Supporting Information

Stereospecific alkenylation of carboranes: copper-catalyzed access to pyridylcarboranyl alkenes

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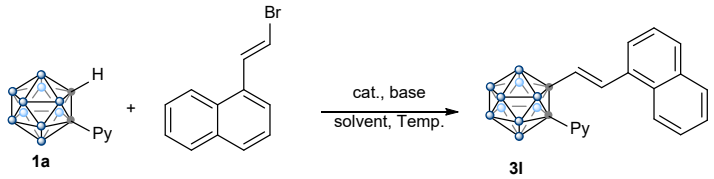
1. General Information

All the commercially available reagents were purchased from commercial sources and used directly. Substituted carboranes and vinyl bromides were synthesized according to literature methods.[1] Analytical thin layer chromatography (TLC) was performed on silica gel (GF 254) plates, while column chromatography was performed on Silica Gel (200−300 mesh). Visualization of the developed chromatogram was performed by UV absorbance (254 nm). ^{1}H, $^{11}B\{^{1}H\}$, ^{13}C, ^{19}F spectra were recorded using Bruker Advance NEO 400 spectrometer under ambient conditions unless otherwise stated. All chemical shifts (δ values) were reported in ppm with the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts.[2] High resolution mass spectra (HRMS) were obtained on a Shimadzu LCMS-IT-TOF spectrometer. Single crystal X-ray crystallography were carried on a Bruker SMART Apex III CCD diffractometer by means of graphitemonochromated (Mo-Kα radiation, λ = 0.7107 Å and Cu-Kα radiation, λ = 1.5406 Å). APEX III program was used to determine the unit cell parameters and for data collection. The data were integrated and corrected for Lorentz and polarization effects using SAINT. Absorption correction was applied with SADABS. The structure was solved by direct method and refined by full-matrix leastsquares method on F^2 using the SHELXTL[3]or Olex-2[4] crystallographic software package. All nonhydrogen atom positions were determined to utilize the difference Fourier synthesis, while the hydrogen atoms were placed at geometrically calculated positions using a riding model. Melting points were measured using a SGW® X-4A.

2. Experimental Section

2.1 Condition Optimization

Table S1. Optimization of reaction conditions[a,b]

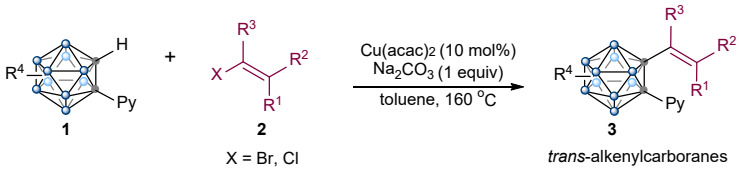


Entry	Cat.	Solvent	Base	Yield
1	CuF_2	DCE	K_2CO_3	40%
2	$Cu(CF_3CO_2)_2$	DCE	K_2CO_3	40%
3	$Cu(OAc)_2$	DCE	K_2CO_3	39%
4	$Cu(acac)_2$	DCE	K_2CO_3	53%
5	CuCl	DCE	K_2CO_3	32%
6	Cu_2O	DCE	K_2CO_3	40%
7	CuI	DCE	K_2CO_3	13%
8	-	DCE	K_2CO_3	-
9	$Cu(acac)_2$	1,1,2,2-tetrachloroethane	K_2CO_3	30%
10	$Cu(acac)_2$	1,4-dioxane	K_2CO_3	5%
11	$Cu(acac)_2$	toluene	K_2CO_3	84%
12	$Cu(acac)_2$	$PhCF_3$	K_2CO_3	73%
13	$Cu(acac)_2$	*p*-xylene	K_2CO_3	80%
14	$Cu(acac)_2$	*m*-xylene	K_2CO_3	82%
15	$Cu(acac)_2$	*o*-xylene	K_2CO_3	83%
16	$Cu(acac)_2$	mesitylene	K_2CO_3	78%
17	$Cu(acac)_2$	toluene	-	5%
18	$Cu(acac)_2$	toluene	$KHCO_3$	81%
19	$Cu(acac)_2$	toluene	Na_2CO_3	91%
20	$Cu(acac)_2$	toluene	$NaHCO_3$	65%
21	$Cu(acac)_2$	toluene	Li_2CO_3	40%
22	$Cu(acac)_2$	toluene	Cs_2CO_3	10%
23	$Cu(acac)_2$	toluene	KH_2PO_4	54%
24	$Cu(acac)_2$	toluene	K_2HPO_4	55%
25	$Cu(acac)_2$	toluene	KOAc	62%
26[c]	**$Cu(acac)_2$**	**toluene**	**Na_2CO_3**	**90%**
27[c,d]	$Cu(acac)_2$	toluene	Na_2CO_3	78%
28[c,e]	**$Cu(acac)_2$**	**toluene**	**Na_2CO_3**	**90%**
29[c,e,f]	$Cu(acac)_2$	toluene	Na_2CO_3	58%

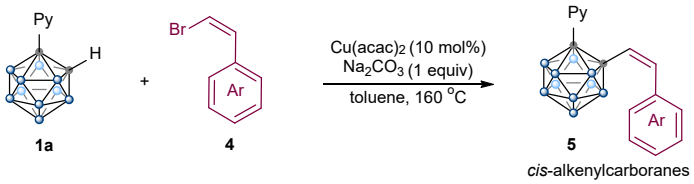
[a] Conditions: **1a** (0.05 mmol), (*E*)-1-(2-bromovinyl)naphthalene (3.0 equiv), cat. (10 mol%), base (2 equiv), solvent (0.5 mL), 160 °C, 12 h. [b] Yield of isolated product. [c] Na_2CO_3 (1 equiv). [d] cat. (5 mol%). [e] (*E*)-1-(2-bromovinyl)naphthalene (1.5 equiv). [f] 150 °C, 48 h.

2.2 General Procedures

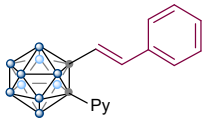
General procedure for C–H *trans*-alkenylation of carboranes: carboranes (0.1 mmol, 1 equiv), **2** (0.15 mmol or 0.3 mmol), $Cu(acac)_2$ (10 mol%) and Na_2CO_3 (1 equiv) were mixed in toluene (1 mL) in a closable Schlenk tube equipped with a magnetic stirrer and the resulting reaction mixture was stirred at 160 °C for 12 h to 24 h. After completion of the reaction, concentrated in vacuo. The crude product was purified by column chromatography on silica gel using petroleum ether and dichloromethane as the eluent to give the desired products **3**.



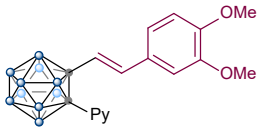
General procedure for C–H *cis*-alkenylation of carboranes: 1a (0.1 mmol, 1 equiv), **4** (0.3 mmol), $Cu(acac)_2$ (10 mol%) and Na_2CO_3 (1 equiv) were mixed in toluene (1 mL) in a closable Schlenk tube equipped with a magnetic stirrer and the resulting reaction mixture was stirred at 160 °C for 12 h to 24 h. After completion of the reaction, concentrated in vacuo. The crude product was purified by column chromatography on silica gel using petroleum ether and dichloromethane as the eluent to give the desired products **5**.



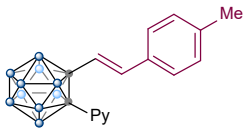
2.3 Characterization Data of Products



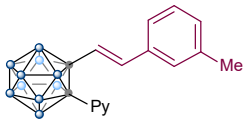
3a: 32 mg, Yield 99%. White solid, mp 85–88 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (dt, *J* = 4.7, 1.4 Hz, 1H), 7.78 – 7.66 (m, 2H), 7.32 – 7.28 (m, 1H), 7.27 – 7.22 (m, 3H), 7.17 – 7.11 (m, 2H), 6.81 (d, *J* = 15.7 Hz, 1H), 6.06 (d, *J* = 15.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.2, 149.2, 139.3, 137.2, 134.7, 129.4, 128.8, 127.0, 125.4, 124.8, 121.3, 82.3, 80.9. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.60 (1B), -3.36 (1B), -10.18 (8B). HRMS (ESI): *m/z* calcd for $C_{15}H_{22}B_{10}N$ $[M+H]^+$: 324.2750. Found: 324.2767.



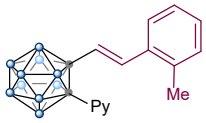
3b: 35 mg, Yield 91%. White solid, mp 79–81 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 4.7 Hz, 1H), 7.76 – 7.64 (m, 2H), 7.29 (t, *J* = 5.6 Hz, 1H), 6.79 – 6.68 (m, 3H), 6.63 (s, 1H), 5.94 (d, *J* = 15.6 Hz, 1H), 3.82 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.2, 149.3, 149.1, 139.2, 137.1, 127.6, 125.4, 124.7, 120.6, 119.1, 111.1, 109.3, 82.5, 81.5, 56.0, 55.9. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.59 (2B), -10.20 (8B). HRMS (ESI): *m/z* calcd for $C_{17}H_{26}B_{10}NO_2$ $[M+H]^+$: 384.2962. Found: 384.2979.



3c: 29 mg, Yield 86%. White solid, mp 90–93 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (dt, *J* = 4.8, 0.9 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.34 – 7.27 (m, 1H), 7.11 – 7.01 (m, 4H), 6.79 (d, *J* = 15.7 Hz, 1H), 6.03 (d, *J* = 15.7 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 149.2, 139.6, 139.3, 137.2, 131.9, 129.5, 126.9, 125.4, 124.7, 120.2, 82.5, 81.3, 21.4. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.58 (1B), -3.32 (1B), -10.12 (8B). HRMS (ESI): *m/z* calcd for $C_{16}H_{24}B_{10}N$ $[M+H]^+$: 338.2907. Found: 338.2918.

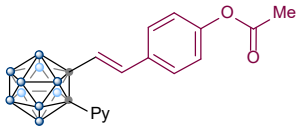


3d: 31 mg, Yield 92%. White solid, mp 82–84 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 4.8 Hz, 1H), 7.77 – 7.65 (m, 3H), 7.36 – 7.27 (m, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.99 – 6.91 (m, 2H), 6.79 (d, *J* = 15.7 Hz, 1H), 6.06 (d, *J* = 15.8 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 149.2, 139.5, 138.5, 137.2, 134.6, 130.2, 128.7, 127.8, 125.4, 124.8, 124.1, 121.1, 82.4, 81.1, 21.4. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.58 (1B), -3.32 (1B), -10.09 (8B). HRMS (ESI): *m/z* calcd for $C_{16}H_{24}B_{10}N$ $[M+H]^+$: 338.2907. Found: 338.2931.

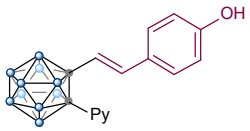


3e: 31 mg, Yield 92%. White solid, mp 85–87 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 4.7 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.35 – 7.30 (m, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.11 – 7.02 (m, 3H), 6.97

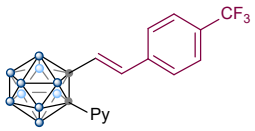
(d, J = 7.6 Hz, 1H), 5.93 (d, J = 15.6 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 149.3, 137.8, 137.2, 136.4, 134.0, 130.5, 129.2, 126.3, 125.9, 125.4, 124.8, 122.7, 82.5, 81.1, 19.6. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.57 (1B), -3.31 (1B), -10.08 (8B). HRMS (ESI): *m/z* calcd for $C_{16}H_{24}B_{10}N$ $[M+H]^+$: 338.2907. Found: 338.2926.



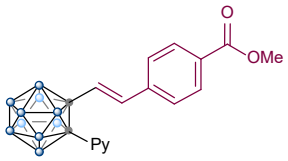
3f: 16 mg, Yield 42%. White solid, mp 154–156 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (d, J = 4.7 Hz, 1H), 7.75 – 7.66 (m, 2H), 7.35 – 7.28 (m, 1H), 7.15 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 6.78 (d, J = 15.7 Hz, 1H), 6.03 (d, J = 15.7 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.4, 151.3, 149.3, 138.3, 137.3, 132.5, 128.1, 125.4, 124.9, 122.1, 121.6, 82.4, 80.7, 21.2. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.68 (2B), -10.16 (8B). HRMS (ESI): *m/z* calcd for $C_{17}H_{24}B_{10}NO_2$ $[M+H]^+$: 382.2805. Found: 382.2818.



3g: 18 mg, Yield 53%. White solid, mp 63–65 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (dt, J = 4.7, 1.4 Hz, 1H), 7.77 – 7.65 (m, 2H), 7.35 – 7.29 (m, 1H), 7.07 – 6.99 (m, 2H), 6.77 – 6.66 (m, 3H), 5.91 (d, J = 15.7 Hz, 1H), 5.47 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.8, 149.3, 149.2, 138.9, 137.3, 128.7, 127.5, 125.5, 124.8, 118.9, 115.8, 82.4, 81.6. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.61 (1B), -3.57 (1B), -10.32 (8B). HRMS (ESI): *m/z* calcd for $C_{15}H_{22}B_{10}NO$ $[M+H]^+$: 340.2700. Found: 340.2719.

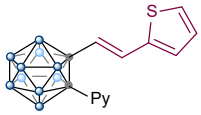


3h: 34 mg, Yield 87%. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, J = 4.7 Hz, 1H), 7.79 – 7.67 (m, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.24 (d, J = 8.1 Hz, 2H), 6.84 (d, J = 15.8 Hz, 1H), 6.17 (d, J = 15.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.2, 138.1, 138.1, 137.5, 137.3, 131.0 (q, $^{2}J_{C\text{-}F}$ = 32.7 Hz), 127.2, 125.8 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 125.4, 124.9, 124.1, 123.9 (q, $^{1}J_{C\text{-}F}$ = 272.4 Hz), 82.2, 80.0. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.67 (2B), -9.99 (8B). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.78 (3F). HRMS (ESI): *m/z* calcd for $C_{16}H_{21}B_{10}F_3N$ $[M+H]^+$: 392.2624. Found: 392.2633.

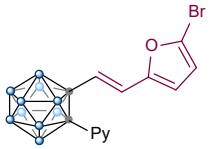


3i: 19 mg, Yield 50%. White solid, mp 144–146 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (dt, J = 4.6, 1.3 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.76 – 7.68 (m, 2H), 7.35 – 7.28 (m, 1H), 7.19 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 15.8 Hz, 1H), 6.17 (d, J = 15.8 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 149.2, 149.2, 139.0, 138.0, 137.3, 130.6, 130.1, 126.9, 125.4, 124.9, 123.9, 82.2, 80.1, 52.4. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.65 (2B), -9.96 (8B). HRMS (ESI): *m/z*

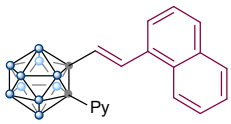
calcd for $C_{17}H_{24}B_{10}NO_2$ $[M+H]^+$: 382.2805. Found: 382.2825.



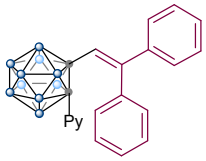
3j: 20 mg, Yield 61%. White solid, mp 116–118 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.34 – 7.27 (m, 1H), 7.16 (d, *J* = 5.0 Hz, 1H), 6.96 – 6.87 (m, 3H), 5.90 (d, *J* = 15.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.2, 149.2, 139.4, 137.2, 132.2, 128.7, 127.8, 126.6, 125.3, 124.8, 120.3, 82.4, 80.8. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.66 (1B), -3.41 (1B), -10.19 (8B). HRMS (ESI): *m/z* calcd for $C_{13}H_{20}B_{10}NS$ $[M+H]^+$: 330.2315. Found: 330.2335.



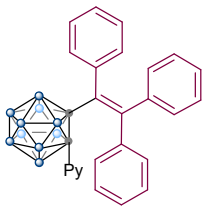
3k: 23 mg, Yield 58%. White solid, mp 117–119 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (dt, *J* = 4.8, 1.4 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.37 – 7.29 (m, 1H), 6.48 (d, *J* = 15.5 Hz, 1H), 6.25 (q, *J* = 3.4 Hz, 2H), 5.95 (d, *J* = 15.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.3, 149.3, 149.1, 137.3, 125.6, 125.4, 124.9, 123.9, 119.7, 114.2, 113.7, 82.6, 80.6. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.70 (2B), -10.12 (8B). HRMS (ESI): *m/z* calcd for $C_{13}H_{19}B_{10}NOBr$ $[M+H]^+$: 394.1622. Found: 394.1643.



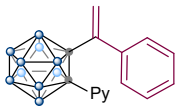
3l: 34 mg, Yield 90%. White solid, mp 130–133 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 – 8.59 (m, 1H), 7.84 – 7.68 (m, 5H), 7.59 (d, *J* = 15.5 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.35 – 7.29 (m, 2H), 7.15 (d, *J* = 7.1 Hz, 1H), 6.09 (d, *J* = 15.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 149.3, 137.4, 137.3, 133.5, 132.5, 131.0, 129.6, 128.7, 126.7, 126.3, 125.5, 125.5, 124.8, 124.3, 123.5, 82.6, 81.0. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.55 (1B), -3.24 (1B), -10.05 (8B). HRMS (ESI): *m/z* calcd for $C_{19}H_{24}B_{10}N$ $[M+H]^+$: 374.2907. Found: 374.2930.



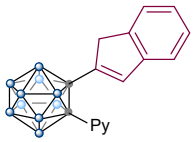
3m: 33 mg, Yield 82%. White solid, mp 151–153 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 – 8.68 (m, 1H), 7.78 (td, *J* = 7.7, 1.9 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.34 (m, 4H), 7.23 – 7.13 (m, 3H), 6.94 (dd, *J* = 7.7, 1.9 Hz, 2H), 6.82 – 6.77 (m, 2H), 5.96 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.5, 149.7, 149.3, 141.5, 137.2, 136.6, 129.8, 128.7, 128.4, 128.4, 128.3, 127.3, 125.8, 124.8, 120.6, 84.1, 80.0. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.79 (2B), -9.96 (8B). HRMS (ESI): *m/z* calcd for $C_{21}H_{26}B_{10}N$ $[M+H]^+$: 400.3063. Found: 400.3085.



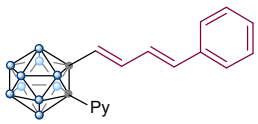
3n: 36 mg, Yield 76%. White solid, mp 198–200 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.91 (d, *J* = 3.9 Hz, 1H), 7.75 (td, *J* = 7.8, 1.8 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.37 – 7.27 (m, 3H), 7.24 (d, *J* = 7.7 Hz, 2H), 6.95 – 6.79 (m, 5H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.0 Hz, 2H), 6.52 (d, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.2, 150.1, 148.9, 144.7, 141.1, 140.3, 137.1, 131.5, 131.0, 128.9, 127.9, 127.7, 127.6, 127.4, 127.0, 126.9, 126.4, 126.0, 125.2, 85.0, 84.7. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -1.45 (1B), -3.16 (1B), -9.82 (8B). HRMS (ESI): *m/z* calcd for $C_{27}H_{30}B_{10}N$ $[M+H]^+$: 476.3376. Found: 476.3365.



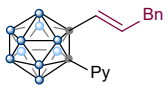
3o: 20 mg, Yield 62%. White solid, mp 100–102 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 4.7 Hz, 1H), 7.65 (td, *J* = 7.9, 1.8 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.37 (dd, *J* = 7.6, 4.9 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 2H), 6.54 (d, *J* = 7.0 Hz, 2H), 5.83 (s, 1H), 5.24 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 149.1, 141.4, 139.7, 137.0 , 128.7, 128.5, 128.1, 127.6, 125.8, 124.9, 84.1, 83.7. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.30 (2B), -9.44 (4B), -10.40 (4B). HRMS (ESI): *m/z* calcd for $C_{15}H_{22}B_{10}N$ $[M+H]^+$: 324.2750. Found: 324.2777.



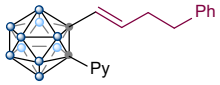
3p: 28 mg, Yield 83%. White solid, mp 152–154 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 – 8.39 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.60 (td, *J* = 7.8, 1.9 Hz, 1H), 7.29 (d, *J* = 6.1 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.22 – 7.14 (m, 3H), 6.91 (s, 1H), 3.35 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.2, 149.2, 143.4, 142.6, 138.3, 137.9, 137.1, 126.9, 126.6, 125.3, 124.8, 123.7, 122.2, 84.1, 81.2, 42.9. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.41 (2B), -10.28 (8B). HRMS (ESI): *m/z* calcd for $C_{16}H_{22}B_{10}N$ $[M+H]^+$: 336.2750. Found: 336.2778.



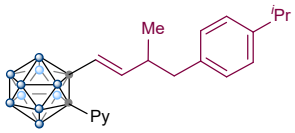
3q: 18 mg, Yield 51%. White solid, mp 107–109 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (dt, *J* = 4.9, 1.4 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.34 – 7.23 (m, 6H), 6.63 – 6.56 (m, 2H), 6.43 (dd, *J* = 15.3, 10.8 Hz, 1H), 5.62 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 149.2, 139.5, 137.3, 137.2, 136.2, 128.8, 128.7, 126.9, 126.1, 125.4, 124.8, 124.1, 82.5, 81.2. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.68 (2B), -9.94 (8B). HRMS (ESI): *m/z* calcd for $C_{17}H_{24}B_{10}N$ $[M+H]^+$: 350.2907. Found: 350.2927.



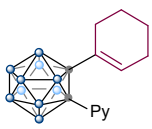
3r: 29 mg, Yield 86%. White solid, mp 72–75 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (dt, *J* = 4.9, 1.4 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.31 (ddd, *J* = 6.6, 4.8, 1.9 Hz, 1H), 7.19 – 7.14 (m, 3H), 6.77 – 6.71 (m, 2H), 6.13 (dt, *J* = 15.3, 7.0 Hz, 1H), 5.44 (dt, *J* = 15.2, 1.6 Hz, 1H), 3.16 (dd, *J* = 7.0, 1.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 140.7, 138.0, 137.0, 128.6, 128.4, 126.6, 125.5, 124.6, 124.1, 82.4, 80.6, 38.2. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.59 (1B), -3.44 (1B), -10.27 (8B). HRMS (ESI): *m/z* calcd for $C_{16}H_{24}B_{10}N$ $[M+H]^+$: 338.2907. Found: 338.2919.



3s: 31 mg, Yield 88%. White solid, mp 55–57 °C. As the starting vinyl bromide was an isomeric mixture (*trans*:*cis* = 9:1), the product was obtained as a mixture of isomers with a nearly identical ratio (*trans*:*cis* = 9:1). The two isomers were difficult to separate. ^{1}H NMR for the *trans* isomer (400 MHz, Chloroform-*d*) δ 8.55 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.68 (td, *J* = 7.7, 1.9 Hz, 1H), 7.62 (dt, *J* = 8.1, 1.2 Hz, 1H), 7.31 (ddd, *J* = 7.4, 4.8, 1.3 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.19 – 7.10 (m, 1H), 7.01 – 6.97 (m, 2H), 6.01 (dt, *J* = 15.4, 7.0 Hz, 1H), 5.35 (dt, *J* = 15.3, 1.5 Hz, 1H), 2.41 (t, *J* = 7.6 Hz, 2H), 2.16 – 2.10 (m, 2H). ^{1}H NMR for the *cis* isomer (400 MHz, Chloroform-*d*) δ 8.58 (dd, *J* = 1.9, 1.0 Hz, 1H), 7.68 (td, *J* = 7.7, 1.9 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.31 (ddd, *J* = 7.4, 4.8, 1.3 Hz, 1H), 7.27 (d, *J* = 1.4 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.15 – 7.12 (m, 2H), 5.48 (dt, *J* = 12.0, 7.4 Hz, 1H), 5.15 (dt, *J* = 11.9, 1.7 Hz, 1H), 2.68 (m, 2H), 2.62 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 149.3, 149.2, 141.2, 140.8, 140.6, 140.5, 137.1, 137.1, 128.6, 128.5, 128.4, 126.3, 126.2, 125.4, 125.4, 124.7, 124.6, 123.3, 121.6, 83.3, 82.1, 80.7, 79.4, 35.3, 34.9, 33.8. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.74 (1B), -3.54 (1B), -10.25 (8B). HRMS (ESI): *m/z* calcd for $C_{17}H_{26}B_{10}N$ $[M+H]^+$: 352.3063. Found: 352.3078.

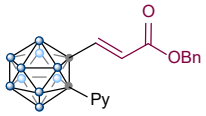


3t: 32 mg, Yield 78%. colourless oil. As the starting vinyl bromide was an isomeric mixture (*trans*/*cis* = 3.2:1), the product was obtained as a mixture of isomers with a comparable ratio (*trans*/*cis* = 3.7:1). The two isomers were difficult to separate. ^{1}H NMR for the *trans* isomer (400 MHz, Chloroform-*d*) δ 8.57 – 8.54 (m, 1H), 7.67 (td, *J* = 7.8, 1.8 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.29 (ddd, *J* = 7.4, 4.8, 1.3 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 5.91 (dd, *J* = 15.4, 7.7 Hz, 1H), 5.24 (d, *J* = 15.5 Hz, 1H), 2.89 – 2.83 (m, 1H), 2.34 – 2.28 (m, 2H), 2.20 – 2.14 (m, 1H), 1.23 (d, *J* = 7.0 Hz, 6H), 0.70 (d, *J* = 6.6 Hz, 3H). ^{1}H NMR for the *cis* isomer (400 MHz, Chloroform-*d*) δ 8.59 – 8.57 (m, 1H), 7.67 (td, *J* = 7.8, 1.8 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.33 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 5.30 (d, *J* = 12.0 Hz, 1H), 5.06 (d, *J* = 11.9 Hz, 1H), 3.37 (dt, *J* = 12.0, 6.4 Hz, 1H), 2.55 (dd, *J* = 13.3, 5.8 Hz, 2H), 2.36 (dd, *J* = 13.0, 7.5 Hz, 1H), 1.26 (s, 6H), 0.86 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 149.3, 149.2, 147.2, 146.9, 146.8, 137.1, 137.0, 136.7, 136.6, 129.4, 129.1, 126.4, 126.4, 125.4, 125.3, 124.7, 124.6, 121.2, 119.6, 82.3, 81.0, 79.5, 42.4, 42.3, 38.3, 33.9, 33.8, 33.2, 29.8, 24.2, 24.2, 24.2, 19.4, 19.0. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.73 (1B), -3.63 (1B), -10.23 (8B). HRMS (ESI): *m/z* calcd for $C_{21}H_{34}B_{10}N$ $[M+H]^+$: 408.3689. Found: 408.3703.

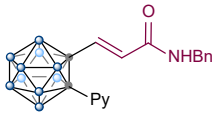


3u: 20 mg, Yield 66%. White solid, mp 125–127 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 – 8.50 (m, 1H), 7.68 (td, *J* = 7.7, 1.8 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.30 (ddd, *J* = 7.4, 4.8, 1.3 Hz, 1H), 6.24 – 6.16 (m, 1H), 1.93 – 1.87 (m, 2H), 1.86 – 1.81 (m, 2H), 1.39 – 1.31 (m, 2H), 1.25 – 1.17 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.5, 149.1, 137.4, 136.8, 129.0, 125.0, 124.5, 87.5, 83.1, 30.1,

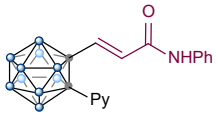
26.2, 22.9, 21.0. $^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) δ -2.79 (1B), -3.28 (1B), -9.96 (3B), -10.79 (5B). HRMS (ESI): *m/z* calcd for $C_{13}H_{24}B_{10}N$ $[M+H]^+$: 302.2907. Found: 302.2927.



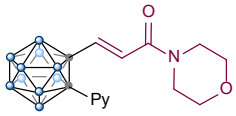
3v: 13 mg, Yield 34%. White solid, mp 63–65 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 – 8.44 (m, 1H), 7.70 – 7.61 (m, 2H), 7.31 – 7.25 (m, 4H), 7.23 – 7.18 (m, 2H), 6.62 (d, *J* = 15.5 Hz, 1H), 6.16 (d, *J* = 15.5 Hz, 1H), 5.02 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.4, 149.3, 148.8, 138.7, 137.5, 135.3, 128.7, 128.6, 128.4, 128.3, 125.3, 125.0, 81.4, 77.1, 67.0. $^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) δ -2.77 (2B), -9.64 (8B). HRMS (ESI): *m/z* calcd for $C_{17}H_{24}B_{10}NO_2$ $[M+H]^+$: 382.2805. Found: 382.2825.



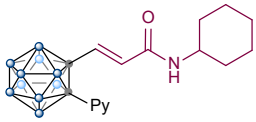
3w: 17 mg, Yield 45%. White solid, mp 167–169 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 – 8.53 (m, 1H), 7.78 – 7.67 (m, 2H), 7.36 – 7.27 (m, 4H), 7.25 – 7.18 (m, 2H), 6.58 (d, *J* = 15.0 Hz, 1H), 6.18 (d, *J* = 15.0 Hz, 1H), 5.93 (t, *J* = 5.9 Hz, 1H), 4.39 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.0, 149.5, 148.7, 137.5, 137.4, 135.0, 130.7, 129.0 , 128.1, 128.0, 125.4, 125.1, 81.5, 77.8, 44.1. $^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) δ -2.87 (2B), -9.66 (8B). HRMS (ESI): *m/z* calcd for $C_{17}H_{25}B_{10}N_2O$ $[M+H]^+$: 381.2965. Found: 381.2979.



3x: 17 mg, Yield 46%. White solid, mp 158–160 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.47 (s, 1H), 8.63 (d, *J* = 4.5 Hz, 1H), 7.98 – 7.90 (m, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.57 – 7.50 (m, 1H), 7.32 – 7.25 (m, 2H), 7.13 – 7.02 (m, 1H), 6.69 (d, *J* = 15.0 Hz, 1H), 6.60 (d, *J* = 15.0 Hz, 1H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 161.6, 150.4, 148.9, 139.6, 138.9, 134.4, 134.0, 129.7, 126.5, 126.4, 125.0, 120.3, 83.3, 79.5. $^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) δ -3.18 (2B), -9.94 (8B). HRMS (ESI): *m/z* calcd for $C_{16}H_{23}B_{10}N_2O$ $[M+H]^+$: 367.2809. Found: 367.2821.

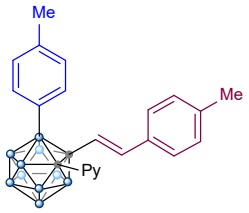


3y: 13 mg, Yield 36%. White solid, mp 107–109 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 – 8.55 (m, 1H), 7.77 – 7.69 (m, 2H), 7.38 – 7.33 (m, 1H), 6.60 (d, *J* = 15.0 Hz, 1H), 6.51 (d, *J* = 15.0 Hz, 1H), 3.65 – 3.59 (m, 4H), 3.59 – 3.52 (m, 2H), 3.41 – 3.34 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.0, 149.4, 148.8, 137.5, 135.8, 127.5, 125.5, 125.1, 81.7, 66.7, 46.2, 42.5. $^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) δ -2.80 (2B), -9.64 (8B). HRMS (ESI): *m/z* calcd for $C_{14}H_{25}B_{10}N_2O_2$ $[M+H]^+$: 361.2914. Found: 361.2904.

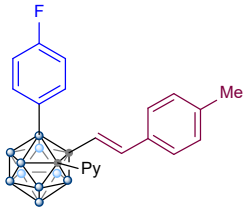


3z: 8 mg, Yield 21%. White solid, mp 208–210 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 – 8.53 (m, 1H), 7.77 – 7.67 (m, 2H), 7.38 – 7.30 (m, 1H), 6.50 (d, *J* = 14.9 Hz, 1H), 6.13 (d, *J* = 14.9 Hz, 1H), 5.49 (d, *J* = 8.2 Hz, 1H), 3.77 – 3.63 (m, 1H), 1.89 – 1.82 (m, 2H), 1.72 – 1.64 (m, 2H), 1.64 – 1.56 (m,

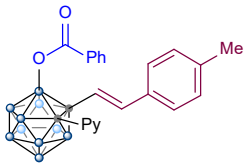
1H), 1.37 – 1.25 (m, 2H), 1.20 – 1.04 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.1, 149.4, 148.7, 137.4, 134.2, 131.3, 125.4, 125.1, 81.5, 78.1, 48.8, 33.0, 25.5, 24.8. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.90 (2B), -9.77 (8B). HRMS (ESI): *m/z* calcd for $C_{16}H_{29}B_{10}NO$ $[M+H]^+$: 373.3278. Found: 373.3294.



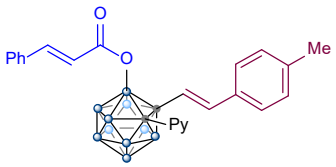
3aa: 25 mg, Yield 58%. colourless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 4.5 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.15 – 7.08 (m, 4H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 15.9 Hz, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 2.32 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.1, 148.5, 139.0, 138.9, 136.7, 136.7, 135.0, 132.9 , 129.6, 128.5, 126.9, 125.2, 124.2, 121.1, 79.8, 78.8, 21.4, 21.4. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -1.36 (1B), -3.38 (1B), -4.43 (1B), -8.84 (3B), -10.98 (4B). HRMS (ESI): *m/z* calcd for $C_2H_{30}B_{10}N$ $[M+H]^+$: 428.3376. Found: 428.3398.



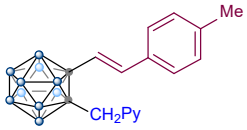
3ab: 24 mg, Yield 56%. White solid, mp 162–164 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 – 8.43 (m, 1H), 7.58 (td, *J* = 7.8, 1.8 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.21 (m, 3H), 7.16 – 7.08 (m, 4H), 6.87 – 6.79 (m, 3H), 6.66 (d, *J* = 15.9 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6 (d, $^{1}J_{C\text{-}F}$ = 249.7 Hz), 150.0, 148.5, 139.2, 137.0, 137.0, 136.8, 132.8, 129.7, 126.9, 125.0, 124.3, 120.8, 114.7 (d, $^{2}J_{C\text{-}F}$ = 19.7 Hz), 79.9, 78.8, 21.4. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -3.22 (2B), -4.33 (1B), -8.82 (3B), -10.81 (4B). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.02 (1F). HRMS (ESI): *m/z* calcd for $C_{22}H_{27}B_{10}FN$ $[M+H]^+$: 432.3126. Found: 432.3137.



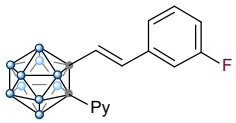
3ac: 25 mg, Yield 55%. White solid, mp 112–114 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (d, *J* = 4.8 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.64 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.25 (m, 3H), 7.09 (s, 4H), 6.93 (d, *J* = 15.9 Hz, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.7, 149.2, 147.9, 139.5, 139.1, 137.0, 133.6, 132.3, 130.2, 129.6, 128.6, 126.9, 125.5, 124.7, 117.8, 80.3, 79.8, 21.4. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -1.62 (1B), -4.93 (2B), -11.65 (5B), -15.00 (2B). HRMS (ESI): *m/z* calcd for $C_{23}H_{28}B_{10}NO_2$ $[M+H]^+$: 458.3118. Found: 458.3129.



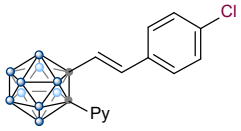
3ad: 27 mg, Yield 56%. colourless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (dt, *J* = 4.8, 1.4 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.39 – 7.29 (m, 5H), 7.25 – 7.21 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 15.9 Hz, 1H), 6.32 (d, *J* = 5.6 Hz, 1H), 6.28 (d, *J* = 5.5 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.5, 149.2, 147.9, 146.7, 139.5, 138.9, 137.0, 133.9, 132.4, 130.8, 129.6, 129.0, 128.3, 127.0, 125.5, 124.7, 118.3, 117.9, 80.1, 79.7, 21.4. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -1.78 (1B), -5.13 (2B), -11.86 (5B), -15.18 (2B). HRMS (ESI): *m/z* calcd for $C_{25}H_{30}B_{10}NO_2$ $[M+H]^+$: 484.3275. Found: 484.3291.



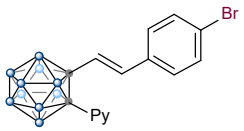
3ae: 22 mg, Yield 62%. White solid, mp 50–52 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 4.6 Hz, 1H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.23 – 7.15 (m, 4H), 7.03 (d, *J* = 15.7 Hz, 1H), 6.53 (d, *J* = 15.7 Hz, 1H), 3.61 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.5, 149.7, 141.5, 140.1, 136.7, 131.9, 129.8, 127.4, 125.0, 122.9, 120.1, 80.2, 79.3, 43.5, 21.5. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -3.98 (2B), -10.19 (8B). HRMS (ESI): *m/z* calcd for $C_{17}H_{26}B_{10}N$ $[M+H]^+$: 352.3063. Found: 352.3076.



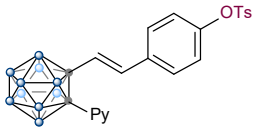
3af: 30 mg, Yield 88%. White solid, mp 69–72 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 – 8.55 (m, 1H), 7.76 – 7.67 (m, 2H), 7.36 – 7.28 (m, 1H), 7.22 (q, *J* = 7.9 Hz, 1H), 7.00 – 6.88 (m, 2H), 6.82 (d, *J* = 10.1 Hz, 1H), 6.77 (d, *J* = 15.8 Hz, 1H), 6.08 (d, *J* = 15.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.0 (d, $^{1}J_{C\text{-}F}$ = 246.4 Hz), 149.2, 137.9 (d, $^{4}J_{C\text{-}F}$ = 2.4 Hz), 137.3, 136.9 (d, $^{3}J_{C\text{-}F}$ = 7.4 Hz), 130.4 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 125.3, 124.9, 123.1 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 122.8, 116.2 (d, $^{2}J_{C\text{-}F}$ = 21.2 Hz), 113.3 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 82.2, 80.2. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.60 (2B), -9.94 (8B). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.65 (1F). HRMS (ESI): *m/z* calcd for $C_{15}H_{21}B_{10}FN$ $[M+H]^+$: 342.2656. Found: 342.2675.



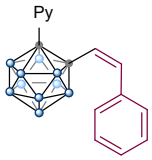
3ag: 31 mg, Yield 87%. White solid, mp 88–91 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (dt, *J* = 4.7, 1.5 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.34 – 7.29 (m, 1H), 7.24 – 7.19 (m, 2H), 7.09 – 7.04 (m, 2H), 6.75 (d, *J* = 15.7 Hz, 1H), 6.05 (d, *J* = 15.8 Hz, 1H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 149.2, 137.9, 137.3, 135.2, 133.2, 129.1, 128.2, 125.4, 124.8, 122.0, 82.3, 80.5. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.63 (2B), -10.07 (8B). HRMS (ESI): *m/z* calcd for $C_{15}H_{21}B_{10}ClN$ $[M+H]^+$: 358.2361. Found: 358.2376.



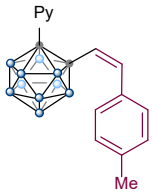
3ah: 143 mg, Yield 71%. White solid, mp 101–103 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 4.7 Hz, 1H), 7.78 – 7.65 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 15.8 Hz, 1H), 6.06 (d, *J* = 15.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 149.2, 138.0, 137.3, 133.6, 132.0, 128.4, 125.4, 124.8, 123.4, 122.1, 82.2, 80.5. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.66 (2B), -10.08 (8B). HRMS (ESI): *m/z* calcd for $C_{15}H_{21}B_{10}BrN$ $[M+H]^+$: 402.1856. Found: 402.1873.



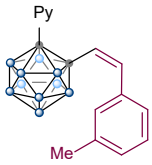
3ai: 38 mg, Yield 77%. Yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 4.8 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.27 (m, 3H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 15.7 Hz, 1H), 6.02 (d, *J* = 15.8 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.0, 149.2, 149.1, 145.7, 137.6, 137.3, 133.6, 132.3, 130.0, 128.5, 128.2, 125.4, 124.9, 122.8, 122.4, 82.1, 80.3, 21.8. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.71 (2B), -10.06 (8B). HRMS (ESI): *m/z* calcd for $C_{22}H_{28}B_{10}NO_3S$ $[M+H]^+$: 494.2788. Found: 494.2802.



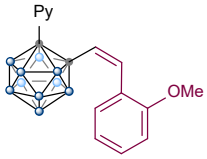
5a: 28 mg, Yield 86%. colourless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.71 – 8.62 (m, 1H), 7.77 (td, *J* = 7.8, 1.8 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 7.6, 4.9 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.07 – 6.98 (m, 2H), 6.63 (d, *J* = 12.5 Hz, 1H), 5.49 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 149.4, 138.9, 137.2, 134.6, 128.3, 128.1, 127.9, 125.6, 124.8, 123.6, 83.4, 78.8. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.60 (2B), -9.89 (8B). HRMS (ESI): *m/z* calcd for $C_{15}H_{22}B_{10}N$ $[M+H]^+$: 324.2750. Found: 324.2761.



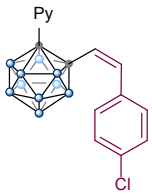
5b: 26 mg, Yield 77%. White solid, mp 94–96 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.65 (dd, *J* = 4.8, 1.0 Hz, 1H), 7.76 (td, *J* = 7.8, 1.9 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 7.7 Hz, 2H), 6.58 (d, *J* = 12.5 Hz, 1H), 5.45 (d, *J* = 12.5 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 139.1, 137.8, 137.2, 131.6, 128.8, 128.2, 125.6, 124.8, 123.4, 83.5, 79.0, 21.4. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.79 (2B), -9.90 (8B). HRMS (ESI): *m/z* calcd for $C_{16}H_{24}B_{10}N$ $[M+H]^+$: 338.2907. Found: 338.2923.



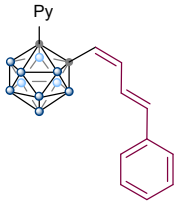
5c: 21 mg, Yield 62%. White solid, mp 86–88 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 4.2 Hz, 1H), 7.76 (td, *J* = 7.8, 1.9 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 7.5, 4.7 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.85 – 6.76 (m, 2H), 6.59 (d, *J* = 12.5 Hz, 1H), 5.47 (d, *J* = 12.5 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.5, 149.4, 139.0, 137.7, 137.1, 134.6, 128.9, 128.6, 128.0, 125.7, 125.3, 124.8, 123.5, 83.4, 78.9, 21.6. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.84 (2B), -9.90 (8B). HRMS (ESI): *m/z* calcd for $C_{16}H_{24}B_{10}N$ $[M+H]^+$: 338.2907. Found: 338.2931.



5d: 23 mg, Yield 65%. White solid, mp 119–121 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.68 – 8.61 (m, 1H), 7.75 (td, *J* = 7.8, 1.9 Hz, 1H), 7.67 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.38 (ddd, *J* = 7.4, 4.7, 1.1 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.07 (dt, *J* = 7.4, 1.4 Hz, 1H), 6.96 – 6.89 (m, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.47 (d, *J* = 12.4 Hz, 1H), 5.52 (d, *J* = 12.4 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.7, 149.4, 137.0, 135.7, 130.4, 129.7, 125.6, 124.7, 123.9, 123.3, 119.9, 110.2, 83.3, 79.1, 55.3. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.90 (2B), -9.97 (8B). HRMS (ESI): *m/z* calcd for $C_{16}H_{24}B_{10}NO$ $[M+H]^+$: 354.2856. Found: 354.2877.

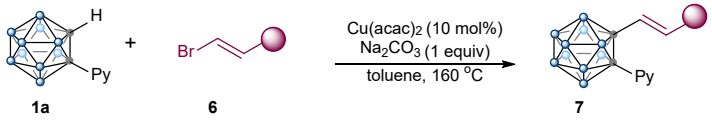


5e: 23 mg, Yield 63%. White solid, mp 96–98 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 – 8.62 (m, 1H), 7.77 (td, *J* = 7.8, 1.9 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.32 – 7.27 (m, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.53 (d, *J* = 12.5 Hz, 1H), 5.49 (d, *J* = 12.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.5, 149.4, 137.5, 137.3, 134.0, 133.0, 129.7, 128.4, 125.6, 124.9, 124.5, 83.3, 78.4. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.32 (1B), -2.83 (1B), -9.86 (8B). HRMS (ESI): *m/z* calcd for $C_{15}H_{21}B_{10}ClN$ $[M+H]^+$: 358.2361. Found: 358.2385.



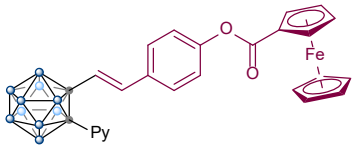
5f: 18 mg, Yield 50%. White solid, mp 155–157 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 – 8.57 (m, 1H), 7.75 – 7.67 (m, 2H), 7.53 (ddd, *J* = 15.4, 11.8, 1.2 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.39 – 7.29 (m, 4H), 6.61 (d, *J* = 15.4 Hz, 1H), 6.17 – 6.07 (m, 1H), 5.15 (d, *J* = 11.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 149.3, 139.9, 137.3, 137.2, 136.3, 129.0, 129.0, 127.3, 125.4, 124.8, 122.1, 120.0, 83.8, 80.0. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.54 (2B), -9.84 (8B). HRMS (ESI): *m/z* calcd for $C_{17}H_{24}B_{10}N$ $[M+H]^+$: 350.2907. Found: 350.2915.

3. Synthetic Applications



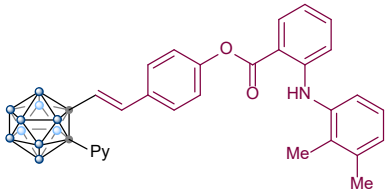
A mixture of **1a** (0.1 mmol, 1 equiv), **6** (0.15 mmol, 1.5 equiv), $Cu(acac)_2$ (10 mol%), Na_2CO_3 (1 equiv) and toluene (1 mL) was stirred at 160 °C for 12 h. After completion of the reaction, concentrated in vacuo. The crude product was purified by column chromatography on silica gel using petroleum ether and dichloromethane as the eluent to give the desired products **7**.

3.1 Synthesis of Carborane-Based Ferrocene

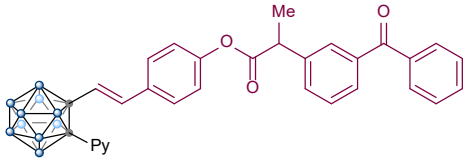


7a: 22 mg, Yield 40%. Orange solid, mp 171–173 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 4.7 Hz, 1H), 7.81 – 7.64 (m, 2H), 7.40 – 7.28 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 15.7 Hz, 1H), 6.05 (d, *J* = 15.7 Hz, 1H), 4.94 (s, 2H), 4.51 (s, 2H), 4.28 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.3, 151.7, 149.2, 138.4, 137.2, 132.2, 128.1, 125.4, 124.8, 122.2, 121.4, 82.4, 80.8, 72.2, 70.8, 70.1, 69.8. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.58 (2B), -10.08 (8B). HRMS (ESI): *m/z* calcd for $C_{26}H_{30}B_{10}FeNO_2$ $[M+H]^+$: 552.2618. Found: 552.2634.

3.2 Synthesis of Potential COX-2 Inhibitors

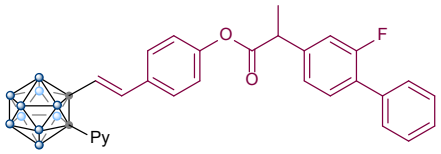


7b: 52 mg, Yield 92%. White solid, mp 166–168 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.12 (s, 1H), 8.60 (dt, *J* = 4.6, 1.4 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.79 – 7.69 (m, 2H), 7.36 – 7.30 (m, 2H), 7.26 – 7.21 (m, 2H), 7.19 – 7.09 (m, 4H), 7.05 (d, *J* = 7.0 Hz, 1H), 6.89 – 6.77 (m, 2H), 6.76 – 6.72 (m, 1H), 6.09 (d, *J* = 15.7 Hz, 1H), 2.34 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 151.5, 150.5, 149.2, 149.2, 138.4, 138.4, 138.3, 137.2, 135.3, 132.7, 132.5, 132.0, 128.2, 127.3, 126.1, 125.4, 124.8, 123.4, 122.5, 121.6, 116.3, 113.9, 109.3, 82.4, 80.8, 20.7, 14.1. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.56 (2B), -10.03 (8B). HRMS (ESI): *m/z* calcd for $C_{30}H_{35}B_{10}N_2O_2$ $[M+H]^+$: 563.3697. Found: 563.3713.

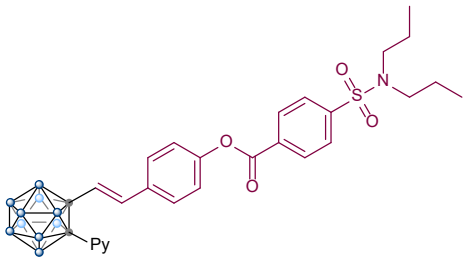


7c: 48 mg, Yield 83%. yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 4.6 Hz, 1H), 7.85 – 7.78 (m, 3H), 7.73 – 7.66 (m, 3H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.48 (td, *J* = 7.6, 3.3 Hz, 3H), 7.32 – 7.27 (m, 1H), 7.15 – 7.09 (m, 2H), 6.93 – 6.88 (m, 2H), 6.77 (d, *J* = 15.7 Hz, 1H), 6.02 (d, *J* = 15.7 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.5, 172.5,

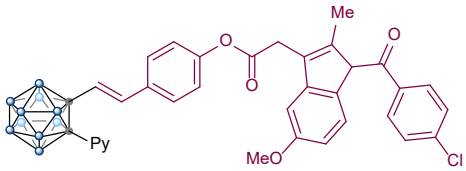
151.3, 149.2, 149.2, 140.2, 138.2, 138.2, 137.5, 137.2, 132.7, 132.5, 131.6, 130.2, 129.4, 129.3, 128.9, 128.5, 128.0, 125.3, 124.8, 121.8, 121.6, 82.3, 80.7, 45.6, 18.5. $^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) δ -2.56 (2B), -10.04 (8B). HRMS (ESI): *m/z* calcd for $C_{31}H_{34}B_{10}NO_3$ $[M+H]^+$: 576.3537. Found: 576.3551.



7d: 43 mg, Yield 76%. colourless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 – 8.53 (m, 1H), 7.76 – 7.66 (m, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.41 – 7.36 (m, 1H), 7.33 – 7.27 (m, 1H), 7.25 – 7.17 (m, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 15.8 Hz, 1H), 6.03 (d, *J* = 15.7 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 1H), 1.64 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 159.9 (d, $^{1}J_{C-F}$ = 249.0 Hz), 151.4, 149.2, 141.1(d, $^{3}J_{C-F}$ = 7.8 Hz), 138.2, 137.2, 135.4, 135.4, 132.5, 131.2 (d, $^{4}J_{C-F}$ = 3.8 Hz), 129.0 (d, $^{4}J_{C-F}$ = 2.9 Hz), 128.6, 128.3 (d, $^{3}J_{C-F}$ = 13.7 Hz), 128.0, 127.9, 125.4, 124.8, 123.7 (d, $^{4}J_{C-F}$ = 3.2 Hz), 121.8, 121.6, 115.4 (d, $^{2}J_{C-F}$ = 23.9 Hz), 82.4, 80.7, 45.2, 18.5. $^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) δ -2.52 (2B), -10.12 (8B). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.15 (1F). HRMS (ESI): *m/z* calcd for $C_{30}H_{33}B_{10}FNO_2$ $[M+H]^+$: 566.3493. Found: 566.3521.

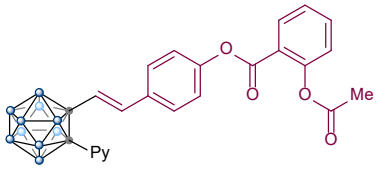


7e: 46 mg, Yield 76%. White solid, mp 152–155 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 4.7 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.75 – 7.68 (m, 2H), 7.36 – 7.29 (m, 1H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 15.7 Hz, 1H), 6.07 (d, *J* = 15.7 Hz, 1H), 3.15 – 3.08 (m, 4H), 1.56 (q, *J* = 7.5 Hz, 4H), 0.87 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.8, 151.2, 149.2, 149.2, 145.2, 138.1, 137.3, 132.8, 132.5, 130.9, 128.2, 127.3, 125.4, 124.9, 122.0, 121.9, 82.4, 80.6, 50.0, 22.0, 11.3. $^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) δ -2.49 (2B), -9.98 (8B). HRMS (ESI): *m/z* calcd for $C_{28}H_{39}B_{10}N_2O_4S$ $[M+H]^+$: 607.3629. Found: 607.3639.



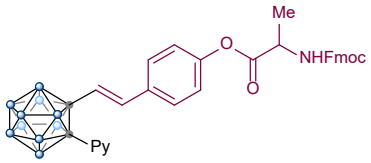
7f: 48 mg, Yield 71%. White solid, mp 48–50 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (dt, *J* = 4.7, 1.4 Hz, 1H), 7.72 – 7.65 (m, 4H), 7.50 – 7.45 (m, 2H), 7.30 (ddd, *J* = 6.7, 4.8, 2.3 Hz, 1H), 7.15 – 7.10 (m, 2H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.77 (d, *J* = 15.7 Hz, 1H), 6.69 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.02 (d, *J* = 15.7 Hz, 1H), 3.88 (s, 2H), 3.82 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.2, 168.4, 156.2, 151.3, 149.2, 139.5, 138.1, 137.2, 136.4, 133.9, 132.6, 131.3, 130.9, 130.5, 129.3, 128.1, 125.4, 124.8, 121.9, 121.7, 115.1, 111.8, 111.8,

101.3, 82.3, 80.7, 55.8, 30.6, 13.5. $^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) δ -2.57 (2B), -10.06 (8B). HRMS (ESI): *m/z* calcd for $C_{34}H_{36}B_{10}ClN_2O_4$ $[M+H]^+$: 679.3362. Found: 679.3386.

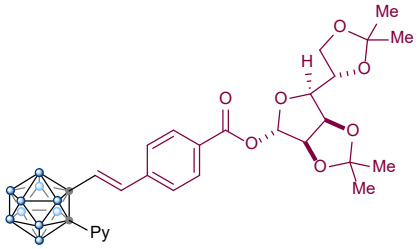


7g: 15 mg, Yield 30%. White solid, mp 166–168 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (dt, *J* = 4.7, 1.4 Hz, 1H), 8.18 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.64 (td, *J* = 7.9, 1.7 Hz, 1H), 7.38 (td, *J* = 7.7, 1.2 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.22 – 7.18 (m, 2H), 7.17 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.09 – 7.04 (m, 2H), 6.81 (d, *J* = 15.7 Hz, 1H), 6.05 (d, *J* = 15.8 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8, 162.9, 151.4, 151.2, 149.3, 149.2, 138.2, 137.3, 135.0, 132.8, 132.3, 128.3, 126.4, 125.4, 124.9, 124.2, 122.3, 122.2, 121.8, 82.4, 80.7, 21.1. $^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) δ -2.62 (2B), -10.00 (8B). HRMS (ESI): *m/z* calcd for $C_{24}H_{28}B_{10}NO_4$ $[M+H]^+$: 502.3016. Found: 502.3036.

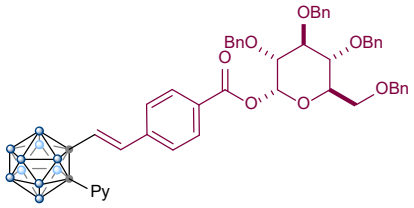
3.3 Construction of the BNCT Drug Candidate



7h: 34 mg, Yield 54%. White solid, mp 55–57 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 – 8.54 (m, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.73 – 7.66 (m, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.34 – 7.26 (m, 3H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.78 (d, *J* = 15.7 Hz, 1H), 6.03 (d, *J* = 15.7 Hz, 1H), 5.33 (d, *J* = 7.8 Hz, 1H), 4.67 – 4.53 (m, 1H), 4.48 – 4.35 (m, 2H), 4.22 (t, *J* = 7.0 Hz, 1H), 1.56 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.7, 155.8, 151.0, 149.2, 143.9, 143.8, 141.4, 138.1, 137.3, 132.8, 128.2, 127.9, 127.2, 125.4, 125.1, 124.8, 121.9, 121.8, 120.2, 82.3, 80.6, 67.3, 49.9, 47.2, 18.5. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.57 (2B), -10.04 (8B). HRMS (ESI): *m/z* calcd for $C_{33}H_{37}B_{10}N_2O_4$ $[M+H]^+$: 633.3751. Found: 633.3767.

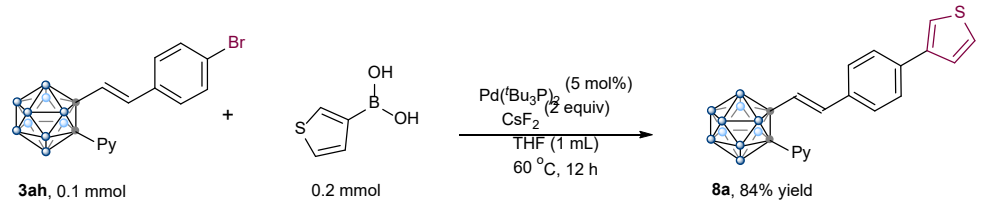


7i: 33 mg, Yield 51%. White solid, mp 152–154 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 – 8.55 (m, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.81 – 7.69 (m, 2H), 7.34 (ddd, *J* = 6.8, 4.7, 1.9 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 15.7 Hz, 1H), 6.35 (s, 1H), 6.21 (d, *J* = 15.7 Hz, 1H), 4.94 (dd, *J* = 5.9, 3.5 Hz, 1H), 4.86 (d, *J* = 5.8 Hz, 1H), 4.45 (ddd, *J* = 7.8, 6.2, 4.2 Hz, 1H), 4.17 – 4.08 (m, 2H), 4.04 (dd, *J* = 8.9, 4.3 Hz, 1H), 1.53 (s, 3H), 1.47 (s, 3H), 1.39 (d, *J* = 5.8 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.4, 149.2, 149.2, 139.6, 137.7, 137.3, 130.3, 129.9, 126.9, 125.4, 124.9, 124.3, 113.5, 109.5, 101.8, 85.3, 82.7, 82.2, 80.0, 79.5, 73.0, 66.9, 27.1, 26.1, 25.2, 24.8. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.55 (2B), -9.81 (8B). HRMS (ESI): *m/z* calcd for $C_{30}H_{48}B_{10}NO_7$ $[M+H]^+$: 642.4429. Found: 642.4441.



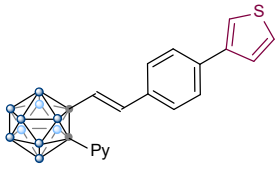
7j: 42 mg, Yield 46%. colourless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 4.7 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 2H), 7.81 – 7.69 (m, 2H), 7.40 – 7.31 (m, 14H), 7.29 (s, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.19 (dd, *J* = 6.2, 2.8 Hz, 2H), 6.87 (d, *J* = 15.9 Hz, 1H), 6.60 (d, *J* = 3.3 Hz, 1H), 6.21 (d, *J* = 15.7 Hz, 1H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.89 (t, *J* = 9.7 Hz, 2H), 4.76 (d, *J* = 11.5 Hz, 1H), 4.71 – 4.61 (m, 2H), 4.57 (d, *J* = 10.4 Hz, 1H), 4.51 (d, *J* = 12.1 Hz, 1H), 4.04 (t, *J* = 9.3 Hz, 1H), 3.96 (dd, *J* = 10.1, 2.4 Hz, 1H), 3.82 (dt, *J* = 13.3, 9.9 Hz, 3H), 3.67 (d, *J* = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.4, 149.2, 139.5, 138.7, 138.0, 137.9, 137.8, 137.7, 137.3, 130.5, 130.1, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 126.9, 125.4, 124.9, 124.3, 91.0, 82.2, 81.9, 80.0, 79.1, 77.0, 75.8, 75.7, 73.7, 73.3, 73.2, 68.2. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.53 (2B), -9.88 (8B). HRMS (ESI): *m/z* calcd for $C_{51}H_{60}B_{10}NO_7$ $[M+H]^+$: 906.5368. Found: 906.5384.

3.4 Construction of Carborane-Based Functionalized Molecules

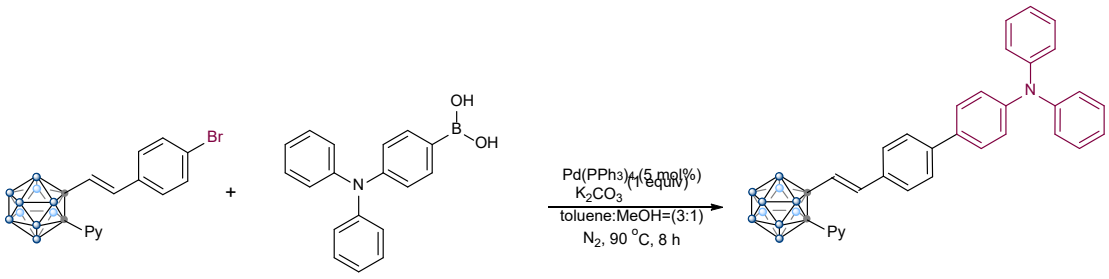


3ah, 0.1 mmol 0.2 mmol **8a**, 84% yield

To a 25 mL dried flask were sequentially added **3ah** (0.1 mmol, 1 equiv), 3-thiopheneboronic acid (0.2 mmol, 2 equiv), $Pd(^tBu_3P)_2$ (5 mol%), CsF (0.2 mmol, 2 equiv) and THF (1 mL) under air atmosphere. The reaction was stirred at 60 °C for 12 h. After the reaction was completed, the solvents were removed under vacuum and purified by silica gel column chromatography (petroleum and ethyl acetate as eluent) to obtain the product **8a** in 84% isolated yield.

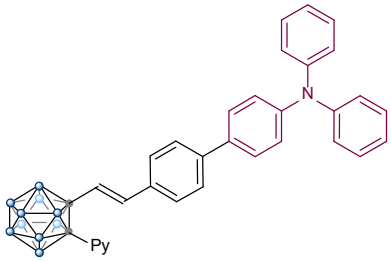


8a: 34 mg, Yield 84%. White solid, mp 140–142 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 – 8.56 (m, 1H), 7.77 – 7.67 (m, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.43 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.36 – 7.28 (m, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 15.7 Hz, 1H), 6.09 (d, *J* = 15.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 149.2, 141.5, 138.8, 137.2, 136.8, 133.5, 127.5, 126.7, 126.7, 126.2, 125.4, 124.8, 121.1, 121.0, 82.4, 81.1. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.60 (2B), -10.06 (8B). HRMS (ESI): *m/z* calcd for $C_{19}H_{24}B_{10}NS$ $[M+H]^+$: 406.2628. Found: 406.2639.

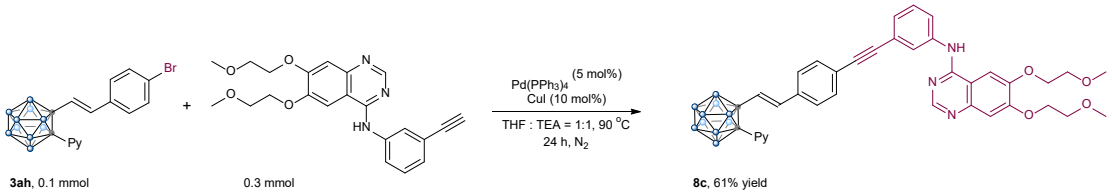


3ah, 0.1 mmol 0.3 mmol **8b**, 80% yield

To a 25 mL sealed tube equipped with a magnetic stir bar was charged with **3ah** (0.1 mmol, 1 equiv), 4-(diphenylamino) phenylboronic acid (0.3 mmol, 3 equiv), $Pd(PPh_3)_4$ (5 mol%), K_2CO_3 (0.1 mmol, 1 equiv) and mixed solvents (toluene:MeOH = 3:1) under N_2 atmosphere. The mixture was maintained stirring at 90 °C for 8 h in a heating mantel. After the reaction was completed, the solvents were removed under vacuum and purified by silica gel column chromatography (petroleum and ethyl acetate as eluent) to obtain the product **8b** in 80% isolated yield.

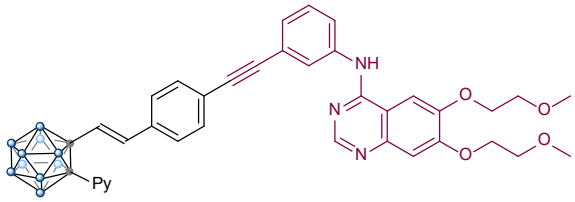


8b: 45 mg, Yield 80%. yellow solid, mp 77–79 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 – 8.53 (m, 1H), 7.76 – 7.65 (m, 2H), 7.42 (dd, *J* = 19.1, 8.5 Hz, 4H), 7.32 – 7.22 (m, 5H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.14 – 7.07 (m, 6H), 7.05 – 7.01 (m, 2H), 6.82 (d, *J* = 15.7 Hz, 1H), 6.09 (d, *J* = 15.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 149.2, 147.8, 147.6, 141.6, 138.9, 137.2, 133.8, 133.1, 129.5, 127.7, 127.5, 126.8, 125.4, 124.8, 124.7, 123.6, 123.3, 120.9, 82.4, 81.2. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.69 (2B), -10.17 (8B). HRMS (ESI): *m/z* calcd for $C_{33}H_{35}B_{10}N_2$ $[M+H]^+$: 567.3798. Found: 567.3814.



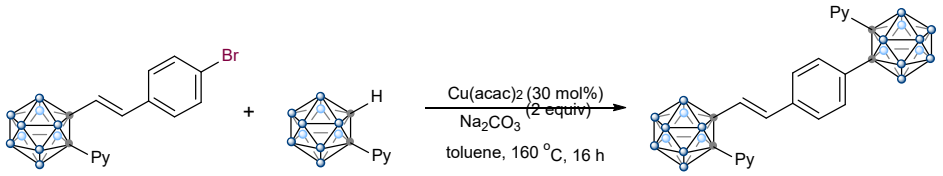
3ah, 0.1 mmol 0.3 mmol **8c**, 61% yield

A mixture of **3ah** (0.1 mmol, 1 equiv) and Erlotinib (0.3 mmol, 3 equiv), $Pd(PPh_3)_4$ (5 mol%), CuI (10 mol%) in mixed solvents (THF:TEA = 1:1) was stirred at 90 °C for 24 h under N_2 atmosphere. After cooling down to room temperature, the solvents were removed under vacuum and the residue was purified by column chromatography on silica gel, using DCM and MeOH as the eluent (volume ratio, DCM/MeOH: = 20:1) to afford the desired product **8c** in 61% isolated yield.



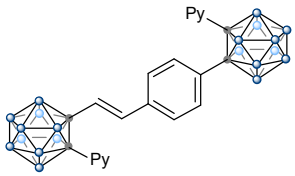
8c: 44 mg, Yield 61%. yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (s, 1H), 8.59 (d, *J* = 4.8 Hz, 1H), 7.92 (t, *J* = 1.8 Hz, 1H), 7.76 – 7.70 (m, 3H), 7.60 – 7.49 (m, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.34 (m, 1H), 7.34 – 7.31 (m, 1H), 7.30 – 7.27 (m, 2H), 7.21 (s, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 15.7 Hz, 1H), 6.11 (d, *J* = 15.7 Hz, 1H), 4.28 (t, *J* = 4.7 Hz, 2H), 4.23 (t, *J* = 4.7 Hz, 2H), 3.83 (d, *J* = 3.9 Hz, 4H), 3.46 (d, *J* = 3.9 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.4, 154.8, 153.5, 149.3, 149.2, 149.1, 139.0, 138.4, 137.2, 134.6, 132.0, 129.2, 127.5, 127.0, 125.4, 124.8, 124.7, 124.1, 123.8, 122.2, 122.1, 109.2, 108.6, 102.8, 91.0, 89.3, 82.3, 80.7, 71.1, 70.5, 69.3, 68.5, 59.4, 59.4. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.60 (2B), -10.02 (8B). HRMS (ESI): *m/z* calcd for $C_{37}H_{43}B_{10}N_4O_4$ $[M+H]^+$: 715.4282. Found: 715.4296.

3.5 Double C-Carboranylation via Iterative Cluster C−H Activation



3ah, 0.1 mmol **1a**, 0.2 mmol **8d**, 77% yield

To a 25 mL sealed tube equipped with a magnetic stir bar was charged with **3ah** (0.1 mmol, 1 equiv), **1a** (0.2 mmol, 2 equiv), $Cu(acac)_2$ (30 mol%), Na_2CO_3 (0.2 mmol, 2 equiv), toluene (1 mL). The mixture was maintained stirring at 160 °C for 16 h in a heating mantel. Upon completion, the reaction mixture was cooled to room temperature, The reaction mixture was purified by flash column chromatography on silica gel using petroleum/ethyl acetate as the eluent to afford the desired product **8d** in 77% isolated yield.



8d: 42 mg, Yield 77%. White solid, mp 206–208 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (dt, *J* = 4.7, 1.4 Hz, 1H), 8.33 (dt, *J* = 4.9, 1.4 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.56 – 7.47 (m, 2H), 7.39 – 7.34 (m, 2H), 7.34 – 7.29 (m, 1H), 7.15 (ddd, *J* = 6.6, 4.7, 2.1 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.65 (d, *J* = 15.7 Hz, 1H), 6.01 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.2, 149.2, 149.1, 148.7, 137.3, 137.2, 136.9, 136.3, 131.6, 131.2, 126.5, 125.4, 125.0, 124.9, 124.6, 123.5, 84.2, 84.0, 82.0, 80.0. ^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) δ -2.74 (4B), -10.11 (16B). HRMS (ESI): *m/z* calcd for $C_{22}H_{35}B_{20}N_2$ $[M+H]^+$: 543.4802. Found: 543.4823.

4. Photophysical Properties

Carboranes have been regarded as excellent building blocks to construct luminescent materials particularly for aggregation induced emission (AIE) luminogens (AIEgens), due to their 3D-aromatic structure, unique electronic properties and large steric hindrance. For a demonstration, we investigated the photophysical properties of the representative products.

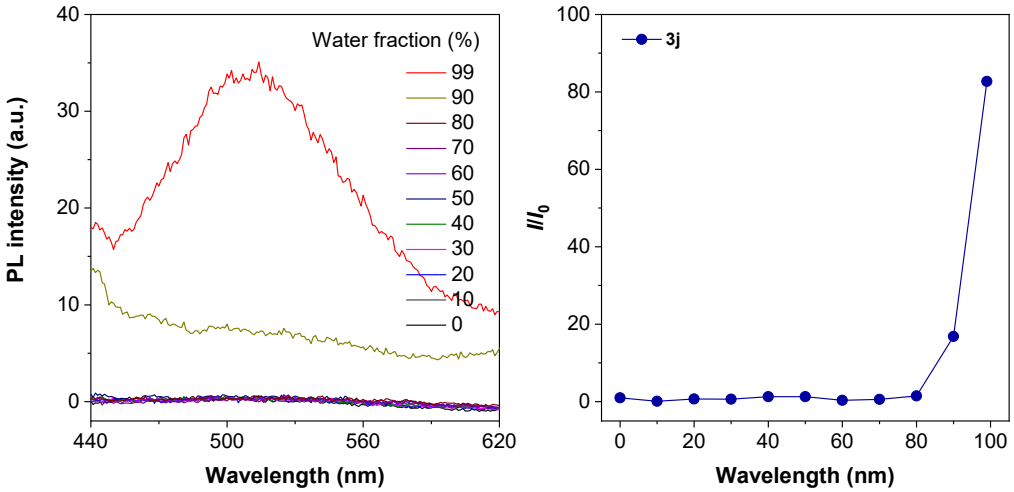


Figure S1. Left: The PL spectra of **3j** in THF/H_2O mixture solvents. Right: The plot of the relative emission intensity (I/I_0) at the emission maximum versus the water fraction for compound **3j**.

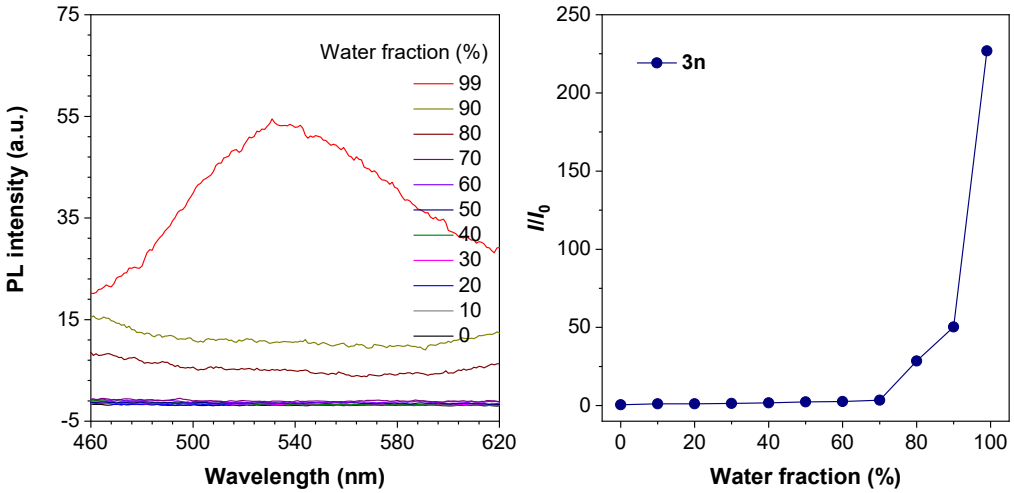


Figure S2. Left: The PL spectra of **3n** in THF/H_2O mixture solvents. Right: The plot of the relative emission intensity (I/I_0) at the emission maximum versus the water fraction for compound **3n**.

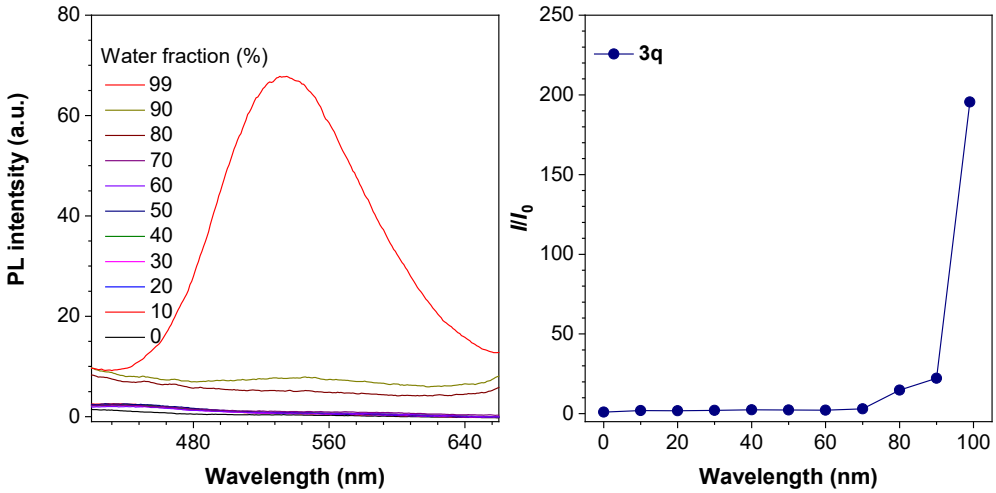


Figure S3. Left: The PL spectra of **3q** in THF/H_2O mixture solvents. Right: The plot of the relative emission intensity (I/I_0) at the emission maximum versus the water fraction for compound **3q**.

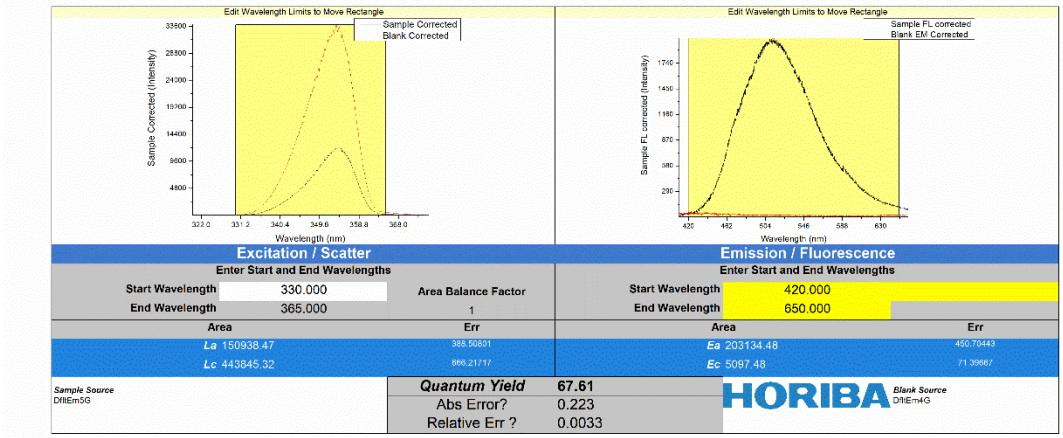


Figure S4. The absolute quantum yields of **3j**.

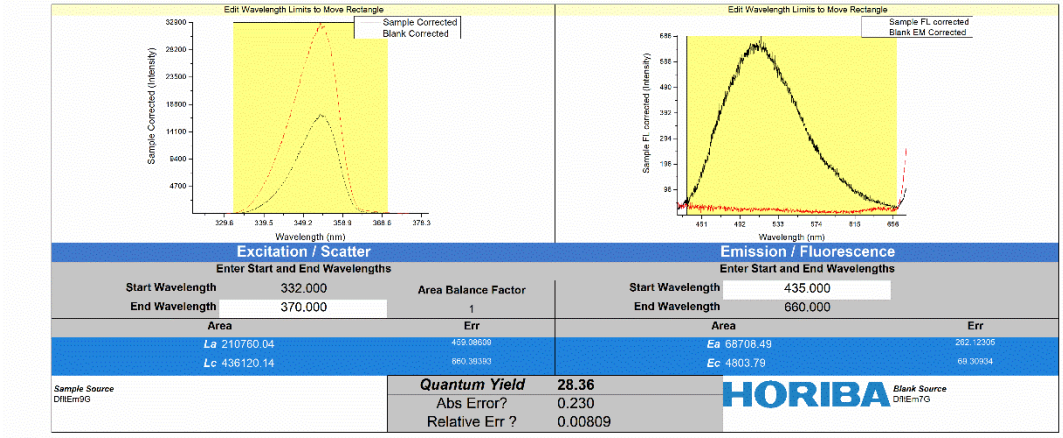


Figure S5. The absolute quantum yields of **3l**.

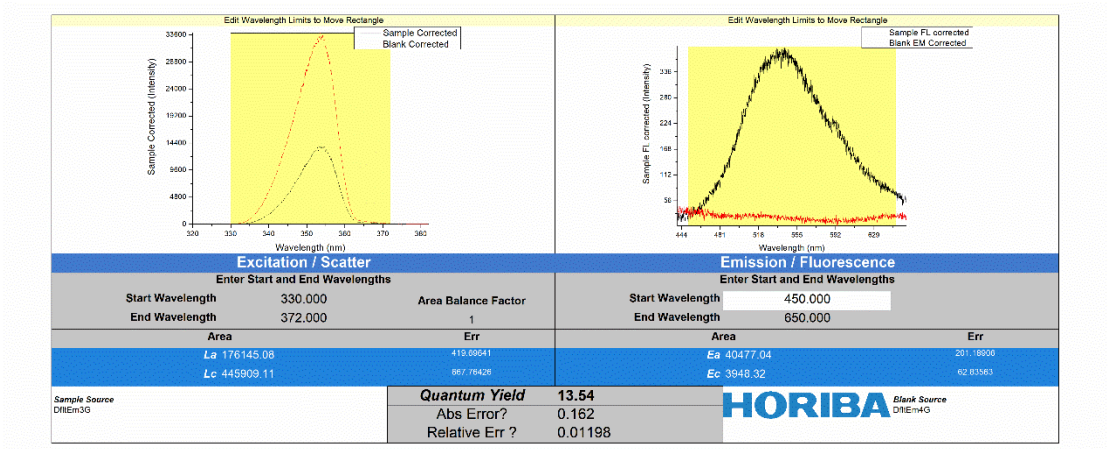


Figure S6. The absolute quantum yields of **3n**.

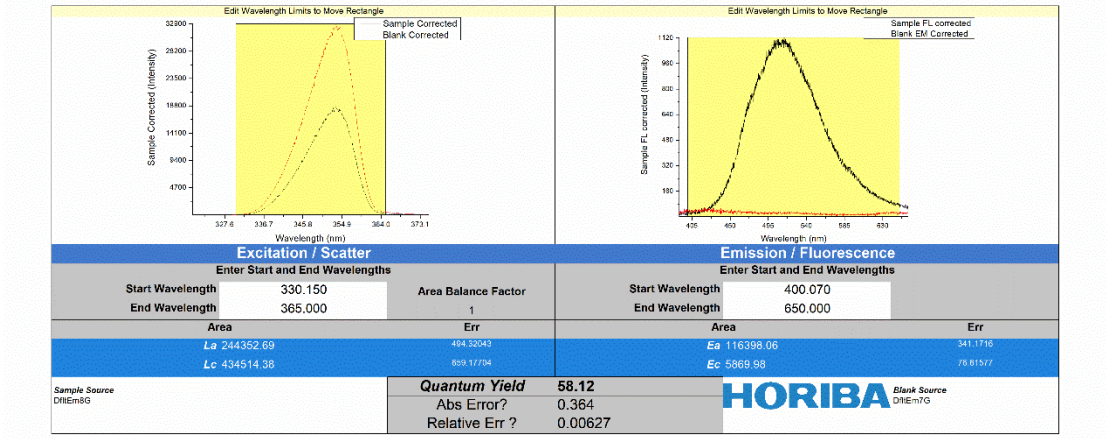


Figure S7. The absolute quantum yields of **3q**.

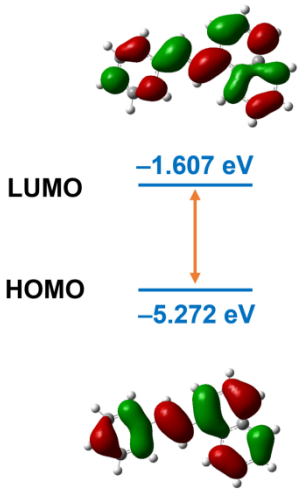
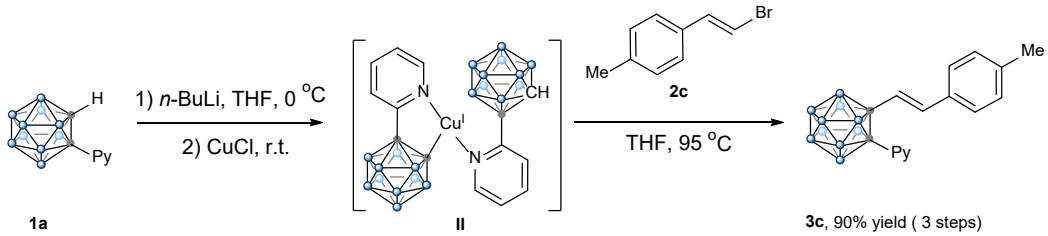


Figure S8. HOMO and LUMO of **1-styrylnaphthalene** in excited state.

5. Preliminary Mechanistic Studies

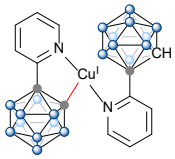
5.1 Metal Intermediate Experiment

To a solution of **1a** (0.1 mmol) in 0.3 mL of THF was added dropwise a 1.6 M solution of *n*-BuLi in *n*-hexane (0.1 mL, 0.16 mmol) at 0 °C under N_2. The mixture was stirred for 30 min. Then, CuCl (13 mg, 0.13 mmol) was added in one portion, and the mixture was stirred at room temperature for 1 h. Pyridine (60 μL, 0.75 mmol) and (*E*)-1-(2-bromovinyl)-4-methylbenzene (29.5 mg, 0.15 mmol) were added in one portion, and the resulting mixture was stirred at 95 °C for 3 h. Upon completion, the reaction mixture was concentrated under vacuo. The crude mixture was purified by column chromatography eluting with petroleum ether and dichloromethane to afford the desired product **3c** in 90% yield.



Scheme S1. Synthesis and reaction of complex **II**.

To a solution of **1a** (0.5 mmol) in 1.5 mL of THF was added dropwise a 1.6 M solution of *n*-BuLi in *n*-hexane (0.5 mL, 0.16 mmol) at 0 °C under N_2. The mixture was stirred for 30 min. Then, CuCl (65 mg, 0.65 mmol) was added in one portion, and the mixture was stirred at room temperature for 1 h. Upon completion, the crude mixture was diluted by ethyl acetate (2.0 mL) and evaporated in vacuo to remove all the volatiles. The resulting mixture was purified by column chromatography (eluting with petroleum ether/ethyl acetate = 1/2) gave the complex **II**. Then, a small portion (about 2 mg) of complex **II** was diluted by EtOH and analyzed by HRMS.



HRMS (ESI): *m/z* calcd for $C_{14}H_{28}B_{20}CuN_2$ $[M-H]^-$: 504.3548. Found: 504.3546.

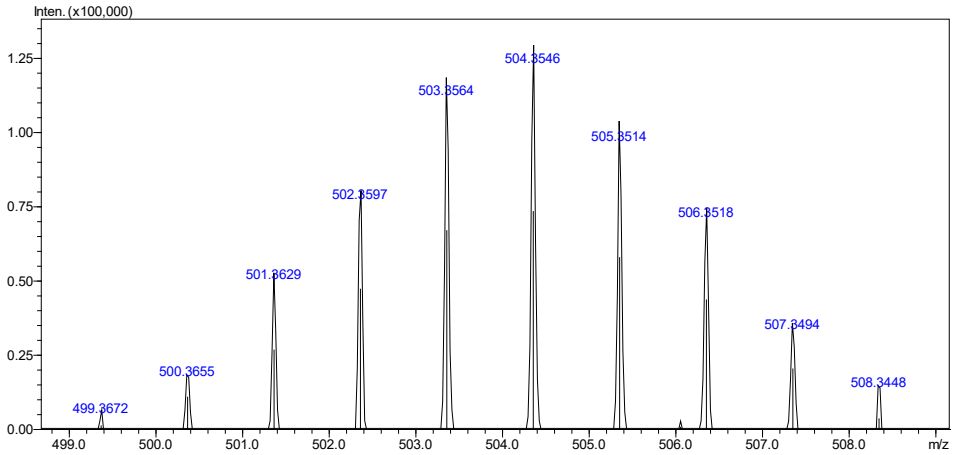


Figure S9. ESI-HRMS of complex **II**

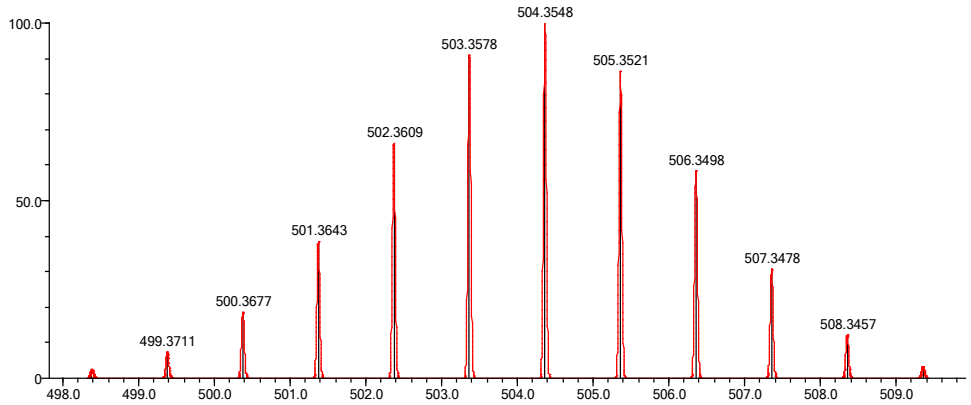
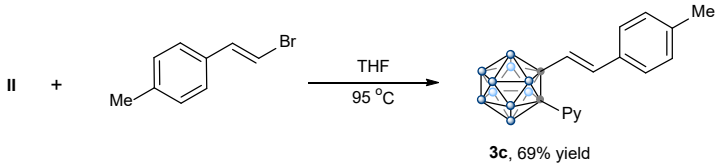


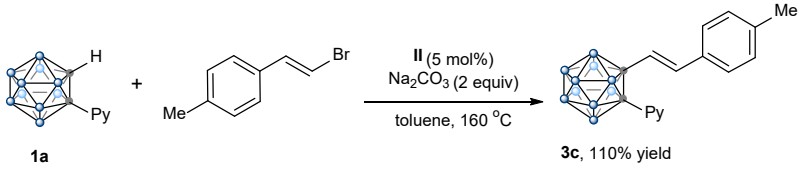
Figure S10. Calculated HRMS of complex **II**

A mixture of complex **II** (0.02 mmol, 1.0 equiv), (*E*)-1-(2-bromovinyl)-4-methylbenzene (0.03 mmol, 1.5 equiv) and THF (0.2 mL) in a closable Schlenk tube equipped with a magnetic stirrer and the resulting reaction mixture was stirred at 95 °C for 3 h. Upon completion, the reaction mixture was concentrated under vacuo. The crude mixture was purified on silica gel eluting with petroleum ether and dichloromethane to afford the desired product **3c** in 69% yield.



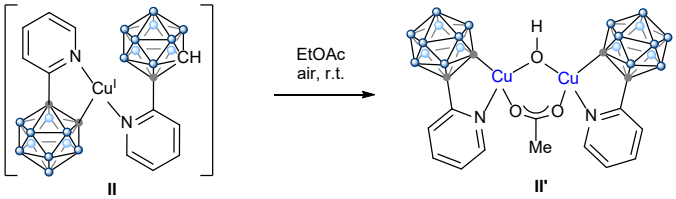
Scheme S2. Reaction of complex **II**.

A mixture of **1a** (0.05 mmol, 1.0 equiv), (*E*)-1-(2-bromovinyl)-4-methylbenzene (0.075 mmol, 1.5 equiv), complex **II** (5 mol%), Na_2CO_3 (0.1 mmol, 2 equiv) and toluene (0.5 mL) in a closable Schlenk tube equipped with a magnetic stirrer and the resulting reaction mixture was stirred at 160 °C for 12 h. Upon completion, the reaction mixture was concentrated under vacuo. The crude mixture was purified on silica gel eluting with petroleum ether and dichloromethane to afford the desired product **3h** in 112% yield.



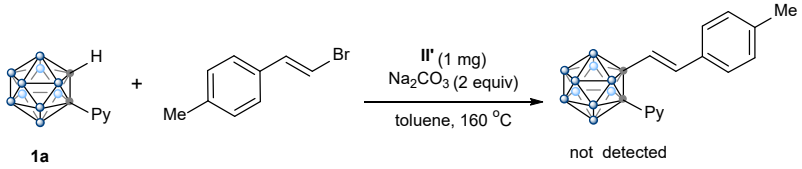
Scheme S3. Evaluation of catalytic activity of complex **II**.

Complex **II** (2 mg) was dissolved in ethyl acetate (1 mL) in 4 mL glass vial. The glass vial was open cap. Vapor diffusion within 2 days at room temperature. we found that the reaction of complex **II** in ethyl acetate at room temperature afforded a rare copper(II)-carborane complex **II'**. The structure of this Cu(II) complex was confirmed by X-ray diffraction.



Scheme S4. Synthesis of complex **II'**.

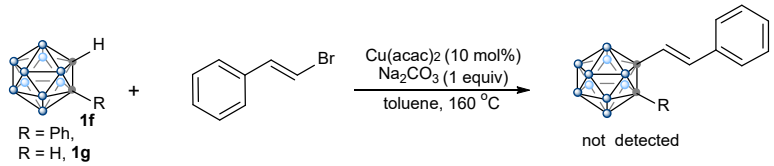
A mixture of **1a** (0.05 mmol, 1.0 equiv), (*E*)-1-(2-bromovinyl)-4-methylbenzene (0.075 mmol, 1.5 equiv), complex **II'** (1 mg), Na_2CO_3 (0.1 mmol, 2 equiv) and toluene (0.5 mL) in a closable Schlenk tube equipped with a magnetic stirrer and the resulting reaction mixture was stirred at 160 ºC for 12 h. No target product was observed.



Scheme S5. Reaction of complex **II'**.

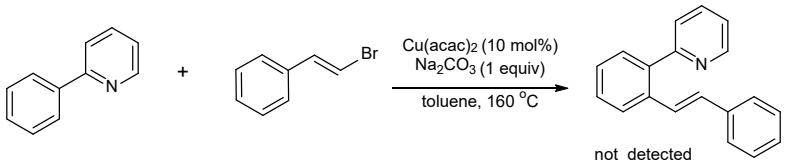
5.2 Control Experiments

A mixture of **1f** or **1g** (0.05 mmol, 1.0 equiv), (*E*)-(2-bromovinyl)benzene (0.075 mmol, 1.5 equiv), $Cu(acac)_2$ (10 mol%), Na_2CO_3 (0.05 mmol, 1 equiv) and toluene (0.5 mL) in a closable Schlenk tube equipped with a magnetic stirrer and the resulting reaction mixture was stirred at 160 °C for 12 h. No desired product was observed.



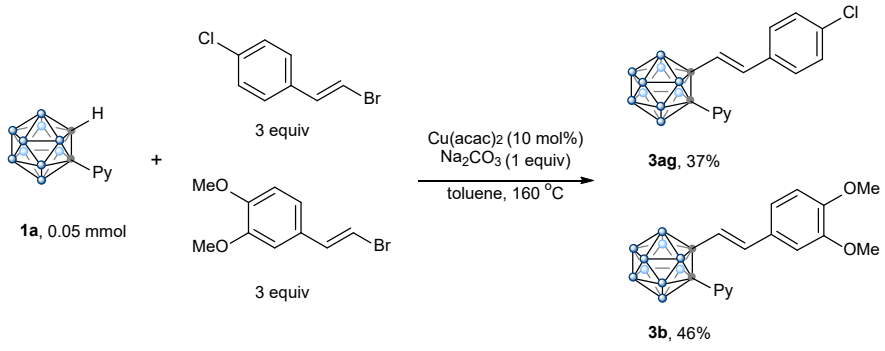
Scheme S6. Comparison of directing groups.

A mixture of 2-phenylpyridine (0.05 mmol, 1.0 equiv), (*E*)-(2-bromovinyl)benzene (0.075 mmol, 1.5 equiv), $Cu(acac)_2$ (10 mol%), Na_2CO_3 (0.05 mmol, 1 equiv) and toluene (0.5 mL) in a closable Schlenk tube equipped with a magnetic stirrer and the resulting reaction mixture was stirred at 160 °C for 12 h. No desired product was observed.



Scheme S7. Reaction of 2-phenylpyridine.

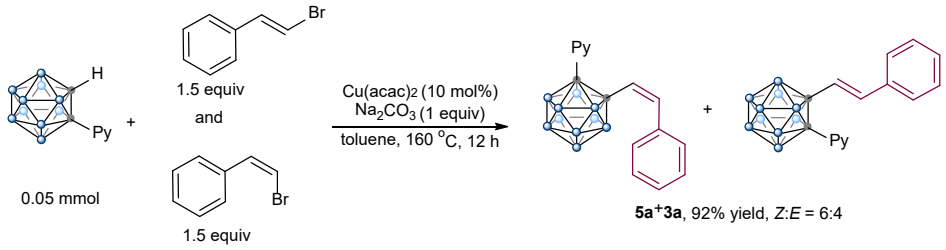
A mixture of **1a** (0.05 mmol, 1 equiv), (*E*)-1-(2-bromovinyl)-4-chlorobenzene (0.15 mmol, 3.0 equiv), (*E*)-4-(2-bromovinyl)-1,2-dimethoxybenzene (0.15 mmol, 3.0 equiv), $Cu(acac)_2$ (10 mol%), Na_2CO_3 (1 equiv) and toluene (0.5 mL) was stirred at 160 °C for 12 h. After completion of the reaction, concentrated in vacuo. The crude product was purified by column chromatography on silica gel using petroleum ether and dichloromethane as the eluent to give the **3ag** in 37% yield and **3b** in 46% yield, respectively.



Scheme S8. Comparison of reactivity of vinyl bromides.

A mixture of **1a** (0.05 mmol, 1 equiv), (*E*)-cinnamic acid (0.075 mmol, 1.5 equiv), (*Z*)-cinnamic acid (0.075 mmol, 1.5 equiv), $Cu(acac)_2$ (10 mol%), Na_2CO_3 (1 equiv) and toluene (0.5 mL) was stirred at 160 °C for 12 h. After completion of the reaction, concentrated in vacuo. The crude product was purified by column chromatography on silica gel using petroleum ether and dichloromethane as the

eluent to give a mixture of *Z*/*E* isomers (**5a**+**3a**, 92% yield, *Z*/*E* = 6:4).



Scheme S9. Comparison of reactivity of (*Z*)- and (*E*)-vinyl bromides.

5a+3a: 15 mg, Yield 92%. Colorless oil. the product was obtained as a mixture of isomers with a comparable ratio (*Z*/*E* = 6:4). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.68 – 8.56 (m, 1H), 7.79 – 7.64 (m, 2H), 7.43 – 7.27 (m, 3H), 7.24 (d, *J* = 3.4 Hz, 1H), 7.16 – 6.99 (m, 2H), 6.81 (d, *J* = 15.8 Hz, 0.4H), 6.62 (d, *J* = 12.5 Hz, 0.6H), 6.06 (d, *J* = 15.7 Hz, 0.4H), 5.48 (d, *J* = 12.5 Hz, 0.6H).

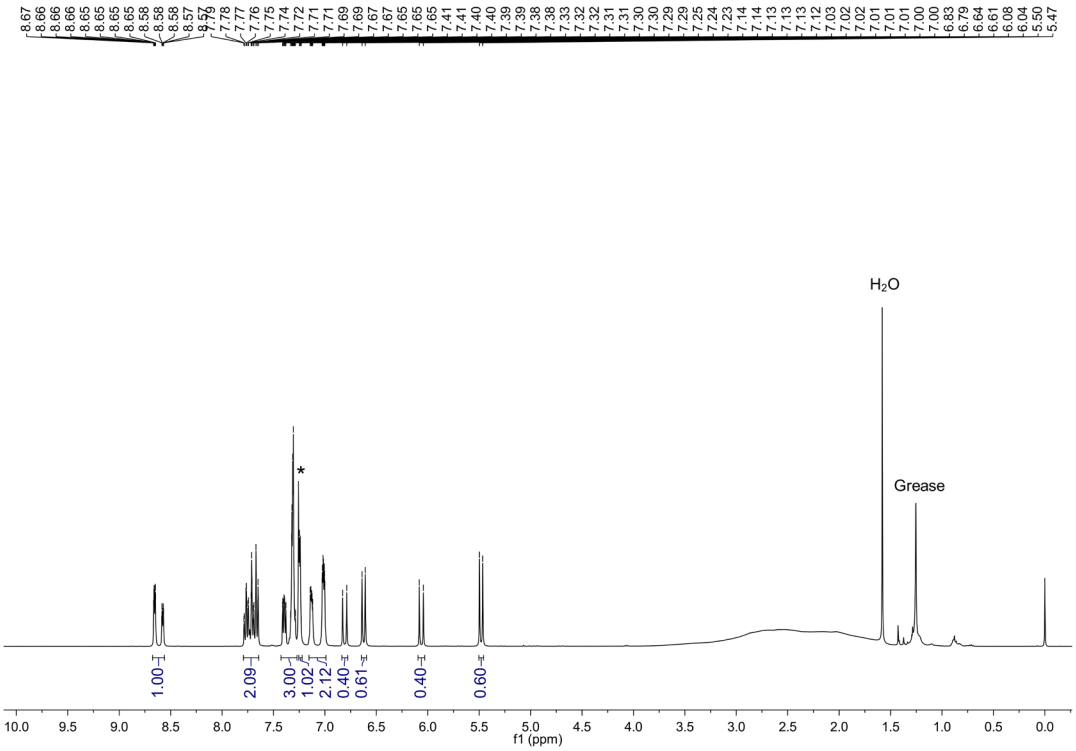
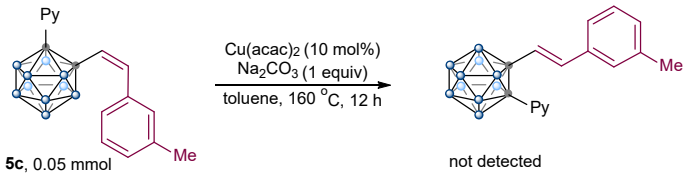


Figure S11. ^{1}H NMR (400 MHz, Chloroform-*d*) **5a**+**3a** (* from residual $CHCl_3$ in Chloroform-*d*)

A mixture of **5c** (0.05 mmol, 1 equiv), $Cu(acac)_2$ (10 mol%), Na_2CO_3 (1 equiv) and toluene (0.5 mL) in a closable Schlenk tube equipped with a magnetic stirrer and the resulting reaction mixture was stirred at 160 °C for 12 h. The trans product **3d** was not detected.

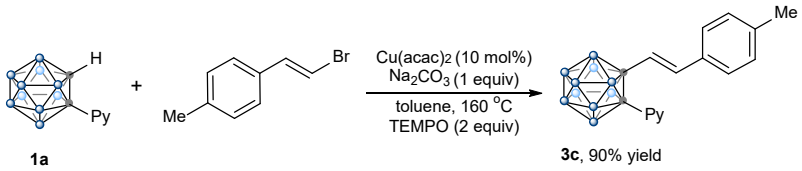


Scheme S10. Stability test of product **5c** configuration.

5.3 Radical Trapping Experiments

1a (0.05 mmol, 1.0 equiv), (*E*)-1-(2-bromovinyl)-4-methylbenzene (0.075 mmol, 1.5 equiv), $Cu(acac)_2$ (10 mol%), Na_2CO_3 (0.05 mmol, 1 equiv) and TEMPO (0.1 mmol, 2 equiv) were mixed in toluene (0.5 mL) in a closable Schlenk tube equipped with a magnetic stirrer and the resulting reaction mixture was stirred at 160 °C for 12 h. Upon completion, the reaction mixture was concentrated under vacuo. The crude mixture was purified on silica gel eluting with petroleum ether and dichloromethane to afford the desired product **3c** in 90% yield.

Radical trapping experiments with TEMPO suggested that the above alkenylation of carboranes might not involve a radical pathway.



Scheme S11. Radical trapping experiment.

5.4 Plausible Catalytic Cycle

On the basis of our observations and previous reports,[5] a plausible reaction mechanism is proposed in Figure S11. Reduction of Cu(II) by *o*-carborane or base forms Cu(I) species.[6] A bidentate chelation of **1a** with Cu(I) occurs to give the intermediate (**I**). Subsequently, in the presence of Na_2CO_3, cage C-H bond metalation of I generates a key cyclometalated intermediate copper(I)-*o*-carborane complex (**II**). Oxidative addition of Cu(I) by alkenyl halide affords the Cu(III) species (**III**), which undergoes C-C reductive elimination to give products **3** and regenerate the catalytically active Cu(I) complex. It is noteworthy that the double bond geometry of alkenyl halide reactants was fully retained in all of the stereospecific cage C-H alkenylation products.

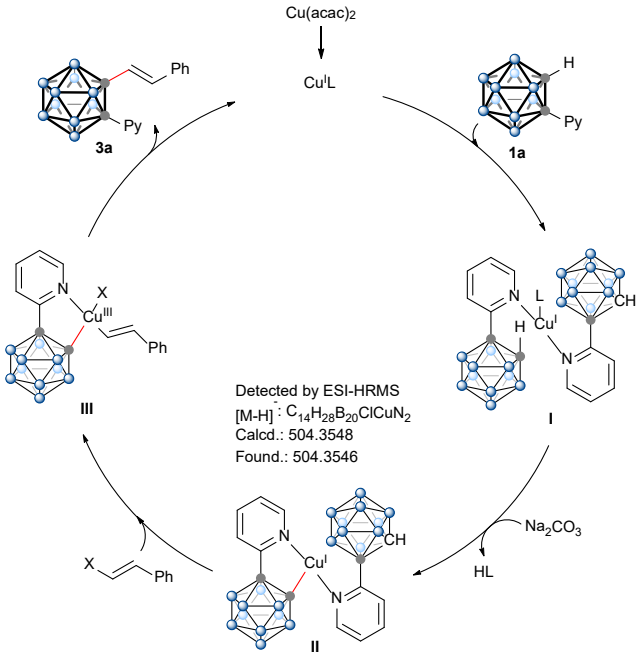


Figure S12. Plausible catalytic cycle.

6. X-Ray Crystallographic Data

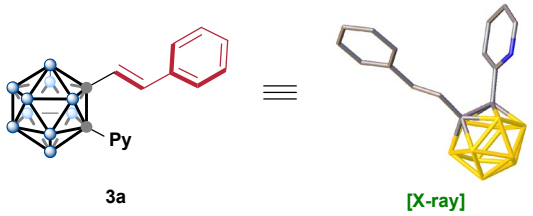


Table S2. Crystal data and structure refinement for **3a**.

Identification code	CCDC 2496932
Empirical formula	$C_{15}H_{21}B_{10}N$
Formula weight	323.43
Temperature/K	193
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.6233(3)
b/Å	12.6036(6)
c/Å	44.544(2)
α/°	90
β/°	90.489(2)
γ/°	90
Volume/Å^3	3718.3(3)
Z	4
ρ_{calc} g/cm^3	1.156
μ/mm^{-1}	0.058
F(000)	1344.0
Crystal size/mm^3	0.15 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.714 to 49.992
Index ranges	$-7 \le h \le 7$, $-14 \le k \le 13$, $-52 \le l \le 52$
Reflections collected	26081
Independent reflections	6513 [R_{int} = 0.0983, R_{sigma} = 0.0918]
Data/restraints/parameters	6513/0/477
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0802, wR_2 = 0.2112
Final R indexes [all data]	R_1 = 0.1090, wR_2 = 0.2267
Largest diff. peak/hole / e Å^{-3}	0.28/-0.32

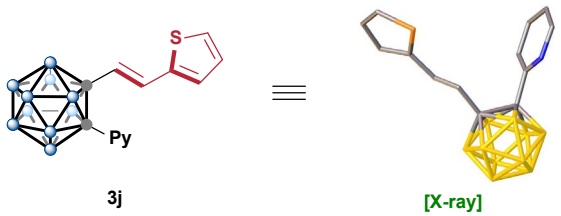
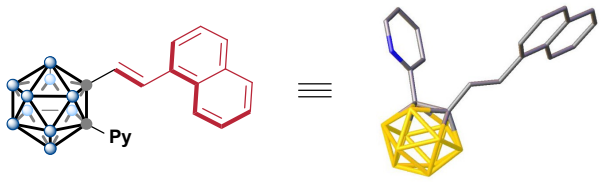


Table S3. Crystal data and structure refinement for **3j**.

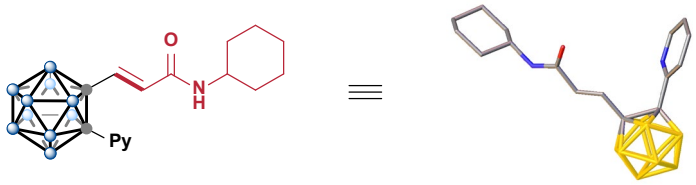
Identification code	CCDC 2496933
Empirical formula	$C_{13}H_{19}B_{10}NS$
Formula weight	329.45
Temperature/K	193
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.800(4)
b/Å	12.420(6)
c/Å	21.506(10)
α/°	90
β/°	90.303(19)
γ/°	90
Volume/Å^3	1816.4(16)
Z	2
ρ_{calc} g/cm^3	1.210
μ/mm-1	0.172
F(000)	686.0
Crystal size/mm^3	0.19 × 0.08 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.786 to 54.934
Index ranges	$-8 \le h \le 7$, $-16 \le k \le 16$, $-26 \le l \le 27$
Reflections collected	15459
Independent reflections	8033 [R_{int} = 0.0664, R_{sigma} = 0.0992]
Data/restraints/parameters	8033/4/459
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0731, wR_2 = 0.1900
Final R indexes [all data]	R_1 = 0.0970, wR_2 = 0.2118
Largest diff. peak/hole / e Å^{-3}	0.57/-0.55



3l [X-ray]

Table S4. Crystal data and structure refinement for **3l**.

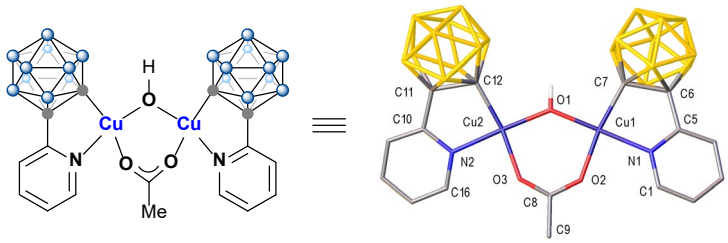
Identification code	CCDC 2496934
Empirical formula	$C_{19}H_{23}B_{10}N$
Formula weight	373.48
Temperature/K	193
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.4659(6)
b/Å	6.6516(3)
c/Å	18.7605(7)
α/°	90
β/°	111.9990(10)
γ/°	90
Volume/Å^3	2020.83(14)
Z	4
ρ_{calc} g/cm^3	1.228
μ/mm^{-1}	0.063
F(000)	776.0
Crystal size/mm^3	0.17 × 0.15 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.684 to 55.072
Index ranges	$-22 \le h \le 22$, $-8 \le k \le 8$, $-24 \le l \le 24$
Reflections collected	18135
Independent reflections	4646 [R_{int} = 0.0592, R_{sigma} = 0.0541]
Data/restraints/parameters	4646/0/271
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0517, wR_2 = 0.1319
Final R indexes [all data]	R_1 = 0.0695, wR_2 = 0.1448
Largest diff. peak/hole / e Å^{-3}	0.27/-0.25



3z ≡ [X-ray]

Table S5. Crystal data and structure refinement for **3z**.

Identification code	CCDC 2496936
Empirical formula	$C_{16}H_{28}B_{10}N_2O$
Formula weight	372.50
Temperature/K	173
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.9890(4)
b/Å	22.5139(9)
c/Å	8.2685(3)
α/°	90
β/°	105.1940(10)
γ/°	90
Volume/Å^3	2153.81(14)
Z	4
ρ_{calc} g/cm^3	1.149
μ/mm^{-1}	0.063
F(000)	784.0
Crystal size/mm^3	0.16 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.958 to 52.748
Index ranges	$-14 \le h \le 14$, $-28 \le k \le 28$, $-10 \le l \le 9$
Reflections collected	22482
Independent reflections	4388 [R_{int} = 0.0740, R_{sigma} = 0.0566]
Data/restraints/parameters	4388/0/266
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0515, wR_2 = 0.1187
Final R indexes [all data]	R_1 = 0.0825, wR_2 = 0.1385
Largest diff. peak/hole / e Å^{-3}	0.22/-0.21



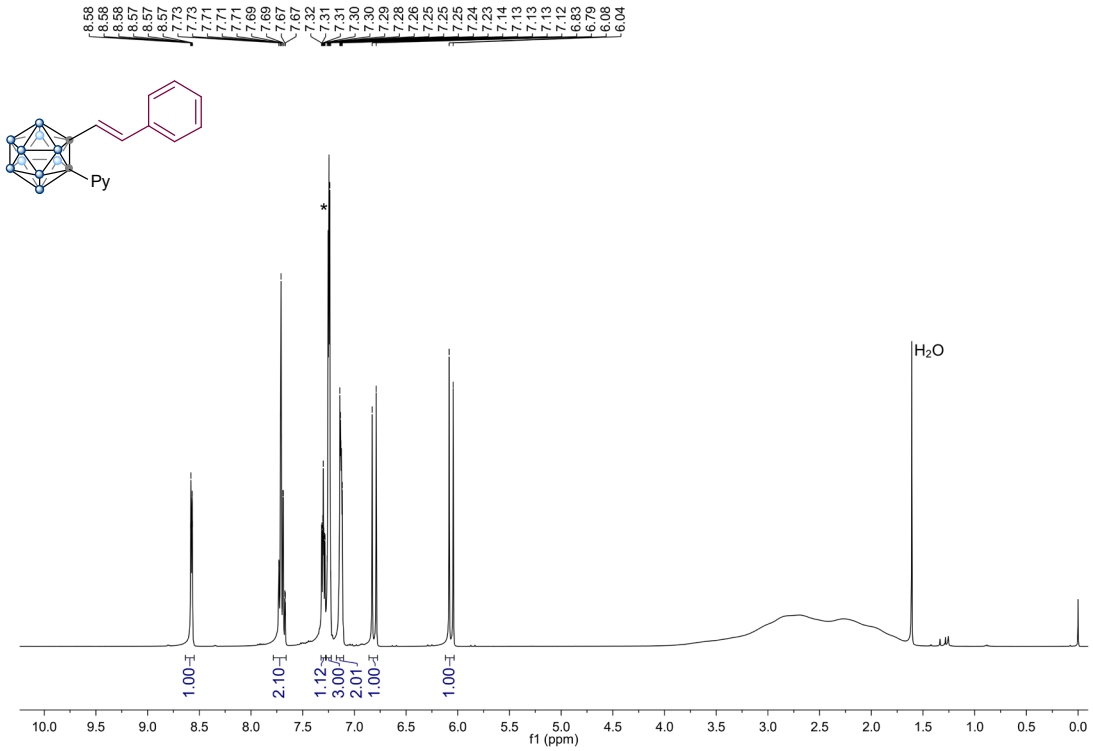
B' **[X-ray]**

Table S6. Crystal data and structure refinement for **B'**.

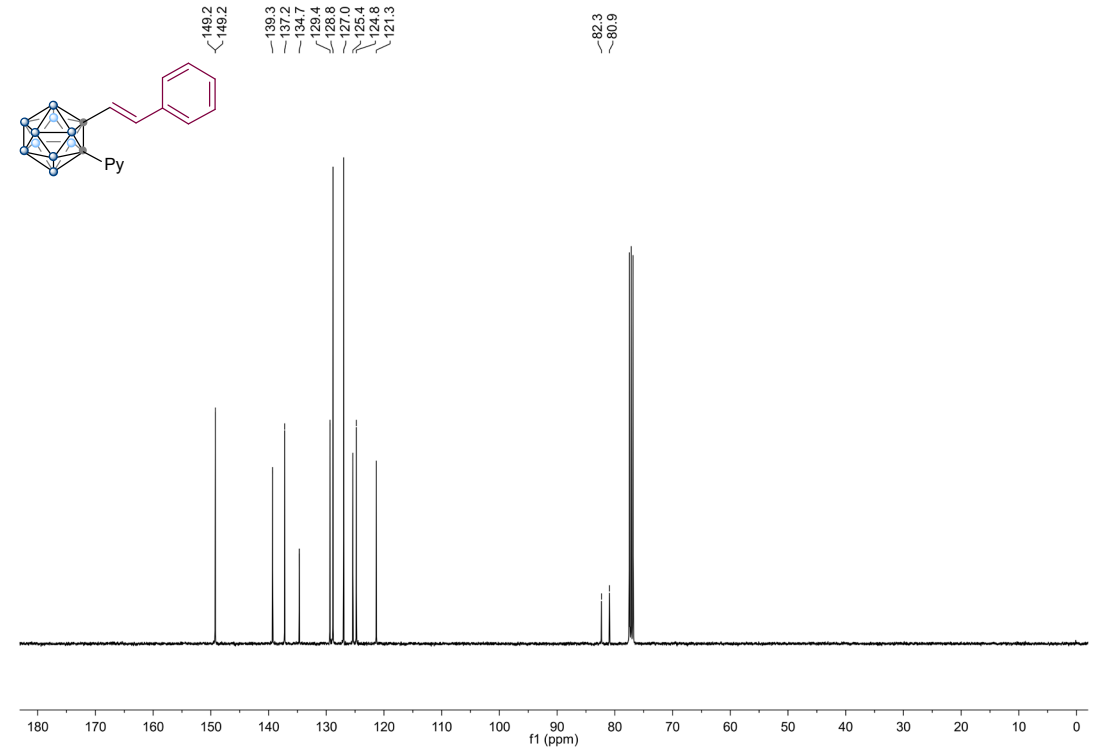
Identification code	CCDC 2496931
Empirical formula	$C_{32}H_{64}B_{40}Cu_4N_4O_6$
Formula weight	1287.43
Temperature/K	170
Crystal system	triclinic
Space group	P-1
a/Å	7.3682(3)
b/Å	10.1761(4)
c/Å	22.8548(10)
α/°	85.791(2)
β/°	86.643(2)
γ/°	70.673(2)
Volume/Å^3	1611.64(12)
Z	1
ρ_{calc} g/cm^3	1.326
μ/mm^{-1}	1.798
F(000)	648.0
Crystal size/mm^3	0.08 × 0.05 × 0.04
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.762 to 127.676
Index ranges	-7 ≤ h ≤ 8, -11 ≤ k ≤ 11, -26 ≤ l ≤ 26
Reflections collected	13973
Independent reflections	5282 [R_{int} = 0.0526, R_{sigma} = 0.0516]
Data/restraints/parameters	5282/1/393
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0398, wR_2 = 0.1095
Final R indexes [all data]	R_1 = 0.0447, wR_2 = 0.1141
Largest diff. peak/hole / e Å^{-3}	0.37/-0.42

7. NMR Spectra

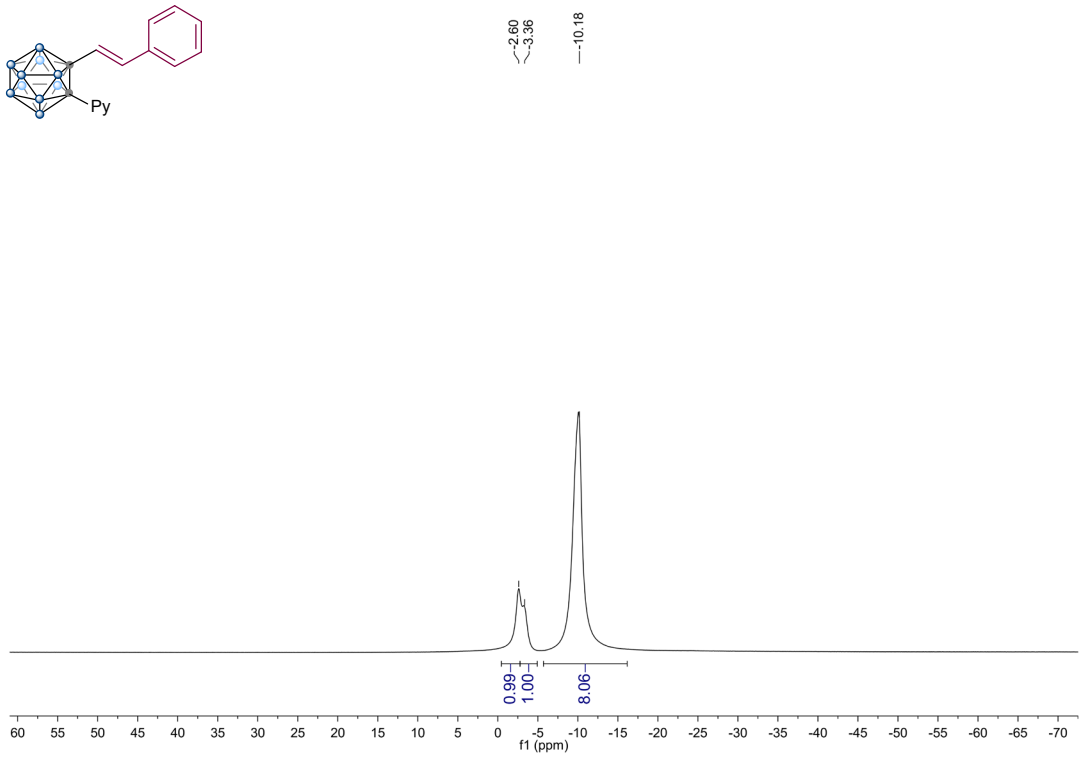
^{1}H NMR (400 MHz, Chloroform-*d*) **3a** (* from residual $CHCl_3$ in Chloroform-*d*)



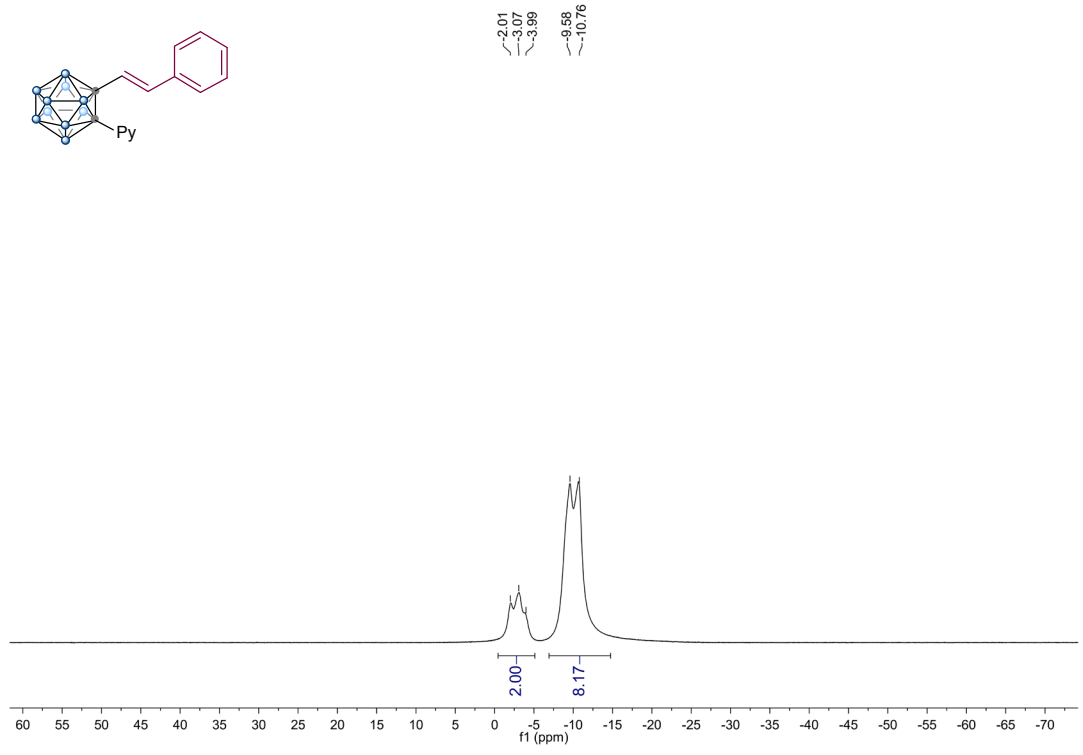
^{13}C NMR (101 MHz, Chloroform-*d*) **3a**



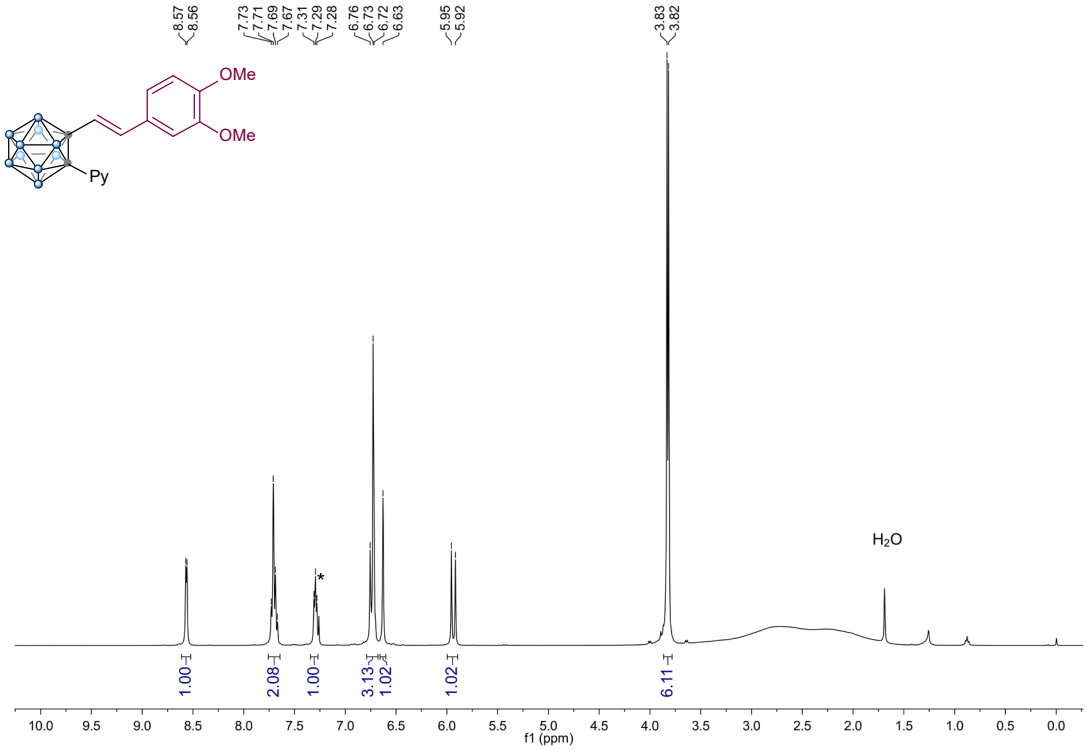
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **3a**



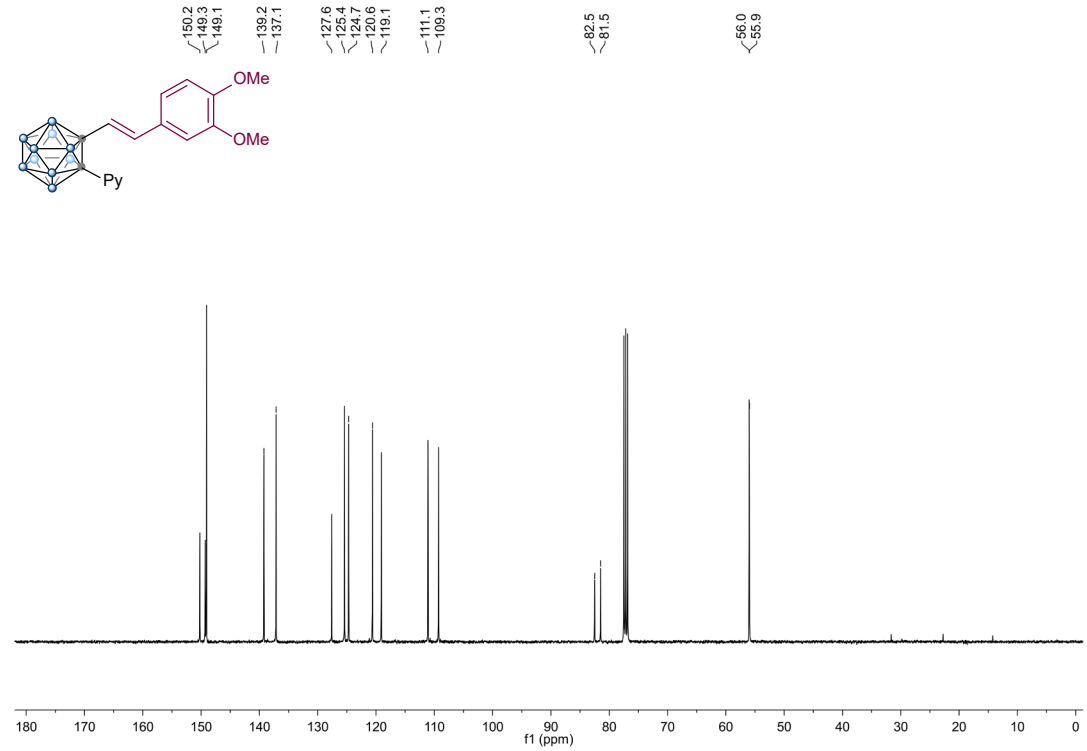
^{11}B NMR (128 MHz, Chloroform-*d*) **3a**



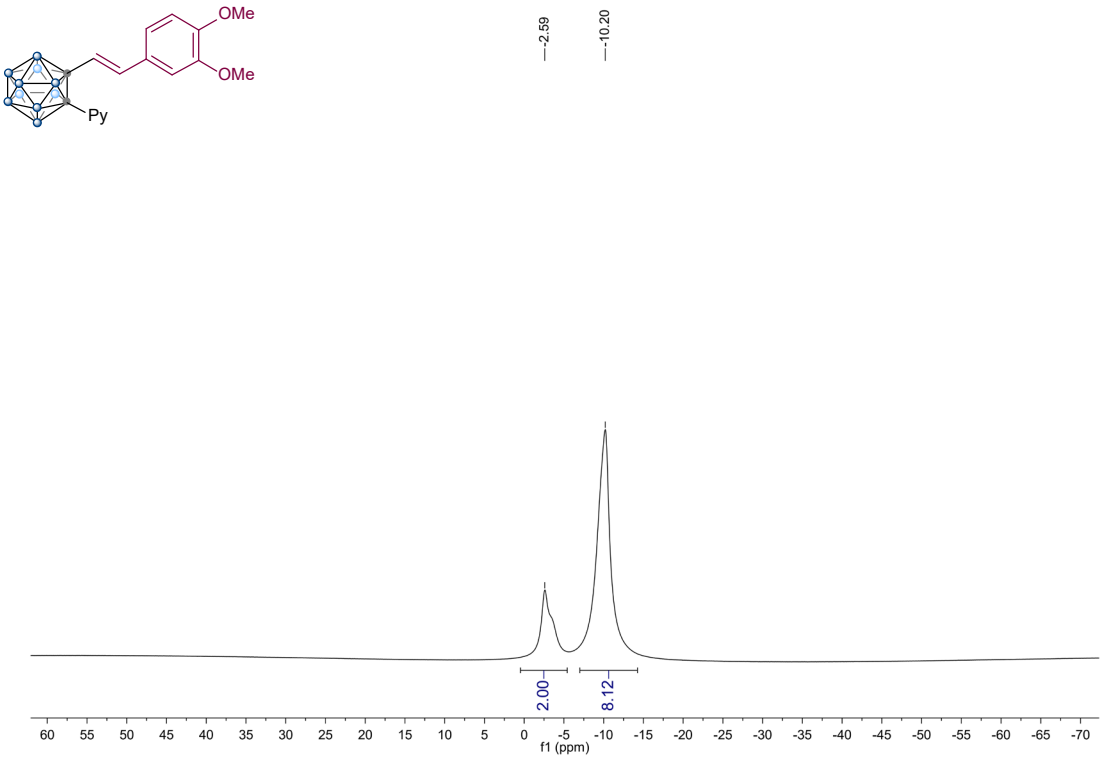
^{1}H NMR (400 MHz, Chloroform-*d*) **3b** (* from residual $CHCl_3$ in Chloroform-*d*)



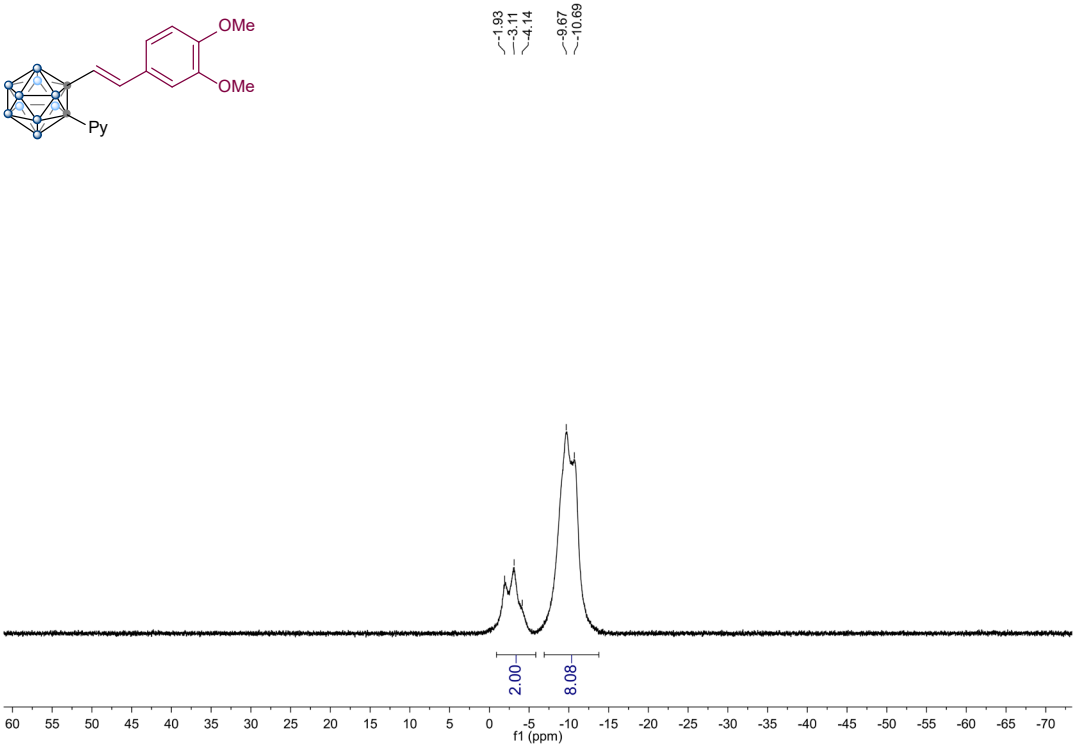
^{13}C NMR (101 MHz, Chloroform-*d*) **3b**



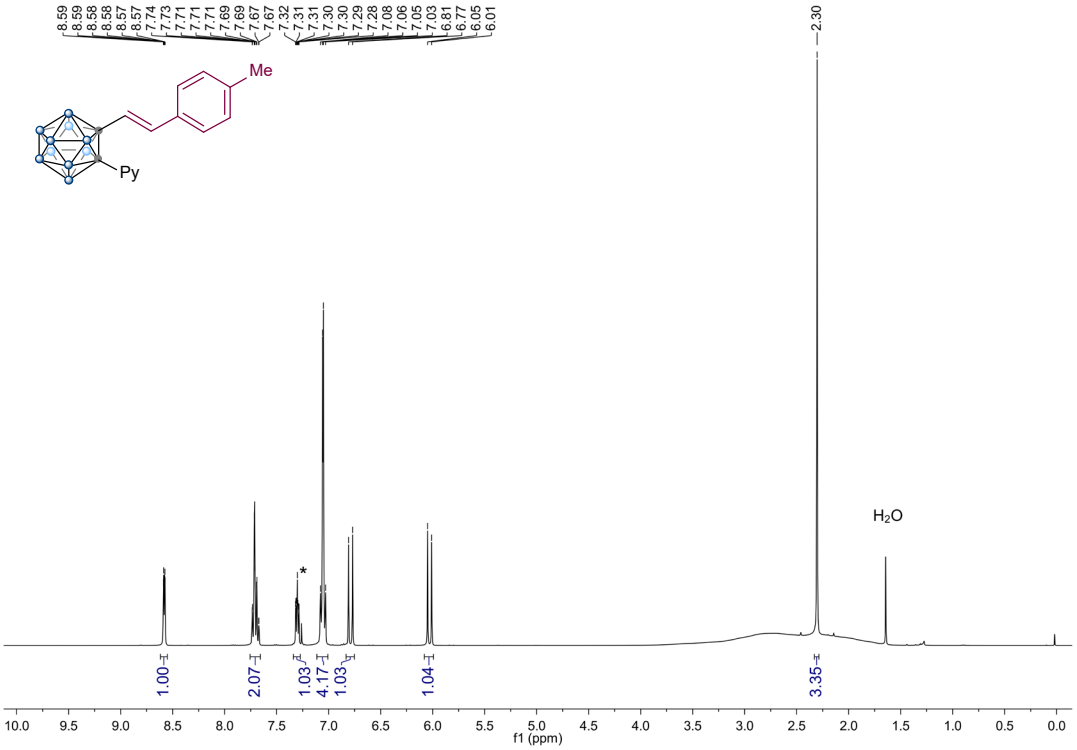
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **3b**



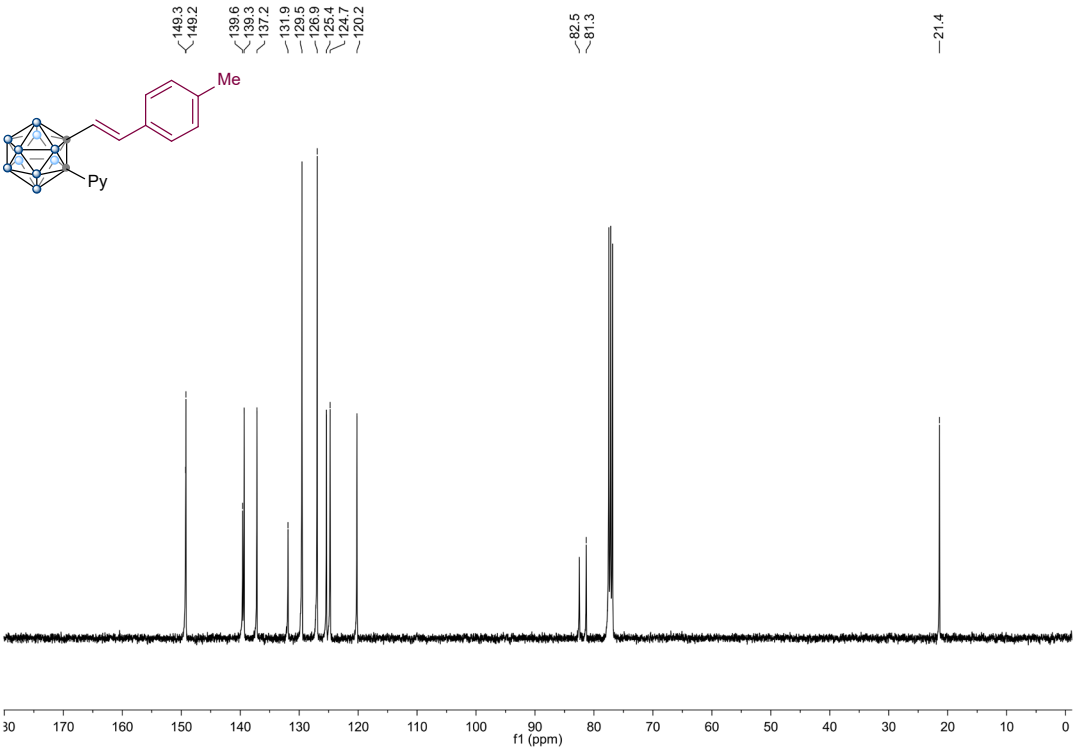
^{11}B NMR (128 MHz, Chloroform-*d*) **3b**



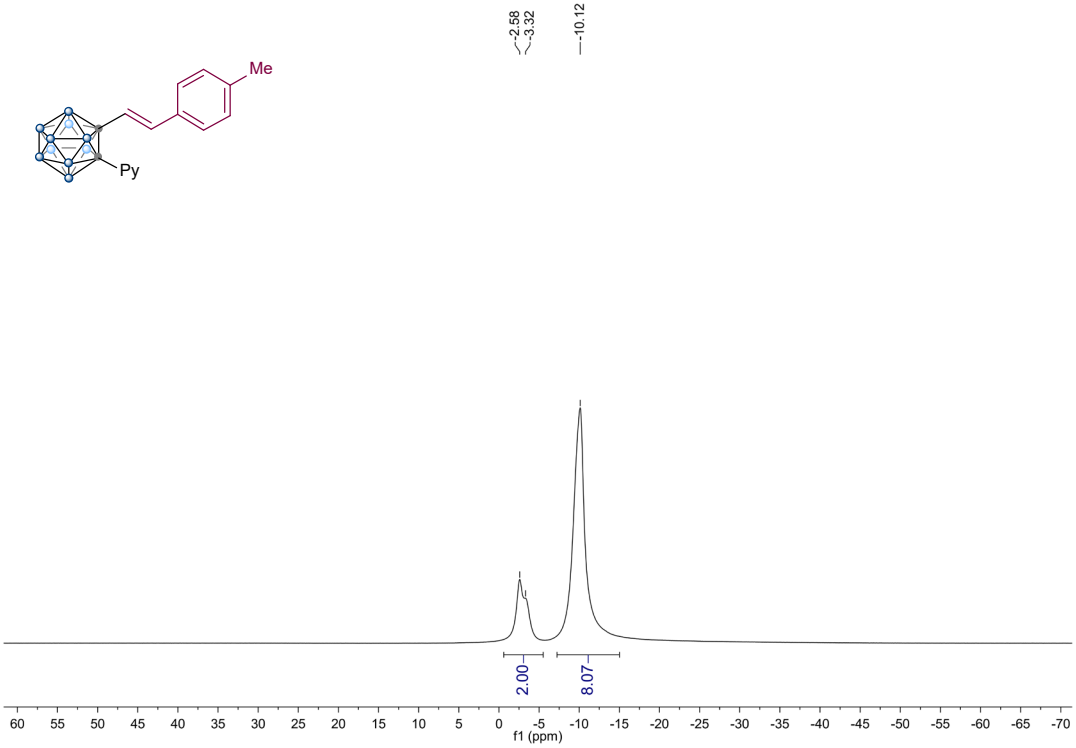
^{1}H NMR (400 MHz, Chloroform-*d*) **3c** (* from residual $CHCl_3$ in Chloroform-*d*)



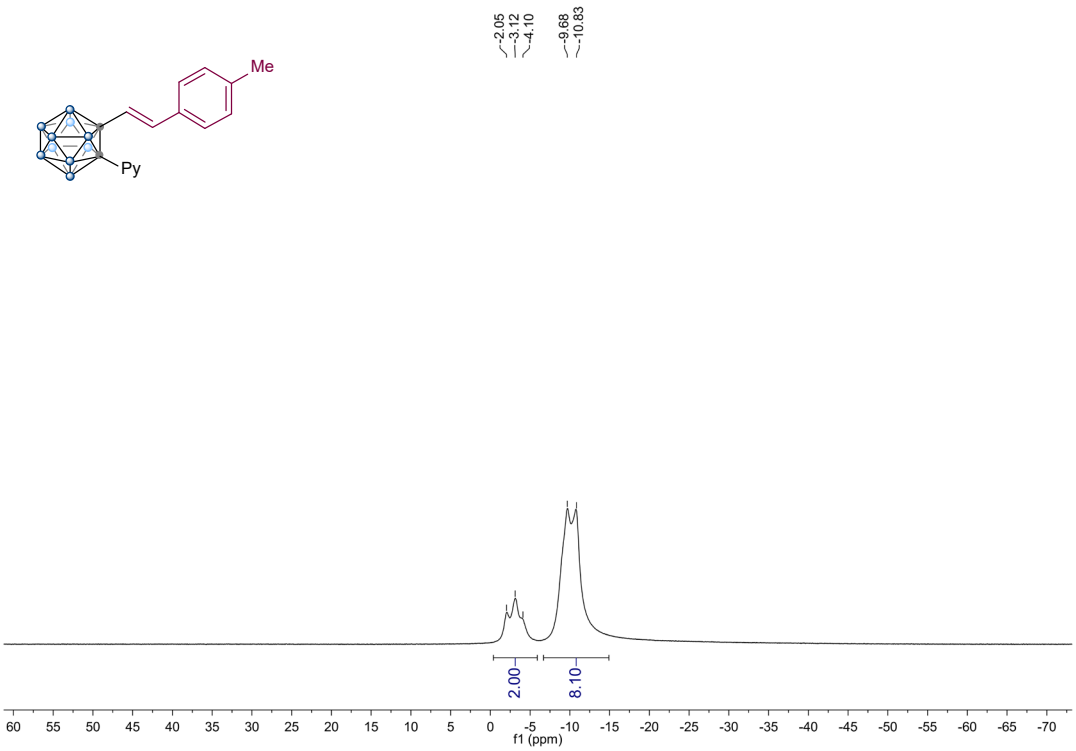
^{13}C NMR (101 MHz, Chloroform-*d*) **3c**



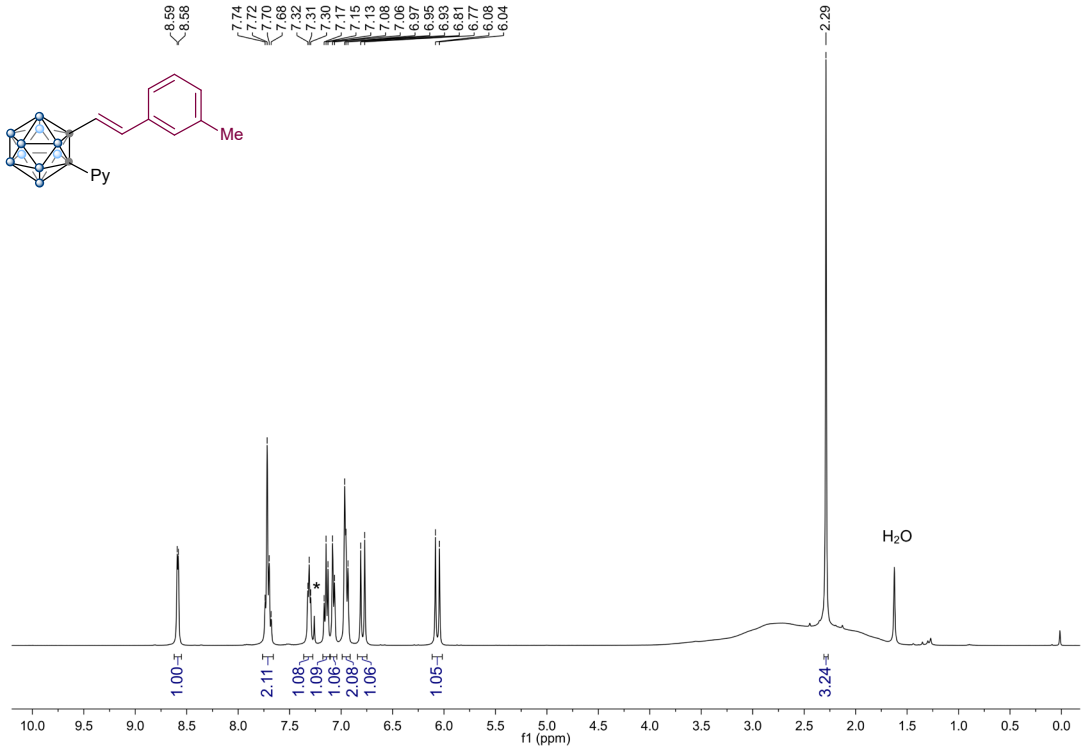
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **3c**



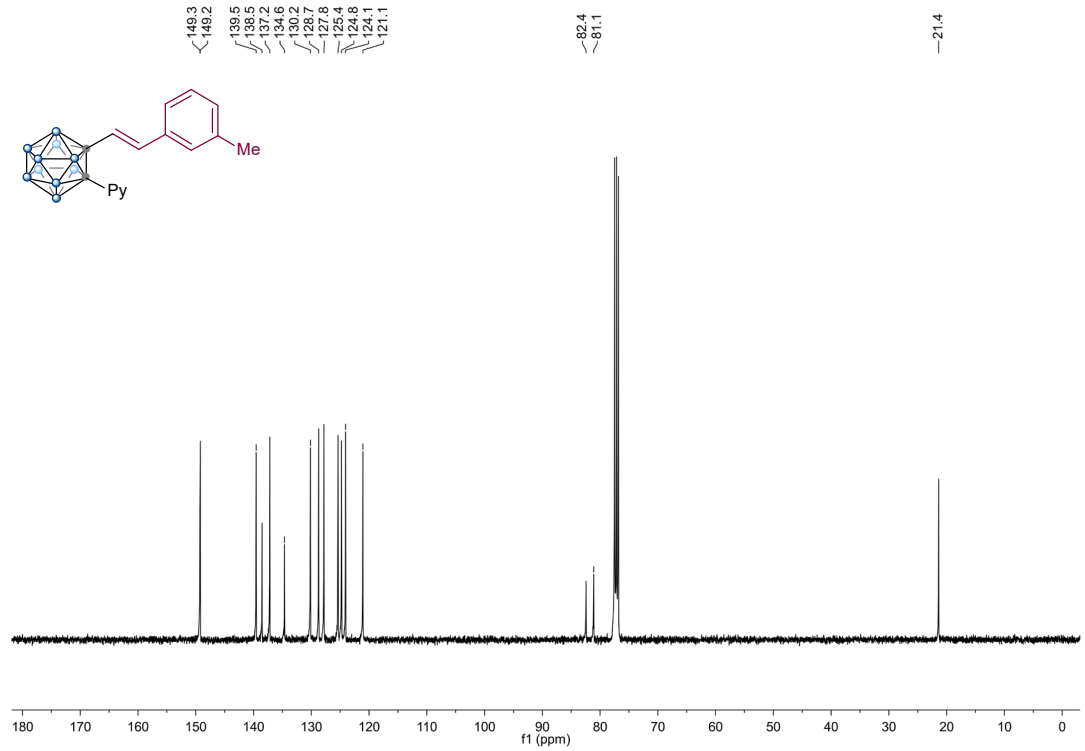
^{11}B NMR (128 MHz, Chloroform-*d*) **3c**



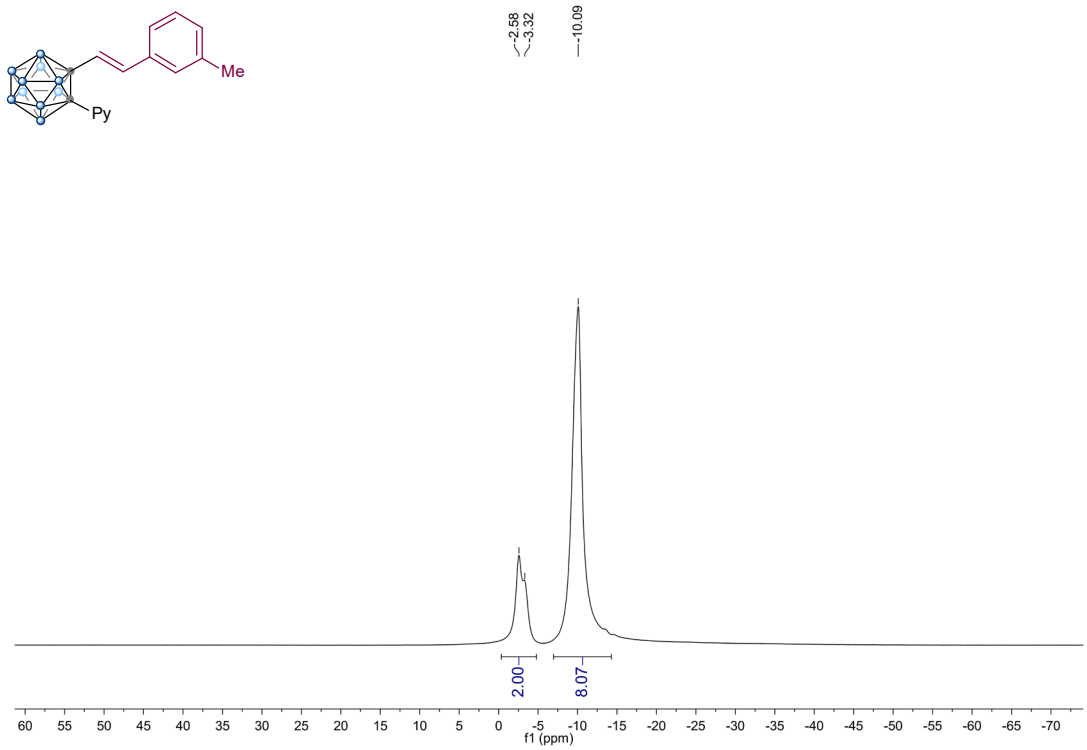
^{1}H NMR (400 MHz, Chloroform-*d*) **3d** (* from residual $CHCl_3$ in Chloroform-*d*)



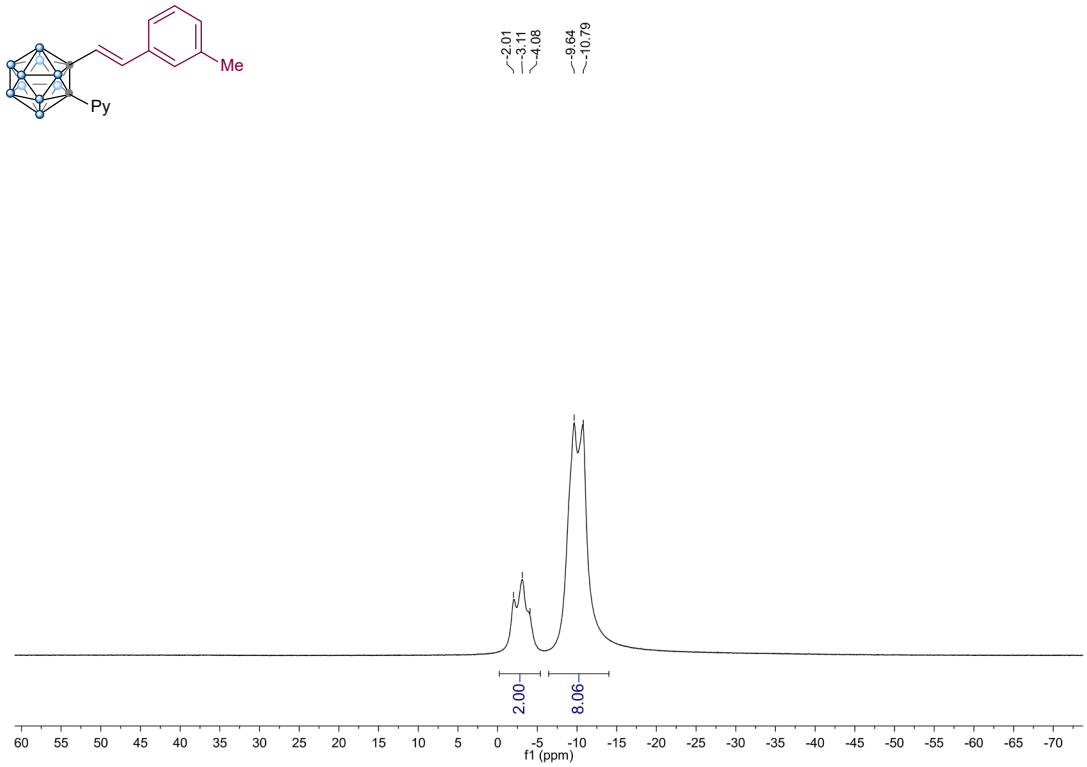
^{13}C NMR (101 MHz, Chloroform-*d*) **3d**



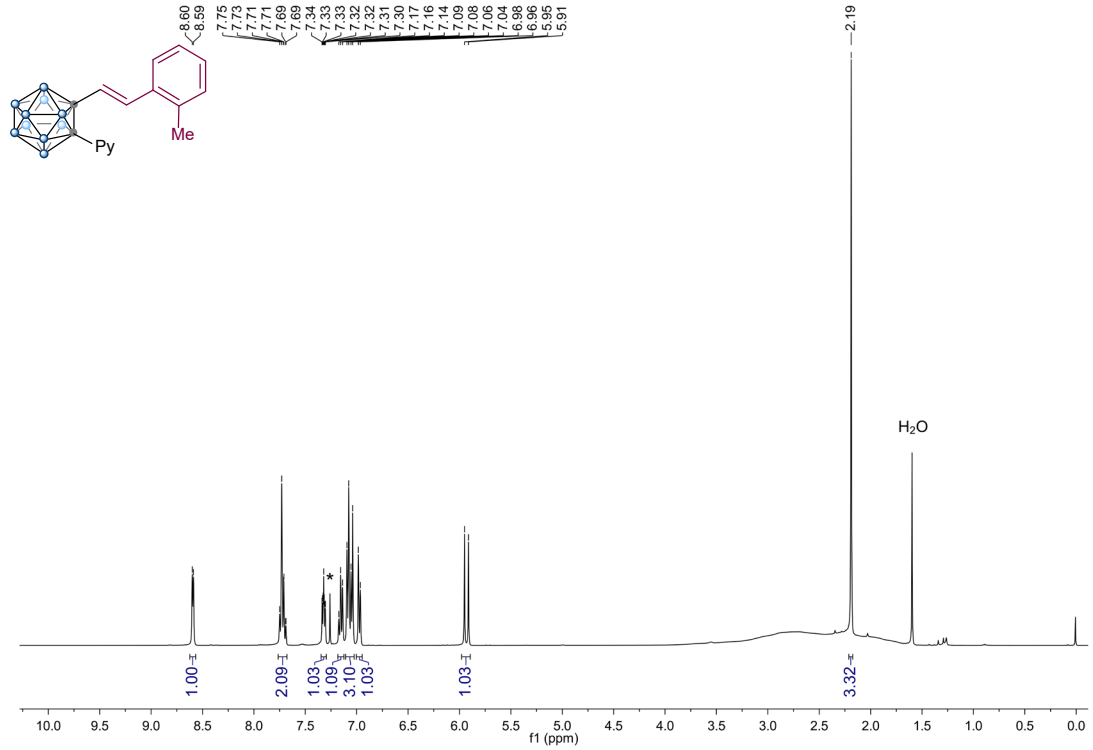
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **3d**



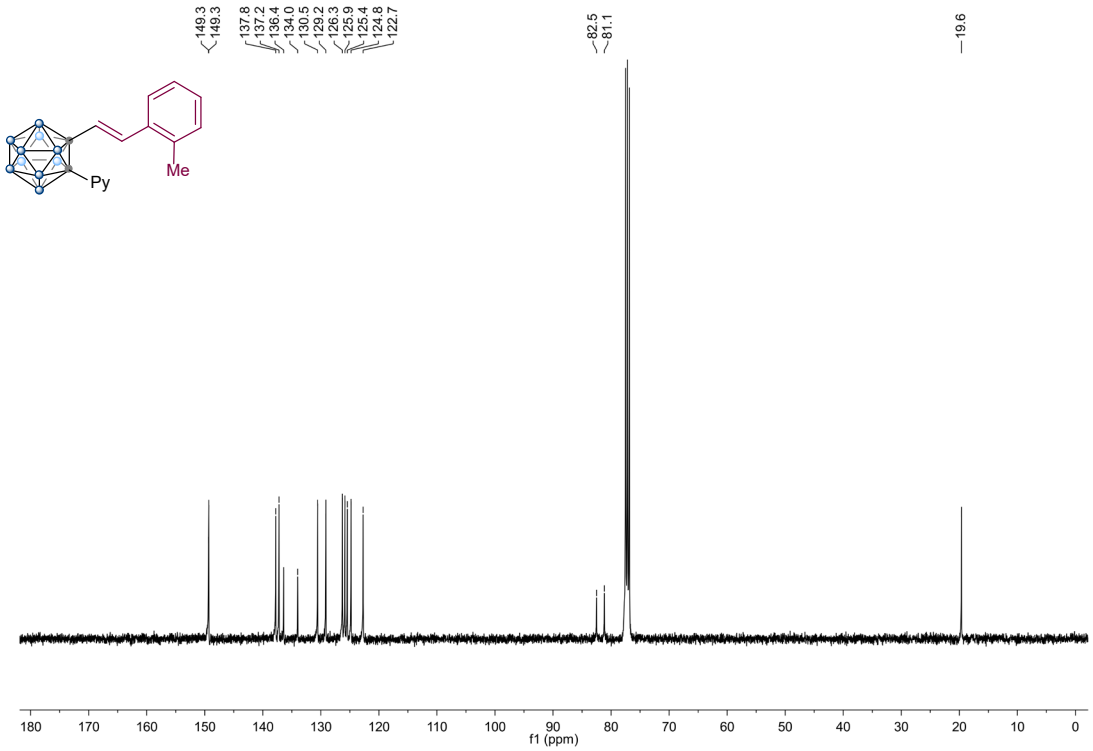
^{11}B NMR (128 MHz, Chloroform-*d*) **3d**



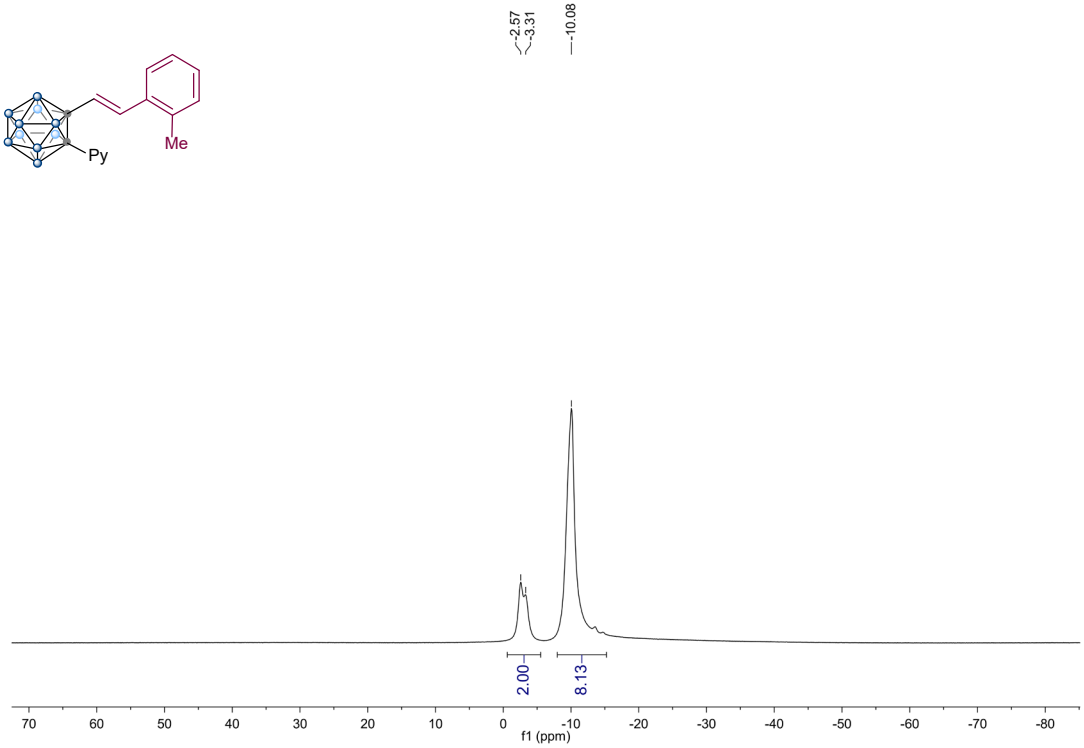
^{1}H NMR (400 MHz, Chloroform-*d*) **3e** (* from residual $CHCl_3$ in Chloroform-*d*)



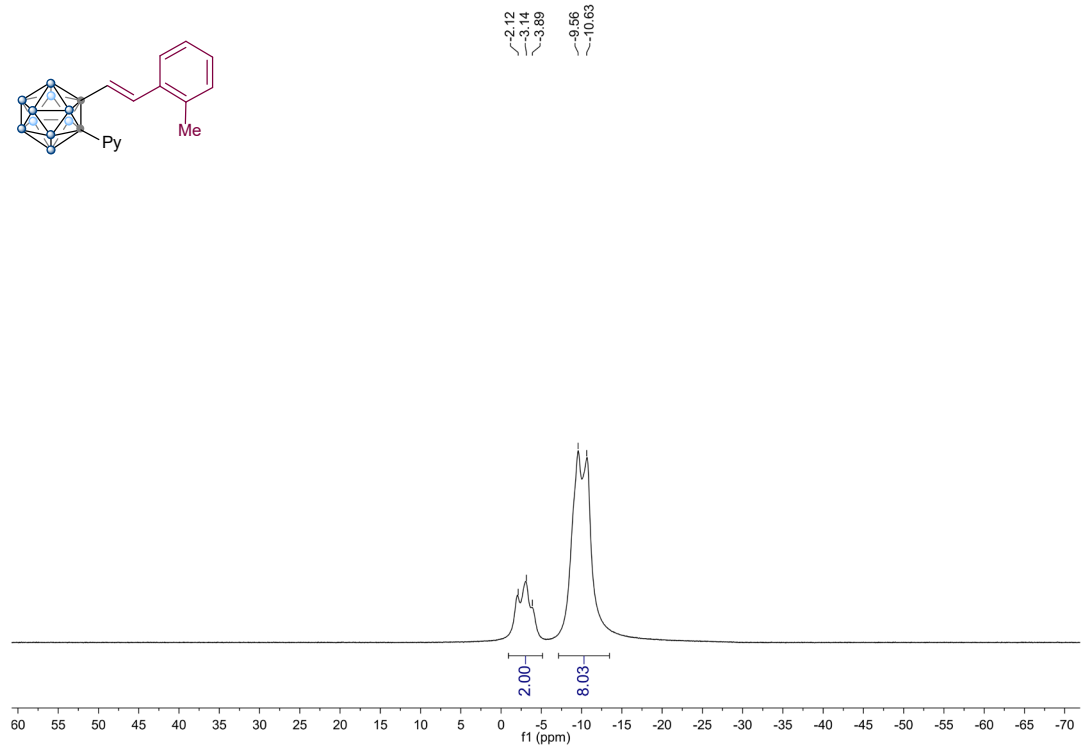
^{13}C NMR (101 MHz, Chloroform-*d*) **3e**



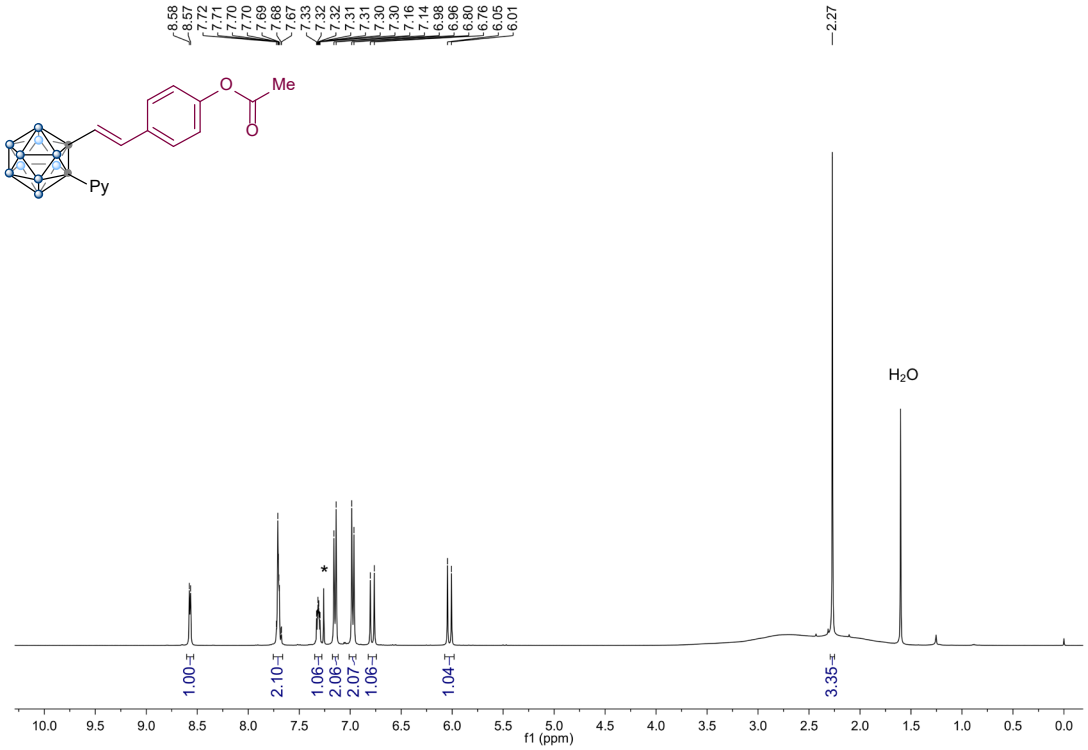
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **3e**



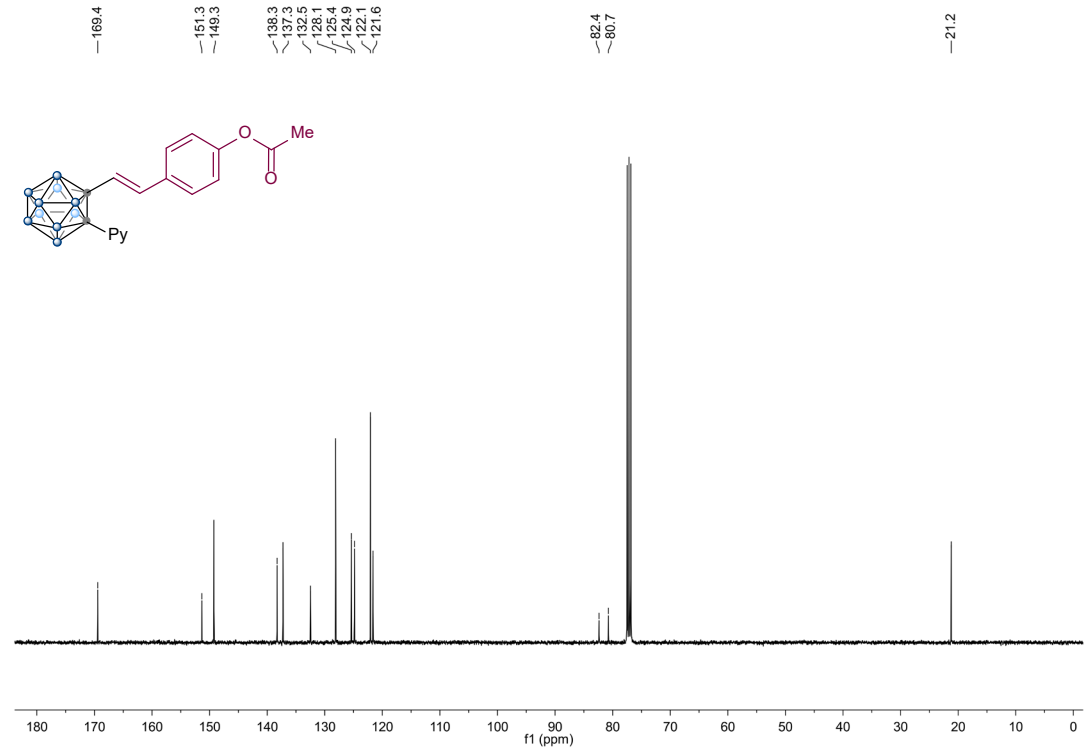
^{11}B NMR (128 MHz, Chloroform-*d*) **3e**



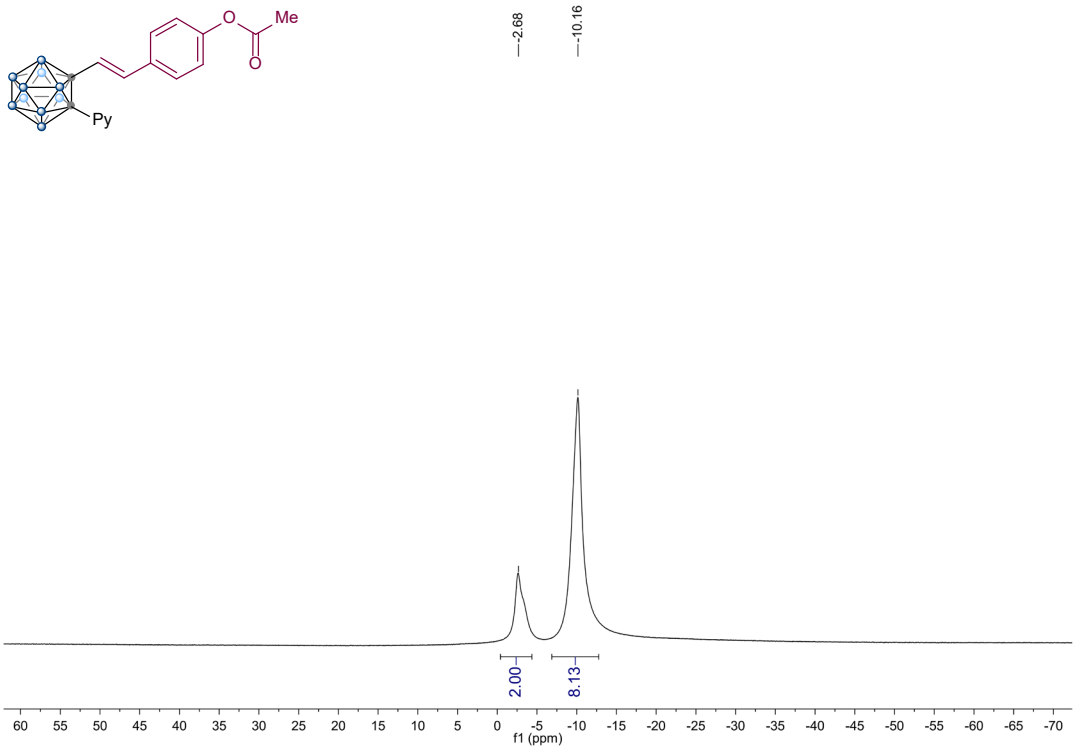
^{1}H NMR (400 MHz, Chloroform-*d*) **3f** (* from residual $CHCl_3$ in Chloroform-*d*)



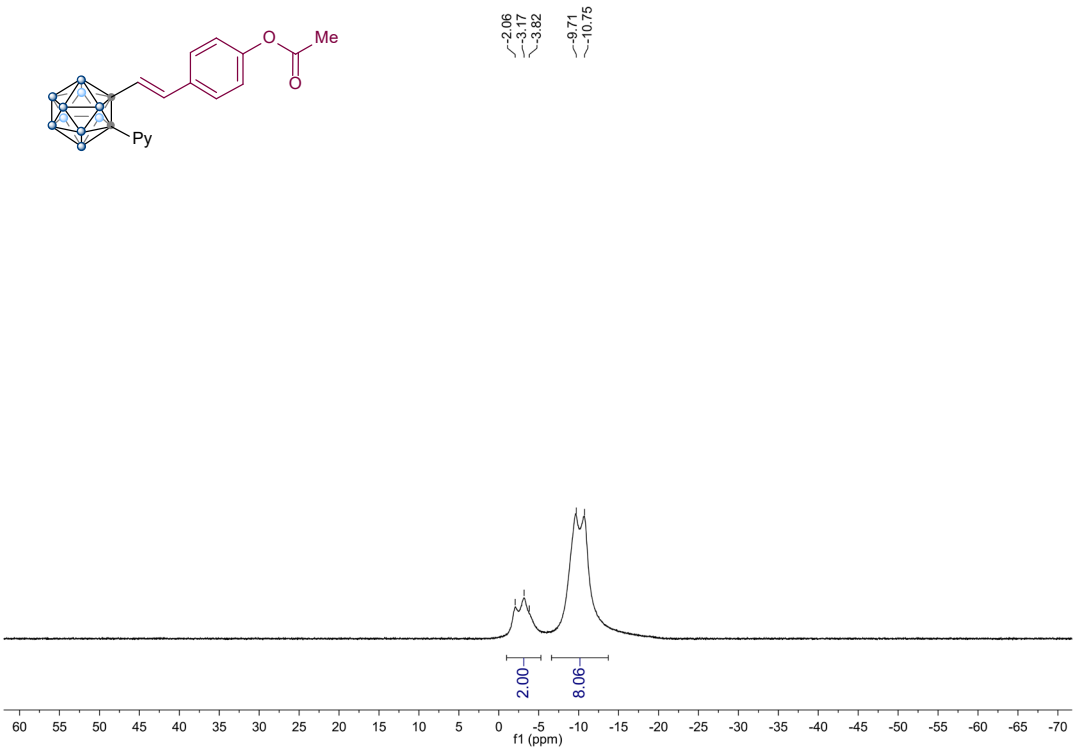
^{13}C NMR (101 MHz, Chloroform-*d*) **3f**



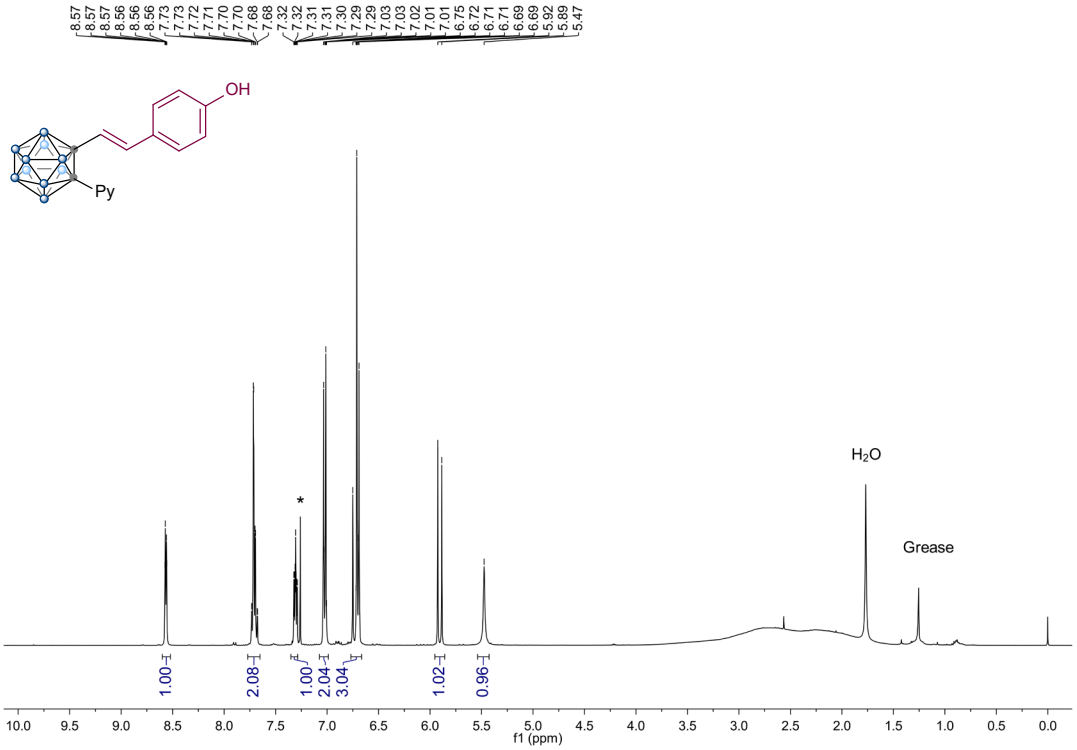
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **3f**



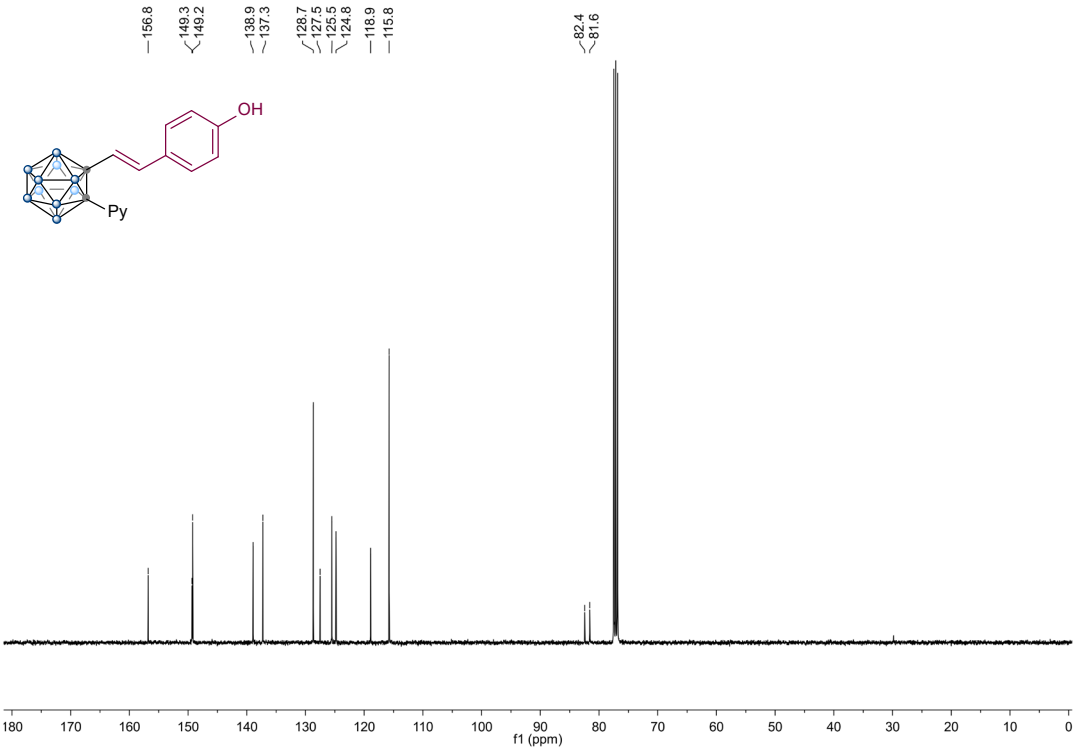
^{11}B NMR (128 MHz, Chloroform-*d*) **3f**



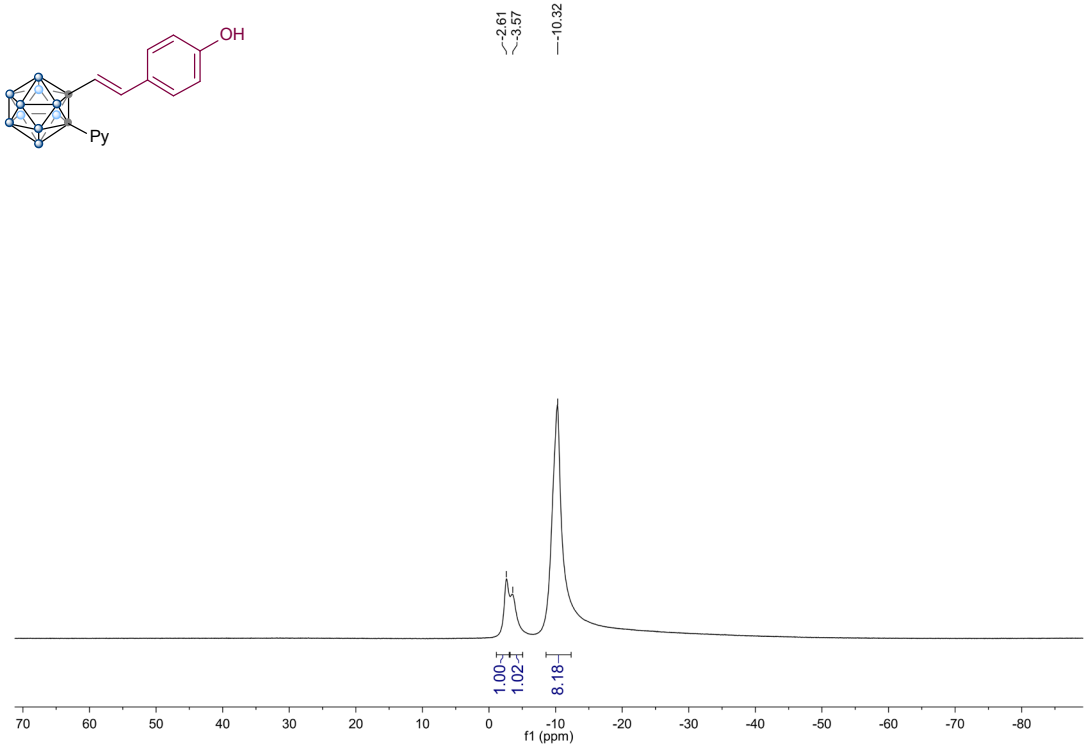
^{1}H NMR (400 MHz, Chloroform-*d*) **3g** (* from residual $CHCl_3$ in Chloroform-*d*)



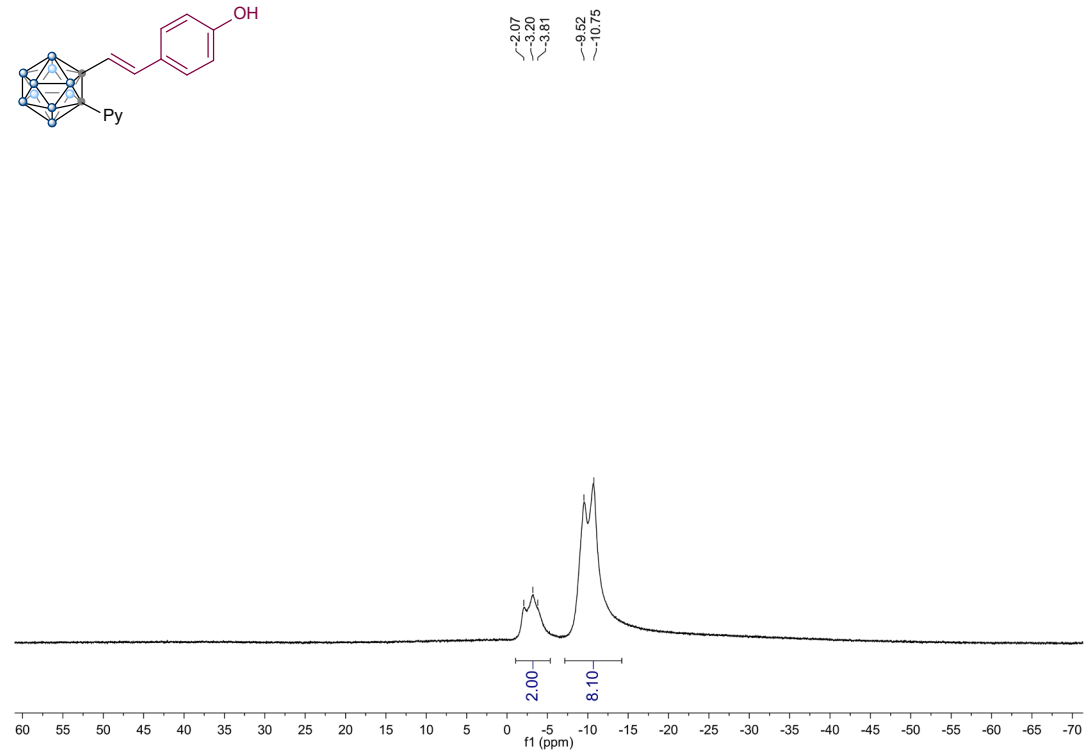
^{13}C NMR (101 MHz, Chloroform-*d*) **3g**



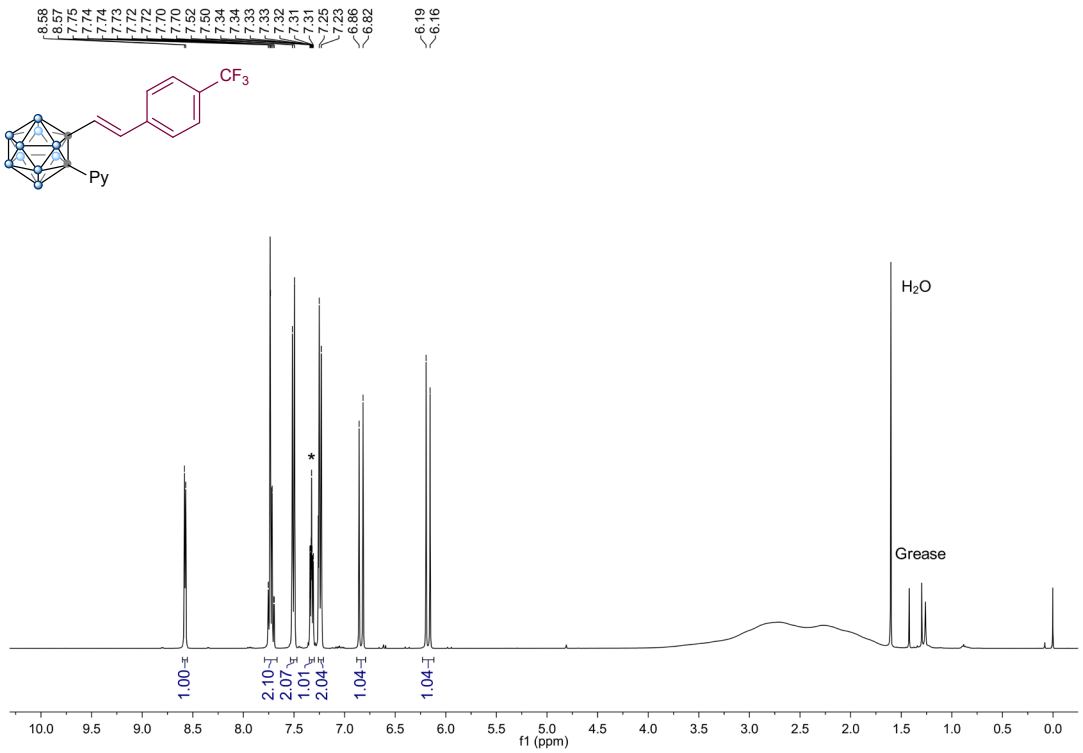
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **3g**



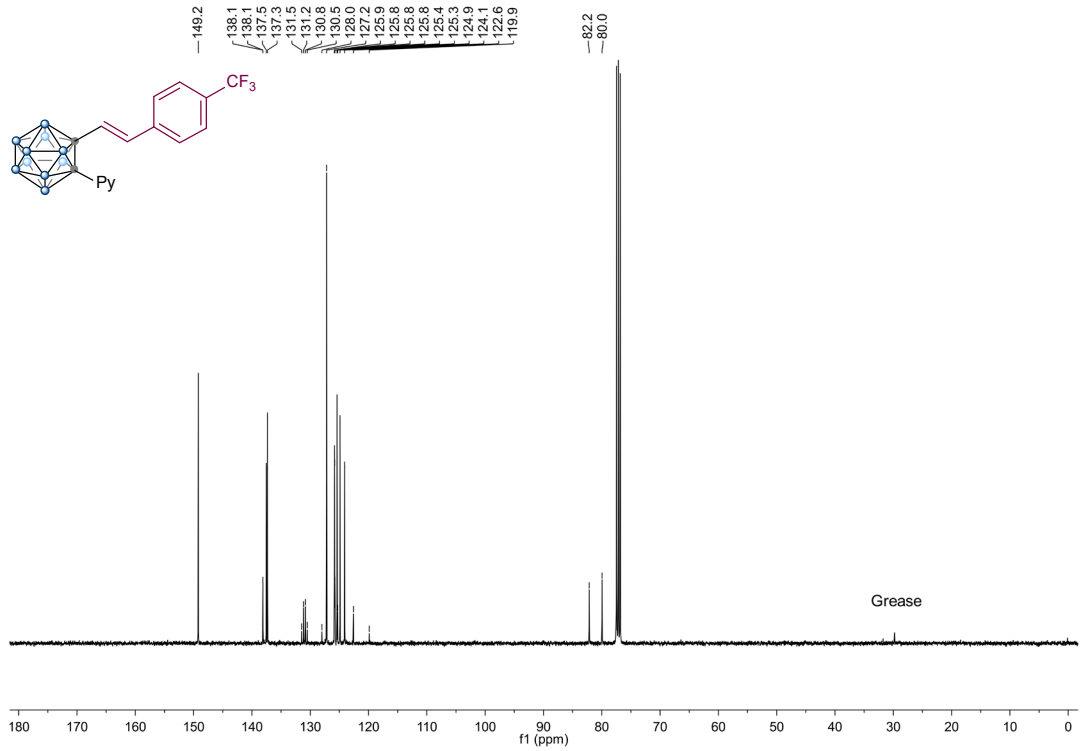
^{11}B NMR (128 MHz, Chloroform-*d*) **3g**



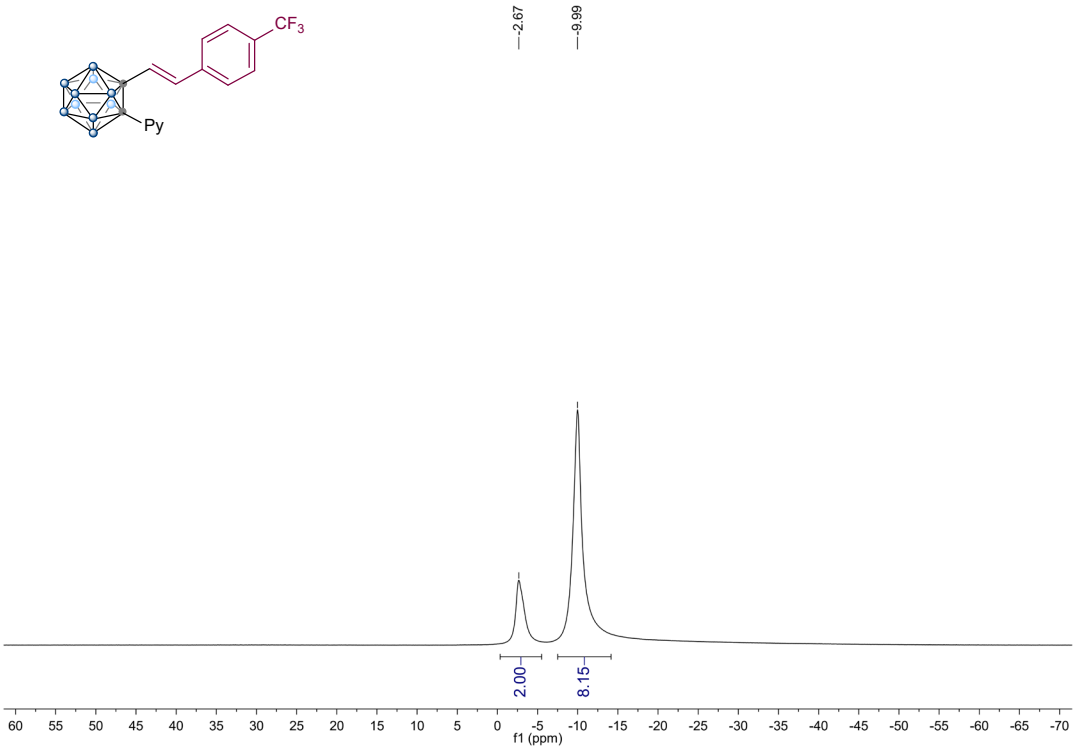
^{1}H NMR (400 MHz, Chloroform-*d*) **3h** (* from residual $CHCl_3$ in Chloroform-*d*)



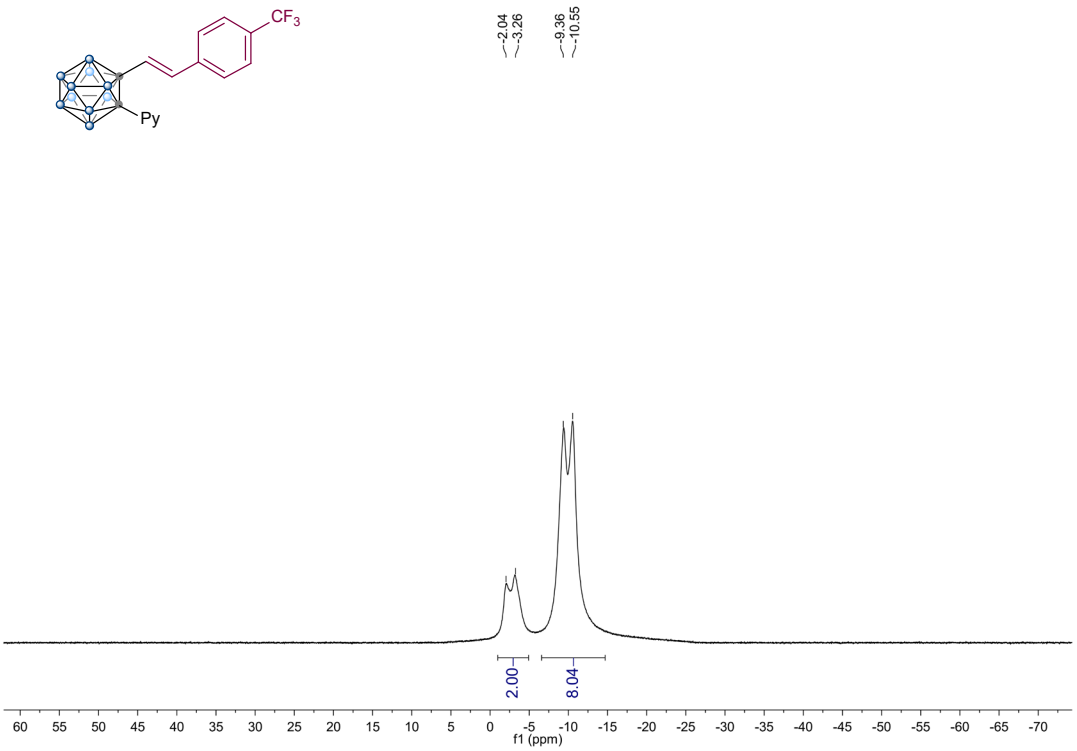
^{13}C NMR (101 MHz, Chloroform-*d*) **3h**



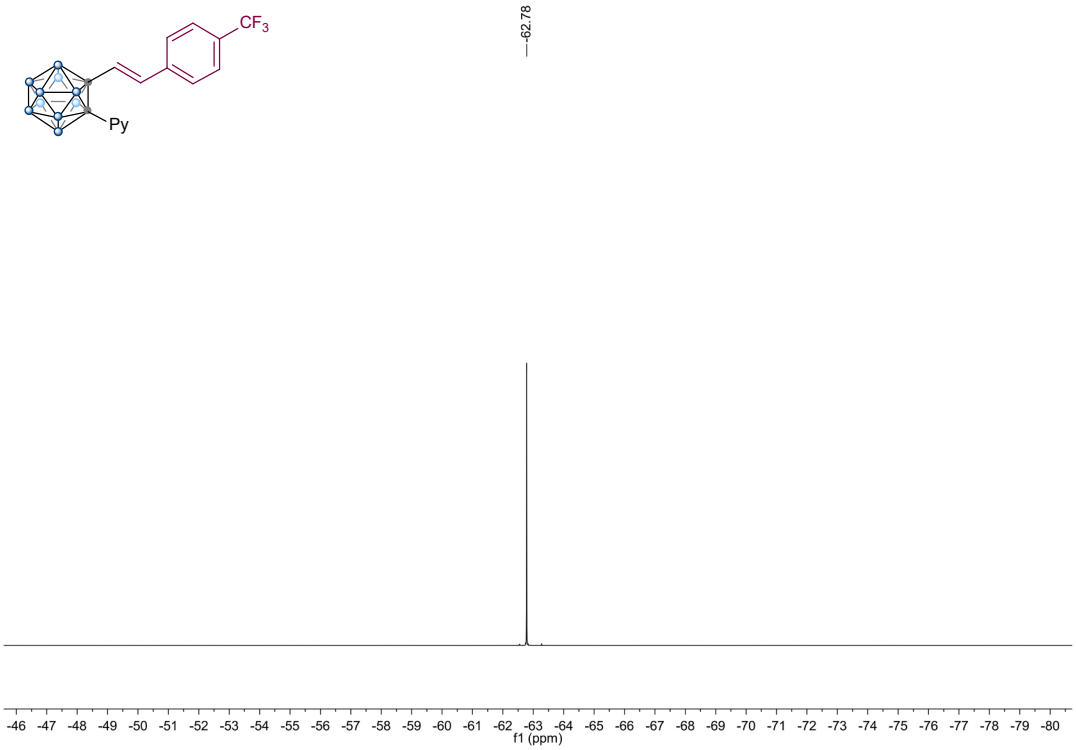
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **3h**



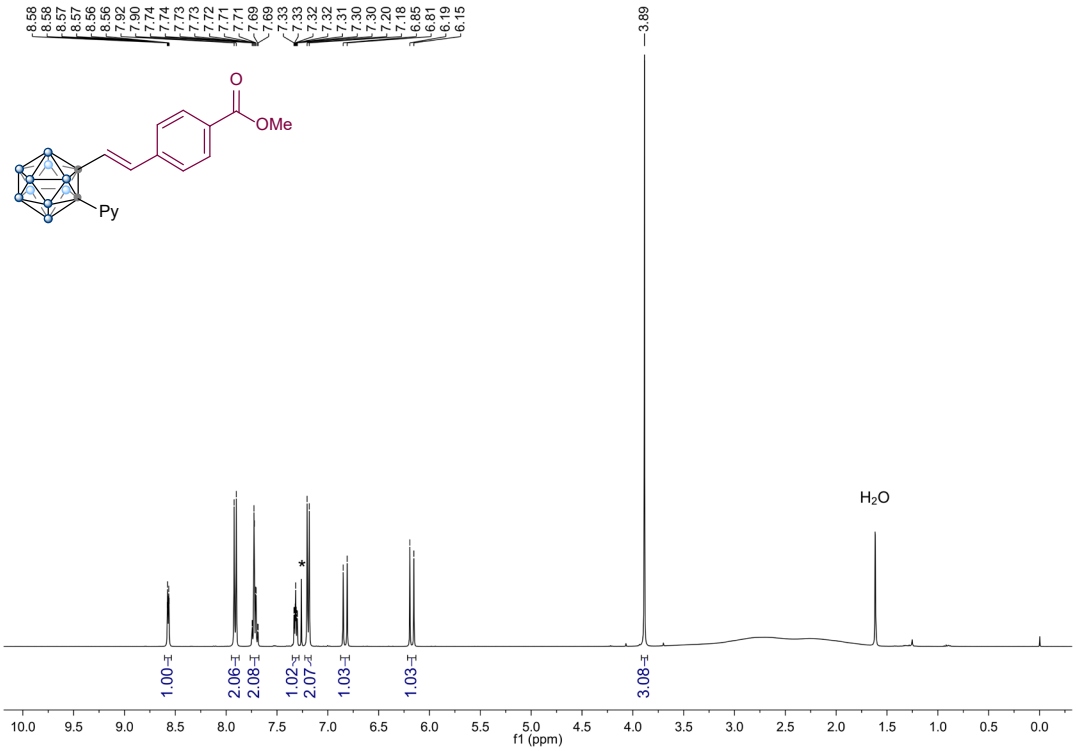
^{11}B NMR (128 MHz, Chloroform-*d*) **3h**



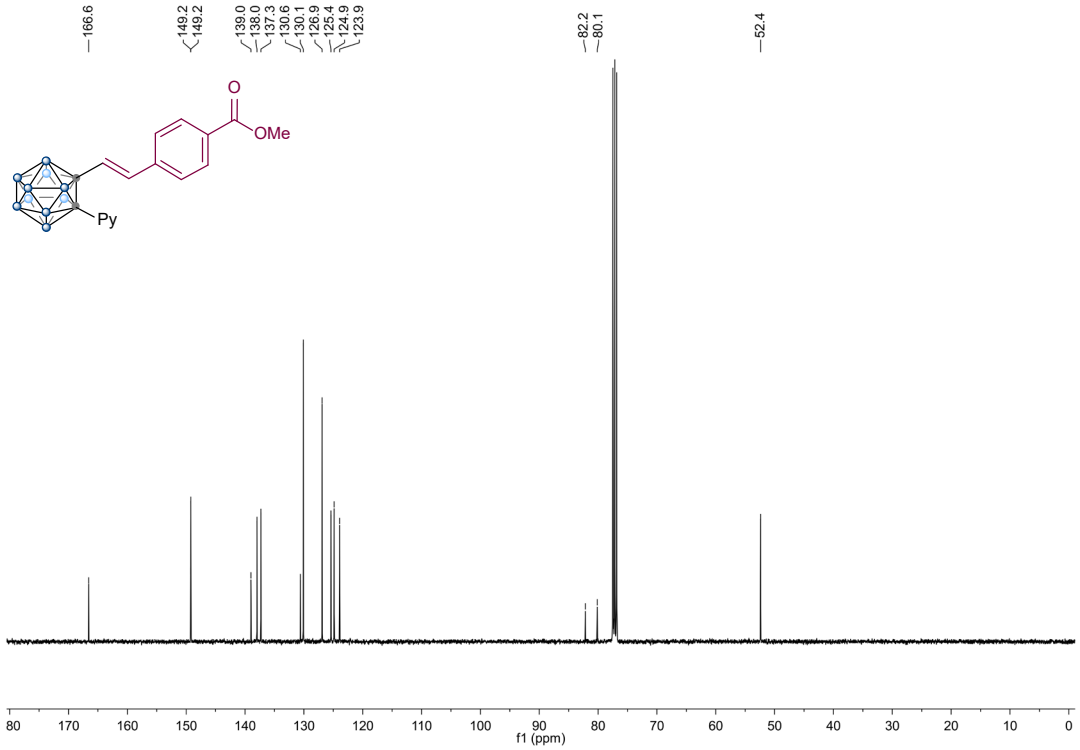
^{19}F NMR (376 MHz, Chloroform-*d*) **3h**



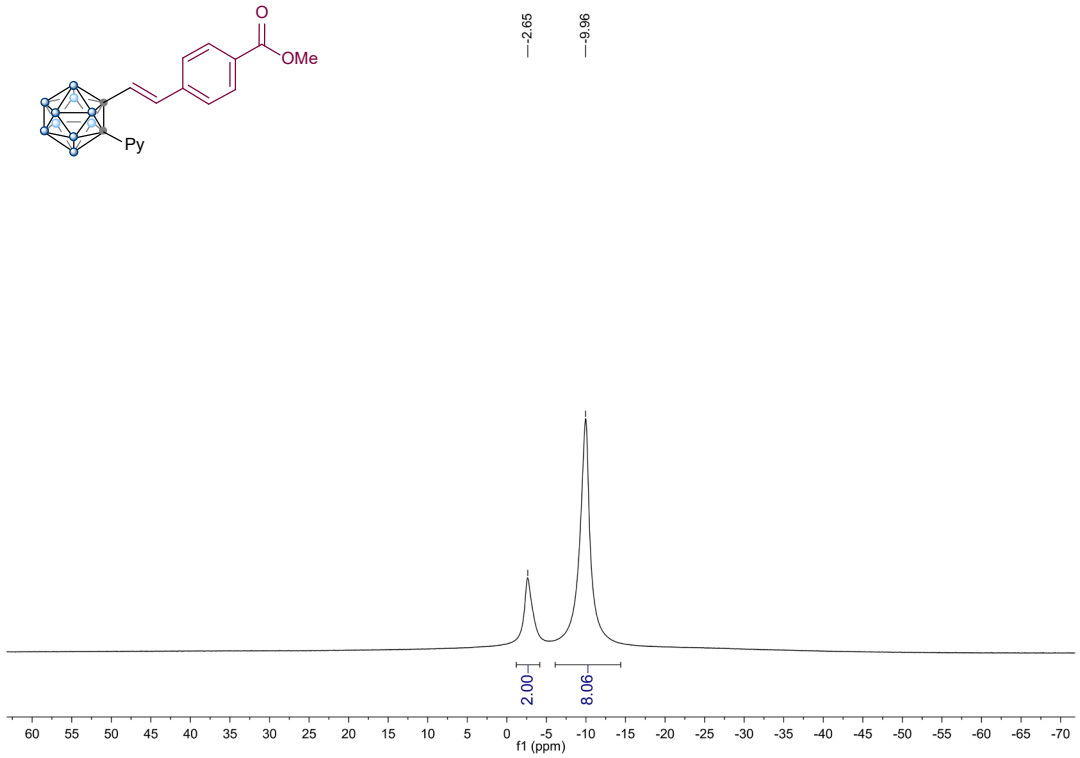
^{1}H NMR (400 MHz, Chloroform-*d*) **3i** (* from residual $CHCl_3$ in Chloroform-*d*)



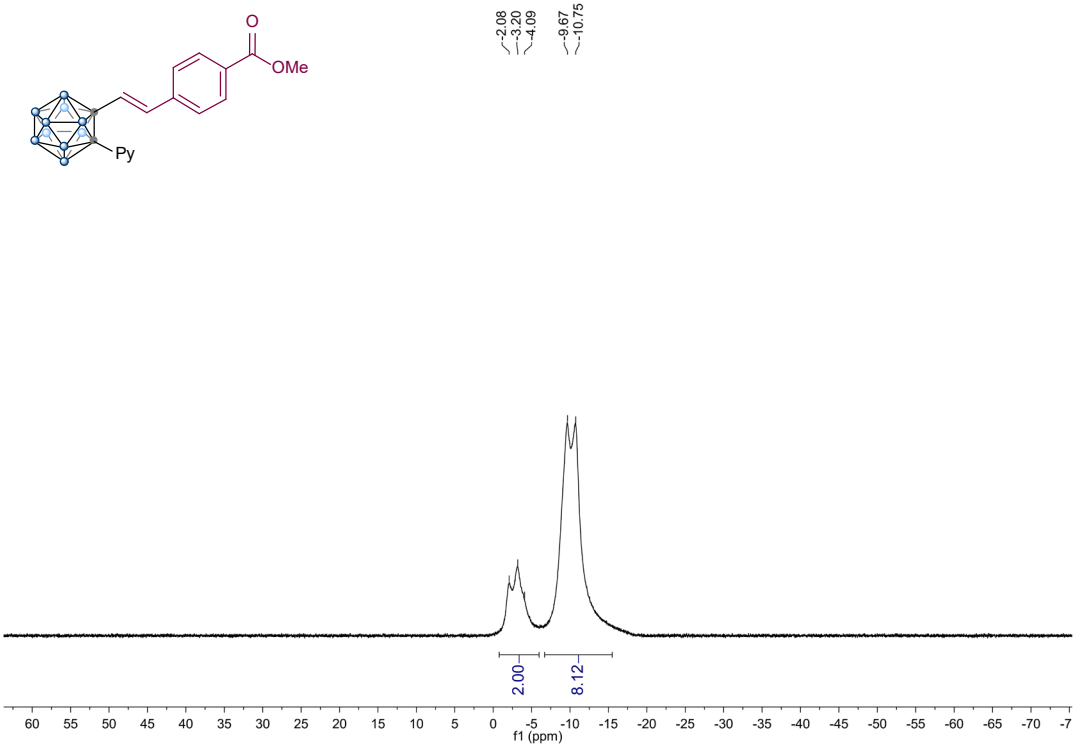
^{13}C NMR (101 MHz, Chloroform-*d*) **3i**



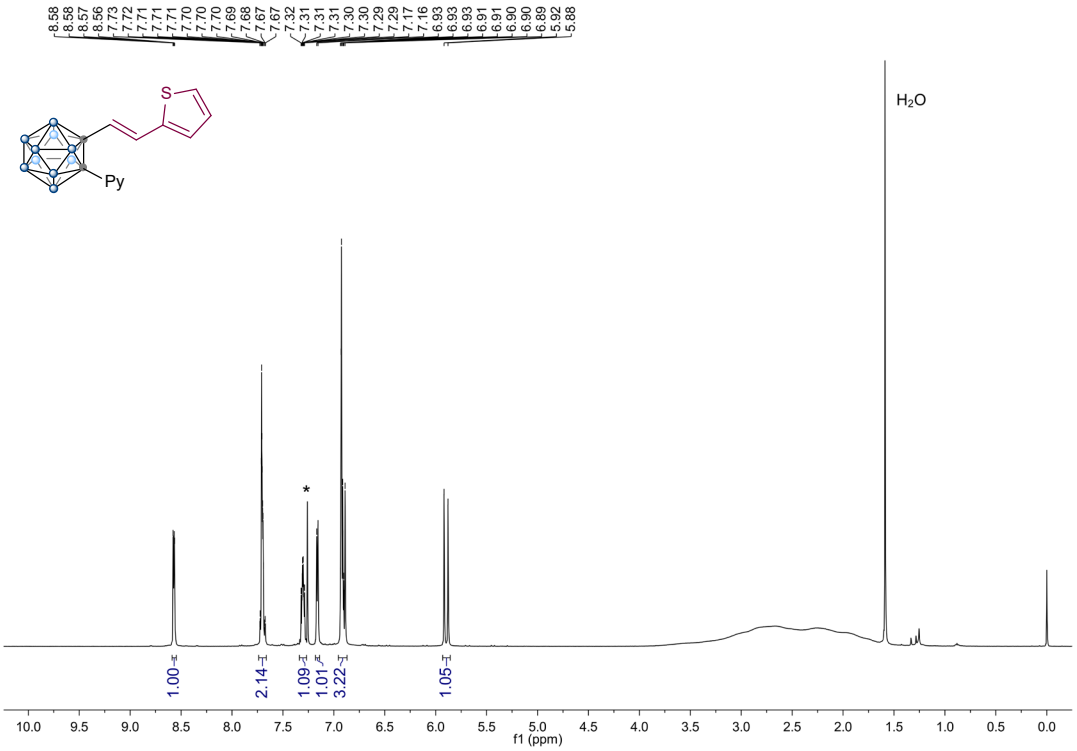
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3i**



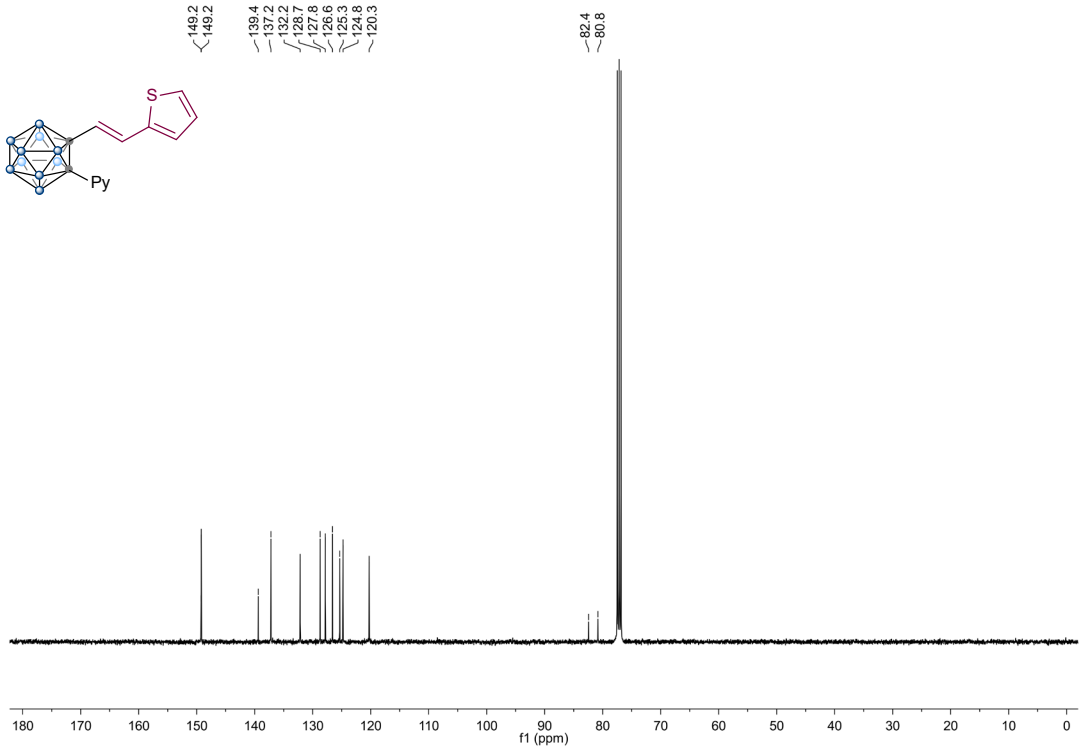
^{11}B NMR (128 MHz, Chloroform-*d*) **3i**



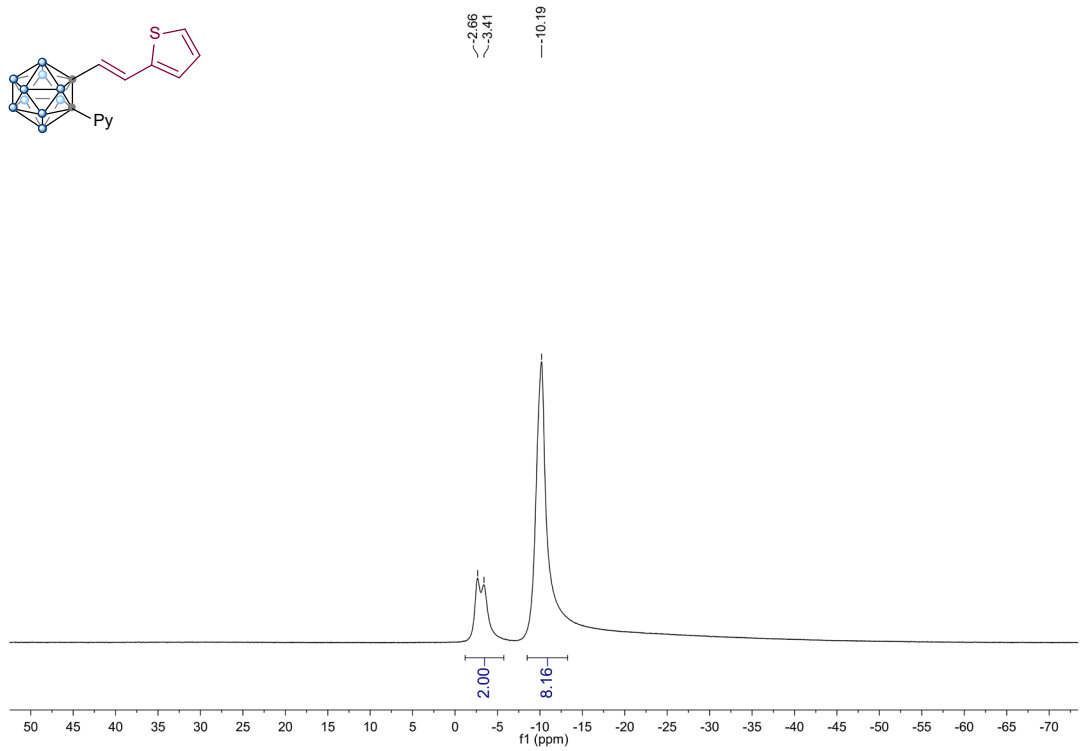
^{1}H NMR (400 MHz, Chloroform-*d*) **3j** (* from residual $CHCl_3$ in Chloroform-*d*)



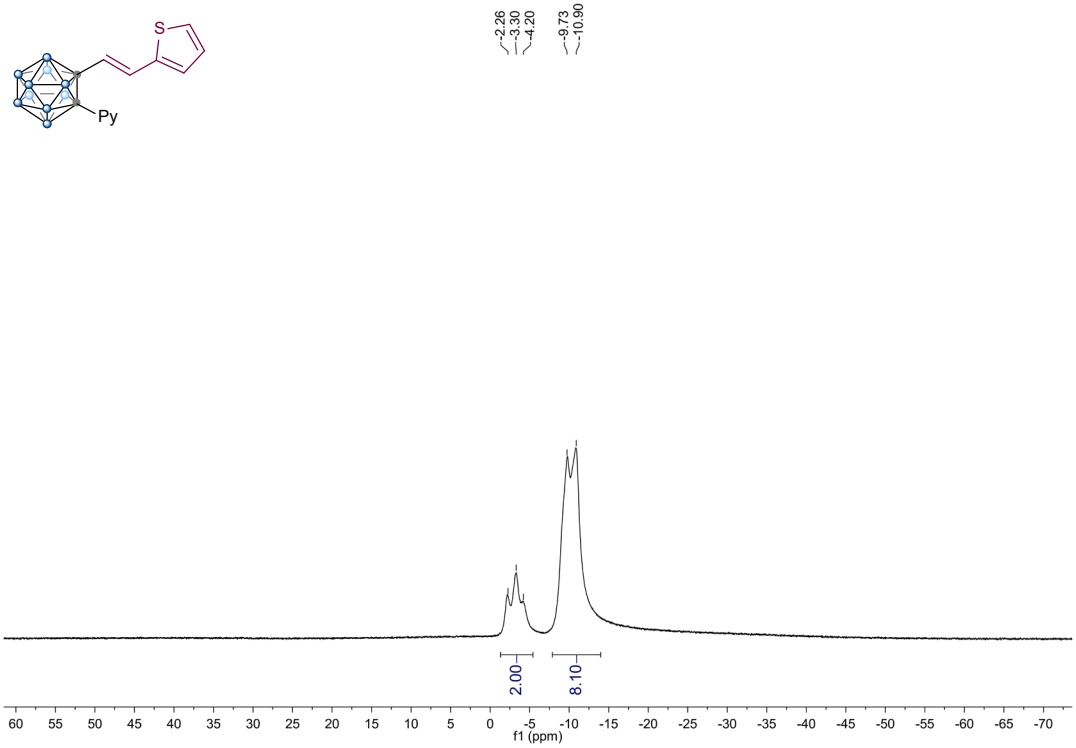
^{13}C NMR (101 MHz, Chloroform-*d*) **3j**



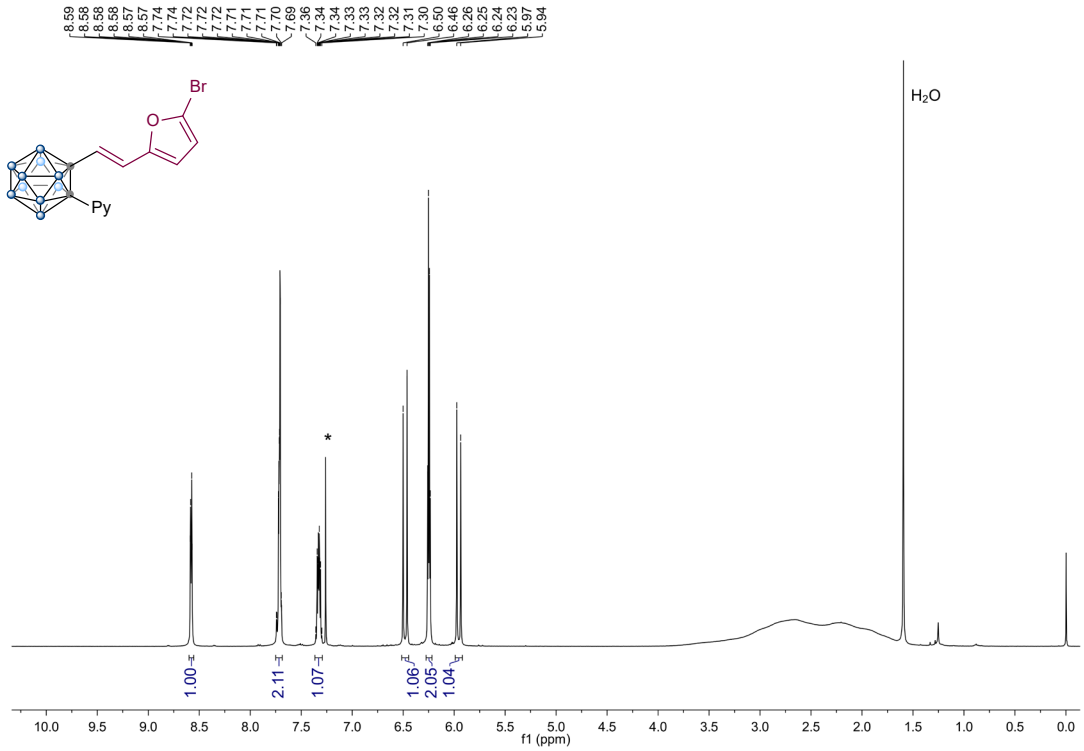
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3j**



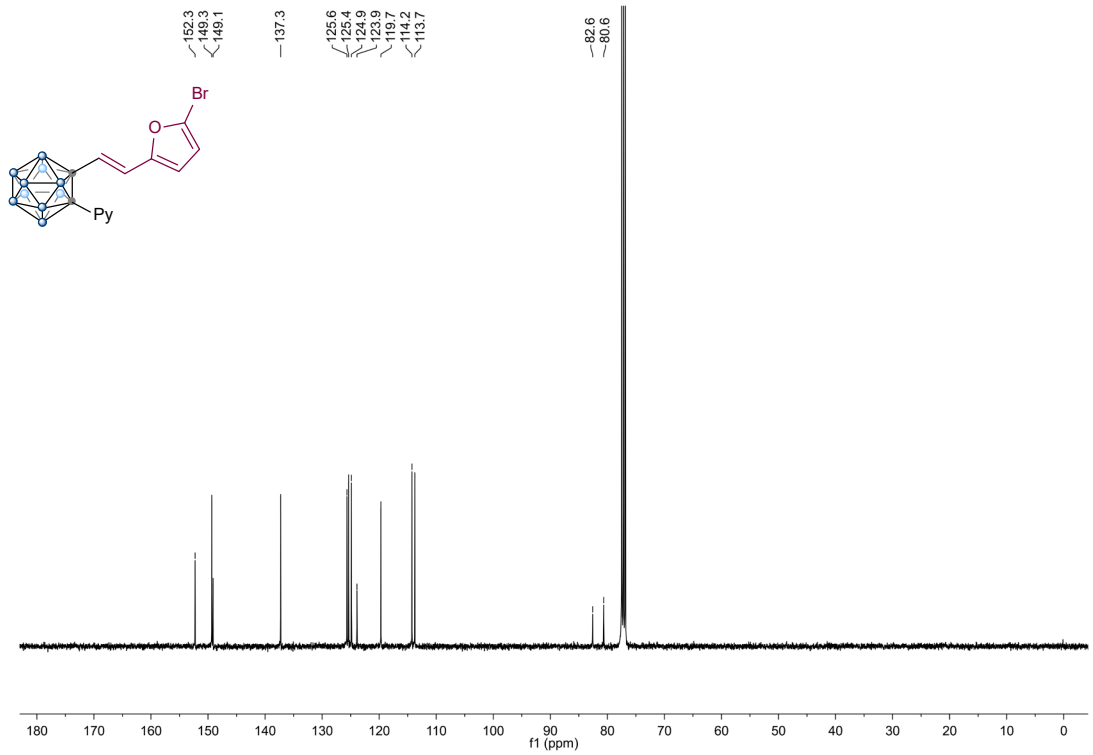
^{11}B NMR (128 MHz, Chloroform-*d*) **3j**



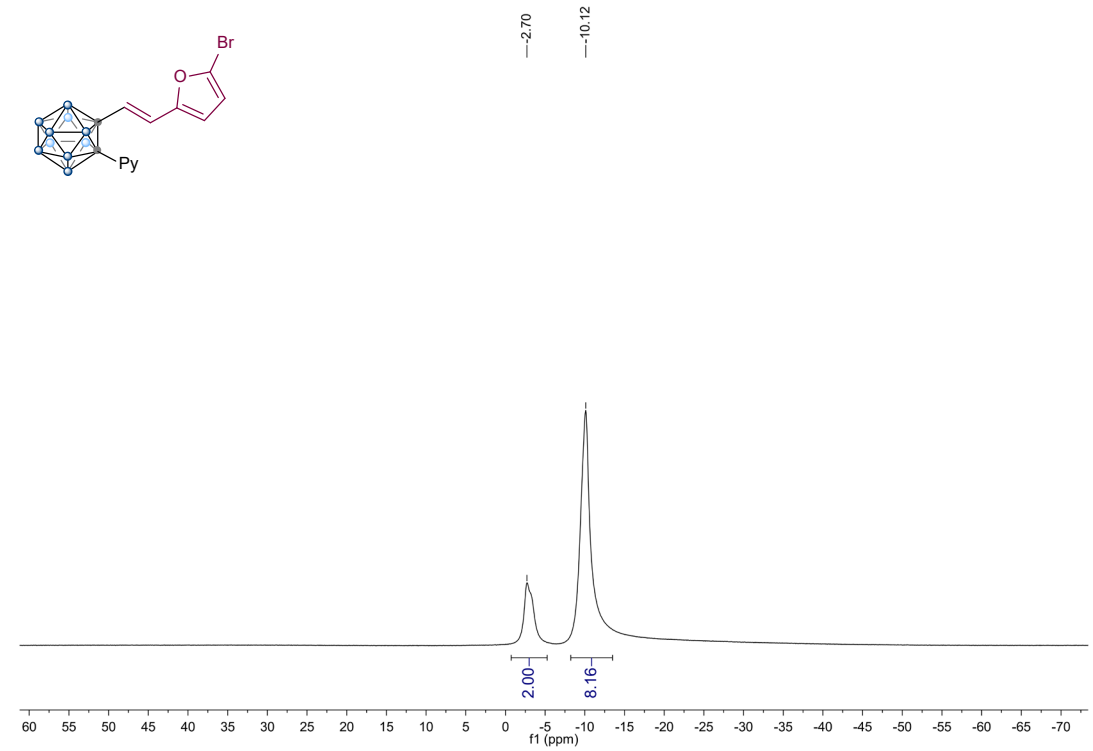
^{1}H NMR (400 MHz, Chloroform-*d*) **3k** (* from residual $CHCl_3$ in Chloroform-*d*)



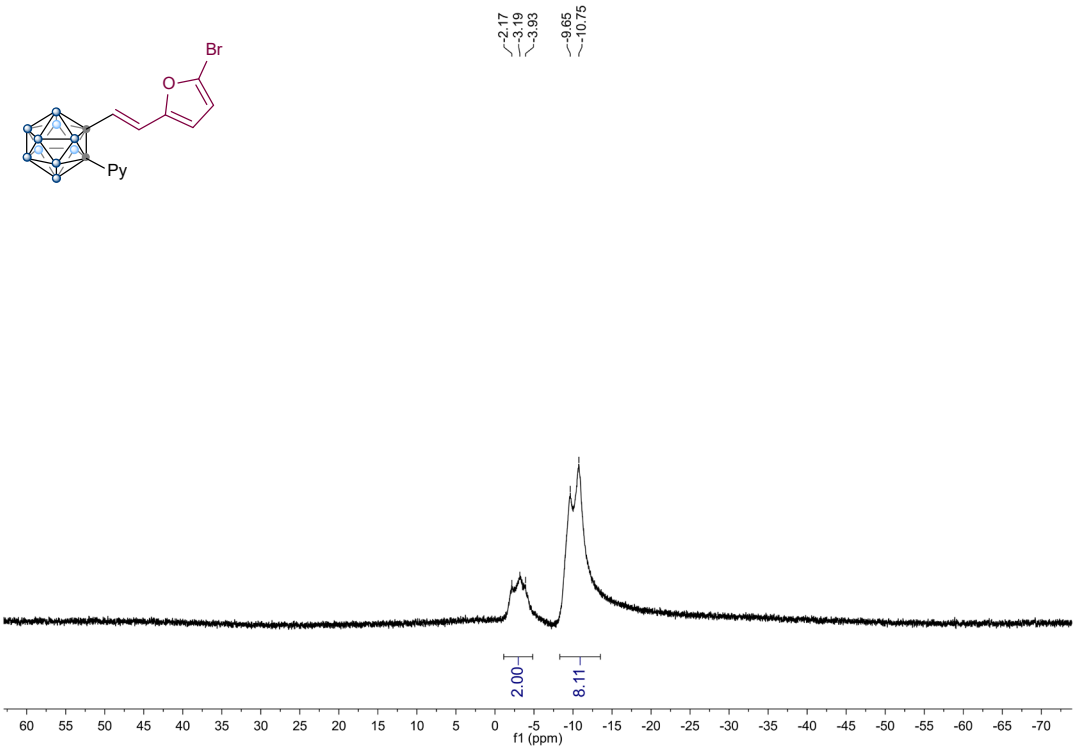
^{13}C NMR (101 MHz, Chloroform-*d*) **3k**



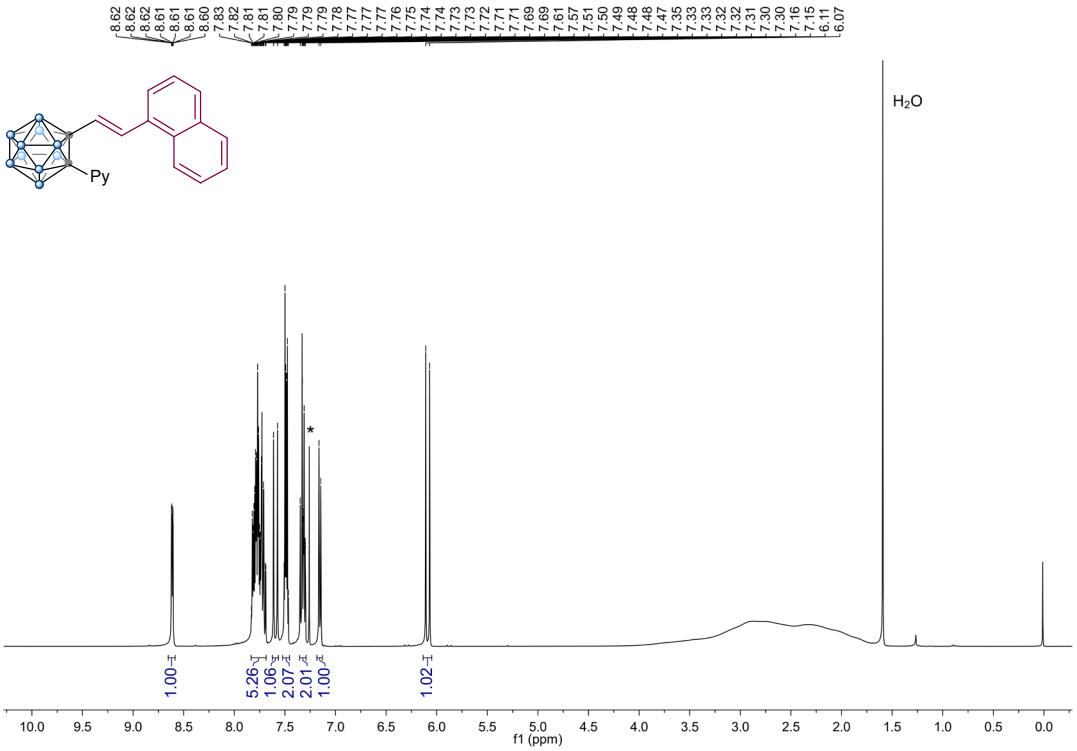
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3k**



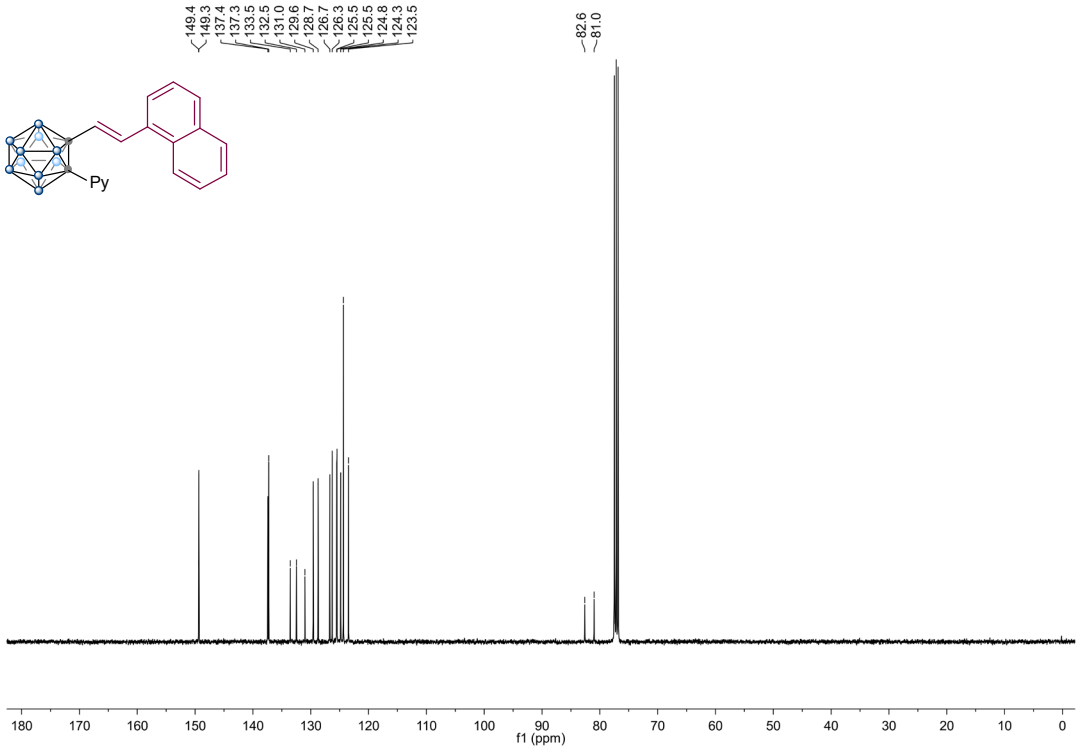
^{11}B NMR (128 MHz, Chloroform-*d*) **3k**



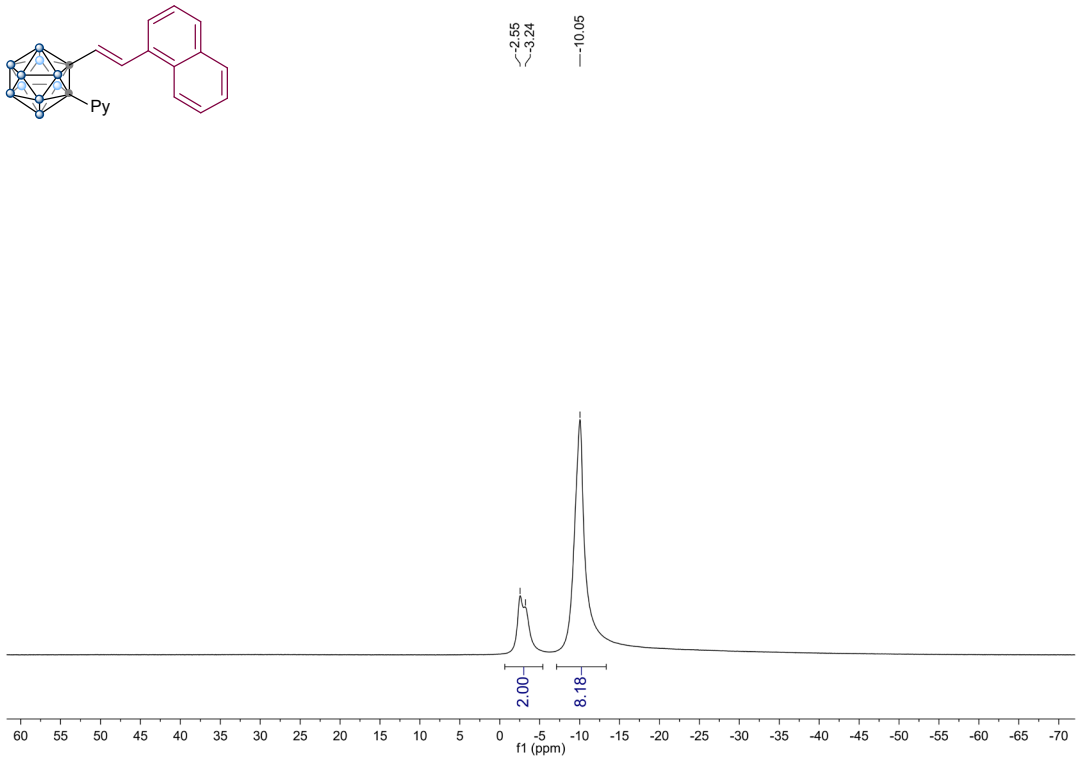
^{1}H NMR (400 MHz, Chloroform-*d*) **3l** (* from residual $CHCl_3$ in Chloroform-*d*)



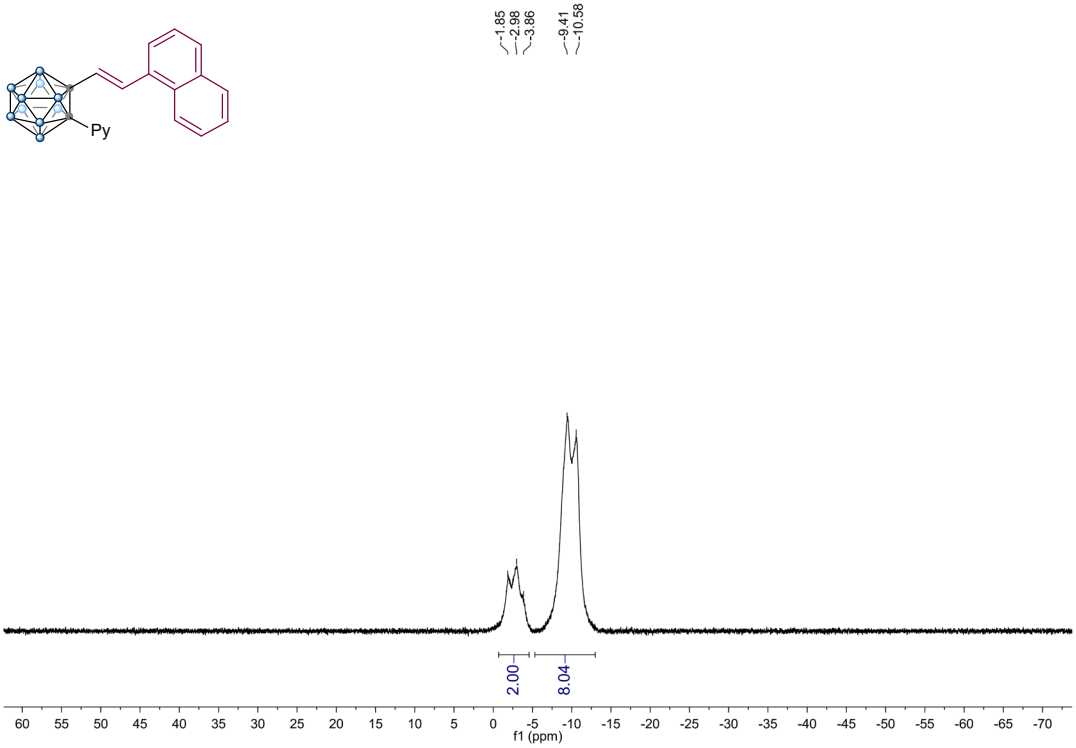
^{13}C NMR (101 MHz, Chloroform-*d*) **3l**



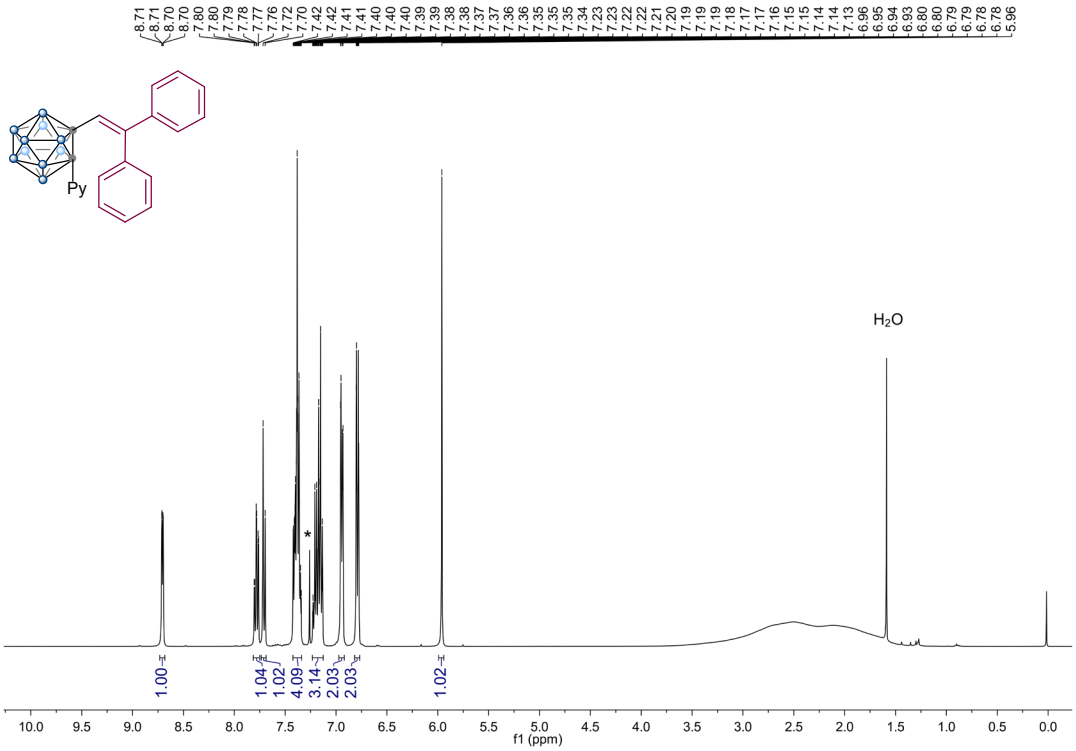
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3l**



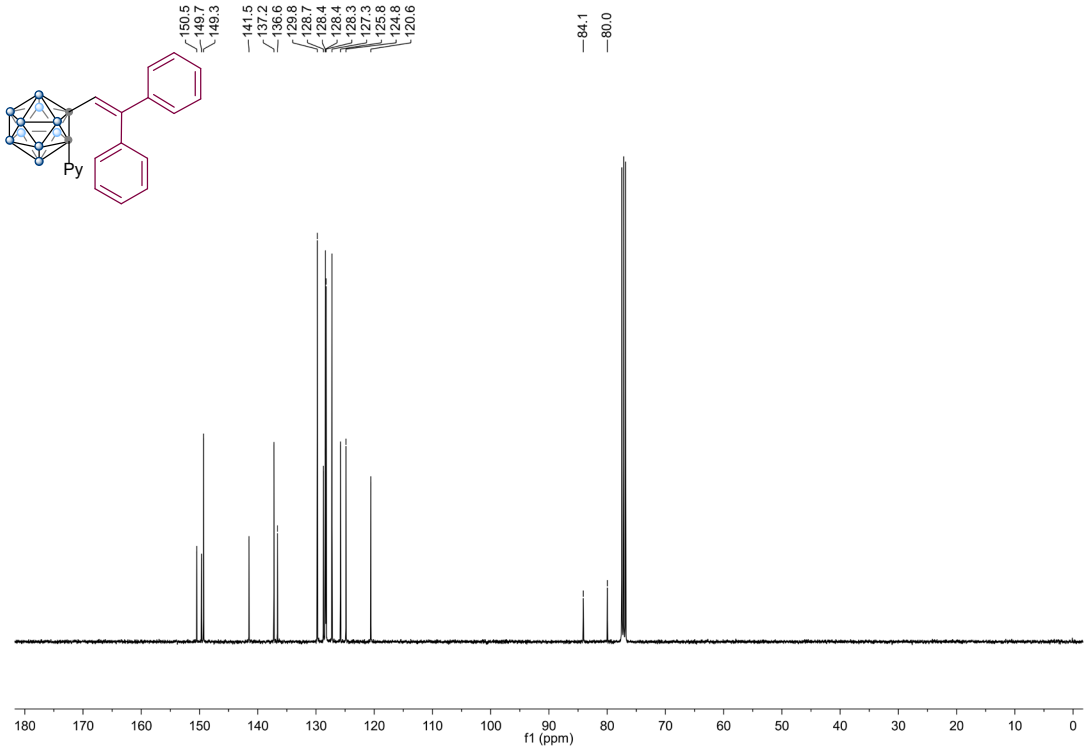
^{11}B NMR (128 MHz, Chloroform-*d*) **3l**



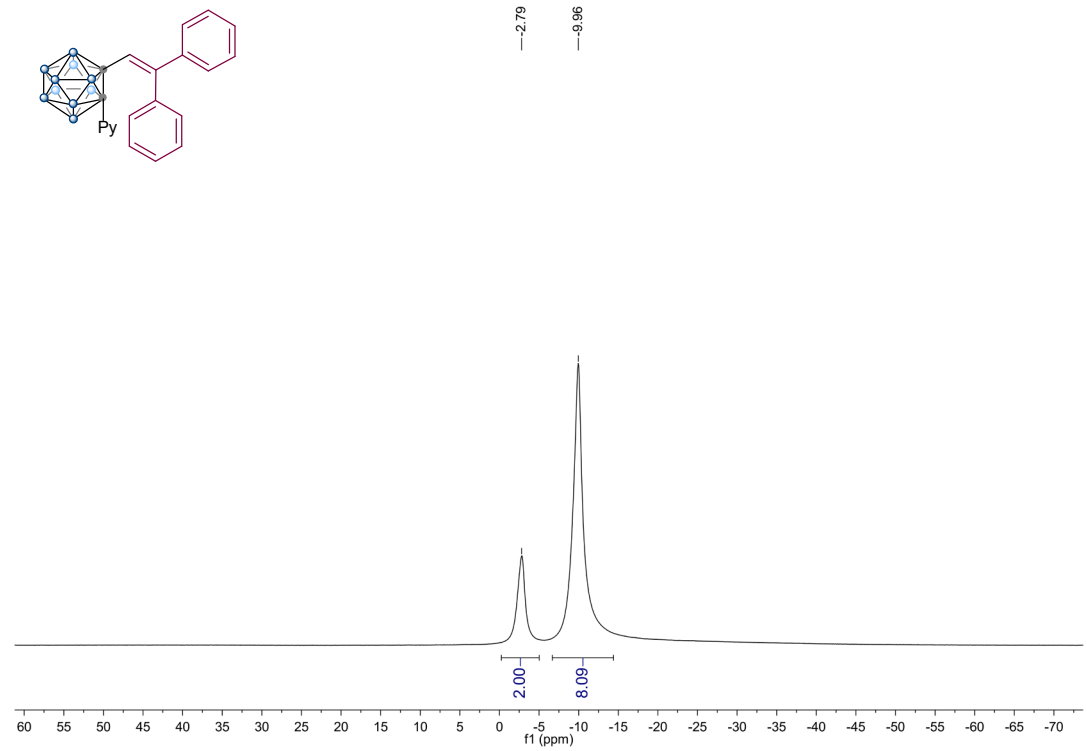
^{1}H NMR (400 MHz, Chloroform-*d*) **3m** (* from residual $CHCl_3$ in Chloroform-*d*)



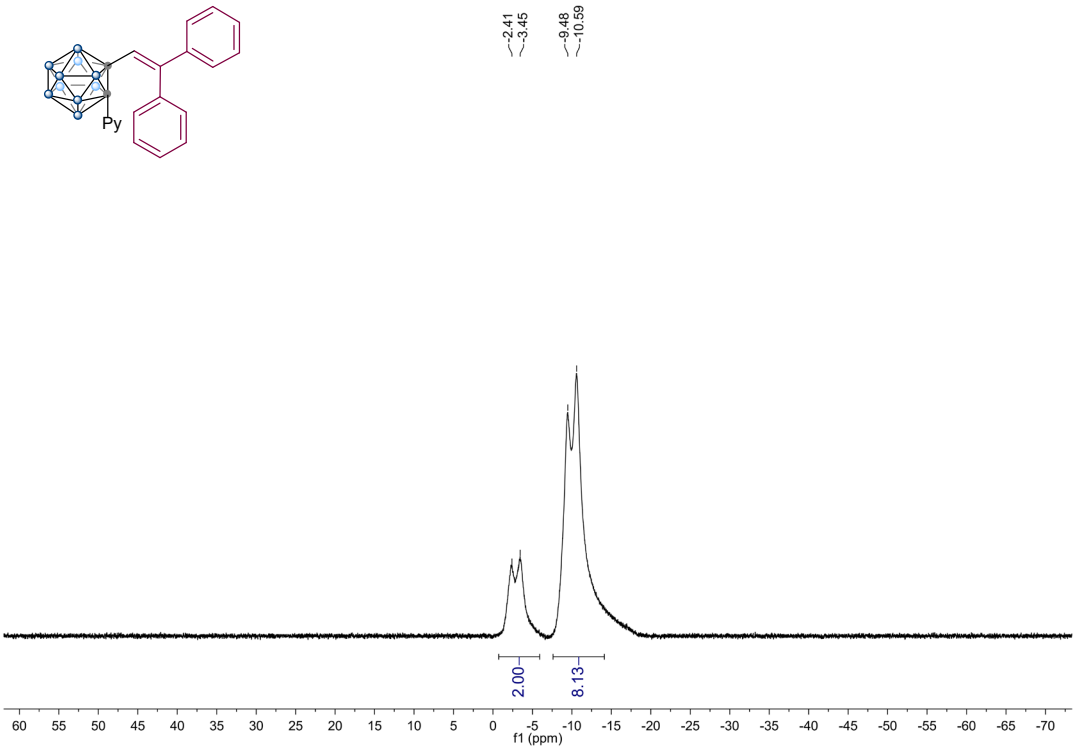
^{13}C NMR (101 MHz, Chloroform-*d*) **3m**



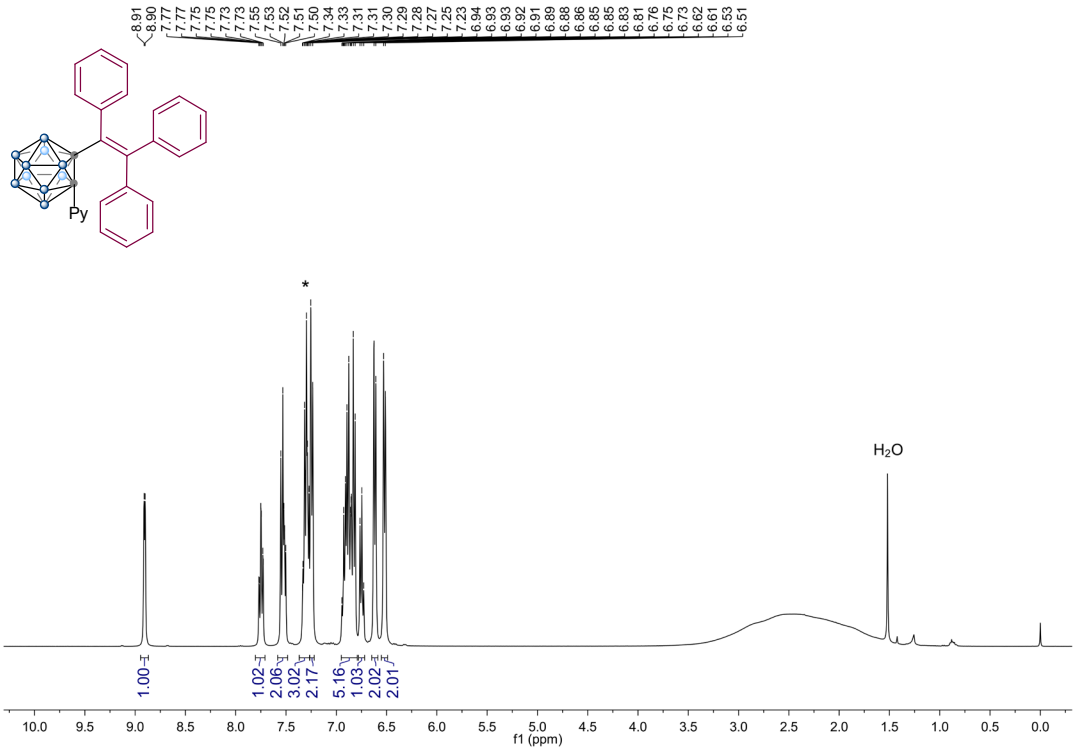
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3m**



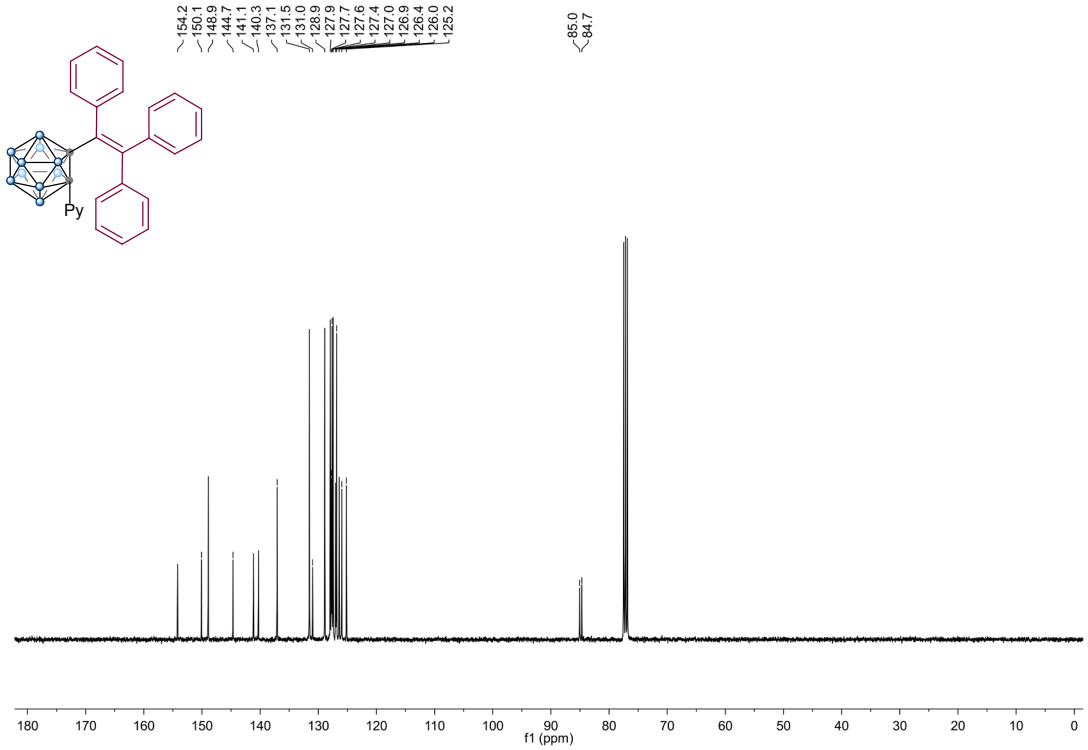
^{11}B NMR (128 MHz, Chloroform-*d*) **3m**



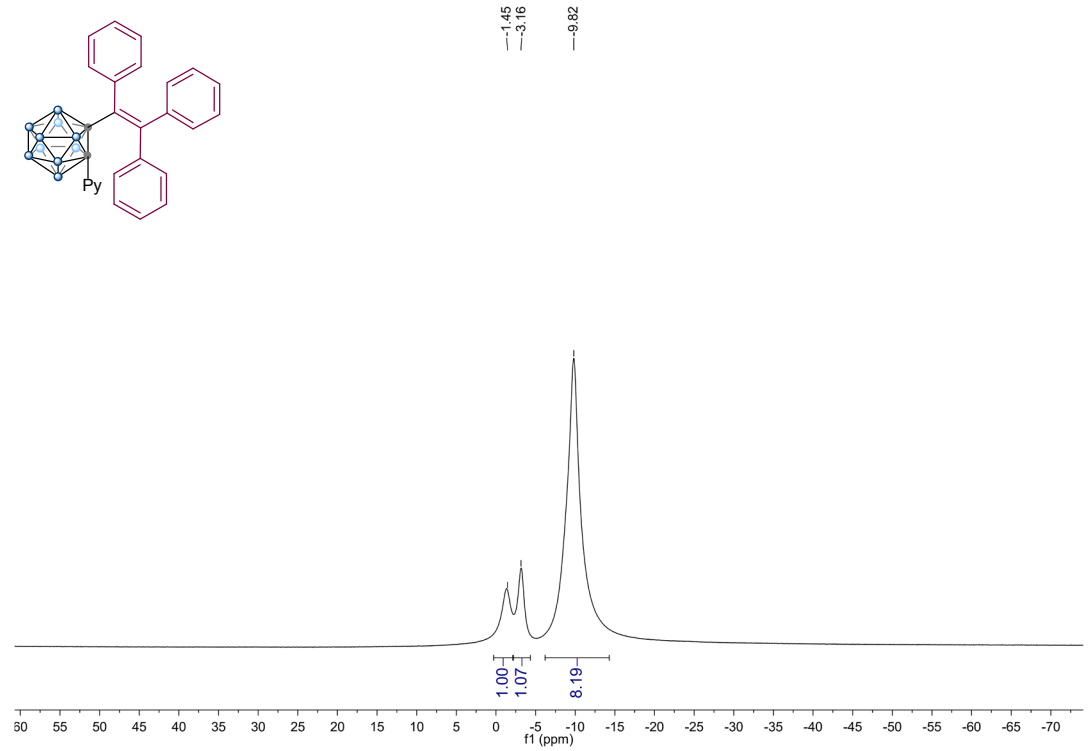
^{1}H NMR (400 MHz, Chloroform-*d*) **3n** (* from residual $CHCl_3$ in Chloroform-*d*)



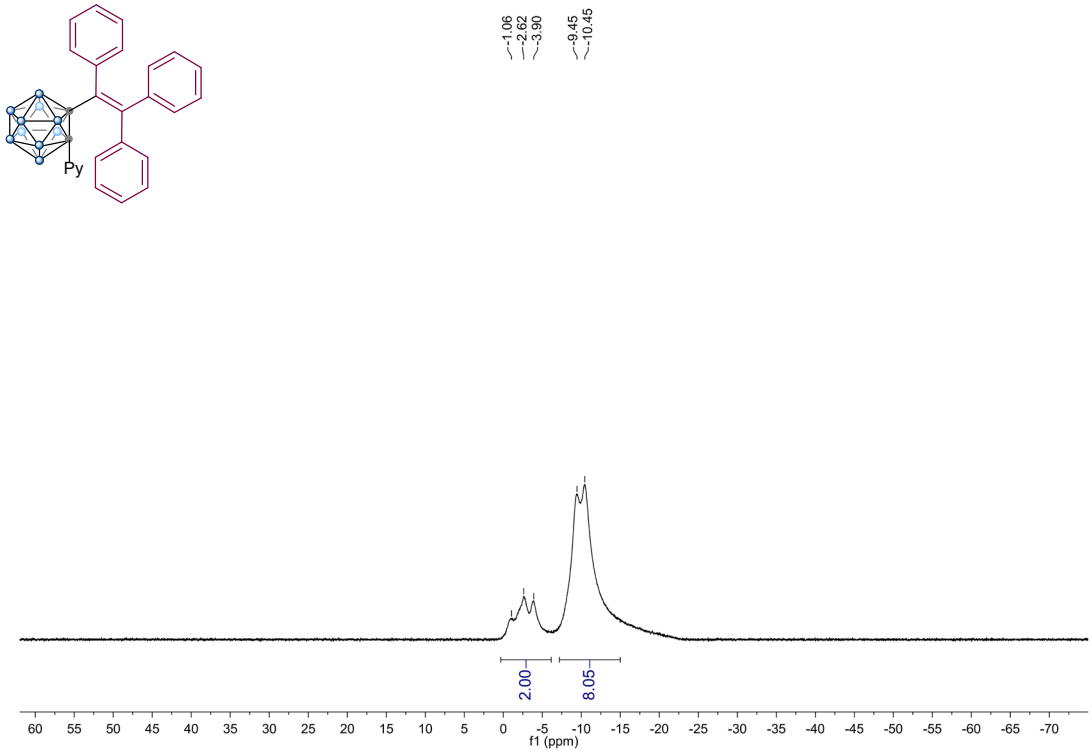
^{13}C NMR (101 MHz, Chloroform-*d*) **3n**



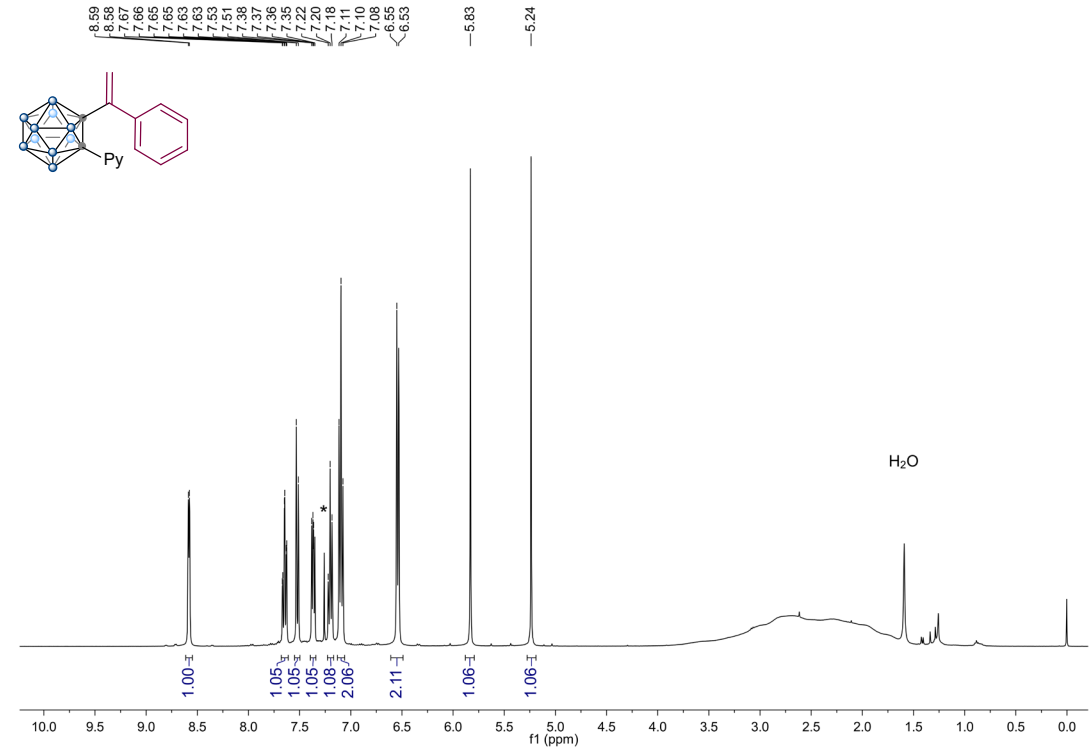
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3n**



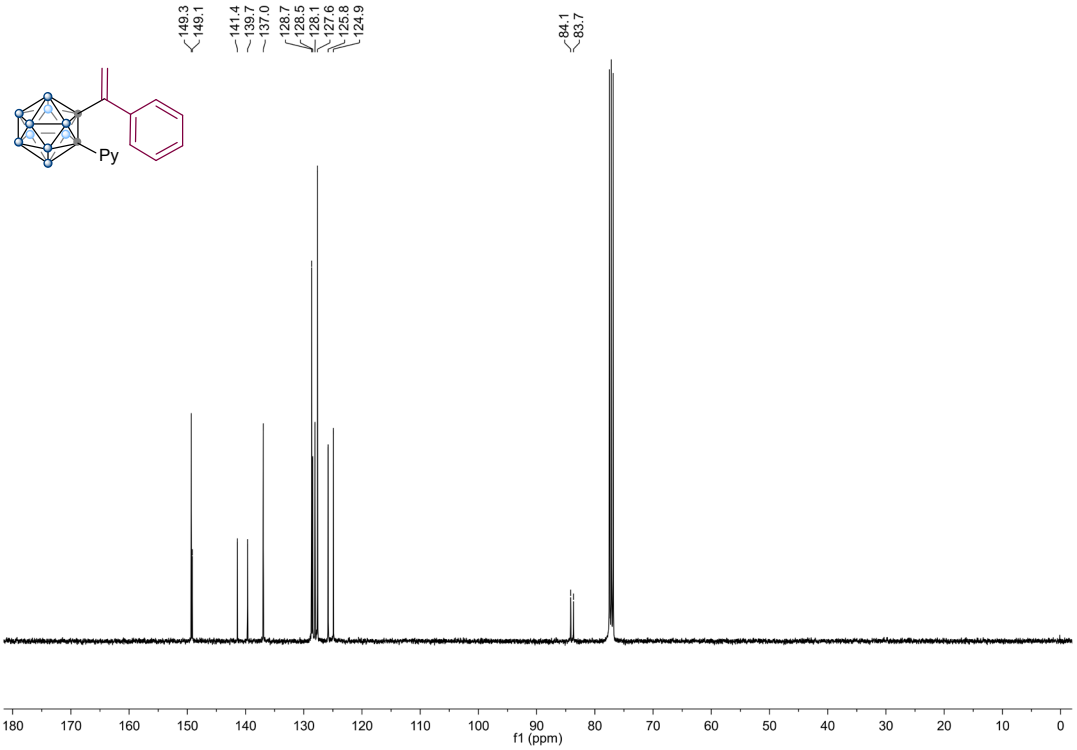
^{11}B NMR (128 MHz, Chloroform-*d*) **3n**



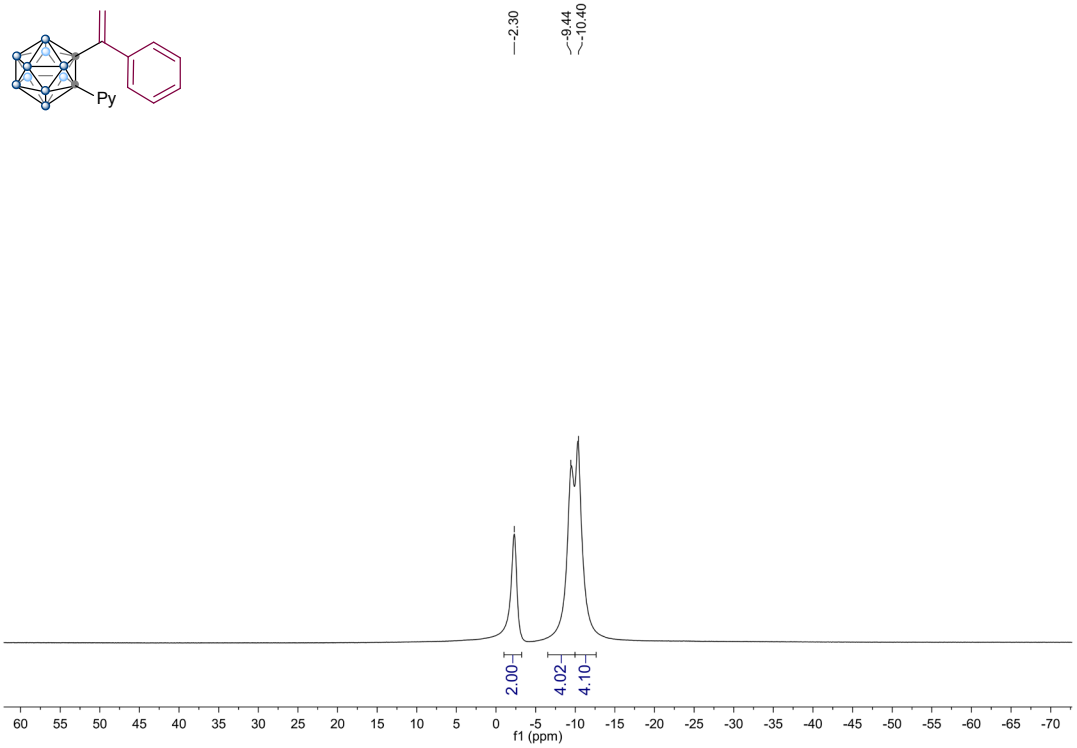
^{1}H NMR (400 MHz, Chloroform-*d*) **3o** (* from residual $CHCl_3$ in Chloroform-*d*)



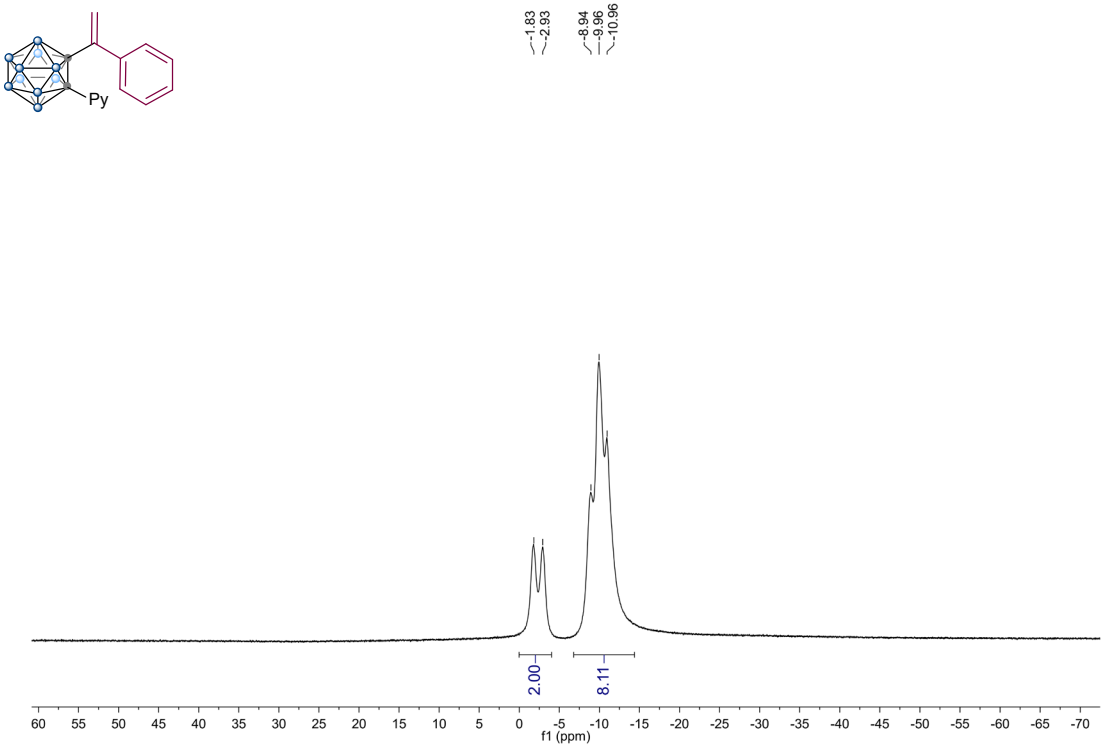
^{13}C NMR (101 MHz, Chloroform-*d*) **3o**



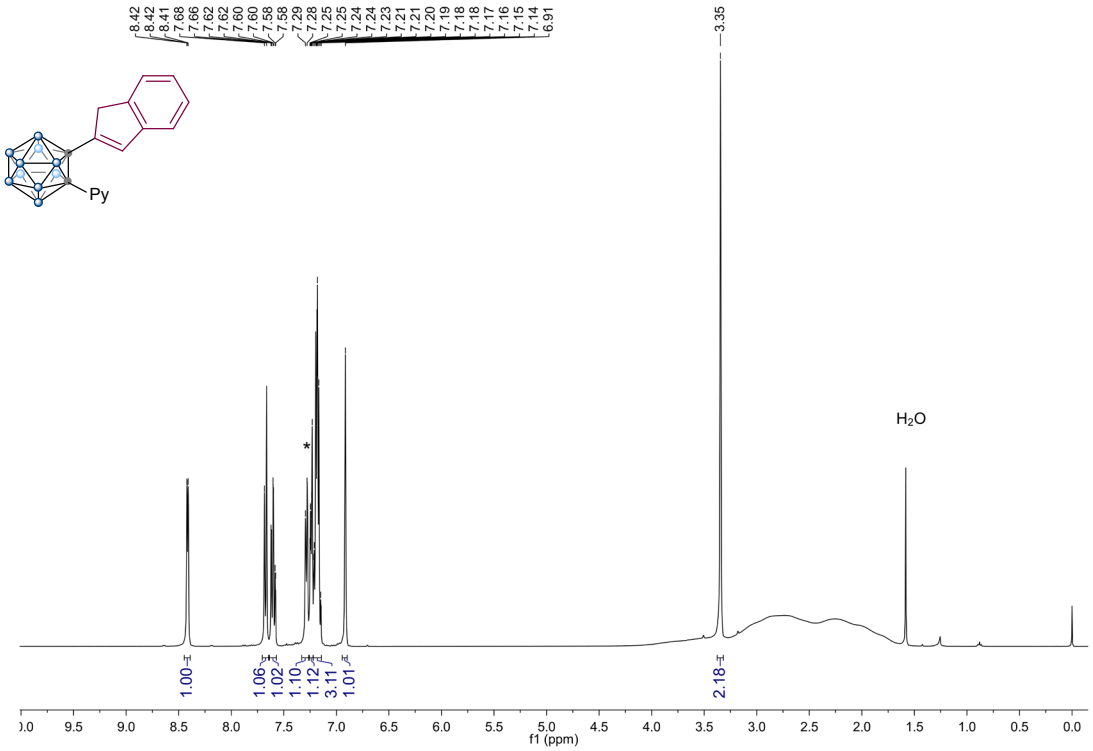
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3o**



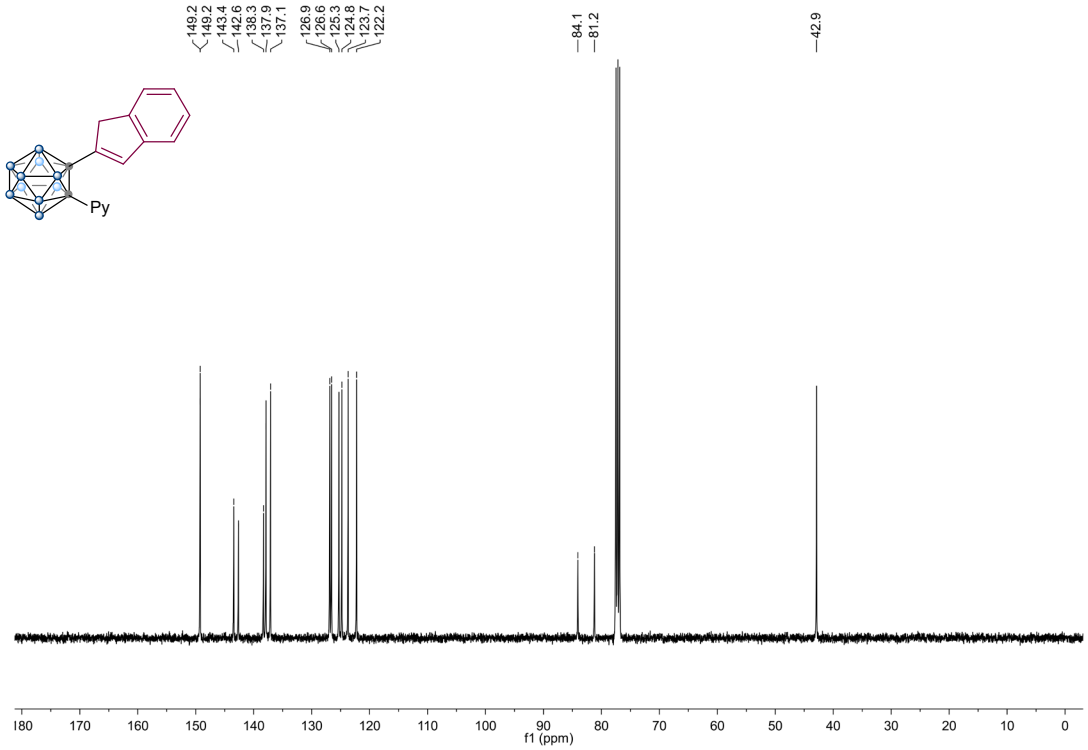
^{11}B NMR (128 MHz, Chloroform-*d*) **3o**



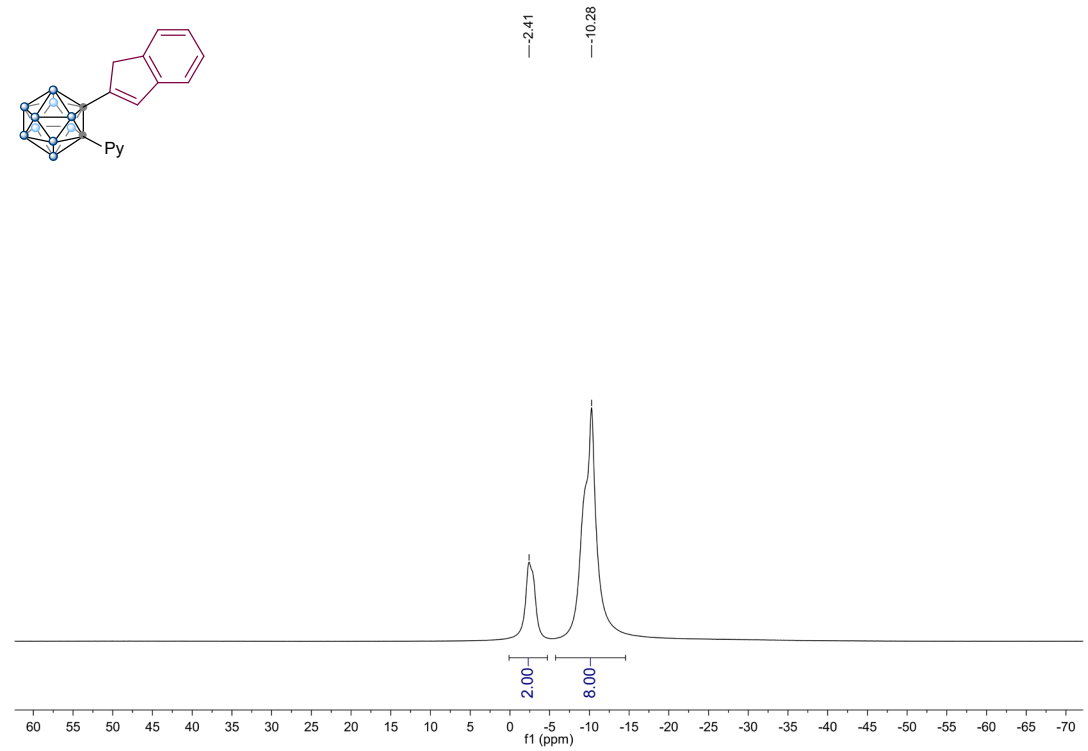
^{1}H NMR (400 MHz, Chloroform-*d*) **3p** (* from residual $CHCl_3$ in Chloroform-*d*)



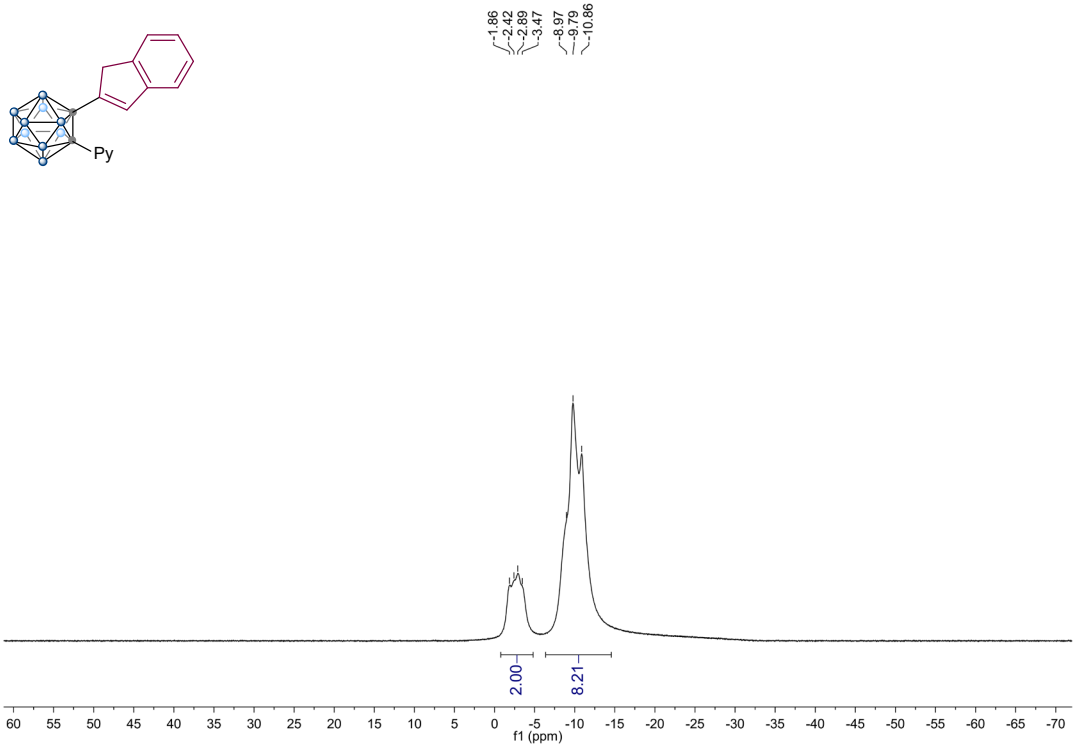
^{13}C NMR (101 MHz, Chloroform-*d*) **3p**



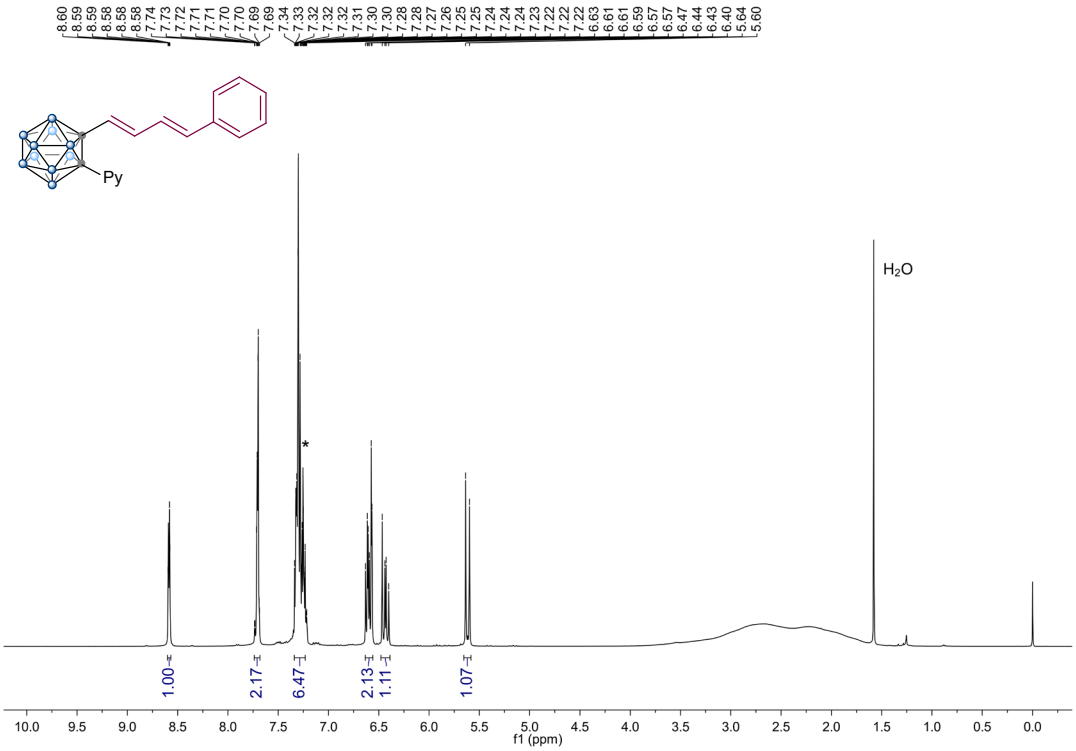
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3p**



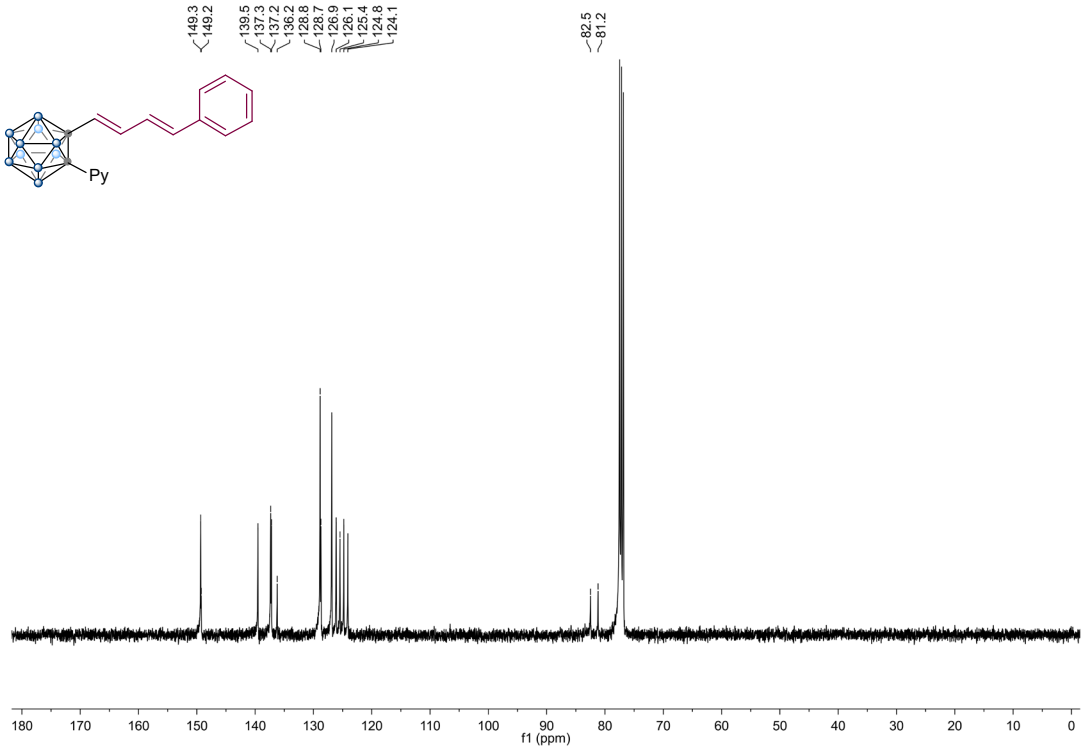
^{11}B NMR (128 MHz, Chloroform-*d*) **3p**



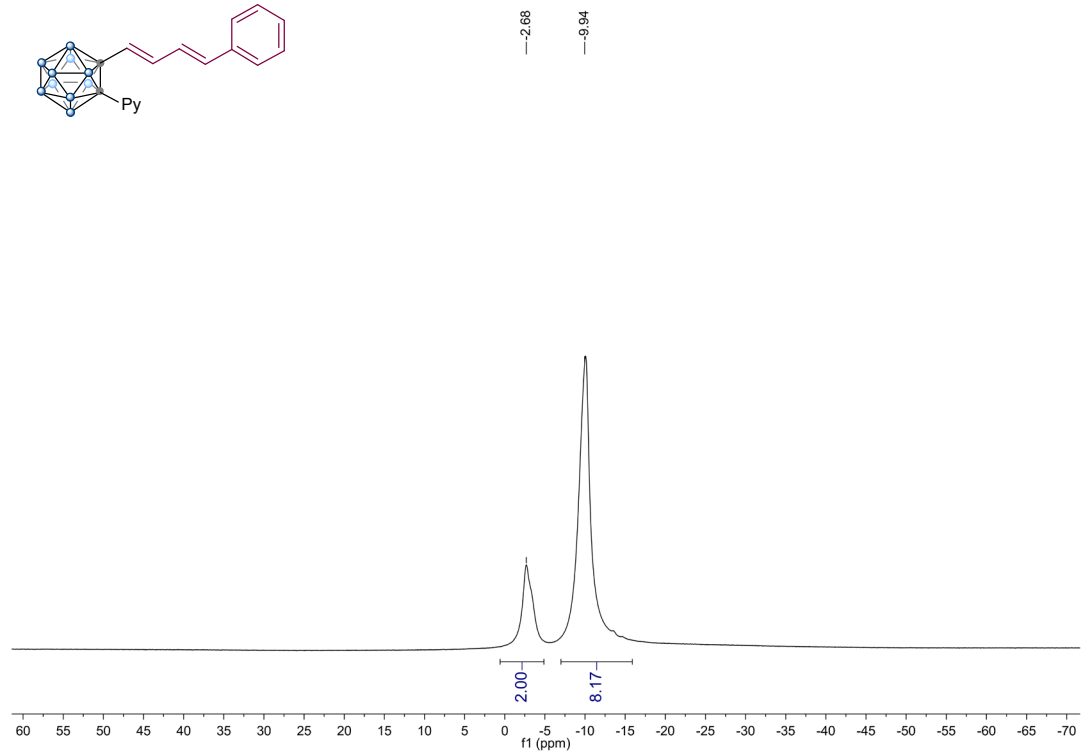
^{1}H NMR (400 MHz, Chloroform-*d*) **3q** (* from residual $CHCl_3$ in Chloroform-*d*)



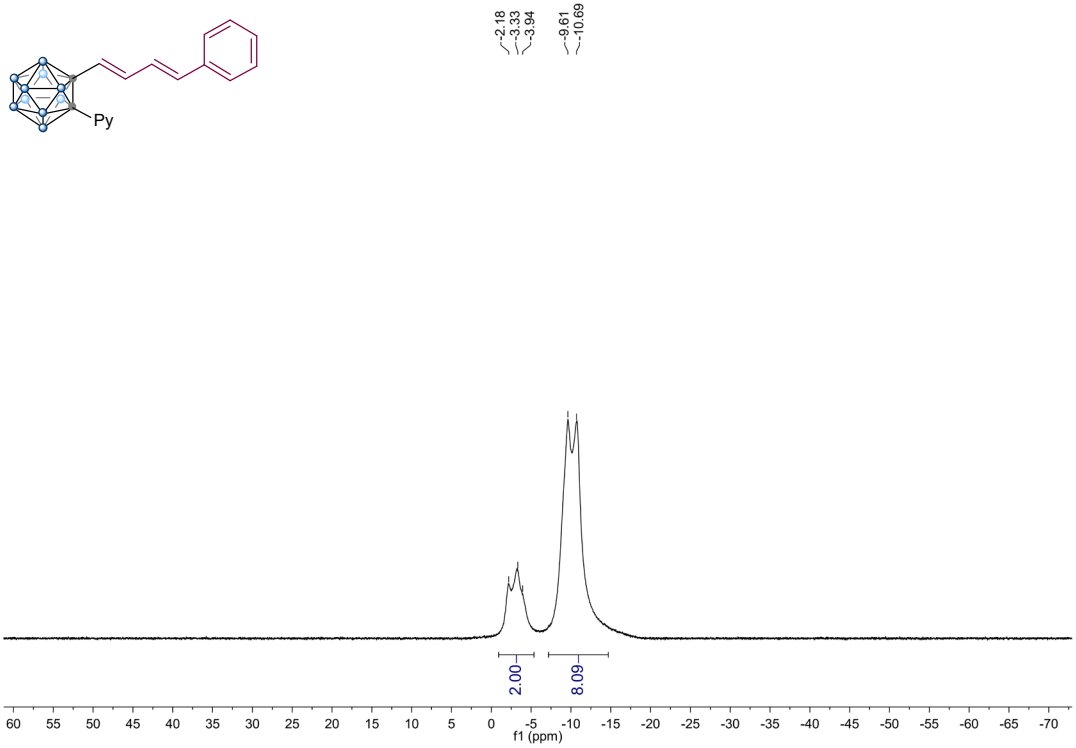
^{13}C NMR (101 MHz, Chloroform-*d*) **3q**



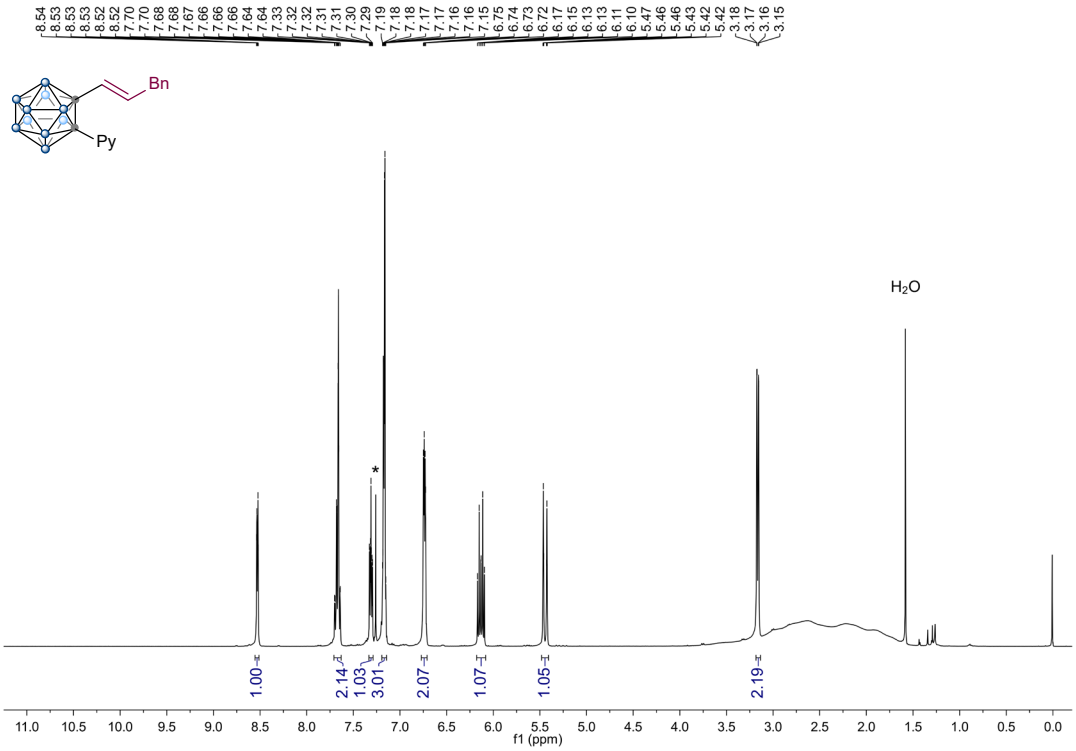
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3q**



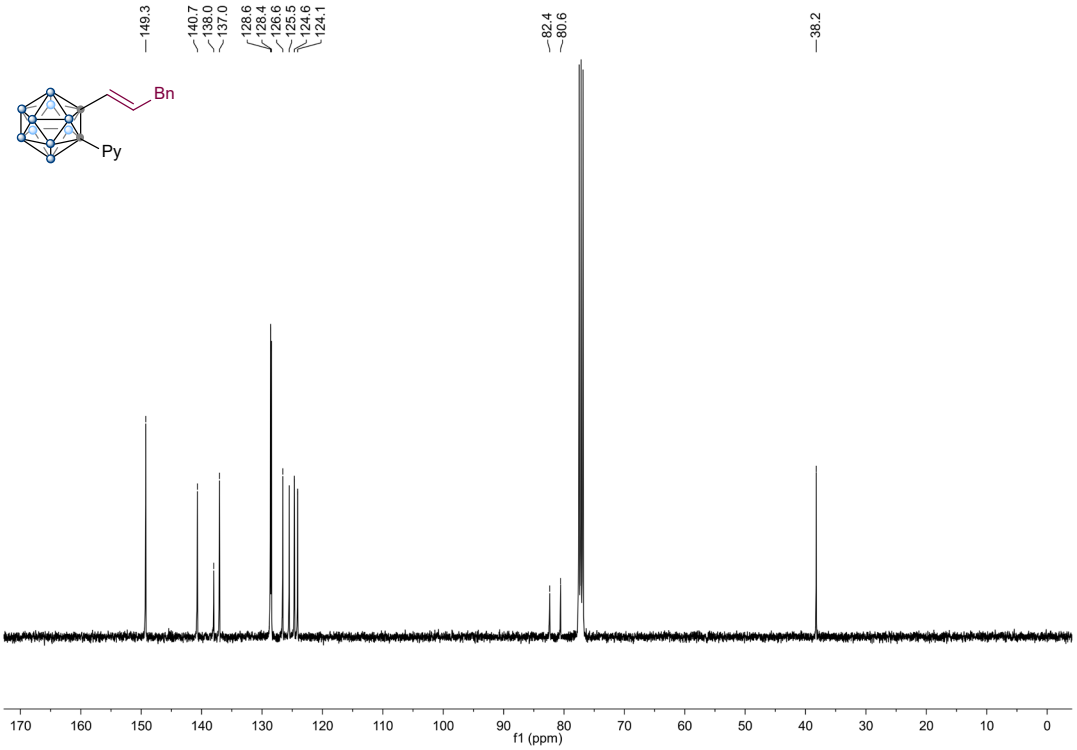
^{11}B NMR (128 MHz, Chloroform-*d*) **3q**



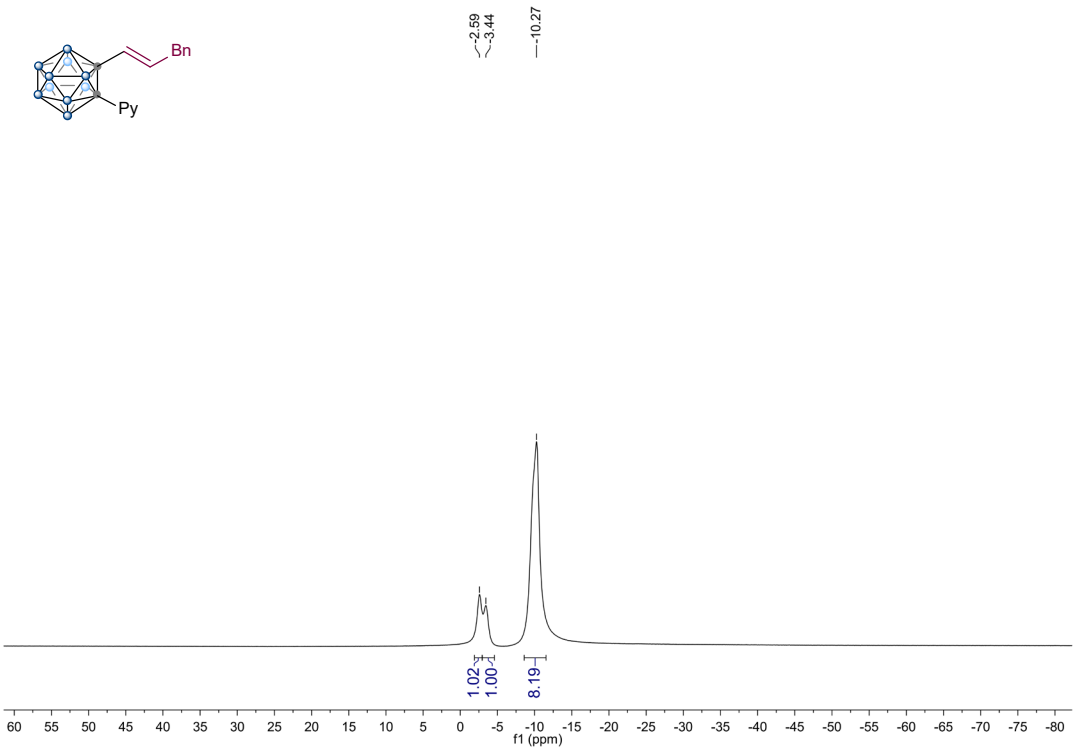
^{1}H NMR (400 MHz, Chloroform-*d*) **3r** (* from residual $CHCl_3$ in Chloroform-*d*)



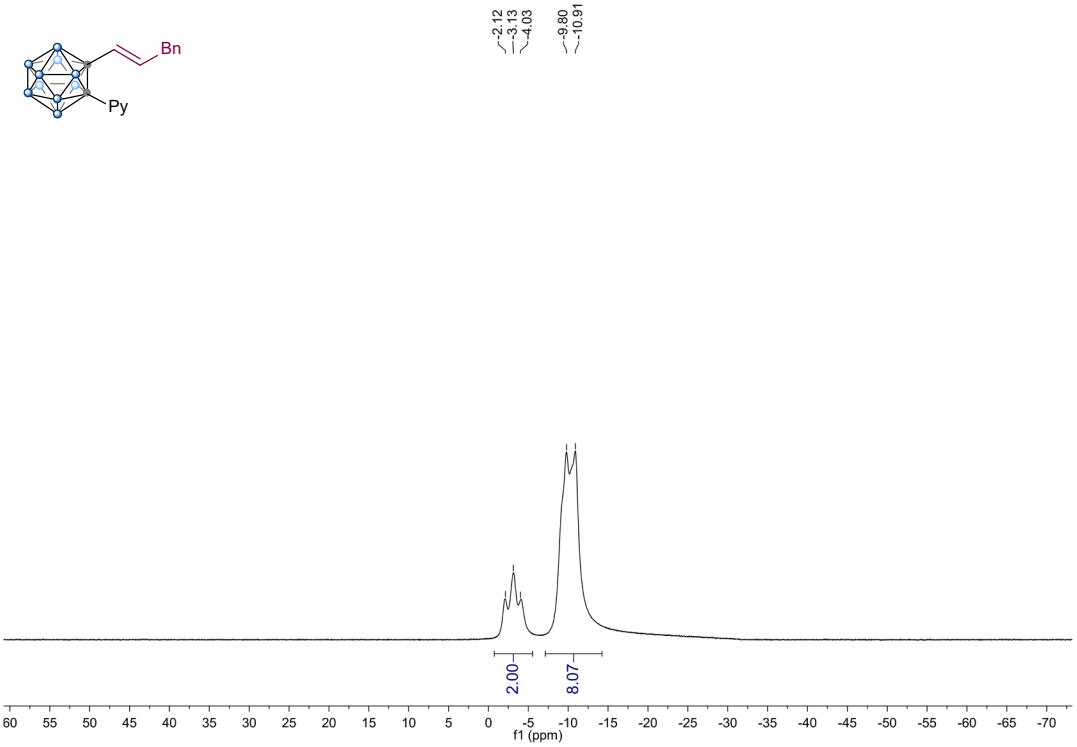
^{13}C NMR (101 MHz, Chloroform-*d*) **3r**



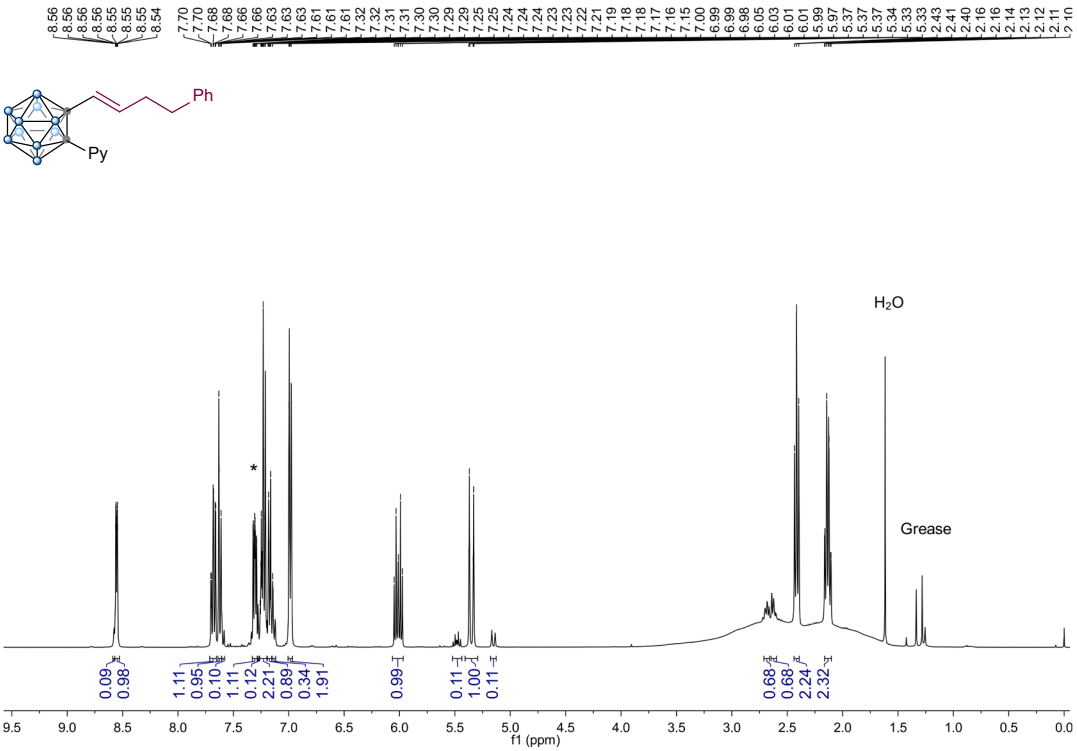
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3r**



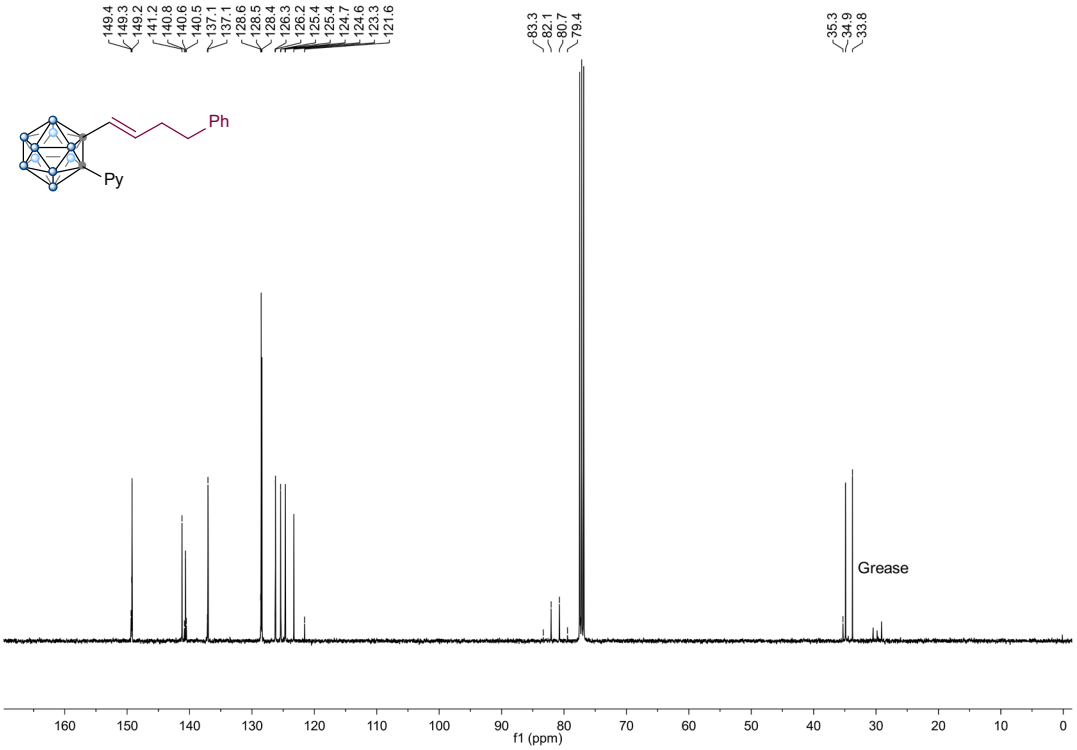
^{11}B NMR (128 MHz, Chloroform-*d*) **3r**



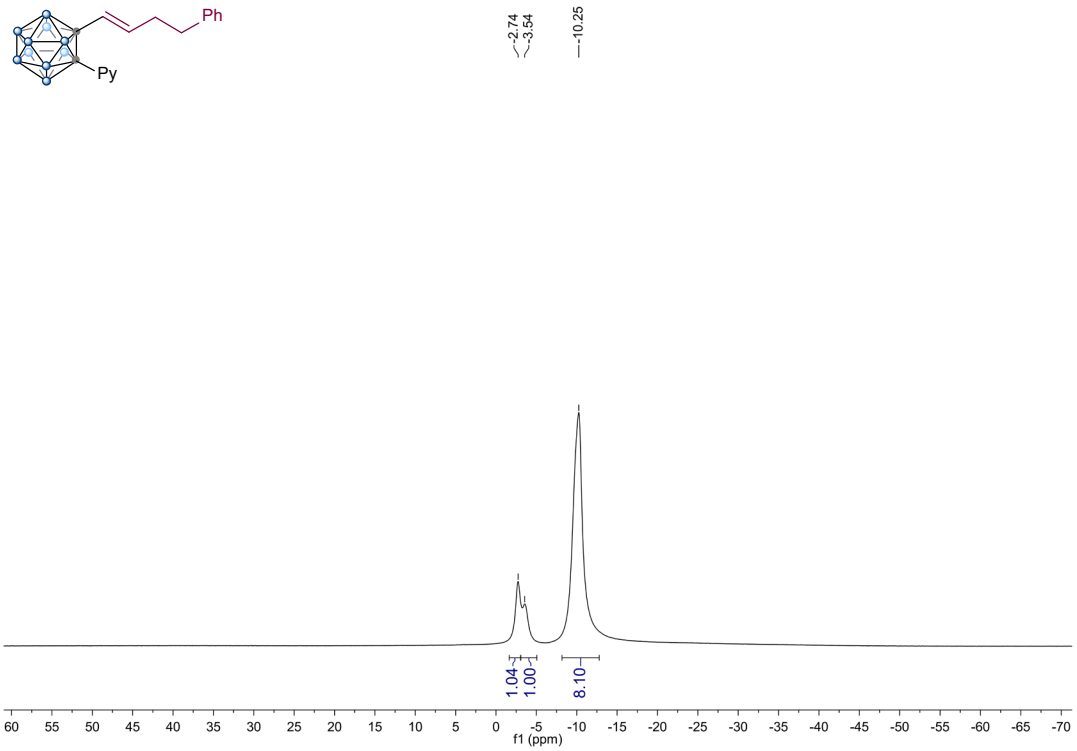
^{1}H NMR (400 MHz, Chloroform-*d*) **3s** (* from residual $CHCl_3$ in Chloroform-*d*)



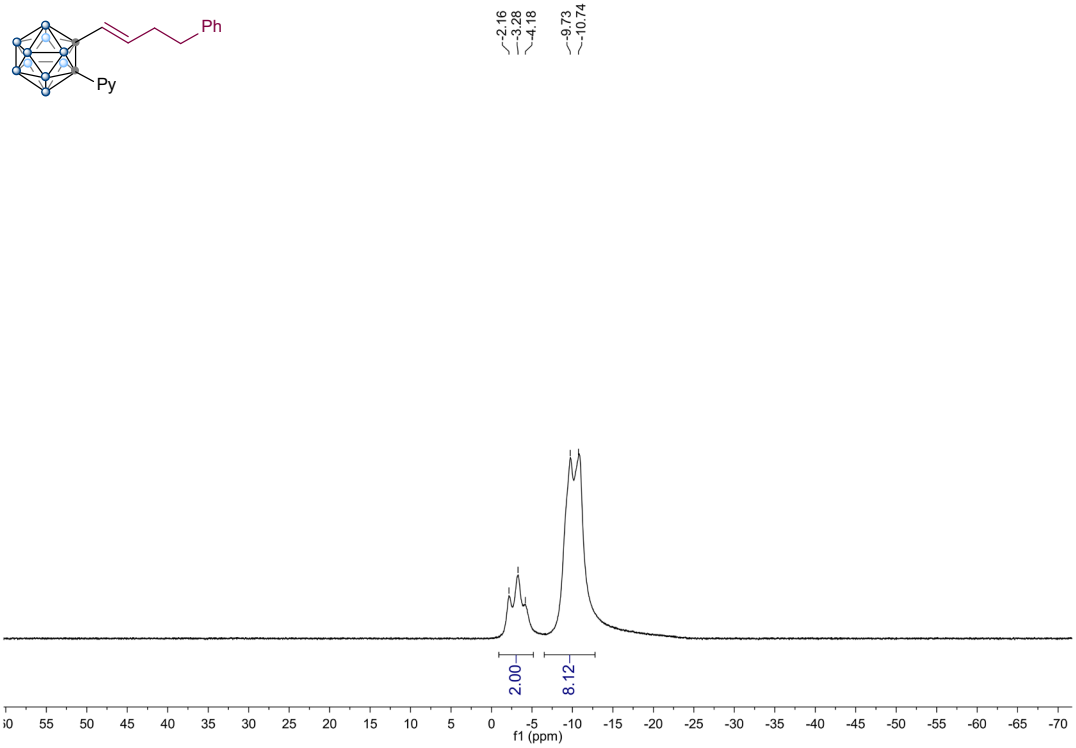
^{13}C NMR (101 MHz, Chloroform-*d*) **3s**



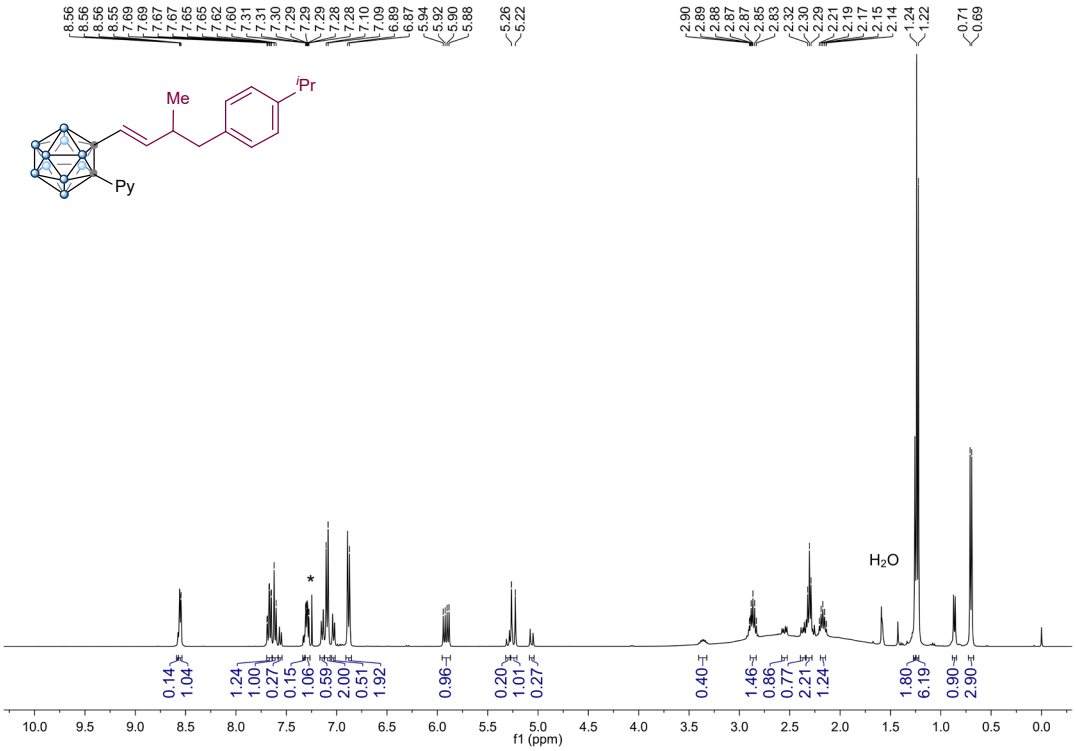
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3s**



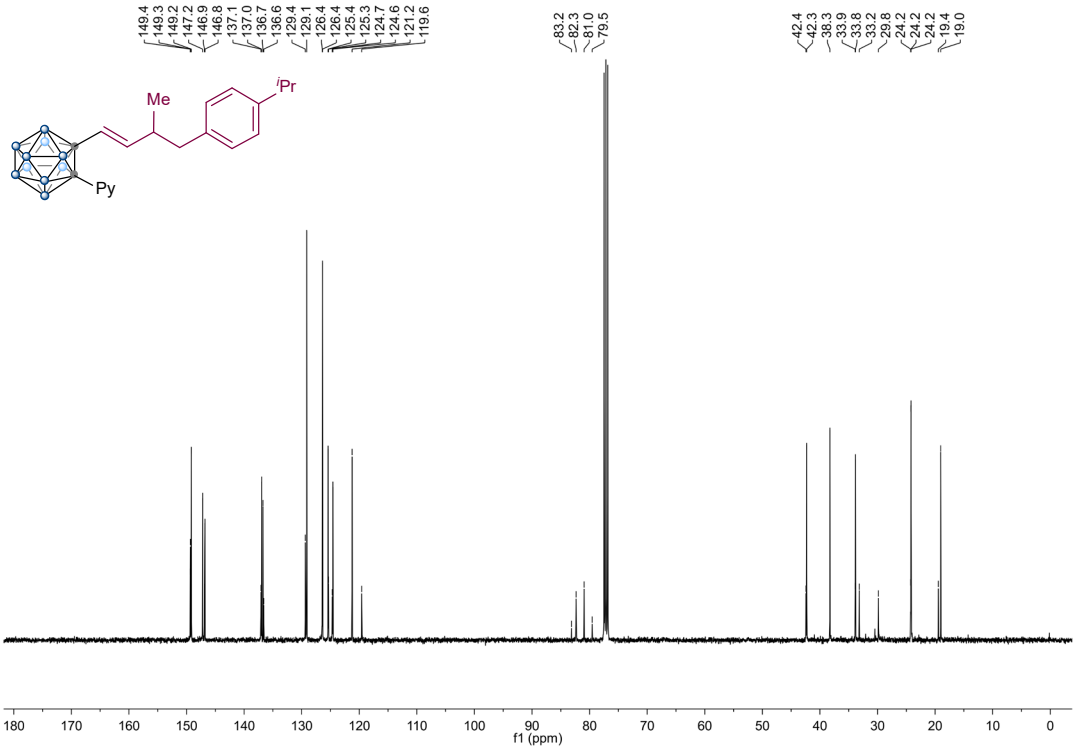
^{11}B NMR (128 MHz, Chloroform-*d*) **3s**



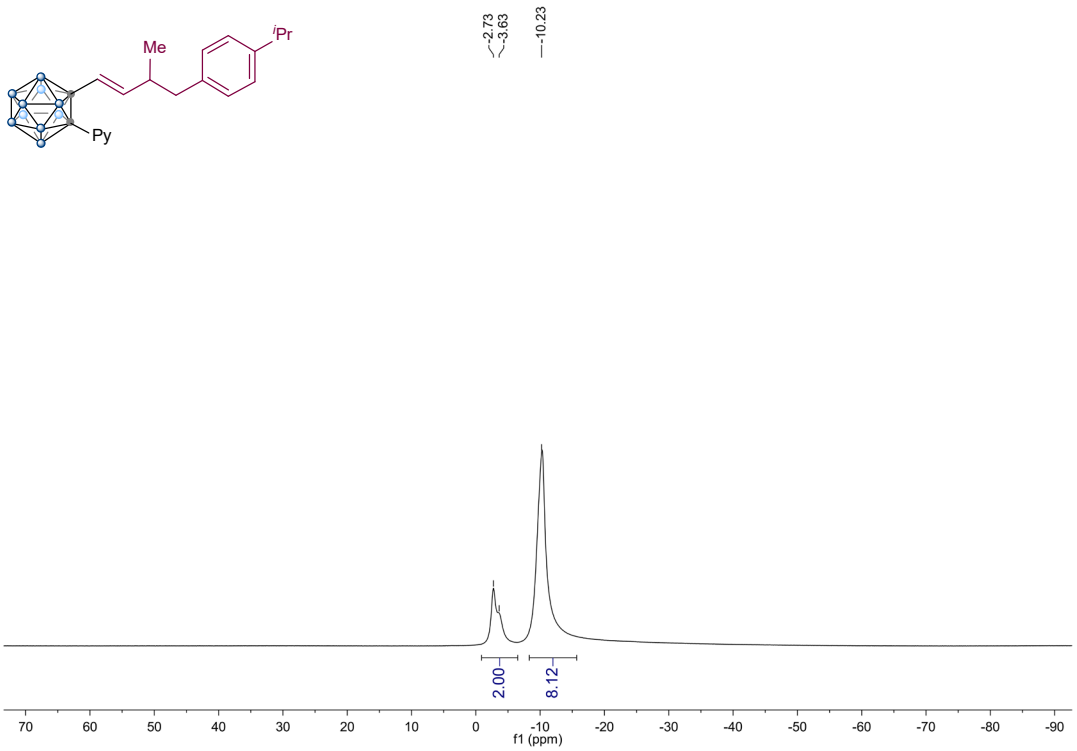
^{1}H NMR (400 MHz, Chloroform-*d*) **3t**(* from residual $CHCl_3$ in Chloroform-*d*)



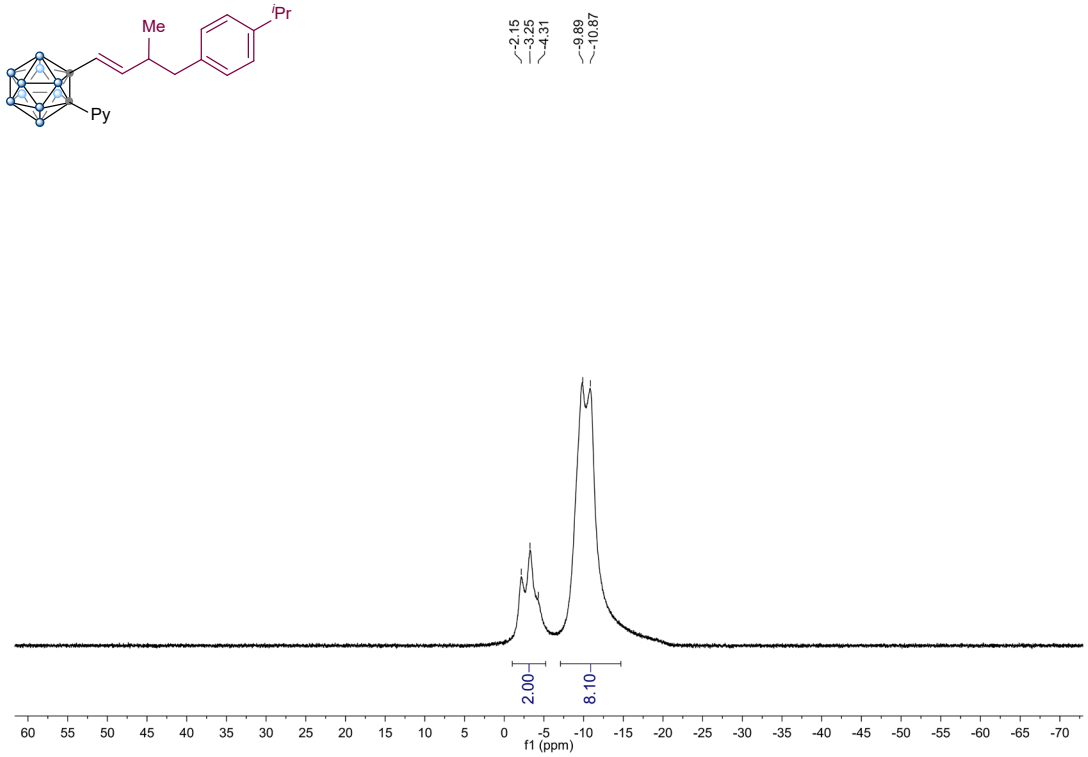
^{13}C NMR (101 MHz, Chloroform-*d*) **3t**



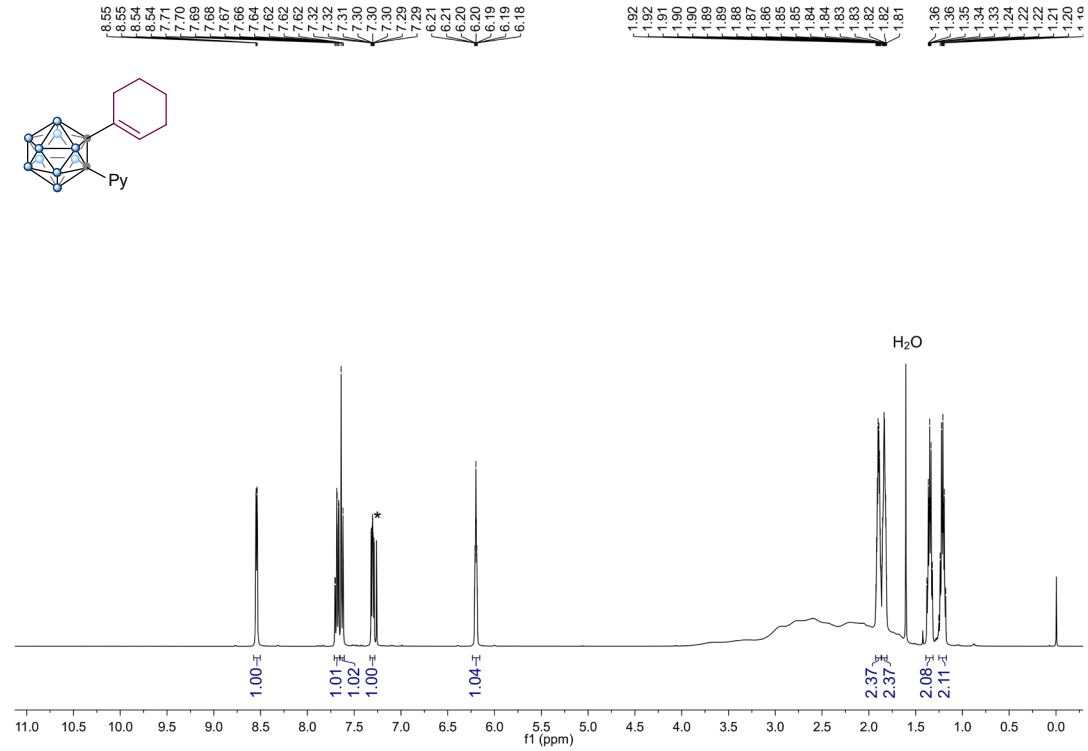
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3t**



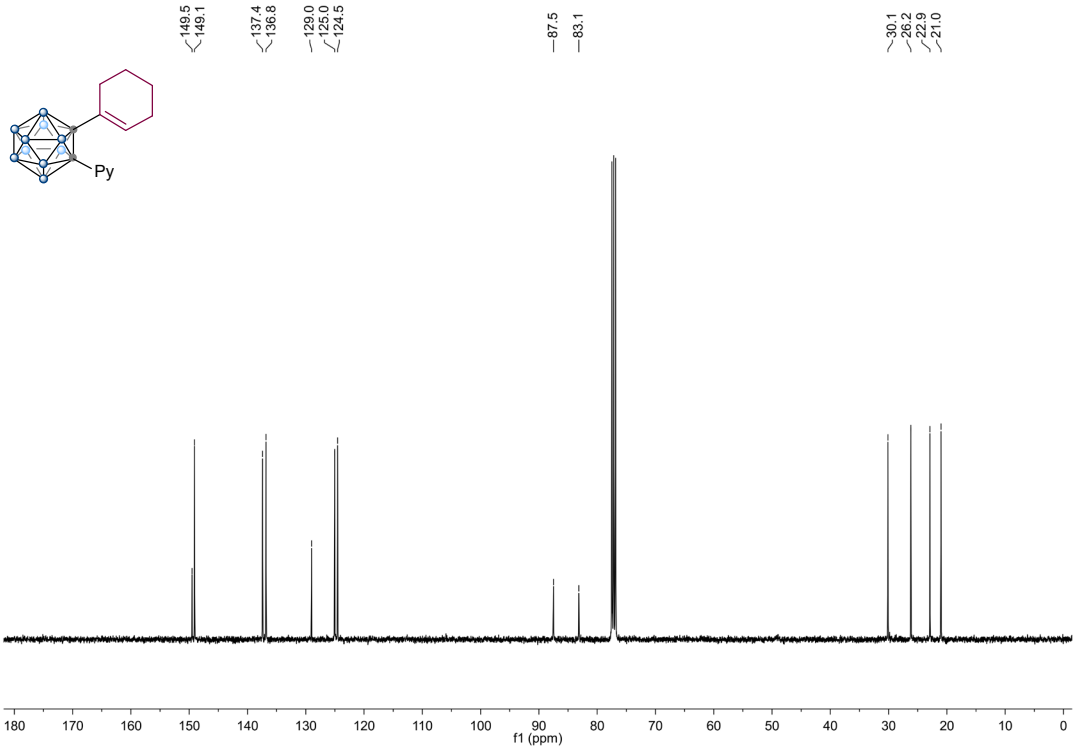
^{11}B NMR (128 MHz, Chloroform-*d*) **3t**



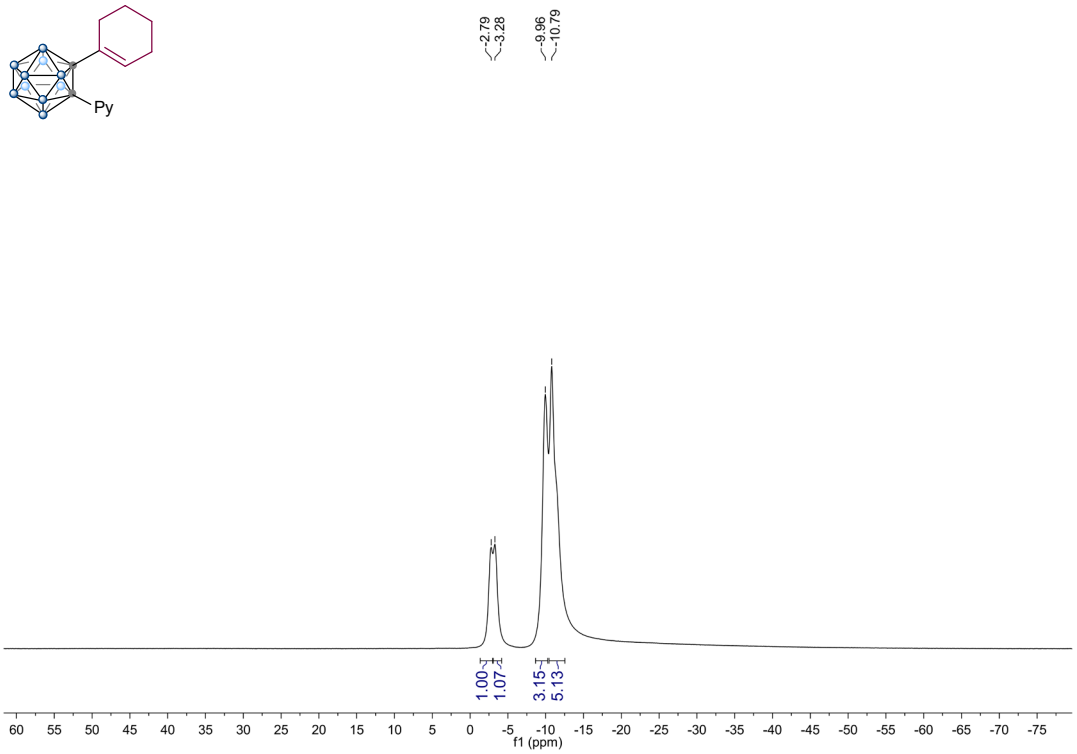
^{1}H NMR (400 MHz, Chloroform-*d*) **3u** (* from residual $CHCl_3$ in Chloroform-*d*)



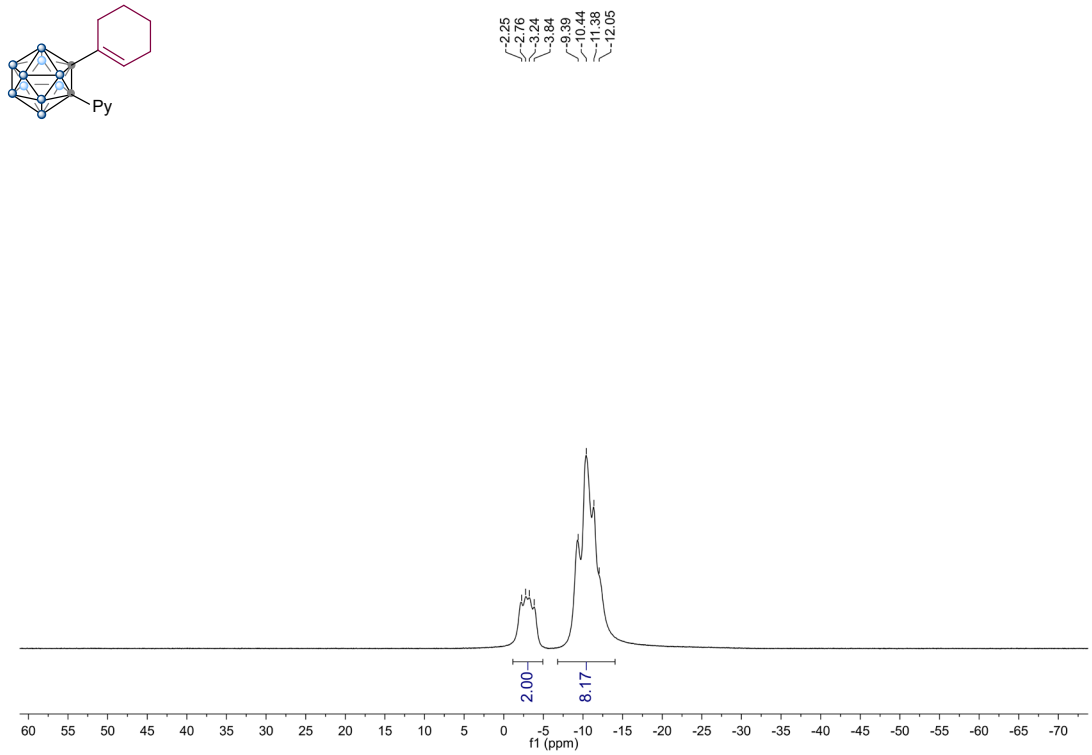
^{13}C NMR (101 MHz, Chloroform-*d*) **3u**



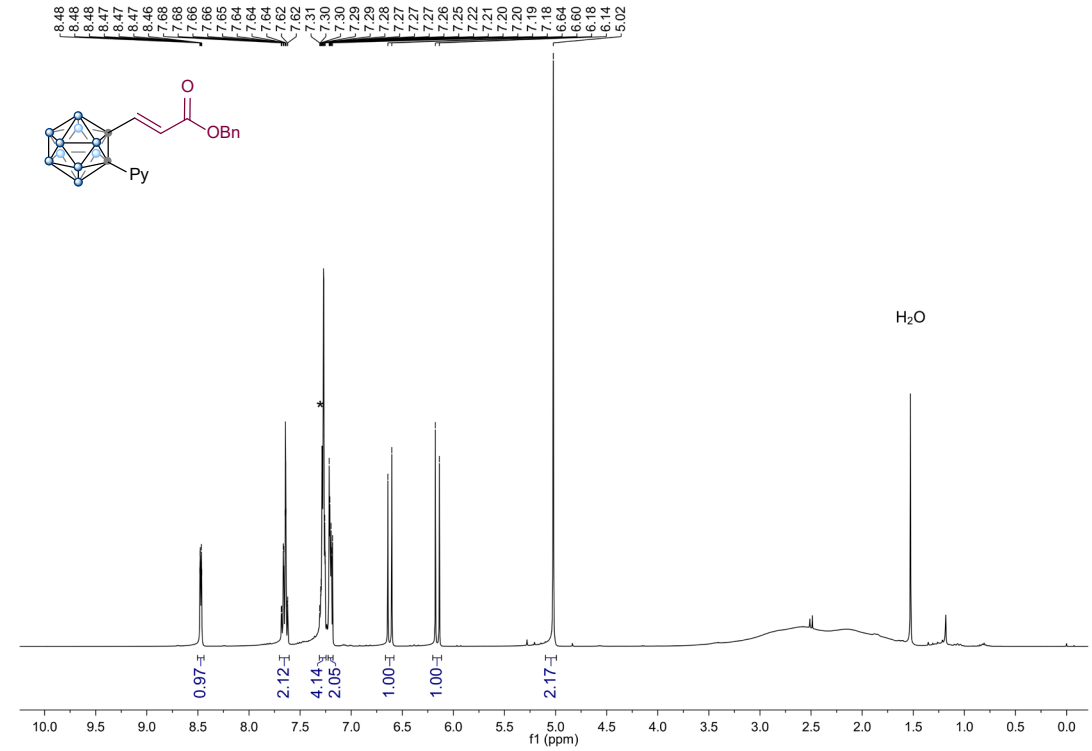
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3u**



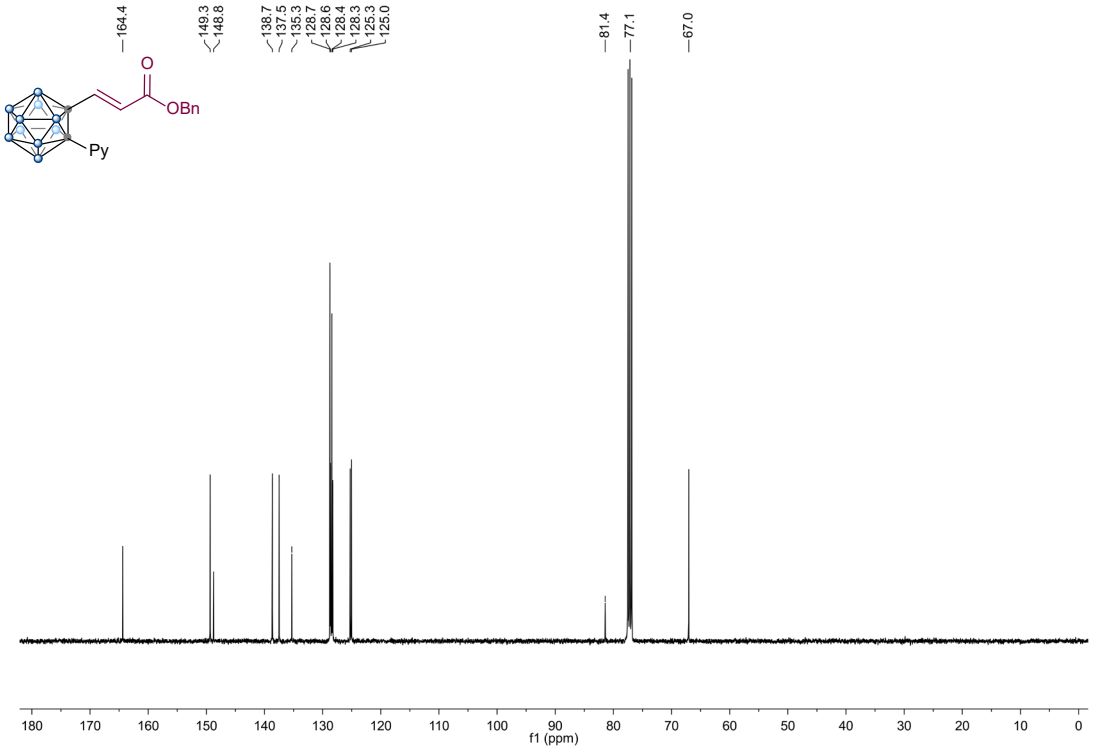
^{11}B NMR (128 MHz, Chloroform-*d*) **3u**



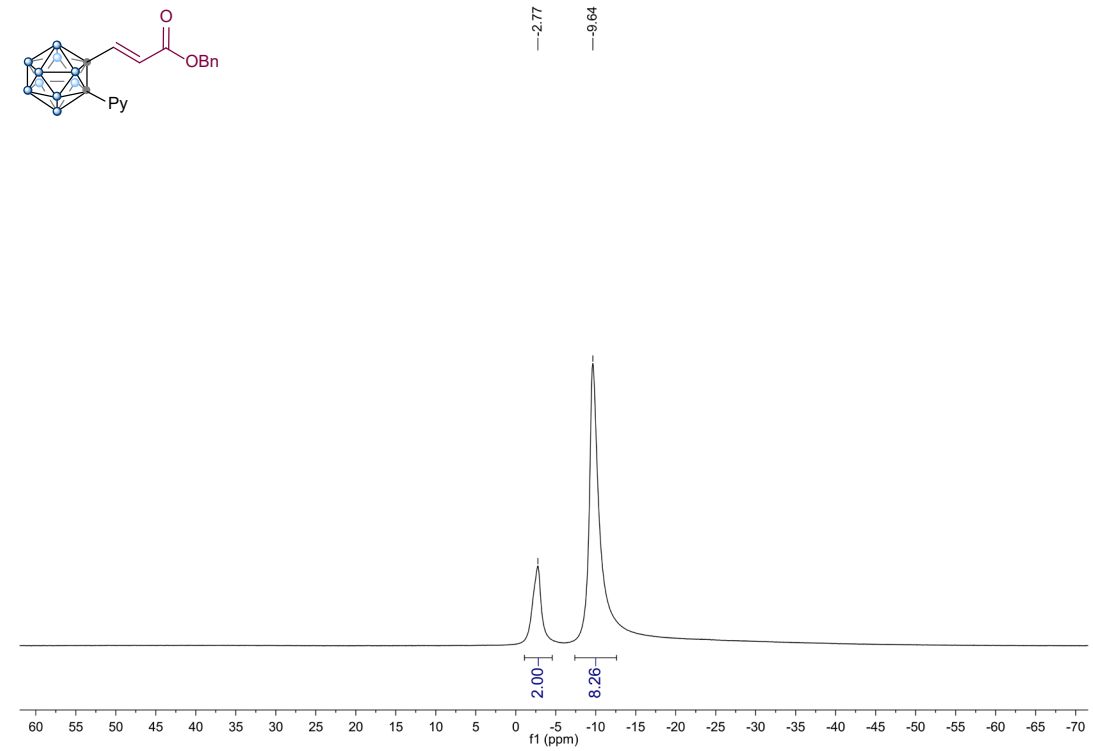
^{1}H NMR (400 MHz, Chloroform-*d*) **3v** (* from residual $CHCl_3$ in Chloroform-*d*)



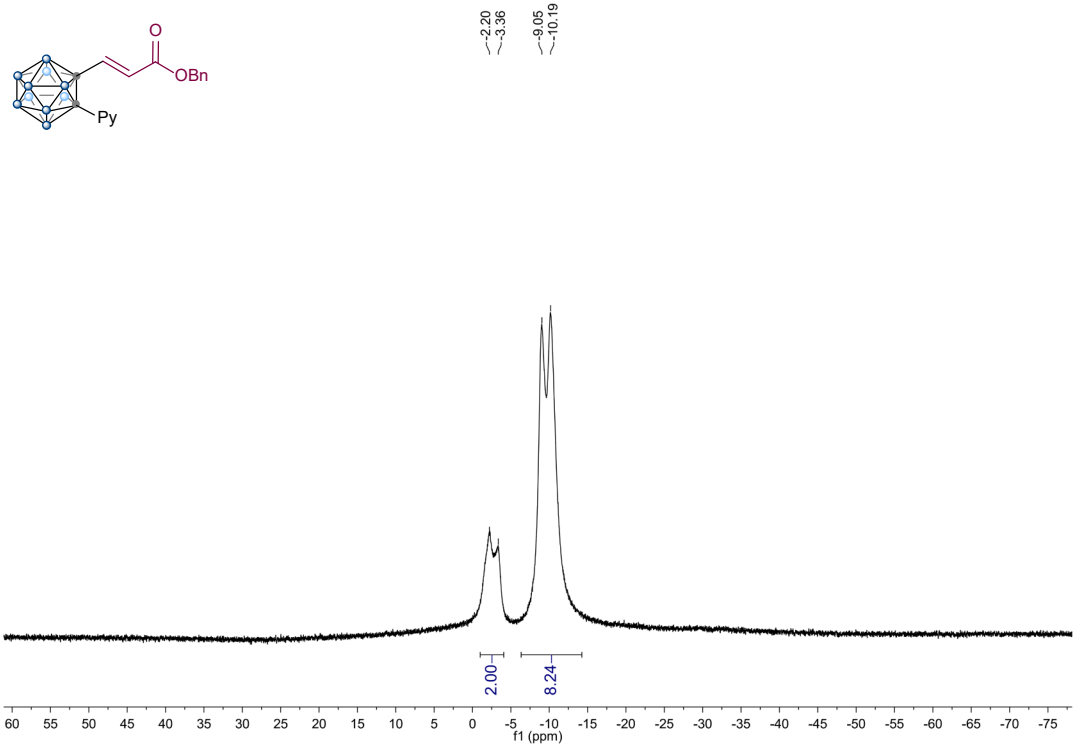
^{13}C NMR (101 MHz, Chloroform-*d*) **3v**



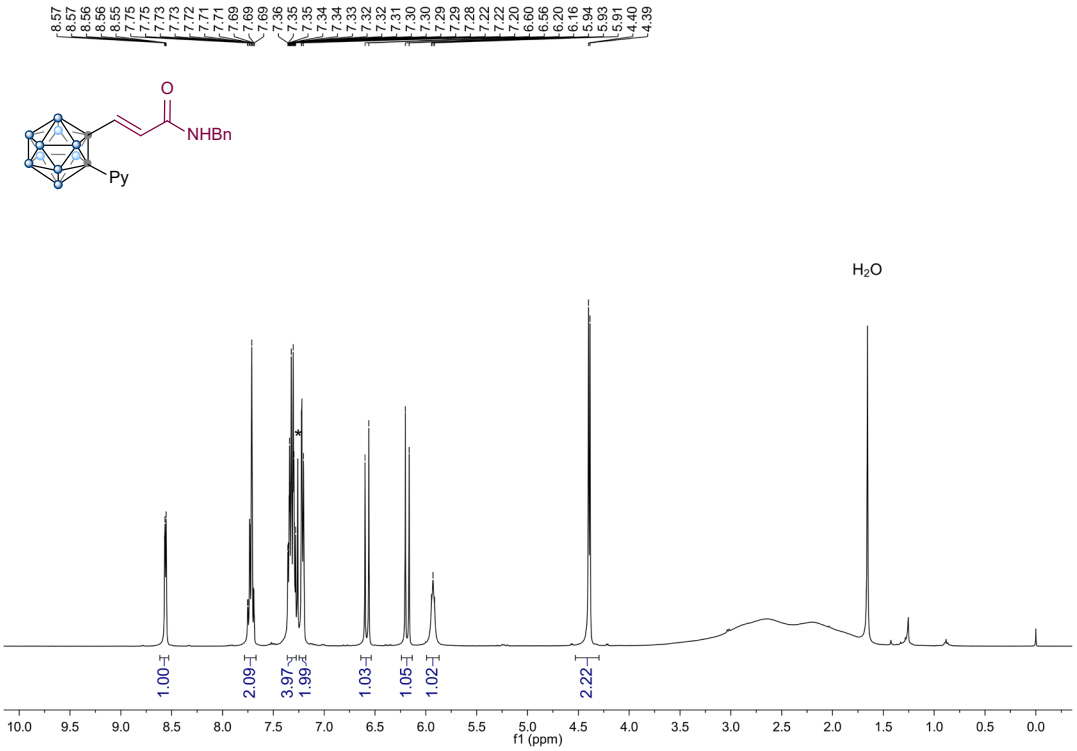
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3v**



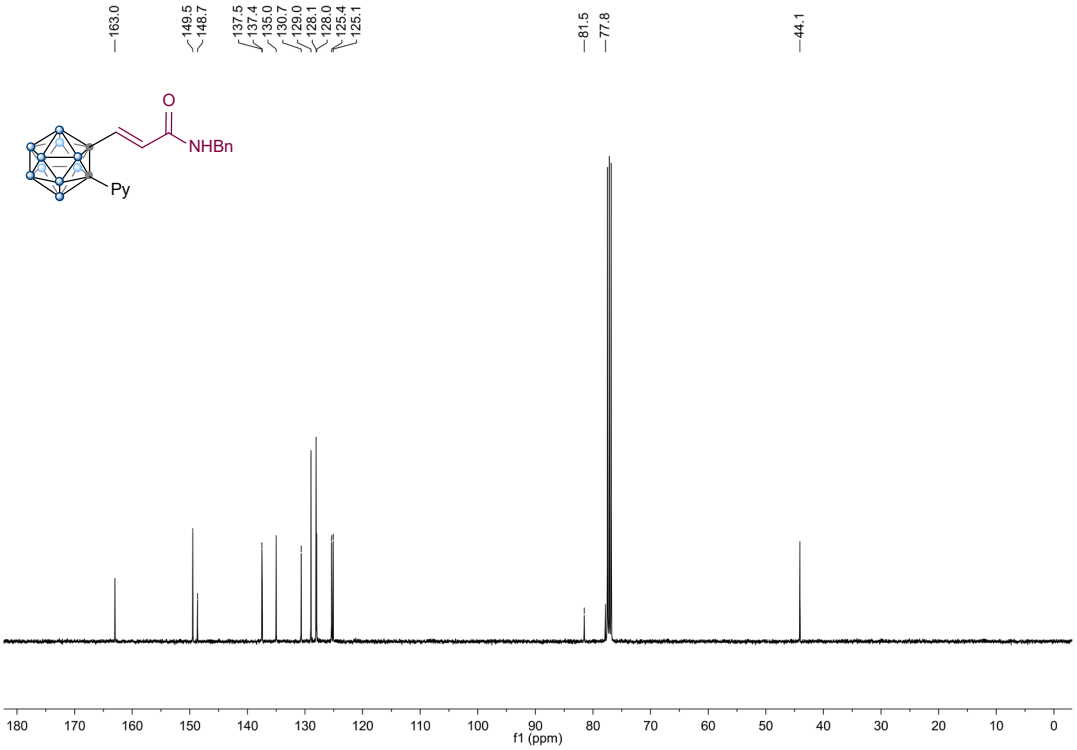
^{11}B NMR (128 MHz, Chloroform-*d*) **3v**



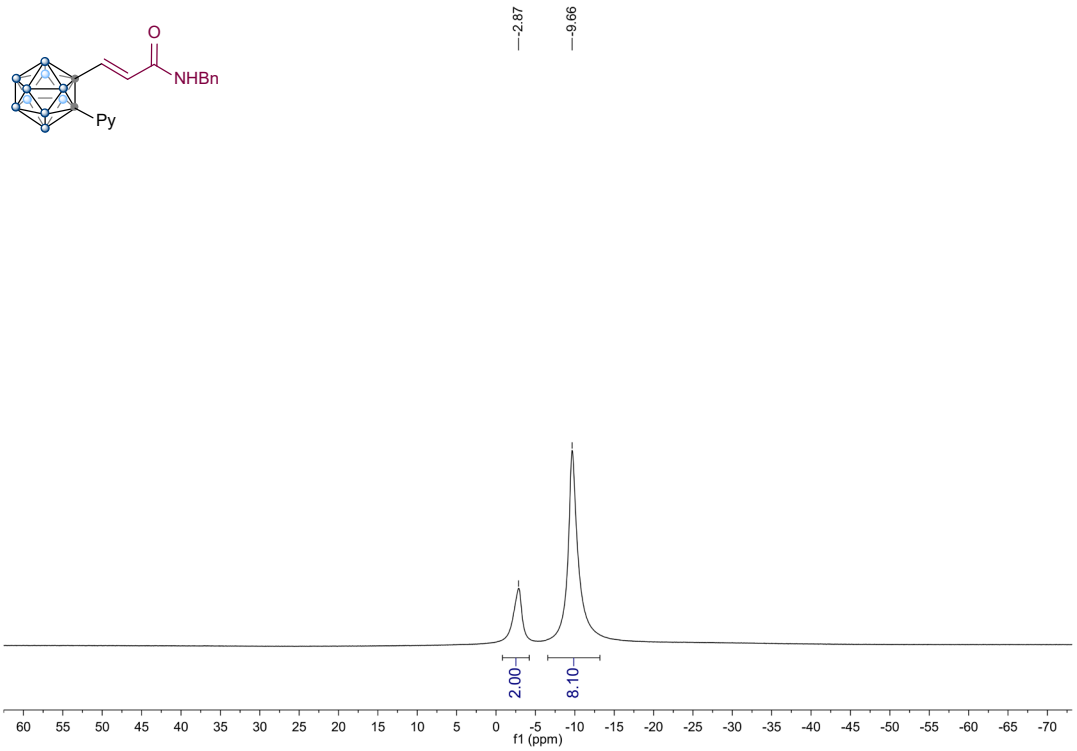
^{1}H NMR (400 MHz, Chloroform-*d*) **3w** (* from residual $CHCl_3$ in Chloroform-*d*)



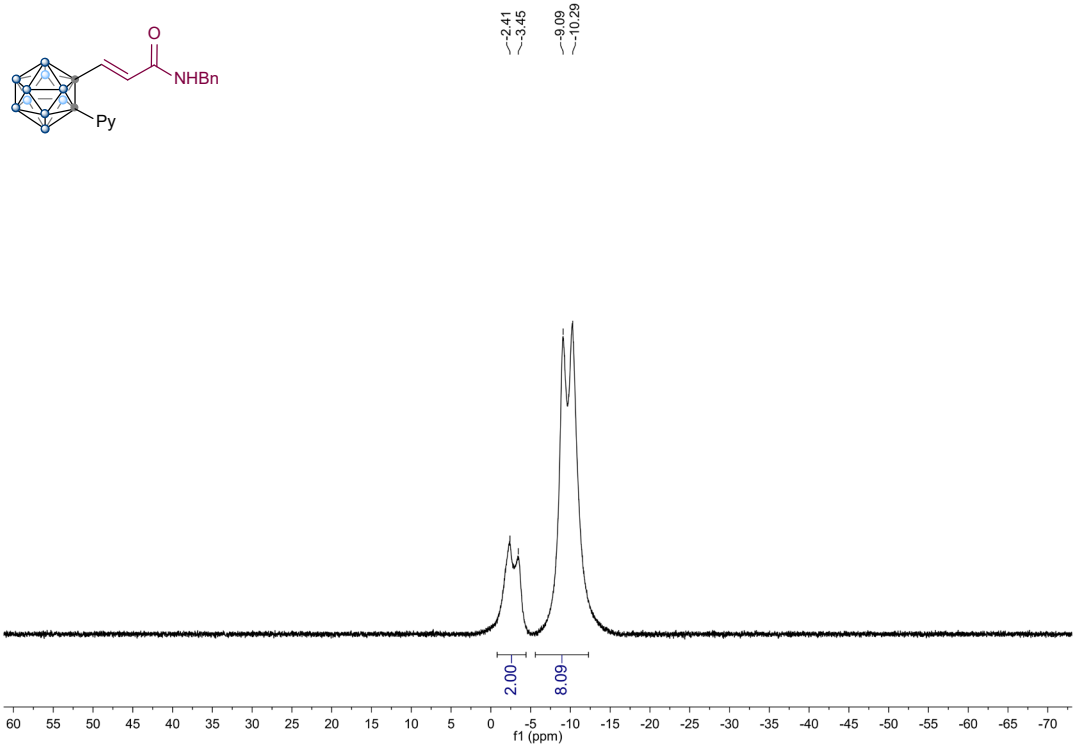
^{13}C NMR (101 MHz, Chloroform-*d*) **3w**



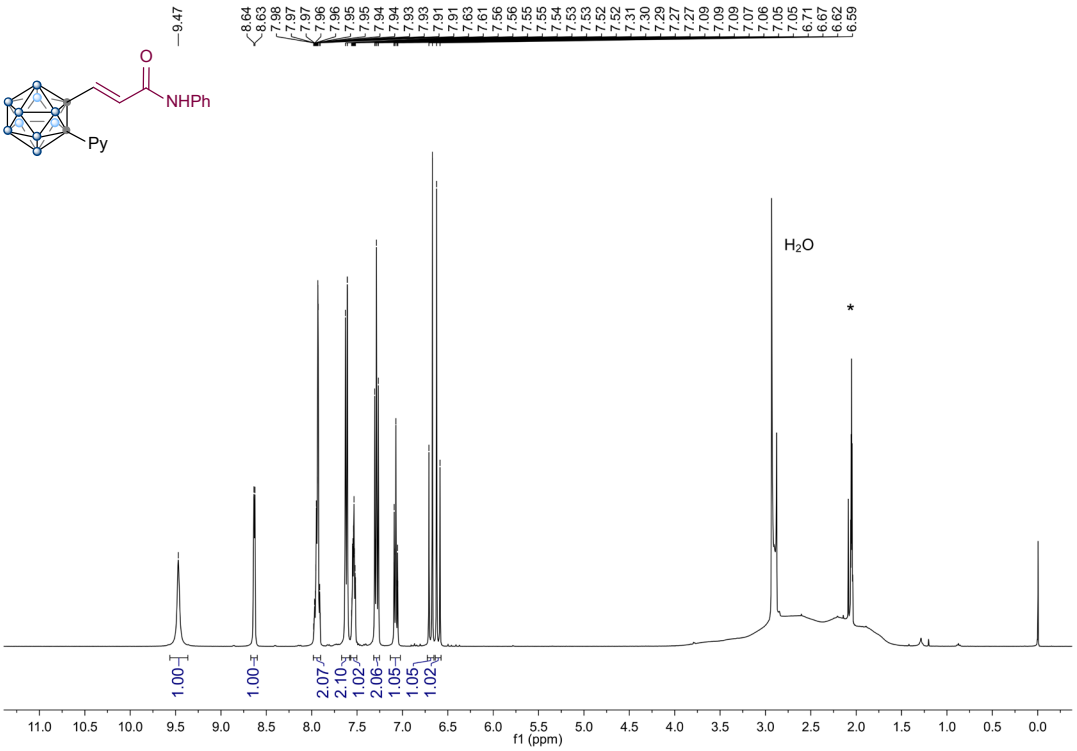
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3w**



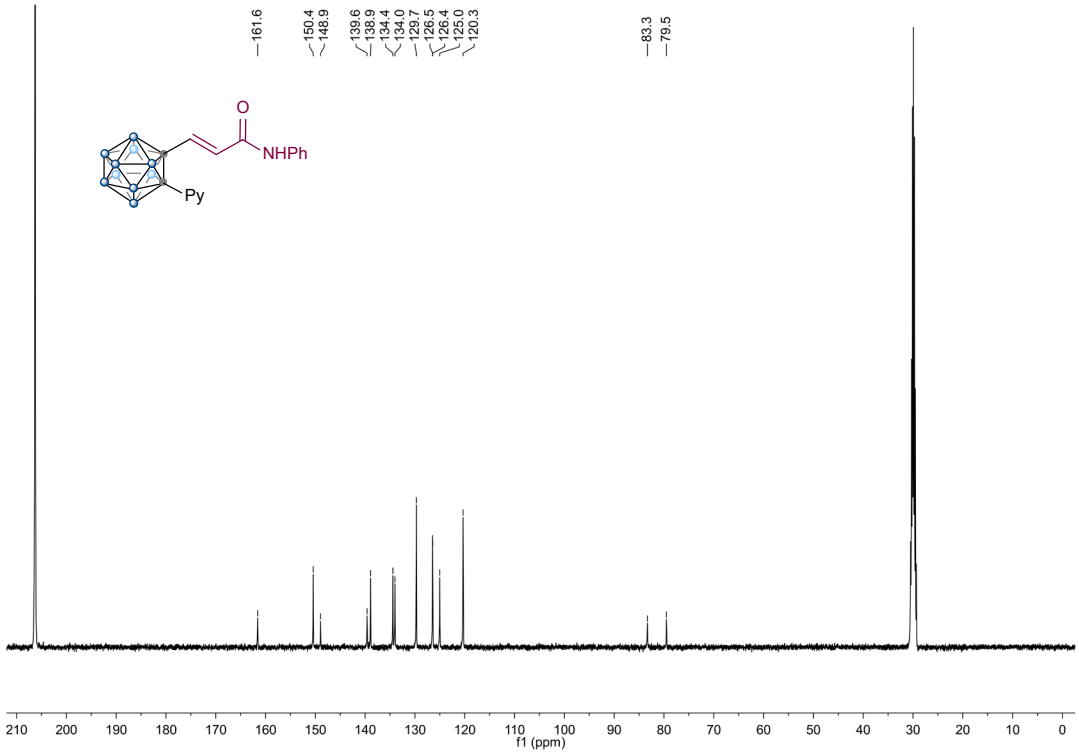
^{11}B NMR (128 MHz, Chloroform-*d*) **3w**



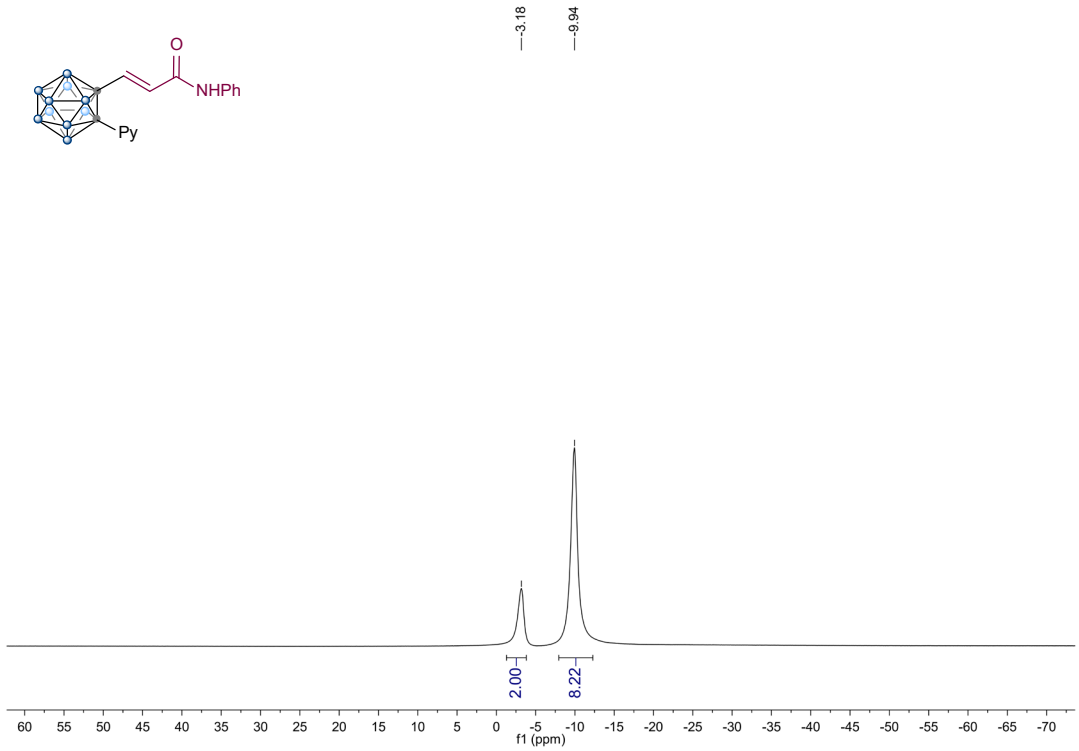
^{1}H NMR (400 MHz, Acetone-*d*$_6$) **3x** (* from residual acetone in Acetone-*d*$_6$)



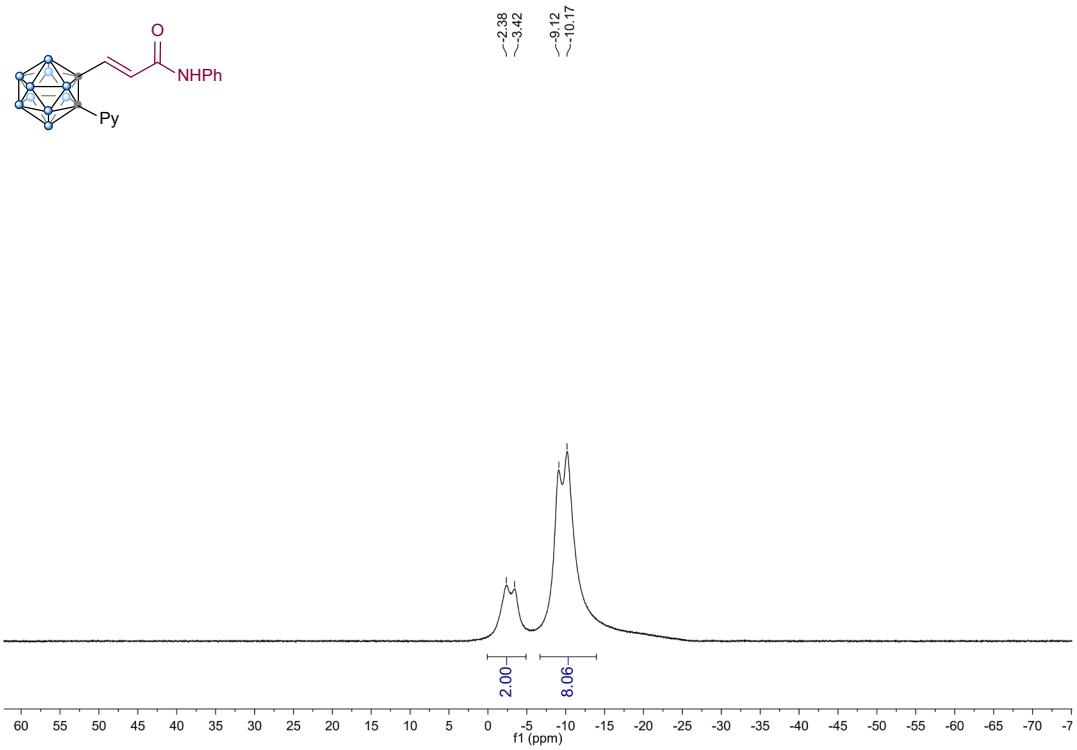
^{13}C NMR (101 MHz, Acetone-d_6) **3x**



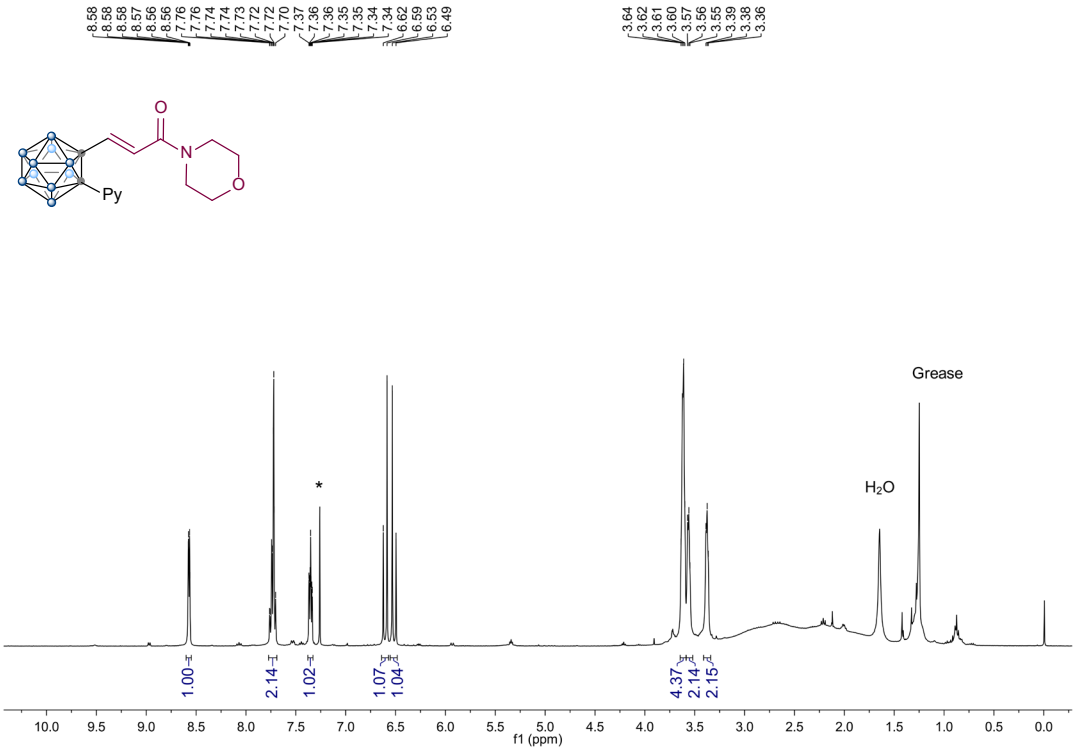
^{11}B{^{1}H} NMR (128 MHz, Chloroform-d) **3x**



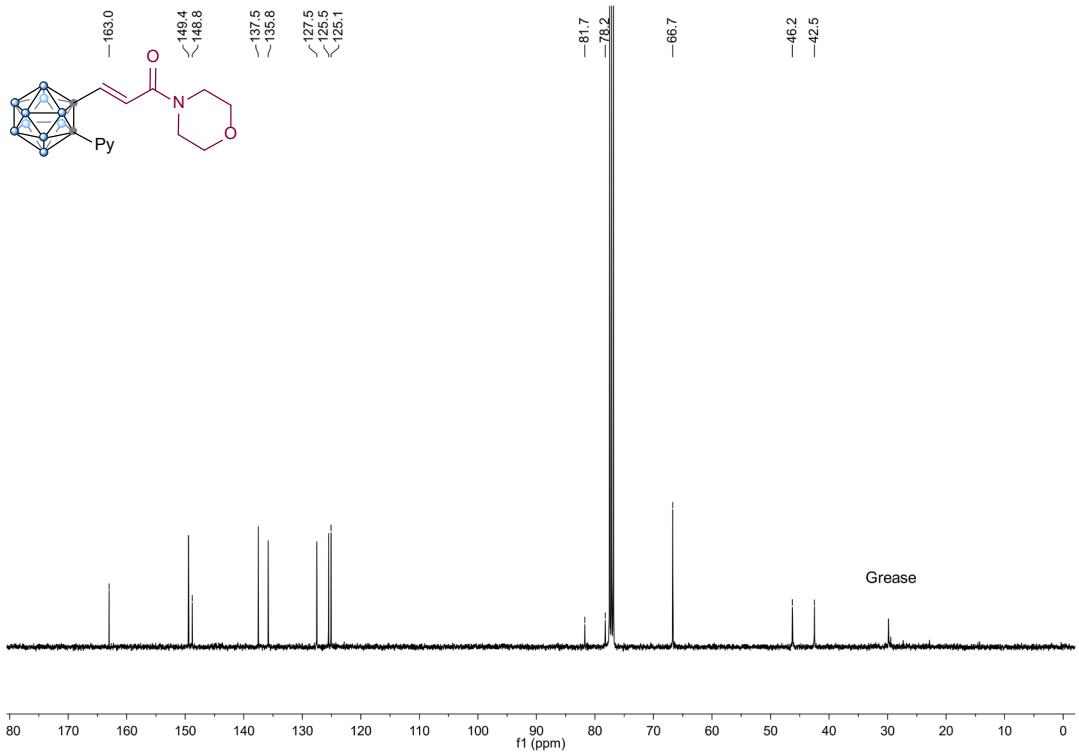
^{11}B NMR (128 MHz, Chloroform-*d*) **3x**



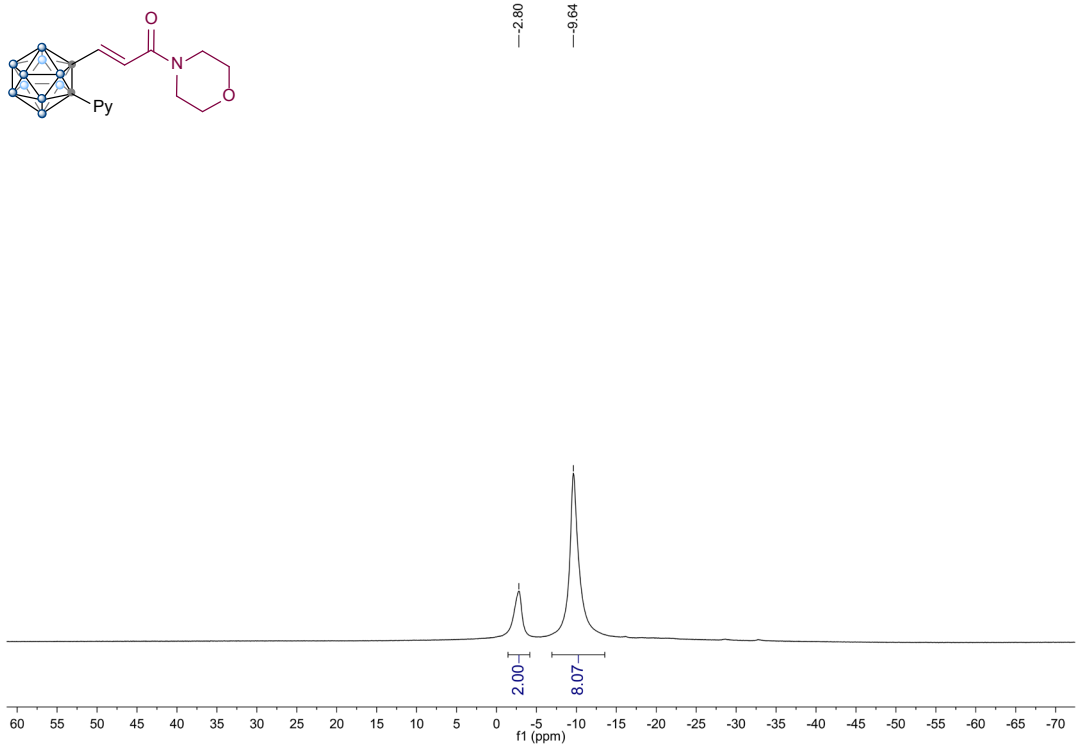
^{1}H NMR (400 MHz, Chloroform-*d*) **3y** (* from residual $CHCl_3$ in Chloroform-*d*)



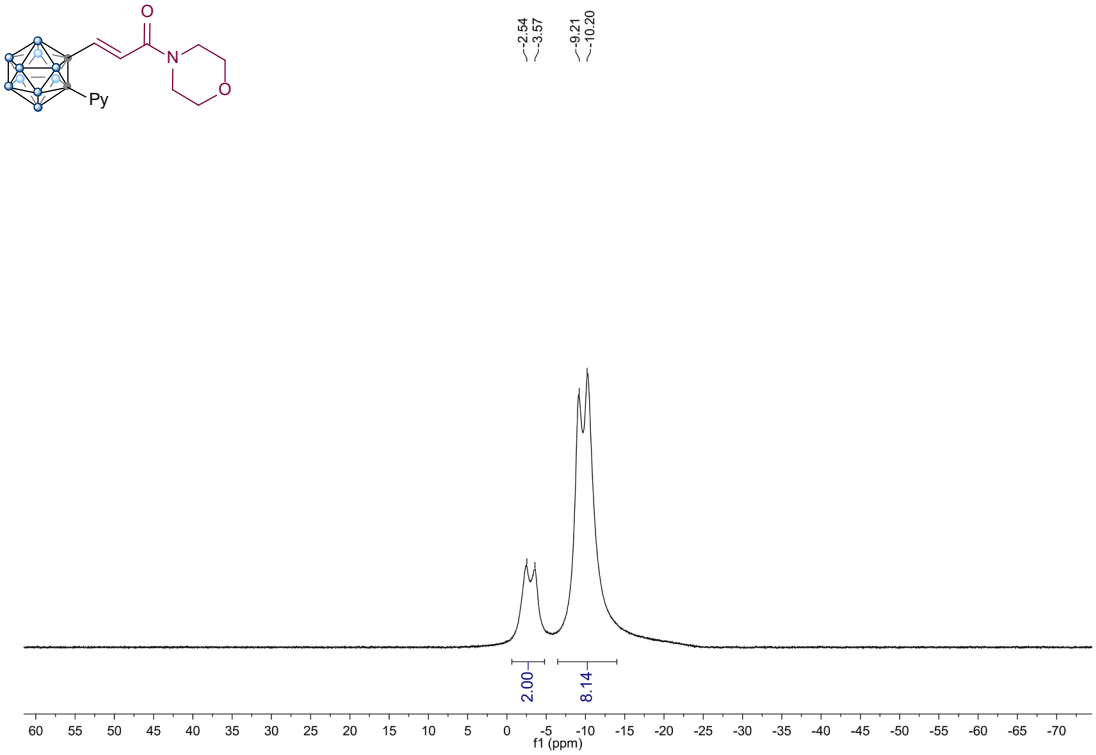
^{13}C NMR (101 MHz, Chloroform-*d*) **3y**



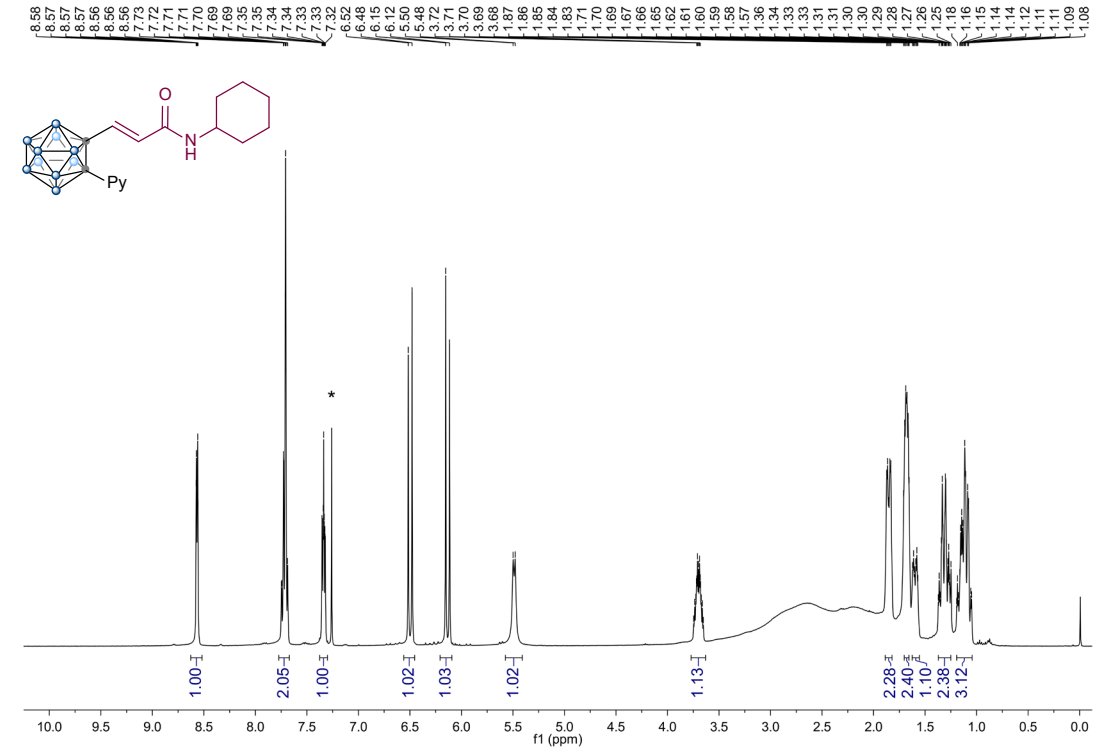
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3y**



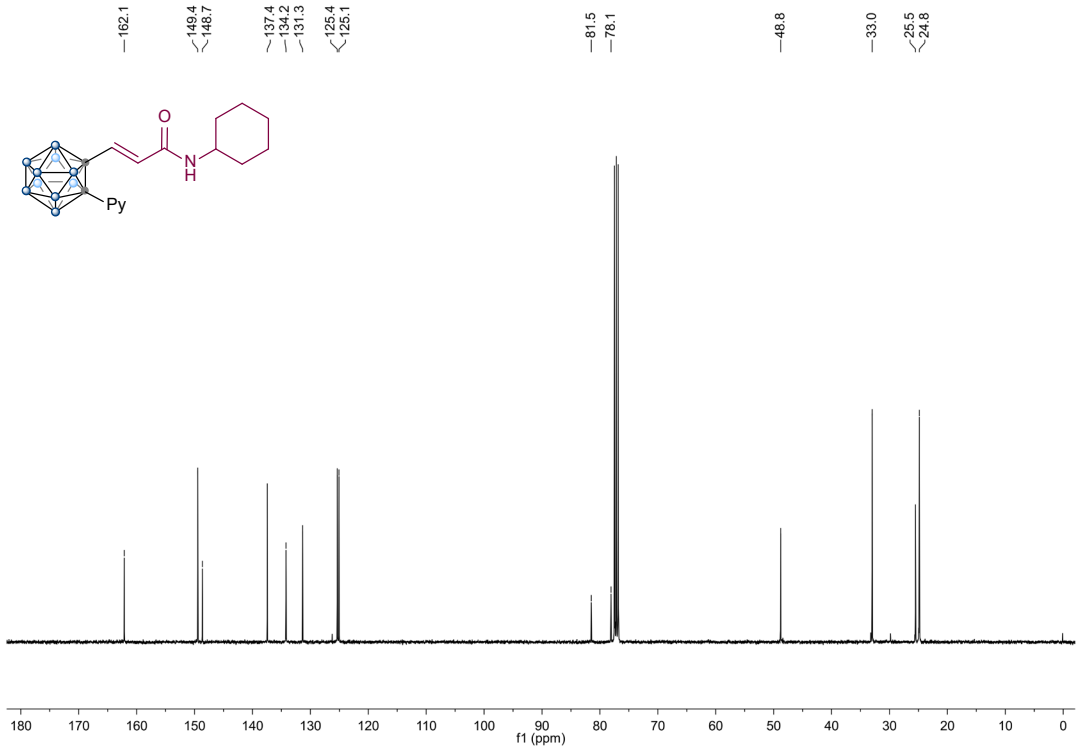
^{11}B NMR (128 MHz, Chloroform-*d*) **3y**



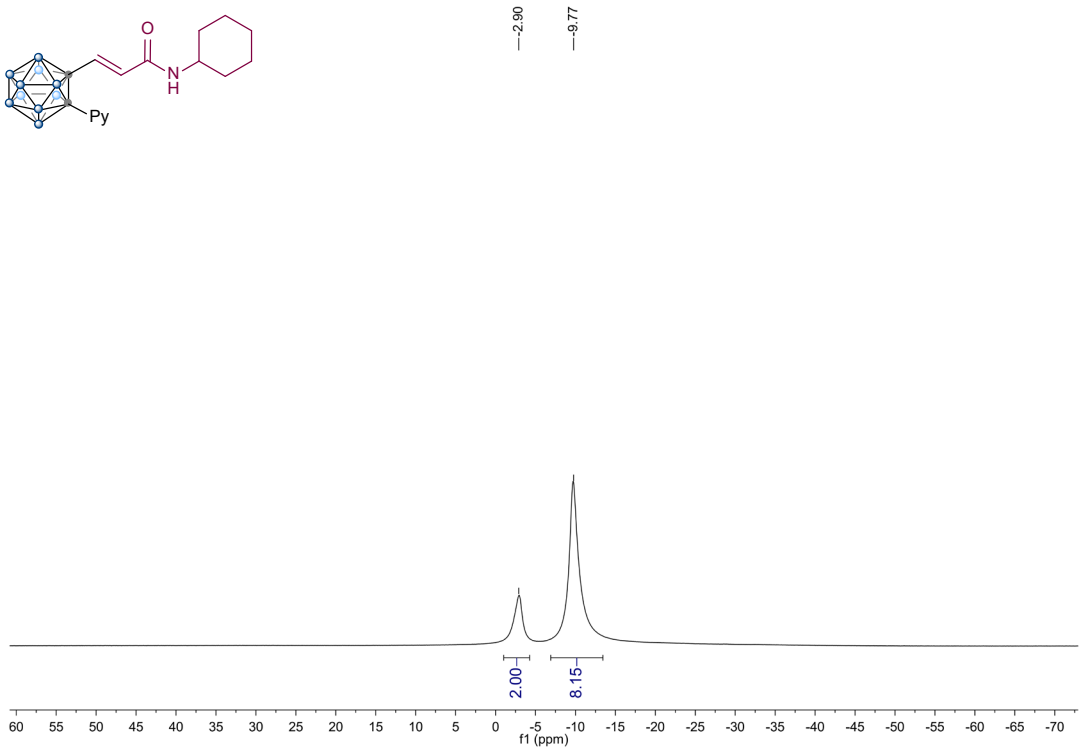
^{1}H NMR (400 MHz, Chloroform-*d*) **3z** (* from residual $CHCl_3$ in Chloroform-*d*)



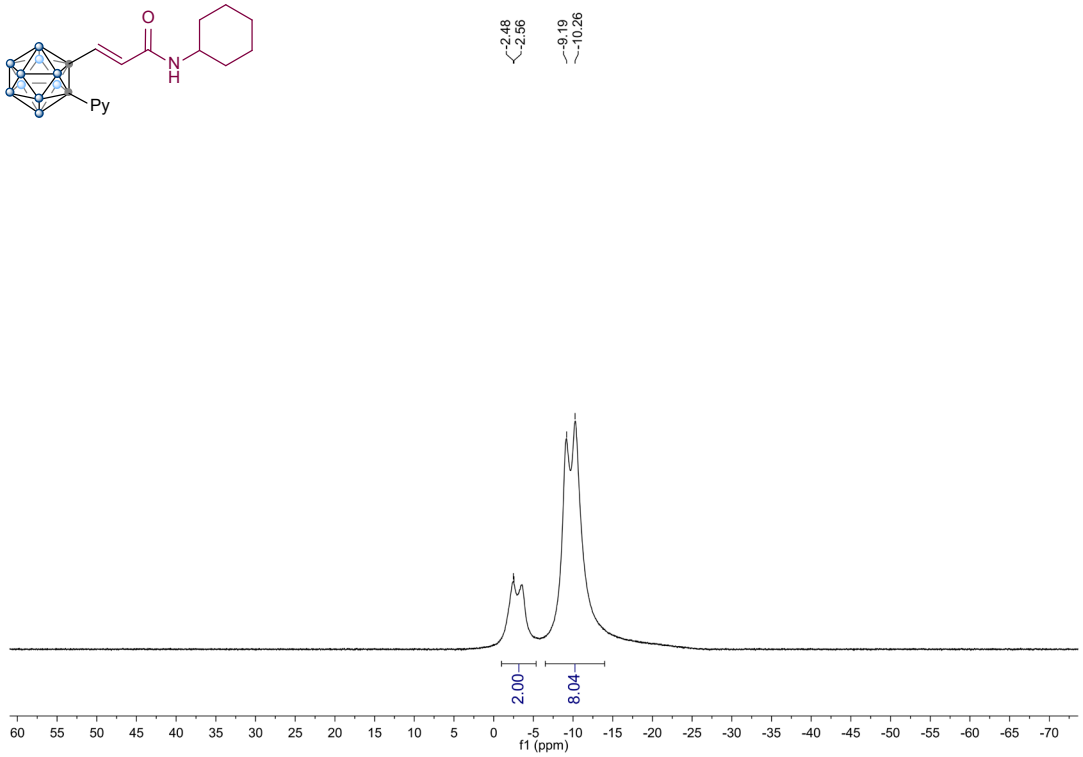
^{13}C NMR (101 MHz, Chloroform-*d*) **3z**



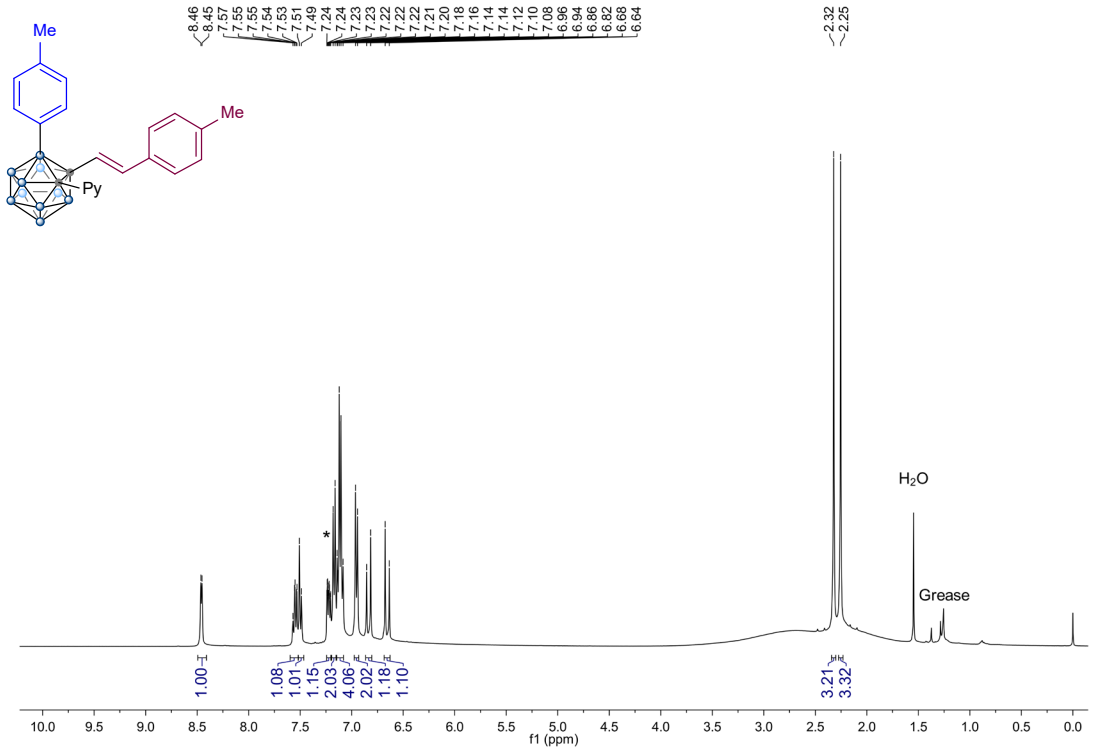
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3z**



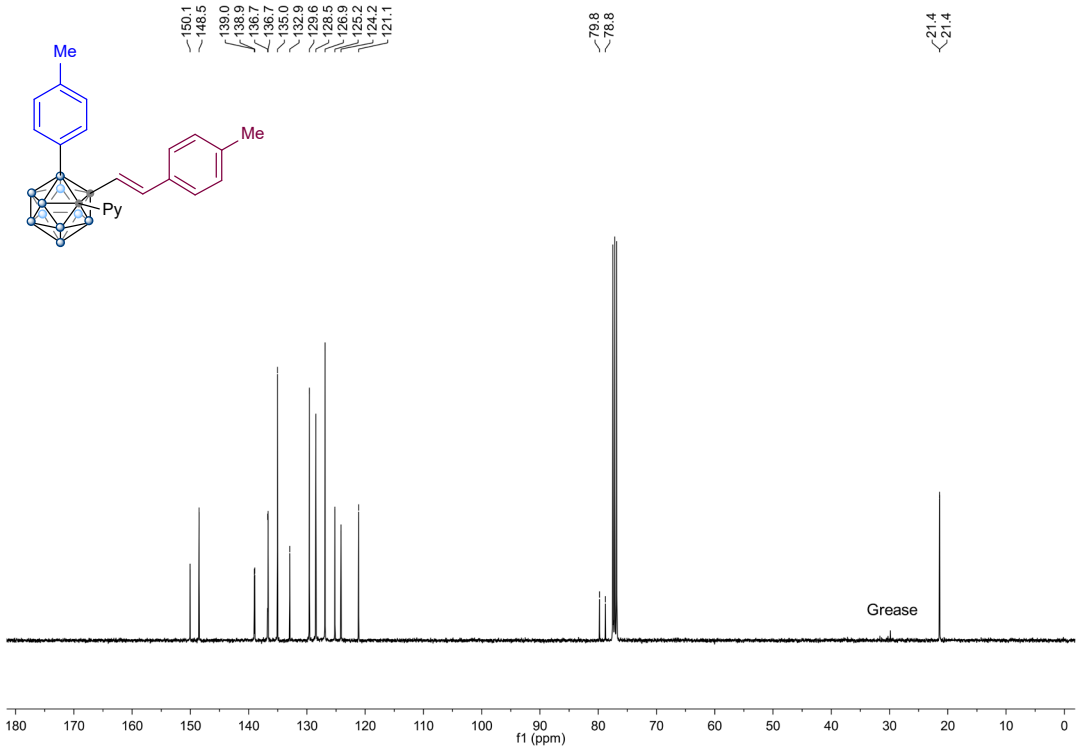
^{11}B NMR (128 MHz, Chloroform-*d*) **3z**



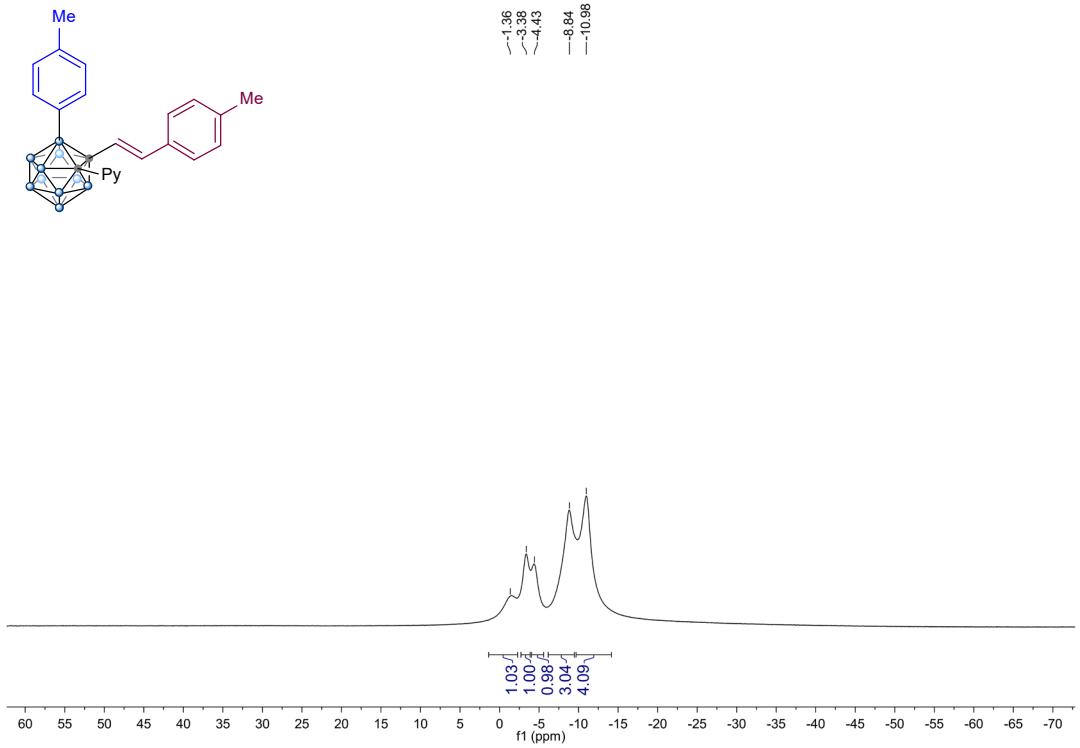
^{1}H NMR (400 MHz, Chloroform-*d*) **3aa** (* from residual $CHCl_3$ in Chloroform-*d*)



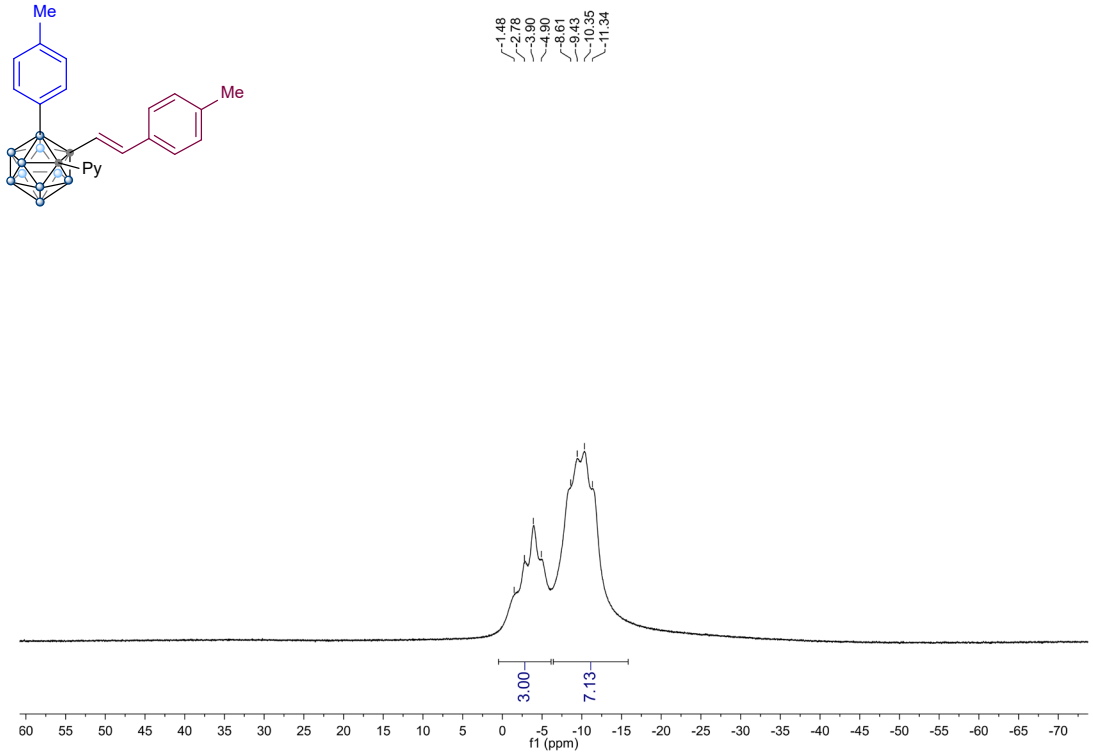
^{13}C NMR (101 MHz, Chloroform-*d*) **3aa**



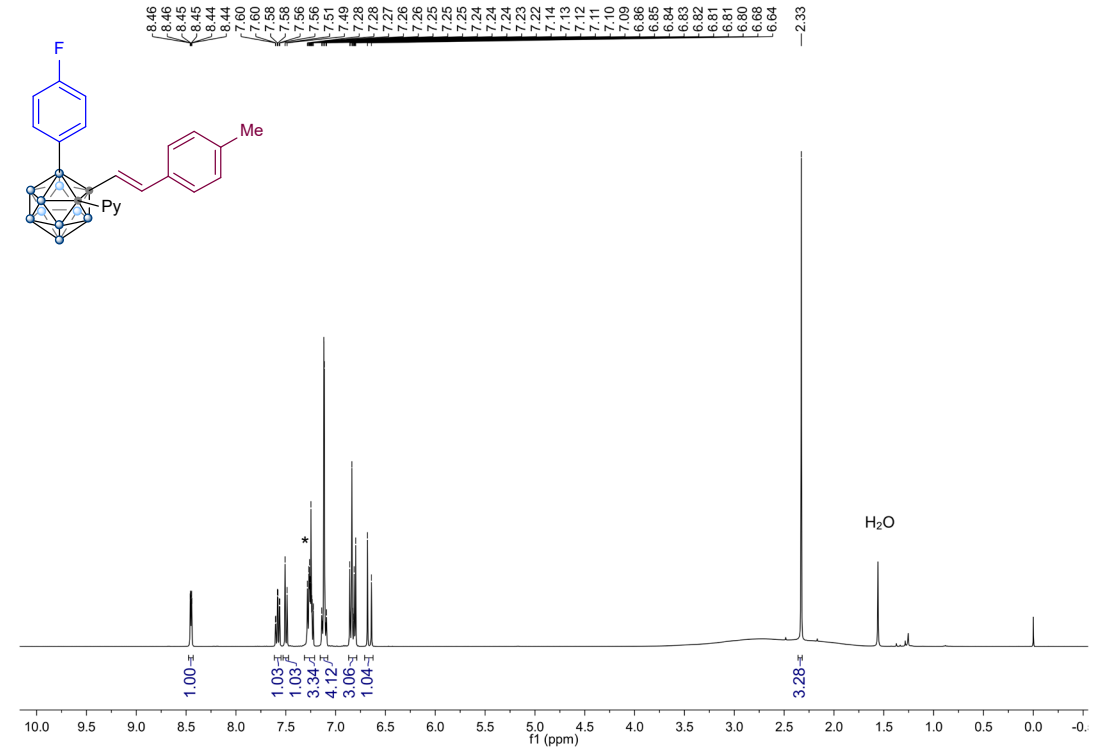
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3aa**



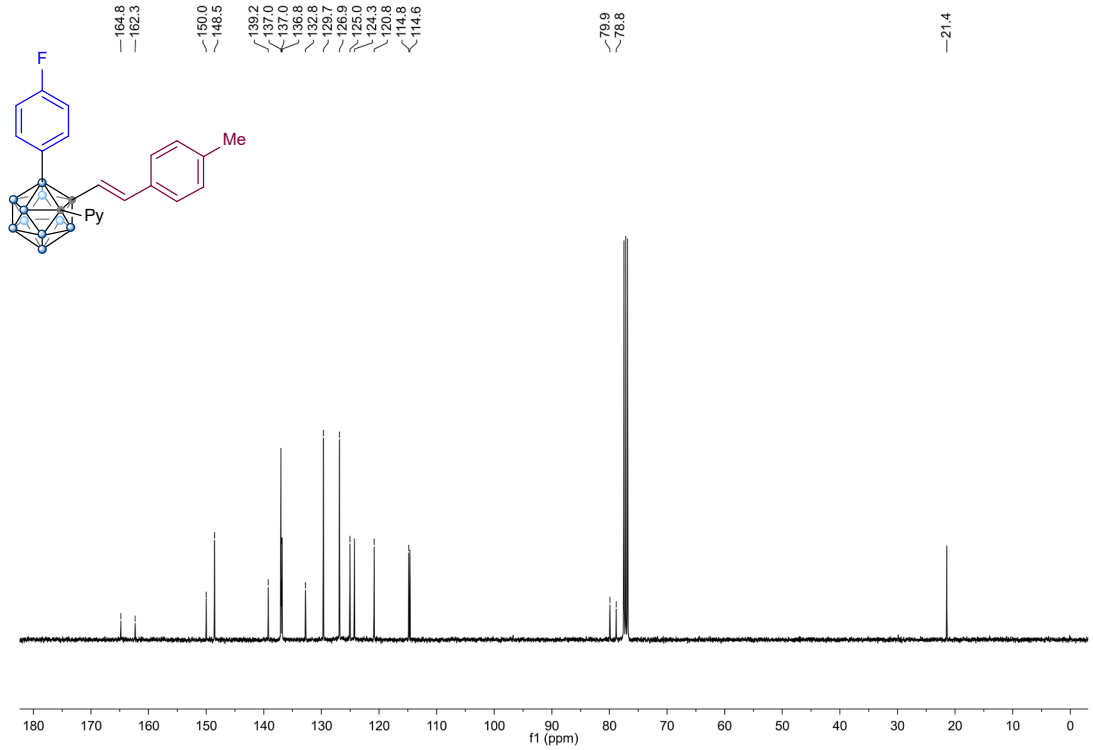
^{11}B NMR (128 MHz, Chloroform-*d*) **3aa**



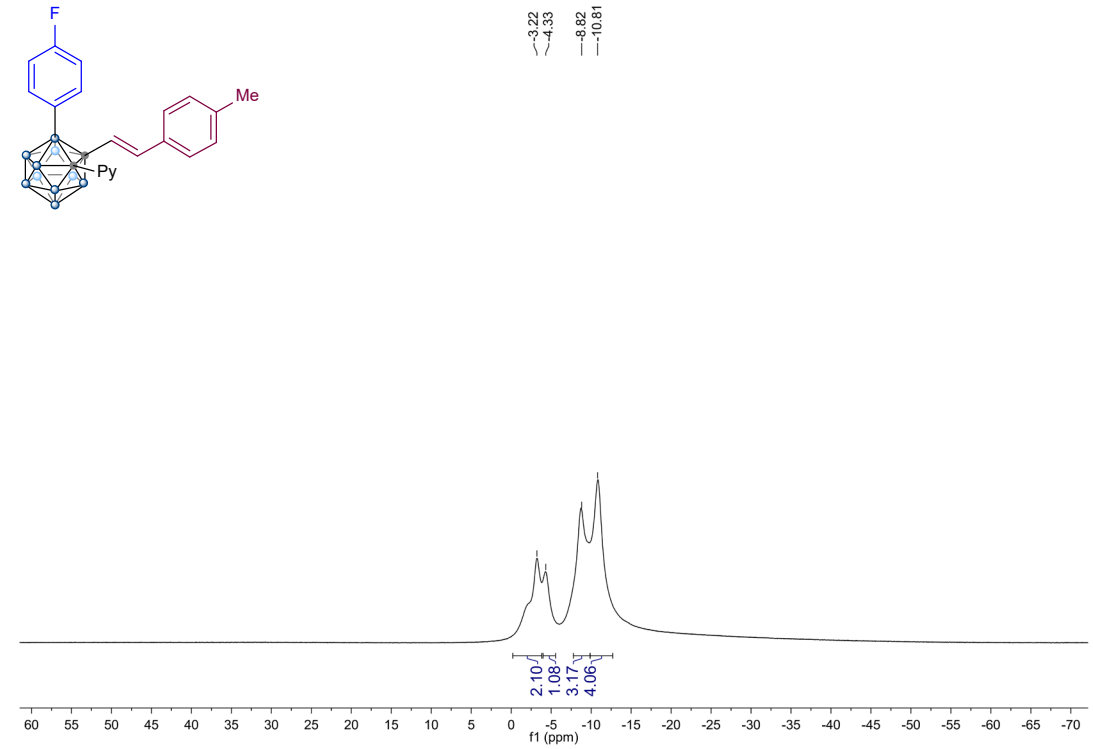
^{1}H NMR (400 MHz, Chloroform-*d*) **3ab** (* from residual $CHCl_3$ in Chloroform-*d*)



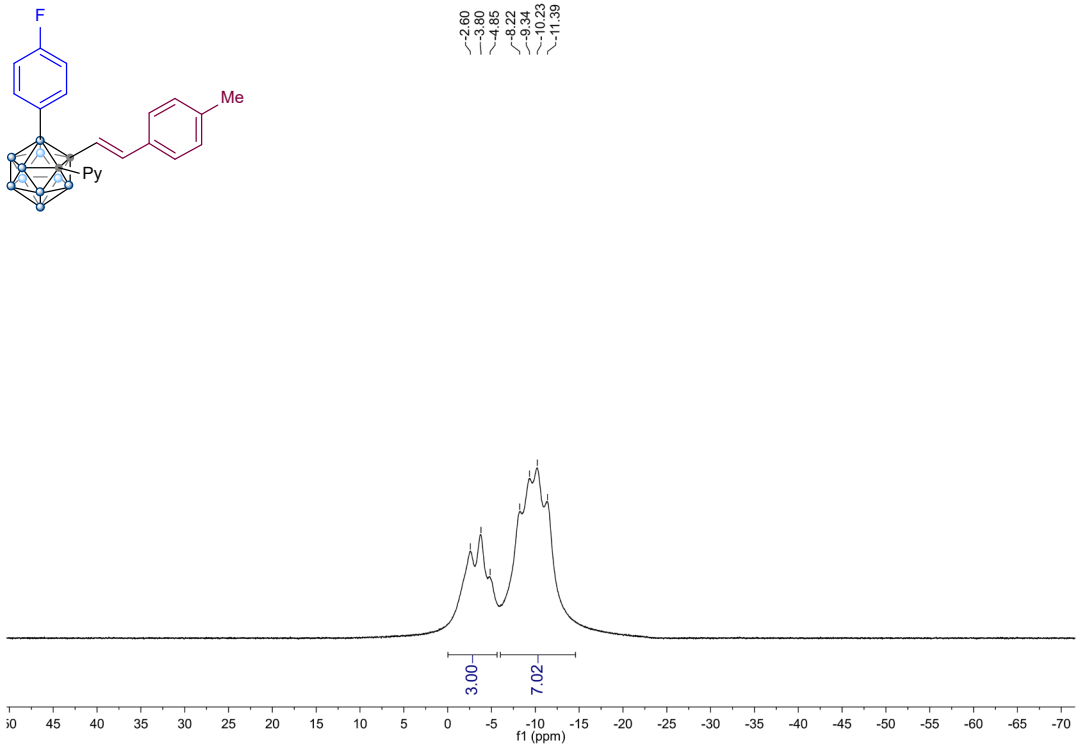
^{13}C NMR (101 MHz, Chloroform-*d*) **3ab**



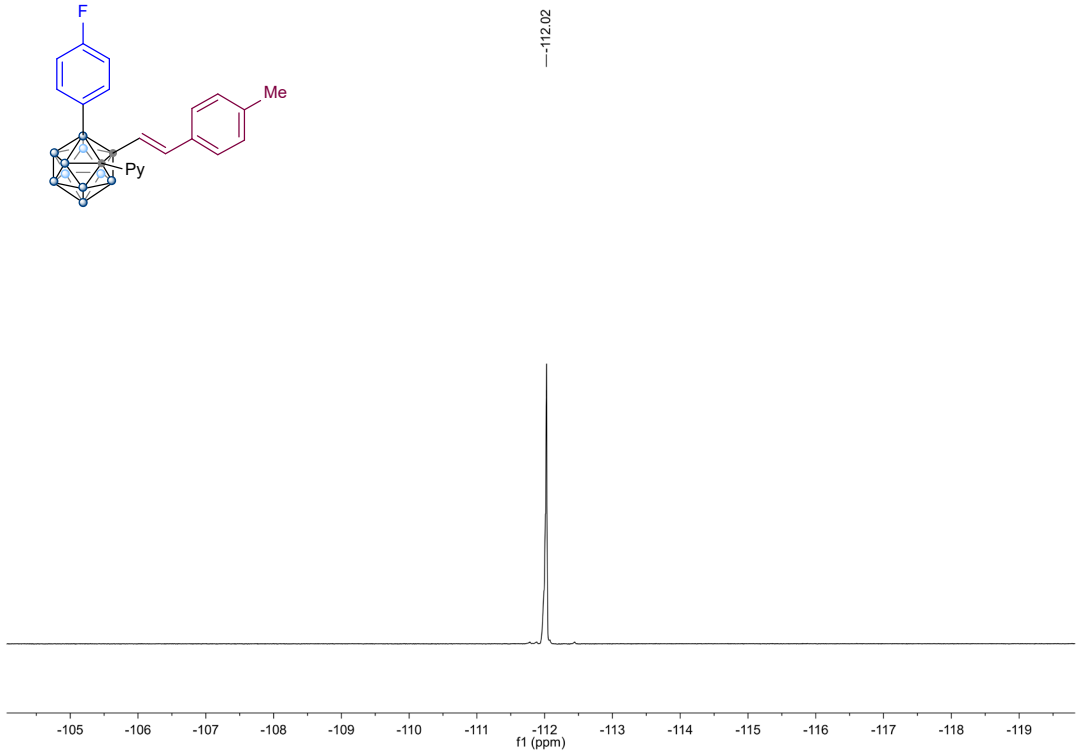
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3ab**



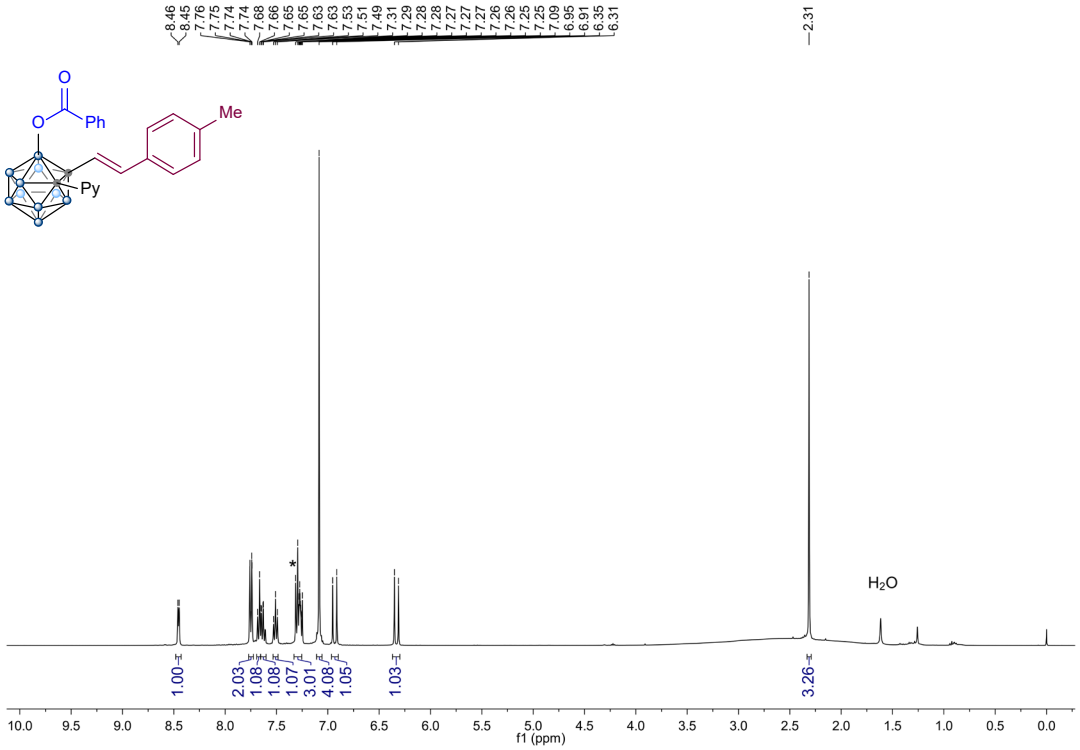
^{11}B NMR (128 MHz, Chloroform-*d*) **3ab**



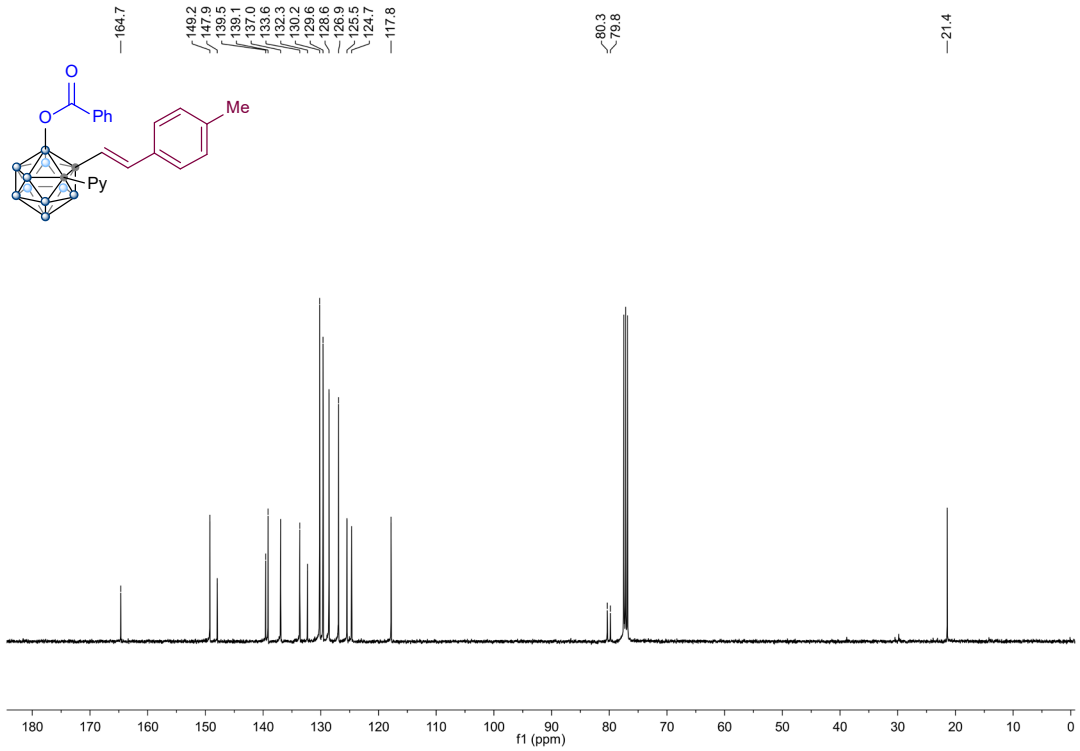
^{19}F NMR (376 MHz, Chloroform-*d*) **3ab**



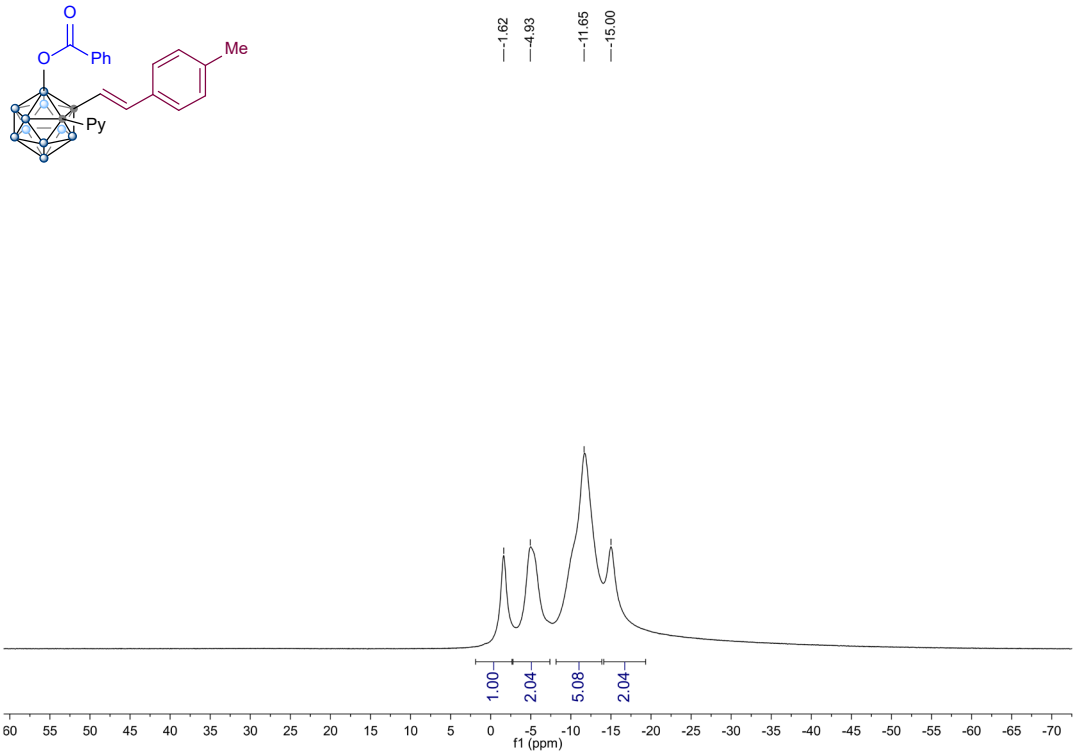
^{1}H NMR (400 MHz, Chloroform-*d*) **3ac** (* from residual $CHCl_3$ in Chloroform-*d*)



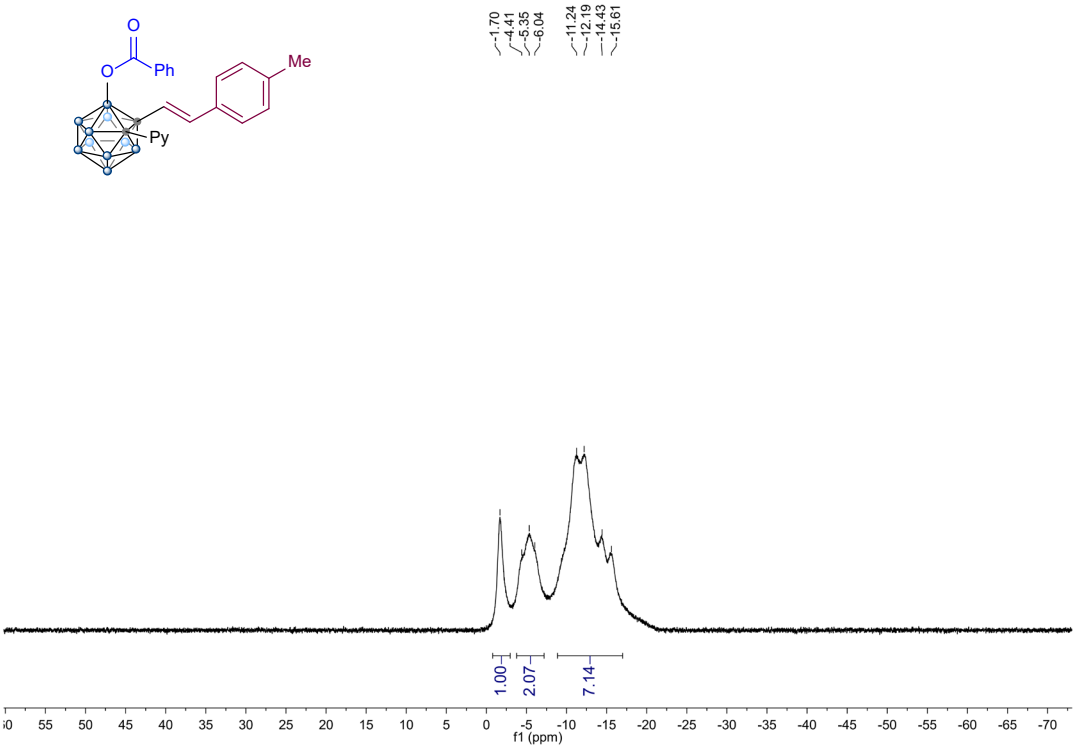
^{13}C NMR (101 MHz, Chloroform-*d*) **3ac**



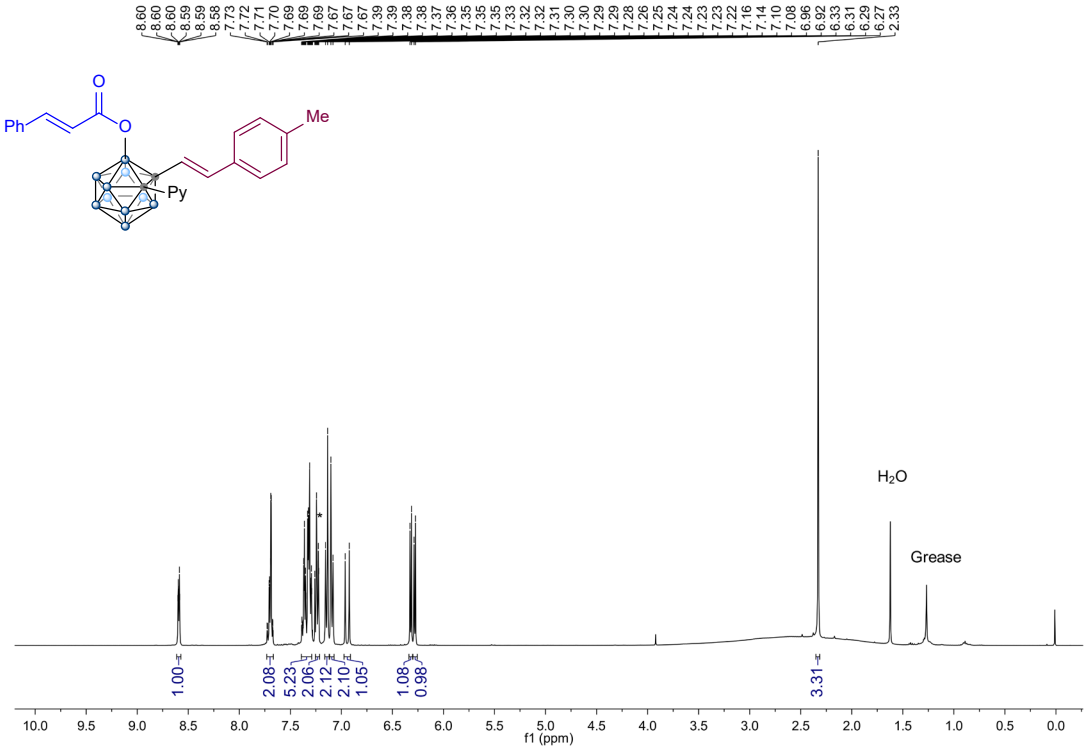
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **3ac**



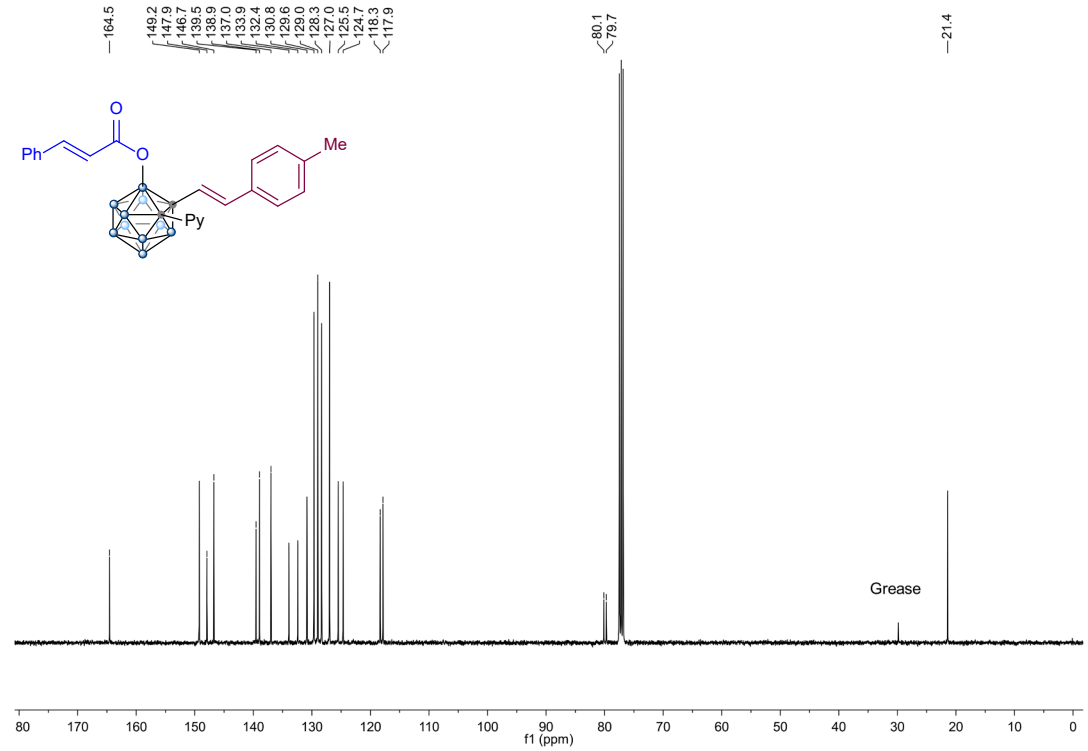
^{11}B NMR (128 MHz, Chloroform-*d*) **3ac**



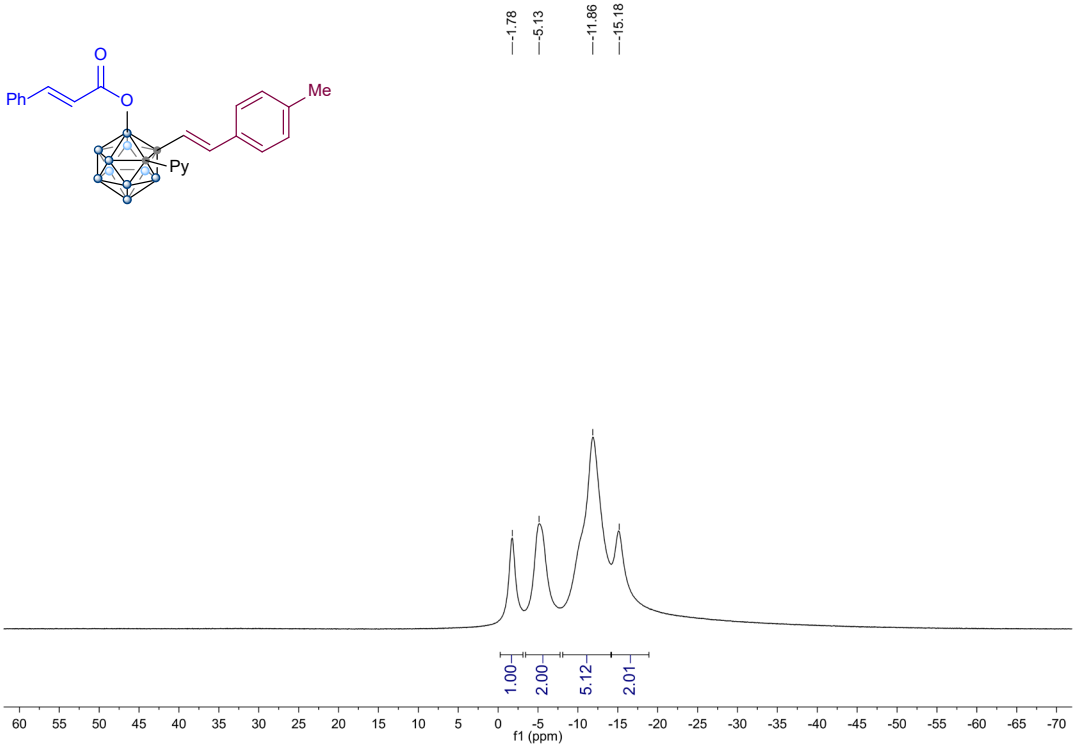
^{1}H NMR (400 MHz, Chloroform-*d*) **3ad** (* from residual $CHCl_3$ in Chloroform-*d*)



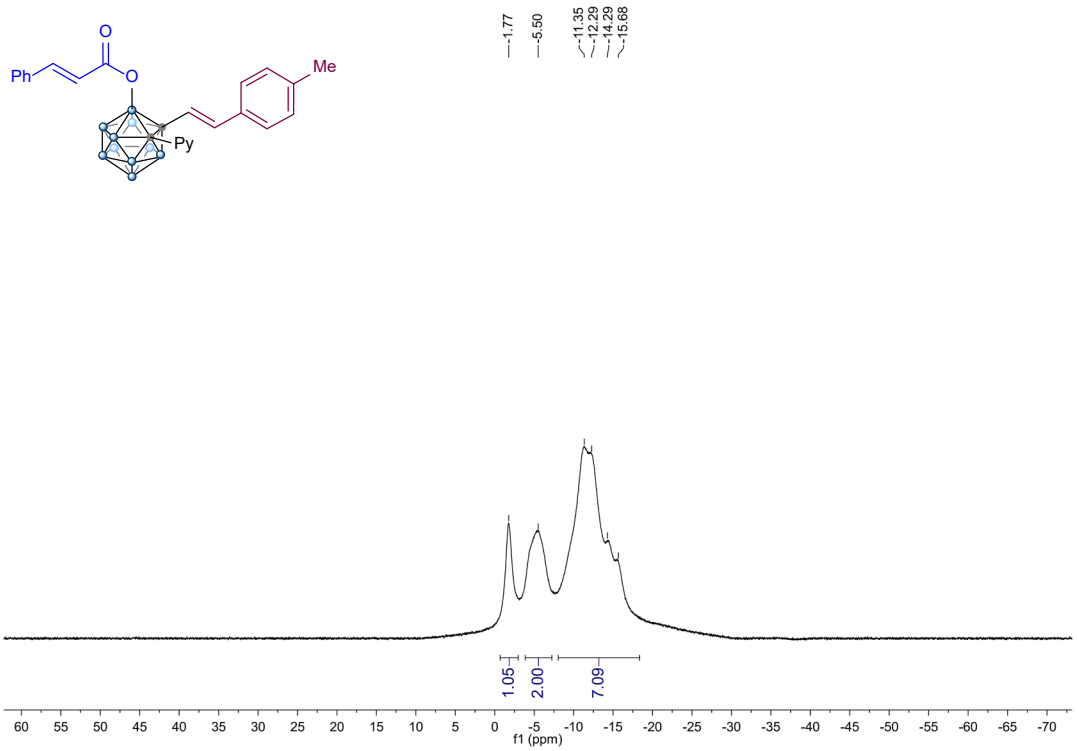
^{13}C NMR (101 MHz, Chloroform-*d*) **3ad**



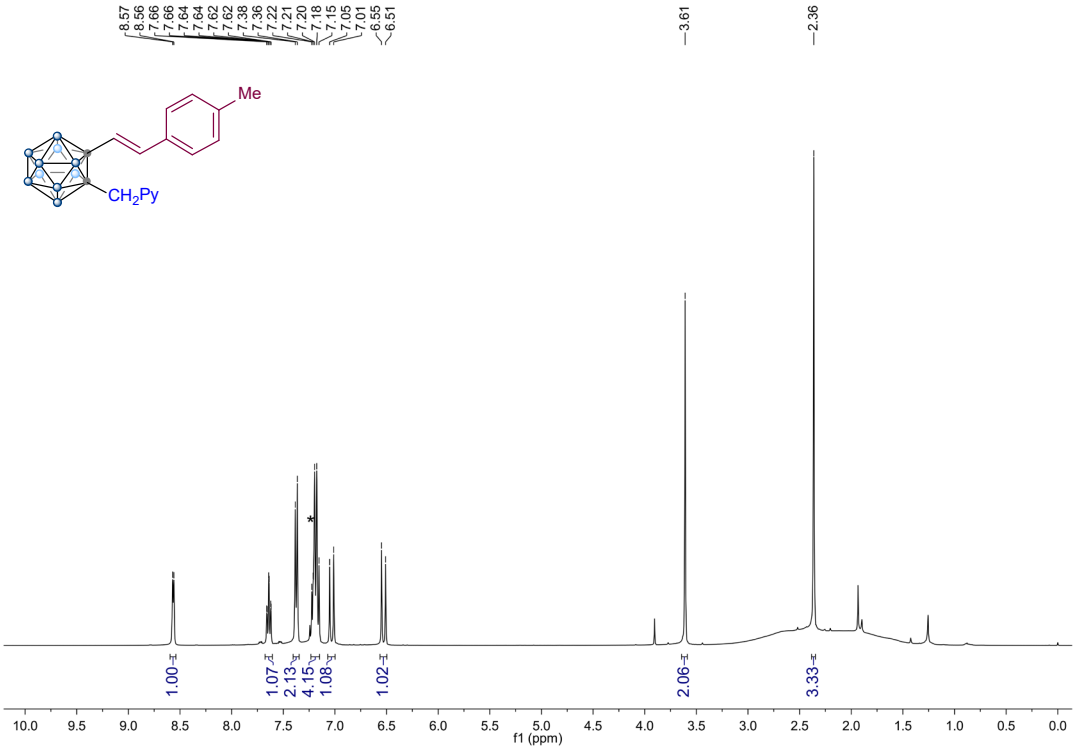
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **3ad**



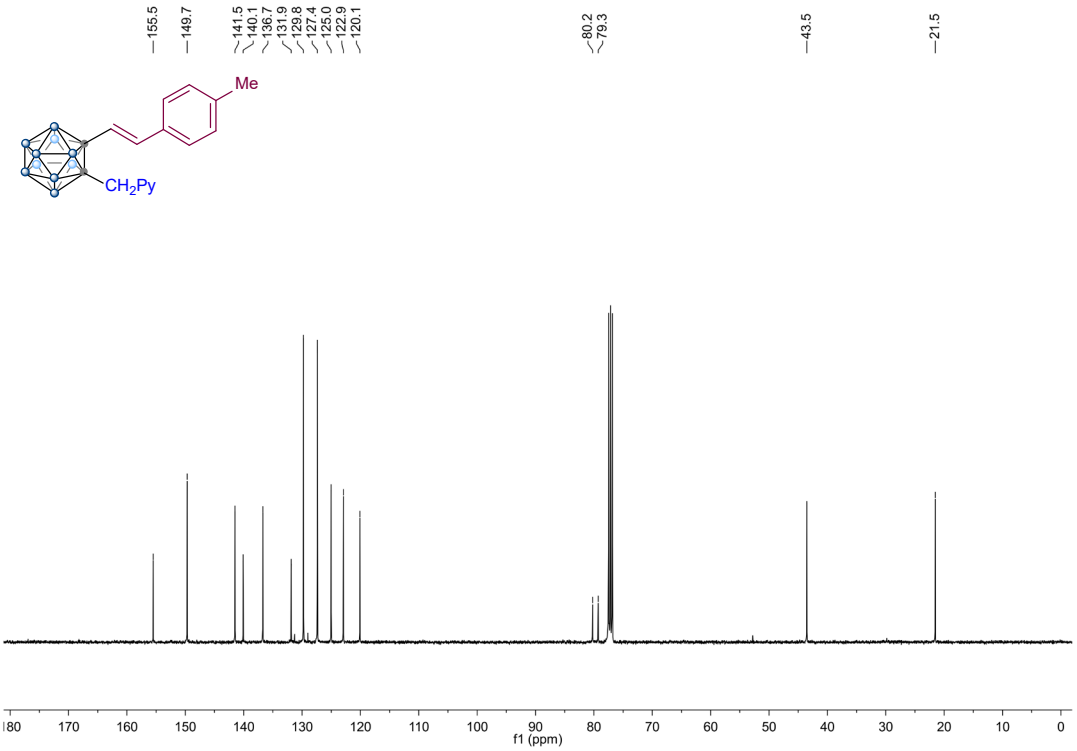
^{11}B NMR (128 MHz, Chloroform-*d*) **3ad**



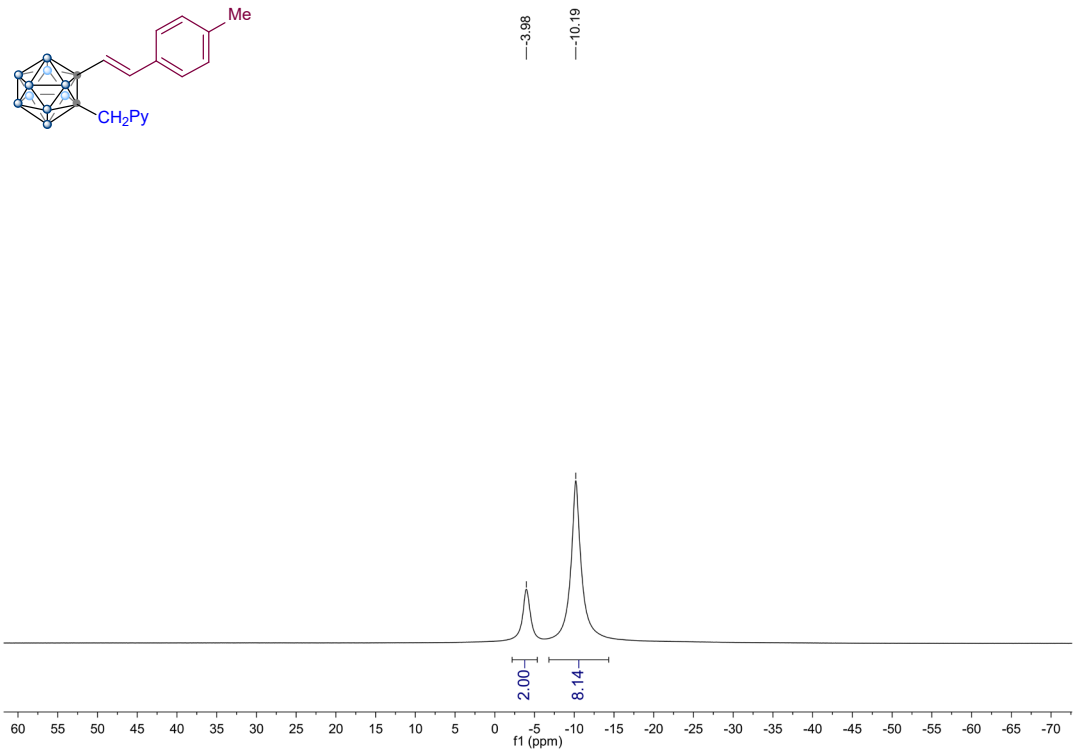
^{1}H NMR (400 MHz, Chloroform-*d*) **3ae** (* from residual $CHCl_3$ in Chloroform-*d*)



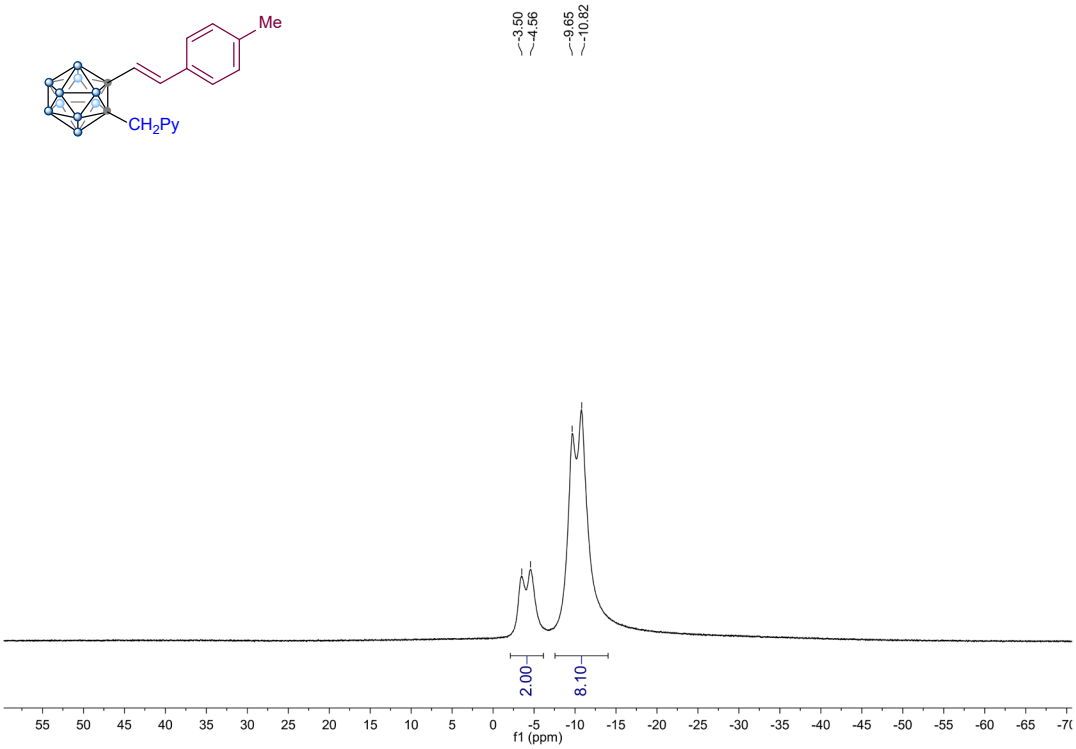
^{13}C NMR (101 MHz, Chloroform-*d*) **3ae**



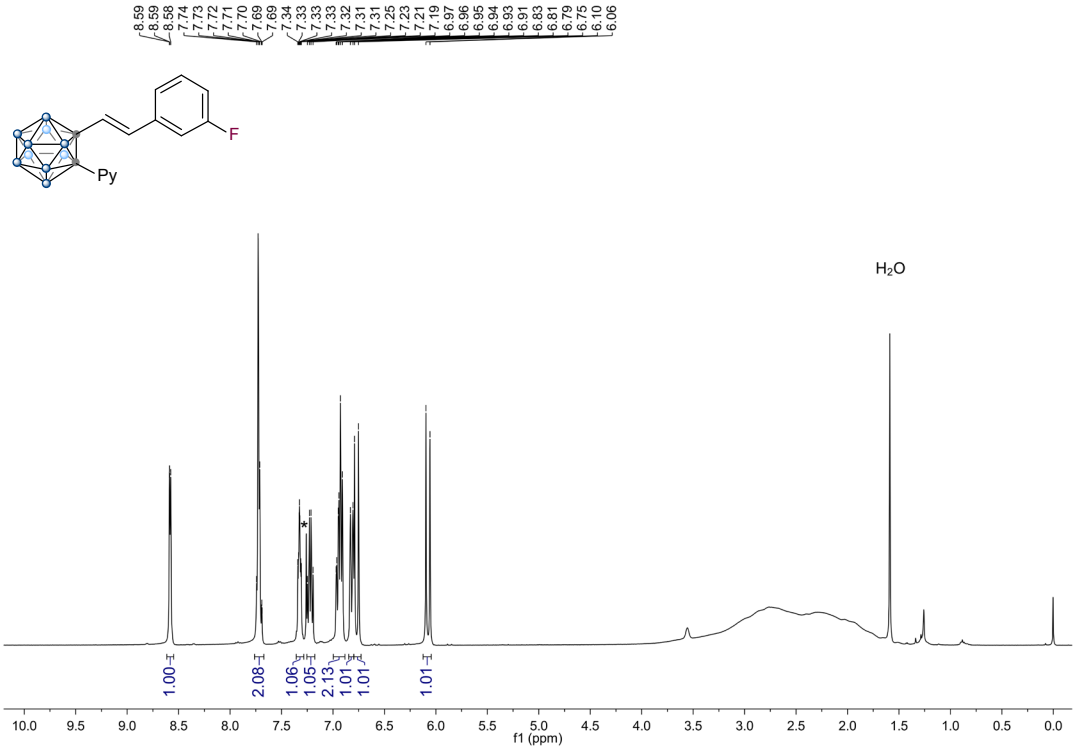
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **3ae**



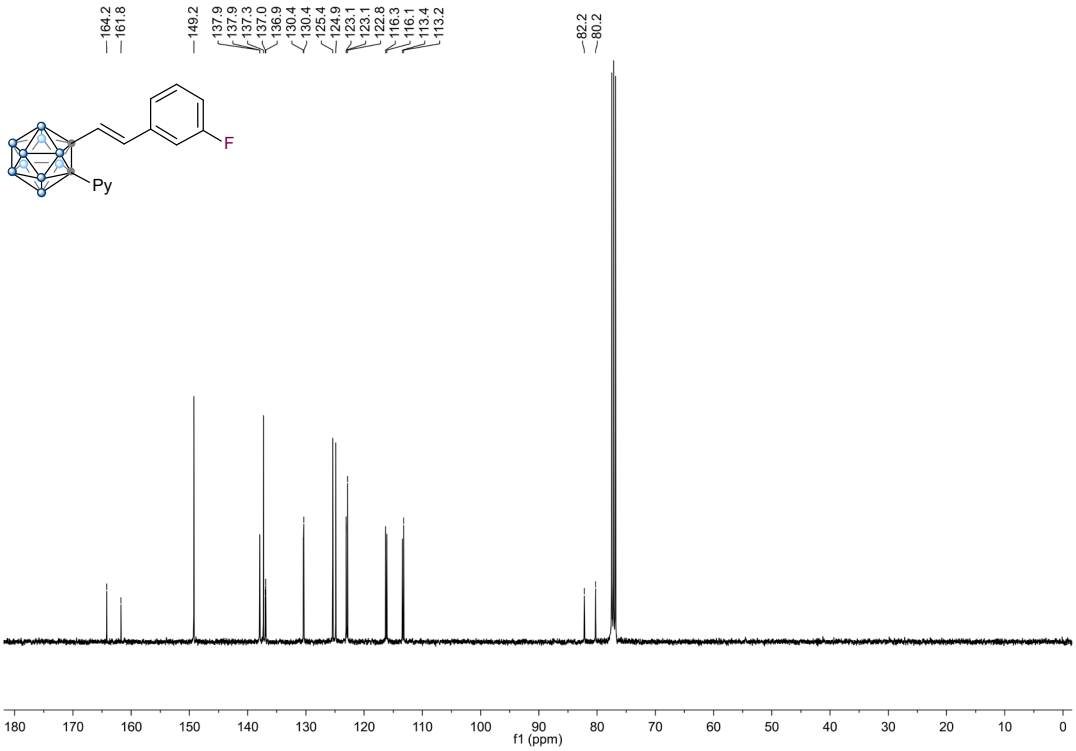
^{11}B NMR (128 MHz, Chloroform-*d*) **3ae**



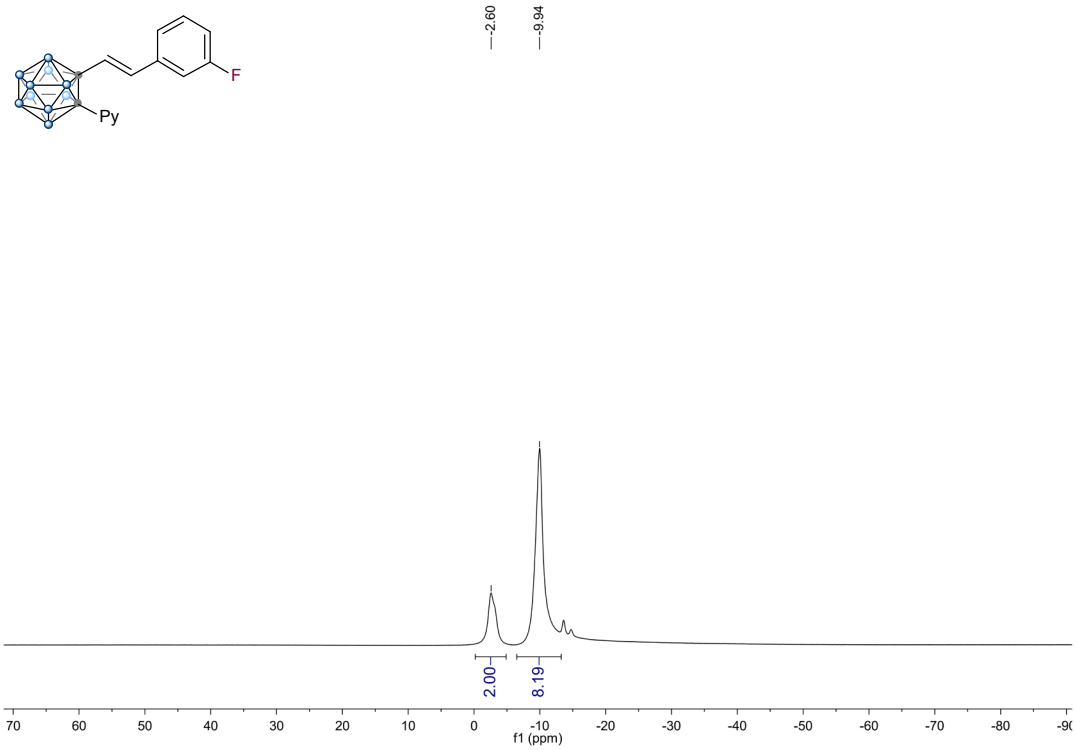
^{1}H NMR (400 MHz, Chloroform-*d*) **3af** (* from residual $CHCl_3$ in Chloroform-*d*)



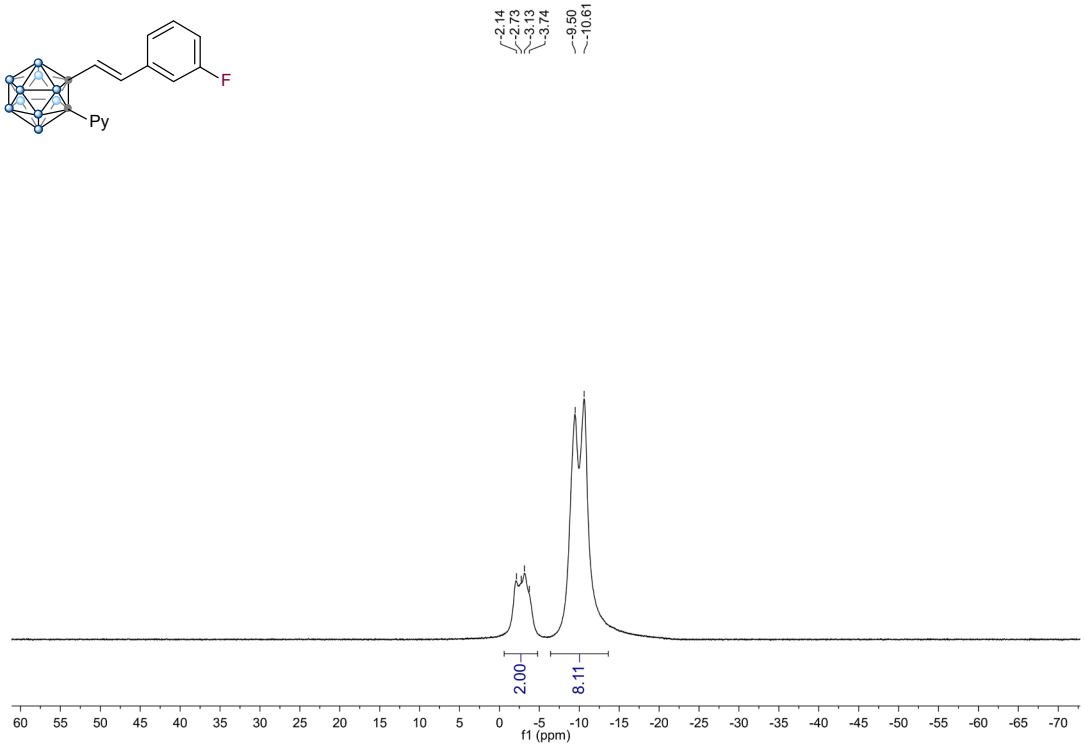
^{13}C NMR (101 MHz, Chloroform-*d*) **3af**



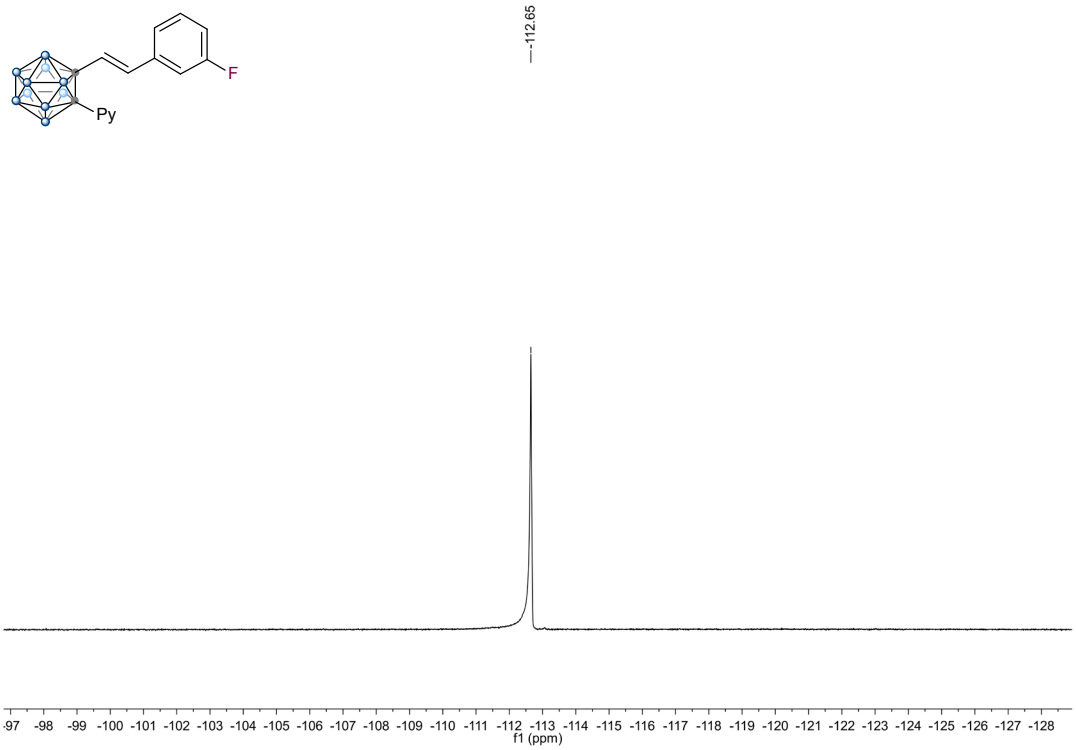
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **3af**



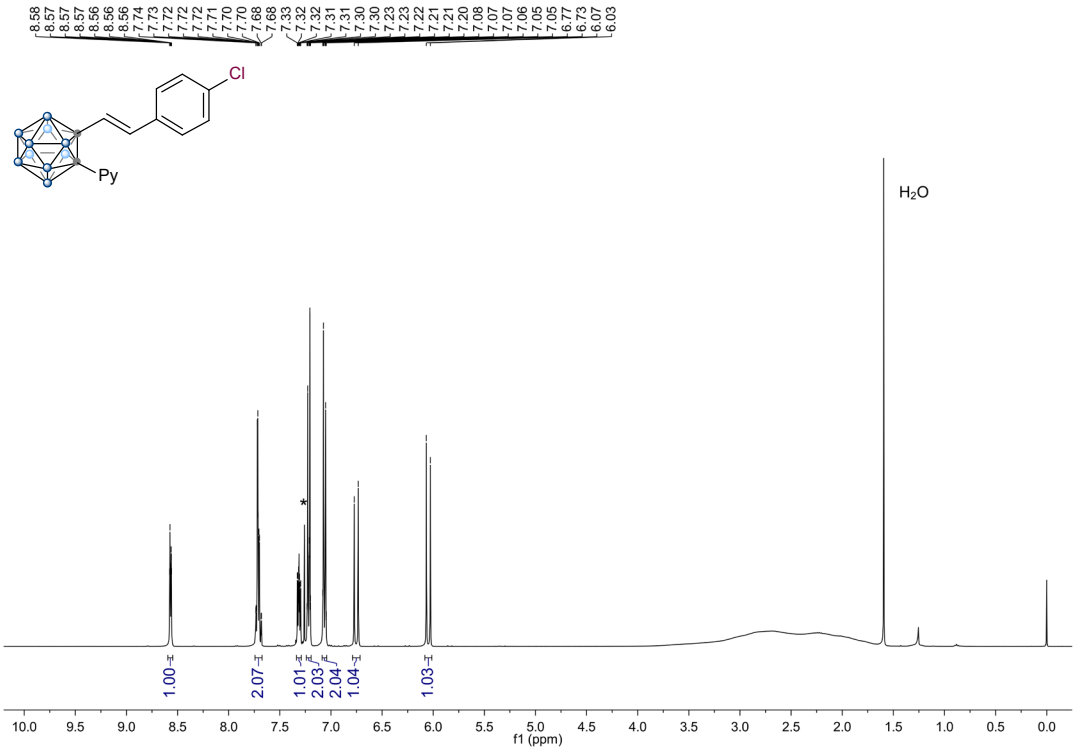
^{11}B NMR (128 MHz, Chloroform-*d*) **3af**



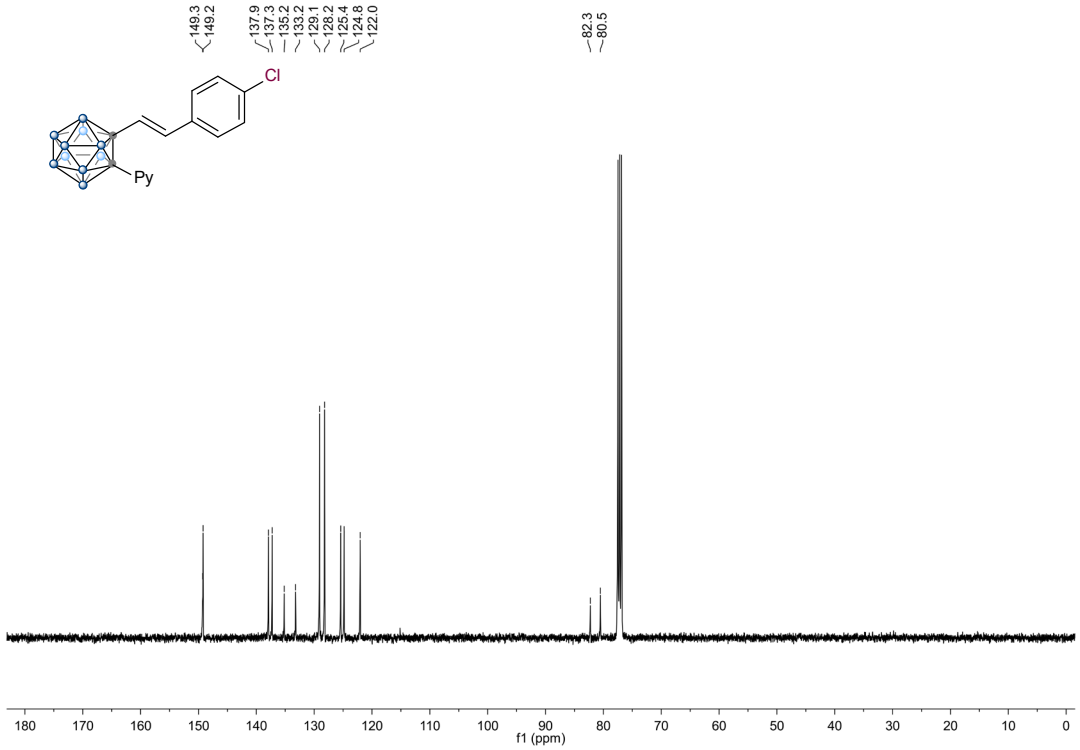
^{19}F NMR (376 MHz, Chloroform-*d*) **3af**



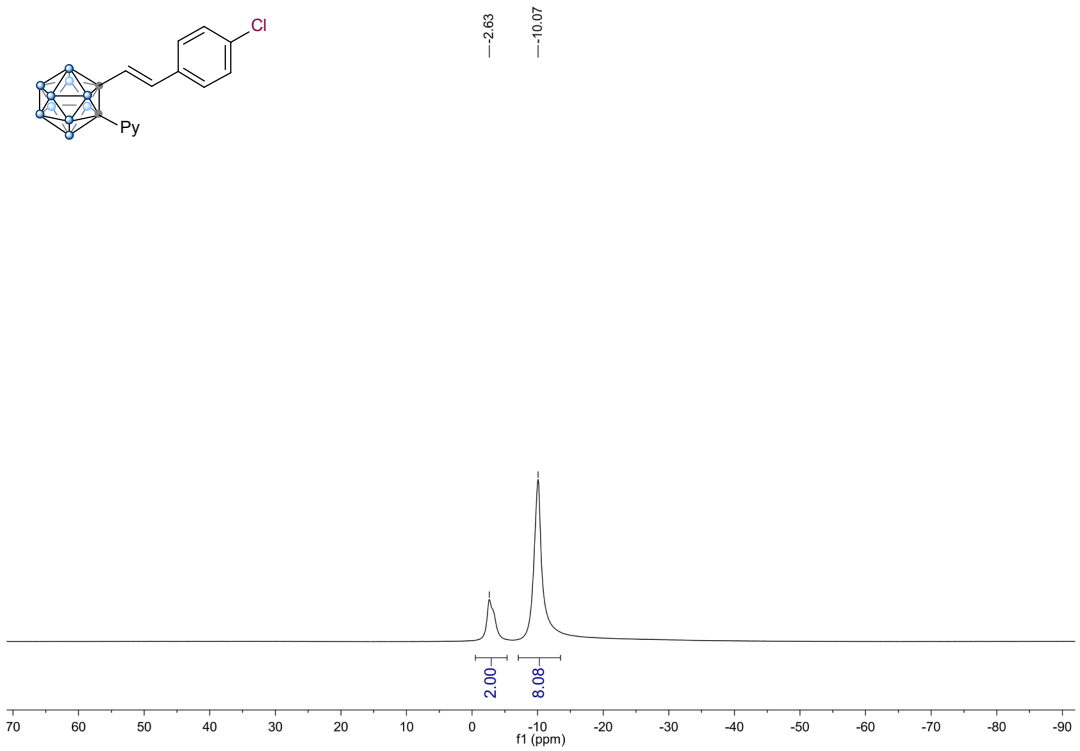
^{1}H NMR (400 MHz, Chloroform-*d*) **3ag** (* from residual $CHCl_3$ in Chloroform-*d*)



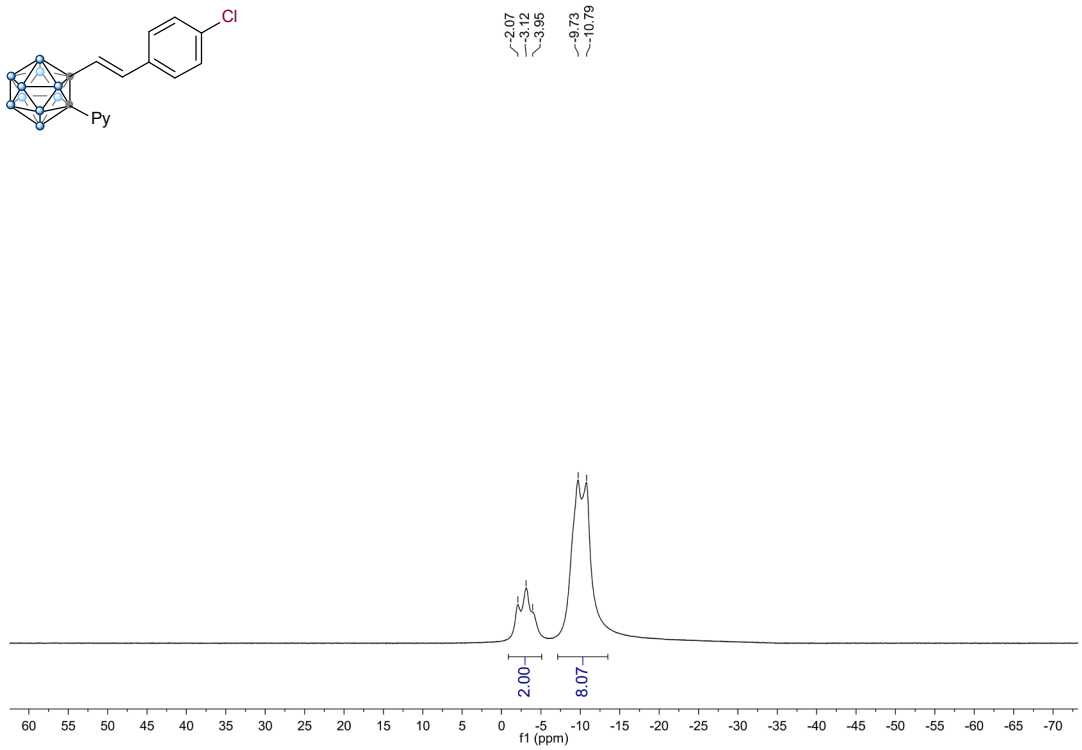
^{13}C NMR (101 MHz, Chloroform-*d*) **3ag**



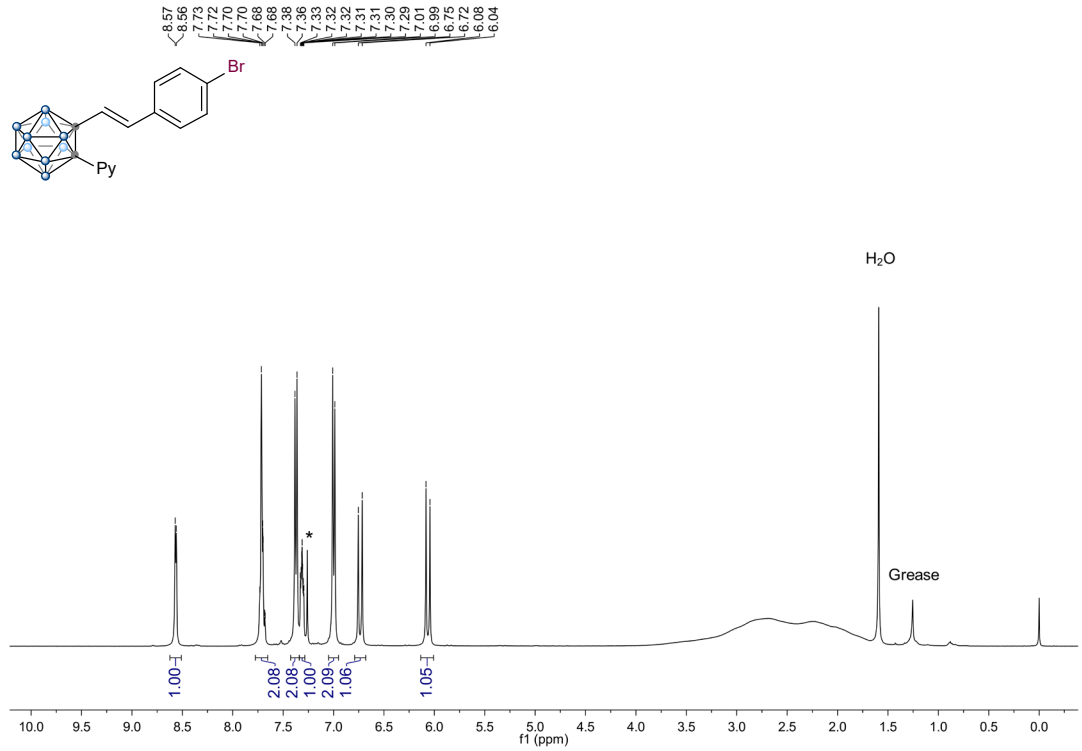
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3ag**



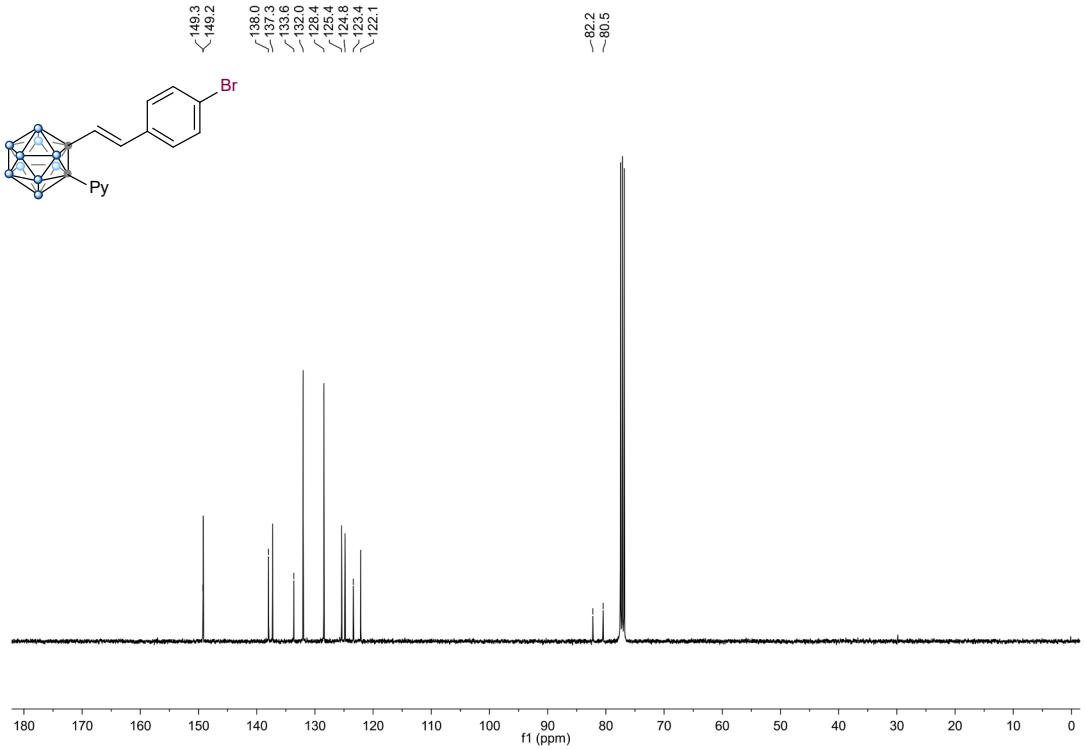
^{11}B NMR (128 MHz, Chloroform-*d*) **3ag**



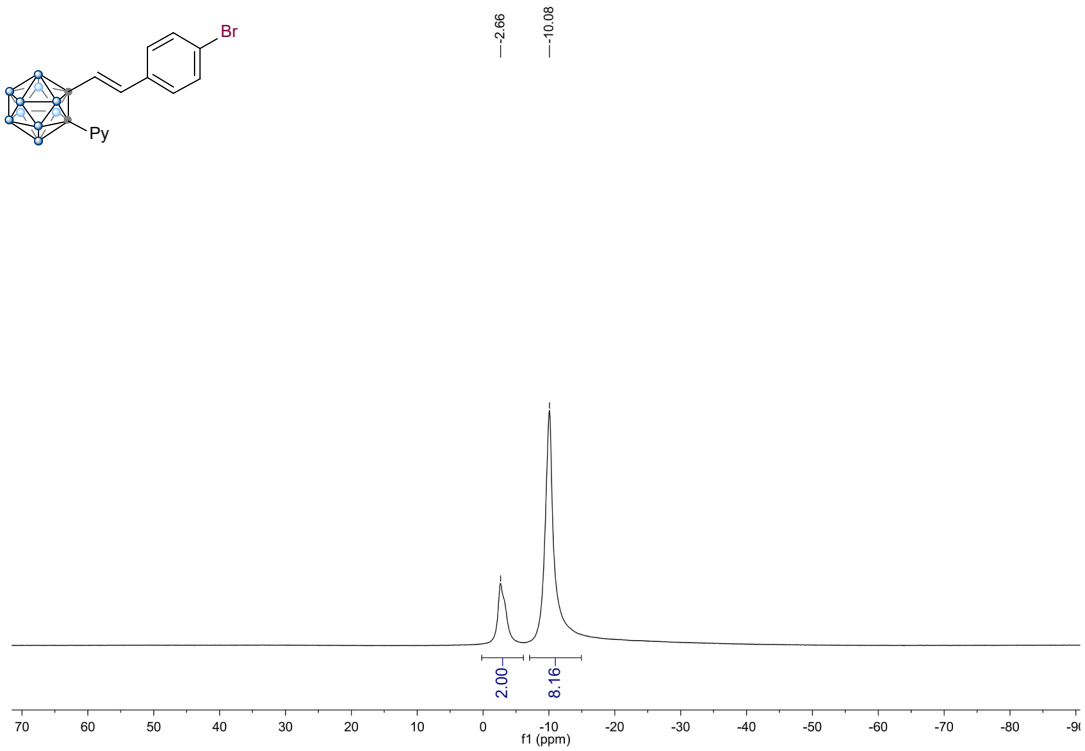
^{1}H NMR (400 MHz, Chloroform-*d*) **3ah** (* from residual $CHCl_3$ in Chloroform-*d*)



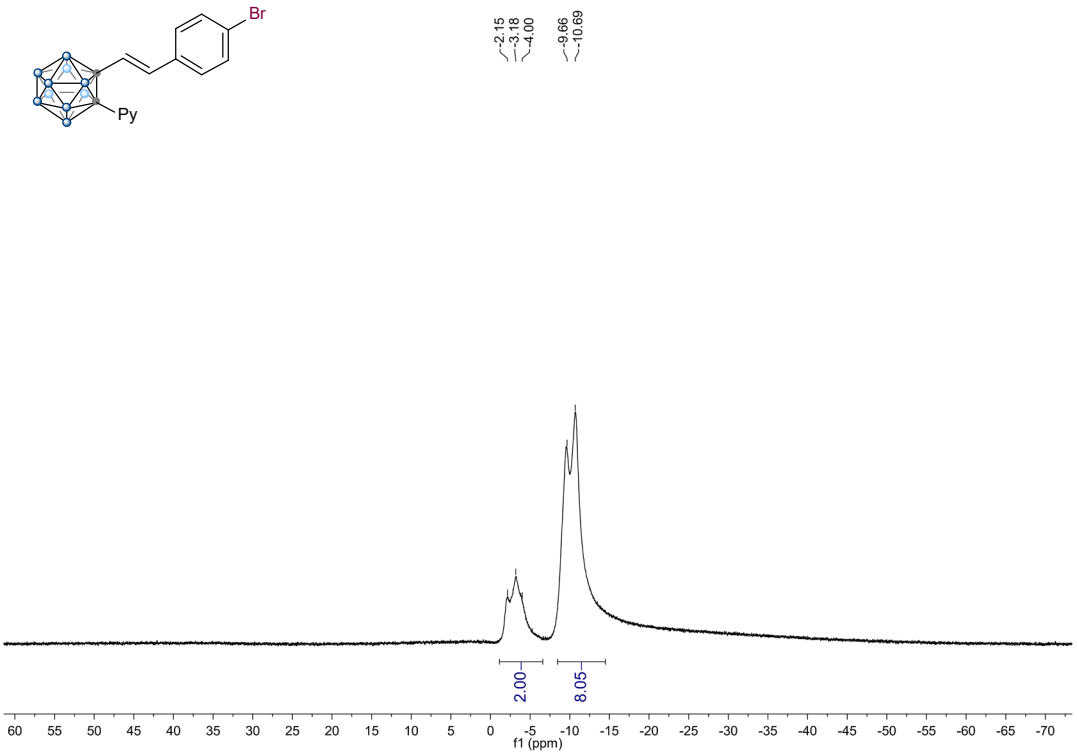
^{13}C NMR (101 MHz, Chloroform-*d*) **3ah**



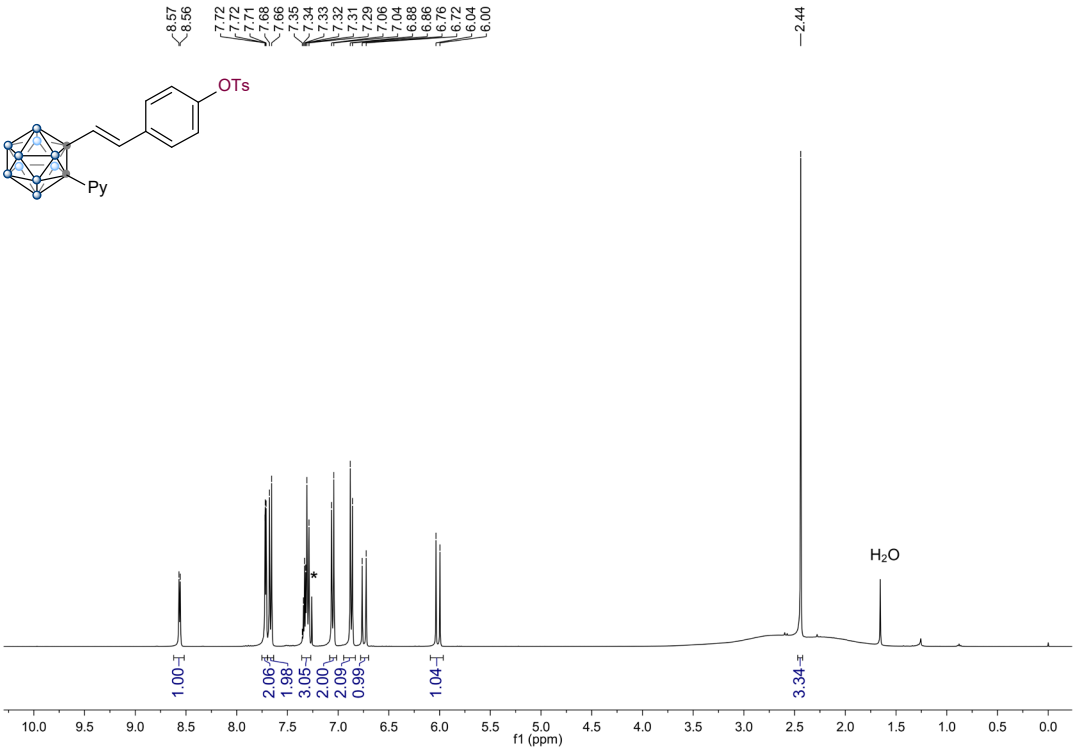
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3ah**



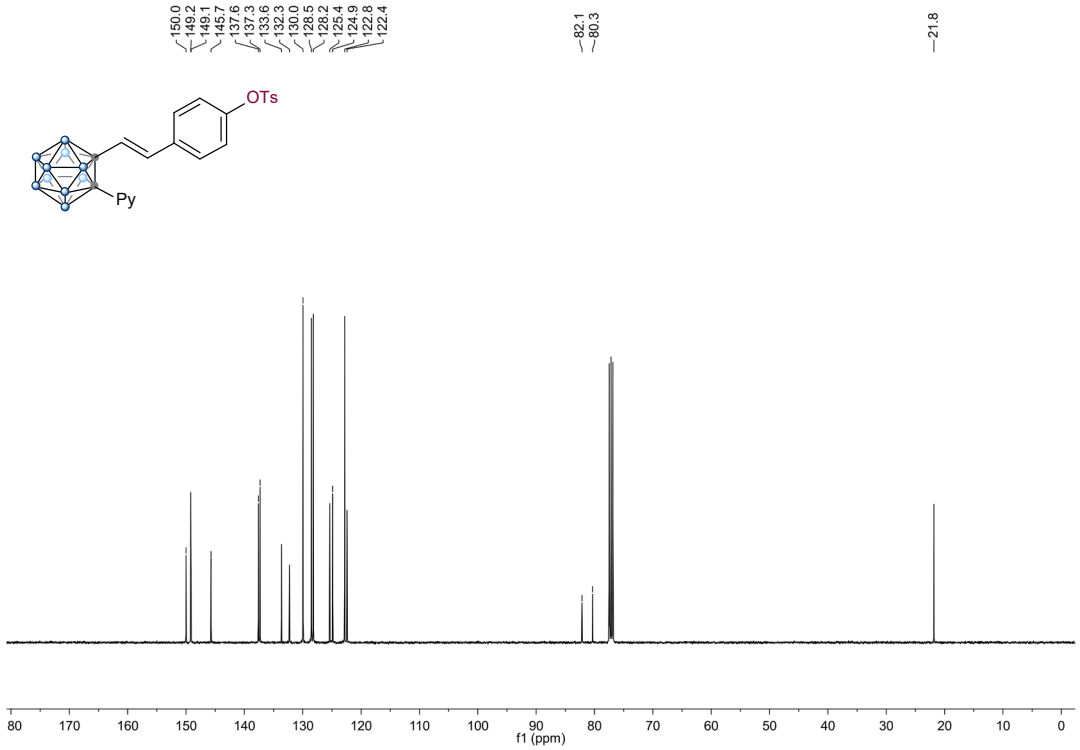
^{11}B NMR (128 MHz, Chloroform-*d*) **3ah**



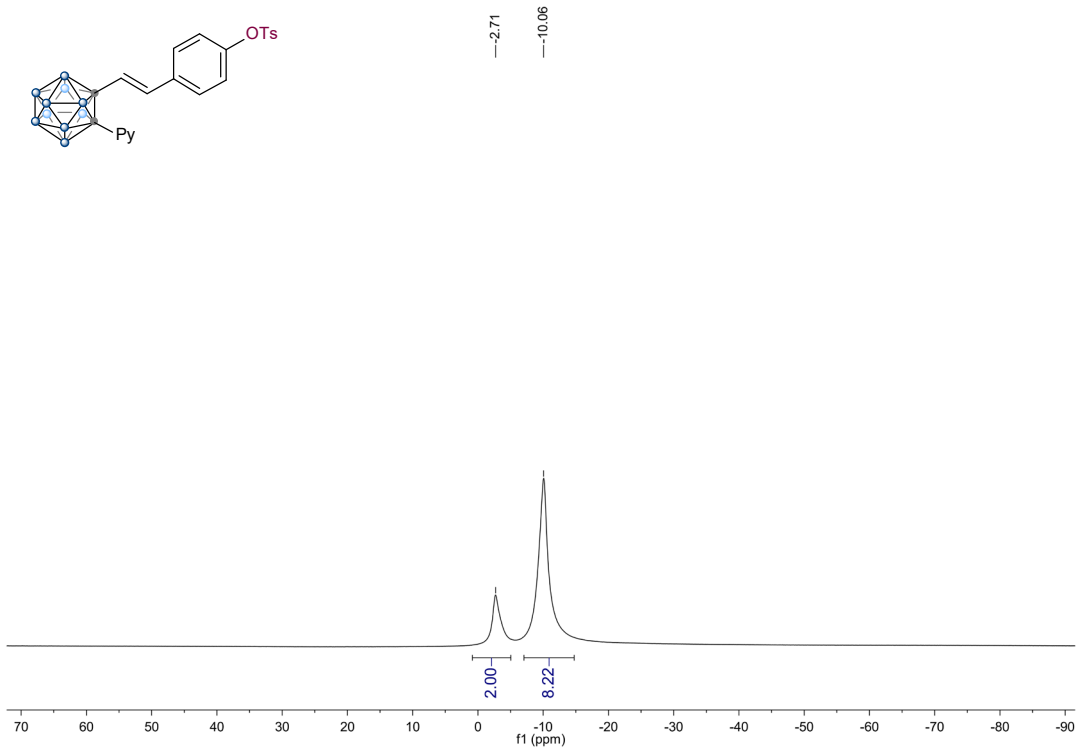
^{1}H NMR (400 MHz, Chloroform-*d*) **3ai** (* from residual $CHCl_3$ in Chloroform-*d*)



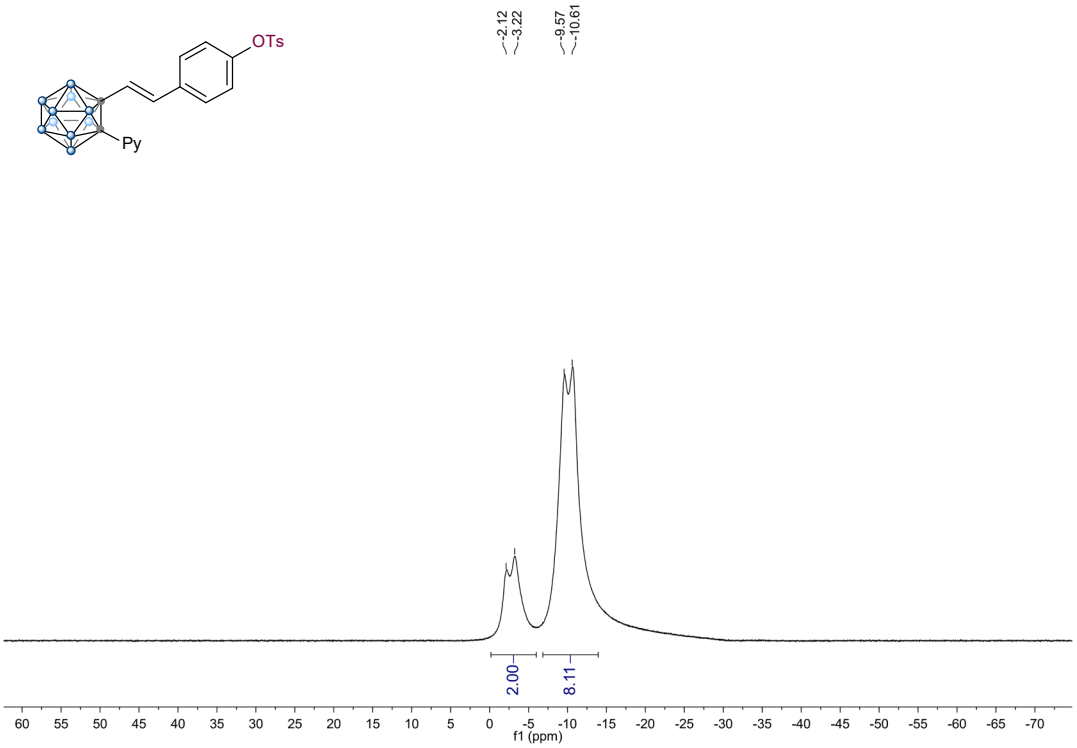
^{13}C NMR (101 MHz, Chloroform-*d*) **3ai**



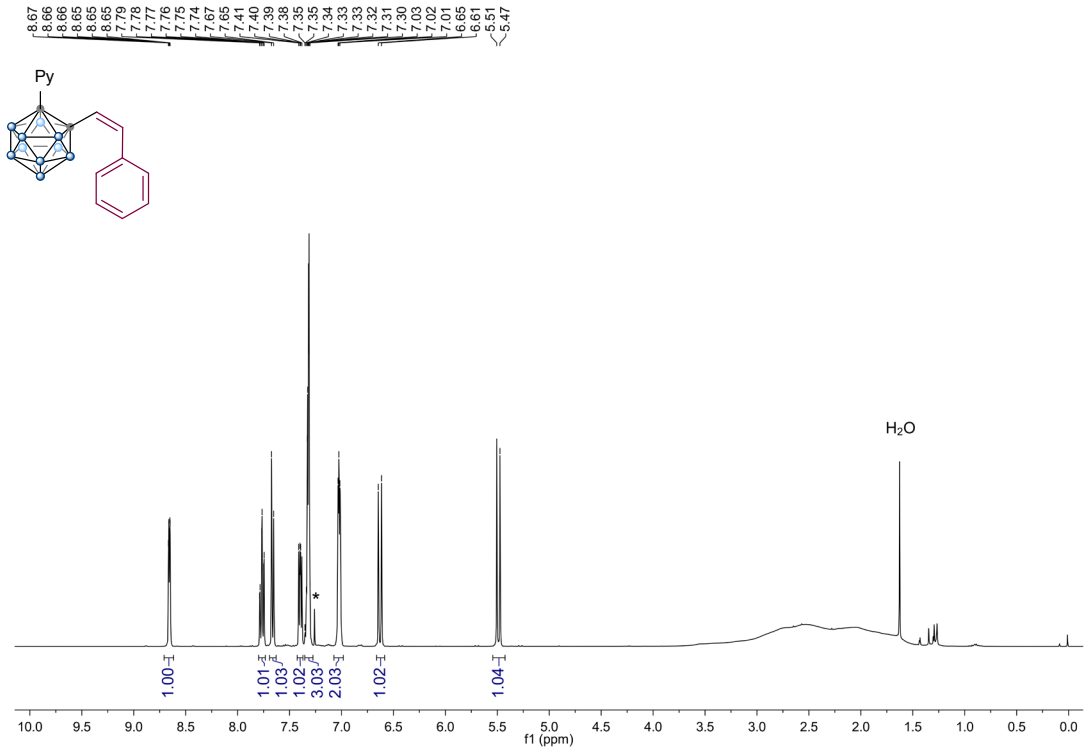
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **3ai**



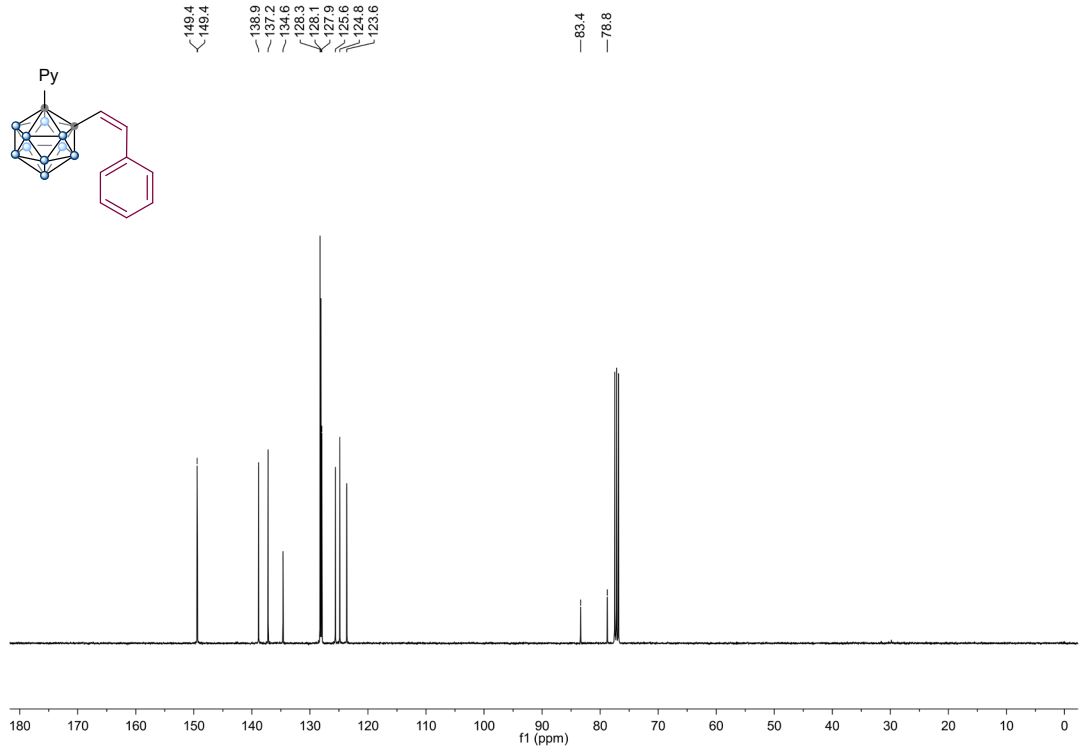
^{11}B NMR (128 MHz, Chloroform-*d*) **3ai**



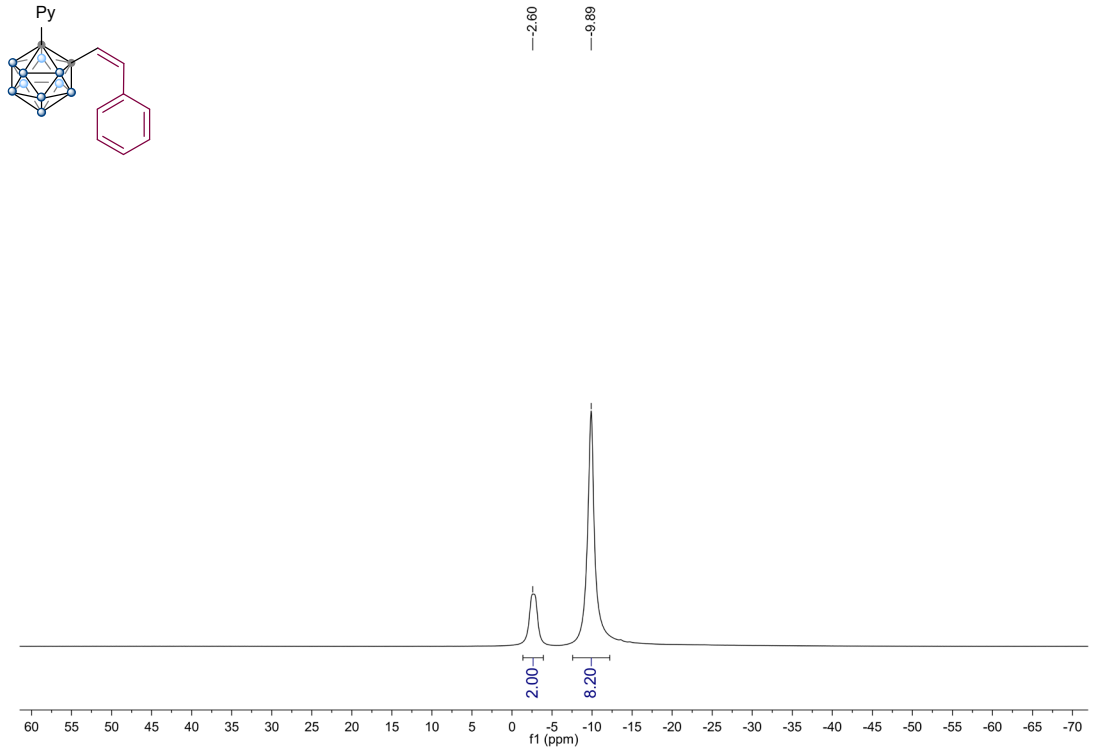
^{1}H NMR (400 MHz, Chloroform-*d*) **5a** (* from residual $CHCl_3$ in Chloroform-*d*)



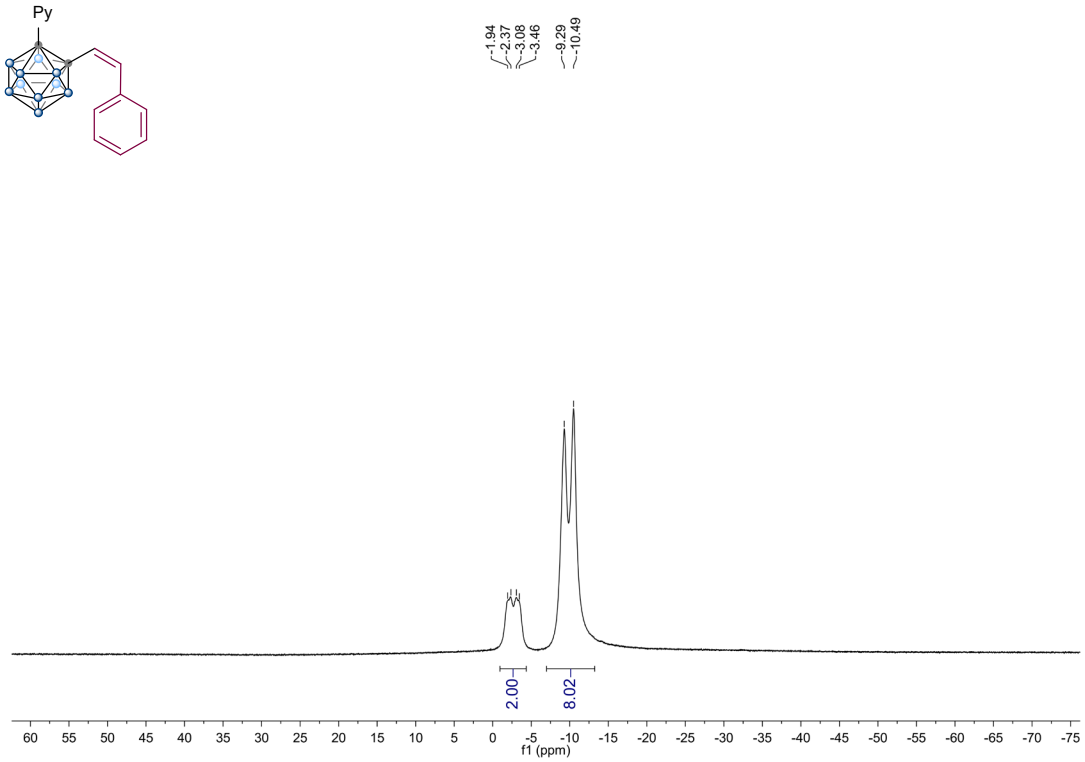
^{13}C NMR (101 MHz, Chloroform-*d*) **5a**



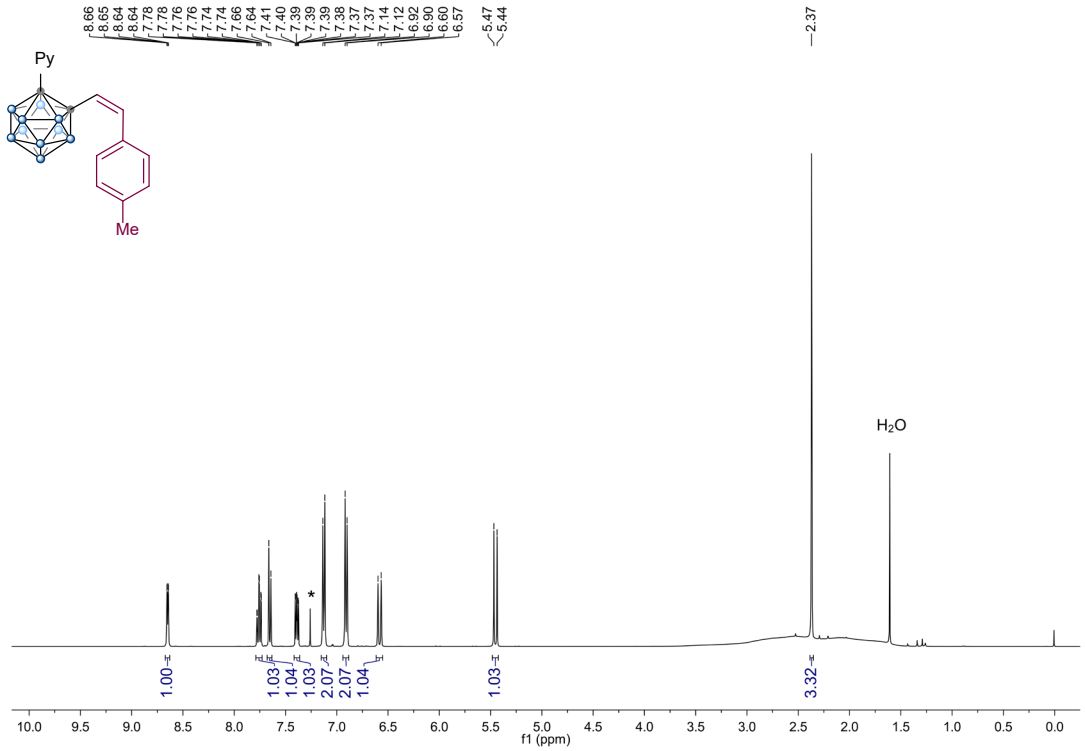
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **5a**



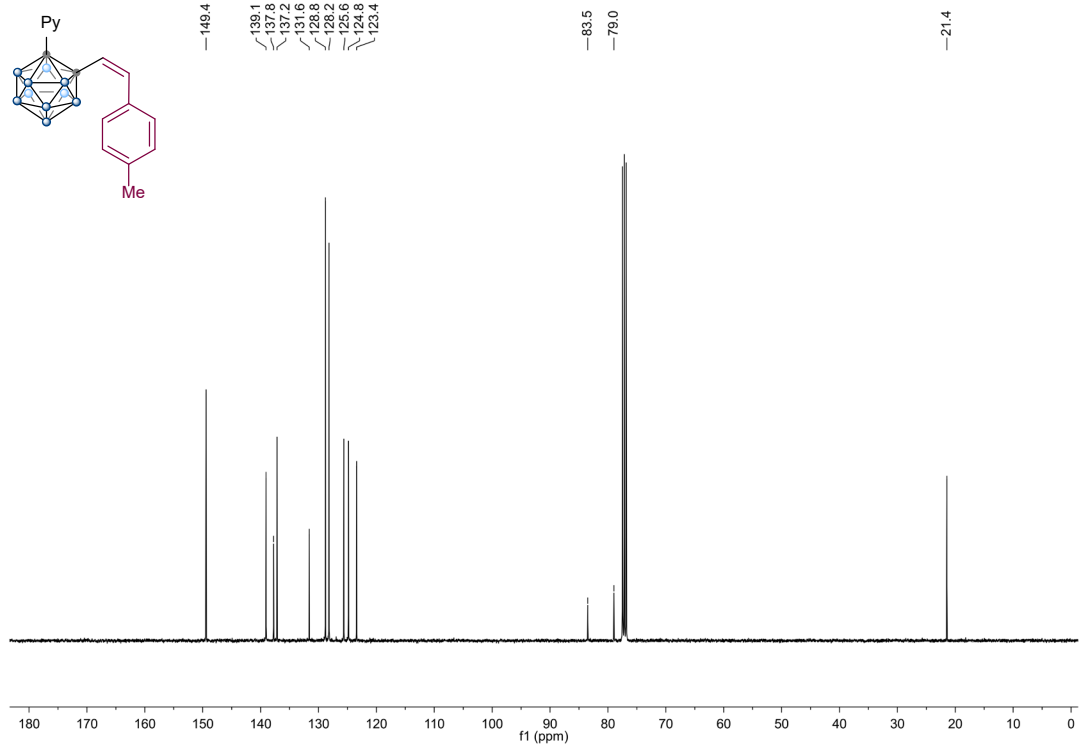
^{11}B NMR (128 MHz, Chloroform-*d*) **5a**



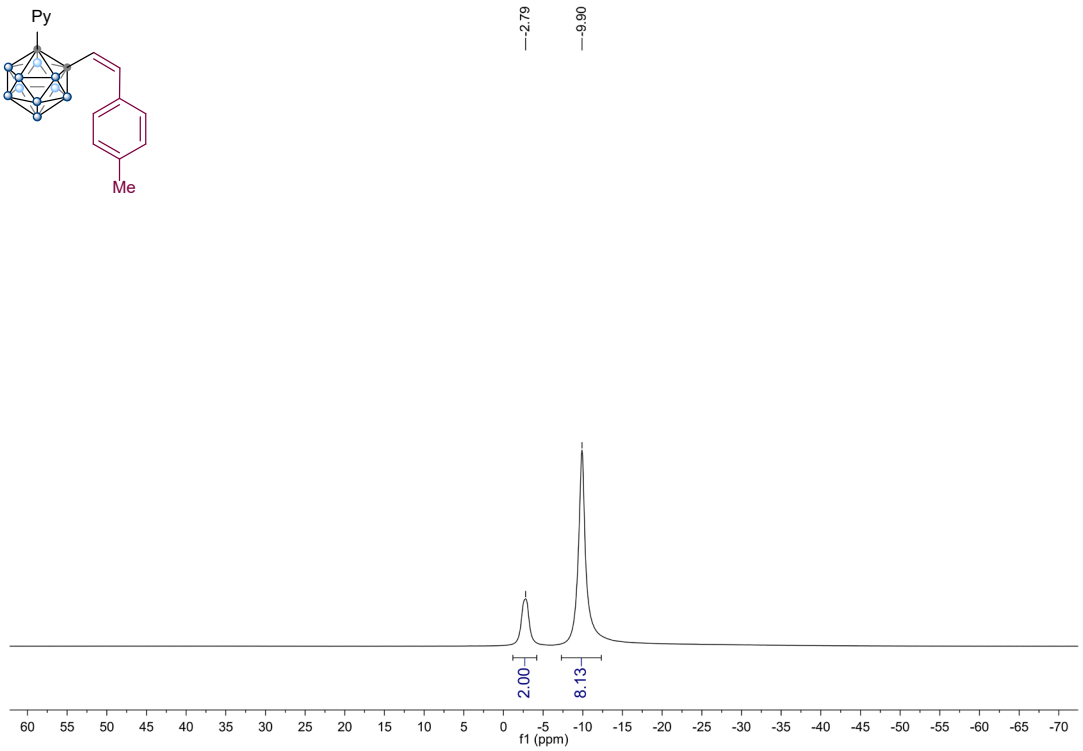
^{1}H NMR (400 MHz, Chloroform-*d*) **5b** (* from residual $CHCl_3$ in Chloroform-*d*)



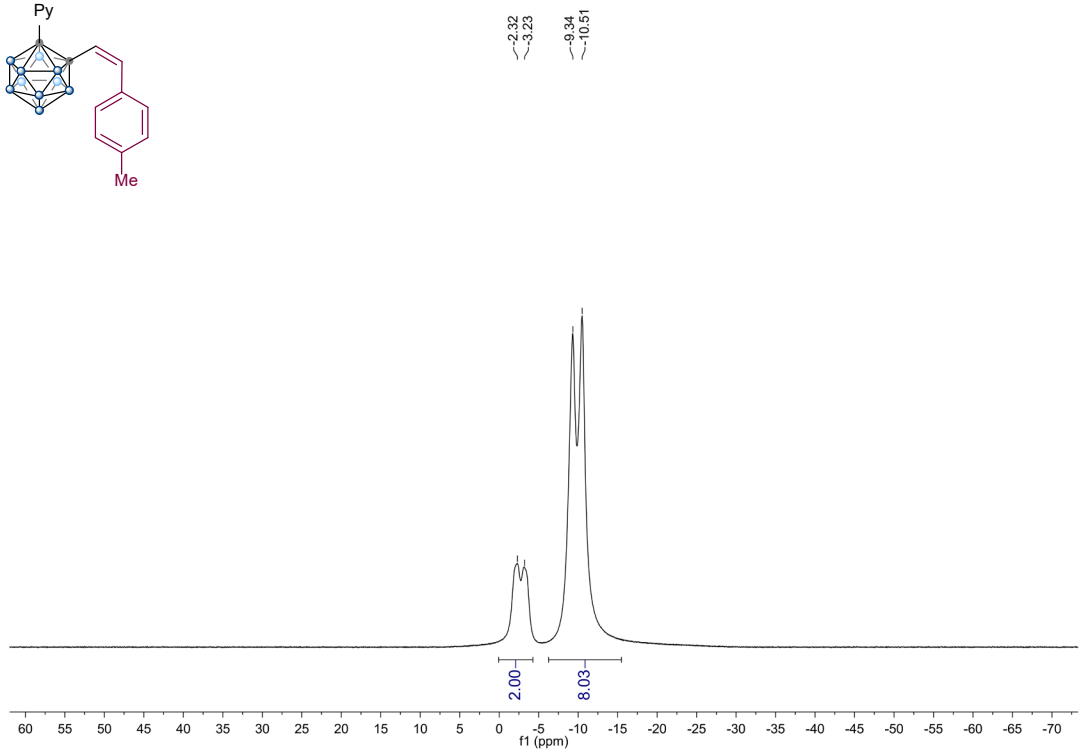
^{13}C NMR (101 MHz, Chloroform-*d*) **5b**



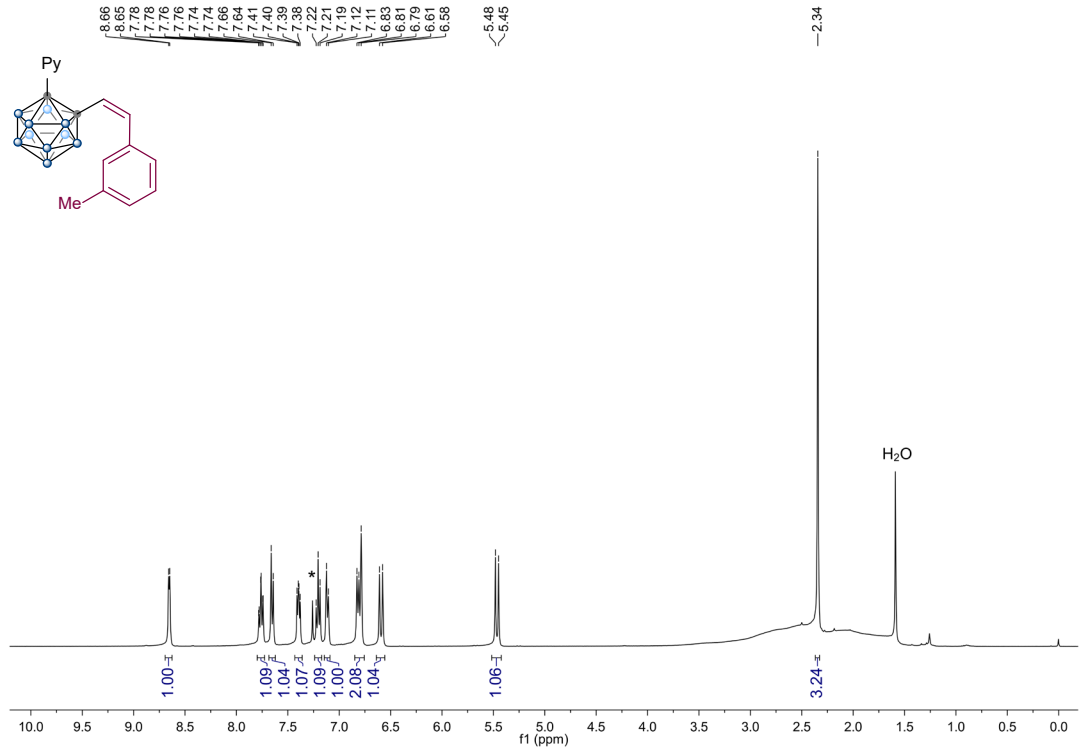
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **5b**



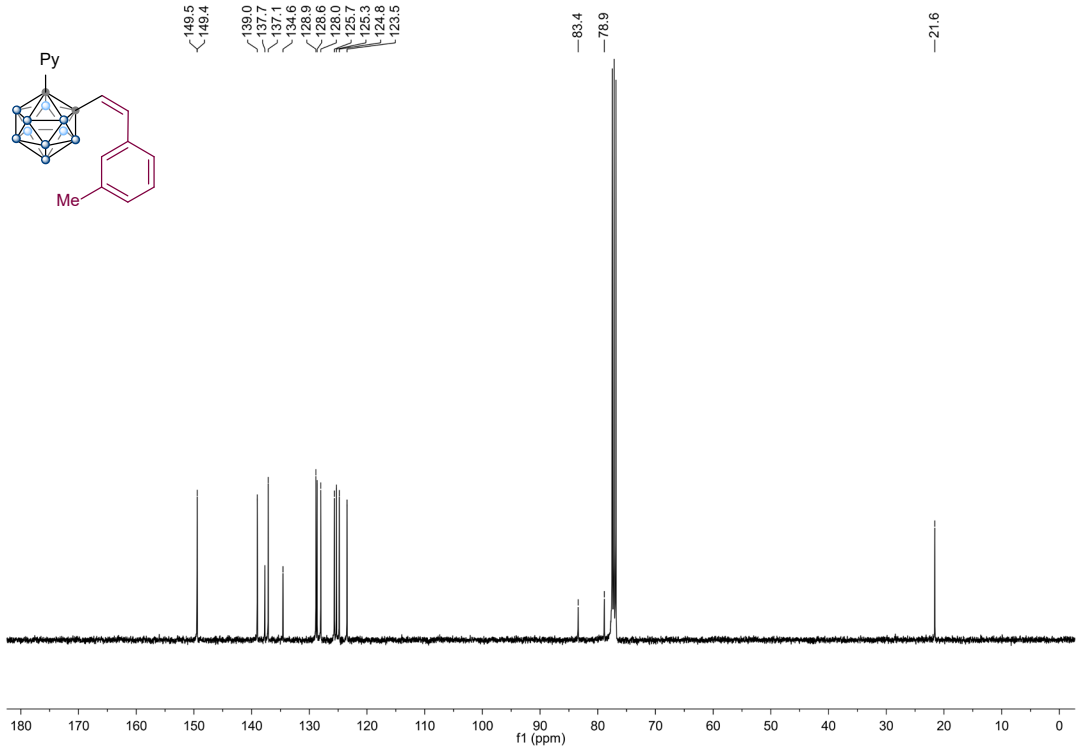
^{11}B NMR (128 MHz, Chloroform-*d*) **5b**



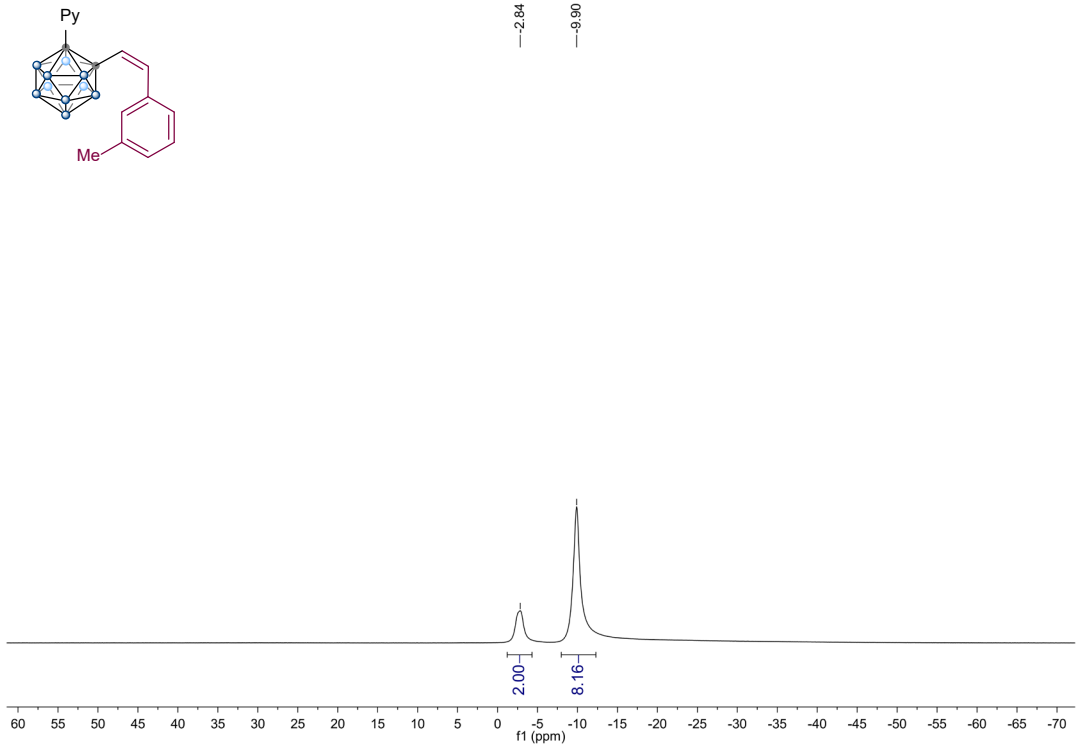
^{1}H NMR (400 MHz, Chloroform-*d*) **5c** (* from residual $CHCl_3$ in Chloroform-*d*)



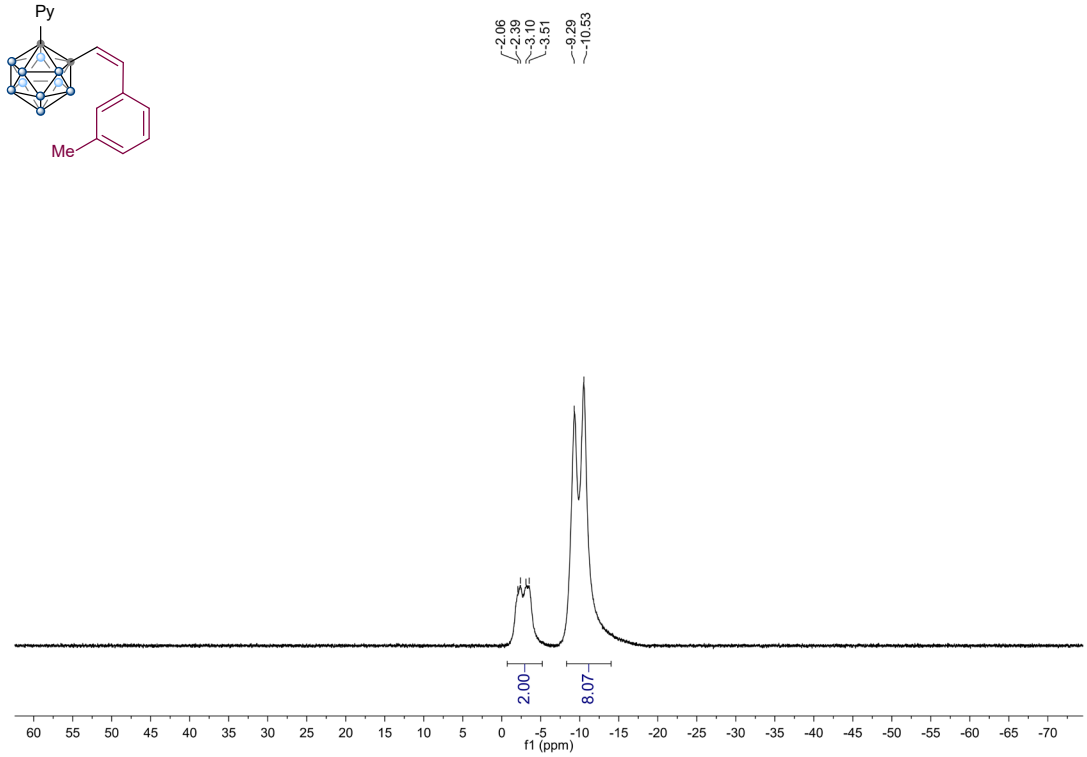
^{13}C NMR (101 MHz, Chloroform-*d*) **5c**



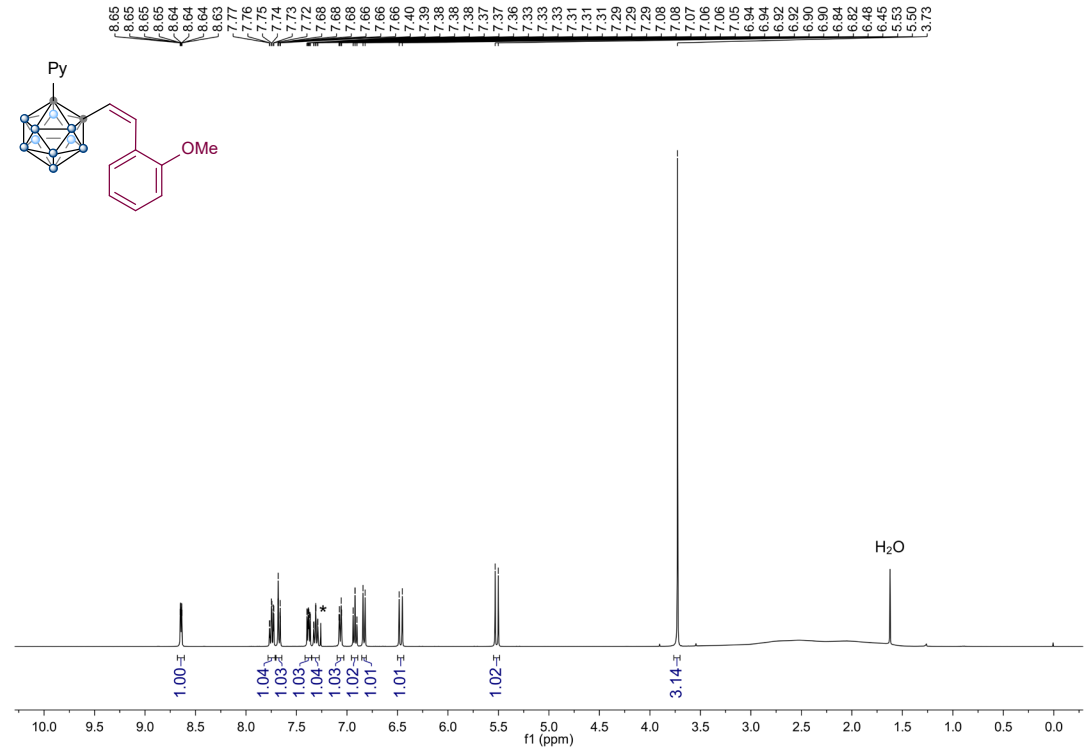
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **5c**



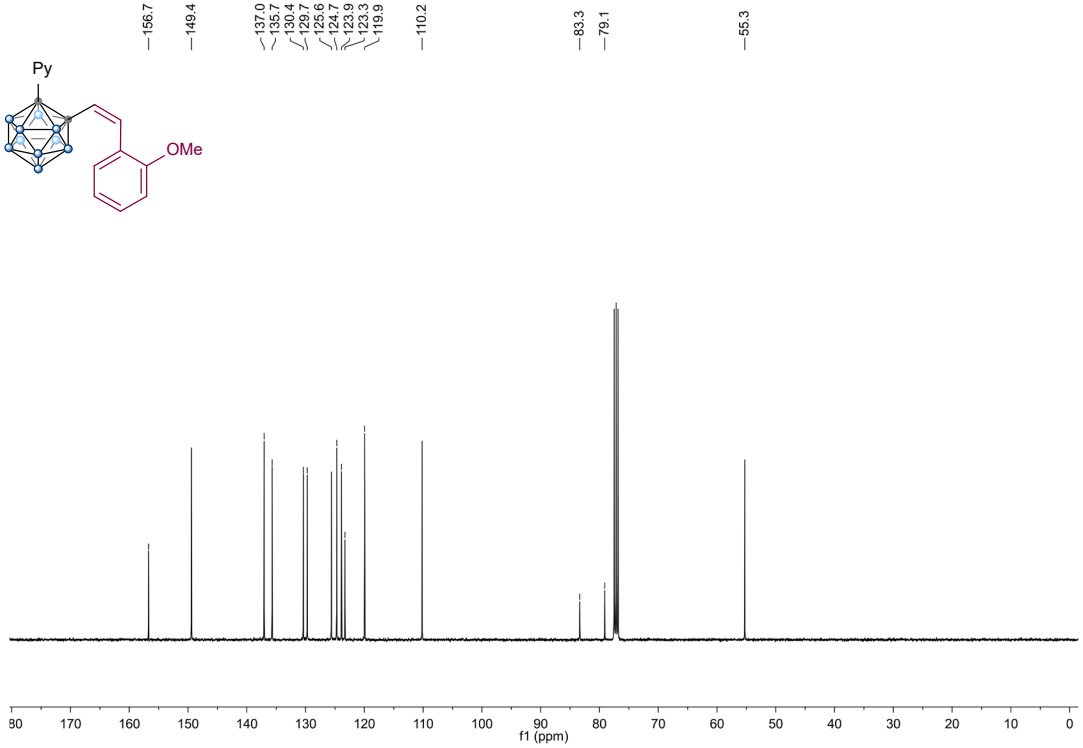
^{11}B NMR (128 MHz, Chloroform-*d*) **5c**



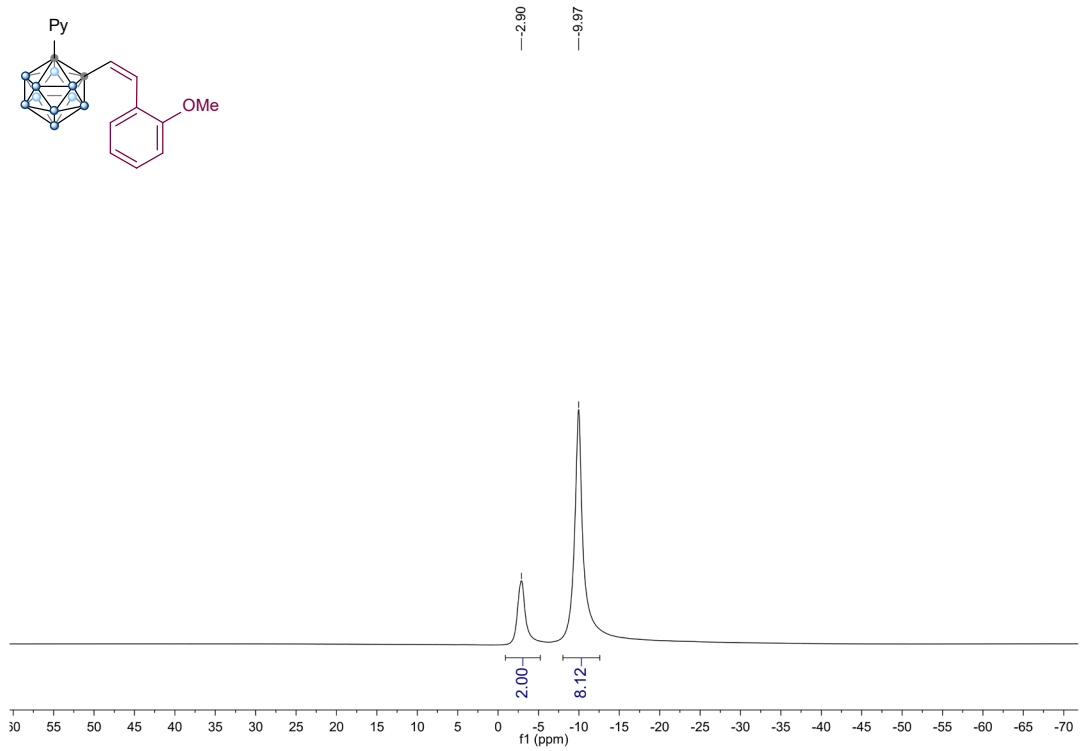
^{1}H NMR (400 MHz, Chloroform-*d*) **5d** (* from residual $CHCl_3$ in Chloroform-*d*)



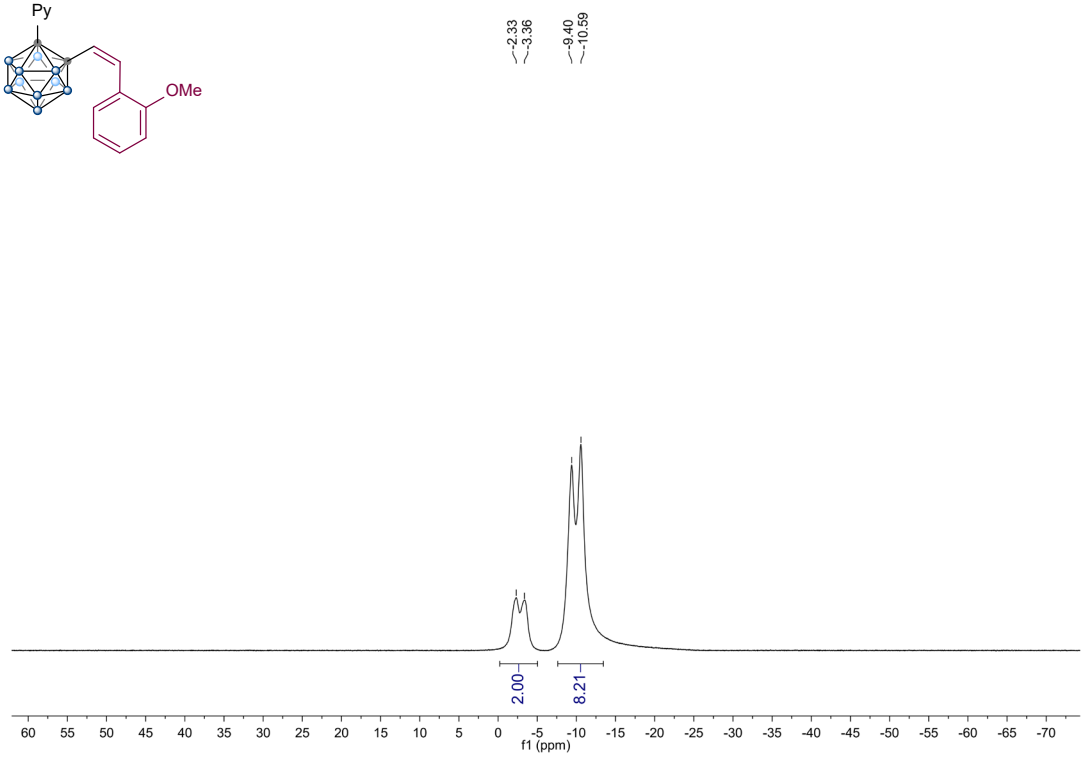
^{13}C NMR (101 MHz, Chloroform-*d*) **5d**



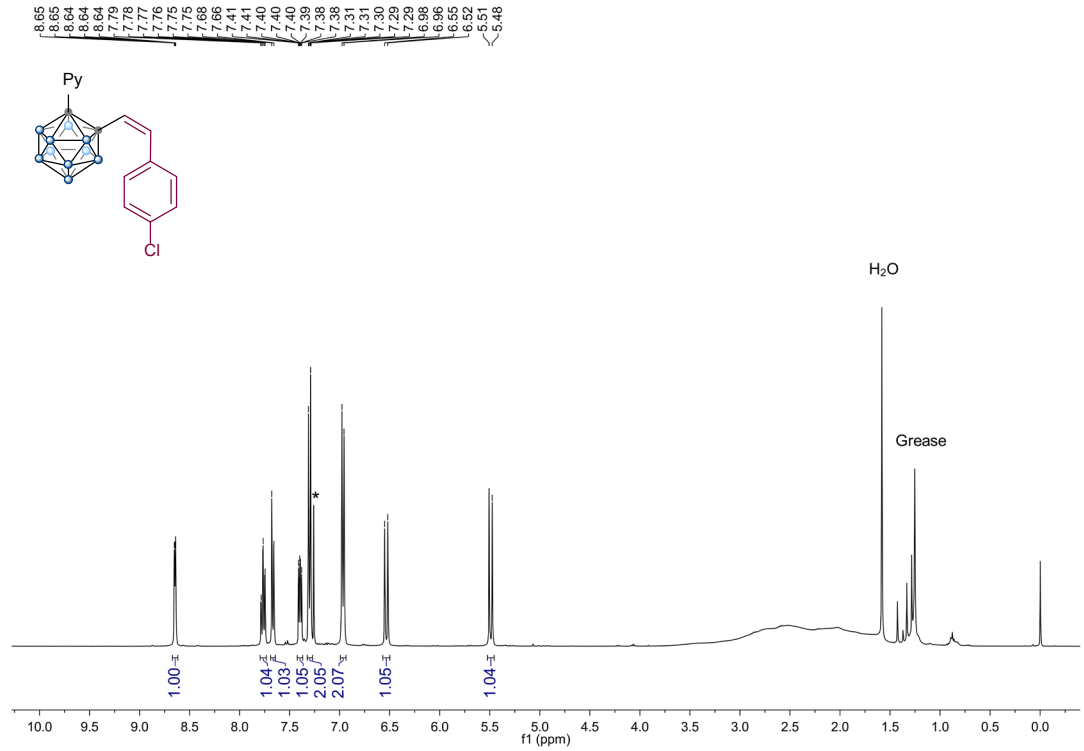
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **5d**



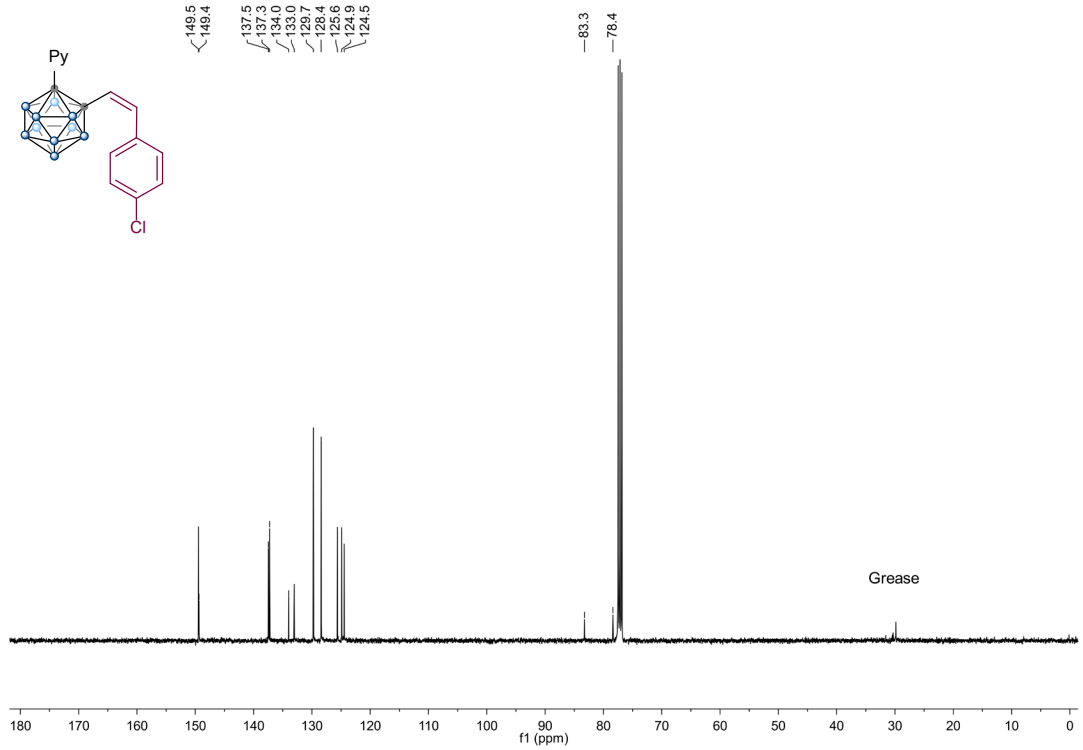
^{11}B NMR (128 MHz, Chloroform-*d*) **5d**



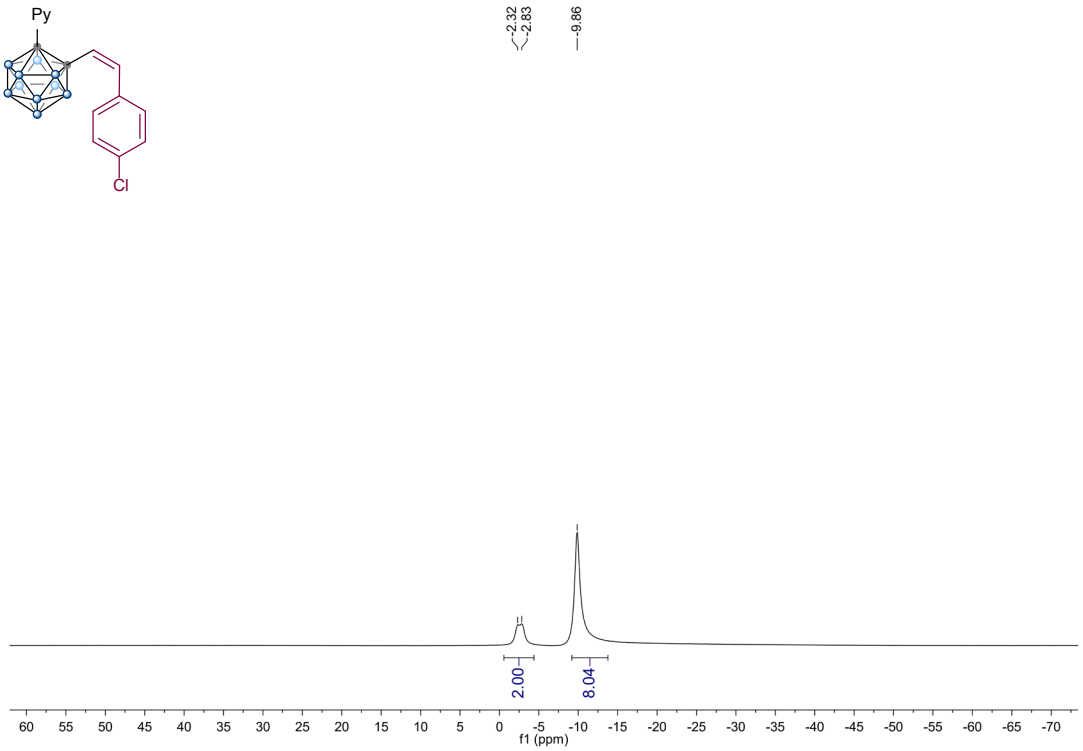
^{1}H NMR (400 MHz, Chloroform-*d*) **5e** (* from residual $CHCl_3$ in Chloroform-*d*)



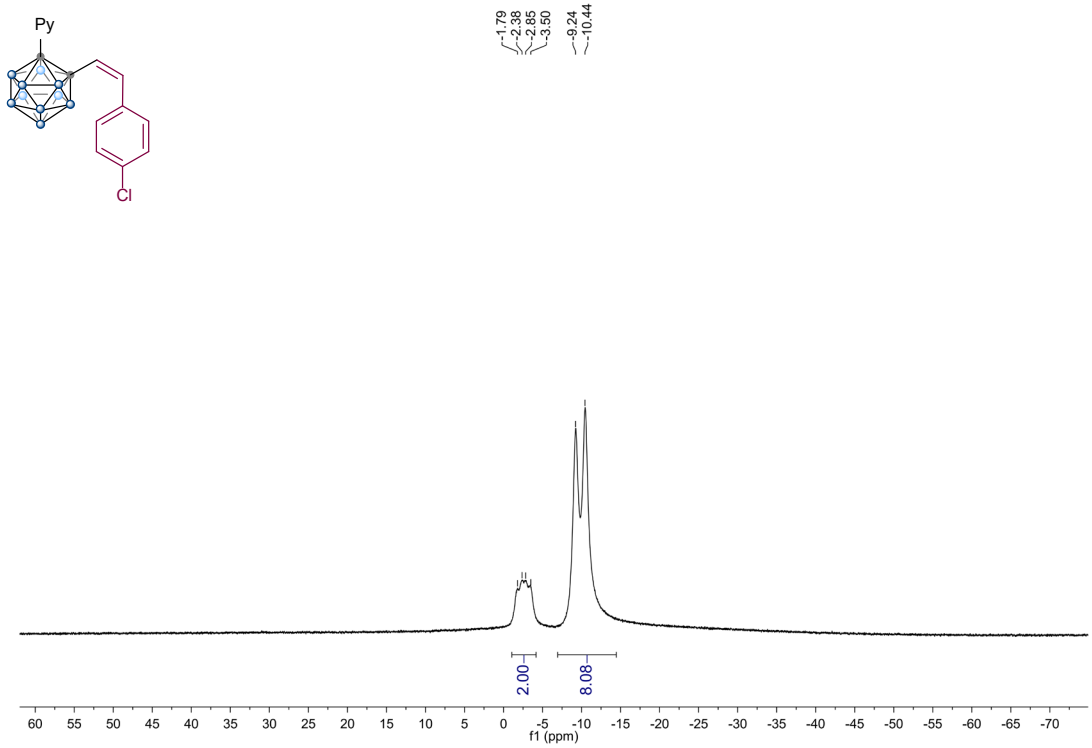
^{13}C NMR (101 MHz, Chloroform-*d*) **5e**



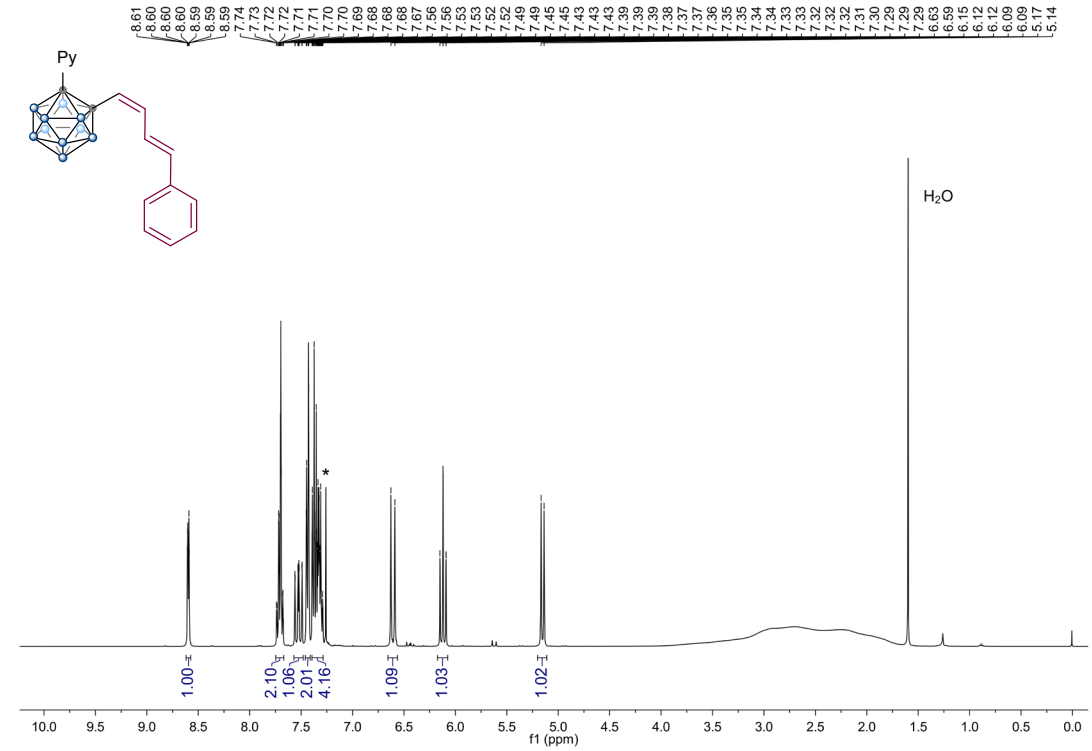
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **5e**



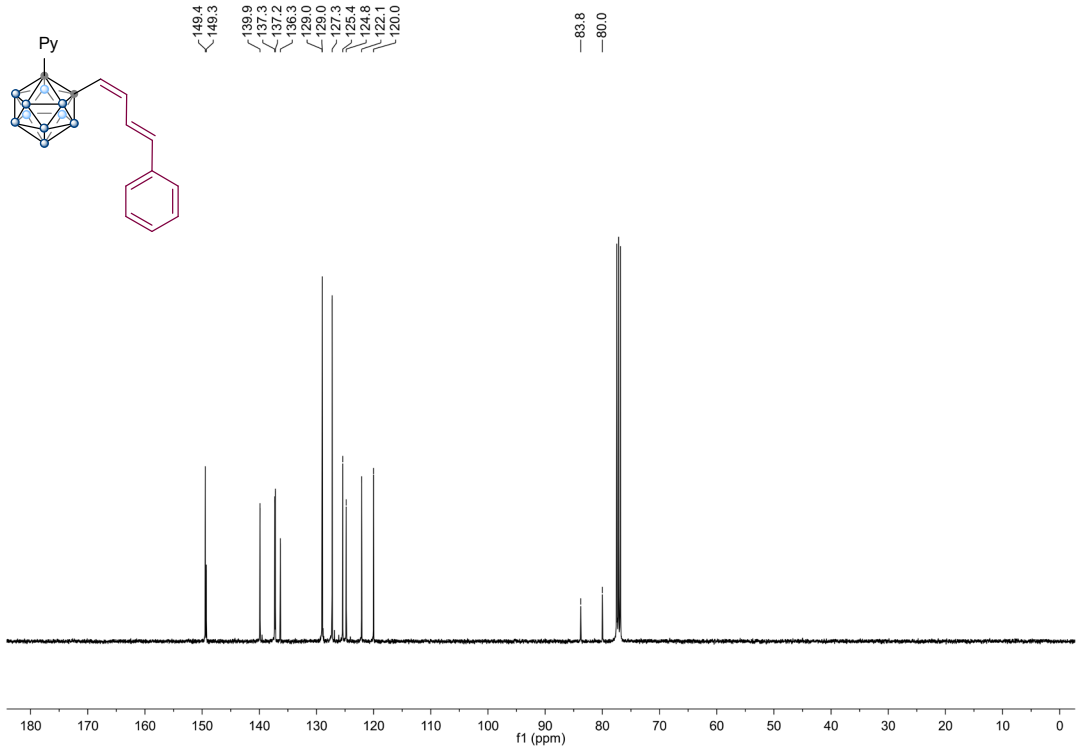
^{11}B NMR (128 MHz, Chloroform-*d*) **5e**



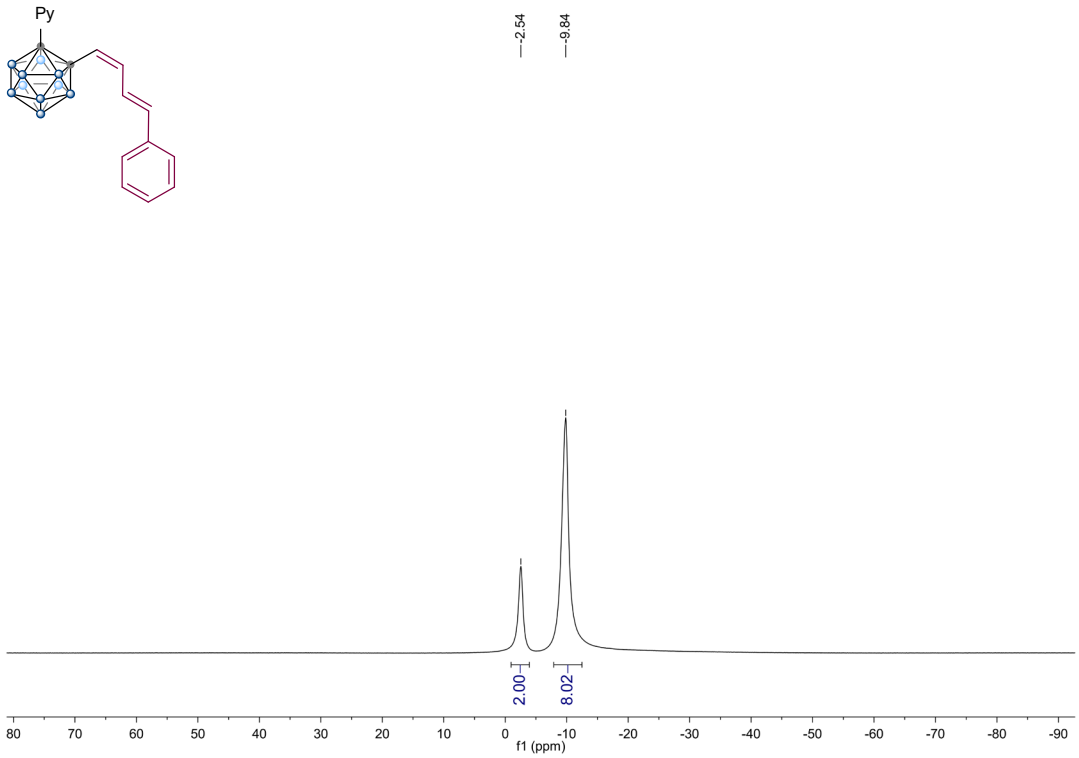
^{1}H NMR (400 MHz, Chloroform-*d*) **5f** (* from residual $CHCl_3$ in Chloroform-*d*)



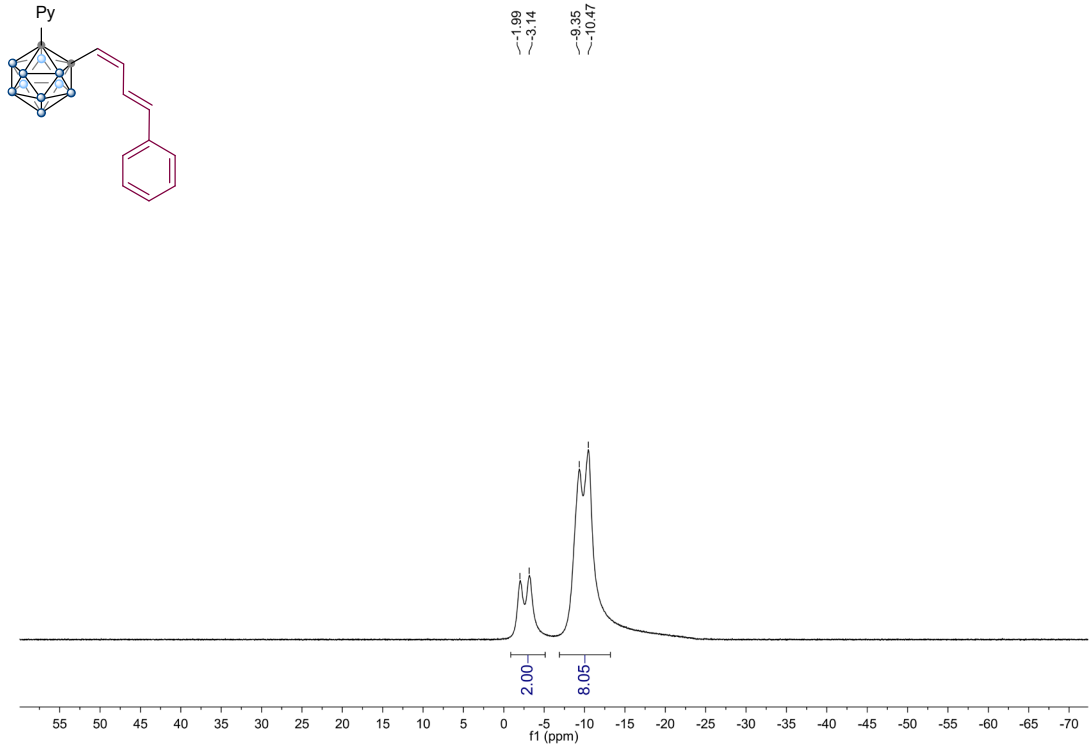
^{13}C NMR (101 MHz, Chloroform-*d*) **5f**



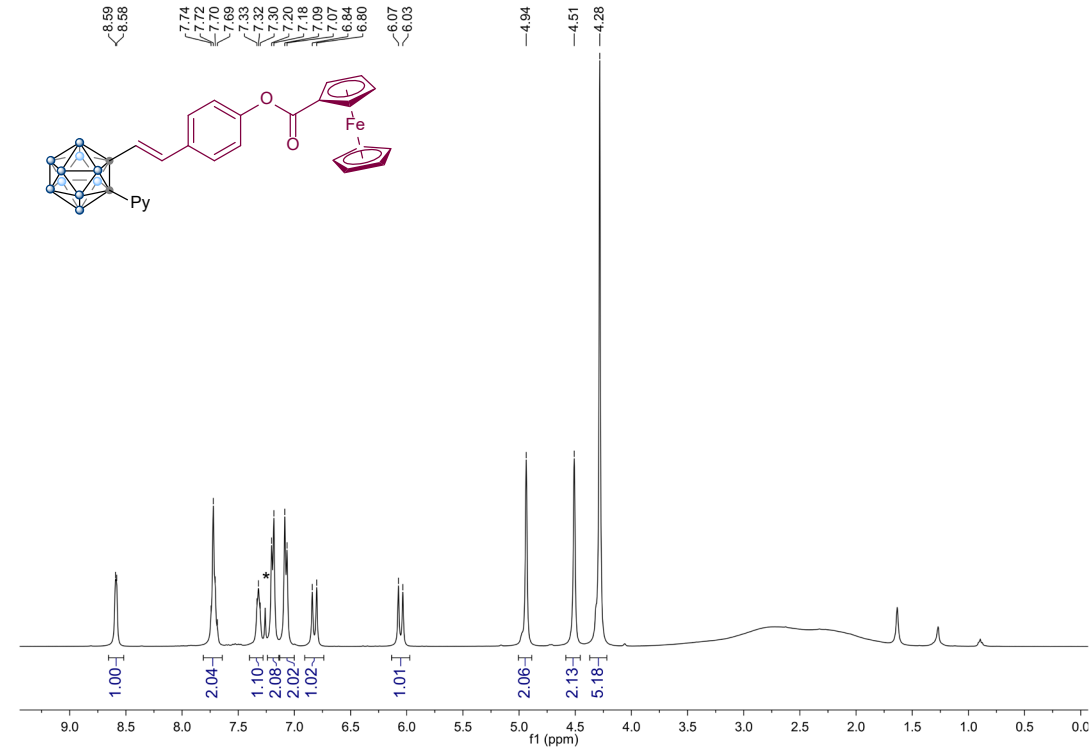
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **5f**



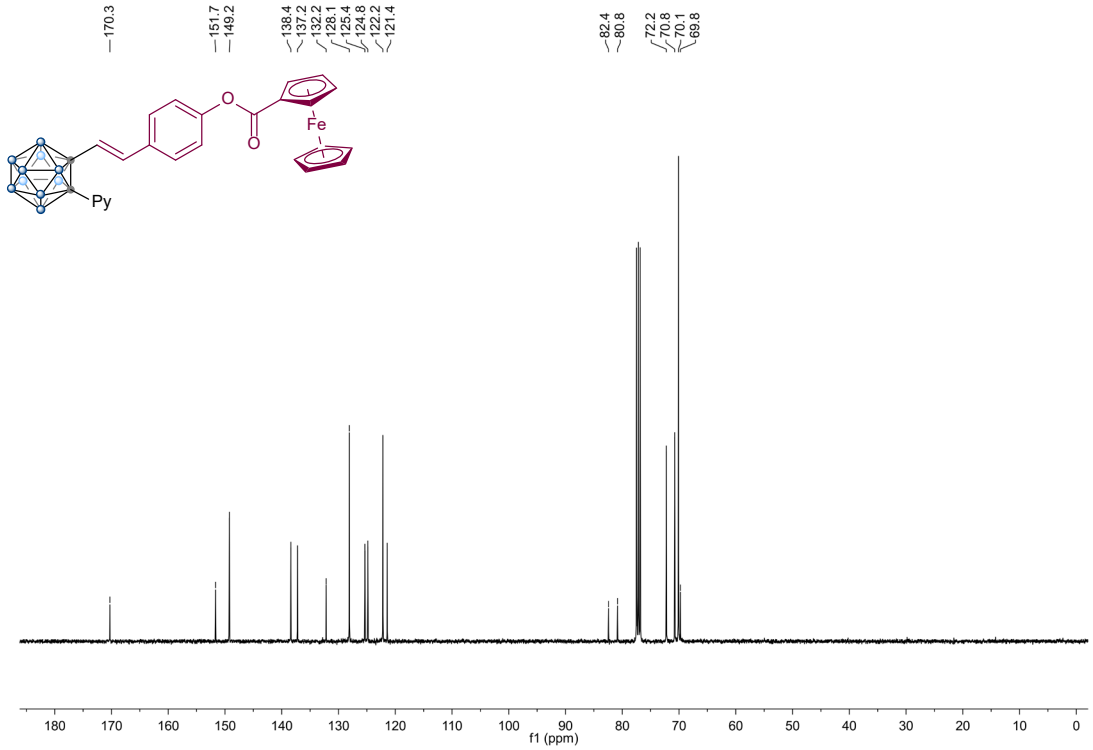
^{11}B NMR (128 MHz, Chloroform-*d*) **5f**



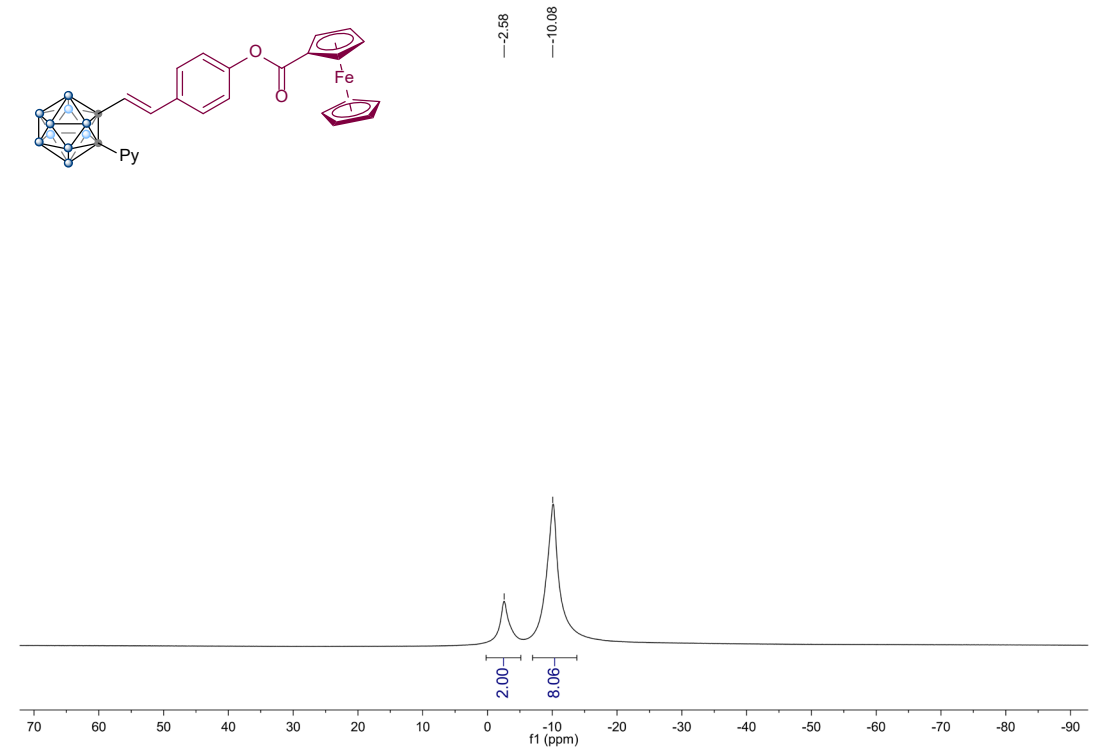
^{1}H NMR (400 MHz, Chloroform-*d*) **7a** (* from residual $CHCl_3$ in Chloroform-*d*)



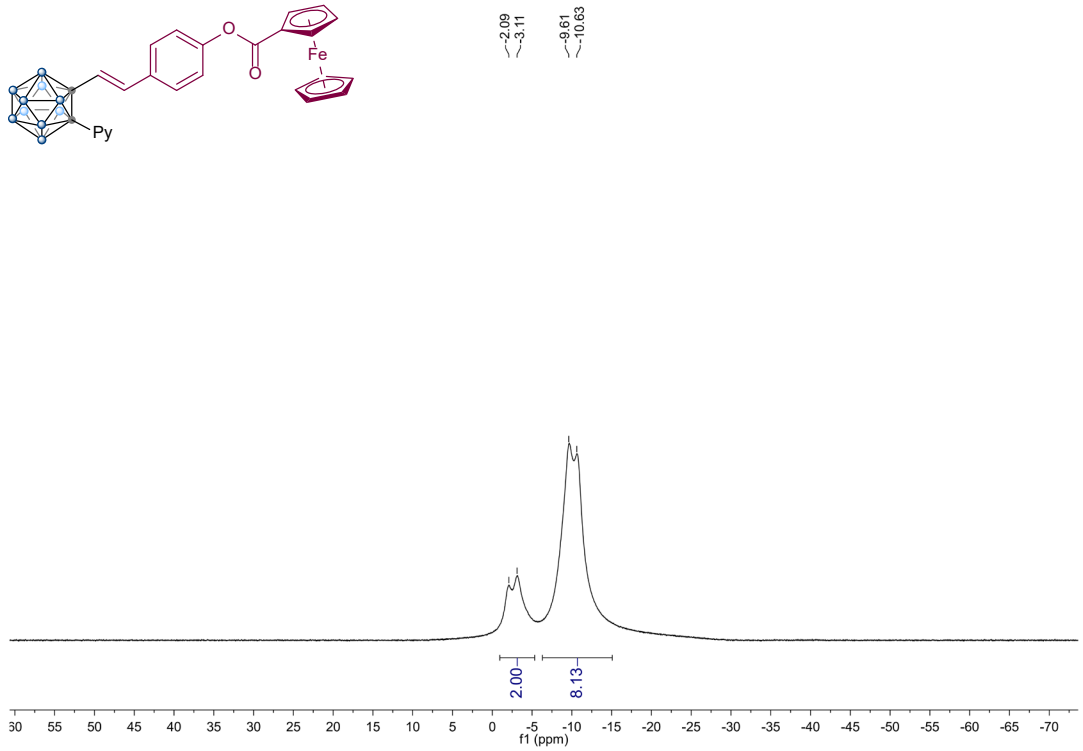
^{13}C NMR (101 MHz, Chloroform-*d*) **7a**



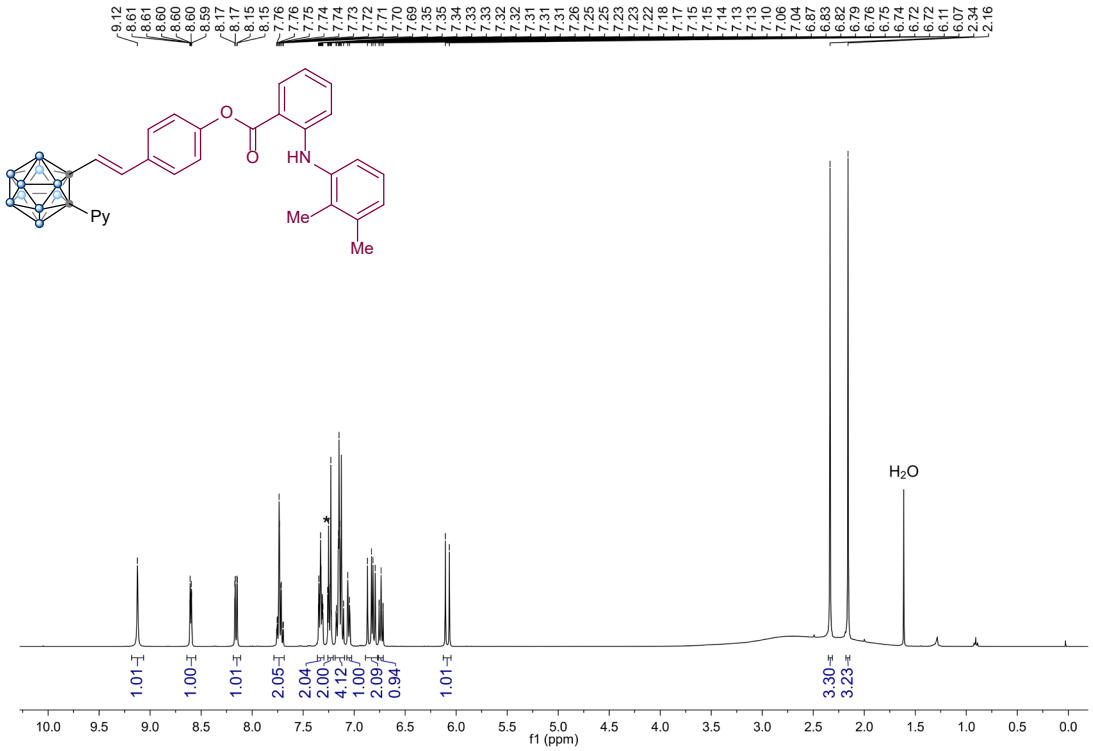
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **7a**



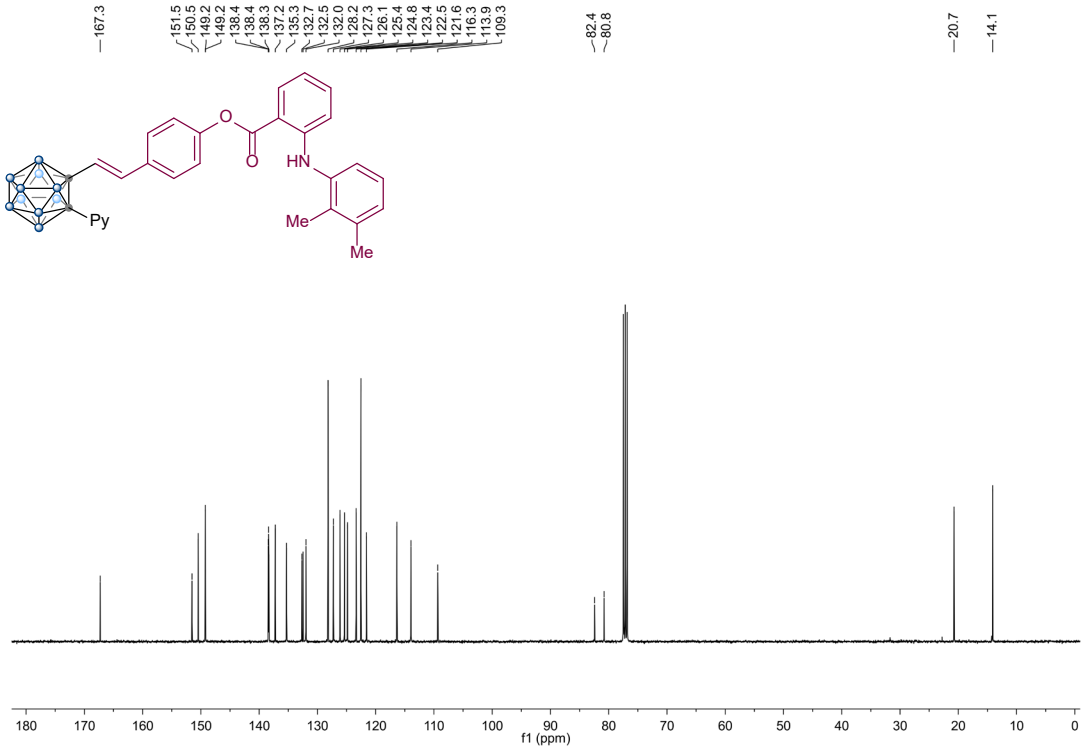
^{11}B NMR (128 MHz, Chloroform-*d*) **7a**



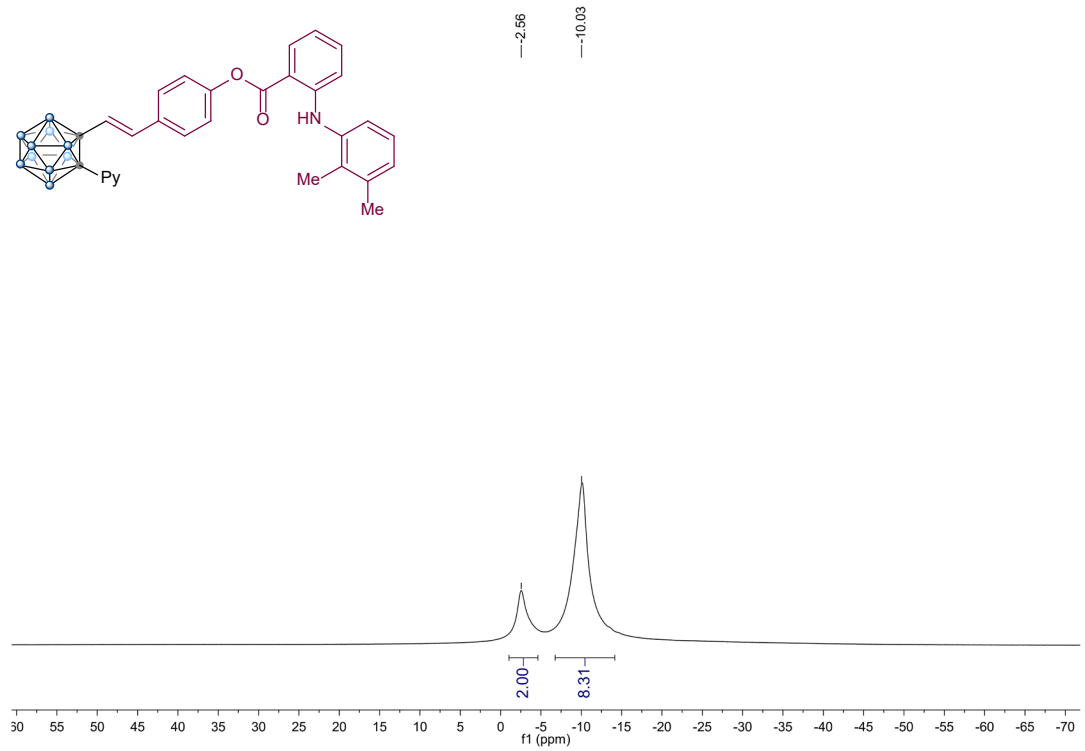
^{1}H NMR (400 MHz, Chloroform-*d*) **7b** (* from residual $CHCl_3$ in Chloroform-*d*)



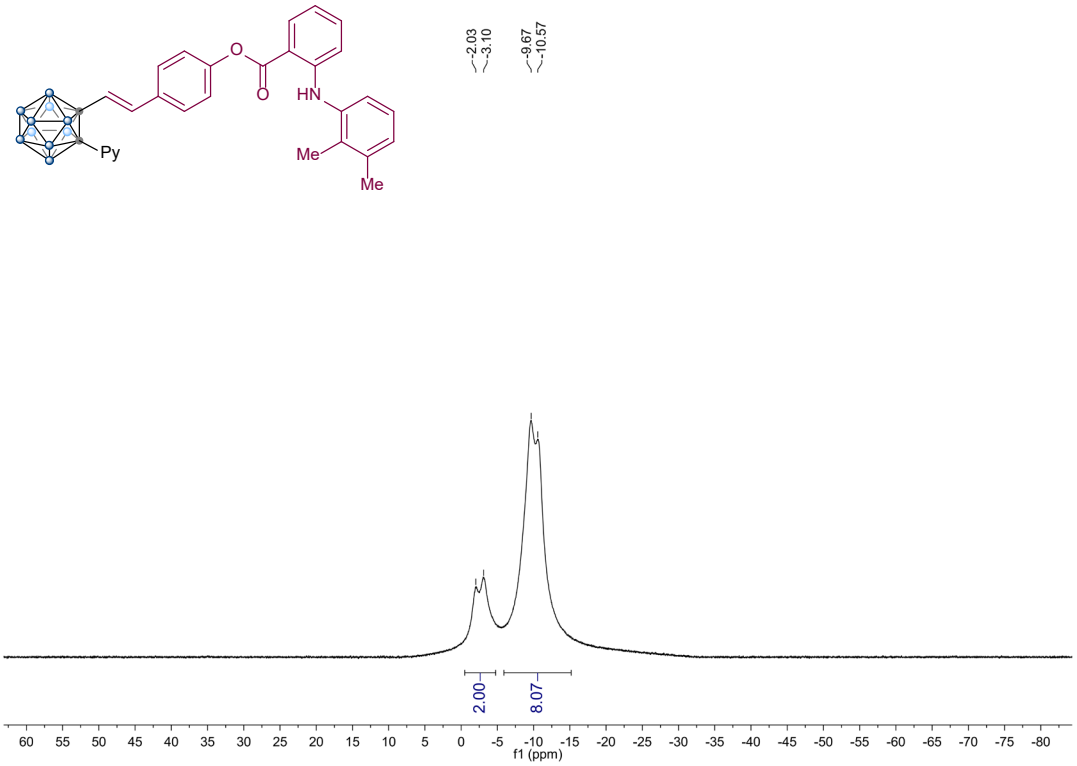
^{13}C NMR (101 MHz, Chloroform-*d*) **7b**



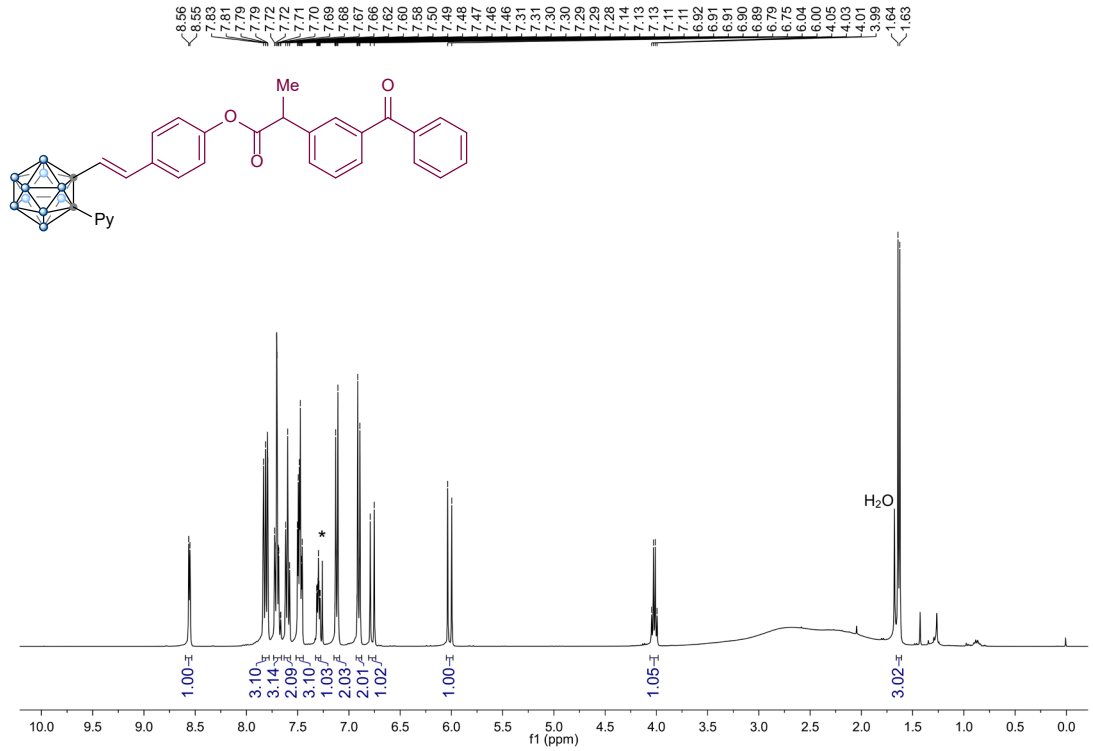
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **7b**



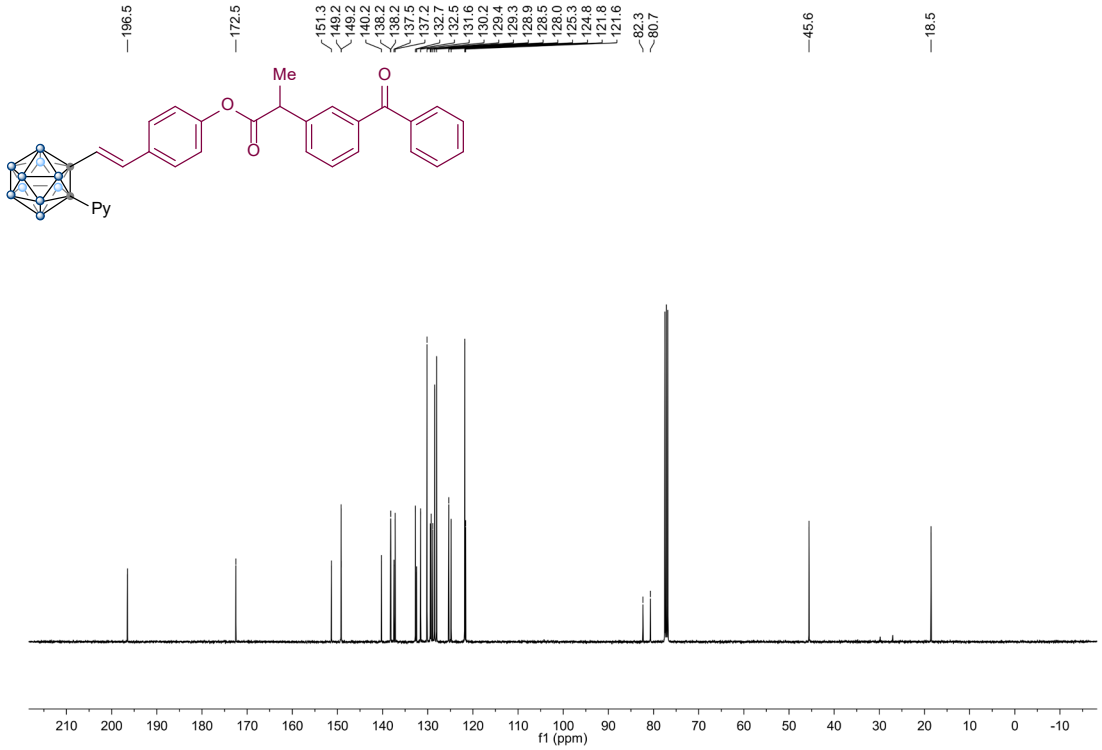
^{11}B NMR (128 MHz, Chloroform-*d*) **7b**



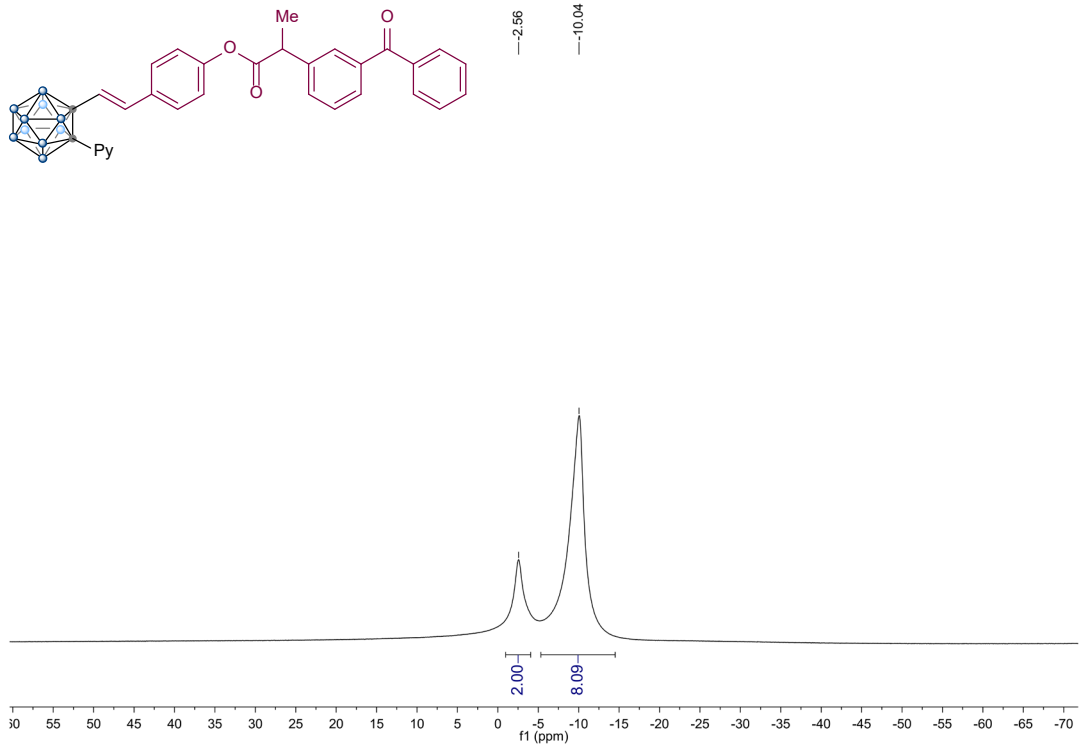
^{1}H NMR (400 MHz, Chloroform-*d*) **7c** (* from residual $CHCl_3$ in Chloroform-*d*)



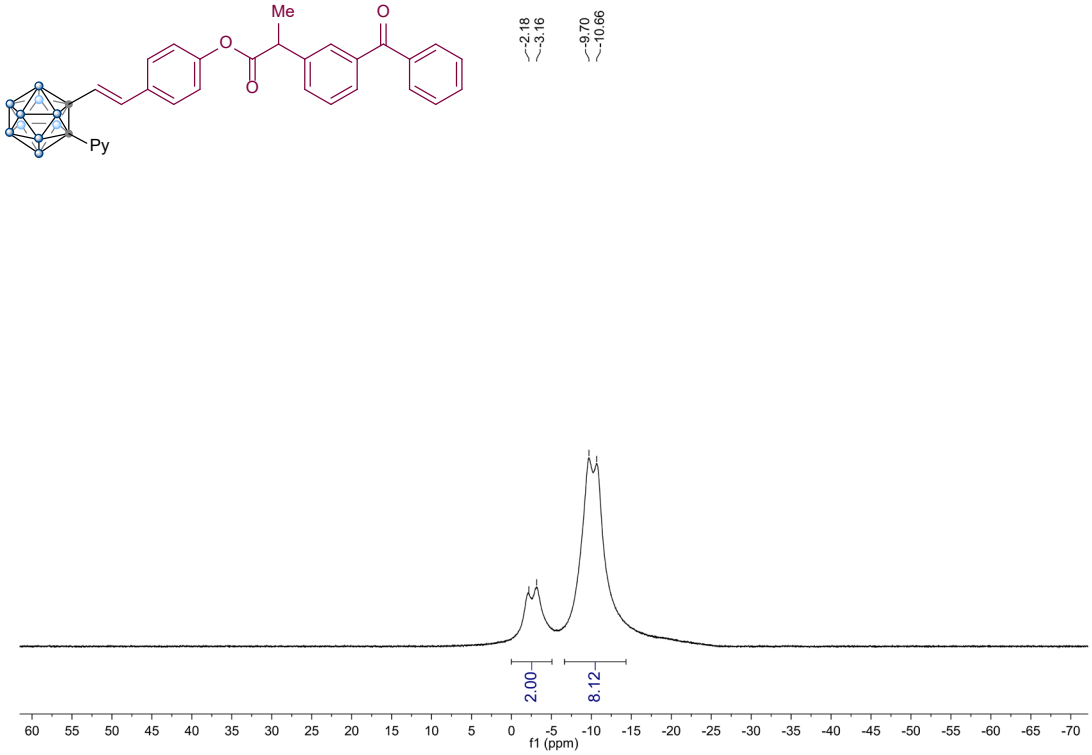
^{13}C NMR (101 MHz, Chloroform-*d*) **7c**



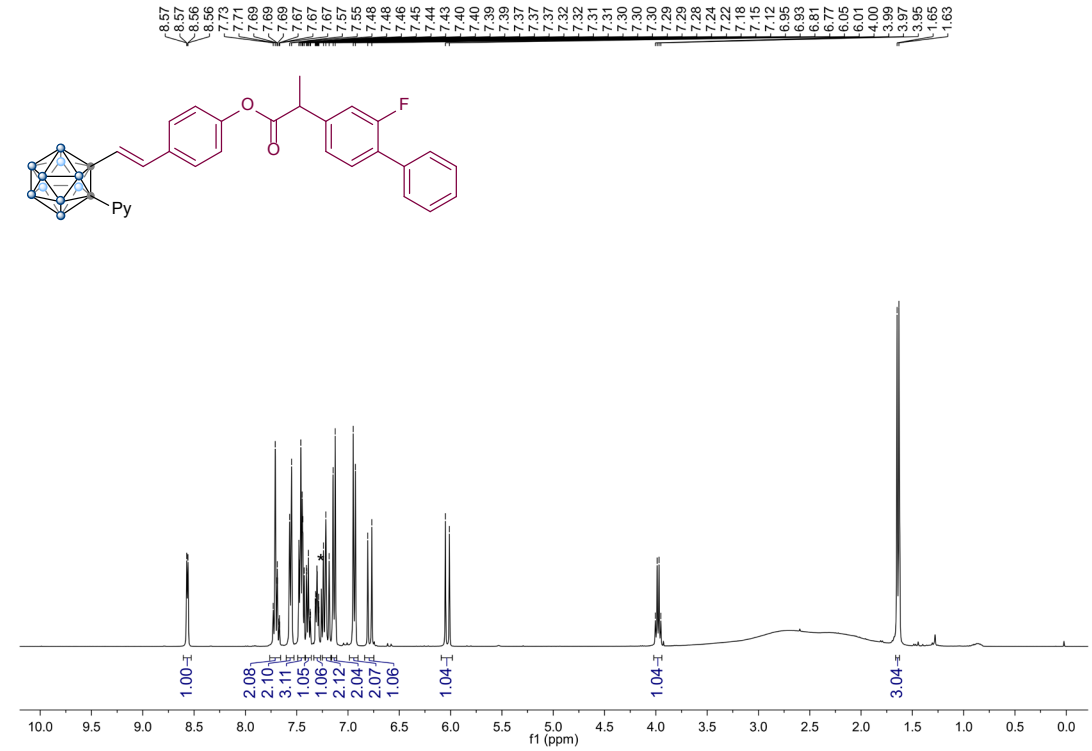
^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **7c**



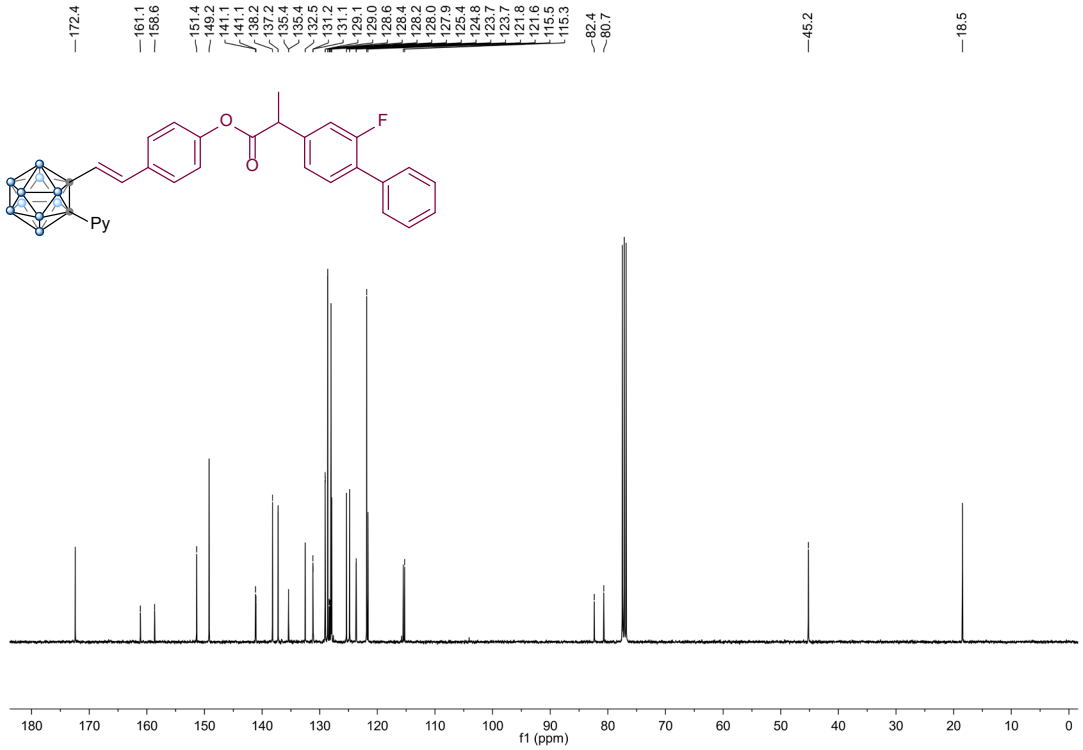
^{11}B NMR (128 MHz, Chloroform-*d*) **7c**



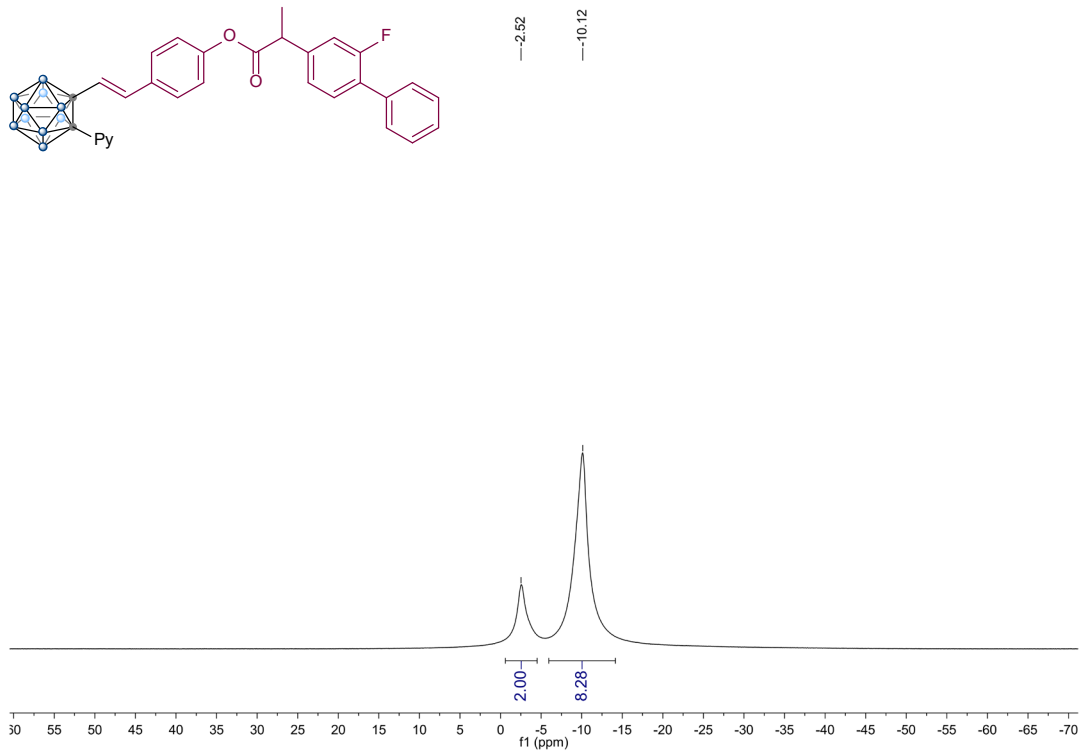
^{1}H NMR (400 MHz, Chloroform-*d*) **7d** (* from residual $CHCl_3$ in Chloroform-*d*)



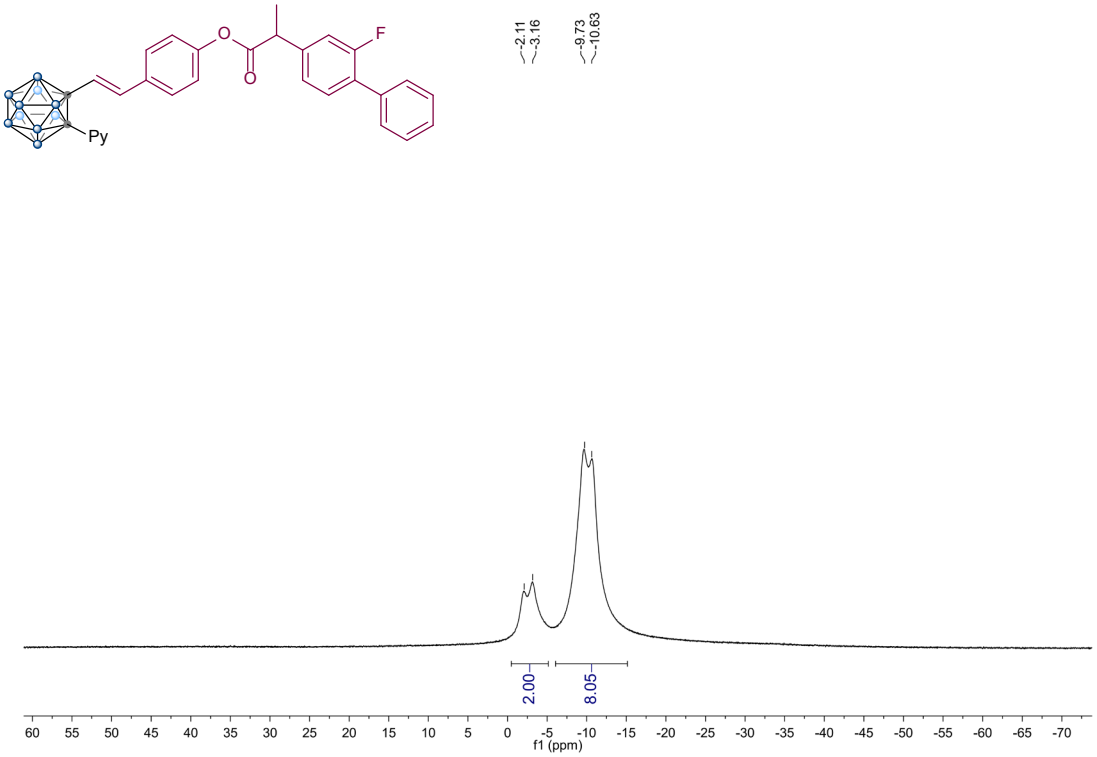
^{13}C NMR (101 MHz, Chloroform-*d*) **7d**



^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*) **7d**

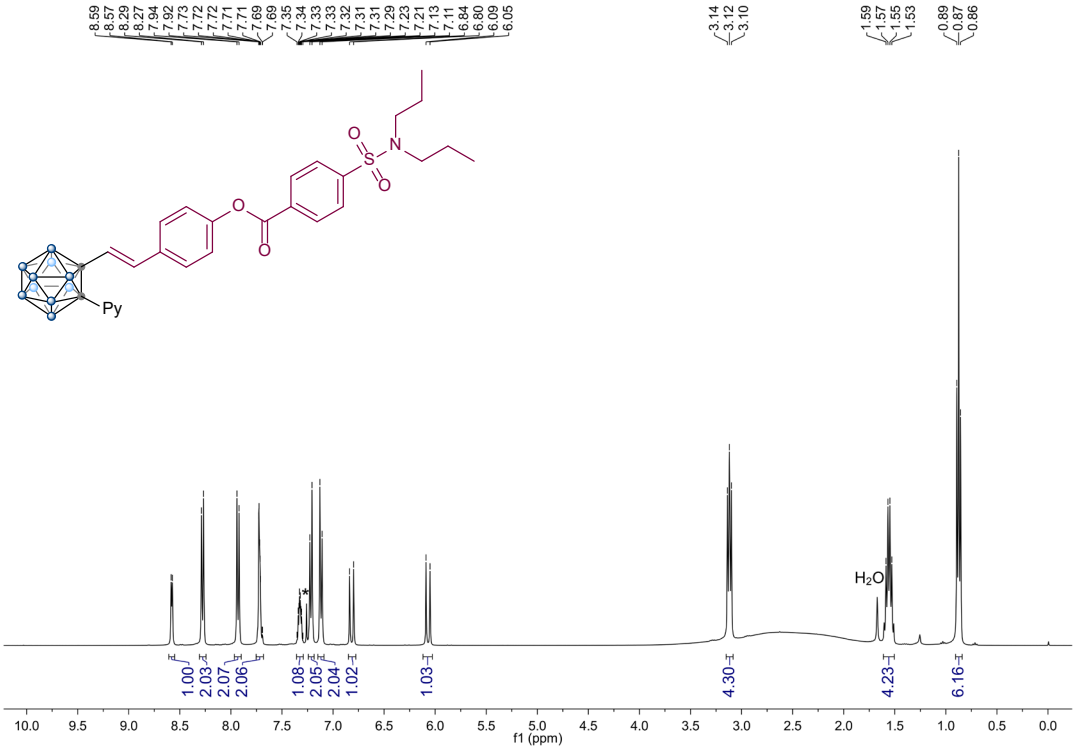


^{11}B NMR (128 MHz, Chloroform-*d*) **7d**

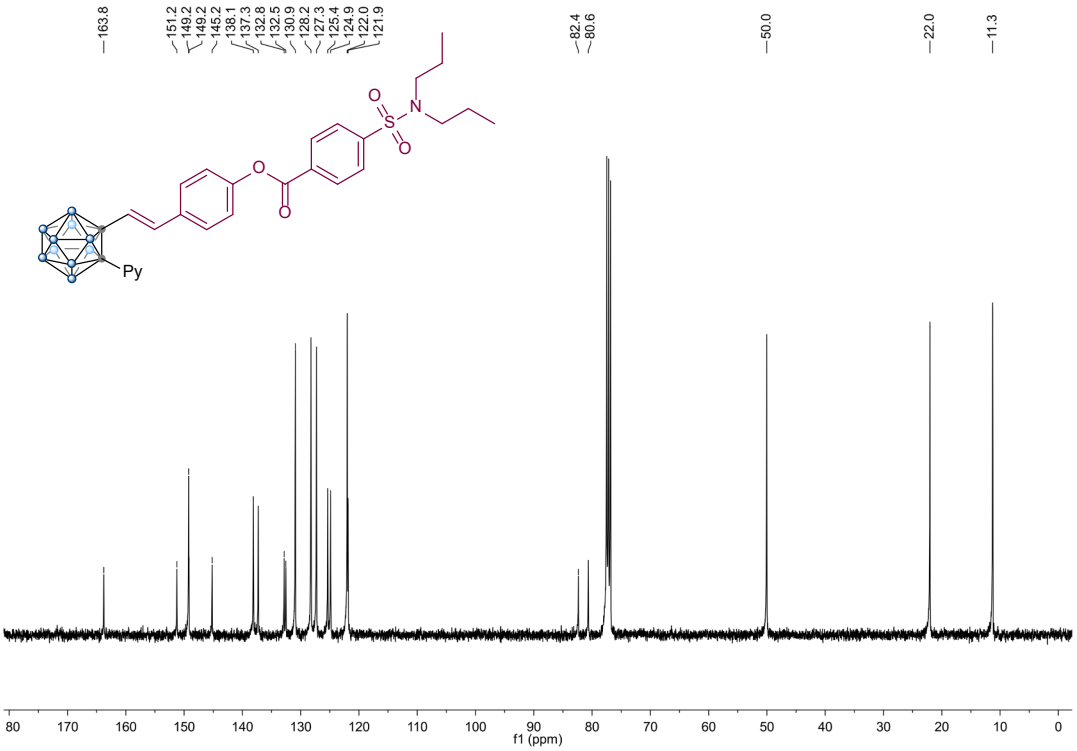


^{19}F NMR (376 MHz, Chloroform-*d*) **7d**

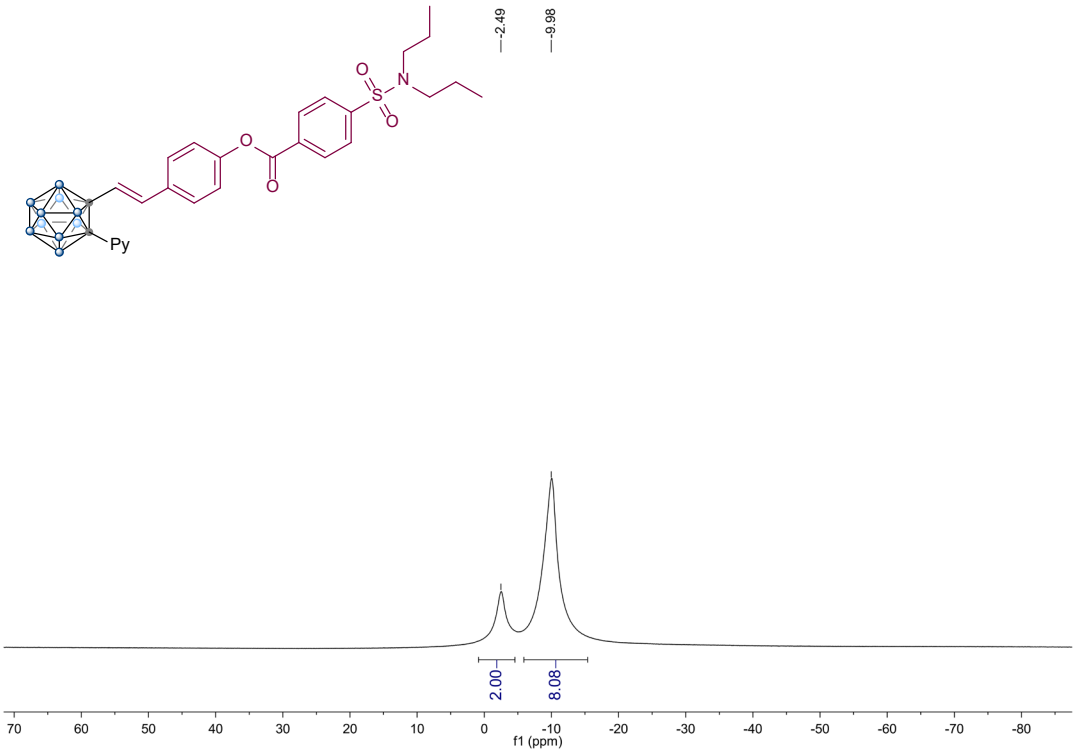
^{1}H NMR (400 MHz, Chloroform-*d*) **7e** (* from residual $CHCl_3$ in Chloroform-*d*)



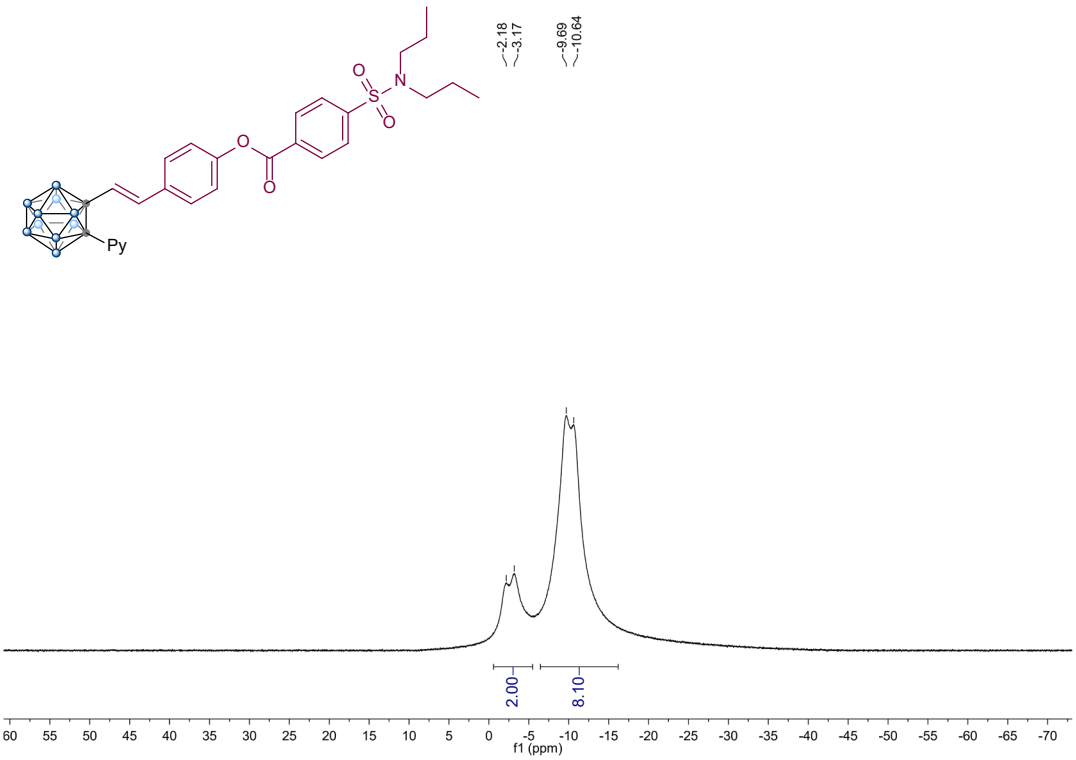
^{13}C NMR (101 MHz, Chloroform-*d*) **7e**



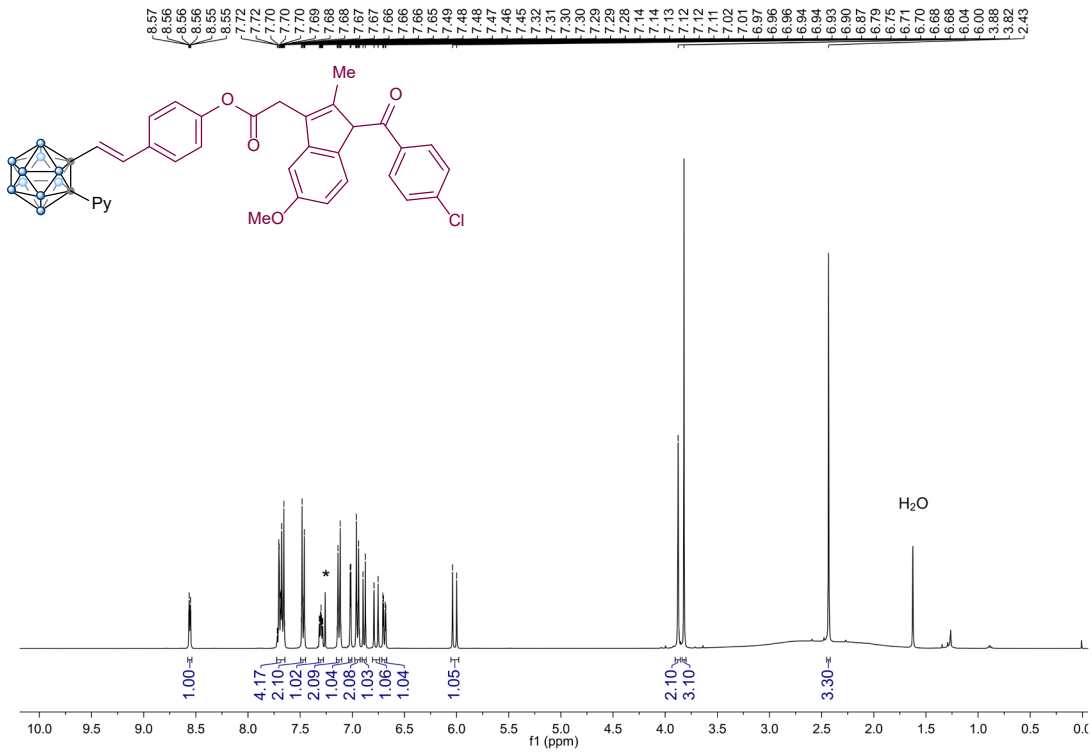
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **7e**



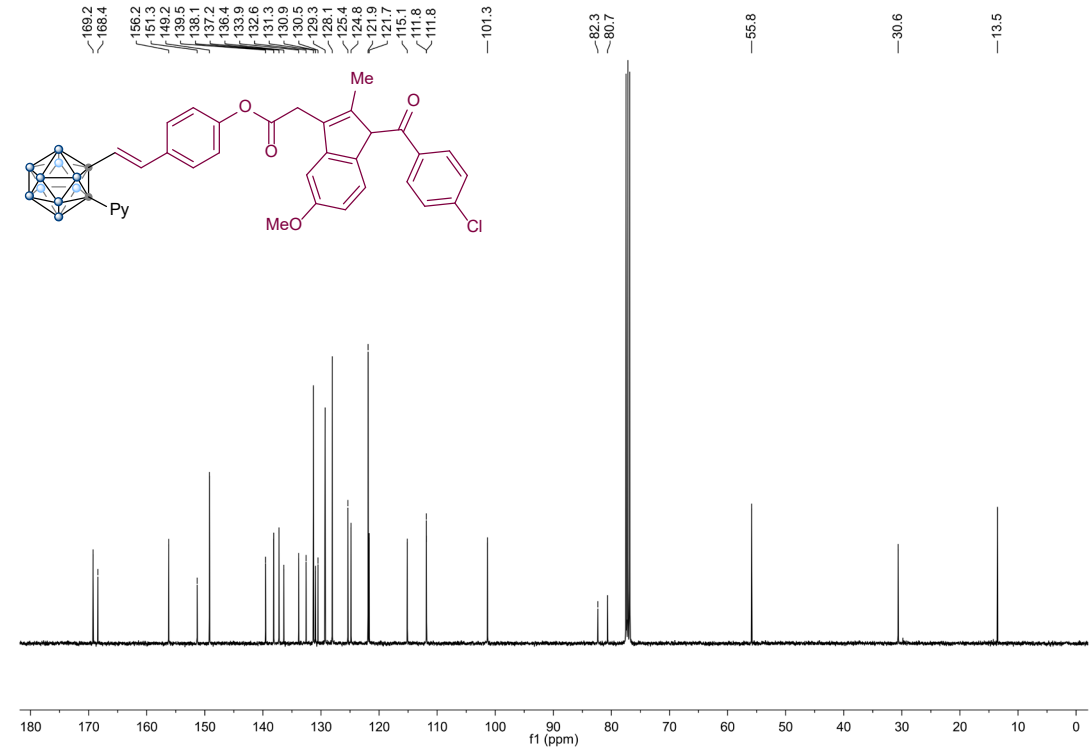
^{11}B NMR (128 MHz, Chloroform-*d*) **7e**



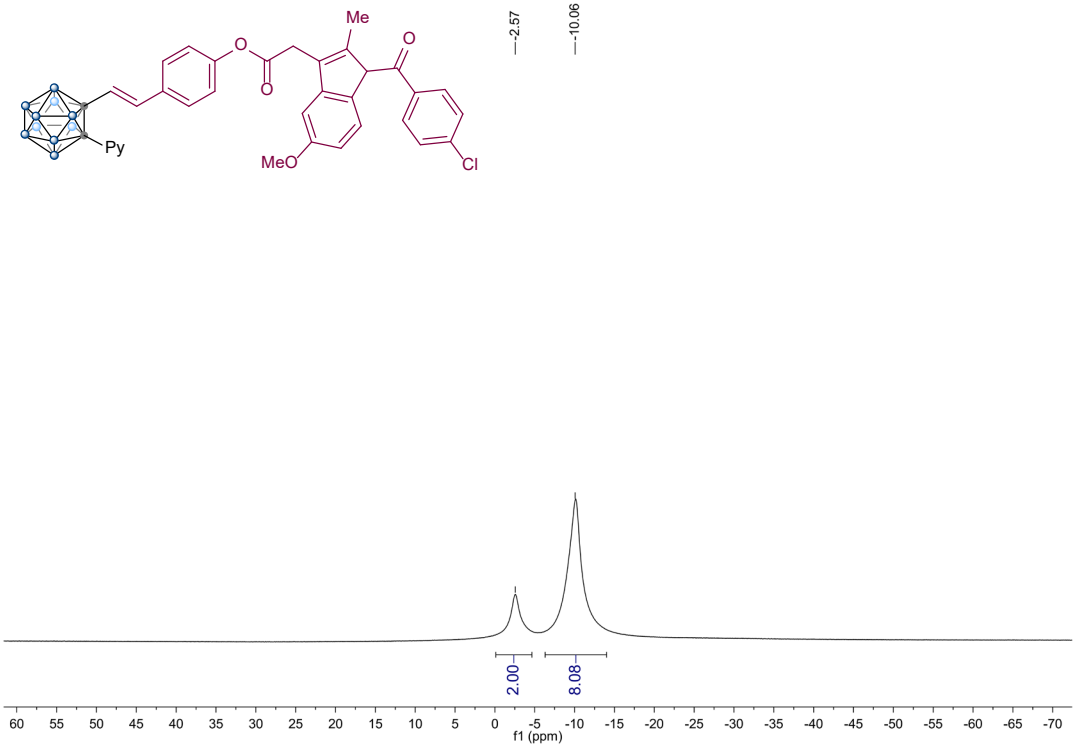
^{1}H NMR (400 MHz, Chloroform-*d*) **7f** (* from residual $CHCl_3$ in Chloroform-*d*)



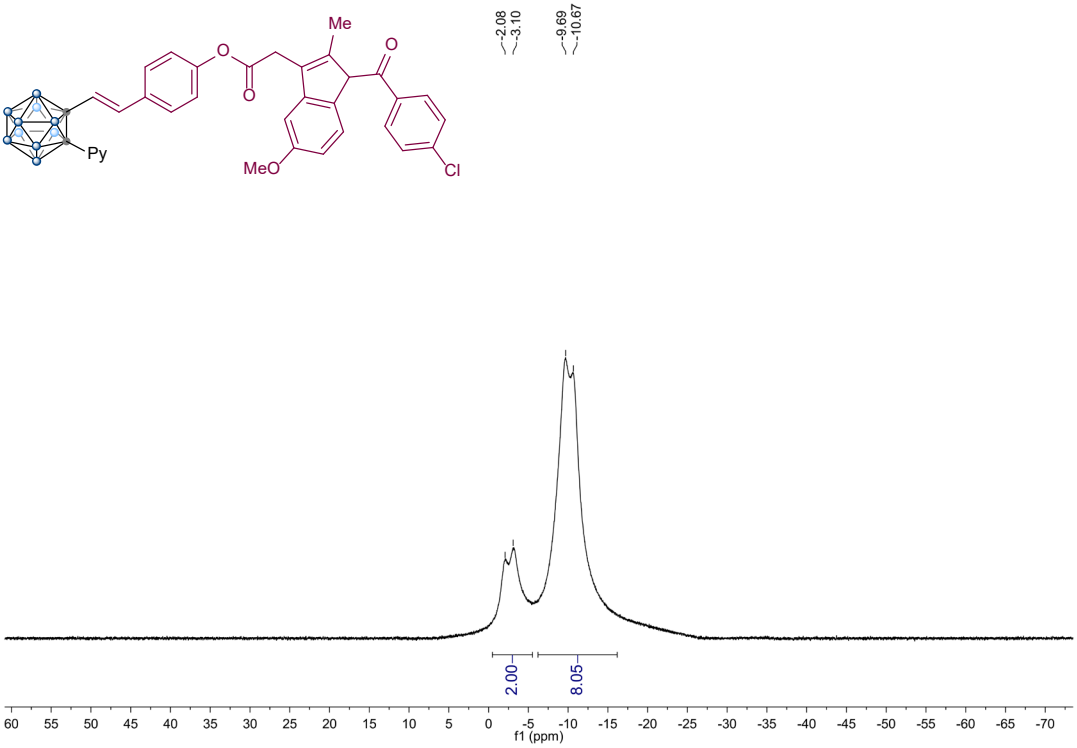
^{13}C NMR (101 MHz, Chloroform-*d*) **7f**



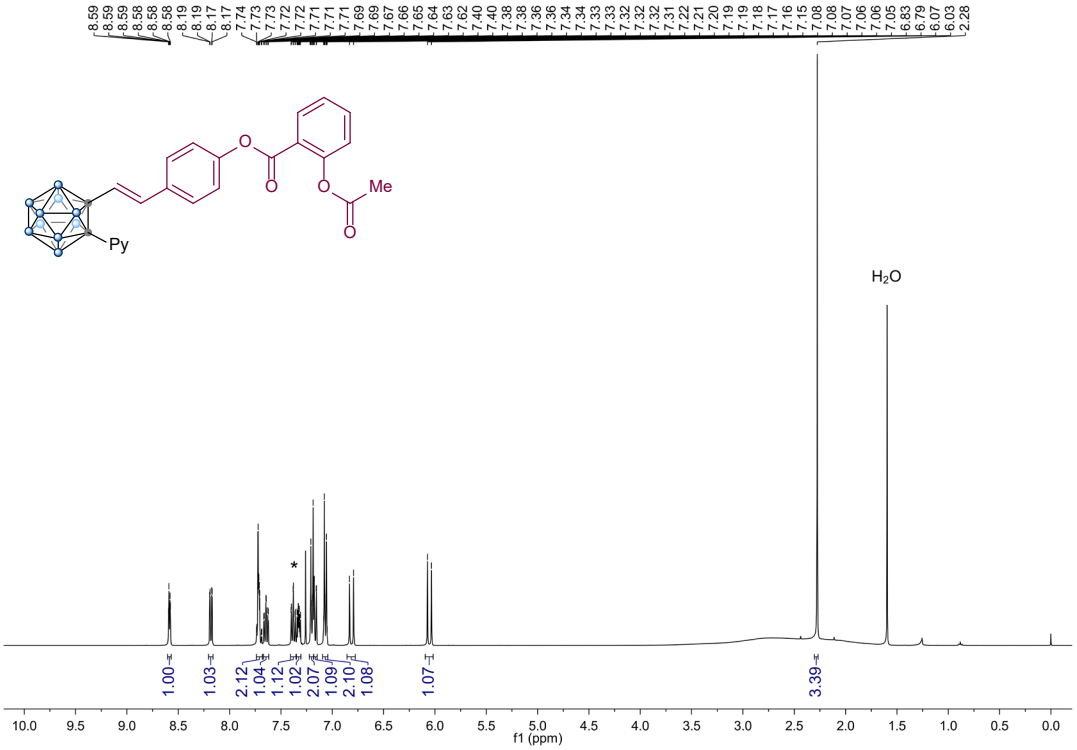
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **7f**



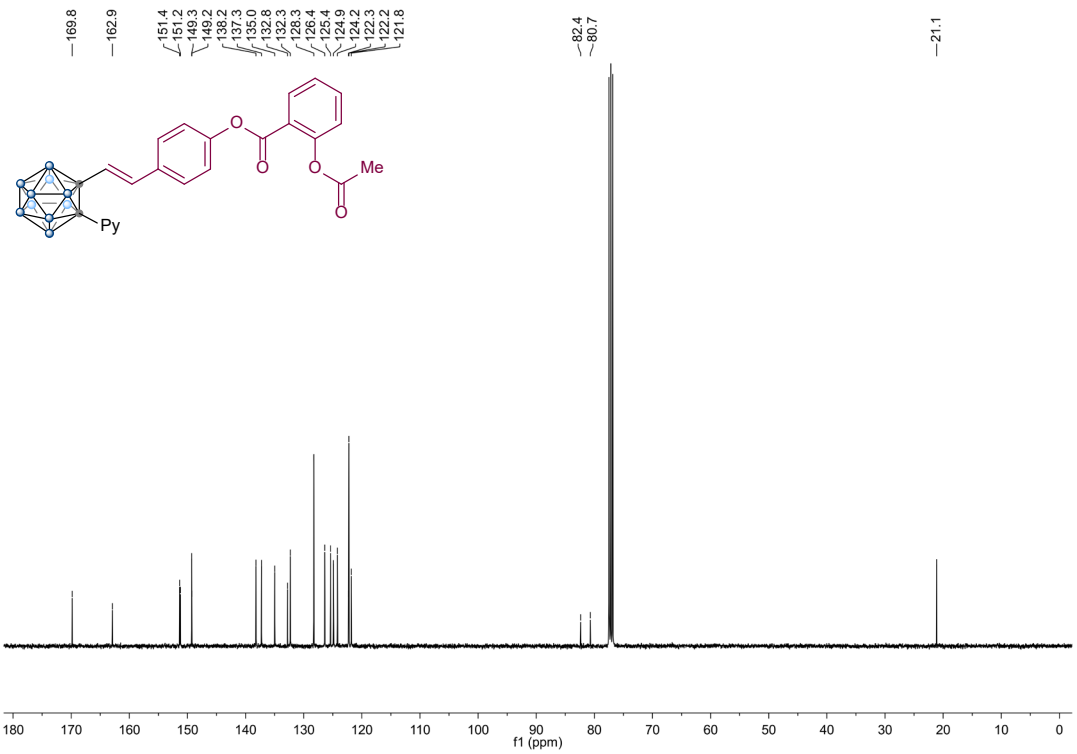
^{11}B NMR (128 MHz, Chloroform-*d*) **7f**



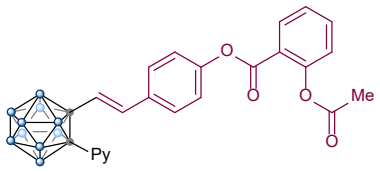
^{1}H NMR (400 MHz, Chloroform-*d*) **7g** (* from residual $CHCl_3$ in Chloroform-*d*)



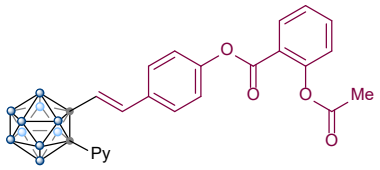
^{13}C NMR (101 MHz, Chloroform-*d*) **7g**



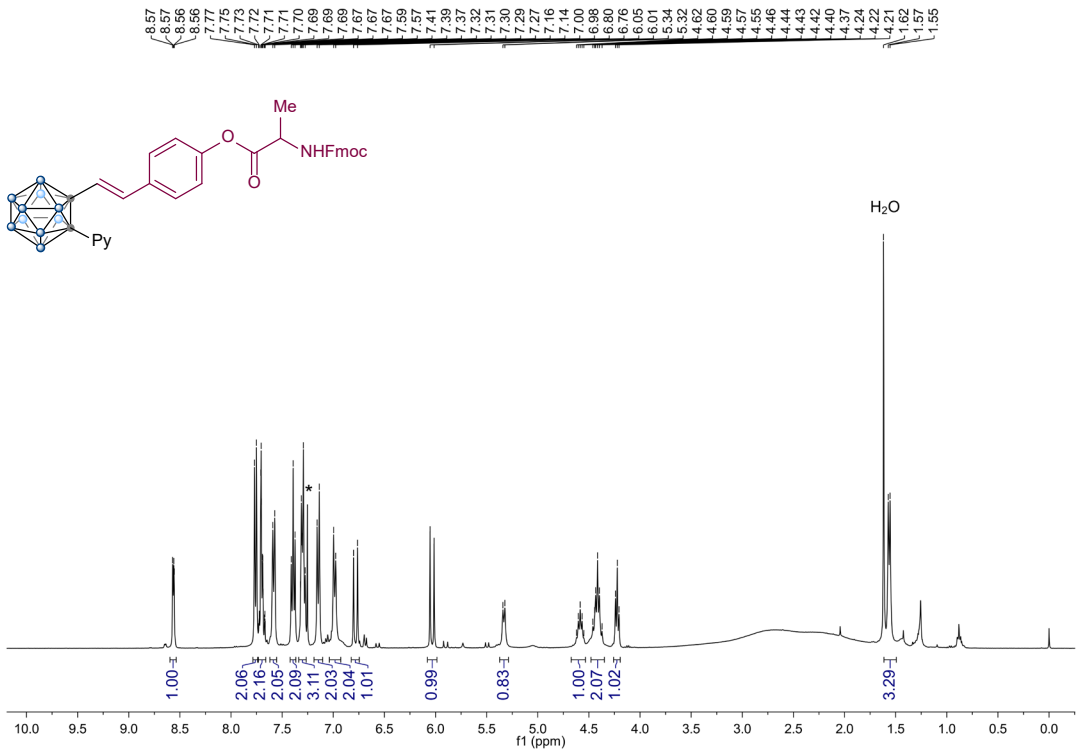
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **7g**



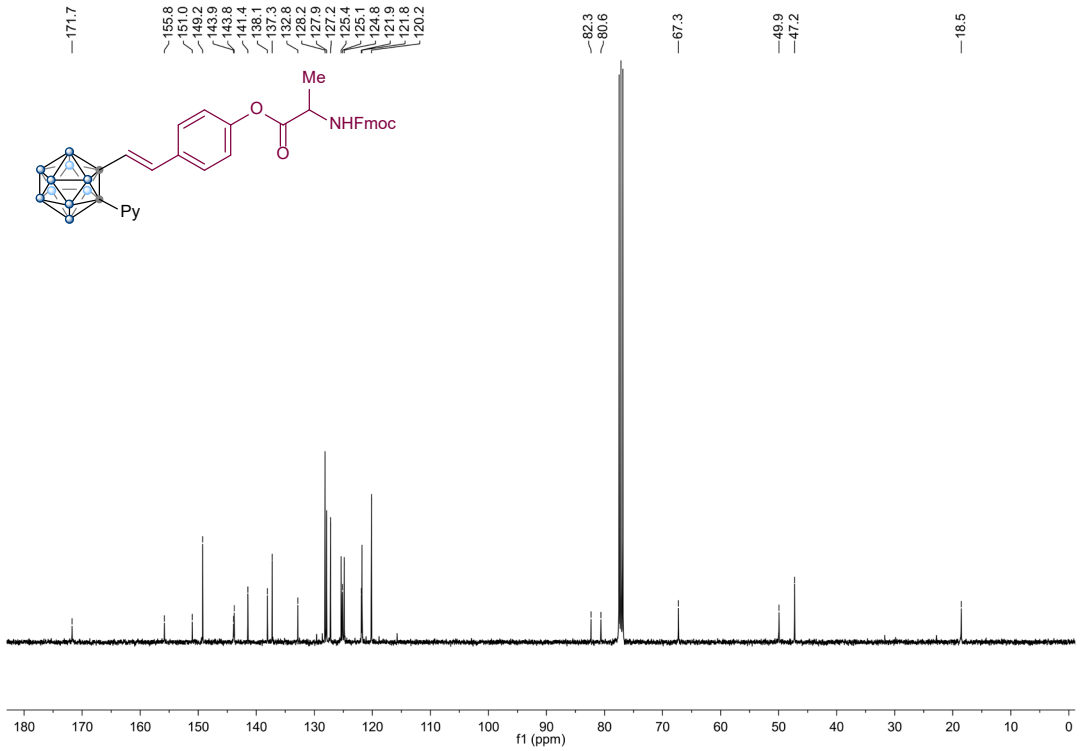
^{11}B NMR (128 MHz, Chloroform-*d*) **7g**



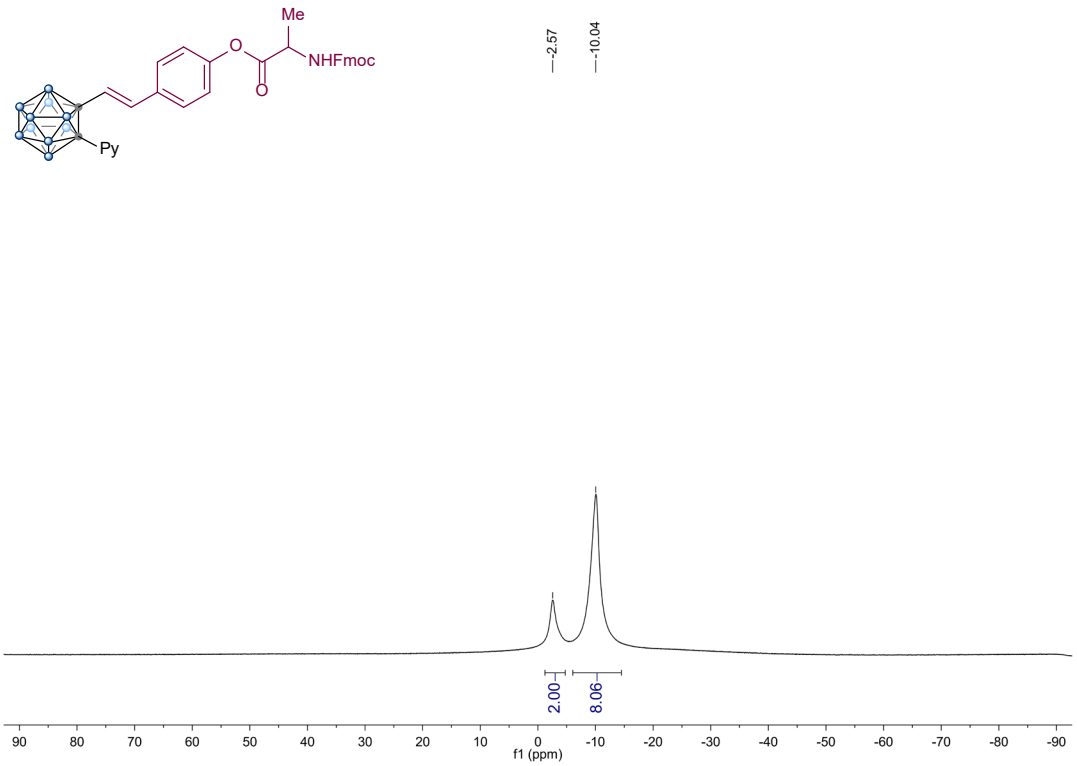
^{1}H NMR (400 MHz, Chloroform-*d*) **7h** (* from residual $CHCl_3$ in Chloroform-*d*)



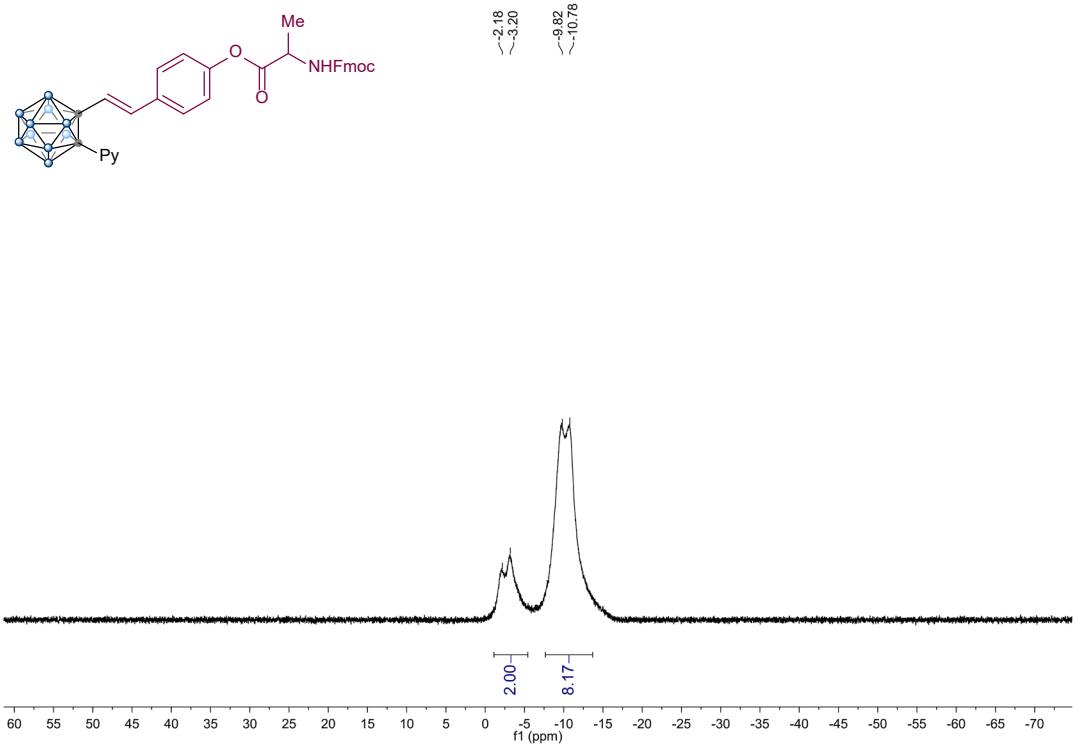
^{13}C NMR (101 MHz, Chloroform-*d*) **7h**



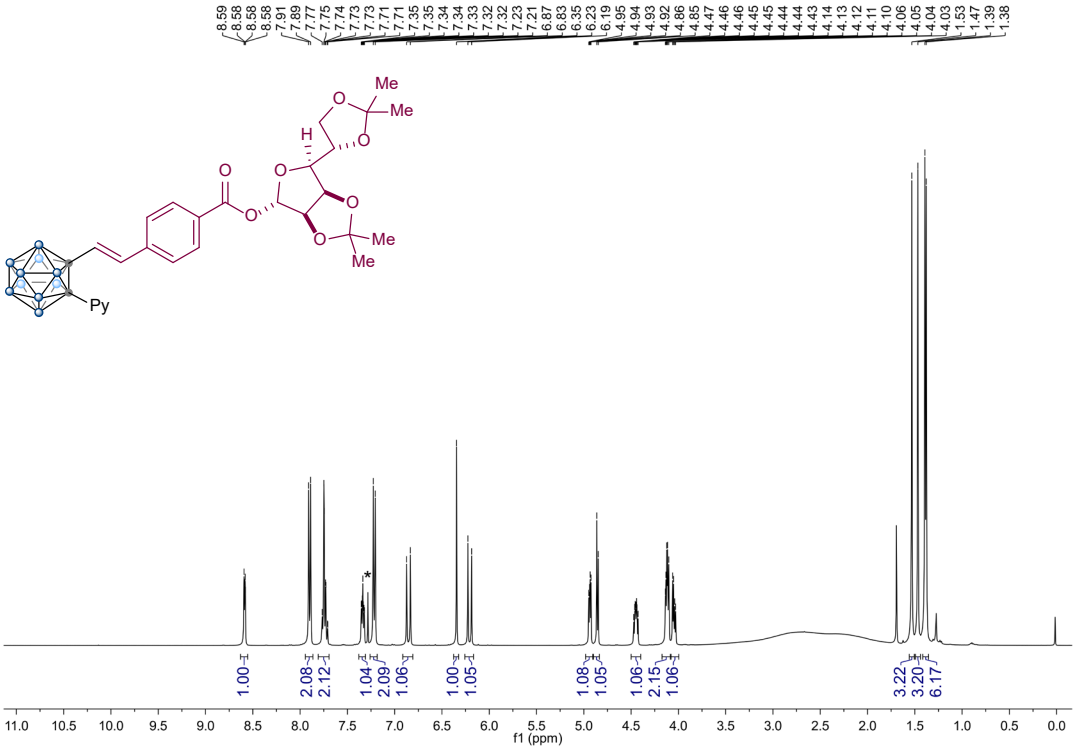
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **7h**



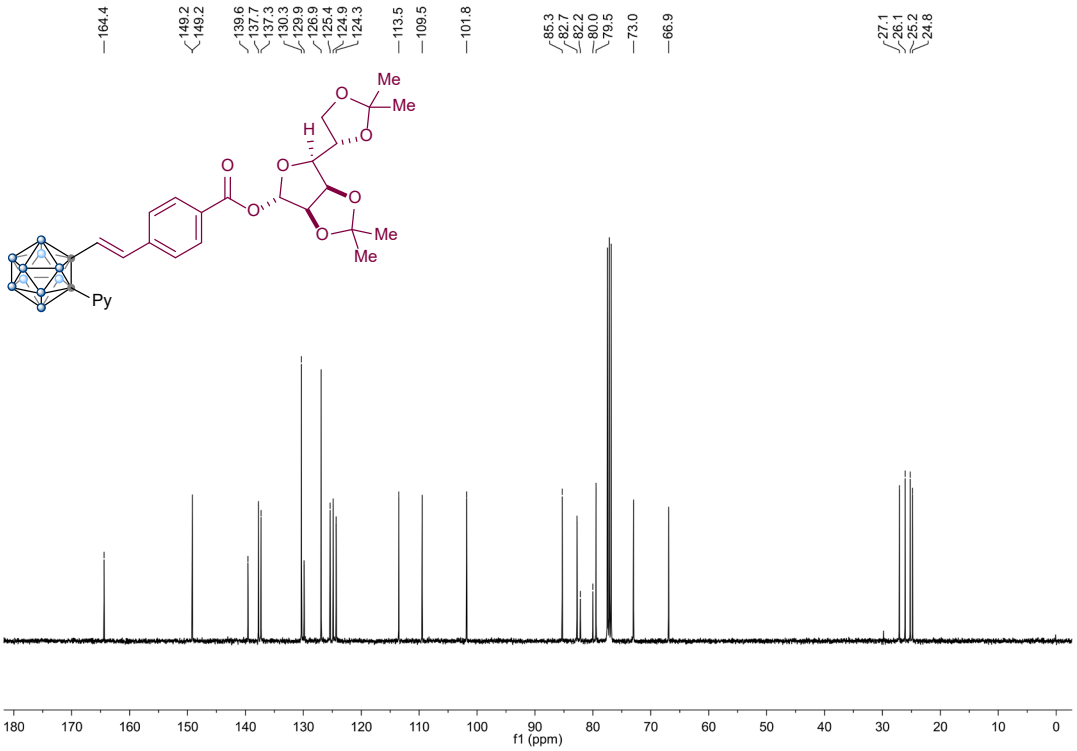
^{11}B NMR (128 MHz, Chloroform-*d*) **7h**



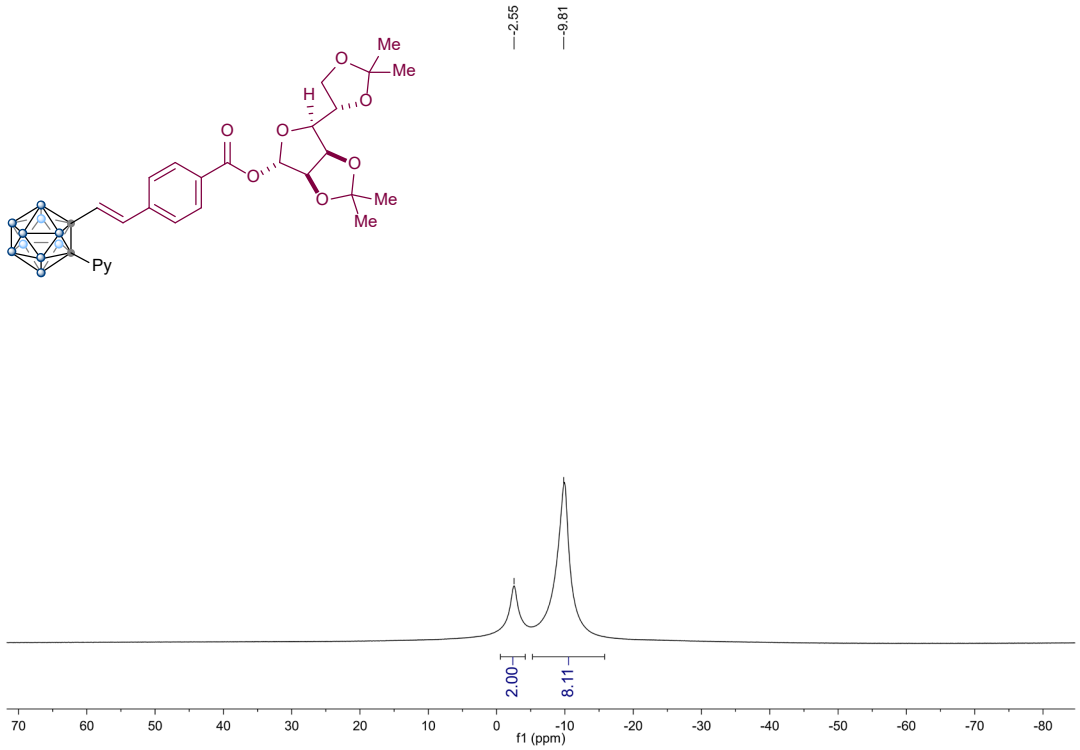
^{1}H NMR (400 MHz, Chloroform-*d*) **7i** (* from residual $CHCl_3$ in Chloroform-*d*)



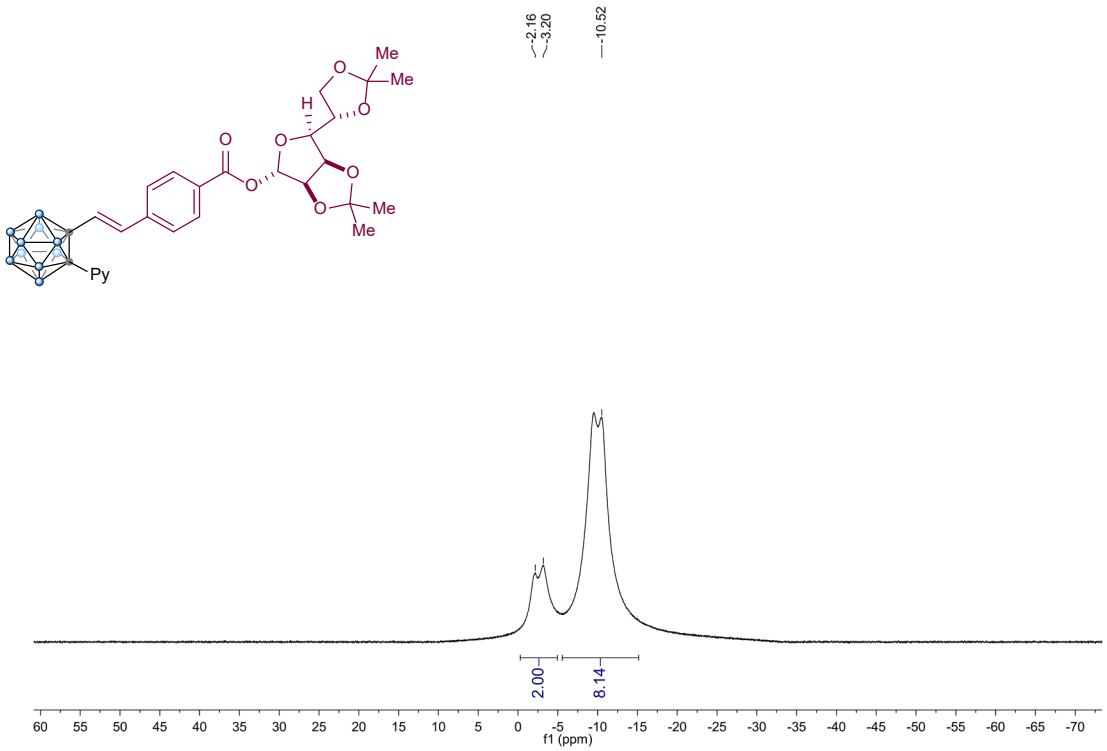
^{13}C NMR (101 MHz, Chloroform-*d*) **7i**



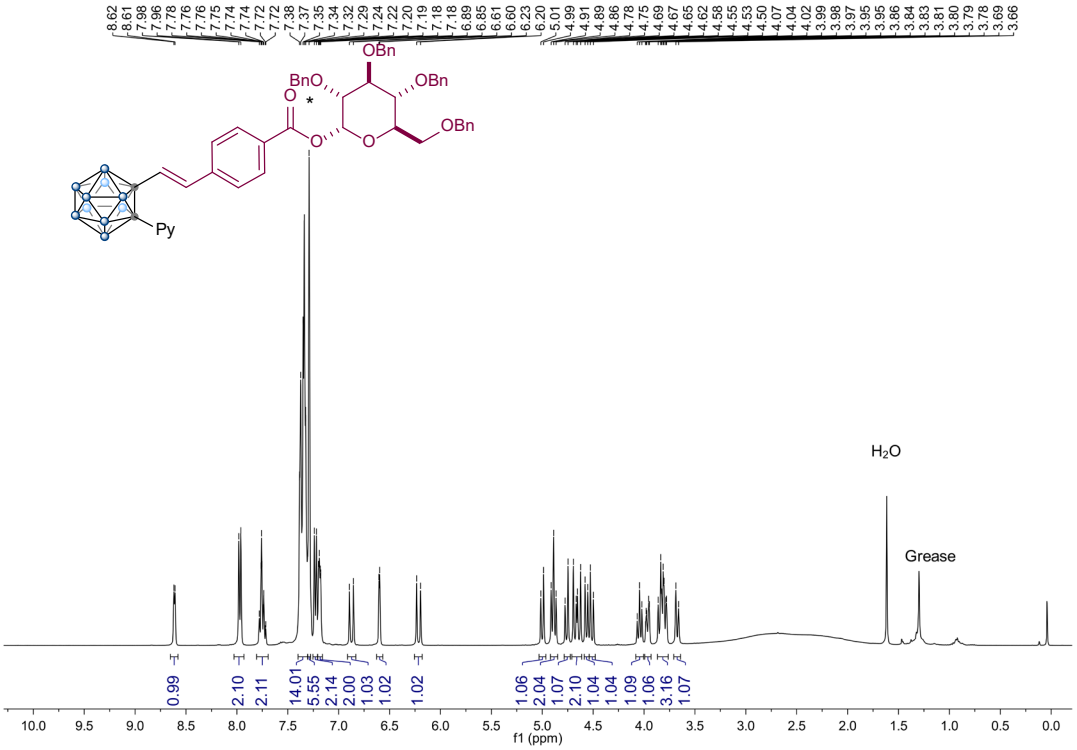
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **7i**



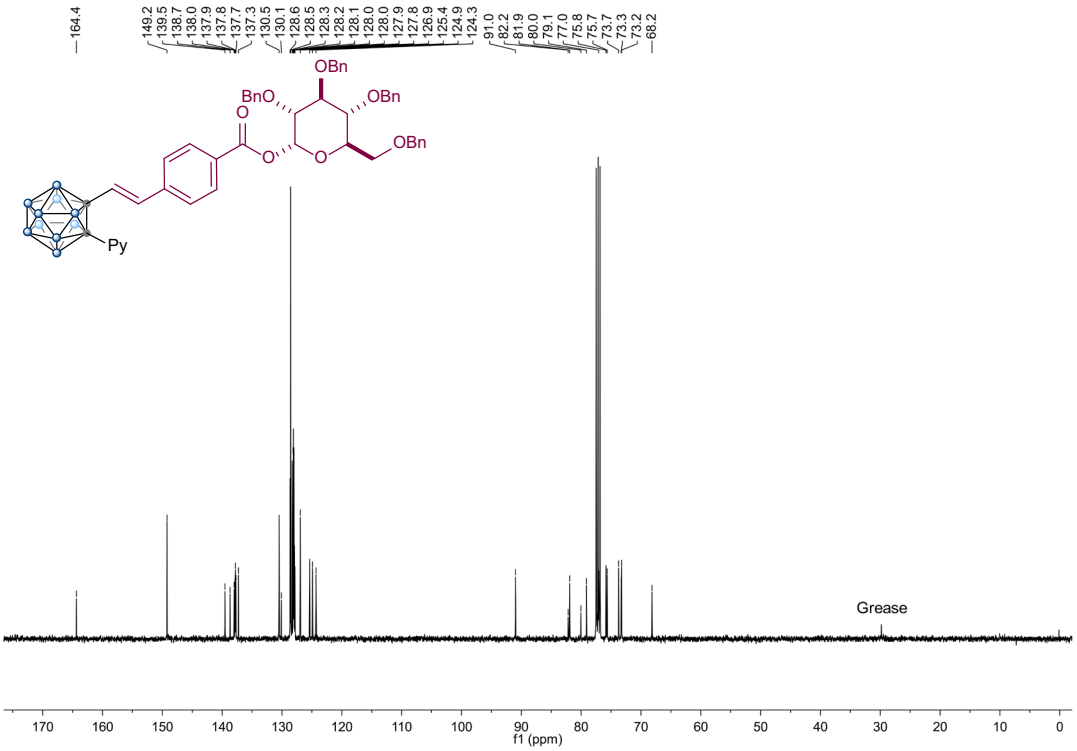
^{11}B NMR (128 MHz, Chloroform-*d*) **7i**



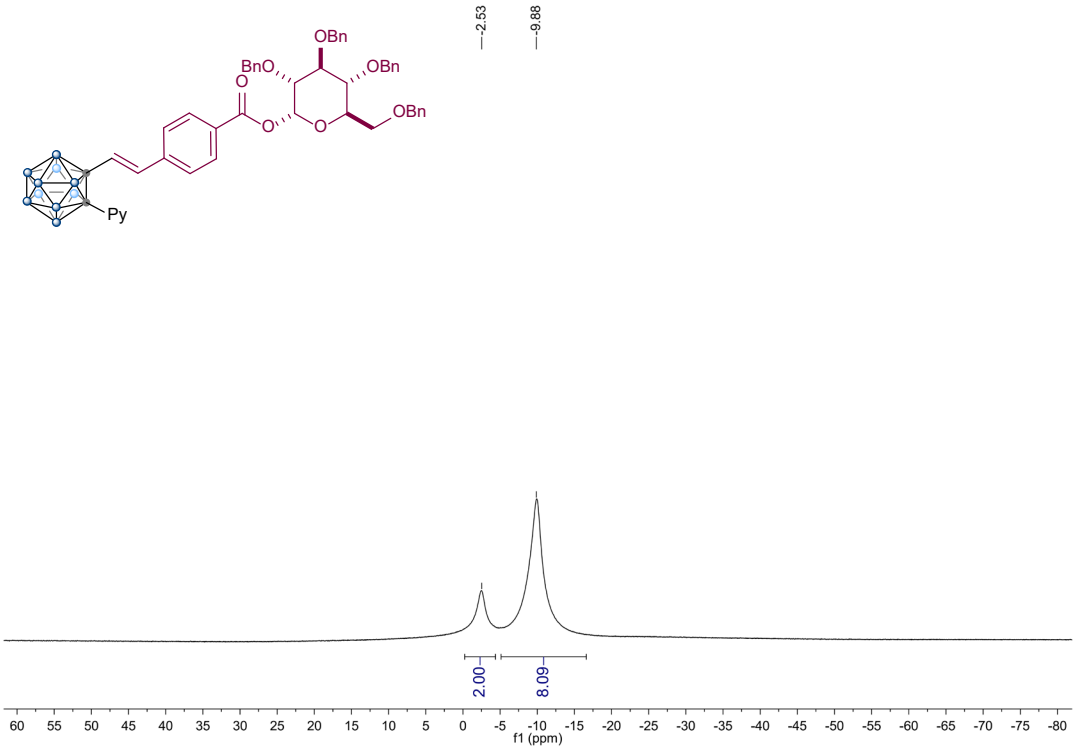
^{1}H NMR (400 MHz, Chloroform-*d*) **7j** (* from residual $CHCl_3$ in Chloroform-*d*)



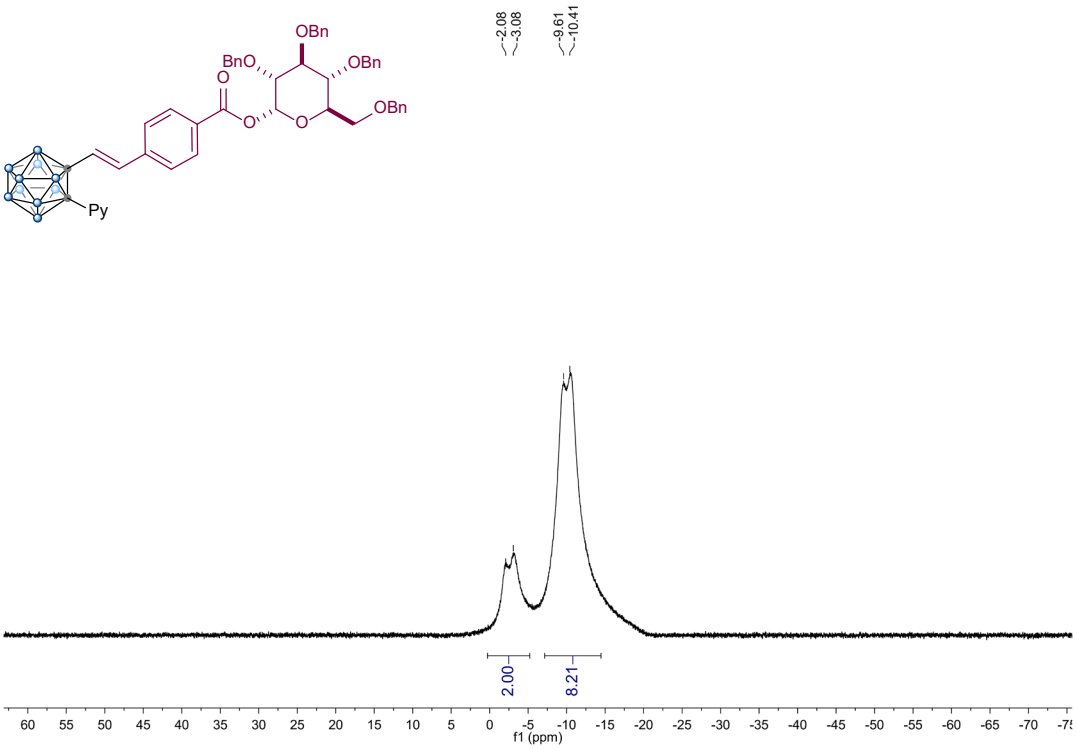
^{13}C NMR (101 MHz, Chloroform-*d*) **7j**



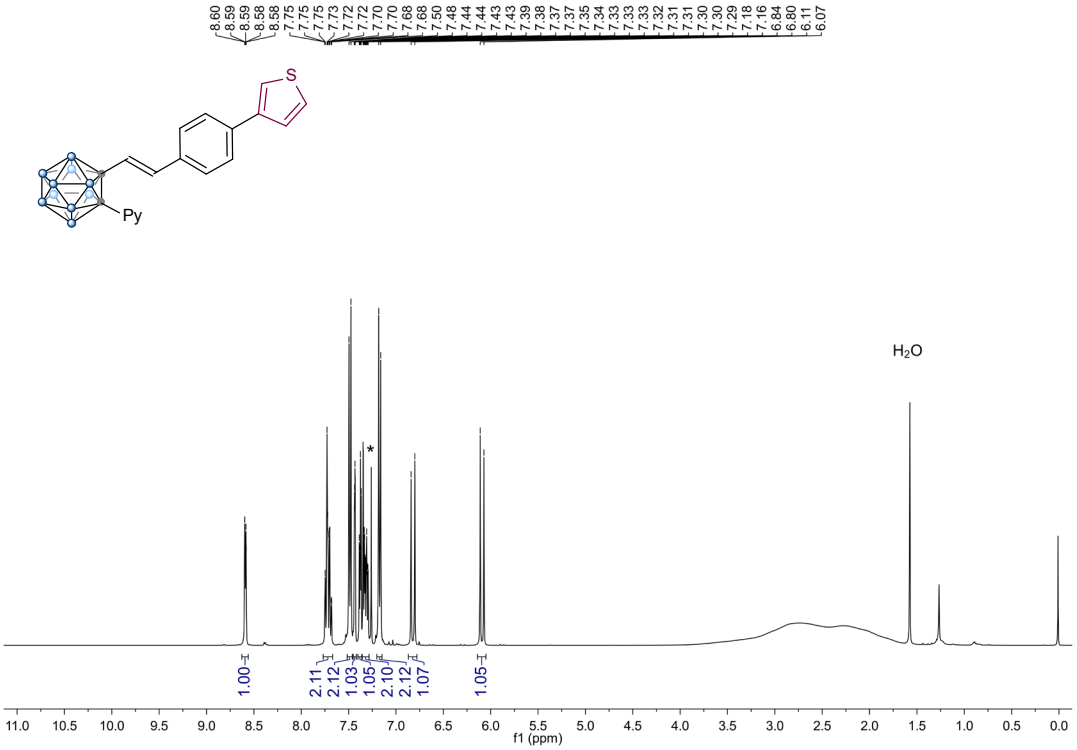
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **7j**



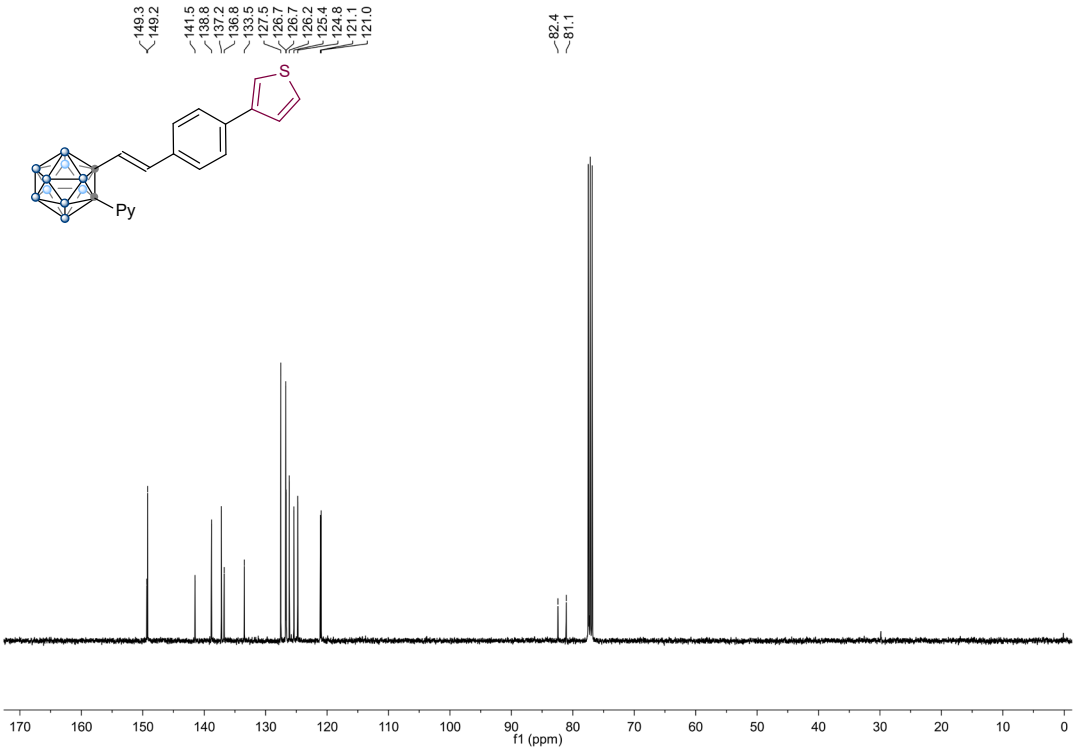
^{11}B NMR (128 MHz, Chloroform-*d*) **7j**



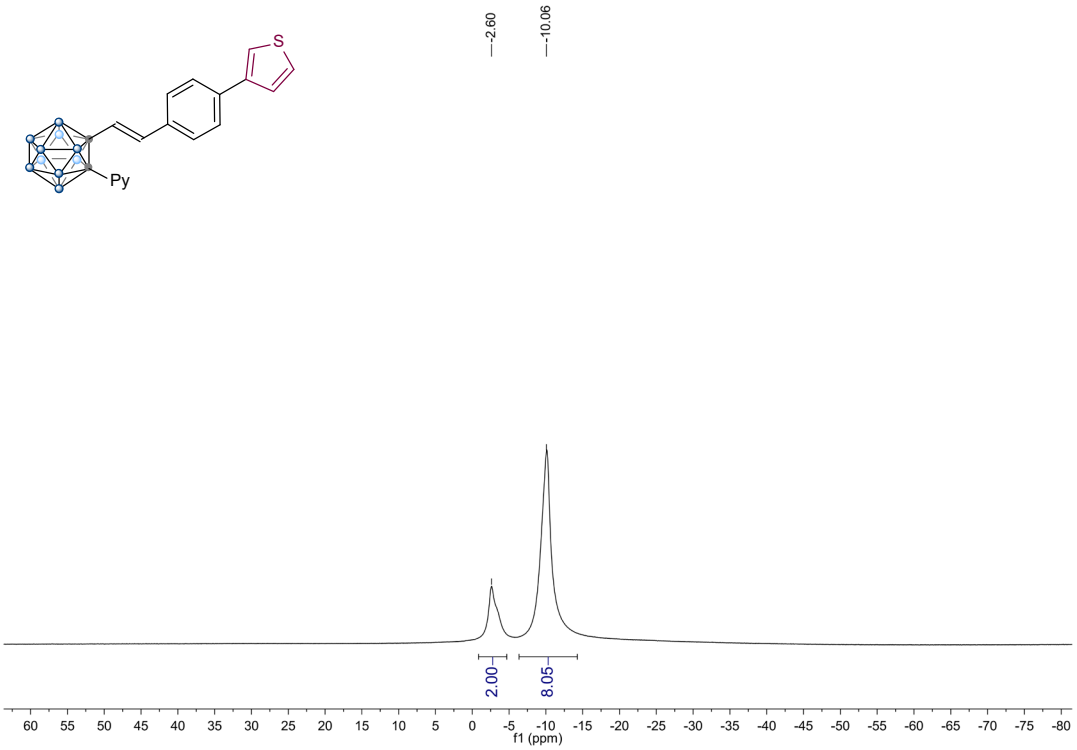
^{1}H NMR (400 MHz, Chloroform-*d*) **8a** (* from residual $CHCl_3$ in Chloroform-*d*)



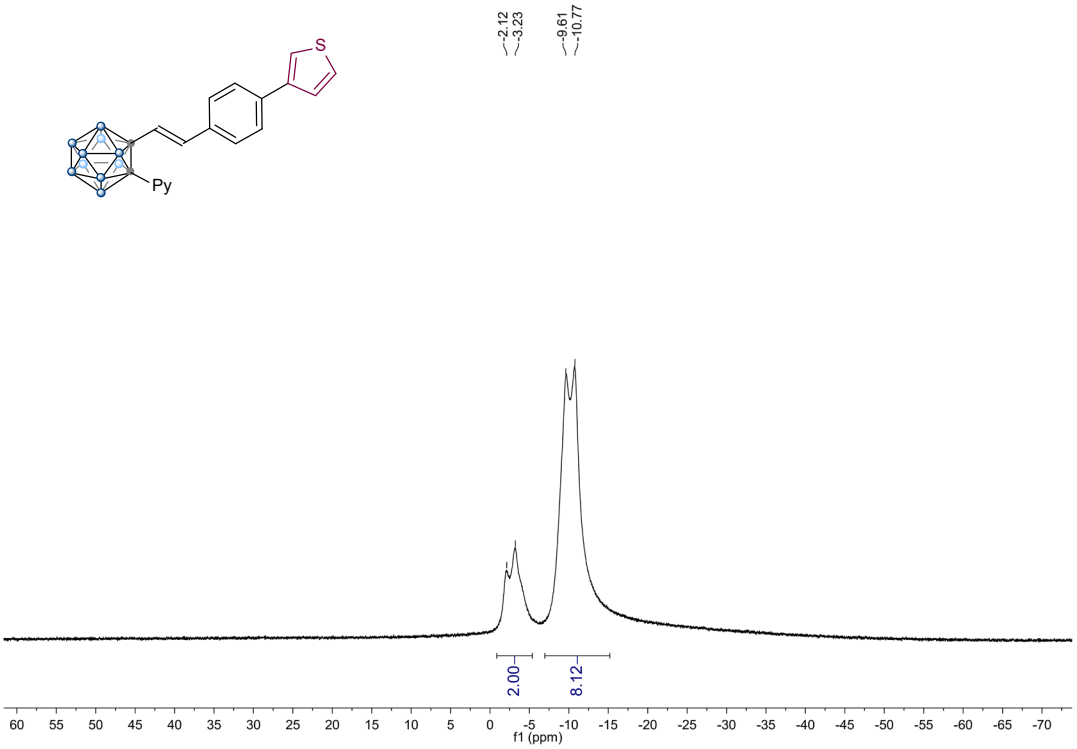
^{13}C NMR (101 MHz, Chloroform-*d*) **8a**



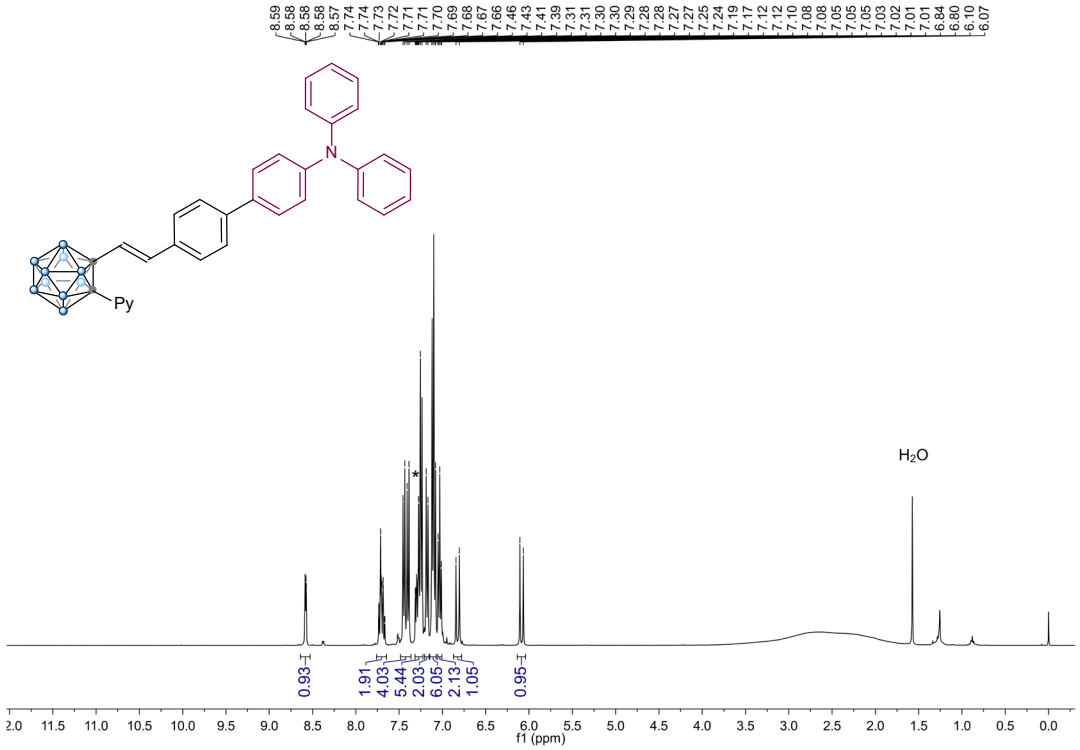
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **8a**



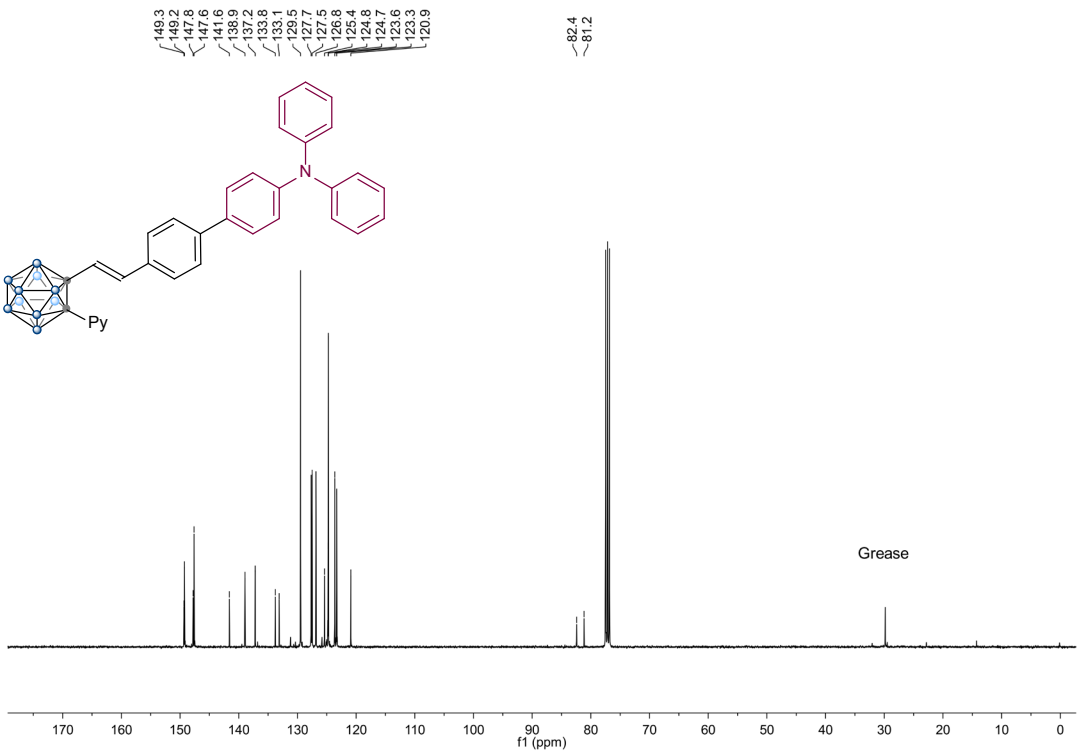
^{11}B NMR (128 MHz, Chloroform-*d*) **8a**



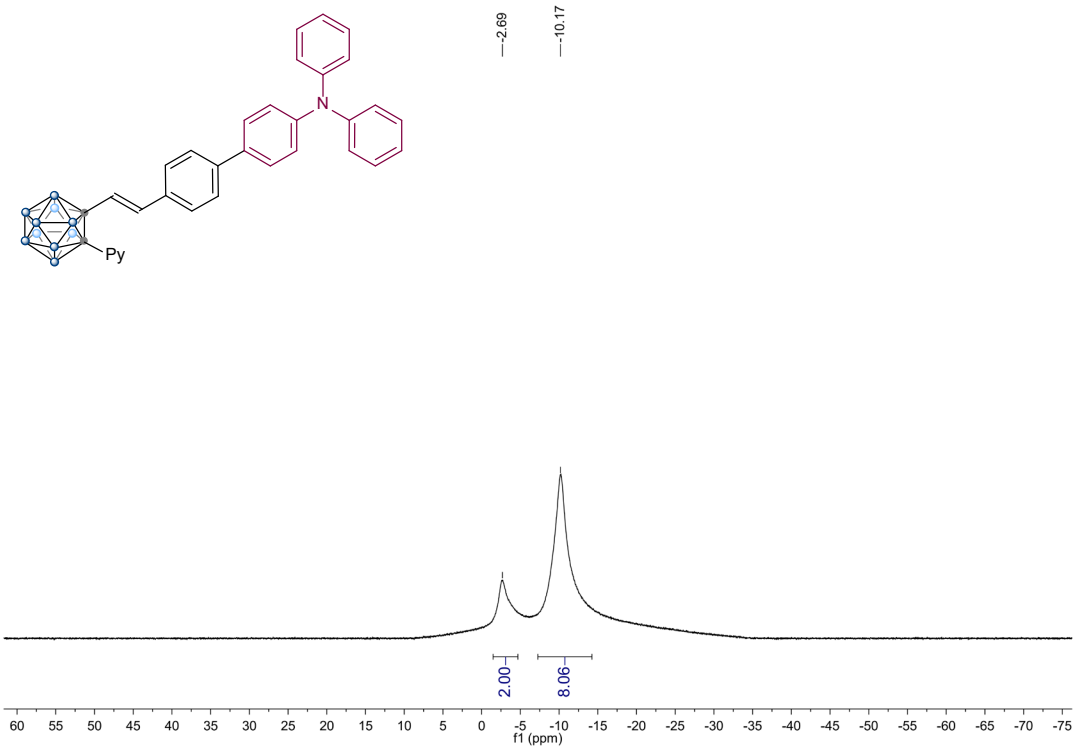
^{1}H NMR (400 MHz, Chloroform-*d*) **8b** (* from residual $CHCl_3$ in Chloroform-*d*)



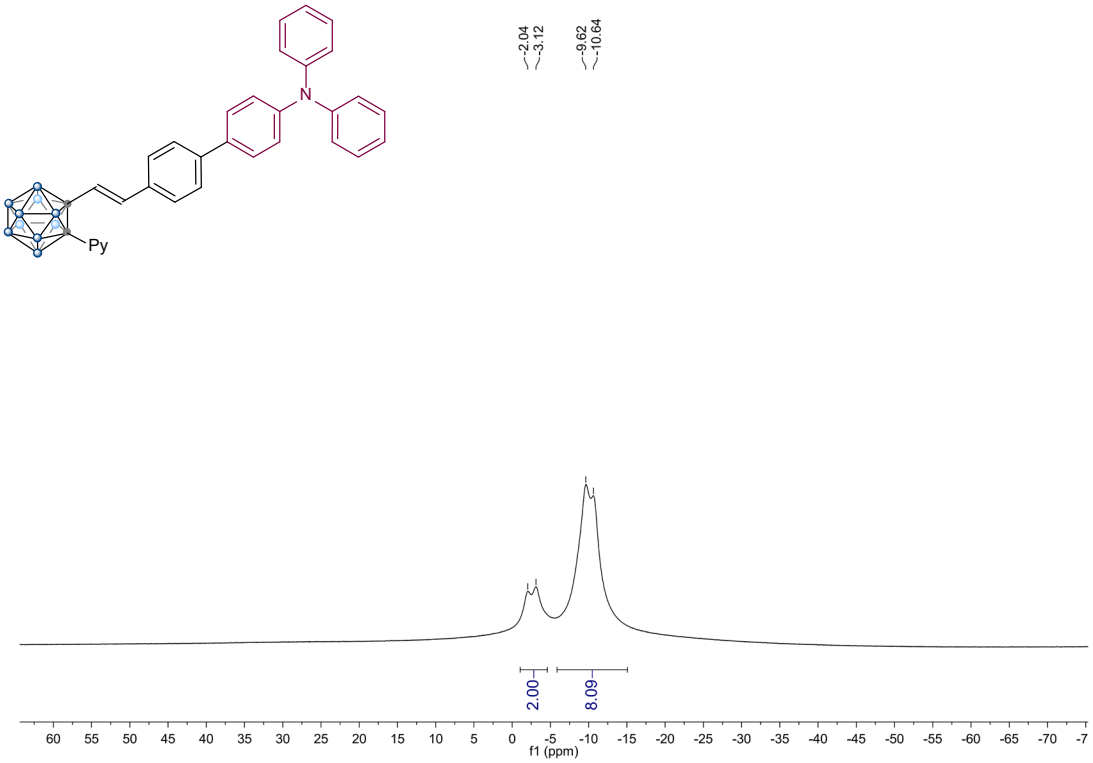
^{13}C NMR (101 MHz, Chloroform-*d*) **8b**



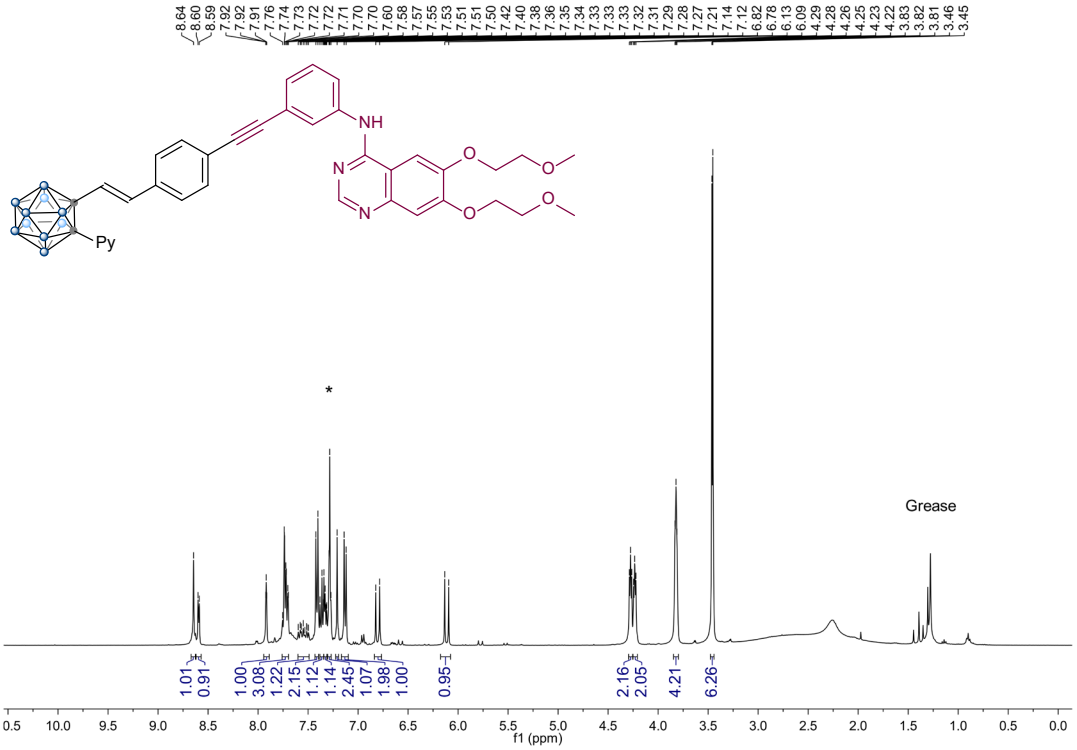
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **8b**



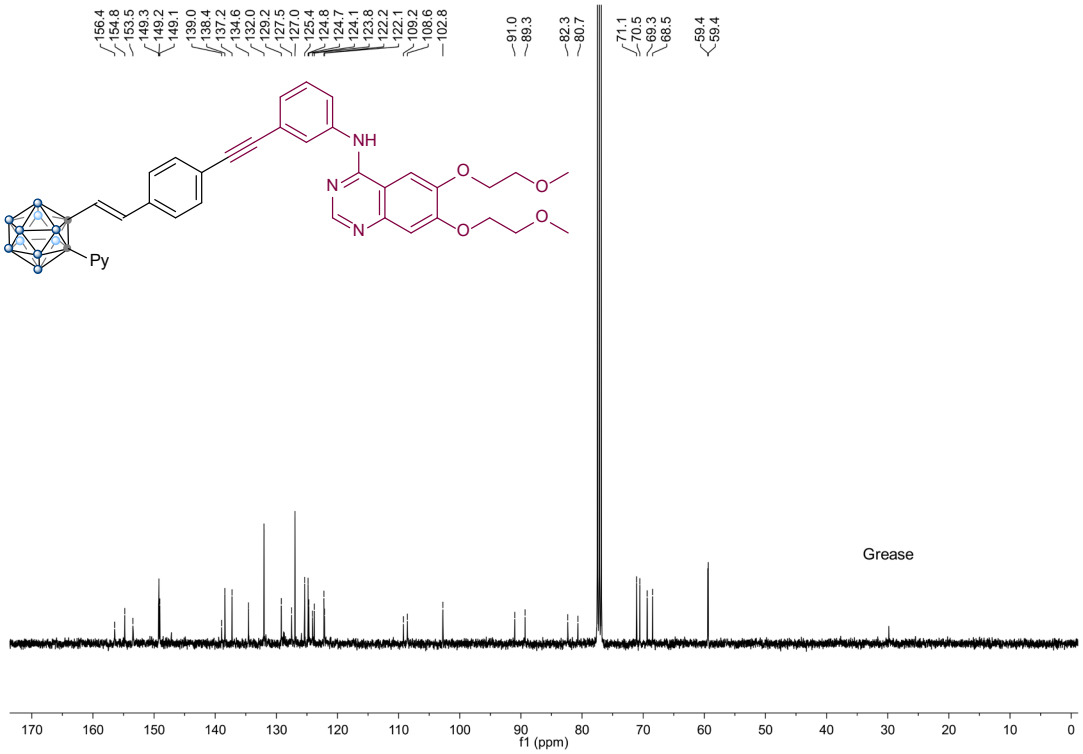
^{11}B NMR (128 MHz, Chloroform-*d*) **8b**



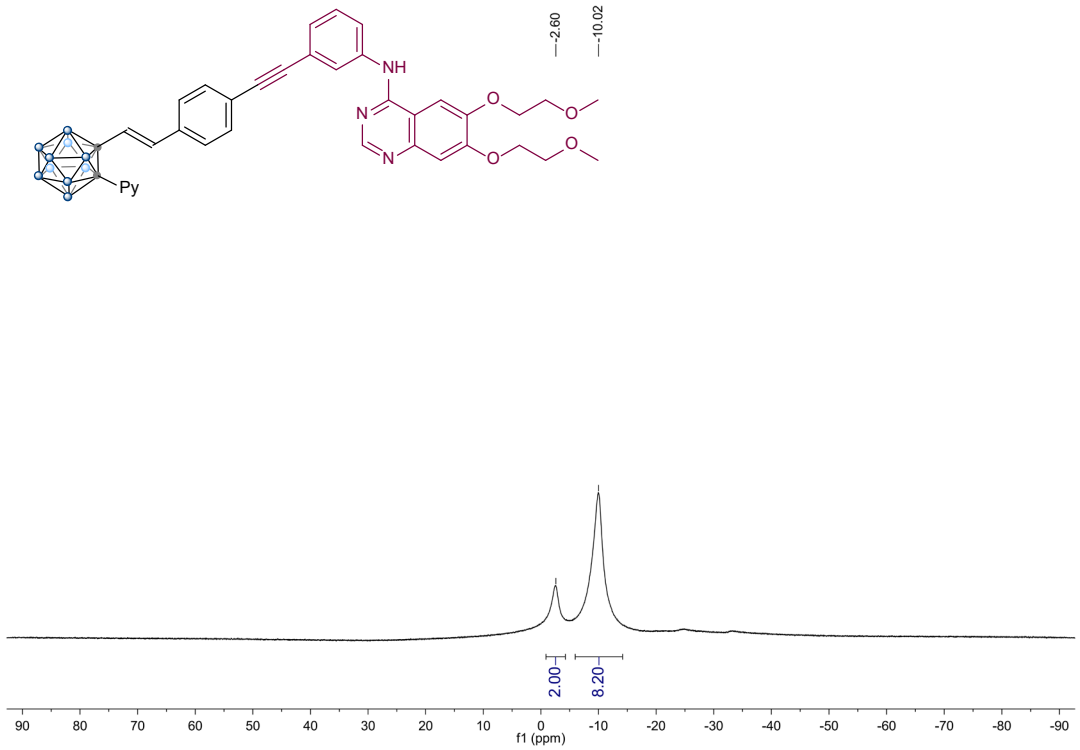
^{1}H NMR (400 MHz, Chloroform-*d*) **8c** (* from residual $CHCl_3$ in Chloroform-*d*)



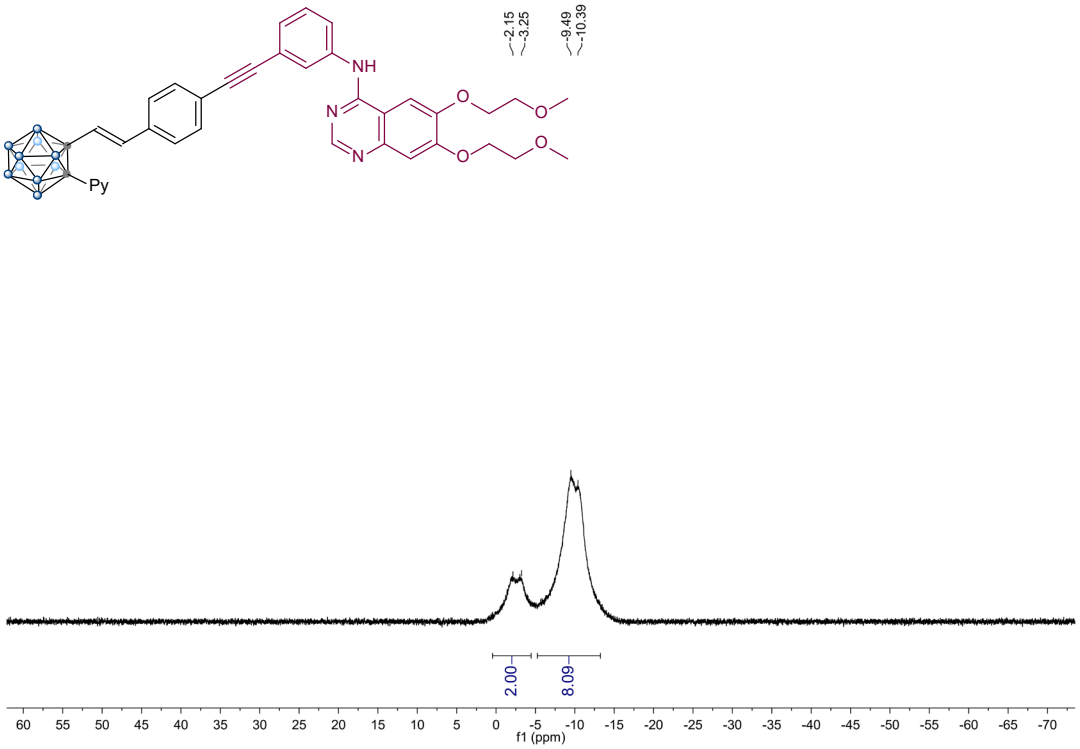
^{13}C NMR (101 MHz, Chloroform-*d*) **8c**



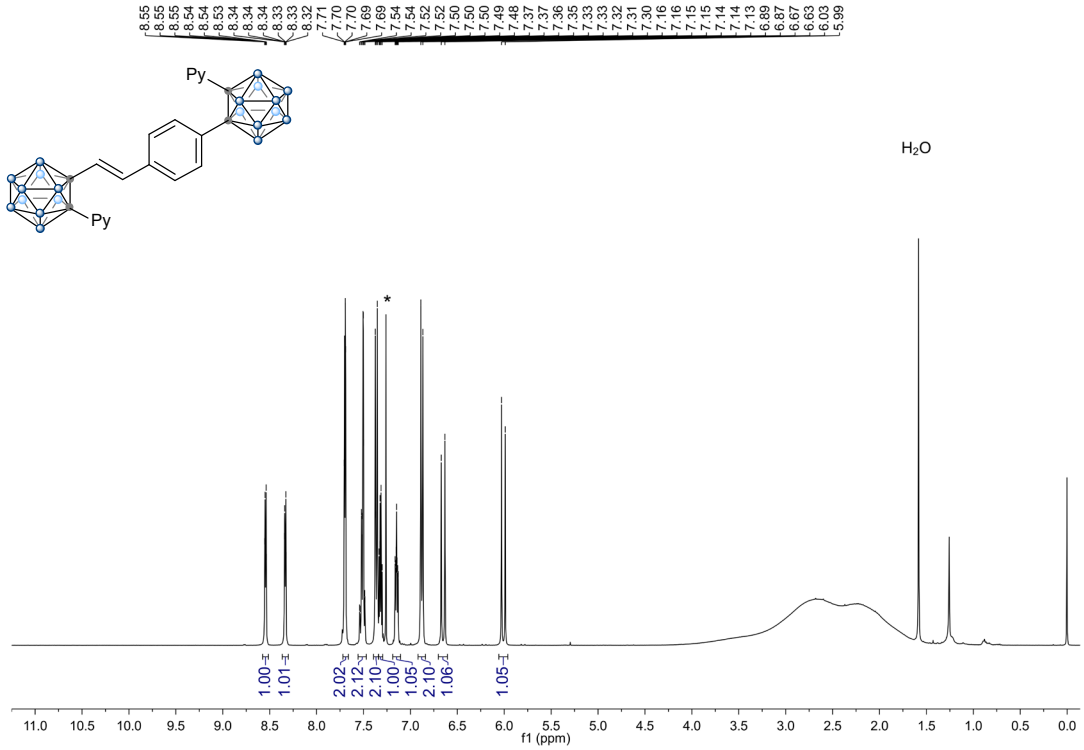
$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **8c**



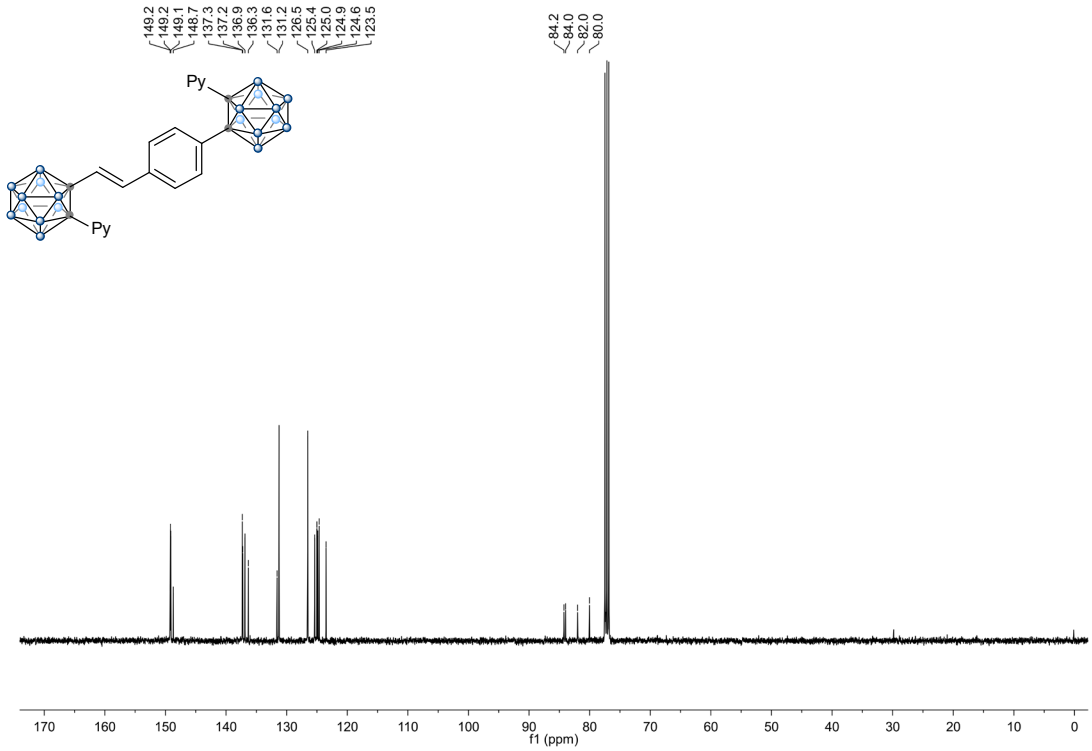
^{11}B NMR (128 MHz, Chloroform-*d*) **8c**



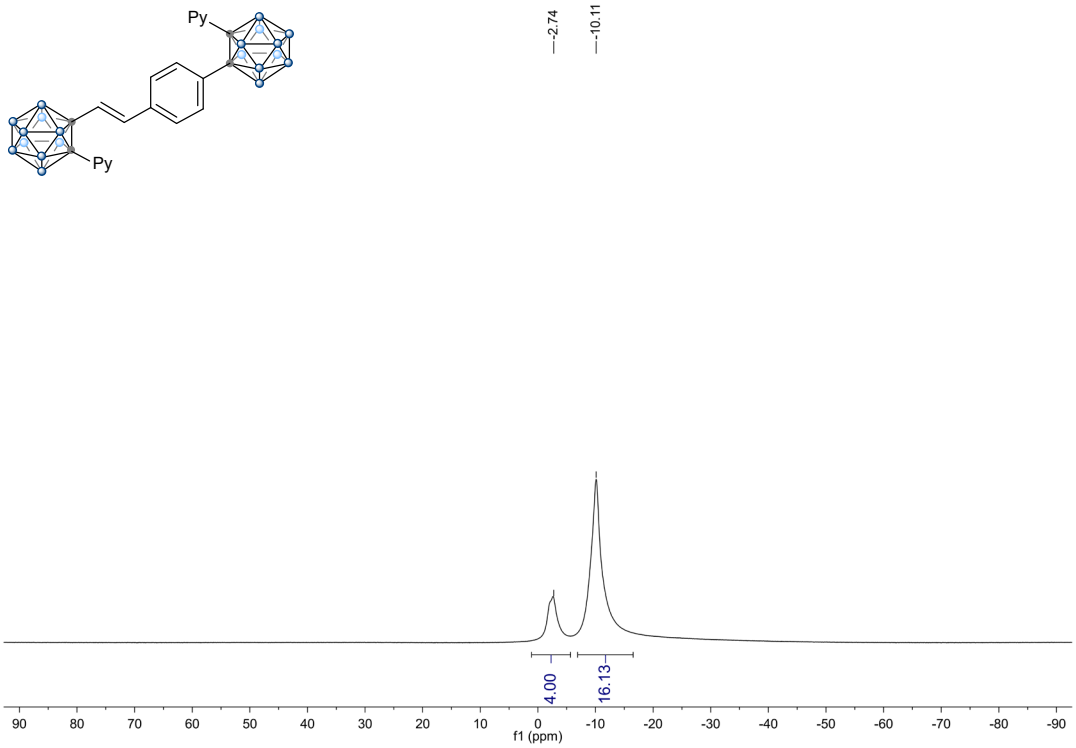
^{1}H NMR (400 MHz, Chloroform-*d*) **8d** (* from residual $CHCl_3$ in Chloroform-*d*)



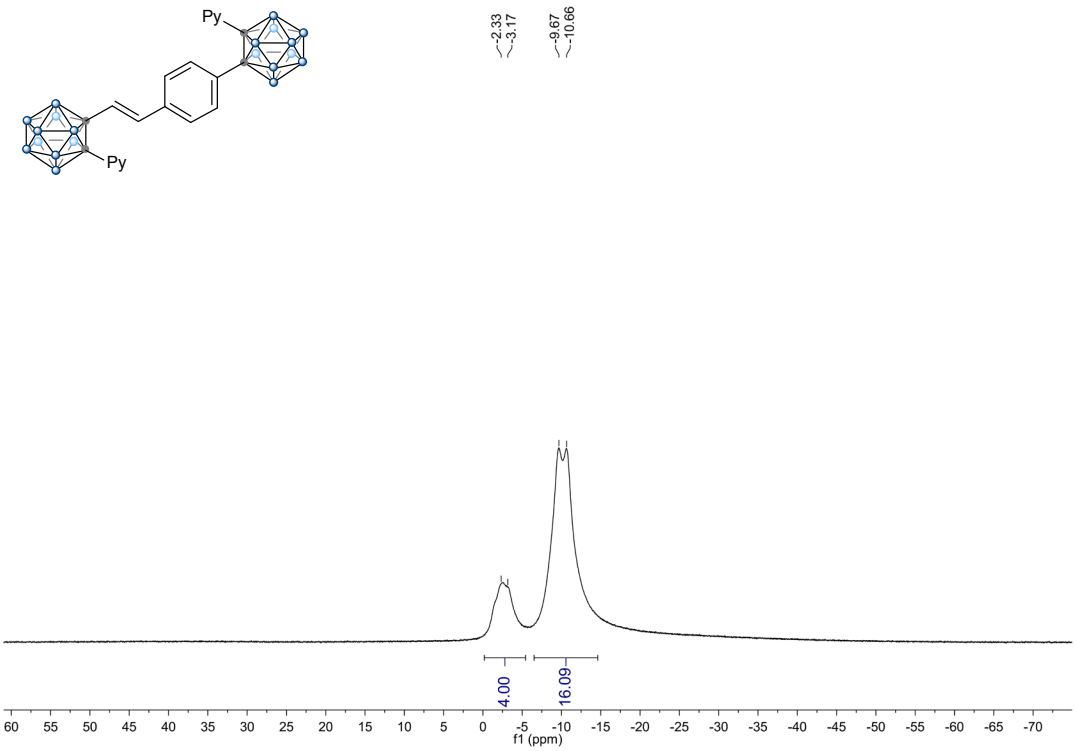
^{13}C NMR (101 MHz, Chloroform-*d*) **8d**



$^{11}B\{^{1}H\}$ NMR (128 MHz, Chloroform-*d*) **8d**



^{11}B NMR (128 MHz, Chloroform-*d*) **8d**



8. References

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