Visible Light Induced C-C Bond Formation

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Table of Contents

1. Copper in Photocatalysis

1.1	Introduction	1
1.2	Photophysical properties of copper catalysts	1
1.3	Early examples of copper catalysis with UV light	5
1.4	Copper as visible light photoredox catalyst	8
1.5	Conclusion	16
1.6	References	16

2. Aim of the work

2.1	Allylation and atom transfer radical radical addition (ATRA) by copper photocatalyst	19
2.2	Vinyl radical generation by visible light photocatalysis and its synthetic applications	19
2.3	References	20

3. Visible Light Mediated Allylation of α-halo carbonyl Compounds

3.1	Introduction	21
3.2	Photochemical allylation of organic halides	21
3.3	Allylation of α-halocarbonyl compounds with visible light	23
3.4	Proposed reaction mechanism	28
3.5	Conclusion	28
3.6	Experimental part	29
3.7	References	48

4. Atom Transfer Radical Addition (ATRA) of Benzyl halides to Styrenes and Silyl enol ethers

4.1	Introduction	50

4.2	Visible light mediated atom transfer radical addition	51
4.3	Benzyl radical by visible light photocatalysis	53
4.4	ATRA of benzyl halides to Olefins	56
4.5	Synthesis of tetrahydroquinolines	63
4.6	Proposed reaction mechanism	64
4.7	Conclusion	65
4.8	Experimental part	66
4.9	References	108

5. Photocatalytic Vinyl Radical Formation and its Synthetic Utility

5.1	Introduction	110
5.2	Vinyl radical by thermal process	110
5.3	Cascade cyclization via visible-light photoredox catalysis	114
5.4	Visible-light induced vinyl radical formation	117
5.5	Cascade cyclizations of α-bromochalcones or -cinnamates with heteroarenes	119
5.6	Mechanistic Investigation	125
5.7	Conclusion	128
5.8	Experimental part	129
5.9	References	188

6. Visible Light Mediated Synthesis of Dihydronaphthalenes

6.1	Introduction	190
6.2	Literature procedures for dihydronaphthalene synthesis	190
6.3	Intermolecular vinyl radical annulations to olefin by photoredox catalysis	190
6.4	Synthetic applications of dihydronaphthalenes	195
6.5	Proposed reaction mechanism	195
6.6	Conclusion	197

6.7 Experimental part 197
6.8 References 233

7. Visible Light triggered α-vinylation of Enol acetates - Access to α-vinyl carbonyls

7.1 Introduction 234
7.2 Literature precedence for α-vinylation of carbonyls 234
7.3 Visible light mediated α-vinylation of enol acetates 235
7.4 Reaction mechanism 240
7.5 Conclusion 240
7.6 Experimental part 241
7.7 References 277

8. Summary 278

9. Zusammenfassung 280

10. Abbreviations 282

11. Acknowledgements 283

12. Curriculum Vitae 284

1. Copper in Photocatalysis

1.1 Introduction

One of the fundamental goals for synthetic organic chemists has been small molecule activation by means of new methodologies and transformations. Among many catalytic processes, light activation of molecules has evoked large attention from the view of its application in rapid and efficient synthesis of fine chemicals. Ciamician,[1] in 1913 addressed the bright future of photochemistry owing to the vast natural abundance of solar energy. Since then photochemistry has turned out as a powerful tool for synthetic organic chemist and several reviews have been published on this field.[2,3]

Most prevalently used photoredox catalysts are metal complexes based on ruthenium or iridium. Though advantageous in terms of stability and activity, these expensive rare transition metal complexes pose severe drawbacks with respect to large scale application and sustainability. Consistent effort has been put to introduce inexpensive dyes as photocatalysts and applied successfully in many transformations.[4] With the rejuvenation of photoredox catalysis, copper complexes as photoredox catalysts has received its due attention recently. Strong reducing power, sufficient life time and high luminescence of such complexes in their excited state has already been explored aiming at practical applications, e.g., for photocatalytic hydrogen production from water,[5] as photosensitizer in photoelectrochemical cells[6] or as active components in organic light emitting diodes (OLED).[7] In contrast, the use of copper complexes as photoredox catalysts for organic synthesis was rare until recently.[8]

1.2 Photophysical properties of copper catalysts

Before discussing the synthetic transformations mediated by copper based photocytalysts, it is necessary to account for the photo physical properties of such complexes and compare them with some of the prevalently used ruthenium and iridium complexes.

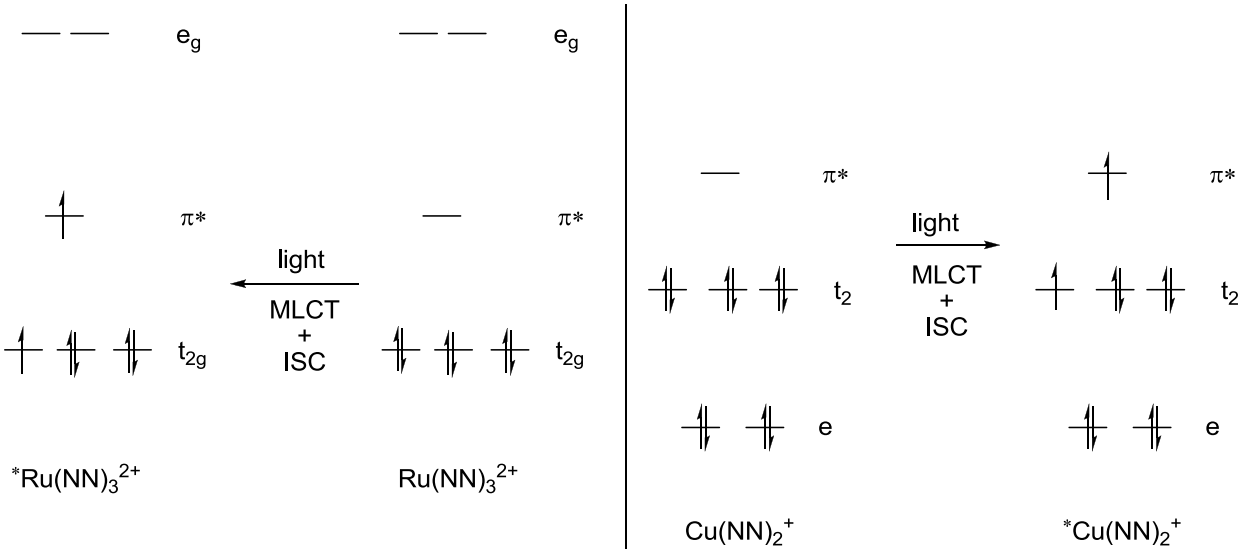
Pioneering work by McMillin and coworkers[9] relating to the excited state properties of Cu^{I}-phenanthroline derivatives **3** has established these complexes as attractive alternatives to ruthenium complexes.

In $[Cu(NN)_2]^+$ **3**, where NN is a bidentate heteroaromatic ligand like 1,10-phenanthroline **1**, the metal centre has a d^{10} electronic configuration with a distorted tetrahedral geometry. When irradiated by light, an electron from the metal centered t_2 orbital is promoted to the lowest energy (LUMO) ligand centered π^* orbital, which is known as metal to ligand charge transfer (MLCT). This effectively results in the oxidation of Cu(I) to Cu(II) and single electron reduction of the ligand within the metal complex (Eq. 1).[10] The primary singlet MLCT state rapidly endures intersystem crossing (ISC) to attain the stable triplet excited MLCT state (Scheme 1.1).

$$[Cu^{I}(NN)_2]^+ \xrightarrow{h\nu} [Cu^{II}(NN)(NN^{-\bullet})]^{+*} \quad \text{..... (1)}$$

For $[Ru(NN)_3]^{2+}$,e.g. $[Ru(bpy)_3]^{2+}$ (bpy = 2,2´-bipyridine), the MLCT triplet excited state is a more potent reductant as well as oxidant than the ground state species. In case of $Cu(NN)_2^+$, the excited state, though a potent reductant, is only a mild oxidant reflecting the general low tendency for reducing ground state copper(I) compounds. Due to this fact, examples for reductive quenching of excited copper complexes are scarce.

Scheme 1.1. Simplified molecular orbital depiction of low-spin d^6 Ru^{2+} and d^{10} Cu^+ complex



To illustrate and compare the potential of excited ruthenium and iridium complexes with that of copper, some of their main photophysical properties are depicted in Table 1. It is evident that excited $[Cu(dap)_2]^+$ (dap=2,9-bis(4-anisyl)-1,10-phenanthroline) is a much stronger reductant

(1.43 V) than excited $[Ru(bpy)_3]^{2+}$ (0.81 V) or $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]^+$ (0.89 V; dF(CF3)ppy = 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine, dtbbpy = 4,4-di-*tert*-butyl-2,2-dipyridyl). Only *fac*-$Ir(ppy)_3$ (ppy = 2-phenylpyridine) has a more negative potential than copper. In terms of excited state life time, however, $[Cu(dap)_2]^+$ is the least stable by a factor of 5 to 10 when compared to related ruthenium or iridium complexes.

Table 1.1. Comparison of reduction potential of copper catalyst with ruthenium and iridium catalysts[a]

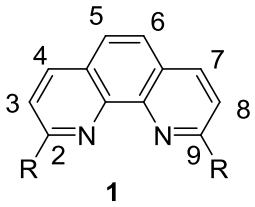
entry	photocatalyst	$E_{1/2}$ (M^*/M^+) (V)	$E_{1/2}$ (M^+/M) (V)	excitation λ_{max} (nm)	excited state lifetime (ns)	reference
1	$[Cu(dap)_2]^+$	-1.43	+0.62	437	270	11a
2	$[Ru(bpy)_3]^{2+}$	-0.81	+1.29	452	1100	11b
3	$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]^+$	-0.89	+1.69	380	2300	11c
4	$[Ir(ppy)_2(dtbbpy)]^+$	-0.96	+1.21		557	11d
5	*fac*-$Ir(ppy)_3$	-1.73	+0.77	375	1900	11e

[a] Potentials are measured against saturated calomel electrode (SCE) in MeCN at room temperature

The short excited state life time of the Cu^I-phenalthroline complexes **3** is rationalized in terms of excited state reorganization from a ground state tetrahedral geometry to a to a square planner geometry resulting in exciplex quenching,[12] and thus limiting their application in photocatalysis. Appropriate substitution at the 2,9-positions of phenanthrolines and incorporation of bulky chelating phosphine ligands have shown to increase the life time of the excited triplet state as well as photostability by preventing excited state structural relaxation and hence exciplex quenching. McMillin and coworkers introduced this new category of $[Cu(NN)(POP)]^+$ complexes **4** (POP = bis[*2*-(diphenylphosphino)phenyl]ether), which have long excited life time due to inefficient exciplex quenching.[14] A comparison of excited state life times and absorption maxima of copper complexes with increasing ligand bulkiness is delineated in Table 1.2. From this analysis it becomes clearly evident that the bulkiness of ligands increases the life time of excited states to the microsecond region (entries 6, 7) concurrent with a blue shifted absorption maximum. Thus one of the significant advantages of photoactive copper complexes is that by

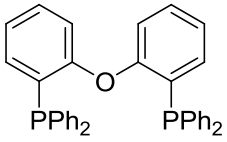
changing the nature of the chelating ligands, they can be widely tuned to meet the requirements for a given photochemical process.

Table 1.2. Effect of ligand substitution for copper complex

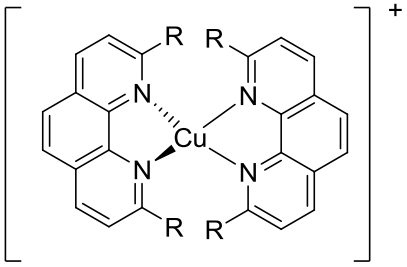


1

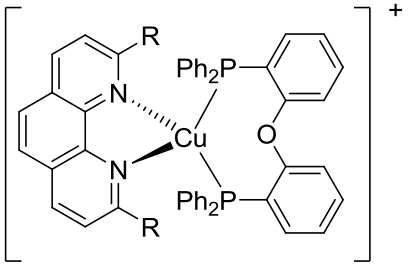
1a, R = H, phen
1b, R = Me, dmp
1c, R = *n*-Bu, dbp
1d, R = Ph, dpp
1e, R = 4-methoxy phenyl, dap



2
POP



3
$[Cu(NN)_2]^+$



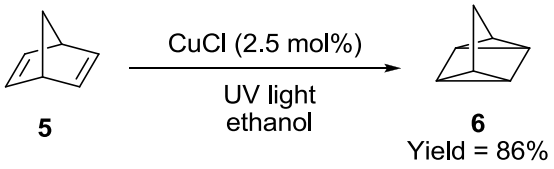
4
$[Cu(NN)(POP)]^+$

R	photocatalyst	excitation λ_{max} (nm)	excited state lifetime (ns)	reference
H	$[Cu(phen)_2]^+$	458	<20	13
Me	$[Cu(dmp)_2]^+$	454	85	13
Ph	$[Cu(dpp)_2]^+$	448	250	13
4-OMe-C_6H_4	$[Cu(dap)_2]^+$	437	270	11a
Ph	$[Cu(phen)(POP)]^+$	391	190	14
Me	$[Cu(dmp)(POP)]^+$	383	14300	14
n-Bu	$[Cu(dbp)(POP)]^+$	378	16100	14

1.3 Early examples of copper catalysis with UV light

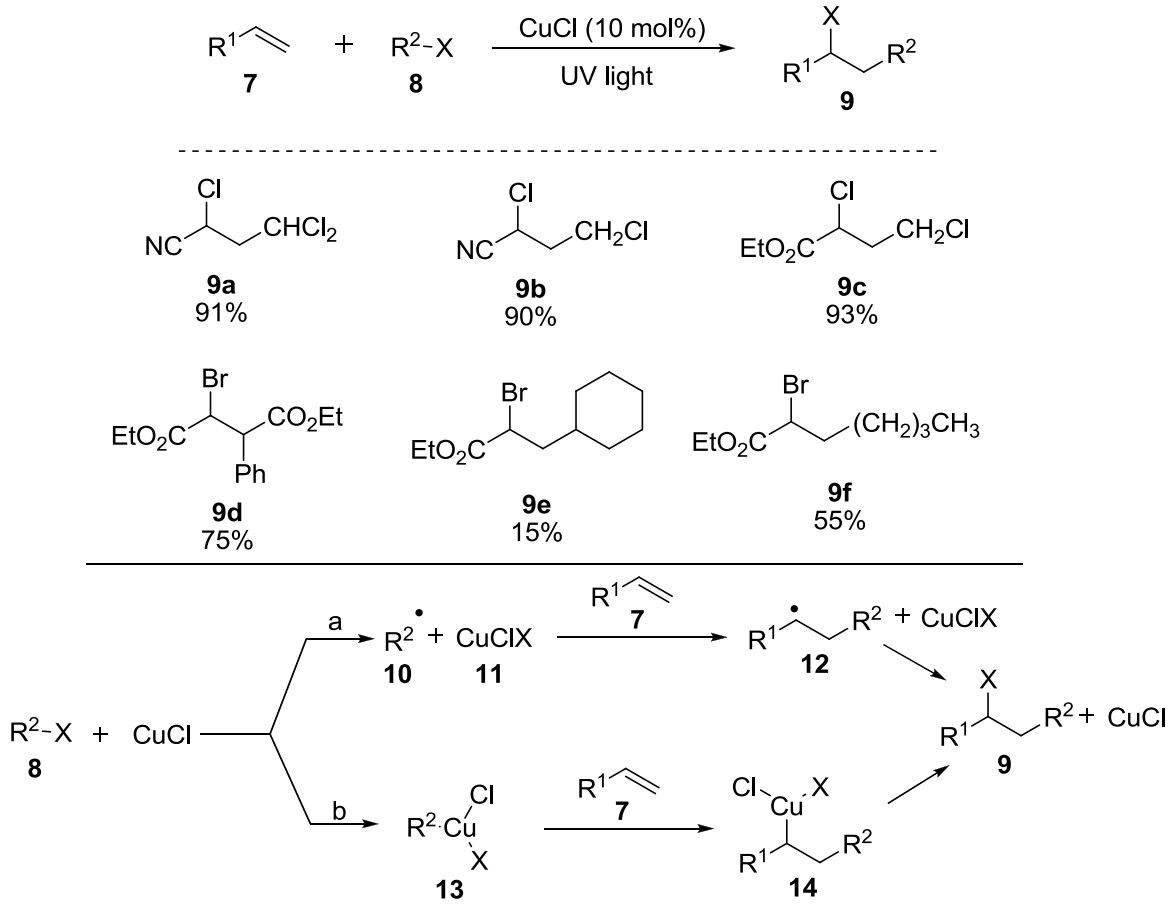
One of the early examples of copper photocatalysis is the valence isomerization of norbornadiene **5** to quadricyclene **6** that was reported by Kutal et al. in (Scheme 1.2).[15] A mechanistic rationale comprises formation of light absorbing 1:1 cuprous chloride-norbornadiene π-complex. This reaction was shown to be catalyzed by a large number of copper(I) salts such as CuCl, CuBr or CuOAc, however, CuCl was preferred with respect to other copper salts because of its ease in handling.

Scheme 1.2. Valence isomerization of norbornadiene under photochemical condition



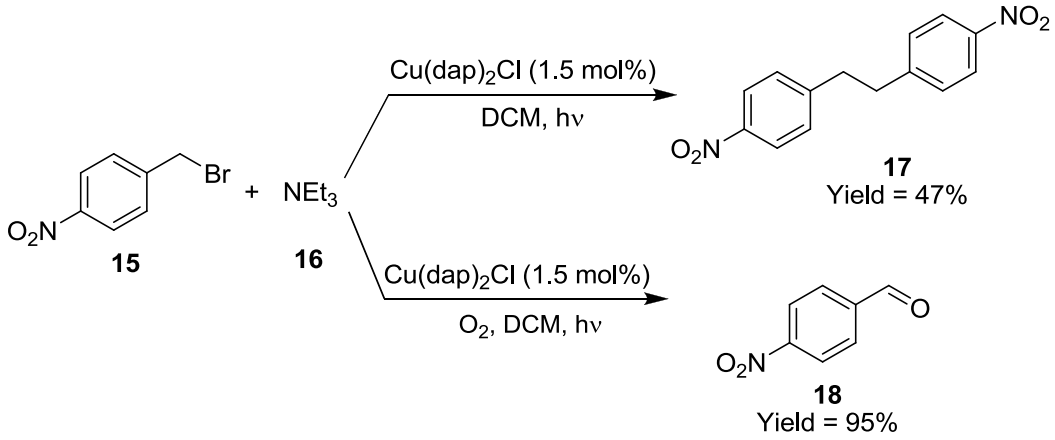
In 1980, Mitani group reported the cuprous chloride catalyzed addition of unactivated alkyl halides to olefins under UV irradiation condition (Scheme 1.3). The reaction works well with a wide range of alkyl halides and olefins. Though in their first report[16] they speculated the reductive cleavage of C-X (halogen) bond by one electron transfer from CuCl to generate a carbon centered radical and copper(II) species (path a), experimental evidence suggested that the reaction might go through the photochemical generation of a Cu(III) species (path b).[17] No suppression of the reaction in the presence of radical quencher e.g. *tert*-butylcatechol and hydroquinone disputed the possibility of a radical mechanism.

Scheme 1.3. ATRA of alkyl halides to Olefin by CuCl under UV irradiation



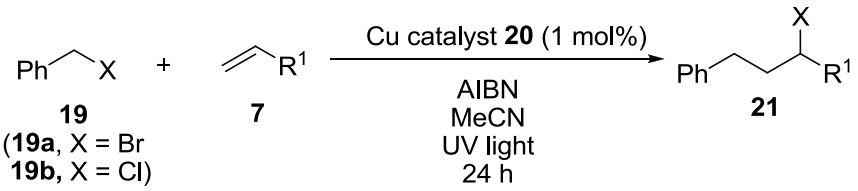
In 1987 Sauvage et al. successfully employed $Cu(dap)_2Cl$ for the C-Br bond activation of 4-nitrobenzyl bromide **15** (Scheme 1.4). In the absence of air with triethylamine **16** as sacrificial electron donor, a reductive coupling led to the formation of bisbenzyl **17**. Conversely, oxidation of the starting benzyl bromide to corresponding aldehyde **18** was achieved in the presence of air in very high yield .[11a] Though detailed mechanistic aspects were not explored it was presumed that bisbenzyl **17** was formed either *via* biradical coupling between two benzyl radicals or *via* a nucleophilic attack on benzyl bromide by a benzyl anion formed through photochemical dielectronic reduction of benzyl bromide. Likewise, the benzyl radical is assumed to react with oxygen when present in reaction, which ultimately leads to aldehyde formation.

Scheme 1.4. Benzyl bromide activation with $Cu(dap)_2Cl$ as photoredox catalyst



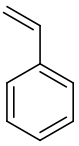
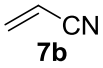
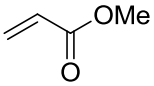
In a related work to Mitani group,[16,17] Pintauer et al. disclosed the atom transfer radical addition (ATRA) and atom transfer radical cyclization (ATRC) of different alkyl halides to highly active alkenes employing the copper(II) photocatalyst **20** in combination with azobisisobutyronitrile (AIBN) under UV light irradiation.[18] Apart from alkyl halides, benzyl halides **19** have been utilized as ATRA reagents (Table 1.3). Despite the low yields of the ATRA products achieved, this study represents an important development in ATRA reactions, disclosing the first examples that involve benzyl halides.

Table 1.3. ATRA of benzyl halides with olefins under UV irradiation



catalyst **20** = $[Cu^{II}(TPMA)X][X]$

TPMA = tris(2-pyridylmethyl)amine

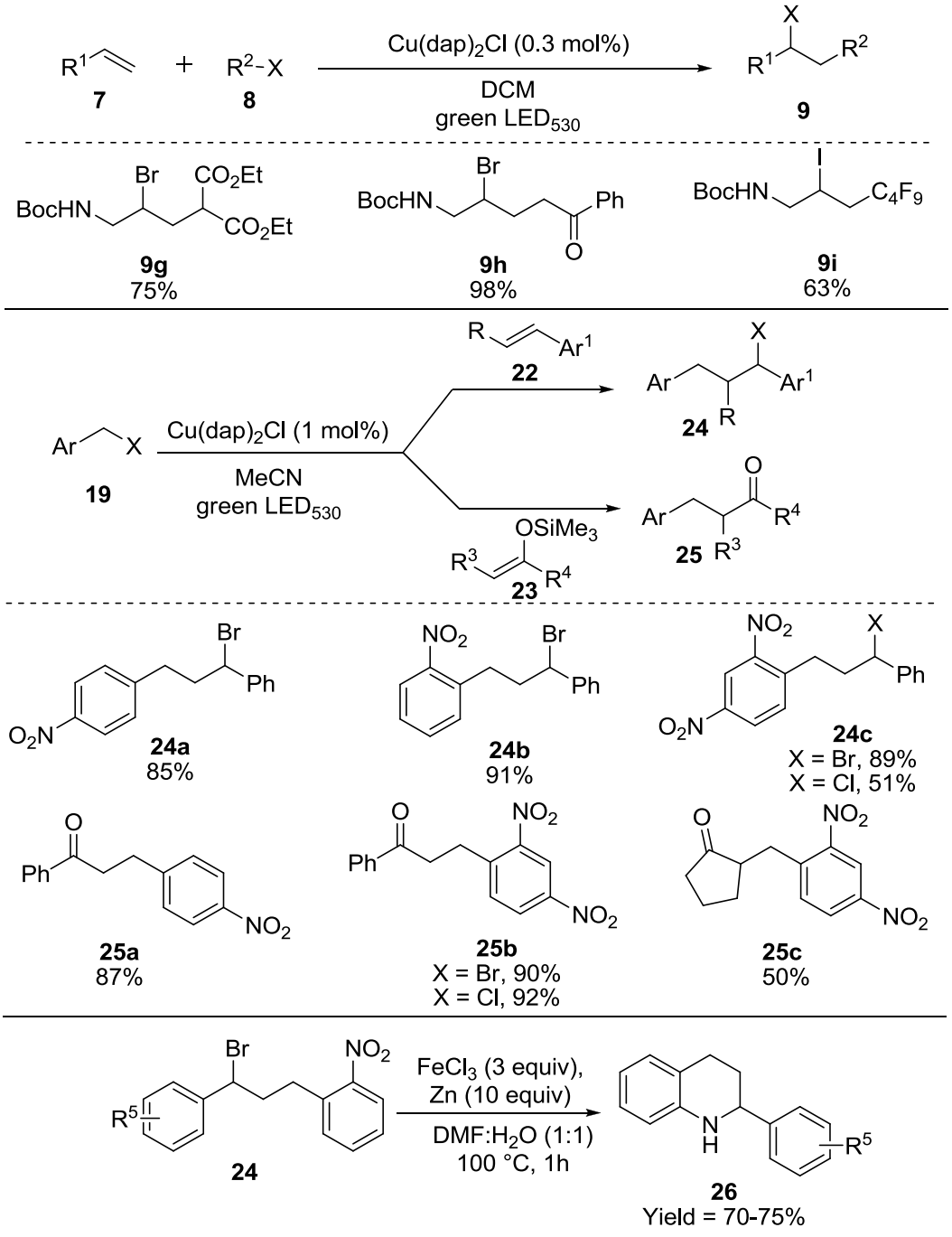
entry	halide (**19**)	alkene (**7**)	yield (%)[a]
1	**19a**	 **7a**	34 (X = Br)
2	**19b**		23 (X = Cl)
3	**19a**	 **7b**	21 (X = Br)
4	**19b**		16 (X = Cl)
5	**19a**	 **7c**	33 (X = Br)
6	**19b**		26 (X = Cl)

[a] Yield was determined using ^{1}H NMR spectroscopy

1.4 Copper as visible light photoredox catalyst

Expanding on the work of Mitani and Pintauer, our group[19] has demonstrated the potential of $[Cu(dap)_2]Cl$ as a visible light photoredox catalyst for ATRA of alkyl halides **8** to olefins **7**. The reaction was amenable to a broad variety of organic halides in combination with terminal alkenes as well as cyclic internal alkenes as coupling partners, providing high yields of **9** with low catalyst loading (Scheme 1.5), rivaling iridium complexes that can also be used as visible light photoredox catalysts for this process.[20] Likewise $[Cu(dap)_2]Cl$ is powerful enough to allow the ATRA of electron deficient benzyl halides **19** to olefins, under visible light irradiation (Scheme 1.5). A wide range of electron rich styrenes **22** or silyl enol ethers **23** can serve as coupling partner in good to excellent yields.[21]Mechanistically it was proposed to proceed *via* oxidative quenching of excited photocatalyst.

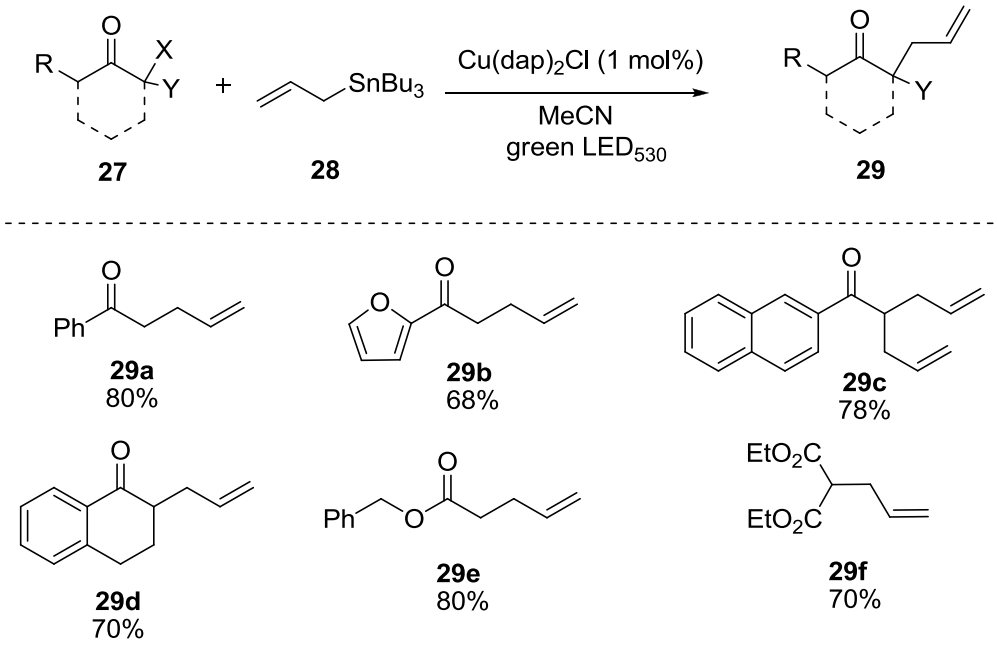
Scheme 1.5. ATRA of alkyl and benzyl halides with $Cu(dap)_2Cl$ as visible light photoredox catalyst



The resulting ATRA products **24** possessing a *ortho*-nitro group were utilized as precursors for the synthesis of biologically important quinolines **26**.

Employing the same catalyst the allylation of α-halo carbonyl compounds **27** with allyltributyltin **28** is also possible (Scheme 1.6),[19] providing an alternative to previously known radical conditions utilizing AIBN at 80 °C or BEt_3 at ambient temperature, as well as to photochemical condition under UV irradiation in absence of any catalysts.

Scheme 1.6. Allylation of α-halo carbonyls by allyltributyltin with $[Cu(dap)_2]Cl$ as photoredox catalyst

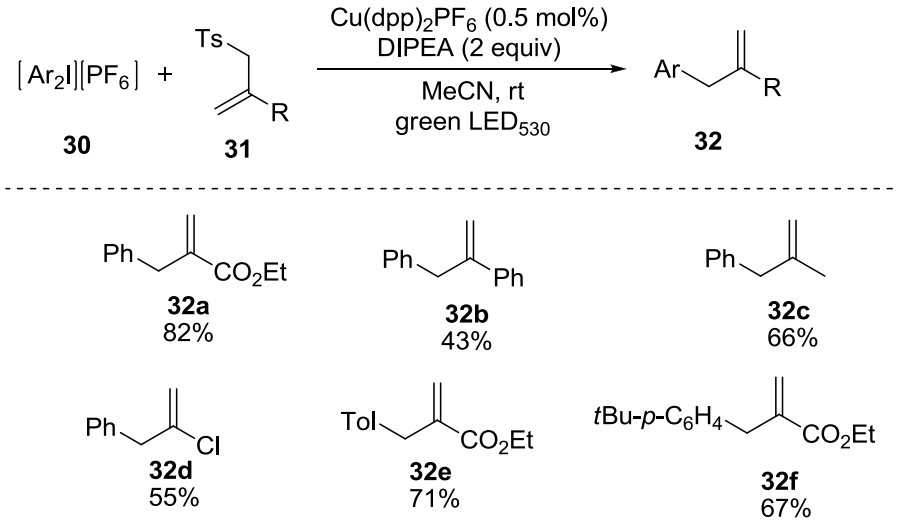


Similar to the ATRA process, it was again assumed that a single electron transfer (SET) between excited catalyst and organic halide initiated the reaction instead of a direct electron transfer between halide and allyltributyltin.

Very recently Ollivier and coworkers reported the allylation of aryl radicals derived from diaryliodonium salts **30**[22] by means of $[Cu(dpp)_2]PF_6$ and allyl tosylate **31** by visible light photoredox catalysis (Scheme 1.7).[23] A variety of diaryliodonium salts as well as allyl tosylates were tolerated under the reaction conditions leading to moderate to good yield of allyl arenes **32**. The authors propose an oxidative quenching cycle for excited $[Cu(dpp)_2]^+$ by an diaryliodinium salts leading to the formation of aryl radicals. The catalytic cycle is closed by electron transfer from Hünig's base (i-Pr_2NEt) which was used as sacrificial electron donor. The presence of

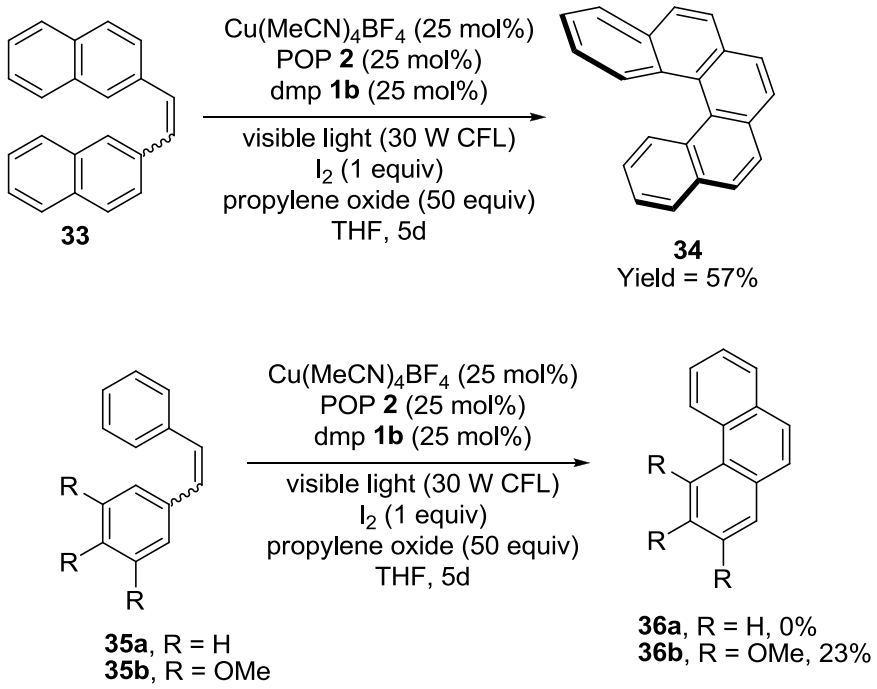
Cu(I) and Cu(II) species in the reaction medium was further verified by in situ monitoring of reaction with ^{1}H NMR.

Scheme 1.7. Allylation of aryl radical under photocatalytic reduction condition



An interesting application of copper based photocatalysis was also recently reported by Collins et al. in the photocyclization of **33** for the synthesis of 5[helicene] **34** triggered by visible light (Scheme 1.8).[24] The photocatalyst was generated *in situ* by mixing $[Cu(MeCN)_4]BF_4$ and POP and dmp. In this process the authors could overcome the limitations of classical UV-light mediated photocyclization e.g. formation of byproducts such as regioisomers resulting from intermolecular [2+2] cyclization. Molecular iodine was used as the oxidant in the transformation.

Scheme 1.8. Visible light mediated photocyclization by in situ generated Cu-based complex

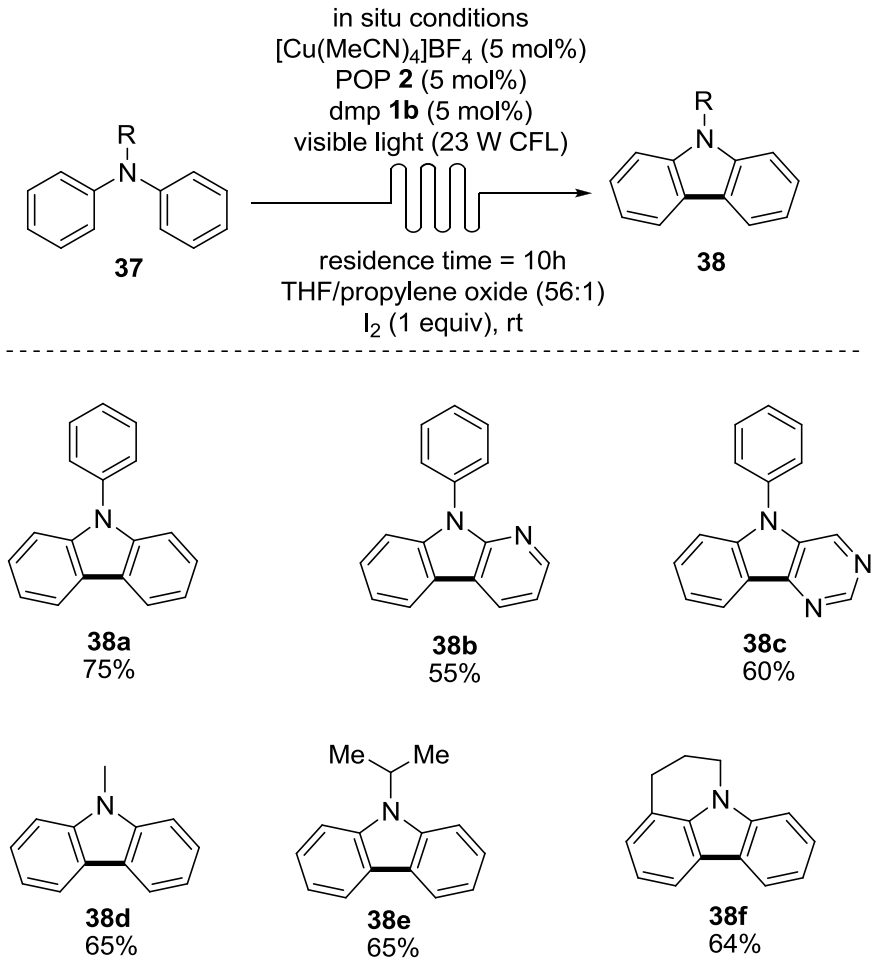


The reaction could be performed in gram scale as a potential synthetic application. Long reaction time of five days could be reduced to ten hours by continuous flow strategy. Though the detailed mechanism for this transformation is still elusive, an oxidative mechanism for the overall process was suggested based on the cyclization of stilbenes **35** under similar reaction conditions.

Another elegant application of copper photocatalysts is the carbazole synthesis from di- or triarylamines by oxidative C-C bond coupling (Scheme 1.9), was reported again from Collins and coworkers.[25] Similar to their previous report of helicene synthesis by photocyclization, visible light mediated oxidative photoredox catalysis was utilized under continuous flow conditions. Remarkably, while widely used $[Ru(bpy)_3](PF_6)_2$ only yielded 27% of the expected carbazole **38**, applying an *in situ* generated $[Cu(dmp)(POP)]BF_4$ complex resulted in 85% of the desired carbazole after five days of reaction time. A continuous flow strategy reduced the reaction time to ten hours. The iodine in the reaction mixture is thought to serve both as an oxidative quencher of the excited photocatalyst and as oxidant for the final re-aromatization step. Another notable advantage of the copper based photocatalyst over commonly used ruthenium or

iridium catalyst was the possibility of rapid screening of different catalyst using an *in situ* synthesis combining a copper salt with diamine and bisphosphine ligand.

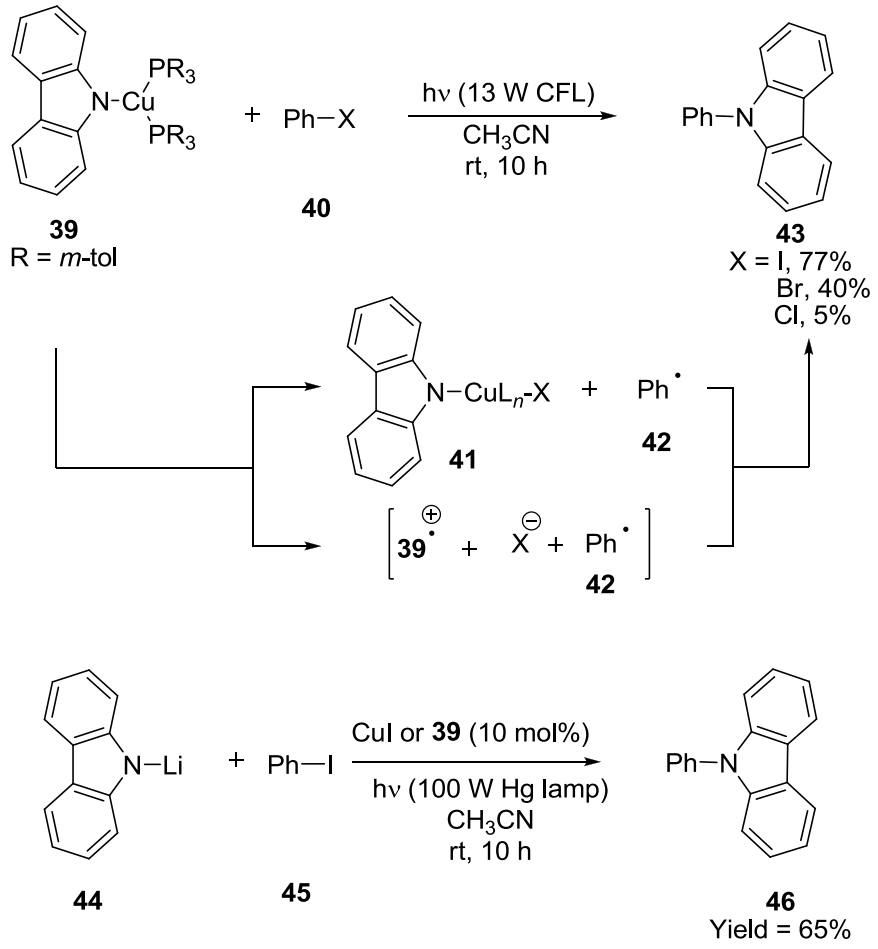
Scheme 1.9. Visible light mediated carbazole synthesis by in situ generated Cu-based complex



Further contributions on copper based photocatalysis were made by Fu and Peters et al. for photoinduced Ullmann C-N coupling reactions (Scheme 1.10).[26] Though there was computational evidence that the process involved the aryl radicals as coupling partners,[27] supportive experimental evidence of single electron transfer (SET) was still elusive. A luminescence quenching of carbazolide complex **39** upon the addition of iodobenzene **45** provided proof of electron transfer from the copper complex to aryl halide **40**, leading to the formation of N-phenyl carbazole **43** in 77% yield. Bromobenzene and chlorobenzene give poor

yields of corresponding carbazoles, which is rationalized on basis of their higher reduction potentials (PhI, –1.91 V *vs* PhBr, –2.43 V and PhCl, –2.76 V). The formation of benzene or iodobiphenyl further underlined the radical mechanism, and EPR analysis showed the presence of Cu(II) species in the reaction medium.

Scheme 1.10. Visible light mediated Ullmann C-N coupling

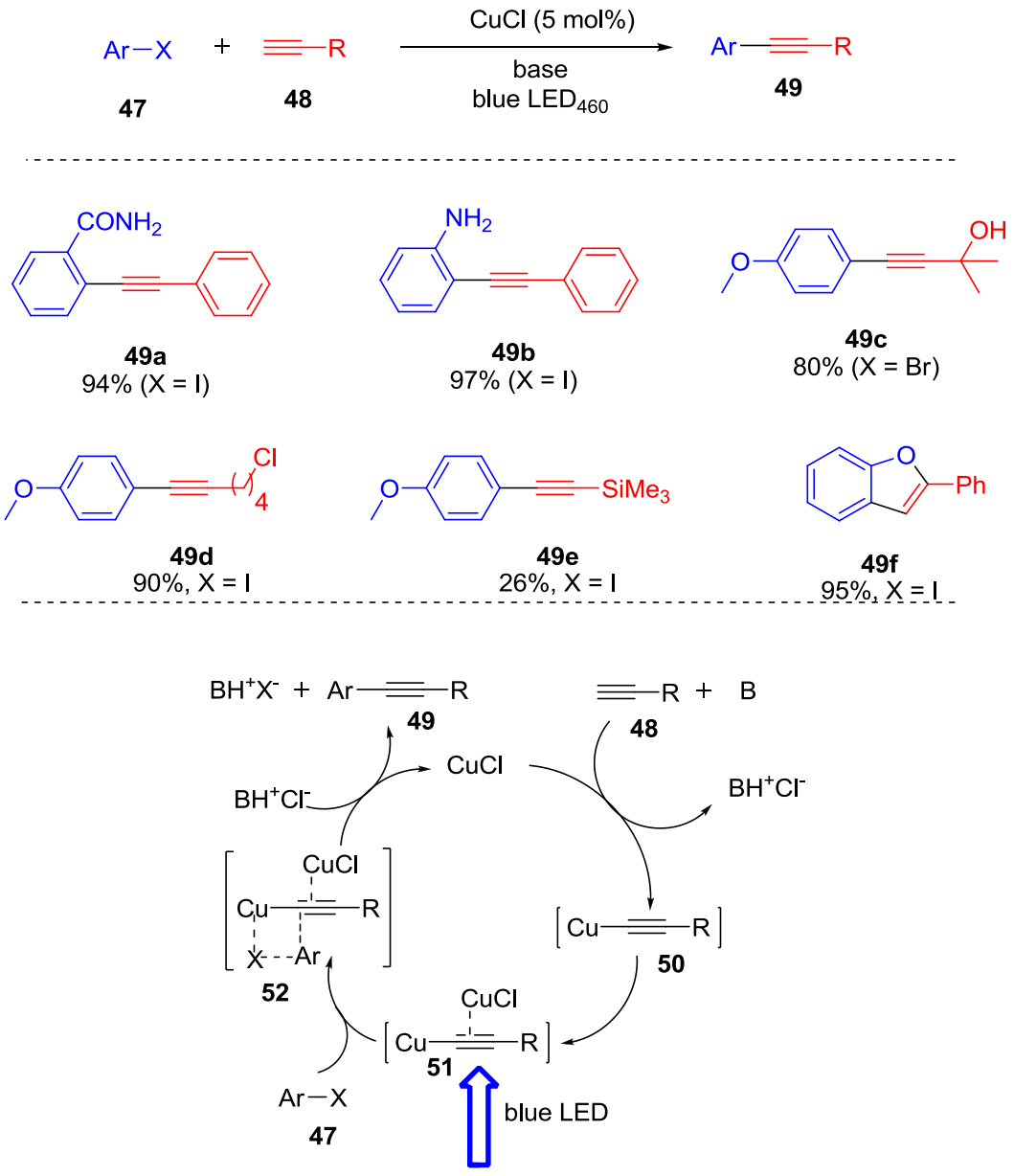


A catalytic procedure employing lithium-carbazolide **44** and iodobenzene **45** as coupling partners was also developed where copper-carbazolide **39** served as catalyst.

Another coupling reaction, i.e. the Sonogashira C-C cross coupling demonstrates the potential of the combination of copper(I) and visible light (Scheme 1.11).[28] Under photoredox catalyzed

conditions using CuCl, alkynylation of aryl halides **47** proceeded at room temperature. Attempts have been made to avoid the use of expensive palladium in Sonogashira cross coupling before, but met with limited success.[29]

Scheme 1.11. Photoinduced Sonogashira coupling by copper(I) chloride salt



Mechanistically it is thought to proceed via copper acetylide complex **51** (λ_{abs} = 425-485 nm) which is the key light absorbing species. Rate acceleration upon addition of 0.1 mol% of CuCl to

the copper(I) phenylacetylide complex **50** bolstered the hypothesis. Photo excitation of copper(I) phenylacetylide is believed to trigger a ligand to metal charge transfer (LMCT), resulting in partial positive charge in the acetylene moiety, thus favoring nucleophilic attack of electron rich aryl halide **47**, nevertheless, as the synthesis of **49a** shows, electron deficient arenes were also suitable substrates.

1.5 Conclusion

With the resurrection of visible light photocatalysis as a powerful tool in organic synthesis, copper based photo sensitizers are coming under limelight due to their economical advantage, as well as efficient tuning of excited state properties with ligand modification over widely used ruthenium or iridium analogues. Though a huge amount of research efforts have been invested in understanding and modification of copper complexes as photocatalysts combined with their utilization in water splitting or as sensitizer in photochemical devices, not much attention was given to the use of these complexes in organic synthesis. Following the early examples of UV light photocatalysis, copper complexes are now being examined and utilized as visible light photocatalysts in many organic transformations with great success. Copper might very well hold the potential to eventually replace ruthenium or iridium complexes as visible light photoredox catalyst in the foreseeable future.

1.6 References

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2. Aim of this Work

Visible light photoredox catalysis has emerged as an elegant tool in synthetic organic chemistry from the point of its application in fine molecules synthesis.[1] Due to the mild, environmentally benign reaction conditions and largely vast natural abundance of solar energy, visible light photocatalysis has a bright future.[2] Aim of this work was to develop efficient and new organic transformations based on single electron transfer (SET) photoredox catalysis.

2.1 Allylation and atom transfer radical radical addition (ATRA) by copper photocatalyst

Most commonly used visible light phototredox catalysts are complexes based on ruthenium and iridium. Due to the rarity of these metals, it is always desirable to develop new catalytic systems which can emulate the role of those complexes. Copper, being abundant in nature and inexpensive provides a viable alternative. We have successfully applied one such copper based photocatalyst $[Cu(dap)_2Cl]$[3] in the allylation of α-halo carbonyl compounds[4] and in ATRA of electron deficient bezyl halides to styrenes and silyl enol ethers and the products have been utilized in synthesizing biologically relevant tetrahydroquinolines.[5]

2.2 Vinyl radical generation by visible light photocatalysis and its synthetic applications

Due to their high reactivity, vinyl radicals have been utilized in many valuable transformations in synthetic organic chemistry as well as in practical applications.[6] Though there are several thermal routes exists in literature for accessing this radical,[7] photochemical processes are rare.[8]

Following our previous experience of reductive debromination[9] of *vic*-dibromoalkene to corresponding alkyne, we envisioned a visible light triggered route to access vinyl radials. Utilizing α-bromo chalcones as vinyl radical source under photochemical conditions, we decided to synthetically exploit these radicals utilizing different trapping agents to synthesize polycyclic frameworks (**2**) by an intermolecular cascade reaction sequence involving heteroarenes,[10] for the synthesis of 3,4-dihydronapthalenes by an intermolecular annulation sequence involving olefins (**3)** and in α- vinylation of ketones (**4**) employing enol acetates as coupling partner (Figure 2.1).

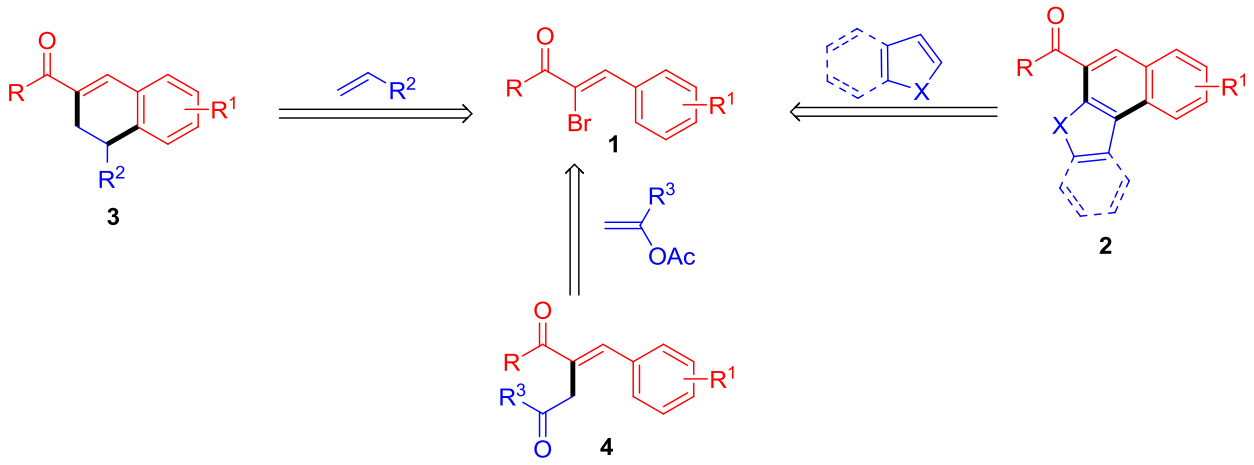

Figure 2.1. Synthetic transformations of photochemically generated vinyl radical

2.3 References

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3. Visible Light Mediated Allylation of α-halo carbonyl Compounds

3.1 Introduction

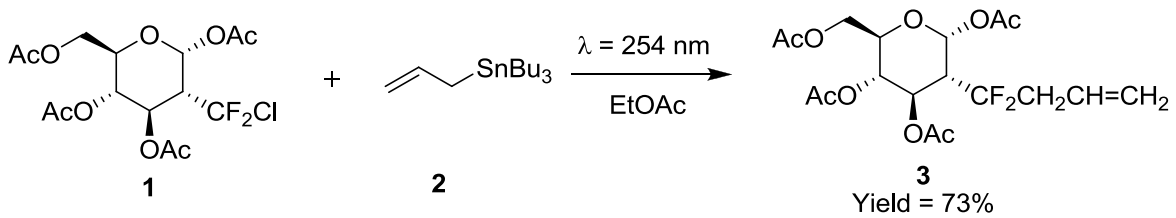
Allylation of organic halides has been established as a powerful tool for introduction of allyl group by selective C-C bond formation.[1,2] Introduction of an allyl functionality in a molecule, paves the way for further synthetically useful transformations (ozonolysis, dihydroxylation, epoxidation, cycloaddition, olefin metathesis etc.), making it a versatile functional group. Among various allylating agents allyltrimethylsilanes,[3] allyl halides,[4,5] allyl Girgnards,[6] allyl boranes or boronates[7,8] etc. are well known. But arguably the most prominent of all is allyl tributyltin which is basically a radical allylating agent.

3.2 Photochemical allylation of organic halides

Usually allylation employing allyl tributyltin proceeds via radical process, and initiated by azobisisobutyronitrile (AIBN) at 80 °C or by Et_3B at ambient temperature.[9] Allylation using allyl tributyltin also proceeds under UV light irradiation without any catalyst. There are several reports of such allylation of organo halides.

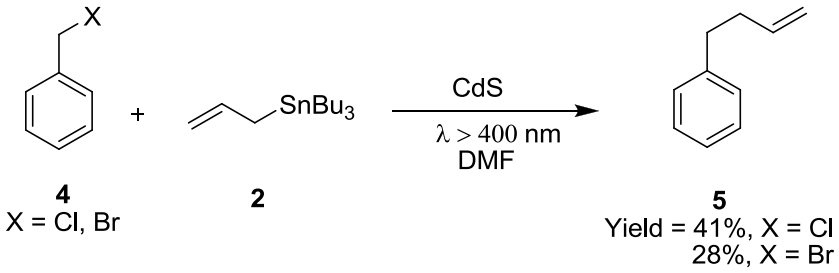
Miethchen and coworkers reported the allylation of C-Cl bond of monosaccharide **1** in moderated yield under UV irradiation by allyl tributyltin **2**. A longer irradiation time led to the formation of unidentifiable byproducts without increasing the amount of desired product (Scheme 3.1).[10]

Scheme 3.1. Allylation of monosaccharides by UV light irradiation



Allylation of benzyl halides **4** by cadmium sulfide nanocrystallities under visible light irradiation using allyl tributyltin **2** as electron donor leading to the formation of homoallyl benzene **5** was reported by Yanagida and coworkers. A bimolecular coupling between benzyl and allyl radical on the surface of cadmium sulfide nanocrystallities has been proposed as the plausible mechanism for the allylation (Scheme 3.2).[11]

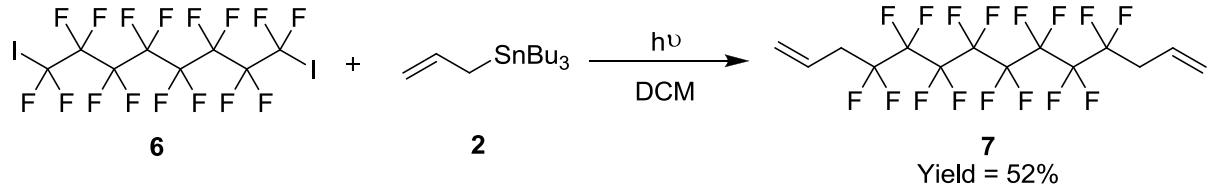
Scheme 3.2. Allylation of benzyl halides with CdS nanocrystallites under visible light irradiation



Explanation behind better yield for benzyl chloride over benzyl bromide was given by higher reduction potential for chloride over bromide, which led to slow formation of benzyl radical in case of benzyl chloride, thus minimizing side reactions.

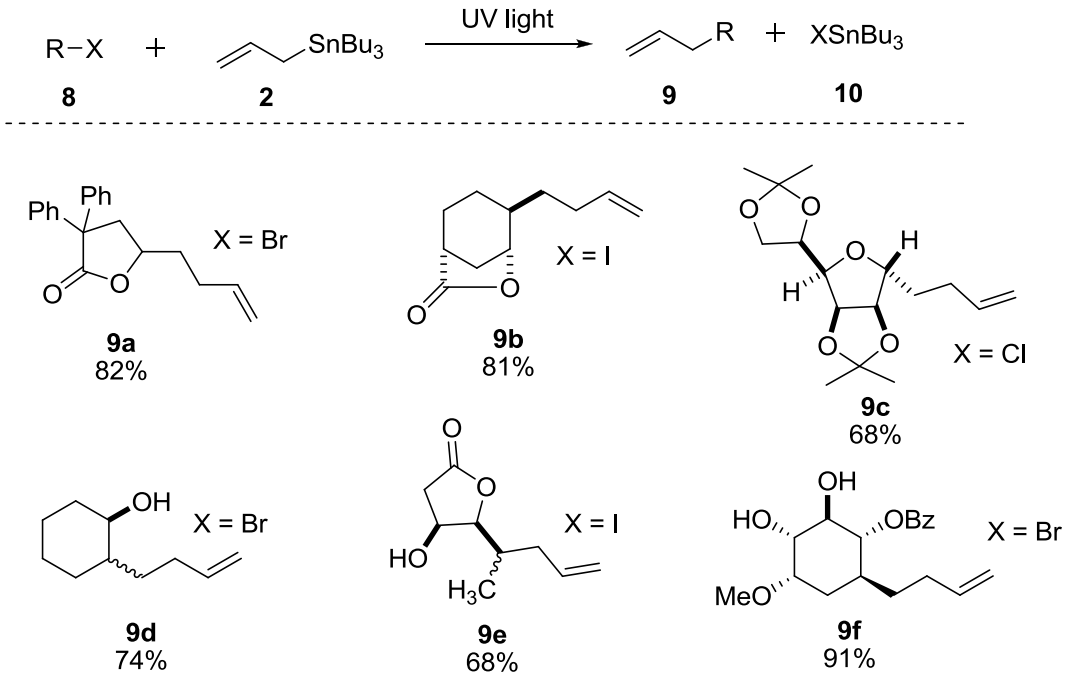
In this context, Gladysz et al. reported the two fold allyaltion of perfluoroalkyl α,ω-diiodide **6** using excess of allyl tributyltin **2** under UV light irradiation (Scheme 3.3).[12]

Scheme 3.3. Two fold allyaltion of perfluoroalkyl α,ω-diiodide



Keck et al. reported the allylation of different organic halides with allyl tributyltin under UV irradiation (Scheme 3.4). The reaction was well tolerant in terms of steric hindrance and complex functionalities. Another notable feature of this allylation was β-hydrogen tolerance where many of the organometallic procedures fail, due to reductive elimination.[13]

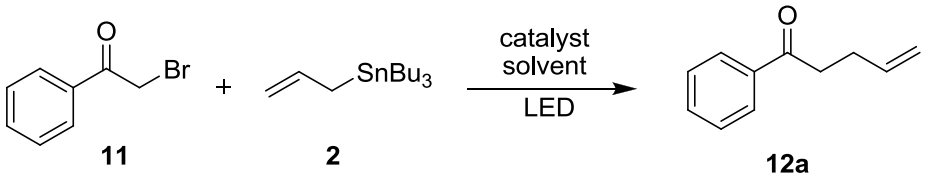
Scheme 3.4. Allyllation of organic halides



3.3 Allylation of α-halocarbonyl compounds with visible light

Though there are reports of allylation utilizing allyl tributyltin of organic halides under thermal or UV light irradiation, allylation of α-halo carbonyl compounds under visible light irradiation was still elusive. In continuation of our quest in visible light photoredox catalysis, we planned to investigate the allylation of α-halocarbonyl compounds under visible light irradiation. Since α-halocarbonyl compounds were already a well known radical precursor under visible light irradiation in presence of a suitable photocatalyst, we started our investigation with 2-bromo acetophenone **11** as model substrate and allyl tributyltin **2** as allylating agent. The desired allylated product **12a** was obtained in 72% of isolated yield after 2 hours of irradiation with 1 mol% $Ru(bpy)_3Cl_2$ in acetonitrile (Table 3.1, entry 1).

Table 3.1. Optimization of reaction conditions: screening of solvents and catalysts[a]



11 **2** **12a**

entry	condition	yield (%)[b]
1	$Ru(bpy)_3Cl_2$ (1 mol%), CH_3CN, 455 nm, 2h	72
2	$Ru(bpy)_3Cl_2$ (1 mol%), DMF, 455 nm, 8h	60
3	$Ru(bpy)_3Cl_2$ (1 mol%), DCM, 455 nm, 15h	50
4	$Ru(bpy)_3Cl_2$ (1 mol%), MeOH, 455 nm, 15h	50
5	**$Cu(dap)_2Cl$ (1 mol%), CH_3CN, 530 nm, 3 h**	**80**
6	no photocatalyst, 455 nm light, 24 h	30
7	no photocatalyst, 530 nm light, 24 h	no reaction
8	with $Cu(dap)_2Cl$, no light, 24 h	trace

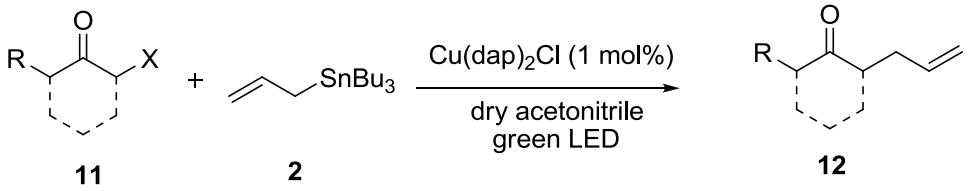
[a] Reaction condition: 2-Bromoacetophenone (1 equiv), allyl tributyltin (1 equiv) irradiated with appropriate LED. [b] Isolated yield after purification on SiO_2

Next we proceeded to optimize the reaction conditions. For that purpose we screened many different solvents and catalysts. Switching to DMF instead of MeCN resulted in inferior yield of 60% after 8 hours (Table 3.1, entry 2). When solvent was changed to DCM or MeOH the reaction became slow, took 15 hours for completion with only 50% yield of the desired product with many undesired side products (Table 3.1, entries 3, 4). $Cu(dap)_2Cl$, being economically advantageous over $Ru(bpy)_3Cl_2$, and having slightly higher reduction potential than later, was screened (Table 3.1, entry 5) as a catalyst. We found that with $Cu(dap)_2Cl$, though the reaction took little longer than $Ru(bpy)_3Cl_2$ (3 hours instead of 2 hours), yield was increased to 80%. When the reaction was performed without any catalyst, but under blue LED irradiation, it led to 30% yield of the product after 24 hours (Table 3.1, entry 6), though, irradiation with only a green LED failed to give any product formation (Table 3.1, entry 7). Reaction with only photocatalyst,

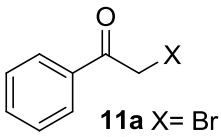
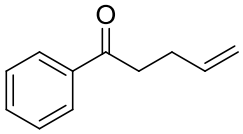
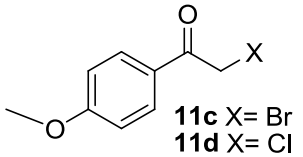
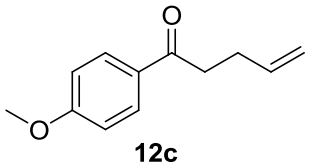
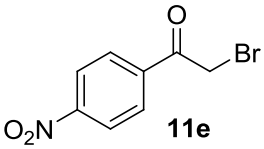
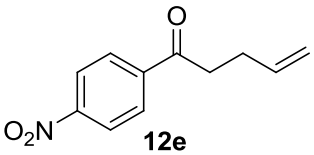
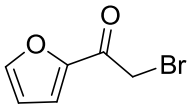
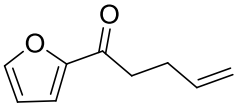
excluding light led to trace amount of product. These control experiments proved that both photocatalyst and light were essential for the reaction to proceed, and $Cu(dap)_2Cl$ was a better choice of catalyst for the allylation reaction.

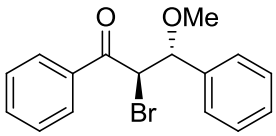
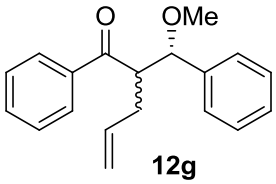
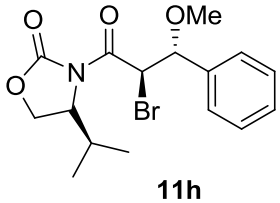
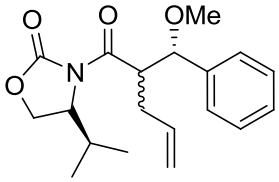
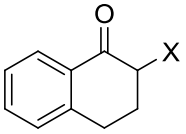
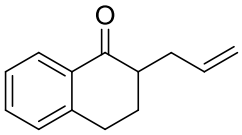
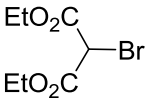
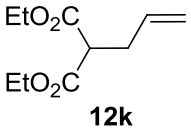
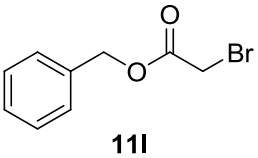
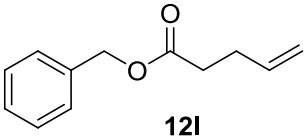
Having the optimized reaction condition in hand, we proceeded to examine the substrate scope for the allylation reaction (Table 3.2).

Table 3.2. Substrate scope for allylation[a]



11 **2** **12**

entry	substrate (**11**)	product (**12**)	time (h)	yield (%)
1	 **11a** X= Br	 **12a**	3	80
2	**11b** X= Cl		5	85
3	 **11c** X= Br	 **12c**	4.5	75
4	**11d** X= Cl		5	79
5	 **11e**	 **12e**	4	74
6	 **11f**	 **12f**	6	68

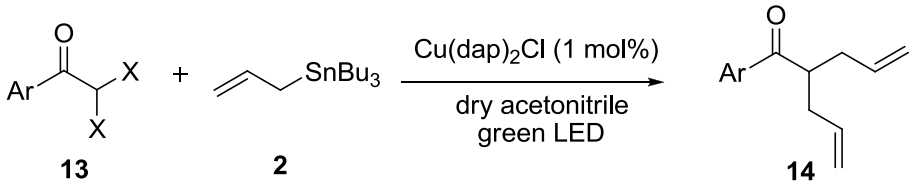
entry	substrate (**11**)	product (**12**)	time (h)	yield (%)[b]
7	 **11g**	 **12g**	12	72% (*syn:anti* = 85:15)
8	 **11h**	 **12h**	15	77% (*anti:syn* = 75:25)
9	 **11i** X= Br	 **12i**	7	70
10	**11j** X= Cl		6	63
11	 **1k**	 **12k**	4.5	70
12	 **11l**	 **12l**	8	80

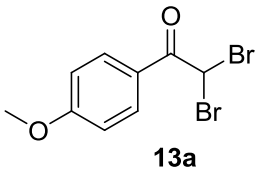
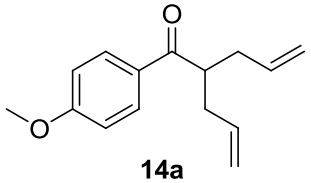
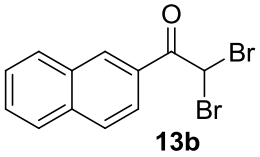
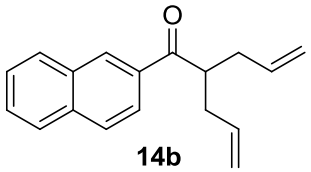
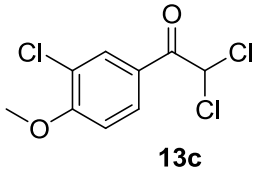
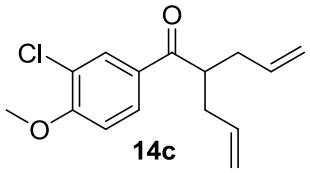
[a] Reaction condition: Organohalide **11** (1 equiv), allyltributyltin **2** (1 equiv), $Cu(dap)_2Cl$ (1 mol%) in acetonitrile irradiated with a green LED. [b] Isolated yield after purification on SiO_2

The reaction was not only efficient for bromide substrates, chlorides were also equally potent substrate for allylation (Table 3.2, entries 2, 4, 10), often giving somewhat better results than bromides which was surprising considering more stable C-Cl bond over C-Br bond. Electron donating (Table 3.2, entries 3, 4) or withdrawing (Table 3.2, entry 5) substituent has no effect on reaction time or yield. Reaction was not stereoselective since an *anti* diastereomer led to mixture of *syn* and *anti* diastereomeric products (Table 3.2, entries 7, 8).

One interesting fact about this allylation was di-allylation of α, α-dibromo and α, α-dichloroketones **13** (Scheme 3.3). Using two equivalent of allyltributyltin, these dihalides were efficiently converted to corresponding doubly allylated products **14**, which could be used as the precursors for ring closing olefin metathesis reaction.

Table 3.3. Di-allylation of α, α-dibromo and α, α-dichloroketones[a]



Entry	Substrate (**13**)	Product (**14**)	Time (h)	Yield (%)[b]
1	 **13a**	 **14a**	7	89
2	 **13b**	 **14b**	6	78
3	 **13c**	 **14c**	5.5	80

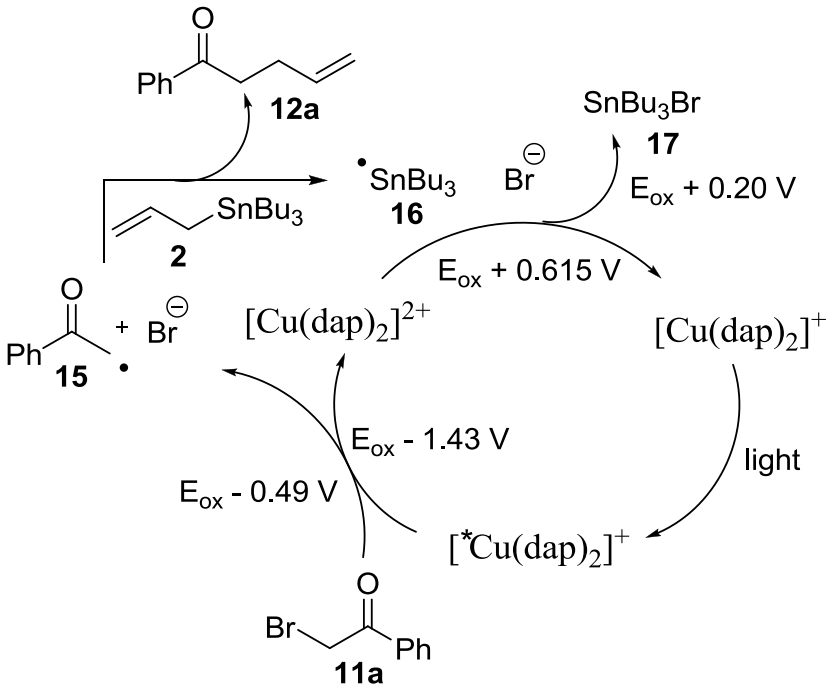
[a] Reaction condition: Organohalide **13** (1 equiv), allyltributyltin **2** (2 equiv), $Cu(dap)_2Cl$ (1 mol%) in acetonitrile irradiated with a green LED. [b] Isolated yield after purification on SiO_2

One advantage of this allylation procedure was that we could avoid the use of excess allylating agent which is prevalent in other literature reports for allylation under thermal or photochemical protocols. As a key structural requirement, a carbonyl functionality alpha to one halogen atom was essential for the above transformation.

3.4 Proposed reaction mechanism

A reaction mechanism is proposed based on the oxidative quenching of photocatalyst (Scheme 3.5). Excited $Cu(dap)_2^+$ transfer an electron to electron deficient **11a**, thus forming the phenacyl radical **15** and goes to $Cu(dap)_2^{2+}$ state. Phenyl acyl radical **15** subsequently adds to the allyl tributyltin **2** to produce product **12a**. A back electron transfer probably from tributyltin radical **16** regenerates the catalyst. A direct electron transfer between organic halide and allyl tributyltin could be overruled on the basis of incompletion of the reaction in absence of photocatalyst. Also, all the steps in the mechanism are thermodynamically favored as judged by oxidation potential of individual step.

Scheme 3.5. Proposed reaction mechanism



3.5 Conclusion

In conclusion, we have successfully demonstrated the allylation of α-halo carbonyl compounds under visible light irradiation employing allyl tributyltin and a economically viable alternative

$Cu(dap)_2Cl$ to widely used ruthenium or iridium photocatalysts. A wide range of α-bromo and chloro carbonyl compounds with different functional moieties were well tolerated in this allylation process. Using two equivalent of allyl tributyltin, di allylation of α, α-dibromo and α, α-dichloroketones were also achieved in good yields. This allylation procedure has advantage of using one equivalent of allyl tributaltin reagent per halide in contrary to use of excess allylating reagens in literature procedures.

3.6 Experimental part

General Procedure A[14]

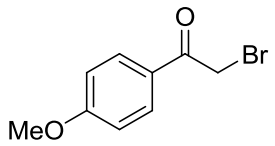
To a stirred solution of the corresponding ketone (1 mmol) in $CHCl_3$ (3 mL), a chloroform solution (0.5 mL) of bromine (1.1 mmol for monobromination and 2.2 mmol for dibromination) was added drop wise at 0°C and after complete addition the reaction mixture brought into room temperature. The stirring was continued at room temperature for another 1h and then gently heated at 65°C. After completion of the reaction (TLC), the reaction mixture was brought to room temperature and unreacted bromine was quenched by addition of saturated solution of $Na_2S_2O_7$ and stirring continued for another 30 min. The reaction mixture was extracted with $CHCl_3$ (2x5 mL) and the combined organic layers washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Depending upon the substrate the desire compound was obtained by crystallization (EA/PE) or by column chromatography.

General Procedure B[15]

Ketone (1 mmol) N-halosuccinimide (NBS/ NCS, 1 mmol) were triturates together with p-toluenesulfonic acid (PTSA, 0.1 mmol) in a porcelain mortar for 20 min. The reaction mixture was then heated to 80°C for 2h, turning into a dense paste. Water was then added (5 mL) followed by extraction with diethyl ether (20 mL). The organic phase was washed with water (10 mL), dried over Na_2SO_4 and solvent evaporated under reduced pressure. Depending upon the

substrate the desire compound was obtained by crystallization (EA/PE) or by column chromatography.

2-Bromo-1-(4-methoxyphenyl)ethanone (11c)[16]

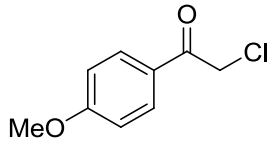


According to general procedure **A**, 1-(4-methoxyphenyl) ethanone (0.15 g, 1 mmol), bromine (0.06 mL, 1.1 mmol) afforded **11c** (0.17 g, 0.75 mmol, 75 %) as crystalline solid after crystallization from EA/PE. R*f* (EtOAc/hexane 1:9): 0.24.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.78 Hz, 2H), 6.95 (d, *J* = 9.05 Hz, 2H), 4.45 (s, 3H), 3.91 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.9, 164.1, 131.4, 126.9, 114.1, 55.6, 30.7.

2-Chloro-1-(4-methoxyphenyl)ethanone (11d)[16]

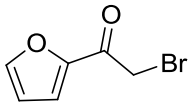


According to general procedure **B**, 1-(4-methoxyphenyl) ethanone (0.5 g, 3.33 mmol), NCS (0.44 g, 3.33 mmol) afforded **11d** (0.45 g, 2.49 mmol, 75 %) as crystalline solid after crystallization from EA/PE. R*f* (EtOAc/hexane 1:9): 0.30.

^{1}H NMR (300 MHz, $CDCl_3$): δ =7.93 (d, *J* = 9.05 Hz, 2H), 6.95 (d, *J* = 9.05 Hz, 2H), 4.66 (s, 2H), 3.89 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.6, 164.1, 130.9, 127.2, 114.1, 55.6, 45.7.

2-bromo-1-(furan-2-yl)ethanone (11f)[17]

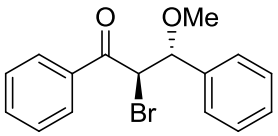


According to general procedure **A**, 1-(furan-2-yl)ethanone (0.30 g, 1 mmol), bromine (0.15 mL, 1.1 mmol) afforded **11f** (0.35 g, 1.89 mmol, 70 %) as black solid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.22.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (dd, *J*=1.6, 0.6 Hz, 1H), 7.34 (dd, *J*=3.7, 0.5 Hz, 1H), 6.65 – 6.55 (m, 1H), 4.32 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.36, 150.36, 147.29, 119.13, 112.87, 30.01.

(2R,3R)-2-bromo-3-methoxy-1,3-diphenylpropan-1-one (11g)[18]

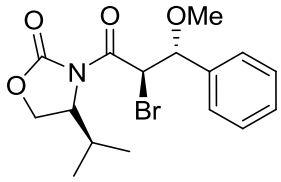


To a stirred methanolic solution of chalcone (0.50 g, 2.40 mmol) was added bromine (1.1 mmol) at ice-cold condition and stirring was continued for 20-30 min. After completion of the reaction (as judged by TLC), the reaction mixture was extracted with Et_2O and dried over Na_2SO_4 and concentrated in vacuo to give the crude product. Column chromatography on silica gel afforded pure **11g** as light yellow solid (0.65 g, 2.03 mmol, 85 %). R*f* (EtOAc/hexane 1:9): 0.48

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 – 8.00 (m, 2H), 7.69 – 7.57 (m, 1H), 7.57 – 7.34 (m, 7H), 5.14 (d, *J*=9.9 Hz, 1H), 4.84 (t, *J*=8.0 Hz, 1H), 3.20 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.34, 137.84, 135.27, 133.74, 128.86, 128.82, 128.39, 128.24, 83.32, 57.72, 47.27.

(R)-3-((2R,3R)-2-bromo-3-methoxy-3-phenylpropanoyl)-4-isopropyloxazolidin-2-one (11h)[19]



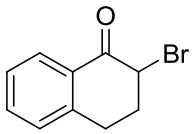
To a stirred methanolic solution of (*S*)-3-cinnamoyl-4-isopropyloxazolidin-2-one (0.30 g, 1.09 mmol) were added $AgNO_3$ (1.2 mmol) and bromine (1.1 mmol) respectively at ice-cold condition and stirring was continued for 20-30 min. The reaction mixture was extracted with Et_2O and dried over Na_2SO_4 and concentrated in vacuo to give the crude product in ratio of 67:33 of two anti diastereomers in favor of **11h**. The two diastereomers were separated by

column chromatography on silica gel with a combined yield of 82% (0.33 g, 0.89 mmol) as white solid. R*f* (EtOAc/hexane 3:7): 0.70

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 – 7.30 (m, 5H), 5.84 (d, *J*=10.1 Hz, 1H), 4.68 (d, *J*=10.1 Hz, 1H), 4.63 – 4.48 (m, 1H), 4.39 – 4.20 (m, 2H), 3.19 (s, 3H), 2.55 – 2.35 (m, 1H), 1.04 – 0.81 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.37, 153.29, 136.95, 128.93, 128.43, 128.39, 83.43, 63.52, 58.60, 57.55, 44.16, 28.17, 17.87, 14.88.

2-Bromo-3,4-dihydronaphthalen-1(2H)-one (11i)[16]

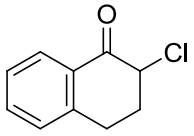


According to general procedure **B**, tetralone (0.5 g, 3.42 mmol), NBS (0.6 g, 3.42 mmol) afforded **11i** (0.44 g, 1.95 mmol, 57 %) as gummy oil after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.39.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (dd, *J* = 1.37, 7.95 Hz, 1H), 7.55-7.45 (m, 1H), 7.37-7.21 (m, 2H), 4.71 (t, *J* = 4.39 Hz, 1H), 3.49-3.22 (m, 1H), 2.95- 2.83 (m, 1H), 2.58- 2.35 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.5, 143.0, 134.2, 129.9, 128.8, 128.6, 127.1, 50.6, 31.9, 26.1.

2-Chloro-3,4-dihydronaphthalen-1(2H)-one (11j)[16]

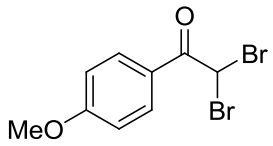


According to general procedure **B**, tetralone (1 g, 6.84 mmol), NCS (0.91 g, 6.84 mmol) afforded **11j** (0.8 g, 4.45 mmol, 65 %) as yellowish oil after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.41.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 7.95 Hz, 1H), 7.58-7.45 (m, 1H), 7.38-7.22 (m, 2H), 4.67-4.57 (m, 1H), 3.33-3.18 (m, 1H), 3.06 -2.90 (m, 1H), 2.67-2.36 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.8, 143.1, 134.1, 130.4, 128.7, 128.5, 127.1, 59.8, 32.4, 26.3.

2,2-Dibromo-1-(4-methoxyphenyl)ethanone (13a)[16]

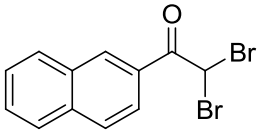


According to general procedure **A**, 1-(4-methoxyphenyl)-ethanone (0.42 g, 2.80 mmol), bromine (0.3 mL, 5.6 mmol) afforded **13a** (0.62 g, 2.01 mmol, 72 %) as crystalline solid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.30.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 9.05 Hz, 2H), 6.97 (d, *J* = 8.78 Hz, 2H), 6.66 (s, 1H), 3.90 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.5, 132.2, 123.3, 114.2, 55.6, 39.8.

2,2-dibromo-1-(naphthalen-6-yl)ethanone (13b)[20]

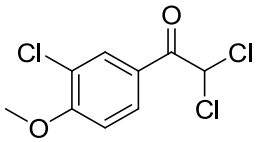


According to general procedure (GP-A), 1-(naphthalen-6-yl)ethanone (0.30 g, 1.76 mmol), bromine (0.18 mL, 3.52 mmol) afforded **13b** (0.40 g, 1.23 mmol, 70 %) as white solid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.48.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.63 (s, 1H), 8.09 (dd, *J*=8.7, 1.8 Hz, 1H), 8.04 – 7.86 (m, 3H), 7.69 – 7.55 (m, 2H), 6.87 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.01, 136.05, 132.30, 131.81, 129.86, 129.47, 128.96, 128.10, 127.90, 127.26, 124.72, 39.79.

2,2-dichloro-1-(3-chloro-4-methoxyphenyl)ethanone (13c)[21]



1-(4-methoxyphenyl)ethanone (0.50 g, 3.33 mmol) was dissolved in a mixture of 31% aq HCl (20 mL, 0.2 mol) and EtOH (20–25 mL). The mixture was heated to reflux (91–93 °C). A solution of 35% aq H_2O_2 in EtOH (1.6 mL, 5 mmol of H_2O_2) was added with stirring over 1 min.

The reaction mixture was refluxed with stirring for 10–15 min and cooled to room temperature. H_2O was added and the mixture was extracted with CH_2Cl_2. The combined organic extracts were washed with H_2O, dried over Na_2SO_4, and concentrated in vacuo. The crude reaction mixture was subjected to column chromatography to obtain pure **13c** (0.67 g, 2.66 mmol, 80 %) as light yellow solid. R*f* (EtOAc/hexane 1:9): 0.29.

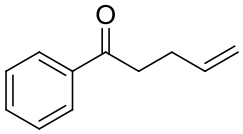
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 – 8.09 (m, 1H), 8.09 – 7.99 (m, 1H), 7.07 – 6.96 (m, 1H), 6.58 (s, 1H), 4.00 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 183.60, 160.03, 132.06, 130.59, 124.40, 123.42, 111.45, 67.62, 56.57.

General procedure for the Photoredeox catalyzed allylation of halides

An oven dried 10 mL vial equipped with a plastic septum and magnetic stir bar was charged with $Cu(dap)_2Cl$ (1 mol%), the corresponding halide (0.25 mmol, 1.0 equiv), allyltri-n-butyltin (0.25 mmol, 1.0 equiv). The flask was purged with a stream of nitrogen and 1.0 mL of solvent (acetonitrile) was added. The resultant mixture was degassed for 5 min by nitrogen sparging and placed at a distance of ~ 0.5 -1.0 cm from a green LED lamp (530 nm). After the completion of the reaction (as judged by TLC analysis), the mixture was directly concentrated in vacuo. The residue was purified by chromatography on silica gel, using PE/ EA as the solvent system.

1-phenylpent-4-in-1-one (12a)[22]



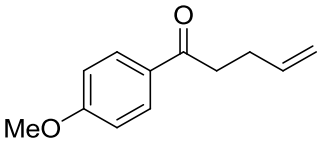
According to the general procedure, 2-bromoacetophenone (0.050 g, 0.25 mmol), $Cu(dap)_2Cl$ (1 mol%) allyltri-n-butyltin (0.083 g, 0.25 mmol) afforded **12a** (0.032 g, 80 %) as colorless liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.51.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99-7.95 (m, 2H), 7.59-7.53 (m, 1H), 7.49-7.43 (m, 2H), 5.97-5.84 (m, 1H), 5.12-4.99 (m, 2H), 3.08 (t, *J* = 7.1 Hz, 2H), 2.54-2.46 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 199.4, 137.3, 136.9, 133.0, 128.6, 128.0, 115.3, 37.7, 28.1.

MS (EI, 70 eV): *m/z* (%) = 160.1 (4.8) [M+], 105.0 (100.0), 77.0 (31.8).

1-(4-methoxyphenyl)pent-4-in-1-one (12c)[23]



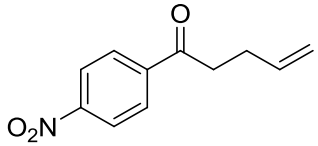
According to the general procedure, **11c** (0.055 g, 0.24 mmol), $Cu(dap)_2Cl$ (1 mol%), allyltri-n-butyltin (0.080 g, 0.24 mmol) afforded **12c** (0.034 g, 75 %) as colorless liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.37.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, *J*=8.9 Hz, 2H), 6.93 (d, 1 *J*=8.9 Hz, 2H), 5.97-5.84 (m, 1H), 5.12-4.99 (m, 2H), 3.87 (s, 3H), 3.03 (t, *J* = 7.2 Hz, 2H), 2.52-2.44 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 198.0, 163.4, 137.5, 130.3, 130.0, 115.1, 113.7, 55.4, 37.4, 28.3.

MS (EI, 70 eV): *m/z* (%) = 190.1 (9.0) [M+], 135.1 (100.0), 107.0 (7.2), 77.0 (11.8).

1-(4-nitrophenyl)pent-4-in-1-one (12e)



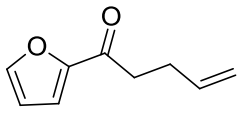
According to the general procedure, **11e** (0.050 g, 0.20 mmol), $Cu(dap)_2Cl$ (1 mol%), allyltri-n-butyltin (0.066 g, 0.20 mmol) afforded **12e** (0.031 g, 74 %) as pale yellow liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.37.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (d, *J*=8.6 Hz, 2H), 8.11 (d, *J*=8.8 Hz, 2H), 5.96-5.82 (m, 1H), 5.13-5.02 (m, 2H), 3.13 (t, *J* = 7.1 Hz, 2H), 2.55-2.48 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 197.8, 150.3, 141.3, 136.6, 129.0, 123.9, 115.8, 38.3, 27.8.

HRMS (ESI): Calcd. For $C_{11}H_{11}NO_3$ *m/z* 205.0739, found *m/z* 205.0744.

1-(furan-2-yl)pent-4-in-1-one (12f)[24]



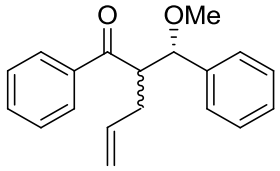
According to the general procedure, **11f** (0.040 g, 0.21 mmol), $Cu(dap)_2Cl$ (1 mol%), allyltri butyltin (0.069g, 0.21 mmol) afforded **12f** (0.021 g, 68 %) as colorless liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.54.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 1.6, 0.6 Hz, 1H), 7.18 (dd, *J* = 3.5, 0.6 Hz, 1H), 6.52 (dd, *J* = 3.5, 1.6 Hz, 1H), 5.94-5.80 (m, 1H), 5.11-4.97 (m, 2H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.51-2.43 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 188.7, 152.7, 146.2, 137.0, 116.9, 115.4, 112.1, 37.5, 28.0.

MS (EI, 70 eV): *m/z* (%) = 150 (15.8) [M+], 94.9 (100.0).

2-(methoxy(phenyl)methyl)-1-phenylpent-4-in-1-one (12g)



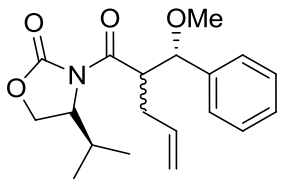
According to the general procedure, **11g** (0.050 g, 0.15 mmol), $Cu(dap)_2Cl$ (1 mol%), allyltri-n-butyltin (0.051 g, 0.15 mmol) afforded **12g** (0.031 g, 72 %) as light yellow gummy liquid after column purification on silica gel (separable mixture of diastereomers (syn:anti=85:15)). R*f* (EtOAc/hexane 1:9): 0.54.

^{1}H NMR (300 MHz, $CDCl_3$): syn isomer δ 8.02-8.00 (m, 2H), 7.56-7.54 (m, 1H), 7.50-7.47 (m, 2H), 7.22-7.08 (m, 5H) 5.51-5.38 (m, 1H), 4.83-4.76 (m, 2H), 4.43 (d, *J* = 9.7 Hz, 1H), 3.86 (dt, *J* = 3.89, 9.98 Hz, 1H), 3.04 (s, 3H), 2.37-2.26 (m, 1H), 1.91-1.83 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 201.8, 139.7, 137.9, 135.3, 132.6, 128.2, 128.2, 128.0, 127.8, 127.5, 117.0, 84.0, 56.8, 53.8, 34.3.

HRMS (ESI): Calcd. For $C_{19}H_{20}O_2$ *m/z* 280.1463, found *m/z* 280.1470.

(R)-3-((R)-2-((S)-methoxy(phenyl)methyl)pent-4-enoyl)-4-isopropyloxazolidin-2-one (12h)



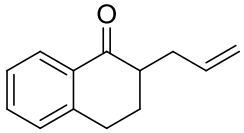
According to the general procedure, **11h** (0.050 g, 0.13 mmol), $Cu(dap)_2Cl$ (1 mol%), allyltri-n-butyltin (0.043 g, 0.13 mmol) afforded **12h** (0.033 g, 77 %) as white solid (separable mixture of diastereomers (syn:anti=25:75)) after column purification on silica gel. R*f* (EtOAc/hexane 2:8): 0.61.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.35 (m, 2H), 7.34-7.28 (m, 2H), 7.27-7.24 (m, 1H), 5.83-5.69 (m, 1H), 5.05-4.94 (m, 2H), 4.56-4.59 (m, 1H), 4.44-4.42 (m, 1H), 4.35-4.30 (m, 1H), 4.15-4.02 (m, 2H), 3.19 (s, 3H), 2.67-2.52 (m, 2H), 1.94-1.83 (m, 1H), 0.72 (d, *J* = 7.0 Hz, 3H), 0.33 (d, *J* = 6.8 Hz, 3H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9, 153.5, 139.1, 135.5, 128.3, 128.0, 127.9, 116.8, 84.0, 62.8, 58.1, 56.8, 49.4, 33.3, 28.3, 17.7, 14.1.

HRMS (ESI): Calcd. For $C_{19}H_{25}NO_4Na$ *m/z* 354.1676, found *m/z* 354.1670.

2-allyl-3,4-dihydronapthalen-1(2H)-one (12i)[25]



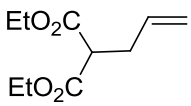
According to the general procedure, **11i** (0.030 g ,0.13 mmol), $Cu(dap)_2Cl$ (1 mol%), allyltri-n-butyltin (0.044 g, 0.13 mmol) afforded **12i** (0.017 g, 70 %) as colorless oil after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.54.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.46 (td, *J* = 7.6, 1.4 Hz, 1H), 7.32-7.27 (m, 1H), 7.26 (d, 1H, *J* = 7.6 Hz,), 5.92-5.78 (m, 1H), 5.14-5.04 (m, 2H), 2.99 (dd, *J* = 7.6, 4.5 Hz, 2H), 2.81-2.71 (m, 1H), 2.61-2.50 (m, 1H), 2.32-2.19 (m, 2H), 1.93-1.79 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 199.5, 144.0, 136.2, 133.2, 132.5, 128.7, 127.4, 126.6, 116.8, 47.1, 34.0, 28.6, 27.9.

MS (EI, 70 eV): *m/z* (%) = 186.1 (100.0) [M+], 145.1 (26.1), 118.1 (59.4), 90.1 (37.4).

Diethyl-2-allyl-malonate (12k)[26]



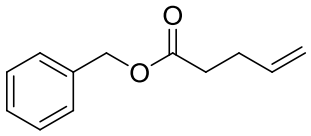
According to the general procedure, diethyl bromomalonate (0.040 g, 0.16 mmol), $Cu(dap)_2Cl$ (1 mol%), allyltri-n-butyltin (0.055 g, 0.16 mmol) afforded **12k** (0.023 g, 70 %) as colorless oil after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.46.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.80-5.67 (m, 1H), 5.11-4.99 (m, 2H), 4.19-4.11 (m, 4H), 3.38 (t, *J* = 7.5 Hz, 1H), 2.62-2.57 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.9, 134.1, 117.5, 61.4, 51.6, 32.8, 14.1.

MS (EI, 70 eV): *m/z* (%) = 200.1 (2.0) [M+], 155.1 (15.1), 127.1 (100.0), 109.0 (78.3).

Benzyl pent-4-enoate (12l)[27]



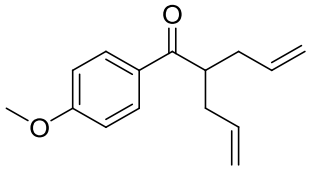
According to the general procedure, benzyl-2-bromoacetate (0.050 g, 0.21 mmol), $Cu(dap)_2Cl$ (1 mol%), allyltri-n-butyltin (0.072 g, 0.21 mmol) afforded **12l** (0.033 g, 80 %) as colorless oil after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.54.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.30 (m, 5H), 5.89-5.76 (m, 1H), 5.13 (s, 2H), 5.09-4.97 (m, 2H), 2.50-2.35 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9, 136.6, 136.0, 128.5, 128.2, 115.5, 66.2, 33.5, 28.8.

MS (EI, 70 eV): *m/z* (%) = 190.1 (3.6) [M+], 130.1 (9.4), 91.1 (100.0), 77.1 (11.4).

2-allyl-1-(4-methoxyphenyl)pent-4-in-1-one (14a)



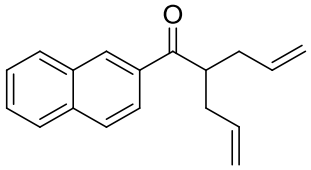
According to the general procedure, **13a** (0.050 g, 0.16 mmol), $Cu(dap)_2Cl$ (1 mol%), allyltri-n-butyltin (0.107 g, 0.16 mmol) afforded **14a** (0.033 g, 89 %) as colorless liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.62.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.80-5.67 (m, 2H), 5.06-4.95 (m, 4H), 3.87 (s, 3H), 3.57-3.48 (m, 1H), 2.56-2.45 (m, 2H), 2.33-2.23 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 201.2, 163.4, 135.6, 130.6, 130.1, 116.8, 113.8, 55.4, 45.2, 36.0.

HRMS (ESI): Calcd. For $C_{15}H_{18}O_2$ *m/z* 230.1307, found *m/z* 230.1305.

2-allyl-1-(napthalen-6-yl)pent-4-in-1-one (14b)



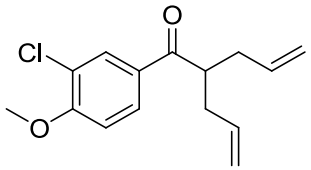
According to the general procedure, **13b** (0.10 g, 0.30 mmol), $Cu(dap)_2Cl$ (1 mol%), allyltri-n-butyltin (0.201g, 0.60 mmol) afforded **14b** (0.059 g, 78 %) as colourless liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.58.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.04-7.87 (m, 4H), 7.63-7.53 (m, 2H), 5.85-5.71 (m, 2H), 5.10-4.97 (m, 4H), 3.80-3.71 (m, 1H), 2.64-2.53 (m, 2H), 2.41-2.31 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 202.7, 135.5, 135.5, 134.4, 132.6, 129.8, 129.6, 128.5, 128.4, 127.7, 126.7, 124.2, 117.0, 45.6, 36.0.

HRMS (ESI): Calcd. For $C_{18}H_{18}O$ *m/z* 250.1358, found *m/z* 250.1357.

2-allyl-1-(3-chloro-4-methoxyphenyl)pent-4-in-1-one (14c)



According to the general procedure, **13c** (0.050 g, 0.19 mmol), $Cu(dap)_2Cl$ (1 mol%), allyltri-n-butyltin (0.130 g, 0.38 mmol) afforded **14c** (0.042 g, 80 %) as colorless liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.37.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, *J* = 2.1 Hz, 1H), 7.85 (dd, *J* = 8.6 Hz, *J* = 2.2 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 1H), 5.79-5.65 (m, 2H), 5.08-4.94 (m, 4H), 3.97 (s, 3H), 3.53-3.44 (m, 1H), 2.56-2.42 (m, 2H), 2.34-2.22 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 200.3, 158.7, 135.3, 130.6, 128.7, 122.9, 117.0, 111.3, 56.3, 45.3.

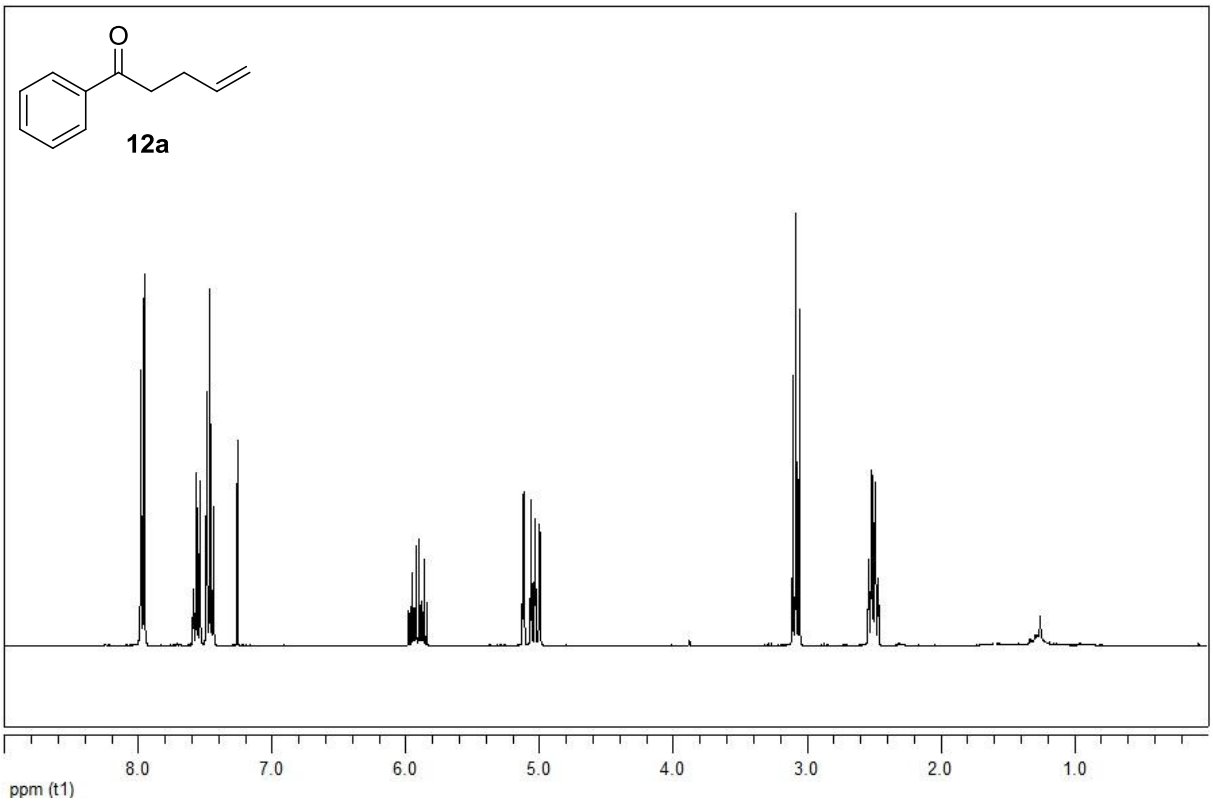
Appendix

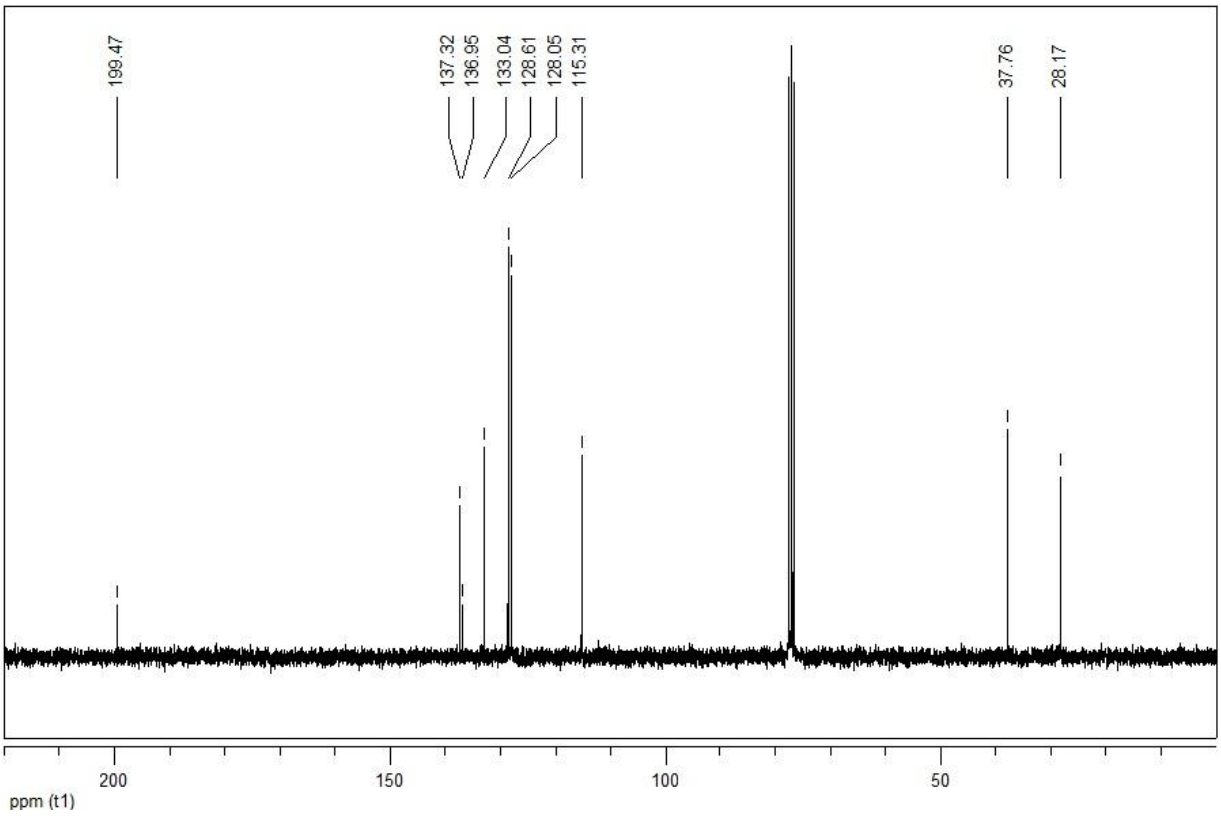
Selected NMR- spectra

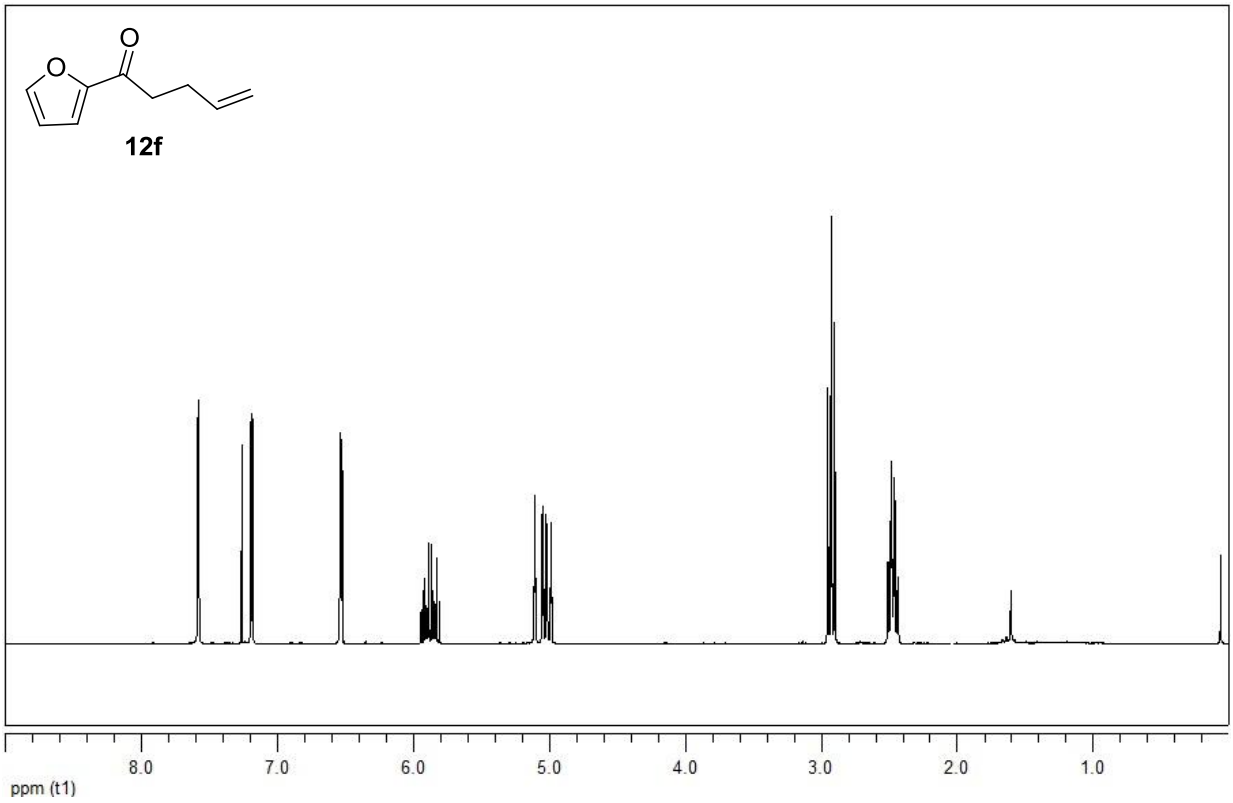
^{1}H-NMR spectra - upper image

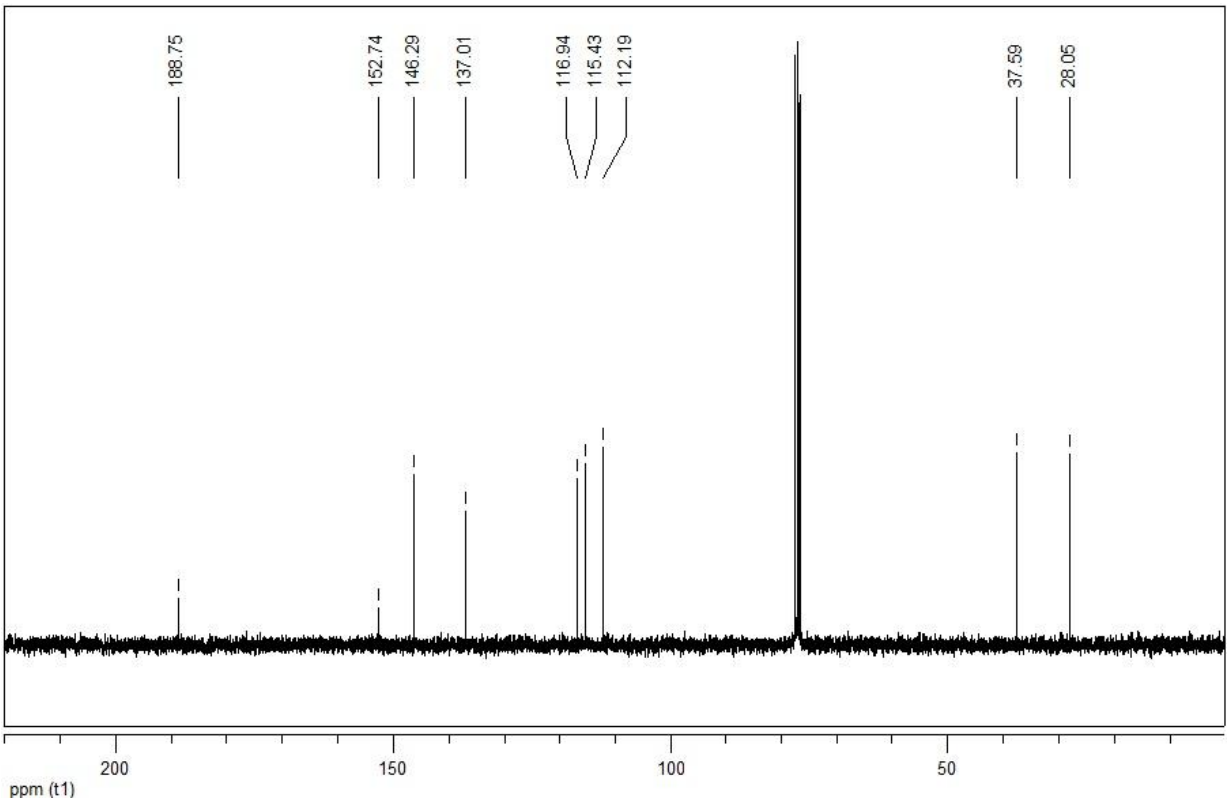
^{13}C-NMR spectra - lower image

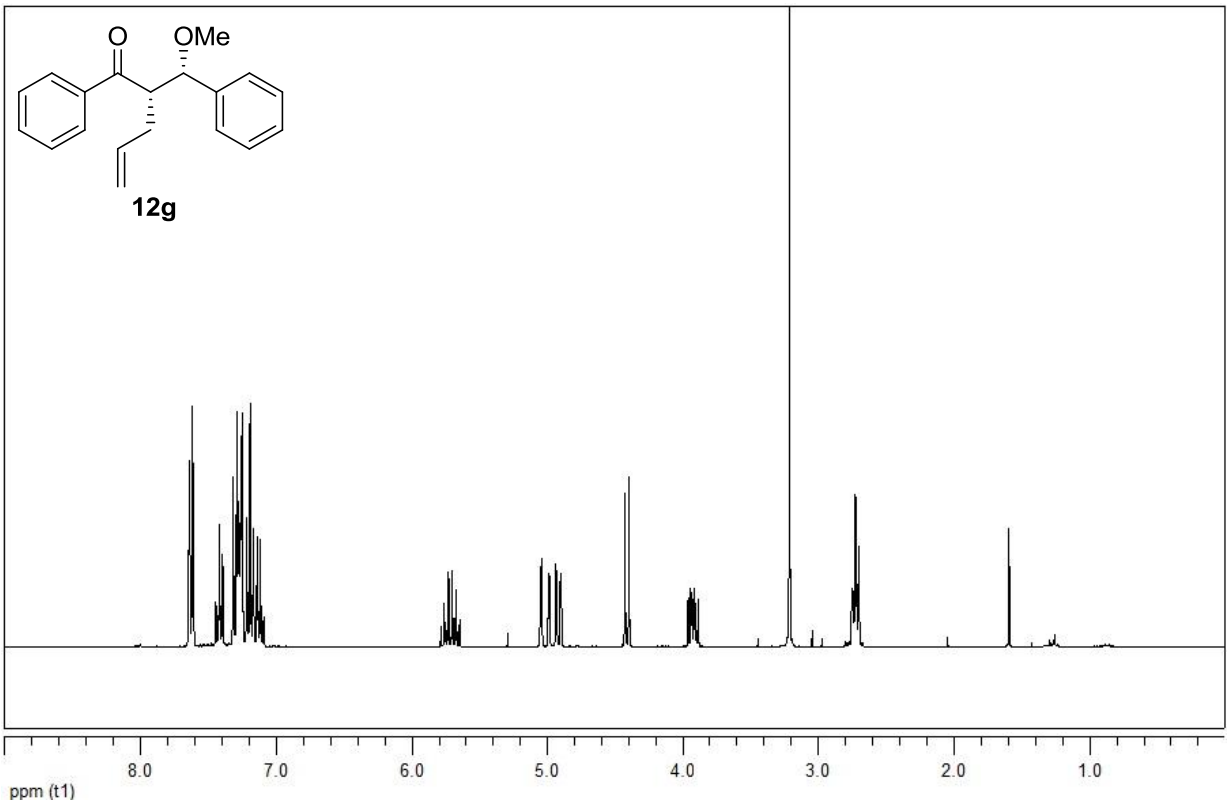
Solvent, if not stated otherwise: $CDCl_3$

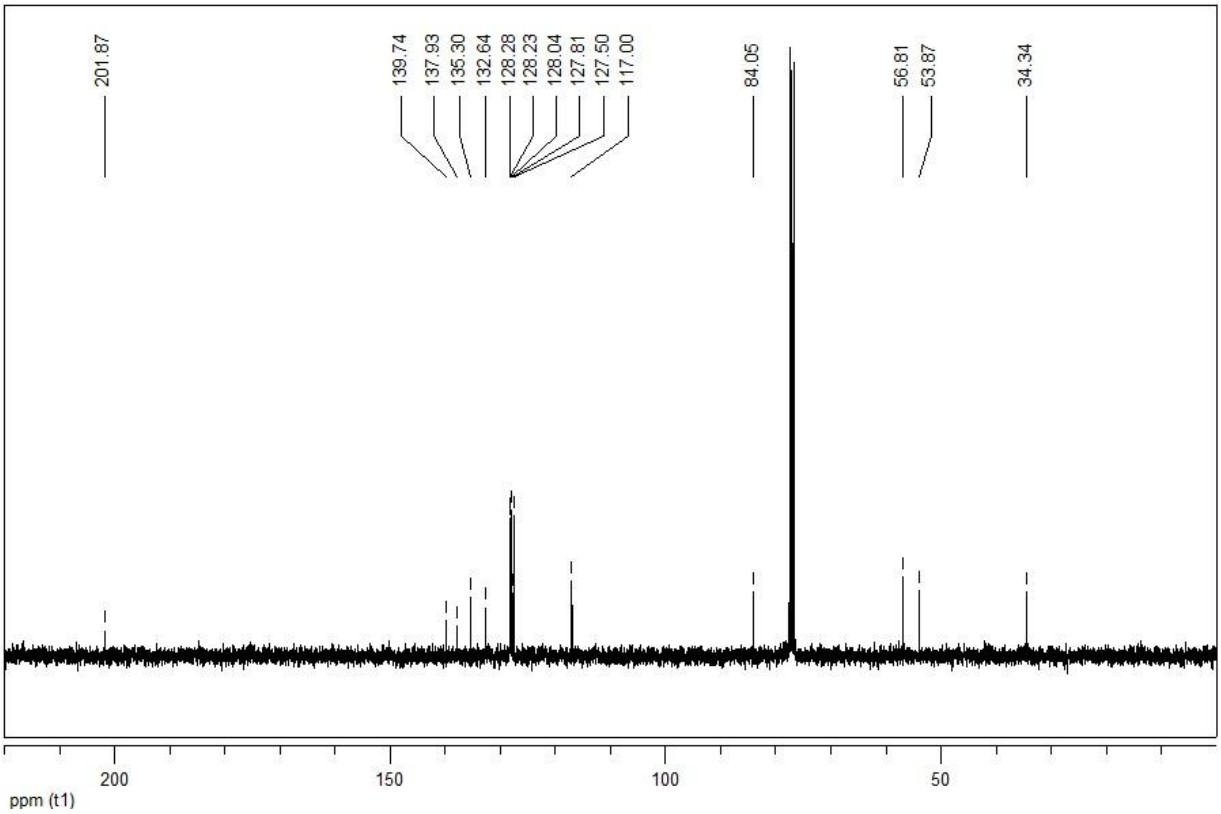

O
12a
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

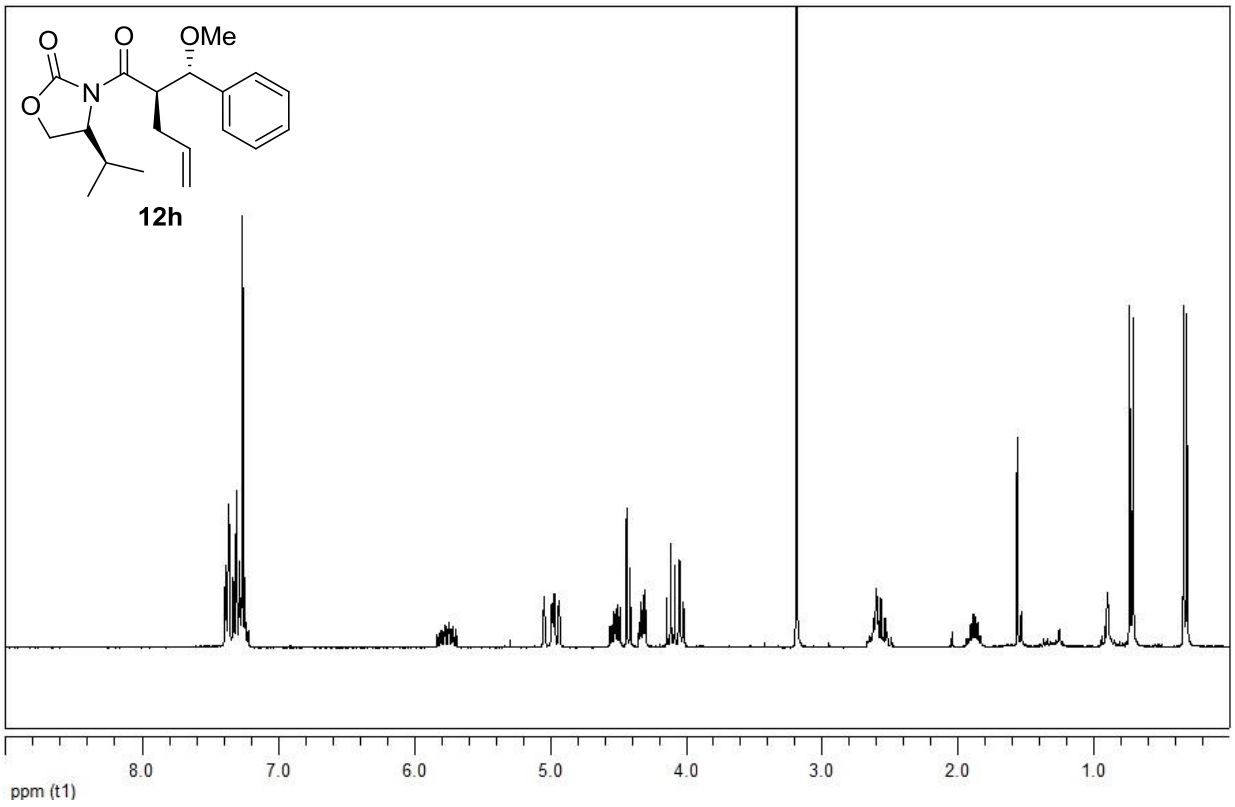

199.47
137.32
136.95
133.04
128.61
128.05
115.31
37.76
28.17
200
150
100
50
ppm (t1)

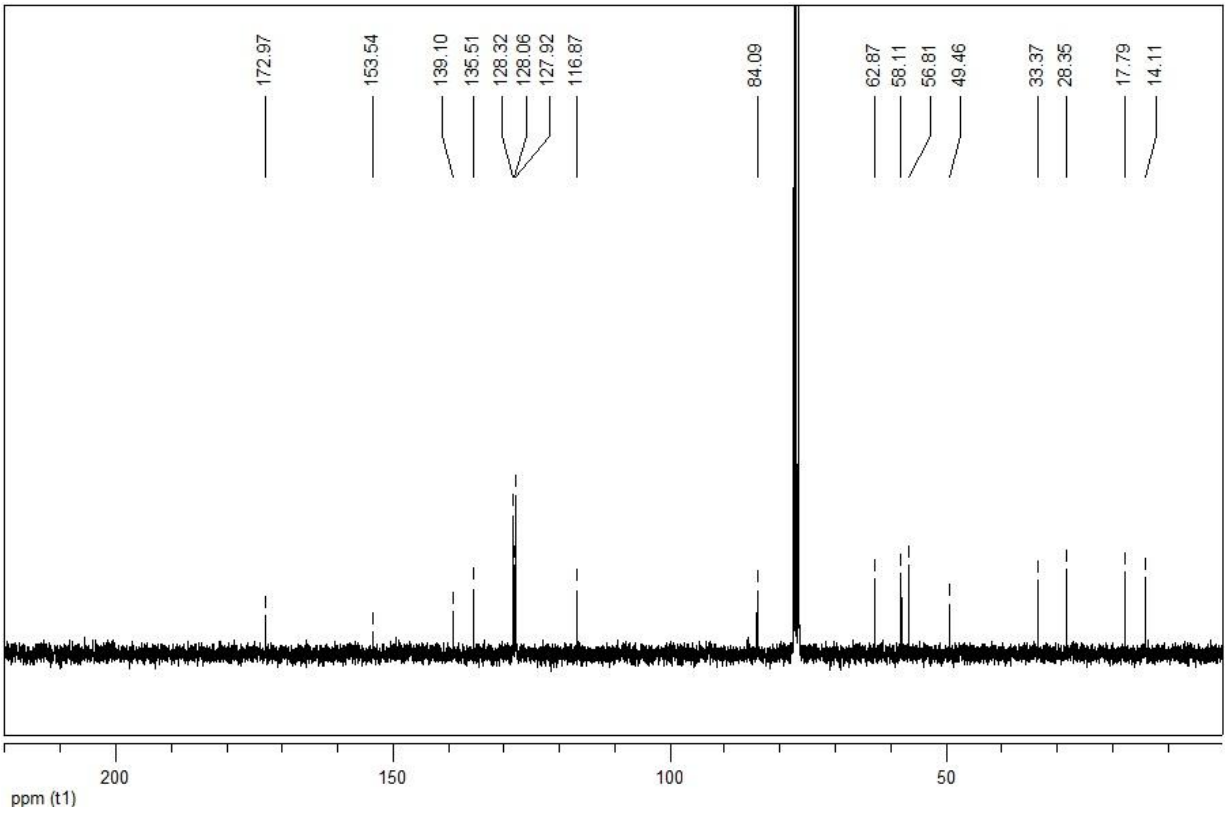

O
O
12f
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


188.75
152.74
146.29
137.01
116.94
115.43
112.19
37.59
28.05
200
150
100
50
ppm (t1)


O
OMe
12g
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


201.87
139.74
137.93
135.30
132.64
128.28
128.23
128.04
127.81
127.50
117.00
84.05
56.81
53.87
34.34
200
150
100
50
ppm (t1)


O
O
OMe
N
O
12h
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


172.97
153.54
139.10
135.51
128.32
128.06
127.92
116.87
84.09
62.87
58.11
56.81
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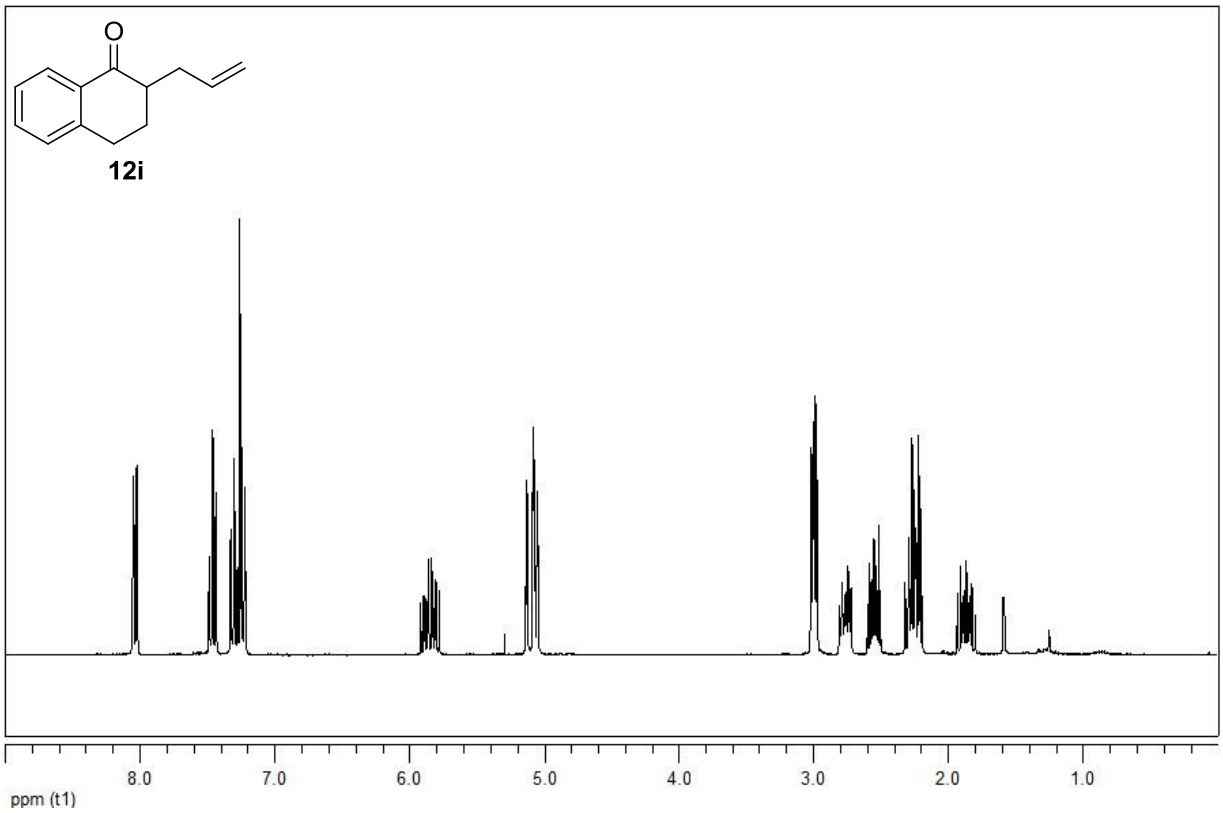
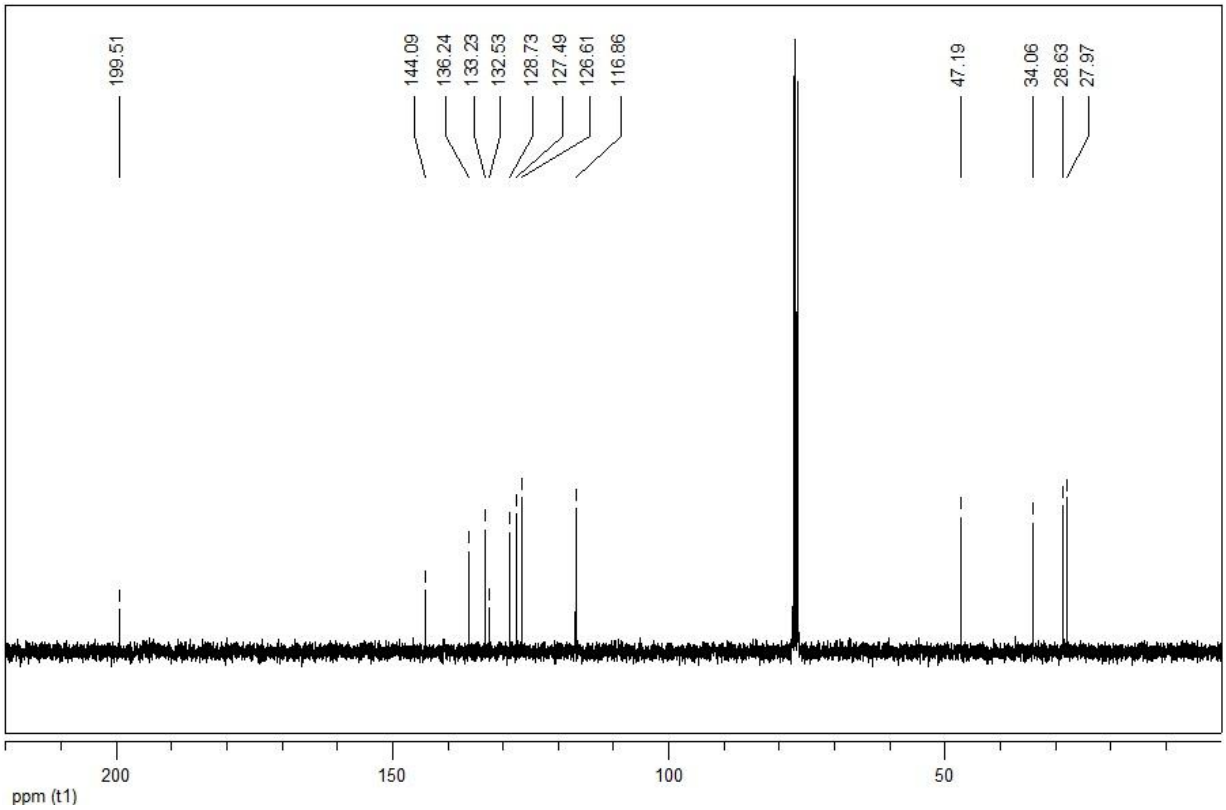
33.37
28.35
17.79
14.11
200
150
100
50
ppm (t1)


O
12i
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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144.09
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133.23
132.53
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27.97
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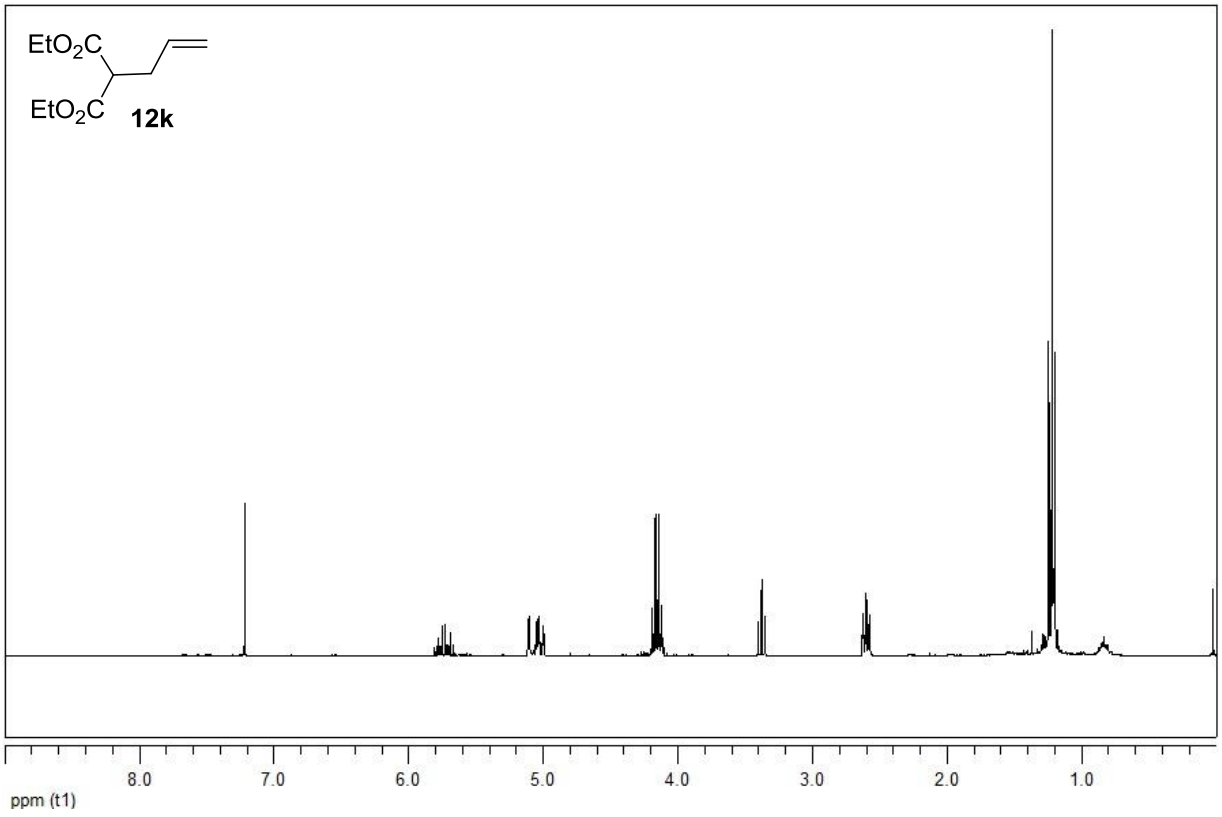
100
50
ppm (t1)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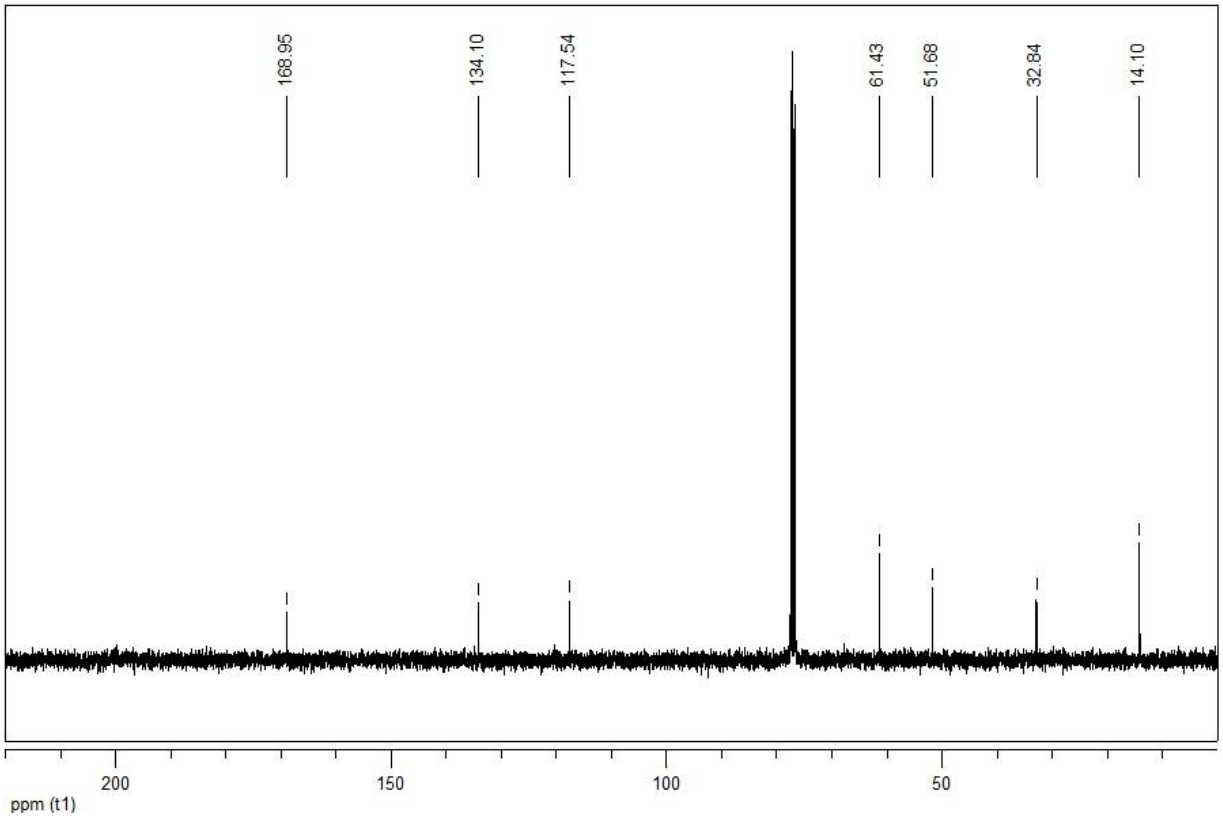
ppm (t1)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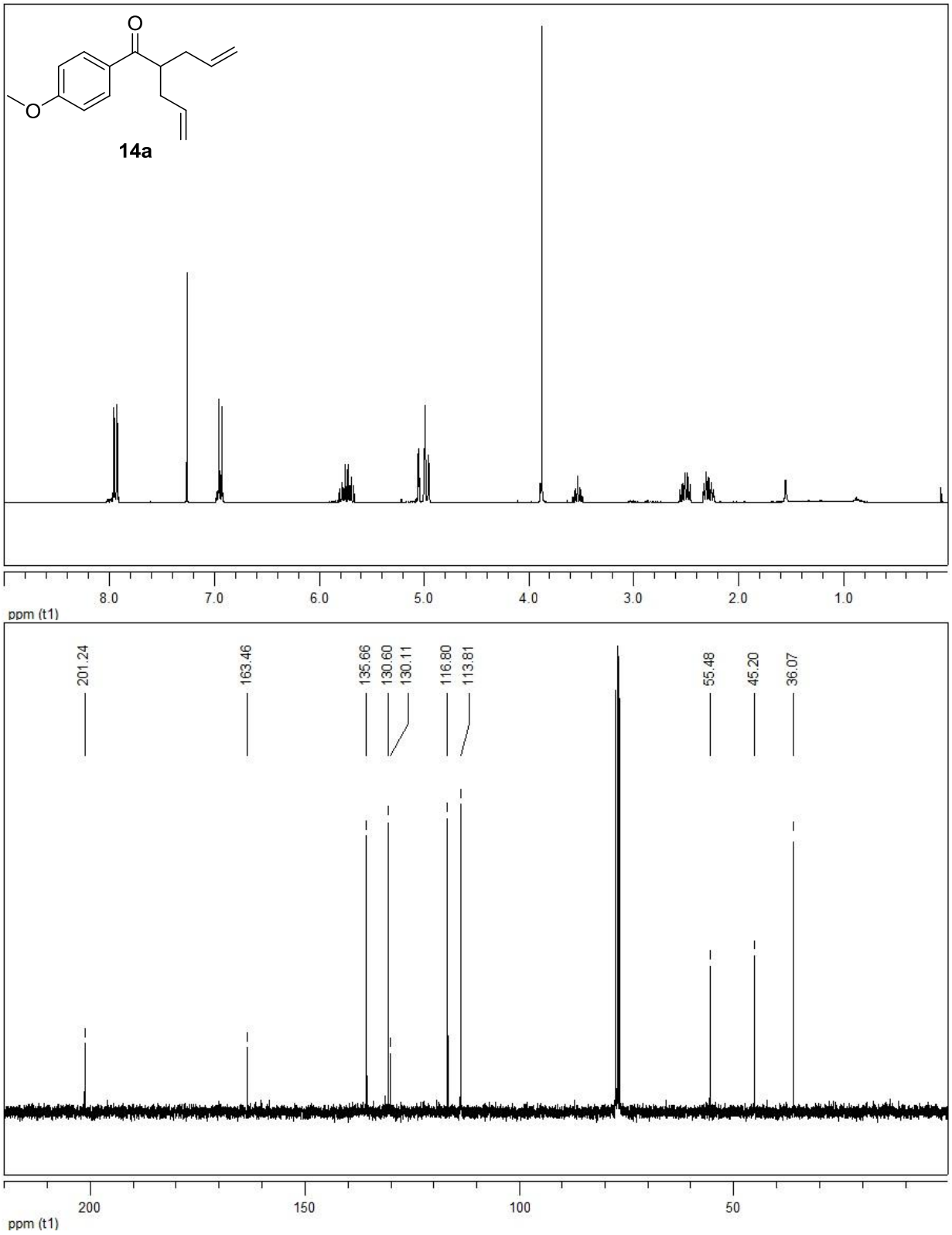
100
50
ppm (t1)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3.0
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135.66
130.60
130.11
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113.81
55.48
45.20
36.07
200
150
100
50
ppm (t1)

3.7 References

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4. Atom Transfer Radical Addition (ATRA) of Benzyl halides to Styrenes and Silyl enol ethers

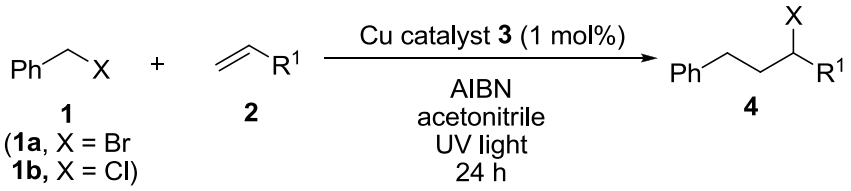
4.1 Introduction

Atom transfer radical addition (ATRA) is a fundamental reaction for C-C bond formation in organic chemistry. The origin of ATRA can be traced back in 1937 when Kharasch et al. reported the peroxide effect on the addition of HBr to olefin.[1]

In mid 1940s, Kharasch and coworkers reported direct addition of halogenated alkenes to olefinic double bonds using radical initiators or light.[2] Such addition of organic halides to double (or triple) bonds is established as a versatile tool in organic synthesis since it results in the formation of a C-C and C-X (halogen) bond simultaneously. Although there are a few reports of ATRA utilizing peroxides,[1] triethylboron[3] and organitin[4] reagents as initiators, typically used initiators in ATRA are different transition metal complexes of copper,[5] ruthenium,[6] iron,[7] or nickel.[8]

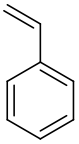
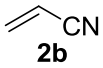
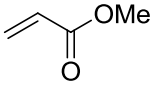
Despite tremendous advancement in the area of ATRA, demonstrating the synthetic potential of these processes, use of benzyl halides **1** as ATRA reagent was elusive until recently when Pintauer and coworkers reported the addition of benzyl bromides and -chlorides to olefinic double bonds **2** using a Cu (II) catalyst and AIBN under UV light irradiation albeit in low yields (Scheme 4.1).[9]

Scheme 4.1. ATRA of benzyl halides to olefins by UV light irradiation



catalyst **3** = $[Cu^{II}(TPMA)X][X]$

TPMA = tris(2-pyridylmethyl)amine

entry	halide (**1**)	alkene (**2**)	yield (%)[a]
1	**1a**	 **2a**	34 (X = Br)
2	**1b**		23 (X = Cl)
3	**1a**	 **2b**	21 (X = Br)
4	**1b**		16 (X = Cl)
5	**1a**	 **2c**	33 (X = Br)
6	**1b**		26 (X = Cl)

[a] Yield was determined using ^{1}H NMR spectroscopy

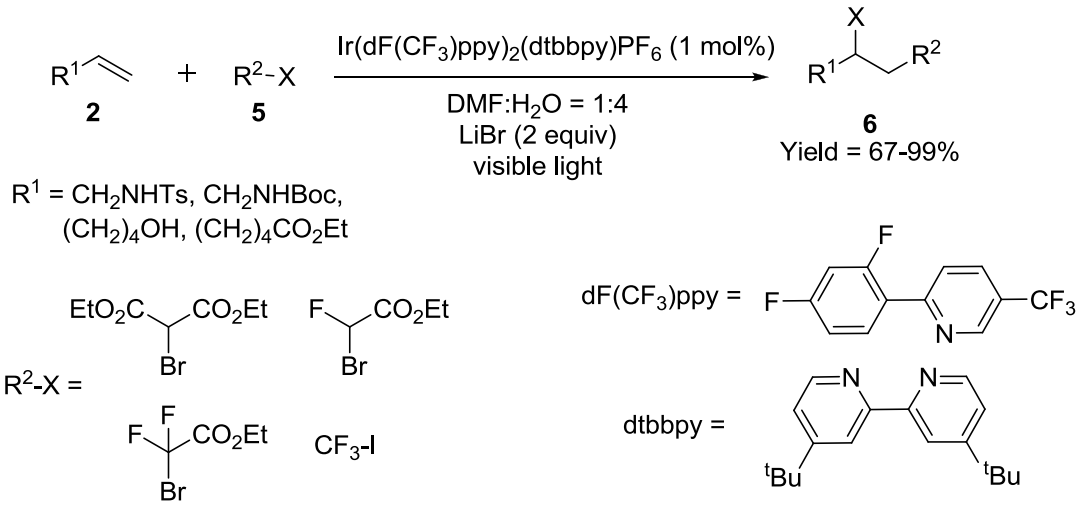
4.2 Visible light mediated atom transfer radical addition

The main drawbacks for many of the above mentioned ATRA are harsh, environmentally malign reaction conditions, high catalyst loading, and complex purification procedures. Visible light driven ATRA could overcome many of these limitations using mild and ease to handle reaction conditions with high catalytic efficiency. With the abundance of sunlight, an ATRA, triggered by visible-light definitely has a tremendous potential.

In 2011, Stephenson et al. first reported the visible light mediated intermolecular ATRA between olefins **2** and activated alkyl halides **5** using an iridium catalyst $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (Scheme 4.2).[10] Lithium bromide was presumed to assist bromo ester activation towards reduction, whereas water played a role in faster reaction rate. A wide range of halogenated

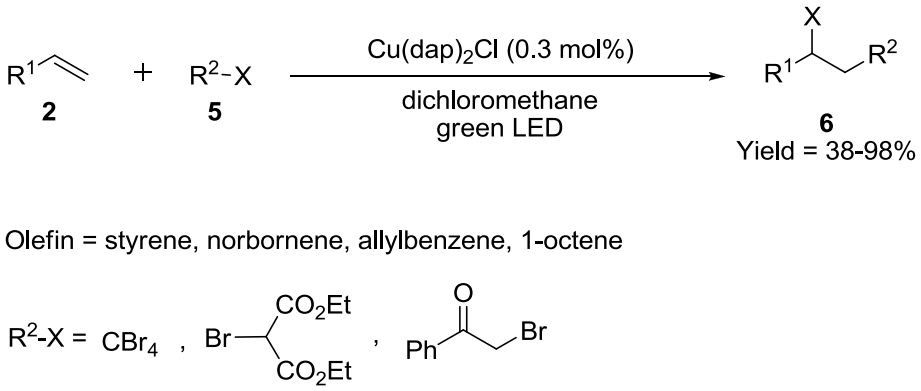
compounds and olefins were capable of producing ATRA under the reaction conditions resulted in good to excellent yields of the ATRA product **6**.

Scheme 4.2. ATRA of organic halides to olefins by visible light irradiation



In this context, our group[11] has accomplished similar ATRA reactions as Stephenson et al. utilizing an inexpensive copper based photocatalyst $Cu(dap)_2Cl$.[12] Notable features of this ATRA were catalyst loading as low as 0.3 mol%, compatible with a variety of organic halides as ATRA reagents, with good to excellent yields of the product (Scheme 4.3).

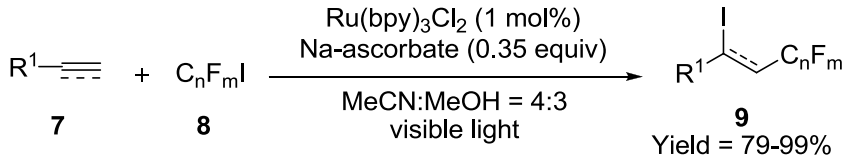
Scheme 4.3. ATRA of organic halides to olefins with $Cu(dap)_2Cl$



The products obtained from the ATRA reactions have been shown to be valuable synthons for further transformations. A mechanism has been proposed based on the oxidative quenching of excited photocatalyst.

Although photocatalytic ATRA reactions are based on oxidative quenching cycle of the catalyst, in 2012, Stephenson et al. came up with a more vigorous study on ATRA using both oxidative and reductive quenching of photocatalysis cycle and thus expanding the scope of ATRA.[13] By using sodium ascorbate as reductive quencher in the photocatalytic cycle of $Ru(bpy)_3Cl_2$ they could accomplish the ATRA of perfluoroalkyl iodides **7** to olefins and alkynes **8** in excellent yields. Use of sub-stoichiometric sodium ascorbate denoted its role as an initiator in the overall process (Scheme 4.4).

Scheme 4.4. ATRA of perfluoroalkyl iodides



7 **8** **9**

Yield = 79-99%

R^1 = $(CH_2)_4OH$, $(CH_2)_4I$, $(CH_2)_4CO_2Et$, $(CH_2)_2OH$

C_nF_mI = CF_3I, $C_6H_{13}I$, $C_8H_{17}I$, $C_{10}H_{21}I$

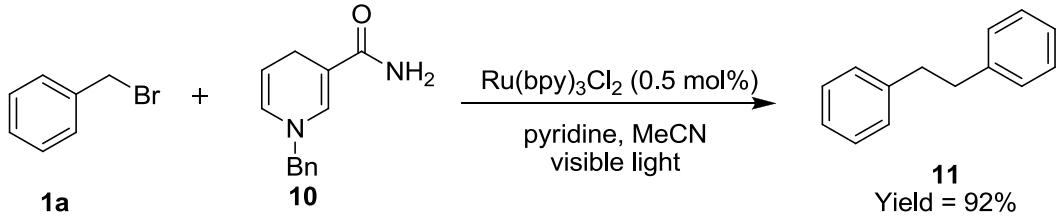
Oxidative quenching cycle was employed to expand the scope of organic halides to CCl_3Br, CBr_4, CCl_4 and TsCl.

4.3 Benzyl radical by visible light photocatalysis

Formation of benzyl radicals from benzyl halides is a well studied area in literature. Among the various established methods, electrochemical reduction of benzyl halides,[14] samarium iodide (SmI_2) mediated radical reaction,[15] metal mediated processes[16] or silica promoted photo irradiation[17] are well known procedures for the generation of benzyl radical. But arguably most exciting and elegant of all the process are visible light promoted activation of benzyl halides.

In 1984, Tanaka et al. reported the synthesis of bibenzyl **11** from benzyl bromide **1a** under visible light irradiation using of $Ru(bpy)_3Cl_2$ as sensitizer.[18] Interestingly, when the reaction was carried out in presence of only 1-benzyl-l,4-dihydronicotinamide (BNAH) **10**, in the absence of sensitizer, toluene was formed as the sole product, whereas employing $Ru(bpy)_3Cl_2$ with BNAH resulted in bibenzyl formation (Scheme 4.5).

Scheme 4.5. Bibenzyl formation from benzyl bromide in presence of $Ru(bpy)_3Cl_2$ and BNAH

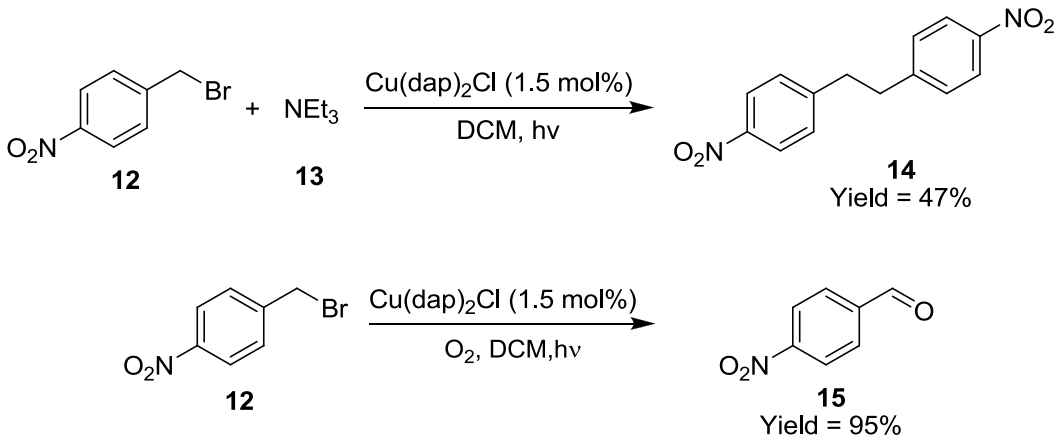


1a **10** **11** Yield = 92%

According to the authors, two different mechanisms were active under different reaction conditions. In presence of only BNAH, it's a radical chain process which was operative involving benzyl radical as chain carrier. When a photosensitizer $Ru(bpy)_3Cl_2$ was present, a two electron reduction of benzyl bromide took place by reductive quenching of excited sensitizer.

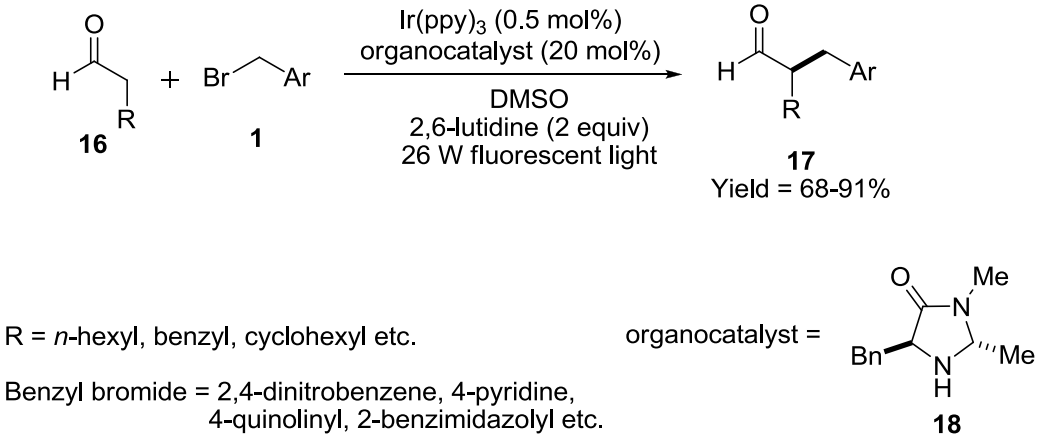
Sauvage and coworkers reported the cleavage of cleavage of benzylic C-Br bond of 4-nitrobenzyl bromide **12** by means of photoredox catalysis using the $Cu(dap)_2Cl$ (Scheme 4.6) . Depending upon the reaction condition, they could achieve bibenzyl **14** formation (in absence of air) or oxidation to aldehyde **15** of the starting benzyl bromide (with air).[12]

Scheme 4.6. Benzyl bromide activation with $Cu(dap)_2Cl$ as photoredox catalyst



In 2010, McMillan et al. achieved α-benzylation of aldehydes by merging of photoredox catalysis and organocatalysis.[19] Employing a highly reducing iridium catalyst $Ir(ppy)_3$, and imidazolidinone organocatalyst **18** α-benzylation was accomplished for a wide range of aldehydes **16** with a variety of electron deficient benzyl halides **1** in good yields and high enentioselectivity (Scheme 4.7).

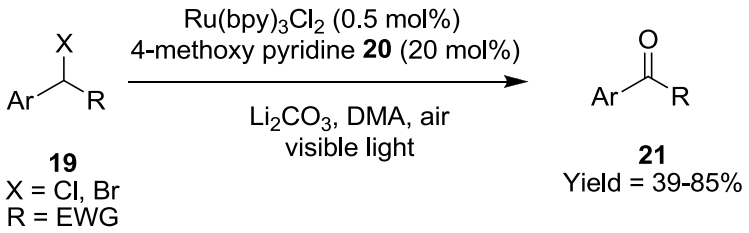
Scheme 4.7. Enantioselective α-benzylation of aldehydes



Following the same route of McMillan et al. Jiao and coworkers reported the oxidation of different α-aryl halogen derivatives **19** to corresponding α-aryl carbonyl compounds **21**

combining photoredox catalysis and organocatalysis at room temperature in presence of air and $Ru(bpy)_3Cl_2$, where 4-methoxy pyridine **20** played the role of organocatalyt (Scheme 4.8).[20]

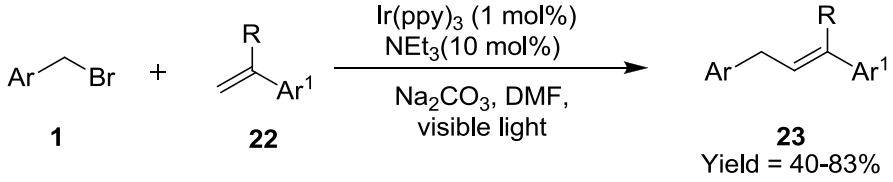
Scheme 4.8. Oxidation of α-aryl halogen derivatives to corresponding α-aryl carbonyl compounds



Both chloride and bromide as leaving group were well tolerated in the reaction. Based on EPR study, the authors speculated the presence of Ru^{+1} in the reaction mixture, which corroborated the reductive quenching cycle of the photocatylyst.

Recently, Lei and coworkers reported the alkenylation of benzyl halides **1** using highly reducing *fac*-$Ir(ppy)_3$ as photocatalyst (Scheme 4.9).[21] An oxidative quenching cycle was proposed for the transformation. This intermolecular alkenylation reaction was well compatible with secondary benzyl halides bearing a β-hydrogen.

Scheme 4.9. Alkenylation of benzyl halides

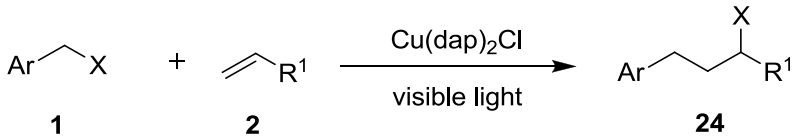


4.4 ATRA of benzyl halides to Olefins

Among all the above mentioned report of benzyl radical formation from benzyl halides by visible light photoredox catalysis, ATRA of benzyl halides to olefins were still elusive. Keeping in mind

that copper is an inexpensive metal compared to ruthenium or iridium, and $Cu(dap)_2Cl$ as a visible light photoredox catalyst can promote benzyl C-Br cleavage, we envisioned a ATRA between different benzyl halides **1** with olefins **2** (Scheme 4.10) . We were also interested in the fact that oxidative photocatalytic cycles have some added advantages over reductive counterpart like no sacrificial electron donor is necessary, less number of possible side reactions from reagents (reduction of starting material is the prominent side reaction in reductive quenching cycle) and excellent yields.

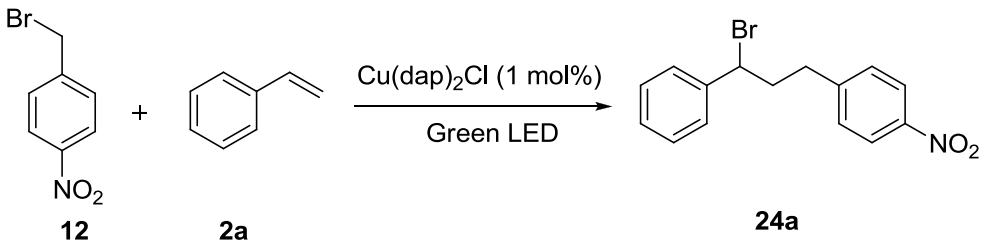
Scheme 4.10. Proposed ATRA of benzyl halides with olefins



1 **2** **24**

As a model system we investigated the ATRA between 4-nitrobenzyl bromide **12** and styrene **2a**. Using 1 mol% of $Cu(dap)_2Cl$ and 10 equiv. of styrene, the ATRA product **24a** was obtained in 85% isolated yield after 24h of irradiation with a green LED under nitrogen atmosphere in acetonitrile. Next we turned our attention to optimize the reaction conditions by screening different solvents and photocatalysts. When acetonitrile was replaced by dichloromethane as solvent the reaction was incomplete after 24 hours (Table 4.1, entry 1). Finally 1 mol% $Cu(dap)_2Cl$, with 5 equiv. of styrene in acetonitrile for 12 hours of irradiation was found to be optimal condition for the reaction giving 85% isolated yield (Table 4.1, entry 3). It is worthy to mention that $Ir(ppy)_2(dtbbpy)PF_6$ was also a competent photocatalyst (Table 1, entry 4) with similar result as $Cu(dap)_2Cl$. But copper being cost effective (cost per mol Cu/Ir = 1:10000) was the catalyst of our choice.

Table 4.1. Optimization of reaction conditions: screening of solvents and catalysts



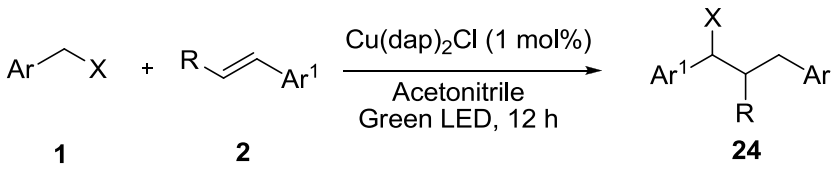
12 **2a** **24a**

entry	condition	yield (%)[a]
1	$Cu(dap)_2Cl$ (1 mol%), styrene (10 equiv), DCM, 530 nm, 24 h	60
2	$Cu(dap)_2Cl$ (1 mol%), styrene (10 equiv), CH_3CN, 530 nm, 24 h	85
3	**$Cu(dap)_2Cl$ (1 mol%), styrene (5 equiv), CH_3CN, 530 nm, 12 h**	**85**
4	$Ir(ppy)_2(dtbbpy)PF_6$ (1 mol%), styrene (5 equiv), CH_3CN, 455 nm, 12 h	85
5	$Ru(bpy)_3Cl_2$ (1 mol%), styrene (5 equiv), CH_3CN, 455 nm, 12 h	69
6	no photocatalyst, 530 nm light, 24 h	no reaction
7	with $Cu(dap)_2Cl$, no light, 24 h	no reaction

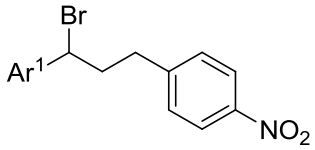
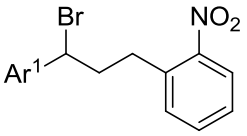
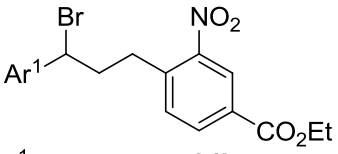
[a] Isolated yield after purification on SiO_2

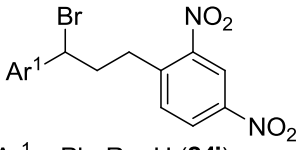
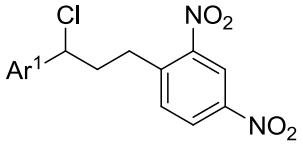
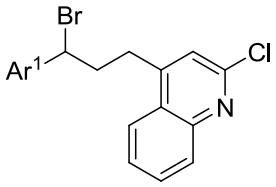
$Ru(bpy)_3Cl_2$ was less effective for the above transformation giving 69% yield of expected product after 12 hours of irradiation with blue LED (Table 4.1, entry 5). When the reaction was performed without any photocatalyst, no product was obtained even after 24 hours of irradiation (Table 4.1, entry 6). Similarly when light was excluded from the reaction, keeping other parameters unchanged, no conversion was achieved (Table 4.1, entry 7). These two control experiments proved that both light and photocatalst were essential for the above mentioned ATRA reaction.

Table 4.2. Substrate Scope of the ATRA Reaction between Nitrobenzyl Halides and Styrenes[a]



1 **2** **24**

entry	Ar	X	product	yield (%) [b]
	4-NO_2-Ph	Br		
1			Ar^1 = Ph, R = H (**24a**)	85[c]
2			Ar^1 = 4-Br-Ph, R = H (**24b**)	90
3			Ar^1 = 3-Cl-Ph, R = H (**24c**)	87 (84)[c]
4			Ar^1 = 2-napthyl, R = H (**24d**)	85 (83)[c]
	2-NO_2-Ph	Br		
5			Ar^1 = Ph, R = H (**24e**)	91 (80)[d]
6			Ar^1 = 4-Br-Ph, R = H (**24f**)	87
7			Ar^1 = 3-Cl-Ph, R = H (**24g**)	80 (79)[c]
8			Ar^1 = biphenyl, R = H(**24h**)	82
	4-CO_2Et-2-NO_2-Ph	Br		
9			Ar^1 = Ph, R = H (**24i**)	70

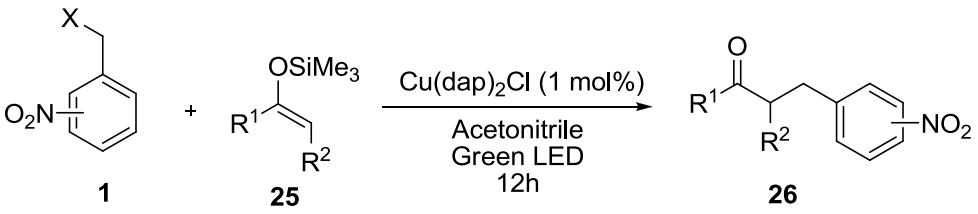
entry	Ar	X	product	yield (%) [b]
	2,4-di-NO_2-Ph	Br		
10			Ar^1 = Ph, R = H (**24j**)	89
11			Ar^1 = Ph, R = Me (**24k**)	35[c,e,f]
12			Ar^1 = 4-Br-Ph, R = H (**24l**)	86
13			Ar^1 = 3-Cl-Ph, R = H (**24m**)	95
14			Ar^1 = 2-napthyl, R = H (**24n**)	81
15			Ar^1 = biphenyl, R = H (**24o**)	90
	2,4-di-NO_2-Ph	Cl		
16			Ar^1 = Ph, R = H (**24p**)	51
17			Ar^1 = 3-Cl-Ph, R = H (**24q**)	92
18			Ar^1 = 4-methyl, R = H (**24r**)	93
	4-quinolinyl	Br		
19			Ar^1 = 2-napthyl, R = H (**24s**)	66
20	4-CN-Ph	Br	------	no reaction
21	4-CF_3-Ph	Br	------	no reaction
22	Ph	Br	------	no reaction

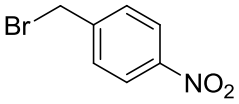
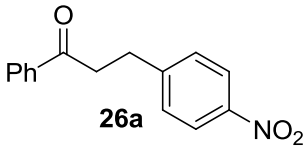
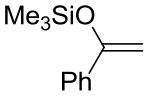
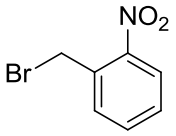
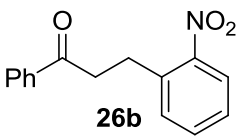
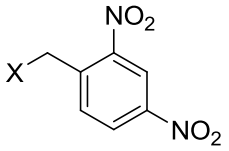
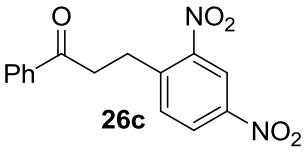
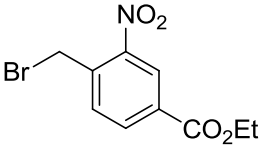
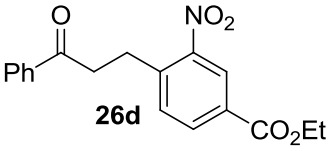
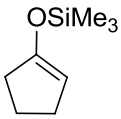
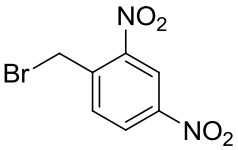
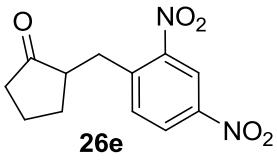
[a] Benzyl halide (0.2 mmol, 1 equiv), styrene (2-5 equiv), $Cu(dap)_2Cl$ (1 mol%) in degassed acetonitrile (1.0 mL), external irradiation at 530 nm for 12 h. [b] Yield of isolated product. [c] 1 mmol of benzylbromide. [d] 2 mmol of benzylbromide with 0.5 mol% of catalyst loading [e] Internal irradiation at 60°C for 20 h (see experimental section for details). [f] Combined yield of two diastereomers (dr = 1.3:1)

Having the optimized reaction condition in hand, we proceeded to evaluate the scope of the reaction (Table 4.2). Presence of an strongly electron withdrawing nitro group (Table 4.2, entries 1-18) in phenyl ring of benzylic moiety or a electron poor heteroarene (Table 4.2, entry 19) was essential requisite for the radical formation. 2,4-Dinitrobenzyl chloride, though resulted in moderate yield when reacted with styrene (Table 4.2, entry 16), led to excellent yield with substituted styrenes (Table 4.2, entries 17-18). Attempts to use 4-Cyano (Table 4.2, entry 20), 4-Trifluoromethylbenzyl bromide (Table 4.2, entry 21) or benzyl bromide itself (Table 4.2, entry 22), resulted in complete recovery of the starting material presumably due to the high reduction potential of initial C-Br bond cleavage step for electro-neutral or partially electron deficient benzylic sytem. ($E_{1/2}$ = –1.85 V vs SCE for benzyl bromide in MeCN).[22]

In case of alkenes, apart from styrene, 2-vinylnaphthalene (Table 4.2, entries 4, 14, 19) and 4-vinylbiphenyl (Table 4.2, entries 8, 15) proved to be good substrates for the above mentioned transformation. Substitution at the β-position of styrene resulted in low yield of the product (Table 4.2, entry 11) after 20 hours of irradiation at 60 °C. Halide substitutions at *para* (Table 4.2, entries 2, 6, 12) or *meta* position (Table 4.2, entries 3, 7, 13, 17) of styrene were well tolerated showing no cross reactivity.

Table 4.3. Reaction of benzyl halides with silyl enol ethers[a]



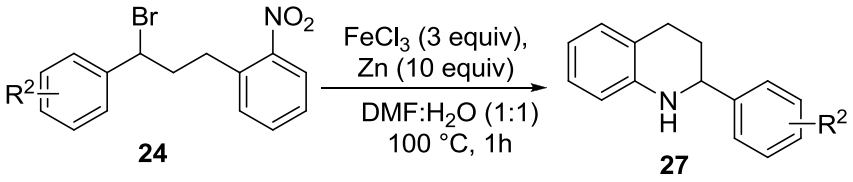
entry	silyl enol ether	benzyl halide	product(**26**)	yield (%)[b]
1				87%
2				78%
3				90%, X=Br 92%, X=Cl
4				81%
5				50%

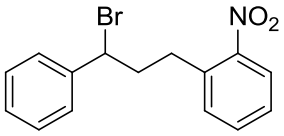
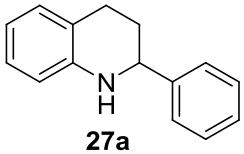
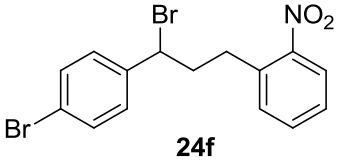
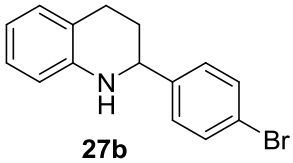
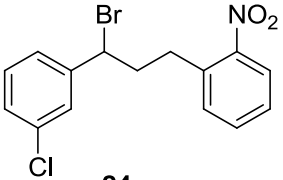
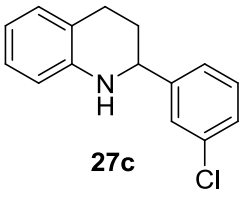
[a] Reaction conditions: Benzyl halide (1 equiv), silyl enol ether (3 equiv), $Cu(dap)_2Cl$ (1 mol%) in degassed acetonitrile, irradiation at 530 nm for 12 h. [b] Yield of isolated product.

4.5 Synthesis of tetrahydroquinolines

To further illustrate the applicability of the titled methodology, ATRA products obtained from the reaction of *o*-nitrobenzyl bromide were converted to corresponding tetrahydroquinolines. Treatment of the ATRA products **24** with $FeCl_3$/Zn in DMF–H_2O (1:1) under reflux conditions smoothly resulted in the reduction of the nitro to the amino functionality with concurrent cyclization to 2-substituted tetrahydroquinolines **27** in good yields.[23]

Table 4.4. Application of ATRA products to the synthesis of tetrahydroquinolines[a]

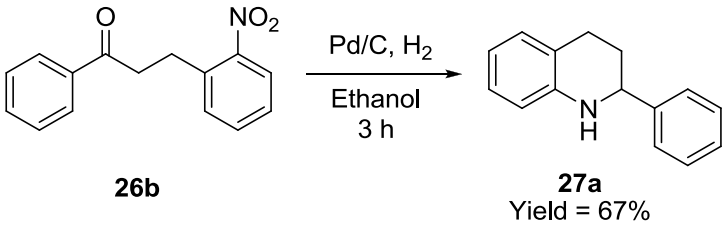


entry	starting material	product	yield (%)[b]
1	 **24e**	 **27a**	75
2	 **24f**	 **27b**	72
3	 **24g**	 **27c**	70

[a] Reaction conditions: ATRA product (1 equiv), $FeCl_3 \cdot 6H_2O$ (3 equiv), Zn dust (10 equiv) in 1:1 DMF-H_2O refluxed at 100 °C for 1 h. [b] Yield of isolated product.

Alternatively, ketone **26b** was converted to tetrahydroquinoline **27a** by subjecting it to catalytic reduction using Pd/Carbon in ethanol (Scheme 4.11).[24]

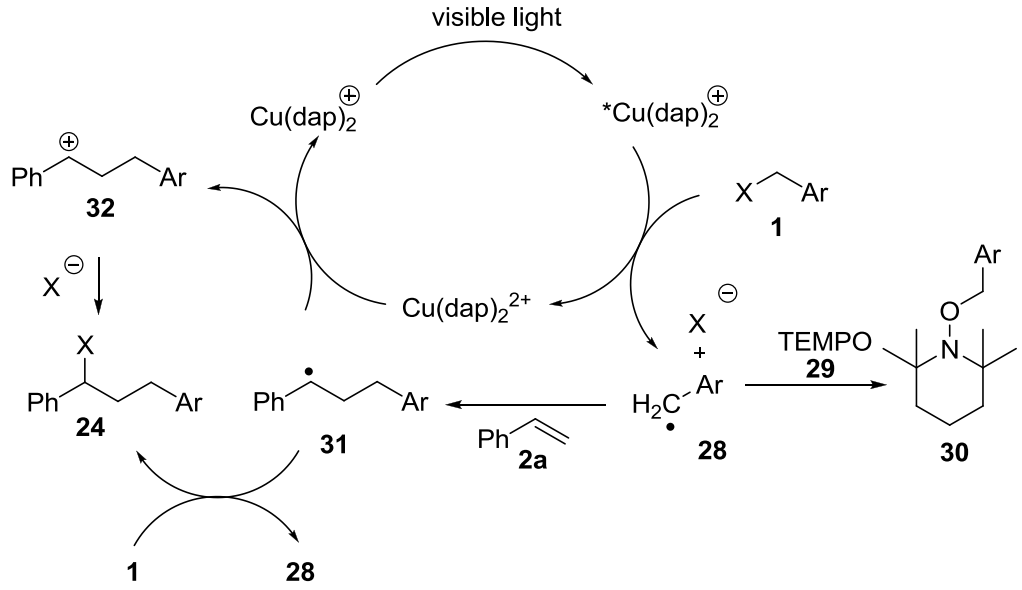
Scheme 4.11. Synthesis of tetrahydroquinoline from ketone 26b



4.6 Proposed reaction mechanism

Mechanism for the above transformation is in consistent with the oxidative quenching cycle of Copper catalyst (Scheme 4.12). $Cu(dap)_2Cl$, when irradiated with the green LED light source, goes to excited state forming $*Cu(dap)_2^+$. This excited species now has sufficient reduction potential to transfer an electron to electron deficient benzyl halide **1**, thus forming the benzyl radical **28** and goes to $Cu(dap)_2^{2+}$ state.

Scheme 4.12. Proposed reaction mechanism



Benzyl radical **28** subsequently adds to the olefin **2a** to produce radical intermediate **31**. The expected ATRA product now can be formed by two possible pathways, by a back electron transfer to the Cu^{2+}, thus closing the catalytic cycle and forming carbocation **32** (radical polar crossover), which then trapped by the halide anion. This mechanistic proposal demands the

electron transfer between two species whose concentrations are very low in reaction mixture. Alternatively, product **27** can be formed from **31** by reaction with benzyl halide **1**, which regenarates **28** (radical propagation). While both the mechanisms are viable, Stepehnson and coworkers have shown that radical polar crossover plays significant role and radical propagation mechanism might operate with very short chain length.[13] The existence of benzyl radical in reaction medium was unambiguously established by 2,2,6,6-tetramethylpiperidinoxyl (**29**, TEMPO) trapping experiment. A TEMPO trapped adduct **30** was detected by mass spectrometry which proves overall radical mechanism for the ATRA reaction.

4.7 Conclusion

In conclusion, we have achieved so far elusive ATRA of electron deficient benzyl halides to styrenes and silyl enol ethers. $Cu(dap)_2Cl$ was used as the photoredox catalyst for the ATRA reaction. Alongside its economical advantage, this catalyst is as or more efficient than some other well known Ru or Ir based photocatalysts. 2-substituted tetrahydroquinolines were synthesized by subjecting the ATRA products derived from *o*-nitrobenzyl halides. A nitro substitution at *ortho* or *para* position of benzyl halides was essential structural requirement for the ATRA to proceed.

4.8 Experimental Part

General Information

All reactions were performed using common dry, inert atmosphere techniques. Reactions were monitored by TLC and visualized by a dual short/long wave UV lamp and stained with an ethanolic solution of vanillin. Column flash chromatography was performed using 230-400 mesh silica gel. NMR spectra were recorded on 300 MHz spectrometer. Chemical shifts for ^{1}H NMR were reported as δ, parts per million, relative to the signal of $CDCl_3$ at 7.26 ppm. Chemical shifts for ^{13}C NMR were reported as δ, parts per million, relative to the center line signal of the $CDCl_3$ triplet at 77 ppm. Proton and carbon assignments were established using spectral data of similar compounds. The abbreviations s, d, dd, t, q and m stand for the resonance multiplicity singlet, doublet, doublet of doublets, triplet, quartet and multiplet respectively.

Some of the ATRA products were unstable under mass spectrometric analysis. So HRMS of the corresponding methoxides has been obtained converting the ATRA bromides to methoxides.

General procedure (GP-A) for the Photoredeox catalyzed ATRA reaction

An oven dried 10 mL vial equipped with a plastic septum and magnetic stir bar was charged with $Cu(dap)_2Cl$ (1 mol%) and the corresponding benzyl halide (1.0 equiv). The flask was purged with a stream of nitrogen and 1.0 mL acetonitrile was added. The resultant mixture was degassed for 5 min by nitrogen sparging and the respective styrene (2- 5 equiv) or silyl enol ether (3 equiv) was added to the vial. The vial was placed at a distance of ~ 0.5 -1.0 cm from a green LED lamp (530 nm) and stirred for 12 h. After the completion of the reaction (as judged by TLC analysis), the mixture was directly concentrated in vacuo. The residue was purified by chromatography on silica gel, using PE/ EA as the solvent system.

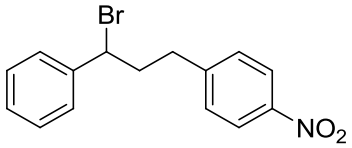
General procedure (GP-B) for bromide to methoxide transformation

The purified bromide (0.10 mmol) was dissolved in 1ml of MeOH and refluxed at 60 °C for 2h. After completion of the reaction (as judged by TLC analysis), MeOH was removed in vacuo. The residue was purified by chromatography on silica gel, using PE/ EA as the solvent system to afford the methoxide.

General procedure (GP-C) for the synthesis of tetrahydroquinolines[23]

In a round bottom flask, Ferric chloride hexahydrate (3 equiv) and Zinc dust (10 equiv) were added to the ATRA product (0.46 mmol) in 2.5 mL of dimethyl formamide and water 1:1. The mixture was heated for 1 h in an oil bath at 100 °C. After completion of the reaction (monitored by TLC), the reaction mixture was filtered and filtrate was diluted with water and basified with saturated sodium carbonate solution. It was then extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4; solvent was removed in vacuo and subjected to colum chromatography on silica gel, using PE/EA as solvent system to get the pure product

1-(3-bromo-3-phenylpropyl)-4-nitrobenzene (24a)

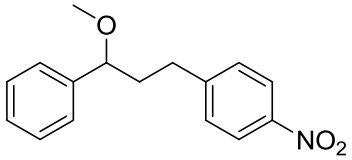


According to the general procedure (GP-A), 4-nitro benzylbromide (0.216 g, 1.00 mmol, 1 equiv), $Cu(dap)_2Cl$ (8.8 mg, 1 mol %), styrene (0.520 g, 5.00 mmol, 5 equiv) afforded **24a** (0.272 g, 85 %) as colorless liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.45.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.20 – 8.11 (m, 2H), 7.42 – 7.27 (m, 7H), 4.87 (dd, *J* = 8.6, 6.1 Hz, 1H), 2.95 (ddd, *J* = 14.4, 9.1, 5.7 Hz, 1H), 2.88 – 2.74 (m, 1H), 2.71 – 2.55 (m, 1H), 2.51 – 2.37 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 148.27, 146.67, 141.42, 129.38, 128.90, 128.69, 127.23, 123.85, 53.96, 40.79, 34.20.

1-(3-methoxy-3-phenylpropyl)-4-nitrobenzene (24a´)



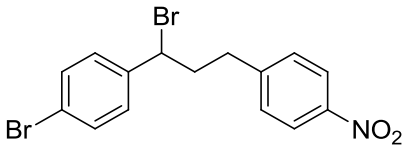
According to the general procedure (GP-B), 1-(3-bromo-3-phenylpropyl)-4-nitrobenzene **24a** (0.040 g, 0.12 mmol) in 1 mL of MeOH afforded **24a´** (0.025 g, 74 %) as colorless liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.53.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.16 – 8.10 (m, 2H), 7.40 – 7.22 (m, 7H), 4.07 (dd, *J* = 8.1, 5.1 Hz, 1H), 3.22 (s, 3H), 2.91 – 2.70 (m, 2H), 2.21 – 2.05 (m, 1H), 2.02 – 1.87 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.99, 141.59, 129.94, 129.26, 128.56, 127.84, 126.61, 123.67, 82.74, 56.68, 39.24, 32.01.

HRMS (ESI): Calcd. For $C_{16}H_{17}NO_3$ *m/z* 271.1208, found *m/z* 271.1207.

1-(3-bromo-3-(4-bromopropyl)propyl)-4-nitrobenzene (24b)



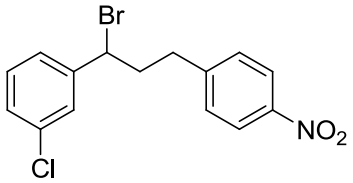
According to the general procedure (GP-A), 4-nitro benzylbromide (0.050 g, 0.23 mmol, 1 equiv), $Cu(dap)_2Cl$ (2 mg, 1 mol %), 4-bromostyrene (0.126 g, 0.69 mmol, 3 equiv) afforded **24b** (0.082 g, 90 %) as colorless oil after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.45.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.21 – 8.13 (m, 2H), 7.52 – 7.44 (m, 2H), 7.38 – 7.29 (m, 2H), 7.29 – 7.20 (m, 2H), 4.80 (dd, *J* = 8.7, 6.1 Hz, 1H), 2.94 (ddd, *J* = 14.4, 9.0, 5.7 Hz, 1H), 2.87 – 2.75 (m, 1H), 2.67 – 2.52 (m, 1H), 2.47 – 2.31 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.96, 146.73, 140.48, 132.07, 129.36, 128.90, 123.91, 122.56, 52.67, 40.65, 34.09.

HRMS (ESI): Calcd. For $C_{15}H_{13}Br_2NO_2$ *m/z* 396.9313, found *m/z* 396.9310.

1-(3-bromo-3-(3-chlorophenyl)propyl)-4-nitrobenzene (24c)



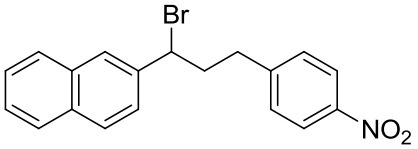
According to the general procedure (GP-A), 4-nitro benzylbromide (0.050 g, 0.23 mmol, 1 equiv), $Cu(dap)_2Cl$ (2 mg, 1 mol %), 3-chlorostyrene (0.095 g, 0.69 mmol, 3 equiv) afforded **24c** (0.071 g, 87 %) as colorless oil after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.30.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21 – 8.11 (m, 2H), 7.40 – 7.31 (m, 3H), 7.31 – 7.19 (m, 3H), 4.79 (dd, *J* = 8.8, 5.9 Hz, 1H), 3.03 – 2.89 (m, 1H), 2.88 – 2.75 (m, 1H), 2.67 – 2.48 (m, 1H), 2.48 – 2.29 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.93, 146.74, 143.38, 134.63, 130.17, 129.36, 128.82, 127.45, 125.44, 123.90, 52.44, 40.63, 34.08.

HRMS (ESI): Calcd. For $C_{15}H_{13}ClBrNO_2$ *m/z* 352.9818, found *m/z* 352.9817.

2-(1-bromo-3-(4-nitrophenyl)propyl)naphthalene (24d)

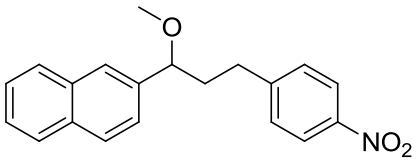


According to the general procedure (GP-A), 4-nitro benzylchloride (0.040 g, 0.18 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.5 mg, 1 mol %), 2-vinylnapthalene (0.055 g, 0.36 mmol, 2 equiv) afforded **24d** (0.057 g, 85 %) as colorless liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.30.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.20 – 8.12 (m, 2H), 7.90 – 7.73 (m, 4H), 7.58 – 7.47 (m, 3H), 7.35 (d, *J*=8.7 Hz, 2H), 5.05 (dd, *J* = 8.1, 6.5 Hz, 1H), 3.04 – 2.91 (m, 1H), 2.90 – 2.66 (m, 2H), 2.62 – 2.46 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 148.23, 146.68, 138.56, 133.28, 133.02, 129.39, 129.06, 128.05, 127.76, 126.74, 126.69, 126.10, 124.85, 123.87, 54.35, 40.68, 34.22.

2-(1-methoxy-3-(4-nitrophenyl)propyl)naphthalene (24d´)



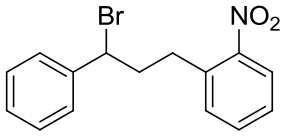
According to the general procedure (GP-B), 2-(1-bromo-3-(4-nitrophenyl)propyl)naphthalene **24d** (0.040 g, 0.10 mmol) in 1 mL of MeOH afforded **24d´** (0.027 g, 78 %) as yellow liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.43.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 (m, 2H), 7.91 – 7.78 (m, 3H), 7.70 (s, 1H), 7.58 – 7.38 (m, 3H), 7.38 – 7.23 (m, 2H), 4.24 (dd, *J* = 7.9 , 5.3 Hz, 1H), 3.25 (s, 3H), 2.96 – 2.70 (m, 2H), 2.33 – 2.14 (m, 1H), 2.13 – 1.95 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.92, 146.35, 138.96, 133.21, 129.27, 128.60, 127.80, 127.77, 127.69, 126.29, 126.00, 125.94, 124.17, 123.68, 82.88, 56.76, 39.05, 32.00.

HRMS (ESI): Calcd. For $C_{20}H_{19}NO_3$ *m/z* 321.1365, found *m/z* 321.1367.

1-(3-bromo-3-phenylpropyl)-2-nitrobenzene (24e)



According to the general procedure (GP-A), 2-nitro benzylbromide (0.050 g, 0.23 mmol, 1 equiv), $Cu(dap)_2Cl$ (2 mg, 1 mol %), styrene (0.119 g, 1.15 mmol, 5 equiv) afforded **24e** (0.067 g, 91 %) as yellow liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.44.

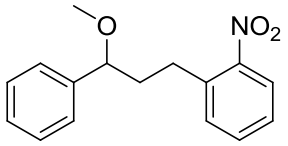
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.98 – 7.90 (m, 1H), 7.54 (td, *J* =7.7, 1.3 Hz, 1H), 7.46 – 7.28 (m, 7H), 4.99 (dd, *J* = 8.5, 6.4 Hz, 1H), 3.12 (ddd, *J* = 13.4, 9.8, 5.3 Hz, 1H), 2.93 (ddd, *J* = 13.3, 9.6, 6.1 Hz, 1H), 2.71 – 2.44 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 141.51, 135.78, 133.20, 132.20, 128.83, 128.60, 127.54, 127.29, 125.83, 125.02, 54.59, 40.49, 32.10.

Large scale reaction with low catalyst loading

According to the general procedure (GP-A), 2-nitro benzylbromide (0.432 g, 2.0 mmol, 1 equiv), $Cu(dap)_2Cl$ (8.8 mg, 0.5 mol %), styrene (1.04 g, 10.0 mmol, 5 equiv) in 5 mL of acetonitrile was irradiated for 12 h to get **24e** (0.510 g, 80 %) as yellow liquid after column purification on silica gel.

1-(3-methoxy-3-phenylpropyl)-2-nitrobenzene (24e´)



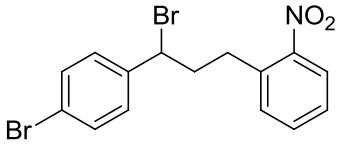
According to the general procedure (GP-B), 1-(3-bromo-3-phenylpropyl)-2-nitrobenzene **24e** (0.040 g, 0.12 mmol) in 1 mL of MeOH afforded **24e´** (0.030 g, 89 %) as colorless oil after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.42.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.93 – 7.85 (m, 1H), 7.50 (t, *J*=7.5, 1H), 7.41 – 7.23 (m, 7H), 4.14 (dd, *J*=8.1, 5.1, 1H), 3.23 (s, 3H), 3.11 – 2.98 (m, 1H), 2.98 – 2.84 (m, 1H), 2.19 – 1.92 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.44, 141.74, 137.09, 132.87, 131.99, 128.48, 127.72, 127.00, 126.62, 124.71, 83.23, 56.67, 38.85, 29.56.

HRMS (ESI): Calcd. For $C_{16}H_{17}NO_3$ *m/z* 271.1208, found *m/z* 271.1201.

1-(3-bromo-3-(4-bromophenyl)propyl)-2-nitrobenzene (24f)



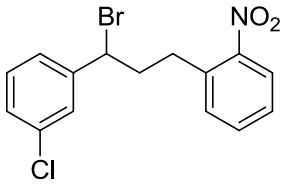
According to the general procedure (GP-A), 2-nitro benzylbromide (0.040 g, 0.18 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.5 mg, 1 mol %), 4-bromostyrene (0.098 g, 0.54 mmol, 3 equiv) afforded **24f** (0.064 g, 87 %) as colorless liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.44.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.95 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.59 – 7.43 (m, 3H), 7.42 – 7.33 (m, 2H), 7.31 – 7.27 (m, 2H), 4.93 (dd, *J* = 8.4, 6.5 Hz, 1H), 3.10 (ddd, *J* = 13.3, 9.9, 5.3 Hz, 1H), 2.92 (ddd, *J* = 13.3, 9.7, 6.1 Hz, 1H), 2.66 – 2.41 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 140.55, 135.56, 133.28, 132.19, 131.99, 128.97, 127.65, 125.09, 122.23, 53.28, 40.37, 32.10.

HRMS (ESI): Calcd. For $C_{15}H_{13}Br_2NO_2$ *m/z* 396.9313, found *m/z* 396.9314.

1-(3-bromo-3-(3-chlorophenyl)propyl)-2-nitrobenzene (24g)



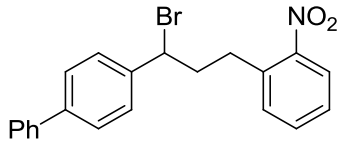
According to the general procedure (GP-A), 2-nitro benzylbromide (0.040 g, 0.18 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.5 mg, 1 mol %), 3-chlorostyrene (0.074 g, 0.54 mmol, 3 equiv) afforded **24g** (0.053 g, 80 %) as colorless liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.48.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.95 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.63 – 7.46 (m, 1H), 7.44 – 7.33 (m, 3H), 7.32 – 7.22 (m, 3H), 4.91 (dd, *J* = 8.6, 6.2 Hz, 1H), 3.13 (ddd, *J* = 13.4, 9.8, 5.2 Hz, 1H), 2.93 (ddd, *J* = 13.3, 9.6, 6.1 Hz, 1H), 2.66 – 2.39 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.12, 143.48, 135.53, 134.56, 133.29, 132.20, 130.12, 128.73, 127.68, 127.52, 125.51, 125.09, 53.08, 40.35, 32.07.

HRMS (ESI): Calcd. For $C_{15}H_{13}ClBrNO_2$ *m/z* 352.9818, found *m/z* 352.9818.

1-(3-bromo-3-(biphenyl)propyl)-2-nitrobenzene (24h)

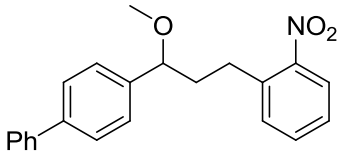


According to the general procedure (GP-A), 2-nitro benzylbromide (0.030 g, 0.13 mmol,1 equiv), $Cu(dap)_2Cl$ (1.1 mg, 1 mol %), 4-vinylbiphenyl (0.046 g, 0.26 mmol, 2 equiv) afforded **24h** (0.045 g, 82 %) as colorless oil after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.36.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.95 (dd, *J* =8.5, 1.4 Hz, 1H), 7.63 – 7.30 (m, 12H), 5.05 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.21 – 3.08 (m, 1H), 2.98 (ddd, *J* = 13.3, 9.5, 6.2 Hz, 1H), 2.74 – 2.49 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 141.52, 140.47, 140.42, 135.78, 133.71, 133.23, 132.24, 129.63, 128.84, 127.74, 127.57, 127.13, 125.53, 125.05, 54.40, 40.41, 32.18.

1-(3-methoxy-3-(biphenyl)propyl)-2-nitrobenzene (24h´)



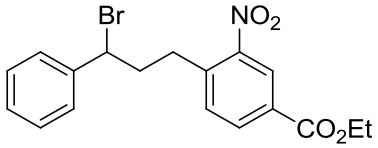
According to the general procedure (GP-B), 1-(3-bromo-3-(biphenyl)propyl)-2-nitrobenzene **24h** (0.040 g, 0.10 mmol) in 1 mL of MeOH afforded **24h´** (0.022 g, 63 %) as yellow gummy liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.40.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.54 (m, 4H), 7.48 (m, 3H), 7.35 (m, 5H), 4.20 (dd, *J* = 8.2, 5.0 Hz, 1H), 3.27 (s, 3H), 3.14 – 3.02 (m, 1H), 3.02 – 2.92 (m, 1H), 2.24 – 1.95 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.45, 140.86, 140.82, 140.63, 137.08, 132.89, 132.02, 128.77, 127.28, 127.24, 127.09, 127.07, 127.02, 124.73, 82.99, 56.74, 38.83, 29.61.

HRMS (ESI): Calcd. For $C_{22}H_{21}ClNNaO_3$ $[M+Na]^+$ *m/z* 370.1414, found *m/z* 370.1412.

ethyl 4-(3-bromo-3-phenylpropyl)-3-nitrobenzoate (24i)



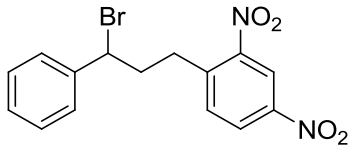
According to the general procedure (GP-A), ethyl 4-(bromomethyl)-3-nitrobenzoate (0.10 g, 0.34 mmol, 1 equiv), $Cu(dap)_2Cl$ (3 mg, 1 mol %), styrene (0.176 g, 1.7 mmol, 5 equiv) afforded **24i** (0.093 g, 70 %) as light yellow liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:8): 0.67.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.56 (d, *J* = 1.7 Hz, 1H), 8.18 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.49 – 7.27 (m, 6H), 4.98 (dd, *J*=8.5, 6.3 Hz, 1H), 4.41 (q, *J* = 7.13 Hz, 2H), 3.17 (ddd, *J* = 13.4, 9.9, 5.2 Hz, 1H), 2.98 (ddd, *J* = 13.3, 9.7, 6.1 Hz, 1H), 2.70 – 2.44 (m, 2H), 1.41 (t, *J*=7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.41, 149.14, 141.28, 140.33, 133.61, 132.44, 130.35, 128.89, 128.70, 127.26, 126.11, 125.79, 61.84, 54.26, 40.27, 32.20, 14.29.

HRMS (ESI): Calcd. For $C_{18}H_{18}BrNO_4$ *m/z* 391.0419, found *m/z* 391.0417.

1-(3-bromo-3-phenylpropyl)-2,4-dinitrobenzene (24j)

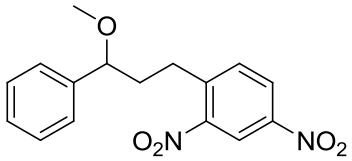


According to the general procedure (GP-A), 2, 4-dinitro benzylbromide (0.040 g, 0.15 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.3 mg, 1 mol %), styrene (0.078 g, 0.75 mmol, 5 equiv) afforded **24j** (0.045 g, 82 %) as yellow liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.51.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.79 (s, 1H), 8.38 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.47 – 7.27 (m, 5H), 4.98 (dd, *J* = 8.5, 6.3Hz, 1H), 3.25 (ddd, *J* = 13.5, 10.0, 5.2 Hz, 1H), 3.05 (ddd, *J* = 13.4, 9.9, 6.1 Hz, 1H), 2.72 – 2.45 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.06, 146.64, 142.78, 141.00, 133.54, 128.96, 128.84, 128.73, 127.22, 120.58, 53.92, 40.17, 32.27.

1-(3-methoxy-3-phenylpropyl)-2,4-dinitrobenzene (24j´)



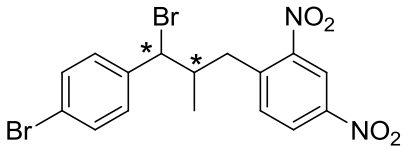
According to the general procedure (GP-B), 1-(3-bromo-3-phenylpropyl)-2,4-dinitrobenzene **24j** (0.040 g, 0.10 mmol) in 1 mL of MeOH afforded **24j´** (0.026 g, 75 %) as light yellow liquid after column purification on silica gel. R*f* (EtOAc/hexane 2:8): 0.51.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.75 (d, *J* = 2.4 Hz, 1H), 8.34 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.56 (d, *J* = 8.5, 1H), 7.47 – 7.19 (m, 5H), 4.15 (dd, *J* = 8.2, 4.8 Hz, 1H), 3.21 (s, 3H), 3.20 – 3.11 (m, 1H), 3.11 – 2.96 (m, 1H), 2.20 – 1.94 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.24, 146.28, 144.39, 141.19, 133.32, 128.63, 127.97, 126.86, 126.52, 120.30, 82.93, 56.69, 38.53, 29.75.

HRMS (ESI): Calcd. For $C_{16}H_{16}N_2NaO_5$ $[M+Na]^+$ *m/z* 339.0951, found *m/z* 339.0952.

1-(3-bromo-2-methyl-3-phenylpropyl)-2,4-dinitrobenzene (3k)



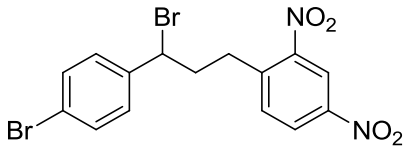
An oven dried Schlenck flask equipped with magnetic stir bar was charged with 2,4-dinitro-benzyl bromide (0.261 mg 1.00 mmol, 1.0 equiv), trans-β-methylstyrene (0.590 mg, 5.0 mmol, 5.0 equiv) and $Cu(dap)_2Cl$ (8.8 mg, 1 mol %). The flask was purged with a stream of nitrogen and 10.0 mL acetonitrile was added. The resultant mixture was degassed using freeze-pump-thaw cycles (5x) and flushed with N_2. The reaction mixture was internally irradiated using blue LED rods at 530 nm. After 20 h of irradiation, solvent was evaporated under reduced pressure, and the crude reaction mixture was purified by chromatography on flash silica gel to afford 3k (0.133 g, 35 %) as colorless oil as diasteriomeric ratio of 1.3:1. R_f (EtOAc/hexane 1:3): 0.63; ^1H

NMR (400 MHz, $CDCl_3$, major diastereomer marked with *) δ = 8.78* (d, *J* = 2.3 Hz, 1H), 8.74 (d, *J* = 2.4 Hz, 1H), 8.39 – 8.33 (m, 2H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.55* (d, *J* = 8.5 Hz, 1H), 7.34 (m, 10H), 4.93* (d, *J* = 5.8 Hz, 1H), 4.89 (d, *J* = 8.1 Hz, 1H), 3.78 (dd, *J* = 13.5, 3.7 Hz, 1H), 3.19* (dd, *J* = 13.4, 5.5 Hz, 1H), 2.89 (dd, *J* = 12.3, 7.6 Hz, 1H), 2.83 (dd, *J* = 12.4, 9.2 Hz, 1H), 2.62 – 2.51 (m, 1H), 2.43-2.35* (m, 1H), 1.05* (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 2H).

^{13}C NMR (100 MHz, CDCl3) δ = 146.67, 146.53, 142.30, 142.08, 140.05,139.96, 134.23, 133.98, 128.72, 128.58, 128.52, 128.37, 128.02, 127.86, 126.72, 126.58, 120.53, 120.30, 61.93, 61.59, 42.58, 42.25, 38.70, 37.80, 17.23, 16.61.

HRMS (ESI): Calcd. For $C_{16}H_{16}BrN_2O$ $[M]^+$ *m/z* 379.0288, found *m/z* 379.0278.

1-(3-bromo-3-(4-bromophenyl)propyl)-2,4-dinitrobenzene (24l)

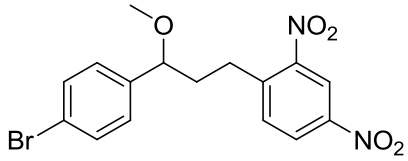


According to the general procedure (GP-A), 2, 4-dinitro benzylbromide (0.040 g, 0.15 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.3 mg, 1 mol %), 4-bromostyrene (0.082 g, 0.45 mmol, 3 equiv) afforded **24l** (0.057 g, 86 %) as colorless oil after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.17.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.81 (d, *J* = 2.3 Hz, 1H), 8.39 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.29 (m, 2H), 4.93 (dd, *J* = 8.6, 6.2 Hz, 1H), 3.23 (ddd, *J* = 13.4, 10.1, 5.2 Hz, 1H), 3.03 (ddd, *J* = 13.3, 10.0, 6.0 Hz, 1H), 2.67 – 2.41 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.04, 146.72, 142.52, 140.05, 133.53, 132.13, 128.88, 127.28, 122.74, 120.65, 52.66, 40.06, 32.26.

1-(3-methoxy-3-(4-bromophenyl)propyl)-2,4-dinitrobenzene (24l´)



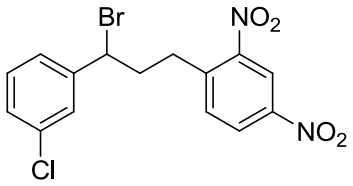
According to the general procedure (GP-B), 1-(3-bromo-3-(4-bromophenyl)propyl)-2,4-dinitrobenzene **24l** (0.040 g, 0.09 mmol) in 1 mL of MeOH afforded **24l´** (0.029 g, 82 %) as yellow oil after column purification on silica gel. R*f* (EtOAc/hexane 2:8): 0.46.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.76 (d, *J* = 2.4 Hz, 1H), 8.35 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.20 – 7.13 (m, 2H), 4.12 (dd, *J* = 8.2, 4.7 Hz, 1H), 3.21 (s, 3H), 3.18 – 2.96 (m, 2H), 2.14 – 1.92 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.23, 146.34, 144.14, 140.31, 133.33, 131.79, 128.21, 126.93, 121.76, 120.35, 82.33, 56.78, 38.46, 29.69.

HRMS (ESI): Calcd. For $C_{16}H_{15}BrN_2O_5$ *m/z* 394.0164, found *m/z* 394.0150.

1-(3-bromo-3-(3-chlorophenyl)propyl)-2,4-dinitrobenzene (24m)

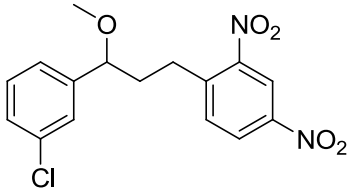


According to the general procedure (GP-A), 2, 4-dinitro benzylbromide (0.040 g, 0.15 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.3 mg, 1 mol %), 3-chlorostyrene (0.062 g, 0.45 mmol, 3 equiv) afforded **24m** (0.058 g, 95 %) as very light yellow oil after column purification on silica gel. R*f* (EtOAc/hexane 2:8): 0.63.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.81 (d, *J* = 2.3 Hz, 1H), 8.40 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 15.3 Hz, 1H), 7.34 – 7.27 (m, 3H), 4.91 (dd, *J* = 8.7, 6.0 Hz, 1H), 3.26 (ddd, *J* = 13.4, 10.0, 5.1 Hz, 1H), 3.05 (ddd, *J* = 13.3, 9.9, 6.1 Hz, 1H), 2.69 – 2.40 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.04, 146.73, 142.95, 142.50, 134.72, 133.53, 130.25, 128.97, 127.45, 127.27, 125.43, 120.65, 52.43, 40.03, 32.23.

1-(3-methoxy-3-(3-chlorophenyl)propyl)-2,4-dinitrobenzene (24m´)



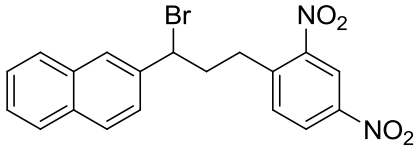
According to the general procedure (GP-B), 1-(3-bromo-3-(3-chlorophenyl)propyl)-2,4-dinitrobenzene **24m** (0.040 g, 0.10 mmol) in 1 mL of MeOH afforded **24m´** (0.027 g, 77 %) as yellow gummy liquid after column purification on silica gel. R*f* (EtOAc/hexane 2:8): 0.58.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.76 (d, *J* = 2.3 Hz, 1H), 8.35 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.32 – 7.24 (m, 3H), 7.19 – 7.13 (m, 1H), 4.13 (dd, *J* = 8.1, 4.8 Hz, 1H), 3.23 (s, 3H), 3.20 – 2.98 (m, 2H), 2.18 – 1.92 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.25, 146.36, 144.11, 143.53, 134.63, 133.34, 129.98, 128.12, 126.92, 126.56, 124.67, 120.35, 82.36, 56.91, 38.49, 29.68.

HRMS (ESI): Calcd. For $C_{16}H_{15}ClN_2NaO_5$ $[M+Na]^+$ *m/z* 373.0562, found *m/z* 373.0561.

2-(1-bromo-3-(2,4-dinitrophenyl)propyl)naphthalene (24n)

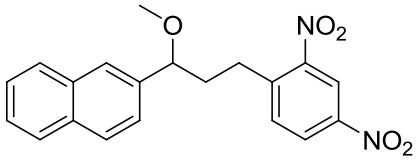


According to the general procedure (GP-A), 2, 4-dinitro benzylbromide (0.040 g, 0.15 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.3 mg, 1 mol %), 2-vinylnapthalene (0.082 g, 0.30 mmol, 2 equiv) afforded **24n** (0.064 g, 81 %) as yellow liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.23.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.79 (d, *J* = 2.4 Hz, 1H), 8.36 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.91 – 7.76 (m, 4H), 7.64 – 7.46 (m, 4H), 5.17 (dd, *J* = 8.3, 6.6 Hz, 1H), 3.28 (ddd, *J* = 13.4, 10.0, 5.2 Hz, 1H), 3.06 (ddd, *J* = 13.3, 9.8, 6.2 Hz, 1H), 2.82 – 2.56 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.04, 146.61, 142.74, 138.12, 133.54, 133.31, 132.99, 129.13, 128.08, 127.76, 127.16, 126.83, 126.75, 126.17, 124.74, 120.58, 54.25, 40.05, 32.34.

2-(1-methoxy-3-(2,4-dinitrophenyl)propyl)naphthalene (24n´)



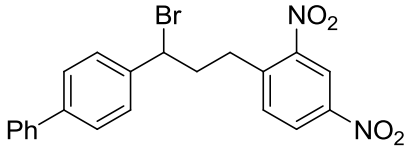
According to the general procedure (GP-B), 2-(1-bromo-3-(2,4-dinitrophenyl)propyl)naphthalene **24n** (0.040 g, 0.09 mmol) in 1 mL of MeOH afforded **24n´** (0.025 g, 71 %) as light yellow liquid after column purification on silica gel. R*f* (EtOAc/hexane 2:8): 0.53.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.70 (d, *J* = 2.4 Hz, 1H), 8.28 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.87 – 7.72 (m, 3H), 7.67 (s, 1H), 7.54 – 7.33 (m, 4H), 4.28 (dd, *J* = 8.2, 4.9 Hz, 1H), 3.21 (s, 3H), 3.20 – 3.10 (m, 1H), 3.02 (ddd, *J* = 13.4, 9.5, 6.3 Hz, 1H), 2.25 – 1.99 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 148.20, 145.23, 143.30, 137.52, 132.29, 132.19, 127.63, 126.79, 126.73, 125.81, 125.29, 125.04, 124.85, 122.98, 121.16, 119.27, 82.05, 55.74, 37.30, 28.77.

HRMS (ESI): Calcd. For $C_{20}H_{18}N_2O_5$ *m/z* 366.1216, found *m/z* 366.1215.

2-(1-bromo-3-(biphenyl)propyl)-2,4-dinitrobenzene (24o)

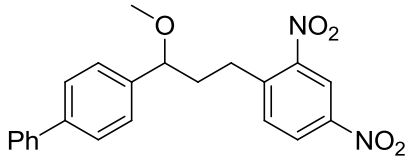


According to the general procedure (GP-A), 2, 4-dinitro benzylbromide (0.040 g, 0.15 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.3 mg, 1 mol %), 4-vinylbiphenyl (0.055 g, 0.30 mmol, 2 equiv) afforded **24o** (0.061 g, 90 %) as light yellow liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.38.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.81 (d, *J* = 2.3 Hz, 1H), 8.39 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.68 – 7.52 (m, 6H), 7.51 – 7.31 (m, 6H), 5.04 (dd, *J* = 8.5, 6.3 Hz, 1H), 3.28 (ddd, *J* = 13.3, 10.0, 5.2 Hz, 1H), 3.09 (ddd, *J* = 13.3, 9.8, 6.1 Hz, 1H), 2.76 – 2.50 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.07, 146.66, 142.77, 141.79, 140.23, 139.93, 133.57, 128.89, 127.67, 127.60, 127.35, 127.22, 127.11, 120.62, 53.72, 40.10, 32.34.

2-(1-methoxy-3-(biphenyl)propyl)-2,4-dinitrobenzene (24o´)



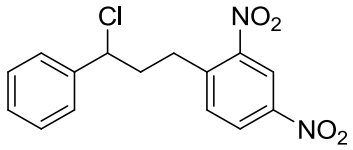
According to the general procedure (GP-B), 2-(1-bromo-3-(biphenyl)propyl)-2,4-dinitrobenzene **24o** (0.040 g, 0.09 mmol) in 1 mL of MeOH afforded **24o´** (0.021 g, 59 %) as yellow oil after column purification on silica gel. R*f* (EtOAc/hexane 2:8): 0.42.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.76 (d, *J* = 2.3 Hz, 1H), 8.35 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.59 (dd, *J* = 8.3, 2.6 Hz, 5H), 7.49 – 7.39 (m, 2H), 7.39 – 7.31 (m, 3H), 4.21 (dd, *J* = 8.2, 4.8 Hz, 1H), 3.26 (s, 3H), 3.24 – 3.15 (m, 1H), 3.14 – 3.01 (m, 1H), 2.25 – 1.96 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.28, 146.29, 144.38, 140.92, 140.69, 140.22, 133.34, 128.82, 127.39, 127.37, 127.08, 126.97, 126.87, 120.32, 82.69, 56.77, 38.52, 29.80.

HRMS (ESI): Calcd. For $C_{22}H_{20}N_2NaO_5$ $[M+Na]^+$ *m/z* 415.1264, found *m/z* 415.1266.

1-(3-chloro-3-phenylpropyl)-2,4-dinitrobenzene (24p)



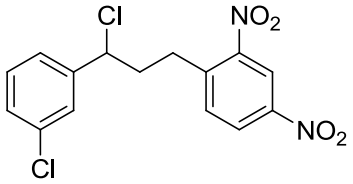
According to the general procedure (GP-A), 2, 4-dinitro benzylchloride (0.049 g, 0.23 mmol, 1 equiv), $Cu(dap)_2Cl$ (2.0 mg, 1 mol %), styrene (0.119 g, 1.15 mmol, 5 equiv) afforded **24p** (0.038 g, 51 %) as light yellow liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.32.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (d, *J*=2.3 Hz, 1H), 8.38 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.62 (m, 1H), 7.48 – 7.28 (m, 5H), 4.91 (dd, *J* = 8.3, 5.9 Hz, 1H), 3.26 (ddd, *J* = 13.5, 9.5, 5.7 Hz, 1H), 3.07 (ddd, *J* = 13.4, 9.4, 6.6 Hz, 1H), 2.59 – 2.30 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.10, 146.62, 142.98, 140.61, 133.53, 128.89, 128.75, 127.17, 126.86, 120.57, 62.63, 40.22, 31.12.

HRMS (ESI): Calcd. For $C_{18}H_{13}ClN_2O_4$ *m/z* 320.0522, found *m/z* 320.0524.

1-(3-chloro-3-(3-chlorophenyl)propyl)-2,4-dinitrobenzene (24q)



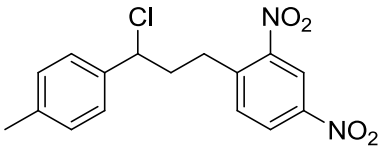
According to the general procedure (GP-A), 2, 4-dinitro benzylchloride (0.040 g, 0.18 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.5 mg, 1 mol %), 3-chlorostyrene (0.074 g, 0.54 mmol, 3 equiv) afforded **24q** (0.060 g, 92 %) as light yellow oil after column purification on silica gel. R*f* (EtOAc/hexane 2:8): 0.70.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.80 (d, *J* =2.3 Hz, 1H), 8.39 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.61 (d, *J* = 8.5Hz, 1H), 7.39 (s, 1H), 7.34 – 7.22 (m, 3H), 4.87 (dd, *J* = 8.1, 6.0 Hz, 1H), 3.27 (ddd, *J* = 13.4, 9.3, 6.0 Hz, 1H), 3.08 (ddd, *J* = 13.4, 9.1, 6.9 Hz, 1H), 2.48 – 2.37 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.08, 146.70, 142.68, 142.56, 134.73, 133.54, 130.18, 128.89, 127.24, 127.12, 125.06, 120.63, 61.62, 40.13, 31.05.

HRMS (ESI): Calcd. For $C_{15}H_{12}Cl_2N_2NaO_4$ $[M+Na]^+$ *m/z* 377.0778, found *m/z* 377.0777

1-(3-chloro-3-p-tolylpropyl)-2,4-dinitrobenzene (24r)



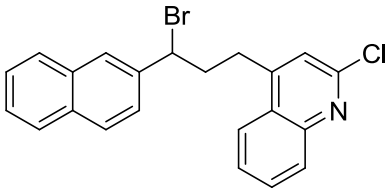
According to the general procedure (GP-A), 2, 4-dinitro benzylchloride (0.030 g, 0.13 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.1 mg, 1 mol %), 4-methylstyrene (0.046 g, 0.39 mmol, 3 equiv) afforded **24r** (0.043 g, 93 %) as light yellow oil after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.25.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.79 (d, *J* = 2.4 Hz, 1H), 8.38 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.21 – 7.14 (m, 2H), 4.89 (dd, *J* = 8.3, 6.0 Hz, 1H), 3.24 (ddd, *J* = 13.5, 9.6, 5.6 Hz, 1H), 3.12 – 2.99 (m, 1H), 2.51 – 2.38 (m, 2H), 2.38 – 2.30 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.11, 146.59, 143.05, 138.71, 137.66, 133.53, 129.54, 127.15, 126.78, 120.55, 62.62, 40.13, 31.15, 21.18.

HRMS (ESI): Calcd. For $C_{16}H_{16}ClN_2O_4$ $[M+H]^+$ *m/z* 335.0793, found *m/z* 335.0797.

4-(3-bromo-3-(naphthalen-6-yl)propyl)-2-chloroquinoline (24s)

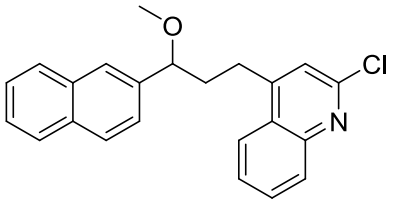


According to the general procedure (GP-A), 4-(bromomethyl)-2-chloroquinoline (0.040 g, 0.11 mmol, 1 equiv), $Cu(dap)_2Cl$ (0.98 mg, 1 mol %), 2-vinylnapthalene (0.033 g, 0.22 mmol, 2 equiv) afforded **24s** (0.030 g, 66 %) as colorless oil after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.28.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.06 – 8.01 (m, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.91 – 7.67 (m, 6H), 7.61 – 7.47 (m, 4H), 5.19 (dd, *J* = 8.5, 6.2 Hz, 1H), 3.43 – 3.30 (m, 1H), 3.17 – 3.04 (m, 1H), 2.91 – 2.75 (m, 1H), 2.64 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.61, 149.90, 148.13, 138.41, 133.32, 133.02, 130.44, 129.51, 129.11, 128.09, 127.77, 127.03, 126.79, 126.73, 126.18, 125.98, 124.81, 123.42, 121.86, 54.65, 39.66, 30.72.

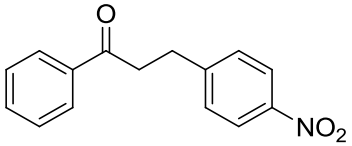
4-(3-methoxy-3-(naphthalen-6-yl)propyl)-2-chloroquinoline (24s´)



According to the general procedure (GP-B), 4-(3-bromo-3-(naphthalen-6-yl)propyl)-2-chloroquinoline **24s** (0.025 g, 0.06 mmol) in 1 mL of MeOH afforded **24s´** (0.018 g, 83 %) as colorless oil after column purification on silica gel. R*f* (EtOAc/hexane 2:8): 0.71.

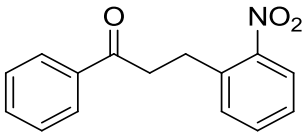
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.02 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.98 – 7.91 (m, 1H), 7.90 – 7.80 (m, 3H), 7.76 – 7.66 (m, 2H), 7.56 – 7.42 (m, 4H), 7.24 (s, 1H), 4.33 (dd, *J* = 8.0, 4.9 Hz, 1H), 3.30 (s, 3H), 3.27 – 3.18 (m, 1H), 3.18 – 3.03 (m, 1H), 2.40 – 2.23 (m, 1H), 2.22 – 2.06 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.59, 150.64, 148.07, 138.82, 133.23, 130.23, 129.34, 128.64, 127.84, 127.78, 126.75, 126.32, 126.26, 126.04, 125.97, 124.14, 123.69, 121.68, 82.95, 56.85, 38.02, 28.22.
HRMS (ESI): Calcd. For $C_{23}H_{21}ClNO$ $[M+H]^+$ *m/z* 362.1306, found *m/z* 362.1309.

3-(4-nitrophenyl)-1-phenylpropan-1-one (26a)[25]



According to the general procedure, 4-nitro benzylbromide (0.040 g, 0.18 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.5 mg, 1 mol %), (1-phenylvinyloxy)trimethylsilane (0.103 g, 0.54 mmol, 3 equiv) afforded **26a** (0.041 g, 87 %) as yellow solid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.30.
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.15 (dd, *J* = 8.9, 2.2 Hz, 2H), 7.95 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.60 – 7.41 (m, 5H), 3.37 (dd, *J* = 10.8, 4.0 Hz, 2H), 3.19 (t, *J* = 7.2 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.14, 149.21, 136.51, 133.42, 129.39, 128.74, 128.01, 124.34, 123.80, 39.42, 29.74.
MS (EI, 70 eV): m/z = 105.1 (100.0), 255.1 (24.7) [M+].

3-(2-nitrophenyl)-1-phenylpropan-1-one (26b)[25]



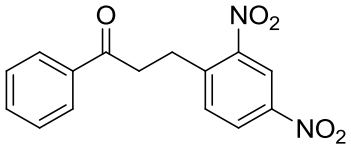
According to the general procedure, 2-nitro benzylbromide (0.216 g, 1.00 mmol, 1 equiv), $Cu(dap)_2Cl$ (8.8 mg, 1 mol %), (1-phenylvinyloxy)trimethylsilane (0.576 g, 3.00 mmol, 3 equiv) afforded **26b** (0.198 g, 78 %) as light yellow solid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.40.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.20 – 7.92 (m, 3H), 7.75 – 7.36 (m, 6H), 3.65 – 3.27 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.54, 149.34, 136.59, 136.57, 133.33, 133.27, 132.66, 128.67, 128.10, 127.49, 124.93, 39.46, 27.79.

MS (EI, 70 eV): m/z = 105.1 (100.0), 255.1 (24.7) [M+].

3-(2,4-dinitrophenyl)-1-phenylpropan-1-one (26c)



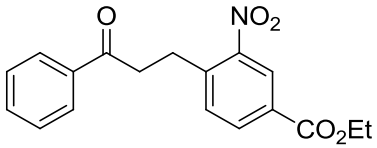
According to the general procedure, 2, 4-dinitro benzylbromide (0.040 g, 0.15 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.3 mg, 1 mol %), (1-phenylvinyloxy)trimethylsilane (0.086 g, 0.45 mmol, 3 equiv) afforded **26c** (0.040 g, 90 %) as yellow liquid after column purification on silica gel. R*f* (EtOAc/hexane 2:8): 0.46.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.79 (d, *J* = 2.4 Hz, 1H), 8.36 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.92 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.56 (ddd, *J* = 6.6, 3.8, 1.2 Hz, 1H), 7.44 (dd, *J* = 10.4, 4.7 Hz, 2H), 3.44 (s, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.54, 149.28, 146.57, 143.64, 136.20, 134.26, 133.61, 128.79, 128.05, 127.09, 120.42, 38.71, 27.54.

HRMS (ESI): Calcd. For $C_{15}H_{12}N_2O_5$ $[M]^+$ *m/z* 300.0746, found *m/z* 300.0751.

ethyl 3-nitro-4-(3-oxo-3-phenylpropyl)benzoate (26d)



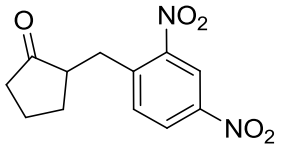
According to the general procedure, ethyl 4-(bromomethyl)-3-nitrobenzoate (0.050 g, 0.17 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.5 mg, 1 mol %), (1-phenylvinyloxy)trimethylsilane (0.098 g, 0.51 mmol, 3 equiv) afforded **26d** (0.046 g, 81 %) as yellow liquid after column purification on silica gel. R*f* (EtOAc/hexane 1:9): 0.20.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.54 (d, *J* =1.7 Hz, 1H), 8.13 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.56 – 7.49 (m, 2H), 7.45 – 7.37 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.42 – 3.29 (m, 4H), 1.37 (t, *J*=7.13 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.04, 164.46, 149.33, 141.19, 136.41, 133.62, 133.40, 132.95, 130.25, 128.72, 128.07, 126.01, 61.79, 39.09, 27.72, 14.30.

HRMS (ESI): Calcd. For $C_{18}H_{18}NO_5$ $[M+H]^+$ *m/z* 328.1179, found *m/z* 328.1184.

2-(2,4-dinitrobenzyl)cyclopentanone (26e)



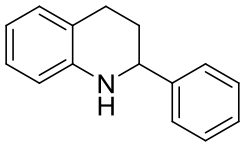
According to the general procedure, 2, 4-dinitro benzylbromide (0.050 g, 0.19 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.6 mg, 1 mol %), (cyclopentenyloxy)trimethylsilane (0.089 g, 0.57 mmol, 3 equiv) afforded **26e** (0.025 g, 50 %) as yellow liquid after column purification on silica gel. R*f* (EtOAc/hexane 2:8): 0.21.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.78 (d, *J* = 2.3 Hz, 1H), 8.37 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 3.47 (dd, *J* = 13.8, 6.1 Hz, 1H), 2.99 (dd, *J* = 13.8, 7.6 Hz, 1H), 2.59 – 2.25 (m, 2H), 2.25 – 1.99 (m, 3H), 1.91 – 1.70 (m, 1H), 1.70 – 1.47 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 218.27, 149.29, 146.57, 142.45, 134.17, 126.88, 120.38, 49.90, 37.48, 32.61, 29.62, 20.44.

HRMS (ESI): Calcd. For $C_{12}H_{13}N_2O_5$ $[M+H]^+$ *m/z* 265.0819, found *m/z* 265.0819.

1,2,3,4-tetrahydro-2-phenylquinoline (27a)[26]



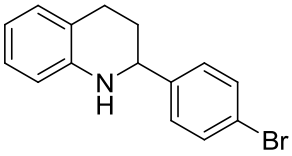
According to the general procedure (GP-C), ATRA product **24e** (0.150 g, 0.46 mmol, 1 equiv), $FeCl_3.6H_2O$ (0.379 g, 1.40 mmol, 3 equiv), Zinc dust (0.305 g, 4.68 mmol, 10 equiv) afforded **27a** (0.075 g, 75 %) as colorless liquid after column purification on silica gel.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.45 – 7.24 (m, 5H), 7.02 (t, *J* = 7.0 Hz, 2H), 6.67 (td, *J* = 7.4, 1.0 Hz, 1H), 6.60 – 6.53 (m, 1H), 4.45 (dd, *J* = 9.3, 3.3 Hz, 1H), 4.16 (b, 1H), 2.94 (ddd, *J* = 16.2, 10.5, 5.5 Hz, 1H), 2.75 (dt, *J* = 16.4, 4.8 Hz, 1H), 2.20 – 1.93 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 144.65, 144.51, 129.33, 128.60, 127.49, 126.93, 126.60, 121.05, 117.36, 114.16, 56.30, 30.93, 26.39.

MS (ESI) Calculated for $C_{16}H_{17}N$ $[M+H]^+$ 210.1, found 210.0

2-(4-bromophenyl)-1,2,3,4-tetrahydroquinoline (27b)[26]



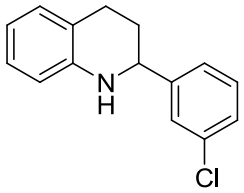
According to the general procedure (GP-C), ATRA product **24f** (0.053 g, 0.13 mmol, 1 equiv), $FeCl_3.6H_2O$ (0.107 g, 0.39 mmol, 3 equiv), Zinc dust (0.086 g, 1.32 mmol, 10 equiv) afforded **27b** (0.027 g, 72 %) as colorless liquid after column purification on silica gel.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.52 – 7.44 (m, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.02 (t, *J* = 7.8 Hz, 2H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 7.9 Hz, 1H), 4.41 (dd, *J* = 9.1, 3.3 Hz, 1H), 3.03 – 2.82 (m, 1H), 2.72 (dt, *J* = 16.5 , 4.9 Hz, 1H), 2.22 – 2.04 (m, 1H), 2.04 – 1.86 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 141.02, 143.58, 131.64, 129.31, 128.33, 126.98, 121.13, 121.03, 117.73, 114.33, 55.69, 30.78, 26.06.

MS (ESI) Calculated for $C_{15}H_{15}BrN$ $[M+H]^+$ 288.0, found 288.0

2-(3-chlorophenyl)-1,2,3,4-tetrahydroquinoline (27c)[27]



According to the general procedure (GP-C), ATRA product **24g** (0.038 g, 0.10 mmol, 1 equiv), $FeCl_3.6H_2O$ (0.086 g, 0.30 mmol, 3 equiv), Zinc dust (0.069 g, 1.0 mmol, 10 equiv) afforded **27c** (0.018 g, 70 %) as yellow oil after column purification on silica gel.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.36 (s, 1H), 7.27 – 7.18 (m, 3H), 6.98 (m, 2H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 4.38 (dd, *J* = 9.1, 3.4 Hz, 1H), 2.87 (ddd, *J* = 16.0, 10.4, 5.5 Hz, 1H), 2.68 (dt, *J* = 16.4, 4.9 Hz, 1H), 2.08 (ddd, *J* = 10.1, 8.6, 5.1 Hz, 1H), 2.02 – 1.86 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 146.79, 144.07, 134.45, 129.87, 129.34, 127.61, 127.02, 126.77, 124.80, 120.99, 117.69, 114.30, 55.82, 30.86, 26.12.

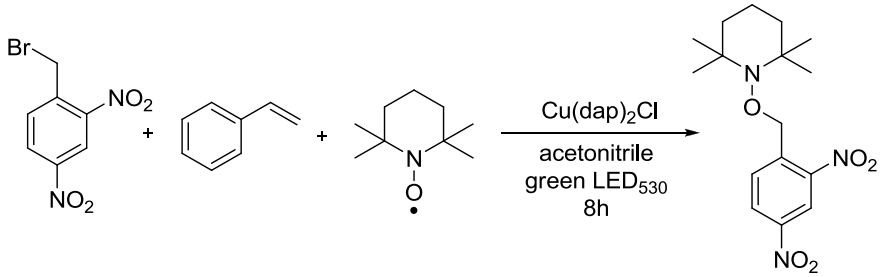
MS (ESI) Calculated for $C_{15}H_{15}ClN$ $[M+H]^+$ 244.0, found 244.0

Procedure for the Reduction of Ketone with Pd/C[24]

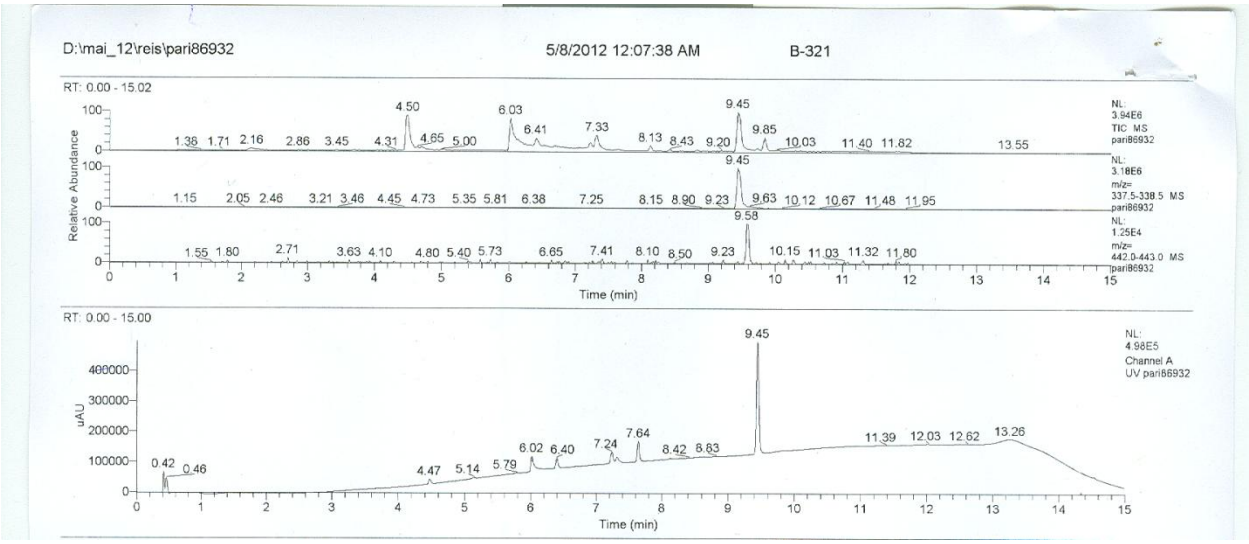
Ketone **5b** (150 mg, 0.58 mmol, 1 equiv) was dissolve in 3 mL of ethanol and 23.2 mg of 5% Pd/C was added. Hydrogen gas was passed through the solution for 5 minutes and stirred at room temperature for 3 h under hydrogen atmosphere. After completion of the reaction (as judged by TLC), the reaction mixture was filtered through a celite bed, the filtrate was concentrated in vacuo and subjected to column chromatography to obtain **6a** (81 mg, 67 %) as colorless liquid.

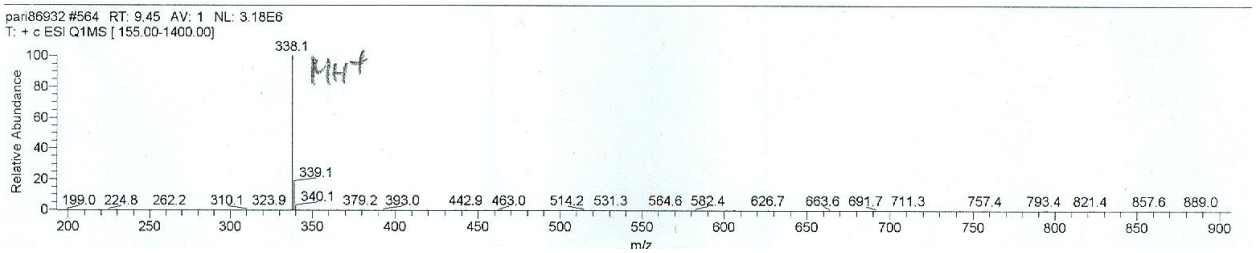
Experimental procedure to trap radical with TEMPO

An oven dried 10 mL vial equipped with a plastic septum and magnetic stir bar was charged with $Cu(dap)_2Cl$ (20 mol%) and 2, 4 -dinitro benzylbromide (0.030 g, 0.11 mmol, 1 equiv) . The flask was purged with a stream of nitrogen and 1.0 mL acetonitrile was added. The resultant mixture was degassed for 5 min by nitrogen sparging and styrene (0.057 g, 0.55 mmol, 5.0 equiv) was added to the vial. The vial was placed at a distance of ~ 0.5 -1.0 cm from a green LED lamp (530 nm). After 8 h of irradiation, TEMPO trapped compound **13** was detected by mass spectra.


Br
NO2
NO2
+
+
N
O
Cu(dap)2Cl
acetonitrile
green LED530
8h
N
O
NO2
NO2

13
M.W. = 337.37


D:\mai_12\reis\pari86932
5/8/2012 12:07:38 AM
B-321
RT: 0.00 - 15.02
Relative Abundance
Time (min)
NL: 3.94E6 TIC MS pari86932
NL: 3.18E6 m/z= 337.5-338.5 MS pari86932
NL: 1.25E4 m/z= 442.0-443.0 MS pari86932
RT: 0.00 - 15.00
uAU
NL: 4.98E5 Channel A UV pari86932


pari86932 #564 RT: 9.45 AV: 1 NL: 3.18E6
T: + c ESI Q1MS [155.00-1400.00]
Relative Abundance
m/z
338.1
MH+
339.1
340.1

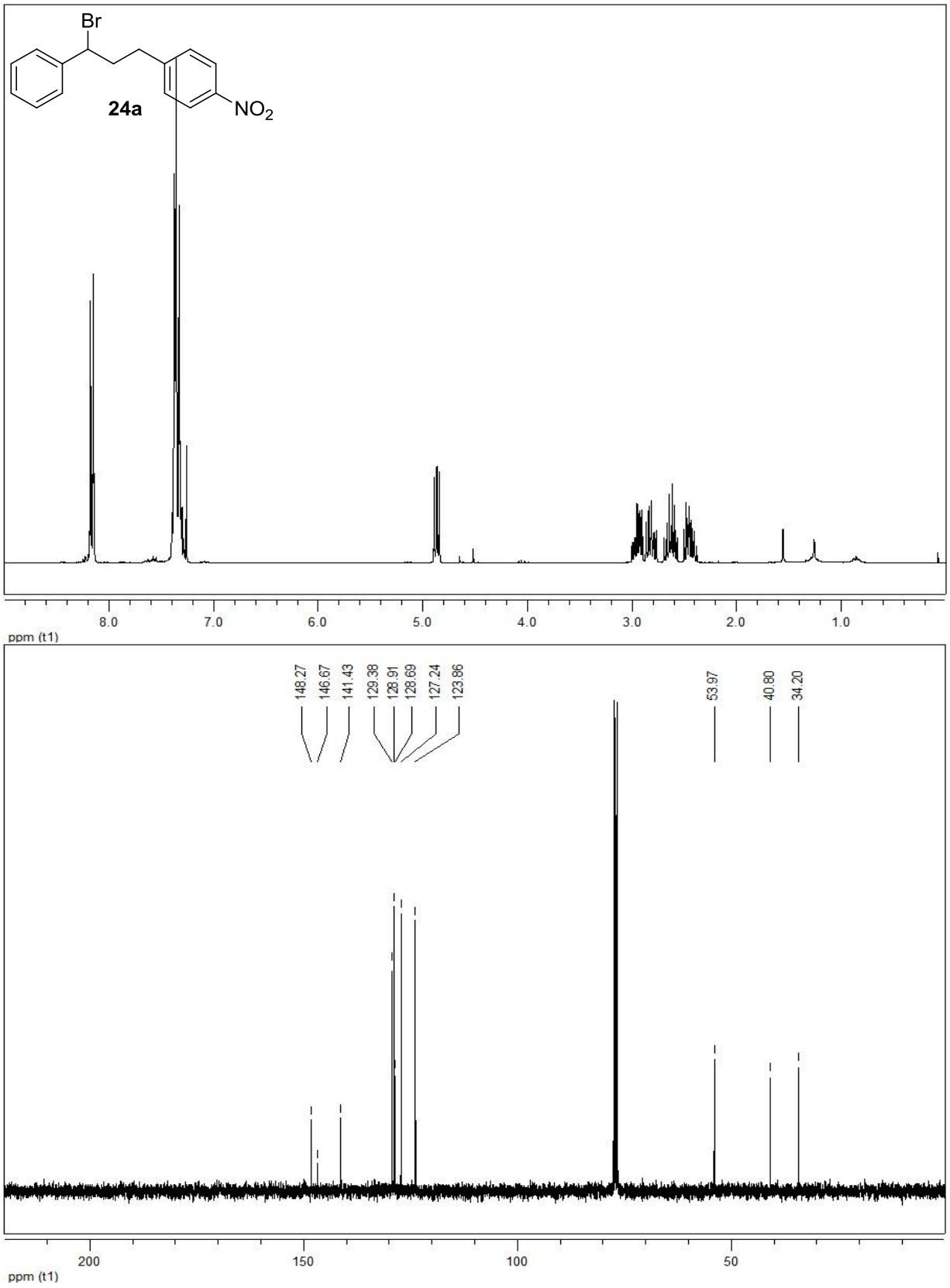
Appendix

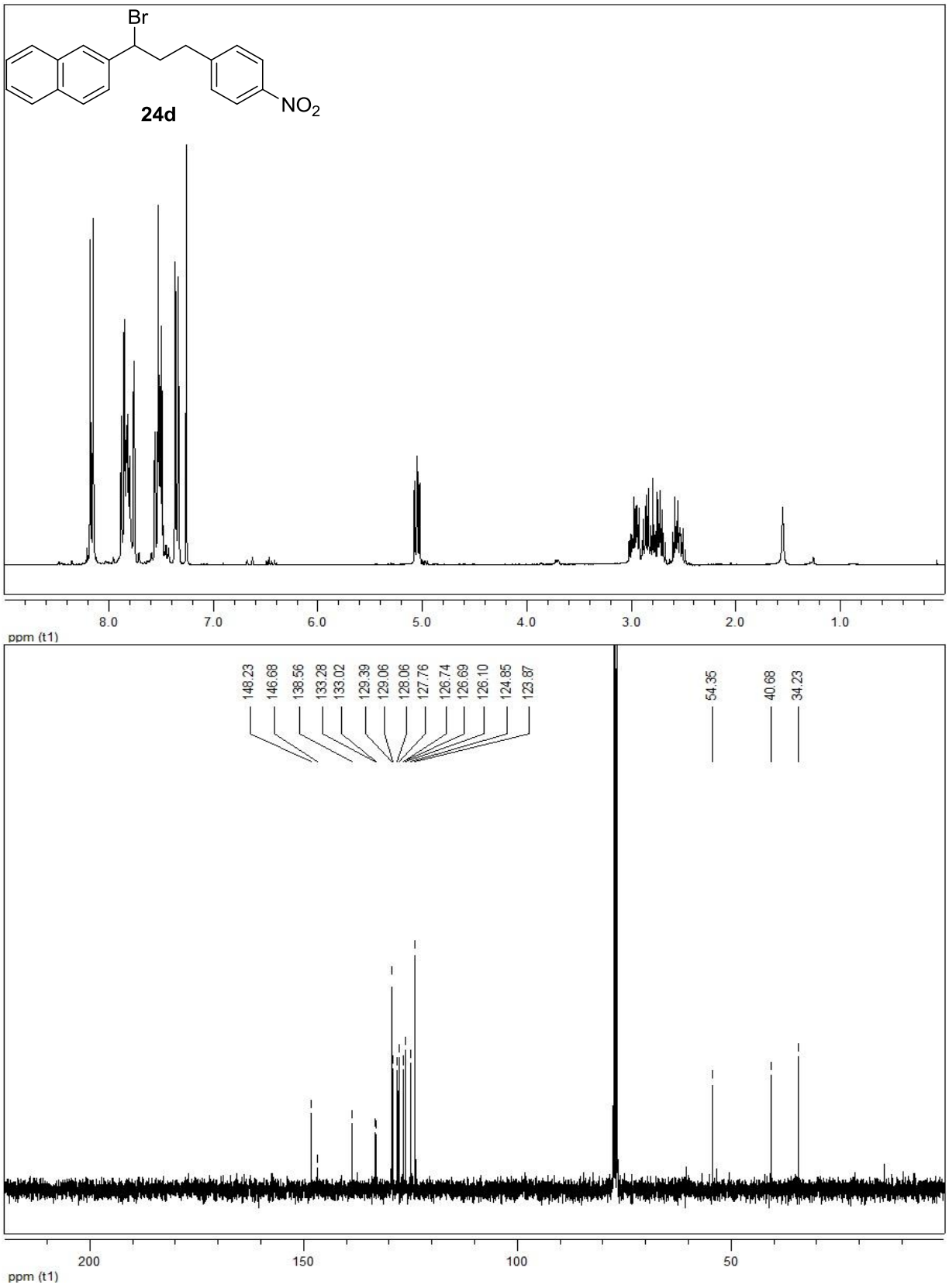
Selected NMR- spectra

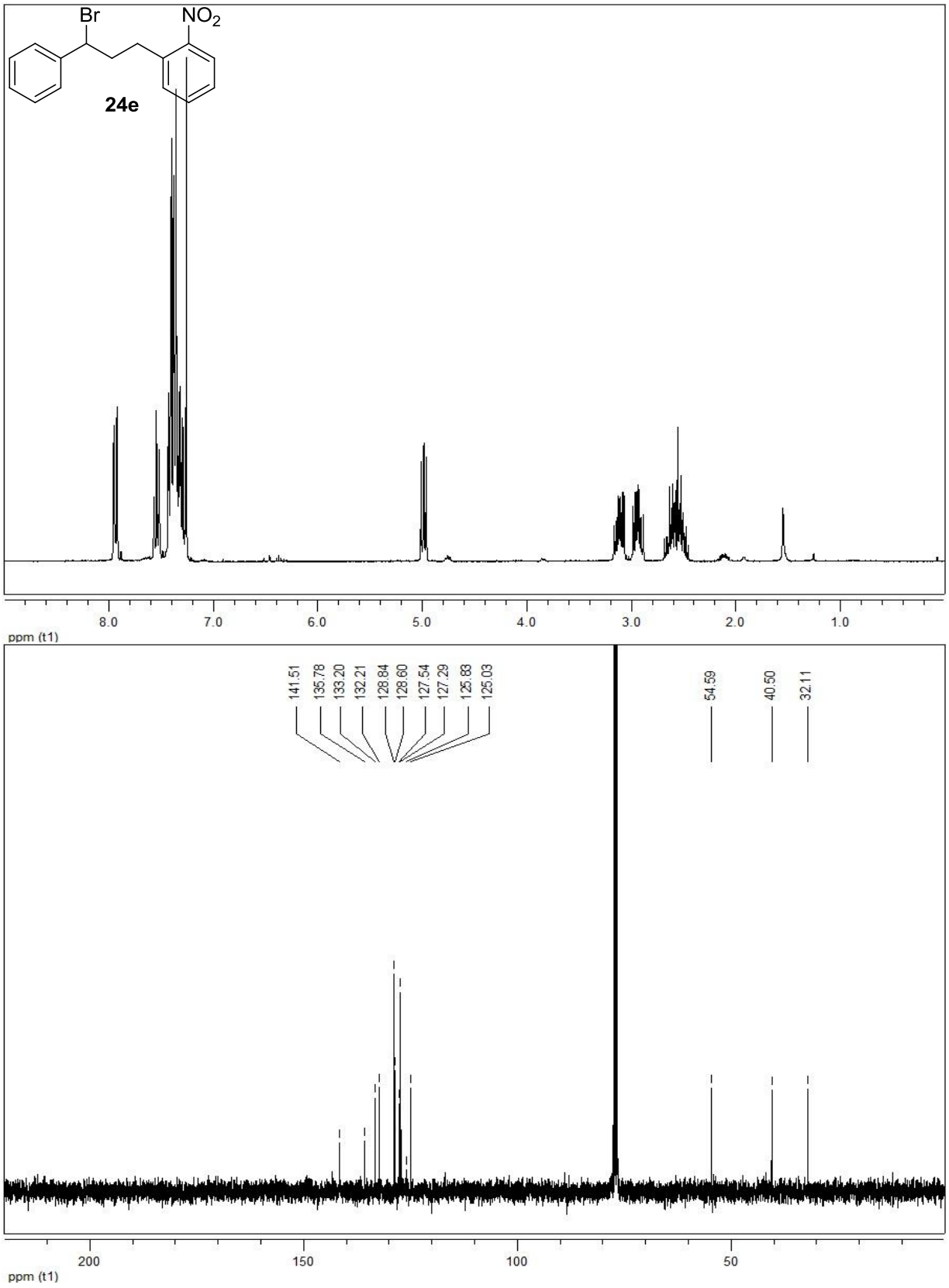
^{1}H-NMR spectra - upper image

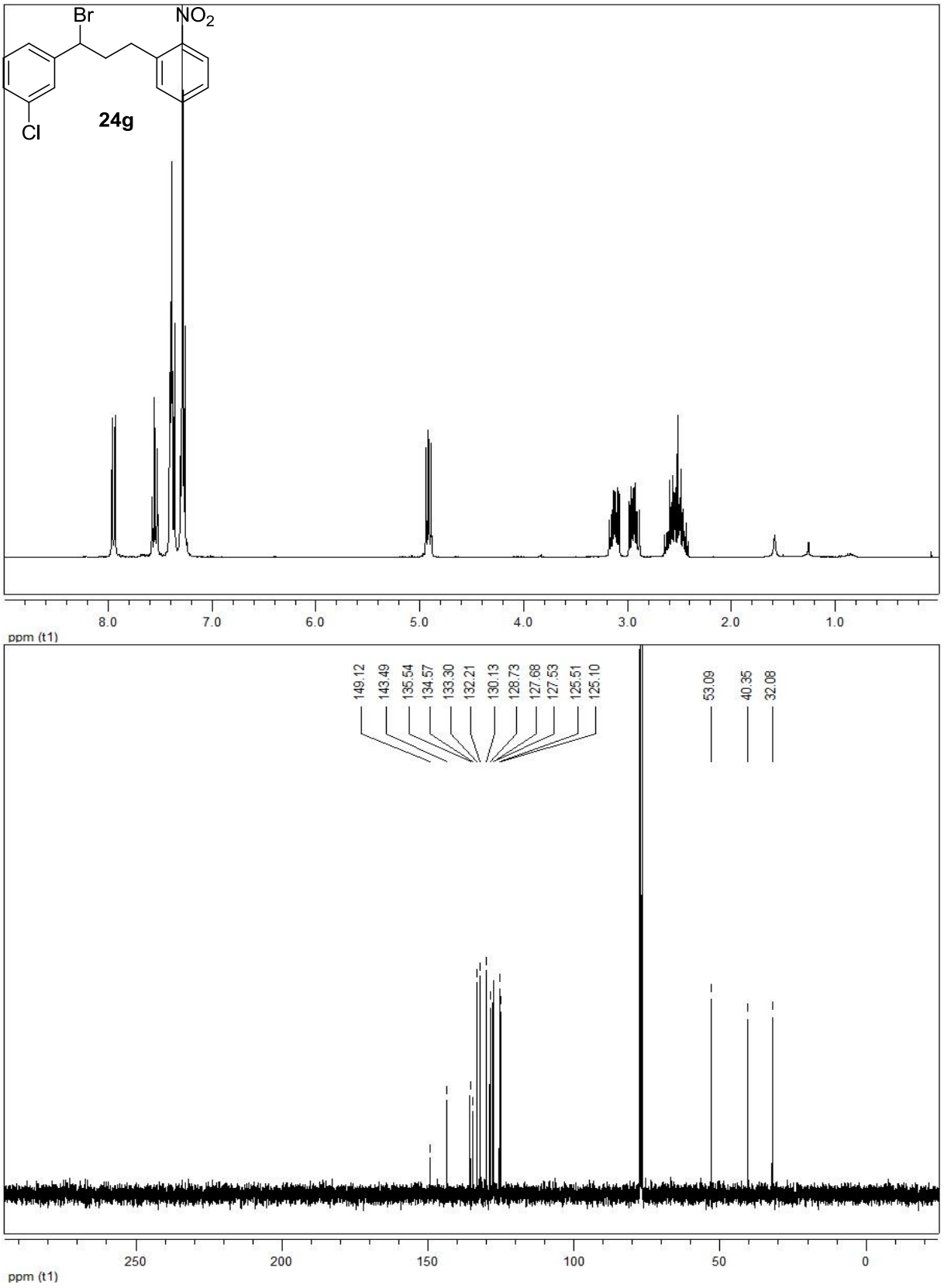
^{13}C-NMR spectra - lower image

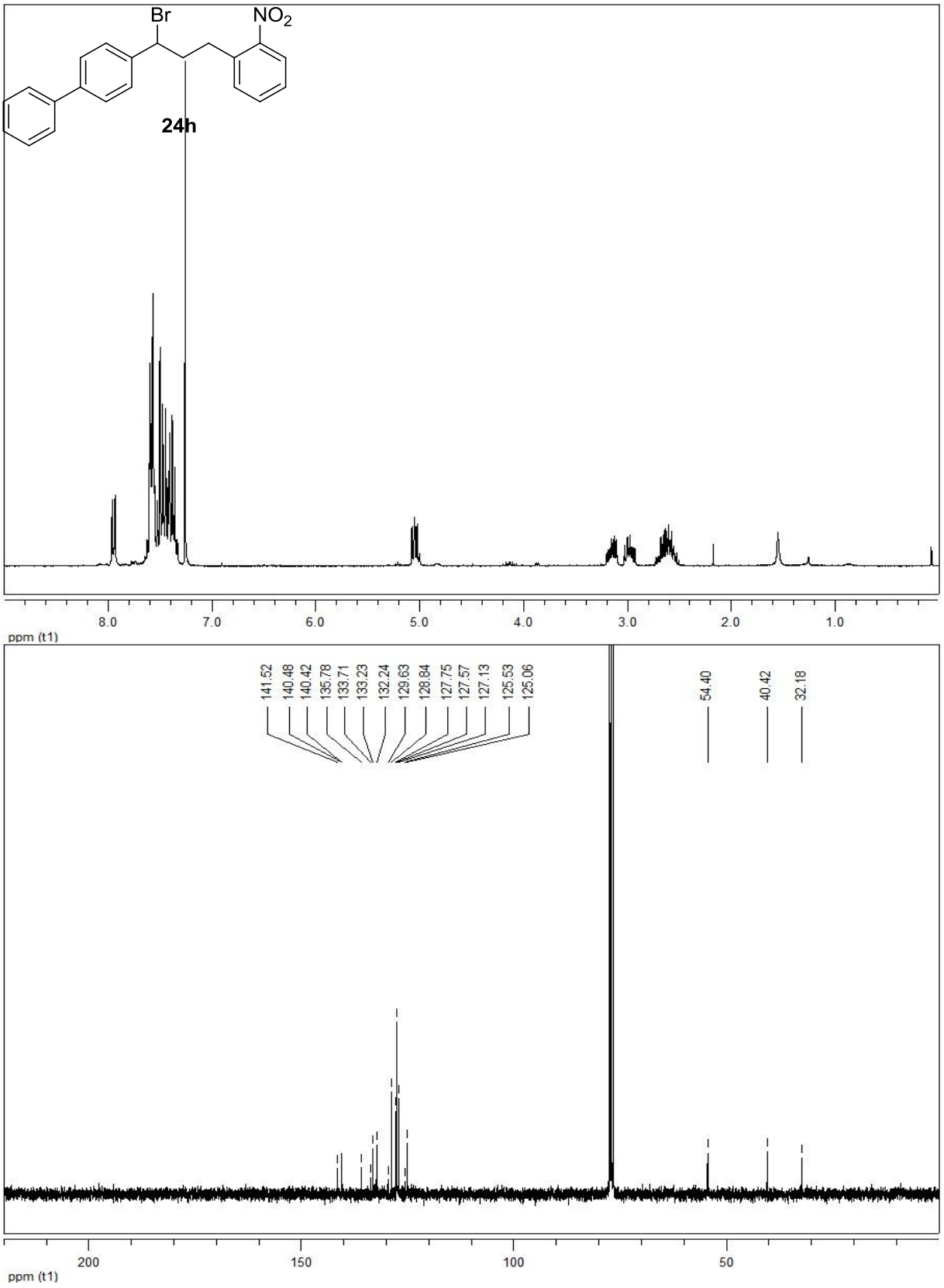
Solvent, if not stated otherwise: $CDCl_3$

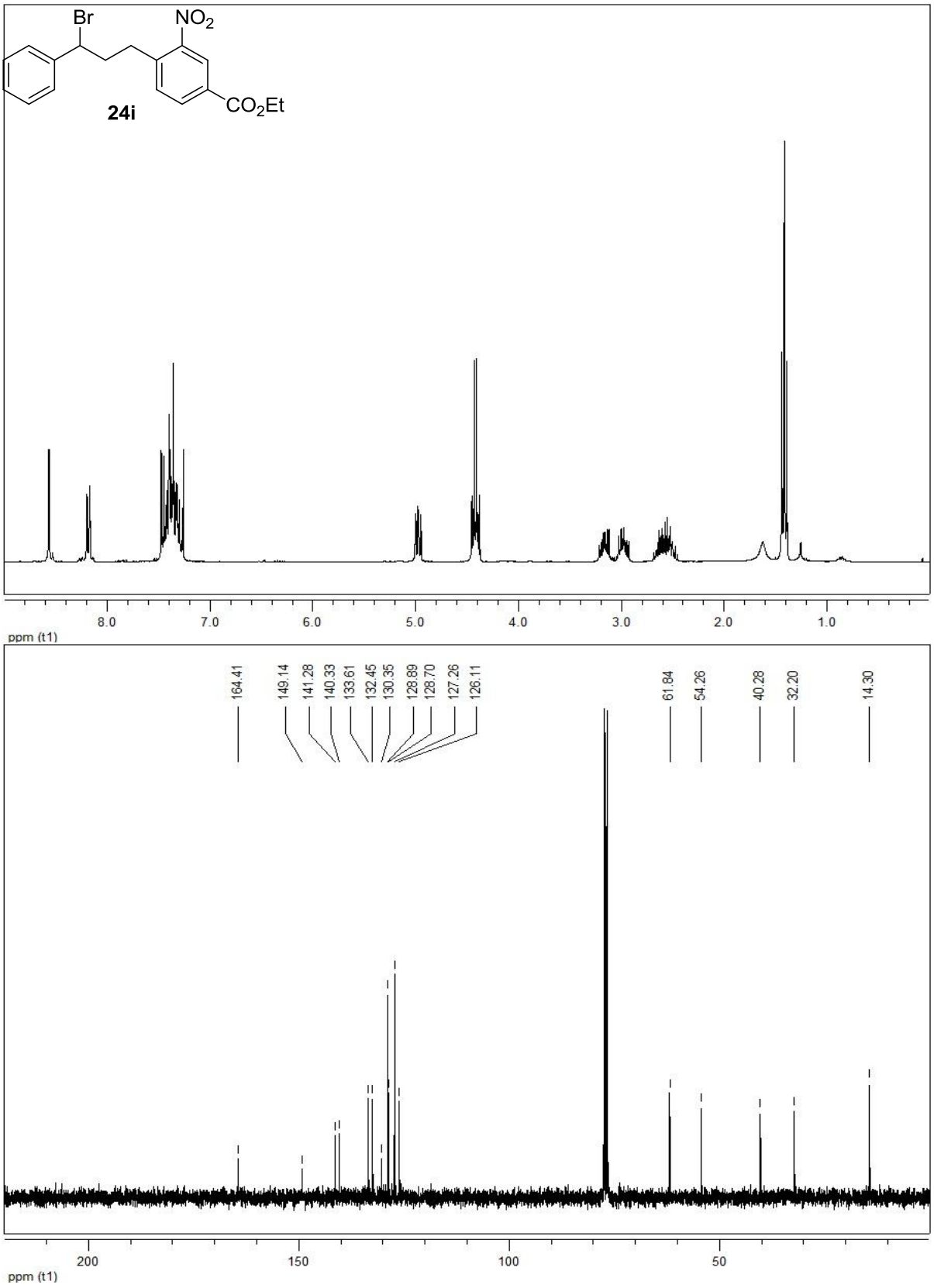

Br
24a
NO_2
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
148.27
146.67
141.43
129.38
128.91
128.69
127.24
123.86
53.97
40.80
34.20
200
150
100
50
ppm (t1)

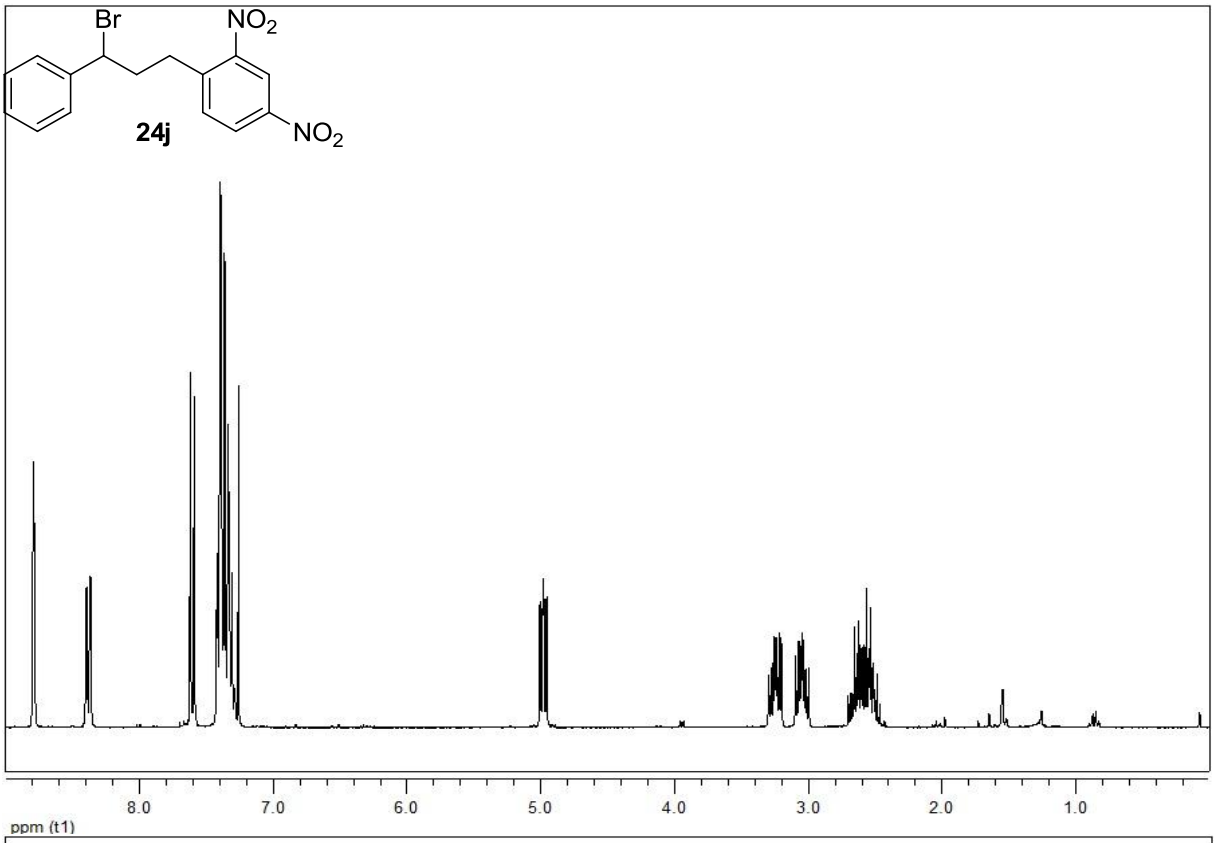

Br
NO2
24d
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
148.23
146.68
138.56
133.28
133.02
129.39
129.06
128.06
127.76
126.74
126.69
126.10
124.85
123.87
54.35
40.68
34.23
200
150
100
50
ppm (t1)

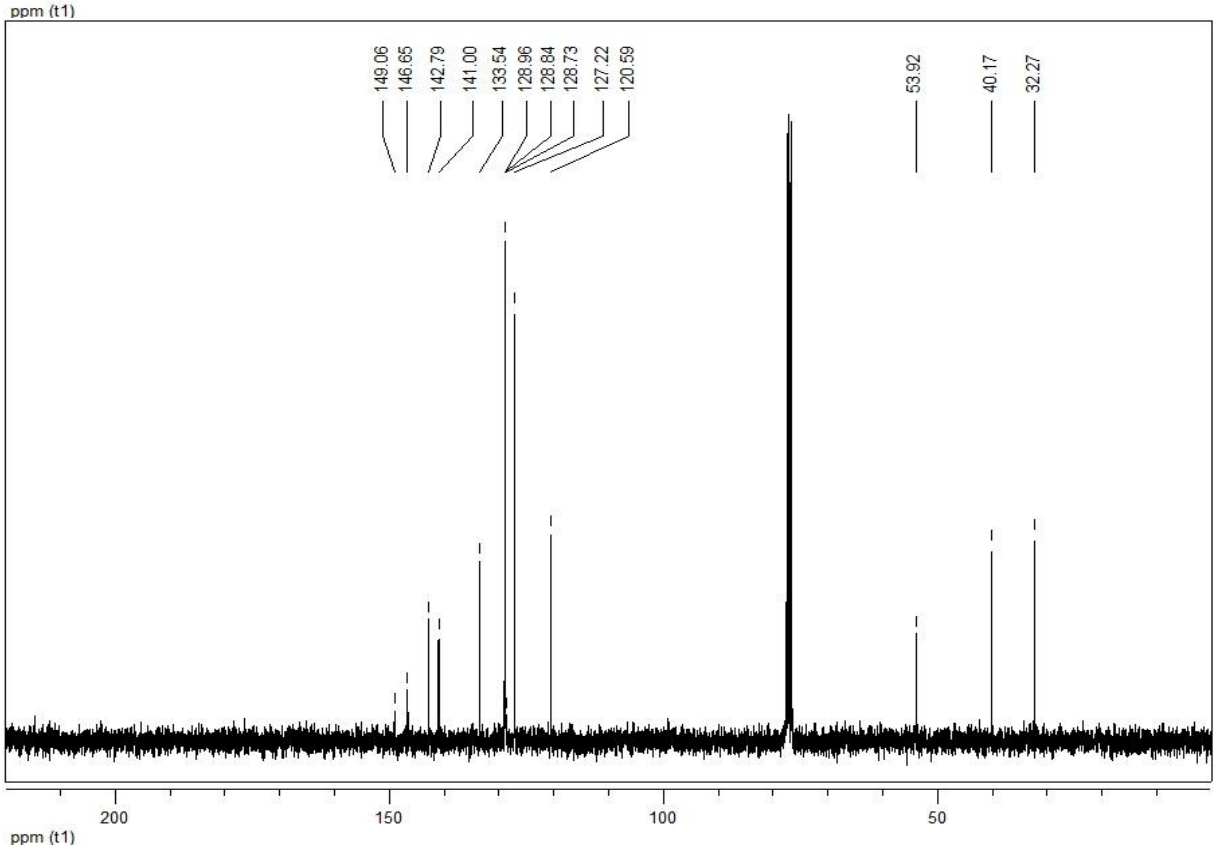

Br
NO2
24e
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
141.51
135.78
133.20
132.21
128.84
128.60
127.54
127.29
125.88
125.03
54.59
40.50
32.11
200
150
100
50
ppm (t1)

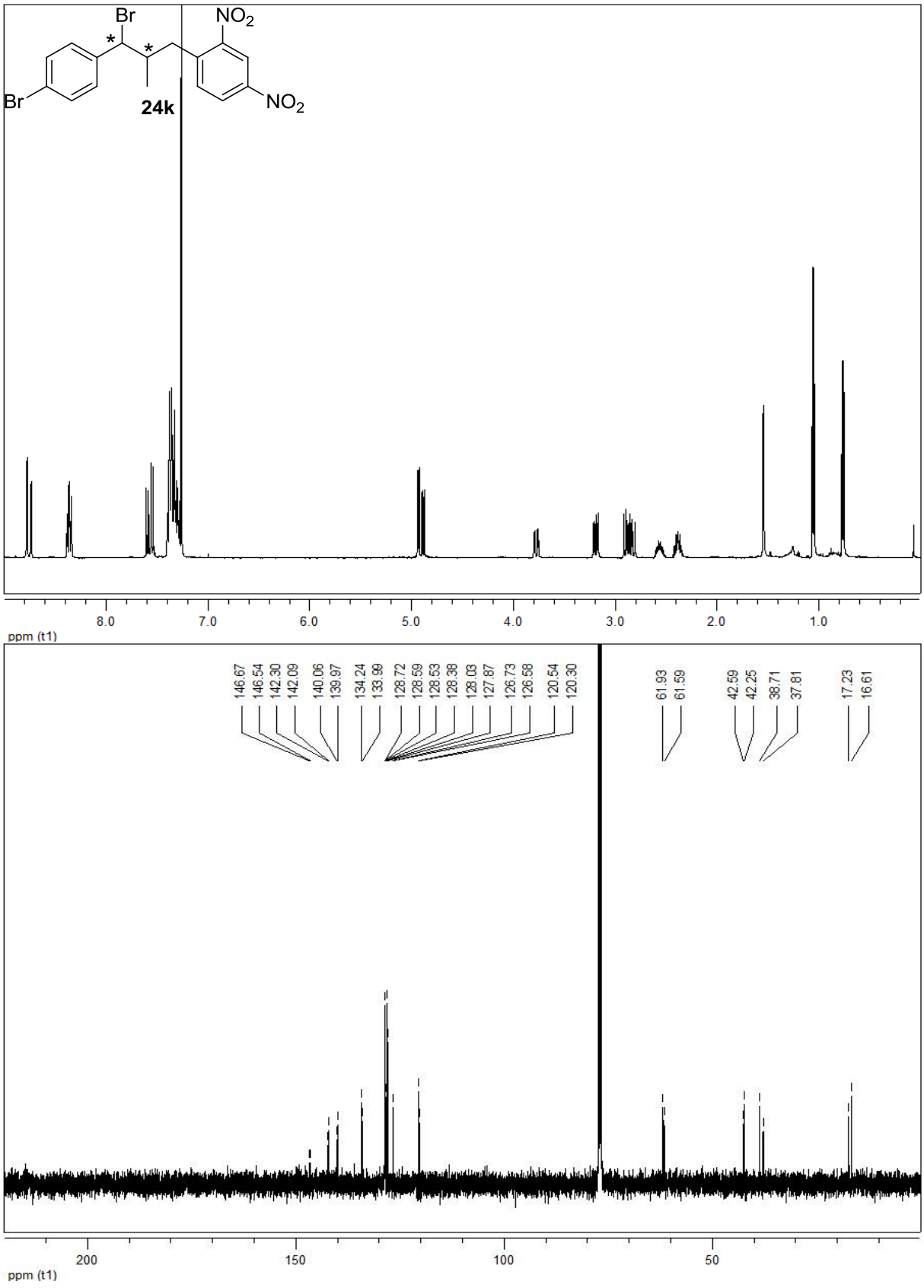

Br
NO2
Cl
24g
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
149.12
143.49
135.54
134.57
133.30
132.21
130.13
128.73
127.68
127.53
125.51
125.10
53.09
40.35
32.08
250
200
150
100
50
0
ppm (t1)


Br
NO2
24h
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
141.52
140.48
140.42
135.78
133.71
133.23
132.24
129.63
128.84
127.75
127.57
127.13
125.53
125.06
54.40
40.42
32.18
200
150
100
50
ppm (t1)


Br
NO2
CO2Et
24i
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
164.41
149.14
141.28
140.33
133.61
132.45
130.35
128.89
128.70
127.26
126.11
61.84
54.26
40.28
32.20
14.30
200
150
100
50
ppm (t1)


Br
NO2
NO2
24j
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


149.06
146.65
142.79
141.00
133.54
128.96
128.84
128.73
127.22
120.59
53.92
40.17
32.27
200
150
100
50
ppm (t1)


Br
NO2
*
*
Br
NO2
24k
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
146.67
146.54
142.30
142.09
140.06
139.97
134.24
133.99
128.72
128.59
128.53
128.38
128.03
127.87
126.73
126.58
120.54
120.30
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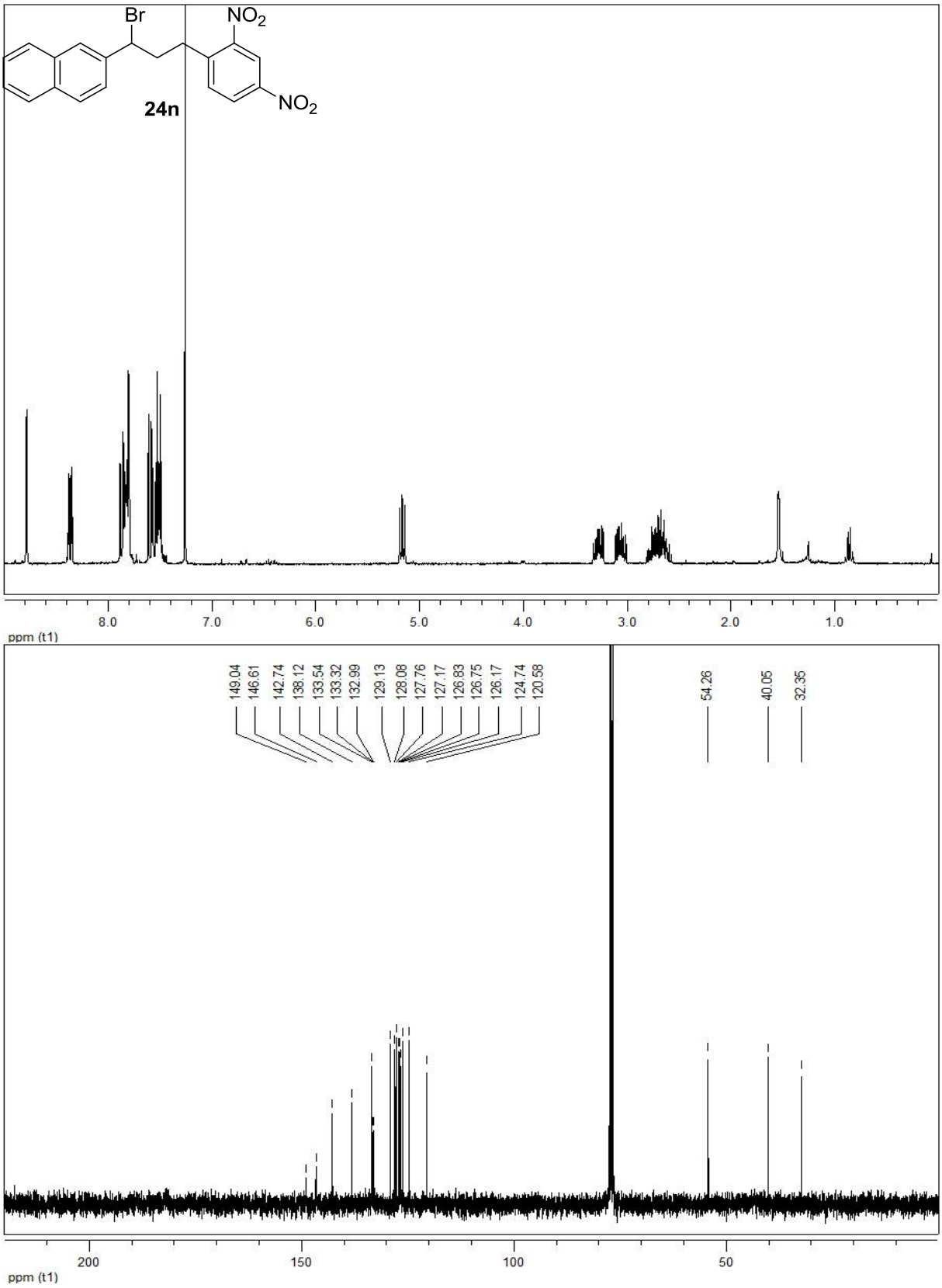
17.23
16.61
200
150
100
50
ppm (t1)


Br
NO2
NO2
24n
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
149.04
146.61
142.74
138.12
133.54
133.32
132.99
129.13
128.08
127.76
127.17
126.83
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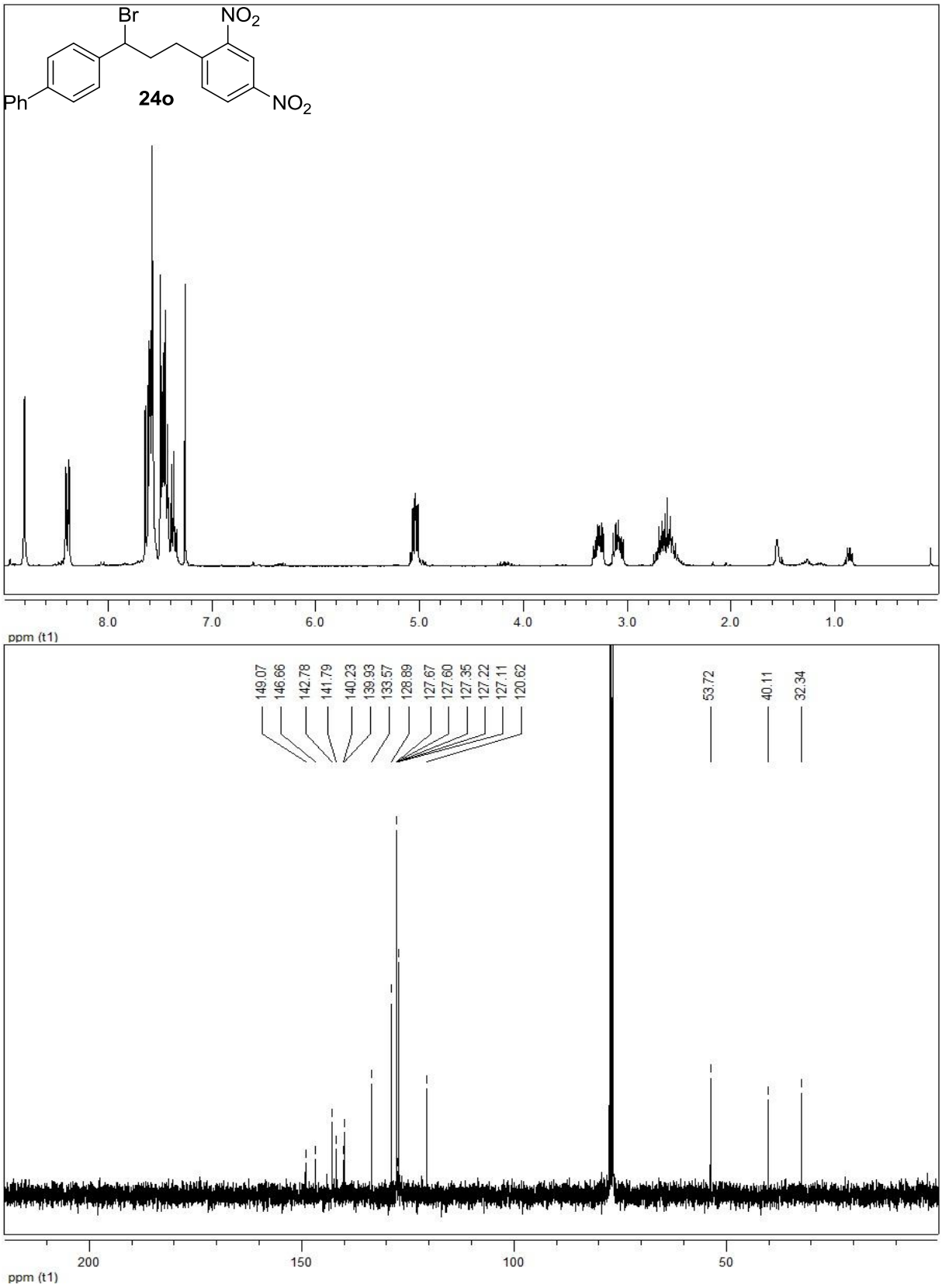
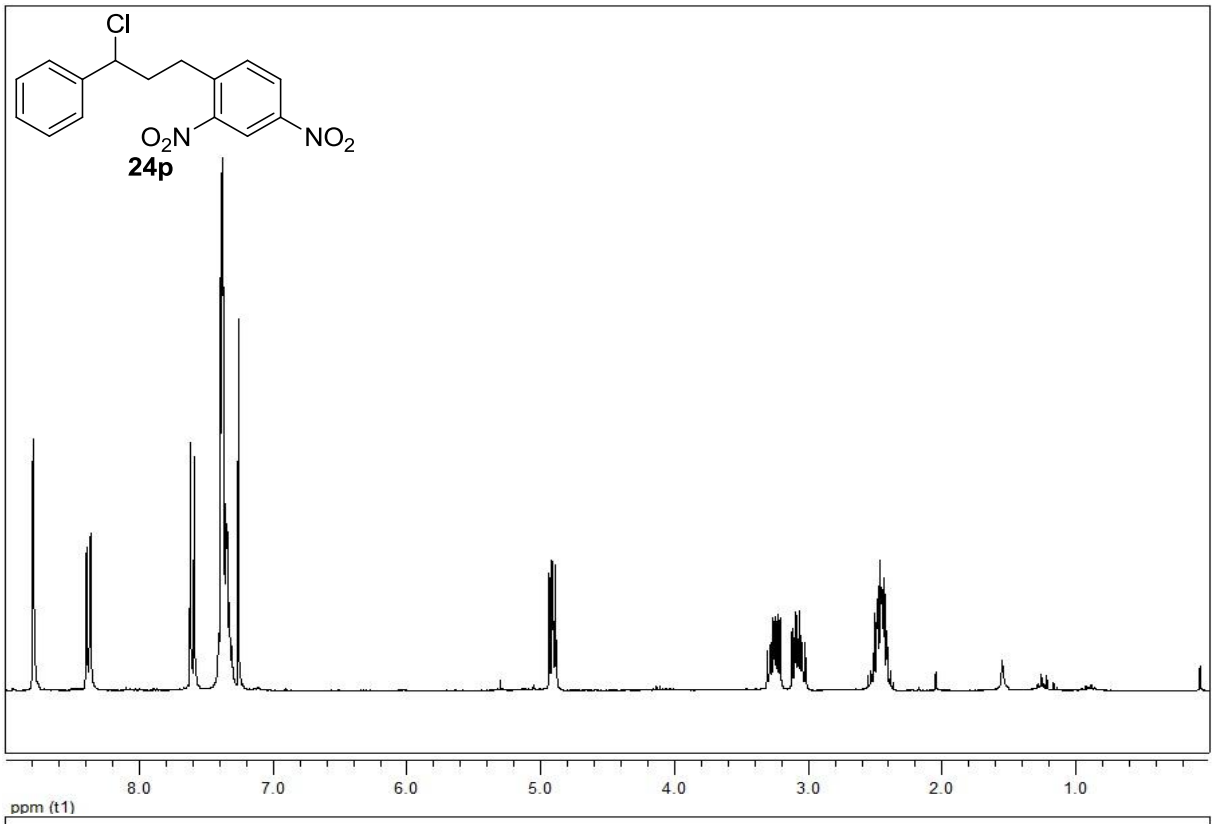
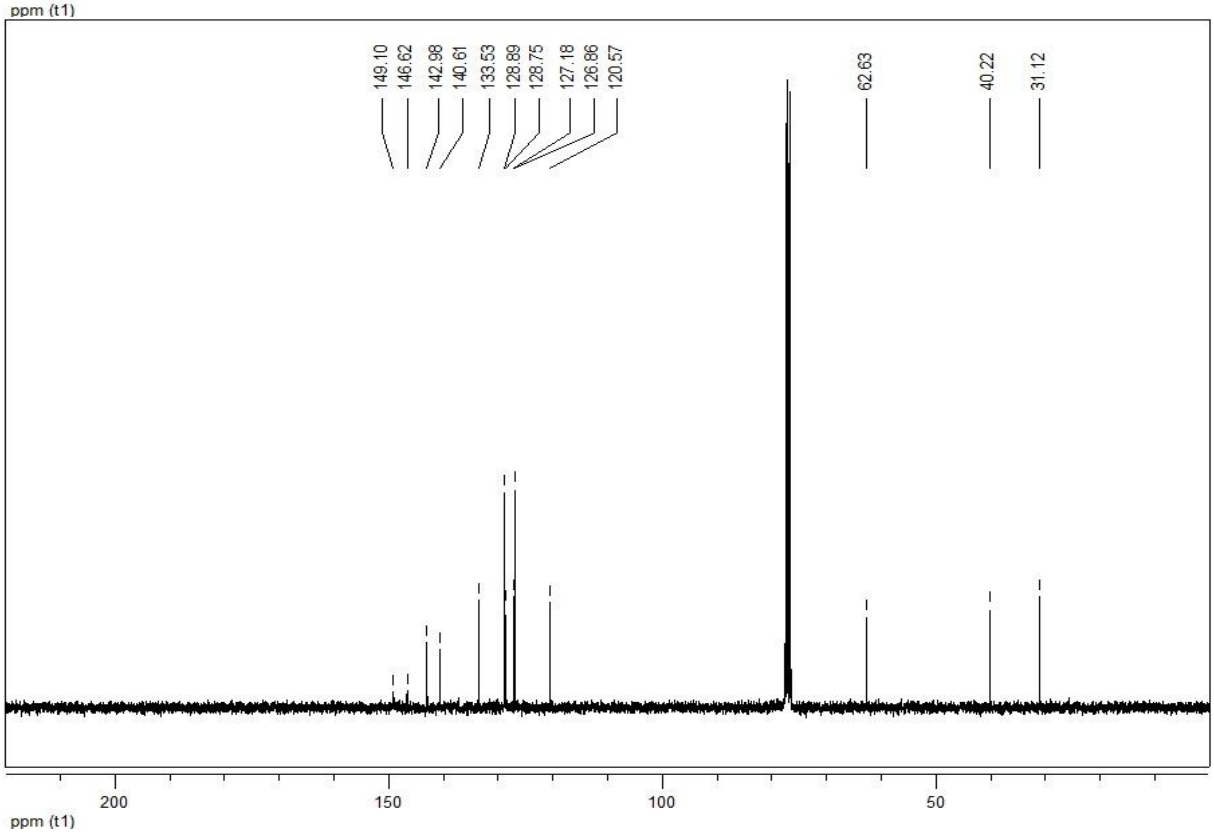
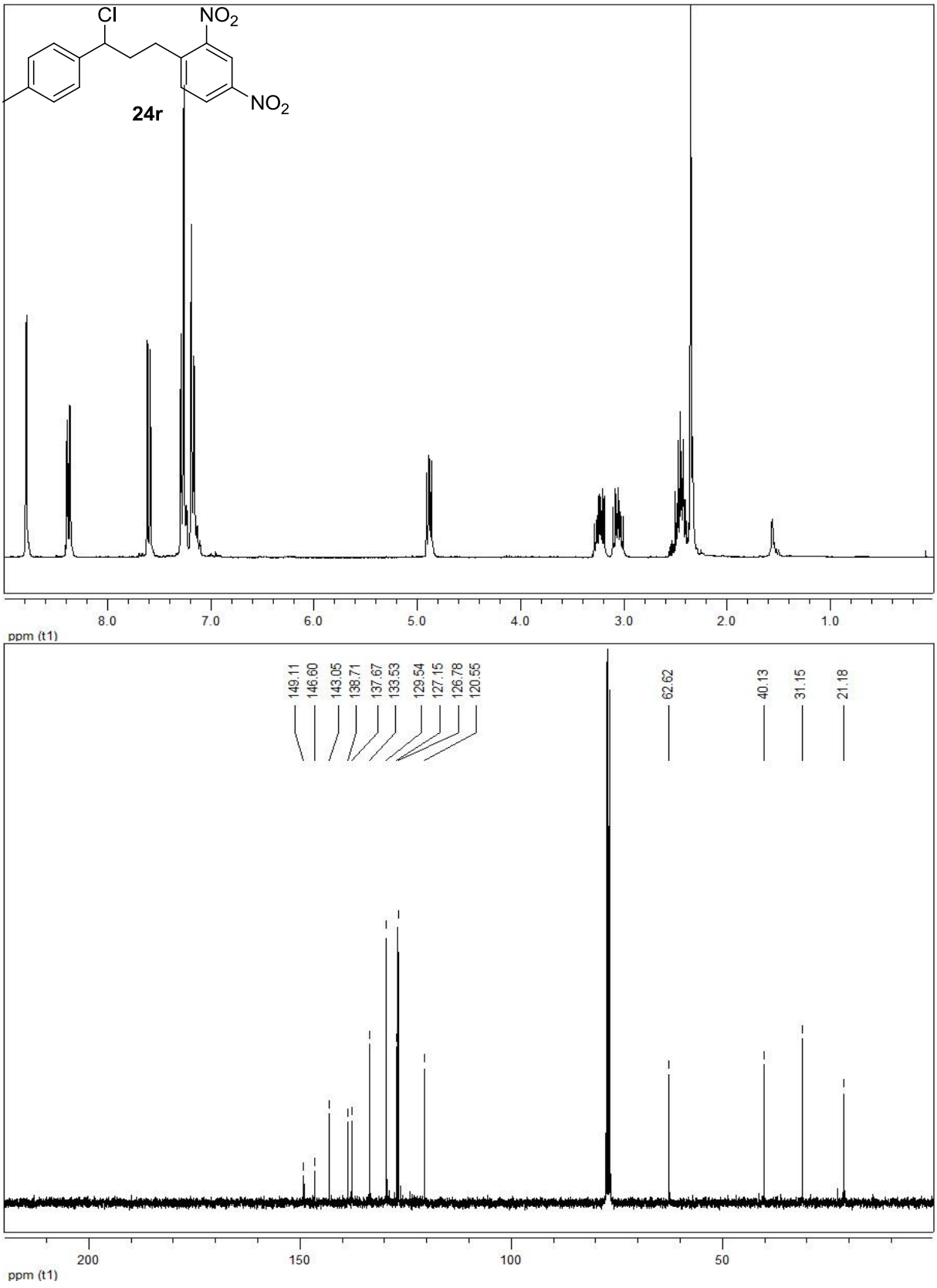
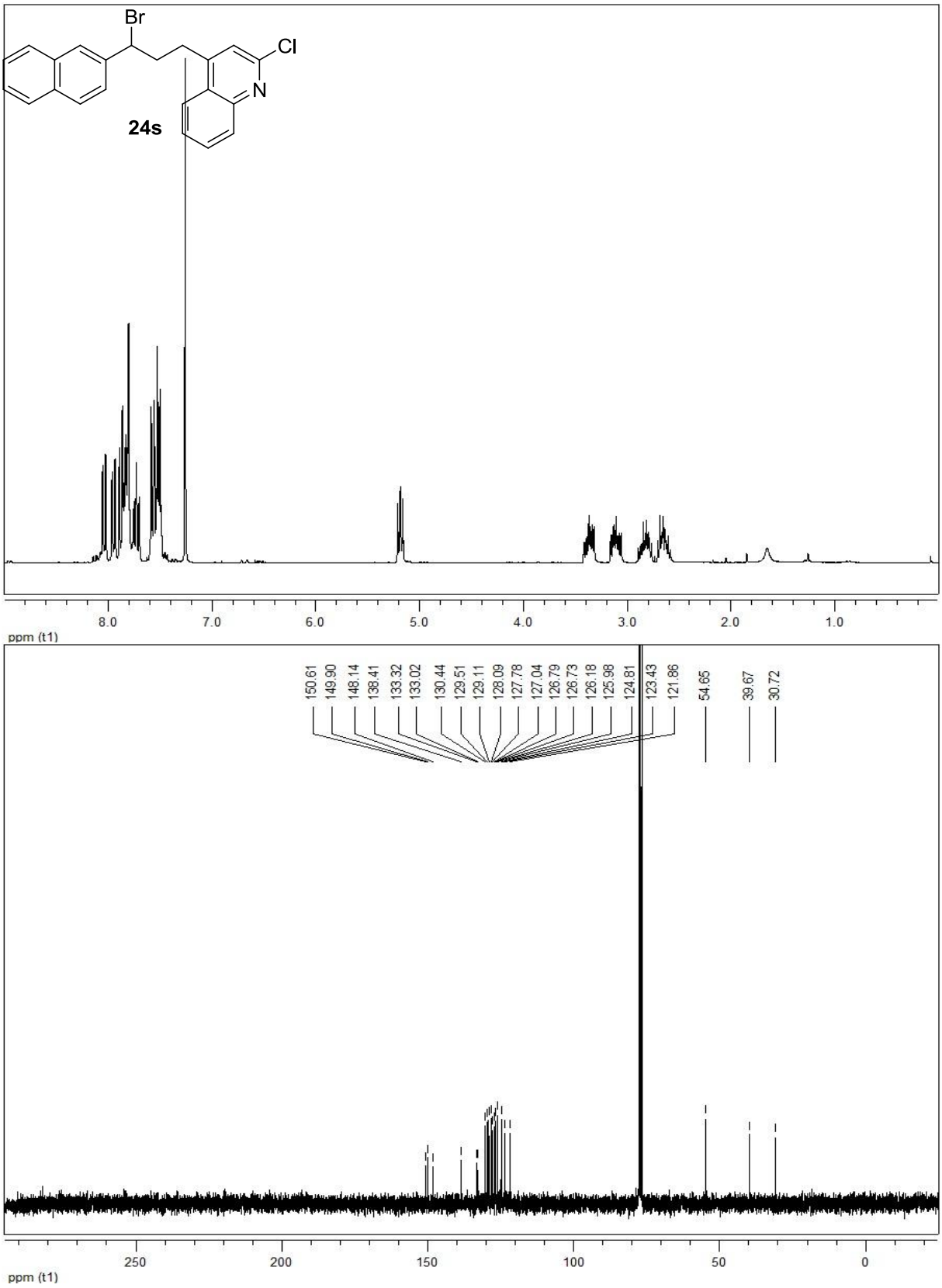
40.05
32.35
200
150
100
50
ppm (t1)


Br
NO2
Ph
24o
NO2
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
149.07
146.66
142.78
141.79
140.23
139.93
133.57
128.89
127.67
127.60
127.35
127.22
127.11
120.62
53.72
40.11
32.34
200
150
100
50
ppm (t1)


Cl
O_2N
NO_2
24p
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


149.10
146.62
142.98
140.61
133.53
128.89
128.75
127.18
126.86
120.57
62.63
40.22
31.12
200
150
100
50
ppm (t1)


Cl
NO2
NO2
24r
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
149.11
146.60
143.05
138.71
137.67
133.53
129.54
127.15
126.78
120.55
62.62
40.13
31.15
21.18
200
150
100
50
ppm (t1)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N
24s
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6.0
5.0
4.0
3.0
2.0
1.0
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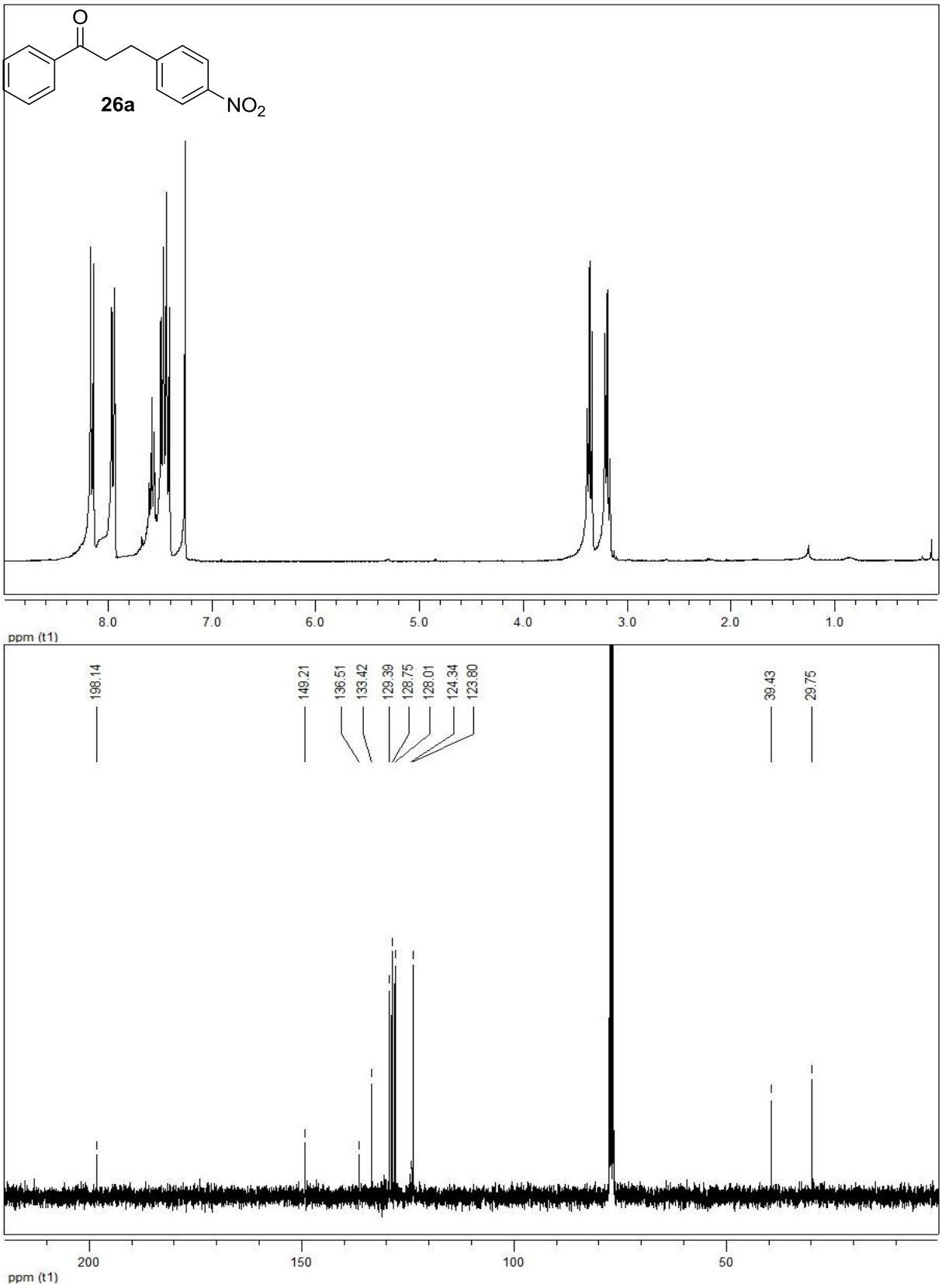
149.90
148.14
138.41
133.32
133.02
130.44
129.51
129.11
128.09
127.78
127.04
126.79
126.73
126.18
125.98
124.81
123.43
121.86
54.65
39.67
30.72
250
200
150
100
50
0
ppm (t1)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26a
NO_2
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6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
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149.21
136.51
133.42
129.39
128.75
128.01
124.34
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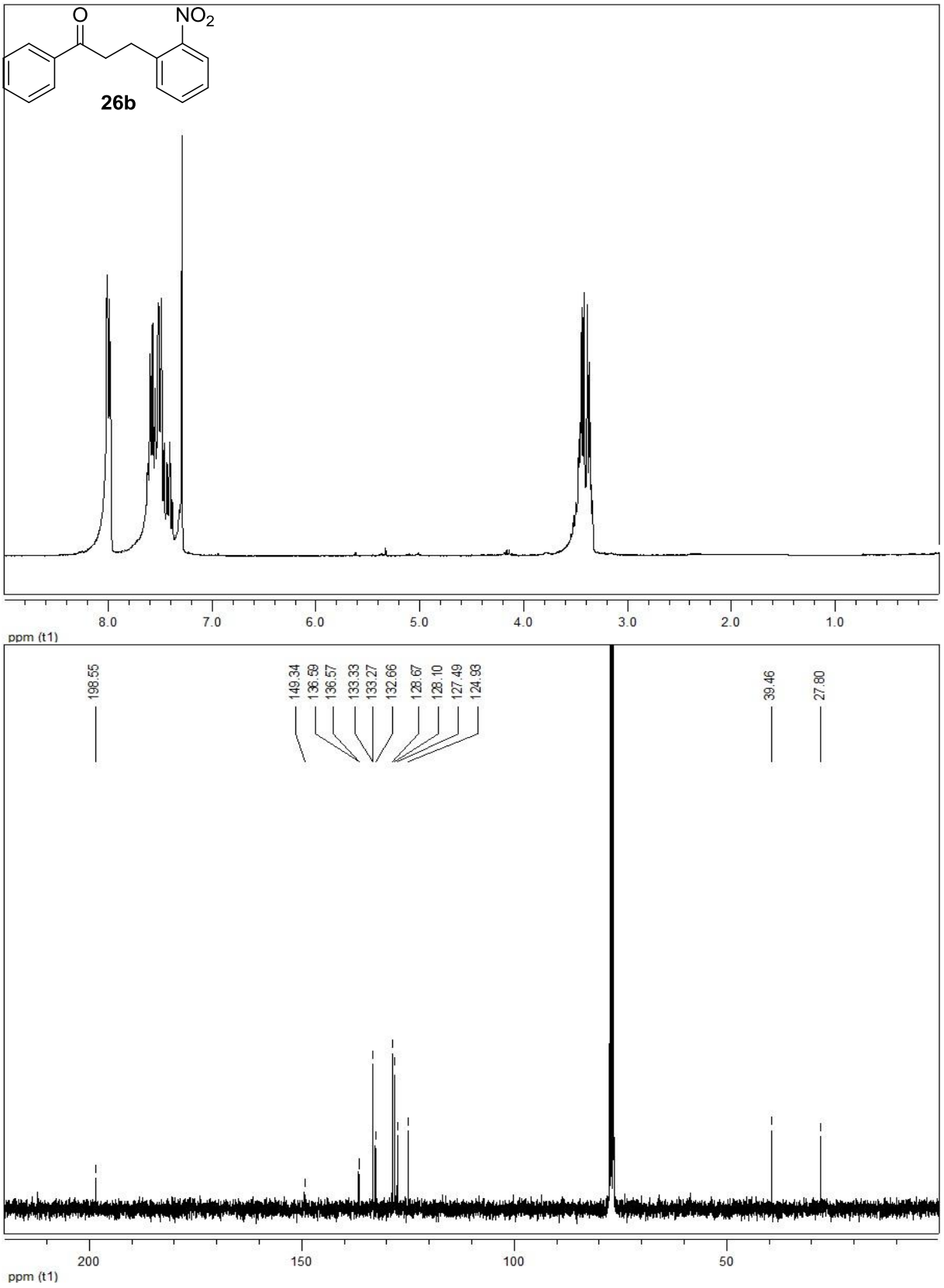
39.43
29.75
200
150
100
50
ppm (t1)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NO2
26b
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5.0
4.0
3.0
2.0
1.0
ppm (t1)
198.55
149.34
136.59
136.57
133.33
133.27
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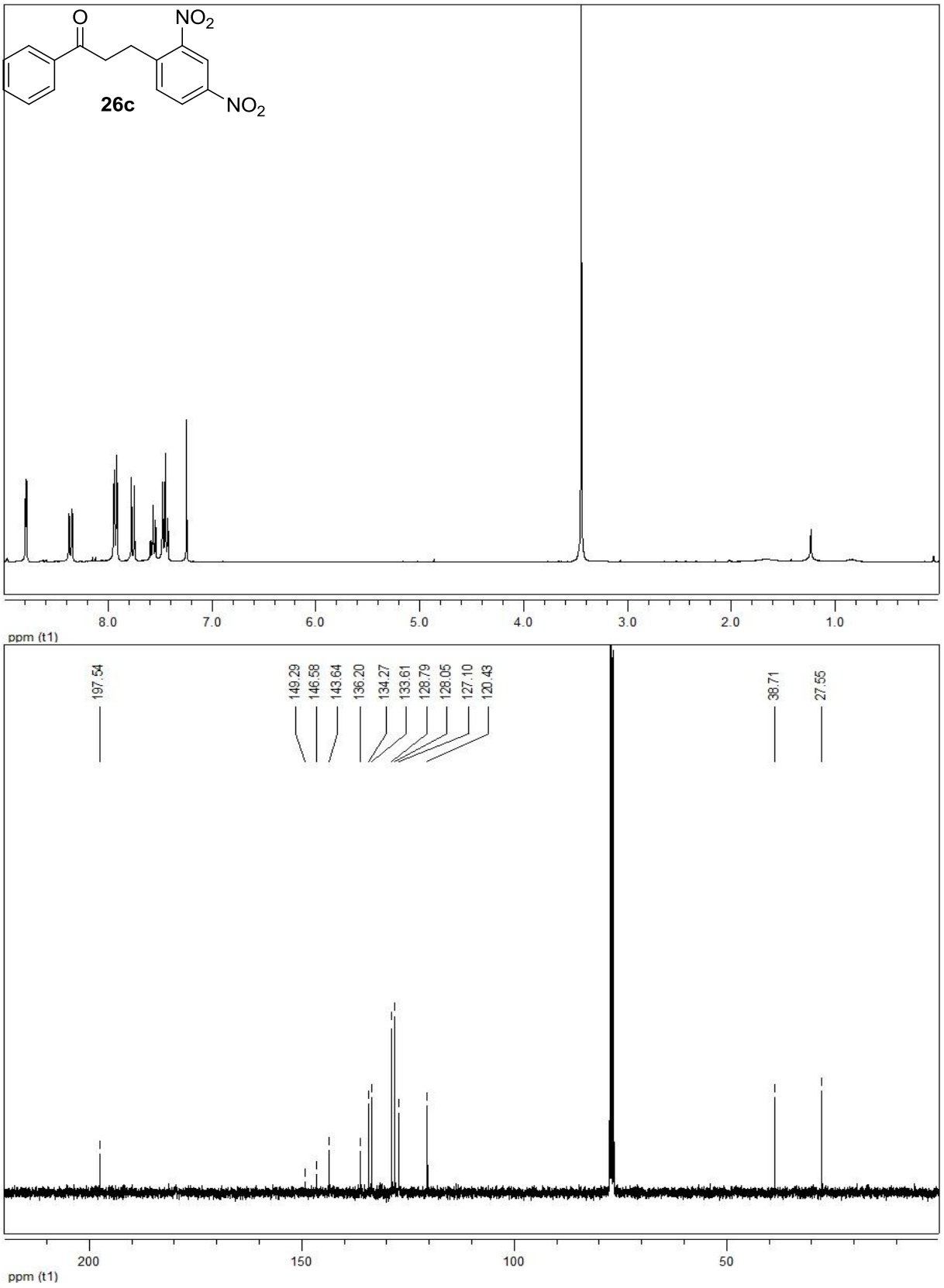
128.67
128.10
127.49
124.93
39.46
27.80
200
150
100
50
ppm (t1)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NO2
NO2
26c
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
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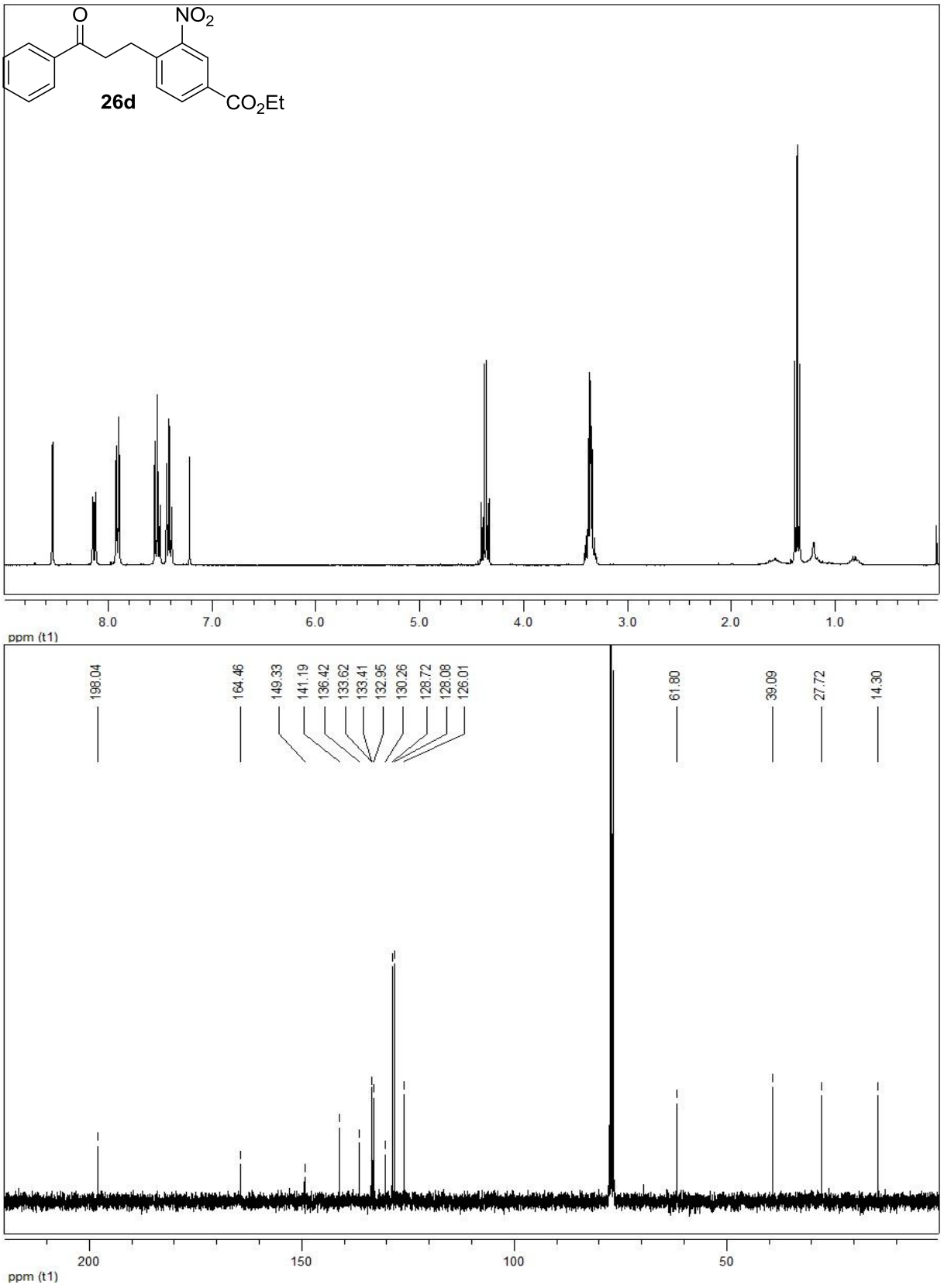
149.29
146.58
143.64
136.20
134.27
133.61
128.79
128.05
127.10
120.43
38.71
27.55
200
150
100
50
ppm (t1)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CO2Et
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
198.04
164.46
149.33
141.19
136.42
133.62
133.41
132.95
130.26
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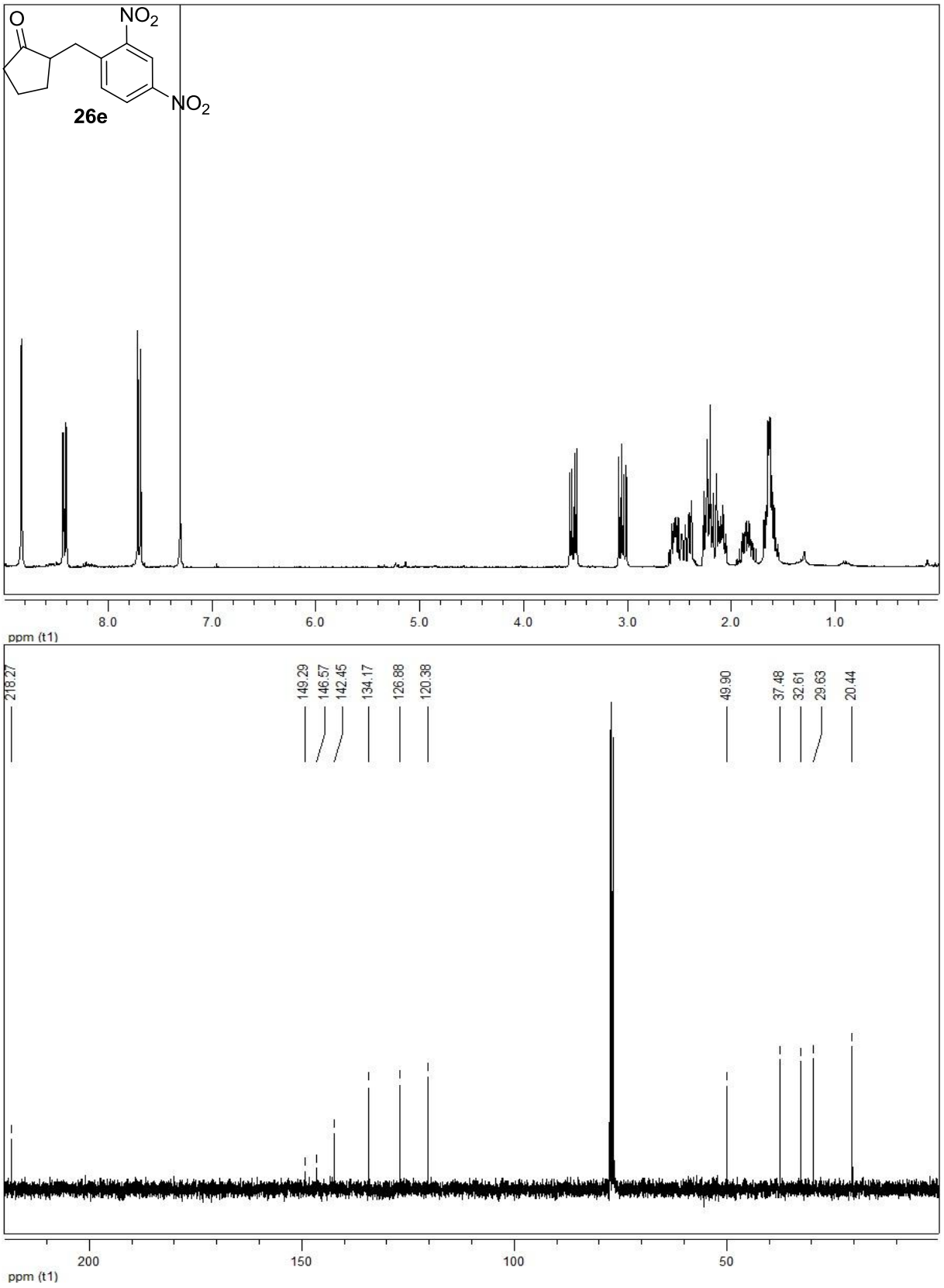
128.08
126.01
61.80
39.09
27.72
14.30
200
150
100
50
ppm (t1)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NO2
NO2
26e
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6.0
5.0
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3.0
2.0
1.0
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149.29
146.57
142.45
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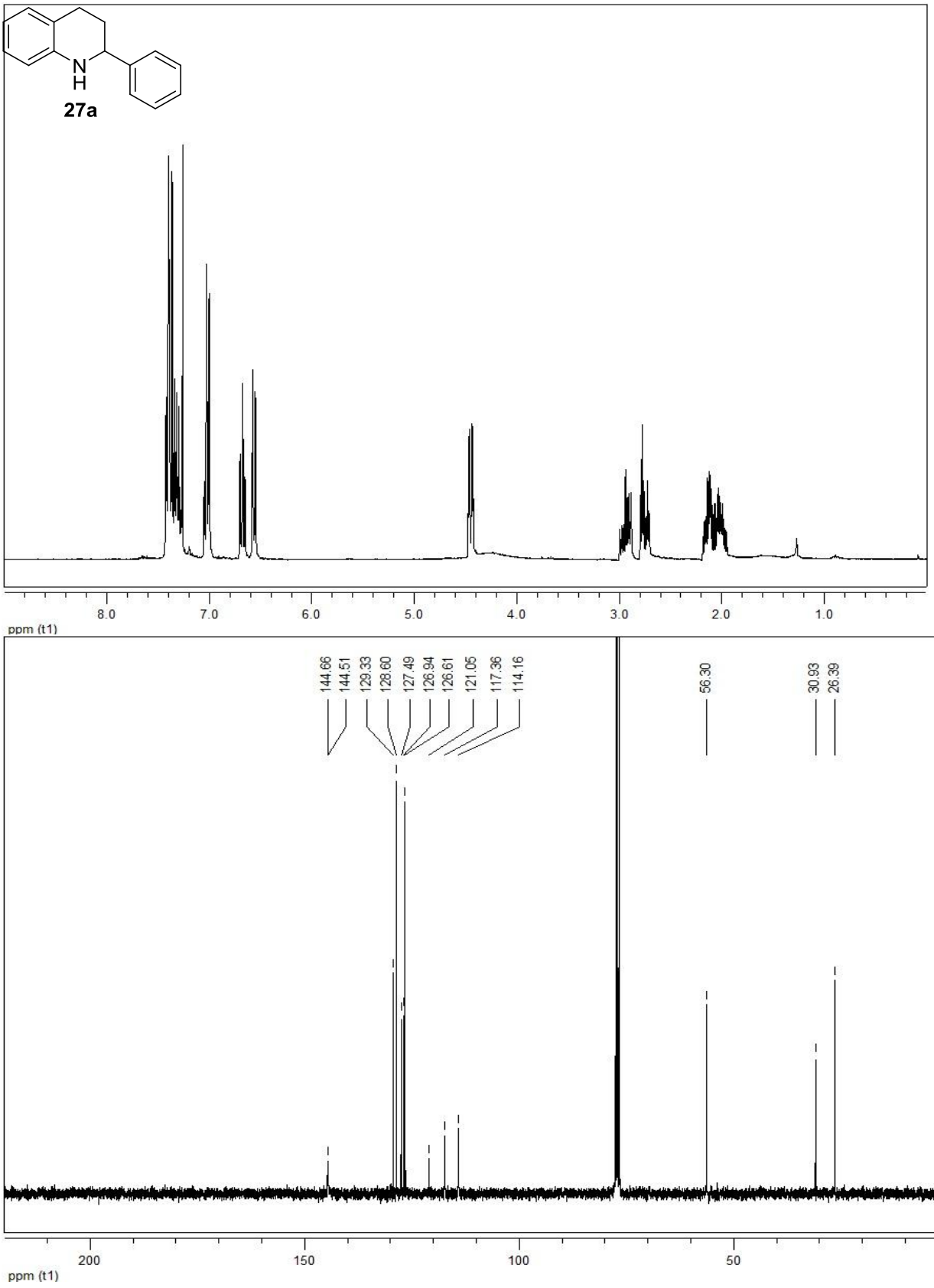
29.63
20.44
200
150
100
50
ppm (t1)


27a
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
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144.51
129.33
128.60
127.49
126.94
126.61
121.05
117.36
114.16
56.30
30.93
26.39
200
150
100
50
ppm (t1)

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18. Hironaka, K.; Fukuzumi, S.; Tanaka, T. *J. Chem. Soc., Perkin Trans. 2*, **1984**, 1705.
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20. Su, Y.; Zhang, L.; Jiao, N. *Org. Lett*. **2011**, *13*, 2168.
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5. Photocatalytic Vinyl Radical Formation and its Synthetic Utility

5.1 Introduction

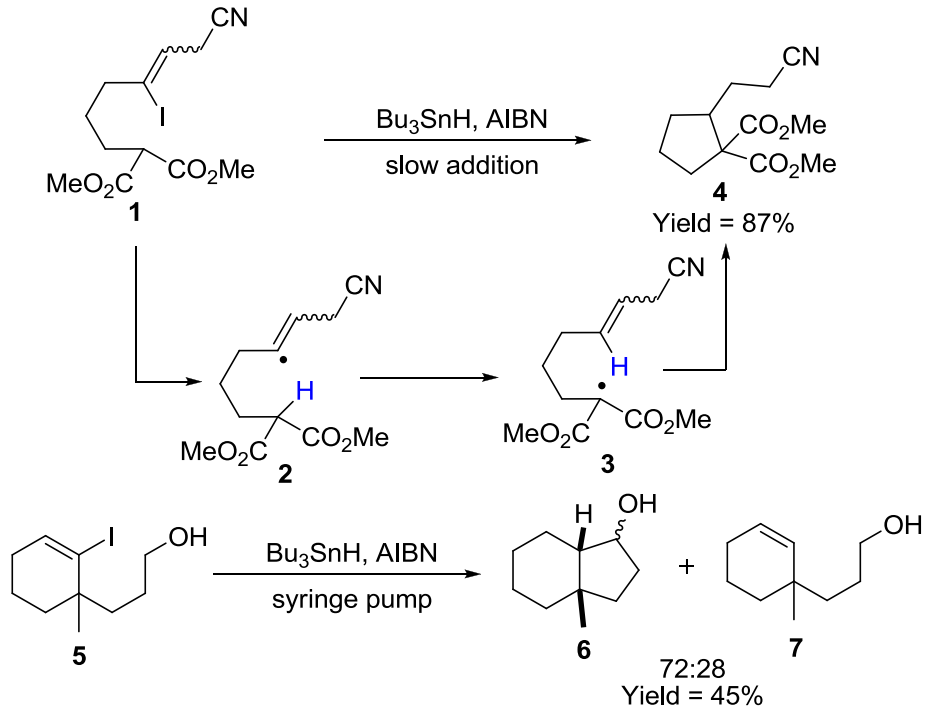
Synthetic utility of vinyl radical is already well established in literature. Since the pioneering work of Stork et al.[1] vinyl radical reactions have been developed as a versatile tool in synthetic organic chemistry.[2] Considering their high reactivity, they have been utilized in the process of cyclization in organic synthesis, recognized as important intermediate in hydrocarbon combustion processes[3] or in radical polymerization processes.[4]

5.2 Vinyl radical by thermal process

Thermal vinyl radical generation from vinyl halides is traditionally carried out using tributyltin hydride and a radical initiator such as AIBN. Vinyl radical formation by electrochemical processes[5] or by photolysis of vinyl halides[4] is also well established in literature.

One of the notable processes involving vinyl radical is radical translocation cyclization process starting from a vinyl halide as vinyl radical source. Curran et al. in 1988 reported a 1, 5-hydrogen transfer to vinyl radical **2**, thus generating an alkyl radical **3** which was suitably positioned to undergo intramolecular cyclization with alkenes to furnish **4** (Scheme 5.1).[6]

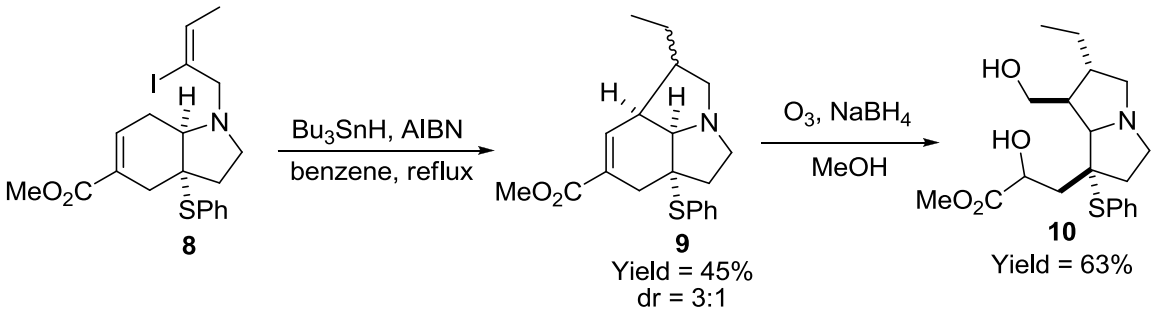
Scheme 5.1. 1, 5 hydrogen transfer to vinyl radicals derived from vinyl halides



A wide range of cyclopentane derivatives were efficiently prepared in moderate to good yields utilizing this methodology. In the second example, beside desired translocation cyclization product **6**, reduced product **7** was obtained in 28% yield. The ratio of the cyclization product and the reduced product was influenced by nature of substituent. Slow addition technique and in situ generated tributyltin hydride were used to achieve good yields.

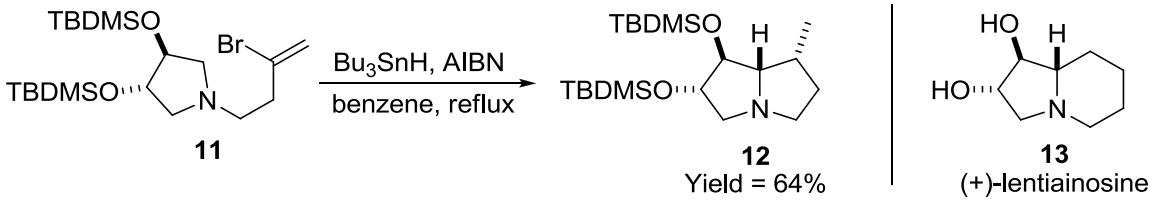
Parsons et al. in their pioneering work in 1988 developed an innovative method for the synthesis of pyrrolizidine alkaloid precursors using a translocation and cyclization process. In this transformation a stabilized allylic radical was generated via a 1, 5-hydrogen transfer from vinyl iodide. The tricyclic amine product **9** was converted to substituted pyrrolizidine derivative **10** by ozonolysis followed by reductive work up with sodium borohydride (Scheme 5.2).[7]

Scheme 5.2. Translocation-cyclization involving allyl radical intermediate



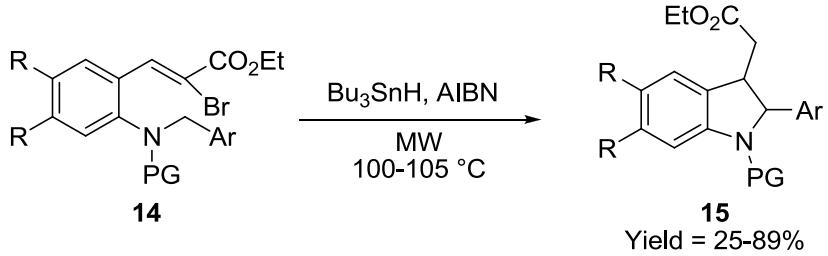
Robertson et al. successfully employed the translocation-cyclization reaction in the synthesis of optically pure silyl protected (6*S*, 7*S*)-dihydroxyheliotridane **12**, a close structural isomer of lentiginosine **13**, a potent amyloglucosidase inhibitor (Scheme 5.3).[8]

Scheme 5.3. Translocation-cyclization for the synthesis of optically pure (6*S*, 7*S*)-dihydroxyheliotridane



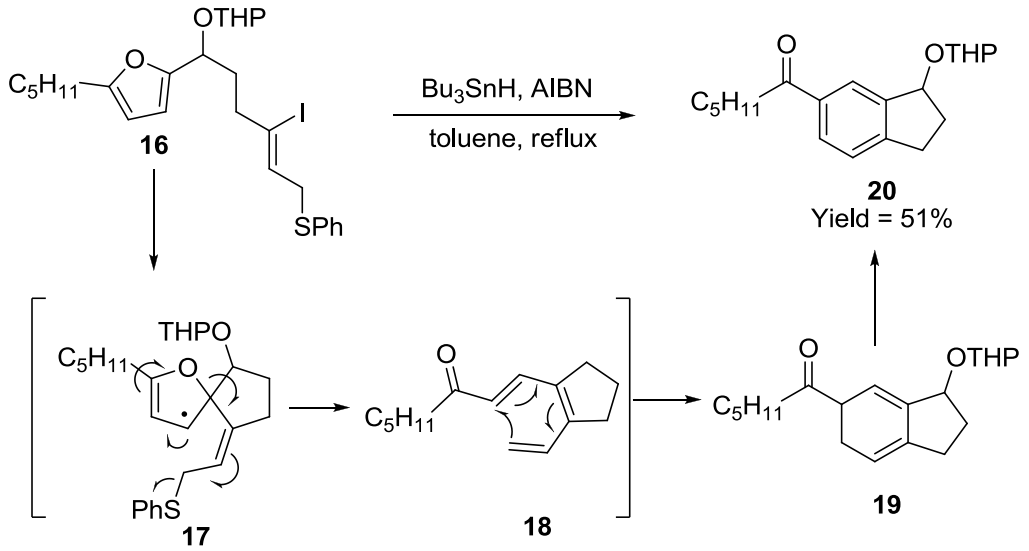
Synthesis of 3-aryl indolines **15** has been reported from our group by tandem radical cyclization of α-keto vinyl radical involving an unusual 1, 6-hydrogen transfer followed by 5-*exo*-trig ring closure from precursor **14** (Scheme 5.4).[9]

Scheme 5.4. Access to indolins via 1,6-hydrogen transfer



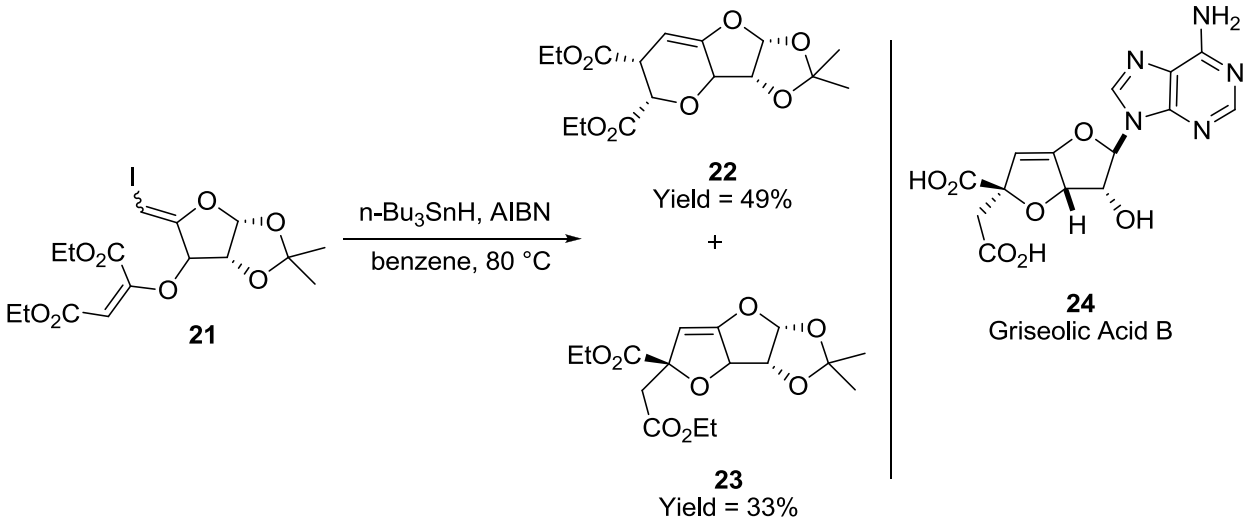
Parsons et al. also reported an intramolecular cascade reaction sequence involving vinyl radical and furan under typical tributyltin hydride and AIBN condition which led to the formation of aromatic ketone **20** (Scheme 5.5).[10]

Scheme 5.5. Intramolecular vinyl radical addition to furan



Vinyl radical cyclization was used as key step in the total synthesis of griseolic acid B **24** by Doss et al. Subjecting **21** under usual tributyltin hydride and AIBN reaction condition, they could isolate **22** and **23** as 6-*endo*-trig and 5-*exo*-trig cyclization products respectively in 3:2 ratio and 82% combined yield (Scheme 5.6).[11]

Scheme 5.6. Radical cyclization in the synthesis of Griseolic Acid B

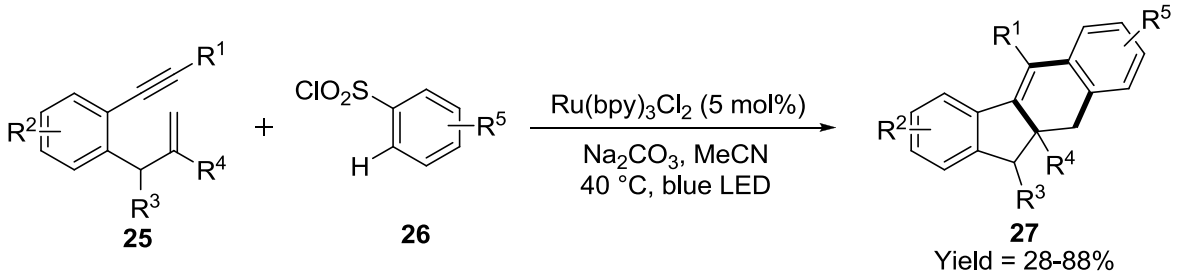


5.3 Cascade cyclization via visible-light photoredox catalysis

Cascade cyclizations are efficient and powerful tools in organic chemistry[12,13] for the synthesis of polycyclic compounds involving multiple bond formations. In this regard visible-light mediated cascade cyclizations are a growing field of interest in organic chemistry due to abundance of sunlight and a greener approach compared to other existing methodologies.

An elegant example of such cascade cyclization involving 1, 6-enynes **25** with aryl radicals generated from aryl sulfonyl chlorides **26** triggered by visible-light was reported by Li et al. The reaction thus involved in one C-S bond cleavage and three new C-C bonds formation in one step (Scheme 5.7).[14]

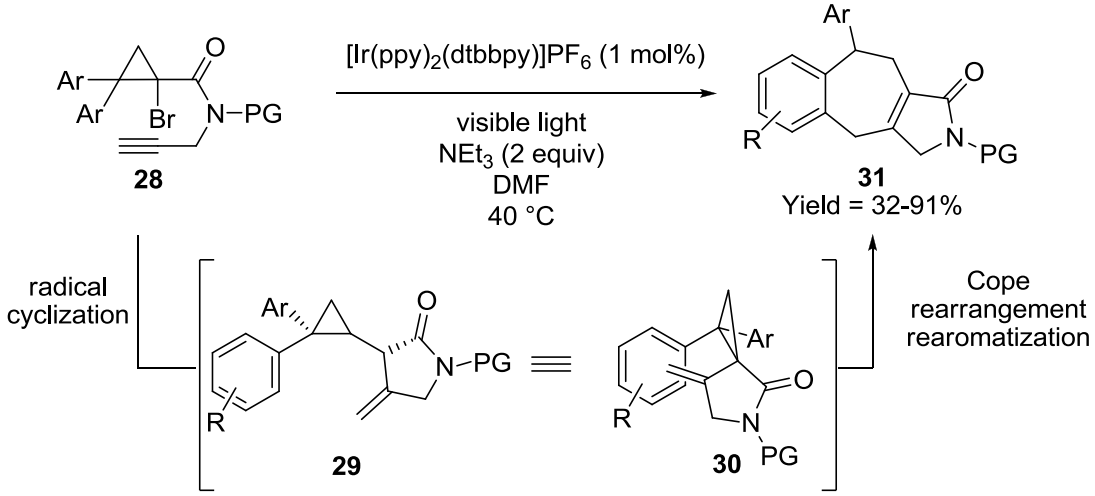
Scheme 5.7. Tandem cyclizations of 1,6-enynes with arylsulfonyl chlorides



The reaction was exemplified by excellent functional group tolerance and represented an alternative aryl radical source under visible-light irradiation.

In this context, Stephenson et al. described the rearrangement of divinylcyclopropanes **28** to tricyclic pyrrolidinones **31**. From mechanistic point of view, the reaction proceeded via radical tandem cyclization followed by Cope rearrangement leading to pyrrolidinones (Scheme 5.8).[15]

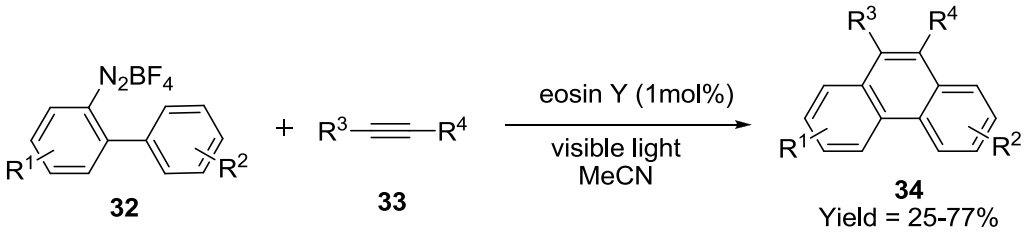
Scheme 5.8. Divinylcyclopropane rearrangement to tricyclic pyrrolidinones



The reaction is an example of accessing significant molecular complexity starting form relatively simple starting material in a single step. In contrast to the previously mentioned enyne cyclization, reductive quenching of the photoredox catalyst was explored here.

More recently, Zhou et al. reported the phenanthrene **34** synthesis[16] by [4+2] benzannulation of biaryl diazonuim salts **32** with alkynes **33** utilizing Eosin Y as the photocatalyst.[17] In this reaction diazonium salts were used as the oxidative quencher of the excited photocatalyst (Scheme 5.9).

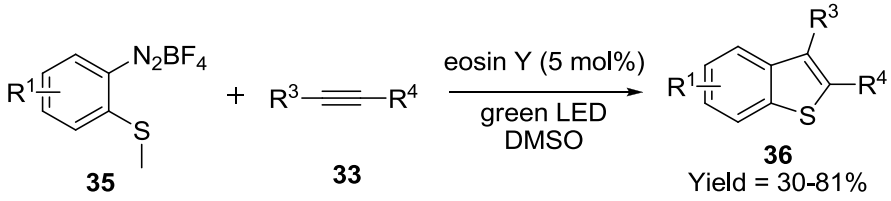
Scheme 5.9. Visible light-induced [4+2] benzannulation of biaryldiazonium salts with alkynes



Notable feature of the reaction was excellent functional group tolerance in terms of aryl substituent and both terminal and internal alkynes.

Synthesis of substituted benzothiophenes **36** was reported by König et al. by radical annulations of 2-methylthio arene diazonium salts **35** with alkynes **32** (5.10).[18]

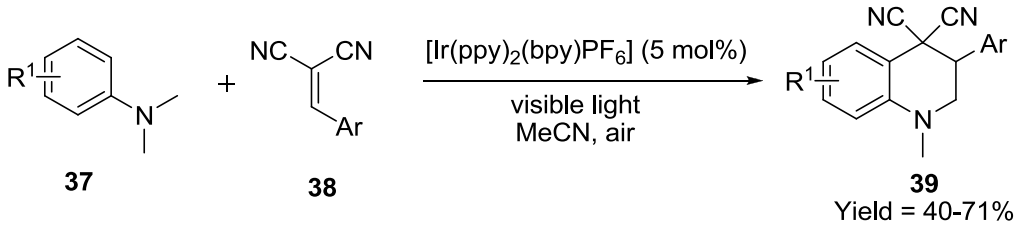
Scheme 5.10. Visible-light photocatalytic synthesis of benzothiophenes



The shortcomings of regioselectivity problem and rather low yield in direct arylation of benzothiophenes with aryl diazonium salts employing Eosin Y as photoredox catalyst were overcome by this annulation method. This reaction was also compatible with a wide range of functional groups and both terminal and internal alkynes were tolerated well similar to the above example of phenanthrene synthesis. Isolation of TEMPO trapped radical intermediates validated the overall radical process.

Very recently, Rueping et al. demonstrated the visible-light induced α-amino radical[19] cascade to electron deficient alkenes **38** forming tetrahydroquinolines **39** (Scheme 5.11).[20]

Scheme 5.11. photoredox catalyzed radical addition/cyclization reaction



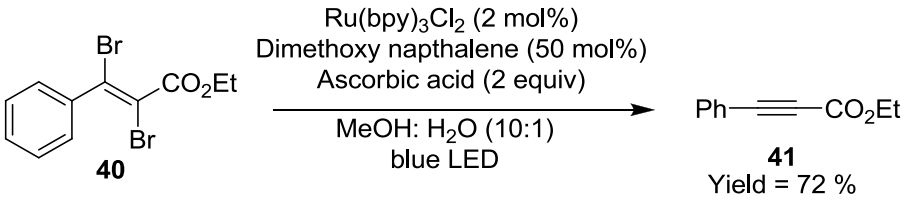
The authors demonstrated the role of oxygen as a switch, formation of addition product in the absence of it, whereas addition/cyclization to aromatic rings in the presence of it.

5.4 Visible-light induced vinyl radical formation

Despite the tremendous progress in the area of visible light photocatalysis demonstrating impressively the synthetic potential of such processes, there are only a few examples for the formation of vinyl radicals by photoredox activation of C(sp^2)-X (halogen) bonds.

One of the early examples of vinyl radical formation by visible-light photoredox catalysis was reported from our group[21] in the process of reductive debromination[22] of *vic*-dibromoalkene **40** to corresponding alkyne **41** (Scheme 5.12).

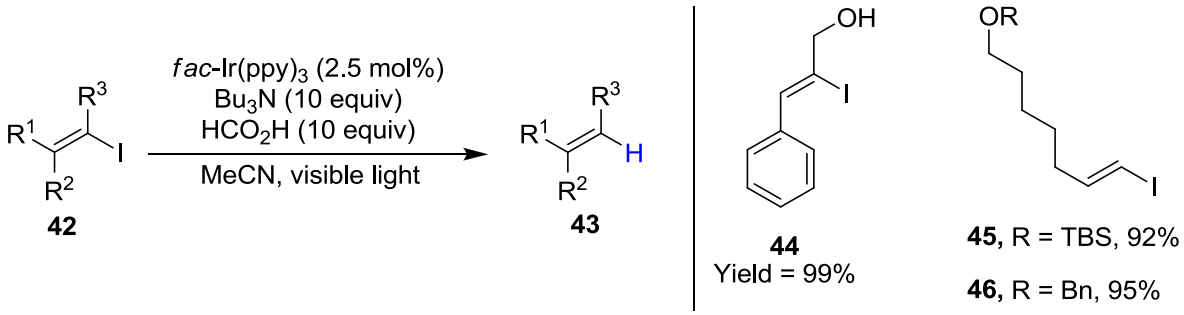
Scheme 5.12. Photocatalytic reductive debromination of a *vic*-dibromoalkene.



The reaction was carried out in presence of a combination of 1,5-dimethoxynaphthalene and ascorbic acid[23] as reductive quencher of exited $Ru(bpy)_3Cl_2$.

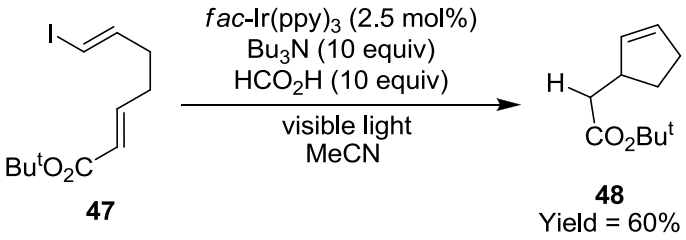
Recently visible-light mediated photoredox catalysis was successfully utilized by Stephenson et al. for vinyl radical generation by engaging unactivated alkenyl iodides in radical reactions. They could reduce the alkenyl iodides **42** to alkenes **43** in good to excellent yields employing a strongly reducing $Ir(ppy)_3$ as the photocatalyst and tributylamine and formic acid as the proton source (Scheme 5.13).[24]

Scheme 5.13. Visible-light mediated reduction of unactivated alkenyl iodides



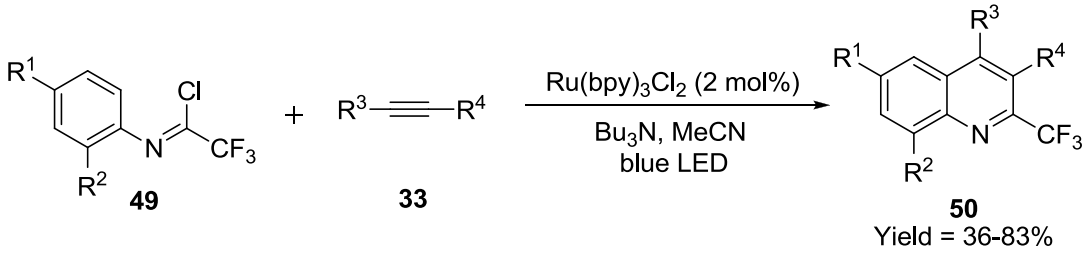
In the same report, they also demonstrated an intramolecular cyclization process involving vinyl radical from precursor **47** leading to carbocycle **48** (Scheme 5.14).

Scheme 5.14. Intramolecular radical cyclization of alkenyl iodide 47



One elegant example of vinyl radical by the cleavage of (sp^2) C-Cl bond of trifluoromethyl imidoyl chloride **49** and follow up intermolecular cyclization involving alkynes **33** thus leading to formation of 2-trifluoromethyl quinolines **50** was reported by Zhou et al (Scheme 5.15).[25]

Scheme 5.15. Radical cyclization of trifluoroacetimidoyl chlorides with alkynes

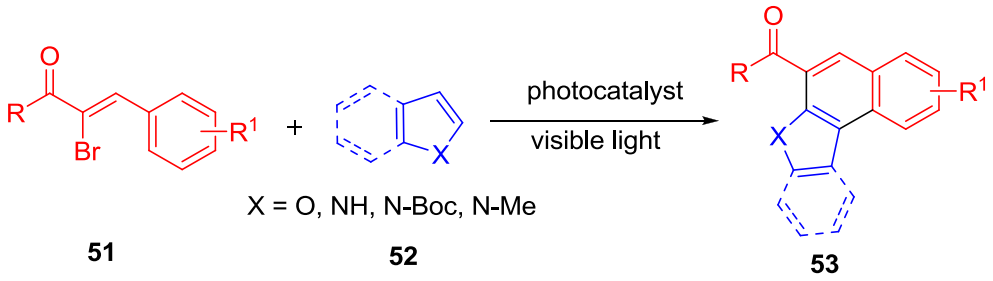


The reaction has been proposed to proceed via reductive quenching of the excited photocatalyst. Following a light/dark experiment, the authors excluded a possible radical chain mechanism for the process. Complete suppression of the reaction in presence of TEMPO, established a single electron transfer (SET) process in the catalytic cycle.

5.5 Cascade cyclizations of α-bromochalcones or -cinnamates with heteroarenes

Although there are reports of cascade cyclization as well as vinyl radical formation triggered by visible-light photocatalysis, the combination of both concepts is rare. In continuation of our study on visible-light photoredox catalysis, we envisioned that it might be possible to engage the α-keto vinyl radicals obtained from bromoalkene **51** in C-C bond formation (Scheme 5.16) by effectively blocking the elimination pathway leading to the alkynes.[21]

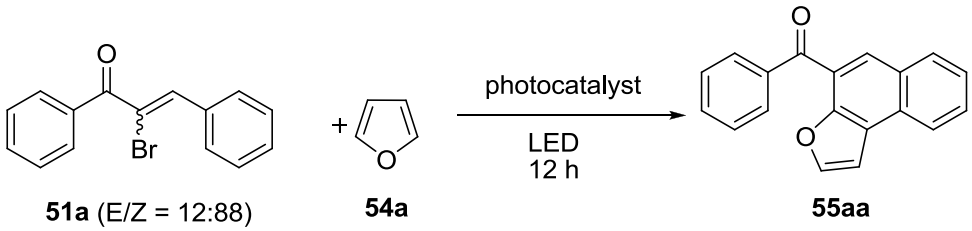
Scheme 5.16. Photoredox catalyzed cascade cyclization between α-bromo chalcones or –cinnamates with heteroarenes.



We initiated our investigation with the reaction between α-bromochalcone **51a** and furan **54a** in the presence of 1 mol% of $Ru(bpy)_3Cl_2$. When the reaction was carried out in presence of an amine (condition typical for a reductive quenching cycle), dehalogenation of the starting material to chalcone took place without any formation of desired C-C coupling product with furan **54a** (Table 5.1, entries 1, 2). In contrast, a oxidative quenching cycle utilizing $Ru(bpy)_3Cl_2$ resulted in the formation of desired polycyclic compound **55aa** albeit only 5% yield. The product formation is associated with an intermolecular cyclization with concurrent activation of three C, H-bonds in which α-bromo chalcone **51a** served both as a precursor for vinyl radicals and provide *ortho*-C_{aryl}-H bonds for the cyclization. Nevertheless, the low conversion of **51a** resulting in a poor yield made optimization of the process necessary. Employing some other well established photoredox catalysts such as $Cu(dap)_2Cl$ (Table 5.1, entry 4), Eosin Y (Table 5.1, entry 5) or $Ir[(ppy)_2(dtbbpy)]PF_6$ (Table 5.1, entry 6) which all have been utilized in oxidative quenching successfully before, resulted in no product formation. To our delight, 1 mol% of $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ led to full consumption of **51a** after 12h of reaction time giving rise to 91% NMR yield of **55aa** (Table 5.1, entry 7). DMF, proved to be essential solvent for the

reaction, employing MeCN resulted in no reaction (Table 5.1, entry 8). Likewise, both light and catalyst were essential (Table 5.1, entry 9 and 10) for the reaction.

Table 5.1. Optimization of reaction conditions for the cascade cyclization of 51 and 54[a]



51a (E/Z = 12:88) **54a** **55aa**

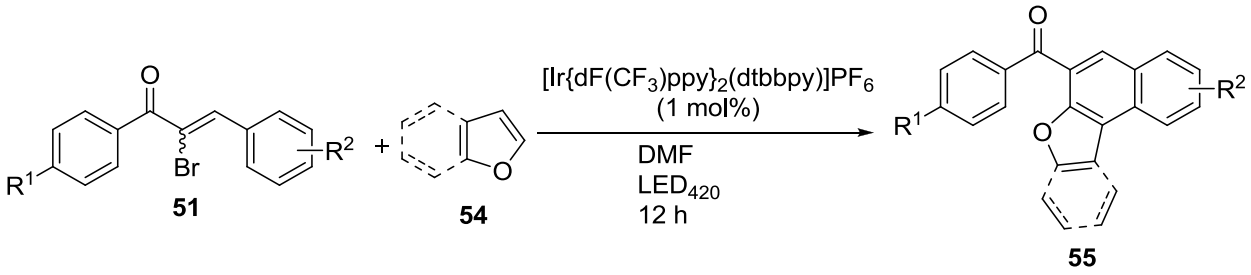
entry	photocatalyst	solvent	yield (%)[b]
1	$Ru(bpy)_3Cl_2$, NEt_3, 455 nm	DMF	dehalogenation, >95
2	$Ru(bpy)_3Cl_2$, NEt_3, 455 nm	MeCN	dehalogenation, 70
3	$Ru(bpy)_3Cl_2$, 455 nm	DMF	≤ 5
4	$Cu(dap)_2Cl$, 530 nm	DMF	no reaction
5	Eosin Y, 530 nm	DMF	no reaction
6	$Ir[(ppy)_2(dtbbpy)]PF_6$, 455 nm	DMF	no reaction
7	**$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$, 420 nm**	**DMF**	**91**
8	$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$, 420 nm	MeCN	no reaction
9[c]	$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$	DMF	no reaction
10	no photocatalyst, 420 nm	DMF	no reaction

[a] Reaction conditions: **51a** (1 equiv), furan **54a** (5 equiv), photocatalyst (1 mol%). [b] Yields were determined by ^1H NMR analysis. [c] Without light irradiation

Having the optimized reaction condition in hand, we examined the scope of the reaction by varying different electron donating and withdrawing groups in either ring of chalcone (Table 5.2). Limitations were observed with substrates having an *ortho*-substituent as R^2 (Table 5.2, entries 6, 10) thus blocking one reaction site for cyclization. Product **55fa** and **55ja** were still formed in a clean reaction, but conversion of the starting material was incomplete. When R^1 and R^2 (Table 5.2, entry 12 and 13) were strong electron withdrawing groups, no conversion of the corresponding starting material was observed. The halide substituent in either ring of the

chalcone did not show any cross reactivity under the optimized reaction conditions. Other furans such as 2-methylfuran **54b** (Table 5.2, entries 14, 15) and benzofuran **54c** (Table 5.2, entry 16) were also found to be excellent reaction partners for α-bromochalcones **51**.

Table 5.2. Reaction of α-bromo chalcone with furans[a]

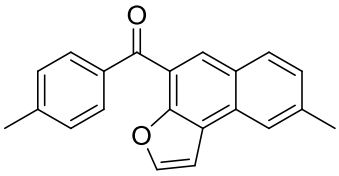


entry	R^1	R^2	**51**	furan (**54**)	product **(55)**	yield (%)[b]
1	H	H	**51a**	furan (**54a**)	**55aa**	85
2	H	4-Cl	**51b**	furan (**54a**)	**55ba**	82
3	Cl	H	**51c**	furan (**54a**)	**55ca**	91
4	Cl	4-Br	**51d**	furan (**54a**)	**55da**	80
5	Cl	4-Me	**51e**	furan (**54a**)	**55ea**	80
6	Cl	2-Me	**51f**	furan (**54a**)	**55fa**	32
7	Me	4-Me	**51g**	furan (**54a**)	**55ga**	83
8	OMe	H	**51h**	furan (**54a**)	**55ha**	60
9	H	4-F	**51i**	furan (**54a**)	**55ia**	82

10	H	2-F	**51j**	furan (**54a**)	**55ja**	42
11	F	H	**51k**	furan (**54a**)	**55ka**	78
12	NO_2	H	**51l**	furan (**54a**)	–	no reaction
13	H	4-NO_2	**51m**	furan (**54a**)	–	no reaction
14	Cl	4-Br	**51d**	2-methyl furan (**54b**)	**55db**	65
15	H	4-Cl	**51b**	2-methyl furan (**54b**)	**55bb**	78
16	Cl	4-Br	**51d**	Benzo-furan (**54c**)	**55dc**	85

[a] Reaction conditions: **51** (0.5 mmol), **54** (5 equiv) and photocatalyst (1 mol%) in dry DMF (2.0 mL) was irradiated for 12 h with a LED light source (420 nm). [b] Yield of isolated product.

The structural assignment of product **55** was confirmed unambiguously by single-crystal X-ray analysis of **55ga** (Figure 5.1).



55ga

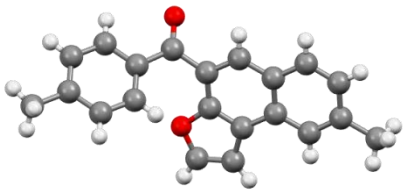
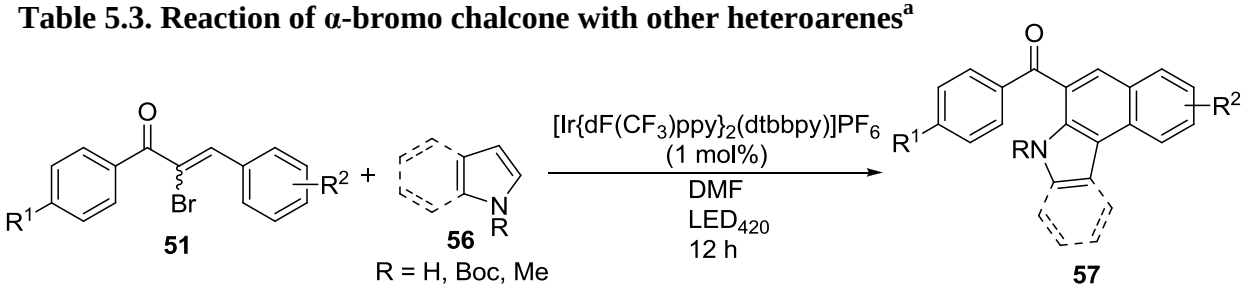


Figure 5.1. X-ray crystal structure of **55ga.**

Next, we examined the substrate generality with respect to heteroarenes other than furans. *N*-heteroaromatic systems such as pyrroles **56a** and indoles, either in *N*-unprotected **56c** or *N*-protected **56e** form, were amenable in the coupling with chalcones **51** (Table 5.3). Besides electronic variations of **51** in a similar way as were done in the coupling with furans, we also demonstrated that an *ortho*-substituent in the arene ring of **51** which is involved in the cyclization process is tolerated well (Table 5.3, entries 4, 7).

Table 5.3. Reaction of α-bromo chalcone with other heteroarenes[a]



Entry	R^1	R^2	**51**	Heteroarene (**56**)	Product (**57**)	Yield (%)[b]
1	H	H	**51a**	pyrrole (**56a**)	**57aa**	89
2	H	4-Cl	**51b**	pyrrole (**56a**)	**57ba**	95
3	Cl	4-Me	**51e**	pyrrole (**56a**)	**57ea**	91
4	Cl	2-Me	**51f**	pyrrole (**56a**)	**57fa**	78
5	OMe	H	**51h**	pyrrole (**56a**)	**57ha**	80
6	H	4-F	**51i**	pyrrole (**56a**)	**57ia**	87
7	H	2-F	**51j**	pyrrole (**56a**)	**57ja**	83
8	F	H	**51k**	pyrrole (**56a**)	**7ka**	84
9	NO_2	H	**51l**	pyrrole (**56a**)	–	no reaction
10	H	NO_2	**51m**	pyrrole (**56a**)	–	no reaction
11	Cl	H	**51c**	N-Bocpyrrole (**56b**)	**57cb**	92
12	H	H	**51a**	N-Bocpyrrole (**56b**)	**57ab**	85
13	Cl	H	**51c**	indole (**56c**)	**57cc**	87

14	H	4-Me	**51n**	indole (**56c**)	**57nc**	72
15	Cl	H	**51c**	5-methoxy indole (**56d**)	**57cd**	70
16	H	H	**51a**	N-methylindole (**56e**)	**57ae**	70

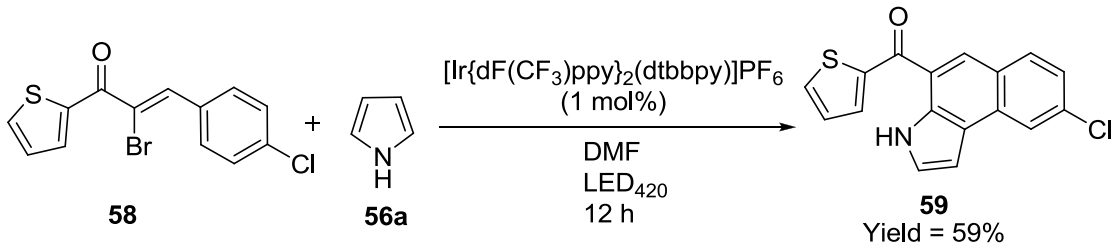
[a] Reaction conditions: **51** (0.5 mmol), **56** (5 equiv) and photocatalyst (1 mol%) in dry DMF (2 mL) irradiated for 12 h with a LED light source (420 nm). [b] Yield of isolated product.

The structural assignment of products **57** was confirmed unambiguously by a single-crystal X-ray analysis (Figure 5.2).

Figure 5.2. X-ray crystal structure of **57ba.**

α-bromo chalcone bearing a thiophene moiety **58** also resulted in high yield of the corresponding cyclized product **59** when coupled with pyrrole **56a** (Scheme 5.17).

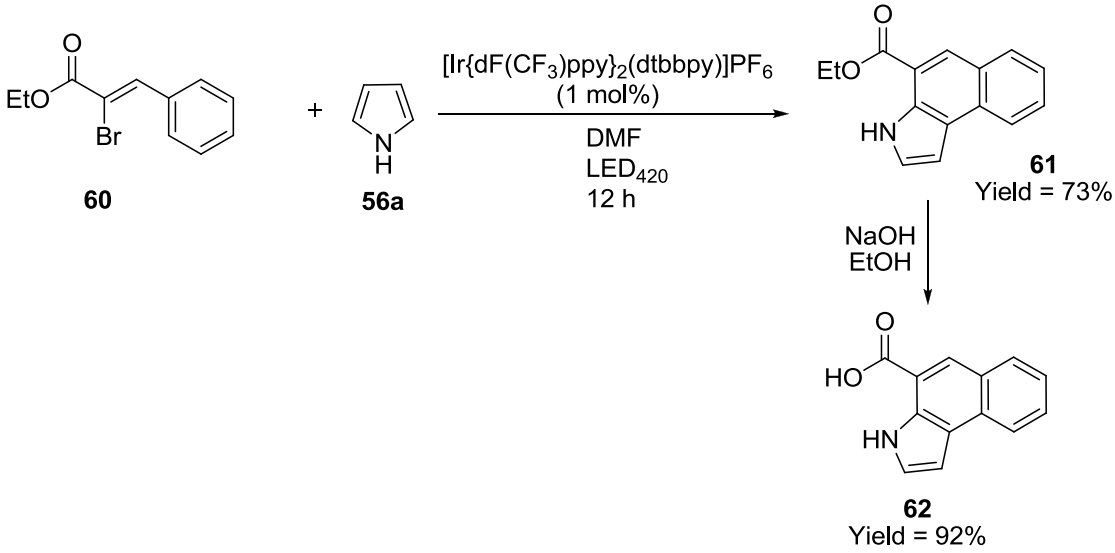
Scheme 5.17. Reaction of α-bromochalcone 58 bearing thiophene moiety with pyrrole



Next we questioned ourselves that the arene ring in α-bromo chalcone, not involved in cyclization process was really necessary for the above photochemical process. So we prepared α-bromo chalcone cinnamate **60** and subjected to coupling with pyrrole. Indeed the reaction

proceeded smoothly to yield benzoanellated 1*H*-indole-7-carboxylates **61**. 1*H*-indole-7-carboxylates have been recognized to display manyfold biological activities and have been identified as EP4 receptor antagonists and PPAR active compounds.[26] The ester group provided the scope for further functionalization, as **61** was hydrolyzed to the corresponding acid **62** in 92% yield (Scheme 5.18).

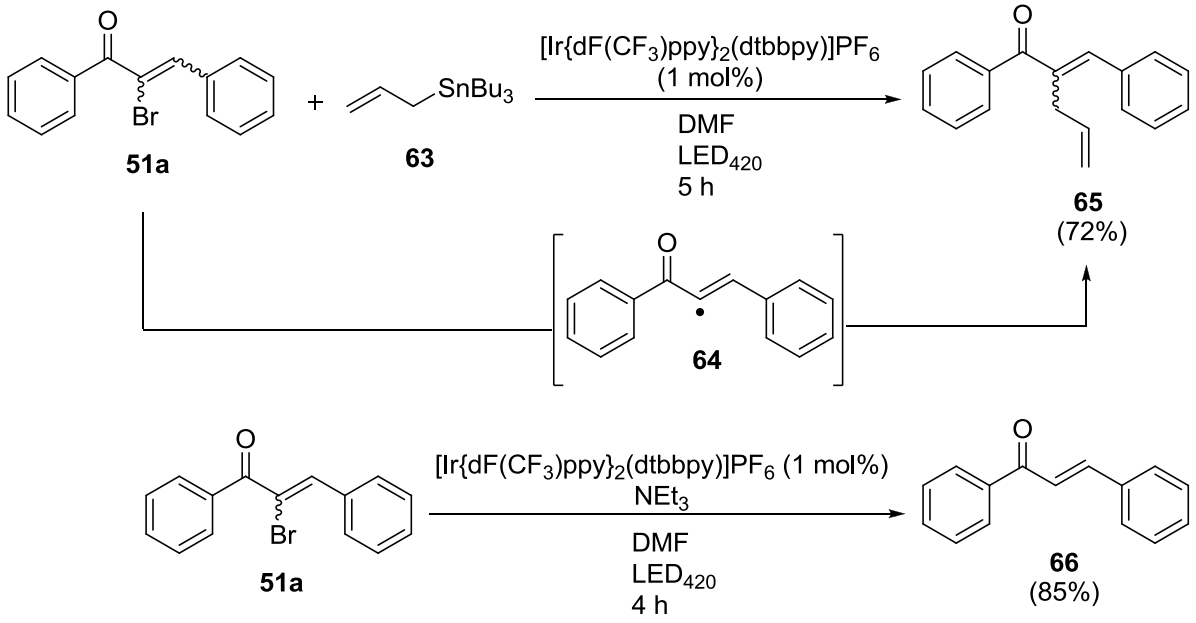
Scheme 5.18. Reaction of α-bromoethyl cinnamate 60 with pyrrole.



5.6 Mechanistic Investigation

To prove the formation of α-keto vinyl radicals from α-bromochalcones under the photochemical reaction conditions, we performed two additional experiments. We presumed that the allyl stannane **63** being a radical allylating agent, should lead to the allylation of α-bromochalcone (**51a**) under the same reaction conditions as the cyclization. Indeed, allylated compound **65** was isolated in 72% yield. This proves formation of vinyl radical **64** as the photochemical key step for the cyclization process (Scheme 5.19).

Scheme 5.19. Allylation and reduction of α-bromo chaconne 51a.

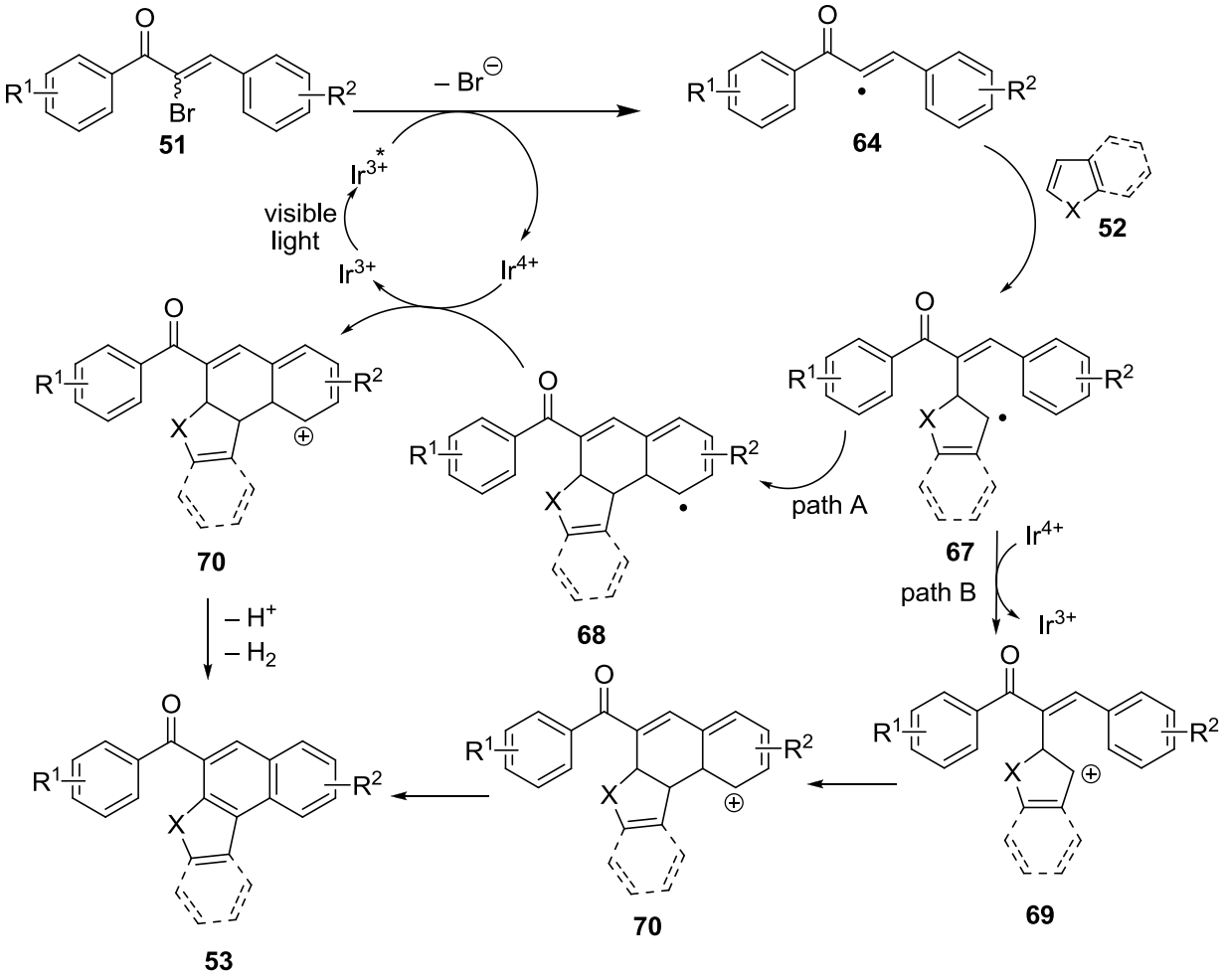


On the other hand, as mentioned before (Table 5.1, entries 1, 2) for $Ru(bpy)_3Cl_2$, switching to reductive quenching cycle for iridium catalyst by addition of triehtylamine as sacrificial electron donor, led to the formation of chalcone **66** being also consistent with the formation of vinyl radical **64**.

Based on the above evidence, a plausible reaction mechanism is proposed for the above cyclization reaction involving the formation of vinyl radical **64** by the transfer of an electron from excited $*Ir^{3+}$ to α-bromochalcone **51** (Scheme 5.20). The radical **64** then adds to the heteroarene **52** to form the radical **67**. Formation of final product could occur by two possible pathways, one by chemoselective addition of the radical **67** to the arene ring of chalcone bearing the vinyl, but not the carbonyl group (path A), thus forming radical **68**. A back electron transfer from **68** to Ir^{4+} closes the catalytic cycle and forms the cation **70**. Alternatively, intermediate **67** could be oxidized by back electron transfer from to Ir^{4+}, thus regenerating the catalyst and cation intermediate **69**. An electrophilic ring closure then should furnish **70**. Carbocation **70** then finally forms product **53**, in which overall one molecule of hydrogen must lost driven by the

aromatization of the final product **53**. The mechanism for this dehydrogenation is still elusive but has been reported in literature before in different processes.[19a, 27]

Scheme 5.20. Proposed reaction mechanism for the photoredox catalyzed cascade cyclization between chalcones and heteroarenes.



We have performed the reaction of α-bromo chalcone **51a** with pyrrole **56a** in DMF-d^7 under deaerated conditions. NMR analysis showed that the dehydrogenation indeed takes place during the reaction and not during the workup procedure. Iridium catalysts are well known for their power to catalyze hydrogenation/dehydrogenation processes, and we therefore assume that here also the iridium photocatalyst employed, can take in addition such a role.

5.7 Conclusion

In conclusion, we have developed an unprecedented methodology for the generation of vinyl radicals by activation of (sp^2)C-Br bond of α-bromochalcones and -cinnamtates triggered by visible-light photoredox catalysis. The vinyl radicals were engaged in a cascade cyclization with heteroarenes in intermolecular fashion forming novel scaffolds such as naphtho[2,1-*b*]furans, 3*H*-benzo[*e*]indoles and related heterocycles. In this transformation, α-bromochalcones and –cinnamtates played a dual role, served as a vinyl radical source as well as provided *ortho*-Caryl-H bonds for the cyclization. The overall transformation is characterized by three fold C-H activation. The reaction was amenable to a broad variety of heteroarenes, ranging from furans, benzofurans to pyrroles, in protected or unprotected form, as well as indoles. Notable features of the above transformation are low catalyst loading, good to excellent yield of the product. An *ortho* substitution in the aryl ring of α-bromochalcones led to poor yield of the furan adducts. The existence of vinyl radical in the reaction medium was proved experimentally.

5.8 Experimental part

General Information

All reactions were performed using common dry, inert atmosphere techniques. Reactions were monitored by TLC and visualized by a dual short/long wave UV lamp and stained with an ethanolic solution of vanillin. Column flash chromatography was performed using 230-400 mesh silica gel. NMR spectra were recorded on 300 MHz spectrometer. Chemical shifts for ^{1}H NMR were reported as δ, parts per million, relative to the signal of $CDCl_3$ at 7.26 ppm. Chemical shifts for ^{13}C NMR were reported as δ, parts per million, relative to the center line signal of the $CDCl_3$ triplet at 77 ppm. Proton and carbon assignments were established using spectral data of similar compounds. The abbreviations s, d, dd, t, q and m stand for the resonance multiplicity singlet, doublet, doublet of doublets, triplet, quartet and multiplet respectively.

General procedure (GP-A) for the preparation of α-bromo chalcone

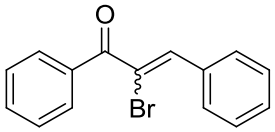
To a mixture of corresponding chalcone (2.0 mmol, 1.0 equiv) and *OXONE* (2.4 mmol, 1.2 equiv) in CH_2Cl_2 (10.0 mL) was added 2 N HBr (10.0 mmol, 2.0 equiv) in one portion resulting in dark red colored solution. The reaction mixture was stirred at room temperature until all chalcone was converted to dibromide (as judged by TLC). Triethylamine (10.0 mmol, 5.0 equiv) was added cautiously and after stirring for further 12 h, the reaction mixture was extracted with CH_2Cl_2 (2 x 10.0 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by silica gel column chromatography afforded pure α-bromo chalcone.

General procedure (GP-B) for the photoredeox catalyzed tandem cyclization reaction

An oven dried 10 mL vial equipped with a plastic septum and magnetic stir bar was charged with $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (1 mol %) and the corresponding α-bromochalcone (0.5 mmol, 1.0 equiv). The flask was purged with a stream of nitrogen and 2.0 mL of dry dimethylformamide was added. The resultant mixture was degassed for 5 min by nitrogen sparging and the furan or pyrrole (2.5 mmol, 5.0 equiv) or indole (1.0 mmol, 2.0 equiv) was added to the vial. The vial was placed at a distance of ~ 0.5 -1.0 cm from a blue LED lamp (420 nm) and irradiated for 12 h. After the completion of the reaction (as judged by TLC analysis), the mixture was transferred to a separating funnel, diluted with 15 mL of ethyl acetate and washed

with 20 mL of water. The aqueous layer was washed with ethyl acetate (3 × 10 mL) and the combined organic layer was dried over anhydrous sodium sulfate, solvent was removed in vacuo and the residue was subjected to colum chromatography on silica gel, using PE/EA as solvent system to get the pure product.

2-bromo-1,3-diphenylprop-2-en-1-one (51a)[28]



According to the general procedure (GP-A), (E)-1,3-diphenylprop-2-en-1-one (1.01 g, 5.0 mmol, 1.0 equiv), *OXONE* (3.68 g, 6.0 mmol, 1.2 equiv), 2 N HBr (10.0 mmol, 2.00 equiv), triethylamine (2.52 g, 25.0 mmol, 5.0 equiv) afforded 5**1a** (1.22 g, 85 %) as colorless solid after column purification on silica gel as a mixture of Z:E = 88:12. R_f (EtOAc/hexane 1:9): 0.57.

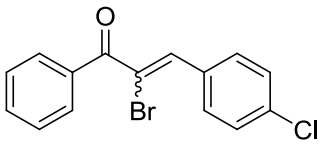
^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 7.89 – 7.77 (m, 4H), 7.71 (s, 1H), 7.64 – 7.56 (m, 1H), 7.53 – 7.40 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 191.66, 142.96, 136.55, 133.63, 132.71, 130.47, 130.32, 129.77, 128.69, 128.56, 122.67.

^{1}H NMR (300 MHz, $CDCl_3$, E isomer) δ = 8.06 – 7.95 (m, 4H), 7.68 – 7.64 (m, 2H), 7.38 (s, 1H), 7.18 (m, 4H).

MS (EI, 70 eV): m/z = 286.04 (M+), 207.10, 105.09.

2-bromo-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (51b)[28]



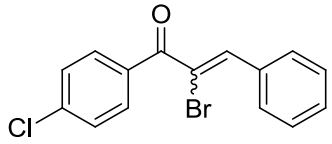
According to the general procedure (GP-A), (E)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (485 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.47 g, 2.4 mmol, 1.2 equiv), 2 N HBr (4.00 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.0 equiv) afforded **51b** (521 mg, 81 %) as white solid after column purification on silica gel as a mixture of Z:E = 91:9. R_f (EtOAc/hexane 1:9): 0.54.

^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 7.80 (m, 4H), 7.64 (s, 1H), 7.62 – 7.56 (m, 1H), 7.54 – 7.45 (m, 2H), 7.41 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$, Z isomer) δ = 191.33, 141.11, 136.32, 132.81, 132.07, 131.49, 129.74, 129.42, 128.83, 128.59, 123.15.

HRMS (EI-MS): Calcd. For $C_{15}H_{10}BrClO$ [$M^{+\cdot}$] m/z 319.9604, found *m/z* 319.9605.

2-bromo-1-(4-chlorophenyl)-3-phenylprop-2-en-1-one (51c)[29]



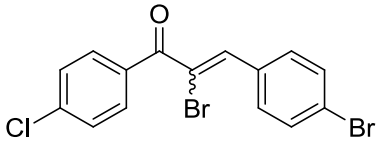
According to the general procedure (GP-A), (E)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (485 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.47 g, 2.4 mmol, 1.2 equiv), 2 N HBr (4.00 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.0 equiv) afforded **51c** (527 mg, 82 %) as white solid after column purification on silica gel as a mixture of Z:E = 86:14. R_f (EtOAc/hexane 1:9): 0.60.

^{1}H NMR (300 MHz, $CDCl_3$, Z isomer) δ = 7.85 (m, 2H), 7.80 – 7.73 (m, 2H), 7.67 (s, 1H), 7.50 – 7.42 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$, Z isomer) δ = 190.43, 142.57, 139.20, 134.77, 133.46, 131.16, 130.58, 130.31, 128.90, 128.59, 121.91.

HRMS (EI-MS): Calcd. For $C_{15}H_{10}BrClO$ [$M^{+\cdot}$] m/z 319.9604, found *m/z* 319.9605.

2-bromo-3-(4-bromophenyl)-1-(4-chlorophenyl)prop-2-en-1-one (51d)



According to the general procedure (GP-A), (E)-3-(4-bromophenyl)-1-(4-chlorophenyl)prop-2-en-1-one (643 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.40 g, 2.4 mmol, 1.2 equiv), 2 N HBr (4.0 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.0 equiv) afforded **51d** (625 mg, 78 %) as white solid after column purification on silica gel as a mixture of Z:E = 89:11. R_f (EtOAc/hexane 1:9): 0.60.

M.P. =79-81 °C

IR (neat): 3095, 1740, 1650, 1586, 1401, 1228, 1067, 748 cm^{-1}.

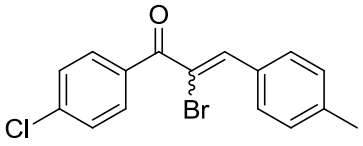
^{1}H NMR (300 MHz, $CDCl_3$, Z isomer) δ = 7.79 – 7.68 (m, 4H), 7.62 – 7.54 (m, 3H), 7.51 – 7.44 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$, Z isomer) δ = 190.19, 140.97, 139.39, 134.48, 132.31, 131.87, 131.64, 131.15, 128.96, 124.93, 122.53.

^{1}H NMR (300 MHz, $CDCl_3$, E isomer) δ = 7.92 – 7.86 (m, 2H), 7.43 – 7.38 (m, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.30 (s, 1H), 7.02 (d, *J* = 8.4 Hz, 2H).

HRMS (EI-MS): Calcd. For $C_{15}H_9Br_2ClO$ [$M^{+\cdot}$] m/z 397.8709, found *m/z* 397.8711.

2-bromo-1-(4-chlorophenyl)-3-p-tolylprop-2-en-1-one (51e)



According to the general procedure (GP-A), (E)-1-(4-chlorophenyl)-3-p-tolylprop-2-en-1-one (513 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.40 g, 2.4 mmol, 1.2 equiv), 2 N HBr (4.0 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.00 equiv) afforded **51e** (462 mg, 69 %) as white solid after column purification on silica gel as a mixture of Z:E = 60:40. R_f (EtOAc/hexane 1:9): 0.62.

M.p. = 81-83 °C

IR (neat): 3030, 1651, 1586, 1220, 1009, 809 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, Z isomer) δ = 7.82 – 7.70 (m, 4H), 7.65 (s, 1H), 7.50 – 7.44 (m, 2H), 7.25 (m, 2H), 2.40 (s, 3H).

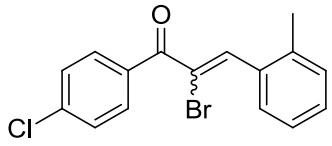
^{13}C NMR (75 MHz, $CDCl_3$, Z isomer) δ = 190.94, 143.14, 136.36, 131.33, 131.09, 130.51, 129.46, 129.33, 129.29, 128.85, 128.16, 21.64.

^{1}H NMR (300 MHz, $CDCl_3$, E isomer) δ = 7.93 – 7.88 (m, 2H), 7.41 – 7.36 (m, 2H), 7.35 (s, 1H), 7.06 – 6.96 (m, 4H), 2.24 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, E isomer) δ = 190.55, 141.36, 139.13, 138.97, 135.05, 131.38, 130.61, 128.93, 121.13, 21.28.

HRMS (EI-MS): Calcd. For $C_{16}H_{12}BrClO$ [$M^{+\cdot}$] m/z 333.9760, found *m/z* 333.9760.

2-bromo-1-(4-chlorophenyl)-3-o-tolylprop-2-en-1-one (51f)



According to the general procedure (GP-A), (E)-1-(4-chlorophenyl)-3-o-tolylprop-2-en-1-one (513 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.40 g, 2.4 mmol, 1.2 equiv), 2 N HBr (4.0 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.0 equiv) afforded **51f** (530 mg, 79 %) as white solid after column purification on silica gel as a mixture of Z:E = 81:19. R_f (EtOAc/hexane 2:8): 0.77.

M.p. = 75-77 °C

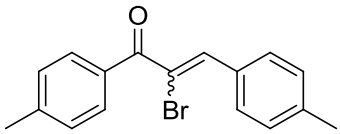
IR (neat): 3062, 1665, 1586, 1397, 1246, 1092, 757 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, *Z* isomer) δ = 7.84 – 7.76 (m, 3H), 7.74 (s, 1H), 7.51 – 7.46 (m, 2H), 7.36 – 7.22 (m, 3H), 2.27 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, *Z* isomer) δ = 190.18, 141.77, 139.38, 136.96, 134.70, 133.35, 131.13, 130.95, 130.32, 129.80, 128.92, 128.72, 125.76, 20.09.

HRMS (EI-MS): Calcd. For $C_{16}H_{12}BrClO$ [$M^{+\cdot}$] m/*z* 333.9760, found *m/z* 333.9759.

2-bromo-1,3-dip-tolylprop-2-en-1-one (51g)



According to the general procedure (GP-A), (E)-1,3-di-*p*-tolylprop-2-en-1-one (473 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.40 g, 2.4 mmol, 1.2 equiv), 2 N HBr (4.0 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.0 equiv) afforded **51g** (454 mg, 72 %) as white solid after column purification on silica gel as a mixture of Z:E = 87:13. R_f (EtOAc/hexane 1:9): 0.48.

M.p. = 77-79 °c

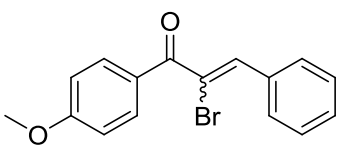
IR (neat): 2919, 1738, 1658, 1604, 1246, 1072, 633 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 7.77 (d, *J* = 8.3 Hz, 2H), 7.74 – 7.69 (m, 2H), 7.66 (s, 1H), 7.29-7.23 (m, 4H), 2.44 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, *Z* isomer) δ = 191.48, 143.46, 142.43, 140.92, 133.91, 130.88, 130.38, 129.97, 129.25, 129.19, 121.75, 21.70, 21.62.

HRMS (EI-MS): Calcd. For $C_{17}H_{15}BrO$ [$M^{+\cdot}$] m/*z* 314.0306, found *m/z* 314.0307.

2-bromo-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (51h)[29]



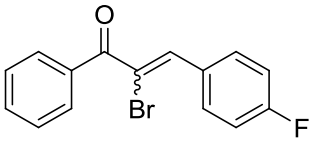
According to the general procedure (GP-A), (E)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (477 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.40 g, 2.4 mmol, 1.2 equiv), 2N HBr (4.0 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.0 equiv) afforded **51h** (507 mg, 80 %) as yellow gummy liquid after column purification on silica gel as a mixture of Z:E = 85:15. R_f (EtOAc/hexane 1:9): 0.34.

^{1}H NMR (300 MHz, $CDCl_3$, Z isomer) δ = 7.92 – 7.79 (m, 4H), 7.60 (s, 1H), 7.50 – 7.36 (m, 3H), 6.98 (dd, *J* = 8.2, 6.2 Hz, 2H), 3.90 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, Z isomer) δ = 190.37, 163.57, 140.41, 133.81, 132.42, 130.07, 128.50, 128.19, 121.94, 114.24, 113.85, 55.58.

MS (EI, 70 eV): m/z = 316.05 (M+), 237.08, 135.10.

2-bromo-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (51i)[28]



According to the general procedure (GP-A), (E)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (452 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.40 g, 2.4 mmol, 1.2 equiv), 2N HBr (4.0 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.0 equiv) afforded **51i** (476 mg, 78 %) as yellow liquid after column purification on silica gel as a mixture of Z:E = 82:18. R_f (EtOAc/hexane 1:9): 0.51.

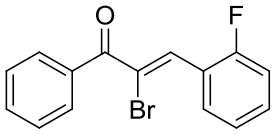
^{1}H NMR (300 MHz, $CDCl_3$, Z isomer) δ = 7.92 – 7.83 (m, 2H), 7.82 – 7.76 (m, 2H), 7.66 (s, 1H), 7.64 – 7.56 (m, 1H), 7.49 (ddd, *J* = 6.7, 4.5, 1.2 Hz, 2H), 7.18 – 7.09 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$, Z isomer) δ = 191.45, 161.94, 141.51, 132.71, 132.55, 132.43, 129.98, 129.70, 128.95, 128.57, 115.89, 115.60.

^{1}H NMR (300 MHz, $CDCl_3$, E isomer) δ = 7.97 (m, 2H), 7.64 – 7.53 (m, 1H), 7.46 – 7.39 (m, 2H), 7.34 (s, 1H), 7.18 – 7.09 (m, 2H), 6.91 – 6.82 (m, 2H).

HRMS (EI-MS): Calcd. For $C_{15}H_{10}BrFO$ [$M^{+\cdot}$] m/z 303.9899, found *m/z* 303.9895.

(E)-2-bromo-3-(2-fluorophenyl)-1-phenylprop-2-en-1-one (51j)



According to the general procedure (GP-A), (E)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-one (452 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.40 g, 2.4 mmol, 1.2 equiv), 2N HBr (4.0 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.0 equiv) afforded **51j** (378 mg, 62 %) as yellow gummy liquid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.51.

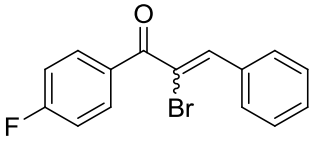
IR (neat): 3064, 1665, 1597, 1448, 1225, 1100, 825, 753 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.83 (s, 2H), 7.65 – 7.56 (m, 1H), 7.56 – 7.46 (m, 3H), 7.42 (m, 2H), 7.16 – 7.07 (m, 2H).

^1H NMR (300 MHz, $CDCl_3$) δ = 8.21 (td, *J* = 7.7, 1.5 Hz, 2H), 7.99 – 7.93 (m, 2H), 7.86 (s, 2H), 7.30 – 7.22 (m, 2H), 7.00 – 6.92 (m, 1H), 6.89 (m, 1H).

HRMS (EI-MS): Calcd. For $C_{15}H_{10}BrFO$ [$M^{+\cdot}$] m/z 303.9899, found *m/z* 303.9895.

2-bromo-1-(4-fluorophenyl)-3-phenylprop-2-en-1-one (51k)[29]



According to the general procedure (GP-A), (E)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-one (452 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.40 g, 2.4 mmol, 1.2 equiv), 2 N HBr (4.0 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.0 equiv) afforded **51k** (439 mg, 72 %) as yellow gummy liquid after column purification on silica gel as a mixture of Z:E = 88:12. R_f (EtOAc/hexane 1:9): 0.62.

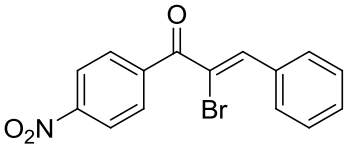
^1H NMR (300 MHz, $CDCl_3$, Z isomer) δ = 7.91 – 7.79 (m, 4H), 7.65 (s, 1H), 7.49 – 7.41 (m, 3H), 7.23 – 7.12 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 190.20, 167.20, 142.05, 133.51, 132.50, 132.38, 130.47, 130.25, 128.57, 121.85, 115.94, 115.64.

^1H NMR (300 MHz, $CDCl_3$, E isomer) δ = 8.03 – 7.96 (m, 2H), 7.38 (s, 1H), 7.23 – 7.12 (m, 5H), 7.07 (m, 2H).

HRMS (EI-MS): Calcd. For $C_{15}H_{10}BrFO$ [$M^{+\cdot}$] m/z 303.9899, found *m/z* 303.9895.

(E)-2-bromo-1-(4-nitrophenyl)-3-phenylprop-2-en-1-one (51l)[30]



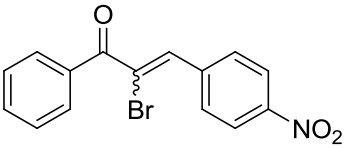
According to the general procedure (GP-A), (E)-1-(4-nitrophenyl)-3-phenylprop-2-en-1-one (507 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.40 g, 2.4 mmol, 1.2 equiv), 2N HBr (4.0 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.0 equiv) afforded **51l** (536 mg, 81 %) as sticky light yellow liquid column purification on silica gel. R_f (EtOAc/hexane 2:8): 0.60.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.38 – 8.30 (m, 2H), 7.97 – 7.84 (m, 4H), 7.72 (s, 1H), 7.50 – 7.44 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 189.94, 149.85, 144.61, 142.25, 133.09, 131.17, 130.60, 130.37, 128.71, 123.75, 121.70.

HRMS (EI-MS): Calcd. For $C_{15}H_{10}BrNO_3$ [$M^{+\cdot}$] m/z 330.9844, found *m/z* 330.9836.

2-bromo-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (51m)[31]



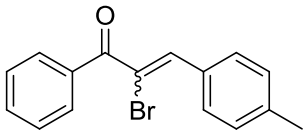
According to the general procedure (GP-A), (E)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (507 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.40 g, 2.4 mmol, 1.2 equiv), 2N HBr (4.0 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.0 equiv) afforded **51m** (551 mg, 83 %) as orange solid after column purification on silica gel. Z:E = 82:18. R_f (EtOAc/hexane 2:8): 0.55.

^{1}H NMR (400 MHz, $CDCl_3$, Z isomer) δ = 8.33 – 8.23 (m, 2H), 8.00 – 7.92 (m, 2H), 7.89 – 7.81 (m, 2H), 7.67 (s, 1H), 7.66 – 7.59 (m, 1H), 7.55 – 7.50 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, Z isomer) δ = 190.77, 148.05, 140.00, 138.50, 135.49, 133.37, 130.64, 129.89, 128.74, 125.79, 123.69.

HRMS (EI-MS): Calcd. For $C_{15}H_{10}BrNO_3$ [$M^{+\cdot}$] m/z 330.9844, found *m/z* 330.9836.

2-bromo-1-phenyl-3-p-tolylprop-2-en-1-one (51n)[28]



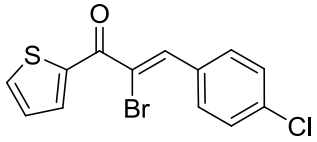
According to the general procedure (GP-A), (E)-1-phenyl-3-p-tolylprop-2-en-1-one (444 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.40 g, 2.4 mmol, 1.2 equiv), 2N HBr (4.0 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.0 equiv) afforded **51n** (465 mg, 75 %) as white solid after column purification on silica gel as a mixture of Z:E = 88:12. R_f (EtOAc/hexane 1:9): 0.58.

^{1}H NMR (300 MHz, $CDCl_3$, Z isomer) δ = 7.79 (m, 4H), 7.69 (s, 1H), 7.59 (m, 1H), 7.52 – 7.47 (m, 2H), 7.25 (d, *J* = 7.9, 2H), 2.40 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, Z isomer) δ = 191.71, 143.32, 141.14, 136.83, 132.48, 130.80, 130.48, 129.68, 129.28, 128.50, 121.84, 21.63.

HRMS (EI-MS): Calcd. For $C_{16}H_{13}BrO$ [$M^{+\cdot}$] m/*z* 300.0150, found *m/z* 300.0149.

(E)-2-bromo-3-(4-chlorophenyl)-1-(thiophen-2-yl)prop-2-en-1-one (58)



According to the general procedure (GP-A), (E)-3-(4-chlorophenyl)-1-(thiophen-2-yl)prop-2-en-1-one (452 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.40 g, 2.4 mmol, 1.2 equiv), 2N HBr (4.0 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.0 equiv) afforded **58** (426 mg, 65 %) as yellow liquid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.32.

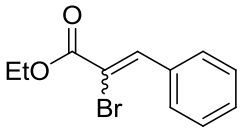
IR (neat): 3095, 1634, 1488, 1408, 1250, 1012, 819, 727 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.84 – 7.73 (m, 5H), 7.46 – 7.38 (m, 2H), 7.21 – 7.14 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 182.86, 141.18, 138.51, 136.12, 135.28, 134.85, 132.08, 131.34, 128.85, 128.14, 121.34.

HRMS (EI-MS): Calcd. For $C_{13}H_8BrClOS$ [$M^{+\cdot}$] m/*z* 325.9168, found *m/z* 325.9168.

ethyl 2-bromo-3-phenylacrylate (60)[32]



According to the general procedure (GP-A), ethyl cinnamate (352 mg, 2.0 mmol, 1.0 equiv), *OXONE* (1.40 g, 2.4 mmol, 1.2 equiv), 2N HBr (4.0 mmol, 2.0 equiv), triethylamine (1.01 g, 10.0 mmol, 5.0 equiv) afforded **60** (454 mg, 89 %) as colorless liquid after column purification on silica gel as a mixture of Z:E = 50:50. R_f (EtOAc/hexane 1:9): 0.57.

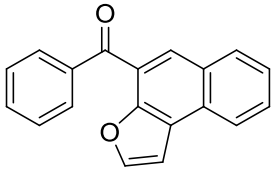
Z isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.22 (s, 1H), 7.90 – 7.81 (m, 2H), 7.46 – 7.39 (m, 3H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1Hz, 3H).

E isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.36 (s, 1H), 7.35 – 7.30 (m, 3H), 7.30 – 7.24 (m, 2H), 4.21 (q, *J*=7.1, 2H), 1.18 (t, *J*=7.1, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.44, 163.39, 140.81, 139.63, 134.89, 133.77, 130.31, 130.20, 128.90, 128.44, 128.41, 128.14, 113.18, 111.80, 62.83, 62.36, 14.26, 13.72.

MS (EI, 70 eV): m/z = 254.0 (M+).

(naphtho[2,1-b]furan-4-yl)(phenyl)methanone (55aa)



According to the general procedure (GP-B), **51a** (144 mg, 0.5 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 1 mol %), furan (170 mg, 2.5 mmol, 5.0 equiv) afforded **55aa** (116 mg, 85 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.38.

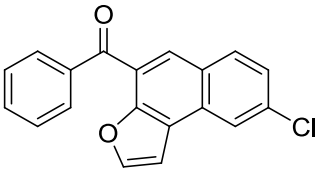
M.p. = 147-149 °C.

IR (neat): 3057, 1658, 1598, 1293, 1265,734, 632 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 10.2 Hz, 2H), 7.95 – 7.89 (m, 2H), 7.82 (d, *J* = 2.1 Hz, 1H), 7.70 (m, 1H), 7.67 – 7.61 (m, 1H), 7.59 – 7.47 (m, 3H), 7.33 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 193.95, 145.32, 137.95, 133.02, 130.23, 129.95, 129.43, 129.37, 128.61, 128.41, 125.39, 124.25, 123.77, 123.48, 105.40.

HRMS (ESI): Calcd. For $C_{19}H_{12}O_2$ $[M+]^+$ *m/z* 272.0837, found *m/z* 272.0837.

(8-chloronaphtho[2,1-b]furan-4-yl)(phenyl)methanone (55ba)



According to the general procedure (GP-B), **51b** (161 mg, 0.5 mmol, 1.0 equiv), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.60 mg, 1 mol %), furan (170 mg, 2.5 mmol, 5.0 equiv) afforded **55ba** (126 mg, 82 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.40.

M.p. = 159-161 °C

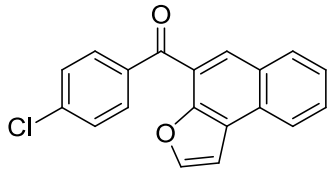
IR (neat): 3025, 1665, 1428, 1255, 786, 538 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 2.1 Hz, 1H), 7.95 (s, 1H), 7.91 – 7.83 (m, 3H), 7.78 (d, *J* = 2.1 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.51 – 7.42 (m, 3H), 7.24 (d, *J* = 2.1 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 193.53, 150.09, 145.64, 137.74, 134.56, 133.14, 131.38, 130.16, 130.07, 128.44, 128.03, 127.63, 126.30, 124.00, 123.61, 122.76, 105.29.

HRMS (ESI): Calcd. For $C_{19}H_{12}ClO_2$ $[M+H]^+$ *m/z* 307.0520, found *m/z* 307.0521.

(4-chlorophenyl)(naphtho[2,1-b]furan-4-yl)methanone (55ca)



According to the general procedure (GP-B), **51c** (161 mg, 0.5 mmol, 1.0 equiv), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.60 mg, 1 mol %), furan (170 mg, 2.5 mmol, 5.0 equiv) afforded **55ca** (140 mg, 91 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.53.

M.p. = 155-157 °C

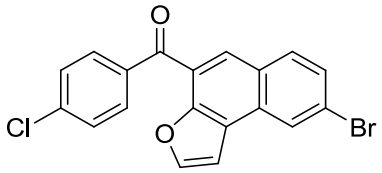
IR (neat): 3098, 1642, 1618, 1586, 1293,738 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 5.7 Hz, 2H), 7.89 – 7.83 (m, 2H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.60 – 7.53 (m, 1H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 2.1 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 192.67, 149.38, 145.35, 139.51, 136.29, 131.57, 129.98, 129.52, 129.38, 128.77, 128.58, 128.50, 125.52, 124.32, 123.50, 123.38, 105.48.

HRMS (ESI): Calcd. For $C_{19}H_{12}ClO_2$ $[M+H]^+$ m/z 307.0520, found *m/z* 307.0521.

(8-bromonaphtho[2,1-b]furan-4-yl)(4-chlorophenyl)methanone (55da)



According to the general procedure (GP-B), **51d** (200 mg, 0.5 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 1 mol %), furan (170 mg, 2.5 mmol, 5.0 equiv) afforded **55da** (154 mg, 80 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.54.

M.p. = 169-171°C

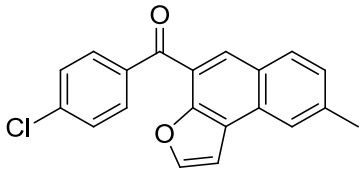
IR (neat): 3108, 2333, 1656, 1622, 1296,786, 538 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.29 (d, *J* = 1.9 Hz, 1H), 7.93 (s, 1H), 7.84 – 7.80 (m, 2H), 7.78 (dd, *J* = 4.3, 2.0 Hz, 2H), 7.60 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.24 (d, *J* = 2.2 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 192.30, 149.81, 145.73, 139.71, 136.05, 131.52, 131.45, 130.49, 129.00, 128.83, 128.03, 127.84, 126.07, 123.75, 123.58, 123.16, 105.39.

HRMS (ESI): Calcd. For $C_{19}H_{11}BrClO_2$ $[M+H]^+$ m/z 384.9625, found *m/z* 384.9623.

(4-chlorophenyl)(8-methylnaphtho[2,1-b]furan-4-yl)methanone (55ea)



According to the general procedure (GP-B), **51e** (168 mg, 0.5 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 1 mol %), furan (170 mg, 2.5 mmol, 5.0 equiv) afforded **55ea** (128 mg, 80 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.51.

M.p. = 125-127 °C

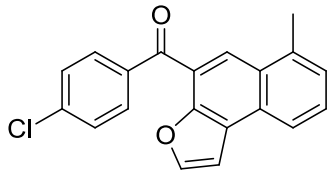
IR (neat): 3053, 1656, 1633, 1588, 1294, 1251, 1090, 740 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 4.8 Hz, 2H), 7.92 – 7.82 (m, 3H), 7.79 (d, *J* =2.1 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.39 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.29 (d, *J* = 2.1 Hz, 1H), 2.62 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 192.75, 149.64, 145.13, 139.32, 139.05, 136.47, 131.55, 129.82, 129.80, 128.71, 128.65, 127.68, 127.43, 123.77, 122.84, 122.47, 105.37, 101.21, 22.16.

HRMS (ESI): Calcd. For $C_{20}H_{13}ClO_2$ $[M+H]^+$ *m/z* 321.0676, found *m/z* 321.0676.

(4-chlorophenyl)(6-methylnaphtho[2,1-b]furan-4-yl)methanone (55fa)



According to the general procedure (GP-B), **51f** (168 mg, 0.5 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 1 mol %), furan (170 mg, 2.5 mmol, 5.0 equiv) afforded **55fa** (54 mg, 32 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.45.

M.p. = 117-119 °C

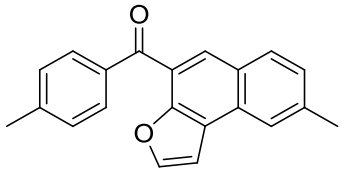
IR (neat): 3058, 1658, 1589, 1288, 1229, 1092, 762 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (s, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.78 (d, *J* = 2.1 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.51 – 7.46 (m, 2H), 7.42 – 7.39 (m, 1H), 7.32 (d, *J* = 2.1 Hz, 1H), 2.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.87, 149.21, 145.27, 139.50, 136.82, 136.45, 131.59, 129.83, 128.72, 128.61, 128.40, 126.49, 124.74, 124.65, 122.83, 121.78, 105.69, 20.16,

HRMS (ESI): Calcd. For $C_{20}H_{13}ClO_2$ $[M+H]^+$ *m/z* 321.0676, found *m/z* 321.0676.

(8-methylnaphtho[2,1-b]furan-4-yl)(p-tolyl)methanone (55ga)



According to the general procedure (GP-B), **51g** (158 mg, 0.5 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 1 mol %), furan (170 mg, 2.5 mmol, 5.0 equiv) afforded **55ga** (125 mg, 83 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.37.

M.p. = 121-123 °C

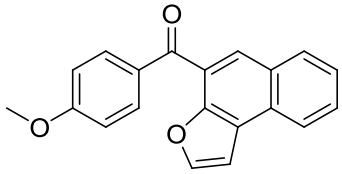
IR (neat): 3059, 1656, 1624, 1455, 1291, 1109, 728, 633 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 3.0 Hz, 2H), 7.91 – 7.75 (m, 4H), 7.37 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.29 (dd, *J* = 8.9, 7.0 Hz, 3H), 2.61 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 193.69, 154.08, 149.87, 145.03, 143.78, 138.62, 135.44, 130.41, 129.71, 129.56, 129.09, 128.36, 127.49, 127.46, 123.17, 122.80, 105.29, 22.13, 21.78.

HRMS (ESI): Calcd. For $C_{21}H_{17}O_2$ $[M+H]^+$ *m/z* 301.1223, found *m/z* 301.1223.

(4-methoxyphenyl)(naphtho[2,1-b]furan-4-yl)methanone (55ha)



According to the general procedure (GP-B), **51h** (159 mg, 0.5 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 1 mol %), furan (170 mg, 2.5 mmol, 5.0 equiv) afforded **55ha** (91 mg, 60 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 2:8): 0.43.

M.p. = 168-170 °C

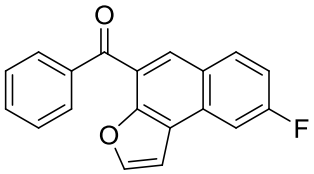
IR (neat): 3058, 1650, 1597, 1250, 1163, 1025, 633 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ = 8.22 – 8.15 (m, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.96 – 7.89 (m, 2H), 7.80 (d, *J* = 2.1 Hz, 1H), 7.69 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.59 – 7.51 (m, 1H), 7.32 (d, *J* = 2.1 Hz, 1H), 7.01 – 6.94 (m, 2H), 3.90 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 192.48, 163.73, 149.58, 145.20, 132.70, 130.60, 129.79, 129.47, 129.14, 128.10, 127.66, 125.32, 124.34, 124.05, 123.47, 113.69, 105.44, 55.55.

HRMS (ESI): Calcd. For $C_{20}H_{15}O_3$ $[M+H]^+$ *m/z* 303.1016, found *m/z* 303.1012.

(8-fluoronaphtho[2,1-b]furan-4-yl)(phenyl)methanone (55ia)



According to the general procedure (GP-B), **51i** (152 mg, 0.5 mmol, 1.0 equiv), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 1 mol %), furan (170 mg, 2.50mmol, 5.0 equiv) afforded **55ia** (119 mg, 82 %) as light yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.40.

M.p. = 103-105 °C

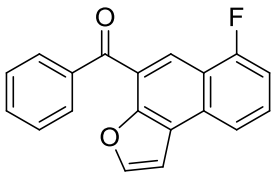
IR (neat): 3351, 1635, 1469, 1289, 1206, 904, 726 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99 (dd, *J* = 8.4, 5.0 Hz, 2H), 7.94 – 7.88 (m, 2H), 7.82 (d, *J* = 2.1 Hz, 1H), 7.78 (dd, *J* = 9.7, 2.6 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.55 – 7.48 (m, 2H), 7.35 – 7.28 (m, 1H), 7.25 (d, *J* = 2.2 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 193.68, 160.84, 150.09, 145.42, 137.87, 133.07, 132.62, 132.49, 130.17, 128.49, 128.47, 128.44, 126.26, 123.94, 115.64, 115.31, 107.95, 107.66, 105.38.

HRMS (ESI): Calcd. For $C_{19}H_{11}FO_2$ $[M+]^+$ *m/z* 290.0743, found *m/z* 290.0748.

(6-fluoronaphtho[2,1-b]furan-4-yl)(phenyl)methanone (55ja)



According to the general procedure (GP-B), **51j** (152 mg, 0.5 mmol, 1.0 equiv), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 1 mol %), furan (170 mg, 2.5 mmol, 5.0 equiv) afforded **55ja** (61 mg, 42 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.30.

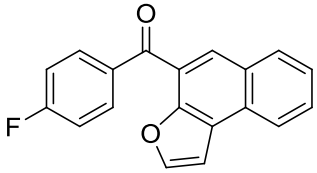
IR (neat): 3348, 1638, 1455, 1271, 1189, 903, 531 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.28 (s, 1H), 8.03 – 7.88 (m, 3H), 7.84 (d, *J* = 2.1 Hz, 1H), 7.70 – 7.58 (m, 2H), 7.51 (m, 2H), 7.31 (d, *J* = 2.1 Hz, 1H), 7.22 (dd, *J* = 10.7, 8.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 193.60, 161.77, 158.39, 150.14, 145.71, 137.61, 133.25, 130.28, 128.83, 128.71, 128.49, 120.88, 120.81, 119.65, 119.40, 119.35, 109.59, 109.33, 105.56.

HRMS (ESI): Calcd. For $C_{19}H_{11}FO_2$ $[M+]^+$ *m/z* 290.0743, found *m/z* 290.0748.

(4-fluorophenyl)(naphtho[2,1-b]furan-4-yl)methanone (55ka)



According to the general procedure (GP-B), **51k** (152 mg, 0.5 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 1 mol %), furan (170 mg, 2.5 mmol, 5.0 equiv) afforded **55ka** (113 mg, 78 %) as colorless solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.33.

M.p. = 93-95 °C

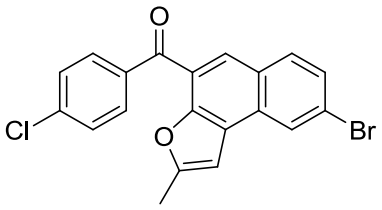
IR (neat): 3331, 1657, 1598, 1241, 1155, 904, 726 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 8.3 Hz, 1H), 8.01 (t, *J* = 4.1 Hz, 2H), 7.99 – 7.91 (m, 2H), 7.81 (d, *J* = 2.1 Hz, 1H), 7.71 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.56 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.33 (d, *J* = 2.1 Hz, 1H), 7.22 – 7.14 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 192.37, 167.49, 164.12, 149.41, 145.32, 134.24, 134.20, 132.90, 132.78, 129.93, 129.42, 129.39, 128.48, 128.28, 125.48, 124.26, 123.59, 123.50, 115.75, 115.47, 105.48.

HRMS (ESI): Calcd. For $C_{19}H_{11}FO_2$ $[M+]^+$ *m/z* 290.0743, found *m/z* 290.0748.

(8-bromo-1-methylnaphtho[2,1-b]furan-4-yl)(4-chlorophenyl)methanone (55db)



According to the general procedure (GP-B), **51d** (100 mg, 0.25 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (2.8 mg, 1 mol %), 2-methyl furan (102 mg, 1.25 mmol, 5 equiv)

afforded **55db** (65 mg, 65 %) as organe liquid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.62.

IR (neat): 2919, 1660, 1587, 1487, 1292, 1089, 804, 735 cm^{-1}.

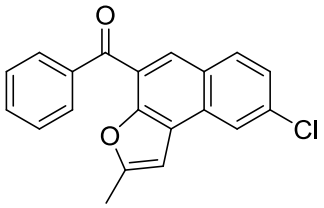
M.p. = 160-162 °C

^1H NMR (300 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 1.9 Hz, 1H), 7.83 – 7.75 (m, 4H), 7.55 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.46 – 7.41 (m, 2H), 6.84 (d, *J* = 1.0 Hz, 1H), 2.48 (d, *J* = 0.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 192.44, 156.69, 136.04, 131.64, 131.33, 128.75, 128.64, 127.63, 126.43, 126.04, 123.31, 122.63, 101.60, 14.37.

HRMS (ESI): Calcd. For $C_{20}H_{13}BrClO_2$ $[M+H]^+$ m/z 398.9782, found *m/z* 398.9779.

(8-chloro-1-methylnaphtho[2,1-b]furan-4-yl)(phenyl)methanone (55bb)



According to the general procedure (GP-B), **51b** (129 mg, 0.4 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (4.5 mg, 1 mol %), 2-methyl furan (410 mg, 2.0 mmol, 5.0 equiv) afforded **55bb** (100 g, 78 %) as yellow liquid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.48.

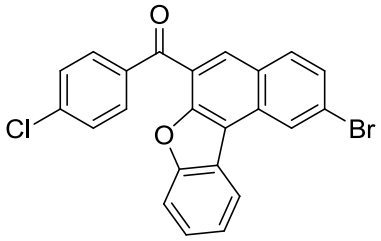
IR (neat): 3057, 1661, 1458, 1367, 1293, 632 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 1.9 Hz, 1H), 7.96 – 7.82 (m, 4H), 7.63 (ddd, *J* = 6.8, 4.0, 1.3 Hz, 1H), 7.50 (dd, *J* = 10.4, 4.6 Hz, 2H), 7.45 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.87 (d, *J* = 0.7 Hz, 1H), 2.53 (d, *J*=0.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 192.79, 155.49, 148.49, 136.67, 132.99, 132.07, 130.23, 129.24, 128.47, 127.33, 126.35, 125.47, 124.92, 124.18, 122.48, 121.68, 100.48, 13.31.

HRMS (ESI): Calcd. For $C_{20}H_{15}ClO_2$ $[M+]^+$ m/z 320.0604, found *m/z* 320.0602.

(2-bromobenzo[d]naphtho[2,1-b]furan-6-yl)(4-chlorophenyl)methanone (55dc)



According to the general procedure (GP-B), **51d** (120 mg, 0.3 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (3.3 mg, 1 mol %), benzofuran (71 mg, 0.6 mmol, 2.0 equiv) afforded **55dc** (111 mg, 85 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.58.

M.p. = 237-239 °C

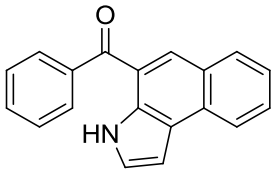
IR (neat): 3319, 1626, 1488, 1292, 1095, 986, 873, 735 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ = 8.81 (d, *J* = 1.8 Hz, 1H), 8.43 – 8.36 (m, 1H), 8.13 (s, 1H), 7.99 – 7.85 (m, 3H), 7.74 – 7.63 (m, 2H), 7.56 – 7.47 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 192.11, 156.10, 151.64, 139.94, 135.82, 132.26, 131.76, 131.62, 131.40, 130.33, 128.90, 128.87, 127.91, 127.01, 125.99, 124.05, 124.03, 123.85, 123.56, 121.81, 118.13.

HRMS (ESI): Calcd. For $C_{23}H_{13}BrClO_2$ $[M+H]^+$ m/z 434.9782, found *m/z* 434.9785.

(3H-benzo[e]indol-4-yl)(phenyl)methanone (57aa)



According to the general procedure (GP-B), **51a** (144 mg, 0.5 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 1 mol %), pyrrole (168 mg, 2.5 mmol, 5.0 equiv) afforded **57aa** (121 mg, 89 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.35.

M.p. = 144-146 °C

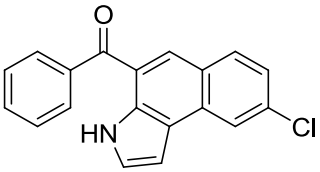
IR (neat): 3486, 3056, 1621, 1576, 1360, 1303, 1101, 730 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.52 (s, 1H), 8.29 (dd, *J* = 8.3, 0.5 Hz, 1H), 8.03 (d, *J* = 6.2 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.89 – 7.82 (m, 2H), 7.73 – 7.62 (m, 2H), 7.61 – 7.53 (m, 2H), 7.48 – 7.41 (m, 2H), 7.15 (dd, *J* = 3.1, 2.4 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.26, 138.93, 131.82, 131.20, 130.92, 130.75, 130.51, 129.59, 128.94, 128.40, 127.81, 124.28, 123.99, 123.57, 123.09, 121.08, 101.41.

HRMS (ESI): Calcd. For $C_{19}H_{14}NO$ $[M+H]^+$ *m/z* 272.1070, found *m/z* 272.1070.

(8-chloro-3H-benzo[e]indol-4-yl)(phenyl)methanone (57ba)



According to the general procedure (GP-B), **51b** (96 mg, 0.3 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (3.3 mg, 1 mol %), pyrrole (101 mg, 1.5 mmol, 5.0 equiv) afforded **57ba** (87 mg, 95 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.36.

M.p. = 182-184 °C

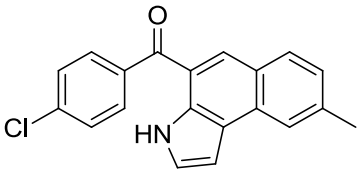
IR (neat): 3319, 1626, 1488, 1381, 1292, 1095, 735 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.54 (s, 1H), 8.24 (d, *J* = 2.1 Hz, 1H), 7.99 (s, 1H), 7.88 – 7.80 (m, 3H), 7.69 – 7.62 (m, 1H), 7.57 (m, 2H), 7.48 – 7.44 (m, 1H), 7.38 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.10 (dd, *J* =3.1, 2.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.94, 137.65, 133.94, 130.89, 130.88, 130.51, 130.15, 129.47, 128.49, 127.40, 124.95, 123.76, 122.94, 122.51, 121.36, 120.11, 100.45.

HRMS (ESI): Calcd. For $C_{19}H_{13}ClNO$ $[M+H]^+$ *m/z* 306.0680, found *m/z* 306.0678.

(4-chlorophenyl)(8-methyl-3H-benzo[e]indol-4-yl)methanone (57ea)



According to the general procedure (GP-B), **51e** (168 mg, 0.5 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 1 mol %), pyrrole (167 mg, 2.5 mmol, 5.0 equiv)

afforded **57ea** (146 mg, 91 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.45.

M.p. = 178-180 °C

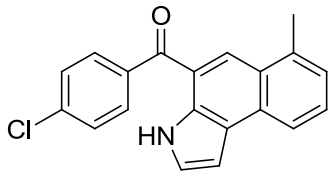
IR (neat): 3424, 3052, 1623, 1478, 1356, 1271, 738 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ = 10.46 (s, 1H), 8.06 (d, *J* = 0.7 Hz, 1H), 7.94 (s, 1H), 7.79 (ddd, *J* = 7.8, 4.8, 2.6 Hz, 3H), 7.57 – 7.49 (m, 2H), 7.45 – 7.40 (m, 1H), 7.28 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.14 – 7.08 (m, 1H), 2.61 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.85, 139.59, 138.05, 137.33, 131.22, 131.01, 130.95, 130.80, 130.35, 128.69, 126.26, 125.81, 123.87, 123.44, 122.53, 120.09, 101.36, 22.29.

HRMS (ESI): Calcd. For $C_{20}H_{15}ClNO$ $[M+H]^+$ *m/z* 320.0837, found *m/z* 320.0836.

(4-chlorophenyl)(6-methyl-3H-benzo[e]indol-4-yl)methanone (57fa)



According to the general procedure (GP-B), **51f** (168 mg, 0.5 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 1 mol %), pyrrole (167 mg, 2.5 mmol, 5.0 equiv) afforded **57fa** (125 mg, 78 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.39.

M.p. = 159-161 °C

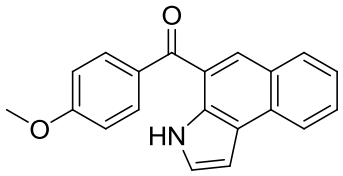
IR (neat): 3440, 3391, 1631, 1590, 1490, 1289, 1100, 763 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ = 10.42 (s, 1H), 8.20 – 8.14 (m, 2H), 7.86 – 7.81 (m, 2H), 7.62 – 7.52 (m, 3H), 7.47 – 7.42 (m, 1H), 7.30 (m, 1H), 7.17 – 7.12 (m, 1H), 2.66 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.92, 138.26, 137.34, 136.93, 131.23, 131.15, 130.54, 128.86, 128.66, 126.98, 126.82, 125.23, 124.97, 123.77, 121.46, 120.23, 101.68, 20.14.

HRMS (ESI): Calcd. For $C_{20}H_{15}ClNO$ $[M+H]^+$ *m/z* 320.0837, found *m/z* 320.0836.

(3H-benzo[e]indol-4-yl)(4-methoxyphenyl)methanone (57ha)



According to the general procedure (GP-B), **51h** (159 mg, 0.5 mmol, 1.0 equiv), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 1 mol %), pyrrole (168 mg, 2.5 mmol, 5.0 equiv) afforded **57ha** (121 mg, 80 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 2:8): 0.38.

M.p. = 108-110 °C

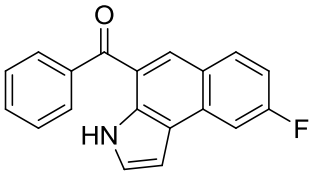
IR (neat): 3380, 2963, 1616, 1592, 1251, 1103, 1020, 738 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.40 (s, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 8.04 (s, 1H), 7.92 (dd, *J* = 11.9, 8.6 Hz, 3H), 7.72 – 7.61 (m, 1H), 7.50 – 7.37 (m, 2H), 7.17 – 7.10 (m, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 3.93 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 195.72, 161.80, 131.05, 130.31, 129.86, 129.60, 129.30, 129.22, 127.59, 126.77, 123.14, 122.87, 122.40, 122.02, 120.41, 112.65, 100.33, 54.50.

HRMS (ESI): Calcd. For $C_{20}H_{16}NO_2$ $[M+H]^+$ *m/z* 302.1176, found *m/z* 302.1175.

(8-fluoro-3H-benzo[e]indol-4-yl)(phenyl)methanone (57ia)



According to the general procedure (GP-B), **51i** (152 mg, 0.5 mmol, 1.0 equiv), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 1 mol %), pyrrole (168 g, 2.5 mmol, 5.0 equiv) afforded **57ia** (126 mg, 87 %) as yellow crystalline solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.33.

M.p. = 179-181 °C

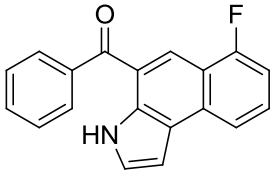
IR (neat): 3372, 1621, 1471, 1362, 1289, 1106, 728 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.56 (s, 1H), 8.01 (s, 1H), 7.95 – 7.79 (m, 4H), 7.69 – 7.61 (m, 1H), 7.57 (m, 2H), 7.47 – 7.41 (m, 1H), 7.19 (td, *J* = 8.7, 2.6 Hz, 1H), 7.07 (dd, *J* = 3.1, 2.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.03, 164.73, 161.42, 138.81, 133.11, 132.98, 131.85, 131.04, 130.87, 129.51, 128.43, 124.64, 123.68, 120.46, 114.05, 113.72, 107.51, 107.23, 101.57.

HRMS (ESI): Calcd. For $C_{19}H_{12}FNO$ $[M+]^+$ m/*z* 289.0903, found *m/z* 289.0898.

(6-fluoro-3H-benzo[e]indol-4-yl)(phenyl)methanone (57ja)



According to the general procedure (GP-B), **51j** (152 mg, 0.5 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 1 mol %), pyrrole (168 mg, 2.5 mmol, 5.0 equiv) afforded **57ja** (120 mg, 83 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.31.

M.p. = 173-175 °C

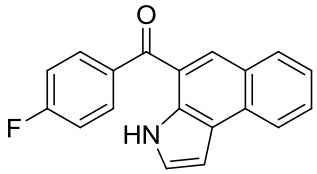
IR (neat): 3332, 1626, 1446, 1359, 1284, 1103, 731 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.57 (s, 1H), 8.32 (s, 1H), 8.05 (d, *J*=8.3, 1H), 7.90 – 7.82 (m, 2H), 7.69 – 7.53 (m, 4H), 7.46 (t, *J* = 2.79 Hz, 1H), 7.15 – 7.05 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.06, 162.19, 158.83, 138.62, 132.20, 132.15, 132.06, 131.21, 129.67, 129.18, 129.06, 128.48, 128.39, 124.06, 123.05, 122.97, 121.12, 118.97, 118.92, 117.93, 117.73, 108.11, 107.85, 101.71.

HRMS (ESI): Calcd. For $C_{19}H_{12}FNO$ $[M+]^+$ m/*z* 289.0903, found *m/z* 289.0898.

(3H-benzo[e]indol-4-yl)(4-fluorophenyl)methanone (57ka)



According to the general procedure (GP-B), **51k** (152 mg, 0.5 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 1 mol %), pyrrole (168 mg, 2.5 mmol, 5.0 equiv) afforded 57**ka** (122 mg, 84 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.28.

M.p. = 163-165 °C

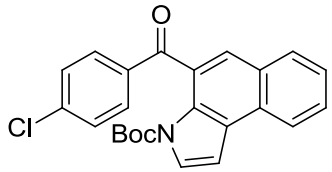
IR (neat): 3348, 1634, 1486, 1305, 1227, 1108, 901, 730 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.45 (s, 1H), 8.32 – 8.26 (m, 1H), 7.99 (s, 1H), 7.96 – 7.85 (m, 3H), 7.69 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.30 – 7.19 (m, 2H), 7.15 (dd, *J* = 3.1, 2.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.68, 166.73, 135.07, 135.02, 132.17, 132.05, 130.92, 130.79, 130.67, 130.45, 129.01, 127.75, 124.36, 124.08, 123.65, 123.12, 120.97, 115.72, 115.43, 101.47.

HRMS (ESI): Calcd. For $C_{19}H_{12}FNO$ $[M+]^+$ m/z 289.0903, found *m/z* 289.0898.

tert-butyl 4-(4-chlorobenzoyl)-3H-benzo[e]indole-3-carboxylate (57cb)



According to the general procedure (GP-B), **51c** (80 mg, 0.25 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (2.8 mg, 1 mol %), N-Boc pyrrole (84 mg, 0.5 mmol, 2.0 equiv) afforded **57cb** (93 mg, 92 %) as light yellow gummy liquid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.35.

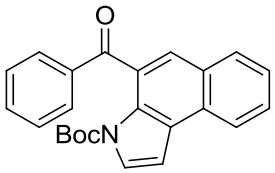
IR (neat): 3436, 3056, 1621, 1576, 1360, 1303, 1255, 971, 876, 730 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.23 – 8.15 (m, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.79 (s, 1H), 7.70 – 7.58 (m, 3H), 7.56 (d, *J* = 3.7 Hz, 1H), 7.49 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.13 (d, *J* = 3.6 Hz, 1H), 1.34 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 192.91, 149.08, 138.55, 136.93, 130.68, 129.54, 129.27, 128.53, 128.42, 128.19, 127.72, 127.14, 127.12, 126.62, 126.19, 125.40, 123.18, 105.77, 84.50, 27.71.

HRMS (ESI): Calcd. For $C_{24}H_{20}ClNO_3$ $[M+]^+$ m/z 405.1126, found *m/z* 405.1114.

tert-butyl 4-benzoyl-3H-benzo[e]indole-3-carboxylate (57ab)



According to the general procedure (GP-B), **51a** (144 mg, 0.50 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 1 mol %), N-Boc pyrrole (167 mg, 1.0 mmol, 2.0 equiv)

afforded **57ab** (157 mg, 85 %) as light yellow liquid after column purification on silica gel. R_f (EtOAc/hexane 2:8): 0.63.

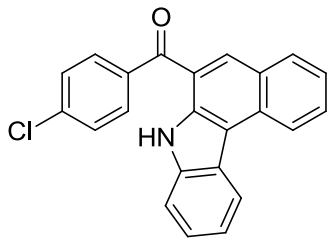
IR (neat): 3057, 2978, 1740, 1666, 1361, 1292, 1172, 752 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.77 – 7.70 (m, 2H), 7.61 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.56 (d, *J* = 3.6 Hz, 1H), 7.52 – 7.41 (m, 2H), 7.39 – 7.30 (m, 2H), 7.13 (d, *J* = 3.7 Hz, 1H), 1.30 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 194.20, 149.12, 138.42, 132.30, 129.61, 129.36, 129.30, 128.40, 128.27, 127.60, 127.04, 126.76, 126.19, 125.30, 123.18, 105.63, 84.41, 27.71.

HRMS (ESI): Calcd. For $C_{24}H_{22}NO_3$ $[M+H]^+$ *m/z* 372.1594, found *m/z* 372.1597.

(7H-benzo[c]carbazol-6-yl)(4-chlorophenyl)methanone (57cc)



According to the general procedure (GP-B), **51c** (80 mg, 0.25 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (2.8 mg, 1 mol %), indole (59 mg, 0.5 mmol, 2.0 equiv) afforded **57cc** (77 mg, 87 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.46.

M.p. = 181-183 °C

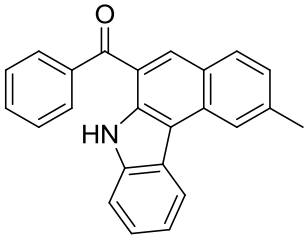
IR (neat): 3431, 3058, 1634, 1468, 1351, 1217, 632 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ = 10.64 (s, 1H), 8.82 (d, *J* = 8.4 Hz, 1H), 8.60 (d, *J* = 7.9 Hz, 1H), 8.23 (s, 1H), 7.99 (dd, *J* = 8.1, 5.0 Hz, 1H), 7.89 – 7.76 (m, 3H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.61 – 7.39 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.88, 145.39, 138.84, 138.44, 137.08, 135.99, 134.14, 132.49, 131.14, 131.10, 130.08, 128.83, 127.49, 125.11, 123.66, 123.26, 122.87, 122.05, 120.62, 120.02, 111.88.

HRMS (ESI): Calcd. For $C_{23}H_{15}ClNO$ $[M+H]^+$ *m/z* 356.0837, found *m/z* 356.0831.

(2-methyl-7H-benzo[c]carbazol-6-yl)(phenyl)methanone (57nc)



According to the general procedure (GP-B), **51n** (150 g, 0.5 mmol, 1.0 equiv), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 1 mol %), indole (117 mg, 1.0 mmol, 2.0 equiv) afforded **57nc** (121 mg, 72 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.67.

M.p. = 186-188 °C

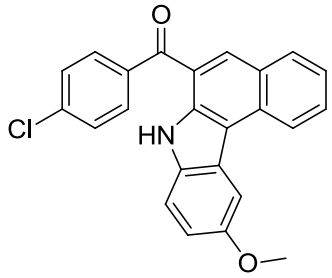
IR (neat): 2926, 2362, 1724, 1661, 1589, 1487, 1091, 768, 631 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.72 (s, 1H), 8.61 (d, *J* = 8.6 Hz, 2H), 8.25 (s, 1H), 7.88 (dd, *J* = 11.7, 4.9 Hz, 3H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.66 (dt, *J* = 2.9, 2.2 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.55 – 7.49 (m, 1H), 7.44 (dd, *J* = 11.0, 4.1 Hz, 1H), 7.36 – 7.30 (m, 1H), 2.71 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.17, 140.45, 138.98, 138.78, 136.43, 134.44, 132.72, 131.80, 130.98, 129.58, 128.41, 125.71, 124.80, 122.98, 122.61, 121.97, 120.39, 119.49, 116.33, 111.78, 22.62.

HRMS (ESI): Calcd. For $C_{24}H_{17}NO$ $[M+]^+$ *m/z* 335.1310, found *m/z* 335.1304.

(4-chlorophenyl)(10-methoxy-7H-benzo[c]carbazol-6-yl)methanone (57cd)



According to the general procedure (GP-B), **51c** (161 mg, 0.5 mmol, 1.0 equiv), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 1 mol %), 5-methoxy indole (147 mg, 1.0 mmol, 2.0 equiv) afforded **57cd** (135 mg, 70 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.35.

M.p. = 195-197 °C

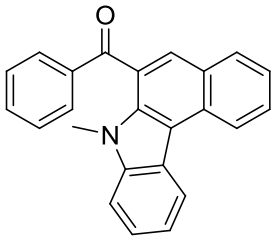
IR (neat): 3433, 1619, 1485, 1312, 1210,981, 631 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.53 (s, 1H), 8.74 (d, *J* = 8.2 Hz, 1H), 8.21 (s, 1H), 8.03 (d, *J* = 2.4 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.88 – 7.78 (m, 3H), 7.64 – 7.46 (m, 4H), 7.20 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.04 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.78, 154.65, 138.39, 137.11, 136.61, 134.14, 133.89, 132.53, 131.15, 131.04, 130.02, 128.79, 127.33, 123.46, 123.23, 122.94, 120.13, 116.84, 114.38, 112.39, 105.11, 56.26.

HRMS (ESI): Calcd. For $C_{24}H_{16}ClNO_2$ $[M+]^+$ *m/z* 385.0870, found *m/z* 385.0869.

(7-methyl-7H-benzo[c]carbazol-6-yl)(phenyl)methanone (57ae)



According to the general procedure (GP-A), **51a** (144 mg, 0.5 mmol, 1.0 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 1 mol %), N-methyl indole (131 mg, 1.0 mmol, 2.0 equiv) afforded **57ae** (117 mg, 70 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.35.

M.p. = 179-181 °C

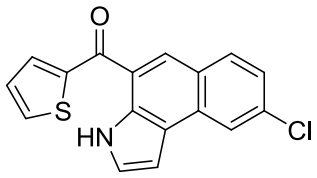
IR (neat): 3054, 2939, 1740, 1654, 1475, 1333, 1264, 1217, 1176, 919, 742 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.89 (d, *J* = 8.1 Hz, 1H), 8.66 (d, *J* = 8.0 Hz, 1H), 8.05 – 7.95 (m, 3H), 7.93 (s, 1H), 7.79 (ddd, *J* = 6.9, 6.2, 1.4 Hz, 1H), 7.66 (ddd, *J* = 6.8, 2.7, 1.3 Hz, 1H), 7.58 – 7.39 (m, 6H), 3.73 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.47, 140.90, 137.98, 136.01, 133.71, 130.88, 130.66, 129.85, 129.04, 128.77, 128.47, 127.40, 125.01, 124.84, 123.58, 123.16, 123.07, 122.14, 120.30, 116.85, 109.66, 33.27.

HRMS (ESI): Calcd. For $C_{24}H_{18}BrNO$ $[M+H]^+$ *m/z* 336.1382, found *m/z* 336.1379.

(8-chloro-3H-benzo[e]indol-4-yl)(thiophen-2-yl)methanone (59)



According to the general procedure (GP-B), **58** (164 mg, 0.5 mmol, 1.0 equiv), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 1 mol %), pyrrole (168 mg, 2.5 mmol, 5.0 equiv) afforded **59** (138 mg, 89 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 2:8): 0.46.

M.p. = 174-176 °C

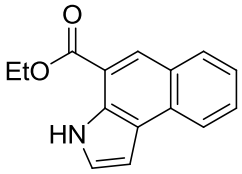
IR (neat): 3438, 3105, 1612, 1513, 1413, 1361, 1298, 1096, 632 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.30 (s, 1H), 8.31 (s, 1H), 8.24 (d, *J* = 2.1 Hz, 1H), 7.93 (d, *J* = 8.7 Hz, 1H), 7.86 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.78 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.27 – 7.23 (m, 2H), 7.08 (dd, *J* = 3.1, 2.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 188.17, 143.36, 134.82, 134.27, 133.68, 131.82, 131.40, 130.95, 128.25, 128.02, 126.12, 124.88, 123.98, 123.57, 122.43, 121.71, 101.59.

HRMS (ESI): Calcd. For $C_{17}H_{10}ClNOS$ $[M+]^+$ m/*z* 311.0172, found *m/z* 311.0166.

ethyl 3H-benzo[e]indole-4-carboxylate (61)



According to the general procedure (GP-A), **60** (128 mg, 0.5 mmol, 1.0 equiv), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 1 mol %), pyrrole (168 g, 2.5 mmol, 5.0 equiv) afforded **61** (87 mg, 73 %) as light orange solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.35.

M.p. = 120-122 °C

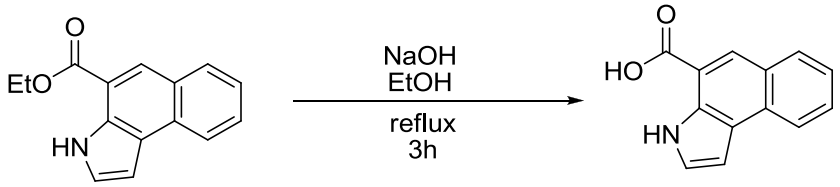
IR (neat): 3398, 2985, 1681, 1620, 1365, 1228, 1089, 730 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.15 (s, 1H), 8.39 (s, 1H), 8.31 – 8.19 (m, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.66 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.46 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.12 (dd, *J* = 3.0, 2.4 Hz, 1H), 4.52 (q, *J* = 7.1 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.38, 130.73, 130.66, 130.17, 128.27, 128.06, 126.78, 123.92, 123.87, 123.07, 114.56, 101.49, 61.17, 14.52.

HRMS (ESI): Calcd. For $C_{15}H_{13}NO_2$ $[M+]^+$ m/z 239.0946, found *m/z* 239.0946.

General procedure for the hydrolysis of ester 61 to acid 62[33]



61 **62**

A suspension of **61** (72 mg, 0.3 mmol, 1 equiv) and 300 mg of NaOH in 6 mL of ethanol and 6 mL of water was refluxed for 3h. The solution was concentrated under reduced pressure up to approximately half and extracted with 10 mL of diethyl ether. The aqueous layer was acidified with 10% HCl to produce an orange precipitate. The precipitate was filtered, washed with 1M HCl, water and hexane, dried overvacuum to yield (58 mg, 92%) of pure **62**.

M.p. = 151-153 °C

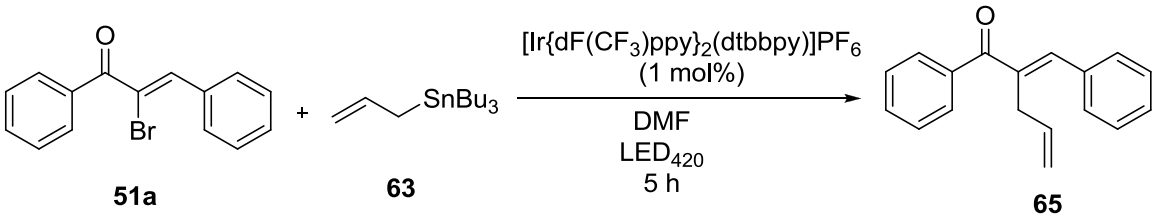
IR (neat): 3422, 1665, 1489, 1309, 1024, 995, 633 cm^{-1}.

^{1}H NMR (300 MHz, DMSO) δ = 13.30 (s, 1H), 11.38 (s, 1H), 8.30 (d, *J* = 8.5 Hz, 2H), 8.07 (t, *J* = 9.1 Hz, 1H), 7.69 – 7.58 (m, 1H), 7.48 – 7.38 (m, 2H), 7.15 (dd, *J* = 3.0, 2.0 Hz, 1H).

^{13}C NMR (75 MHz, DMSO) δ = 167.69, 129.87, 129.79, 129.52, 127.80, 127.27, 125.68, 124.60, 123.76, 123.46, 122.77, 115.60, 100.71.

HRMS (ESI): Calcd. For $C_{13}H_8NO_2$ $[M-H]^+$ m/z 210.0561, found *m/z* 210.0558.

General procedure for the Photoredeox catalyzed allylation reaction



An oven dried 10 mL vial equipped with a plastic septum and magnetic stir bar was charged with [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (1 mol %) and the α-bromochalcone **51a** (144 mg, 0.5 mmol, 1.0 equiv). The flask was purged with a stream of nitrogen and 2.0 mL of dry dimethylformamide was added. The resultant mixture was degassed for 5 min by nitrogen sparging and allyltributyltin (166 mg, 0.5 mmol, 1.0 equiv) was added to the vial. The vial was placed at a distance of ~ 0.5 -1.0 cm from a blue LED lamp (420 nm) and irradiated for 5 h. After the completion of the reaction (as judged by TLC analysis), the mixture was transferred to a separating funnel, diluted with 15 mL of ethyl acetate and washed with 20 mL of water. The aqueous layer was washed with ethyl acetate (3 × 10 mL) and the combined organic layer was dried over anhydrous sodium sulfate, solvent was removed in vacuo and the residue was subjected to colum chromatography on silica gel, using PE/EA as solvent system to get pure **65** (89 mg, 72%).

The compound is reported previously.[34]

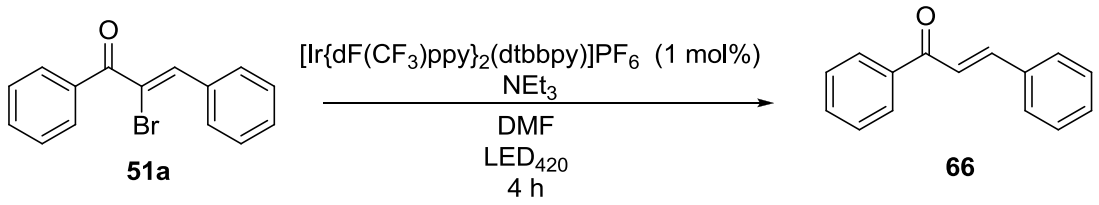
E/*Z* = 11:89

Z isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.91 – 7.82 (m, 2H), 7.49 – 7.39 (m, 2H), 7.35 – 7.24 (m, 2H), 7.16 – 7.03 (m, 5H), 6.77 (t, *J* = 1.4 Hz, 1H), 5.92 (ddt, *J* = 17.0, 10.0, 7.0 Hz, 1H), 5.22 – 5.07 (m, 2H), 3.30 – 3.19 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 200.43, 139.65, 135.67, 134.22, 133.28, 130.56, 129.45, 128.56, 128.47, 128.36, 128.17, 127.57, 117.91, 40.49.

HRMS (ESI): Calcd. For $C_{18}H_{16}NO$ $[M+]^+$ *m/z* 248.1201, found *m/z* 248.1203.

General procedure for the Photoredeox catalyzed reduction of α-bromochalcone



An oven dried 10 mL vial equipped with a plastic septum and magnetic stir bar was charged with $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (1 mol %) and the α-bromochalcone **51a** (144 mg, 0.5 mmol, 1.0 equiv). The flask was purged with a stream of nitrogen and 2.0 mL of dry dimethylformamide was added. The resultant mixture was degassed for 5 min by nitrogen sparging and triethylamine (101 mg, 1.0 mmol, 2.0 equiv) was added to the vial. The vial was placed at a distance of ~ 0.5 - 1.0 cm from a blue LED lamp (420 nm) and irradiated for 4 h. After the completion of the reaction (as judged by TLC analysis), the mixture was transferred to a separating funnel, diluted with 15 mL of ethyl acetate and washed with 20 mL of water. The aqueous layer was washed with ethyl acetate (3 × 10 mL) and the combined organic layer was dried over anhydrous sodium sulfate, solvent was removed in vacuo and the residue was subjected to colum chromatography on silica gel, using PE/EA as solvent system to get pure chalcone **66** (88 mg, 85%).

Reduction potential

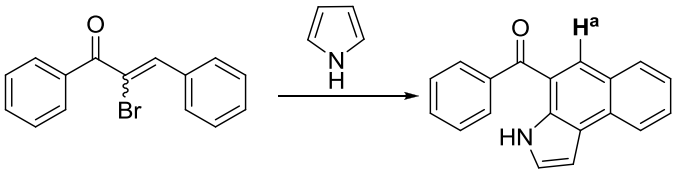
Redox potentials of the α-bromo chalcones were measured by cyclic voltammetry in DMF containing tetrabutylammonium tetrafluoruborate (0.1 M) as supporting electrolyte. All values are given vs. Saturated Calomel Eletrode (SCE).

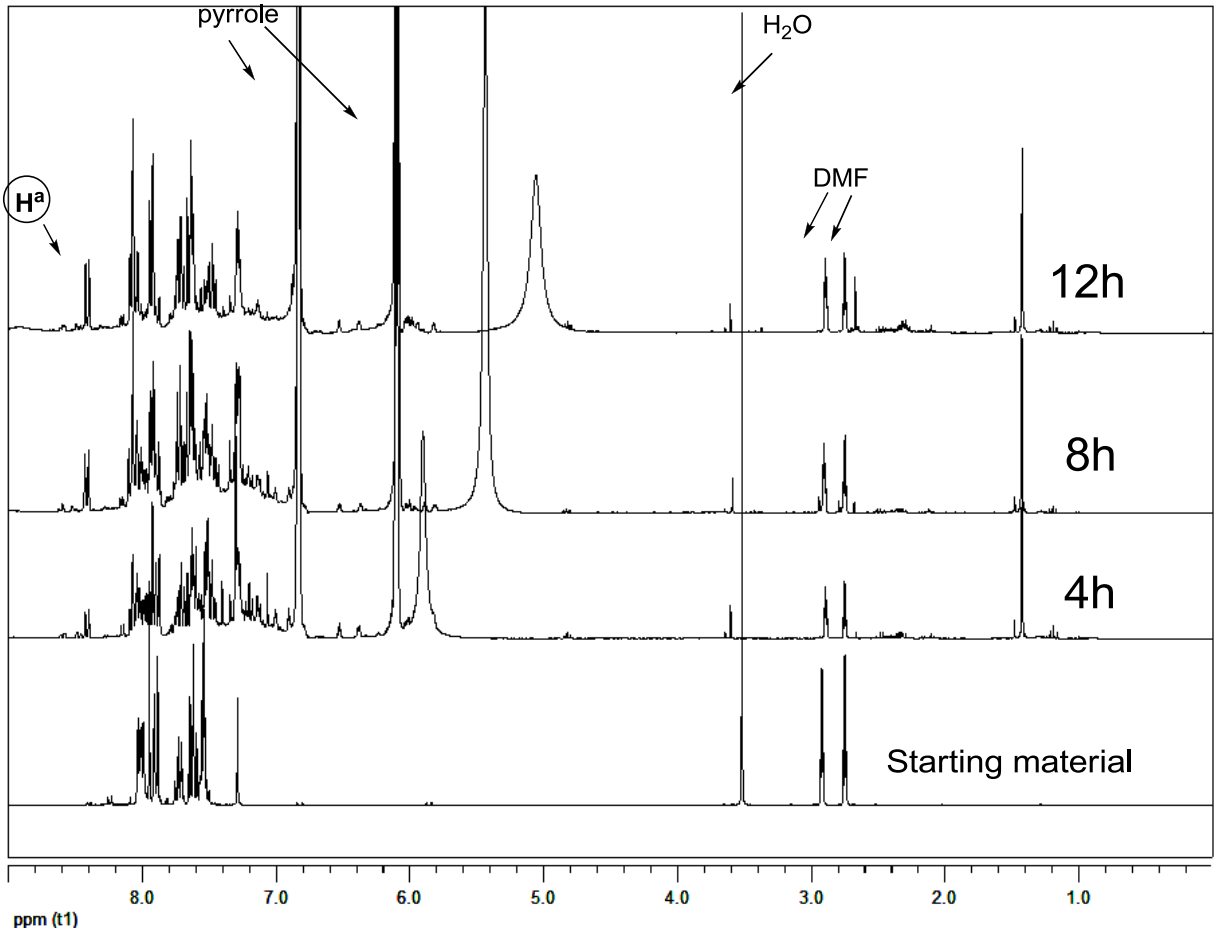
α-bromo chalcone (**51**)	Reduction potential (V)
51a	-0.88
51b	-0.89
51c	-0.90
51d	-0.84
51e	-0.75
51f	-0.89

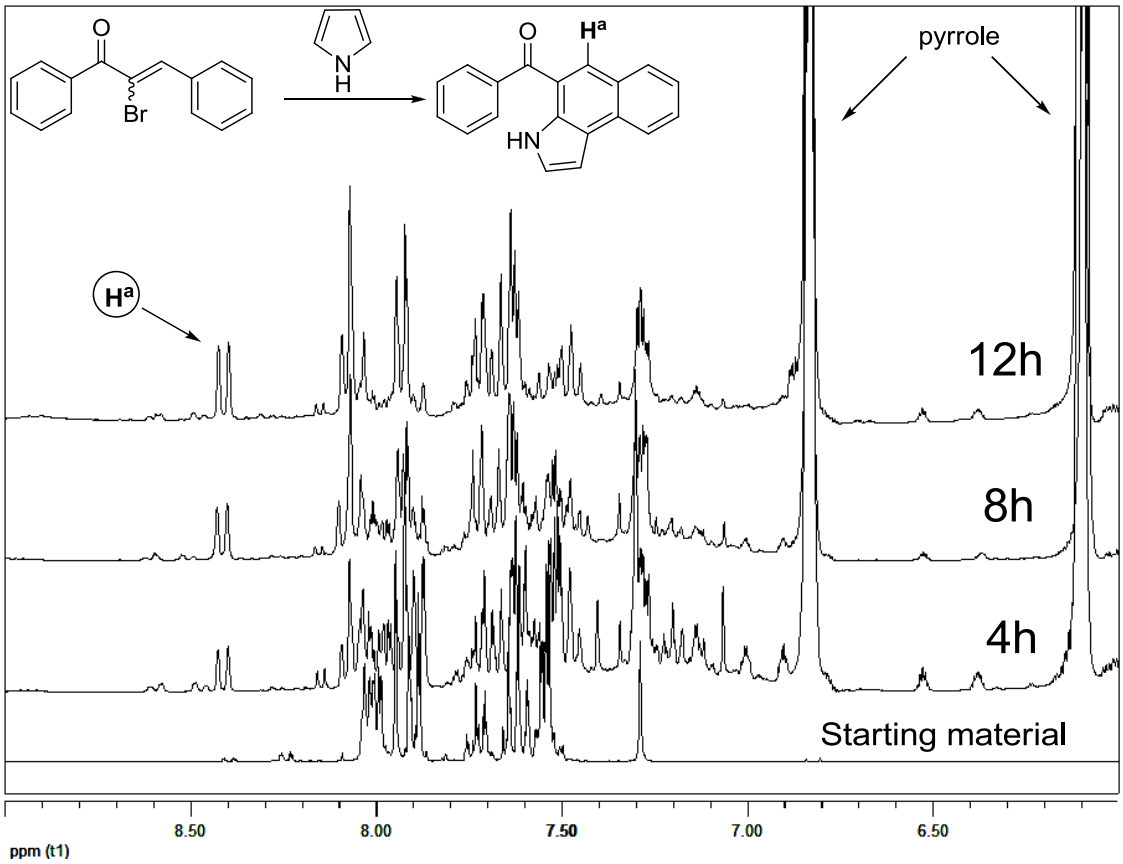
51g	-0.87
51h	-0.93
51i	-0.79
51j	-0.59
51k	-0.79
51l	-1.02
51m	-1.00
51n	-0.92
58	-0.72
60	-0.97

DMF-d^7 Experiment

An oven dried 10 mL vial equipped with a plastic septum and magnetic stir bar was charged with $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (1 mol %) and the α-bromochalcone **1a** (30 mg, 0.10 mmol, 1.0 equiv). The flask was purged with a stream of nitrogen and 0.5 mL of DMF-D^7 was added. The resultant mixture was degassed for 5 min by nitrogen sparging and pyrrole (21 mg, 0.3 mmol, 3.0 equiv) was added to the vial. The vial was placed at a distance of ~ 0.5 -1.0 cm from a blue LED lamp (420 nm) and irradiated for 4 h. The reaction mixture was transferred to an nmr tube under nitrogen and spectra was recorded. The 8h and 12h experiments were performed in separate vials for respective hours. It was clearly visible that characteristic signal for proton $\mathbf{H^a}$ at 8.21 ppm already appeared after 4h of irradiation and the intensity increased with time.


O
Br
N
H
O
Ha
HN


pyrrole
H2O
Ha
DMF
12h
8h
4h
Starting material
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)



Crystallographic information

Table S1. Crystallographic data and structure refinement parameters for compounds **55ga**

Compound	**55ga**	***V* [Å^3]**	1490.40 (8)
Formula	$C_{21}H_{16}O_2$	**Z**	4
Mr	300.34	**ρ_{calcd} [g cm^{-3}]**	1.339
Cryst size[mm]	0.14 × 0.03 × 0.03	***μ*(Cu K*α*) [mm^{-1}]**	0.673
Cryst colour	colorless	***F*(000)**	632

Cryst description	stick	**reflns collected**	8673
Cryst System	orthorhombic	**unique reflns**	2819
Space group	$P2_12_12_1$	R_{int}	0.029
T[K]	123	**reflns with $I > 2\sigma(I)$**	2586
***a* [Å]**	4.0524 (1)	**parameters/restraints**	211/0
***b* [Å]**	14.5480 (5)	**GOF on F^2**	1.04
***c* [Å]**	25.2805 (9)	**R1 [$I > 2\sigma(I)$]**	0.033
***α* [deg]**	90	**wR2 (all data)**	0.085
***β* [deg]**	90	**Largest difference peak/hole [e Å^{-3}]**	+0.16/-0.20

Table S2. Selected geometric parameters (Å, °)

O1-C1	1.2228 (19)	O2—C4	1.3812 (19)
O2—C3	1.3743 (19)		
C3—O2—C4	105.17 (11)	O2—C3—C2	125.40 (13)
O1—C1—C2	118.63 (14)	O2—C3—C6	110.44 (13)
O1—C1—C15	120.35 (14)	O2—C4—C5	112.37 (14)

Table S3 Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O1^{i}	0.9300	2.3700	3.250 (2)	159.00
C16—H16···O2^{ii}	0.9300	2.5700	3.4105 (19)	150.00

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1/2; (ii) *x*+1, *y*, *z*.

Table S2. Crystallographic data and structure refinement parameters for compounds **57ba**

Compound	**57ba**	***V* [Å^3]**	701.02 (7)
Formula	$C_{19}H_{12}ClNO$	**Z**	2
Mr	305.75	**ρ_{calcd} [g cm^{-3}]**	1.449
Cryst size[mm]	0.14 × 0.04 × 0.03	***μ*(Cu K*α*) [mm^{-1}]**	2.40
Cryst colour	faint yellow	***F*(000)**	316
Cryst description	stick	**reflns collected**	6079
Cryst System	triclinic	**unique reflns**	2688
Space group	P_1	**R_{int}**	0.022
T[K]	123	**reflns with *I* > 2σ(I)**	2366
***a* [Å]**	3.8986 (2)	**parameters/restraints**	202/0
***b* [Å]**	12.3782 (7)	**GOF on *F* ^{2}**	1.03
***c* [Å]**	15.1085 (8)	**R1 [*I* > 2σ(I)]**	0.034
***α* [deg]**	76.021 (5)	**wR2 (all data)**	0.040
***β* [deg]**	82.896 (5)	**Largest difference peak/hole [e Å^{-3}]**	+0.24/-0.29
***γ* [deg]**	85.259 (5)	**CCDC number**	

Table 2 Selected geometric parameters (Å, °)

Cl1—C1	1.7426 (16)	N1—C9	1.370 (2)
O1—C13	1.224 (2)	N1—C10	1.366 (2)
C9—N1—C10	108.99 (13)	N1—C10—C7	107.55 (14)
Cl1—C1—C2	117.99 (12)	N1—C10—C11	129.85 (14)
Cl1—C1—C6	119.25 (13)	O1—C13—C11	119.85 (16)
N1—C9—C8	109.72 (14)	O1—C13—C14	118.84 (15)

Table 3 Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O1	0.84 (2)	2.29 (2)	2.7722 (19)	116.5 (17)
N1—H1N···O1^{i}	0.84 (2)	2.13 (2)	2.9417 (18)	162 (2)

Symmetry code: (i) −*x*, −*y*, −*z*+2.

Computing details

Data collection: *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.11 (release 16-05-2011 CrysAlis171 .NET); cell refinement: CrysAlisPro, Agilent Technologies, Version 1.171.35.11 (release 16-05-2011 CrysAlis171 .NET); data reduction: *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.11 (release 16-05-2011 CrysAlis171 .NET); program(s) used to solve structure: *SIR97* (Altomare, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *PLATON* (Spek, 2003).

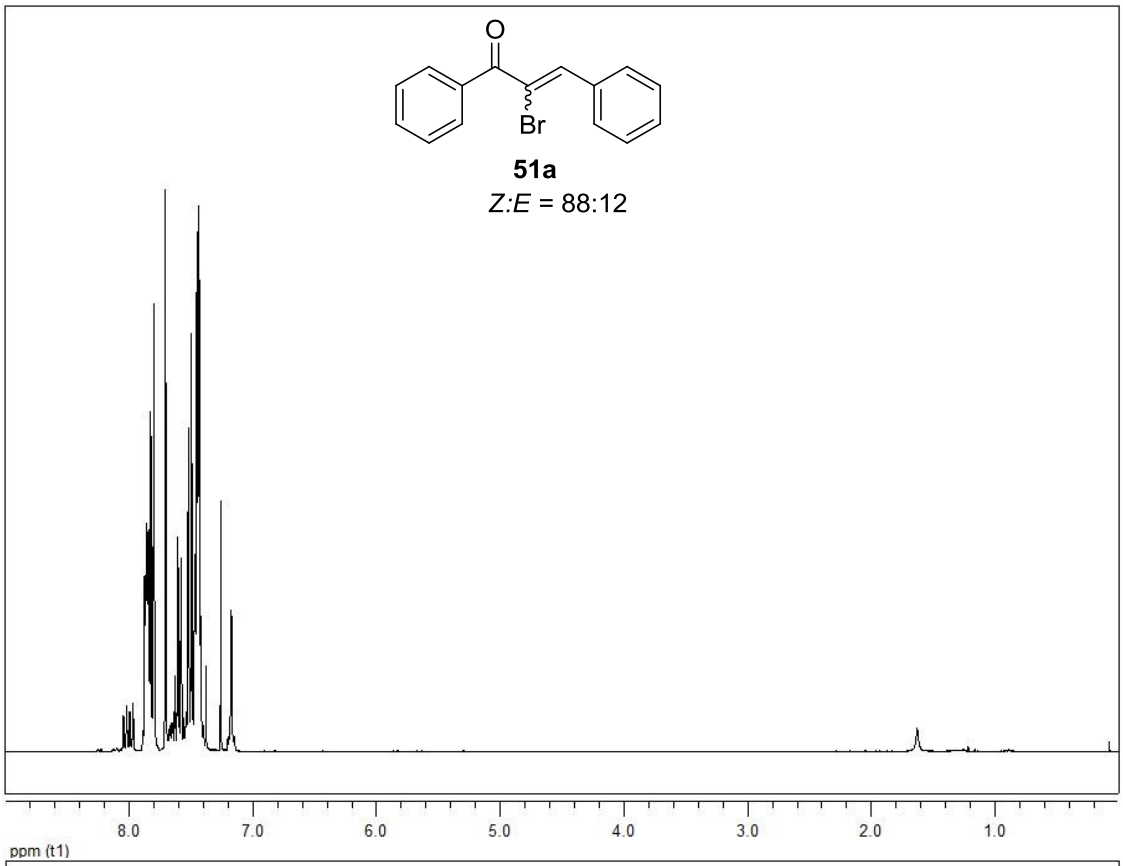
Appendix

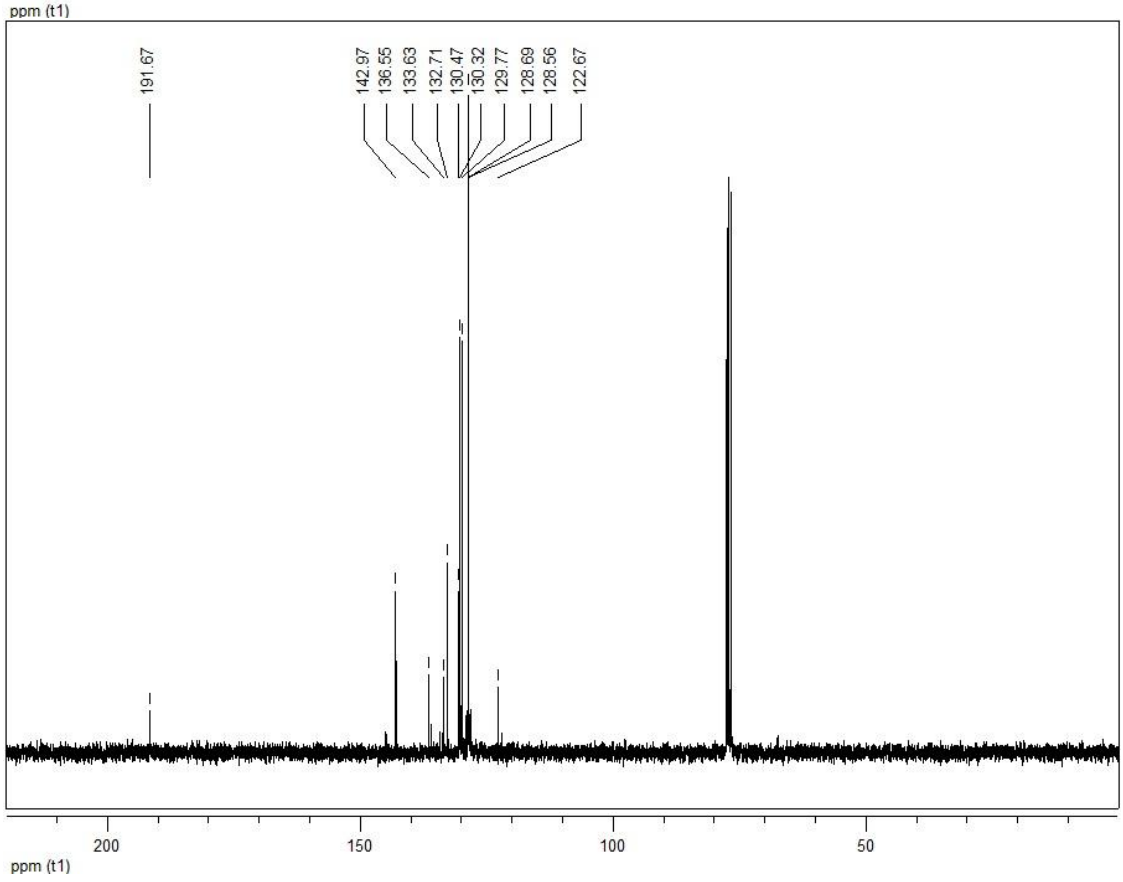
Selected NMR- spectra

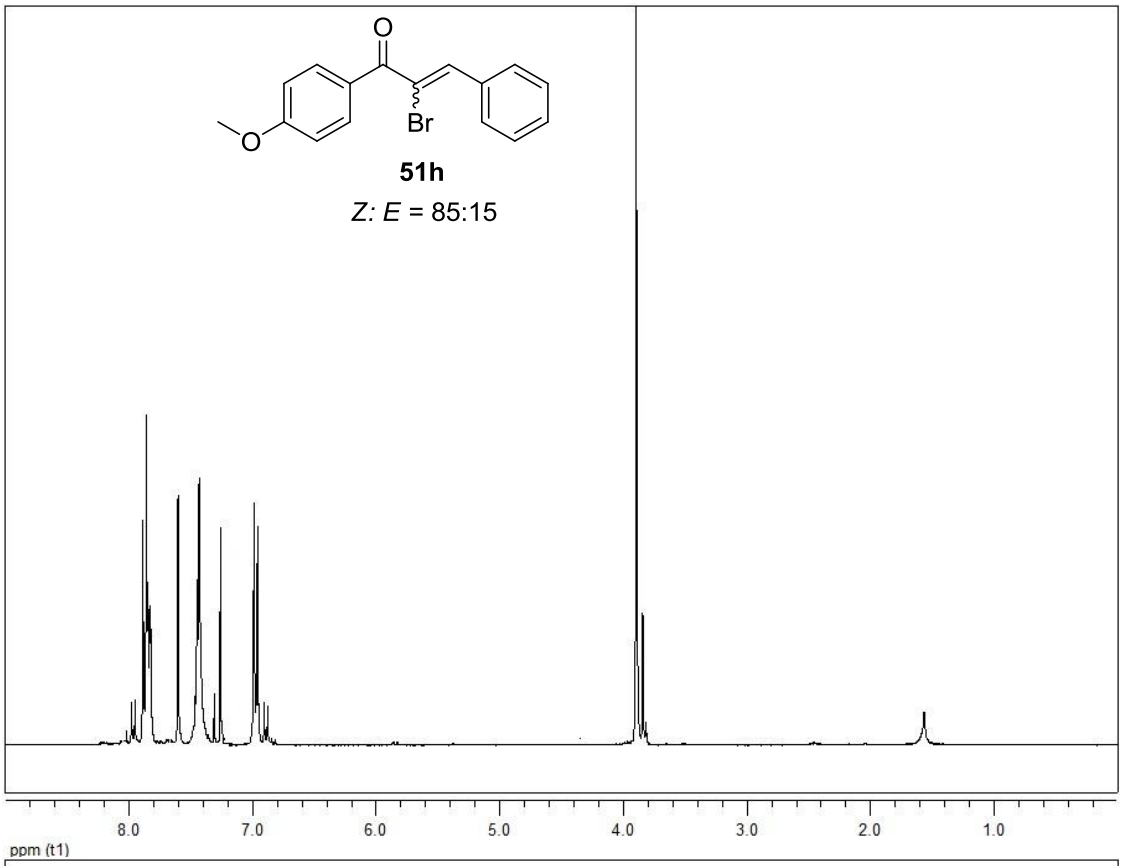
^{1}H-NMR spectra - upper image

^{13}C-NMR spectra - lower image

Solvent, if not stated otherwise: $CDCl_3$

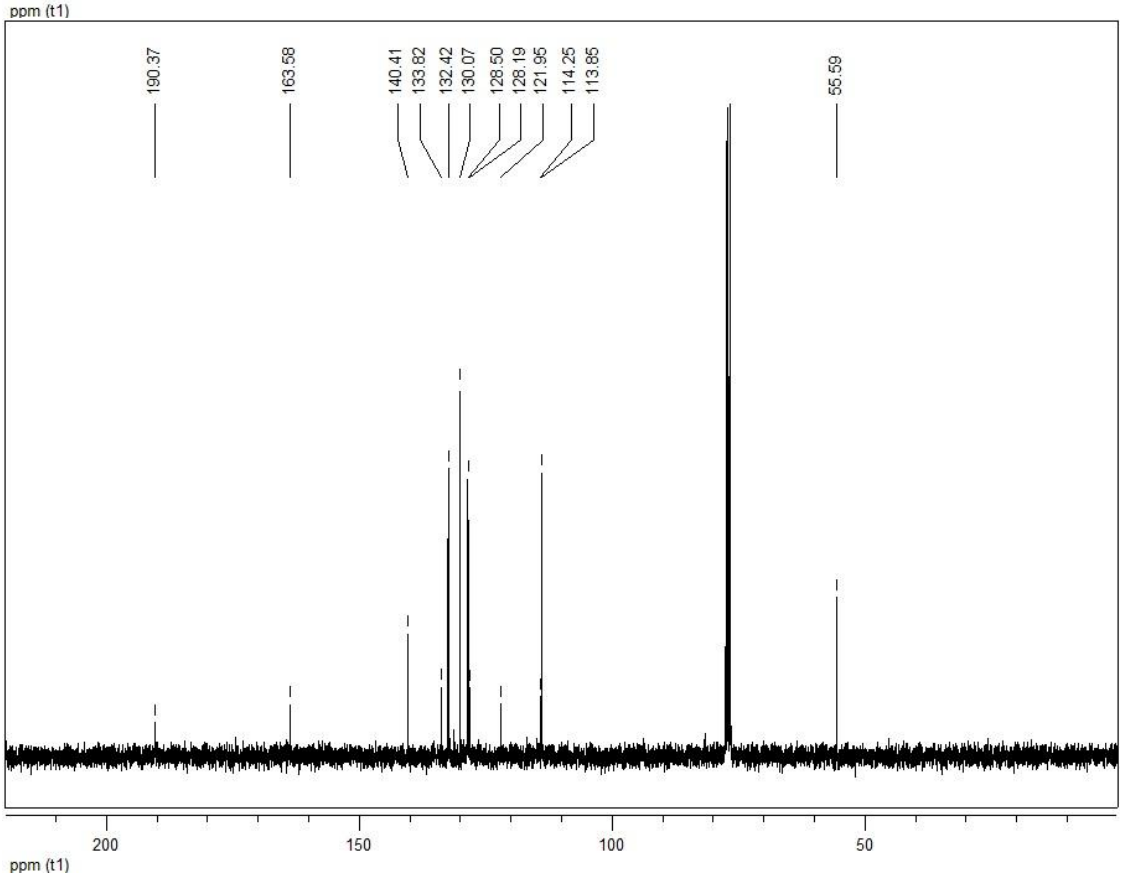

O
Br
51a
Z:E = 88:12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

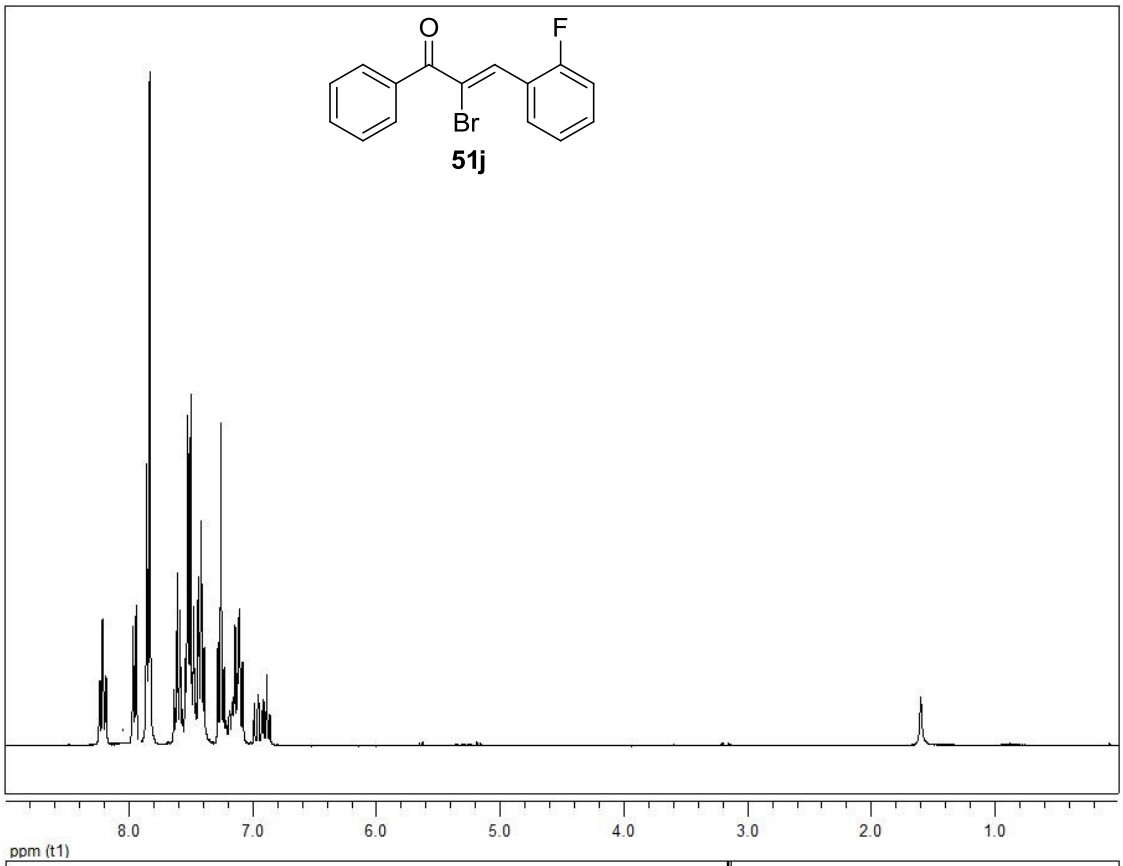

191.67
142.97
136.55
133.63
132.71
130.47
130.32
129.77
128.69
128.56
122.67
200
150
100
50
ppm (t1)


O
Br
O
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

51h

Z: E = 85:15


190.37
163.58
140.41
133.82
132.42
130.07
128.50
128.19
121.95
114.25
113.85
55.59
200
150
100
50
ppm (t1)


O
F
Br
51j
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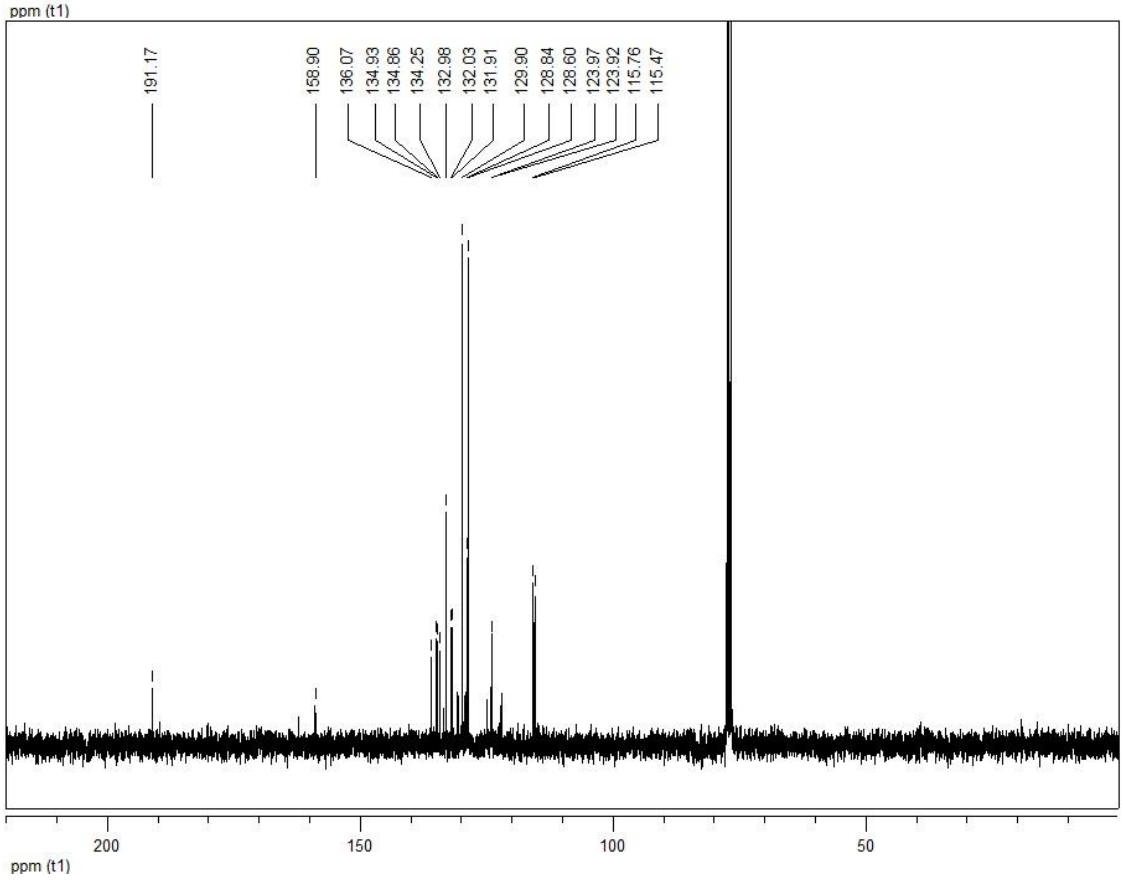
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


191.17
158.90
136.07
134.93
134.86
134.25
132.98
132.03
131.91
129.90
128.84
128.60
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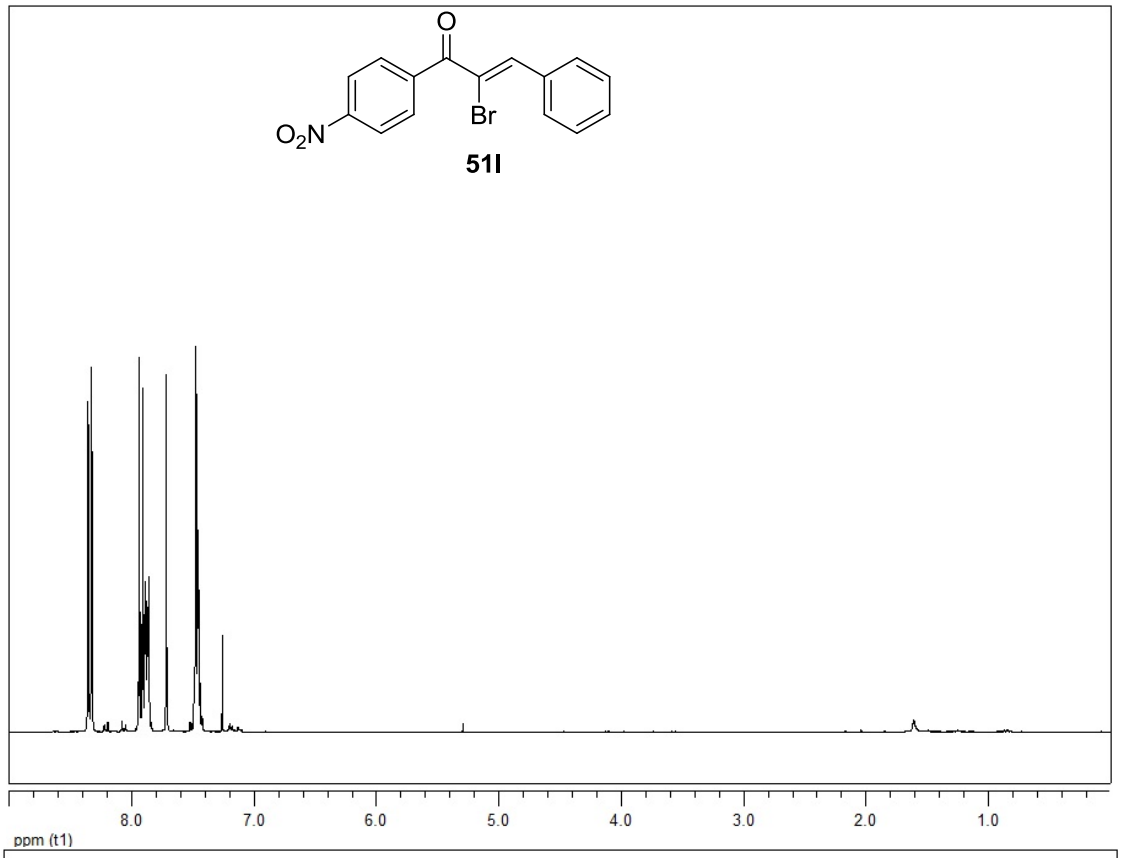
115.76
115.47
200
150
100
50
ppm (t1)


O
Br
O_2N
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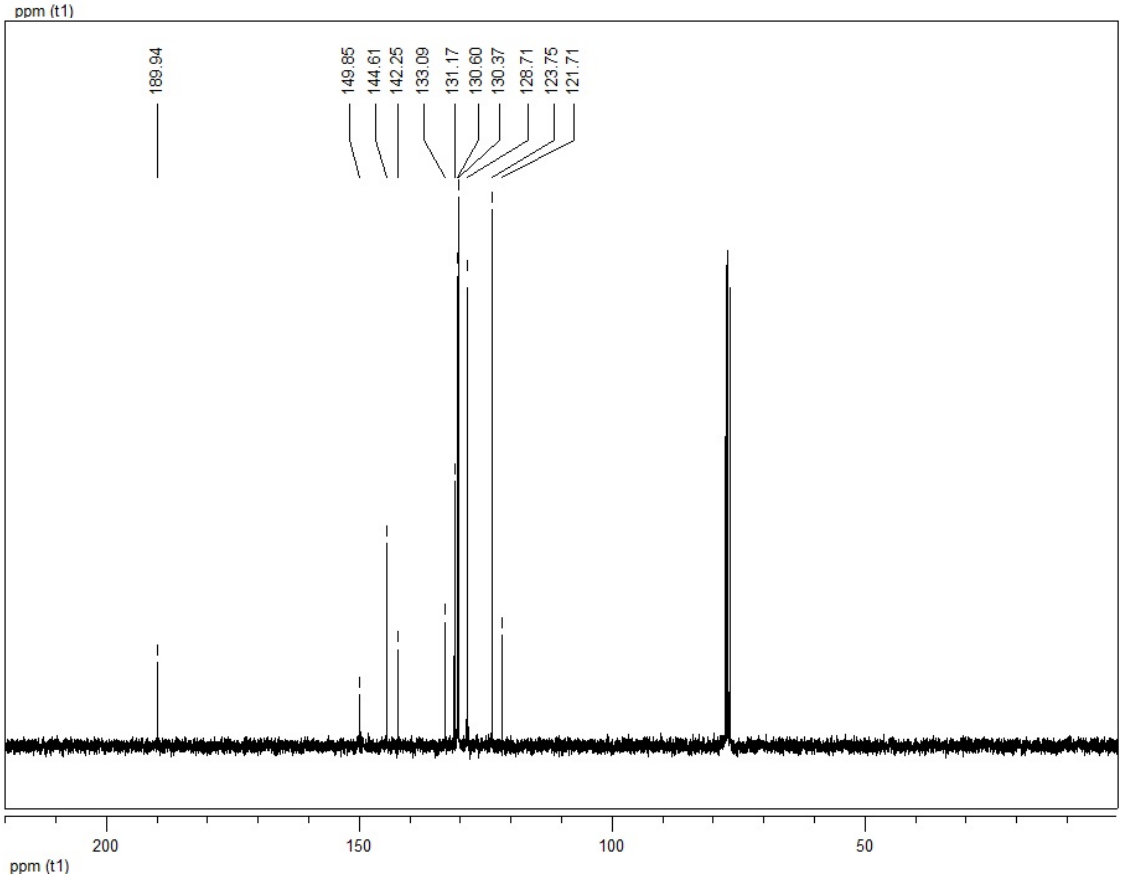
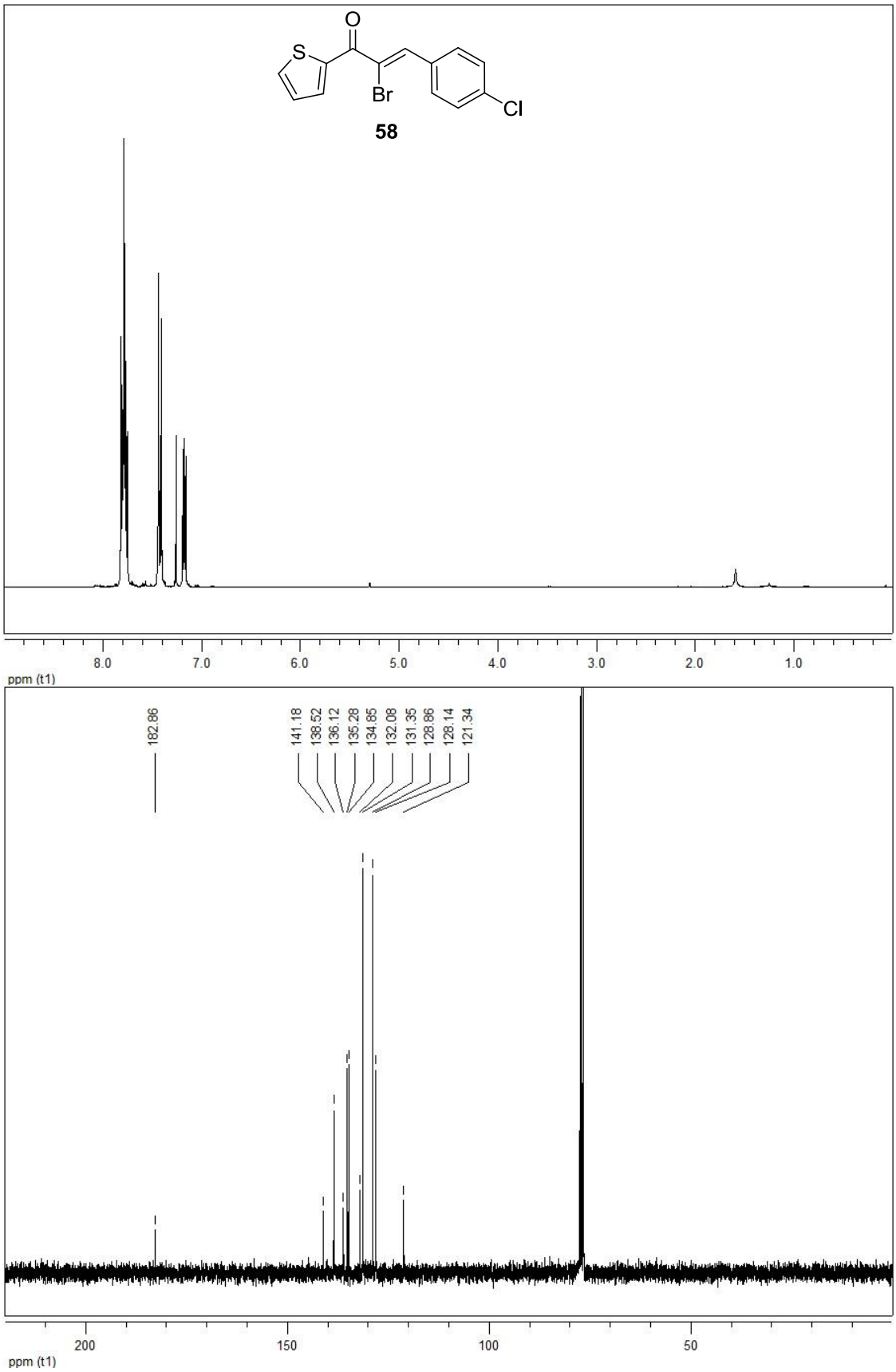
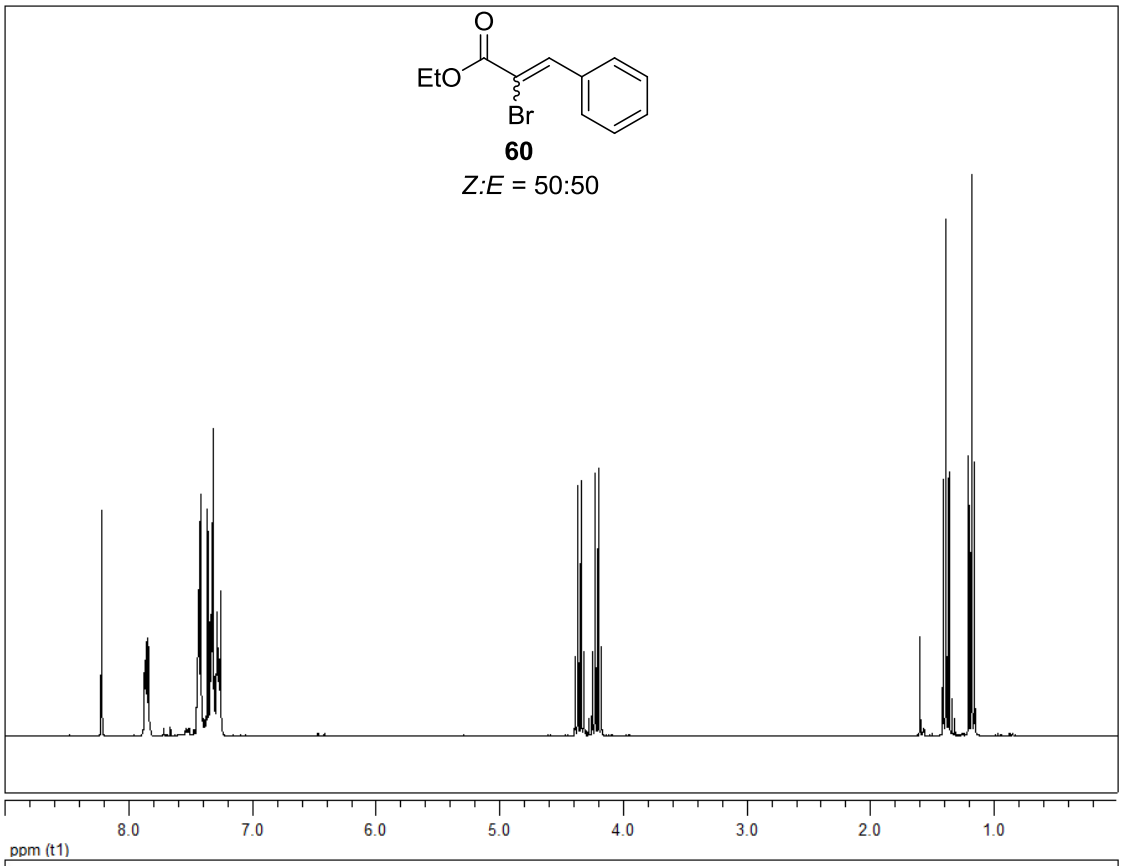
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

51l

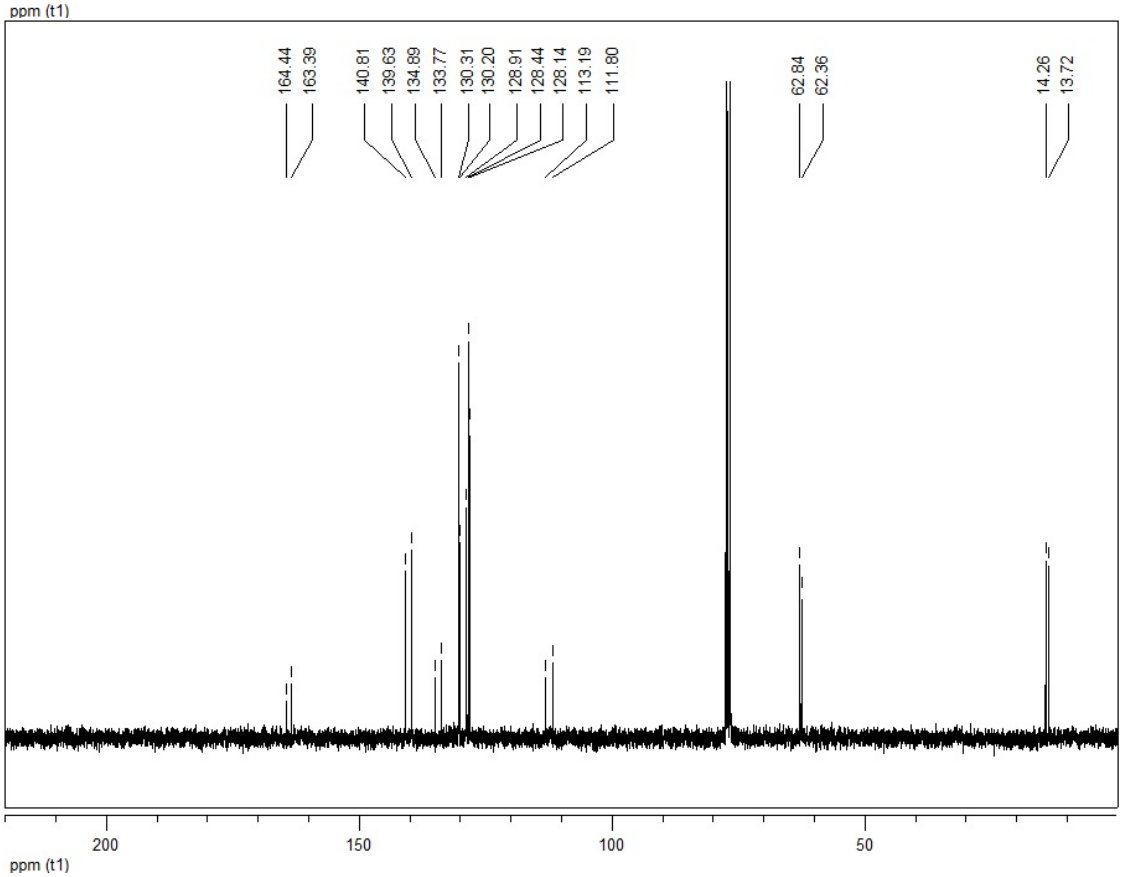

189.94
149.85
144.61
142.25
133.09
131.17
130.60
130.37
128.71
123.75
121.71
200
150
100
50
ppm (t1)


O
S
Br
Cl
58
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
182.86
141.18
138.52
136.12
135.28
134.85
132.08
131.35
128.86
128.14
121.34
200
150
100
50
ppm (t1)


O
EtO
Br
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

60

Z:*E* = 50:50


164.44
163.39
140.81
139.63
134.89
133.77
130.31
130.20
128.91
128.44
128.14
113.19
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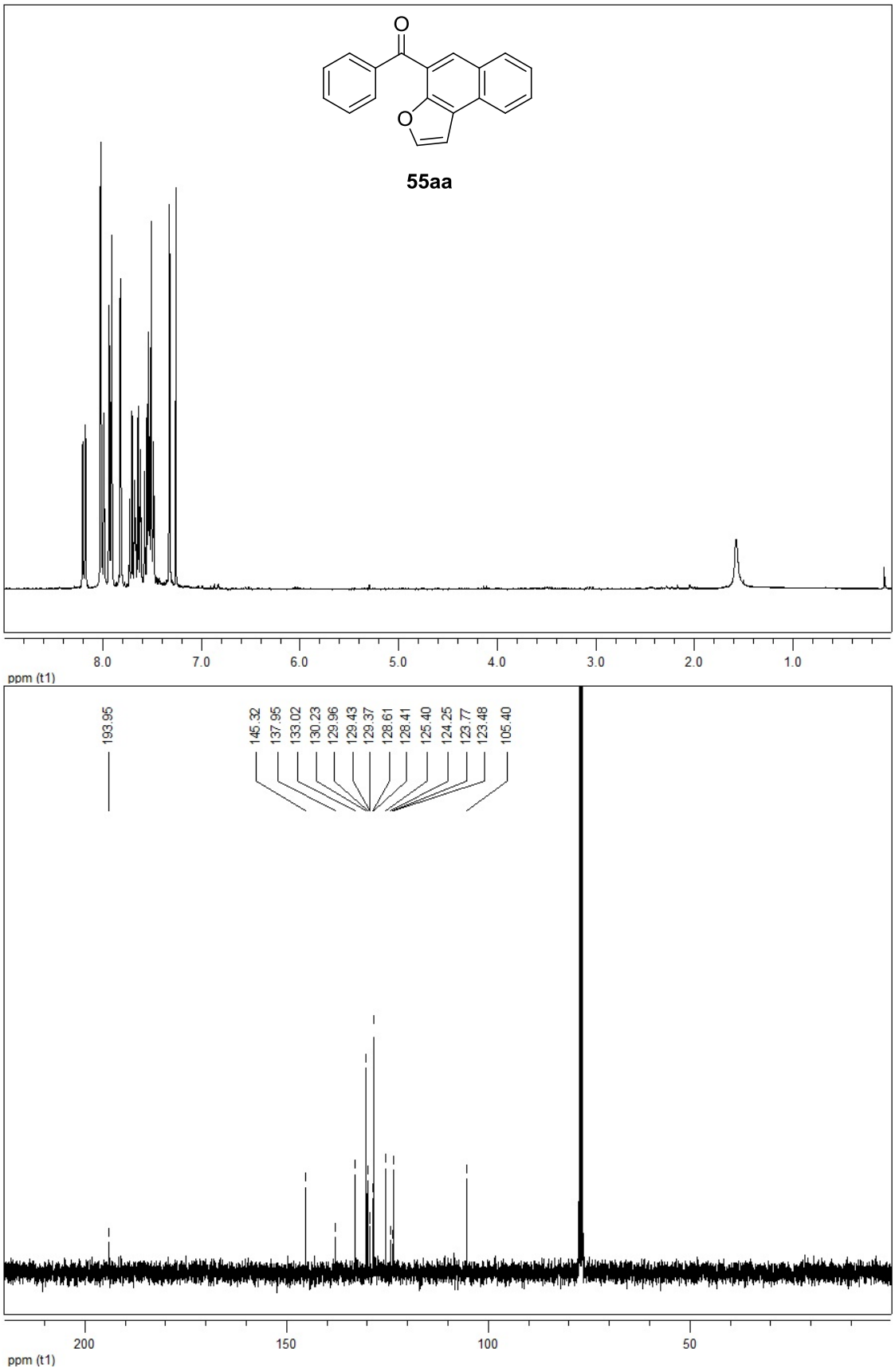
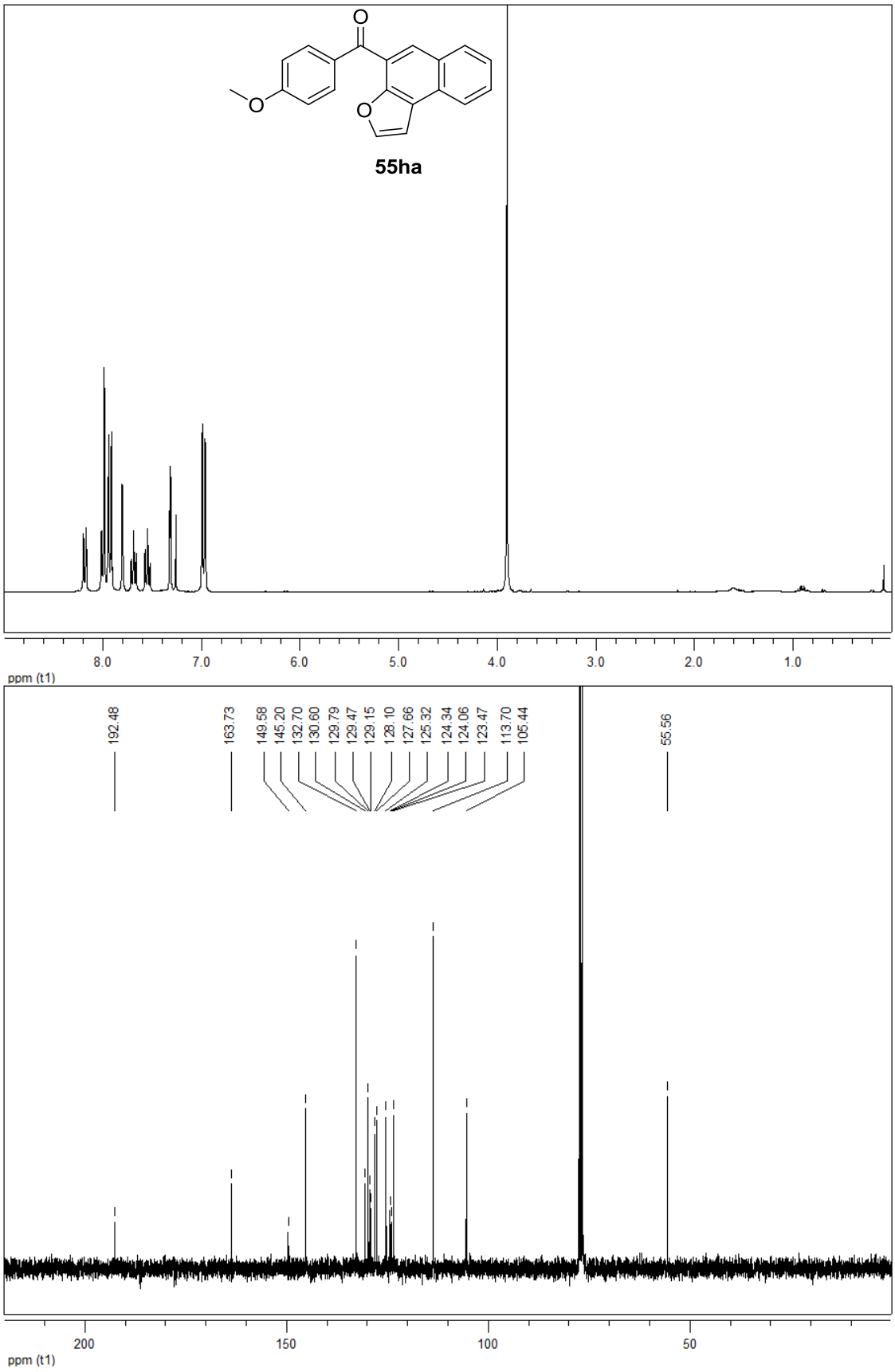
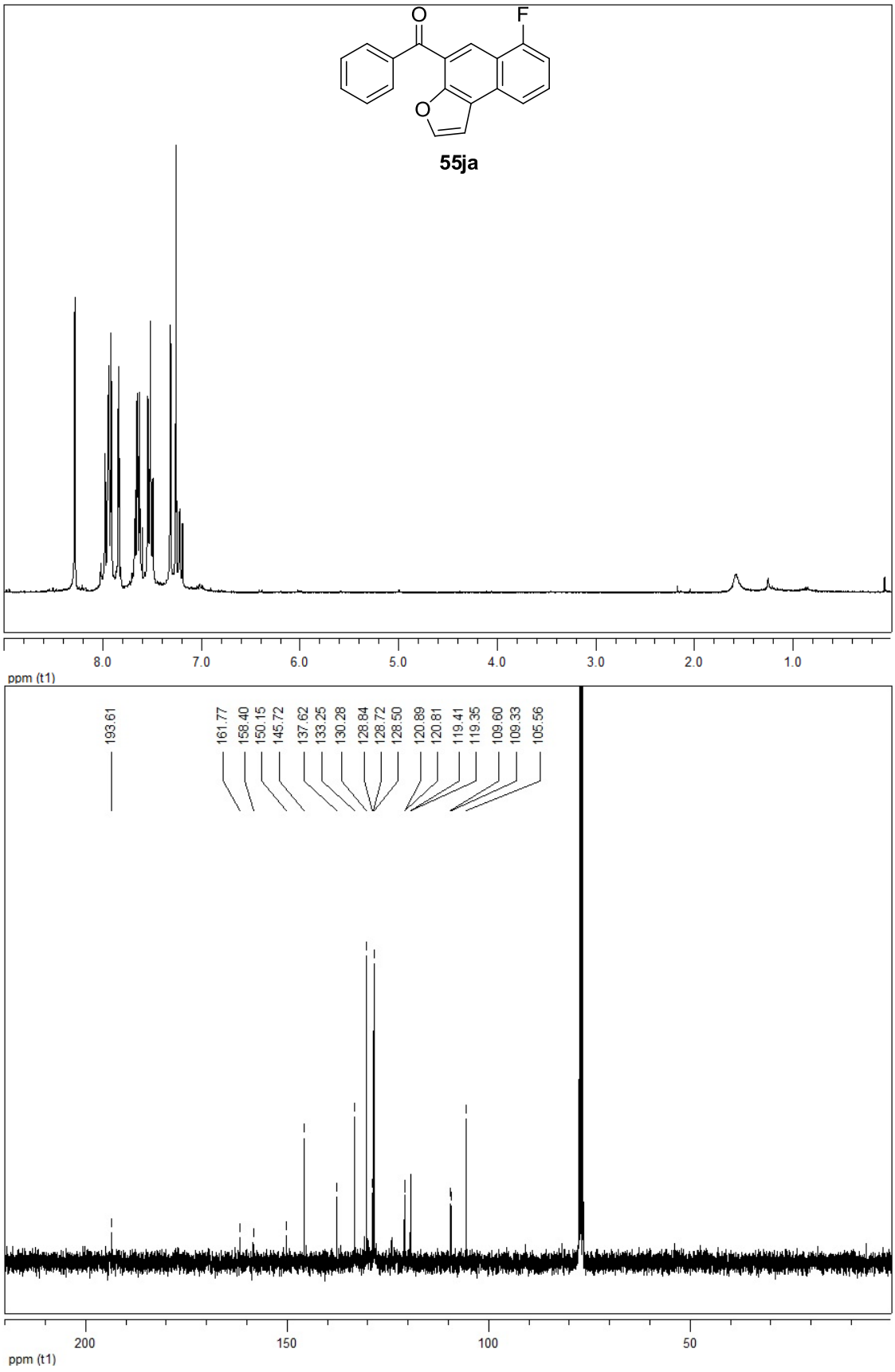
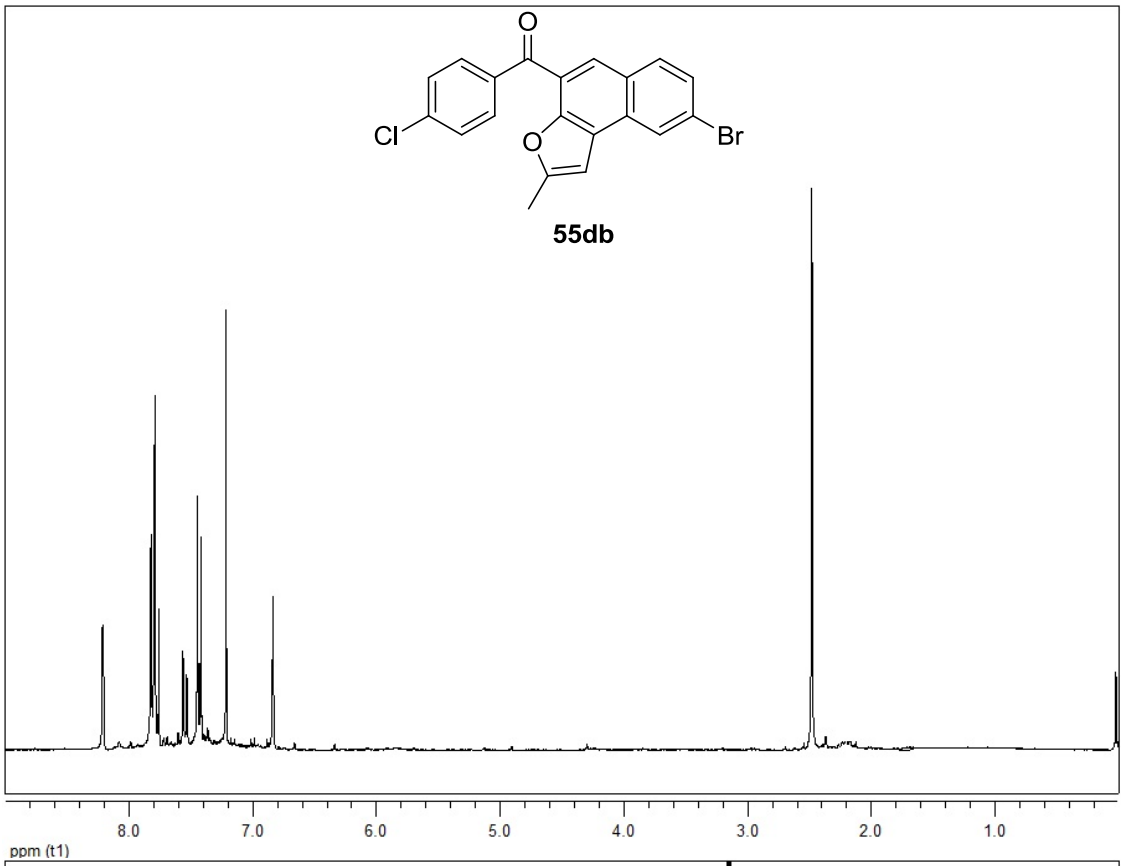
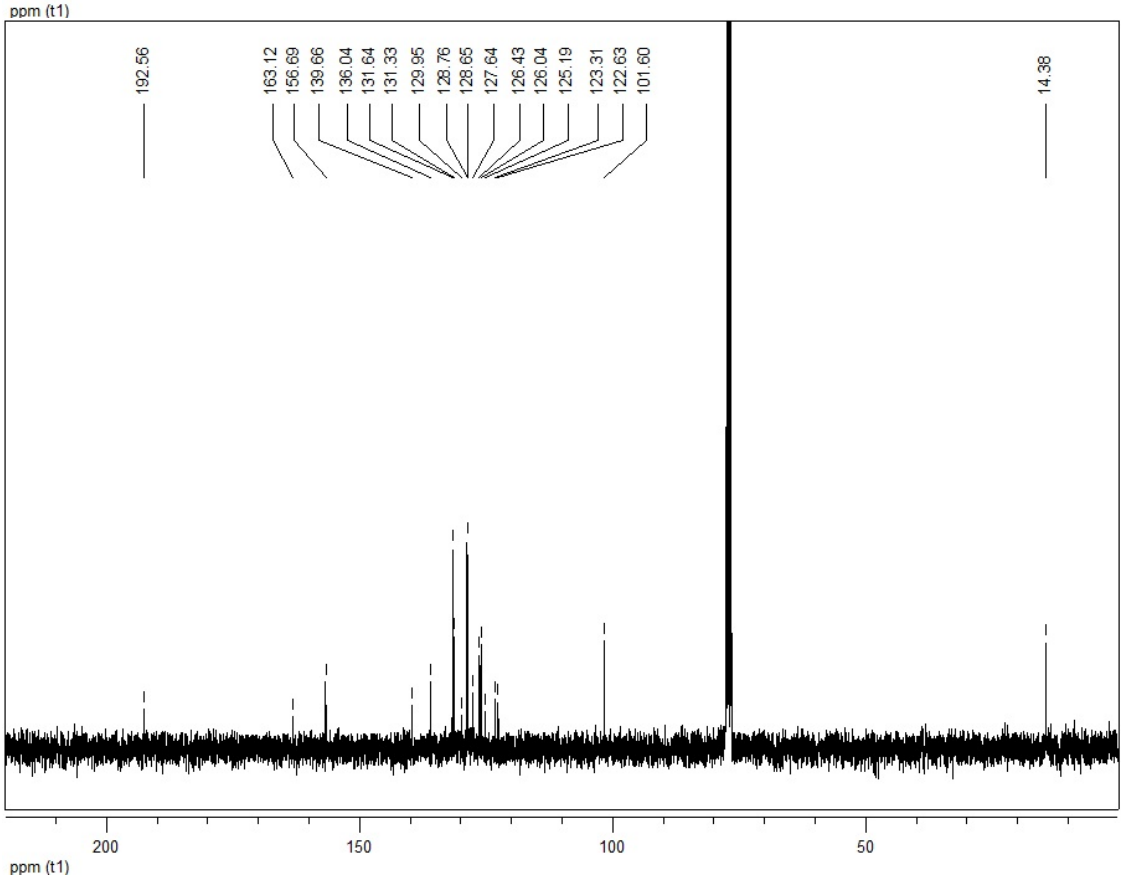
14.26
13.72
200
150
100
50
ppm (t1)

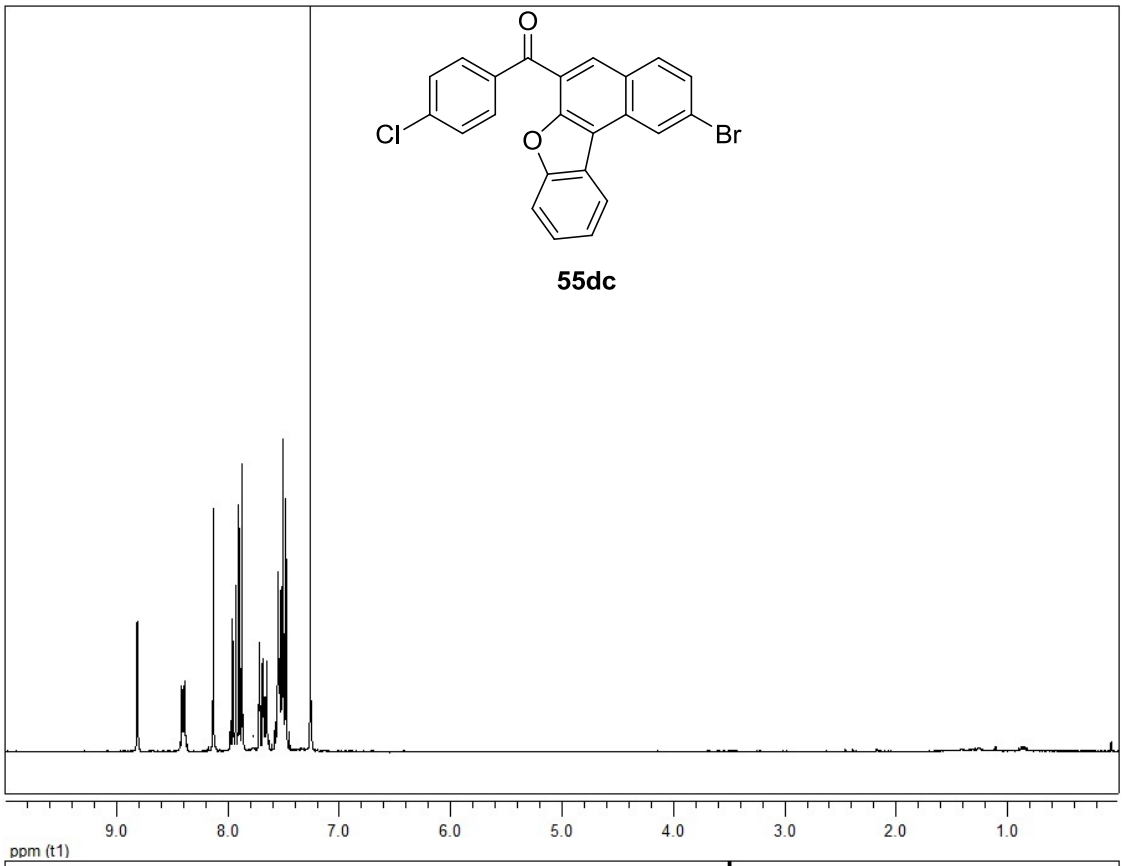

O
O
55aa
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
193.95
145.32
137.95
133.02
130.23
129.96
129.43
129.37
128.61
128.41
125.40
124.25
123.77
123.48
105.40
200
150
100
50
ppm (t1)

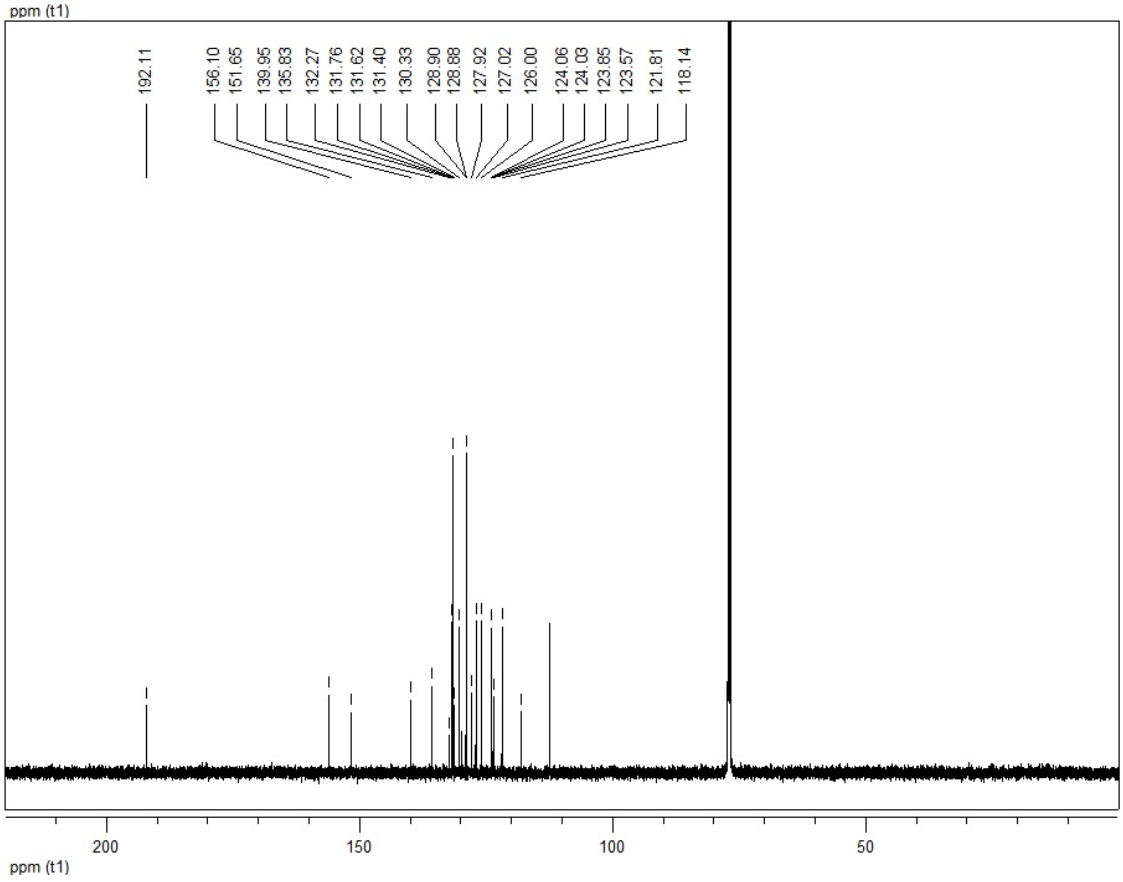

55ha
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
192.48
163.73
149.58
145.20
132.70
130.60
129.79
129.47
129.15
128.10
127.66
125.32
124.34
124.06
123.47
113.70
105.44
55.56
200
150
100
50
ppm (t1)

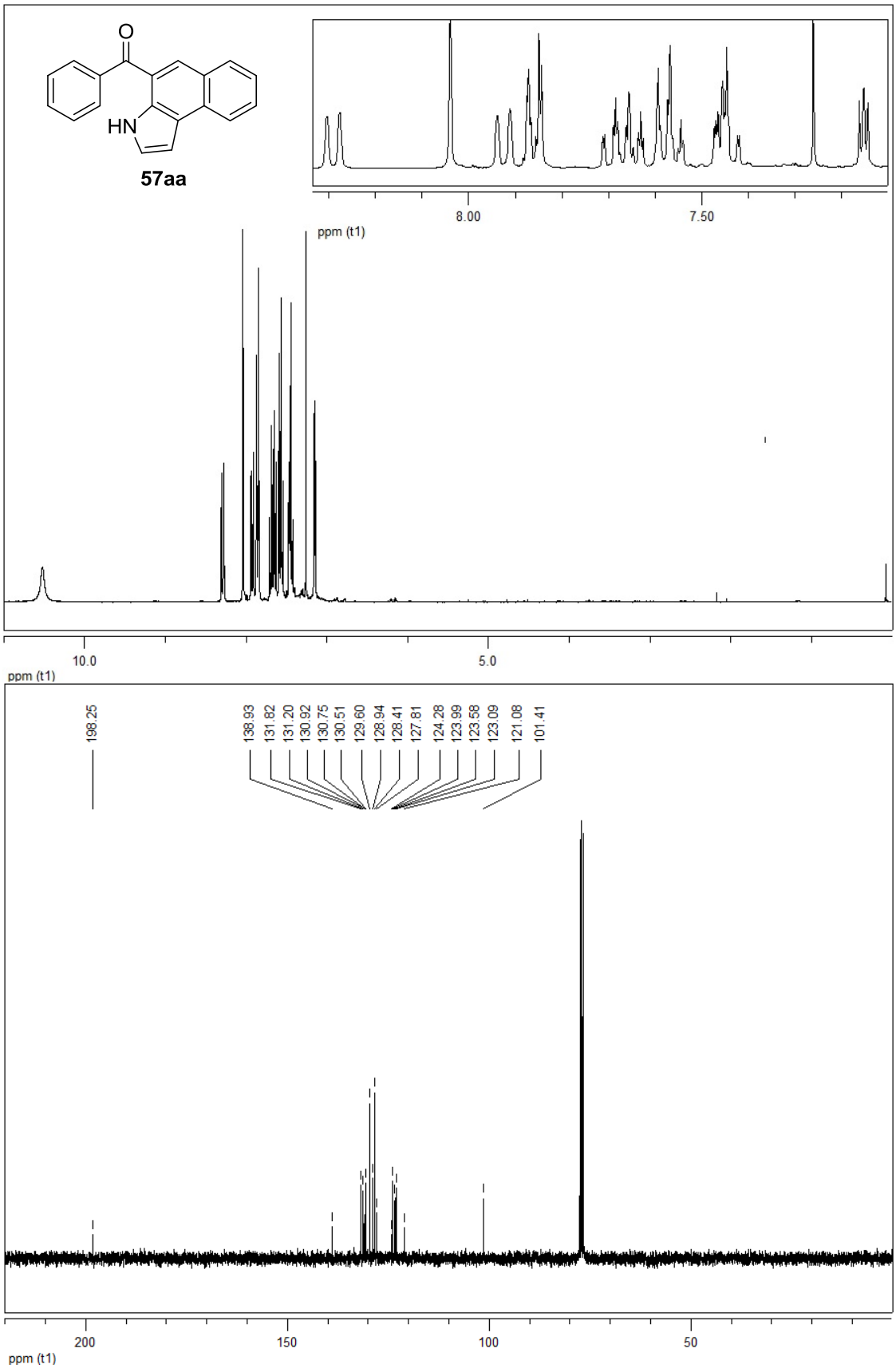

O
F
O
55ja
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
193.61
161.77
158.40
150.15
145.72
137.62
133.25
130.28
128.84
128.72
128.50
120.89
120.81
119.41
119.35
109.60
109.33
105.56
200
150
100
50
ppm (t1)

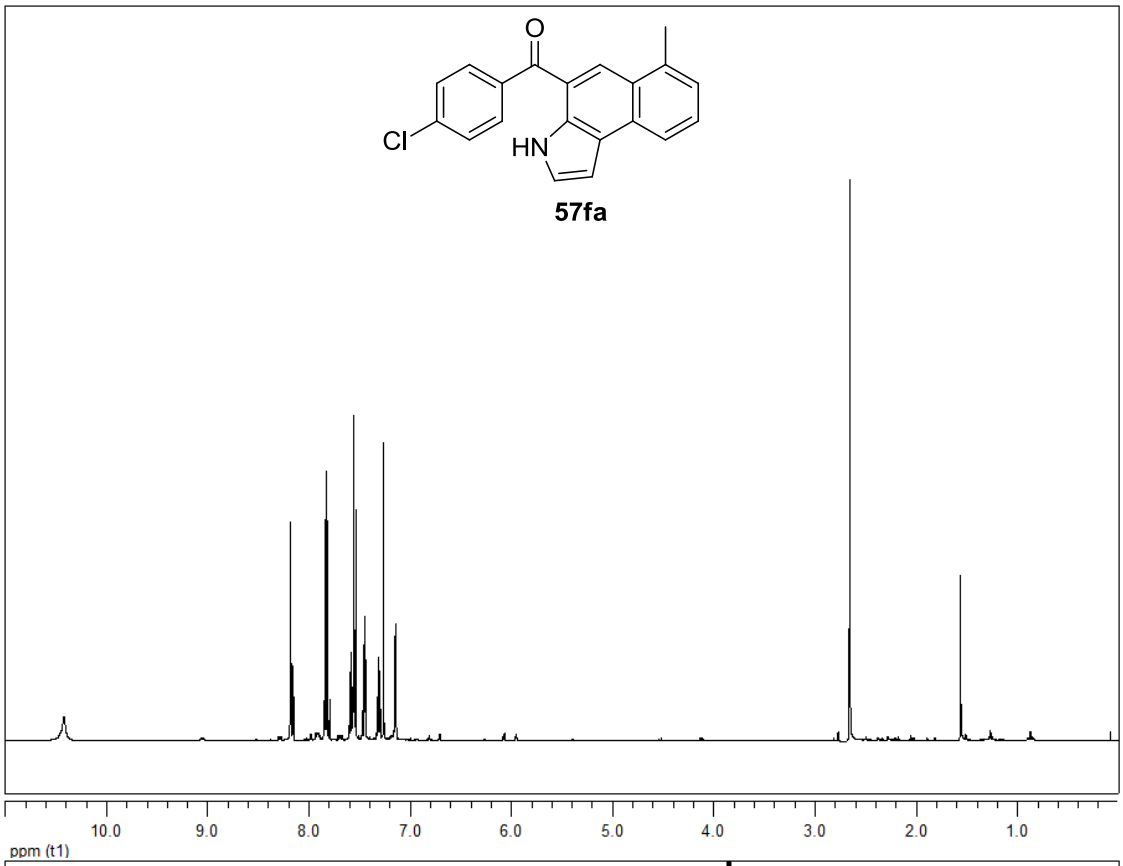

O
Cl
O
Br
55db
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


192.56
163.12
156.69
139.66
136.04
131.64
131.33
129.95
128.76
128.65
127.64
126.43
126.04
125.19
123.31
122.63
101.60
14.38
200
150
100
50
ppm (t1)

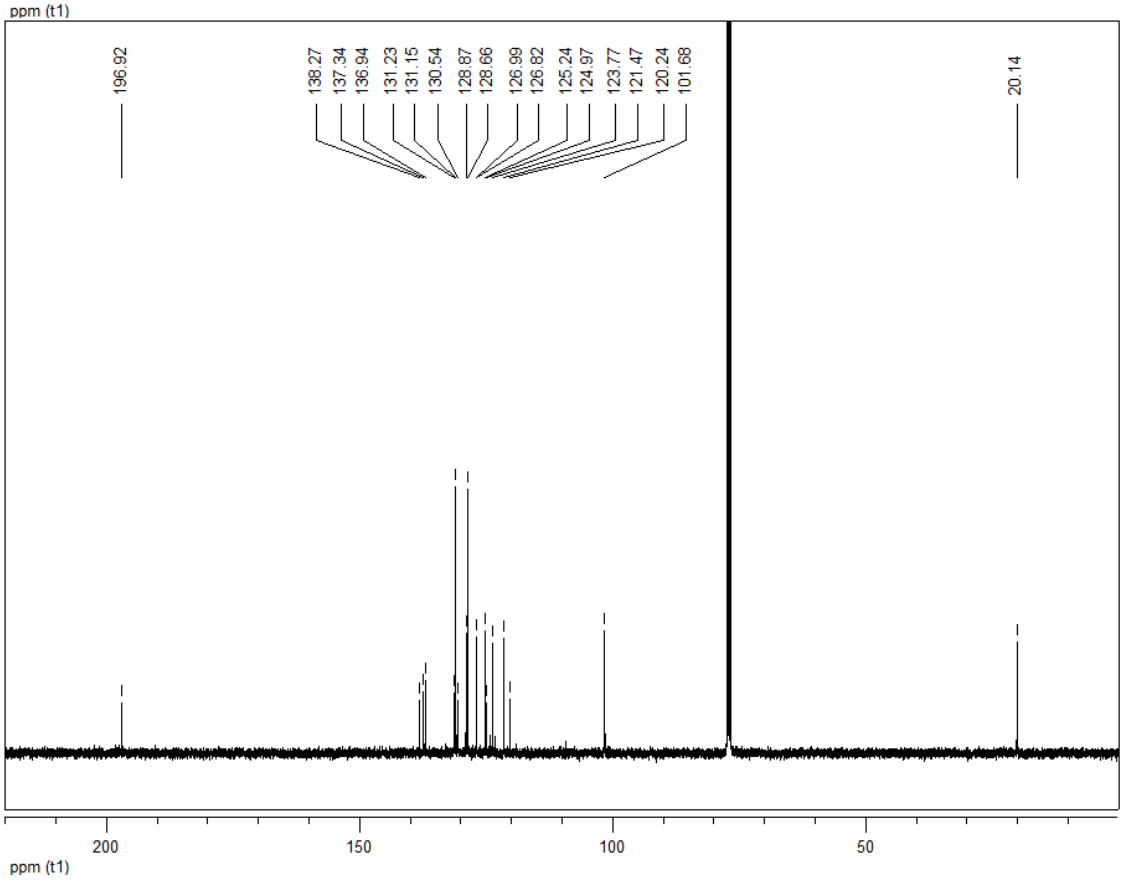

O
Cl
O
Br
55dc
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

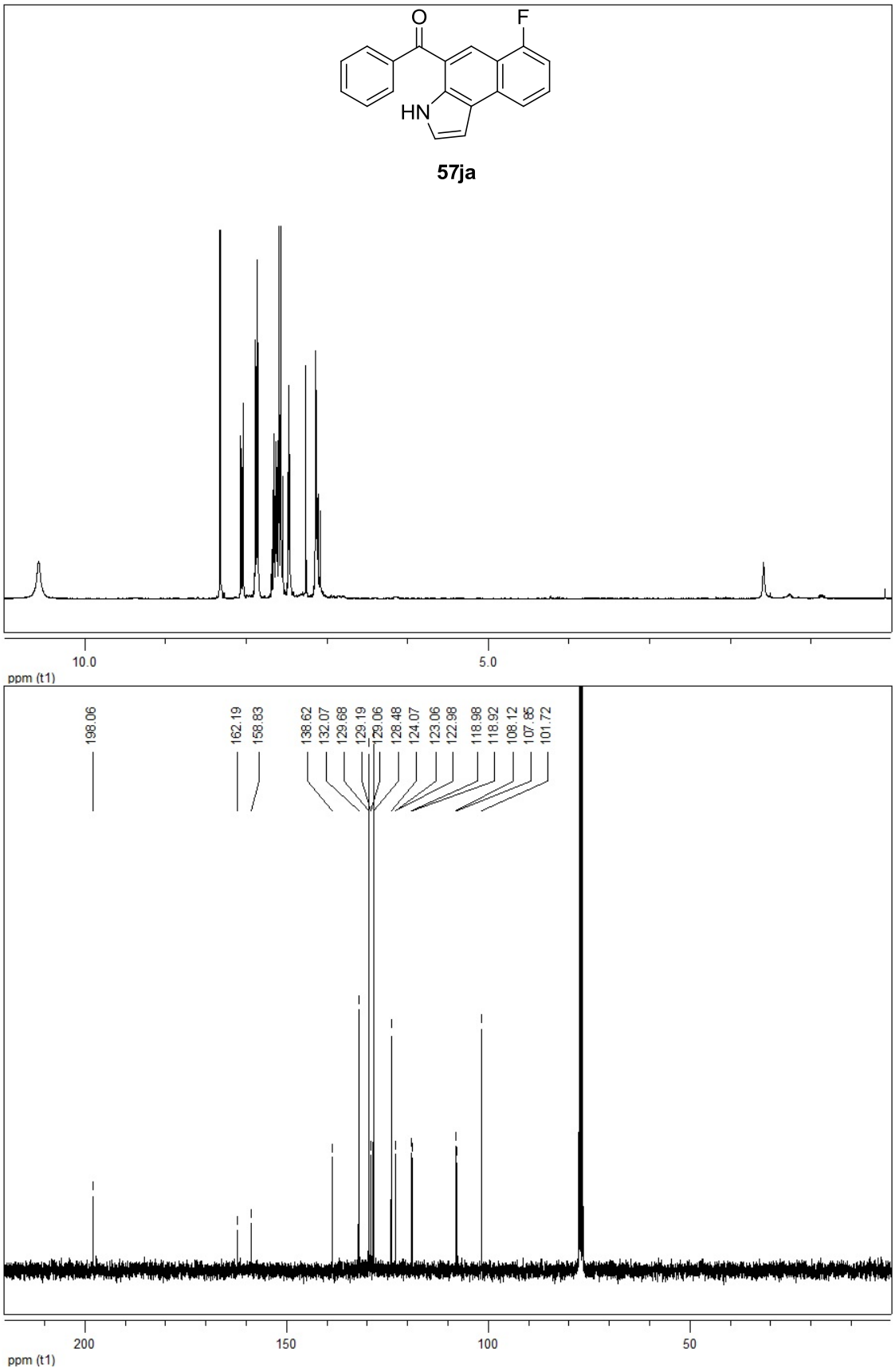

192.11
156.10
151.65
139.95
135.83
132.27
131.76
131.62
131.40
130.33
128.90
128.88
127.92
127.02
126.00
124.06
124.03
123.85
123.57
121.81
118.14
200
150
100
50
ppm (t1)

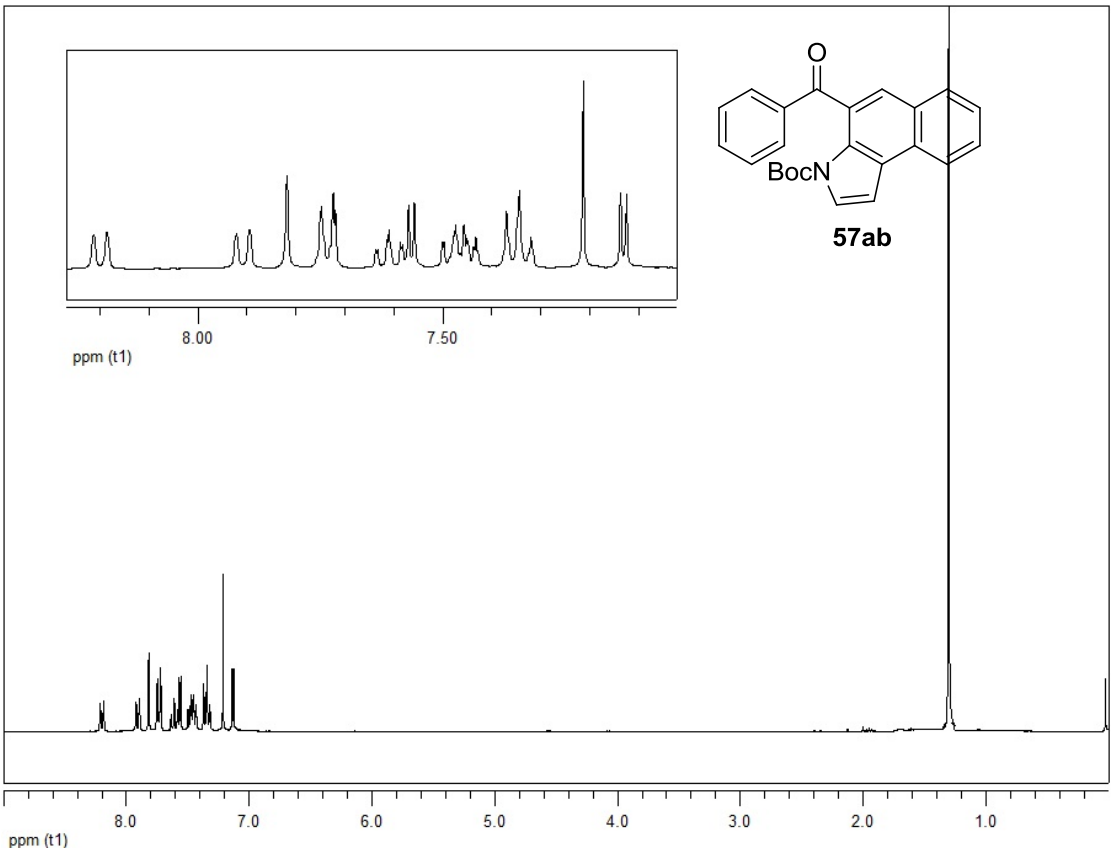

O
HN
57aa
8.00
7.50
ppm (t1)
10.0
5.0
ppm (t1)
198.25
138.93
131.82
131.20
130.92
130.75
130.51
129.60
128.94
128.41
127.81
124.28
123.99
123.58
123.09
121.08
101.41
200
150
100
50
ppm (t1)

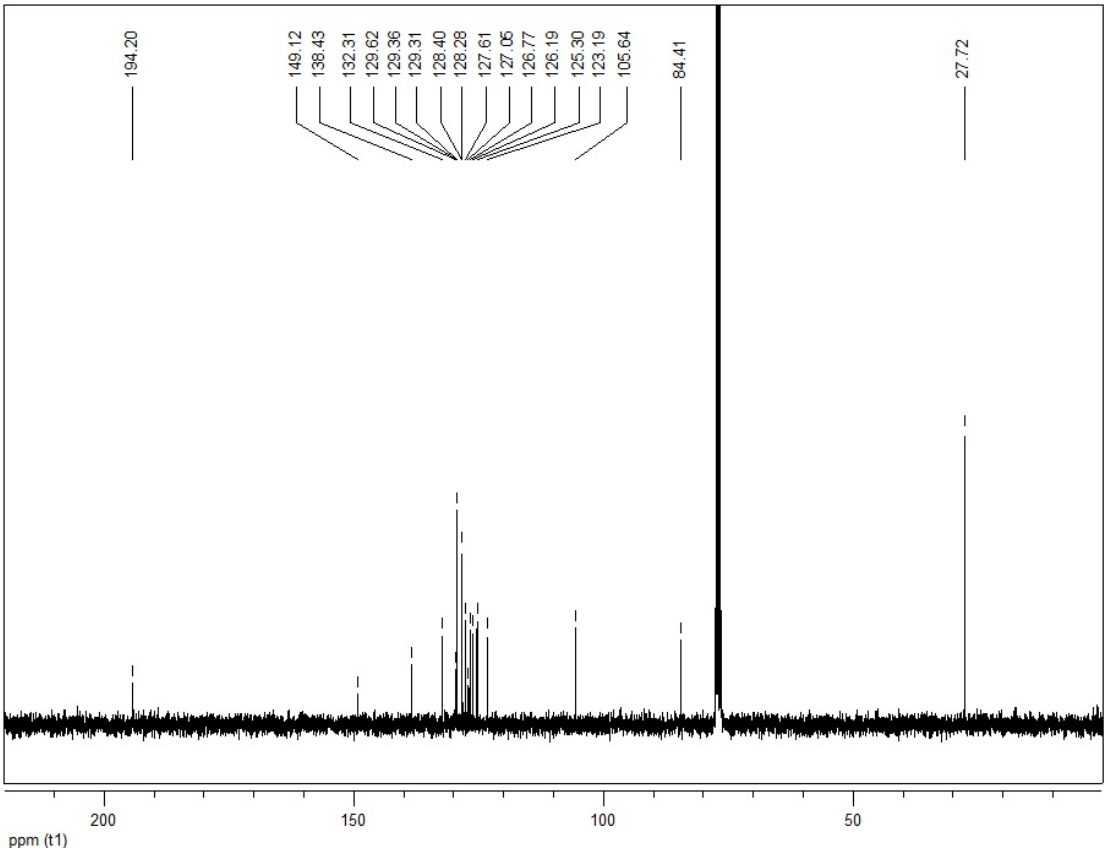

O
Cl
HN
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

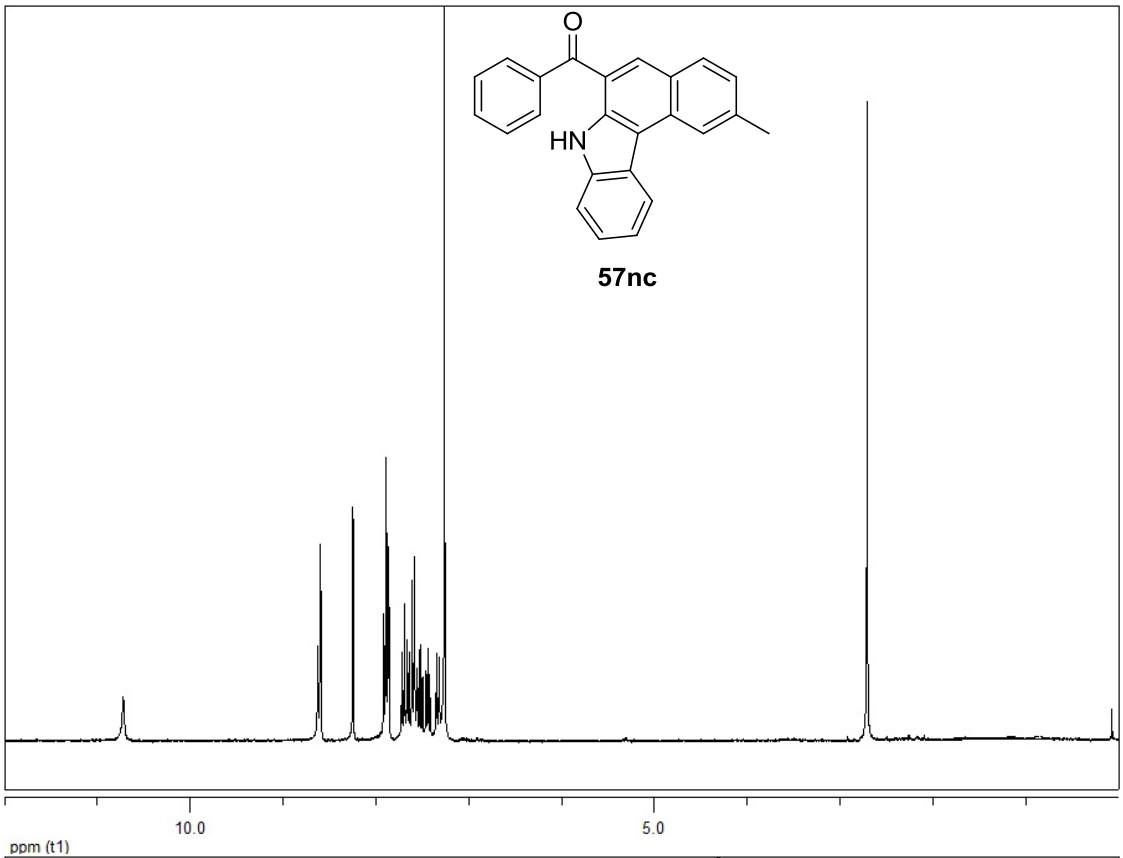
57fa


196.92
138.27
137.34
136.94
131.23
131.15
130.54
128.87
128.66
126.99
126.82
125.24
124.97
123.77
121.47
120.24
101.68
20.14
200
150
100
50
ppm (t1)

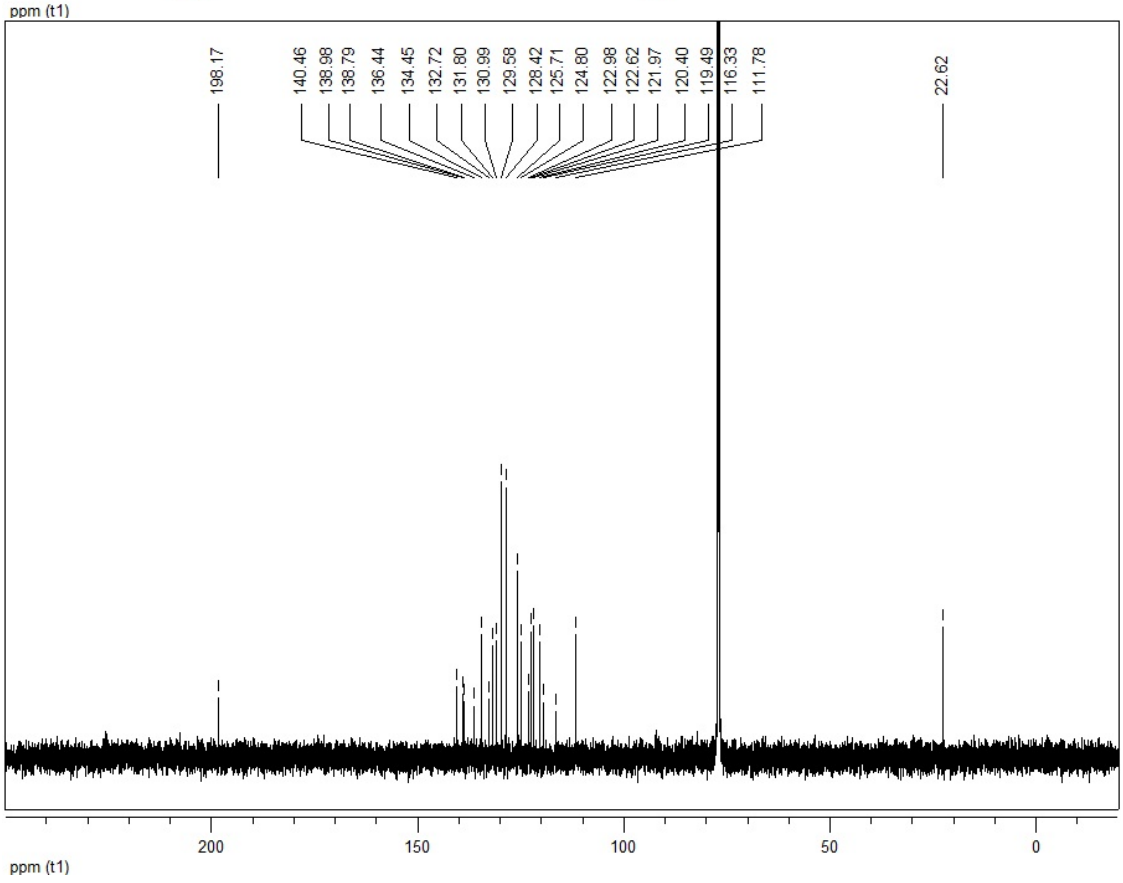

O
F
HN
57ja
10.0
5.0
ppm (t1)
198.06
162.19
158.83
138.62
132.07
129.68
129.19
129.06
128.48
124.07
123.06
122.98
118.98
118.92
108.12
107.85
101.72
200
150
100
50
ppm (t1)

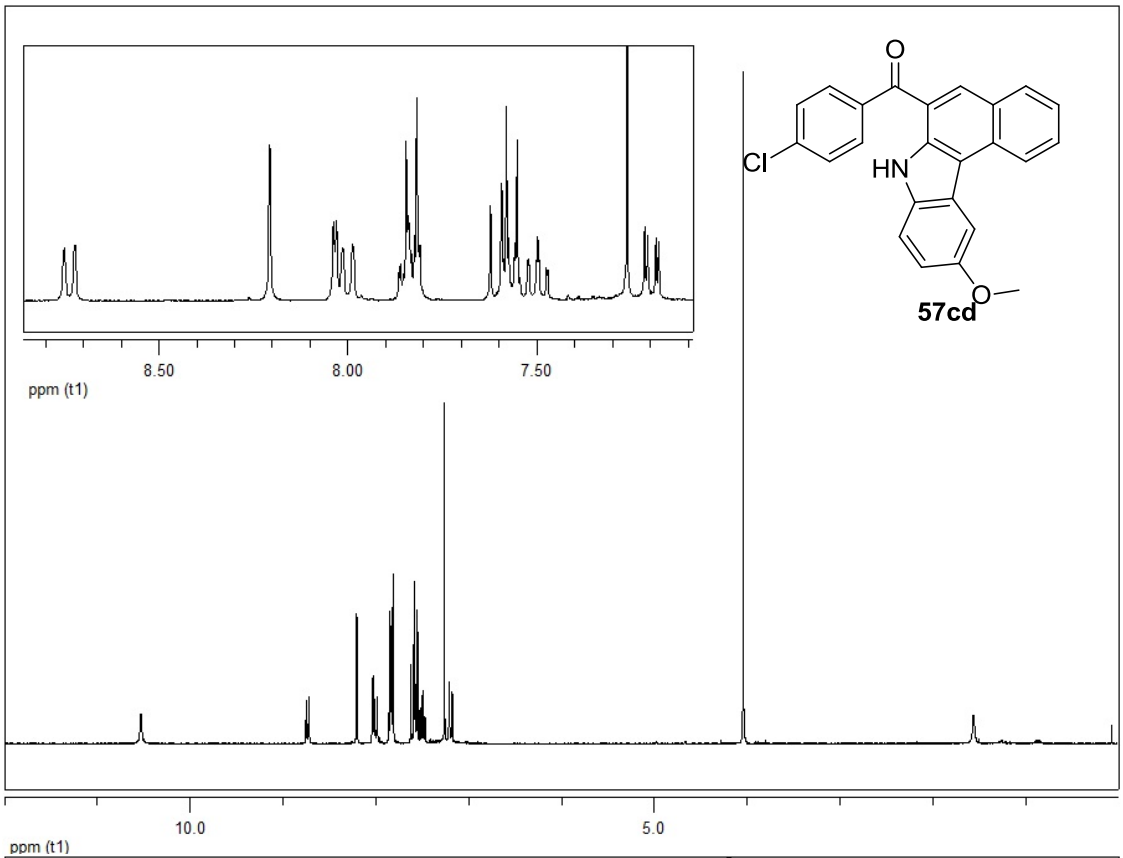

O
BocN
57ab
8.00
7.50
ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

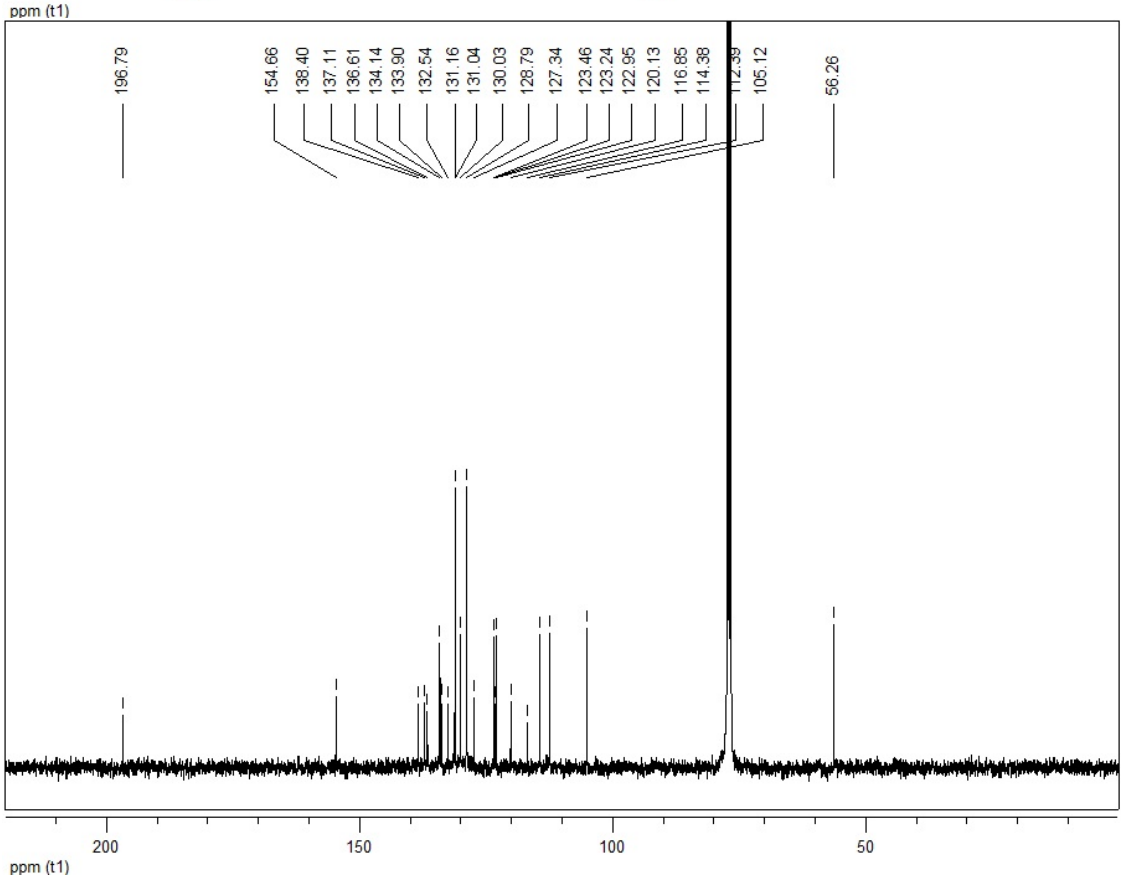

194.20
149.12
138.43
132.31
129.62
129.36
129.31
128.40
128.28
127.61
127.05
126.77
126.19
125.30
123.19
105.64
84.41
27.72
200
150
100
50
ppm (t1)

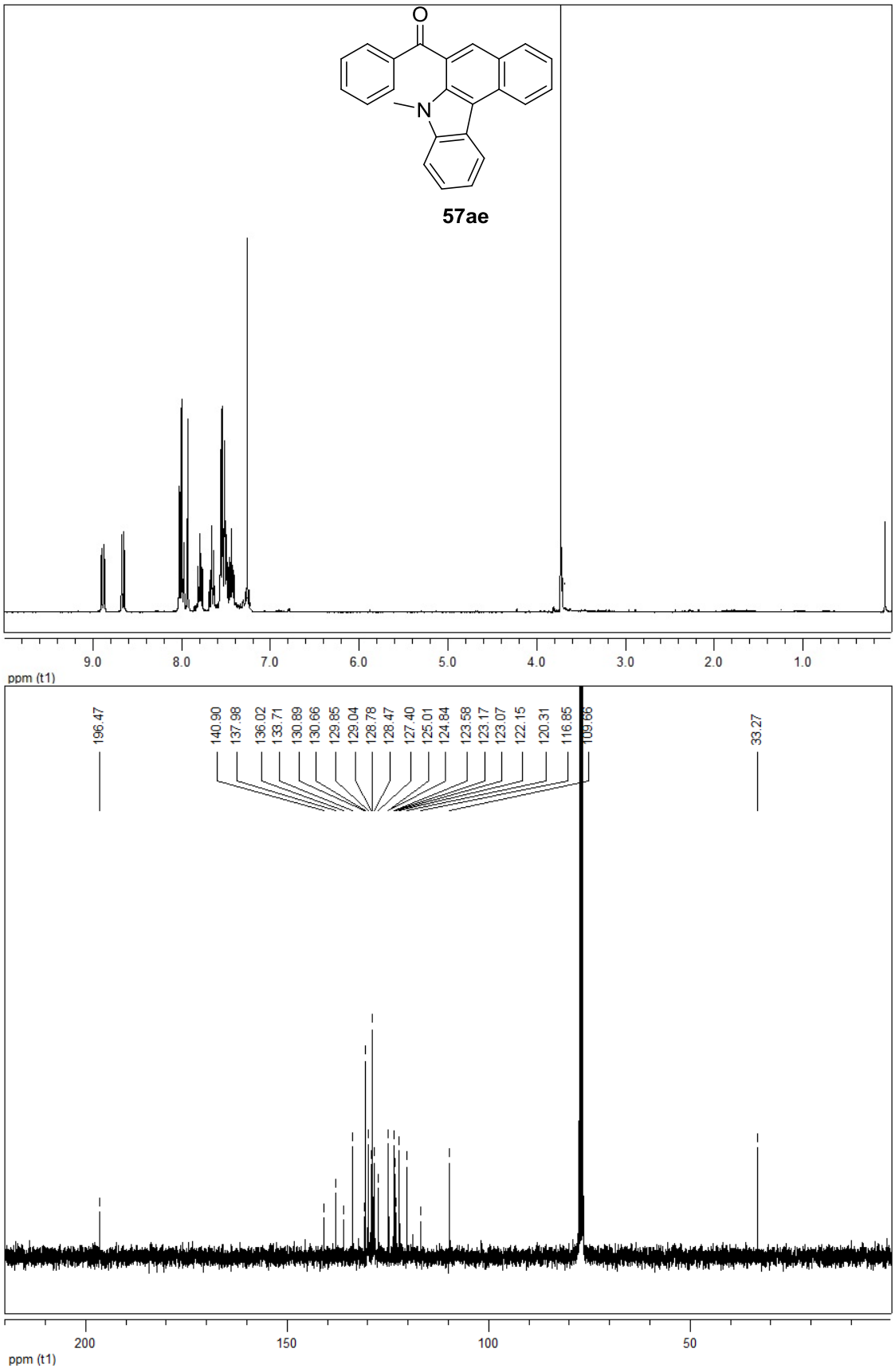

O
HN
10.0
5.0
ppm (t1)

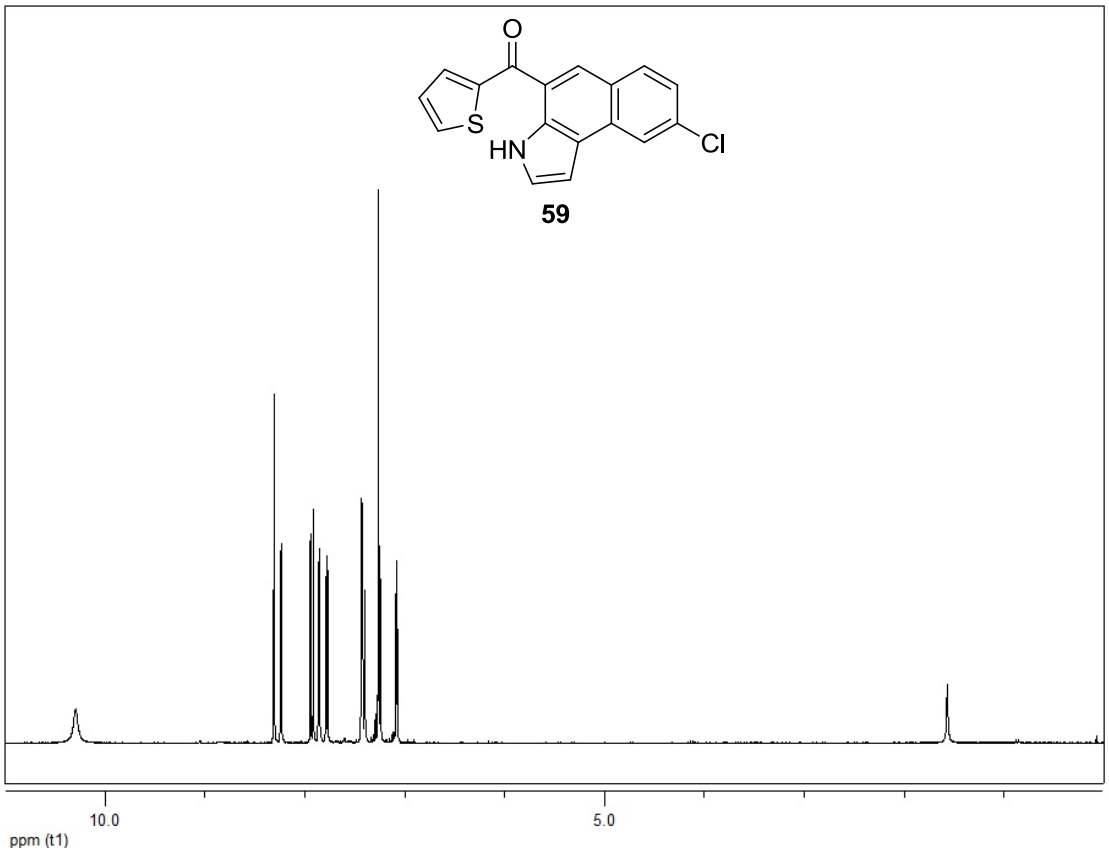
57nc

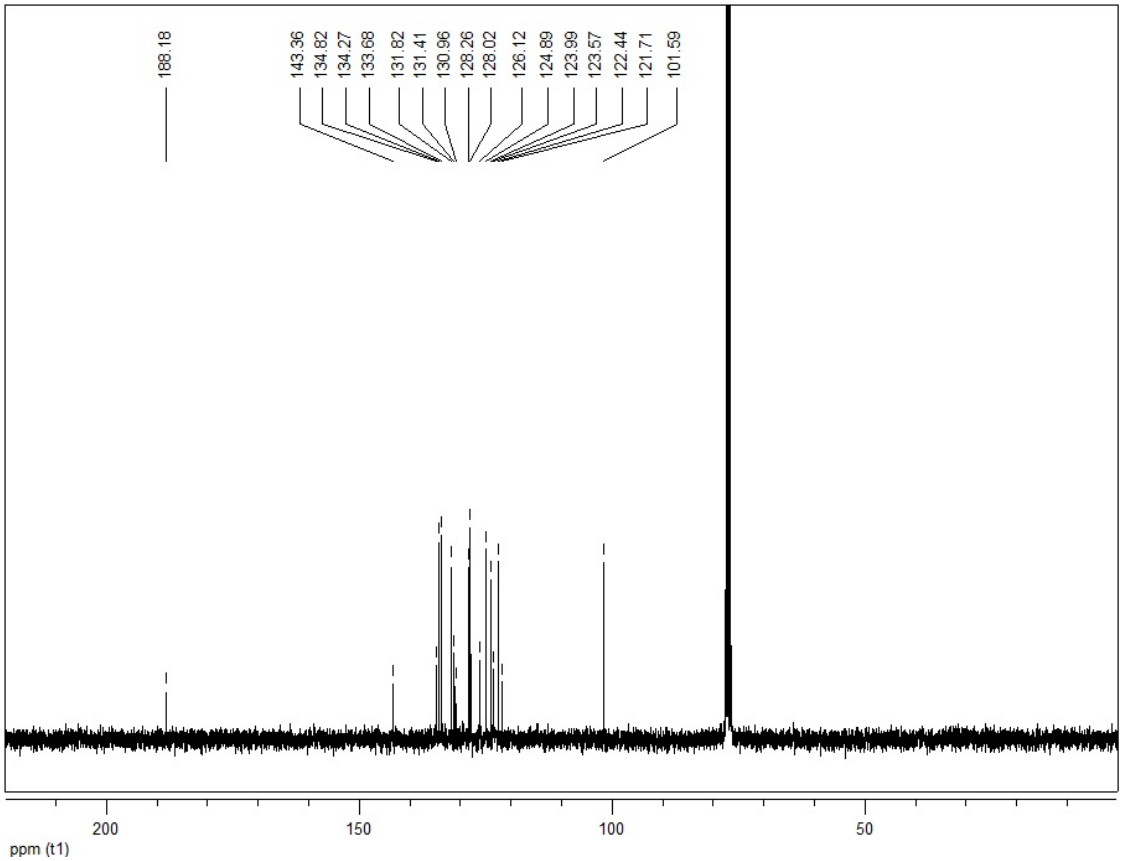

198.17
140.46
138.98
138.79
136.44
134.45
132.72
131.80
130.99
129.58
128.42
125.71
124.80
122.98
122.62
121.97
120.40
119.49
116.33
111.78
22.62
200
150
100
50
0
ppm (t1)

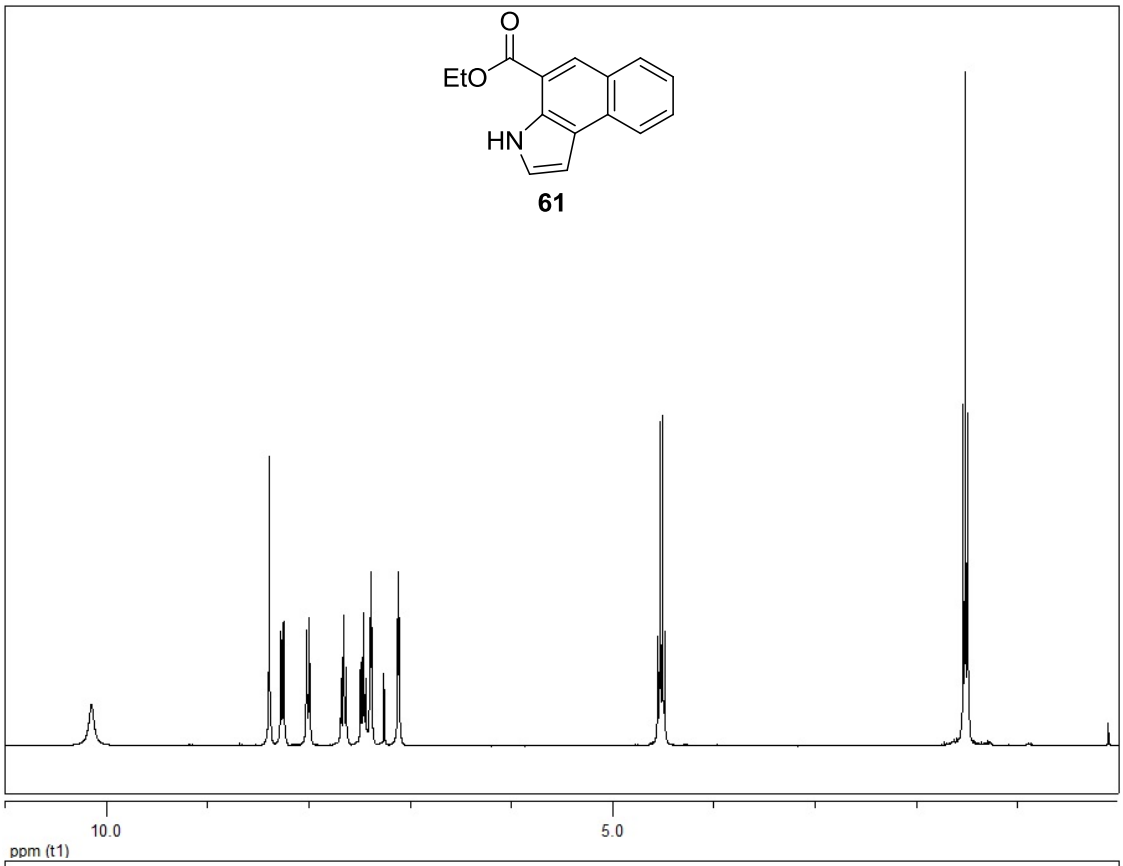

O
Cl
HN
O
57cd
8.50
8.00
7.50
ppm (t1)
10.0
5.0
ppm (t1)


196.79
154.66
138.40
137.11
136.61
134.14
133.90
132.54
131.16
131.04
130.03
128.79
127.34
123.46
123.24
122.95
120.13
116.85
114.38
112.39
105.12
56.26
200
150
100
50
ppm (t1)

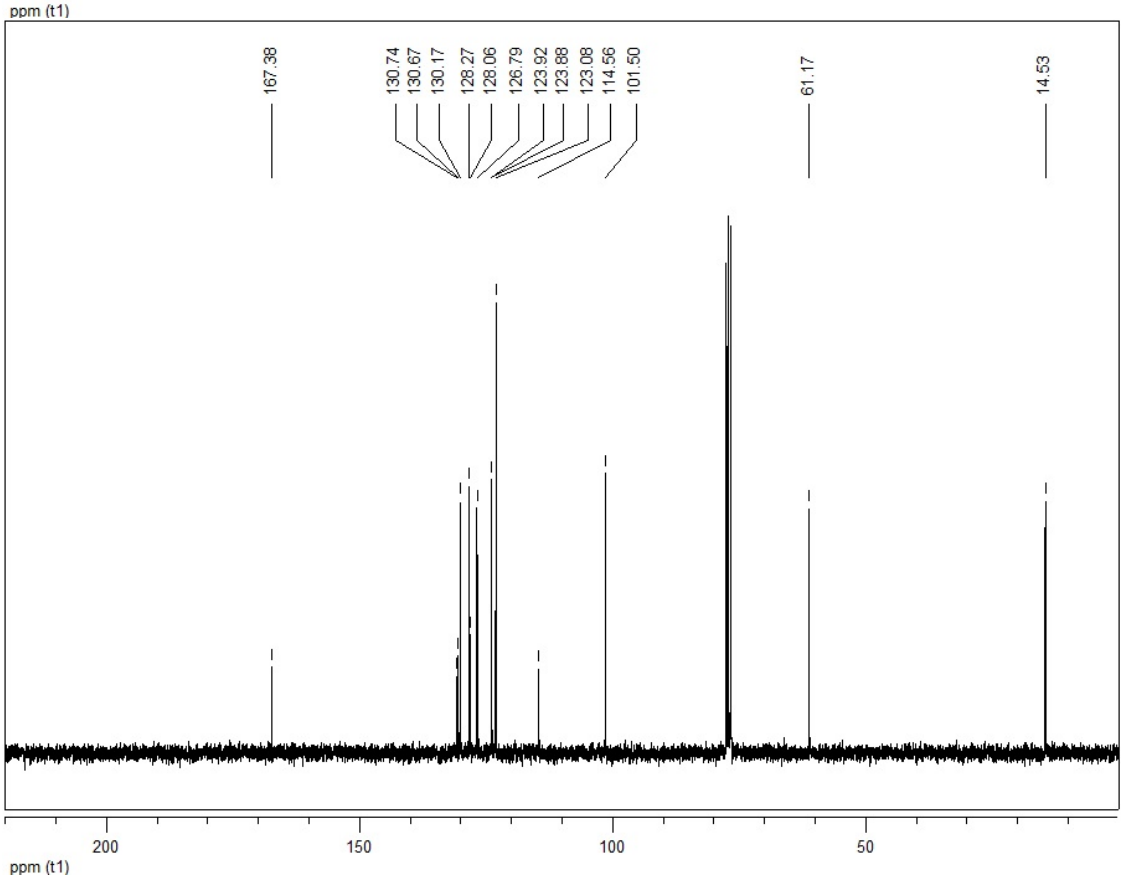

O
N
57ae
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
196.47
140.90
137.98
136.02
133.71
130.89
130.66
129.85
129.04
128.78
128.47
127.40
125.01
124.84
123.58
123.17
123.07
122.15
120.31
116.85
109.66
33.27
200
150
100
50
ppm (t1)

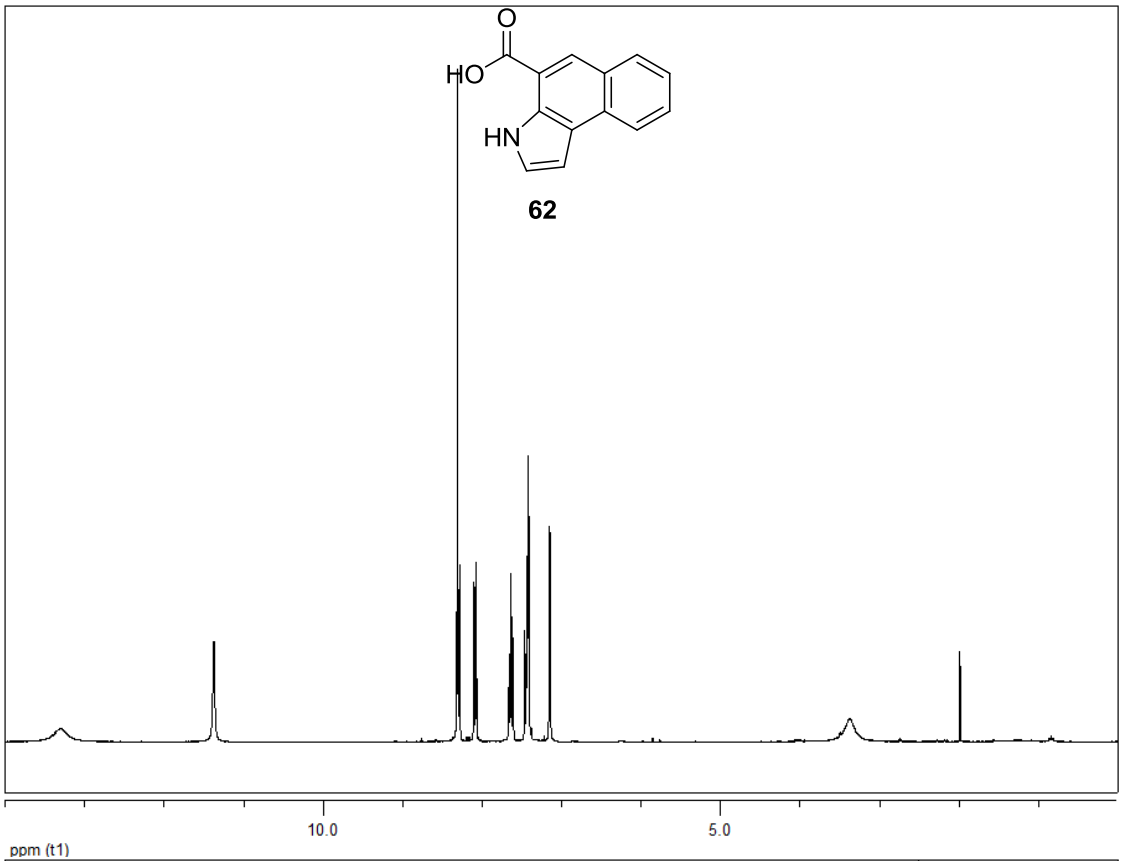

O
S
HN
Cl
59
10.0
5.0
ppm (t1)

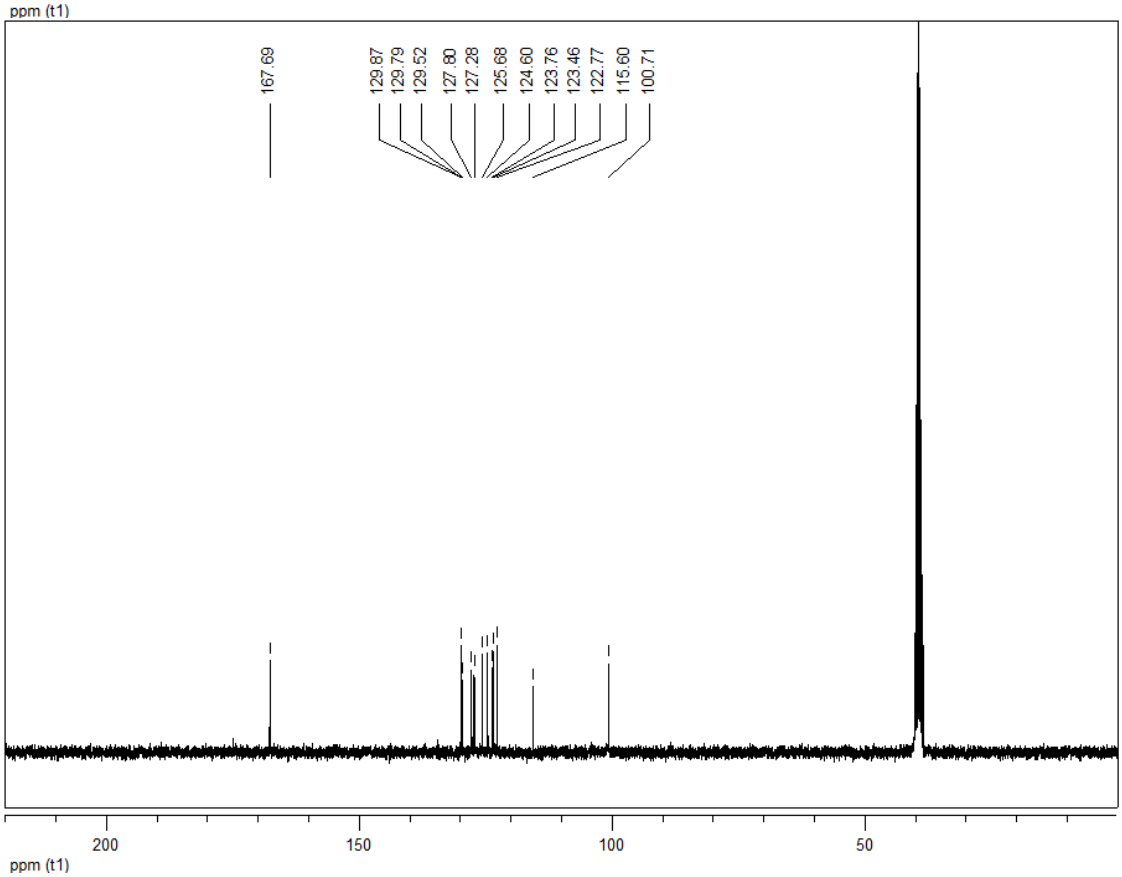

188.18
143.36
134.82
134.27
133.68
131.82
131.41
130.96
128.26
128.02
126.12
124.89
123.99
123.57
122.44
121.71
101.59
200
150
100
50
ppm (t1)

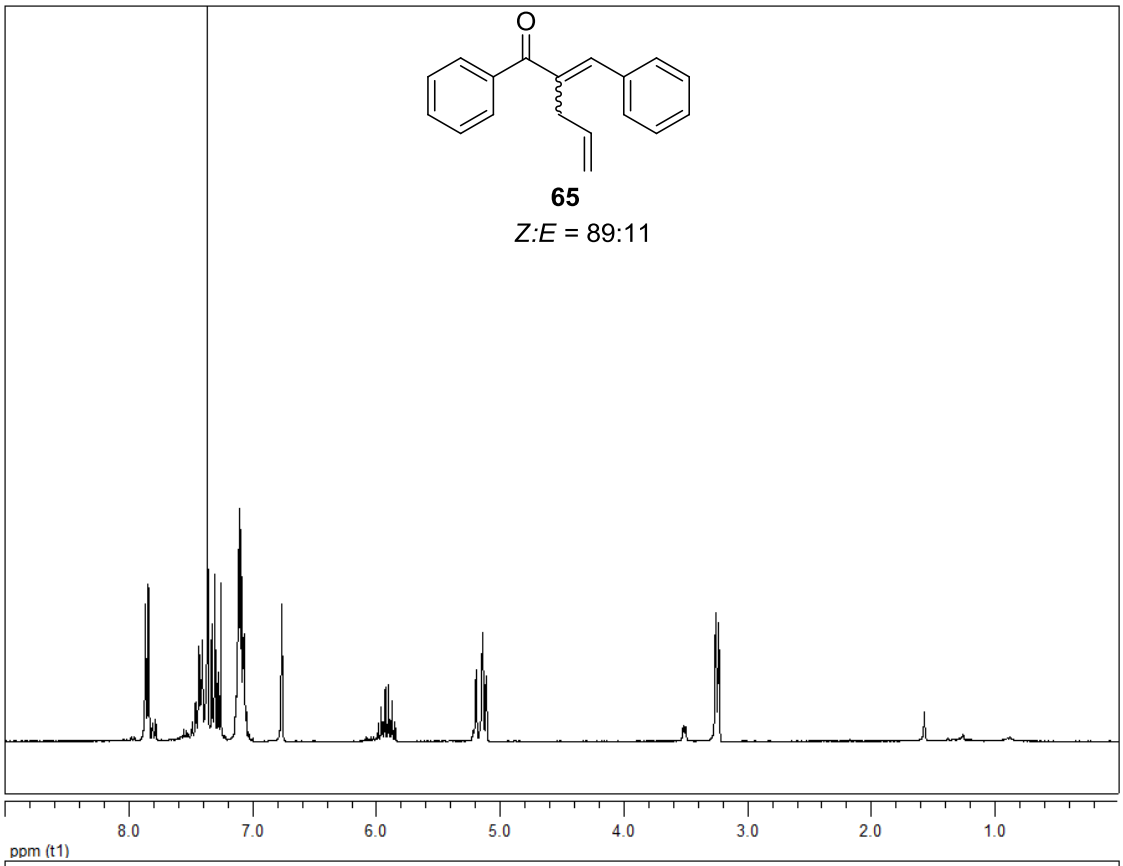

O
EtO
HN
10.0
5.0
ppm (t1)

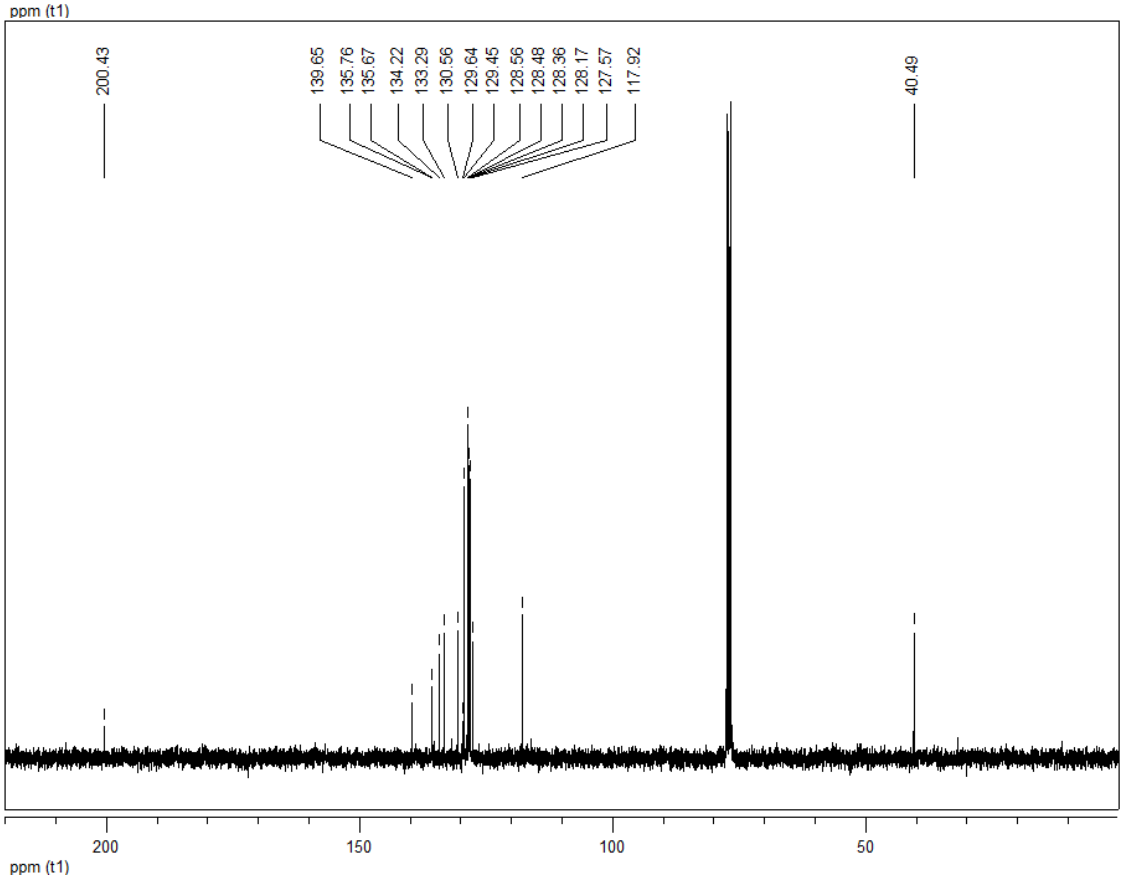
61


167.38
130.74
130.67
130.17
128.27
128.06
126.79
123.92
123.88
123.08
114.56
101.50
61.17
14.53
200
150
100
50
ppm (t1)


O
HO
HN
62
10.0
5.0
ppm (t1)


167.69
129.87
129.79
129.52
127.80
127.28
125.68
124.60
123.76
123.46
122.77
115.60
100.71
200
150
100
50
ppm (t1)


O
65
Z:E = 89:11
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


200.43
139.65
135.76
135.67
134.22
133.29
130.56
129.64
129.45
128.56
128.48
128.36
128.17
127.57
117.92
40.49
200
150
100
50
ppm (t1)

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6. Visible Light Mediated Synthesis of Dihydronaphthalenes

6.1 Introduction

Dihydronaphthalene ring system is a ubiquitous structural motif in various therapeutically relevant natural products.[1] They have been used as starting material in the synthesis of biologically active compounds,[2] applied as fluorescent ligands for the estrogen receptors,[3] used as potent Aldosterone Synthase (CYP11B2) inhibitors for the treatment of congestive heart failure and myocardial fibrosis,[4] and as building blocks in the total synthesis of natural products.[5]

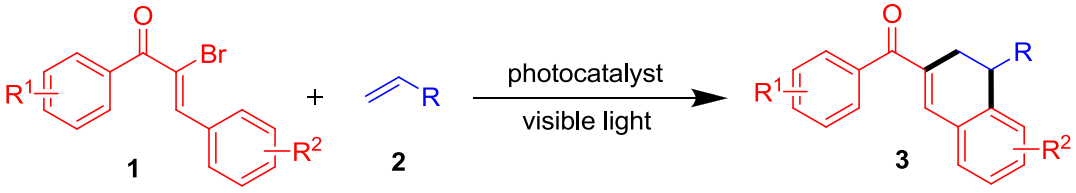
6.2 Literature procedures for dihydronaphthalene synthesis

Due to their wide applications, considerable efforts have been directed for the synthesis of dihydronaphthalenes. One of the most prominent and useful methods has been dearomatization of naphthalenes by nucleophilic addition of organometallic reagents.[6] Among other well established procedures, transition metal catalyzed reactions are noteworthy, coupling of Grignard reagents with in-situ generated enol phosphates by palladium catalysis,[7] gold (I) catalyzed intramolecular vinylidenecyclopropane rearrangement,[8] oxidation of diethyl α-benzylmalonate by manganese (III) in the presence of alkynes,[9] copper (II) catalyzed [4+2] cycloaddition of *o*-alkynyl(oxo)benzenes with alkenes,[10] nickel catalyzed [2+2+2] cycloaddition reaction of arynes, alkenes, and alkynes[11] have been utilized for the synthesis of dihydronaphthalenes. However many of these processes suffer from lack of operational simplicity, regioisomeric problems and low yields.

6.3 Intermolecular vinyl radical annulations to olefin by photoredox catalysis

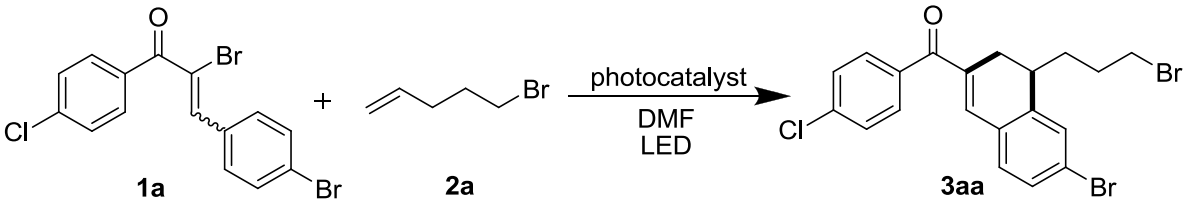
As a continuation of our ongoing study on visible light promoted vinyl radical generation from α-bromochalcones, we have demonstrated its utilization in the synthesis of polycyclic frameworks by cascade cyclization with heteroarenes.[12] Considering the high reactivity and electrophilic nature of such vinyl radicals we envisioned an intermoleular vinyl radical annulations sequence involving an olefin **2** and one aryl ring of the α-bromochalcone **1** (similar to heteroarenes) which should lead to the formation of dihydronaphthalenes **3** (Scheme 6.1).

Scheme 6.1. Intermolecular annulations of vinyl radicals to olefins



Our first attempt focused on the reaction of α-bromochalcone **1a** and 5-bromo-1-pentene **2a** in DMF using [Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$ (1 mol%) as photocatalyst. To our delight, after 36 h of irradiation, expected product **3aa** was formed in 68% isolated yield (Table 6.1, entry 1). Switching to Ru(bpy)$_3$Cl$_2$ (1 mol%) resulted in no conversion (Table 6.1, entry 2). Employing 1 mol% of Ir(ppy)$_3$ though resulted in better yield of 75% after similar reaction time (Table 6.1, entry 3).

Table 6.1. Optimization of reaction conditions[a]



entry	photocatalyst	yield (%)[b]
1	[Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$, 420 nm	68
2	Ru(bpy)$_3$Cl$_2$, 455 nm	no reaction
3	**Ir(ppy)$_3$, 420 nm**	**75**
4	Cu(dap)$_2$Cl, 530 nm	no reaction
5	Eosin Y, 530 nm	no reaction
6	Ir[(ppy)$_2$(dtbbpy)]PF$_6$, 455 nm	traces
7	Ir(ppy)$_3$, no light	no reaction
8	no photocatalyst, 420 nm	no reaction

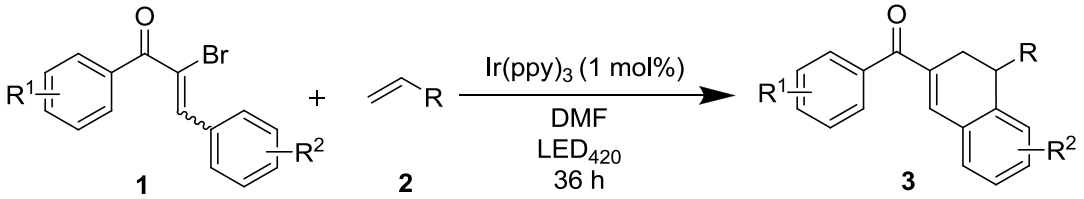
[a] Reactions conditions: **1a** (1 equiv), **2a** (3 equiv), photocatalyst (1 mol%) in DMF irradiated for 36 h.

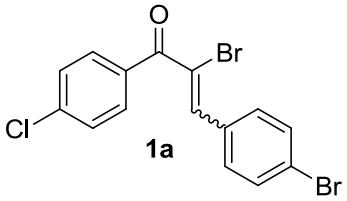
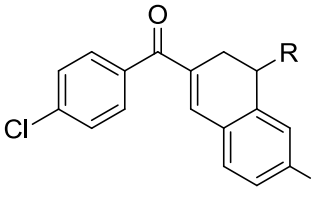
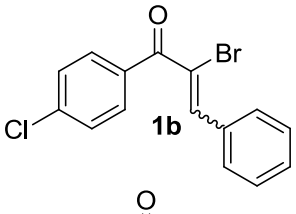
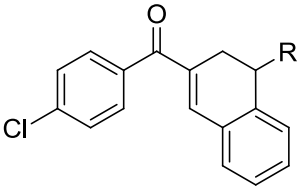
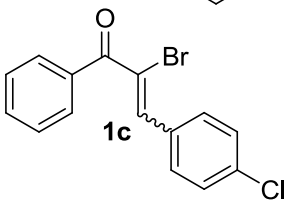
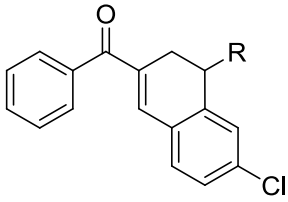
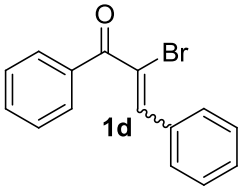
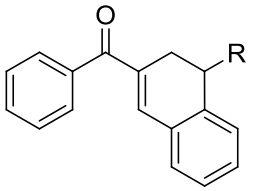
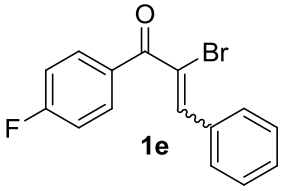
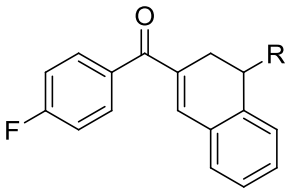
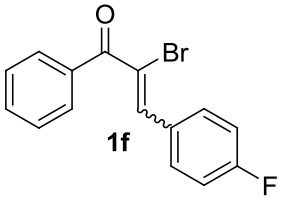
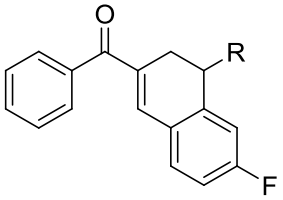
[b] Isolated yield.

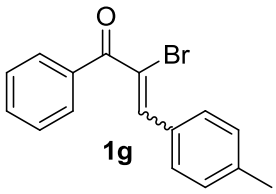
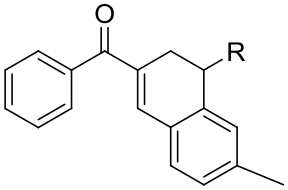
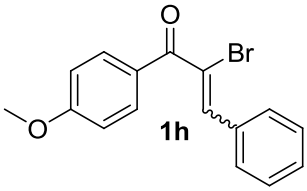
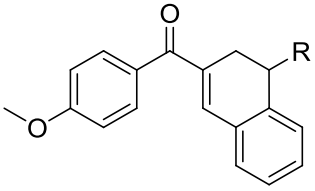
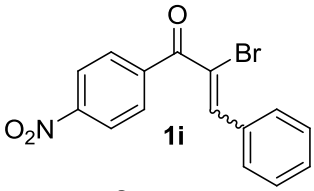
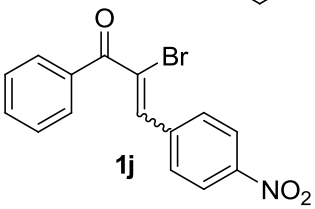
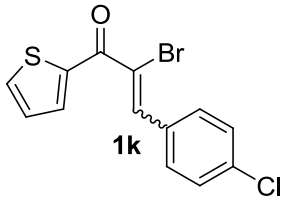
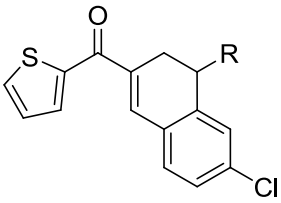
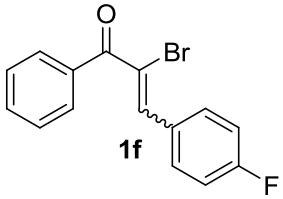
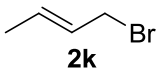
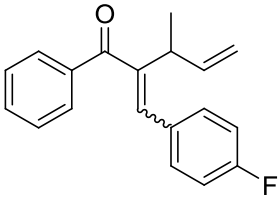
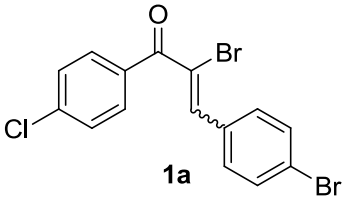
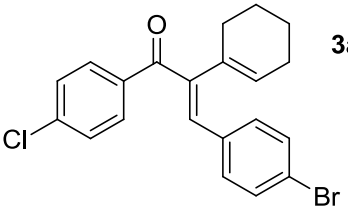
Employing some other well established photocatalysts e.g. $Cu(dap)_2Cl$ (Table 6.1, entry 4), Eosin Y (Table 6.1, entry 5) or $Ir[(ppy)_2(dtbbpy)]PF_6$ (Table 6.1, entry 6) resulted in no product formation. To ensure the role of each of the reaction parameters, additional control experiments were carried out. As expected, no conversion was observed in the absence of light or catalyst (Table 6.1, entries 7, 8).

Having the optimized reaction condition in hand we proceeded to evaluate the substrate scope for this transformation (Table 6.2). Electron donating and electron withdrawing substituent in either ring of the chalcone was varied. Halides in arene rings did not show any cross reactivity under the photochemical condition. However, the process was limited to nitro substituent in either ring (Table 6.2, entries 16, 17), where no conversion of the starting material was observed. In case of olefins, a wide range of functionality was tolerated including alkyl bromides, benzyl ethers, and aromatic rings. For allyl bromide **2k**, bromide elimination was observed leading to allylation of chalcone (Table 6.2, entry 19). When cyclohexene was used as olefin, the second C-C bond formation did not take place presumably due to lack of proper orientation of cyclohexyl moiety forming a Heck type coupling product (Table 6.2. entry 20).

Table 6.2. Substrate scope for the annulation[a]



entry	substrate (**1**)	olefin (**2**)	product (**3**)	yield (%)
				
1 2 3 4 5 6	 **1a**	**2a**, R = $(CH_2)_3Br$ **2b**, R = CH_2OAc **2c**, R = CH_2SiMe3 **2d**, R = CH_2Ph **2e**, R = CH_2NHBoc **2f**, R = $(CH_2)_5CH_3$		**3aa** 75 **3ab** 78 **3ac** 70 **3ad** 82 **3ae** 68 **3af** 73
7 8 9	 **1b**	**2a**, R = $(CH_2)_3Br$ **2g**, R = CH_2Cl **2h**, R = CH_2O-2,4 -di-Cl-C_6H_3		**3ba** 73 **3bg** 60 **3bh** 56
10	 **1c**	**2a**, R = $(CH_2)_3Br$		**3ca** 80
11	 **1d**	**2a**, R = $(CH_2)_3Br$		**3da** 71
12	 **1e**	**2i**, R = $(CH_2)_2Br$		**3ei** 62
13	 **1f**	**2a**, R = $(CH_2)_3Br$		**3fa** 56

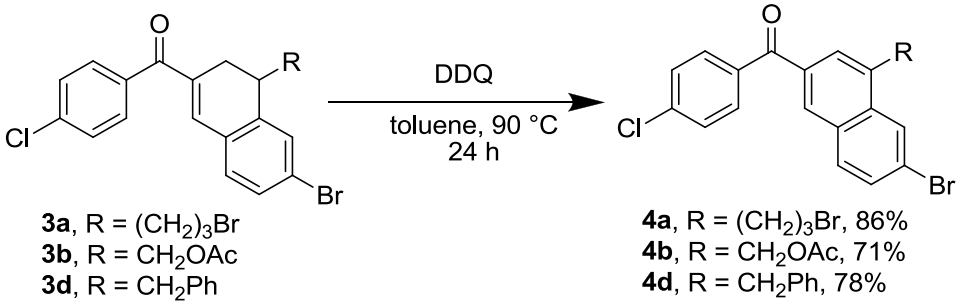
entry	substrate (**1**)	olefin (**2**)	product (**3**)	yield (%)
14	 **1g**	**2j**, R = CH_2SiMe_3	 **3gj**	52
15	 **1h**	**2j**, R = CH_2SiMe_3	 **3hj**	47
16	 **1i**	**2a**, R = $(CH_2)_3Br$	----	
17	 **1j**	**2a**, R = $(CH_2)_3Br$	----	
18	 **1k**	**2j**, R = CH_2SiMe_3	 **3kj**	60
19	 **1f**	 **2k**	 **3fk**	35
20	 **1a**	 **2l**	 **3al**	59

[a] Reactions conditions: **1** (1 equiv), **2** (3 equiv), photocatalyst (1 mol%) in DMF irradiated for 36 h. [b] Isolated yield.

6.4 Synthetic applications of dihydronaphthalenes

To demonstrate the utility of this visible light induced vinyl radical cascade sequence, we showed that dihydronaphthalenes **3** can be easily oxidized to substituted naphthalenes **4**. Subjecting the dihydronaphthalenes under reflux condition in the presence of DDQ in benzene provided naphthalenes in good yields.[13]

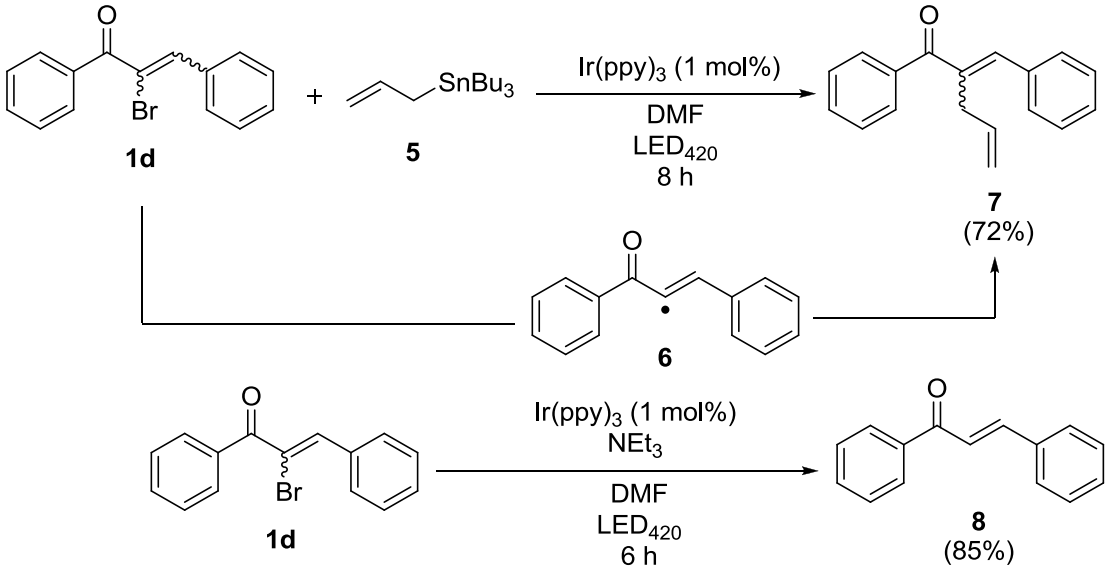
Scheme 6.2. Conversion of dihydronaphthalenes to naphthalenes



6.5 Proposed reaction mechanism

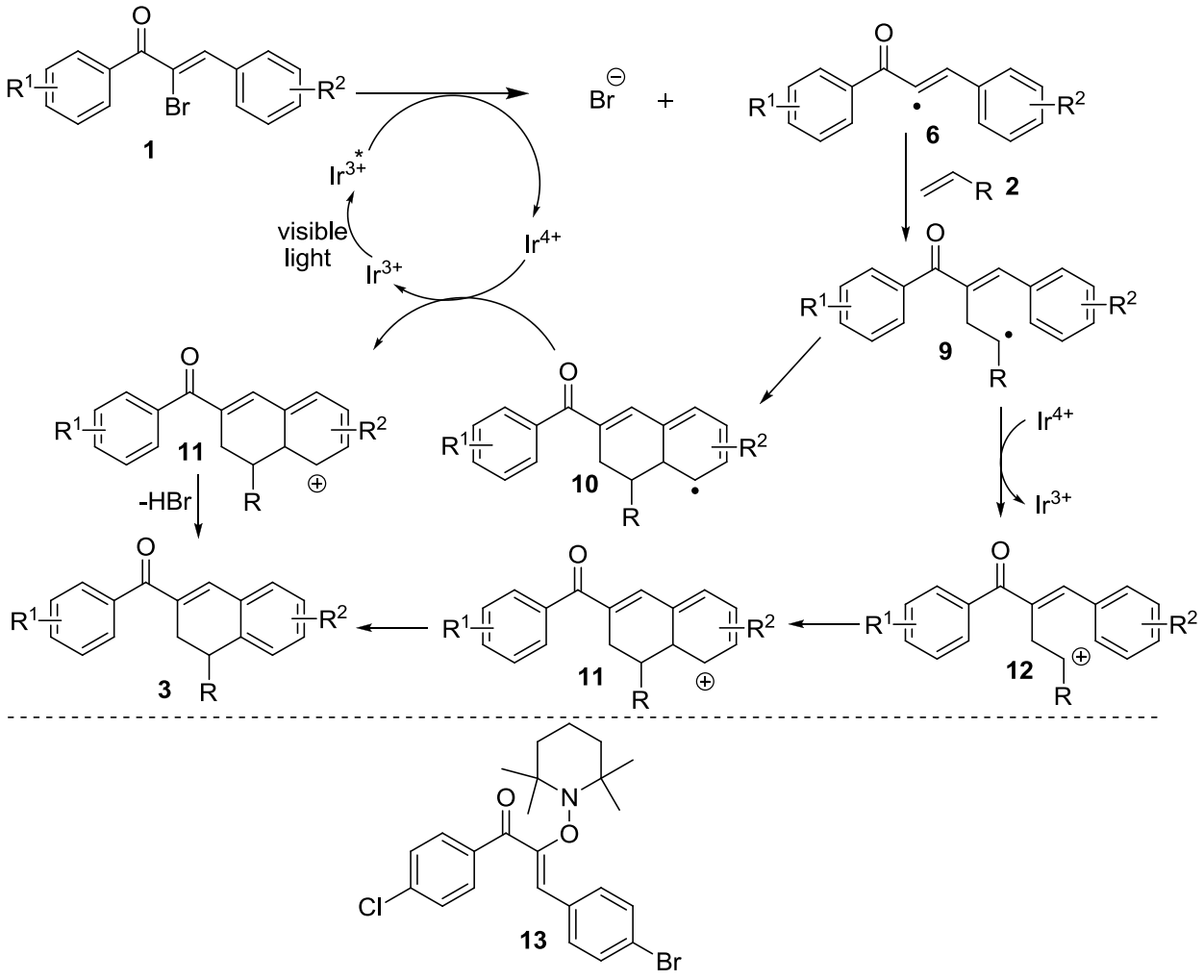
To prove the formation of α-keto vinyl radicals from α-bromochalcones under the photochemical reaction conditions, we performed two additional experiments. We presumed that the allyl stannane **5** being a radical allylating agent should lead to the allylation of α-bromochalcone (**1d**) under the same reaction conditions as the cyclization.

Scheme 6.3. Allylation and reduction of α-bromo chaconne 1d.



Indeed, allylated compound **7** was isolated in 72% yield. This proves formation of vinyl radical **6** as the photochemical key step for the cyclization process (Scheme 6.3). On the other hand, α-bromochalcone **1d** was reduced to chalcone **8** by addition of triehtylamine as sacrificial electron donor, also consistent with the formation of vinyl radical **6**. To further support our hypothesis of presence of vinyl radical **6** in reaction medium, we performed radical trapping experiment and TEMPO adduct **13** was detected by mass spectrometry (see supporting information for more details).

Scheme 6.4. Proposed reaction mechanism for the photoredox catalyzed cascade cyclization between chalcones and olefins.



Based on the above evidence, a plausible reaction mechanism is proposed for the above cyclization reaction involving the formation of vinyl radical **6** by the transfer of an electron from

excited $*Ir^{3+}$ to α-bromochalcone **1** (Scheme 6.4). The radical **6** then adds to the olefin **2** to form the radical **9**. Formation of final product could occur by two possible pathways, one by chemoselective addition of the radical **9** to the arene ring of chalcone bearing the vinyl, but not the carbonyl group (path A), thus forming radical **10**. A back electron transfer from **10** to Ir^{4+} closes the catalytic cycle and forms the cation **11**. Alternatively, intermediate **9** could be oxidized by back electron transfer from to Ir^{4+}, thus regenerating the catalyst and cation intermediate **12**. An electrophilic ring closure then should furnish **11**. Carbocation **11** then finally forms product **3.**

6.6 Conclusion

In conclusion, a photochemical synthesis of dihydronaphthalenes has been achieved by intermolecular vinyl radical annulations to olefins utilizing iridium catalyst and visible light. A wide range of olefins and α-bromochalcones are tolerated giving rise to larger variety of 3,4-dihydronaphthalenes. The dihydronaphthalenes products are converted to substituted naphthalenes as a potential application of the methodology. Mechanistic investigation was performed in support of a radical process.

6.7 Experimental part

General Information

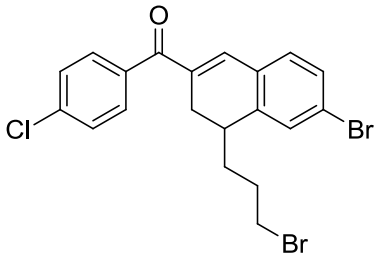
All reactions were performed using common dry, inert atmosphere techniques. Reactions were monitored by TLC and visualized by a dual short/long wave UV lamp and stained with an ethanolic solution of vanillin. Column flash chromatography was performed using 230-400 mesh silica gel. NMR spectra were recorded on 300 MHz spectrometer. Chemical shifts for ^{1}H NMR were reported as δ, parts per million, relative to the signal of $CDCl_3$ at 7.26 ppm. Chemical shifts for ^{13}C NMR were reported as δ, parts per million, relative to the center line signal of the $CDCl_3$ triplet at 77 ppm. Proton and carbon assignments were established using spectral data of similar compounds. The abbreviations s, d, dd, t, q and m stand for the resonance multiplicity singlet, doublet, doublet of doublets, triplet, quartet and multiplet respectively.

Preparation of α-bromo chalcones has been described in Chapter 5.

General procedure (GP-A) for the photoredeox catalyzed dihydronapthalene synthesis

An oven dried 15 mL Schlenk tube equipped with a plastic septum and magnetic stir bar was charged with $Ir(ppy)_3$ (1 mol %), α-bromochalcone (0.5 mmol, 1.0 equiv) and the olefin (1.5 mmol, 3.0 equiv). The flask was purged with a stream of nitrogen and 2.0 mL of dry dimethylformamide was added. The resultant mixture was degassed by freeze-pump-thaw procedure (3 cycles). The tube was sealed with an internal irradiation set up (a LED stick inside, see picture) and irradiated for 36 h. After the completion of the reaction (as judged by TLC analysis), the mixture was transferred to a separating funnel, diluted with 15 mL of ethyl acetate and washed with 20 mL of water. The aqueous layer was washed with ethyl acetate (3 × 10 mL) and the combined organic layer was dried over anhydrous sodium sulfate, solvent was removed in vacuo and the residue was subjected to colum chromatography on silica gel, using PE/EA as solvent system to get the pure product.

(6-bromo-4-(3-bromopropyl)-3,4-dihydronaphthalen-2-yl)(4-chlorophenyl)methanone (3aa)

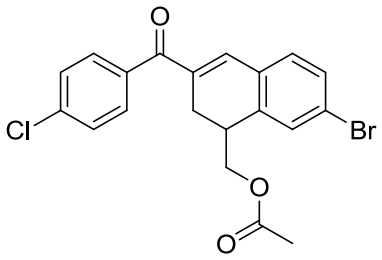


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.71 – 7.63 (m, 2H), 7.49 – 7.42 (m, 2H), 7.40 – 7.33 (m, 2H), 7.03 (dd, *J* = 5.3, 3.2 Hz, 2H), 3.47 – 3.32 (m, 2H), 2.95 (qd, *J* = 6.9, 4.2 Hz, 1H), 2.85 (dd, *J* = 17.2, 4.0 Hz, 1H), 2.72 (ddd, *J* = 17.2, 6.7 Hz, 2.3, 1H), 2.05 – 1.63 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 195.84, 142.77, 138.44, 138.28, 136.28, 135.77, 130.79, 130.66, 130.55, 130.48, 130.29, 128.72, 124.17, 36.59, 33.62, 32.48, 30.15, 27.38.

HRMS (ESI): Calcd. For $C_{20}H_{18}Br_2ClO$ $[M+H]^+$ m/*z* 466.9413, found *m/z* 466.9417.

(7-bromo-3-(4-chlorobenzoyl)-1,2-dihydronaphthalen-1-yl)methyl acetate (3ab)

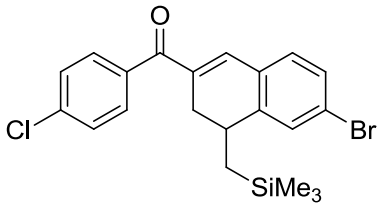


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.66 (dd, *J* = 16.7, 10.0 Hz, 2H), 7.52 – 7.34 (m, 4H), 7.10 – 6.95 (m, 2H), 4.20 – 4.03 (m, 2H), 3.32 (tt, *J* = 10.8, 5.5 Hz, 1H), 2.95 (dd, *J* = 17.6, 3.7 Hz, 1H), 2.74 (ddd, *J* = 17.6, 7.0, 2.3 Hz, 1H), 2.12 – 2.02 (m, 3H).

^{13}C NMR (75MHz, $CDCl_3$) δ = 195.59, 170.83, 138.34, 138.31, 138.07, 136.17, 135.27, 131.56, 130.99, 130.86, 130.59, 130.53, 128.69, 124.21, 64.91, 36.53, 24.68, 20.87.

HRMS (ESI): Calcd. For $C_{20}H_{17}BrClO_3$ $[M+H]^+$ *m/z* 421.0023, found *m/z* 421.0026.

(6-bromo-4-((trimethylsilyl)methyl)-3,4-dihydronaphthalen-2-yl)(4-chlorophenyl)methanone (3ac)

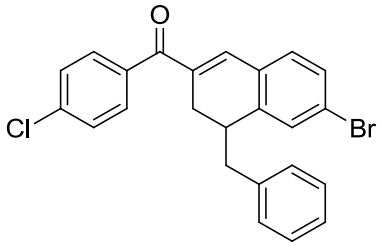


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.68 – 7.60 (m, 2H), 7.47 – 7.23 (m, 3H), 7.05 – 6.92 (m, 3H), 3.05 (td, *J* = 10.5, 5.3 Hz, 1H), 2.70 (d, *J* = 5.5 Hz, 2H), 0.86 (ddd, *J* = 19.9, 14.8, 7.5 Hz, 2H), 0.00 (s, 9H).

^{13}C NMR (75MHz, $CDCl_3$) δ = 196.68, 146.94, 139.39, 132.72, 132.02, 131.34, 131.17, 130.73, 130.41, 130.33, 130.18, 129.40, 124.97, 34.59, 30.59, 23.32, 0.00.

HRMS (ESI): Calcd. For $C_{21}H_{23}BrClOSi$ $[M+H]^+$ *m/z* 433.0390, found *m/z* 433.0392.

(4-benzyl-6-bromo-3,4-dihydronaphthalen-2-yl)(4-chlorophenyl)methanone (3ad)

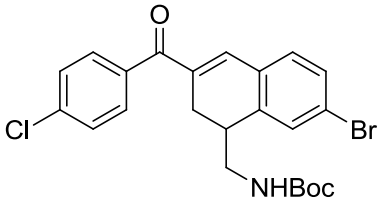


^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 – 7.62 (m, 2H), 7.49 – 7.43 (m, 2H), 7.37 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.29 – 7.16 (m, 4H), 7.06 – 6.97 (m, 4H), 3.18 (ddd, *J* = 15.3, 6.9, 3.1 Hz, 1H), 2.88 (dd, *J* = 17.4, 3.0 Hz, 1H), 2.85 – 2.73 (m, 2H), 2.63 (ddd, *J* = 17.4, 7.0, 2.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.67, 142.50, 139.98, 139.97, 138.96, 138.21, 136.38, 135.57, 131.24, 130.59, 130.50, 130.32, 130.20, 129.24, 128.64, 128.37, 126.43, 123.93, 41.19, 39.46, 26.79.

HRMS (ESI): Calcd. For $C_{24}H_{19}BrClO$ $[M+H]^+$ *m/z* 437.0308, found *m/z* 437.0309.

tert-butyl (7-bromo-3-(4-chlorobenzoyl)-1,2-dihydronaphthalen-1-yl)methylcarbamate (3ae)

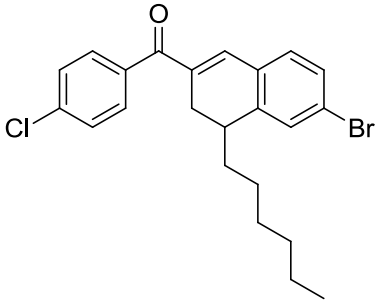


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.74 – 7.64 (m, 2H), 7.50 – 7.42 (m, 2H), 7.42 – 7.36 (m, 2H), 7.03 (m, 2H), 4.69 (m, 1H), 3.31 – 3.06 (m, 3H), 2.93 (d, *J* = 17.7 Hz, 1H), 2.69 (dd, *J* = 17.5, 3.6 Hz, 1H), 1.42 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 195.93, 155.86, 140.12, 138.25, 138.02, 136.24, 135.35, 131.60, 130.67, 130.60, 130.52, 128.68, 124.18, 79.61, 43.28, 37.52, 28.36, 25.11.

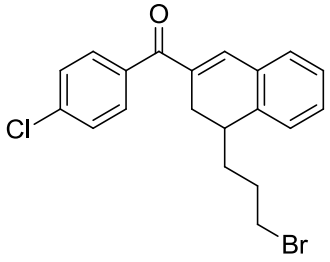
HRMS (ESI): Calcd. For $C_{23}H_{24}BrClNO_3$ $[M+H]^+$ *m/z* 476.0623, found *m/z* 476.0613.

(6-bromo-4-hexyl-3,4-dihydronaphthalen-2-yl)(4-chlorophenyl)methanone (3af)



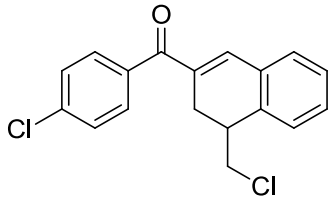
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.70 – 7.65 (m, 2H), 7.48 – 7.44 (m, 2H), 7.38 – 7.33 (m, 2H), 7.03 – 6.98 (m, 2H), 2.90 (m, 1H), 2.82 (dd, *J* = 17.1, 4.3 Hz, 1H), 2.72 (ddd, *J* = 17.1, 6.8, 2.3 Hz, 1H), 1.57 – 1.50 (m, 3H), 1.47-1.33 (m, 1H), 1.32 – 1.21 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (75MHz, $CDCl_3$) δ = 195.94, 143.78, 138.44, 138.14, 136.46, 136.12, 130.76, 130.59, 130.50, 130.32, 129.87, 128.63, 123.97, 37.18, 34.07, 31.71, 29.30, 27.45, 27.02, 22.62, 14.06.
HRMS (ESI): Calcd. For $C_{23}H_{25}BrClO$ $[M+H]^+$ *m/z* 431.0777, found *m/z* 431.0778.

(4-(3-bromopropyl)-3,4-dihydronaphthalen-2-yl) (4-chlorophenyl)methanone (3ba)



^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.71 – 7.67 (m, 2H), 7.48 – 7.44 (m, 2H), 7.33 (td, *J* = 7.5, 1.2 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 2.2 Hz, 1H), 3.42 – 3.35 (m, 2H), 2.98 (m, 1H), 2.87 (dd, *J* = 17.1, 3.9 Hz, 1H), 2.77 (ddd, *J* = 17.1, 6.8, 2.3 Hz, 1H), 1.97 (m, 1H), 1.88 – 1.79 (m, 1H), 1.77 – 1.66 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ = 196.06, 140.80, 139.69, 138.09, 136.57, 135.40, 131.53, 130.63, 130.23, 129.34, 128.62, 127.78, 127.13, 36.67, 33.67, 32.74, 30.35, 27.72.
HRMS (ESI): Calcd. For $C_{20}H_{19}BrClO$ $[M+H]^+$ *m/z* 389.0302, found *m/z* 389.0296.

(4-(chloromethyl)-3,4-dihydronaphthalen-2-yl)(4-chlorophenyl)methanone (3bg)

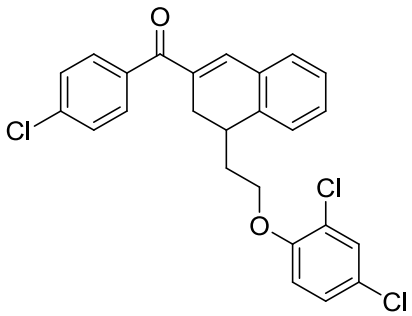


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.72 – 7.65 (m, 2H), 7.49 – 7.44 (m, 2H), 7.41 – 7.27 (m, 3H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 2.3 Hz, 1H), 3.68 – 3.55 (m, 2H), 3.37 – 3.29 (m, 1H), 3.23 (dd, *J* = 17.5, 3.6 Hz, 1H), 2.80 (ddd, *J* = 17.5, 6.8, 2.4 Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$) δ = 195.65, 139.09, 138.23, 136.85, 136.35, 134.76, 131.79, 130.63, 130.46, 129.40, 128.67, 128.56, 128.06, 46.80, 39.83, 25.67.

HRMS (ESI): Calcd. For $C_{18}H_{15}Cl_2O$ $[M+H]^+$ m/z 317.0494, found *m/z* 317.0497.

(4-chlorophenyl)(4-(2-(2,4-dichlorophenoxy)ethyl)-3,4-dihydronaphthalen-2-yl)methanone (3bh)

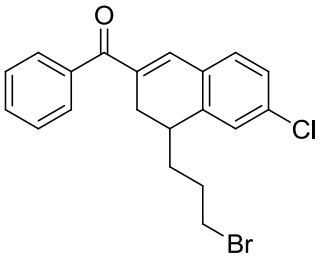


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.73 – 7.65 (m, 2H), 7.50 – 7.42 (m, 2H), 7.38 (d, *J* = 2.5 Hz, 1H), 7.31 – 7.10 (m, 6H), 6.78 (d, *J* = 8.8 Hz, 1H), 4.02 (dt, *J* = 9.5, 5.7 Hz, 1H), 3.88 (ddd, *J* = 9.4, 7.3, 5.7 Hz, 1H), 3.39 (qd, *J* =7.2, 3.0 Hz, 1H), 2.97 (dd, *J* = 17.2, 3.0 Hz, 1H), 2.81 (ddd, *J* = 17.2, 6.7, 2.5 Hz, 1H), 2.15 – 1.95 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.11, 153.08, 140.06, 139.61, 138.16, 136.48, 135.32, 131.49, 130.68, 130.33, 130.02, 129.44, 128.66, 128.17, 127.59, 127.30, 125.65, 123.63, 113.80, 66.38, 33.39, 33.07, 27.80.

HRMS (ESI): Calcd. For $C_{25}H_{20}Cl_3O_2$ $[M+H]^+$ m/z 457.0529, found *m/z* 457.0530.

(4-(3-bromopropyl)-6-chloro-3,4-dihydronaphthalen-2-yl)(phenyl)methanone (3ca)

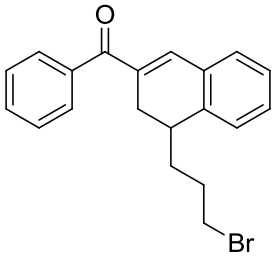


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.77 – 7.68 (m, 2H), 7.63 – 7.53 (m, 1H), 7.48 (m, 2H), 7.24 – 7.16 (m, 2H), 7.15 – 7.04 (m, 2H), 3.44 – 3.36 (m, 2H), 3.02 – 2.93 (m, 1H), 2.88 (dd, *J* = 17.1, 4.1 Hz, 1H), 2.75 (ddd, *J* = 17.1, 6.7, 2.3 Hz, 1H), 2.07 – 1.66 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.16, 142.59, 138.35, 138.07, 135.83, 135.54, 131.92, 130.28, 129.23, 128.38, 127.86, 127.23, 36.74, 33.63, 32.48, 30.18, 27.36.

HRMS (EI-MS): Calcd. For $C_{20}H_{18}BrClO$ $[M+]^+$ *m/z* 388.0230, found *m/z* 388.0216.

(4-(3-bromopropyl)-3,4-dihydronaphthalen-2-yl)(phenyl)methanone (3da)

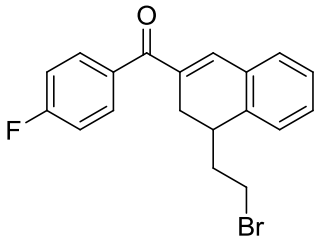


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.77 – 7.71 (m, 2H), 7.61 – 7.53 (m, 1H), 7.53 – 7.45 (m, 2H), 7.36 – 7.28 (m, 1H), 7.24 – 7.14 (m, 3H), 7.13 (d, *J* = 2.1Hz, 1H), 3.39 (t, *J* = 6.6 Hz, 2H), 3.04 – 2.84 (m, 2H), 2.78 (ddd, *J* = 17.1, 6.7, 2.3 Hz, 1H), 2.07 – 1.90 (m, 1H), 1.90 – 1.67 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.45, 140.80, 139.69, 138.32, 135.58, 131.77, 131.73, 130.06, 129.29, 129.25, 128.32, 127.78, 127.08, 36.73, 33.76, 32.74, 30.39, 27.72.

HRMS (ESI): Calcd. For $C_{20}H_{19}BrO$ $[M+]^+$ *m/z* 354.0619, found *m/z* 354.0622.

(4-(2-bromoethyl)-3,4-dihydronaphthalen-2-yl)(4-fluorophenyl)methanone (3ei)

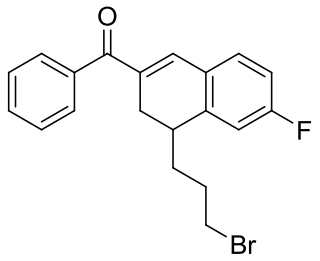


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.77 – 7.68 (m, 2H), 7.33 – 7.18 (m, 3H), 7.18 – 7.08 (m, 3H), 7.05 (d, *J* = 2.4 Hz, 1H), 3.39 (dt, *J* = 10.1, 6.4 Hz, 1H), 3.33 – 3.16 (m, 2H), 2.85 (dd, *J* = 17.2, 3.1 Hz, 1H), 2.74 (ddd, *J* = 17.2, 6.6, 2.5 Hz, 1H), 2.15 – 1.91 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 195.79, 139.49, 139.15, 135.39, 131.80, 131.69, 131.50, 130.24, 129.45, 128.05, 127.44, 115.65, 115.36, 36.71, 35.20, 31.74, 27.70.

HRMS (EI-MS): Calcd. For $C_{19}H_{16}BrFO$ $[M+]^+$ *m/z* 358.0369, found *m/z* 358.0364.

(4-(3-bromopropyl)-6-fluoro-3,4-dihydronaphthalen-2-yl)(phenyl)methanone (3fa)

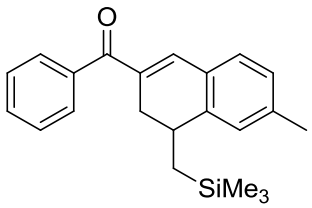


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.76 – 7.69 (m, 2H), 7.61 – 7.54 (m, 1H), 7.48 (m, 2H), 7.15 (dd, *J* = 8.2, 5.8 Hz, 1H), 7.10 (d, *J* = 2.0 Hz, 1H), 6.98 – 6.88 (m, 2H), 3.44 – 3.35 (m, 2H), 3.03 – 2.91 (m, 1H), 2.87 (dd, *J* = 17.1, 4.3 Hz, 1H), 2.75 (ddd, *J* = 17.1, 6.7, 2.0 Hz, 1H), 1.99 (m, 1H), 1.91 – 1.79 (m, 1H), 1.79 – 1.66 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.25, 161.84, 143.70, 143.59, 138.66, 138.22, 134.92, 134.89, 131.80, 131.03, 130.91, 129.20, 128.34, 128.07, 128.03, 115.11, 114.81, 114.08, 113.80, 36.95, 33.61, 32.44, 30.19, 27.19.

HRMS (EI-MS): Calcd. For $C_{20}H_{18}BrFO$ $[M+]^+$ *m/z* 372.0525, found *m/z* 372.0527.

(6-methyl-4-((trimethylsilyl)methyl)-3,4-dihydronaphthalen-2-yl)(phenyl)methanone (3gj)

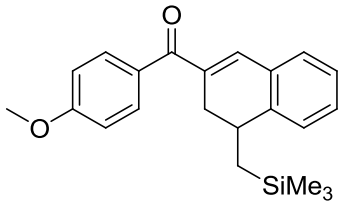


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.67 (dd, *J* = 17.4, 15.9 Hz, 2H), 7.60 – 7.32 (m, 3H), 7.10 (s, 1H), 7.07 – 6.91 (m, 3H), 3.05 (td, *J* = 10.2, 5.3 Hz, 1H), 2.80 – 2.66 (m, 2H), 2.33 (s, 3H), 0.97 (dd, *J* = 14.8, 9.8 Hz, 1H), 0.79 (dd, *J* = 14.7, 5.2 Hz, 1H), 0.00 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.27, 145.14, 141.30, 140.90, 139.41, 135.36, 132.21, 130.74, 129.90, 129.37, 128.94, 128.41, 127.92, 34.71, 30.88, 23.59, 22.42, 0.00.

HRMS (EI-MS): Calcd. For $C_{22}H_{26}OSi$ $[M+]^+$ m/z 334.1753, found *m/z* 334.1749.

(6-chloro-4-((trimethylsilyl)methyl)-3,4-dihydronaphthalen-2-yl)(4-methoxyphenyl)methanone (hj)

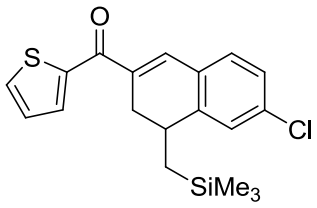


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.81 – 7.74 (m, 2H), 7.30 – 7.06 (m, 4H), 6.99 – 6.91 (m, 2H), 3.87 (s, 3H), 3.10 (dq, *J* = 10.6, 5.4 Hz, 1H), 2.79 – 2.72 (m, 2H), 1.00 (dd, *J* = 14.8, 9.6 Hz, 1H), 0.83 (dd, *J* = 14.8, 5.4 Hz, 1H), 0.00 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.15, 163.44, 144.87, 139.06, 136.64, 132.33, 132.14, 131.62, 130.63, 129.66, 127.54, 127.26, 114.27, 56.22, 34.69, 31.56, 23.44, 0.00.

HRMS (ESI): Calcd. For $C_{22}H_{27}O_2Si$ $[M+H]^+$ m/z 351.1775, found *m/z* 351.1777.

(6-chloro-4-((trimethylsilyl)methyl)-3,4-dihydronaphthalen-2-yl)(thiophen-2-yl)methanone (3kj)

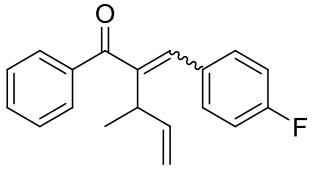


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.66 (ddd, *J* = 6.1, 4.4, 1.1 Hz, 2H), 7.32 (d, *J* = 1.8 Hz, 1H), 7.20 – 7.16 (m, 1H), 7.16 – 7.07 (m, 3H), 3.05 (td, *J* = 10.6, 5.3 Hz, 1H), 2.83 – 2.62 (m, 2H), 0.95 (dt, *J* = 18.5, 9.2 Hz, 1H), 0.79 (dd, *J* = 14.8, 5.0 Hz, 1H), 0.00 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 189.03, 146.61, 144.00, 137.02, 136.75, 136.18, 133.94, 133.55, 130.80, 130.54, 128.50, 127.79, 127.42, 34.71, 31.32, 23.17, 0.00.

HRMS (ESI): Calcd. For $C_{19}H_{22}ClOSSi$ $[M+H]^+$ m/z 361.0844, found *m/z* 361.0849.

2-(4-fluorobenzylidene)-3-methyl-1-phenylpent-4-en-1-one (3fk)

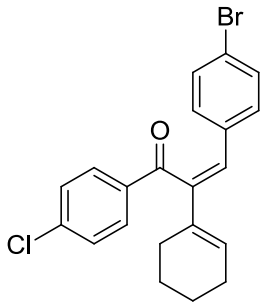


^{1}H NMR (600 MHz, $CDCl_3$, *Z* isomer, major) δ = 7.83 – 7.79 (m, 2H), 7.45 – 7.41 (m, 1H), 7.31 – 7.27 (m, 2H), 7.07 (ddd, *J* = 8.3, 5.1, 2.4 Hz, 2H), 6.80 – 6.73 (m, 2H), 6.68 (d, *J* = 6.9 Hz, 1H), 5.93 (ddd, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.18 – 5.05 (m, 2H), 3.39 (dq, *J* = 7.0, 6.0 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 200.60, 144.61, 144.60, 140.29, 136.18, 133.28, 130.25, 130.20, 129.69, 129.38, 128.43, 127.86, 115.16, 115.02, 42.91, 18.55.

HRMS (ESI): Calcd. For $C_{19}H_{18}FO$ $[M+H]^+$ m/z 281.1342, found *m/z* 281.1345.

(E)-3-(4-bromophenyl)-1-(4-chlorophenyl)-2-cyclohexenylprop-2-en-1-one (3al)

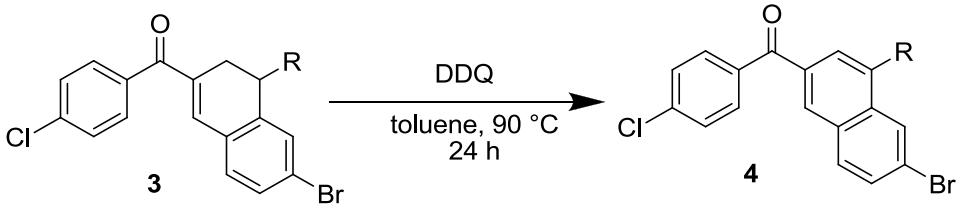


^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 7.83 (d, *J* = 0.6 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.31 – 7.17 (m, 3H), 6.98 – 6.88 (m, 2H), 6.75 (s, 1H), 4.99 (td, *J* = 10.4, 4.7 Hz, 1H), 2.68 (td, *J* = 11.7, 3.6 Hz, 1H), 2.21 – 2.11 (m, 1H), 2.03 (m, 1H), 1.76 (m, 2H), 1.52 – 1.20 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 198.51, 160.49, 141.63, 139.94, 134.28, 134.08, 131.46, 130.76, 130.27, 130.19, 128.86, 122.11, 49.38, 32.25, 31.82, 25.38, 24.30.

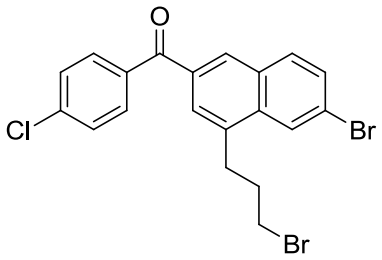
HRMS (EI-MS): Calcd. For $C_{21}H_{18}BrClO$ $[M+]^+$ *m/z* 400.0230, found *m/z* 400.0227.

General procedure (GP-B) for the transformation of dihydronapthalenes to napthalenes[13]



Dihydronapthalene **3** (1 equiv), DDQ (1.5 equiv) in toluene was refluxed for 24 h. After the completion of the reaction (as judged by TLC analysis), the solvent was removed in vacuo and the residue was subjected to colum chromatography on silica gel, using PE/EA as solvent system to get the pure product **4**.

(6-bromo-4-(3-bromopropyl)naphthalen-2-yl)(4-chlorophenyl)methanone (4a)

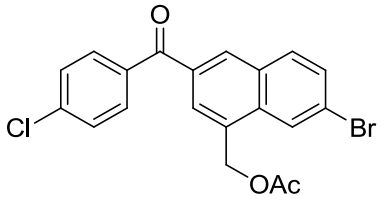


^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.26 (s, 1H), 8.06 (s, 1H), 7.86 – 7.75 (m, 4H), 7.65 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.55 – 7.45 (m, 2H), 3.50 (t, *J* = 6.4 Hz, 2H), 3.30 – 3.21 (m, 2H), 2.32 (dq, *J* = 9.2, 6.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 195.11, 139.07, 137.01, 135.85, 134.90, 134.39, 131.88, 131.47, 131.24, 130.63, 130.23, 128.81, 126.67, 126.34, 123.42, 33.11, 33.06, 31.09.

HRMS (EI-MS): Calcd. For $C_{20}H_{15}Br_2ClO$ $[M+]^+$ m/z 463.9178, found *m/z* 463.9180.

(7-bromo-3-(4-chlorobenzoyl)naphthalen-1-yl)methyl acetate (4b)

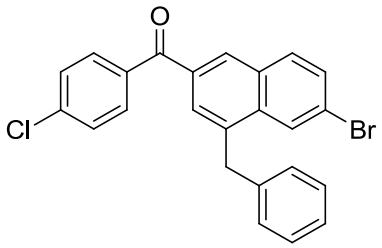


^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 15.8 Hz, 2H), 8.01 (s, 1H), 7.80 (dd, *J* = 12.6, 5.5 Hz, 3H), 7.69 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 5.55 (s, 2H), 2.15 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 194.69, 170.78, 139.24, 135.65, 134.40, 134.28, 132.38, 131.82, 131.70, 131.47, 131.10, 130.64, 128.87, 127.66, 126.29, 123.96, 63.82, 21.03.

HRMS (EI-MS): Calcd. For $C_{20}H_{14}BrClO_3$ $[M+]^+$ m/z 415.9815, found *m/z* 415.9817.

(4-benzyl-6-bromonaphthalen-2-yl)(4-chlorophenyl)methanone (4c)



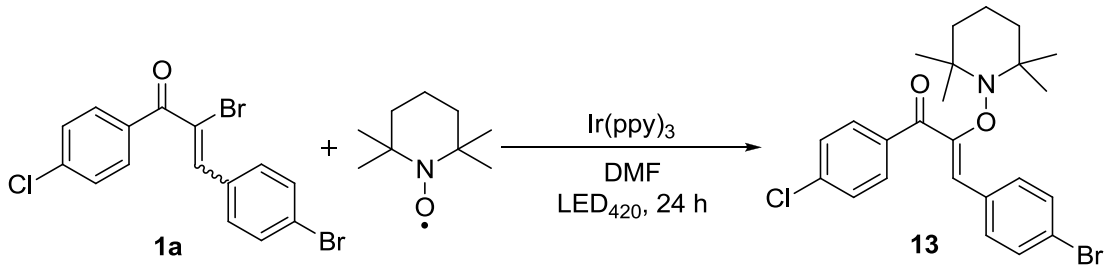
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 1.6 Hz, 1H), 8.09 (s, 1H), 7.78 (dd, *J* = 8.7, 2.2 Hz, 4H), 7.62 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 4.44 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 195.10, 139.33, 139.02, 137.06, 135.87, 135.23, 134.41, 132.29, 131.71, 131.47, 131.27, 130.74, 130.20, 128.75, 128.65, 127.78, 126.99, 126.56, 123.36, 38.90.

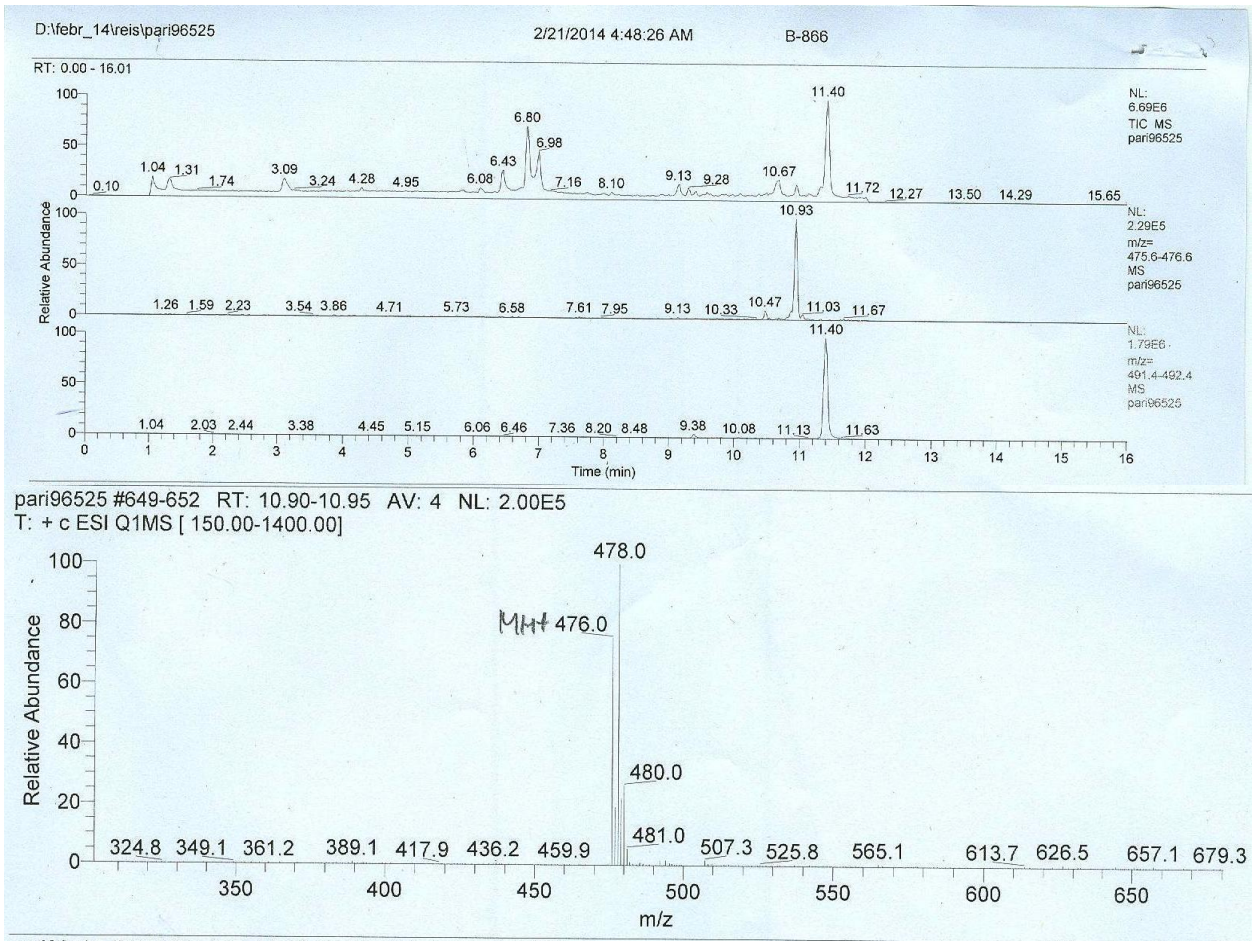
HRMS (EI-MS): Calcd. For $C_{24}H_{16}BrClO$ $[M+]^+$ *m/z* 434.0073, found *m/z* 434.0075.

Experimental procedure to trap radical with TEMPO

An oven dried 15 mL Schlenk tube equipped with a plastic septum and magnetic stir bar was charged with $Ir(ppy)_3$ (20 mol %), α-bromochalcone 1a (0.1 mmol, 1.0 equiv) and TEMPO (0.3 mmol, 3.0 equiv). The flask was purged with a stream of nitrogen and 0.5 mL of dry dimethylformamide was added. The resultant mixture was degassed by freeze-pump-thaw procedure (3 cycles). The tube was sealed with an internal irradiation set up. After 24 h of irradiation, TEMPO trapped compound **13** was detected by mass spectra.



Exact mass = 475.09


D:\febr_14\reis\pari96525
2/21/2014 4:48:26 AM
B-866
RT: 0.00 - 16.01
NL: 6.69E6 TIC MS pari96525
NL: 2.29E5 m/z= 475.6-476.6 MS pari96525
NL: 1.79E6 m/z= 491.4-492.4 MS pari96525
Relative Abundance
Time (min)
pari96525 #649-652 RT: 10.90-10.95 AV: 4 NL: 2.00E5
T: + c ESI Q1MS [150.00-1400.00]
478.0
MH+ 476.0
480.0
481.0
m/z

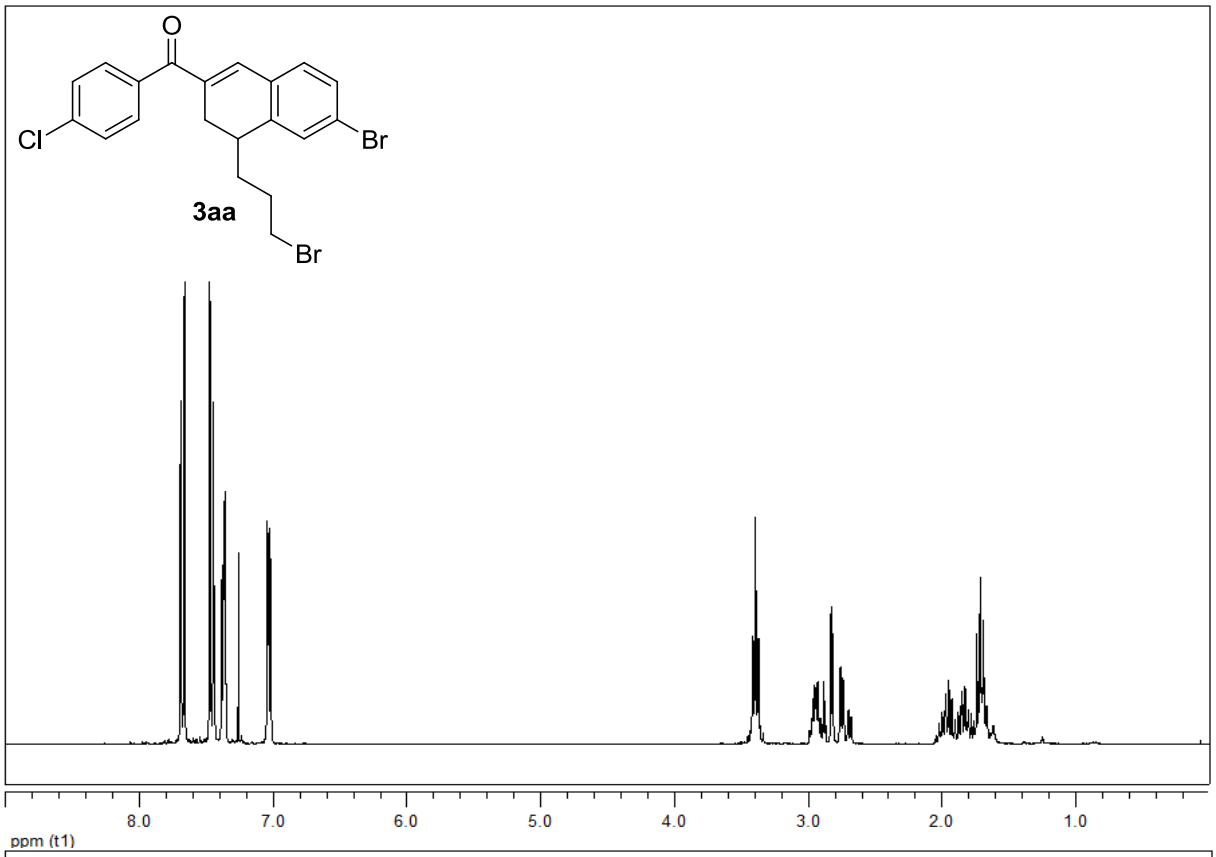
Appendix

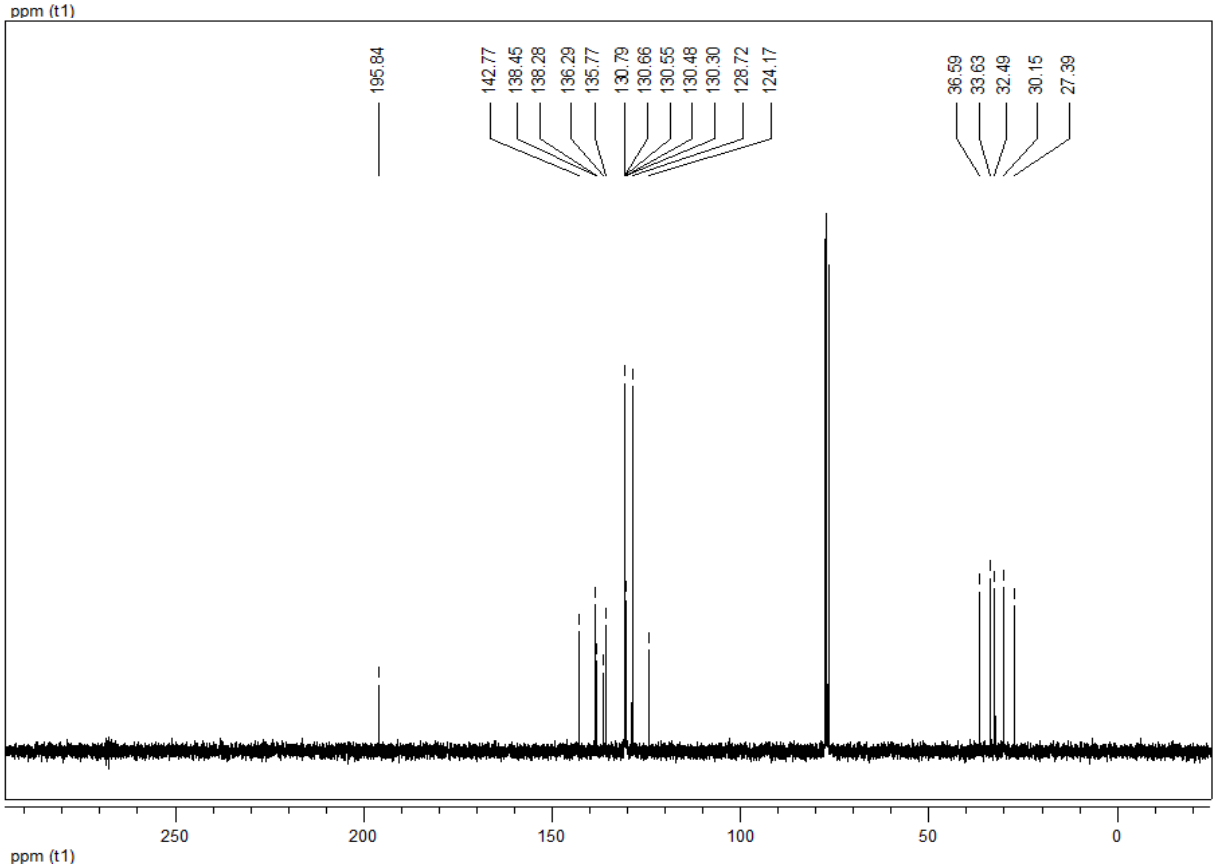
NMR- spectra

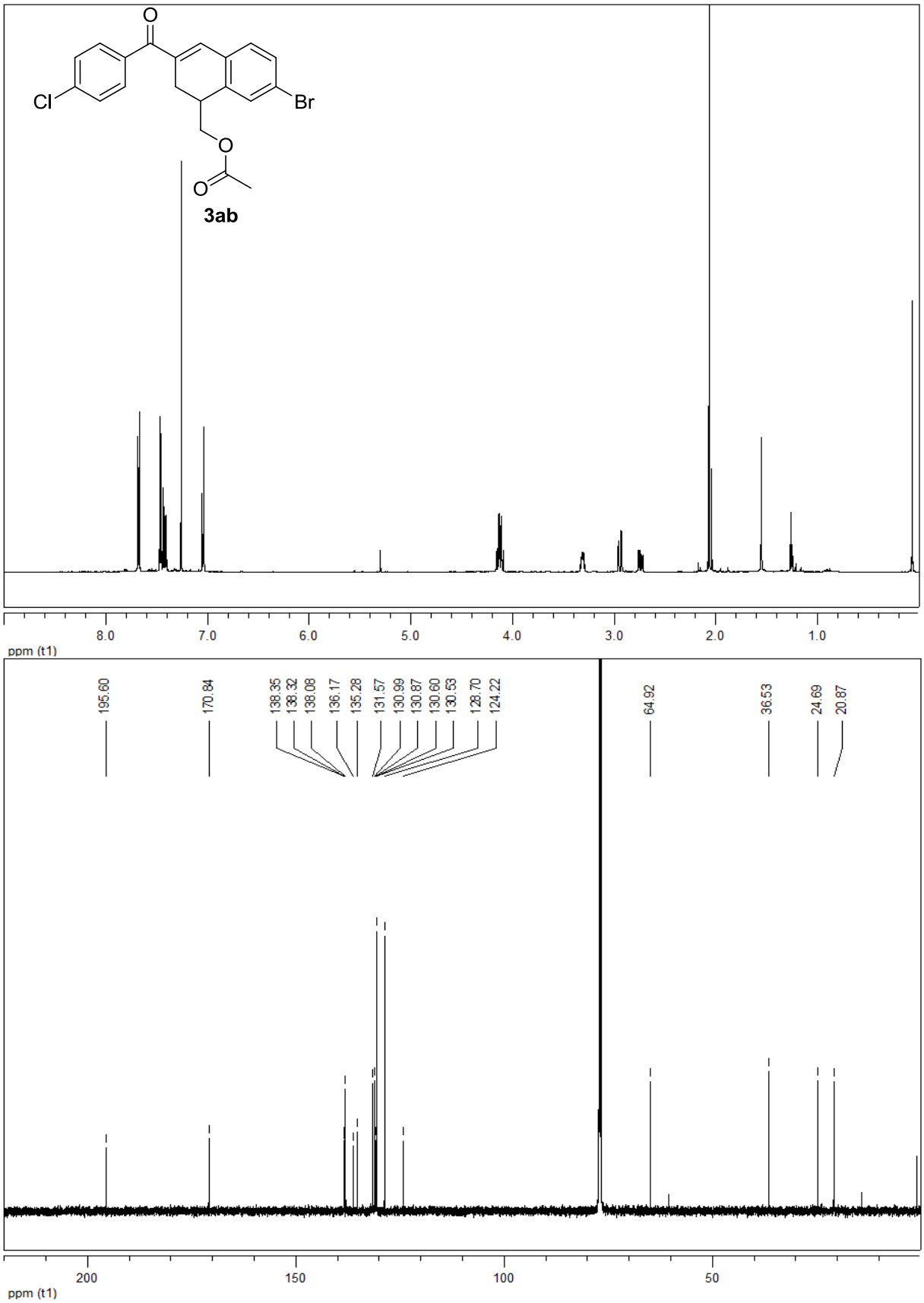
^{1}H-NMR spectra - upper image

^{13}C-NMR spectra - lower image

Solvent, if not stated otherwise: $CDCl_3$


O
Cl
Br
3aa
Br
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


195.84
142.77
138.45
138.28
136.29
135.77
130.79
130.66
130.55
130.48
130.30
128.72
124.17
36.59
33.63
32.49
30.15
27.39
250
200
150
100
50
0
ppm (t1)


O
Cl
Br
O
O
3ab
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
195.60
170.84
138.35
138.32
138.08
136.17
135.28
131.57
130.99
130.87
130.60
130.53
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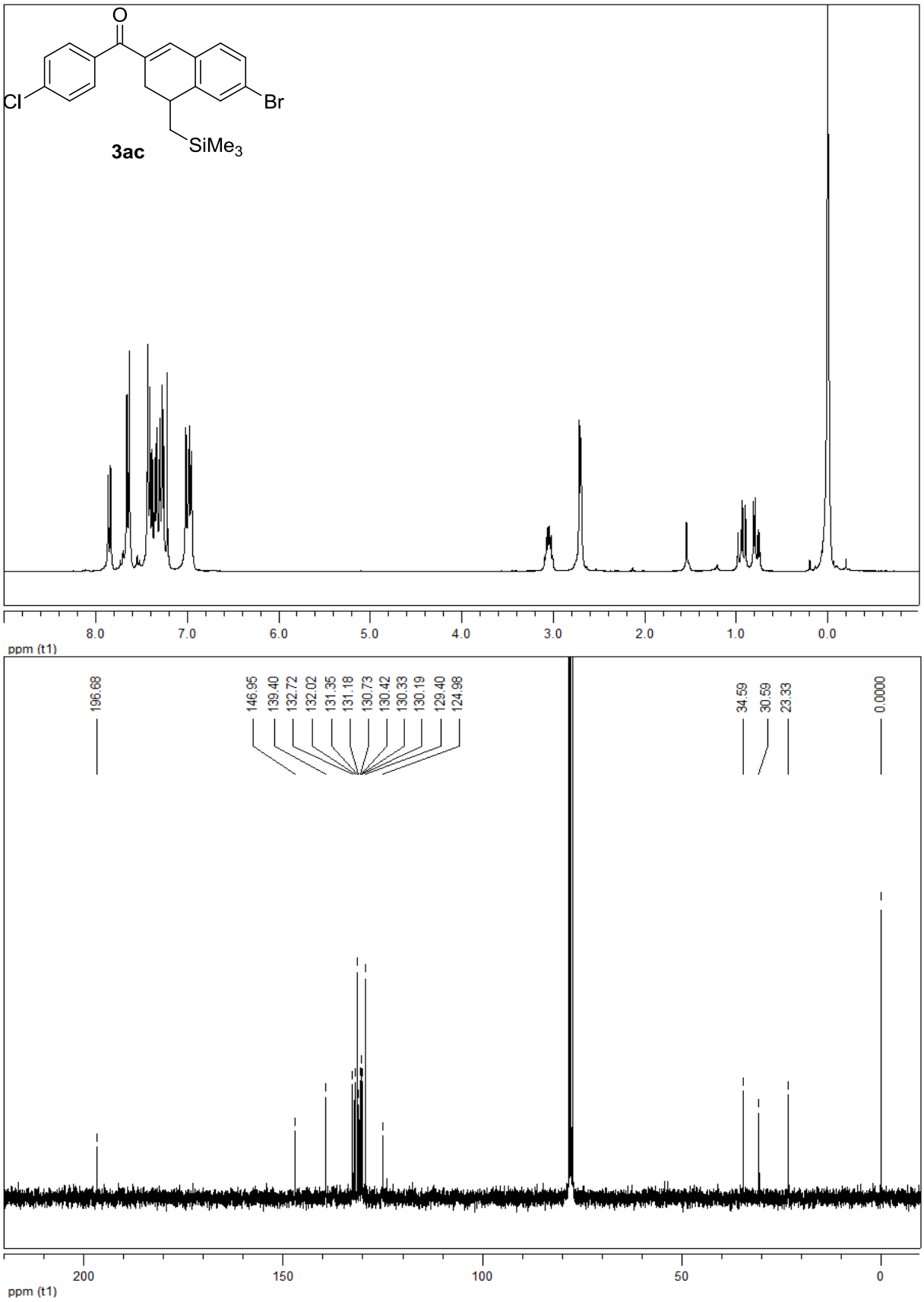
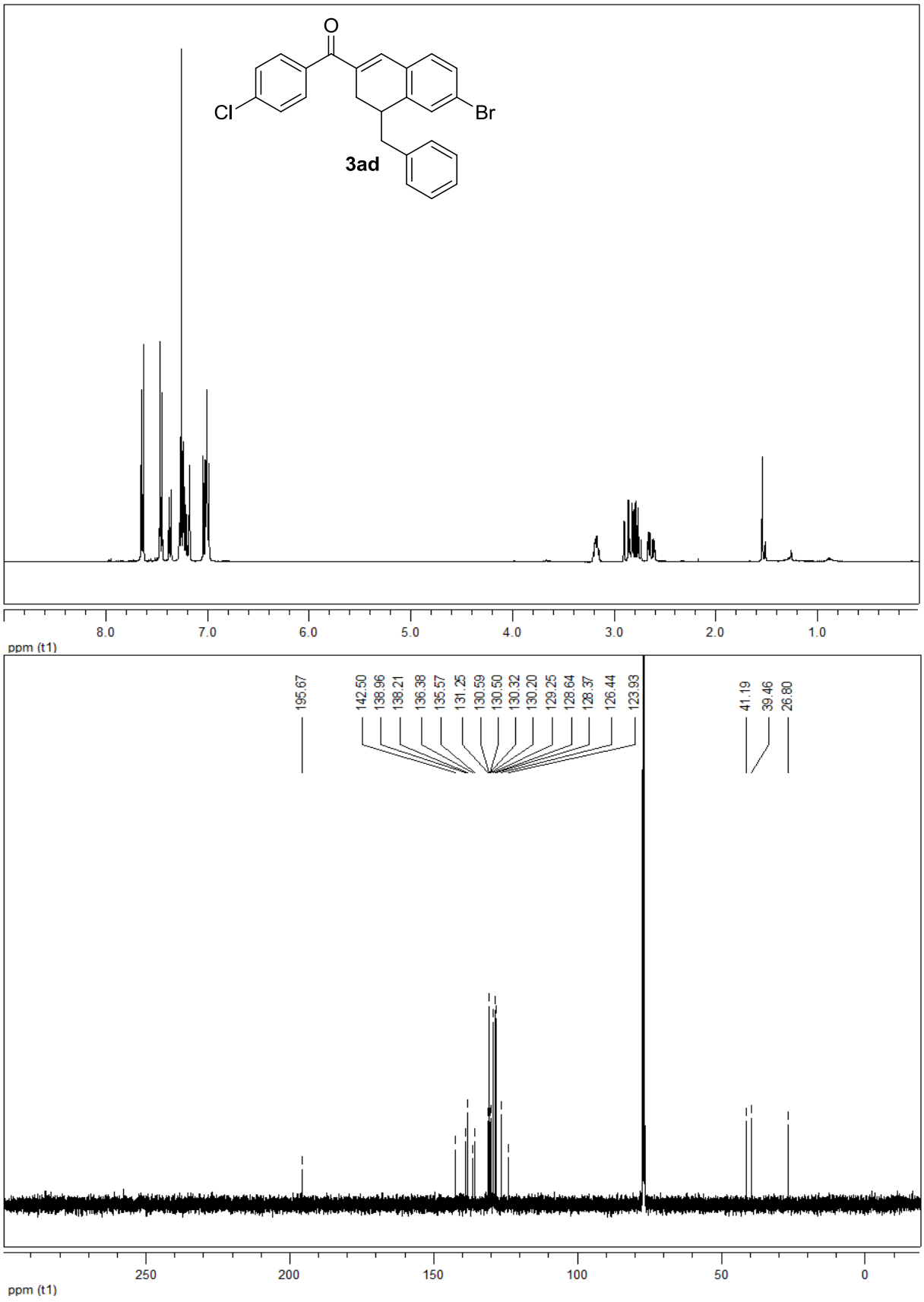
24.69
20.87
200
150
100
50
ppm (t1)


O
Cl
Br
SiMe3
3ac
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
196.68
146.95
139.40
132.72
132.02
131.35
131.18
130.73
130.42
130.33
130.19
129.40
124.98
34.59
30.59
23.33
0.0000
200
150
100
50
0
ppm (t1)


O
Cl
Br
3ad
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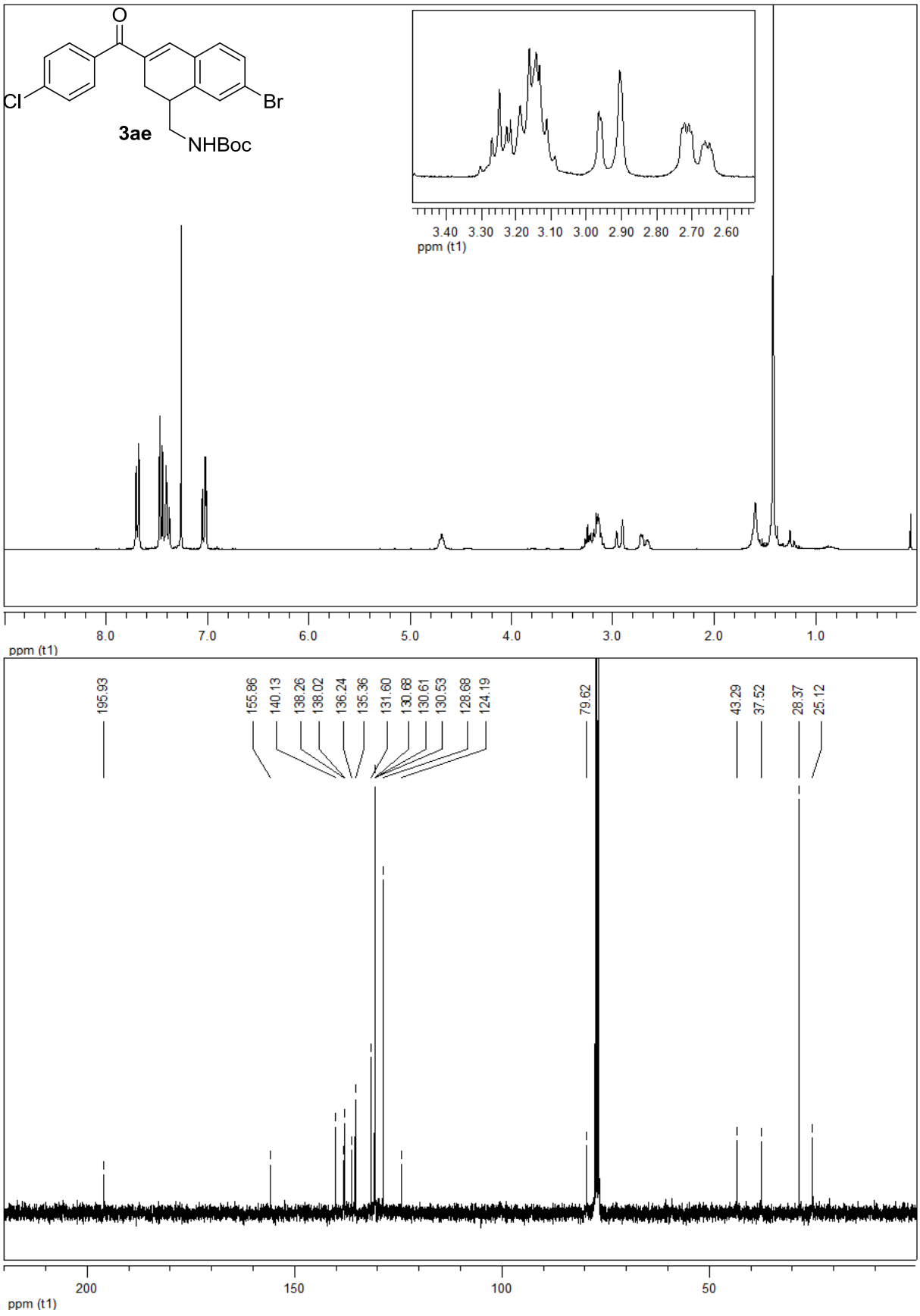
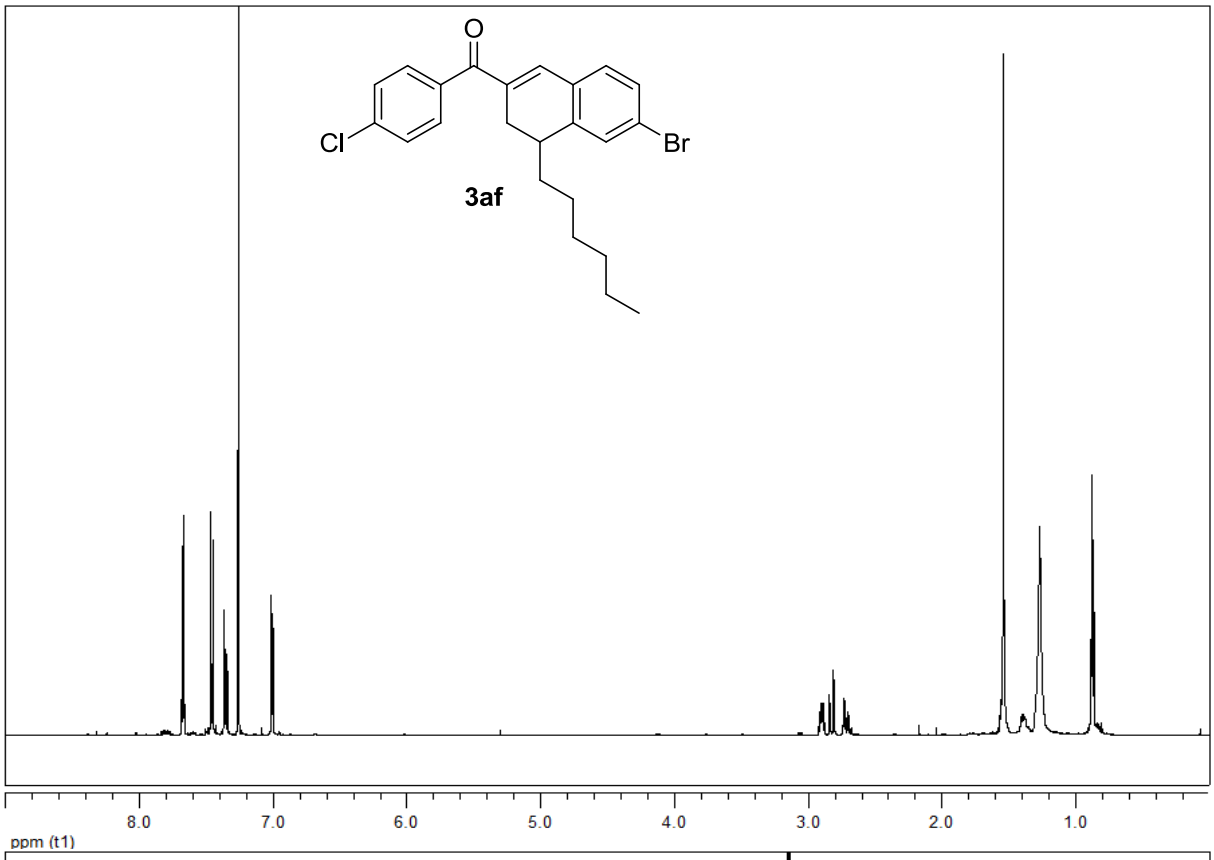
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
195.67
142.50
138.96
138.21
136.38
135.57
131.25
130.59
130.50
130.32
130.20
129.25
128.64
128.37
126.44
123.93
41.19
39.46
26.80
250
200
150
100
50
0
ppm (t1)


O
Cl
Br
3ae
NHBoc
3.40 3.30 3.20 3.10 3.00 2.90 2.80 2.70 2.60
ppm (t1)
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
ppm (t1)
195.93
155.86
140.13
138.26
138.02
136.24
135.36
131.60
130.68
130.61
130.53
128.68
124.19
79.62
43.29
37.52
28.37
25.12
200 150 100 50
ppm (t1)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Cl
Br
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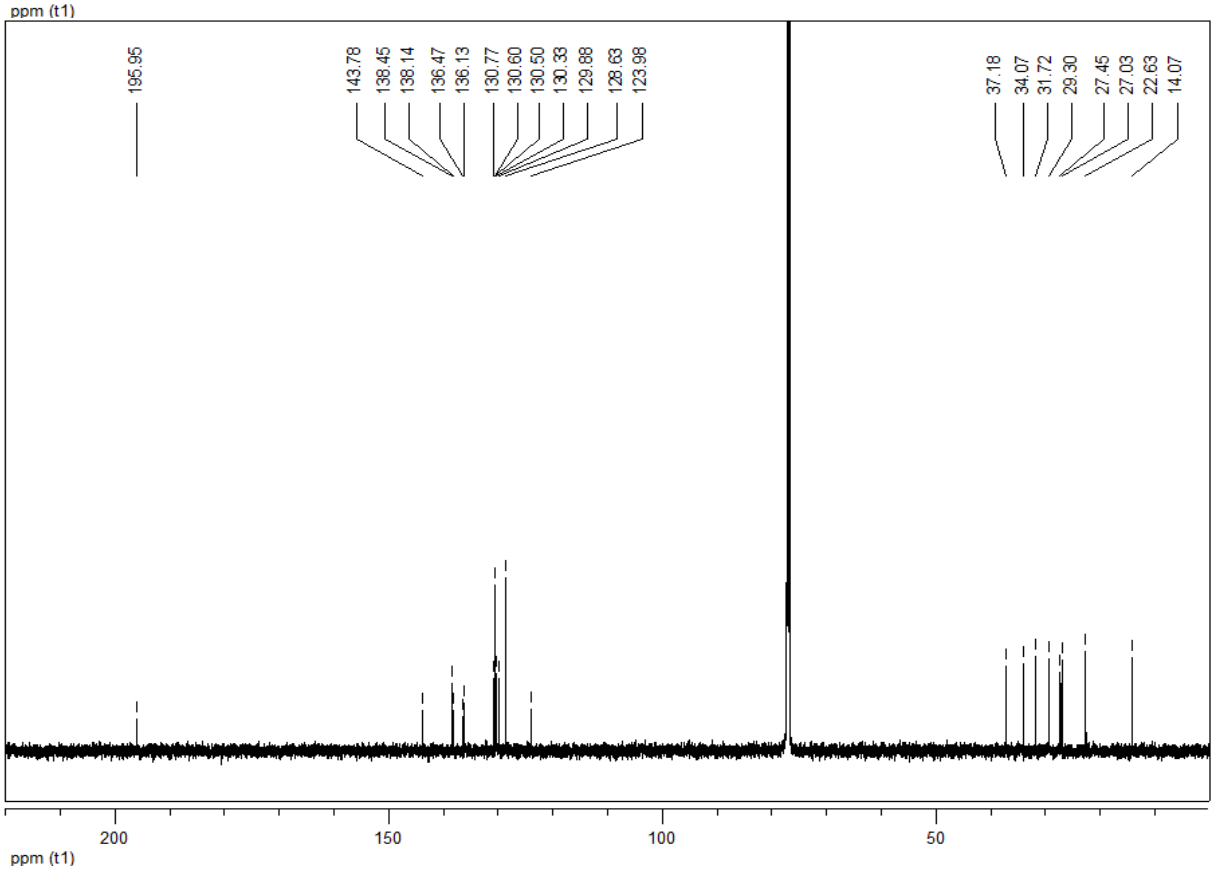
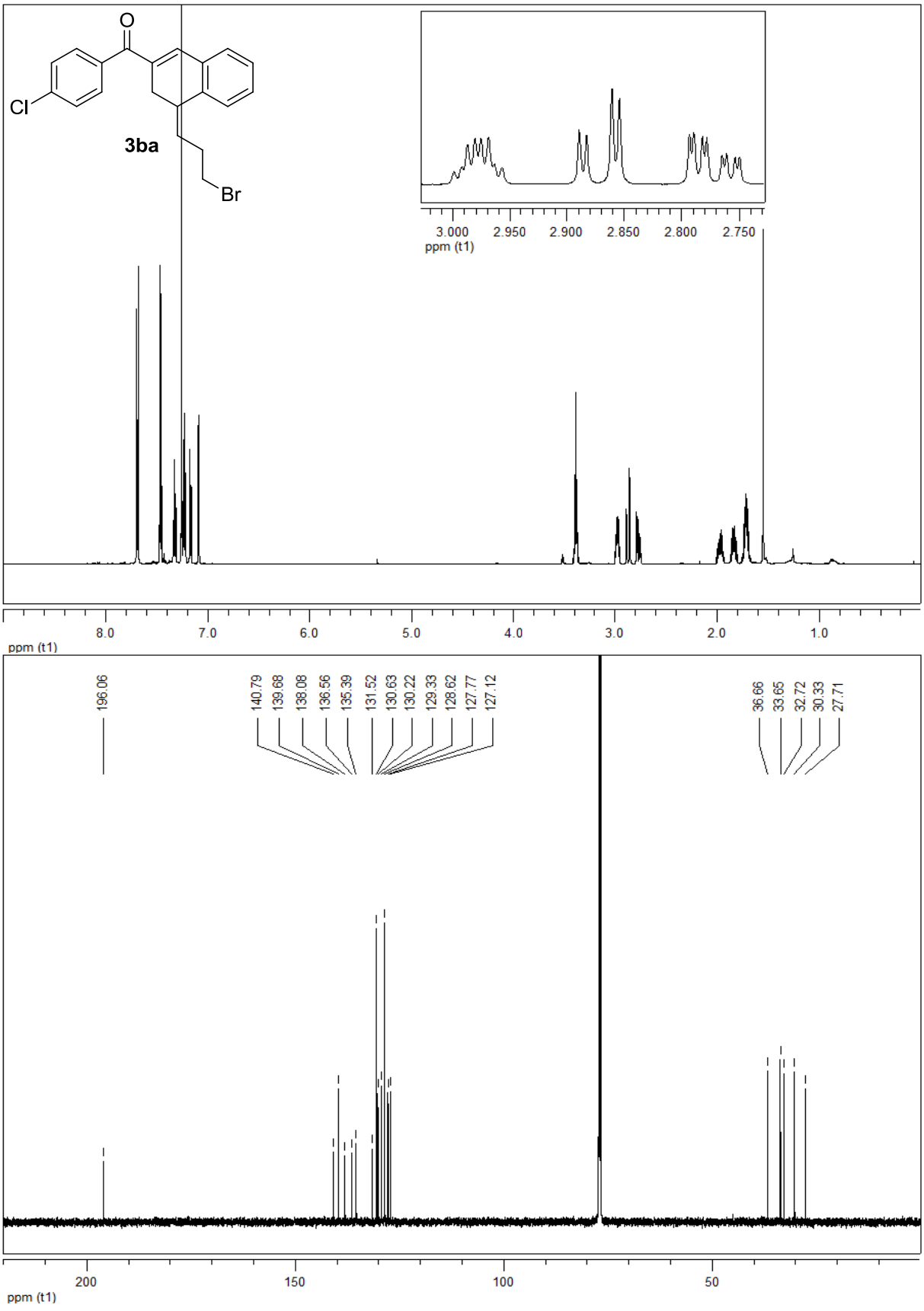
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


195.95
143.78
138.45
138.14
136.47
136.13
130.77
130.60
130.50
130.33
129.88
128.63
123.98
37.18
34.07
31.72
29.30
27.45
27.03
22.63
14.07
200
150
100
50
ppm (t1)


O
Cl
3ba
Br
3.000
2.950
2.900
2.850
2.800
2.750
ppm (t1)
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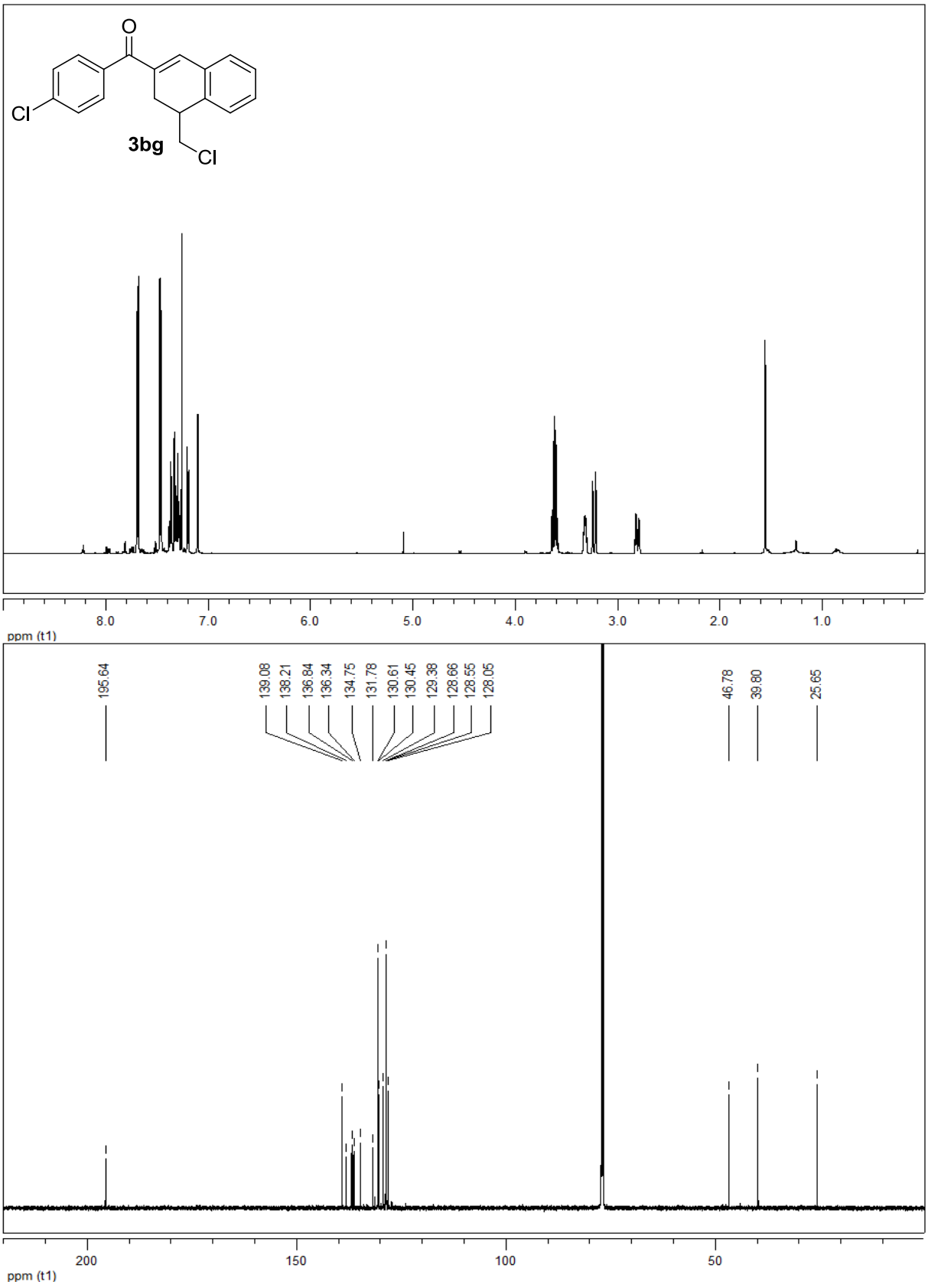
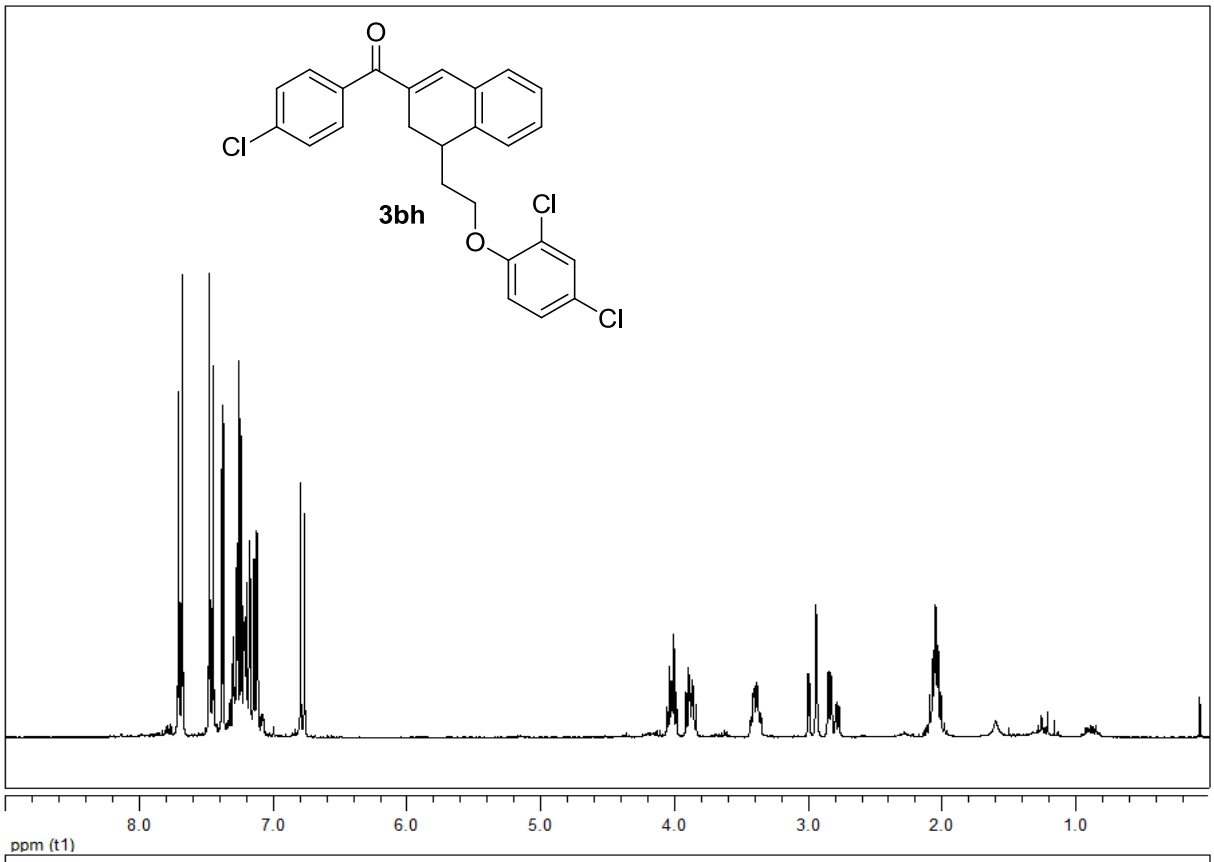
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
196.06
140.79
139.68
138.08
136.56
135.39
131.52
130.63
130.22
129.33
128.62
127.77
127.12
36.66
33.65
32.72
30.33
27.71
200
150
100
50
ppm (t1)


O
Cl
3bg
Cl
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
195.64
139.08
138.21
136.84
136.34
134.75
131.78
130.61
130.45
129.38
128.66
128.55
128.05
46.78
39.80
25.65
200
150
100
50
ppm (t1)


O
Cl
3bh
Cl
O
Cl
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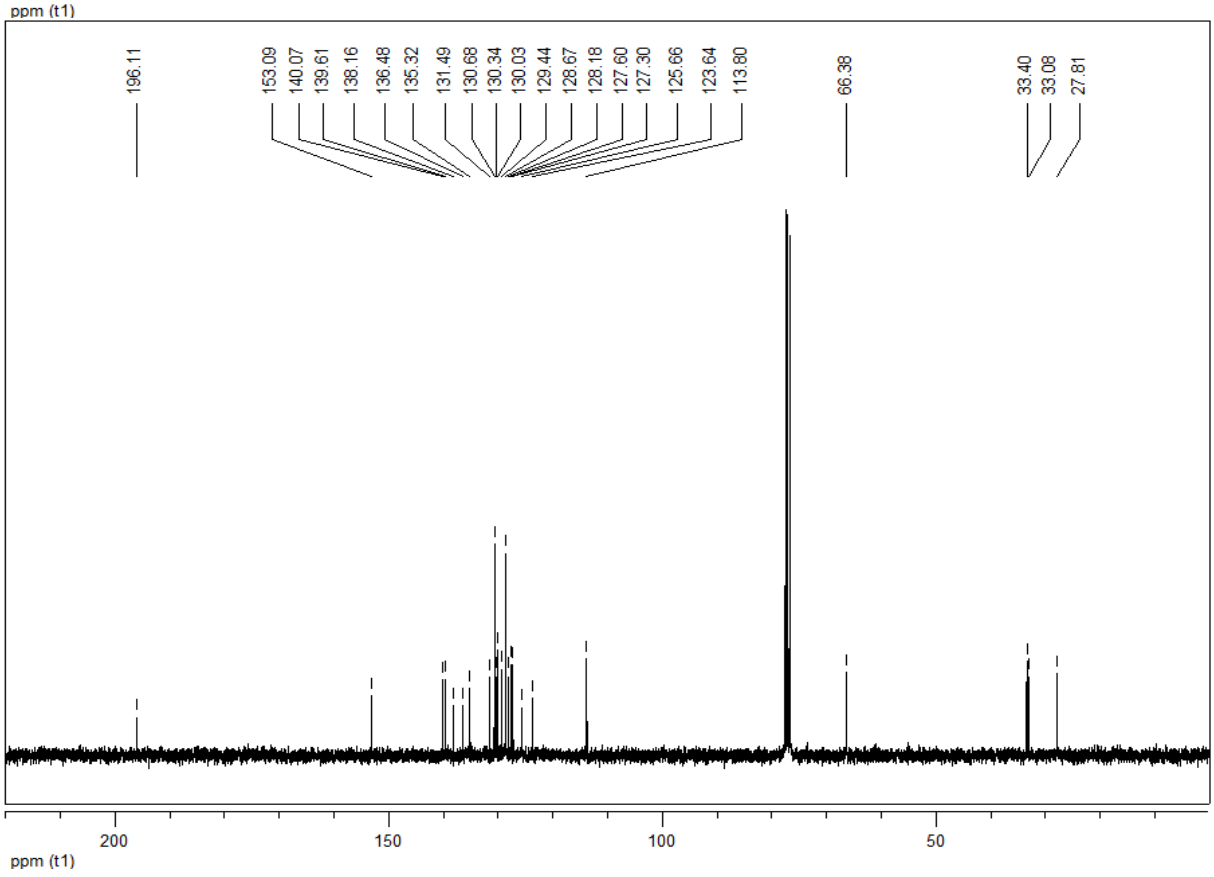
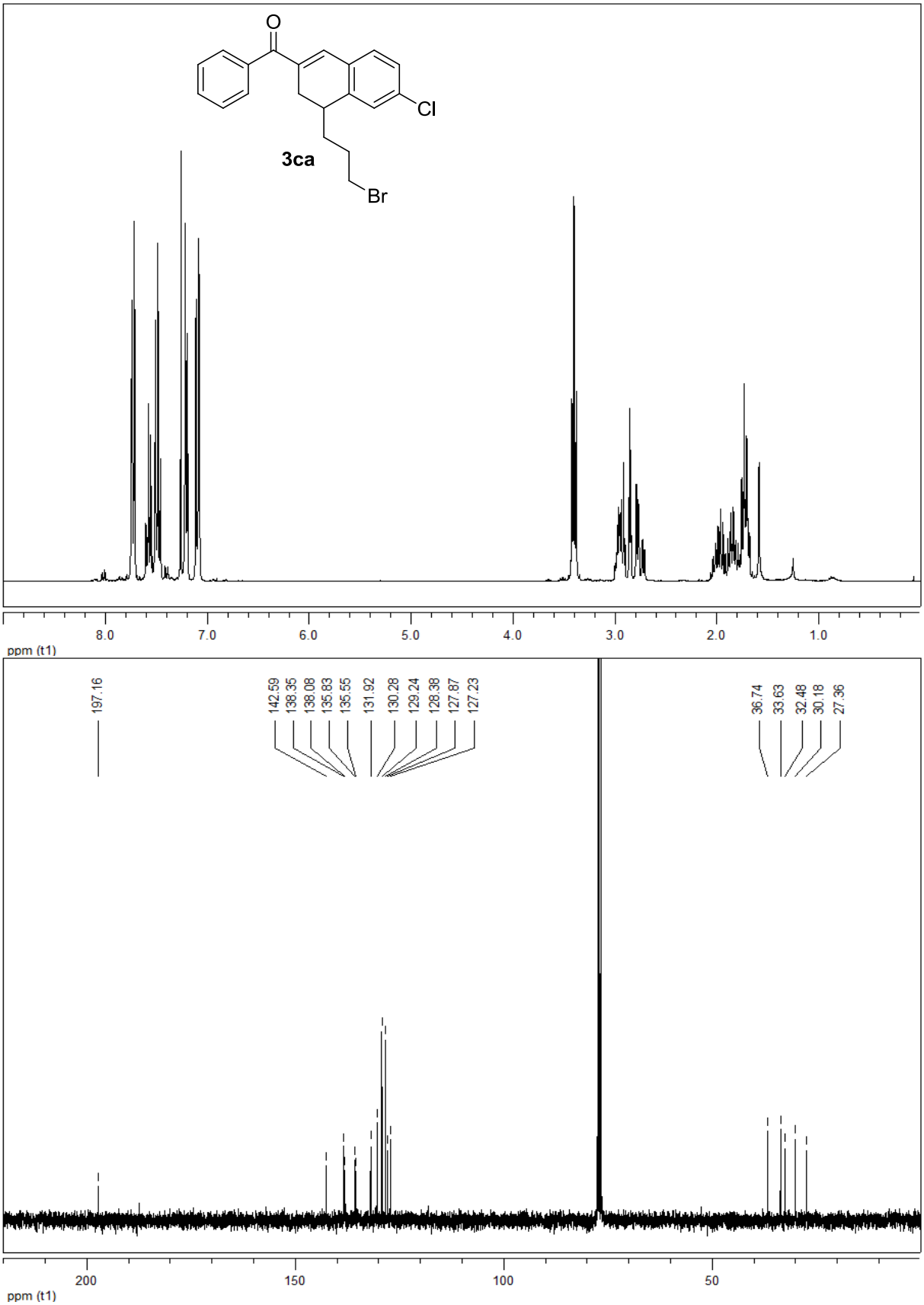
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


196.11
153.09
140.07
139.61
138.16
136.48
135.32
131.49
130.68
130.34
130.03
129.44
128.67
128.18
127.60
127.30
125.66
123.64
113.80
66.38
33.40
33.08
27.81
200
150
100
50
ppm (t1)


O
Cl
3ca
Br
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
197.16
142.59
138.35
138.08
135.83
135.55
131.92
130.28
129.24
128.38
127.87
127.23
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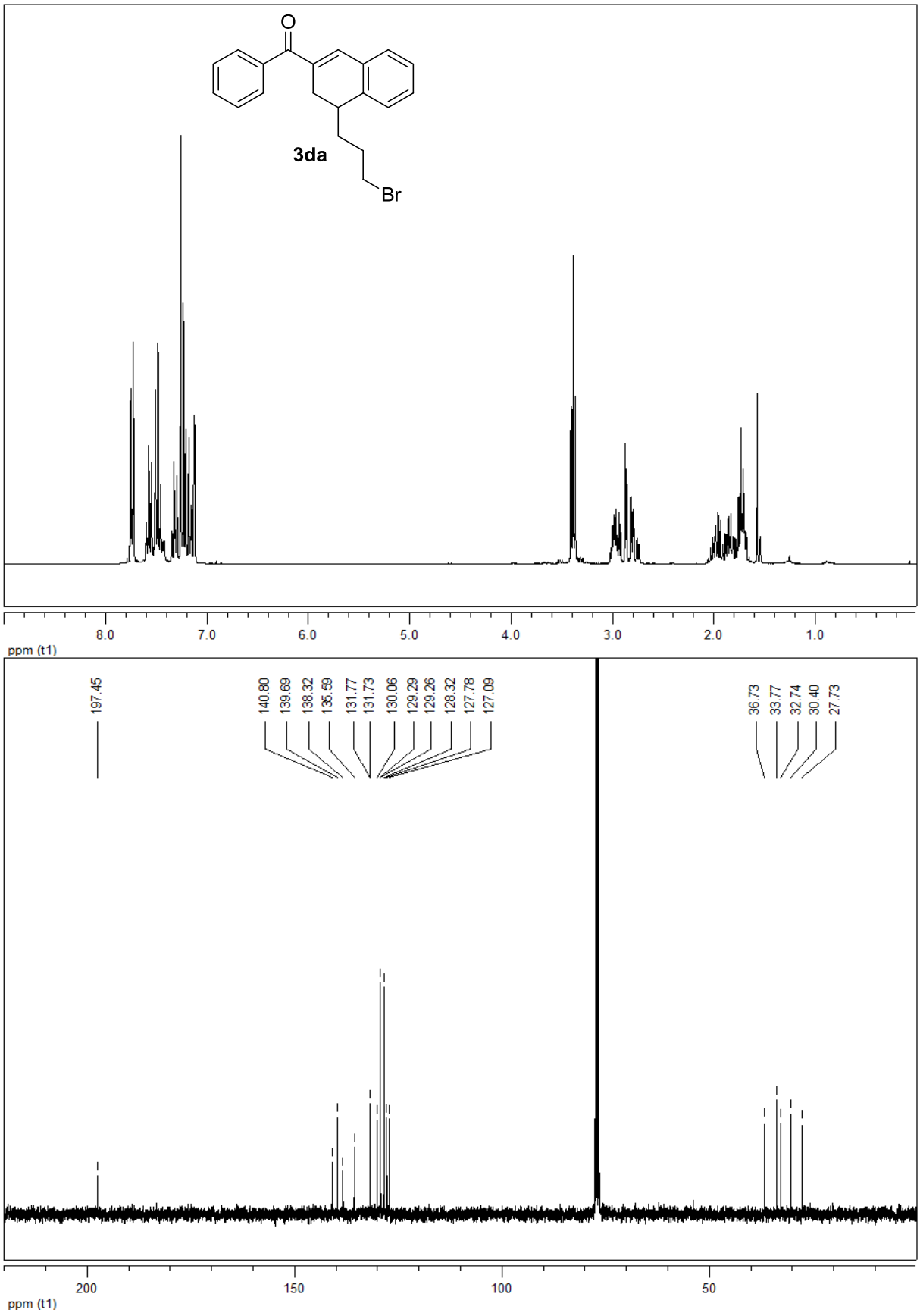
30.18
27.36
200
150
100
50
ppm (t1)


O
3da
Br
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
197.45
140.80
139.69
138.32
135.59
131.77
131.73
130.06
129.29
129.26
128.32
127.78
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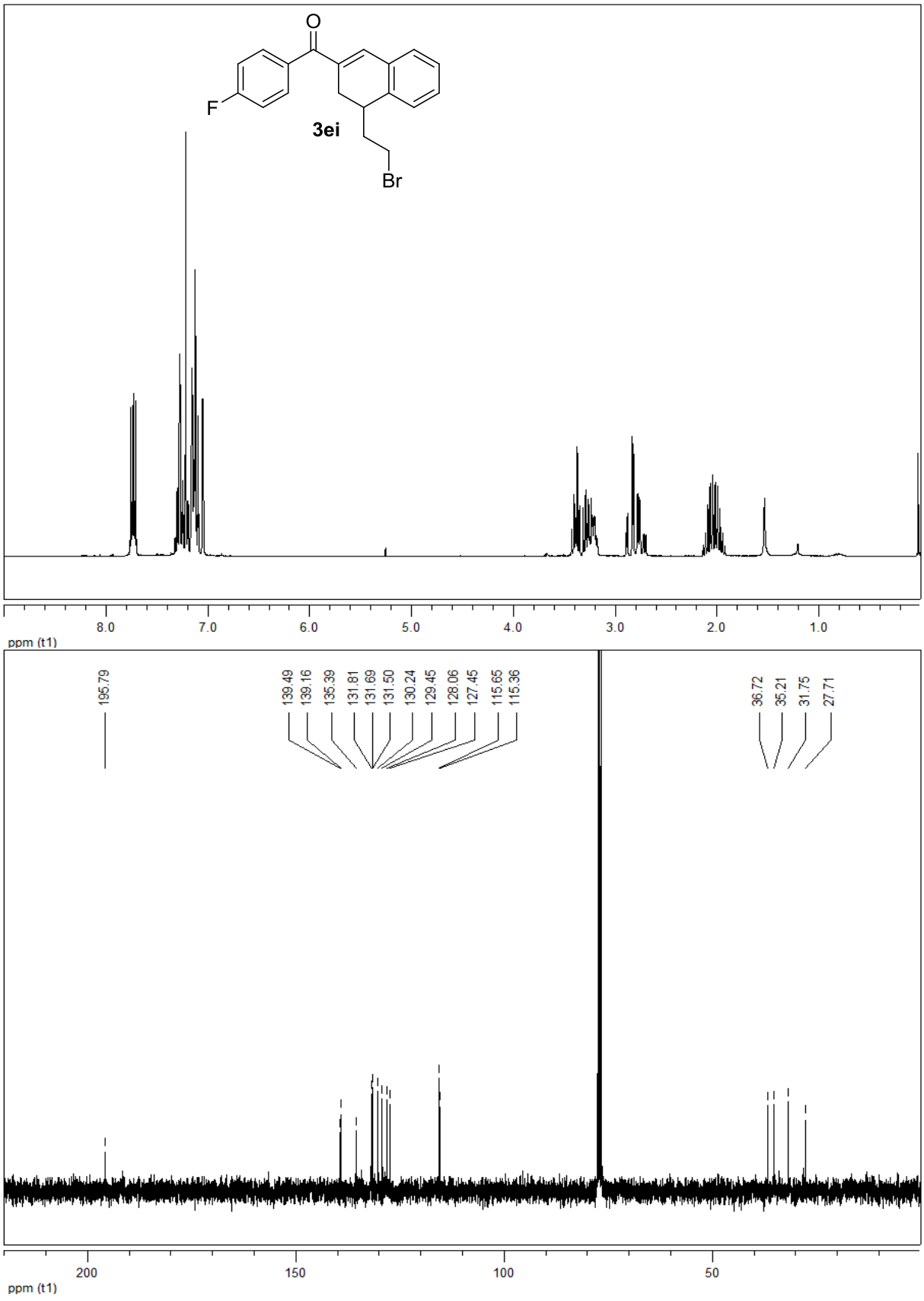
30.40
27.73
200
150
100
50
ppm (t1)


O
F
3ei
Br
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
195.79
139.49
139.16
135.39
131.81
131.69
131.50
130.24
129.45
128.06
127.45
115.65
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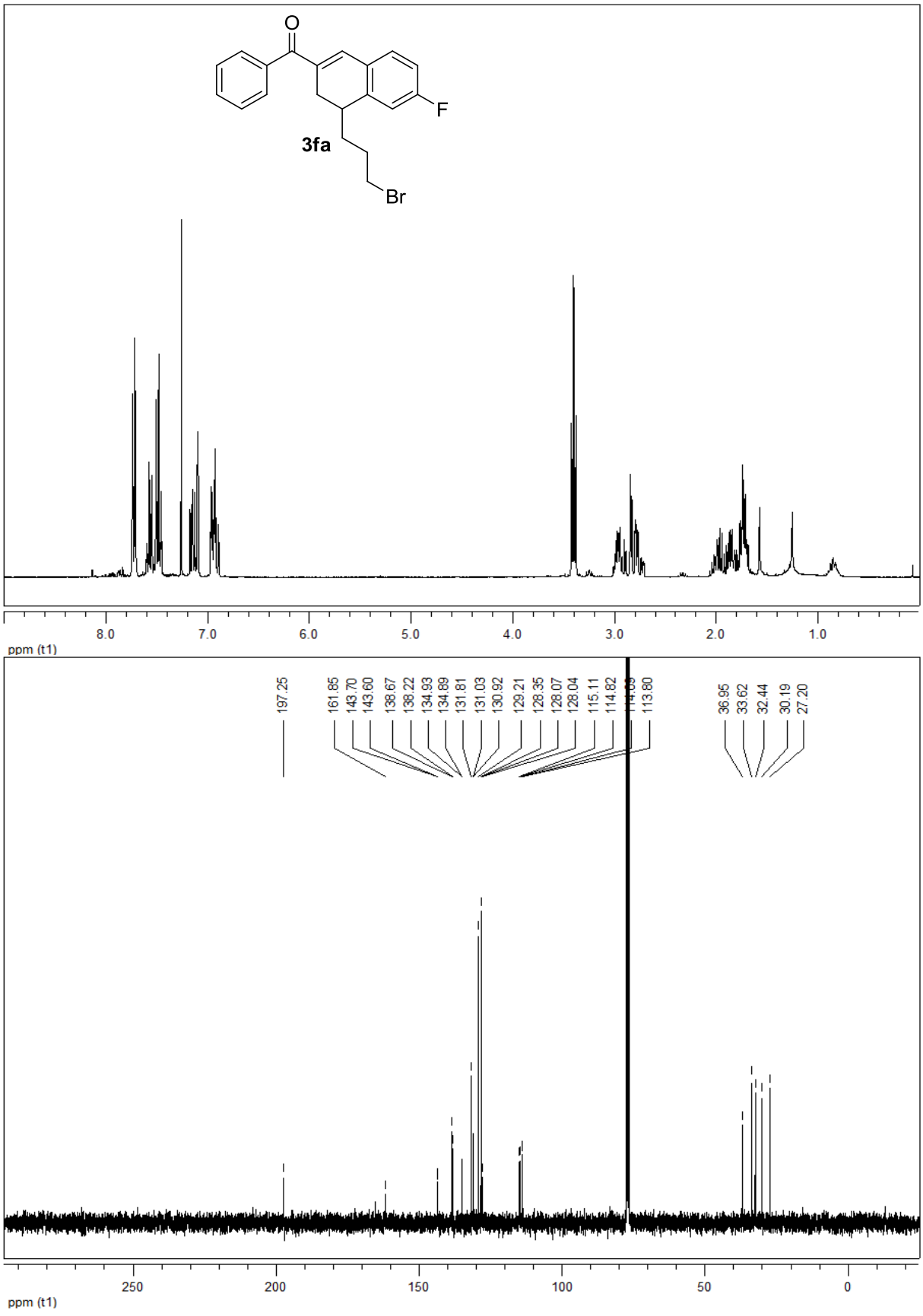
31.75
27.71
200
150
100
50
ppm (t1)


O
F
3fa
Br
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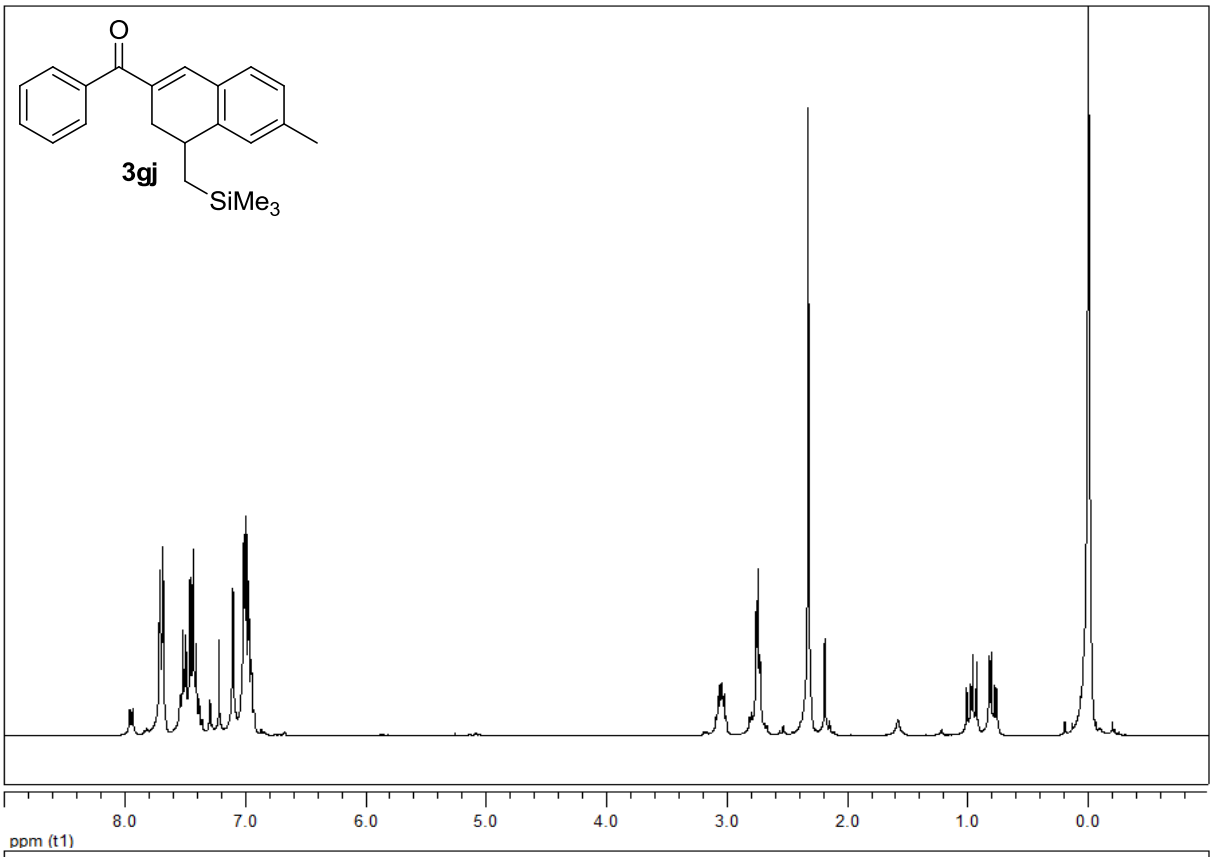
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
197.25
161.85
143.70
143.60
138.67
138.22
134.93
134.89
131.81
131.03
130.92
129.21
128.35
128.07
128.04
115.11
114.82
113.80
36.95
33.62
32.44
30.19
27.20
250
200
150
100
50
0
ppm (t1)


O
3gj
SiMe3
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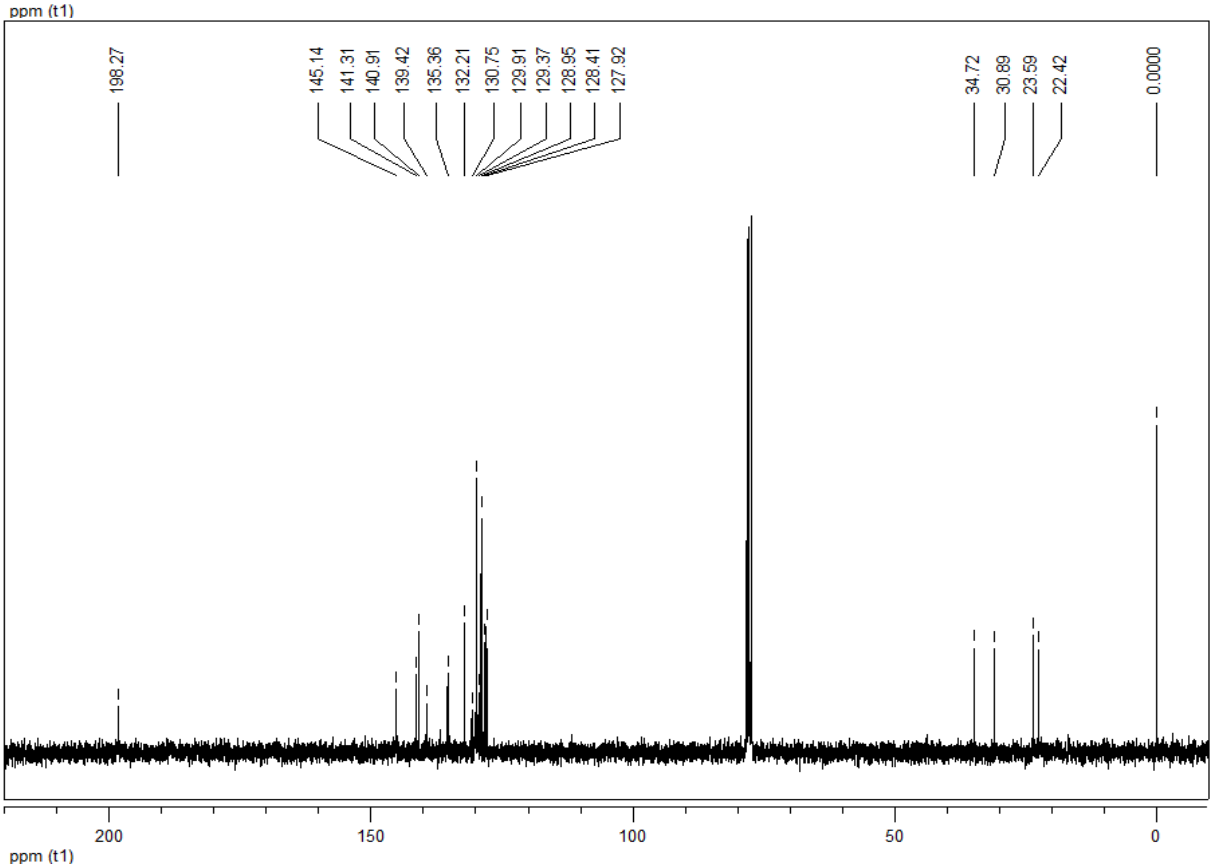
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


198.27
145.14
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140.91
139.42
135.36
132.21
130.75
129.91
129.37
128.95
128.41
127.92
34.72
30.89
23.59
22.42
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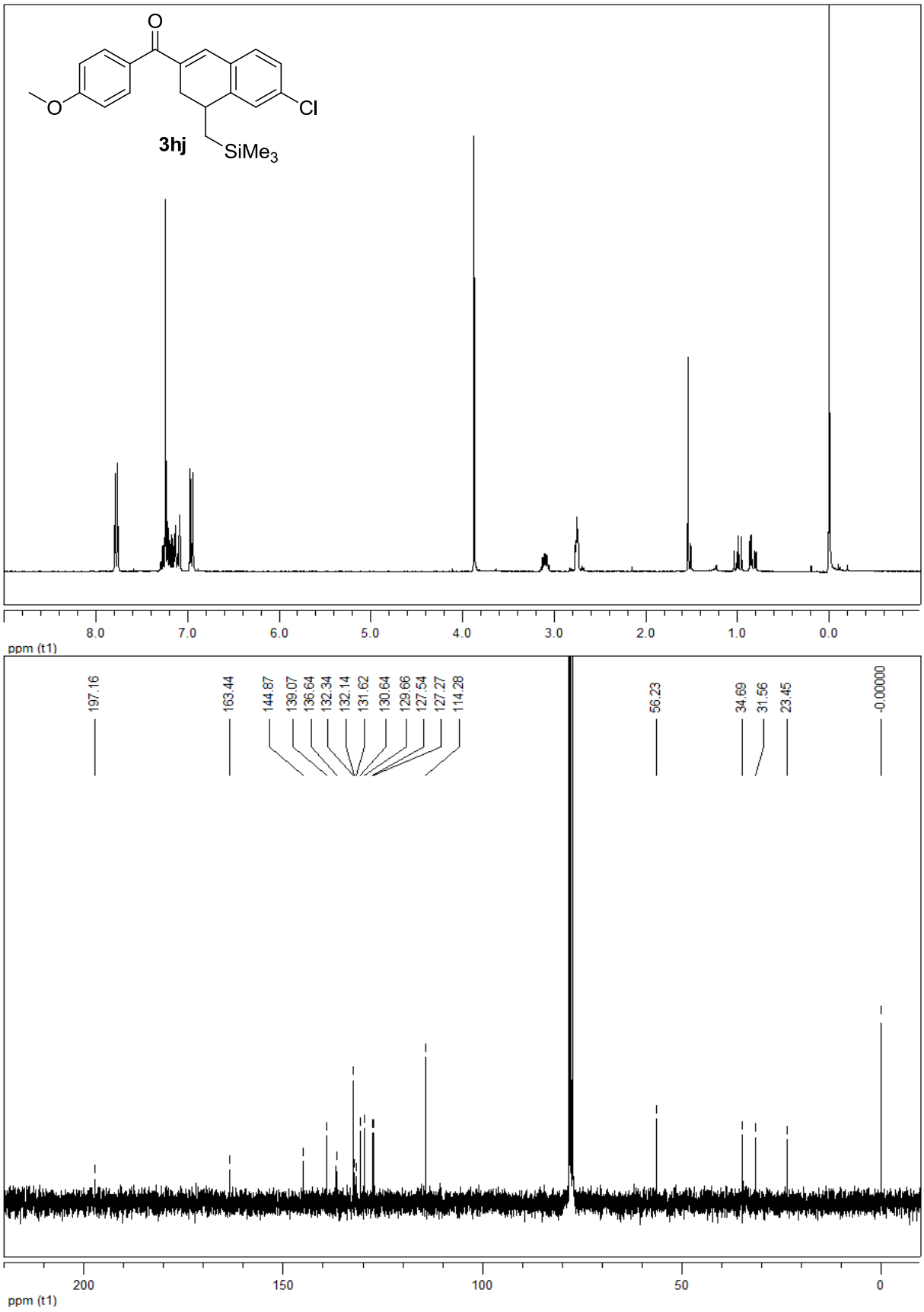
200
150
100
50
0
ppm (t1)


O
O
Cl
3hj
SiMe3
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
197.16
163.44
144.87
139.07
136.64
132.34
132.14
131.62
130.64
129.66
127.54
127.27
114.28
56.23
34.69
31.56
23.45
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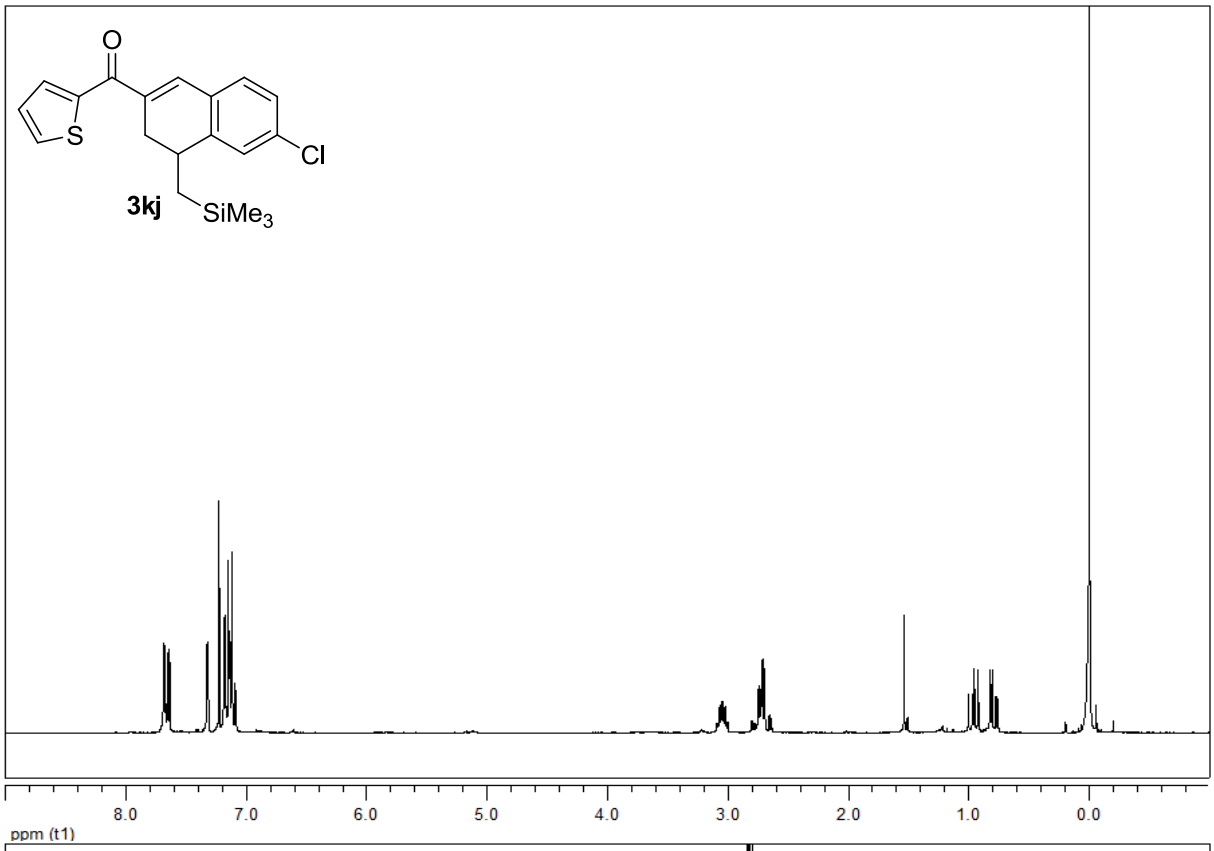
150
100
50
0
ppm (t1)


O
S
Cl
3kj
SiMe3
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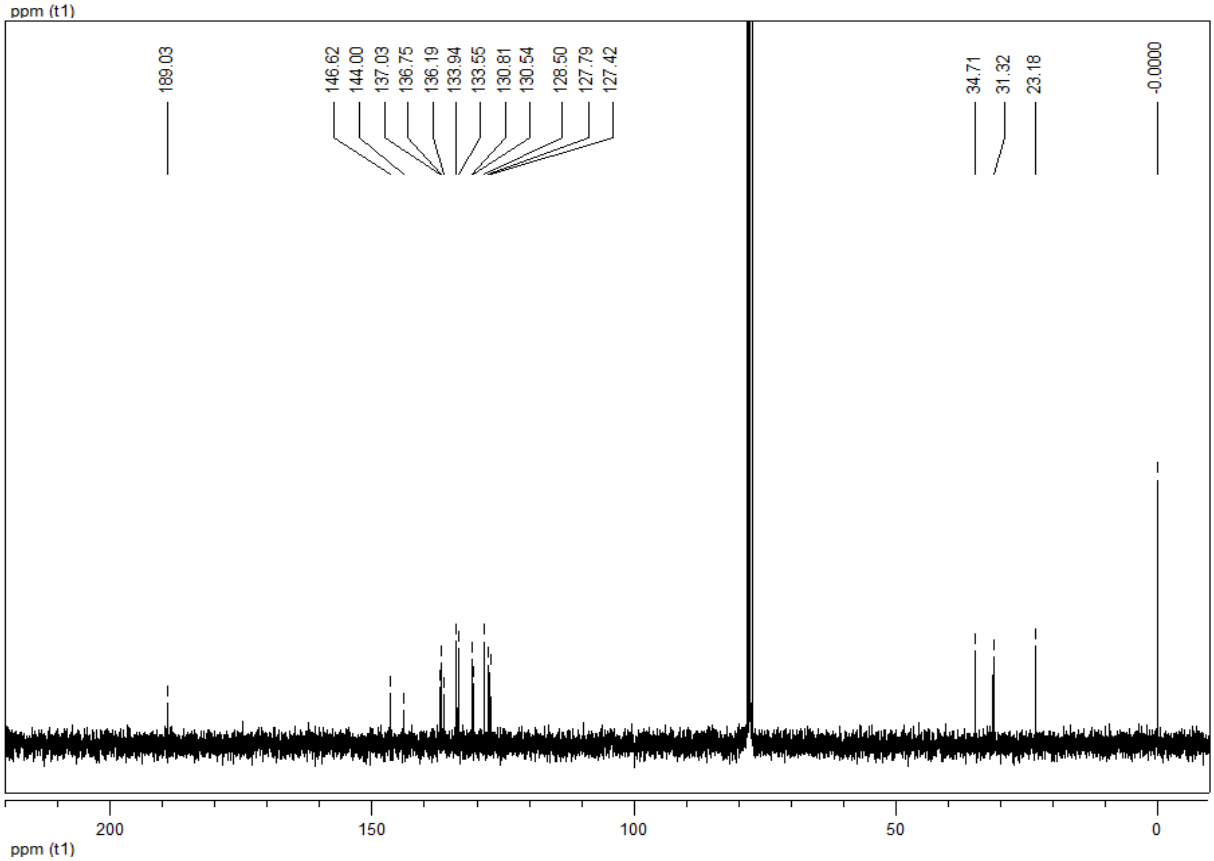
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


189.03
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137.03
136.75
136.19
133.94
133.55
130.81
130.54
128.50
127.79
127.42
34.71
31.32
23.18
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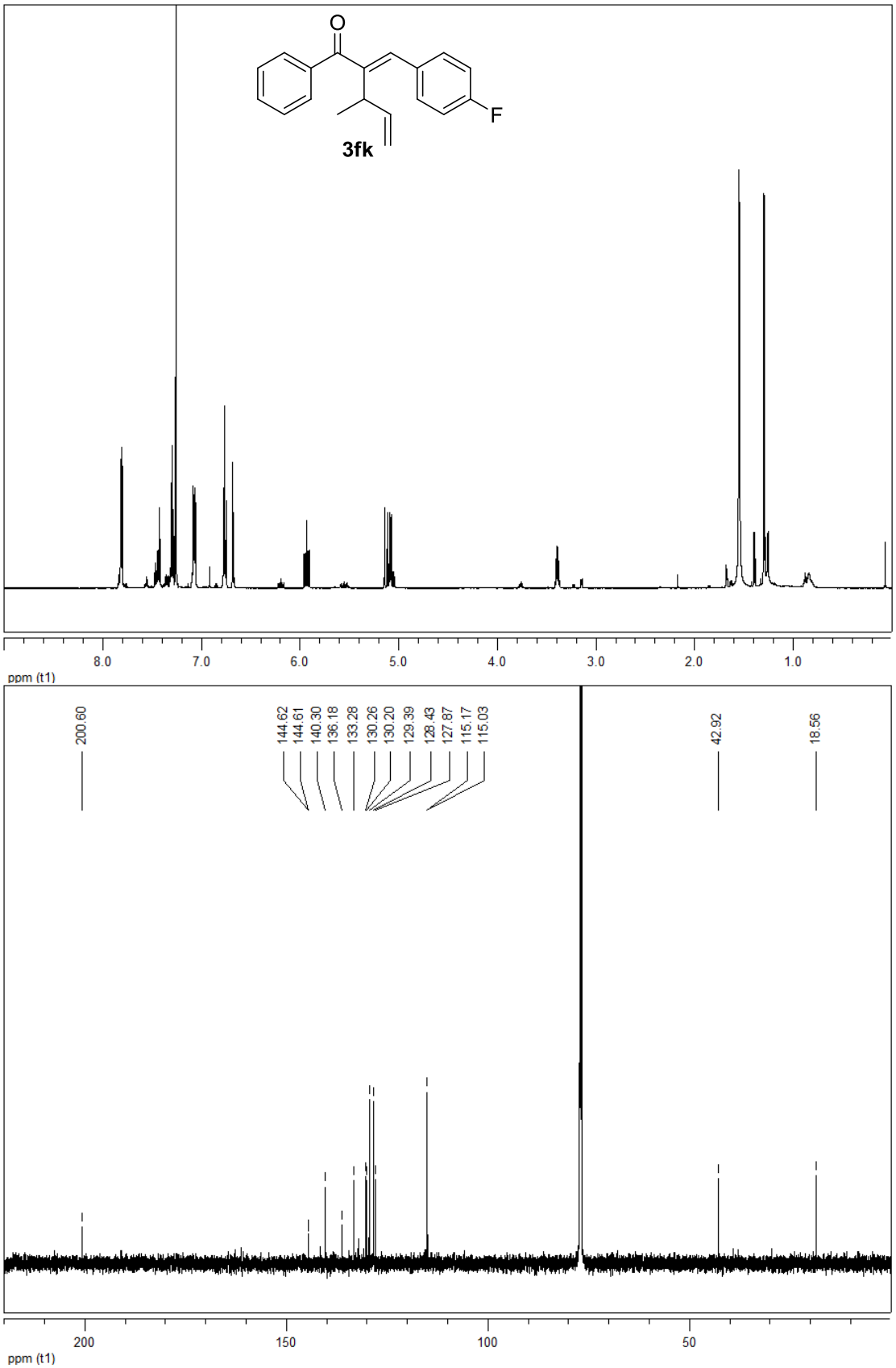
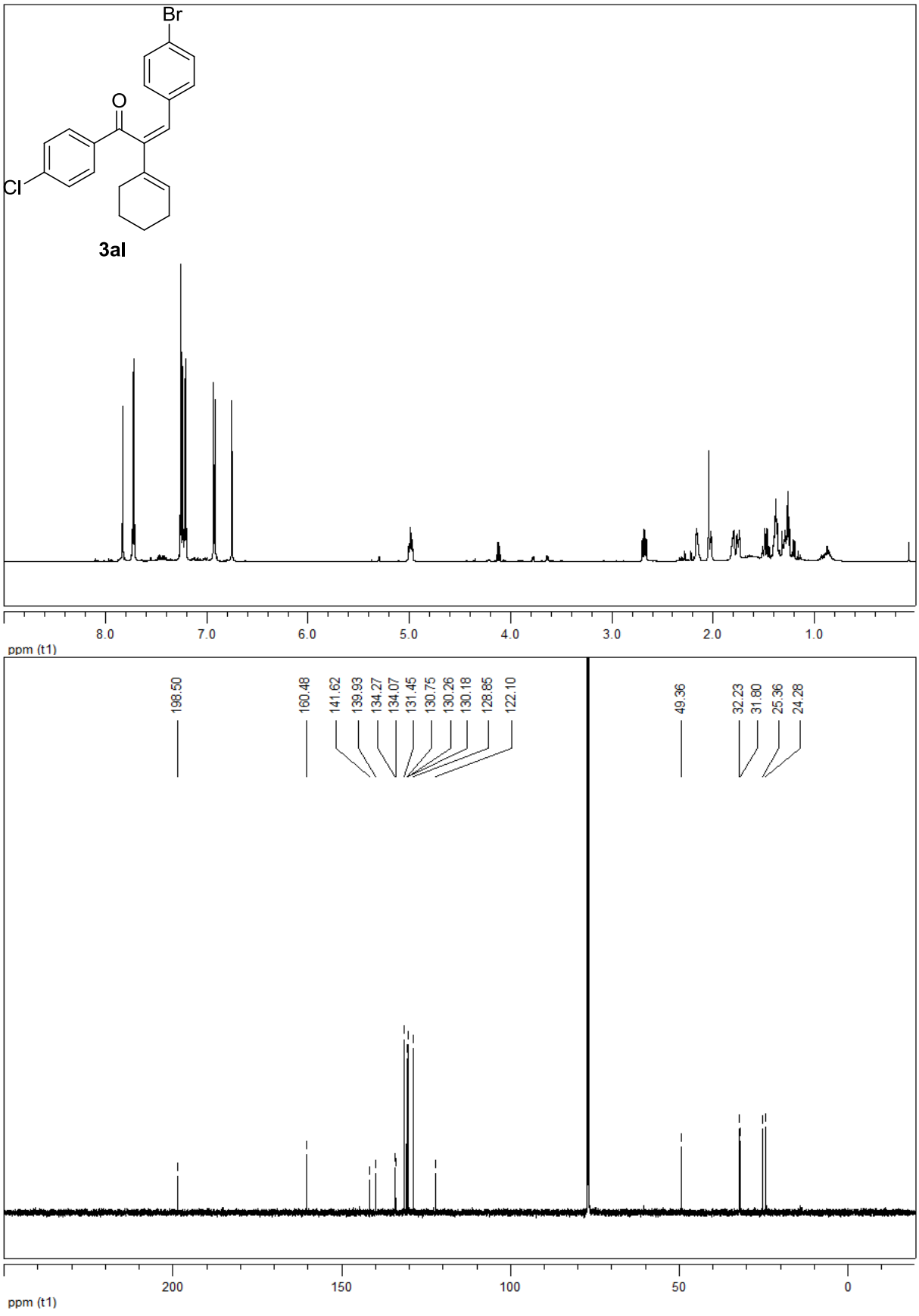
200
150
100
50
0
ppm (t1)


O
F
3fk
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
200.60
144.62
144.61
140.30
136.18
133.28
130.26
130.20
129.39
128.43
127.87
115.17
115.03
42.92
18.56
200
150
100
50
ppm (t1)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O
Cl
3al
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
198.50
160.48
141.62
139.93
134.27
134.07
131.45
130.75
130.26
130.18
128.85
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32.23
31.80
25.36
24.28
200
150
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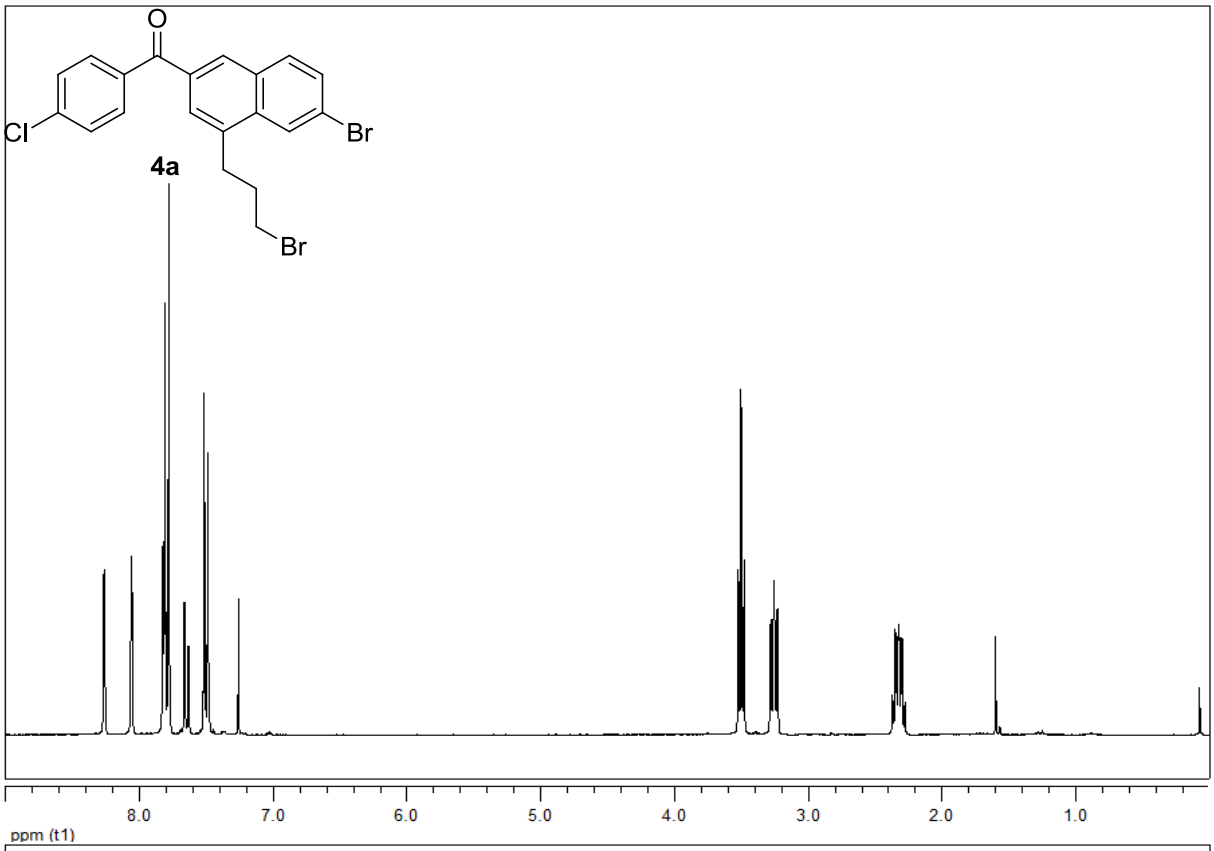
50
0
ppm (t1)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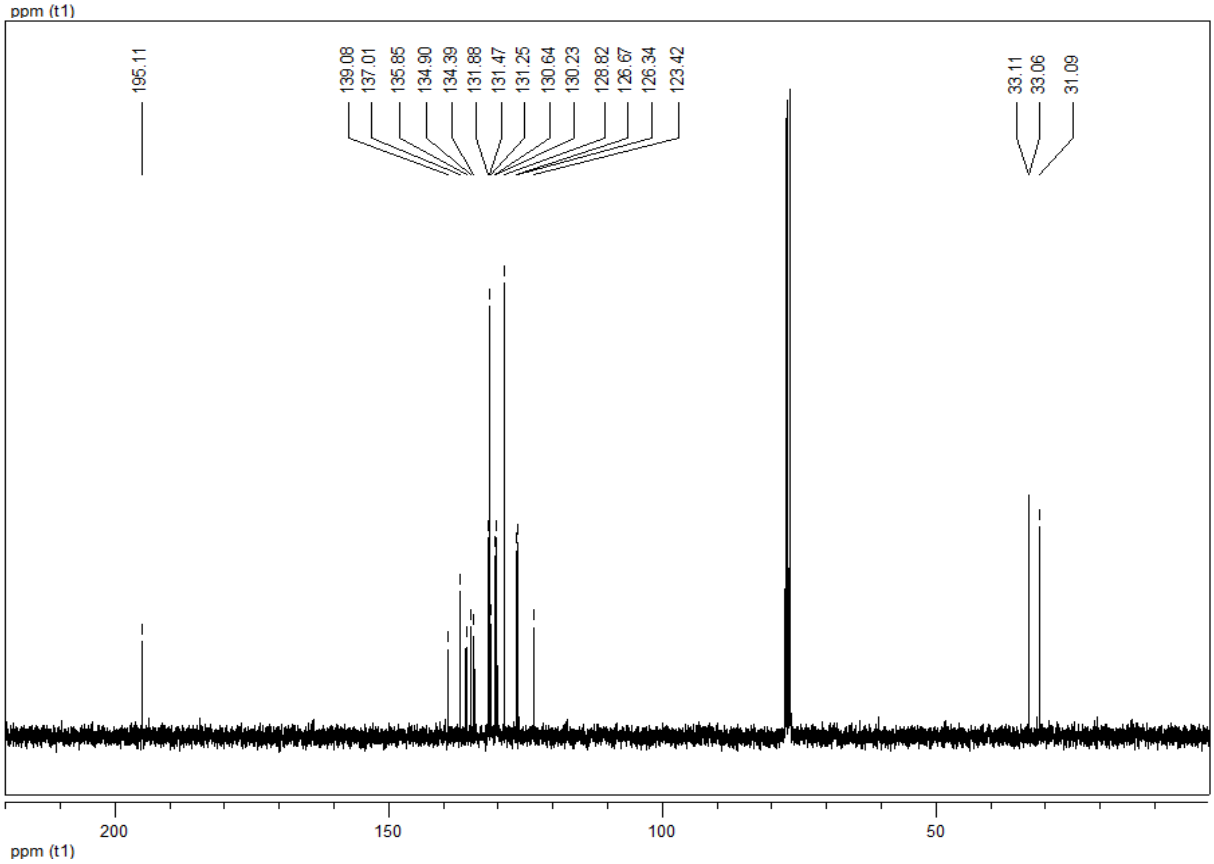
ppm (t1)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139.08
137.01
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131.47
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130.64
130.23
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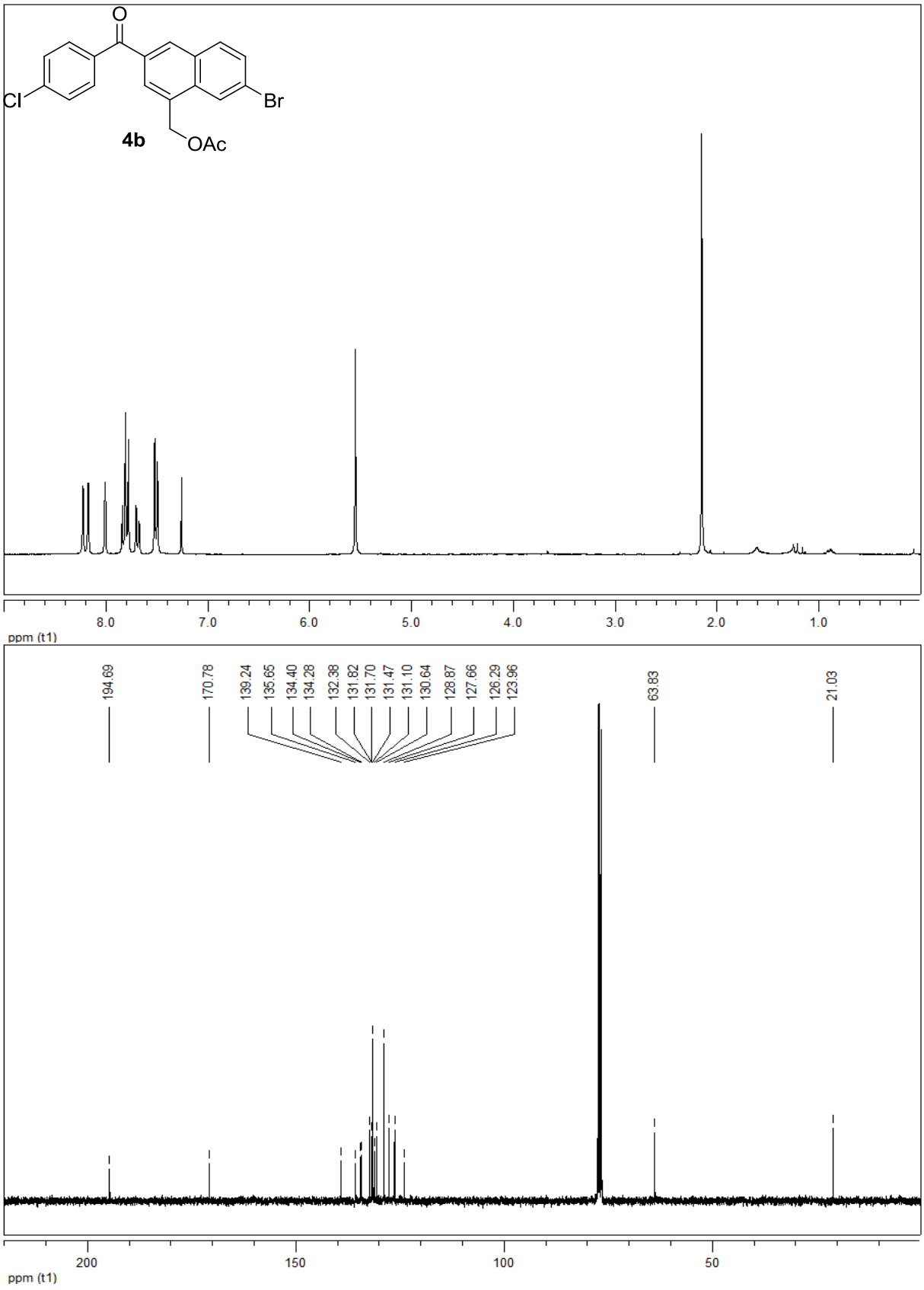
126.34
123.42
33.11
33.06
31.09
200
150
100
50
ppm (t1)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Cl
Br
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OAc
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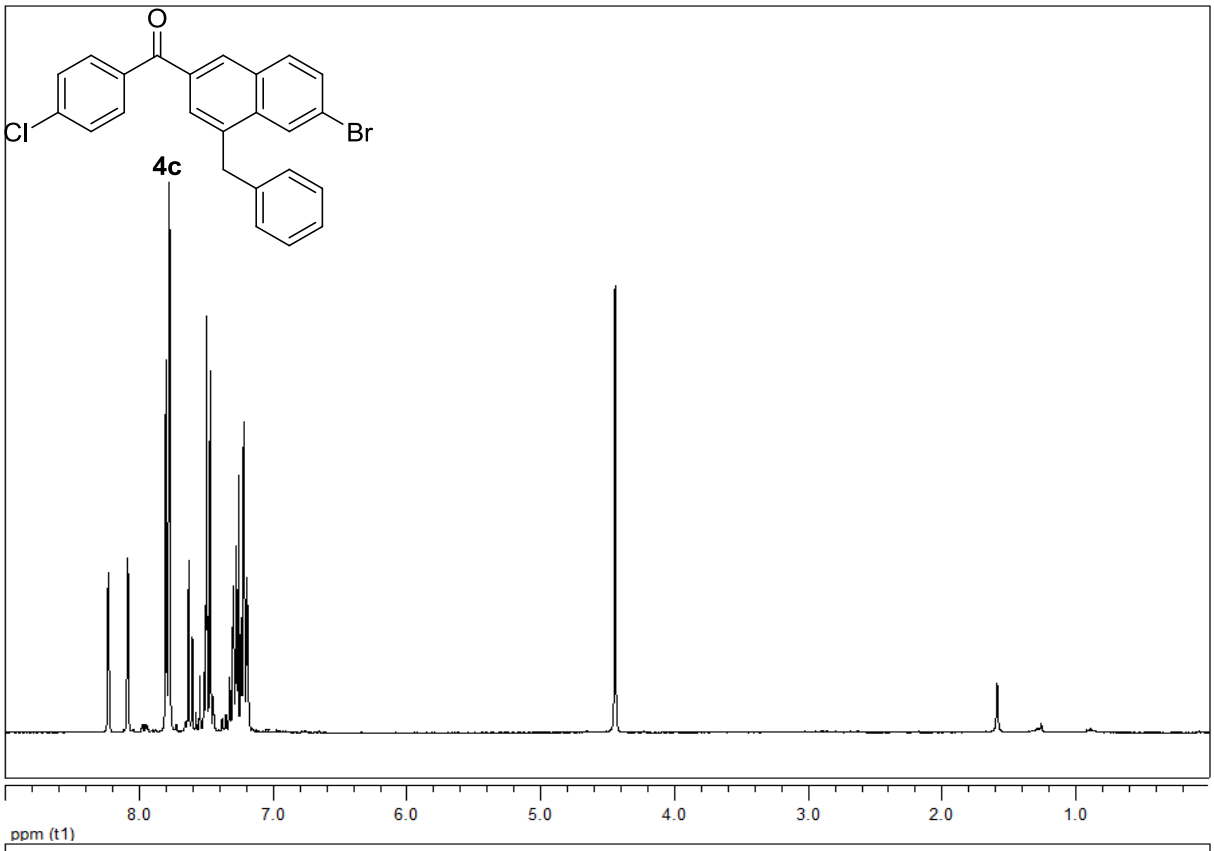
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
194.69
170.78
139.24
135.65
134.40
134.28
132.38
131.82
131.70
131.47
131.10
130.64
128.87
127.66
126.29
123.96
63.83
21.03
200
150
100
50
ppm (t1)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Cl
Br
4c
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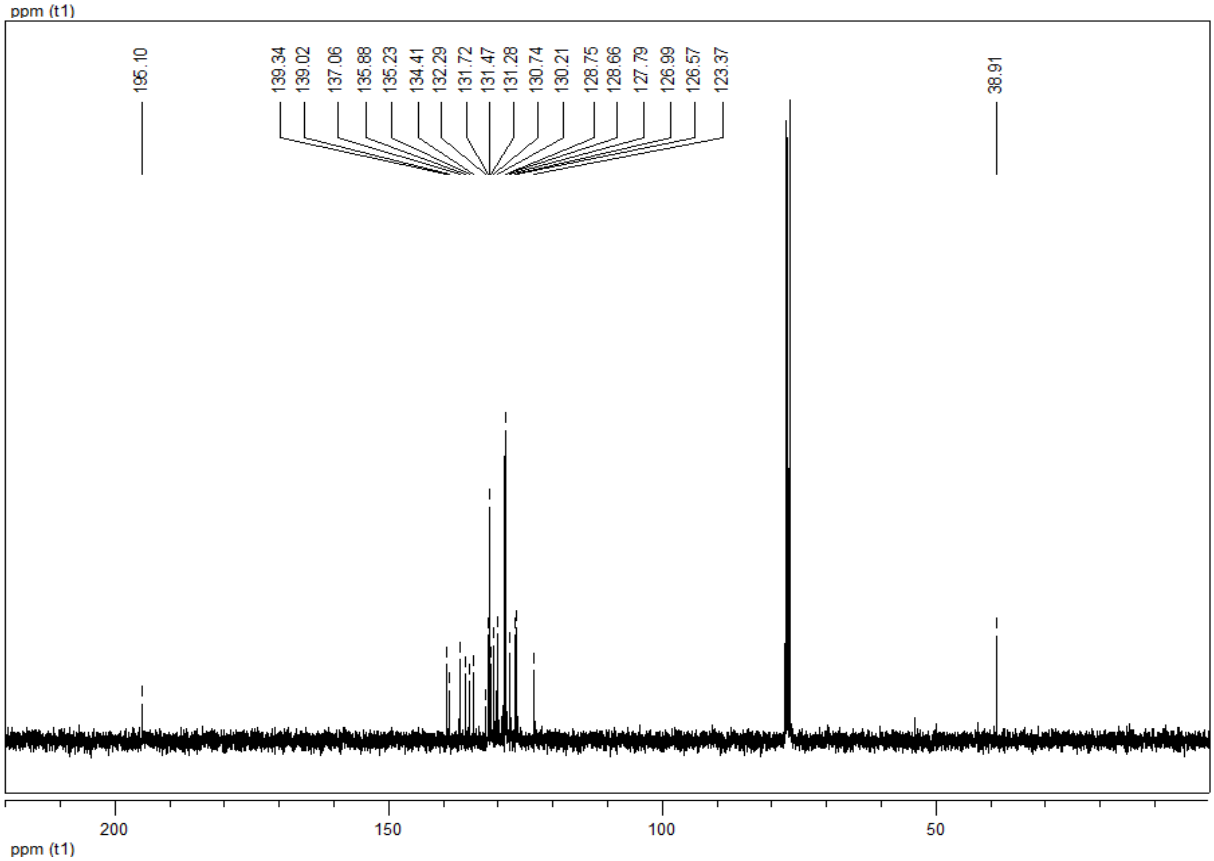
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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139.02
137.06
135.88
135.23
134.41
132.29
131.72
131.47
131.28
130.74
130.21
128.75
128.66
127.79
126.99
126.57
123.37
38.91
200
150
100
50
ppm (t1)

6.8 References

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7. Visible Light triggered α-vinylation of Enol acetates - Access to α-vinyl carbonyls

7.1 Introduction

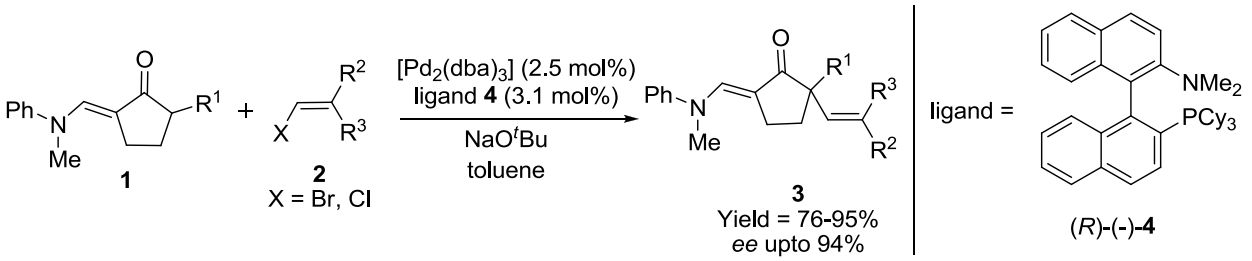
The importance of α-vinylation of ketones is not only arises from frequent appearance of C-C double bonds in various natural products and biologically active compounds but also from rich chemistry of olefins that helps to gain efficient molecular complexity. Thus the α-vinylation of ketones remains a very attractive transformation.

7.2 Literature precedence for α-vinylation of carbonyls

There are many synthetic methodologies documented in literature for α-vinylation of ketones. Most common of them is the transition metal catalyzed cross coupling of ketone enolates with different vinyl reagents. As vinylating reagents vinyl bromides[1], triflates[2] or alkenyl zinc[3] are commonly found in the literature. Enantionselective α-vinylation of aldehydes has been achieved by synergistic catalysis employing vinyl boronic acids[4] or by SOMO catalysis utilizing vinyl potassium trifluouoborate salts.[5] Synthesis of substituted furans by an intramolecular O-vinylation of ketones with vinyl bromides employing copper(I) catalyst was also reported.[6] Bonjoch group reported a palladium catalyzed cyclization of amino tethered vinyl bromides with ketone enolates for the synthesis of nitrogen heterocycles.[7] An elegant example of super base promoted α-vinylation of ketones with diverse arylacetylenes for synthesis of β,γ-unsaturated ketones was reported by Trofimov et al.[8]

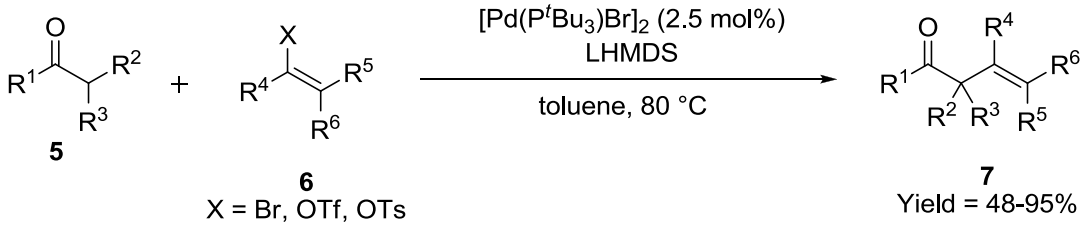
Buchwald reported an asymmetric α-vinylation of ketones **1** employing $Pd_2(dba)_3$ and ligand **4** with high enentioselectivity and good to excellent yield of α-keto vinyl product **3**, however the substrate scope was limited (Scheme 7.1).[1]

Scheme 7.1. Asymmetric vinylation of ketone enolates



In this context, Huang et al. described the α-vinylation of 3-methyloxindole employing palladium catalyst $[Pd(P^tBu_3)Br]_2$ and LHMDS as base (Scheme 7.2).[2] The methodology was extended to the α-vinylation of different ketones and esters **5** as well. Vinyl bromides, triflates or tosylates **6** were used as vinyl source; though lower yields were obtained when tetrasubstituted vinyl sources were used.

Scheme 7.2. Palladium catalyzed α-vinylation of ketones employing vinyl bromides, triflates and tosylates



7.3 Visible light mediated α-vinylation of enol acetates

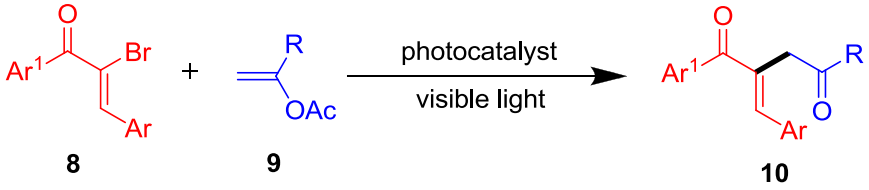
Many of the above mentioned processes, however suffers drawbacks from operational simplicity, use of base or toxic metal enolates and harsh reaction conditions. Conversely, visible light photoredox catalysis being an environmentally benign process provides a superior alternative with the advantage of abundant sunlight, a non-toxic "reagent".

Enol acetates are ketone equivalents and electrophilic in nature. They have been established as radical acceptors both in photochemical[9] reaction conditions providing α-functionalized carbonyl compounds. Eventhough silyl enol ethers have been reported widely as radical acceptors in

photocatalysis providing α-functionalized ketones,[10] stability and ease of preparation of enol acetates make them a better alternative.

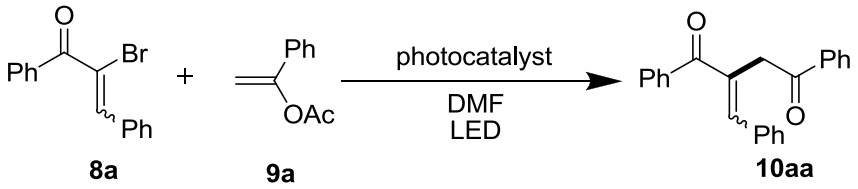
In continuation of our study involving vinyl radical, we envisioned a radical vinylation process for α-vinylation of carbonlys. The vinyl radical generated from α-bromochalcones **8** by photocatalyst under visible light irradiation, should undergo a sp^2(C)-sp^2(C) coupling with enol acetates **9** providing α-vinyl ketones **10** (Scheme 7.3).

Scheme 7.3. Visible light triggered α-vinylation of enolacetates



We initially explored the vinylation of enol acetate **9a** with α-bromochalcone **8a** employing 1 mol% of [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 as photocatalyst in DMF as in the previous cascade cyclization (Chapter 5). After 3 h of reaction time expected α-vinylated ketone **10aa** was obtained in 79% of isolated yield as a mixture of E/Z isomers (Table 7.1, entry 1).

Table 7.1. Optimization of reaction conditions[a]



entry	photocatalyst	yield (%)[b]
1	[Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6, 420 nm	79
2	**Ru(bpy)$_3$Cl$_2$, 455 nm**	**80**
3	Cu(dap)$_2$Cl, 530 nm	no reaction
4	Eosin Y, 530 nm	no reaction
5	Ir[(ppy)$_2$(dtbbpy)]PF_6, 455 nm	negligible

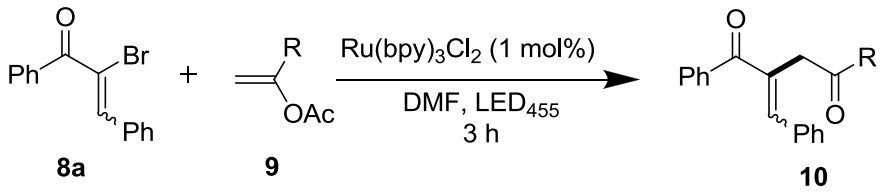
6[c]	$Ru(bpy)_3Cl_2$, 455 nm	no reaction
7	no photocatalyst, 455 nm	no reaction

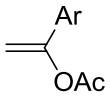
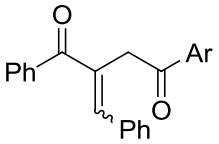
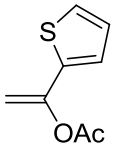
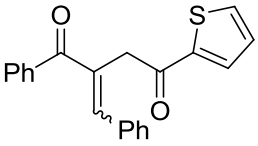
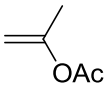
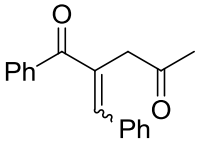
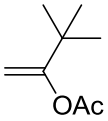
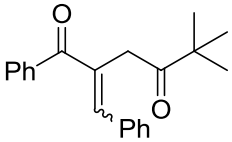
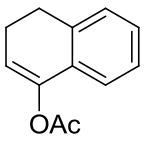
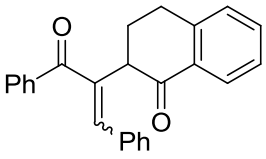
[a] Reaction conditions: **8a** (1 equiv), enol acetate **9a** (5 equiv), photocatalyst (1 mol%) and internal irradiation time of 3 h. [b] Isolated yield. [c] Without light irradiation.

As previously described that $Ru(bpy)_3Cl_2$ also a competent photoredox catalyst for the generation of vinyl radical from α-bromochalcones (Chapter 5), we performed the reaction with 1 mol% of $Ru(bpy)_3Cl_2$, and pleasingly product **10aa** was obtained in 80% yield with same reaction time (Table 7.1, entry 2). The enol acetate was used in excess (5 equiv) for efficient trapping of highly reactive vinyl radical. No product formation was observed in the absence of light or photocatalyst (Table 7.1, entries 6 and 7). Though both $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ and $Ru(bpy)_3Cl_2$ were equally effective for vinylation, we decided to proceed with the later considering the economical advantage of ruthenium over iridium.

With the optimized reaction condition in hand, we proceeded to find out the scope of the reaction. A variety of enol acetates were compatible for the vinylation as shown in Table 7.2. Electron donating or withdrawing substitution in the aryl ring of enol acetates produced moderate to good yields of vinylated product. Surprisingly, 4-methoxy substitution in aryl ring of enol acetate did not give any product formation, but decomposition of the enol acetate (Table 7.2, entry 3). Heteroaryl, aliphatic or alicyclic enol acetates all led to satisfactory yield of the α-vinylated ketones (Table 7.2, entries 7-10).

Table 7.2. Scope of enol acetates[a]

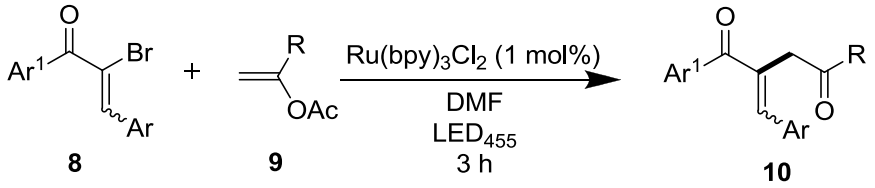


entry	enol acetate	9	product	10[b]	yield (%)[c]
					
1	Ar = C_6H_5	**9a**		**10aa**	80
2	Ar = 4-Me-C_6H_4	**9b**		**10ab**	63
3	Ar = 4-OMe-C_6H_4	**9c**		**10ac**	0
4	Ar = 4-Br-C_6H_4	**9d**		**10ad**	77
5	Ar = 4-Cl-C_6H_4	**9e**		**10ae**	71
6	Ar = 4-F-C_6H_4	**9f**		**10af**	75
7		**9g**		**10ag**	60
8		**9h**		**10ah**	56
9		**9i**		**10ai**	67
10		**9j**		**10aj**	72

[a] Reaction conditions: **8a** (1 equiv), enol acetate **9** (5 equiv), photocatalyst (1 mol%) and internal irradiation time of 3 h. [b] Obtained as *E/Z* mixture (see experimental part) [c] Isolated combined yield of *E* and *Z* isomers.

Next we examined the scope of α-bromochalcones by varying deferent electron donating and withdrawing groups in either ring of chalcone (Table 7.3). Halide substitution in either ring did not show any cross reactivity (Table 7.3, entries 1-10). Substitution with strong electron withdrawing groups (Table 7.2, entry 14 and 15) did not undergo any conversion and the corresponding starting material was fully recovered.

Table 7.3. Scope of α-bromochalcone[a]



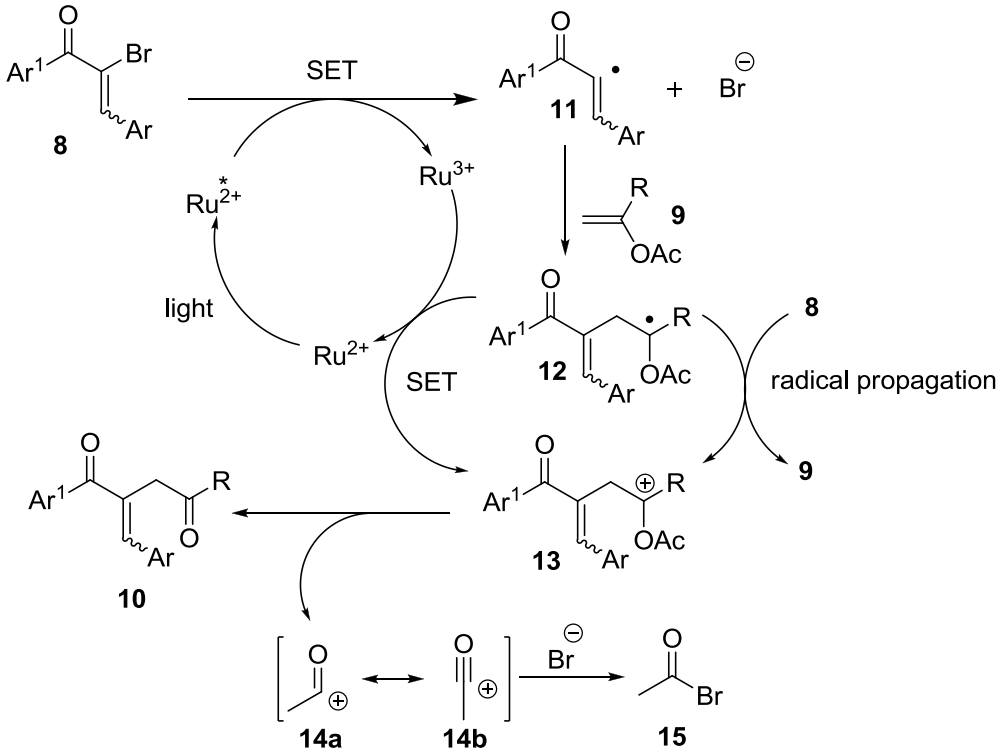
Entry	Ar^1	Ar	**8**	Enol acetate (**9**)	Product (**10**)[b]	Yield (%)[c]
1	4-Cl-C_6H_4	C_6H_5	**8b**	**9a**	**10ba**	62
2				**9h**	**10bh**	51
3	C_6H_5	4-Cl-C_6H_4	**8c**	**9g**	**10cg**	70
4				**9h**	**10ch**	49
5	4-Cl-C_6H_4	4-Br-C_6H_4	**8d**	**9a**	**10da**	83
6				**9h**	**10dh**	56
7	4-F-C_6H_4	C_6H_5	**8e**	**9a**	**10ea**	68
8				**9f**	**10ef**	72
9	C_6H_5	4-F-C_6H_4	**8f**	**9a**	**10fa**	62
10				**9g**	**10fg**	65
11	C_6H_5	4-Me-C_6H_4	**8g**	**9a**	**10ga**	43
12	4-OMe-C_6H_4	C_6H_5	**8h**	**9a**	**10ha**	35
13	2-thienyl	4-Cl-C_6H_4	**8i**	**9a**	**10ia**	78
14	4-NO_2-C_6H_4	C_6H_5	**8j**	**9a**	---	---
15	C_6H_5	4-NO_2-C_6H_4	**8k**	**9a**	---	---

[a] Reaction conditions: **8** (1 equiv), enol acetate **9** (5 equiv), photocatalyst (1 mol%) and internal irradiation time of 3 h. [b] Obtained as *E/Z* mixture (see experimental part) [c] Isolated combined yield of *E* and *Z* isomers.

7.4 Reaction mechanism

A plausible reaction mechanism is proposed based on the oxidative quenching of excited $Ru(bpy)_3Cl_2$ by α-bromochalcone **8** (Scheme 7.4). This led to the formation of vinyl radical **11** which was trapped by enol acetate **9** to give radical intermediate **12**. This intermediate can be oxidized to cationic species **13** by two possible pathways, by a single electron transfer (SET) to Ru^{3+}, thus closing the catalytic cycle or initiating a radical chain process by reducing **8** to **11**. Observed product **10** is formed by an acyl cation **14** transfer from **13** which is trapped by bromide anion to form acetyl bromide **15**.[9b]

Scheme 7.4. Proposed reaction mechanism



7.5 Conclusion

In summary, we have developed a visible light driven methodology for α-vinylation of ketones employing $Ru(bpy)_3Cl_2$ as photocatalyst by coupling a vinyl radical derived from α-

bromochalcone with enol acetate. A broad variety of α-bromochalcones and enol acetates were compatible coupling partners. Low catalyst loading, short reaction time, and good to excellent yields of the products are attractive features of this novel transformation.

7.6 Experimental Part

General Information

All reactions were performed using common dry, inert atmosphere techniques. Reactions were monitored by TLC and visualized by a dual short/long wave UV lamp and stained with an ethanolic solution of vanillin. Column flash chromatography was performed using 230-400 mesh silica gel. NMR spectra were recorded on 300 MHz spectrometer. Chemical shifts for ^{1}H NMR were reported as δ, parts per million, relative to the signal of $CDCl_3$ at 7.26 ppm. Chemical shifts for ^{13}C NMR were reported as δ, parts per million, relative to the center line signal of the $CDCl_3$ triplet at 77 ppm. Proton and carbon assignments were established using spectral data of similar compounds. The abbreviations s, d, dd, t, q and m stand for the resonance multiplicity singlet, doublet, doublet of doublets, triplet, quartet and multiplet respectively.

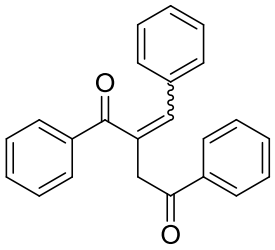
Preparation of α-bromochalcone has been described in Chapter 5.

General procedure (GP-A) for the photoredeox catalyzed α-vinylation of enol acetates

An oven dried 15 mL Schlenk tube equipped with a plastic septum and magnetic stir bar was charged with $Ru(bpy)_3Cl_2$ (1 mol %), α-bromochalcone (0.5 mmol, 1.0 equiv) and the enol acetate (2.5 mmol, 5.0 equiv). The flask was purged with a stream of nitrogen and 2.0 mL of dry dimethylformamide was added. The resultant mixture was degassed by freeze-pump-thaw procedure (3 cycles). The tube was sealed with an internal irradiation set up (a LED stick inside) and irradiated for 3 h. After the completion of the reaction (as judged by TLC analysis), the mixture was transferred to a separating funnel, diluted with 15 mL of ethyl acetate and washed with 20 mL of water. The aqueous layer was washed with ethyl acetate (3 × 10 mL) and the combined organic layer was dried over anhydrous sodium sulfate, solvent was removed in vacuo

and the residue was subjected to colum chromatography on silica gel, using PE/EA as solvent system to get the pure product.

2-benzylidene-1,4-diphenylbutane-1,4-dione (10aa)



E/Z = 15:85.

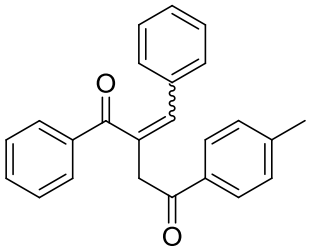
IR (neat): 3063, 1645, 1609, 1482 1338, 1220, 772, 693 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 8.04 (m, 2H), 7.98 – 7.91 (m, 2H), 7.64 – 7.53 (m, 2H), 7.53 – 7.44 (m, 4H), 7.42 (s, 1H), 7.40 – 7.27 (m, 5H), 4.47 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.58, 197.77, 144.00, 138.17, 136.52, 136.04, 135.22, 133.43, 132.05, 130.06, 128.87, 128.76, 128.72, 128.37, 128.25, 38.68.

HRMS (ESI): Calcd. For $C_{23}H_{19}O_2$ $[M+H]^+$ *m/z* 327.1385, found *m/z* 327.1387.

2-benzylidene-1-phenyl-4-p-tolylbutane-1,4-dione (10ab)



E/Z = 24:76

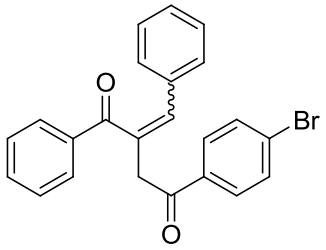
IR (neat): 3055, 2362, 1646, 1606, 1447, 1323, 1222, 1004, 771, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 7.96 (m, 4H), 7.61 – 7.52 (m, 1H), 7.52 – 7.43 (m, 2H), 7.39 (s, 1H), 7.37–7.24 (m, 7H), 4.44 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.62, 197.36, 144.26, 143.74, 138.22, 136.21, 135.27, 134.06, 132.01, 130.08, 129.38, 128.78, 128.68, 128.49, 128.22, 38.59, 21.73.

HRMS (ESI): Calcd. For $C_{24}H_{21}O_2$ $[M+H]^+$ *m/z* 341.1536, found *m/z* 341.1538.

2-benzylidene-4-(4-bromophenyl)-1-phenylbutane-1,4-dione (10ad)



E/Z = 12:88

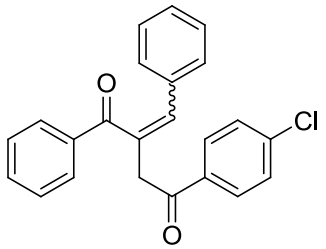
IR (neat): 3059, 2359, 1647, 1584, 1398, 1210, 998, 783, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, *Z* isomer) δ = 7.99 – 7.89 (m, 4H), 7.70 – 7.65 (m, 2H), 7.65 – 7.58 (m, 1H), 7.56 – 7.50 (m, 2H), 7.47 (s, 1H), 7.44 – 7.36 (m, 3H), 7.35 – 7.29 (m, 2H), 4.44 (d, *J* = 0.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 198.35, 196.76, 144.29, 138.06, 135.73, 135.33, 135.13, 132.03, 132.00, 129.94, 129.84, 128.93, 128.71, 128.68, 128.57, 128.24, 38.49.

HRMS (ESI): Calcd. For $C_{23}H_{18}BrO_2$ $[M+H]^+$ *m/z* 405.0485, found *m/z* 405.0481.

2-benzylidene-4-(4-chlorophenyl)-1-phenylbutane-1,4-dione (10ae)



E/Z = 14:86

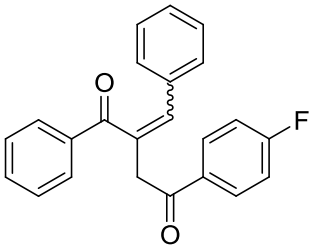
IR (neat): 3059, 2362, 1647, 1589, 1447, 1212, 1092, 1000, 699 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 8.00 – 7.89 (m, 4H), 7.62 – 7.53 (m, 1H), 7.53 – 7.41 (m, 5H), 7.41 – 7.32 (m, 3H), 7.32 – 7.24 (m, 2H), 4.41 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.62, 144.33, 139.87, 138.06, 135.73, 135.13, 134.88, 132.10, 129.99, 129.78, 129.03, 128.97, 128.75, 128.72, 128.28, 38.55.

HRMS (ESI): Calcd. For $C_{23}H_{18}ClO_2$ $[M+H]^+$ *m/z* 361.0990, found *m/z* 361.0988.

2-benzylidene-4-(4-fluorophenyl)-1-phenylbutane-1,4-dione (10af)



E/Z = 17:83.

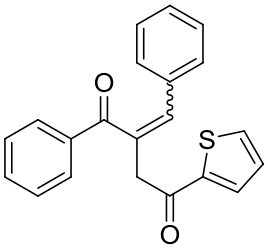
IR (neat): 3057, 1656, 1442, 1330, 1145, 1009, 763, 693 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 8.10 – 8.02 (m, 2H), 7.97 – 7.91 (m, 2H), 7.61 – 7.54 (m, 1H), 7.52 – 7.45 (m, 2H), 7.43 (s, 1H), 7.40 – 7.27 (m, 5H), 7.20 – 7.10 (m, 2H), 4.45 – 4.39 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.48, 196.21, 167.64, 164.26, 144.22, 138.10, 135.86, 135.17, 133.03, 132.99, 132.08, 131.09, 130.96, 130.01, 128.93, 128.73, 128.27, 115.97, 115.68, 38.50.

HRMS (ESI): Calcd. For $C_{23}H_{18}FO_2$ $[M+H]^+$ *m/z* 345.1285, found *m/z* 345.1284.

2-benzylidene-1-phenyl-4-(thiophen-2-yl)butane-1,4-dione (10ag)



E/Z =21:79.

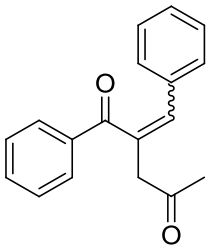
IR (neat): 3086, 1646, 1415, 1220, 960, 771, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 7.96 – 7.88 (m, 2H), 7.83 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.67 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.53 – 7.43 (m, 2H), 7.42 (s, 1H), 7.40 – 7.26 (m, 5H), 7.16 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.40 (d, *J*= 0.4 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.41, 190.53, 144.32, 143.58, 138.09, 135.43, 135.11, 134.05, 132.59, 132.08, 130.03, 128.97, 128.82, 128.73, 128.25, 39.01.

HRMS (ESI): Calcd. For $C_{21}H_{17}O_2S$ $[M+H]^+$ *m/z* 333.0944, found *m/z* 333.0942.

2-benzylidene-1-phenylpentane-1,4-dione (10ah)



E/Z = 11:89.

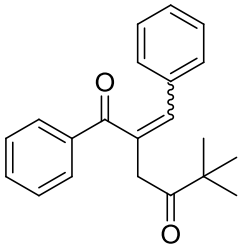
IR (neat): 3055, 2363, 1715, 1645, 1447, 1266, 1019, 758, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 7.87 – 7.80 (m, 2H), 7.60 – 7.52 (m, 1H), 7.51 – 7.43 (m, 2H), 7.43 – 7.32 (m, 4H), 7.29 (m, 2H), 3.85 (s, 2H), 2.29 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 206.20, 198.48, 144.70, 138.09, 135.57, 135.09, 131.98, 129.78, 129.04, 128.80, 128.70, 128.26, 42.94, 30.27.

HRMS (ESI): Calcd. For $C_{18}H_{17}O_2$ $[M+H]^+$ *m/z* 265.1223, found *m/z* 265.1227.

2-benzylidene-5,5-dimethyl-1-phenylhexane-1,4-dione (10ai)



E/Z = 5:95.

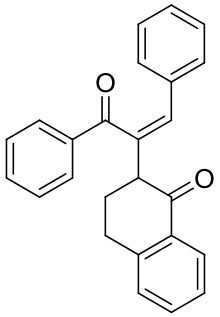
IR (neat): 2962, 1704, 1648, 1447, 1266, 1063, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 7.93 – 7.86 (m, 2H), 7.59 – 7.50 (m, 1H), 7.50 – 7.42 (m, 2H), 7.39 – 7.31 (m, 4H), 7.23 (dd, *J* = 7.3, 1.7 Hz, 2H), 3.97 (d, *J* = 0.5 Hz, 2H), 1.23 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 214.00, 198.71, 143.66, 138.20, 136.56, 135.40, 131.99, 130.02, 128.73, 128.60, 128.58, 128.20, 44.51, 37.18, 29.73, 26.66.

HRMS (ESI): Calcd. For $C_{21}H_{23}O_2$ $[M+H]^+$ *m/z* 307.1693, found *m/z* 307.1688.

2-(3-oxo-1,3-diphenylprop-1-en-2-yl)-3,4-dihydronaphthalen-1(2H)-one (10aj)



Only *Z* isomer was formed.

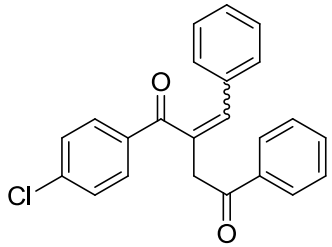
IR (neat): 3056, 2363, 1679, 1647, 1447, 1226, 1013, 750, 698 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ = 8.09 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.95 – 7.84 (m, 2H), 7.60 – 7.53 (m, 1H), 7.53 – 7.18 (m, 10H), 7.08 – 7.00 (m, 1H), 4.07 – 4.00 (m, 1H), 3.21 – 2.97 (m, 2H), 2.97 – 2.77 (m, 1H), 2.29 – 2.17 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.18, 197.46, 144.32, 143.76, 140.88, 135.31, 133.36, 132.65, 131.92, 129.94, 129.82, 129.06, 128.85, 128.77, 128.60, 128.24, 127.72, 126.77, 49.64, 29.63, 29.36.

HRMS (ESI): Calcd. For $C_{25}H_{21}O_2$ $[M+H]^+$ *m/z* 353.1536, found *m/z* 353.1541.

2-benzylidene-1-(4-chlorophenyl)-4-phenylbutane-1,4-dione (10ba)



E/Z = 14:86.

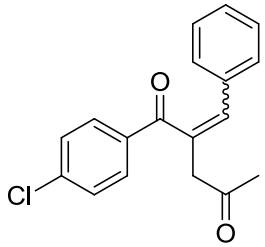
IR (neat): 3055, 2362, 1646, 1606, 1447, 1323, 1222, 1004, 771, 698 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 8.02 (m, 2H), 7.94 – 7.88 (m, 2H), 7.64 – 7.57 (m, 1H), 7.52 – 7.44 (m, 4H), 7.38 – 7.32 (m, 4H), 7.30 – 7.26 (m, 2H), 4.46 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.69, 197.38, 143.68, 138.44, 136.46, 136.40, 135.93, 134.98, 133.51, 131.48, 128.99, 128.75, 128.57, 128.35, 38.76.

HRMS (ESI): Calcd. For $C_{23}H_{18}ClO_2$ $[M+H]^+$ *m/z* 361.0990, found *m/z* 361.0988.

2-benzylidene-1-(4-chlorophenyl)pentane-1,4-dione (10bh)



E/Z = 12:88.

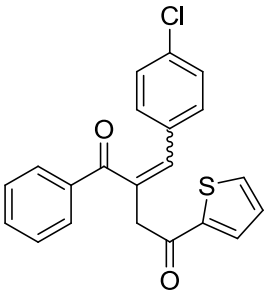
IR (neat): 3056, 2363, 1715, 1641, 1443, 1029, 743, 695 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$. *Z* isomer) δ = 7.79 – 7.71 (m, 2H), 7.43 – 7.37 (m, 2H), 7.37 – 7.30 (m, 3H), 7.25 (d, *J* = 4.3 Hz, 1H), 7.25 – 7.20 (m, 2H), 3.81 (s, 2H), 2.23 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 206.06, 197.29, 144.37, 138.38, 136.38, 135.48, 134.88, 131.22, 129.15, 128.77, 128.75, 128.59, 43.00, 30.20.

HRMS (ESI): Calcd. For $C_{18}H_{16}ClO_2$ $[M+H]^+$ *m/z* 299.0833, found *m/z* 299.0836.

2-(4-chlorobenzylidene)-1-phenyl-4-(thiophen-2-yl)butane-1,4-dione (10cg)



E/Z = 16:84.

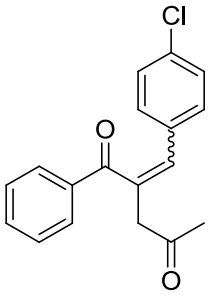
IR (neat): 3057, 2360, 1647, 1580, 1445, 1097, 1030, 698 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 7.92 – 7.87 (m, 2H), 7.84 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.68 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.52 – 7.44 (m, 2H), 7.34 (m, 3H), 7.28 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.16 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.35 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.09, 190.31, 143.44, 142.90, 137.89, 135.97, 135.00, 134.24, 133.51, 132.71, 132.18, 130.09, 129.97, 128.97, 128.30, 38.89.

HRMS (ESI): Calcd. For $C_{21}H_{16}ClO_2S$ $[M+H]^+$ *m/z* 367.0554, found *m/z* 367.0558.

2-(4-chlorobenzylidene)-1-phenylpentane-1,4-dione (10ch)



E/Z =7:93.

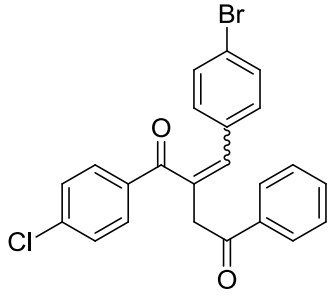
IR (neat): 3056, 2362, 1713, 1645, 1443, 1033, 742, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 7.86 – 7.77 (m, 2H), 7.61 – 7.52 (m, 1H), 7.52 – 7.42 (m, 2H), 7.42 – 7.33 (m, 2H), 7.31 (s, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 2H), 2.29 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 206.01, 198.18, 143.26, 137.89, 136.10, 135.07, 133.49, 132.08, 130.06, 129.73, 128.96, 128.31, 42.82, 30.35.

HRMS (ESI): Calcd. For $C_{18}H_{16}ClO_2$ $[M+H]^+$ *m/z* 299.0833, found *m/z* 299.0836.

2-(4-bromobenzylidene)-1-(4-chlorophenyl)-4-phenylbutane-1,4-dione (10da)



E/Z = 17:83.

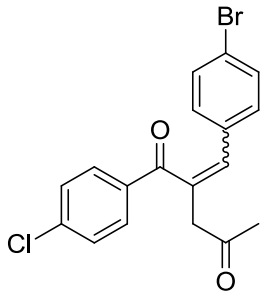
IR (neat): 3057, 2356, 1645, 1584, 1395, 1215, 997, 733, 699 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, Z isomer) δ = 8.05 – 7.97 (m, 2H), 7.93 – 7.86 (m, 2H), 7.61 (m, 1H), 7.54 – 7.43 (m, 7H), 7.17 – 7.11 (m, 2H), 4.43 – 4.39 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.52, 197.10, 142.27, 138.61, 136.55, 136.22, 133.83, 133.68, 131.99, 131.45, 130.25, 128.81, 128.65, 128.36, 123.29, 38.70.

HRMS (ESI): Calcd. For $C_{23}H_{17}BrClO_2$ $[M+H]^+$ *m/z* 439.0100, found *m/z* 439.0103.

2-(4-bromobenzylidene)-1-(4-chlorophenyl)pentane-1,4-dione (10dh)



E/Z = 9:91.

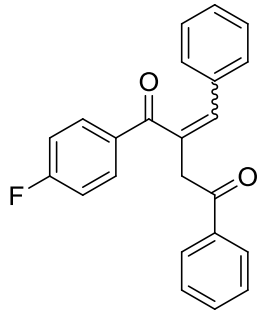
IR (neat): 3059, 2360, 1715, 1647, 1038, 746, 697 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 7.78 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J*= 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.22 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 2H), 2.28 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 205.87, 196.99, 142.93, 138.54, 136.14, 136.08, 133.73, 131.98, 131.17, 130.24, 128.65, 123.45, 42.90, 30.29.

HRMS (ESI): Calcd. For $C_{18}H_{15}BrClO_2$ $[M+H]^+$ *m/z* 376.9938, found *m/z* 376.9939.

2-benzylidene-1-(4-fluorophenyl)-4-phenylbutane-1,4-dione (10ea)



E/Z = 11:89.

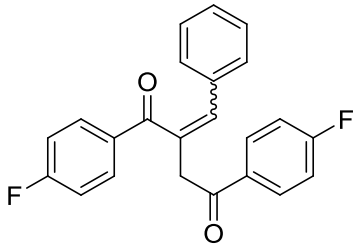
IR (neat): 3057, 1655, 1476, 1345, 1147, 1029, 753, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 8.07 – 7.92 (m, 4H), 7.64 – 7.57 (m, 1H), 7.53 – 7.45 (m, 2H), 7.41 – 7.32 (m, 4H), 7.32 – 7.24 (m, 2H), 7.22 – 7.12 (m, 2H), 4.47 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.78, 197.18, 166.92, 163.57, 143.28, 136.40, 136.01, 135.06, 134.31, 134.27, 133.51, 132.70, 132.58, 128.92, 128.76, 128.74, 128.36, 115.54, 115.25, 38.89.

HRMS (ESI): Calcd. For $C_{23}H_{18}FO_2$ $[M+H]^+$ *m/z* 345.1285, found *m/z* 345.1284.

2-benzylidene-1,4-bis(4-fluorophenyl)butane-1,4-dione (10ef)



E/Z = 33:67.

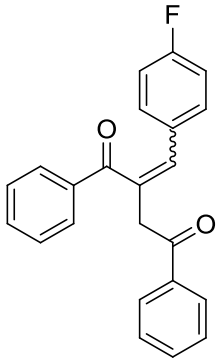
IR (neat): 3057, 1652, 1482, 1352, 1145, 1105, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 8.02 – 7.94 (m, 2H), 7.89 – 7.81 (m, 2H), 7.14 – 7.05 (m, 2H), 7.04 – 6.95 (m, 6H), 6.85 – 6.76 (m, 2H), 4.31 (d, *J* = 1.1 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.63, 194.73, 166.65, 165.98, 163.26, 162.61, 135.18, 134.15, 133.06, 131.78, 131.74, 131.51, 131.39, 130.06, 129.94, 127.95, 127.15, 126.99, 114.99, 114.70, 114.19, 113.90, 45.69.

HRMS (ESI): Calcd. For $C_{23}H_{17}F_2O_2$ $[M+H]^+$ *m/z* 363.1191, found *m/z* 363.1190.

2-(4-fluorobenzylidene)-1,4-diphenylbutane-1,4-dione (10fa)



E/Z = 23:77.

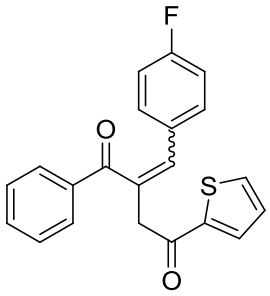
IR (neat): 3052, 1657, 1473, 1342, 1145, 1022, 733, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, Z isomer) δ = 8.04 (dt, *J* = 8.5, 1.7 Hz, 2H), 7.96 – 7.89 (m, 2H), 7.65 – 7.53 (m, 2H), 7.53 – 7.44 (m, 4H), 7.37 (s, 1H), 7.32 – 7.23 (m, 2H), 7.10 – 6.99 (m, 2H), 4.43 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.36, 197.68, 164.52, 142.95, 138.10, 136.47, 136.00, 133.51, 132.07, 131.25, 130.72, 130.61, 129.98, 128.75, 128.37, 128.28, 115.98, 115.70, 38.52.

HRMS (ESI): Calcd. For $C_{23}H_{18}FO_2$ $[M+H]^+$ *m/z* 345.1285, found *m/z* 345.1284.

2-(4-fluorobenzylidene)-1-phenyl-4-(thiophen-2-yl)butane-1,4-dione (10fg)



E/Z =18:82.

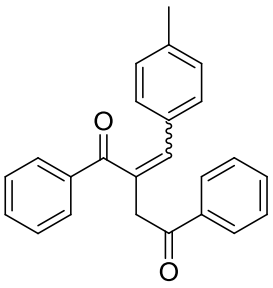
IR (neat): 3085, 2360, 1685, 1632, 1415, 1110, 1093, 688 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$, Z isomer) δ = 7.87 – 7.82 (m, 2H), 7.80 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.63 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.43 (m, 2H), 7.34 – 7.26 (m, 3H), 7.12 (dd, *J* = 4.9, 3.8 Hz, 1H), 7.06 – 6.97 (m, 2H), 4.31 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.26, 190.48, 164.60, 161.29, 143.49, 143.36, 137.99, 135.33, 134.27, 132.75, 132.14, 131.16, 131.11, 130.82, 130.71, 129.98, 128.34, 128.29, 116.01, 115.72, 38.83.

HRMS (ESI): Calcd. For $C_{21}H_{16}FO_2S$ $[M+H]^+$ *m/z* 351.0855, found *m/z* 351.0859.

2-(4-methylbenzylidene)-1,4-diphenylbutane-1,4-dione (10ga)



E/Z = 12:88.

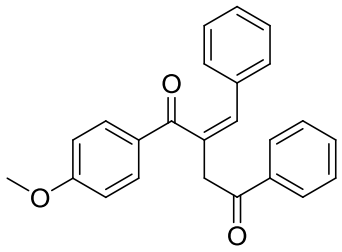
IR (neat): 3059, 2362, 1683, 1646, 1448, 1214, 1002, 716, 690 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 8.04 (dt, 2H), 7.96 – 7.90 (m, 2H), 7.63 – 7.52 (m, 2H), 7.52 – 7.44 (m, 4H), 7.39 (s, 1H), 7.22 – 7.12 (m, 4H), 4.47 (s, 2H), 2.34 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.66, 197.81, 144.37, 139.13, 138.33, 136.59, 135.29, 133.37, 132.31, 131.91, 130.00, 129.42, 128.84, 128.70, 128.36, 128.21, 38.68, 21.36.

HRMS (ESI): Calcd. For $C_{24}H_{21}O_2$ $[M+H]^+$ *m/z* 341.1536, found *m/z* 341.1538.

2-benzylidene-1-(4-methoxyphenyl)-4-phenylbutane-1,4-dione (10ha)



E/Z = 9:91.

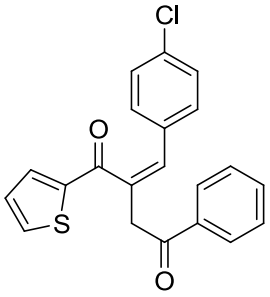
IR (neat): 3060, 2357, 1682, 1597, 1253, 1169, 909, 730, 633 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 8.05 – 7.96 (m, 4H), 7.64 – 7.55 (m, 1H), 7.51 – 7.42 (m, 2H), 7.39 – 7.26 (m, 6H), 7.02 – 6.94 (m, 2H), 4.46 (s, 2H), 3.89 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.92, 197.36, 163.01, 142.25, 136.53, 136.07, 135.37, 133.39, 132.52, 130.55, 128.72, 128.69, 128.45, 128.36, 128.00, 113.52, 55.51, 39.06.

HRMS (ESI): Calcd. For $C_{24}H_{21}O_3$ $[M+H]^+$ *m/z* 357.1491, found *m/z* 357.1493.

2-(4-chlorobenzylidene)-4-phenyl-1-(thiophen-2-yl)butane-1,4-dione (10ia)



E/Z = 38:62.

IR (neat): 3095, 2364, 1683, 1625, 1412, 1213, 1092, 726, 689 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ = 8.00 (dt, *J* = 8.5, 1.7 Hz, 2H), 7.90 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.70 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.52 – 7.42 (m, 2H), 7.39 – 7.31 (m, 2H), 7.31 – 7.22 (m, 2H), 7.18 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.40 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.28, 189.38, 142.98, 140.10, 136.60, 136.26, 134.84, 134.67, 133.94, 133.58, 130.06, 129.00, 128.76, 128.36, 127.93, 39.16.

HRMS (ESI): Calcd. For $C_{21}H_{16}ClO_2S$ $[M+H]^+$ *m/z* 367.0554, found *m/z* 367.0560.

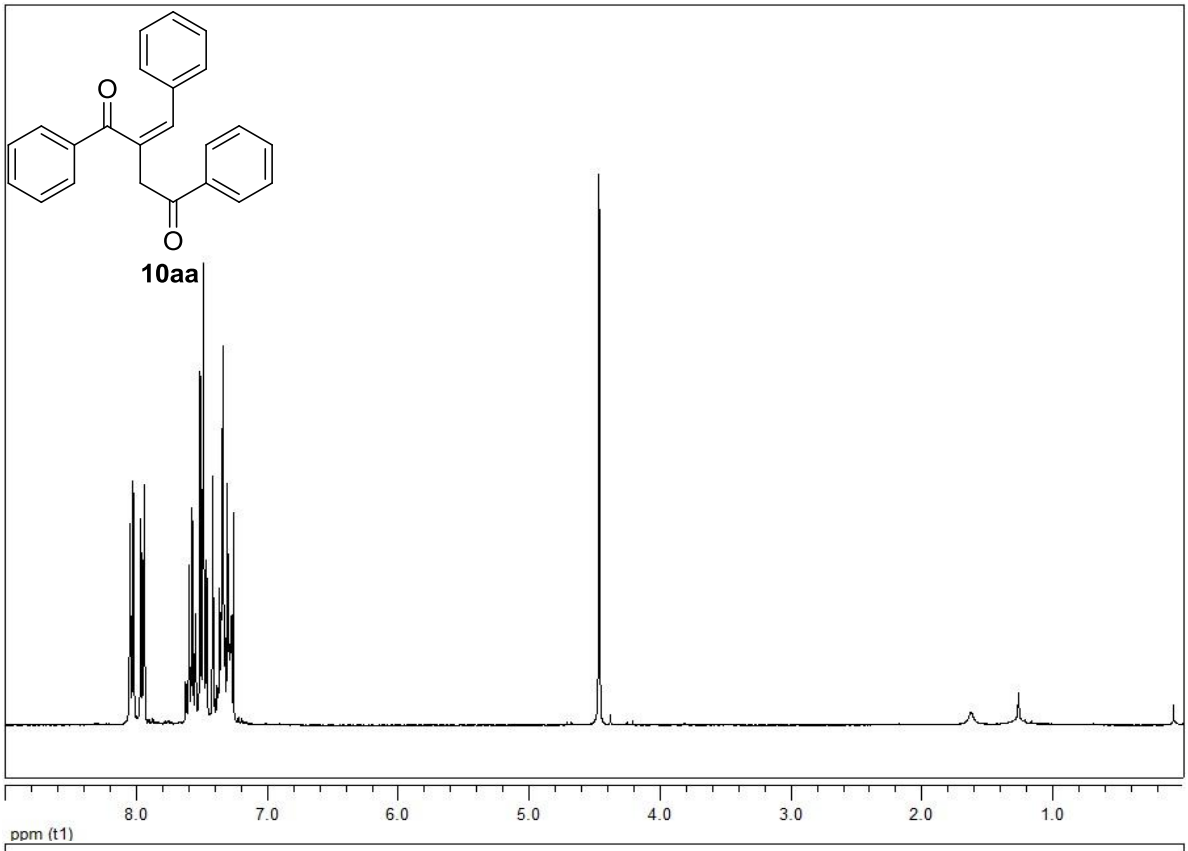
Appendix

NMR- spectra

^{1}H-NMR spectra - upper image

^{13}C-NMR spectra - lower image

Solvent, if not stated otherwise: $CDCl_3$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3.0
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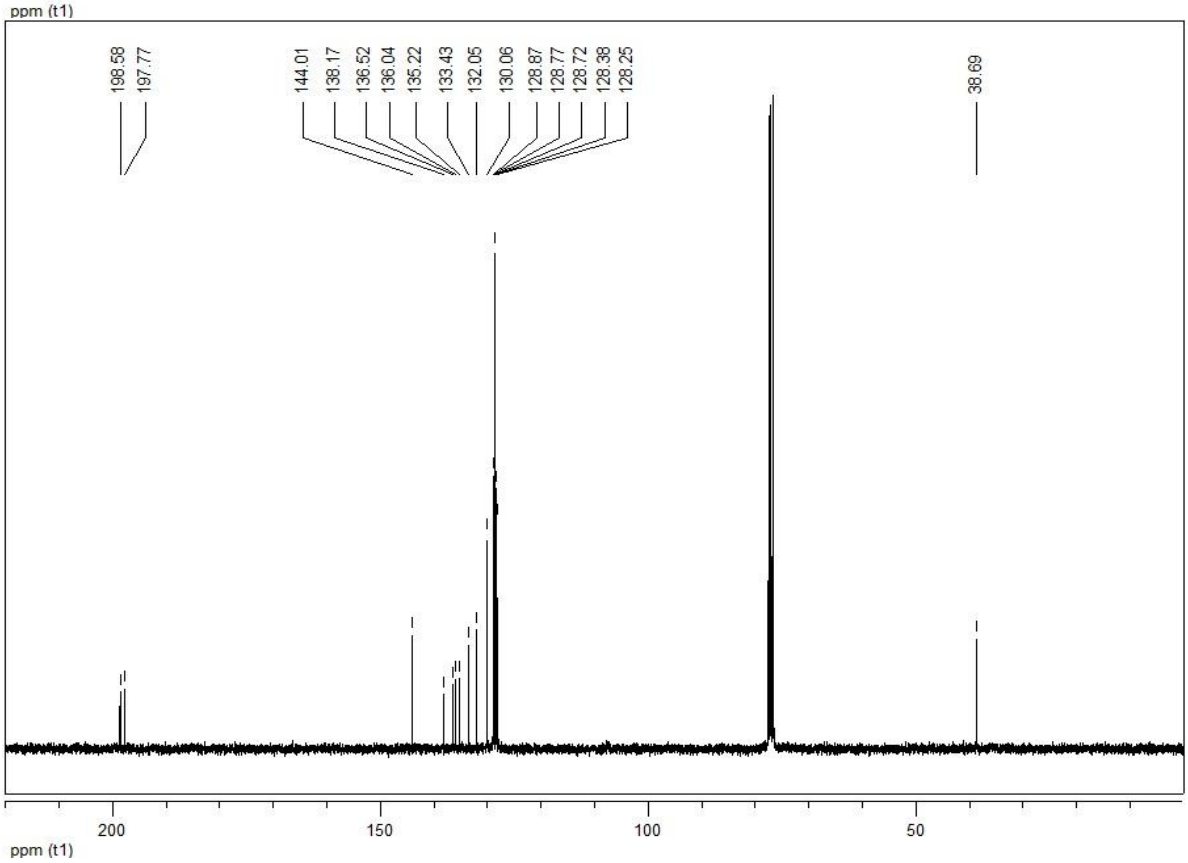
1.0
ppm (t1)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197.77
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128.25
38.69
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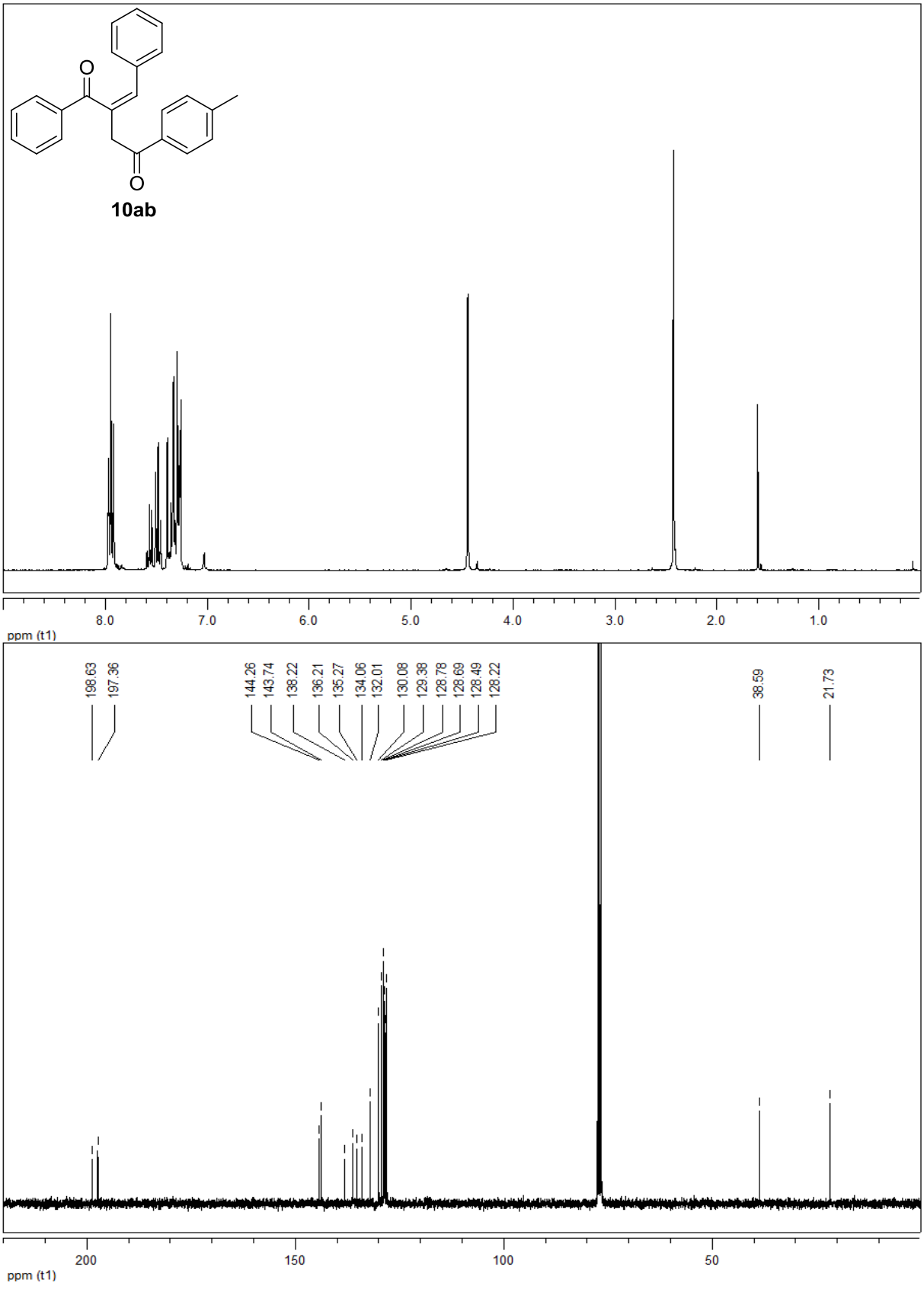
150
100
50
ppm (t1)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4.0
3.0
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1.0
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197.36
144.26
143.74
138.22
136.21
135.27
134.06
132.01
130.08
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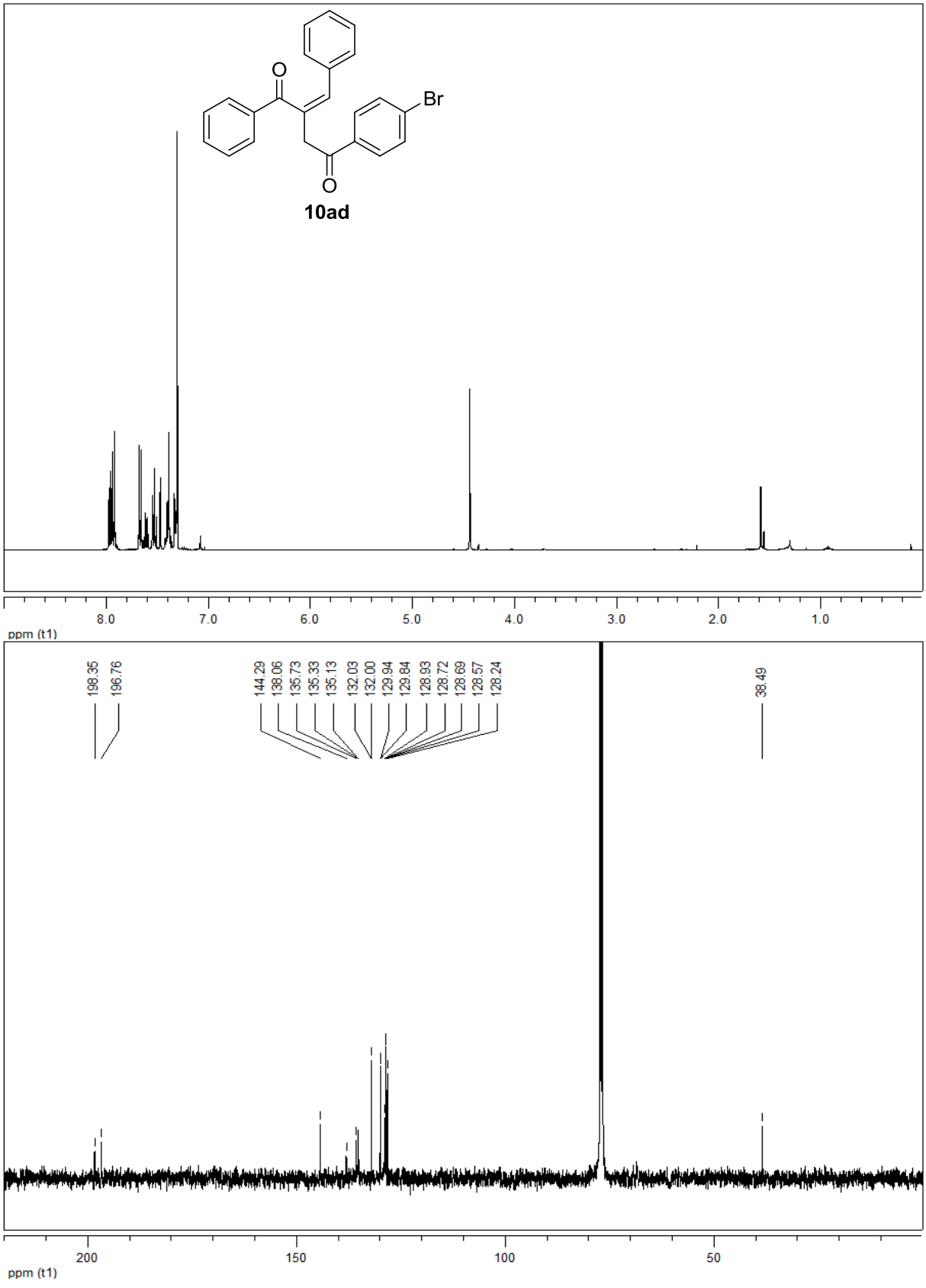
128.78
128.69
128.49
128.22
38.59
21.73
200
150
100
50
ppm (t1)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2.0
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196.76
144.29
138.06
135.73
135.33
135.13
132.03
132.00
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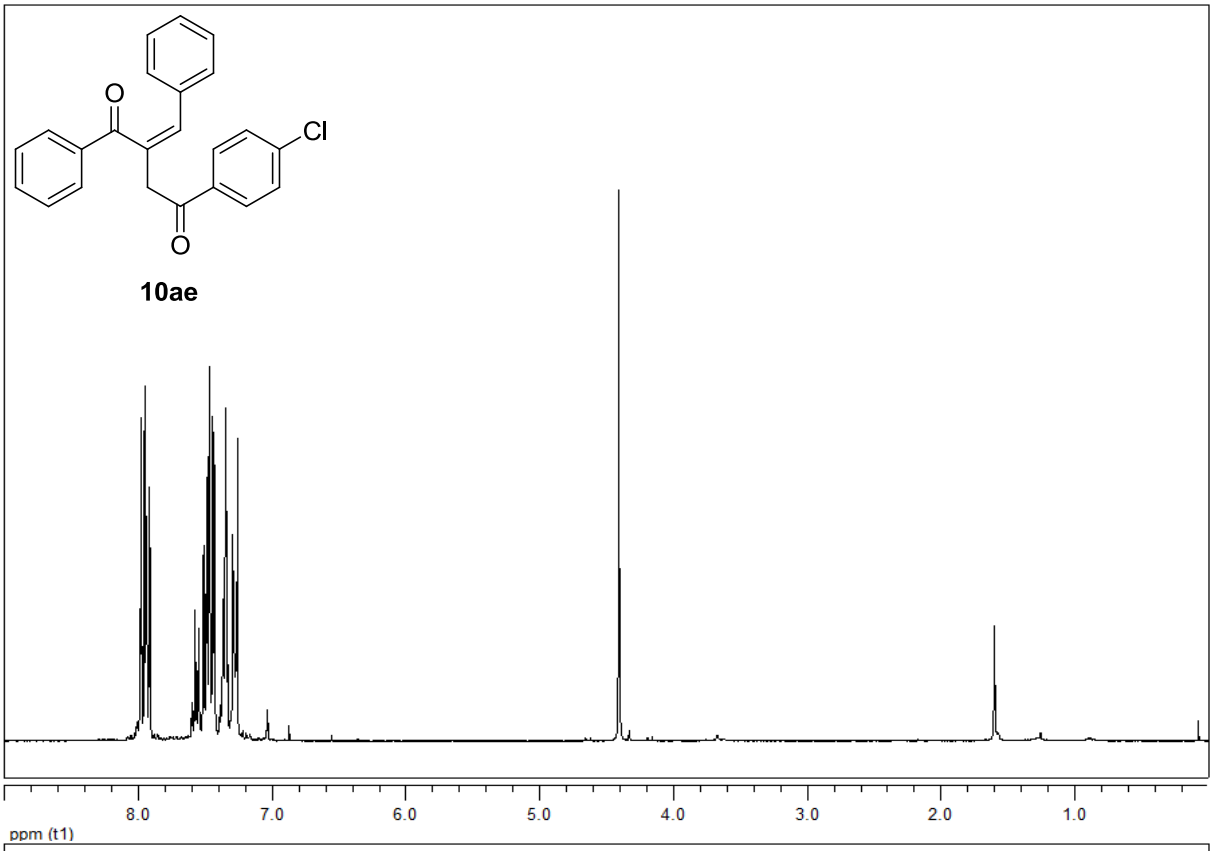
128.69
128.57
128.24
38.49
200
150
100
50
ppm (t1)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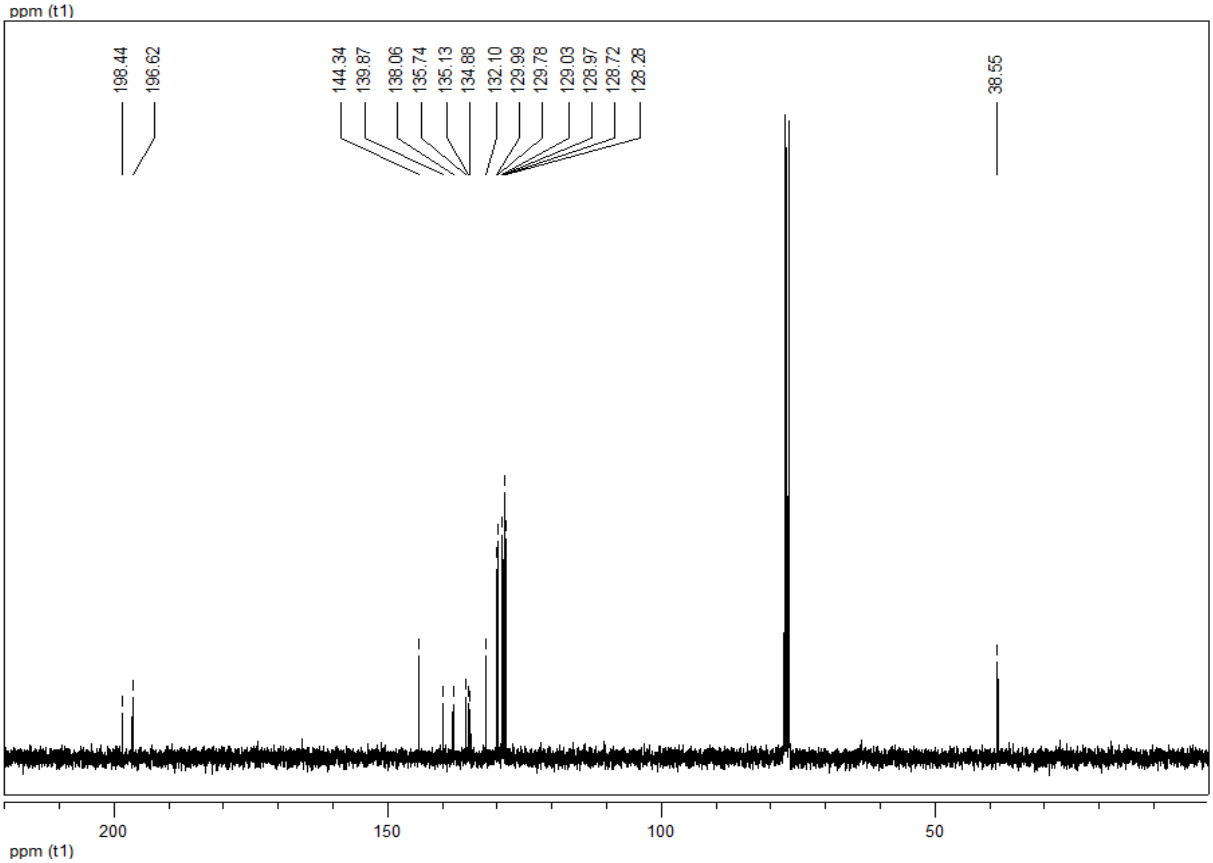
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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139.87
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135.13
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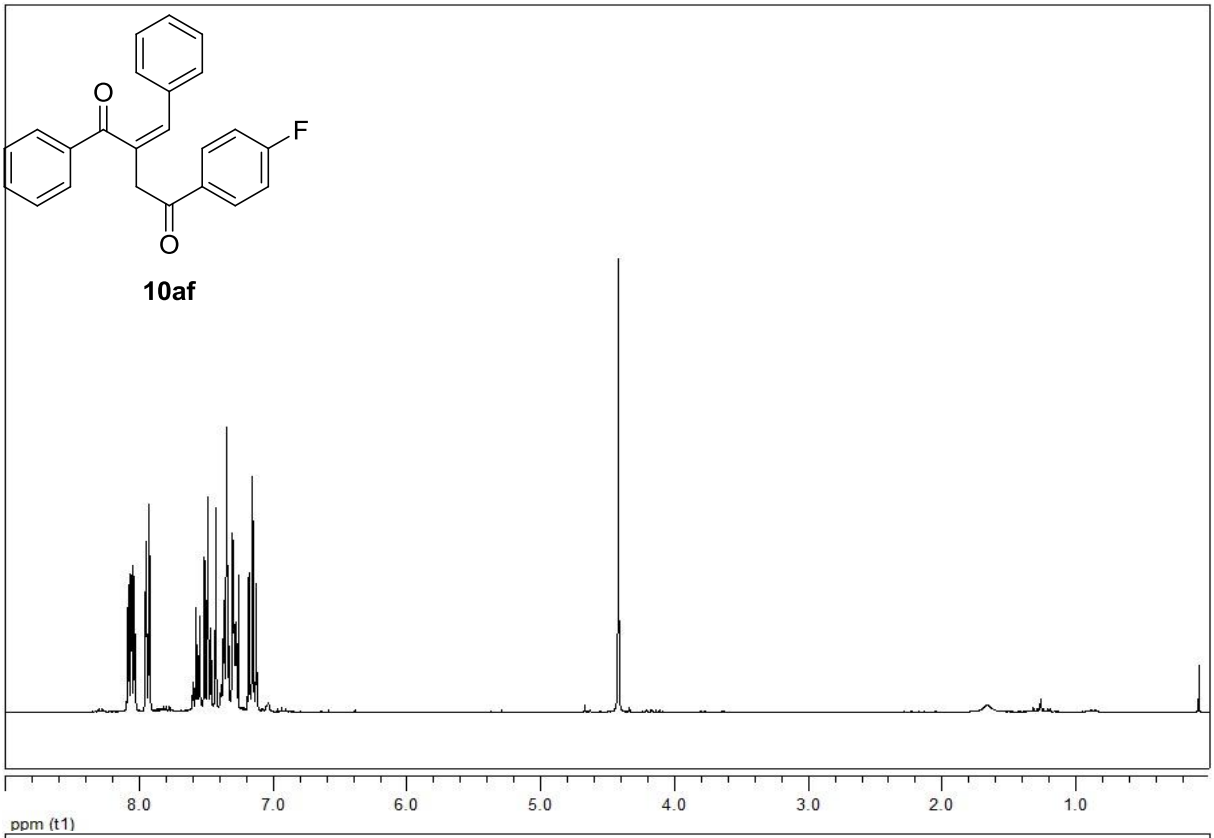
128.28
38.55
200
150
100
50
ppm (t1)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F
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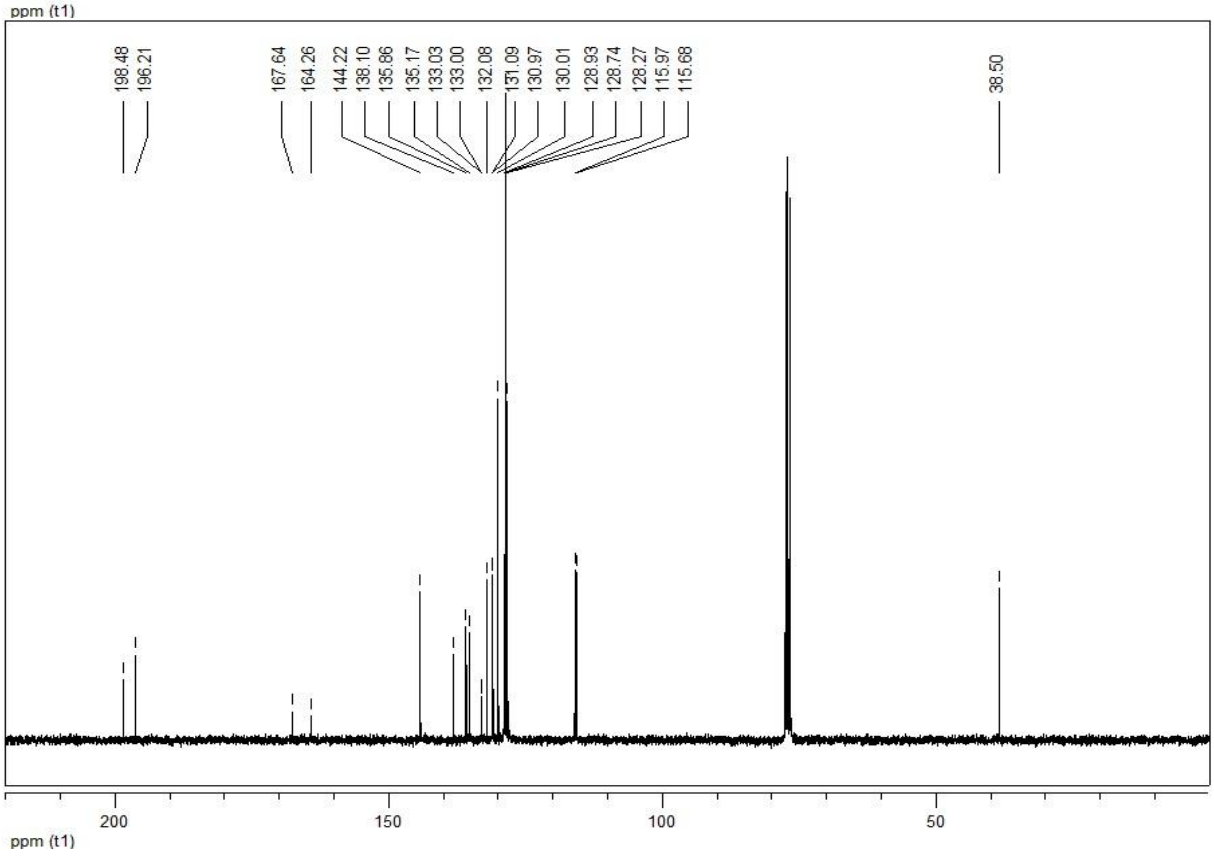
5.0
4.0
3.0
2.0
1.0
ppm (t1)

10af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133.00
132.08
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38.50
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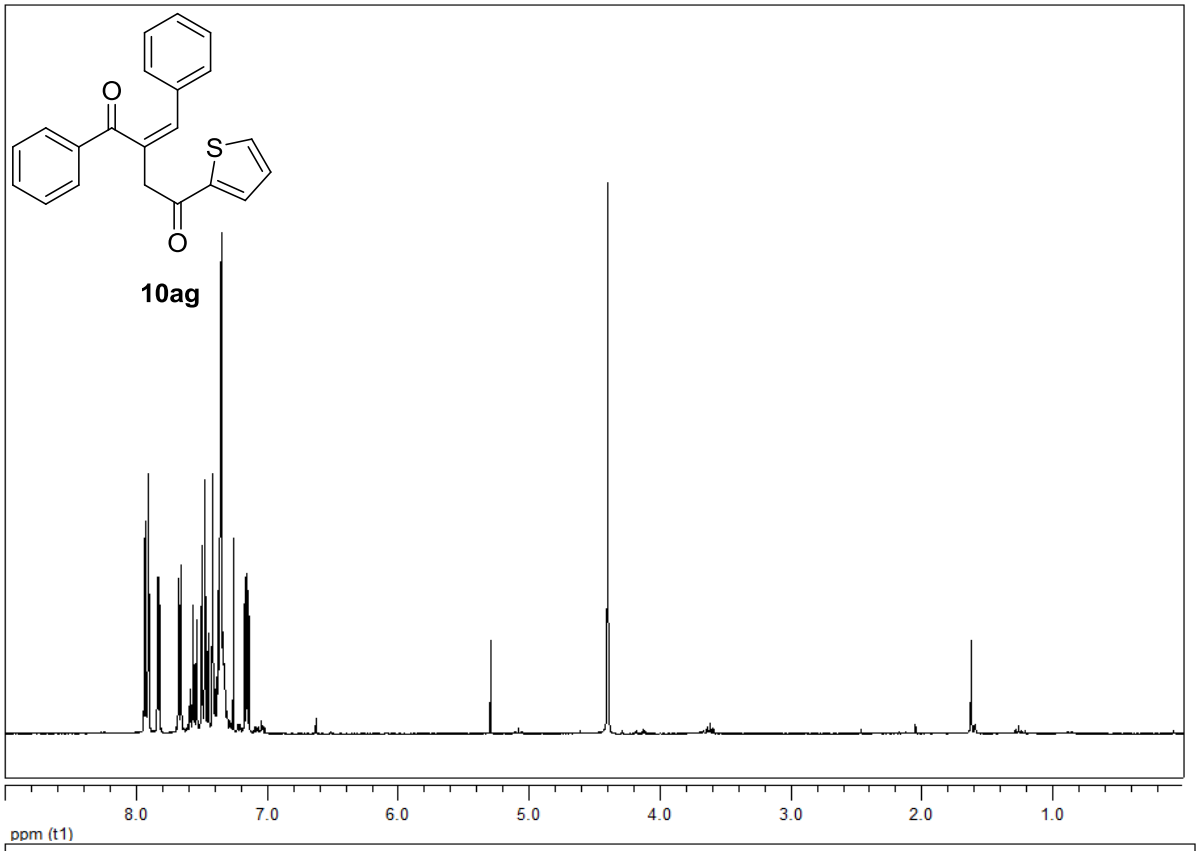
100
50
ppm (t1)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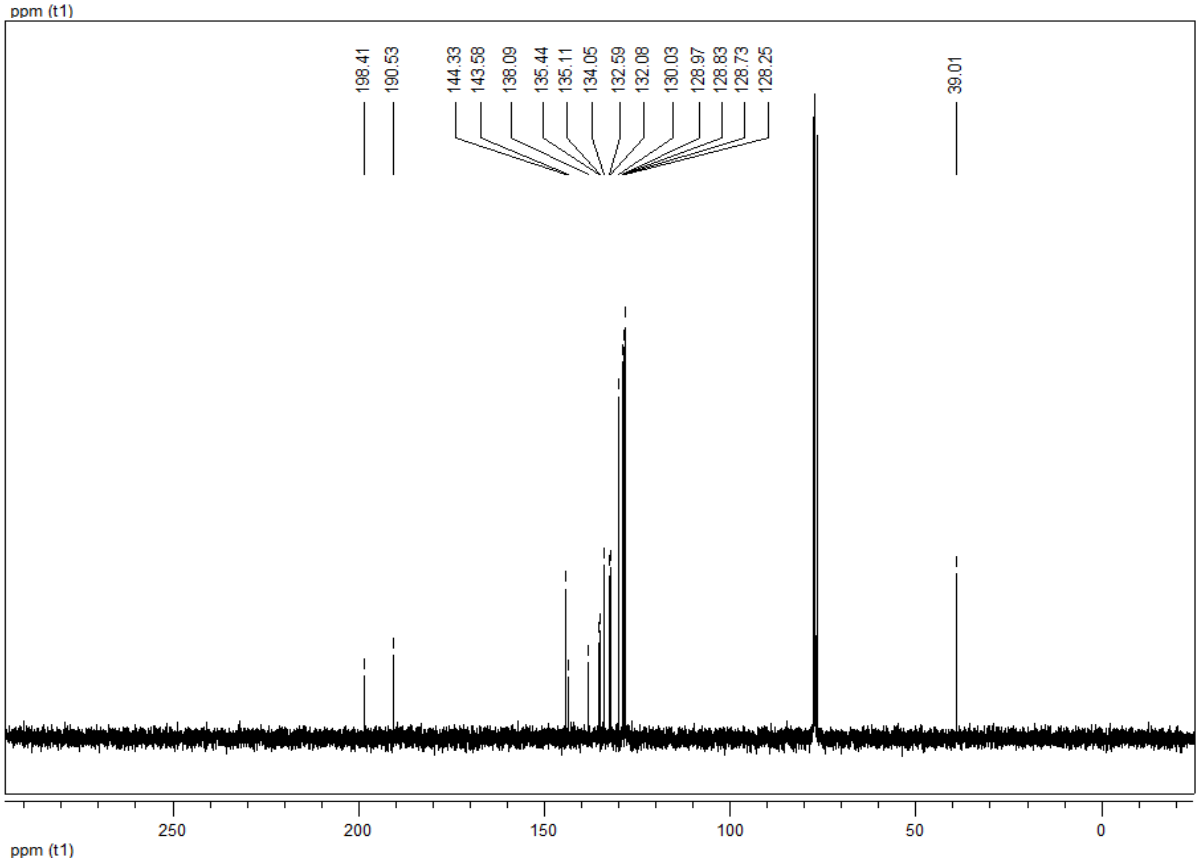
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134.05
132.59
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128.83
128.73
128.25
39.01
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50
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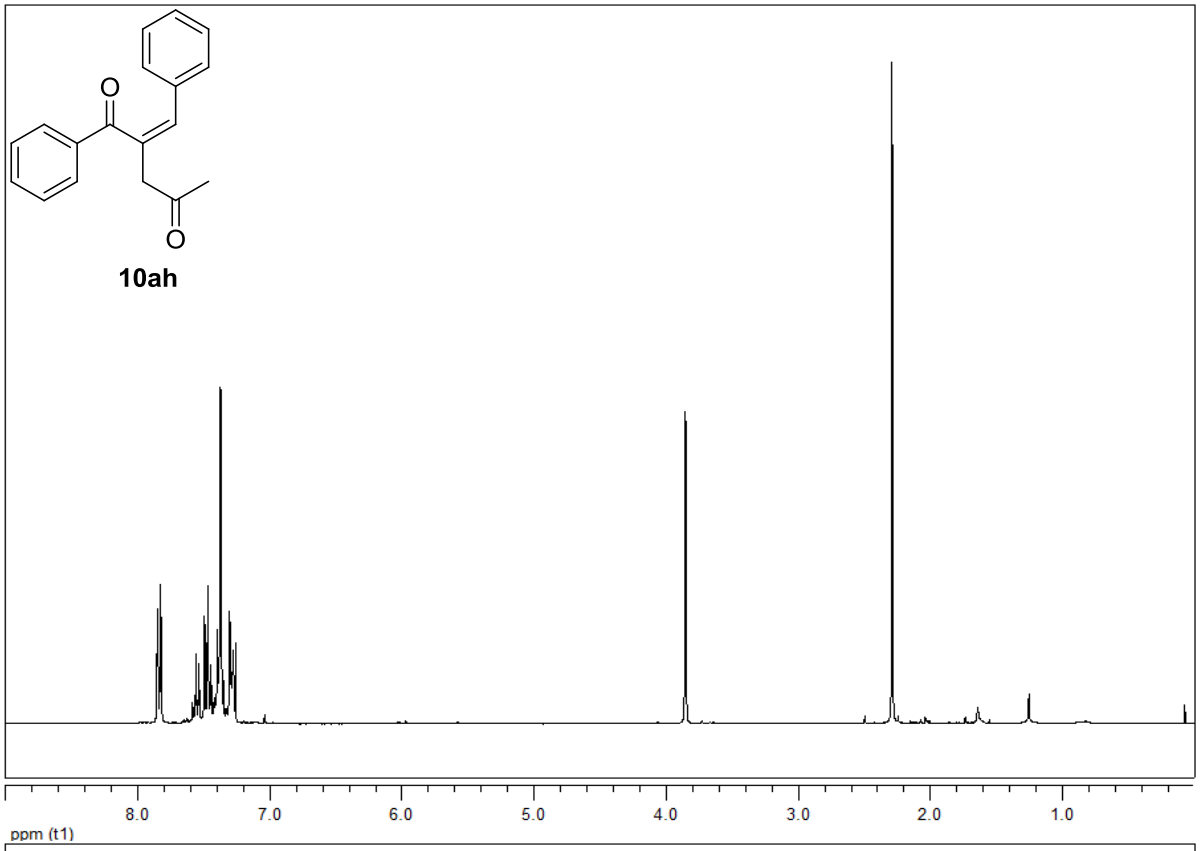
ppm (t1)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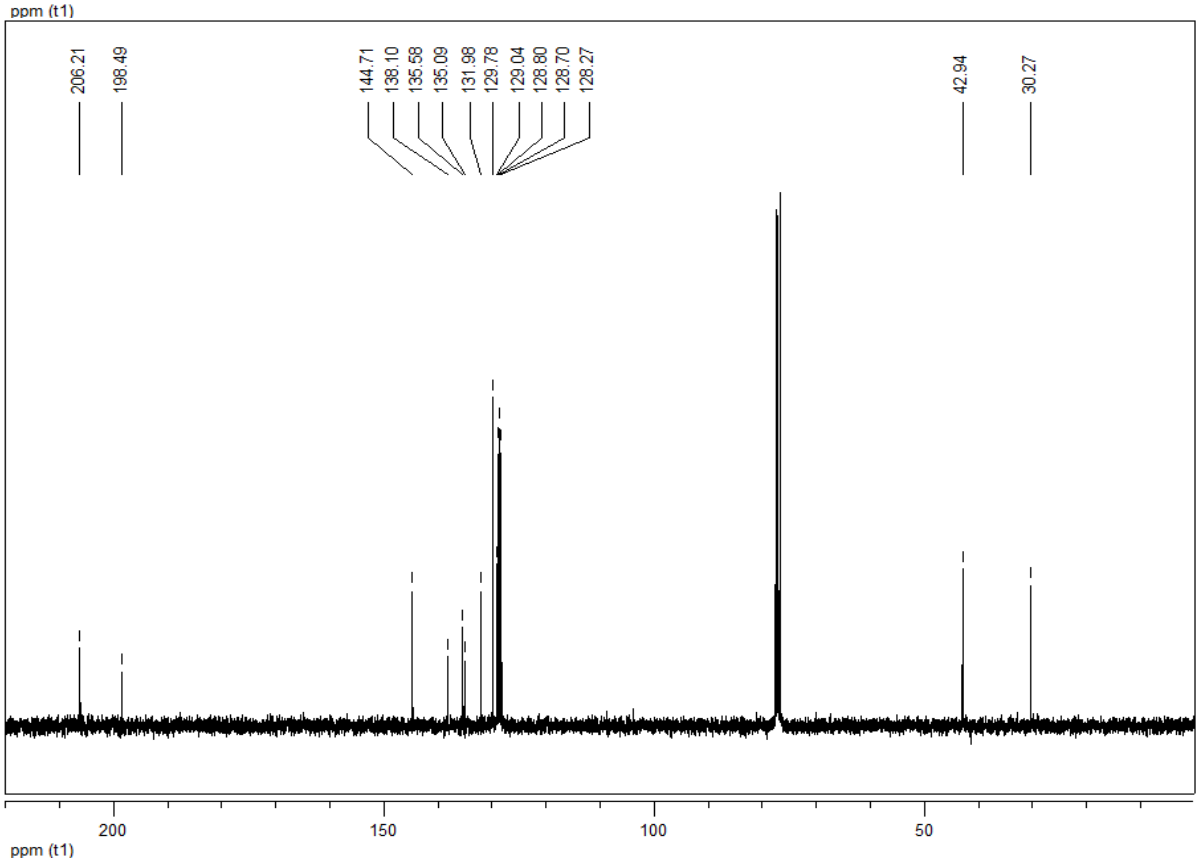
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128.27
42.94
30.27
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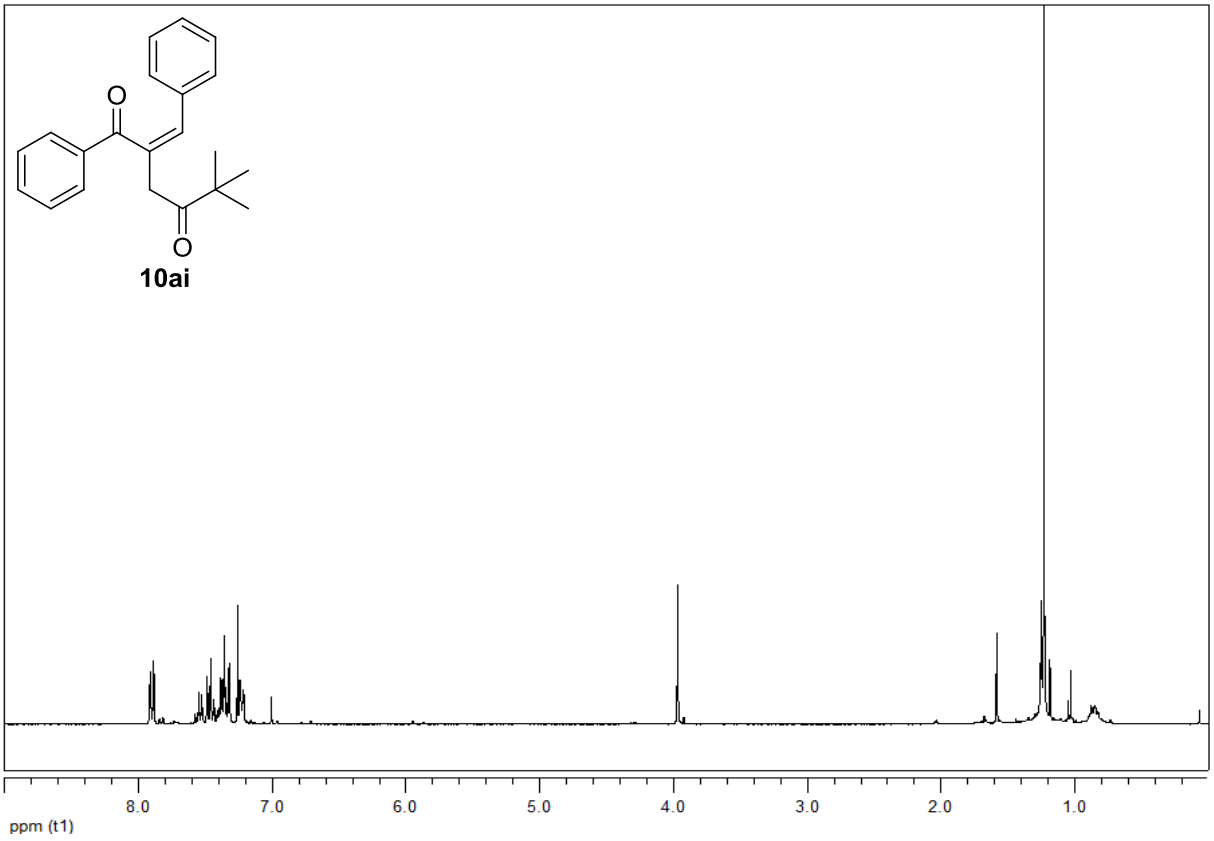
150
100
50
ppm (t1)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O
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4.0
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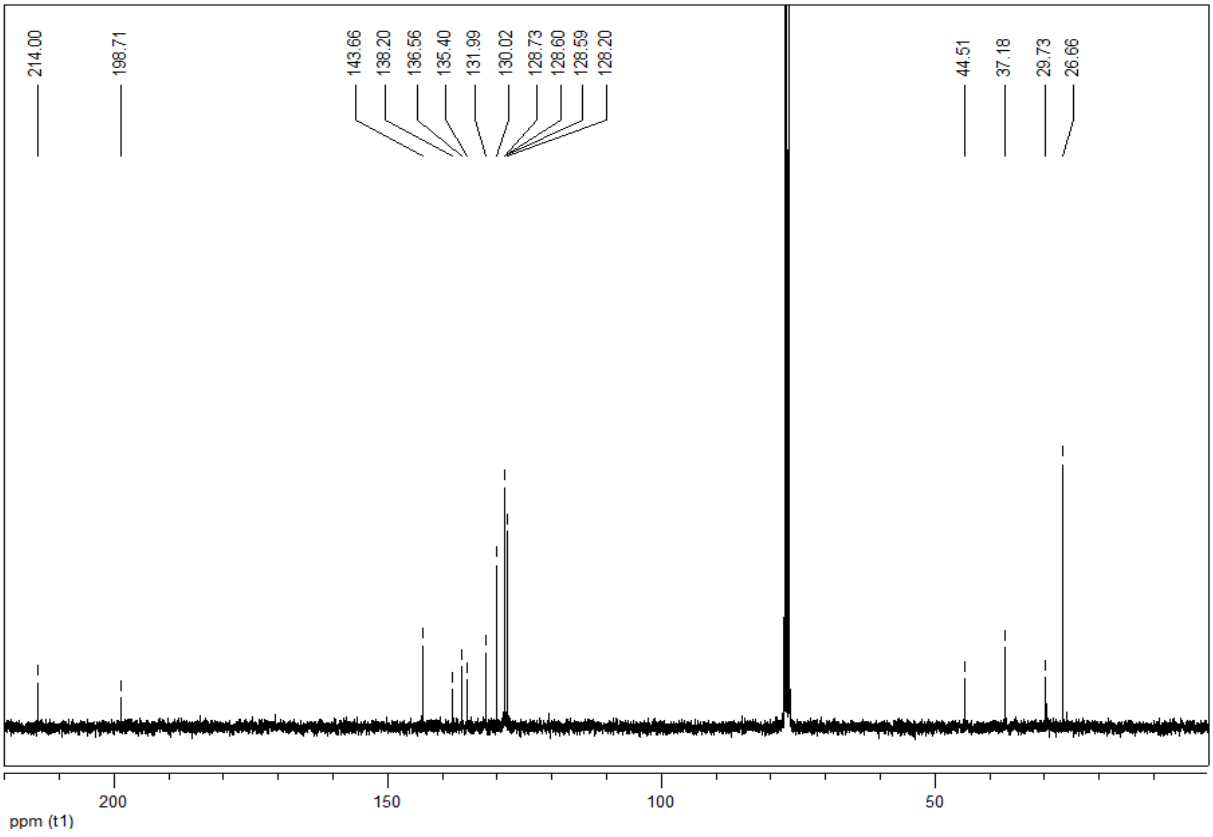
1.0
ppm (t1)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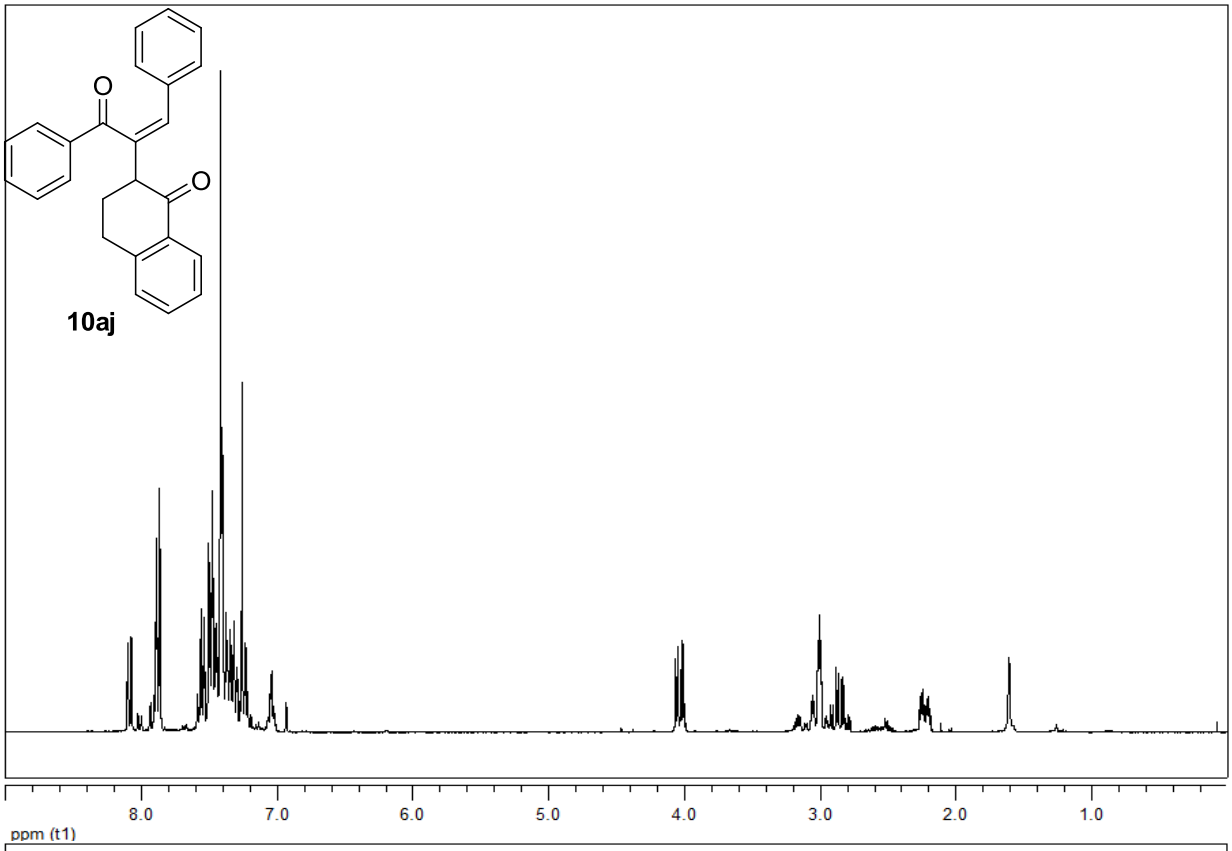
100
50
ppm (t1)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O
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5.0
4.0
3.0
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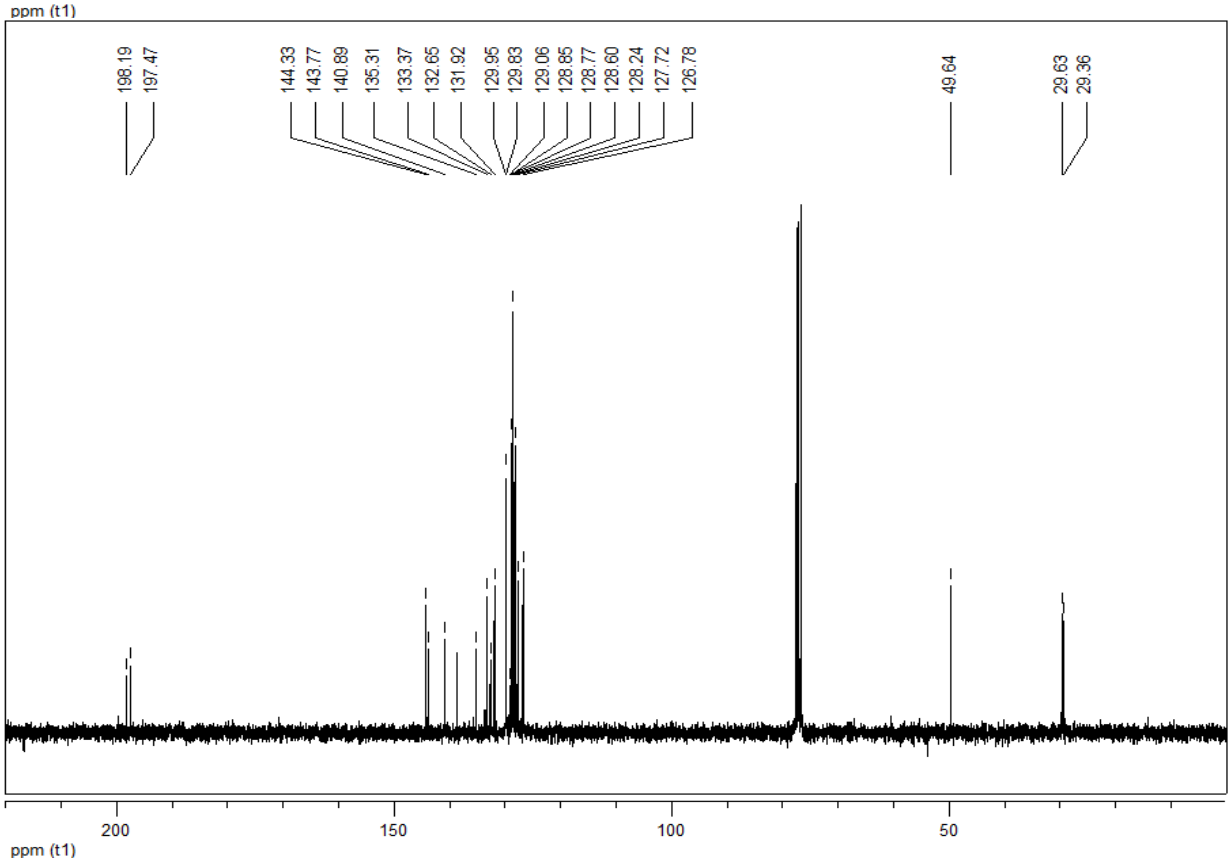
1.0
ppm (t1)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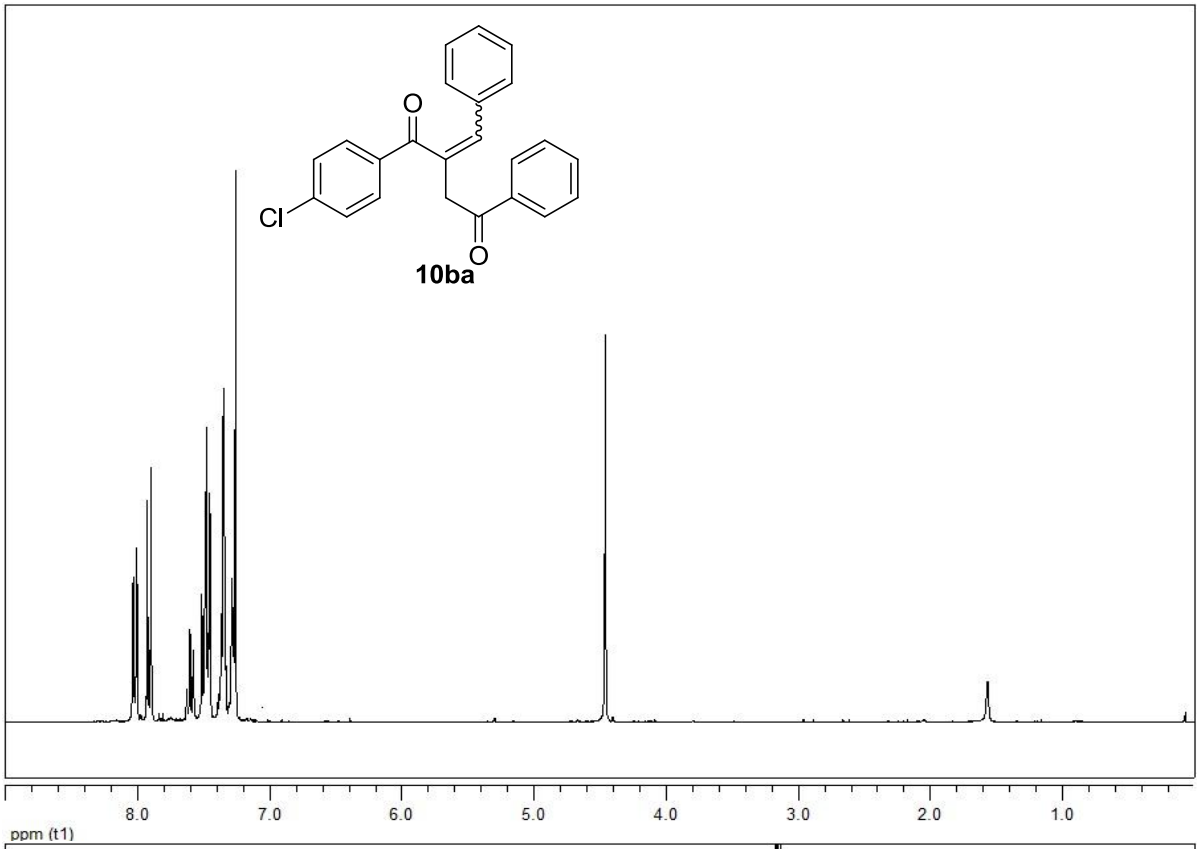
ppm (t1)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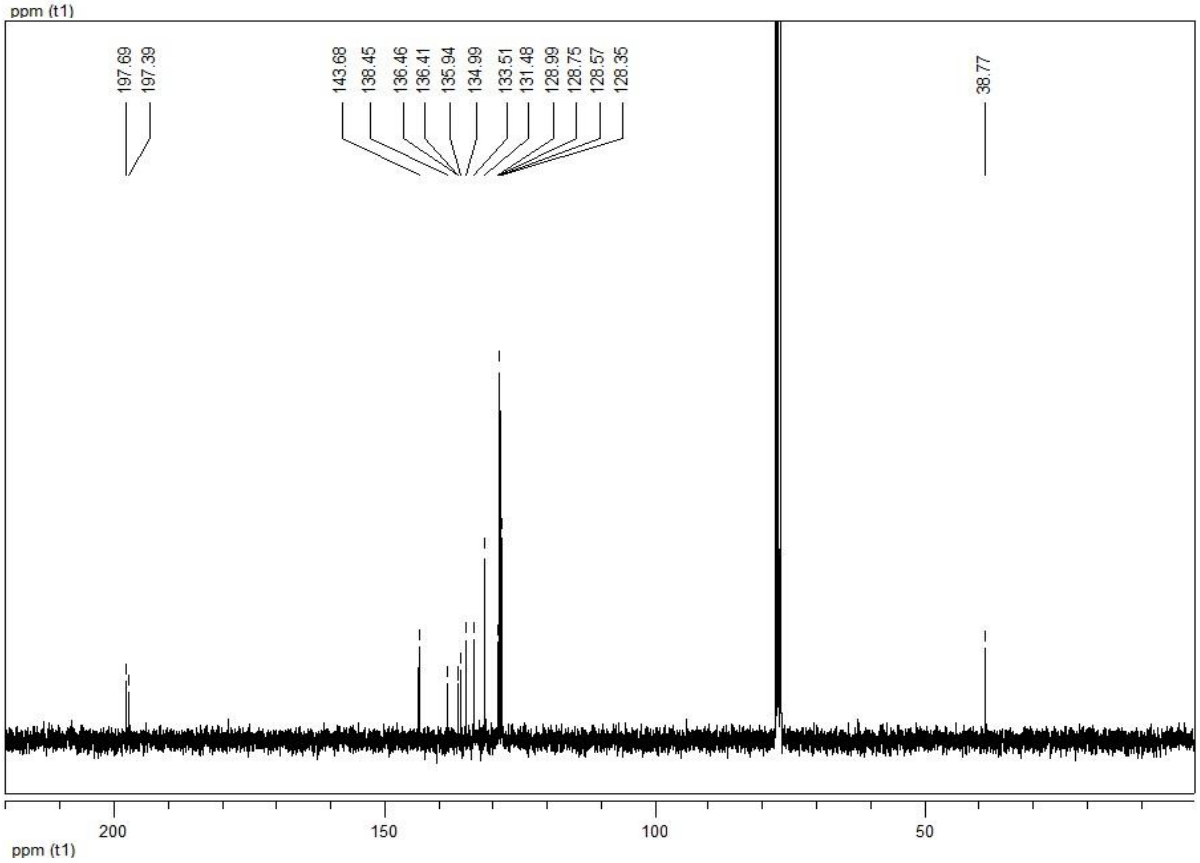
4.0
3.0
2.0
1.0
ppm (t1)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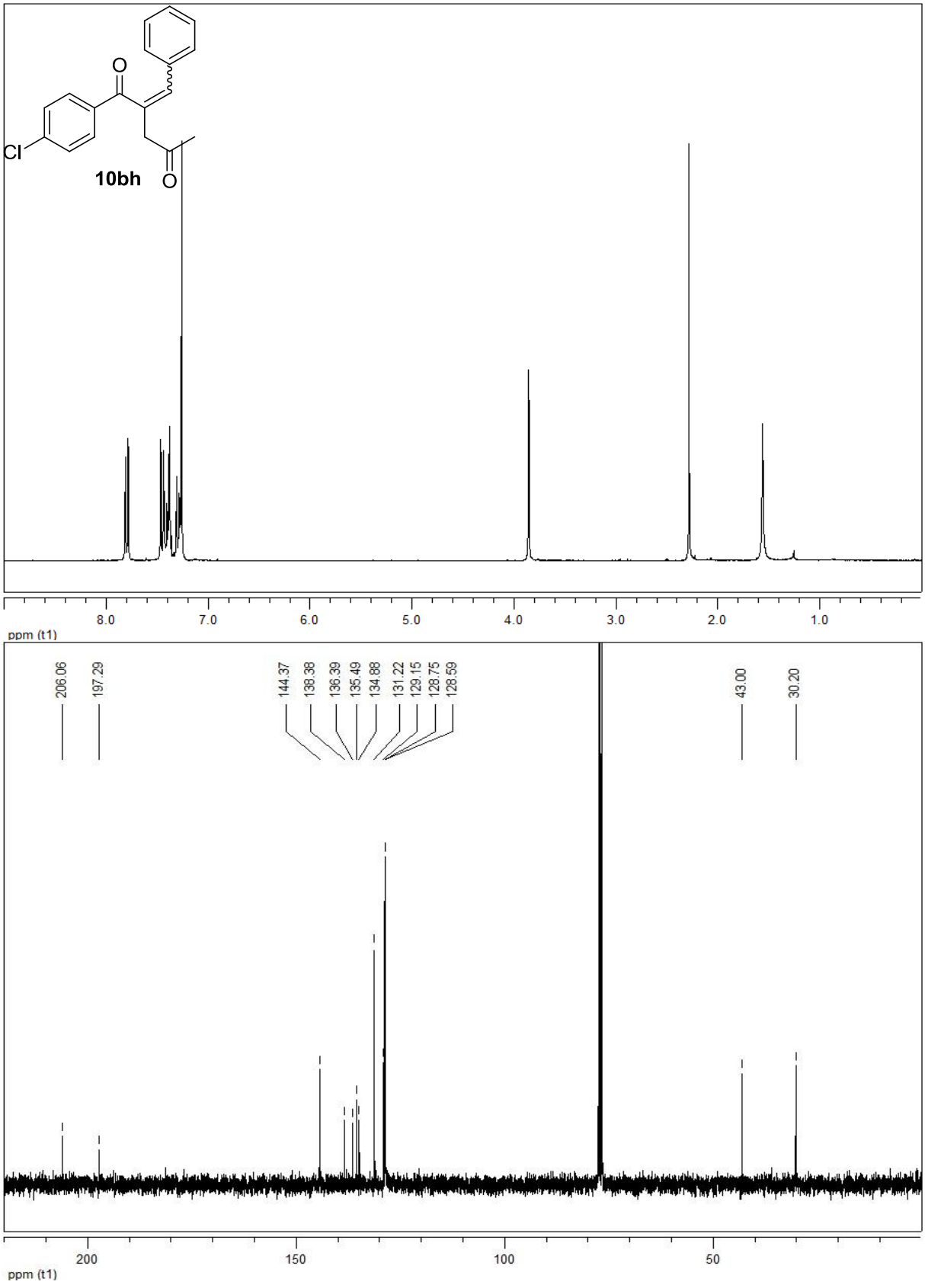
ppm (t1)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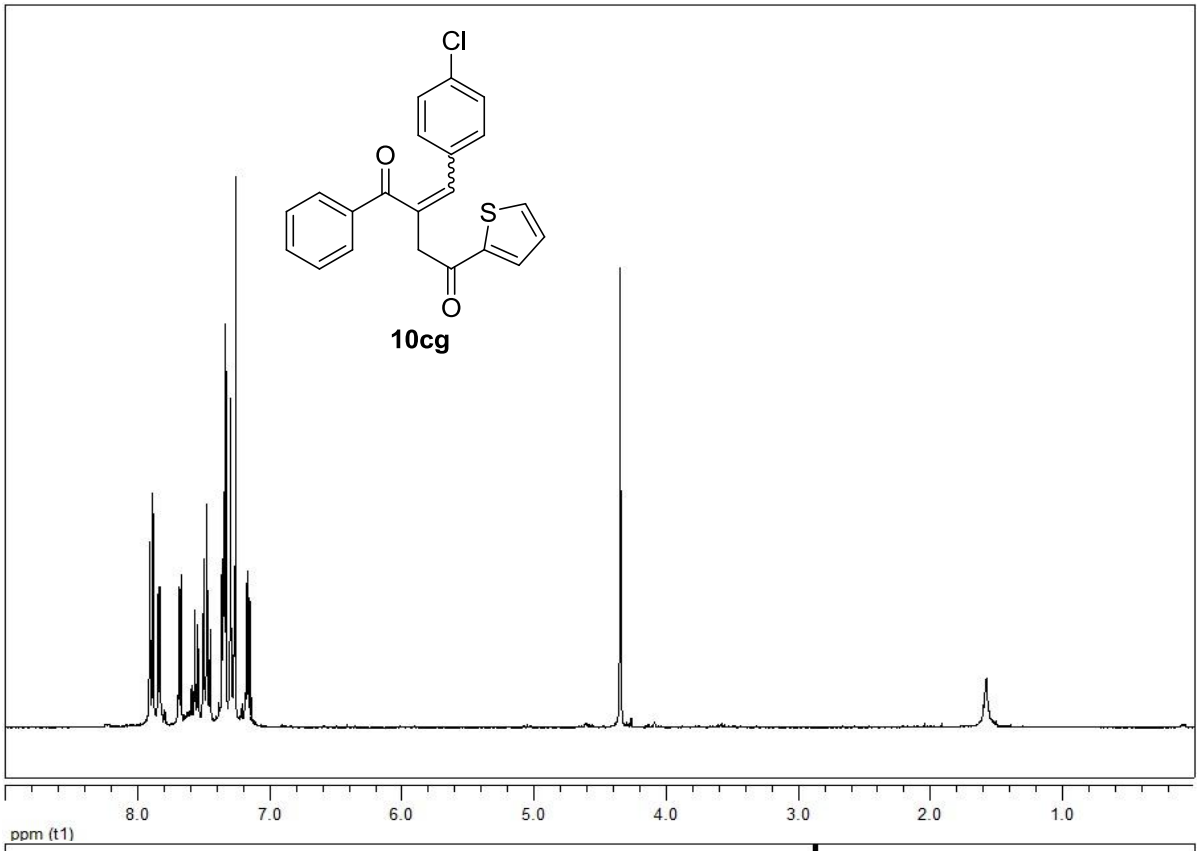
ppm (t1)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S
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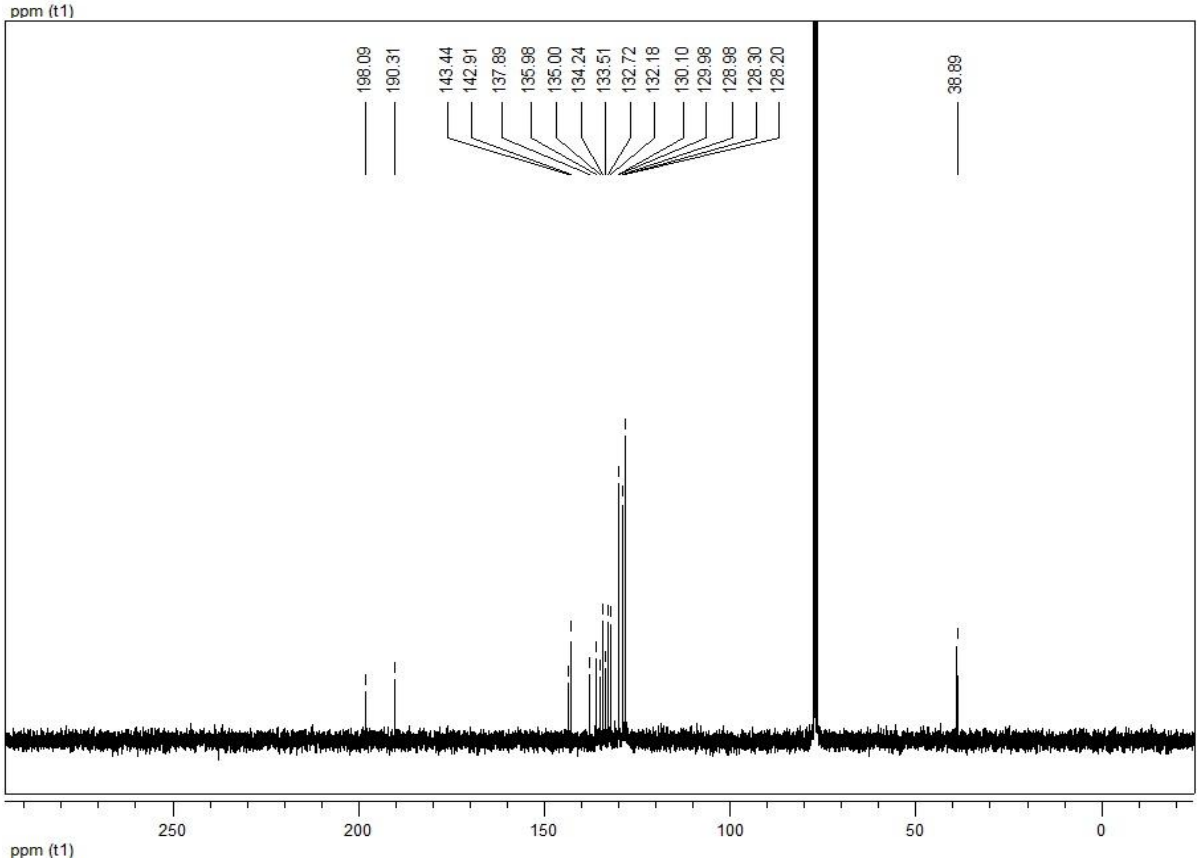
ppm (t1)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200
150
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50
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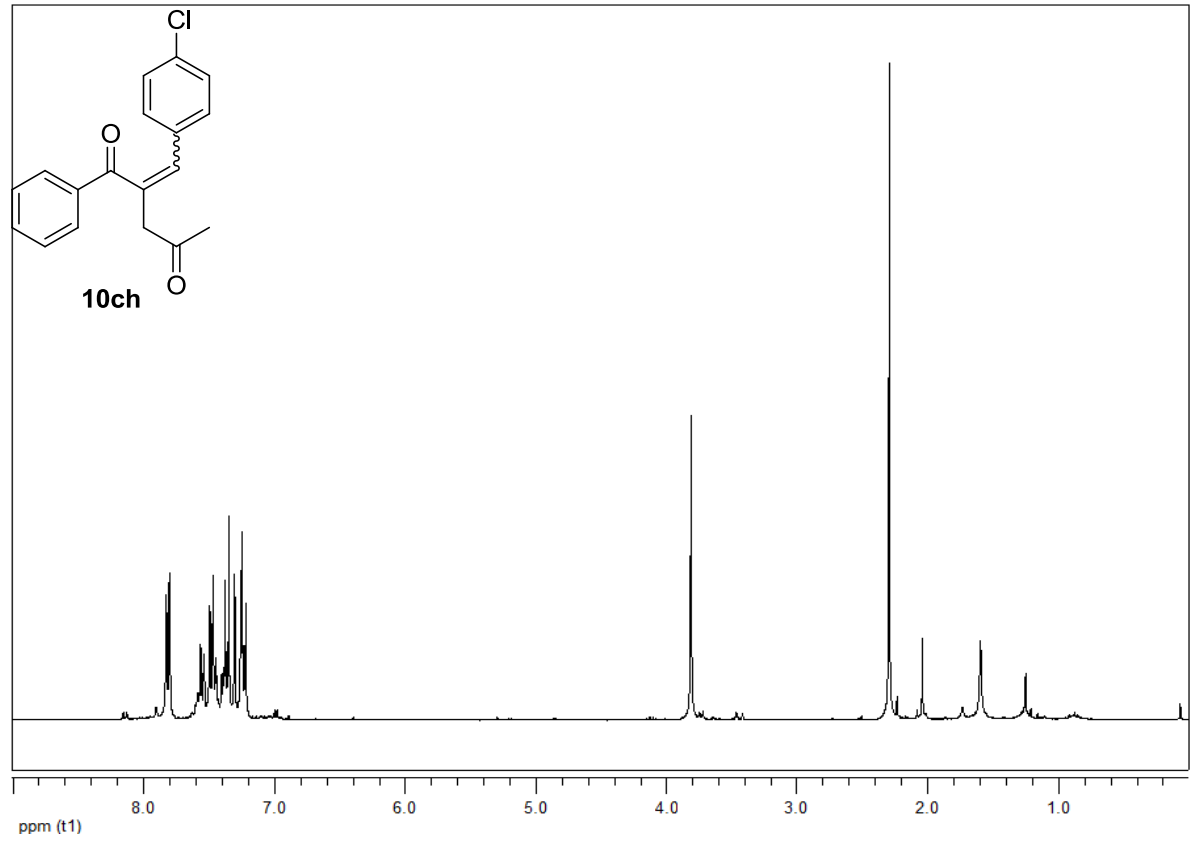
ppm (t1)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O
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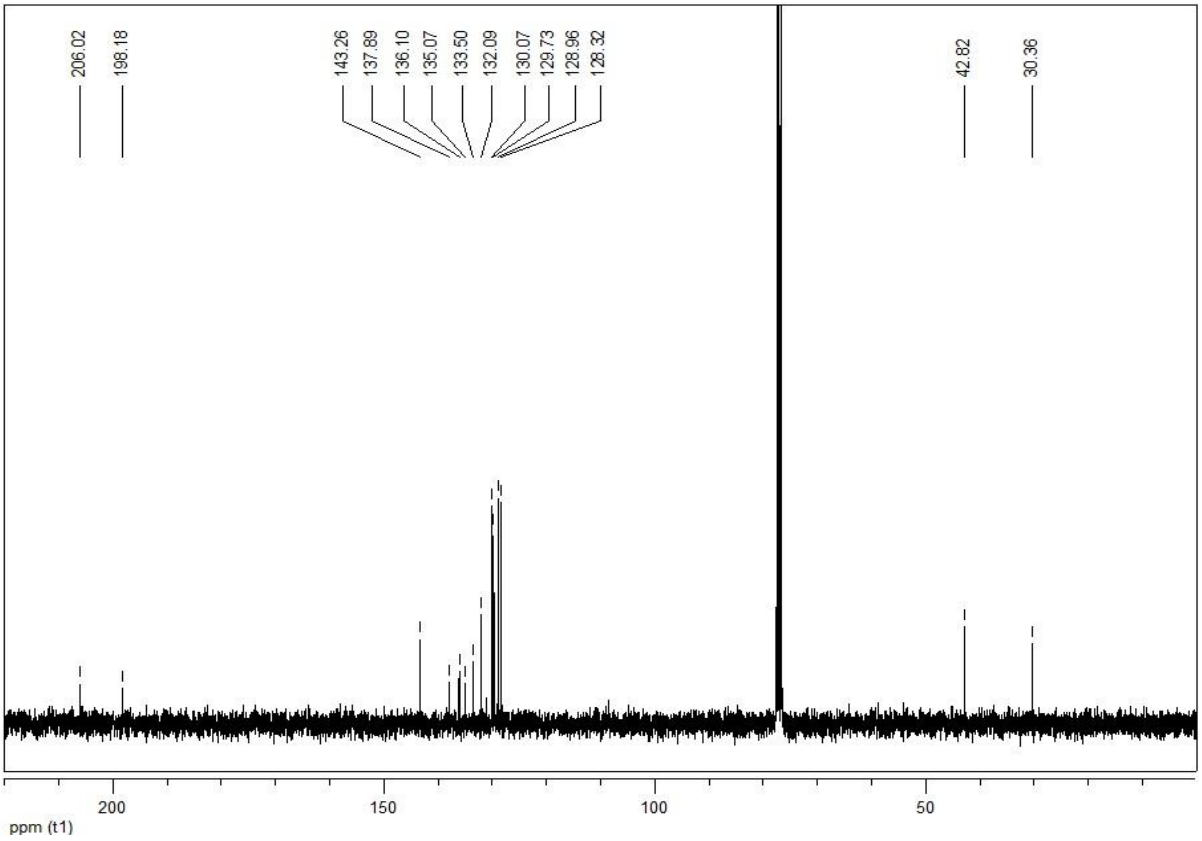
ppm (t1)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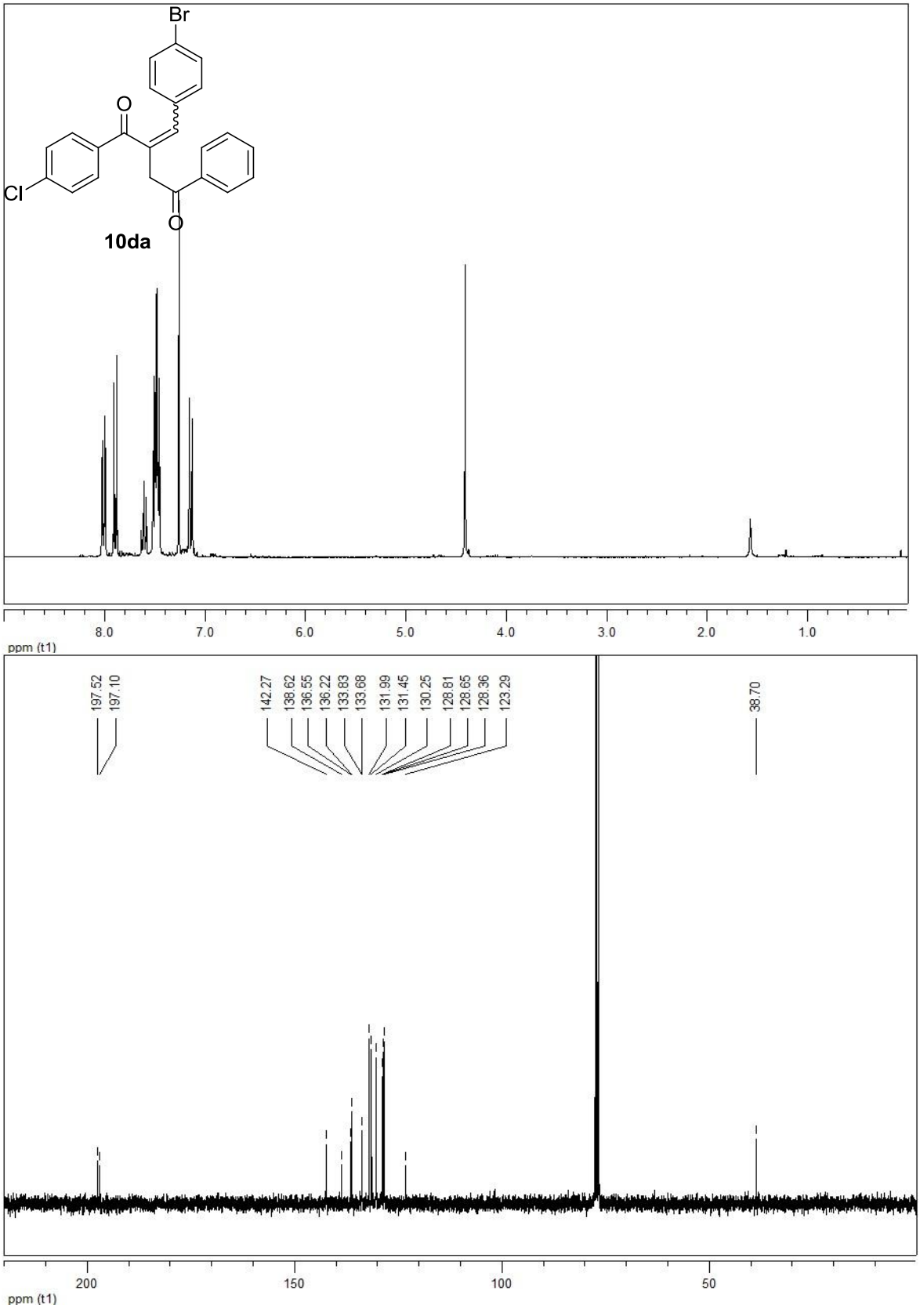
ppm (t1)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7.0
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4.0
3.0
2.0
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ppm (t1)
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197.10
142.27
138.62
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133.83
133.68
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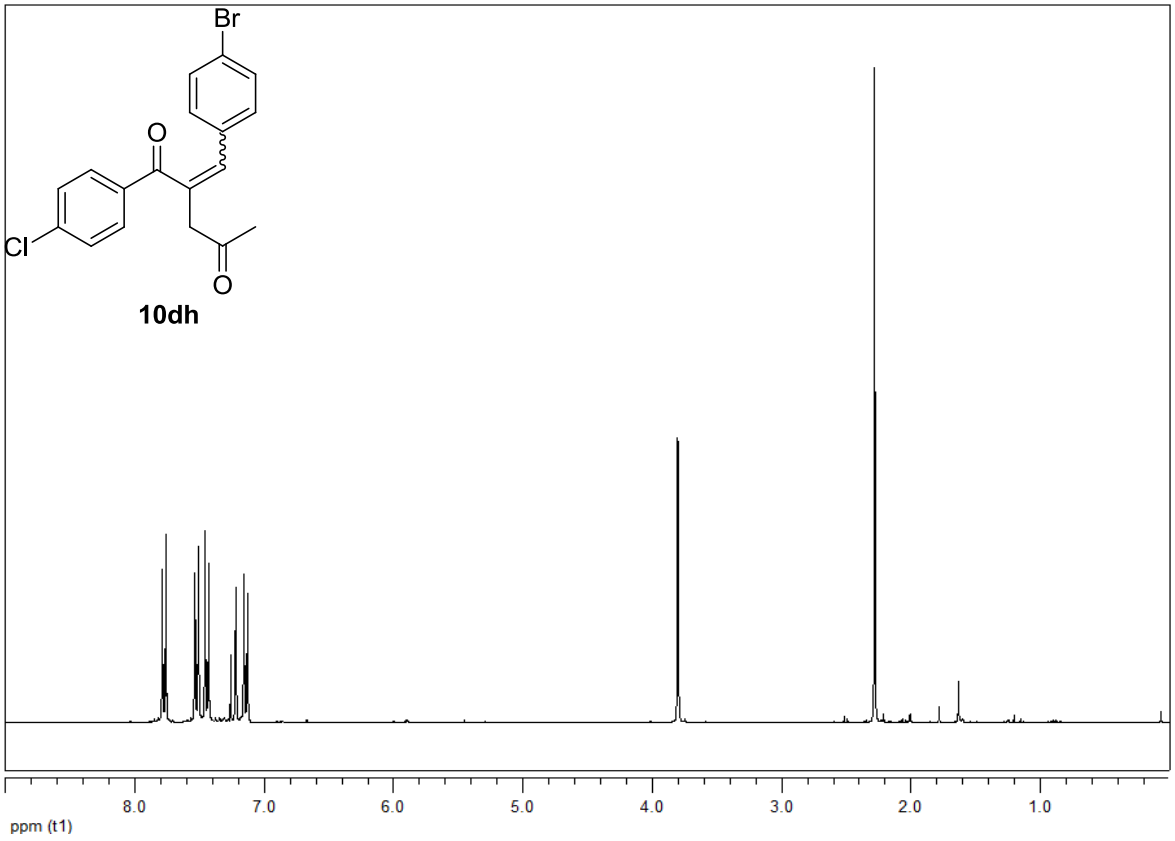
ppm (t1)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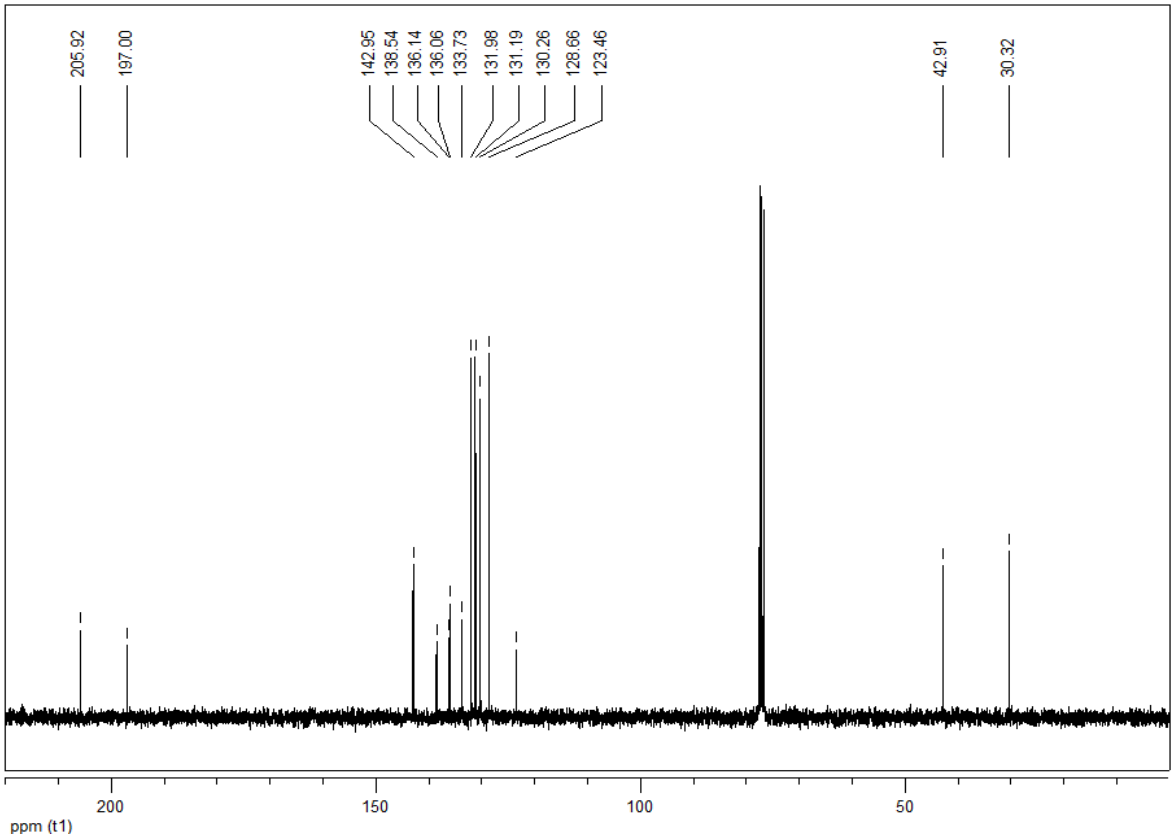
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138.54
136.14
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133.73
131.98
131.19
130.26
128.66
123.46
42.91
30.32
200
150
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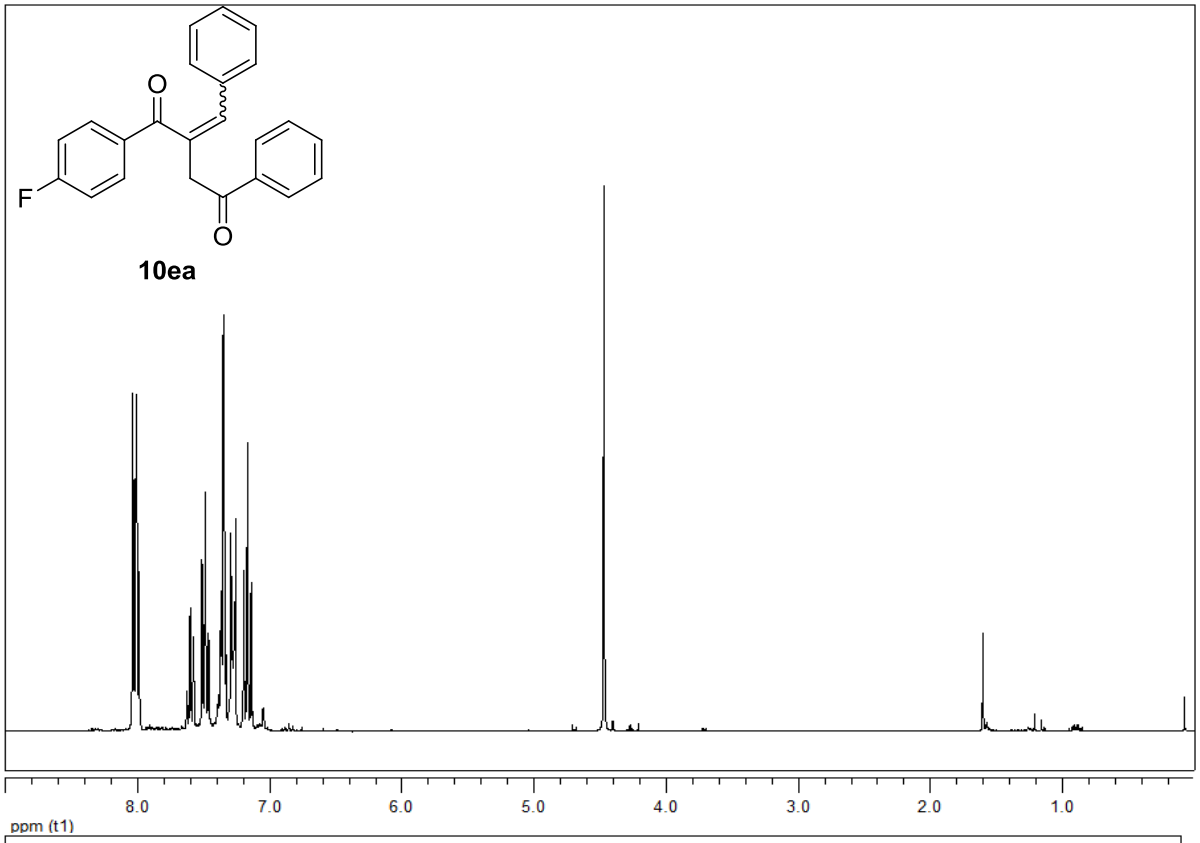
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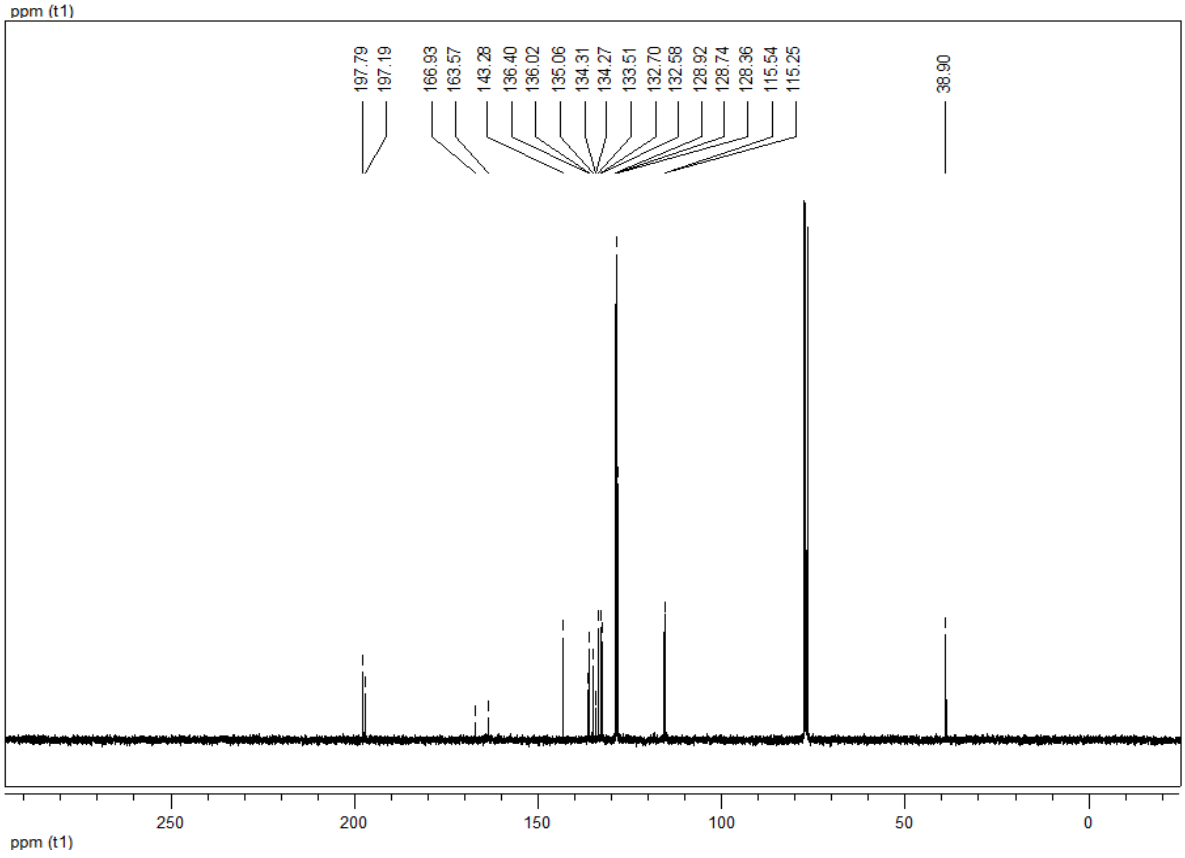
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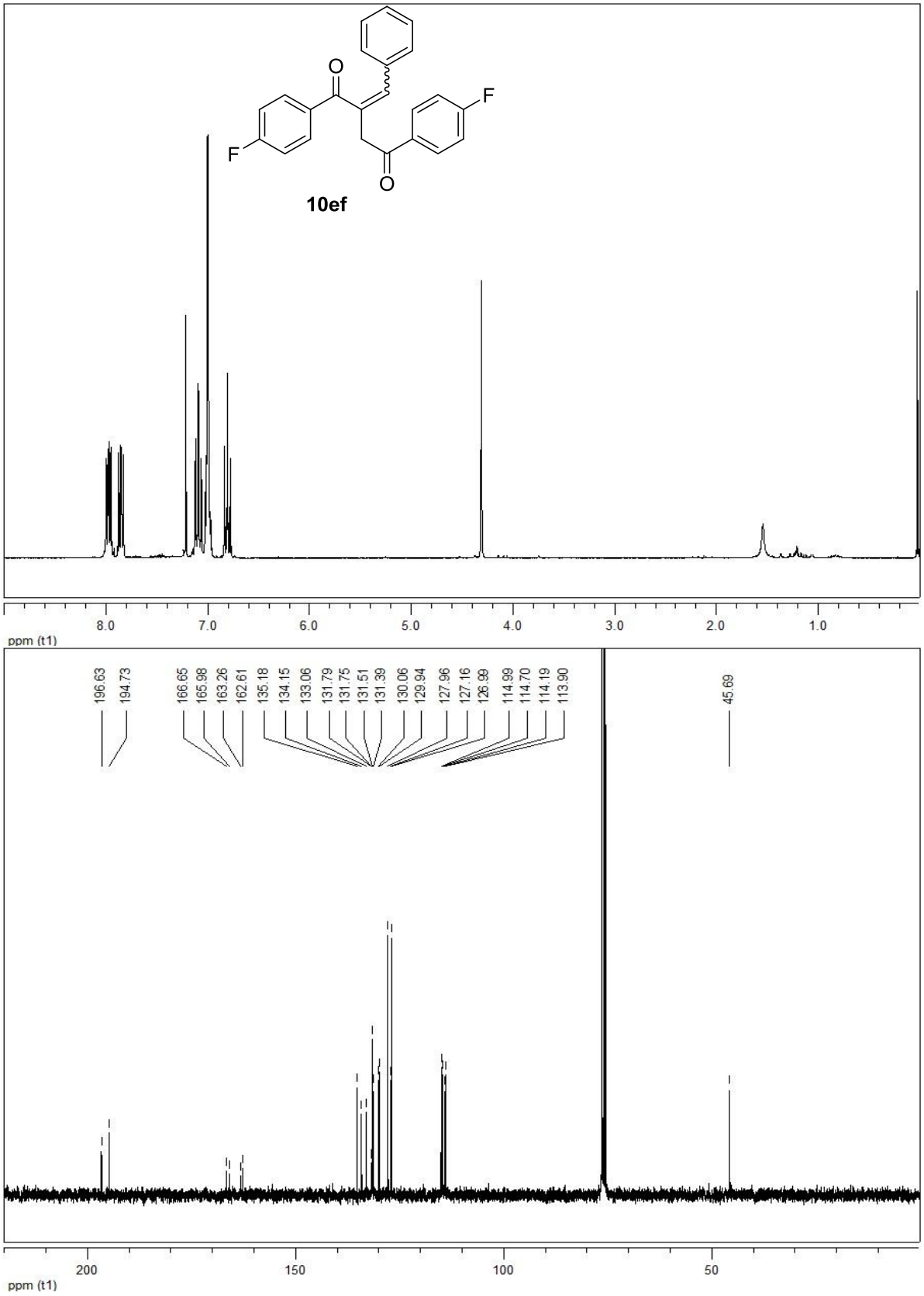
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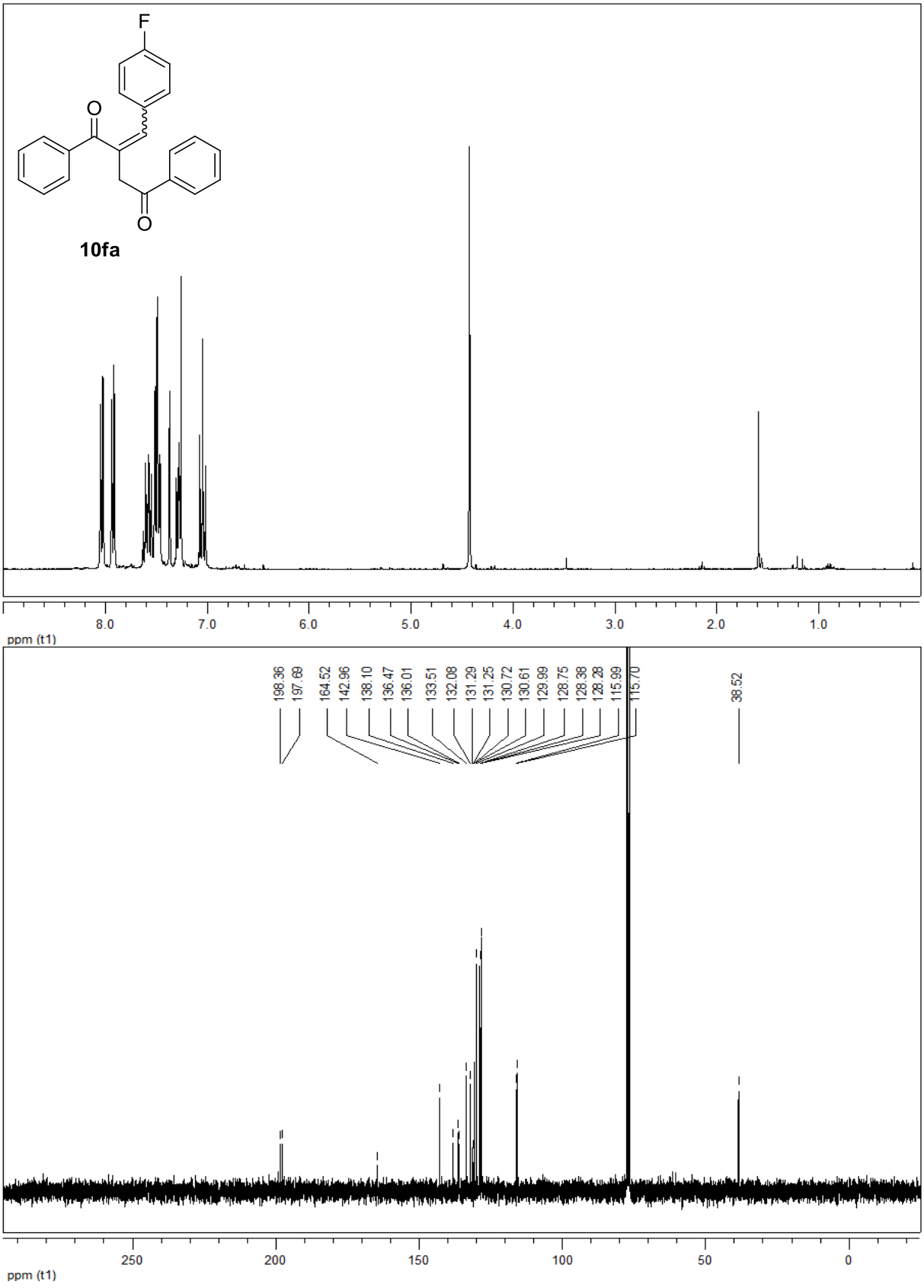
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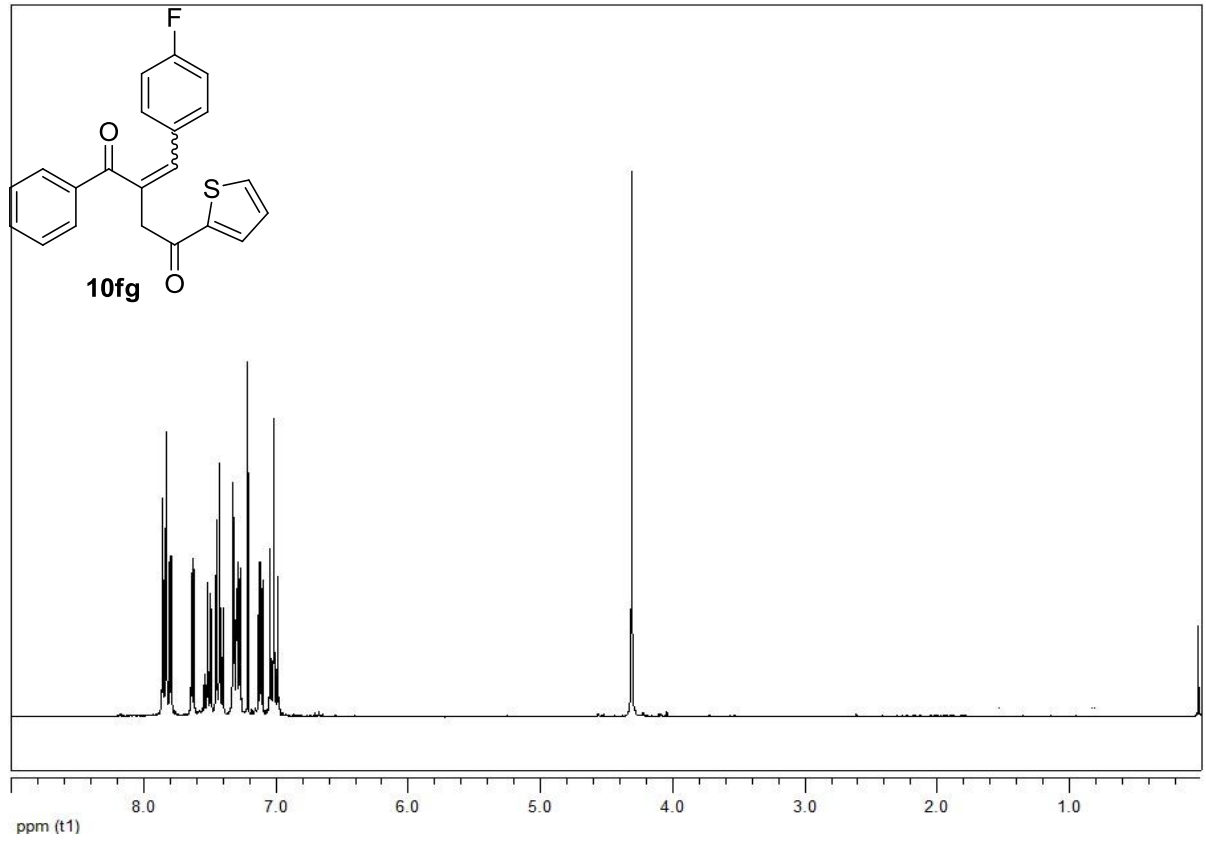
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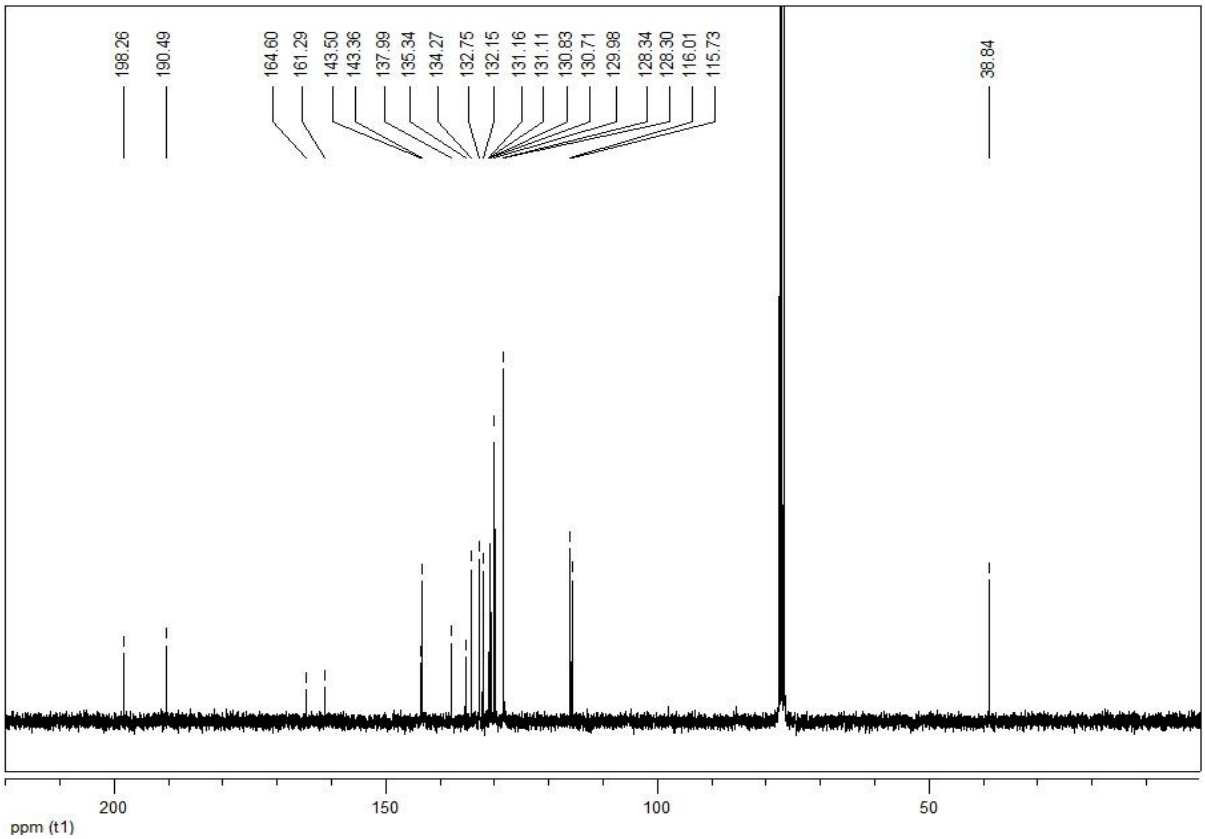
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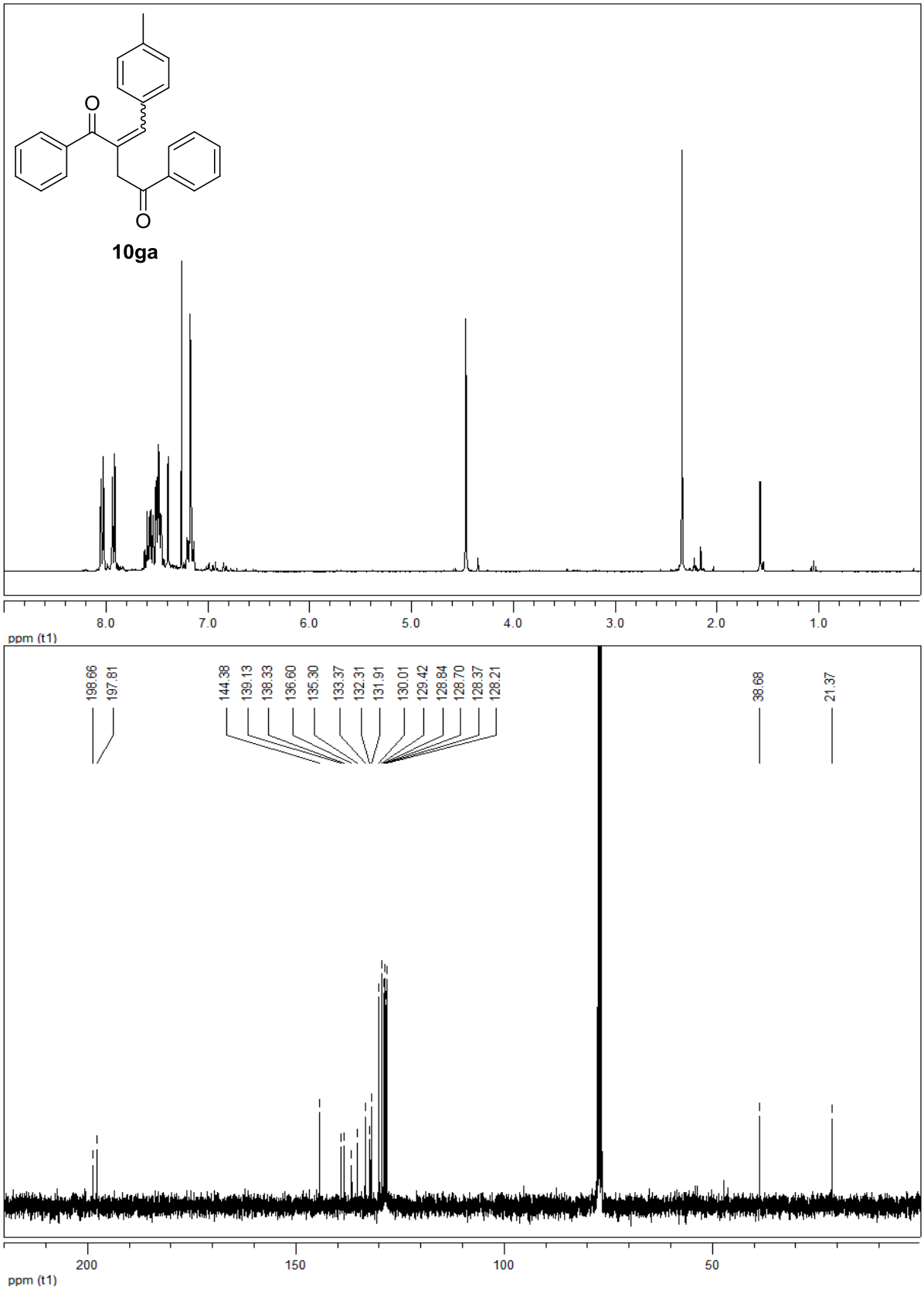
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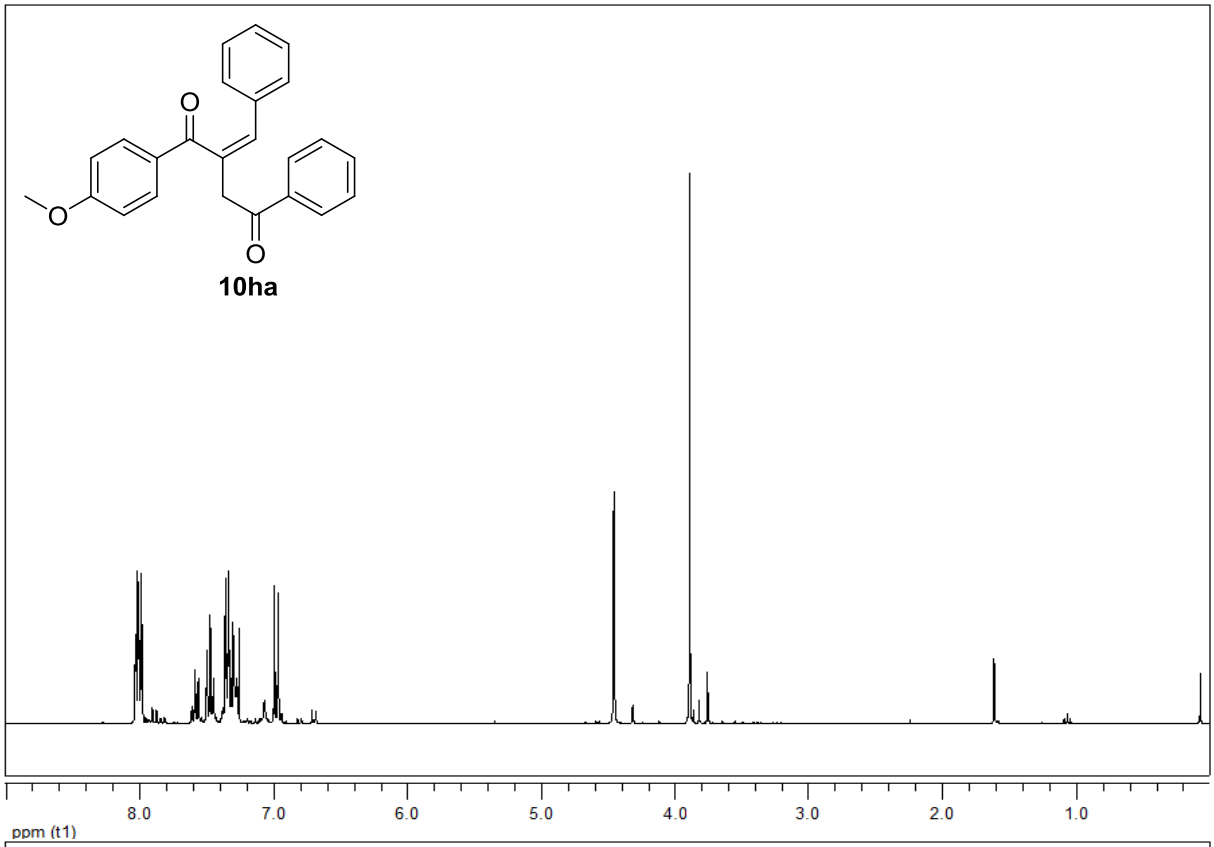
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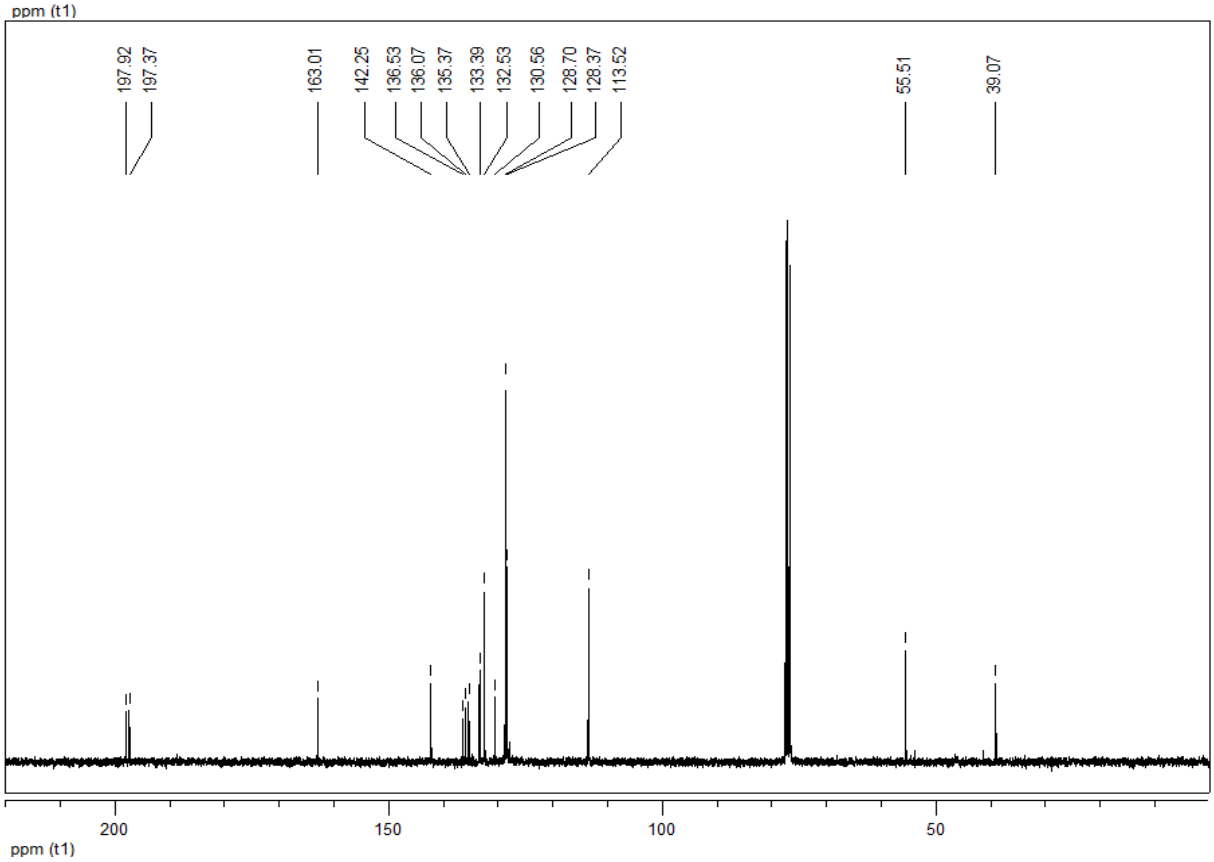
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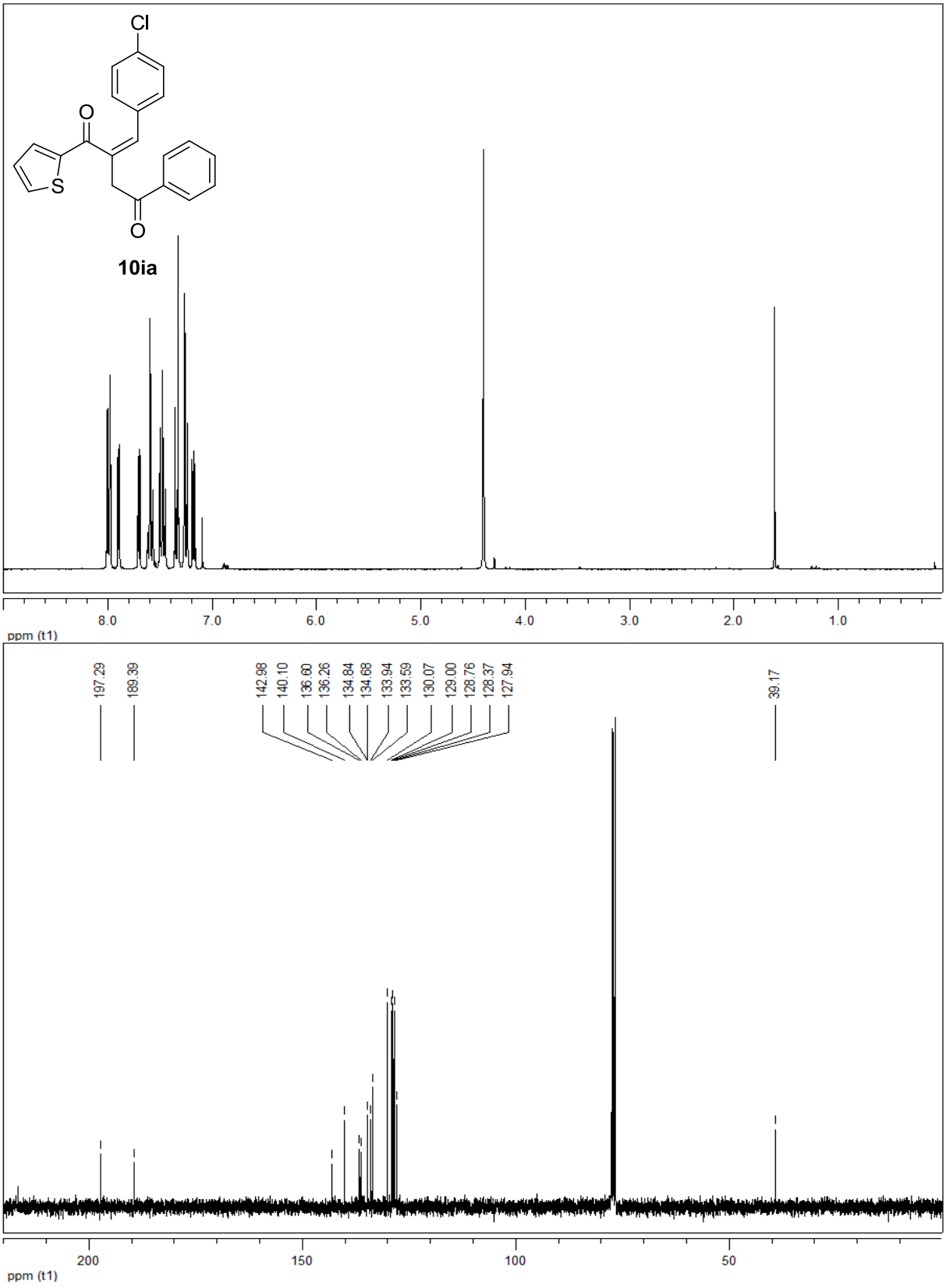
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10. (a) Pham, P. V.; Nagib, D. A.; MacMillan, D. W. C. *Angew. Chem. Int. Ed*. **2011**, *50*, 6119. (b) Paria, S.; Pirtsch, M.; Kais, V.; Reiser, O. *Synthesis* **2013**, *19*, 2689.

8. Summary

This Ph.D thesis demonstrates the developement of new methodologies for C-C bond formation triggered by visible light photoredox catalysis.

In Chapter 1, we have outlined a short overview on Copper in Photocatalysis. Starting from the photophysical properties of copper complexes, a comparison of main excited state aspects of prevalently used ruthenium and iridium complexes with that of copper has been shown. Several UV and visible light mediated synthetic transformation utilizing copper catalysts has been described.

In Chapter 3, allylation of α-halo carbonyl compounds has been described employing allyl tributyltin and $[Cu(dap)_2Cl]$ as visible light photoredox catalyst. Utilizing a very low catalyst loading, mono allylation of α-halo ketones and di-allylation of α, α-dibromo and α, α-dichloroketoneshas has been achieved.

In Chapter 4, we describe the atom transfer radical addition (ATRA) of electron deficient benzyl halides to styrenes and silyl enol ethers utilizing $[Cu(dap)_2Cl]$ as photocatalyst. To further emphasize on the utility of this methodology, products derived from ATRA of 2-nitrobenzyl bromide to different styrenes successfully converted to biologically important tetrahydroquinolines.

In Chapter5, a visible light phototoredox catalyzed methodology for vinyl radical generation from α-bromochalcone and cinnamates utilizing an iridium based photocatalyst has been described. The vinyl radicals were efficiently engaged in cascade cyclization with different heteroarenes like furan, benzofuran, pyrrole and indole for the synthesis of novel polycyclic frameworks in excellent yields. A single electron transfer from photocatalyst to substrate has been proposed. Presence of vinyl radical in reaction medium was corroborated by additional experiments.

In Chapter 6, we have described a vinyl radical annulation sequence to olefins for the synthesis of 3,4-dihydronaphthalenes. A wide range of terminal alkenes with different functional groups were efficiently converted to dihydronaphthalenes. A plausible reaction mechanism based on oxidative quenching of photocatalyst was proposed. Radical trapping experiments with TEMPO

supported the vinyl radical mechanism. To demonstrate further the application of the methodology, some of the dihydronaphthalenes were efficiently converted to naphthalenes.

In Chapter 7, we have described an efficient method for the α-vinylation of ketones. Vinyl radicals, generated by an iridium catalyst from α-bromochalcones under visible light irradiation, were coupled with enol acetates to furnish 1,4-diketones. Aromatic, aliphatic and alicyclic enol acetates were suitable partners for this coupling reaction. A reaction mechanism is proposed involving a photo induced electron transfer from the excited photocatalyst to α-bromochalcones forming vinyl radicals.

9. Zusammenfassung

Diese Dissertation befasste sich mit der Entwicklung neuartiger Methodiken für die Knüpfung von C-C Bindungen ausgelöst durch Photoredoxkatalyse im sichtbaren Licht.

In Kapitel 1 wurde ein kurzer Überblick über die bisherige Verwendung von Kupfer in der Photokatalyse gegeben. Ausgehend von den photophysikalischen Eigenschaften verschiedener Kupferkomplexe wurde ein Vergleich mit den angeregten Zuständen bevorzugt genutzter Ruthenium- und Iridium- basierter Katalysatoren angestellt. Es wurden verschiedene, bereits bekannte, synthetische Anwendungen von Kupfer-basierten Photokatalysatoren sowohl im UV-Bereich als auch im sichtbaren Bereich des Spektrums beschrieben.

Im zweiten Kapitel wurden die genaue Themenstellung und die Ziele dieser Arbeit skizziert.

In Kapitel 3 wurde die Allylierung von α-Halogen Carbonylverbindungen unter Verwendung von Allytributylzinn und $[Cu(dap)_2Cl]$ als Photoredoxkatalysator für sichtbares Licht beschrieben. Mit sehr kleinen Katalysatormengen konnten α-Halogen Ketone erfolgreich einfach allyliert, und α, α-Dibrom als auch α, α-Dichlorketone zweifach allyliert werden.

Atom Transfer Radical Addition (ATRA) Reaktionen von elektronenarmen Benzylhalogeniden an Styrole und Silylenolether mit Hilfe von $[Cu(dap)_2Cl]$ wurden in Kapitel 4 beschrieben. Um den Nutzen dieser Methode zu demonstrieren wurde gezeigt, dass mehrere Produkte der ATRA Reaktionen zu biologisch wichtigen Tetrahydroquinolinen weiter umgesetzt werden konnten.

In Kapitel 5 wurde eine Methode für die Erzeugung von Vinylradiakalen aus α-Bromchalkonen und Cinnamaten mittels eines Iridium-basierten Photokatalysators beschrieben. Diese Radikale wurden effektiv in einer Kaskadenzyklisierung mit unterschiedlichen Heteroaromaten wie Furan, Benzofuran, Pyrrol und Indol zur Synthese neuartiger polyzyklischer Verbindungen in hervorragenden Ausbeuten genutzt. Als wichtiger Schritt im Reaktionsmechanismus wurde ein Ein-Elektronen-Übertrag vom Photokatalysator auf das Substrat postuliert. Die Präsenz der dabei intermediär auftretenden Vinylradikale konnte durch zusätzliche Versuche experimentell gesichert werden.

Ausgehend von Vinylradikalen wurde in Kapitel 6 eine Annelierung an Alkene zur Synthese von 3,4-Dihydronaphthalinen entwickelt. Eine große Bandbreite terminaler Alkene mit unterschiedlichen funktionellen Gruppen konnte erfolgreich verwendet werden. Ein Mechanismus basierend auf oxidativem Quenching des Photokatalysators wurde vorgeschlagen. Radikalabfangreaktionen mit TEMPO untermauern das Auftreten von Vinylradikalspezies. Der synthetische Nutzen der Methode konnte durch effektive Weiterumsetzung einiger der erhaltenen Dihydronaphthalinen zu Naphthalinen gezeigt werden.

Im Kapitel 7 wurde abschließend eine effiziente Methode für die α-Vinylierung von Ketonen erforscht. Vinylradikale, die durch einen Iridiumkatalysator aus α-Bromchalkonen unter Bestrahlung mit sichtbarem Licht erzeugt wurden, konnten mit Enolacetaten zu 1,4-Diketonen gekoppelt werden. Sowohl aromatische als auch aliphatische und alizyklische Enolacetate waren als Kopplungspartner geeignet. Ein Reaktionsmechanismus in dem ausgehend von einem Ein-Elektronen-Übertrag des angeregten Photokatalysators auf α-Bromchalkone Vinylradikale erzeugt werden wurde postuliert.

10. Abbreviations

AIBN	azobisisobutyronitrile
Ar	aryl
Boc	*tert*-butyloxycarbonyl
$CDCl_3$	deuterated chloroform
DCM	dichloromethane
CFL	compact fluorescent lamp
DIPEA	N,N-diisopropylethylamine
DMF	dimethyl formamide
ee	enantiomeric excess
EE	ethylacetate
EI	electron impact (MS)
equiv	equivalents
ESI	electronspray ionization (MS)
EtOH	ethanol
Et	ethyl
eV	electron volts
h	hour (s)
HRMS	high resolution mass spectrometry
^{i}Pr	*iso*-propyl
IR	infrared spectroscopy
ISC	inter system crossing
M	metal
MCR	multicomponent reaction
Me	methyl
MeCN	acetonitrile
MHz	mega hertz
min	minutes
mL	milliliter
MLCT	metal to ligand charge transfer
mmol	millimole
mol%	mole percent
Mp	melting point
Na_2SO_4	sodium sulfate
^{n}Bu	*n*-butyl
nm	nanometer
NMR	nuclear magnetic resonance
Nu	nucleophile
^{n}Pr	*n*-propyl
o-	*ortho*-
OAc	acetate
OTf	triflate
p-	*para*
PE	petroleum ether
Ph	phenyl
rt	room temperature
SCE	saturated calomel electrode
SET	single electron transfer
^{t}Bu	*tert-butyl*
TEMPO	(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
Ts	tosyl
UV	ultraviolet
V	volt
W	watt
X	arbitrary anion

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I will miss University of Regensburg, but it was a wonderful experience as a graduate student during my M.Sc days in Indian Institute of Technology, Madras (IIT-M), India as well. I deeply acknowledge Prof. Dr. S. Sankararaman, Department of Organic Chemistry (IITM) for giving me an opportunity to carry out my first research career in his laboratory during my M.Sc study.

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Master of Science (M.Sc.) in Chemistry, 07/2007–05/ 2009
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Bachelor of Science (B.Sc.) in Chemistry Honours, 07/2004 – 06/2007
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1. Fellowship for pursuing Ph.D. from GRK 1626 (Chemical Photocatalysis) – **2010-2013**.

2. Scholarship from the Gesellschaft Deutscher Chemiker (GDCh) to attend ORCHEM **2012**, Weimar, Germany.

3. Qualified Graduate Aptitude Test in Engineering (GATE, **2009**), with 98 percentile (for Ph.D. in India).

4. Qualified CSIR-NET Examination (for Ph.D. in India) and awarded Junior research Fellowship – **2008**.

5. Institute Merit Scholarship for outstanding academic performance throughout all four semesters, Indian Institute of Technology Madras, 2007-2009.

6. Ranked 128th in the all India Joint Admission Test for M.Sc Examination f conducted by Indian Institute of Technology (2007)

List of Publications

1. M. Pirtsch, **S. Paria,** T. Matsuno, H. Isobe, O. Reiser, "$Cu(dap)_2Cl$ as efficient visible light driven photoredox catalyst in carbon carbon bond forming reactions" *Chem. Eur. J.* **2012**, *18*, 7336.

2. **S. Paria,** M. Pirtsch, V. Kais, O. Reiser, "Visible light induced intermolecular atom-transfer radical addition of benzyl halides to olefins: facile synthesis of tetrahydroquinolines" *Synthesis* **2013**, *19*, 2689.

3. **S. Paria**, O. Reiser, "Visible light photoredox catalyzed cascade cyclizations of α-bromochalcones or -cinnamates with heteroarenes" *Adv. Syn. Cat*. **2014**, *356*, 557.

4. Contribution to book chapter: "Homogeneous visible light-mediated transition metal photoredox catalysis other than ruthenium and iridium" in "**Chemical Photocatalysis**", Burkhard König (ed.), *De Gruyter*. **2013**.

5. **S. Paria**, O. Reiser, "Visible light mediated tandem cyclization of vinyl radicals with olefins - synthesis of di-hydronapthalenes" **2014** (manuscript under preparation).

Conferences and Presentations

1. **Suva Paria**, Michael Pirtsch and Prof. Dr. Oliver Reiser: Visible Light Driven Atom Transfer Radical Addition of Benzyl halides to Styrenes (**Poster Presentation**) – ORCHEM **2012**, Weimar, Germany.

2. **Suva Paria** and Prof. Dr. Oliver Reiser: Visible Light Mediated Tandem Cyclization of Vinyl Radical to Heteroarenes (**Poster Presentation**) – 7th Heidelberg Forum on Molecular Catalysis **2013**, Heidelberg, Germany.

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