Electronic Supplementary Information

Synthesis of a Carborane-substituted Bis(phosphanido) Cobaltate(I), Ligand Substitution, and Unusual P_4 Fragmentation

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Oxidative addition of the P–P single bond of an *ortho*-carborane-derived 1,2-diphosphetane (1,2-$C_2(PMes)_2B_{10}H_{10}$) (Mes = 2,4,6-$Me_3C_6H_2$) to cobalt(-I) and nickel(0) sources affords the first heteroleptic complexes of a carborane-bridged bis(phosphanido) ligand. The complexes also incorporate labile ligands suitable for further functionalisation. Thus, the cobalt complex [K([18]crown-6)][Co{1,2-$(PMes)_2C_2B_{10}H_{10}$}(cod)] (cod = 1,5-cyclooctadiene) bearing a labile cyclooctadiene ligand undergoes facile ligand exchange reactions with isonitriles and *tert*-butyl phosphaalkyne with retention of the bis(phosphanido) ligand. However, in the reaction with one equivalent of P_4, the electron-rich bis(phosphanido) moiety abstracts a single phosphorus atom with formation of a new P_3 chain, while the remaining three P atoms derived from P_4 form an η^3-coordinating *cyclo*-P_3 ligand. In contrast, when the same reaction is performed with two equivalents of the cobalt(I) complex, a dinuclear product is formed which features an unusual P_4 chain in its molecular structure.

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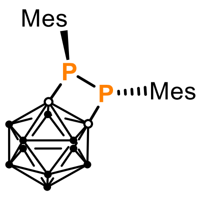
1. Experimental Section

General Methods. All reactions and manipulations were carried out under an argon atmosphere using standard Schlenk and glovebox techniques unless stated otherwise. Solvents were either obtained from an MBraun Solvent Purification System, or dried and stored according to common procedures.[1] *Tert*-butyl phosphaalkyne,[2] $[K(thf)_{0.2}][Co(\eta^4\text{-cod})_2)]$,[3] KC_8[4] and $[Ni(IMes)(\eta^2\text{-}H_2C{=}CHSiMe_3)_2]$[5] were synthesised according to literature procedures. The synthesis of dibromo(mesityl)phosphane was adapted from a protocol for the synthesis of dichloro(mesityl)phosphane by using PBr_3 instead of PCl_3 as the phosphorus source.[6] All other compounds are commercially available. NMR spectra were recorded with a Bruker AVANCE DRX 400 MHz NMR spectrometer at room temperature unless stated otherwise. All isolated compounds were measured in deuterated tetrahdrofuran except for *rac*-**5**, which was measured in C_6D_6. Tetramethylsilane was used as internal standard for ^{1}H and ^{13}C{^{1}H} NMR spectra. 85% H_3PO_4 was used as external standard for ^{31}P{^{1}H} NMR spectra and $BF_3{\cdot}OEt_2$ was used as external standard for ^{11}B{^{1}H} NMR spectra. NMR spectra were recorded at the following frequencies: ^{1}H: 400.13 MHz, ^{13}C: 100.63 MHz, ^{11}B: 128.38 MHz, ^{31}P: 161.99 MHz. The solid-state ^{31}P NMR spectroscopic measurements were performed on an Infinity$_{plus}$ spectrometer system (Agilent) operated at 7 Tesla, equipped with a variable-temperature Chemagnetics-Varian 6 mm pencil CPMAS probe. ^{31}P{^{1}H} CP NMR spectra were recorded with a cross polarisation time of 4 ms, a 90°-pulse length of 4.0 µs, and a repetition time of 20 s. Magic angle spinning (MAS) rates of 5750 Hz and 5010 Hz were used. The spectrum was indirectly referenced to H_3PO_4 (85% in H_2O). The numerical NMR parameters have been extracted from the experimentally obtained spectrum using the WSolids1 program package.[7] UV-vis spectra were recorded on a Varian Cary 50 spectrometer. Elemental analyses were determined by the analytical department of Regensburg University.

Single crystal X-ray diffraction. The single-crystal X-ray diffraction data were recorded on Agilent Technologies SuperNova and GV1000, TitanS2 diffractometers with Cu-K_α radiation (λ = 1.54184 Å) except for [K(18-c-6)(dme)$_2$]**8**, where Cu-K_β radiation (λ = 1.39225 Å) was used. Semiempirical multi-scan absorption corrections were applied to the data. The structures were solved with SHELXS[8] and least-square refinements on F^2 were carried out with SHELXL.[8] The hydrogen atoms were located in idealised positions and refined isotropically with a riding model. Crystallographic data for has been deposited at the CCDC under 2086046 ([K(dme)$_4$][*rac*-**1**], 2086047 (*rac*-**2**), 2086048 ([K(18-c-6)(dme)][*rac*-**6**]), 2086049 ([K(dme)**4**][*rac*-**7**]), 2086050 [K(18-c-6)(dme)**2**][*meso*-**8**] and 2086051 ([K(dme)][K(dme)$_2$][*rac*-**9**]) and can be obtained from https://www.ccdc.cam.ac.uk/structures/. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

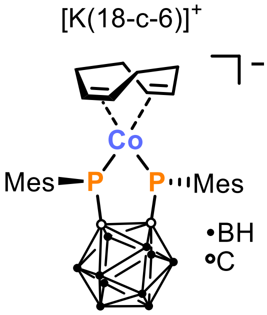
Synthesis of *rac*-1,2-(PMes)$_2$C$_2$B$_{10}$H$_{10}$ (*rac*-5). At 0°C, *n*BuLi (14 mL of a 1.56 M solution in hexanes, 21.8 mmol, 2.02 equiv.) was added slowly to a solution of *ortho*-carborane **3** (1.56 g, 10.8 mmol, 1.00 equiv.) in diethyl ether (30 mL). The mixture was stirred at 0°C for 0.5 h and then for 2 h at room temperature. The resulting suspension was added to a solution of MesPBr$_2$ (6.62 g, 21.6 mmol, 2.00 equiv.) in diethyl ether (40 mL) over a period of 2 h. The mixture was then stirred for a further 17 h. Afterwards, the solvent was replaced with toluene and LiBr was removed *via* filtration over celite. Volatiles were removed from the filtrate to afford a red oil. After washing of the oil with acetonitrile (3 x 5 mL), crude bis(phosphane) **4** (3 g of a mixture of the *rac* and *meso* isomer) was obtained as a



rac-**5**

yellow solid. Afterwards, 4 and KC_8 (1.347 g, 9.96 mmol, 2.00 eq) were suspended in diethyl ether (15 mL) and stirred for 21 d. Subsequent work-up of the reaction mixture was performed under air. The solvent was replaced with toluene (40 mL) and KBr was removed *via* filtration over silica. Volatiles were removed from the filtrate under reduced pressure to afford crude diphosphetane *rac*-**5** as a yellow solid. Recrystallisation of the crude product by layering a saturated toluene solution with acetonitrile afforded pure *rac*-**5** (1.56 g, 33% starting from **3**) as colourless crystals. $C_{20}H_{32}B_{10}P_2$, calculated (%): C 54.28, H 7.29; found (%): C 54.59, H 7.35. ^{1}H NMR: δ = 1.90 – 3.60 (m, 10H, BH), 2.04 (s, 6H, *para*-CH_3), 2.37 – 2.39 (m, 12H, *ortho*-CH_3), 6.63 (s, 4H, mesityl-CH) ppm. ^{13}C{^{1}H} NMR: δ = 20.5 (s, *para*-CH_3), 24.3 (s, *ortho*-CH_3), 73.6 – 74.1 (m, $C_2B_{10}H_{10}$), 129.2 – 129.6 (m, *ipso*-C), 130.1 (s, mesityl-CH), 139.7 (s, *para*-C), 140.2 (bs, *ortho*-C) ppm. ^{11}B{^{1}H} NMR: δ = −10.9 (bs), −8.3 (bs), −7.2 (bs), −2.3 (bs) ppm. ^{31}P{^{1}H} NMR: δ = 38.7 (s) ppm.

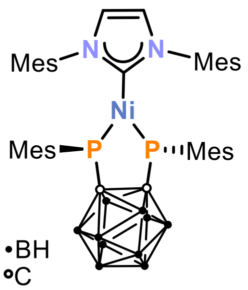
Synthesis of [K(18-c-6)][Co(cod){$B_{10}H_{10}C_2(PMes)_2$}] ([K(18-c-6)(thf)][*rac*-1]).



[K(18-6)][*rac*-**1**]

Diphosphetane *rac*-**5** (120 mg, 0.27 mmol, 1.00 equiv.) and [K(thf)$_{0.2}$][Co(η^4-cod)$_2$)] (90 mg, 0.27 mmol, 1.00 eq) were suspended in a mixture of diethyl ether and *n*-hexane (2 mL/5 mL). After 24 h of stirring, 18-c-6 (75 mg, 0.27 mmol, 1.00 eq) was added to the suspension and stirring was continued for an additional 24 h. Then, volatiles were removed *in vacuo* and the residue was recrystallised from THF/*n*-hexane to afford [K(18-c-6)(thf)][*rac*-**1**] (180 mg, 67%) as orange crystals. A solution of [K(dme)$_4$)][*rac*-**1**] in DME with sufficient purity for further experiments can be obtained when, instead of adding 18-c-6 to the initial reaction mixture, volatiles are instead removed *in vacuo* and the residue is dissolved in DME. Crystals of [K(dme)$_4$)][*rac*-**1**] suitable for single crystal X-ray diffraction were obtained by layering such a solution of [K(dme)$_4$][*rac*-**1**] in DME with *n*-hexane. $C_{44}H_{76}B_{10}CoKO_7P_2$, calculated (%): C 53.64, H 7.78; found (%): C 53.41, H 7.71. ^{1}H NMR: δ = 1.18 – 1.26 (m, 4H, cod-CH_2), 2.19 (s, 6H, *para*-CH_3), 2.25 – 2.32 (m, 4H, cod-CH_2), 2.56 (s, 12H, *ortho*-CH_3), 2.93 (bs, 4H, cod-CH), 3.58 (s, 24H, 18-c-6), 6.78 (s, 4H, mesityl-CH) ppm.) ^{13}C{^{1}H} NMR: δ = 21.2 (s, *para*-CH_3), 26.3 (s, *ortho*-CH_3), 32.3 (s, cod-CH_2), 70.4 (s, cod-CH_2), 71.1 (s, 18-c-6), 91.5 – 92.0 (m, $C_2B_{10}H_{10}$), 128.4 (s, mesityl-CH), 136.3 (s, *para*-C), 141.1 – 141.4 (m, *ipso*-C), 145.2 – 145.3 (m, *ortho*-C) ppm. ^{11}B{^{1}H} NMR: δ = −9.4 (bs), −7.9 (bs) ppm. ^{31}P{^{1}H} NMR: δ = 101.3 (bs) ppm. UV-vis: λ_{max} = 337 nm (ε = 13300 L·mol^{-1}·cm^{-1}), 435 nm (ε = 6150 L·mol^{-1}·cm^{-1}), 768 nm (ε = 1880 L·mol^{-1}·cm^{-1}).

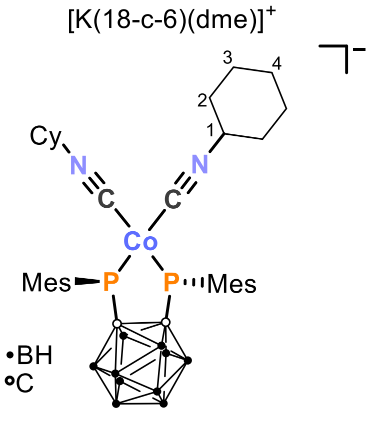
Synthesis of [Ni(IMes){$B_{10}H_{10}C_2(PMes)_2$}] (*rac*-2). A solution of [Ni(IMes)(η^2-H_2C=CHSiMe_3)$_2$] (60 mg, 0.106 mmol, 1.04 equiv.) in *n*-hexane was added dropwise to an *n*-hexane solution of diphosphetane *rac*-**5** (45 mg, 0.102 mmol, 1.00 equiv.) and the mixture was stirred for 24 h. Afterwards, the resulting suspension was filtered and the residue was washed with *n*-hexane (3 x 2 mL). After drying the residue in vacuo, *rac*-**2** was obtained as a dark purple solid (60 mg, 74% yield). Crystals suitable for single crystal X-ray diffraction were obtained by dissolving both reactants in toluene and letting the resulting solution stand at room temperature for 24 h. Elemental analysis: $C_{40}H_{56}B_{10}N_2NiP_2$, calculated (%): C 61.12, H 7.01, N 3.48; found (%): C 61.55, H 6.80, N 3.20. ^{31}P{^{1}H} (CP-MAS, solid state): δ_{11} = 424 ppm; δ_{22} = 33 ppm; δ_{33} = −67 ppm; δ_{iso} = 130 ppm. UV-vis: λ_{max} = 271 nm (ε = 8790



rac-**2**

L·mol^{-1}·cm^{-1}), 340 nm (ε = 9720 L·mol^{-1}·cm^{-1}), 424 nm (ε = 1670 L·mol^{-1}·cm^{-1}), 527 nm (ε = 1860 L·mol^{-1}·cm^{-1}), 898 nm (ε = 680 L·mol^{-1}·cm^{-1}).

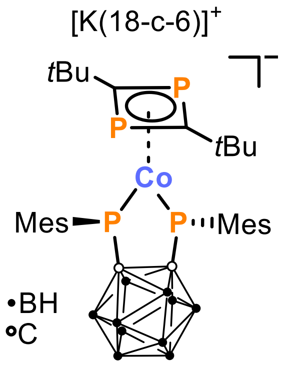
Synthesis of [K(18-c-6)(dme)][Co($C_6H_{11}NC)_2${$B_{10}H_{10}C_2$(PMes)$_2$}] ([K(18-c-6)(dme)][*rac*-6]



[K(18-c-6)(dme)][rac-**6**]

Cyclohexyl isonitrile (25 µL, 0.20 mmol, 2.00 eq) was added to a solution of [K(18-c-6)(thf)][*rac*-**1**] (100 mg, 0.10 mmol, 1.00 eq) in THF (5 mL). After 15 h of stirring, the mixture was filtered and volatiles were removed *in vacuo*. The residue was dissolved in DME and the resulting solution was layered with *n*-hexane. After 3 d, [K(18-c-6)(dme)][*rac*-**6**] was obtained as red crystals suitable for single-crystal X-ray diffraction studies. Drying of the crystals *in vacuo* resulted in partial removal of dme molecules, affording [K(18-c-6)(dme)$_{0.8}$][*rac*-**6**] (60 mg, 55%) according to ^{1}H NMR spectroscopy and elemental analysis. $C_{46}H_{78}B_{10}CoKN_2O_6P_2$·$(C_4H_{10}O_2)_{0.8}$, calculated (%): C 53.99, H 7.71, N 2.72; found (%): C 54.32, H 7.72, N 2.40. ^{1}H NMR: δ = 0.96 – 1.14 (m, 10H, H^{2,3,4}), 1.20 – 1.30 (m, 2H, H^4), 1.31 – 1.40 (m, 4H, H^2), 1.42 – 1.52 (m, 4H, H^3), 2.17 (s, 6H, *para*-CH_3), 2.87 (s, 12H, *ortho*-CH_3), 2.92 – 2.98 (m, 2H, 1), 3.27 (s, 4.8H, dme-CH_3), 3.43 (s, 3.6H, dme-CH_2). 3.64 (s, 24H, 18-c-6), 6.77 (s, 4H, mesityl-CH) ppm.) ^{13}C{^{1}H} NMR: δ = 21.1 (s, *para*-CH_3), 24.1 (s, C^3), 26.3 (s, C^4), 27.9 (s, *ortho*-CH_3), 34.0 (s, C^2), 53.7 (s, C^1), 58.8 (s, dme-CH_3), 71.1 (s, 18-c-6), 72.7 (s, dme-CH_2), 97.1 – 98.8 (m, $C_2B_{10}H_{10}$), 128.2 (s, mesityl-CH), 135.5 (s, *para*-C), 142.8 – 143.8 (m, *ipso*-C), 145.3 (m, *ortho*-C) ppm. ^{11}B{^{1}H} NMR: δ = −9.0 (bs), −6.7 (bs) ppm. ^{31}P{^{1}H} NMR: δ = 103.3 (bs) ppm. UV-vis: λ_{max} = 277 nm (ε = 11640 L·mol^{-1}·cm^{-1}), 342 nm (ε = 8580 L·mol^{-1}·cm^{-1}), 490 nm (ε = 3430 L·mol^{-1}·cm^{-1}), 655 nm (ε = 740 L·mol^{-1}·cm^{-1}).

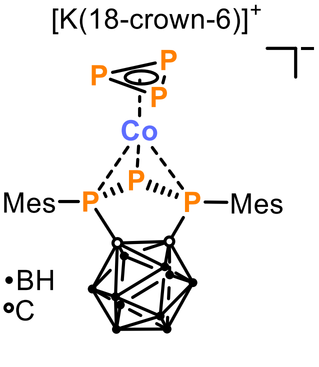
Synthesis of [K(18-c-6)][Co(*t*Bu-C_2P_2){B_{10}H10C_2(PMes)$_2$}] ([K(18-c-6)][*rac*-7]). A solution of *tert*-butyl phosphaalkyne in *n*-hexane (0.30 mL, 2.6 M, 6.00 equiv.) was added to a solution of [K(18-c-6)(thf)][*rac*-**1**] (130 mg, 0.13 mmol, 1.00 equiv.) in THF (5 mL). After stirring for 15 h, volatiles were removed *in vacuo*. The residue was washed with a mixture of diethyl ether and *n*-hexane (1:4 v/v, 3 x 3 mL) to afford [K(18-c-6)][*rac*-**7**] (87 mg, 65%) as a red solid. Crystals of [K(dme)$_4$)][*rac*-**7**] suitable for single crystal X-ray diffraction were obtained by adding the *tert*-butyl phosphaalkyne solution to a solution of [K(dme)$_4$][*rac*-**1**] in DME and layering the mixture with *n*-hexane after 15 h of stirring. $C_{42}H_{74}B_{10}CoKO_6P_4$, calculated (%): C 50.19, H 7.42; found (%): C 50.28, H 6.99. ^{1}H NMR: δ = 0.84 (s, 18H, *t*Bu-CH_3), 2.25 (s, 6H, *para*-CH_3), 2.84 (s, 12H, *ortho*-CH_3), 3.59 (s, 24H, 18-c-6), 6.86 (s, 4H, mesityl-CH) ppm.)



[K(18-c-6)][*rac*-**7**]

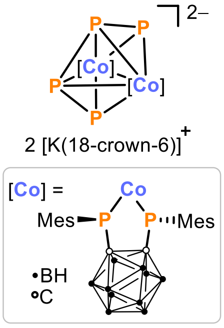
^{13}C{^{1}H} NMR: δ = 21.3 (s, *para*-CH_3), 27.3 (s, *ortho*-CH_3), 30.8 (s, *t*Bu-CH_3), 35.3 (s, *t*Bu-*C*(CH_3)), 71.1 (s, 18-c-6), 93.7 – 94.5 (m, $C_2B_{10}H_{10}$), 99.1 – 100.5 (m, *t*$Bu_2C_2P_2$), 128.7 (s, mesityl-CH), 137.1 (s, *para*-C), 141.9 – 142.1 (m, *ipso*-C), 145.1 (s, *ortho*-C) ppm. ^{11}B{^{1}H} NMR: δ = −9.7 to −7.7 (m) ppm. ^{31}P{^{1}H} NMR: δ = 15.3 (t, $^2J_{PP}$ = 14 Hz, *t*$Bu_2C_2P_2$), 104.1 (bs) ppm. UV-vis: λ_{max} = 354 nm (ε = 11450 L·mol^{-1}·cm^{-1}), 404 nm (ε = 6250 L·mol^{-1}·cm^{-1}), 513 nm (ε = 4290 L·mol^{-1}·cm^{-1}), 810 nm (ε = 2290 L·mol^{-1}·cm^{-1}).

Synthesis of [K(18-c-6)][Co(*cyclo*-P_3){$B_{10}H_{10}C_2(P_3Mes_2)$}] ([K(18-c-6)][*meso*-8]). A solution of white phosphorus in benzene (0.44 mL, 0.19 M, 1.00 equiv.) was added to a solution of [K(18-c-6)(thf)][*rac*-**1**] (87 mg, 0.088 mmol, 1.05 equiv.) in THF (5 mL). After stirring for 25 h, volatiles were removed *in vacuo*. The residue was dissolved in THF/toluene (4 mL/1 mL) and the resulting solution was layered with *n*-hexane (3 mL). After 3 d, [K(18-c-6)][*meso*-**8**] (45 mg, 49%) was obtained as yellow crystals. The final product contained ca. 8% of [K(18-c-6)]$_2$[*rac*-**9**] as indicated by ^{1}H NMR spectroscopy and elemental analysis. Crystals of [K(18-c-6)(dme)$_2$][*meso*-**8**] suitable for single crystal X-ray diffraction were obtained by dissolving [K(18-c-6)][*meso*-**8**] in a 2:1 mixture of DME/toluene and layering the resulting solution with *n*-hexane. $C_{32}H_{56}B_{10}CoKO_6P_6$, calculated (%): C 41.38, H 6.08; found (%): C 42.0, H 5.95. ^{1}H NMR: δ = 2.24 (s, 6H, *para*-CH_3), 2.80 (s, 6H, *ortho*-CH_3), 2.82 (s, 6H, *ortho*-CH_3), 3.59 (s, 24H, 18-c-6), 6.83 (s, 2H, mesityl-CH), 6.87 (d, 2H, $^4J_{PP}$ = 5 Hz, mesityl-CH) ppm. ^{13}C{^{1}H} NMR: δ = 20.3 (s, *para*-CH_3), 25.4 (s, *ortho*-CH_3), 70.0 (s, 18-c-6), 73.2 – 74.2 (m, $C_2B_{10}H_{10}$), 124.6 – 124.9 (m, *ipso*-C), 128.3 (s, mesityl-CH), 129.2 (d, $^3J_{CP}$ = 10 Hz, mesityl-CH), 140.0 (s, *para*-C), 142.3 (s, *ortho*-C), 146.2 (d, $^2J_{PP}$ = 27 Hz, *ortho*-C) ppm. ^{11}B{^{1}H} NMR: δ = −12.5 (bs, 4B), −8.6 (bs, 2B), −2.3 (bs, 4B) ppm. ^{31}P{^{1}H} NMR: δ = −250.9 (s, *cyclo*-P_3), −250.8 (t, $^1J_{PP}$ = 330 Hz, $C_2(PMes)_2$*P*), 30.0 (d, $^1J_{PP}$ = 330 Hz, C_2(*PMes*)$_2$P) ppm. UV-vis: λ_{max} = 287 nm (ε = 16280 L·mol^{-1}·cm^{-1}), 337 nm (ε = 18340 L·mol^{-1}·cm^{-1}), 398 nm (ε = 6760 L·mol^{-1}·cm^{-1}).



[K(18-crown-6)]**8**

Synthesis of [K(18-c-6]$_2$[{$B_{10}H_{10}C_2(P_2Mes_2)$Co}$_2$(μ-η^4:η^4-$P_4$)] ([K(18-c-6]$_2$[*rac*-9]) A solution of white phosphorus in benzene (0.8 mL, 0.19 M, 0.56 equiv.) was added to a solution of K[*rac*-**1**] in THF (3 mL, 0.09 M, 1.00 equiv.). After stirring for 12 d, 18-c-6 (75 mg, 0.27 mmol, 1.00 equiv.) was added to the reaction mixture. After stirring for additional 15 h, 7 mL of *n*-hexane were added to precipitate the product. After stirring for another 15 h, the mixture was filtered and the residue was washed with diethyl ether (8x3 mL) to afford [K(18-c-6)]$_2$[*rac*-**9**] (50 mg, 21%) as a purple solid. Crystals of [K(dme)$_3$]$_2$[*rac*-**9**] suitable for single crystal X-ray diffraction were obtained by stirring the reaction mixture for 12 d, removal of the solvent in vacuo and subsequent recrystallization of the resulting residue from DME/*n*-hexane. $C_{64}H_{112}B_{20}Co_2K_2O_{12}P_8$, calculated (%): C 44.34, H 6.51; found (%): C 44.30, H 6.38. ^{1}H NMR: δ = 2.14 (s, 6H, *para*-CH_3), 2.50 – 2.60 (m, 12H, *ortho*-CH_3), 3.62 (s, 24H, 18-c-6), 6.63 (s, 4H, mesityl-CH) ppm. ^{13}C{^{1}H} NMR: δ = 21.2 (s, *para*-CH_3), 26.3 (s, *ortho*-CH_3), 71.2 (s, 18-c-6), 128.6 (s, mesityl-CH), 136.1 (bs, *para*-C), 145.6 (bs, *ortho*-C) ppm. ^{11}B{^{1}H} NMR: δ = −7.1 (bs) ppm. ^{31}P{^{1}H} NMR (298 K): δ = −42.0 (bs, P4, P5), 58.0 (bs, PMes), 119.2 (bs, PMes), 223.1 (bs, P6), 423.6 (bs, P3) ppm (labels according to Figure 4). ^{31}P{^{1}H} NMR (233 K): δ = −49.1 (dd, $^1J_{PP}$ = 379 Hz, 217 Hz, P4), −42.3 (dd, $^1J_{PP}$ = 478 Hz, 217 Hz, P5), 55.0 – 56.2 (m, PMes), 117.8 (bs, PMes), 216.5 (d, $^1J_{PP}$ = 478 Hz, P6), 418.8 (d, $^1J_{PP}$ = 379 Hz, P3) ppm (labels according to Figure 4). UV-vis: λ_{max} = 357 nm (ε = 20140 L·mol^{-1}·cm^{-1}), 533 nm (ε = 14370 L·mol^{-1}·cm^{-1}).



[K(18-crown-6)]$_2$[**9**]

2. Computational Details

All calculations were carried out with the ORCA program package.[9,10] Unless stated otherwise, all calculations were carried out in the gas phase. Density fitting techniques, also called resolution-of-identity approximation (RI)[11], were used for *meta*-GGA calculations and the RIJCOSX[12] approximation was used for hybrid-GGA, DLPNO-CCSD(T) and CASSCF calculations. Atom-pairwise dispersion corrections with the Becke-Johnson damping (D3BJ)[13,14] were used for all DFT calculations. Orbital pictures were rendered with the software Chimaera.[15] All geometries were obtained at the TPSS-D3BJ/def2-TZVP[16,17] level of theory. For the formation of complex **8**$^{-}$, relaxed surface scans with subsequent geometry optimisations were carried out to find the relevant minima and saddle points. Subsequently, single point calculations at the DLPNO-CCSD(T)/cc-pVDZ and DLPNO-CCSD(T)/cc-pVTZ level of theory were conducted.[18,19] The DLPNO-CCSD(T) energies obtained with the two basis sets were used for an extrapolation of the energies to the basis-set limit following a standard extrapolation scheme. ^{31}P NMR chemical shifts of **9**$^{2-}$ were calculated with the TPSS0[20] functional using the def2-SVP, def2-TZVP and pcSseg-2[21] basis sets (see the Supporting Information). TDDFT calculations were performed at the ωB97X-D3/def2-TZVP CPCM(THF)[22] level of theory. EDA-NOCV calculations were performed at the ωB97X-D3/def2-QZVP[17,23] level of theory.

CASSCF calculations were performed using the def2-TZVP basis set. For [*rac*-**1**]$^{-}$, [*rac*-**6**]$^{-}$, [*rac*-**7**]$^{-}$ and [*meso*-**8**]$^{-}$, the initial guess orbitals (obtained from a DFT calculation) contained the five 3d orbitals of cobalt, and two ligand-based orbitals. In addition, three orbitals of the 4d sub-shell of cobalt (so called "double-shell") were included in the case of [*rac*-**1**]$^{-}$ and [*rac*-**6**]$^{-}$ to aid convergence. Thus, [*rac*-**1**]$^{-}$ and [*rac*-**6**]$^{-}$ are described with an active space of ten electrons in ten orbitals, whereas [*rac*-**7**]$^{-}$ and [*meso*-**8**]$^{-}$ are described with an active space of ten electrons in seven orbitals. In all cases, three 3d orbitals with occupation numbers close to 2.0 are found on the cobalt centres. Furthermore, two orbital pairs are obtained which describe the metal-ligand interactions (σ/π-donating and π-accepting) in every case. The metal-ligand bonding interactions are highly covalent in nature, making the assignment of an oxidation state of the cobalt centres somewhat ambiguous. However, TDDFT calculations and UV-vis spectroscopy support the assignment of a d^{8} configuration to the cobalt centre in [*rac*-**1**]$^{-}$, [*rac*-**6**]$^{-}$ and [*rac*-**7**]$^{-}$, since lowest-energy electron excitations in these anions correspond to MLCT transitions. If the configuration at the cobalt atoms would be closer to a d^{6} configuration, LMCT transitions would be expected to occur instead (see the main text for a detailed discussion of [*rac*-**7**]$^{-}$).

For nickel complex *rac*-**2**, the final active space consists of the five 3d orbitals of Ni, an orbital localised at the bisphosphanido moiety and four orbitals of the 4d shell of Ni. Here, four 3d orbitals on Ni with occupation numbers close to 2.0 are found allowing for an assignment of a d^{8} to the nickel centre.

Representative natural orbitals obtained from the CASSCF calculations are given further below.

3. Crystal structure tables

Crystal data and structure refinement for [K(dme)$_4$][*rac*-**1**]

Empirical formula	$C_{44}H_{84}B_{10}Co_1K_1O_8P_2$	
Formula weight	1009.17	
Temperature	123 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	*C*2	
Unit cell dimensions	a = 17.3818(5) Å	a= 90°.
	b = 12.4973(3) Å	b= 121.991(3)°.
	c = 15.0604(4) Å	g = 90°.
Volume	2774.66(15) Å^3	
Z	2	
Density (calculated)	1.208 Mg/m^3	
Absorption coefficient	3.995 mm^{-1}	
F(000)	1076	
Crystal size	0.3 x 0.15 x 0.05 mm^3	
Theta range for data collection	3.460 to 73.936°.	
Index ranges	-21<=h<=20, -15<=k<=15, -18<=l<=18	
Reflections collected	9514	
Independent reflections	5348 [R(int) = 0.0258]	
Completeness to theta = 73.936°	98.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.76256	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5348 / 1 / 307	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2σ(I)]	R_1 = 0.0354, wR_2 = 0.0917	
R indices (all data)	R_1 = 0.0361, wR_2 = 0.0925	
Absolute structure parameter	0.261(4)	
Largest diff. peak and hole	0.582 and -0.233 e·Å^{-3}	

Crystal data and structure refinement for *rac*-**2**

Empirical formula	$C_{41}H_{56}B_{10}N_2NiP_2$	
Formula weight	805.62	
Temperature	123 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	a = 17.5999(5) Å	α = 90°.
	b = 14.7143(4) Å	β = 104.342(3)°.
	c = 16.7284(5) Å	γ = 90°.
Volume	4197.1(2) Å^3	
Z	4	
Density (calculated)	1.275 Mg/m^3	
Absorption coefficient	1.620 mm^{-1}	
F(000)	1696	
Crystal size	0.35 x 0.2 x 0.2 mm^3	
Theta range for data collection	3.968 to 68.245°.	
Index ranges	-17<=h<=21, -14<=k<=17, -20<=l<=14	
Reflections collected	8371	
Independent reflections	3838 [R(int) = 0.0121]	
Completeness to theta = 68.245°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.92333	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3838 / 0 / 260	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2σ(I)]	R_1 = 0.0309, wR_2 = 0.0834	
R indices (all data)	R_1 = 0.0316, wR_2 = 0.0839	
Largest diff. peak and hole	0.267 and -0.263 e·Å^{-3}	

Crystal data and structure refinement for [K(18-c-6)(dme)][*rac*-**6**]

Empirical formula	$C_{50}H_{88}B_{10}CoKN_2O_8P_2$	
Formula weight	1113.29	
Temperature	123 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 20.6366(3) Å	α = 90°.
	b = 13.1049(2) Å	β = 90.4440(10)°.
	c = 21.8850(3) Å	γ = 90°.
Volume	5918.41(15) $Å^3$	
Z	4	
Density (calculated)	1.249 Mg/m^3	
Absorption coefficient	3.805 mm^{-1}	
F(000)	2368	
Crystal size	0.4 x 0.2 x 0.05 mm^3	
Theta range for data collection	2.932 to 89.548°.	
Index ranges	-19<=h<=26, -16<=k<=7, -26<=l<=28	
Reflections collected	27740	
Independent reflections	13400 [R(int) = 0.0249]	
Completeness to theta = 89.548°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.82770	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13400 / 7 / 784	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R_1 = 0.0388, wR_2 = 0.0992	
R indices (all data)	R_1 = 0.0490, wR_2 = 0.1080	
Largest diff. peak and hole	0.853 and -0.307 e·$Å^{-3}$	

Crystal data and structure refinement for $[K(dme)_4][rac\text{-}\mathbf{7}]$

Empirical formula	$C_{46}H_{90}B_{10}CoKO_8P_4$	
Formula weight	1101.18	
Temperature	123 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 10.5646(2) Å	α = 91.272(1)°.
	b = 16.0317(3) Å	β = 103.576(1)°.
	c = 18.5427(3) Å	γ = 93.528(1)°.
Volume	3044.84(10) $Å^3$	
Z	2	
Density (calculated)	1.201 Mg/m^3	
Absorption coefficient	4.162 mm^{-1}	
F(000)	1172	
Crystal size	0.35 x 0.1 x 0.1 mm^3	
Theta range for data collection	3.626 to 73.903°.	
Index ranges	-13<=h<=12, -18<=k<=19, -20<=l<=23	
Reflections collected	50649	
Independent reflections	12295 [R(int) = 0.0391]	
Completeness to theta = 73.903°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.60305	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12295 / 0 / 651	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2σ(I)]	R_1 = 0.0357, wR_2 = 0.0971	
R indices (all data)	R_1 = 0.0362, wR_2 = 0.0977	
Largest diff. peak and hole	0.669 and -0.475 $e·Å^{-3}$	

Crystal data and structure refinement for [K(18-c-6)(dme)$_2$][*meso*-**8**]

Empirical formula	$C_{40}H_{76}B_{10}CoKO_{10}P_6$	
Formula weight	1108.95	
Temperature	123 K	
Wavelength	1.39222 Å	
Crystal system	Monoclinic	
Space group	*P*2$_1$	
Unit cell dimensions	a = 13.2511(4) Å	α = 90°.
	b = 18.2870(3) Å	β = 103.026(3)°.
	c = 13.4608(3) Å	γ = 90°.
Volume	3177.93(14) Å^3	
Z	2	
Density (calculated)	1.159 Mg/m^3	
Absorption coefficient	3.343 mm^{-1}	
F(000)	1164	
Crystal size	0.6 x 0.2528 x 0.0806 mm^3	
Theta range for data collection	3.745 to 57.000°.	
Index ranges	-15<=h<=15, -14<=k<=21, -16<=l<=13	
Reflections collected	11905	
Independent reflections	8212 [R(int) = 0.0356]	
Completeness to theta = 57.000°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.54908	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8212 / 19 / 624	
Goodness-of-fit on F^2	0.993	
Final R indices [I>2sigma(I)]	R_1 = 0.0520, wR_2 = 0.1328	
R indices (all data)	R_1 = 0.0660, wR_2 = 0.1432	
Absolute structure parameter	0.47 (1)	
Largest diff. peak and hole	0.899 and -0.386 e·Å^{-3}	

Crystal data and structure refinement for [K(dme)][K(dme)$_2$][*rac*-**9**]

Empirical formula	$C_{96}H_{168}B_{40}Co_4K_2O_8P_{16}$	
Formula weight	2692.13	
Temperature	123 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/m$	
Unit cell dimensions	a = 19.3026(8) Å	α = 90°.
	b = 20.5879(7) Å	β = 112.895(4)°.
	c = 24.2008(8) Å	γ = 90°.
Volume	8859.7(6) Å^3	
Z	2	
Density (calculated)	1.009 Mg/m^3	
Absorption coefficient	4.951 mm^{-1}	
F(000)	2788	
Crystal size	0.15 x 0.05 x 0.05 mm^3	
Theta range for data collection	3.773 to 74.215°.	
Index ranges	-23<=h<=21, -25<=k<=25, -30<=l<=28	
Reflections collected	36055	
Independent reflections	17876 [R(int) = 0.0642]	
Completeness to theta = 74.215°	96.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.73552	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17876 / 0 / 858	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R_1 = 0.0830, wR_2 = 0.2090	
R indices (all data)	R_1 = 0.1185, wR_2 = 0.2318	
Largest diff. peak and hole	2.418 and -0.603 e·Å^{-3}	

4. NMR spectra

rac-5

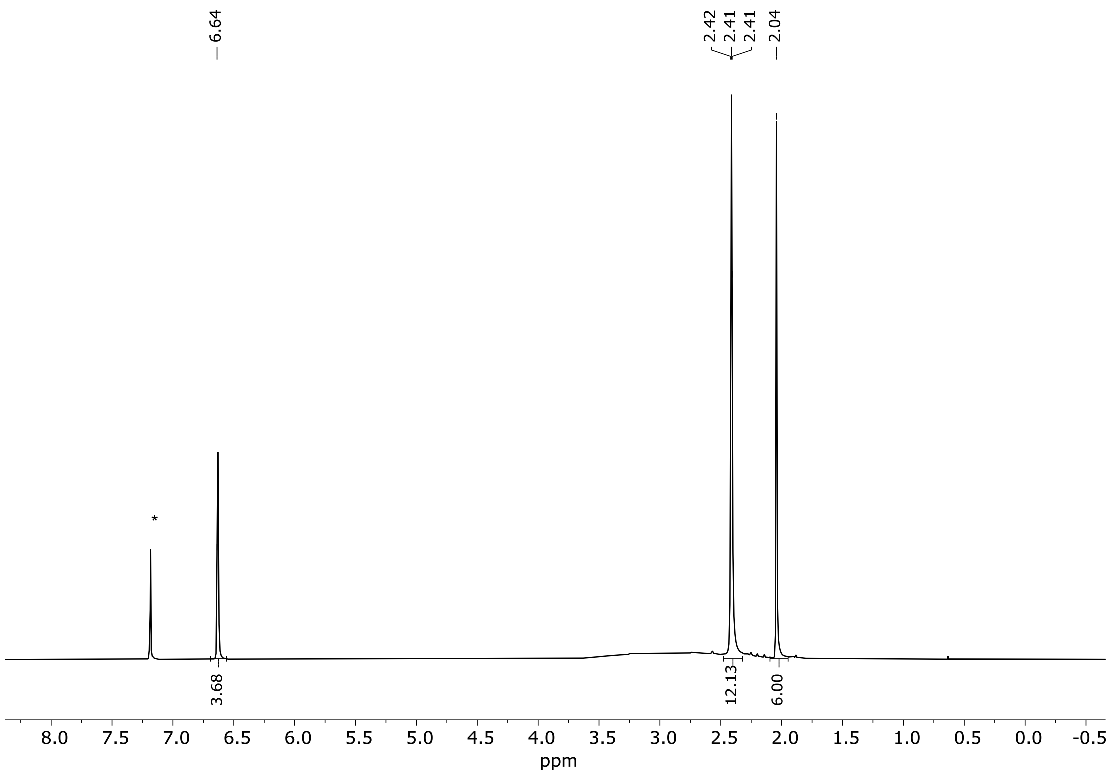


Figure S1: ^{1}H NMR spectrum of *rac*-**5** in C_6D_6. (*: C_6D_6).

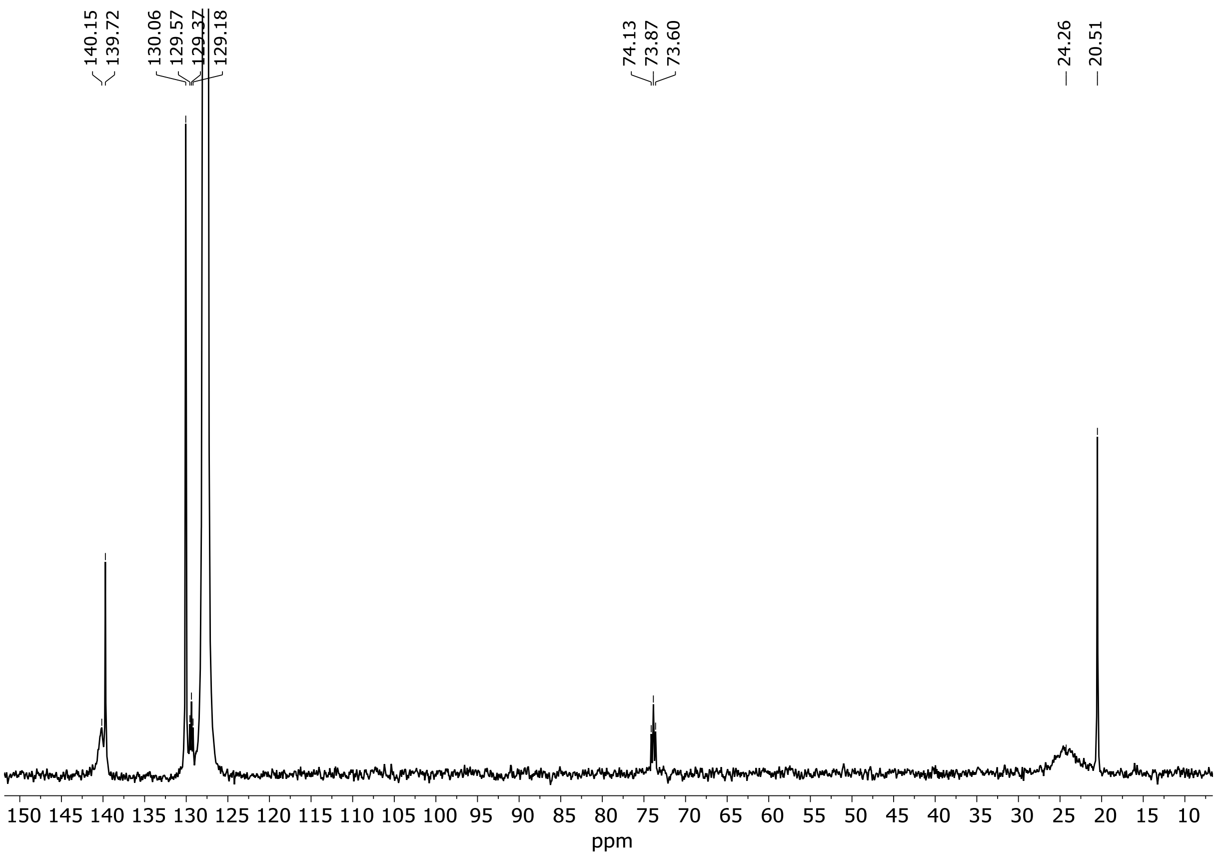


Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum of *rac*-**5** in C_6D_6. (*: C_6D_6).

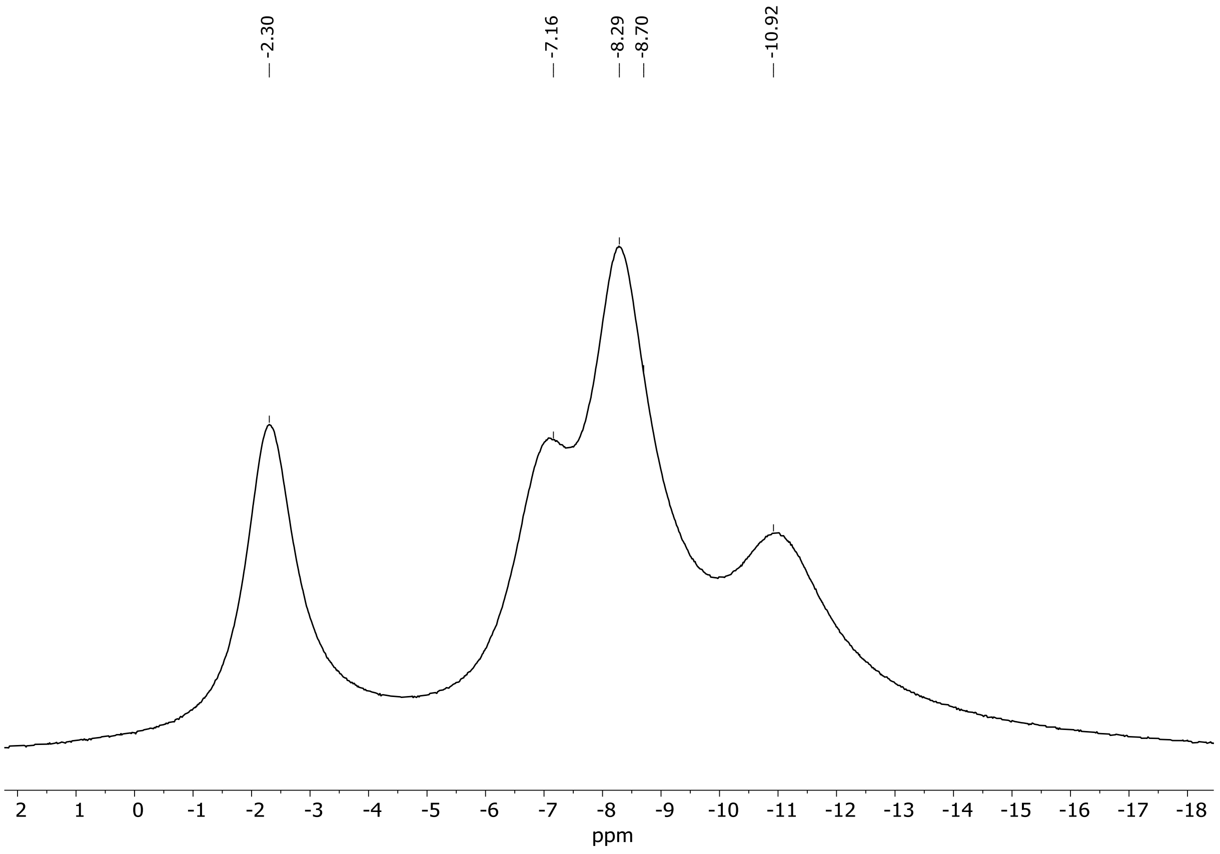


Figure S3: $^{11}B\{^{1}H\}$ NMR spectrum of *rac*-**5** in C_6D_6.

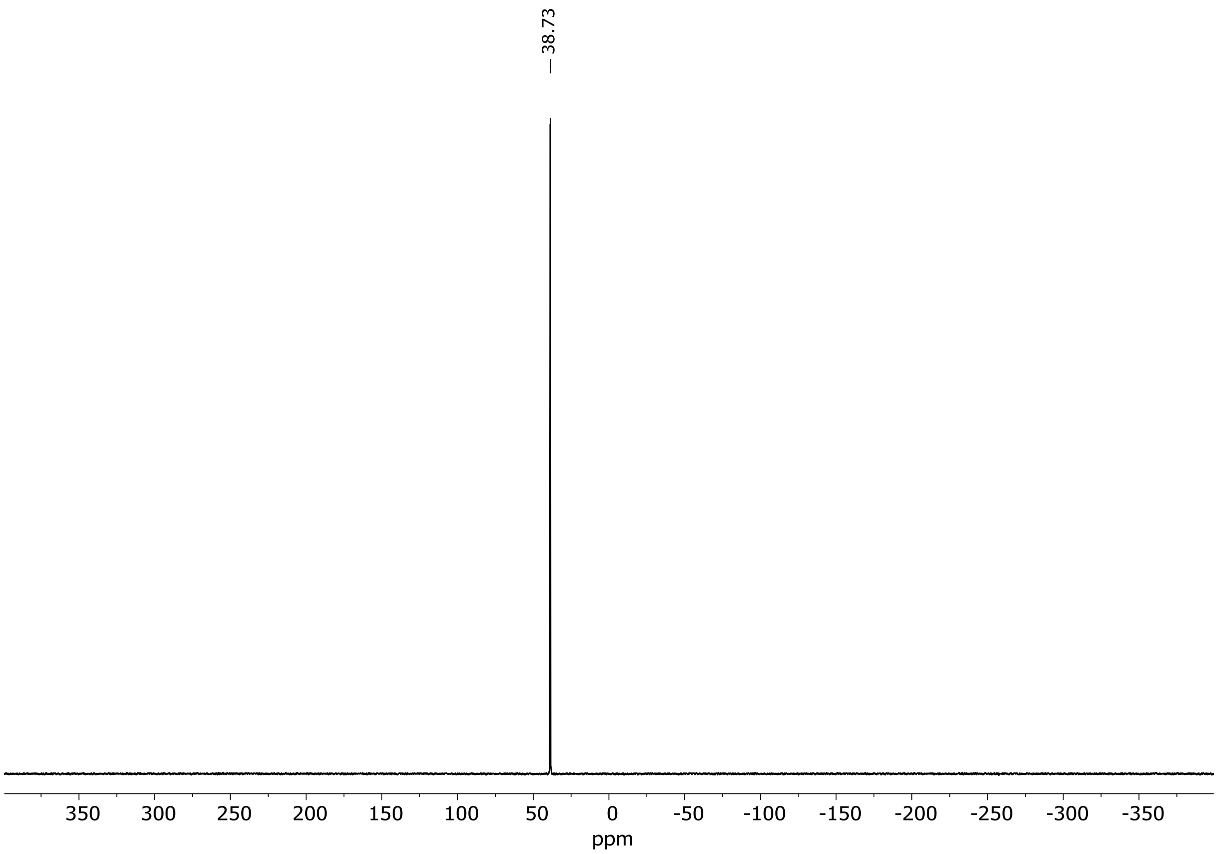


Figure S4: $^{31}P\{^{1}H\}$ NMR spectrum of *rac*-**5** in C_6D_6.

[K(18-c-6)(thf)][*rac*-**1**]

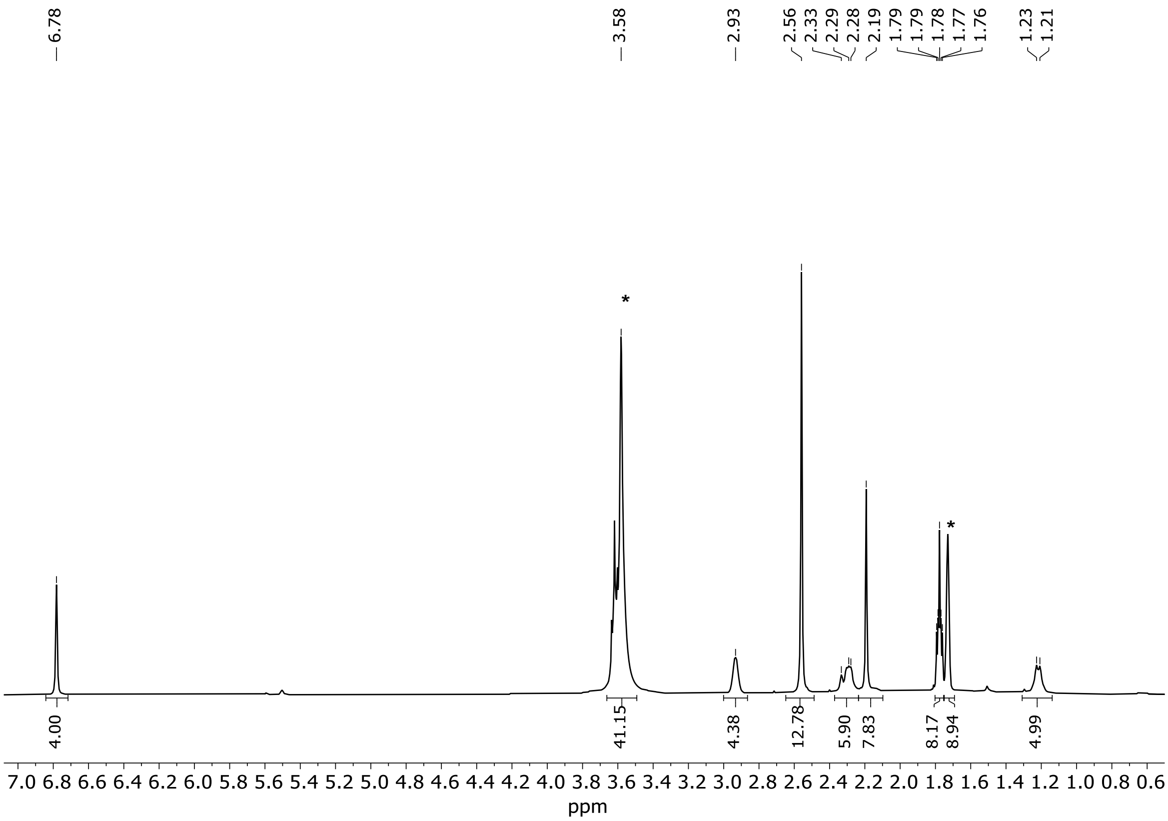


Figure S5: ^{1}H NMR spectrum of [K(18-c-6)(thf)][*rac*-**1**] in THF-d_8. (*: THF-d_8)

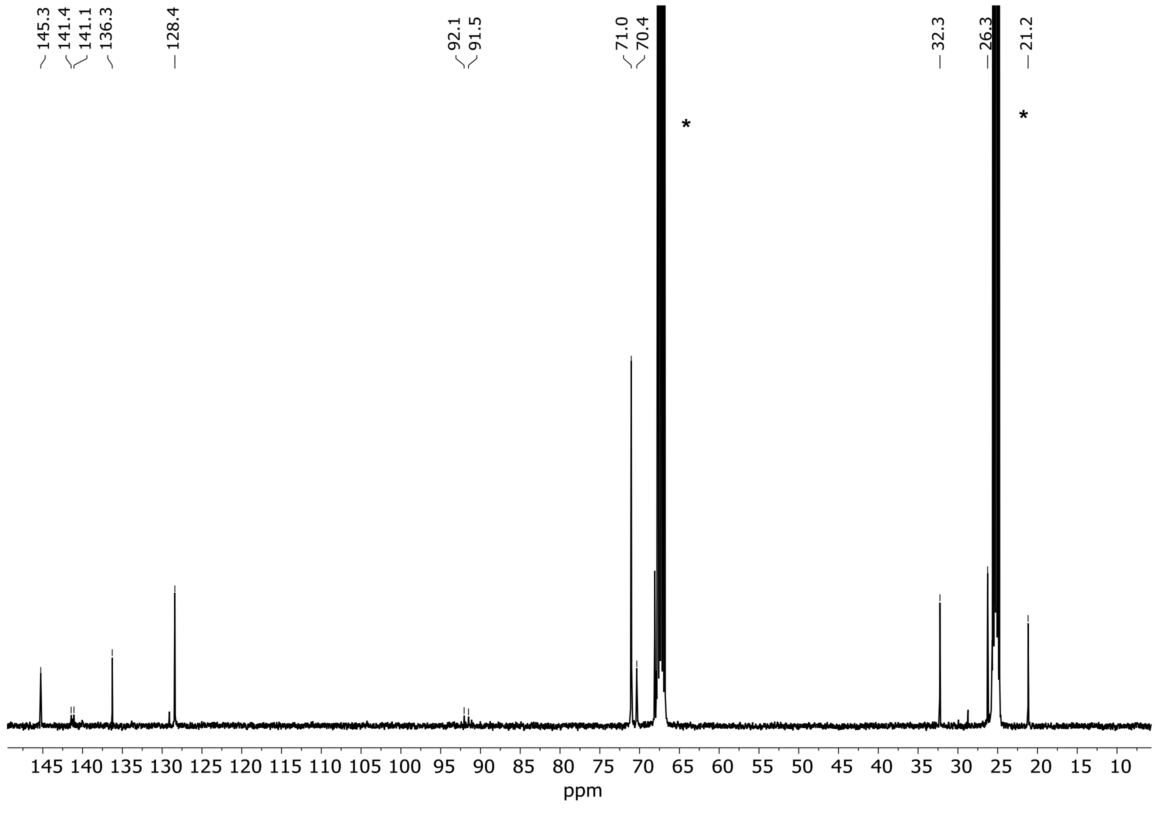


Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of [K(18-c-6)(thf)][*rac*-**1**] in THF-d_8. (*: THF-d_8)

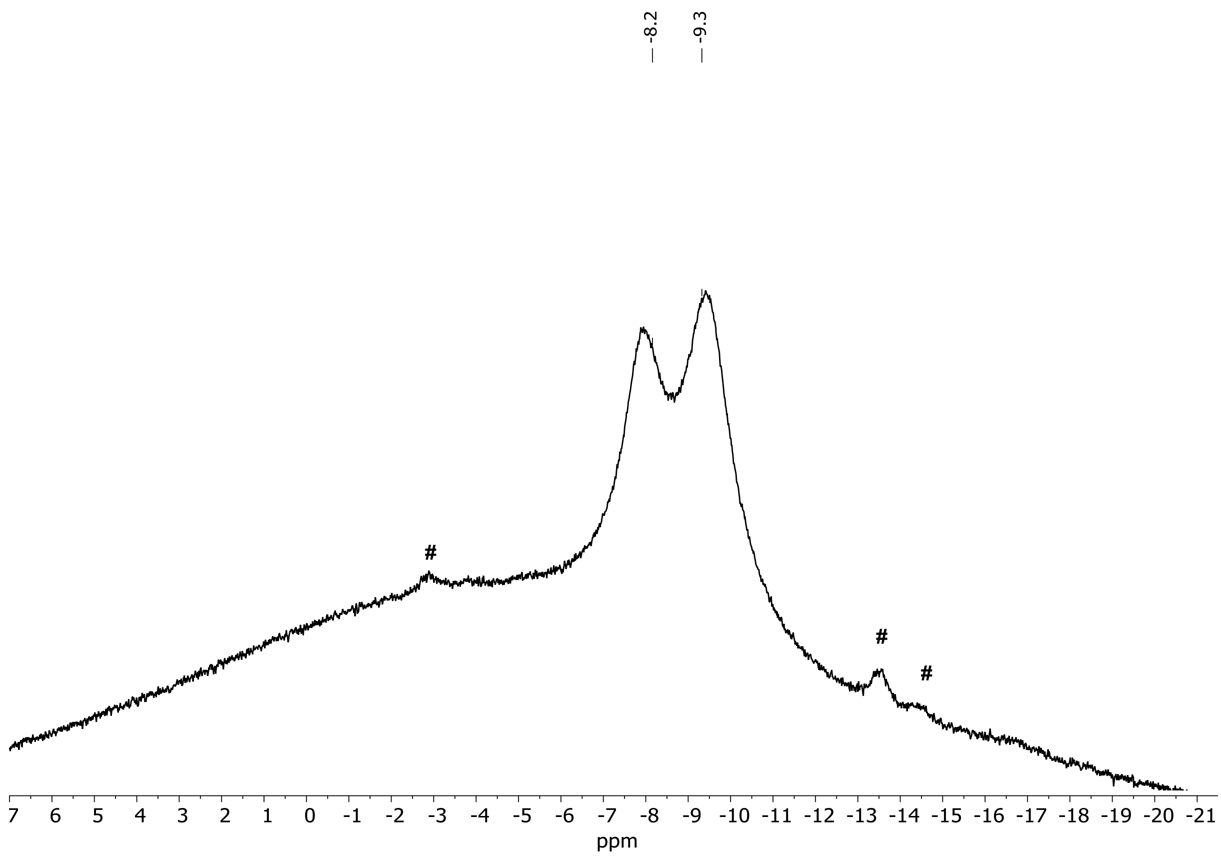


Figure S7: $^{11}B\{^1H\}$ NMR spectrum of [K(18-c-6)(thf)][*rac*-**1**] in THF-d$_8$. (#: unindentified impurity)

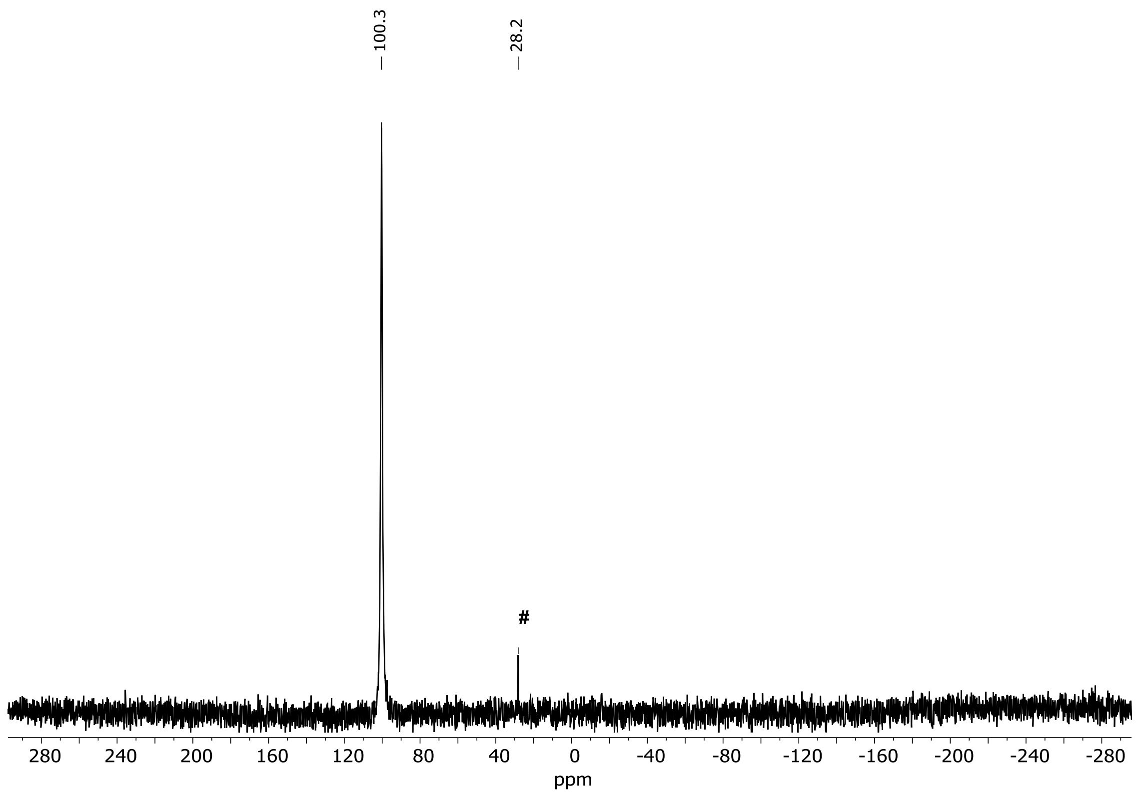


Figure S8: $^{31}P\{^1H\}$ NMR spectrum of [K(18-c-6)(thf)][*rac*-**1**] in THF-d$_8$. (#: unindentified impurity)

***rac*-2**

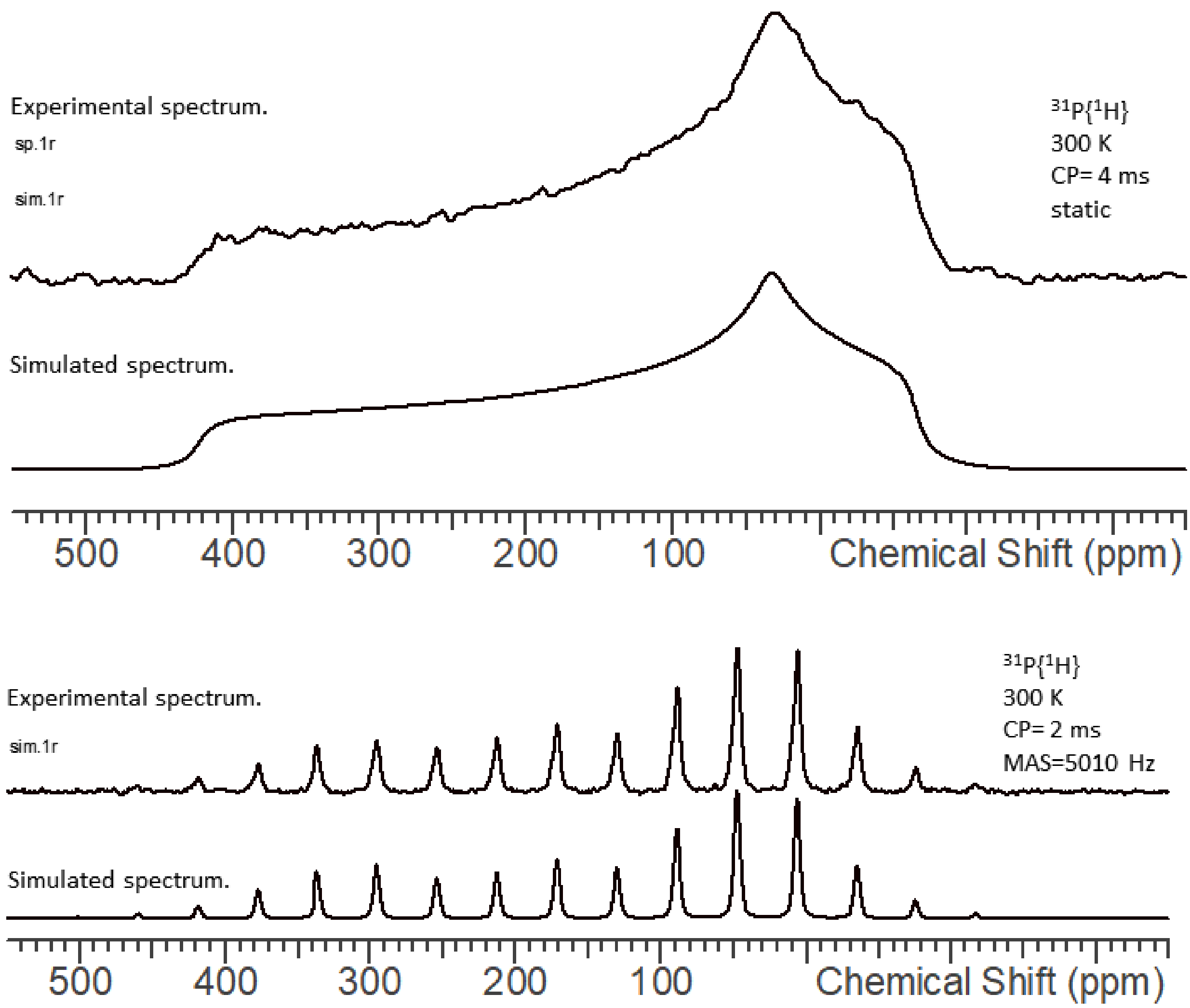


Figure S9: $^{31}P\{^1H\}$ NMR spectrum of *rac*-**2** in the solid-state (top: static, bottom: magic-angle spinning at 5010 Hz).

[K(18-c-6)(dme)][*rac*-**6**]

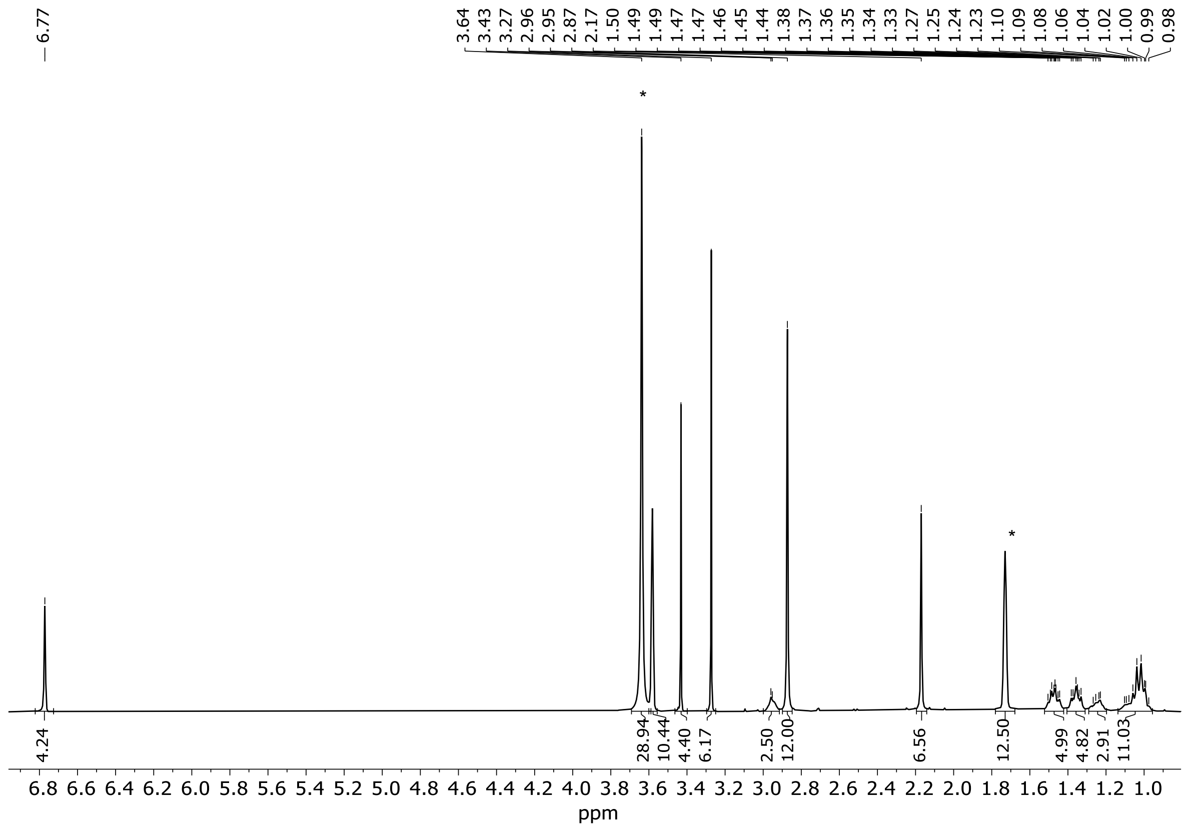


Figure S10: ^{1}H NMR spectrum of [K(18-c-6)(dme)][*rac*-**6**] in THF-d_8. (*: THF-d_8)

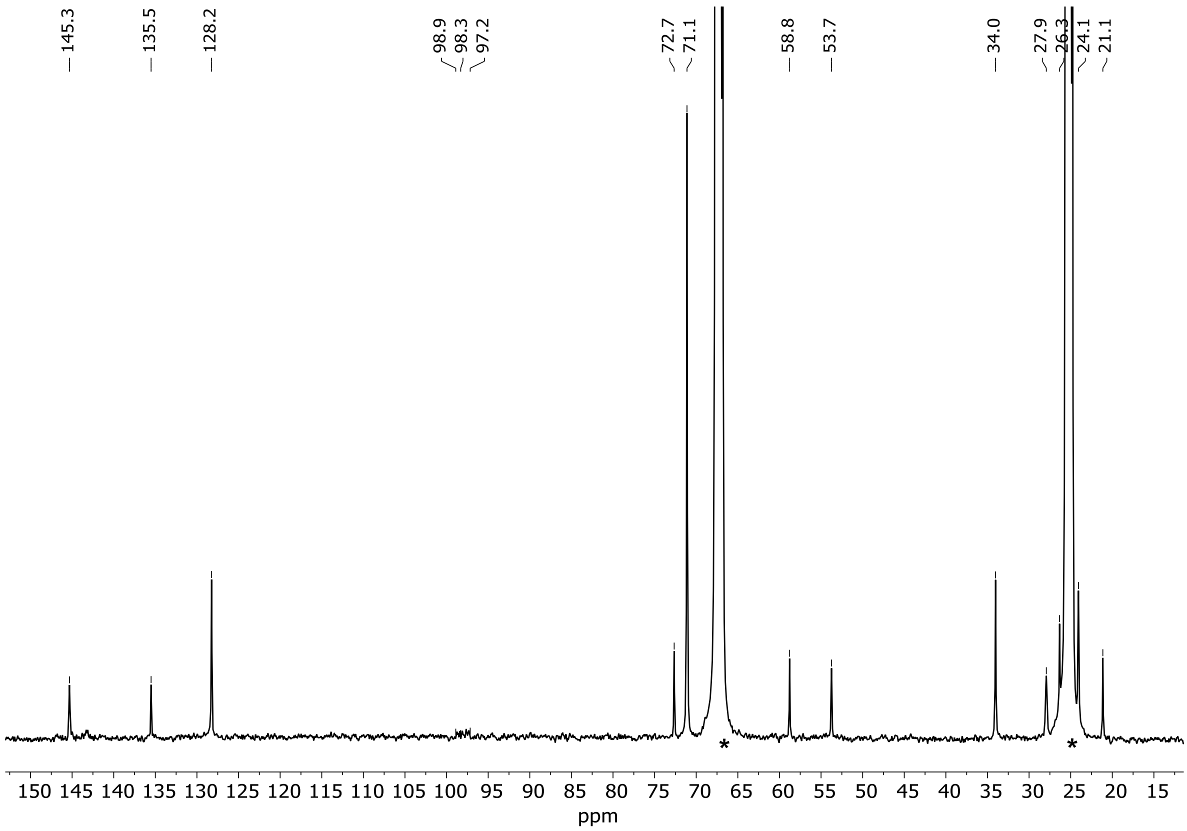


Figure S11: $^{13}C\{^{1}H\}$ NMR spectrum of [K(18-c-6)(dme)][*rac*-**6**] in THF-d_8. (*: THF-d_8)

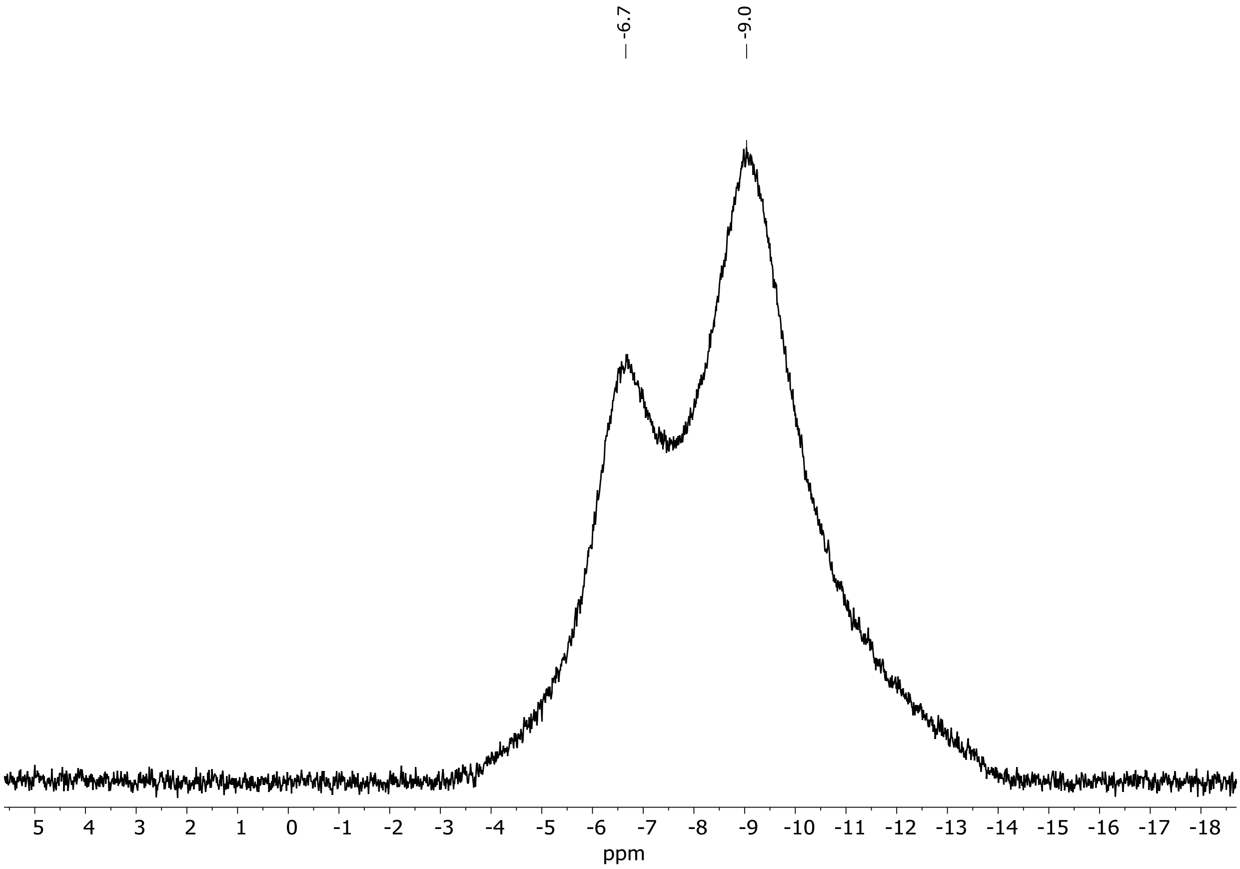


Figure S12: $^{11}B\{^{1}H\}$ NMR spectrum of [K(18-c-6)(dme)][*rac*-**6**] in THF-d_8.

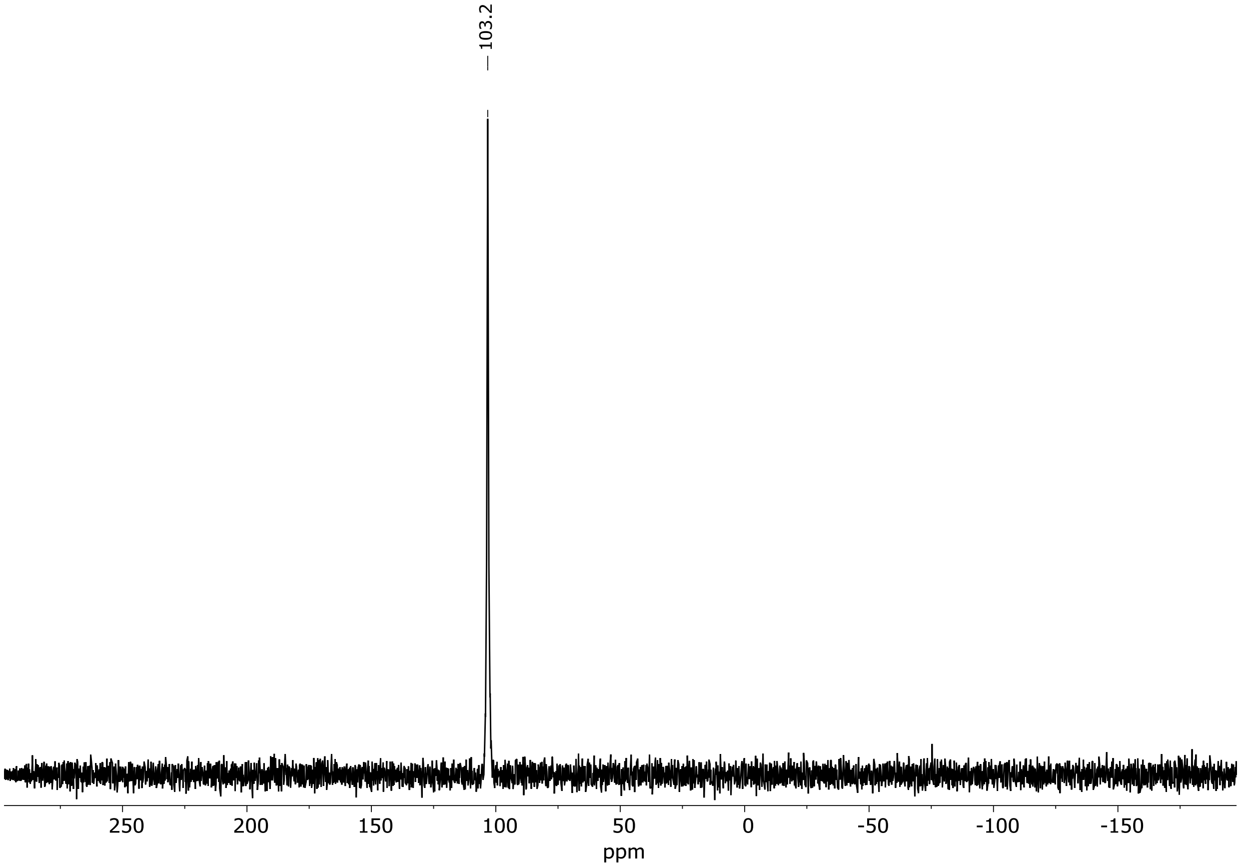


Figure S13: $^{31}P\{^{1}H\}$ NMR spectrum of [K(18-c-6)(dme)][*rac*-**6**] in THF-d_8.

[K(18-c-6)][*rac*-**7**]

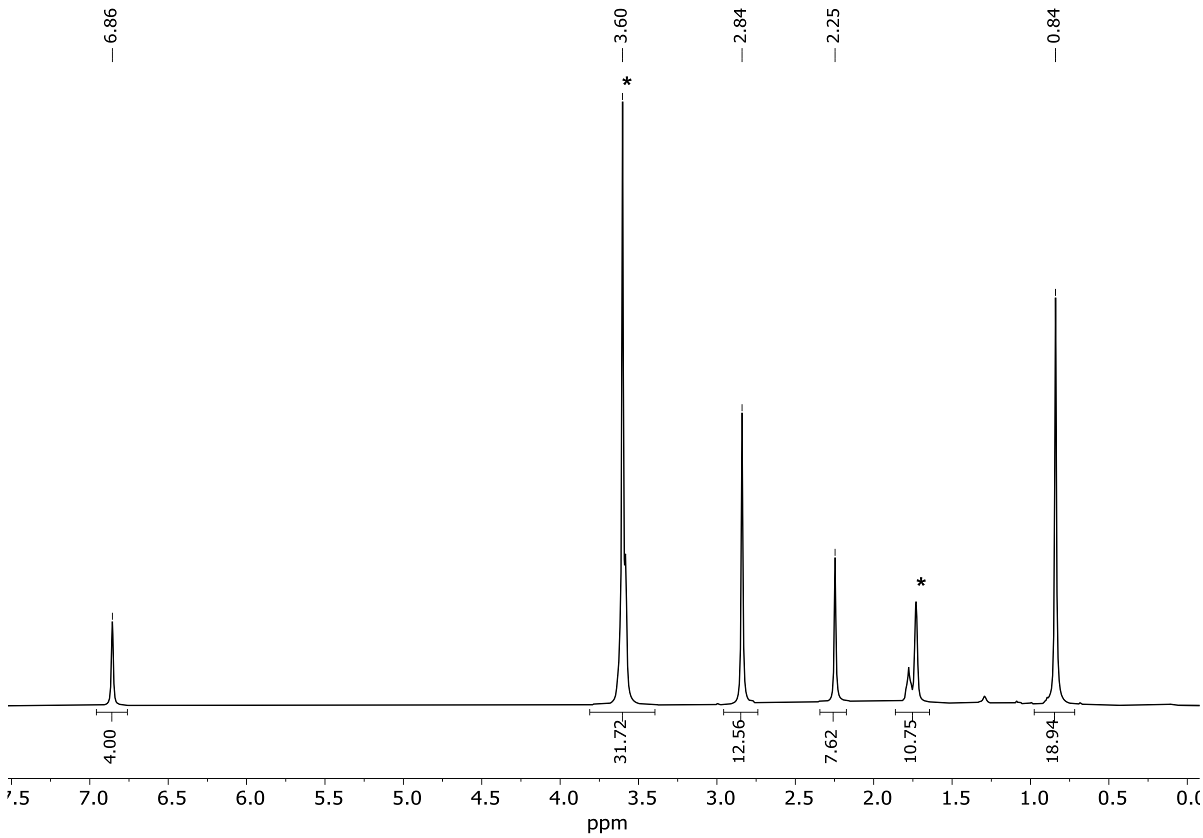


Figure S14: ^{1}H NMR spectrum of [K(18-c-6)][*rac*-**7**] in THF-d_8. (*: THF-d_8)

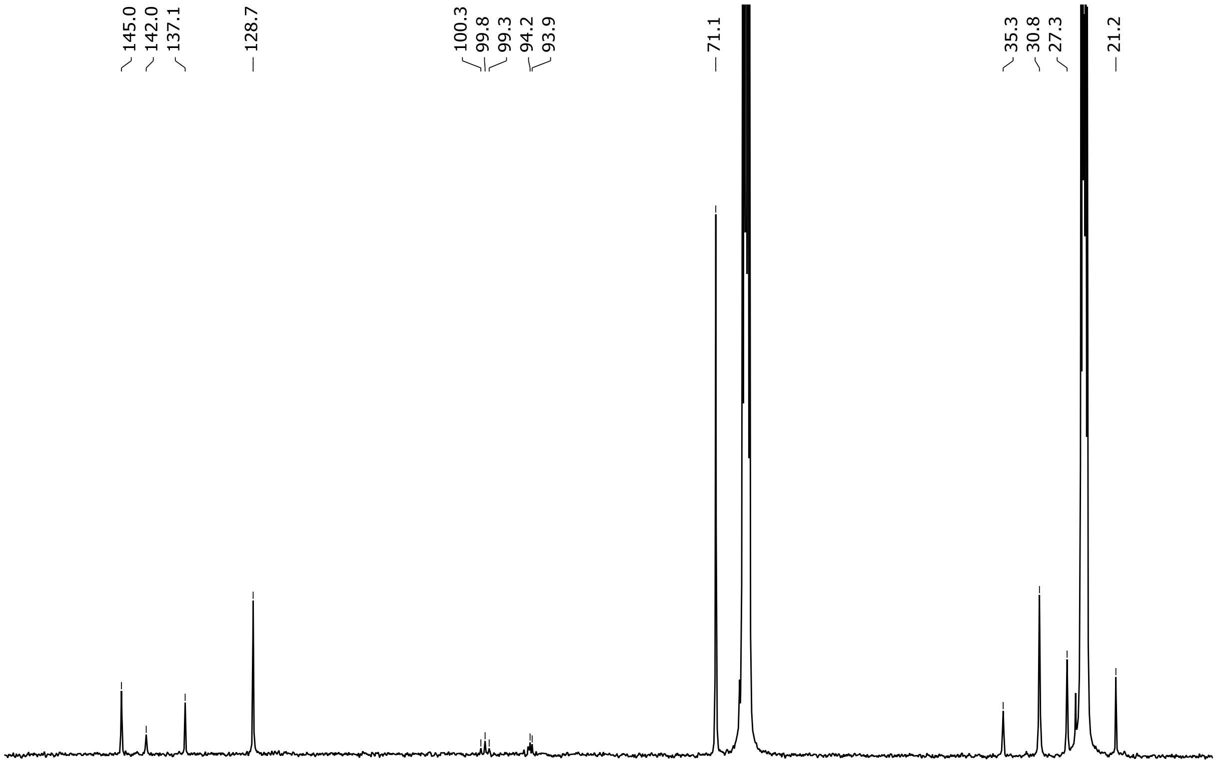


Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum of [K(18-c-6)][*rac*-**7**] in THF-d_8. (*: THF-d_8)

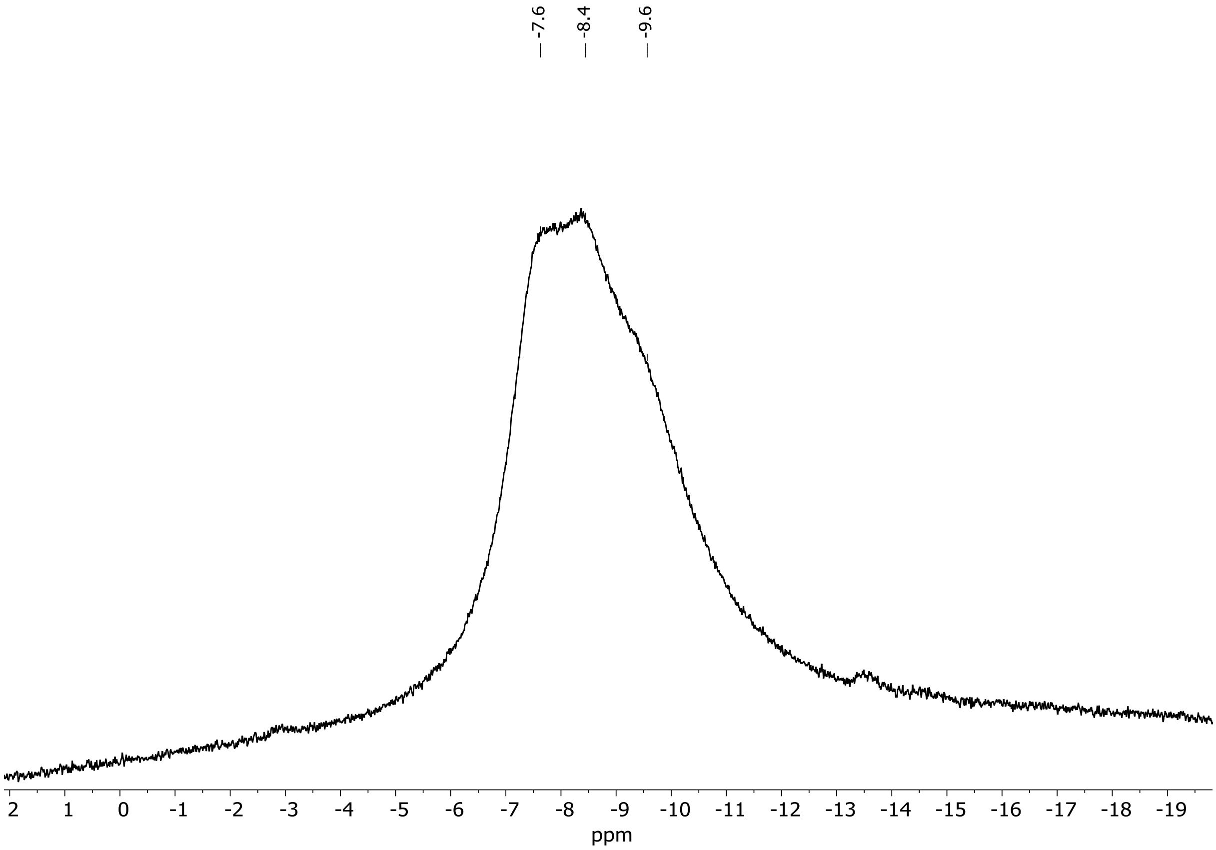


Figure S16: $^{11}B\{^{1}H\}$ NMR spectrum of [K(18-c-6)][*rac*-**7**] in THF-d_8.

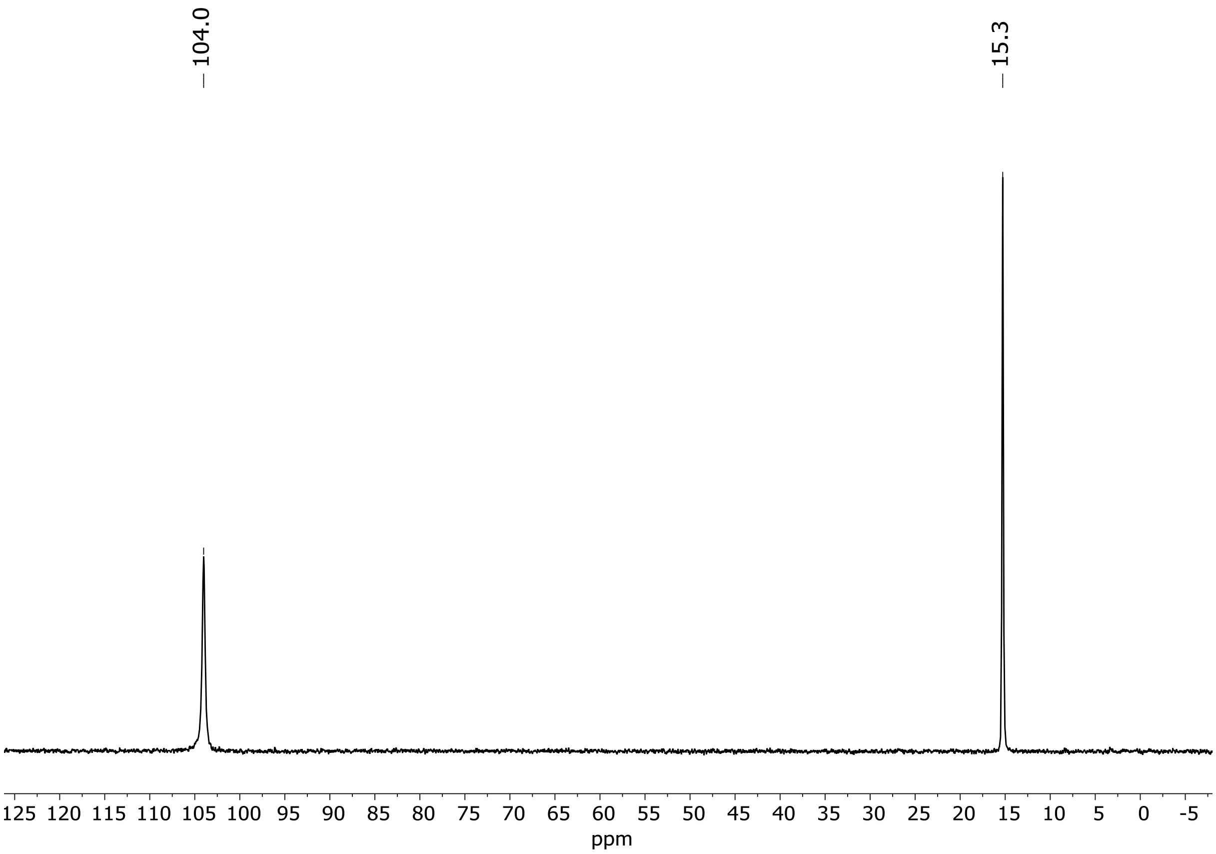


Figure S17: $^{31}P\{^{1}H\}$ NMR spectrum of [K(18-c-6)][*rac*-**7**] in THF-d_8.

[K(18-c-6)][*meso*-**8**]

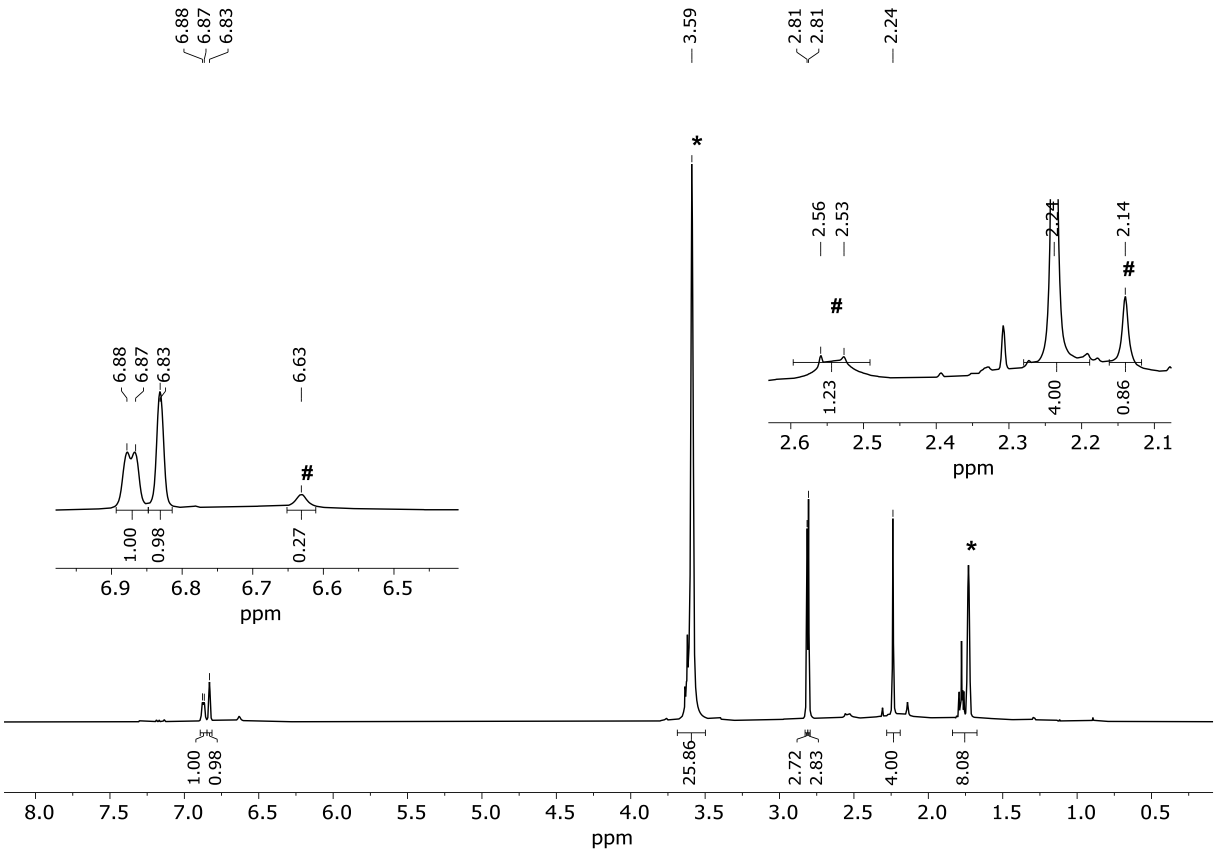


Figure S18: ^{1}H NMR spectrum of [K(18-c-6)][*meso*-**8**] in THF-d_8. Enlarged areas show contaminations of $[K(18\text{-c-}6)]_2$[*rac*-**9**] (#). (*: THF-d_8)

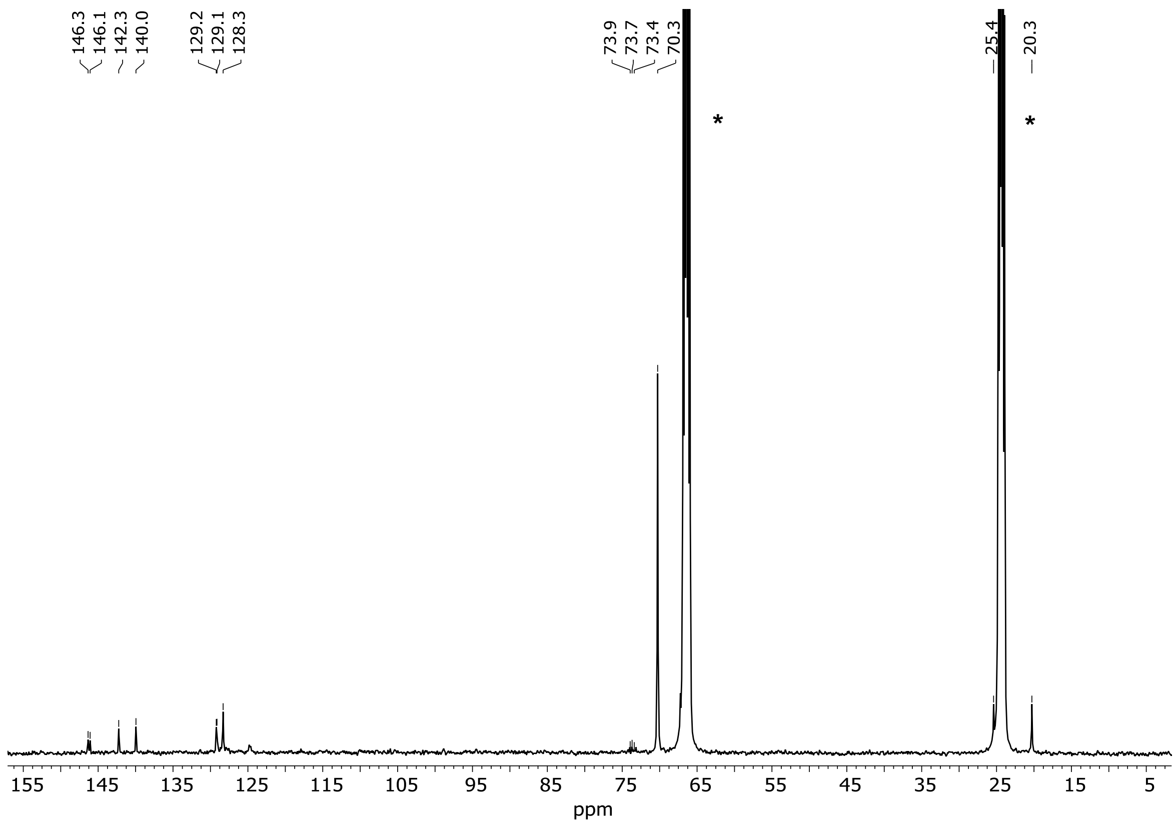


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of [K(18-c-6)][*meso*-**8**] in THF-d_8. (*: THF-d_8)

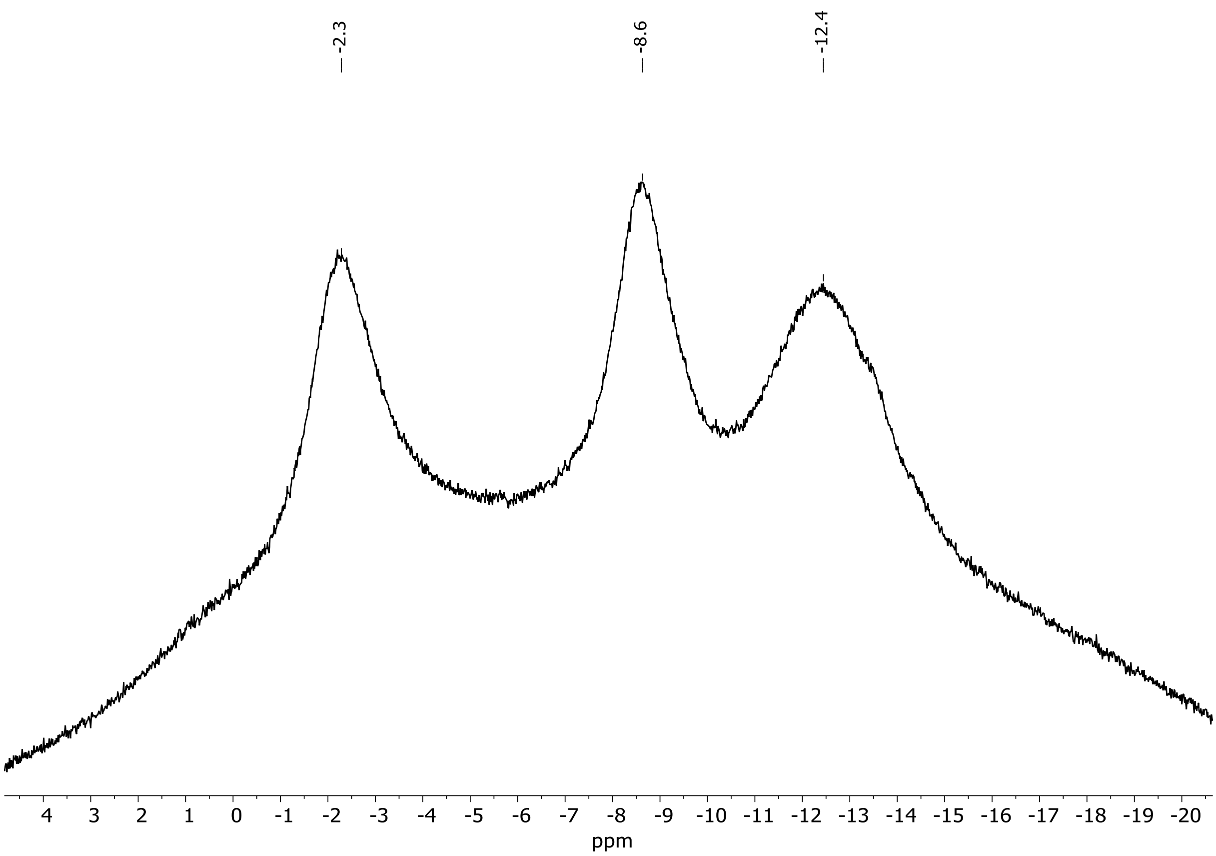


Figure S20: $^{11}B\{^{1}H\}$ NMR spectrum of [K(18-c-6)][*meso*-**8**] in THF-d_8.

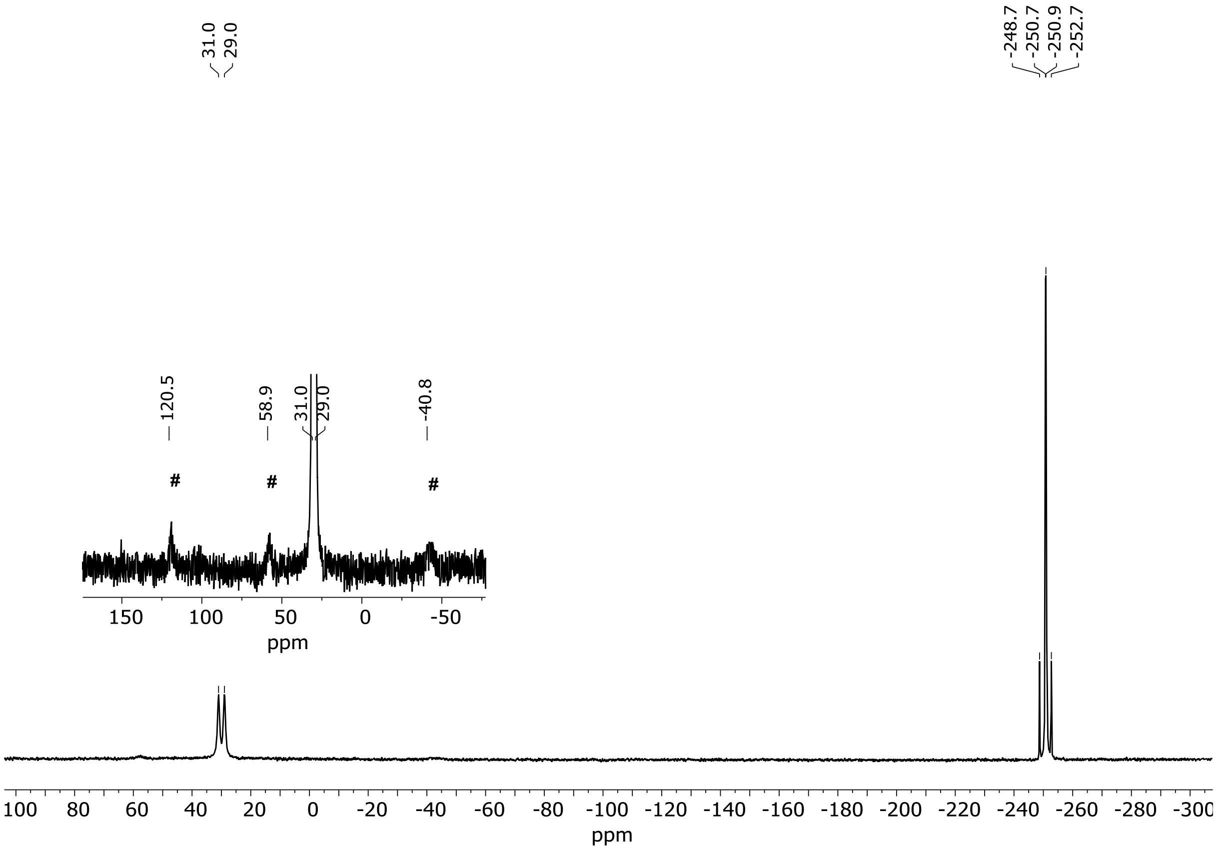


Figure S21: $^{31}P\{^{1}H\}$ NMR spectrum of [K(18-c-6][*meso*-**8**] in THF-d_8. Enlarged areas show contaminations of $[K(18\text{-}c\text{-}6)]_2$**9** (#).

[K(18-c-6)]$_2$[rac-**9**]

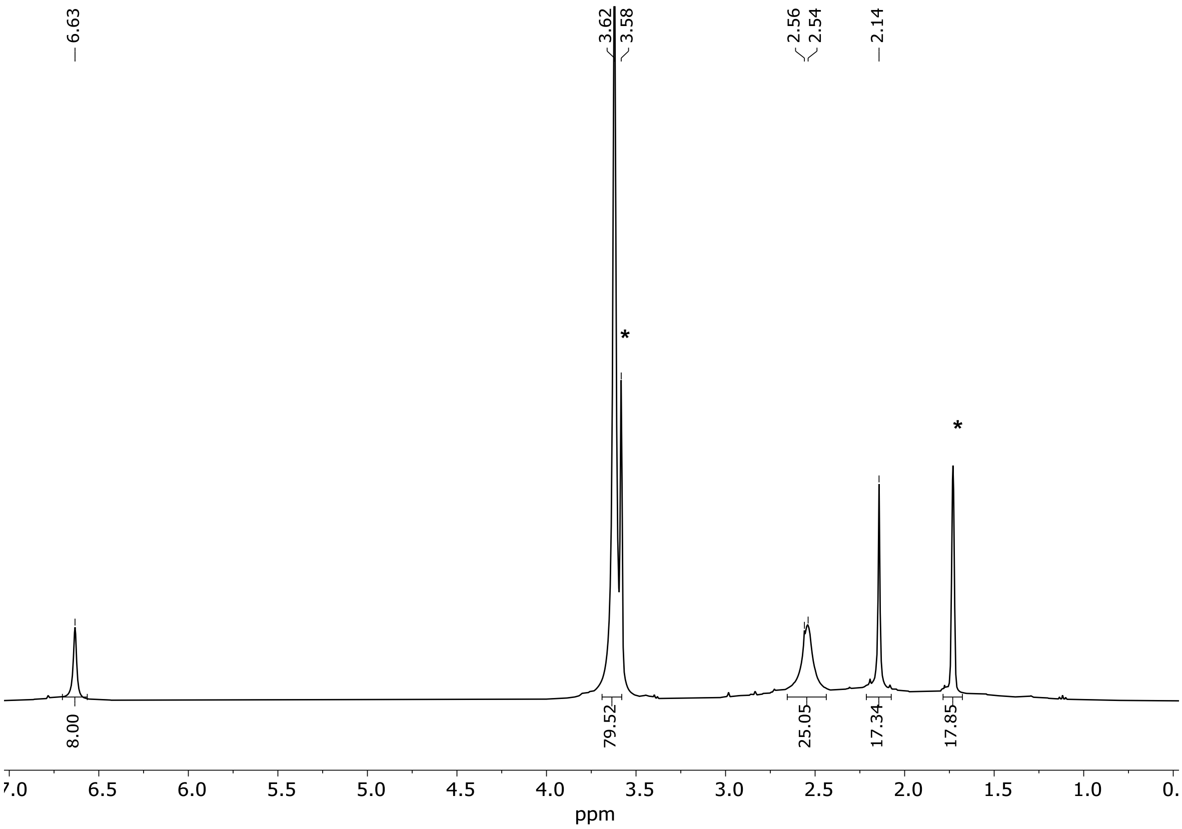


Figure S22: ^{1}H NMR spectrum of [K(18-c-6)]$_2$[*rac*-**9**] in THF-d$_8$. (*: THF-d$_8$)

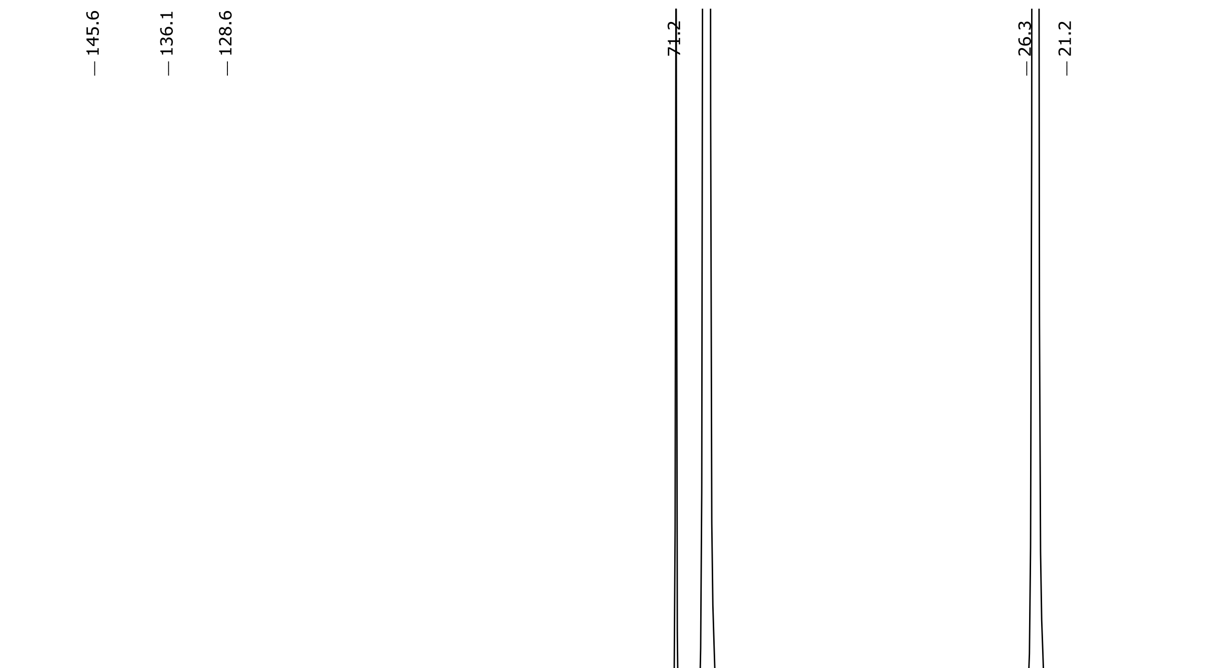


Figure S23: ^{13}C{^{1}H} NMR spectrum of [K(18-c-6)]$_2$[*rac*-**9**] in THF-d$_8$. (*: THF-d$_8$)

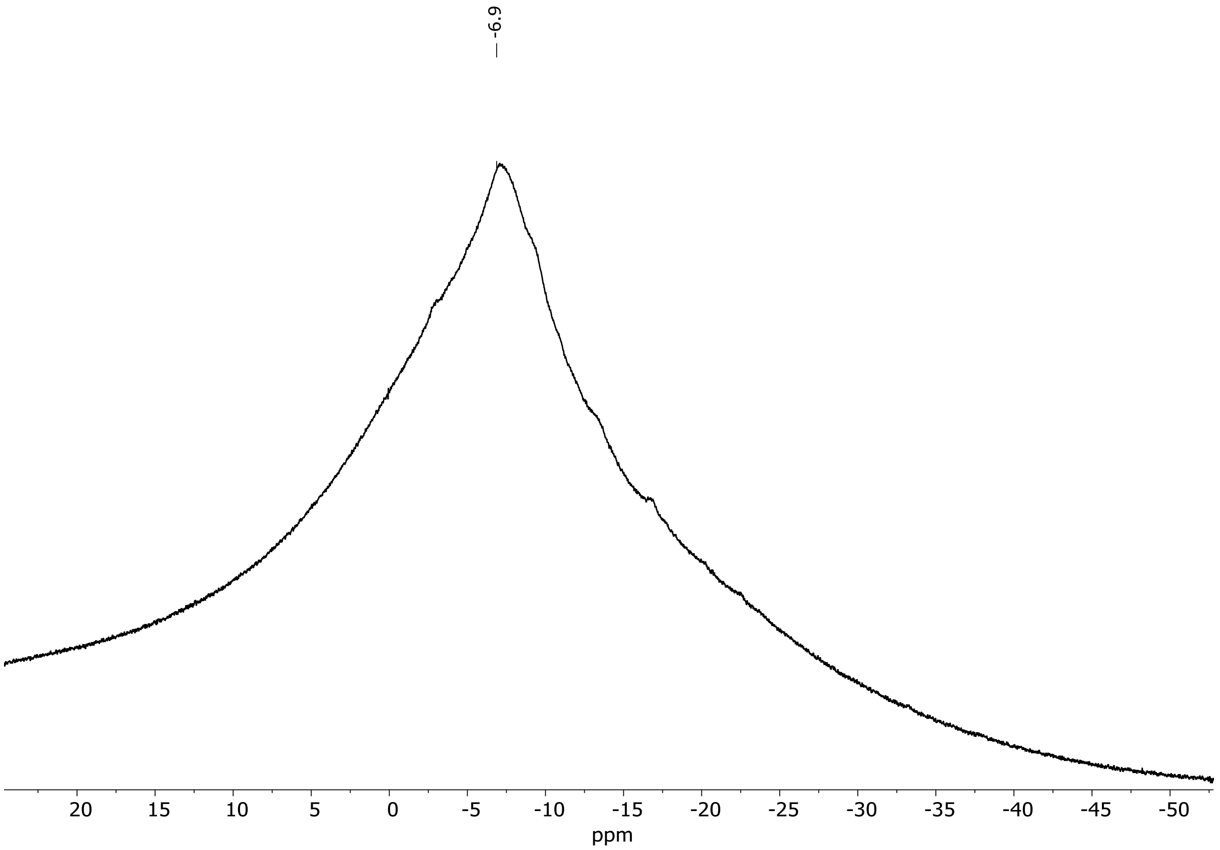


Figure S24: $^{11}B\{^{1}H\}$ NMR spectrum of $[K(18\text{-}c\text{-}6)]_2$[*rac*-**9**] in THF-$d_8$.

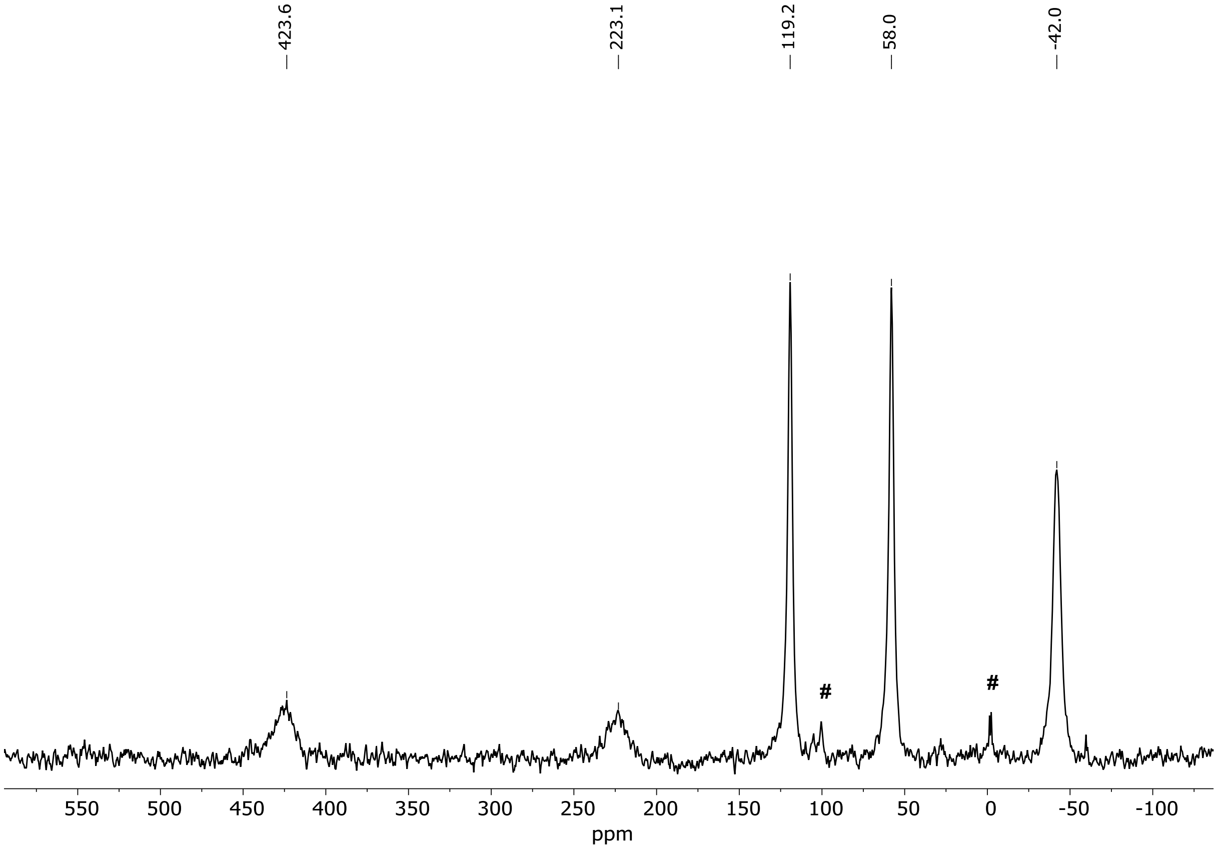


Figure S25: $^{31}P\{^{1}H\}$ NMR spectrum of $[K(18\text{-}c\text{-}6)]_2$[*rac*-**9**] in THF-$d_8$.(#: unindentified impurity).

5. NMR spectroscopic monitoring of the reaction between [K(18-c-6)(thf)][*rac*-1] and P_4

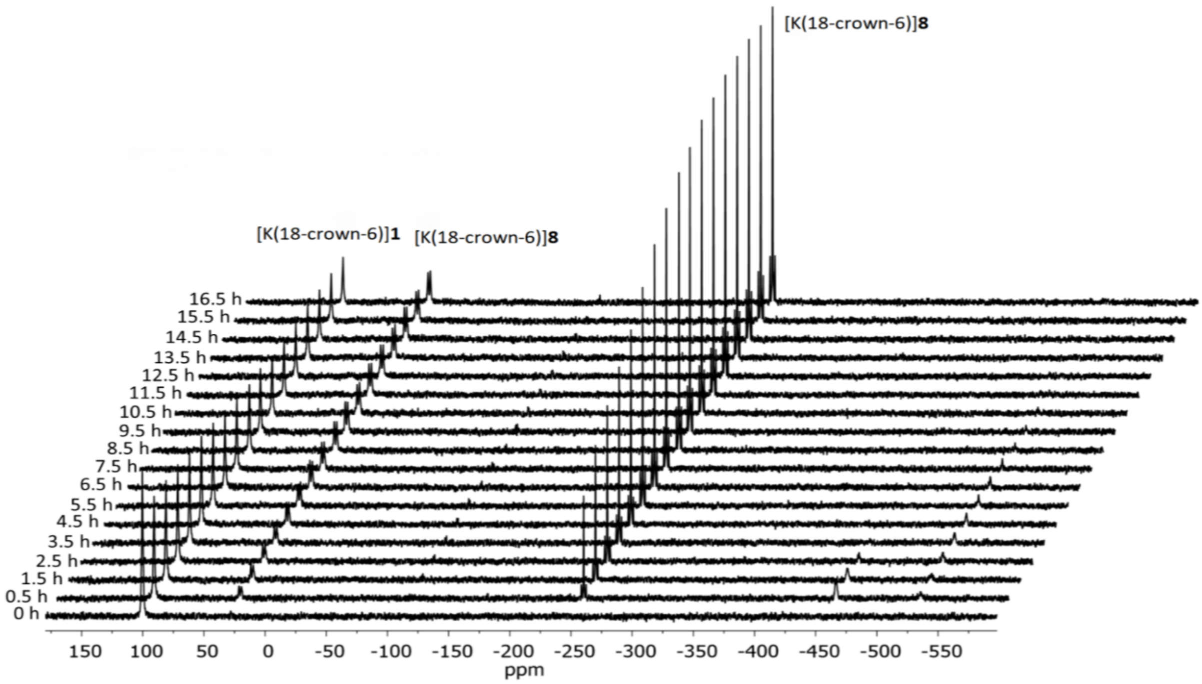


Figure S26: $^{31}P\{^1H\}$ NMR spectroscopic monitoring of the reaction between [K(18-c-6)(thf)][*rac*-**1**] and P_4 (THF-d_8). Stack angle = 15°.

6. NMR spectroscopic monitoring of the reaction between [K(18-c-6][*rac*-1] and [K(18-c-6][*meso*-8]

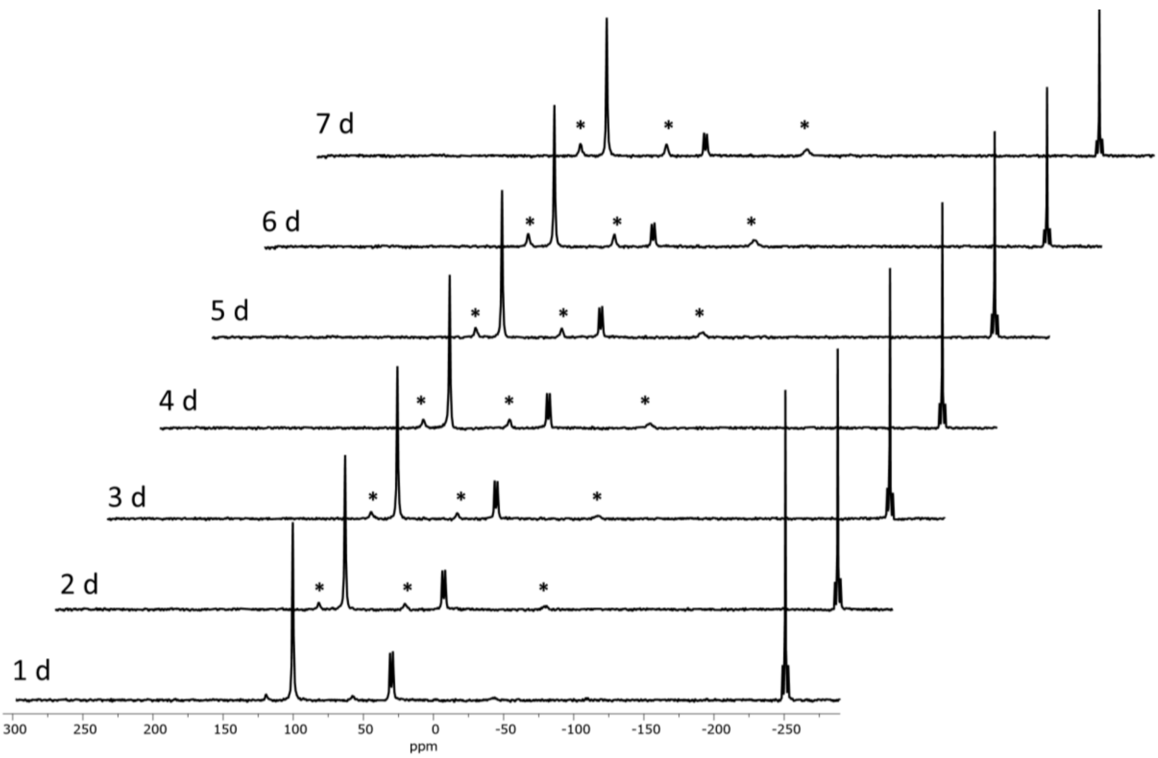


Figure S27: $^{31}P\{^1H\}$ NMR spectroscopic monitoring of the reaction between [K(18-c-6)(thf)][*rac*-**1**] and [K(18-c-6][*meso*-**8**] in THF-d_8. A star (*) denotes signals corresponding to $[K(18\text{-}c\text{-}6)]_2$[*rac*-**9**]. Stack angle = 30°.

7. Variable temperature NMR spectroscopic measurements on [K(18-c-6][*rac*-**7**]

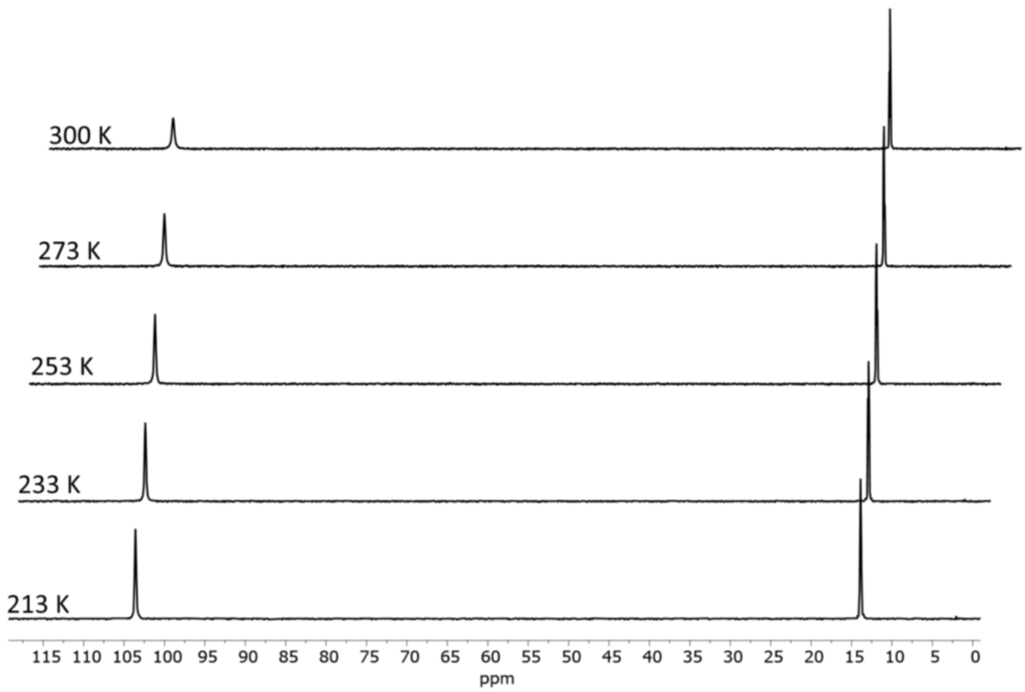


Figure S28: Variable temperature NMR spectra of [K(18-c-6][*rac*-**7**] ($^{31}P\{^{1}H\}$, THF-d_8). Stack angle = 5°.

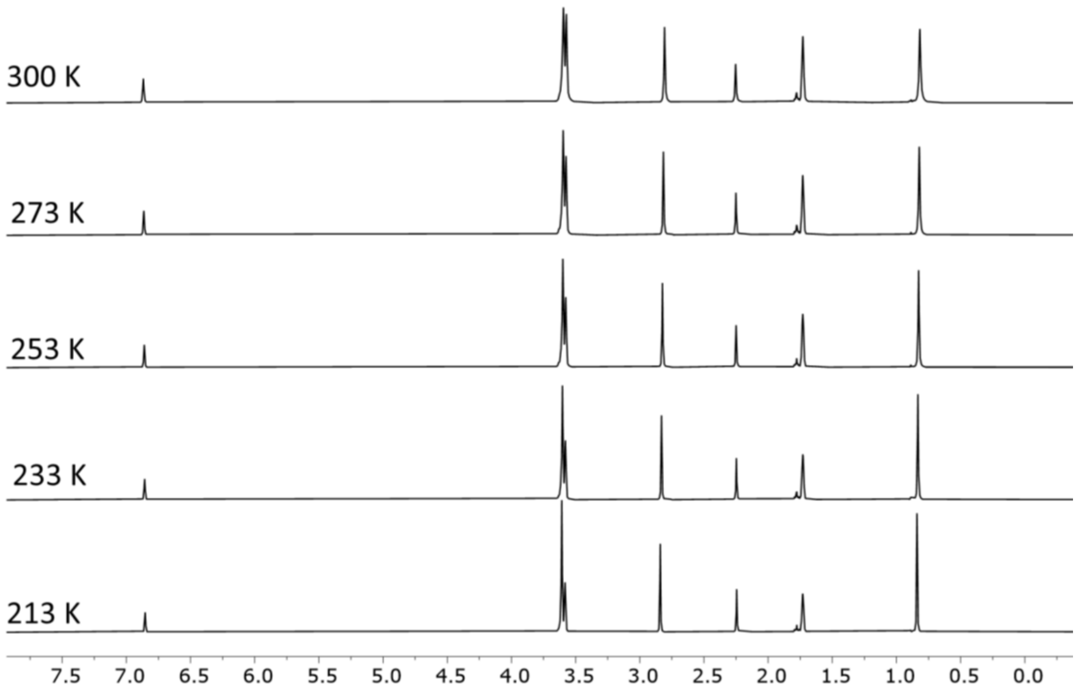


Figure S29*:* Variable temperature NMR spectra of [K(18-c-6][*rac*-**7**] (^{1}H, THF-d_8). Stack angle = 0°.

8. Variable temperature NMR spectroscopic measurements on [K(18-c-6]$_2$[rac-9]

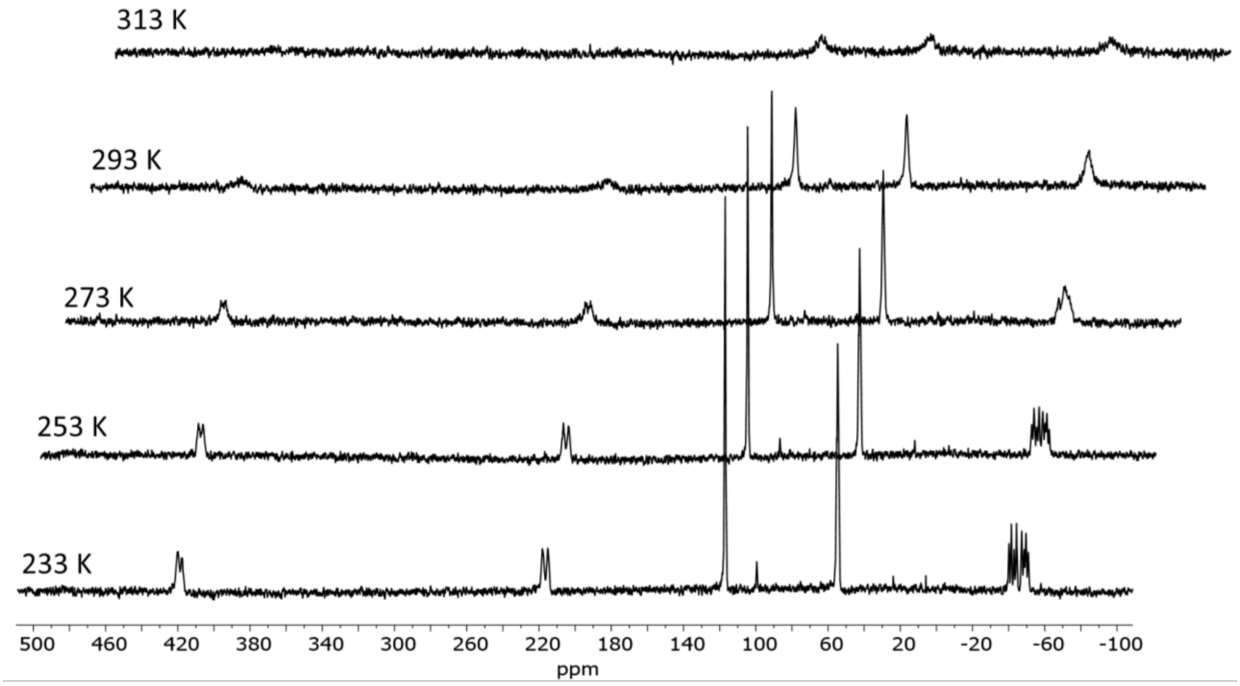


Figure S30: Variable temperature NMR spectra of [K(18-c-6)]$_2$[*rac*-**9**] ($^{31}P\{^1H\}$, THF-d$_8$). Stack angle = 15°.

Table 1: Calculated ^{31}P NMR shifts of [*rac*-**9**]$^{2-}$ with various basis sets (BS = broken-symmetry). Atom labels refer to Figure 4 in the main text. The calculated shifts were referenced internally against P2.

	Exp.	def2-SVP	def2-SVP	def2-TZVP	def2-TZVP	pcSseg-2	pcSseg-2
		S = 0, BS	S = 0	S = 0, BS	S = 0	S = 0, BS	S = 0
P4	−49.1	−5	−32	−28	−54	4	−53
P5	−42.3	7	21	−16	−2	13	−2
P1	55.2	49/49	64/64	50/51	59/59	47/48	59/59
P2	116.9	117/116	117/116	117/115	117/116	117/117	117/117
P6	216.5	302	268	215	258	281	254
P3	418.8	527	209	433	218	492	213

Figure S30 shows the variable temperature $^{31}P\{^1H\}$ NMR spectra of [K(18-c-6]$_2$[*rac*-**9**]. In addition, Table 1 shows the calculated ^{31}P NMR shifts of the dianion [*rac*-**9**]$^{2-}$ (TPSS0 functional, basis sets are given in Table 1). Clearly, a reasonable agreement between measured and calculated shifts is only reached when a broken-symmetry wavefunction is used. This is particularly visible when comparing the calculated shifts of P3.

9. Cyclic voltammetry measurements

Cyclic voltammograms (CV) were recorded with a CH Instruments potentiometerand software from CH Instruments. CV was measured with an electrode cell equipped with a Pt-working electrode, Pt-counter electrode and an Ag/$AgNO_3$-reference electrode. The Ag/AgNO3reference electrode was referenced against ferrocene in tetrahydrofuran. The analytes and the conducting salt [nBu4N]PF6 (2 mmol) were dissolved in tetrahydrofuran (10mL) for the CV measurements.

[K(18-c-6)(thf)][*rac*-**1**]

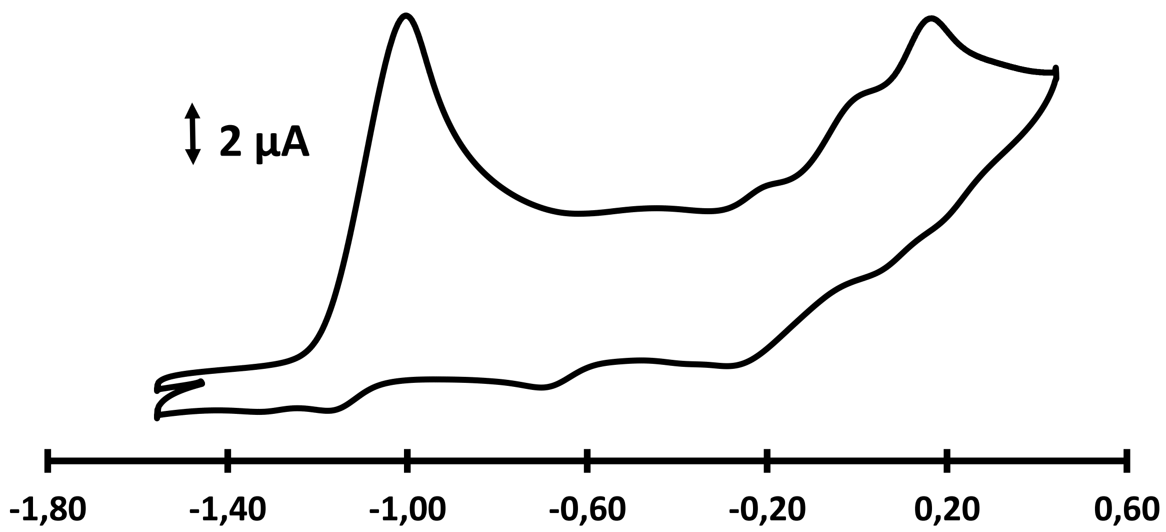


Figure S31: Cyclic voltammogram of [K(18-c-6)(thf)][*rac*-**1**], scan rate 200mV, range from E(V)=−1.8 to +0.6, E vs. FcH/FcH⁺.

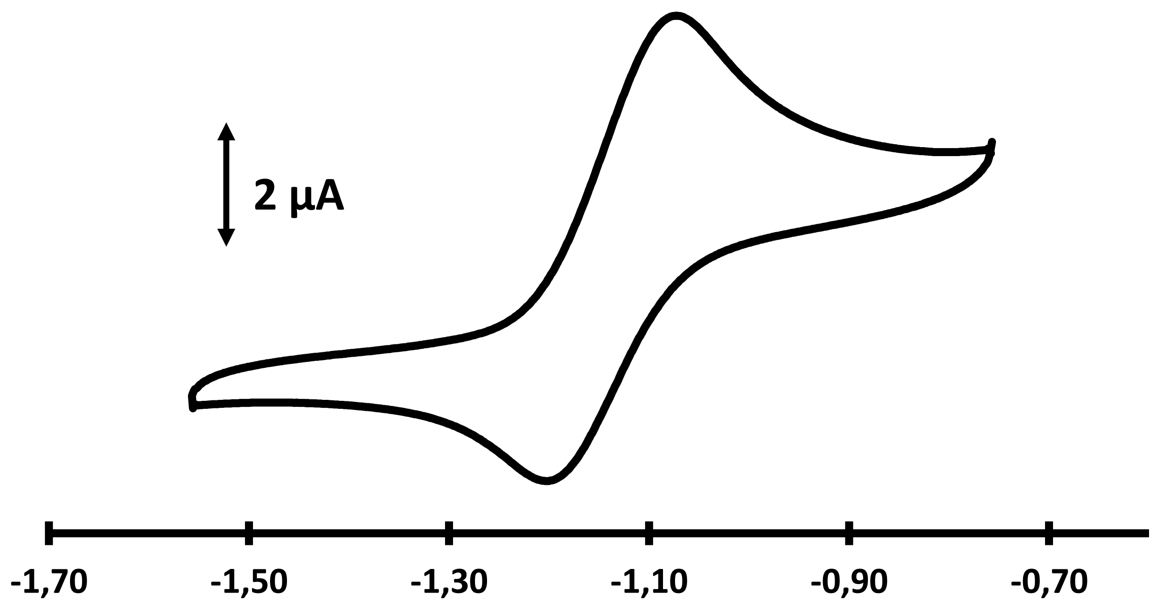


Figure S32: Cyclic voltammogram of [K(18-c-6)(thf)][*rac*-**1**], scan rate 200mV, range from E(V)=−1.7 to −0.8, E vs. FcH/FcH⁺.

[K(18-c-6)(dme)][*rac*-**6**]

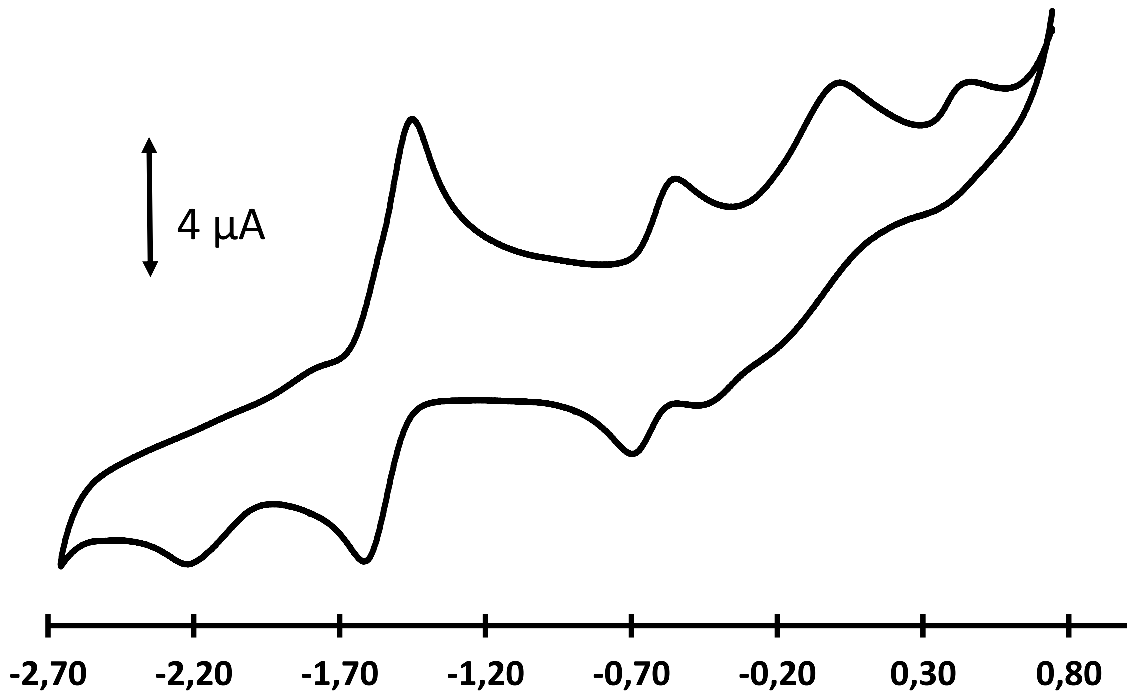


Figure S33: Cyclic voltammogram of [K(18-c-6)(dme)][*rac*-**6**], scan rate 200mV, range from E(V)=−2.7 to +0.8, E vs. FcH/FcH+.

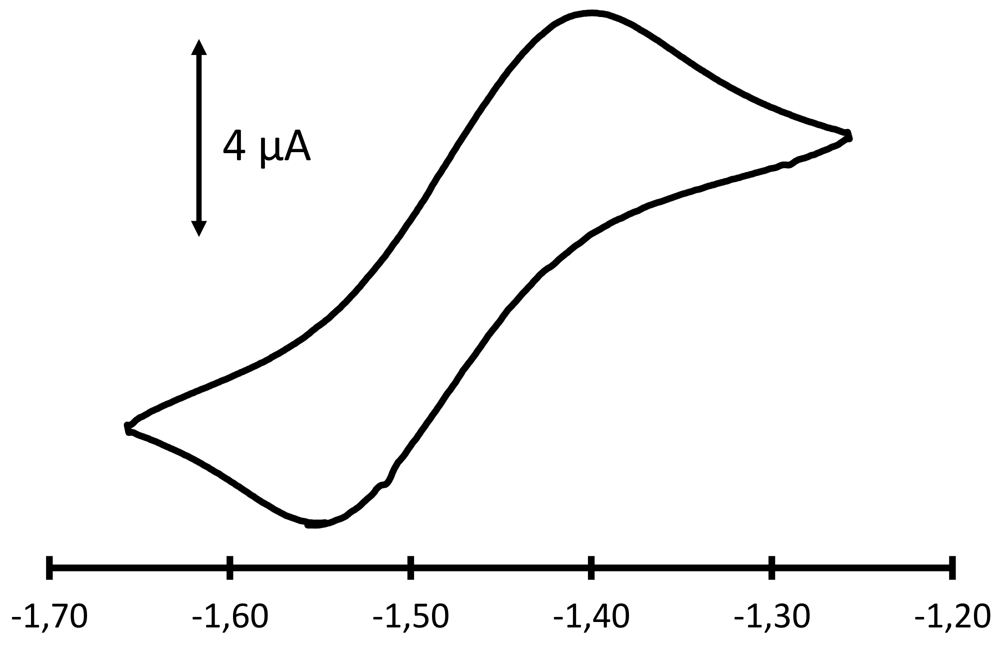


Figure S34: Cyclic voltammogram of [K(18-c-6)(dme)][*rac*-**6**], scan rate 200mV, range from E(V)=−1.7 to −1.2, E vs. FcH/FcH+.

[K(18-c-6][*rac*-**7**]

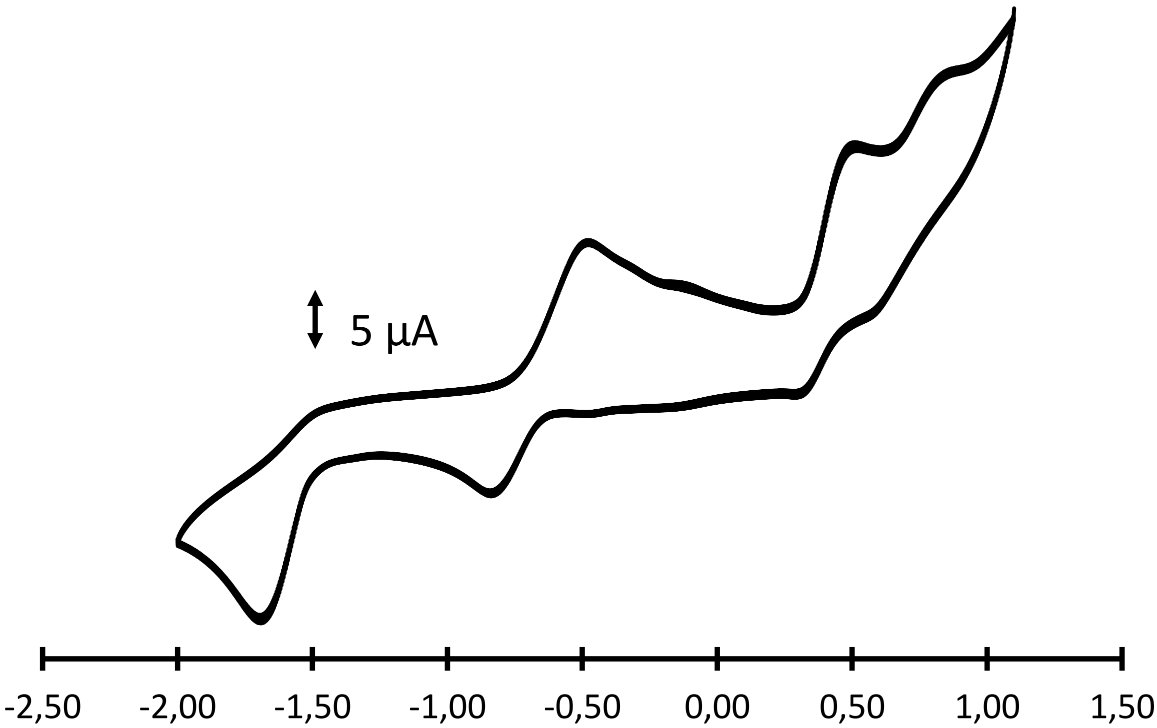


Figure S35: Cyclic voltammogram of [K(18-c-6)][*rac*-**7**], scan rate 200mV, range from E(V)=−2.5 to +1.0, E vs. FcH/FcH$^+$.

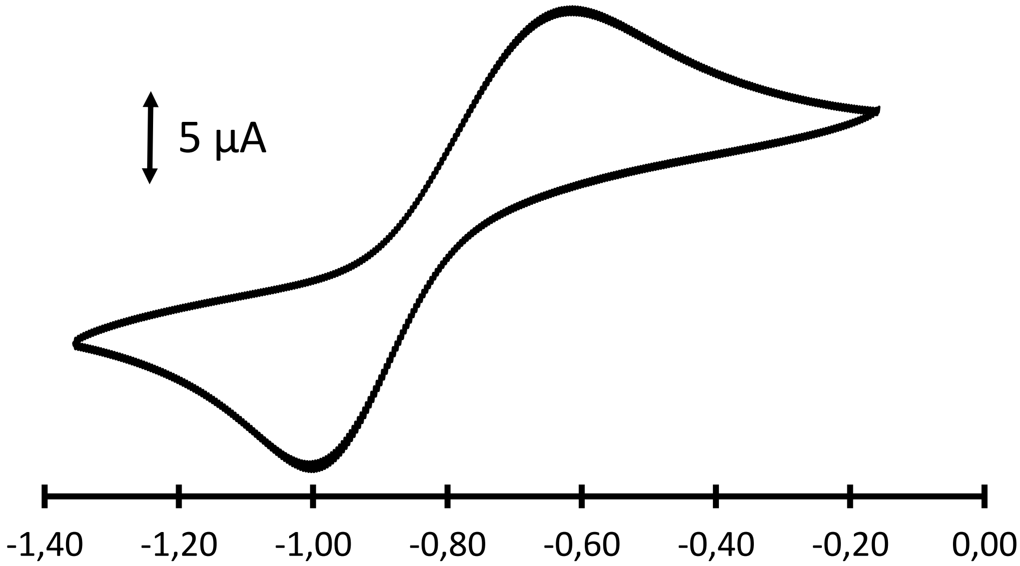


Figure S36: Cyclic voltammogram of [K(18-c-6)][*rac*-**7**], scan rate 200mV, range from E(V)=−1.4 to 0.0, E vs. FcH/FcH$^+$.

[K(18-c-6)][*meso*-**8**]

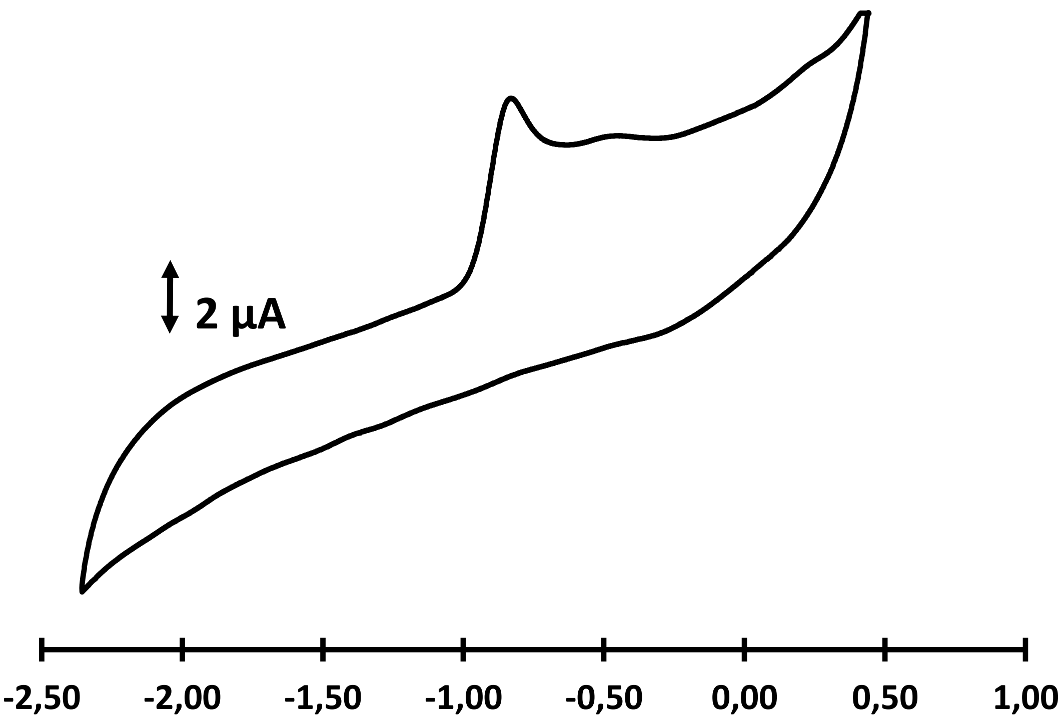


Figure S37: Cyclic voltammogram of [K(18-c-6)][*meso*-**8**], scan rate 200mV, range from E(V)=−2.5 to +1.0, E vs. FcH/FcH$^+$.

[K(18-c-6)]$_2$[*rac*-**9**]

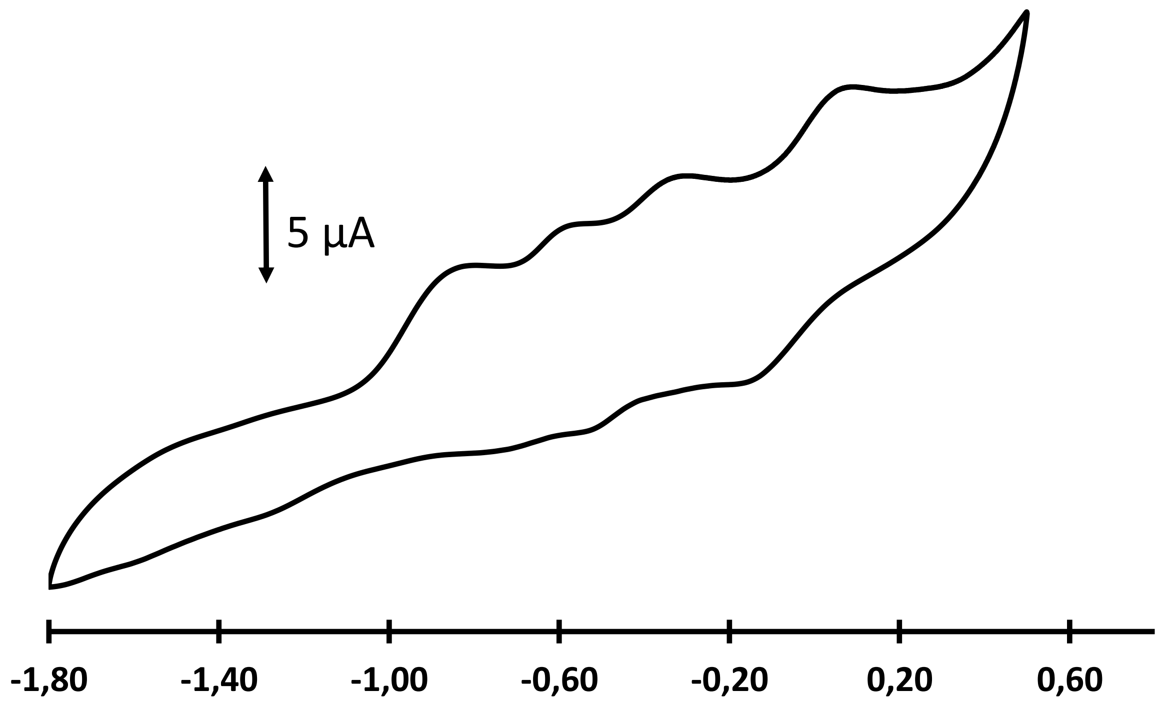
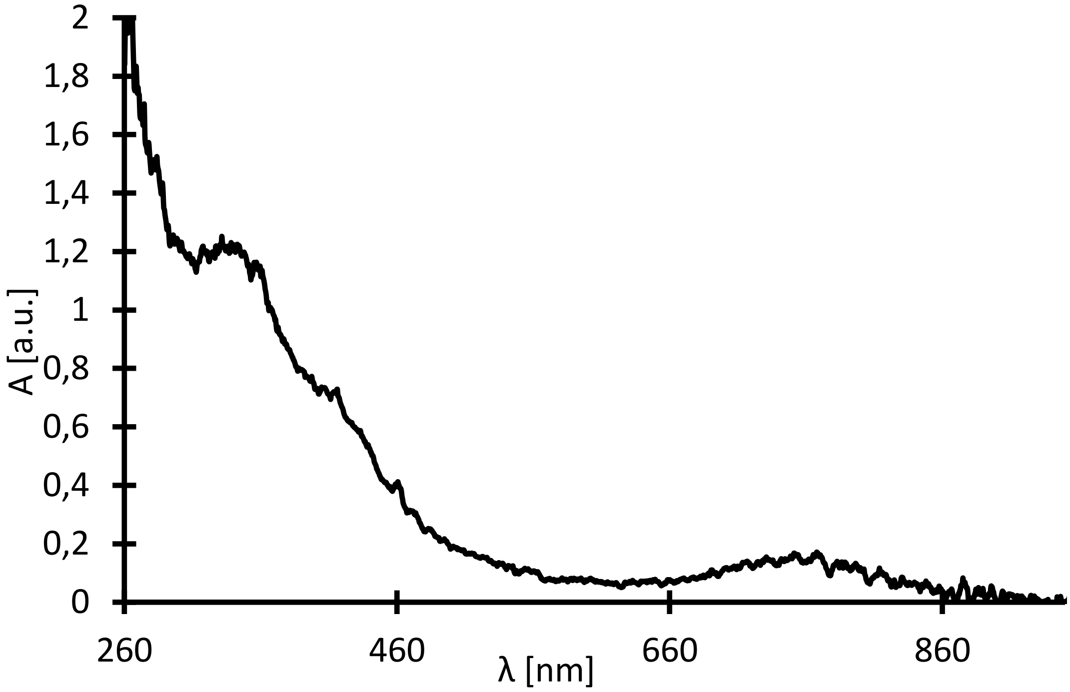


Figure S38: Cyclic voltammogram of [K(18-c-6)]$_2$[*rac*-**9**], scan rate 200mV, range from E(V)=−1.8 to +0.6, E vs. FcH/FcH$^+$.

10.UV-vis spectra and TDDFT results

The following section contains the measured and calculated UV-vis spectra of all complexes. The calculated spectra are in reasonable agreement with the experimental spectra and show the typical blue-shift when using range-separated hybrid functionals. In addition, the difference densities of selected transitions are given to identify the nature of the observed maxima. For **9**$^{2-}$, spectra were calculated using a standard closed-shell wavefunction and a broken-symmetry wavefunction. However, the differences between both spectra are neglicible, indicating that the antiferromagnetic coupling between the cobalt atoms in [*rac*-**9**]$^{2-}$ does not influence the transition energies significantly.

[K(18-c-6)(thf)][**rac-1**]



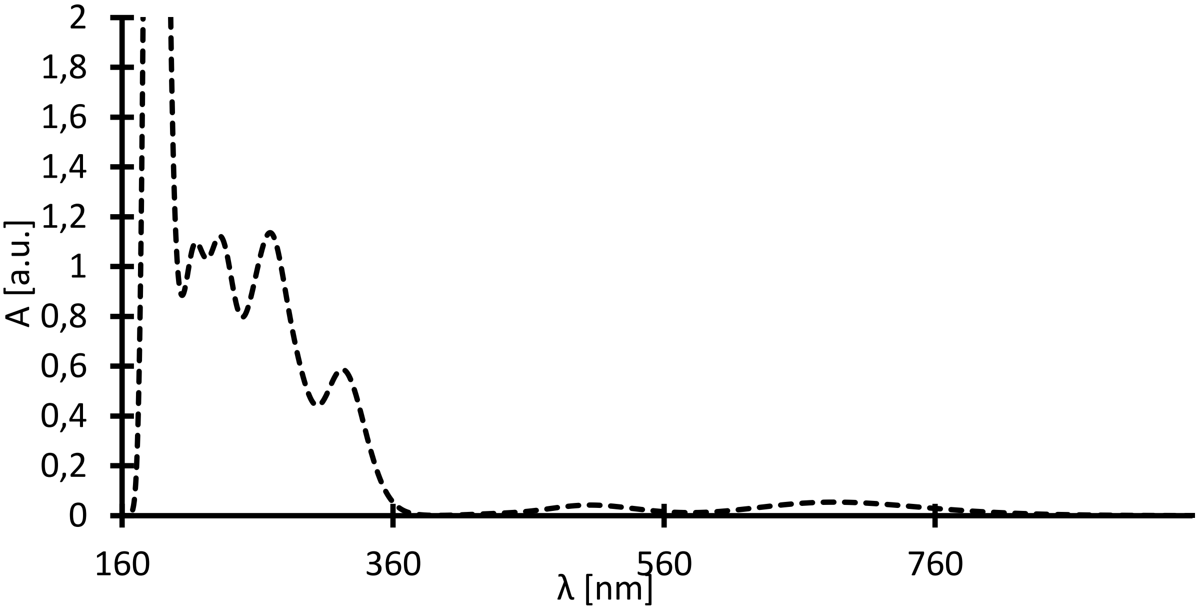
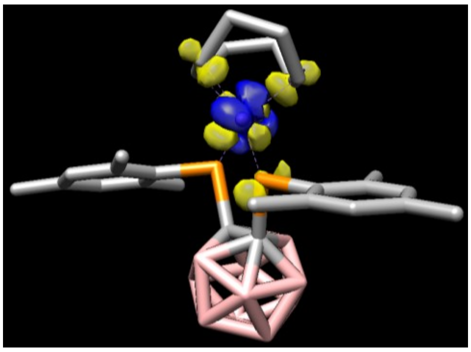
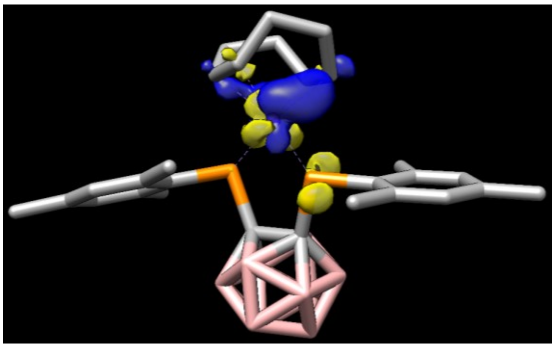


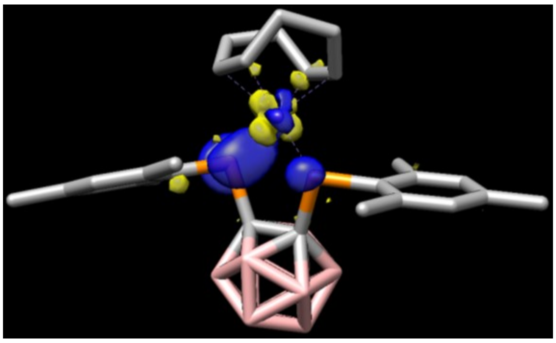
Figure S39: UV-vis spectrum of [K(18-c-6)(thf)][*rac*-**1**] in THF (line: experimental data, dotted: calculated spectrum).



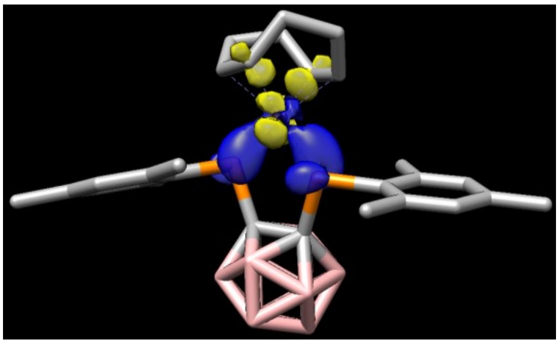
2 (683 nm, f_{osc} = 0.012)



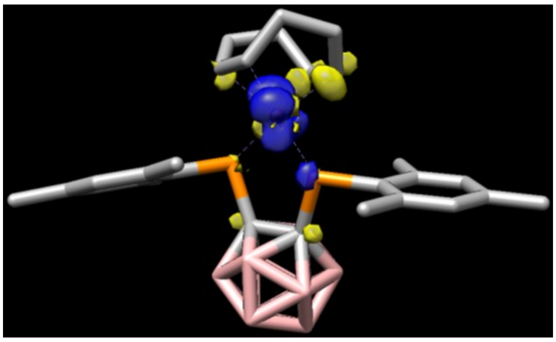
3 (506 nm, f_{osc} = 0.011)



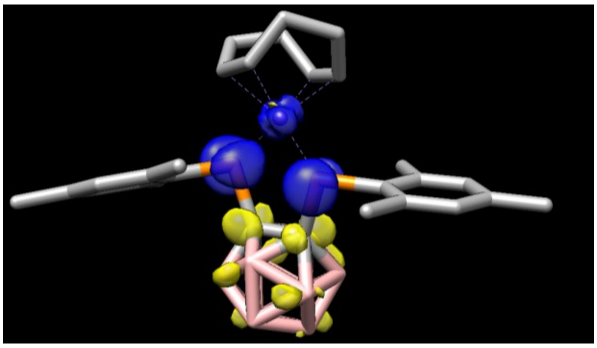
6 (332 nm, f_{osc} = 0.056)



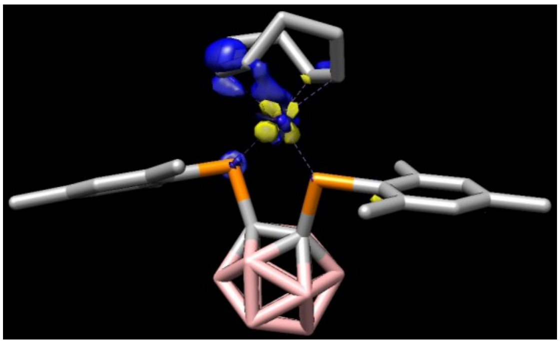
7 (320 nm, f_{osc} = 0.091)



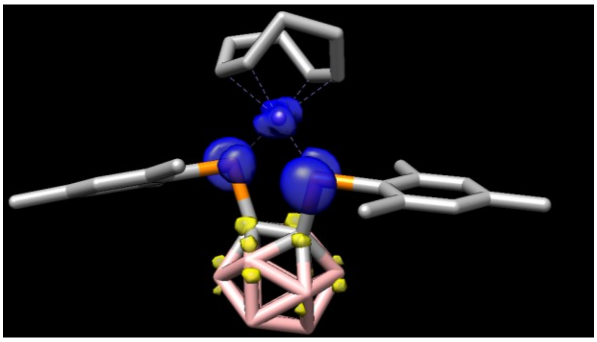
12 (270 nm, f_{osc} = 0.140)



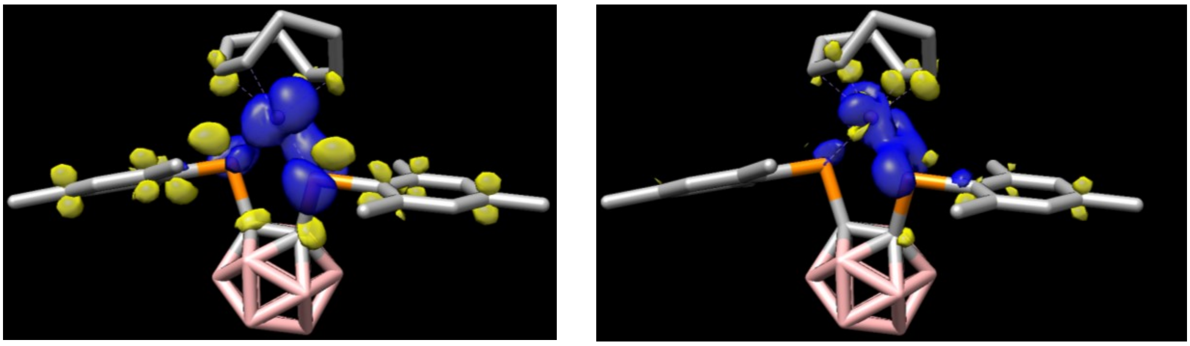
13 (274 nm, f_{osc} = 0.075)



25 (233 nm, f_{osc} = 0.054)



28 (230 nm, f_{osc} = 0.095)

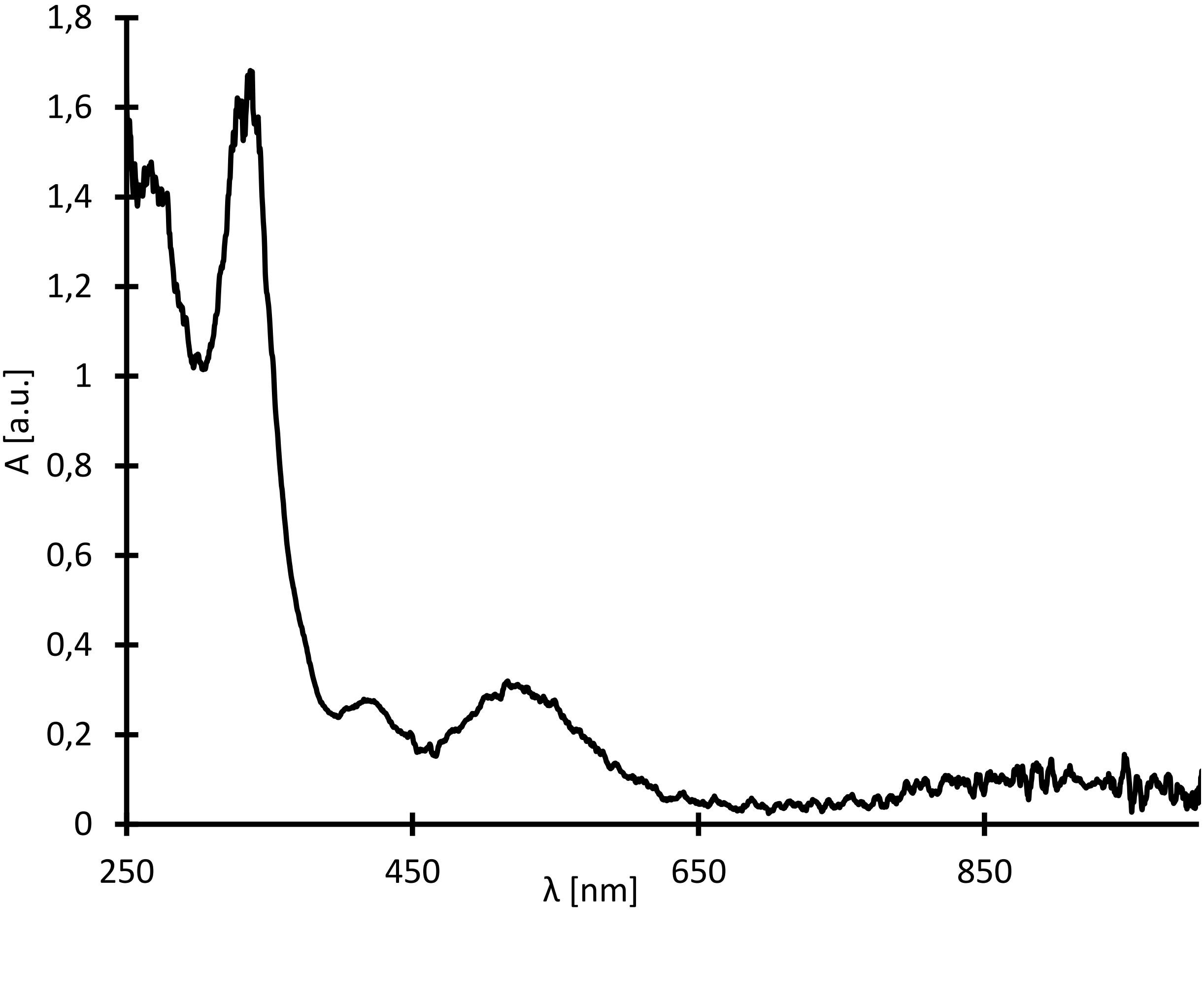


30 (223 nm, f_{osc} = 0.032)

35 (214 nm, f_{osc} = 0.033)

Figure S40: Difference densities of calculated excited states of [*rac*-**1**]⁻ (transitions proceed from blue to yellow). The calculated wavelength of the absorption and the oscillator strength are given in parentheses.

***rac*-2**



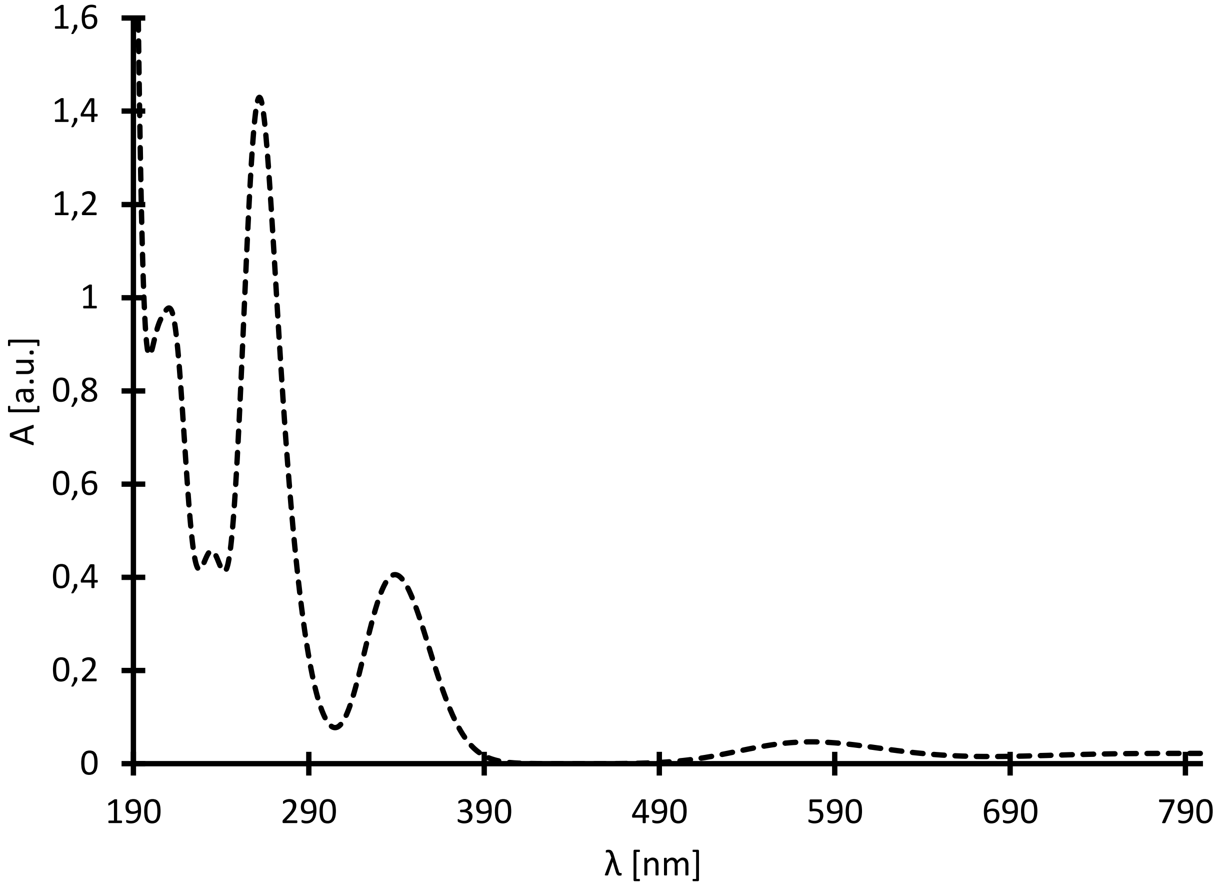
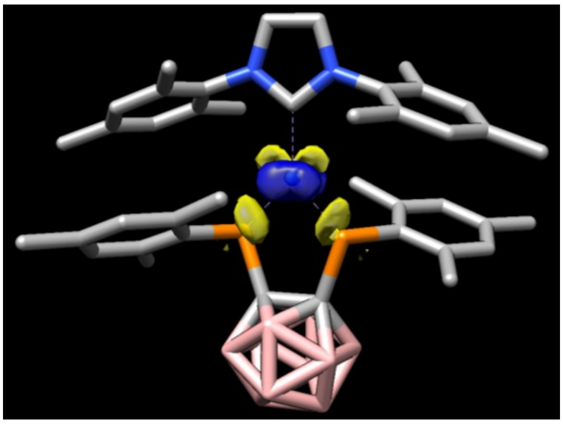
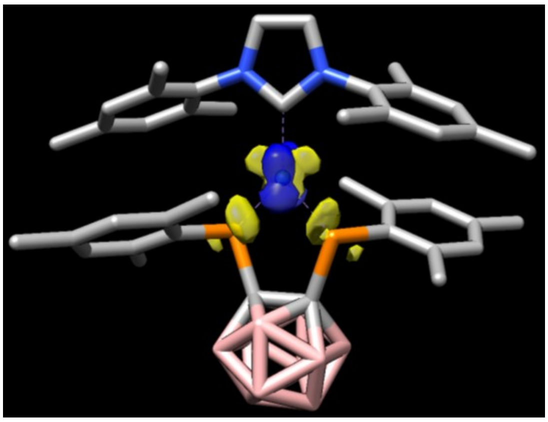


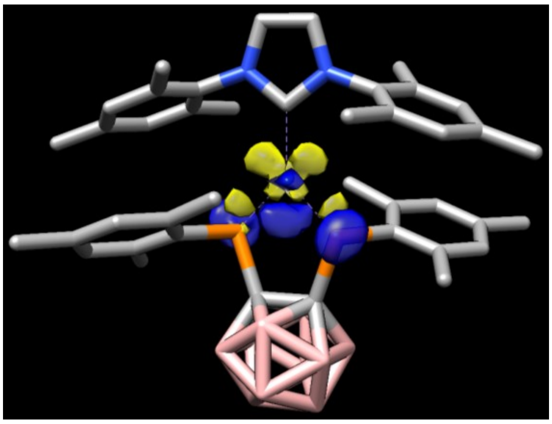
Figure S41: UV-vis spectrum of *rac*-**2** in THF (line: experimental data, dotted: calculated spectrum).



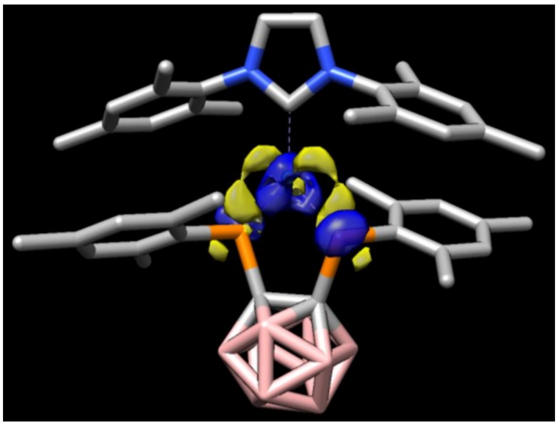
2 (771 nm, f_{osc} = 0.004)



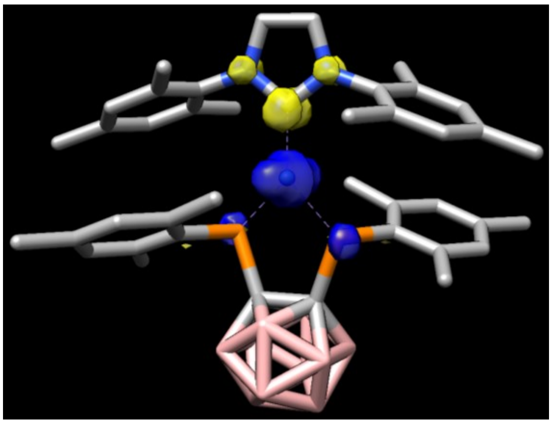
3 (741 nm, f_{osc} = 0.002)



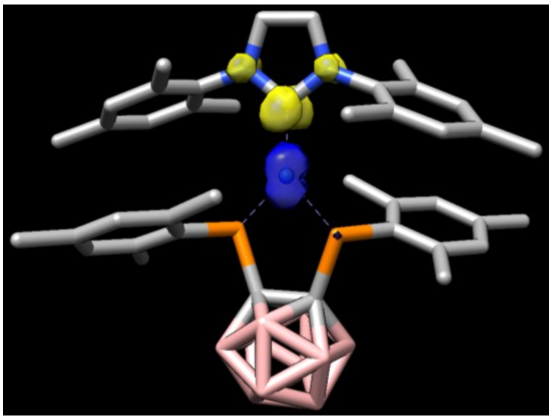
5 (350 nm, f_{osc} = 0.064)



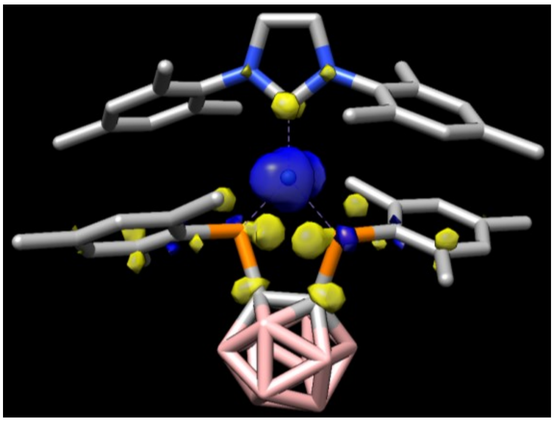
6 (332 nm, f_{osc} = 0.083)



11 (263 nm, f_{osc} = 0.232)



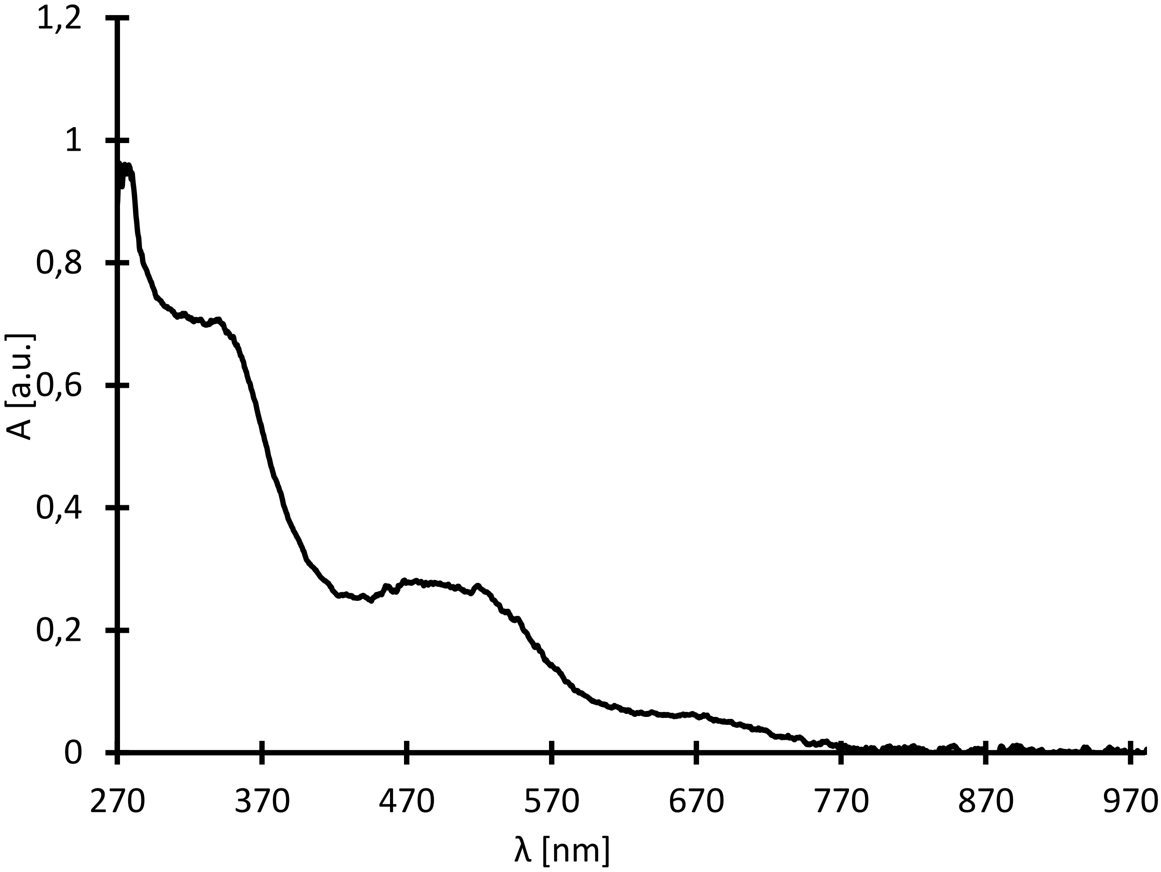
12 (258 nm, f_{osc} = 0.161)



36 (213 nm, f_{osc} = 0.114)

Figure S42: Difference densities of calculated excited states of *rac*-**2** (transitions proceed from blue to yellow). The calculated wavelength of the absorption and the oscillator strength are given in parentheses.

[K(18-c-6)(dme)][*rac*-**6**]



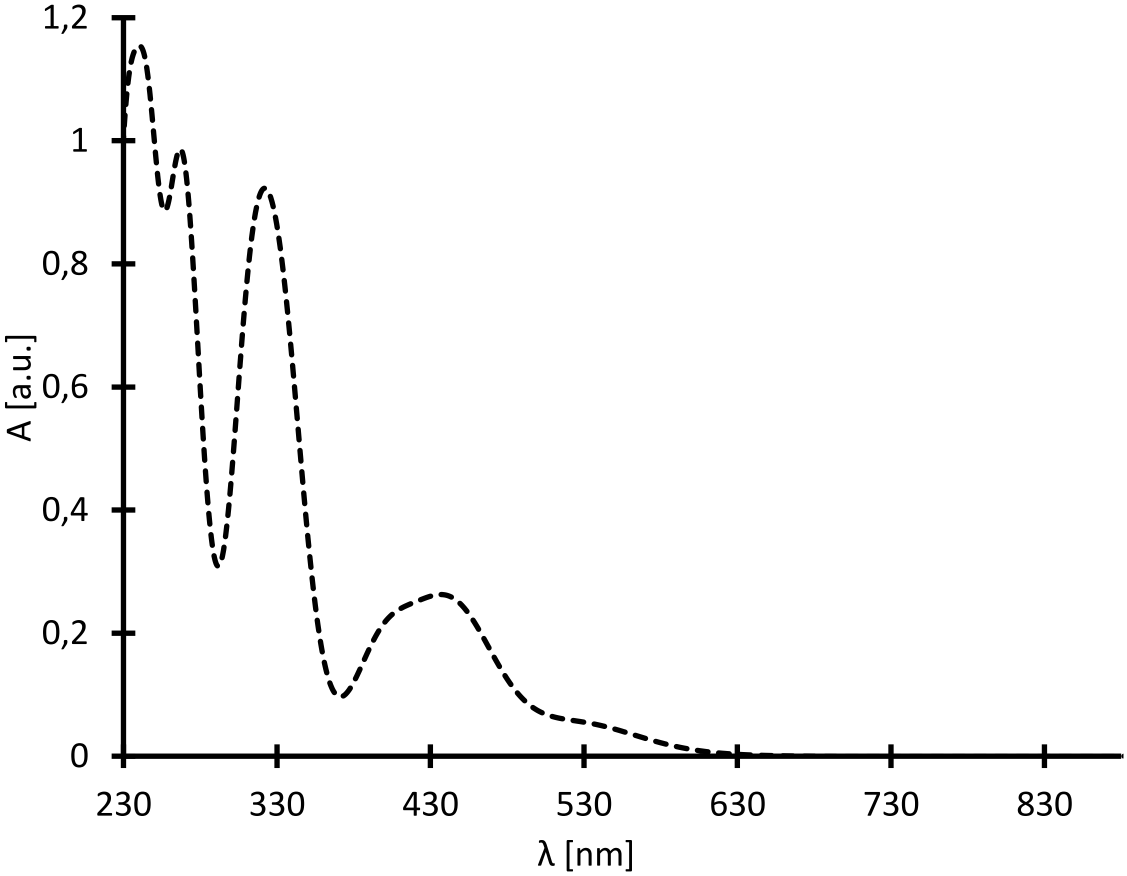
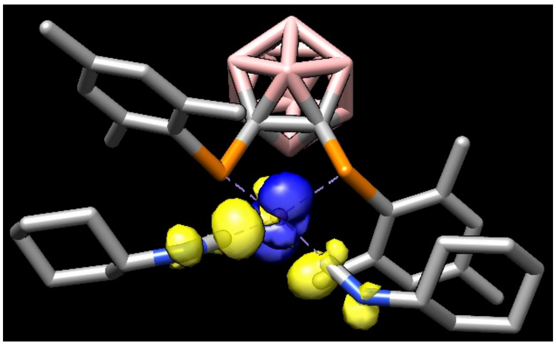
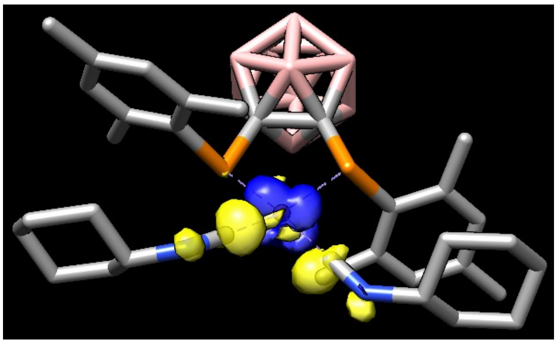


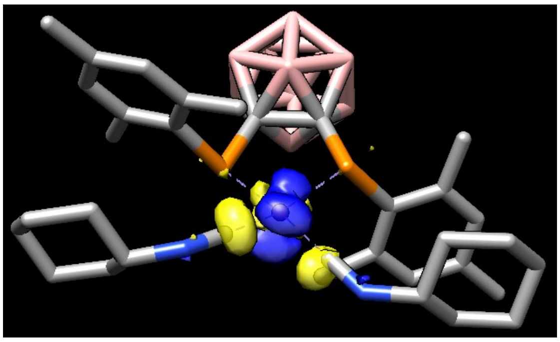
Figure S43: UV-vis spectrum of [K(18-c-6)(dme)][*rac*-**6**] in THF (line: experimental data, dotted: calculated spectrum).



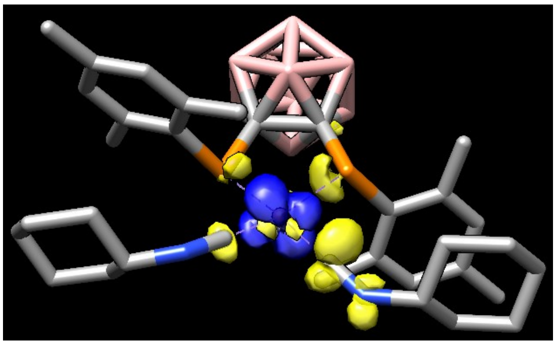
1 (529 nm, f_{osc} = 0.009)



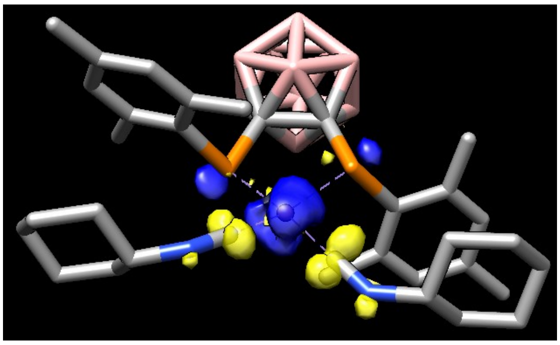
2 (447 nm, f_{osc} = 0.039)



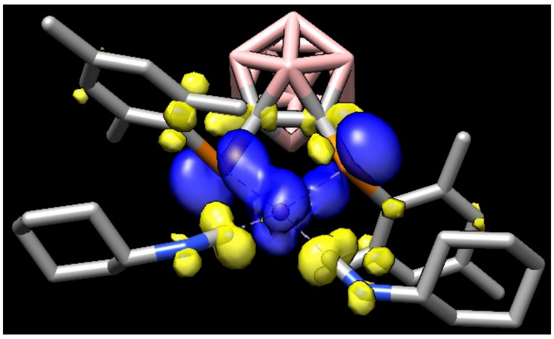
3 (403 nm, f_{osc} = 0.030)



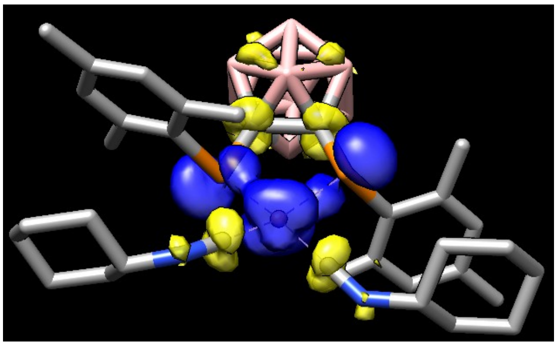
7 (334 nm, f_{osc} = 0.084)



9 (314 nm, f_{osc} = 0.081)



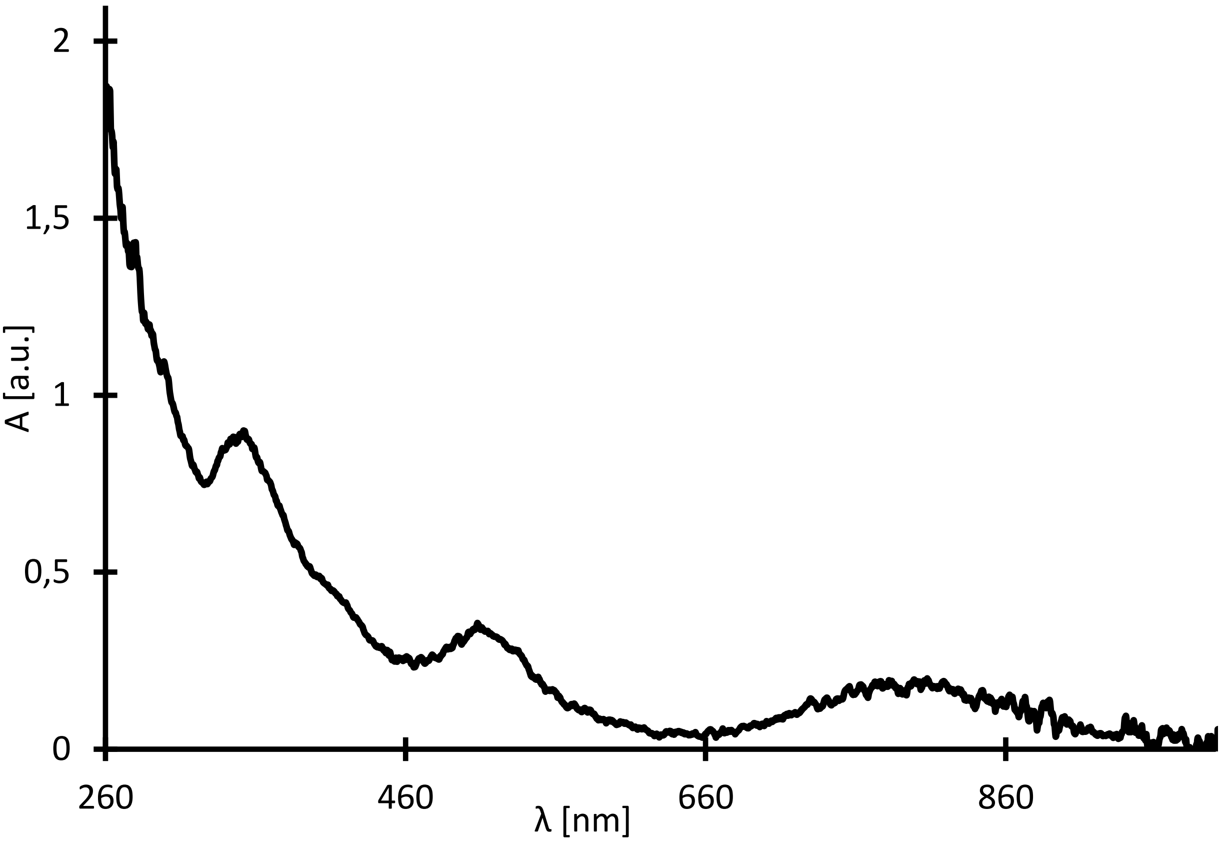
19 (267nm, f_{osc} = 0.071)



26 (243nm, f_{osc} = 0.057)

Figure S44: Difference densities of calculated excited states of [*rac*-**6**]$^{-}$ (transitions proceed from blue to yellow). The calculated wavelength of the absorption and the oscillator strength are given in parentheses.

[K(18-c-6][*rac*-**7**]



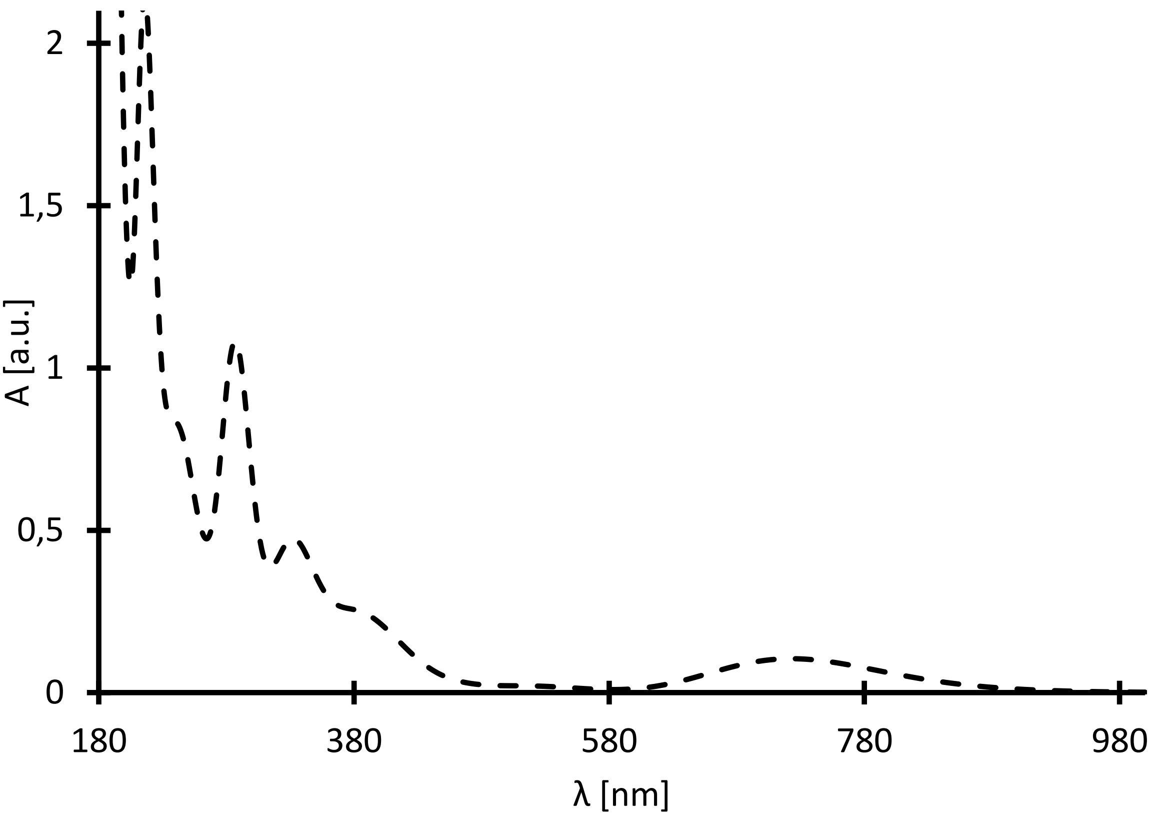
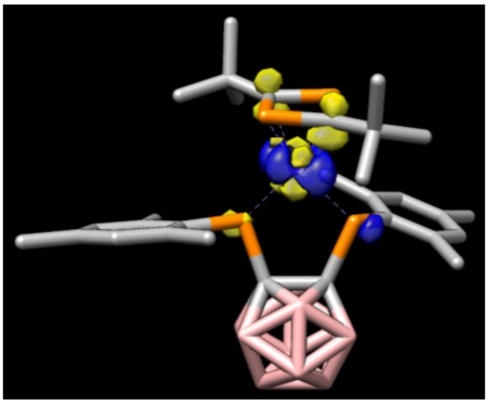
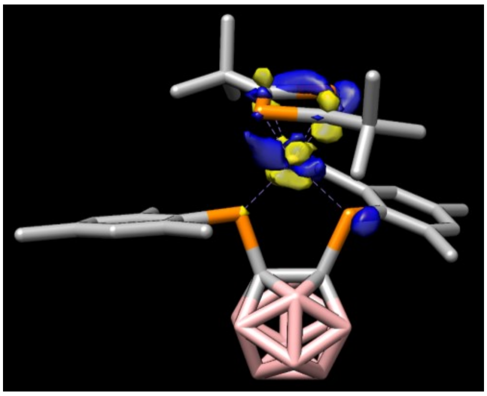


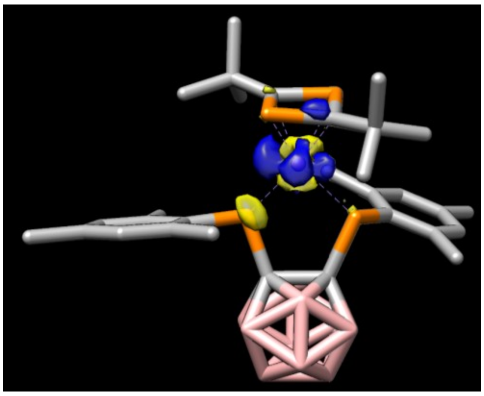
Figure S45: UV-vis spectrum of [K(18-c-6][*rac*-**7**] in THF (line: experimental data, dotted: calculated spectrum).



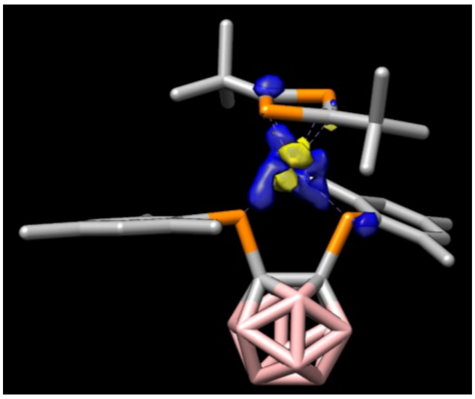
2 (722 nm, f_{osc} = 0.029)



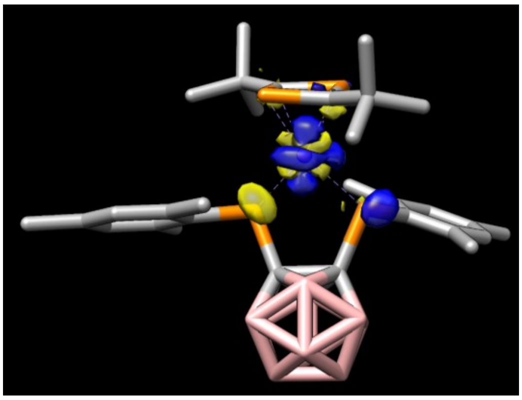
5 (418 nm, f_{osc} = 0.011)



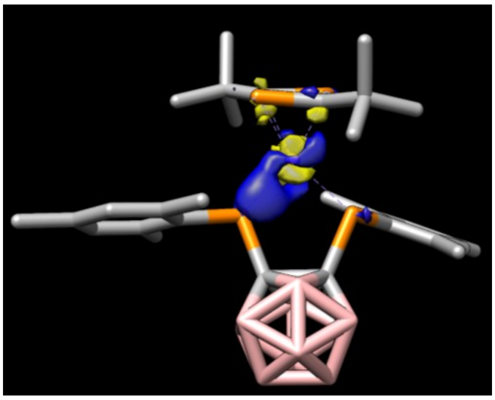
6 (408 nm, f_{osc} = 0.020)



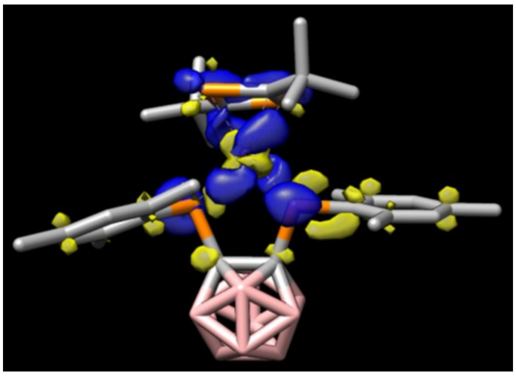
8 (380 nm, f_{osc} = 0.047)



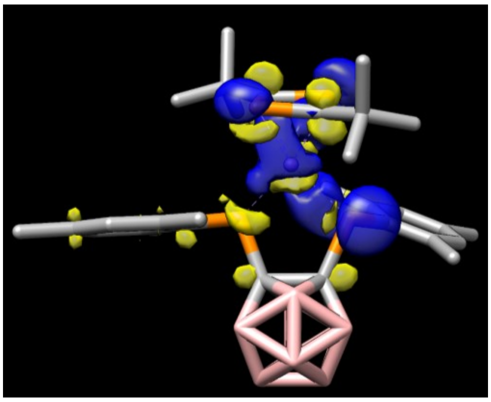
9 (351 nm, f_{osc} = 0.048)



10 (330 nm, f_{osc} = 0.099)



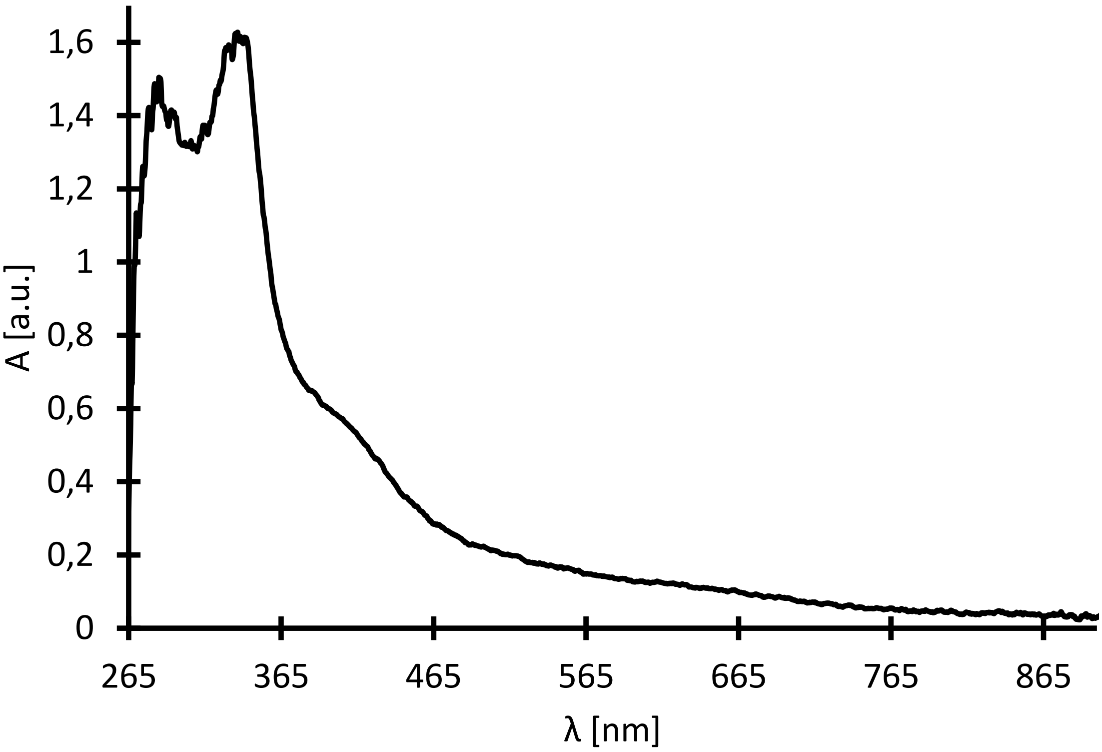
14 (288 nm, f_{osc} = 0.160)



15 (284 nm, f_{osc} = 0.113)

Figure S46: Difference densities of calculated excited states of [*rac*-**7**]$^{-}$ (transitions proceed from blue to yellow). The calculated wavelength of the absorption and the oscillator strength are given in parentheses.

[K(18-c-6)][*meso*-**8**]



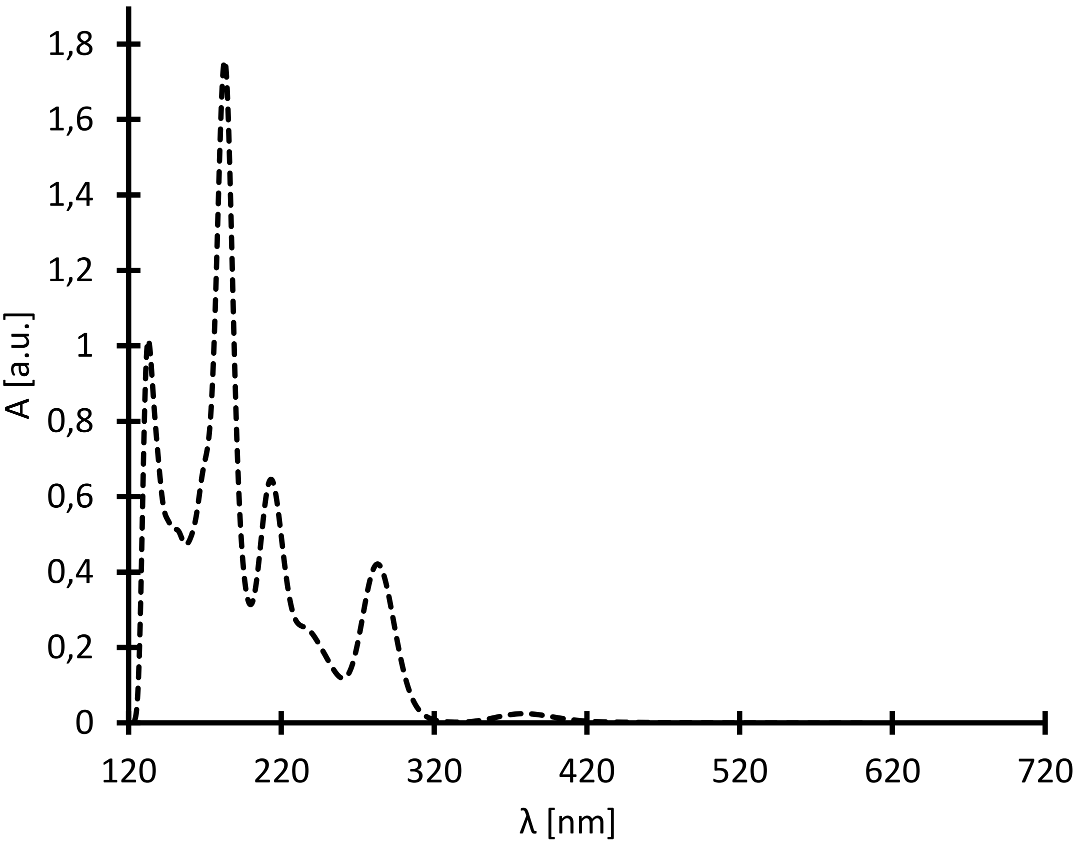
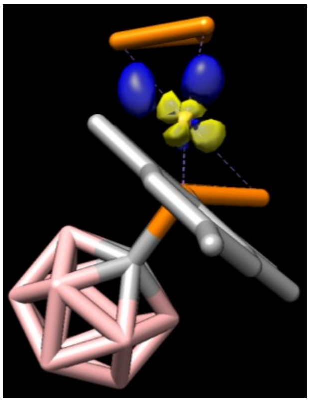
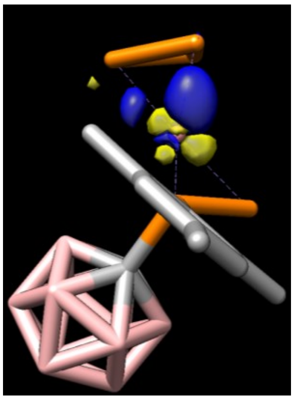


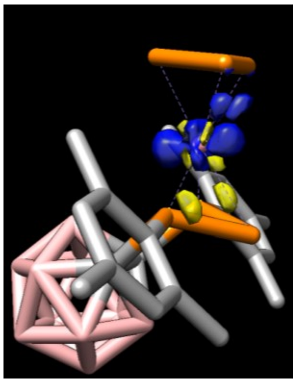
Figure S47: UV-vis spectrum of [K(18-c-6)][*meso*-**8**] in THF (line: experimental data, dotted: calculated spectrum).



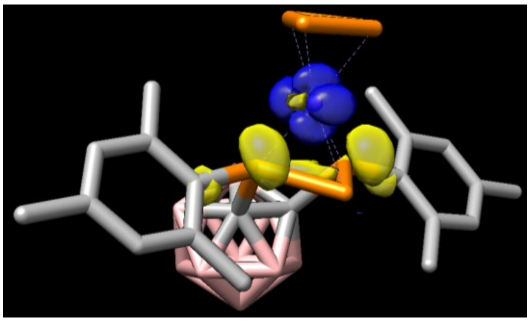
7 (384 nm, f_{osc} = 0.015)



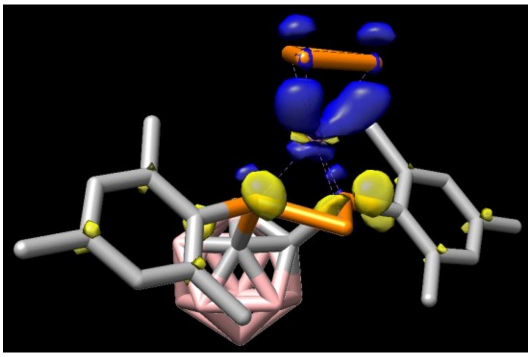
8 (375 nm, f_{osc} = 0.019)



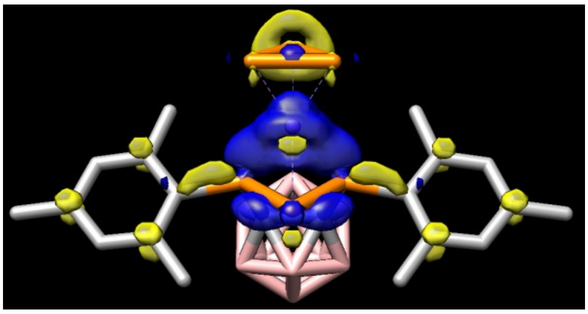
13 (283 nm, f_{osc} = 0.403)



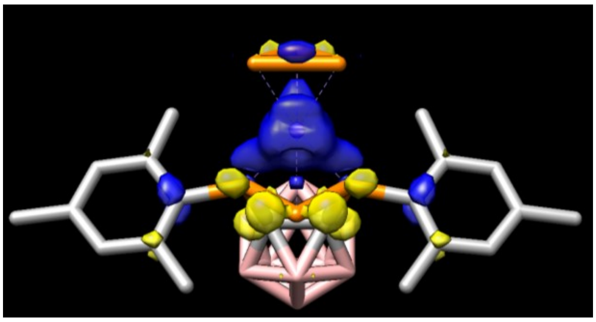
14 (280 nm, f_{osc} = 0.104)



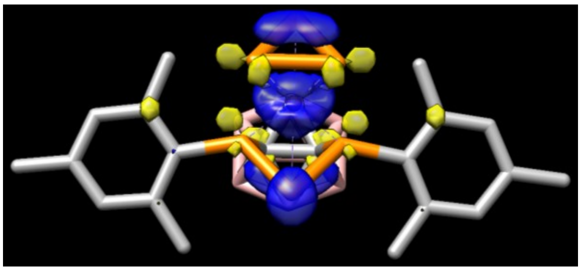
15 (286 nm, f_{osc} = 0.056)



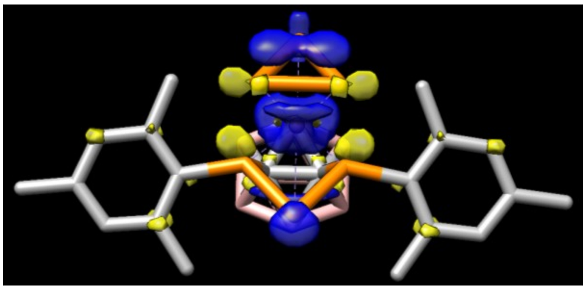
52 (215nm, f_{osc} = 0.220)



53 (215nm, f_{osc} = 0.101)



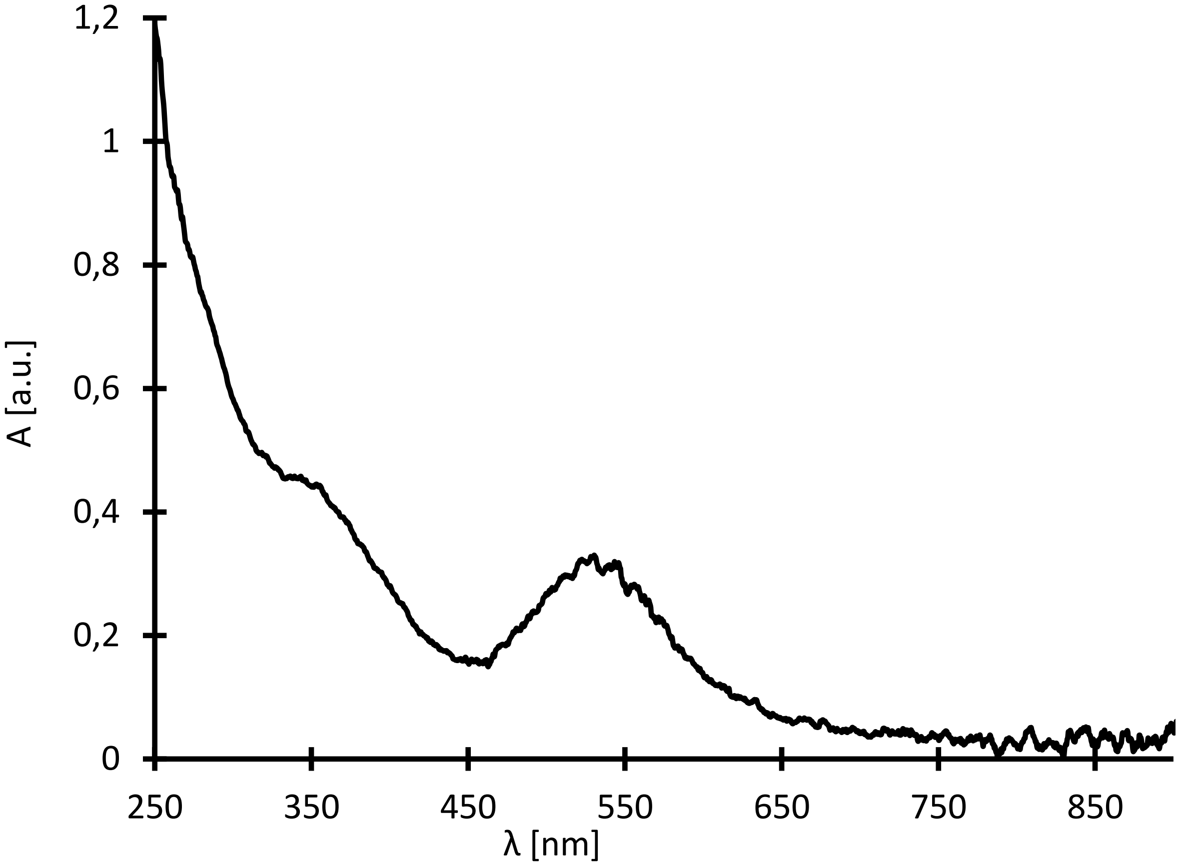
97 (184 nm, f_{osc} = 0.127)



98 (184 nm, f_{osc} = 0.217)

Figure S48: Difference densities for selected transitions of [*meso*-**8**]$^{–}$ (transitions proceed from blue to yellow). The calculated wavelength of the absorption and the oscillator strength are given in parentheses.

[K(18-c-6)]$_2$[*rac*-**9**]



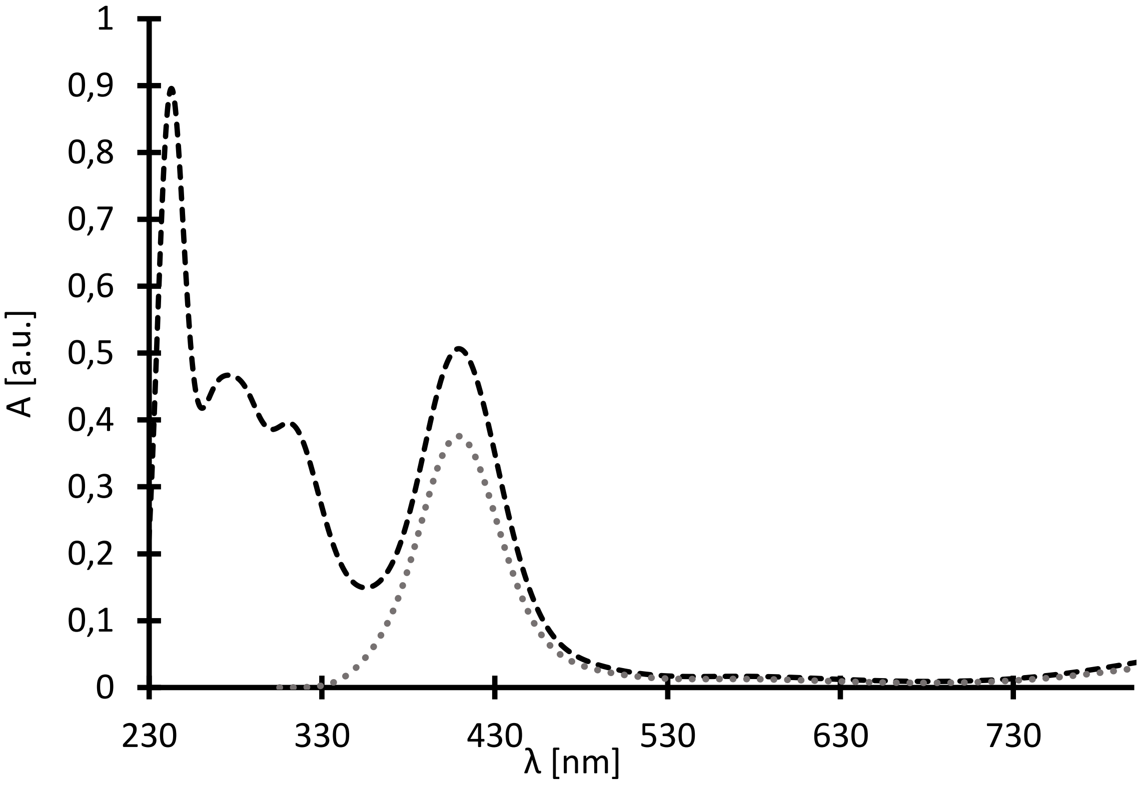
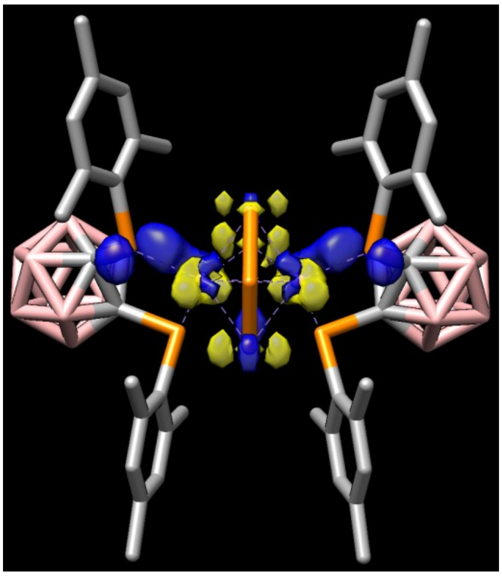
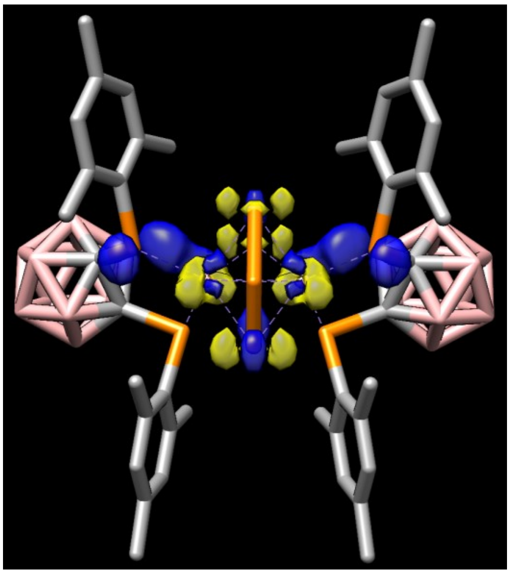


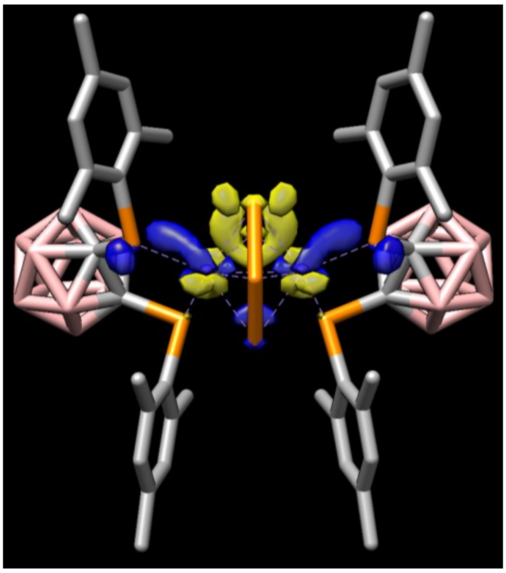
Figure S49: UV-vis spectrum of [K(18-c-6)]$_2$[*rac*-**9**] in THF (line: experimental data, dotted: calculated spectrum (black: standard DFT, grey: BS-DFT).



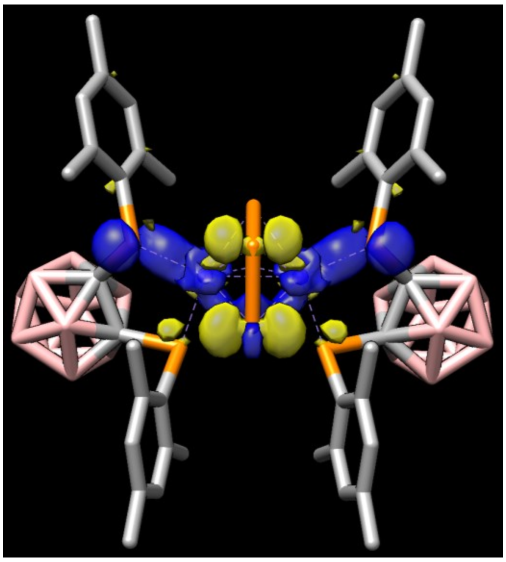
34 (BS, 410 nm, f_{osc} = 0.279)



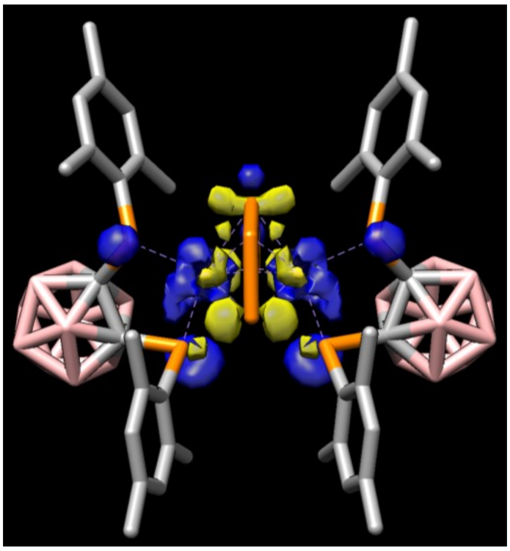
14 (410 nm, f_{osc} = 0.308)

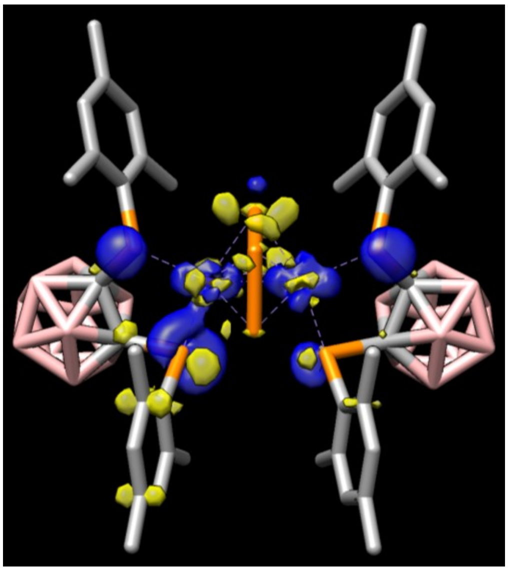


32 (314 nm, f_{osc} = 0.076)



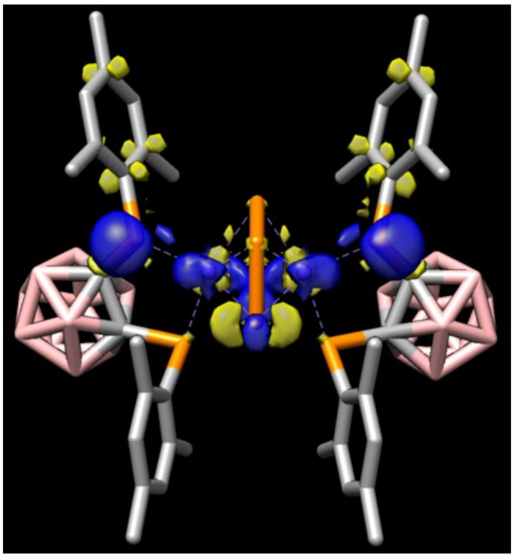
34 (308 nm, f_{osc} = 0.082)





39 (292 nm, f_{osc} = 0.080)

41 (286nm, f_{osc} = 0.049)

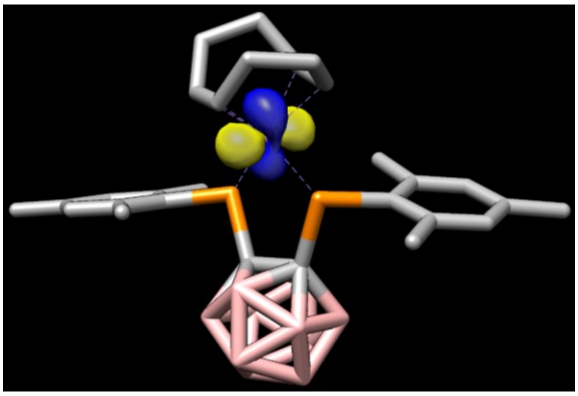


43 (282nm, f_{osc} = 0.071)

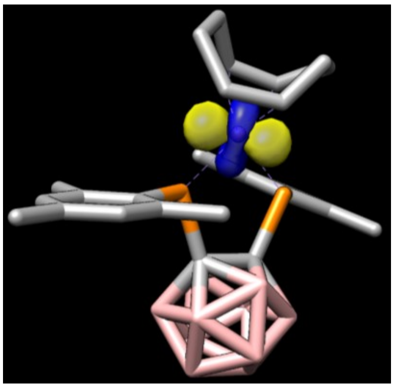
Figure S50: Difference densities for selected transitions of [*rac*-**9**]$^{2-}$ (transitions proceed from blue to yellow). The calculated wavelength of the absorption and the oscillator strength are given in parentheses.

11.Relevant Natural Orbitals obtained from CASSCF calculations

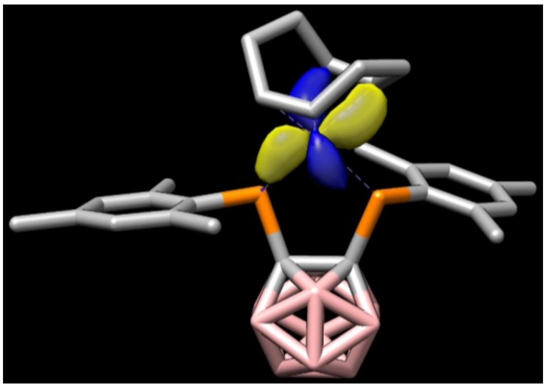
[*rac*-1]⁻



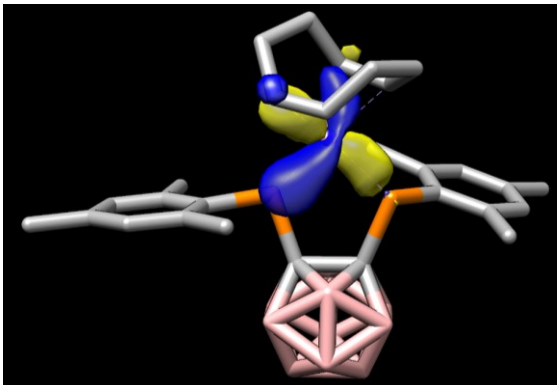
155 (1.969, 84%)



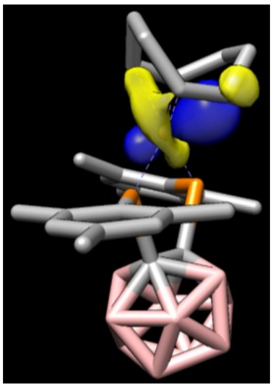
156 (1.960, 92%)



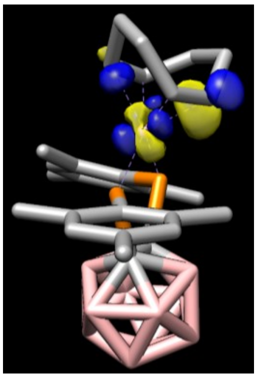
157 (1.931, 77%)



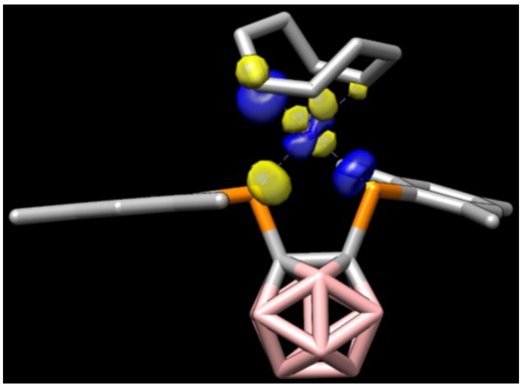
158 (1.927, 57%)



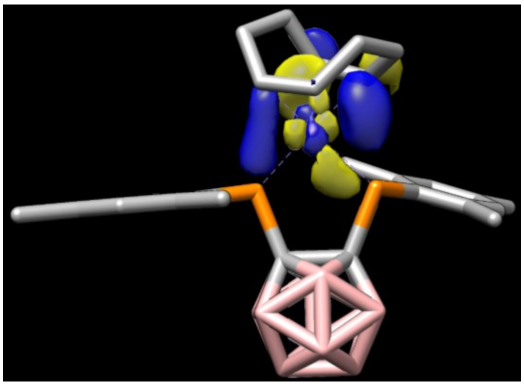
159 (1.906, 62%)



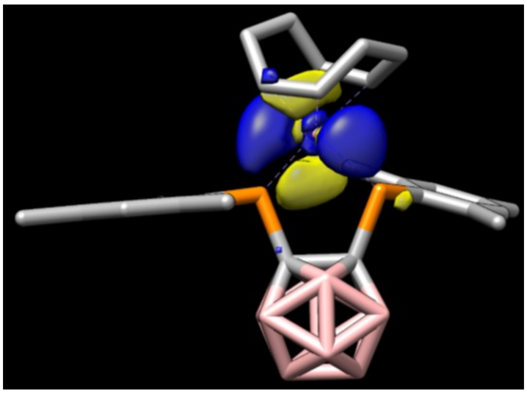
160 (0.099, 59%)



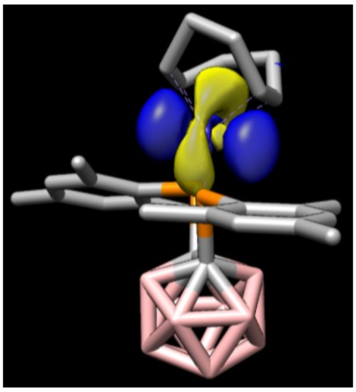
161 (0.080, 61%)



162 (0.067)



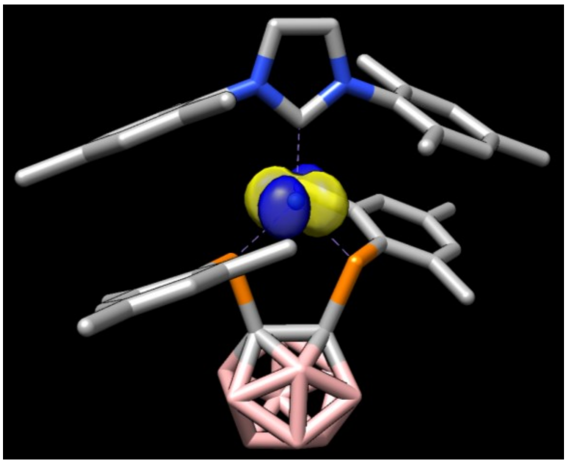
163 (0.034)



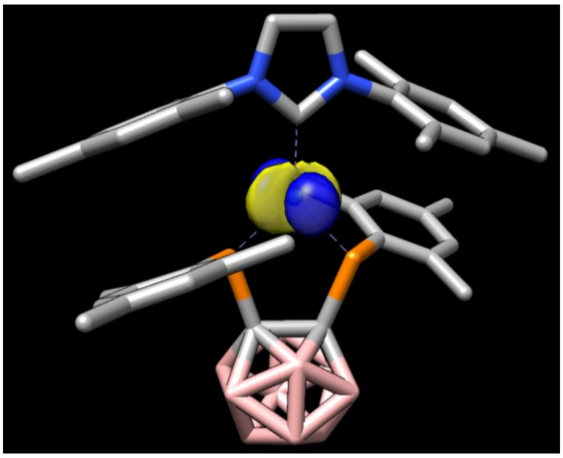
164 (0.028)

Figure S51: Natural orbitals of the active space describing the ground-state of [*rac*-**1**]⁻. Contributions of 3d orbitals on cobalt and orbital occupations are given in parentheses.

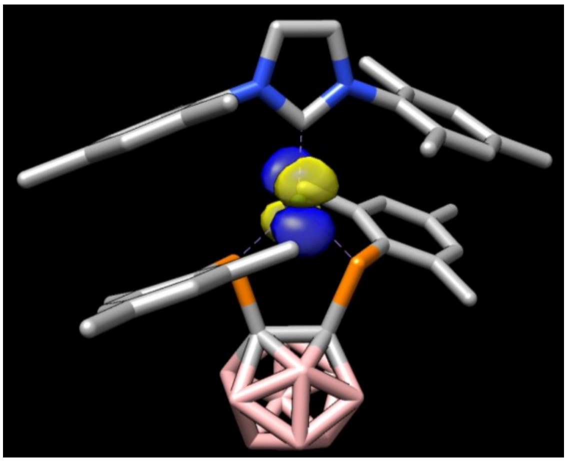
***rac*-2**



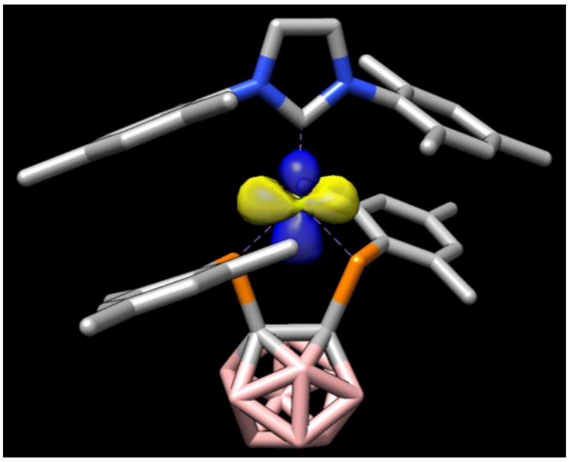
207 (1.976, 97%)



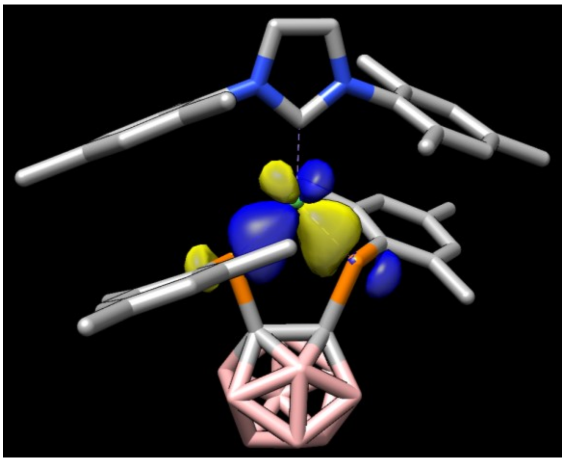
208 (1.974, 96%)



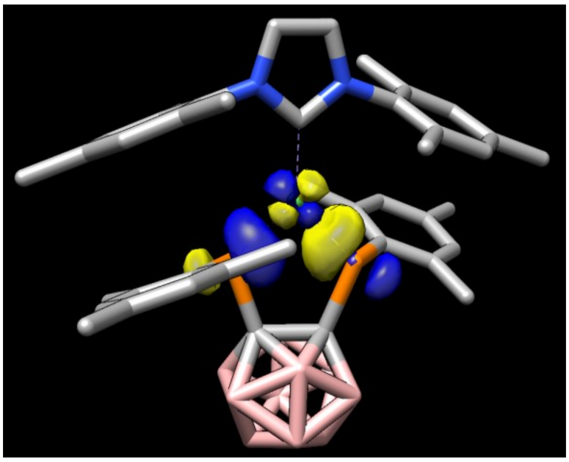
209 (1.971, 93%)



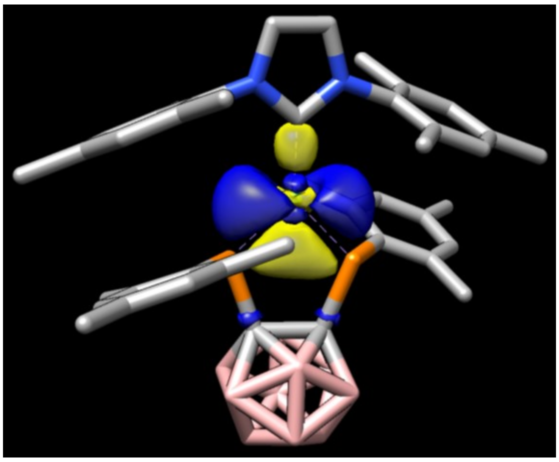
210 (1.965, 89%)



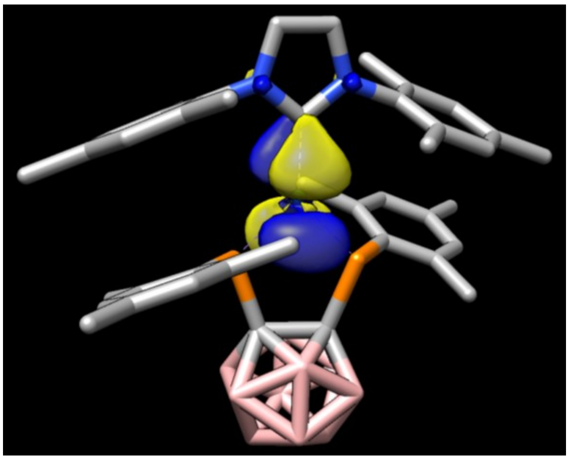
211 (1.912, 61%)



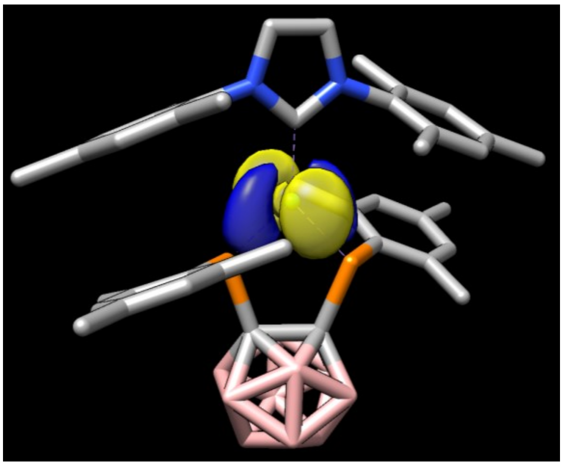
212 (0.093, 56%)



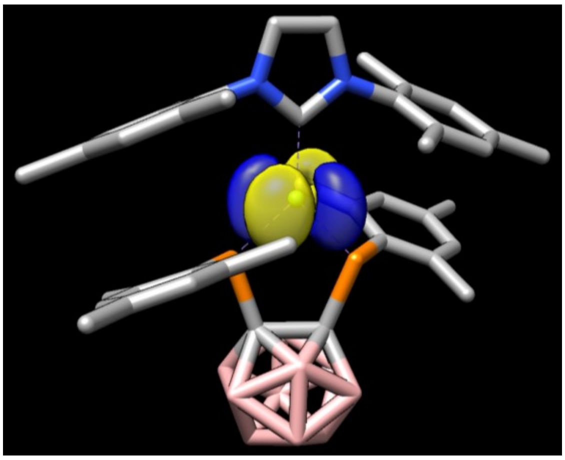
213 (0.035)



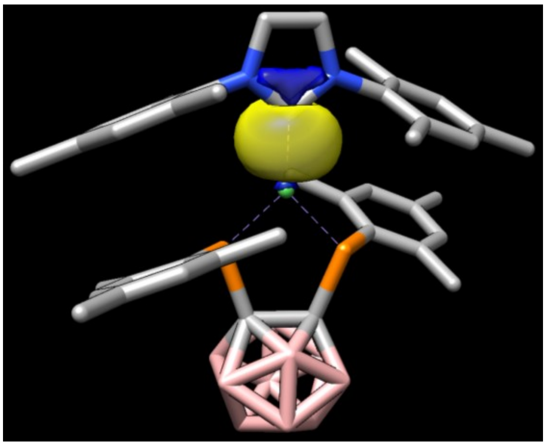
214 (0.028)



215 (0.024)



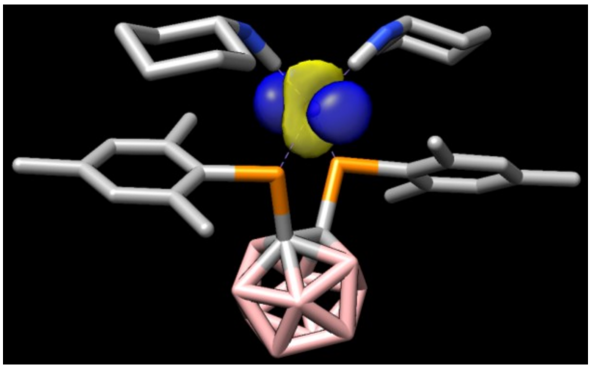
216 (0.022)



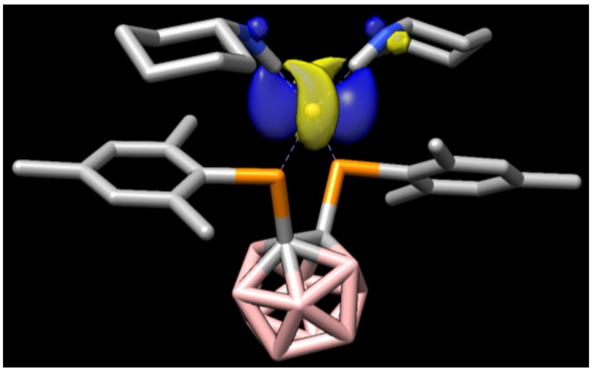
128 (2.000)

Figure S52: Natural orbitals of the active space describing the ground-state of *rac*-**2**. In addition, the nickel-carbene bonding orbital is shown as well (128). Contributions of 3d orbitals on cobalt and orbital occupations are given in parentheses.

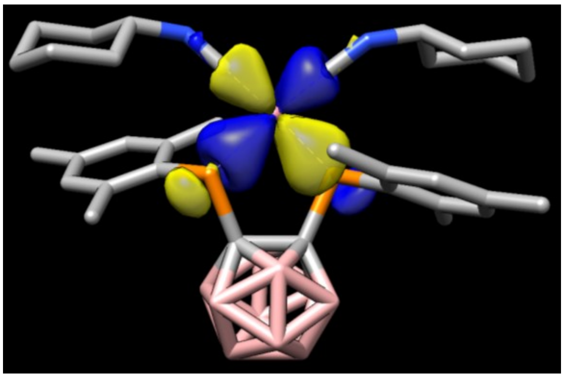
[*rac*-6]⁻



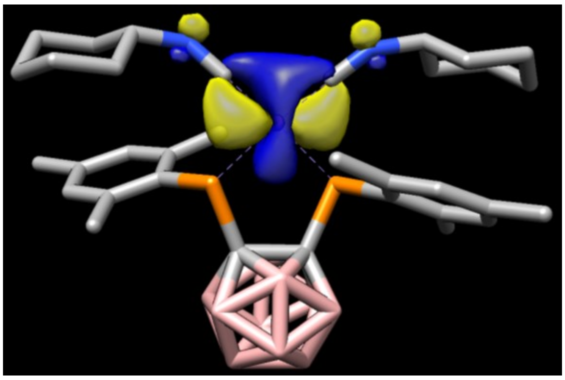
185 (1.959, 91%)



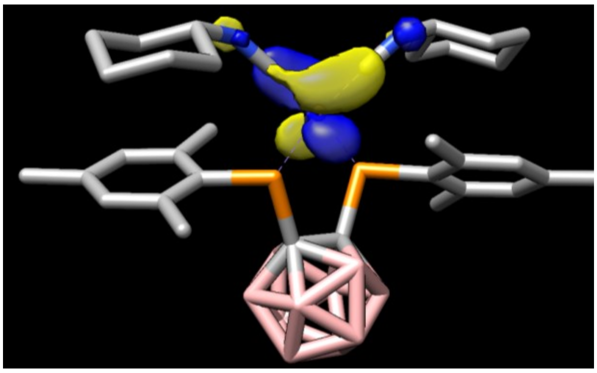
186 (1.948, 87%)



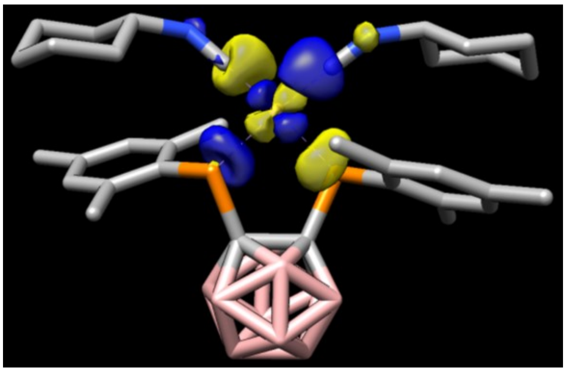
187 (1.944, 54%)



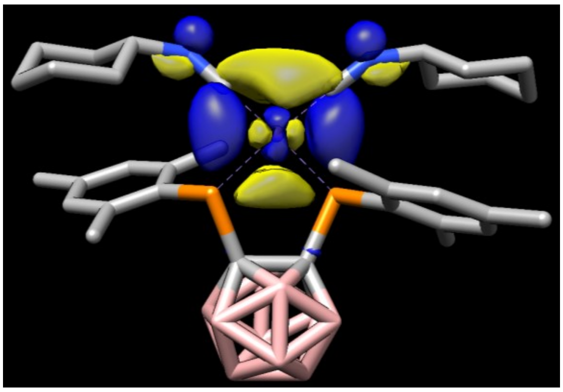
188 (1.937, 80%)



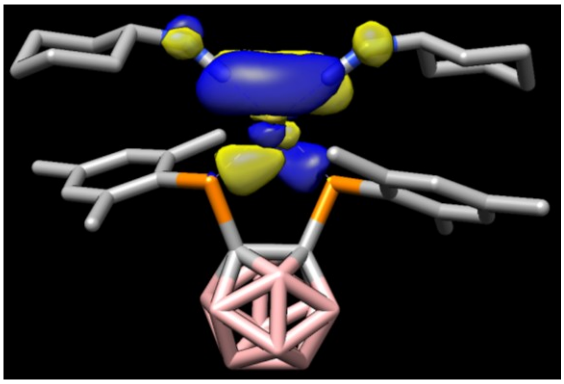
189 (1.934, 81%)



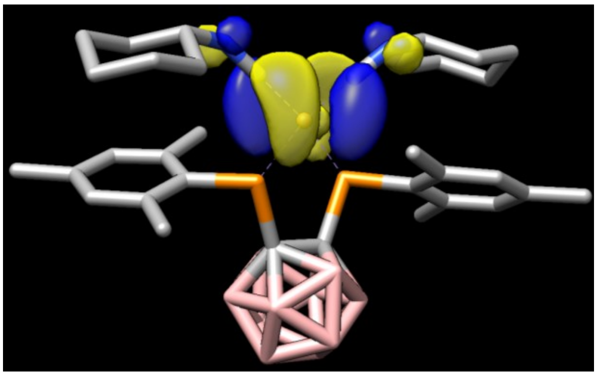
190 (0.069, 69%)



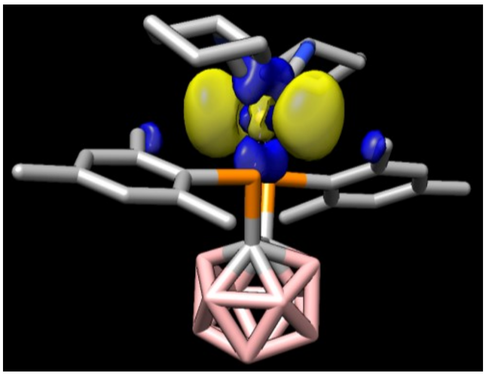
191 (0.064, 61%)



192 (0.063)



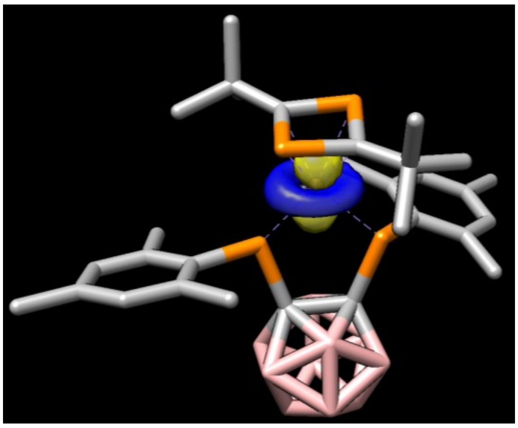
193 (0.049)



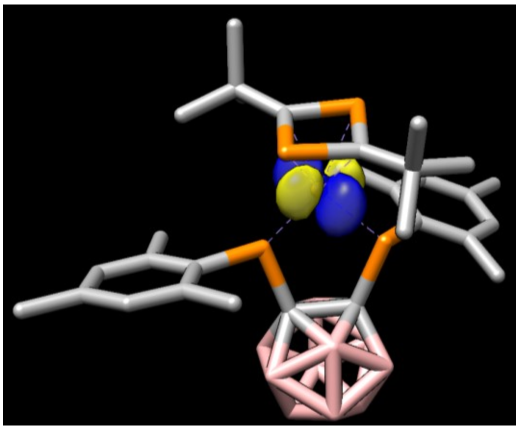
194 (0.036)

Figure S53: Natural orbitals of the active space describing the ground-state of [*rac*-**6**]⁻. Contributions of 3d orbitals on cobalt and orbital occupations are given in parentheses.

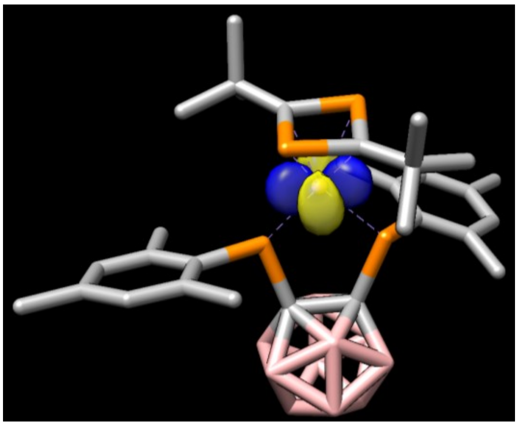
[*rac*-**7**]⁻



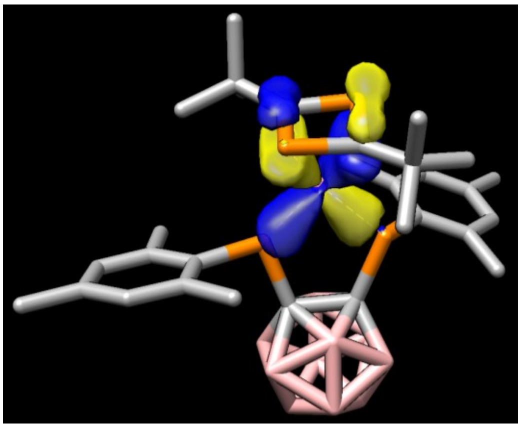
179 (1.997, 92%)



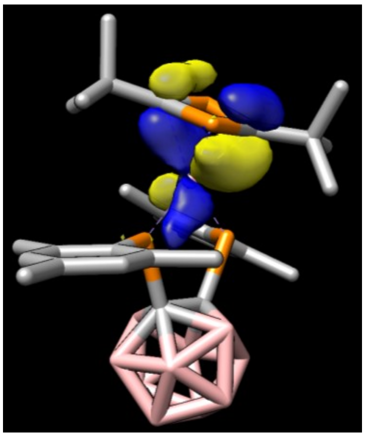
180 (1.978, 93%)



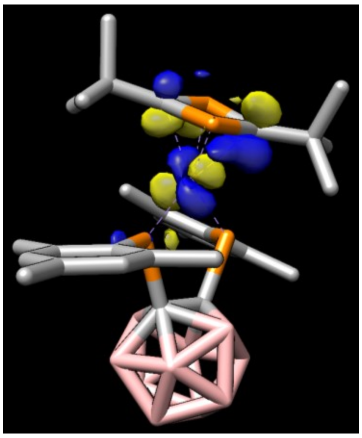
181 (1.977, 95%)



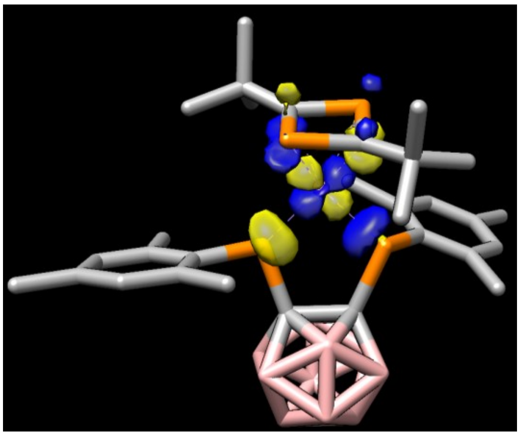
182 (1.899, 49%)



183 (1.864, 44%)



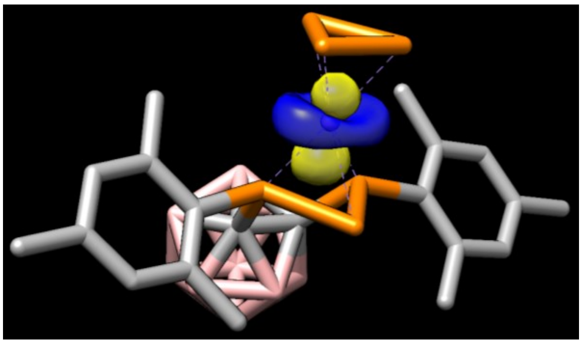
184 (0.163, 63%)



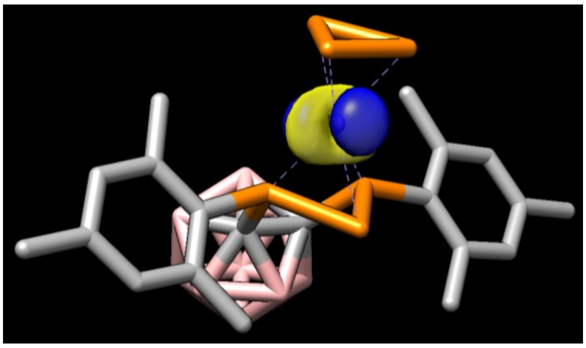
185 (0.122, 64%)

Figure S54: Natural orbitals of the active space describing the ground-state of [*rac*-**7**]⁻. Contributions of 3d orbitals on cobalt and orbital occupations are given in parentheses.

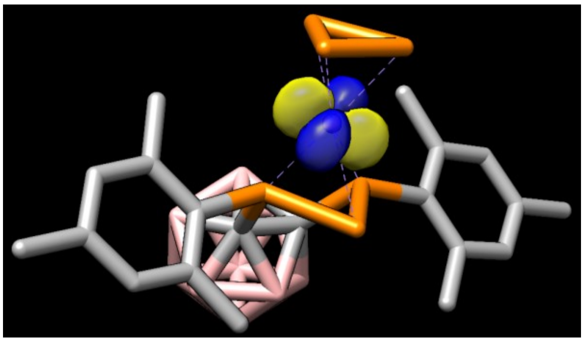
[*meso*-**8**]⁻



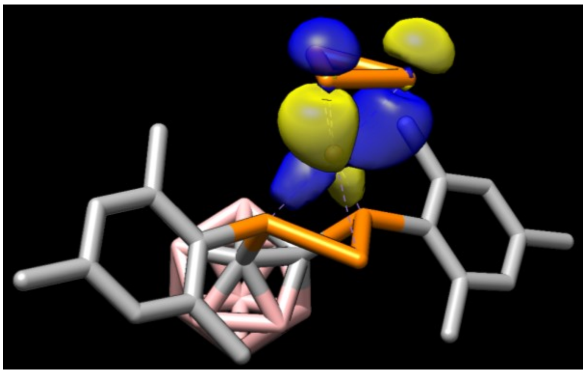
155 (1.997, 83%)



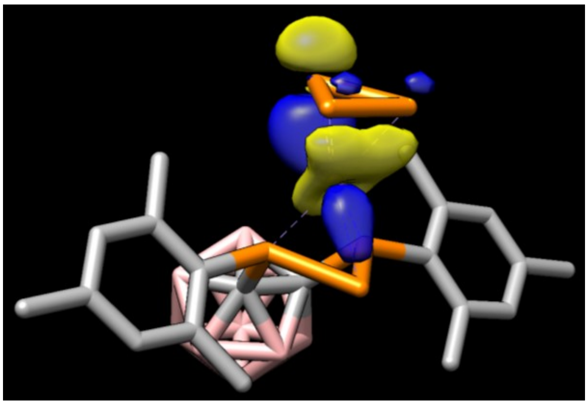
156 (1.992, 90%)



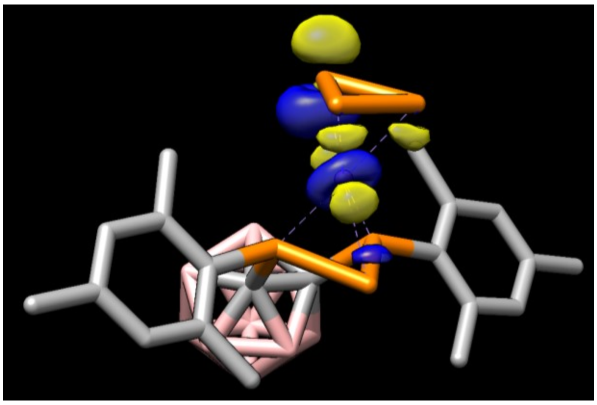
157 (1.992, 94%)



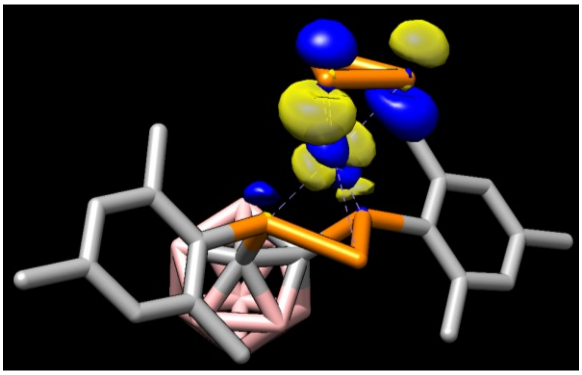
158 (1.862, 51%)



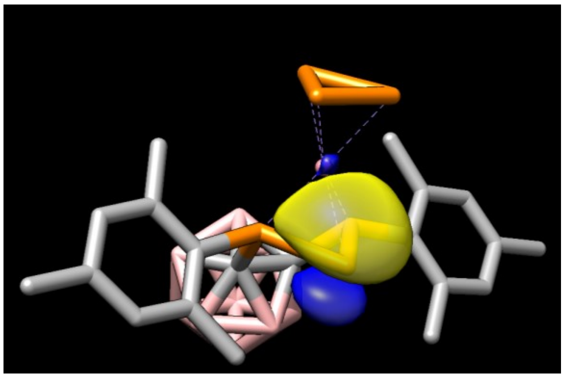
159 (1.854, 50%)



160 (0.155, 60%)



161 (0.147, 60%)

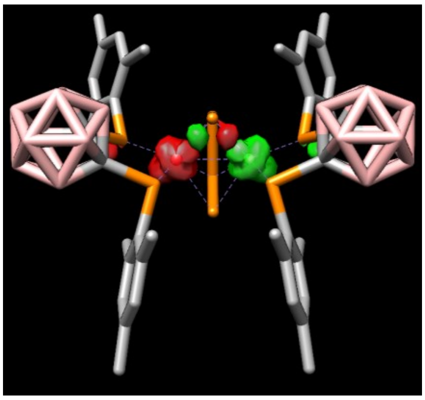


76 (2.000)

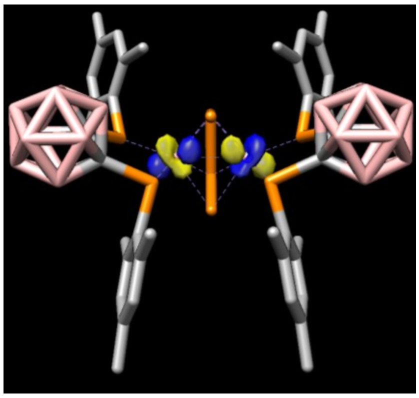
Figure S55: Natural orbitals of the active space describing the ground-state of [*meso*-**8**]$^-$. In addition the orbital describing the bonding interaction between cobalt and P2 (referring to Figure 4 in the main text) is shown as well. Contributions of 3d orbitals on cobalt and orbital occupations are given in parentheses.

12.Broken-symmetry DFT calculations on [*rac*-9]$^{2-}$

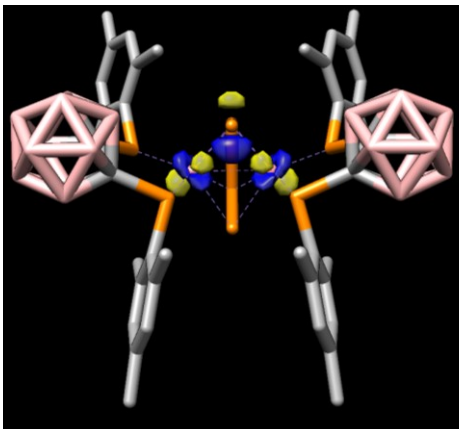
Due to its molecular size and the presence of two interacting metal centres in [*rac*-**9**]$^{2-}$, broken-symmetry DFT was used to analyse its electronic structure (TPSS0/def2-TZVP). Figure S56 contains the obtained spin density and the natural orbitals of the broken-symmetry solution. Here, the doubly-occupied natural orbitals were further localised using intrinsic bond orbitals (IBO). The spin density and the orbital pair 289/290 show the antiferromagnetic coupling of two spins localised equally on the cobalt atoms. In addition, three doubly occupied 3d orbitals are found for each cobalt centre (9, 128, 131, 85, 188, 189). The remaining seven orbitals in Figure SXX describe bonding interactions within the Co2P4 fragment. Thus, 14 electrons are located within this cluster, making it a *closo*-cluster.



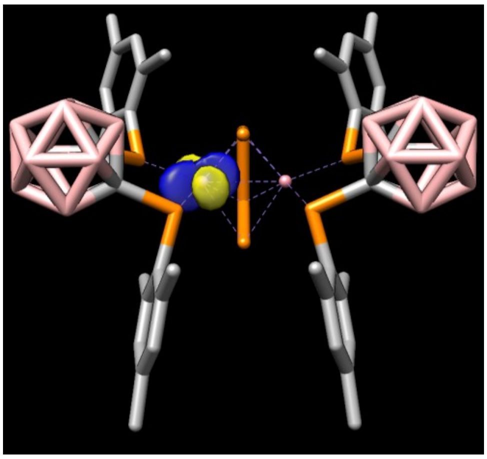
spin density



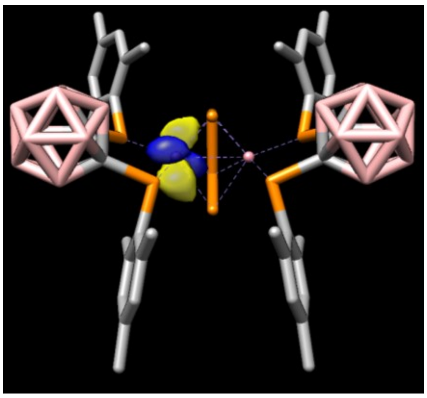
289 (1.673)



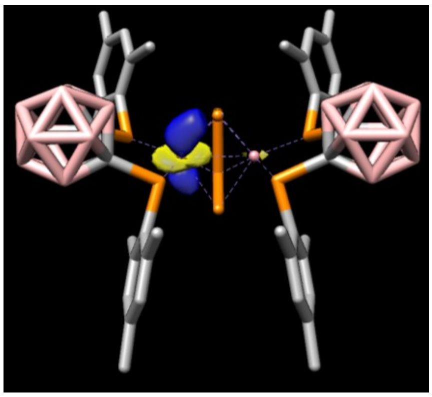
290 (0.327)



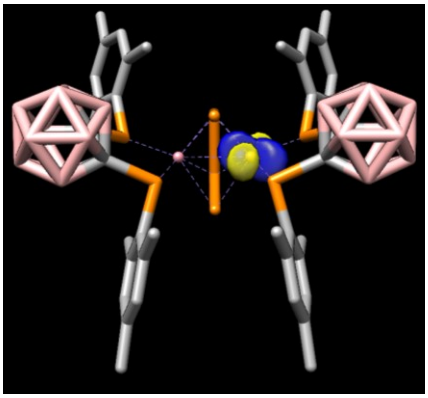
9 (2.000)

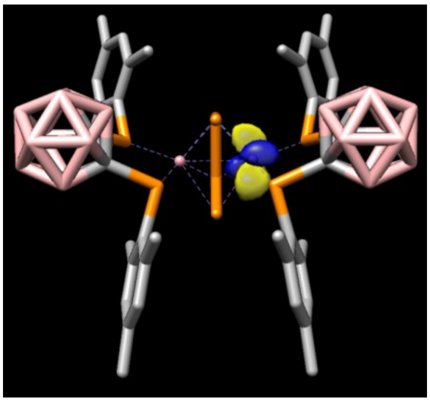


128 (2.000)



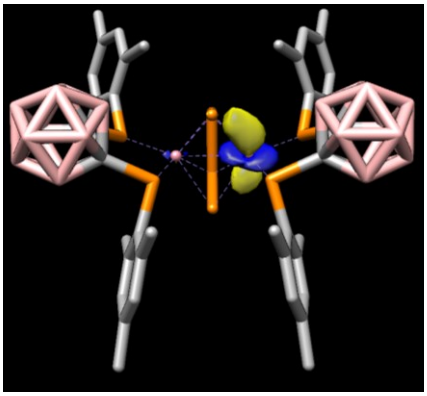
131 (2.000)

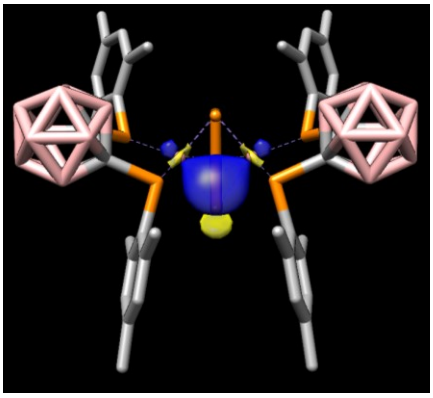




85 (2.000)

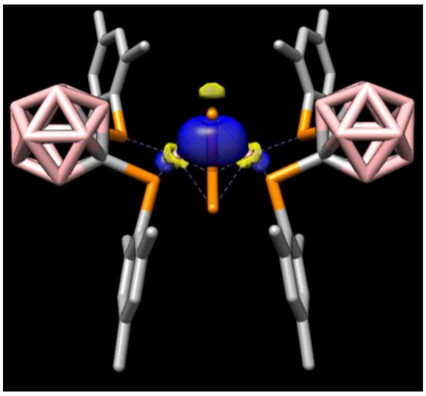
188 (2.000)

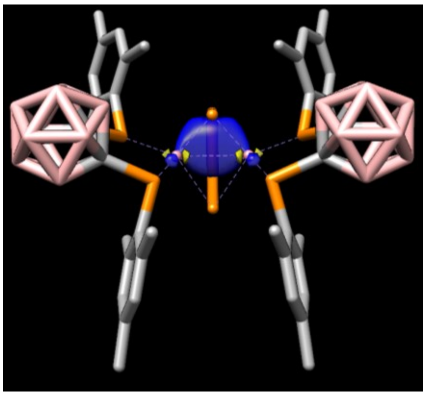




189 (2.000)

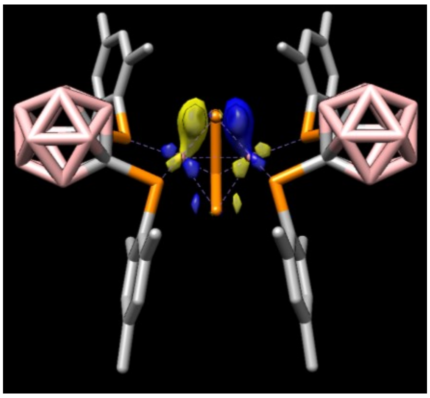
260 (2.000)

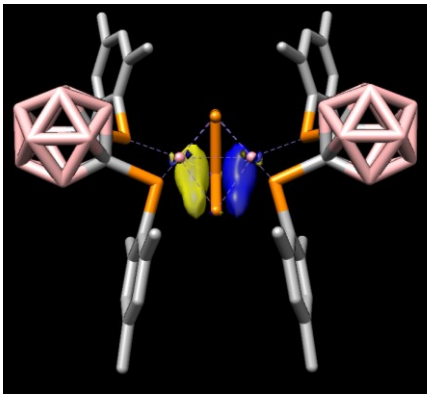




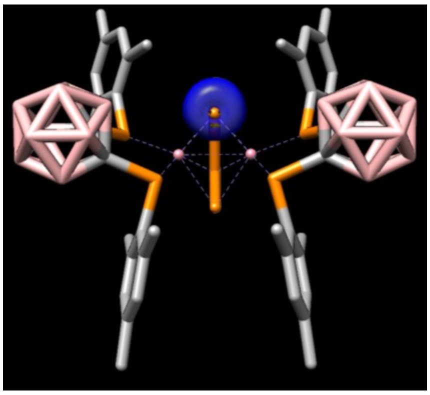
261 (2.000)

184 (2.000)



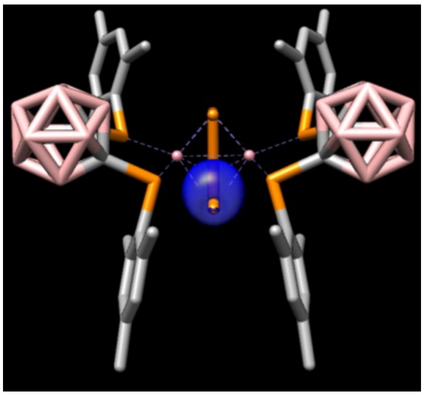


249 (2.000)



134 (2.000)

283 (2.000)



183 (2.000)

Figure S56: Spin density and partially localised natural orbitals obtained from a broken-symmetry calculation on [*rac*-**9**]$^{2-}$.

13. Cartesian coordinates of optimised structures

1,5-cyclooctadiene

C	-5.45590039892631	2.99690419217797	24.45027085052491
C	-4.67979378607789	2.19622062260459	25.18989698299774
H	-5.19395255838294	1.49567127129746	25.84824031158754
C	-2.92226969336024	1.52925562470352	22.68119310132205
H	-2.77289215370744	0.70383722338273	21.98403288009005
C	-5.08225190257622	4.04172065647996	23.43149779086462
H	-5.25081723462233	5.04042245083204	23.86423619979026
H	-5.79665457790654	3.96250480479228	22.60003705348275
C	-3.34634549769932	2.68317089467879	22.15288406948664
C	-3.65218593483618	3.98696385339144	22.85014920943096
H	-3.56303177949733	4.79989852798295	22.11983754876374
H	-2.92138725191036	4.20349258955286	23.63133858816488
C	-2.61093721275382	1.17165398986843	24.11100480768754
H	-1.51864482948152	1.09940920535364	24.23249193424367
H	-2.98931818080172	0.15485792583036	24.28688265516372
C	-3.17340512329229	2.09663722015192	25.21288251863363
H	-2.86829112151560	1.67912958827983	26.17970732877286
H	-2.70669530373081	3.08124176573939	25.15013646603275
H	-6.53240552060855	2.89221716780197	24.59113603393315
H	-3.52686993831259	2.68685042509784	21.07773366902657

P_4

P	-5.25697938367335	0.50769329439178	0.41808719253640
P	-3.28377231162797	-0.40840836051755	0.75551900577241
P	-3.52712524825019	1.14502298802634	-0.78531713752198
P	-3.64262305644849	1.68165207809943	1.34666093921318

1^{-}

Co	-5.11231793008454	1.29230068372103	23.15419884860417
C	-6.56709044828123	-1.59135499411762	22.13374709273761
C	-3.20476514287236	-2.81174107813507	21.71585545463637
C	-9.14836171807898	2.14937614248555	24.10171396728146
C	-5.55479534353824	2.79168989429899	24.46227338144379
C	-3.50027349482977	-0.88979453137876	20.25691977031311
C	-9.11537216747173	3.06724845272170	21.84669082837368
C	-4.95787361963332	1.66403521321831	25.09353025277367
H	-5.62928188410300	0.96955281598041	25.59786552384115
C	-3.81388524630409	-1.55144943492706	21.46673019223301
C	-2.64531260275900	-1.50289787040427	19.32884140133096
H	-2.42943929467764	-0.97958133626109	18.39708780246163
C	-8.62799142996894	1.24374325774850	25.18608949461701
H	-9.24098934733356	0.33760805457699	25.25627677280411
H	-8.65499756646936	1.74609627230773	26.15935038527635
H	-7.60509446627792	0.92912733707233	24.96899825011555
C	-3.03596848012111	1.24529371980461	23.13127232594683
H	-2.64844786804018	0.54599972768629	22.39368760587251
C	-4.82304372881677	4.07735676717083	24.13521148974605
H	-4.69453499259478	4.71997158448972	25.02542517950954
H	-5.44776874943719	4.64298128981804	23.43324943115420
C	-3.54038005636448	2.47947806685365	22.67661004652513
C	-2.06882501258040	-2.74790112724630	19.55575334072730
C	-3.46694431534646	3.77680361555044	23.47155849616522
H	-3.18256475285947	4.59797350374853	22.80081042897987
H	-2.67371132090746	3.70896391588047	24.22404063864332
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H	-1.53370114782023	1.38584832083940	24.70008761461684
H	-2.51962667940788	-0.07803626730203	24.70173891757229
C	-2.35385861567611	-3.38141182470239	20.76740490871461
H	-1.90432836089652	-4.35068654909061	20.98249089271971
C	-4.01627622629783	0.47987524552908	19.89159814870610
H	-3.18866035627643	1.20120840907663	19.88069833380143
H	-4.77170751219529	0.83318368066996	20.59704991902684
H	-4.45269603112068	0.46929685389197	18.88614817554597
C	-3.51869990591206	1.62249149858732	25.59730761548824
H	-3.47643872792352	1.02729321285234	26.51740030948776
H	-3.18894782624715	2.63213063345126	25.87015538903347
C	-10.26085291439208	2.95348869422956	24.38462350678148
H	-10.69937102149335	2.90888495899638	25.38141895594835
C	-10.82211350273290	3.79915189903257	23.43214743708378
C	-8.52504723826462	3.18391046310099	20.45989732803908
H	-8.53698799148098	2.22081041535603	19.93993048091486
H	-7.47720149841027	3.49989119779020	20.50259968695974
H	-9.09274327784771	3.91050780980603	19.86728457397197
C	-10.23033278024178	3.84305783433725	22.16571344996472
H	-10.64670379428186	4.50142665818590	21.40359245145394
C	-3.45741604472388	-3.58681805626669	22.98723022960195
H	-4.47844104936401	-3.98045022061650	23.01174420757005
H	-3.35404280101147	-2.94776735549431	23.86932950717232
H	-2.76077564042160	-4.43022815058438	23.05932168539891
C	-1.18040105310855	-3.40225870599189	18.52548256729419

H	-1.70844057215351	-4.21458543087707	18.00860952307524
H	-0.28724122980032	-3.83894446327815	18.98773050643142
H	-0.85715024679373	-2.68092492076384	17.76788968216858
C	-12.03311085805731	4.64277455802546	23.75011884308663
H	-11.83877876741020	5.70634609710458	23.56395552092422
H	-12.32660665395786	4.52934697822764	24.79847079440669
H	-12.88959456735330	4.35621535002491	23.12673879094909
C	-7.76830811250747	-0.44461096987216	22.03158843987498
C	-8.56407105546273	2.19328767833196	22.81888002897026
B	-7.23252955705280	-3.09130966281913	22.66479391433258
H	-6.55790181215373	-3.77687241167716	23.35422074224650
B	-8.36616719442785	-3.58698994826188	21.40565146618294
H	-8.56290155290958	-4.73704659110897	21.17679333071856
B	-8.31107189498335	-2.36603508844104	20.11035683554082
H	-8.46727850609111	-2.62520308837908	18.96101612931483
B	-8.88539781841854	-0.83207379209225	20.79225027028765
H	-9.38219183011267	0.06412703506588	20.19727805499156
B	-9.64085296333292	-2.34619271141814	21.29945413795532
H	-10.76319701435433	-2.59845169449919	20.99915298878373
B	-7.78594390537522	-1.56350251948908	23.33478544468865
H	-7.46626853270832	-1.18559253370548	24.40400604068727
B	-9.27081634625646	-1.08816501115022	22.50198504976655
H	-10.04214312646447	-0.37900934492988	23.05101240804711
B	-7.15513204993562	-1.12788435394171	20.58352168822450
H	-6.47027741712004	-0.45391428110100	19.90423834838785
B	-6.81846732333363	-2.81658816703534	20.96848378012437
H	-5.87116246365030	-3.33310632694490	20.48375759568136
B	-8.96317326807594	-2.79784876746581	22.88370190532824
H	-9.58388482598777	-3.36169328053873	23.72616178233743
P	-7.04277396879211	1.26272795740053	22.32895099371337
P	-4.93862901210321	-0.88396024302191	22.79852261544805
H	-6.62688872444394	2.92171002947698	24.59837728604787
H	-3.62119376112000	2.60534574022856	21.59764074022979

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C	-6.65250843653916	-1.72204789336610	22.18195707804119
C	-3.30492090254015	-2.87429915383943	21.67788010053868
C	-9.00812493079406	2.18250915708947	24.07115708711541
C	-3.41095824891051	-0.74941059483528	20.49109182494171
C	-8.99081458607164	3.09265845698874	21.80949270148515
C	-3.84979825529781	-1.56652521211857	21.55914930930360
C	-2.49335436607218	-1.26212966715845	19.56317095541074
H	-2.18072608601125	-0.62398236376074	18.73724700382139
C	-8.51620753249497	1.25984308874439	25.15110289333671
H	-9.13984583560289	0.35994312010774	25.19985106270060
H	-8.55955745863315	1.75268672930119	26.12848994219797
H	-7.48952531179071	0.94251548157242	24.95561523477258
C	-1.97551946518011	-2.55066998289431	19.65690137529414
C	-2.39035677202646	-3.33926376037804	20.73144279767824

H	-1.99539670642283	-4.34910569791721	20.83975914443385
C	-3.85510456536215	0.67553117162733	20.29668812575244
H	-3.26276153929904	1.35466772412357	20.92217000145744
H	-4.90002724061890	0.82722990854626	20.57716035953710
H	-3.71771989785401	0.97605989829509	19.25187634525178
C	-10.04970456198705	3.06519579041994	24.38563694362316
H	-10.45024149032398	3.05757137742234	25.39903301184933
C	-10.58438785657442	3.94644149408514	23.44990102363274
C	-8.44551231073399	3.17564380368037	20.40110109011623
H	-8.55296657186901	2.22266363146852	19.87368313516608
H	-7.37623051698775	3.41248506831839	20.40196010685405
H	-8.97862192761000	3.95063692295223	19.83871039320843
C	-10.03557539468969	3.94680537533851	22.16472504962914
H	-10.42683880202265	4.63505484968382	21.41614114701700
C	-3.69498317472866	-3.80768716306279	22.79796067756815
H	-4.70745316799316	-4.19789433956083	22.65125707800668
H	-3.69791989839915	-3.28996861390750	23.76225410725363
H	-3.00526703823696	-4.65803305741179	22.83894606768056
C	-0.99796833988563	-3.07975581978090	18.63554759983021
H	-1.40028025158844	-3.96192164752682	18.12194141235585
H	-0.05440976994303	-3.38189019063163	19.10697649689555
H	-0.77169439715631	-2.32175973483457	17.87912114098950
C	-11.72755689565172	4.86600435747256	23.80467806230165
H	-11.54355107077207	5.88626319983778	23.44849364215731
H	-11.88199919996550	4.90270966609688	24.88762651643801
H	-12.66410191216671	4.52496833944677	23.34435431258418
C	-7.81538765776801	-0.54889645792577	22.01172385815992
C	-8.46937617666302	2.18237096234979	22.76648701622387
B	-7.36987813653387	-3.18653892423423	22.74226784143364
H	-6.73082464943684	-3.86184679304931	23.47417453748784
B	-8.47928580029363	-3.68840918270074	21.46440932328064
H	-8.70231471260006	-4.83867552260869	21.26500976540839
B	-8.34833831887555	-2.51183230093404	20.13265020895050
H	-8.47851327698532	-2.80305434796783	18.98839120284184
B	-8.89925140107037	-0.94102177862647	20.75003295622451
H	-9.34465946297532	-0.04748366187186	20.11212260302969
B	-9.71311896584938	-2.41650600002868	21.27976738415640
H	-10.83150918680754	-2.64886062636895	20.95176409896055
B	-7.89900486473285	-1.62122138454423	23.34779554938512
H	-7.59246580052122	-1.22094524819521	24.41133231879878
B	-9.34555789433175	-1.13005051790316	22.45491302643564
H	-10.10681084307294	-0.37896438947733	22.96125564104641
B	-7.17016547240452	-1.29291687556272	20.60170183227617
H	-6.43458005172397	-0.66154861596094	19.93077932234183
B	-6.89756054757826	-2.97711124409583	21.05101486825388
H	-5.94792557937314	-3.52826049711344	20.61066083273304
B	-9.09698657824468	-2.83593956112277	22.89888492680658
H	-9.75862762372150	-3.35558498824559	23.73768740604366
P	-7.04904633138342	1.15803029627167	22.18005585692165
P	-5.03561861394365	-1.04730403316676	22.88940509620159
Co	-5.21832782573017	1.13957899051506	23.25953384194493
P	-4.79975262990145	1.51633332220420	25.29038273490776

P	-4.42182111788117	3.11901320556523	23.10046289098945
P	-2.94002547439050	1.65250502762346	23.94161238780111
P	-3.64316231839807	3.39073742754068	25.16360831272642

TS1

P	-7.00186168830540	1.19723897938500	22.06359430853063
P	-4.92491055294872	-1.02865997142716	22.80656407706498
Co	-5.20298044720083	1.07060139536152	23.26704403691577
P	-4.43858170501888	0.11309282368215	24.94992156414032
P	-5.19789294406684	3.25692146216017	23.72525971517926
P	-3.33666467057855	2.17270830490989	24.20461887449729
P	-4.97467882202743	2.21115618718373	25.69374447307710
C	-6.59239795203824	-1.71962040721751	22.28567787068217
C	-3.24343331348893	-2.86321053882276	21.53269618857311
C	-8.92083858848484	2.32173796665853	23.94682387717200
C	-3.37759668716824	-0.69441964001023	20.41368529810028
C	-9.01397486101817	3.06257504071196	21.62916716403580
C	-3.79050818877578	-1.55915565736156	21.45581625344452
C	-2.48098722823226	-1.17147454639016	19.45204626594927
H	-2.17543763184287	-0.50116402949079	18.64941431437882
C	-8.37251593469015	1.47669050108623	25.06219169810086
H	-9.00330311754562	0.59475834954742	25.22308820327469
H	-8.33895354411169	2.04326419828736	25.99847709229448
H	-7.36624765322015	1.12249955748501	24.81809060823303
C	-1.96893005249102	-2.46944213085408	19.48853413401963
C	-2.35410761674382	-3.29529687359667	20.54438481607355
H	-1.94584274685814	-4.30311022578508	20.61185729268794
C	-3.85935238241692	0.72655673805403	20.29853844359320
H	-3.70263064772203	1.27325275606466	21.23775037244516
H	-4.93716741319870	0.77519951040630	20.11200638232438
H	-3.33418838153586	1.24199834674787	19.48688537063887
C	-9.96341192598782	3.20836038602157	24.24409121723342
H	-10.32029978664812	3.26769934769985	25.27210091980558
C	-10.55061173840405	4.01368031422999	23.27177536625890
C	-8.53250187977769	3.05235267107204	20.19529013686724
H	-8.59619603179749	2.05058623574500	19.75967786097792
H	-7.48225914382119	3.35502804980224	20.12587225256102
H	-9.13724319865057	3.73989575952034	19.59284345206634
C	-10.05679449734530	3.92705226911585	21.96776674168657
H	-10.49043197515595	4.55467440053952	21.18968339851926
C	-3.58354361118365	-3.80842137158150	22.65812434109055
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H	-3.51702126533134	-3.30208721407323	23.62646552673098
H	-2.90675105248767	-4.66954099674300	22.64772449012602
C	-1.03712727015248	-2.96760541036385	18.41081800770091
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H	-1.60239720334723	-3.39036424051509	17.56940690374788
H	-0.37638375572217	-3.75404546791362	18.79055980358966
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H	-11.74472634558787	5.12811368554859	24.68674139321505
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B	-7.27503725864129	-3.13269041659493	22.98542540923672
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B	-8.45677661975074	-3.71496404774028	21.80712021375967
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B	-8.39357625633709	-2.63465416360917	20.39117504190367
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H	-9.38279633954763	-0.17395394832238	20.24710374893999
B	-9.69256996031177	-2.44998806885356	21.60166097553418
H	-10.82770063169068	-2.69782014304652	21.35251811917915
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B	-9.25807864381060	-1.08531031346006	22.65832420116034
H	-9.99244157026122	-0.30012805584322	23.15069955689031
B	-7.18719167954397	-1.39160971738193	20.71134239198286
H	-6.48203409565011	-0.82006686275906	19.95857234717119
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H	-5.97797844071421	-3.62839656250286	20.80093907600389
B	-8.98851268989563	-2.75708415502769	23.21043777092506
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P	-4.93571724301575	-0.89432034469891	22.71893385973832
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P	-4.40537590678722	-0.65705361870095	24.70031557245813
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P	-3.49535145059591	2.41508995636499	23.27164097109312
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C	-3.79041891095005	-1.55439284400776	21.46099994624034
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H	-2.21830683420649	-0.72140644970874	18.56418414191122
C	-8.16171410357419	1.56549919158337	25.15683044873740
H	-8.77538062346356	0.71494779509295	25.47499385615840
H	-8.01286180957562	2.21978294539852	26.02279934135949
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H	-1.94639576016107	-4.34728321930054	20.83449650087774
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H	-4.95589180730455	0.75634323765577	20.27799539130395
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C -7.70260439668290 -0.41453429482967 22.03701364199928
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P -7.37198614811417 1.56196340769492 21.90269449568449
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Co -5.18458628377703 1.74568948147172 22.19777817372321
P -5.04457784780320 0.45083999178651 23.88077396433501
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C	-8.95766004210022	1.98821548642372	24.37343189552029
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H	-4.79755045198684	-0.61507236688939	18.86549861648661
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H	-9.95085095279401	4.46183735468275	20.64674361129938
C	-10.42243081376487	3.98048903556662	23.07929096418322
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C	-3.59575375841635	-2.59796232515971	23.71398020148077
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H	-3.15763847892084	-3.48949832154192	24.17430411452542
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H	0.07515401324234	-4.52294695328895	20.86121706709449
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H	-1.02367687144244	-5.11138883136543	19.60701113268196
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C	-8.67024724967944	2.27999526545828	23.01850404230129
B	-6.99359507651592	-2.91388066133055	21.91275479960037
H	-6.15171505783276	-3.60161650084673	22.37926318676502
B	-8.24565970283953	-3.36651032740385	20.74847759813851
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H	-8.78585901982585	-2.11212015049483	18.50076253477393
B	-9.09995445778589	-0.62789806803465	20.61276613416674
H	-9.74810682464114	0.28258545662808	20.22235455843808
B	-9.63142589041658	-2.27014096645621	20.98751442242694

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B	-7.60242142376547	-1.56501392209425	22.87505605648627
H	-7.17583537334381	-1.30492272274272	23.93820668770397
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H	-9.96979354404454	-0.59651139418779	23.03684559833498
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H	-6.86882894909397	0.13229275292355	19.49920950806355
B	-6.85982995524690	-2.37674660799152	20.23086009097115
H	-5.93195477610948	-2.71195062513654	19.57729781835154
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P	11.36648664276162	13.71310827981878	6.80682313140730
P	12.32156011532845	12.35845879109798	3.32576295907844
P	13.99696444503330	13.71308761301178	2.99347275041056
C	11.04129929357071	12.90120399463888	2.00490950981794
C	13.30888167983590	10.00445270563121	2.03130211121613
C	10.82069295201641	10.28329979890261	4.95215120367249
H	10.29641720393155	9.46896499804751	5.46215242868165
H	10.07533646602938	10.97522336740049	4.54676347532399
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C	11.71096713565261	9.72759816500423	3.86830111064929
C	11.78558739445209	8.34439904635271	3.69051831766399
H	11.19093284666608	7.70338146928208	4.33973695450065
C	12.59562426778194	7.76753915079830	2.71022589429168
C	13.35085461226319	8.61315234999128	1.89714655634395
H	13.99116832932515	8.18211830550961	1.12875294011102
C	14.16301115944522	10.84695363997959	1.11926101294788
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H	14.97849498301661	11.32625863424847	1.67214948168887
H	13.58563074272194	11.65066637017536	0.65594253965168
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B	11.67209782807663	13.71306585518115	0.62761651593861
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B	9.00526679545605	12.82166412981826	0.14380776014993
H	8.26864021775199	12.17953977278252	-0.53167093555432

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P	12.32155007948784	15.06770860858748	3.32574416031617
C	11.04129051932720	14.52493442417036	2.00490089693160
C	13.30835479359108	17.42169019538257	2.03083640524351
C	10.82172824589715	17.14288278241138	4.95301265688304
H	10.29777378975743	17.95722337746666	5.46333391223276
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C	13.35034764406193	18.81299309191785	1.89671339863319
H	13.99028106670696	19.24401594851230	1.12799580429131
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H	14.59591239850144	17.19974248529788	0.32775215753298
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C	12.63163872469625	21.15536893575680	2.51988626698279
H	13.51143326395137	21.45972515966802	1.94433455978341
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B	10.66571819473906	15.14965242692154	0.46091982380304
H	11.17307601331353	16.16606771603491	0.12870808879387
B	9.46992509734900	15.14888211026854	1.76955444744591
H	9.18407955633266	16.16680874119368	2.30150193106488
B	9.00525680952714	14.60443046860127	0.14379652461732
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P	13.26084364390272	12.63669916020167	6.79832492727804

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H	1.02393223861685	-2.66087467856648	2.98652037354733
C	-1.87833146305021	2.09560582959981	0.95924104458296
B	-2.49498013043711	-4.27263251036002	3.19509698212553
H	-3.49357333869868	-4.11863964094296	2.58200012237029
C	-2.50210922711123	2.61458637349541	2.10387378034432
B	-1.46196991664944	-5.71676531369921	3.28045753771912
H	-1.76226372319543	-6.71384577863348	2.71280671271325
C	-3.93804098579597	-0.02023178044492	4.80570585235403
H	-3.13208473034237	0.71352031305876	4.64876407833380
H	-3.53579123927725	-0.77612503277234	5.48627741502496
H	-4.77365742388549	0.48122974970376	5.30356877815660
B	0.23092881204465	-5.17313356053911	3.41129389424510
H	1.14800175730909	-5.76027343442763	2.94248607560627
C	-6.27646776157317	-1.10926041704986	2.02713712054700
B	-0.91878780656017	-4.29054308600149	2.38512655843061
H	-0.83329905048518	-4.13389868364498	1.21540594285382

C	-3.89416170000099	2.64955421271777	2.24921552630129
C	-4.38160251746800	-0.61210085903527	3.49559889064126
C	-3.48506558166641	-1.13211411169368	2.53572922717456
C	-1.42829991383259	4.42888537250254	3.49353847368008
H	-1.85687779123513	5.23614754202089	2.92208043242705
C	-1.42362367425465	-2.95837738982479	3.33518737046242
C	-4.54681334839233	3.20500171554718	3.48933463795887
H	-4.62439060238763	4.29840973512565	3.44206064827804
H	-3.97677675299198	2.95686291927912	4.38845947387540
H	-5.55687583052827	2.80179582805287	3.59576359758950
C	-5.37713025294557	-1.59372838707382	1.07736987943880
H	-5.75158345243260	-1.96690124498834	0.12548663280295
C	-2.69878186834822	1.60847279919800	-0.05833518185323
H	-2.23259015743464	1.19713352832507	-0.95097926838519
C	-0.37877520755449	2.03464958501245	0.83610227068000
H	-0.08926729268568	1.85238187700441	-0.20185114504129
H	0.01565752868047	1.21777239226957	1.45095011020672
H	0.09366745108676	2.96236637727498	1.17512732338210
C	-3.10115246827234	-2.13615649159935	0.21247678631574
H	-3.66099326991660	-2.24997136687334	-0.72106891554782
H	-2.68963713285092	-3.11537712762943	0.47780351721646
H	-2.24900882324645	-1.46913677279647	0.04042436586048
C	-4.09335467655906	1.62570820265925	0.04310034743459
C	-5.75372422666831	-0.61612236437738	3.22154180266215
H	-6.43334151602238	-0.21438458846413	3.97150568371279
C	-4.67012681516842	2.14492169343797	1.20250361349733
H	-5.75188923693196	2.13909023451729	1.30944599690818
C	-3.99971597260692	-1.60460431237016	1.30150175192526
C	-7.76197497225406	-1.11846160366068	1.76709361332274
H	-7.99343993672170	-0.73668209388456	0.76618011315946
H	-8.29591846496929	-0.50752942144984	2.50090451254742
H	-8.16253561260081	-2.13800377282069	1.82499238992644
C	-4.95053058261013	1.11063309021800	-1.08487503105741
H	-5.00503475027011	1.84610163253600	-1.89742663007670
H	-5.96866814655343	0.90783227838596	-0.74331762796482
H	-4.53723318009582	0.18804728499718	-1.50338139885718
C	-1.02615860973498	2.25188166135867	4.04290431311255
P	-1.63852080105673	-1.18574705983896	2.68728647278746
Ni	-1.03705555319133	0.31295880843066	4.05033751218000
N	-0.36869801695246	3.09583252601269	4.89448111760864
C	-0.17569047148552	2.11200328083364	7.12658074816586
C	0.45324662893566	2.61727603959742	5.97861384803894
C	1.84566232054979	2.64133781157481	5.83496336146886
C	-0.60206829712891	4.42967008696231	4.57221564352054
H	-0.16535564145000	5.23777724484504	5.13626754730171
C	2.50417939492282	3.18362871913968	4.59212369701122
H	2.59164939050716	4.27655201371120	4.63309064997165
H	1.93269997570024	2.93535358651780	3.69396876131604
H	3.51064664312058	2.77070580518309	4.48893145646837
C	0.63991017552242	1.62644993334418	8.14877524362139
H	0.16960613110637	1.22508666896252	9.04380349614048
C	-1.67582057465812	2.06391290845127	7.24861262813559

H	-1.96771441451100	1.88968337579399	8.28726988823233
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C	2.03471281254828	1.63199705190321	8.04866857216921
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H	3.69841063965150	2.12343977498703	6.78046320598358
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H	2.94241314419807	1.86054181948072	9.99026249087535
H	3.90481063337789	0.91086563906154	8.84440326985312
H	2.46829328498057	0.20218425989580	9.60518630199207
B	-2.31864277538629	-3.40130566414589	4.72239901216697
H	-3.11347518724530	-2.63856291091647	5.13515832144938
B	0.39463290469401	-4.27513459037888	4.93967114256459
H	1.39424982534249	-4.12325255602048	5.55161461580397
B	-0.64794571756774	-5.71311402141494	4.86587157126345
H	-0.35420440434581	-6.70758088508230	5.44147816890412
C	1.86287754595969	-0.04325437017467	3.29411452771480
H	1.06411461895918	0.69877966401258	3.44725566561563
H	1.45196286746809	-0.80088369167823	2.62066859072368
H	2.70185259098922	0.44649430866779	2.79024289850852
B	-2.33721117461227	-5.15926515308615	4.73065646596788
H	-3.25817298077854	-5.73643241033642	5.20420304754872
C	4.19733208669728	-1.12642053708247	6.07851081975578
B	-1.18159921512145	-4.27626585314230	5.74972375429377
H	-1.26600383401833	-4.10968000840893	6.91815602743064
C	2.30429865304643	-0.62850621920273	4.60790835398670
C	1.40547158670829	-1.13602086514916	5.57229026482069
C	-0.66786473655056	-2.95505982384553	4.78909870502059
C	3.29586445869829	-1.59831453501189	7.03257936290819
H	3.66883783080758	-1.96677902707521	7.98687725222833
C	1.01734273368925	-2.12065865690829	7.90318301031067
H	1.57740953305946	-2.23164722843035	8.83694542475630
H	0.59924597047442	-3.09902198709670	7.64506634737701
H	0.16974162896985	-1.44694111757755	8.07151026436390
C	3.67658298111710	-0.63884741942969	4.88093327890261
H	4.35800719865919	-0.24685798529027	4.12745890737238
C	1.91820778355993	-1.60227194756157	6.80968204613886
C	5.68301829696102	-1.14327386064609	6.33713403816910
H	5.91773616468261	-0.75885289918819	7.33626097470258
H	6.21981033426113	-0.53849492285827	5.60030316765077
H	6.07752043080815	-2.16538611877355	6.28289497298084
P	-0.44139287982314	-1.17883293710257	5.42289919515472

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H	9.40674867589052	9.19376482889031	2.74129683181519
P	10.76578367748425	9.53740887865064	5.67197933853363
N	14.96225993783344	11.62516659080674	3.60853037595754
B	11.53246657694070	6.76793832057879	4.80440997531794

H	12.48344202335258	6.98606411070080	5.46363163811440
P	12.47655875323851	9.12935755375076	3.02139809179355
B	9.92826323033466	6.47730986640812	5.47830290632143
H	9.82181452198494	6.47285658852388	6.65712828721625
C	14.08192167219445	8.18367027274181	3.00143851050824
B	8.76270279694865	7.33049052194808	4.45860172927380
H	7.83815648717211	7.89871489466454	4.92956853127686
C	11.29368787936130	7.69870890773287	3.38758340100672
B	8.98449883220588	5.57350160902571	4.28888817583013
H	8.13645268565020	4.81365256777484	4.63126260916564
B	10.71938620722420	5.22798971634966	4.50636723162579
H	11.13212531831774	4.22967388878538	5.00154059306219
B	8.80470746194570	6.59624089293609	2.84072284247827
H	7.84085533691787	6.58008031941642	2.14580757614392
B	11.60043124431854	6.03805283356177	3.19266400975499
H	12.65423098907035	5.70769729832135	2.76863813647190
C	8.67005398156733	11.31100289398616	4.70534972790381
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C	16.58082551870005	6.83591372379215	2.74584748194605
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H	9.92710407115758	4.32222167749139	2.18647148851398
C	15.73989653779578	7.00659891263617	1.64392406825793
H	16.04521379147689	6.62022853342305	0.67169542208652
C	14.50872523337149	7.65540124103010	1.75143513120033
C	9.09760372546864	10.36725187795891	5.67086246337363
C	13.89044450889482	11.25198133820676	4.00687466904371
C	6.99551550497455	10.72597257296777	6.86639579135947
H	6.35293312859365	10.49138286026414	7.71477319729056
C	14.93229741583417	8.01965858344440	4.12153130642312
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H	16.23712178501018	12.68911551384903	2.38039656113418
C	7.41312276245309	11.91906495047533	4.84479041346527
H	7.09878185906910	12.63643702439697	4.08678600981160
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C	8.57724566087897	9.06089212900073	7.81640348761444
H	8.43810106607967	8.04434395336778	7.43270916778075
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C	16.81431301195425	10.43447152370653	-0.06430889333385
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H	9.37797894791204	14.54748462987568	6.69396231932490
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C	17.91692764651900	6.14790153430175	2.60582896660505
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H	16.78848150026871	7.21866207585091	4.84422321852509
C	13.65620034348479	7.74718568845471	0.50959361428225
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C	10.92788679058100	13.30385404381177	7.54959999315168
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C	16.86939676363305	10.62753075180332	2.45493289828408
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C	8.78554305315557	13.98464321962586	8.71799145366833
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H	10.91598702803509	13.24342290473997	10.37323768140950
C	10.31770365758776	7.96730585593846	4.71596120202979

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B	11.89211526578032	23.04168004961147	6.70751660109032
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H	8.94168750794635	22.13328049286435	9.16630068376118
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C	13.42849595814229	18.64489026333125	11.16450054136074
C	15.32353145322392	19.58233255437842	9.96091867877489
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H	11.38675450882270	18.40216070547233	10.48663132382672
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C	15.48892103016921	19.19402805987943	12.36635912652709
C	16.04354311448466	19.61548693535654	11.15703254959707
H	17.06657243963960	19.99086721178269	11.13884516620957
C	14.18395850042683	18.71133143712305	12.34319943190788
H	13.72746546003456	18.36964727576601	13.27196076734011
C	8.47993815219713	19.38214868943070	7.11116154184485
C	13.67589416156135	16.39842433662884	5.94919486487367
C	8.13229352344803	15.82025425325827	8.23359572923893
H	8.05237677481422	15.39020733066415	7.22862996229388
H	8.14582246752197	16.90844205244689	8.12870346401381
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C	12.48885216163440	16.25538620239034	6.87051366148515
C	10.62674744785493	15.72754771316948	8.14761829558523
C	7.30808314551566	19.48055963139252	7.90182774714237
C	10.76520372448182	20.87595177459751	8.01090017128158
C	8.37143731342238	19.40011254910864	5.70362443447617
C	7.10234420684562	19.50603661112833	5.12130897213365
H	7.02623443530654	19.50899046393000	4.03451009530284
C	16.01288227961583	20.10589592478865	8.72419441753194
H	15.75399682468146	19.51861247654407	7.83904828082977
H	17.09926867616654	20.10171420748371	8.86678853643154
H	15.70311795284403	21.13566439150838	8.51556856509608
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H	17.23376863283325	18.73651052681572	13.56286783697901
H	15.71773846526711	18.82070142426218	14.48070131498933
H	16.50576254810340	20.30563929180508	13.91873743429515
C	12.39908479931262	20.81627005199018	8.30469498853965
C	13.75451295328976	15.10175823251416	5.10731188343318
H	12.84724803263047	14.97802385147210	4.50610103755699
H	13.85610573145365	14.22722999989199	5.75941970939127

H	14.62058266712950	15.14004278490809	4.43378464424036
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H	6.36257753660870	19.59152417621594	9.83072001137652
H	8.02101463120064	20.23430002417772	9.80159115804431
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H	13.48036978721420	18.52961185705068	5.57954626725841
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C	9.57393778546552	19.34122785862538	4.80072122790431
H	9.31603920510880	18.87245456894726	3.84556500787339
H	10.38740595543229	18.78188646221599	5.26865969734271
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C	14.98160479252657	16.54838731406375	6.74659867748409
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H	15.11659304448284	15.70105794401758	7.42927395134568
H	14.96245995197078	17.47021128690971	7.33537906321225
C	9.40453548739841	15.32506685401907	8.93931365588029
C	5.94153137851499	19.60957698115513	5.88459671070188
C	4.58862508119082	19.75305848895222	5.23067235931692
H	4.23320585382471	20.79030594919901	5.28720227869727
H	3.83871371888183	19.12492031596509	5.72480091788058
H	4.63015115965315	19.47240094843310	4.17356058798480
C	9.45686270196599	15.88968732134513	10.36841836746551
H	10.35458021842553	15.54258529584531	10.89099316545635
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H	9.48214193046887	16.98273704706748	10.34092613940993
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H	8.49412932030718	13.43669289227961	9.56087017232923
H	10.27514373227714	13.40403777173250	9.51057592445621
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P	10.07453691468608	19.14639060505420	7.98743285623324
P	10.73047586204057	16.19560207716818	6.42743589092049
P	12.38820220966837	15.62852172690360	8.56496130178969
Co	11.47642763486001	17.61712921283312	7.98566120348307

[*rac*-9]$^{2-}$

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H	16.30037412200027	13.30576353415172	-9.50015432272516
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Co	8.50772119115641	14.16057158311703	-8.18826568900478
B	7.80905015950967	21.41100130771661	-9.37473727469925
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H	8.94490222364144	21.83313456601563	-13.12204624204644
B	6.58393331084706	20.49052418163790	-10.26099616253943
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H	10.05409990474567	20.39137687375180	-8.53854007351866
B	7.08274791758233	20.40633966781546	-11.96579008772844
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B	9.83303815265077	20.40044763030746	-11.14002517449139
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C	7.26880515957569	20.27161722414209	-5.29643181184888
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H	4.33741954337967	18.44491149848954	-9.80815937784932
C	14.29053501355423	18.36228262284145	-9.63394366203741
C	12.28927040953837	17.73912954742145	-10.88354760731561
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C	3.56923431898653	19.59469060367621	-5.85652821460493
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H	11.74757957119830	19.43047343495763	-6.73411294236799
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H	14.26085975474052	17.83059274579042	-11.71907737292075
P	9.69228592887107	17.40096404027343	-9.94366374717318
Co	8.50866869217052	16.71801510607506	-8.18818574163254

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