Triazole vs Triazolium Carbene Ligands in the Site-Selective Cyclometallation of *o*-Carboranes by M(III) (M=Ir,Rh) Complexes

María Frutos,[a] Mar Gómez-Gallego,*,[a] Elena A. Giner,[a] Miguel A. Sierra,*,[a] Carmen Ramírez de Arellano[b]

[a]Departamento de Química Orgánica, Facultad de Ciencias Químicas, Centro de Innovación en Química Avanzada (ORFEO-CINQA). Universidad Complutense, 28040 Madrid, Spain.

[b]Departamento de Química Orgánica, Facultad de Química, Centro de Innovación en Química Avanzada (ORFEO-CINQA). Universidad de Valencia, 46100-Valencia, Spain.

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1. Experimental General

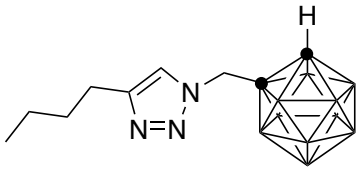
Unless noted otherwise, all manipulations were carried out under an argon atmosphere using standard Schlenk techniques. CH_2Cl_2 was dried by passage through solvent purification columns containing activated alumina. MeCN and toluene were HPLC grade and were used without further purification. All reagents were obtained from commercial sources and used without further purification, unless noted otherwise. Flash column chromatography was performed using silica gel (Merck, n° 9385, 230-400 mesh). ^{1}H and $^{13}C\{^{1}H\}$ and $^{11}B\{^{1}H\}$ NMR spectra were recorded at 300 or 500 MHz (^{1}H NMR), at 75 or 125 MHz ($^{13}C\{^{1}H\}$NMR) and at 160 MHz ($^{11}B\{^{1}H\}$ NMR) using $CDCl_3$ and acetone-d_6, as solvents with the residual solvent signal as internal reference ($CDCl_3$, 7.26 and 77.2 ppm), (acetone-d_6, 2.05 and 29.84 ppm). The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), quint (quintet), sept (septet), ddt (doublet of doublet of triplets) and br (broad). High-resolution mass spectrometry (HRMS) by the ESI technique was performed with an Agilent 6500 accurate mass apparatus with a Q-TOF analyser. IR spectra were recorded on a MIR (8000-400 cm^{-1}) spectrometer as solid films by slow evaporation of the solvent using the attenuated total reflectance (ATR) technique. Cyclic voltammograms were recorded using a Metrohm Autolab Potentiostat model PGSTAT302N with a glassy carbon working electrode, Ag/AgCl 3 M as reference and a Pt wire counter electrode. All the measurements were performed under Ar, at room temperature from CH_3CN solutions containing 0.1 M $[NBu_4]PF_6$ as supporting electrolyte, with analyte concentrations of 1 mM (scan rate 0.1 V/s).

Phenylacetylene **1a** and 1-hexyne **1b** were obtained from commercial sources and used without any further purification. *o*-Carboranylmethyl azide was synthetized from *o*-carborane in two steps as previously described.[1] Compounds **1c**,[2] **1d**,[3] **2a**,[1c] **2c**,[4] $[IrCp^*Cl_2]_2$[5] and $[RhCp^*Cl_2]_2$[5] were prepared following previously reported methods.

2. General procedure for the synthesis of 1,2,3-triazoles 2

A mixture of organic azide (1.10 equiv), alkyne (1.00–1.50 equiv) and $Cu(OAc)_2 \cdot H_2O$ (0.08 equiv) was stirred in toluene at 50 °C overnight. The reaction was allowed to reach rt. The crude was filtered through a plug of celite. The solvent was removed under *vacuum* to afford the corresponding reaction products, which were purified through a short pad of SiO_2 when needed.

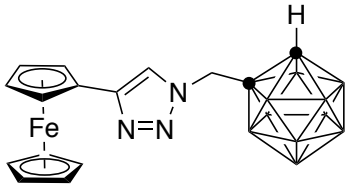
Compound 2b



Following the general procedure, a mixture of azide (300 mg, 1.50 mmol, 1.00 equiv), alkyne **1b** (371 mg, 4.50 mmol, 3.00 equiv) and $Cu(OAc)_2 \cdot H_2O$ (24 mg, 0.12 mmol, 0.08 equiv) was stirred in toluene (20 mL) at 50 °C overnight. The crude was diluted in CH_2Cl_2 and filtered through a plug of celite. The solvent was removed under *vacuum* and the resulting residue was purified (SiO_2, Hex/AcOEt 8:2) to yield **2b** as a white solid (372 mg, 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (s, 1H, N_3C=CH), 4.97 (s, 2H, NCH_2), 3.87 (br s, 1H, CH carborane), 2.74 (t, *J* = 7.64 Hz, 2H, CH_2), 1.67 (quint, *J* = 7.64 Hz, 2H, CH_2), 1.39 (sep, *J* = 7.37 Hz, 2H, CH_2), 0.95 (t, *J* = 7.37 Hz, 3H, CH_3), 2.85–0.82 (m, 10H, BH carborane). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 149.9 (C, N_3C=CH, seen in HMBC), 122.4 (CH, N_3C=CH, seen in HMQC), 71.6 (C, carborane), 58.8 (CH, carborane), 53.9 (NCH_2), 31.4 (CH_2), 25.3 (CH_2), 22.4 (CH_2), 13.9 (CH_3). **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$) δ –1.1, –4.4, –9.5, –11.7, –12.4. **IR (CH_2Cl_2) $\nu_{máx}$** 2959, 2923, 2586, 1460, 1225, 1047, 726. **HRMS (ESI)** *m/z* calculated for $C_9H_{24}B_{10}N_3$: 282.29725 $[M+H]^+$, found: 282.29606.

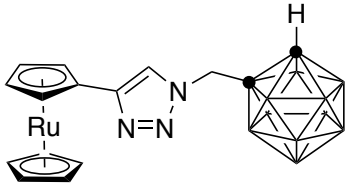
Compound 2c



Following the general procedure, a mixture of azide (200 mg, 1.00 mmol, 1.10 equiv), alkyne **1c** (192 mg, 0.91 mmol, 1.00 equiv) and $Cu(OAc)_2 \cdot H_2O$ (15 mg, 0.07 mmol, 0.08 equiv) in toluene (15 mL) was stirred at 50 °C overnight. The reaction was allowed to reach rt. The crude was filtered through a plug of celite. The solvent was removed under *vacuum* and the resulting residue was purified (SiO_2, Hex/AcOEt 8:2) to yield **2c** as an orange solid (338 mg, 91%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (s, 1H, N_3C=CH), 5.00 (s, 2H, NCH_2), 4.76 (br s, 2H, Cp), 4.36 (br s, 2H, Cp), 4.09 (s, 5H, Cp), 3.91 (br s, 1H, CH carborane), 3.29–0.99 (m, 10H, BH carborane). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 148.3 (C, N_3C=CH), 119.8 (CH, N_3C=CH), 74.1 (C, Cp), 71.7 (C, carborane), 69.8 (5CH, Cp), 69.2 (2CH, Cp), 66.9 (2CH, Cp), 58.9 (CH, carborane), 54.0 (NCH_2). **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$) δ –0.6, –1.5, –3.9, –4.8, –9.0, –12.1, –12.9 . **IR (CH_2Cl_2) $\nu_{máx}$** 3050, 2925, 2855, 2598, 1711, 1463, 1225, 1047, 823. **HRMS (ESI)** *m/z* calculated for $C_{15}H_{24}B_{10}N_3Fe$: 410.23251 $[M+H]^+$, found: 410.23326.

Compound 2d



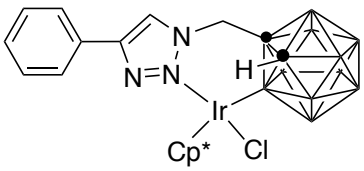
Following the general procedure, a mixture of azide (86 mg, 0.43 mmol, 1.10 equiv), alkyne

1d (100 mg, 0.39 mmol, 1.00 equiv) and $Cu(OAc)_2 \cdot H_2O$ (6 mg, 0.03 mmol, 0.08 equiv) in toluene (10 mL) was stirred at 50 °C overnight. The reaction was allowed to reach rt. The crude was filtered through a plug of celite. The solvent was removed under *vacuum* and the resulting residue was purified (SiO_2, Hex/AcOEt 7:3) to yield **2d** as a white solid (146 mg, 82%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (s, 1H, N_3C=CH), 5.14 (t, *J* = 1.69 Hz, 2H, Cp), 4.95 (s, 2H, NCH_2), 4.68 (t, *J* = 1.69 Hz, 2H, Cp), 4.48 (s, 5H, Cp), 3.88 (br s, 1H, CH carborane), 3.12–0.64 (m, 10H, BH carborane). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 147.6 (C, N_3C=CH), 120.0 (CH, N_3C=CH), 77.7 (C, Cp), 71.7 (C, carborane), 71.6 (5CH, Cp), 71.1 (2CH, Cp), 69.4 (2CH, Cp), 58.9 (CH, carborane), 53.9 (NCH_2). **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$) δ –1.1, –4.3, –9.4, –12.4. **IR (CH_2Cl_2) $\nu_{máx}$** 2580, 1717, 1334, 1224, 1102, 811, 738. **HRMS (ESI)** *m/z* calculated for $C_{15}H_{24}B_{10}N_3Ru$: 456.20141 $[M+H]^+$, found: 456.20171.

3. Synthesis of metallacycles 3 and 4

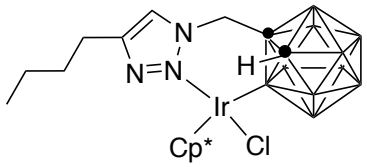
Compound 3a



A mixture of triazole **2a** (50 mg, 0.17 mmol, 1.00 equiv), NaOAc (41 mg, 0.50 mmol, 3.00 equiv) and $[IrCl_2(Cp^*)]_2$ (66 mg, 0.08 mmol, 0.50 equiv) in CH_2Cl_2 (6.5 mL) was stirred at rt overnight. The crude was filtered through a pad of celite. The solvent was removed under *vacuum* and the resulting residue was purified (SiO_2, Hex/AcOEt 8:2) to yield **3a** as a yellow solid (79 mg, 74%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 1H, N_3C=CH), 7.75–7.72 (m, 2H, Ar), 7.50–7.38 (m, 5H, Ar), 6.06 (d, *J* = 14.48 Hz, 1H, NCH_2), 5.06 (br s, 1H, CH carborane), 4.66 (d, *J* = 14.48 Hz, 1H, NCH_2), 1.76 (s, 15H, Cp*), 3.26–0.63 (m, 9H, BH carborane). **^{13}C{^{1}H} NMR** (125 MHz, *d*$_6$-acetone) δ 149.0 (C, N_3C=CH), 130.1 (2CH, Ar), 130.0 (C, Ar), 129.9 (CH, Ar), 126.8 (CH, N_3C=CH), 126.4 (2CH, Ar), 93.5 (5C, Cp*), 69.1 (C, carborane), 63.5 (CH, carborane), 55.2 (NCH_2), 9.2 ($5CH_3$, Cp*). **^{11}B{^{1}H} NMR** (160 MHz, *d*$_6$-acetone) δ –3.9, –5.4, –9.8, –10.6, – 12.2, –13.3. **IR (acetone) $\nu_{máx}$** 2957, 2573, 1466, 1092, 1018, 810, 759, 690. **HRMS (ESI)** *m/z* calculated for $C_{21}H_{33}B_{10}N_3Ir$: 628.32939 $[M–Cl]^+$, found: 628.33059

Compound 3b

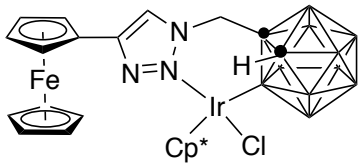


A mixture of triazole **2b** (40 mg, 0.14 mmol, 1.00 equiv), NaOAc (35 mg, 0.43 mmol, 3.00 equiv) and $[IrCl_2(Cp^*)]_2$ (57 mg, 0.07 mmol, 0.50 equiv) in CH_2Cl_2 (5 mL) was stirred at rt overnight. The crude was filtered through a pad of celite. The solvent was removed under *vacuum* and the resulting residue was purified (SiO_2, CH_2Cl_2) to yield **3b** as a yellow solid (47 mg, 52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (s, 1H, N_3C=CH), 5.93 (d, *J* = 14.50 Hz, 1H, NCH_2), 5.02 (br s, 1H, CH carborane), 4.54 (d, *J* = 14.50 Hz, 1H, NCH_2), 2.68 (t, *J* = 7.57 Hz, 2H, CH_2), 1.70 (s, 15H, Cp*), 1.66 (ddt, *J* = 3.30 Hz, *J* = 7.40 Hz, *J* = 10.73 Hz, 2H, CH_2), 1.38 (sep, *J* = 7.40 Hz, 2H, CH_2), 0.95 (t, *J* = 7.40 Hz, 3H, CH_3), 3.02–1.46 (m, 9H, BH carborane). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 149.3 (C, N_3C=CH), 125.7 (CH, N_3C=CH), 92.8 (5C, Cp*), 67.7 (C, carborane), 62.8 (CH, carborane), 54.6 (NCH_2), 30.7 (CH_2), 25.0 (CH_2), 22.2 (CH_2), 13.9 (CH_3), 9.1 ($5CH_3$, Cp*). **^{11}B{^{1}H} NMR** (160 MHz, *d*$_6$-acetone) δ –

3.8, –5.2, –7.4, –11.8, –13.0. **IR (CH_2Cl_2) $\nu_{máx}$** 2957, 2924, 2581, 1458, 1033, 813. **HRMS (ESI)** *m/z* calculated for $C_{19}H_{37}B_{10}IrN_3$: 608.36060 $[M–Cl]^+$, found: 608.36061.

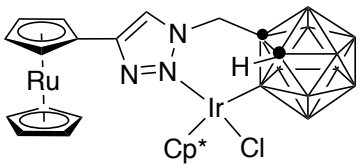
Compound 3c



A mixture of triazole **2c** (50 mg, 0.12 mmol, 1.00 equiv), Cs_2CO_3 (52 mg, 0.16 mmol, 1.30 equiv) and $[IrCl_2(Cp^*)]_2$ (49 mg, 0.06 mmol, 0.50 equiv) in CH_3CN (2.50 mL) was stirred at 60 °C in a sealed tube for 4 days. The reaction mixture was allowed to reach rt. The crude was filtered through a pad of celite. The solvent was removed under *vacuum* and the resulting residue was purified (SiO_2, Hex/AcOEt 7:3, AcOEt, CH_2Cl_2) to yield **3c** as an orange solid (41 mg, 44%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (s, 1H, N_3C=CH), 5.98 (d, *J* = 14.46 Hz, 1H, NCH_2), 5.07 (br s, 1H, CH carborane), 4.74 (br s, 1H, Cp), 4.61 (br s, 1H, Cp), 4.57 (d, *J* = 14.46 Hz, 1H, NCH_2), 4.37 (br s, 2H, Cp), 4.09 (s, 5H, Cp), 1.76 (s, 15H, Cp*), 3.48–0.66 (m, 9H, BH carborane). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 148.4 (C, N_3C=CH), 123.2 (CH, N_3C=CH), 93.0 (5C, Cp*), 73.3 (C, carborane), 69.9 (5CH, Cp), 69.4 (2CH, Cp), 67.7 (C, carborane), 66.9 (CH, Cp), 66.6 (CH, Cp), 62.8 (CH, carborane), 54.7 (NCH_2), 9.1 ($5CH_3$, Cp*). **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$) δ –3.3, –4.4, –5.5, –6.9, –7.8, –11.3, –12.3. **IR (CH_2Cl_2) $\nu_{máx}$** 3102, 3041, 2959, 2921, 2856, 2578, 1518, 1031, 817, 737. **HRMS (ESI)** *m/z* calculated for $C_{25}H_{38}B_{10}N_3FeIr$: 736.30465 $[M–Cl]^+$, found: 736.30553.

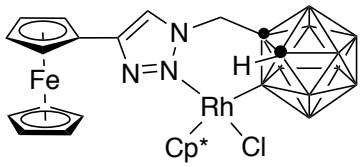
Compound 3d



A mixture of triazole **2d** (40 mg, 0.09 mmol, 1.00 equiv), Cs_2CO_3 (37 mg, 0.11 mmol, 1.30 equiv) and $[IrCl_2(Cp^*)]_2$ (35 mg, 0.04 mmol, 0.50 equiv) in CH_3CN (2 mL) was stirred at 60 °C in a sealed tube for 4 days. The reaction mixture was allowed to reach rt. The crude was filtered through a pad of celite. The solvent was removed under *vacuum* and the resulting residue was purified (SiO_2, Hex/AcOEt 7:3, AcOEt, CH_2Cl_2) to yield **3d** as an orange solid (30 mg, 46%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 1H, N_3C=CH), 5.94 (d, *J* = 14.49 Hz, 1H, NCH_2), 5.09 (dt, *J* = 1.20 Hz, 2.35 Hz, 1H, Cp), 5.32 (br s, 1H, CH carborane), 5.02 (dt, *J* = 1.20 Hz, 2.35 Hz, 1H, Cp), 4.69 (dt, *J* = 1.20 Hz, 2.35 Hz, 2H, Cp), 4.52 (d, *J* = 14.49 Hz, 1H, NCH_2), 4.48 (s, 5H, Cp), 1.73 (s, 15H, Cp*), 3.41–0.15 (m, 9H, BH carborane). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 147.6 (C, N_3C=CH), 123.2 (CH, N_3C=CH), 92.9 (5C, Cp*), 77.0 (C, Cp), 71.8 (5CH, Cp), 71.2 (CH, Cp), 71.1 (CH, Cp), 69.3 (CH, Cp), 69.1 (CH, Cp), 67.5 (C, carborane seen in HMBC), 62.7 (CH, carborane), 54.7 (NCH_2), 9.1 ($5CH_3$, Cp*). **^{11}B{^{1}H} NMR** (160 MHz, *d*$_6$-acetone) δ –3.9, –5.2, –7.6, –11.8, –12.2, –13.3. **IR (CH_2Cl_2) $\nu_{máx}$** 3105, 3041, 2957, 2918, 2856, 2578, 1450, 1029, 811, 737. **HRMS (ESI)** *m/z* calculated for $C_{25}H_{38}B_{10}N_3RuIr$: 782.27386 $[M–Cl]^+$, found: 782.27575.

Compound 4c

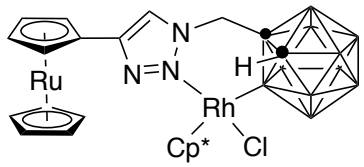


A mixture of triazole **2c** (50 mg, 0.12 mmol, 1.00 equiv), Cs_2CO_3 (52 mg, 0.16 mmol, 1.30 equiv) and $[RhCl_2(Cp^*)]_2$ (38 mg, 0.06 mmol, 0.50 equiv) in CH_3CN (2.50 mL) was stirred at 65 °C in a sealed tube for 4 days. The reaction mixture was allowed to reach rt. The crude was

filtered through a pad of celite. The solvent was removed under *vacuum* and the resulting residue was purified (SiO_2, Hex/AcOEt 7:3, AcOEt, CH_2Cl_2) to yield **4c** as an orange solid (29 mg, 35%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (s, 1H, N_3C=CH), 5.00 (d, *J* = 14.95 Hz, 1H, NCH_2), 4.76 (q, *J* = 1.66 Hz, 1H, Cp), 4.71 (q, *J* = 1.66 Hz, 1.50 Hz, 1H, Cp), 4.66 (d, *J* = 14.95 Hz, 1H, NCH_2), 4.30 (t, *J* = 1.83 Hz, 2H, Cp), 4.08 (s, 5H, Cp), 3.71 (br s, 1H, CH carborane), 2.08 (s, 15H, Cp*), 3.42–0.73 (m, 9H, BH carborane). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 147.2 (C, N_3C=CH), 120.5 (CH, N_3C=CH), 104.0 (5C, Cp*, $J_{Rh,C}$ = 6.54 Hz), 74.9 (C, Cp), 70.8 (C, carborane, seen in HMBC) 69.8 (5CH, Cp), 68.9 (2CH, Cp), 66.8 (2CH, Cp), 58.1 (NCH_2), 56.6 (CH, carborane, $J_{Rh,C}$ = 12.13 Hz), 9.8 ($5CH_3$, Cp*). **^{11}B{^{1}H} NMR** (160 MHz, *d*$_6$-acetone) δ 9.2, –1.3, –7.0, –9.4, –11.8, – 16.9, –18.2, –21.6. **IR (CH_2Cl_2) $\nu_{máx}$** 3098, 2958, 2923, 2855, 2538, 1469, 1381, 1033, 819. **HRMS (ESI)** *m/z* calculated for $C_{25}H_{38}B_{10}N_3FeRh$: 647.24804 $[M–Cl]^+$, found: 647.24613.

Compound 4d



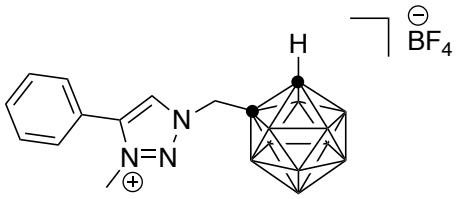
A mixture of triazole **2d** (40 mg, 0.09 mmol, 1.00 equiv), Cs_2CO_3 (37 mg, 0.11 mmol, 1.30 equiv) and $[RhCl_2(Cp^*)]_2$ (27 mg, 0.04 mmol, 0.50 equiv) in CH_3CN (2 mL) was stirred at 65 °C in a sealed tube for 4 days. The reaction mixture was allowed to reach rt. The crude was filtered through a pad of celite. The solvent was removed under *vacuum* and the resulting residue was purified (SiO_2, Hex/AcOEt 7:3, AcOEt, CH_2Cl_2) to yield **4d** as an orange solid (27 mg, 46%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (s, 1H, N_3C=CH), 5.16 (q, *J* = 1.45 Hz, 1H, Cp), 5.12 (q, *J* = 1.45 Hz, 1H, Cp), 4.99 (d, *J* = 14.94 Hz, 1H, NCH_2), 4.66 (t, *J* = 1.73 Hz, 2H, Cp) , 4.61 (d, *J* = 14.94 Hz, 1H, NCH_2), 4.49 (s, 5H, Cp), 3.68 (br s, 1H, CH carborane), 2.08 (s, 15H, Cp*), 3.11–0.50 (m, 9H, BH carborane). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 146.5 (C, N_3C=CH), 120.6 (CH, N_3C=CH), 103.9 (C, Cp*, $J_{Rh,C}$ = 6.44 Hz), 78.5 (C, Cp), 71.7 (5CH, Cp), 70.9 (2CH, Cp, $J_{Rh,C}$ = 1.39 Hz), 69.6 (C, carborane), 69.4 (2CH, Cp), 58.1 (NCH_2), 56.5 (CH, carborane), 9.8 ($5CH_3$, Cp*). **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$) δ 9.2, –1.5, –9.5, –11.7, –18.3, –21.5. **IR (CH_2Cl_2) $\nu_{máx}$** 2959, 2922, 2856, 2536, 1468, 1381, 1095, 1028, 809, 735. **HRMS (ESI)** *m/z* calculated for $C_{25}H_{38}B_{10}N_3RuRh$: 693.21693 $[M–Cl]^+$, found: 693.21645.

4. General procedure for the synthesis of triazolium salts 5

Triazole (1.00 equiv) and Meerwein's salt (1.30 equiv) were stirred under argon at rt in anhydrous CH_2Cl_2 until complete consumption of the starting material (^{1}H NMR analysis). The reaction was quenched with some drops of methanol. The volatiles were removed under *vacuum* to afford the corresponding reaction product without further purification. In some cases, the product was washed with a mixture of CH_2Cl_2:pentane to remove traces of starting material.

Compound 5a

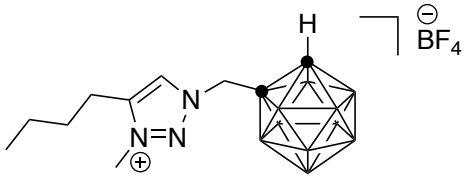


Following the general procedure, a mixture of **2a** (179 mg, 0.59 mmol, 1.00 equiv) and Me_3OBF_4 (114 mg, 0.77 mmol, 1.30 equiv) in CH_2Cl_2 (39 mL) was stirred under argon at rt

overnight. The reaction was quenched with some drops of methanol. The volatiles were removed under *vacuum* to yield **5a** as a white solid (220 mg, 92%).

^{1}H NMR (300 MHz, d_6-acetone) δ 9.17 (s, 1H, N_3C=CH), 7.88–7.86 (m, 2H, Ar), 7.85–7.83 (m, 3H, Ar), 5.84 (s, 2H, NCH_2), 5.08 (br s, 1H, CH carborane), 4.59 (s, 3H, CH_3), 3.10–1.29 (m, 10H, BH carborane). **^{13}C{^{1}H} NMR** (75 MHz, d_6-acetone) δ l45.1 (C, N_3C=CH), 132.8 (CH, Ar), 131.2 (CH, N_3C=CH), 130.6 (2CH, Ar), 130.4 (2CH, Ar), 123.2 (C, Ar), 71.1 (C, carborane), 63.0 (CH, carborane), 56.7 (CH_2, NCH_2), 40.2 (CH_3, NCH_3). **^{11}B{^{1}H} NMR** (160 MHz, d_6-acetone) δ –0.6, –1.0, –2.2, –4.2, –9.0, –11.6, –12.5. **IR (d_6-acetone) $\nu_{máx}$** 3129, 3066, 2594, 1441, 1054, 765, 730, 697. **HRMS (ESI)** *m/z* calculated for $C_{12}H_{22}B_{10}N_3$: 316.28174 $[M]^+$, found: 316.28187.

Compound 5b

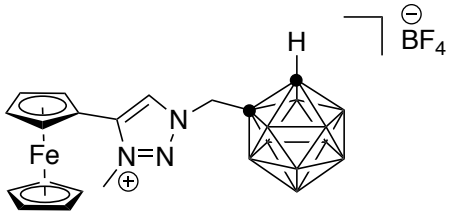


Following the general procedure, a mixture of **2b** (278 mg, 0.99 mmol, 1.00 equiv) and Me_3OBF_4 (190 mg, 1.28 mmol, 1.30 equiv) in anh CH_2Cl_2 (33 mL) was stirred under argon at rt overnight. The reaction was quenched with some drops of methanol. The volatiles were removed under *vacuum* to yield **5b** as brown solid (306 mg, 81%).

^{1}H NMR (500 MHz, d_6-acetone) δ 8.82 (s, 1H, N_3C=CH), 5.70 (s, 2H, NCH_2), 5.01 (br s, 1H, CH carborane), 4.49 (s, 3H, NCH_3), 3.08 (t, J = 7.77 Hz, 2H, CH_2), 1.81 (quint, J = 7.77 Hz, 2H, CH_2), 1.48 (sep, J = 7.39 Hz, 2H, CH_2), 0.96 (t, J = 7.39 Hz, 3H, CH_3), 2.93–1.29 (m, 10H, BH carborane). **^{13}C{^{1}H} NMR** (75 MHz, d_6-acetone) δ 146.8 (C, N_3C=CH,), 130.6 (CH, N_3C=CH), 71.1 (C, carborane), 62.8 (CH, carborane), 56.3 (NCH_2), 38.6 (NCH_3), 29.2 (CH_2),

23.4 (CH_2), 22.5 (CH_2), 13.7 (CH_3). **$^{11}B\{^1H\}$ NMR** (160 MHz, *d_6*-acetone) δ 20.3, 17.4, –0.9, –2.3, –4.3, –9.1, –11.7, –12.6. **IR (*d_6*-acetone) $\nu_{máx}$** 2583, 845, 729. **HRMS (ESI)** *m/z* calculated for $C_{10}H_{26}B_{10}N_3$: 296.31295 $[M]^+$, found: 296.31258.

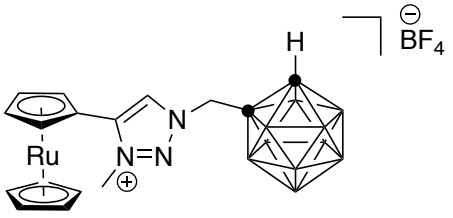
Compound 5c



Following the general procedure, a mixture of **2c** (100 mg, 0.24 mmol, 1.00 equiv) and Me_3OBF_4 (47 mg, 0.32 mmol, 1.30 equiv) in dry CH_2Cl_2 (16 mL) was stirred under argon at rt overnight. The reaction was quenched with some drops of methanol. The volatiles were removed under *vacuum* to yield **5c** as an orange solid (111 mg, 90%).

^1H NMR (300 MHz, *d_6*-acetone) δ 9.08 (s, 1H, N_3C=CH), 5.69 (s, 2H, NCH_2), 5.07 (br s, 3H, CH carborane+2H Cp), 4.70 (br s, 2H, Cp), 4.59 (s, 3H, NCH_3), 4.34 (s, 5H, Cp), 3.29–0.88 (m, 10H, BH carborane). **$^{13}C\{^1H\}$ NMR** (75 MHz, *d_6*-acetone) δ 146.2 (C, N_3C=CH), 129.8 (CH, N_3C=CH), 72.5 (2CH, Cp), 71.3 (5CH, Cp), 71.2 (C, carborane), 70.2 (2CH, Cp), 66.2 (C, Cp), 62.9 (CH, carborane), 56.5 (NCH_2), 40.4 (NCH_3). **$^{11}B\{^1H\}$ NMR** (160 MHz, *d_6*-acetone) δ 20.3, –1.0, –2.3, –4.3, –9.1, –11.7, –12.6. **IR (*d_6*-acetone) $\nu_{máx}$** 3135, 3062, 2922, 2853, 2595, 1598, 1059, 829, 754. **HRMS (ESI)** *m/z* calculated for $C_{16}H_{26}B_{10}N_3Fe$: 424.24820 $[M]^+$, found: 424.24786.

Compound 5d



Following the general procedure, a mixture of **2d** (84 mg, 0.18 mmol, 1.00 equiv) and Me_3OBF_4 (36 mg, 0.24 mmol, 1.30 equiv) in anh CH_2Cl_2 (12 mL) was stirred under argon at rt overnight. The reaction was quenched with some drops of methanol. The volatiles were removed under *vacuum* to yield **5d** as a white solid (82 mg, 82%).

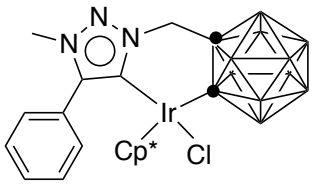
^{1}H NMR (500 MHz, d_6-acetone) δ 8.95 (s, 1H, N_3C=CH), 5.66 (s, 2H, NCH_2), 5.35 (t, J = 1.80 Hz, 2H, Cp), 5.02 (br s, 1H, CH carborane), 4.97 (t, J = 1.80 Hz, 2H, Cp), 4.73 (s, 5H, Cp), 4.53 (s, 3H, NCH_3), 2.95–1.40 (m, 10H, BH carborane). **^{13}C{^{1}H} NMR** (75 MHz, d_6-acetone) δ 144.8 (C, N_3C=CH), 130.1 (CH, N_3C=CH), 74.0 (2CH, Cp), 73.2 (5CH, Cp), 72.3 (2CH, Cp), 71.2 (C, carborane), 70.1 (C, Cp), 63.0 (CH, carborane), 56.5 (NCH_2), 40.3 (NCH_3). **^{11}B{^{1}H} NMR** (160 MHz, d_6-acetone) δ –1.0, –2.3, –4.2, –9.1, –11.7, –12.5. **IR (d_6-acetone) $\nu_{máx}$** 3034, 2924, 2864, 1602, 1313, 1075, 818. **HRMS (ESI)** *m/z* calculated for $C_{16}H_{26}B_{10}N_3Ru$: 470.21711 $[M]^+$, found: 470.21709.

5. General procedure for the synthesis of MIC carbenes

In a flask charged with 4 Å molecular sieves, a mixture of triazolium salt (1.00 equiv), NMe_4Cl (1.50 equiv) and Ag_2O (0.75 equiv) was stirred at rt, in CH_2Cl_2, in the dark, until the formation of the silver carbene (^{1}H NMR analysis). Then, the metallic salt (1.00 equiv) was added and the reaction was stirred at rt until completion (^{1}H NMR analysis). The reaction was filtered through a pad of Celite and the volatiles were removed under *vacuum* to afford the corresponding reaction products, which were purified through a short pad of SiO_2.

6. Synthesis of metallacycles 6

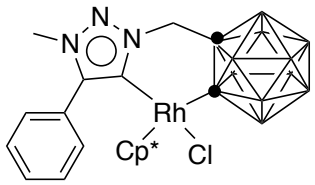
Compound 6a



Following the general procedure, a mixture of salt **5a** (60 mg, 0.15 mmol, 1.00 equiv), NMe_4Cl (24 mg, 0.22 mmol, 1.50 equiv) and Ag_2O (26 mg, 0.11 mmol, 0.75 equiv) in CH_2Cl_2 (14 mL) was stirred under argon, at rt, overnight. Next, NMe_4Cl (24 mg, 0.22 mmol, 1.50 equiv) and Ag_2O (26 mg, 0.11 mmol, 0.75 equiv) were added to the solution that was stirred at rt for other 24 h. $[IrCl_2(Cp^*)]_2$ (53 mg, 0.07 mmol, 0.45 equiv) was added and the reaction was stirred for three hours. The resulting residue was purified (SiO_2, Hex/AcOEt 7:3, CH_2Cl_2, CH_2Cl_2:9% MeOH) to yield **6a** as a yellow solid (75 mg, 79%).

^{1}H NMR (500 MHz, *d*$_6$-acetone) δ 8.02–8.00 (m, 2H, Ar), 7.56–7.48 (m, 3H, Ar), 5.10 (d, *J* = 14.57 Hz, 1H, NCH_2), 4.47 (d, *J* = 14.57 Hz, 1H, NCH_2), 4.00 (s, 3H, NCH_3), 3.46–0.61 (m, 10H, BH carborane), 1.36 (s, 15H, CH_3). **^{13}C{^{1}H} NMR** (125 MHz, *d*$_6$-acetone) δ 150.7 (C, N_3C=*C*Ir), 142.1 (C, N_3*C*=CIr), 134.1 (2CH, Ar), 130.7 (CH, Ar), 128.4 (2CH, Ar), 127.8 (C, Ar), 92.4 (C, Cp*), 73.9 (C, carborane), 58.9 (NCH_2), 48.1 (C, carborane), 38.1 (NCH_3), 9.0 (5CH_3, Cp*). **^{11}B{^{1}H} NMR** (160 MHz, *d*$_6$-acetona) δ –2.8, –5.0. –7.7, –10.0, –10.4, –12.2. **IR (*d*$_6$-acetone) $\nu_{máx}$** 3061, 2958, 2916, 2855, 2620, 2561, 1439, 1072, 10267, 766, 735, 702. **HRMS (ESI)** *m/z* calculated for $C_{22}H_{35}B_{10}IrN_3$: 642.34508 $[M–Cl]^+$, found: 642.34594.

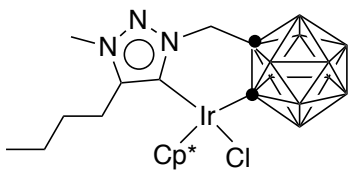
Compound 6b



Following the general procedure, a mixture of salt **5a** (70 mg, 0.17 mmol, 1.00 equiv), NMe_4Cl (29 mg, 0.26 mmol, 1.50 equiv) and Ag_2O (30 mg, 0.13 mmol, 0.75 equiv) in CH_2Cl_2 (16 mL) was stirred under argon, at rt, overnight. Next, NMe_4Cl (29 mg, 0.26 mmol, 1.50 equiv) and Ag_2O (30 mg, 0.13 mmol, 0.75 equiv) were added to the solution that was stirred at rt for other 24 h. $[RhCl_2(Cp^*)]_2$ (43 mg, 0.07 mmol, 0.40 equiv) was added and the reaction was stirred overnight. The resulting residue was purified (SiO_2, CH_2Cl_2 to CH_2Cl_2:9% MeOH) to yield **6b** as a yellow solid (59 mg, 72%).

^{1}H NMR (500 MHz, *d*$_6$-acetone) δ 8.09–8.07 (m, 2H, Ar), 7.57–7.49 (m, 3H, Ar), 5.15 (d, *J* = 14.63 Hz, 1H, NCH_2), 4.54 (d, *J* = 14.63 Hz, 1H, NCH_2), 4.03 (s, 3H, NCH_3), 3.31–0.55 (m, 10H, BH carborane), 1.34 (s, 15H, CH_3). **^{13}C{^{1}H} NMR** (125 MHz, *d*$_6$-acetone) δ 160.0 (C, N_3C=*C*Rh, $J_{Rh,C}$ = 51.85 Hz), 149.9 (C, N_3*C*=CRh), 134.0 (2CH, Ar), 130.7 (CH, Ar), 128.5 (2CH, Ar), 127.9 (C, Ar), 98.9 (C, Cp*, $J_{Rh,C}$ = 5.59 Hz), 74.6 (C, carborane), 67.7 (C, carborane), 58.9 (NCH_2), 38.2 (NCH_3), 9.4 (5CH_3, Cp*). **^{11}B{^{1}H} NMR** (160 MHz *d*$_6$-acetona) δ –2.6, –4.8, –6.3, –6.3, –8.1, –9.5, –10.0, –12.2. **IR (*d*$_6$-acetone) $\nu_{máx}$** 2920, 2852, 2572, 1437, 1167, 1067, 764, 698. **HRMS (ESI)** *m/z* calculated for $C_{22}H_{35}B_{10}N_3Rh$: 552.28944 $[M–Cl]^+$, found: 552.29047.

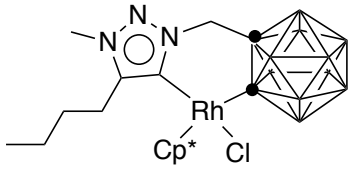
Compound 6c



Following the general procedure, a mixture of **5b** (100 mg, 0.26 mmol, 1.00 equiv), NMe_4Cl (43 mg, 0.39 mmol, 1.50 equiv) and Ag_2O (45 mg, 0.20 mmol, 0.75 equiv) in CH_2Cl_2 (24 mL) was stirred under argon, at rt, overnight. Next, NMe_4Cl (43 mg, 0.39 mmol, 1.50 equiv) and Ag_2O (45 mg, 0.20 mmol, 0.75 equiv) were added to the solution that was stirred at rt for other 24 h. $[IrCl_2(Cp^*)]_2$ (83 mg, 0.10 mmol, 0.40 equiv) was added and the reaction was stirred for three hours. The resulting residue was purified (SiO_2, Hex/AcOEt, 8:2) to yield **6c** as a yellow solid (74 mg, 54%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.87 (d, *J* = 14.07 Hz, 1H, NCH_2), 4.23 (d, *J* = 14.07 Hz, 1H, NCH_2), 4.05 (s, 3H, NCH_3), 2.92–2.86 (m, 1H, CH_2), 2.67–2.61 (m, 1H, CH_2), 2.01–1.90 (m, 3H, CH_2), 1.59 (s, 15H, CH_3), 1.53–1.42 (m, 3H, CH_2), 0.98 (t, *J* = 6.91 Hz, CH_3), 3.21–0.71 (m, 10H, BH carborane). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 149.3 (C, N_3C=CIr), 144.1 (C, N_3C=*C*Ir), 91.7 (C, Cp*), 72.2 (C, carborane), 57.9 (NCH_2), 46.5 (C, carborane), 36.8 (NCH_3), 31.8 (CH_2), 25.0 (CH_2), 23.3 (CH_2), 13.9 (CH_3), 9.2 ($5CH_3$, Cp*). **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$) δ –2.6, –4.5, –5.6, –7.8, –10.0, –12.3. **IR (*d*$_6$-acetone) $\nu_{máx}$** 2958, 2922, 2855, 2620, 2560, 1453, 1351, 1029, 735. **HRMS (ESI)** *m/z* calculated for $C_{20}H_{39}B_{10}N_3Ir$: 622.37630 $[M–Cl]^+$, found: 622.37753.

Compound 6d

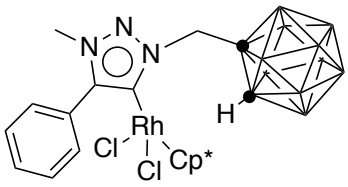


Following the general procedure, a mixture of **5b** (100 mg, 0.26 mmol, 1.00 equiv), NMe_4Cl (43 mg, 0.39 mmol, 1.50 equiv) and Ag_2O (45 mg, 0.20 mmol, 0.75 equiv) in CH_2Cl_2 (24 mL) was stirred under argon, at rt, overnight. Next, NMe_4Cl (43 mg, 0.39 mmol, 1.50 equiv)

and Ag_2O (45 mg, 0.20 mmol, 0.75 equiv) were added to the solution that was stirred at rt for other 24 h. $[RhCl_2(Cp^*)]_2$ (64 mg, 0.10 mmol, 0.40 equiv) was added and the reaction was stirred for two hours. The resulting residue was purified (SiO_2, CH_2Cl_2) to yield **6d** as a yellow solid (101 mg, 89%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.91 (d, J = 14.20 Hz, 1H, NCH_2), 4.29 (d, J = 14.20 Hz, 1H, NCH_2), 4.06 (s, 3H, NCH_3), 3.01–2.91 (m, 1H, CH_2), 2.74–2.64 (m, 1H, CH_2), 2.03–1.91 (m, 2H, CH_2), 1.56 (s, 15H, CH_3), 1.53–1.42 (m, 2H, CH_2), 0.98 (t, J = 7.04 Hz, CH_3), 3.51–0.75 (m, 10H, BH carborane). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 161.2 (C, N_3C=*C*Rh, $J_{Rh,C}$ = 50.69 Hz), 148.9 (C, N_3*C*=CRh), 98.4 (C, Cp*, $J_{Rh,C}$ = 5.63 Hz), 73.2 (C, carborane), 68.8 (C, carborane, seen in HMBC), 57.9 (NCH_2), 36.9 (NCH_3), 31.1 (CH_2), 25.6 (CH_2), 23.3 (CH_2), 13.9 (CH_3), 9.6 ($5CH_3$, Cp*). **^{11}B{^{1}H} NMR** (160 MHz *d*$_6$-acetona) δ –2.3, –4.3, –6.3, –8.2, –9.6, –12.2. **IR (*d*$_6$-acetone) $\nu_{máx}$**, 2958, 2924, 2867, 2619, 2562, 1452, 1351, 1025, 735. **HRMS (ESI)** *m/z* calculated for $C_{20}H_{39}B_{10}N_3Rh$: 532.32065 $[M–Cl]^+$, found: 532.32329.

7. Synthesis of compound 7

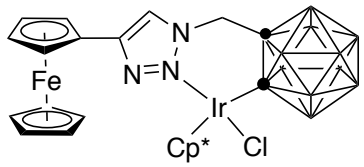


Following the general procedure, a mixture of **5a** (60 mg, 0.15 mmol, 1.00 equiv), NMe_4Cl (24 mg, 0.22 mmol, 1.50 equiv) and Ag_2O (26 mg, 0.11 mmol, 0.75 equiv) in CH_2Cl_2 (14 mL) was stirred under argon, at rt, overnight. Next, $[RhCl_2(Cp^*)]_2$ (41 mg, 0.07 mmol, 0.45 equiv) was added and the reaction was stirred overnight. The resulting residue was purified (SiO_2, CH_2Cl_2:2% MeOH) to yield **7** as a yellow solid (52 mg, 60%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76–7.74 (m, 2H, Ar), 7.51–7.50 (m, 3H, Ar), 5.74 (s, 2H,

NCH_2), 5.59 (br s, 1H, CH carborane), 3.89 (s, 3H, NCH_3), 1.31 (s, 15H, CH_3), 3.21–0.39 (m, 10H, BH carborane). **IR (d_6-acetone) $\nu_{máx}$** 2923, 2576, 1450, 1262, 1062, 1021, 811, 730, 699. **HRMS (ESI)** *m/z* calculated for $C_{22}H_{36}B_{10}ClN_3Rh$: 589.26369 $[M–Cl]^+$, found: 589.26400.

8. Synthesis of compound 8



Triazole **2c** (150 mg, 0.37 mmol, 1.00 equiv) was dissolved in dry THF (9 mL) under Ar. The solution was kept at 0 ºC. Then, ^{n}BuLi (solution 1.6 M in hexanes) (460 µL, 0.73 mmol, 2.00 equiv) was added dropwise. The reaction mixture was stirred at 0 ºC for 1 h. Next, $[IrCp^*Cl_2]_2$ (146 mg, 0.18 mmol, 0.50 equiv) was added in one portion and the resulting mixture was stirred at rt overnight. The crude was filtered through a plug of celite, and the volatiles were removed under *vaccum*. The resulting residue was purified (SiO_2, Hex/AcOEt 8:2) to yield **8** as a yellow solid (106 mg, 43%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (s, 1H, N_3C=CH), 6.17 (d, *J* = 14.41 Hz, 1H, NCH_2), 4.69 (br s, 1H, Cp), 4.63 (br s, 1H, Cp), 4.47 (d, *J* = 14.41 Hz, 1H, NCH_2), 4.37 (br s, 2H, Cp), 4.09 (s, 5H, Cp), 1.64 (s, 15H, Cp*), 3.58–0.27 (m, 10H, BH carborane). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 148.9 (C, N_3C=CH), 123.6 (CH, N_3C=CH), 91.4 (5C, Cp*), 72.9 (C, carborane), 72.8 (C, Cp), 69.9 (5CH, Cp), 69.5 (2CH, Cp), 67.0 (CH, Cp), 66.8 (CH, Cp), 54.3 (NCH_2), 53.3 (C, carborane), 9.1 ($5CH_3$, Cp*). **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$) δ –2.5, –3.8, –7.1, –7.9, –9.1, –10.0, –11.7. **IR (CH_2Cl_2) $\nu_{máx}$** 2558, 1589, 1446, 1324, 1264, 1106, 1026, 878, 820, 735. **HRMS (ESI)** *m/z* calculated for $C_{25}H_{37}B_{10}N_3FeIr$: 736.29587 $[M–Cl]^+$, found: 736.2971.

9. Single crystal X-ray diffraction results and discussion

Crystals of **3c** suitable for single crystal X-ray diffraction were grown from a slow diffusion of *n*-pentane into a Cl_2CH_2 solution and its structure unambiguously established (Figure S1). The geometry around the iridium atom (frequently described as a *three-legged piano-stool geometry),* can be rationalized as a distorted octahedron with the cyclopentadienyl ligand occupying the three positions of a face while the opposite is occupied by a bidentated κ^2-(*o*-carboranylmethyl)triazolyl moiety and a chlorine atom. The κ^2-(*o*-carboranylmethyl)triazolyl moiety bonds to the iridium center through both, the carborane B(3) position and the triazolyl nitrogen atom N(2). The triazolyl moiety bonds to a ferrocenyl group through C(4) atom.The bidentated ligand and the Iridium atom form a six-membered metallacycle having a boat conformation, with dihedral angles of 45.26(15)º and 31.02(14)º between the N(1), N(2), B(3), C(1) plane (mean deviation 0.0106 Å) and the N(1)-C(3)-C(1) plane and the N(2)-Ir(1)-B(3) plane, respectively and, a trans-annular Ir(1)···C(3) distance of 3.469(2) Å. An intramolecular C-H···Cl hydrogen bond [C(3)-H(3B)···Cl(1): C(3)···Cl(1) 3.235(3) Å, H(3B)···Cl(1) 2.49 Å, C(3)-H(3B)···Cl(1) 131.6º] could contribute to stabilize the six-membered ring boat conformation. This is the first crystal structure reported for a metallacycle with a -B-C-C-N-N-M- sequence.[6]

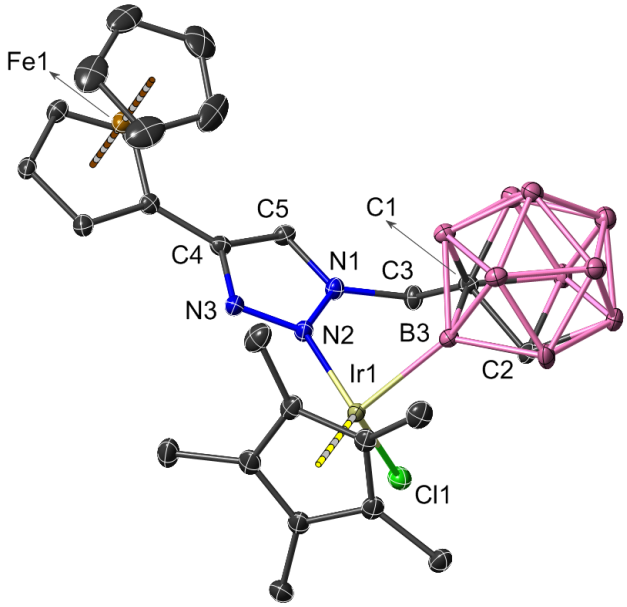


Figure S1. X-ray thermal ellipsoid plot for **3c** (50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (º): Ir(1)-N(2) 2.083(2), Ir(1)-B(3) 2.086(3), Ir(1)-Cl(1) 2.4266(6), N(1)-N(2) 1.354(3), N(2)-N(3) 1.315(3), N(3)-C(4) 1.365(3), C(4)-C(5) 1.382(3), N(1)-C(3) 1.457(3), C(1)-C(3) 1.521(3), C(1)-B(3) 1.793(3), N(2)-Ir(1)-B(3) 85.08(9), Ir(1)-N(2)-N(1) 128.47(15), N(2)-N(1)-C(3) 123.01(19), N(1)-C(3)-C(1) 110.93(19), C(3)-C(1)-B(3) 115.39(19) and C(1)-B(3)-Ir(1) 118.42(16).

Crystals of **6a** suitable for single crystal X-ray diffraction were grown from a Cl_2CH_2 / Et_2O solution and its structure unambiguously established (Figure S3). The crystal presents two independent molecules of **6a**. The geometry around the iridium atom (frequently described as a *three-legged piano-stool geometry),* can be rationalized as a distorted octahedron with the cyclopentadienyl ligand occupying the three positions of a face while the opposite is occupied by a bidentated κ^2-(*o*-carboranylmethyl)triazolyl moiety and a chlorine atom. The κ^2-(*o*-carboranylmethyl)triazolyl moiety bonds to the iridium center through both the carborane carbon atom in the C(2) position and the C(5) triazolylidene carbon atom. The triazolylidene moiety bonds to a phenyl group through C(4) atom. In both independent

molecules, the bidentated ligand and the Iridium atom form a six-membered metallacycle having a boat conformation. The Ir(1) labeled molecule shows dihedral angles of 43.5(9)º and 29.6(4)º between the N(1), C(5), C(2), C(1) plane (mean deviation 0.0162 Å) and the N(1)-C(3)-C(1) plane and the C(5)-Ir(1)-C(2) plane, respectively, together with a trans-annular Ir(1)···C(3) distance of 3.417(11) Å. Similar values are observed for the Ir(2) labeled molecule.

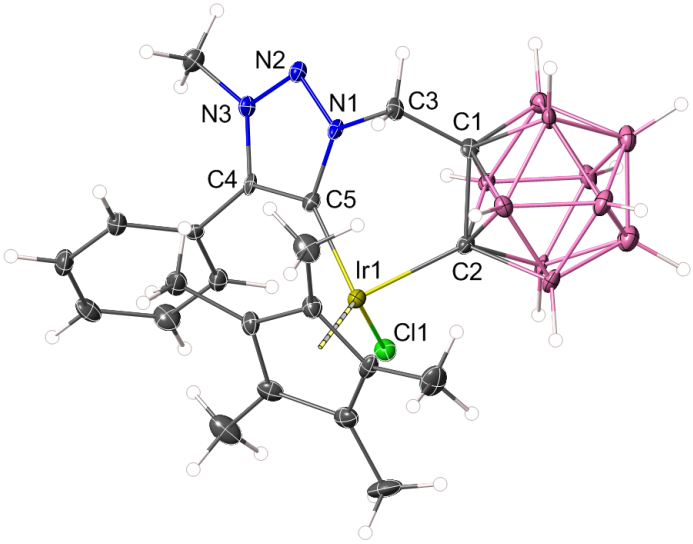


Figure S3. X-ray thermal ellipsoid plot for **6a** (40% probability level). Selected bond lengths (Å) and angles (º): Ir(1)-C(2) 2.125(10), Ir(1)-C(5) 2.026(10), Ir(1)-Cl(1) 2.421(2), N(1)-N(2) 1.338(12), N(2)-N(3) 1.298(11), N(3)-C(4) 1.365(13), C(4)-C(5) 1.404(13), N(1)-C(3) 1.464(12), C(1)-C(3) 1.508(14), C(1)-C(2) 1.698(14), C(2)-Ir(1)-C(5) 88.5(4), Ir(1)-C(2)-C(1) 118.4(6), C(2)-C(1)-C(3) 116.3(8), N(1)-C(3)-C(1) 111.2(8), C(3)-N(1)-C(5) 127.5(9) and N(1)-C(5)-Ir(1) 123.0(7).

Single crystal X-ray diffraction experimental data

Crystal data for compound 3c: $C_{25}H_{37}B_{10}ClFeIrN_3$, M = 771.17, monoclinic, a = 10.7280(10), b = 12.2730(10), c = 23.362(2) Å, β = 97.602(6)º, V = 3048.9(5) Å^3, space

group $P_{2(1)/n}$, $Z = 4$, $T = 120(2)$ K, $\lambda = 0.71073$ Å, $D_{calcd} = 1.680$ gcm^{-3}, $\mu = 4.946$ cm^{-1}, 31205 reflections measured, 8899 unique ($R_{int} = 0.0422$), orange crystals obtained by CH_2Cl_2 evaporation, crystal structure solved by direct methods and all non-hydrogen atoms refined anisotropically on F^2 using the programs SHELXS-2013 and SHELXL-2017/2[8] carborane C-H atom was located in a difference Fourier synthesis and refined as free, methyl group hydrogen atoms were included as *rigid* and others using a *riding* model, GOF = 1.039, R (F_o, $I > 2\sigma(I)$) = 0.0273, R_w (F_o^2, all data) = 0.0671.

Crystal data for compound 6a: $C_{22}H_{35}B_{10}ClIrN_3$, $M = 677.28$, orthorhombic, $a = 31.5605(9)$, $b = 8.6073(2)$, $c = 20.2755(5)$ Å, $V = 5507.9(2)$ Å^3, space group $P_{na2(1)}$, $Z = 8$, $T = 120(2)$ K, $\lambda = 0.71073$ Å, $D_{calcd} = 1.634$ gcm^{-3}, $\mu = 4.964$ cm^{-1}, 43285 reflections measured, 15524 unique ($R_{int} = 0.0707$), yellow crystals obtained by CH_2Cl_2/Et_2O evaporation, crystal structure solved by direct methods and all non-hydrogen atoms refined anisotropically on F^2 using the programs SHELXT[9] and SHELXL-2017/2[8], methyl group hydrogen atoms were included as *rigid* and others using a *riding* model, GOF = 1.053, R (F_o, $I > 2\sigma(I)$) = 0.0501, R_w (F_o^2, all data) = 0.1059.

CCDC-1824868 and CCDC-1824870 contain the full supplementary crystallographic data for compounds **3c** and **7a**. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

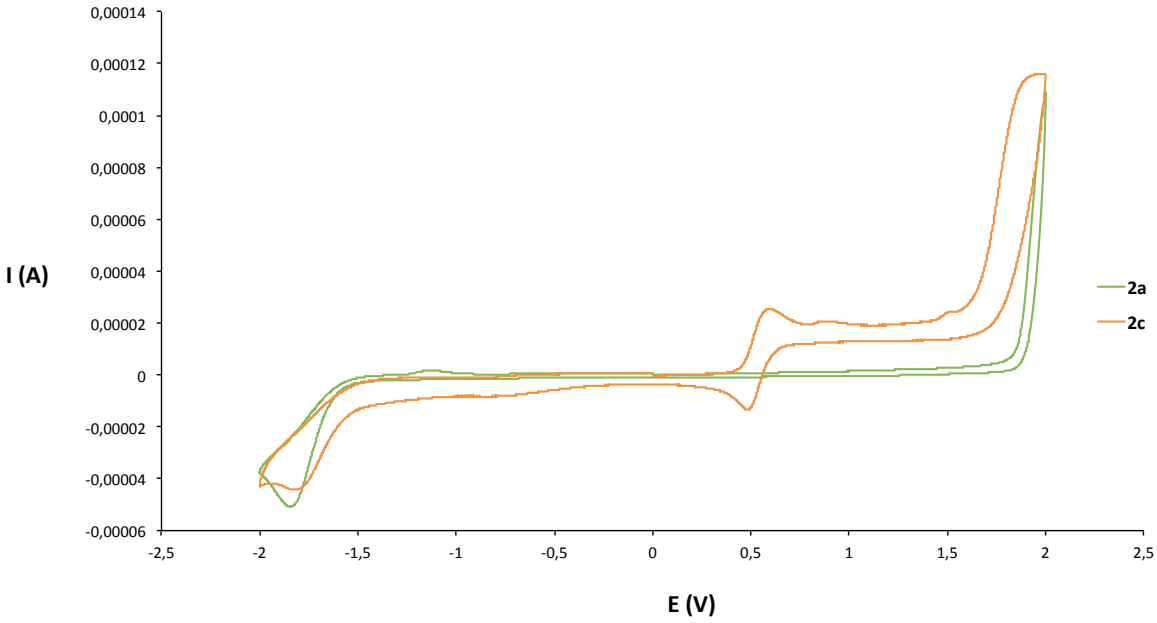
10. Electrochemical Studies

Table S1.[a] Cyclic voltammetry data of triazoles **2a–c**, triazolium salts **5a–c** and Ir(III) complexes **3a–c**, **6a** and **6c**.

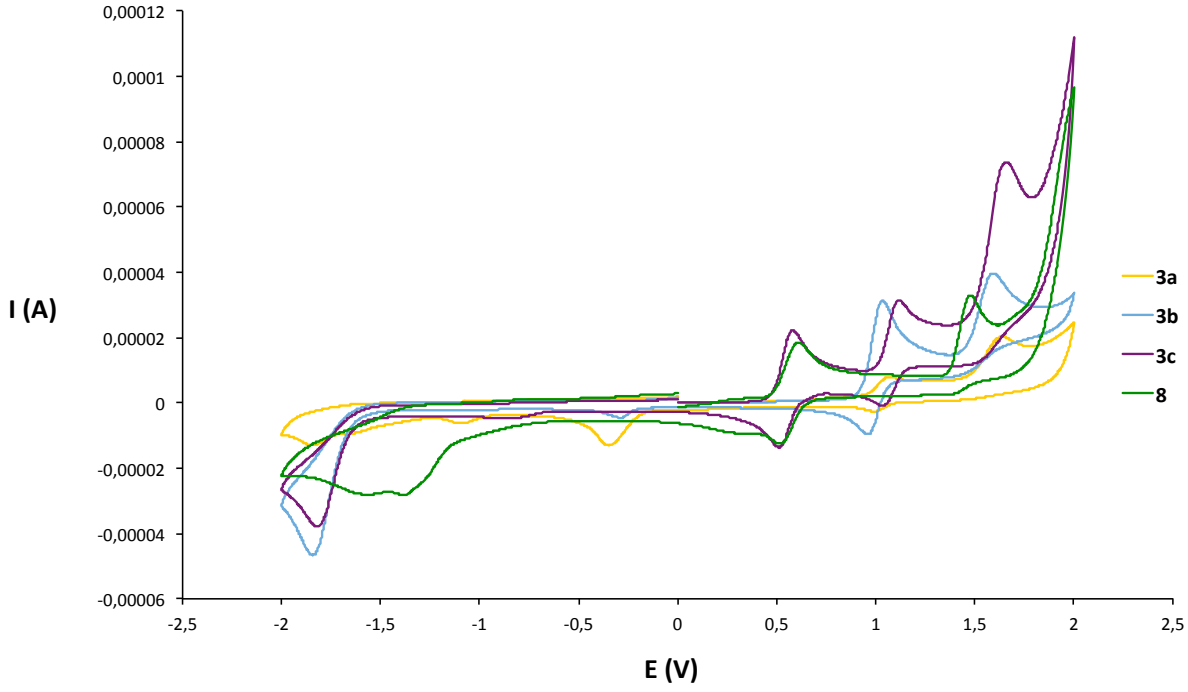
	Oxidation		**Reduction**
Compound	E_{pa1} (ΔVmV)	E_{pa2}	E_{pc}
3a	1.02** (60)	1.61	-1.84
3b	1.00** (70)	1.60	-1.84
3c*	1.07** (100)	1.68	-1.82
6a	1.12	-	-1.64
6c	1.06	-	-1.60
2a			-1.84
2b			*b*
2c			-1.81
5a			-1.42
5b			-1.53
5c			-1.40

[a] Data (V) obtained from $1x10^{-3}$ M acetonitrile solutions, containing 0.1 M $[N(^nBu)_4]ClO_4$ as supporting electrolyte at 20 ºC. Potentials are relative to Ag/AgCl. * $E_{1/2}$ Fc/Fc^+ = 0.54 V for compound **3c**. **$E_{1/2.}$ [b] not observed in the acetonitrile window frame.

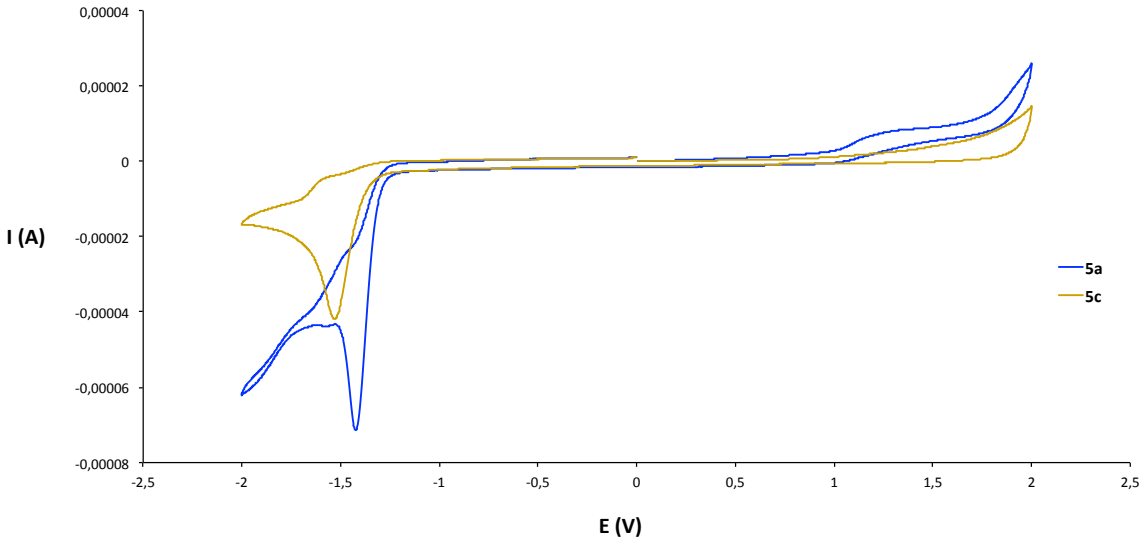
CVs of compounds 2a,2c



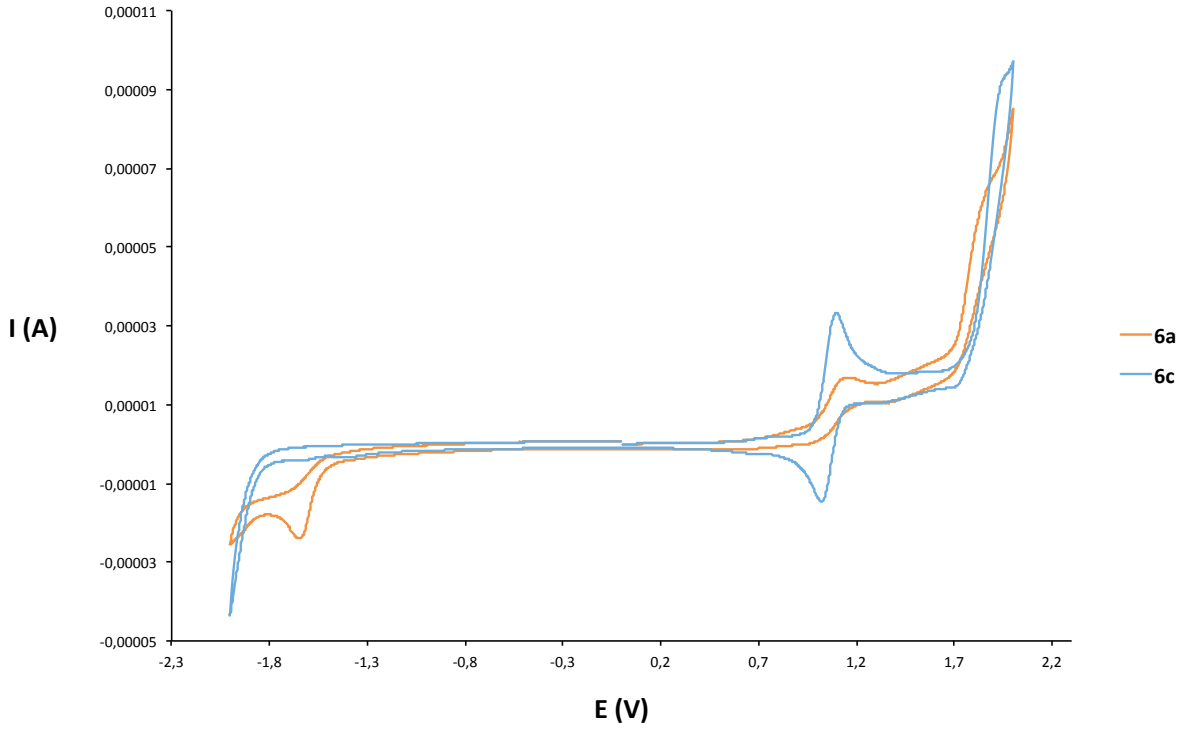
CVs of compounds 3a–c and 8



CVs of compounds 5a,5c



CVs of compounds 6a,6c



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6. CSD version 4.39 (November 2017; 931,333 entries).

7. CSD, V5.39, 14 hits analyzed.

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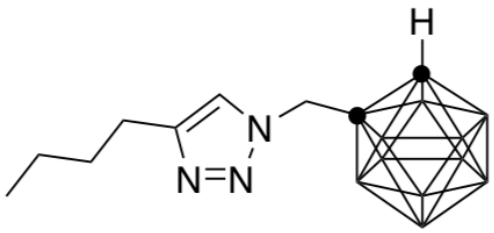
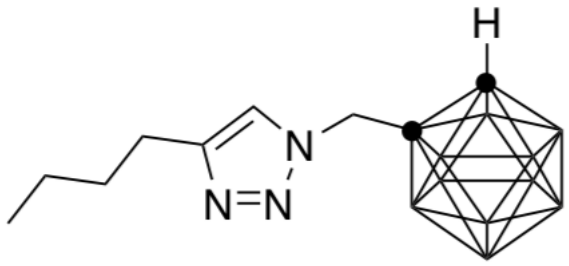


2b

^{1}H NMR (500 MHz, $CDCl_3$)

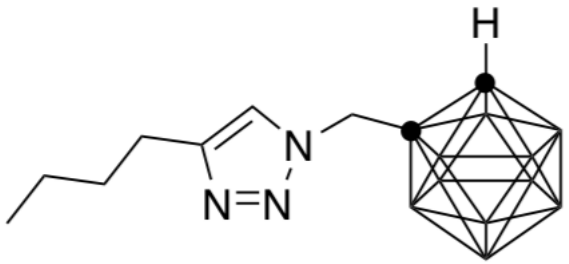


2b

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

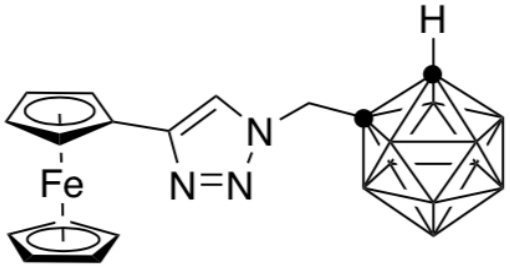
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
71.6
58.8
53.9
31.4
25.3
22.4
13.9

f1 (ppm)



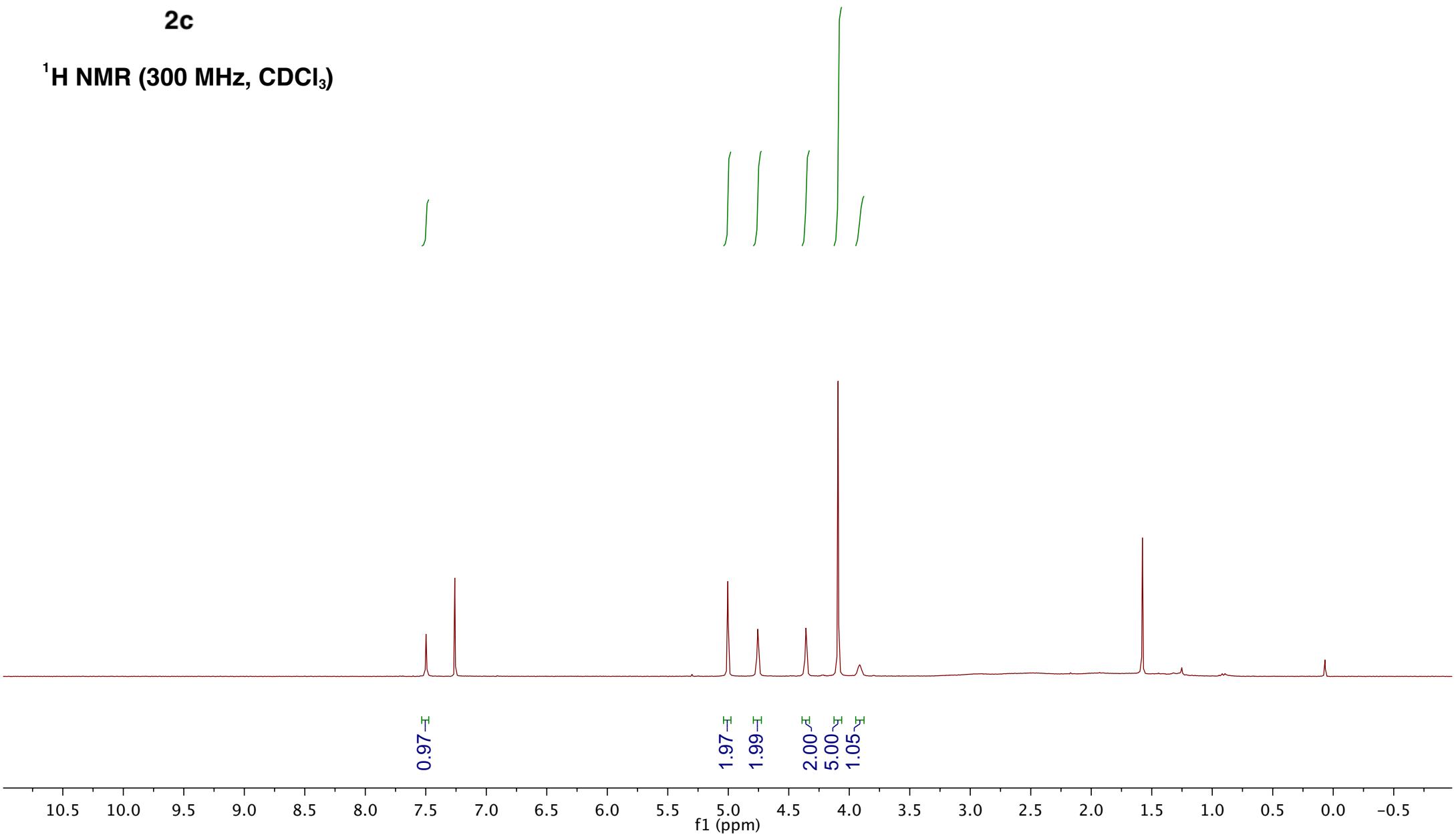
2b

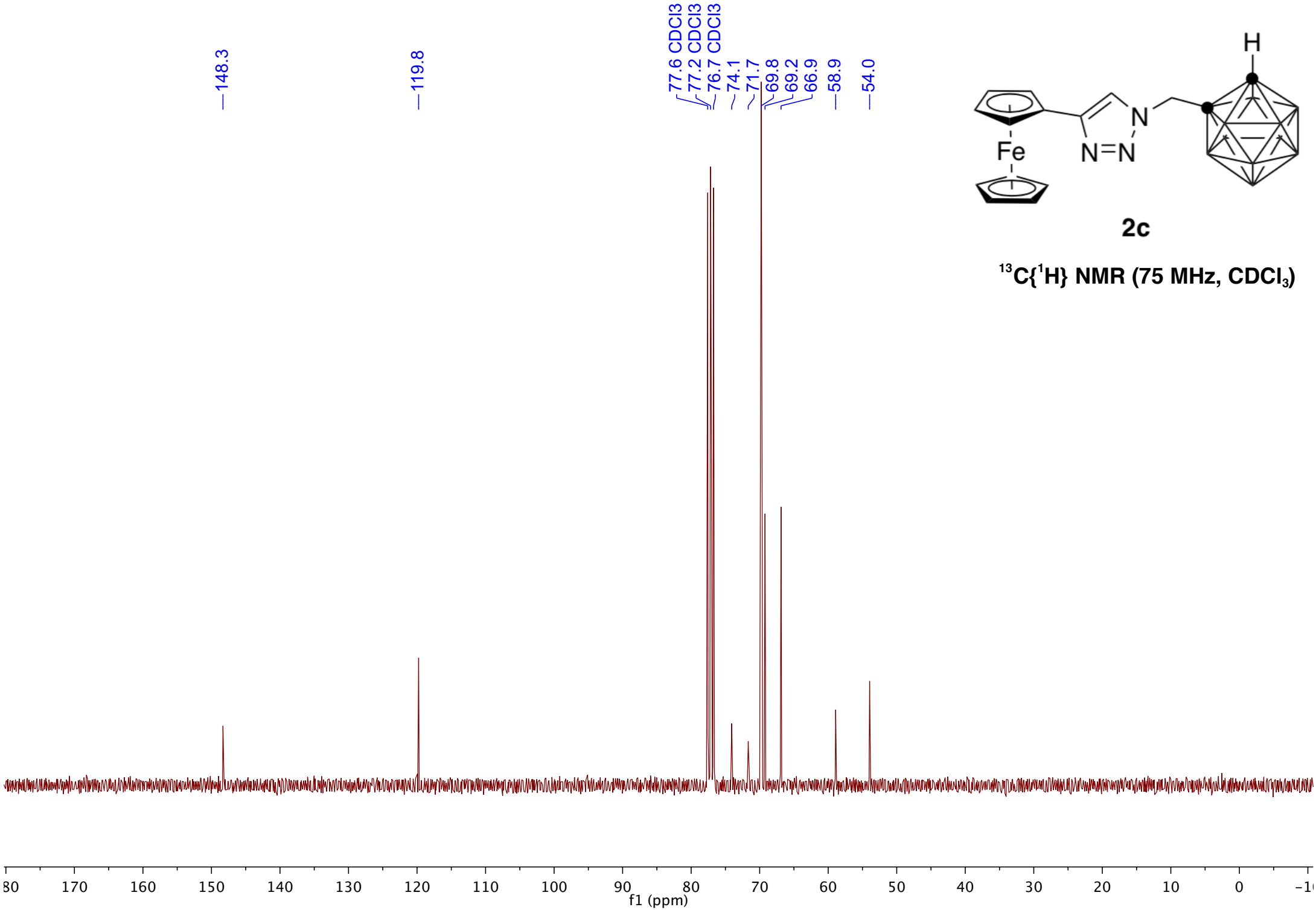
$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$)



2c

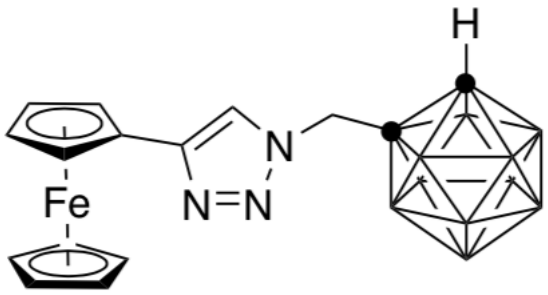
^{1}H NMR (300 MHz, $CDCl_3$)





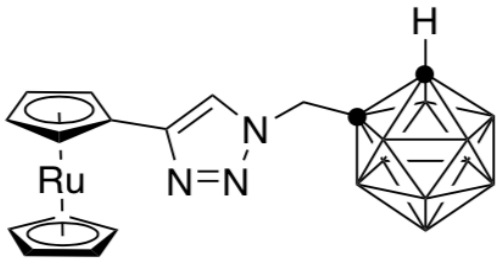
2c

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



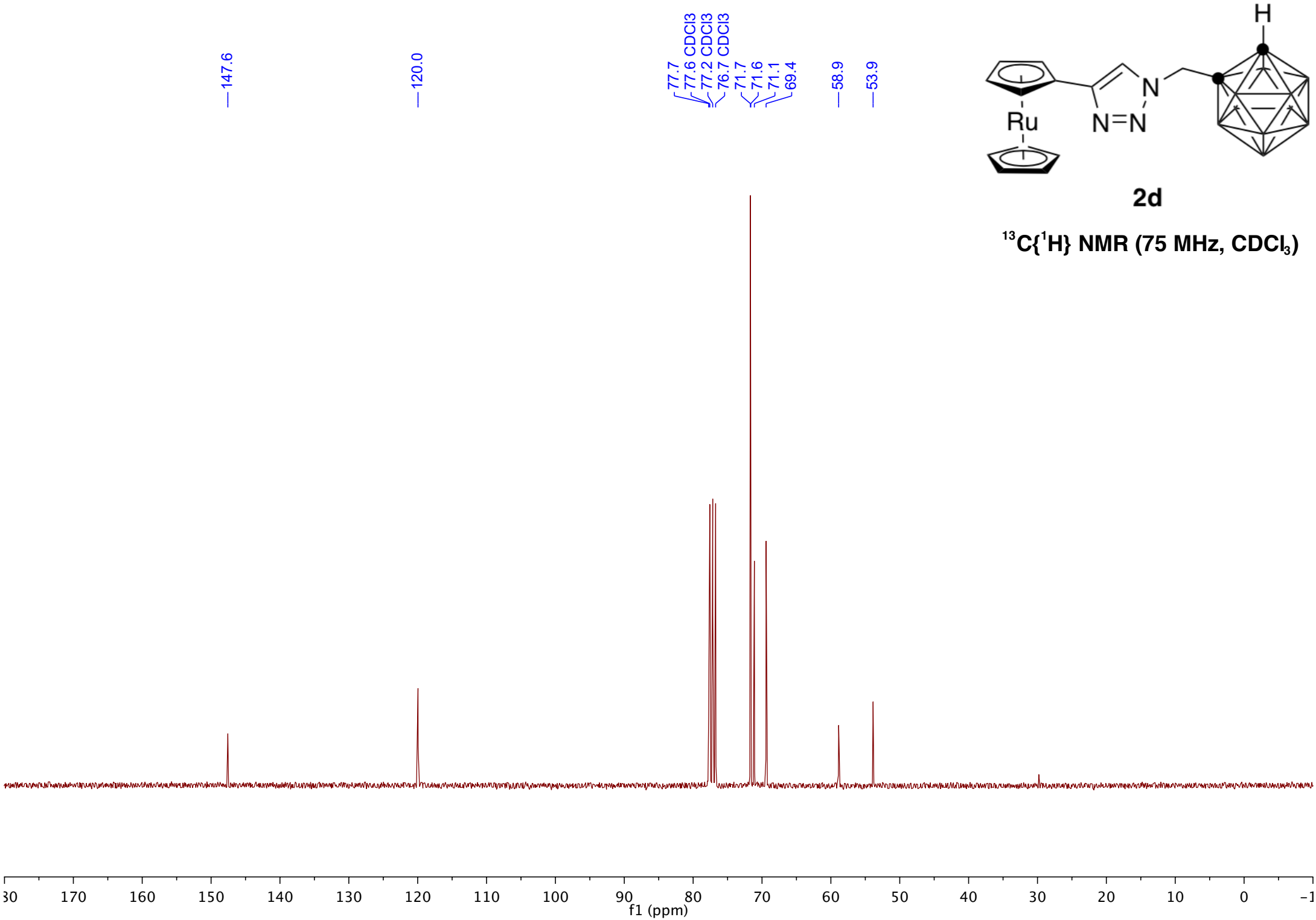
2c

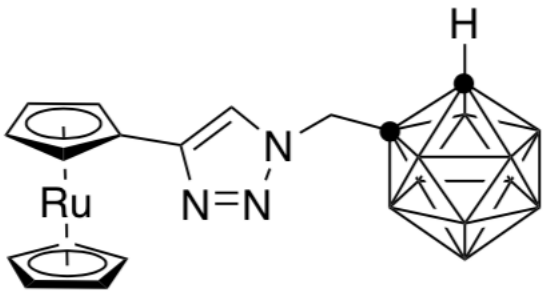
$^{11}B\{^{1}H\}$NMR (160 MHz, $CDCl_3$)



2d

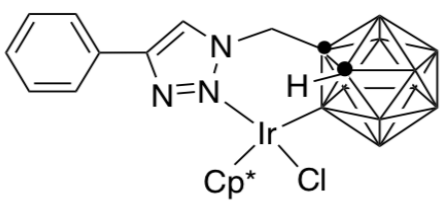
^{1}H NMR (300 MHz, $CDCl_3$)


147.6
120.0
77.7
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
71.7
71.6
71.1
69.4
58.9
53.9
H
N
N=N
Ru
2d
13C{1H} NMR (75 MHz, CDCl3)
f1 (ppm)



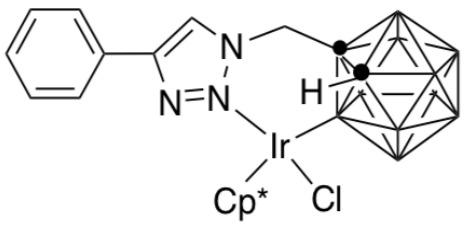
2d

$^{11}B\{^{1}H\}$NMR (160 MHz, $CDCl_3$)



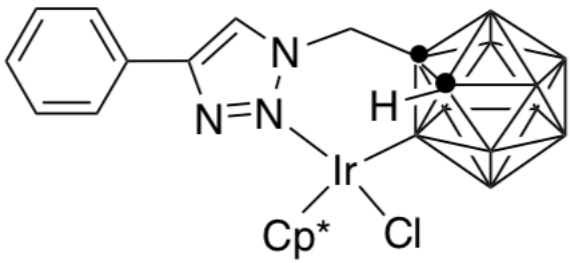
3a

^{1}H NMR (300 MHz, $CDCl_3$)



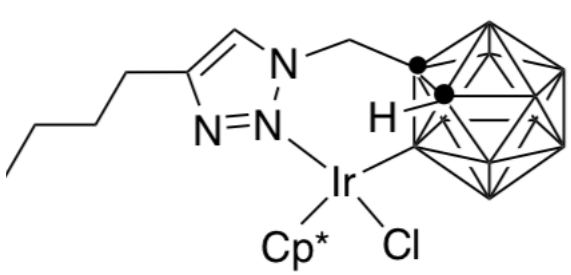
3a

$^{13}C\{^{1}H\}$ NMR (125 MHz, d_6-acetone)



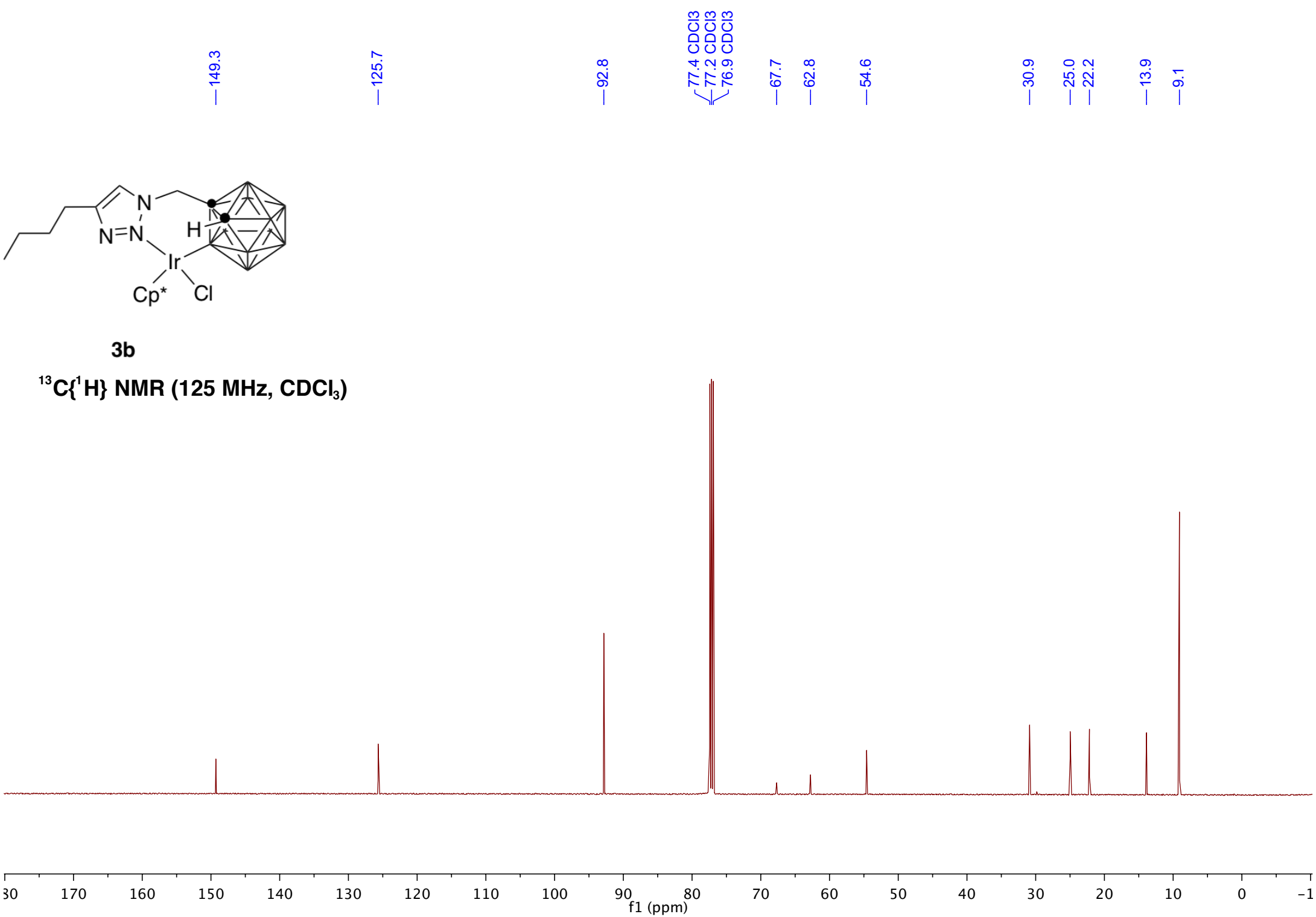
3a

$^{11}B\{^{1}H\}$ NMR (160 MHz, d_6-acetone)



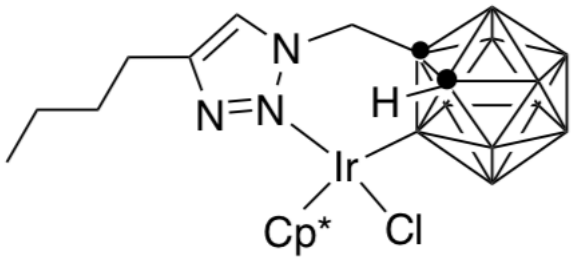
3b

^{1}H NMR (500 MHz, $CDCl_3$)



3b

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



3b

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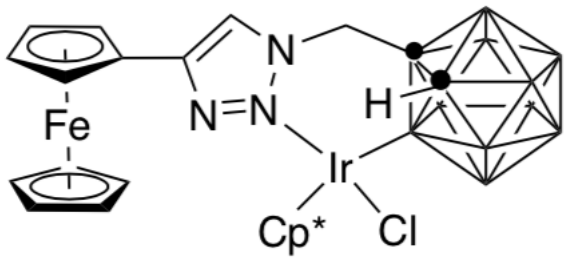
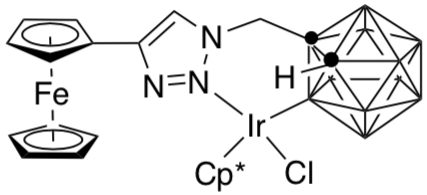


3c

^{1}H NMR (300 MHz, $CDCl_3$)

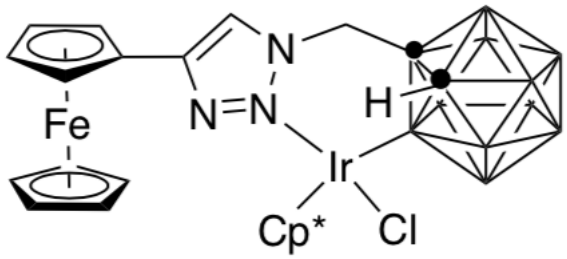


3c

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

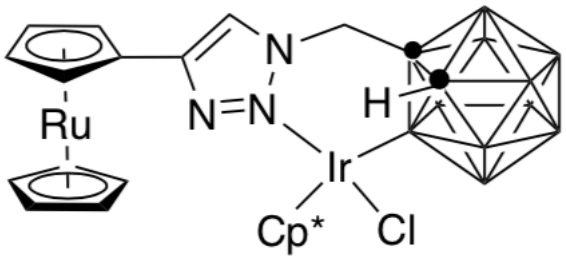
148.4
123.2
93.0
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
73.3
69.9
69.4
67.7
66.9
66.6
62.8
54.7
9.1

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



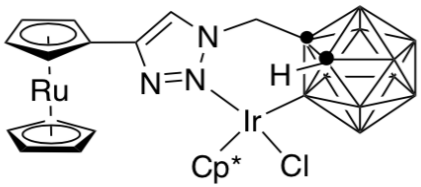
3c

$^{11}B\{^{1}H\}$NMR (160 MHz, $CDCl_3$)



3d

^{1}H NMR (300 MHz, $CDCl_3$)

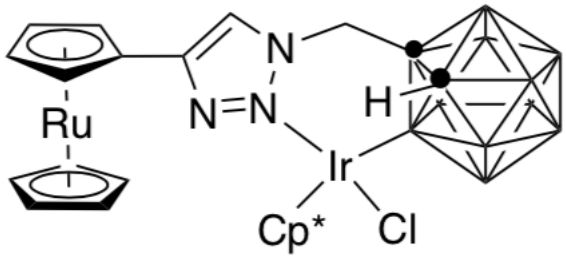


3d

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

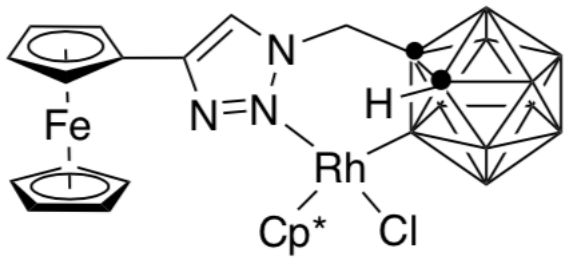
147.6
123.2
92.9
77.6 CDCl3
77.2 CDCl3
77.0
76.7 CDCl3
71.8
71.2
71.2
69.3
69.1
62.7
54.7
9.1

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



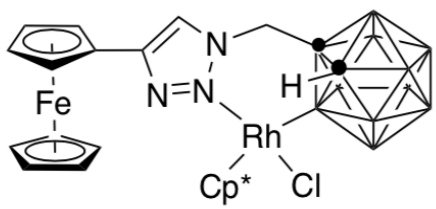
3d

$^{11}B\{^{1}H\}$ NMR (160 MHz, d_6-acetone)



4c

^{1}H NMR (300 MHz, $CDCl_3$)



4c

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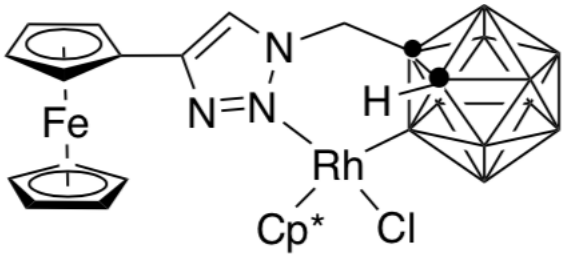
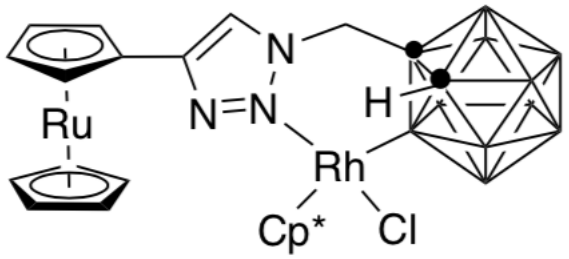


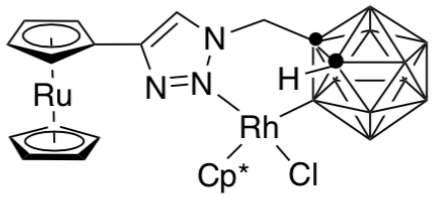
4c

$^{11}B\{^{1}H\}$NMR (160 MHz, d_6-acetone)



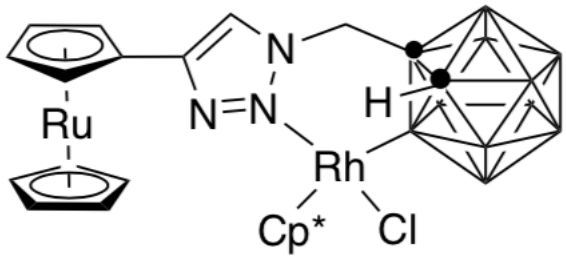
4d

^{1}H NMR (300 MHz, $CDCl_3$)



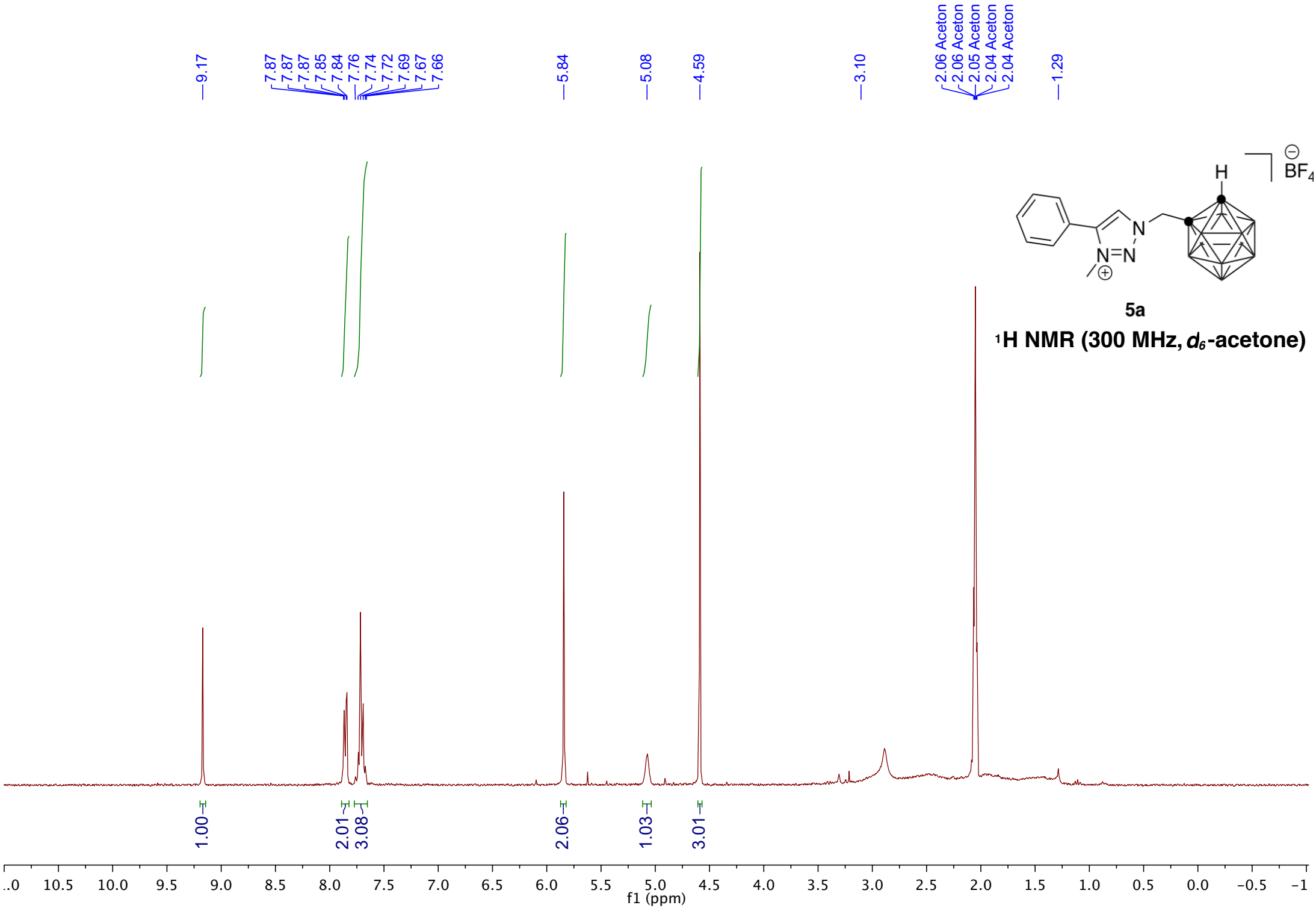
4d

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



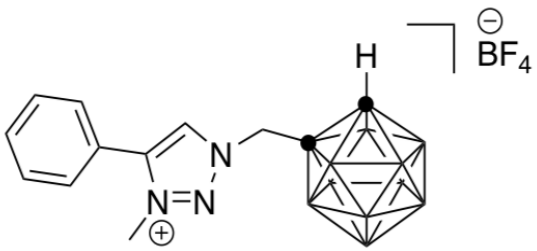
4d

$^{11}B\{^{1}H\}$NMR (160 MHz, $CDCl_3$)



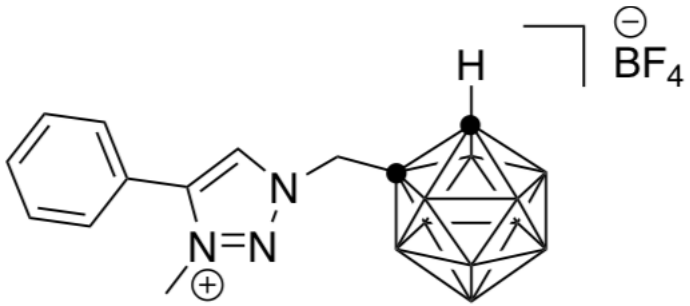
5a

^{1}H NMR (300 MHz, d_6-acetone)



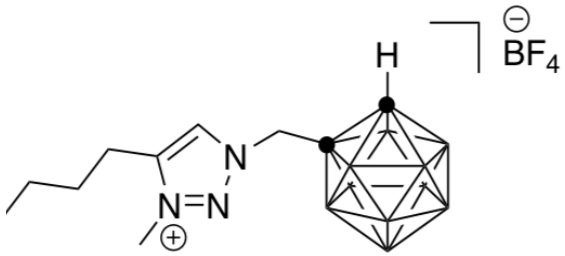
5a

$^{13}C\{^{1}H\}$ NMR (75 MHz, d_6-acetone)



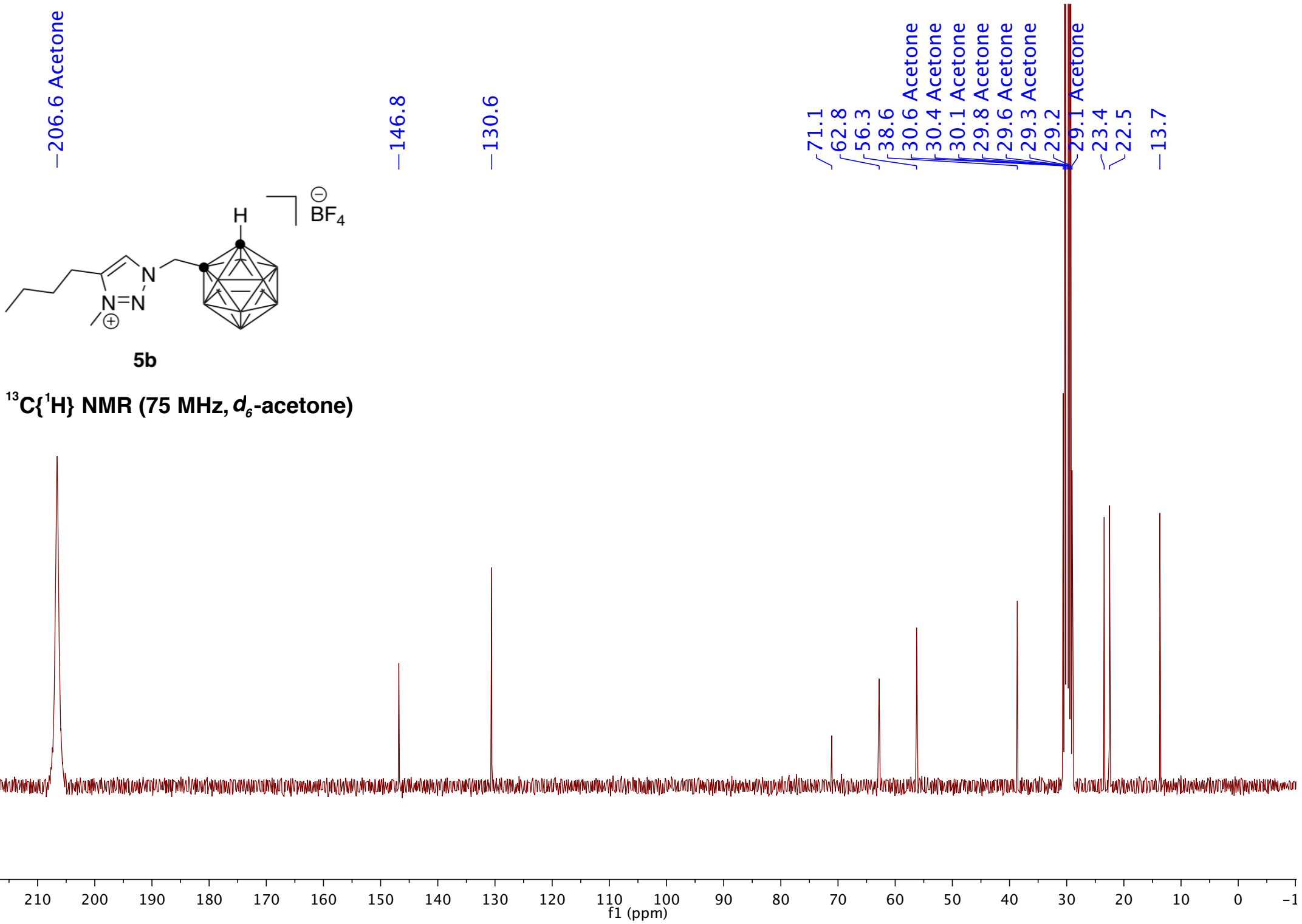
5a

$^{11}B\{^{1}H\}$ NMR (160 MHz, d_6-acetone)



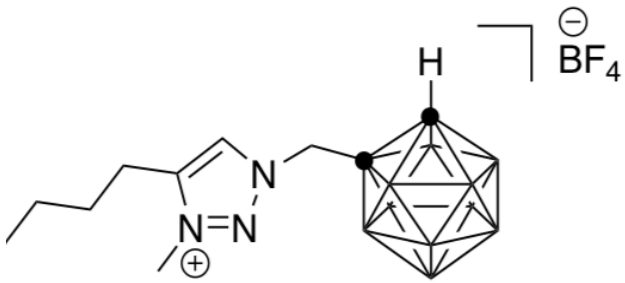
5b

^{1}H NMR (500 MHz, d_6-acetone)



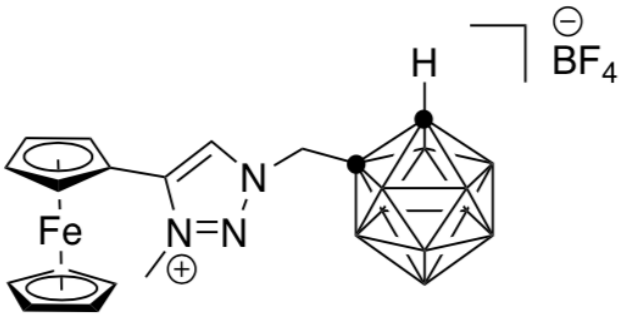
5b

$^{13}C\{^{1}H\}$ NMR (75 MHz, d_6-acetone)



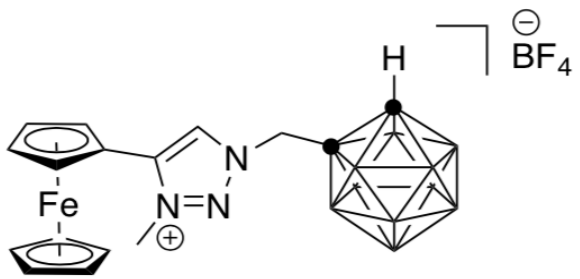
5b

$^{11}B\{^{1}H\}$ NMR (160 MHz, d_6-acetone)



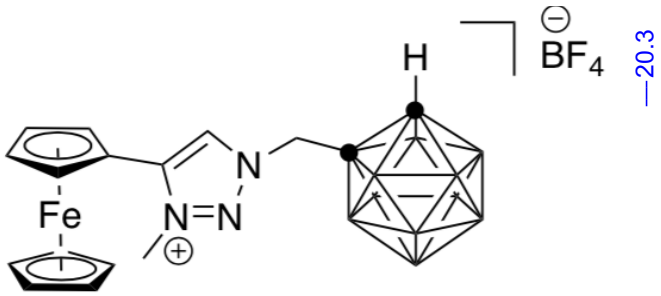
5c

^{1}H NMR (300 MHz, d_6-acetone)



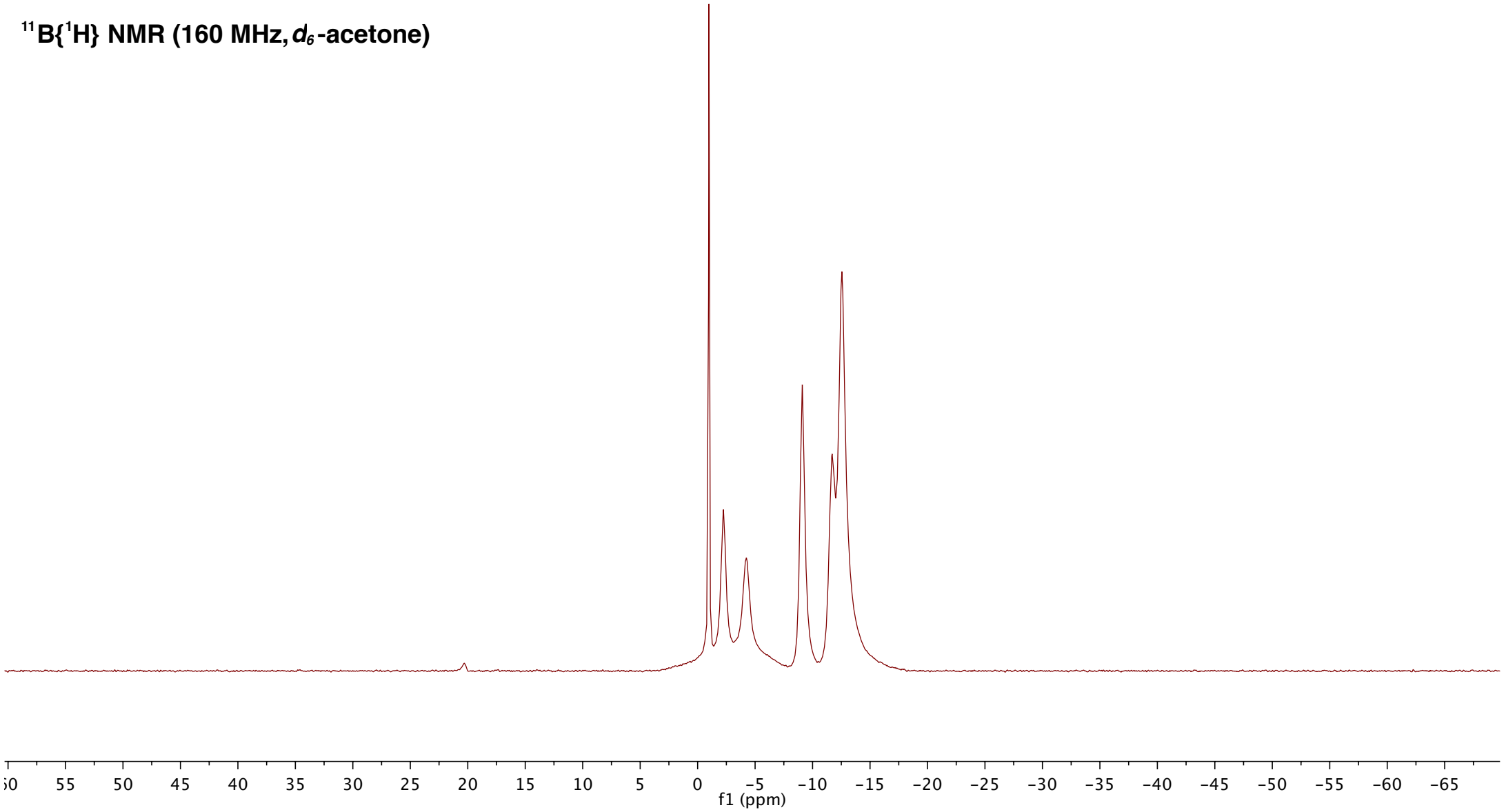
5c

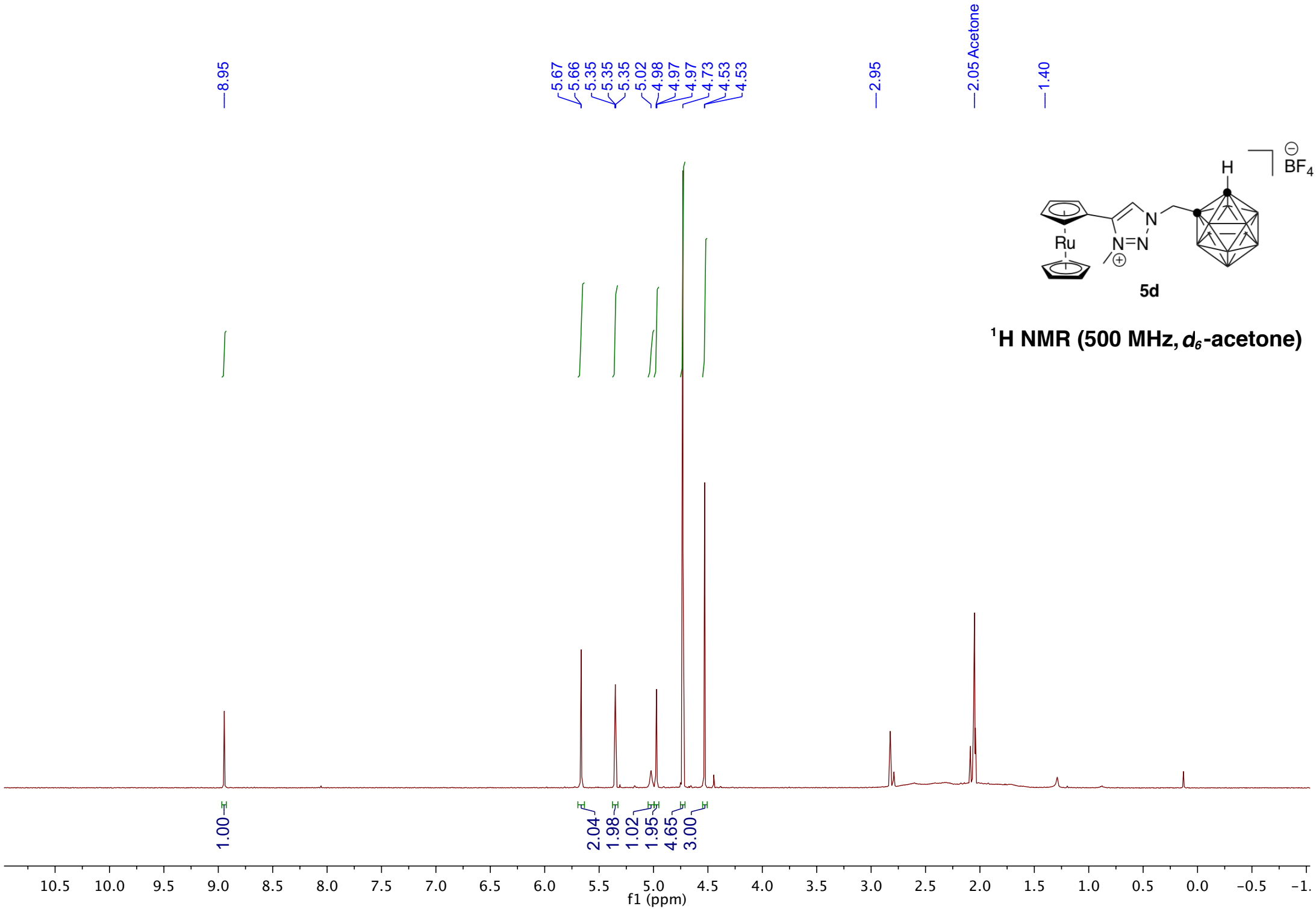
$^{13}C\{^{1}H\}$ NMR (75 MHz, d_6-acetone)

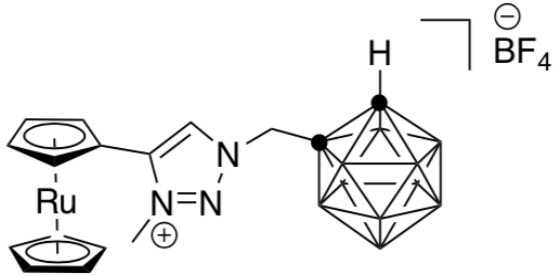


5c

$^{11}B\{^{1}H\}$ NMR (160 MHz, d_6-acetone)

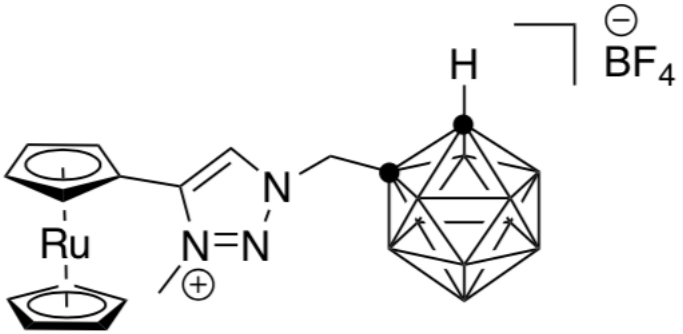



8.95
5.67
5.66
5.35
5.35
5.35
5.02
4.98
4.97
4.97
4.73
4.53
4.53
2.95
2.05 Acetone
1.40
1.00
2.04
1.98
1.02
1.95
4.65
3.00
f1 (ppm)
H
BF4
Ru
N
N=N
5d
1H NMR (500 MHz, d6-acetone)



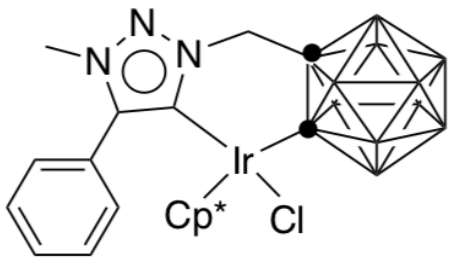
5d

$^{13}C\{^{1}H\}$ NMR (75 MHz, d_6-acetone)



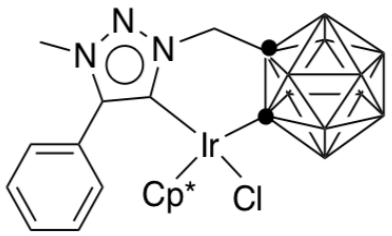
5d

$^{11}B\{^{1}H\}$ NMR (160 MHz, d_6-acetone)



6a

^{1}H NMR (500 MHz, d_6-acetone)

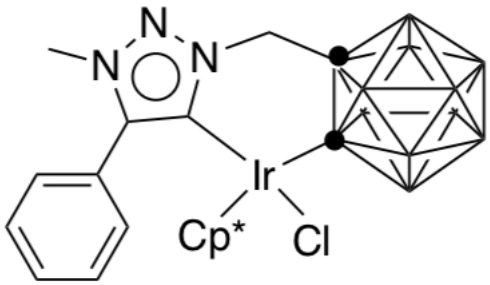


6a

$^{13}C\{^{1}H\}$ NMR (125 MHz, d_6-acetone)

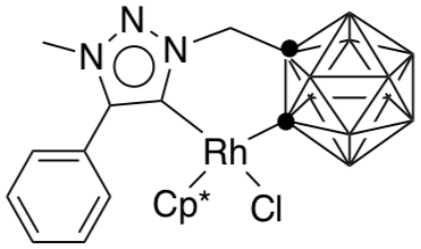
206.1 Acetone
150.7
142.1
134.1
130.7
128.4
127.8
92.4
73.9
58.9
48.1
38.1
30.3 Acetone
30.1 Acetone
30.0 Acetone
29.8 Acetone
29.8 (CD3)2CO
29.7 Acetone
29.5 Acetone
29.4 Acetone
9.0

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



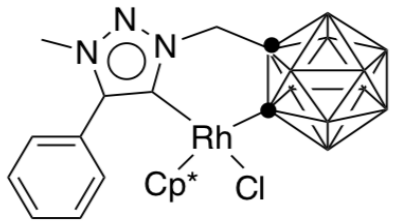
6a

$^{11}B\{^{1}H\}$ NMR (160 MHz, d_6-acetone)



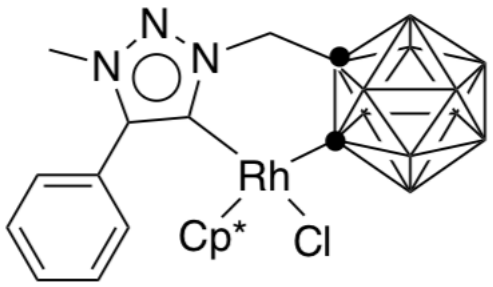
6b

^{1}H NMR (500 MHz, d_6-acetone)



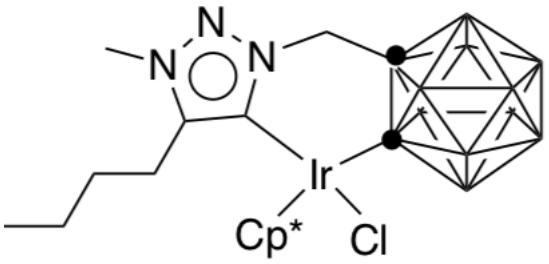
6b

$^{13}C\{^{1}H\}$ NMR (125 MHz, d_6-acetone)



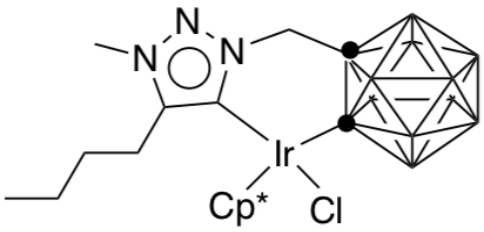
6b

$^{11}B\{^{1}H\}$ NMR (160 MHz, d_6-acetone)



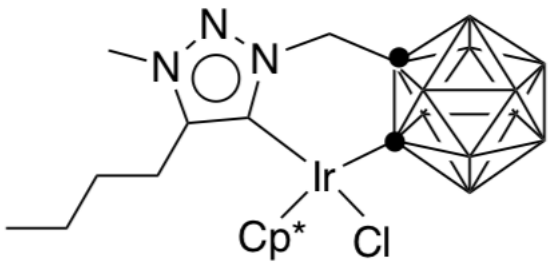
6c

^{1}H NMR (500 MHz, $CDCl_3$)



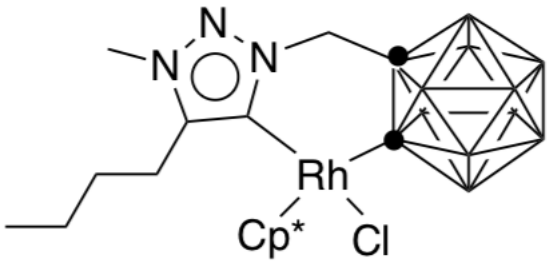
6c

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



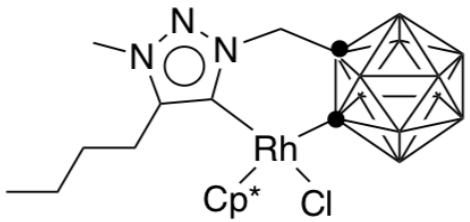
6c

$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$)



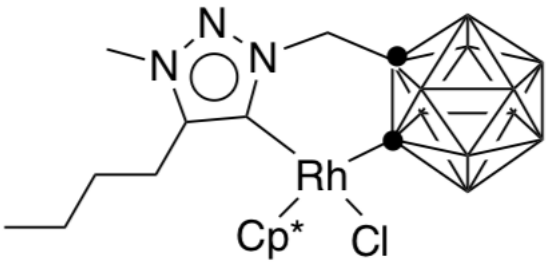
6d

^{1}H NMR (300 MHz, $CDCl_3$)



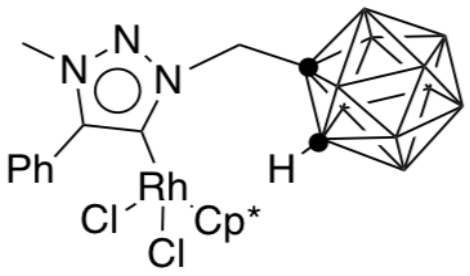
6d

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



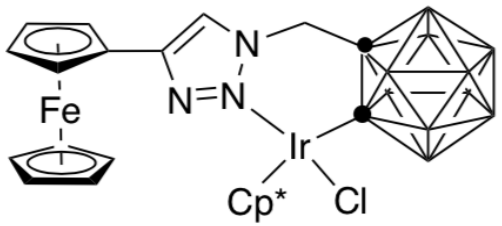
6d

$^{11}B\{^{1}H\}$ NMR (160 MHz, d_6-acetone)



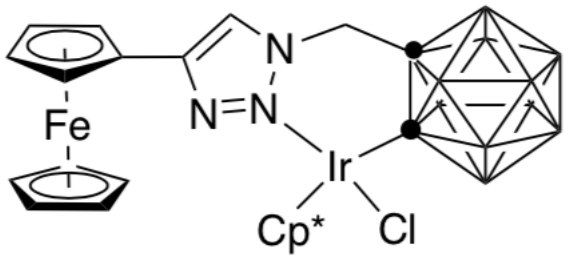
7

^{1}H NMR (300 MHz, $CDCl_3$)



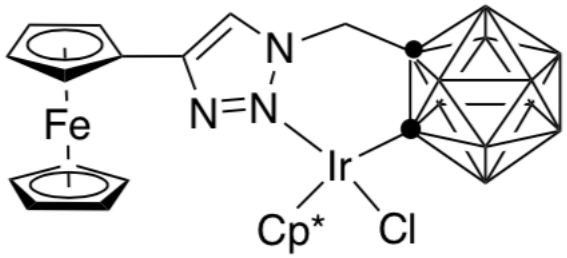
8

^{1}H NMR (300 MHz, $CDCl_3$)



8

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



8

$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$)