Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information for:

Toward Asymmetric Aziridination with an Iron Complex Supported by a D_2-symmetric tetra-NHC

Kevin M. Blatchford, Carson J. Mize, Sharani Roy, and David M. Jenkins*

Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996, United States

Table of Contents:

Experimental section

General Considerations for Synthesis:

All reactions and workups for NHC ligands were conducted under air unless otherwise stated. All reactions, workups and manipulations involving the NHC metal complexes and subsequent reactions were done using standard Schlenk techniques under N_2 or in an MBraun Unilab glovebox under N_2 unless otherwise stated. All glassware for glovebox reactions were dried at 170 °C overnight before use. For air sensitive reactions, tetrahydrofuran (THF), hexanes, and diethyl ether were dried on an Innovative Technologies Pure Solv MD-7 Solvent Purification System, degassed by three freeze-pump-thaw cycles on a Schlenk line, and subsequently stored under activated 4 Å molecular sieves prior to use. Anhydrous acetonitrile was prepared by distillation over phosphorous pentoxide, followed by degassing by three freeze-pump-thaw cycles and stored over activated 4 Å molecular sieves prior to use. Benzene and pentane were purchased anhydrous from Sigma-Aldrich, degassed by three freeze-pump-thaw cycles and subsequently stored over activated 4 Å molecular sieves prior to use. Anhydrous NMR solvents, chloroform-d ($CDCl_3$) and acetonitrile-d_3 (CD_3CN) were degassed by three freeze-pump-thaw cycles and subsequently stored over activated 4 Å molecular sieves prior to use. Celite used in the synthesis of metal complexes were dried overnight at 240 °C and subsequently stored in the glovebox prior to use. All reagents were purchased from commercial vendors at high purity. (1*S*,2*S*)-(-)-1,2-Diphenylethylenediamine was purchased from Combi-Blocks at highest available purity (96%). 1,1-diethoxy-2-isothiocyanatoethane[1] and methylene bis(trifluoromethanesulfonate)[2] were synthesized via previously reported methods.

General Considerations for Molecule Characterization:

Solution ^1H NMR and $^{13}C\{^1H\}$ NMR were performed on a Varian VNMRS 500 MHz narrow-bore broadband system at 298 K. All ^1H and ^{13}C shifts were referenced to the residual solvent. All mass spectrometry analyses were conducted at the Biological and Small Molecule Mass Spectrometry Center located in the Department of Chemistry at the University of Tennessee. The ESI MS analyses on organic molecules were performed via direct infusion into a Waters Synapt G2-Si mass spectrometer. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance (ATR) using pure samples of each complex. UV-vis measurements were taken inside a dry glovebox on an Ocean Optics USB4000 UV-vis system with 1 cm path length quartz crystal cell.

General Considerations for Crystallography:

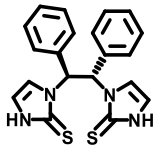
All X-ray data collections were performed on single crystals coated in Paratone oil on glass slides and mounted on nylon fibers. Crystals were coated in Paratone oil, which had previously been degassed with N_2 and dried with a piece of sodium metal inside the glovebox. X-ray data for complexes **5**, **6a** and **6b** were collected with the use of a Mo microsource and X-ray data for **2** and **7** was collected using a Cu microsource on a Bruker D8 Venture diffractometer. Crystals were mounted in a 100 K cold stream provided by an Oxford Cryostream low-temperature apparatus. All data sets were reduced with Bruker SAINT and were corrected for absorption using SADABS. Structures were solved and refined using SHELXT and SHELXLE64, respectively. Compound **7** was treated with

PLATON SQUEEZE command to remove nonsensical disordered solvent voids and remove heavily disordered solvent molecules.

General Considerations of Electrochemical Studies:
Cyclic voltammetry measurements were made inside a dry glovebox at ambient temperature using a BASi Epsilon electrochemical analyzer with a platinum working electrode, platinum wire counter electrode, and $Ag/AgNO_3$ reference electrode. For all samples, a 0.1M solution tetrabutylammonium hexafluorophosphate ($(TBA)(PF_6)$) in the appropriate solvent was used as the supporting electrolyte. All peaks were referenced to an external standard of ferrocene. Unless overwise stated, all experiments were initiated at more oxidizing potentials, followed by reduction.

General Considerations for Separation of Chiral Aziridines:
All chiral UHPLC mass spectrometry analyses were conducted at the Biological and Small Molecule Mass Spectrometry Center located in the Department of Chemistry at the University of Tennessee. Samples were analyzed using the same ultra-high performance liquid chromatography combined with high resolution mass spectrometry (UHPLC-HRMS) method. Autosampler vials were kept at 4 °C in a Dionex Ultimate 3000 RS Autosampler. Injections of 10 µL were made onto a Phenomenex Lux 3 µm Cellulose-1 (150 x 4.6 mm) column kept at 40 °C. Analytes were eluted over 20 minutes at 0.500 mL/min with 0.1% formic acid in water and 0.1% formic acid in acetonitrile (B) using the following isocratic gradient: 25% A and 75% B. Mass analysis was performed using a ThermoFisher Orbitrap Exactive Plus. Samples were ionized using heated electrospray ionization in positive mode with the following parameters: resolution of 140,000, automatic gain control of 1e6, maximum inject time of 50 ms, sheath gas of 25, aux gas of 10, sweep gas of 3, spray voltage at 3.25 kV, capillary temperature of 320°C, S-lens at 50, and aux gas heater at 50°C. Analytes were detected as $[M+H]^+$ with a less than 5 ppm mass error using Xcalibur.

Synthesis of 1,1'-((1*S*,2*S*)-1,2-diphenylethane)bis(1,3-dihydro-2H-imidazole-2-thione), 1.



Synthesis of **1** was performed by modifying a previously published procedure.[1] (1*S*,2*S*)-(-)-1,2-diphenylethylenediamine (10.02 g, 57.17 mmol, 1 eq.) was added to a 500 mL round bottom flask with 230 mL of dry acetonitrile while stirring. 1,1-Diethoxy-2-isothiocyanatoethane (24.27 g, 114.3 mmol, 2 eq.) was added quickly to the round bottom while stirring. The resulting solution was brought to reflux at 85 °C. The reaction was allowed to cool to ambient temperature over 3 hours. This solution was then concentrated in the round bottom flask under high vacuum, resulting in a sticky light-yellow foam. To the yellow foam was added 1M HCl (230 mL) and the mixture was refluxed at 100 °C overnight. The reaction was then cooled to room temperature and kept in a -20 °C freezer overnight. The brown/yellow precipitate was then filtered over a medium porosity frit and

washed with three times with ice cold water (300 mL) and dried under high vacuum, which yielded a brown powder (20.3 g, 94.5% yield).

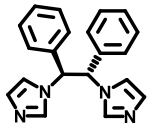
^{1}H NMR ($CDCl_3$, 499.74 MHz): δ 11.19 (s, 2H), 7.56-7.51 (m, 4H), 7.31-7.20 (m, 6H), 7.16-7.12 (m, 4H), 6.44 (t, J = 2.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125.66 MHz) δ 160.80, 135.84, 129.28, 129.05, 128.31, 116.99, 114.32, 59.90.

IR: 3130, 3089, 3019, 2910, 1568, 1495, 1460, 1412, 1276, 1261, 1157, 1123, 1101, 1076, 917, 880, 812, 740, 726, 694, 671, 628 cm^{-1}.

ESI HR MS (*m/z*): $[M+H]^+$: $(C_{20}H_{19}N_4S_2)^+$: 379.1031 (found), $[M+H]^+$: $(C_{20}H_{19}N_4S_2)^+$: 379.1051 (calculated).

Synthesis of 1,1'-[(1*S*,2*S*)-1,2-diphenyl-1,2-ethanediyl]bis-imidazole, 2.

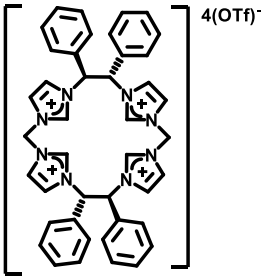


This compound was previously reported by a different synthetic method.[3] To a 1 L round bottom flask, the cyclic thiourea (23.4 g, 62.3 mmol, 1 eq) was added along with 625 mL of 2.5 M HNO_3 solution. The resulting slurry is stirred while cooling to 0 °C in an ice bath. To this solution $NaNO_2$ (4.25 g, 62.3 mmol, 1 eq) dissolved in 20mL of H_2O and was added. The solution was allowed to warm up to room temperature over 4 hours while covered with a septum. [**Caution**]: Over time, the sealed flask builds pressure due to NO_x gases formed. The flask must be vented periodically to prevent the septum bursting off and releasing NO_x gases. After the reaction is completed, saturated K_2CO_3 was slowly added while stirring until the solution was fully basified. The solution was diluted with its equivalent volume of deionized water to approximately 2000 mL, then it was extract three times with 600 mL of CH_2Cl_2. The resulting organic fractions were combined and dried over anhydrous $MgSO_4$ then filtered and concentrated in vacuum to yield a yellow powdery residue. This residue was purified by gradient column chromatography using gradient silica column of 5-10% methanol in CH_2Cl_2 yielding the pure off-white product (8.85 g, 45.5% yield). NMR spectra match the previously reported spectra.

^{1}H NMR ($CDCl_3$, 499.74 MHz): δ 7.29-7.26 (m, 6H), 7.25-7.20 (m, 4H), 6.99 (t, *J* = 1.0 Hz, 2H), 6.75 (t, *J* = 1.4 Hz, 2H), 5.86 (s, 2H).

^{13}C NMR ($CDCl_3$, 125.66 MHz): δ 136.41, 135.66, 130.29, 129.34, 129.18, 128.10, 117.44, 64.84.

Synthesis of ($^{(S,S)\text{-}1,2\text{-}Ph_2\text{-}Et,\ Me}TC^{H}$)$(OTf)_4$, 3.



Diimidazole **2** (1.00 g, 3.18 mmol, 2 eq), dry acetonitrile (160 mL), and a stir bar were added to a 250 mL round bottom flask. Ditriflatomethane (0.995 g, 3.18 mmol, 2 eq) and dry acetonitrile (10 mL) were added to a 20 mL vial. Both solutions were cooled to 0 °C while stirring in an ice bath. The chilled solution of ditriflatomethane (clear and colorless) in acetonitrile was added dropwise to the stirring diimidazole solution (clear and slightly yellow) over the course of one hour. The reaction mixture was then allowed to warm slowly to room temperature overnight while stirring. All volatiles were then removed from the reaction by rotary evaporation, resulting in a beige powdery film. 50 mL of THF was then added to the beige solid resulting in a brown solution which contained a white suspended solid. This solution was filtered through a fine porosity 30mL frit and the collected solid was washed with an additional 50 mL of THF until filtrate was colorless. The white powder collected was dried under high vacuum to remove lingering volatiles resulting in pure product (0.906 g, 45.5% yield).

^{1}H NMR (CD_3CN, 499.74 MHz): δ 9.54 (t, *J* = 1.7 Hz, 4H), 8.14 (t, *J* = 2.0 Hz, 4H), 7.89 (t, *J* = 1.9 Hz, 4H), 7.64-7.60 (m, 8H), 7.40-7.33 (m, 12H), 7.07 (s, 4H), 6.34 (s, 4H)

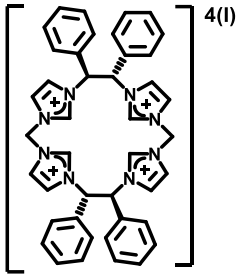
^{13}C NMR (CD_3CN, 125.66 MHz): δ 137.83, 133.91, 131.54, 130.79, 128.96, 126.07, 122.90, 66.10, 59.92.

^{19}F NMR (CD_3CN, 470 MHz): δ 77.69

IR: 3124, 3055, 2985, 1544, 1497, 1461, 1380, 1299, 1255, 1224, 1150, 1025, 954, 847, 805, 768, 749, 710, 694, 663, 650, 634 cm^{-1}.

ESI HR MS (*m/z*): $[M\text{-}(OTf)]^+$: $(C_{45}H_{40}F_9N_8O_9S_3)^+$: 1103.1936 (found), $[M\text{-}(OTf)]^+$: $(C_{45}H_{40}F_9N_8O_9S_3)^+$: 1103.1937 (calculated).

Synthesis of ($^{(S,S)\text{-}1,2\text{-}Ph_2\text{-}Et,\ Me}TC^{H}$)$(I)_4$, 4.



Tetrabutylammonium iodide (0.605 g, 1.60 mmol, 4 eq), 20 mL of acetonitrile, and a stir bar was added to a 50 mL round bottom flask. Compound **3** (0.501 g, 0.400 mmol, 1 eq) was added as a powder to this colorless solution. The white solid slowly dissolved, resulting in a colorless and clear solution. After 10 min of stirring a white precipitate began to form. The solution was stirred overnight, filtered over a fine porosity 30 mL frit, washed with an additional 30 mL of acetonitrile, and dried under high vacuum resulting in pure product in the form of a white powder (0.466 g, 100% yield).

^{1}H NMR (DMSO-d_6, 499.74 MHz,) δ 9.91 (s, 4H), 8.35 (s, 4H), 8.07 (s, 4H), 7.76 (d, *J* = 7.6 Hz, 8H), 7.61 (s, 4H), 7.45 (t, *J* = 7.7 Hz, 8H), 7.38 (t, *J* = 7.4 Hz, 4H), 6.65 (s, 4H).

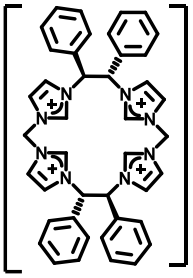
^{13}C NMR (DMSO-d_6, 125.66 MHz): δ 136.79, 132.85, 130.28, 129.65, 128.26, 124.70, 121.36, 63.39, 48.47.

^{19}F NMR (DMSO-d_6, 470 MHz): δ No resonances observed.

IR: 3422, 3064, 1540, 1496, 1457, 1296, 1233, 1149, 1031, 924, 841, 806, 766, 745, 718, 695, 659 cm^{-1}.

ESI HR MS (*m/z*): $[M\text{-}I]^+$: $(C_{42}H_{40}I_3N_8)^+$:1037.0537 (found), $[M\text{-}I]^+$: $(C_{42}H_{40}I_3N_8)^+$: 1037.0510 (calculated).

Synthesis of ($^{(S,S)\text{-}1,2\text{-}Ph_2\text{-}Et,\ Me}TC^{H}$)$(PF_6)_4$, 5.



Compound **4** (0.5006 g, 0.430 mmol, 1 eq), dimethylsulfoxide (30 mL), and a stir bar were added to a 1 L Erlenmeyer flask. Potassium hexafluorophosphate (1.266 g, 6.878 mmol, 16 eq), DI H_2O (350 ml), and a stir bar were added to a 0.5 L beaker. After both solutions had stirred for 5 min, the KPF_6 solution was slowly added to the solution with compound **4** which immediately resulted in the precipitation of a white solid. This suspension was stirred for 5 min and then filtered over a fine porosity 30 mL frit. The resulting white powder was washed with an additional 60 mL of DI H_2O and 90 mL of diethyl ether subsequently before being dried under high vacuum until all volatiles were removed, yielding a pure product (0.532 g, 100% yield).

^{1}H NMR (CD_3CN, 499.74 MHz): δ 8.97 (s, 4H), 7.90 (t, *J* = 2.0 Hz, 4H), 7.81 (t, *J* = 2.0 Hz, 4H), 7.56 (dd, *J* = 8.1, 1.5 Hz, 8H), 7.45 – 7.35 (m, 12H), 6.80 (s, 4H), 6.31 (s, 4H).

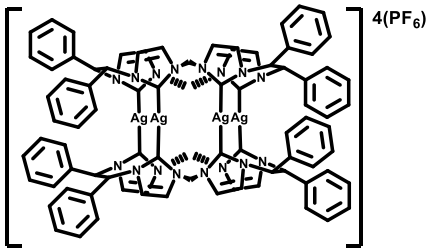
^{13}C NMR (CD_3CN, 125.66 MHz): δ 137.21, 133.18, 131.74, 130.90, 129.06, 126.28, 122.79, 66.38, 59.21.

^{19}F NMR (CD_3CN, 470 MHz): δ -71.73 (d, *J* = 707.2 Hz).

IR: 3413, 3040, 1545, 1497, 1458, 1436, 1189, 1153, 1031, 952, 830, 768, 719, 696, 660 cm^{-1}.

ESI HR MS (*m/z*): $[M\text{-}(PF_6)]^+$:$(C_{42}H_{40}F_{18}N_8P_3)^+$:1091.2274 (found), $[M\text{-}(PF_6)]^+$:$(C_{42}H_{40}F_{18}N_8P_3)^+$: 1091.2301 (calculated).

Synthesis of [($^{(S,S)\text{-}1,2\text{-}Ph_2\text{-}Et,\ Me}TC^{H}$)$_2Ag_4$](PF$_6$)$_4$, 6.



Silver hexafluorophosphate (0.280 g, 1.105 mmol, 2.1 eq), compound **5** (0.650 g, 0.526 mmol, 1 eq), and DMSO (10 mL) were added to a 20 mL vial. This solution was heated to 90 °C for ten minutes and then triethylamine (0.266 g, 2.630 mmol, 5 eq) was added. The reaction mixture was then stirred for 48 hours at 90 °C. After cooling to room temperature, the resulting brown solution was removed from the glovebox and poured into 200 mL of DI H_2O. A precipitate immediately formed and after 5 min of stirring, was filtered over a fine porosity 15 mL frit. The collected precipitate was washed with 45 mL of H_2O followed by 45 mL of diethyl ether, and 30mL. At this point, the collected off-white solid consists of a pure mixture of two conformers of the desired product. (0.548 g, 45% yield).

This mixture was then washed with 30 mL of THF and 30 mL of acetonitrile, collecting filtrates separately. Both conformers are soluble in acetonitrile, but the staggered conformer is also slightly soluble in THF (the eclipsed conformer is not). By collecting separately, the conformers can effectively be separated via solvent exclusion. Each of these fractions were individually dried under high vacuum, redissolved in acetonitrile, and crystalized via vapor diffusion of diethyl ether.

Eclipsed Conformer (6a)

^{1}H NMR (CD_3CN, 499.74 MHz): δ 7.80 (s, 4H), 7.70 (s, 4H), 7.65 (s, 4H), 7.46 (s, 4H), 7.29 (d, J = 11.9 Hz, 4H), 7.26 – 7.20 (m, 16H), 7.01 – 6.92 (m, 16H), 6.89 (d, J = 7.2 Hz, 8H), 6.67 (d, J = 14.3 Hz, 4H), 6.51 (d, J = 11.9 Hz, 4H), 6.40 (d, J = 14.4 Hz, 4H).

^{13}C NMR (CD_3CN, 125.66 MHz): δ 135.82, 134.40, 130.66, 130.60, 130.34, 130.14, 128.62, 128.56, 124.20, 124.15, 123.58, 123.45, 123.02, 122.98, 68.18, 68.02, 67.55.

IR: 3153, 2970, 2870, 1548, 1500, 1457, 1232, 1154, 1030, 825, 739, 696, 661 cm^{-1}.

ESI HR MS (*m/z*): $[M\text{-}4(PF_6)]^{4+}$:$(C_{84}H_{72}Ag_4N_{16})^{4+}$:434.0592 (found), $(C_{84}H_{72}Ag_4N_{16})^{4+}$:434.0575 (calculated).

Staggered Conformer (6b)

^{1}H NMR (CD_3CN, 499.74 MHz): δ 7.75 (t, *J* = 1.8 Hz, 4H), 7.60 (t, *J* = 2.0 Hz, 4H), 7.54 – 7.46 (m, 14H), 7.42 (dd, *J* = 6.4, 2.6 Hz, 16H), 7.22 – 7.16 (m, 9H), 7.10 (dd, *J* = 5.1, 1.9

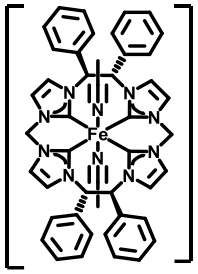
Hz, 12H), 7.03 (d, *J* = 11.6 Hz, 4H), 6.73 (d, *J* = 11.6 Hz, 4H), 6.32 (d, *J* = 14.5 Hz, 4H), 6.21 (d, *J* = 14.5 Hz, 4H).

^{13}C NMR (CD_3CN, 125.66 MHz): δ 136.41, 135.31, 131.57, 131.17, 130.83, 130.66, 130.55, 129.00, 128.74, 127.98, 122.36, 122.31, 69.53, 67.19, 66.18, 63.52, 59.94.

IR: 3116, 1545, 1498, 1458, 1369, 1228, 1153, 1030, 815, 767, 740, 718, 695, 661, 639 cm^{-1}.

ESI HR MS (*m/z*): $[M\text{-}4(PF_6)]^{4+}$:$(C_{84}H_{72}Ag_4N_{16})^{4+}$:434.0584 (found), $(C_{84}H_{72}Ag_4N_{16})^{4+}$:434.0575 (calculated).

Synthesis of [($^{(S,S)\text{-}1,2\text{-}Ph_2\text{-}Et,\ Me}TC^{H}$)Fe($CH_3CN$)$_2$]($PF_6$)$_2$, 7.



[($^{(S,S)\text{-}1,2\text{-}Ph2\text{-}Et,\ Me}TC^{H}$)$_2Ag_4$]($PF_6$)$_4$ (0.340 g, 0.147 mmol, 1 eq) and 40 mL of acetonitrile were added to a 100 mL round bottom flask containing FeI_2 (0.0909 g, 0.294 mmol, 2 eq). Within 5 minutes of stirring, silver halide precipitate began to form slowly. The reaction was stirred for 48 hours while stirring vigorously at room temperature. The reaction mixture (now a red/yellow solution with a large amount of white precipitate) was filtered through a Celite plug in a medium porosity 30 mL frit. All volatiles were then removed from the filtrate under high vacuum and the resulting red solid was crystallized via vapor diffusion of diethyl ether into acetonitrile (0.292 g, 95% yield).

Single crystals of higher quality for SCXRD analysis were obtained by vapor diffusion of diethyl ether into benzonitrile.

^{1}H NMR (CD_3CN, 499.74 MHz): δ 7.56 (s, 4H), 7.46 – 7.37 (m, 9H), 7.34 (s, 2H), 7.18 – 7.07 (m, 14H), 6.88 (d, *J* = 11.6 Hz, 2H), 6.79 (d, *J* = 11.9 Hz, 2H), 6.24 (d, *J* = 13.5 Hz, 2H), 5.79 (d, *J* = 13.3 Hz, 2H).

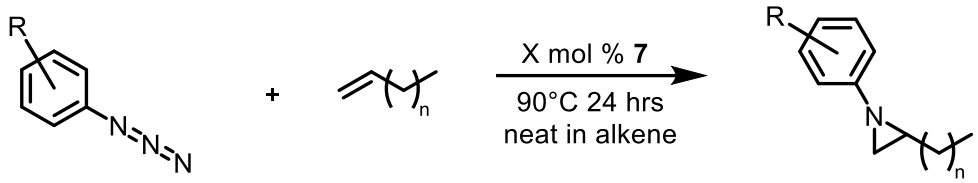
^{13}C NMR (CD_3CN, 125.66 MHz): δ 141.06, 135.04, 130.89, 130.67, 130.28, 130.17, 129.80, 129.55, 129.21, 128.51, 128.27, 127.49, 126.70, 123.62, 122.66, 121.74, 68.74, 63.82, 63.08.

^{19}F NMR (CD_3CN, 470 MHz): δ -72.82 (d, *J* = 706.5 Hz).

IR: 3151, 2935, 2850, 1657, 1485, 1421, 1286, 1145, 1033, 990, 940, 825, 740, 718, 677, 662 cm^{-1}.

ESI HR MS (*m/z*): $[M]^{2+}$:$(C_{42}H_{36}FeN_8)^{2+}$: 354.1220 (found), $(C_{42}H_{36}FeN_8)^{2+}$: 354.1201 (calculated).

General Catalytic Reaction:

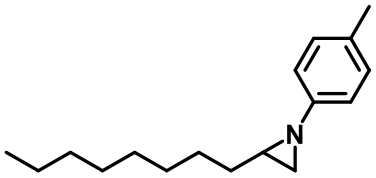


R = Methyl or Isopropyl

[($^{(S,S)}$-1,2-Ph$_2$-Et, ^{Me}TC^{H})Fe(CH$_3$CN)$_2$](PF$_6$)$_2$, **7** was added to a 20 mL vial followed by the addition of the alkene of choice. The reaction mixture was heated to the desired temperature and stirred for 10 min. The organic azide was then added to the reaction which was then stabilized to the designated temperature. Once the organic azide was no longer present (as determined by TLC) the mixture was removed from heat, filtered through Celite and washed through with hexanes. This crude product was purified by column chromatography on silica gel using a gradient elution of a mixture of ethyl acetate and hexanes. The corresponding excess alkene can be recovered from the column as it comes out with pure hexanes as eluent. The catalyst can be recovered from the celite by washing with acetonitrile (40-60% recovery).

Control Reactions:
Control reactions following the method of the general catalytic reaction were attempted for every reaction and tabulated concurrently.

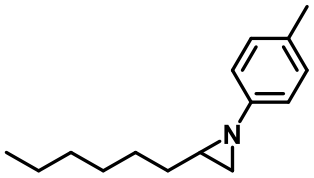
Synthesis of 2-octyl-1-(*p*-tolyl)aziridine, **8**.



p-tolyl azide (0.048 g, 0.36 mmol) and 1-decene (1.53 g, 2.06 mL) were used in the general catalytic reaction as described above and at 2% catalyst loading, yielding 0.089 g of product (55% yield). Control reaction produced 32% yield of the aziridine. ^{1}H and ^{13}C NMR matched previous reports.[4]

Chiral UHPLC-MS: showed no enantiomeric excess (<2%).
Peak 1: eluted at 8.541 min with an area of 1,418,103,607
Peak 2: eluted at 9.133 min with an area of 1,433,327,319

Synthesis of 2-hexyl-1-(*p*-tolyl)aziridine, 9.



p-tolyl azide (0.063 g, 0.47 mmol) and 1-octene (1.43 g, 2.00 mL, 12.74 mmol) were used in the General Catalytic Reaction described above and at 2% catalyst loading, yielding 0.067 g of product (65% yield). Control reaction produced 60% yield.

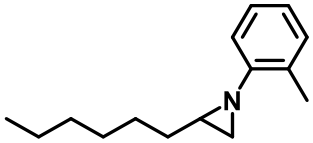
^{1}H NMR ($CDCl_3$, 499.74 MHz): δ 7.04 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.3 Hz, 2H), 2.29 (s, 3H), 2.09 – 2.00 (m, 3H), 1.66 – 1.52 (m, 4H), 1.46 – 1.39 (m, 2H), 1.35 (m, 4H), 0.93 (t, J = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125.66 MHz): δ 152.74, 131.45, 129.50, 120.64, 40.32, 34.15, 33.38, 31.97, 29.33, 27.79, 22.73, 20.76, 14.20.

HR MS (*m/z*): $[M+H]^+$:$(C_{15}H_{24}N)^+$: 218.1897(found), $(C_{15}H_{24}N)^+$: 218.1909 (calculated).

Chiral UHPLC-MS: showed no enantiomeric excess (<2%).
Peak 1: eluted at 7.8659 min with an area of 95,878,004
Peak 2: eluted at 8.7907 min with an area of 98,732,044

Synthesis of 2-hexyl-1-(*o*-tolyl)aziridine, 10.



o-tolyl azide (0.050 g, 0.292 mmol) and 1-octene (1.43 g, 2.00 mL, 12.74 mmol) were used in the General Catalytic Reaction described above and at 2% catalyst loading, yielding (0.0525 g) 64% yield. Control reaction produced 52% yield.

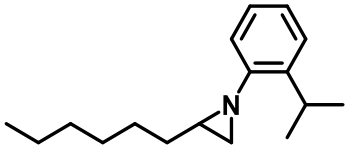
^{1}H NMR ($CDCl_3$, 499.74 MHz): δ 7.12 – 7.07 (m, 2H), 6.90 (td, *J* = 7.4, 1.3 Hz, 1H), 6.84 (d, *J* = 7.3 Hz, 1H), 2.35 (s, 3H), 2.12 (d, *J* = 1.3 Hz, 1H), 1.96 (d, *J* = 7.2 Hz, 1H), 1.85 – 1.78 (m, 1H), 1.55 – 1.52 (m, 2H), 1.43 – 1.38 (m, 2H), 1.37 – 1.28 (m, 6H), 0.93 – 0.89 (m, 3H).

^{13}C NMR ($CDCl_3$, 125.66 MHz): δ 152.18, 130.65, 130.55, 126.45, 122.21, 119.48, 40.16, 34.44, 33.02, 32.00, 29.39, 27.45, 22.75, 18.28, 14.22.

HR MS (*m/z*): $[M+H]^+$:$(C_{15}H_{24}N)^+$: 218.1895 (found), $(C_{15}H_{24}N)^+$: 218.1909 (calculated).

Chiral UHPLC-MS: showed 3% enantiomeric excess.
Peak 1: eluted at 7.787 min with an area of 3,346,018,745
Peak 2: eluted at 8.124 min with an area of 3,546,749,954

Synthesis of 2-hexyl-1-(2-isopropylphenyl)aziridine, 11.



(2-isopropylphenyl)azide (0.067 g, 0.416 mmol) and 1-octene (1.43 g, 2.00 mL, 12.74 mmol) were used in the General Catalytic Reaction described above and at 2% catalyst loading, yielding 0.0153 g (15% yield).

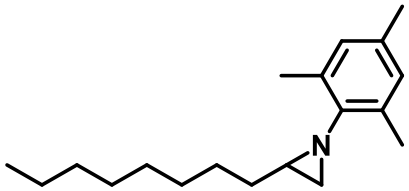
^{1}H NMR ($CDCl_3$, 499.74 MHz): δ 7.23 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.09 (td, *J* = 7.5, 1.6 Hz, 1H), 7.00 (td, *J* = 7.4, 1.3 Hz, 1H), 6.85 (dd, *J* = 7.9, 1.5 Hz, 1H), 3.53 (hept, *J* = 6.8 Hz, 1H), 2.16 – 2.09 (m, 2H), 2.02 (d, *J* = 7.2 Hz, 1H), 1.90 – 1.81 (m, 1H), 1.58 – 1.49 (m, 3H), 1.46 – 1.39 (m, 2H), 1.35 (m, 4H), 1.31 – 1.28 (m, 6H), 0.93 (t, *J* = 7.1 Hz 3H).

^{13}C NMR ($CDCl_3$, 125.66 MHz): δ 151.31, 141.39, 126.16, 125.89, 122.63, 119.76, 40.29, 34.41, 32.99, 31.98, 29.37, 27.31, 26.91, 23.87, 23.51, 22.74, 14.21.

HR MS (*m/z*): $[M+H]^+$:$(C_{17}H_{27}N)^+$: 246.2211 (found), $(C_{15}H_{24}N)^+$: 246.2222 (calculated).

Chiral UHPLC-MS: showed 4% enantiomeric excess.
Peak 1: eluted at 9.2531 min with an area of 35,730,646
Peak 2: eluted at 10.0819 min with an area of 33,075,040

Synthesis of 2-octyl-1-(mesityl)aziridine, 12.



Mesityl azide (0.069 g, 0.43 mmol) and 1-decene (1.48 g, 2 mL) were used in the General Catalytic Reaction described above and at 2% catalyst loading, but no reaction was observed with **7**.

Annotated spectra and other analytical data for compounds

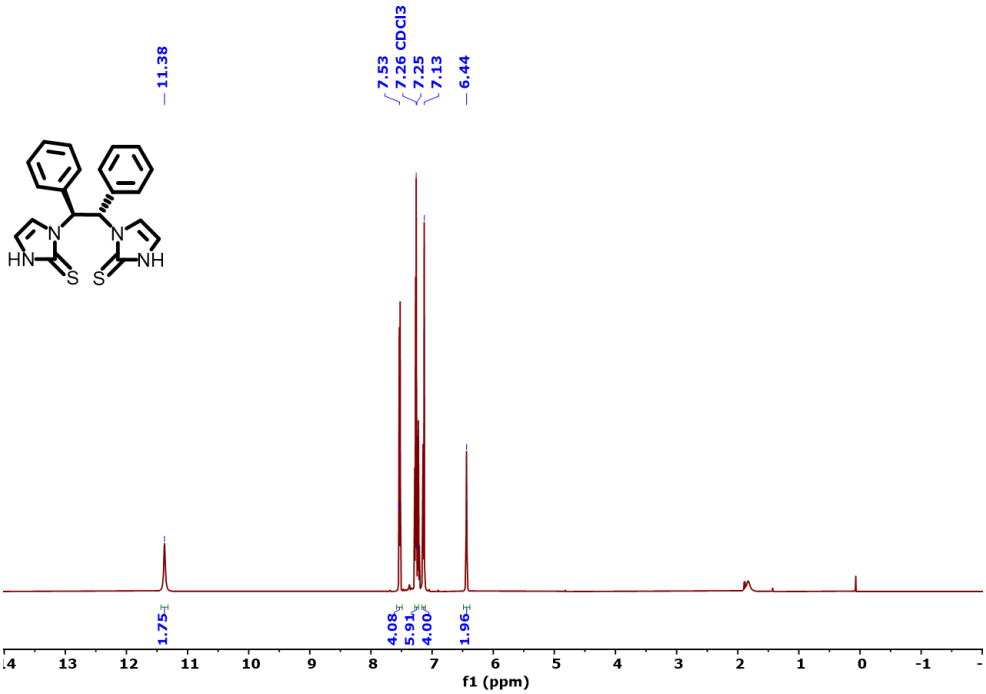


Figure S1. ^{1}H NMR of **1** in $CDCl_3$.

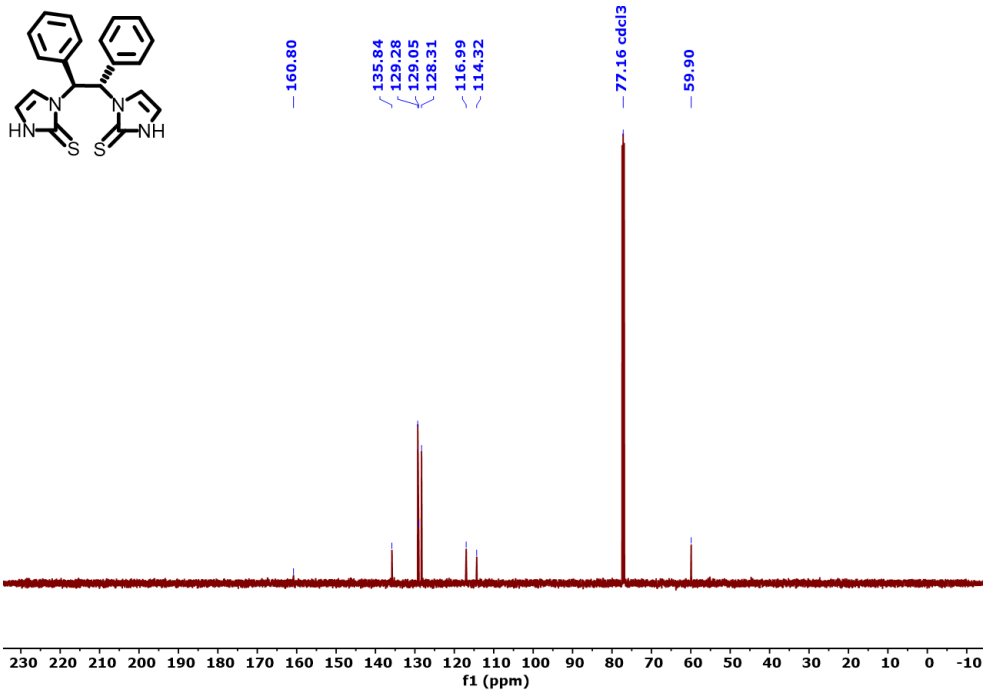


Figure S2. ^{13}C NMR of **1** in $CDCl_3$.

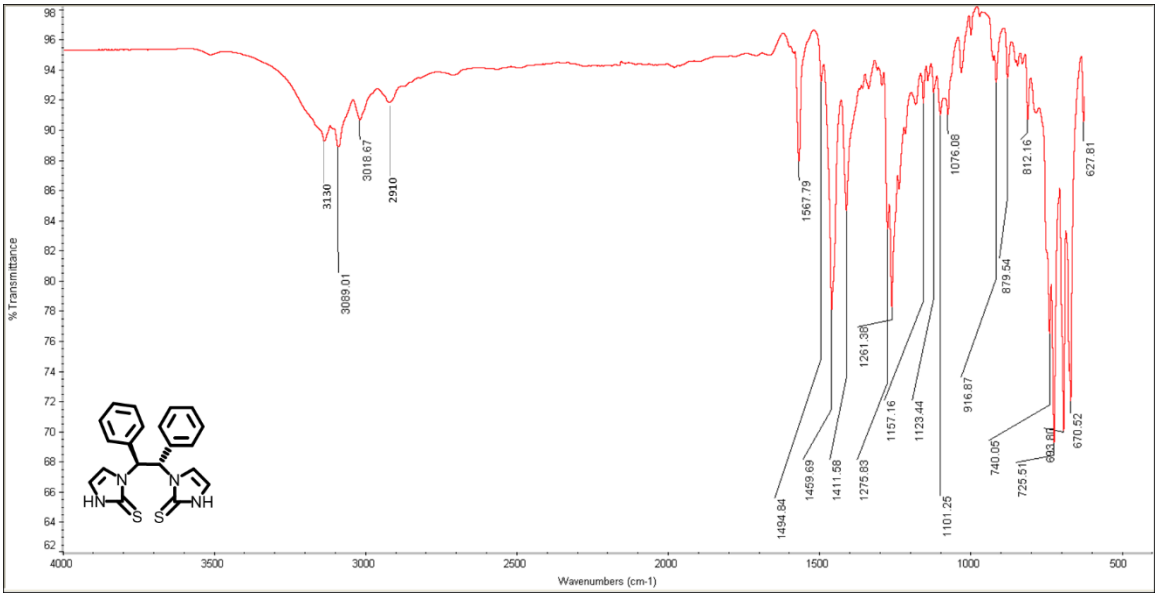


Figure S3. IR of **1**.

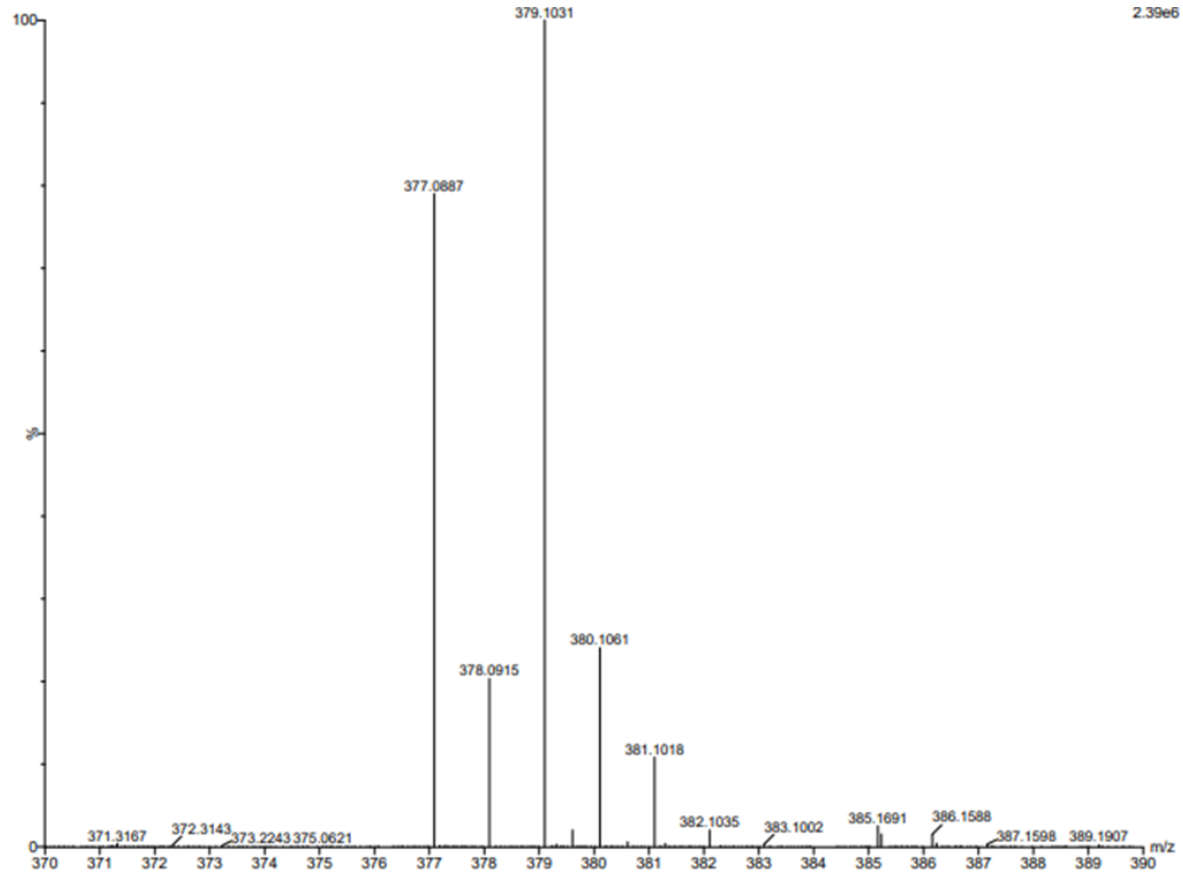


Figure S4. ESI HRMS of **1**.

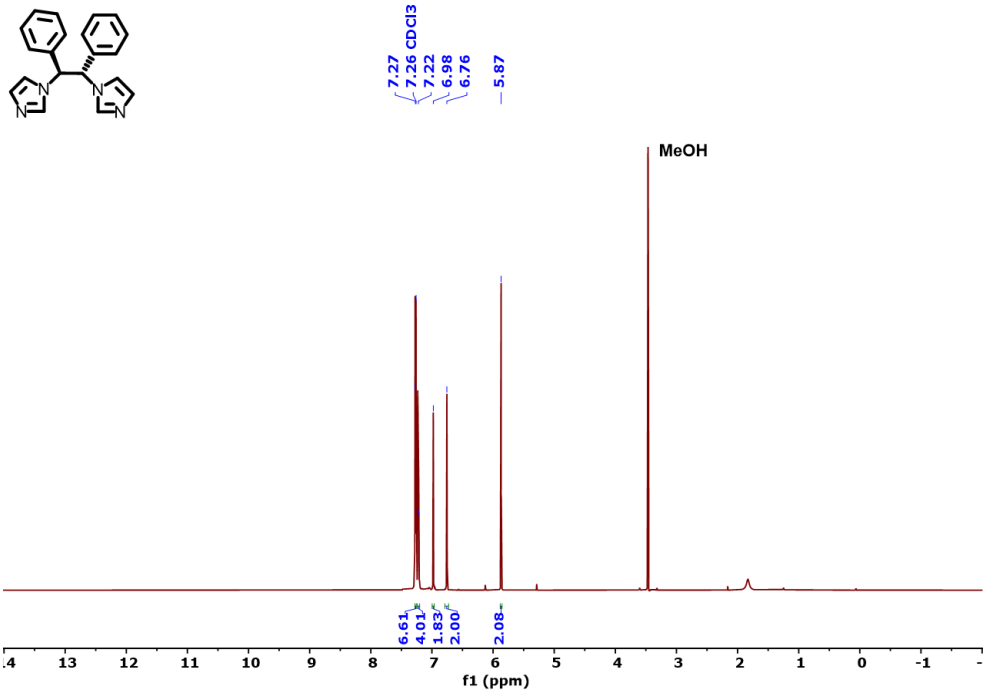


Figure S5. ^{1}H NMR of **2** in $CDCl_3$.

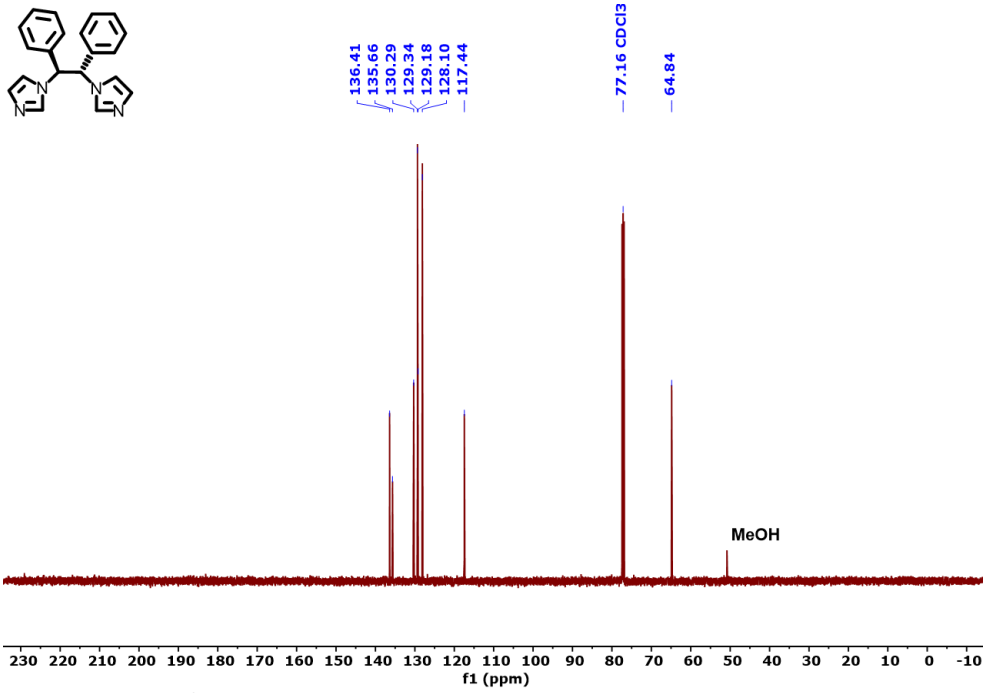


Figure S6. ^{13}C NMR of **2** in $CDCl_3$.

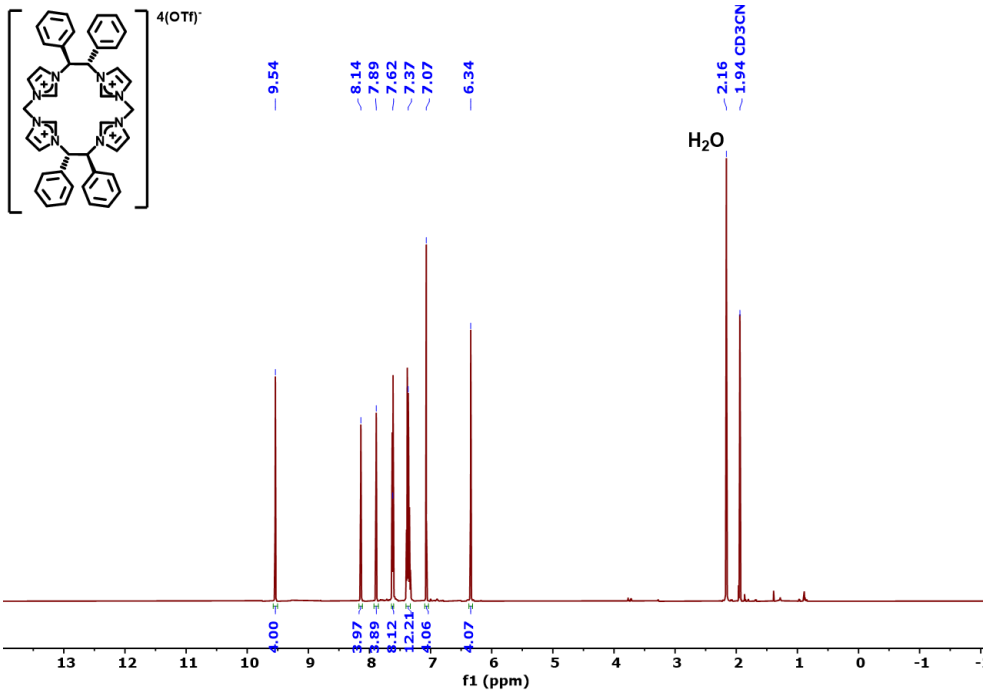


Figure S7. ^{1}H NMR of **3** in CD_3CN.

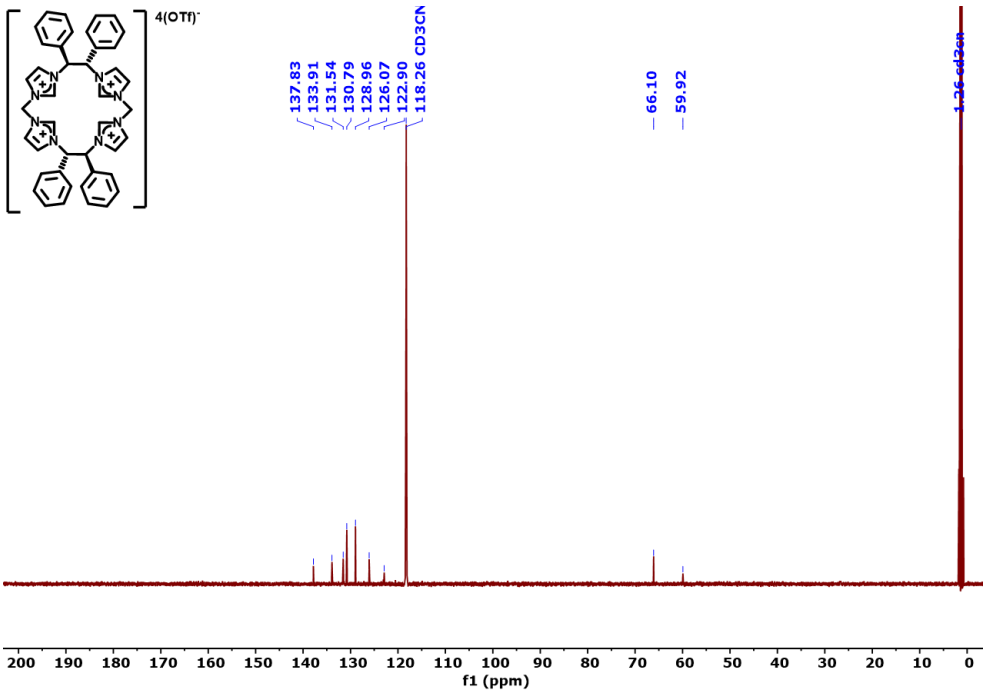


Figure S8. ^{13}C NMR of **3** in CD_3CN.

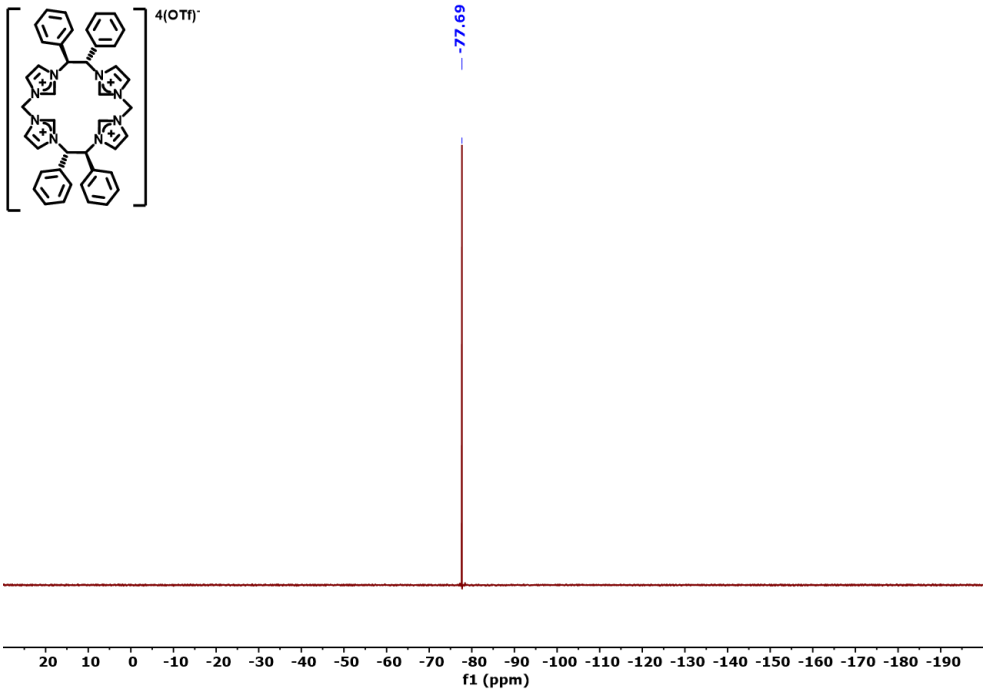


Figure S9. ^{19}F NMR of **3** in CD_3CN.

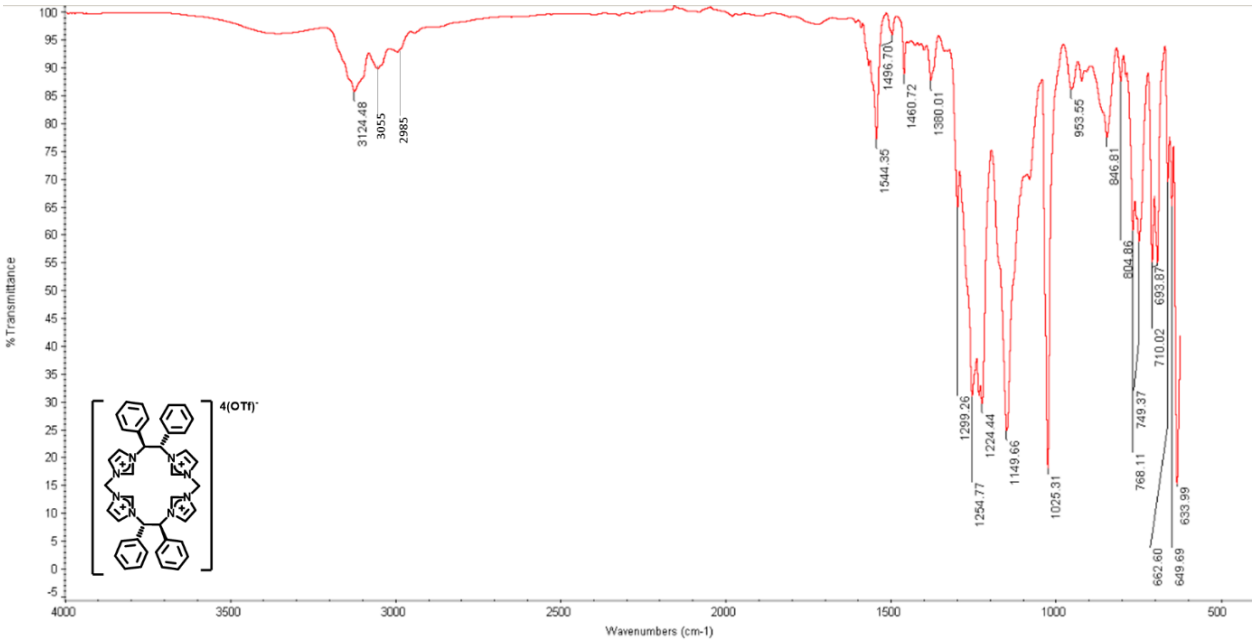


Figure S10. IR of compound **3**.

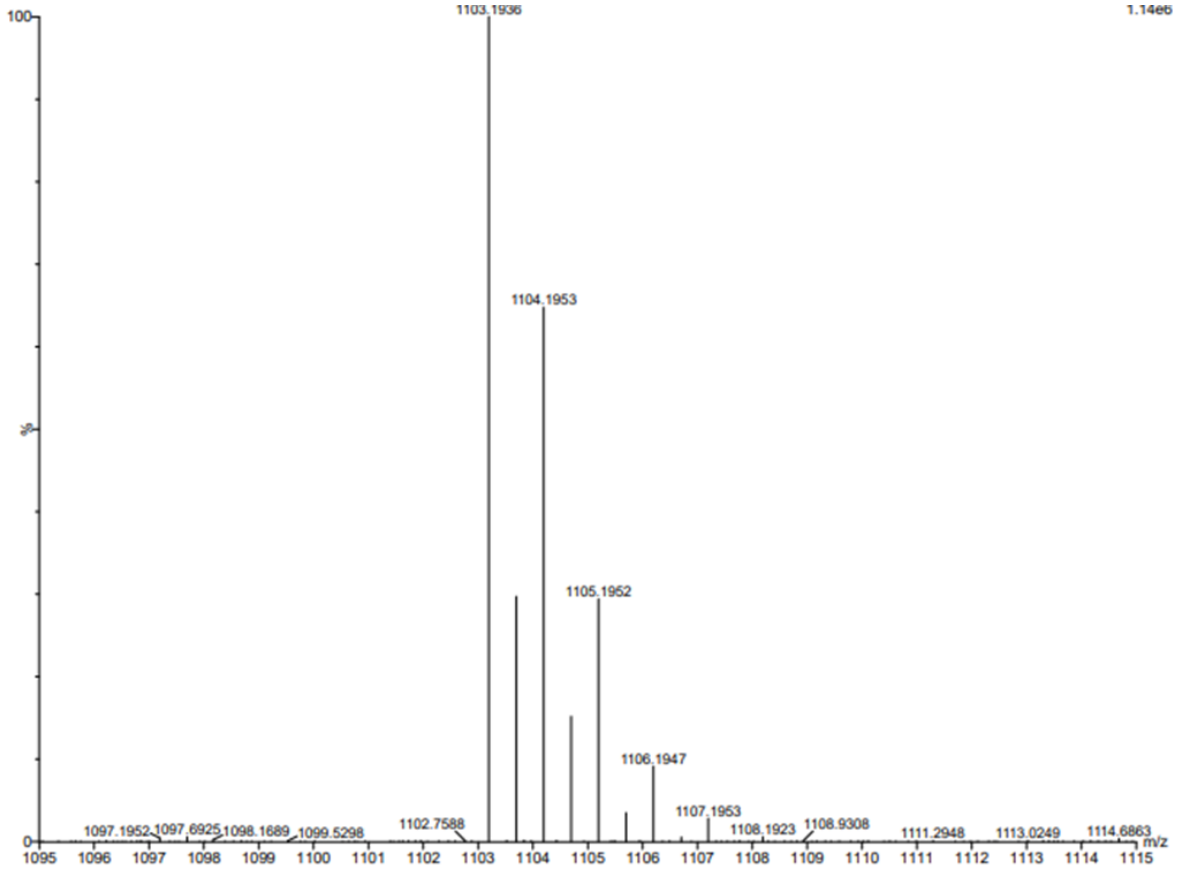


Figure S11. ESI HRMS of **3**

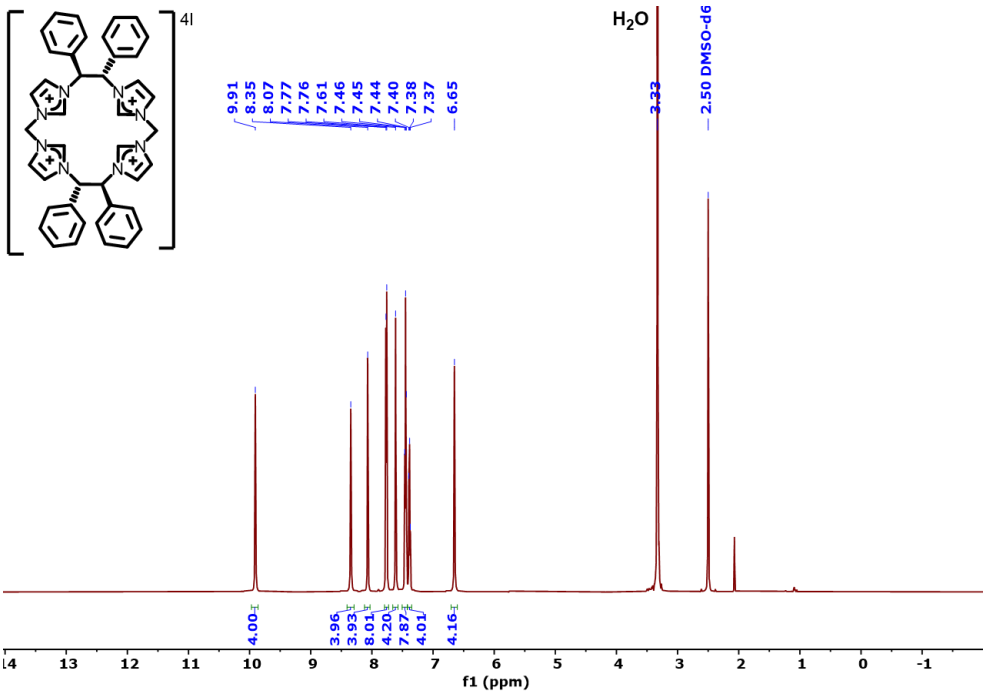


Figure S12. ^{1}H NMR of **4** in DMSO-d$_6$.

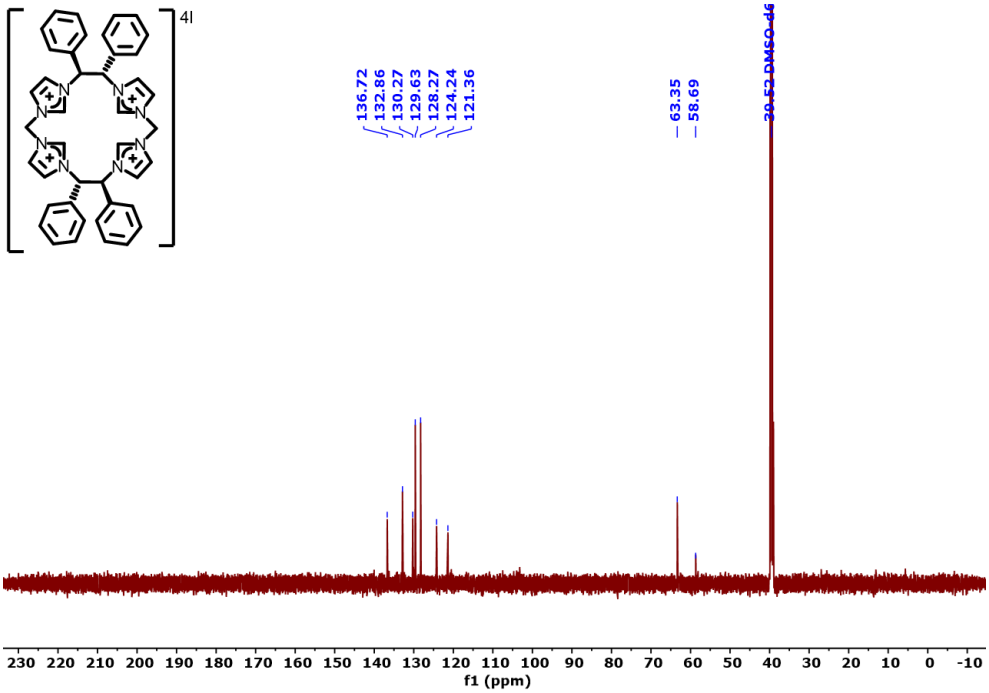
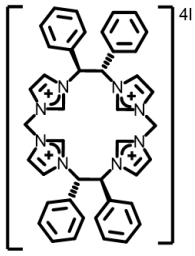


Figure S13. ^{13}C NMR of **4** in DMSO-d$_6$.



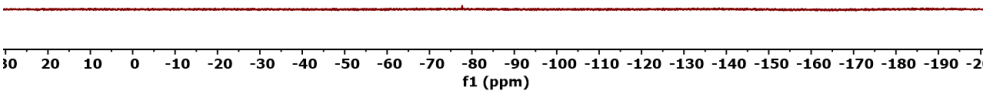


Figure S14. ^{19}F NMR of **4** in DMSO-d_6.

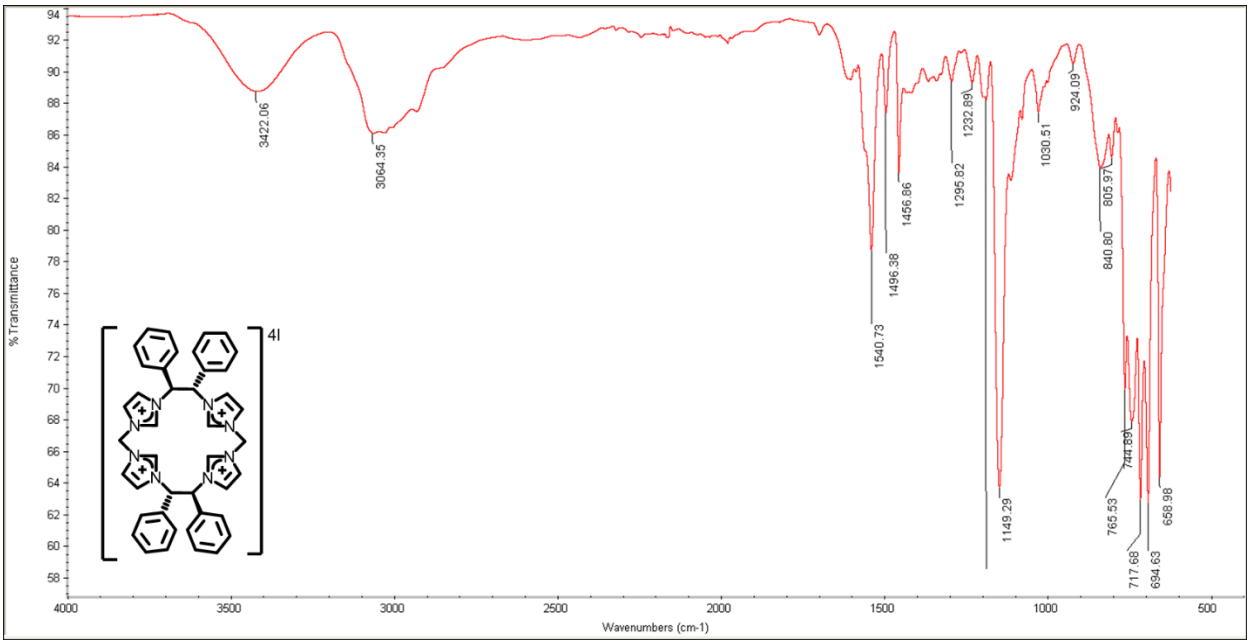


Figure S15. IR of **4**.

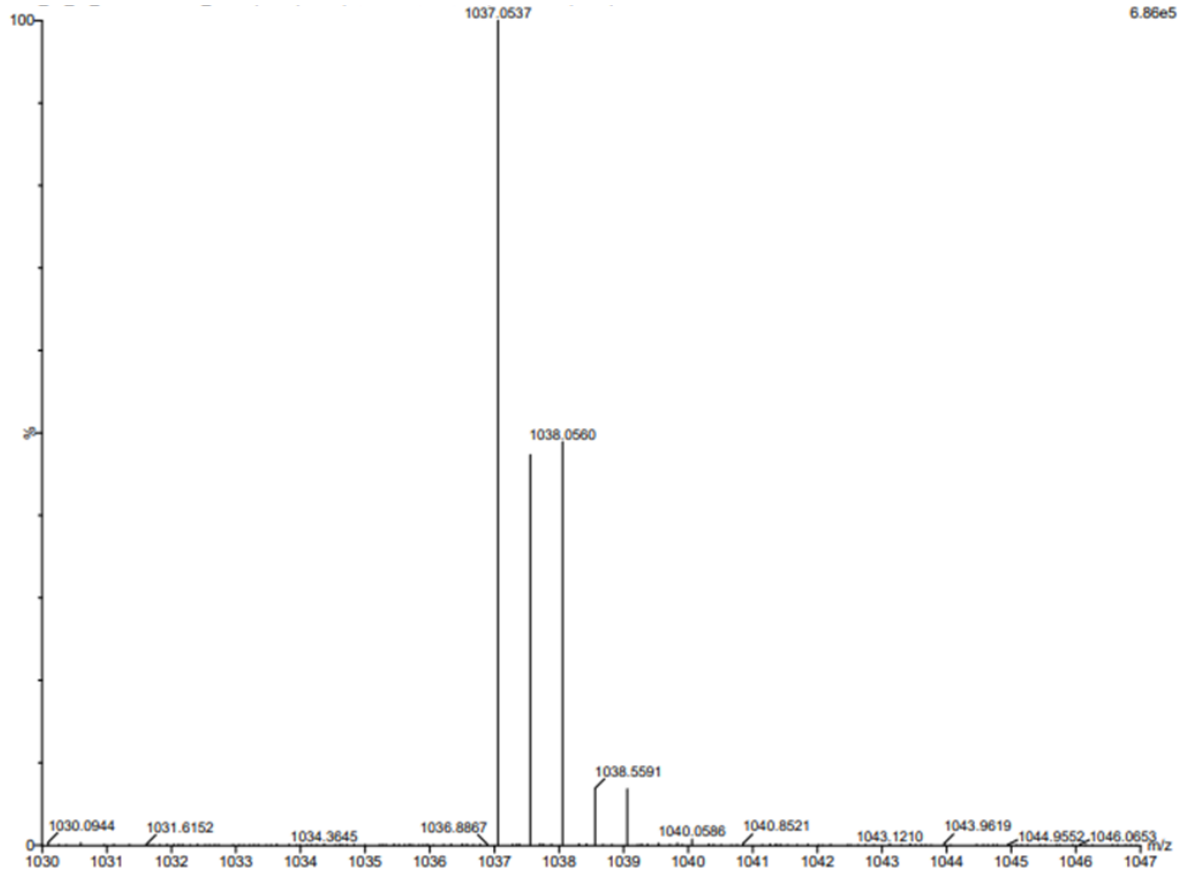


Figure S16 ESI HRMS of **4**.

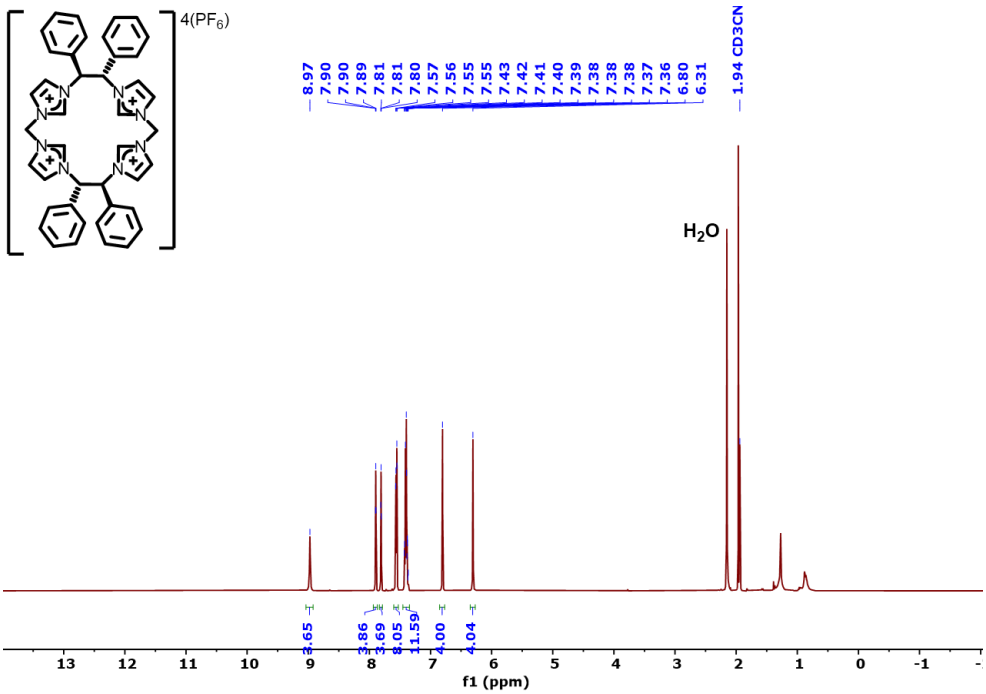


Figure S17. ^{1}H NMR of **5** in CD_3CN.

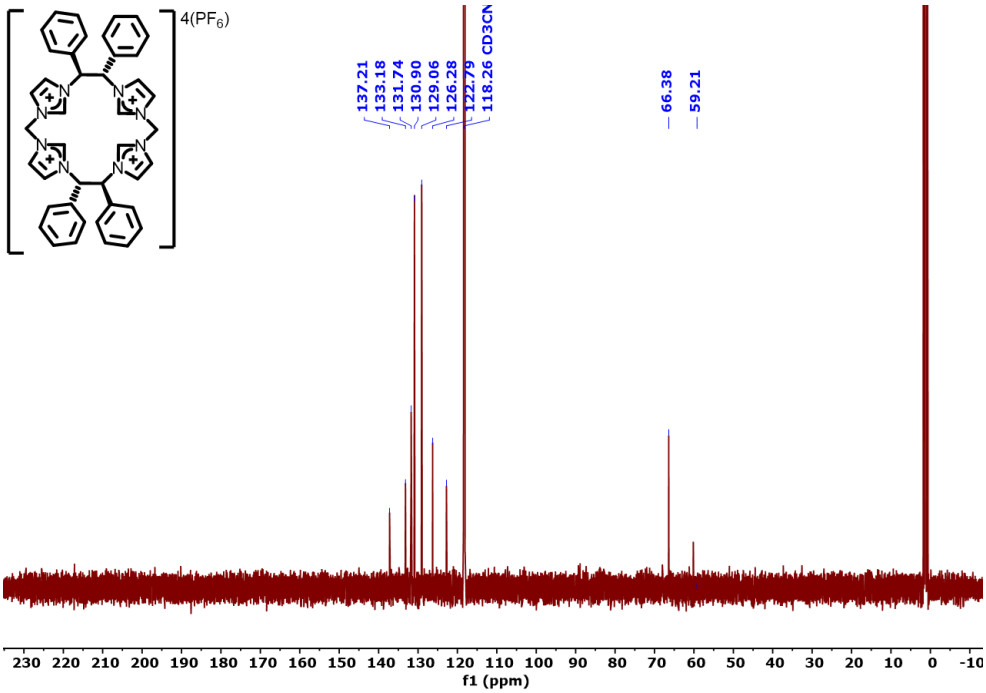


Figure S18. ^{13}C NMR of **5** in CD_3CN.

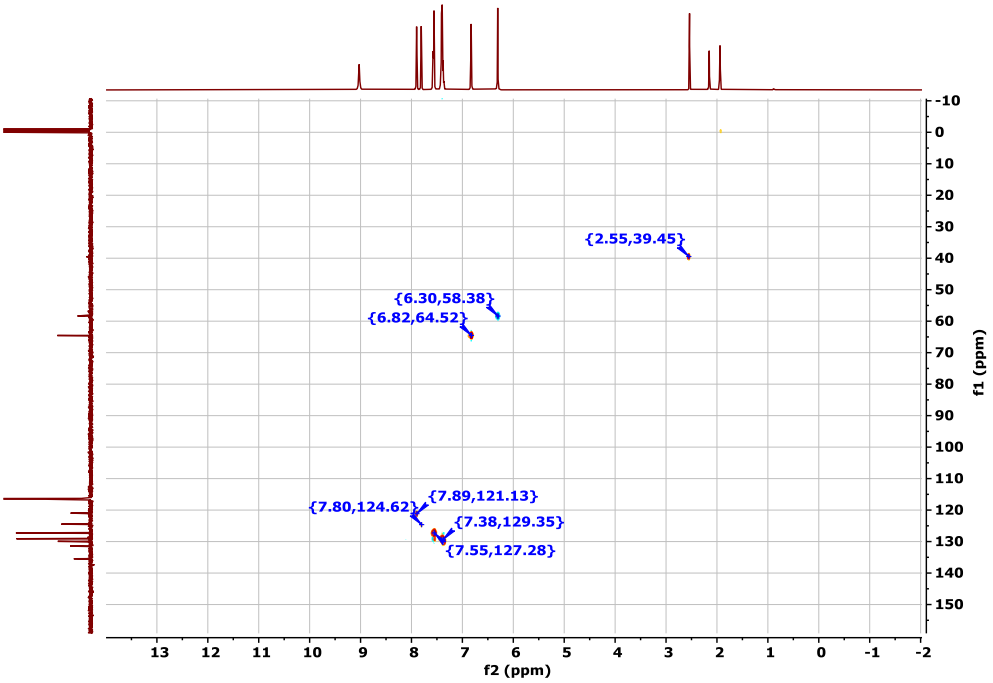


Figure S19. HSQC NMR of **5** in CD_3CN.

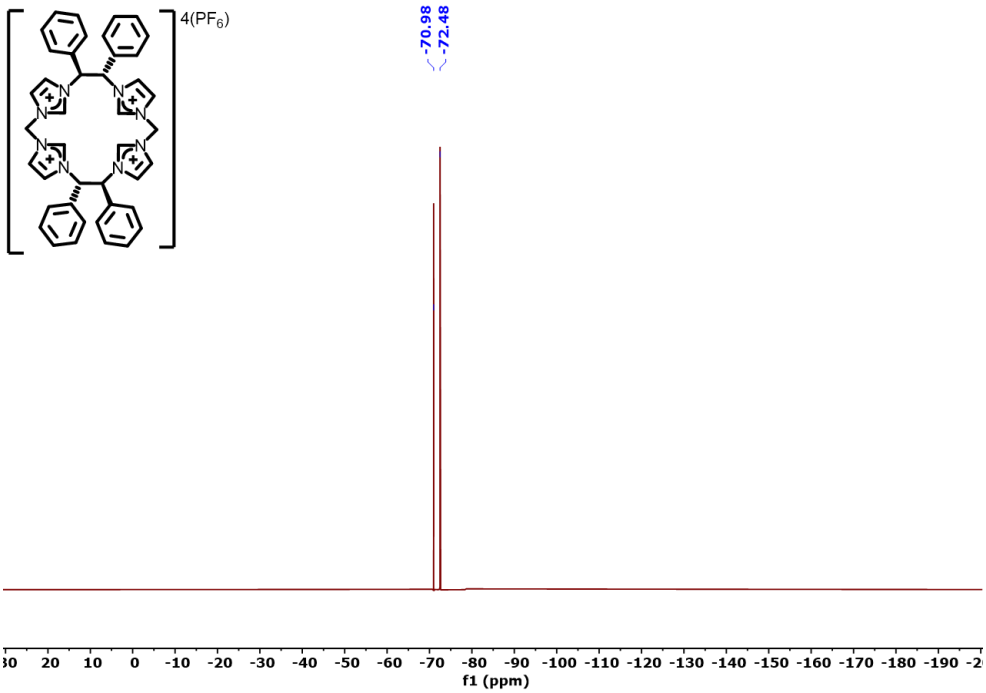


Figure S20. ^{19}F NMR of **5** in CD_3CN.

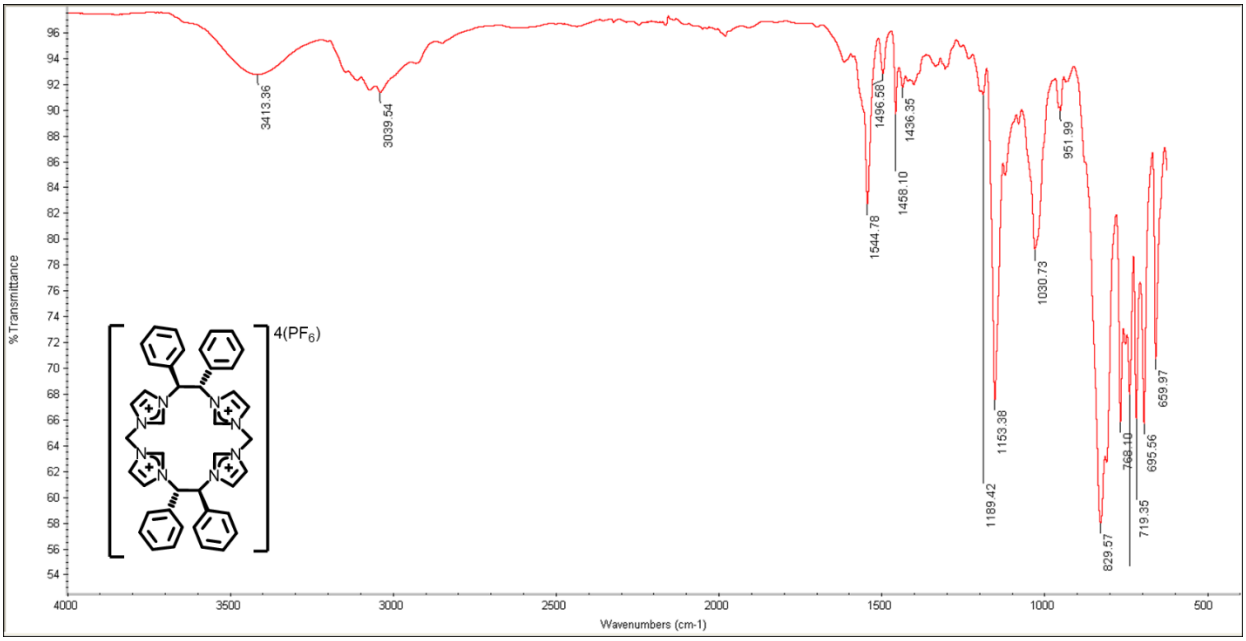


Figure S21. IR of **5**.

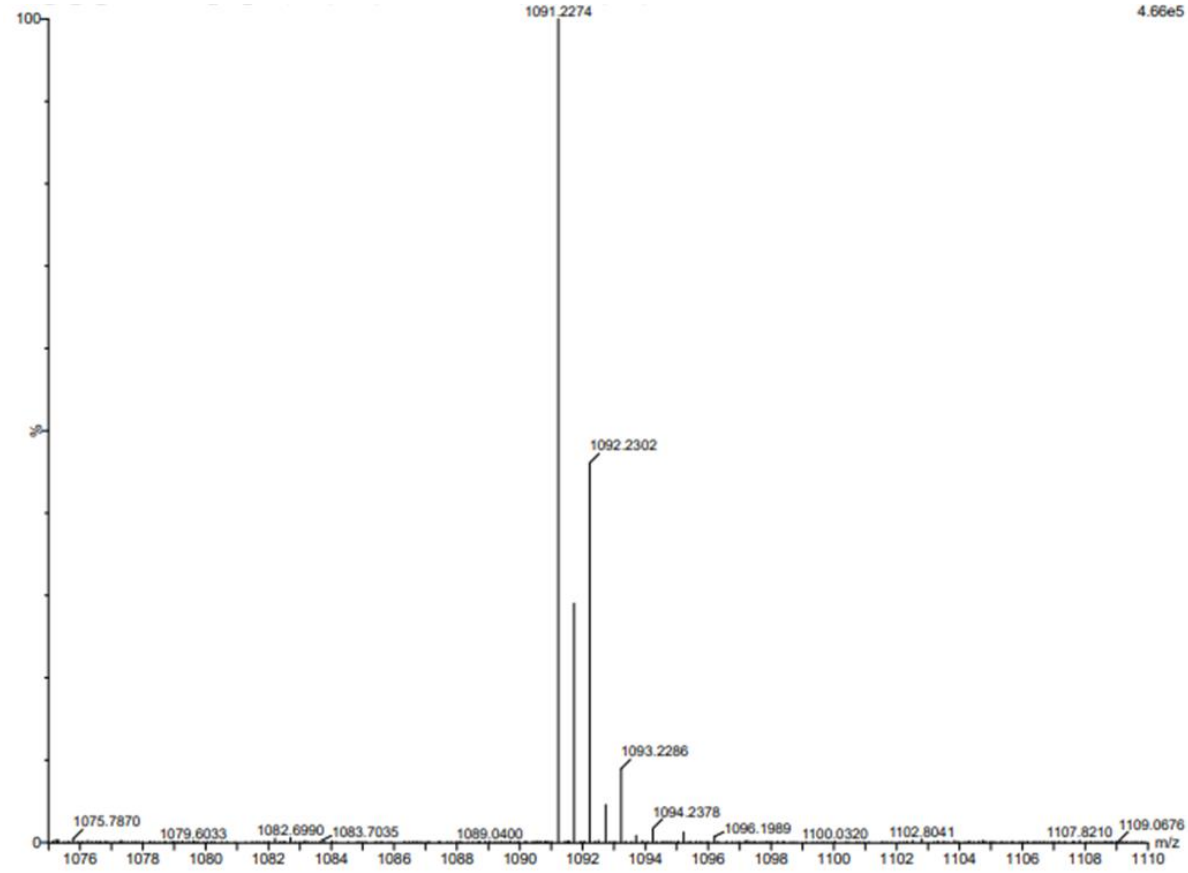


Figure S22 ESI HRMS of **5**.

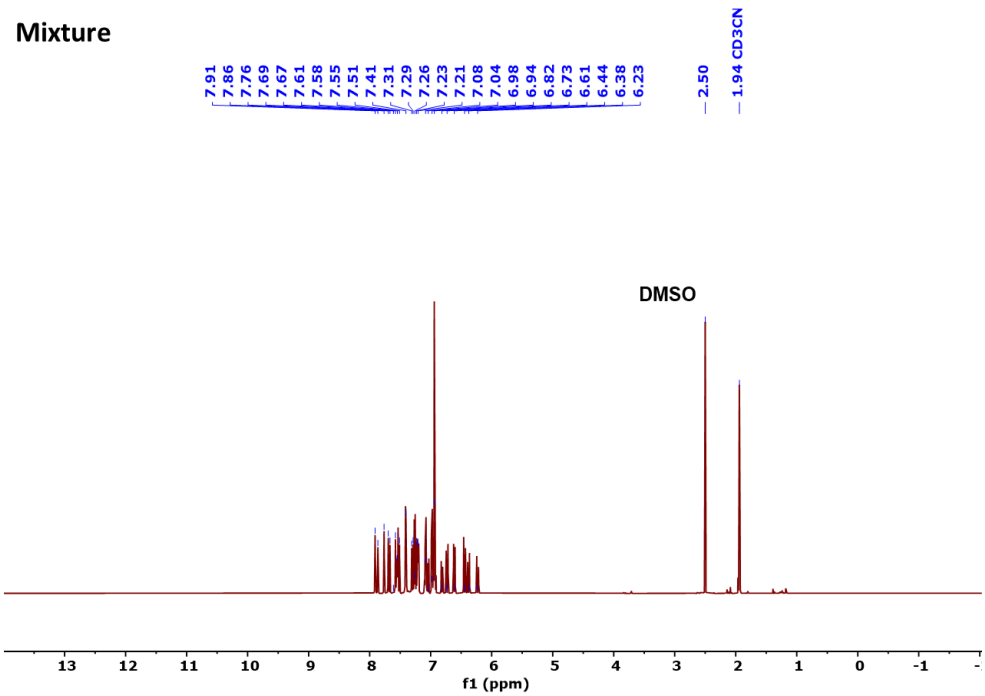


Figure S23. ^{1}H NMR of **6**(a+b) in CD_3CN.

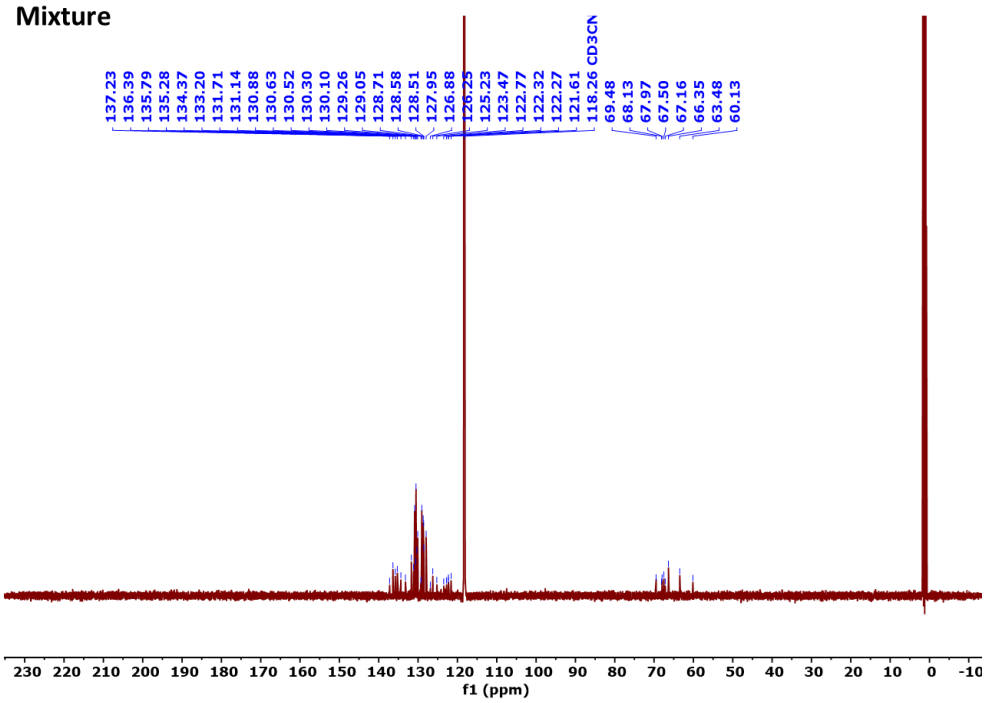


Figure S24. ^{13}C NMR of **6**(a+b) in CD_3CN.

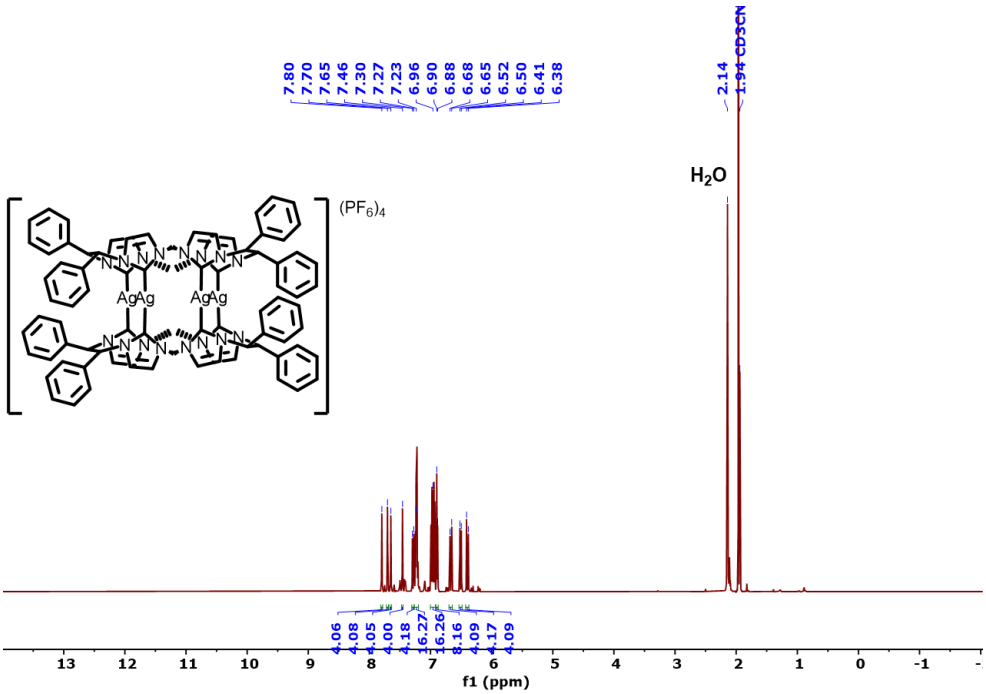


Figure S25. ^{1}H NMR of **6a** in CD_3CN.

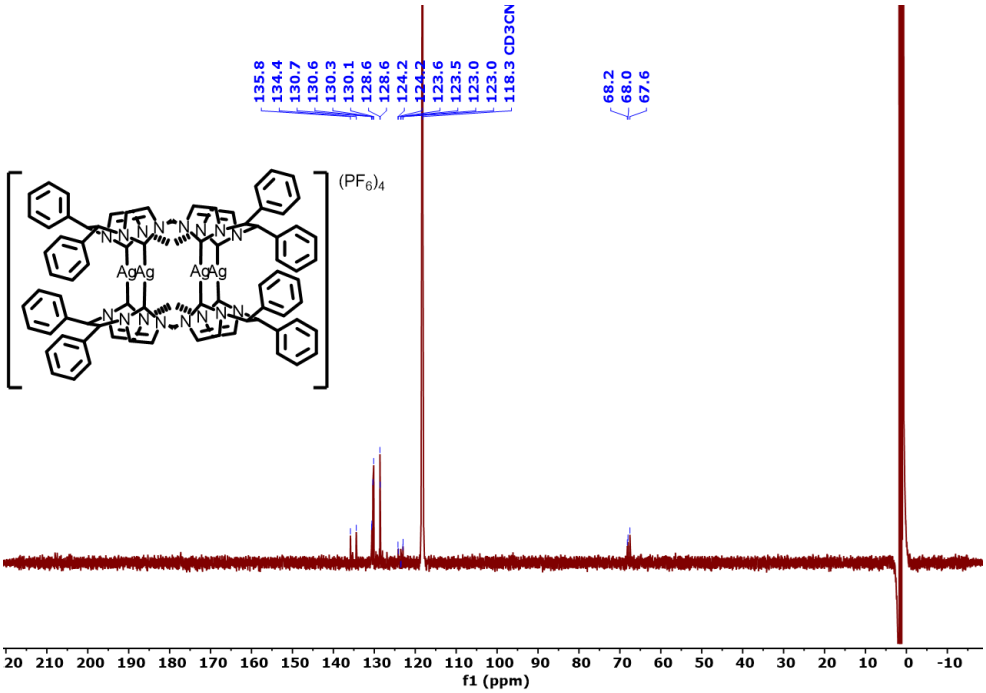


Figure S26. ^{13}C NMR of **6a** in CD_3CN.

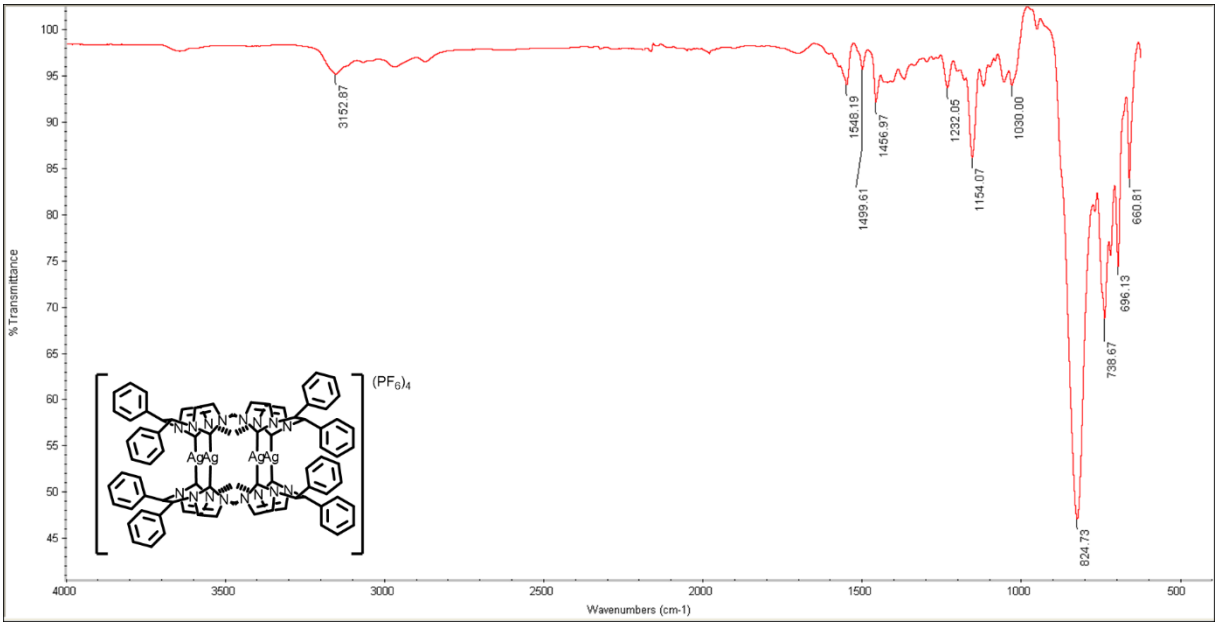


Figure S27. IR of **6a**.

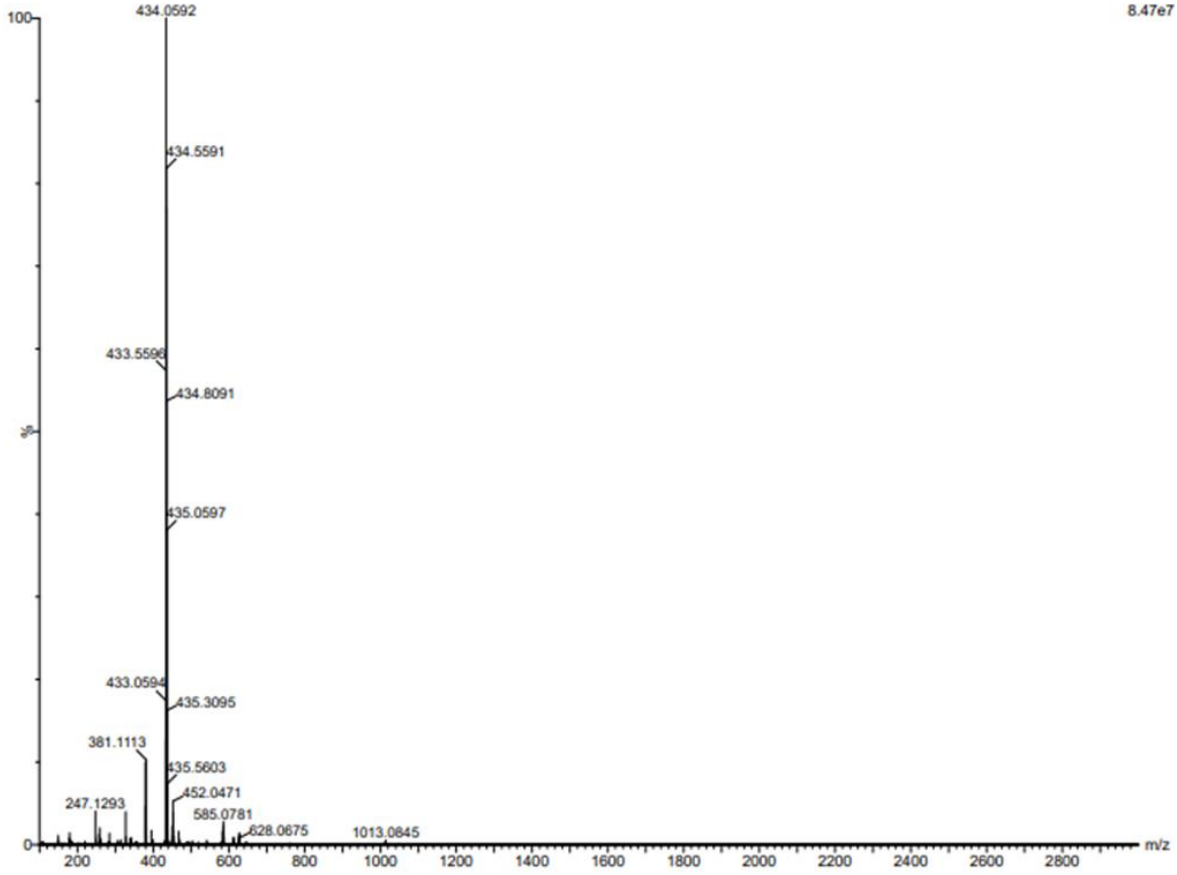


Figure S28. ESI-HRMS of **6a**.

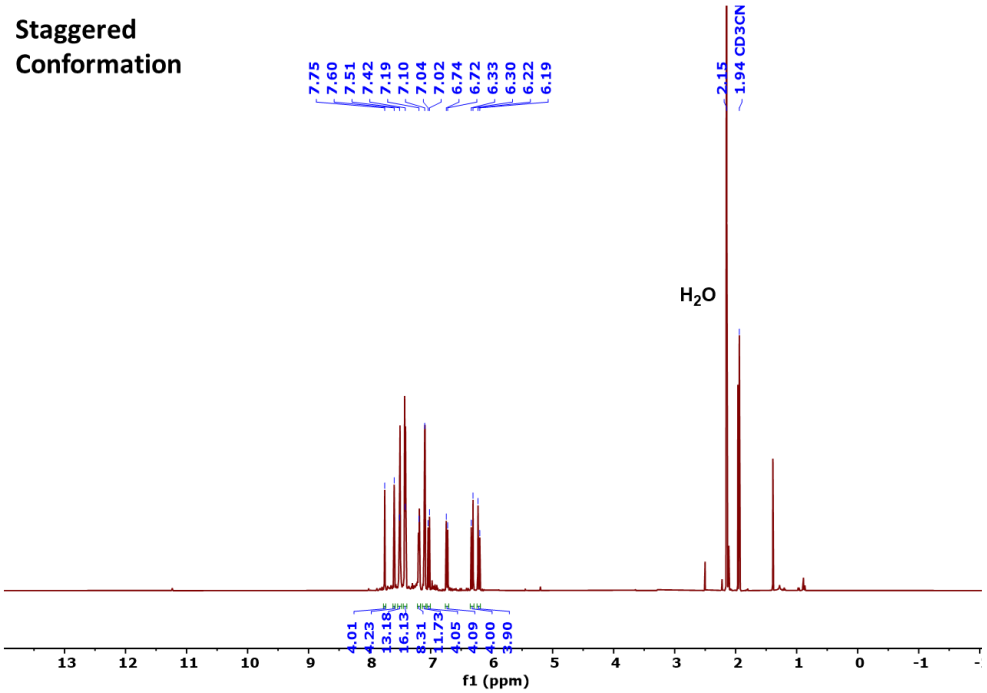


Figure S29. ^{1}H NMR of **6b** in CD_3CN.

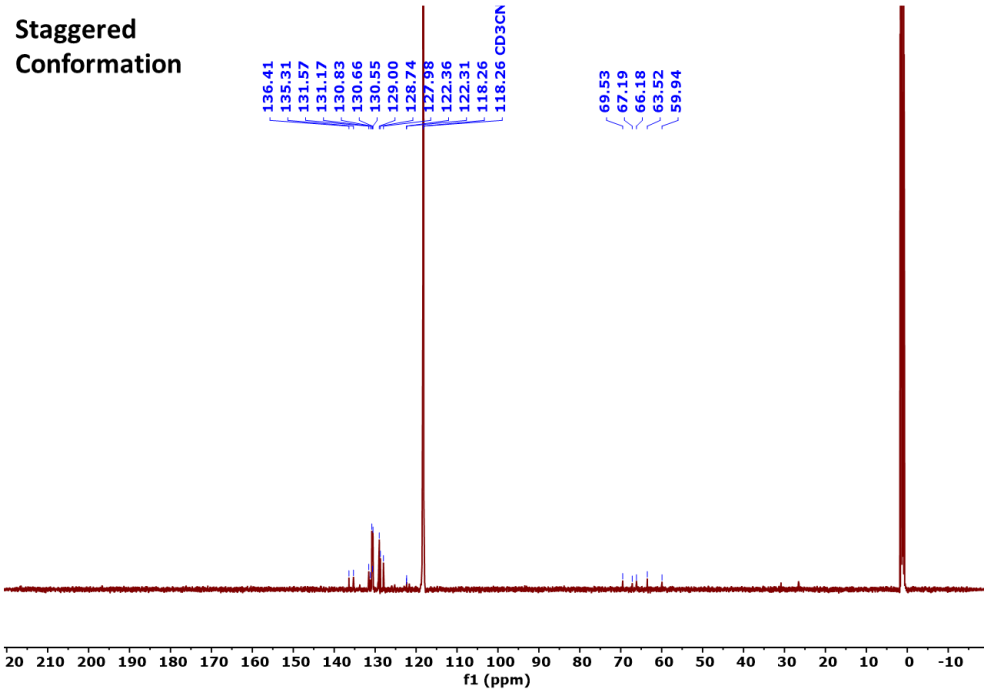


Figure S30. ^{13}C NMR of **6b** in CD_3CN.

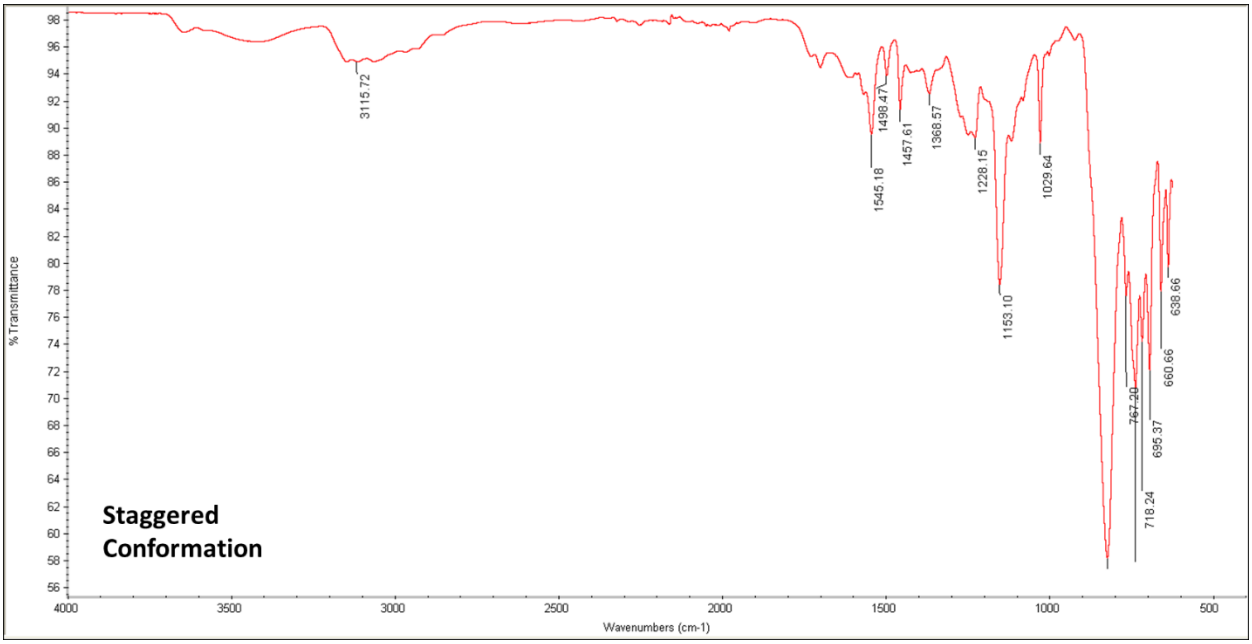


Figure S31. IR of **6b.**

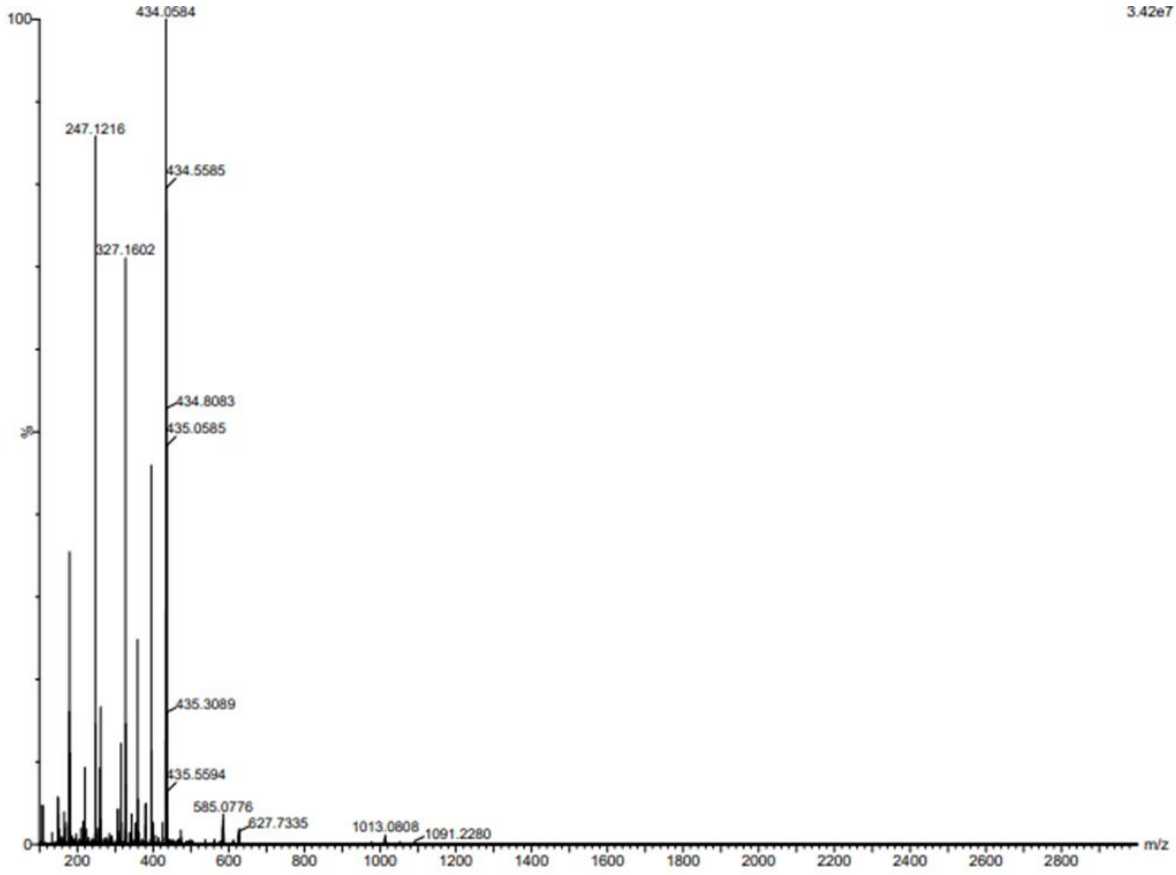


Figure S32. ESI HRMS of **6b**.

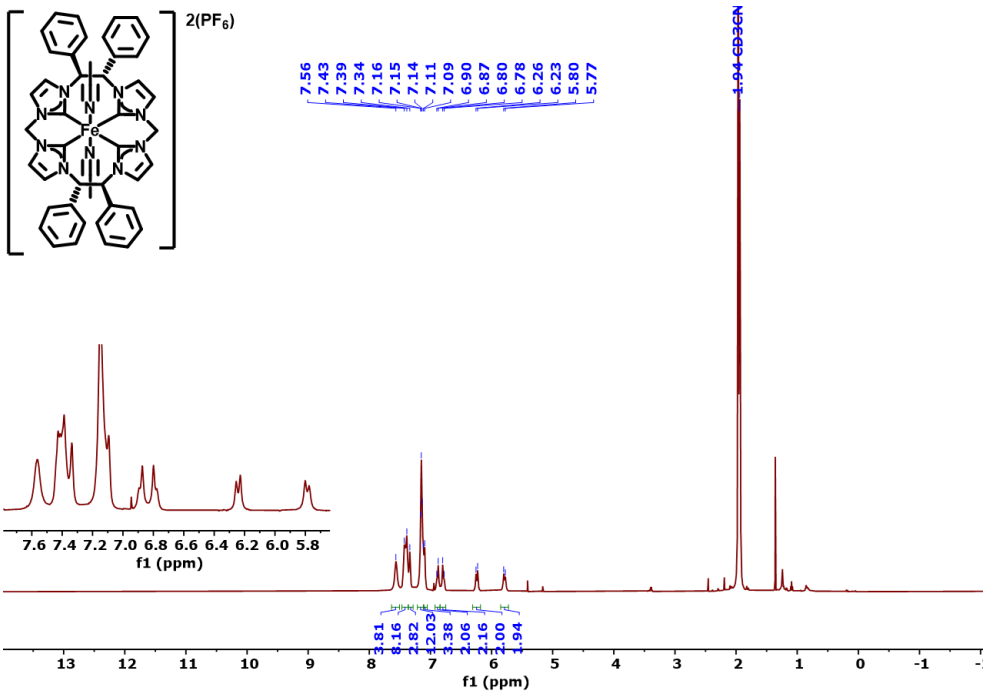


Figure S33. ^{1}H NMR of **7** in CD_3CN.

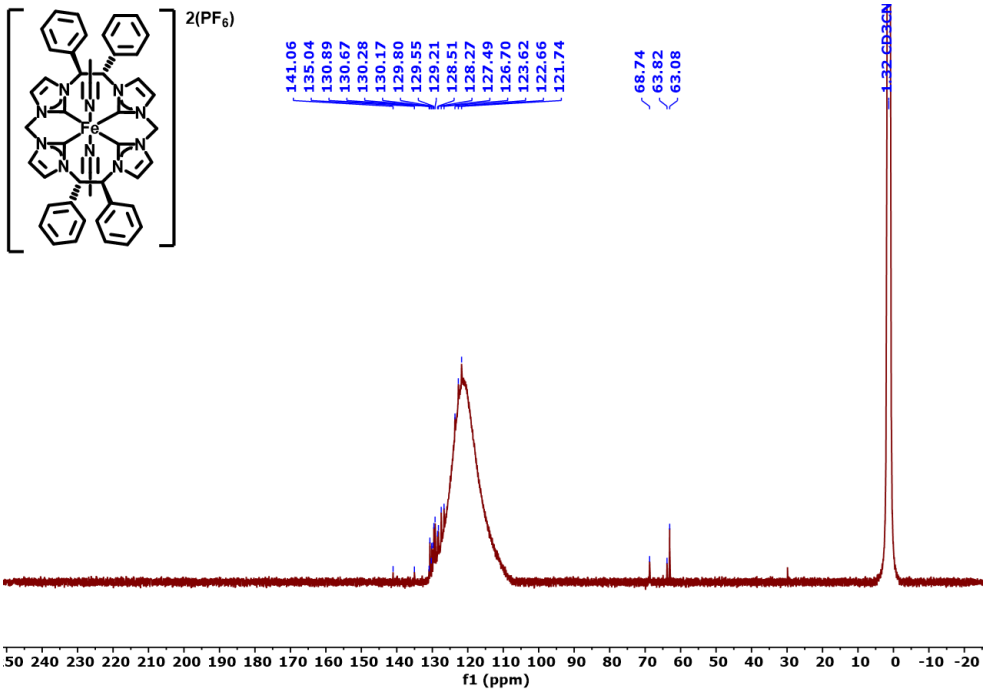


Figure S34. ^{13}C NMR of **7** in CD_3CN.

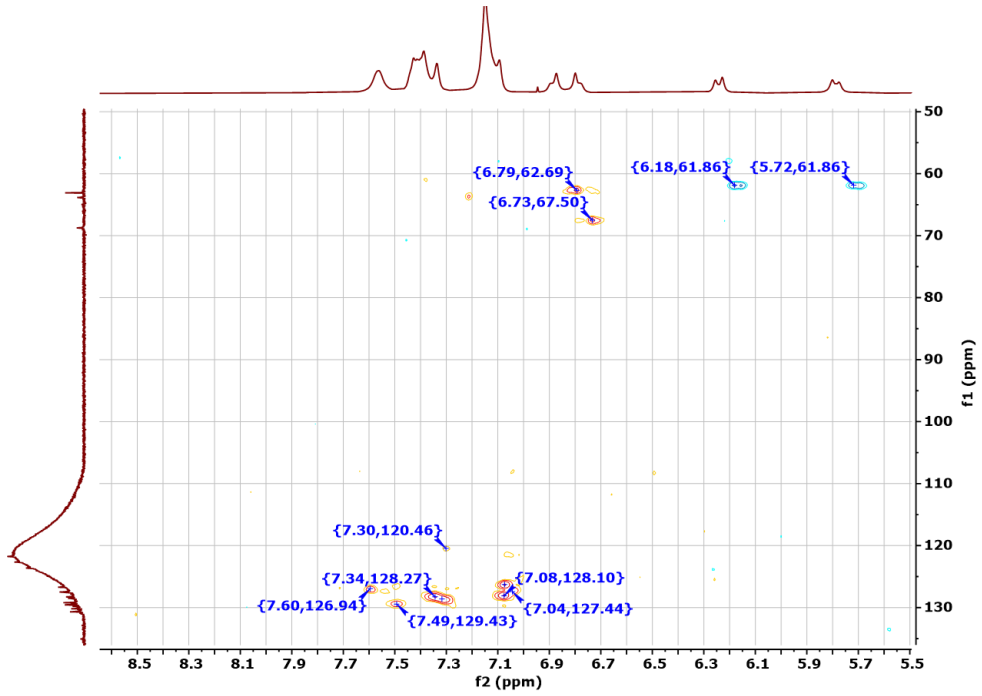


Figure S35. HSQC NMR of **7** in CD_3CN.

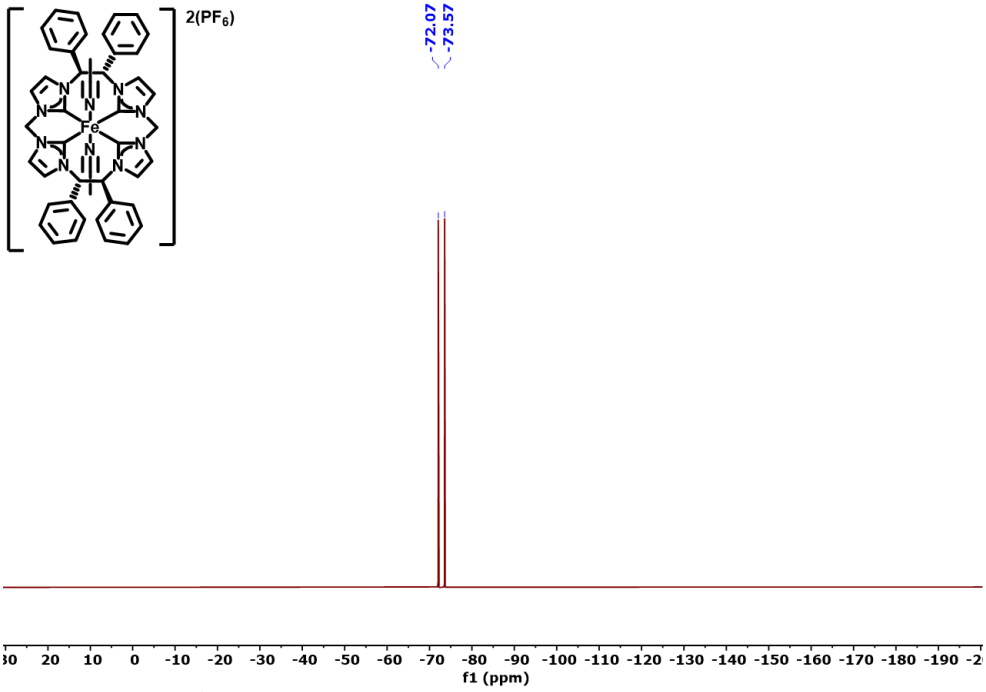


Figure S36. ^{19}F NMR of **7** in CD_3CN.

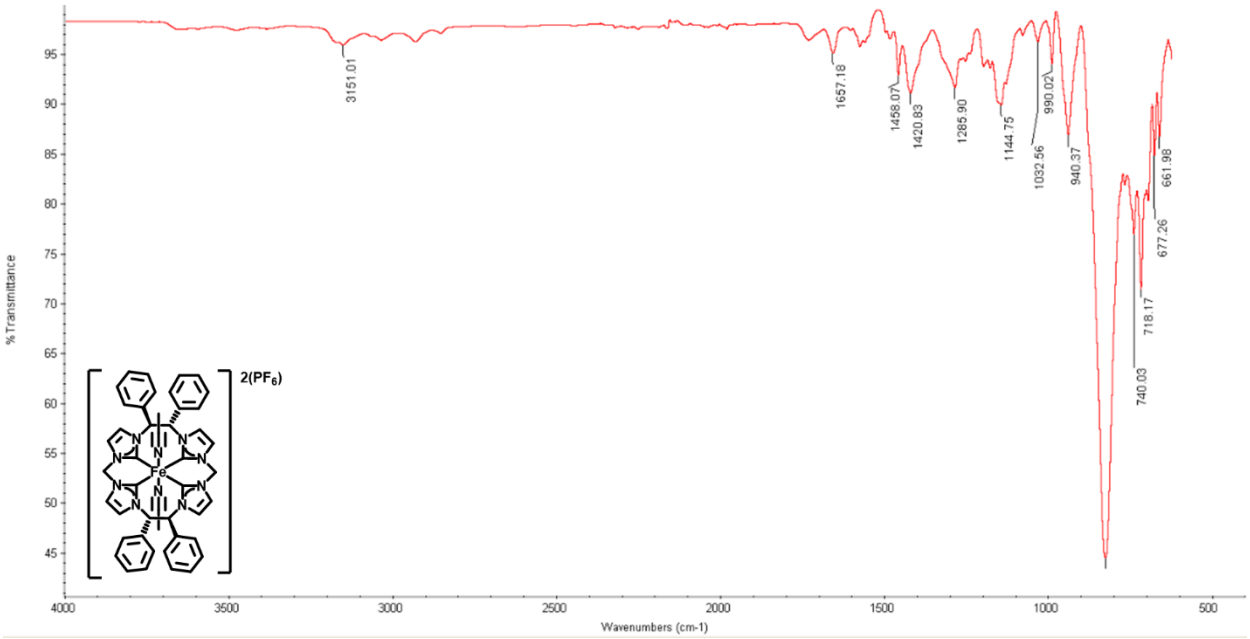


Figure S37. IR of **7**.

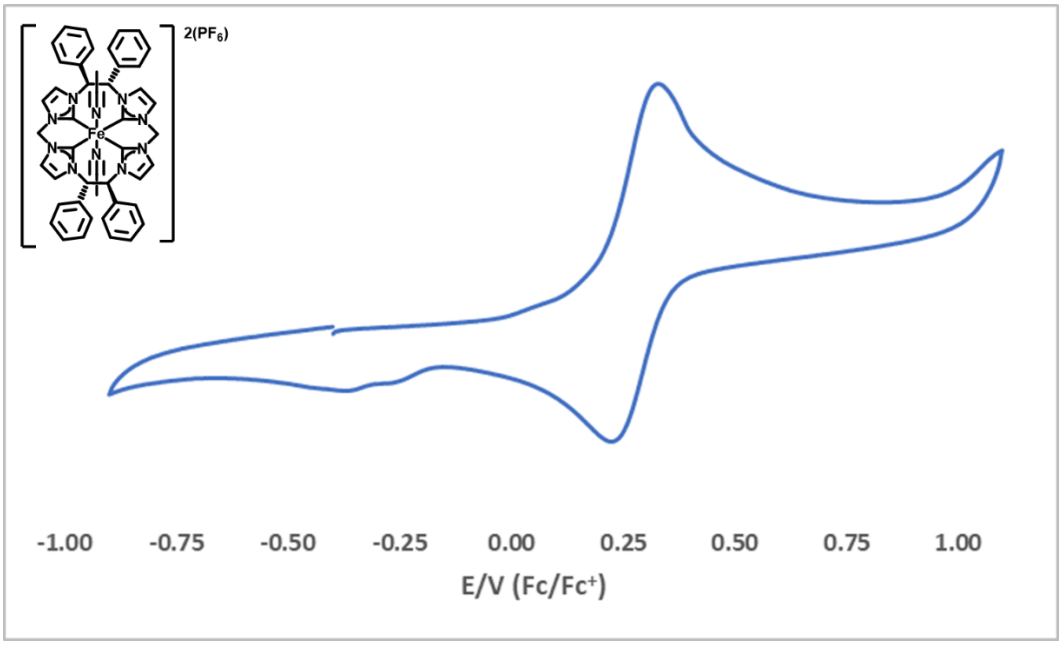


Figure S38. Cyclic Voltammogram of **7** in acetonitrile.

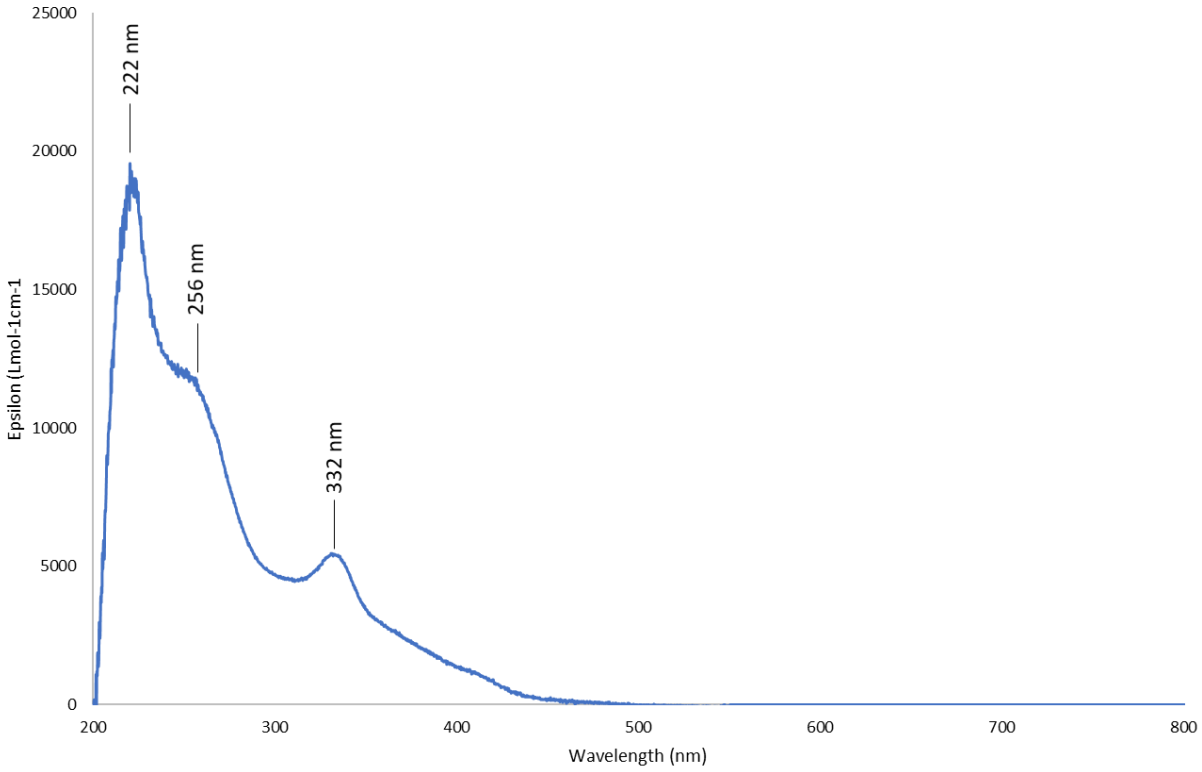


Figure S39. UV-vis of **7** in acetonitrile.

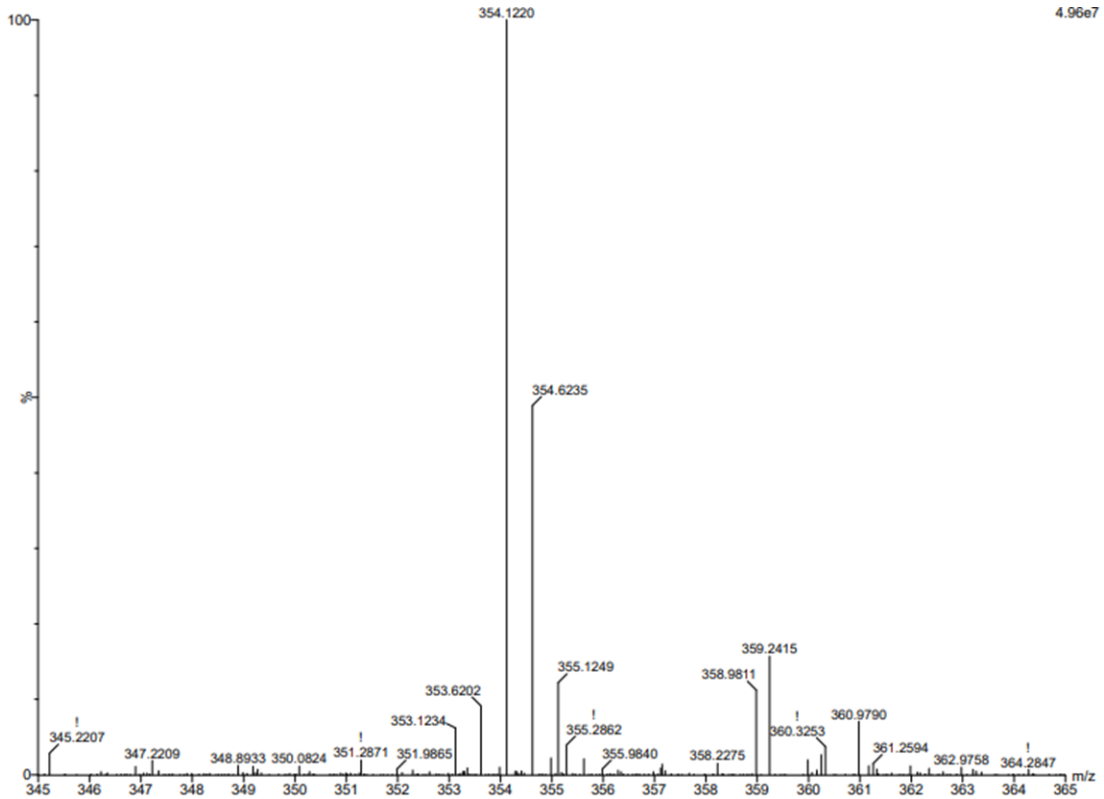


Figure S40. ESI HRMS of **7.**

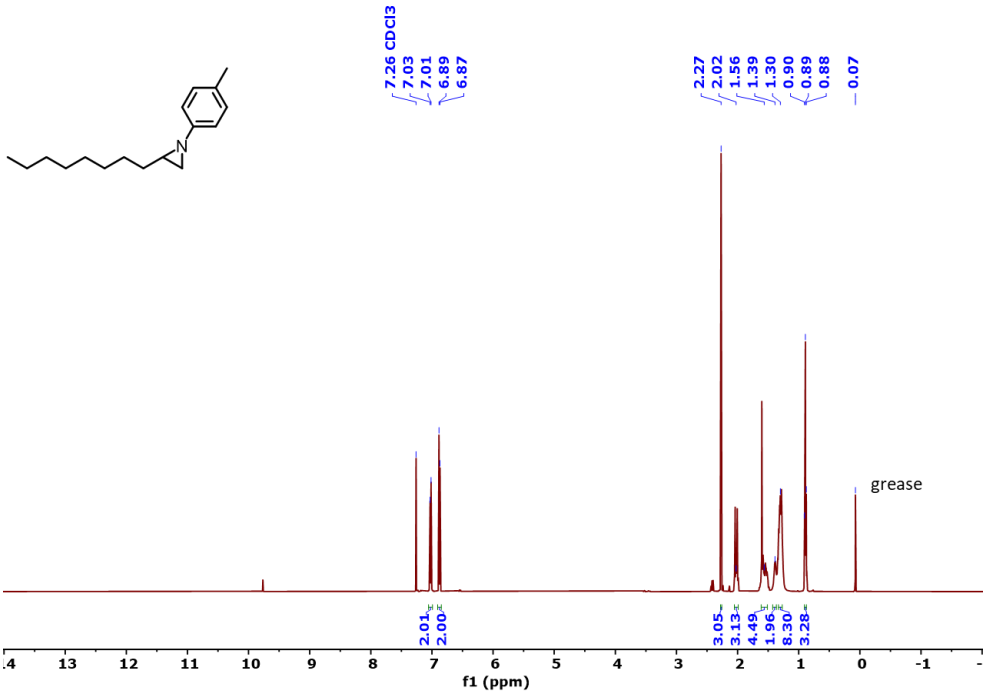


Figure S41. ^{1}H NMR of **8** in $CDCl_3$.

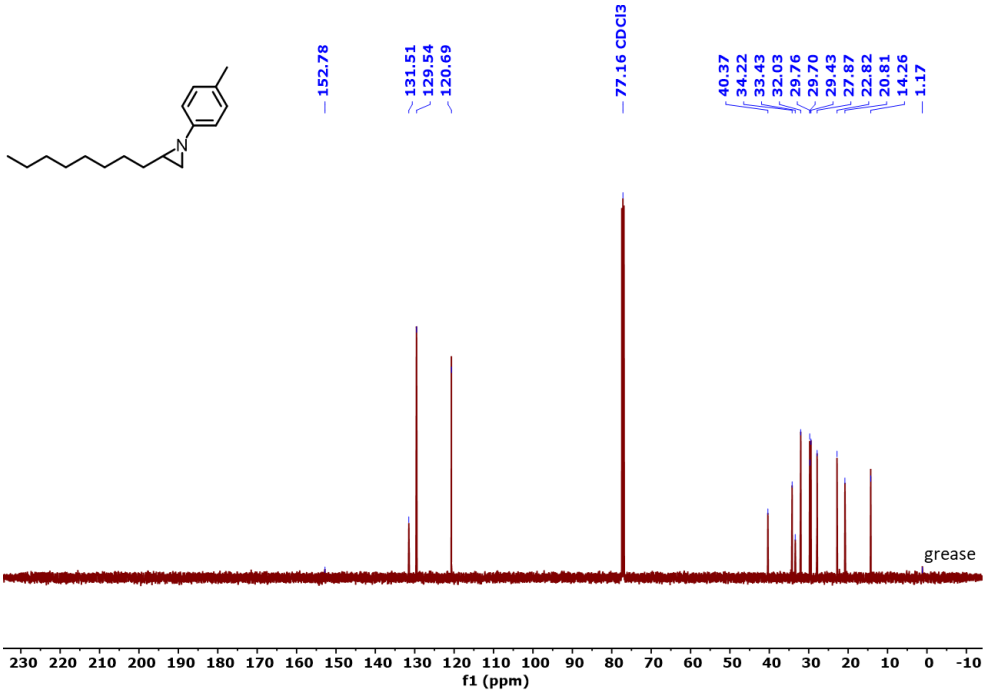


Figure S42. ^{13}C NMR of **8** in $CDCl_3$.

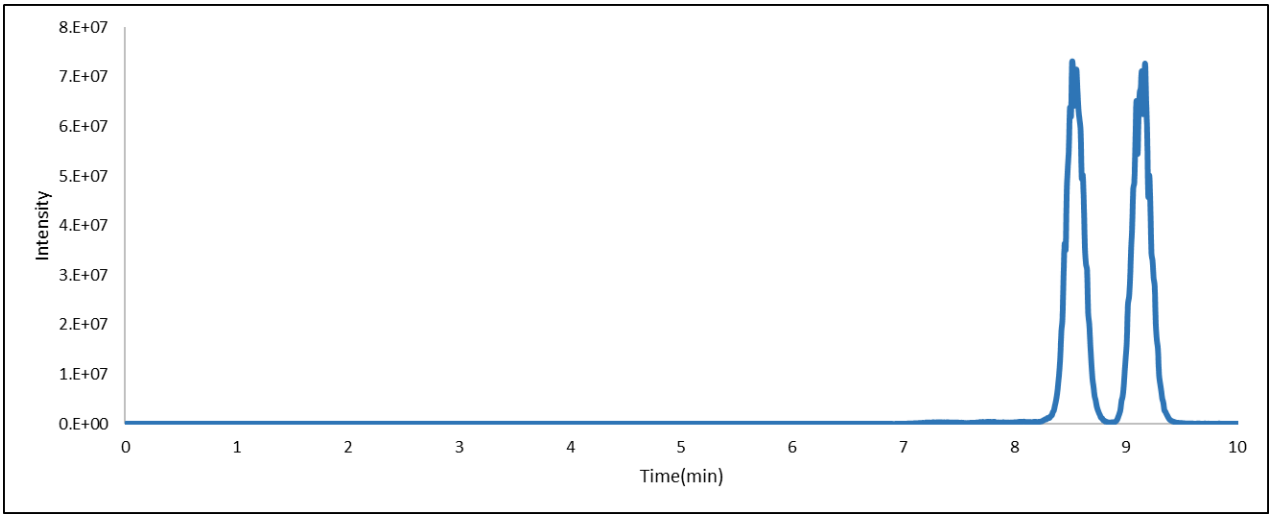


Figure S43. UHPLC Chromatogram of **8**.

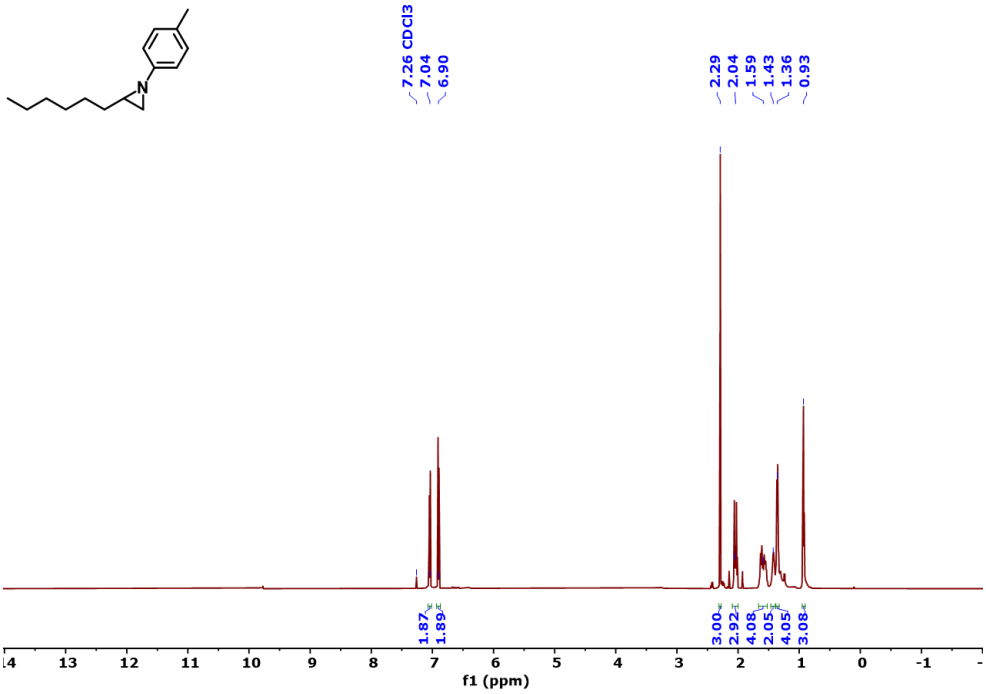


Figure S44. ^{1}H NMR of **9** in $CDCl_3$.

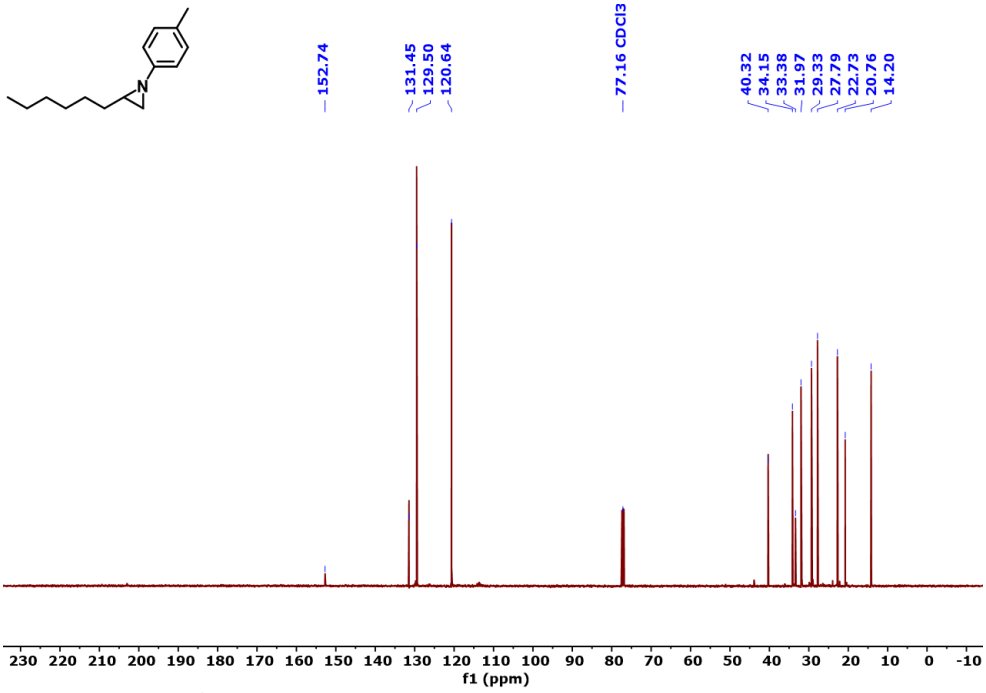


Figure S45. ^{13}C NMR of **9** in $CDCl_3$.

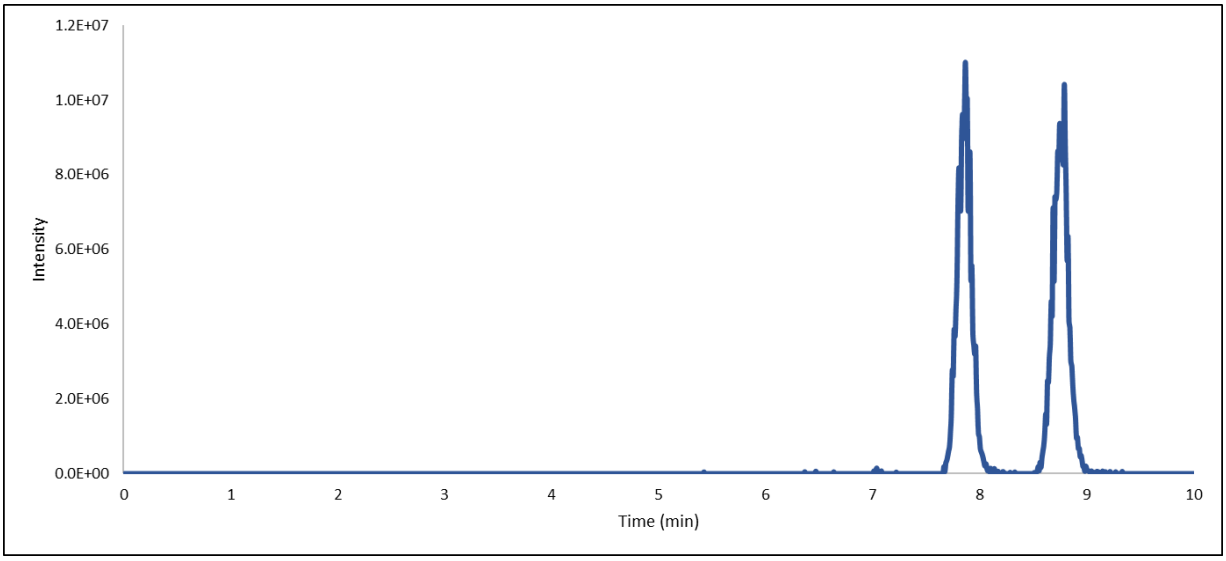


Figure S46. UHPLC Chromatogram of **9**.

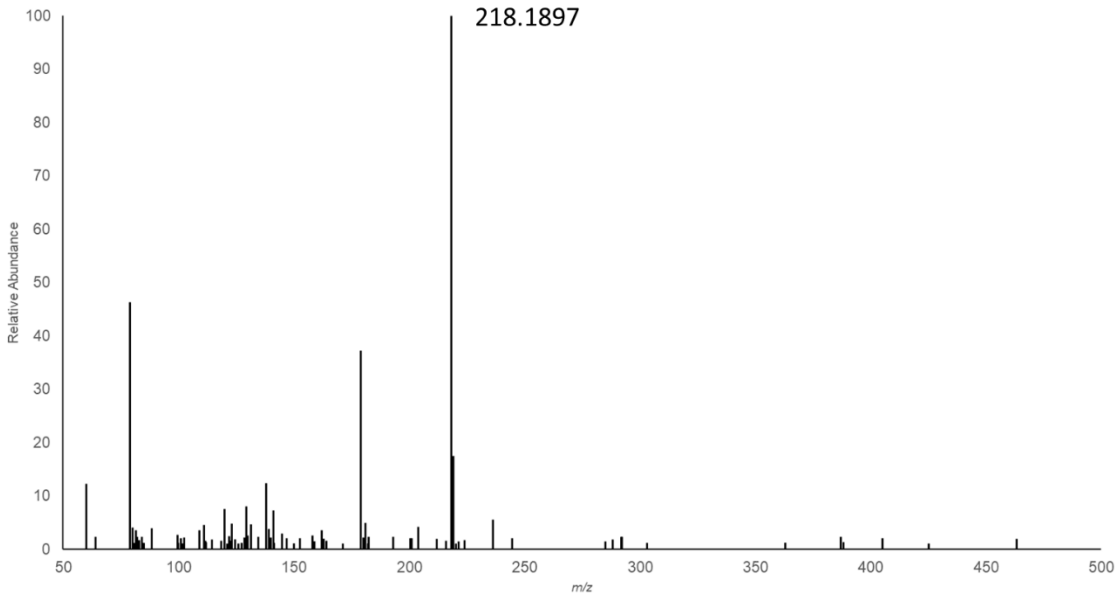


Figure S47. HRMS of **9**.

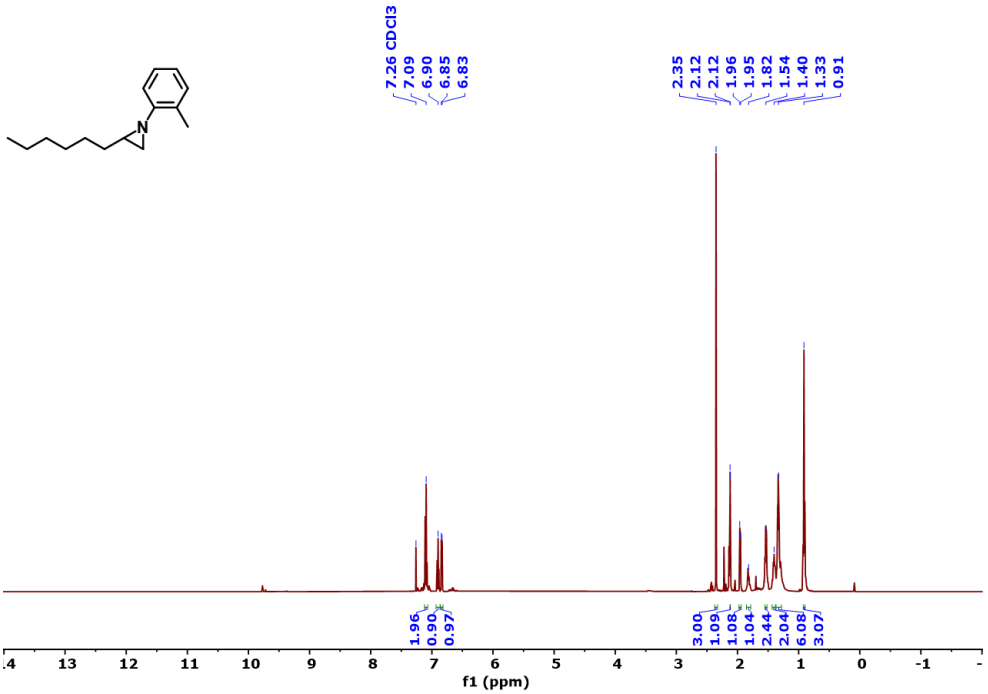


Figure S48. ^{1}H NMR of **10** in $CDCl_3$.

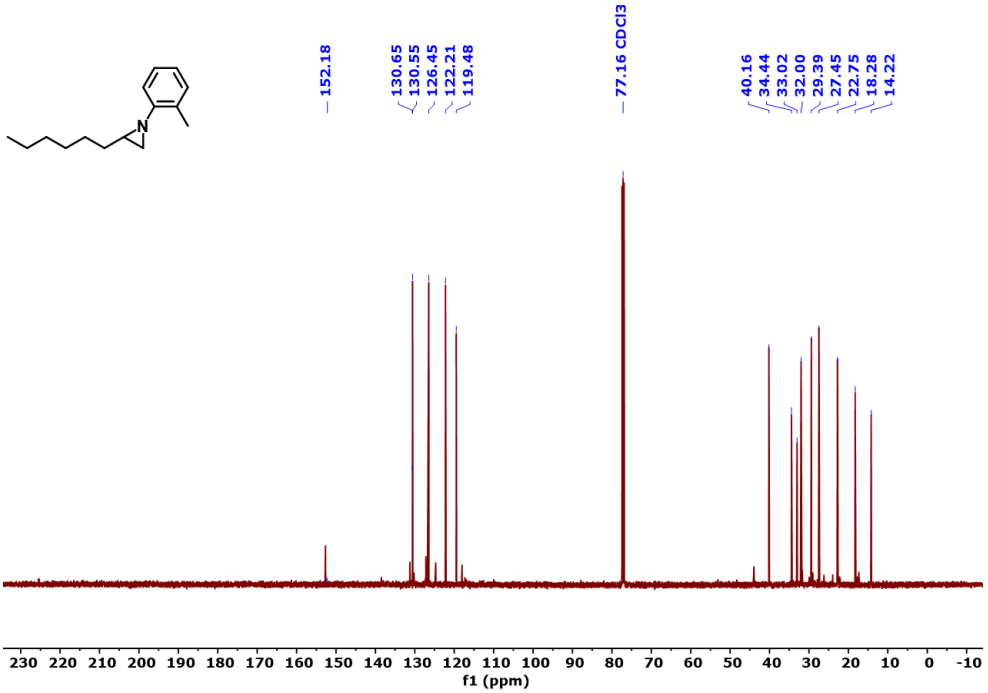


Figure S49. ^{13}C NMR of **10** in $CDCl_3$.

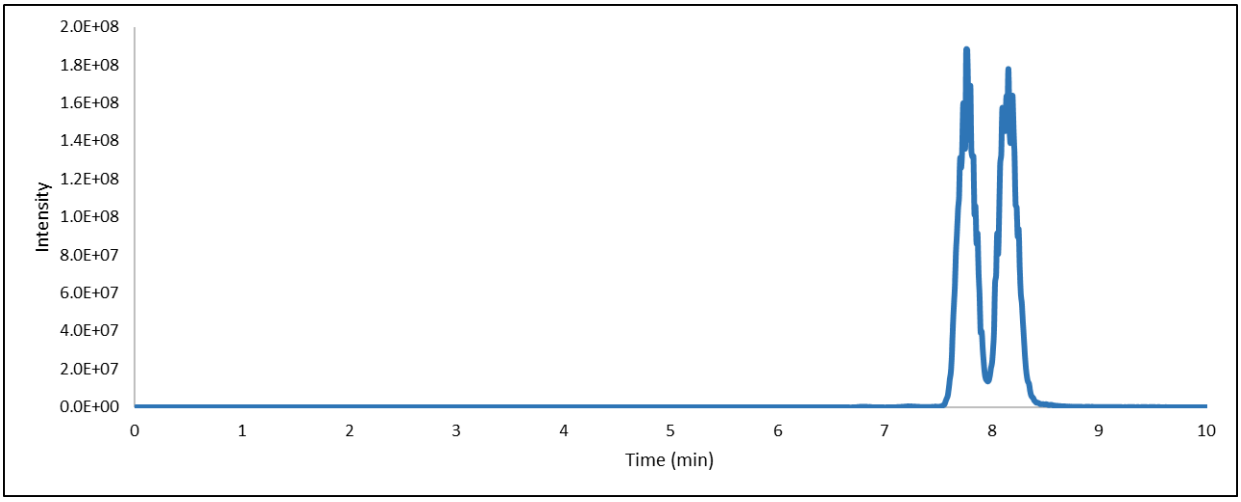


Figure S50. UHPLC Chromatogram of **10**.

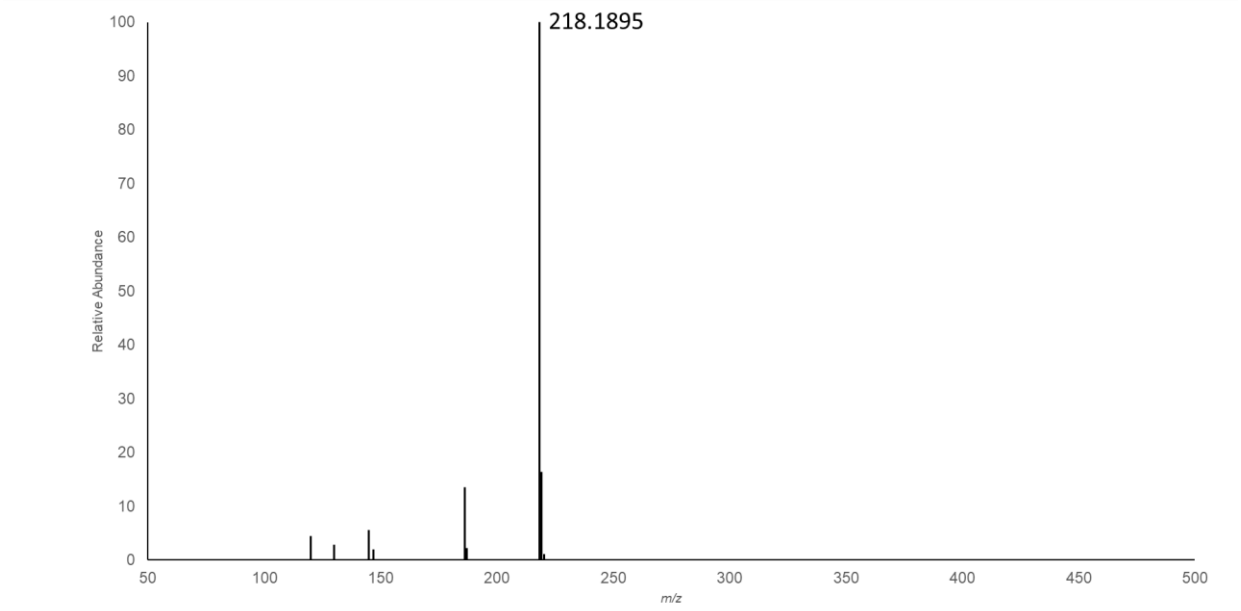


Figure S51. HRMS of **10**.

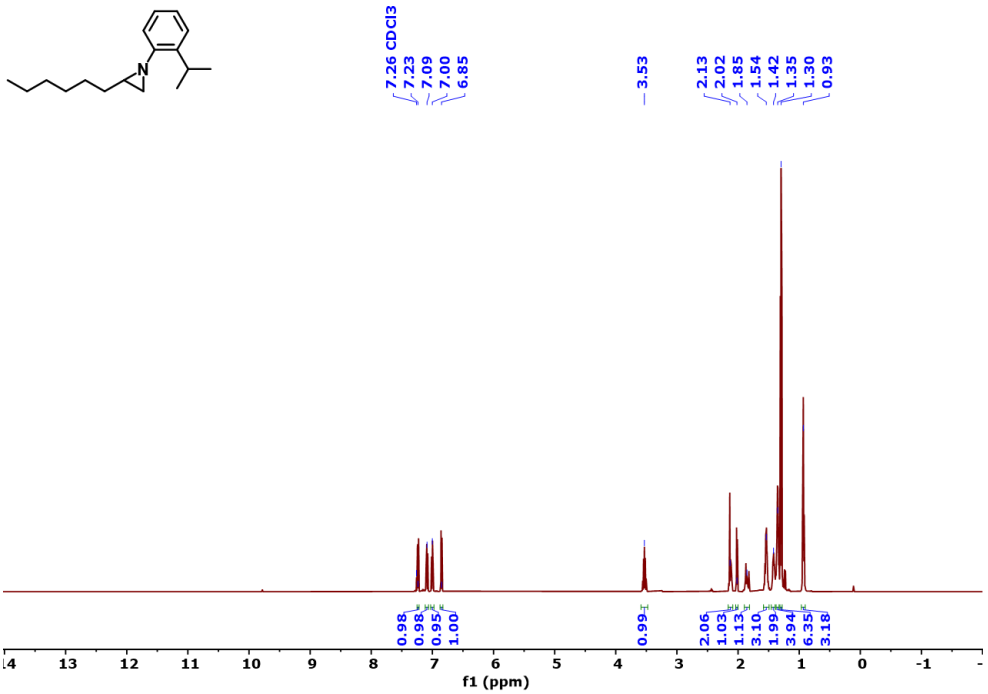


Figure S52. ^{1}H NMR of **11** in $CDCl_3$.

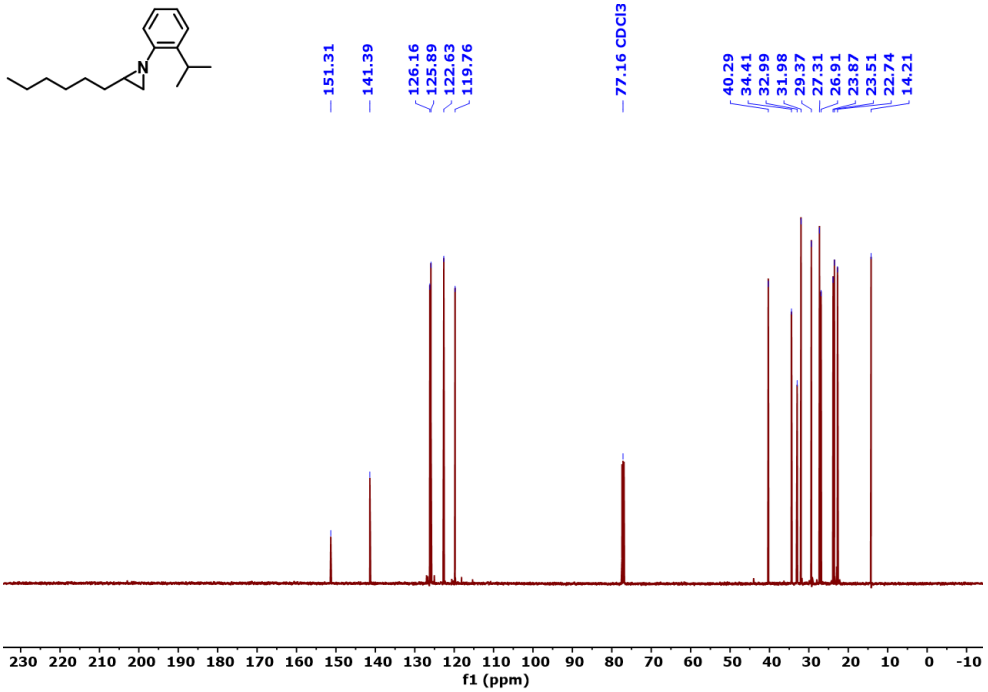


Figure S53. ^{13}C NMR of **11** in $CDCl_3$.

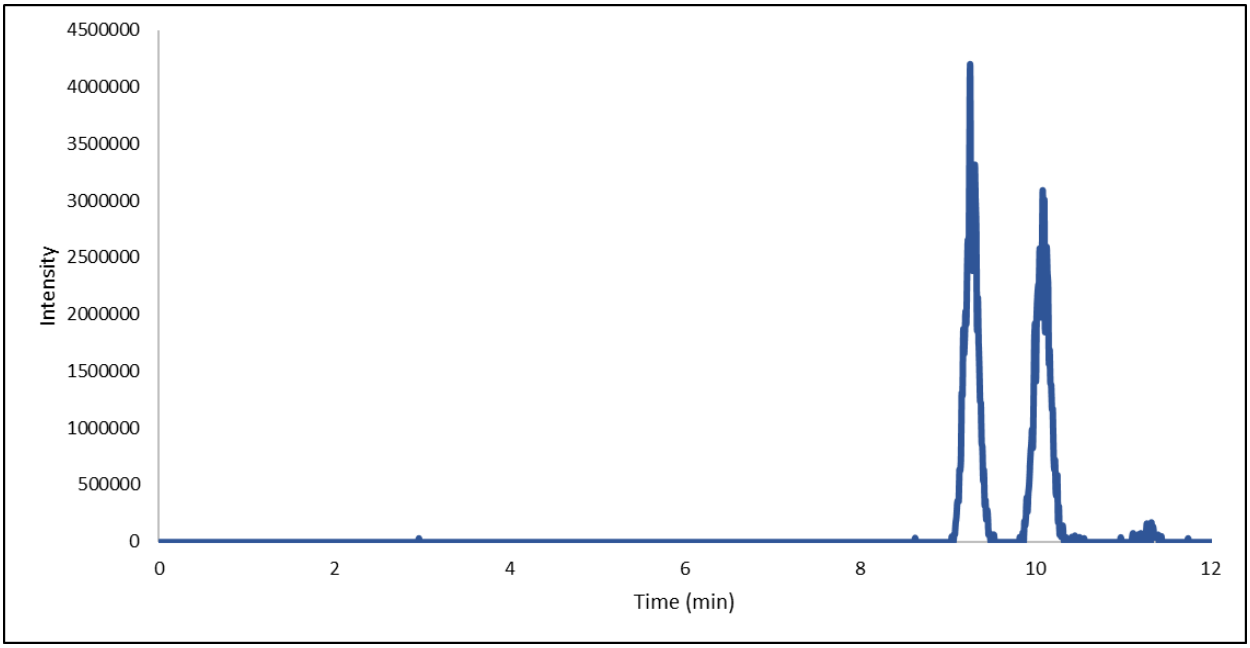


Figure S54. UHPLC Chromatogram of **11.**

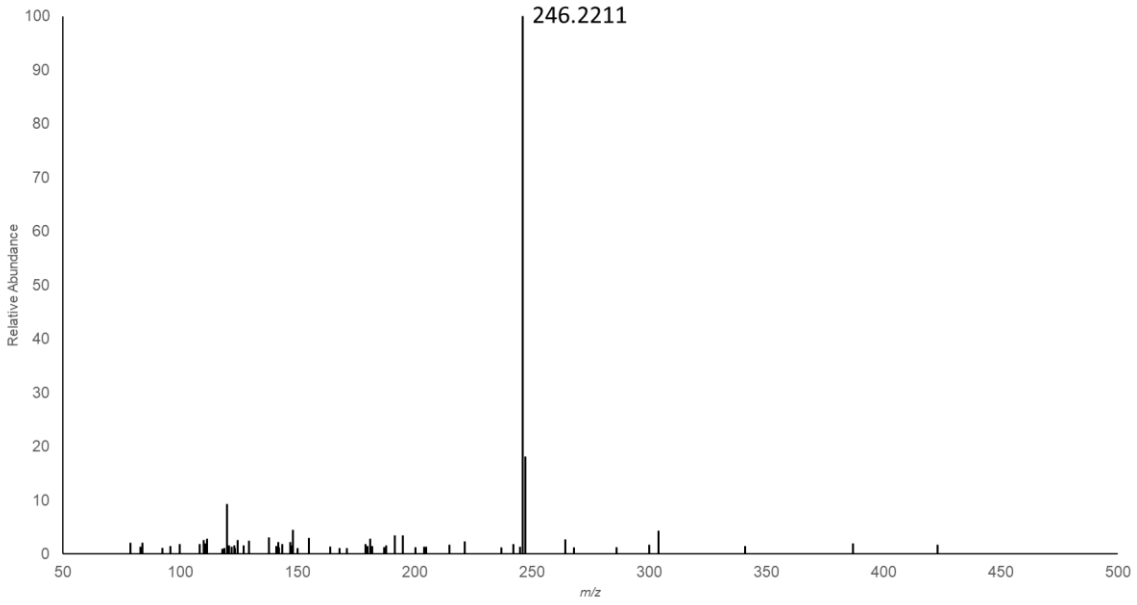


Figure S55. HRMS of **11**.

Additional single crystal X-ray structures

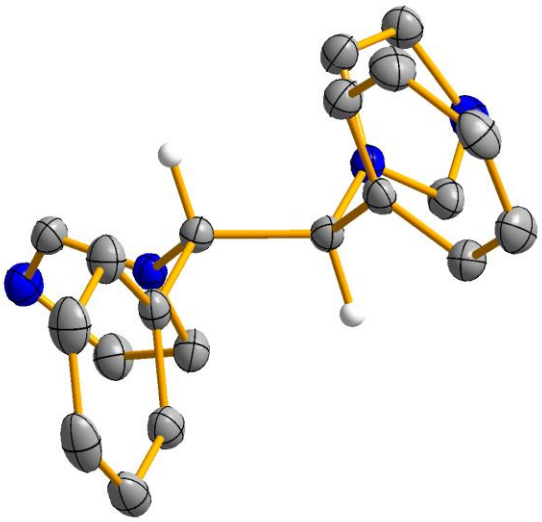


Figure S56. Solid state structures of **2**. Blue, grey, and white ellipsoids (50% probability) represent N, C, and H atoms, respectively. Solvent molecules and H-atoms on non-stereogenic atoms are omitted for clarity.

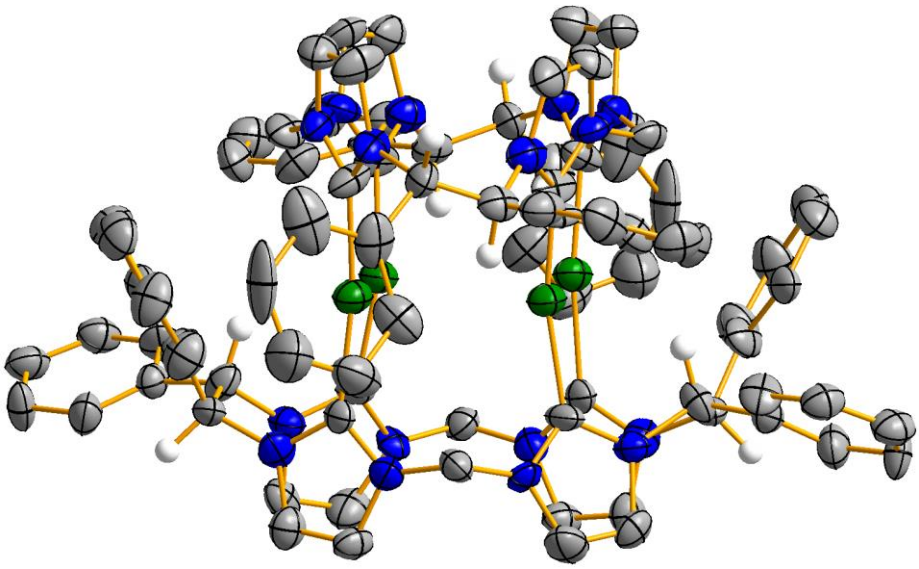


Figure S57. Solid state structures of **6b**. Green, blue, grey, and white ellipsoids (50% probability) represent Ag, N, C, and H atoms, respectively. Solvent molecules, anions and H-atoms on non-stereogenic atoms are omitted for clarity

Computational methods

Computations were performed using DFT as implemented within the Gaussian 16 quantum-chemistry software package.[5] The DFT method described below is the same as that used in our previous mechanistic study of catalytic aziridination using tetracarbene complexes. Geometries were optimized and vibrational frequencies were calculated using a combination of the TPSS exchange-correlation functional[6, 7] and the Ahlrichs def2svp basis set[8] with density fitting.[9] Following optimization, the electronic energies of the relaxed geometries were computed using the TPPSh functional[10, 11] and the Ahlrichs def2tzvpp basis set.[8] Dispersion corrections were added to the TPSS/def2svp and TPSSh/def2tzvpp computations using the Grimme's D3 method[12] with Becke-Johnson damping parameters.[13] The standard free energy of a species was calculated by adding a free-energy correction to the electronic energy, calculated using TPSS/def2svp for the standard conditions of 1 atm and 298 K. All electronic wavefunctions were checked for stability and the success of geometry optimizations was verified by ensuring that minimum-energy geometries had real vibrational frequencies whereas transition-state geometries had a single imaginary vibrational frequency along the reaction coordinate and real frequencies along the other coordinates. Free energies are reported relative to the sum of free energies of the tetracarbene iron complex and reactants.

Additional computational results

Figure S58 shows the free-energy pathway for the reaction between the new tetracarbene iron complex (**7**) and *p*-tolyl azide to form an iron imide. Overall, the *p*-tolyl iron imide formed with **7** is considerably less thermally stable compared to the *p*-tolyl iron imides formed with $[(^{Et,Me}TC^{H})Fe(NCCH_3)_2](PF_6)_2$.[14] In further contrast to $[(^{Et,Me}TC^{H})Fe(NCCH_3)_2](PF_6)_2$, the *S* = 0 (singlet) *p*-tolyl iron imide is slightly more stable (ΔG = -28.0 kcal/mol) than the *S* = 1 (triplet) *p*-tolyl imide (ΔG = -26.5 kcal/mol) for **7**. Finally, the free energy of activation to form the *S* = 1 (triplet) *p*-tolyl imide ($\Delta G^{‡}$ = 20.7 kcal/mol) is significantly greater with **7** than with $[(^{Et,Me}TC^{H})Fe(NCCH_3)_2](PF_6)_2$.

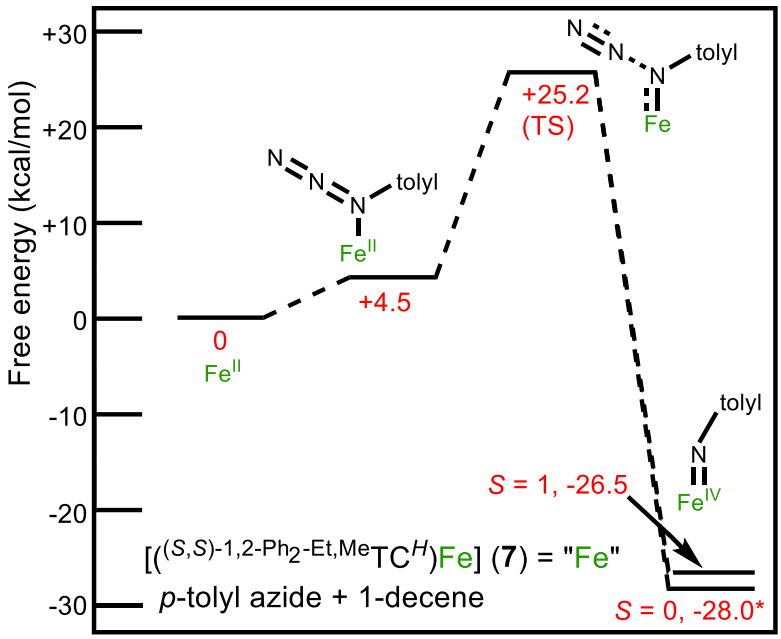


Figure S58. Free-energy pathway of formation of *p*-tolyl imide from the reaction of **7** with *p*-tolyl azide. The species in (*S* = 0) singlet state is indicated with an "*"; all other species are in the (*S* = 1) triplet state.

Table S1 shows the energetics of iron imide formation from reactions of **7** with *p*-tolyl azide, **7** with *o*-tolyl azide, and **7** with mesityl azide. The free energy of activation to form the iron imide ($\Delta G^{\ddagger} = \Delta G_{TS} - \Delta G_{\alpha\text{-bound azide}}$) increases in the order *p*-tolyl azide < *o*-tolyl azide < mesityl azide, whereas the thermal stability of the iron imide increases in the order *o*-tolyl azide < *p*-tolyl azide < mesityl azide. We note that the (*S* = 1) triplet state is more stable than the (*S* = 0) singlet state for *o*-tolyl imide and mesityl imide.

Table S1. Free energies of intermediates and transition state in the pathways to form iron imides from reactions of **7** with *p*-tolyl azide, **7** with *o*-tolyl azide, and **7** with mesityl azide.

Azide	$\Delta G_{\alpha\text{-bound azide}}$ (kcal/mol)	ΔG_{TS} (kcal/mol)	$\Delta G^{\ddagger}$ (kcal/mol)	ΔG_{Imide} (*S* = 1) (kcal/mol)	ΔG_{Imide} (*S* = 0) (kcal/mol)
p-tolyl azide	4.5	25.2	20.7	-26.5	-28.0
o-tolyl azide	10.0	31.2	21.2	-22.7	-19.3
mesityl azide	12.1	40.0	27.9	-30.6	-25.6

References

1. J. F. DeJesus and D. M. Jenkins, *Eur. J. Chem.*, 2020, **26**, 1429-1435.
2. M. R. Anneser, S. Haslinger, A. Pothig, M. Cokoja, J. M. Basset and F. E. Kuhn, *Inorg. Chem.*, 2015, **54**, 3797-3804.
3. J. Liu, J. Chen, J. Zhao, Y. Zhao, L. Li and H. Zhang, *Synthesis*, 2003, 2661-2666.
4. S. A. Cramer and D. M. Jenkins, *J. Am. Chem. Soc.*, 2011, **133**, 19342-19345.
5. 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, Gaussian, Inc., Wallingford CT, 2016.
6. J. P. Perdew, J. Tao, V. N. Staroverov and G. E. Scuseria, *J. Chem. Phys.*, 2004, **120**, 6898-6911.
7. J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Let.*, 2003, **91**, 146401.
8. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
9. F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057-1065.
10. V. N. Staroverov, G. E. Scuseria, J. Tao and J. P. Perdew, *J. Chem. Phys.*, 2003, **119**, 12129-12137.
11. V. N. Staroverov, G. E. Scuseria, J. Tao and J. P. Perdew, *J. Chem. Phys.*, 2004, **121**, 11507-11507.
12. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
13. S. Grimme, S. Ehrlich and L. Goerigk, *J. Computat. Chem.*, 2011, **32**, 1456-1465.
14. S. B. Isbill, P. P. Chandrachud, J. L. Kern, D. M. Jenkins and S. Roy, *ACS Catal.*, 2019, **9**, 6223-6233.