Mechanistic Investigations on Copper(I) and Copper(II) Photoredox Catalysis: Unique Opportunities via Inner Sphere Mechanisms

DISSERTATION

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Table of Contents

Abbreviations

Ac	acetyl
ATRA	atom transfer radical addition
BHT	butylated hydroxytoluene
(±)-BINAP	(±)-(1,1′-binaphthalene-2,2′-diyl)-bis(diphenylphosphine)
(±)-BINOL	(±)-1,1′-bi-2-naphthol
Bn	benzyl
Bphen	bathophenanthrolin
bpy	2,2′-bipyridine
bpydc	dimethyl-2,2′-bipyridine-4,4′-dicarboxylate
^{t}Bu	*tert*-butyl
^{t}Bu-TERPY	4,4′,4″-tri-*tert*-Butyl-2,2′:6′,2″-terpyridine
CAS	complete active space
cat.	catalytic amounts
CI	conical intersection
COSMO	conductor-like screening model
CW	continuous wave
d	doublet (spectroscopy)
dap	2,9-bis(*para*-anisyl)-1,10- phenanthroline
DFT	density functional theory
DMF	N,N-Dimethylformamide
dmp	2,9-dimethyl-1,10-phenanthroline
DMPO	5,5-dimethyl-1-pyrroline-N-oxide
DPEPhos	bis[(2-diphenylphosphino)-phenyl]-ether
dpp	2,9-diphenyl-1,10-phenanthroline
d.r.	diastereomeric ratio
dtbbpy	4,4’-di-*tert*-butyl-2,2’-bipyridine
DZ	double zeta
ECP	effective core potentials
EPR	electron paramagnetic resonance
equiv.	equivalent
Et	ethyl
GGA	generalized gradient approximation
GTO	gaussian type orbitals

HF	Hartree-Fock
HOMO	highest occupied molecular orbital
IC	internal conversion
IRC	intrinsic reaction coordinate
ISC	inter system crossing
LDA	local density approximation
LED	light emitting diode
LIH	light-induced homolysis
LMCT	ligand-to-metal charge transfer
LUMO	lowest unoccupied molecular orbital
m	multiplet (spectroscopy)
Me	methyl
MEP	minimum energy path
MLCT	metal-to-ligand charge transfer
MO	molecular orbital
NEB	nudged elastic bond
NMR	nuclear magnetic resonance
PBN	N-*tert*-butyl-α-phenylnitrone
PCM	polarizable continuum model
PES	potential energy surface
Ph	phenyl
phen	1,10-phenanthroline
ppm	parts per million
ppy	2-phenylpyridine
PT2	second-order perturbation theory
PTFE	Polytetrafluorethylen
(±)-QUINAP	(±)-1-(2-diphenylphosphino-1-naphthyl)isoquinoline
QZ	quadruple zeta
RAS	restricted active space
RSE	radical stabilization energy
S	singlet state
s	singlet (spectroscopy)
SCE	saturated calomel electrode
SCF	self-consistent field
SET	single electron transfer

SOC	spin-orbit coupling
SOMO	singly occupied molecular orbital
SVP	split valence polarization
T	triplet state
TD	time-dependent
TEMPO	(2,2,6,6-tetramethylpiperidin-1-yl)oxyl
TZ	triple zeta
UV	ultraviolet
vis	visible light
Xantphos	4,5-bis-(diphenylphosphino)-9,9-dimethylxanthen
ZPE	zero-point energy

A. Introduction

1. Photocatalysis

1.1. General

For a long time, mankind considered the interaction of matter with light to be only causing physical phenomena. While photoinduced reactions such as the bleaching effect of the sun, the deleterious effects on beer and the spoiling of gun cotton were noticed, the impact of light on chemical transformations was only recognized in the 18th century.[1] One of the major obstacles to the advancement of photochemistry was the lack of a reliable light source and analytical techniques to investigate photochemical processes.[2] Driven by the desire to mimic the astounding capabilities of photosynthesis and to harvest the immense amounts of Energy available through sunlight, photochemical transformations became more abundant in the 20th century. Nevertheless, it wasn't until the late 1970s for photocatalysts to be used as a tool for chemical transformations. In 1972 Fujishima and Honda reported the electrochemical photocatalysis of water with TiO_2.[3] A few years later Carey et al. managed to utilize TiO_2 for the photodechlorination of PCB's[4] and Inoue et al. published their results on the photoelectrocatalytic reduction of CO_2.[5]

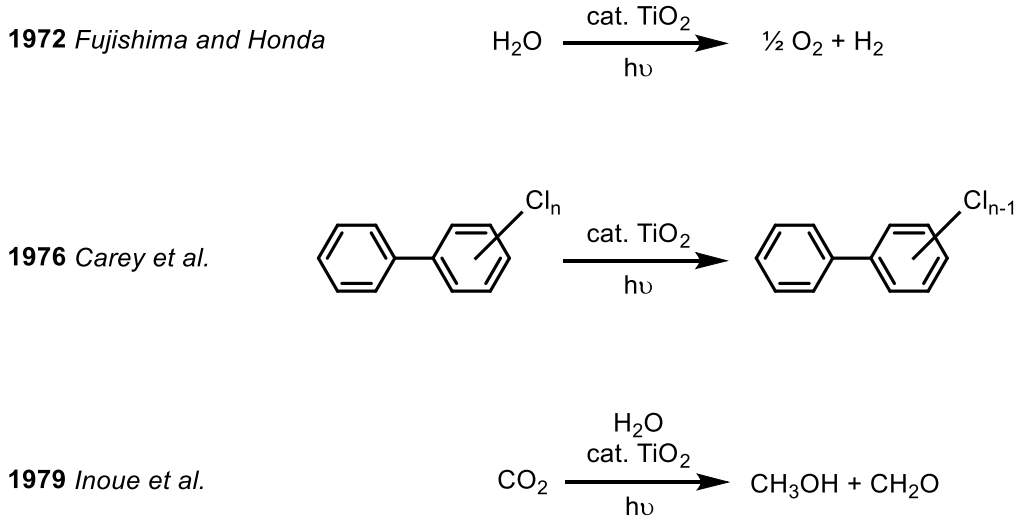


Figure 1: Selection of photocatalytic reactions discovered in the late 20th century.[3–5]

In these reactions the photocatalyst is "able to produce, upon absorption of light, chemical transformations […] and regenerates itself" (IUPAC).[6] By using the energy provided by light, photocatalysis can enable reactions far from thermal equilibrium and thereby open new pathways for chemical transformations. The energy of a photon is used to form intermediates with much higher energy content than the reactants, circumnavigating high potential energy

barriers and even enabling the formation of thermodynamically stable products in an otherwise endergonic reaction.

The fundamentals of photochemistry explained in Sýkoras and Šimas review "Photochemistry of coordination compounds" is summarised in the following.[7] Irradiation of a molecule leads to an electronically excited state if the energy of the photon is equivalent to the energy difference between the electronical ground state E_{GS} and an excited state E_{ES}.

$$E_{ES} - E_{GS} = h\nu = \frac{hc}{\lambda}$$

The energy of a photon can be described by the Planck constant h and the frequency ν or its wavelength λ, with c being the speed of light. The probability of light absorption can be expressed by the oscillator strength f:

$$f = \frac{8\pi^2 m\nu g}{3he^2}\left(\int \Psi_{GS}\hat{R}\Psi_{ES}d\tau\right)^2$$

where g corresponds to the degeneracy of the states Ψ_{GS} and Ψ_{ES} and $\hat{R}$ being the dipole moment operator, e the charge and m the mass of an electron. An experimental description of the absorption of light in a homogeneous solution can be done with the Lamber-Beer law:

$$A_\lambda = \varepsilon_\lambda cd = \log\left(\frac{I_{0,\lambda}}{I_{0,\lambda} - I_{a,\lambda}}\right)$$

The absorbance A of a solute with the concentration c at a given wavelength λ is being measured. With the help of the optical path length d and the intensity of light before (I_0) and after transmitting through the sample (I_a) the molar absorption coefficient ε can be determined. Photoexcitation of a molecule,

$$A + h\nu \rightarrow A^*$$

to an electronically excited state can be understood as a shift in the distribution of electron density to energetically higher lying orbitals. Due to relatively slow nuclear motion, the molecular geometry of the excited molecule is not in a thermodynamic minimum on the excited state potential energy surface (PES), as the atoms could not rearrange as fast as the electrons. This induces molecular motion to adjust to the new electronic state and enables a wide selection of pathways to relax to a thermodynamically stable product. An overview of the different processes that can occur upon excitation is shown in *Figure 2*.[8]

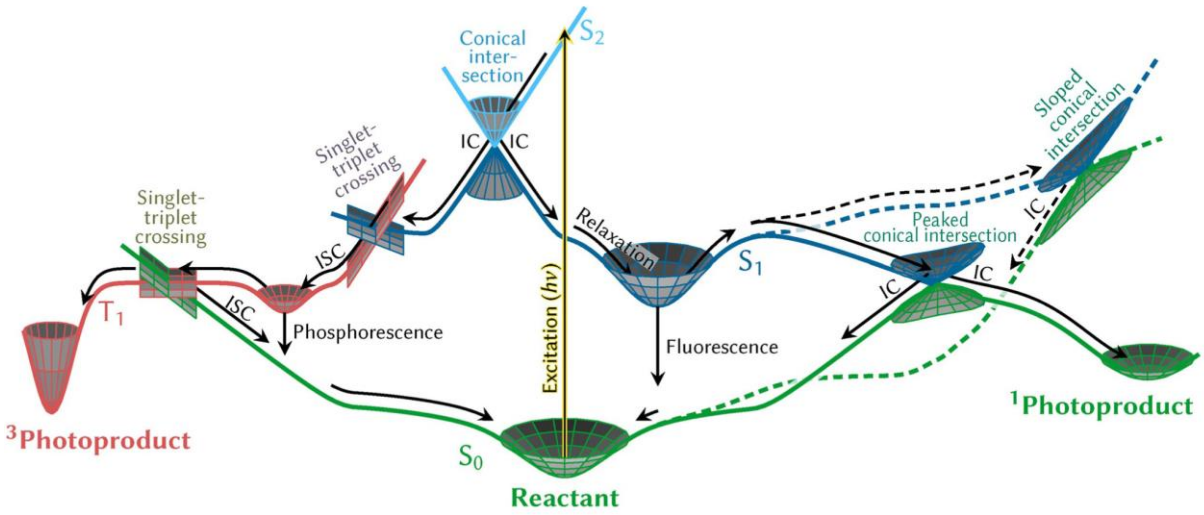


Figure 2: Summary of processes upon excitation of a molecule in the electronical ground state S_0 to an excited state S_2. The green line shows the PES of the ground state, the blue lines the PES of the excited singlet states S_1 and S_2 and the red line the PES of an excited triplet state T_1. Figure adapted from Mai and González. [8]

Absorption of a photon leads to excitation from the electronical ground state S_0 to an electronically excited state S_2. By relaxation of the geometry on the excited state PES the molecule might either transition to a different electronical state (S_1 or T_1) or reach a local minimum to form a long-lived excited state. From there it can overcome potential energy barriers to change its chemical nature or eventually decay back to the ground state PES via fluorescence, releasing energy in the form of radiation. Via internal conversion (IC, $k_{IC} \approx 10^{12}\ s^{-1}$)[7] at conical intersections or intersystem crossing (ISC, $k_{ISC} \approx 10^{9} - 10^{13}\ s^{-1}$)[7] radiationless transitions to different excited states or to the ground state are possible. ISC involves a change in multiplicity and can yield long-lived states, which can either form a new product or relax to the ground state via phosphorescence – releasing energy in form of radiation – or radiationless via ISC.

To utilize the different processes of photochemistry, different types of photocatalysts have been developed. Their different mechanisms can be differentiated as followed:

a) Photogenerated Catalysis $A \xrightarrow{h\nu} A^* \rightarrow K$

In photogenerated catalysis a catalytically inactive precursor *A* gets excited by light and transforms into the active catalyst *K*. The following catalytic cycle does not need to involve light absorption and can be exclusively of thermodynamic nature.

b) Catalysed Photolysis $K + R \rightarrow KR \xrightarrow{h\nu} KR^* \rightarrow K + P$

In catalysed photolysis excitation of a reactant *R* is enabled by coordination to a catalyst *K*, resulting in the formation of product *P* and regenerating the catalyst *K*.

c) Photosensitized Reactions $K \xrightarrow{h\nu} K^* \xrightarrow{R} (K-R)^* \; or \; K + R^* \longrightarrow K + P$

Photosensitized Reactions start by excitation of the catalyst *K* followed by formation of an exciplex or energy transfer to the reactant *R*, which then reacts to product *P*.

Energy transfer between two molecules can occur by simultaneous excitation of the reactant and quenching of the excited state of the catalyst or by electron transfer. Since an excited molecule consists of both an empty low-lying orbital and an occupied higher lying orbital, excited molecules can act both as oxidizing and reducing agent. Whether a photoredox reaction is possible can be expressed by the redox potentials:

$$E^{*0}_{(Ox/Red^*)} - E^{0}_{(Ox/Red)} = h\nu_{Red}\frac{N}{nF}$$

$$E^{*0}_{(Ox^*/Red)} - E^{0}_{(Ox/Red)} = h\nu_{Ox}\frac{N}{nF}$$

The redox potential E^{*0} of the respective oxidized ground state and reduced excited state and vice versa and the redox potential of the ground states are used in this equation, as well as the Avogadro constant *N* and the Faraday constant *F*. The number of exchanged electrons is *n* and $h\nu_{Red}$ and $h\nu_{Ox}$ are the energies of the transition to the reduced or oxidized states. Experimentally, the excited state redox potentials can be determined by phase-modulated voltammetry. More commonly however, the ground state redox potentials are corrected by the energy difference between the lowest lying excited state and the ground state $E_{0,0}$:[9]

$$E^*_{red} = E_{red} + E_{0,0}(Photooxidant)$$

$$E^*_{ox} = E_{ox} - E_{0,0}(Photoreductant)$$

$E_{0,0}$ can both be estimated by absorption and emission maxima of the photocatalyst.

Photoredox catalysis is a powerful tool for organic synthesis as it produces radicals, which are highly reactive intermediates. The photocatalyst undergoes oxidative or reductive quenching of the excited state, exchanging electrons either with the substrate or a sacrificial electron donor/acceptor.[10] Typically, photocatalysts consist of a metal centre coupled with an organic ligand but also metal free organocatalysts are well known (*Figure 3*).

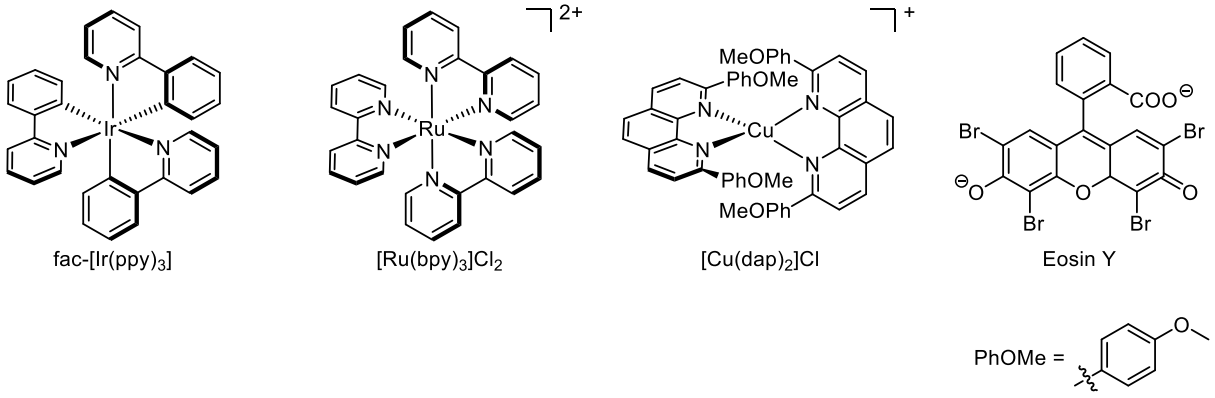


Figure 3: Selection of commonly used photocatalysts in organic synthesis.[10,11]

Their capabilities to absorb light can be attributed to at least one of the following transitions between molecular orbitals (MOs):

a) Transition between AOs of the central atom

These transitions typically occur at or between multiple metal centres. Electron density can be shifted between d- and f-orbitals, metal centres or Rydberg states.

b) Transition between MOs of the ligands

These transitions occur either between MOs localized on one ligand or between the HOMO of one ligand and the LUMO of another ligand.

c) Transition between metal and ligand MOs

Transitions from ligand to metal orbitals are known as ligand-to-metal charge transfer (LMCT). The opposite transition is known as metal-to-ligand charge transfer (MLCT).

d) Transition between complex and environmental particles

An electron is ejected to an unspecified molecule in its environment or an ionic component in its secondary coordination sphere.

Apart from its light absorbing capabilities properties such as oxidation and reduction potentials, excited state lifetime and coordination to substrates are key features of photocatalysts, as well as their ability to be regenerated in the course of the reaction. In the following chapter these features will be discussed thoroughly for copper based photocatalysts.

1.2. Copper Photocatalysis

While heavy transition metals such as Ir or Ru are widely studied and highly capable in photocatalysis, their scarcity has pushed research on earth abundant elements, such as the 3d metals Fe, Co, Ni, Cu and Zn.[12] Their ability to also coordinate to the substrate and influence

the reaction even after the photocatalytic step, renders them a promising choice for selective transformations. Copper in particular excels at rapid ligand exchange and coordination to a wide selection of Ligands. Various heteroleptic N- and P-based multidentate ligands can be used to fine tune the photocatalytic features of Cu-complexes (*Figure 4*).[13]

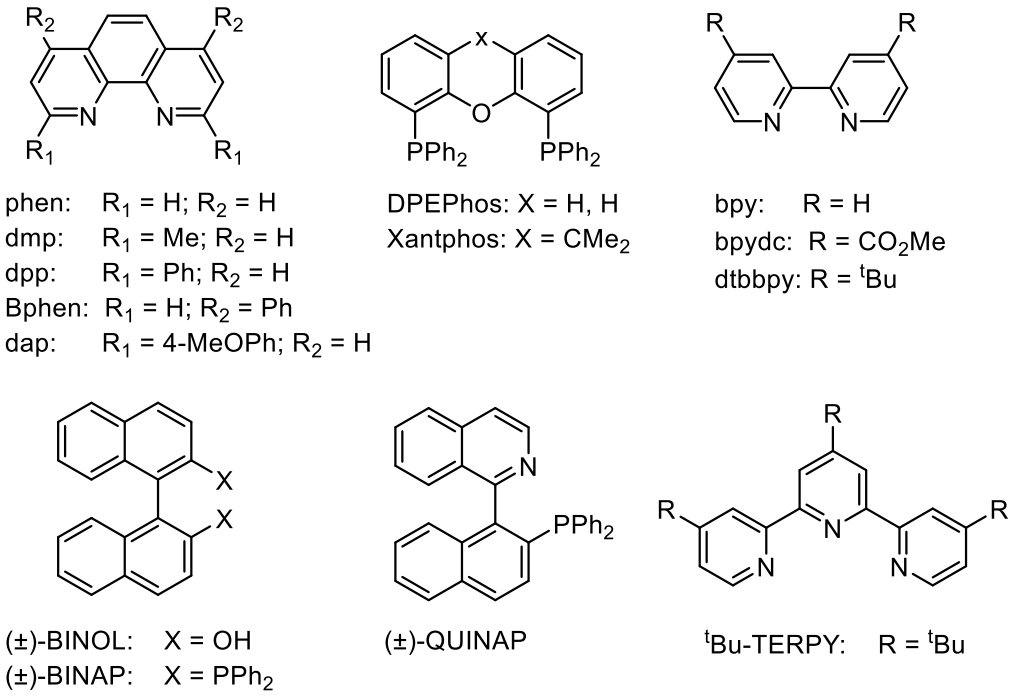


Figure 4: Selection of different ligands to form Cu-complexes.[13]

Copper in its +1-oxidation state can form two-, three-, and tetra-coordinated complexes.[14] Due to its d^{10} configuration, the electron density on the metal centre is distributed evenly, which favours the formation of symmetrical complexes. While two- and three-coordinated complexes of Cu(I) are well known, they are usually stabilized by sterically blocking additional coordination sites to the Cu-centre. With less steric bulk at the ligands, a tetra-coordination in a pseudo-tetrahedral geometry is favoured.[14] Extensive research on the photoexcitation of these complexes has been done since McMillin's report of the $[Cu(dmp)_2]^+$ complex.[15] Two major transitions are observed upon photoexcitation: π-π* ligand centred transitions and MLCT, with the Cu centre being oxidized to a formal oxidation state of +2. This either induces a flattening of the tetrahedral geometry to a stable singlet state or causes ISC to a triplet state, which relaxes to an even more stable flattened geometry than the singlet state.[14] The flattening of the ligands opens up a new coordination site and even favours dissociation of a ligand, enabling coordination of substrates or intermediates.[16] Formation of an exciplex with a solvent molecule gives rise to a non-radiative deactivation pathway, effectively shortening the excited state lifetime. By addition of steric bulk to the phenanthroline ligands at the 2 and 9 positions, a deactivation pathway via exciplex formation is hampered, thus the short excited state lifetime

of $[Cu(dmp)_2]^+$ (τ_{Em} = 90 ns) could be increased ($[Cu(dpp)_2]^+$: τ_{Em} = 250 ns).[14] The Steric bulk hinders the flattening of the geometry, preventing the formation of an exciplex and favours ISC to a long-lived triplet state. Since the backbone of the ligand can be finetuned, a wide selection of different complexes with elongated lifetime, absorption in the region of visible light (450 - 700 nm) and enhanced emission properties has been synthesized.[14] Furthermore, the reduction potential of the MLCT state can be tuned, which is generally used to catalyse reactions via single electron transfer (SET).[14] With oxidation potentials around +0.5 V to +1.0 V vs SCE and reduction potentials of -1.4 V to -1.8 V vs SCE homoleptic Cu-complexes are already good electron donors in the ground state.[14] In the excited state the redox properties are heavily increased. In case of $[Cu(dmp)_2]^+$ complexes the ground state reduction potential of $E_{red} = -1.74\ V$ is increased to $E^*_{red} = -0.07$ V (vs SCE in acetonitrile, counterion: BF_4^-) and the excited state oxidation potential is shifted from its ground state oxidation potential $E_{ox} = +0.93\ V$ to $E^*_{ox} = -0.72$ V (vs SCE in acetonitrile, counterion: BF_4^-).[14] While potent as both reducing and oxidizing agent, Cu(I) is typically used as electron donor. Two possible mechanisms of Cu(I) as a photocatalyst were postulated by Reiser et al.[17]:

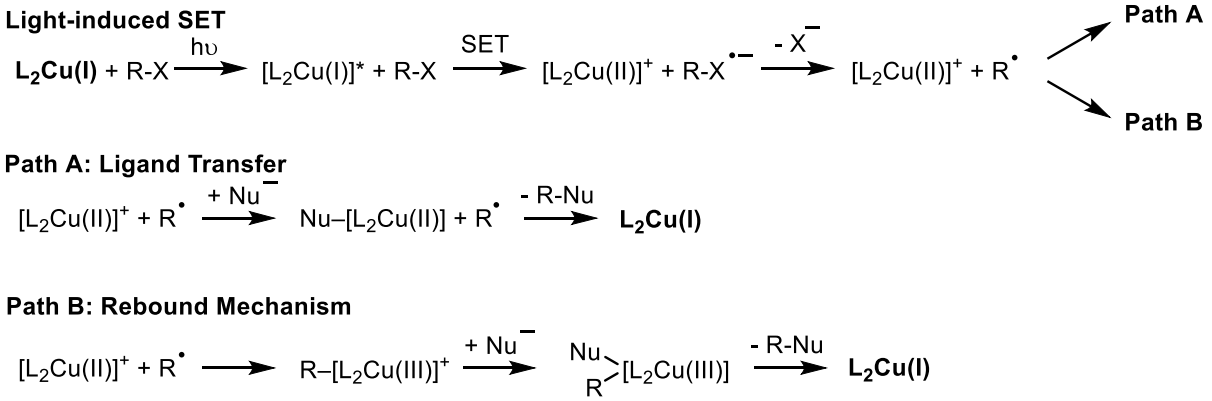


Figure 5: General scheme of the Cu(I) light-induced SET mechanism and two possible pathways via ligand transfer and a rebound mechanism.[13]

Single electron transfer (SET) from the MLCT state generates a radical *R* and oxidizes the Cu(I) complex to Cu(II). Via ligand exchange pathway **A** the Cu(II) intermediate can transfer a nucleophile *Nu* to the radical, regenerating its +1 oxidation state and forming a Nu-R bond.[13] Alternatively, a rebound mechanism **B** of the radical to the copper centre has been proposed[17], to form a Cu(III) intermediate. After ligand exchange with a nucleophile *Nu*, reductive elimination to Cu(I) and Nu-R occurs.[13] Another mechanism via oxidation of the radical *R* to a cation, followed by recombination with an anion could be excluded. Comparison to the $[Ru(bpy)_3]Cl_2$ catalysed reaction, which assumably should proceed via a photoredox cycle, showed very low yields (≥ 10%).[17]

Opposed to Cu(I) photocatalysis, Cu(II) complexes undergo LMCT upon photoexcitation. The d^9 configuration of Cu(II) leaves one d-orbital half filled, which can be occupied by an electron from a ligand. The LMCT states induce both homolytic and heterolytic cleavage of a Cu-X bond.[18] In the latter case the metal centre is reduced to Cu(I) and the newly formed radical can initiate organic transformations. The resulting Cu(I) complex gets either oxidized by O_2 or in the course of the organic transformation to regenerate the Cu(II) oxidation state.[19]

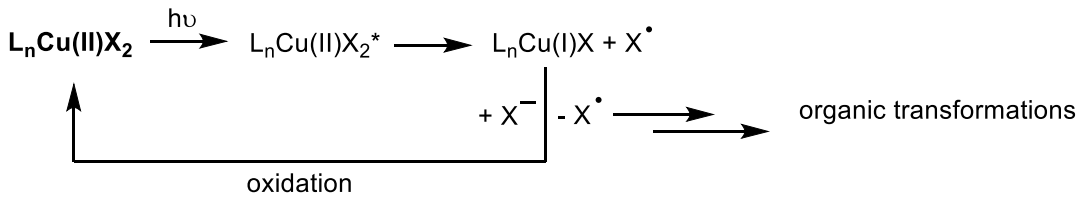


Figure 6: General scheme of the Cu(II) light-induced homolysis mechanism. [19]

Cu(II) photocatalysis gives access to radical intermediates build from a nucleophile or anion, while Cu(I) photocatalysis is able to reduce molecules that can split off a leaving group to form a neutral radical. Both pathways give rise to a wide selection of transformations, making Cu-photocatalysis a versatile tool for organic synthesis.[13] The rather short excited state lifetimes are compensated by a strong tendency for Lewis acid interactions and π-coordination with various substrates. The ability to interact with intermediates and the wide selection of compatible ligands enable unique pathways for selective transformations. However, these features can result in complex interactions with several intermediates, rendering a deep understanding and prediction of reaction behaviour difficult. Understanding these specific reaction mechanisms, interactions with molecules in the inner sphere and formation of intermediates, could elevate Cu-photoredox catalysis to another level and enable a more elaborate reaction design.

2. CW-EPR Spectroscopy

Electron Paramagnetic Resonance (EPR) spectroscopy detects unpaired electrons and is therefore a powerful tool for the observation of radical intermediates and paramagnetic compounds. This chapter will focus on the fundamental principles of continuous wave EPR (CW-EPR) spectroscopy. Formulas and physical explanations are taken from Daniella Goldfarbs and Stefan Stolls book “EPR Spectroscopy – Fundamentals and Methods”, unless stated otherwise.[20]

EPR spectroscopy is based on the electron Zeeman effect, which splits the degenerate energy levels of the two electron spin states $m_s = \pm\frac{1}{2}$ of an unpaired electron by exerting an external magnetic field.

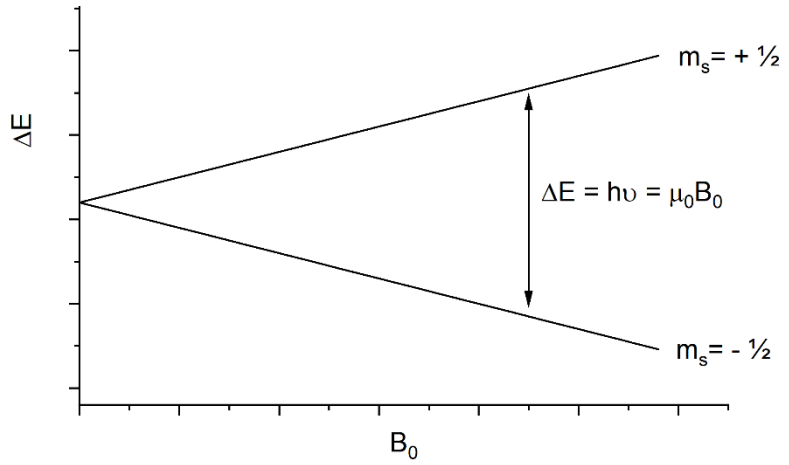


Figure 7: Electron Zeeman effect. The energy difference of the electron spin states m_s are shown in dependency of the magnetic field B_0, the g-value and the Bohr magneton μ_B.[20]

In CW-EPR continuous microwave irradiation is used on a fixed frequency and the magnetic field is varied. Resonance is observed when the energy difference of the electron spin states $m_s = \pm\frac{1}{2}$ matches the energy of the microwave frequency. There are different commonly used microwave frequencies, assigned to different letters. As the linewidths do not scale proportional to the frequency, a better resolution of the spectrum can be achieved at higher frequencies. Yet the X-band frequency of 9-10 GHz is widely used because of its low cost and, in many cases, sufficient resolution. Q-band spectrometers (33-35 GHz) also use electromagnets and are therefore easily accessible. Despite its need for a superconducting magnet, W-band spectrometers (95 GHz) are also popular. The choice of band type is most often set by the specific compound under investigation and sometimes measurements at multiple bands are done to interpret a signal. Commonly the signal is presented in its 1st derivative due to the use of a modulation-amplitude detection method. A schematic overview of a CW-EPR spectrometer and its core components is shown in *Figure 8*.

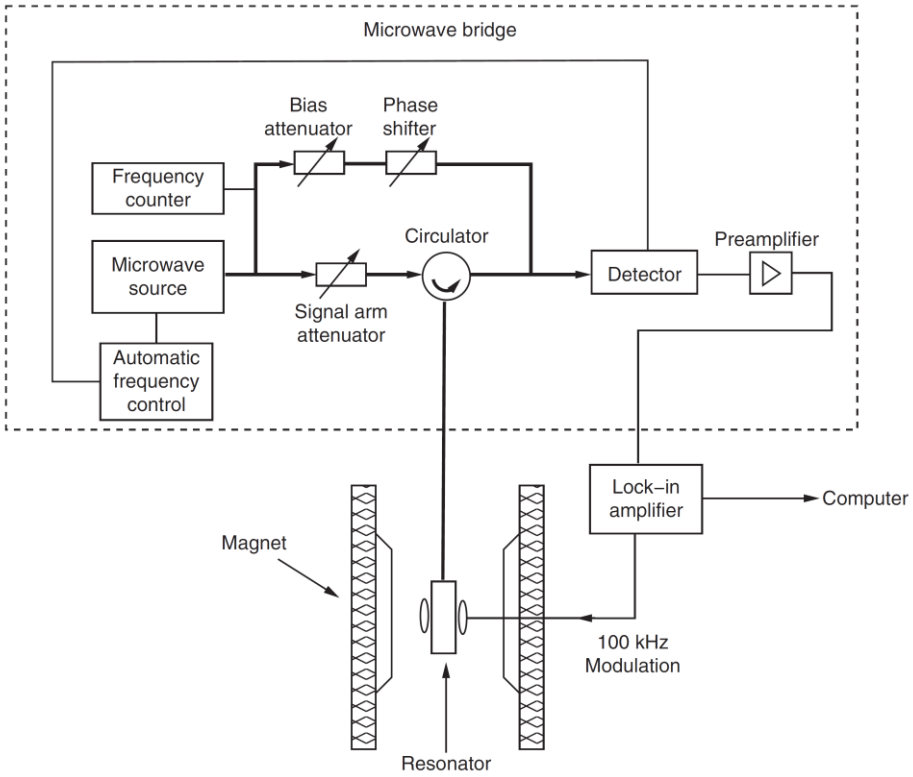


Figure 8: Scheme of a CW-EPR spectrometer adapted from D. Goldfarb and S. Stoll .[20]

The radiation source and the detector are located in the microwave bridge, whereas the sample is in the microwave cavity. The emitted microwaves from the microwave source are split into signal and reference arms and their microwave power can be tuned by attenuators. In the signal arm the microwaves are passed through a circulator to the resonator. This is useful to prevent microwave radiation coming from the source to directly reach the detector. A coupling element can be tuned to ensure, that no power is reflected at the resonance frequency of the resonator. Now the magnetic field is swept and as soon as an EPR transition occurs, the microwave gets absorbed by the sample, disturbing the critical coupling of the resonator and reflecting some of the incoming microwaves. These are converted into an electrical current, which is then transformed into a sine wave with its amplitude being proportional to the slope of the signal. The resulting EPR spectrum is then shown in its first derivative form. The signal intensity is proportional to the square root of the microwave power at low power levels. At higher microwave power levels this linear behaviour changes and eventually the signal intensity decreases. As the signal intensity is dependent on the population difference of the lower and upper energy level, the signal intensity is saturated at high microwave powers due to the populations getting equalized. At lower microwave power however, relaxation to the thermal equilibrium can occur. It is therefore important to find the sweet spot between sufficient microwave power, while maintaining sufficient relaxation. This is usually done by plotting the

signal intensity against the square root of the microwave power, where the effect of saturation can be seen at the deviation from a linear relationship. It becomes clear that the relaxation time has a strong influence on signal intensity. Relaxation is classified in two terms: The spin-lattice or longitudinal relaxation time T_1 and the spin-spin or transverse relaxation time T_2. T_1 describes the relaxation from a higher spin state to the thermal equilibrium and T_2 describes the redistribution of energy.[21] Both relaxation time and population difference of the spin states are temperature dependent. While the population difference becomes more pronounced at lower temperatures, positively effecting the signal intensity, too low temperatures elongate relaxation times. This results in a lower microwave power to prevent saturation and negatively impacts the signal intensity.

EPR often gets compared to NMR, which uses the same approach as EPR for nuclear magnetic resonance.[21] In accordance with the chemical shift in NMR the primary information gained in EPR is the g-factor of the unpaired electron(s), which serves as a fingerprint of the paramagnetic species and its electronic environment. The g-factor of a free electron is:

$$g_e = 2.0023$$

This value deviates depending on its chemical surrounding, by coupling of the spin and orbital angular momenta (Spin-orbit coupling). Carbon centred organic radicals are usually very close to the free electron g-value. With an oxygen atom being adjacent, the g-factor shifts to 2.003 - 2.004, while oxygen centred radicals usually have a g-value higher than 2.004.[22] As spin-orbit coupling scales with the atomic number, much larger deviations are observed for electrons at a metal centre. In addition to the external magnetic field, the movement of other charged particles such as electrons and atomic nuclei exert a local magnetic field, which can further split the energy levels of an electron. The different effects on the energy levels of the spin system can be expressed with the spin Hamiltonian H_0:[21]

$$H_0 = H_{EZ} + H_{NZ} + H_{HF} + H_{NQ} + H_{NN} + H_{ZFS}$$

The energy terms used to describe the spin Hamiltonian H_0 are the electron Zeeman H_{EZ}, nuclear Zeeman H_{NZ}, hyperfine H_{HF}, nuclear quadrupole H_{NQ}, nuclear-nuclear H_{NN} and the zero field splitting H_{ZFS}.[21]

Magnetic interaction of an electron with the nuclear spin, called hyperfine coupling, is one of the most important sources of chemical information in CW-EPR. Opposed to the nucleus, the electron is not localized in space, but delocalized over multiple atoms, resulting in magnetic coupling to these nuclei. Coupling of an electron to *n* nuclei with nuclear spin *I* splits the EPR signal in 2nI +1 lines:

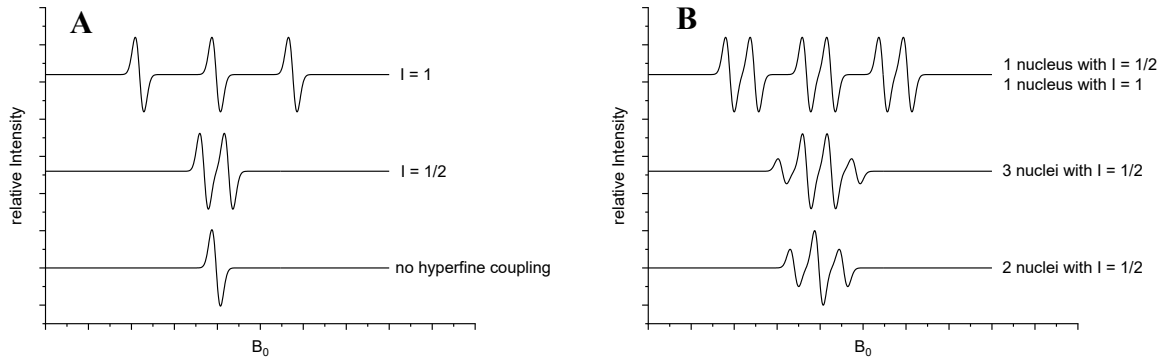


Figure 9: Hyperfine splitting patterns of the coupling between an electron and multiple nuclei of varying nuclear spin.[23] Simulations were done using the EasySpin 6.0.0-dev.53 package for Matlab (9.7.0.1190202 (R2019b)).[24]

Typical Nuclei that contribute to hyperfine interactions in CW-EPR include ^{1}H, ^{13}C, ^{14}N, ^{31}P, ^{51}V, ^{63}Cu, ^{65}Cu.[21] Another effect to consider is the anisotropy of the radical centre. In solution-phase organic radicals appear usually as narrow, isotropic EPR lines, as rapid molecular tumbling averages out anisotropic interactions, such as g-anisotropy and hyperfine anisotropy. Paramagnetic metal centres however often possess very large g-anisotropy, which is not averaged out completely by tumbling motion because of spin-orbit coupling. This gives rise to multiple signals corresponding to the same paramagnetic specie. Their spectra are classified according to their symmetry as:

Isotropic	$g_x = g_y = g_z$
Axial	$g_x = g_y \neq g_z$
Rhombic	$g_x \neq g_y \neq g_z$

Particularly for metal complexes information on the symmetry of the metal centre is highly valuable. The anisotropy effect is even more pronounced in solid powders or frozen solutions as molecular motion is more limited. The g-value of a gaseous metal ion can be expressed with the Landé factor:[25]

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

This formula uses the total angular momentum *j*, the orbital angular momentum *l* and the spin angular momentum *s*. In the ground state the perturbing effect of the ligands quenches the orbital angular momentum, but due to orbital mixing the excited state of a molecule reintroduces some orbital contribution to the g-value. The following formula addresses this effect by introducing the variable *k* for orbital mixing and including the energy difference between ground state E_0 and excited states E_n:[25]

$$g_i = 2.0023 \pm \frac{k\lambda}{E_0 - E_n}$$

The g value is now dependent on the orientation *i*, which can be *x*,*y* and *z* and the spin-orbit coupling constant λ is used. λ is either positive for d^1-d^4 configurations or negative for d^6-d^9 configurations, which results in a positive deviation from the free electron g-value for d^6-d^9 configured metal centres and a negative deviation for d^1-d^4 configured metal centres.[25] Using the anisotropic g-values geometric information of the paramagnetic metal centre can be gained. The "magic pentagon" serves as a good tool for the determination of the *k* value.[25]

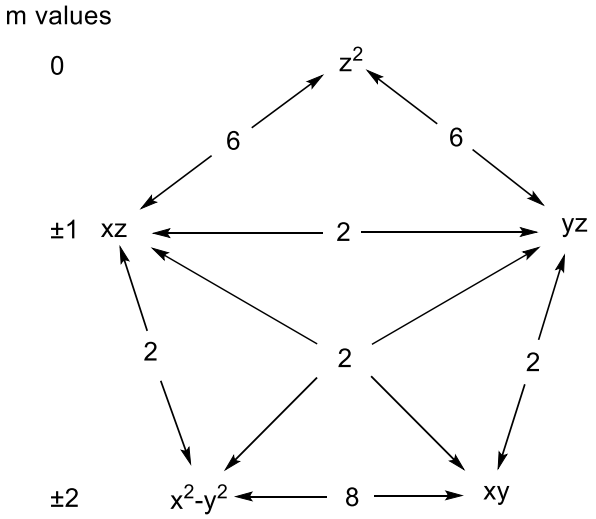


Figure 10: Magic pentagon to determine the value of k. Figure adapted from Garribba and Micera.[25]

In the case of an elongated octahedral, square pyramidal or square planar geometry, the ground state is the $d_{x^2-y^2}$ orbital. Two different g-values derive from this geometry as the *x* and *y* orientation is equivalent:[25]

$$g_{\parallel} = g_z = 2.0023 \pm \frac{8\lambda}{E(d_{x^2-y^2}) - E(d_{xy})}$$

$$g_{\perp} = g_x = g_z = 2.0023 \pm \frac{2\lambda}{E(d_{x^2-y^2}) - E(d_{xz})} = 2.0023 \pm \frac{2\lambda}{E(d_{x^2-y^2}) - E(d_{yz})}$$

From these equations follows an axial spectrum with $g_{\parallel} > g_{\perp} > 2.0023$.

The inverse relationship $g_{\perp} > g_{\parallel} = 2.0023$ is true for compressed octahedral or trigonal bipyramidal geometries, where the ground state is the d_{z^2} orbital. A rhombic spectrum with three different g-values can be observed for intermediate geometries, where the ground state is a linear combination of the $d_{x^2-y^2}$ and the d_{z^2} orbitals. The predominant contribution of these orbitals can be extracted with the *R* parameter:[25]

$$R = \frac{g_y - g_z}{g_x - g_y}$$

Assigning the g values from the rhombic spectrum with $g_x > g_y > g_z$, the predominant contribution comes from the $d_{x^2-y^2}$ orbital for $R < 1$ and from the d_{z^2} orbital for $R > 1$.

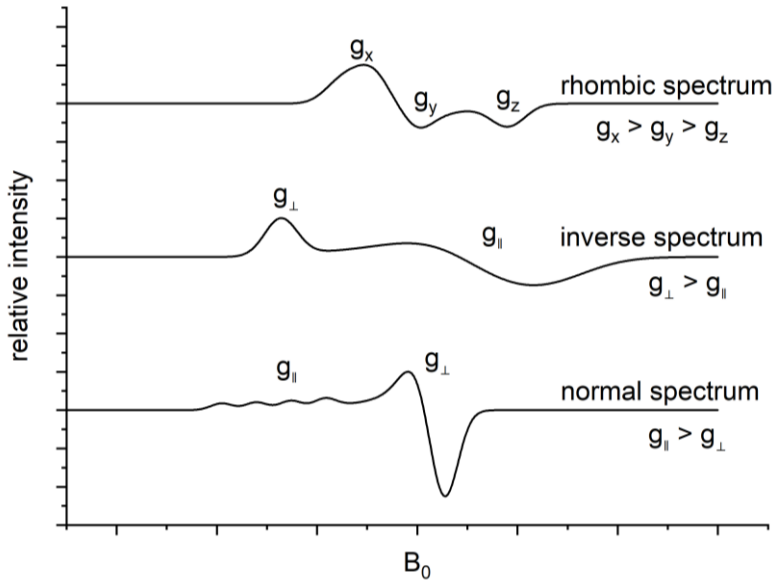
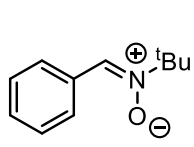
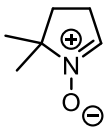


Figure 11: Simulated Cu^{2+}-spectra of normal, inverse and rhombic symmetry. Simulations were done using the EasySpin 6.0.0-dev.53 package for Matlab (9.7.0.1190202 (R2019b)).[24]

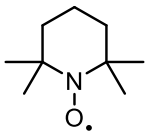
Gaining insight into the geometry of a complex is highly valuable for mechanistic research, as changes of the geometry at the metal centre have implications on the coordination behaviour of the paramagnetic species (e.g. the catalyst) during the reaction. Coupled with the possibility to track the formation of organic radicals that are sufficiently populated for observation, highly valuable information about intermediates and reaction paths can be gained. For short-lived radicals that escape the resolution of the EPR spectrometer a commonly used strategy is the use of a spin or radical trap. Spin traps are compounds with a high reactivity towards radicals and form stable radicals that can be observed by EPR spectroscopy. Widely used spin traps are N-tert-Butyl-α-phenylnitrone (PBN) and 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO).[26] The opposite strategy is to introduce a stable radical that is quenched by the formation of another radical, resulting in a decrease of the EPR signal. Molecules like (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) fulfil this purpose as the EPR signature is already visible at relatively low concentrations.



N tert-Butyl-α-phenylnitrone
PBN



5,5-Dimethyl-1-pyrroline-N-oxide
DMPO



(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl
TEMPO

Figure 12: Commonly used spin and radical traps for EPR spectroscopy: PBN, DMPO and TEMPO.

Investigating the signal intensity provides valuable quantitative information of the paramagnetic species under investigation. This can result in kinetic information of the reaction process observed when following the change of signal intensity over time. As was shown in this chapter EPR spectroscopy is a powerful tool for mechanistic research whenever radical intermediates and paramagnetic complexes are involved. On the other hand, spectra are often complex to interpret without the use of elaborate tools. Therefore, EPR spectroscopy is often coupled with spectrum simulations and experimental comparisons of similar spin systems.

3. Computational Chemistry

3.1. Introduction

With the technological advances of computers, sufficient computing power has become available to use the principles of theoretical chemistry for detailed simulations in chemistry. Additionally, the approximations made by theoretical chemists render otherwise decade long calculations for the description of molecules and their physical behaviour to be only a matter of hours. The scientific use ranges from calculations on energy profiles over simulations of spectra to modelling of molecular systems prior to synthesis and gives insight to multiple scientific problems from a theoretical point of view. Hypothetically, Quantum mechanics is able to exactly predict any property of an atom, but in practice only one electron systems have been solved exactly. A wide selection of approximations and methods to describe atoms and molecules has been developed of which density functional theory has become one of the most used methods for computational calculations. In this chapter the theory behind computational chemistry with a focus on DFT will be elucidated. Formulas and theoretical explanations are based on David Youngs book “Computational Chemistry”.[27] As a basis for all computational models stands the Schrödinger equation:

$$\hat{H}\Psi = E\Psi$$

Ψ is a wave function, which is a function of electron and nuclear positions, E the energy and $\hat{H}$ is the Hamilton operator,

$$\hat{H} = -\sum_{i}^{particles} \frac{\nabla_i^2}{2m_i} + \sum_{i<j}^{particles} \sum \frac{q_i q_j}{r_{ij}}$$

where ∇_i^2 is the Laplacian operator, m the mass and q the charge of particle i, with a distance of r_{ij} between particles. This operator includes a description for the kinetic energy and Coulomb attraction and repulsion. Using the Born-Oppenheimer approximation the nuclear and electron motions can be separated, as nuclear motion is relatively slow compared to electron motion:

$$\hat{H} = -\sum_{i}^{electrons} \frac{\nabla_i^2}{2} + \sum_{i}^{nuclei} \sum_{j}^{electrons} \frac{Z_i}{r_{ij}} + \sum_{i<j}^{electrons} \sum \frac{1}{r_{ij}}$$

The first term now only describes the kinetic energy of electrons, followed by the attraction of electrons to nuclei and the repulsion between electrons. With the wavefunction of a molecule these equations can be used to determine any property of the molecule using the expectation value of the corresponding operator, e.g. the energy:

$$\langle E \rangle = \int \Psi^* \hat{H} \Psi$$

Based on a theory by Hohenberg and Kohn[28], DFT uses the electron density instead of a wavefunction for the calculation of the energy. A linear combination of basis functions is used for the electron density and its determinant – the Kohn-Sham orbitals[29], named after their inventors – is then used by a functional to calculate the ground state electronic energy of a given molecule. To sufficiently describe a multitude of different chemical systems, a wide range of functionals has been developed, using fundamental quantum mechanics and parameterized functions to match experimental results, giving rise to *ab initio* (purely theoretical) and semiempirical variations of DFT. A big advantage of DFT is its calculation speed, without forfeiting accuracy. While wavefunction based methods have to integrate the whole wavefunction for coulomb repulsion, DFT only uses the electron density, scaling down the computational cost from N^4 to N^3 (N is the number of basis functions). This enables calculations on large systems and heavy atoms, that otherwise would be too expensive in computational cost. A wide selection of functionals has been developed to optimize accuracy, while maintaining low computational cost. The simplest form of DFT is solely based on the electron density, called local density approximation (LDA). More elaborate methods also include gradients of the spin densities and are called generalized gradient approximation (GGA). Notable examples include BP86[30], BLYP[31] and PBE[32]. Both LDA and GGA functionals predict too small HOMO-LUMO gaps and underestimate the population of high-spin states due to the inclusion of self-exchange and self-correlation.[33] To decrease self-exchange and self-correlation, partial Hartree-Fock exchange and kinetic energy density is used by hybrid

functionals. The popular functional B3LYP[31,34–36] uses 20% Hartree-Fock exchange while others use 25% (PBE0), 27% (M06[37]) or even 100% (M06-HF[38]). The best performing functional is heavily dependent on the investigated molecules and the desired information. While some functionals perform well for main group elements other functionals are much better suited for the description of transition-metals.[33] This is problematic for computations on metalorganic catalysts, where both groups of elements are present. One major challenge is the multiconfigurational character of transition-metals. Careful benchmarking and comparison to experimental values has to be done to gain valuable results.[33,39] Despite this weakness DFT performs reasonably well in some cases, a common strategy however is the application of multi-reference methods on the DFT-optimized geometries.[40,41] By allowing configuration interaction for a user defined set of orbitals and electrons, the multireference character of a molecule can be accounted for. These computationally demanding multireference methods will be discussed in the next chapter.

Fundamental to the description of wavefunctions, molecular orbitals and the electron density are basis sets. They are equally important to the choice of method, when it comes to the accuracy and cost of a calculation. Basis sets are a set of functions used to depict the shape of the atomic orbitals:

$$\varphi = Y_{lm} \sum_i C_i \sum_j C_{ij} e^{-\zeta_{ij} r^2}$$

Y_{lm} is a function for the orbital symmetry, C_i corresponds to the molecular orbital coefficients, which will be optimized during a calculation. The contraction coefficients C_{ij} and the exponent ζ_{ij} on the other hand are fixed parameters provided by a data base. The exponent $-r^2$ is a Gaussian primitive function. While the exact solution of the hydrogen atom uses a slater type orbital, gaussian type orbitals (GTO) can be used analytically opposed to the numeric integrals over slater type orbitals, which speeds up the calculation drastically. Apart from rare cases, where the accuracy is maximized, gaussian type orbitals are mainly used. A widely used family of basis sets are the Pople basis sets. Different specifications can be made via the basis set notation, e.g. the 6-31G basis set contains six GTO primitives for core orbitals and two contractions of three and one GTO primitive respectively for valence shell orbitals. There is also the possibility of adding polarization functions (*) and diffuse functions (+) to tailor the basis set to the molecules described. A similar family of basis sets is the Ahlrichs def2-XVP basis set.[42] Analogous to the Pople basis sets specifications can be made through the notation with X, standing for S (split), DZ (double zeta), TZ (triple zeta) or QZ (quadruple zeta) for valence orbitals or by adding another polarization function P (e.g def2-TZVPP). These basis

sets are widely used for DFT calculations. They are available for almost all atoms and deliver sufficient results for the optimization of basic structural parameters using the cheap def2-SVP basis set and yield results close to the basis set limit with the def2-TZVP basis set.[42] While def2-TZVPP and def2-QZVP perform even better, the increase in accuracy usually does not justify the computational cost. This changes for post-HF methods like MP2, where a larger basis set is needed to reach the same level of accuracy.[42] Another feature is the inclusion of effective core potentials (ECP) in the basis set to deal with relativistic effects. These become more pronounced for heavier atoms and are therefore included for atoms beyond Kr and are treated by replacing the core electrons with an effective potential.[42] A case can be made for the treatment of relativistic effects for Cu atoms, as mass defect and spin-orbit coupling can become relevant.[27] However the use of ECPs for 3d transition metals has shown varying success and performs poorly compared to the all electron treatment with the def2-TZVP basis set.[43] This comes with a significant increase in computational cost, which has to be balanced with the desired accuracy.

Up to now, the calculation of a single isolated molecule has been addressed. In reality, the molecule interacts with nearby molecules through van der Waals forces, dispersion and hydrogen bonding interactions or dielectric shielding of electrostatic interactions. In homogeneous catalysis interactions occur mainly with the solvent and it can have a significant effect on different properties of a molecule, including the geometry, energy or the stabilization of charge separation.[27] Interactions with a solvent can be treated explicitly, by adding solvent molecules to the calculation. An accurate description can be achieved by molecular-mechanics or Monte Carlo calculations, but a more practical and less time and resource consuming treatment can be done by adding a small number of solvent molecules to the geometry. Either the most stable geometry or a Boltzmann averaged result of multiple stable geometries can then be used. Solvent effects can also be treated implicitly by modelling the solvent as a continuum with a dielectric constant. Frequently used models include the conductor-like screening model COSMO and the polarized continuum method PCM. COSMO is based on a solvent accessible surface and is considered to be a simple and efficient model, while PCM uses a self-consistent reaction field calculation and is based on the Poisson Equation:

$$\nabla^2\phi = \frac{-4\pi\rho(r)}{\varepsilon}$$

The equation uses the Laplace operator ∇^2, the electric potential ϕ, the charge density $\rho(r)$ and the dielectric permittivity ε. PCM enables a more differentiated description of the shape of the solvent cavity and the solute and is considered a more accurate model than COSMO. For the systems under investigation in this work solvent effects play an important role and a proper

treatment of solvent effects becomes even more important for the calculation of photochemical processes, which will be covered in the next chapter.[44,45]

3.2. Computational Photochemistry

Many properties and spectroscopic phenomena include the electronic excitation of a molecule to electronically higher states. Yet standard DFT is formulated to optimize the ground-state electronic configuration, i.e. the state of lowest energy. While imposing a specific symmetry different from the ground state may yield the lowest excited state of the given symmetry, more sophisticated methods have been developed to generate excited state wavefunctions.[27] DFT has been extended by a linear response formalism, which is known as time-dependent DFT (TD-DFT).[46] Vertical excitation of closed shell ground state geometries is used to predict excitation energies. Using first order perturbation theory the response of the ground state to a perturbation in form of a time-oscillating field is calculated.[47] Even though TD-DFT generally struggles with a proper description of Rydberg states, delocalized states over large π-systems, doubly excited states, charge transfer states and conical intersections, it has shown to accurately predict excited state properties of a large variety of molecules.[45,48] A more elaborate treatment of excited states and the coverage of static correlation can be achieved with multiconfigurational wavefunctions. By splitting the orbitals into core, active and virtual orbitals, the CASSCF method (Complete Active Space Self-Consistent Field) considers all allowed arrangements of electrons in the active space.[49] A good description of the active space covers all orbitals, that change occupation in the course of the observed transformation.[50] This can be an excitation to another electronic state or the change to a geometry with a different ground state electronic configuration. The active space however has to be chosen by the scientist himself, which introduces the danger of inaccurate active space selection, resulting in an incorrect description of chemical processes. Furthermore, a small active space leads to the overestimation of static correlation.[41] This problem can be dealt with to some degree by adding dynamic correlation with CAS second-order Perturbation Theory (CASPT2).[51] Increasing the active space can also yield in a sufficient amount of active orbitals to include dynamic correlation, but this comes at computational cost, which is already high for CASSCF/CASPT2.[41] To decrease computational cost the restricted active space method (RASSCF/RASPT2) divides the active space into three additional groups (RAS1, RAS2, RAS3).[52,53] The RAS2 space is similar to the active space in CASSCF and allows full configuration interaction, the RAS1 and RAS3 space however is restricted by the number of allowed electron holes (RAS1) and electrons (RAS3). This enables the use of a much larger

active space, while reducing computational cost. Even more so than with CASSCF, the choice of the restricted active space has a tremendous impact on the accuracy of the calculation.[54]

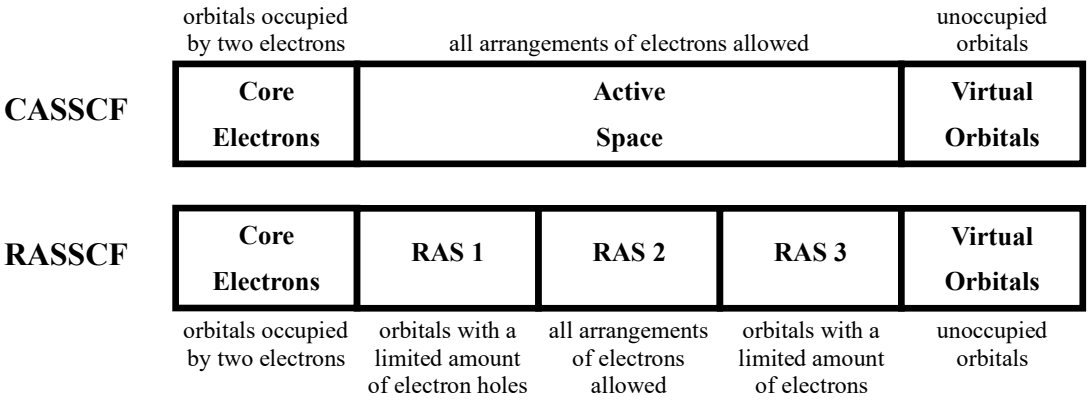


Figure 13: Separation of orbital spaces in CASSCF (Core electrons, active space, virtual orbitals) and RASSCF (core electrons, RAS1, RAS2, RAS3 and virtual orbitals).[53]

Both CASSCF and RASSCF have the potential to yield a fundamentally better description of molecules, especially when static correlation plays a significant role. This is often the case for transition metals, conjugated aromatic systems, excited states and transition states in chemical reactions, where bond formation and bond breaking occurs.[41] These effects are all relevant to mechanistic investigations on Cu-catalysis involving photoexcitation. However, these multireference methods come at a high computational cost when compared to DFT and require careful selection and thorough testing of active spaces. As the geometry of a molecule changes to an intermediate and finally forms the product, the electronic configuration can change drastically, which makes selection of a common active space very challenging.[55] An established strategy is the exploration of the PES using DFT and specifically investigating crucial geometries with CASSCF/CASPT2 or the RAS equivalent.[55]

As the focus of this thesis is on mechanistic investigations on Cu-photocatalysis including large ligands, a method tailored to compute excited state behaviour, spectroscopic properties as well as accurate ground state energies, while maintaining low computational cost is needed. Beckes B3LYP[31,34–36] functional has proven to be a reliable functional for a wide selection of computations[56] and is able to give reasonable results for TD-DFT calculations on similar systems[48] and will therefore be the method of choice for computational calculations in this thesis. The computational investigations conducted will be of adiabatic nature, not accounting for dynamic effects. Following vertical excitation and investigation of the PES from the Franck Condon point to different relaxation paths provides information about the minimum energy path (MEP) to the photoproducts.[57] This can be done via intrinsic reaction coordinate (IRC),

scanning a range of geometric parameters or using sophisticated methods to extrapolate a MEP between optimized structures, e.g. the nudged elastic bond method (NEB).[57,58] Local properties of interest for photophysical processes were discussed in chapter 1.1 and include conical intersections, funnels to lower electronical states and intersystem crossing. Exploration of these local properties on the potential energy surface allows for the rationalization of product formation, selectivity and barriers, as well as photophysical properties such as excited-state lifetimes, quantum yields, transient absorption and emission bands.[57]

4. Aim of this Work

In the introduction, the great potential of Cu-photoredox catalysis has been highlighted. Basic concepts of its mechanisms have already been established, yet the detailed description of the proposed inner sphere pathways is still incomplete. In this thesis different tools of physical organic chemistry will be used to investigate key intermediates to develop a deeper understanding of the unique traits of Cu(I)- and Cu(II)-photoredox catalysis. This involves computational, spectroscopical and synthetical approaches, cooperating closely with organic synthetics with valuable experience of this chemistry through daily use. The main questions addressed here are: i) How large is the effect of pre-coordination to the catalyst? Because of its short excited-state lifetime, Cu-photocatalysis might be dependent on coordination to substrates prior to excitation. A detailed description of the deactivation pathway could be valuable to understand the substrate scope of Cu-photocatalysis.

ii) Which specific role is the Cu-catalyst playing after excitation? Two different pathways have been proposed for Cu(I) photocatalysis. A rebound mechanism, involving formation of a Cu(III) intermediate and a ligand-exchange pathway of a Cu(II) intermediate. Especially EPR-spectroscopy might be very useful in identifying and tracking long-lived radical or paramagnetic intermediates, to shine light on the intricacies of these inner sphere processes. Understanding these is essential for understanding the selective formation of products, possible limitations and unknown opportunities of Cu-photoredox catalysis.

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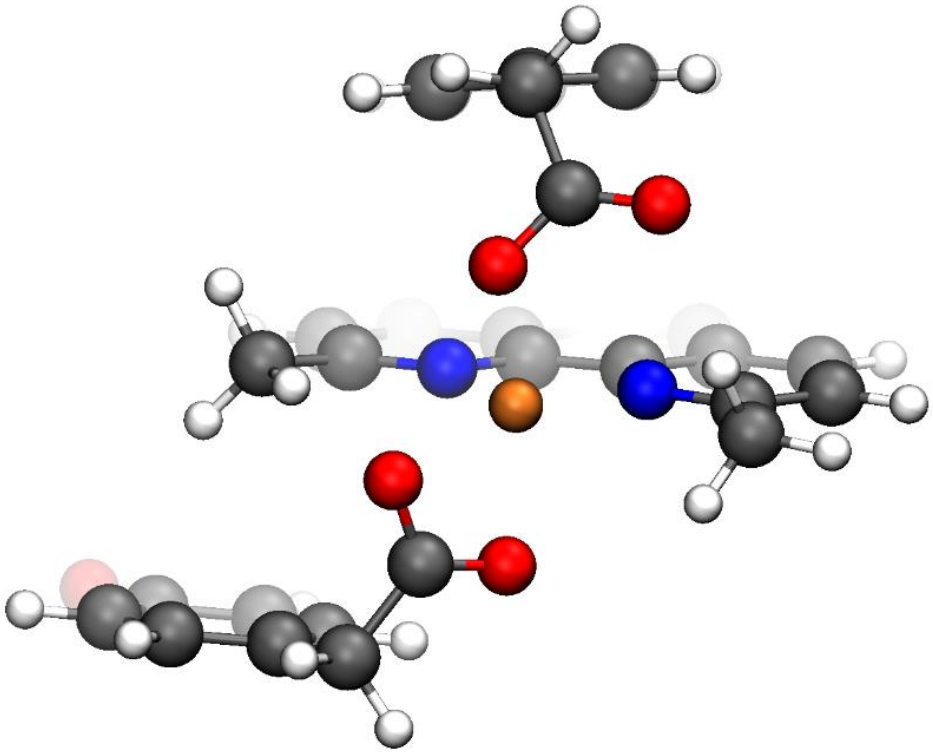
B. Mechanistic investigations on Copper(II)-photocatalyzed Decarboxylative Oxygenation of Phenylacetic Acids



Published in *Chemical communications (Cambridge, England)*: Copper(II)-photocatalyzed decarboxylative oxygenation of carboxylic acids.[1]

O. Reiser, J. Rehbein, F. N. Castellano: Supervision of the project

H. Sterzel: EPR Experiments, DFT and TD-DFT calculations, mechanistic explanation

A. Reichle, P. Kreitmeier, R. Fayad: Synthesis, Reaction optimization, control Experiments and additional spectroscopic investigations

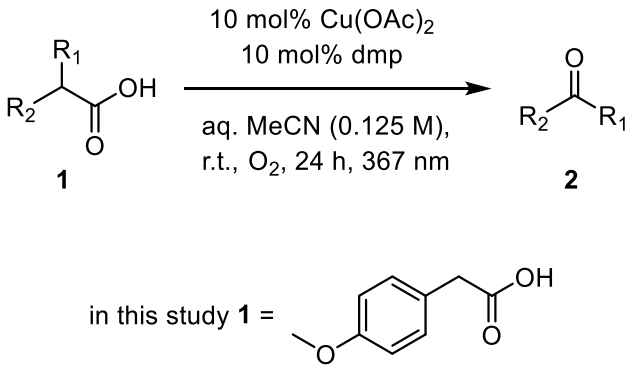
Additional support as stated in the paper.

1. Introduction

This thesis includes work that led to the publication of a paper on the Cu(II)-photocatalyzed decarboxylative oxygenation of phenylacetic acids, carried out in collaboration with the Reiser group.[1] The benefit of a Cu(II) based photocatalyst is in its pre-coordination to the substrate, outweighing the short excited state lifetimes of copper complexes[2] by involving the substrate in the excitation process. Via light-induced homolysis (LIH) the substrate molecule is being transformed into a reactive intermediate in the form of an organic radical. This is well known for a long time in the case of Cu(II)-chloride complexes. Already in 1962 Kochi proposed the homolysis of $Cu(II)Cl_2$ upon UV-irradiation to form a Cl-radical and Cu(I)Cl. Apart from halogens also azide-,[3] alkyl-,[4] enolate-[5] and carboxylate-ligands[6,7] seem to be suitable for homolytic bond cleavage. The decarboxylation in particular seems to be a promising source of alkyl radicals, which could then be coupled with a different functional group or to form a C-C bond.[8] In the paper by Li *et al.*[7] they showed that without an oxidant, no regeneration of the Cu(II) complex occurs, which resulted in a stoichiometric use of the Cu(II) salt. The Reiser group managed to close the catalytic cycle by the use of oxygen and could therefore reduce the use of Cu(II) salt to catalytic amounts. With the use of EPR- and UV/vis spectroscopy, as well as computational investigations, the mechanism of this transformation was explored, and the results will be discussed in the following.

2. Results and Discussion

The photocatalyzed decarboxylative oxygenation of phenylacetic acids by the Reiser group is shown in Scheme 1. A carboxylic acid **1** gets reduced to an aldehyde **2** by catalytic amounts of $Cu(dmp)(OAc)_2$ under irradiation at 367 nm. The reaction proceeds at room temperature under oxygen atmosphere for 24 h.



Scheme 1: General scheme of the photocatalyzed decarboxylative oxygenation of phenylacetic acid.[1]

It was shown that no reaction occurs in the absence of irradiation and only traces of product could be isolated in the absence of oxygen atmosphere. The addition of the dmp ligand increased the yield from 15% to 93% and the substrate scope ranged from primary and secondary phenyl acetic acids to cyclohexyl substituted carboxylic acids. In the following investigations the 4-methoxyphenylacetic acid will be used as the standard substrate. The investigations can be divided into three parts: i) Identification of the catalytically active species ii) Observation of the irradiation step from Cu(II) to Cu(I) iii) Identification of the nature of the organic radical intermediate.

Starting with the identification of the catalytically active specie, one has to consider that Cu(II)-acetates are prone to form different oligomers in solution, bridged by one or multiple acetate molecules.[9] Indeed, the Reiser group managed to crystallize the paddle-wheel structure **3** from a mixture of $CuSO_4$ and 4-methoxyphenylacetic acid (*Figure 14 A*). Subjecting paddle-wheel structure **3** to the reaction conditions lead to much lower conversion. This result could be rationalized by a rebound mechanism after Cu-O bond homolysis. As the one oxygen atom of **1** is still coordinated to the other Cu-centre of the dimer, decarboxylation is disfavoured resulting in an unproductive rebinding of the carboxyl radical to the formerly bound Cu-centre. As a consequence, catalytically active Cu(II)(**1**)$_2$ complexes would need to comprise of at least one monodentate coordination to the carboxylic acid. A paper by Schröder el al. revealed that small fractions of H_2O could break up $Cu(OAc)_2$ oligomers,[10] which indeed led to an ideal ratio of 2.2 vol% of H_2O in acetonitrile. As can be seen in *Figure 14*, while no considerably large effect on the UV/vis absorption could be observed (C), the EPR spectrum (D) shows an increase in intensity of the Cu-signal, with increasing H_2O content. A maximum is reached at 10.3 vol% and the intensity decreases again with higher water fractions. Presumably the water helps breaking up Cu-oligomers and as a result, the isotropic spectrum at low H_2O content changes to a complex anisotropic spectrum of Cu-monomers. In fact, EPR measurements of **3** yielded no EPR signal at all, opposed to **4** with a distinct signal at g = 2.13 (*Figure 14 B*). While the maximum effect of water on the formation of monomeric Cu is seen at ~10 vol%, the optimal reaction conditions need only 2.2 vol%. As the water content becomes too large, the effect of acetonitrile as the solvent might get diminished. Also, an excessive amount of water molecules might block several coordination sites of the Cu-centre, reducing the effectiveness of the photocatalyst. Considering these results, monomeric Cu(II)(**1**)$_2$ complex **4** was concluded to be the active catalyst in this reaction.

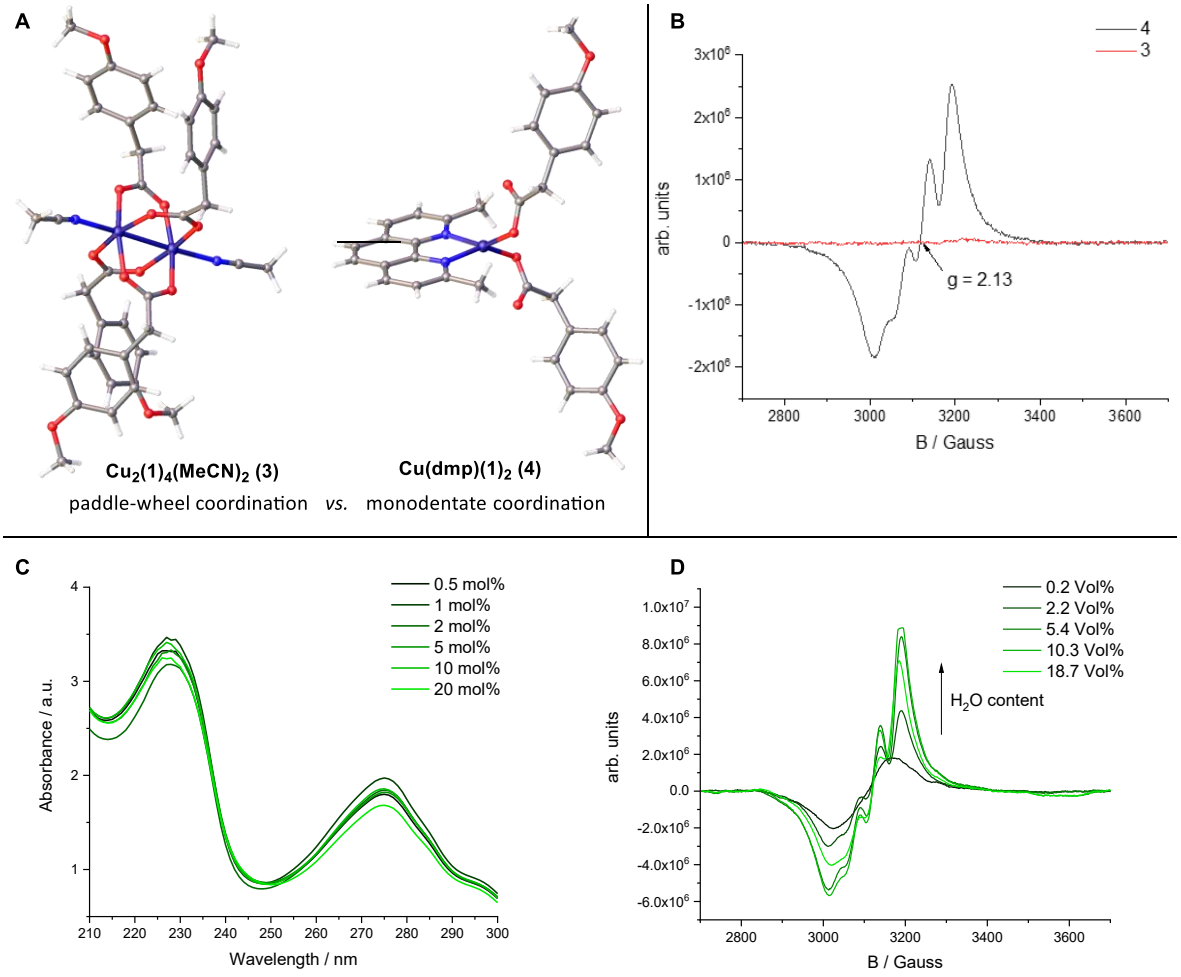


Figure 14: ***A)*** *Paddle-wheel structure 3 and monodentate coordination of Cu(II)dmp and 4-methoxyphenylacetic acid.*[1] ***B)*** *Cu(II)-complex* ***3*** *(6.25 mmol/L) and* ***4*** *(12.5 mmol/L) formed in situ in MeCN (2.0 mL), water (45 µL, 2.2 vol%) from Copper(II)-carboxylate at room temperature (25 °C).* ***C)*** *UV/Vis absorption spectrum of a H_2O-titration series of the reaction solution. Cu^{II}-complex* ***4*** *(12.5 mmol/L) formed in situ in MeCN (2.0 mL at room temperature (25 °C).* ***D)*** *EPR spectrum of Cu^{II}-complex* ***4*** *(12.5 mmol/L) formed in situ in MeCN (2.0 mL) at room temperature (25 °C). Microfwave frequency 9.33 GHz, modulation amplitude 25 G, Microwave Power 60 mW.*[1]

The photochemical behaviour of the reaction mixture was investigated using UV/vis and EPR spectroscopy as well as TD-DFT calculations. The experimental and simulated UV/vis spectra can be seen in *Figure 15*. The reaction mixture prior to irradiation (red line) fits the simulated spectrum of **4** (red dotted line), which shows an absorption maximum at 367 nm, and weak absorption above 400 nm. These excitations correspond to ligand-to-ligand charge transfer states from one carboxylic acid molecule to the dmp ligand and the other carboxylic acid.

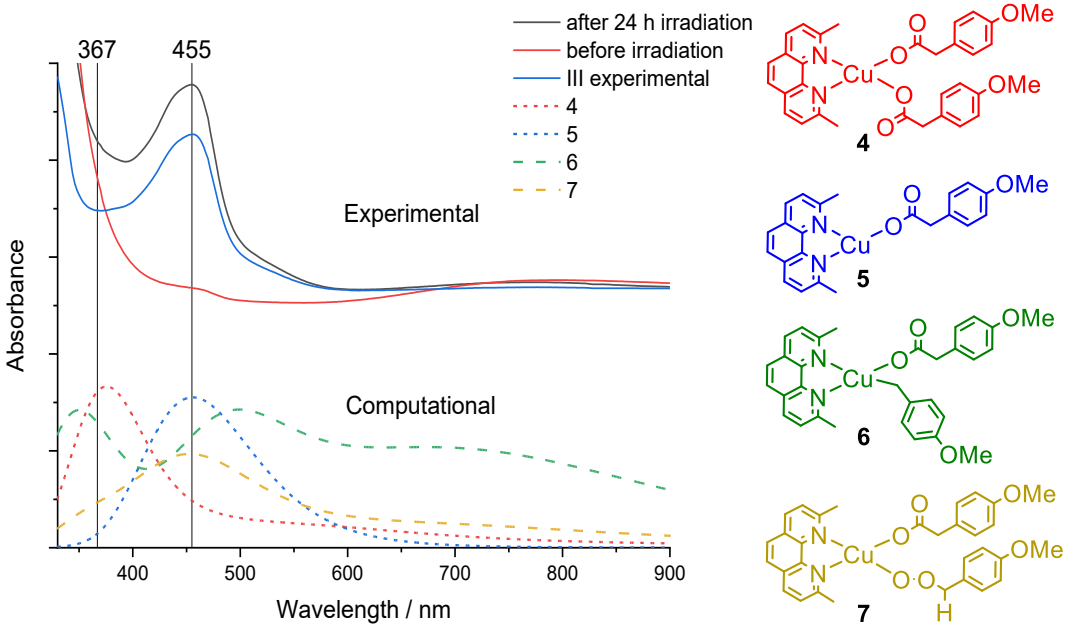
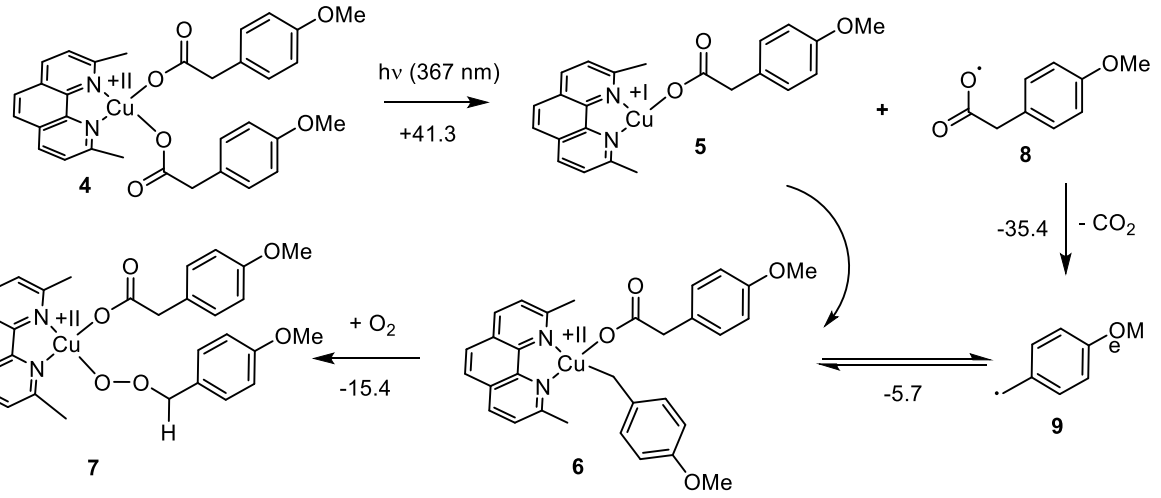


Figure 15: Comparison between experimental and calculated UV/vis spectra.[1]

After 24 h of irradiation at 367 nm, an absorption band at 455 nm appears (black line). We compared the new absorption band with **5** and both the experimental and the simulated spectrum (straight and dotted blue lines) fit the absorption maximum at 455 nm. They could however not reproduce the transient appearing in the 700 - 900 nm region. Considering intermediates **6** and **7**, the transient might be due to a rebound mechanism of the radical **9** to the Cu(I) centre after decarboxylation (*Scheme 2*). After initial LIH, which DFT calculations show to be energetically uphill, radical **8** may release CO_2 in a strongly exergonic process and form the alkyl radical **9** as reactive intermediate. **9** will eventually react with oxygen, but might be stabilized by binding to **5** to form Cu(II)-complex **6** and **7**. Since formation of a new Cu(II) species could not be detected by the means of EPR spectroscopy, this intermediate might be too short lived for a detection with EPR.



*Scheme 2: Postulated reaction pathway. Irradiation of **4** leads to LIH, forming Cu(I) complex **5** and radical **8**. Decarboxylation of **8** sets free the alkyl radical **9**, which can bind to the Cu(I) centre to form a Cu(II) complex **6** or **7**. $\Delta_R G$ values depicted are in kcal mol^{-1}.[1]*

The emergence of a pronounced Cu(I) absorption band in the UV/vis spectra, suggests that the re-oxidized Cu(II)-complex is less populated during irradiation. This was supported by a kinetic EPR measurement of the reaction mixture (*Figure 16*).

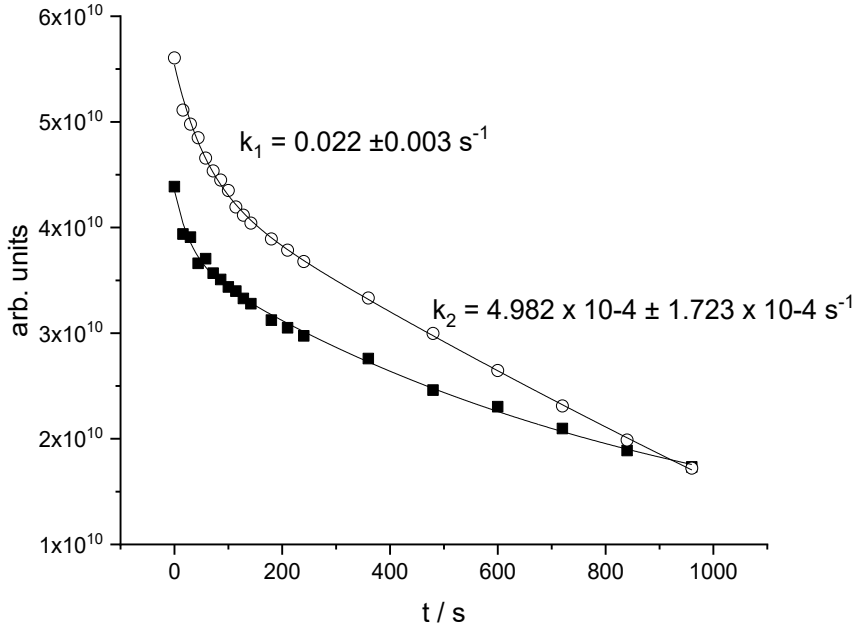


*Figure 16: Kinetic measurement of Cu(II) signal intensity during the reaction. The signal intensity was double integrated for the plot. The red and black data points resemble two independent measurements. For the determination of k-values the average of both measurements was used. k_1 resembles the kinetic in the early stage of the reaction and k_2 after 5 min reaction time. **1** (125 mmol/L), Cu^{II}-complex **4** (12.5 mmol/L) in MeCN (2.0 mL), water (45 µL, 2.2 vol%) at room temperature (25 °C). Irradiation at 365 nm with a radiant power of 30 mW under O_2 atmosphere.[1]*

The reaction mixture was irradiated for 15 min and the Cu(II) signal intensity was observed. After initial exponential decrease in intensity (~10^{-2}) during the first 5 min the signal decreases slower (~10^{-4}) and almost linearly. The absence of an organic radical in the EPR spectra suggests that either no organic radical is formed, or it is too short lived for detection. With the aim to trap the hypothesized organic radical the radical trap PBN and the spin trap TEMPO were used. PBN is known to react with radicals to form a stable radical, while TEMPO is a stable radical that can recombine with another radical, hence quenching its radical signature in the EPR spectrum. In *Figure 17* the EPR spectra prior to irradiation and after 20 min of irradiation of the reaction mixture including the corresponding radical/spin trap is shown. As the reaction proceeds the formation of a stable PBN-radical is observed as well as a decrease of the TEMPO signal, which confirms the formation of a radical.

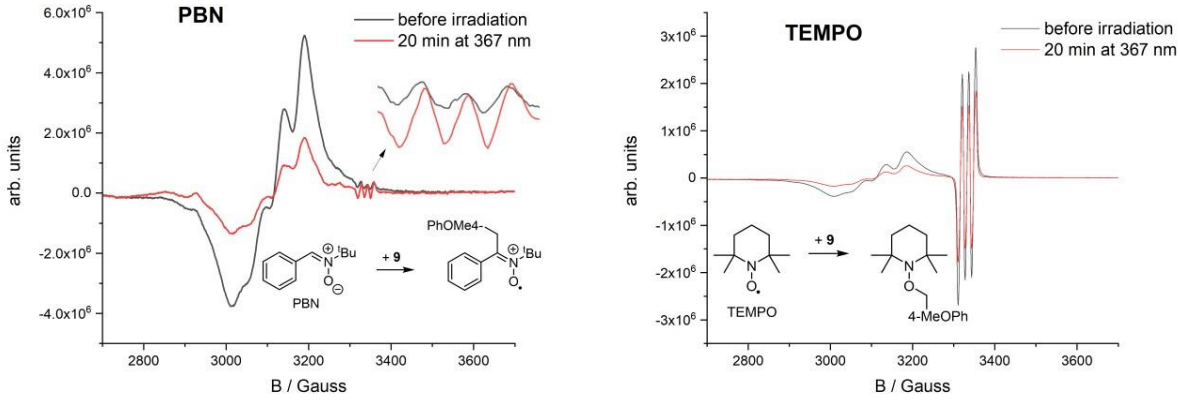


Figure 17: ***1*** *(125 mmol/L, 1 eq.), Cu^{II}-complex* ***4*** *(12.5 mmol/L, 0.1 eq) in MeCN (2.0 mL), water (45 µL, 2.2 vol%) at room temperature (25 °C). Irradiation at 367 nm with a radiant power of 30 mW.* ***PBN:*** *N-tert-Butyl-α-phenylnitrone (150 mmol/L, 1.2 eq.),* ***TEMPO:*** *TEMPO (12.5 mmol/L, 0.1 eq.*[1]

The calculated energetics and the kinetic studies suggest that the decarboxylation process of radical **8** and the following conversion to aldehyde **2** is energetically favoured and faster than the reoxidation procedure of the Cu-catalyst. Oxygen is being used both as a reagent for the aldehyde formation and to regenerate the catalyst. The question remains, whether radical **9** can also be coupled with different substrates before oxidation by O_2. Curiously in the absence of oxygen the Reiser group could identify the formation of a side product formed by reaction of radical **8** and **9**.[1] This product is not being formed in the presence of oxygen, which advocates the idea that oxidation of **9** by oxygen is in fact too fast for different coupling partners. Before radical **9** can get into close proximity of another coupling partner oxygen has already transformed the radical to complex **7**. In accordance with this hypothesis the attempt by the Reiser group to trap the radical with different nucleophiles in the presence of oxygen was

unsuccessful.[1] The efficient trapping of organic radical **9** was used to elucidate the kinetics of the reaction process (*Figure 18 A*). The kinetics of PBN-radical formation as well as the decrease of Cu(II) complex **4** show a mono-exponential behaviour in the same order of magnitude (Cu(II): 0.015 s^{-1}; PBN-R: 0.013 s^{-1}). The irradiation of complex **4** yields an EPR-silent molecule, presumably Cu(I). This transformation might be directly involved in the radical formation as the kinetics suggest. In a light on/off experiment (*Figure 18 B*) a slowdown of radical formation can be seen, whenever irradiation is paused. It is curious to note, that radical formation does not come to a complete halt, which could be rationalized by a delayed decay of the active intermediates. When irradiation is put back on, the formation of PBN-radical increases again. Presumably the interruption of the reaction did not damage the catalytic system or interfere with intermediates. This also confirms the presumption of repeated LIH to generate the reactive intermediate **8**, instead of initiation of a radical chain mechanism.

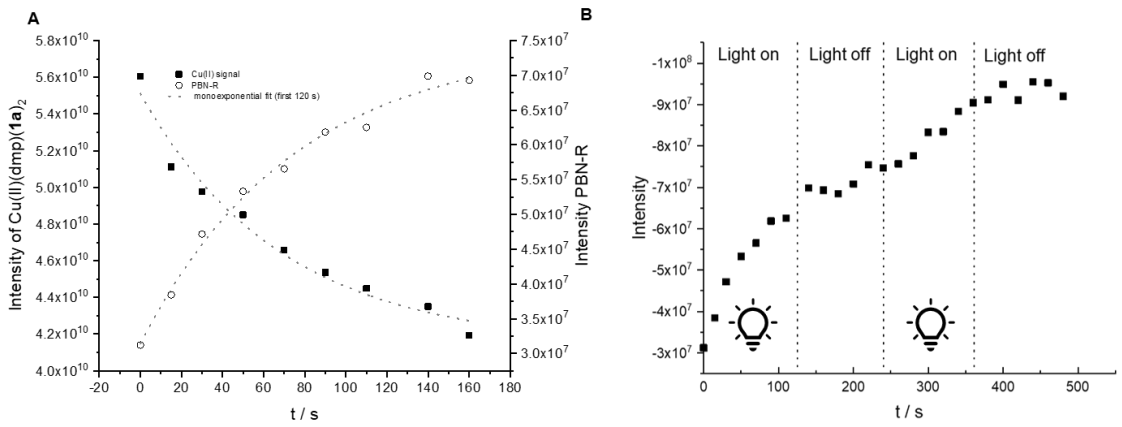


*Figure 18: **A)** Kinetic traces of the Cu(II) signal (black squares) with kinetial = 0.015 ± 0.004 s^{-1} and of the growth of the PBN-R signals (circles) with kinetial = 0.013 ± 0.002 s^{-1}. Fitted at early times with a single exponential function and assuming pseudo-first order conditions for the PBN-R formation. **B)** Light on/off cycle experiment, showing the PBN-R signal intensity.[1]*

The findings of the discussed experiments are condensed in *Figure 19*. Supported by our H_2O-titration study, the addition of small water fractions helps breaking up aggregates of Cu-complexes to produce the active catalyst **4**. LIH at 367 nm overcomes the barrier of 41.3 kcal mol^{-1} and reduces the Cu(II)-catalyst to Cu(I) (**5**). This has been backed up by UV/vis, TD-DFT and kinetic EPR studies. The decarboxylation from **8** to **9** is strongly exergonic (-35.4 kcal mol^{-1}) as well as oxidation under O_2 atmosphere (-21.1 kcal mol^{-1}). This is supported by radical trapping experiments with PBN and TEMPO. Formation of a stabilizing complex **6** is theoretically feasible and could fit the observed transient in the 700-900 nm region in the UV/vis spectrum. Formation of complex **7** eventually leads to a strongly exergonic

cleavage of the peroxide bond (-57.2 kcal mol^{-1}) to form product **2** and complex **10**, which can regenerate the catalyst **4** by ligand exchange (-24.2 kcal mol^{-1}).

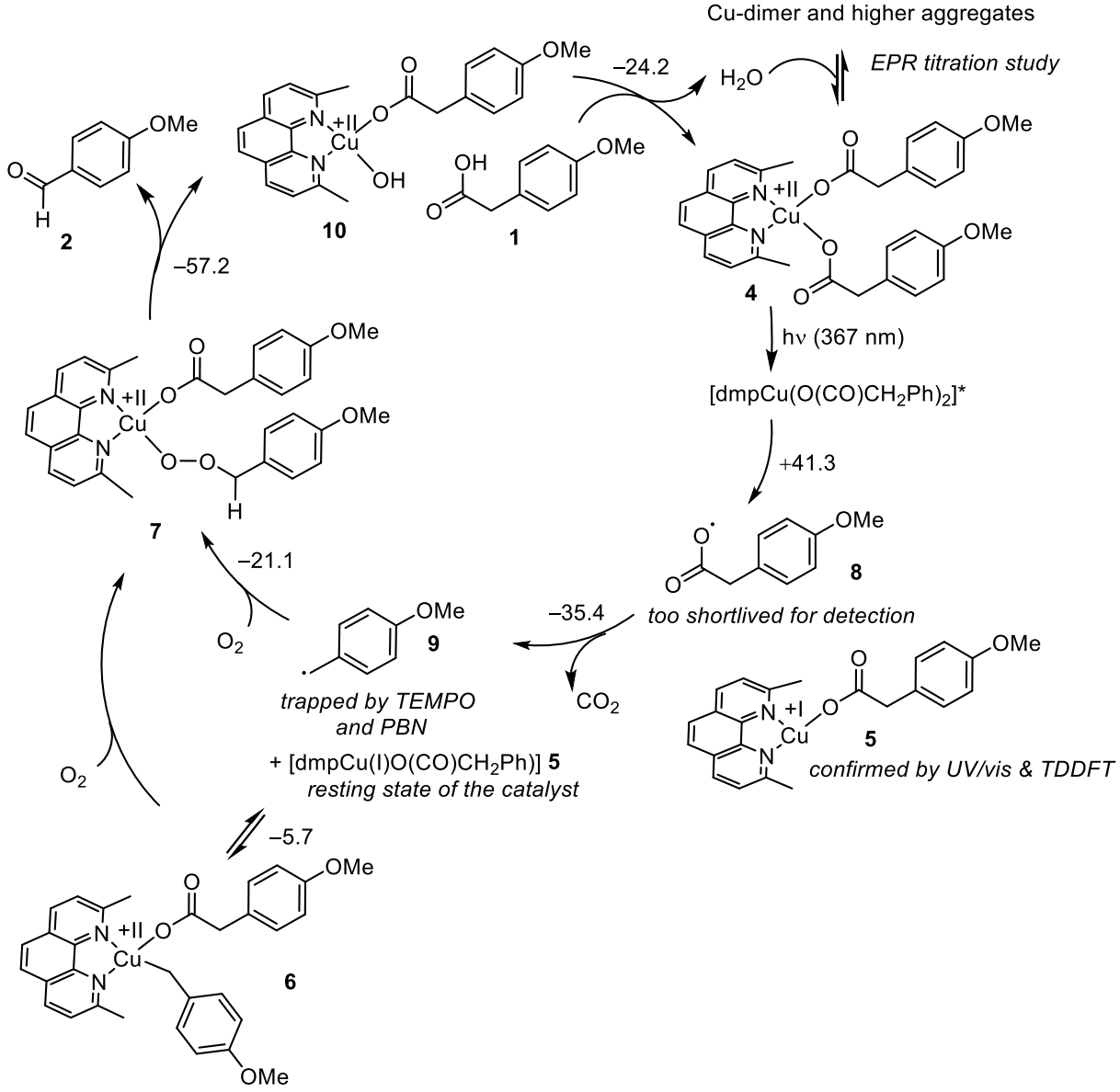


Figure 19: Proposed mechanism based on experimental and computational investigations. $\Delta_R G$ values depicted are in kcal mol^{-1}.[1]

3. Conclusion

Mechanistic studies on the Cu(II)-photocatalyzed decarboxylative oxygenation of phenylacetic acids were conducted. The mechanistic proposal for Cu(II) based photoredox catalysis from chapter 1.2 fits our findings. Crucially, we were able to identify the formation of alkyl radical **9** and reinforced the presumption of a stabilizing effect of the Cu-catalyst on intermediate **6**, enhancing the selectivity of the reaction. A rational for the inaccessibility of **9** for other

nucleophiles in the presence of oxygen was found. While we could show that intermediate **9** is indeed being formed, oxidation by oxygen seems to be too fast for other coupling partners. Finding alternative oxidants with slower or no reactivity towards intermediate **9** will be the key in enabling a wide range of coupling partners to the substrate molecule. Great caution needs to be exercised in the choice of the Cu-salt and its reaction conditions. The coordinating behaviour of copper and its paramagnetic nature in its +2-oxidation state enables formation of a variety of different aggregates, which could hinder its potential of LIH. As the pre-coordination of the substrate to the catalyst is a key feature of enabling the photocatalytic properties of Cu(II) with its short excited state lifetimes, more detailed information on the coordination of different substrates and the prerequisites for LIH bears high potential for new transformations. This was shown in this work by the inactive paddlewheel structure, which does not lead to LIH opposed to a monomeric coordination. Already many groups have pushed research on Cu(II)-photoredox catalysis and with increasing knowledge of the intricacies of these transformations, its potential is more and more recognized.[11]

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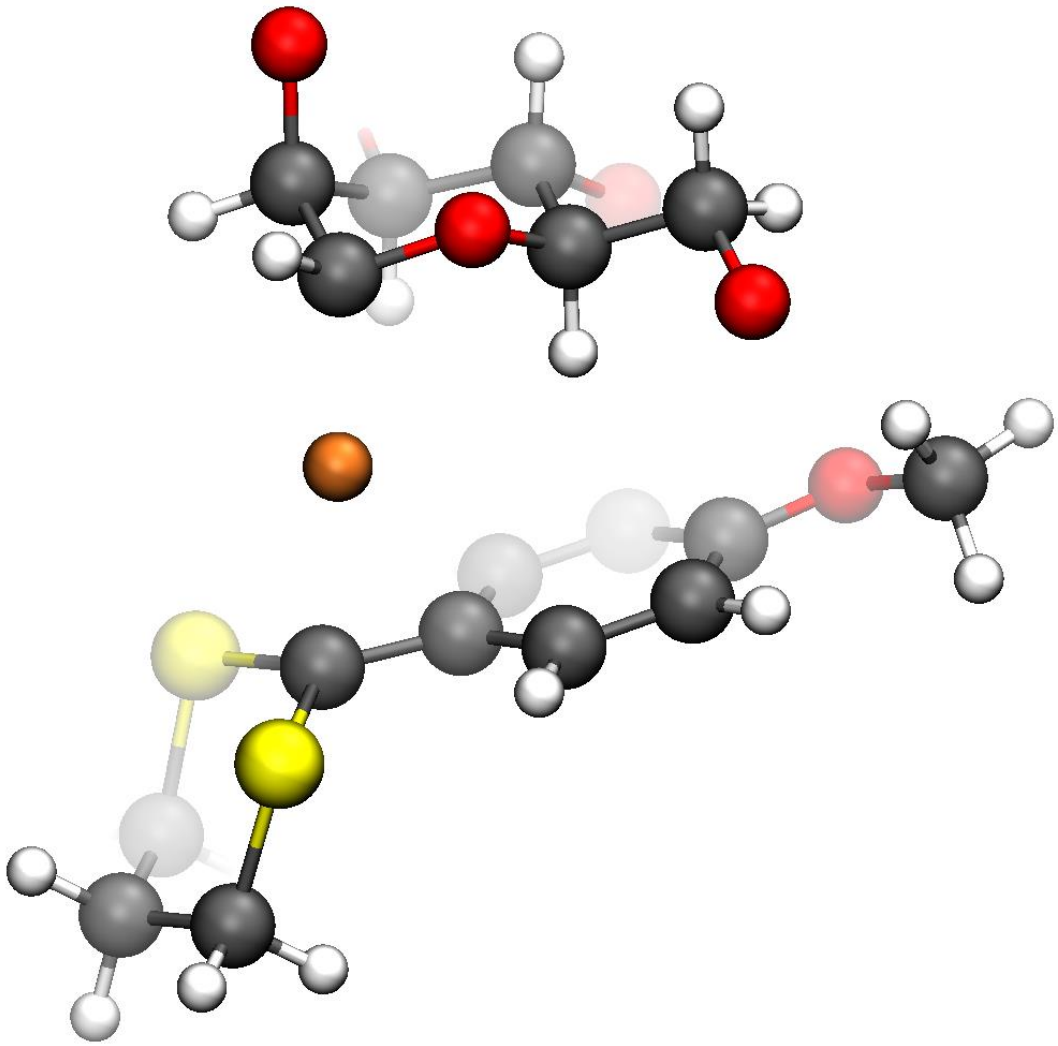
C. Investigations on the Radical Mechanism in the Stereoselective Synthesis of α- Mannosides



Published in Chem. Eur. J.: Efficient Copper-Catalyzed Highly Stereoselective Synthesis of Unprotected C-Acyl Manno-, Rhamno- and Lyxopyranosides.[1]

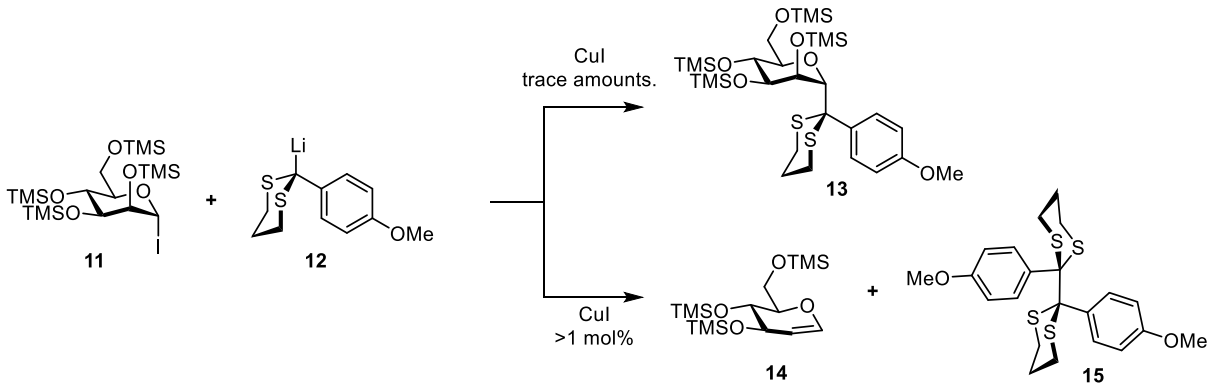
J. Rehbein, N. Schützenmeister: Supervision of the project

H. Sterzel: Mechanistic investigations, EPR Spectroscopy, UV/vis Absorption, Computational Chemistry

J. Boehlich: Synthesis, corresponding analytics, sample preparation for mechanistic investigations

1. Introduction

In their effort to create one pot syntheses for the creation of C-acyl manno-, rhamno- and lyxopyranosides, Boehlich and Schützenmeister developed an efficient stereoselective Cu-catalysed synthesis.[1] Previous protocols for β-selective synthesis of C-acyl glycosidic compounds[2] revolved around generation of α-glycosyl iodide[3] of several monosaccharides and subsequent S_N2 reaction with a lithiated dithiane.[4] By the means of Cu-catalysis however, α-selective C-acylation of D-mannose was achieved (*Scheme 3*). While high catalyst loadings inhibited the reaction and increased formation of byproducts glucal **14** and dithiane dimer **15**, trace amounts of CuI yielded exclusively the α-anomer. Addition of the radical inhibitor butylated hydroxytoluene (BHT) leads to lower yields, hinting at a radical mechanism. In the previous chapter we were able to reinforce the idea of Cu being able to stabilize radical intermediates. To get deeper insight into the effect of CuI in this transformation and expand the understanding of Cu-chemistry related to radical intermediates, investigations by the means of UV/vis, CW-EPR as well as DFT and TD-DFT studies were carried out.

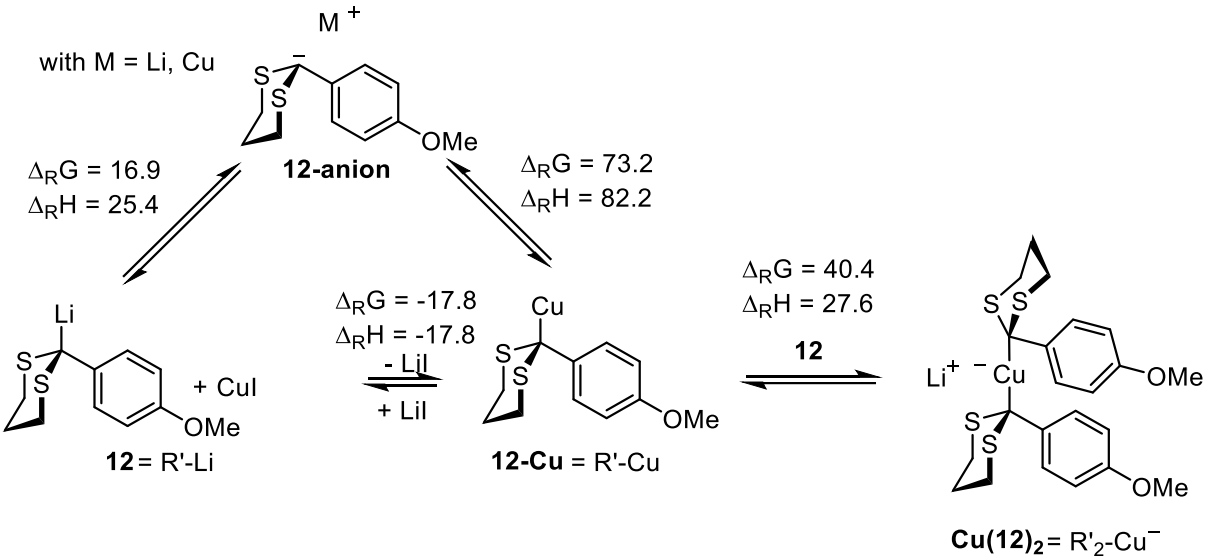


*Scheme 3: General scheme of the Cu-catalysed reaction of α-mannosyl iodide **11** with lithiated dithiane **12**.*

2. Results and Discussion

Based on the experimental observations, five possible mechanistic scenarios have been evaluated by DFT and TD-DFT calculations. In addition to a Cu(I)/Cu(III) cycle the formation of free radicals via SET, a S_RN-Mechanism[5] and an ionic pathway were evaluated. Furthermore, formation of Gilman-Cuprates is known for mixtures of Cu(I) and organolithium compounds[6] and could lead to a Corey–Posner–Whitesides–House reaction.[7] In principle, the formation of Gilman Cuprates (**Cu(12)$_2$**, *Scheme 4*) was seen as an option, although the nucleophilicity of these is lower than for the original lithiated dithiane and the stereoselectivity would be determined by the S_N2 mechanism to lead to the β-anomer (**13β**). In addition, the

thermodynamic evaluation of forming **Cu(12)$_2$** suggests it is actually not a feasible process, which excludes this mechanistic option altogether.



Scheme 4: Formation of different dithiane-species. Energies in kcal mol^{-1}.[1]

This leaves the scenario of the Cu-dithiane **12-Cu** playing a key role in the mechanism of the alkylation. Since transmetallation of **12** to **12-Cu** is favoured by -17.8 kcal/mol formation of **12-Cu** in solution is possible. Although an uphill reaction, dissociation of **12** to **12-anion** is to be expected in solution of a coordinating solvent like glyme. Further indication is provided by experimental UV/vis spectra. In the reference spectrum of **12** with and without CuI a shoulder at 504 nm is visible (*Figure 20*).

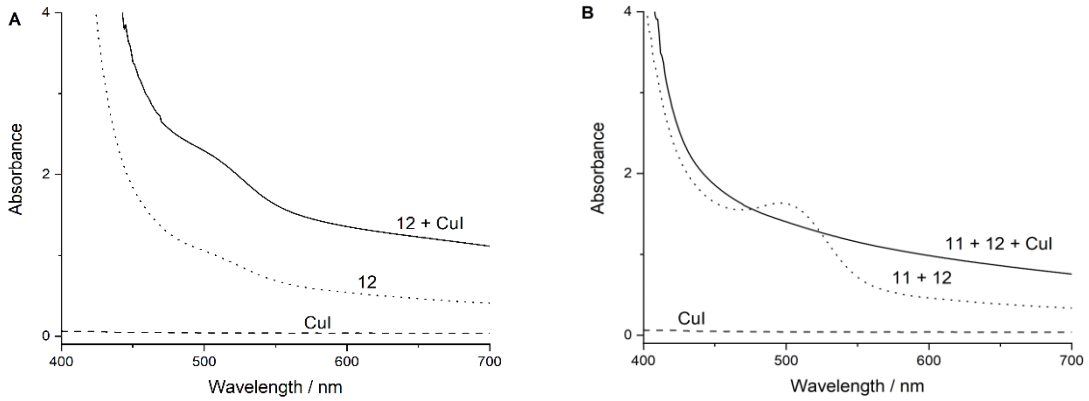


*Figure 20: A) Solutions of **12** (185 mmol/L, 2 equiv.) and CuI (0.925 mmol/L, 1 mol%) in glyme; B) Solutions of **11** (92.5 mmol/L, 1 equiv.), **12** (185 mmol/L, 2 equiv.) and CuI (0.925 mmol/L, 1 mol%) in glyme.[1]*

Similar dithianyl-anions have shown to absorb in the same region (λ_{max} for similar dithianyl ions: 506 nm).[5] This UV/vis signature appears in both Cu-free and Cu-catalysed reactions of

11 and **12**. After initial formation of a Lewis acid-base complex multiple different pathways can be considered (*Figure 21* and *Figure 22*).

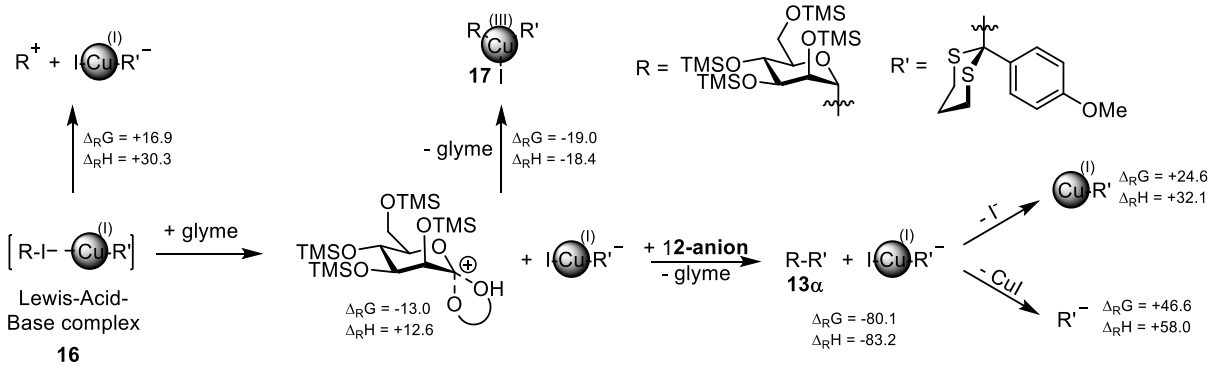


Figure 21: Ionic mechanism after heterogenic dissociation of the Lewis acid-base complex. Energies in kcal mol^{-1}.[1]

Heterolytic dissociation of the Lewis acid-base complex (*Figure 21*) is thermodynamically uphill. Considering a stabilizing effect of the solvent to the mannosyl ion the dissociation is kinetically favoured ($\Delta_R G = -13.0\ \frac{kcal}{mol}$). While free **12-anion** could react with the mannosyl cation to **13α**, the anionic dithianyl-CuI-complex is unlikely to release CuI or iodine. Since only traces of CuI are present in the solution, this step might stop the Cu-catalysed reaction. Taking the experimental results of BAT disrupting the reaction into consideration, an anionic pathway is unlikely.

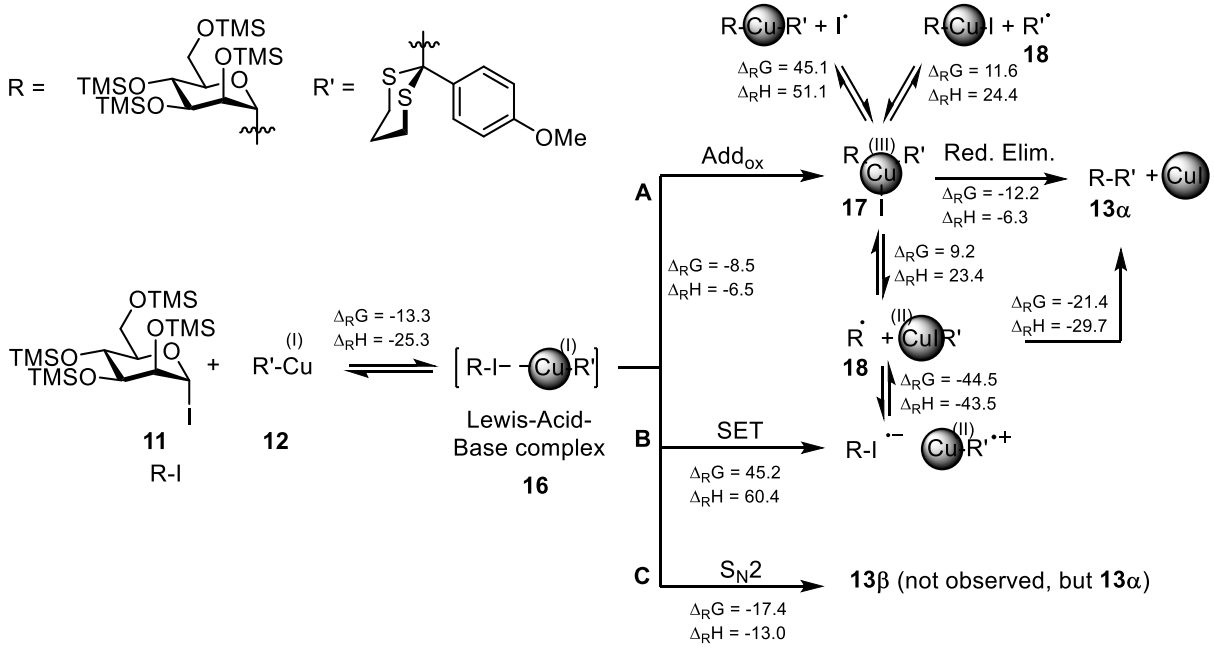


Figure 22: Comparison of Cu-catalysed pathways. Energies in kcal mol^{-1}.[1]

Oxidative addition (*Figure 22* **A**) under formation of a Cu(III) intermediate, followed by reductive elimination to **13α** is thermodynamically feasible. While homolysis from Cu(III) to Cu(II) is uphill, the energy difference could be small enough to allow for the formation of side products via **18** and **19**. Even though the S_N2 reaction (**C**) is thermodynamically feasible, this mechanism can be excluded due to the absence of **13β**. A radical pathway via initial single electron transfer (SET) (**B**) has a high barrier in the Cu-catalysed reaction. However, SET between **11** and **12** in the Cu-free reaction (*Figure 23*) seems to be much more likely, as the barrier is significantly lower and entropic effects favour the overall reaction to **18** and **19**.

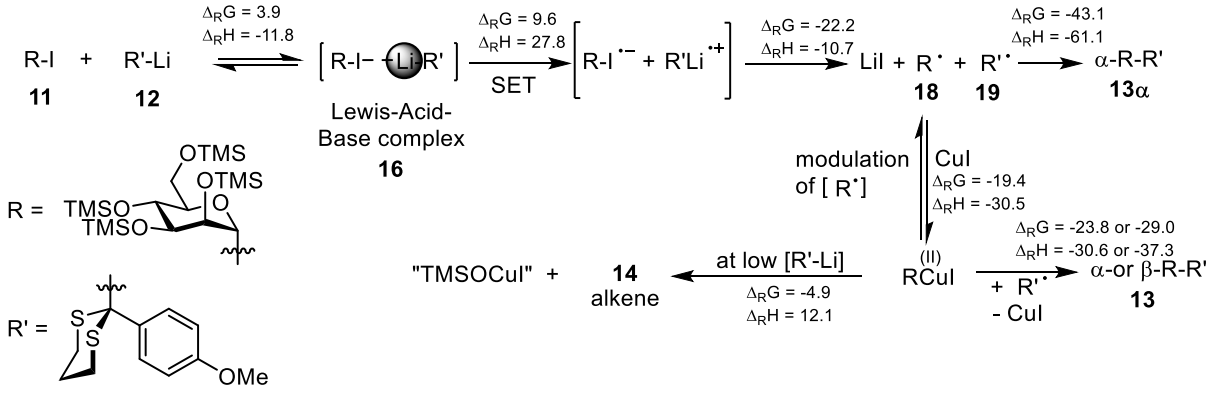


*Figure 23: SET mechanism of the Cu-free reaction between **1** and **2**. Energies in kcal mol^{-1}.*[1]

Comparison of HOMO-LUMO energy gaps of **11** and different dithianyl species show, that SET from **12-anion** has a significantly smaller HOMO-LUMO gap than **12** and **12-Cu** (**12**: Δε = 5.44 eV; **12-Cu**: Δε = 5.99 eV; **12-anion**: Δε = 2.18 eV).

Following the CW-EPR signature over an extended period of time gave further insight into the formation of Cu(II) and radical intermediates. Monitoring of the reaction solution at room temperature indicated no presence of a Cu(II) species. The high dilution and low catalyst loading renders the dimerization/aggregation of a Cu(II) species to diamagnetic compounds[8] rather unlikely. Even though the optimized reaction conditions use only 0.26 mol% CuI, a higher catalytic loading of 1.0 mol% was used in the mechanistic studies to ensure that all possible radicals were formed and can be detected during the EPR experiment. Given the sensitivity of the EPR, lack of a Cu(II) signal supports a Cu(I)/Cu(III) cycle. Interestingly, instead of an originally expected Cu(II) specie an organic radical signal appears at the onset of both Cu-catalysed and Cu-free reactions (*Figure 24*). While this radical signal has no resolved hyperfine coupling, in the course of the Cu-catalysed reaction a second signal overlaps with the first one, featuring hyperfine splitting of $\alpha_I = 15.7\ G$ and $\alpha_{II} = 12.6\ G$.

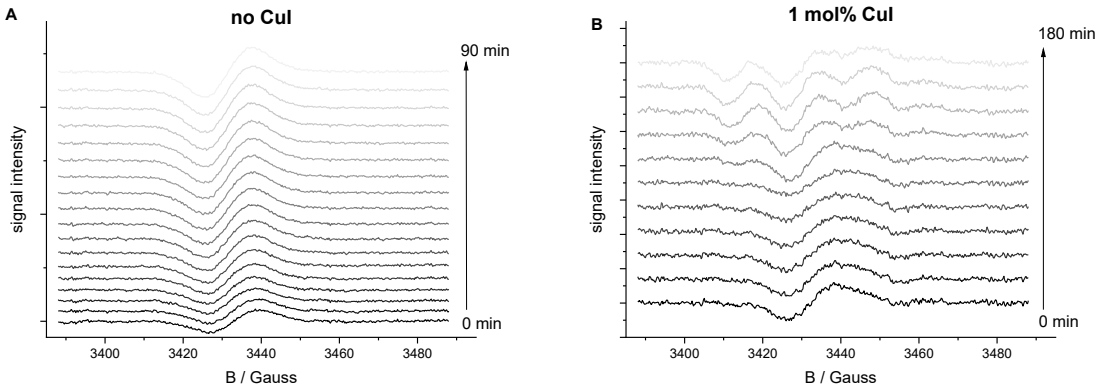


*Figure 24: A) Solution of **11** (92.5 mmol/L, 1 equiv.) and **12** (185 mmol/L, 2 equiv.) in glyme. measurement over 90 min in 5 min intervals; B) Solution of **11** (92.5 mmol/L, 1 equiv.), **12** (185 mmol/L, 2 equiv.) and CuI (0.925 mmol/L, 1 mol%) in glyme. measurement over 180 min (from bottom to top): First three measurements in 5 min intervals, subsequent measurements in 15 min intervals.[1]*

The first radical signal appearing in the Cu and Cu-free reaction mixtures is identical (*Figure 25*) and is therefore independent of the presence of copper in the mixture. This fits the previous statement that SET from **12-anion** and **11** is possible. However, this would produce two different radicals, while only one signal can be observed in the early stages of the reaction. A rational for this could be the lower inertness under the reaction conditions for the mannosyl radical (RSE (**18**) = -8.6 kcal/mol, RSE (**19**) = -24.6 kcal/mol).

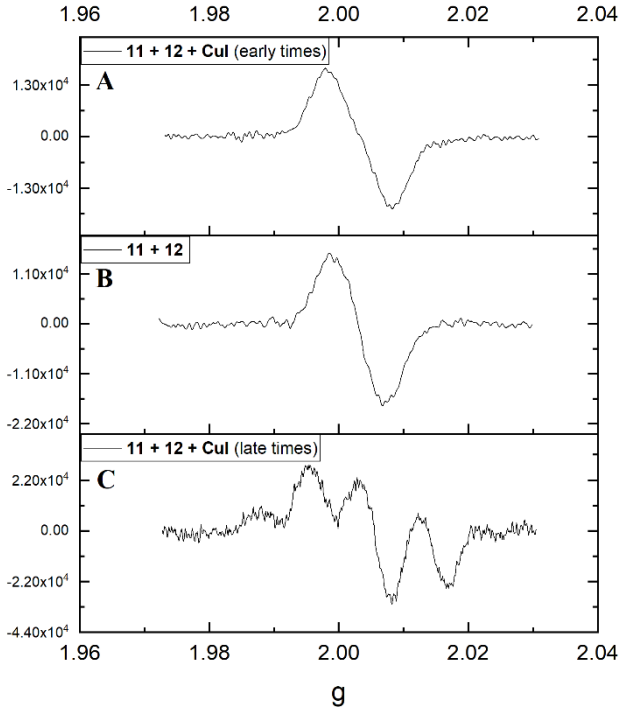


*Figure 25: CW-EPR spectra A) and C) **11** (1 equiv.), **12** (2 equiv.) and CuI (1 mol%); B) **11** (1 equiv.), **12** (2 equiv.) and CuI (1 mol%).[1]*

Due to its instable nature mannosyl-radical **18** is unlikely to be persistent enough given the reaction conditions, hence the observed radical in the early stages has to be the dithianyl-radical **19**. Although recombination of the radicals to furnish **13** is predicted to be a thermodynamically steep downhill process ($\Delta_R G = -43.1\ kcal/mol$), product formation is not observed from this two-component reaction. Surprisingly, the characteristics of the emerging second radical signal in the presence of copper fit the mannosyl radical, as literature data of carbohydrate radicals feature similar coupling constants.[9] At later stages of the reaction, less dithianyl-radical is present to converge copper bound mannosyl radical **18** into **13**, **14** or any other unidentified side product, which enhances its lifetime. Complementary UV/vis studies of the two- and multicomponent mixtures in combination with TD-DFT calculations provided further evidence of the discussed intermediates (*Figure 26*).

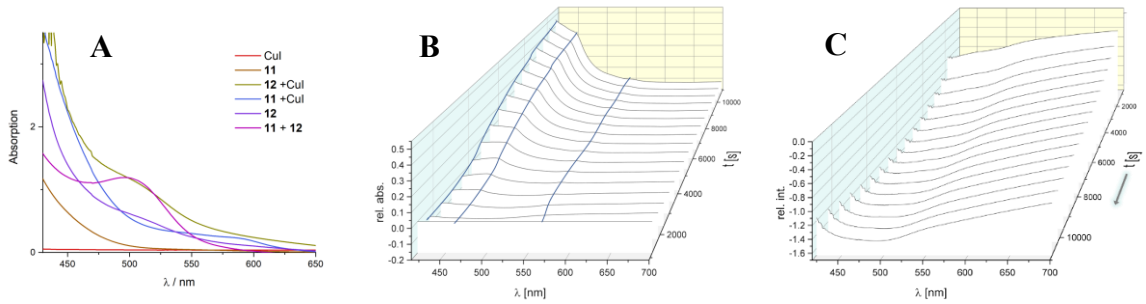
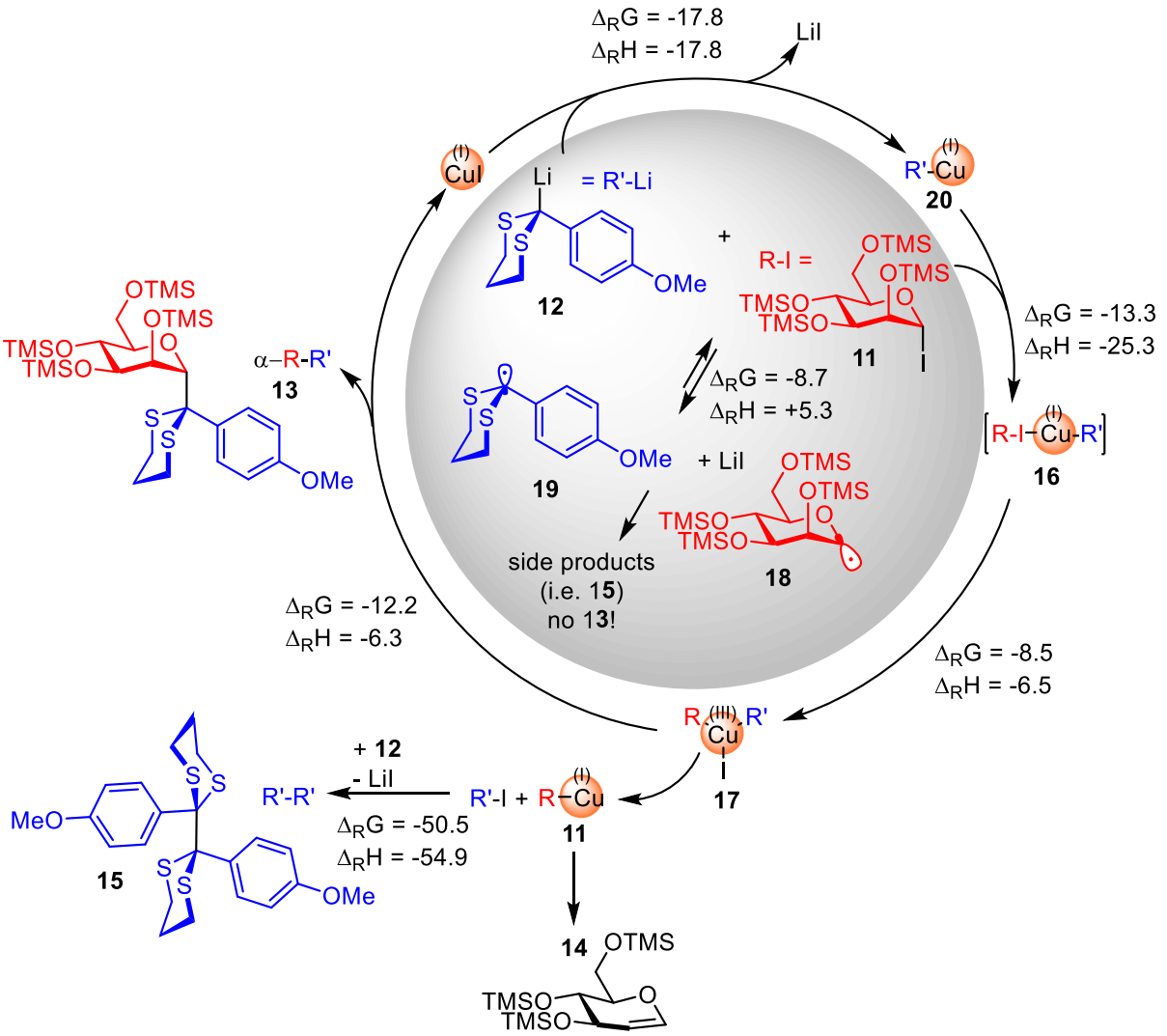


*Figure 26: UV/Vis spectra of A) Single and two-component solutions in glyme; B) reaction mixture of **11** (1.00 equiv.) and **12** (2.00 equiv.); C) **11** (1.00 equiv.), **12** (2.00 equiv.) and CuI (1.00 mol%).*[1]

In the two-component mixture (without CuI) a steady increase of the UV/vis signature at 420 nm can be observed. This matches the accumulation of radical **19** and fits TD-DFT simulations of its UV/vis absorption. In the presence of CuI however, a sharp decline of the instantaneously occurring band can be seen. The proposed diamagnetic Cu-complexes turn up in the multi-component solution with typical kinetics of a transient followed by a slow reoccurrence at the end of the transformation with broad absorptions >550 nm. Based on the findings from EPR, UV/vis as well as DFT and TD-DFT calculations a catalytic cycle can be formulated as shown in *Scheme 5*.



*Scheme 5: Competing pathways of the reaction. Within the circle the uncatalyzed spontaneous SET is described. Outside the circle CuI catalysed reaction to selective formation of **3** is shown. Energies are given in kcal mol^{-1}.[1]*

3. Conclusion

Two pathways are most likely happening simultaneously in the multi-component reaction mixture. While a pathway without CuI leads to the observed side products **14** and **15**, a productive path involves most likely a Cu(I)/Cu(III) cycle. Copper takes on the dual role of stabilizing the mannosyl radical **18** and ensures close proximity of the reaction partners by forming a formal Cu(III) specie **17**. Reductive elimination regenerates CuI and furnishes **13** with formal retention of configuration (i.e. **13α**). The astounding capabilities of Cu to both stabilize radical intermediates and to selectively find a coupling partner were shown. It is notable, that trace amounts of CuI were sufficient to impact the product formation. This implies

a high affinity of Cu to interact with these organic radicals and provides a strong contrast to the higher catalyst loadings in photocatalytic reactions using Cu.

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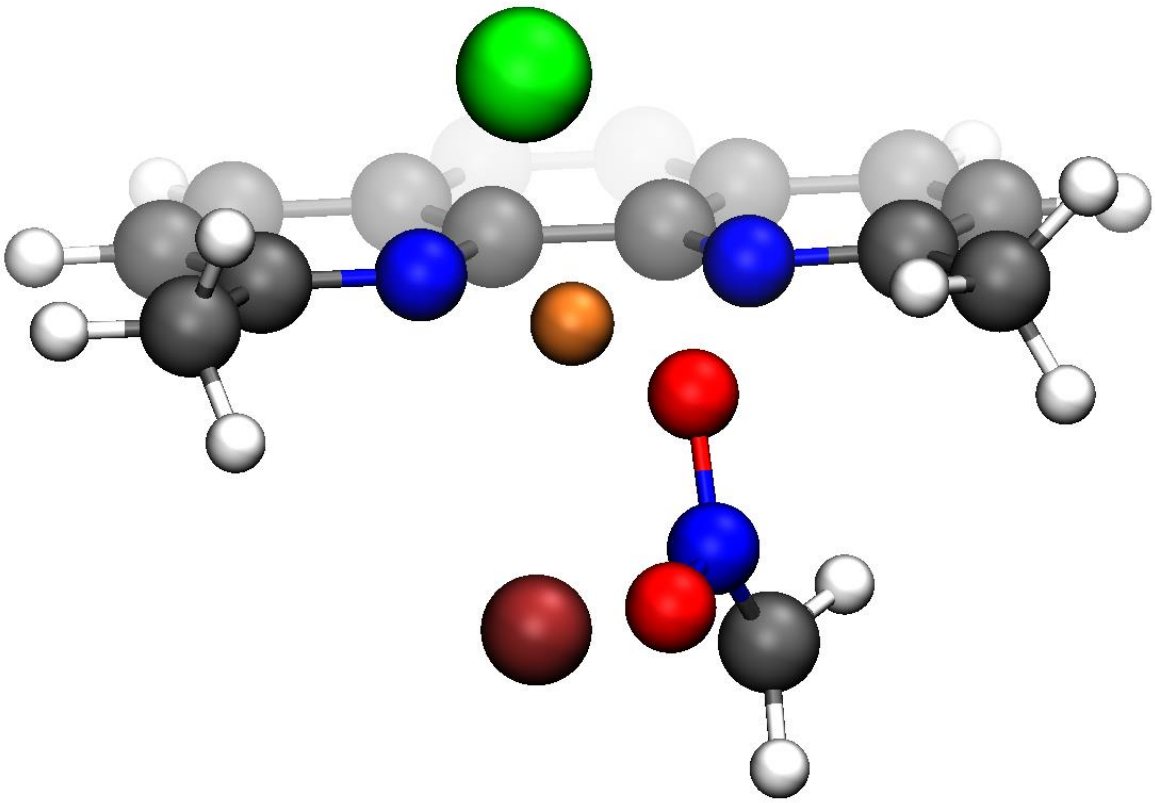
D. Cu(I)-photocatalyzed Bromonitroalkylation of Olefins: New Evidence for Highly Efficient Inner Sphere Pathways



Published in *Angew. Chem. Int. Ed.*: Cu(I)-photocatalyzed Bromonitroalkylation of Olefins: New Evidence for Highly Efficient Inner Sphere Pathways.[1]

J. Rehbein, O. Reiser: Supervision of the project

Hannes Sterzel: Mechanistic investigations, EPR experiments, computational chemistry

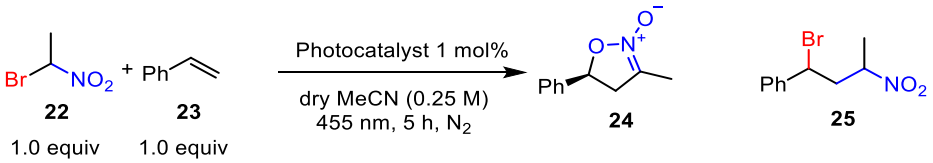
A. Reichle, M. Koch, L. Großkopf, J. Floss: Synthesis, reaction optimization and control experiments and corresponding analytics, UV/vis Absorption, quantum yield and fluorescence quenching measurements

Unpublished Results by H. Sterzel: EPR spin-trapping experiments, synthesis and experiments with Cyclopropyl-bromonitromethane, NMR and MEP calculations, mechanism (refined from previous publication[1])

1. Introduction

The Cu(I)-photoredox chemistry was introduced in chapter 1.2 and is subject of investigation in this chapter. With various different transformations possible, the key feature of its chemistry is the ability of coordination to intermediates after initial SET to further influence the reaction process.[2] As has been established in the previous chapter, already very low concentrations of Cu(I) (< 1 mol%) in the solution are sufficient to dramatically change the reaction path of radical intermediates. Cu(I) photocatalysis however, usually requires higher catalyst loadings (> 1 mol%), conceivably due to the excitation process. To gain more information on key intermediates and examine the details of the proposed inner sphere mechanism, the Cu(I)-photocatalyzed Bromonitroalkylation of olefins was investigated. This reaction is especially suitable, as it can be compared to the Ir-catalysed reaction by Ooi *et al.*, which shows a different selectivity.[3] In *Table 1* the direct comparison from the Reiser group between both catalysed reactions is shown.[1]

Table 1: Difference between Ir- and Cu-catalysed reaction of Bromo-nitroethane with styrene.[1,3]

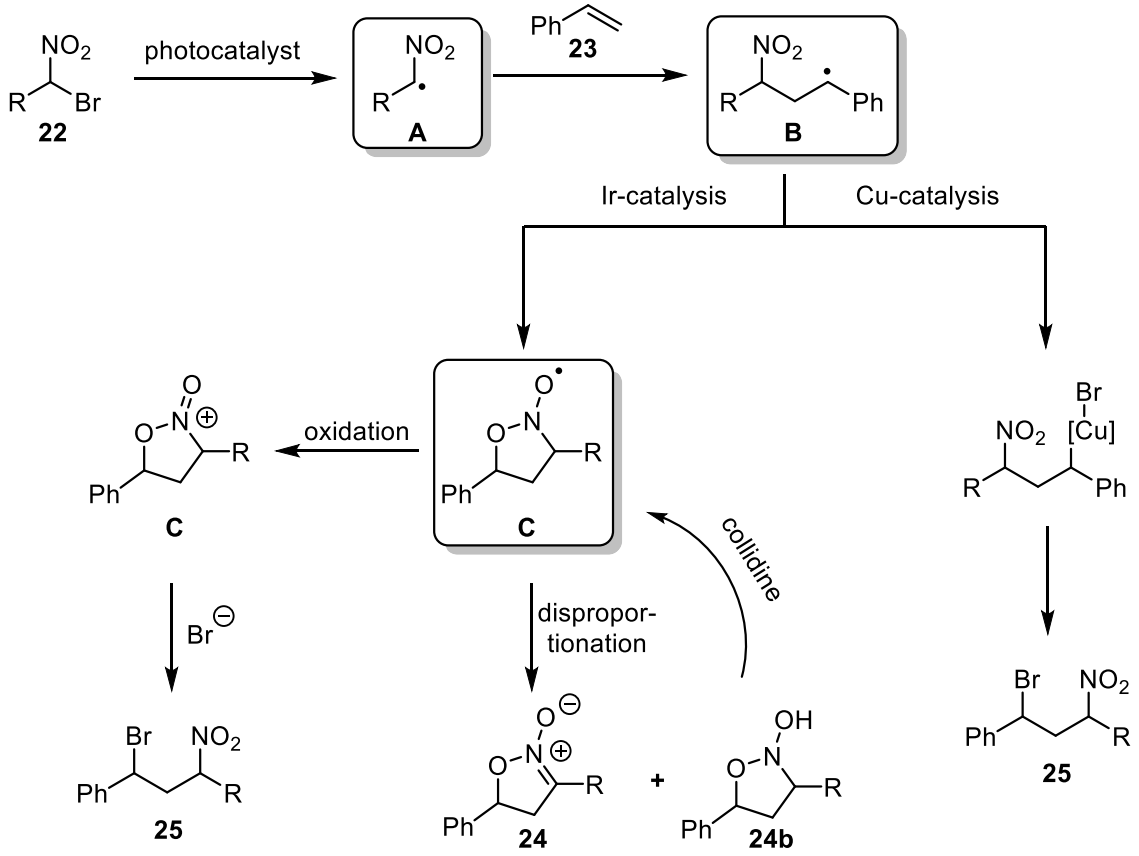


Catalyst	$E_{1/2}(M^+/M)$ V vs. SCE	Additive (1.0 equiv)	Yield 24 [%]	Yield 25 [%]
$[Cu(dap)_2]Cl$	+0.62	-	0	88[1]
$Ir(ppy)_3$	+0.78	-	7	31
$[Cu(dap)_2]Cl$	+0.62	Collidine	0	90
$Ir(ppy)_3$	+0.78	Collidine	57	traces

[1]H-NMR-yield using 1,1,2,2-tetrachloroethane as internal standard. [1] after 2h.

Two different products **24** and **25** are formed. While the $Ir(ppy)_3$ catalysed reaction yields a mixture of both products and with addition of collidine shifts its reactivity to almost form the cyclized product **24** exclusively, the Cu-catalysed reaction forms only product **25** and increases the yields to ~90%, without switching reactivity in presence of collidine. The Ooi group rationalized the Ir-catalysed reactivity with the formation of radical **A** after initial SET, which then reacts with the olefin to form radical **B** (*Scheme 6*). This radical then undergoes spontaneous cyclization to form nitroxyl-radical **C** as persistent radical intermediate. Depending on the redox ability of the catalyst different reaction paths can be accessed. Oxidation of radical **C** enables ring-opening via addition of a bromide ion to yield product **25**.

Under reductive conditions disproportionation of radical **C** is enabled yielding product **24**. The addition of collidine aids in the reactivation of side product **24b** to intermediate **C** and therefore increases the conversion to product **24**. As the oxidation potential of $Cu(dap)_2Cl$ is even smaller than the oxidation potential of $Ir(ppy)_3$ (*Table 1*), the afore mentioned mechanism would favour formation of product **24** in the Cu-catalysed reaction. Since no traces of product **24** are formed, the question arises, whether the Cu-catalyst already interferes with the formation of intermediate **C** and selectively adds bromine to the radical intermediate **B** instead, producing product **25**.



Scheme 6: Reaction scheme of Ir- and Cu-catalysed reaction of Bromo-nitroalkane with styrene.

The specific nature of the Cu-catalysed bromonitroalkylation of olefins will be investigated, with a focus on rationalizing the selectivity by finding key intermediates and looking into the excitation process of the catalyst.

2. Results and Discussion

As formation of intermediates **A**, **B** and **C** is central to the reaction process, identification of radical intermediates in both Ir- and Cu-catalysed reactions was the first target. Therefore, EPR measurements of the respective reaction mixtures were carried out (*Figure 27*).

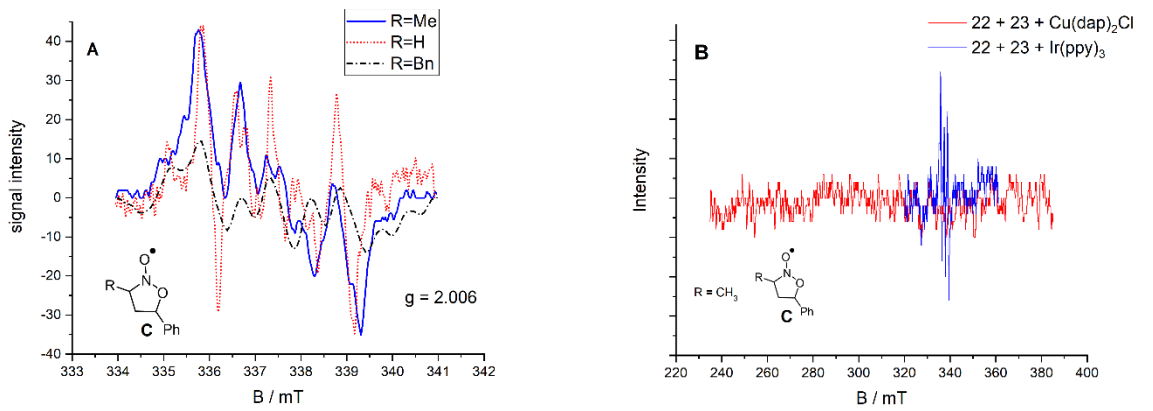


*Figure 27: Comparison between EPR spectra using $Ir(ppy)_3$ and $Cu(dap)_2Cl$ as catalyst. A) Ir-catalysed reaction using three different substrates **22**: Bromonitromethane (**22a**), Bromonitroethane (**22b**), Bromonitrobenzylmethane (**22c**); B) Comparison between Ir-and Cu-catalysed reaction using **22b** as substrate; Irradiation at 455 nm.*[1]

Three different ATRA (atom transfer radical addition) reagents were used (**22a**, **22b**, **22c**) and all of them developed a radical signature in the Ir-catalysed reaction (g = 2.006). The signal grew steadily over a period of more than 15 min, indicating its persistent character as an intermediate. The Cu-catalysed reaction in comparison did not show any radical signature in this region. To find out, which of the proposed radicals **A**-**C** was detected, further experiments were performed.

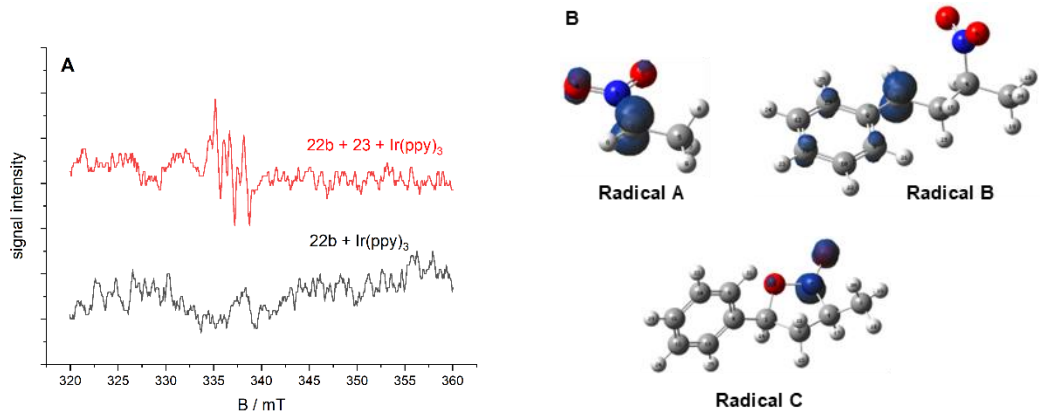


*Figure 28: A) EPR spectra of Ir-catalysed reaction with and without styrene; B) Calculated spin density at radicals **A**, **B** and **C**, for bromonitroethane **22b**; Irradiation at 455 nm.*[1]

In the absence of styrene, no radical signature could be detected (*Figure 28A*). As formation of radical **A** should be independent of the presence of any styrene, the radical intermediate **A** can be ruled out as the persistent radical. Further evidence is provided by the calculated spin densities of Radical **A**-**C** (*Figure 28B*). Most of the spin density in the intermediates **A** and **B** is located on a carbon atom, whereas the spin density in radical **C** is located on the NO_2-group. The typical triplet signature of a nitrogen centred radical (α_N = 1.4 mT) and the g-value are

quite similar to related nitronic ester radicals.[4] These findings suggest that the persistent radical intermediate detected in the Ir-catalysed reaction is radical **C**. Turning the attention to the Cu-catalysed reaction however, instead of an organic radical a Cu(II)-signature was observed when the concentration of $Cu(dap)_2Cl$ was increased (*Figure 29*).

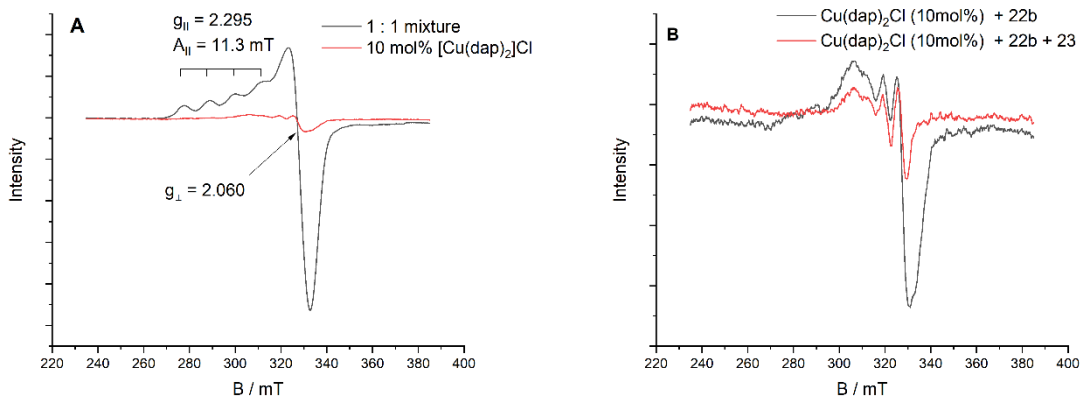


*Figure 29: A) EPR spectra of stoichiometric $Cu(dap)_2Cl$ and **22b**; B) Addition of styrene after mixing $Cu(dap)_2Cl$ with **22b**.[1]*

A stoichiometric mixture of $Cu(dap)_2Cl$ and **22b** showed a well resolved signal with $g_{\perp} = 2.060$, $g_{\parallel} = 2.295$ and hyperfine coupling of $A_{\parallel} = 11.3\ mT$. This signal decreases, when only 10 mol% of catalyst are used, but remains visible. Considering the small intensity at 10 mol%, it is comprehensible, that no signal was detected at the low catalyst loading of 1 mol% in the standard reaction. Additionally, the formed Cu(II)-complex after initial SET, is most likely regenerated to Cu(I) in the course of the reaction. Higher amounts of catalyst might increase the population of the Cu(II)-species, as not enough substrate is available for the onward reaction. The following investigations were conducted using the $Cu(dmp)_2Cl$ catalyst and bromonitromethane **22a**, to reduce computational cost for simulations on the observed reactions and spectra. It was shown by the Reiser group, that $Cu(dmp)_2Cl$ is also feasible for this reaction.[1] To further examine the reaction mechanism of the Cu-photocatalysed bromonitromethylation of styrene, spin-trapping reagent PBN was used (*Figure 30*). Indeed, a radical signal at $g = 1.997$ and hyperfine coupling $\alpha_N = 14.8\ Gauss$ and $\alpha_H = 5.1\ Gauss$ was detected during the reaction. Importantly, no radical was formed in the absence of ATRA reagent **22a** or Cu-catalyst (*Figure 30B*). This is a marked contrast to the Ir-catalysed reaction, where the absence of styrene resulted in no detectable radical formation (without the use of a spin trap). From these findings it can be concluded that formation of radical **A** is indeed occurring after SET from Cu(I). This radical is then being trapped by PBN. Whether reaction to intermediate **B** occurs in the presence of styrene before the radical is trapped by PBN is

unclear. The formation of radical **C** can also be excluded, as the Ir-catalysed reaction showed its persistent character, rendering the use of a spin trap unnecessary for its detection. This was not the case in the Cu-catalysed reaction.

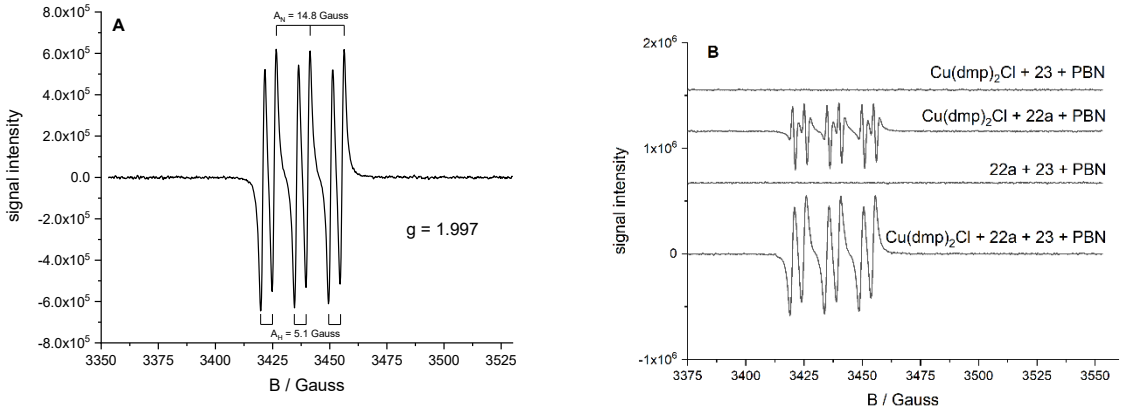


*Figure 30: A) EPR spectrum of Cu(dmp)$_2$Cl, **22a**, **23** and PBN after irradiation at 455 nm; B) Reference spectra, leaving out different components of the reaction.*[1]

Kinetic studies of the PBN-radical formation with and without styrene (*Figure 31*) revealed, that radical formation can only be observed in the first 10 min. While this might be due to the nature of the measurement setup – no stirring of the reaction solution during EPR measurements – a clear distinction between both experiments can be observed.

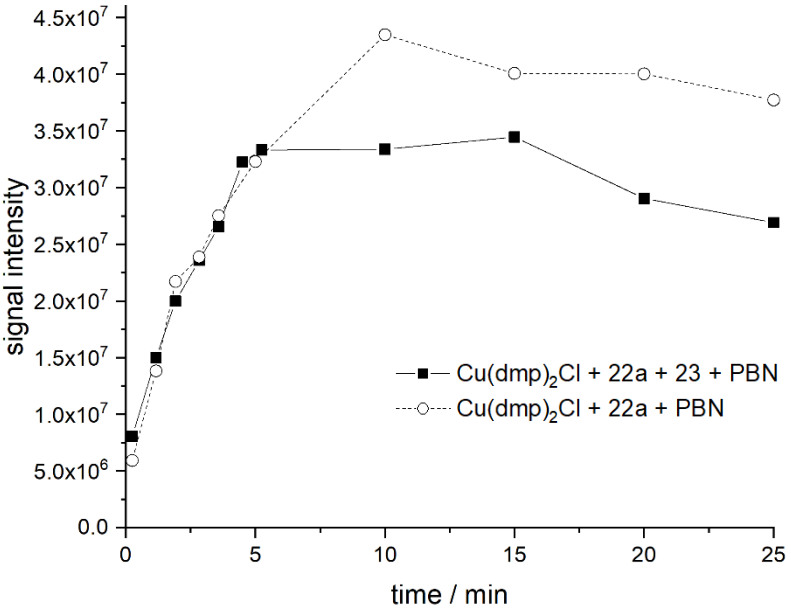


Figure 31: Kinetic study of radical trapping by PBN in the presence and absence of styrene.

The PBN-radical formation during the first 5 min proceeds equally in both experiments, but while signal intensity increases further without styrene, the styrene containing reaction exhibits no more radical formation post the 5 min mark. A rational would be that styrene and PBN compete in the reaction with radical **A**. In the first 5 min sufficient amounts of radical **A** are produced to fuel both reactions, but as the ATRA reagent **22a** is used up, the formation of PBN-radical also comes to a halt. This occurs earlier in the presence of styrene, as some of radical **A** has been used up, without producing a radical, that can be trapped by PBN. The question remains, why radical **B** is not being trapped by PBN. By introducing a cyclopropyl-ring to the ATRA reagent (**22d**) information on the lifetime of the radical intermediate can be gained. In case of fast conversion of the radical intermediate, the cyclopropyl-ring stays intact and can be identified in the product (**25d**). In case of a longer lifetime on the other hand, ring opening occurs resulting in formation of product **25e**. The NMR spectra of the substrates **22d** and **23**, as well as the reaction mixture is shown in *Figure 32*.

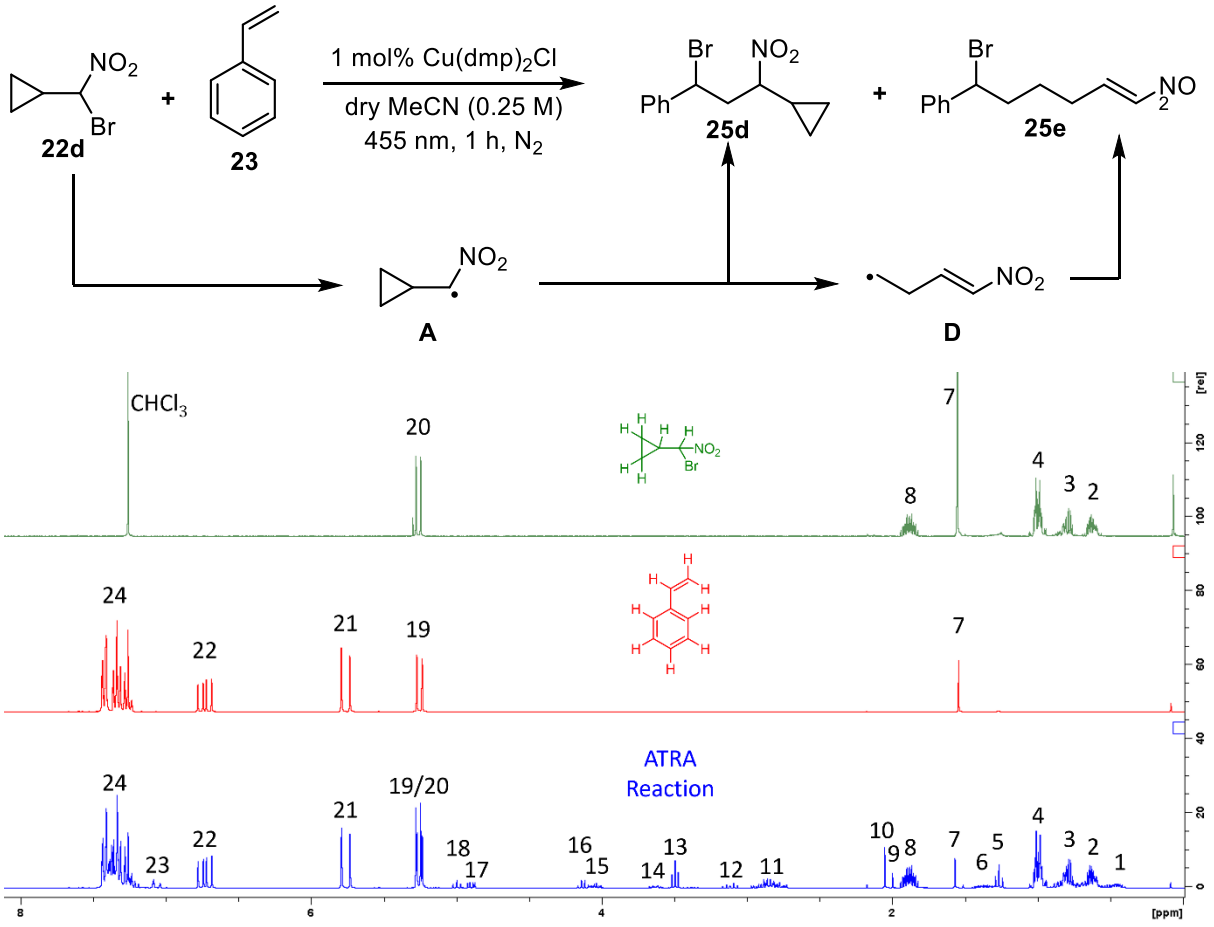


*Figure 32: Radical clock experiment. NMR spectra of **22d**, **23** and the reaction mixture after 1 h of irradiation at 455 nm.*

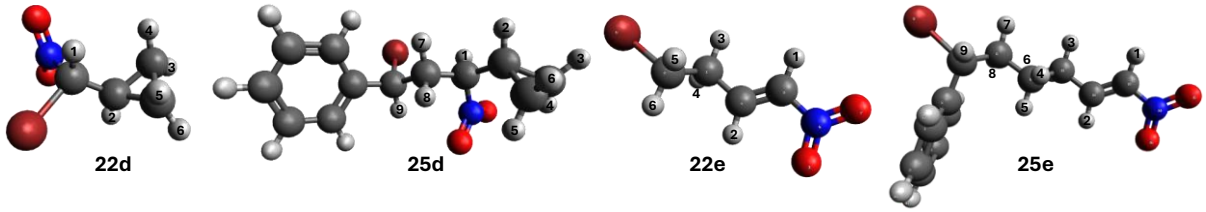
After 1 h reaction time, a large proportion of the starting materials is still present. Ruling out signals from remaining solvents (ethyl acetate, chloroform), the new product peaks 1, 6, 9, 11-

15, 17, 18, 23 are present. Additionally signals 2, 3 and 24 exhibit considerably more noise, indicating overlapping peaks. To assign the signals of the reaction, DFT calculations of the NMR spectra were carried out (Table 2).

*Table 2: Experimental and calculated NMR chemical shifts of **22d**, **22e**, **25d** and **25e**.*

Hydrogen Atom	22d experimental	22d calculated	22e calculated	25d calculated	25e calculated
1	5.26	6.29	7.37 (*7.07*) [1]	4.73	7.24
2	1.88	1.78	7.34 (*7.23*) [1]	1.41	7.42
3	0.99	0.89	3.10 (*2.87*) [1]	0.63	2.62
4	0.79	0.81	3.11 (*2.87*) [1]	0.42	2.53
5	0.62	0.81	3.76 (*3.51*) [1]	0.58	0.98
6	0.99	0.89	3.75 (*3.51*) [1]	0.68	1.27
7	-	-	-	2.96	2.43
8	-	-	-	3.01	2.77
9	-	-	-	5.44	5.43

[1]Experimental shifts[5]



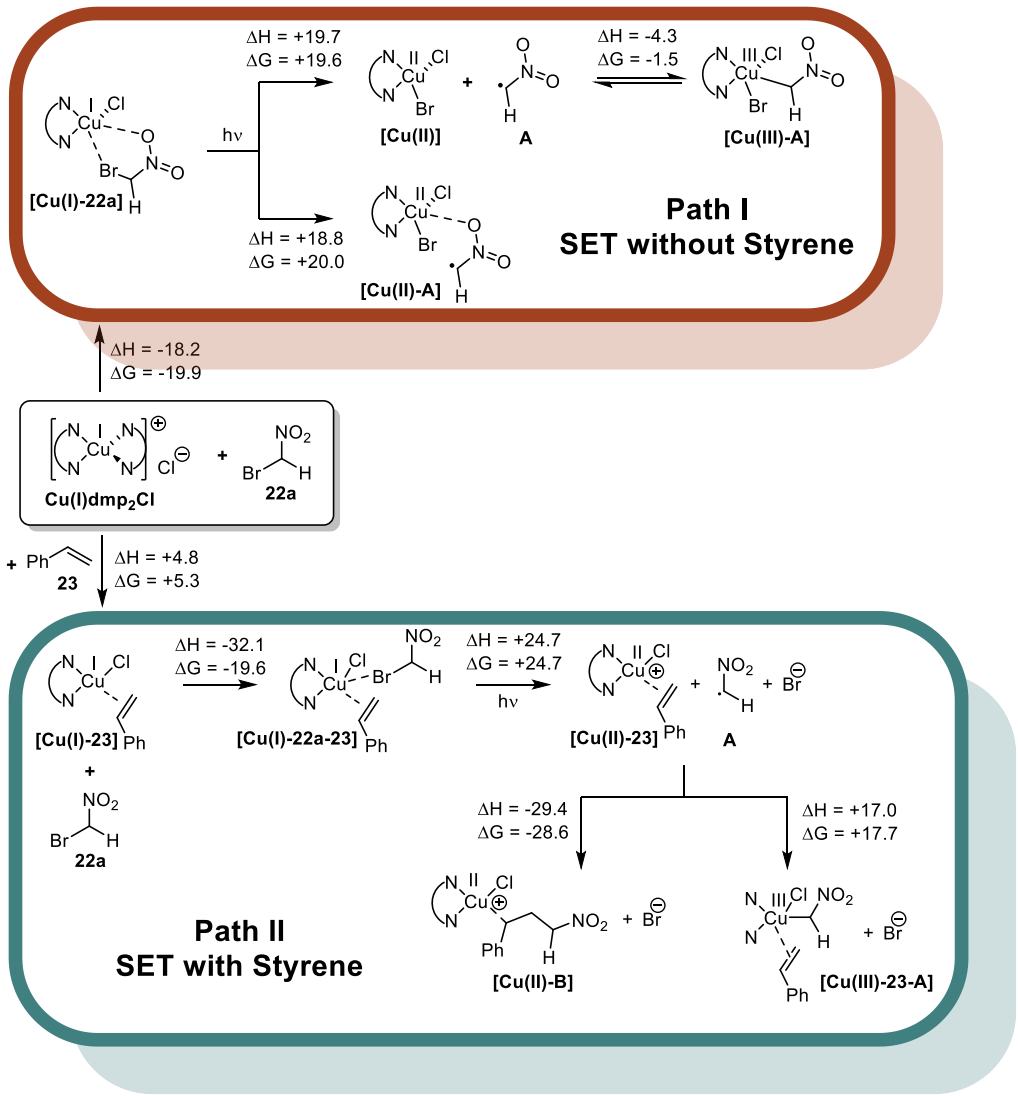
Considerable deviation from the experimental NMR shifts for **22d** is only revealed for the hydrogen atom located next to the nitro-group and the bromine atom. As the shown values of the simulated NMR shifts are the average of the diastereomers, the three different chemical shifts for hydrogen atoms 3 - 6 are averaged out to only two different chemical shifts. Reaction to product **25d** is predicted to shift these peaks upfield, which fits the emerging peak 1 and the increased noise at peaks 2 and 3. Importantly the appearance of peak 6 does match the lower chemical shift of hydrogen atom 2 in product **25d**. Also, Hydrogen atom 1 has a lower chemical shift in the calculated NMR spectrum of **25d**, as the bromine atom is no longer in close proximity. Interestingly, several peaks of the calculated spectrum for ring opening product **25e** cannot be assigned to any peaks in the experimental spectrum. While peak 23 could account for one of the hydrogens 1 or 2, there is a lack of peaks in the region of 2 - 3 ppm for the CH_2 groups. Instead ring opening product **22e**, produced by formation of **A**, ring opening to **D** and recreation of a bromine-bond at the new radical centre, fits the NMR spectrum. Both calculated and experimental[5] chemical shifts match the peaks 11, 13 and 23, with Hydrogen atom 2 overlapping with the aromatic peaks 24. Indeed, comparing the integrals of the peaks reveals a matching distribution of 1:1.3 (d.r.) for product **25d** and 1.4 for product **22e** (*Table 3*). The NMR radical-clock-experiment implicates, that either no intermediate **B** is formed, or it is

converted immediately to product **25**. On the other hand, intermediate **A** is long-lived enough to partially undergo ring-opening. Instead of reaction with styrene however it is quenched by bromine. A rational for these observations would be that radical **A** is not leaving the inner sphere after SET.

*Table 3: Assignment of NMR signals to the products **25d** and **22e**.*

NMR signal	Chemical shift (Integral)	25d (r/s) (ratio: 1)	25d (s/r) (ratio: 1.3)	22e (ratio: 1.4)	Total Integral (25d+22e)
11	2.85 (6.55)	8 (1.0)	7/8 (2.6)	7/8 (2.8)	6.4
12	3.12 (0.95)	7 (1.0)			1.0
13	3.49 (2.78)			6 (2.8)	2.8
14	3.63 (1.03)	1 (1.0)			1.0
15	4.04 (1.54)		1 (1.3)		1.3
17	4.89 (1.31)		9 (1.3)		1.3
18	4.99 (1.0)	9 (1.0)			1.0
23	7.06 (1.54)			1.4	1.4

If no styrene is available, the radical is either quenched before or after ring-opening, leading to the unproductive regeneration of **22d** and the ring opened equivalent **22e**. If on the other hand styrene is present, reaction with styrene immediately results in formation of **25**, without the possibility for intermediate **B** to leave the inner sphere or undergo ring-opening. It is therefore likely, that a productive reaction to **25** requires pre-coordination of styrene to copper. After SET the radical **A** either rebinds to the Cu-centre, creating a formal Cu(III) intermediate or reacts with styrene. Instead of forming a Cu-C bond between the metastable radical **B** and Cu(II), immediate oxidation to product **25** and Cu(I) closes the catalytic cycle. To further substantiate this mechanism, the excited state PES was explored by the means of TD-DFT. The minimum energy path (MEP) between two stable geometries was calculated using the nudged elastic bond (NEB) method.



Scheme 7: Calculated pathway after SET in the presence and absence of styrene. Energies are in kcal mol^{-1}.

Two different pathways were considered (*Scheme 7*). The first pathway via coordination of **22a** to the Cu-catalyst to form the pre-coordinated specie **[Cu(I)-22a]**, followed by SET to overcome the uphill process to either **[Cu(II)-A]** or uncoordinated **[Cu(II)]** and **A**. Rebinding of **A** to Cu(II) yields **[Cu(III)-A]** and results in a slightly more stable structure. The MEP between **[Cu(I)-22a]** and **[Cu(II)]** and **A** shown in *Figure 33* bears a relatively flat minimum in the ground state (S_0).

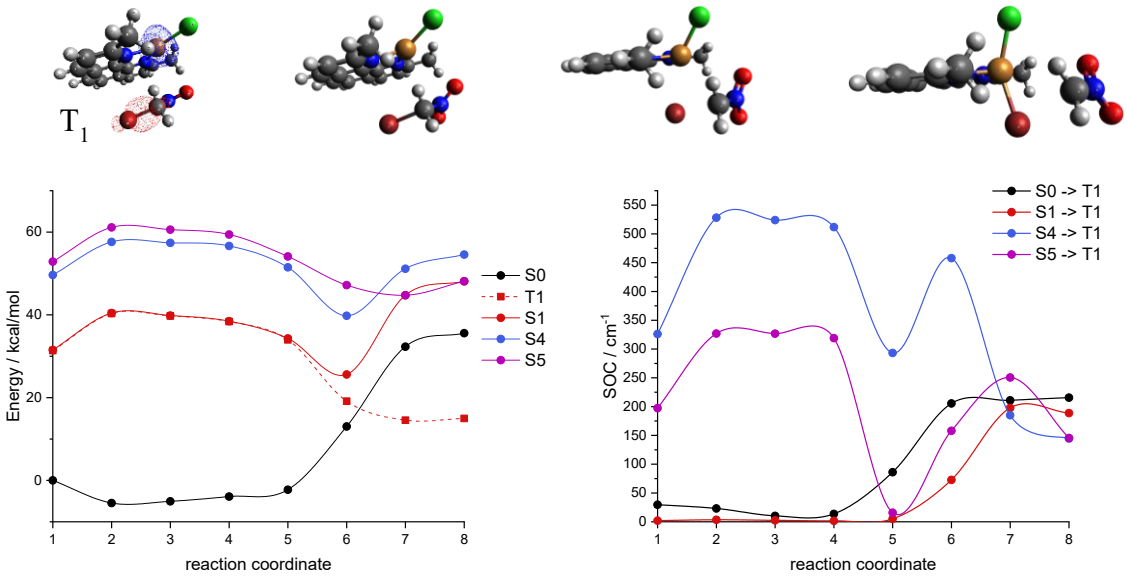


*Figure 33: MEP from **[Cu(I)-22a]** to **[Cu(II)]** and **A**. Geometries of reaction coordinates 1,3,6 and 8 shown from left to right. Excited state difference density of **[Cu(I)-22a]** (T_1, Isovalue 0.006). SOC was calculated by taking the root mean square value of the xyz SOC components from the orca calculation (Keyword: DOSOC true).*

Excitations to the singlet states S_1, S_4 and S_5 lead to a minimum at coordinate 6/7, where the C-Br bond is already elongated to more than 2.6 Å and the nitro-group has already rotated to almost reach the flat geometry of radical **A**. Spin-orbit-coupling (SOC) to the lowest triplet state T_1 is especially high from S_4 and S_5 states, but increases also in the S_1 state from coordinate 5 onwards. Both ISC to the triplet state T_1 or IC back to the ground state is therefore possible. As SOC between ground state and triplet state is strong, ISC back to the ground state is also very likely, showing that radical **A** is likely to be quenched if it does not leave the inner sphere or reacts rapidly. Similarly, the MEP to a coordinated specie **[Cu(II)-A]** shows an initially flat PES in the ground state, strong SOC between T_1 and S_4/S_5 states and a shared minimum of the S_1, S_4 and S_5 states, where SOC between S_1 and T_1 increases (*Figure 34*). Again, excitations to the singlet states S_1, S_4 and S_5 lead to a shared minimum (coordinate 4/5). The nitro-group rotates and one of the oxygen atoms coordinates to the Cu-centre. At this point the C-Br bond is not elongated yet, but SOC to the T_1 state enables ISC. The T_1 path is energetically downhill and results in the cleavage of the bond and coordination of bromine to the Cu-centre.

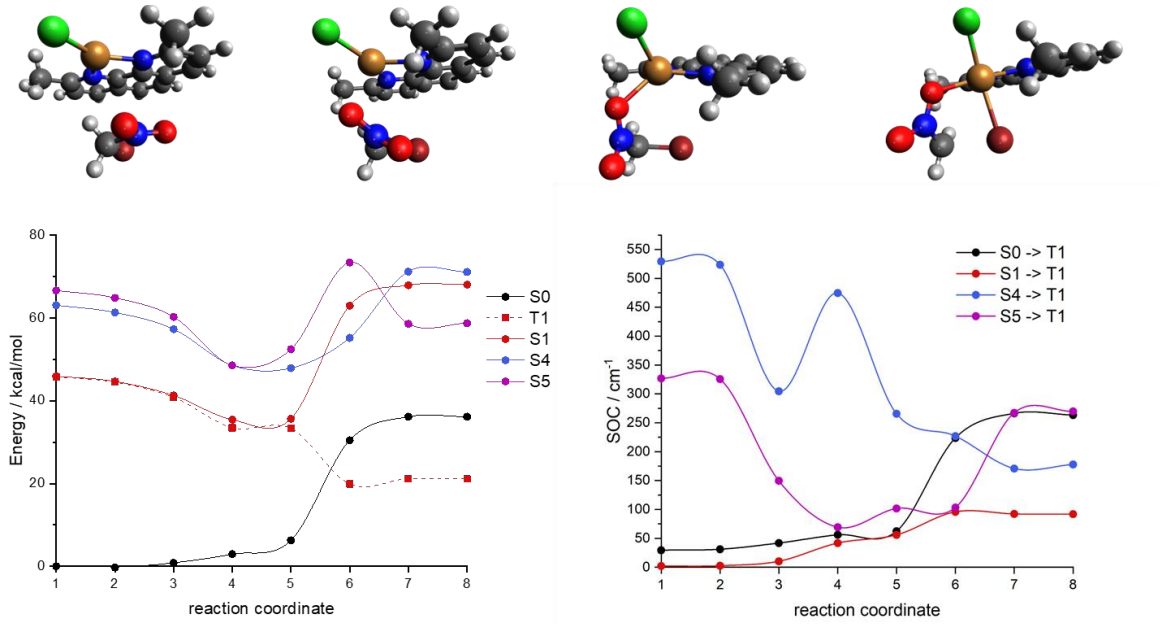


*Figure 34: MEP from **[Cu(I)-22a]** to **[Cu(II)-A]**. Geometries of reaction coordinates 1,3,5 and 8 shown from left to right. SOC was calculated by taking the root mean square value of the xyz SOC components from the orca calculation (Keyword: DOSOC true).*

IC from the excited singlet states back to the ground state can also occur, as well as quenching of the radical **A** back to **22a**, due to strong SOC between ground and triplet state. Rebinding of radical **A** to the Cu-centre to form **[Cu(III)-A]**, shows an unexpected minimum in the ground state before reaching the end of the calculated path (*Figure 35*).

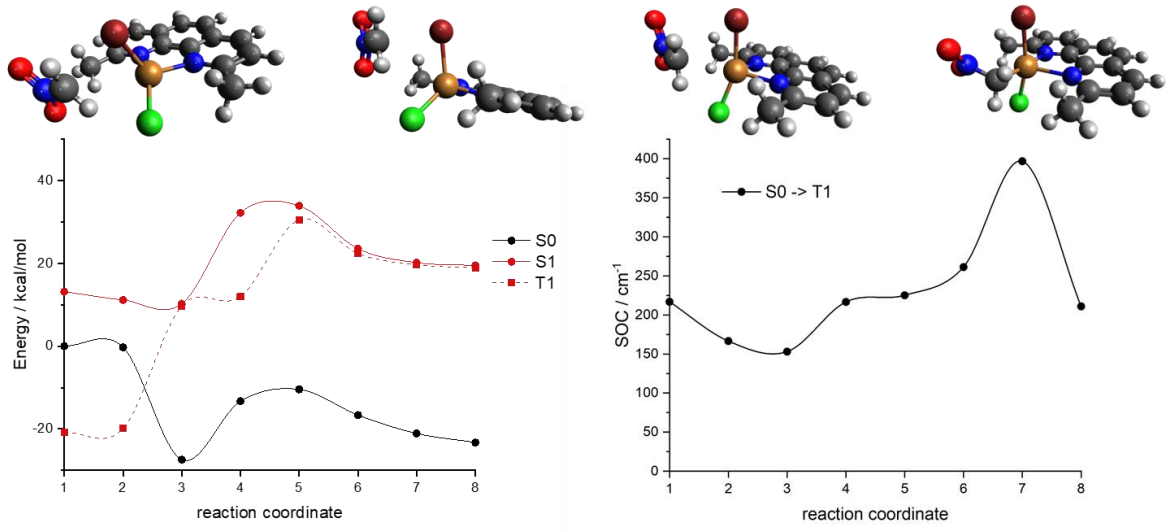


*Figure 35: MEP from **[Cu(II)]** and **A** to **[Cu(III)-A]**. Geometries of reaction coordinates 1,3,6 and 8 shown from left to right. SOC was calculated by taking the root mean square value of the xyz SOC components from the orca calculation (Keyword: DOSOC true).*

The triplet state shows a high barrier (ca. 60 kcal/mol) and with strong SOC to the S_0 state ISC to the ground state is more likely. Excited singlet states e.g. the S_1 state also possess high barriers and are energetically uphill. Interestingly the starting geometries (reaction coordinates 1-3) feature coordination of the radical **A** to the bromine atom. Instead of overcoming the barrier to proceed to a Cu(III) complex, oxidation to **22a** and Cu(I) could occur, again quenching radical **A** by regenerating the starting material.

Having explored the MEPs without precoordinated styrene, the second reaction path includes styrene coordination to yield **[Cu(I)-23]** (*Scheme 7*). Despite endergonic, excitation of $Cu(dmp)_2Cl$ is known to flatten the geometry, which favours the release of one ligand.[6] This leaves open a coordination site for styrene. Additionally, styrene possesses an aromatic ring, which can interact with the ligand system. It is therefore likely, that styrene is present in the inner sphere of the catalyst complex when excitation takes place. SET from **[Cu(I)-23]** to **22b** to form **A** can either be followed by rebinding to the Cu-centre to yield **[Cu(III)-23-A]** or by reaction of **A** with styrene to form **[Cu(II)-B]** (*Scheme 7*).

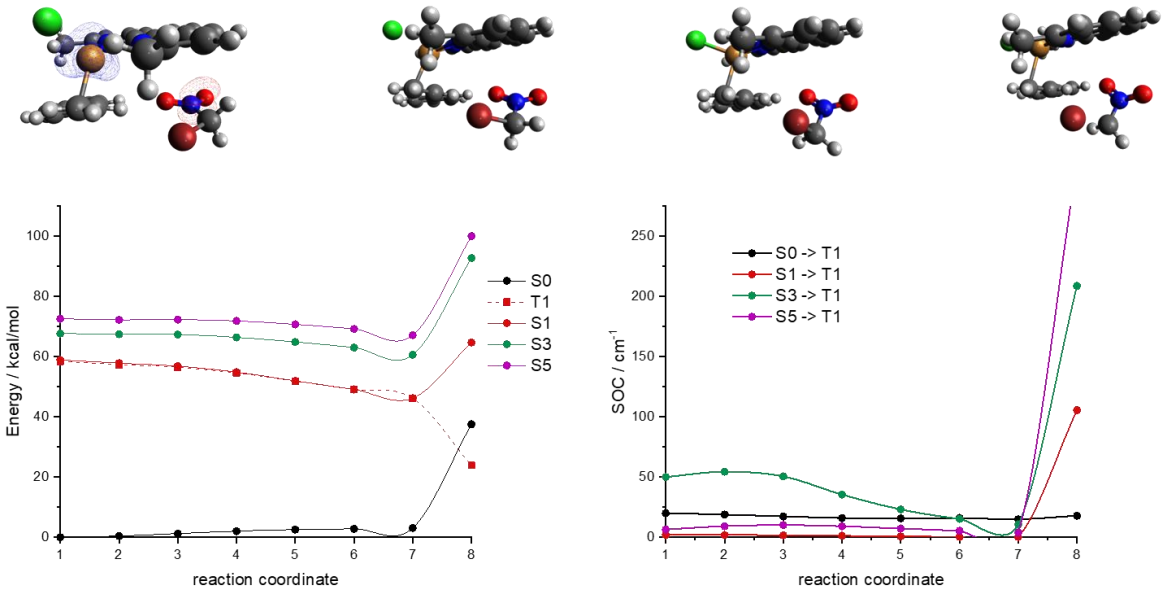


*Figure 36: MEP of **[Cu(I)-22a-23]** C-Br bond cleavage to **[Cu(II)-23]** and **A**. Geometries of reaction coordinates 1,4,7 and 8 shown from left to right. Excited state difference density **[Cu(I)-22a-23]** (T_1, Isovalue 0.006). SOC was calculated by taking the root mean square value of the xyz SOC components from the orca calculation (Keyword: DOSOC true).*

The C-Br bond cleavage in **[Cu(I)-22a-23]** is shown in *Figure 36*. All plotted excited states slowly sink into a minimum right before reaching the T_1 state minimum. This slow degression is represented by the rotation of the nitro-group to match the flat geometry of **A**. The C-Br bond is fully intact until the last step. Despite only moderate SOC, ISC to yield **A** is possible. S_1, S_3 and S_5 state show productive paths and especially the S_3 state shows sufficient SOC in the early

stages. Interestingly SOC between the ground and T_1 state is not drastically increasing, potentially improving the lifetime of the triplet state. Following the C-Br bond cleavage, coordination of radical **A** to the Cu-centre to yield **[Cu(III)-23-A]** is uphill (*Scheme 7*). Presumably this intermediate yields similar results as shown for the rebound mechanism to **[Cu(III)-A]**, where quenching of the radical **A** leads to the unproductive regeneration of **22a**. Instead, reaction of **A** with Styrene to form **[Cu(II)-B]** features a productive MEP (*Figure 37*).

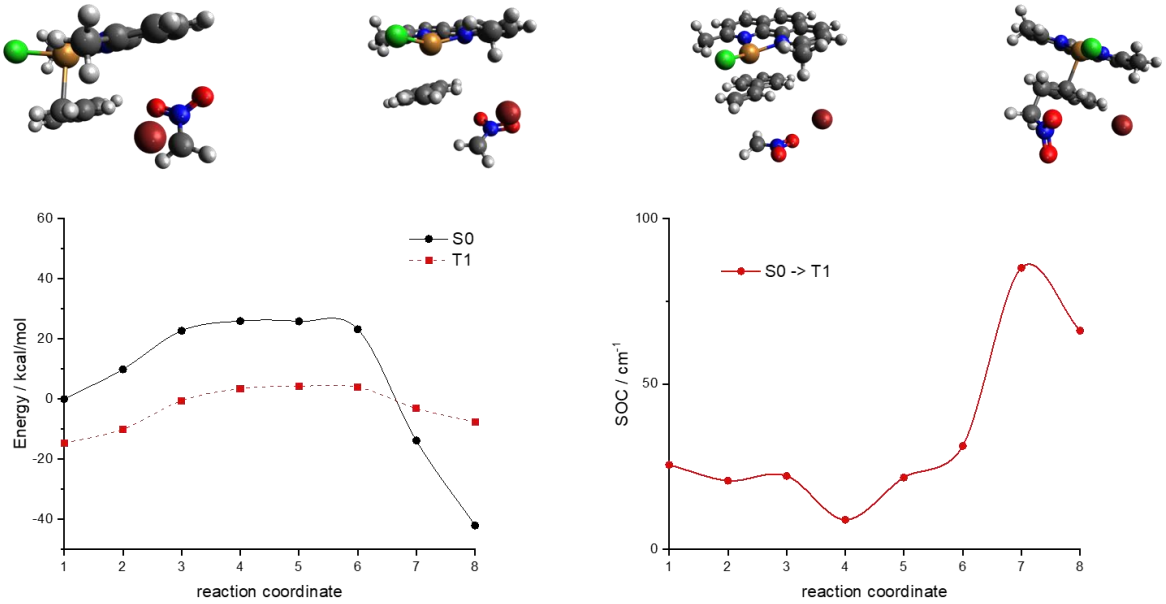
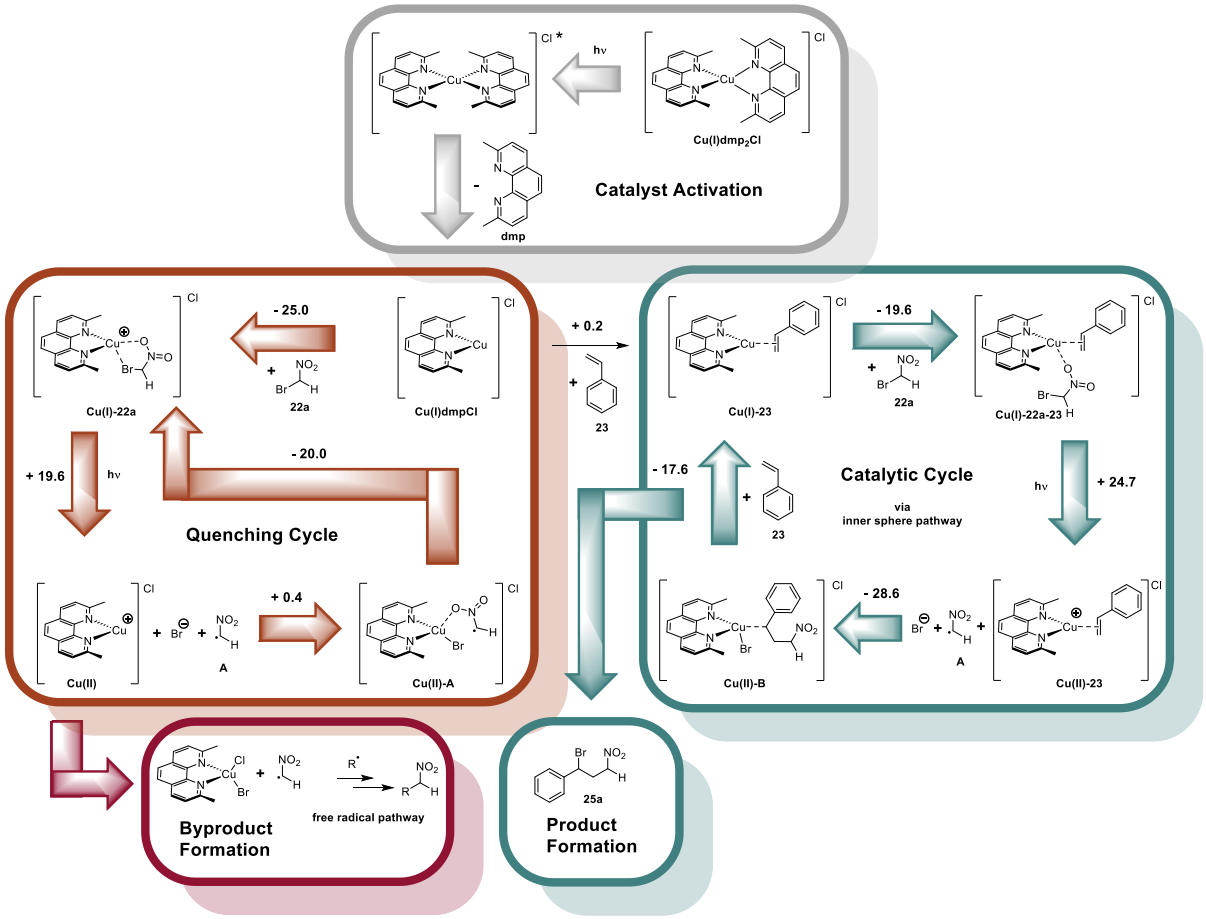


*Figure 37: MEP from **[Cu(II)-23]** to **[Cu(II)-B]**. Geometries of reaction coordinates 1,3,6 and 8 shown from left to right. SOC was calculated by taking the root mean square value of the xyz SOC components from the orca calculation (Keyword: DOSOC true).*

From reaction coordinates 1-6 radical **A** is traversing towards styrene, followed by the formation of a C-C bond (coordinates 7 and 8). A relatively low barrier in the triplet state and strong SOC in the later parts of the MEP seem to enable this reaction path. This process is also highly exergonic as soon as the singlet state is recovered. To close the catalytic cycle, oxidation by the Cu(II)-complex then yields product **25** and regenerates the catalyst. An overview of the different pathways established in this chapter is given in *Scheme 8*.



Scheme 8: Reaction mechanism of Cu(I)-photoredox catalysed bromonitromethylation. Gibbs free energies are in kcal mol^{-1}.

3. Conclusion

Radical **A** and the formation of **B** was identified as key intermediates and investigated theoretically and experimentally. Considering the evidence collected by the means of EPR, spin-trapping and radical clock experiments as well as DFT and TD-DFT calculations, the mechanism of the Cu(I)-photocatalyzed Bromonitroalkylation can be summed up as in *Scheme 8*. Two parallel catalytic cycles are taking place, preceded by an activation phase to free up a coordination site for substrate coordination. Irradiation of the catalyst favours release of a ligand and enables coordination to substrates, such as styrene. After initial activation of the catalyst a quenching mechanism stabilizes ATRA reagent **22** when no reaction partner is available, preventing formation of byproducts. This mechanism also regenerates the catalyst and proceeds as long until coordination of styrene enables reaction of intermediate **A** with styrene. The dependency of pre-coordination might very well be a rational for the use of higher catalyst loadings then in transformations, where Cu only functions as a mediator (e.g. Chapter C).

Increasing catalyst loadings will increase the population of pre-coordinated catalyst, which leads to a productive reaction path. Following the reaction of styrene with intermediate **A**, the resulting radical **B** is then immediately oxidized to product **25**, closing the catalytic cycle. A rebound mechanism to a formal Cu(III) complex seems to be interrupted by coordination of a bromine ligand to the radical centre, hence reducing the Cu-complex to Cu(I) before a Cu(III) complex can be formed. This interesting mechanism could provide a rational for the unsuccessful search for a proposed Cu(III) intermediate and is certainly worth further investigation. However, it has to be noted that DFT does not properly describe the multireference character of these transformations. Hence, the use of a multireference method (e.g. CASSCF or RASSCF) on these geometries can yield a more nuanced description of the discussed interactions and is therefore a promising approach to gain more information on prerequisites and boundaries of the inner sphere pathway.

4. References

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[3] Y. Tsuchiya, R. Onai, D. Uraguchi, T. Ooi, *Chem. Comm.* **2020**, *56*, 11014.

[4] J. E. T. Corrie, B. C. Gilbert, V. R. N. Munasinghe, A. C. Whitwood, *J. Chem. Soc., Perkin Trans. 2* **2000**, *12*, 2483.

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E. Summary

The versatility, selective nature and tunability of redox properties with a wide selection of ligands renders Cu-photoredox catalysis a valuable tool for synthesis. The unique traits of copper chemistry have shown useful for Cu(I)/Cu(II), Cu(I)/Cu(III) and Cu(II)/Cu(I) cycles. In this thesis substantial progress has been made in understanding reaction mechanisms specific to Cu-photoredox chemistry. Spectroscopic techniques were coupled with computational chemistry and targeted experiments for mechanistic insights into three different Cu-catalysed reactions. The employment of UV/vis, NMR and EPR spectroscopy, accompanied with computational simulations of spectra, reaction energies and excited state behaviour has proven powerful in entangling the intricacies of the investigated transformations. The importance of ligand exchange and substrate coordination was established in the Copper(II)-photocatalysed decarboxylative oxygenation of phenylacetic acids. Evidence for the formation and coordination of a radical intermediate by copper was found, hinting to a stabilizing characteristic additionally to its photocatalytic properties. This characteristic was further investigated in the stereoselective synthesis of α-mannosides, as the Cu-catalysed reaction stabilized the reactive radical intermediates to selectively form the product and stopped byproduct formation. In the third project the nature of intermediates was thoroughly investigated and revealed a stabilizing quenching cycle by copper in absence of a suitable reaction partner. Coordination of a substrate provides said reaction partner, which is selectively coupled with the ATRA reagent. Exploration of the excited state PES suggests that prior to formation of a Cu(III) intermediate reduction of the Cu(II) complex and product formation takes place. The radical intermediate is prone to react with a reactive ligand instead of rebinding to the copper centre. These findings might spark further investigations with more sophisticated computational methods than TD-DFT. While proven accurate and efficient, more exact calculations on excited state transitions of found intermediates could give further insight into the redox and binding behaviour of Cu-intermediate-complexes. Multi reference methods such as CASSCF or RASSCF can improve the description of transformations where a bond is being cleaved or formed homolytically. On top of that a better description of the multireference character of the investigated Cu-complexes enhances the simulation of the excited state PES. It is also important to note, that the investigations in this thesis are focused on a static description of processes and did not include dynamic treatment of the investigated reactions. Building on the static description of the excited state PES in this thesis, excited state dynamics could help quantify the stabilizing effect of a quenching cycle and the efficiency of LIH

followed by different deactivation pathways. Implementation of these ideas could round out the investigations on the inner-sphere pathway and give way to *in silico* design of Cu-photoredox transformations.

F. Zusammenfassung

Die Vielfalt, Selektivität und Flexibilität der Redoxeigenschaften, ermöglicht durch eine große Bandbreite an Liganden, machen Kupfer Photoredox Katalyse zu einem wertvollen Werkzeug der Synthesechemie. Die einzigartigen Charakteristika der Kupferchemie haben sich in verschiedenen Cu(I)/Cu(II), Cu(I)/Cu(III) and Cu(II)/Cu(I) Zyklen als nützlich erwiesen. In dieser Dissertation wurden wesentliche Fortschritte gemacht, ein tiefergehendes Verständnis für die Kupfer-spezifischen Reaktionsmechanismen unter photokatalytischen Bedingungen zu erlangen. Spektroskopie, gekoppelt mit computerchemischen Untersuchungen und gezielten Experimenten haben eine detaillierte Analyse der Reaktionsprozesse dreier verschiedener Kupfer-katalysierten Reaktionen ermöglicht. Die Kombination von UV/vis, NMR und EPR-Spektroskopie, deren computerchemische Simulation, sowie die Berechnung von Reaktionsenergien im elektronischen Grundzustand und angeregter Zustände hat sich als potent erwiesen, um Feinheiten (photo-)chemischer Transformationen aufzuschlüsseln. Die Wichtigkeit des Ligandenaustauschs und die Ausbildung von vorkoordinierten Substrat-Katalysator-Komplexen ist in Kapitel B (Copper(II)-photocatalysed decarboxylative oxygenation of phenylacetic acids) deutlich geworden. Es wurden Nachweise auf die Bildung eines radikalischen Intermediats und dessen Koordination am Kupferzentrum gefunden, die den Rückschluss auf einen Stabilisierungseffekt von Kupfer zusätzlich zu dessen photochemischen Funktion zulassen. Diese Interaktion wurde tiefergehend in der stereoselektiven Synthese von α-Mannosiden untersucht, bei der Kupfer radikalische Zwischenprodukte stabilisiert, zur selektiven Produktbildung beiträgt und Nebenreaktionen verhindert, indem es die Reaktionspartner zusammenbringt. Im dritten Projekt wurde die Radikalbildung, Stabilität und der Effekt des Kupfers auf diese Prozesse weitergehend untersucht und ein stabilisierender Quench-Mechanismus in Abwesenheit eines Reaktionspartners aufgedeckt. Dadurch wird das gebildete Radikal zum Edukt zurückgebildet und somit eine Nebenreaktion unterdrückt. Koordination eines Reaktionspartners in der Liganden Sphäre ermöglicht dann bei erneuter Radikalbildung eine selektive Reaktion. Untersuchungen der Potentialhyperfläche von Grund- und angeregten Zuständen ergaben, dass an Stelle einer Bindung des Radikals am Kupferzentrum zu einem Cu(III)-Intermediat die Reduktion des Cu(II) Komplexes zu Cu(I) und die gleichzeitige Produktbildung stattfindet. Dieses Ergebnis bietet eine exzellente Grundlage für elaboriertere computerchemische Methoden. Während TD-DFT einen exzellenten Kompromiss zwischen Effizienz und Genauigkeit eingeht, können exaktere Berechnungen der Übergänge zwischen den gefundenen Zwischenprodukten einen tiefergehenden Einblick in das Redox- und Bindungsverhalten der Kupfer-Intermediat-Komplexe bieten. Multireferenz

Methoden wie CASSCF und RASSCF sind hervorragend geeignet, um die Beschreibung der homolytischen Bindungsbildung und Bindungsspaltung zu verbessern. Darüber hinaus kann der Multireferenz Charakter der Kupferkomplexe besser abgebildet werden, was unter anderem zu einer verbesserten Simulation der angeregten Zustände führt. Weiterhin ist wichtig zu erwähnen, dass die durchgeführten Untersuchungen lediglich eine statische Betrachtung der Prozesse abbilden. Dynamische Effekte, insbesondere bei angeregten Zuständen, können zur Quantifizierung der Stabilisierungseffekte des Kupfers und des Quench-Vorgangs beitragen und die Effizienz der lichtinduzierten Homolyse inklusive der Deaktivierungspfade aufdecken. Die Implementierung dieser Ideen könnten die Untersuchungen des „Inner-Sphere"-Mechanismus vervollständigen und es ermöglichen Cu-Photoredox Reaktionen *in silico* zu designen.

G. Experimental

1. Chapter B

1.1. General Information

Commercially available chemicals were used without further purifications. Synthesized compounds were provided by the Reiser group and are well documented in the quoted publication. All photochemical reactions were carried out in oven-dried glassware. Reactions were carried out under atmospheric conditions unless stated otherwise. Reaction mixtures were degassed using three freeze-pump-thaw cycles.

1.2. Standard experiment

A flame-dried Schlenk tube (10.0 mL size) equipped with a magnetic stirring bar was charged with anhydrous $Cu(OAc)_2$ (4.5 mg, 25 µmol, 10 mol%) and dmp (5.2 mg, 25 µmol, 10 mol%) and the 4-methoxyphenylacetic acid (41.6 mg, 0.25 mmol, 1.0 equiv). Subsequently, the solvent mixture MeCN (2 mL) and water (46.0 µL, 2.2 vol%) was added. Depending on the atmosphere used, the reaction tube was flushed with oxygen and a balloon containing oxygen was added. A Teflon sealed inlet for a glass rod was placed on the reaction tube, through which irradiation with LED took place from above.

1.3. UV/Vis Absorption Spectroscopy

All UV/vis measurements were recorded on a SPECTRORECORD 200 PLUS of the company analytikjena using a Macro cell type 110-QS quartz cuvette with PTFE stopper (Hellma Analytics quartz cuvette, 10 × 10 mm, 3.5 mL).

For UV/vis spectra of the Cu-complexes **4** and **5**, stock solutions with a concentration of 25.0 µmol/10 mL (referred to Cu(II)) were prepared. From this stock solution, 200 µL were transferred to a cuvette, containing acetonitrile (2mL) and water (45 µL). Then the spectra were recorded. For UV/vis monitoring, 4-methoxyphenylacetic acid (**1**) (41.5 mg, 0.25 mmol, 1.0 equiv) and Cu(dmp)(**1**)$_2$ (**4**) (15.1 mg, 25.0 µmol, 10 mol%) were dissolved in dry MeCN (2.0 mL, 0.125 M) and water (45 µL, 2.2 vol%). Then, it was irradiated at 367 nm under O_2 atmosphere, provided by an oxygen balloon, for 24 h at room temperature (25°C). After given time, 10 µL of the reaction mixture was dissolved into 2 mL of acetonitrile for measurement. Further, UV/vis spectra of **1** and the product **2** showed no increased absorbance at 367 nm. Water titration experiments were carried out exactly the same, with varying water content.

1.4. EPR Spectroscopy

Continuous-wave (CW) electron paramagnetic resonance (EPR) experiments were carried out in acetonitrile solutions on a Bruker EMX Spectrometer (X-Band, 9-10 GHz) equipped with an ER 083 (200/60) power source electromagnet (0-6000 G). For the measurements, an ER 4104 OR/9009 resonant cavity with a resonance frequency of 9.66 GHz was used. Samples were measured in glass pipettes, which were evacuated and flushed with dry N_2 several times before being filled with 0.3 mL solution. Solvents were degassed by three freeze-pump-thaw cycles and stored under dry N_2 for no more than one week. Between preparation and the first obtained spectrum 10-15 min went by. To exclude light, samples were covered with tin foil during this time.

Irradiation during measurements was performed with a Luminus SST-10 (3 W, 720 mA, λ_{max} = 365 nm) LED and by the use of an optical fibre cable FP1500URT (0.50 NA, 300-1200 nm, 1500 µm, multimode, end A SMA, end B flat cleave) into the cavity.

For measurements under oxygen atmosphere the samples were connected to a balloon containing oxygen.

EPR spectra were obtained as a first order derivative plot. Raw data were exported in the ASCII file format and processed with Origin 2019b (Version 9.6.5.169). All spectra are baseline and solvent corrected. For quantitative comparisons the spectra were integrated twice.

For all measurements a stock solution of 2 mL was prepared. All measurements were done in acetonitrile unless stated otherwise.

1.4.1. Comparison of 3 and 4

Comparison of the EPR spectra of the Paddlewheel complex **3** and monomeric complex **4** were done using the following measurement parameters.

Spectrum	Resonance Frequency	Microwave Power	Modulation Amplitude	Conversion Time	Time Constant	Receiver gain	Resolution
3	9.325 GHz	62.10 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024
4	9.318 GHz	60.61 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024

Cu(II)-complex **3** (6.25 mmol/L) or **4** (12.5 mmol/L) formed in situ in MeCN (2.0 mL), water (45 µL, 2.2 vol%) from Copper(II)-carboxylate at room temperature (25 °C).

1.4.2. Water Titration Experiment

A water titration experiment was done using the following measurement parameters:

Spectrum	Resonance Frequency	Microwave Power	Modulation Amplitude	Conversion Time	Time Constant	Receiver gain	Resolution
0.2 vol%	9.328 GHz	59.82 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024
2.2 vol%	9.318 GHz	60.61 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024
5.4 vol%	9.327 GHz	59.82 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024
10.3 vol%	9.328 GHz	60.06 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024
18.7 vol%	9.327 GHz	60.21 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024

Cu(II)-complex **4** (12.5 mmol/L) formed in situ in MeCN (2.0 mL) at room temperature (25 °C). Water: 0.2 vol% (4.5 µL), 2.2 vol% (45 µL), 5.4 vol% (115 µL), 10.3 vol% (230 µL), 18.7 vol% (461 µL).

1.4.3. Reaction kinetic measurement of Cu(II)

The kinetic measurements were done using the following measurement parameters.

Spectrum	Resonance Frequency	Microwave Power	Modulation Amplitude	Conversion Time	Time Constant	Receiver gain	Resolution
Run7	9.304 GHz	63.32 mW	25 G	21.0 ms	20.48 ms	2.0×10^4	512
Run8	9.304 GHz	63.40 mW	25 G	21.0 ms	20.48 ms	2.0×10^4	512

1 (125 mmol/L), Cu^{II}-complex **4** (12.5 mmol/L) in MeCN (2.0 mL), water (45 µL, 2.2 vol%) at room temperature (25 °C). Irradiation at 365 nm with a radiant power of 30 mW under O_2 atmosphere. For the determination of k_1 and k_2, the averages from both measurements were used.

$k_1 = 0.022 \pm 0.003\ s^{-1}$

$k_2 = 4.982 \times 10^{-4} \pm 1.723 \times 10^{-4}\ s^{-1}$

1.4.4. Radical trapping Experiment

Radical trapping Experiments were done using the following measurement parameters.

Spectrum	Resonance Frequency	Microwave Power	Modulation Amplitude	Conversion Time	Time Constant	Receiver gain	Resolution
PBN	9.322 GHz	62.59 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024
TEMPO	9.306 GHz	61.86 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024

N-tert-Butyl-α-phenylnitrone (150 mmol/L, 1.2 eq.) **1** (125 mmol/L, 1 eq.), Cu^{II}-complex **4** (12.5 mmol/L, 0.1 eq) in MeCN (2.0 mL), water (45 µL, 2.2 vol%) at room temperature (25 °C). Irradiation at 367 nm with a radiant power of 30 mW.

TEMPO (12.5 mmol/L, 0.1 eq.), **1** (125 mmol/L, 1 eq.), Cu^{II}-complex **4** (12.5 mmol/L, 0.1 eq) in MeCN (2.0 mL), water (45 µL, 2.2 vol%) at room temperature (25 °C). Irradiation at 367 nm with a radiant power of 30 mW.

1.4.5. Light-on/off-cycle Experiment

Spectrum	Resonance Frequency	Microwave Power	Modulation Amplitude	Conversion Time	Time Constant	Receiver gain	Resolution
PBN	9.304 GHz	62.27 mW	25 G	41.0 ms	40.96 ms	2.0×10^4	256

N-tert-Butyl-α-phenylnitrone (150 mmol/L, 1.2 eq.) **1** (125 mmol/L, 1 eq.), Cu(II)-complex **4** (12.5 mmol/L, 0.1 eq) in MeCN (2.0 mL), water (45 µL, 2.2 vol%) at room temperature (25 °C). Irradiation at 365 nm with a radiant power of 30 mW.

1.5. Computational Chemistry

1.5.1. General Information

All calculations were conducted using the Gaussian16[1] (Revision C.01) software package. Density functional theory calculations were carried out with the Becke-style 3-Parameter Density Functional using the Lee-Yang-Parr correlation functional (B3LYP).[2–5] The final structures were calculated with the addition of *Grimme's* empirical dispersion correction D3.[6] For the atoms H, C, N, O the Pople-type triple zeta valence basis set 6-311G(d,p)[7–9] was used, while for Cu atoms the Ahlrichs-Weigend triple zeta valence polarisation basis set def2-TZVP[10,11] was used. Stationary points were confirmed as local minima by frequency calculations (no imaginary frequencies). Wavefunctions of open shell molecules were checked for stability by using the keyword stable. Gibbs free energies were obtained by the sum of electronic and thermal free energies. UV/vis simulations were done with the TD-DFT approach using the same level of theory stated above (B3LYP/6-311G(d,p) and B3LYP/def2-TZVP). Visualization of geometries was achieved with GaussView[12] (Version 6.0.16). Visualization for the titlepage was done with VMD.[13–20]

1.5.2. Simulated UV/Vis Absorption Spectra

All data for the calculated UV/vis spectra were printed from GaussView and visualized with Origin 2019b (Version 9.6.5.169).

1.5.3. Calculation Examples

Geometry optimization and frequency calculation:

 # opt ub3lyp/gen pseudo=read
int=ultrafine
SCF(tight)
empiricaldispersion=gd3
freq(noraman)

opt_freq

0 2

C H O N 0
6-311G(d,p)
****
Cu 0
def2tzvp
****

Cu 0
def2tzvp

Stability of the wavefunction:

 # ub3lyp/chkbas gfinput pseudo=read stable
int=ultrafine
empiricaldispersion=gd3
geom(check)
guess(read)

stable

0 2

TD-DFT calculation:

 # ub3lyp/chkbas
int(ultrafine)
SCF(tight)
empiricaldispersion=gd3
td=(NStates=30)

tddft

0 2

NBO calculation:

 # ub3lyp/chkbas pop=(nbo7,savenbos,reg)

int(ultrafine)

SCF(tight)

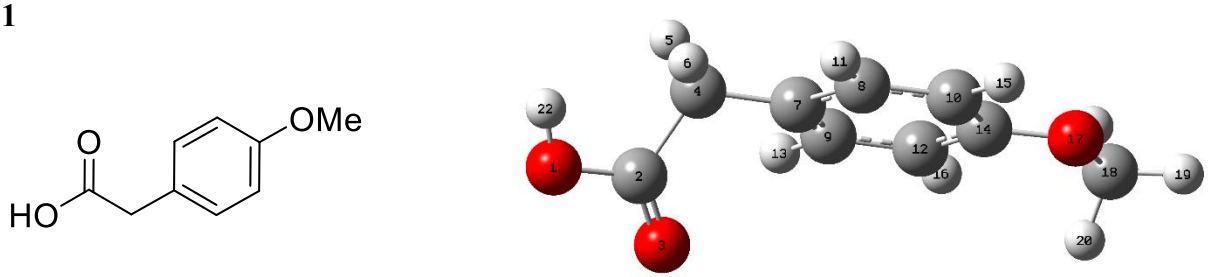
empiricaldispersion=gd3

nbo

0 2

1.5.1. Optimized xyz-Matrices and Thermodynamic Data

1



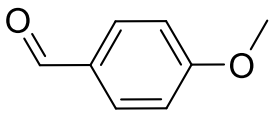
0 1

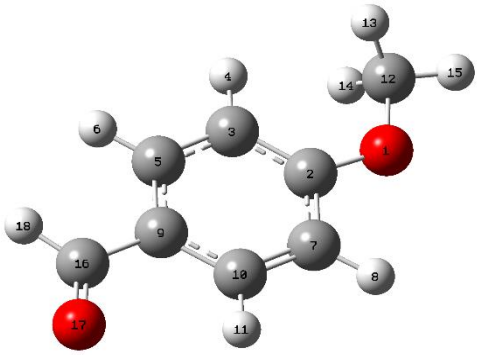
O	-4.33175400	-0.09427400	0.19068700
C	-2.99961900	-0.38276500	0.20305900
O	-2.60360500	-1.35672900	0.77159200
C	-2.13564300	0.59852600	-0.59529900
H	-2.37664600	0.42224700	-1.65251600
H	-2.46679000	1.61923100	-0.37627200
C	-0.65192500	0.47564700	-0.35923400
C	0.08925900	1.56349200	0.11363400
C	0.02140200	-0.71844300	-0.61346400
C	1.45714900	1.46624500	0.32143000
H	-0.41009600	2.50385900	0.32504800
C	1.39458100	-0.83471200	-0.40923100
H	-0.53471400	-1.58238900	-0.95589300
C	2.12166000	0.26348100	0.06081100
H	2.03482800	2.30550300	0.68860200
H	1.87911600	-1.77975300	-0.61270700
O	3.46437000	0.26490400	0.29600300
C	4.19261000	-0.93465000	0.07073100
H	5.22603300	-0.70781700	0.32811800
H	3.83197800	-1.75040500	0.70804400
H	4.14219200	-1.24578600	-0.97938000

H	-4.49483900	0.72317300	-0.29393100

Zero-point correction= 0.175188 (Hartree/Particle)
Thermal correction to Energy= 0.186441
Thermal correction to Enthalpy= 0.187386
Thermal correction to Gibbs Free Energy= 0.136514
Sum of electronic and zero-point Energies= -574.643943
Sum of electronic and thermal Energies= -574.632690
Sum of electronic and thermal Enthalpies= -574.631745
Sum of electronic and thermal Free Energies= -574.682617

2



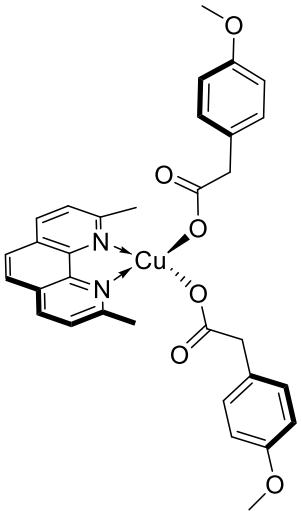


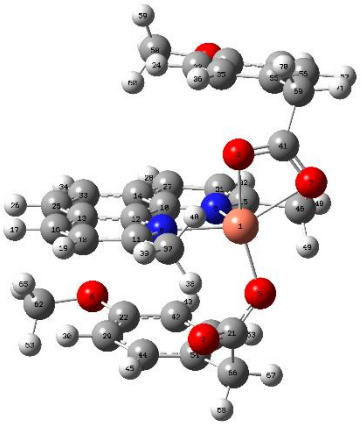
0 1

O	2.59839700	0.64050500	-0.00033200
C	1.29252500	0.27929600	-0.00037200
C	0.83239500	-1.04322400	-0.00028100
H	1.52319000	-1.87476200	-0.00034000
C	-0.53824900	-1.28541600	-0.00026600
H	-0.89735800	-2.31019500	-0.00014500
C	0.37295200	1.34423200	-0.00022800
H	0.76316300	2.35450000	-0.00015400
C	-1.45693900	-0.23522800	-0.00013500
C	-0.98153700	1.08781300	-0.00014600
H	-1.70490100	1.89464100	-0.00007700
C	3.59467800	-0.37766700	0.00073900
H	3.52483400	-1.00568800	-0.89417100
H	3.52318800	-1.00546000	0.89567700
H	4.54963400	0.14438500	0.00153800
C	-2.90467400	-0.50896200	-0.00004600
O	-3.77095300	0.33800700	0.00070100
H	-3.16820800	-1.59057700	-0.00086900

Zero-point correction= 0.142038 (Hartree/Particle)
Thermal correction to Energy= 0.150822
Thermal correction to Enthalpy= 0.151766
Thermal correction to Gibbs Free Energy= 0.108138
Sum of electronic and zero-point Energies= -460.089443
Sum of electronic and thermal Energies= -460.080659
Sum of electronic and thermal Enthalpies= -460.079715
Sum of electronic and thermal Free Energies= -460.123343

4





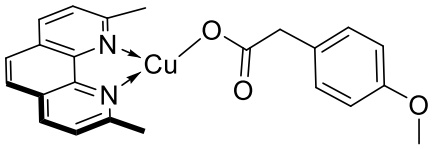
0 2

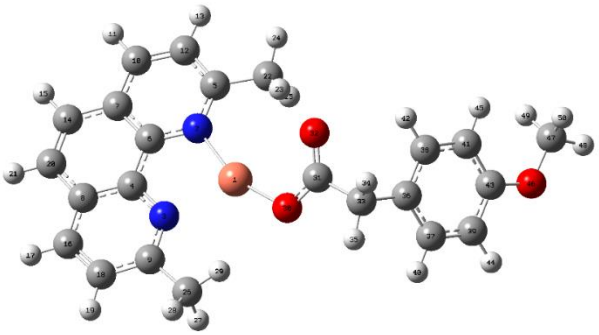
Cu	0.19018800	-2.30269300	-0.27220500
O	-2.91495800	-2.97641100	-0.52741600
O	1.76710900	-2.62434800	0.94263200
O	3.98422000	3.30960200	-0.02110900
O	-1.08763600	-2.34337900	-1.68928900
O	-2.91065000	3.74810800	-0.51695900
O	2.05874200	-2.87156300	-1.21443300
N	-0.87515400	-1.50340100	1.31296500
N	0.43031900	-0.00467600	-0.57680200
C	-0.16331800	0.63892100	0.44548400
C	-1.46485900	-2.26725700	2.23023500
C	-0.85814900	-0.15350000	1.43803800
C	-1.49817600	0.50017500	2.51612700
C	-0.14978200	2.04732900	0.56913400
C	1.00705900	0.68451800	-1.55297500
C	-2.15692900	-0.31203800	3.46101500
H	-2.66832200	0.15154500	4.29816100
C	-2.13526300	-1.67927500	3.32380300
H	-2.62306800	-2.32003300	4.04712400
C	4.02128500	1.94992800	0.11441000
C	-2.36252600	-2.41524100	-1.46898400
C	-3.05794600	2.45373300	-0.94840500
C	3.50496200	1.24872900	1.20683800
H	3.04526500	1.76615800	2.03746400
C	-1.45179000	1.92910300	2.61204700
H	-1.94887100	2.40475600	3.45059400
C	0.50844600	2.76853000	-0.44726800
H	0.53808900	3.85110700	-0.39939500
C	-3.78021800	1.47003200	-0.27022700
H	-4.28798200	1.69100300	0.65873000
C	1.07626900	2.09565500	-1.50097500
H	1.57830900	2.63297600	-2.29509000
C	-0.80333400	2.67264200	1.67674800
H	-0.78448700	3.75429300	1.74347700
C	3.54832500	-0.14267900	1.21330200
H	3.09792300	-0.68464600	2.03598900
C	-1.37695900	-3.74995500	2.04989400
H	-1.89379400	-4.00674200	1.12028100

H	-1.82530200	-4.28670600	2.88622500
H	-0.32635100	-4.04040000	1.95541100
C	2.54542500	-2.70081500	-0.06805600
C	-2.39639400	2.12770800	-2.13407800
H	-1.83417400	2.90195400	-2.64053700
C	-3.83308600	0.17614600	-0.78697900
H	-4.36615100	-0.59594600	-0.24341500
C	1.52858400	-0.09761600	-2.72046300
H	2.28617300	-0.81029500	-2.39423000
H	1.94491200	0.55433000	-3.48907500
H	0.71003700	-0.69173100	-3.13626800
C	4.59706900	1.24532400	-0.94634900
H	4.99603700	1.80641900	-1.78258200
C	-2.45473600	0.83335600	-2.63182700
H	-1.92296600	0.59003900	-3.54518500
C	-3.18062100	-0.16422900	-1.97328400
C	4.10513400	-0.86045100	0.15382200
C	4.63440300	-0.14276700	-0.92301700
H	5.06498900	-0.67628200	-1.76360600
C	3.53176800	4.08108900	1.08292600
H	4.14829800	3.90735600	1.97252400
H	2.48430600	3.86725000	1.32375100
H	3.62449400	5.12240100	0.77729200
C	-3.75454400	4.19875500	0.53275900
H	-4.81234300	4.05572800	0.28392800
H	-3.55107500	5.26326300	0.64612400
H	-3.53322000	3.68775300	1.47658200
C	-3.19245900	-1.59652800	-2.46554400
H	-2.75354000	-1.66205700	-3.46182300
H	-4.20798100	-1.99571500	-2.48626500
C	4.01202000	-2.37869100	0.12830300
H	4.35243200	-2.80890600	1.07262800
H	4.59420200	-2.79409300	-0.69416000

Zero-point correction=	0.558181 (Hartree/Particle)
Thermal correction to Energy=	0.596279
Thermal correction to Enthalpy=	0.597223
Thermal correction to Gibbs Free Energy=	0.485403
Sum of electronic and zero-point Energies=	-3439.014861
Sum of electronic and thermal Energies=	-3438.976763
Sum of electronic and thermal Enthalpies=	-3438.975819
Sum of electronic and thermal Free Energies=	-3439.087638

5





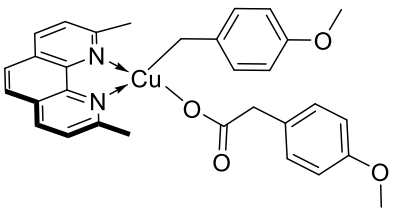
0 1

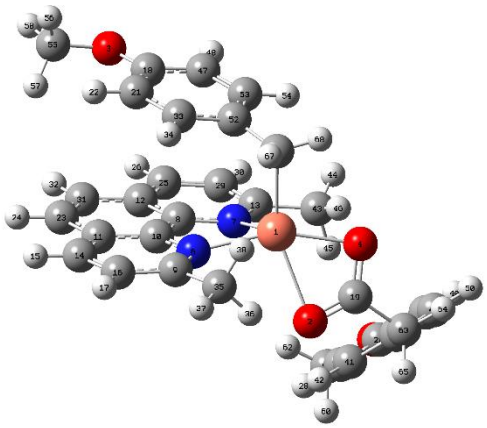
Cu	-0.74350100	-0.34362600	0.20152400
N	-1.91213200	1.29295600	0.04552400
N	-2.69910700	-1.28506900	-0.23402600
C	-3.65355400	-0.32942200	-0.29685800
C	-1.48422900	2.54976700	0.19198600
C	-3.23419100	1.04542300	-0.14706600
C	-4.20279300	2.07149000	-0.19784800
C	-5.02069800	-0.62507800	-0.49138300
C	-3.02857400	-2.56427600	-0.35261400
C	-3.74000900	3.39458100	-0.03476500
H	-4.44742500	4.21653900	-0.06188200
C	-2.39923900	3.62752800	0.15877700
H	-2.02569500	4.63572300	0.28677800
C	-5.58108700	1.73604000	-0.40113500
H	-6.30759200	2.54028700	-0.43791500
C	-5.36100300	-1.99052000	-0.61943900
H	-6.39843400	-2.27071000	-0.76843400
C	-4.37805500	-2.94892200	-0.54879500
H	-4.62120700	-4.00081800	-0.64062100
C	-5.97526900	0.44133600	-0.54252900
H	-7.02075900	0.19634200	-0.69402500
C	-0.01203800	2.76945600	0.36685800
H	0.42087500	2.03017200	1.04966900
H	0.20074300	3.77972200	0.72018800
H	0.49194800	2.62893900	-0.59559500
C	-1.92237700	-3.57977600	-0.29048400
H	-1.69059800	-3.94038800	-1.29856400
H	-2.21900400	-4.44585500	0.30660200
H	-1.01660600	-3.13638300	0.12669600
O	0.80331100	-1.39391100	0.58709700
C	1.68446700	-0.82614500	1.34222300
O	1.58004400	0.28367600	1.87235300
C	2.97368100	-1.63473800	1.54658600
H	3.21378800	-1.60176300	2.61348000
H	2.80423400	-2.67226100	1.25762300
C	4.11693200	-1.04649100	0.74534700
C	4.73875200	-1.77246600	-0.27645400
C	4.57102900	0.24981500	0.99455600
C	5.78151000	-1.23071000	-1.01668100

H	4.39929900	-2.77913400	-0.49770100
C	5.61650700	0.80960800	0.26099600
H	4.07503300	0.83436600	1.76021300
C	6.23005200	0.06567300	-0.75094900
H	6.26531900	-1.79151700	-1.80751500
H	5.93820500	1.81763800	0.48683900
O	7.26461300	0.51068200	-1.53094100
C	7.76025500	1.81936700	-1.30340500
H	8.56775300	1.96312200	-2.02057800
H	6.98887700	2.58095900	-1.47258500
H	8.15730100	1.93215600	-0.28696900

Zero-point correction= 0.391205 (Hartree/Particle)
Thermal correction to Energy= 0.418152
Thermal correction to Enthalpy= 0.419096
Thermal correction to Gibbs Free Energy= 0.328289
Sum of electronic and zero-point Energies= -2864.928845
Sum of electronic and thermal Energies= -2864.901898
Sum of electronic and thermal Enthalpies= -2864.900954
Sum of electronic and thermal Free Energies= -2864.991762

6





0 2

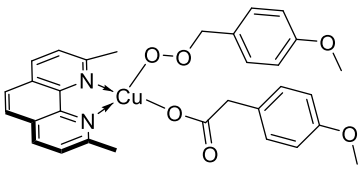
Cu	-0.01179000	1.73332700	-0.62723400
O	1.78940400	2.56381300	0.52121400
O	-4.32746400	-2.94146500	-1.20259200
O	1.74426800	2.08080800	-1.63754600
O	5.86273700	-2.72966600	0.62321800
N	-1.36294300	1.69821600	0.94682300
N	-0.01806500	-0.49736100	0.05540300
C	-1.10394700	-0.69001700	0.83595200
C	-1.93772900	2.80064200	1.42171200
C	-1.79894000	0.47643700	1.33221700
C	-2.90950800	0.31353200	2.19306100
C	-1.59199800	-1.97307000	1.16909100
C	0.63573600	-1.54319100	-0.43314900
C	-3.52269100	1.48619100	2.67574500
H	-4.37728600	1.40776000	3.33952500

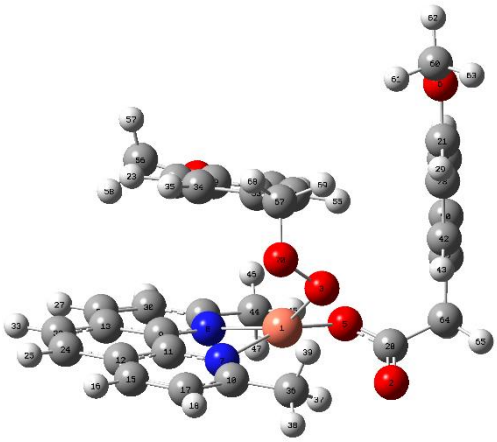
C	-3.03284300	2.71954200	2.30569400
H	-3.48295700	3.63143400	2.67791300
C	-3.72611600	-1.74331700	-1.49146100
C	2.37489400	2.40053900	-0.57708600
C	5.37701000	-1.47104500	0.40103100
C	-4.17619700	-0.49694000	-1.05357500
H	-5.08064300	-0.40378000	-0.46779700
C	-3.36983300	-1.00494600	2.51181100
H	-4.23392000	-1.10865200	3.15913700
C	-0.89476200	-3.07691900	0.63487400
H	-1.24556800	-4.08169800	0.84389100
C	4.66014100	-0.71598800	1.33469200
H	4.44495300	-1.10384200	2.32121500
C	0.20989900	-2.86451300	-0.15304400
H	0.75839800	-3.69708800	-0.57708000
C	-2.74462300	-2.10255300	2.00800900
H	-3.10600400	-3.09876100	2.23802800
C	-3.43283100	0.64591100	-1.34082300
H	-3.77767300	1.60238100	-0.96107400
C	-1.36704800	4.10948200	0.95835200
H	-0.27749600	4.08222000	1.04506300
H	-1.76690800	4.95105000	1.52518700
H	-1.59712900	4.25679600	-0.10163600
C	5.62800100	-0.93586600	-0.86625300
H	6.18087700	-1.53627900	-1.57854300
C	4.20656800	0.55725400	0.99153500
H	3.62213400	1.12826800	1.70366100
C	1.84238200	-1.28228500	-1.28520500
H	1.93409500	-2.02983000	-2.07662400
H	2.74911700	-1.33269300	-0.67480100
H	1.79981800	-0.28325800	-1.71878800
C	-2.55897800	-1.81622300	-2.26305100
H	-2.23358500	-2.78977600	-2.60945700
C	5.16726900	0.33308700	-1.19139500
H	5.35832300	0.72835300	-2.18332400
C	4.45151300	1.10351700	-0.26908600
C	-2.22640400	0.59633900	-2.06081400
C	-1.83304500	-0.67418900	-2.54214000
H	-0.91403000	-0.75322900	-3.11325800
C	-5.54783800	-2.91630500	-0.47984900
H	-6.32422200	-2.35860300	-1.01755100
H	-5.41605600	-2.47892600	0.51727900
H	-5.85871200	-3.95562400	-0.37846200
C	5.63090500	-3.32538300	1.89046400
H	6.08772700	-2.74459000	2.70070300
H	6.09704600	-4.30887400	1.84809500
H	4.55905300	-3.44234500	2.09257600
C	3.89525600	2.46693000	-0.63593000
H	4.20991500	2.74831100	-1.64131700
H	4.23671200	3.22389200	0.07425300
C	-1.36114500	1.76156900	-2.20100700
H	-1.87377800	2.72189000	-2.12337800

H	-0.67338800	1.73577700	-3.04581400

Zero-point correction= 0.541133 (Hartree/Particle)
Thermal correction to Energy= 0.577080
Thermal correction to Enthalpy= 0.578025
Thermal correction to Gibbs Free Energy= 0.470346
Sum of electronic and zero-point Energies= -3250.366158
Sum of electronic and thermal Energies= -3250.330210
Sum of electronic and thermal Enthalpies= -3250.329266
Sum of electronic and thermal Free Energies= -3250.436945

7





0 2

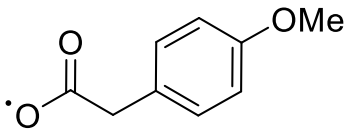
Cu	-0.39388100	-1.06411900	-0.79715700
O	1.27407700	-2.83521200	-2.35211500
O	0.78611800	-1.89140900	0.50236000
O	-0.33383500	4.26940800	-0.16397200
O	1.02973000	-0.62817400	-2.01900800
O	5.60085200	1.07416900	1.82425300
N	-2.08195600	-1.93140000	-0.02724700
N	-1.87421600	0.51388500	-1.16800400
C	-2.96573100	0.26236000	-0.39781700
C	-2.16484000	-3.17915100	0.42787300
C	-3.07555100	-1.04115000	0.20821300
C	-4.21088300	-1.36026000	0.98184300
C	-3.99975800	1.20123100	-0.19898400
C	-1.77013600	1.67869000	-1.79912500
C	-4.28102500	-2.67567100	1.49186700
H	-5.13311900	-2.96958000	2.09565300
C	-3.28342200	-3.57306600	1.20293100
H	-3.33095900	-4.59158500	1.56752600
C	-0.09744000	3.11509100	0.53900100
C	1.70684700	-1.68800600	-2.35494200
C	5.02808300	0.41183000	0.77285800
C	-0.92128600	2.63288700	1.55908000
H	-1.80448600	3.17479700	1.86871300
C	-5.22268500	-0.37059900	1.19285200
H	-6.08006600	-0.62752900	1.80498300

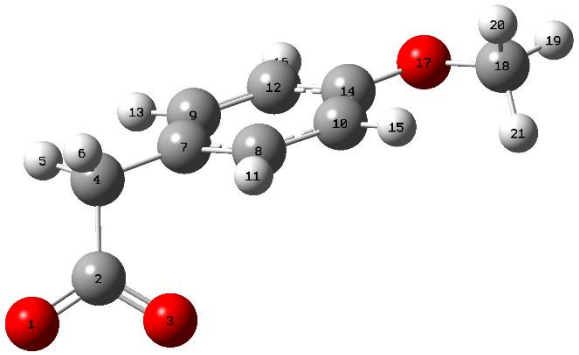
C	-3.86539600	2.44339300	-0.85851600
H	-4.63376300	3.19981000	-0.73629300
C	4.52682100	-0.89146500	0.82898600
H	4.56165600	-1.46634900	1.74448500
C	-2.77239000	2.67210300	-1.65252000
H	-2.64656800	3.61304000	-2.17281000
C	-5.11993500	0.86220300	0.62504600
H	-5.89436200	1.60598100	0.77705700
C	-0.60107400	1.42539900	2.17963700
H	-1.24695700	1.05090400	2.96777400
C	-1.05910700	-4.14228600	0.12532000
H	-0.53203000	-3.87544200	-0.79181600
H	-1.44927700	-5.16061500	0.06146600
H	-0.31771000	-4.08939200	0.92632100
C	4.94338600	1.12764500	-0.42509100
H	5.32824200	2.14007600	-0.44824600
C	3.94864000	-1.45975000	-0.30563300
H	3.51401200	-2.45002200	-0.23509400
C	-0.59512200	1.93784400	-2.69113000
H	0.18651600	1.19517900	-2.54389800
H	-0.20731100	2.94097700	-2.50052800
H	-0.92194800	1.89850200	-3.73661400
C	1.02870300	2.38567400	0.14942700
H	1.65017100	2.76614400	-0.65060600
C	4.36520700	0.54426100	-1.54506100
H	4.29249400	1.11816900	-2.46306900
C	3.86092500	-0.76015700	-1.50949500
C	0.52419500	0.69166300	1.80688400
C	1.33077100	1.18540500	0.77251800
H	2.18519700	0.61275200	0.44023700
C	-1.29971900	5.17779000	0.34543900
H	-1.07052100	5.46530500	1.37775100
H	-2.31174500	4.75877200	0.30419300
H	-1.25128500	6.05791200	-0.29478600
C	5.63916000	0.42285000	3.08374300
H	4.63148300	0.18046500	3.44333700
H	6.10509400	1.12766600	3.77138100
H	6.23841500	-0.49514800	3.04894700
C	3.16902200	-1.38413100	-2.70263300
H	3.64958300	-2.31775900	-3.00110600
H	3.19320400	-0.69421700	-3.55044200
C	0.83679500	-0.63568100	2.44620700
H	0.45490400	-0.67839400	3.47101900
H	1.91651000	-0.81598800	2.45244600
O	0.19581500	-1.73803800	1.79518800

Zero-point correction= 0.551196 (Hartree/Particle)
Thermal correction to Energy= 0.588741
Thermal correction to Enthalpy= 0.589685
Thermal correction to Gibbs Free Energy= 0.478509
Sum of electronic and zero-point Energies= -3400.769760

```
 Sum of electronic and thermal Energies=           -3400.732215
 Sum of electronic and thermal Enthalpies=         -3400.731271
 Sum of electronic and thermal Free Energies=      -3400.842447
```

8





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0 2
 O                -4.21888100    0.24169300    0.37288800
 C                -2.98794200    0.30273600    0.20909900
 O                -2.38757600    1.17022000    0.90639300
 C                -2.22542200   -0.56734500   -0.77074300
 H                -2.60365000   -1.58908100   -0.69334200
 H                -2.47562900   -0.21456500   -1.77688200
 C                -0.74630400   -0.47961400   -0.49913300
 C                -0.04258700    0.69786600   -0.77842600
 C                -0.04812000   -1.54592800    0.08455300
 C                 1.31707400    0.81541900   -0.50533000
 H                -0.56670600    1.53831000   -1.21803700
 C                 1.30346300   -1.44703900    0.35976500
 H                -0.57346500   -2.46491900    0.32113700
 C                 1.99898900   -0.26190100    0.06826000
 H                 1.82597200    1.74059100   -0.73706400
 H                 1.85381200   -2.26792000    0.80242600
 O                 3.31977400   -0.26900000    0.37771500
 C                 4.08611300    0.90634000    0.13344900
 H                 5.09649500    0.67442400    0.46497300
 H                 4.10265600    1.15794400   -0.93284500
 H                 3.70238800    1.75870400    0.70471000
```

```
Zero-point correction=                0.161477 (Hartree/Particle)
 Thermal correction to Energy=                  0.172561
 Thermal correction to Enthalpy=                0.173506
 Thermal correction to Gibbs Free Energy=       0.122488
 Sum of electronic and zero-point Energies=          -573.991090
 Sum of electronic and thermal Energies=             -573.980006
 Sum of electronic and thermal Enthalpies=           -573.979062
 Sum of electronic and thermal Free Energies=        -574.030079
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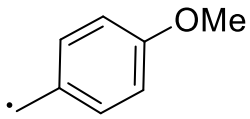
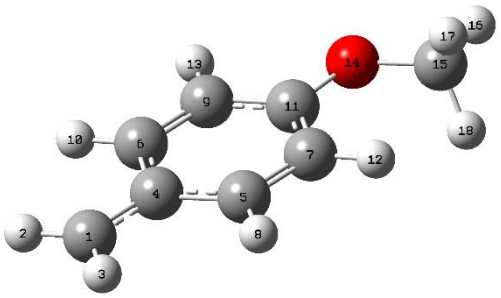
9



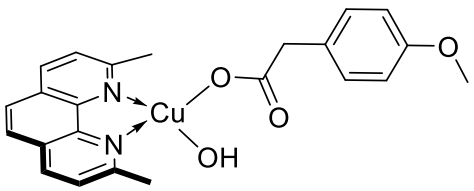


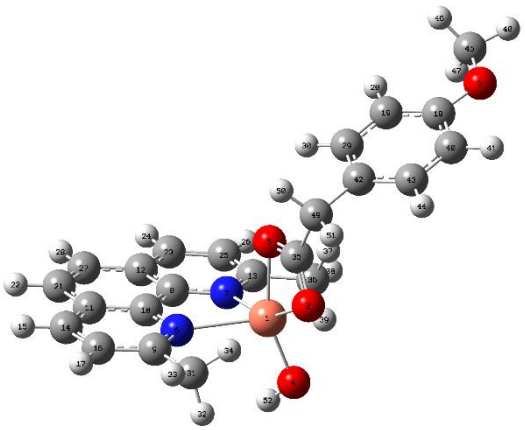
0 2

C	-3.30009000	-0.31693700	0.00042900
H	-3.98295000	0.52325400	0.00063400
H	-3.72452900	-1.31303500	0.00049700
C	-1.91180000	-0.12128400	-0.00000100
C	-0.99947200	-1.21281800	-0.00024900
C	-1.33771900	1.18715700	-0.00008900
C	0.37320000	-1.02395800	-0.00035000
H	-1.39420900	-2.22321600	-0.00041900
C	0.02427900	1.37726000	-0.00014100
H	-1.99814900	2.04767300	-0.00011300
C	0.90043700	0.27572900	-0.00018200
H	1.02536900	-1.88711900	-0.00069600
H	0.45659800	2.37072100	-0.00021200
O	2.22760700	0.57968700	-0.00003700
C	3.16936000	-0.48511200	0.00041400
H	4.15097600	-0.01403100	0.00100500
H	3.06796400	-1.11107400	0.89459900
H	3.06889800	-1.11089600	-0.89398500

Zero-point correction=	0.146717 (Hartree/Particle)
Thermal correction to Energy=	0.154910
Thermal correction to Enthalpy=	0.155855
Thermal correction to Gibbs Free Energy=	0.113506
Sum of electronic and zero-point Energies=	-385.402916
Sum of electronic and thermal Energies=	-385.394722
Sum of electronic and thermal Enthalpies=	-385.393778
Sum of electronic and thermal Free Energies=	-385.436127

10





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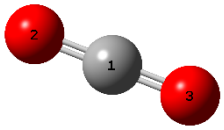
0 2
 Cu                  0.67077500    0.58570200   -1.24073300
 O                  -0.69021300    2.27435100   -0.96929100
 O                  -6.92021900   -0.94698400    0.35829600
 O                   1.11725400    0.58184000   -3.04283300
 O                  -0.53120500    0.57926300    0.41625400
 N                   2.59025100    1.10597900   -0.02822500
 N                   1.49336400   -1.28686300   -0.73479200
 C                   2.55945000   -1.28807300    0.09445500
 C                   3.09507900    2.29233000    0.28137100
 C                   3.13853100   -0.01763600    0.47645800
 C                   4.25228500   -0.00132400    1.34762600
 C                   3.12554800   -2.48681400    0.58582900
 C                   0.93475800   -2.42645700   -1.13004300
 C                   4.77465300    1.26674500    1.68204700
 H                   5.62519500    1.33425500    2.35222900
 C                   4.20396200    2.40179100    1.15507900
 H                   4.59393400    3.38267400    1.39841500
 C                  -5.75572700   -0.25125100    0.52603800
 C                  -4.59971800   -0.76243200    1.12363000
 H                  -4.56578100   -1.77708400    1.49718200
 C                   4.79162300   -1.23519700    1.83727700
 H                   5.64433500   -1.19870500    2.50641800
 C                   2.53022900   -3.69378600    0.16239800
 H                   2.93290700   -4.63836200    0.51260000
 C                   1.44967000   -3.66543400   -0.68894400
 H                   0.98204500   -4.58238900   -1.02510800
 C                   4.25275700   -2.42856400    1.46903300
 H                   4.66863900   -3.35940100    1.83854100
 C                  -3.46876200    0.04444500    1.24338300
 H                  -2.56578500   -0.36082900    1.68409300
 C                   2.46206000    3.49472400   -0.35820300
 H                   2.84535700    3.60770100   -1.37772200
 H                   2.68270800    4.40913000    0.19523900
 H                   1.38254800    3.35872600   -0.44521600
 C                  -1.07981900    1.67580300    0.06571600
 C                  -0.25316600   -2.31334100   -2.03821000
 H                  -1.09097400   -1.88236900   -1.47971300
 H                  -0.55478400   -3.28080700   -2.44040700
 H                  -0.02053500   -1.61330100   -2.84757600
 C                  -5.75894300    1.06380300    0.05189300
 H                  -6.66127100    1.44167400   -0.41328900
 C                  -3.46115900    1.36015300    0.77923800
 C                  -4.62416400    1.85296200    0.17783900
 H                  -4.64095300    2.86919200   -0.20155300
 C                  -6.97365100   -2.29017000    0.81246500
 H                  -6.81050600   -2.35850900    1.89494100
 H                  -6.23901700   -2.92110700    0.29738700
 H                  -7.97653200   -2.64505000    0.57866500
 C                  -2.22031500    2.22376600    0.90452000
 H                  -1.88432500    2.24809100    1.94595500
 H                  -2.42841500    3.24352000    0.58072100
```

```
 H                  1.98740400    0.19978500   -3.19419600


Zero-point correction=                0.404617 (Hartree/Particle)
 Thermal correction to Energy=                    0.433531
 Thermal correction to Enthalpy=                  0.434475
 Thermal correction to Gibbs Free Energy=         0.340307
 Sum of electronic and zero-point Energies=         -2940.745962
 Sum of electronic and thermal Energies=            -2940.717048
 Sum of electronic and thermal Enthalpies=          -2940.716104
 Sum of electronic and thermal Free Energies=       -2940.810272
```

CO_2

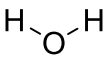
O=C=O

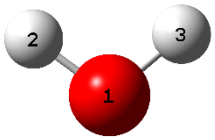



```
0 1
 C                  0.00000000    0.00000000    0.00000000
 O                  0.00000000    0.00000000    1.16052400
 O                  0.00000000    0.00000000   -1.16052400


Zero-point correction=                0.011717 (Hartree/Particle)
 Thermal correction to Energy=                    0.014340
 Thermal correction to Enthalpy=                  0.015284
 Thermal correction to Gibbs Free Energy=        -0.008977
 Sum of electronic and zero-point Energies=           -188.629601
 Sum of electronic and thermal Energies=              -188.626979
 Sum of electronic and thermal Enthalpies=            -188.626035
 Sum of electronic and thermal Free Energies=         -188.650295
```

H_2O





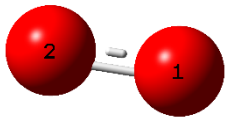

```
0 1
 O                  0.00000000    0.00000000    0.11865100
 H                  0.00000000    0.75700000   -0.47460500
 H                  0.00000000   -0.75700000   -0.47460500


Zero-point correction=                0.021323 (Hartree/Particle)
 Thermal correction to Energy=                    0.024158
 Thermal correction to Enthalpy=                  0.025102
 Thermal correction to Gibbs Free Energy=         0.003676
 Sum of electronic and zero-point Energies=            -76.426134
 Sum of electronic and thermal Energies=               -76.423299
```

```
 Sum of electronic and thermal Enthalpies=            -76.422354
 Sum of electronic and thermal Free Energies=         -76.443780
```

O_2

O=O




```
0 3
 O                  0.00000000    0.00000000    0.60281900
 O                  0.00000000    0.00000000   -0.60281900
```

```
Zero-point correction=                0.003738 (Hartree/Particle)
 Thermal correction to Energy=                    0.006101
 Thermal correction to Enthalpy=                  0.007045
 Thermal correction to Gibbs Free Energy=        -0.016227
 Sum of electronic and zero-point Energies=        -150.361051
 Sum of electronic and thermal Energies=           -150.358688
 Sum of electronic and thermal Enthalpies=         -150.357743
 Sum of electronic and thermal Free Energies=      -150.381016
```

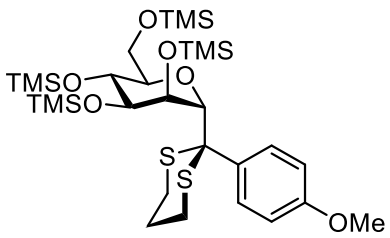
2. Chapter C

2.1. General Information

All reactions were run under anhydrous conditions under nitrogen atmosphere unless stated otherwise. Reactions carried out at 0 °C employed an ice bath. All commercially purchased chemicals were used without further purification, unless stated otherwise. The concentrations of *tert*-butyllithium solutions were determined by titration of menthol in THF with 1,10-phenantroline as indicator.[21]

2.2. Standard reaction procedure

2-(α-D-mannopyranosyl)-2-(4-methoxyphenyl)-1,3-dithiane **13**



TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) was added to neat 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-mannopyranose (1.00 g, 1.85 mmol, 1.00 equiv.) and the mixture was stirred

at room temperature for 15 min to give 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **11** as orange oil, which was dissolved in glyme (5.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-methoxyphenyl)-1,3-dithiane (837 mg, 3.70 mmol, 2.00 equiv.) in glyme (7.9 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.74 M in *n*-pentane, 2.10 mL, 3.65 mmol, 1.98 equiv.) was added. The mixture was stirred at 0 °C for 5 min to form the lithiated dithiane **12**. A solution of CuI (3.5 mg, 18.5 µmol, 1.0 mol%) in glyme (5.0 mL) was prepared and cooled to 0 °C. The precooled solutions of CuI, 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **11** and glyme (5 mL) were added to the dithiane solution **12** and samples for measurements were taken.

2.3. UV/Vis Absorption Spectroscopy

UV/Vis spectra were recorded using an analytikjena SPECORD 50 PLUS spectrometer, using a sealed, nitrogen flushed quartz cuvette (10 mm by 10 mm). Sample preparation was done according to the synthesis procedure of **13** (see Chapter 2.2 Standard reaction procedure). Measurements were started 5 min after sample preparation.

2.3.1. Reference Spectra

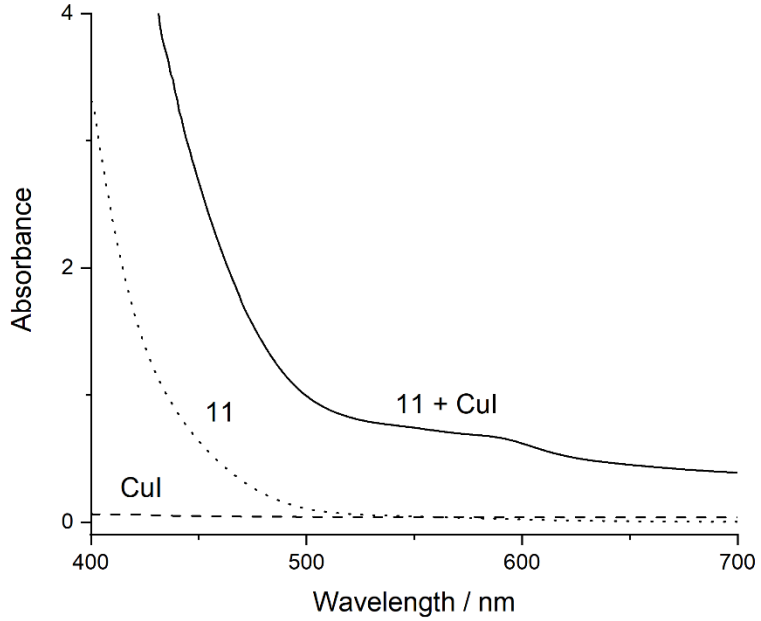


*Figure 38: Solutions of **11** (92.5 mmol/L, 1 equiv.) and CuI (0.925 mmol/L, 1 mol%) in glyme.*

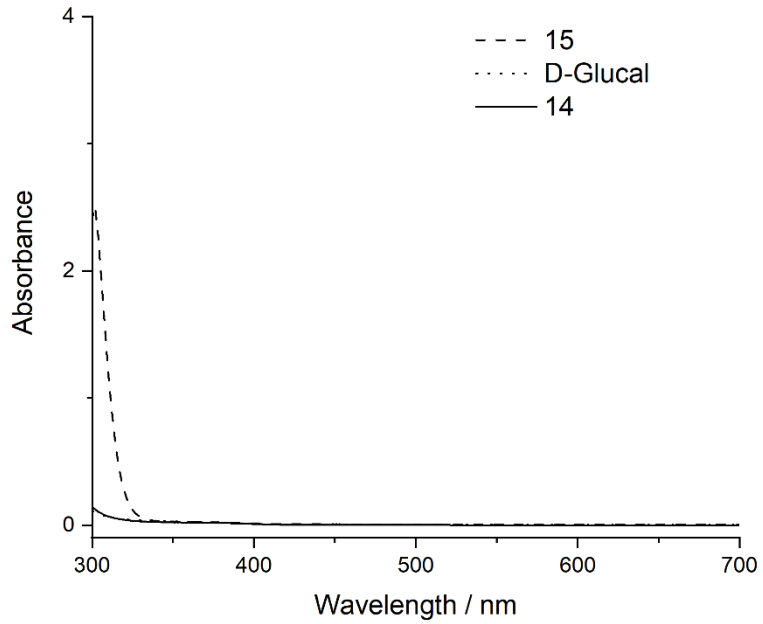


*Figure 39: Solutions of **15** (5 mmol/L), D-Glucal (5 mmol/L) and **14** (5 mmol/L) in glyme.*

2.3.2. Kinetic studies

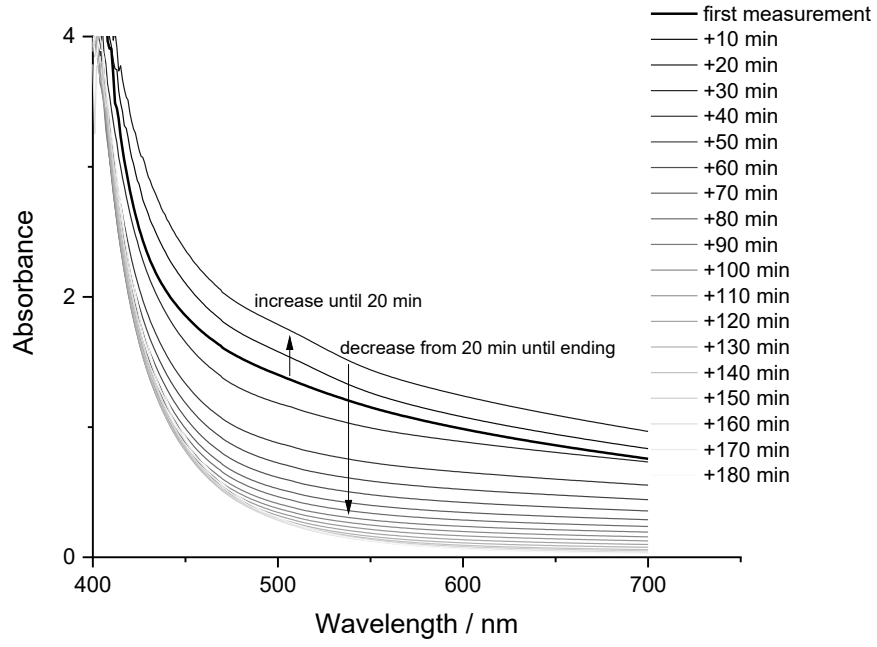


*Figure 40: Solution of **11** (92.5 mmol/L, 1 equiv.), **12** (185 mmol/L, 2 equiv.) and CuI (0.925 mmol/L, 1 mol%) in glyme. Measurement over 180 min in 10 min intervals.*

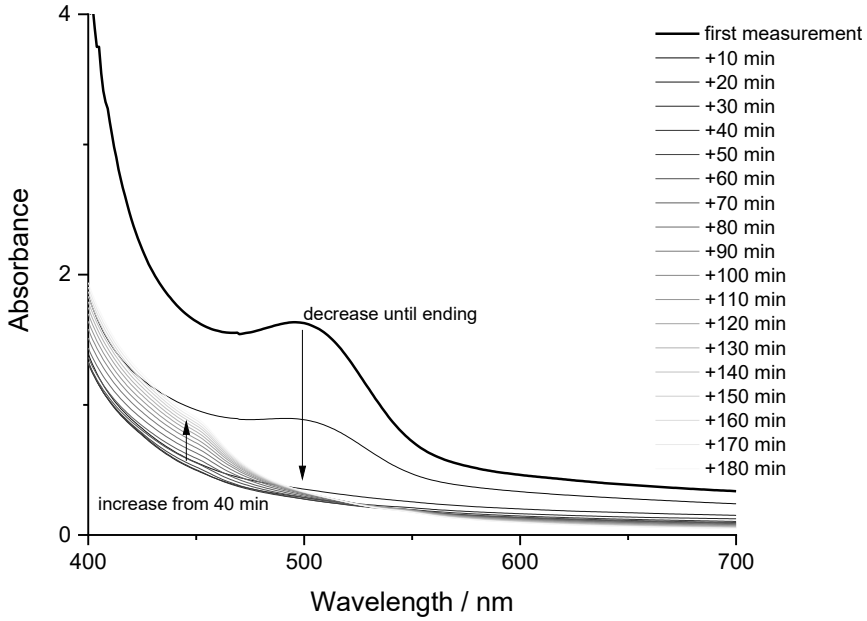


*Figure 41: Solution of **11** (92.5 mmol/L, 1 equiv.) and **12** (185 mmol/L, 2 equiv.) in glyme. Measurement over 180 min in 10 min intervals.*

2.4. EPR Spectroscopy

CW-EPR experiments were carried out on a Bruker EMX Spectrometer (X-Band, 9-10 GHz) equipped with an ER 083 (200/60) power source electromagnet (0-6000 G). For the measurements, an ER 4104 OR/9009 resonant cavity with a resonance frequency of 9.63 GHz was used. Samples were measured in quartz cuvettes, which were evacuated and flushed with dry N_2 several times before being filled with 0.3 mL of the specified solutions. Solvents were degassed by three freeze-pump-thaw cycles and stored under dry N_2 for no more than one week. Between preparation and the first obtained spectrum 10 min went by unless stated otherwise.
EPR spectra were obtained as a first order derivative plot. Raw data were exported in the ASCII file format and processed with Origin 2019b (Version 9.6.5.169). All spectra are baseline and solvent corrected. For quantitative comparisons the spectra were integrated twice. TEMPO was used as an external standard and all spectra were referenced via the TEMPO g-value (exp.: g_{iso}=1.997, lit.: g_{iso}=2.006).[22]
Sample preparation was done according to the synthesis procedure of **13** (see Chapter 2.2 Standard reaction procedure). Measurements were started 10 min after sample preparation. For kinetic measurements samples were frozen in liquid nitrogen and warmed to room temperature directly before the measurement.

2.4.1. Reference Spectra

Spectrum	Resonance Frequency	Microwave Power	Modulation Amplitude	Conversion Time	Time Constant	Receiver gain	Resolution
Figure 42 **11** + **12** + CuI	9.629 GHz	26.08 mW	25 G	80.0 ms	81.92 ms	2.0 x 10^3	1024
Figure 42 **11** + CuI	9.630 GHz	26.14 mW	25 G	83.0 ms	81.92 ms	2.0 x 10^4	1024
Figure 42 **12** + CuI	9.631 GHz	26.27 mW	25 G	83.0 ms	81.92 ms	2.0 x 10^4	1024
Figure 43	9.629 GHz	26.08 mW	25 G	80.0 ms	81.92 ms	2.0 x 10^3	1024
Figure 44	9.628 GHz	26.56 mW	25 G	80.0 ms	81.92 ms	2.0 x 10^3	1024
Figure 45	9.625 GHz	26.49 mW	25 G	80.0 ms	81.92 ms	2.0 x 10^3	1024

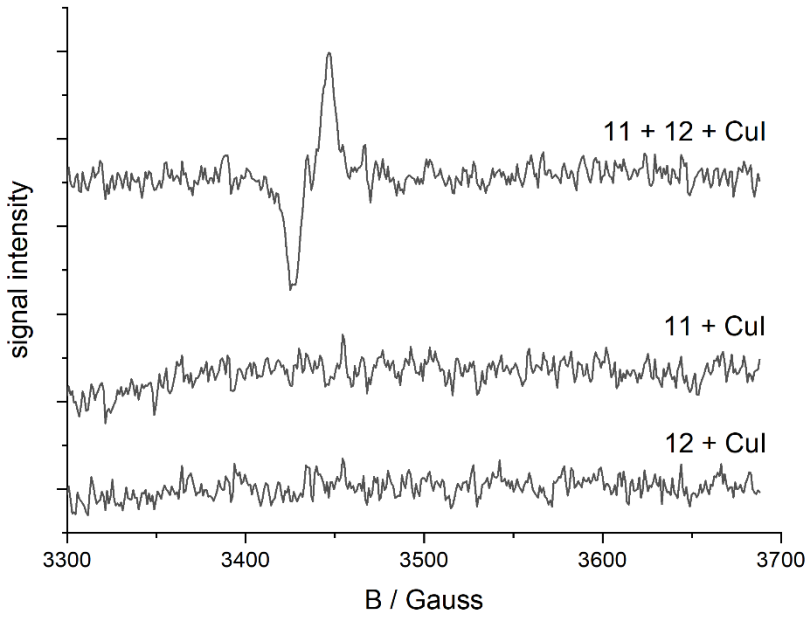


*Figure 42: EPR spectra of solutions in glyme consisting mixtures of **11** (92.5 mmol/L, 1 equiv.), **12** (185 mmol/L, 2 equiv.) and CuI (0.925 mmol/L, 1 mol%).*

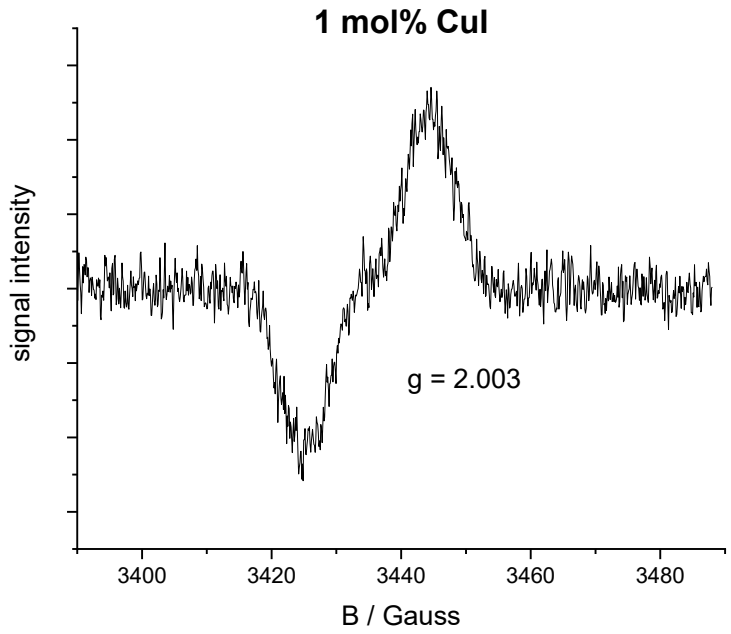


*Figure 43: Solution of **11** (92.5 mmol/L, 1 equiv.), **12** (185 mmol/L, 2 equiv.) and CuI (0.925 mmol/L, 1 mol%) in glyme.*

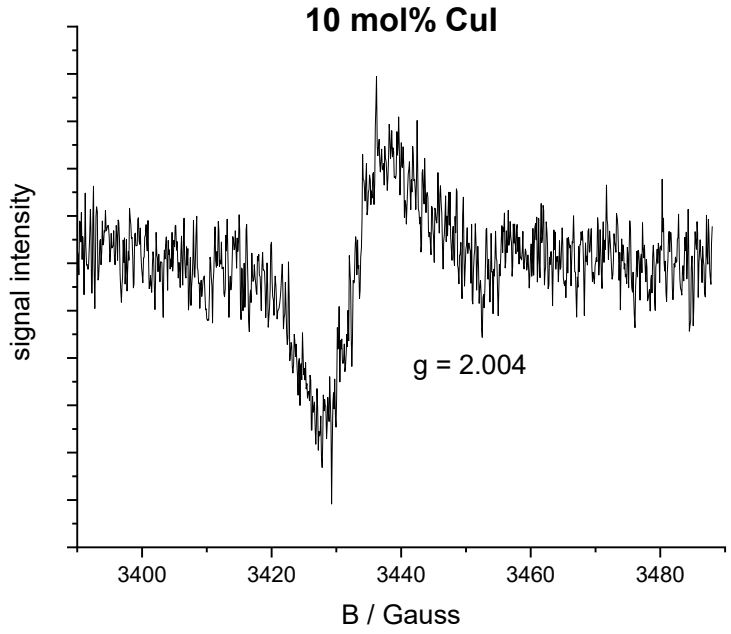


*Figure 44: Solution of **11** (92.5 mmol/L, 1 equiv.), **12** (185 mmol/L, 2 equiv.) and CuI (9.25 mmol/L, 10 mol%) in glyme.*

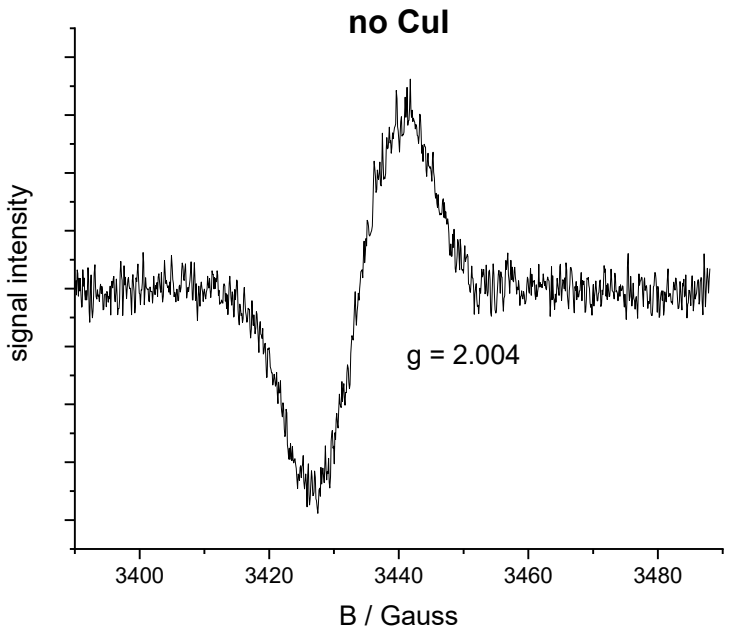


*Figure 45: Solution of **11** (92.5 mmol/L, 1 equiv.) and **12** (185 mmol/L, 2 equiv.) in glyme.*

2.4.2. Kinetic studies

Spectrum	Resonance Frequency	Microwave Power	Modulation Amplitude	Conversion Time	Time Constant	Receiver gain	Resolution
Figure 24A	9.629 GHz	26.91 mW	25 G	80.0 ms	81.92 ms	2.0×10^3	512
Figure 24B	9.625 GHz	26.75 mW	25 G	80.0 ms	81.92 ms	2.0×10^3	512

2.5. Computational Chemistry

All calculations were conducted using the Gaussian16[1] (Revision C.01) software package. Density functional theory calculations were carried out with the Becke-style 3-parameter exchange functional with the Lee-Yang-Parr correlation functional (B3LYP).[2–5] The final structures were calculated with the addition of Grimme's empirical dispersion correction D3.[6] For the atoms H, Li, C, N, O, Si , S the Pople-type triple zeta split-valence basis set 6-311G(d,p)[7–9] was used, whereas for Cu and I atoms the Ahlrichs-Weigend triple zeta valence polarisation basis set def2-TZVP[10,11] was used. Stationary points were confirmed as local minima by frequency calculations (no imaginary frequencies). Wavefunctions of open-shell molecules were checked for stability by using the keyword ***stable***. Enthalpies were obtained by the sum of electronic and thermal enthalpies and Gibbs free energies were obtained by the sum of electronic and thermal free energies both corrected for zero-point energies (ZPE). UV/Vis absorption spectra were simulated by TD-DFT calculations using the same level of theory as stated above. Visualization of geometries was achieved with GaussView[12] (Version 6.0.16). Visualization for the titlepage was done with VMD.[13–20]

2.5.1. Simulated UV/Vis Absorption Spectra

All data for the calculated UV/vis spectra were exported from GaussView and visualized with Origin 2019b (Version 9.6.5.169).

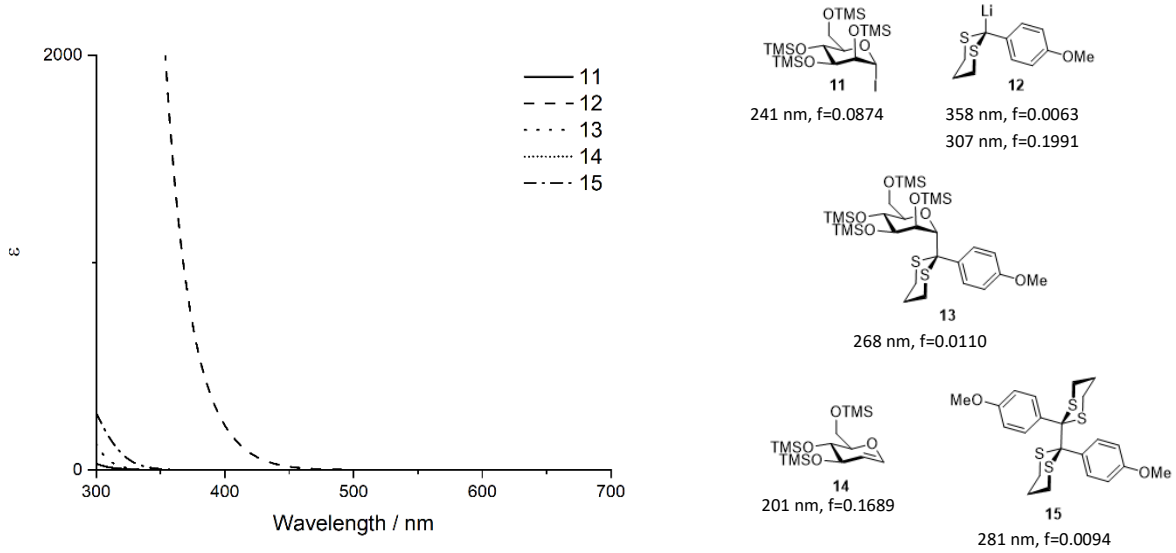


*Figure 46: Simulated UV/vis spectrum of **11**, **12**, **13**, **14** and **15**.*

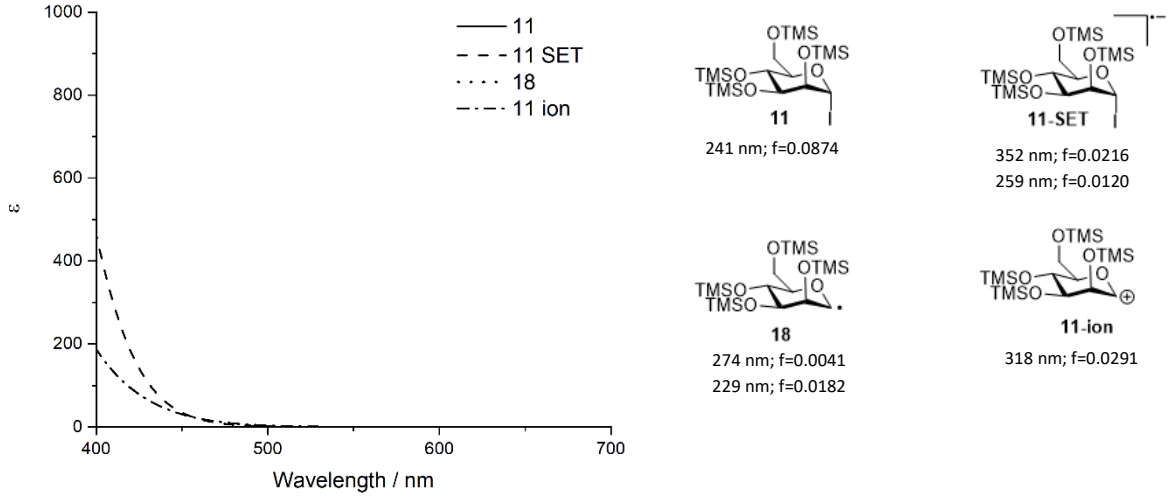


*Figure 47: Simulated UV/vis spectrum of **11**, **11-SET**, **18** and **11-ion**.*

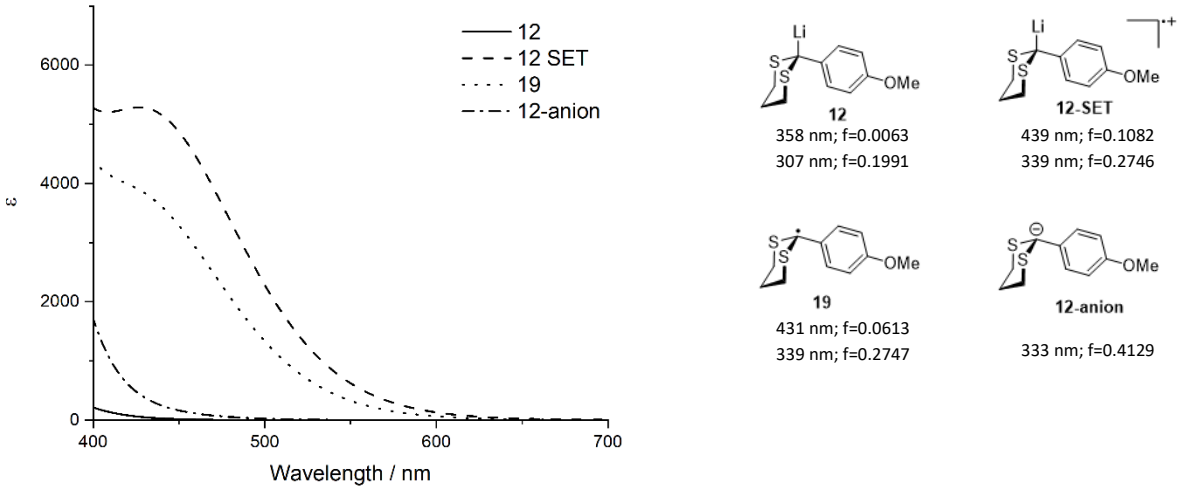


*Figure 48: Simulated UV/vis spectrum of **12**, **12-SET**, **19** and **12-anion**.*

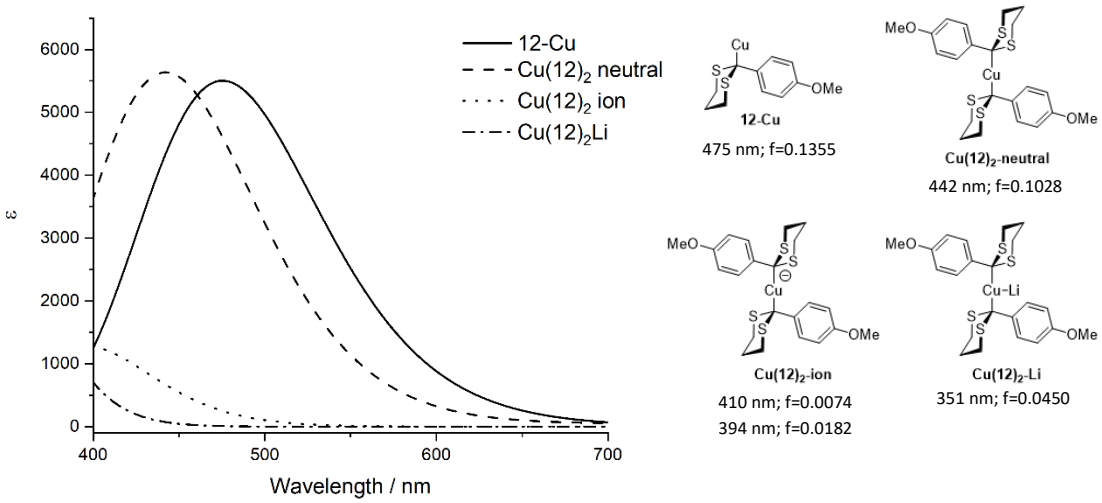


*Figure 49: Simulated UV/vis spectrum of **12-Cu**, **Cu(12)$_2$-neutral**, **Cu(12)$_2$-ion** and **Cu(12)$_2$-Li**.*

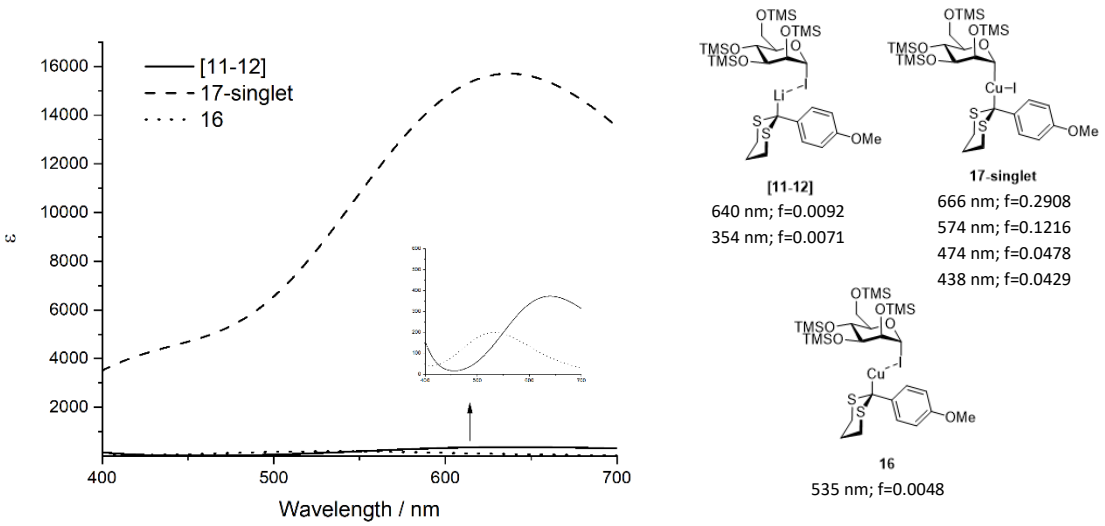


*Figure 50: Simulated UV/vis spectrum of **[11-12]**, **17-singlet** and **16**.*

2.5.2. Calculation Examples

Geometry optimization and frequency calculation:

 # b3lyp/chkbas opt freq(noraman)
int(ultrafine)
SCF(tight)
empiricaldispersion=gd3
scrf(read)

opt_freq

0 1

EPS=7.2
EPSINF=1.379

Stability of the wavefunction:

 # ub3lyp/chkbas gfinput pseudo=read stable
int=ultrafine
empiricaldispersion=gd3
geom(check)

guess(read)
scrf(read)

stable

0 2

EPS=7.2
EPSINF=1.379

TD-DFT calculation:

 # ub3lyp/chkbas
int(ultrafine)
SCF(tight)
empiricaldispersion=gd3
td=(NStates=10)
scrf(read)

tddft

0 1

EPS=7.2
EPSINF=1.379

NBO calculation:

 # ub3lyp/chkbas pop=(nbo7,savenbos,reg)
int(ultrafine)
SCF(tight)
empiricaldispersion=gd3
scrf(read)

nbo

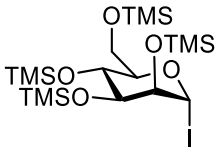
0 1

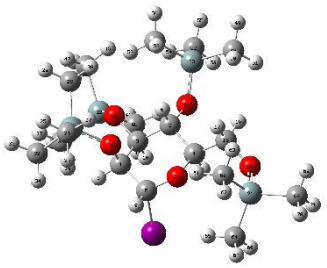
EPS=7.2

EPSINF=1.379

2.5.3. Optimized xyz-Matrices and Thermodynamic Data

11





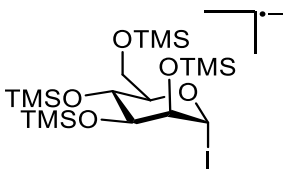
0 1

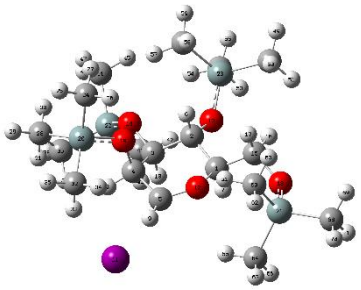
C	1.26620000	0.82275800	-0.28555600
C	-0.22934800	1.06096900	-0.01105800
C	-1.00895600	-0.19790400	-0.39845400
C	-0.46956400	-1.38813400	0.40529000
C	1.04567100	-1.51678200	0.21751500
H	-0.37277200	1.23381100	1.06067700
H	1.41774800	0.67043800	-1.36075000
H	-0.95793100	-2.30810300	0.07358800
H	1.46987500	-2.27719500	0.86472900
H	-0.81997100	-0.38605900	-1.46111800
I	1.45162100	-2.43692700	-1.85343300
O	1.73519500	-0.35951100	0.40385000
O	-0.66280300	2.16377200	-0.78534100
O	-2.39142700	-0.03233600	-0.15354000
C	2.14349500	1.96866900	0.19029400
H	1.77025300	2.88585900	-0.26554100
H	2.04074100	2.06051600	1.27929000
O	3.49660900	1.81346300	-0.19225600
O	-0.64344400	-1.18039000	1.79452900
Si	-1.88313400	-1.73818900	2.79919500
Si	4.70601800	0.94358300	0.59699800
Si	-3.58927200	-0.18076300	-1.33681200
Si	-1.46551500	3.52998600	-0.19506100
C	-1.03236200	-2.13963400	4.42120000
H	-1.76116600	-2.45968800	5.17234500
H	-0.30054100	-2.94232000	4.29355500
H	-0.50959900	-1.26247900	4.81376500
C	-3.16277700	-0.39349000	3.04829200
H	-3.94209600	-0.72574900	3.74158800
H	-2.70365500	0.50956600	3.46030000
H	-3.62163200	-0.12929700	2.09482300
C	-2.65294600	-3.27492100	2.04403400
H	-3.13725100	-3.05998700	1.08900200
H	-1.90644000	-4.05773400	1.87985400
H	-3.41428900	-3.67626700	2.72003200
C	-4.07115200	-1.98662200	-1.52512200
H	-4.54422200	-2.37027700	-0.61712900

H	-4.78112600	-2.10874800	-2.34948100
H	-3.19727900	-2.60781300	-1.74433500
C	-2.94041900	0.48338400	-2.96966400
H	-3.77052500	0.68109000	-3.65468600
H	-2.38575000	1.41155300	-2.81685100
H	-2.27211900	-0.23200300	-3.45754500
C	-5.03264900	0.81765900	-0.68311500
H	-4.78726800	1.87950700	-0.60760600
H	-5.89861500	0.71538800	-1.34412800
H	-5.32667100	0.46797000	0.31066100
C	-0.20584700	4.85328600	0.24501300
H	-0.71628700	5.76704700	0.56632100
H	0.44469100	4.53137000	1.06329200
H	0.42456200	5.10485200	-0.61280600
C	-2.54313400	4.11896700	-1.60970700
H	-1.94871700	4.25100800	-2.51832200
H	-3.34577200	3.41210900	-1.83128200
H	-2.99929400	5.08271900	-1.36356300
C	-2.47265700	3.07468600	1.32136500
H	-3.04635400	2.16367300	1.14478600
H	-1.83375900	2.90323200	2.19239700
H	-3.16397800	3.88538800	1.57127400
C	4.22371100	0.64136700	2.38737300
H	3.31260300	0.04167900	2.44761200
H	5.02472100	0.10132200	2.90181400
H	4.05577600	1.57948800	2.92497300
C	5.00910200	-0.67797900	-0.29535000
H	4.11725700	-1.30691800	-0.27090900
H	5.27088600	-0.50455200	-1.34337200
H	5.83445900	-1.22584300	0.17102100
C	6.23984800	2.02119900	0.49201900
H	6.09686200	2.96412400	1.02776300
H	7.10275700	1.50946800	0.93008600
H	6.48226300	2.25546100	-0.54879200

Zero-point correction=	0.586003 (Hartree/Particle)
Thermal correction to Energy=	0.629202
Thermal correction to Enthalpy=	0.630146
Thermal correction to Gibbs Free Energy=	0.509265
Sum of electronic and zero-point Energies=	-2543.935687
Sum of electronic and thermal Energies=	-2543.892489
Sum of electronic and thermal Enthalpies=	-2543.891544
Sum of electronic and thermal Free Energies=	-2544.012426

11-SET





-1 2

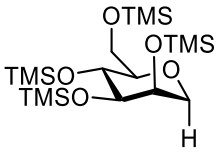
C	1.79777400	-0.31347200	0.48856400
C	0.61290800	-1.19366900	0.05627900
C	-0.66424900	-0.35006600	0.03823100
C	-0.47003400	0.83307700	-0.91648700

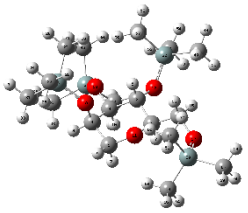
C	0.77836900	1.57299300	-0.57258100
H	0.78944300	-1.56266700	-0.96014800
H	1.62816400	0.02166300	1.51884000
H	-1.32543400	1.50792200	-0.81500000
H	0.98798800	2.53463700	-1.02465200
H	-0.81384200	0.06654900	1.04125900
I	-2.00955500	2.94368400	2.13716100
O	1.91915600	0.85124600	-0.35316700
O	0.48818200	-2.26024100	0.98489700
O	-1.76630900	-1.15041400	-0.35022000
C	3.12802400	-1.04380200	0.40880000
H	3.03590100	-1.98047100	0.95852200
H	3.33390800	-1.27915900	-0.64397500
O	4.19803500	-0.31486000	0.98864000
O	-0.37606400	0.31270300	-2.26715200
Si	-1.12415100	1.00962400	-3.59587900
Si	5.04854300	0.98583600	0.34214400
Si	-3.20460600	-1.31994800	0.50835300
Si	0.38067000	-3.89817500	0.60928100
C	-0.57719600	-0.03353400	-5.05434900
H	-1.02074300	0.33567700	-5.98435200
H	0.51060200	-0.01043700	-5.16562500
H	-0.88392700	-1.07518400	-4.92353600
C	-2.99171100	0.96014600	-3.39511400
H	-3.48494900	1.39900800	-4.26837900
H	-3.34340300	-0.06920200	-3.28378000
H	-3.31200300	1.52103000	-2.51308700
C	-0.55866000	2.79373100	-3.78624500
H	-0.83448700	3.38876500	-2.91018100
H	0.52726500	2.85019300	-3.90471800
H	-1.02169400	3.25857700	-4.66257800
C	-4.39117900	0.06900700	0.07924300
H	-4.63432600	0.06744700	-0.98644900
H	-5.32462200	-0.03743100	0.64217500
H	-3.95369300	1.03791300	0.33731800
C	-2.84989700	-1.32459600	2.35200300
H	-3.72467500	-1.67537300	2.90880900
H	-2.00417900	-1.97554900	2.58640400
H	-2.61169500	-0.31498900	2.69918500
C	-3.91016700	-2.95945700	-0.07779700
H	-3.27004100	-3.80109200	0.19685200
H	-4.89916000	-3.12794500	0.35985500
H	-4.02026500	-2.96213800	-1.16642100
C	2.09869700	-4.66303600	0.67429600
H	2.04259600	-5.74272900	0.50052700
H	2.75378400	-4.23659500	-0.09109000
H	2.56776600	-4.50328100	1.64963100
C	-0.69324800	-4.65312400	1.94735600
H	-0.28655500	-4.42875900	2.93770200
H	-1.71506300	-4.26978400	1.90904000
H	-0.73349200	-5.74144700	1.83848100
C	-0.34986200	-4.13010700	-1.10460700
H	-1.22844800	-3.49541800	-1.23094500
H	0.37092700	-3.86657800	-1.88418700
H	-0.63839200	-5.17493500	-1.25631200
C	4.99952800	0.93163700	-1.53547000

H	3.97245700	1.02707900	-1.89390800
H	5.58875500	1.75525300	-1.95099800
H	5.41541600	-0.00467500	-1.92025500
C	4.36022500	2.60666800	0.99058500
H	3.31857600	2.72909100	0.68840700
H	4.40567400	2.63867400	2.08335200
H	4.93778000	3.45369400	0.60564500
C	6.80875400	0.76141700	0.96080400
H	7.24838600	-0.16326500	0.57550400
H	7.44017800	1.59637300	0.64011500
H	6.83707400	0.72122600	2.05379800

Zero-point correction=	0.583218 (Hartree/Particle)
Thermal correction to Energy=	0.627276
Thermal correction to Enthalpy=	0.628220
Thermal correction to Gibbs Free Energy=	0.502511
Sum of electronic and zero-point Energies=	-2544.048286
Sum of electronic and thermal Energies=	-2544.004228
Sum of electronic and thermal Enthalpies=	-2544.003284
Sum of electronic and thermal Free Energies=	-2544.128993

11-H





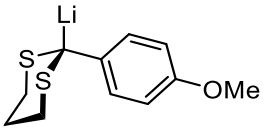
0 1

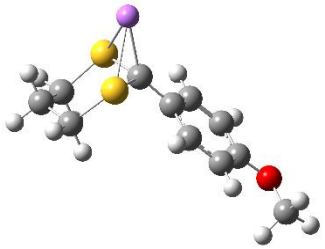
C	-1.57372200	-0.41178800	-0.61049700
C	-0.14594700	-0.63666400	-0.07384500
C	0.83242600	0.17735500	-0.92842500
C	0.42354400	1.65796700	-0.91185700
C	-1.02468200	1.77286600	-1.38378700
H	-0.09425100	-0.25638500	0.95180800
H	-1.62418700	-0.78347100	-1.64613200
H	1.07043300	2.20753700	-1.60783000
H	-1.36661700	2.80276100	-1.28172000
H	0.73768100	-0.18266900	-1.96205900
O	-1.89133200	0.97949500	-0.58140900
O	0.18208600	-2.01676700	-0.13935400
O	2.16228700	0.01780700	-0.46528600
C	-2.63121100	-1.12886400	0.21256500
H	-2.36597400	-2.18403700	0.27295900
H	-2.62577100	-0.71325000	1.22888800
O	-3.92339900	-1.04773400	-0.36796400
O	0.50828000	2.20119800	0.39499700
Si	1.79691900	2.97199000	1.15010200
Si	-5.00273900	0.24313600	-0.31654200
Si	3.42410000	-0.63901600	-1.37094400
Si	0.69034400	-2.97331600	1.15437500
C	1.00441600	4.31790800	2.19214400
H	1.76027100	4.85707900	2.77194100
H	0.47671900	5.04185700	1.56455800
H	0.28367100	3.89118600	2.89600900
C	2.73517500	1.78523400	2.25738000

H	3.51630500	2.31382300	2.81351700
H	2.06420900	1.31374400	2.98111300
H	3.19372800	0.99480800	1.66236400
C	2.93765600	3.72168000	-0.14099700
H	3.37922100	2.95334800	-0.77860500
H	2.40615500	4.43232300	-0.78110400
H	3.75439400	4.25991400	0.35005400
C	4.23981300	0.70451600	-2.40251700
H	4.75419700	1.43721200	-1.77507100
H	4.97961500	0.26694300	-3.08072600
H	3.50224900	1.23600200	-3.01183900
C	2.76139700	-1.98430500	-2.50346600
H	3.57863600	-2.62442400	-2.84980300
H	2.02920100	-2.60224400	-1.98037500
H	2.27589300	-1.56096900	-3.38768100
C	4.63659900	-1.30566400	-0.10755100
H	4.21062300	-2.13049300	0.46801800
H	5.54228800	-1.66943100	-0.60246700
H	4.93132900	-0.52104800	0.59527300
C	-0.79899500	-3.74570900	2.00320700
H	-0.46891100	-4.41672000	2.80305200
H	-1.44361600	-2.98499500	2.45249000
H	-1.40081100	-4.33054600	1.30153800
C	1.74858400	-4.31837500	0.38989100
H	1.20406300	-4.82943600	-0.40938800
H	2.67235600	-3.91864400	-0.03405100
H	2.01708600	-5.06480300	1.14379400
C	1.65123400	-1.93538500	2.38777900
H	2.39332400	-1.31720200	1.88089000
H	0.99258000	-1.26886800	2.95175200
H	2.16306300	-2.58287600	3.10650200
C	-4.66415600	1.32222700	1.18250900
H	-3.65998600	1.74745100	1.12362600
H	-5.38704000	2.14291400	1.22677700
H	-4.74680800	0.75336500	2.11368900
C	-4.90165300	1.24478400	-1.90219500
H	-3.92053800	1.71442100	-1.99148700
H	-5.06128200	0.60723000	-2.77712900
H	-5.66652600	2.02823100	-1.91434500
C	-6.70015600	-0.55338100	-0.19425200
H	-6.80117700	-1.12629400	0.73214900
H	-7.48682100	0.20787000	-0.20932300
H	-6.87583600	-1.23262000	-1.03384200
H	-1.09917000	1.47388500	-2.44002900

Zero-point correction=	0.596360 (Hartree/Particle)
Thermal correction to Energy=	0.637827
Thermal correction to Enthalpy=	0.638771
Thermal correction to Gibbs Free Energy=	0.522658
Sum of electronic and zero-point Energies=	-2246.714181
Sum of electronic and thermal Energies=	-2246.672714
Sum of electronic and thermal Enthalpies=	-2246.671770
Sum of electronic and thermal Free Energies=	-2246.787883

12



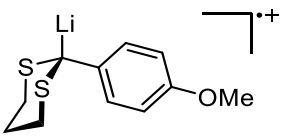


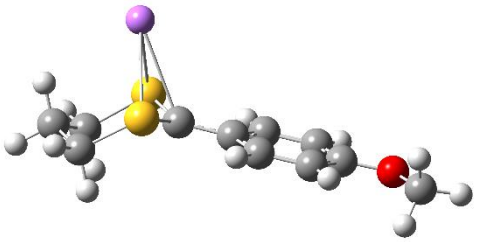
0 1

C	3.51004300	-0.40653100	1.32719400
C	2.76557700	0.92857100	1.39970500
C	1.11972000	0.18421900	-0.86477200
C	2.63081200	-1.57402800	0.87240500
H	1.90084000	0.85679700	2.06486800
H	3.42072600	1.72065600	1.77006900
H	4.36986000	-0.31093400	0.65478700
H	3.90522900	-0.63791200	2.32387000
H	1.76523300	-1.68760500	1.53064200
H	3.19337600	-2.51055700	0.87790300
S	1.99183900	-1.38510300	-0.86006600
S	2.15072000	1.52341000	-0.24730300
Li	2.54196200	0.44936600	-2.48124800
C	-0.31482000	0.19139400	-0.49159300
C	-1.02297900	1.40549100	-0.31504900
C	-1.08273900	-0.98042100	-0.35894600
C	-2.37957100	1.43812700	-0.03394200
H	-0.48948100	2.34445900	-0.40038200
C	-2.45314700	-0.95944900	-0.08250200
H	-0.59947500	-1.94231900	-0.47597300
C	-3.11714000	0.25455200	0.08478800
H	-2.89472800	2.38370300	0.09677800
H	-2.97956100	-1.90118200	0.00657000
O	-4.45693300	0.39755500	0.36118200
C	-5.23541700	-0.78443500	0.49792500
H	-4.87839100	-1.41004200	1.32464000
H	-6.25111600	-0.45415000	0.71164400
H	-5.23591800	-1.37731300	-0.42449900

Zero-point correction=	0.215805 (Hartree/Particle)
Thermal correction to Energy=	0.230834
Thermal correction to Enthalpy=	0.231778
Thermal correction to Gibbs Free Energy=	0.173238
Sum of electronic and zero-point Energies=	-1306.149370
Sum of electronic and thermal Energies=	-1306.134342
Sum of electronic and thermal Enthalpies=	-1306.133398
Sum of electronic and thermal Free Energies=	-1306.191938

12-SET





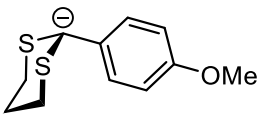
1 2

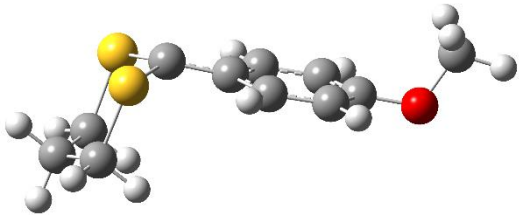
C	4.12301500	-0.16967300	0.50242200
C	3.39432700	1.13920100	0.78617400
C	0.98617700	0.01878100	-0.14082700

C	3.25679600	-1.40768700	0.71129700
H	2.99732400	1.16498000	1.80237100
H	4.05583200	1.99580600	0.65127000
H	4.53462700	-0.15750100	-0.51225300
H	4.97294000	-0.23658900	1.19059600
H	2.86480300	-1.45118100	1.72888800
H	3.82294800	-2.32023000	0.51985600
S	1.80793900	-1.53519900	-0.43170300
S	1.97906000	1.48385500	-0.35424300
Li	2.41921800	0.10440900	-2.56474200
C	-0.43946900	0.10087500	-0.05059000
C	-1.11525500	1.35563300	0.00642200
C	-1.25717100	-1.06020200	-0.02071800
C	-2.48733500	1.43209000	0.07459800
H	-0.54104500	2.27251200	0.00529500
C	-2.63866200	-0.98475500	0.04812800
H	-0.79472300	-2.03814800	-0.04199900
C	-3.27390600	0.26545100	0.09007700
H	-2.98927700	2.39093500	0.11963300
H	-3.21239500	-1.90093000	0.07195400
O	-4.61096500	0.45636300	0.14860100
C	-5.47325800	-0.68639200	0.16535900
H	-5.28631800	-1.30843300	1.04569000
H	-6.48507000	-0.28968900	0.20841700
H	-5.35311000	-1.28409300	-0.74320100

Zero-point correction=	0.218293 (Hartree/Particle)
Thermal correction to Energy=	0.232937
Thermal correction to Enthalpy=	0.233881
Thermal correction to Gibbs Free Energy=	0.176273
Sum of electronic and zero-point Energies=	-1306.011828
Sum of electronic and thermal Energies=	-1305.997184
Sum of electronic and thermal Enthalpies=	-1305.996240
Sum of electronic and thermal Free Energies=	-1306.053848

12-anion





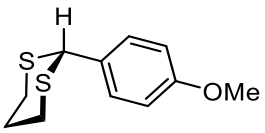
-1 1

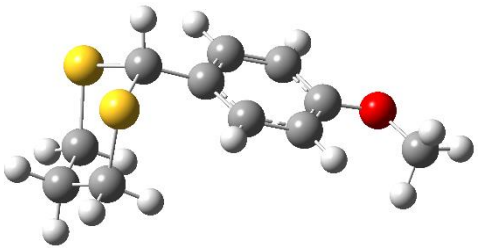
C	3.71673600	0.00000000	1.03777100
C	2.89332500	1.28952100	0.91362200
C	1.10217700	0.00000000	-0.82762400
C	2.89332500	-1.28952100	0.91362200
H	2.10715700	1.31865400	1.67428800
H	3.53460600	2.16604500	1.04678300
H	4.50171100	0.00000000	0.27257900
H	4.21892100	0.00000000	2.01473700
H	2.10715700	-1.31865400	1.67428800
H	3.53460600	-2.16604500	1.04678400
S	2.08556100	-1.47260600	-0.75155000
S	2.08556100	1.47260600	-0.75155000
C	-0.26994200	0.00000000	-0.37448000
C	-1.01105500	1.20172800	-0.15731500

C	-1.01105500	-1.20172800	-0.15731500
C	-2.34961200	1.19806200	0.21367300
H	-0.50819700	2.15178300	-0.28882300
C	-2.34961200	-1.19806200	0.21367300
H	-0.50819700	-2.15178300	-0.28882400
C	-3.03772200	0.00000000	0.40545800
H	-2.87468400	2.13575400	0.37259500
H	-2.87468400	-2.13575400	0.37259500
O	-4.37501500	0.00000000	0.80567900
C	-5.29780400	0.00000000	-0.28357800
H	-5.17339100	-0.89132300	-0.91158500
H	-6.30200200	0.00000000	0.14529900
H	-5.17339100	0.89132400	-0.91158500

Zero-point correction=	0.212450 (Hartree/Particle)
Thermal correction to Energy=	0.226360
Thermal correction to Enthalpy=	0.227305
Thermal correction to Gibbs Free Energy=	0.170367
Sum of electronic and zero-point Energies=	-1298.656182
Sum of electronic and thermal Energies=	-1298.642271
Sum of electronic and thermal Enthalpies=	-1298.641327
Sum of electronic and thermal Free Energies=	-1298.698265

12-H





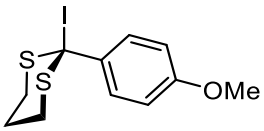
0 1

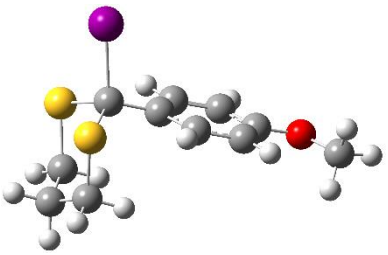
C	3.03333900	-0.53302400	1.52721800
C	2.32112000	0.82025400	1.49764200
C	1.29192700	0.30127300	-1.06220800
C	2.30548200	-1.62645300	0.74416600
H	1.29433200	0.73222300	1.86316300
H	2.84033200	1.54531500	2.12606200
H	4.05493100	-0.42214700	1.15382300
H	3.09946700	-0.85962300	2.57200900
H	1.30010000	-1.77813900	1.14362500
H	2.84105500	-2.57438900	0.81665900
S	2.17961600	-1.31553200	-1.06645300
S	2.27483300	1.59475900	-0.16726100
C	-0.17673400	0.25412600	-0.63823600
C	-0.89538400	1.45369500	-0.49481300
C	-0.87469600	-0.93774000	-0.45095900
C	-2.24107100	1.45522900	-0.16974100
H	-0.38880800	2.40063200	-0.63305500
C	-2.23087100	-0.95455100	-0.11500800
H	-0.36372900	-1.88274200	-0.57984900
C	-2.92412000	0.24756700	0.03054600
H	-2.78861800	2.38399200	-0.06221400
H	-2.72405900	-1.90666500	0.02449100
O	-4.24144400	0.35588000	0.35729400
C	-4.98739800	-0.84178600	0.57442300
H	-4.57608100	-1.42235500	1.40690100
H	-5.99757500	-0.52131900	0.82198300

H	-5.01427300	-1.46385300	-0.32636900
H	1.35373400	0.62285000	-2.10433800

Zero-point correction=	0.228077 (Hartree/Particle)
Thermal correction to Energy=	0.241536
Thermal correction to Enthalpy=	0.242481
Thermal correction to Gibbs Free Energy=	0.186813
Sum of electronic and zero-point Energies=	-1299.177949
Sum of electronic and thermal Energies=	-1299.164490
Sum of electronic and thermal Enthalpies=	-1299.163546
Sum of electronic and thermal Free Energies=	-1299.219214

12-I



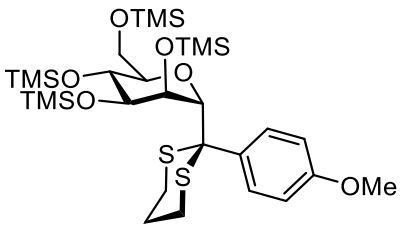


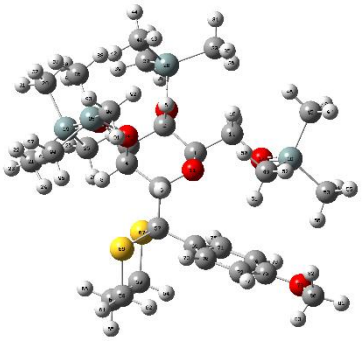
0 1

C	-1.44186000	3.37681400	-0.06588800
C	-1.03028500	2.71205600	1.24712500
C	-0.85271600	0.22195900	-0.00590700
C	-0.86629900	2.69703700	-1.30755900
H	0.05685200	2.68347000	1.35360100
H	-1.43941800	3.25272200	2.10245400
H	-2.53195000	3.41735100	-0.13590100
H	-1.07577100	4.41025500	-0.04892800
H	0.22562100	2.67414300	-1.27577800
H	-1.16729400	3.22419000	-2.21471700
S	-1.47466500	0.97546600	-1.57250300
S	-1.67756800	0.99728200	1.45360200
C	0.65138700	0.11796200	0.09982300
C	1.28527000	0.01086600	1.35104400
C	1.45927600	0.06201400	-1.04109000
C	2.65770900	-0.12452900	1.45157700
H	0.69061600	0.03357400	2.25432500
C	2.84190200	-0.07392500	-0.95523500
H	1.00314100	0.12377000	-2.02003900
C	3.45473200	-0.16621700	0.29864600
H	3.14086800	-0.20212800	2.41790600
H	3.42292500	-0.10715600	-1.86628200
O	4.78890800	-0.29628200	0.50355800
C	5.65401800	-0.35808200	-0.63328600
H	5.59205700	0.55795400	-1.22918600
H	6.66014600	-0.46232900	-0.23260300
H	5.42061300	-1.22279500	-1.26232100
I	-1.71231600	-1.85721600	-0.04913300

Zero-point correction=	0.216872 (Hartree/Particle)
Thermal correction to Energy=	0.232166
Thermal correction to Enthalpy=	0.233111
Thermal correction to Gibbs Free Energy=	0.172494
Sum of electronic and zero-point Energies=	-1596.386382
Sum of electronic and thermal Energies=	-1596.371088
Sum of electronic and thermal Enthalpies=	-1596.370144
Sum of electronic and thermal Free Energies=	-1596.430761

13





0 1

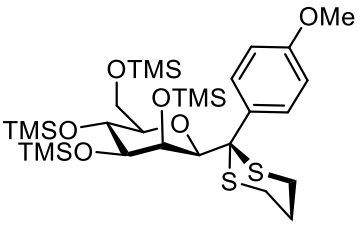
C	0.15769100	1.28869400	-0.45823500
C	-1.36584300	1.25632300	-0.23761400
C	-1.82894800	-0.19604700	-0.28331000
C	-1.09596500	-1.01083100	0.78996500
C	0.43702500	-0.86459700	0.67675600
H	-1.58527800	1.65610700	0.75819600
H	0.38227600	0.92089600	-1.46712300
H	-1.36711600	-2.06374300	0.67251000
H	0.82835900	-1.12762100	1.66194300
H	-1.55199700	-0.58664000	-1.26541100
O	0.82217500	0.49131200	0.52516800
O	-2.00862600	2.00599000	-1.25800900
O	-3.23222200	-0.29717900	-0.10032400
C	0.69842700	2.70243800	-0.30976200
H	0.17290900	3.34362800	-1.01983800
H	0.45657400	3.05124800	0.70334200
O	2.09260500	2.77875900	-0.57272400
Si	3.22205300	3.20303600	0.60164700
Si	-4.25422300	-1.02870700	-1.22623700
Si	-3.13206300	3.23748300	-1.00080900
C	-4.26471900	-2.88933500	-0.96118700
H	-4.71295500	-3.15338500	0.00045200
H	-4.84184300	-3.38631600	-1.74771100
H	-3.24794300	-3.29331600	-0.98735000
C	-3.65834100	-0.64233300	-2.96627600
H	-4.45076700	-0.84571400	-3.69309700
H	-3.36649600	0.40661200	-3.05059000
H	-2.79337700	-1.25489200	-3.23694700
C	-5.94762800	-0.30498300	-0.88029600
H	-5.96837100	0.77199000	-1.06343700
H	-6.70279800	-0.77299600	-1.51909400
H	-6.23724000	-0.47493800	0.16059600
C	-2.23552800	4.88536900	-0.87091200
H	-2.95548200	5.70267800	-0.75897500
H	-1.56889600	4.90746800	-0.00394600
H	-1.63647700	5.08443000	-1.76429300
C	-4.23400400	3.22570800	-2.51701900
H	-3.63587900	3.30146600	-3.42971800
H	-4.82692200	2.31013600	-2.57751300
H	-4.92354300	4.07521900	-2.49524300
C	-4.10030700	2.91417600	0.57442500
H	-4.44168100	1.87849000	0.60821400
H	-3.48989300	3.09250800	1.46437900
H	-4.96868800	3.57815200	0.62792500
C	2.73065700	4.86952200	1.33354900
H	1.75467500	4.82750800	1.82628800

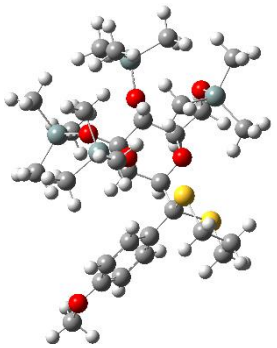
H	3.46339900	5.18719200	2.08240900
H	2.68438100	5.64092900	0.55887200
C	3.29395500	1.91710300	1.96384100
H	2.31561700	1.79765000	2.43555400
H	3.58117900	0.94555600	1.55822600
H	4.01961700	2.20844300	2.73062900
C	4.86345100	3.36171200	-0.28855000
H	4.75952100	3.97138700	-1.19063000
H	5.58989400	3.85465800	0.36603300
H	5.27486200	2.39102400	-0.57047300
C	1.18852500	-1.85640500	-0.29420700
C	1.91960900	-4.59037600	-0.63651000
C	1.41566000	-3.26055200	-2.75689700
C	1.34486400	-4.61264500	-2.05164300
H	1.88123800	-5.58381800	-0.18636400
H	2.96188300	-4.26222800	-0.64152300
H	1.02255100	-3.33089500	-3.77259600
H	2.44569600	-2.90198000	-2.81798200
H	1.92609800	-5.33193500	-2.64105000
H	0.31089700	-4.96717400	-2.02828200
S	0.38919900	-1.95066000	-1.97695600
S	0.98805500	-3.52994800	0.53705100
C	2.65914100	-1.42746300	-0.37703700
C	3.56966400	-1.76670200	0.62545900
C	3.11451600	-0.58759100	-1.40302500
C	4.88321900	-1.29594000	0.61961600
H	3.25486300	-2.40862000	1.43789700
C	4.41604100	-0.11766800	-1.42890100
H	2.43630400	-0.28603700	-2.18875000
C	5.31333800	-0.45995600	-0.41255400
H	5.54693000	-1.58164500	1.42397900
H	4.75290000	0.53671100	-2.22322200
O	6.55923700	0.08402600	-0.51097600
C	7.48957300	-0.15841000	0.54444300
H	8.39107300	0.38952500	0.27727000
H	7.10815800	0.21142200	1.50179900
H	7.72515000	-1.22407500	0.63144200
O	-1.44743100	-0.53587700	2.08205900
Si	-2.57852800	-1.16139800	3.15752800
C	-4.18846200	-0.20615900	3.05540000
H	-4.90511000	-0.57102800	3.79828900
H	-4.01888400	0.85851400	3.24034800
H	-4.62358700	-0.30419800	2.06023100
C	-1.80515500	-0.93204200	4.85271300
H	-0.87960200	-1.50818300	4.94161400
H	-1.56729400	0.12066300	5.03247000
H	-2.48872800	-1.26107700	5.64172700
C	-2.85076800	-2.98579700	2.79884500
H	-3.30035800	-3.14689600	1.81677300
H	-1.90852300	-3.54079400	2.83419800
H	-3.52270900	-3.41568400	3.54822700

Zero-point correction=	0.804592 (Hartree/Particle)
Thermal correction to Energy=	0.860033
Thermal correction to Enthalpy=	0.860977
Thermal correction to Gibbs Free Energy=	0.714890

Sum of electronic and zero-point Energies=	-3544.712325
Sum of electronic and thermal Energies=	-3544.656884
Sum of electronic and thermal Enthalpies=	-3544.655939
Sum of electronic and thermal Free Energies=	-3544.802026

13β





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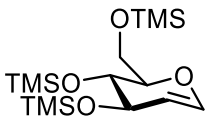
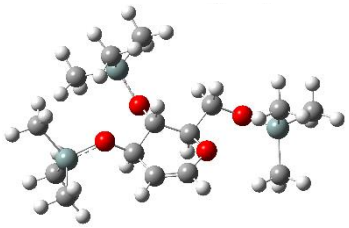
C	1.41505100	-0.94068200	-1.65291100
C	1.94515400	0.22172600	-0.79801600
C	0.83711700	1.26472500	-0.63263400
C	-0.41535400	0.60706000	-0.02236600
C	-0.82091300	-0.55280800	-0.95019400
H	2.19835400	-0.16555600	0.19049800
H	1.17077400	-0.55364300	-2.65579400
H	-1.21788300	1.35202100	-0.00689000
H	0.57083300	1.63211400	-1.63333200
O	0.23692900	-1.49296500	-1.05897900
O	3.07195100	0.80291700	-1.43776300
O	1.26990800	2.33329900	0.19028100
C	2.41801500	-2.07012200	-1.83512200
H	1.90465600	-2.89922100	-2.33518500
H	3.21278300	-1.71513900	-2.49426100
O	3.02483500	-2.49231600	-0.62657600
Si	2.42589900	-3.56581300	0.52908300
Si	1.45827300	3.93127900	-0.31047200
Si	4.64850400	0.83866000	-0.83704700
C	-0.17137100	4.85815600	-0.15225700
H	-0.46411600	5.00083700	0.89095000
H	-0.08847400	5.84741800	-0.61442100
H	-0.97818900	4.32033800	-0.66008800
C	2.01098200	3.98254000	-2.10530000
H	2.42786800	4.96522300	-2.34660500
H	2.76649200	3.22031800	-2.29938700
H	1.16987000	3.80502800	-2.78220600
C	2.73194900	4.64037900	0.86624500
H	3.68110500	4.10356900	0.79657900
H	2.91958000	5.69655500	0.65088300
H	2.37906400	4.56501100	1.89891600
C	5.63482500	-0.61597800	-1.49659700
H	6.67260800	-0.55560600	-1.15221900
H	5.20687800	-1.55820300	-1.14650900
H	5.64571300	-0.62214400	-2.59081700
C	5.39388800	2.43567600	-1.48367100
H	5.31149200	2.48867900	-2.57329400
H	4.90299300	3.31732400	-1.06603200
H	6.45666800	2.48567000	-1.22646400
C	4.61812100	0.81020500	1.03938500
H	3.95506200	1.58393600	1.43213200

H	4.27240000	-0.15456900	1.41996200
H	5.62445200	0.98432000	1.43269100
C	1.08421800	-4.63965800	-0.22275400
H	1.45410000	-5.18920200	-1.09411800
H	0.73552800	-5.37264300	0.51187800
H	0.23159400	-4.02747700	-0.52403200
C	3.91173100	-4.59746700	1.04038100
H	4.28725400	-5.19320200	0.20318700
H	4.72574500	-3.95601700	1.39174500
H	3.64953600	-5.28193900	1.85358500
C	1.79649500	-2.58516200	1.99474100
H	1.00596400	-1.90219100	1.68128800
H	1.39706500	-3.24908300	2.76828200
H	2.60427400	-1.99621600	2.44097200
C	-2.14270700	-1.29378300	-0.60923400
C	-3.99635500	-3.21741200	-1.57902500
C	-3.56131200	-3.20374400	0.93208200
C	-3.87404900	-4.04706200	-0.30199800
H	-4.27071800	-3.84578200	-2.42832600
H	-4.76001900	-2.44195500	-1.47358600
H	-3.50212500	-3.83351600	1.82226200
H	-4.35224100	-2.46808900	1.09996900
H	-4.83020500	-4.55673600	-0.13055500
H	-3.10980500	-4.81789100	-0.43316600
S	-1.93765900	-2.33902900	0.91388900
S	-2.41944800	-2.43030600	-2.08234100
C	-3.25863000	-0.24659800	-0.48503800
C	-3.76006000	0.39592800	-1.62114000
C	-3.73094800	0.19006200	0.76051200
C	-4.69242400	1.42860700	-1.53475400
H	-3.42509900	0.08324700	-2.60188800
C	-4.66388900	1.21038500	0.86517600
H	-3.34940400	-0.27152600	1.66096800
C	-5.15454100	1.84376700	-0.28206700
H	-5.04883700	1.89127500	-2.44477700
H	-5.02305200	1.53891000	1.83305000
O	-6.06531300	2.83290900	-0.07606300
C	-6.58981900	3.52253100	-1.21137400
H	-7.28328300	4.26141200	-0.81463900
H	-5.79702600	4.03112900	-1.76971200
H	-7.12757400	2.84081200	-1.87834800
O	-0.15590600	0.11309200	1.27105100
Si	-0.21263100	0.88150200	2.76621300
C	1.51591900	1.36183200	3.31184800
H	1.50191600	1.77663600	4.32506300
H	2.17614700	0.49007900	3.31119500
H	1.93242100	2.10266300	2.62865900
C	-0.90788100	-0.39310100	3.95529500
H	-1.92313300	-0.68339600	3.67568400
H	-0.29106000	-1.29574100	3.94976000
H	-0.92542100	0.00344700	4.97564400
C	-1.32931900	2.38770100	2.67797600
H	-0.93493300	3.12285200	1.97548400
H	-2.34044100	2.12305800	2.35940300
H	-1.39640300	2.86161000	3.66237800
H	-1.00123900	-0.09995400	-1.93878000

Zero-point correction=	0.805046 (Hartree/Particle)
Thermal correction to Energy=	0.860042
Thermal correction to Enthalpy=	0.860986
Thermal correction to Gibbs Free Energy=	0.717284
Sum of electronic and zero-point Energies=	-3544.722545
Sum of electronic and thermal Energies=	-3544.667549
Sum of electronic and thermal Enthalpies=	-3544.666605
Sum of electronic and thermal Free Energies=	-3544.810307

14





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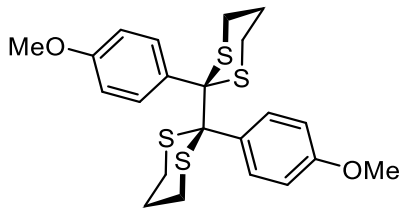
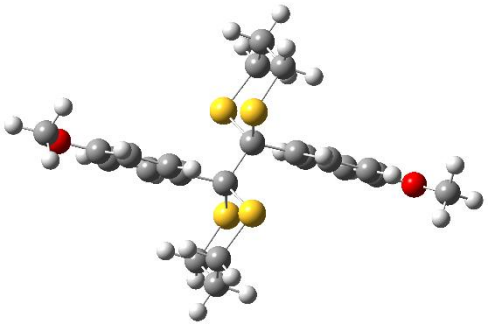
C	-1.21761600	-0.24977800	0.37354400
C	0.21026100	0.08857200	-0.07050500
C	1.14220700	-1.08348700	0.2 4306000
C	0.48676100	-2.37420500	-0.17623400
C	-0.81560700	-2.44665400	-0.45059500
H	0.20934900	0.22380400	-1.15932900
H	-1.22360200	-0.48039500	1.44624700
H	1.10302900	-3.25643600	-0.28925200
H	-1.30735900	-3.34666700	-0.80005500
H	1.32556000	-1.07062200	1.32594000
O	-1.69782300	-1.41384100	-0.33585600
O	0.63946100	1.25644700	0.59950200
O	2.37031700	-0.86707600	-0.45009800
C	-2.20077400	0.87573700	0.09676000
H	-1.80303800	1.78876000	0.54103100
H	-2.26697900	1.02161200	-0.98940000
O	-3.47700100	0.63885500	0.66566800
Si	-4.73856900	-0.29670600	0.05837600
Si	3.90291400	-1.33446900	0.06399800
Si	1.45653700	2.58038100	-0.05331900
C	4.15660600	-3.17109300	-0.24684000
H	3.98036100	-3.41885600	-1.29753900
H	5.18024300	-3.46773900	0.00351600
H	3.47794200	-3.77484000	0.36321500
C	4.10991300	-0.97375600	1.89727600
H	5.14382700	-1.16946600	2.19887500
H	3.88030500	0.06825200	2.13365600
H	3.46304900	-1.60902600	2.50924000
C	5.07416400	-0.31442700	-0.98298900
H	4.93448500	0.75499200	-0.80469900
H	6.11513000	-0.56402900	-0.75667200
H	4.90502400	-0.50379800	-2.04682700
C	0.29354200	4.05170200	0.04755100
H	0.78364300	4.96191600	-0.31234800
H	-0.59987300	3.88681900	-0.56217100
H	-0.02859000	4.22757600	1.07817100
C	2.96680100	2.87936300	1.01656100
H	2.69019700	2.94956500	2.07248100
H	3.69312700	2.07062300	0.90849400
H	3.45868900	3.81547700	0.73425900

C	1.94263100	2.23651400	-1.83207300
H	2.49831000	1.29849400	-1.89781300
H	1.06933100	2.16585700	-2.48712500
H	2.57555500	3.04681800	-2.20705300
C	-6.30303300	0.63370400	0.51809800
H	-6.33855200	1.61135000	0.02875800
H	-7.19119800	0.07007900	0.21493700
H	-6.35998000	0.79265200	1.59901900
C	-4.58320700	-0.46673000	-1.80562100
H	-4.58382100	0.50888500	-2.30108300
H	-3.65917200	-0.98695200	-2.06779400
H	-5.42588800	-1.04274300	-2.20059500
C	-4.73831600	-1.98336500	0.88270400
H	-4.82115200	-1.88685700	1.96948600
H	-5.58316300	-2.58597900	0.53363500
H	-3.81276900	-2.51567600	0.65411500

Zero-point correction=	0.466410 (Hartree/Particle)
Thermal correction to Energy=	0.499211
Thermal correction to Enthalpy=	0.500155
Thermal correction to Gibbs Free Energy=	0.401819
Sum of electronic and zero-point Energies=	-1761.580169
Sum of electronic and thermal Energies=	-1761.547368
Sum of electronic and thermal Enthalpies=	-1761.546424
Sum of electronic and thermal Free Energies=	-1761.644760

15





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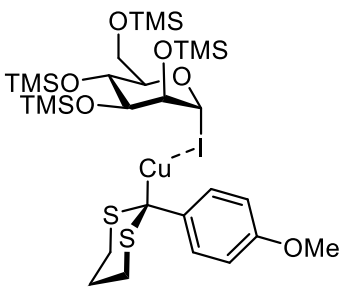
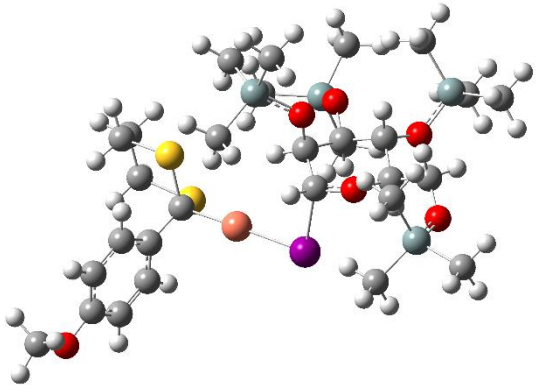
C	-0.65897300	-3.94338700	0.00943900
C	-1.00884400	-3.14033400	1.25938800
C	-0.44275400	-0.66848300	-0.04054800
C	-0.93420700	-3.18615900	-1.28683800
H	-2.06249100	-2.85176600	1.25839700
H	-0.82240400	-3.72609400	2.16162100
H	0.38949500	-4.25087700	0.04562300
H	-1.27029000	-4.85395900	0.00815800
H	-1.98671500	-2.90331000	-1.36036400
H	-0.69166800	-3.80231100	-2.15483400
S	0.10662300	-1.69129100	-1.52080800
S	0.01617600	-1.63668100	1.50679900
C	-1.95626700	-0.38492000	-0.08778500
C	-2.69957300	-0.18501900	1.07891900
C	-2.64692000	-0.27666000	-1.30669600
C	-4.05856400	0.12378400	1.05069700
H	-2.21670500	-0.27731600	2.04151200
C	-3.99717100	0.02812100	-1.35445700
H	-2.11784700	-0.43558900	-2.23601300
C	-4.71999300	0.23641600	-0.17429600

H	-4.58100600	0.26892200	1.98612600
H	-4.51513800	0.10961300	-2.30243700
O	-6.04013800	0.52809400	-0.32438300
C	-6.82164000	0.76427100	0.84727200
H	-6.43907400	1.61844700	1.41537700
H	-7.82653700	0.98629200	0.49332300
H	-6.85089900	-0.12017500	1.49218000
C	0.65885100	3.94337000	0.00942600
C	1.00874500	3.14034200	1.25938500
C	0.44277700	0.66844500	-0.04054600
C	0.93414200	3.18614800	-1.28684100
H	2.06240600	2.85182800	1.25841000
H	0.82226300	3.72609900	2.16161100
H	-0.38963300	4.25080700	0.04559400
H	1.27012200	4.85397300	0.00814900
H	1.98666400	2.90335000	-1.36034900
H	0.69158500	3.80228300	-2.15484300
S	-0.10661200	1.69122800	-1.52081900
S	-0.01620300	1.63663900	1.50679200
C	1.95629700	0.38490500	-0.08777600
C	2.69961000	0.18502100	1.07892700
C	2.64695500	0.27666800	-1.30668700
C	4.05860700	-0.12375600	1.05070400
H	2.21674400	0.27731000	2.04152100
C	3.99721200	-0.02808700	-1.35444900
H	2.11788000	0.43559200	-2.23600300
C	4.72003800	-0.23637200	-0.17429000
H	4.58105200	-0.26888500	1.98613200
H	4.51518100	-0.10956300	-2.30243000
O	6.04018900	-0.52802300	-0.32437900
C	6.82170000	-0.76418900	0.84727200
H	6.43915400	-1.61837500	1.41537400
H	7.82660100	-0.98618800	0.49331900
H	6.85094400	0.12025500	1.49218400

Zero-point correction=	0.435345 (Hartree/Particle)
Thermal correction to Energy=	0.462674
Thermal correction to Enthalpy=	0.463618
Thermal correction to Gibbs Free Energy=	0.378529
Sum of electronic and zero-point Energies=	-2597.161374
Sum of electronic and thermal Energies=	-2597.134045
Sum of electronic and thermal Enthalpies=	-2597.133101
Sum of electronic and thermal Free Energies=	-2597.218190

16





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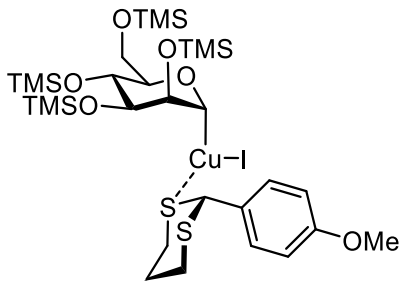
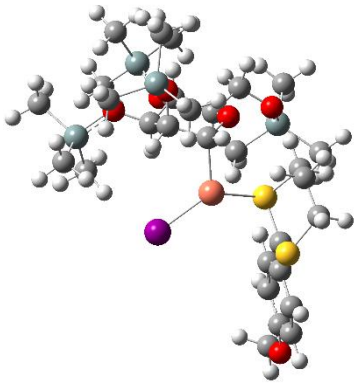
C	-3.35684200	1.02267600	-0.39446100
C	-3.37461500	-0.48575200	-0.09921700
C	-1.94797600	-1.04168700	-0.15265400
C	-1.06020500	-0.25976700	0.82222200
C	-1.18239200	1.24802100	0.58488800
H	-3.77137200	-0.65871400	0.90687100
H	-3.02823300	1.18108100	-1.42744000
H	-0.01674400	-0.57298600	0.70473600
H	-0.60532900	1.85541800	1.27312200
H	-1.57246700	-0.87115200	-1.16791300
I	0.07137100	1.77651100	-1.41719600
O	-2.41680100	1.73141600	0.46384800
O	-4.16578800	-1.09458100	-1.09756900
O	-1.94861000	-2.41199300	0.16622300
C	-4.70268300	1.69346900	-0.18200400
H	-5.44457700	1.13388600	-0.75221900
H	-4.96458300	1.62589900	0.88155900
O	-4.71487600	3.02993200	-0.64093700
O	-1.52829700	-0.43533600	2.14309400
Si	-0.53864500	-0.67926200	3.50467300
Si	-4.23966100	4.42472400	0.18045500
Si	-1.19611600	-3.64750800	-0.71262700
Si	-5.44601200	-2.17612800	-0.87200900
C	-1.71166200	-0.47671700	4.94622500
H	-1.18610600	-0.62594700	5.89420800
H	-2.15154800	0.52429700	4.95577600
H	-2.52341300	-1.20742100	4.89187100
C	0.19366700	-2.39863500	3.42798400
H	0.79123400	-2.59631600	4.32365800
H	-0.59442000	-3.15390700	3.36695600
H	0.84707400	-2.50780200	2.56012800
C	0.80563700	0.63183700	3.49795800
H	1.40750900	0.58666600	2.58525000
H	0.38131500	1.63590500	3.59157600
H	1.48986400	0.47806200	4.33790200
C	0.52030200	-3.96549700	-0.03957700
H	0.47313600	-4.30670600	0.99806800
H	1.01452300	-4.74526900	-0.62861100
H	1.15861800	-3.07932700	-0.07461000
C	-1.12136400	-3.15247400	-2.52362400
H	-0.80707400	-4.00841500	-3.12852000
H	-2.09777700	-2.81924000	-2.88595100
H	-0.39992400	-2.34806600	-2.69494300
C	-2.26581200	-5.16342300	-0.44277100
H	-3.26574000	-5.04801100	-0.86566800
H	-1.79986600	-6.03874900	-0.90598900
H	-2.37319000	-5.36943500	0.62626600
C	-7.06191400	-1.21689600	-0.85962500
H	-7.91111900	-1.90544500	-0.80098400
H	-7.12142700	-0.54371900	0.00067400
H	-7.17663100	-0.61982500	-1.76900800
C	-5.38204500	-3.30476000	-2.36502300
H	-5.50603900	-2.72612900	-3.28503400
H	-4.42904800	-3.83463700	-2.42808800
H	-6.18401500	-4.04801500	-2.32448600
C	-5.23407200	-3.09012600	0.75211500

H	-4.21389900	-3.46142200	0.85825900
H	-5.44664500	-2.43732200	1.60386900
H	-5.92615000	-3.93632700	0.80172900
C	-4.22235800	4.10851200	2.03189200
H	-3.49729000	3.33346300	2.29165200
H	-3.94455500	5.02539300	2.56100800
H	-5.20522700	3.79751100	2.39834200
C	-2.54406000	4.96218800	-0.41766700
H	-1.78149300	4.22940500	-0.14657700
H	-2.53158800	5.07792000	-1.50543400
H	-2.26778900	5.92448300	0.02525400
C	-5.51531900	5.72366700	-0.27013400
H	-6.50928400	5.43960900	0.08716300
H	-5.25763000	6.68979300	0.17513900
H	-5.56957900	5.85809900	-1.35444200
C	4.85750300	-3.63552400	0.50312600
C	5.13512100	-3.07939600	-0.89679000
C	3.63325100	-0.72740000	-0.34125100
C	4.71157400	-2.55034200	1.57375300
H	6.03509200	-2.45759000	-0.89465800
H	5.28699800	-3.89060900	-1.61222000
H	3.95596300	-4.25516400	0.48056900
H	5.69377500	-4.28700300	0.78728000
H	5.61464600	-1.93565300	1.62382100
H	4.55124900	-2.99624200	2.55796000
S	3.26544400	-1.43392400	1.30911400
S	3.74536200	-2.07826100	-1.58386900
C	4.82047500	0.22326400	-0.36859200
C	5.44062000	0.57670000	-1.58497500
C	5.30929300	0.85421600	0.78210300
C	6.47659500	1.49518000	-1.64126400
H	5.09707500	0.11710600	-2.50294900
C	6.35253600	1.78347300	0.74201000
H	4.86139600	0.62023900	1.73930900
C	6.94801000	2.11131900	-0.47574800
H	6.93990300	1.75308900	-2.58689800
H	6.68603700	2.23416300	1.66743200
O	7.97552600	3.00098700	-0.63752200
C	8.48213600	3.65803500	0.52047600
H	8.89427500	2.94233200	1.24066200
H	9.27792300	4.31287800	0.16920200
H	7.70885200	4.25952800	1.01147800
Cu	2.04193800	0.34352600	-0.83065100

Zero-point correction=	0.803965 (Hartree/Particle)
Thermal correction to Energy=	0.864455
Thermal correction to Enthalpy=	0.865399
Thermal correction to Gibbs Free Energy=	0.702867
Sum of electronic and zero-point Energies=	-5483.129445
Sum of electronic and thermal Energies=	-5483.068955
Sum of electronic and thermal Enthalpies=	-5483.068011
Sum of electronic and thermal Free Energies=	-5483.230543

17





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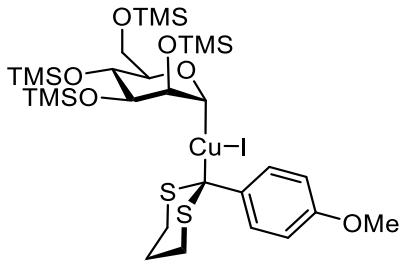
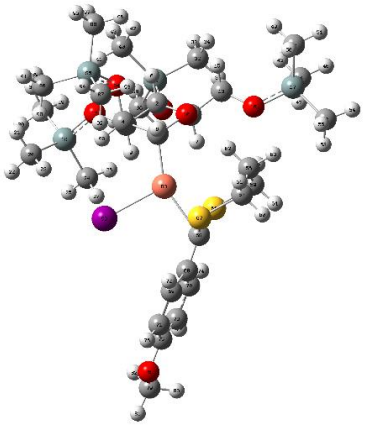
C	-1.02585500	1.42103500	1.12882800
C	-2.32895400	1.40279200	0.31445700
C	-2.43823000	0.05945600	-0.41097400
C	-2.37004000	-1.07877900	0.61002800
C	-1.10875100	-0.94813500	1.44857200
H	-3.19063500	1.50896300	0.98132300
H	-0.19822300	1.35733900	0.41244100
H	-1.03430100	-1.70040500	2.23438700
H	-1.55515500	-0.03140900	-1.05706600
O	-0.93293300	0.29761600	2.02670400
O	-2.25053400	2.45850600	-0.62800400
O	-3.62730200	0.01038700	-1.17117400
C	-0.84445300	2.67002000	1.97116900
H	-1.20057600	3.52972500	1.39884600
H	-1.45808800	2.58010600	2.87225200
O	0.51738200	2.82718100	2.36220700
Si	1.54045200	3.91208700	1.56849900
Si	-3.71882700	-0.45703500	-2.78951800
Si	-3.43085700	3.61644600	-0.96222100
C	-3.81248200	-2.32629200	-2.92311900
H	-4.70590400	-2.71433900	-2.42778200
H	-3.84536700	-2.63254100	-3.97391600
H	-2.93373400	-2.79193200	-2.46769800
C	-2.20617400	0.17420300	-3.70806900
H	-2.35544200	0.08323000	-4.78842500
H	-2.01024500	1.22363100	-3.47475400
H	-1.31706400	-0.40655700	-3.44534900
C	-5.30807700	0.31866700	-3.41239400
H	-5.26761500	1.41000800	-3.38057300
H	-5.50465400	0.01555800	-4.44532600
H	-6.15550400	-0.00455500	-2.80063900
C	-3.02083900	5.18298700	-0.00438200
H	-3.71538600	5.98706800	-0.26800800
H	-3.09311900	5.02374700	1.07564600
H	-2.00749000	5.52842700	-0.23066100
C	-3.29750400	3.94847900	-2.80128600
H	-2.27361200	4.22725400	-3.06713900
H	-3.56997900	3.06888700	-3.38847500
H	-3.95735700	4.77085100	-3.09407500
C	-5.12373200	2.97534400	-0.47110200
H	-5.27662700	1.96959600	-0.86701300
H	-5.23510300	2.93108300	0.61629500
H	-5.90674000	3.63371600	-0.85966800
C	1.46479400	3.60366600	-0.28472900

H	0.44074600	3.68768900	-0.66037400
H	2.08201600	4.33116200	-0.82083700
H	1.82751200	2.60258000	-0.53123500
C	0.96946300	5.66308300	1.94315100
H	-0.06109000	5.82585200	1.61335500
H	1.01726000	5.86911300	3.01635500
H	1.60069800	6.39473400	1.42911800
C	3.24729700	3.58756000	2.26344200
H	3.61117200	2.60001700	1.97058100
H	3.95725800	4.33268200	1.89166200
H	3.24107400	3.64414600	3.35545900
C	2.03105100	-1.42164100	3.55059700
C	3.29448300	-2.25801500	3.37454500
C	3.76911100	-1.03268900	0.90281100
C	2.14041900	-0.01941300	2.96695600
H	4.15815000	-1.76549800	3.82556300
H	3.17785400	-3.24056400	3.83398700
H	1.17406400	-1.94038200	3.11214600
H	1.83539200	-1.32278200	4.62417900
H	3.00094100	0.52097000	3.36571300
H	1.24261000	0.57314600	3.13002600
S	2.32469600	0.00191200	1.13037700
S	3.72270200	-2.64238200	1.61682800
C	4.77766100	-0.63713300	-0.02919700
C	5.92685900	-1.44668400	-0.27131900
C	4.69421200	0.57592800	-0.76381900
C	6.89728000	-1.06871700	-1.17067700
H	6.04546400	-2.37550800	0.27042700
C	5.67162500	0.95868400	-1.66800000
H	3.84685500	1.23200200	-0.61852100
C	6.78668400	0.13752100	-1.88650600
H	7.76719000	-1.69072100	-1.34389700
H	5.55547000	1.89341900	-2.19885200
O	7.79667700	0.41005900	-2.74699400
C	7.74030100	1.61621800	-3.51396500
H	7.73852300	2.49775200	-2.86543500
H	8.63949700	1.61794900	-4.12626400
H	6.85782200	1.63229800	-4.16092000
Cu	0.60263800	-1.36506800	0.28905300
O	-3.50704900	-0.99577000	1.47312300
Si	-4.39328700	-2.32635200	2.00271300
C	-5.17792200	-3.19128400	0.53368600
C	-3.25402500	-3.51739800	2.90843200
C	-5.68532800	-1.60401500	3.14803200
H	-5.80316900	-2.49902500	-0.03646100
H	-4.42006600	-3.59533100	-0.14247200
H	-5.80452600	-4.02374500	0.86890500
H	-2.46218500	-3.88691000	2.24919400
H	-2.78296600	-3.03450300	3.76949100
H	-3.81274600	-4.38585100	3.27121500
H	-6.32748200	-2.39200700	3.55317800
H	-5.21631600	-1.08390000	3.98791400
H	-6.32026700	-0.89002500	2.61609800
H	-2.33869200	-2.03277100	0.07571500
I	0.22032200	-2.92070800	-1.63562200

Zero-point correction=	0.802167 (Hartree/Particle)
Thermal correction to Energy=	0.863292
Thermal correction to Enthalpy=	0.864236
Thermal correction to Gibbs Free Energy=	0.698379
Sum of electronic and zero-point Energies=	-5483.140357
Sum of electronic and thermal Energies=	-5483.079232
Sum of electronic and thermal Enthalpies=	-5483.078288
Sum of electronic and thermal Free Energies=	-5483.244145

17-singlet





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C	-1.94269500	-1.07361000	0.08900700
C	-2.49531200	0.27898600	0.58357900
C	-1.50693000	1.39620200	0.25180300
C	-1.19143500	1.36864200	-1.24484900
C	-0.64015500	-0.00143000	-1.62060700
H	-3.43587600	0.49646000	0.06699800
H	-1.05988400	-1.30729700	0.70298900
H	-0.52048900	-0.07134100	-2.70362300
H	-0.57253000	1.18050700	0.78358100
O	-1.56068300	-1.02933200	-1.27921700
O	-2.67837500	0.19201600	1.99015500
O	-2.04200600	2.64358200	0.66008000
C	-2.96711000	-2.17924300	0.24687900
H	-3.41281200	-2.09654800	1.24071300
H	-3.75210400	-2.03135500	-0.50588500
O	-2.34969700	-3.45416300	0.08889700
Si	-3.20792900	-4.90058700	0.18168400
Si	-1.23630100	3.81402900	1.56135700
Si	-4.05887800	0.60818700	2.85934900
C	-0.26417400	4.96008300	0.43722800
H	-0.92709100	5.49017200	-0.25142000
H	0.27860700	5.70499100	1.02868100
H	0.46788000	4.39860800	-0.14923800
C	-0.08493400	2.98173700	2.79138300
H	0.29443500	3.71465700	3.51028300
H	-0.60258100	2.19360300	3.34441200
H	0.77476100	2.53653600	2.28235500
C	-2.59616300	4.78255200	2.41930300
H	-3.15521800	4.16535500	3.12625200
H	-2.17367800	5.63019400	2.96785600
H	-3.30449400	5.17822400	1.68529300
C	-5.08247900	-0.94147600	3.16859000
H	-5.92635300	-0.71592700	3.82876600
H	-5.48990400	-1.34295000	2.23588200

H	-4.48470500	-1.72524600	3.64331700
C	-3.43420900	1.28256800	4.49344400
H	-2.80656700	0.54244300	4.99861300
H	-2.83877500	2.18738200	4.35267100
H	-4.26967500	1.52448300	5.15759200
C	-5.08419700	1.86070600	1.91033400
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H	-5.86508500	2.27711400	2.55422300
C	-4.05728600	-5.01198600	1.85440000
H	-4.78171300	-4.20363500	1.99061600
H	-4.59516100	-5.95999300	1.95258700
H	-3.32785700	-4.95140100	2.66753300
C	-4.47584500	-4.96905200	-1.20222200
H	-5.21082600	-4.16380800	-1.11140900
H	-3.99175200	-4.87634400	-2.17871900
H	-5.01978700	-5.91854500	-1.18211100
C	-1.90576200	-6.23258100	-0.01524500
H	-1.13208400	-6.14189700	0.75224300
H	-2.35483200	-7.22611400	0.07545400
H	-1.42514600	-6.17077100	-0.99542400
C	0.60425800	-3.56128000	-1.66561200
C	1.89464800	-3.42179000	-2.45520000
C	2.96268400	-1.69929200	-0.41400200
C	0.81799000	-3.63365400	-0.16451100
H	2.60049000	-4.22654800	-2.24242100
H	1.70170700	-3.40056800	-3.52859000
H	-0.08299200	-2.74512400	-1.89214200
H	0.11464900	-4.49131100	-1.97196200
H	1.45258100	-4.47151600	0.12939500
H	-0.14252000	-3.69675200	0.34543100
S	1.58797400	-2.13233800	0.58947400
S	2.79104300	-1.83163000	-2.16953900
C	4.21210500	-1.26343700	0.18995700
C	5.28247100	-0.78363400	-0.60152200
C	4.39325600	-1.25585900	1.58673000
C	6.45388000	-0.33555400	-0.02906600
H	5.19071200	-0.76242500	-1.67907700
C	5.56604400	-0.80012300	2.17150600
H	3.60751500	-1.62128500	2.23462900
C	6.61274000	-0.33374200	1.36579800
H	7.26872900	0.02910100	-0.64210600
H	5.65627500	-0.81997600	3.24848200
O	7.79986200	0.12497700	1.82604500
C	8.01881100	0.17300500	3.23914600
H	7.97155100	-0.82724200	3.68072500
H	9.01956300	0.57956200	3.36779300
H	7.29219900	0.82812900	3.72915100
Cu	1.22043500	-0.29963100	-0.89981800
O	-2.40082500	1.63597700	-1.97204300
Si	-2.47285800	2.61331700	-3.33307700
C	-2.03978400	4.38383100	-2.87924700
C	-1.26729800	1.98647800	-4.63497000
C	-4.24506300	2.48025100	-3.92629800
H	-2.70790100	4.75852500	-2.09890500
H	-1.01463100	4.45833000	-2.50713600

H	-2.12859900	5.03891700	-3.75170600
H	-0.24045500	1.99395900	-4.25617500
H	-1.50994900	0.96329200	-4.93606900
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H	-4.40408600	3.09606100	-4.81691000
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H	-4.94000800	2.81897300	-3.15264600
H	-0.43041700	2.12444100	-1.45690000
I	2.47167500	1.93610400	-0.54979100

Zero-point correction=	0.802931 (Hartree/Particle)
Thermal correction to Energy=	0.863794
Thermal correction to Enthalpy=	0.864739
Thermal correction to Gibbs Free Energy=	0.701617
Sum of electronic and zero-point Energies=	-5483.139074
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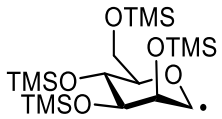
18



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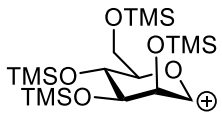
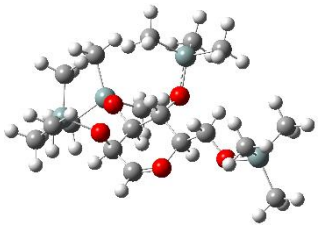
C	-1.57900900	-0.43951000	-0.59131900
C	-0.15960900	-0.64483700	-0.03697300
C	0.82482000	0.11525600	-0.93378000
C	0.46861700	1.60718800	-0.86684600
C	-0.96585000	1.79607200	-1.24087300
H	-0.10421700	-0.20537000	0.96409300
H	-1.63519100	-0.87360700	-1.59727100
H	1.10230200	2.16460600	-1.56453600
H	-1.35840400	2.79564500	-1.38776100
H	0.66723400	-0.22229600	-1.96723200
O	-1.89891800	0.96654000	-0.68785600
O	0.13836200	-2.02985000	-0.01701700
O	2.15907900	-0.11187200	-0.52673000
C	-2.65187600	-1.06901500	0.28121600
H	-2.38590800	-2.11370000	0.44371700
H	-2.65655400	-0.55955600	1.25363100
O	-3.93380300	-1.04102800	-0.32257800
O	0.67112800	2.06724500	0.48107800
Si	1.86733900	3.06378300	1.10855800
Si	-5.03533200	0.23230400	-0.37255900
Si	3.33337800	-0.79519700	-1.52673600
Si	0.71977400	-2.85803900	1.33767000
C	1.22832800	4.83245100	1.11581600
H	1.95819100	5.51331200	1.56552700
H	1.02936300	5.17972600	0.09697200
H	0.29761800	4.90914600	1.68562200
C	2.14550800	2.44651400	2.85657300
H	2.88507000	3.06175400	3.37842800
H	1.21629000	2.47363100	3.43306700
H	2.50554900	1.41404000	2.84289900

C	3.45147800	2.96453700	0.10686200
H	3.86285400	1.95485200	0.14627000
H	3.29339900	3.22512000	-0.94318400
H	4.19226000	3.65981900	0.51446500
C	3.97448800	0.49854900	-2.73031000
H	4.47109700	1.32084300	-2.20999500
H	4.69095500	0.05255300	-3.42769800
H	3.15435800	0.91843500	-3.32150400
C	2.59304100	-2.22927800	-2.49025900
H	3.38436200	-2.87591800	-2.88185000
H	1.93601500	-2.82377400	-1.85313700
H	2.00361200	-1.87524400	-3.34110400
C	4.68268200	-1.34585400	-0.35003000
H	4.33012600	-2.13185300	0.32256900
H	5.54389300	-1.73293900	-0.90277900
H	5.02540400	-0.50710100	0.26281400
C	-0.73574700	-3.50287200	2.33736800
H	-0.38064100	-4.08360300	3.19488900
H	-1.34880900	-2.68266800	2.72223000
H	-1.37711800	-4.15178400	1.73388200
C	1.71868300	-4.28950500	0.65646200
H	1.13322400	-4.86062000	-0.06975800
H	2.63048200	-3.94730700	0.16145900
H	2.00712600	-4.96877400	1.46451100
C	1.76738000	-1.71462400	2.39593500
H	2.48498900	-1.17483300	1.77564600
H	1.15577600	-0.97458700	2.91957700
H	2.31006900	-2.29271300	3.15031800
C	-6.72203400	-0.57538500	-0.20384200
H	-6.82445500	-1.07655400	0.76303900
H	-7.51822600	0.17159500	-0.28470800
H	-6.87986800	-1.31938400	-0.99031600
C	-4.71846300	1.42163500	1.04606200
H	-4.78823000	0.91872600	2.01537100
H	-3.72509700	1.86739500	0.95917100
H	-5.45977000	2.22676700	1.03317800
C	-4.92291600	1.11629900	-2.02507900
H	-5.09933000	0.42137600	-2.85172900
H	-5.67264700	1.91165700	-2.08978800
H	-3.93331800	1.55930200	-2.15312700

Zero-point correction=	0.582541 (Hartree/Particle)
Thermal correction to Energy=	0.624274
Thermal correction to Enthalpy=	0.625219
Thermal correction to Gibbs Free Energy=	0.507125
Sum of electronic and zero-point Energies=	-2246.062812
Sum of electronic and thermal Energies=	-2246.021078
Sum of electronic and thermal Enthalpies=	-2246.020134
Sum of electronic and thermal Free Energies=	-2246.138227

18-ion





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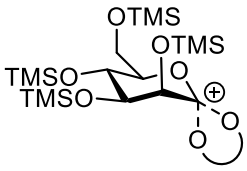
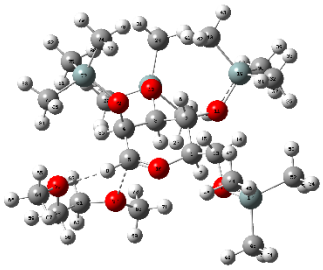
C	1.40488000	-0.28564700	-0.85209700
C	0.14679500	0.27898700	-0.17773300
C	-1.08783600	-0.10448400	-1.00361300
C	-1.18973100	-1.63180100	-1.03964400
C	0.11648200	-2.29608100	-1.34799300
H	0.03356600	-0.15958800	0.81967500
H	1.56967400	0.18241200	-1.82257600
H	-1.96045000	-1.95831600	-1.74380900
H	0.14515700	-3.35707400	-1.58938700
H	-0.93531400	0.25342200	-2.03123600
O	1.23427800	-1.75684100	-1.20803700
O	0.31072100	1.67172800	-0.13548400
O	-2.25360300	0.42077100	-0.43330200
C	2.66123600	-0.23100400	-0.01676200
H	2.74341700	0.79952600	0.34292700
H	2.54244800	-0.88870200	0.85471200
O	3.76182200	-0.60205500	-0.81111900
O	-1.33374100	-2.19906000	0.24519800
Si	-2.77956600	-2.74766900	1.01646200
Si	5.36976200	-0.55275600	-0.27471800
Si	-3.32564700	1.50113300	-1.19890200
Si	0.19964800	2.65807900	1.25307500
C	-2.26228100	-4.31421600	1.89101100
H	-3.09560200	-4.71654800	2.47473900
H	-1.94726600	-5.08042500	1.17750200
H	-1.43412800	-4.12229100	2.57877900
C	-3.29702700	-1.40775100	2.20809200
H	-4.20527400	-1.70371200	2.74199900
H	-2.51379600	-1.21865000	2.94673200
H	-3.48786500	-0.47844100	1.66962800
C	-4.05879300	-3.05987900	-0.31237300
H	-4.32296100	-2.14575100	-0.84866400
H	-3.71889700	-3.80409200	-1.03842000
H	-4.97182100	-3.44475300	0.15202000
C	-4.56658200	0.52069100	-2.20740400
H	-5.19787700	-0.10107800	-1.56703600
H	-5.22152900	1.19867300	-2.76370800
H	-4.06858500	-0.12851400	-2.93421700
C	-2.33496700	2.64324600	-2.30954500
H	-2.93739700	3.51450000	-2.58319900
H	-1.43044600	2.99208900	-1.80754100
H	-2.03806800	2.14549400	-3.23722300
C	-4.16962000	2.39176900	0.21110100
H	-3.46616400	2.98194000	0.80225600
H	-4.93783600	3.06775500	-0.17581200
H	-4.65913000	1.67825700	0.88003000
C	1.91631600	2.87290400	1.97949500
H	1.88424700	3.59223700	2.80387500
H	2.31000400	1.93374800	2.37847100

H	2.62032400	3.25211100	1.23319100
C	-0.45538200	4.29344100	0.62775100
H	0.15901000	4.66710700	-0.19615200
H	-1.48515600	4.21353100	0.27355200
H	-0.43062700	5.03785200	1.42920200
C	-0.94680900	1.83975000	2.49002900
H	-1.86407300	1.49748700	2.00751400
H	-0.47673200	0.97755200	2.97170200
H	-1.21244900	2.55160500	3.27730500
C	5.78572600	1.20628700	0.22955700
H	5.16139800	1.55006700	1.05959800
H	6.82894700	1.26952000	0.55400800
H	5.65084700	1.89774200	-0.60705700
C	5.56185200	-1.71726100	1.18451200
H	4.93782900	-1.41240800	2.03004700
H	5.29056000	-2.74091200	0.91097700
H	6.60056200	-1.72507400	1.52894000
C	6.36740400	-1.11262200	-1.75169600
H	6.21554200	-0.44434900	-2.60368700
H	7.43491100	-1.11638200	-1.51191900
H	6.08644800	-2.12489800	-2.05475500

Zero-point correction=	0.585106 (Hartree/Particle)
Thermal correction to Energy=	0.626599
Thermal correction to Enthalpy=	0.627544
Thermal correction to Gibbs Free Energy=	0.511805
Sum of electronic and zero-point Energies=	-2245.896250
Sum of electronic and thermal Energies=	-2245.854756
Sum of electronic and thermal Enthalpies=	-2245.853812
Sum of electronic and thermal Free Energies=	-2245.969551

18-ion-glyme





1 1

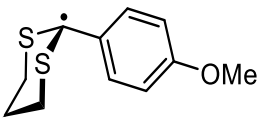
C	-1.49017500	0.12756700	-0.44946400
C	-0.50018000	-0.94746100	0.01928800
C	0.89244800	-0.61404800	-0.52586900
C	1.31885500	0.72864900	0.07285400
C	0.26913700	1.78593900	-0.12834000
H	-0.44362900	-0.94381300	1.11228600
H	-1.64306200	0.05577000	-1.52596200
H	0.51327200	2.81934100	0.10056600
H	0.80495700	-0.49648200	-1.61355000
O	-0.96127900	1.52096500	-0.24229600
O	-0.96352400	-2.17496200	-0.48530800
O	1.81902300	-1.60982400	-0.18985700
C	-2.82227200	0.09742600	0.26172300
H	-3.16631200	-0.94143700	0.23960600
H	-2.67042800	0.38595900	1.31066600
O	-3.72337700	0.95837600	-0.39729500
Si	-5.33545000	1.16291000	0.07837000

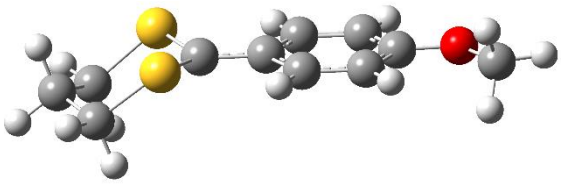
Si	2.75996300	-2.44161700	-1.33474500
Si	-1.19428500	-3.59002500	0.43556900
C	4.19188200	-1.34866700	-1.86372400
H	4.86968200	-1.14916000	-1.03059700
H	4.76572500	-1.83236000	-2.66049600
H	3.83583300	-0.38825000	-2.25066200
C	1.68409000	-2.85030000	-2.81891600
H	2.14074300	-3.65317600	-3.40534100
H	0.69067500	-3.17504600	-2.50251100
H	1.56419100	-1.98841500	-3.48190200
C	3.35133400	-3.96230200	-0.42440300
H	2.51846600	-4.61862100	-0.16052900
H	4.04930500	-4.53246700	-1.04448100
H	3.86983300	-3.68431500	0.49744100
C	-2.96187600	-3.61332500	1.06909100
H	-3.16681100	-4.56259500	1.57416400
H	-3.14207200	-2.81182300	1.79161900
H	-3.68114700	-3.50720600	0.25181300
C	-0.90223800	-4.99403500	-0.76451900
H	-1.51511500	-4.87262400	-1.66204600
H	0.14440400	-5.05017800	-1.07228400
H	-1.16989500	-5.94848700	-0.30146500
C	0.01629900	-3.60732500	1.86775200
H	1.02834100	-3.39271300	1.51938600
H	-0.24248800	-2.86629000	2.62953300
H	0.00912000	-4.59072800	2.34765500
C	-5.37710700	1.93700100	1.78799700
H	-4.86705400	2.90454800	1.79487200
H	-6.41128400	2.09874500	2.10752200
H	-4.89893700	1.29398100	2.53308100
C	-6.06493000	2.29701700	-1.21552400
H	-5.53465900	3.25289800	-1.24339900
H	-6.00973400	1.84481300	-2.20950900
H	-7.11704800	2.50128100	-0.99538400
C	-6.17659400	-0.51543300	0.10026600
H	-5.70647200	-1.19363900	0.81891800
H	-7.22801300	-0.41021600	0.38467900
H	-6.13980300	-0.98742300	-0.88579200
O	1.94428900	4.25596600	-0.18028900
O	0.88352300	2.46661600	-2.20800100
C	2.06162000	4.48482000	-1.57992100
H	2.97309800	5.05871500	-1.79630400
H	1.19802200	5.05399200	-1.94855000
C	2.13934300	3.16516000	-2.30973400
H	2.35165900	3.36349400	-3.36434300
H	2.94508700	2.53942300	-1.90876200
C	1.81153900	5.46465100	0.56646500
H	1.73400500	5.18441500	1.61566600
H	2.68833300	6.10830200	0.42826300
H	0.91181000	6.01554000	0.26731100
C	0.61080900	1.62166500	-3.33312800
H	0.53599000	2.22472100	-4.24242900
H	1.38939400	0.86287400	-3.46277700
H	-0.34859600	1.14174100	-3.15034600
O	1.34299800	0.66663500	1.48454200
Si	2.71039300	0.84066000	2.50334800

C	2.16548700	-0.00068300	4.07818100
C	4.17043000	-0.01212600	1.70316800
C	3.03147200	2.67077500	2.72012900
H	1.26358700	0.46836500	4.48076000
H	1.95192200	-1.05732700	3.89565200
H	2.94821300	0.06307700	4.83983100
H	3.92958500	-1.05284400	1.47956000
H	4.47205100	0.47795200	0.77379300
H	5.02800100	0.01101000	2.38239600
H	3.92993200	2.84102300	3.32066900
H	3.17189200	3.14935800	1.74706700
H	2.19057300	3.15877400	3.22108500
H	2.26673900	1.06057900	-0.35421400

Zero-point correction=	0.729625 (Hartree/Particle)
Thermal correction to Energy=	0.779874
Thermal correction to Enthalpy=	0.780819
Thermal correction to Gibbs Free Energy=	0.645634
Sum of electronic and zero-point Energies=	-2554.742548
Sum of electronic and thermal Energies=	-2554.692299
Sum of electronic and thermal Enthalpies=	-2554.691354
Sum of electronic and thermal Free Energies=	-2554.826539

19





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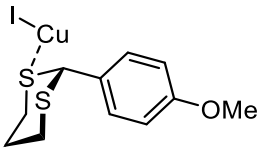
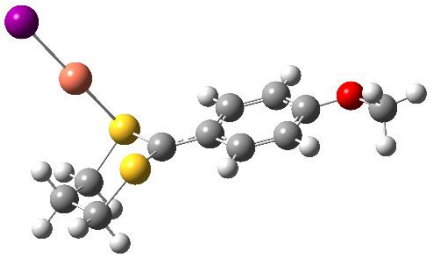
C	4.20873500	-0.16760500	0.27296500
C	3.50394100	1.14197700	0.61246900
C	1.05360500	0.02377600	-0.20393000
C	3.35551900	-1.39509500	0.57682600
H	3.19610700	1.16083000	1.66027000
H	4.15709900	1.99690800	0.43058000
H	4.51349100	-0.17073100	-0.77730100
H	5.12019400	-0.22938700	0.87895100
H	3.04573600	-1.40731100	1.62412800
H	3.90495200	-2.31490800	0.37006300
S	1.83947600	-1.54379500	-0.46531500
S	2.01736200	1.49538800	-0.42266200
C	-0.37941200	0.10590100	-0.11194900
C	-1.05855600	1.35655200	-0.04460700
C	-1.19825900	-1.05206800	-0.07677600
C	-2.43192600	1.43209100	0.04640300
H	-0.48672800	2.27486400	-0.05357600
C	-2.58103200	-0.97886300	0.01463300
H	-0.73737100	-2.03030700	-0.11031200
C	-3.21695900	0.26760900	0.07444000
H	-2.93238000	2.39163300	0.10096700
H	-3.15175900	-1.89717500	0.04135400
O	-4.56005300	0.45654800	0.16327400
C	-5.41002700	-0.69118100	0.19400300
H	-5.20002900	-1.31811500	1.06663900
H	-6.42544000	-0.30578700	0.26146800

H	-5.30663200	-1.28694600	-0.71864400

Zero-point correction=	0.215149 (Hartree/Particle)
Thermal correction to Energy=	0.228802
Thermal correction to Enthalpy=	0.229746
Thermal correction to Gibbs Free Energy=	0.173075
Sum of electronic and zero-point Energies=	-1298.553011
Sum of electronic and thermal Energies=	-1298.539359
Sum of electronic and thermal Enthalpies=	-1298.538414
Sum of electronic and thermal Free Energies=	-1298.595086

19-CuI



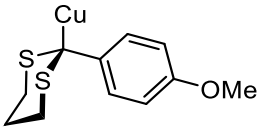


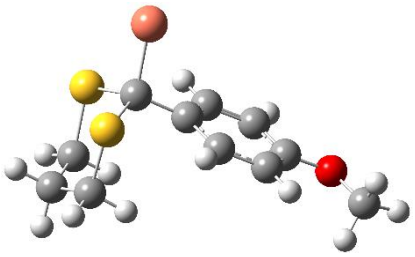
0 2

C	-1.23698700	3.23168200	0.14154500
C	-0.66289400	2.70608000	1.45151600
C	1.08740800	1.04060400	-0.01170300
C	-0.20474200	3.33529400	-0.97590800
H	0.18609600	3.30031300	1.79364200
H	-1.41708700	2.68136000	2.23840400
H	-2.07602900	2.60366400	-0.17382500
H	-1.63462200	4.23470200	0.33132400
H	0.62962200	3.97566900	-0.68389100
H	-0.65467700	3.74484700	-1.88120000
S	0.49643000	1.71675600	-1.52649300
S	-0.06198200	0.95688700	1.36356100
C	2.33165500	0.33729900	0.06834700
C	2.69432100	-0.44262100	1.20517700
C	3.27450600	0.38445500	-0.99255500
C	3.89588600	-1.11131900	1.26675400
H	2.01649700	-0.51827500	2.04497600
C	4.48335400	-0.28892300	-0.93276300
H	3.05365900	0.97493200	-1.87159400
C	4.81007400	-1.04879600	0.19987100
H	4.15935700	-1.70147400	2.13602800
H	5.16611900	-0.21268600	-1.76765100
O	5.95930600	-1.74458300	0.36408100
C	6.92967600	-1.73147900	-0.68762500
H	7.29321900	-0.71691500	-0.87712100
H	7.75139900	-2.35204400	-0.33697100
H	6.51897700	-2.15527300	-1.60903600
Cu	-1.80737200	-0.17848500	0.49641800
I	-3.72863900	-1.43354800	-0.34794100

Zero-point correction=	0.217153 (Hartree/Particle)
Thermal correction to Energy=	0.235055
Thermal correction to Enthalpy=	0.235999
Thermal correction to Gibbs Free Energy=	0.165634
Sum of electronic and zero-point Energies=	-3237.039710
Sum of electronic and thermal Energies=	-3237.021807
Sum of electronic and thermal Enthalpies=	-3237.020863
Sum of electronic and thermal Free Energies=	-3237.091228

20





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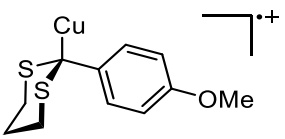
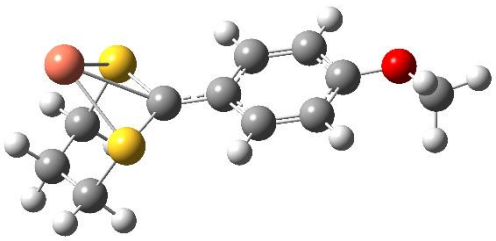
C	2.32375500	-2.65511800	0.09477900
C	1.76486000	-2.00763600	1.36458500
C	1.12044500	0.36380000	-0.04132000
C	1.63804700	-2.18125800	-1.18927300
H	0.69048600	-2.18996200	1.45467700
H	2.25219200	-2.41320300	2.25364100
H	3.39970800	-2.46814700	0.02932400
H	2.18602800	-3.74083300	0.17436400
H	0.56443800	-2.38348700	-1.15186400
H	2.04872300	-2.69563300	-2.06062900
S	1.87474100	-0.38327800	-1.54361900
S	2.04576500	-0.18531600	1.45462700
C	-0.38421000	0.17986000	0.07122500
C	-1.04581800	0.34001800	1.30529400
C	-1.19155300	-0.09385100	-1.03919300
C	-2.42163400	0.22877200	1.41737100
H	-0.46381000	0.55692500	2.19165800
C	-2.58002800	-0.20929000	-0.94291300
H	-0.72899000	-0.21756100	-2.00972800
C	-3.20857700	-0.05007400	0.29275500
H	-2.91348000	0.35392100	2.37513800
H	-3.14946400	-0.42613800	-1.83676200
O	-4.55357000	-0.14468700	0.50951400
C	-5.39746200	-0.42914500	-0.60400200
H	-5.15413400	-1.39798700	-1.05362700
H	-6.41162400	-0.45969200	-0.20955400
H	-5.32923200	0.35275100	-1.36822800
Cu	1.48285100	2.29198500	-0.20056900

Zero-point correction=	0.216031 (Hartree/Particle)
Thermal correction to Energy=	0.231450
Thermal correction to Enthalpy=	0.232394
Thermal correction to Gibbs Free Energy=	0.171632
Sum of electronic and zero-point Energies=	-2939.152491
Sum of electronic and thermal Energies=	-2939.137072
Sum of electronic and thermal Enthalpies=	-2939.136128
Sum of electronic and thermal Free Energies=	-2939.196890

20-SET





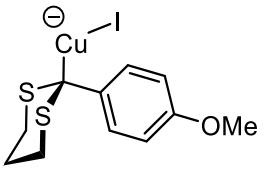
1 2

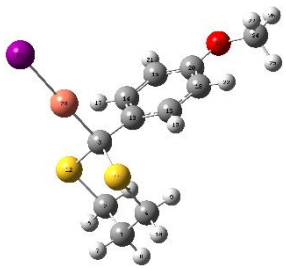
C	3.25209800	0.06908700	-1.63357400
C	2.50892400	-1.26065300	-1.54038500

C	0.44769400	-0.04579900	-0.11605600
C	2.37397900	1.31699000	-1.59648400
H	1.80307000	-1.39571000	-2.36059200
H	3.20677500	-2.09830400	-1.53444200
H	4.00828100	0.12614500	-0.84184600
H	3.79678700	0.07696900	-2.58399900
H	1.66129700	1.34325200	-2.42140500
H	2.98140100	2.22194000	-1.62622800
S	1.35534700	1.49424300	-0.04963600
S	1.51324900	-1.47627800	0.01622600
C	-0.96801000	-0.11977300	-0.06995100
C	-1.64983700	-1.37419600	-0.02652000
C	-1.77720600	1.05084700	-0.07522100
C	-3.02084000	-1.44035500	0.00659500
H	-1.07909700	-2.29325700	-0.02495000
C	-3.15697000	0.98392500	-0.04176200
H	-1.30621700	2.02426000	-0.11141100
C	-3.79983900	-0.26514500	0.00071700
H	-3.53244800	-2.39433800	0.03697100
H	-3.72736800	1.90218400	-0.04986900
O	-5.13309700	-0.44630800	0.03705000
C	-5.99514500	0.70009500	0.03534700
H	-5.86212900	1.28833900	-0.87676300
H	-7.00696600	0.30367700	0.07015000
H	-5.81524100	1.32623900	0.91359800
Cu	2.64655200	0.10901700	1.44802500

Zero-point correction=	0.216851 (Hartree/Particle)
Thermal correction to Energy=	0.232320
Thermal correction to Enthalpy=	0.233265
Thermal correction to Gibbs Free Energy=	0.172223
Sum of electronic and zero-point Energies=	-2938.984853
Sum of electronic and thermal Energies=	-2938.969383
Sum of electronic and thermal Enthalpies=	-2938.968439
Sum of electronic and thermal Free Energies=	-2939.029481

20-I-ion





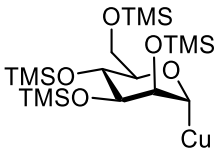
-1 1

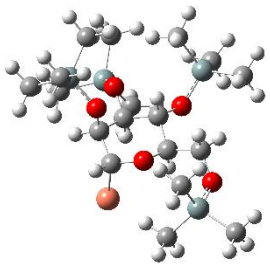
C	-2.01699600	-3.86746600	-0.08388200
C	-1.91403200	-3.08853900	1.23151800
C	-0.31622500	-1.07432400	0.00656400
C	-1.96966200	-2.97785500	-1.33037500
H	-2.71616100	-2.34798900	1.30402000
H	-1.99957700	-3.76300200	2.08671800
H	-1.21564800	-4.61152800	-0.13280300
H	-2.96904100	-4.41456700	-0.08766300
H	-2.78103700	-2.24470900	-1.30813300
H	-2.08172200	-3.57738800	-2.23682000
S	-0.37478000	-2.06712200	-1.53657500
S	-0.30352800	-2.21160500	1.45193600

C	-1.38796900	-0.00103000	0.09732000
C	-1.73500300	0.58092200	1.33492200
C	-2.02754700	0.52849000	-1.03156900
C	-2.65415600	1.61368200	1.43183800
H	-1.26443600	0.21245400	2.23732800
C	-2.95454100	1.57168100	-0.95110000
H	-1.78981000	0.12382700	-2.00683700
C	-3.27864900	2.12304300	0.28774300
H	-2.90308100	2.04691200	2.39424400
H	-3.41087400	1.93521300	-1.86251900
O	-4.17512800	3.14125500	0.49024900
C	-4.81351100	3.70500100	-0.65008100
H	-5.41774300	2.96145400	-1.18265200
H	-5.46469000	4.49168600	-0.27167400
H	-4.08595800	4.14079900	-1.34429200
Cu	1.43435900	-0.12129200	-0.00078300
I	3.60692600	1.07947700	-0.04134600

Zero-point correction=	0.216334 (Hartree/Particle)
Thermal correction to Energy=	0.233995
Thermal correction to Enthalpy=	0.234940
Thermal correction to Gibbs Free Energy=	0.166888
Sum of electronic and zero-point Energies=	-3237.184597
Sum of electronic and thermal Energies=	-3237.166935
Sum of electronic and thermal Enthalpies=	-3237.165991
Sum of electronic and thermal Free Energies=	-3237.234042

21





0 1

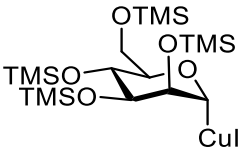
C	1.45895200	0.56151700	-0.18377800
C	-0.02107700	0.83246000	0.15270400
C	-0.88920900	-0.18457400	-0.59351700
C	-0.44177900	-1.60672800	-0.23047100
C	1.04414400	-1.76865500	-0.53532200
H	-0.16948500	0.68012100	1.22695400
H	1.60051200	0.71102300	-1.26874600
H	-1.00686400	-2.32309700	-0.83772500
H	1.38903600	-2.72416400	-0.13449500
H	-0.70109500	-0.04699000	-1.66591200
O	1.80350000	-0.77667600	0.15065800
O	-0.36880500	2.15294600	-0.24141800
O	-2.26291900	0.01463900	-0.29674400
C	2.41442400	1.47622700	0.56389300
H	2.08228900	2.50608900	0.43667400
H	2.37315600	1.22836600	1.63278700
O	3.74546600	1.40143200	0.07356700
O	-0.65615000	-1.84968200	1.16227700
Si	-1.96581000	-2.56292100	1.92883800
Si	4.86848600	0.16599700	0.27926200
Si	-3.43918600	0.34744000	-1.45514800

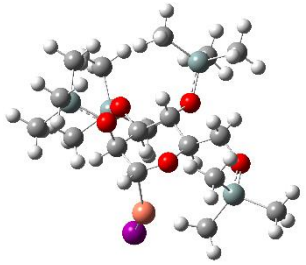
Si	-1.06990500	3.31984400	0.75389800
C	-3.13732400	-1.26692800	2.61327200
H	-3.95222000	-1.73755600	3.17307200
H	-2.61127900	-0.58537500	3.28800300
H	-3.55786200	-0.67194500	1.80178500
C	-2.86685700	-3.70540200	0.73751600
H	-3.68965000	-4.20960900	1.25411900
H	-3.28943200	-3.15712700	-0.10709500
H	-2.19785600	-4.47585400	0.34223300
C	-1.22435600	-3.55060000	3.34460900
H	-0.56462400	-4.33886400	2.97052700
H	-0.63818500	-2.90402000	4.00449500
H	-2.00932200	-4.02019000	3.94602500
C	-4.07017800	-1.25551000	-2.20854300
H	-4.60214600	-1.86138800	-1.47014200
H	-4.76161100	-1.04639400	-3.03131700
H	-3.24574500	-1.85354400	-2.60917400
C	-2.71292900	1.43419700	-2.80657100
H	-3.51268600	1.90984300	-3.38252100
H	-2.08067500	2.21326900	-2.37586300
H	-2.10287600	0.85339300	-3.50461500
C	-4.81750800	1.20851200	-0.52196200
H	-4.49547500	2.17423800	-0.12552700
H	-5.67542900	1.38030000	-1.17922900
H	-5.15671600	0.59599700	0.31834900
C	0.27563600	4.33887400	1.58312700
H	-0.17219000	5.14060000	2.17949300
H	0.88451900	3.72619100	2.25411900
H	0.94021900	4.79937800	0.84627700
C	-2.07415500	4.41318300	-0.39116600
H	-1.45417400	4.78451600	-1.21234500
H	-2.92163900	3.87737300	-0.82444000
H	-2.46355300	5.27875900	0.15363200
C	-2.13860900	2.50103300	2.06169300
H	-2.77760400	1.73833300	1.61459300
H	-1.53017500	2.01607700	2.83040600
H	-2.76819000	3.24682300	2.55691700
C	4.57051800	-0.73592800	1.89856000
H	3.58055100	-1.19629000	1.89680300
H	5.32003400	-1.52123100	2.03876200
H	4.63623500	-0.05404300	2.75199900
C	4.81033100	-1.01745100	-1.17847200
H	3.82431800	-1.48399800	-1.24598800
H	5.00724600	-0.48974100	-2.11666900
H	5.56176100	-1.80669500	-1.07225100
C	6.53252100	1.03895100	0.30178900
H	6.61020700	1.71857200	1.15544700
H	7.34888700	0.31277400	0.37160600
H	6.68126000	1.62281900	-0.61149800
Cu	1.39290800	-1.77972900	-2.47573500

Zero-point correction=	0.584633 (Hartree/Particle)
Thermal correction to Energy=	0.627728
Thermal correction to Enthalpy=	0.628672
Thermal correction to Gibbs Free Energy=	0.508848
Sum of electronic and zero-point Energies=	-3886.684537

Sum of electronic and thermal Energies=	-3886.641442
Sum of electronic and thermal Enthalpies=	-3886.640498
Sum of electronic and thermal Free Energies=	-3886.760322

21-I





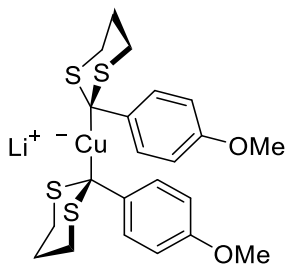
0 2

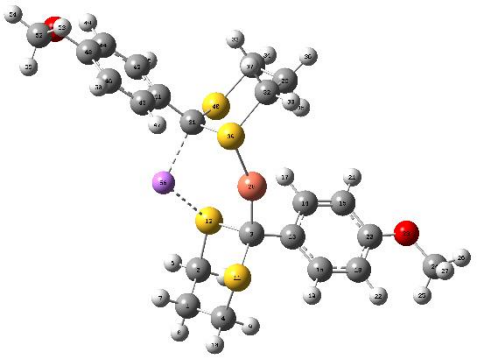
C	-1.15594100	-1.31215200	-0.25996200
C	0.37537900	-1.41725100	-0.32716700
C	0.94984800	-0.02974700	-0.01527800
C	0.52226200	0.38262300	1.39762200
C	-0.99218800	0.31248000	1.52386700
H	0.72885700	-2.11970500	0.43498900
H	-1.48438300	-0.58764300	-1.01520800
H	0.84285200	1.41271400	1.58212200
H	-1.36137100	0.49530700	2.53559300
H	0.48811200	0.67750300	-0.71751700
O	-1.58507600	-0.82418900	1.03972100
O	0.73491200	-1.81973400	-1.63223900
O	2.35476000	-0.01548500	-0.13745600
C	-1.90637300	-2.61102300	-0.48188000
H	-1.48972400	-3.10108200	-1.36146600
H	-1.75220400	-3.26431800	0.38671500
O	-3.28438400	-2.39186600	-0.72812900
O	1.05380100	-0.50403900	2.37142400
Si	2.43811800	-0.30633700	3.32263200
Si	-4.49462900	-1.87194900	0.32103700
Si	3.17676100	1.03112100	-1.18405400
Si	1.76943000	-3.10190500	-2.01760400
C	3.87693100	-1.22792900	2.55583100
H	4.77058100	-1.13792300	3.18165500
H	3.64503800	-2.29079400	2.44418500
H	4.09306100	-0.82770800	1.56447900
C	2.82389300	1.52332500	3.49324900
H	3.67569800	1.65833100	4.16694400
H	3.08515300	1.97567500	2.53399200
H	1.97723700	2.07571700	3.91166800
C	1.98744500	-1.05526900	4.98165400
H	1.16487900	-0.50762500	5.45040200
H	1.67950800	-2.09874700	4.86707100
H	2.84368300	-1.03147800	5.66290900
C	3.34297900	2.71901100	-0.37821100
H	3.96079300	2.67627800	0.52275200
H	3.80778000	3.42828200	-1.07060800
H	2.36091100	3.11885900	-0.10665500
C	2.21854600	1.18778300	-2.79079000
H	2.85501800	1.61681500	-3.57083000
H	1.86321800	0.21171000	-3.12733700
H	1.34987300	1.84246100	-2.67308800
C	4.85244100	0.22923000	-1.42196500
H	4.76492400	-0.73912700	-1.92092100

H	5.50054300	0.86705000	-2.03045500
H	5.34693700	0.06929800	-0.45960900
C	0.75299000	-4.67199900	-2.19894200
H	1.39444900	-5.50957000	-2.49135500
H	0.26420100	-4.94125600	-1.25786000
H	-0.02067200	-4.55841900	-2.96391600
C	2.54140400	-2.63141000	-3.65726600
H	1.76984800	-2.37732100	-4.38961100
H	3.20795000	-1.77174400	-3.55610700
H	3.12396900	-3.46663100	-4.05779200
C	3.05443600	-3.31507100	-0.66794900
H	3.51432400	-2.35686600	-0.42105300
H	2.61513700	-3.71962400	0.24831900
H	3.83432100	-4.00879200	-0.99693100
C	-4.25460400	-2.63502600	2.01841500
H	-3.30083100	-2.32034100	2.44907400
H	-5.05403300	-2.31397800	2.69369500
H	-4.27127400	-3.72783000	1.97299300
C	-4.52368600	0.01254200	0.44797300
H	-3.91938000	0.35215900	1.29334900
H	-4.13673700	0.46689100	-0.47054200
H	-5.54237300	0.38323900	0.59399400
C	-6.07792400	-2.46489800	-0.48778600
H	-6.08641400	-3.55417100	-0.58363100
H	-6.94787900	-2.16829600	0.10627200
H	-6.19099300	-2.03399300	-1.48685200
Cu	-1.79749100	1.86362700	0.46357500
I	-1.16637700	3.68150300	-1.07925900

Zero-point correction=	0.585293 (Hartree/Particle)
Thermal correction to Energy=	0.630991
Thermal correction to Enthalpy=	0.631936
Thermal correction to Gibbs Free Energy=	0.502400
Sum of electronic and zero-point Energies=	-4184.547684
Sum of electronic and thermal Energies=	-4184.501985
Sum of electronic and thermal Enthalpies=	-4184.501041
Sum of electronic and thermal Free Energies=	-4184.630576

Cu(12)$_2$





0 1

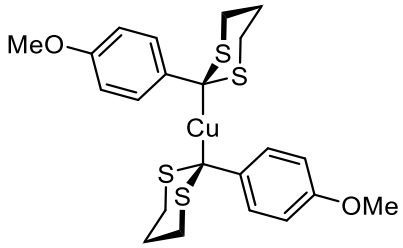
C	-2.39713700	-4.14326900	0.79728700
C	-2.29345100	-3.02048600	1.83023600
C	-1.91720000	-1.04513400	-0.26799800
C	-3.04645000	-3.69640400	-0.51381100
H	-3.27915000	-2.59591100	2.03905500
H	-1.87768500	-3.38774800	2.77082100
H	-1.40314100	-4.55619300	0.59684000

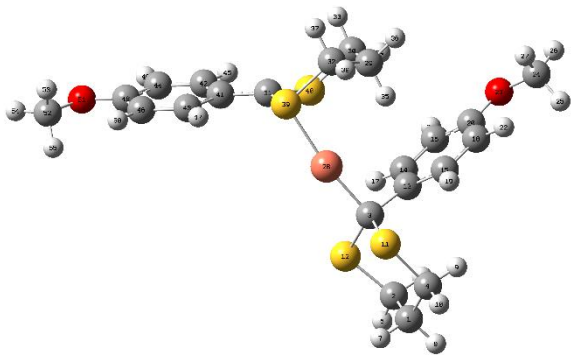
H	-3.00253200	-4.94998500	1.22855800
H	-4.04505400	-3.29394200	-0.32640400
H	-3.14438400	-4.53609500	-1.20521000
S	-2.05211600	-2.43891700	-1.43342800
S	-1.19570700	-1.62139400	1.33671800
C	-3.16250200	-0.21611100	-0.05622500
C	-3.10443300	0.88769700	0.82200200
C	-4.37121000	-0.41992500	-0.72427200
C	-4.19261500	1.71502400	1.03049300
H	-2.17674500	1.08933700	1.34505800
C	-5.47941000	0.41532600	-0.53427000
H	-4.45729000	-1.23519600	-1.43102000
C	-5.39886400	1.48722300	0.35176600
H	-4.13142000	2.55896500	1.70819500
H	-6.38915500	0.20951200	-1.08247800
O	-6.41280000	2.36595200	0.62229100
C	-7.65433200	2.18503000	-0.05224100
H	-8.10361600	1.21457700	0.18670200
H	-8.30709100	2.98068500	0.30317100
H	-7.53711300	2.27094000	-1.13836900
Cu	-0.49572100	0.08528800	-0.96001200
C	0.89346600	3.35548400	-0.43668200
C	1.50092000	3.05036100	0.93560800
C	2.11520800	0.35134400	0.13024500
C	1.61638900	2.65954800	-1.58837500
H	2.56630100	3.29586700	0.95538300
H	1.00046200	3.63022800	1.71424500
H	-0.16052700	3.05513900	-0.44269000
H	0.92728600	4.43730400	-0.60923100
H	2.68186900	2.90040400	-1.59944900
H	1.18535800	2.93211300	-2.55376600
S	1.49903200	0.81251300	-1.51019900
S	1.28387200	1.28177700	1.42809500
C	3.59850800	0.21927200	0.20970800
C	4.32914000	0.50152100	1.38466900
C	4.34928700	-0.29280700	-0.86685700
C	5.69730000	0.28004300	1.47528300
H	3.80671800	0.90432800	2.24323800
C	5.72441900	-0.51293800	-0.79060200
H	3.84402200	-0.53019500	-1.79560900
C	6.41527300	-0.22870400	0.38991900
H	6.23416800	0.50842000	2.38948500
H	6.23810900	-0.90535400	-1.65854500
O	7.76309400	-0.40665600	0.57993300
C	8.52734200	-0.92280600	-0.50389800
H	8.48909200	-0.26019400	-1.37627800
H	9.55383100	-0.98446500	-0.14550400
H	8.18718600	-1.92285300	-0.79730400
Li	1.27162800	-1.72559800	0.54425500

Zero-point correction=	0.433836 (Hartree/Particle)
Thermal correction to Energy=	0.465753
Thermal correction to Enthalpy=	0.466697
Thermal correction to Gibbs Free Energy=	0.367905
Sum of electronic and zero-point Energies=	-4245.258458
Sum of electronic and thermal Energies=	-4245.226542

Sum of electronic and thermal Enthalpies= -4245.225597
Sum of electronic and thermal Free Energies= -4245.324389

Cu(12)$_2$-neutral





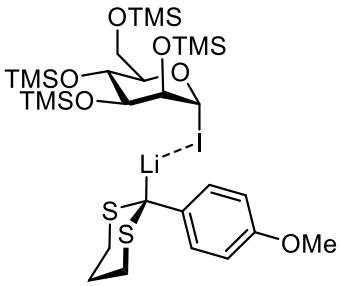
0 2

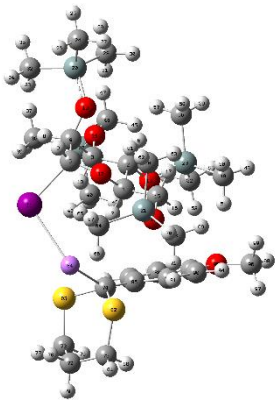
C	3.84166200	3.97295400	0.83650100
C	3.07380400	3.15214800	1.87751900
C	1.85980400	1.58388500	-0.14981600
C	4.19115800	3.18771500	-0.43168600
H	3.64230100	2.26252200	2.16403100
H	2.89379500	3.74246100	2.77863800
H	3.26121900	4.86187700	0.57065100
H	4.77751800	4.32011800	1.29310300
H	4.79379900	2.30941600	-0.18421300
H	4.76585300	3.80736300	-1.12358800
S	2.71496900	2.62393300	-1.38796300
S	1.40726700	2.60492700	1.30547400
C	2.58516200	0.29753200	0.21055000
C	2.19691700	-0.44971600	1.34332700
C	3.56320800	-0.28635000	-0.60544500
C	2.72879300	-1.69698800	1.62131800
H	1.43861000	-0.04478500	1.99915300
C	4.10514300	-1.54849000	-0.34288200
H	3.89351800	0.24312600	-1.48980900
C	3.68498700	-2.26974200	0.77395100
H	2.40407600	-2.25706400	2.49093400
H	4.84889100	-1.94749200	-1.01979300
O	4.12685200	-3.51857000	1.12149400
C	5.09521100	-4.14274600	0.28366600
H	6.02286200	-3.56136400	0.23964100
H	5.30005700	-5.11289300	0.73344000
H	4.71218800	-4.28860600	-0.73277000
Cu	0.26549200	0.77522300	-0.91545900
C	0.48465300	-2.52454700	-1.23667300
C	-0.24134100	-3.06028100	-0.00884200
C	-2.15662200	-1.01192100	-0.24278800
C	-0.44428400	-1.94125800	-2.29498600
H	-0.95281600	-3.84379500	-0.27630500
H	0.47647600	-3.46524800	0.70531900
H	1.23326000	-1.78919900	-0.93777000
H	1.02559100	-3.35923500	-1.69585200
H	-1.19218200	-2.66145300	-2.62978000
H	0.11899600	-1.58432400	-3.15756700
S	-1.37008200	-0.43780800	-1.74503600
S	-1.15562500	-1.79117100	0.97349100

C	-3.50003000	-0.60407000	0.03651800
C	-4.20174100	-1.08947500	1.17746600
C	-4.19705600	0.31042200	-0.79421200
C	-5.49153200	-0.69307400	1.45096400
H	-3.71685600	-1.79822700	1.83546500
C	-5.49569600	0.71006600	-0.52120600
H	-3.70716800	0.71726000	-1.66900600
C	-6.15996600	0.21375700	0.60910400
H	-6.01910200	-1.07566100	2.31637300
H	-5.97805500	1.41090200	-1.18842500
O	-7.42455400	0.53747300	0.97282100
C	-8.15876000	1.45893400	0.16185700
H	-8.29555400	1.07147200	-0.85248700
H	-9.12858500	1.56651200	0.64289300
H	-7.66163500	2.43298200	0.12081700

Zero-point correction=	0.432970 (Hartree/Particle)
Thermal correction to Energy=	0.463631
Thermal correction to Enthalpy=	0.464575
Thermal correction to Gibbs Free Energy=	0.367141
Sum of electronic and zero-point Energies=	-4237.646156
Sum of electronic and thermal Energies=	-4237.615494
Sum of electronic and thermal Enthalpies=	-4237.614550
Sum of electronic and thermal Free Energies=	-4237.711984

[11-12]





0 1

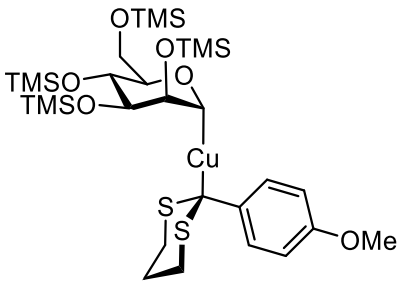
C	-0.08313300	0.42687800	-1.03652200
C	-1.27702700	-0.49556200	-0.74303700
C	-1.95026500	-0.01503800	0.54483200
C	-2.44984000	1.41909800	0.32780600
C	-1.30869100	2.31621300	-0.16060200
H	-2.00290800	-0.40163200	-1.55778600
H	0.64987100	0.36572200	-0.22414300
H	-2.84924900	1.81548200	1.26422200
H	-1.65156100	3.30265200	-0.45383100
H	-1.18817800	0.00037500	1.33279100
I	-0.06755500	2.90633800	1.74230200
O	-0.53033800	1.81094800	-1.13664200
O	-0.81721400	-1.82230700	-0.60167600
O	-3.03217000	-0.84922600	0.90057100
C	0.59490100	0.10389600	-2.35772400
H	0.95096000	-0.92402500	-2.29451800
H	-0.14848100	0.16779000	-3.16304000
O	1.70921200	0.93484100	-2.61798400
O	-3.41324400	1.47347400	-0.70647600

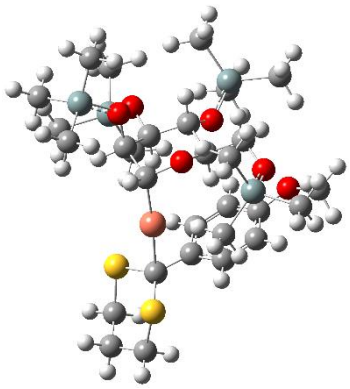
Si	-5.10004700	1.48452300	-0.55564600
Si	1.75254700	2.43478500	-3.37795100
Si	-3.09966600	-1.74074400	2.33634900
Si	-1.40287200	-3.15206400	-1.46714300
C	-5.68534500	2.67657800	-1.87895500
H	-6.77866500	2.71405500	-1.91044100
H	-5.31550800	3.68823100	-1.68926700
H	-5.33210200	2.36497400	-2.86632000
C	-5.78363700	-0.23013100	-0.86414300
H	-6.87748200	-0.22049100	-0.82178500
H	-5.48373400	-0.60270900	-1.84722300
H	-5.40356200	-0.92372200	-0.11307600
C	-5.56584400	2.09177100	1.15886400
H	-5.21698900	1.41012100	1.93823300
H	-5.15431800	3.08473100	1.36270900
H	-6.65514100	2.15964500	1.23994700
C	-3.80545600	-0.65689600	3.69967600
H	-4.83458900	-0.36033600	3.47846400
H	-3.80813700	-1.19133900	4.65512900
H	-3.20889000	0.25149000	3.82859000
C	-1.37552300	-2.32208700	2.79954400
H	-1.43284500	-3.13549600	3.52944300
H	-0.83316800	-2.67695700	1.92114200
H	-0.78695900	-1.51647900	3.24821100
C	-4.26677600	-3.15687700	1.96041700
H	-3.87277800	-3.80769100	1.17671800
H	-4.43312500	-3.76458000	2.85503600
H	-5.23747000	-2.77804100	1.62759700
C	-0.38847800	-3.35027500	-3.03631000
H	-0.64678800	-4.28307600	-3.54766700
H	-0.56452000	-2.52553900	-3.73288000
H	0.67801500	-3.37362100	-2.80001600
C	-1.19638000	-4.64606900	-0.36107800
H	-0.14290400	-4.86558900	-0.17895300
H	-1.69326000	-4.50603800	0.60120700
H	-1.64262400	-5.52086200	-0.84583500
C	-3.20924100	-2.87163400	-1.89943000
H	-3.77159700	-2.56334900	-1.01661400
H	-3.33315200	-2.09574300	-2.66018200
H	-3.64768700	-3.79430300	-2.29213900
C	0.12617700	2.76791500	-4.25737200
H	-0.70431900	2.78233200	-3.54789400
H	0.16509700	3.73858000	-4.76144900
H	-0.08350700	2.00787200	-5.01609800
C	2.10903400	3.76313800	-2.09789900
H	1.35841400	3.74336900	-1.30330200
H	3.09754400	3.60867300	-1.65305900
H	2.10011700	4.75791200	-2.55429700
C	3.17393000	2.34669000	-4.59977400
H	2.97969300	1.60112600	-5.37626900
H	3.33031700	3.31371400	-5.08834000
H	4.10237800	2.07216400	-4.09038600
C	6.00195900	1.19054400	2.48600200
C	4.96229300	0.39640300	3.27970000
C	3.29096700	0.15690600	0.93004500
C	6.12181900	0.75220300	1.02498100

H	5.18375100	-0.67392200	3.25047700
H	4.94247100	0.71626400	4.32432000
H	5.75882900	2.25826300	2.52980900
H	6.97914800	1.06347700	2.96761600
H	6.36389100	-0.31185600	0.95672400
H	6.90382000	1.31716500	0.51180000
S	4.57884900	1.03363500	0.03276000
S	3.22979800	0.62842200	2.65568200
Li	2.62300500	2.19415600	0.86971400
C	3.02543200	-1.24924400	0.56352800
C	2.48436400	-2.18670900	1.47322200
C	3.24907400	-1.72915200	-0.74331700
C	2.21853400	-3.50010000	1.11164200
H	2.27215400	-1.87595700	2.48824500
C	2.99356800	-3.04969400	-1.11390200
H	3.63307900	-1.04985900	-1.49344900
C	2.48413500	-3.95390100	-0.18145000
H	1.80830700	-4.19775400	1.83335100
H	3.19905100	-3.35348700	-2.13250900
O	2.19300200	-5.27748400	-0.43502700
C	2.54244300	-5.80598700	-1.70832400
H	3.61591500	-5.70202200	-1.90393900
H	2.28276200	-6.86335400	-1.67755200
H	1.98223100	-5.32389600	-2.51688900

Zero-point correction=	0.805070 (Hartree/Particle)
Thermal correction to Energy=	0.864173
Thermal correction to Enthalpy=	0.865118
Thermal correction to Gibbs Free Energy=	0.710727
Sum of electronic and zero-point Energies=	-3850.103845
Sum of electronic and thermal Energies=	-3850.044742
Sum of electronic and thermal Enthalpies=	-3850.043797
Sum of electronic and thermal Free Energies=	-3850.198188

[18-Cu-19]





0 2

C	-0.56177800	-1.54973000	-0.33686700
C	-1.73810800	-0.79865700	0.31641100
C	-1.58421400	0.70894800	0.10546900
C	-1.32881800	1.02417200	-1.37424800
C	-0.10444400	0.24316900	-1.84412700
H	-2.67739400	-1.11184100	-0.15195200
H	0.34292600	-1.29340400	0.23039200
H	-0.00059600	0.37685800	-2.92291900
H	-0.69040500	1.01273200	0.66358700
O	-0.39696200	-1.17518000	-1.69064600

O	-1.72501400	-1.07876100	1.71044300
O	-2.72990100	1.37552400	0.61981700
C	-0.74002900	-3.05693300	-0.28262300
H	-1.00641200	-3.34121100	0.73548700
H	-1.56244900	-3.34356400	-0.95069900
O	0.45041000	-3.76589000	-0.61421800
Si	1.17208200	-3.90609800	-2.12993000
Si	-2.68104600	2.75312700	1.57668700
Si	-2.98170900	-1.59799700	2.68923500
C	-2.48312600	4.29188500	0.51526500
H	-3.31750200	4.40527400	-0.18087800
H	-2.43730800	5.18843400	1.14228800
H	-1.55928700	4.24663900	-0.06967900
C	-1.23346900	2.65525600	2.77686800
H	-1.37640700	3.36446800	3.59798800
H	-1.13564200	1.65360200	3.20163000
H	-0.29318000	2.91093700	2.28062600
C	-4.32883300	2.77881600	2.46982200
H	-4.43806400	1.91483800	3.13021900
H	-4.42870400	3.68507000	3.07489600
H	-5.15406500	2.75963700	1.75213500
C	-2.80415400	-3.45169800	2.95973400
H	-3.52452000	-3.81200300	3.70106800
H	-2.96942300	-4.00903900	2.03300200
H	-1.79809400	-3.68554300	3.32126600
C	-2.75321600	-0.71135600	4.32760400
H	-1.74776200	-0.88899300	4.72093800
H	-2.88901100	0.36741800	4.22176200
H	-3.47174200	-1.07287600	5.06974000
C	-4.63566100	-1.19216400	1.90031500
H	-4.64919700	-0.14771400	1.58129900
H	-4.82344200	-1.81542900	1.02110200
H	-5.45251100	-1.35844200	2.60938300
C	-0.13622000	-3.88028200	-3.47581600
H	-0.66013800	-2.92253500	-3.46334300
H	0.32352000	-4.01553400	-4.45991500
H	-0.86818700	-4.68135400	-3.33372100
C	2.46206400	-2.56832600	-2.40462900
H	2.02601400	-1.57998200	-2.24507000
H	3.30726900	-2.69149700	-1.72253000
H	2.84848300	-2.61632400	-3.42809300
C	2.03438100	-5.57613800	-2.06430700
H	1.31320500	-6.39069700	-1.95046000
H	2.60617400	-5.75467900	-2.98065300
H	2.73181000	-5.62089200	-1.22198000
C	5.44185400	3.84227100	0.28527700
C	4.29306300	3.91747600	1.28637600
C	3.21272100	1.53940000	0.22639400
C	5.87325800	2.41358600	-0.03258500
H	4.54613500	3.40719900	2.21860000
H	4.04083400	4.95373500	1.51763800
H	5.17228400	4.36629600	-0.63573700
H	6.30196100	4.36615200	0.71941200
H	6.14913300	1.87168000	0.87499700
H	6.72647600	2.40377800	-0.71293400
S	4.58816700	1.41613200	-0.91902300

S	2.70089700	3.20030500	0.66662300
C	2.79776600	0.39664400	1.02737500
C	1.85654900	0.52226600	2.09886300
C	3.24069600	-0.92547500	0.72589600
C	1.36283900	-0.57809400	2.75290200
H	1.51559400	1.50719400	2.38083800
C	2.73773200	-2.03222600	1.38011900
H	3.97203000	-1.06097800	-0.05751300
C	1.76769300	-1.87635600	2.38437800
H	0.62141100	-0.47363700	3.53351700
H	3.07543500	-3.01487100	1.08540900
O	1.16332000	-2.88909800	3.03186200
C	1.42708600	-4.23825000	2.60705300
H	2.46758700	-4.50999700	2.80724000
H	0.76827500	-4.86273200	3.20630000
H	1.19774000	-4.35587900	1.54501900
Cu	1.53997500	0.78877400	-0.85547300
O	-2.51587800	0.67461900	-2.10565700
Si	-3.12138200	1.48377300	-3.43454700
C	-3.65533700	3.22182000	-2.95189000
C	-1.82800900	1.59379000	-4.79824200
C	-4.59313700	0.46539500	-3.99228300
H	-4.41909100	3.19212200	-2.16989100
H	-2.81284100	3.80888900	-2.57607200
H	-4.07154000	3.75042600	-3.81556600
H	-0.95263700	2.16271300	-4.47017200
H	-1.48925600	0.59851000	-5.09954300
H	-2.23968000	2.09515200	-5.68027400
H	-5.07322200	0.91863600	-4.86517600
H	-4.28401900	-0.54809600	-4.26341300
H	-5.33907800	0.39123400	-3.19588600
H	-1.11971200	2.09842100	-1.47060500

Zero-point correction=	0.801182 (Hartree/Particle)
Thermal correction to Energy=	0.859643
Thermal correction to Enthalpy=	0.860587
Thermal correction to Gibbs Free Energy=	0.705049
Sum of electronic and zero-point Energies=	-5185.279165
Sum of electronic and thermal Energies=	-5185.220703
Sum of electronic and thermal Enthalpies=	-5185.219759
Sum of electronic and thermal Free Energies=	-5185.375297

CuI

Cu—I

0 1

Cu	0.00000000	0.00000000	-1.56934500
I	0.00000000	0.00000000	0.85869800

Zero-point correction=	0.000519 (Hartree/Particle)
Thermal correction to Energy=	0.003398
Thermal correction to Enthalpy=	0.004342
Thermal correction to Gibbs Free Energy=	-0.024856
Sum of electronic and zero-point Energies=	-1938.436139
Sum of electronic and thermal Energies=	-1938.433260
Sum of electronic and thermal Enthalpies=	-1938.432316

Sum of electronic and thermal Free Energies= -1938.461514

I_radical

0 2

I	0.00000000	0.00000000	0.00000000

Zero-point correction=	0.000000 (Hartree/Particle)
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.017503
Sum of electronic and zero-point Energies=	-297.779521
Sum of electronic and thermal Energies=	-297.778105
Sum of electronic and thermal Enthalpies=	-297.777161
Sum of electronic and thermal Free Energies=	-297.797024

Li_ion

1 1

Li	0.00000000	0.00000000	0.00000000

Zero-point correction=	0.000000 (Hartree/Particle)
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.012748
Sum of electronic and zero-point Energies=	-7.453963
Sum of electronic and thermal Energies=	-7.452547
Sum of electronic and thermal Enthalpies=	-7.451603
Sum of electronic and thermal Free Energies=	-7.466711

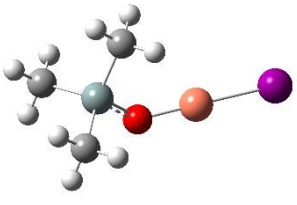
LiI

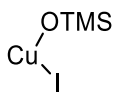
0 1

Li	0.00000000	0.00000000	-2.59651100
I	0.00000000	0.00000000	0.14697200

Zero-point correction=	0.000677 (Hartree/Particle)
Thermal correction to Energy=	0.003461
Thermal correction to Enthalpy=	0.004405
Thermal correction to Gibbs Free Energy=	-0.022568
Sum of electronic and zero-point Energies=	-305.461676
Sum of electronic and thermal Energies=	-305.458892
Sum of electronic and thermal Enthalpies=	-305.457948
Sum of electronic and thermal Free Energies=	-305.484921

CuOTMSI





0 2

Si	-2.93246100	0.08917300	-0.00045800
C	-3.86859200	-0.42183100	1.54967400
H	-3.31730200	-0.13626300	2.44960700
H	-4.84499400	0.07235300	1.57637500
H	-4.02915100	-1.50273800	1.57125200
C	-2.62934300	1.94230400	-0.01523600
H	-2.05741300	2.23589300	-0.90069600
H	-3.57221300	2.49811800	-0.02417300
H	-2.06485800	2.25176900	0.86957300
C	-3.85620900	-0.44799100	-1.54946900
H	-4.01588800	-1.52922500	-1.55434600
H	-4.83263300	0.04505600	-1.59182000
H	-3.29785500	-0.17687100	-2.44949500
Cu	0.26798400	-0.37056200	0.00355600
O	-1.47645700	-0.74207400	0.01076000
I	2.62739200	0.09889600	-0.00073300

Zero-point correction=	0.114490 (Hartree/Particle)
Thermal correction to Energy=	0.127040
Thermal correction to Enthalpy=	0.127984
Thermal correction to Gibbs Free Energy=	0.069631
Sum of electronic and zero-point Energies=	-2422.948785
Sum of electronic and thermal Energies=	-2422.936235
Sum of electronic and thermal Enthalpies=	-2422.935291
Sum of electronic and thermal Free Energies=	-2422.993644

Cu_ion

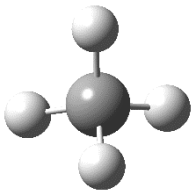
$Cu^{\oplus}$

1 1

Cu	0.00000000	0.00000000	0.00000000

Zero-point correction=	0.000000 (Hartree/Particle)
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.015855
Sum of electronic and zero-point Energies=	-1640.366141
Sum of electronic and thermal Energies=	-1640.364725
Sum of electronic and thermal Enthalpies=	-1640.363781
Sum of electronic and thermal Free Energies=	-1640.381996

CH_4



CH_4

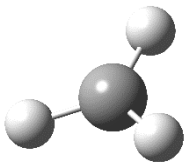
0 1

C	0.00000000	0.00000000	0.00000000
H	0.62969200	0.62969200	0.62969200
H	-0.62969200	-0.62969200	0.62969200
H	-0.62969200	0.62969200	-0.62969200
H	0.62969200	-0.62969200	-0.62969200

Zero-point correction=	0.044417 (Hartree/Particle)
Thermal correction to Energy=	0.047287
Thermal correction to Enthalpy=	0.048232

Thermal correction to Gibbs Free Energy=	0.027100
Sum of electronic and zero-point Energies=	-40.489634
Sum of electronic and thermal Energies=	-40.486764
Sum of electronic and thermal Enthalpies=	-40.485820
Sum of electronic and thermal Free Energies=	-40.506952

CH_3_radical



$^{\bullet}CH_3$

0 2

C	0.00000000	0.00000000	0.00005900
H	0.00000000	1.08069000	-0.00011800
H	0.93590500	-0.54034500	-0.00011800
H	-0.93590500	-0.54034500	-0.00011800

Zero-point correction=	0.029482 (Hartree/Particle)
Thermal correction to Energy=	0.032554
Thermal correction to Enthalpy=	0.033498
Thermal correction to Gibbs Free Energy=	0.010722
Sum of electronic and zero-point Energies=	-39.824896
Sum of electronic and thermal Energies=	-39.821825
Sum of electronic and thermal Enthalpies=	-39.820880
Sum of electronic and thermal Free Energies=	-39.843657

3. Chapter D

3.1. General Information

Commercially available chemicals were used without further purifications. All photochemical reactions were carried out in oven-dried glassware and were run under anhydrous conditions under nitrogen atmosphere using standard Schlenk technique. Reaction mixtures were degassed using three freeze-pump-thaw cycles. Petroleum ether (hexanes) and ethyl acetate (EtOAc) were distilled prior to use.

3.2. Standard experiment

An oven dried Schlenk tube (10 mL size) equipped with a stirring bar was charged with $[Cu(dap)_2]Cl$ (4.4 mg, 1 mol%, 0.01 equiv), $[Cu(dmp)_2]Cl$ (2.6 mg, 1 mol%, 0.01 equiv) or $Ir(ppy)_3$ (3.3 mg, 1 mol%, 0.01 equiv) and then degassed by three freeze-pump-thaw cycles. Then dry MeCN (2 mL, 0.25 M) was added under positive nitrogen atmosphere and bromonitroalkane **22** (0.5 mmol, 1.0 equiv) and styrene **23** (57 µL, 0.5 mmol, 1.0 equiv) was added under nitrogen atmosphere. A Teflon sealed inlet for a glass rod was placed on the reaction tube, through which irradiation with LED_{455nm} took place from above. The mixture was stirred at room temperature (25 °C).

3.3. EPR Spectroscopy

Continuous-wave (CW) electron paramagnetic resonance (EPR) experiments were carried out on two different spectrometers. A Magnettech Miniscope MS 400 spectrometer (X-Band, 9-10 GHz) and a Bruker EMX Spectrometer (X-Band, 9-10 GHz) equipped with an ER 083 (200/60) power source electromagnet (0-6000 G) and an ER 4104 OR/9009 resonant cavity with a resonance frequency of 9.63 GHz. Samples were measured in glass pipettes, which were evacuated and flushed with dry nitrogen several times before being filled with 0.3 mL of the specified solutions. Solvents were degassed by three freeze-pump-thaw cycles.

EPR spectra were obtained as a first order derivative plot. Raw data were exported in the ASCII file format and processed with Origin 2019b (Version 9.6.5.169). All spectra are baseline corrected and referenced against TEMPO as an external standard (g-value exp.: g_{iso}=2.006, lit.: g_{iso}=2.006).[[22]] To decrease noise, all spectra were subtracted by the corresponding spectra before irradiation.

Sample preparation was done according to the standard experiment (chapter 3.2). Between sample preparation and the first obtained spectrum 5 min went by unless stated otherwise.

3.3.1. EPR Spectra (Magnettech Miniscope)

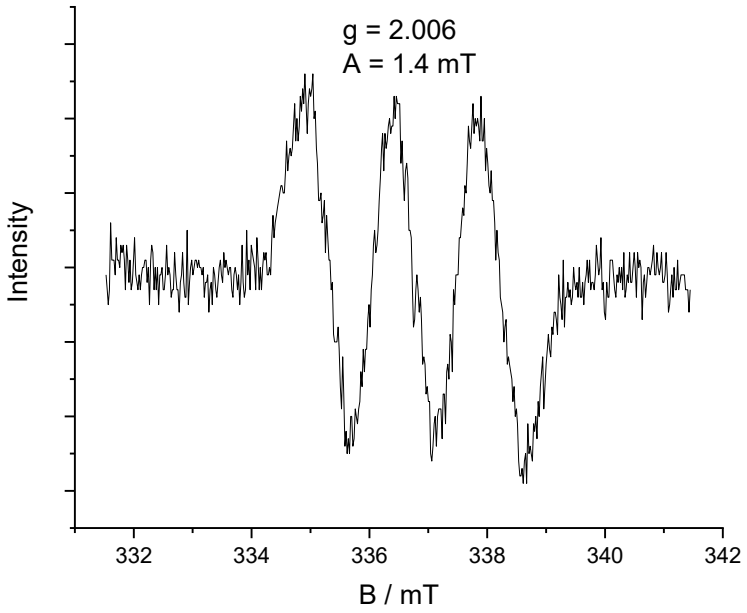


*Figure 51: EPR Spectra of Ir(ppy)$_3$ (5 µmol, 1 mol%), bromonitromethane **22a** (0.5 mmol, 1 equiv) and styrene **23** (0.5 mmol, 1 equiv) in acetonitrile (2 mL); Frequency: 0.4570 GHz; Modulation amplitude: 0.7 mT; MW attenuation: 10 dB; Gain: 10; Time constant: 0 s; B_0-field: 337 mT; B_0-sweep: 10 mT; Average of 5 runs.*

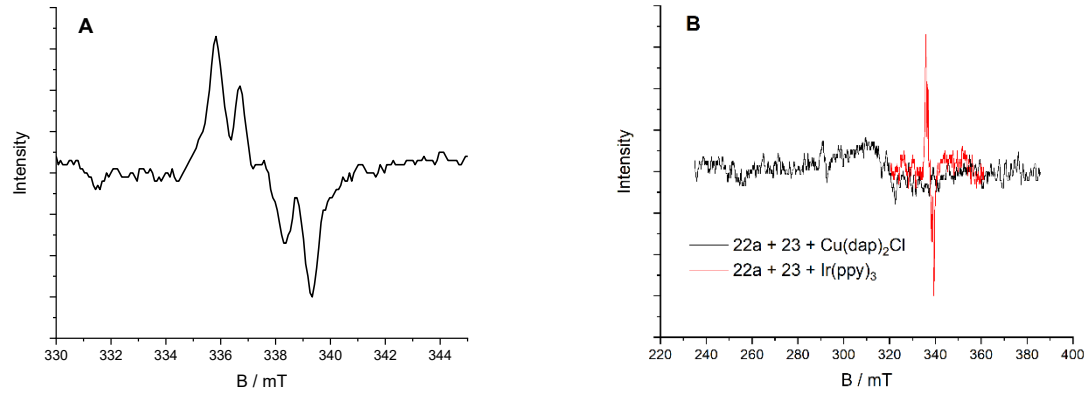


*Figure 52: EPR spectra of photocatalyst (5 µmol, 1 mol%), bromonitromethane **22a** (0.5 mmol, 1 equiv) and styrene **23** (0.5 mmol, 1 equiv) in acetonitrile (2 mL); Frequency: 0.4577 GHz; Modulation amplitude: 0.7 mT; MW attenuation: 10 dB; Gain: 10; Time constant: 1 s; Average of 3 runs; A) Photocatalyst: $Ir(ppy)_3$; 60 min irradiation at 455 nm; B_0-field: 340 mT; B_0-sweep: 40 mT; B) Comparison between photocatalyst $[Cu^I(dap)_2]Cl$ (B_0-field: 310 mT; B_0-sweep: 150 mT) and $Ir(ppy)_3$ after irradiation at 455 nm.*

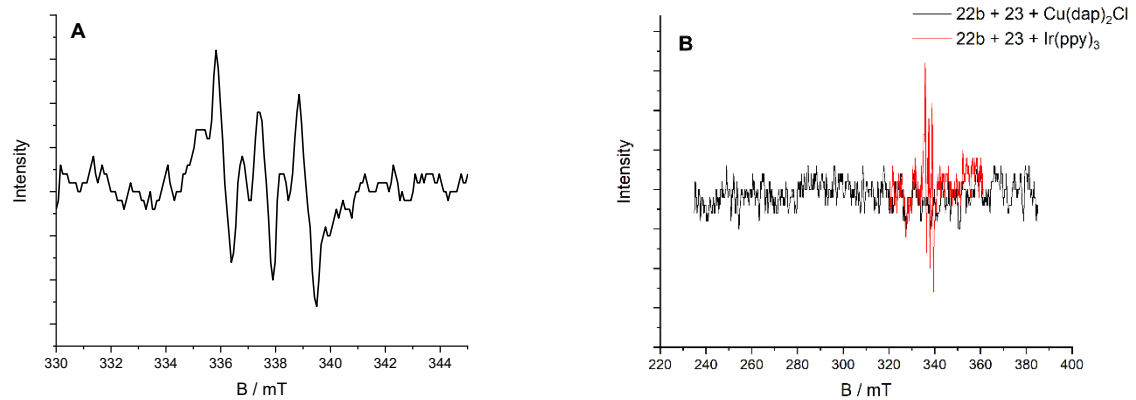


*Figure 53: EPR spectra of photocatalyst (5 µmol, 1 mol%), bromonitroethane **22b** (0.5 mmol, 1 equiv) and styrene **23** (0.5 mmol, 1 equiv) in acetonitrile (2 mL); Frequency: 0.4568 GHz; Modulation amplitude: 0.7 mT; MW attenuation: 10 dB; Gain: 10; Time constant: 1 s; Average of 3 runs; A) Photocatalyst: $Ir(ppy)_3$: 30 min irradiation at 455 nm; B_0-field: 340 mT; B_0-sweep: 40 mT; B) Comparison between Photocatalyst $[Cu^I(dap)_2]Cl$ (B_0-field: 310 mT; B_0-sweep: 150 mT) and $Ir(ppy)_3$ after irradiation at 455 nm.*

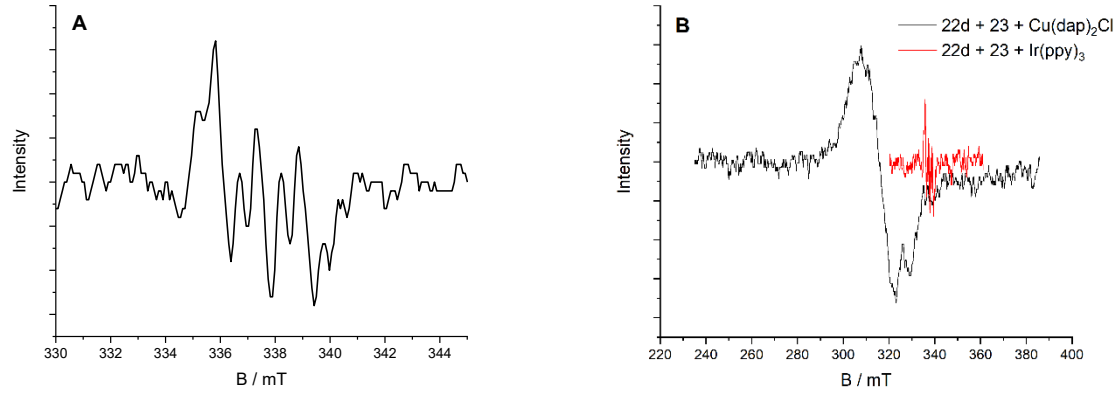


*Figure 54: EPR spectra of photocatalyst (5 µmol, 1 mol%), bromonitrobenzylmethane **22d** (0.5 mmol, 1 equiv) and styrene **23** (0.5 mmol, 1 equiv) in acetonitrile (2 mL); Frequency: 0.4569 GHz; Modulation amplitude: 0.7 mT; MW attenuation: 10 dB; Gain: 10; Time constant: 1 s, average of 3 runs; A) Photocatalyst: $Ir(ppy)_3$: 60 min irradiation at 455 nm; B_0-field: 340 mT; B_0-sweep: 40 mT; B) Comparison between photocatalyst $[Cu^I(dap)_2]Cl$ (B_0-field: 310 mT; B_0-sweep: 150 mT) and $Ir(ppy)_3$ after irradiation at 455 nm.*

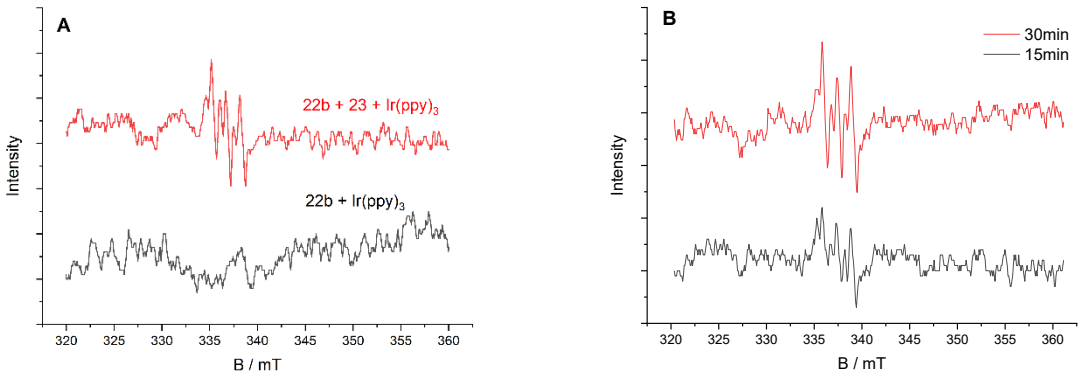


*Figure 55: EPR spectra of $Ir(ppy)_3$ (5 µmol, 1 mol%), bromonitroethane **22b** (0.5 mmol, 1 equiv) and styrene **23** (0.5 mmol, 1 equiv) in acetonitrile (2 mL); Frequency: 0.4568 GHz; Modulation amplitude: 0.7 mT; MW attenuation: 10 dB; Gain: 10; Time constant: 1 s; B0-field: 340 mT; B0-sweep; Average of 3 runs; A) Comparison of the spectra with (red line) and without styrene **23** (black line) after 45 min irradiation at 455 nm. B) Signal growth from 15 min to 30 min irradiation at 455 nm.*

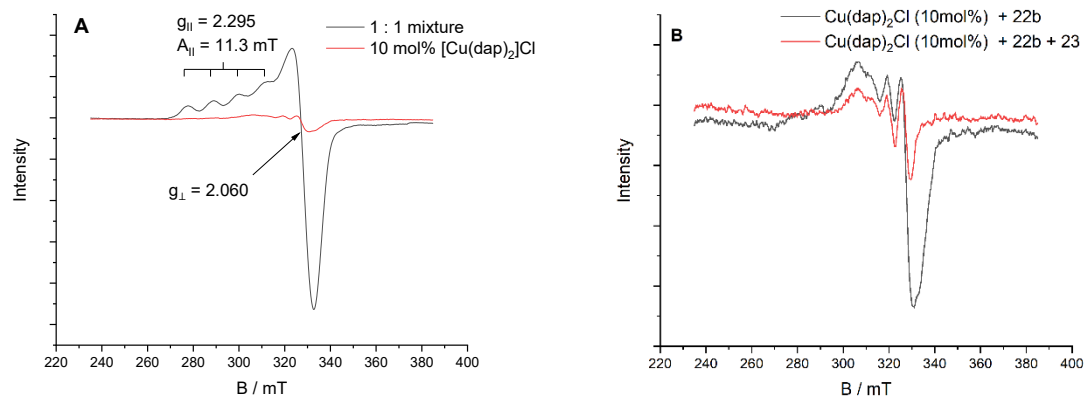


*Figure 56: EPR spectra of A) [Cu(dap)$_2$]Cl (50 µmol, 1 equiv), bromonitroethane **22b** (50 µmol, 1 equiv) (black line) and [Cu(dap)$_2$]Cl (50 µmol, 10 mol%), bromonitroethane **22b** (0.5 mmol, 1 equiv) (red line) in acetonitrile (2 mL); B) Addition of styrene **23** (0.5 mmol, 1 equiv) to a mixture of [Cu(dap)$_2$]Cl (50 µmol, 10 mol%), bromonitroethane **22b** (0.5 mmol, 1 equiv) in acetonitrile (2 mL); Frequency: 0.4575 GHz; Modulation amplitude: 0.7 mT; MW attenuation: 10 dB; Gain: 10; Time constant: 1 s; B0-field: 340 mT; B0-sweep; Average of 3 runs.*

3.3.2. EPR Spectra (Bruker EMX)

Spectrum	Resonance Frequency	Microwave Power	Modulation Amplitude	Conversion Time	Time Constant	Receiver gain	Resolution
Figure 57A	9.607 GHz	6.63 mW	10 G	40.0 ms	40.96 ms	5.0 x 10^3	1024
Figure 57B **Cu(dmp)$_2$Cl +22a + 23** + PBN	9.605 GHz	6.59 mW	10 G	40.0 ms	40.96 ms	5.0 x 10^3	1024
Figure 57B **22a + 23** + PBN	9.605 GHz	6.78 mW	10 G	40.0 ms	40.96 ms	5.0 x 10^3	1024
Figure 57B **Cu(dmp)$_2$Cl +22a** + PBN	9.607 GHz	6.80 mW	10 G	40.0 ms	40.96 ms	5.0 x 10^3	1024
Figure 57B **Cu(dmp)$_2$Cl + 23** + PBN	9.626 GHz	6.73 mW	10 G	40.0 ms	40.96 ms	5.0 x 10^3	1024
Figure 58 **Cu(dmp)$_2$Cl +22a + 23** + PBN	9.605 GHz	6.60 mW	10 G	40.0 ms	40.96 ms	5.0 x 10^3	1024
Figure 58 **Cu(dmp)$_2$Cl +22a** + PBN	9.605 GHz	6.82 mW	10 G	40.0 ms	40.96 ms	5.0 x 10^3	1024

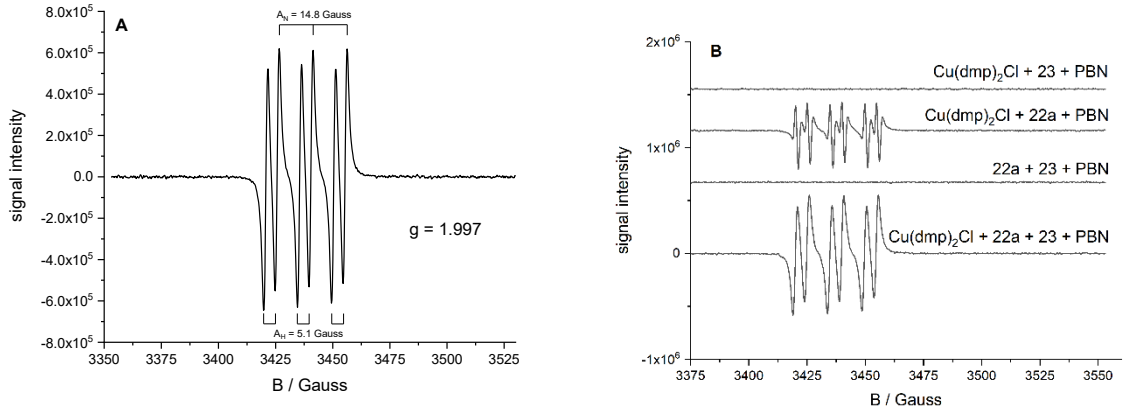


*Figure 57: EPR spectra of A) [Cu(dmp)$_2$]Cl (50 µmol, 1 equiv), bromonitromethane **22a** (50 µmol, 1 equiv), styrene **23** (0.5 mmol, 1 equiv) and PBN (50 µmol, 1 equiv) in acetonitrile (2 mL); B) Multicomponent mixtures as labeled in the spectrum. [Cu(dmp)$_2$]Cl (50 µmol, 1 equiv), bromonitromethane **22a** (50 µmol, 1 equiv), styrene **23** (0.5 mmol, 1 equiv) and PBN (50 µmol, 1 equiv) in acetonitrile (2 mL).*

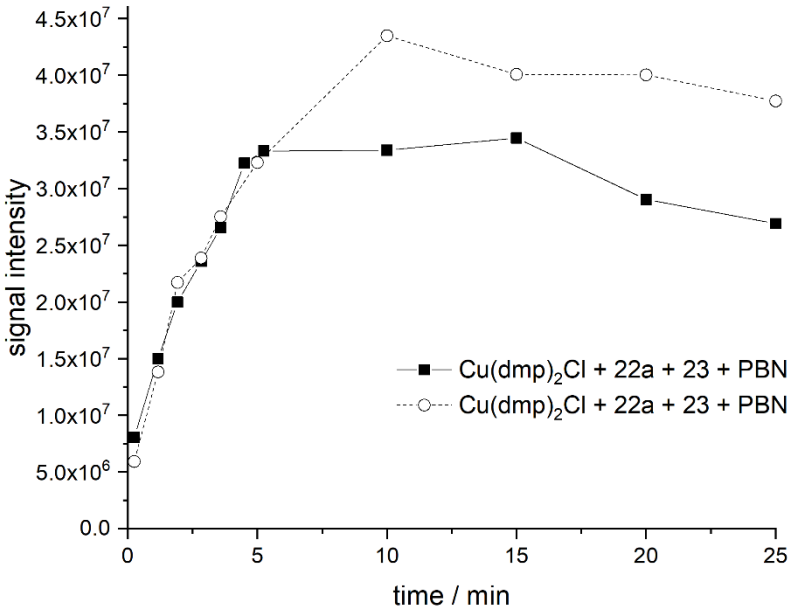
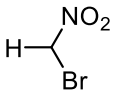


*Figure 58: Kinetik EPR spectra of [Cu(dmp)$_2$]Cl (50 µmol, 1 equiv), bromonitromethane **22a** (50 µmol, 1 equiv), styrene **23** (0.5 mmol, 1 equiv) and PBN (50 µmol, 1 equiv) in acetonitrile (2 mL) (black line) and [Cu(dmp)$_2$]Cl (50 µmol, 1 equiv), bromonitromethane **22a** (50 µmol, 1 equiv) and PBN (50 µmol, 1 equiv) in acetonitrile (2 mL) (red line).*

3.4. Synthesis

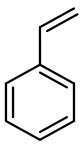
3.4.1. Bromonitromethane 22a



Commercially available, technical grade bromonitromethane was further purified by vacuum distillation at 45 °C and a pressure of 9.6 mbar.

^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 5.71 (s, 2H).

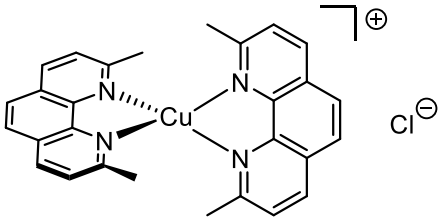
3.4.2. Styrene 23



Commercially available styrene was further purified by vacuum distillation at 32 °C and a pressure of 7 mbar.

^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 7.45 – 7.22 (m, 5H), 6.73 (dd, *J* = 17.6, 10.9 Hz 1H), 5.76 (dd, *J* = 17.6, 0.9 Hz 1H), 5.25 (dd, *J* = 10.9, 0.9 Hz 1H).

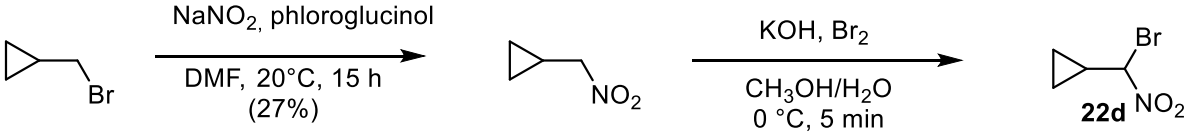
3.4.3. Cu(dmp)$_2$Cl



According to the literature procedure,[23] a round-bottom flask equipped with a magnetic stirring bar was charged with 2,9-dimethyl-1,10-phenanthroline (624.8 mg, 3.0 mmol, 2.0 equiv.), dissolved in chloroform (40 mL) and stirred at room temperature (25 °C) for 30 min. CuCl (148.5 mg, 1.5 mmol, 1.0 equiv.) was added and the resulting mixture was stirred for 18 h at room temperature (25 °C). Afterwards it was concentrated *in vacuo* to a volume of 10 mL and the complex was precipitated using diethylether (10 mL). The red precipitate was collected by vacuum filtration using a fritted funnel. The solid was washed with cold diethyl ether and dried *in vacuo* to yield 744.2 mg (1.46 mmol, 97%) of [Cu(dmp)$_2$]Cl as a bright red solid. Spectral data are in accordance with literature.[23]

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 8.54 (d, *J* = 8.3 Hz, 2H), 8.05 (s, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 2.41 (s, 6H).

3.4.4. Cyclopropyl-bromonitromethane 22d



According to slightly modified literature procedure,[24] a round bottom flask equipped with a magnetic stirring bar was charged with sodium nitrite (4.35 g, 63 mmol, 2.1 equiv.) and phloroglucinol dihydrate (6.32 g, 39 mmol, 1.3 equiv.) dissolved in DMF (180 mL). Bromomethyl-cyclopropane (6.05 g, 30 mmol, 1.0 equiv.) was added and the resulting mixture was stirred for 16 h at room temperature (25 °C) before diluting with ice water (60 mL). The mixture was extracted with diethyl ether and the combined organic phase were washed with water, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by

flash column chromatography (hexanes / EtOAc 1:1) to yield 194.0 mg (1.92 mmol, 6.4%) of cis-2-(Nitromethyl)cyclopropane as a light-yellow liquid.

According to slightly modified literature procedure,[23] cis-2-(Nitromethyl)cyclopropane (189 mg, 1.9 mmol, 1.0 equiv.) was added to a mixture of solid KOH (104.9 mg, 1.9 mmol, 1.0 equiv.), MeOH (1.6 mL) and H_2O (3.2 mL) at room temperature (25°C). The mixture was vigorously stirred until complete dissolution of the starting nitro compound (30 min), and then cooled to 0 °C. Bromine (96 µL, 1.9 mmol, 1.0 equiv.) in CH_2Cl_2 (3.2 mL, precooled to − 78 °C) was slowly added to the mixture. The cooling bath was removed, and the mixture was vigorously stirred for 5 min. The mixture was poured in a separation funnel and shaken, subsequently adding small portions of $Na_2S_2O_3$ until all remaining bromine was quenched. The phases were separated, and the organic phase was washed with water (4 mL) and brine (4 mL), dried over $MgSO_4$ and concentrated via rotary evaporation. After filtration with silica and washing with hexanes, the solvent was removed, and the remaining liquid was further purified by vacuum distillation at 40 °C and a pressure of 1.2 mbar to yield 57.3 mg (0.32 mmol, 6%) Cyclopropyl-bromonitromethane as colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 5.26 (d, *J* = 9.7 Hz, 1H), 1.88 (m, 1H), 0.99 (m, 2H), 0.79 (m, 1H), 0.62 (m, 1H).

3.4.5. NMR Spectra

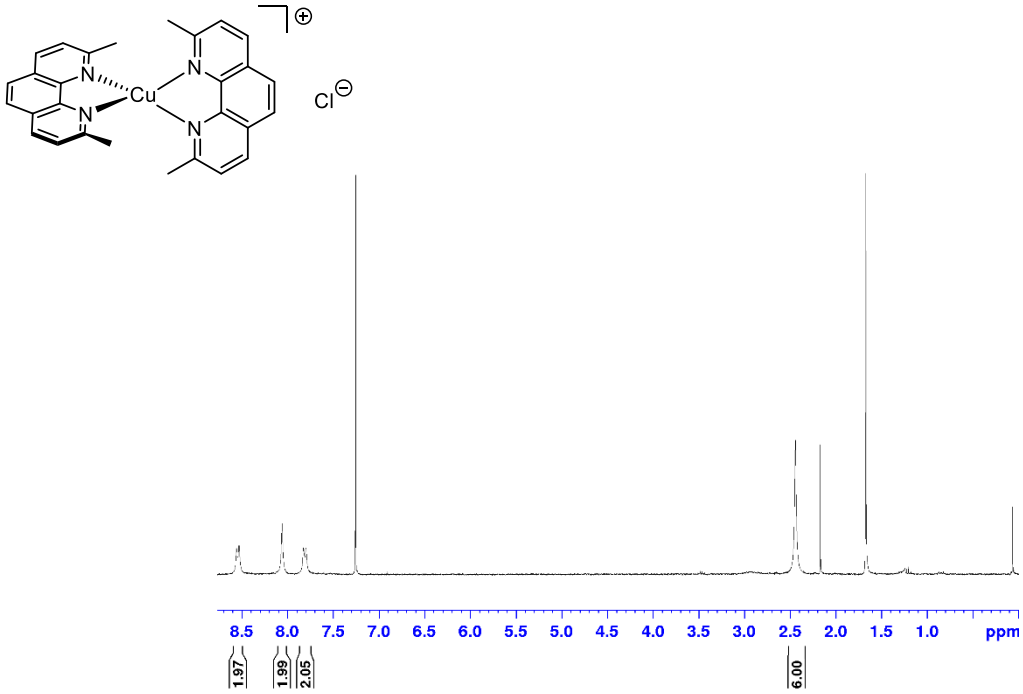


Figure 59: ^{1}H-NMR of Cu(dmp)$_2$Cl; Solvent: $CDCl_3$.

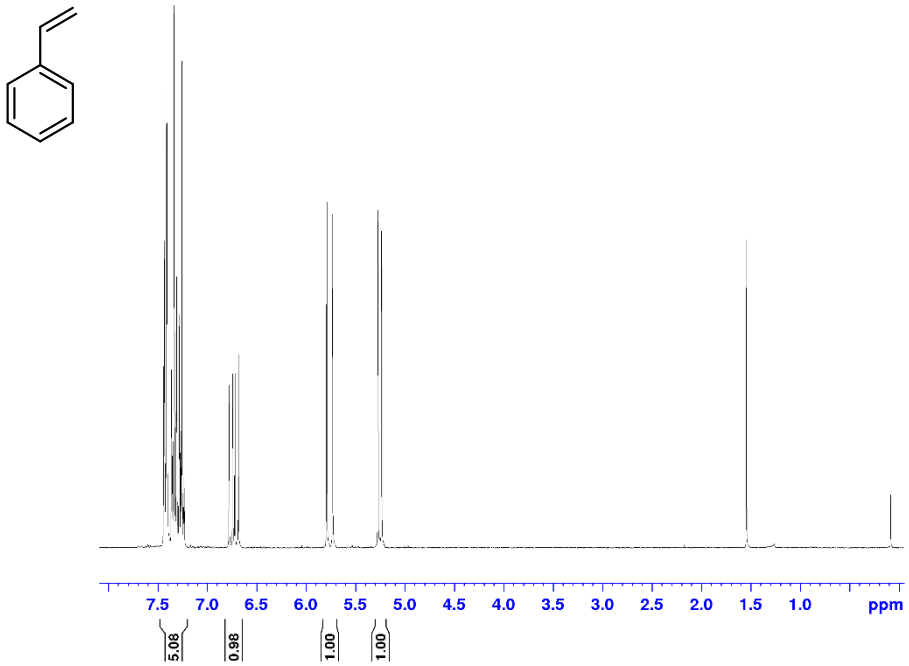


*Figure 60: ^{1}H-NMR of Styrene **23**; Solvent: $CDCl_3$.*

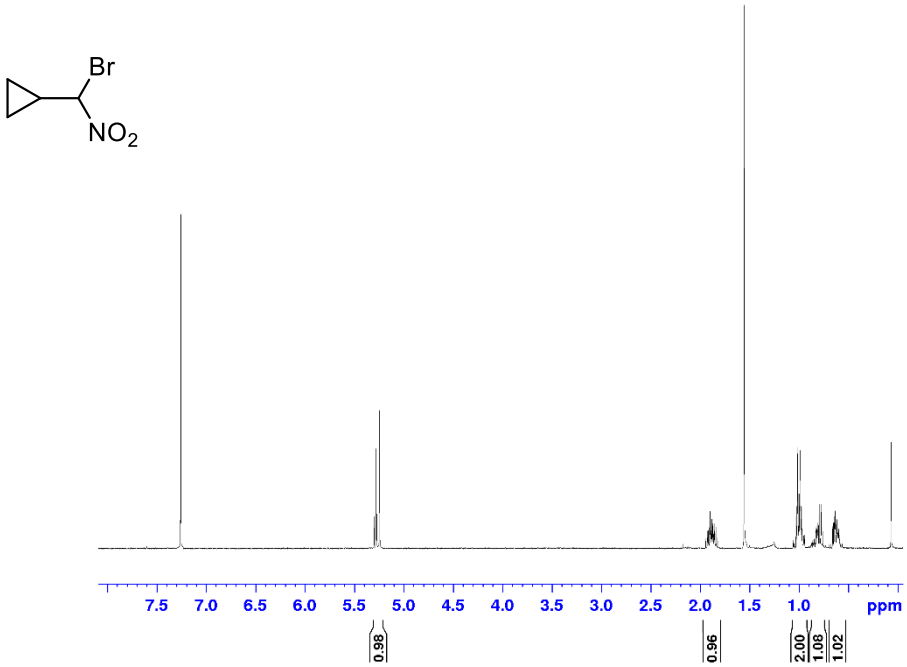


*Figure 61: ^{1}H-NMR of Cyclopropyl-bromonitromethane **22d**; Solvent: $CDCl_3$.*

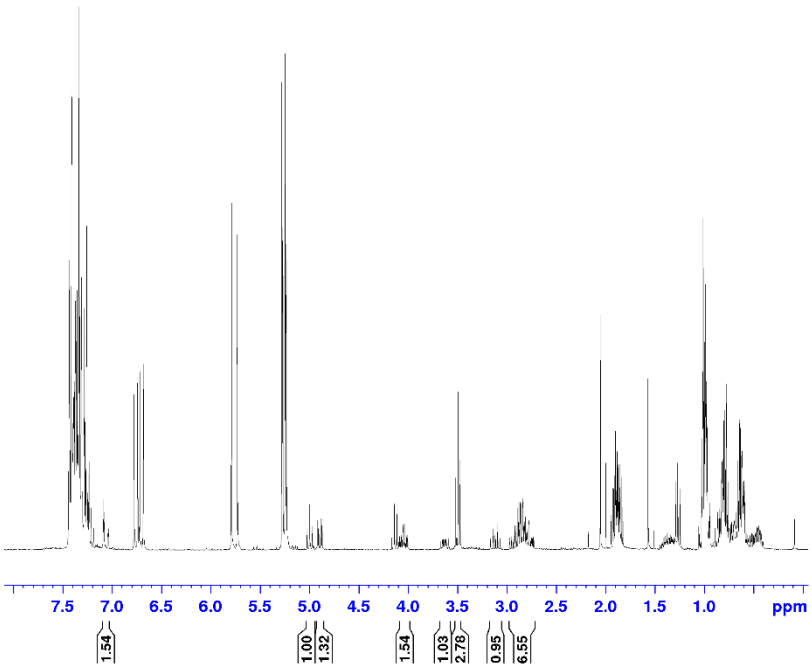


*Figure 62: ^{1}H-NMR of the reaction mixture **22d**, **23**, Cu(dmp)$_2$Cl after 1h irradiation at 451 nm. The solvent was removed and the liquid mixture purified by flash-chromatography (ethylacetate/hexanes 1:1); Solvent: $CDCl_3$.*

3.5. Computational Chemistry

All calculations were conducted using the Orca 5 software package (version 5.0.4)[25]. Density functional theory calculations were carried out with the Becke-style 3-parameter exchange functional with the Lee-Yang-Parr correlation functional (B3LYP).[2–5] The structures were calculated with the addition of Grimme's empirical dispersion correction D4[26]. Ahlrichs-Weigend split valence polarisation basis set def2-SVP[10,11] and triple zeta valence polarisation basis set def2-TZVP[10,11] were used with the auxiliary basis def2/J[10]. Stationary points were confirmed as local minima by frequency calculations (no imaginary frequencies). Wavefunctions of open-shell molecules were checked for stability by using the keyword *stable*. TD-DFT calculations were conducted using the same level of theory as stated above. Population analysis was carried out with NBO 7.0.[27] Simulations of NMR spectra were carried out using the segmented contracted basis set pcSseg-2[28] with the automatically generated auxiliary basis Aux/J, Aux/C, Aux/JK[29] and the chemical shifts are the Boltzmann weighed shifts of the calculated stereoisomers. Nudged-Elastic-Band calculations (NEB)[30] were carried out on the B3LYP-D4/def2-SVP level of theory, accompanied by TD-DFT calculations on the B3LYP-D4/def2-TZVP level of theory on the respective geometries. All NEB calculations were carried out in the broken symmetry singlet state (scf BrokenSym 1,1) and including optimization of the

first and last geometry (Free_End true). Visualization of geometries was achieved with the Orca enhanced version of Avogadro.[31] Visualization for the titlepage was done with VMD.[13–20]

3.5.1. Calculation Examples

Geometry optimization and frequency calculation:

```
! UKS B3LYP D4 def2-TZVP opt freq TightSCF
! CPCM(Acetonitrile) DEFGRID3

%maxcore 180
%pal
  nprocs 4
end

* xyzfile 0 1 opt_freq.xyz
```

TD-DFT and NBO calculation:

```
! B3LYP D4 def2-TZVP NBO TightSCF KEEPDENS
! CPCM(Acetonitrile) DEFGRID3

%maxcore 500
%pal
  nprocs 8
end

%tddft NROOTS 20
      DOSOC TRUE
      TRIPLETS TRUE
end

* xyzfile 0 1 tddft.xyz
```

NMR calculation:

```
! B3LYP pcSseg-2 AUTOAUX NMR
! CPCM(Chloroform)
```

```
%maxcore 300
%pal
  nprocs 4
end

* xyzfile 0 1 nmr.xyz

%EPRNMR
  NUCLEI = ALL H {SHIFT, SSALL}
END
```

NEB calculation and broken symmetry:

```
! UKS B3LYP D4 def2-SVP NEB TightSCF
! CPCM(Acetonitrile) DEFGRID3

%maxcore 500
%pal
  nprocs 8
end

%neb NEB_END_XYZFILE "neb_end.xyz"
Free_End true
Free_End_Type Perp
Nimages 8
end

%scf BrokenSym 1,1
end

* xyzfile 0 1 neb_start.xyz

%geom
 Fragments
```

2 {46:51} end # atoms x to y belong to Fragment 2, the rest belongs to Fragment 1 by #default

end

end

3.5.2. NMR xyz-Matrices

22d-r-1

```
0 1
H       -9.57814        0.63110        0.23830
C      -10.02785        1.55926       -0.09098
C      -11.29633        1.38711       -0.83677
C      -11.45397        0.16055       -1.69164
C      -12.21944        0.26897       -0.40630
H      -11.74993        2.30482       -1.18178
H      -11.98557        0.28217       -2.62418
H      -10.62607       -0.53451       -1.72767
H      -11.90673       -0.35246        0.42157
H      -13.27938        0.47411       -0.44619
Br      -8.64881        2.49755       -1.13654
N      -10.24252        2.37933        1.17755
O      -10.83287        3.43685        1.08096
O       -9.82228        1.89535        2.21322
```

22d-r-2

```
0 1
H      -10.66439        1.70529        1.67553
C      -10.36295        1.24195        0.74525
C      -11.51834        0.65586       -0.00494
C      -12.25469        1.41226       -1.08419
C      -11.44299        0.19493       -1.43080
H      -12.13125        0.06292        0.66098
H      -13.33269        1.33885       -1.07577
H      -11.87577        2.37542       -1.39664
H      -10.51745        0.35110       -1.96512
H      -11.96119       -0.72219       -1.67181
Br      -9.02911       -0.11829        1.23200
N       -9.67424        2.35022       -0.03779
O       -8.95660        2.05828       -0.97244
O       -9.94824        3.48363        0.31529
```

22d-r-3

```
0 1
H      -10.10737        0.81522        1.46190
C      -10.17620        1.23212        0.46493
C      -11.51145        0.99001       -0.17508
C      -11.75228        1.10668       -1.65125
C      -11.81407       -0.23974       -0.98465
```

H	-12.30698	1.33517	0.47598
H	-12.67413	1.57629	-1.96236
H	-10.90068	1.30824	-2.28492
H	-11.00686	-0.93072	-1.17908
H	-12.77934	-0.69815	-0.82480
Br	-8.63013	0.56292	-0.51704
N	-10.01721	2.74483	0.66456
O	-9.71248	3.43788	-0.28252
O	-10.28072	3.14948	1.78389

22d-s-1

0 1

H	-9.36803	2.35721	-0.80515
C	-9.97495	1.70759	-0.18709
C	-11.29529	1.37655	-0.81710
C	-11.49091	0.19411	-1.72429
C	-12.15689	0.23022	-0.37684
H	-11.80841	2.28643	-1.10853
H	-12.09167	0.35617	-2.60757
H	-10.66339	-0.48797	-1.85401
H	-11.76813	-0.42645	0.38792
H	-13.22133	0.40831	-0.32741
Br	-8.84672	0.18616	0.27857
N	-10.24639	2.52291	1.08325
O	-10.10050	3.72780	0.96908
O	-10.63728	1.95118	2.07872

22d-s-2

0 1

H	-9.63528	0.51335	1.15672
C	-10.32765	1.22390	0.72475
C	-11.43287	0.56018	-0.03552
C	-12.38214	1.28982	-0.93982
C	-11.37309	0.34368	-1.52866
H	-11.84992	-0.25181	0.54540
H	-13.41799	0.98434	-0.90191
H	-12.22222	2.34656	-1.09515
H	-10.54801	0.76967	-2.08222
H	-11.70488	-0.61836	-1.89175
Br	-10.99969	2.29725	2.22983
N	-9.47077	2.11129	-0.16622
O	-8.39131	1.64353	-0.48288
O	-9.91409	3.17684	-0.54300

22d-s-3

0 1

H	-9.36841	1.02458	-0.37202
C	-10.16007	1.32056	0.30446
C	-11.52037	0.96013	-0.16039
C	-11.79949	1.03624	-1.64505
C	-11.68439	-0.29729	-0.96811

H	-12.31907	1.23541	0.51292
H	-12.77750	1.39120	-1.93600
H	-10.99138	1.34443	-2.29420
H	-10.79866	-0.88642	-1.16338
H	-12.58334	-0.87168	-0.79764
Br	-9.71396	0.53107	2.05147
N	-10.01857	2.83203	0.45954
O	-9.07707	3.34958	-0.11418
O	-10.85760	3.42041	1.11214

22e-cis-1

0 1

C	-10.69266	-0.57679	-0.01670
C	-12.20699	-0.47242	0.01349
C	-10.06936	0.78389	-0.02098
C	-8.78426	1.13222	-0.00631
Br	-13.03068	-2.26433	0.01268
N	-7.68653	0.19282	0.01771
O	-6.55659	0.67345	0.05251
O	-7.91602	-1.01183	0.00216
H	-10.32953	-1.14785	0.83903
H	-10.36485	-1.13225	-0.89751
H	-12.60569	0.02889	-0.86295
H	-12.57132	0.01219	0.91392
H	-10.74936	1.63009	-0.03887
H	-8.43682	2.15191	-0.00818

22e-cis-2

0 1

C	-10.75758	-0.53633	0.72252
C	-11.77198	-0.54449	-0.41642
C	-10.02647	0.77138	0.72800
C	-8.90023	1.12122	0.11145
Br	-12.81902	-2.22139	-0.40599
N	-8.10854	0.23577	-0.72173
O	-6.95620	0.59170	-0.94631
O	-8.60436	-0.79464	-1.16229
H	-11.28037	-0.64346	1.67254
H	-10.07250	-1.37067	0.60196
H	-11.29071	-0.51091	-1.38673
H	-12.50481	0.25068	-0.32788
H	-10.47447	1.56405	1.31737
H	-8.43341	2.08709	0.21350

22e-cis-3

0 1

C	-11.06581	-0.08858	0.57914
C	-11.15278	-1.44017	-0.12223
C	-9.63716	0.20658	0.92120
C	-8.70054	0.82925	0.20976
Br	-13.03518	-1.90238	-0.51189

N	-8.90706	1.39150	-1.11132
O	-8.05992	2.19030	-1.49773
O	-9.88120	1.05409	-1.77393
H	-11.48261	0.67979	-0.06598
H	-11.64153	-0.12394	1.50348
H	-10.78033	-2.25386	0.49120
H	-10.65318	-1.42954	-1.08371
H	-9.30008	-0.13688	1.89322
H	-7.70326	1.02383	0.56879

22e-trans-1

0 1

C	-10.62532	-1.05488	0.34563
C	-12.02084	-0.98573	-0.26190
C	-10.02630	0.31222	0.40304
C	-8.89540	0.63724	-0.20877
Br	-12.87005	-2.76946	-0.27319
N	-8.35273	1.98186	-0.12047
O	-7.29972	2.17911	-0.71930
O	-8.94461	2.83826	0.52316
H	-10.69921	-1.44445	1.36453
H	-9.99409	-1.73179	-0.22862
H	-12.00255	-0.66938	-1.29958
H	-12.68993	-0.35124	0.31048
H	-10.54987	1.07311	0.97012
H	-8.27807	-0.01488	-0.80513

22e-trans-2

0 1

C	-10.83021	-0.93807	0.70665
C	-11.53192	-1.15041	-0.61845
C	-9.81665	0.15662	0.71134
C	-9.49546	0.92456	-0.32270
Br	-12.84608	-2.61764	-0.47840
N	-8.48868	1.96289	-0.18971
O	-8.25647	2.62081	-1.19974
O	-7.92814	2.13909	0.88400
H	-11.55975	-0.72076	1.49275
H	-10.32950	-1.85807	1.02350
H	-10.85240	-1.45200	-1.40900
H	-12.10555	-0.28418	-0.93202
H	-9.30485	0.32872	1.65067
H	-9.90306	0.88844	-1.31888

22e-trans-3

0 1

C	-11.07592	-0.63699	0.51772
C	-11.24447	-1.70574	-0.55500
C	-9.78967	0.09407	0.31241
C	-9.72165	1.40158	0.10116
Br	-12.89844	-2.74378	-0.25612

N	-8.44405	2.06702	-0.08788
O	-8.48952	3.27909	-0.27475
O	-7.40711	1.41776	-0.05569
H	-11.92035	0.05098	0.50426
H	-11.04814	-1.11865	1.49874
H	-10.43998	-2.43417	-0.54317
H	-11.34741	-1.27954	-1.54740
H	-8.86998	-0.47889	0.33404
H	-10.55199	2.08724	0.05167

25d-s,s-1

0 1

C	-6.83258	-1.99370	0.73088
C	-6.20968	-2.94746	1.52324
C	-5.54769	-2.56734	2.68826
C	-5.51150	-1.22707	3.05458
C	-6.13399	-0.27200	2.25878
C	-6.80198	-0.64521	1.09283
C	-7.47801	0.40666	0.27435
C	-8.89979	0.06996	-0.14346
C	-9.65217	1.16610	-0.88139
C	-11.03320	0.70976	-1.31883
C	-12.17548	0.49882	-0.36787
C	-12.23340	1.60690	-1.39058
H	-7.33248	-2.30060	-0.17802
H	-6.23882	-3.98918	1.23196
H	-5.06288	-3.31280	3.30467
H	-4.99955	-0.92329	3.95817
H	-6.10440	0.77205	2.54422
H	-8.90794	-0.80831	-0.78817
H	-9.45040	-0.19277	0.76125
H	-10.93994	-0.01608	-2.11715
H	-12.79363	-0.37544	-0.51576
H	-12.03862	0.78711	0.66467
H	-12.14449	2.62294	-1.03151
H	-12.88953	1.49340	-2.24178
H	-9.09674	1.51375	-1.74811
N	-9.76608	2.41022	-0.01543
O	-9.62650	3.48829	-0.56644
O	-10.01560	2.27121	1.17148
H	-7.43004	1.35950	0.79065
Br	-6.35574	0.77670	-1.37518

25d-s,s-2

0 1

C	-7.52783	-1.71197	2.54319
C	-6.70711	-2.79928	2.26506
C	-5.73494	-2.70208	1.27650
C	-5.58786	-1.51115	0.57207
C	-6.40977	-0.42630	0.84897
C	-7.39345	-0.51737	1.83433
C	-8.36723	0.58740	2.13673

C	-9.57304	0.66430	1.19944
C	-9.31717	0.78515	-0.29748
C	-10.51314	0.31567	-1.11059
C	-11.81946	1.05100	-1.18998
C	-10.94294	0.92559	-2.41213
H	-8.27937	-1.79055	3.31897
H	-6.82336	-3.71682	2.82674
H	-5.09024	-3.54408	1.06189
H	-4.82707	-1.42316	-0.19228
H	-6.26850	0.49975	0.30923
H	-10.10685	-0.27955	1.33976
H	-10.24846	1.45558	1.51942
H	-10.58396	-0.76363	-1.05290
H	-12.72404	0.46114	-1.14085
H	-11.88621	2.02606	-0.72999
H	-10.44186	1.81952	-2.75806
H	-11.24518	0.25325	-3.20244
H	-8.44526	0.21581	-0.60331
N	-8.96665	2.20993	-0.68979
O	-8.01338	2.36491	-1.43507
O	-9.67764	3.11328	-0.28424
H	-8.74834	0.46248	3.14488
Br	-7.43257	2.35723	2.27223

25d-s,s-3

0 1

C	-7.26810	-1.82281	1.97313
C	-6.07651	-2.39371	1.54059
C	-5.08742	-1.59406	0.98168
C	-5.29321	-0.22147	0.86048
C	-6.48266	0.34594	1.29028
C	-7.48529	-0.45158	1.84541
C	-8.79860	0.11978	2.27300
C	-9.56433	0.92465	1.23040
C	-10.01853	0.06960	0.04534
C	-11.19352	0.69284	-0.68940
C	-11.09781	1.93526	-1.52626
C	-11.40338	0.60647	-2.17290
H	-8.04000	-2.44646	2.40601
H	-5.92361	-3.46019	1.63955
H	-4.15917	-2.03484	0.64290
H	-4.52482	0.40549	0.42802
H	-6.63256	1.41292	1.19568
H	-10.46638	1.32541	1.69058
H	-8.98366	1.77126	0.86970
H	-12.08636	0.60194	-0.08310
H	-11.89536	2.65882	-1.43194
H	-10.11937	2.35626	-1.70511
H	-10.62910	0.16002	-2.78208
H	-12.40776	0.41733	-2.52425
H	-10.29289	-0.93283	0.36568
N	-8.87707	-0.17468	-0.92880
O	-8.70311	-1.31887	-1.31255
O	-8.22848	0.78508	-1.30945

H	-9.43277	-0.66481	2.67405
Br	-8.53106	1.30934	3.88367

25d-s,s-4

0 1

C	-6.00127	-0.72161	0.16472
C	-4.67184	-0.69801	0.57124
C	-4.35472	-0.40904	1.89327
C	-5.37312	-0.14412	2.80560
C	-6.69958	-0.16637	2.39839
C	-7.02642	-0.45374	1.07130
C	-8.44273	-0.46828	0.59200
C	-9.25807	0.73919	1.02213
C	-10.62649	0.93846	0.35425
C	-10.57927	0.82162	-1.15175
C	-10.76302	-0.41634	-1.98586
C	-11.75443	0.71740	-2.08074
H	-6.24759	-0.94950	-0.86478
H	-3.88685	-0.90592	-0.14380
H	-3.32133	-0.39179	2.21348
H	-5.13214	0.07789	3.83683
H	-7.48183	0.02721	3.11994
H	-9.37332	0.77613	2.10242
H	-8.66493	1.61411	0.74273
H	-9.79580	1.48150	-1.50851
H	-10.06939	-0.56099	-2.80277
H	-11.09113	-1.32125	-1.50068
H	-12.73265	0.55160	-1.65718
H	-11.73853	1.34190	-2.96325
H	-10.95204	1.94641	0.61666
N	-11.68934	0.10134	1.07099
O	-11.77542	0.27159	2.27587
O	-12.41105	-0.64207	0.43455
H	-8.47052	-0.59413	-0.48344
Br	-9.31803	-2.18109	1.22672

25d-s,s-5

0 1

C	-6.74269	-1.86908	0.45631
C	-5.97818	-2.90015	0.98309
C	-5.25863	-2.70883	2.16020
C	-5.30695	-1.47886	2.80532
C	-6.07107	-0.44525	2.27509
C	-6.79798	-0.63070	1.09976
C	-7.62897	0.49445	0.57341
C	-9.05829	0.11577	0.22234
C	-9.95593	1.25869	-0.22237
C	-11.35975	0.81085	-0.52796
C	-12.25641	1.68497	-1.36011
C	-11.68612	0.42327	-1.94524
H	-7.28587	-2.02655	-0.46588
H	-5.94117	-3.85455	0.47467

H	-4.66311	-3.51441	2.56891
H	-4.75051	-1.32156	3.71980
H	-6.10715	0.51300	2.77778
H	-9.07198	-0.62536	-0.57578
H	-9.49304	-0.35621	1.10600
H	-11.82465	0.23284	0.26035
H	-13.30645	1.70653	-1.10622
H	-11.85470	2.62727	-1.70706
H	-10.90148	0.52061	-2.68344
H	-12.34193	-0.42313	-2.09070
H	-9.53294	1.79366	-1.06791
N	-10.03892	2.31811	0.87457
O	-9.89982	3.48335	0.54487
O	-10.27364	1.94539	2.01303
H	-7.59884	1.32907	1.26626
Br	-6.71566	1.27893	-1.05877

25d-s,s-6

0 1

C	-6.58101	-1.39560	0.01916
C	-5.82679	-2.52770	0.29216
C	-5.35089	-2.75909	1.58054
C	-5.63243	-1.84972	2.59304
C	-6.38590	-0.71405	2.31770
C	-6.86922	-0.47770	1.03143
C	-7.69754	0.74046	0.77986
C	-8.99703	0.47130	0.03674
C	-9.90328	1.67313	-0.15729
C	-11.23000	1.41573	-0.84275
C	-11.42980	0.29014	-1.82233
C	-12.11243	0.25220	-0.48350
H	-6.93349	-1.22067	-0.98849
H	-5.60754	-3.23062	-0.50066
H	-4.76282	-3.64254	1.79111
H	-5.26632	-2.02174	3.59653
H	-6.60445	-0.00557	3.10667
H	-8.77557	0.07160	-0.95078
H	-9.51900	-0.30858	0.59295
H	-11.74380	2.33671	-1.08542
H	-12.02026	0.50941	-2.70051
H	-10.62035	-0.40451	-1.99147
H	-11.74661	-0.46020	0.24237
H	-13.17662	0.43388	-0.43650
H	-9.37799	2.47048	-0.67634
N	-10.25553	2.30290	1.19368
O	-10.39525	3.51357	1.22107
O	-10.42211	1.56651	2.15196
H	-7.87147	1.26465	1.71244
Br	-6.58733	2.08770	-0.25306

25d-r,r-1

0 1

C	-5.67232	-1.49250	0.52932
C	-4.98029	-2.42926	1.28890
C	-5.38127	-2.70001	2.59190
C	-6.47779	-2.03064	3.13091
C	-7.16955	-1.09818	2.37114
C	-6.77338	-0.82138	1.06072
C	-7.50827	0.15978	0.20607
C	-9.01704	-0.02242	0.18423
C	-9.77505	0.88139	-0.77439
C	-11.25894	0.63212	-0.76045
C	-12.10671	1.46120	0.16680
C	-12.19393	1.66856	-1.31937
H	-5.35852	-1.28127	-0.48533
H	-4.12963	-2.94477	0.86247
H	-4.84338	-3.42669	3.18633
H	-6.79240	-2.23544	4.14589
H	-8.01160	-0.57566	2.80556
H	-9.21279	-1.06431	-0.07818
H	-9.43726	0.14300	1.17568
H	-11.53786	-0.40605	-0.88732
H	-12.92454	0.96515	0.66966
H	-11.60871	2.22177	0.75305
H	-11.75637	2.56901	-1.72876
H	-13.07441	1.31693	-1.83773
H	-9.56109	1.93026	-0.58905
N	-9.28262	0.65658	-2.20297
O	-9.02142	1.64292	-2.87127
O	-9.20873	-0.49320	-2.60847
H	-7.09403	0.15463	-0.79688
Br	-7.06330	2.03847	0.82604

25d-r,r-2

0 1

C	-5.89392	-0.38201	0.35613
C	-5.17634	-1.56167	0.19712
C	-5.51714	-2.68598	0.93932
C	-6.57479	-2.62406	1.84363
C	-7.29030	-1.44687	2.00047
C	-6.96076	-0.31569	1.25141
C	-7.74093	0.95365	1.36050
C	-9.25278	0.84422	1.21433
C	-9.68707	0.41731	-0.18918
C	-11.13937	0.71252	-0.45511
C	-11.48908	2.01423	-1.12238
C	-11.64978	0.71791	-1.86884
H	-5.63180	0.49280	-0.22542
H	-4.35549	-1.60189	-0.50658
H	-4.96259	-3.60690	0.81633
H	-6.84237	-3.49639	2.42499
H	-8.10718	-1.40746	2.70817
H	-9.67775	0.16487	1.95157
H	-9.69362	1.82521	1.38543
H	-11.81283	0.35531	0.31296
H	-12.37623	2.52687	-0.77896

H	-10.67459	2.66426	-1.41281
H	-10.94276	0.50155	-2.65845
H	-12.64834	0.34229	-2.04023
H	-9.05962	0.86694	-0.95530
N	-9.48851	-1.08387	-0.39094
O	-8.82647	-1.44431	-1.34923
O	-10.04051	-1.83853	0.39108
H	-7.35243	1.69226	0.66618
Br	-7.36785	1.82343	3.14831

25d-r,r-3

0 1

C	-5.84785	0.26549	0.67874
C	-4.99758	-0.50766	-0.10395
C	-5.27878	-1.85201	-0.31716
C	-6.41194	-2.41721	0.25987
C	-7.26205	-1.64365	1.03958
C	-6.99170	-0.29130	1.25232
C	-7.90664	0.62327	2.01733
C	-9.09842	1.15935	1.22416
C	-10.01780	0.16239	0.53205
C	-10.86644	0.81548	-0.52788
C	-10.35203	0.81698	-1.94147
C	-11.53489	-0.03556	-1.57070
H	-5.62152	1.31110	0.84679
H	-4.11342	-0.06020	-0.53861
H	-4.61581	-2.45792	-0.92047
H	-6.63311	-3.46537	0.10751
H	-8.12706	-2.10135	1.49902
H	-9.68850	1.83295	1.84404
H	-8.66407	1.76506	0.42399
H	-11.39687	1.69790	-0.19413
H	-10.52050	1.70629	-2.53189
H	-9.41166	0.31757	-2.13308
H	-11.38601	-1.10557	-1.51531
H	-12.51500	0.26766	-1.90982
H	-9.46671	-0.67098	0.10787
N	-10.97340	-0.49450	1.52457
O	-11.02949	-1.71309	1.53092
O	-11.66452	0.23302	2.21582
H	-7.34302	1.47927	2.37329
Br	-8.49642	-0.21741	3.74110

25d-r,r-4

0 1

C	-5.83367	-0.30723	1.40719
C	-4.77261	-1.08205	1.86196
C	-4.99557	-2.38810	2.28212
C	-6.28404	-2.91539	2.24369
C	-7.34210	-2.14182	1.78804
C	-7.12575	-0.82900	1.36395
C	-8.24472	0.02611	0.85950

C	-9.21247	-0.68551	-0.08119
C	-9.91979	0.24551	-1.06690
C	-10.94627	1.18823	-0.50350
C	-10.56667	2.62532	-0.27656
C	-11.50462	2.26965	-1.39286
H	-5.65914	0.71076	1.08212
H	-3.77438	-0.66535	1.88680
H	-4.17202	-2.99322	2.63742
H	-6.46370	-3.93121	2.57025
H	-8.33990	-2.55942	1.77076
H	-8.61646	-1.39019	-0.66583
H	-9.94322	-1.27018	0.47397
H	-11.62401	0.74196	0.21106
H	-10.96508	3.10519	0.60518
H	-9.56116	2.92599	-0.53784
H	-11.13245	2.33076	-2.40690
H	-12.55241	2.50911	-1.28167
H	-9.19020	0.78943	-1.66299
N	-10.62517	-0.64382	-2.09139
O	-10.32842	-0.50441	-3.26625
O	-11.46180	-1.42936	-1.67862
H	-7.84761	0.93028	0.40915
Br	-9.22777	0.75794	2.47384

25d-r,r-5

0 1

C	-6.54146	-0.19539	2.19708
C	-5.32488	-0.70695	2.63521
C	-4.99083	-2.02926	2.36833
C	-5.87867	-2.83687	1.66150
C	-7.09123	-2.32470	1.22274
C	-7.43336	-0.99634	1.48503
C	-8.72156	-0.40489	1.00889
C	-9.00750	-0.64423	-0.46296
C	-10.20890	0.08650	-1.07202
C	-10.39797	1.50419	-0.63485
C	-9.51688	2.54986	-1.27113
C	-10.98643	2.50708	-1.58413
H	-6.80210	0.83416	2.40807
H	-4.64158	-0.07316	3.18489
H	-4.04618	-2.43121	2.71007
H	-5.62551	-3.86832	1.45458
H	-7.77902	-2.96551	0.68758
H	-8.12934	-0.27310	-0.99787
H	-9.07919	-1.70631	-0.68426
H	-10.63046	1.63958	0.41193
H	-9.14634	3.34213	-0.63657
H	-8.82636	2.22781	-2.03912
H	-11.28414	2.15507	-2.56286
H	-11.62375	3.27322	-1.16644
H	-10.09022	0.04500	-2.15577
N	-11.49905	-0.73341	-0.88008
O	-12.49262	-0.17714	-0.45459
O	-11.45617	-1.90610	-1.21542

H	-8.75088	0.65259	1.24443
Br	-10.23061	-1.12432	2.15226

25d-r,r-6

0 1

C	-5.67818	-1.11540	0.38409
C	-5.02572	-2.30290	0.69555
C	-5.57337	-3.17160	1.63203
C	-6.77632	-2.84718	2.25448
C	-7.42782	-1.66279	1.94118
C	-6.88477	-0.78540	1.00015
C	-7.56696	0.48947	0.62240
C	-9.04957	0.34312	0.31655
C	-9.74760	1.60400	-0.15836
C	-11.21573	1.47187	-0.50966
C	-11.74978	0.32793	-1.32673
C	-12.11017	0.44277	0.12824
H	-5.25041	-0.43856	-0.34463
H	-4.09160	-2.54717	0.20726
H	-5.06706	-4.09560	1.87811
H	-7.20564	-3.51833	2.98661
H	-8.35442	-1.41642	2.44199
H	-9.13822	-0.44173	-0.43578
H	-9.57329	-0.00052	1.20609
H	-11.67504	2.43450	-0.69277
H	-12.50112	0.55743	-2.06875
H	-11.06562	-0.45937	-1.61027
H	-11.67740	-0.27461	0.80983
H	-13.10799	0.76291	0.39258
H	-9.61923	2.40905	0.56033
N	-9.07163	2.14711	-1.42117
O	-9.04683	3.35815	-1.55902
O	-8.63782	1.35039	-2.23678
H	-7.03478	0.96132	-0.19574
Br	-7.30911	1.83756	2.11668

25d-r,r-7

0 1

C	-5.45649	-0.84693	0.62443
C	-4.61267	-1.94504	0.74720
C	-5.10080	-3.14304	1.25520
C	-6.43633	-3.23764	1.63886
C	-7.27826	-2.14187	1.51370
C	-6.79567	-0.93508	1.00273
C	-7.67819	0.25869	0.83389
C	-9.00873	-0.02496	0.15626
C	-9.87538	1.18956	-0.13523
C	-11.17032	0.83062	-0.81228
C	-12.37640	0.58241	0.05307
C	-12.31015	1.81120	-0.81033
H	-5.07547	0.08643	0.22960
H	-3.57651	-1.86319	0.44667

H	-4.44613	-3.99880	1.35386
H	-6.82084	-4.16703	2.03776
H	-8.31022	-2.22455	1.82723
H	-8.79024	-0.53949	-0.78194
H	-9.60880	-0.70329	0.76139
H	-11.05630	0.20665	-1.68941
H	-13.04005	-0.21959	-0.23673
H	-12.25997	0.71094	1.12075
H	-12.15173	2.76263	-0.32100
H	-12.93134	1.85459	-1.69337
H	-10.06142	1.77251	0.76241
N	-9.12907	2.15847	-1.05051
O	-9.12015	3.33661	-0.73755
O	-8.61158	1.70759	-2.05983
H	-7.13383	1.04762	0.32512
Br	-8.01016	1.09398	2.65258

25d-r,s-1

0 1

C	-5.92869	-1.78554	0.44706
C	-5.32200	-2.71734	1.28186
C	-5.56941	-2.69012	2.64929
C	-6.42658	-1.72761	3.17709
C	-7.03327	-0.79946	2.34287
C	-6.79108	-0.82134	0.96760
C	-7.44162	0.15303	0.03925
C	-8.94131	0.30191	0.23068
C	-9.66073	1.15362	-0.81049
C	-11.09790	0.69838	-1.01483
C	-12.18497	0.89716	0.00179
C	-12.24447	1.61407	-1.32510
H	-5.73283	-1.80556	-0.61771
H	-4.65693	-3.46145	0.86383
H	-5.09695	-3.41232	3.30191
H	-6.62013	-1.69952	4.24131
H	-7.68562	-0.04778	2.76645
H	-9.35069	-0.70837	0.14983
H	-9.18971	0.65738	1.22809
H	-11.10465	-0.25367	-1.53123
H	-12.86137	0.07217	0.17591
H	-11.96413	1.49481	0.87443
H	-12.07376	2.68190	-1.32312
H	-12.96067	1.28113	-2.06288
H	-9.14274	1.13777	-1.76668
N	-9.65741	2.62691	-0.43286
O	-9.48862	3.43022	-1.33412
O	-9.88093	2.92973	0.72687
H	-7.21527	-0.10261	-0.99125
Br	-6.51025	1.94373	0.22335

25d-r,s-2

0 1

C	-5.93819	-0.59300	0.41848
C	-5.39852	-1.87454	0.39713
C	-5.87683	-2.84410	1.26984
C	-6.89786	-2.52717	2.16319
C	-7.43755	-1.24956	2.18111
C	-6.96230	-0.26940	1.30696
C	-7.54918	1.10529	1.27423
C	-9.06614	1.17353	1.16254
C	-9.60277	0.47859	-0.08598
C	-11.12055	0.47741	-0.12478
C	-11.94487	1.70279	-0.39242
C	-11.92852	0.56746	-1.38624
H	-5.56721	0.16160	-0.26349
H	-4.60656	-2.11283	-0.30043
H	-5.45775	-3.84153	1.25695
H	-7.27181	-3.27795	2.84675
H	-8.22315	-1.01093	2.88590
H	-9.52917	0.67899	2.01631
H	-9.39368	2.21038	1.16882
H	-11.50269	-0.19540	0.63298
H	-12.82929	1.85005	0.21123
H	-11.43088	2.61119	-0.67246
H	-11.41247	0.73181	-2.32229
H	-12.80031	-0.06623	-1.46605
H	-9.24091	-0.54357	-0.15826
N	-9.04816	1.13473	-1.34008
O	-8.69717	0.39921	-2.24712
O	-9.00652	2.35365	-1.38633
H	-7.07694	1.69522	0.49562
Br	-7.01675	2.11553	2.93707

25d-r,s-3

0 1			
C	-5.80882	0.08633	0.66315
C	-5.06122	-0.96117	0.14041
C	-5.45495	-2.27619	0.36326
C	-6.59507	-2.53366	1.11642
C	-7.34226	-1.48533	1.63812
C	-6.96318	-0.16472	1.40707
C	-7.77109	1.02258	1.85090
C	-8.90580	1.44515	0.91982
C	-10.00477	0.43068	0.63657
C	-11.26264	1.11282	0.11972
C	-11.36407	1.72942	-1.24565
C	-12.19986	0.52298	-0.89101
H	-5.49900	1.10899	0.48738
H	-4.16980	-0.74953	-0.43526
H	-4.87309	-3.09435	-0.04008
H	-6.90467	-3.55367	1.30153
H	-8.21865	-1.70101	2.23253
H	-9.38368	2.32899	1.34057
H	-8.45686	1.75065	-0.02670
H	-11.72829	1.66735	0.92509
H	-11.84974	2.69184	-1.32462

H	-10.54703	1.57640	-1.93654
H	-11.93991	-0.41758	-1.35642
H	-13.25899	0.65778	-0.72335
H	-10.25505	-0.15378	1.51817
N	-9.56077	-0.62009	-0.37144
O	-9.98947	-1.75060	-0.21322
O	-8.85506	-0.27683	-1.30445
H	-7.11418	1.87649	1.98102
Br	-8.49668	0.77128	3.70621

25d-r,s-4

0 1

C	-6.13316	-0.14489	1.42755
C	-4.96760	-0.83964	1.73134
C	-5.02392	-2.19635	2.02776
C	-6.25108	-2.85535	2.01657
C	-7.41296	-2.16161	1.71021
C	-7.36472	-0.79793	1.41213
C	-8.59576	-0.02552	1.06427
C	-9.53699	-0.72686	0.08444
C	-10.37231	0.15215	-0.84810
C	-11.09214	1.31778	-0.19511
C	-10.49355	2.67937	0.00329
C	-11.64178	2.48800	-0.95731
H	-6.08804	0.91187	1.19654
H	-4.01812	-0.32080	1.73527
H	-4.11875	-2.73912	2.26599
H	-6.30092	-3.91128	2.24761
H	-8.36191	-2.68143	1.71281
H	-8.93691	-1.39202	-0.53827
H	-10.23284	-1.36870	0.62333
H	-11.71011	0.95609	0.61632
H	-10.68029	3.16908	0.94807
H	-9.52136	2.88372	-0.42267
H	-11.42837	2.56626	-2.01392
H	-12.61923	2.84873	-0.66969
H	-11.10486	-0.47717	-1.34908
N	-9.51490	0.65445	-2.00122
O	-8.36320	0.98599	-1.76934
O	-10.03911	0.71829	-3.10039
H	-8.33014	0.96567	0.72557
Br	-9.57963	0.38242	2.79523

25d-r,s-5

0 1

C	-6.59835	-0.19586	2.35744
C	-5.34453	-0.71059	2.66711
C	-4.99200	-1.98501	2.23910
C	-5.89872	-2.74097	1.50007
C	-7.14894	-2.22530	1.18946
C	-7.50993	-0.94484	1.61403
C	-8.83894	-0.34670	1.28388

C	-9.24363	-0.46683	-0.17404
C	-10.55615	0.23729	-0.50686
C	-10.56808	1.71971	-0.17423
C	-9.66065	2.71581	-0.83731
C	-11.14949	2.78055	-1.06467
H	-6.87319	0.79623	2.69299
H	-4.64635	-0.11681	3.24209
H	-4.01790	-2.38956	2.48017
H	-5.63056	-3.73490	1.16706
H	-7.84857	-2.82793	0.62627
H	-8.44105	-0.01255	-0.75739
H	-9.30754	-1.51465	-0.46601
H	-10.74149	1.86595	0.88395
H	-9.19734	3.46593	-0.21193
H	-9.05268	2.37361	-1.66297
H	-11.51909	2.49863	-2.04104
H	-11.71333	3.57049	-0.58946
H	-11.39271	-0.24510	-0.01024
N	-10.85862	0.03695	-1.98002
O	-9.95016	0.17902	-2.78305
O	-12.01042	-0.22189	-2.28450
H	-8.87153	0.68475	1.61530
Br	-10.25276	-1.20424	2.46401

25d-r,s-6

0 1

C	-5.98071	-1.54123	0.17553
C	-5.29475	-2.61242	0.73729
C	-5.43201	-2.89175	2.09176
C	-6.25824	-2.09521	2.88098
C	-6.94418	-1.02791	2.31909
C	-6.81309	-0.74210	0.95824
C	-7.55367	0.38749	0.31717
C	-9.04117	0.41959	0.62578
C	-9.86728	1.41762	-0.17650
C	-11.31753	1.01402	-0.27312
C	-12.19828	1.62740	-1.32397
C	-11.75303	0.19637	-1.45798
H	-5.87063	-1.32269	-0.87927
H	-4.65394	-3.22532	0.11729
H	-4.89774	-3.72300	2.53250
H	-6.36558	-2.30573	3.93687
H	-7.57111	-0.40741	2.94529
H	-9.41840	-0.57243	0.36390
H	-9.23084	0.55500	1.68883
H	-11.77400	0.78084	0.68049
H	-13.22754	1.82439	-1.06056
H	-11.75336	2.35669	-1.98723
H	-11.01001	-0.02998	-2.21092
H	-12.47423	-0.58924	-1.28351
H	-9.45241	1.58089	-1.16851
N	-9.85407	2.80688	0.45950
O	-9.71101	3.76134	-0.28514
O	-10.05799	2.88935	1.65847

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 H       -7.39058        0.38156       -0.75604
Br       -6.66729        2.12822        0.85294
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25d-r,s-7

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 0 1
 C       -5.87194       -1.16712        0.01605
 C       -5.21593       -2.33231        0.39701
 C       -5.54094       -2.95159        1.59807
 C       -6.52465       -2.40030        2.41550
 C       -7.18009       -1.23847        2.03350
 C       -6.86075       -0.61151        0.82703
 C       -7.56046        0.63004        0.37701
 C       -9.07604        0.56697        0.46552
 C       -9.80354        1.76626       -0.12670
 C      -11.17109        1.49484       -0.72337
 C      -11.44736        0.27698       -1.56044
 C      -12.08158        0.41998       -0.20284
 H       -5.61592       -0.68364       -0.91830
 H       -4.45219       -2.75345       -0.24332
 H       -5.03074       -3.85719        1.89848
 H       -6.77897       -2.87619        3.35336
 H       -7.93183       -0.81158        2.68368
 H       -9.35789       -0.32277       -0.09973
 H       -9.40944        0.40306        1.48713
 H      -11.65150        2.40356       -1.06310
 H      -12.06349        0.42001       -2.43680
 H      -10.66878       -0.46313       -1.68091
 H      -11.71411       -0.21834        0.58837
 H      -13.13704        0.64381       -0.14441
 H       -9.18769        2.28359       -0.85924
 N      -10.05079        2.83954        0.94239
 O       -9.96579        4.00176        0.58342
 O      -10.38508        2.48447        2.05823
 H       -7.24951        0.89308       -0.62920
Br       -6.84955        2.20089        1.44279
```

25d-s,r-1

```
 0 1
 C       -6.59249       -1.97911        0.63598
 C       -5.93363       -2.94617        1.38183
 C       -5.54541       -2.67751        2.69212
 C       -5.81896       -1.43463        3.25090
 C       -6.47740       -0.46561        2.50211
 C       -6.87271       -0.72851        1.19097
 C       -7.59573        0.32957        0.42116
 C       -8.85751       -0.14871       -0.27679
 C       -9.72493        0.93777       -0.90108
 C      -11.17061        0.52218       -1.01542
 C      -12.10421        0.87542        0.10959
 C      -12.23522        1.56115       -1.22332
 H       -6.87607       -2.19491       -0.38531
 H       -5.72010       -3.91077        0.94052
```

H	-5.03127	-3.43295	3.27150
H	-5.52003	-1.21736	4.26785
H	-6.68734	0.50338	2.93737
H	-8.64402	-0.91829	-1.01591
H	-9.46430	-0.62012	0.50074
H	-11.31606	-0.43872	-1.49261
H	-12.84665	0.14205	0.39027
H	-11.70200	1.45007	0.93317
H	-11.92114	2.59388	-1.29066
H	-13.07093	1.30063	-1.85683
H	-9.64281	1.88014	-0.36431
N	-9.26827	1.28243	-2.31808
O	-9.03372	0.36330	-3.08369
O	-9.23386	2.46216	-2.62298
H	-7.81677	1.17572	1.06421
Br	-6.30746	1.15534	-0.90716

25d-s,r-2

0 1

C	-7.32610	-2.39535	1.72836
C	-6.10652	-2.92099	1.32136
C	-5.11395	-2.07834	0.83263
C	-5.34861	-0.70975	0.76074
C	-6.56898	-0.18526	1.16727
C	-7.57379	-1.02388	1.64465
C	-8.95199	-0.54728	2.01007
C	-9.94292	-0.42264	0.85438
C	-9.59603	0.53757	-0.27277
C	-10.80072	0.88364	-1.11203
C	-11.60808	2.09351	-0.72668
C	-10.78504	2.10528	-1.98554
H	-8.09616	-3.05484	2.10894
H	-5.93083	-3.98638	1.39147
H	-4.16188	-2.48443	0.51752
H	-4.57967	-0.04581	0.38866
H	-6.73296	0.88174	1.11666
H	-10.08604	-1.42118	0.43675
H	-10.90394	-0.10667	1.25825
H	-11.34833	0.02216	-1.47358
H	-12.68312	2.02212	-0.81052
H	-11.25705	2.68214	0.11029
H	-9.88419	2.70327	-1.99286
H	-11.29620	2.04581	-2.93579
H	-9.12102	1.44434	0.09237
N	-8.56176	-0.05690	-1.23135
O	-8.64474	-1.23863	-1.51841
O	-7.74625	0.71309	-1.70985
H	-9.38207	-1.22028	2.74463
Br	-8.89270	1.18578	3.02051

25d-s,r-3

0 1

C	-6.91568	-2.11411	1.03266
C	-5.56757	-2.00241	0.70975
C	-4.90620	-0.79492	0.89716
C	-5.59854	0.30069	1.40838
C	-6.94377	0.18876	1.72756
C	-7.61577	-1.02144	1.54135
C	-9.07447	-1.16301	1.83644
C	-9.97699	-0.10268	1.22078
C	-9.87624	-0.05221	-0.30068
C	-10.75551	1.00807	-0.90580
C	-10.15864	2.36807	-1.14874
C	-10.49701	1.47661	-2.31103
H	-7.43153	-3.05403	0.88273
H	-5.03730	-2.85768	0.31243
H	-3.85702	-0.70525	0.64841
H	-5.08722	1.24230	1.55900
H	-7.46915	1.04291	2.13382
H	-11.01077	-0.28119	1.50968
H	-9.70087	0.88731	1.58230
H	-11.78590	0.97322	-0.57651
H	-10.78487	3.22717	-0.95530
H	-9.11319	2.50585	-0.90768
H	-9.67821	1.01841	-2.84902
H	-11.35533	1.72528	-2.91846
H	-8.84829	0.06975	-0.63090
N	-10.29163	-1.39464	-0.89929
O	-11.34572	-1.88413	-0.52825
O	-9.55887	-1.88782	-1.74022
H	-9.41421	-2.15985	1.57465
Br	-9.37515	-1.13720	3.83092

25d-s,r-4

0 1

C	-6.10683	-1.36862	0.61335
C	-5.27970	-2.27192	1.26563
C	-5.51320	-2.60043	2.59871
C	-6.57840	-2.01834	3.27577
C	-7.40515	-1.11197	2.62196
C	-7.18038	-0.78123	1.28596
C	-8.10348	0.18222	0.61346
C	-8.58808	-0.25291	-0.75788
C	-9.64671	0.67194	-1.35307
C	-10.93501	0.72477	-0.57807
C	-11.16243	1.86287	0.38388
C	-11.94743	1.79295	-0.89306
H	-5.90708	-1.11267	-0.41839
H	-4.45037	-2.72004	0.73453
H	-4.86693	-3.30503	3.10517
H	-6.76672	-2.26801	4.31156
H	-8.23362	-0.65717	3.15032
H	-7.74856	-0.34171	-1.44689
H	-9.01926	-1.24945	-0.63993
H	-11.32029	-0.24482	-0.28969
H	-11.66340	1.63118	1.31303

H	-10.39174	2.61691	0.46101
H	-11.70216	2.50002	-1.67397
H	-12.99109	1.51773	-0.84372
H	-9.25206	1.67030	-1.51740
N	-9.96716	0.17342	-2.75835
O	-10.33343	-0.98382	-2.88248
O	-9.86458	0.96723	-3.67846
H	-8.93604	0.41829	1.26576
Br	-7.17033	1.98013	0.46738

25d-s,r-5

0 1

C	-6.06471	-0.76686	1.05322
C	-4.99880	-1.57045	1.43185
C	-5.22643	-2.75169	2.13393
C	-6.52671	-3.12316	2.45497
C	-7.59394	-2.31624	2.07688
C	-7.37401	-1.13383	1.37194
C	-8.54540	-0.29781	0.96657
C	-8.49338	0.21597	-0.47010
C	-9.83324	0.52185	-1.15396
C	-10.73180	1.52533	-0.50092
C	-10.53380	2.97223	-0.85792
C	-11.75419	2.23798	-1.34257
H	-5.87507	0.15317	0.51639
H	-3.98846	-1.27597	1.18023
H	-4.39391	-3.37713	2.42783
H	-6.71224	-4.04019	2.99843
H	-8.60680	-2.60589	2.32693
H	-7.88518	1.11686	-0.53817
H	-7.98870	-0.54349	-1.07040
H	-11.00562	1.31409	0.52079
H	-10.64589	3.69700	-0.06441
H	-9.76914	3.21411	-1.58405
H	-11.80715	1.98678	-2.39383
H	-12.70620	2.46398	-0.88401
H	-9.61456	0.82211	-2.17648
N	-10.56604	-0.80988	-1.33153
O	-11.33231	-1.17002	-0.45333
O	-10.31302	-1.45803	-2.33342
H	-9.46716	-0.83313	1.16583
Br	-8.67778	1.25414	2.26545

25d-s,r-6

0 1

C	-6.09912	-1.35774	0.61605
C	-5.27395	-2.26328	1.26751
C	-5.51501	-2.60100	2.59706
C	-6.58554	-2.02569	3.27130
C	-7.41043	-1.11678	2.61827
C	-7.17821	-0.77721	1.28592
C	-8.10044	0.18666	0.61243

C	-8.59148	-0.25674	-0.75434
C	-9.64810	0.66804	-1.35309
C	-10.93618	0.72530	-0.57801
C	-11.15963	1.86472	0.38374
C	-11.94565	1.79606	-0.89290
H	-5.89384	-1.09409	-0.41269
H	-4.44016	-2.70600	0.73886
H	-4.87016	-3.30738	3.10285
H	-6.77955	-2.28224	4.30436
H	-8.24298	-0.66717	3.14464
H	-7.75415	-0.35599	-1.44450
H	-9.02703	-1.25005	-0.62537
H	-11.32388	-0.24291	-0.28824
H	-11.66080	1.63487	1.31321
H	-10.38692	2.61681	0.45968
H	-11.69893	2.50203	-1.67433
H	-12.98996	1.52357	-0.84234
H	-9.25167	1.66530	-1.51999
N	-9.96994	0.16654	-2.75671
O	-10.33170	-0.99244	-2.87823
O	-9.87272	0.95948	-3.67804
H	-8.92993	0.42860	1.26646
Br	-7.16357	1.98056	0.45259

25d-s,r-7

0 1

C	-6.53821	-1.57291	0.12102
C	-5.85002	-2.74155	0.41441
C	-5.61059	-3.10082	1.73855
C	-6.06205	-2.28248	2.76722
C	-6.74990	-1.11072	2.47224
C	-6.99755	-0.74663	1.14915
C	-7.76094	0.50728	0.86852
C	-8.89941	0.34327	-0.12422
C	-9.77921	1.57349	-0.29894
C	-11.23488	1.31462	-0.63627
C	-11.68144	0.12075	-1.43049
C	-12.02388	0.22313	0.03168
H	-6.70535	-1.29748	-0.91156
H	-5.49755	-3.37298	-0.39043
H	-5.07349	-4.01242	1.96477
H	-5.87939	-2.55379	3.79857
H	-7.09902	-0.47270	3.27439
H	-8.53795	0.00984	-1.09365
H	-9.51184	-0.46709	0.27427
H	-11.77965	2.23385	-0.81000
H	-12.46600	0.26981	-2.15832
H	-10.93594	-0.60732	-1.71796
H	-11.51887	-0.44191	0.71799
H	-13.04118	0.45945	0.30971
H	-9.72211	2.23010	0.56656
N	-9.26410	2.45819	-1.44303
O	-8.85377	1.92114	-2.45607
O	-9.36638	3.66389	-1.29285

```
 H       -8.12435        0.94094        1.79488
Br       -6.46661        1.93287        0.23599
```

25e-cis-1

```
 0 1
 C       -3.85291       -0.32232        0.05492
 C       -3.19234       -1.51922       -0.20064
 C       -3.54503       -2.66943        0.49493
 C       -4.56159       -2.61639        1.44607
 C       -5.22085       -1.42200        1.69769
 C       -4.87337       -0.26130        1.00279
 C       -5.58243        1.03393        1.23417
 C       -7.10024        0.97573        1.25613
Br       -4.95278        1.81973        2.99735
 C       -7.65658        0.51860       -0.09483
 C       -9.19712        0.52453       -0.08875
 C       -9.74040        0.01571       -1.38048
 C      -10.10973        0.66758       -2.48249
 N      -10.07218        2.10537       -2.64554
 O      -10.69541        2.55855       -3.60231
 O       -9.43453        2.79834       -1.86023
 H       -3.57673        0.57345       -0.48706
 H       -2.40410       -1.55124       -0.94126
 H       -3.03215       -3.60204        0.30003
 H       -4.83885       -3.50836        1.99245
 H       -6.00216       -1.39037        2.44526
 H       -5.23842        1.78152        0.52628
 H       -7.44025        0.30304        2.04507
 H       -7.48832        1.96748        1.49114
 H       -7.30204        1.18148       -0.88632
 H       -7.29451       -0.48401       -0.32906
 H       -9.54650       -0.13417        0.70912
 H       -9.54984        1.53196        0.11749
 H       -9.84764       -1.06176       -1.45614
 H      -10.51732        0.18563       -3.35576
```

25e-cis-2

```
 0 1
 C       -3.88747        0.45523        0.24904
 C       -3.11940       -0.43342       -0.49518
 C       -3.42772       -1.78863       -0.49243
 C       -4.50704       -2.24942        0.25792
 C       -5.27289       -1.36095        0.99866
 C       -4.97148        0.00271        1.00017
 C       -5.79496        0.98820        1.76470
 C       -7.30207        0.84453        1.64156
Br       -5.30610        0.86450        3.73243
 C       -7.76265        1.05738        0.19751
 C       -9.29126        0.90728        0.07821
 C       -9.74665        1.12162       -1.32555
 C       -9.89394        0.25454       -2.32699
 N       -9.64496       -1.16792       -2.23301
```

O	-10.05449	-1.85309	-3.16728
O	-9.04704	-1.62681	-1.26572
H	-3.64700	1.51107	0.24595
H	-2.28320	-0.06668	-1.07584
H	-2.83260	-2.48323	-1.07045
H	-4.75190	-3.30339	0.26382
H	-6.10479	-1.73208	1.58187
H	-5.48426	2.00069	1.52642
H	-7.61502	-0.14238	1.98516
H	-7.78210	1.57678	2.29199
H	-7.46094	2.05029	-0.14557
H	-7.28461	0.33117	-0.45924
H	-9.57655	-0.08065	0.43254
H	-9.77262	1.65358	0.71288
H	-9.98752	2.14444	-1.59725
H	-10.25310	0.52464	-3.30629

25e-trans-1

0 1

C	-4.10363	-0.54987	0.44587
C	-3.57957	-1.81656	0.21156
C	-4.15977	-2.92948	0.80813
C	-5.26644	-2.76913	1.63892
C	-5.78921	-1.50496	1.86941
C	-5.21305	-0.38094	1.27317
C	-5.76924	0.99038	1.48296
C	-7.27418	1.13605	1.33552
Br	-5.24938	1.63202	3.33802
C	-7.72744	0.80671	-0.08945
C	-9.24324	0.99974	-0.25251
C	-9.70246	0.62037	-1.61602
C	-10.30531	1.45774	-2.45139
N	-10.72188	1.03408	-3.77405
O	-11.27292	1.88532	-4.46720
O	-10.51739	-0.11616	-4.14208
H	-3.65003	0.31670	-0.01872
H	-2.71990	-1.93196	-0.43533
H	-3.75365	-3.91636	0.62957
H	-5.72079	-3.63192	2.10805
H	-6.64298	-1.39177	2.52403
H	-5.25131	1.70608	0.85220
H	-7.78713	0.48634	2.04637
H	-7.55520	2.16133	1.57926
H	-7.20235	1.44836	-0.80153
H	-7.46447	-0.22331	-0.33755
H	-9.75499	0.35625	0.47128
H	-9.52060	2.03052	-0.02650
H	-9.51832	-0.39614	-1.94473
H	-10.54507	2.49058	-2.25726

25e-trans-2

0 1

C	-4.24559	-0.28221	0.28526
C	-3.68358	-1.48095	-0.14068
C	-4.18036	-2.68844	0.33488
C	-5.24178	-2.69084	1.23729
C	-5.80251	-1.49411	1.65910
C	-5.31029	-0.27591	1.18521
C	-5.91251	1.02813	1.59805
C	-7.42760	1.11898	1.53268
Br	-5.33299	1.44847	3.49737
C	-7.93554	0.93864	0.09932
C	-9.45087	1.08982	0.02581
C	-10.07190	0.92206	-1.31650
C	-9.41631	0.64434	-2.43793
N	-10.12162	0.50009	-3.69666
O	-9.43037	0.23610	-4.67724
O	-11.33768	0.64042	-3.73988
H	-3.85729	0.65809	-0.08560
H	-2.85964	-1.46972	-0.84199
H	-3.74465	-3.62298	0.00697
H	-5.63107	-3.62816	1.61255
H	-6.62032	-1.50780	2.36722
H	-5.45615	1.84314	1.04497
H	-7.87753	0.36649	2.18240
H	-7.73880	2.09385	1.91054
H	-7.45819	1.67624	-0.55160
H	-7.64412	-0.04554	-0.27236
H	-9.93509	0.37369	0.70073
H	-9.75379	2.07279	0.40562
H	-11.14793	1.03685	-1.37457
H	-8.35582	0.49846	-2.55096

25e-trans-3

0 1

C	-4.08589	-0.08144	0.52462
C	-3.40907	-1.18880	0.02473
C	-3.88316	-2.46875	0.28593
C	-5.03727	-2.63520	1.04830
C	-5.71233	-1.52921	1.54397
C	-5.24362	-0.23916	1.28527
C	-5.96399	0.97221	1.78225
C	-7.46610	1.00051	1.55742
Br	-5.61702	1.17203	3.77326
C	-7.80331	1.00467	0.06370
C	-9.32203	1.05918	-0.16645
C	-9.65550	1.13109	-1.61487
C	-10.36494	0.20953	-2.25523
N	-10.64653	0.32461	-3.67275
O	-11.29915	-0.58857	-4.17169
O	-10.23883	1.29322	-4.30198
H	-3.71531	0.91549	0.32126
H	-2.51362	-1.05028	-0.56674
H	-3.35832	-3.33268	-0.09997
H	-5.40975	-3.62961	1.25663
H	-6.60206	-1.67109	2.14275

H	-5.50028	1.87159	1.38922
H	-7.93473	0.14210	2.04118
H	-7.87803	1.89576	2.02487
H	-7.32981	1.86401	-0.41854
H	-7.39973	0.11060	-0.41433
H	-9.80216	0.19521	0.29585
H	-9.71873	1.95586	0.32138
H	-9.28053	1.97910	-2.17663
H	-10.79007	-0.68199	-1.82343

3.5.3. Minimum Energy Path xyz-Matrices

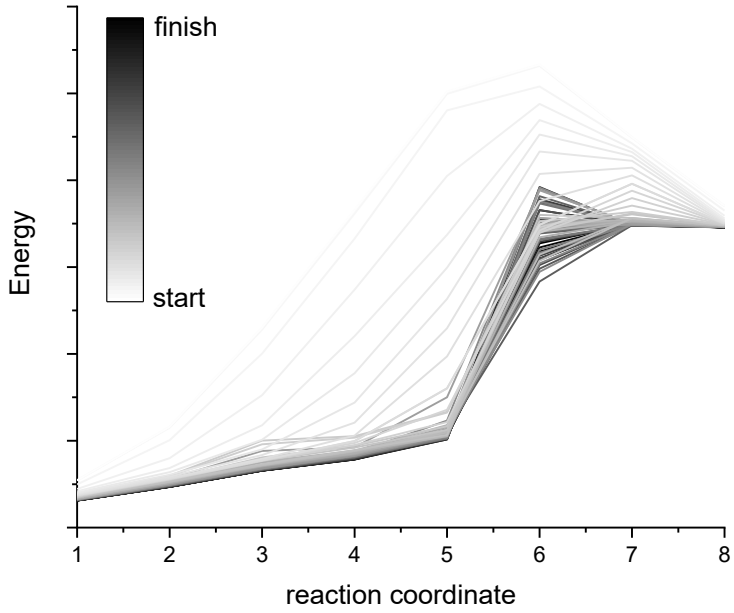


*Figure 63: NEB calculation cycles of **Cu(I)-22a** to **Cu(II)** + **A**.*

1-Cu(I)-22a to Cu(II) + A

Cu	-1.848237	0.926090	0.650896
N	-0.768411	0.881794	-1.132576
N	-0.001090	0.514947	1.443072
C	0.956166	0.482393	0.480640
C	-1.195050	1.031078	-2.386634
C	0.552330	0.692332	-0.882767
C	1.525623	0.665827	-1.908005
C	2.317163	0.240604	0.769459
C	0.319532	0.278696	2.712485
C	1.068875	0.847443	-3.232807
H	1.786103	0.834219	-4.055920
C	-0.278568	1.021716	-3.468184
H	-0.651523	1.152489	-4.483630
C	2.901835	0.434400	-1.582456
H	3.633398	0.419053	-2.390748
C	2.656247	0.017037	2.124027

H	3.697921	-0.171740	2.392279
C	1.667483	0.034147	3.081840
H	1.906699	-0.143692	4.129499
C	3.282720	0.224770	-0.289632
H	4.327040	0.038139	-0.037831
C	-0.774213	0.247904	3.732121
C	-2.663941	1.211249	-2.613830
Cl	-3.948959	1.368875	1.206318
O	-0.055381	-2.704519	1.715360
N	-1.165023	-2.495664	1.171974
O	-2.280177	-2.264701	1.735884
C	-1.328693	-2.523576	-0.319027
H	-1.695962	-1.551631	-0.650263
H	-2.016132	-3.323470	-0.603088
Br	0.359073	-2.837863	-1.269085
H	-0.374563	0.382779	4.745013
H	-1.520990	1.023299	3.518041
H	-1.275498	-0.731189	3.670176
H	-3.217987	0.389231	-2.139551
H	-3.000627	2.148978	-2.148246
H	-2.897187	1.238556	-3.684802

2-Cu(I)-22a to Cu(II) + A

Cu	-1.784679	0.790593	0.605025
N	-0.674978	0.863573	-1.196981
N	0.084958	0.460082	1.386712
C	1.050079	0.506280	0.434343
C	-1.094198	1.048830	-2.447592
C	0.646323	0.734894	-0.936091
C	1.634390	0.798186	-1.949070
C	2.423513	0.337691	0.732791
C	0.414155	0.240971	2.660450
C	1.181989	1.006107	-3.272239
H	1.908649	1.065355	-4.086664
C	-0.170602	1.125436	-3.519907
H	-0.541497	1.278423	-4.535122
C	3.019207	0.640461	-1.608858
H	3.760905	0.700235	-2.409047
C	2.762365	0.099287	2.084985
H	3.811131	-0.039643	2.360150
C	1.766705	0.049526	3.038317
H	2.006568	-0.130703	4.087862
C	3.398962	0.414454	-0.317007
H	4.452517	0.287952	-0.056244
C	-0.686438	0.183805	3.678687
C	-2.571572	1.175094	-2.683914
Cl	-3.912711	1.116363	1.041692
O	-0.518466	-3.003990	1.881906
N	-1.573480	-2.685533	1.378728
O	-2.580909	-2.361388	1.982494
C	-1.737738	-2.686465	-0.126411
H	-2.245200	-1.746659	-0.372903
H	-2.362680	-3.556593	-0.366764
Br	-0.070462	-2.802975	-1.076328

H	-0.299803	0.368476	4.691234
H	-1.471976	0.914783	3.437140
H	-1.154659	-0.815102	3.667153
H	-3.100776	0.296787	-2.282030
H	-2.973093	2.052507	-2.151565
H	-2.796498	1.272901	-3.754933

3-Cu(I)-22a to Cu(II) + A

Cu	-1.702656	0.701808	0.556414
N	-0.594800	0.852755	-1.266150
N	0.160359	0.413178	1.321974
C	1.129479	0.536089	0.377775
C	-1.008310	1.062132	-2.514210
C	0.727995	0.786979	-0.990444
C	1.723231	0.944047	-1.987063
C	2.507637	0.433128	0.685629
C	0.492778	0.170973	2.591339
C	1.275827	1.178574	-3.307860
H	2.008086	1.311492	-4.108353
C	-0.077753	1.232068	-3.570126
H	-0.444817	1.404179	-4.583686
C	3.110906	0.856271	-1.634934
H	3.856330	0.991118	-2.422317
C	2.849136	0.166858	2.032062
H	3.901886	0.076454	2.312112
C	1.850892	0.032567	2.973405
H	2.092051	-0.168462	4.018885
C	3.488548	0.604818	-0.347372
H	4.544509	0.531868	-0.076358
C	-0.602573	0.040503	3.608515
C	-2.486884	1.115396	-2.770857
Cl	-3.860560	1.007190	0.844677
O	-0.976886	-3.319097	2.141058
N	-1.952440	-2.803618	1.636800
O	-2.878170	-2.294954	2.242026
C	-2.107787	-2.803448	0.132626
H	-2.663974	-1.894409	-0.118573
H	-2.668107	-3.713734	-0.120404
Br	-0.415090	-2.820412	-0.785281
H	-0.232763	0.281955	4.615747
H	-1.447018	0.695767	3.350361
H	-0.981716	-0.995269	3.629935
H	-2.975546	0.202772	-2.395910
H	-2.942805	1.958836	-2.227868
H	-2.698996	1.223626	-3.843574

4-Cu(I)-22a to Cu(II) + A

Cu	-1.600420	0.534396	0.454270
N	-0.488436	0.823041	-1.357262
N	0.260247	0.338701	1.229760
C	1.230153	0.567208	0.304940
C	-0.899812	1.065823	-2.599598

C	0.830689	0.845212	-1.059402
C	1.825131	1.125834	-2.029666
C	2.607921	0.553095	0.631566
C	0.594700	0.066594	2.492488
C	1.379348	1.393653	-3.344900
H	2.110324	1.620905	-4.124797
C	0.029498	1.360788	-3.628436
H	-0.336150	1.558119	-4.637867
C	3.209916	1.125533	-1.657252
H	3.953893	1.352986	-2.424159
C	2.951399	0.257548	1.971571
H	4.004046	0.233594	2.264925
C	1.954051	0.011741	2.890333
H	2.194990	-0.212985	3.931055
C	3.587057	0.842978	-0.375961
H	4.641273	0.837015	-0.089339
C	-0.497433	-0.193324	3.486699
C	-2.374274	1.023546	-2.880112
Cl	-3.777621	0.831026	0.600364
O	-1.590412	-3.605441	2.490830
N	-2.417119	-2.876031	1.977788
O	-3.178376	-2.141124	2.576986
C	-2.561148	-2.890866	0.476085
H	-3.151366	-2.010928	0.201301
H	-3.045376	-3.840928	0.214996
Br	-0.837346	-2.813122	-0.394733
H	-0.172571	0.074881	4.502734
H	-1.403908	0.367588	3.218445
H	-0.756400	-1.265396	3.496857
H	-2.806900	0.075453	-2.526234
H	-2.894059	1.824371	-2.330083
H	-2.575508	1.138515	-3.954196

5-Cu(I)-22a to Cu(II) + A

Cu	-1.447044	0.164216	0.223446
N	-0.335869	0.765972	-1.487849
N	0.404274	0.192568	1.076673
C	1.364117	0.593504	0.202619
C	-0.751513	1.063284	-2.717055
C	0.965593	0.919673	-1.151043
C	1.941288	1.377741	-2.070995
C	2.725980	0.713840	0.572230
C	0.732596	-0.120332	2.330875
C	1.492635	1.689524	-3.375836
H	2.208150	2.044688	-4.121482
C	0.158618	1.536560	-3.694580
H	-0.209132	1.766540	-4.696194
C	3.310620	1.495907	-1.659983
H	4.043032	1.847384	-2.390588
C	3.063792	0.377346	1.904528
H	4.103557	0.453354	2.233044
C	2.076016	-0.036027	2.773641
H	2.311261	-0.291844	3.808527
C	3.689163	1.171249	-0.388469

H	4.732503	1.257675	-0.075443
C	-0.351653	-0.582398	3.257777
C	-2.207932	0.889502	-3.038659
Cl	-3.638675	0.524221	0.270328
O	-2.454331	-3.783270	3.040307
N	-2.994522	-2.847857	2.477780
O	-3.422489	-1.849340	3.025480
C	-3.148347	-2.933907	0.984151
H	-3.771458	-2.095687	0.652229
H	-3.533195	-3.932414	0.751549
Br	-1.402046	-2.759290	0.123435
H	-0.099340	-0.358292	4.304304
H	-1.312064	-0.118605	2.992197
H	-0.476195	-1.675598	3.176340
H	-2.563147	-0.097956	-2.708635
H	-2.814201	1.628011	-2.489212
H	-2.390041	1.010060	-4.115437

6-Cu(I)-22a to Cu(II) + A

Cu	-1.325173	-0.119440	0.066806
N	-0.281379	0.767035	-1.525511
N	0.475305	0.114498	1.002669
C	1.419876	0.602675	0.160681
C	-0.702072	1.073439	-2.751993
C	1.014207	0.962337	-1.178562
C	1.975764	1.484869	-2.077347
C	2.767141	0.777928	0.553581
C	0.785102	-0.213084	2.254442
C	1.522118	1.809851	-3.376887
H	2.224952	2.214266	-4.109300
C	0.198548	1.605763	-3.708180
H	-0.171278	1.839376	-4.707780
C	3.336074	1.646670	-1.649902
H	4.059279	2.046685	-2.364593
C	3.094465	0.419101	1.883059
H	4.122733	0.534635	2.234225
C	2.113018	-0.063742	2.723909
H	2.340636	-0.330322	3.756892
C	3.717706	1.306215	-0.382821
H	4.753189	1.431277	-0.057285
C	-0.293594	-0.752295	3.147063
C	-2.141514	0.841143	-3.105538
Cl	-3.502001	0.410286	0.074683
O	-2.814313	-3.791717	3.302134
N	-3.246495	-2.812548	2.700088
O	-3.458763	-1.718284	3.217423
C	-3.476512	-2.946899	1.269658
H	-4.050538	-2.106324	0.862604
H	-3.724929	-3.978922	0.999317
Br	-1.466651	-2.682796	0.208971
H	-0.060733	-0.551334	4.202182
H	-1.273452	-0.323241	2.894948
H	-0.379098	-1.845247	3.023261
H	-2.460069	-0.165043	-2.796140

H	-2.790127	1.546619	-2.561932
H	-2.301421	0.966572	-4.184825

7-Cu(I)-22a to Cu(II) + A

Cu	-1.288748	-0.143760	0.068990
N	-0.282719	0.783449	-1.519239
N	0.483797	0.096677	0.985661
C	1.426948	0.603930	0.150167
C	-0.703240	1.075652	-2.750938
C	1.019782	0.969254	-1.178987
C	1.978389	1.492843	-2.077592
C	2.770023	0.783824	0.550525
C	0.782979	-0.225801	2.244934
C	1.522476	1.819334	-3.376130
H	2.224002	2.229320	-4.107126
C	0.200894	1.607499	-3.706756
H	-0.169157	1.843229	-4.705968
C	3.337400	1.658726	-1.649250
H	4.059383	2.063724	-2.362116
C	3.093582	0.421878	1.880038
H	4.120917	0.540281	2.234148
C	2.110713	-0.064487	2.716237
H	2.337870	-0.332896	3.749402
C	3.719335	1.318470	-0.382180
H	4.753535	1.446920	-0.054579
C	-0.291211	-0.769110	3.135576
C	-2.138027	0.837656	-3.110884
Cl	-3.455580	0.389714	0.035599
O	-2.833382	-3.791833	3.328333
N	-3.310444	-2.816477	2.720554
O	-3.451909	-1.696430	3.247355
C	-3.673081	-2.973109	1.388707
H	-4.088072	-2.101128	0.888116
H	-3.745731	-3.995052	1.025209
Br	-1.274468	-2.633174	0.110196
H	-0.056032	-0.565925	4.189764
H	-1.274229	-0.344662	2.890454
H	-0.372971	-1.861332	3.008516
H	-2.451101	-0.171908	-2.806259
H	-2.789477	1.541573	-2.569845
H	-2.292449	0.963129	-4.190634

8-Cu(I)-22a to Cu(II) + A

Cu	-1.260152	-0.189853	0.033127
N	-0.262510	0.776932	-1.539499
N	0.505265	0.067048	0.957256
C	1.443425	0.601895	0.133480
C	-0.682202	1.076187	-2.769677
C	1.035743	0.978230	-1.192409
C	1.989587	1.528492	-2.080032
C	2.780540	0.802722	0.543527
C	0.801394	-0.259909	2.215991

C	1.533833	1.862963	-3.376559
H	2.231441	2.293509	-4.099419
C	0.217395	1.633015	-3.715416
H	-0.152225	1.873884	-4.713458
C	3.343592	1.712494	-1.643207
H	4.061893	2.138091	-2.347787
C	3.102117	0.433743	1.871536
H	4.124535	0.568266	2.233764
C	2.122950	-0.078068	2.696888
H	2.348129	-0.350758	3.729229
C	3.725023	1.365106	-0.377871
H	4.754935	1.508905	-0.043194
C	-0.268565	-0.826099	3.097806
C	-2.111133	0.818993	-3.139270
Cl	-3.429015	0.342616	-0.014082
O	-2.938056	-3.785554	3.417523
N	-3.386783	-2.803640	2.802353
O	-3.471357	-1.669427	3.306936
C	-3.793104	-2.973024	1.483181
H	-4.159980	-2.091079	0.961779
H	-3.848631	-3.995791	1.117832
Br	-1.278681	-2.660835	0.141321
H	-0.040894	-0.625940	4.154076
H	-1.257612	-0.416460	2.851426
H	-0.333037	-1.918233	2.961586
H	-2.411058	-0.196588	-2.841632
H	-2.775732	1.510171	-2.597888
H	-2.261070	0.947996	-4.219217

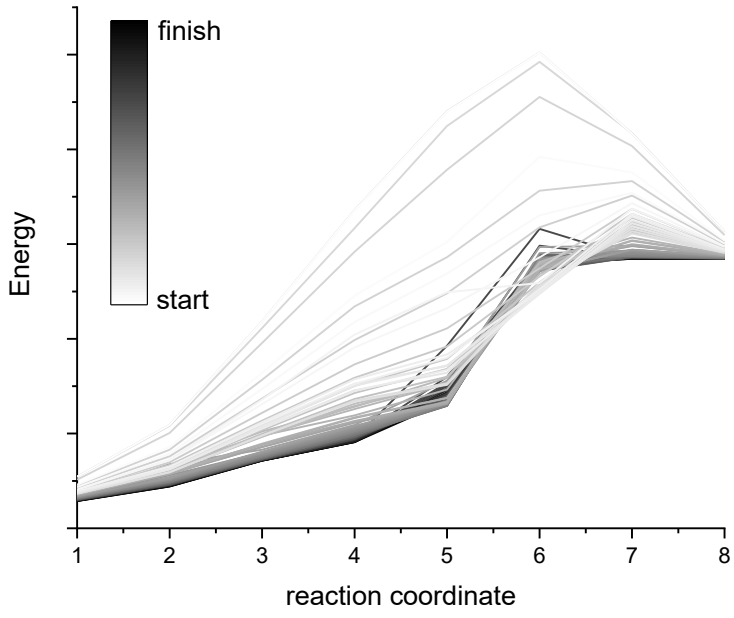


*Figure 64: NEB calculation cycles of **Cu(I)-22a** to **Cu(II)-A**.*

1-Cu(I)-22a to Cu(II)-A

Cu	-1.852580	0.872422	0.645385
N	-0.740376	0.858616	-1.134867
N	0.023951	0.500369	1.439528
C	0.984013	0.474751	0.484229
C	-1.171195	1.023336	-2.384800
C	0.577682	0.680988	-0.887451
C	1.552672	0.664942	-1.913511
C	2.348861	0.245863	0.778008
C	0.345921	0.298533	2.716531
C	1.089446	0.849686	-3.236245
H	1.804136	0.844587	-4.063319
C	-0.260755	1.024214	-3.470050
H	-0.639170	1.161522	-4.484677
C	2.930503	0.441874	-1.580567
H	3.666014	0.433760	-2.388698
C	2.683104	0.037223	2.136833
H	3.725298	-0.142247	2.413616
C	1.690999	0.064044	3.096082
H	1.928093	-0.093969	4.149857
C	3.313105	0.235681	-0.285267
H	4.361829	0.059993	-0.033296
C	-0.766118	0.291526	3.723129
C	-2.646787	1.207130	-2.589788
Cl	-3.944635	1.210609	1.215585
O	-0.141795	-2.689056	1.642536
N	-1.233339	-2.530134	1.139411
O	-2.273252	-2.331442	1.740720
C	-1.399829	-2.548927	-0.365260
H	-1.842238	-1.578448	-0.623697
H	-2.085509	-3.373993	-0.591572
Br	0.249721	-2.782311	-1.322852
H	-0.387487	0.435456	4.744764
H	-1.506707	1.068193	3.481540
H	-1.290004	-0.678567	3.678595
H	-3.199531	0.356263	-2.160403
H	-2.995964	2.105416	-2.055119
H	-2.898075	1.302097	-3.654908

2-Cu(I)-22a to Cu(II)- A

Cu	-1.796938	0.850229	0.641872
N	-0.703055	0.778167	-1.126771
N	0.090409	0.432767	1.444960
C	1.045838	0.468037	0.486305
C	-1.141683	0.941000	-2.375051
C	0.623542	0.658098	-0.883373
C	1.596165	0.707516	-1.910873
C	2.425134	0.333289	0.775541
C	0.431086	0.261197	2.721676
C	1.122943	0.884034	-3.231213
H	1.836782	0.930278	-4.057756
C	-0.234109	0.995956	-3.461190
H	-0.620017	1.131506	-4.473174
C	2.987103	0.575784	-1.582431
H	3.719065	0.625847	-2.392275

C	2.778442	0.151864	2.132966
H	3.831872	0.046682	2.405659
C	1.790292	0.115649	3.096517
H	2.042690	-0.018377	4.150102
C	3.386262	0.394016	-0.288942
H	4.445491	0.295699	-0.038716
C	-0.672893	0.215997	3.737061
C	-2.623729	1.055745	-2.582430
Cl	-3.780007	1.472134	1.362731
O	-0.712100	-2.936204	1.758559
N	-1.643745	-2.530601	1.090698
O	-2.676685	-2.061779	1.525773
C	-1.588906	-2.607858	-0.419308
H	-1.992184	-1.657311	-0.783699
H	-2.224914	-3.454667	-0.708483
Br	0.188214	-2.865913	-1.106530
H	-0.282211	0.306471	4.760207
H	-1.402245	1.016980	3.542313
H	-1.217148	-0.739381	3.650447
H	-3.116185	0.100961	-2.332406
H	-3.046575	1.814561	-1.905833
H	-2.866001	1.311623	-3.622933

3-Cu(I)-22a to Cu(II)- A

Cu	-1.743969	0.770349	0.664177
N	-0.665938	0.701890	-1.116471
N	0.162295	0.369817	1.451486
C	1.107833	0.470695	0.487806
C	-1.114090	0.861211	-2.362127
C	0.667650	0.643763	-0.878850
C	1.632501	0.758087	-1.908997
C	2.495129	0.426296	0.770679
C	0.521050	0.225757	2.726711
C	1.147169	0.924539	-3.226579
H	1.855801	1.019928	-4.053445
C	-0.213864	0.972002	-3.450758
H	-0.609648	1.103595	-4.459501
C	3.030636	0.712506	-1.587453
H	3.753828	0.814818	-2.400280
C	2.867049	0.267764	2.125747
H	3.926710	0.231730	2.392233
C	1.888579	0.168586	3.094871
H	2.155083	0.053277	4.147202
C	3.446408	0.553262	-0.296538
H	4.510790	0.525104	-0.050368
C	-0.573162	0.129499	3.749683
C	-2.599343	0.908937	-2.572269
Cl	-3.576957	1.692206	1.489021
O	-1.491658	-3.179156	1.828465
N	-2.069658	-2.496975	1.007543
O	-2.928856	-1.666611	1.254020
C	-1.758369	-2.682743	-0.456124
H	-2.085244	-1.773746	-0.966043
H	-2.312217	-3.570423	-0.789335

Br	0.126025	-2.954113	-0.759600
H	-0.171782	0.169154	4.771807
H	-1.298640	0.945130	3.603593
H	-1.127783	-0.814933	3.621793
H	-3.024106	-0.108190	-2.513738
H	-3.078066	1.503847	-1.779912
H	-2.851186	1.323141	-3.558448

4-Cu(I)-22a to Cu(II)- A

Cu	-1.703048	0.558061	0.712966
N	-0.623068	0.614732	-1.103249
N	0.243985	0.297096	1.460199
C	1.172590	0.475798	0.491057
C	-1.083203	0.767287	-2.344652
C	0.713787	0.631494	-0.871590
C	1.665030	0.819547	-1.904621
C	2.561917	0.531138	0.767187
C	0.620668	0.181745	2.733074
C	1.165299	0.973032	-3.218776
H	1.864060	1.122195	-4.046182
C	-0.196557	0.944314	-3.436538
H	-0.604580	1.068129	-4.441518
C	3.064878	0.864850	-1.591120
H	3.774930	1.020492	-2.407138
C	2.953030	0.396719	2.119254
H	4.014329	0.436003	2.378743
C	1.990179	0.226731	3.094168
H	2.270415	0.130317	4.144811
C	3.497166	0.728777	-0.303170
H	4.562205	0.772922	-0.062048
C	-0.460071	0.016109	3.761203
C	-2.568886	0.734800	-2.554686
Cl	-3.270251	1.901883	1.610642
O	-2.500855	-3.213952	1.740609
N	-2.531594	-2.390159	0.844711
O	-3.003497	-1.257341	0.945356
C	-1.939395	-2.757976	-0.476429
H	-2.131184	-1.938112	-1.170591
H	-2.386351	-3.707612	-0.792316
Br	-0.024236	-2.999080	-0.290183
H	-0.047556	-0.002852	4.779320
H	-1.188106	0.838651	3.671475
H	-1.016853	-0.918388	3.582449
H	-2.912487	-0.306366	-2.686916
H	-3.087509	1.147523	-1.677089
H	-2.855182	1.291494	-3.458413

5-Cu(I)-22a to Cu(II)- A

Cu	-1.600402	0.409915	0.743604
N	-0.553898	0.511625	-1.091216
N	0.356501	0.230199	1.470895
C	1.258540	0.494165	0.496658

C	-1.030355	0.648363	-2.327615
C	0.780201	0.624258	-0.863694
C	1.707829	0.899395	-1.899019
C	2.640173	0.662944	0.766694
C	0.747554	0.140355	2.741215
C	1.190324	1.034341	-3.208977
H	1.870881	1.249100	-4.036859
C	-0.166106	0.907154	-3.421068
H	-0.589663	1.017565	-4.421373
C	3.101236	1.051952	-1.591944
H	3.792285	1.269402	-2.409876
C	3.048461	0.554762	2.116278
H	4.104130	0.680366	2.370344
C	2.109499	0.299340	3.095623
H	2.402251	0.219022	4.144273
C	3.550065	0.942136	-0.306735
H	4.609310	1.069599	-0.070729
C	-0.310677	-0.120092	3.772818
C	-2.510116	0.513318	-2.540830
Cl	-2.864180	1.975592	1.773919
O	-3.583369	-3.023117	1.405616
N	-3.081125	-2.264435	0.608671
O	-3.224125	-1.032241	0.606965
C	-2.176823	-2.836868	-0.444765
H	-2.172850	-2.146072	-1.297312
H	-2.559634	-3.836491	-0.693832
Br	-0.386072	-2.987473	0.254302
H	0.119180	-0.206767	4.780383
H	-1.051370	0.696824	3.754104
H	-0.857325	-1.046540	3.532774
H	-2.757264	-0.511087	-2.874904
H	-3.054185	0.710543	-1.606242
H	-2.858881	1.198949	-3.328146

6-Cu(I)-22a to Cu(II)- A

Cu	-1.460248	-0.146258	0.863161
N	-0.500564	0.412056	-1.085787
N	0.432619	0.227742	1.487346
C	1.305868	0.541768	0.501226
C	-0.992539	0.546985	-2.312853
C	0.818412	0.634192	-0.856656
C	1.726265	0.973876	-1.888561
C	2.675113	0.781801	0.770926
C	0.824428	0.137199	2.759361
C	1.198055	1.085692	-3.197437
H	1.861917	1.342248	-4.026253
C	-0.149379	0.883847	-3.404877
H	-0.583979	0.981296	-4.401103
C	3.109411	1.200197	-1.587054
H	3.786551	1.452422	-2.404792
C	3.093427	0.681053	2.118717
H	4.143028	0.854001	2.368112
C	2.177982	0.366040	3.100123
H	2.480745	0.282387	4.145282

C	3.568432	1.106936	-0.301098
H	4.619807	1.280888	-0.068208
C	-0.199156	-0.207130	3.798409
C	-2.460485	0.333470	-2.541948
Cl	-2.325322	1.775594	1.756723
O	-4.264477	-2.714848	1.073503
N	-3.458231	-2.129116	0.326130
O	-3.287796	-0.838330	0.407106
C	-2.572622	-2.836871	-0.473145
H	-2.231603	-2.301043	-1.356551
H	-2.796071	-3.901969	-0.550171
Br	-0.615714	-2.732186	0.678572
H	0.265456	-0.349687	4.782669
H	-0.949964	0.597650	3.852437
H	-0.737020	-1.126928	3.516981
H	-2.630471	-0.643877	-3.026957
H	-3.015556	0.349652	-1.597034
H	-2.856317	1.099253	-3.226298

7-Cu(I)-22a to Cu(II)- A

Cu	-1.431694	-0.187210	0.864667
N	-0.496927	0.413352	-1.085964
N	0.436702	0.232704	1.489706
C	1.307872	0.547751	0.500349
C	-0.990217	0.545227	-2.312854
C	0.820754	0.638495	-0.856502
C	1.728287	0.978859	-1.889218
C	2.677393	0.788751	0.771787
C	0.827732	0.140213	2.761072
C	1.198411	1.088308	-3.197906
H	1.862698	1.345672	-4.026940
C	-0.147338	0.883654	-3.405171
H	-0.582679	0.979536	-4.401972
C	3.111042	1.206594	-1.585637
H	3.787937	1.459436	-2.405220
C	3.096281	0.687377	2.118732
H	4.146178	0.860158	2.368195
C	2.181639	0.370629	3.101616
H	2.485205	0.285794	4.146294
C	3.569298	1.114508	-0.302575
H	4.621908	1.289283	-0.068186
C	-0.194532	-0.208729	3.799335
C	-2.457909	0.327460	-2.540272
Cl	-2.290024	1.760932	1.716719
O	-4.316658	-2.718639	1.034843
N	-3.478819	-2.141051	0.325403
O	-3.287619	-0.861245	0.447677
C	-2.655516	-2.841022	-0.513329
H	-2.228117	-2.289805	-1.346794
H	-2.844496	-3.911919	-0.575051
Br	-0.554618	-2.684039	0.757933
H	0.270372	-0.353435	4.782924
H	-0.947039	0.594296	3.855858
H	-0.729671	-1.129199	3.514373

H	-2.626108	-0.648321	-3.029116
H	-3.011557	0.340864	-1.594166
H	-2.858173	1.094760	-3.220610

8-Cu(I)-22a to Cu(II)- A

Cu	-1.423855	-0.198079	0.867436
N	-0.487382	0.389333	-1.087237
N	0.449582	0.211401	1.488917
C	1.316240	0.540320	0.499780
C	-0.981667	0.521693	-2.313885
C	0.827766	0.629596	-0.856650
C	1.730680	0.987501	-1.887733
C	2.682090	0.802109	0.771784
C	0.842636	0.124486	2.760182
C	1.199939	1.096520	-3.195971
H	1.860957	1.367140	-4.023358
C	-0.142773	0.875478	-3.404342
H	-0.579553	0.970733	-4.400514
C	3.109758	1.234905	-1.583618
H	3.782341	1.501939	-2.402206
C	3.102671	0.706505	2.118429
H	4.149309	0.897617	2.368206
C	2.193089	0.374537	3.100730
H	2.497670	0.295058	4.145509
C	3.569190	1.145476	-0.300910
H	4.618583	1.337029	-0.065313
C	-0.173789	-0.233404	3.800905
C	-2.446430	0.290228	-2.545537
Cl	-2.253082	1.762843	1.721606
O	-4.396552	-2.651809	0.985294
N	-3.517877	-2.103887	0.302853
O	-3.292291	-0.830544	0.427478
C	-2.691632	-2.833330	-0.507283
H	-2.225170	-2.303854	-1.333457
H	-2.906908	-3.899609	-0.562934
Br	-0.615963	-2.709290	0.815134
H	0.297006	-0.385551	4.780615
H	-0.924666	0.570373	3.868475
H	-0.711466	-1.150886	3.512240
H	-2.602225	-0.677613	-3.053750
H	-3.000634	0.279065	-1.600011
H	-2.855593	1.065971	-3.210864

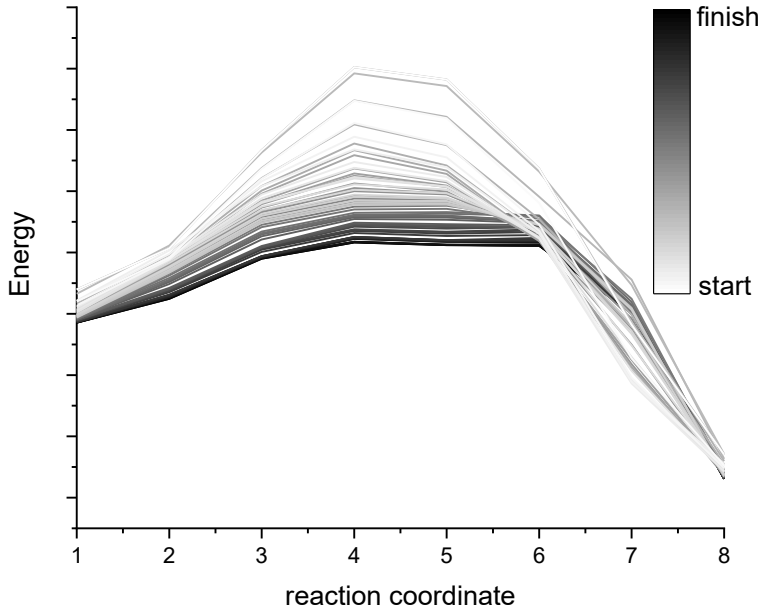


*Figure 65: NEB calculation cycles of **Cu(II)** + **A** to **Cu(III)- A**.*

1-Cu(II) + A to Cu(III)- A

Cu	-1.242424	0.257623	-0.137261
N	0.216790	0.684984	-1.586108
N	0.375302	-0.038390	1.016106
C	1.533895	0.058861	0.314210
C	0.081032	1.010012	-2.872398
C	1.449167	0.441749	-1.068522
C	2.634670	0.540917	-1.833422
C	2.794395	-0.192882	0.900858
C	0.381379	-0.341784	2.314763
C	2.486106	0.903737	-3.192547
H	3.371603	0.994868	-3.826752
C	1.225321	1.128906	-3.703134
H	1.087441	1.399797	-4.751107
C	3.901676	0.268376	-1.217923
H	4.803104	0.348723	-1.829976
C	2.800537	-0.538158	2.273651
H	3.751170	-0.744921	2.771767
C	1.612025	-0.598680	2.970642
H	1.598714	-0.845720	4.033556
C	3.979690	-0.082880	0.100454
H	4.944844	-0.286974	0.569685
C	-0.918206	-0.418459	3.054309
C	-1.290811	1.248353	-3.425134
Cl	-3.063665	1.485757	-0.543526
O	-4.448039	-2.172839	3.102327
N	-4.441152	-1.152038	2.394409
O	-4.150063	-0.025142	2.834254
C	-4.750943	-1.275510	1.044105
H	-4.694335	-0.372506	0.439053

H	-5.155417	-2.232293	0.722052
Br	-2.151422	-2.034850	0.058102
H	-0.766275	-0.209900	4.122458
H	-1.660358	0.280584	2.646259
H	-1.347710	-1.429580	2.960290
H	-1.971115	0.434852	-3.133433
H	-1.716088	2.171940	-3.002864
H	-1.260839	1.333465	-4.519206

2-Cu(II) + A to Cu(III)- A

Cu	-1.211271	0.313561	0.020636
N	0.165027	0.625018	-1.492617
N	0.417056	-0.038301	1.109523
C	1.551624	0.066309	0.372280
C	-0.034245	0.897923	-2.781667
C	1.416796	0.413777	-1.014597
C	2.569530	0.510820	-1.825096
C	2.831644	-0.150486	0.926222
C	0.457863	-0.330503	2.409634
C	2.359618	0.830532	-3.187617
H	3.217470	0.924677	-3.858059
C	1.074931	1.011404	-3.658487
H	0.892496	1.246192	-4.708378
C	3.860443	0.281969	-1.241134
H	4.740933	0.366648	-1.882041
C	2.880065	-0.467818	2.305200
H	3.847304	-0.640887	2.783406
C	1.711040	-0.548378	3.035188
H	1.732167	-0.780233	4.101373
C	3.987422	-0.032780	0.083484
H	4.971588	-0.201891	0.525919
C	-0.830305	-0.438324	3.167192
C	-1.438983	1.068733	-3.274822
Cl	-2.840133	1.823182	-0.198444
O	-4.684772	-2.260922	2.585266
N	-4.484676	-1.157465	2.050846
O	-4.154905	-0.144388	2.694548
C	-4.607847	-1.053731	0.669799
H	-4.395802	-0.081411	0.227158
H	-5.042628	-1.904556	0.152469
Br	-2.032492	-2.035426	-0.007510
H	-0.655386	-0.352929	4.248048
H	-1.549341	0.330774	2.849670
H	-1.303656	-1.413697	2.965316
H	-2.037490	0.176995	-3.027160
H	-1.921446	1.916159	-2.765268
H	-1.459636	1.229456	-4.360280

3-Cu(II) + A to Cu(III)- A

Cu	-1.218178	0.249918	0.067315
N	0.133420	0.562080	-1.482172
N	0.414061	-0.051479	1.133977

C	1.538436	0.054313	0.381745
C	-0.079340	0.839682	-2.767187
C	1.389653	0.378282	-1.009904
C	2.535520	0.491371	-1.827440
C	2.824296	-0.137255	0.930317
C	0.465265	-0.323172	2.438333
C	2.311549	0.805857	-3.189116
H	3.164350	0.912791	-3.864068
C	1.021306	0.971949	-3.652257
H	0.830960	1.210470	-4.700167
C	3.832933	0.287776	-1.248801
H	4.708432	0.381023	-1.895101
C	2.887187	-0.436911	2.312401
H	3.860319	-0.595665	2.783284
C	1.725876	-0.520408	3.054698
H	1.758942	-0.740766	4.123020
C	3.972158	-0.013312	0.077756
H	4.960872	-0.164233	0.516149
C	-0.817302	-0.431750	3.205973
C	-1.494560	1.000488	-3.237148
Cl	-2.639117	1.980452	0.125855
O	-4.714512	-2.284959	2.360509
N	-4.482772	-1.149655	1.918597
O	-4.187764	-0.186071	2.645782
C	-4.537225	-0.946572	0.540538
H	-4.282776	0.049782	0.179978
H	-4.926283	-1.763458	-0.060803
Br	-1.899325	-2.125060	-0.020253
H	-0.630996	-0.382184	4.287047
H	-1.522898	0.361312	2.916797
H	-1.309978	-1.391565	2.977653
H	-2.068478	0.082538	-3.027890
H	-1.988213	1.812960	-2.681721
H	-1.535818	1.211433	-4.313695

4-Cu(II) + A to Cu(III)- A

Cu	-1.339516	0.096381	0.062425
N	0.097637	0.499743	-1.518261
N	0.379971	-0.029441	1.159701
C	1.491160	0.059239	0.389338
C	-0.094091	0.806954	-2.797349
C	1.343949	0.354517	-1.019907
C	2.502011	0.484701	-1.825500
C	2.786008	-0.125299	0.930937
C	0.451636	-0.303439	2.460982
C	2.295294	0.802919	-3.188900
H	3.158041	0.916537	-3.850459
C	1.011366	0.970662	-3.669166
H	0.833919	1.224094	-4.715923
C	3.800191	0.293779	-1.245014
H	4.677122	0.391680	-1.889436
C	2.866540	-0.420630	2.312515
H	3.846434	-0.579179	2.770020
C	1.714945	-0.505589	3.068722

H	1.759598	-0.731423	4.135471
C	3.936409	-0.005715	0.080857
H	4.924427	-0.155185	0.522419
C	-0.828426	-0.420799	3.231233
C	-1.510731	0.978194	-3.261921
Cl	-2.312301	2.069974	0.385256
O	-4.655642	-2.284148	2.303095
N	-4.458534	-1.132896	1.897471
O	-4.202007	-0.177906	2.643134
C	-4.522011	-0.894074	0.517745
H	-4.275151	0.112761	0.181659
H	-4.847732	-1.720437	-0.110023
Br	-1.691585	-2.247312	-0.126922
H	-0.646417	-0.383297	4.313500
H	-1.530013	0.376405	2.944288
H	-1.319078	-1.379797	2.992408
H	-2.088908	0.062334	-3.056394
H	-1.991443	1.790859	-2.693114
H	-1.563072	1.204834	-4.334889

5-Cu(II) + A to Cu(III)- A

Cu	-1.363297	0.069270	0.080290
N	0.060062	0.466698	-1.485298
N	0.376751	-0.045816	1.195764
C	1.477618	0.049846	0.414864
C	-0.147108	0.767007	-2.763952
C	1.311841	0.335213	-0.995375
C	2.460247	0.473031	-1.813532
C	2.780812	-0.116587	0.942851
C	0.465571	-0.310711	2.496732
C	2.238369	0.782547	-3.176291
H	3.094263	0.901584	-3.845705
C	0.948970	0.936522	-3.645801
H	0.759483	1.184193	-4.691737
C	3.766597	0.299787	-1.245885
H	4.634916	0.403785	-1.900824
C	2.879269	-0.401290	2.325529
H	3.865894	-0.544371	2.773538
C	1.736447	-0.494999	3.094428
H	1.794991	-0.712786	4.162189
C	3.920738	0.010341	0.080130
H	4.915167	-0.124809	0.511760
C	-0.808995	-0.433273	3.276025
C	-1.568060	0.924518	-3.218850
Cl	-2.201934	2.099315	0.430148
O	-4.671056	-2.273618	2.093747
N	-4.421200	-1.107240	1.771883
O	-4.188124	-0.205092	2.586975
C	-4.393745	-0.786651	0.405412
H	-4.171145	0.248837	0.147704
H	-4.672824	-1.575909	-0.288474
Br	-1.629007	-2.281359	-0.154012
H	-0.619433	-0.427652	4.357548
H	-1.500009	0.382492	3.015597

H	-1.315869	-1.377350	3.013188
H	-2.130012	-0.005788	-3.033450
H	-2.059164	1.716770	-2.630648
H	-1.627022	1.173549	-4.286469

6-Cu(II) + A to Cu(III)- A

Cu	-1.426844	0.006146	0.103276
N	0.015241	0.428297	-1.464891
N	0.351332	-0.074908	1.212697
C	1.447550	0.030159	0.428047
C	-0.197103	0.733504	-2.741914
C	1.271266	0.309334	-0.981699
C	2.415511	0.460172	-1.804808
C	2.756515	-0.115786	0.950114
C	0.453058	-0.323356	2.515673
C	2.186475	0.769071	-3.166074
H	3.038748	0.896667	-3.838765
C	0.893836	0.914172	-3.628435
H	0.697973	1.164238	-4.672653
C	3.726931	0.302940	-1.244009
H	4.590776	0.415509	-1.903635
C	2.866671	-0.388487	2.333994
H	3.857401	-0.516587	2.777697
C	1.728847	-0.487433	3.109345
H	1.795696	-0.694085	4.178852
C	3.891165	0.020176	0.081947
H	4.889439	-0.101224	0.509092
C	-0.815261	-0.445879	3.305090
C	-1.619066	0.888863	-3.193630
Cl	-2.113524	2.096332	0.489250
O	-4.629634	-2.233794	1.918877
N	-4.322322	-1.064576	1.677327
O	-4.154766	-0.203673	2.546595
C	-4.149445	-0.687888	0.325302
H	-4.053925	0.380051	0.131465
H	-4.410421	-1.442356	-0.412978
Br	-1.565405	-2.357550	-0.145596
H	-0.616551	-0.455926	4.384915
H	-1.498797	0.381372	3.061228
H	-1.333548	-1.381002	3.033439
H	-2.176076	-0.047087	-3.022964
H	-2.112809	1.671168	-2.594611
H	-1.678936	1.153427	-4.257559

7-Cu(II) + A to Cu(III)- A

Cu	-1.645682	-0.115387	0.170321
N	-0.020948	0.401467	-1.454900
N	0.313450	-0.097735	1.204624
C	1.414290	0.013665	0.427635
C	-0.222245	0.718992	-2.730931
C	1.237982	0.291559	-0.979842
C	2.386879	0.453069	-1.800286

C	2.728449	-0.120363	0.949233
C	0.430841	-0.331596	2.509918
C	2.162015	0.766402	-3.160187
H	3.015643	0.898581	-3.831254
C	0.868509	0.910172	-3.618869
H	0.672776	1.165606	-4.662150
C	3.700436	0.302024	-1.241784
H	4.564520	0.419034	-1.901471
C	2.845822	-0.387903	2.332363
H	3.838572	-0.511392	2.774369
C	1.708009	-0.485878	3.106551
H	1.776525	-0.687205	4.177231
C	3.865172	0.020001	0.083629
H	4.864323	-0.096936	0.511780
C	-0.829131	-0.451694	3.311988
C	-1.640952	0.881409	-3.189599
Cl	-2.113846	2.039409	0.513809
O	-4.563900	-2.164103	1.801108
N	-4.181300	-1.011352	1.644651
O	-4.118186	-0.181783	2.543627
C	-3.803553	-0.592605	0.287714
H	-4.100943	0.440997	0.114678
H	-4.137680	-1.347858	-0.430122
Br	-1.506595	-2.431481	-0.105653
H	-0.620303	-0.461325	4.389841
H	-1.511337	0.378219	3.074980
H	-1.349476	-1.387107	3.046397
H	-2.202412	-0.052231	-3.024605
H	-2.132496	1.665482	-2.591546
H	-1.693229	1.149845	-4.253249

8-Cu(II) + A to Cu(III)- A

Cu	-1.485218	-0.122571	0.502004
N	-0.145134	0.319291	-1.317419
N	0.340374	-0.162131	1.339327
C	1.392195	0.002670	0.501330
C	-0.414023	0.568473	-2.595093
C	1.139033	0.244784	-0.899885
C	2.241189	0.410161	-1.776972
C	2.726798	-0.054219	0.974181
C	0.512293	-0.368609	2.645579
C	1.943791	0.657287	-3.137155
H	2.760295	0.788470	-3.851885
C	0.628068	0.739679	-3.541854
H	0.374257	0.939601	-4.584503
C	3.581347	0.333792	-1.271245
H	4.409228	0.462275	-1.972661
C	2.913719	-0.278002	2.357382
H	3.928500	-0.328529	2.760242
C	1.819301	-0.428244	3.183822
H	1.942572	-0.598334	4.254558
C	3.815692	0.112571	0.055130
H	4.835028	0.058914	0.444550
C	-0.701527	-0.528789	3.509163

C	-1.853087	0.662083	-3.011838
Cl	-1.799876	2.005462	1.151974
O	-4.895136	-1.809037	0.507792
N	-4.195941	-0.887893	0.900840
O	-4.160380	-0.494558	2.058260
C	-3.369281	-0.196799	-0.101765
H	-3.677967	0.851199	-0.147671
H	-3.414408	-0.744137	-1.043288
Br	-1.448463	-2.494660	0.290515
H	-0.421949	-0.735592	4.550175
H	-1.309733	0.388928	3.470390
H	-1.331375	-1.351551	3.134655
H	-2.326624	-0.332876	-2.974417
H	-2.405581	1.323899	-2.328383
H	-1.947979	1.046994	-4.035836

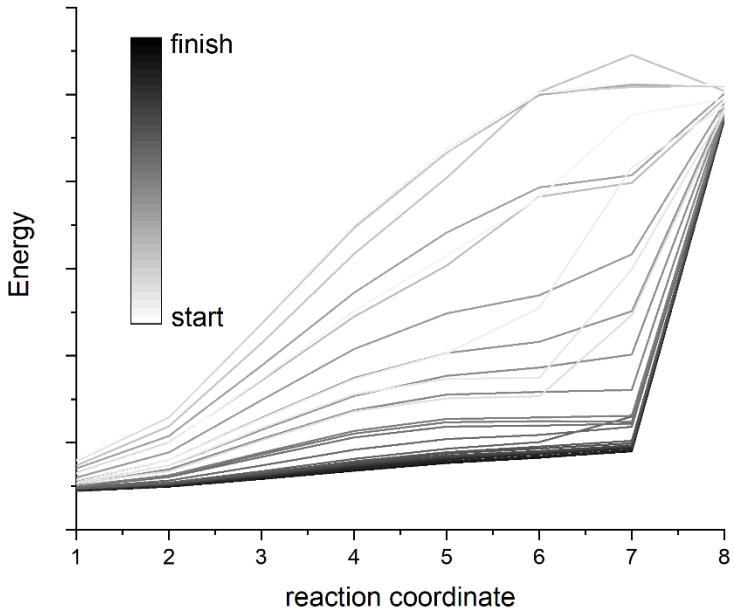


*Figure 66: NEB calculation cycles of **Cu(I)-22a-23** to **Cu(II)-23** + A.*

1-Cu(I)-22a-23 to Cu(II)-23 + A

Cu	-1.403574	-1.420599	-0.458433
N	0.440221	-1.303894	-1.698755
N	0.076955	-1.341098	1.011983
C	1.298892	-1.000447	0.525676
C	0.582884	-1.338164	-3.018970
C	1.491743	-0.988462	-0.908095
C	2.769242	-0.666711	-1.433292
C	2.385969	-0.673055	1.371989
C	-0.125981	-1.402672	2.325713
C	2.909986	-0.698637	-2.841370
H	3.878174	-0.461009	-3.290178
C	1.828753	-1.036433	-3.627768
H	1.917711	-1.074361	-4.715395

C	3.844719	-0.330455	-0.547483
H	4.815914	-0.076599	-0.978870
C	2.152474	-0.715827	2.767945
H	2.963447	-0.465389	3.456873
C	0.912148	-1.084590	3.239049
H	0.711733	-1.137103	4.311200
C	3.657414	-0.328823	0.805223
H	4.476370	-0.075759	1.483013
C	-1.471803	-1.824188	2.836145
C	-0.617308	-1.681343	-3.853561
Cl	-2.419505	-3.463838	-0.706186
H	-1.928753	-1.013646	3.425204
H	-2.140198	-2.089352	2.007216
H	-1.366513	-2.694068	3.505728
H	-0.323225	-2.200952	-4.777580
H	-1.320025	-2.301771	-3.280368
H	-1.141953	-0.756337	-4.151220
C	-2.346322	1.009890	1.005852
C	-3.600338	0.769370	1.601204
C	-3.838163	1.118684	2.930499
C	-2.829051	1.715290	3.697573
C	-1.581995	1.968302	3.115842
C	-1.345661	1.623279	1.784111
H	-4.401835	0.311165	1.017325
H	-4.819729	0.927425	3.372945
H	-3.017614	1.987266	4.739424
H	-0.788285	2.437873	3.703015
H	-0.369609	1.820553	1.335071
C	-2.044712	0.655742	-0.393909
H	-1.157536	1.141129	-0.809973
C	-2.845943	-0.080177	-1.236125
H	-2.634095	-0.108843	-2.307540
H	-3.815708	-0.475064	-0.922438
C	1.750094	2.788501	-2.807141
H	2.483014	2.175701	-3.344236
H	1.888707	3.853598	-3.027575
N	2.063571	2.619549	-1.334034
O	1.229630	2.179113	-0.571777
O	3.193155	2.957921	-1.035287
Br	-0.027484	2.249316	-3.298258

2-Cu(I)-22a-23 to Cu(II)-23 + A

Cu	-1.391136	-1.414661	-0.456773
N	0.449867	-1.341341	-1.686551
N	0.083543	-1.348500	1.021939
C	1.309316	-1.023135	0.535122
C	0.592495	-1.381793	-3.006595
C	1.502656	-1.022129	-0.898229
C	2.780704	-0.707527	-1.425473
C	2.398212	-0.698557	1.380158
C	-0.121309	-1.399482	2.335741
C	2.921024	-0.746318	-2.833270
H	3.889846	-0.514502	-3.283495
C	1.838512	-1.085025	-3.617197

H	1.926521	-1.128749	-4.704697
C	3.857996	-0.373035	-0.541216
H	4.830868	-0.127776	-0.973880
C	2.163058	-0.730696	2.776064
H	2.975272	-0.482222	3.464325
C	0.918875	-1.085360	3.248128
H	0.716949	-1.128989	4.320390
C	3.671885	-0.365870	0.811659
H	4.493081	-0.116105	1.488016
C	-1.468406	-1.816337	2.846589
C	-0.608615	-1.725954	-3.839334
Cl	-2.532555	-3.401008	-0.624648
H	-1.871301	-1.058614	3.536149
H	-2.172030	-1.969895	2.019163
H	-1.377881	-2.759346	3.412539
H	-0.318774	-2.276823	-4.746454
H	-1.326916	-2.316291	-3.254094
H	-1.113728	-0.800490	-4.167806
C	-2.310888	1.030334	0.980728
C	-3.575705	0.796167	1.554618
C	-3.829541	1.134947	2.883306
C	-2.826226	1.715107	3.670405
C	-1.568743	1.962803	3.109437
C	-1.315945	1.627778	1.778379
H	-4.372013	0.351613	0.953277
H	-4.819229	0.948502	3.309192
H	-3.027361	1.978287	4.712045
H	-0.779243	2.419459	3.712283
H	-0.331972	1.819766	1.344932
C	-1.990907	0.682478	-0.415218
H	-1.087220	1.153233	-0.809905
C	-2.784936	-0.037524	-1.276011
H	-2.548102	-0.067955	-2.342232
H	-3.765903	-0.421759	-0.985845
C	1.616817	2.917044	-2.773919
H	2.411980	2.513518	-3.409274
H	1.567297	4.011225	-2.843623
N	2.016569	2.607318	-1.344704
O	1.214440	2.123561	-0.574477
O	3.162962	2.912939	-1.076813
Br	-0.074159	2.167686	-3.292849

3-Cu(I)-22a-23 to Cu(II)-23 + A

Cu	-1.381615	-1.408437	-0.455586
N	0.457472	-1.374710	-1.674869
N	0.088818	-1.353700	1.031783
C	1.317793	-1.043069	0.544320
C	0.600008	-1.422206	-2.994667
C	1.511483	-1.052538	-0.888696
C	2.790078	-0.744950	-1.417856
C	2.408903	-0.721534	1.387890
C	-0.117238	-1.395122	2.345853

C	2.929636	-0.790420	-2.825250
H	3.898807	-0.563030	-3.276922
C	1.846370	-1.131072	-3.606941
H	1.933381	-1.178853	-4.694332
C	3.869350	-0.412201	-0.535337
H	4.843629	-0.174967	-0.969352
C	2.172716	-0.743528	2.783606
H	2.986233	-0.496968	3.471082
C	0.925034	-1.084816	3.256936
H	0.722253	-1.119809	4.329316
C	3.684624	-0.400019	0.817638
H	4.508047	-0.153515	1.492539
C	-1.465865	-1.807654	2.856036
C	-0.602592	-1.765874	-3.825533
Cl	-2.615881	-3.344015	-0.547176
H	-1.816744	-1.113924	3.634695
H	-2.198000	-1.851290	2.040760
H	-1.397904	-2.810288	3.313404
H	-0.317972	-2.344491	-4.716903
H	-1.335309	-2.327280	-3.229882
H	-1.089464	-0.840795	-4.181784
C	-2.279856	1.051584	0.955769
C	-3.553951	0.823583	1.510803
C	-3.821416	1.152006	2.839152
C	-2.823047	1.716211	3.643955
C	-1.556745	1.959009	3.101201
C	-1.289947	1.634022	1.770530
H	-4.345554	0.391091	0.894584
H	-4.817678	0.969194	3.250862
H	-3.034737	1.970350	4.685664
H	-0.770732	2.402601	3.718200
H	-0.299071	1.820944	1.350827
C	-1.943610	0.707919	-0.436357
H	-1.026977	1.166857	-0.813245
C	-2.730511	0.000287	-1.312285
H	-2.472484	-0.031478	-2.373552
H	-3.720448	-0.374786	-1.042294
C	1.486923	3.036009	-2.727002
H	2.309958	2.884137	-3.430963
H	1.233868	4.100001	-2.625663
N	1.988003	2.592160	-1.368080
O	1.224816	2.064209	-0.586730
O	3.153530	2.860279	-1.146642
Br	-0.066382	2.074884	-3.323509

4-Cu(I)-22a-23 to Cu(II)-23 + A

Cu	-1.369658	-1.413873	-0.458186
N	0.464408	-1.404337	-1.663493
N	0.094898	-1.359718	1.041815
C	1.326002	-1.060708	0.553612
C	0.607189	-1.459098	-2.983203
C	1.519862	-1.080153	-0.879196
C	2.799297	-0.780260	-1.410200
C	2.419206	-0.740688	1.395512

C	-0.111869	-1.391285	2.356363
C	2.938638	-0.833627	-2.817097
H	3.908080	-0.610346	-3.270177
C	1.854333	-1.175026	-3.596736
H	1.940259	-1.226070	-4.684028
C	3.880298	-0.447947	-0.529519
H	4.855649	-0.217986	-0.965029
C	2.182502	-0.752741	2.790969
H	2.997190	-0.507310	3.477529
C	0.931942	-1.082413	3.265839
H	0.728794	-1.109066	4.338362
C	3.696704	-0.429533	0.823408
H	4.522020	-0.184994	1.496778
C	-1.461981	-1.799965	2.865455
C	-0.596589	-1.801923	-3.812902
Cl	-2.716979	-3.273753	-0.478107
H	-1.764492	-1.177131	3.719862
H	-2.216181	-1.738923	2.071954
H	-1.422272	-2.847020	3.214794
H	-0.316749	-2.404470	-4.689792
H	-1.341391	-2.337922	-3.209010
H	-1.068072	-0.878508	-4.193694
C	-2.251645	1.073587	0.929730
C	-3.533459	0.849693	1.468634
C	-3.812717	1.167419	2.797025
C	-2.819092	1.717231	3.617562
C	-1.545298	1.955862	3.090957
C	-1.266415	1.641384	1.760299
H	-4.320557	0.426667	0.840171
H	-4.814315	0.986937	3.196590
H	-3.040183	1.963114	4.659270
H	-0.762561	2.387137	3.720730
H	-0.269504	1.823609	1.353004
C	-1.901312	0.735609	-0.459499
H	-0.972007	1.181378	-0.820389
C	-2.679626	0.036708	-1.346962
H	-2.401726	0.000146	-2.402829
H	-3.675685	-0.332735	-1.093485
C	1.353794	3.141656	-2.664733
H	2.160094	3.255279	-3.393460
H	0.906664	4.107481	-2.391461
N	1.969526	2.584832	-1.399715
O	1.255086	2.018576	-0.597485
O	3.156309	2.805675	-1.252964
Br	-0.016406	1.999551	-3.382871

5-Cu(I)-22a-23 to Cu(II)-23 + A

Cu	-1.356609	-1.431890	-0.457901
N	0.469769	-1.428845	-1.652252
N	0.101218	-1.364731	1.052284
C	1.333560	-1.075635	0.562944
C	0.612731	-1.490862	-2.972023
C	1.527054	-1.103806	-0.869871
C	2.807637	-0.812622	-1.402659

C	2.429087	-0.757993	1.403104
C	-0.106072	-1.388057	2.367255
C	2.946944	-0.874885	-2.808956
H	3.917124	-0.657686	-3.263382
C	1.861129	-1.215695	-3.586638
H	1.946509	-1.271184	-4.673737
C	3.890744	-0.481960	-0.523722
H	4.867266	-0.259870	-0.960674
C	2.192157	-0.761172	2.798211
H	3.007955	-0.516907	3.483821
C	0.939133	-1.080360	3.274856
H	0.735806	-1.099634	4.347419
C	3.708370	-0.457559	0.829097
H	4.535635	-0.215727	1.501070
C	-1.458103	-1.792282	2.874506
C	-0.592130	-1.832978	-3.800628
Cl	-2.814322	-3.204708	-0.393797
H	-1.713494	-1.248839	3.795250
H	-2.229091	-1.626395	2.112888
H	-1.453831	-2.871184	3.111417
H	-0.317315	-2.459160	-4.662441
H	-1.347961	-2.344155	-3.189061
H	-1.048538	-0.912141	-4.205241
C	-2.222887	1.095954	0.901293
C	-3.511760	0.874848	1.424965
C	-3.802689	1.181712	2.753328
C	-2.814262	1.717649	3.589228
C	-1.533335	1.952089	3.078515
C	-1.242535	1.648506	1.747818
H	-4.294083	0.459841	0.785367
H	-4.809415	1.003685	3.140923
H	-3.044842	1.955647	4.630729
H	-0.754325	2.371584	3.720776
H	-0.239798	1.826318	1.353178
C	-1.859795	0.765434	-0.486017
H	-0.915007	1.192569	-0.829410
C	-2.629245	0.075822	-1.384458
H	-2.330283	0.030964	-2.433884
H	-3.631495	-0.287057	-1.147275
C	1.212859	3.232247	-2.585542
H	1.961024	3.600752	-3.291245
H	0.596114	4.037401	-2.163845
N	1.950930	2.591505	-1.432828
O	1.300284	1.995032	-0.595951
O	3.154938	2.755834	-1.399074
Br	0.067248	1.960587	-3.467732

6-Cu(I)-22a-23 to Cu(II)-23 + A

Cu	-1.340502	-1.444721	-0.455252
N	0.475052	-1.450869	-1.640621
N	0.108688	-1.369819	1.063352
C	1.341858	-1.090155	0.572690
C	0.617264	-1.519785	-2.960605
C	1.534613	-1.126198	-0.860284

C	2.816288	-0.844414	-1.394964
C	2.439727	-0.775320	1.411088
C	-0.099243	-1.386521	2.378697
C	2.954897	-0.915184	-2.800805
H	3.926331	-0.706722	-3.256635
C	1.866956	-1.254057	-3.576465
H	1.952377	-1.316775	-4.663176
C	3.901864	-0.516552	-0.517758
H	4.879650	-0.302977	-0.956164
C	2.202389	-0.769552	2.805738
H	3.018972	-0.525791	3.490486
C	0.947193	-1.079273	3.284201
H	0.743683	-1.091117	4.356721
C	3.720740	-0.485947	0.834956
H	4.549963	-0.246963	1.505549
C	-1.453788	-1.784761	2.883961
C	-0.588354	-1.863123	-3.787558
Cl	-2.908465	-3.109112	-0.302263
H	-1.660006	-1.333737	3.864409
H	-2.237270	-1.507717	2.168743
H	-1.495004	-2.882467	2.998261
H	-0.318405	-2.514409	-4.632275
H	-1.354652	-2.348775	-3.168133
H	-1.028516	-0.945877	-4.217047
C	-2.191076	1.117517	0.870615
C	-3.487475	0.899298	1.377382
C	-3.791496	1.195127	2.705313
C	-2.809495	1.716637	3.557749
C	-1.521061	1.946790	3.064410
C	-1.216927	1.654599	1.734137
H	-4.264153	0.491912	0.726241
H	-4.803668	1.019967	3.079816
H	-3.050621	1.946308	4.598750
H	-0.746706	2.354380	3.719845
H	-0.208330	1.828275	1.353041
C	-1.813177	0.795519	-0.514510
H	-0.851044	1.200479	-0.836406
C	-2.573374	0.118920	-1.427037
H	-2.250418	0.063545	-2.468471
H	-3.581663	-0.238112	-1.207872
C	1.059289	3.298846	-2.492324
H	1.713413	3.897517	-3.131267
H	0.314331	3.897292	-1.953369
N	1.922669	2.608653	-1.464532
O	1.359574	1.992338	-0.576877
O	3.126714	2.724636	-1.580127
Br	0.150392	1.978247	-3.563355

7-Cu(I)-22a-23 to Cu(II)-23 + A

Cu	-1.316864	-1.468525	-0.455523
N	0.480200	-1.471310	-1.627314
N	0.118274	-1.378052	1.075111
C	1.351583	-1.105285	0.583388
C	0.620272	-1.547832	-2.947505

C	1.543032	-1.148144	-0.849597
C	2.825507	-0.877458	-1.386715
C	2.451703	-0.792911	1.419775
C	-0.090806	-1.387612	2.390558
C	2.962172	-0.957237	-2.792347
H	3.935008	-0.760827	-3.250197
C	1.871099	-1.292863	-3.565118
H	1.956210	-1.366381	-4.651064
C	3.914382	-0.554161	-0.511612
H	4.893706	-0.351116	-0.951517
C	2.213646	-0.778232	2.813852
H	3.030739	-0.535165	3.497949
C	0.956367	-1.078971	3.293810
H	0.752385	-1.083211	4.366060
C	3.734428	-0.515739	0.841257
H	4.565912	-0.280110	1.510121
C	-1.448570	-1.776488	2.894265
C	-0.585273	-1.894309	-3.772824
Cl	-3.011735	-2.979915	-0.209501
H	-1.601777	-1.435134	3.926927
H	-2.238036	-1.377868	2.245765
H	-1.549058	-2.875549	2.873609
H	-0.319176	-2.574314	-4.596121
H	-1.363757	-2.351232	-3.146491
H	-1.005533	-0.982116	-4.231401
C	-2.151843	1.138317	0.836681
C	-3.457335	0.925518	1.322589
C	-3.776944	1.209339	2.649477
C	-2.802774	1.713847	3.520916
C	-1.506094	1.939886	3.047942
C	-1.186010	1.660171	1.718710
H	-4.227098	0.527451	0.657846
H	-4.795238	1.037705	3.008668
H	-3.056134	1.932792	4.561291
H	-0.737836	2.334163	3.718522
H	-0.171618	1.830948	1.352315
C	-1.755518	0.824098	-0.544385
H	-0.774163	1.202526	-0.839068
C	-2.504586	0.166473	-1.475205
H	-2.153147	0.100416	-2.506354
H	-3.519066	-0.185219	-1.277578
C	0.889054	3.339738	-2.388994
H	1.427726	4.127547	-2.925714
H	0.065821	3.712866	-1.768997
N	1.875315	2.638931	-1.485847
O	1.423365	2.012611	-0.541071
O	3.052095	2.730772	-1.765700
Br	0.195986	2.057170	-3.663645

8-Cu(I)-22a-23 to Cu(II)-23 + A

Cu	-1.178170	-1.622423	-0.527263
N	0.480330	-1.424511	-1.609187
N	0.130357	-1.404841	1.071544
C	1.365871	-1.105409	0.589009

C	0.600334	-1.544454	-2.931017
C	1.556570	-1.129544	-0.832412
C	2.834439	-0.889084	-1.378623
C	2.460078	-0.797955	1.428218
C	-0.098930	-1.406613	2.384999
C	2.956246	-0.988742	-2.784870
H	3.926914	-0.812251	-3.255011
C	1.858152	-1.324513	-3.545971
H	1.935521	-1.423567	-4.630195
C	3.926361	-0.580851	-0.504139
H	4.908579	-0.394842	-0.944317
C	2.208588	-0.786883	2.820097
H	3.019176	-0.548343	3.513551
C	0.946224	-1.082661	3.288244
H	0.732609	-1.080933	4.358396
C	3.744336	-0.532118	0.848868
H	4.577257	-0.302807	1.517472
C	-1.454118	-1.781477	2.898388
C	-0.596805	-1.903194	-3.756864
Cl	-3.008591	-2.748274	-0.027654
H	-1.556588	-1.510921	3.956972
H	-2.246113	-1.297325	2.313932
H	-1.603899	-2.868900	2.796543
H	-0.310868	-2.604548	-4.554747
H	-1.392889	-2.355969	-3.150051
H	-0.990601	-0.994799	-4.243475
C	-2.119940	1.151222	0.807615
C	-3.433094	0.935622	1.276656
C	-3.761808	1.213924	2.600603
C	-2.788140	1.706487	3.481126
C	-1.484538	1.931412	3.025619
C	-1.154137	1.665503	1.696458
H	-4.198909	0.548673	0.601708
H	-4.783047	1.048340	2.953223
H	-3.050091	1.918878	4.520967
H	-0.724429	2.317057	3.709260
H	-0.141914	1.845665	1.326854
C	-1.709389	0.855714	-0.566652
H	-0.709707	1.215542	-0.835670
C	-2.435485	0.197777	-1.512461
H	-2.056450	0.146361	-2.534987
H	-3.448119	-0.166763	-1.327178
C	0.868659	3.483549	-2.126300
H	1.271278	4.239526	-2.793844
H	-0.092807	3.603557	-1.636988
N	1.802384	2.720774	-1.451182
O	1.420887	1.984627	-0.504575
O	2.988976	2.732473	-1.841885
Br	0.009453	1.952827	-3.978803

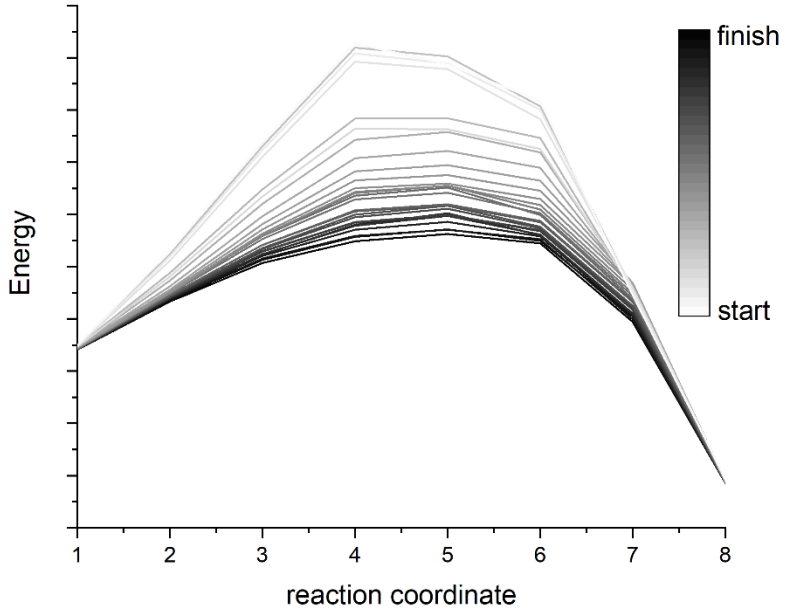


*Figure 67: NEB calculation cycles of **Cu(II)-23** + **A** to **Cu(II)-B**.*

1-Cu(II)-23 + A to Cu(II)-B

Cu	-1.220929	-1.717312	-0.517345
N	0.451326	-1.442802	-1.549348
N	0.036826	-1.500959	1.117830
C	1.263763	-1.117703	0.674168
C	0.609106	-1.525852	-2.869115
C	1.489120	-1.096076	-0.740851
C	2.757799	-0.755978	-1.250924
C	2.315508	-0.761086	1.547430
C	-0.222261	-1.547751	2.424413
C	2.918097	-0.814942	-2.655819
H	3.884590	-0.559255	-3.095874
C	1.864275	-1.210883	-3.448458
H	1.970933	-1.282072	-4.531704
C	3.804195	-0.390246	-0.344199
H	4.777758	-0.120386	-0.758266
C	2.033994	-0.806465	2.932492
H	2.812763	-0.535322	3.649537
C	0.783284	-1.194887	3.360558
H	0.543816	-1.237853	4.423830
C	3.589518	-0.388975	1.005157
H	4.386280	-0.114552	1.700144
C	-1.573296	-1.985383	2.893465
C	-0.544099	-1.936642	-3.729606
Cl	-3.061396	-2.841740	-0.073697
H	-1.668689	-1.842192	3.977128
H	-2.364504	-1.425648	2.376878
H	-1.730332	-3.049417	2.655568
H	-0.195949	-2.600151	-4.534844
H	-1.326991	-2.448831	-3.152786

H	-0.977022	-1.040034	-4.204696
C	-2.027325	1.122808	0.818848
C	-3.327188	0.960150	1.342497
C	-3.585487	1.233134	2.683385
C	-2.552730	1.667337	3.526464
C	-1.261299	1.838827	3.016853
C	-1.002108	1.578959	1.671061
H	-4.139516	0.624550	0.694786
H	-4.597253	1.109314	3.077909
H	-2.759176	1.876412	4.579311
H	-0.453856	2.176666	3.670883
H	0.002176	1.713535	1.263829
C	-1.692537	0.825711	-0.575376
H	-0.711250	1.189020	-0.902486
C	-2.474811	0.171064	-1.474896
H	-2.153939	0.100647	-2.515926
H	-3.478939	-0.180569	-1.228956
C	1.077760	3.586144	-2.624040
H	1.629572	4.049210	-3.438667
H	0.163472	4.018104	-2.225144
N	1.820517	2.818919	-1.751579
O	1.286584	2.418424	-0.684302
O	2.988367	2.497158	-2.069786
Br	-0.158521	1.895867	-4.135736

2-Cu(II)-23 + A to Cu(II)-B

Cu	-1.160199	-1.722042	-0.685993
N	0.653794	-1.489103	-1.479559
N	-0.098162	-1.711931	1.093791
C	1.199202	-1.394844	0.840302
C	0.989688	-1.551179	-2.768007
C	1.595817	-1.256425	-0.527783
C	2.934844	-0.951929	-0.848080
C	2.161451	-1.228012	1.859655
C	-0.514824	-1.876738	2.348309
C	3.272157	-0.928680	-2.222604
H	4.296553	-0.688288	-2.517030
C	2.319822	-1.254576	-3.163558
H	2.573647	-1.303923	-4.223476
C	3.878000	-0.727209	0.206797
H	4.898429	-0.446053	-0.061188
C	1.717638	-1.414184	3.188786
H	2.426777	-1.299145	4.011839
C	0.397795	-1.729880	3.425610
H	0.031992	-1.871147	4.443418
C	3.506379	-0.872639	1.514530
H	4.224130	-0.718206	2.322606
C	-1.938475	-2.252332	2.609661
C	-0.038897	-1.954361	-3.773549
Cl	-3.016298	-2.905506	-0.698696
H	-2.206542	-2.030640	3.651065
H	-2.618795	-1.729490	1.925304
H	-2.068843	-3.334885	2.441136
H	0.439732	-2.521778	-4.585103

H	-0.823775	-2.570483	-3.312389
H	-0.501222	-1.052909	-4.212553
C	-1.659250	1.235149	0.758559
C	-2.840774	1.245814	1.528029
C	-2.820406	1.710012	2.842540
C	-1.625515	2.175274	3.408748
C	-0.448333	2.172061	2.653043
C	-0.464298	1.696799	1.342469
H	-3.788928	0.933034	1.084055
H	-3.746768	1.743589	3.422338
H	-1.618322	2.563102	4.430635
H	0.476448	2.574768	3.072536
H	0.442258	1.712847	0.736643
C	-1.620067	0.844510	-0.653486
H	-0.698893	1.109201	-1.177476
C	-2.622956	0.268838	-1.368810
H	-2.518375	0.141791	-2.447634
H	-3.584675	0.020800	-0.917439
C	-0.427854	3.989981	-2.802626
H	-0.388986	4.563248	-3.724256
H	-1.248305	4.059080	-2.088263
N	0.786496	3.568126	-2.271125
O	0.834882	3.335378	-1.043125
O	1.765258	3.422172	-3.014931
Br	-0.714455	1.702947	-4.573665

3-Cu(II)-23 + A to Cu(II)-B

Cu	-1.090506	-1.725029	-0.762576
N	0.779781	-1.512434	-1.413283
N	-0.182440	-1.796019	1.078091
C	1.145576	-1.533756	0.940326
C	1.212393	-1.537235	-2.674559
C	1.652114	-1.351061	-0.383942
C	3.020568	-1.081335	-0.586867
C	2.031929	-1.468908	2.035640
C	-0.702767	-2.010360	2.286023
C	3.458486	-0.986022	-1.929910
H	4.503768	-0.744073	-2.135505
C	2.572910	-1.242972	-2.954080
H	2.904085	-1.240138	-3.993655
C	3.888584	-0.955193	0.545245
H	4.934851	-0.698828	0.370536
C	1.477069	-1.697557	3.316270
H	2.124564	-1.656048	4.195148
C	0.130122	-1.960359	3.435488
H	-0.318784	-2.135719	4.414195
C	3.413553	-1.160585	1.812146
H	4.073605	-1.083746	2.677787
C	-2.151190	-2.356073	2.418318
C	0.263385	-1.905373	-3.765789
Cl	-2.942308	-2.857033	-1.098078
H	-2.525272	-2.069678	3.410616
H	-2.754833	-1.882277	1.634511
H	-2.267903	-3.449348	2.315649

H	0.811910	-2.412312	-4.573092
H	-0.525608	-2.571566	-3.388423
H	-0.206289	-0.996834	-4.189401
C	-1.409876	1.312362	0.685528
C	-2.472410	1.375555	1.607359
C	-2.269705	1.899298	2.883994
C	-1.003831	2.368297	3.261407
C	0.059218	2.309646	2.355975
C	-0.140784	1.776306	1.081137
H	-3.478623	1.070068	1.307167
H	-3.111749	1.989438	3.575263
H	-0.856498	2.812301	4.249807
H	1.033647	2.725107	2.621292
H	0.672160	1.762326	0.354482
C	-1.567826	0.901410	-0.711079
H	-0.720320	1.104585	-1.358717
C	-2.700241	0.385152	-1.284279
H	-2.738686	0.233245	-2.359561
H	-3.597495	0.188507	-0.705327
C	-1.319751	4.109399	-2.724754
H	-1.665382	4.502359	-3.678329
H	-1.911912	4.081318	-1.810002
N	0.064127	3.945702	-2.546965
O	0.480952	3.927443	-1.378059
O	0.798991	3.841180	-3.529199
Br	-0.875359	1.456869	-4.933968

4-Cu(II)-23 + A to Cu(II)-B

Cu	-1.037167	-1.716629	-0.811363
N	0.869268	-1.522663	-1.356773
N	-0.255795	-1.833879	1.061054
C	1.086730	-1.611191	1.013128
C	1.377751	-1.517342	-2.589850
C	1.679870	-1.410749	-0.271360
C	3.064827	-1.176402	-0.381790
C	1.903517	-1.609357	2.161979
C	-0.857769	-2.078167	2.224790
C	3.584640	-1.036622	-1.691621
H	4.644085	-0.807139	-1.825279
C	2.756465	-1.230672	-2.776092
H	3.147305	-1.185041	-3.793520
C	3.865354	-1.118609	0.803790
H	4.928137	-0.894836	0.701095
C	1.261152	-1.857794	3.398102
H	1.852195	-1.860248	4.316776
C	-0.096795	-2.087632	3.424506
H	-0.609833	-2.284329	4.367065
C	3.306115	-1.345806	2.033111
H	3.914284	-1.319201	2.938357
C	-2.316979	-2.403822	2.255801
C	0.497275	-1.845282	-3.746654
Cl	-2.863662	-2.763449	-1.422646
H	-2.771628	-2.052725	3.192701
H	-2.850417	-1.984649	1.393892

H	-2.431359	-3.501983	2.221933
H	1.095269	-2.307508	-4.545148
H	-0.302178	-2.535138	-3.441786
H	0.038674	-0.926163	-4.163772
C	-1.204538	1.370758	0.596654
C	-2.143300	1.446970	1.641840
C	-1.787835	1.993261	2.874594
C	-0.485930	2.468479	3.086489
C	0.457650	2.393806	2.059200
C	0.104114	1.838582	0.826360
H	-3.178991	1.138241	1.472606
H	-2.541721	2.102666	3.658478
H	-0.221524	2.934180	4.040493
H	1.454658	2.818645	2.193348
H	0.820088	1.817199	0.004504
C	-1.530751	0.959970	-0.768778
H	-0.760059	1.117719	-1.511136
C	-2.753236	0.496205	-1.207728
H	-2.910986	0.328894	-2.266029
H	-3.581828	0.337475	-0.530228
C	-1.987228	4.155048	-2.478906
H	-2.647521	4.283711	-3.336211
H	-2.288315	4.170827	-1.433139
N	-0.608888	4.132264	-2.719678
O	0.157194	4.266152	-1.753520
O	-0.223504	3.980293	-3.884431
Br	-0.616881	1.273679	-5.255207

5-Cu(II)-23 + A to Cu(II)-B

Cu	-1.012534	-1.685498	-0.853671
N	0.918784	-1.516616	-1.314795
N	-0.323049	-1.839381	1.042916
C	1.023821	-1.636681	1.061899
C	1.484466	-1.502888	-2.522466
C	1.679547	-1.432428	-0.190904
C	3.072675	-1.226720	-0.233130
C	1.784832	-1.667391	2.247648
C	-0.982020	-2.106434	2.169987
C	3.656193	-1.080819	-1.514928
H	4.725368	-0.872239	-1.595318
C	2.875698	-1.240847	-2.639897
H	3.314330	-1.186395	-3.636987
C	3.817883	-1.201721	0.989181
H	4.889641	-1.004326	0.938458
C	1.080959	-1.931986	3.446808
H	1.627513	-1.959923	4.392207
C	-0.278281	-2.151479	3.403689
H	-0.835904	-2.368478	4.316036
C	3.196746	-1.430012	2.188400
H	3.762850	-1.428005	3.120914
C	-2.443550	-2.421903	2.126924
C	0.652379	-1.794163	-3.725664
Cl	-2.793330	-2.669025	-1.678744
H	-2.955529	-2.011119	3.008841

H	-2.919947	-2.055709	1.209636
H	-2.563815	-3.519488	2.158260
H	1.282885	-2.234627	-4.511066
H	-0.161737	-2.488164	-3.473798
H	0.226596	-0.858959	-4.137190
C	-1.050031	1.405276	0.503302
C	-1.877036	1.473054	1.637355
C	-1.405313	2.024209	2.827154
C	-0.092404	2.511862	2.906105
C	0.742147	2.445083	1.788925
C	0.272058	1.883730	0.597626
H	-2.922012	1.154632	1.572760
H	-2.078880	2.131229	3.681173
H	0.261154	2.982281	3.828640
H	1.742543	2.882833	1.820043
H	0.900546	1.868300	-0.292490
C	-1.510443	0.999408	-0.822641
H	-0.812868	1.127356	-1.635982
C	-2.792288	0.576399	-1.137644
H	-3.057663	0.403728	-2.170084
H	-3.550781	0.448673	-0.379733
C	-2.404788	4.138156	-2.090778
H	-3.363812	4.144548	-2.606715
H	-2.240434	4.363393	-1.039541
N	-1.269465	4.050042	-2.903227
O	-0.166330	4.323074	-2.410459
O	-1.438954	3.728545	-4.084274
Br	0.311585	1.457616	-5.382762

6-Cu(II)-23 + A to Cu(II)-B

Cu	-0.995914	-1.631526	-0.893728
N	0.976931	-1.505997	-1.274322
N	-0.401486	-1.815955	1.007499
C	0.945544	-1.643309	1.104420
C	1.614793	-1.466726	-2.445447
C	1.673943	-1.446602	-0.107480
C	3.070927	-1.264333	-0.063793
C	1.633075	-1.699473	2.333065
C	-1.129962	-2.094453	2.086624
C	3.732367	-1.108491	-1.304903
H	4.808611	-0.920442	-1.317795
C	3.015323	-1.226619	-2.475189
H	3.512180	-1.154714	-3.443525
C	3.742804	-1.265494	1.200661
H	4.820326	-1.091403	1.213258
C	0.854609	-1.967009	3.484128
H	1.344290	-2.014395	4.459438
C	-0.501685	-2.169861	3.358264
H	-1.115581	-2.393777	4.231854
C	3.049879	-1.490056	2.358676
H	3.560025	-1.507992	3.323266
C	-2.591117	-2.384624	1.952577
C	0.851383	-1.694509	-3.705369
Cl	-2.655196	-2.490450	-2.039100

H	-3.159571	-1.886420	2.751100
H	-2.986721	-2.089551	0.973187
H	-2.744088	-3.471665	2.069685
H	1.524382	-2.080115	-4.483770
H	0.031728	-2.405954	-3.534319
H	0.433191	-0.736219	-4.069577
C	-0.870421	1.423486	0.364411
C	-1.544207	1.491424	1.595406
C	-0.918844	2.040022	2.711645
C	0.394815	2.522666	2.615706
C	1.076916	2.449952	1.400001
C	0.453037	1.890896	0.282192
H	-2.587037	1.170710	1.668012
H	-1.475344	2.147038	3.645287
H	0.865996	2.992289	3.482225
H	2.075689	2.880861	1.300351
H	0.956804	1.867963	-0.685470
C	-1.518295	1.014474	-0.881233
H	-0.911160	1.101789	-1.781741
C	-2.826477	0.657573	-1.019945
H	-3.237209	0.466711	-2.005283
H	-3.494104	0.580990	-0.164693
C	-2.768287	3.913411	-1.821843
H	-3.821919	3.876363	-2.089963
H	-2.363668	4.159600	-0.843344
N	-1.859916	3.898960	-2.887811
O	-0.751034	4.407989	-2.700313
O	-2.228796	3.404076	-3.958167
Br	0.438469	1.758891	-4.974813

7-Cu(II)-23 + A to Cu(II)-B

Cu	-1.039872	-1.446507	-0.968158
N	1.048705	-1.481023	-1.246093
N	-0.471841	-1.779489	0.977793
C	0.868006	-1.639506	1.135851
C	1.754392	-1.414759	-2.371102
C	1.671314	-1.445638	-0.044611
C	3.067725	-1.277856	0.085296
C	1.494073	-1.709582	2.399072
C	-1.249769	-2.063884	2.017425
C	3.802831	-1.112383	-1.112700
H	4.880023	-0.939223	-1.060778
C	3.155416	-1.195552	-2.326459
H	3.704837	-1.104763	-3.263974
C	3.667850	-1.294740	1.385732
H	4.745667	-1.134696	1.459068
C	0.655842	-1.969116	3.510162
H	1.095357	-2.022898	4.508684
C	-0.694921	-2.158257	3.319138
H	-1.356413	-2.375594	4.159004
C	2.910497	-1.516451	2.501837
H	3.367394	-1.544803	3.493129
C	-2.708955	-2.322596	1.794309
C	1.040601	-1.582838	-3.673289

Cl	-2.616939	-2.180317	-2.294564
H	-3.320520	-1.747022	2.505129
H	-3.011461	-2.087668	0.765329
H	-2.916363	-3.391080	1.979388
H	1.741962	-1.916627	-4.450773
H	0.220306	-2.307351	-3.571508
H	0.613078	-0.615276	-3.997906
C	-0.715772	1.385576	0.214086
C	-1.268575	1.485569	1.523805
C	-0.512458	2.020373	2.553020
C	0.793008	2.481903	2.302537
C	1.343970	2.406275	1.016600
C	0.609630	1.840117	-0.014201
H	-2.292796	1.165116	1.717603
H	-0.943694	2.129699	3.550357
H	1.369905	2.934727	3.113079
H	2.329328	2.827914	0.814936
H	0.990705	1.822434	-1.036168
C	-1.474285	1.041996	-0.938416
H	-0.945146	1.039586	-1.898812
C	-2.918241	1.285972	-1.041041
H	-3.362272	0.678932	-1.848284
H	-3.434374	0.988096	-0.095336
C	-2.985586	3.107056	-1.428955
H	-4.026272	3.454221	-1.586193
H	-2.496311	3.739964	-0.668016
N	-2.327532	3.525436	-2.747467
O	-1.427487	4.389503	-2.665782
O	-2.736055	3.067398	-3.751673
Br	0.311486	1.959632	-4.700109

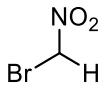
8-Cu(II)-23 + A to Cu(II)-B

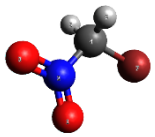
Cu	-0.937566	-1.219600	-1.178836
N	1.223926	-1.363122	-1.124932
N	-0.680135	-1.648464	0.808440
C	0.622111	-1.560678	1.190120
C	2.114565	-1.213569	-2.102155
C	1.626067	-1.390946	0.167209
C	2.982882	-1.257321	0.546824
C	1.015738	-1.627147	2.545715
C	-1.633309	-1.871438	1.711066
C	3.923212	-1.084629	-0.495432
H	4.981767	-0.969915	-0.248497
C	3.494455	-1.067329	-1.805636
H	4.204408	-0.942570	-2.625087
C	3.345769	-1.294641	1.932064
H	4.399393	-1.178523	2.196266
C	-0.006902	-1.830465	3.503809
H	0.255393	-1.882729	4.563495
C	-1.312597	-1.968212	3.089773
H	-2.115537	-2.142610	3.808271
C	2.396583	-1.481211	2.897042
H	2.669518	-1.521828	3.953970
C	-3.054854	-2.015953	1.259631

C	1.616971	-1.176211	-3.514688
Cl	-2.217755	-1.380775	-2.951371
H	-3.678767	-1.218587	1.695309
H	-3.132991	-1.979109	0.165079
H	-3.463908	-2.974660	1.617618
H	2.441750	-1.316604	-4.226844
H	0.851909	-1.949524	-3.675613
H	1.137291	-0.202851	-3.726216
C	-0.330631	1.408799	-0.223955
C	-0.371385	1.489269	1.197852
C	0.766124	1.836870	1.906787
C	1.963474	2.114145	1.223902
C	2.019881	2.061862	-0.176268
C	0.889116	1.711253	-0.896841
H	-1.290761	1.257336	1.737076
H	0.737550	1.886322	2.997079
H	2.858471	2.378213	1.792670
H	2.950638	2.295533	-0.696615
H	0.895360	1.691497	-1.989844
C	-1.459962	1.058352	-1.017019
H	-1.318261	1.129330	-2.104894
C	-2.870139	1.119256	-0.525531
H	-3.502657	0.449409	-1.119888
H	-2.955790	0.833803	0.531076
C	-3.425956	2.544287	-0.632800
H	-4.432200	2.583549	-0.188321
H	-2.789507	3.303417	-0.164817
N	-3.618042	2.976885	-2.066296
O	-3.377251	4.151987	-2.325141
O	-4.027126	2.163013	-2.861574
Br	-0.380334	2.286833	-4.373033

3.5.1. Optimized xyz-Matrices and Thermodynamic Data

22a





0 1

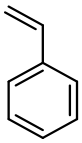
O	-1.15573	-0.41817	0.22424
N	-1.10543	-1.48815	-0.33970
O	-0.74420	-1.66790	-1.49017
C	-1.50070	-2.76475	0.37541
H	-2.29110	-3.21175	-0.21739
H	-0.61057	-3.38464	0.39473
Br	-2.12753	-2.49116	2.17538

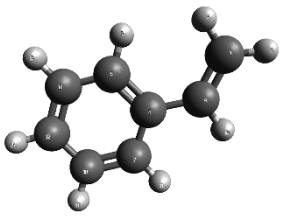
Inner Energy (Hartree): -2818.4091677979

Enthalpy (Hartree): -2818.4082235889

Gibbs Energy (Hartree): -2818.4444397482

23





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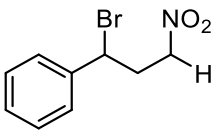
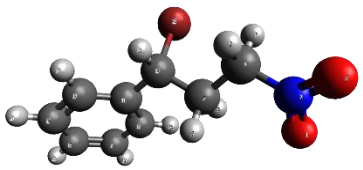
0 1
C       -2.36612        -2.37939        2.39226
H       -2.72603        -1.70449        3.15967
H       -1.31205        -2.32343        2.15241
C       -3.16218        -3.24468        1.76154
C       -4.60239        -3.44199        1.97054
C       -5.35295        -2.69105        2.88650
C       -5.26363        -4.42424        1.22353
C       -6.71138        -2.91892        3.04629
H       -4.87275        -1.92226        3.47817
C       -6.62543        -4.65403        1.38288
H       -4.69797        -5.01274        0.51034
C       -7.35555        -3.90180        2.29578
H       -7.27364        -2.32806        3.75904
H       -7.11485        -5.41986        0.79379
H       -8.41652        -4.07656        2.42355
H       -2.72448        -3.89018        1.00477
```

Inner Energy (Hartree):	-309.4514064371
Enthalpy (Hartree):	-309.4504622280
Gibbs Energy (Hartree):	-309.4889319582

25a





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0 1
O       -1.21122        -0.18873         0.36825
N       -0.74273        -1.23940        -0.03593
O        0.13316        -1.31980        -0.88239
C       -1.24657        -2.53168         0.55021
H       -1.14785        -3.26694        -0.24452
H       -0.52913        -2.76679         1.33763
C       -2.66227        -2.41436         1.07803
H       -2.71049        -1.67700         1.87662
H       -3.31991        -2.07101         0.27376
C       -3.21271        -3.75247         1.54018
C       -4.65566        -3.74654         1.92543
C       -5.20835        -2.72968         2.70748
C       -5.47845        -4.78116         1.47943
C       -6.55830        -2.74773         3.03007
H       -4.58546        -1.92459         3.07521
C       -6.83082        -4.79923         1.80120
```

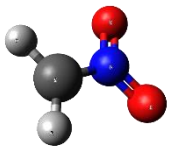
H	-5.05538	-5.57455	0.87482
C	-7.37425	-3.78168	2.57740
H	-6.97572	-1.95333	3.63606
H	-7.45794	-5.60679	1.44480
H	-8.42711	-3.79306	2.83016
H	-3.02255	-4.52925	0.80509
Br	-2.12127	-4.42220	3.12530

Inner Energy (Hartree): -3127.8994173238

Enthalpy (Hartree): -3127.8984731148

Gibbs Energy (Hartree): -3127.9515375536

A-a



0 2

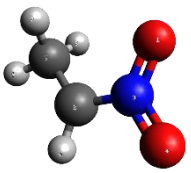
O	-0.50499	1.15504	-0.32414
C	0.40925	-0.90033	-0.08928
O	-1.75655	-0.47904	0.40756
N	-0.67649	-0.02729	0.00299
H	1.33866	-0.48810	-0.44701
H	0.23961	-1.92327	0.20479

Inner Energy (Hartree): -244.3120643759

Enthalpy (Hartree): -244.3111201669

Gibbs Energy (Hartree): -244.3428529154

A-b



0 2

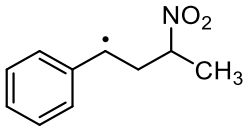
O	-0.55961	1.26694	-0.00008
C	0.59882	-0.69760	0.00003
N	-0.60492	0.02625	-0.00006
O	-1.66653	-0.62568	0.00001
C	1.88646	0.00598	0.00006
H	0.46155	-1.76931	-0.00009
H	1.96938	0.65972	-0.87737
H	1.96856	0.66125	0.87640
H	2.70686	-0.70998	0.00098

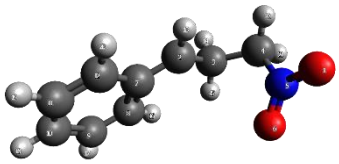
Inner Energy (Hartree): -283.5577756774

Enthalpy (Hartree): -283.5568314683

Gibbs Energy (Hartree): -283.5926650117

B-b





```
0 2
O         3.15460       -1.55798       -0.68710
C        -0.16353       -0.20219        0.76129
C         0.89546        0.84071        0.63974
C         2.29004        0.25279        0.51854
N         2.46129       -0.55510       -0.74740
O         1.92697       -0.15278       -1.76708
C        -1.49979       -0.06616        0.34068
C        -2.00682        1.11007       -0.27534
C        -3.32948        1.19246       -0.66987
C        -4.20225        0.12027       -0.47208
C        -3.72841       -1.04757        0.13371
C        -2.41063       -1.14207        0.53295
H         0.11381       -1.13150        1.24894
H         0.91827        1.47315        1.53878
H         0.70913        1.51508       -0.19569
H        -1.35342        1.95670       -0.43733
H        -3.69099        2.10065       -1.13696
H        -5.23607        0.19291       -0.78458
H        -4.39872       -1.88385        0.29133
H        -2.04905       -2.04943        1.00247
H         3.05188        1.03036        0.44757
H         2.53940       -0.42581        1.32958
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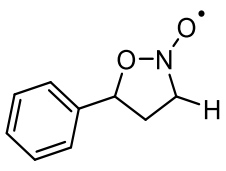
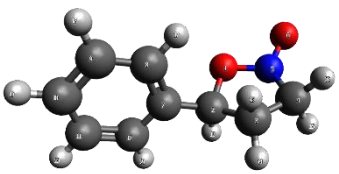
Inner Energy (Hartree): -553.8104947248

Enthalpy (Hartree): -553.8095505158

Gibbs Energy (Hartree): -553.8547736638

C-b





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0 2
O         1.30610        0.38730       -0.83865
C         0.54752       -0.68765       -0.23598
C         1.27101       -0.94082        1.09223
C         2.73276       -0.70281        0.74261
N         2.68120        0.14062       -0.48715
```

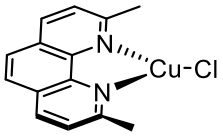
O	3.46781	1.07037	-0.72531
C	-0.88862	-0.26497	-0.12460
C	-1.23865	0.93228	0.50210
C	-2.57264	1.30085	0.61388
C	-3.57260	0.47263	0.10917
C	-3.23013	-0.72161	-0.51404
C	-1.89188	-1.08432	-0.63527
H	0.62428	-1.56771	-0.88012
H	1.08556	-1.94754	1.46056
H	0.93463	-0.22362	1.83997
H	3.26683	-1.61757	0.48749
H	-0.46565	1.57996	0.89603
H	-2.83438	2.23389	1.09723
H	-4.61265	0.76024	0.19997
H	-4.00167	-1.36872	-0.91195
H	-1.62399	-2.01049	-1.12990
H	3.29030	-0.15208	1.49782

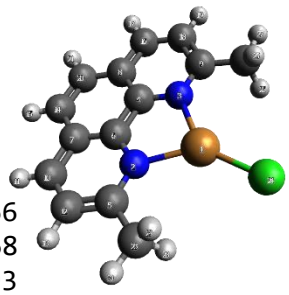
Inner Energy (Hartree): -553.8157138683

Enthalpy (Hartree): -553.8147696592

Gibbs Energy (Hartree): -553.8619070045

Cu(I)dmpCl





0 1

Cu	1.94390	-0.06377	0.01166
N	3.26671	0.08871	-1.59668
N	3.73485	0.00510	1.07493
C	4.79923	0.07272	0.24352
C	2.99728	0.13172	-2.89626
C	4.55078	0.11683	-1.17430
C	5.64024	0.18803	-2.06357
C	6.12678	0.10195	0.71206
C	3.92413	-0.03294	2.38891
C	5.34131	0.23104	-3.43764
H	6.14858	0.28596	-4.15783
C	4.03289	0.20413	-3.84888
H	3.78141	0.23767	-4.90011
C	6.97505	0.21381	-1.55402
H	7.79453	0.26743	-2.25990
C	6.31347	0.05899	2.10573
H	7.31804	0.07899	2.51055
C	5.22268	-0.00679	2.93493
H	5.34400	-0.03946	4.00897
C	7.20916	0.17254	-0.21832
H	8.22025	0.19233	0.16904
C	2.71528	-0.10504	3.26891

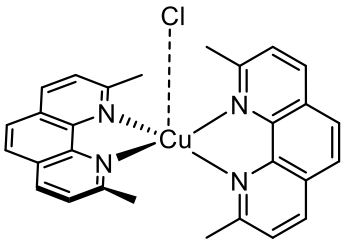
C	1.56043	0.09909	-3.31482
Cl	-0.22160	-0.27287	0.36792
H	2.05881	0.74885	3.07993
H	2.14086	-1.00923	3.04869
H	2.99606	-0.11136	4.32206
H	1.08912	-0.82577	-2.97579
H	1.01409	0.92562	-2.85647
H	1.46488	0.16737	-4.39694

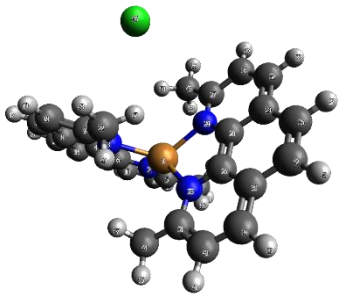
Inner Energy (Hartree): -2750.6679619649

Enthalpy (Hartree): -2750.6670177559

Gibbs Energy (Hartree): -2750.7283343797

Cu(I)dmp$_2$Cl





0 1

Cu	1.64339	0.27912	-0.04220
N	0.03935	-0.99061	-0.00742
N	0.18701	1.66062	0.47789
C	-1.03710	1.08573	0.48604
C	0.00777	-2.29139	-0.27501
C	-1.11706	-0.32276	0.21536
C	-2.37507	-0.95385	0.19267
C	-2.21562	1.81072	0.74381
C	0.31053	2.95477	0.74607
C	-2.39338	-2.33240	-0.08679
H	-3.33890	-2.86003	-0.11413
C	-1.21234	-2.99247	-0.32040
H	-1.20378	-4.05214	-0.53677
C	-3.55431	-0.18845	0.45087
H	-4.51137	-0.69472	0.42957
C	-2.07309	3.18474	1.01086
H	-2.95274	3.78463	1.21006
C	-0.82162	3.74852	1.01563
H	-0.68990	4.80235	1.22011
C	-3.47747	1.14020	0.71870
H	-4.37196	1.71787	0.91640
C	1.69180	3.53004	0.77428
C	1.31274	-2.97343	-0.54170
N	2.76773	0.46562	-1.77362
N	3.49619	0.35422	0.82391
C	4.46417	0.57652	-0.09644
C	2.36831	0.48011	-3.03953
C	4.07811	0.62232	-1.47950

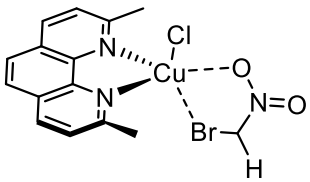
C	5.05918	0.82967	-2.46741
C	5.81545	0.76090	0.25202
C	3.80961	0.32131	2.11436
C	4.62187	0.85554	-3.80427
H	5.34057	1.01604	-4.59866
C	3.29006	0.67781	-4.08594
H	2.93322	0.69301	-5.10676
C	6.42400	1.00656	-2.08175
H	7.16190	1.16814	-2.85782
C	6.13385	0.71823	1.62151
H	7.16134	0.85509	1.93596
C	5.13858	0.50294	2.54246
H	5.36123	0.46631	3.60020
C	6.78700	0.97678	-0.77407
H	7.82100	1.11452	-0.48285
C	2.69656	0.10257	3.09031
C	0.91167	0.26791	-3.30882
Cl	0.98648	4.24950	-3.09489
H	2.27364	3.16646	-0.07275
H	1.66626	4.61848	0.75398
H	2.20614	3.21315	1.68620
H	2.04502	-2.70232	0.22063
H	1.19677	-4.05593	-0.56411
H	1.71359	-2.64729	-1.50526
H	0.62806	-0.75270	-3.04218
H	0.31244	0.94365	-2.69864
H	0.67653	0.43212	-4.35882
H	3.07964	-0.10026	4.08921
H	2.06163	0.99161	3.13625
H	2.06627	-0.72769	2.76722

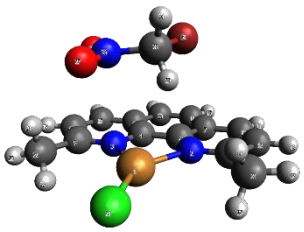
Inner Energy (Hartree): -3400.6135469899

Enthalpy (Hartree): -3400.6126027809

Gibbs Energy (Hartree): -3400.7042222670

Cu(I)-22a





0 1

Cu	1.70748	0.42261	0.45464
N	2.82011	0.40645	-1.32410
N	3.58467	0.04615	1.25319
C	4.53927	0.01902	0.29428
C	2.40236	0.55991	-2.57520
C	4.13506	0.22426	-1.07129
C	5.10607	0.19871	-2.09016
C	5.89573	-0.21817	0.58241

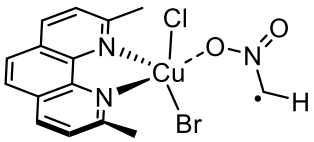
C	3.91678	-0.16350	2.52138
C	4.65292	0.37599	-3.40926
H	5.36557	0.36250	-4.22488
C	3.31363	0.55037	-3.64923
H	2.94266	0.67872	-4.65686
C	6.47657	-0.02994	-1.76117
H	7.20370	-0.04471	-2.56350
C	6.23508	-0.43381	1.93089
H	7.26848	-0.61867	2.19791
C	5.25523	-0.40712	2.88898
H	5.49361	-0.57058	3.93106
C	6.85613	-0.23479	-0.47475
H	7.89398	-0.41613	-0.22425
C	2.82732	-0.16063	3.54671
C	0.93431	0.73968	-2.80522
Cl	-0.38938	0.74109	1.05464
O	3.41700	-3.23126	1.44562
N	2.32873	-3.07157	0.94014
O	1.28356	-2.90689	1.54483
C	2.16267	-3.05553	-0.56380
H	1.73044	-2.08926	-0.80472
H	1.48861	-3.87086	-0.80357
Br	3.81018	-3.27379	-1.53200
H	3.23282	-0.03044	4.54904
H	2.10623	0.62938	3.33775
H	2.28910	-1.11186	3.51710
H	0.38108	-0.10389	-2.38773
H	0.57919	1.63977	-2.29898
H	0.70987	0.82071	-3.86739

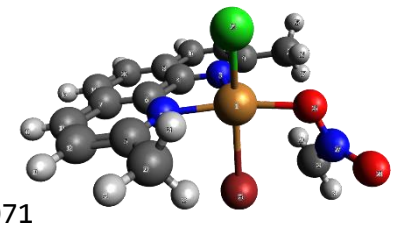
Inner Energy (Hartree): -5569.0883796565

Enthalpy (Hartree): -5569.0874354475

Gibbs Energy (Hartree): -5569.1652905920

Cu(II)-A





0 3

Cu	1.73379	0.01788	-0.39071
N	3.18340	0.15427	-1.73623
N	3.48043	-0.11501	0.96272
C	4.59382	-0.09375	0.19023
C	2.98182	0.29218	-3.04267
C	4.43423	0.04993	-1.22775
C	5.57072	0.08573	-2.05786
C	5.89212	-0.18536	0.72468
C	3.59794	-0.19084	2.27959
C	5.35528	0.23442	-3.43962

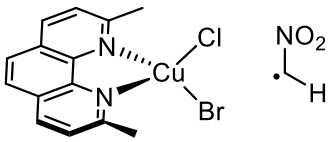
H	6.20553	0.26686	-4.10969
C	4.07728	0.33664	-3.92400
H	3.88987	0.45040	-4.98238
C	6.87187	-0.02385	-1.48230
H	7.72963	0.00367	-2.14225
C	6.00059	-0.29398	2.12501
H	6.98080	-0.36927	2.57950
C	4.86779	-0.28774	2.89150
H	4.92585	-0.35301	3.96976
C	7.02643	-0.15368	-0.14066
H	8.01239	-0.23096	0.30008
C	2.36700	-0.17305	3.13041
C	1.57851	0.38722	-3.54505
Cl	1.24784	2.30316	-0.47487
Br	1.65894	-2.60202	-1.04954
O	0.06164	-0.27047	0.66941
N	-0.46335	-1.46278	0.75208
O	-1.67345	-1.61642	0.50006
C	0.34519	-2.52190	1.01409
H	1.22685	-2.32571	1.59713
H	-0.14137	-3.48312	1.03891
H	1.56342	0.51264	-4.62543
H	1.02300	-0.51735	-3.28714
H	1.06815	1.22964	-3.07544
H	2.50771	0.49830	3.97898
H	1.49634	0.14059	2.56130
H	2.17849	-1.16960	3.54044

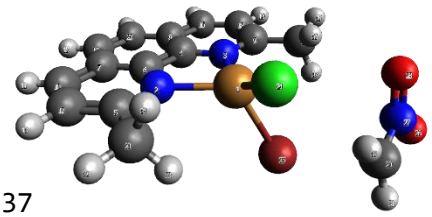
Inner Energy (Hartree): -5569.0584821506

Enthalpy (Hartree): -5569.0575379415

Gibbs Energy (Hartree): -5569.1333709211

Cu(II) + A





0 3

Cu	2.09768	0.40876	-0.33637
N	3.53250	0.79191	-1.79181
N	3.69197	0.07212	0.79745
C	4.84869	0.16588	0.09597
C	3.40321	1.11884	-3.07345
C	4.76386	0.54734	-1.27726
C	5.94116	0.64828	-2.03771
C	6.10104	-0.08525	0.67861
C	3.70683	-0.22940	2.09173
C	5.79552	1.01304	-3.38861
H	6.67372	1.10536	-4.01564
C	4.54343	1.23787	-3.89613

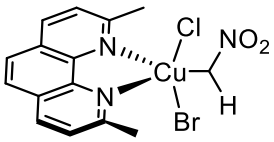
H	4.40662	1.50883	-4.93360
C	7.20270	0.37681	-1.42657
H	8.09556	0.45896	-2.03328
C	6.11133	-0.42913	2.04377
H	7.05440	-0.63368	2.53527
C	4.93212	-0.48776	2.73872
H	4.91942	-0.73133	3.79198
C	7.28070	0.02576	-0.11746
H	8.23705	-0.17585	0.34786
C	2.41950	-0.29906	2.84454
C	2.04161	1.35906	-3.63970
Cl	0.29501	1.66286	-0.71314
Br	1.11878	-1.88937	-0.13854
O	-1.20585	-2.09136	2.90653
N	-1.18387	-1.06971	2.18749
O	-0.92396	0.06452	2.64235
C	-1.43240	-1.19983	0.83944
H	-1.42316	-0.29741	0.25321
H	-1.80338	-2.15158	0.50290
H	2.09171	1.43992	-4.72367
H	1.36277	0.55130	-3.36729
H	1.62043	2.28083	-3.23595
H	2.59237	-0.11379	3.90357
H	1.69559	0.42067	2.46683
H	1.97850	-1.29277	2.73918

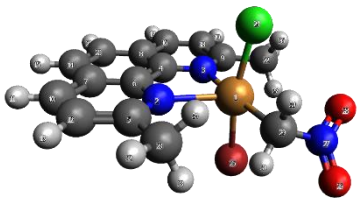
Inner Energy (Hartree): -5569.0569217964

Enthalpy (Hartree): -5569.0559775874

Gibbs Energy (Hartree): -5569.1340629734

Cu(III)-A





0 1

Cu	1.84054	-0.02506	0.34378
N	3.13231	0.40619	-1.53016
N	3.67881	-0.01070	1.12219
C	4.70656	0.15410	0.25672
C	2.84332	0.62232	-2.80466
C	4.42301	0.36224	-1.13626
C	5.49877	0.52571	-2.03303
C	6.04432	0.12648	0.69797
C	3.89278	-0.18933	2.42206
C	5.17608	0.73925	-3.38536
H	5.97141	0.86779	-4.10933
C	3.86107	0.79122	-3.76650
H	3.58859	0.96374	-4.79878
C	6.84394	0.48085	-1.55766

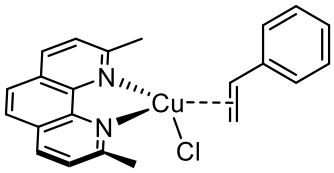
H	7.64748	0.60686	-2.27244
C	6.26945	-0.06601	2.07199
H	7.28578	-0.09266	2.44535
C	5.20625	-0.21709	2.92317
H	5.35631	-0.36364	3.98346
C	7.10687	0.29078	-0.24130
H	8.12484	0.26023	0.12600
C	2.71822	-0.35901	3.33033
C	1.40213	0.67837	-3.20674
Cl	1.49773	2.11076	0.93416
Br	1.92652	-2.39633	0.17561
O	-1.53529	-1.79394	0.44251
N	-0.86732	-0.83387	0.80058
O	-0.85888	-0.39546	1.94182
C	-0.05146	-0.15962	-0.22271
H	-0.38642	0.86752	-0.29844
H	-0.09488	-0.72964	-1.13821
H	1.29649	1.04302	-4.22687
H	0.95569	-0.31742	-3.15415
H	0.84245	1.33304	-2.53829
H	3.04531	-0.55081	4.34979
H	2.10081	0.54118	3.31873
H	2.09354	-1.18943	2.99594

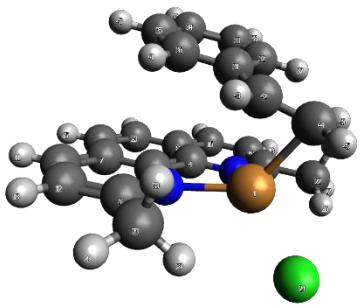
Inner Energy (Hartree): -5569.0637395706

Enthalpy (Hartree): -5569.0627953616

Gibbs Energy (Hartree): -5569.1364995942

Cu(I)-23





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Cu	1.90677	0.40229	-0.10129
N	2.99169	-0.22312	-1.77679
N	3.91947	0.27306	0.73537
C	4.81965	0.11718	-0.26045
C	2.50729	-0.46671	-2.98810
C	4.32962	-0.15734	-1.58562
C	5.24969	-0.32997	-2.63829
C	6.20763	0.22275	-0.04870
C	4.33680	0.52681	1.96616
C	4.72318	-0.59084	-3.91566
H	5.39755	-0.73008	-4.75195
C	3.36460	-0.66248	-4.08800
H	2.93741	-0.86282	-5.06127
C	6.65047	-0.21893	-2.38631
H	7.33462	-0.34935	-3.21567
C	6.63647	0.49920	1.26252

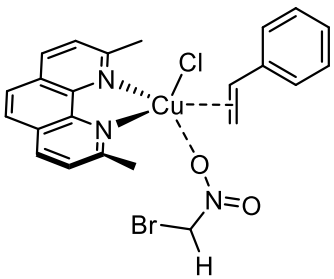
H	7.69605	0.59153	1.46810
C	5.71035	0.64476	2.26146
H	6.01697	0.85194	3.27811
C	7.11167	0.05132	-1.13969
H	8.17378	0.14256	-0.94852
C	3.30696	0.71716	3.03606
C	1.02002	-0.49224	-3.15580
Cl	0.41200	-1.11560	0.81181
H	3.05929	1.77885	3.12904
H	2.39262	0.18026	2.78850
H	3.68180	0.38173	4.00318
H	0.73553	-1.03186	-4.05800
H	0.54432	-0.94932	-2.28854
H	0.63829	0.52942	-3.23919
C	3.20769	3.03763	-0.82209
C	3.91965	3.46017	0.30725
C	5.25826	3.80488	0.21044
C	5.91435	3.74479	-1.01705
C	5.21355	3.35004	-2.15064
C	3.87269	3.00467	-2.05290
H	3.42716	3.50807	1.26934
H	5.79648	4.11629	1.09692
H	6.96336	4.00379	-1.08662
H	5.71359	3.29882	-3.10963
H	3.33388	2.67689	-2.93386
C	1.81317	2.58423	-0.76130
H	1.32804	2.47475	-1.72633
C	1.06395	2.37652	0.35677
H	0.00303	2.18382	0.27147
H	1.44148	2.58287	1.35026

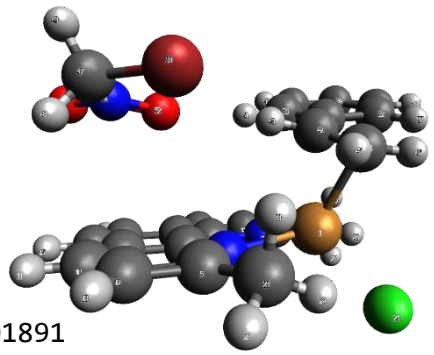
Inner Energy (Hartree): -3060.1412110506

Enthalpy (Hartree): -3060.1402668416

Gibbs Energy (Hartree): -3060.2170074372

Cu(I)-22a-23





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Cu	1.38365	-0.43538	-1.01891
N	3.22282	-0.30170	-2.24648
N	2.86095	-0.33820	0.45907
C	4.08100	-0.00024	-0.02855
C	3.37306	-0.32725	-3.56143

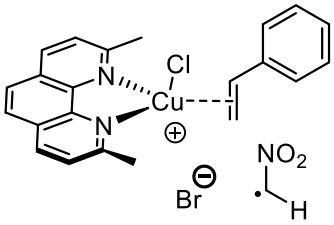
C	4.27282	0.01022	-1.45486
C	5.54258	0.33262	-1.97624
C	5.16177	0.32828	0.81161
C	2.66755	-0.39255	1.76929
C	5.68617	0.30646	-3.37669
H	6.64619	0.54621	-3.81781
C	4.61362	-0.02508	-4.16162
H	4.70228	-0.05724	-5.23924
C	6.61319	0.66847	-1.09537
H	7.57421	0.92331	-1.52446
C	4.93321	0.29218	2.20118
H	5.73817	0.54590	2.88020
C	3.70234	-0.07248	2.67330
H	3.50446	-0.11891	3.73589
C	6.42747	0.67116	0.24845
H	7.23726	0.92683	0.92055
C	1.32799	-0.80537	2.28999
C	2.18201	-0.66065	-4.40477
Cl	0.38605	-2.52226	-1.24134
H	0.88715	-0.00155	2.88150
H	0.65272	-1.05680	1.47600
H	1.43317	-1.67277	2.94580
H	2.48314	-1.17209	-5.31902
H	1.47990	-1.28085	-3.85062
H	1.66430	0.25773	-4.69715
C	0.42271	2.03448	0.45876
C	-0.82225	1.79396	1.05269
C	-1.05415	2.13946	2.37538
C	-0.04794	2.73225	3.13537
C	1.19059	2.98364	2.55495
C	1.42064	2.64182	1.22925
H	-1.61597	1.33640	0.47701
H	-2.02334	1.94588	2.81796
H	-0.23084	2.99757	4.16901
H	1.97995	3.44353	3.13620
H	2.38875	2.83055	0.78407
C	0.72100	1.68146	-0.93627
H	1.61001	2.14906	-1.34276
C	-0.07193	0.95913	-1.77936
H	0.15035	0.92395	-2.83749
H	-1.03842	0.57809	-1.47662
C	4.53901	3.81675	-3.36570
H	5.25745	3.19948	-3.89436
H	4.67084	4.86945	-3.59167
Br	2.75676	3.27537	-3.84403
N	4.85273	3.66201	-1.89195
O	4.02296	3.23032	-1.12281
O	5.98432	4.00342	-1.59619

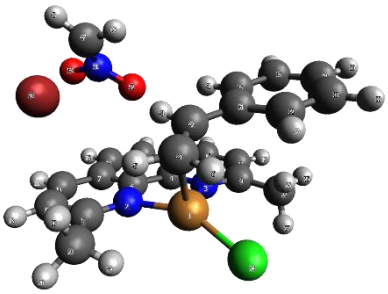
Inner Energy (Hartree): -5878.5532251142

Enthalpy (Hartree): -5878.5522809052

Gibbs Energy (Hartree): -5878.6453617695

Cu(II)-23 + A





0 3			
Cu	1.63026	-0.64319	-1.06777
N	3.26804	-0.42761	-2.14151
N	2.91287	-0.39455	0.52297
C	4.14929	-0.10011	0.04544
C	3.39650	-0.54941	-3.45761
C	4.34281	-0.13433	-1.36546
C	5.61477	0.09850	-1.90640
C	5.23218	0.21294	0.88220
C	2.68497	-0.38460	1.83153
C	5.74075	-0.00295	-3.30491
H	6.70375	0.17278	-3.76782
C	4.65058	-0.33456	-4.06310
H	4.72895	-0.43501	-5.13653
C	6.69993	0.40847	-1.03431
H	7.67347	0.59372	-1.46956
C	4.97760	0.23892	2.26574
H	5.77788	0.48594	2.95235
C	3.72221	-0.05289	2.72815
H	3.50409	-0.03968	3.78671
C	6.51294	0.47284	0.30877
H	7.33376	0.71298	0.97257
C	1.33478	-0.74948	2.35138
C	2.21092	-0.90949	-4.29117
Cl	-0.18462	-1.79387	-0.58118
H	1.24364	-0.46764	3.39787
H	0.54843	-0.26815	1.77566
H	1.18511	-1.82831	2.26706
H	2.50793	-1.60414	-5.07708
H	1.41886	-1.36532	-3.69946
H	1.81662	-0.01310	-4.77659
C	0.64893	2.17631	0.24670
C	-0.65765	1.96610	0.71123
C	-0.98746	2.24949	2.02588
C	-0.02088	2.74301	2.90179
C	1.27645	2.96192	2.45123
C	1.60729	2.68733	1.13201
H	-1.41551	1.58077	0.04229
H	-1.99893	2.08383	2.37464
H	-0.28229	2.95694	3.93053
H	2.03004	3.34433	3.12786
H	2.61454	2.85367	0.77266
C	1.06371	1.87025	-1.11806
H	2.05729	2.21894	-1.38043

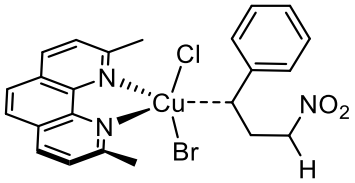
C	0.34865	1.21342	-2.05774
H	0.73177	1.14117	-3.06538
H	-0.66081	0.86752	-1.88466
C	3.65876	4.51064	-2.70334
H	4.04284	5.24960	-3.38363
H	2.69705	4.60660	-2.23173
Br	2.80926	2.98057	-4.56218
N	4.59218	3.77983	-2.02175
O	4.21838	3.05457	-1.05910
O	5.79154	3.80053	-2.40707

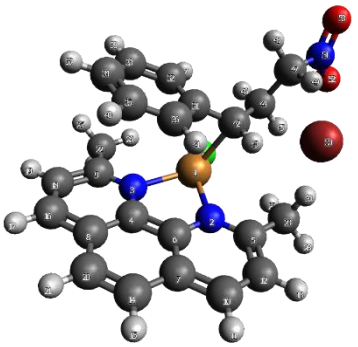
Inner Energy (Hartree): -5878.5139507291

Enthalpy (Hartree): -5878.5130065200

Gibbs Energy (Hartree): -5878.6060803648

Cu(II)-B





0 1

Cu	1.36118	-0.18256	-0.83358
N	3.07649	0.13816	-1.84832
N	2.70326	-0.44562	0.78542
C	3.93296	-0.03073	0.38661
C	3.23968	0.29835	-3.15631
C	4.13602	0.24999	-1.00453
C	5.41547	0.61144	-1.46010
C	5.00629	0.12418	1.28163
C	2.48040	-0.71392	2.06397
C	5.57279	0.80742	-2.84644
H	6.54404	1.08477	-3.23724
C	4.50456	0.63154	-3.68300
H	4.60741	0.75558	-4.75207
C	6.48517	0.75412	-0.52747
H	7.45897	1.04408	-0.90130
C	4.74864	-0.13924	2.64170
H	5.54270	-0.01622	3.36792
C	3.50185	-0.54885	3.02603
H	3.28135	-0.76197	4.06322
C	6.28422	0.53131	0.79675
H	7.09238	0.64635	1.50798
C	1.14358	-1.23503	2.48305
C	2.06489	0.13859	-4.06454
Cl	-0.44097	-1.49250	-0.89051
H	0.82299	-0.76308	3.41216
H	0.39531	-1.07729	1.71146
H	1.21715	-2.31032	2.67234
H	2.37154	-0.33850	-4.99552

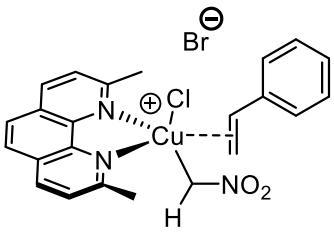
H	1.28163	-0.45519	-3.59705
H	1.66040	1.12260	-4.31886
C	0.69447	2.04996	-0.10628
C	-0.23339	1.81981	0.94176
C	0.10363	2.13039	2.23974
C	1.35927	2.67411	2.52646
C	2.27817	2.93378	1.50880
C	1.95580	2.62479	0.20669
H	-1.19269	1.37458	0.72127
H	-0.59692	1.94048	3.04144
H	1.62050	2.89877	3.55273
H	3.24091	3.36673	1.74345
H	2.64921	2.82644	-0.59847
C	0.43164	1.70344	-1.45969
H	1.19686	2.00967	-2.16553
C	-0.92255	1.53473	-2.05821
H	-0.85233	0.89853	-2.93765
H	-1.63811	1.09292	-1.37082
C	-1.39556	2.92481	-2.49122
H	-1.63061	3.57243	-1.65111
H	-0.66341	3.42458	-3.13097
Br	2.08136	4.07045	-3.63741
N	-2.65476	2.85899	-3.31714
O	-2.89333	1.84895	-3.95483
O	-3.35426	3.85891	-3.32285

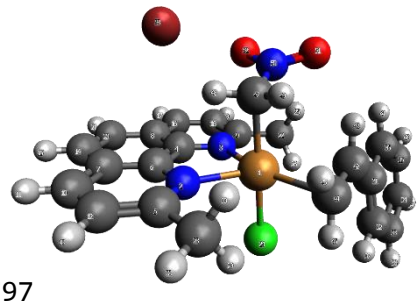
Inner Energy (Hartree): -5878.5608658722

Enthalpy (Hartree): -5878.5599216631

Gibbs Energy (Hartree): -5878.6516022999

Cu(III)-23-A





0 1

Cu	1.69444	-0.54089	-0.93797
N	3.39874	-0.05382	-2.25485
N	3.21157	-0.35205	0.46573
C	4.40188	-0.01341	-0.07381
C	3.45870	0.07508	-3.57253
C	4.49936	0.15171	-1.50099
C	5.73900	0.51577	-2.06499
C	5.55026	0.17263	0.72066
C	3.09125	-0.54703	1.77249
C	5.79014	0.65639	-3.46323
H	6.72380	0.93591	-3.93591
C	4.66256	0.43368	-4.21033

H	4.68091	0.53073	-5.28719
C	6.87671	0.71752	-1.22722
H	7.81352	1.00102	-1.69030
C	5.41357	-0.02185	2.10570
H	6.27400	0.11453	2.74927
C	4.19875	-0.38606	2.62473
H	4.07232	-0.55074	3.68574
C	6.78626	0.54776	0.11496
H	7.64850	0.69242	0.75374
C	1.75512	-0.94249	2.31141
C	2.20972	-0.16216	-4.36160
Cl	2.05655	-2.82695	-1.10439
H	1.04791	-0.11574	2.22652
H	1.35056	-1.77847	1.74008
H	1.82495	-1.22537	3.35986
H	2.41375	-0.15405	-5.43060
H	1.76564	-1.12078	-4.08999
H	1.47387	0.61596	-4.14480
C	-1.25036	-1.74631	0.29470
C	-1.24957	-3.11039	-0.02814
C	-1.62613	-4.05311	0.91420
C	-2.01461	-3.65372	2.19239
C	-2.03060	-2.30223	2.52231
C	-1.65245	-1.35762	1.57949
H	-0.94879	-3.43228	-1.01452
H	-1.62019	-5.10438	0.65495
H	-2.30841	-4.39508	2.92500
H	-2.33504	-1.98672	3.51215
H	-1.65561	-0.30496	1.83414
C	-0.86377	-0.70522	-0.64776
H	-1.00678	0.30539	-0.28229
C	-0.40998	-0.86587	-1.91617
H	-0.31722	-0.00974	-2.57013
H	-0.30661	-1.83954	-2.37237
C	1.35167	1.63773	-0.84869
H	2.32124	1.96633	-1.18340
H	0.51127	1.78640	-1.51062
N	1.07353	2.04768	0.44107
O	-0.09273	2.09793	0.86813
O	2.02643	2.32828	1.23861
Br	4.03542	3.62194	0.34497

Inner Energy (Hartree): -5878.4868736773

Enthalpy (Hartree): -5878.4859294682

Gibbs Energy (Hartree): -5878.5778106869

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