Electronic Supplementary Material (ESI) for Chemical Science.

Placing gold on a π^+-surface: Ligand design and impact on reactivity

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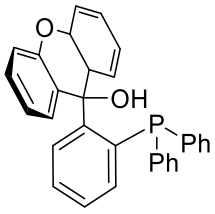
Supporting Information

Contents

1. General Considerations

All experiments were carried out under an atmosphere of nitrogen using standard Schlenk techniques or inside a glovebox unless otherwise noted. Diethylether (Et_2O) and hexanes were dried using potassium and distilled under nitrogen. Dichloromethane (CH_2Cl_2) was dried using calcium hydride and distilled under nitrogen. The starting material 5-bromo-6-diphenylphosphinoacenaphthenee,[1] N-methylacridone,[2] 10-bromo-9-oxa-10-boraanthracene,[3] compound **A**,[2] and 2-(phenylethynyl)phenylboronic acid were prepared according to literature procedures. Xanthone, tetrafluoroboric acid diethyl ether complex (HBF_4▪Et_2O) and trimethylsilyl trifluoromethanesulfonate (TMSOTf) were obtained commerically and used without further purification. Mass spectrometry analyses were performed in-house at the Center for Mass Spectrometry at Texas A&M University. Elemental analyses were performed by Atlantic Microlab (Norcross, GA).



A

1.1 NMR spectroscopy

NMR spectra were recorded at room temperature using a Varian Inova 500 FT NMR (499.41 MHz for ^1H) spectrometer, a Bruker Avance 500 NMR spectrometer (500.13 MHz for ^1H and 125.76 MHz for ^{13}C), or a Bruker Ascend 400 NMR (400.20 MHz for ^1H, 128.36 MHz for ^{11}B and 161.96 MHz for ^{31}P) spectrometer. Chemical shifts are given in ppm. ^1H and ^{13}C signals were referenced to residual ^1H or ^{13}C solvent signals.[4] ^{11}B signals are referenced using $BF_3{\cdot}Et_2O$ solution as external standard (0.0 ppm). The ^{31}P signals are referenced using an 85% H_3PO_4 aqueous solution as external standard (0.0 ppm). The following abbreviations are used in the compilation of NMR data provided for each compound:

• s, singlet; brs, broad singlet; d, doublet; dd, doublet of doublet; ddd, doublet of doublet of doublet; t, triplet; td, triplet of doublet; m, multiplet.

• $^mJ_{X\text{-}Y}$, coupling constant between nucleus X and Y separated by m bonds. The nuclei involved in the coupling reported are: ^1H for H, ^{11}B for B, ^{13}C for C and ^{31}P for P.

1.2 Single crystal X-ray diffraction measurement

The crystallographic measurements were performed at 110 K using a Bruker D8 Venture (Cu source) or Bruker D8 Quest (Mo source) diffractometer equipped with Photon III detectors. Semi-empirical absorption corrections were applied using the Bruker SADABS software package.[5] The structures were solved by direct methods with SHELXT[6] to locate all non-hydrogen atoms. Subsequent refinement using a difference map on F^2 with the SHEXL package[7] allowed for the location of the remaining non-hydrogen atoms which were refined anisotropically. H atoms were added in calculated positions using a riding model. CCDC 2191151-2191157 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk.

1.3 Quantum chemical computations

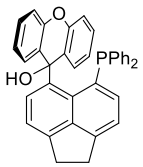
All calculations were performed using DFT methods as implemented in the Gaussian 16 software[8] or ADF

2017 program for energy decomposition analyses.[9] Optimizations were carried out using the crystal structures as initial guesses. The level of theory employed was as follows: Functional: MPW1PW91; Basis sets: mixed with cc-pVTZ-PP for Au, 6-311G+(2d,p) for Ni,[10] 6-31G(d,p) for P/Cl and 6-31G(d') for C/H/B/N/O. Frequency calculations, which were conducted using at the same level of theory, found no imaginary frequencies. NBO analyses were performed with the NBO 7.0 program.[11] The resulting electrostatic potential surface maps and NBOs were visualized using the GaussView 6.0 program. The Mutliwfn program was also used to identify the positions of maximum electrostatic potential ($V_{S,\,max}$).[12] EDA analyses were performed using the ADF 2017 program, the PBE-D3(BJ) functional and the TZ2P basis set.[9]

2. Experimental Procedures

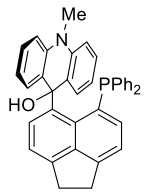
2.1 Syntheses

2.1.1 Synthesis of $\mathbf{1}_{xant}$



N-butyllithium (2.5 M hexanes, 1.02 mL, 3.1 mmol) was slowly added to a solution of 5-bromo-6-diphenylphosphinoacenaphthene (1.06 g, 2.6 mmol) in anhydrous Et_2O (20 mL) at -78 °C. The reaction mixture was stirred for 30 minutes then gradually warmed to ambient temperature. After stirring for another hour, the resulting solution was cooled to -78 °C and xanthone (608 mg, 3.1 mmol) was added in one portion as a solid. The reaction mixture was stirred at -78 °C for another hour and then warmed to ambient temperature. After stirring for 18 hours, the reaction was quenched with a saturated aqueous ammonium chloride solution (30 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over $MgSO_4$ and brought to dryness under vacuum to afford a pale-yellow residue which was washed with minimal acetonitrile to give the pure product as a white solid (1.13 g, 2.1 mmol, 81% yield). Single crystals suitable for X-ray crystal structure analysis were grown by slow evaporation of a CH_2Cl_2 solution of $\mathbf{1}_{xant}$ under an ambient atmosphere. **^{1}H NMR** (400.20 MHz, CD_2Cl_2) δ = 8.79 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.54 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.16 (d, *J* = 1.9 Hz, 2H, Ar-*H*), 7.10-7.15 (m, 2H, Ar-*H*), 7.04-7.10 (m, 4H, Ar-*H*), 6.96 (td, *J* = 7.5, 1.6 Hz, 4H, Ar-*H*), 6.75 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 6.60 (td, *J* = 7.3, 1.4 Hz, 2H, Ar-*H*), 6.32-6.40 (m, 4H, Ar-*H*), 3.47-3.54 (m, 2H, -C*H*$_2$), 3.40-3.47 (m, 2H, -C*H*$_2$), 2.12 (brs, 1H, -O*H*). **^{13}C{^{1}H} NMR** (100.60 MHz, $CDCl_3$) δ: 151.06 (d, *J* = 3.6 Hz), 149.76(s), 148.43 (d, *J* = 1.4 Hz), 141.97 (s), 141.24 (d, *J* = 8.3 Hz), 139.48 (s), 139.28 (s), 134.27 (d, *J* = 2.2 Hz), 134.01 (d, *J* = 28.9 Hz), 132.71 (d, *J* = 20.37 Hz), 131.55 (s), 129.23 (s), 129.17 (s), 128.30 (d, *J* = 27.7 Hz), 127.49 (d, *J* = 5.3 Hz), 127.30 (s), 126.44 (d, *J* = 2.9 Hz), 122.63 (s), 120.20 (s), 118.81 (s), 116.25 (s), 73.45 (d, *J* = 9.4 Hz), 30.44 (s), 29.68 (s). **^{31}P{^{1}H} NMR** (161.96 MHz, $CDCl_3$) δ = -11.38. **HRMS (ESI):** $[M\text{-}OH]^+$ $C_{37}H_{26}OP$ calc. 517.1716 m/z, found 517.1700 m/z; $[M+H]^+$ $C_{37}H_{28}O_2P$ calc. 535.1821 m/z, found 535.1810 m/z; $[M+Na]^+$ $C_{37}H_{27}NaO_2P$ calc. 557.1641 m/z, found 557.1626 m/z; $[M+K]^+$ $C_{37}H_{27}KO_2P$ calc. 573.1380 m/z, found 573.1363 m/z. **Elemental Analysis** calculated: C: 83.13, H: 5.09, found: C: 82.83, H: 5.02.

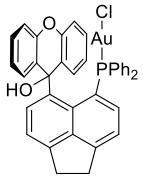
2.1.2 Synthesis of $\mathbf{1}_{acr}$



N-butyllithium (2.5 M hexanes, 1.02 mL, 3.1 mmol) was slowly added to a solution of 5-bromo-6-diphenylphosphinoacenaphthene (1.06 g, 2.6 mmol) in anhydrous Et_2O (20 mL) at -78 °C. The reaction mixture was stirred for 30 minutes and then gradually warmed to ambient temperature. After stirring for another hour, the resulting solution was cooled to -78 °C and N-methyl acridone (648 mg, 3.1 mmol) was added in one portion as a solid. The reaction mixture was stirred at -78 °C for another hour and then warmed to ambient temperature. After stirring for 18 hours, the reaction was quenched with a saturated aqueous ammonium chloride solution (30 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over $MgSO_4$ and brought to dryness under vacuum to afford a pale orange residue which was washed with a minimal amount of acetonitrile to give the pure product as a pale-yellow solid (925 mg, 1.7 mmol, 65% yield). **^{1}H NMR** (500.13 MHz, d_6-DMSO) δ = 8.67 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.54 (d, *J* = 7.4 Hz, 1H, Ar-*H*), 7.19 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 7.05

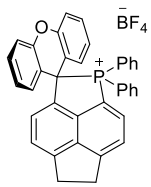
(t, *J* = 7.1 Hz, 1H, Ar-*H*), 6.89-7.02 (m, 9H, Ar-*H*), 6.41 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 6.30 (t, *J* = 7.2 Hz, 2H, Ar-*H*), 6.21 (t, *J* = 6.8 Hz, 4H, Ar-*H*), 5.16 (s, 1H, Ar_3C-O*H*), 3.59 (s, 3H, N-*Me*), 3.42-3.47 (m, 2H, -CH_2), 3.37-3.42 (m, 2H, -CH_2). **$^{13}C\{^1H\}$ NMR** (125.76 MHz, CD_2Cl_2) δ: 149.46 (s), 147.23 (s), 141.53 (s), 140.55 (d, *J* = 4.4 Hz), 140.41 (d, *J* = 8.3 Hz), 139.618 (d, *J* = 22.4 Hz), 136.63 (d, *J* = 2.5 Hz), 133.88 (d, *J* = 28.2 Hz), 132.03 (d, *J* = 20.7 Hz), 131.01 (s), 130.24 (d, *J* = 5.3 Hz), 128.23 (d, *J* = 28.9 Hz), 127.55 (s), 127.24 (d, *J* = 5.5 Hz), 127.02 (s), 126.33 (d, *J* = 3.2 Hz), 119.54 (s), 118.45 (s), 118.35 (s), 111.89 (s), 74.15 (d, *J* = 8.1 Hz, Ar_3C-OH), 33.53 (s, N-CH_3), 29.75 (s, -CH_2), 28.92 (s, -CH_2). **$^{31}P\{^1H\}$ NMR** (162.00 MHz, CD_2Cl_2) δ = -12.90. **HRMS (ESI):** $[M\text{-}OH]^+$ $C_{38}H_{29}NP$ calc. 530.2032 m/z, found 530.2037 m/z; $[M+H]^+$ $C_{38}H_{31}NOP$ calc. 548.2138 m/z, found 548.2150 m/z.

2.1.3 Synthesis of $\mathbf{1_{xant}}$-AuCl



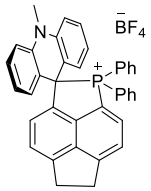
(tht)AuCl (60 mg, 0.19 mmol) was added to a solution of **$\mathbf{1_{xant}}$** (100 mg, 0.19 mmol) in CH_2Cl_2 (10mL). The resulting mixture was stirred at ambient temperature for 1 hour, during which a white powdery solid gradually formed. The product was then collected and washed with CH_2Cl_2 (2 x 2 mL) to afford the pure product as an off-white solid (149 mg, 0.18 mmol, 93% yield). **^1H NMR** (400.20 MHz, d_6-DMSO) δ = 7.42-7.58 (m, 12H, Ar-*H*), 7.30 (d, *J* = 7.4 Hz, 1H, Ar-*H*), 7.23-7.40 (brs, 1H, -O*H*), 7.15-7.22 (m, 3H, Ar-*H*), 7.07 (d, *J* = 7.8, 2H, Ar-*H*), 6.86 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 6.72 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 3.31-3.38 (m, 2H, -CH_2), 3.22-3.30 (m, 2H, -CH_2). **$^{13}C\{^1H\}$ NMR** (125.76 MHz, d_6-DMSO) δ: 151.67 (d, *J* = 3.5 Hz), 148.38 (s), 146.82 (s), 142.34 (d, *J* = 10.9 Hz), 141.85 (s), 140.48 (d, *J* = 10.5 Hz), 132.99 (s), 132.65 (d, *J* = 13.5 Hz), 130.79 (d, *J* = 13.7 Hz), 130.19 (s), 129.51 (s), 129.46 (s), 128.89 (d, *J* = 11.2 Hz), 128.35 (s), 122.95 (s), 121.09 (s), 120.56 (s), 120.48 (s), 118.47 (d, *J* = 12.6 Hz), 115.39 (s), 72.54 (d, *J* = 2.7 Hz), 29.50 (s), 29.01 (s). **$^{31}P\{^1H\}$ NMR** (162.00 MHz, d_6-DMSO) δ = 40.56.

2.1.4 Synthesis of [2_{xant}]BF_4



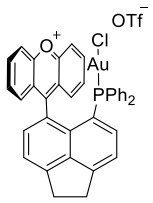
HBF_4▪Et_2O (52% w/w in Et_2O, 59 mg, 0.37 mmol) was added to a solution of $\mathbf{1}_{xant}$ (200 mg, 0.37 mmol) in Et_2O (10mL) at ambient temperature. The resulting mixture was stirred for 1 hour during which a pale green solid gradually formed. The solid was then collected through filtration and washed with Et_2O (2 x 10 mL) to afford the pure product as a white solid (208 mg, 0.34 mmol, 93% yield). Single crystals suitable for X-ray crystal structure analysis were grown by layering hexane in a CH_2Cl_2 solution of [$\mathbf{2}_{xant}$]BF_4 under an ambient atmosphere. **^{1}H NMR** (500.13 MHz, $CDCl_3$) δ = 8.41 (dd, *J* = 9.3, 7.3 Hz, 1H, Ar-*H*), 8.14 (dd, *J* = 7.4, 3.5 Hz, 1H, Ar-*H*), 7.70 (d, *J* = 7.1 Hz, 1H, Ar-*H*), 7.54-7.60 (m, 2H, Ar-*H*), 7.50 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 7.31-7.42 (m, 8H, Ar-*H*), 7.19-7.26 (m, 4H, Ar-*H*), 6.66-6.72 (m, 2H, Ar-*H*), 6.22-6.27 (m, 2H, Ar-*H*), 3.81-3.89 (m, 2H, -CH_2), 3.69-3.78 (m, 2H, -CH_2). **^{13}C{^{1}H} NMR** (125.76 MHz, $CDCl_3$) δ = 156.06 (d, *J* =2.8 Hz), 152.29 (d, *J* = 4.6 Hz), 147.79 (s), 139.54 (d, *J* = 23.7 Hz), 138.47 (d, *J* = 11.7 Hz), 136.98 (d, *J* = 2.7 Hz), 134.80 (d, *J* = 3.6 Hz), 133.86 (s), 133.72 (s), 133.12 (s), 133.05 (s), 130.71 (d, *J* = 3.6 Hz), 129.95 (s),129.85 (s), 128.97 (d, *J* = 4.6 Hz), 128.88 (s), 125.11 (d, *J* = 11.9Hz), 124.30 (d, *J* = 3.0 Hz), 123.72 (s), 119.86 (s), 117.25 (d, *J* = 3.0 Hz), 117.00 (s), 116.39 (s), 106.72 (s), 106.04 (s), 64.18 (d, *J* = 48.1 Hz), 32.64 (s), 31.46 (s). **^{31}P{^{1}H} NMR** (161.96 MHz, $CDCl_3$) δ = 51.99. **Elemental Analysis** calculated: C: 72.53, H: 4.34, found: C: 72.37, H: 4.48.

2.1.5 Synthesis [2_{acr}]BF_4



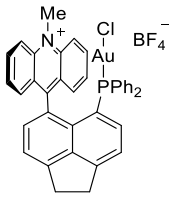
HBF_4▪Et_2O (52% w/w in Et_2O, 58 mg, 0.36 mmol) was added to a solution of $\mathbf{1}_{acr}$ (200 mg, 0.36 mmol) in Et_2O (10mL) at ambient temperature. The resulting mixture was stirred for 1 hour during which a white powdery solid gradually formed. The solid was then collected through filtration and washed with Et_2O (2 x 10 mL) to afford the pure product as a pale-yellow solid (214 mg, 0.35 mmol, 95% yield). Single crystals suitable for X-ray crystal structure analysis were grown by layering hexane in a CH_2Cl_2 solution of [$\mathbf{2}_{acr}$]BF_4 under an ambient atmosphere. **^{1}H NMR** (400.09 MHz, d_3-MeCN) δ = 8.10 (dd, *J* = 9.6, 7.2 Hz, 1H, Ar-*H*), 7.90-7.95 (m, 1H, Ar-*H*), 7.82 (dd, *J* = 7.2, 0.74 Hz, 1H, Ar-*H*), 7.70 (d, *J* = 7.3 Hz, 1H, Ar-*H*), 7.55-7.61 (m, 2H, Ar-*H*), 7.30-7.37 (m, 4H, Ar-*H*), 7.16-7.29 (m, 6H, Ar-*H*), 7.04 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 6.70 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 6.49 (ddd, *J* = 7.9, 3.1, 1.4 Hz, 2H, Ar-*H*), 3.78-3.84 (m, 2H, -CH_2), 3.72-3.78 (m, 2H, -CH_2), 3.40 (d, *J* = 0.83 Hz, 3H, N-*Me)*. **^{13}C{^{1}H} NMR** (100.60 MHz, d_3-MeCN) δ = 156.17 (d, *J* = 2.9 Hz), 148.25 (d, *J* = 1.4 Hz), 143.90 (d, *J* = 5.2 Hz), 140.18 (s), 139.93 (s), 139.26 (s), 139.14 (s), 136.32 (d, *J* = 2.8 Hz), 134.77 (d, *J* = 3.5 Hz), 134.00 (s), 133.95 (s), 132.99 (d, *J* = 16.1 Hz) 130.79 (d, *J* = 8.7 Hz), 130.22 (d, *J* = 3.7 Hz), 129.85 (s), 129.73 (s), 128.37 (d, *J* = 5.2 Hz), 124.41 (d, *J* = 11.7 Hz), 123.76 (s), 122.25 (s), 122.08 (d, *J* = 2.9 Hz), 114.29 (d, *J* = 2.9 Hz), 109.78 (s), 108.95 (s), 70.07 (d, *J* = 41.6 Hz), 33.81 (s), 32.75 (d, *J* = 1.4 Hz), 31.67 (s). **^{31}P{^{1}H} NMR** (161.96 MHz, d_3-MeCN) δ = 50.01. **Elemental Analysis** calculated: C: 73.92, H: 4.73, found: C: 74.05, H: 4.86.

2.1.6 Synthesis of [3_{xant}]OTf



TMSOTf (29 mg, 0.13 mmol) was added to a solution of **1_{xant}-AuCl** (100 mg, 0.13 mmol) in CH_2Cl_2 (10mL) at ambient temperature. An immediate color change from colorless to deep purple ensued. The resulting mixture was stirred for 1 hour and then brought to dryness under vacuum to afford a purple oil. This oil was then triturated in Et_2O (20 mL) to give a solid which was washed by Et_2O (3 x 10 mL) and dried under vacuum to give the pure product as a purple solid (134 mg, 0.16 mmol, 92% yield). Single crystals suitable for X-ray analysis were grown by layering hexanes on a CH_2Cl_2 solution of [**3_{xant}**]OTf at room temperature. **^{1}H NMR** (499.33 MHz, $CDCl_3$) δ = 8.34 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 8.25 (d, *J* = 8.9 Hz, 2H, Ar-*H*), 7.87 (d, *J* = 7.4 Hz, 1H, Ar-*H*), 7.60-7.72 (m, 7H, Ar-*H*), 7.57 (t, *J* = 7.1 Hz, 2H, Ar-*H*), 7.41 (td, *J* = 7.9, 3.9 Hz, 4H, Ar-*H*), 6.99 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 6.96 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 3.76 (brs, 4H, -C*H*$_2$). **^{13}C{^{1}H} NMR** (125.56 MHz, $CDCl_3$) δ = 176.28 (s), 160.39 (d, *J* = 3.0 Hz), 157.98 (s), 155.68 (d, *J* = 2.5 Hz), 144.84 (s), 144.57 (d, *J* = 18.4 Hz), 140.94 (d, *J* = 11.4 Hz), 137.08 (s), 136.28 (s), 132.03 (d, *J* = 11.9 Hz), 131.34 (s), 130.71 (d, *J* = 8.1 Hz), 130.39 (d, *J* = 14.1 Hz), 129.92 (s), 124.59 (s), 123.39 (d, *J* = 2.7 Hz), 122.32 (d, *J* = 37.5 Hz), 121.62 (s), 120.30 (d, *J* = 16.6 Hz), 120.03 (s), 118.59 (d, *J* = 317.5 Hz), 110.61 (s), 109.71 (s), 31.21 (s), 30.68 (s). **^{31}P{^{1}H} NMR** (161.96 MHz, $CDCl_3$) δ = 30.46. **Elemental Analysis** calculated: C: 50.77, H: 2.92, found: C: 50.45, H: 2.87.

2.1.7 Synthesis of [3_{acr}]BF_4

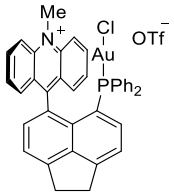


Method 1: (tht)AuCl (60 mg, 0.19 mmol) was added to a solution of **1_{acr}** (103 mg, 0.19 mmol) in CH_2Cl_2 (10mL). The resulting mixture was stirred at ambient temperature for 1 hour before being treated with HBF_4▪Et_2O (52% w/w in Et_2O, 31 mg, 0.19 mmol). The solution was stirred for another hour and brought to dryness under vacuum to afford an orange residue. This residue was washed with Et_2O (3 x 10 mL), affording the pure product as an orange solid (134 mg, 0.16 mmol, 88% yield). Single crystals suitable for X-ray analysis were grown by layering hexanes on a CH_2Cl_2 solution of [**3_{acr}**]BF_4 under an ambient atmosphere. **^{1}H NMR** (500.13 MHz, $CDCl_3$) δ = 8.53 (d, *J* = 9.2 Hz, 2H, Ar-*H*), 8.19 (dd, *J* = 9.3, 1.7 Hz, 2H, Ar-*H*), 7.63 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 7.37-7.47 (m, 3H, Ar-*H*), 7.27-7.37 (m, 5H, Ar-*H*), 7.21 (dd, *J* = 7.9, 2.6 Hz, 4H, Ar-*H*), 7.14 (dd, *J* = 16.0, 7.7 Hz, 1H, Ar-*H*), 6.85 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 6.82 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 4.99 (s, 3H, N-*Me),* 3.67 (brs, 4H, -C*H*$_2$). **^{13}C{^{1}H} NMR** (125.76 MHz, $CDCl_3$) δ = 161.11 (s), 154.30 (d, *J* = 2.2 Hz), 151.61 (s), 141.70 (s), 141.17 (d, *J* = 8.6 Hz), 140.66 (d, *J* = 8.7 Hz), 138.48 (s), 136.56 (s), 134.13 (d, *J* = 14.5 Hz), 132.47 (d, *J* = 2.5 Hz), 131.89 (d, *J* = 11.3 Hz), 130.21 (s), 129.69 (d, *J* = 6.5 Hz), 129.51 (d, *J* = 15.7 Hz), 128.02 (s), 127.43 (s), 126.13 (d, *J* = 3.2 Hz), 121.39 (s), 120.61 (d, *J* = 11.6 Hz), 119.43 (s), 119.36 (s), 118.94 (s), 39.40 (s), 30.63 (s), 30.54 (s). **^{31}P{^{1}H} NMR** (162.00 MHz, $CDCl_3$) δ = 30.66. **Elemental Analysis** calculated: C: 53.71, H: 3.44, found: C: 53.44, H: 3.52.

Method 2: (tht)AuCl (51 mg, 0.16 mmol) was added to a solution of [**2_{acr}**]BF_4 (100 mg, 0.16 mmol) in CH_2Cl_2 (10mL) at ambient temperature. The resulting mixture was stirred for 1 hour during which solution turned from colorless to deep orange. Upon completion, the resulting mixture was concentrated under reduced pressure, washed with Et_2O (3 x 10 mL), and dried under vacuum to afford the pure product as an orange solid (124 mg,

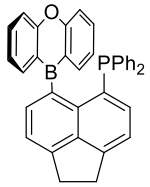
0.13 mmol, 82% yield).

2.1.8 Synthesis of [3_{acr}]OTf



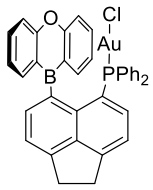
(tht)AuCl (60 mg, 0.19 mmol) was added to a solution of $\mathbf{1}_{acr}$ (103 mg, 0.19 mmol) in CH_2Cl_2 (10mL). The resulting mixture was stirred at room temperature for 1 hour before being treated with TMSOTf (49 mg, 0.22 mmol). After stirring for another hour, the solution was brought to dryness under vacuum to afford a residue which was washed by Et_2O (3 x 10 mL) to give the pure product as an orange solid (123 mg, 0.15 mmol, 76% yield). **^{1}H NMR** (500.13 MHz, $CDCl_3$) δ = 8.53 (d, *J* = 9.5 Hz, 2H, Ar-*H*), 8.18 (ddd, *J* = 9.2, 6.2, 2.4 Hz, 2H, Ar-*H*), 7.64 (d, *J* = 7.4 Hz, 1H, Ar-*H*), 7.43 (t, *J* = 7.1 Hz, 2H, Ar-*H*), 7.40 (d, *J* = 7.3 Hz, 1H, Ar-*H*), 7.31-7.36 (m, 4H, Ar-*H*), 7.21 (td, *J* = 7.6, 2.3 Hz, 4H, Ar-*H*), 7.13 (dd, *J* = 16.2, 7.3 Hz, 1H, Ar-*H*), 6.84 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 6.82 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 5.00 (s, 3H, N-*Me),* 3.67 (brs, 4H, -C*H*$_2$). **^{13}C{^{1}H} NMR** (125.76 MHz, $CDCl_3$) δ = 161.21 (s), 154.32 (d, *J* = 2.7 Hz), 151.64 (s), 141.70 (s), 141.18 (d, *J* = 8.3 Hz), 140.65 (d, *J* = 8.9 Hz), 138.49 (s), 136.61 (s), 134.16 (d, *J* = 14.3 Hz), 132.47 (d, *J* = 2.5 Hz), 131.85 (d, *J* = 10.8 Hz), 130.29 (s), 129.79 (s), 129.66 (s), 129.57 (s), 129.47 (s), 127.97 (s), 127.44 (s), 126.10 (d, *J* = 2.8 Hz), 121.39 (s), 120.61 (d, *J* = 11.6 Hz), 121.43 (s), 120.71 (q, *J* = 319.7 Hz), 120.62 (d, *J* = 12.5 Hz), 119.45 (s), 119.34 (s), 118.90 (s), 39.57 (s), 30.64 (s), 30.55 (s). **^{31}P{^{1}H} NMR** (162.00 MHz, $CDCl_3$) δ = 30.65.

2.1.9 Synthesis of 5



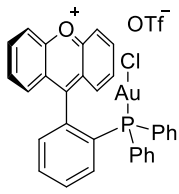
N-butyllithium (2.5 M hexanes, 1.02 mL, 3.1 mmol) was slowly added to a solution of 5-bromo-6-diphenylphosphinoacenaphthene (1.06 g, 2.6 mmol) in anhydrous Et_2O (20 mL) at -78 °C. The reaction mixture was stirred for 30 minutes and then gradually warmed to ambient temperature over the course of 15 minutes. After stirring for another hour at room temperature, the resulting solution was cooled to -78 °C and an Et_2O (10mL) solution of 10-bromo-9-oxa-10-boraanthracene (800 mg, 3.1 mmol) was slowly added. The reaction mixture was stirred at -78 °C for another hour then allowed to warm to ambient temperature. After stirring for 18 hours, the reaction was quenched with saturated aqueous ammonium chloride solution (30 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over $MgSO_4$ and brought to dryness under vacuum to afford a pale-yellow residue which was washed with minimal acetonitrile to give the pure product as a white solid (0.98 g, 1.9 mmol, 72% yield). **^{1}H NMR** (500.13 MHz, $CDCl_3$) δ = 7.59 (t, *J* = 7.3 Hz, 1H, Ar-*H*), 7.54 (d, *J* = 6.9 Hz, 1H, Ar-*H*), 7.42 (t, *J* = 6.6 Hz, 2H, Ar-*H*), 7.15 (td, *J* = 7.6, 1.6 Hz, 2H, Ar-*H*), 6.95-7.02 (m, 8H, Ar-*H*), 6.84-6.90 (m, 4H, Ar-*H*), 6.52-6.61 (m, 4H, Ar-*H*), 3.48 (brs, 4H, -C*H*$_2$). **^{11}B{^{1}H} NMR** (128.36 MHz, $CDCl_3$) δ: -3.31. **^{13}C{^{1}H} NMR** (125.76 MHz, $CDCl_3$) δ: 158.20 (d, *J* = 5.5 Hz), 151.46(s), 151.44(s), 145.19 (s), 144.88 (s), 142.61 (d, *J* = 1.9 Hz), 138.32 (d, *J* = 11.7 Hz), 134.46 (d, *J* = 5.0 Hz), 132.88 (s), 132.75 (s), 132.36 (s), 130.48 (d, *J* = 2.7 Hz), 128.43 (s), 128.36 (s), 127.48 (d, *J* = 16.6 Hz), 127.28 (d, *J* = 23.5 Hz), 122.58 (d, *J* = 2.7 Hz), 122.13 (d, *J* = 2.7 Hz), 121.71 (s), 120.43 (d, *J* = 7.3 Hz), 115.46 (d, *J* = 3.6 Hz), 31.68 (s), 30.94 (s). **^{31}P{^{1}H} NMR** (161.96 MHz, $CDCl_3$) δ = 6.95. **HRMS (ESI):** $[M+H]^+$ $C_{36}H_{27}BOP$ calc. 517.1887 m/z, found 517.1885 m/z; $[M+Na]^+$ $C_{36}H_{26}BNaOP$ calc. 539.1707 m/z, found 539.1707 m/z

2.1.10 Synthesis 6



(tht)AuCl (62 mg, 0.19 mmol) was added to a solution of **5** (100 mg, 0.19 mmol) in CH_2Cl_2 (10mL). The resulting mixture was stirred at ambient temperature for 1 hour and brought to dryness under vacuum to yield an off-white powder. This powder was washed with Et_2O (2 x 10 mL) to afford the pure product as a white solid (125 mg, 0.17 mmol, 86% yield). Single crystals suitable for X-ray analysis were grown by slow evaporation of a CH_2Cl_2 solution of **6** in air. **^{1}H NMR** (500.13 MHz, $CDCl_3$) δ = 7.51-7.57 (m, 3H, Ar-*H*), 7.49 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.44 (d, *J* = 6.9 Hz, 1H, Ar-*H*), 7.26-7.37 (m, 4H, Ar-*H*), 7.19 (td, *J* = 8.2, 2.4 Hz, 4H, Ar-*H*), 7.08-7.16 (m, 6H, Ar-*H*), 6.76 (t, *J* = 7.2 Hz, 2H, Ar-*H*), 3.53 (brs, 4H, -C*H*$_2$). **^{11}B{^{1}H} NMR** (128.36 MHz, $CDCl_3$) δ: 49.62. **^{13}C{^{1}H} NMR** (125.76 MHz, $CDCl_3$) δ: 159.94 (s), 153.34 (d, *J* = 2.8 Hz), 147.48 (d, *J* = 2.5 Hz), 139.93 (d, *J* = 11.0 Hz), 139.12 (d, *J* = 7.0 Hz), 136.76 (d, *J* = 15.7 Hz), 136.25 (s), 135.61 (s), 134.19 (s), 134.09 (s), 131.34 (d, *J* = 2.7 Hz), 131.13 (s), 130.62 (s), 128.98 (d, *J* = 11.8 Hz), 125.52 (brs), 122.34 (s), 120.45 (s), 120.20 (s), 120.00 (s), 119.16 (d, *J* = 10.8 Hz), 117.89 (s), 30.45 (s), 30.29 (s). **^{31}P{^{1}H} NMR** (161.96 MHz, $CDCl_3$) δ = 26.10 ppm. **Elemental Analysis** calculated: C: 57.74, H: 3.50, found: C: 57.44, H: 3.38.

2.1.11 Synthesis of [4$_{Xant}$]OTf



This compound was prepared by adding (tht)AuCl (70 mg, 0.22 mmol) to a solution of **A** (100 mg, 0.22 mmol) in CH_2Cl_2 (10mL). The resulting mixture was stirred at ambient temperature for 1 hour before being treated with TMSOTf (55.6 mg, 0.25 mmol). After stirring for another hour, the solution was brought to dryness under vacuum to afford an orange residue. This residue was washed with Et_2O (3 x 10 mL), affording the pure product as a bright yellow solid (149 mg, 0.18 mmol, 82% yield). Single crystals suitable for X-ray analysis were grown by layering Et_2O in a MeCN solution of [**4$_{Xant}$**]OTf under an ambient atmosphere. **^{1}H NMR** (500.13 MHz, $CDCl_3$) δ = 8.42 (ddd, *J* = 8.8, 6.0, 2.3 Hz, 2H, Ar-*H*), 8.33 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.99-8.05 (m, 1H, Ar-*H*), 7.97 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.85 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 7.50-7.61 (m, 7H, Ar-*H*), 7.44 (td, *J* = 7.9, 2.8 Hz, 4H, Ar-*H*), 7.35 (dd, *J* = 13.7, 8.1 Hz, 4H, Ar-*H*). **^{13}C{^{1}H} NMR** (125.76 MHz, $CDCl_3$) δ = 172.77 (d, *J* = 6.6 Hz), 158.34 (s), 144.57 (s), 136.04 (d, *J* = 14.6 Hz), 135.06 (d, *J* = 5.1 Hz), 134.40 (d, *J* = 13.9 Hz), 133.10 (d, *J* = 2.8 Hz), 132.93 (d, *J* = 2.8 Hz), 132.28 (d, *J* = 8.2 Hz), 131.94 (d, *J* = 8.2 Hz), 130.52 (s), 129.85 (d, *J* = 11.9 Hz), 129.37 (s), 128.71 (s), 128.24 (s), 127.37 (s), 126.86 (s), 125.76 (s), 121.68 (s), 120.70 (s), 119.13 (s). **^{31}P{^{1}H} NMR** (162.00 MHz, $CDCl_3$) δ = 24.46.

2.2 NMR spectra

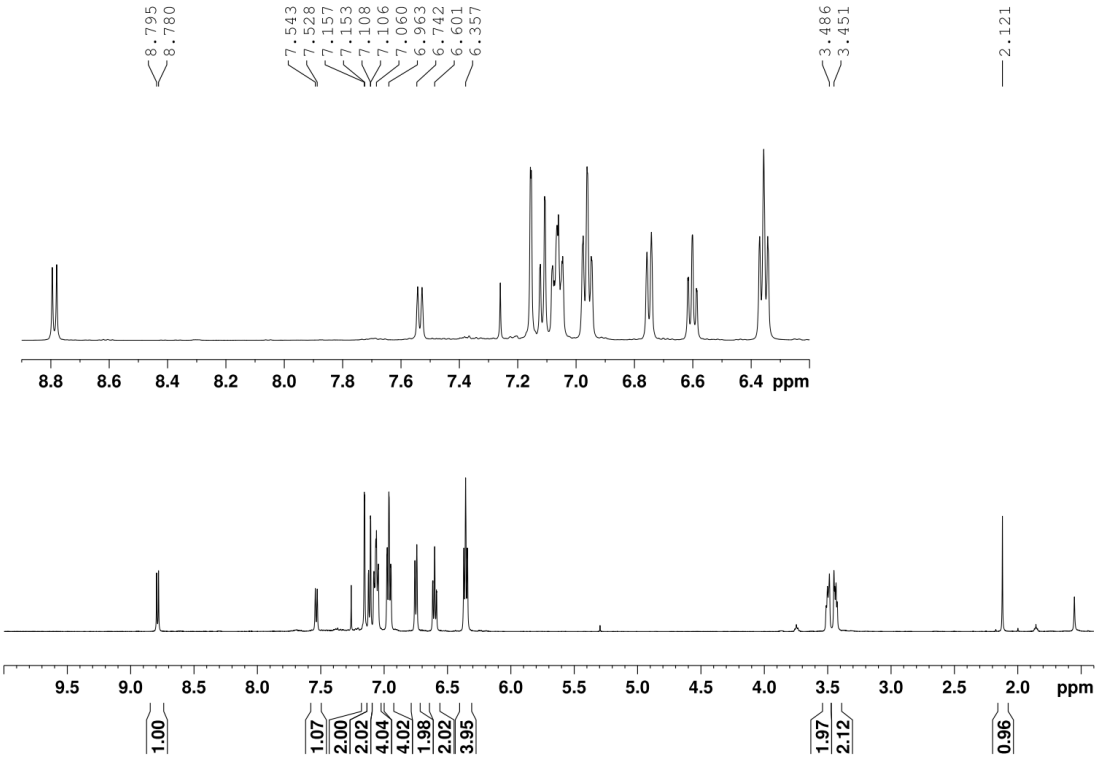


Figure S1. ^{1}H NMR spectrum of **1**$_{xant}$ in $CDCl_3$.

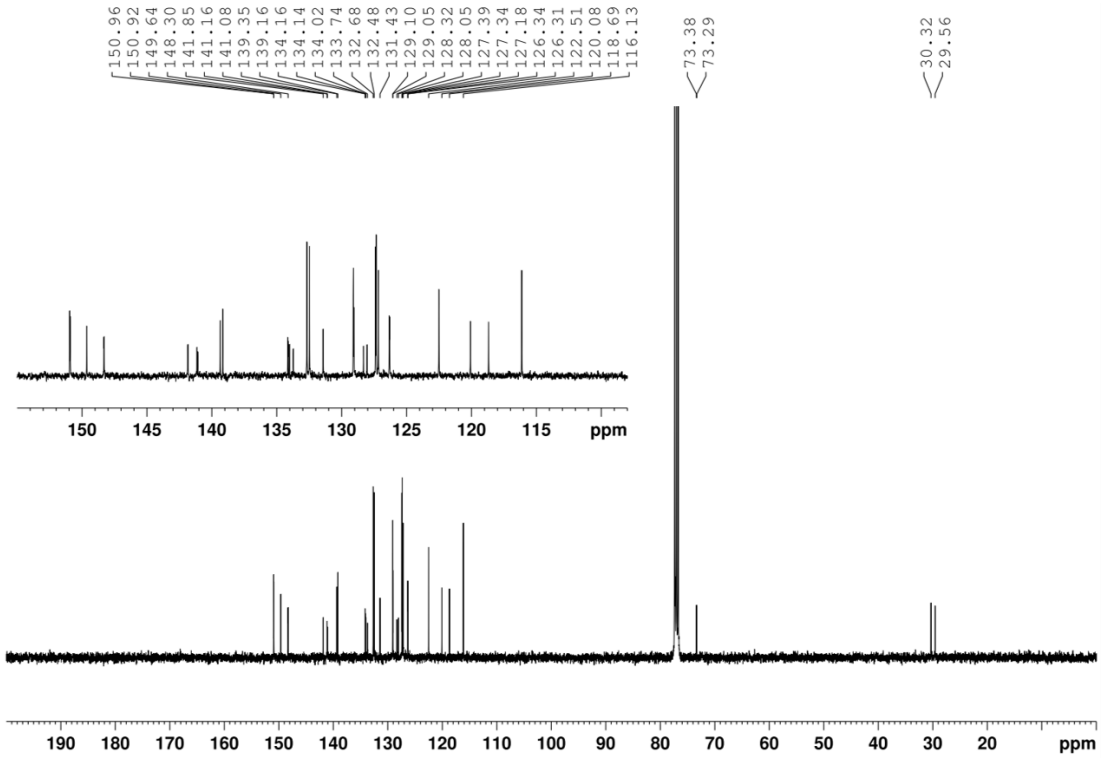


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1**$_{xant}$ in $CDCl_3$.

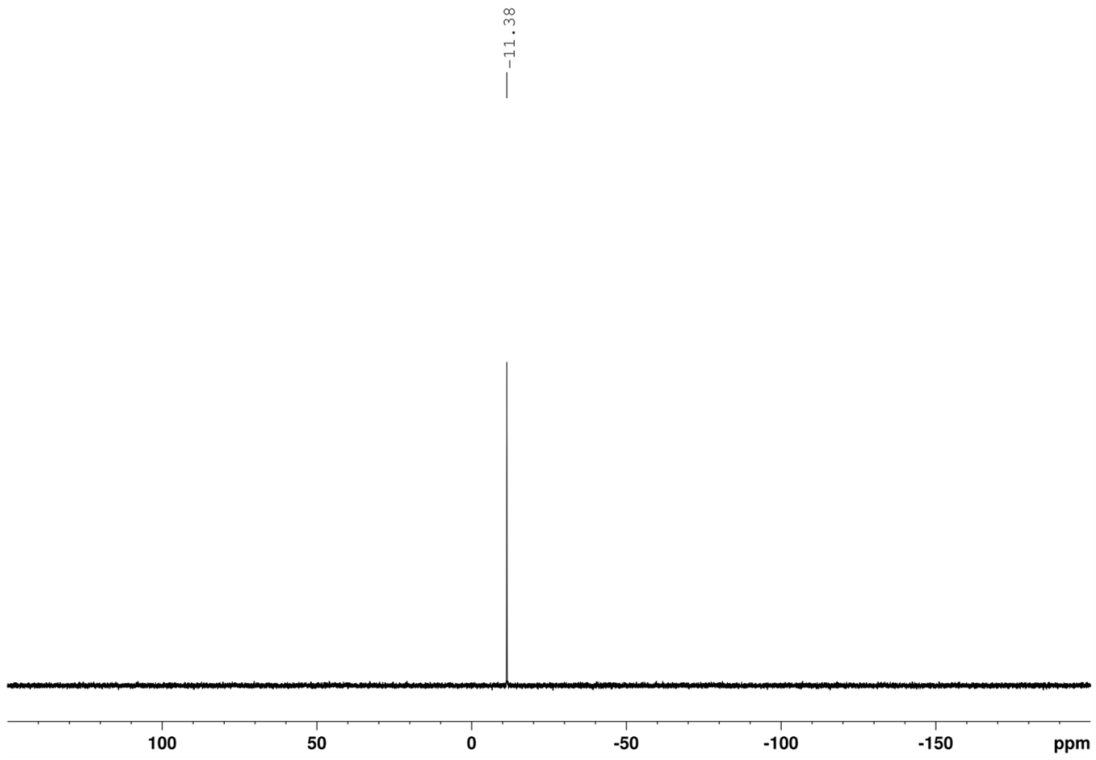


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of $\mathbf{1}_{xant}$ in $CDCl_3$.

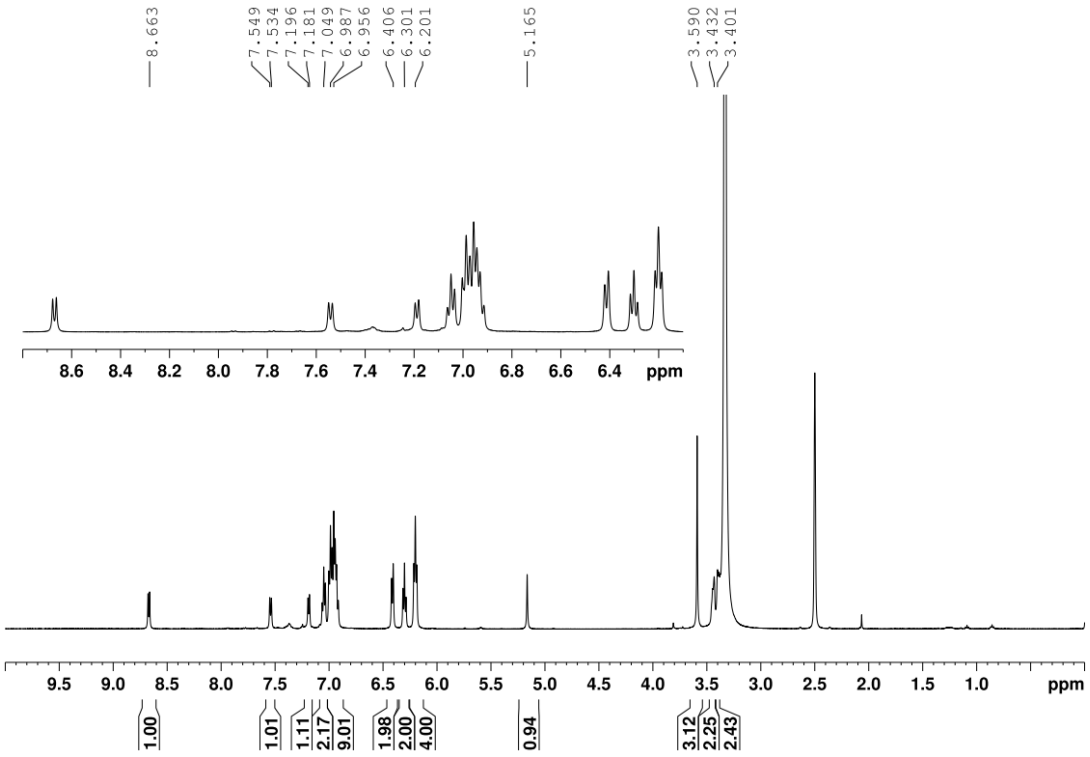


Figure S4. ^{1}H NMR spectrum of $\mathbf{1}_{acr}$ in d_6-DMSO.

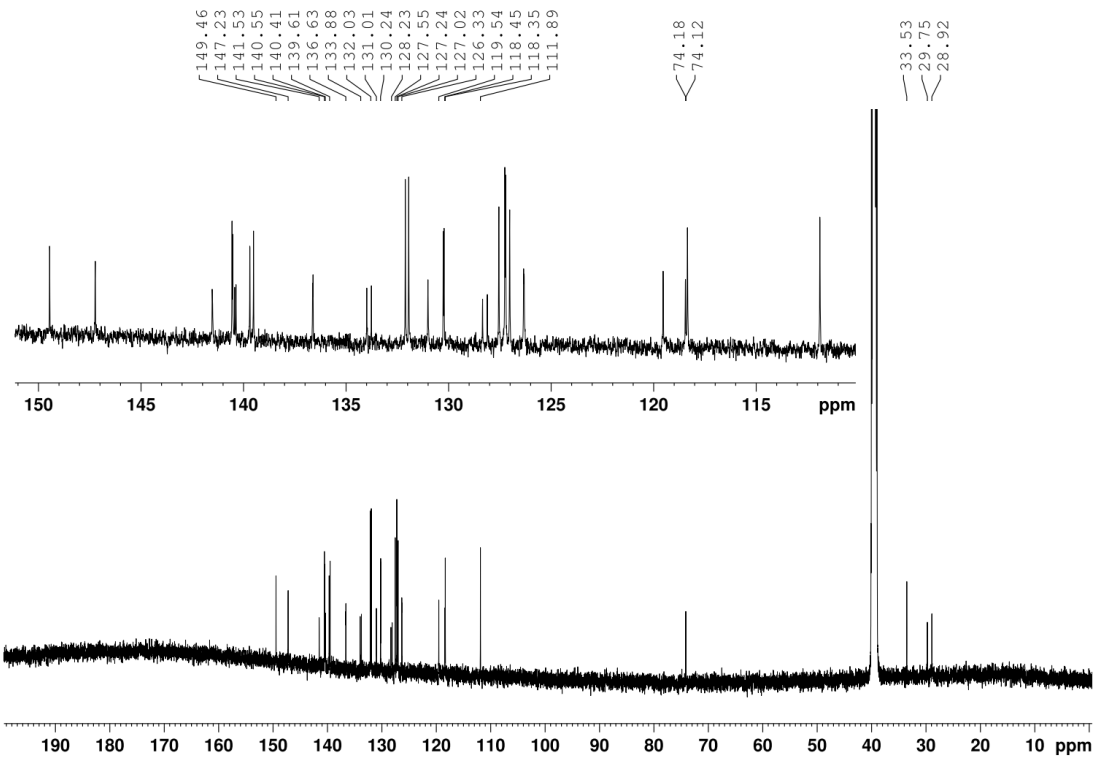


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{1}_{acr}$ in d_6-DMSO.

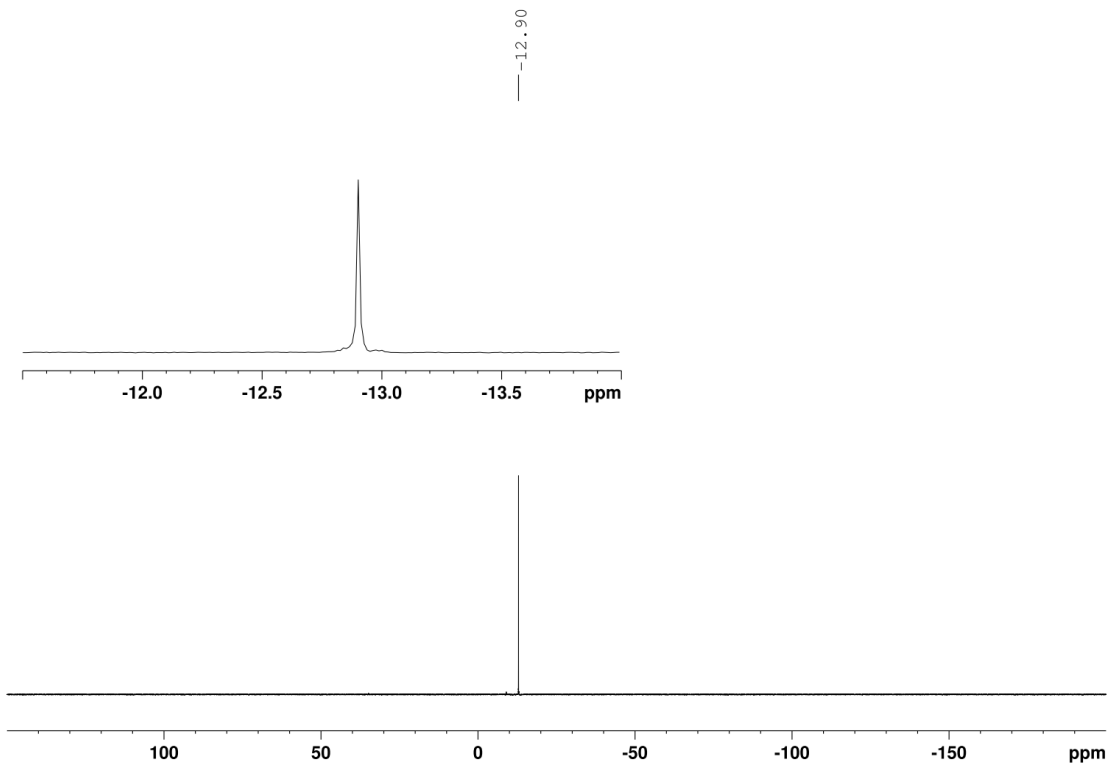


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of $\mathbf{1}_{acr}$ in d_6-DMSO.

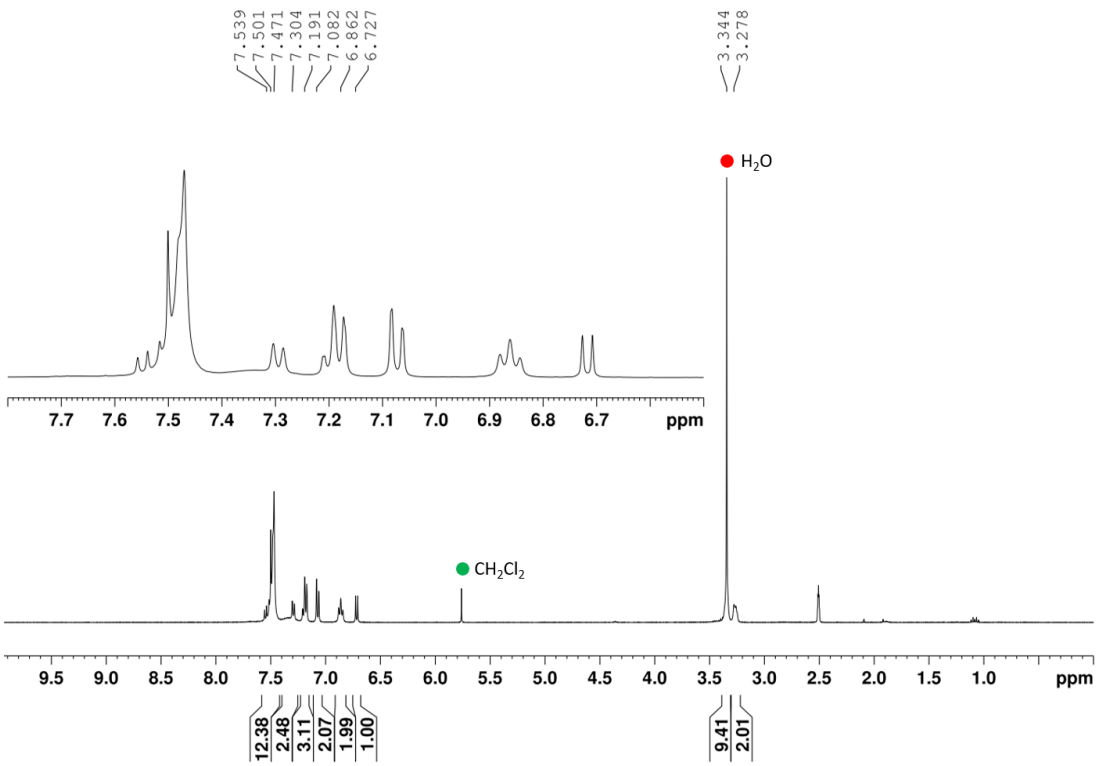


Figure S7. ^{1}H NMR spectrum of **1**$_{xant}$-AuCl in d_6-DMSO.

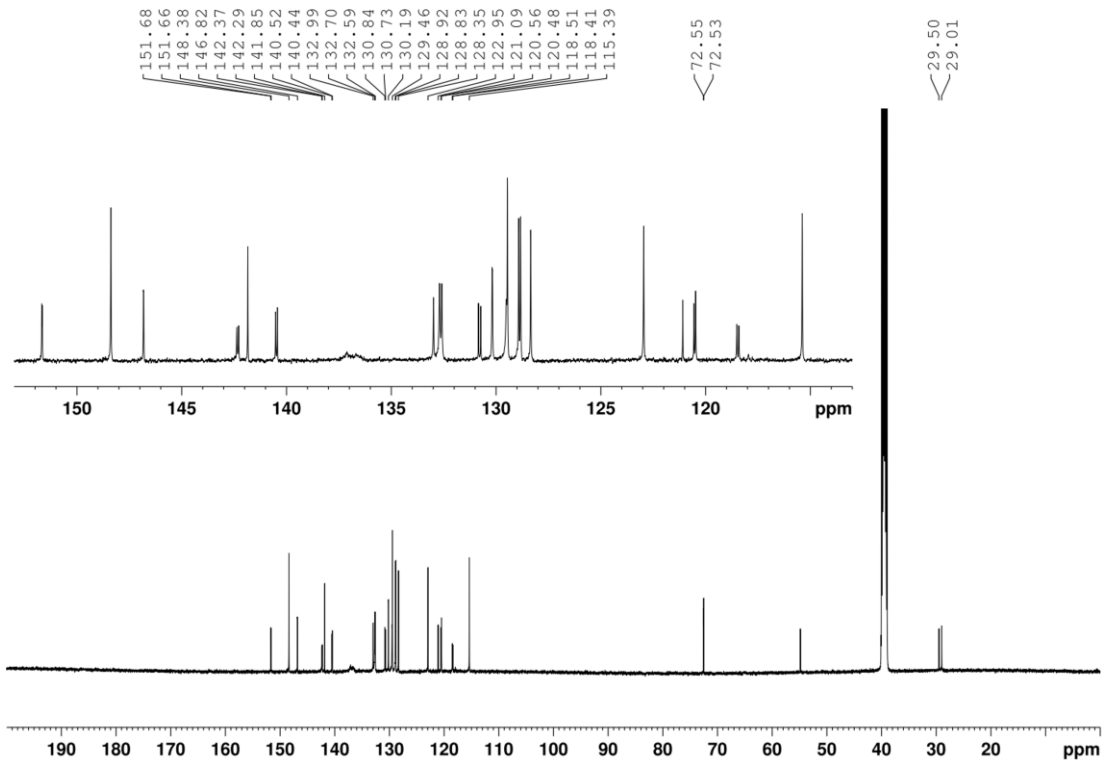


Figure S8. ^{13}C{^{1}H} NMR spectrum of **1**$_{xant}$-AuCl in d_6-DMSO.

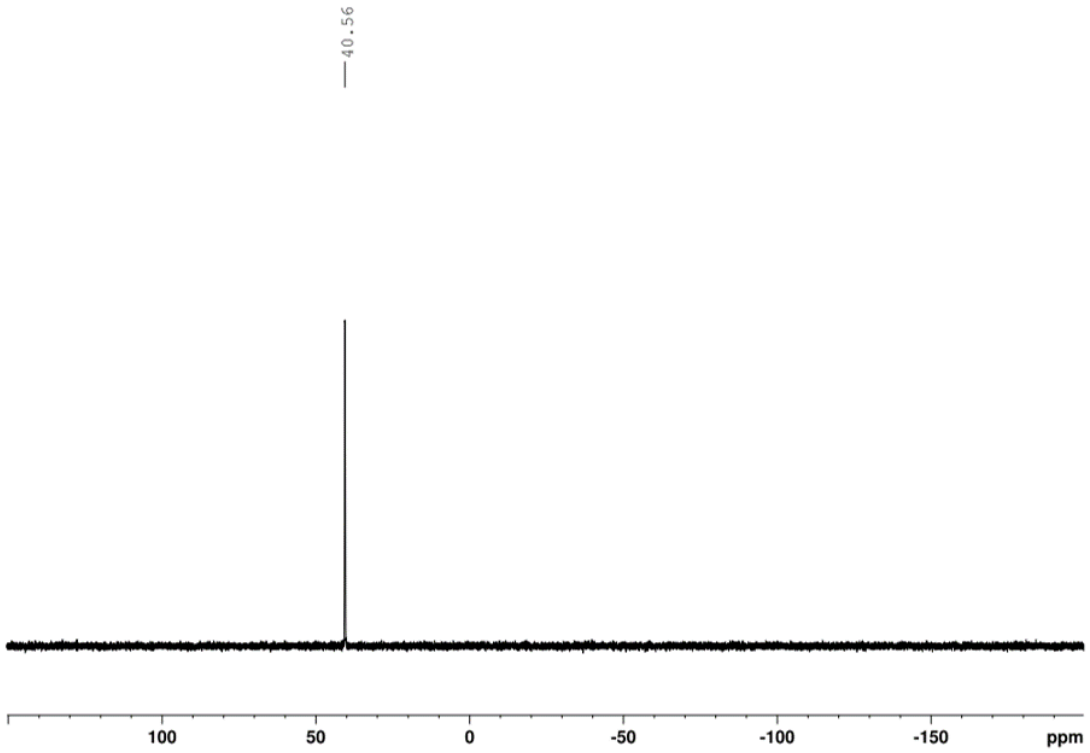


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of $\mathbf{1}_{xant}$-AuCl in d_6-DMSO.

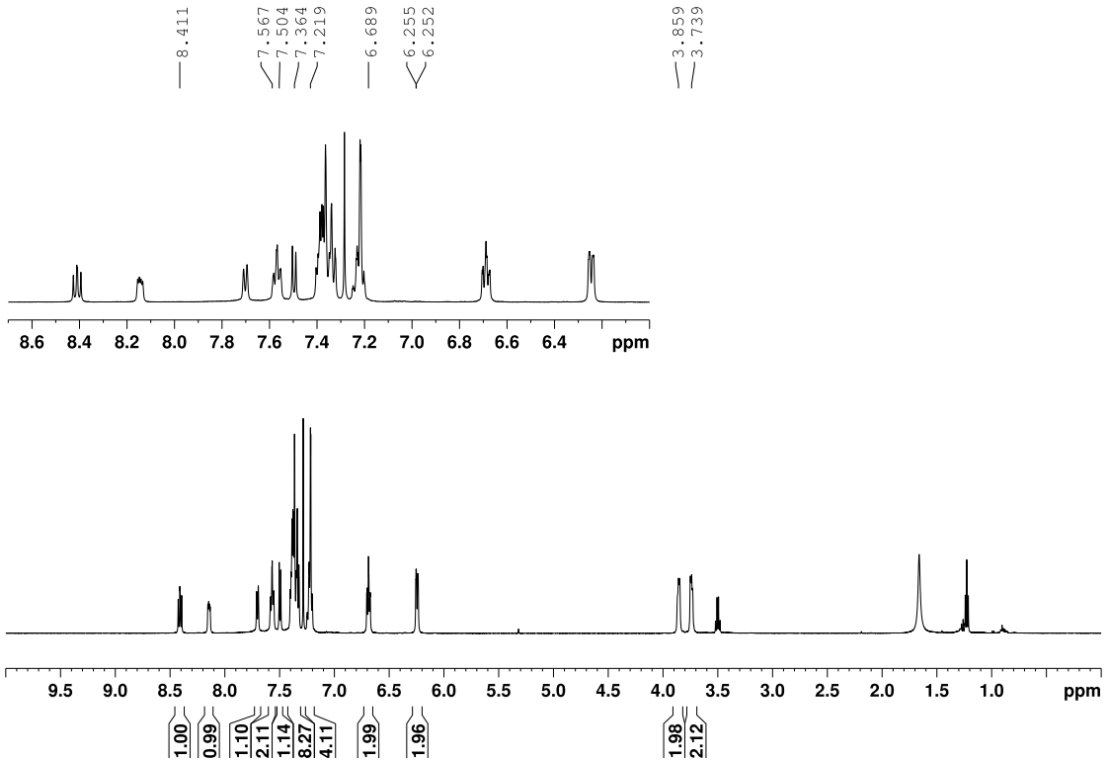


Figure S10. ^{1}H NMR spectrum of $[\mathbf{2}_{xant}]BF_4$ in $CDCl_3$

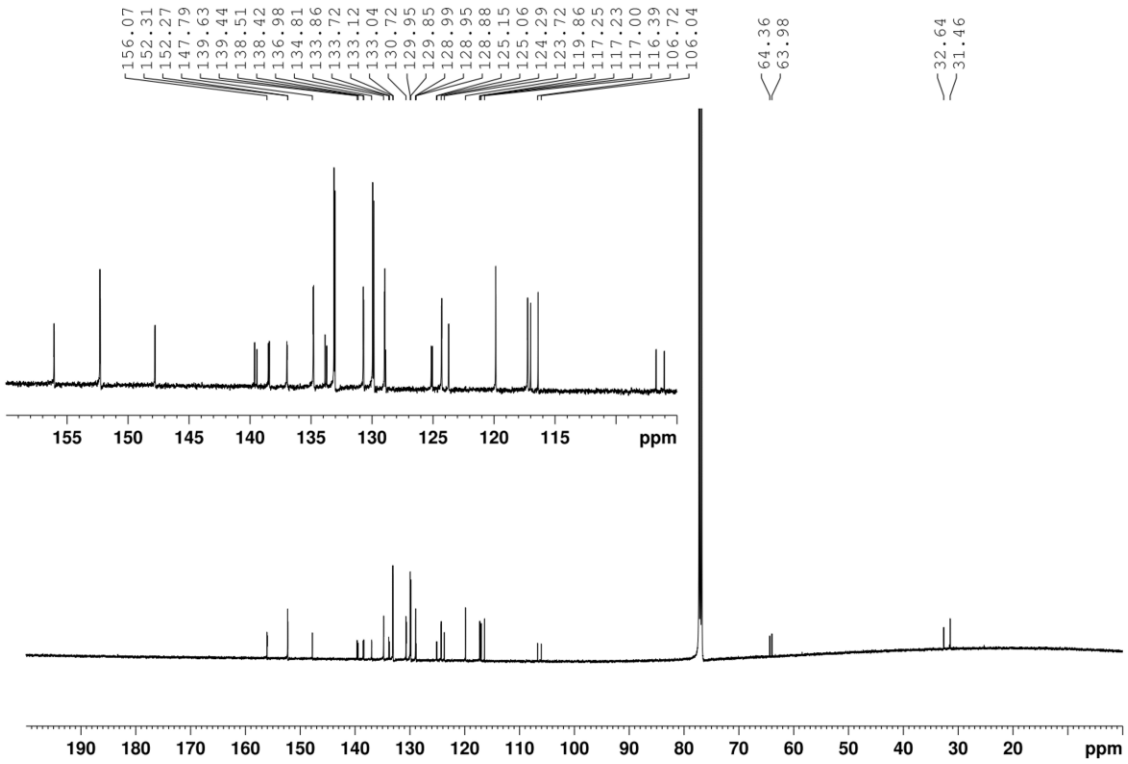


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of [**2**$_{xant}$]BF_4 in $CDCl_3$.

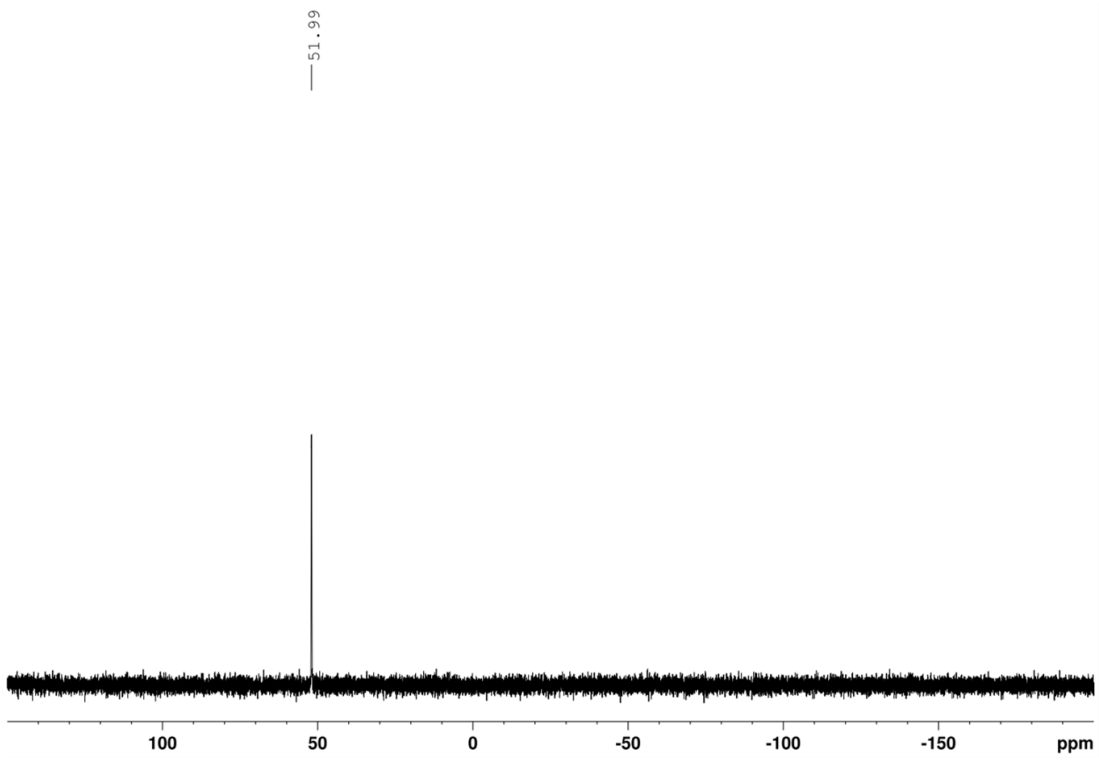


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of [**2**$_{xant}$]BF_4 in $CDCl_3$

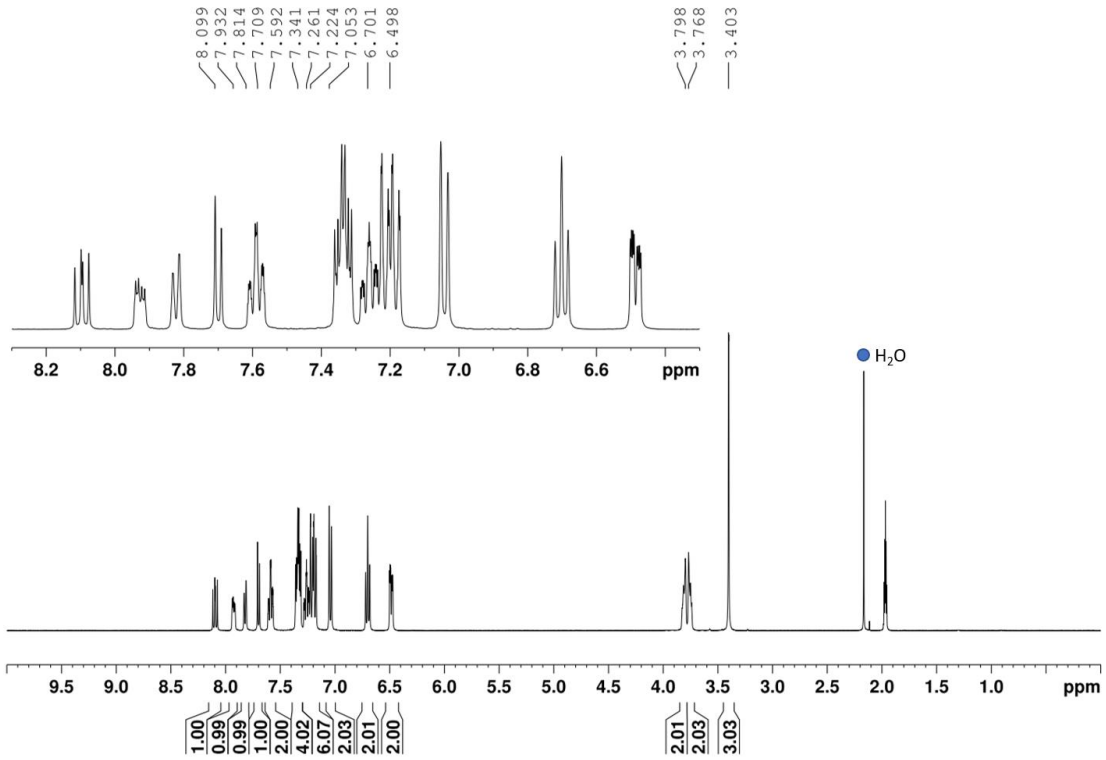


Figure S13. ^{1}H NMR spectrum of [**2**$_{acr}$]BF_4 in d_3-MeCN.

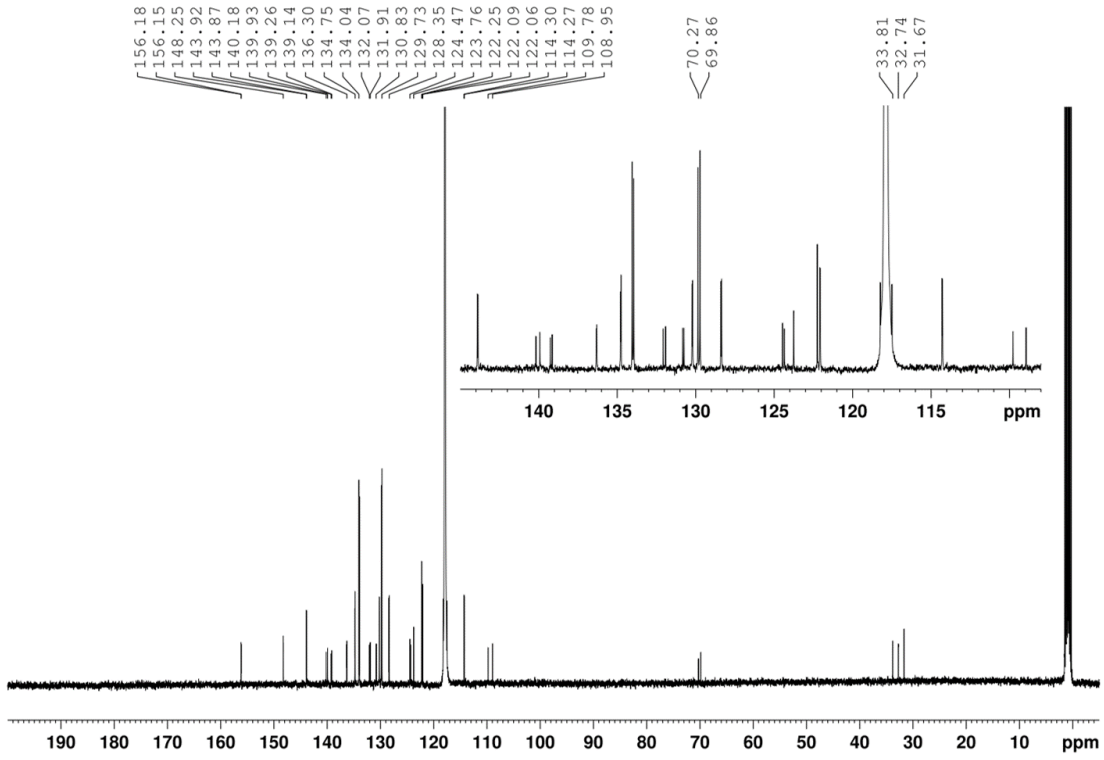


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of [**2**$_{acr}$]BF_4 in d_3-MeCN.

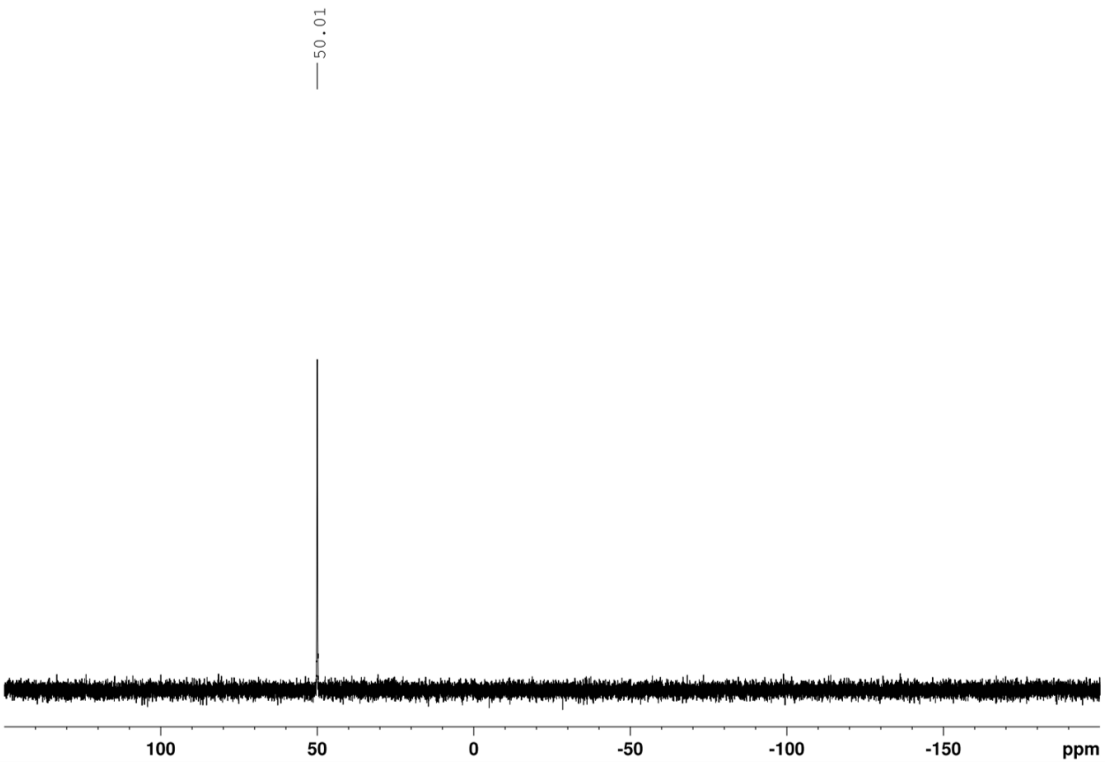


Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum of [**2**$_{acr}$]BF_4 in d_3-MeCN.

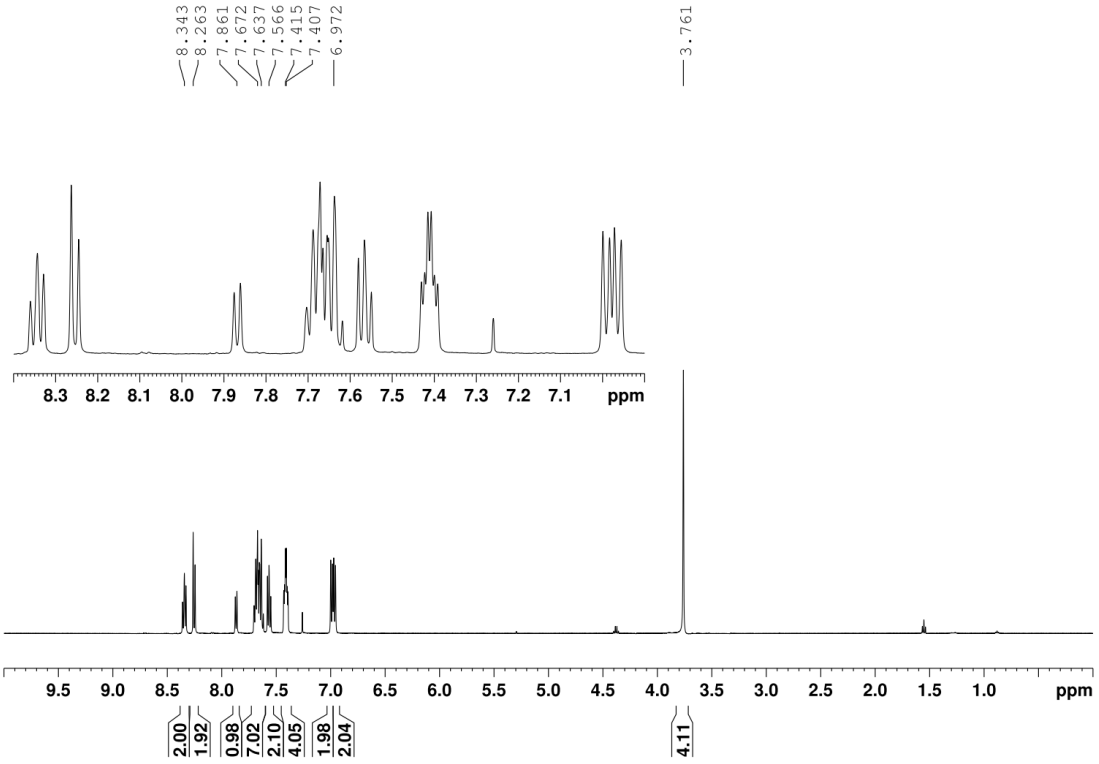


Figure S16. ^{1}H NMR spectrum of [**3**$_{xant}$]OTf in $CDCl_3$.

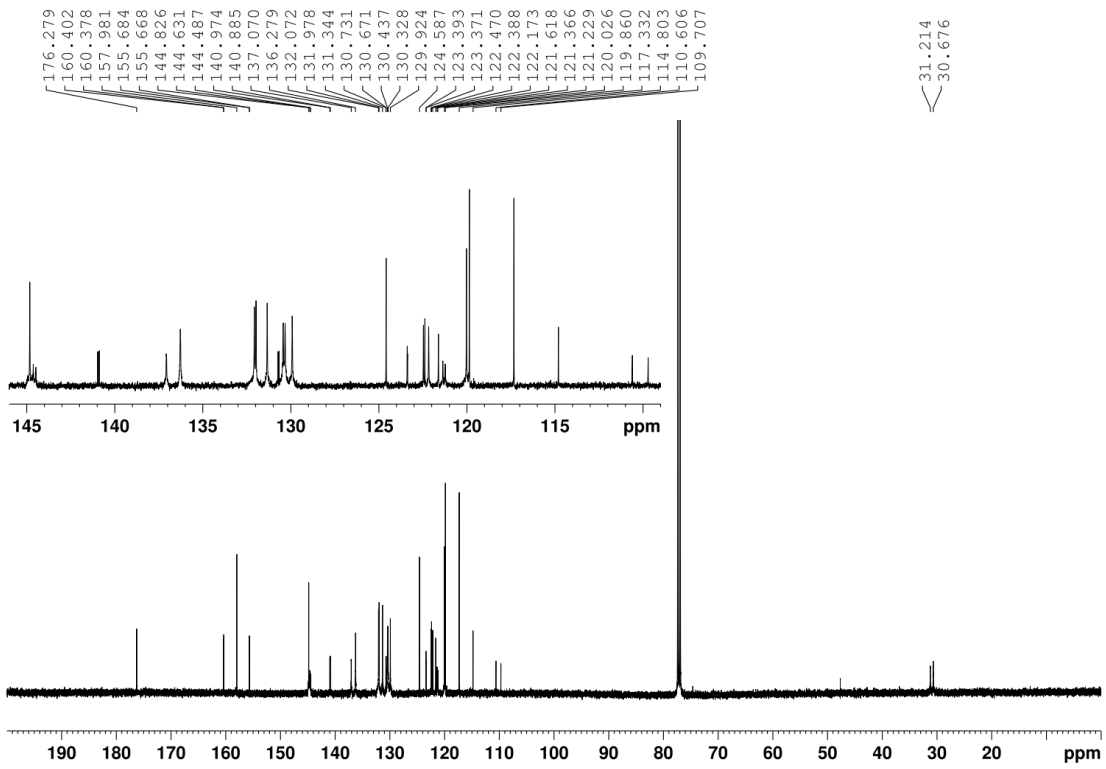


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of [**3**$_{xant}$]OTf in $CDCl_3$.

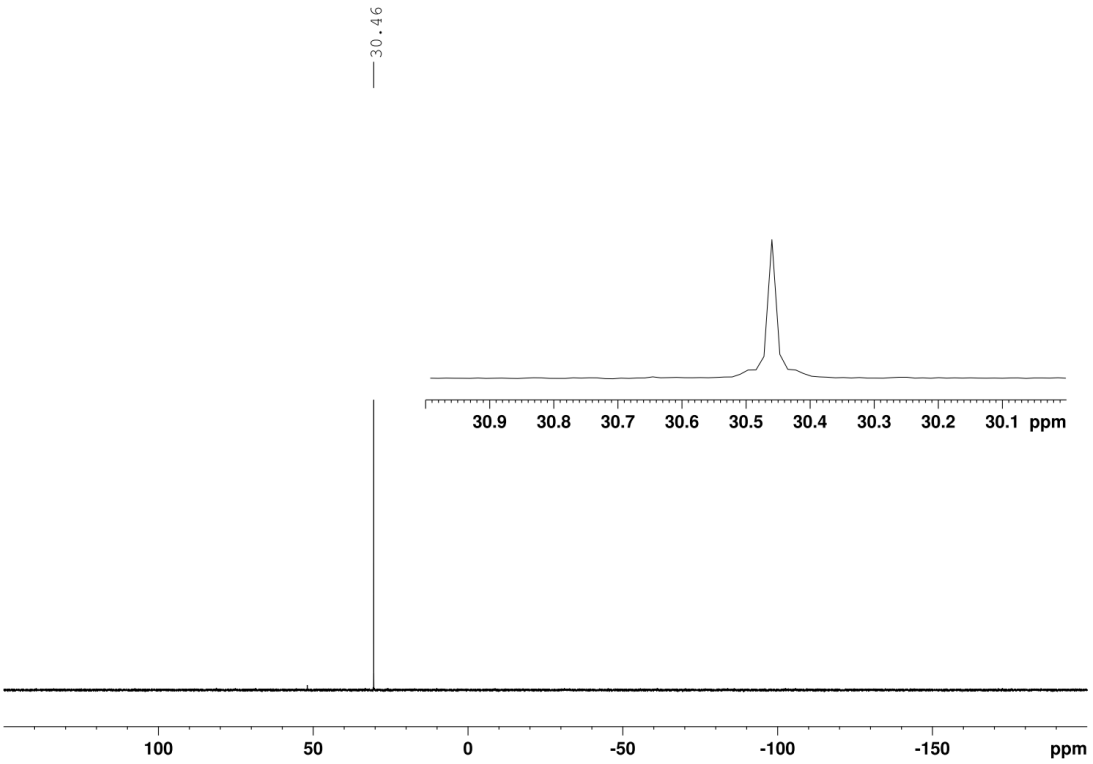


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of [**3**$_{xant}$]OTf in $CDCl_3$.

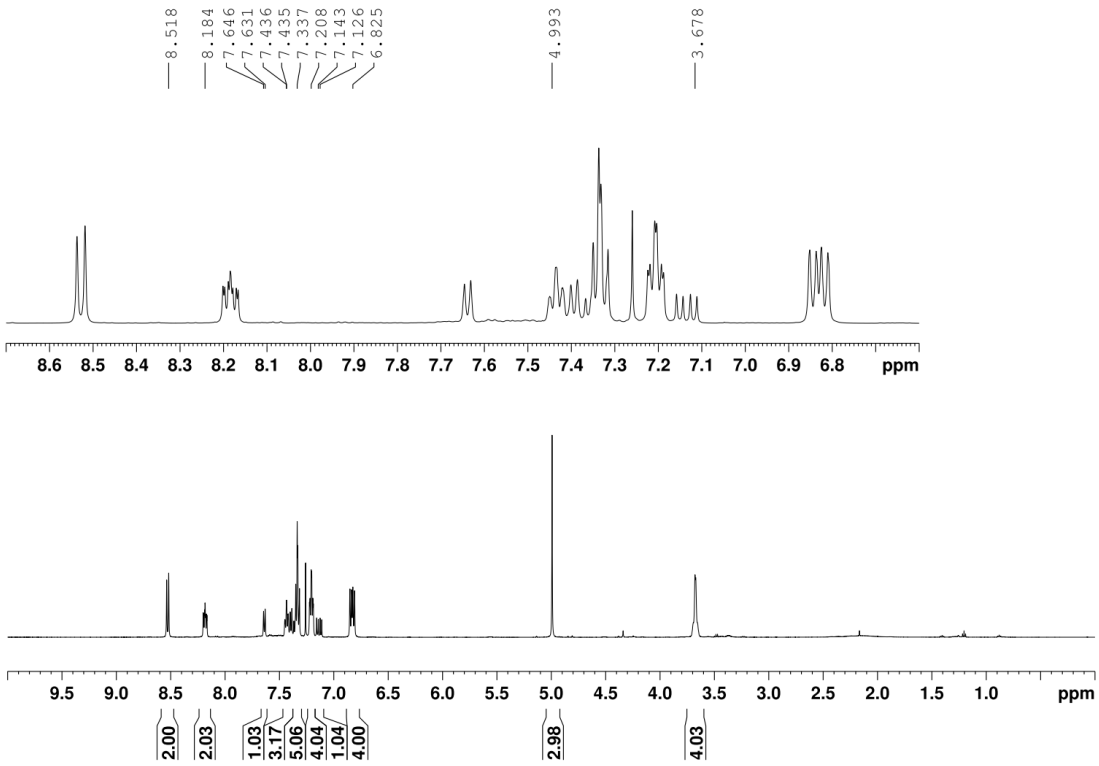


Figure S19. ^{1}H NMR spectrum of [**3**$_{acr}$]BF_4 in $CDCl_3$.

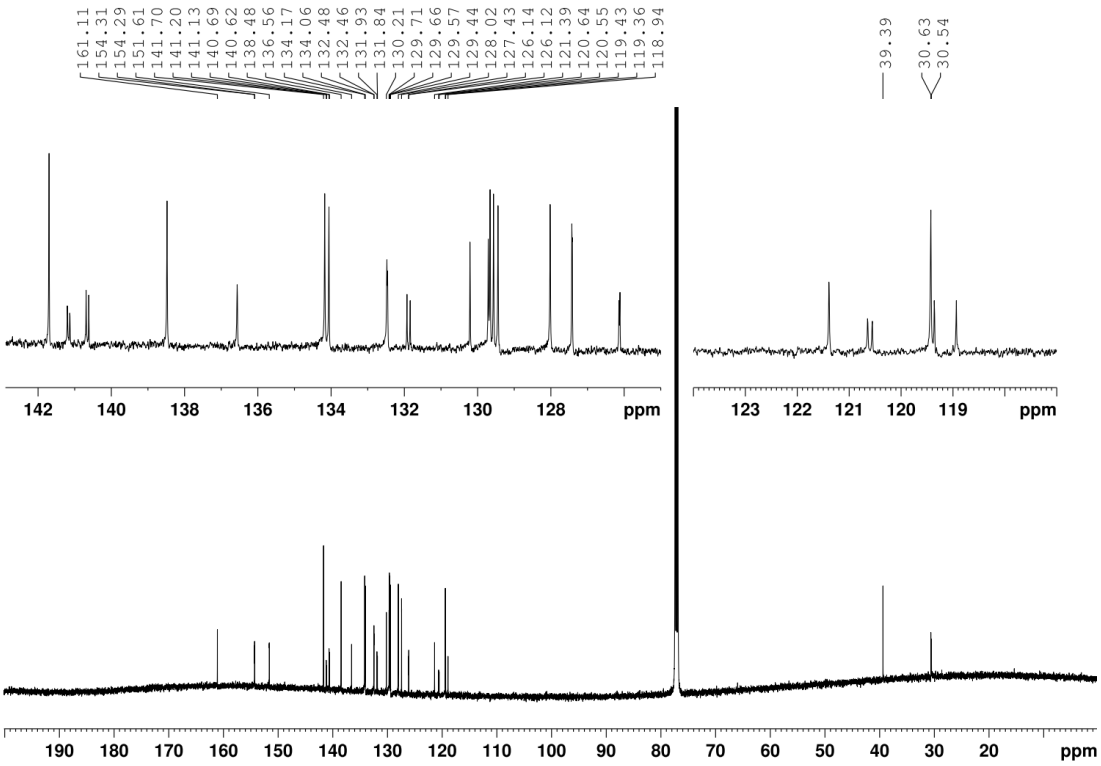


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of [**3**$_{acr}$]BF_4 in $CDCl_3$.

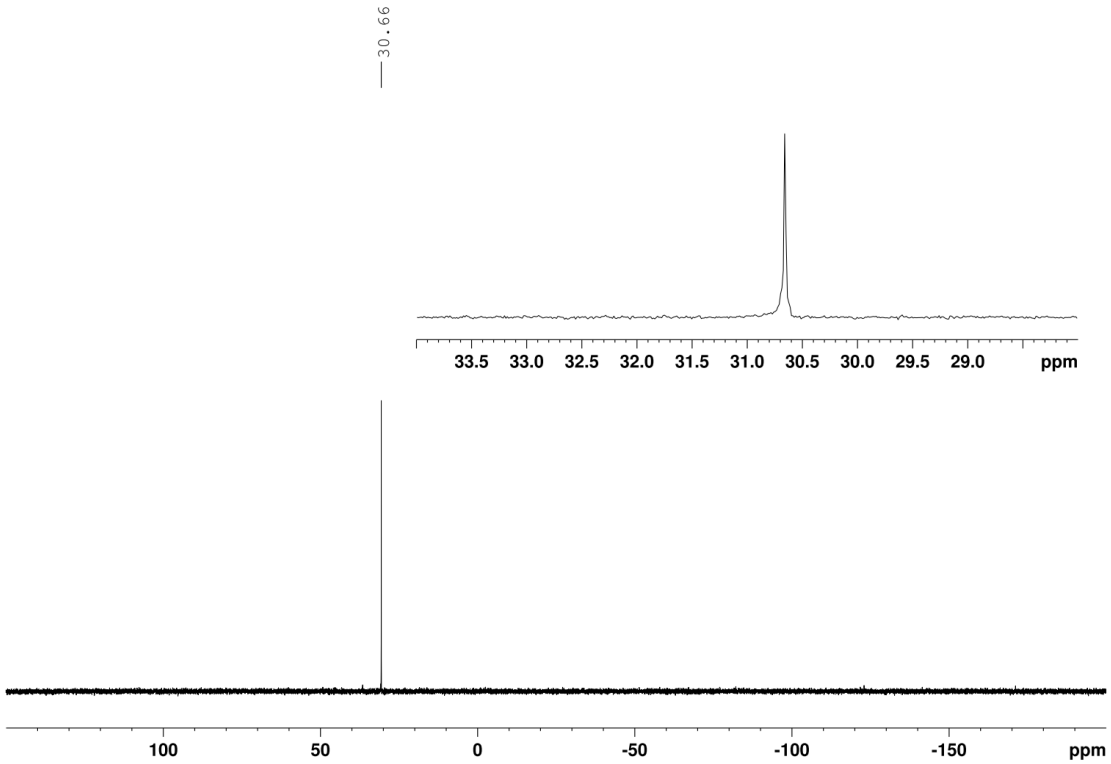


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of [**3**$_{acr}$]BF_4 in $CDCl_3$

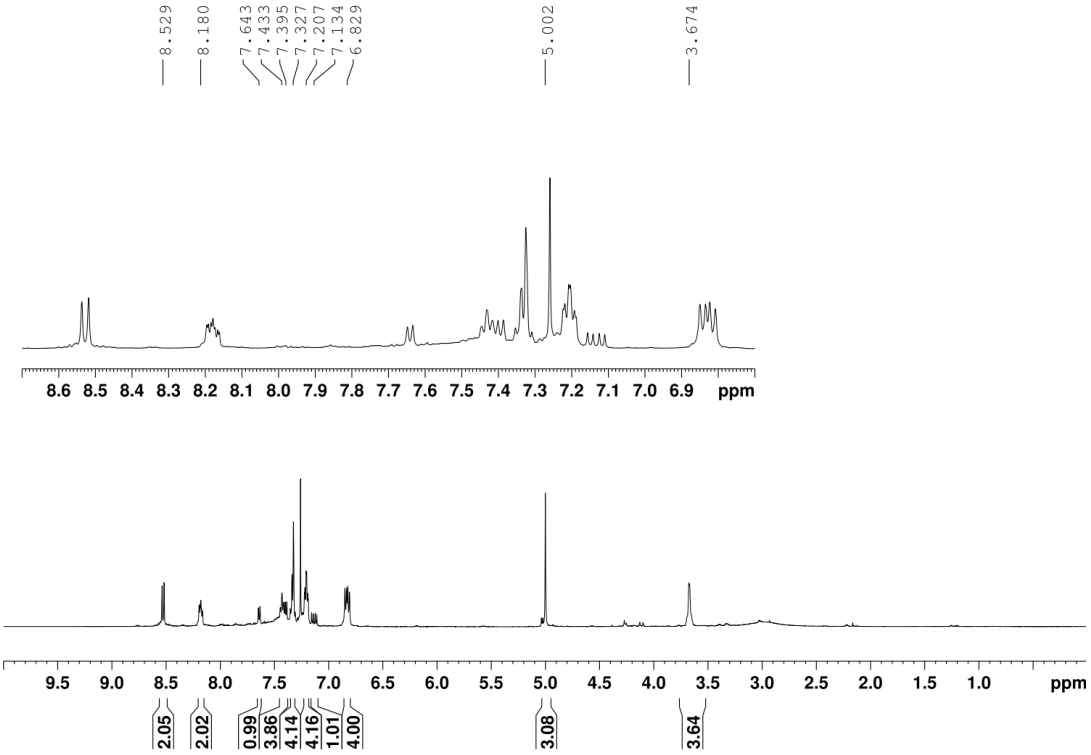


Figure S22. ^{1}H NMR spectrum of [**3**$_{acr}$]OTf in $CDCl_3$

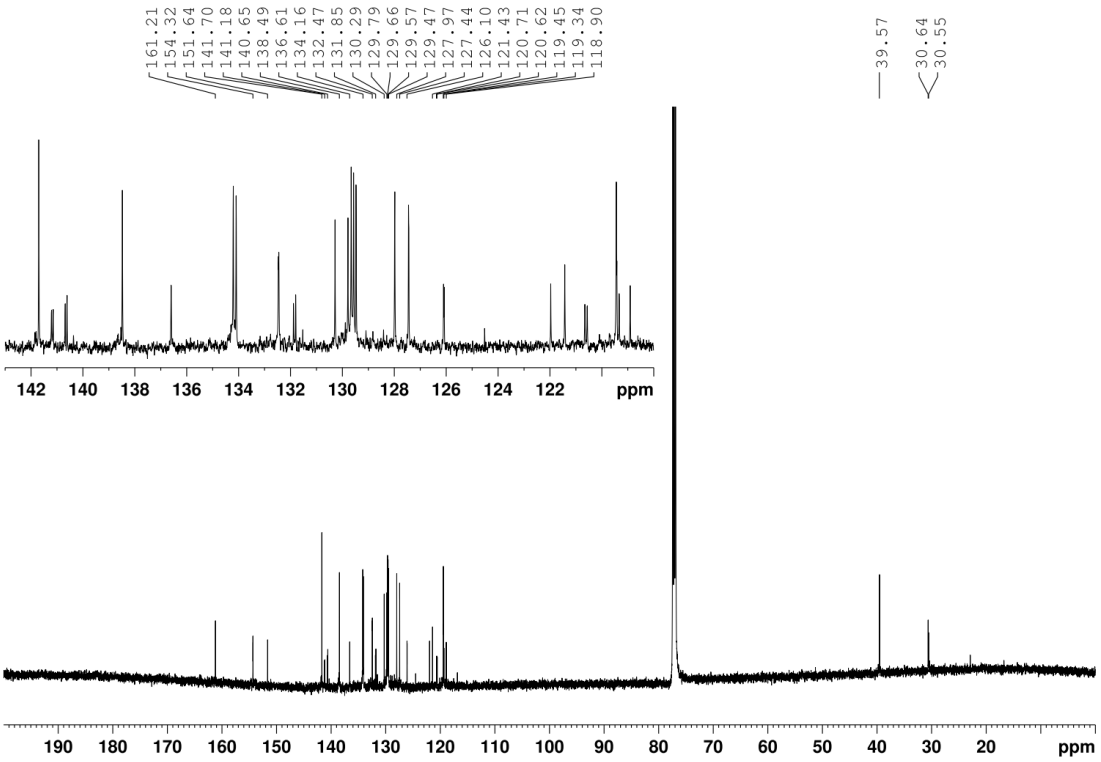


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of [**3**$_{acr}$]OTf in $CDCl_3$

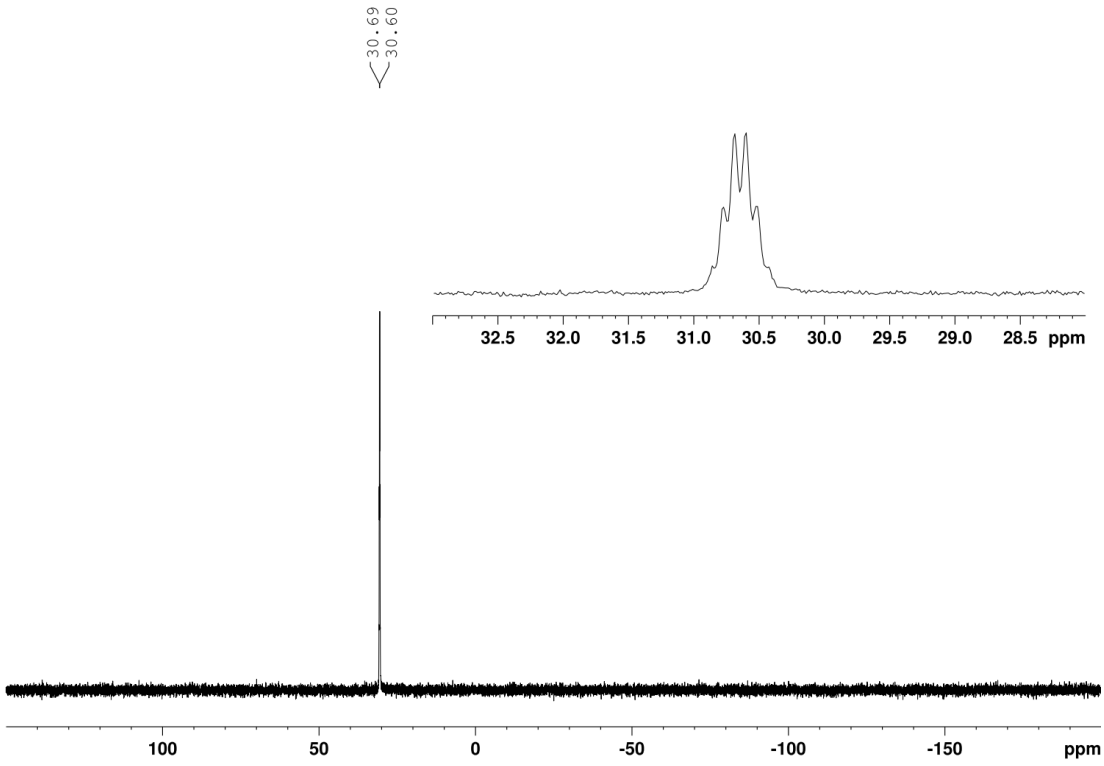


Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum of [**3**$_{acr}$]OTf in $CDCl_3$

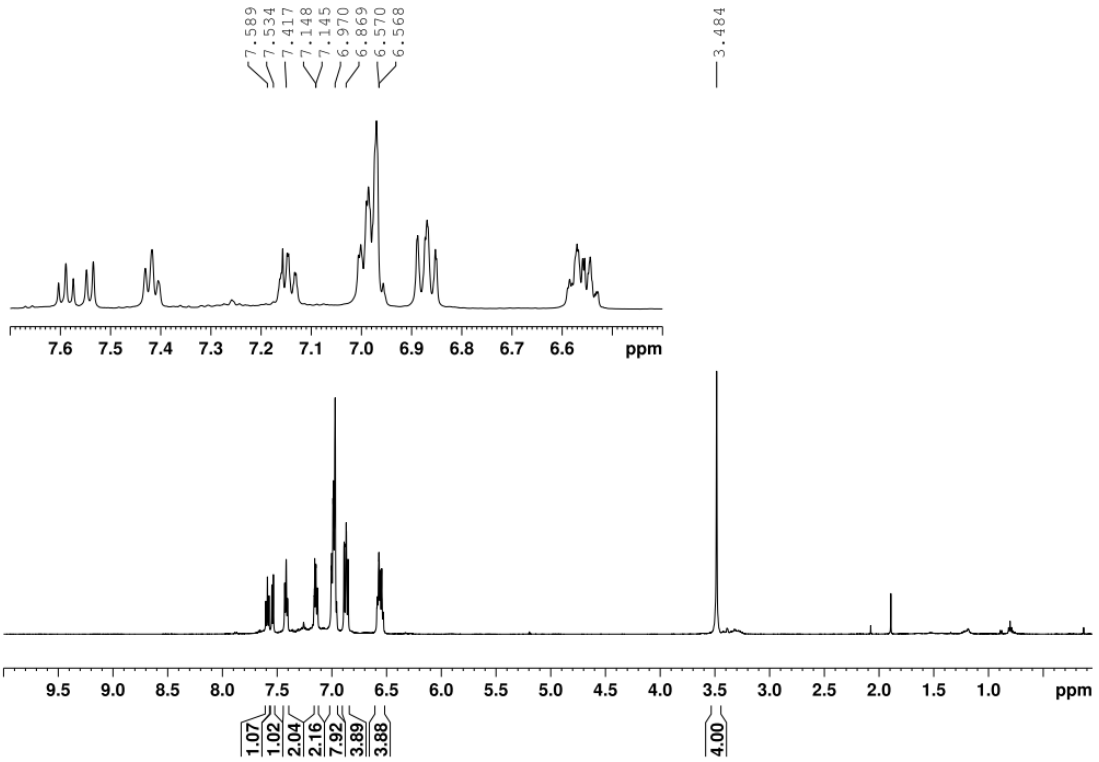


Figure S25. ^{1}H NMR spectrum of **5** in $CDCl_3$

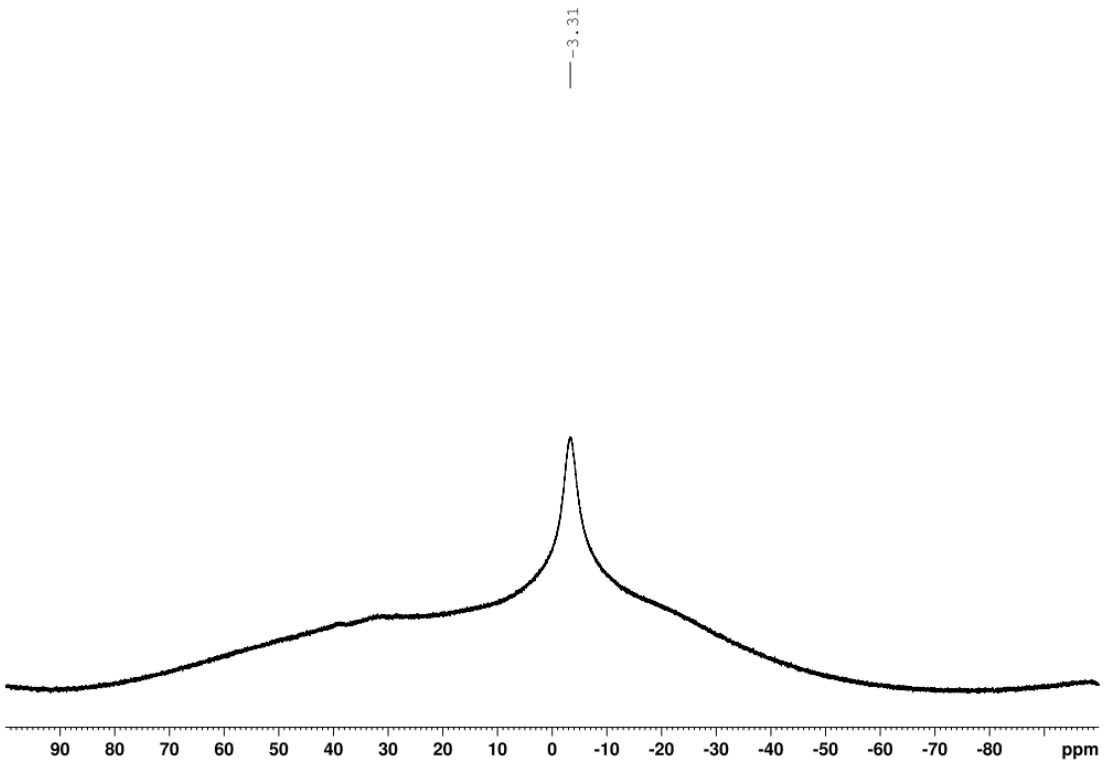


Figure S26. $^{11}B\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$

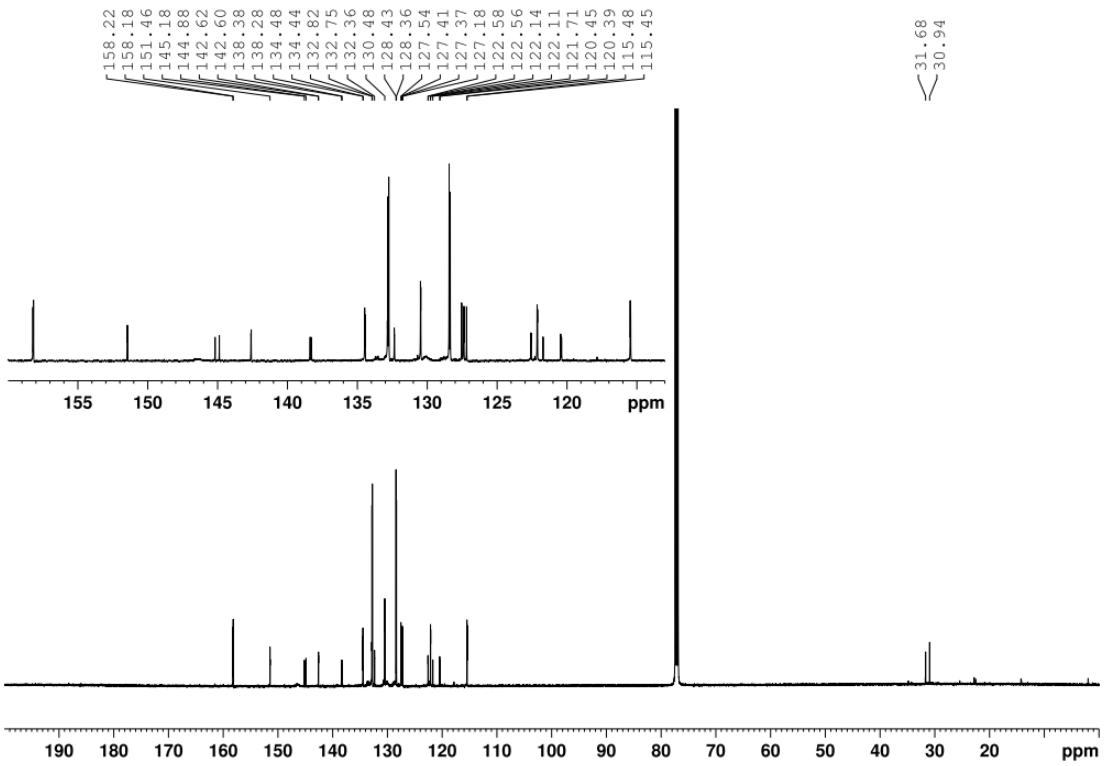


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$

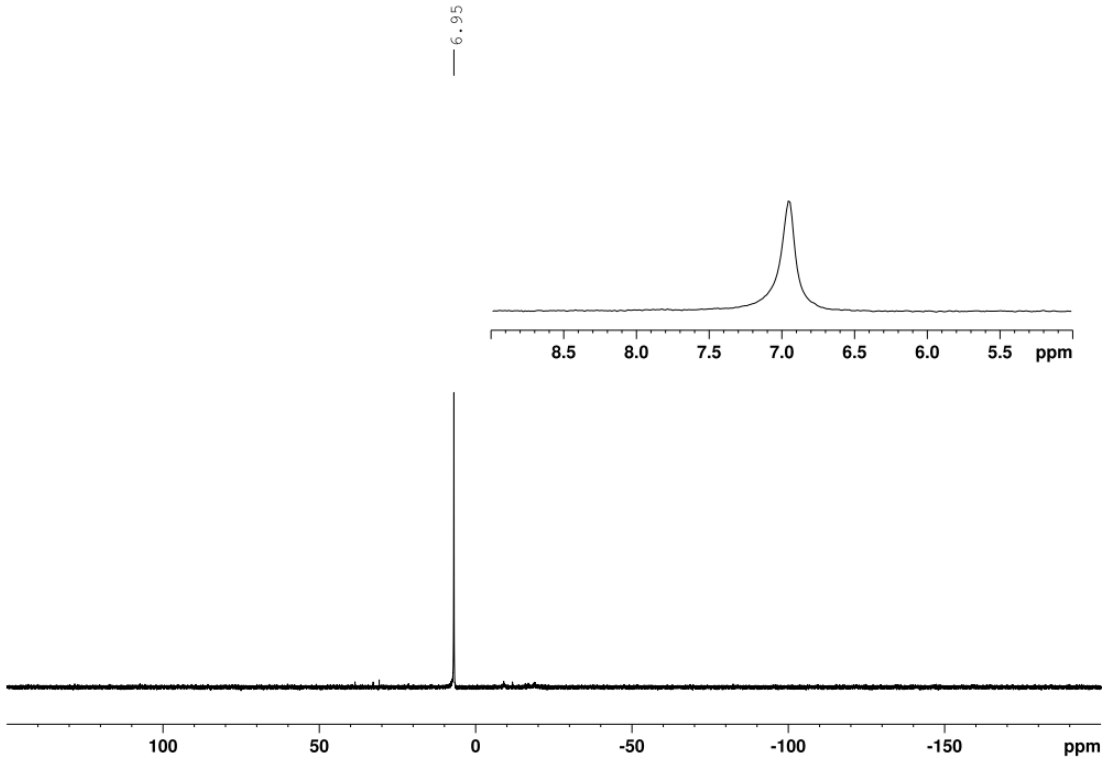


Figure S28. $^{31}P\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$

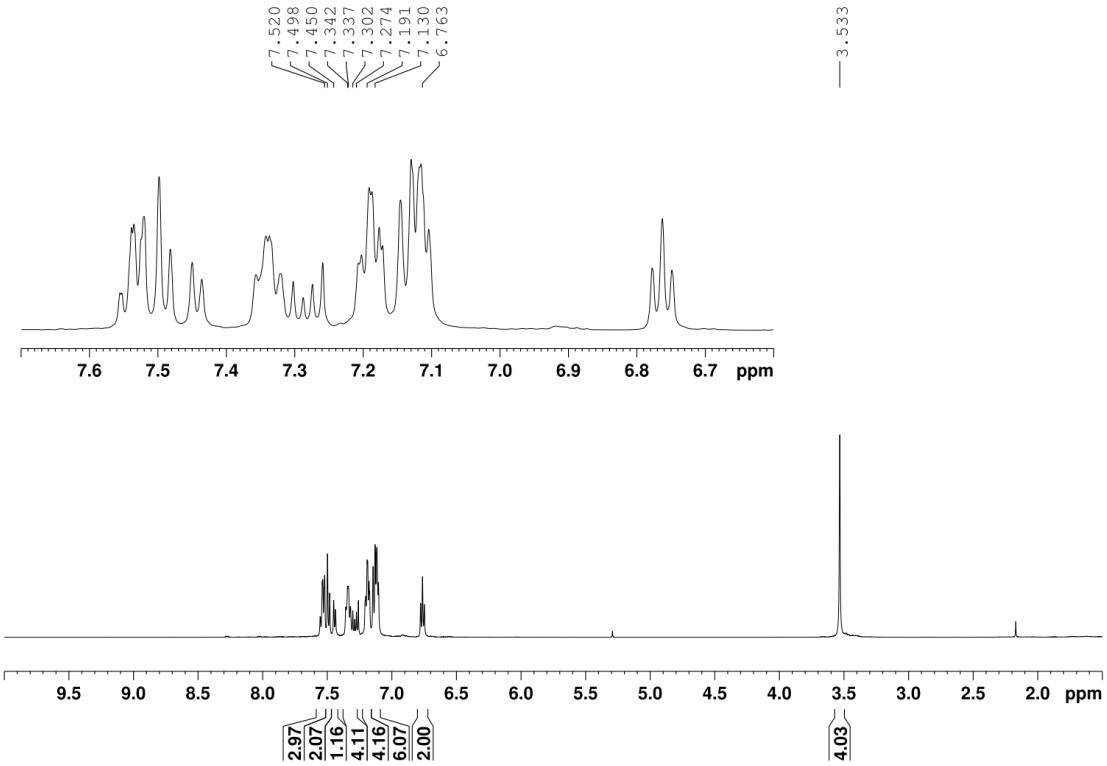


Figure S29. ^{1}H NMR spectrum of **6** in $CDCl_3$

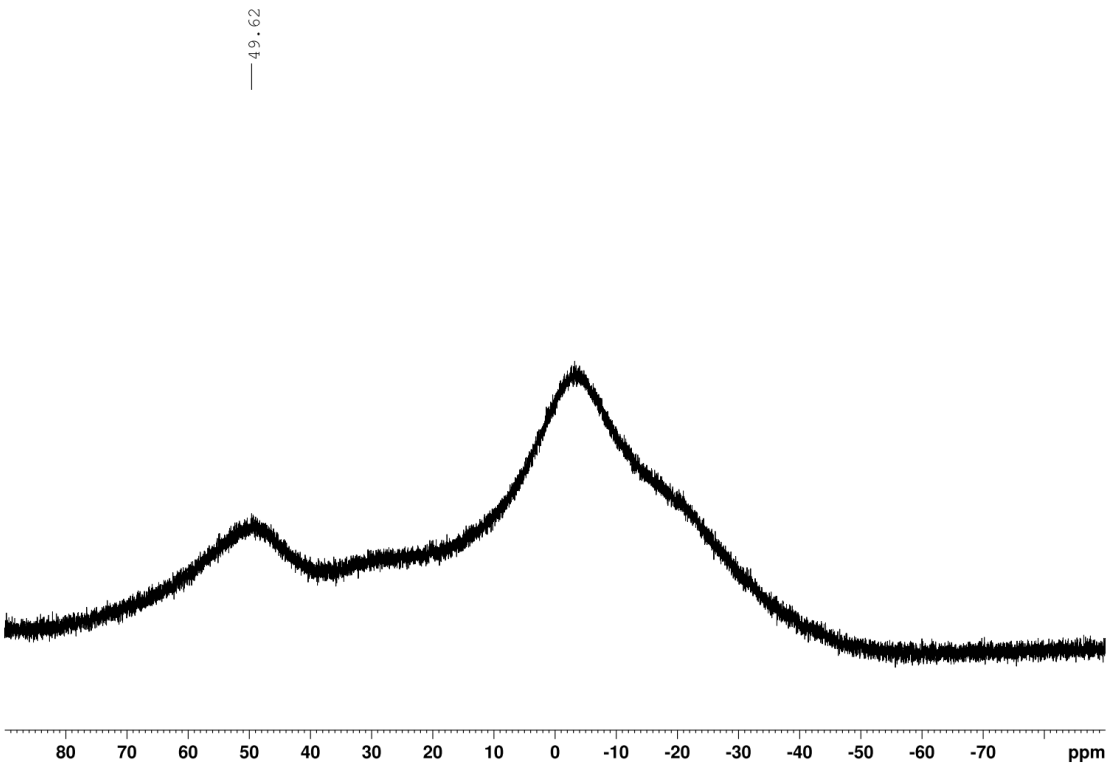


Figure S30. $^{11}B\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$

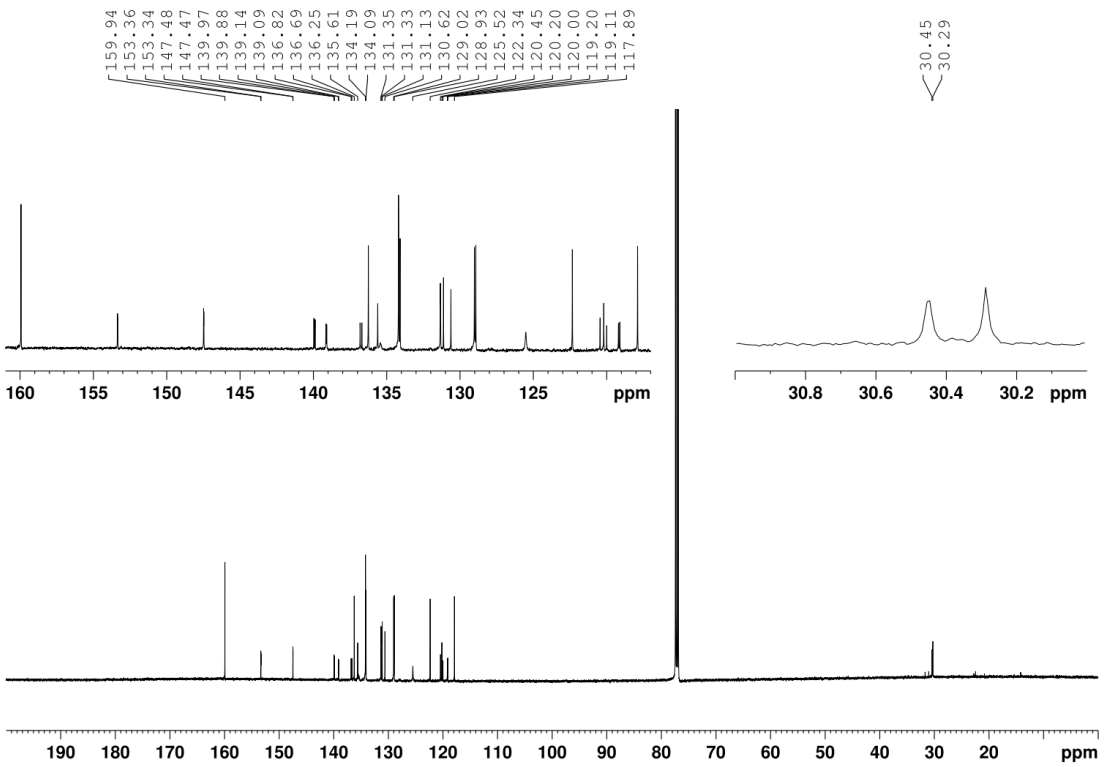


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$

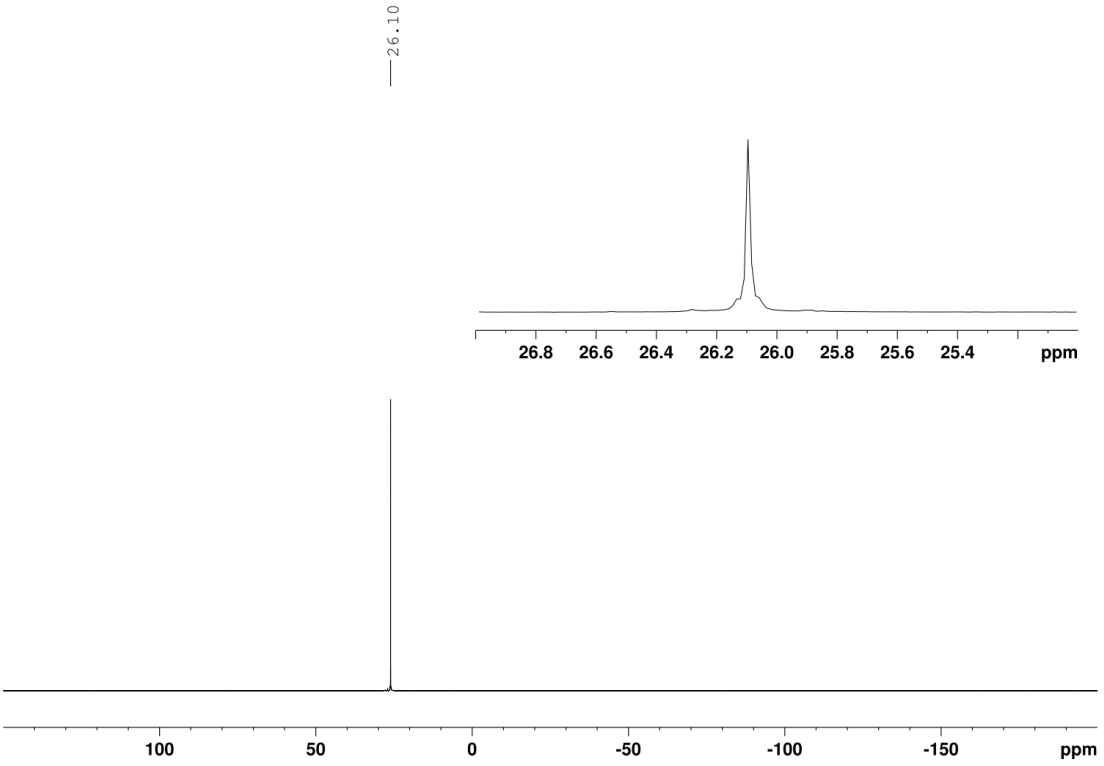


Figure S32. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$

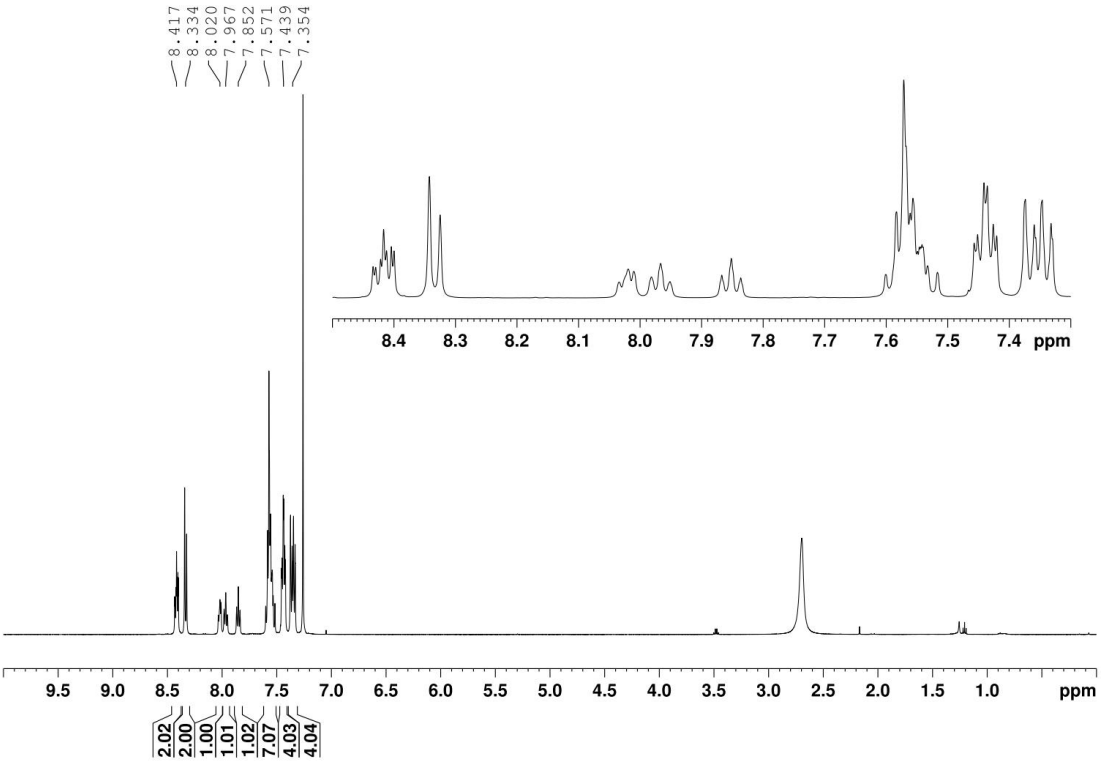


Figure S33. ^{1}H NMR spectrum of [$\mathbf{4}_{\mathbf{xant}}$]OTf in $CDCl_3$

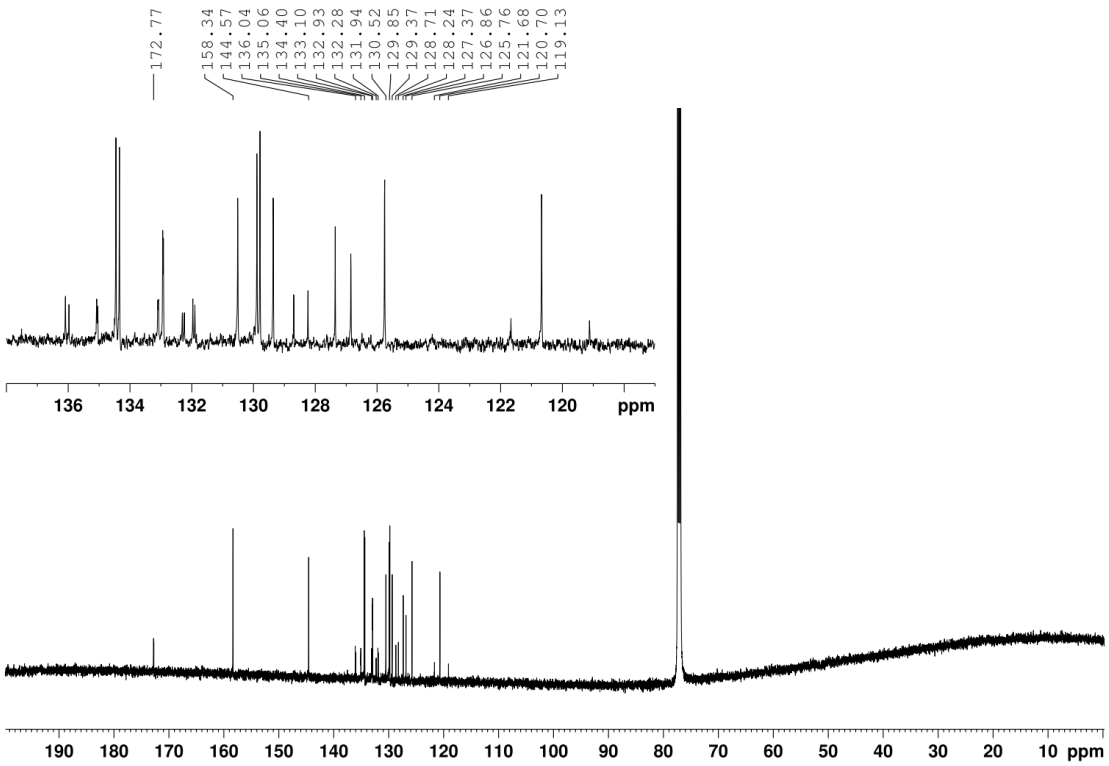


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of [$\mathbf{4}_{\mathbf{xant}}$]OTf in $CDCl_3$

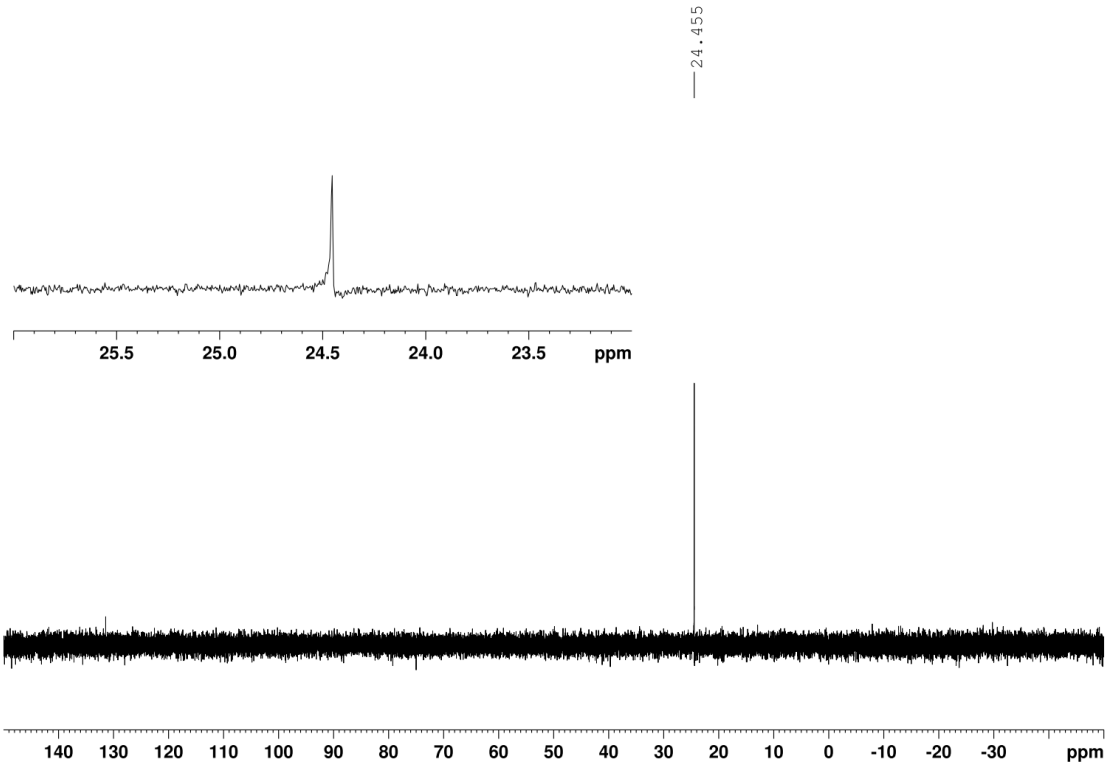
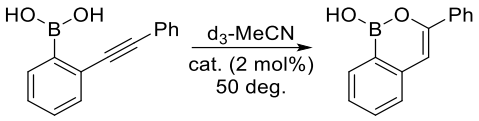


Figure S35. $^{31}P\{^{1}H\}$ NMR spectrum of [**4**$_{xant}$]OTf in $CDCl_3$

3. Catalytic Studies

3.1 Cycloisomerization of 2-(phenylethynyl)phenylboronic acid



a **b**

2-(Phenylethynyl)phenylboronic acid (**a**, 22 mg, 0.1 mmol) was dissolved in d_3-MeCN (0.5 mL) in the presence of the catalyst (2 µmol, 2 mol%). The mixture was then transferred to an NMR tube and the conversion was measured by *in situ* ^{1}H NMR spectroscopy. Between measurements, the NMR tube was immersed in an oil bath kept at 50°C. The NMR spectroscopic data corresponding to **b** were consistent with previous literature values.[13] **^{1}H NMR** (499.32 MHz, d3-MeCN) δ: 7.99 (d, *J* = 7.4 Hz, 1H, Ar-*H*), 7.89–7.94 (m, 2H, Ar-*H*), 7.61 (td, J = 7.5, 1.4 Hz, 1H, Ar-*H*), 7.51 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.44-7.49 (m, 2H, Ar-*H*), 7.36–7.41 (m, 2H, Ar-*H*), 7.00 (s, 1H, ArC*H*=C).

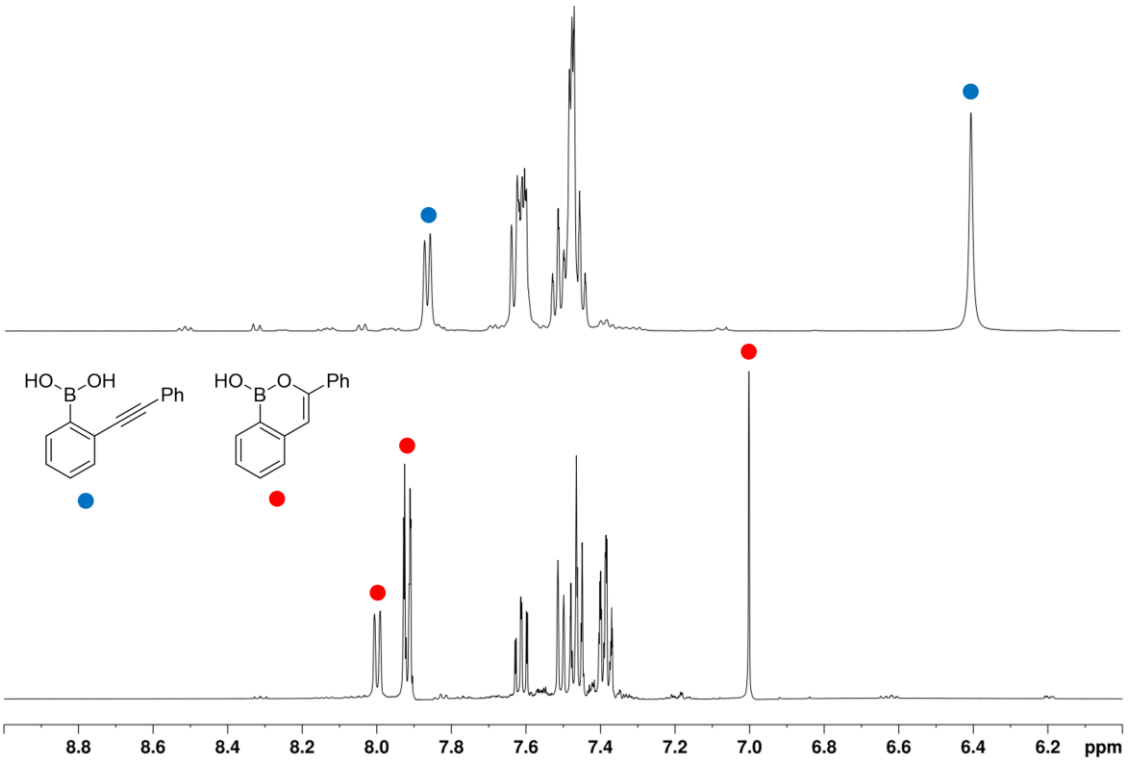


Figure S36. ^{1}H NMR spectra obtained with [**3**$_{xant}$]OTf as the catalyst (2 mol%). The resulting spectrum was collected 2 hours after the start of the reaction. Integration of the ^{1}H resonance afforded a conversion of 99%.

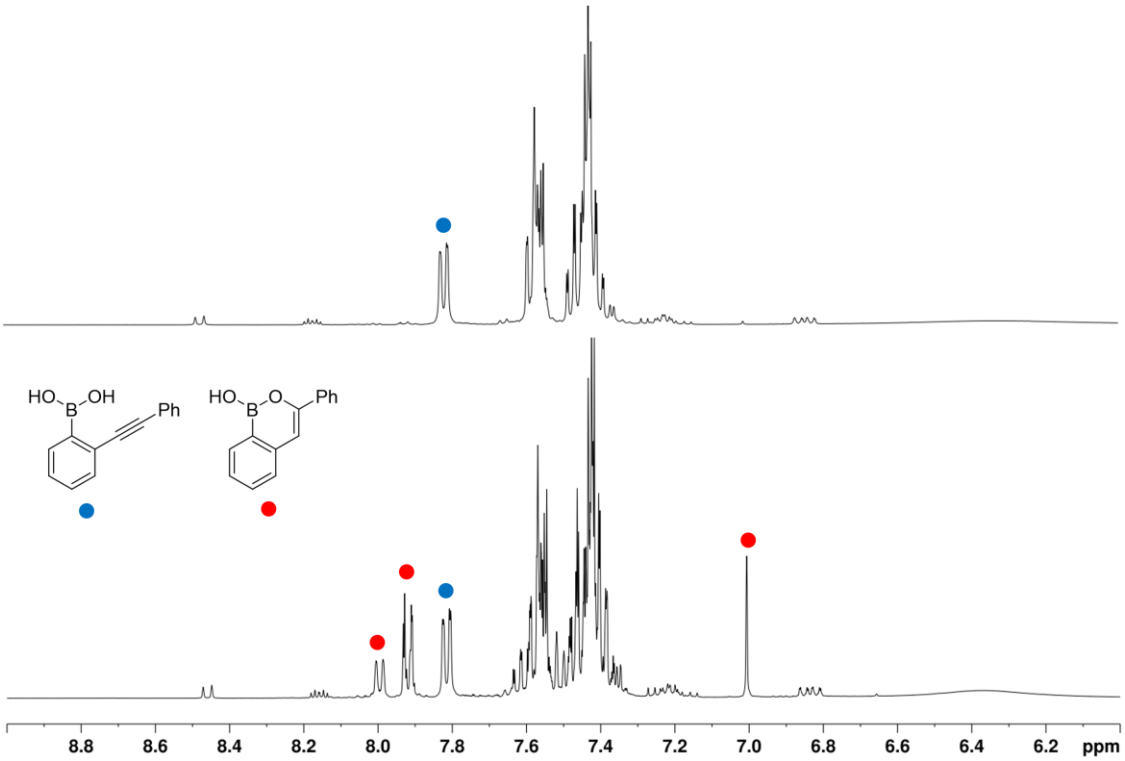


Figure S37. ^{1}H NMR spectra obtained with [**3**$_{acr}$]BF_4 as the catalyst (2 mol%). The resulting spectrum was collected 2 hours after the start of the reaction. Integration of the ^{1}H resonance afforded a conversion of 29%.

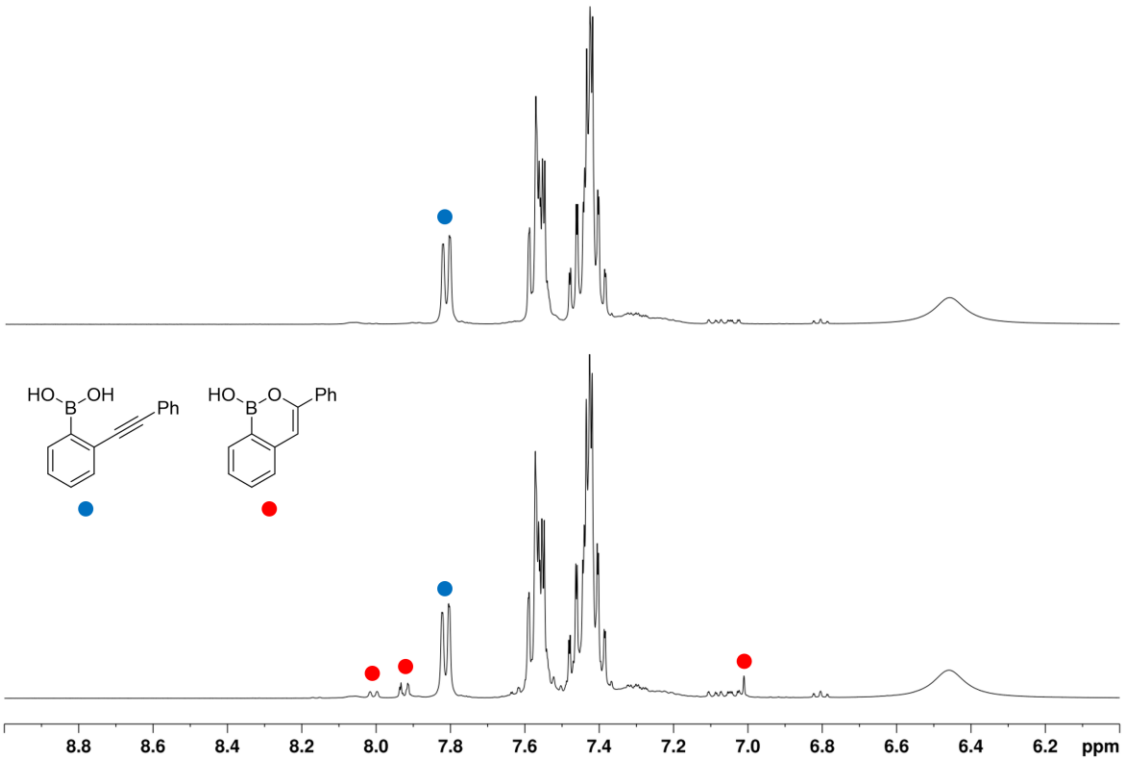


Figure S38. ^{1}H NMR spectra obtained with **6** as the catalyst (2 mol%). The resulting spectrum was collected 2 hours after the start of the reaction. Integration of the ^{1}H resonance afforded a conversion of 6.5%.

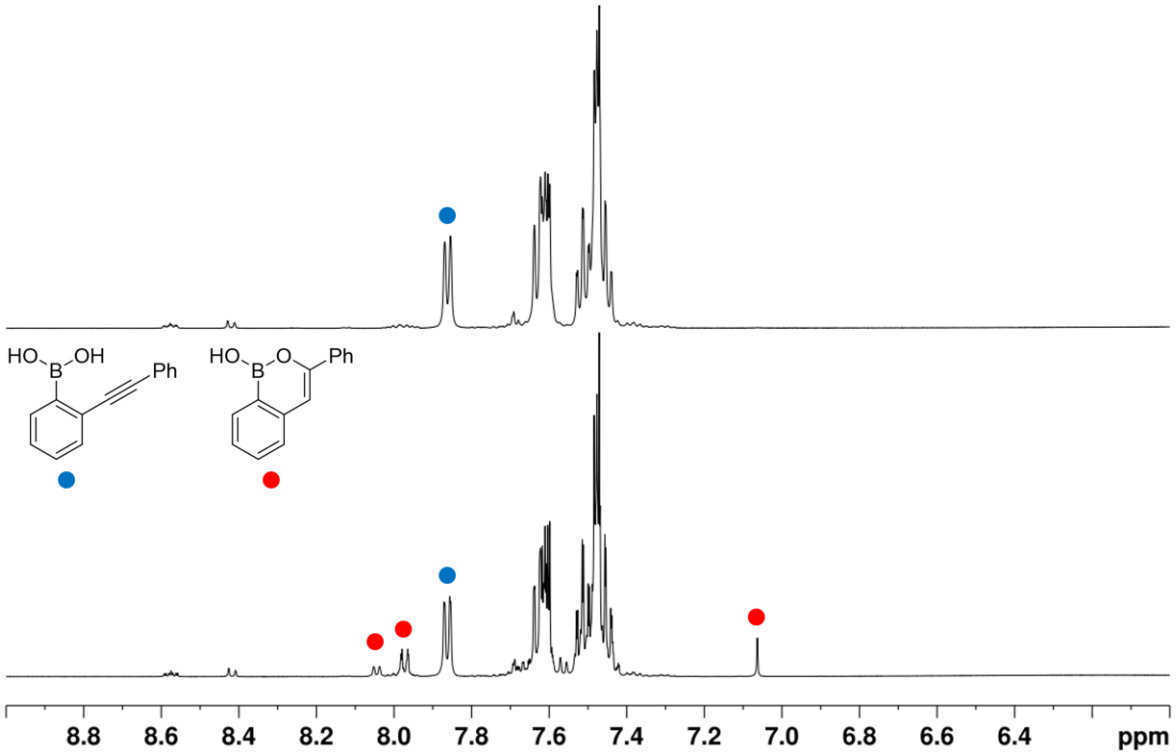


Figure S39. ^{1}H NMR spectra obtained with [**4**$_{xant}$]OTf as the catalyst (2 mol%). The resulting spectrum was collected 2 hours after the start of the reaction. Integration of the ^{1}H resonance afforded a conversion of 11%.

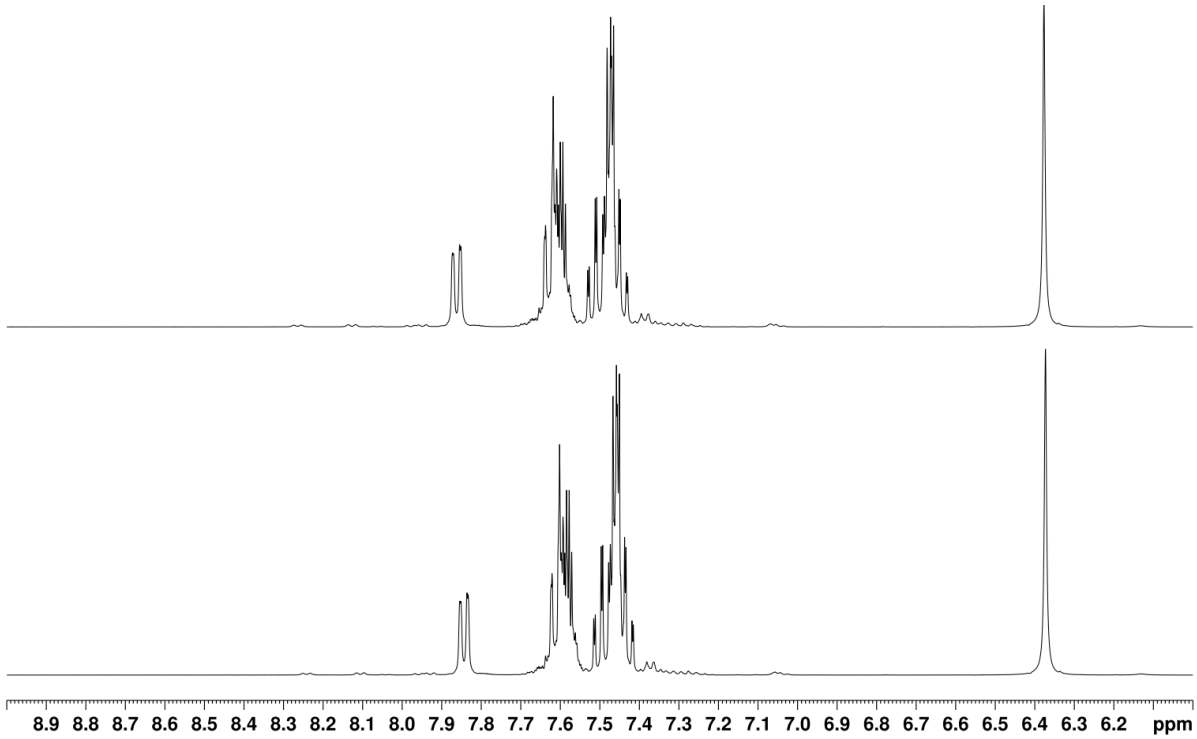


Figure S40. ^{1}H NMR spectra obtained with **PPh$_3$AuCl** as the catalyst (2 mol%). The resulting spectrum was collected 2 hours after the start of the reaction, showing no conversion.

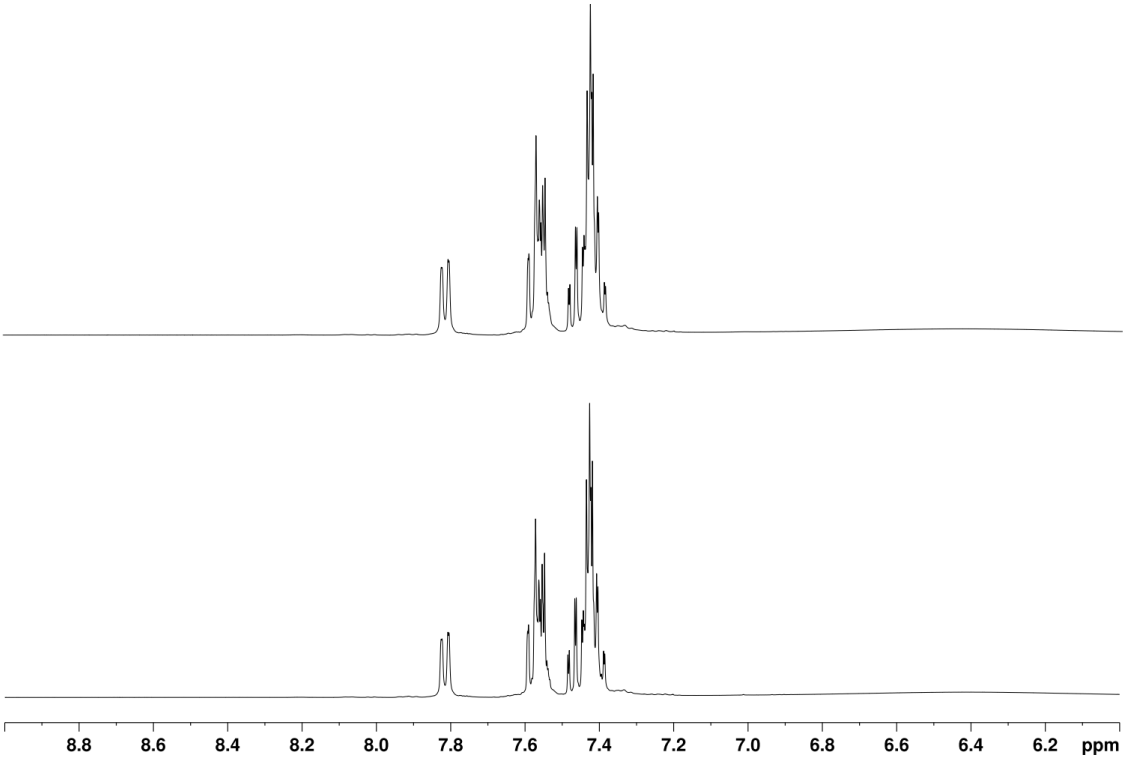
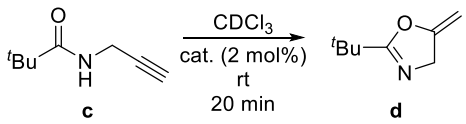


Figure S41. ^{1}H NMR spectra obtained with HBF_4 as the catalyst (2 mol%). The resulting spectrum was collected 2 hours after the start of the reaction, showing no conversion.

3.2 Cycloisomerization of propargyl amide



Model propargyl amide (**c**, 14 mg, 0.1 mmol) was dissolved in $CDCl_3$ (0.5 mL) in the presence of the catalyst (2 µmol, 2 mol%). The mixture was then transferred to an NMR tube and the conversion was measured by *in situ* ^{1}H NMR spectroscopy. **^{1}H NMR** (499.32 MHz, $CDCl_3$) δ: 4.62 (td, *J* = 2.9, 2.7 Hz, 1H, -C=C*H*$_2$), 4.39 (t, J = 2.7 Hz, 2H, -NC*H*$_2$), 4.21 (td, J = 2.7, 2.5 Hz, 1H, -C=C*H*$_2$), 1.24 (s, 9H, -C*H*$_3$).

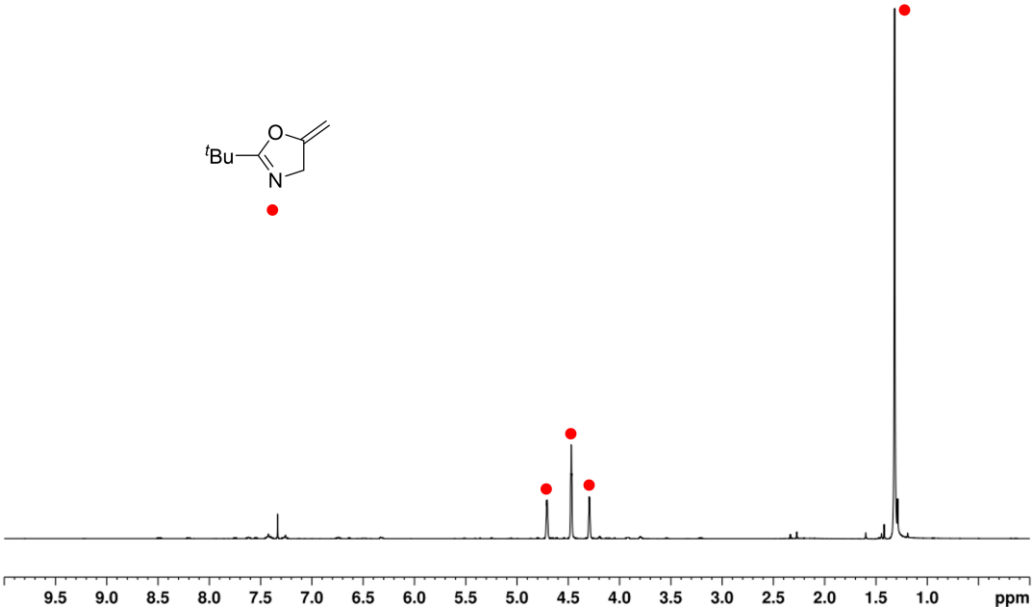


Figure S 42. ^{1}H NMR spectra obtained with [**3**$_{xant}$]OTf as the catalyst (2 mol%). The resulting spectrum was collected 20 mins after the start of the reaction. Integration of the ^{1}H resonance afforded a conversion of 99%.

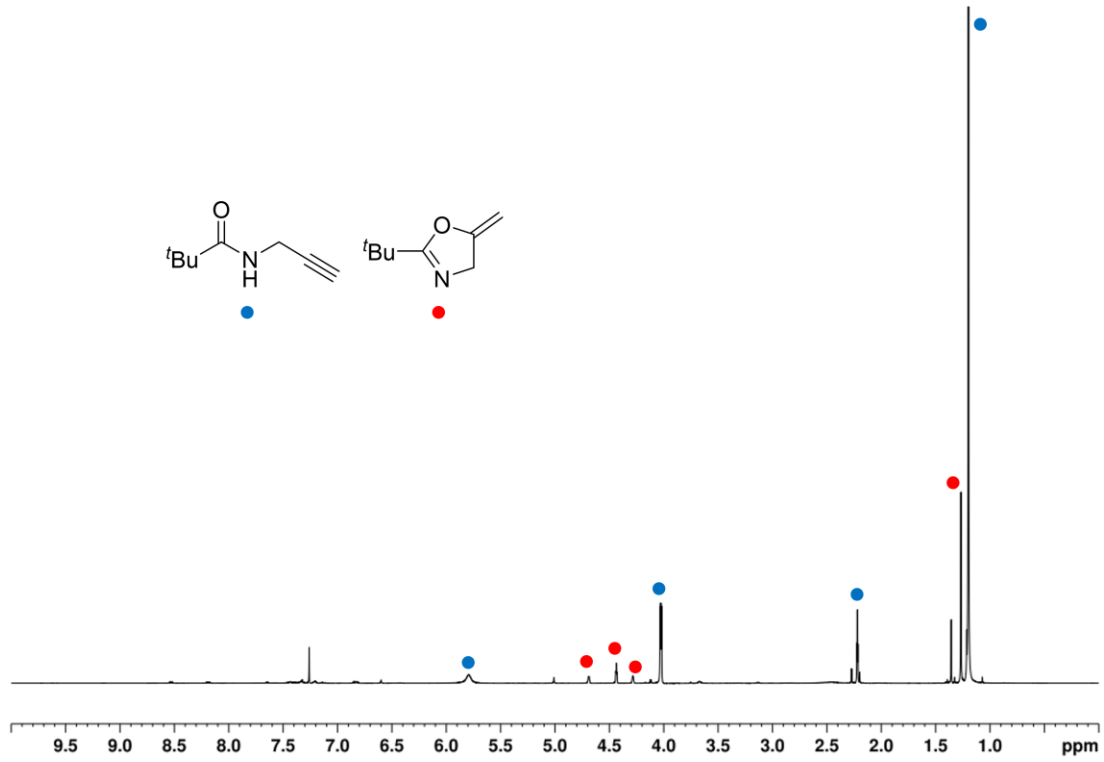


Figure S 43. ^{1}H NMR spectra obtained with [**3**$_{acr}$]BF_4 as the catalyst (2 mol%). The resulting spectrum was collected 20 mins after the start of the reaction. Integration of the ^{1}H resonance afforded a conversion of 16%.

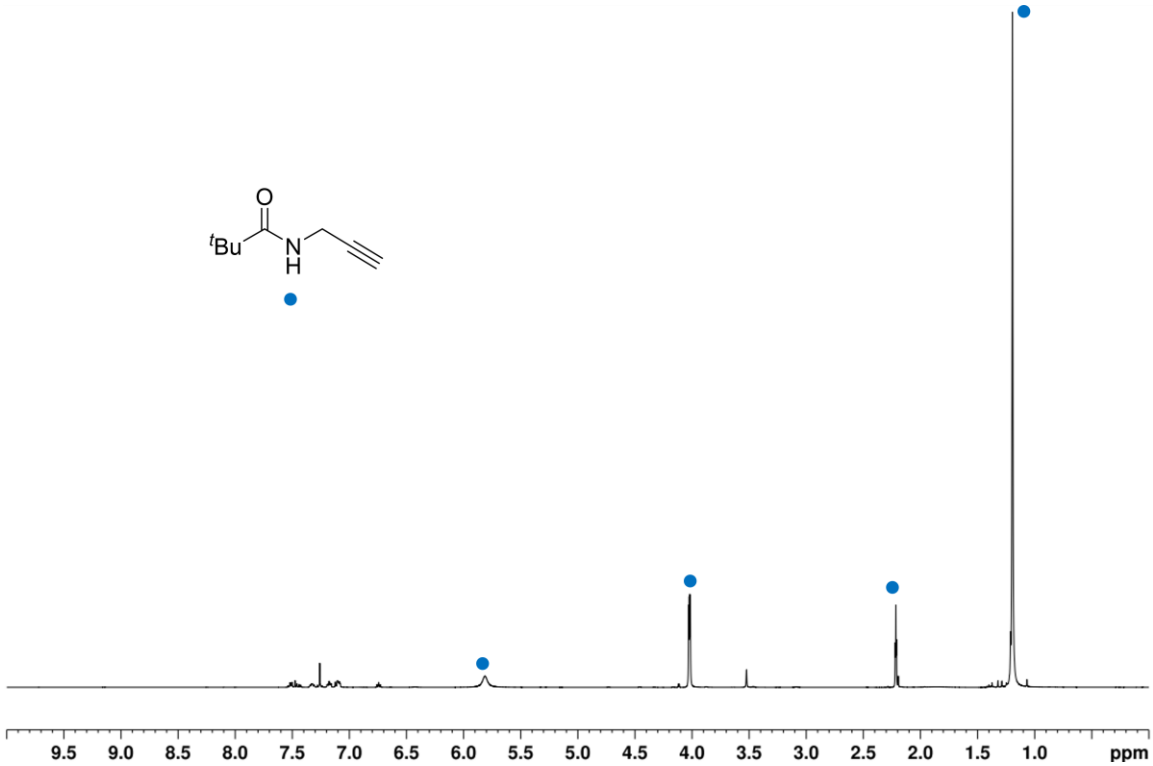


Figure S 44. ^{1}H NMR spectra obtained with **6** as the catalyst (2 mol%). The resulting spectrum was collected 20 mins after the start of the reaction. Integration of the ^{1}H resonance afforded a conversion of 1%.

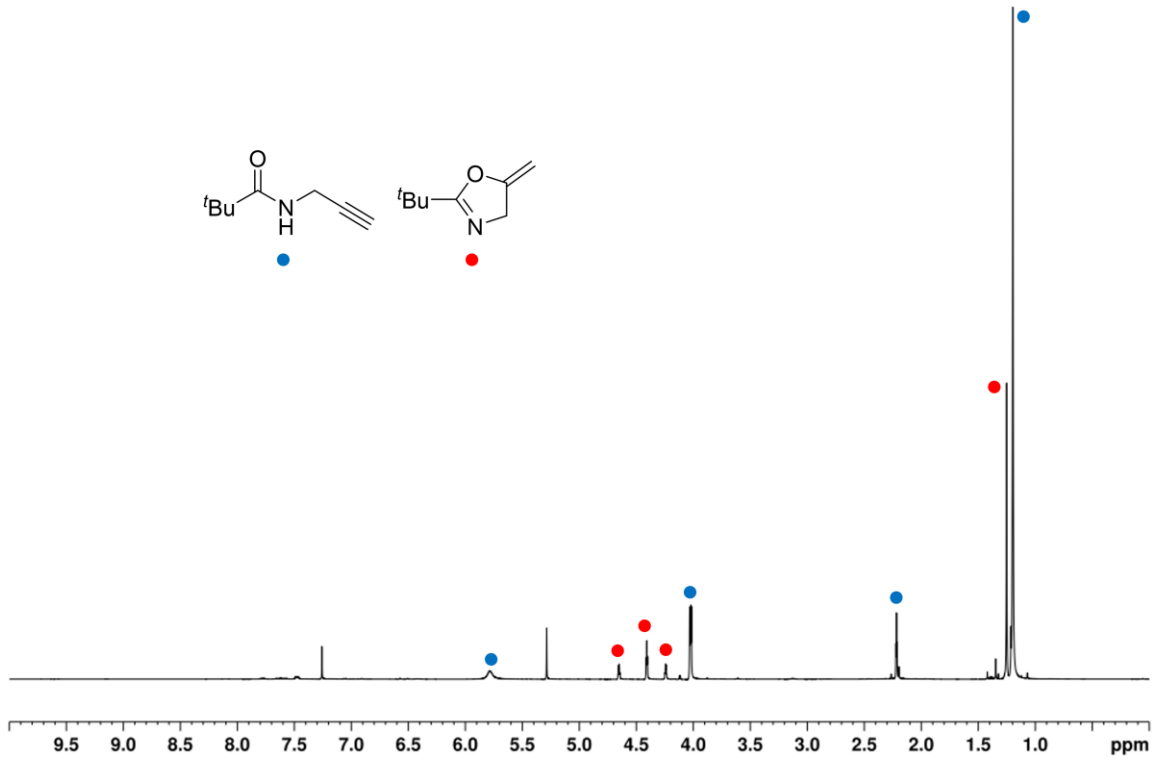


Figure S 45. ^{1}H NMR spectra obtained with [**4**$_{xant}$]OTf as the catalyst (2 mol%). The resulting spectrum was collected 20 mins after the start of the reaction. Integration of the ^{1}H resonance afforded a conversion of 21%.

3.3 Cycloisomerization of Diethyl 2-allyl-2-(2-propynyl)malonate

2-(Phenylethynyl)phenylboronic acid (**e**, 24 mg, 0.1 mmol) was dissolved in $CDCl_3$ (0.5 mL) in the presence of the catalyst (2 µmol, 2 mol%). The mixture was then transferred to an NMR tube and the conversion was measured by *in situ* ^{1}H NMR spectroscopy. Between measurements, the NMR tube was immersed in an oil bath kept at 50°C. The NMR spectroscopic data corresponding to **f** were consistent with previous literature values.[14]

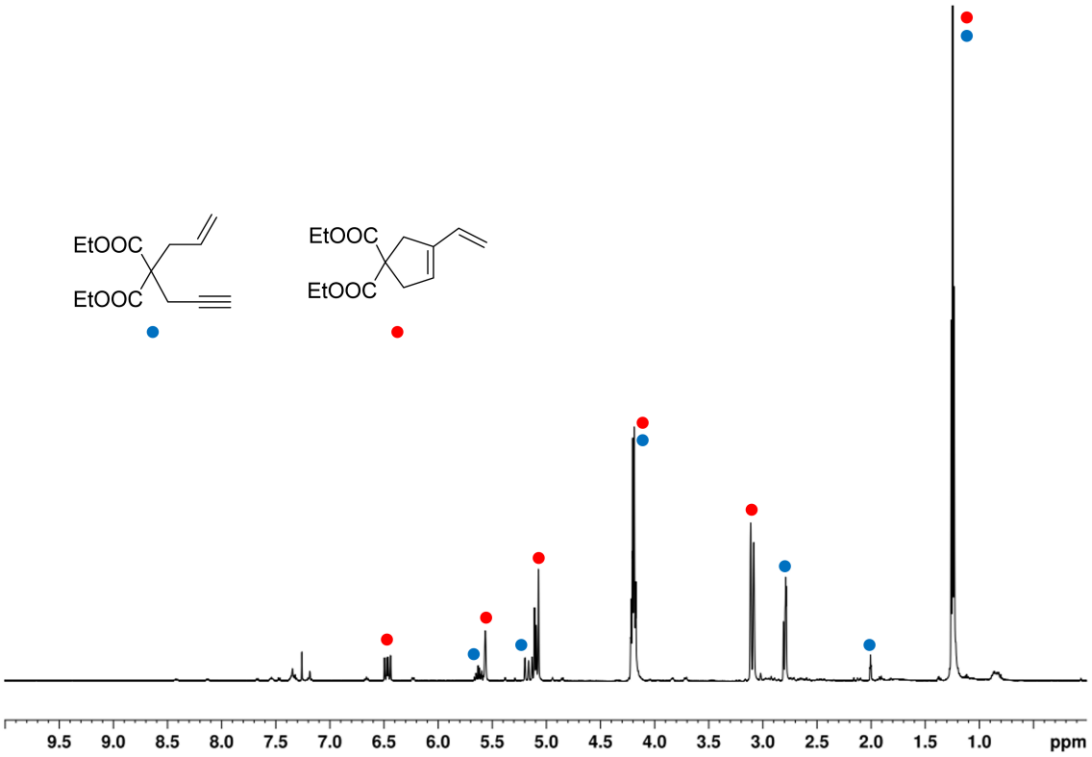


Figure S 46. ^{1}H NMR spectra obtained with [**3**$_{xant}$]OTf as the catalyst (2 mol%). The resulting spectrum was collected 1 hour after the start of the reaction. Integration of the ^{1}H resonance afforded a conversion of 69%.

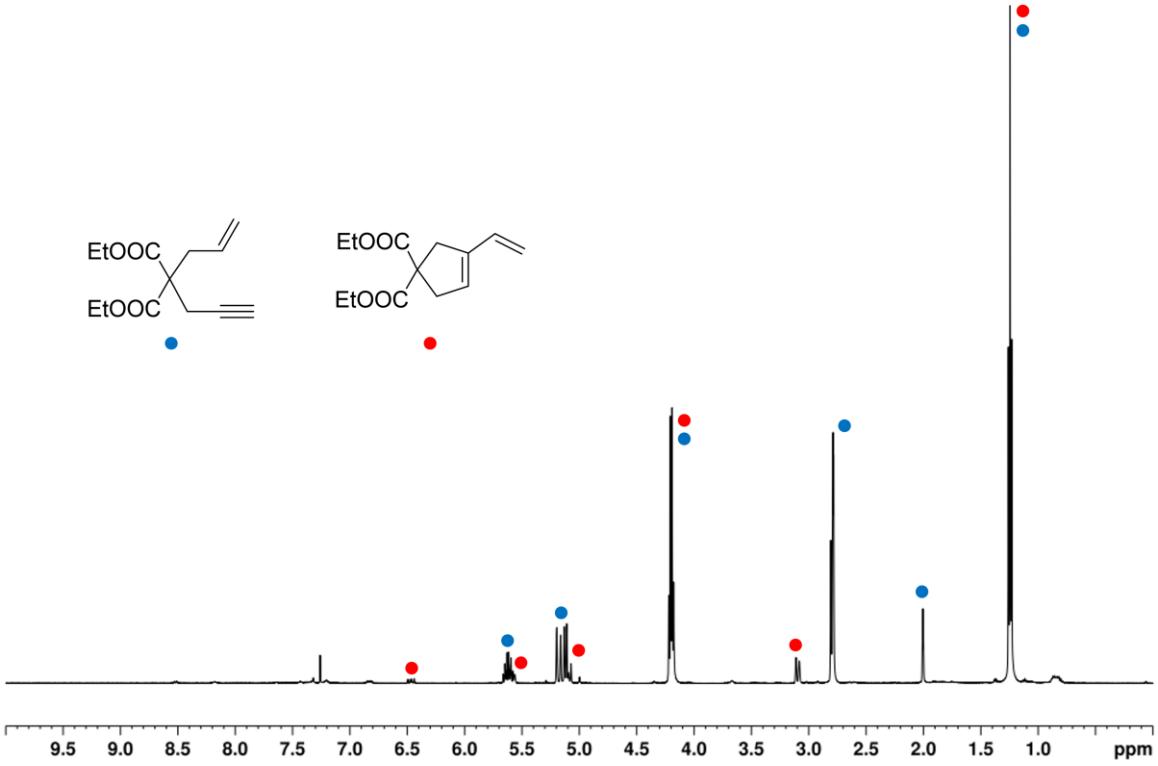


Figure S 47. ^{1}H NMR spectra obtained with [**3**$_{acr}$]BF_4 as the catalyst (2 mol%). The resulting spectrum was collected 1 hour after the start of the reaction. Integration of the ^{1}H resonance afforded a conversion of 11%.

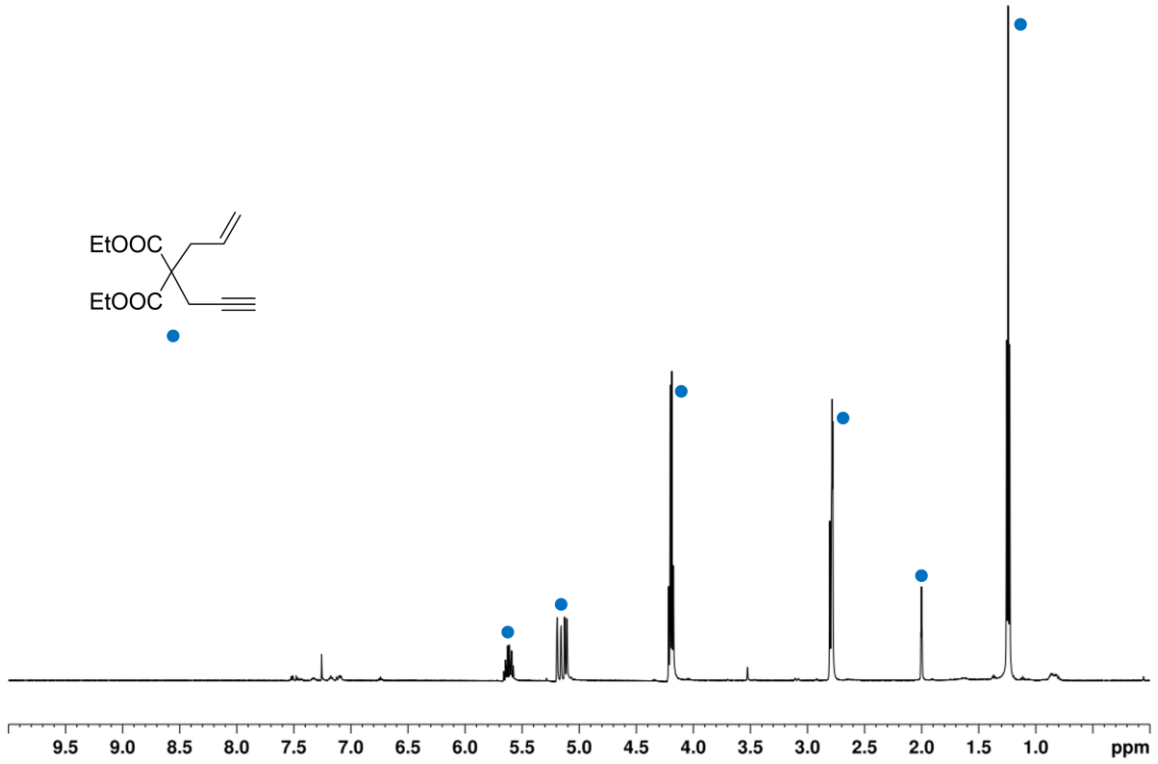


Figure S 48. ^{1}H NMR spectra obtained with **6** as the catalyst (2 mol%). The resulting spectrum was collected 1 hour after the start of the reaction. Integration of the ^{1}H resonance afforded a conversion of 0%.

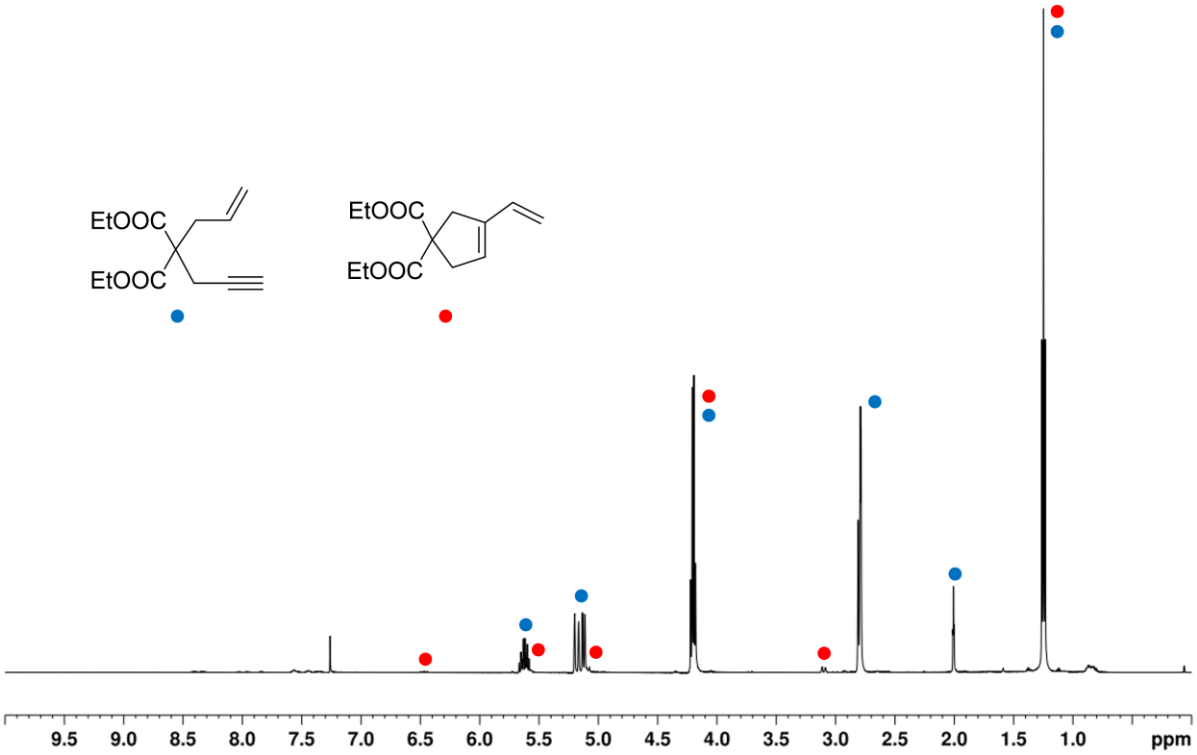
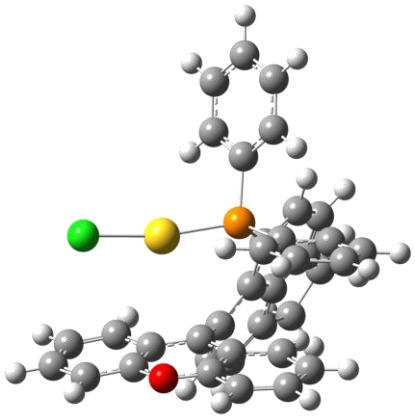


Figure S 49. ^{1}H NMR spectra obtained with [**4**$_{xant}$]OTf as the catalyst (2 mol%). The resulting spectrum was collected 1 hour after the start of the reaction. Integration of the ^{1}H resonance afforded a conversion of 2%.

4. DFT Simulation

4.1 Geometry optimized structure

$[\mathbf{3}_{xant}]^{+}$:



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Sum of electronic and thermal Energies= -2437.206041
Sum of electronic and thermal Enthalpies= -2437.205097
Sum of electronic and thermal Free Energies= -2437.308747

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P	-1.0992	-0.8366	-0.00176	C	-1.82954	0.851069	-0.05938
O	3.633632	0.239997	1.410427	C	-1.1336	2.111343	-0.13295
C	2.617291	1.791392	-1.75497	C	-1.96903	3.242545	-0.35417
H	1.754423	2.252684	-2.22111	C	-2.6763	5.492869	-0.75962
C	3.777407	1.607042	-2.46698	H	-2.61853	5.981976	-1.73851
H	3.837433	1.933806	-3.49965	H	-2.67123	6.29386	-0.01206
C	4.889145	0.980056	-1.86595	C	-3.92744	4.589003	-0.6381
H	5.801693	0.841576	-2.43746	H	-4.57285	4.893921	0.193395
C	4.829894	0.523389	-0.56447	H	-4.54758	4.620412	-1.54052
H	5.666472	0.024357	-0.08823	C	-1.12377	-1.3887	1.737327
C	2.70656	-0.01285	3.526194	C	-2.14023	-0.98708	2.614915
H	3.615438	-0.525	3.822023	H	-2.89459	-0.27438	2.29493
C	1.680776	0.240155	4.415423	C	-2.18424	-1.49483	3.909923
H	1.775135	-0.09046	5.445045	H	-2.97525	-1.1794	4.584134
C	0.527845	0.943872	4.011234	C	-1.21503	-2.40112	4.340236
H	-0.2541	1.154612	4.732264	H	-1.25055	-2.79386	5.352485
C	0.392085	1.362824	2.709922	C	-0.2004	-2.80161	3.472767
H	-0.48885	1.914439	2.402863	H	0.557757	-3.50477	3.804971
C	1.368937	1.563729	0.409938	C	-0.15309	-2.29831	2.174753
C	2.524964	1.370673	-0.39979	H	0.639593	-2.61128	1.499322
C	3.650907	0.713559	0.156366	C	-2.3467	-1.88401	-0.84875
C	1.410509	1.102429	1.754464	C	-2.52502	-1.71172	-2.23016
C	2.575765	0.434048	2.211213	H	-1.95757	-0.95254	-2.7635
C	0.271318	2.424165	-0.068	C	-3.43015	-2.50779	-2.9229
C	0.702767	3.732267	-0.32026	H	-3.56481	-2.36429	-3.99115
H	1.76728	3.938354	-0.25904	C	-4.15637	-3.49138	-2.24855
C	-0.15934	4.81203	-0.56391	H	-4.85912	-4.11649	-2.79206
H	0.249725	5.804647	-0.72385	C	-3.97567	-3.6717	-0.88008

C	-1.50995	4.563924	-0.55991	H	-4.53661	-4.43658	-0.35067
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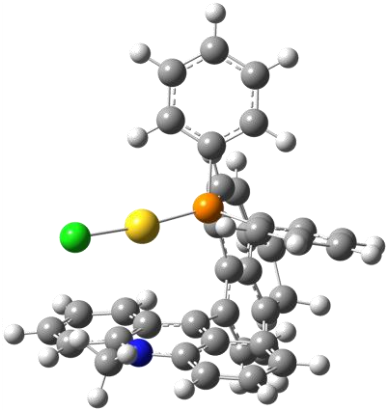
C	-4.01969	2.002243	-0.25498	H	-2.94503	-3.01902	0.890234
H	-5.10133	1.911776	-0.27822				

$[\mathbf{3}_{acr}]^{+}$:



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Sum of electronic and thermal Enthalpies= -2456.625161
Sum of electronic and thermal Free Energies= -2456.731526

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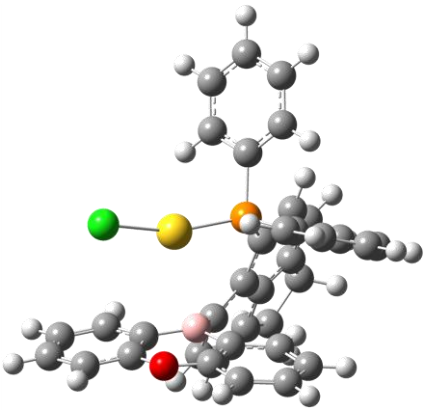
Cl	-3.34944	2.172909	-1.3372	H	5.06888	0.267448	-2.1059
P	0.842862	1.132361	0.196785	C	3.121024	0.494978	-1.19326
N	-3.40512	-1.48308	0.024053	H	3.190065	1.574264	-1.26957
C	-0.71596	-1.75946	-2.51426	C	1.984017	-0.0642	-0.6154
H	0.351698	-1.93677	-2.5575	C	1.886221	-1.50316	-0.53287
C	-1.43258	-1.59328	-3.66822	C	3.064714	-2.20568	-0.90338
H	-0.9352	-1.62525	-4.63194	C	4.625549	-3.98318	-1.24981
C	-2.83222	-1.41433	-3.60043	H	4.579484	-4.74908	-2.03156
H	-3.40748	-1.31901	-4.51626	H	5.210689	-4.41235	-0.42832
C	-3.48915	-1.37822	-2.39415	C	5.248727	-2.65978	-1.76345
H	-4.56539	-1.27362	-2.38674	H	6.201305	-2.43316	-1.27252
C	-3.46753	-1.96612	2.400221	H	5.455767	-2.70151	-2.839
H	-4.54326	-1.86149	2.436163	C	0.873762	0.691057	1.968037
C	-2.79747	-2.30736	3.551242	C	-0.16548	1.146771	2.78936
H	-3.36349	-2.4342	4.469142	H	-1.01052	1.673394	2.351956
C	-1.39848	-2.50036	3.559768	C	-0.11914	0.927198	4.163133
H	-0.88917	-2.74804	4.484801	H	-0.92879	1.284411	4.792879
C	-0.69477	-2.37543	2.393616	C	0.959461	0.245521	4.725814
H	0.378581	-2.51995	2.381046	H	0.992822	0.07171	5.797654
C	-0.63641	-1.96933	-0.04468	C	1.994049	-0.215	3.912898
C	-1.35234	-1.73188	-1.24008	H	2.835875	-0.74622	4.347642
C	-2.76649	-1.52084	-1.18657	C	1.956392	0.00812	2.537616
C	-1.34737	-2.05328	1.169232	H	2.772269	-0.34561	1.91401
C	-2.76062	-1.8188	1.183256	C	1.716244	2.744609	0.130549
C	-4.81099	-1.06484	0.069463	C	2.654432	3.112856	1.1029
H	-4.97444	-0.30368	-0.69062	H	2.884138	2.442867	1.925816
H	-5.01783	-0.60081	1.030299	C	3.293829	4.347812	1.024494

H	-5.47708	-1.91773	-0.08701	H	4.015304	4.627235	1.786949
C	0.800311	-2.34828	-0.12111	C	3.008787	5.221074	-0.02431
C	1.010122	-3.71884	0.028078	H	3.508414	6.184042	-0.08102
H	0.167142	-4.33169	0.336673	C	2.077927	4.859611	-0.99695
C	2.225026	-4.36419	-0.26847	H	1.848801	5.536882	-1.81462
H	2.312495	-5.43833	-0.13578	C	1.428967	3.629815	-0.91793
C	3.24751	-3.60093	-0.77557	H	0.697284	3.356367	-1.6745
C	4.21473	-1.6062	-1.46491				

6:

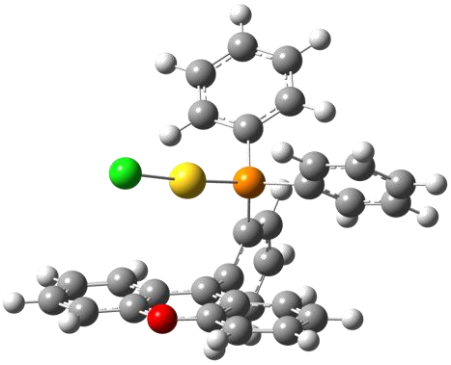


Sum of electronic and zero-point Energies= -2424.196127
Sum of electronic and thermal Energies= -2424.161701
Sum of electronic and thermal Enthalpies= -2424.160756
Sum of electronic and thermal Free Energies= -2424.266157

Au	0.772321	-1.22243	-1.02358	H	-3.87146	0.018845	-0.10177
Cl	2.51515	-2.25334	-2.18875	C	-1.92803	0.917521	-0.04431
P	-1.21448	-0.7646	-0.04057	C	-1.17988	2.149106	-0.05453
O	3.862458	0.066713	1.231058	C	-1.98068	3.319909	-0.16726
C	2.800214	1.808561	-1.82433	C	-2.6048	5.622113	-0.36153
H	1.933637	2.306589	-2.25208	H	-2.53842	6.200996	-1.28984
C	3.972242	1.722059	-2.55531	H	-2.57729	6.348281	0.458889
H	4.031424	2.146142	-3.55354	C	-3.88911	4.753018	-0.31889
C	5.088855	1.081337	-1.99633	H	-4.5272	5.009381	0.534695
H	6.015558	1.012405	-2.55969	H	-4.50465	4.886494	-1.21569
C	5.022	0.534746	-0.7254	C	-2.42191	-1.75868	-1.00589
H	5.874721	0.036677	-0.27412	C	-2.49743	-1.5452	-2.3905
C	3.111141	-0.30291	3.396419	H	-1.86197	-0.79893	-2.86192
H	4.068931	-0.77708	3.588074	C	-3.38333	-2.28468	-3.16658
C	2.159342	-0.1571	4.3928	H	-3.43581	-2.10984	-4.23748
H	2.368132	-0.5347	5.390203	C	-4.19545	-3.25222	-2.57188
C	0.943943	0.489401	4.126082	H	-4.88302	-3.83351	-3.1798
H	0.208714	0.613773	4.915325	C	-4.11966	-3.47249	-1.19927
C	0.688398	0.959303	2.849322	H	-4.74849	-4.22443	-0.73082
H	-0.25158	1.464131	2.641639	C	-3.23712	-2.72845	-0.41471
C	2.686364	1.271827	-0.52139	H	-3.18943	-2.90724	0.655023
C	3.827214	0.632692	-0.00415	C	-1.33618	-1.42838	1.656302
C	1.617981	0.816428	1.796336	C	-0.53155	-2.51923	2.009875
C	2.840181	0.198304	2.118346	H	0.195798	-2.90814	1.300912

C	0.241047	2.354268	0.001218	C	-0.65818	-3.10525	3.266283
C	0.706445	3.667329	-0.12383	H	-0.03001	-3.95077	3.531839
H	1.781981	3.83006	-0.09708	C	-1.58407	-2.60361	4.180486
C	-0.11034	4.812641	-0.24499	H	-1.67994	-3.05904	5.162233
H	0.344439	5.796834	-0.32153	C	-2.38444	-1.51586	3.835165
C	-1.46999	4.63442	-0.25523	H	-3.10506	-1.12046	4.545474
C	-3.39184	3.334573	-0.20951	C	-2.26393	-0.9289	2.577463
C	-4.07427	2.14405	-0.15673	H	-2.88913	-0.07925	2.319375
H	-5.15896	2.094636	-0.18637	B	1.424922	1.379088	0.369976
C	-3.32133	0.955479	-0.09355				

$[\mathbf{4}_{\mathbf{xant}}]^{+}$:

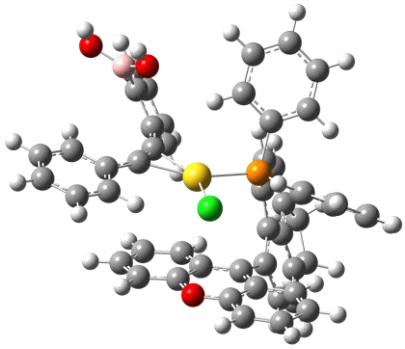


Sum of electronic and zero-point Energies= -2206.313526
Sum of electronic and thermal Energies= -2206.283622
Sum of electronic and thermal Enthalpies= -2206.282678
Sum of electronic and thermal Free Energies= -2206.378918

Au	-0.21567	-0.89016	-1.30744	C	-0.63245	0.416417	3.660441
P	1.383027	-0.0634	0.057951	H	-1.64789	0.60048	3.998868
Cl	-1.7469	-1.7661	-2.81032	C	1.804262	1.979616	-1.77974
O	-3.83796	0.74832	-0.18587	H	1.334766	1.302937	-2.48941
C	2.662771	-2.52521	0.183541	C	-3.22505	-2.86676	1.681675
H	1.659368	-2.92752	0.301645	H	-3.09036	-3.8344	2.152934
C	2.855036	-1.14365	0.0367	C	1.954651	-0.07876	2.790817
C	0.938592	0.072177	1.837782	H	2.966542	-0.29891	2.464122
C	-3.00675	1.787337	-0.04646	C	-4.56517	-1.42027	0.252466
C	1.949221	1.597764	-0.43934	H	-5.42801	-1.22811	-0.3752
C	-0.3756	0.316581	2.287864	C	0.39607	0.286918	4.588981
C	-2.47033	-0.60362	1.255695	H	0.175918	0.372174	5.648521
C	-1.55621	0.465466	1.394959	C	-1.3674	4.012452	0.236527
C	-2.29576	-1.87452	1.869974	H	-0.74828	4.896754	0.341772
H	-1.42073	-2.04413	2.487107	C	4.147812	-0.63696	-0.13224
C	-1.03314	2.856389	0.896211	H	4.308506	0.429904	-0.25446
H	-0.15768	2.816736	1.534081	C	2.990578	3.729212	0.040464
C	-3.34369	2.960254	-0.72267	H	3.448851	4.40981	0.751987
H	-4.23941	2.983709	-1.33303	C	2.254173	3.227043	-2.20435
C	-1.84139	1.694627	0.761654	H	2.136241	3.515413	-3.24476
C	-4.36159	-2.63618	0.873482	C	-2.52007	4.059319	-0.57971
H	-5.08843	-3.43048	0.735022	H	-2.77078	4.979936	-1.09744
C	2.546654	2.480952	0.470284	C	5.044403	-2.87695	0.007325
H	2.662144	2.204426	1.514437	H	5.896188	-3.55093	-0.00676

C	3.755653	-3.38559	0.174795	C	2.844974	4.103043	-1.29502
H	3.6002	-4.45424	0.290834	H	3.189511	5.078631	-1.62595
C	-3.61938	-0.41253	0.443006	C	5.238093	-1.50634	-0.14801
C	1.692185	0.034784	4.153135	H	6.239294	-1.10746	-0.28279
H	2.500669	-0.08195	4.868046				

[3$_{xant}$-a]$^{+}$:

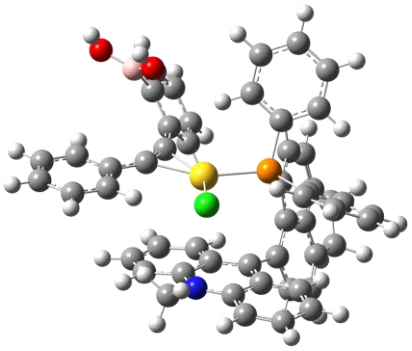


Sum of electronic and zero-point Energies= -3152.293013
Sum of electronic and thermal Energies= -3152.242892
Sum of electronic and thermal Enthalpies= -3152.247348
Sum of electronic and thermal Free Energies= -3152.387840

Au	-1.02711	-0.54449	0.535218	C	-1.71815	2.424587	-1.78973
B	-4.91017	2.179724	0.468359	C	-3.82524	2.643722	-0.57214
C	0.511674	-0.64398	-2.80742	C	-1.86955	3.704289	-2.312
C	-0.62853	-0.88754	-3.53292	C	-3.95849	3.921364	-1.13207
C	-1.30131	-2.12266	-3.41232	C	-2.99783	4.455612	-1.98859
C	-0.81397	-3.11552	-2.58867	Cl	-0.5898	-2.71675	1.654095
C	2.36729	-4.9127	0.269076	H	1.040155	0.294968	-2.92128
C	3.537689	-4.84772	0.996854	H	-1.01034	-0.13247	-4.21197
C	4.304084	-3.66245	1.040709	H	-2.20227	-2.30313	-3.99031
C	3.899014	-2.54989	0.346286	H	-1.29608	-4.08262	-2.50042
C	2.246097	-1.47285	-1.19136	H	1.760646	-5.81031	0.227043
C	1.031683	-1.62457	-1.9187	H	3.867887	-5.72064	1.551555
C	0.352319	-2.86938	-1.85911	H	5.209817	-3.62986	1.636565
C	2.709004	-2.57637	-0.43142	H	4.470525	-1.63086	0.395147
C	1.956496	-3.78002	-0.43619	H	4.520089	-1.61915	-2.268
C	3.092315	-0.28258	-1.40615	H	5.923956	0.096776	-3.32301
C	4.255796	-0.57528	-2.12431	H	1.911458	4.968656	-1.26478
C	5.043729	0.398852	-2.76396	H	0.723163	3.464493	0.246446
C	4.623651	1.705653	-2.70364	H	5.253976	2.864908	-4.41202
C	3.22558	3.415082	-1.98148	H	6.21006	3.134383	-2.96497
C	2.176016	3.915459	-1.25157	H	4.748255	4.899672	-2.36688
C	1.479071	3.033326	-0.40103	H	3.720843	4.544438	-3.74555
C	1.731147	1.665793	-0.31174	H	3.84654	1.355929	1.194462
C	2.714486	1.091491	-1.19432	H	5.622782	0.536927	2.685121
C	3.484705	2.028136	-1.93056	H	5.122112	-1.1898	4.401817
C	5.189268	2.956543	-3.32232	H	2.815603	-2.09212	4.60729
C	4.22459	4.089191	-2.88508	H	1.029894	-1.29172	3.099586
C	2.309696	0.084195	2.039815	H	-1.76647	1.731824	1.864383
C	3.611755	0.593663	1.930947	H	-2.54518	3.484959	3.395526

C	4.618391	0.133279	2.777903	H	-0.9037	4.884234	4.640074
C	4.336016	-0.83368	3.741754	H	1.531664	4.496479	4.326073
C	3.042297	-1.3389	3.85788	H	2.321267	2.738545	2.798559
C	2.032114	-0.88396	3.013173	H	-2.81854	-3.28763	0.399587
C	0.334236	2.113326	2.207929	H	-4.60754	-4.9924	0.121409
C	-1.03492	2.33486	2.393389	H	-7.20534	-1.98819	-1.52771
C	-1.4781	3.330121	3.264415	H	-6.80465	-4.34352	-0.83967
C	-0.55897	4.110909	3.959191	H	-0.85033	1.827601	-2.04859
C	0.808799	3.894046	3.783171	H	-1.10942	4.109392	-2.97409
C	1.254092	2.901254	2.916781	H	-4.83294	4.514864	-0.87738
C	-2.97956	-0.67274	-0.28037	H	-3.12691	5.453858	-2.39752
C	-2.56125	0.511851	-0.48848	H	-5.42324	-0.29697	-1.25948
C	-3.99857	-1.68707	-0.41464	H	-6.8445	2.216186	0.85154
C	-3.77972	-3.0164	-0.02701	H	-5.20481	1.347111	2.233966
C	-5.2459	-1.32528	-0.95718	O	0.828222	-3.89397	-1.14351
C	-4.7871	-3.96462	-0.18213	O	-6.21356	2.45059	0.162758
C	-6.24624	-2.27834	-1.10764	O	-4.49564	1.597194	1.63208
C	-6.02042	-3.60091	-0.72144	P	0.906871	0.775547	1.080297
C	-2.6884	1.882491	-0.93516				

[3$_{acr}$-a]$^{+}$:

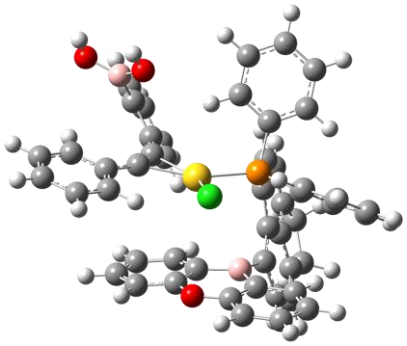


Sum of electronic and zero-point Energies= -3171.713599
Sum of electronic and thermal Energies= -3171.661882
Sum of electronic and thermal Enthalpies= -3171.660938
Sum of electronic and thermal Free Energies= -3171.804990

Au	-1.0153	-0.44653	0.608133	C	-3.59645	2.880943	-0.60087
B	-4.71317	2.489633	0.436206	C	-1.56424	3.813497	-2.32571
C	0.402613	-0.57921	-2.92714	C	-3.65544	4.155616	-1.17934
C	-0.7466	-0.74448	-3.65172	C	-2.65628	4.626704	-2.02925
C	-1.50464	-1.9252	-3.4946	Cl	-0.79186	-2.58064	1.867503
C	-1.1121	-2.91469	-2.62545	H	1.013612	0.304745	-3.06672
C	2.249102	-4.82754	0.264785	H	-1.06421	0.015428	-4.358
C	3.493749	-4.76286	0.844201	H	-2.40305	-2.07111	-4.08651
C	4.279457	-3.59115	0.772514	H	-1.69448	-3.82448	-2.5758
C	3.807097	-2.50475	0.089332	H	1.697048	-5.75597	0.317463
C	2.066297	-1.43734	-1.30456	H	3.877411	-5.63673	1.362105
C	0.845092	-1.56998	-2.00512	H	5.25121	-3.55761	1.253187
C	0.069819	-2.76474	-1.86072	H	4.397269	-1.59966	0.020052
C	2.534528	-2.53103	-0.54993	H	4.131131	-1.60879	-2.72871
C	1.732288	-3.71238	-0.43658	H	5.547237	0.091669	-3.80131

C	2.938623	-0.26229	-1.58539	H	2.187954	5.032103	-0.91466
C	3.970087	-0.56452	-2.47351	H	1.005043	3.491895	0.560999
C	4.76527	0.403441	-3.11537	H	5.0295	2.99049	-4.54482
C	4.474893	1.724665	-2.88326	H	6.14088	3.053625	-3.18745
C	3.302202	3.455147	-1.8744	H	4.89291	4.856859	-2.29386
C	2.367656	3.965285	-1.01075	H	3.708382	4.703568	-3.58035
C	1.672489	3.063686	-0.17858	H	3.95395	1.211717	1.162186
C	1.818514	1.680123	-0.22225	H	5.760396	0.278944	2.550113
C	2.688966	1.108028	-1.22407	H	5.266679	-1.48911	4.22589
C	3.455973	2.052749	-1.96038	H	2.940007	-2.32031	4.493028
C	5.079136	2.98307	-3.45054	H	1.123808	-1.40317	3.089698
C	4.257183	4.136313	-2.81973	H	-1.60097	1.912583	1.868975
C	2.410336	-0.0366	2.026274	H	-2.29475	3.614761	3.492532
C	3.724079	0.431151	1.880959	H	-0.60424	4.729969	4.943026
C	4.746634	-0.09308	2.669835	H	1.794072	4.109758	4.73571
C	4.468409	-1.08339	3.610475	H	2.499164	2.403634	3.11036
C	3.163094	-1.54879	3.761236	H	-0.22547	-5.69755	-1.47088
C	2.136777	-1.02928	2.975608	H	-0.20035	-5.24761	0.263788
C	0.502149	2.03818	2.360834	H	-1.41769	-4.55661	-0.775
C	-0.84707	2.390824	2.486757	H	-3.11688	-2.96941	0.768236
C	-1.24252	3.357944	3.410061	H	-5.247	-0.00925	-1.50655
C	-0.2961	3.979726	4.220056	H	-5.02918	-4.53868	0.507658
C	1.050329	3.632038	4.104084	H	-7.15103	-1.56624	-1.76286
C	1.448517	2.667802	3.183119	H	-7.04877	-3.83816	-0.75828
C	-2.9623	-0.4556	-0.22726	H	-0.64947	1.888639	-2.02287
C	-2.45415	0.686595	-0.4711	H	-0.77448	4.169737	-2.98115
C	-0.38468	-4.89363	-0.74687	H	-4.50048	4.798085	-0.94465
C	-4.05339	-1.39347	-0.35292	H	-2.72729	5.624573	-2.45316
C	-4.00254	-2.67538	0.212239	H	-6.64885	2.603283	0.793258
C	-5.20151	-1.00146	-1.06626	H	-5.05699	1.732354	2.226392
C	-5.07781	-3.54758	0.064803	N	0.500463	-3.75871	-1.02624
C	-6.26997	-1.87885	-1.20919	O	-6.00266	2.793727	0.104838
C	-6.2118	-3.15471	-0.6451	O	-4.33237	1.937606	1.626194
C	-2.49661	2.055749	-0.9388	P	1.004211	0.746087	1.146728
C	-1.48724	2.534608	-1.78508				

6-a:

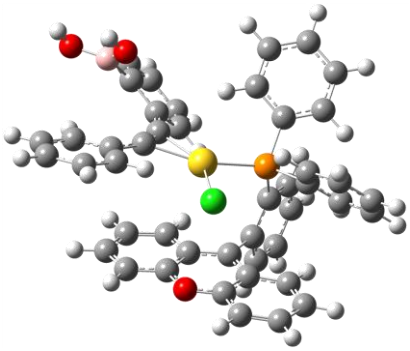


Sum of electronic and zero-point Energies= -3139.245630
Sum of electronic and thermal Energies= -3139.195065
Sum of electronic and thermal Enthalpies= -3139.194121
Sum of electronic and thermal Free Energies= -3139.336370

Au	0.978242	0.519614	0.594585	C	1.562074	-2.37712	-1.85759
B	-2.13547	1.500132	-1.24195	C	3.664527	-2.71535	-0.65899
B	4.764873	-2.33122	0.39704	C	1.672792	-3.63706	-2.43543
C	-0.2661	0.814676	-2.94177	C	3.756538	-3.97105	-1.27389
C	0.852158	1.116129	-3.69804	C	2.777673	-4.4368	-2.14977
C	1.442688	2.384503	-3.58082	Cl	0.737876	2.61546	1.923884
C	0.900784	3.336864	-2.73422	H	-0.73976	-0.15853	-3.04337
C	-2.30244	5.100886	0.095502	H	1.270119	0.382466	-4.38121
C	-3.49121	5.1027	0.805434	H	2.322096	2.631656	-4.16937
C	-4.27821	3.943098	0.882159	H	1.327924	4.331279	-2.64798
C	-3.85624	2.789711	0.245162	H	-1.68159	5.988339	0.020124
C	-0.84196	1.744546	-2.04657	H	-3.81316	6.012616	1.304939
C	-0.24096	3.015594	-1.98909	H	-5.20734	3.953111	1.444542
C	-2.6528	2.73992	-0.49312	H	-4.45436	1.885148	0.31103
C	-1.89843	3.925963	-0.54934	H	-4.31727	1.493377	-2.5029
C	-2.9778	0.187866	-1.46976	H	-5.62194	-0.23406	-3.65572
C	-4.05663	0.452497	-2.31729	H	-1.93952	-5.08927	-1.02527
C	-4.80128	-0.53157	-3.00798	H	-0.82912	-3.5323	0.497768
C	-4.4271	-1.84307	-2.86026	H	-4.92652	-3.07618	-4.57002
C	-3.13803	-3.54341	-1.93515	H	-6.01351	-3.26542	-3.20479
C	-2.17504	-4.03037	-1.08736	H	-4.64535	-5.0235	-2.40685
C	-1.52334	-3.12002	-0.22669	H	-3.48758	-4.73788	-3.69458
C	-1.74821	-1.74725	-0.23649	H	-3.92298	-1.30709	1.116454
C	-2.65913	-1.18971	-1.20764	H	-5.75557	-0.44126	2.515941
C	-3.37421	-2.15128	-1.96903	H	-5.30583	1.301039	4.230774
C	-4.96199	-3.11322	-3.47544	H	-2.99757	2.175171	4.524085
C	-4.06084	-4.24081	-2.90304	H	-1.15851	1.326219	3.107423
C	-2.4106	-0.04883	2.0154	H	1.68119	-1.80514	1.872209
C	-3.71338	-0.53923	1.854244	H	2.443219	-3.48592	3.488119
C	-4.74981	-0.05189	2.64868	H	0.795717	-4.70008	4.909106
C	-4.49654	0.924153	3.611217	H	-1.6289	-4.20216	4.677933
C	-3.20185	1.413139	3.776855	H	-2.40132	-2.51765	3.058249
C	-2.16271	0.93129	2.984129	H	2.851148	3.21807	0.48431
C	-0.41743	-2.04267	2.338405	H	5.394292	0.157285	-1.1401
C	0.946084	-2.32724	2.477145	H	4.703399	4.863635	0.269614
C	1.380157	-3.28207	3.396365	H	7.239631	1.787607	-1.3425

C	0.457862	-3.95948	4.18936	H	6.902377	4.14879	-0.63977
C	-0.90338	-3.68034	4.059982	H	0.713092	-1.74212	-2.08514
C	-1.3394	-2.72886	3.142818	H	0.898168	-3.98942	-3.11077
C	2.93661	0.608626	-0.22502	H	4.61225	-4.60255	-1.04814
C	2.4729	-0.54853	-0.48203	H	2.874376	-5.41985	-2.60238
C	3.995461	1.586378	-0.31711	H	6.699098	-2.42764	0.768769
C	3.812996	2.918863	0.078873	H	5.088928	-1.59921	2.201217
C	5.244031	1.187673	-0.83045	O	-0.73301	4.032142	-1.23858
C	4.856006	3.833159	-0.03966	O	6.061753	-2.61118	0.070351
C	6.280355	2.106822	-0.94429	O	4.370169	-1.80464	1.59399
C	6.090226	3.432604	-0.55009	P	-0.97949	-0.77412	1.124714
C	2.551716	-1.90284	-0.98536				

$[\mathbf{4}_{\mathbf{xant}}\text{-}\mathbf{a}]^+$:



Sum of electronic and zero-point Energies= -2921.363175
Sum of electronic and thermal Energies= -2921.317332
Sum of electronic and thermal Enthalpies= -2921.316387
Sum of electronic and thermal Free Energies= -2921.448304

Au	0.423835	-0.212	-0.69746	C	4.10976	1.993813	0.657491
B	5.115819	1.504889	-0.44963	C	2.389317	3.136504	2.587057
C	0.331081	-1.15802	2.828117	C	4.539558	3.020061	1.509471
C	1.50641	-1.8056	3.114335	C	3.69996	3.592484	2.46318
C	1.721813	-3.12633	2.65975	Cl	-0.69981	-2.0782	-1.87908
C	0.757227	-3.80147	1.93958	H	0.155799	-0.14821	3.180026
C	-3.48184	-4.15503	0.071951	H	2.276777	-1.30445	3.690488
C	-4.74524	-3.66545	-0.18852	H	2.659138	-3.62414	2.887827
C	-5.11918	-2.35708	0.194779	H	0.898938	-4.81954	1.594605
C	-4.21702	-1.53591	0.821571	H	-3.18281	-5.16091	-0.20034
C	-1.92087	-1.20885	1.742286	H	-5.46881	-4.30293	-0.68707
C	-0.68639	-1.81064	2.079169	H	-6.12553	-2.0062	-0.00665
C	-0.44445	-3.14719	1.66236	H	-4.49982	-0.53911	1.136407
C	-2.8979	-1.99059	1.093777	H	-2.80874	-0.5747	4.096396
C	-2.56802	-3.32251	0.719618	H	-3.26053	1.647895	5.073867
C	-2.2035	0.188785	2.180367	H	-4.34513	1.730561	0.179322
C	-2.6584	0.319054	3.497629	H	-6.35268	1.471999	-1.22333
C	-2.90955	1.572074	4.049441	H	-6.15848	0.56999	-3.53123
C	-2.69327	2.712441	3.286104	H	-3.93019	-0.0667	-4.42586
C	-2.00732	1.343886	1.386024	H	-1.91322	0.171558	-3.01957
C	-2.24804	2.593575	1.97177	H	1.082222	2.597555	-0.93978
C	-2.98813	0.95951	-1.32195	H	1.673755	4.88228	-1.65358

C	-4.24601	1.326413	-0.82493	H	-0.10985	6.575489	-2.01999
C	-5.38239	1.185303	-1.61876	H	-2.49133	5.951476	-1.67626
C	-5.27162	0.681395	-2.91371	H	-3.08815	3.672635	-0.97805
C	-4.02133	0.323963	-3.41632	H	-2.87006	3.698263	3.705091
C	-2.88222	0.461722	-2.62651	H	-2.08213	3.495035	1.391815
C	-1.03838	2.977232	-0.87286	H	1.824133	-2.70275	-2.2916
C	0.298338	3.332909	-1.08449	H	4.924013	-1.26282	0.316728
C	0.631202	4.623369	-1.49265	H	3.289356	-4.58612	-2.98403
C	-0.3685	5.570362	-1.69899	H	6.37579	-3.14289	-0.36008
C	-1.70528	5.221619	-1.50511	H	5.56668	-4.81162	-2.01654
C	-2.04106	3.932698	-1.10188	H	0.920169	1.743391	1.86637
C	2.466767	-0.72917	-0.55318	H	1.718537	3.576715	3.319462
C	2.316904	0.382505	0.053684	H	5.55785	3.386915	1.409841
C	3.278619	-1.85227	-0.9569	H	4.064567	4.393121	3.1006
C	2.825679	-2.80139	-1.88409	H	7.025712	1.149272	-0.78914
C	4.568697	-1.98718	-0.4105	H	5.325056	0.994417	-2.34075
C	3.649344	-3.85774	-2.26258	O	-1.36993	-3.84343	0.995839
C	5.382642	-3.04775	-0.79032	O	6.423972	1.380879	-0.07392
C	4.927324	-3.98492	-1.71958	O	4.6553	1.291602	-1.71581
C	2.784247	1.518773	0.817675	P	-1.45032	1.258127	-0.37604
C	1.938306	2.106851	1.769684				

4.2 General procedure used to determine the Gibbs free energy change upon exchnage of the alkyne substrate bewteen two gold complexes.

(1) $[\mathbf{3}_{acr}\text{-}\mathbf{a}]^+ + [\mathbf{3}_{xant}]^+ \rightarrow [\mathbf{3}_{acr}]^+ + [\mathbf{3}_{xant}\text{-}\mathbf{a}]^+$

ΔG = (-3152.38784) + (-2456.731526) – (-2437.308747) – (-3171.80499) = -0.005628 a.u.

= -3.53 kcal mol^{-1}

(2) $\mathbf{6\text{-}a} + [\mathbf{3}_{xant}]^+ \rightarrow \mathbf{6} + [\mathbf{3}_{xant}\text{-}\mathbf{a}]^+$

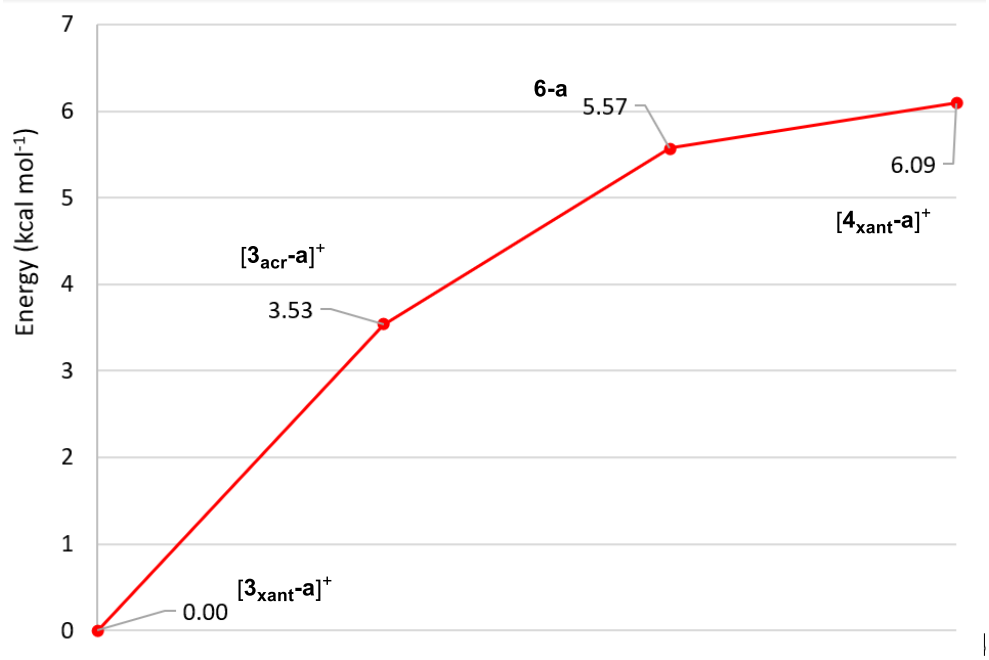
ΔG = (-3152.38784) + (-2424.266157) – (-2437.308747) – (-3139.33637) = -0.008879 a.u.

= -5.57 kcal mol^{-1}

(3) $[\mathbf{4}_{xant}\text{-}\mathbf{a}]^+ + [\mathbf{3}_{xant}]^+ \rightarrow [\mathbf{4}_{xant}]^+ + [\mathbf{3}_{xant}\text{-}\mathbf{a}]^+$

ΔG = (-3152.38784) + (-2206.378918) – (-2437.308747) – (-2921.448304) = -0.009706 a.u.

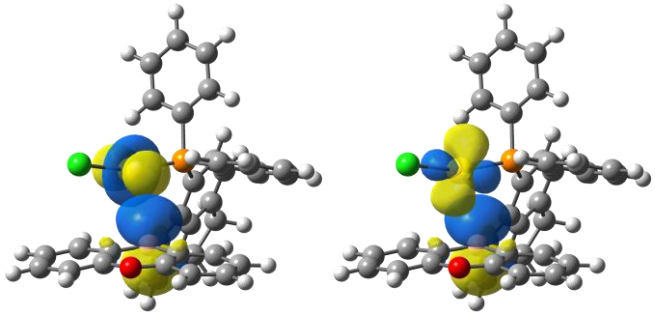
= -6.09 kcal mol^{-1}



4.3 Natural bond orbital (NBO) analysis

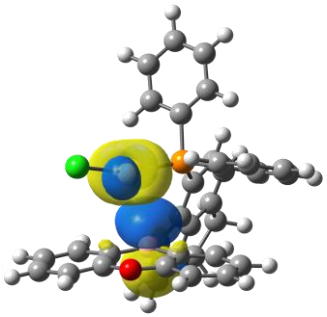
Selected donor and acceptor NBOs and E_{SOPT} values (kcal/mol) for **6**. SOPT stands for second order perturbation theory.

Donor NBO	Acceptor NBO	E_{SOPT}
54. LP (2)Au 1	155. LV (1) B 67	0.06
55. LP (3)Au 1	155. LV (1) B 67	1.51
56. LP (4)Au 1	155. LV (1) B 67	0.49
57. LP (5)Au 1	155. LV (1) B 67	3.67

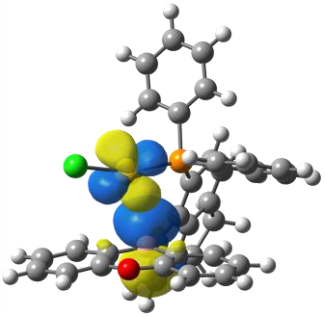


$Au_1 \longrightarrow B_{67}$
0.06 kcal/mol

$Au_1 \longrightarrow B_{67}$
1.51 kcal/mol



$Au_1 \longrightarrow B_{67}$
0.49 kcal/mol



$Cl_2 \longrightarrow B_{67}$
3.67 kcal/mol

Determination of NBO deletion energy using the above second order perturbation

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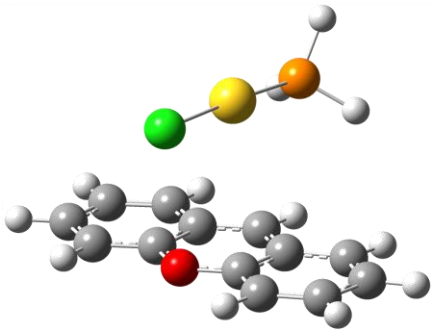
Energy of deletion : -2424.710142333
Total SCF energy : -2424.718437256
Energy change : 0.008295 a.u., 5.205 kcal/mol

4.4 Energy decomposition analysis

[H_3PAuCl-Xant]$^+$:

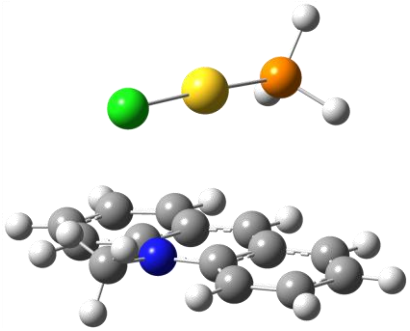


Sum of electronic and zero-point Energies= -1514.650042
Sum of electronic and thermal Energies= -1514.633875
Sum of electronic and thermal Enthalpies= -1514.632931
Sum of electronic and thermal Free Energies= -1514.698600

Au	-1.52177	-0.15103	-0.26469	H	0.810075	2.610538	2.666673
C	1.131608	2.602518	1.628942	H	1.007237	4.71933	1.378305
C	1.245086	3.767458	0.914924	H	1.749249	4.669958	-0.98745
C	1.674725	3.737995	-0.43503	H	2.325012	2.518573	-2.10061
C	2.001339	2.554888	-1.06643	H	2.791928	-1.96529	-2.13533
C	2.484304	-2.08345	-1.10234	H	2.674575	-4.20597	-1.05595
C	2.410167	-3.31799	-0.48951	H	1.963658	-4.44328	1.308007
C	1.998698	-3.45594	0.859342	H	1.337998	-2.44039	2.628098
C	1.648506	-2.35042	1.590864	H	1.025928	0.079821	2.695334
C	1.343656	0.120925	1.654665	H	-1.472	-1.27803	2.674721
C	1.447822	1.359941	1.013885	H	-3.38789	-0.39442	2.286011
C	1.890543	1.369058	-0.33924	H	-1.69901	0.857818	2.712367
C	1.700002	-1.06018	0.995183	O	2.223285	0.232706	-0.95795
C	2.132728	-0.95712	-0.35721	P	-2.0417	-0.24474	1.906738
Cl	-0.86607	-0.042	-2.42972				

	hartree	eV	kcal/mol	kJ/mol
Pauli Repulsion				
Kinetic (Delta T^0):	0.266915269304841	7.2631	167.49	700.79
Delta V^Pauli Coulomb:	-0.206837764209463	-5.6283	-129.79	-543.05
Delta V^Pauli LDA-XC:	-0.052411216244069	-1.4262	-32.89	-137.61
Delta V^Pauli GGA-Exchange:	0.013509162175851	0.3676	8.48	35.47
Delta V^Pauli GGA-Correlation:	-0.004686630622771	-0.1275	-2.94	-12.30
Total Pauli Repulsion: (Total Pauli Repulsion = Delta E^Pauli in BB paper)	0.016488820404388	0.4487	10.35	43.29
Steric Interaction				
Pauli Repulsion (Delta E^Pauli):	0.016488820404388	0.4487	10.35	43.29
Electrostatic Interaction: (Electrostatic Interaction = Delta V_elstat in the BB paper)	-0.008621118678661	-0.2346	-5.41	-22.63
Total Steric Interaction: (Total Steric Interaction = Delta E^0 in the BB paper)	0.007867701725727	0.2141	4.94	20.66
Orbital Interactions				
A:	-0.009224534792025	-0.2510	-5.79	-24.22
Total Orbital Interactions:	-0.009224534791990	-0.2510	-5.79	-24.22
Alternative Decomposition Orb.Int.				
Kinetic:	-0.275811561554836	-7.5052	-173.07	-724.14
Coulomb:	0.235786248993887	6.4161	147.96	619.06
XC:	0.030800777768959	0.8381	19.33	80.87
Total Orbital Interactions:	-0.009224534791990	-0.2510	-5.79	-24.22
Residu (E=Steric+OrbInt+Res):	-0.000000065963119	-0.0000	-0.00	-0.00
Dispersion Energy:	-0.011271252843513	-0.3067	-7.07	-29.59
Total Bonding Energy:	-0.012628151872895	-0.3436	-7.92	-33.16

[H_3PAuCl-Acr]$^+$:

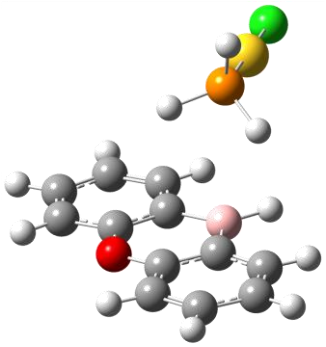


Sum of electronic and zero-point Energies= -1534.078717
Sum of electronic and thermal Energies= -1534.061078
Sum of electronic and thermal Enthalpies= -1534.060133
Sum of electronic and thermal Free Energies= -1534.127796

Au	1.661284	0.001039	-0.20141	H	-1.6161	-4.58506	1.665826
C	-1.48442	-2.45707	1.802457	H	-2.20559	-4.54903	-0.75135
C	-1.68964	-3.637	1.143339	H	-2.4129	-2.4759	-1.97765
C	-2.02093	-3.61297	-0.23274	H	-2.41669	2.472168	-1.9782
C	-2.12881	-2.4352	-0.93491	H	-2.21233	4.545919	-0.7524
C	-2.13245	2.432151	-0.93546	H	-1.62263	4.583389	1.664698
C	-2.02624	3.610247	-0.23358	H	-1.25923	2.441425	2.864104
C	-1.69485	3.635093	1.142454	H	-1.67068	-0.86809	-2.82231
C	-1.48787	2.455622	1.801846	H	-1.67183	0.865276	-2.82249
C	-1.40412	-0.00067	1.773071	H	-3.23682	-0.00243	-2.65306
C	-1.5906	-1.21495	1.11579	H	-1.17515	-0.00037	2.837212
C	-1.90484	-1.20019	-0.28257	H	1.417731	1.078179	2.7463
C	-1.59232	1.213178	1.115497	H	1.418902	-1.07466	2.747041
C	-1.90661	1.197634	-0.28284	H	3.262743	0.00268	2.524849
C	-2.17222	-0.0017	-2.39978	N	-1.99205	-0.00142	-0.94117
Cl	1.26448	0.000259	-2.43707	P	1.951913	0.001797	2.014473
H	-1.25587	-2.44227	2.864727				

	hartree	eV	kcal/mol	kJ/mol
Pauli Repulsion				
Kinetic (Delta T^0):	0.255144606446611	6.9428	160.11	669.88
Delta V^Pauli Coulomb:	-0.194507146382749	-5.2928	-122.06	-510.68
Delta V^Pauli LDA-XC:	-0.054149682775582	-1.4735	-33.98	-142.17
Delta V^Pauli GGA-Exchange:	0.014625080473262	0.3980	9.18	38.40
Delta V^Pauli GGA-Correlation:	-0.005043669720991	-0.1372	-3.16	-13.24
Total Pauli Repulsion: (Total Pauli Repulsion = Delta E^Pauli in BB paper)	0.016069188040551	0.4373	10.08	42.19
Steric Interaction				
Pauli Repulsion (Delta E^Pauli):	0.016069188040551	0.4373	10.08	42.19
Electrostatic Interaction: (Electrostatic Interaction = Delta V_elstat in the BB paper)	-0.010845975977986	-0.2951	-6.81	-28.48
Total Steric Interaction: (Total Steric Interaction = Delta E^0 in the BB paper)	0.005223212062565	0.1421	3.28	13.71
Orbital Interactions				
A:	-0.009358612493731	-0.2547	-5.87	-24.57
Total Orbital Interactions:	-0.009358612493765	-0.2547	-5.87	-24.57
Alternative Decomposition Orb.Int.				
Kinetic:	-0.259103563699290	-7.0506	-162.59	-680.28
Coulomb:	0.222117632895755	6.0441	139.38	583.17
XC:	0.027627318309771	0.7518	17.34	72.54
Total Orbital Interactions:	-0.009358612493765	-0.2547	-5.87	-24.57
Residu (E=Steric+OrbInt+Res):	0.000000111708272	0.0000	0.00	0.00
Dispersion Energy:	-0.012027598447602	-0.3273	-7.55	-31.58
Total Bonding Energy:	-0.016162887170530	-0.4398	-10.14	-42.44

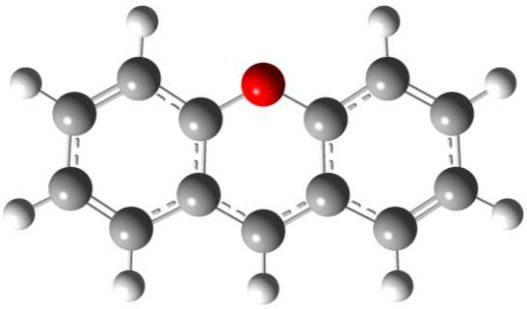
H_3PAuCl-OxaB:



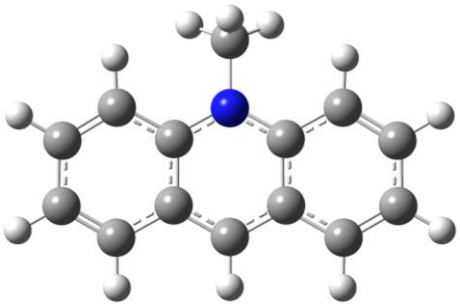
Sum of electronic and zero-point Energies= -1501.656400
Sum of electronic and thermal Energies= -1501.640880
Sum of electronic and thermal Enthalpies= -1501.639936
Sum of electronic and thermal Free Energies= -1501.703346

Au	-2.18933	-0.55516	-0.17951	H	-0.61874	1.66981	1.595954
B	1.552715	-0.08416	1.217811	H	-0.91382	3.934751	0.641939
C	0.146912	2.093892	0.95088	H	0.849462	4.890455	-0.83308
C	-0.02013	3.359563	0.419865	H	2.900691	3.576924	-1.34687
C	0.974932	3.89605	-0.41264	H	5.57107	0.115031	-1.15537
C	2.120421	3.175759	-0.70767	H	6.289953	-2.15815	-0.44094
C	4.949937	-0.49363	-0.5057	H	4.840651	-3.51615	1.057112
C	5.338068	-1.75899	-0.10055	H	2.673705	-2.59097	1.834605
C	4.520215	-2.52679	0.743878	H	0.770714	-0.65186	1.931458
C	3.312217	-2.00913	1.173468	H	0.544248	-2.12078	-0.47174
C	1.297512	1.318679	0.67492	H	-0.58897	-2.24375	-2.29058
C	2.271137	1.896167	-0.16285	H	0.498613	-0.45102	-1.82549
C	2.872132	-0.72355	0.784986	O	3.420853	1.257838	-0.5064
C	3.723258	0.012825	-0.0606	P	-0.37835	-1.36187	-1.21177
Cl	-4.02089	0.2791	0.872649				

4.5 [Xant]$^+$ and [Acr]$^+$ model



C	3.635796	0.6519	-2.8E-05	C	-2.34585	-1.42405	0.000002
C	2.48974	1.404906	0.00002	H	-2.531	2.487761	-3.9E-05
C	1.217814	0.764457	0.000036	H	-2E-06	2.538882	0.000024
C	1.179698	-0.65997	0.000067	H	4.605748	1.132759	-6.1E-05
C	2.34585	-1.42405	-1.8E-05	H	2.530999	2.48776	0.000024
C	3.559722	-0.76194	-0.00007	H	2.27995	-2.50438	-0.00002
C	0.000001	1.452987	0.000027	H	4.475988	-1.34058	-0.00011
C	-1.1797	-0.65997	0.000031	H	-4.60575	1.132761	-6.4E-05
C	-1.21781	0.764456	0.000006	H	-4.47599	-1.34058	-5.4E-05
C	-2.48974	1.404906	-0.00002	H	-2.27995	-2.50438	0.000019
C	-3.6358	0.6519	-3.7E-05	O	0	-1.31394	0.000046
C	-3.55972	-0.76194	-3.1E-05				



C	-3.64047	-0.97101	0.039124	H	2.440329	-2.73749	-0.06309
C	-2.45823	-1.65445	-0.02735	H	-2.9E-05	-2.72267	-0.11668
C	-1.21535	-0.95751	-0.04055	H	-4.58538	-1.4991	0.053052
C	-1.20631	0.477191	-0.00599	H	-2.44035	-2.73746	-0.06314
C	-2.44393	1.1562	0.081768	H	-2.48931	2.231403	0.161128
C	-3.62129	0.441934	0.105153	H	-4.55758	0.98206	0.183643
C	-1.6E-05	-1.63813	-0.07694	H	4.585353	-1.49913	0.053108
C	1.2063	0.477165	-0.006	H	4.557573	0.982027	0.183614
C	1.215329	-0.95753	-0.04054	H	2.489293	2.231385	0.161029
C	2.458202	-1.65448	-0.02732	H	0.000887	3.078457	0.832674
C	3.64045	-0.97104	0.039153	H	0.873549	2.940647	-0.7156
C	3.621284	0.441908	0.105138	H	-0.87416	2.940878	-0.71424
C	2.443925	1.15618	0.081726	N	-2E-06	1.144588	-0.05318
C	0.000078	2.619717	-0.15792				

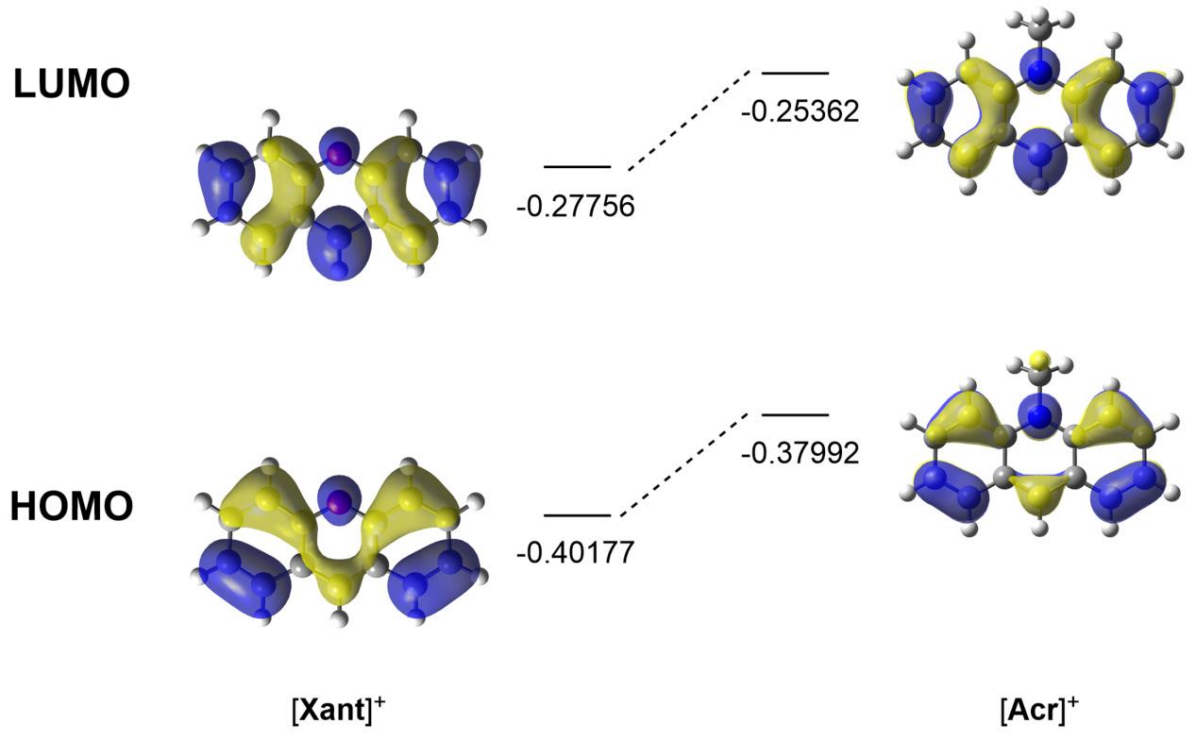
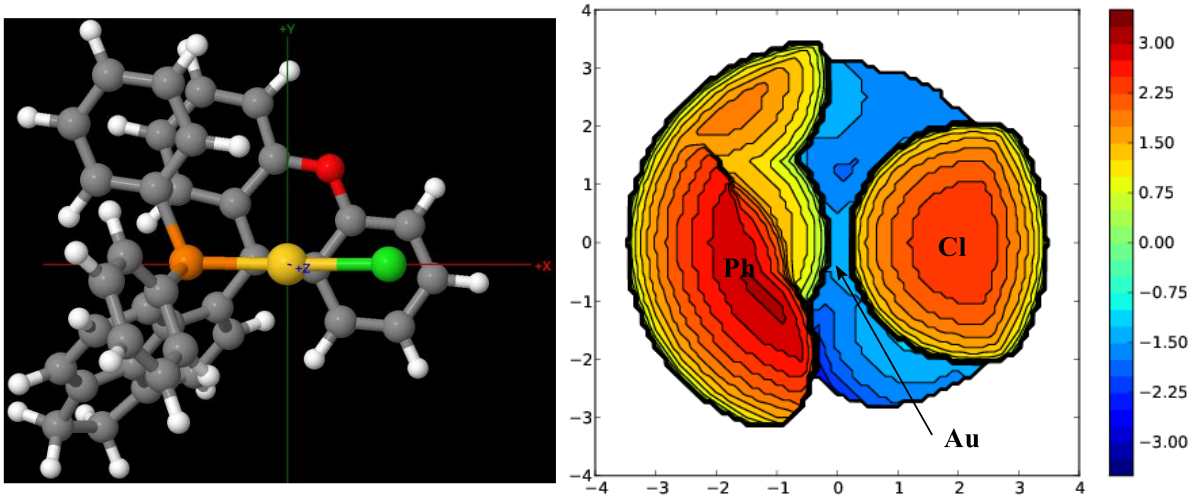


Figure S 50. Selected molecular orbital of [**Xant**]$^+$ and [**Acr**]$^+$ and corresponding orbital energies in a.u. The isovalues used to draw the orbitals are set as 0.02.

4.6 $\%V_{Bur}$ and steric map of $[\mathbf{3}_{xant}]^+$, $[\mathbf{3}_{acr}]^+$, **6** and $[\mathbf{4}_{xant}]^+$

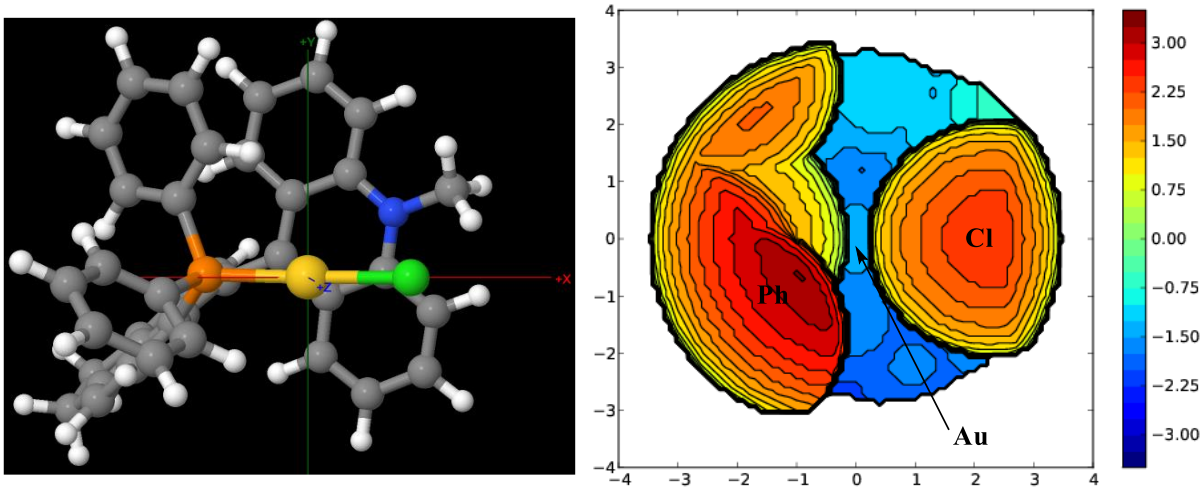
The buried volumes and the steric maps of gold complexes were obtained using the SambVca 2 Web application: "https://www.molnac.unisa.it/OMtools/sambvca2.1/".[15] The input files of the optimized structures were in the XYZ format. For all structures, sphere radius = 3.5 Å, SambVca. mesh spacing was 0.10, all H atoms were omitted, and bond radii were scaled by 1.17. As described by Nolan and coworker, $\%V_{Bur}$ is correlated to the cone angle.[16]



%V Free	%V Buried	% V Tot/V Ex
36.7	**63.3**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	13.6	31.2	44.9	**30.4**	69.6
NW	11.3	33.6	44.9	**25.2**	74.8
NE	20.5	24.3	44.9	**45.8**	54.2
SE	20.4	24.5	44.9	**45.4**	54.6

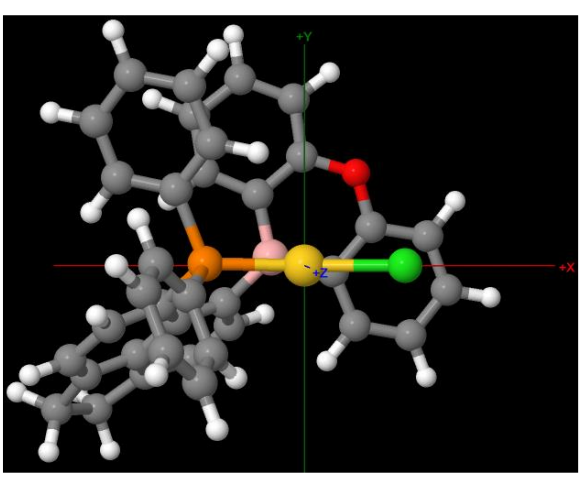
Figure S 51. Buried volumes and the steric maps of $[\mathbf{3}_{xant}]^+$

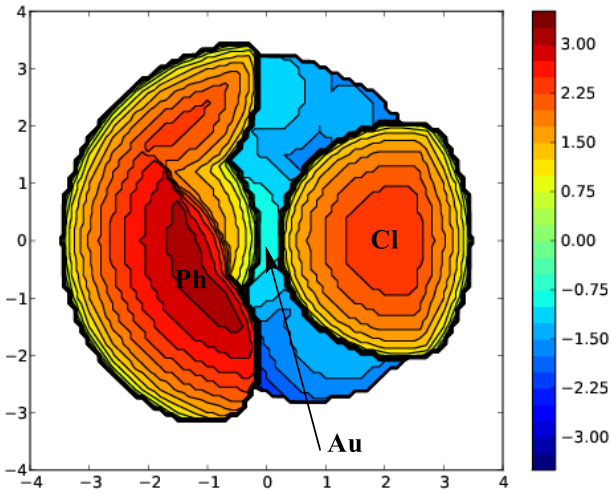


%V Free	**%V Buried**	% V Tot/V Ex
36.6	**63.4**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	12.8	32.1	44.9	**28.4**	71.6
NW	11.8	33.1	44.9	**26.3**	73.7
NE	18.9	25.9	44.9	**42.2**	57.8
SE	22.2	22.6	44.9	**49.5**	50.5

Figure S 52. Buried volumes and the steric maps of $[\mathbf{3}_{acr}]^{+}$

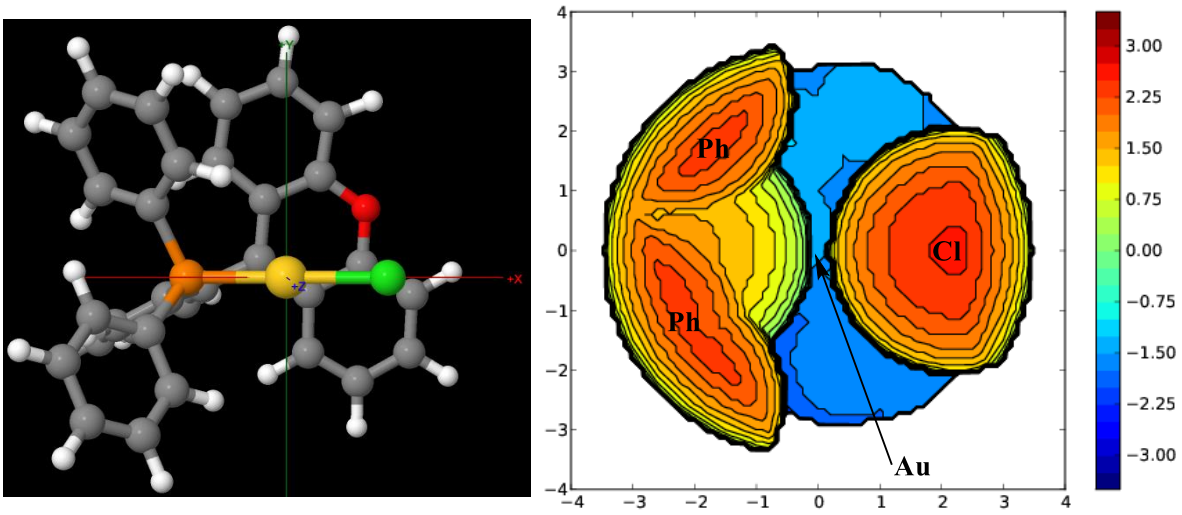




%V Free	%V Buried	% V Tot/V Ex
34.4	**65.6**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	11.9	32.9	44.9	**26.6**	73.4
NW	9.0	35.9	44.9	**20.0**	80.0
NE	20.1	24.8	44.9	**44.7**	55.3
SE	20.8	24.1	44.9	**46.3**	53.7

Figure S 53. Buried volumes and the steric maps of **6**



%V Free	%V Buried	% V Tot/V Ex
39.8	**60.2**	99.9

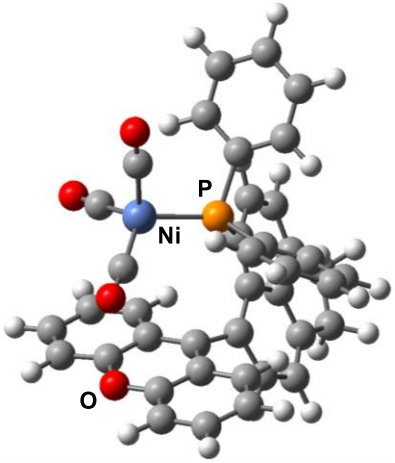
Quadrant	V f	V b	V t	%V f	%V b
SW	15.4	29.5	44.9	**34.3**	65.7
NW	13.1	31.7	44.9	**29.2**	70.8
NE	21.0	23.8	44.9	**46.9**	53.1
SE	21.9	23.0	44.9	**48.8**	51.2

Figure S 54. Buried volumes and the steric maps of [**4**$_{xant}$]$^{+}$

4.7 Electronic parameter of $[2'_{xant}]^+$-Ni(CO)$_3$, $[2'_{acr}]^+$-Ni(CO)$_3$, 5'-Ni(CO)$_3$, L-Ni(CO)$_3$

($[2'_{xant}]^+$, $[2'_{acr}]^+$ and 5': Open-form of $[2_{xant}]^+$, $[2_{acr}]^+$ and 5; L: AcePPh$_2$)

$[2'_{xant}]^+$-Ni(CO)$_3$:

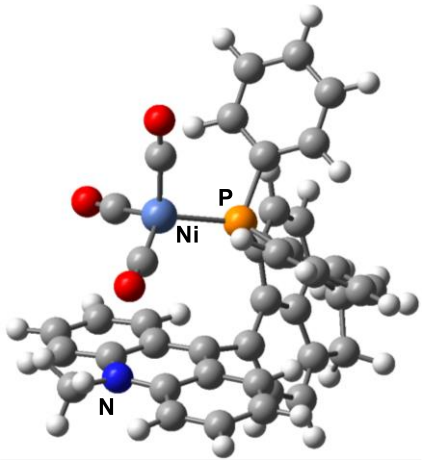


ν(CO) = 2085.44 cm^{-1}
2116.59 cm^{-1}
2170.42 cm^{-1}

P	-1.30191	-0.48093	0.149235	H	0.428045	6.491416	-1.27871
C	1.591823	0.663816	-2.59093	H	-0.3476	6.51309	0.28793
H	0.845134	1.436669	-2.4884	C	-1.54429	5.502981	-1.2555
C	1.896453	0.167448	-3.82627	H	-2.39552	5.969352	-0.75664
H	1.384318	0.544405	-4.70125	H	-1.5917	5.811717	-2.30216
C	2.872199	-0.83328	-3.96985	C	-0.85123	-0.22362	1.912078
H	3.101405	-1.22273	-4.95362	C	-0.9978	0.997351	2.571796
C	3.549327	-1.31325	-2.87741	H	-1.32427	1.874639	2.028226
H	4.318563	-2.06886	-2.96175	C	-0.74805	1.096868	3.93302
C	4.592719	-1.37483	1.631444	H	-0.87359	2.049547	4.433391
H	5.331449	-2.11495	1.355917	C	-0.35965	-0.02339	4.655441
C	4.418443	-0.9619	2.929537	H	-0.17949	0.05298	5.720834
H	5.040725	-1.38392	3.708746	C	-0.21393	-1.24178	4.009078
C	3.432225	-0.01785	3.262685	H	0.081679	-2.12233	4.566016
H	3.290538	0.267139	4.296424	C	-0.45157	-1.33832	2.645911
C	2.638852	0.522898	2.290343	H	-0.33838	-2.29261	2.145928
H	1.855813	1.223198	2.544752	C	-3.12908	-0.70487	0.265338
C	2.242838	0.179217	-1.43058	C	-3.7976	-1.28622	-0.81336
C	3.241871	-0.80071	-1.62079	H	-3.23902	-1.60495	-1.68486
C	2.803801	0.149637	0.934058	C	-5.17114	-1.4667	-0.78177
C	3.78236	-0.82555	0.644337	H	-5.67287	-1.91712	-1.62919
C	1.250612	1.92114	0.077388	C	-5.89605	-1.08667	0.338393
C	2.05162	2.996572	0.46109	H	-6.96752	-1.23983	0.370758
H	3.061757	2.787034	0.790227	C	-5.23978	-0.52114	1.420533
C	1.672677	4.337362	0.326394	H	-5.79675	-0.23243	2.303356
H	2.357661	5.122121	0.621329	C	-3.86661	-0.32507	1.383815
C	0.460336	4.601032	-0.2501	H	-3.37504	0.113406	2.241579
C	-1.59071	4.005514	-1.14026	C	2.039234	0.700881	-0.12449
C	-2.55563	3.097207	-1.47069	Ni	-0.48498	-2.36438	-0.83659
H	-3.49232	3.390007	-1.92878	C	1.094948	-2.93148	-0.20051

C	-2.35141	1.754352	-1.11405	C	-1.66467	-3.65602	-0.3344
H	-3.18353	1.081329	-1.2645	C	-0.55917	-2.14995	-2.6249
C	-1.19557	1.255234	-0.53091	O	2.04505	-3.41046	0.209732
C	-0.09873	2.163764	-0.35662	O	-2.35217	-4.5046	-0.03072
C	-0.39342	3.529246	-0.57834	O	-0.64824	-2.06397	-3.75572
C	-0.19842	5.902722	-0.60572	O	3.985526	-1.25694	-0.60466

[**2'**$_{acr}$]$^{+}$-Ni(CO)$_3$:

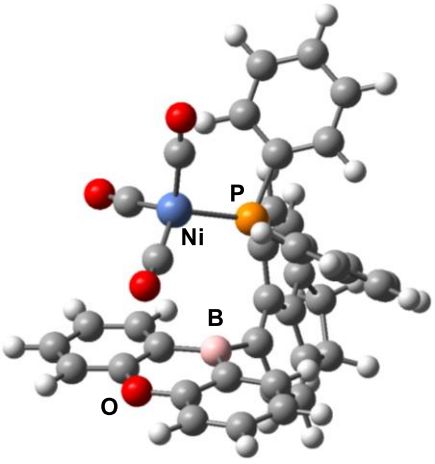


ν(CO) = 2072.29 cm^{-1}
2115.80 cm^{-1}
2168.88 cm^{-1}

P	-1.26493	-0.73612	0.087792	C	-2.89555	5.049905	-1.21021
C	1.503538	1.303639	-2.47924	H	-3.84481	5.290086	-0.72833
H	0.631225	1.929429	-2.36628	H	-2.99216	5.356126	-2.25426
C	1.970532	1.003911	-3.72241	C	-1.05262	-0.43318	1.887408
H	1.467021	1.381027	-4.6023	C	-1.53571	0.706151	2.531617
C	3.121313	0.210247	-3.85682	H	-2.00589	1.496195	1.960436
H	3.506771	-0.01542	-4.84309	C	-1.43626	0.830857	3.910049
C	3.782036	-0.26911	-2.75928	H	-1.82073	1.71878	4.39736
H	4.685392	-0.83866	-2.90759	C	-0.86514	-0.18519	4.663968
C	4.445664	-0.31773	2.016305	H	-0.8005	-0.09182	5.741222
H	5.381263	-0.84064	1.898824	C	-0.38793	-1.32444	4.032783
C	4.062358	0.073593	3.27021	H	0.051482	-2.12586	4.613864
H	4.699434	-0.16761	4.112068	C	-0.47566	-1.44311	2.65384
C	2.861923	0.772573	3.482699	H	-0.10368	-2.33577	2.16601
H	2.559184	1.038785	4.486254	C	-2.97157	-1.43381	0.033736
C	2.085815	1.110316	2.416138	C	-3.38995	-2.08177	-1.1301
H	1.156929	1.642658	2.560018	H	-2.71256	-2.17028	-1.97089
C	2.143862	0.819842	-1.31005	C	-4.6643	-2.61681	-1.22402
C	3.313763	0.020867	-1.462	H	-4.97268	-3.11246	-2.13618
C	2.461988	0.764741	1.092264	C	-5.5349	-2.53108	-0.14674
C	3.645475	-0.00552	0.8995	H	-6.52653	-2.96099	-0.21317
C	0.651674	2.214146	0.130605	C	-5.12459	-1.90169	1.017758
C	1.177274	3.444285	0.508244	H	-5.79434	-1.83919	1.866593
H	2.207277	3.473978	0.843165	C	-3.85412	-1.34974	1.107004
C	0.491641	4.660532	0.390258	H	-3.55423	-0.86371	2.025471
H	0.97165	5.581946	0.695139	N	3.996015	-0.40946	-0.35718
C	-0.74972	4.634956	-0.18	C	1.707199	1.185529	-0.01853

C	-2.58489	3.582651	-1.11474	C	5.115255	-1.3368	-0.5212
C	-3.29431	2.481052	-1.49241	H	4.92881	-1.97781	-1.37505
H	-4.26216	2.552547	-1.97322	H	6.054658	-0.79959	-0.6574
C	-2.77909	1.21622	-1.16093	H	5.175015	-1.98142	0.347535
H	-3.42116	0.36944	-1.35436	Ni	0.078018	-2.34404	-0.829
C	-1.55298	0.991922	-0.55586	C	1.624217	-2.63637	0.024845
C	-0.70868	2.133263	-0.31996	C	-0.8446	-3.88854	-0.54854
C	-1.31969	3.394794	-0.52765	C	0.191448	-2.0406	-2.60311
C	-1.699	5.748476	-0.5225	O	2.570127	-2.98389	0.562962
H	-1.22572	6.490166	-1.1685	O	-1.35088	-4.8879	-0.37577
H	-2.00897	6.278791	0.380884	O	0.227364	-1.91465	-3.73301

5'-Ni(CO)$_3$:

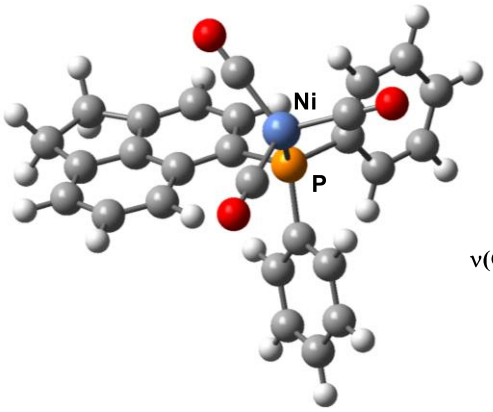


ν(CO) = 2096.78 cm^{-1}
2098.18 cm^{-1}
2158.40 cm^{-1}

P	-1.34511	-0.54659	0.099555	H	-0.05454	6.569483	-1.01213
C	1.832765	0.824502	-2.58822	H	-0.857514	6.48928	0.541852
H	0.960005	1.461601	-2.51055	C	-1.959275	5.460505	-1.05554
C	2.317055	0.484725	-3.83029	H	-2.845503	5.875976	-0.57162
H	1.827042	0.84305	-4.72667	H	-1.994575	5.783373	-2.099
C	3.445479	-0.33276	-3.92955	C	-0.938394	-0.41042	1.885392
H	3.831594	-0.60786	-4.90378	C	-1.161137	0.744574	2.633883
C	4.078632	-0.78918	-2.79553	H	-1.515793	1.644704	2.14861
H	4.959267	-1.41625	-2.84826	C	-0.935117	0.749236	4.002442
C	4.804684	-1.18146	1.744429	H	-1.110679	1.654464	4.571499
H	5.637148	-1.79173	1.419104	C	-0.489926	-0.40002	4.640892
C	4.559553	-0.94159	3.07774	H	-0.316696	-0.39519	5.710398
H	5.214989	-1.37209	3.825639	C	-0.261121	-1.55153	3.903123
C	3.474794	-0.15306	3.469874	H	0.095633	-2.4502	4.391146
H	3.285235	0.024527	4.521047	C	-0.47805	-1.55323	2.5336
C	2.648006	0.387679	2.511574	H	-0.289138	-2.451	1.95738
H	1.800409	0.992931	2.809715	C	-3.153174	-0.93441	0.188171
C	2.4348	0.368283	-1.40088	C	-3.772946	-1.49441	-0.9293
C	3.574982	-0.43106	-1.54542	H	-3.187303	-1.70474	-1.81567
C	2.860054	0.172654	1.137234	C	-5.126933	-1.79069	-0.91898
C	3.956764	-0.62412	0.787924	H	-5.58808	-2.2222	-1.79912
C	1.006299	1.970844	0.236911	C	-5.882738	-1.54949	0.218901

C	1.73887	3.084419	0.634317	H	-6.938327	-1.79227	0.234091
H	2.748376	2.923886	0.998129	C	-5.275051	-1.00549	1.339765
C	1.298685	4.417856	0.525608	H	-5.854083	-0.82168	2.236879
H	1.942001	5.227003	0.851561	C	-3.922655	-0.69452	1.323464
C	0.079943	4.642588	-0.04321	H	-3.467955	-0.27229	2.20946
C	-1.93085	3.958457	-0.96648	Ni	-0.385664	-2.26555	-1.0401
C	-2.84539	3.013337	-1.32798	C	1.262392	-2.74026	-0.4729
H	-3.79472	3.270344	-1.78292	C	-1.423554	-3.69817	-0.6793
C	-2.56628	1.668882	-1.02155	C	-0.458775	-1.83952	-2.78999
H	-3.35522	0.954784	-1.20884	O	2.251478	-3.19135	-0.13746
C	-1.38386	1.225756	-0.45465	O	-2.027303	-4.63906	-0.46601
C	-0.33844	2.185105	-0.2127	O	-0.557235	-1.6166	-3.90182
C	-0.71484	3.536385	-0.40062	O	4.288176	-0.90606	-0.49443
C	-0.64953	5.919575	-0.36724	B	1.993669	0.768155	0.017936

L-Ni(CO)$_3$:



ν(CO) = 2047.10 cm^{-1}
2052.20 cm^{-1}
2111.07 cm^{-1}

P	0.777913	-0.10886	0.100082	C	1.361866	1.699345	4.328627
C	-2.06057	1.504166	0.247758	H	1.51279	2.130322	5.314809
C	-3.25089	2.20667	0.24875	C	2.203205	2.053867	3.275299
H	-3.21829	3.288275	0.353663	H	3.012347	2.761253	3.436163
C	-4.51067	1.572191	0.120677	C	2.001362	1.511199	2.009242
H	-5.41923	2.169221	0.127265	H	2.64882	1.799122	1.184086
C	-4.54522	0.203535	-0.00587	C	1.835327	-1.61223	0.16335
C	-3.53703	-1.89995	-0.13904	C	2.249666	-2.18479	-1.04669
C	-2.44237	-2.72863	-0.1464	H	1.951272	-1.72584	-1.98619
H	-2.53803	-3.80754	-0.23957	C	3.040362	-3.33067	-1.05383
C	-1.15085	-2.1558	-0.03099	H	3.353172	-3.76357	-2.00026
H	-0.29794	-2.8277	-0.04321	C	3.44013	-3.90999	0.149161
C	-0.92886	-0.79083	0.088828	H	4.066905	-4.79779	0.144744
C	-2.05994	0.092426	0.108974	C	3.038918	-3.34375	1.357015
C	-3.33031	-0.51165	-0.00806	H	3.35075	-3.78867	2.29833
C	-5.69228	-0.77071	-0.15122	C	2.237191	-2.20409	1.366285
H	-6.2915	-0.55107	-1.04271	H	1.928603	-1.77102	2.313381
H	-6.37688	-0.71122	0.703389	H	-1.12661	2.04375	0.360508
C	-5.01905	-2.17193	-0.24666	Ni	1.298713	1.272247	-1.61002
H	-5.36108	-2.84059	0.552257	C	0.229032	0.759306	-2.96329

H	-5.26153	-2.67183	-1.19198	C	3.048978	1.040396	-1.9529
C	0.963847	0.597432	1.785048	C	0.97045	2.96727	-1.11639
C	0.125015	0.244736	2.848654	O	-0.45983	0.432363	-3.81677
H	-0.68642	-0.4595	2.685542	O	4.166302	0.9145	-2.16988
C	0.32288	0.796467	4.112959	O	0.770719	4.054404	-0.81546
H	-0.3385	0.520401	4.930045				

5. Crystal Structures

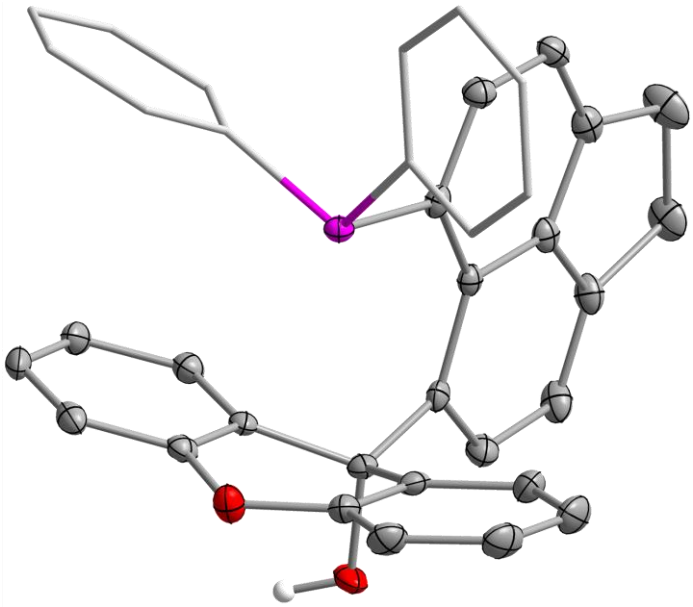


Figure S 55. Molecular structure of $\mathbf{1}_{xant}$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability.

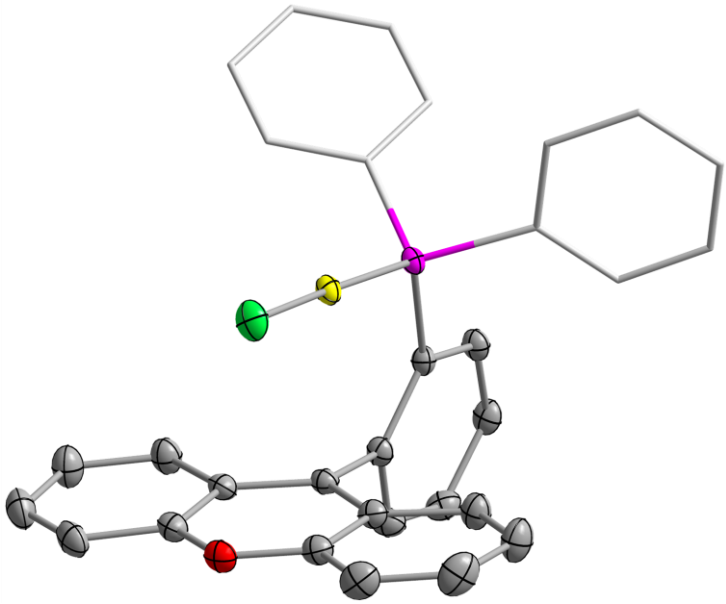


Figure S 56. Molecular structure of $\mathbf{[4}_{xant}\mathbf{]}$OTf. Hydrogen atoms, counter anion and co-crystallized solvent are omitted for clarity. Thermal ellipsoids are set at 50% probability.

6. References

1. R. Kumar and C. Nevado, *Angewandte Chemie International Edition*, 2017, **56**, 1994-2015.
2. L. C. Wilkins, Y. Kim, E. D. Litle and F. P. Gabbaï, *Angewandte Chemie International Edition*, 2019, **58**, 18266-18270.
3. M. Melaïmi, S. Sole, C.-W. Chiu, H. Wang and F. P. Gabbaï, *Inorganic Chemistry*, 2006, **45**, 8136-8143.
4. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
5. G. M. Sheldrick, *SADABS, Version 2007/4, Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA*, 2007.
6. G. M. Sheldrick, *Acta Crystallographica Section A*, 2015, **71**, 3-8.
7. G. M. Sheldrick, *Journal*, 2000.
8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Journal*, 2016.
9. G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. F. Guerra, S. J. A. v. Gisbergen, J. G. Snijders and T. Ziegler, *Journal of Computational Chemistry*, 2001, **22**, 931-967.
10. D. G. Gusev, *Organometallics*, 2009, **28**, 6458-6461.
11. personal communication.
12. T. Lu and F. Chen, *Journal of Computational Chemistry*, 2012, **33**, 580-592.
13. C. Körner, P. Starkov and T. D. Sheppard, *Journal of the American Chemical Society*, 2010, **132**, 5968-5969.
14. B. Zhou and F. P. Gabbaï, *Journal of the American Chemical Society*, 2021, **143**, 8625-8630.
15. L. Falivene, Z. Cao, A. Petta, L. Serra, A. Poater, R. Oliva, V. Scarano and L. Cavallo, *Nature Chemistry*, 2019, **11**, 872-879.
16. H. Clavier and S. P. Nolan, *Chemical Communications*, 2010, **46**, 841-861.