Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Palladium-Catalyzed Selective B(3)–H Arylation of *o*-Carboranes with Arylboronic Acids at Room Temperature

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Table of Contents

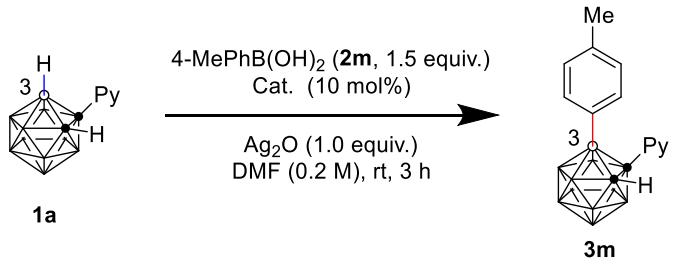
1. General Procedures

All reactions were carried out in a sealed tube under air atmosphere at room temperature. All organic solvents were used as received unless otherwise specified. ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded on a Bruker Advance NEO 400 spectrometer at 400 MHz, 100 MHz, 128 MHz, and 376 MHz, respectively. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, to external $BF_3 \cdot OEt_2$ (0.00 ppm) for boron chemical shifts, and to $CFCl_3$ (0.00 ppm) for fluorine chemical shifts. High resolution mass spectra (HRMS) were obtained on a Shimadzu LCMS-IT-TOF spectrometer. Elemental analyses were performed on an Elementar Vario Pyro Cube instrument. Compounds **1a**,[1] **1b**,[1] and **1c** [2] were prepared according to literature methods.

2. Experimental Section

2.1 Optimization of Reaction Conditions

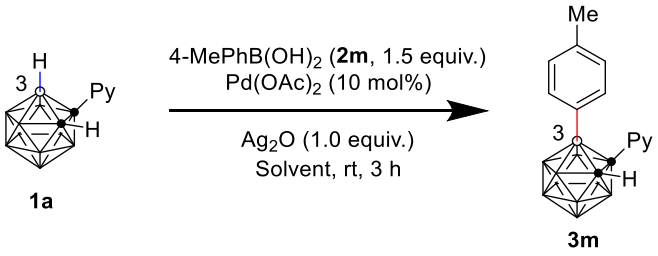
Table S1 Catalyst Investigation [a,b]



Entry	Catalyst	Yield (%)
1	none	0
2	$PdCl_2$	10
3	**$Pd(OAc)_2$**	**85**
4	$Pd(t\text{-}Bu_3P)_2$	25
5	$Pd(PPh_3)_4$	trace
6	$FeCl_3$	0
7	$NiCl_2$	0
8	$Cu(OAc)_2$	0
9	$[RuCl_2(p\text{-cymene})]_2$	trace

[a] Conditions: **1a** (0.1 mmol), **2m** (1.5 equiv.), catalyst (10 mol%), Ag_2O (1.0 equiv.), DMF (0.2 M), air atmosphere, rt, 3 h. [b] Isolated yields.

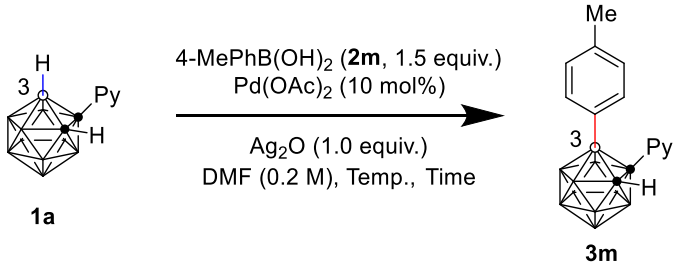
Table S2 Solvent Investigation [a,b]



Entry	Solvent	Conc. (M)	Yield (%)
1	THF	0.2	55
2	1,4-dioxane	0.2	27
3	CH_2Cl_2	0.2	40
4	**DMF**	**0.2**	**85**
5	DMAc	0.2	70
6	toluene	0.2	50
7	DMF	0.05	75
8	DMF	0.1	80
9	DMF	0.33	83

[a] Conditions: **1a** (0.1 mmol), **2m** (1.5 equiv.), $Pd(OAc)_2$ (10 mol%), Ag_2O (1.0 equiv.), air atmosphere, rt, 3 h. [b] Isolated yields.

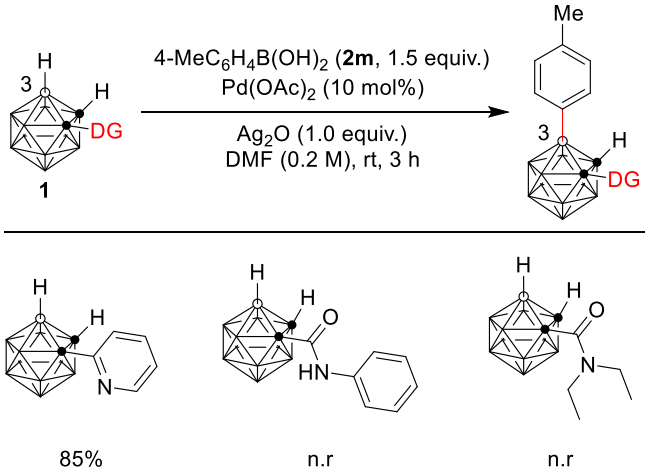
Table S3 Temperature and Reaction Time Investigation [a,b]



Entry	Temp. (℃)	Time (h)	Yield (%)
1	**rt**	**3**	**85**
2	40	3	83
3	50	3	81
4	rt	1	55
5	rt	2	70
6	rt	6	85

[a] Conditions: **1a** (0.1 mmol), **2m** (1.5 equiv.), $Pd(OAc)_2$ (10 mol%), Ag_2O (1.0 equiv.), DMF (0.2 M), air atmosphere. [b] Isolated yield.

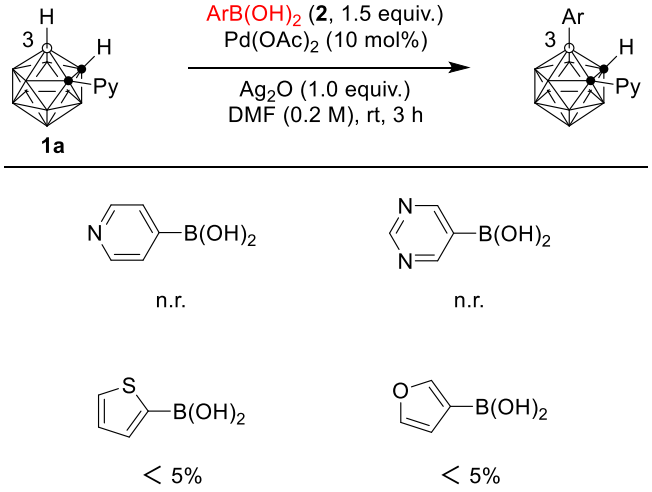
Scheme S4. Screening of Directing Groups [a, b]



[a] Conditions: **1** (0.1 mmol), **2m** (1.5 equiv.), $Pd(OAc)_2$ (10 mol%), Ag_2O (1.0 equiv.), DMF (0.2 M), air atmosphere, rt, 3 h. [b] Isolated yield.

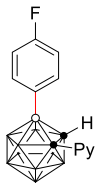
2.2 B(3)–H Arylation of *o*-Carboranes with Heteroarylboronic Acids

Scheme S5. Scope of Heteroarylboronic Acids [a, b]



[a] Conditions: **1a** (0.1 mmol), **2** (1.5 equiv.), $Pd(OAc)_2$ (10 mol%), Ag_2O (1.0 equiv.), DMF (0.2 M), air atmosphere, rt, 3 h. [b] Isolated yield.

2.3 General procedure for cage B(3)–H arylation of *o*-carboranes with arylboronic acids. To a 25 mL dried flask were sequentially added **1** (0.1 mmol), arylboronic acids **2** (0.15 mmol), $Pd(OAc)_2$ (0.01 mmol, 2.24 mg), Ag_2O (0.1 mmol, 23.1 mg), and DMF (0.2 M) under air atmosphere. The reaction was carried out in a sealed tube and stirred at room tempeature for 3 h. After the reaction was completed, a saturated solution of aqueous NaCl was added and the mixture was extracted three times with ethyl acetate. The organic phases were collected, and solvent evaporation under reduced pressure afforded the crude product, which was then purified by column chromatography to provide the target products, by using silica gel as stationary phase and petroleum ether and ethyl acetate as eluent.



3a: Yield 91%. White solid, mp 87-89 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H), 7.57 (td, J = 7.8, 1.8 Hz, 1H), 7.45 (dt, J = 8.0, 1.0 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.12 (ddd, J = 7.6, 4.8, 1.1 Hz, 1H), 6.83 – 6.76 (m, 2H) (Aryl *H*), 5.17 (s, 1H) (Cage C*H*).

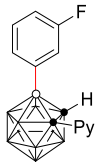
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.72 (d, J = 248.9 Hz), 149.74, 148.49, 137.17, 135.80 (d, J = 8.0 Hz), 124.05, 122.19, 114.76 (d, J = 20.4 Hz) (Aryl *C*), 76.43, 57.00 (Cage *C*), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 0.50 – -6.04 (m, 4B), -7.61 (s, 1B), -9.20 – -13.17 (m, 4B), -14.48 (s, 1B).

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.92 (s, 1F).

HRMS (ESI) *m/z* Calcd for $C_{13}H_{19}B_{10}NF$ $[M+H]^+$ 316.2505, found 316.2501.

Elemental analysis for $C_{13}H_{18}B_{10}NF$ Calcd C, 49.51%; N, 4.44%. Found C, 49.72%; N 4.52%.



3b: Yield 76%. White solid, mp 111-113 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.58 (td, J = 7.8, 1.8 Hz, 1H), 7.46 (dt, J = 8.0, 1.1 Hz, 1H), 7.13 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H), 7.11 – 7.06 (m, 2H), 7.01 (dd, J = 10.1, 2.0 Hz, 1H), 6.90 – 6.84 (m, 1H) (Aryl *H*), 5.19 (s, 1H) (Cage C*H*).

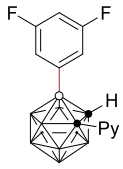
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.17 (d, J = 246.4 Hz), 149.56, 148.51, 137.23, 129.56 (d, J = 2.9 Hz), 129.33 (d, J = 7.6 Hz), 124.12, 122.20, 120.43 (d, J = 20.6 Hz), 116.15 (d, J = 20.9 Hz) (Aryl *C*), 77.36, 57.03 (Cage *C*), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.65 (d, J = 140.1 Hz, 3B), -7.65(s, 1B), -9.61(s, 1B), -10.53(s, 2B), -12.29(s, 2B), -14.40(s, 1B).

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.12 (s, 1F).

HRMS (ESI) *m/z* Calcd for $C_{13}H_{19}B_{10}NF$ $[M+H]^+$ 316.2505, found 316.2506.

Elemental analysis for $C_{13}H_{18}B_{10}NF$ Calcd C, 49.51%; N, 4.44%. Found C, 49.63%; N 4.32%.



3c: Yield 82%. White solid, mp 142-144 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.61 (td, J = 7.8, 1.8 Hz, 1H), 7.47 (dt, J = 8.0, 1.1 Hz, 1H), 7.16 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H), 6.86 – 6.80 (m, 2H), 6.66 – 6.58 (m, 1H) (Aryl *H*), 5.17 (s, 1H) (Cage C*H*).

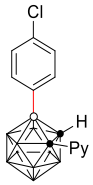
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.40 (d, J = 238.8 Hz), 149.32, 148.61, 137.40, 124.31, 122.23 116.40 (d, J = 24.2 Hz) (Aryl *C*), 116.40 (d, J = 11.3 Hz) (B_{cage}–*C*), 104.70 (t, J = 25.1 Hz) (Aryl *C*), 77.36, 57.01 (Cage *C*).

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.53 (d, J = 115.4 Hz, 3B), -7.56(s, 1B), -8.22 – -11.59 (m, 3B), -12.42(s, 2B), -14.25(s, 1B).

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.56 (s, 2F).

HRMS (ESI) *m/z* Calcd for $C_{13}H_{18}B_{10}NF_2$ $[M+H]^+$ 334.2410, found 334.2415.

Elemental analysis for $C_{13}H_{17}B_{10}NF_2$ Calcd C, 46.84%; N, 4.20%. Found C, 47.02%; N 4.17%.



3d: Yield 68%. White solid, mp 129-130 ℃.

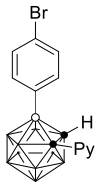
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 7.58 (td, J = 7.8, 1.8 Hz, 1H), 7.45 (dt, J = 8.0, 1.1 Hz, 1H), 7.27 (m, 1H), 7.25 (m, 1H), 7.13 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H), 7.11 – 7.05 (m, 2H) (Aryl *H*), 5.18 (s, 1H) (Cage C*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.63, 148.55, 137.23, 135.64, 135.19, 127.88, 124.15, 122.18 (Aryl *C*), 76.43, 56.89 (Cage *C*), the B_{cage}–*C* was not observed.

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ -3.04(s, 2B), -4.26(s, 2B), -7.66(s, 1B), -9.97 (m, 2B), -12.37(s, 2B), -14.43(s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{13}H_{19}B_{10}NCl$ $[M+H]^+$ 332.2209, found 332.2215.

Elemental analysis for $C_{13}H_{18}B_{10}NCl$ Calcd C, 47.05%; N, 4.22%. Found C, 47.12%; N 4.33%.



3e: Yield 75%. Yellow solid, mp 122-124 ℃.

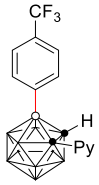
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H), 7.58 (td, J = 7.8, 1.8 Hz, 1H), 7.45 (dt, J = 8.0, 1.0 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.21 – 7.17 (m, 2H), 7.14 (ddd, J = 7.6, 4.8, 1.1 Hz, 1H) (Aryl *H*), 5.18 (s, 1H) (Cage C*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.62, 148.56, 137.25, 135.43, 130.82, 124.17, 122.18 (Aryl *C*), 76.41, 56.85 (Cage *C*), the B_{cage}–*C* was not observed.

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ -3.72 (d, J = 154.0 Hz, 3B), -7.66(s, 1B), -8.40 – -11.60 (m, 3B), -12.33(s, 2B), -14.38(s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{13}H_{19}B_{10}NBr$ $[M+H]^+$ 376.1704, found 376.1709.

Elemental analysis for $C_{13}H_{18}B_{10}NBr$ Calcd C, 41.49%; N, 3.72%. Found C, 41.31%; N 3.88%.



3f: Yield 80%. White solid, mp 90-91 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 7.58 (td, J = 7.7, 1.8 Hz, 1H), 7.46 (m, 3H), 7.39 – 7.33 (m, 2H), 7.13 (ddd, J = 7.6, 4.8, 1.1 Hz, 1H) (Aryl *H*), 5.24 (s, 1H) (Cage C*H*).

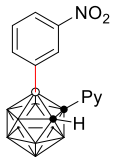
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.43, 148.56, 137.33, 134.18, 131.09 (q, J = 32.3 Hz), 124.26 (q, J = 3.2 Hz) (Aryl *C*), 124.25, 124.09 (q, J = 272.4 Hz) (*C*F_3), 122.18 (Aryl *C*), 76.53, 56.90 (Cage *C*), the B_{cage}–*C* was not observed.

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ -3.04(s, 2B), -4.05(s, 1B), -7.58(s, 1B), -8.47 – -11.55 (m, 3B), -12.21(s, 2B), -14.24(s, 1B).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.99 (s, 3F).

HRMS (ESI) *m/z* Calcd for $C_{14}H_{19}B_{10}NF_3$ $[M+H]^+$ 366.2473, found 366.2476.

Elemental analysis for $C_{14}H_{18}B_{10}NF_3$ Calcd C, 46.02%; N, 3.83%. Found C, 46.28%; N 3.98%.



3g: Yield 77%. Yellow solid, mp 110-113 ℃.

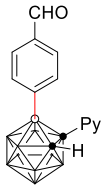
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (ddd, J = 4.8, 1.6, 0.9 Hz, 1H), 8.13 (s, 1H), 8.04 (ddd, J = 8.2, 2.3, 1.0 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.60 (td, J = 7.8, 1.7 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.32 (t, J = 7.9 Hz, 1H), 7.13 (ddd, J = 7.5, 4.8, 1.0 Hz, 1H) (Aryl *H*), 5.29 (s, 1H) (Cage C*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.16, 148.62, 147.50, 140.07, 137.51, 128.73, 128.28, 124.36, 124.07, 122.26 (Aryl *C*), 76.60, 56.98 (Cage *C*), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.43 (d, J = 113.7 Hz, 3B), -7.54(s, 1B), -8.56 – -11.12 (m, 3B), -12.19 (d, J = 69.8 Hz, 2B), -14.07(s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{13}H_{19}B_{10}N_2O_2$ $[M+H]^+$ 343.2450, found 343.2455.

Elemental analysis for $C_{13}H_{18}B_{10}N_2O_2$ Calcd C, 45.60%; N, 8.18%. Found C, 45.66%; N 8.06%.



3h: Yield 85%. White solid, mp 176-178 ℃.

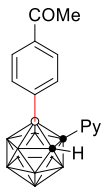
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H) (*C*HO), 8.16 (ddd, J = 4.8, 1.6, 0.9 Hz, 1H), 7.63 – 7.59 (m, 2H), 7.57 (td, J = 7.8, 1.8 Hz, 1H), 7.52 (d, J = 8.1 Hz, 2H), 7.49 – 7.44 (m, 1H), 7.11 (ddd, J = 7.5, 4.8, 1.0 Hz, 1H) (Aryl *H*), 5.25 (s, 1H) (Cage C*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.41(*C*HO), 149.42, 148.54, 137.31, 136.51, 134.50, 128.57, 124.23, 122.18 (Aryl *C*),76.62, 56.97 (Cage *C*), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.47 (d, J = 112.9 Hz, 3B), -7.59(s, 1B), -8.58 – -11.30 (m, 3B), -12.21(s, 2B), -14.19(s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{14}H_{20}B_{10}NO$ $[M+H]^+$ 326.2548, found 326.2547.

Elemental analysis for $C_{14}H_{19}B_{10}NO$ Calcd C, 51.67%; N, 4.30%. Found C, 51.52%; N 4.42%.



3i: Yield 75%. White solid, mp 182-185 ℃.

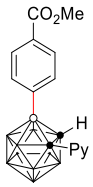
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.16 (m, 1H), 7.69 – 7.66 (m, 2H), 7.56 (td, J = 7.8, 1.7 Hz, 1H), 7.47 – 7.42 (m, 3H), 7.13 – 7.09 (m, 1H) (Aryl *H*), 5.24 (s, 1H) (Cage C*H*), 2.51 (s, 3H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.24 (*C*O), 149.46, 148.53, 137.30, 137.25, 134.13, 127.20, 124.18, 122.14 (Aryl *C*), 76.56, 56.94 (Cage *C*), 26.71 (*C*H$_3$), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.57 (d, J = 117.0 Hz, 3B), -7.61(s, 1B), -8.42 – -11.43 (m, 3B), -12.19(s, 2B), -14.17(s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{15}H_{22}B_{10}NO$ $[M+H]^+$ 340.2705, found 340.2708.

Elemental analysis for $C_{15}H_{21}B_{10}NO$ Calcd C, 53.08%; N, 4.13%. Found C, 53.01%; N 4.33%.



3j. Yield 76%. White solid, mp 160-161 ℃.

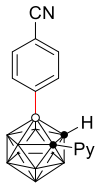
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.13 (m, 1H), 7.76 (d, J = 7.9 Hz, 2H), 7.60 – 7.51 (m, 1H), 7.47 – 7.39 (m, 3H), 7.12 – 7.07 (m, 1H) (Aryl *H*), 5.23 (s, 1H) (Cage C*H*), 3.85 (s, 3H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.05 (*C*OO), 149.52, 148.52, 137.21, 133.91, 130.62, 128.48, 124.15, 122.16 (Aryl *C*), 77.37, 57.00 (Cage *C*), 52.26 (O*C*H$_3$), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.51 (d, J = 129.6 Hz, 3B), -7.64(s, 1B), -8.66 – -11.19 (m, 3B), -12.27(s, 2B), -14.33(s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{15}H_{22}B_{10}NO_2$ $[M+H]^+$ 356.2654, found 356.2655.

Elemental analysis for $C_{15}H_{21}B_{10}NO_2$ Calcd C, 50.69%; N, 3.94%. Found C, 50.89%; N 4.06%.



3k: Yield 65%. White solid, mp 174-175 ℃.

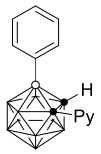
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H), 7.59 (td, J = 7.8, 1.8 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.41 – 7.36 (m, 2H), 7.14 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H) (Aryl *H*), 5.23 (s, 1H) (Cage C*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.20, 148.56, 137.40, 134.36, 130.99, 124.32, 122.15 (Aryl *C*), 118.65 (*C*N), 112.88 (Aryl *C*), 76.60, 56.87 (Cage *C*), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.43 (d, J = 115.7 Hz, 3B), -7.51(s, 1B), -10.04(s, 3B), -12.15(s, 2B), -14.07(s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{14}H_{19}B_{10}N_2$ $[M+H]^+$ 323.2551, found 323.2549.

Elemental analysis for $C_{14}H_{18}B_{10}N_2$ Calcd C, 52.16%; N, 8.69%. Found C, 52.01%; N 8.65%.



3l: Yield 85%. White solid, mp 124-127 ℃.

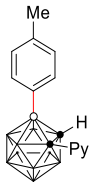
^{1}H NMR (400 MHz, CDCl3) δ 8.19 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 7.55 (td, J = 7.8, 1.8 Hz, 1H), 7.46 (dt, J = 8.0, 1.1 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.21 – 7.15 (m, 1H), 7.14 – 7.06 (m, 3H) (Aryl *H*), 5.21 (s, 1H) (Cage C*H*).

^{13}C NMR (101 MHz, CDCl3) δ 149.83, 148.41, 137.06, 133.88, 129.13, 127.58, 123.93, 122.18 (Aryl *C*), 76.47, 57.02 (Cage *C*), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -1.45 – -5.26 (m, 3B), -6.41 – -8.38 (m, 1B), -8.76 – -11.67 (m, 3B), -12.32(s, 2B), -14.46(s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{13}H_{20}B_{10}N$ $[M+H]^+$ 298.2599, found 298.2595.

Elemental analysis for $C_{13}H_{19}B_{10}N$ Calcd C, 52.50%; N, 4.71%. Found C, 52.55%; N 4.79%.



3m: Yield 85%. White solid, mp 133-135 ℃.

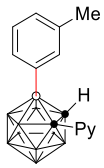
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.56 (td, *J* = 7.8, 1.8 Hz, 1H), 7.46 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.11 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 2H) (Aryl *H*), 5.18 (s, 1H) (Cage C*H*), 2.21 (s, 3H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.93, 148.43, 139.04, 137.05, 133.84, 128.43, 123.93, 122.17 (Aryl *C*), 76.37, 56.95 (Cage *C*), 21.37 (CH_3) , the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -0.91 – -5.13 (m, 3B), -7.68(s, 1B), -8.68 – -11.60 (m, 3B), -12.24(s, 2B), -14.46(s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{14}H_{22}B_{10}N$ $[M+H]^+$ 312.2757, found 312.2758.

Elemental analysis for $C_{14}H_{21}B_{10}N$ Calcd C, 53.99%; N, 4.50%. Found C, 54.19%; N 4.22%.



3n: Yield 69%. White solid, mp 71-74 ℃.

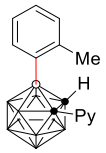
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 7.55 (td, J = 7.8, 1.8 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.13 (s, 1H), 7.12 – 7.08 (m, 2H), 7.00 – 6.97 (m, 2H) (Aryl *H*), 5.17 (s, 1H) (Cage C*H*), 2.19 (s, 3H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.95, 148.36, 137.01, 136.69, 134.69, 130.92, 129.90, 127.47, 123.92, 122.25 (Aryl *C*), 76.39, 57.02 (Cage *C*), 21.42 (*C*H_3), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -1.61 – -4.99 (m, 3B), -7.80 (s, 1B), -8.85 – -11.53 (m, 3B), -12.24(s, 2B), -14.48 (s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{14}H_{22}B_{10}N$ $[M+H]^+$ 312.2757, found 312.2757.

Elemental analysis for $C_{14}H_{21}B_{10}N$ Calcd C, 53.99%; N, 4.50%. Found C, 54.08%; N 4.62%.



3o: Yield 46%. White solid, mp 136-138 ℃.

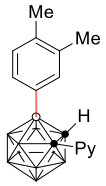
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (ddd, J = 4.8, 1.8, 1.0 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.39 (dt, J = 8.1, 1.1 Hz, 1H), 7.10 – 7.02 (m, 2H), 6.99 – 6.91 (m, 2H) (Aryl *H*), 5.45 (s, 1H) (Cage C*H*), 2.56 (s, 3H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.96, 148.30, 143.07, 137.08, 136.98, 130.72, 129.19, 125.05, 123.99, 121.78 (Aryl *C*), 77.36, 56.56 (Cage *C*), 22.99 (*C*H_3), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -1.40 (s, 1B), -2.78 – -5.89 (m, 2B), -7.57 (s, 1B), -8.59 – -12.98 (m, 4B), -14.32 (s, 2B).

HRMS (ESI) *m/z* Calcd for $C_{14}H_{22}B_{10}N$ $[M+H]^+$ 312.2757, found 312.2754.

Elemental analysis for $C_{14}H_{21}B_{10}N$ Calcd C, 53.99%; N, 4.50%. Found C, 54.11%; N 4.55%.



3p: Yield 63%. White solid, mp 112-115 ℃.

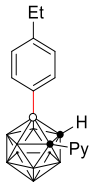
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 4.5 Hz, 1H), 7.56 (td, J = 7.8, 1.8 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.14 – 7.08 (m, 2H), 7.04 (d, J = 7.6 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H) (Aryl *H*), 5.19 (s, 1H) (Cage C*H*), 2.13 (s, 3H) (CH_3), 2.12 (s, 3H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.99, 148.38, 137.75, 137.02, 135.66, 135.21, 131.36, 128.99, 123.92, 122.22 (Aryl *C*), 76.30, 56.94 (Cage *C*), 19.69, 19.68 (*C*H_3), the B_{cage}–*C* was not observed.

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ -1.66 (s, 1B), -3.93 (d, J = 149.7 Hz, 2B), -7.77 (s, 1B), -8.61 – -13.35 (m, 5B), -14.50 (s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{15}H_{24}B_{10}N$ $[M+H]^+$ 326.2912, found 326.2910.

Elemental analysis for $C_{15}H_{23}B_{10}N$ Calcd C, 55.36%; N, 4.30%. Found C, 55.10%; N 4.52%.



3q: Yield 68%. White solid, mp 117-119 ℃.

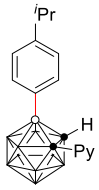
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 7.55 (td, J = 7.8, 1.8 Hz, 1H), 7.45 (dt, J = 8.0, 1.0 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.10 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H), 6.99 – 6.88 (m, 2H) (Aryl *H*), 5.16 (s, 1H) (Cage C*H*), 2.50 (q, J = 7.6 Hz, 2H) (CH_2), 1.12 (t, J = 7.6 Hz, 3H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.00, 148.41, 145.28, 137.05, 133.93, 127.19, 123.89, 122.22 (Aryl *C*), 76.36, 56.98 (Cage *C*), 28.69 (*C*H_2), 15.30 (*C*H_3), the B_{cage}–*C* was not observed.

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ -0.99 – -5.19 (m, 3B), -7.76 (s, 1B), -8.62 – -11.40 (m, 2B), -12.37 (s, 2B), -14.59 (s, 2B).

HRMS (ESI) *m/z* Calcd for $C_{15}H_{24}B_{10}N$ $[M+H]^+$ 326.2912, found 326.2918.

Elemental analysis for $C_{15}H_{23}B_{10}N$ Calcd C, 55.36%; N, 4.30%. Found C, 55.44%; N 4.57%.



3r: Yield 65%. White solid, mp 133-135 ℃.

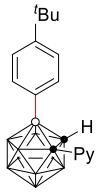
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 7.55 (td, J = 7.8, 1.8 Hz, 1H), 7.45 (dt, J = 8.0, 1.1 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.10 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H), 6.98 – 6.93 (m, 2H) (Aryl *H*), 5.16 (s, 1H) (Cage C*H*), 2.75 (m, 1H) (C*H*), 1.13 (d, J = 6.9, 1.1 Hz, 6H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.96, 149.86, 148.37, 137.05, 133.92, 125.74, 123.85, 122.23 (Aryl *C*), 76.34, 57.00 (Cage *C*), 33.89 (*C*H), 23.83 (*C*H_3), the B_{cage}–*C* was not observed.

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ -0.77 – -5.16 (m, 3B), -7.74 (s, 1B), -8.04 – -11.48 (m, 3B), -12.28 (s, 2B), -14.47 (s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{16}H_{26}B_{10}N$ $[M+H]^+$ 340.3071, found 340.3079.

Elemental analysis for $C_{16}H_{25}B_{10}N$ Calcd C, 56.61%; N, 4.13%. Found C, 56.82%; N 4.32%.



3s: Yield 74%. White solid, mp 140-144 ℃.

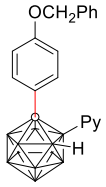
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (ddd, J = 4.8, 1.8, 1.0 Hz, 1H), 7.55 (td, J = 7.8, 1.8 Hz, 1H), 7.46 (dt, J = 8.0, 1.0 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.14 – 7.07 (m, 3H) (Aryl *H*), 5.17 (s, 1H) (Cage C*H*), 1.20 (s, 9H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.12, 149.99, 148.37, 137.05, 133.70, 124.53, 123.84, 122.24 (Aryl *C*), 76.34, 57.04 (Cage *C*), 34.59 (^{t}Bu), 31.22 (*C*H$_3$), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -0.95 – -5.19 (m, 3B), -7.76 (s, 1B), -8.78 – -11.55 (m, 3B), -12.29 (s, 2B), -14.45 (s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{17}H_{28}B_{10}N$ $[M+H]^+$ 354.3225, found 354.3226.

Elemental analysis for $C_{17}H_{27}B_{10}N$ Calcd C, 57.76%; N, 3.96%. Found C, 57.61%; N 4.12%.



3t: Yield 84%. White solid, mp 154-155 ℃.

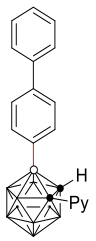
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (ddd, J = 4.8, 1.6, 0.8 Hz, 1H), 7.56 (td, J = 7.8, 1.7 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.38 – 7.34 (m, 4H), 7.34 – 7.29 (m, 1H), 7.26 – 7.23 (m, 2H), 7.11 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H), 6.75 – 6.69 (m, 2H) (Aryl *H*), 5.15 (s, 1H) (Cage C*H*), 4.96 (s, 2H) (CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.68, 149.97, 148.44, 137.05, 136.84, 135.33, 128.69, 128.14, 127.58, 123.91, 122.19, 114.16 (Aryl *C*), 76.33 (Cage *C*), 69.82 (*C*H$_2$), 56.95 (Cage *C*), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -0.98 – -5.39 (m, 3B), -7.78 (s,1B), -8.31 – -11.56 (m, 3B), -12.36 (s,2B), -14.57 (s,1B).

HRMS (ESI) *m/z* Calcd for $C_{20}H_{26}B_{10}NO$ $[M+H]^+$ 404.3018, found 404.3020.

Elemental analysis for $C_{20}H_{25}B_{10}NO$ Calcd C, 59.53%; N, 3.47%. Found C, 59.81%; N 3.30%.



3u: Yield 68%. White solid, mp 121-124 ℃.

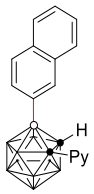
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (ddd, J = 4.8, 1.7, 0.8 Hz, 1H), 7.57 (td, J = 7.8, 1.8 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.42 – 7.31 (m, 7H), 7.10 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H) (Aryl *H*), 5.23 (s, 1H) (Cage C*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.86, 148.48, 141.69, 140.57, 137.13, 134.36, 128.88, 127.65, 127.07, 126.23, 124.01, 122.23 (Aryl *C*), 76.46, 56.99 (Cage *C*), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -0.98 – -4.90 (m, 3B), -7.60 (s, 1B), -8.34 – -11.61 (m, 3B), -12.12 (s, 2B), -14.38 (s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{19}H_{24}B_{10}N$ $[M+H]^+$ 374.2912, found 374.2912.

Elemental analysis for $C_{19}H_{23}B_{10}N$ Calcd C, 61.10%; N, 3.75%. Found C, 61.24%; N 3.61%.



3v: Yield 64%. Red solid, mp 83-85 °C.

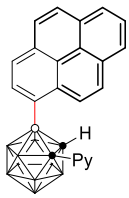
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.11 (m, 1H), 7.87 (s, 1H), 7.72 – 7.68 (m, 2H), 7.57 (d, J = 8.3 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.43 – 7.40 (m, 2H), 7.39 (dd, J = 8.3, 1.5 Hz, 1H), 7.04 – 7.00 (m, 1H) (Aryl *H*), 5.33 (s, 1H) (Cage C*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.85, 148.44, 137.08, 134.92, 133.54, 132.67, 130.07, 128.24, 127.59, 126.91, 126.68, 126.08, 124.01, 122.20 (Aryl *C*), 76.58, 57.03 (Cage *C*), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 0.22 – -6.19 (m, 4B), -7.60 (s, 1B), -8.97 – -13.19 (m, 4B), -14.43 (s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{17}H_{22}B_{10}N$ $[M+H]^+$ 348.2755, found 348.2757.

Elemental analysis for $C_{17}H_{21}B_{10}N$ Calcd C, 58.77%; N, 4.03%. Found C, 58.98%; N 3.87%.



3w: Yield 60%. Yellow solid, mp 193-196 °C.

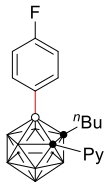
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, J = 9.4 Hz, 1H), 8.37 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.24 – 8.15 (m, 4H), 8.09 – 7.91 (m, 4H), 7.03 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H), 6.93 (td, J = 7.8, 1.8 Hz, 1H), 6.50 (dt, J = 8.0, 1.0 Hz, 1H) (Aryl *H*), 5.24 (s, 1H) (Cage C*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.51, 148.85, 136.64, 135.60, 134.90, 132.01, 131.47, 130.72, 128.27, 127.58, 127.53, 127.17, 126.01, 125.32, 125.19, 125.11, 124.96, 124.26, 124.07, 122.38 (Aryl *C*), 77.36, 57.44 (Cage *C*), the B_{cage}–*C* was not observed.

$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -0.21 – -3.80 (m, 3B), -6.28 (s, 1B), -7.76 – -13.27 (m, 4B), -14.06 (s, 2B).

HRMS (ESI) *m/z* Calcd for $C_{23}H_{24}B_{10}N$ $[M+H]^+$ 422.2912, found 422.2913.

Elemental analysis for $C_{23}H_{23}B_{10}N$ Calcd C, 65.53%; N, 3.32%. Found C, 65.55%; N 3.61%.



4a: Yield 77%. White solid, mp 130-133 ℃.

^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (dt, J = 4.7, 1.4 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.30 – 7.26 (m, 1H), 7.22 – 7.15 (m, 2H), 6.91 – 6.84 (m, 2H) (Aryl *H*), 2.80 – 2.71 (m, 1H), 2.17 – 2.09 (m, 1H), 1.80 – 1.67 (m, 1H), 1.56 – 1.47 (m, 1H), 1.29 – 1.19 (m, 2H) (C*H*$_2$), 0.85 (t, J = 7.4 Hz, 3H) (C*H*$_3$).

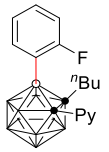
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.53 (d, J = 249.2 Hz), 151.28, 148.21, 136.91, 136.44 (d, J = 7.7 Hz), 125.32, 124.05, 114.85 (d, J = 20.1 Hz) (Aryl *C*), 82.77, 78.87 (Cage *C*), 35.09, 32.15, 22.54 (*C*H$_2$), 13.88 (*C*H$_3$), the B_{cage}–*C* was not observed.

$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -2.36 (s, 1B), -4.11 (d, J = 193.0 Hz, 2B), -9.65 (d, J = 251.8 Hz, 5B), -12.07 (s, 2B).

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.22 (s, 1F).

HRMS (ESI) *m/z* Calcd for $C_{17}H_{27}B_{10}NF$ $[M+H]^+$ 372.3131, found 372.3129.

Elemental analysis for $C_{17}H_{26}B_{10}NF$ Calcd C, 54.96%; N, 3.77%. Found C, 55.05%; N 3.67%.



4b: Yield 48%. Colorless oil.

^1H NMR (400 MHz, CDCl3) δ 8.22 – 8.19 (m, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.67 (td, J = 7.9, 1.8 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.32 – 7.26 (m, 1H), 7.22 – 7.18 (m, 1H), 7.04 – 6.96 (m, 1H), 6.88 – 6.82 (m, 1H) (Aryl *H*), 2.86 – 2.78 (m, 1H), 2.36 – 2.28 (m, 1H), 1.56 – 1.51 (m, 2H), 1.27 – 1.18 (m, 2H) (C*H*$_2$), 0.83 (t, J = 7.4 Hz, 3H) (C*H*$_3$).

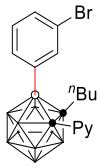
^{13}C NMR (101 MHz, CDCl3) δ 165.81 (d, J = 249.0 Hz), 152.16, 147.51, 137.35, 137.28, 136.75, 125.12 (d, J = 1.9 Hz), 123.76, 123.57 (d, J = 3.0 Hz), 115.71 (d, J = 25.9 Hz) (Aryl *C*), 83.03, 78.41 (Cage *C*), 35.40, 32.31, 22.55 (*C*H$_2$), 13.88 (*C*H$_3$), the B_{cage}–*C* was not observed.

$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -2.87(s, 2B), -4.85 (s, 1B), -6.91 – -9.88 (m, 4B), -10.17 – -12.51 (m, 3B).

^{19}F NMR (376 MHz, $CDCl_3$) δ -99.97 (s, 1F).

HRMS (ESI) *m/z* Calcd for $C_{17}H_{27}B_{10}NF$ $[M+H]^+$ 372.3131, found 372.3133.

Elemental analysis for $C_{17}H_{26}B_{10}NF$ Calcd C, 54.96%; N, 3.77%. Found C, 54.85%; N 3.92%.



4c Yield 71%. White solid, mp 95-99 ℃.

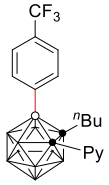
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dt, J = 4.8, 1.3 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.37 (ddd, J = 7.9, 1.9, 1.1 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.11 (m, 1H), 7.02 (t, J = 7.8 Hz, 1H) (Aryl *H*), 2.71 (m, 1H), 2.11 (m, 1H), 1.69 (m, 1H), 1.54 – 1.44 (m, 1H), 1.21 (m, 2H) (CH_2), 0.82 (t, J = 7.4 Hz, 3H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.04, 148.23, 137.30, 136.97, 132.95, 131.95, 129.33, 125.33, 124.16, 122.30 (Aryl *C*), 82.91, 79.00 (Cage *C*), 35.00, 32.12, 22.50 (*C*H_2), 13.87 (*C*H_3), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.17 (s, 2B), -4.74 (s, 1B), -8.66 (s, 3B), -10.38 (s, 3B), -12.03 (s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{17}H_{27}B_{10}NBr$ $[M+H]^+$ 432.2330, found 432.2337.

Elemental analysis for $C_{17}H_{26}B_{10}NBr$ Calcd C, 47.22%; N, 3.24%. Found C, 47.29%; N 3.36%.



4d: Yield 65%. White solid, mp 72-73 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dt, J = 4.7, 1.4 Hz, 1H), 7.72 (m, 2H), 7.44 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.31 – 7.27 (m, 1H) (Aryl *H*), 2.77 (ddd, J = 14.9, 12.3, 4.6 Hz, 1H), 2.17 (ddd, J = 14.9, 12.3, 4.5 Hz, 1H), 1.72 (m, 1H), 1.61 – 1.50 (m, 1H), 1.25 (m, 2H) (CH_2), 0.85 (t, J = 7.4 Hz, 3H) (CH_3).

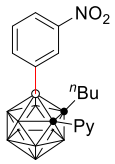
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.89, 148.05, 136.88, 134.57, 130.61 (q, J = 32.4 Hz), 125.08, 124.09 (q, J = 3.9 Hz) (Aryl *C*), 124.01 (*C*F_3), 124.00 (q, J = 272.3 Hz) (Aryl *C*), 82.77, 78.85 (Cage *C*), 34.86, 31.98, 22.31 (*C*H_2), 13.66 (*C*H_3), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.01 (s, 2B), -4.62 (s, 1B), -8.52 (s, 3B), -10.24 (s, 3B), -11.68 (s, 1B).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.91 (s, 3F).

HRMS (ESI) *m/z* Calcd for $C_{18}H_{27}B_{10}NF_3$ $[M+H]^+$ 422.3099, found 422.3095.

Elemental analysis for $C_{18}H_{26}B_{10}NF_3$ Calcd C, 51.29%; N, 3.32%. Found C, 51.39%; N 3.10%.



4e: Yield 62%. Colorless oil.

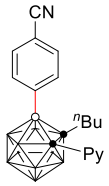
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dt, J = 4.7, 1.4 Hz, 1H), 8.13 (ddd, J = 8.2, 2.3, 1.0 Hz, 1H), 7.94 (s, 1H), 7.77 – 7.72 (m, 3H), 7.45 – 7.39 (m, 1H), 7.32 – 7.28 (m, 1H) (Aryl *H*), 2.74 – 2.66 (m, 1H), 2.20 – 2.12 (m, 1H), 1.74 – 1.62 (m, 1H), 1.58 – 1.49 (m, 1H), 1.26 – 1.19 (m, 2H) (CH_2), 0.83 (t, J = 7.4 Hz, 3H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.80, 148.26, 147.58, 140.91, 137.32, 128.71, 128.64, 125.28, 124.42, 123.78 (Aryl *C*), 82.98, 79.10 (Cage *C*), 35.02, 32.10, 22.45 (*C*H_2), 13.79 (*C*H_3). the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -2.94 (s, 2B), -4.43 (s, 1B), -8.53 (s, 3B), -10.19 (s, 3B), -11.67 (s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{17}H_{27}B_{10}N_2O_2$ $[M+H]^+$ 399.3076, found 399.3075.

Elemental analysis for $C_{17}H_{26}B_{10}N_2O_2$ Calcd C, 51.24%; N, 7.03%. Found C, 51.02%; N 7.11%.



4f: Yield 72%. White solid, mp 145-146 ℃.

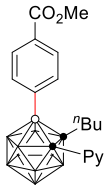
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.28 (m, 1H), 7.75 – 7.69 (m, 2H), 7.50 – 7.43 (m, 2H), 7.38 – 7.31 (m, 2H), 7.28 (ddd, J = 5.4, 4.8, 3.0 Hz, 1H) (Aryl *H*), 2.75 – 2.67 (m, 1H), 2.20 – 2.12 (m, 1H), 1.68 – 1.57 (m, 1H), 1.57 – 1.46 (m, 1H), 1.28 – 1.17 (m, 2H) (CH_2), 0.83 (t, J = 7.4 Hz, 3H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.86, 148.13, 137.17, 134.88, 130.95, 125.20, 124.27 (Aryl *C*), 118.77 (*C*N), 112.53 (Aryl *C*), 82.88, 78.94 (Cage *C*), 34.99, 32.10, 22.42 (*C*H_2), 13.79 (*C*H_3), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -2.97 (s, 2B), -4.56 (s, 1B), -8.58 (s, 3B), -10.27 (s, 3B), -11.61 (s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{18}H_{27}B_{10}N_2$ $[M+H]^+$ 379.3177, found 379.3176.

Elemental analysis for $C_{18}H_{26}B_{10}N_2$ Calcd C, 57.12%; N, 7.40%. Found C, 56.82%; N 7.33%.



4g: Yield 66%. Colorless oil.

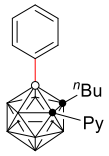
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.25 (m, 1H), 7.80 – 7.75 (m, 2H), 7.65 – 7.59 (m, 2H), 7.26 (s, 1H), 7.24 (s, 1H), 7.22 – 7.17 (m, 1H) (Aryl *H*), 3.82 (s, 3H) (C*H*$_3$), 2.73 – 2.64 (m, 1H), 2.15 – 2.07 (m, 1H), 1.70 – 1.58 (m, 1H), 1.53 – 1.41 (m, 1H), 1.21 – 1.13 (m, 2H) (C*H*$_2$), 0.77 (t, *J* = 7.4 Hz, 3H) (C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.05 (*C*OO), 151.04, 148.14, 136.96, 134.45, 130.33, 128.47, 125.26, 124.11 (Aryl *C*), 82.92, 79.04 (Cage *C*), 52.22 (O*C*H$_3$), 35.06, 32.10, 22.45 (*C*H$_2$), 13.81 (*C*H$_3$) , the B_{cage}–*C* was not observed.

^{11}B NMR (128 MHz, $CDCl_3$) δ -3.07 (s, 2B), -4.65 (s, 1B), -8.63 (s, 3B), -10.23 (s, 3B), -11.54 (s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{19}H_{30}B_{10}NO_2$ $[M+H]^+$ 412.3280, found 412.3283.

Elemental analysis for $C_{19}H_{29}B_{10}NO_2$ Calcd C, 55.45%; N, 3.40%. Found C, 55.43%; N 3.50%.



4h: Yield 69%. White solid, mp 85-88 ℃.

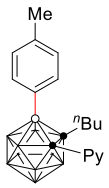
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.40 (m, 1H), 7.74 – 7.70 (m, 1H), 7.67 (td, *J* = 7.7, 1.8 Hz, 1H), 7.33 – 7.25 (m, 4H), 7.24 – 7.18 (m, 2H) (Aryl *H*), 2.82 (m, 1H), 2.25 – 2.16 (m, 1H), 1.87 – 1.74 (m, 1H), 1.65 – 1.56 (m, 1H), 1.33 – 1.22 (m, 2H) (C*H*$_2$), 0.88 (t, *J* = 7.4 Hz, 3H) (C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.11, 148.17, 136.80, 134.53, 128.95, 127.69, 125.35, 124.00 (Aryl *C*), 82.80, 79.07 (Cage *C*), 34.96, 32.12, 22.51 (*C*H$_2$), 13.87 (*C*H$_3$), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ-1.78 (s 1B), -4.10 (d, *J* = 187.4 Hz, 2B), -8.76 (s 3B), -10.53 (s 3B), -12.01 (s 1B).

HRMS (ESI) *m/z* Calcd for $C_{17}H_{28}B_{10}N$ $[M+H]^+$ 354.3225, found 354.3225.

Elemental analysis for $C_{17}H_{27}B_{10}N$ Calcd C, 57.76%; N, 3.96%. Found C, 58.06%; N 3.86 %.



4i: Yield 63%. White solid, mp 125-128 ℃.

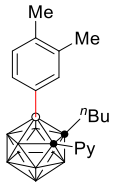
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (ddd, J = 4.7, 1.7, 1.0 Hz, 1H), 7.74 – 7.63 (m, 2H), 7.28 (ddd, J = 7.1, 4.8, 1.5 Hz, 1H), 7.14 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H) (Aryl *H*), 2.84 – 2.76 (m, 1H) (CH_2), 2.31 (s, 3H) (CH_3), 2.21 – 2.13 (m, 1H), 1.87 – 1.75 (m, 1H), 1.64 – 1.52 (m, 1H) (CH_2), 1.32 – 1.22 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.15, 148.21, 138.89, 136.76, 134.54, 128.58, 125.40, 123.97 (Aryl *C*), 82.69, 79.02 (Cage *C*), 34.90, 32.12, 22.54 (*C*H$_2$), 21.36, 13.90 (*C*H$_3$), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -1.63 (s, 1B), -4.20 (d, J = 181.4 Hz, 2B), -8.82 (s, 3B), -10.49 (s, 3B), -12.14 (s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{18}H_{30}B_{10}N$ $[M+H]^+$ 368.3381, found 368.3386.

Elemental analysis for $C_{18}H_{29}B_{10}N$ Calcd C, 58.82%; N, 3.81%. Found C, 59.01%; N 3.59%.



4j: Yield 60%. White solid, mp 157-162 ℃.

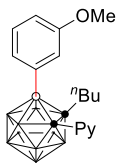
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (ddd, J = 4.7, 1.8, 1.0 Hz, 1H), 7.76 – 7.64 (m, 2H), 7.29 (ddd, J = 7.2, 4.8, 1.4 Hz, 1H), 7.02 (s, 1H), 6.99 – 6.86 (m, 2H) (Aryl *H*), 2.83 – 2.76 (m, 1H) (CH_2), 2.21 (s, 3H) (CH_3), 2.20 – 2.15 (m, 1H) (CH_2), 2.14 (s, 3H) (CH_3), 1.88 – 1.76 (m, 1H) (CH_2), 1.64 – 1.52 (m, 1H), 1.30 – 1.24 (m, 2H) (CH_2), 0.88 (t, J = 7.4 Hz, 3H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.26, 148.21, 137.62, 136.67, 136.09, 135.78, 131.98, 129.09, 125.49, 123.92 (Aryl *C*), 82.69, 78.99 (Cage *C*), 34.83, 32.10, 22.54 (*C*H$_2$), 19.89, 19.69, 13.91 (CH_3), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -1.58 (s, 1B), -4.23 (d, J = 175.3 Hz, 2B), -6.44 – -9.62 (m, 3B), -10.69 (s, 3B), -12.17 (s, 1B).

HRMS (ESI) *m/z* Calcd for $C_{19}H_{32}B_{10}N$ $[M+H]^+$ 382.3538, found 382.3534.

Elemental analysis for $C_{19}H_{31}B_{10}N$ Calcd C, 59.81%; N, 3.67%. Found C, 59.97%; N 3.42%.



4k: Yield 54%. White solid, mp 157-162 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.39 (m, 1H), 7.73 – 7.65 (m, 2H), 7.29 – 7.25 (m, 1H), 7.13 – 7.08 (m, 1H), 6.84 – 6.78 (m, 2H), 6.77 – 6.73 (m, 1H) (Aryl *H*), 3.63 (s, 3H) (OCH_3), 2.80 (ddd,

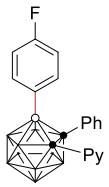
J = 15.0, 12.4, 4.6 Hz, 1H), 2.16 (ddd, *J* = 15.0, 12.3, 4.5 Hz, 1H), 1.83 – 1.72 (m, 1H), 1.60 – 1.49 (m, 1H), 1.28 – 1.21 (m, 2H) (CH_2), 0.85 (t, *J* = 7.4 Hz, 3H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.83, 152.47, 149.29, 137.86, 129.88, 128.07, 126.50, 125.03, 121.06, 115.68 (Aryl *C*), 83.95, 80.05(Cage *C*), 56.13 (O*C*H$_3$), 36.11, 33.20, 23.61 (*C*H$_2$), 14.95 (C*H*$_3$), the B_{cage}–*C* was not observed.

^{11}B NMR (128 MHz, $CDCl_3$) δ -2.11 (s, 1B), -4.16 (d, *J* = 190.2 Hz, 2B), -6.71 – -11.13 (m, 5B), -12.08 (s, 2B).

HRMS (ESI) *m/z* Calcd for $C_{18}H_{30}B_{10}NO$ $[M+H]^+$ 384.3331, found 384.3332.

Elemental analysis for $C_{18}H_{29}B_{10}NO$ Calcd C, 56.37%; N, 3.65%. Found C, 56.45%; N 3.42%.



4l: Yield 81%. White solid, mp 232-234 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (ddd, *J* = 4.7, 1.9, 0.9 Hz, 1H), 7.52 (m, 2H), 7.41 (td, *J* = 7.9, 1.9 Hz, 1H), 7.27 (m, 1H), 7.22 (ddd, *J* = 7.6, 4.7, 1.0 Hz, 1H), 7.14 – 7.07 (m, 3H), 6.89 (m, 2H), 6.79 – 6.72 (m, 2H) (Aryl *H*).

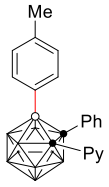
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.52 (d, *J* = 249.8 Hz), 149.29, 148.65, 137.86 (d, *J* = 7.7 Hz), 136.20, 132.28, 130.61, 129.91, 127.46, 126.16, 124.50, 114.27 (d, *J* = 20.1 Hz) (Aryl *C*), 84.05, 82.98 (Cage *C*), the B_{cage}–*C* was not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.21 (s, 3B), -7.82 (s, 2B), -8.76 – -11.29 (m, 5B).

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.08 (s, 1F).

HRMS (ESI) *m/z* Calcd for $C_{19}H_{23}B_{10}NF$ $[M+H]^+$ 392.2818, found 392.2815.

Elemental analysis for $C_{19}H_{22}B_{10}NF$ Calcd C, 58.29%; N, 3.58%. Found C, 58.35%; N 3.53%.



4m: Yield 73%. White solid, mp 242-243 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (ddd, *J* = 4.8, 2.0, 0.9 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.39 (td, *J* = 7.9, 1.9 Hz, 1H), 7.26 – 7.18 (m, 2H), 7.17 – 7.07 (m, 3H), 6.87 (m, 2H), 6.78 (m, 2H) (Aryl *H*), 2.27 (s, 3H) (C*H*$_3$).

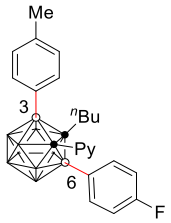
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.42, 148.53, 138.90, 136.07, 135.88, 132.34, 130.88, 129.73, 128.00, 127.35, 126.34, 124.36 (Aryl *C*), 83.86, 82.85 (Cage *C*), 21.40 (*C*H$_3$), the B_{cage}–*C* was not observed.

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ -1.53 (s, 1B), -3.35 (s, 2B), -7.89 (s, 2B), -8.65 – -13.03 (m, 5B).

HRMS (ESI) *m/z* Calcd for $C_{20}H_{26}B_{10}N$ $[M+H]^+$ 388.3068, found 388.3068.

Elemental analysis for $C_{20}H_{25}B_{10}N$ Calcd C, 61.99%; N, 3.61%. Found C, 62.11%; N 3.59%.

2.4 General procedure for synthesis of asymmetric 3,6-diaryl-*o*-carborane 5. To a 25 mL dried flask were sequentially added **4i** (0.1 mmol), 4-fluorophenylboronic acid (0.15 mmol), $Pd(OAc)_2$ (0.01 mmol, 2.24 mg), Ag_2O (0.1 mmol, 23.1 mg), and DMF (0.2 M) under air atmosphere. The reaction was carried out in a sealed tube and stirred at room tempeature for 3 h. After the reaction was completed, a saturated solution of aqueous NaCl was added and the mixture was extracted three times with ethyl acetate. The organic phases were collected, and solvent evaporation under reduced pressure afforded the crude product, which was then purified by column chromatography to provide the target products, by using silica gel as stationary phase and petroleum ether and ethyl acetate as eluent.



5: Yield 70%. White solid, mp 133-136 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (ddd, J = 4.8, 1.8, 0.7 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.76 (td, J = 7.9, 1.9 Hz, 1H), 7.14 (ddd, J = 7.5, 4.7, 0.8 Hz, 1H), 7.08 – 7.02 (m, 2H), 6.94 (q, J = 8.2 Hz, 4H), 6.84 – 6.77 (m, 2H) (Aryl *H*), 2.58 – 2.51 (m, 2H) (CH_2), 2.25 (s, 3H) (CH_3), 1.72 – 1.61 (m, 2H), 1.27 – 1.17 (m, 2H) (CH_2), 0.83 (t, J = 7.3 Hz, 3H) (CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.40 (d, J = 248.9 Hz), 152.82, 147.07, 138.78, 136.58, 135.81 (d, J = 7.8 Hz), 133.87, 128.50, 126.30, 123.24, 114.71 (d, J = 20.2 Hz) (Aryl *C*), 83.49, 78.39 (Cage *C*), 33.80, 32.48, 22.77 (*C*H_2), 21.29, 13.85 (*C*H_3), two B_{cage}–*C* were not observed.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 0.24 (s, 3B), -3.88 (d, J = 160.6 Hz, 2B), -10.06 (s, 3B), -12.96 (s, 2B).

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.36 (s, 1F).

HRMS (ESI) *m/z* Calcd for $C_{24}H_{33}B_{10}NF$ $[M+H]^+$ 462.3600, found 462.3601.

Elemental analysis for $C_{24}H_{32}B_{10}NF$ Calcd C, 62.45%; N, 3.03%. Found C, 62.56%; N 3.07%.

2.5 X-ray Structure Determination.

Single-crystal X-ray data of compounds **3l** and **4j** was collected on a Rigaku XtaLAB PRO 007HF diffractometer using Mo-K radiation. The structure was solved by direct methods and refined on F^2 by the SHELXL 97 program.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were treated as riding atoms using the SHELX 97 default parameters.

Table S4 Crystal data and structure refinement for **3l** (CCDC 2031426)

Empirical formula	$C_{13}H_{19}B_{10}N$
Formula weight	297.39
Temperature/K	180
Radiation type	MoKa
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	P2(1)/n
a/Å	6.5832(2)
b/Å	12.9279(4)
c/Å	19.4223(7)
a/°	90
b/°	92.067(3)
g/°	90
Volume/$Å^3$	1651.90(9)
Z	4
Density (calculated)/g cm^{-3}	1.196
Absorption coefficient/mm^{-1}	0.060
F(000)	616
Crystal size/mm^3	0.4 x 0.37 x 0.21
Theta range for data collection/°	2.624 to 27.484
Index ranges	$-8 \le h \le 5$, $-16 \le k \le 16$, $-24 \le l \le 25$
Reflections collected	10939
Independent reflections	2989 [R_{int} = 0.0631]
Data / restraints / parameters	3782 / 0 / 242
Goodness-of-fit on F^2	1.020
Final R indices [I>4sigma(I)]	R_1 = 0.0631
R indices (all data)	R_1 = 0.0774, wR_2 = 0.1673
Largest diff. peak and hole/e $Å^{-3}$	0.664 and -0.628

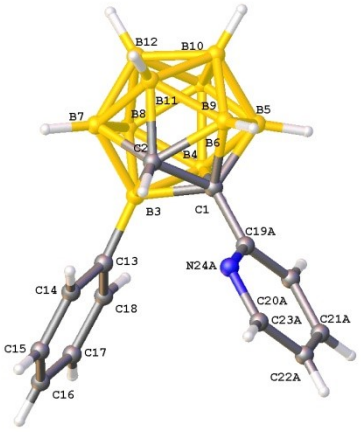


Figure S1 Molecular structure of **3l**

Table S5 Crystal data and structure refinement for **4j** (CCDC 2043212)

Empirical formula	$C_{19}H_{31}B_{10}N$
Formula weight	382.56
Temperature/K	298(2)
Radiation type	MoKa
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	P2(1)/n
a/Å	10.8652(9)
b/Å	10.6399(9)
c/Å	19.5358(15)
a/°	90
b/°	100.152(3)
g/°	90
Volume/Å^3	2223.1(3)
Z	4
Density (calculated)/g cm^{-3}	1.143
Absorption coefficient/mm^{-1}	0.058
F(000)	812
Crystal size/mm^3	0.43 x 0.40 x 0.38
Theta range for data collection/°	2.12 to 25.02
Index ranges	$-12 \le h \le 9$, $-12 \le k \le 10$, $-22 \le l \le 23$
Reflections collected	10960
Independent reflections	3912 [R_{int} = 0.0614]
Data / restraints / parameters	3912 / 0 / 274
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R_1 = 0.0695, wR_2 = 0.1842
R indices (all data)	R_1 = 0.1329, wR_2 = 0.2162
Largest diff. peak and hole/e Å^{-3}	0.198 and -0.262

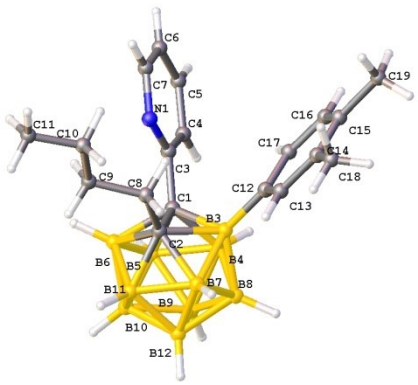


Figure S2 Molecular structure of **4j**

3. References

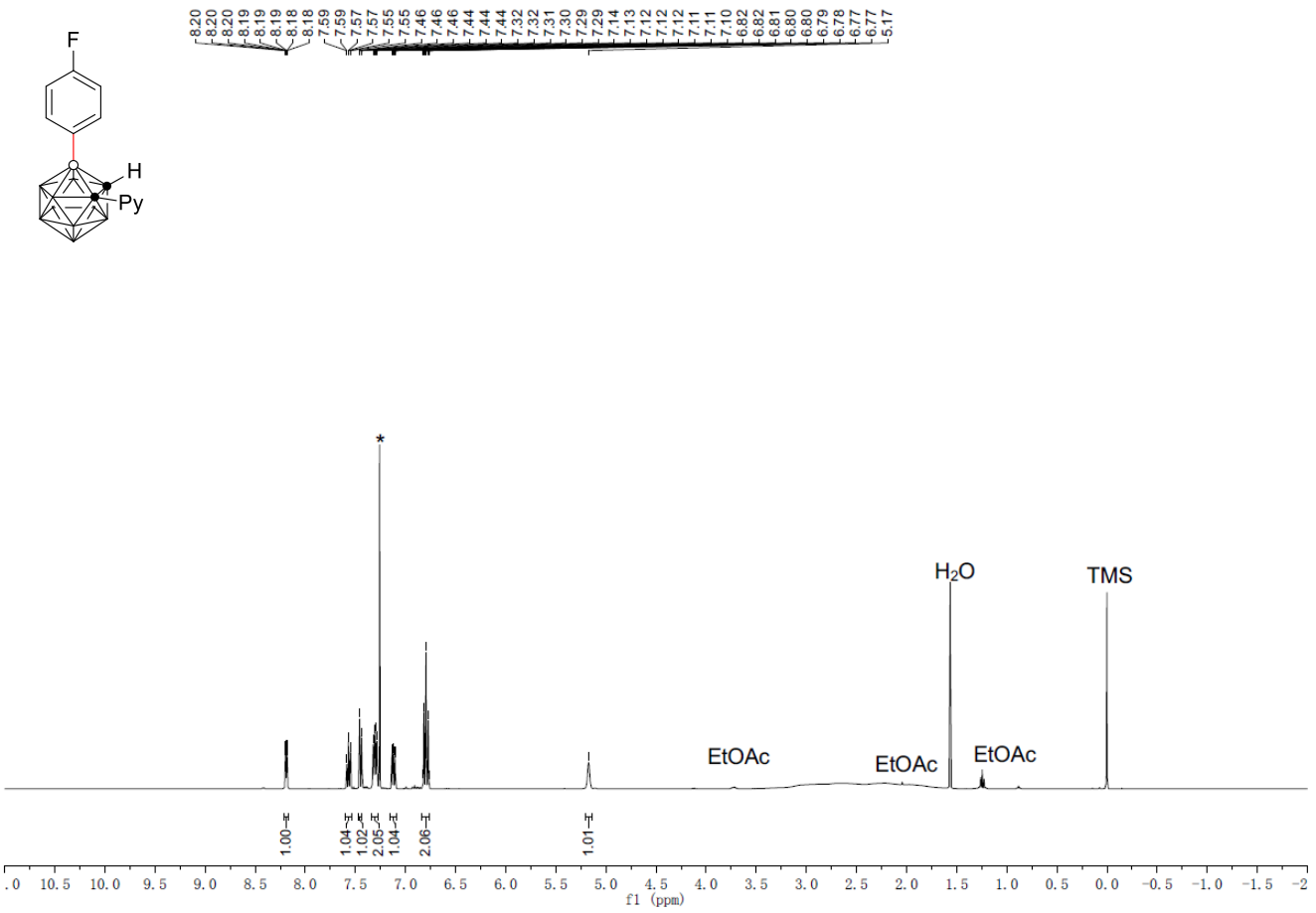
(1) Lu, J. Y.; Zhao, B.; Du, Y. ; Yang, J.; Lu, J. Transition-metal-free direct nucleophilic substitution of carboranyllithium and 2-halopyridines. *Org. Biomol. Chem.* **2019**, *32*, 7438−7441.

(2) Coult, R.; Fox, M. A.; Gill, W. R.; Herbertson, P. L.; MacBride, J. A. H.; Wade, K. C-Arylation and C-heteroArylation of icosahedral carboranes via their copper(I) derivatives. *J. Organomet. Chem.* **1993**, *462*, 19–29.

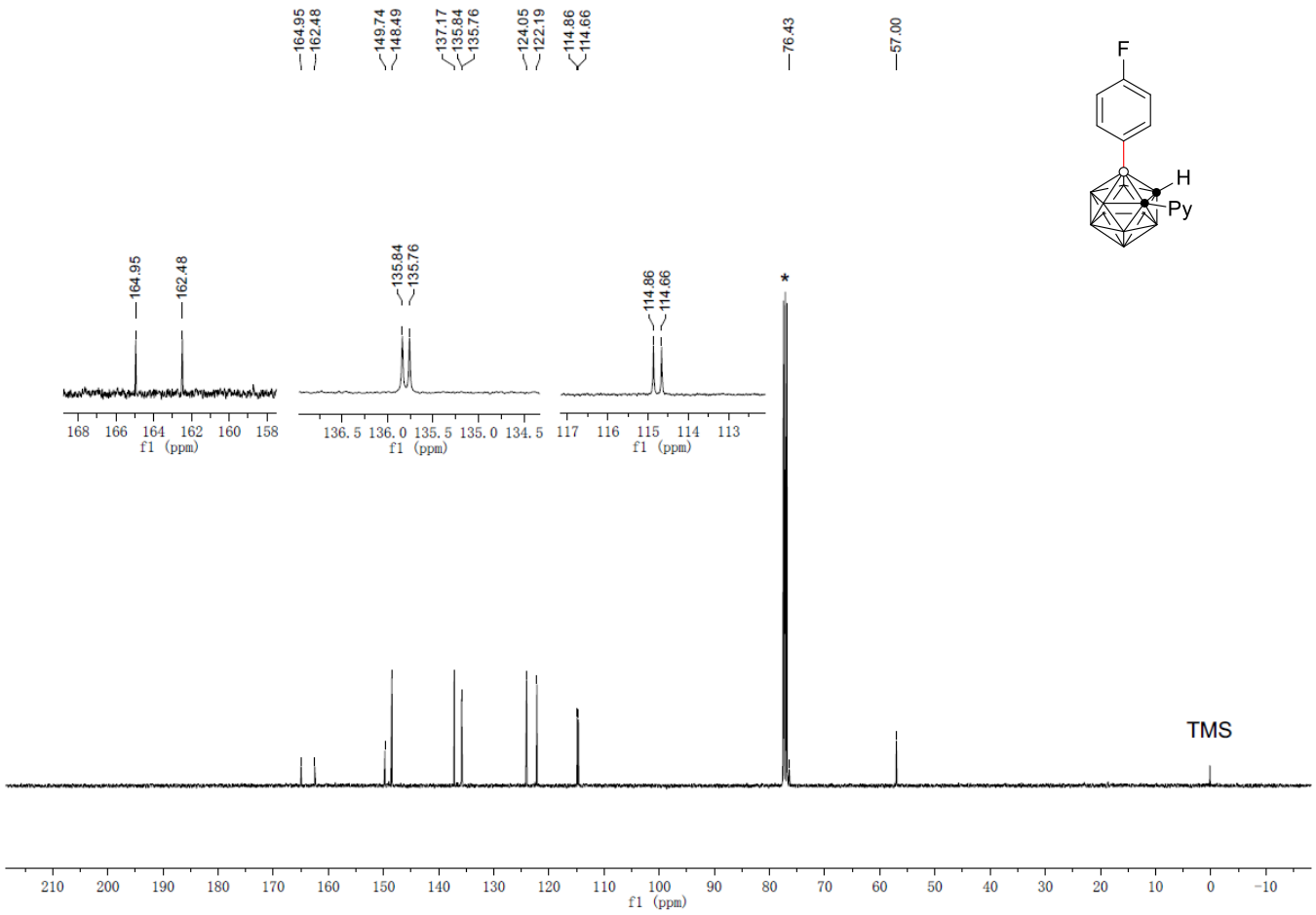
(3) Sheldrick, G. M. SHELX97. University of Göttingen, Germany, 1997.

4. NMR Spectra

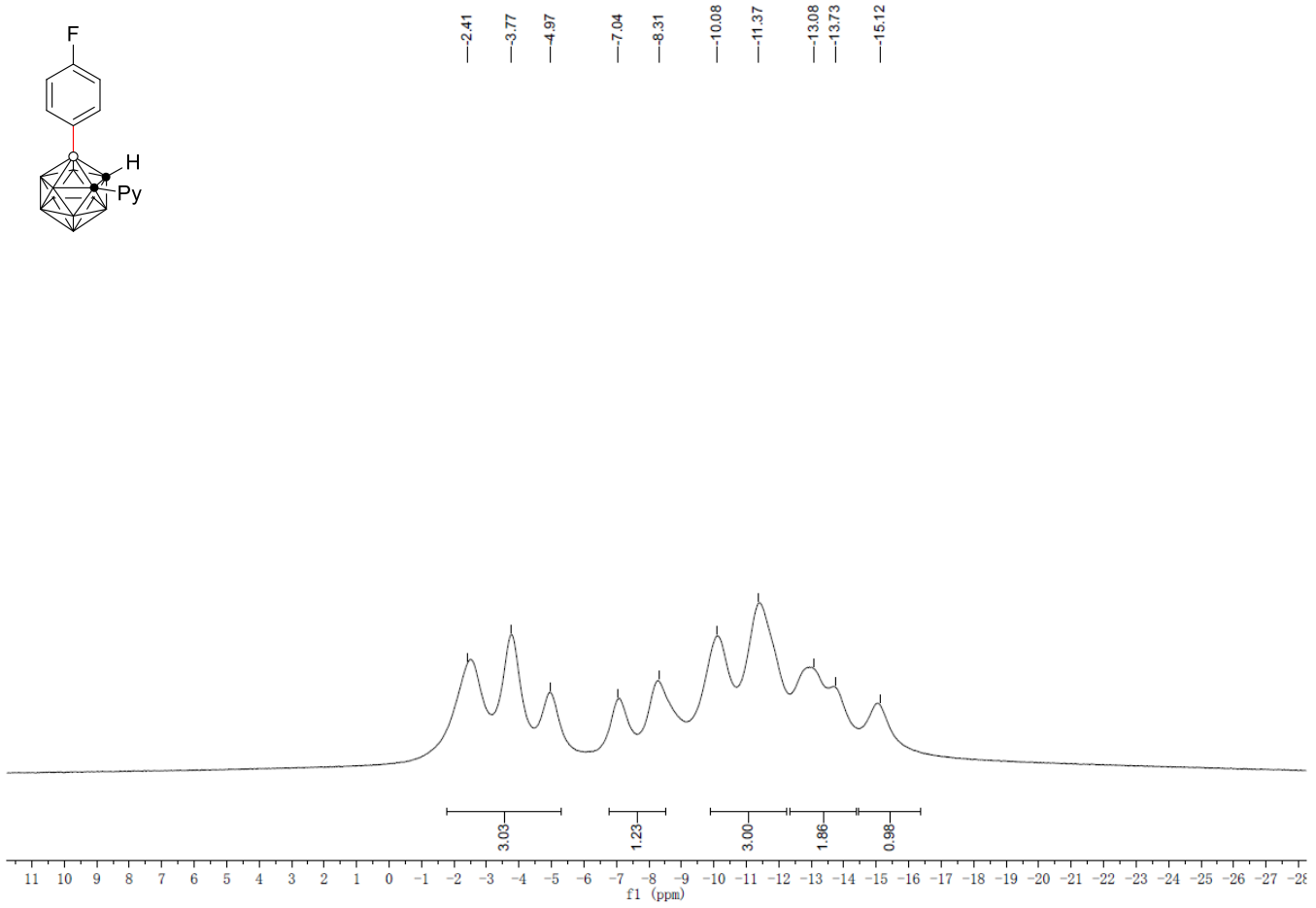
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3a**



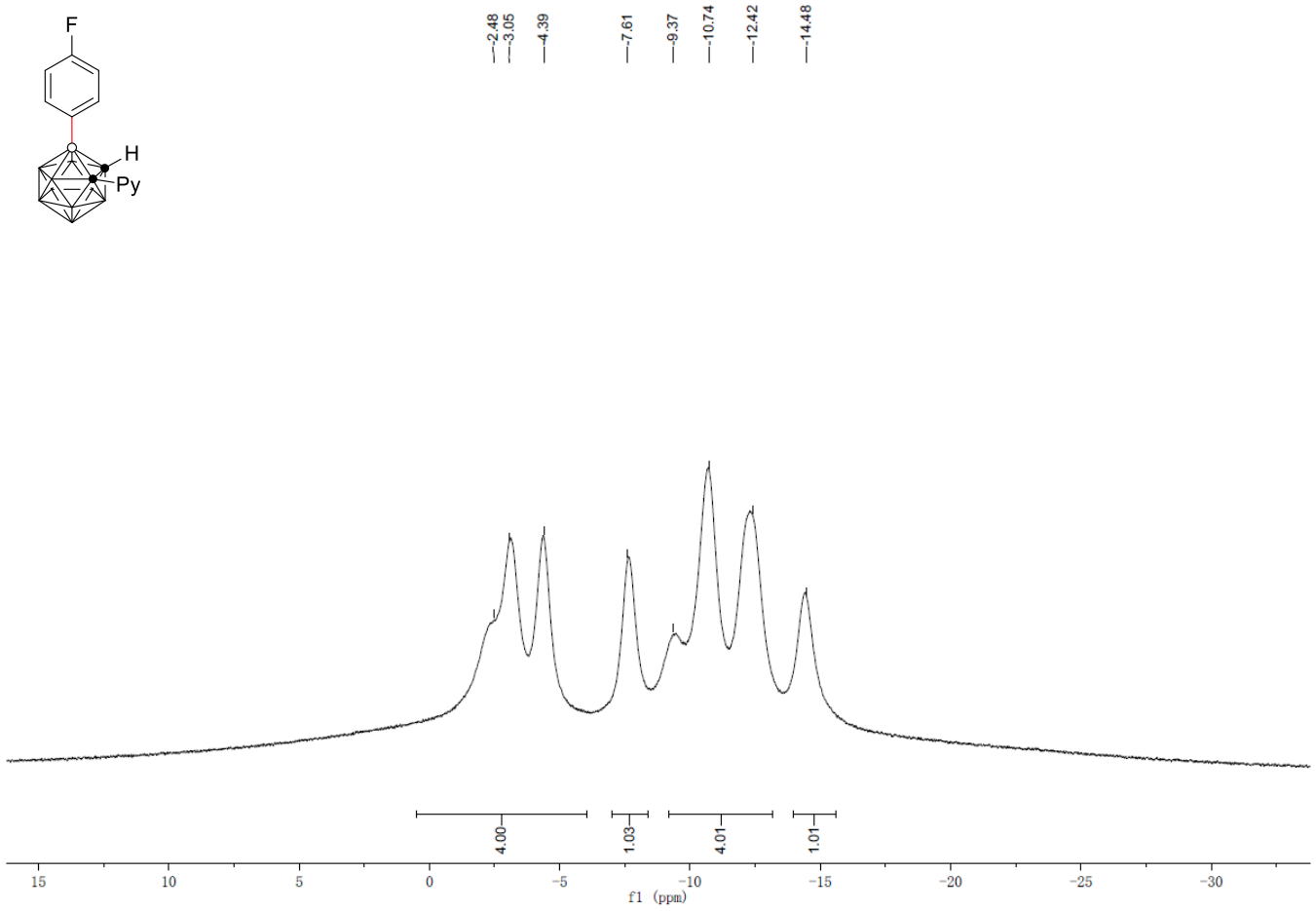
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3a**



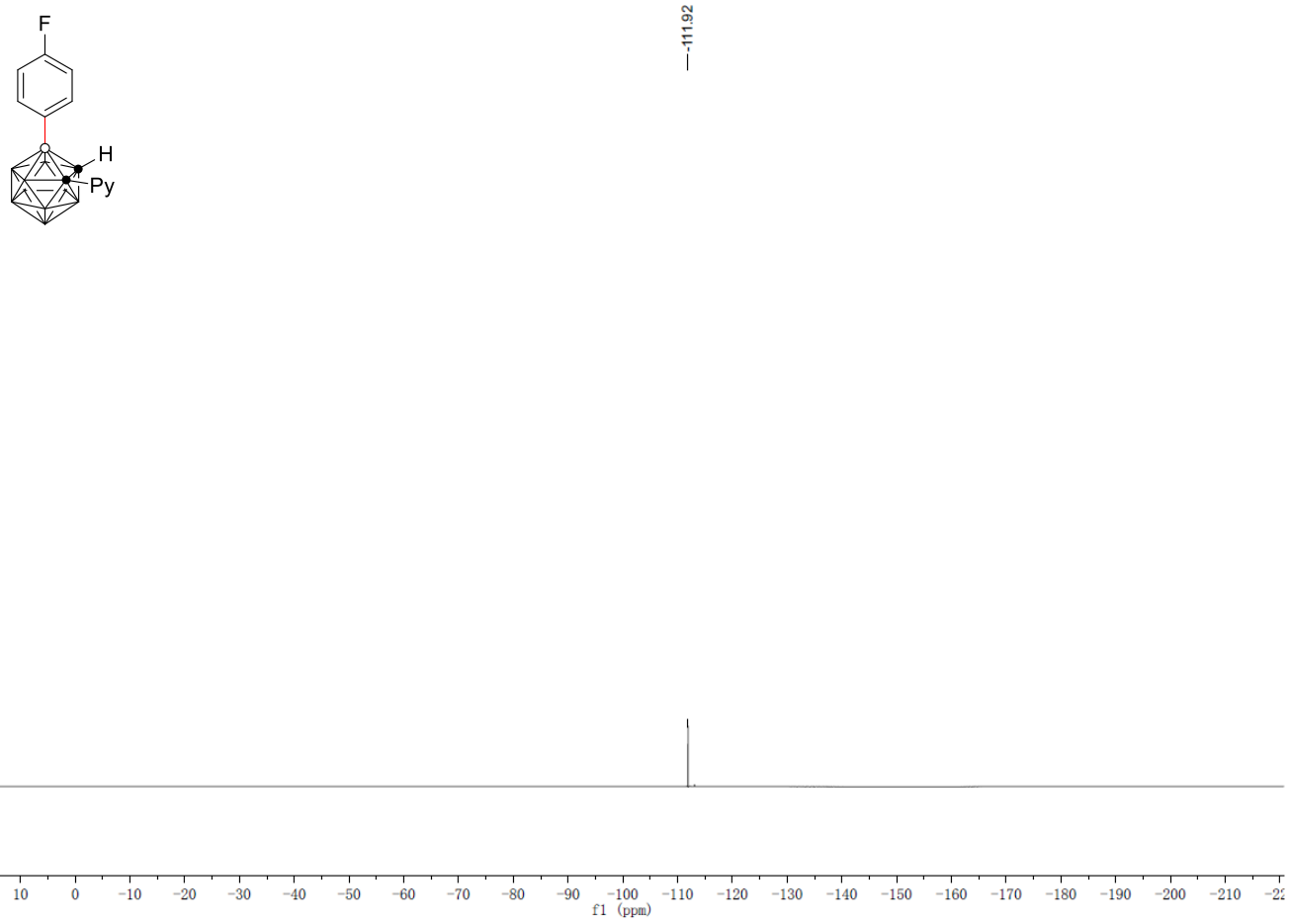
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3a**



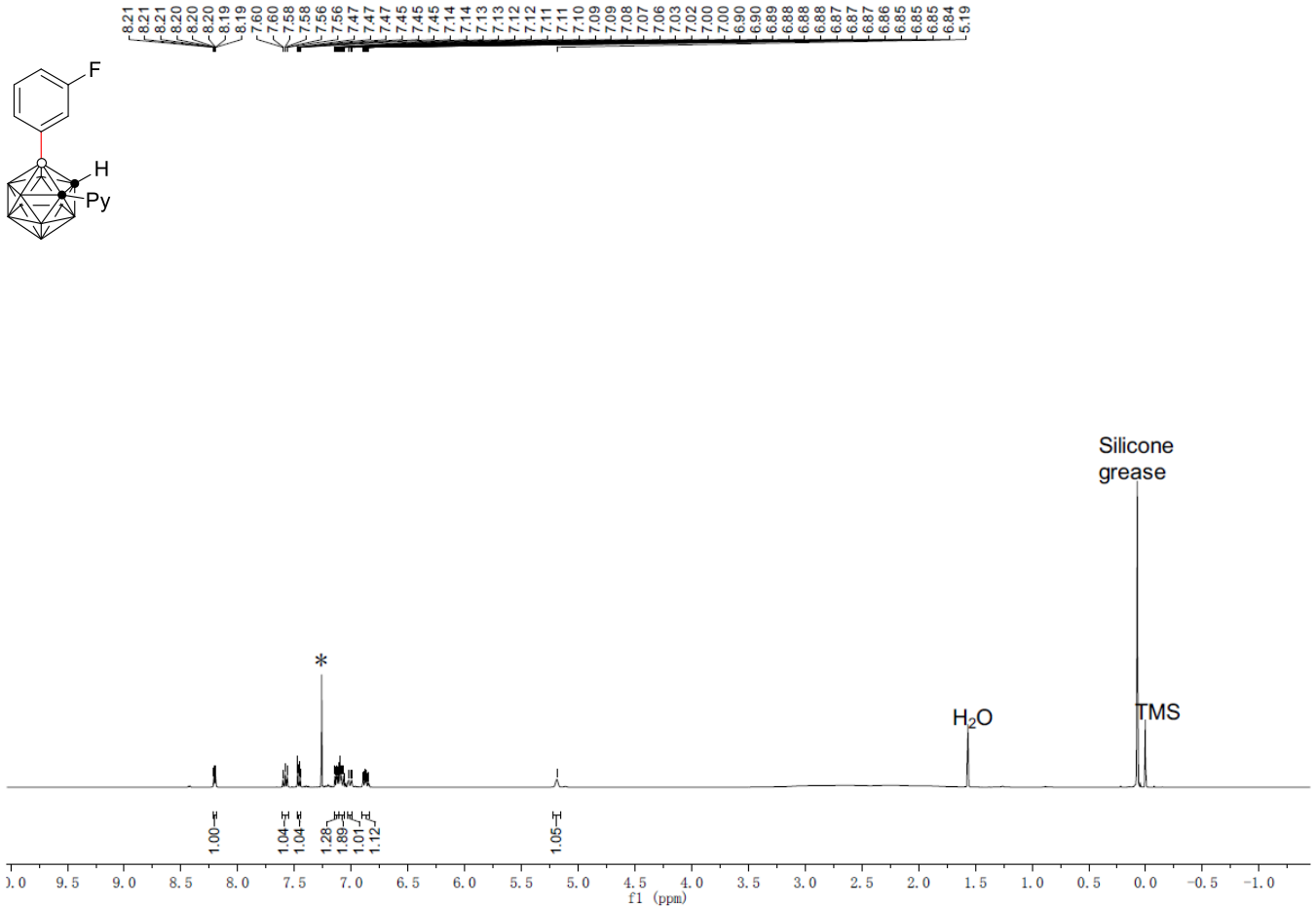
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3a**



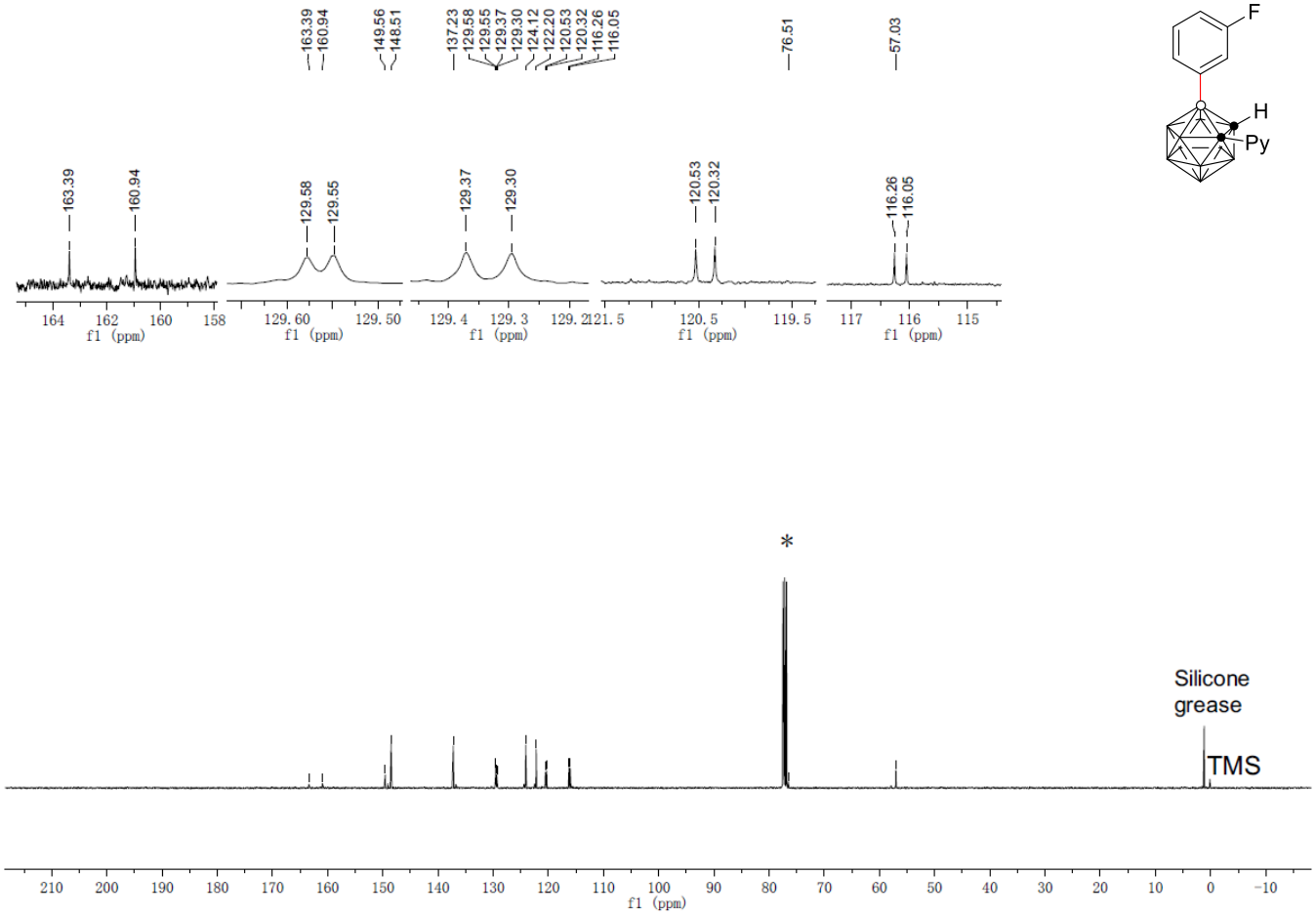
^{19}F NMR (376 MHz, $CDCl_3$ *) of **3a**



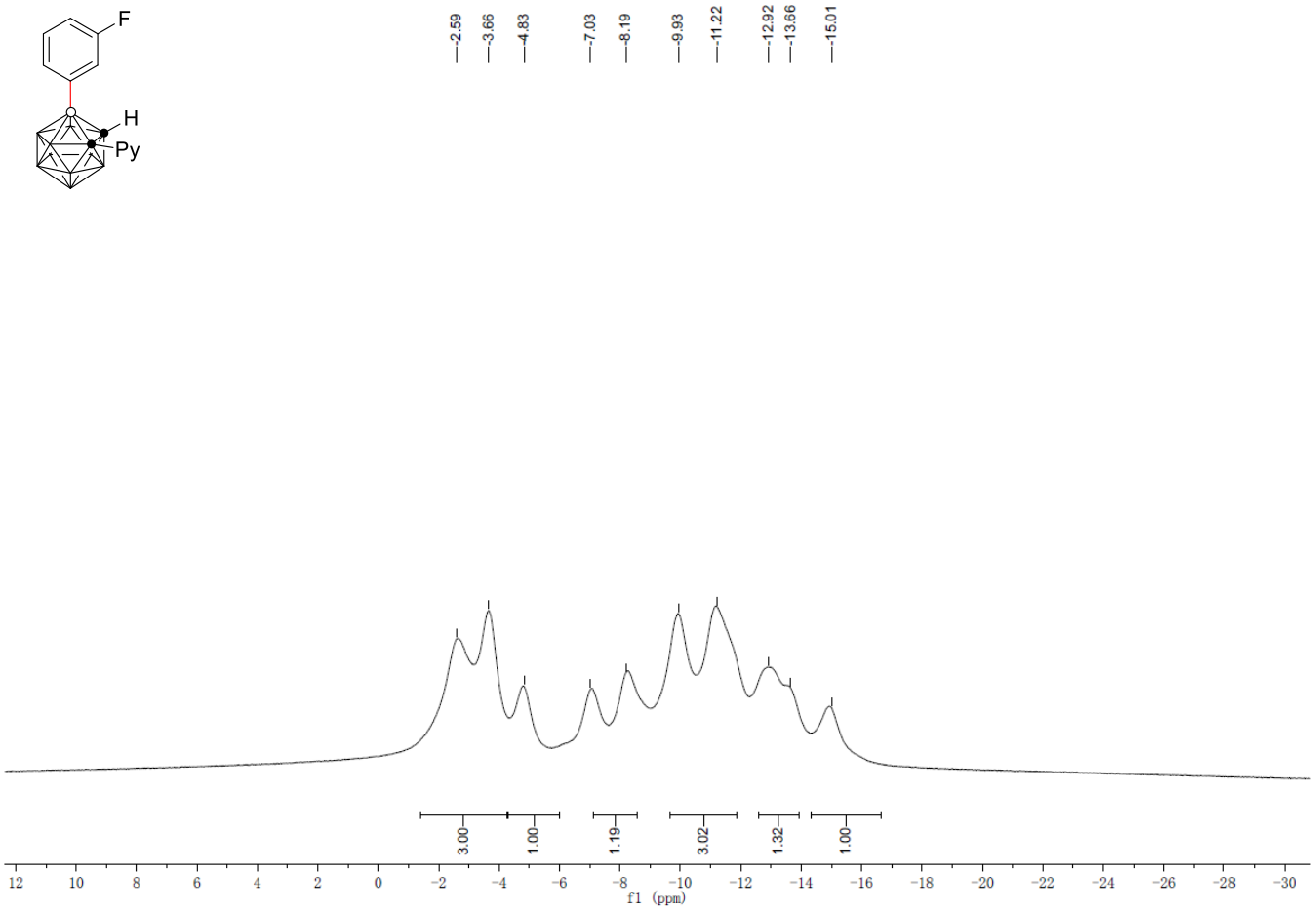
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3b**



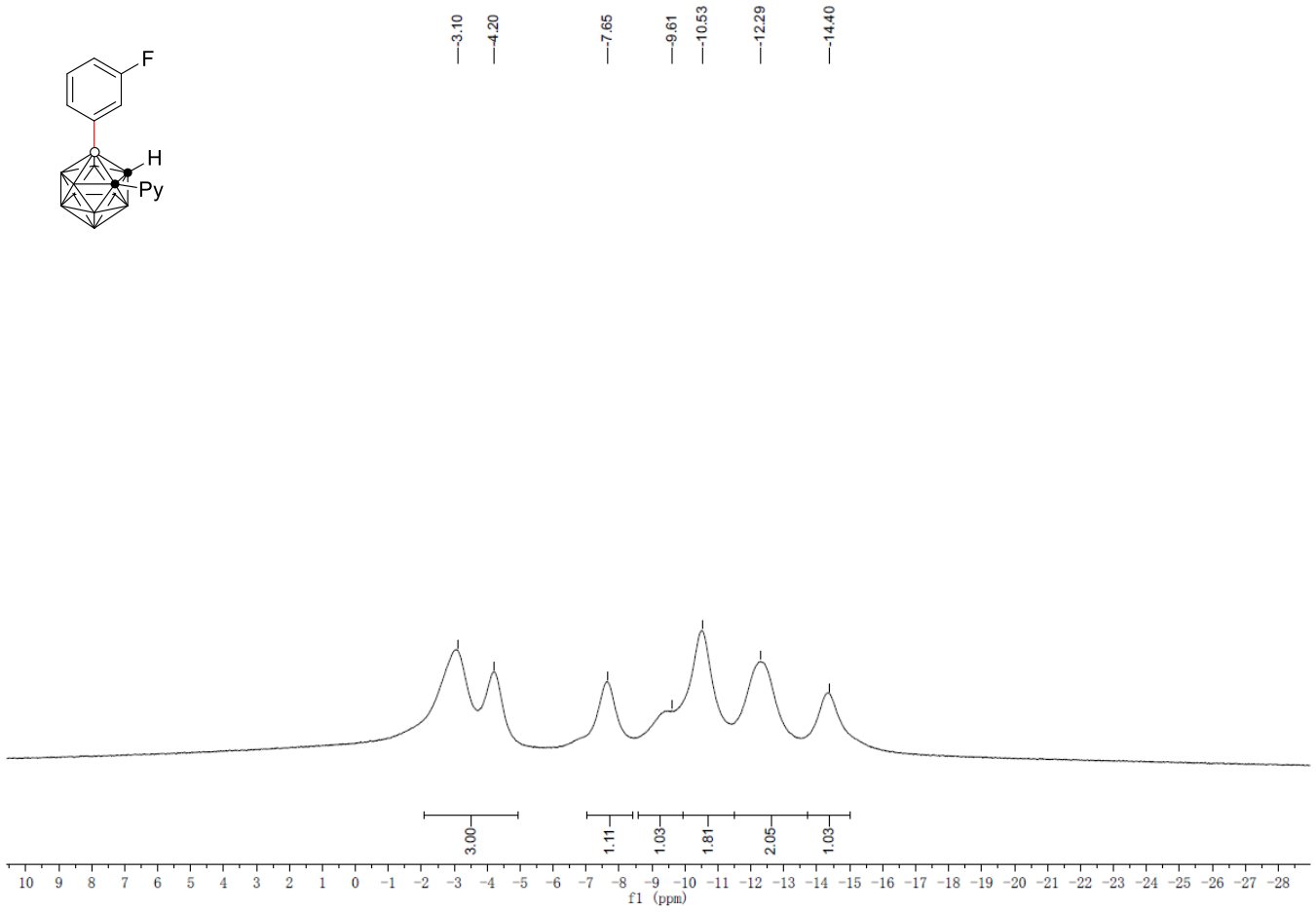
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3b**



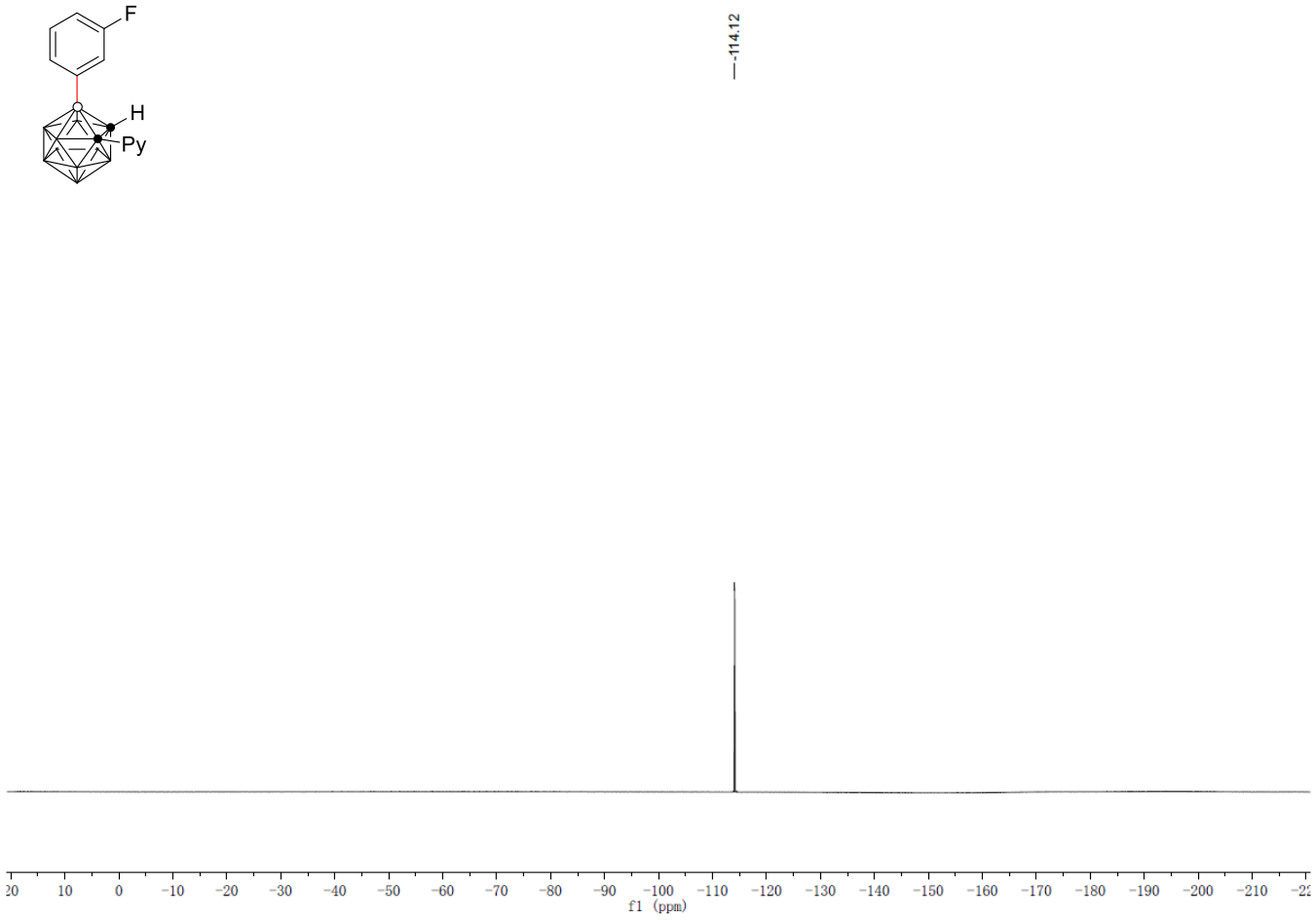
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3b**



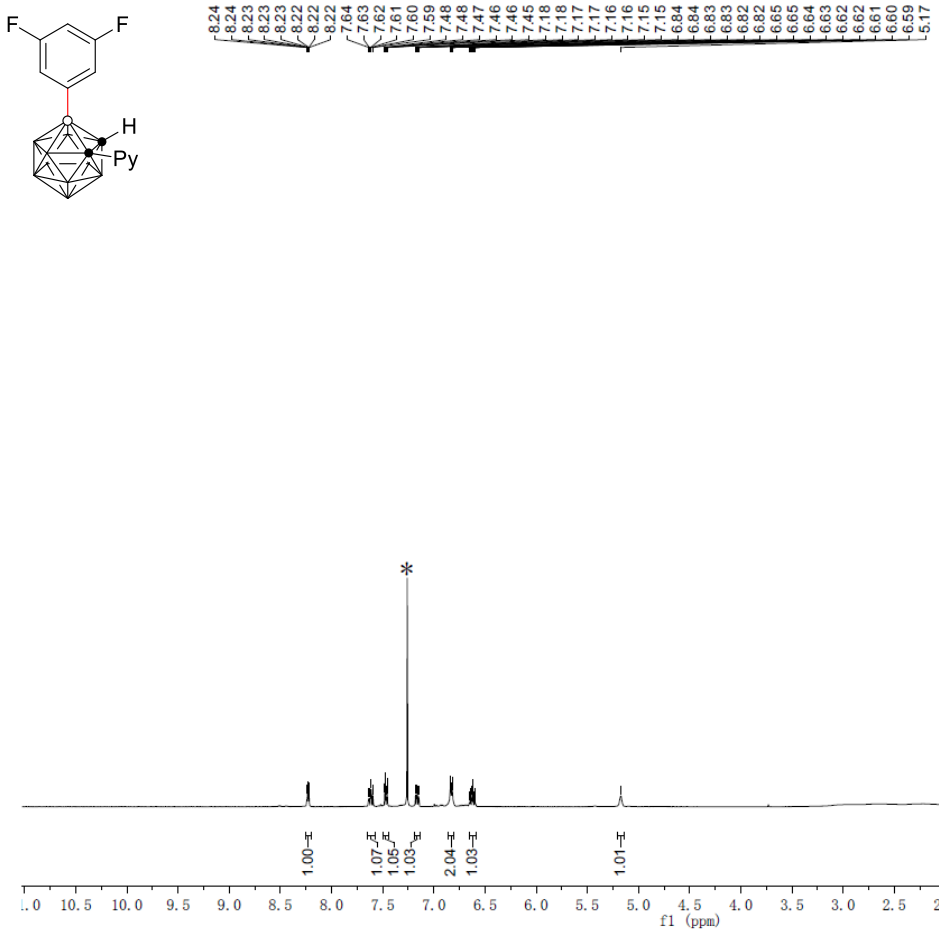
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3b**



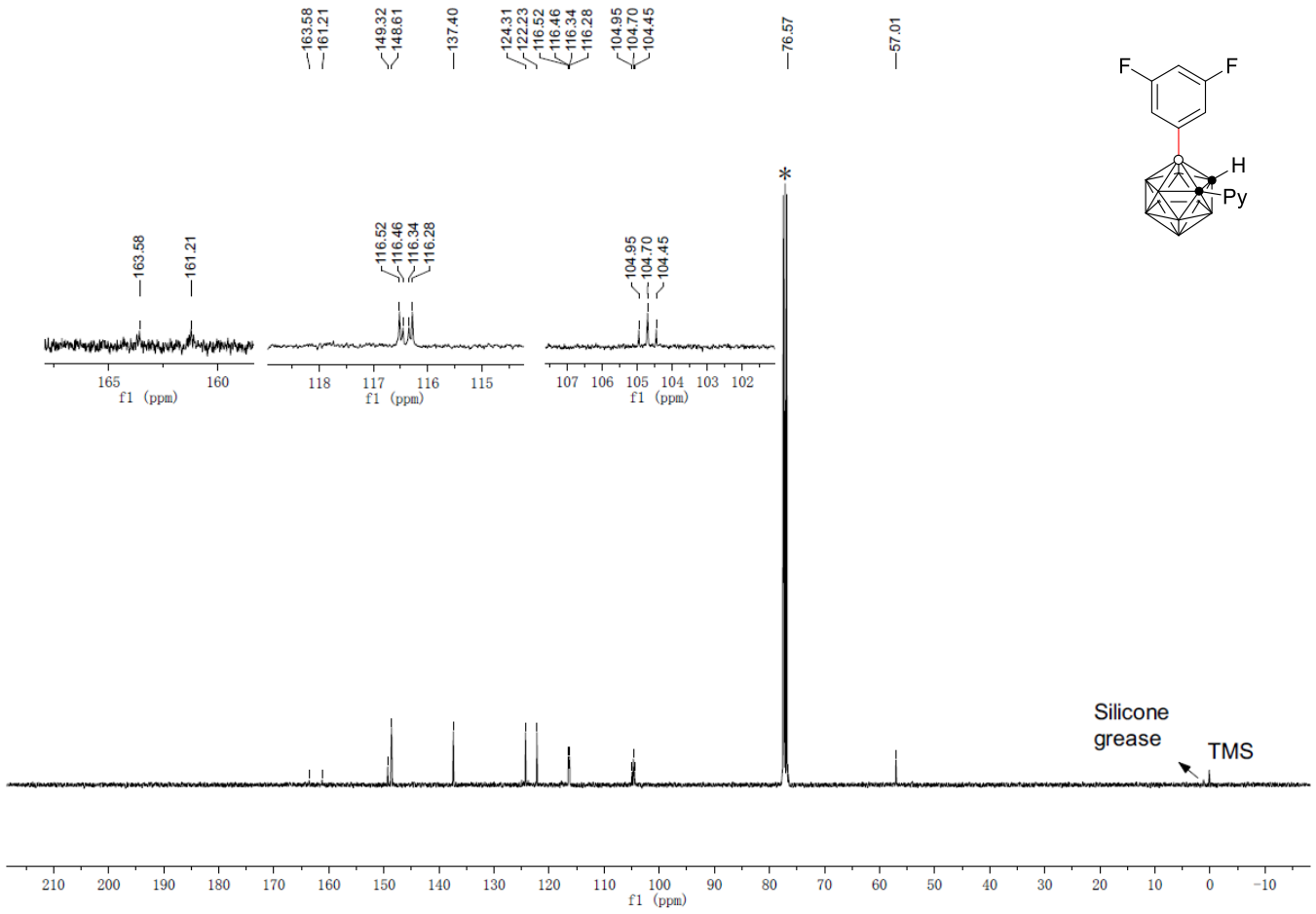
^{19}F NMR (376 MHz, $CDCl_3$ *) of **3b**



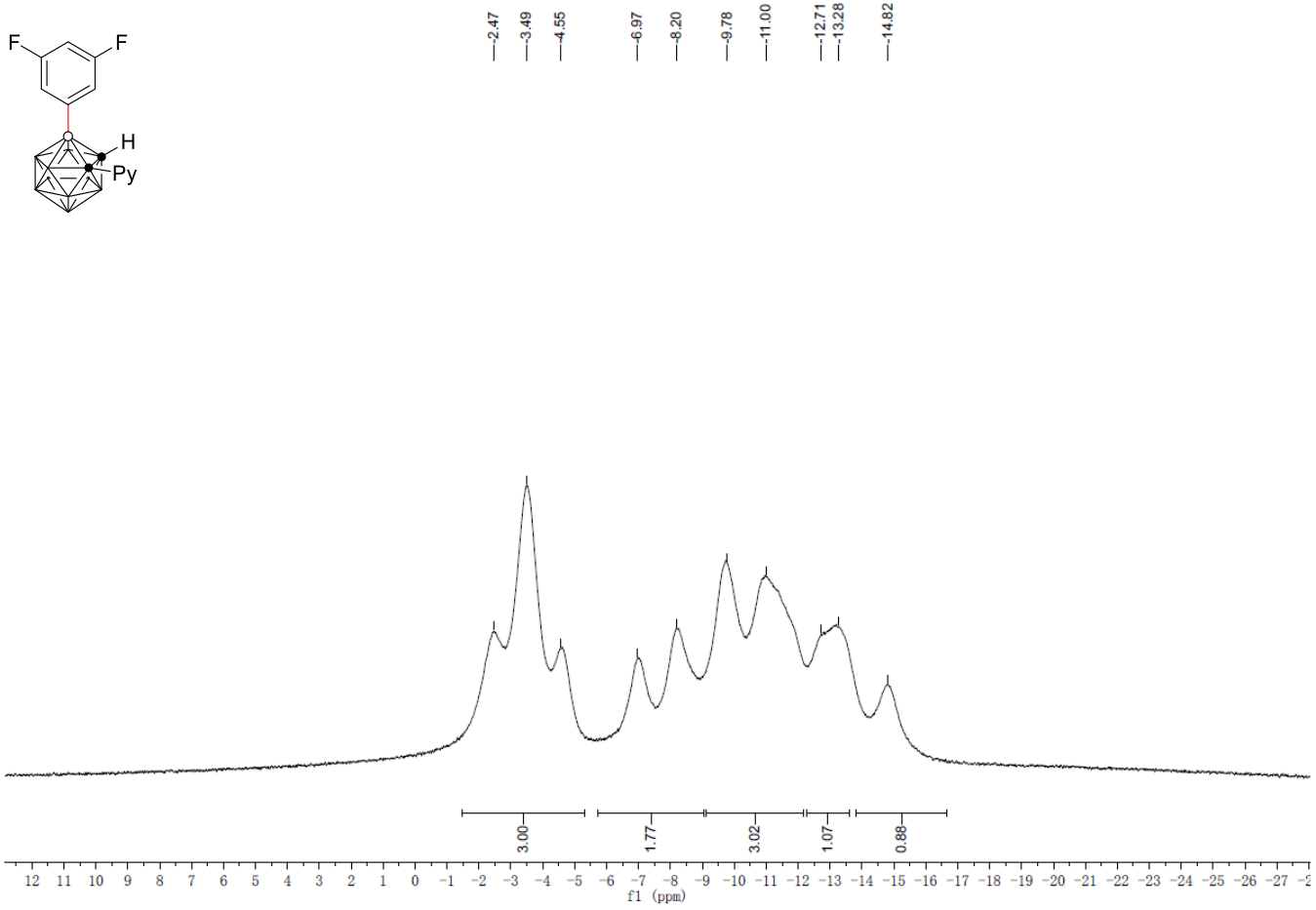
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3c**



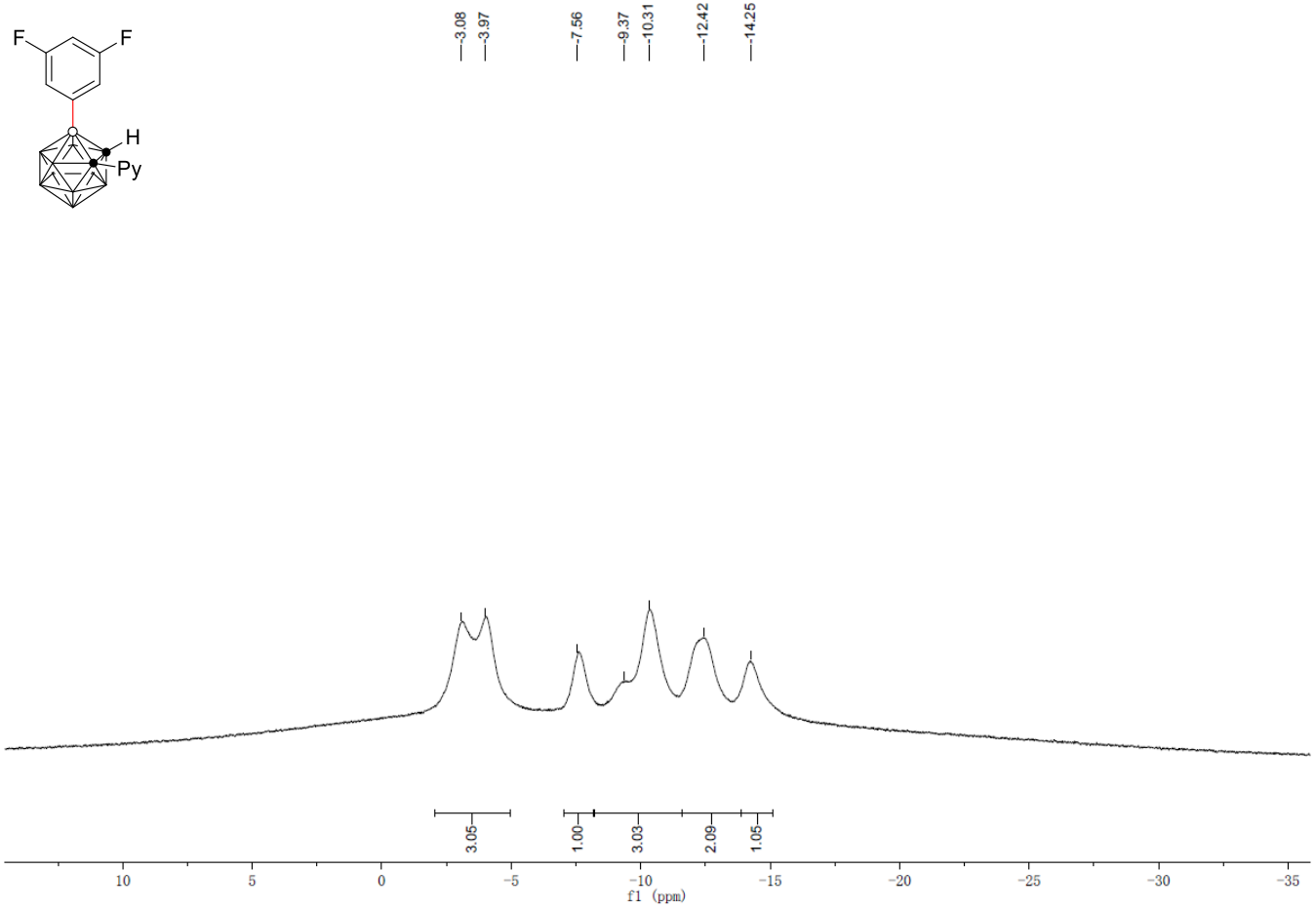
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3c**



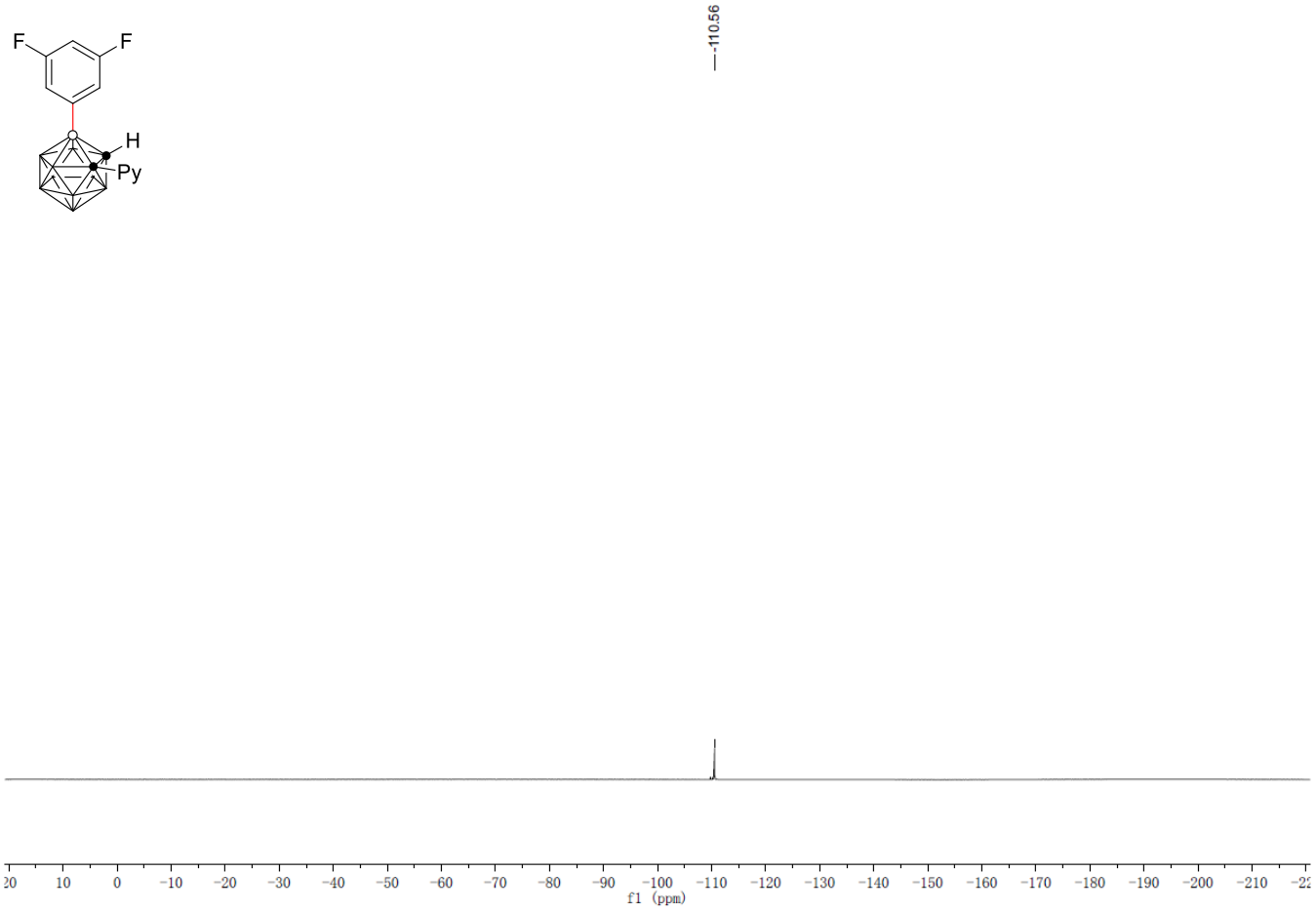
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3c**



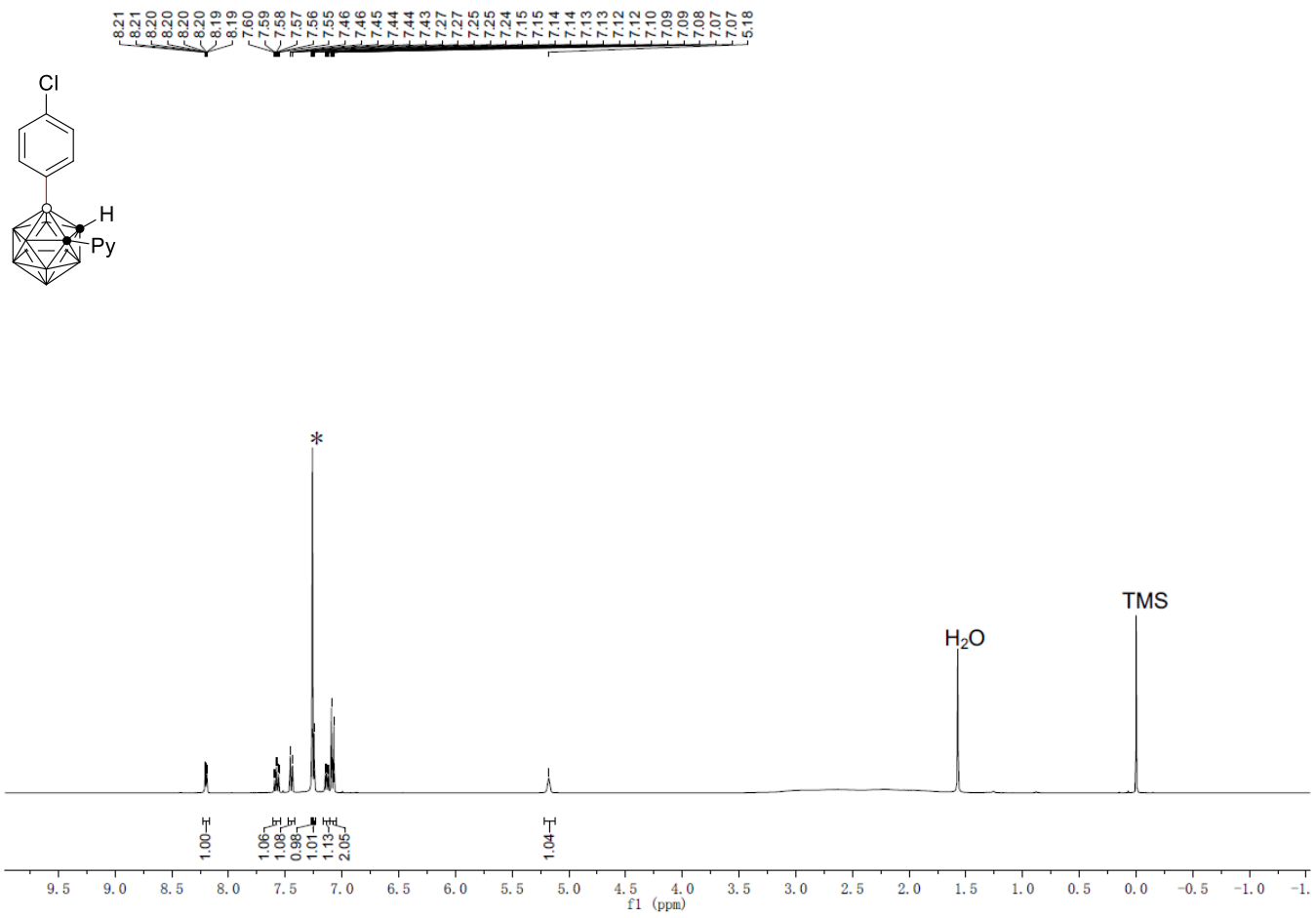
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3c**



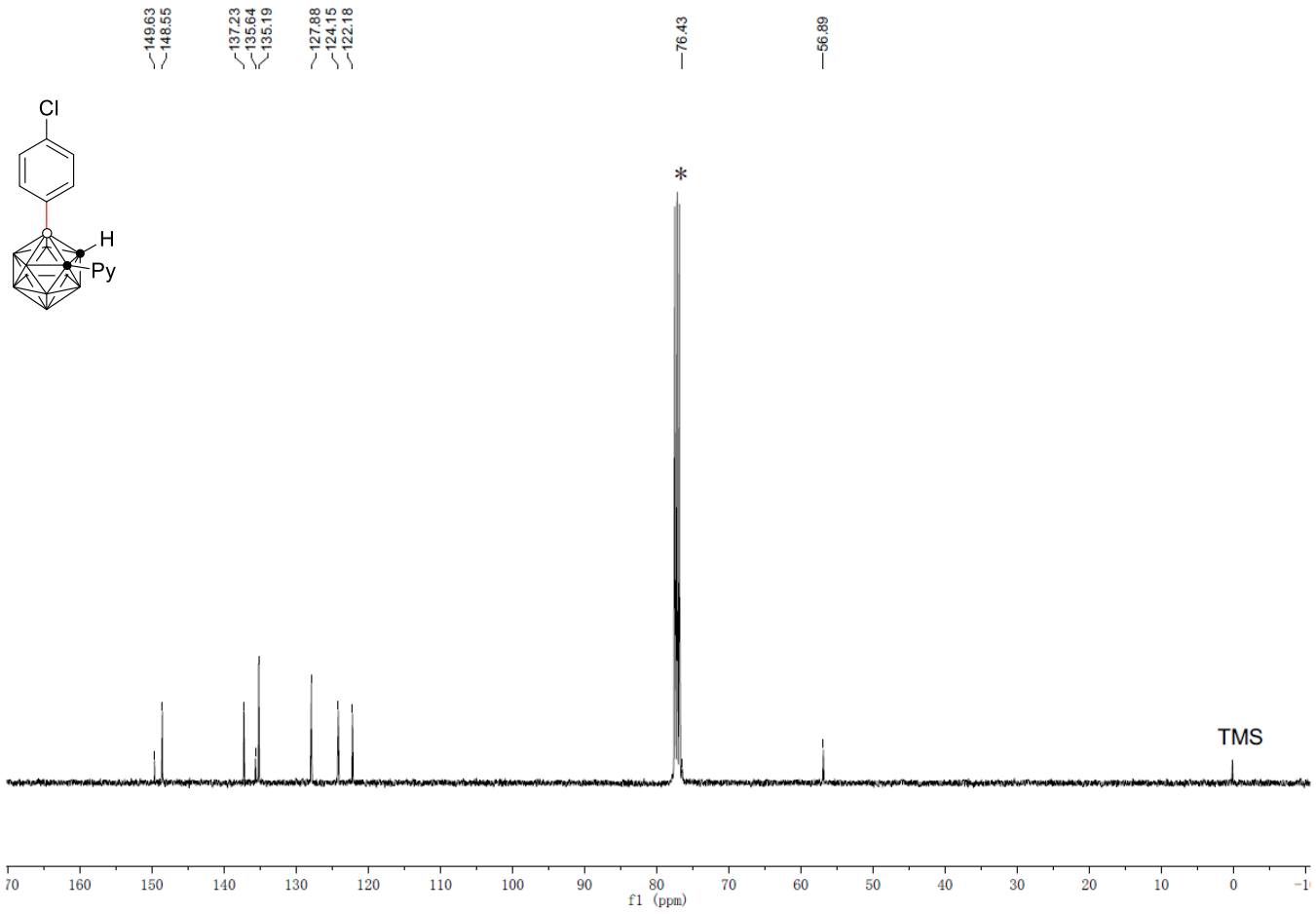
^{19}F NMR (376 MHz, $CDCl_3$ *) of **3c**



^{1}H NMR (400 MHz, $CDCl_3$ *) of **3d**



^{13}C NMR (101 MHz, $CDCl_3$ *) of **3d**



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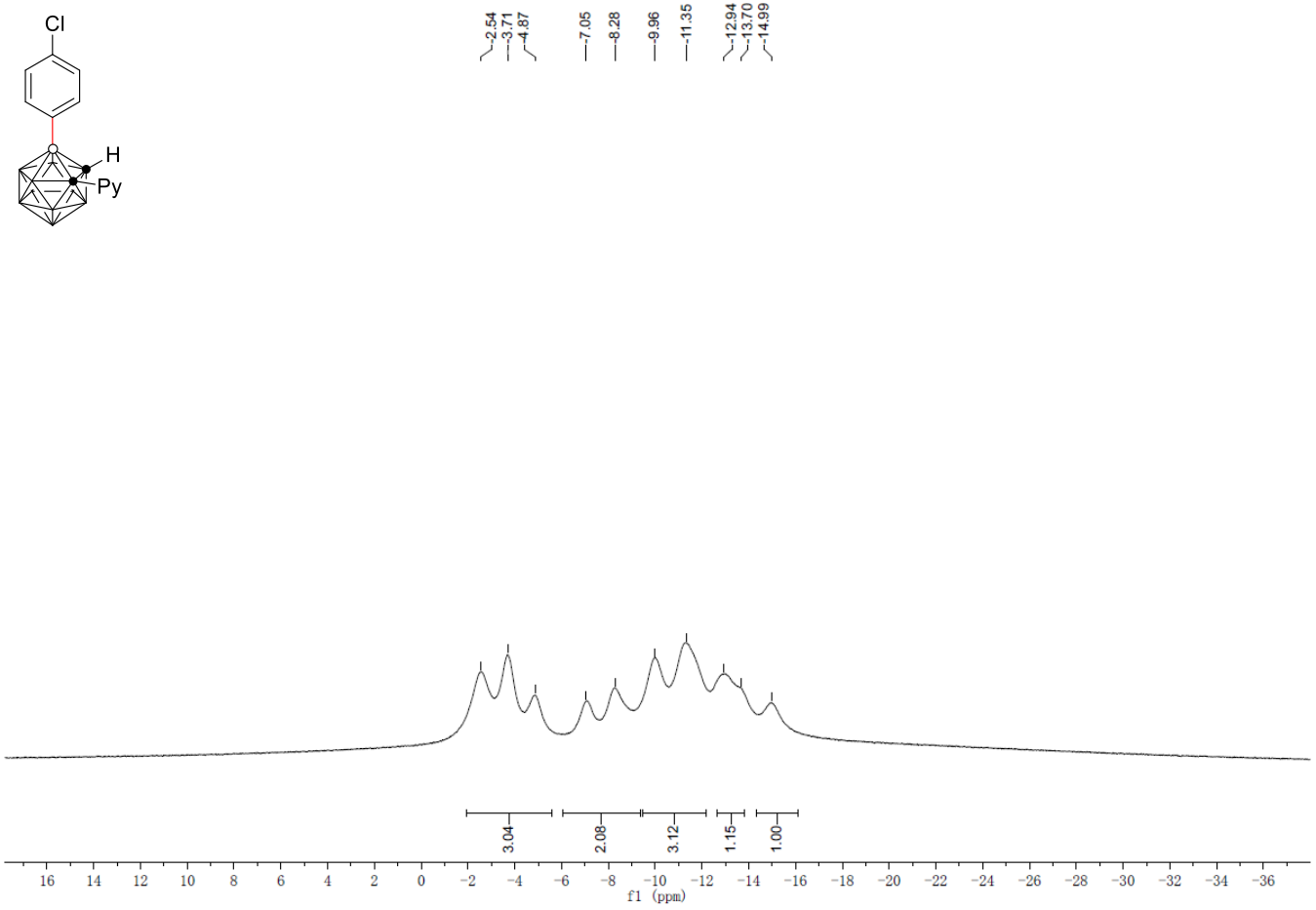

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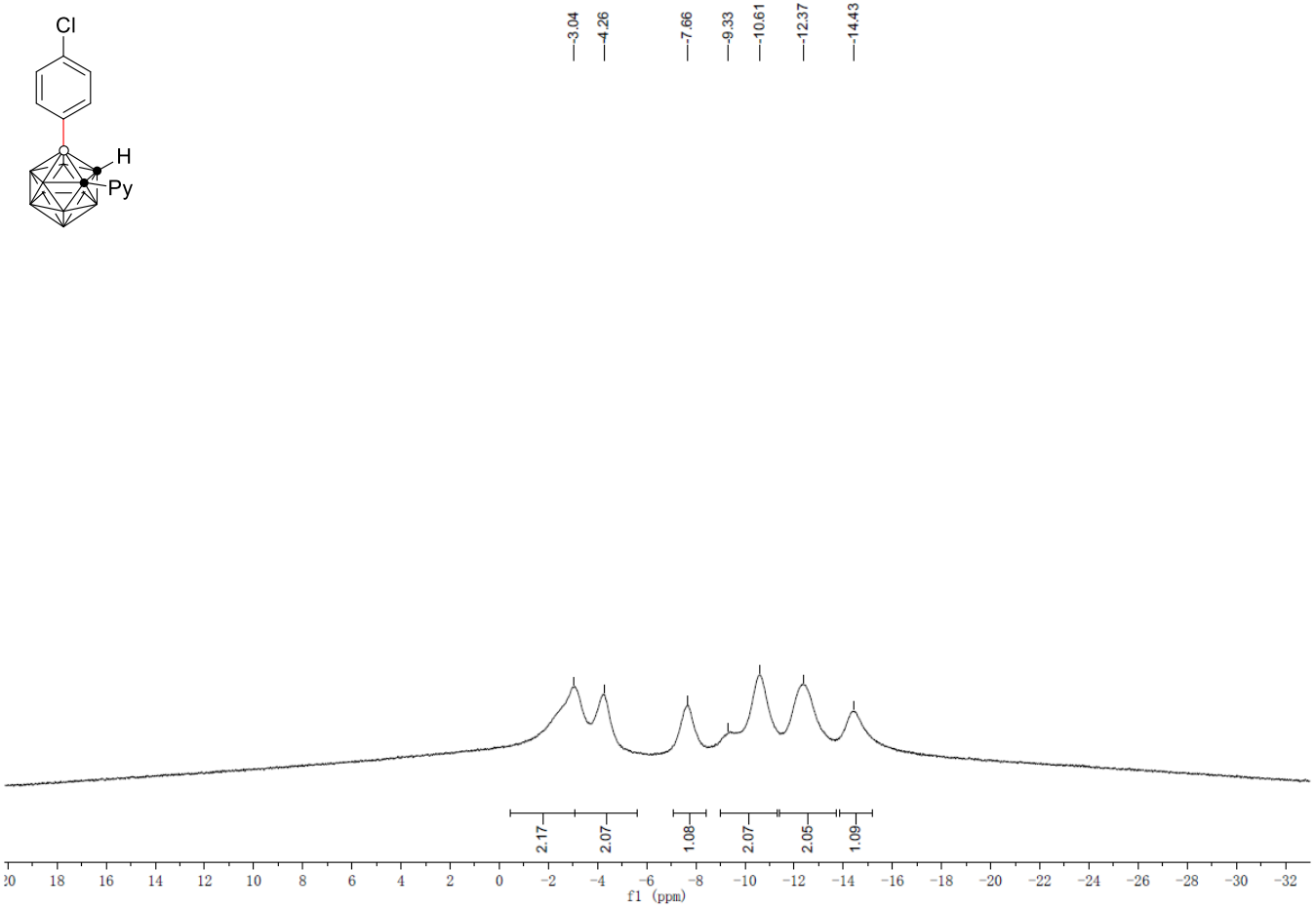

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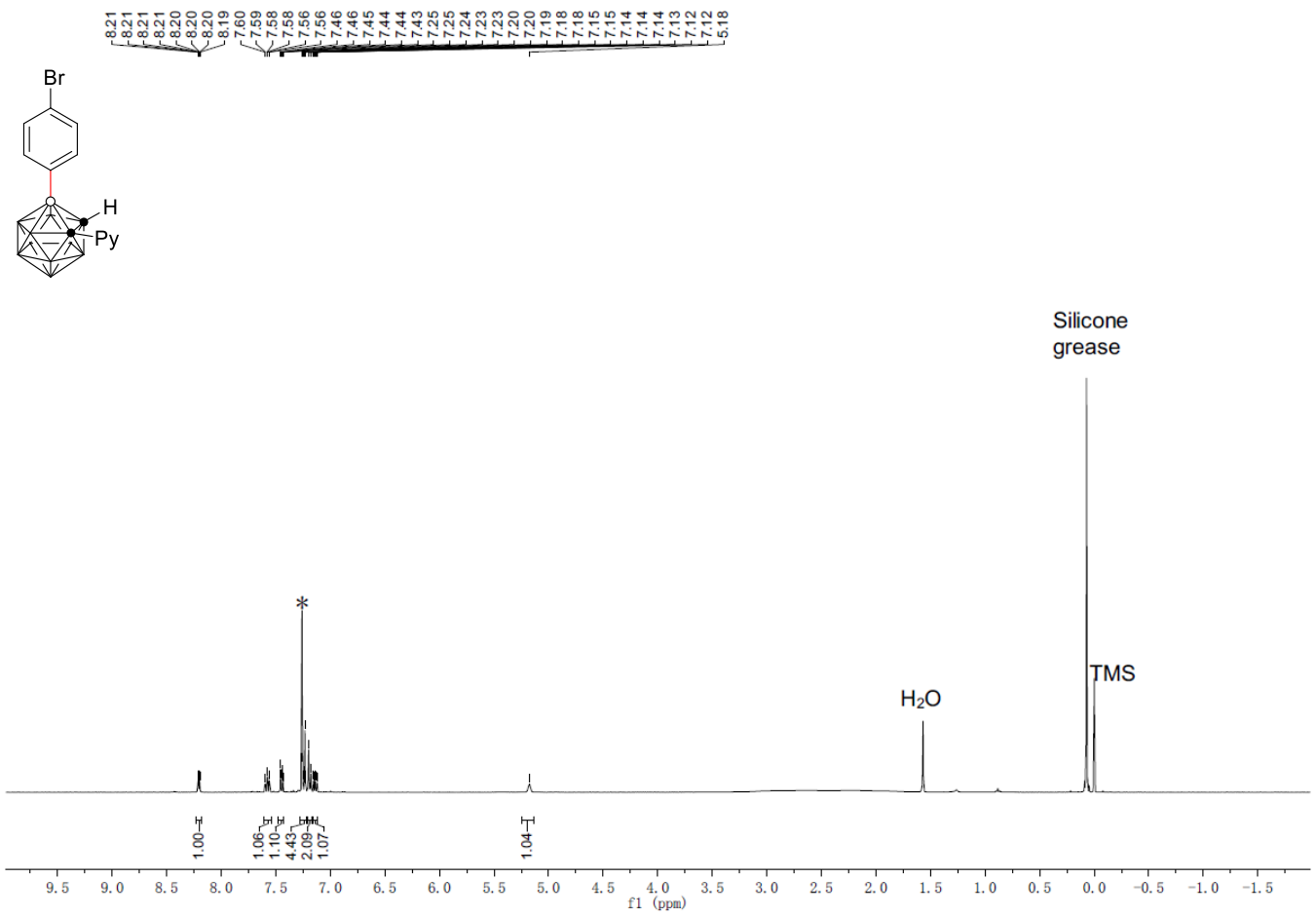
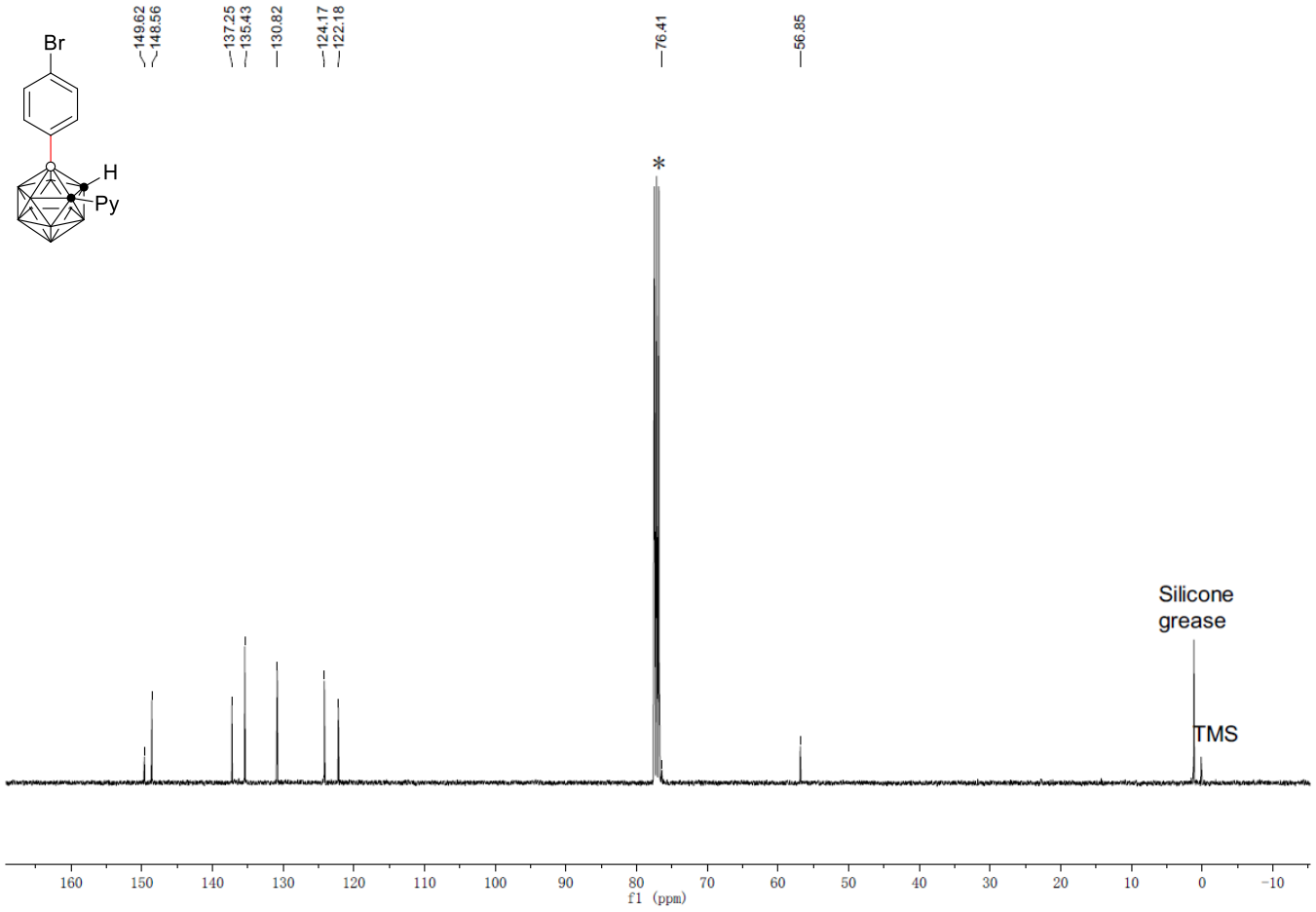
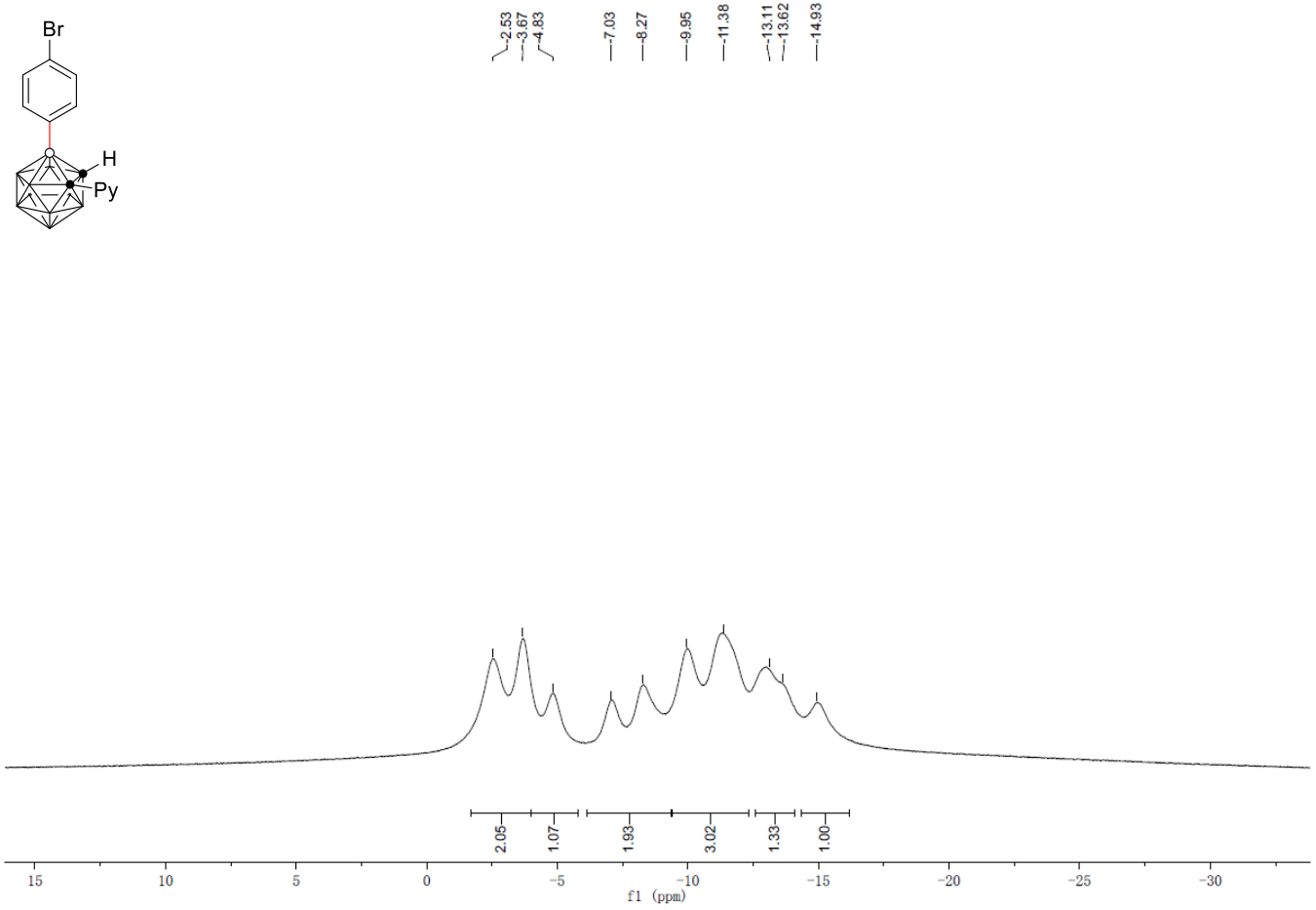


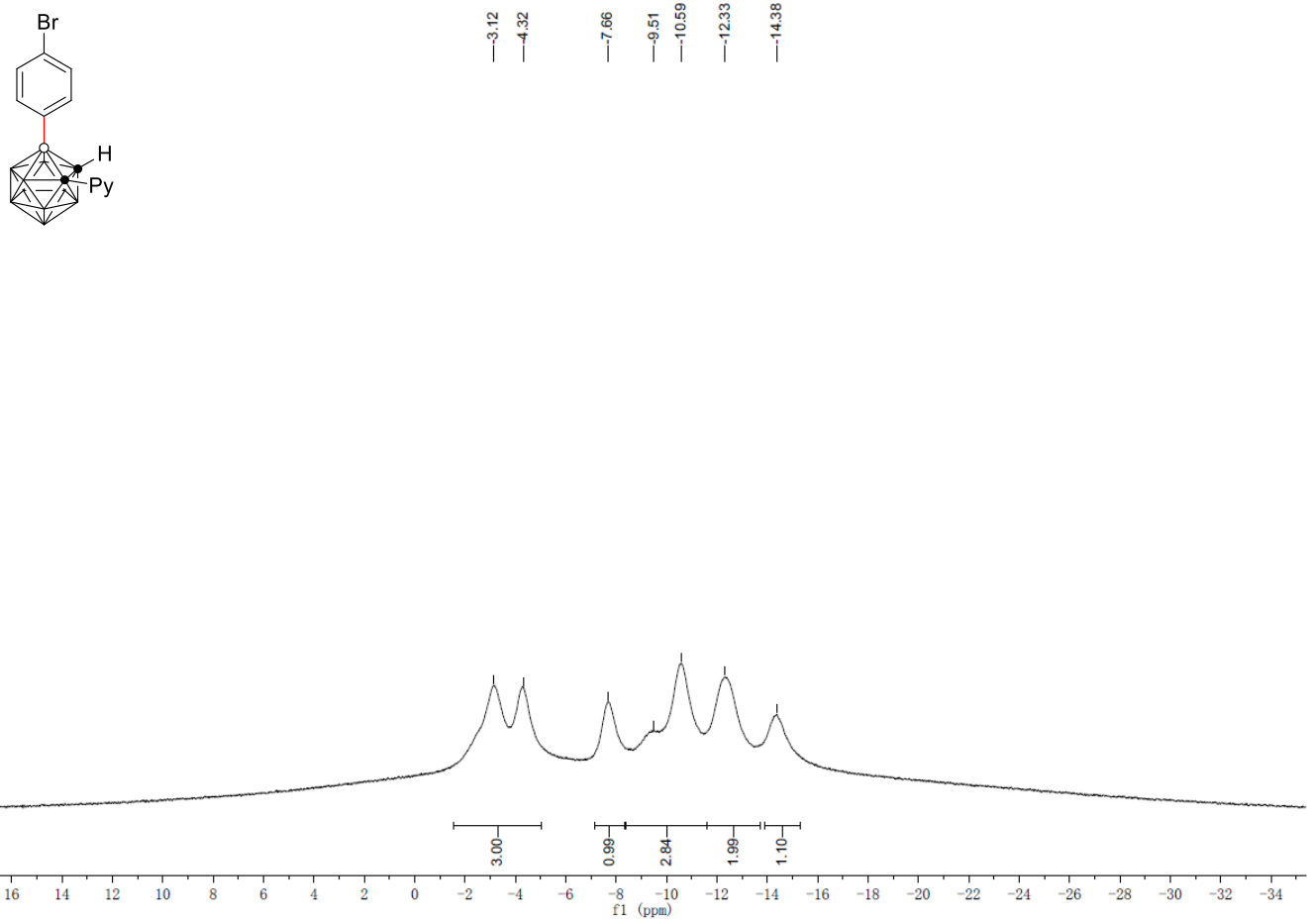
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3e**



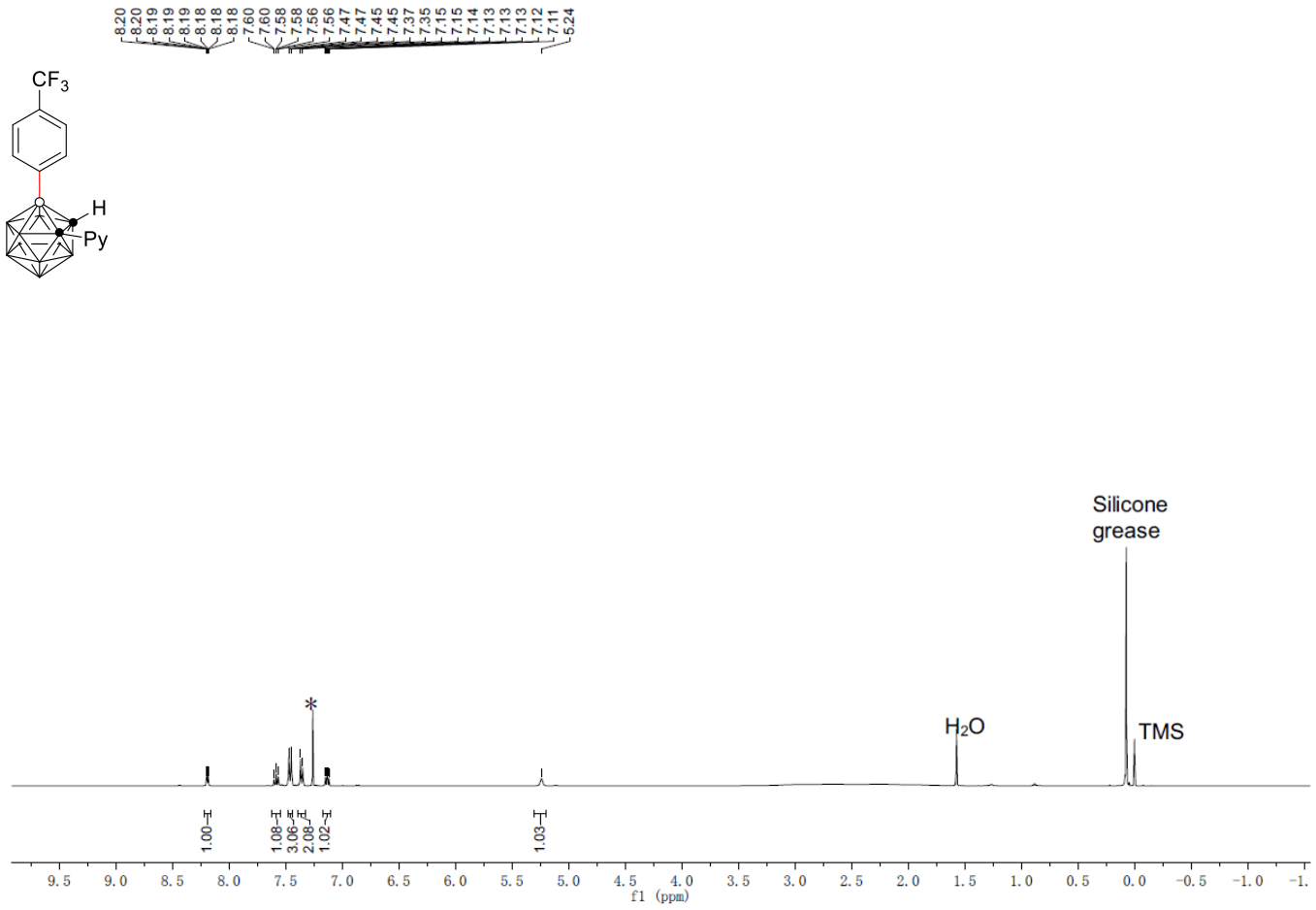
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3e**



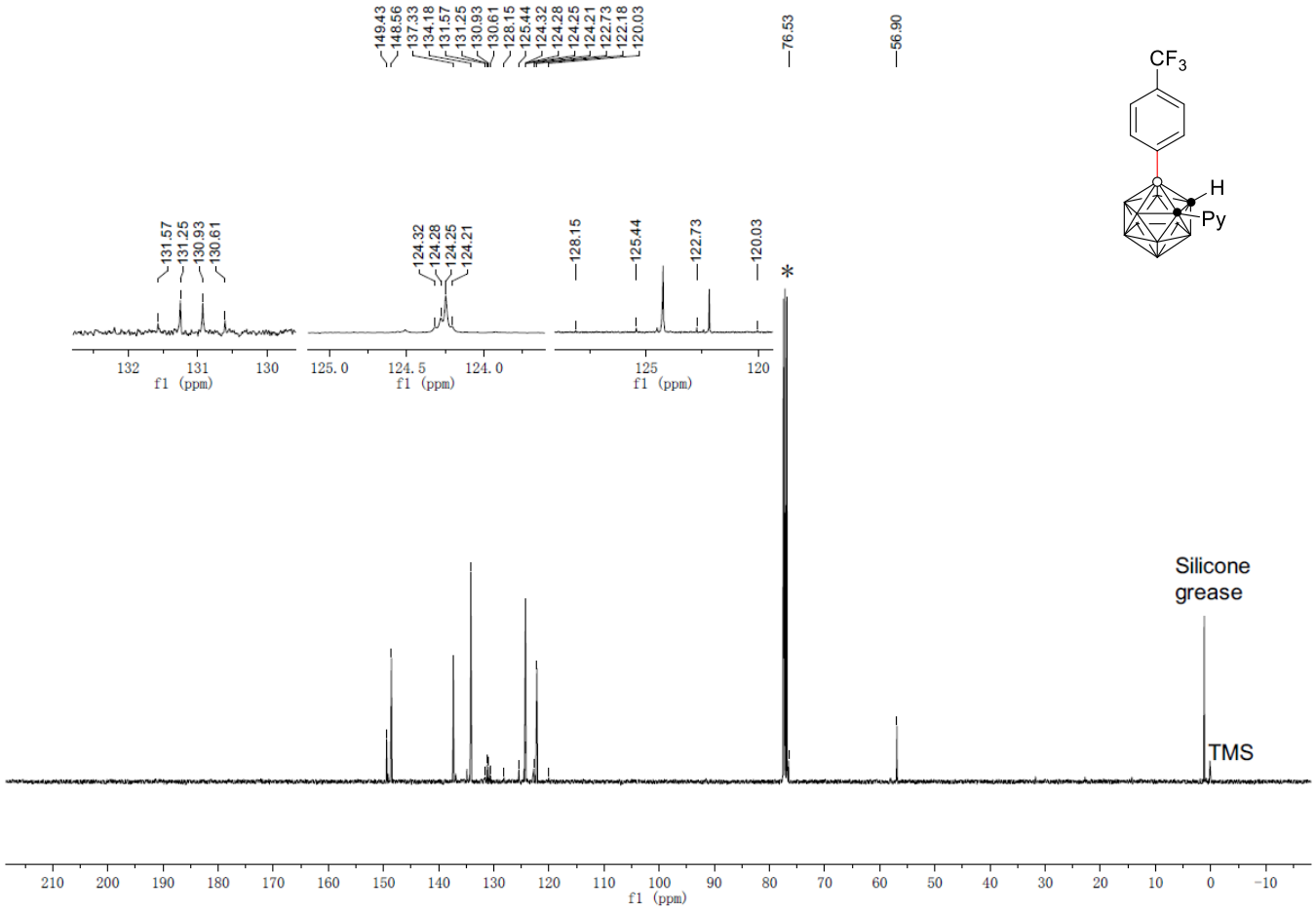
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3e**



^{1}H NMR (400 MHz, $CDCl_3$ *) of **3f**



^{13}C NMR (101 MHz, $CDCl_3$ *) of **3f**



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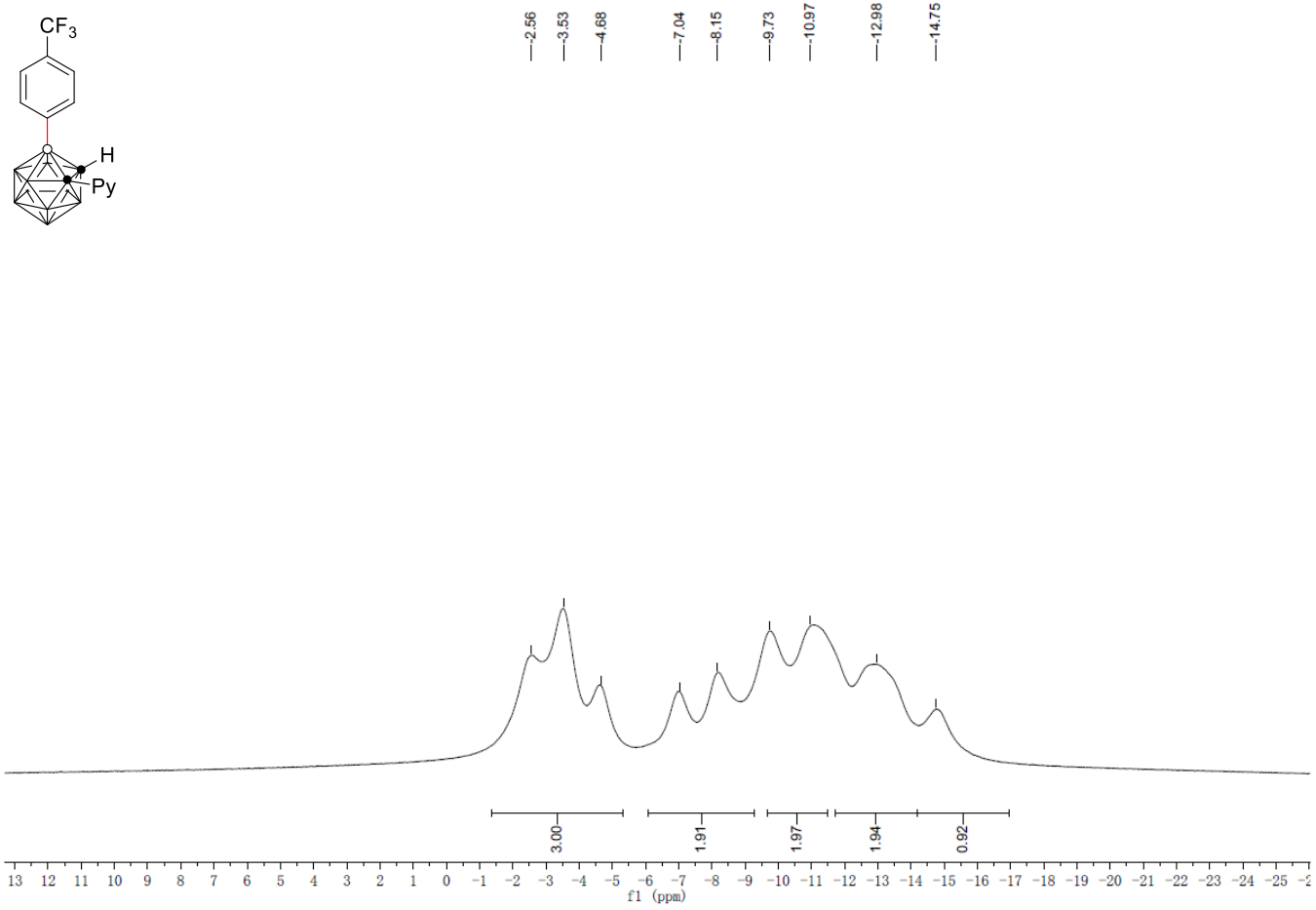
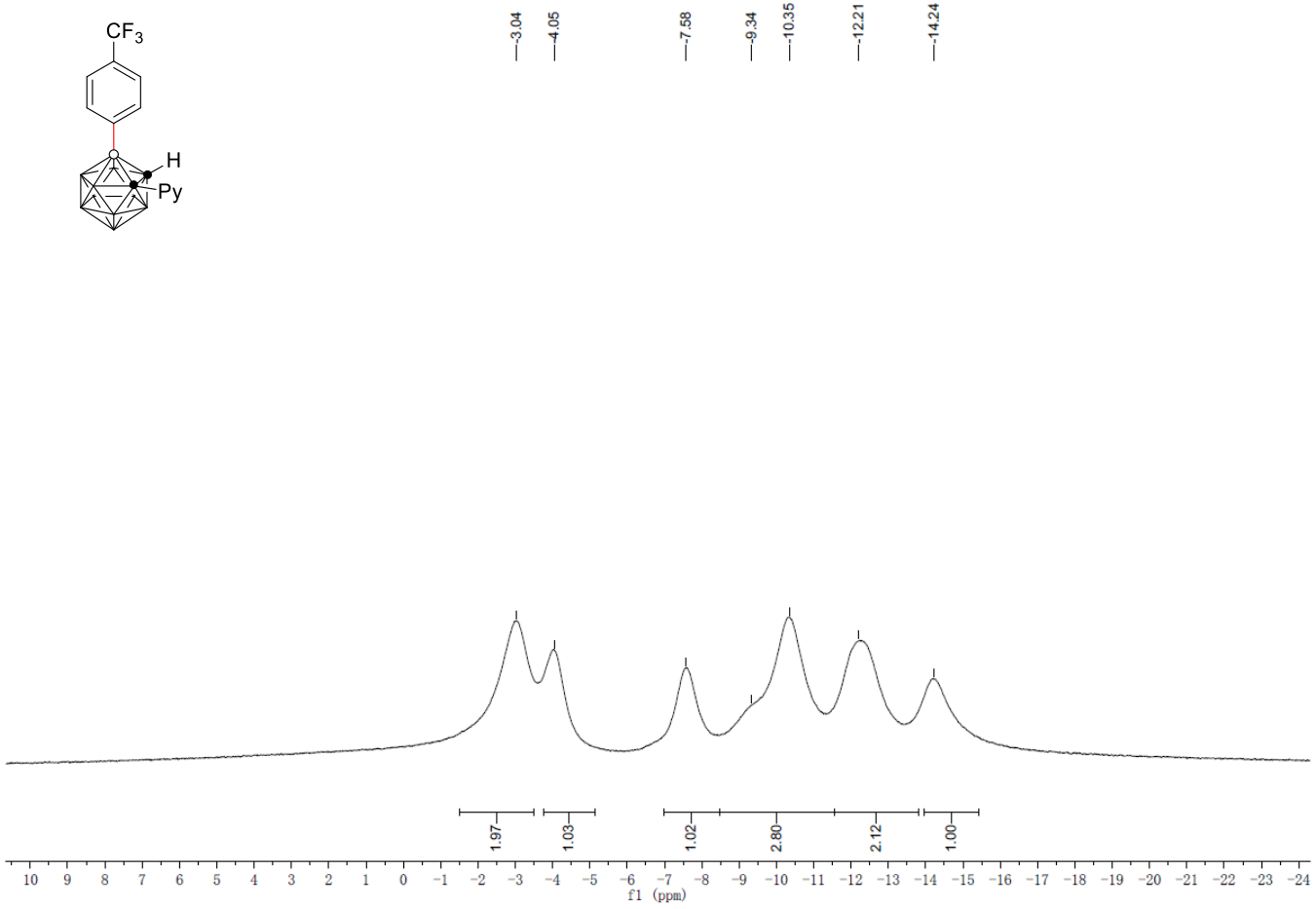
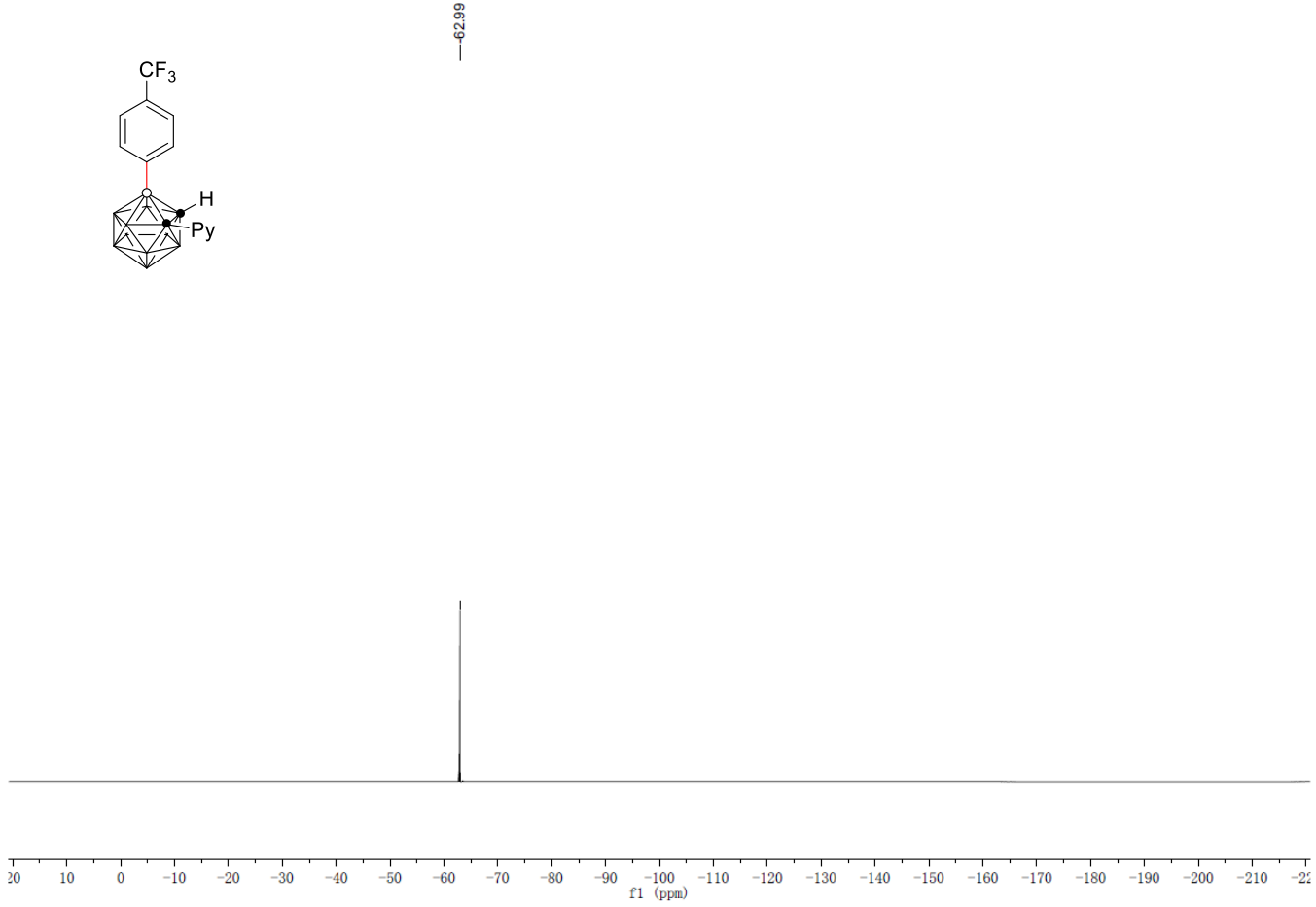


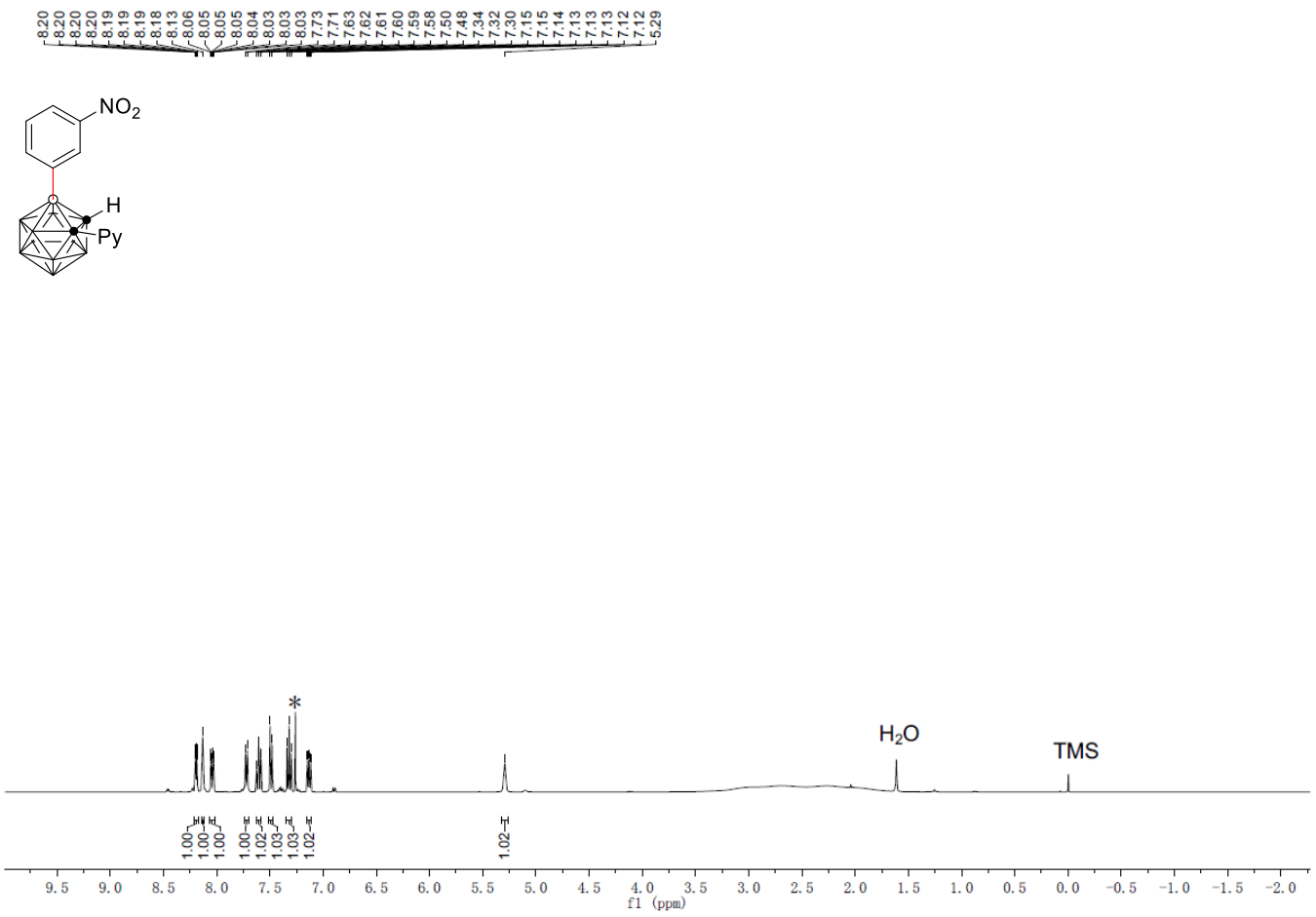
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3f**



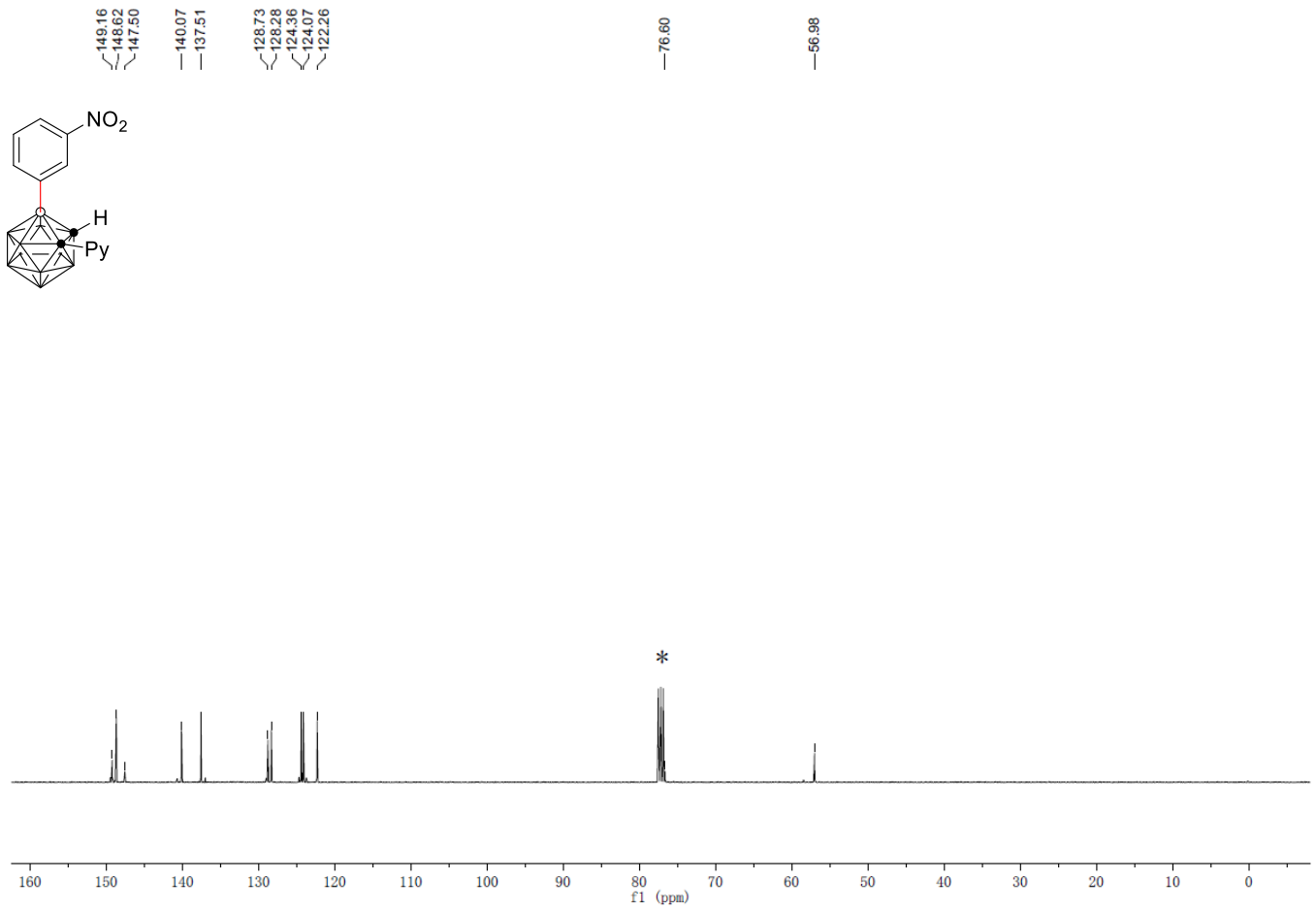
^{19}F NMR (376 MHz, $CDCl_3$*) of **3f**



^{1}H NMR (400 MHz, $CDCl_3$ *) of **3g**



^{13}C NMR (101 MHz, $CDCl_3$ *) of **3g**



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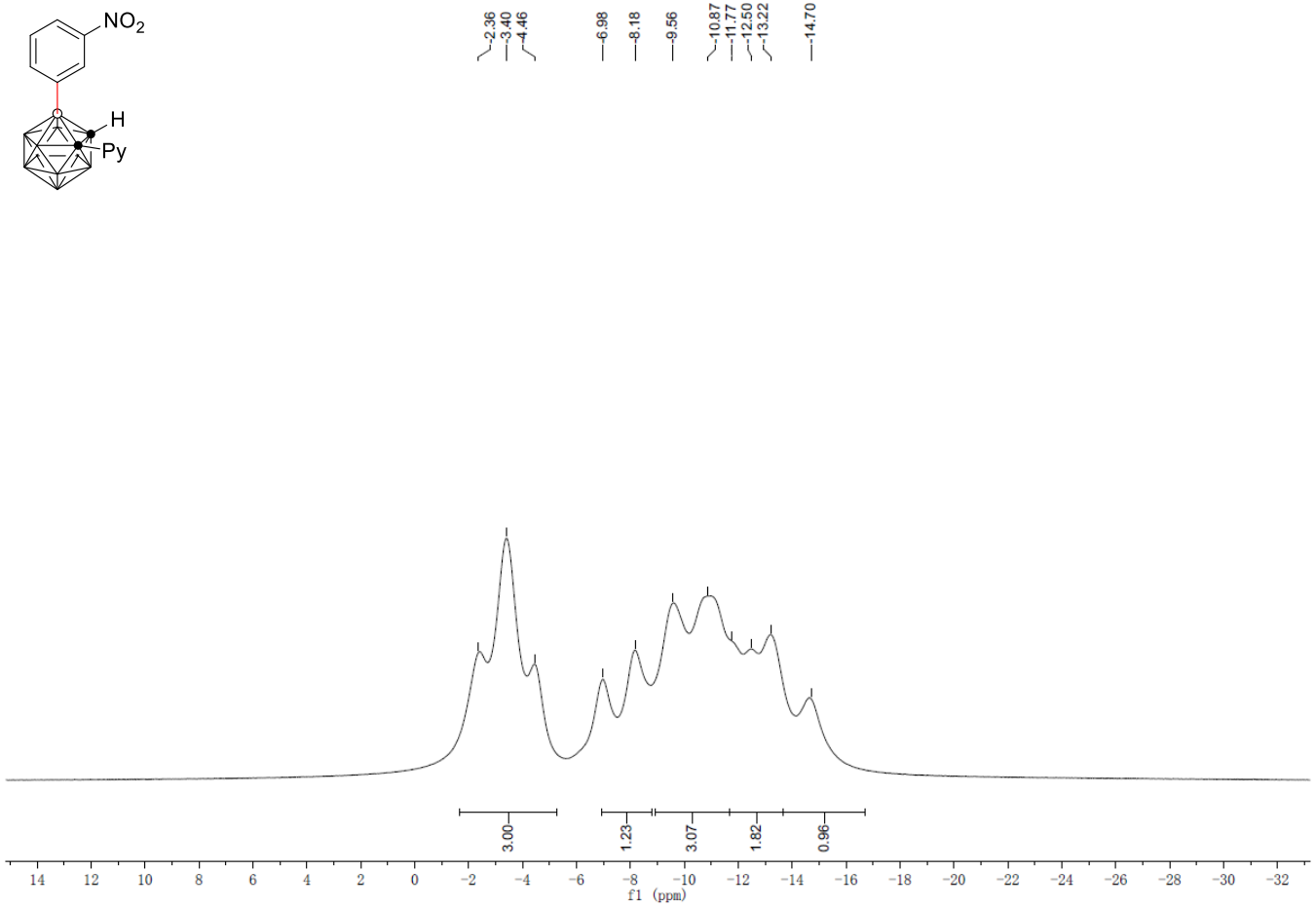
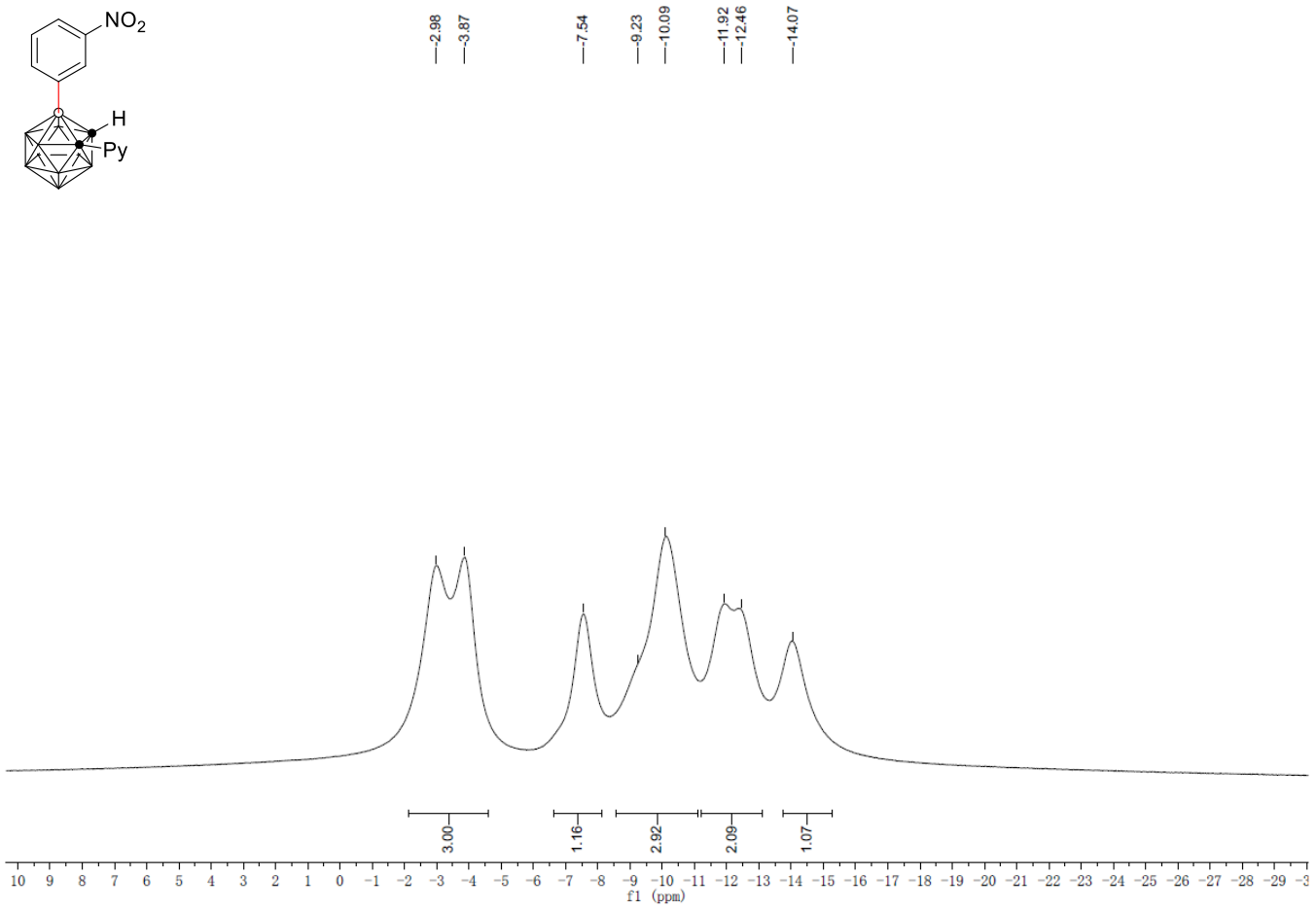
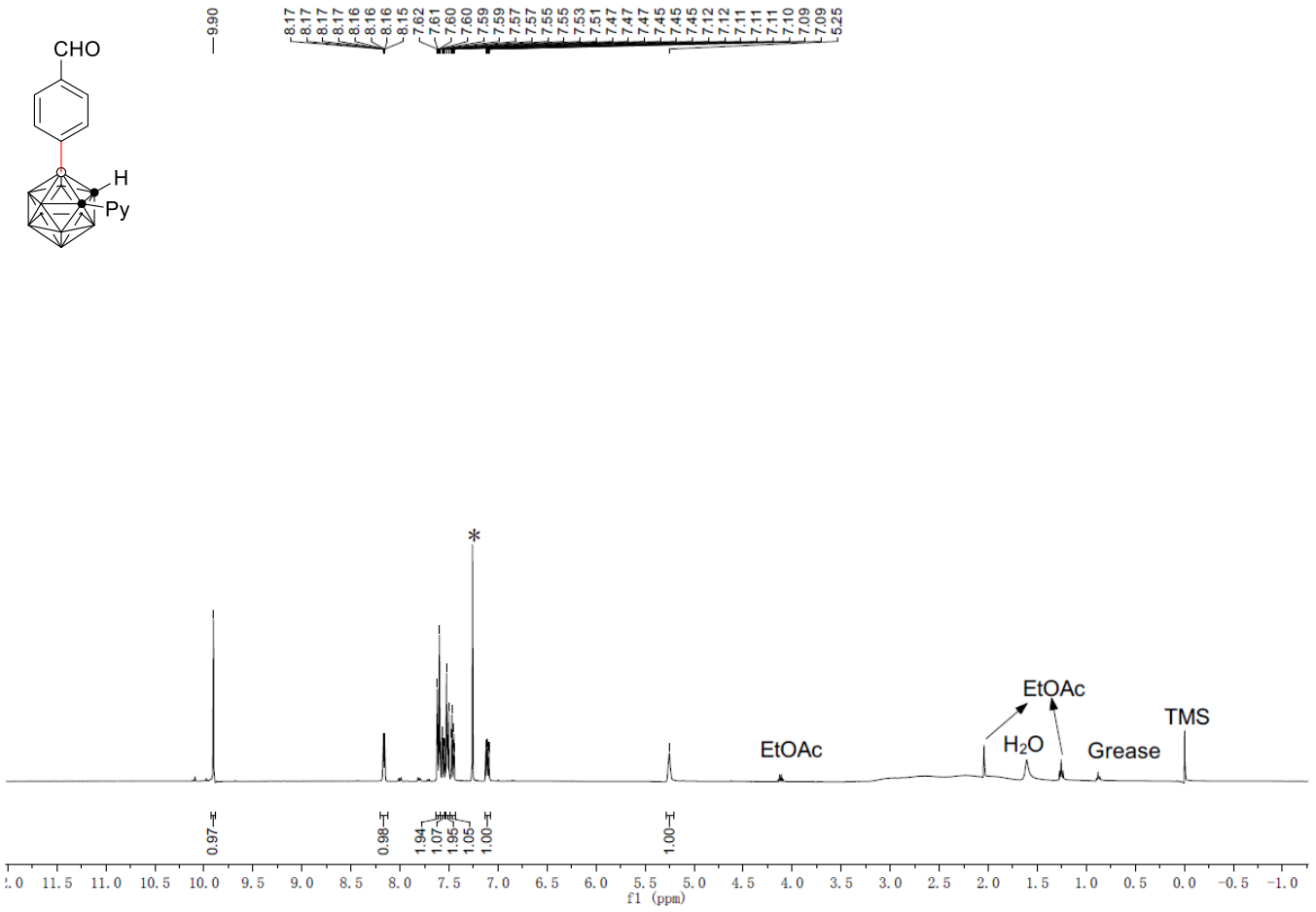


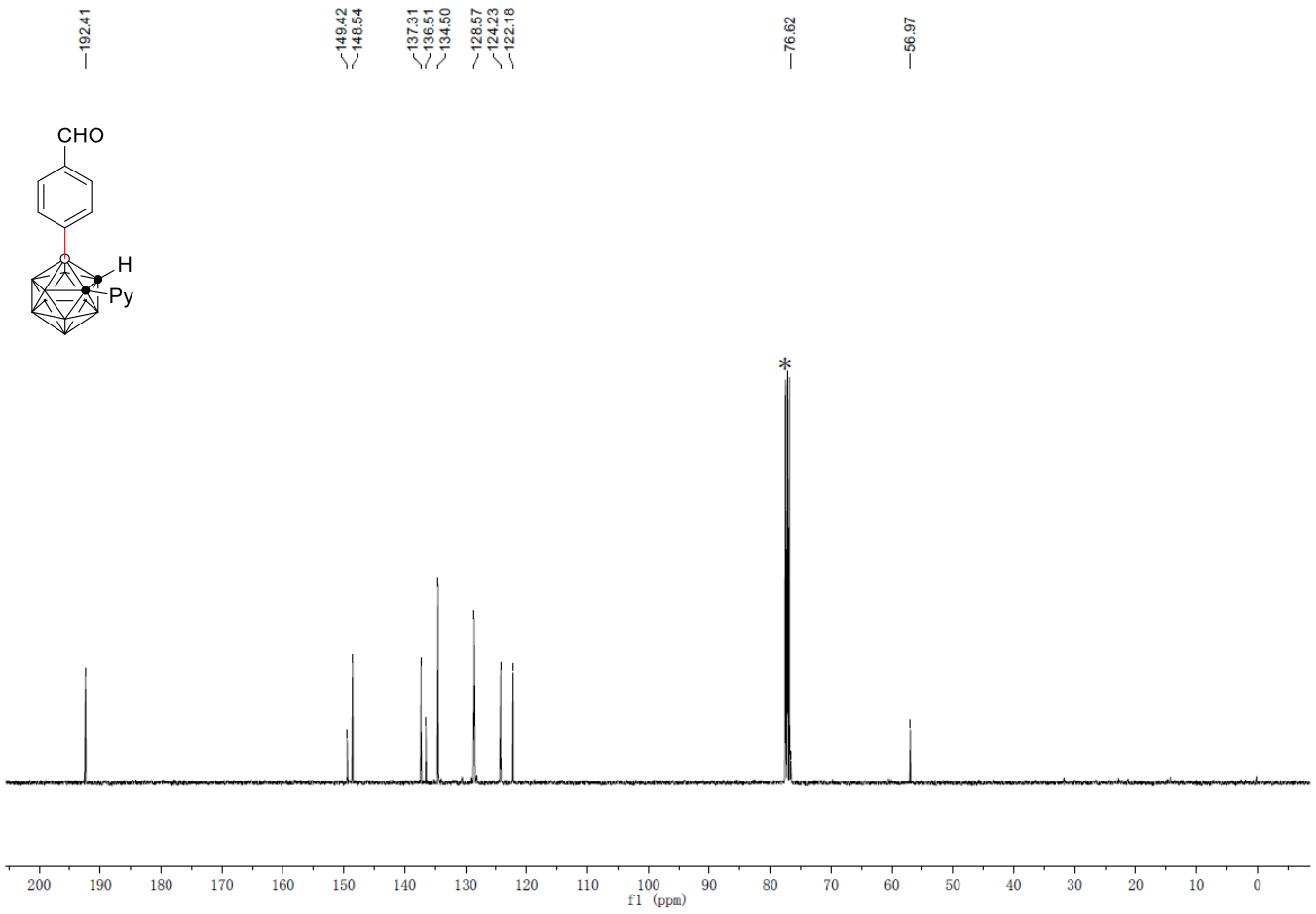
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3g**



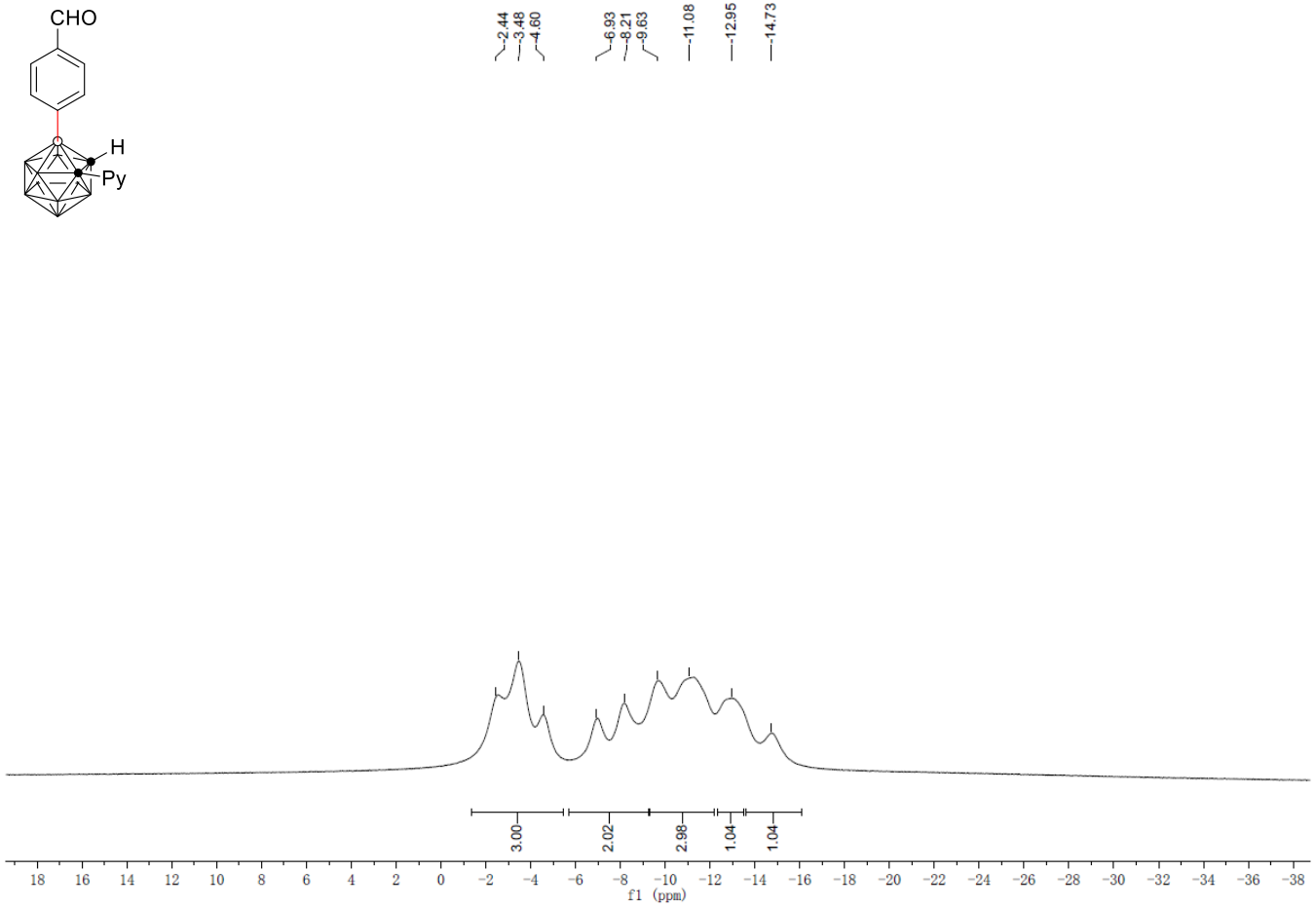
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3h**



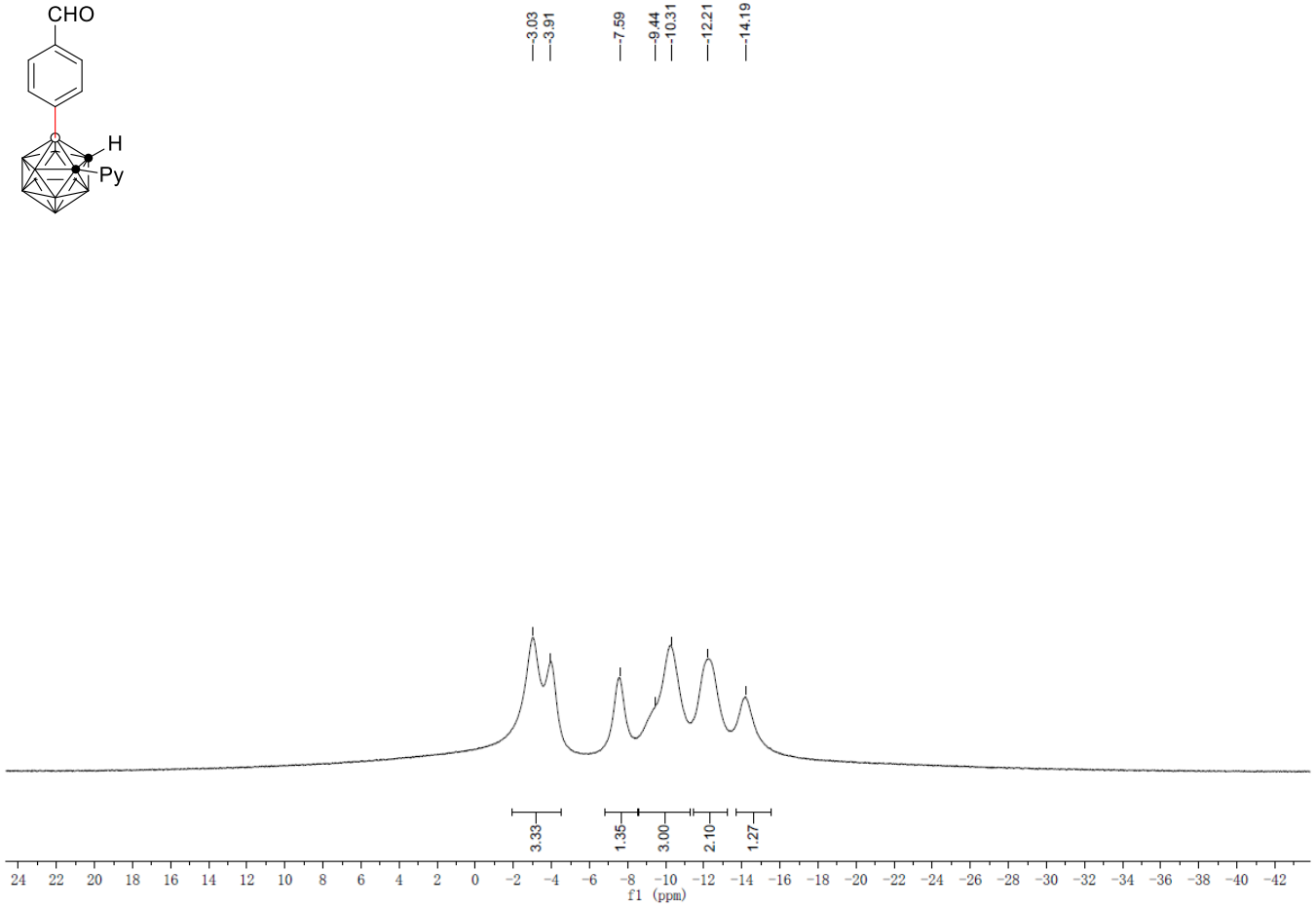
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3h**



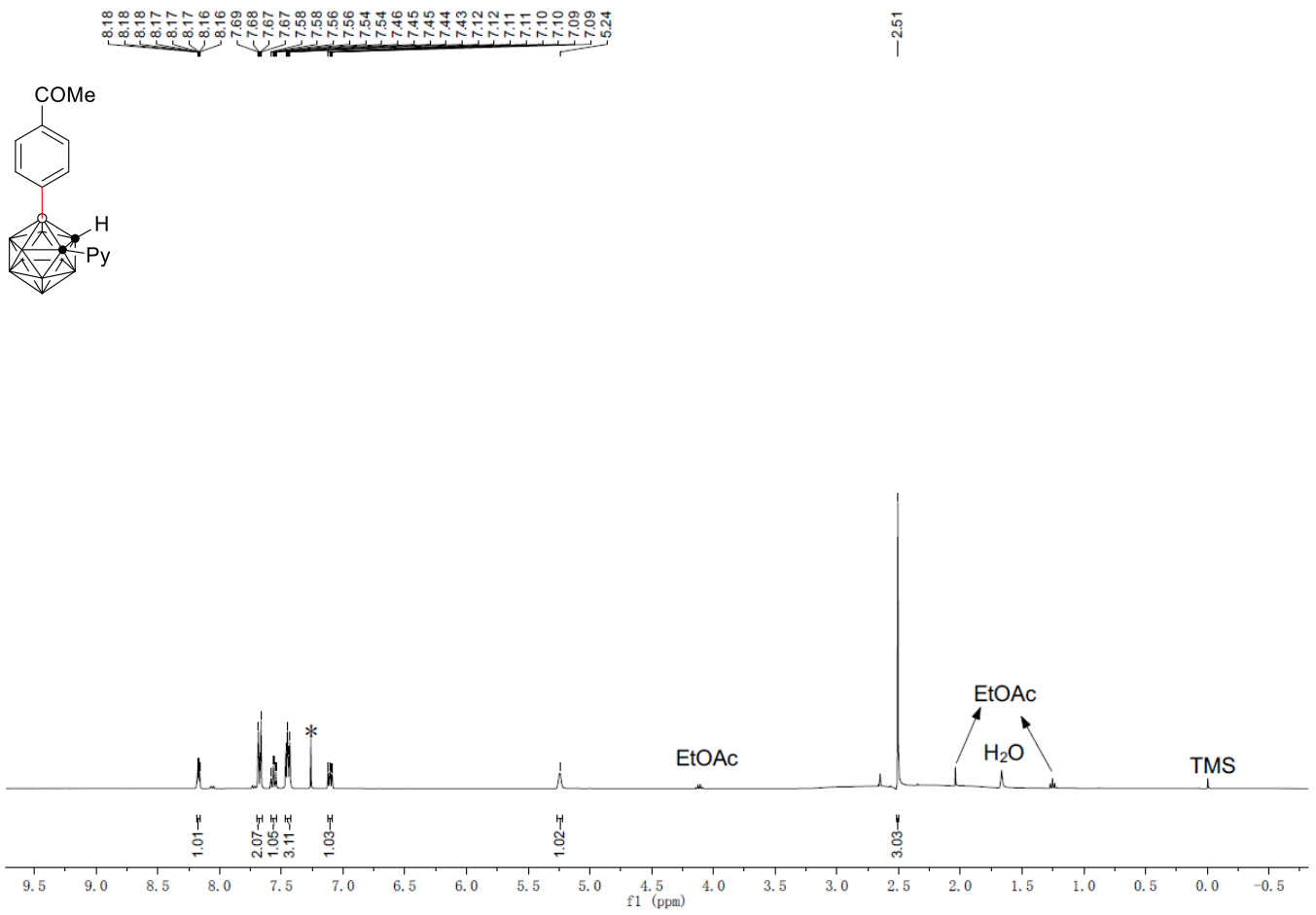
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3h**



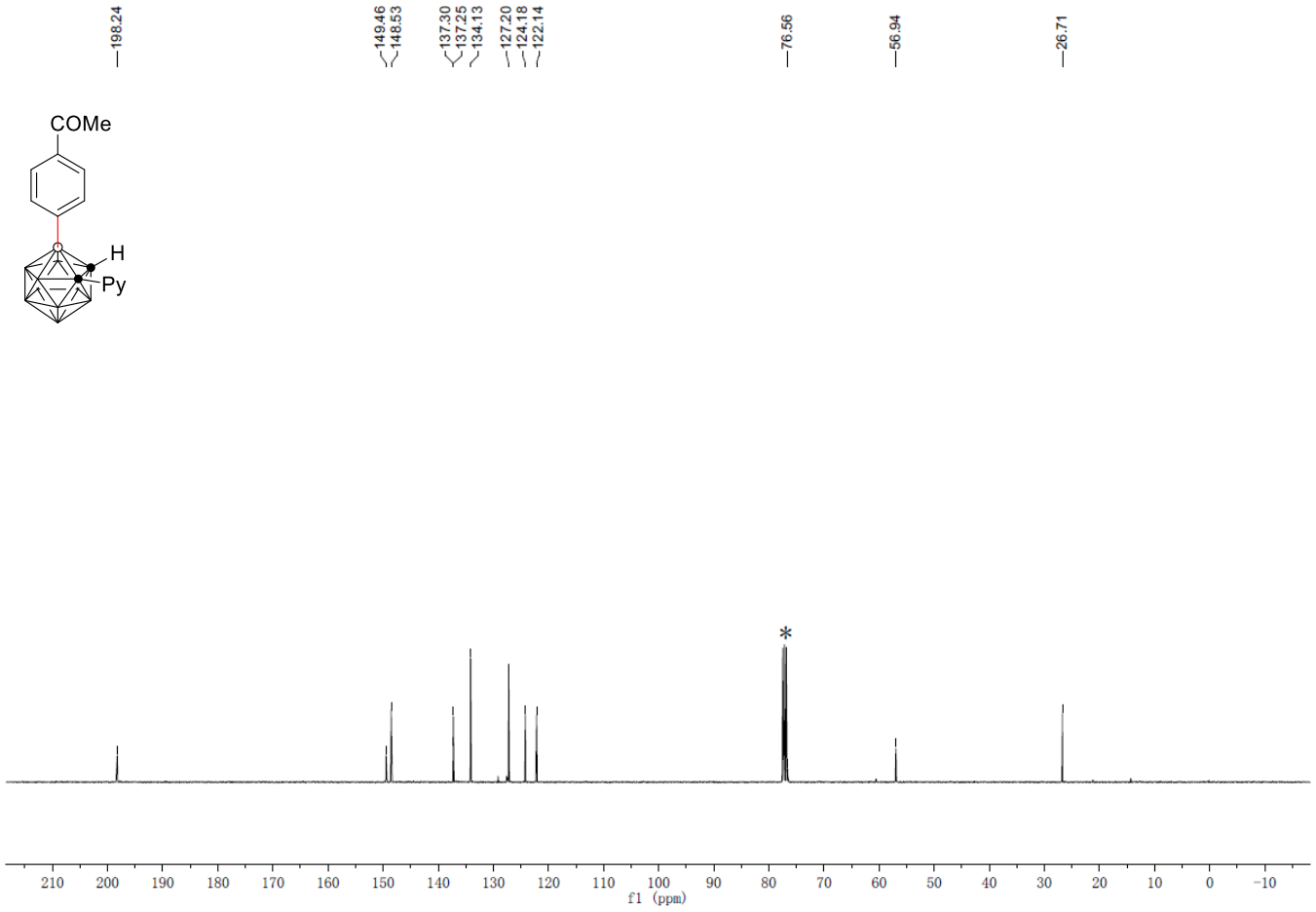
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3h**



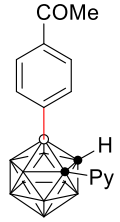
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3i**



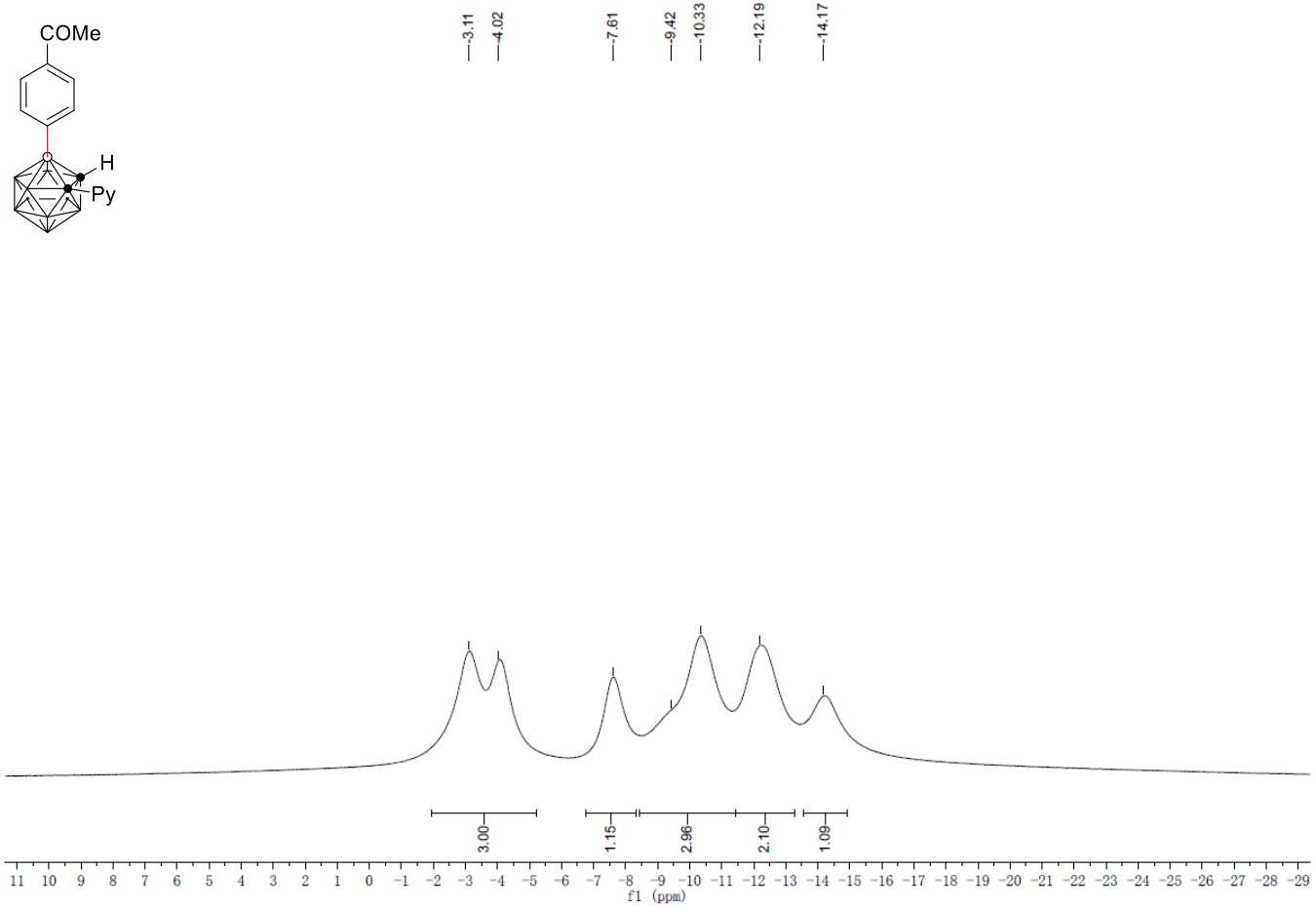
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3i**



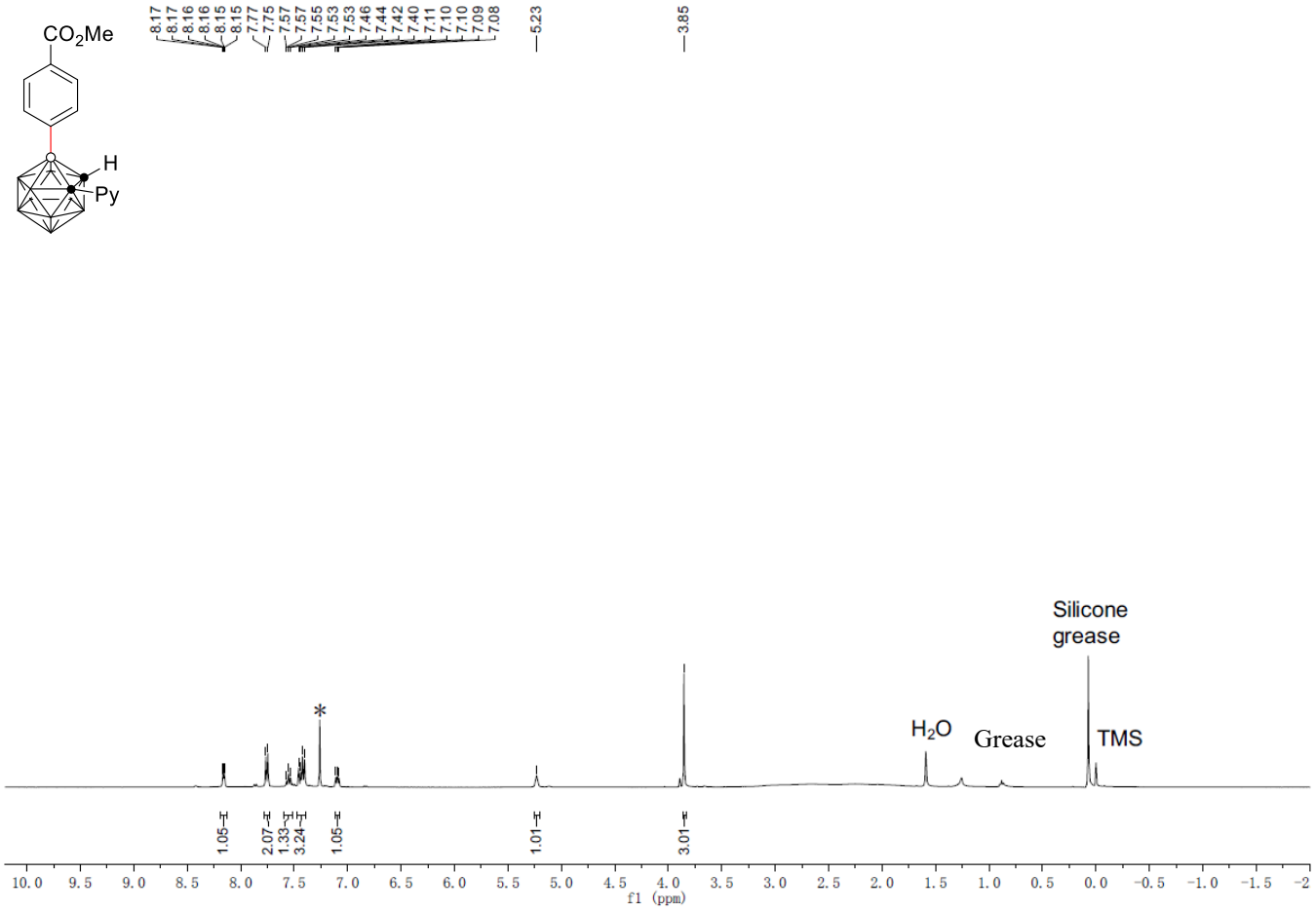
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3i**



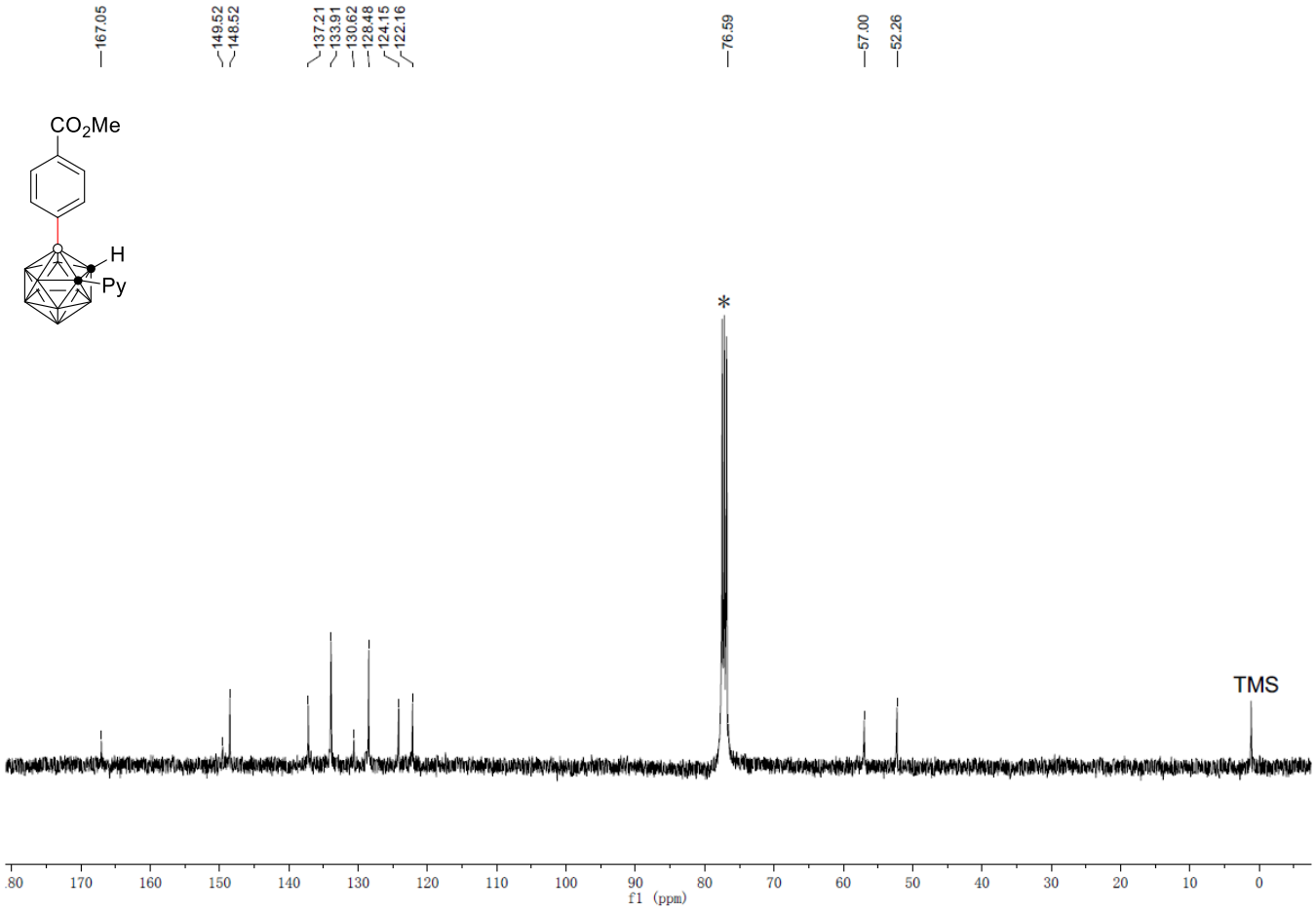
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3i**



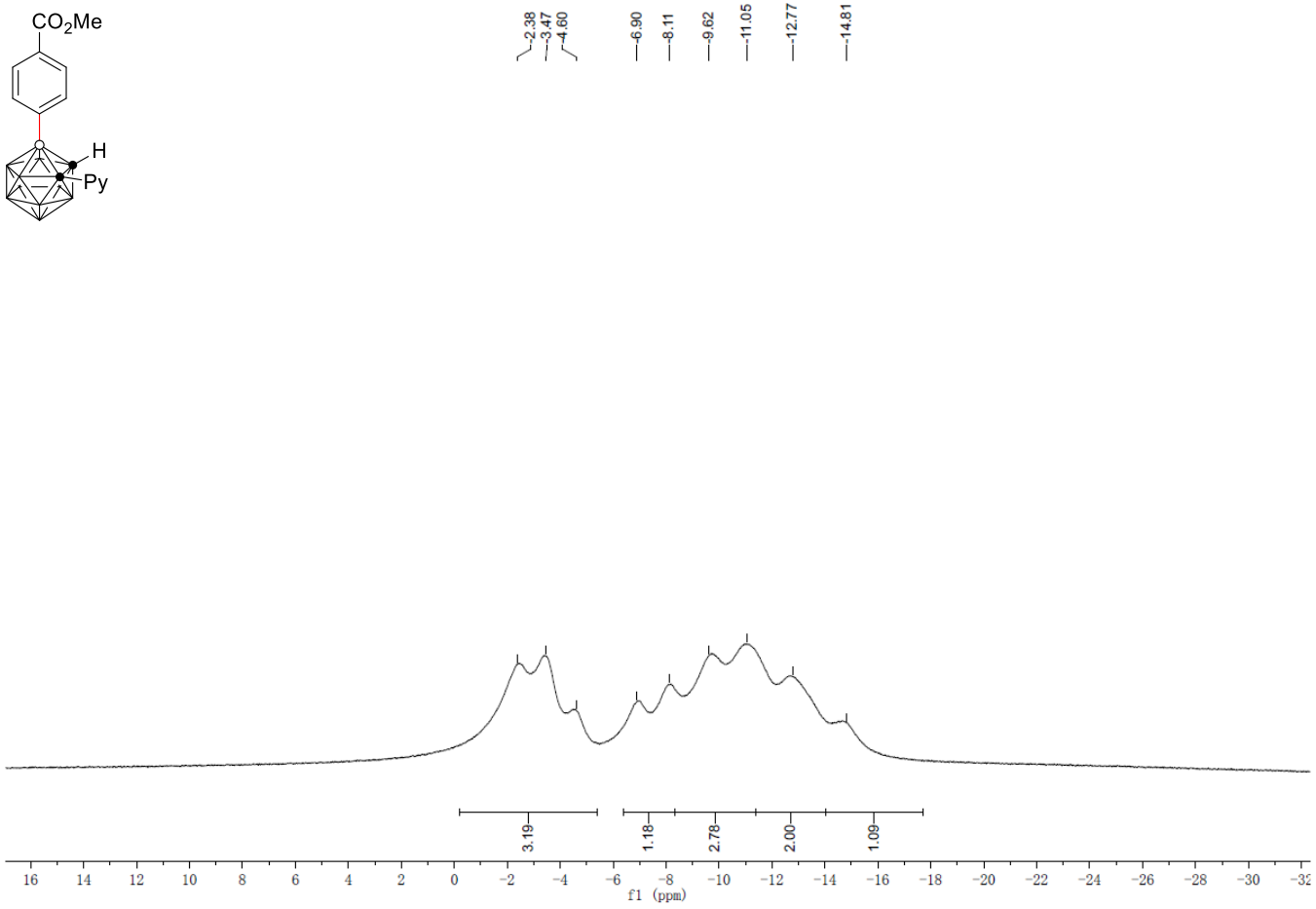
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3j**



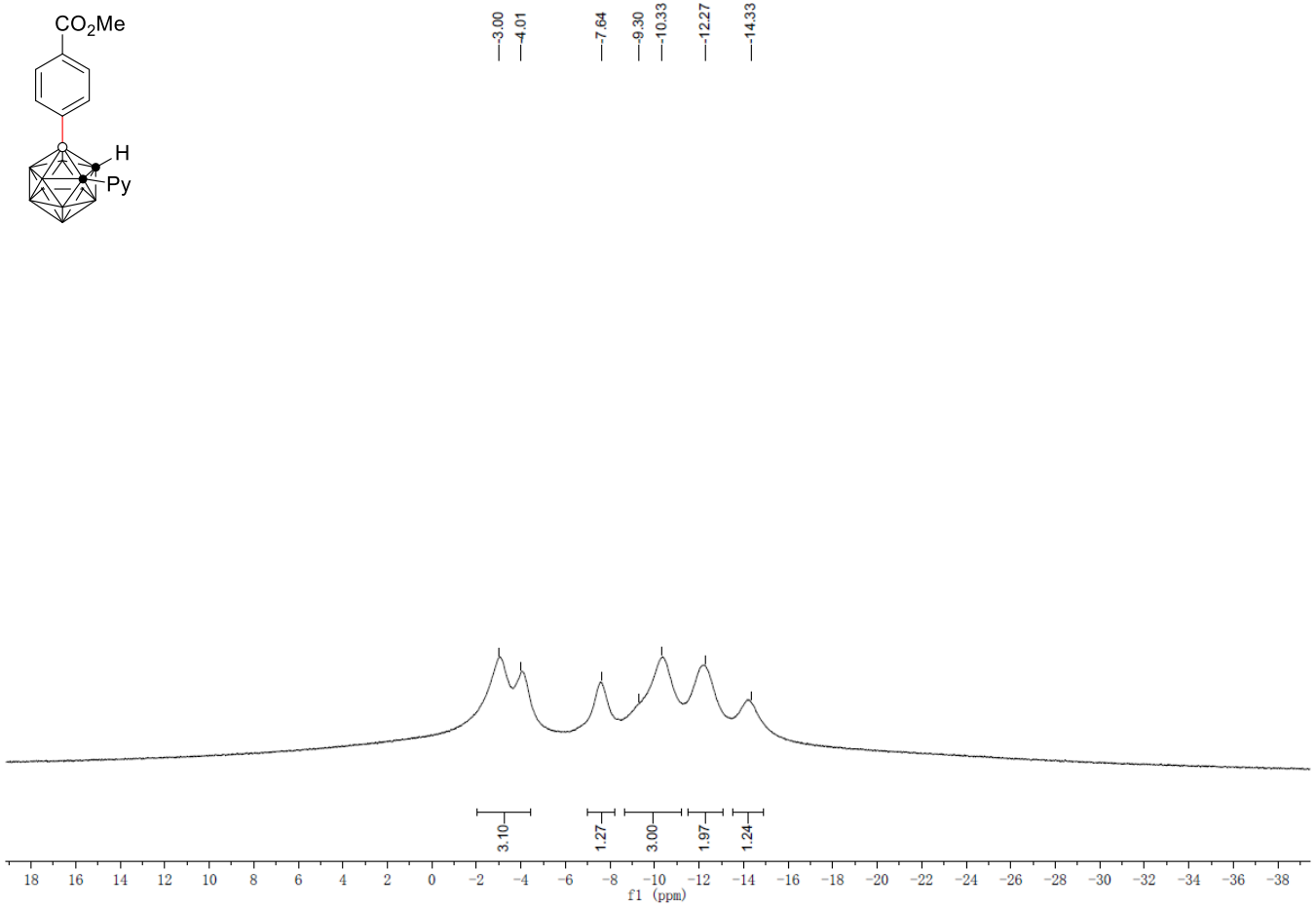
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3j**



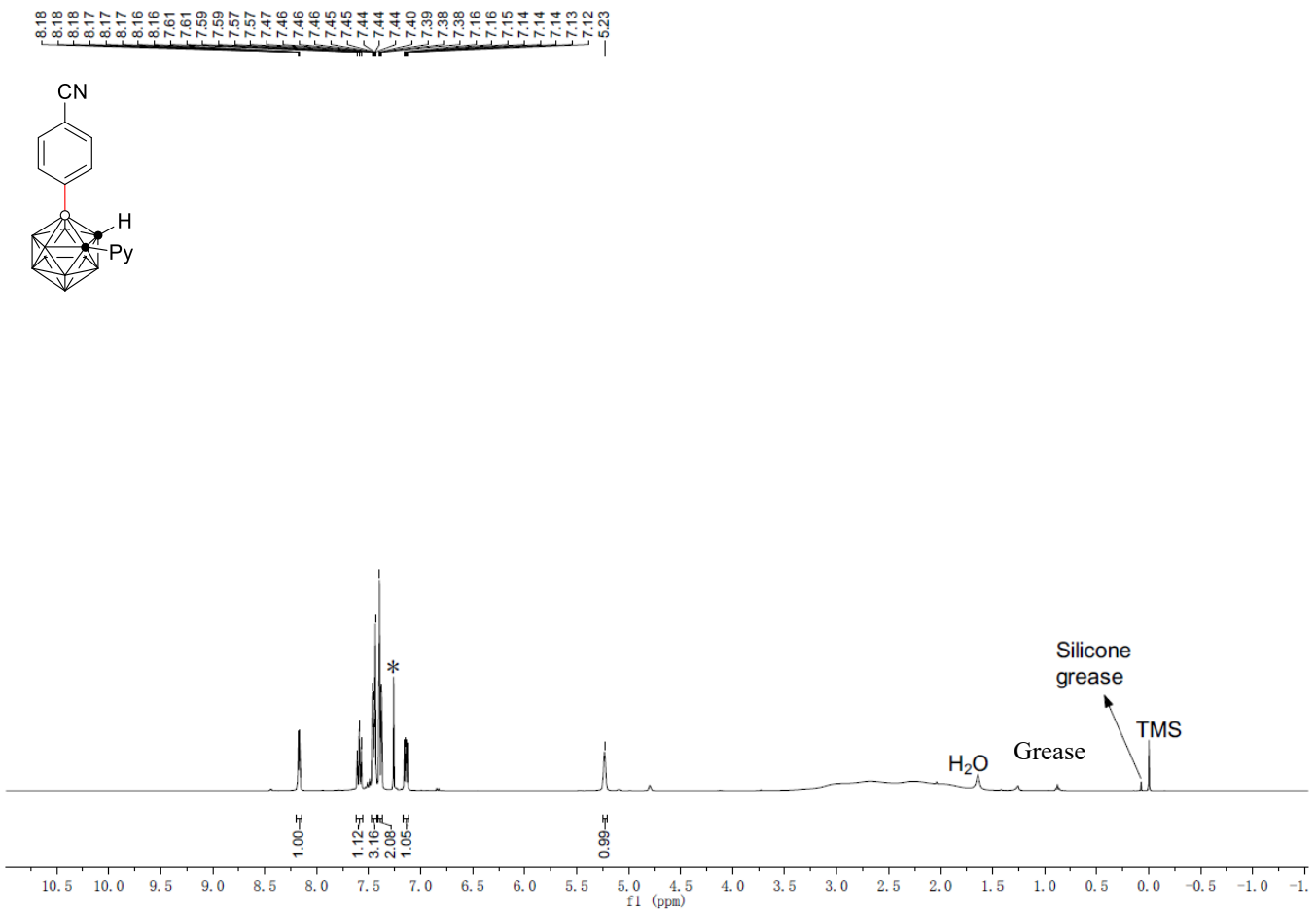
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3j**



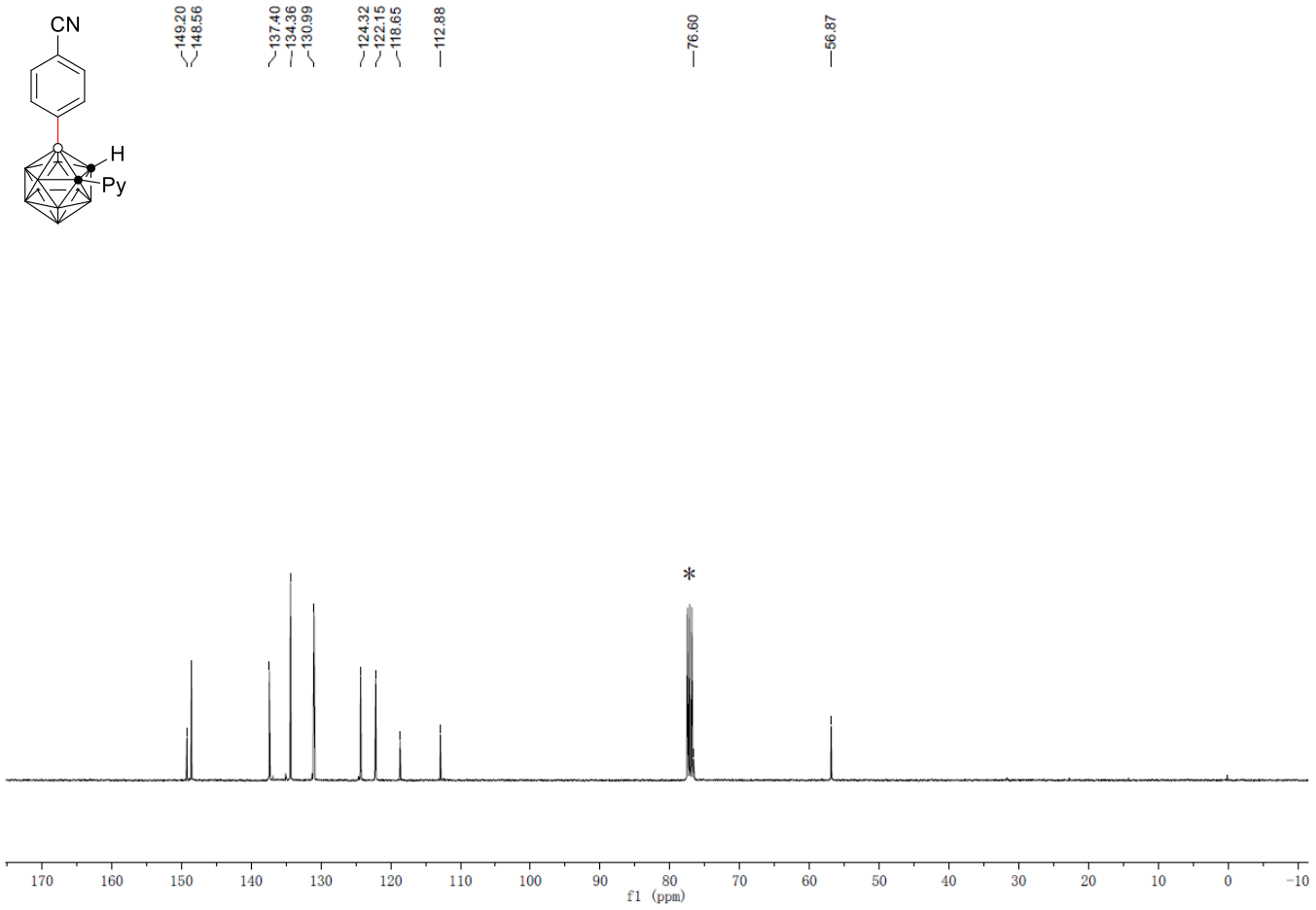
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3j**



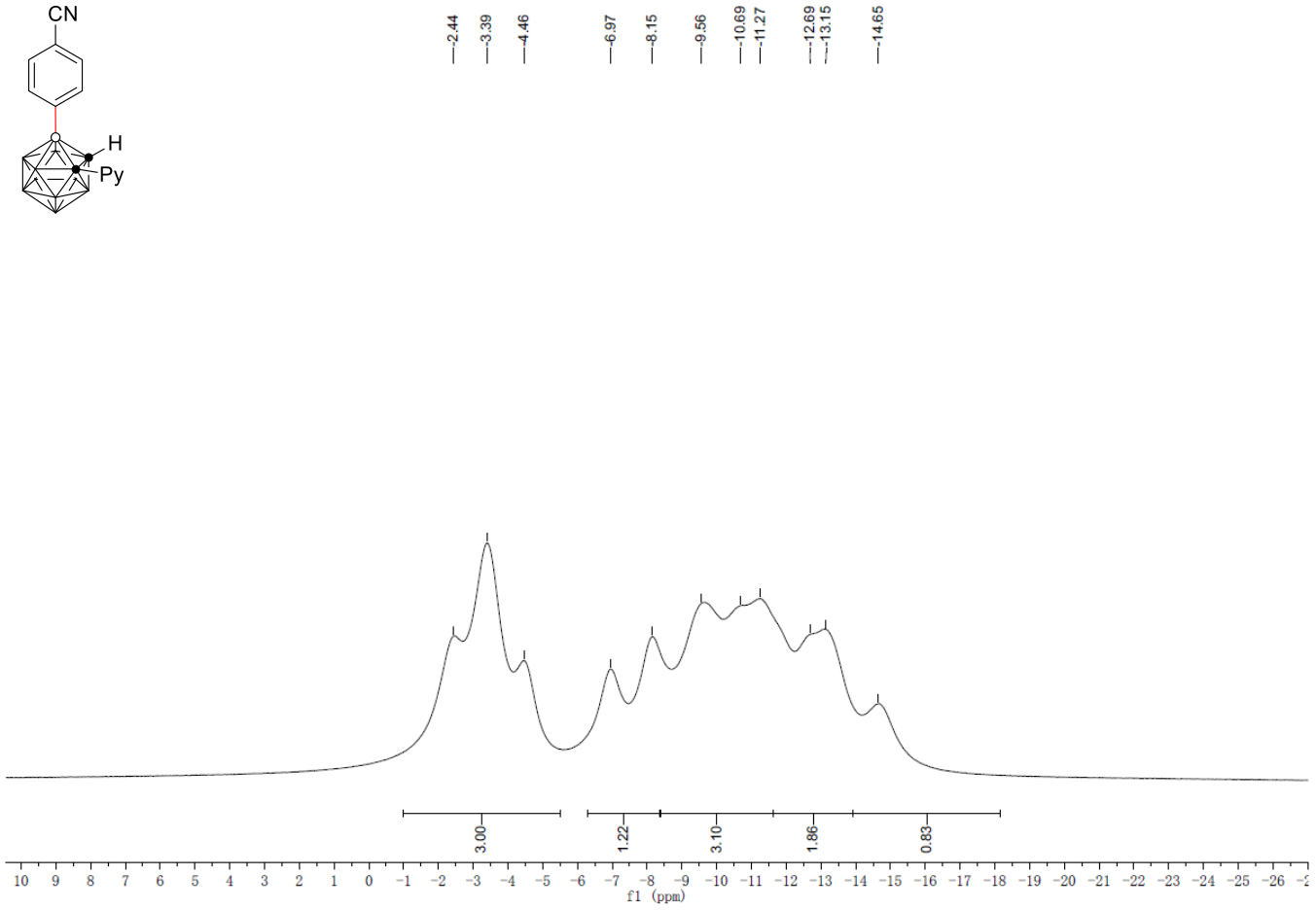
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3k**



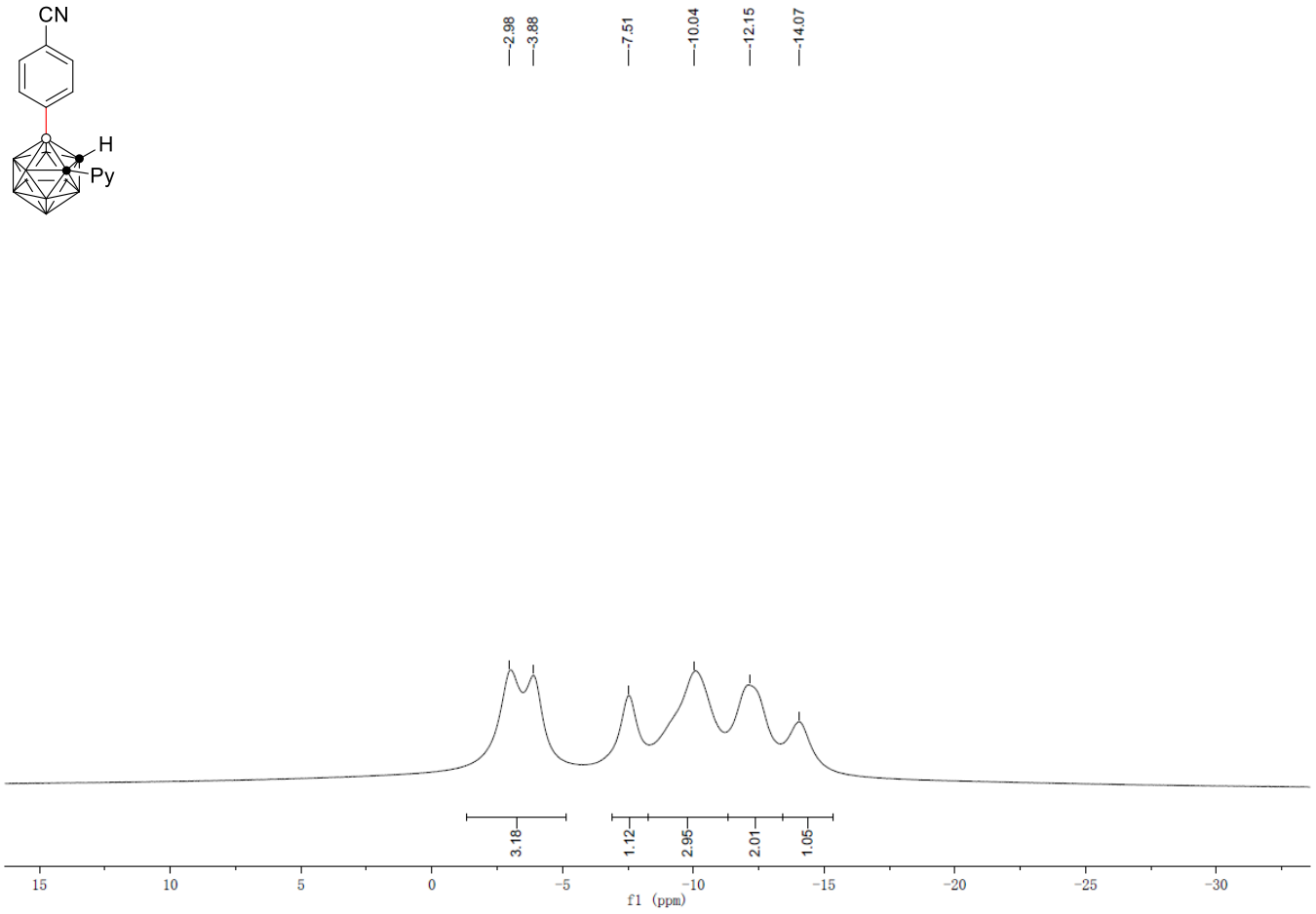
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3k**



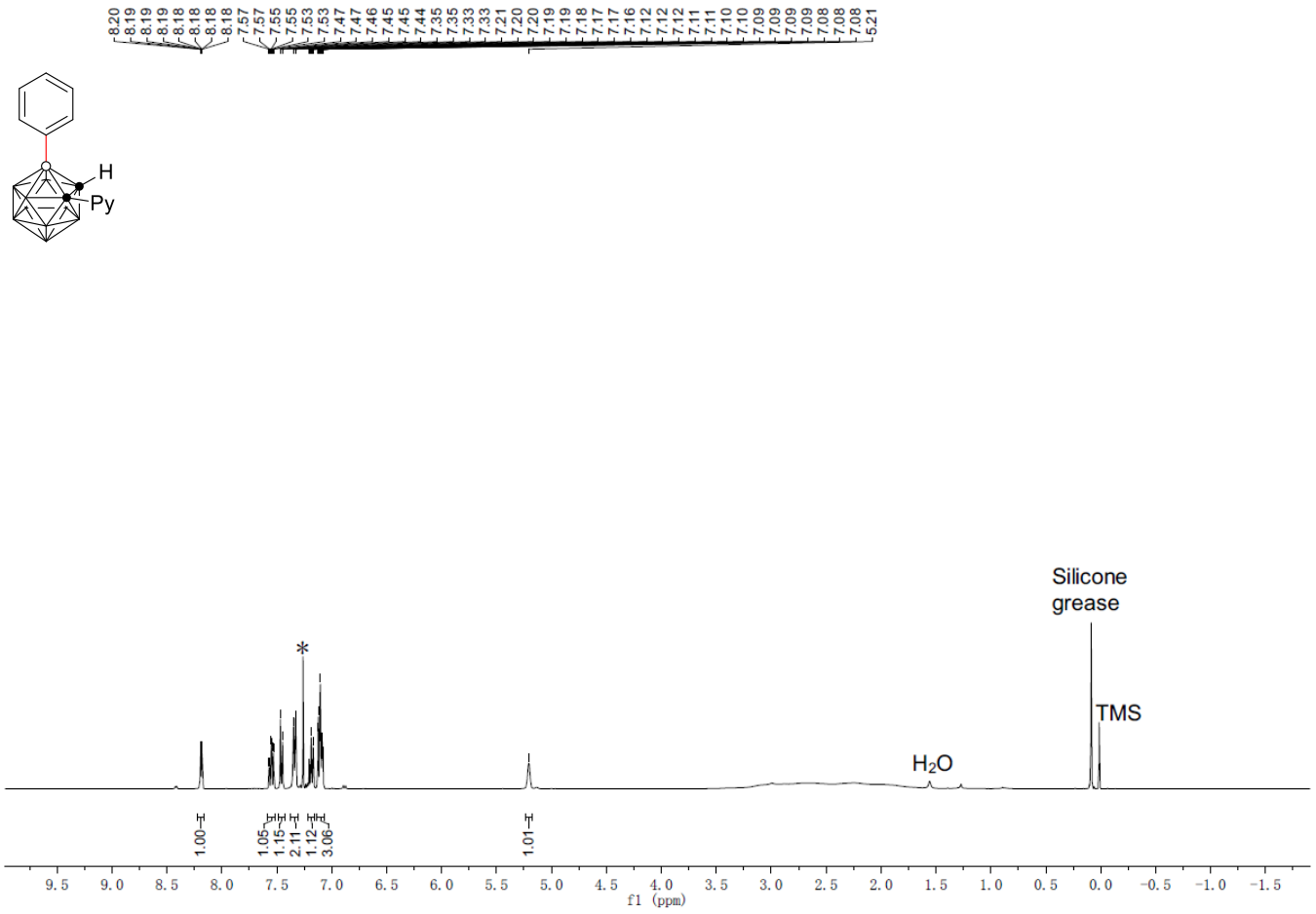
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3k**



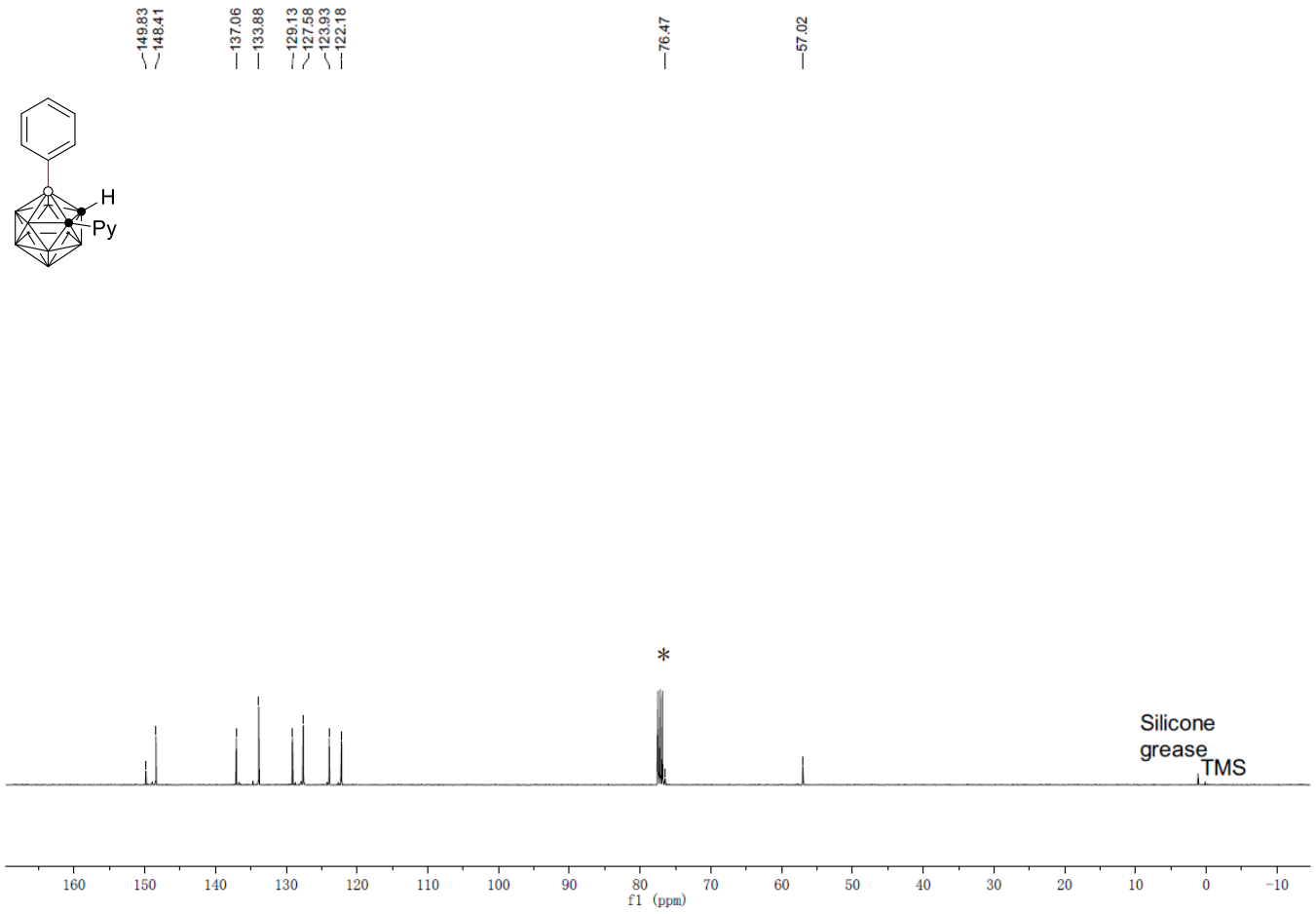
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3k**



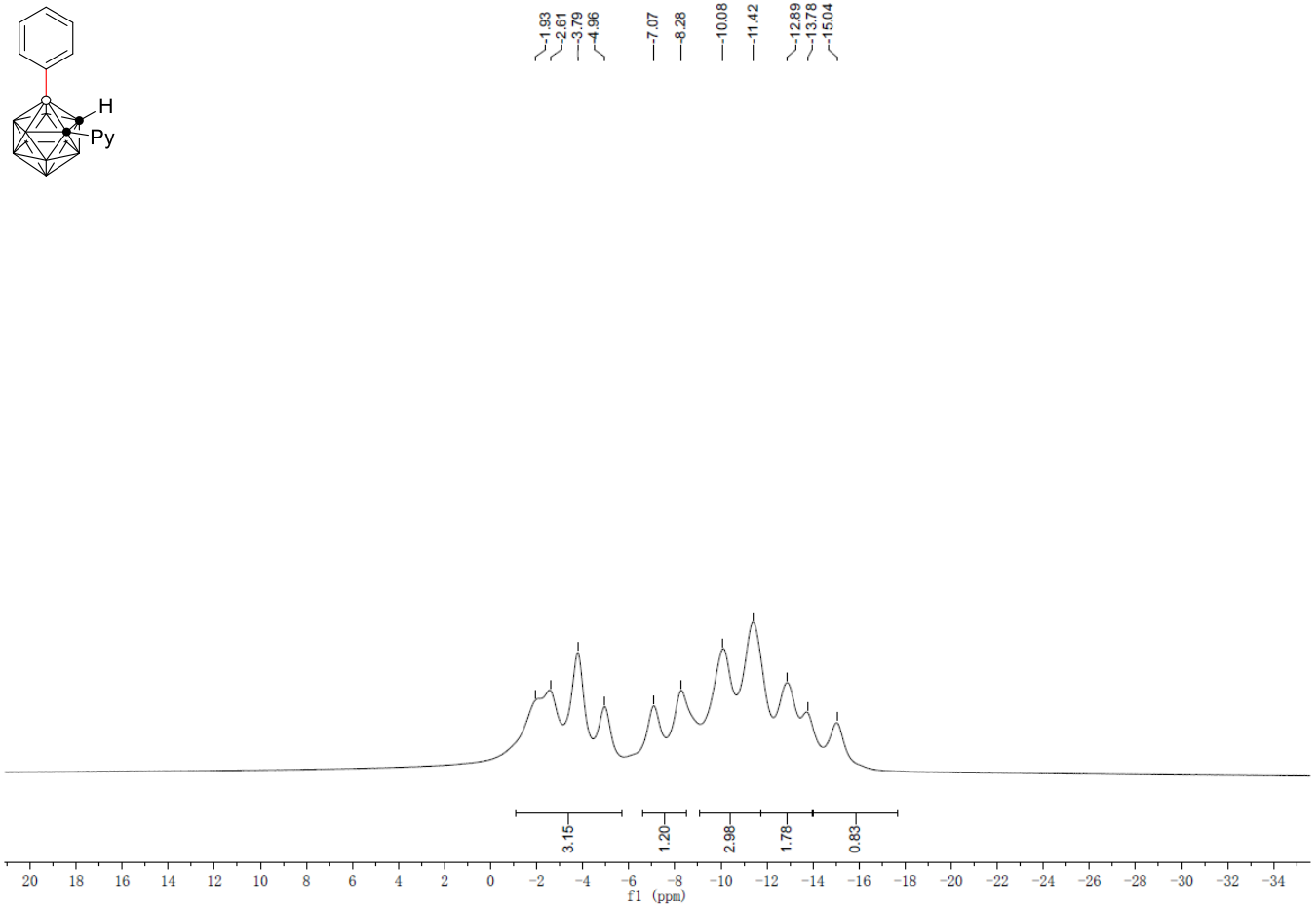
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3l**



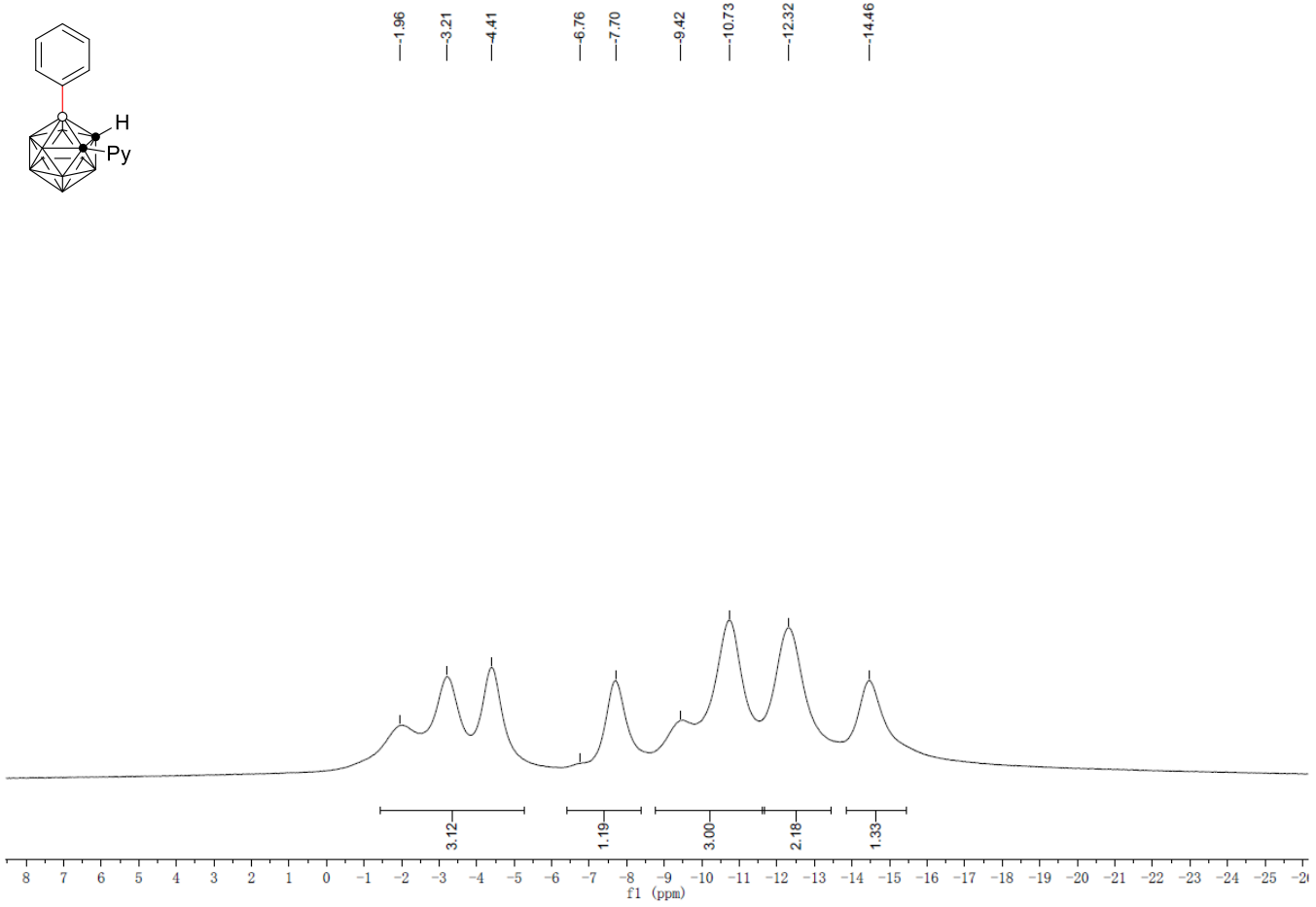
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3l**



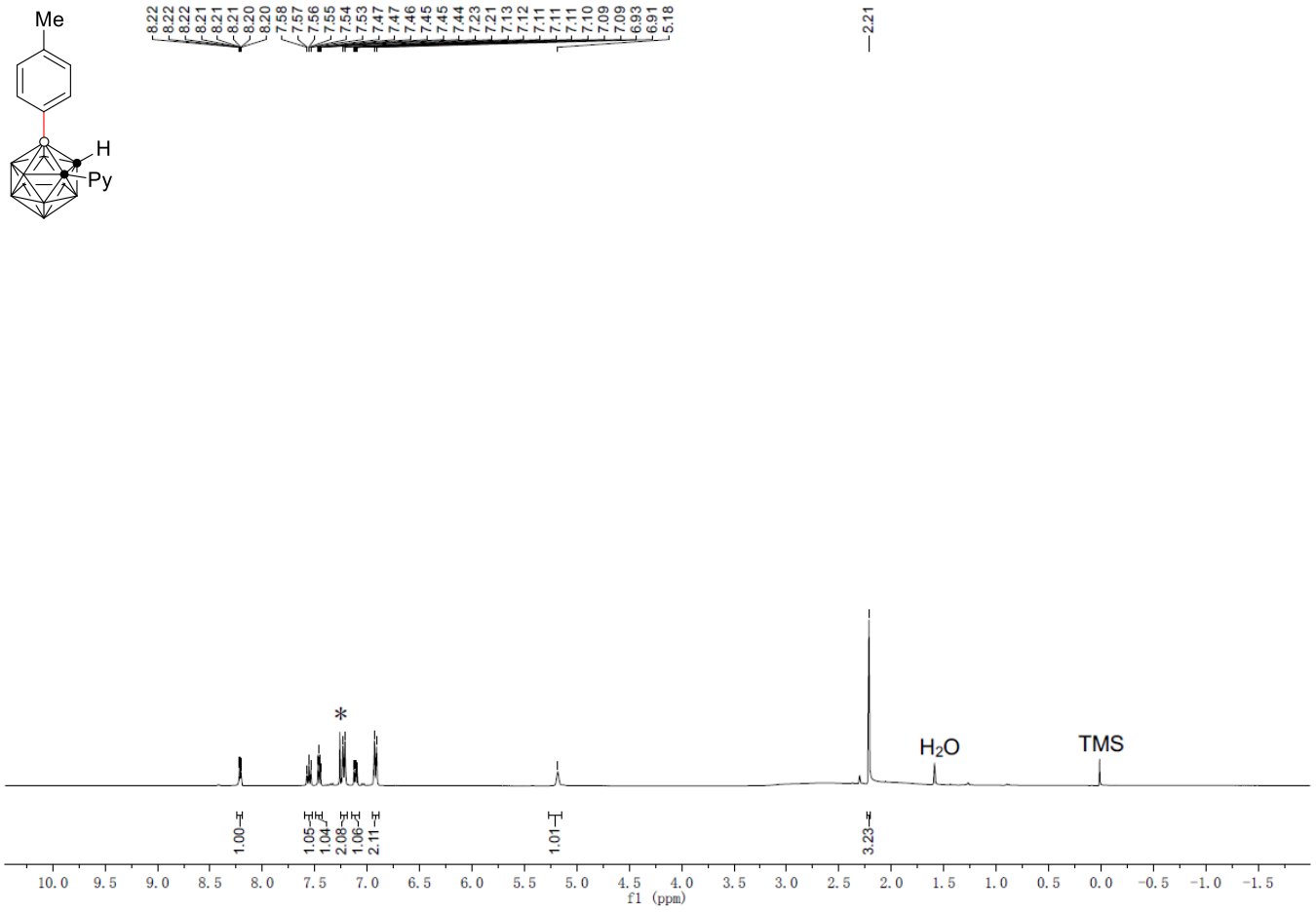
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3l**



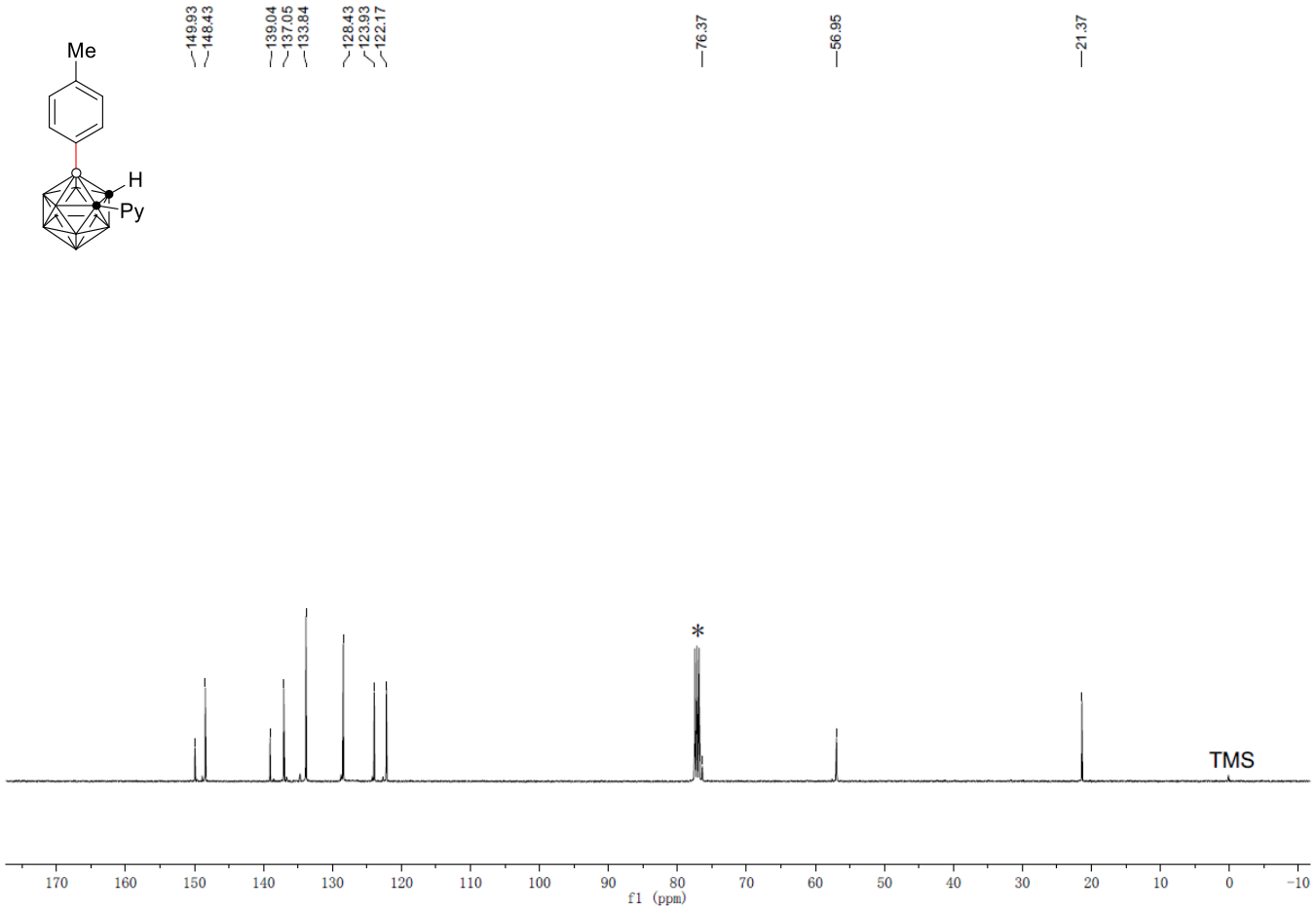
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3l**



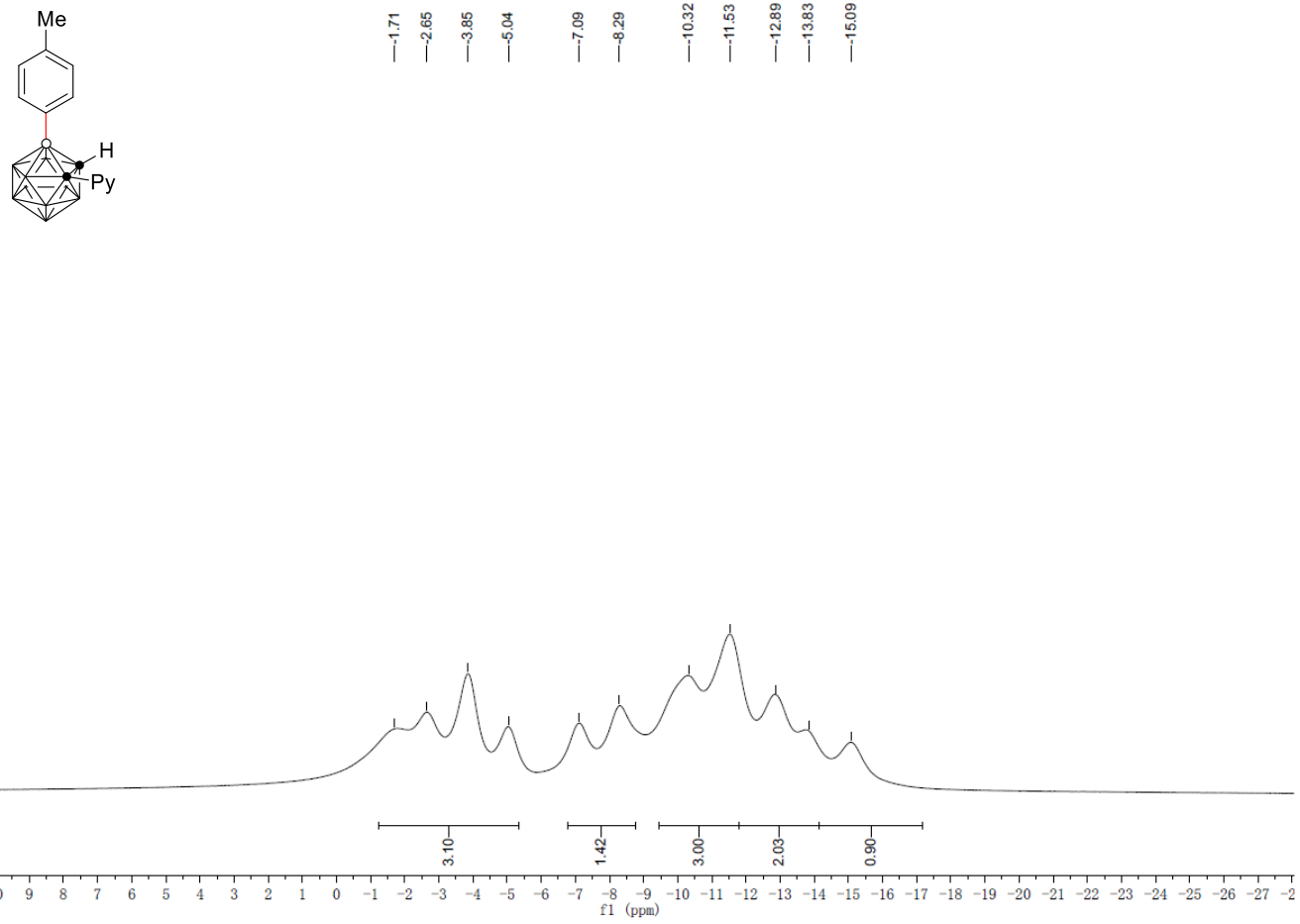
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3m**



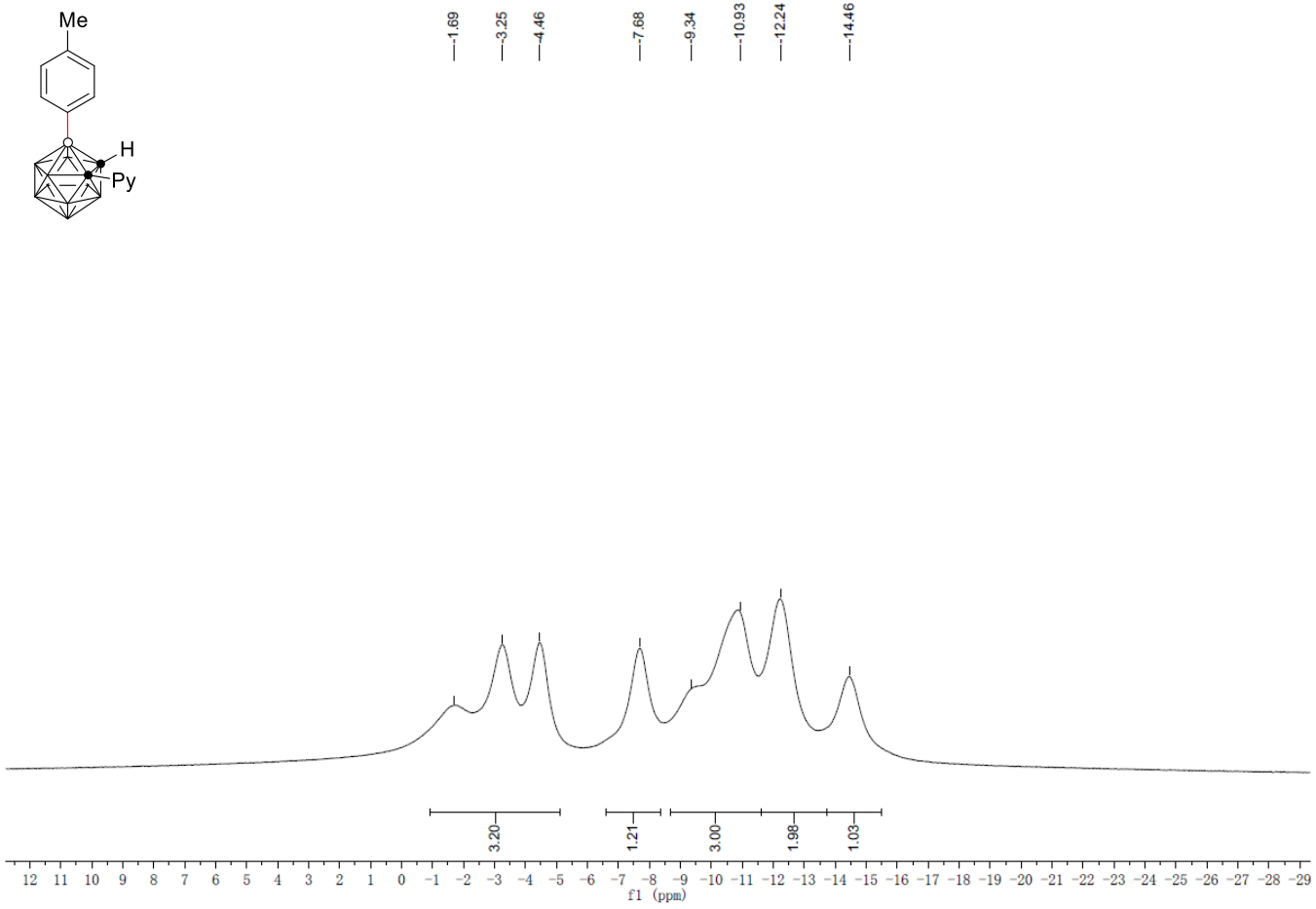
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3m**



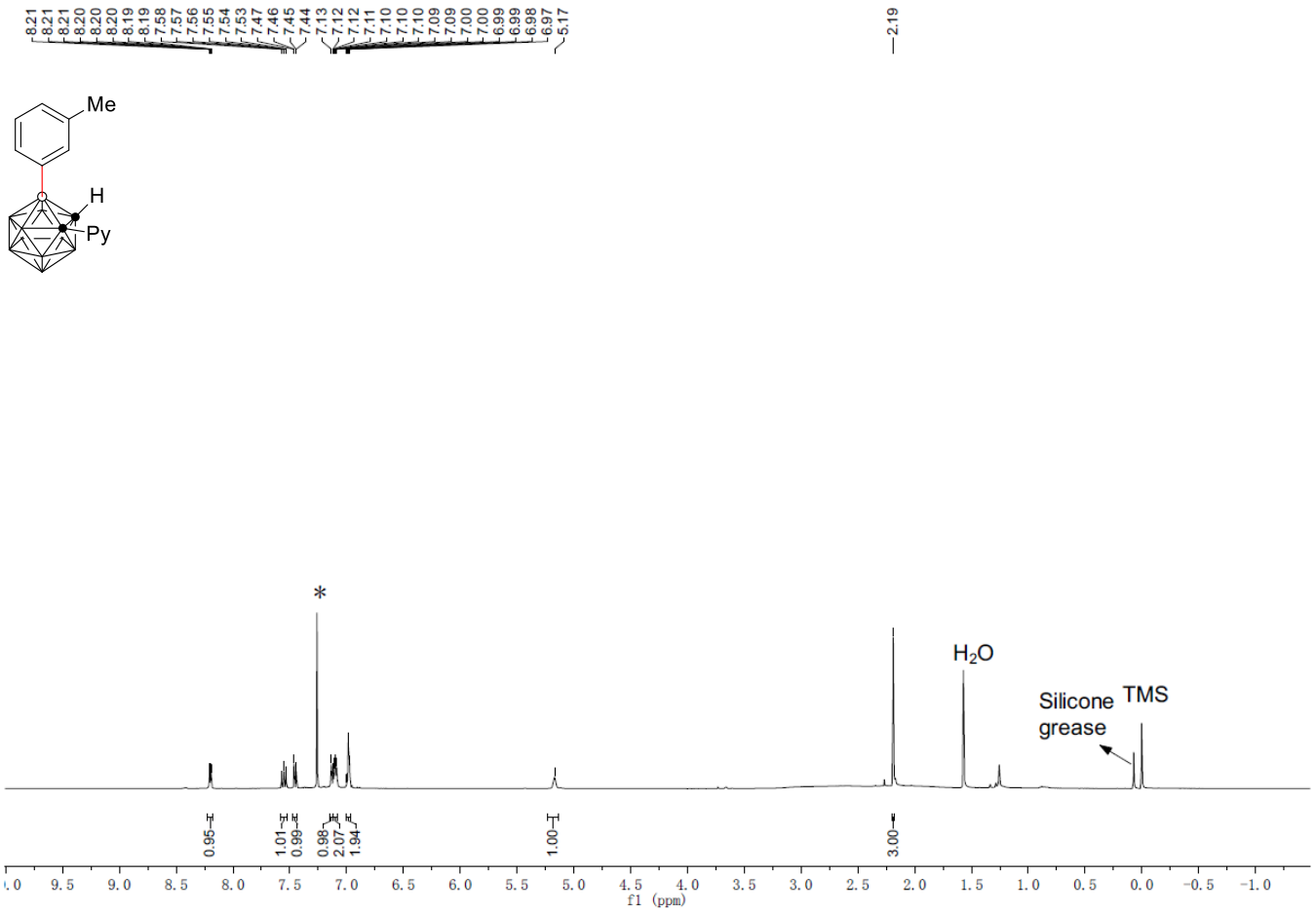
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3m**



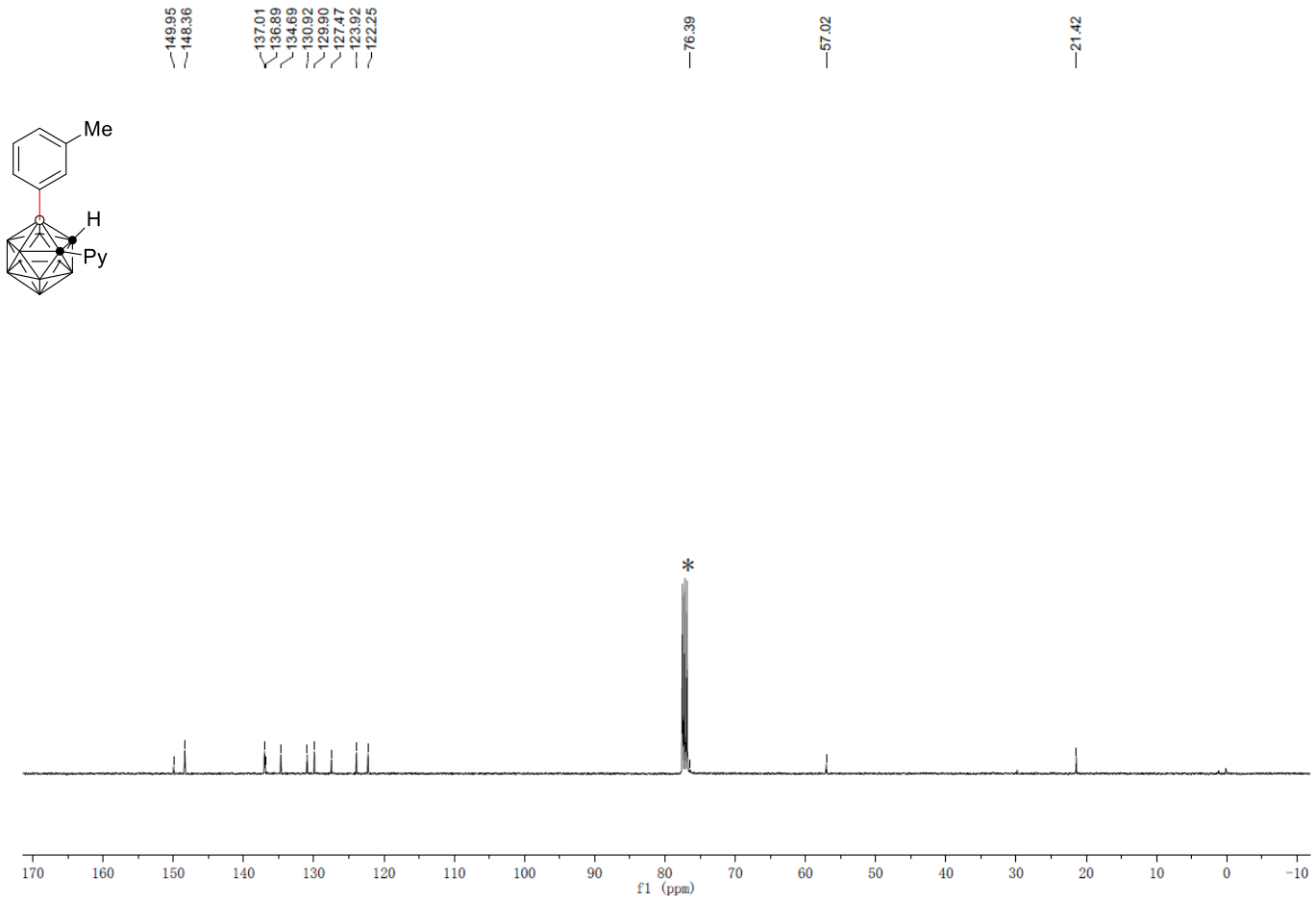
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3m**



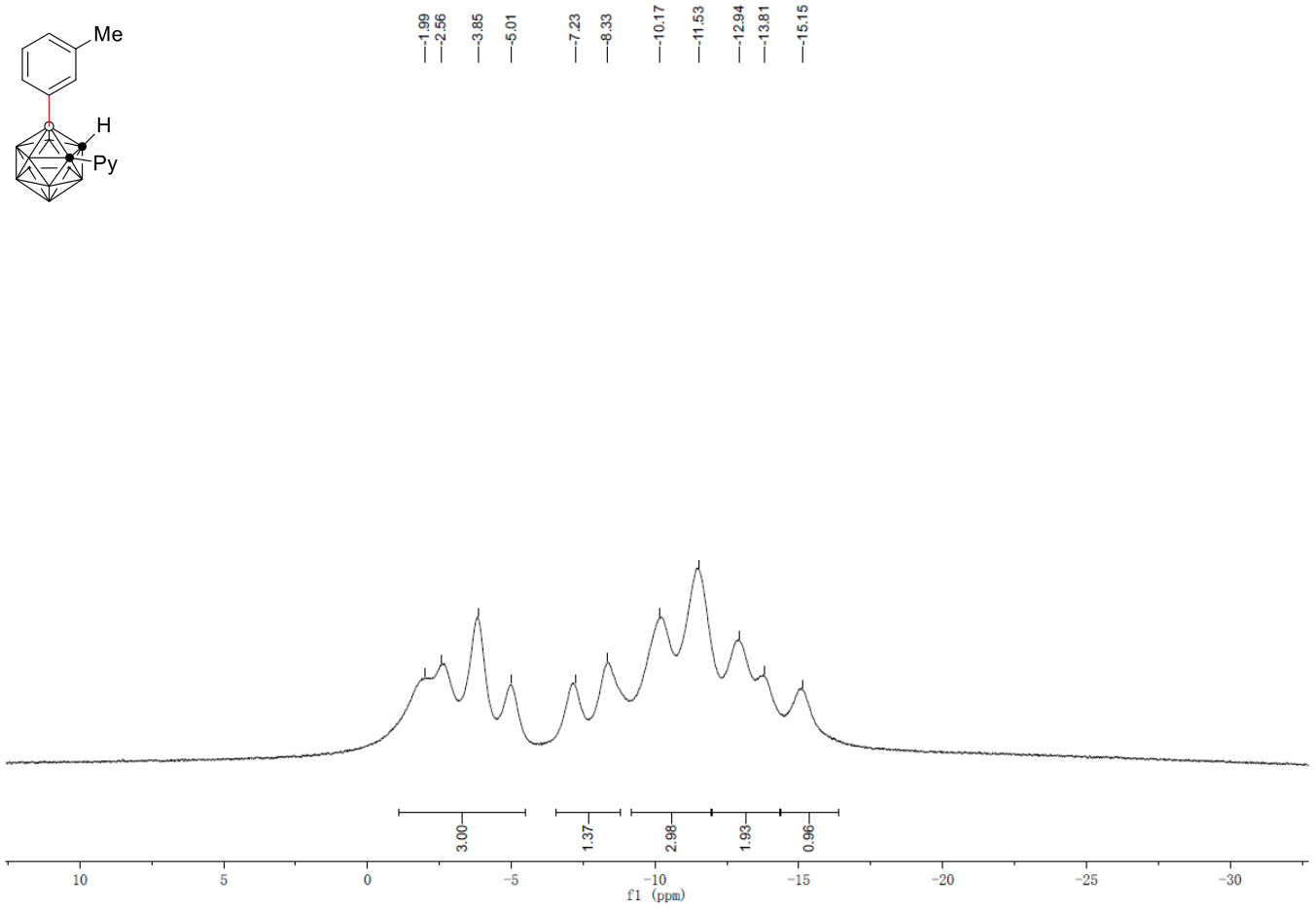
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3n**



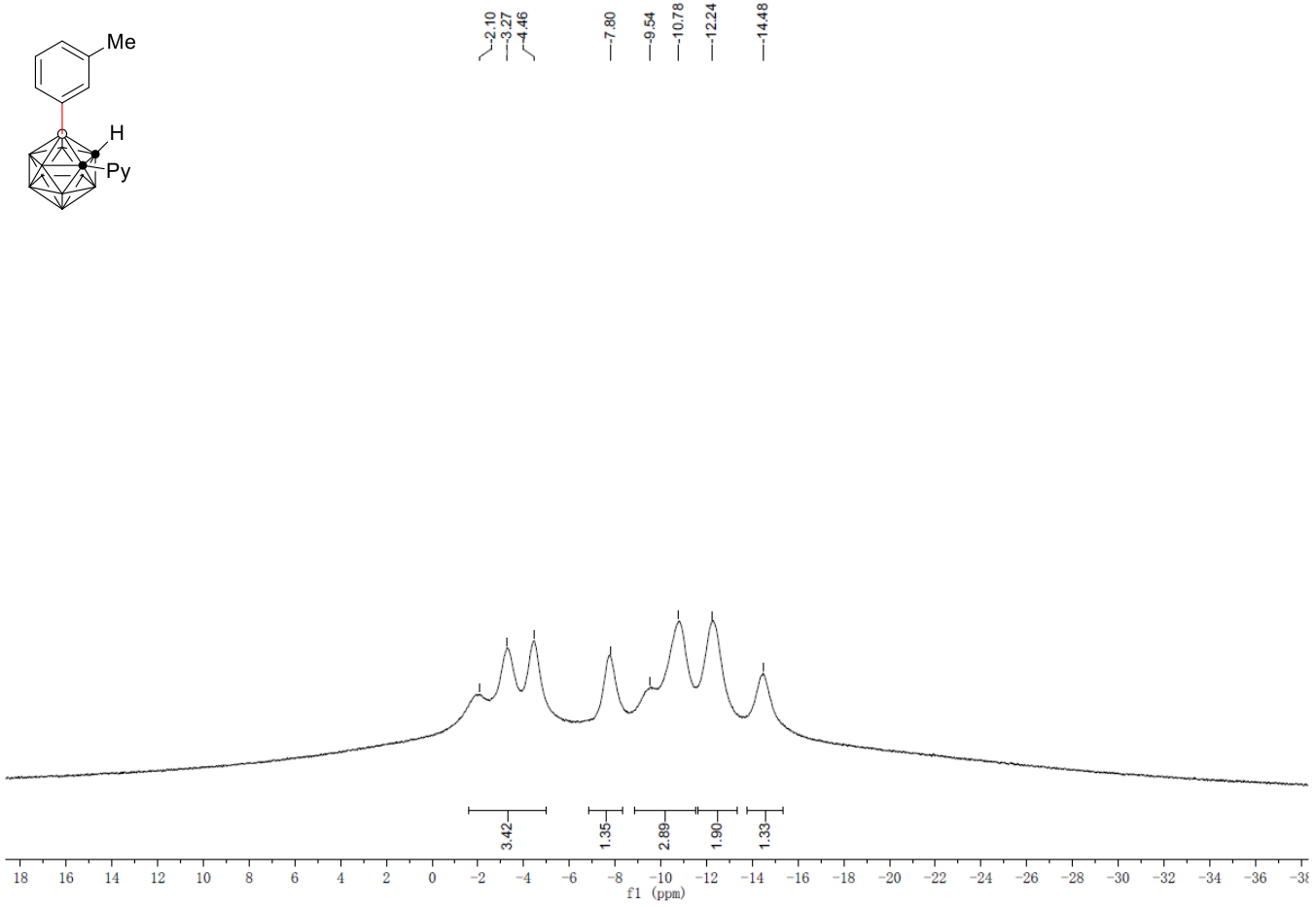
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3n**



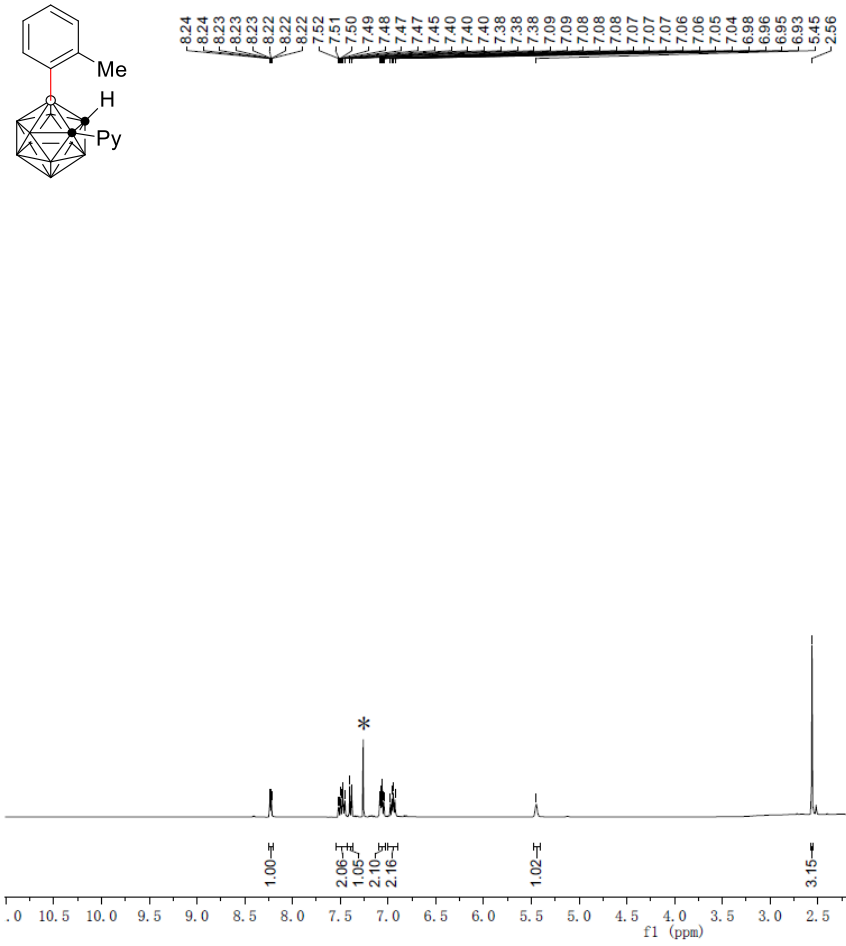
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3n**



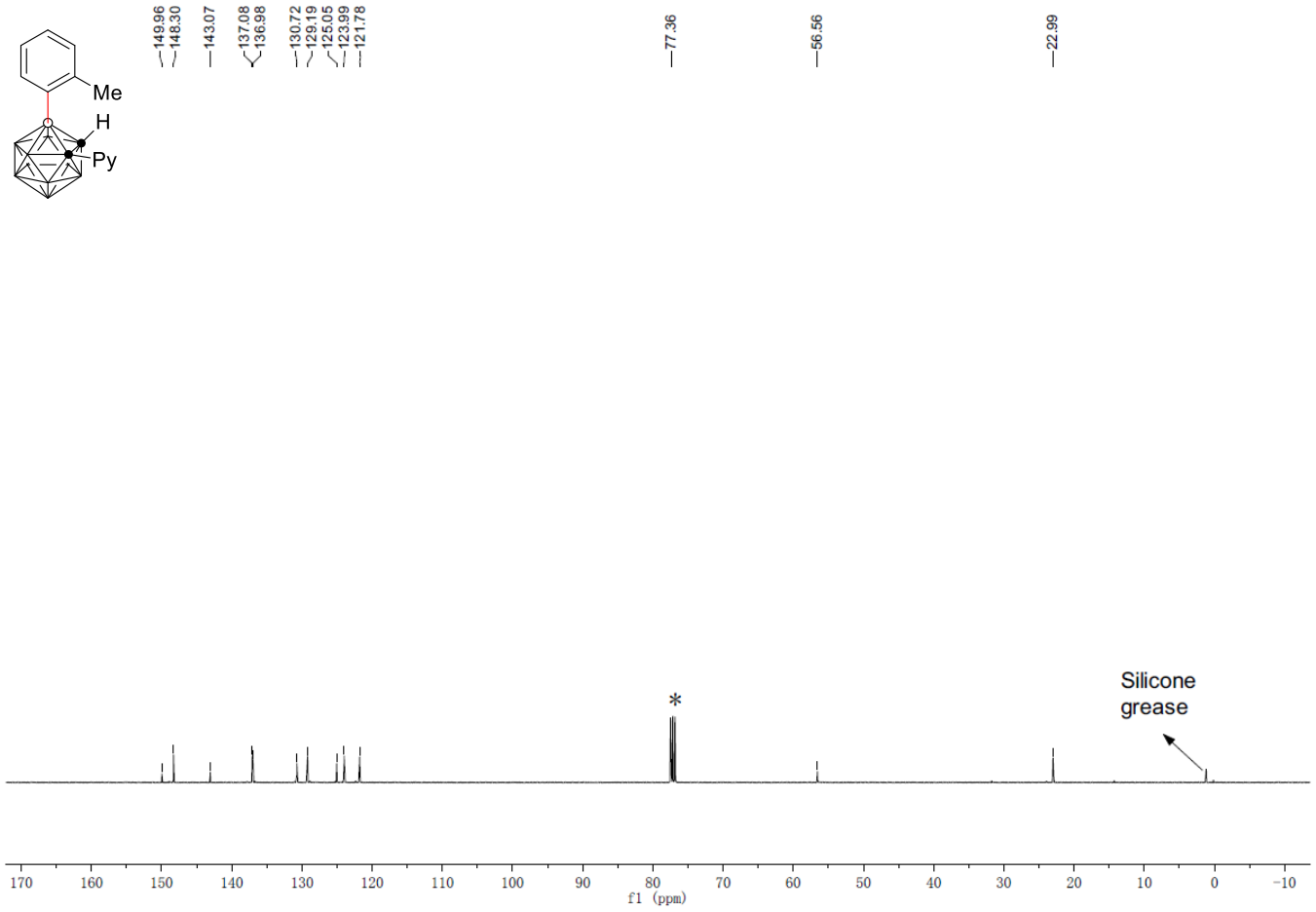
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3n**



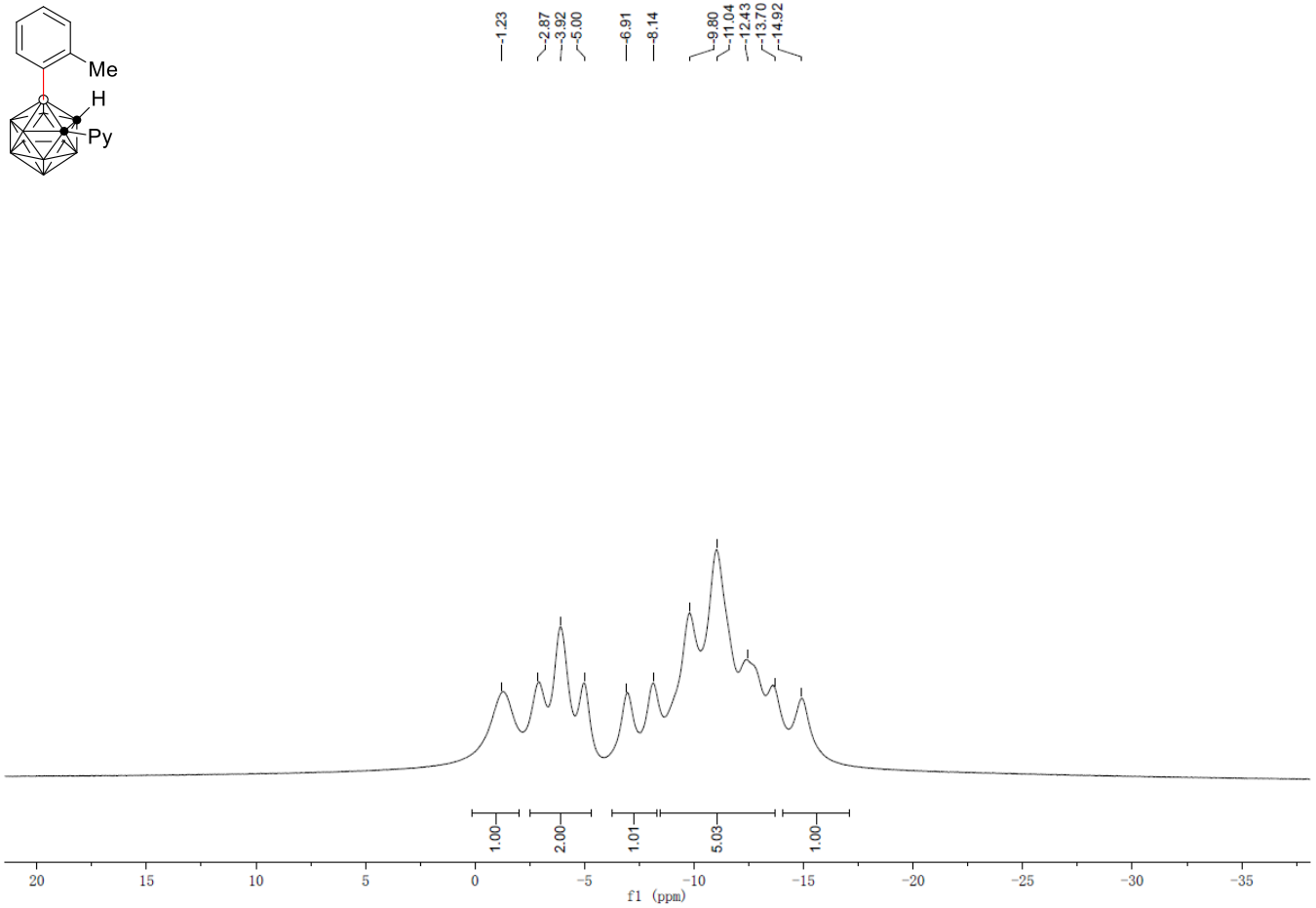
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3o**



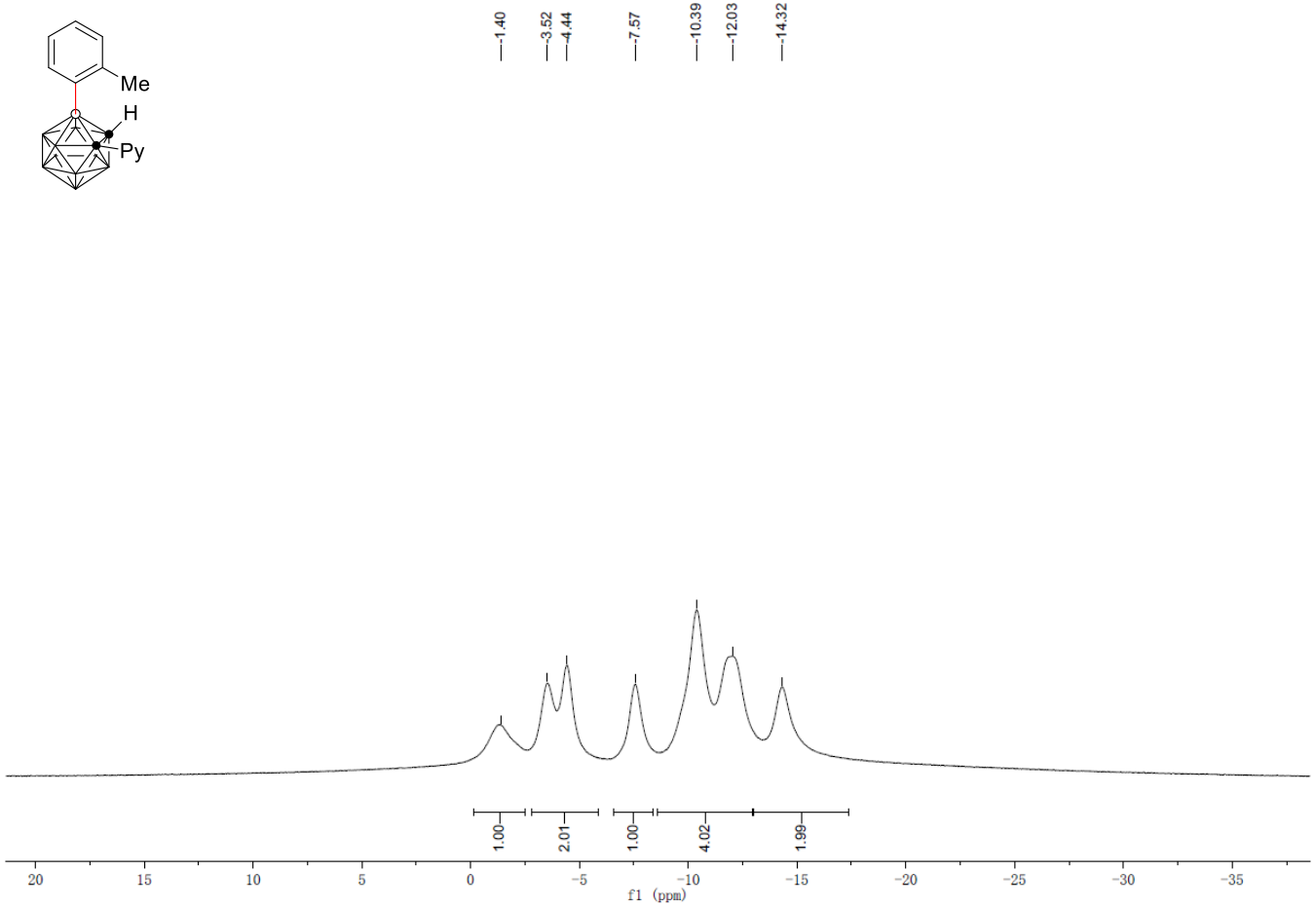
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3o**



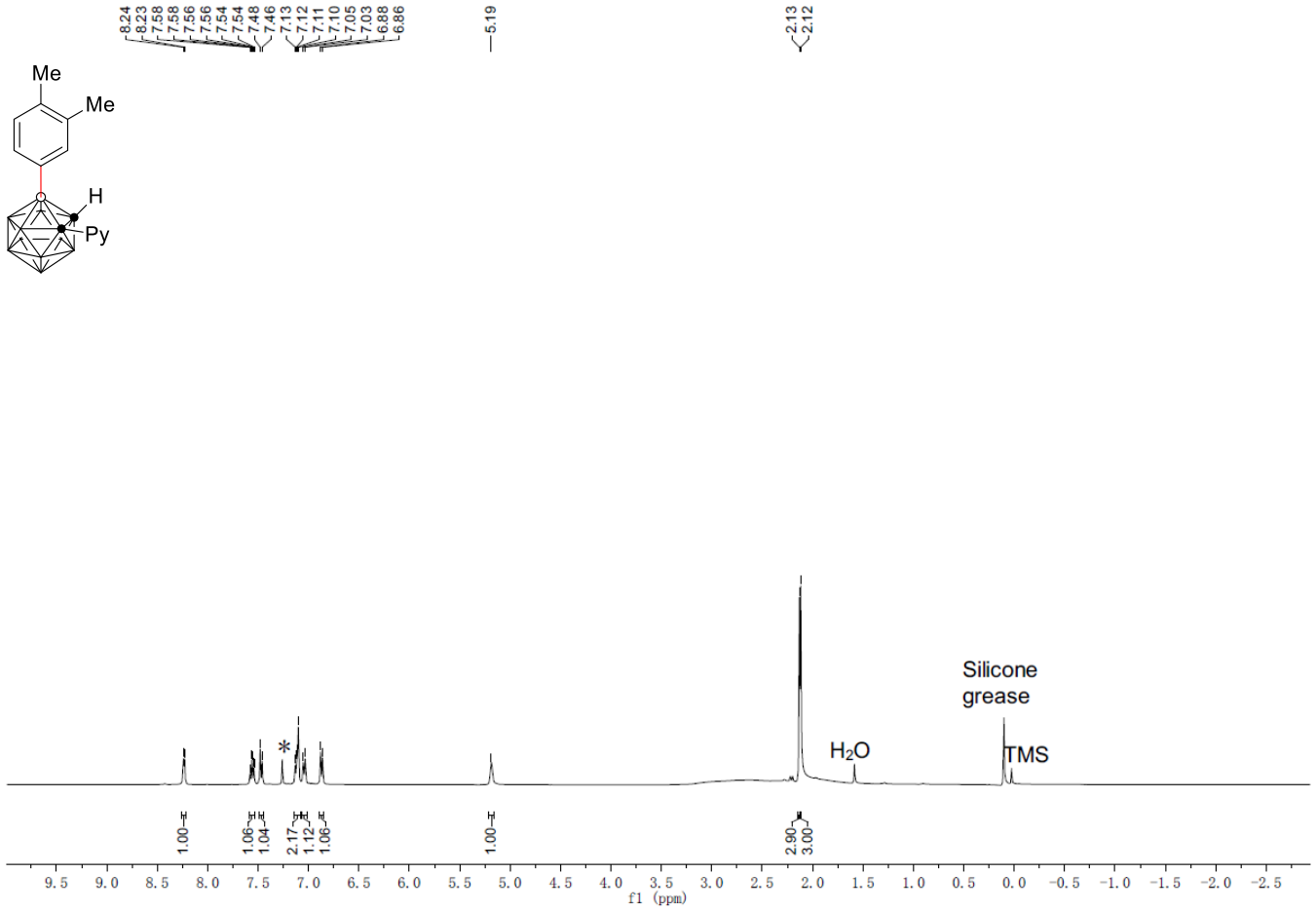
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3o**



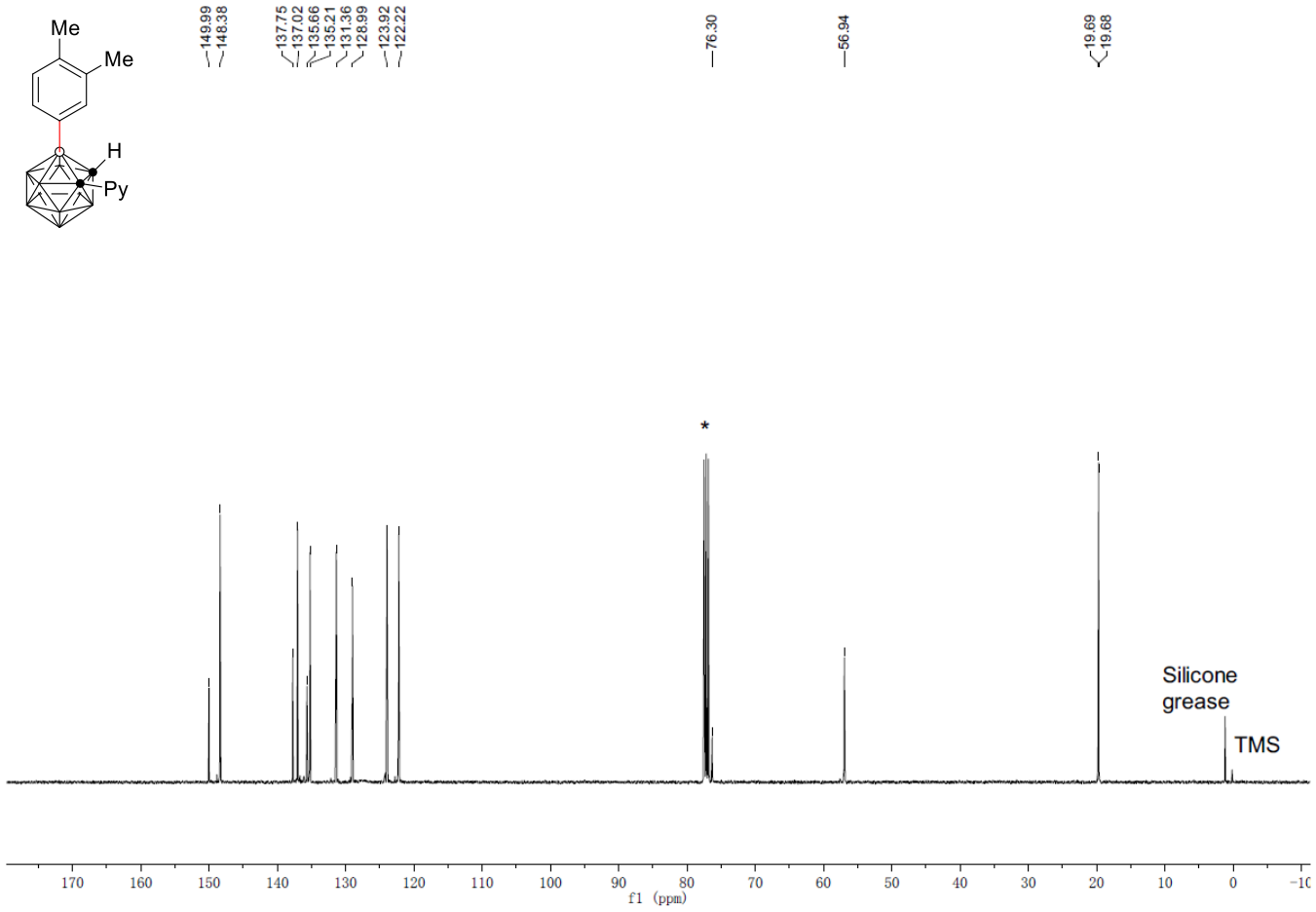
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3o**



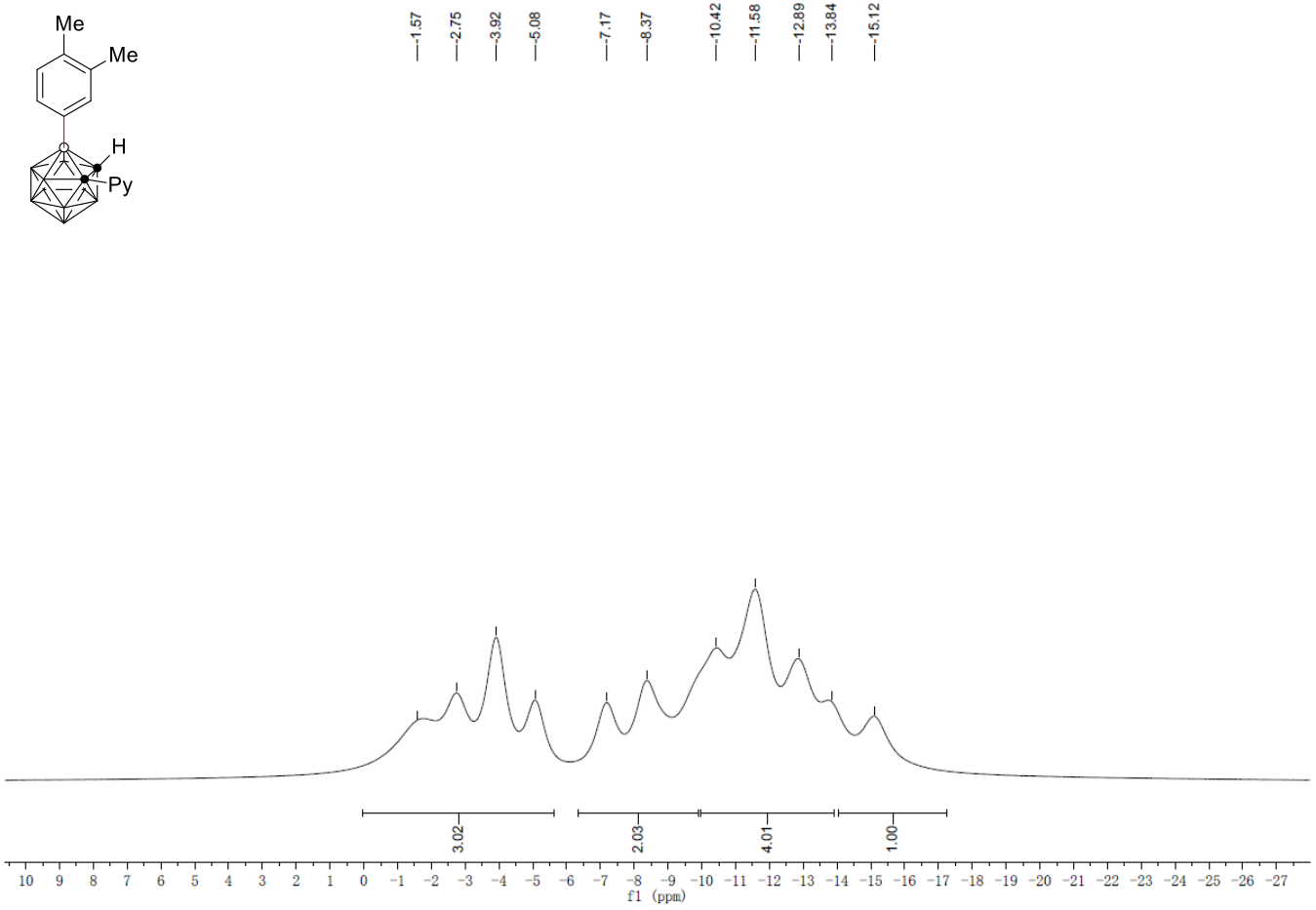
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3p**



^{13}C NMR (101 MHz, $CDCl_3$ *) of **3p**



^{11}B NMR (128 MHz, $CDCl_3$ *) of **3p**



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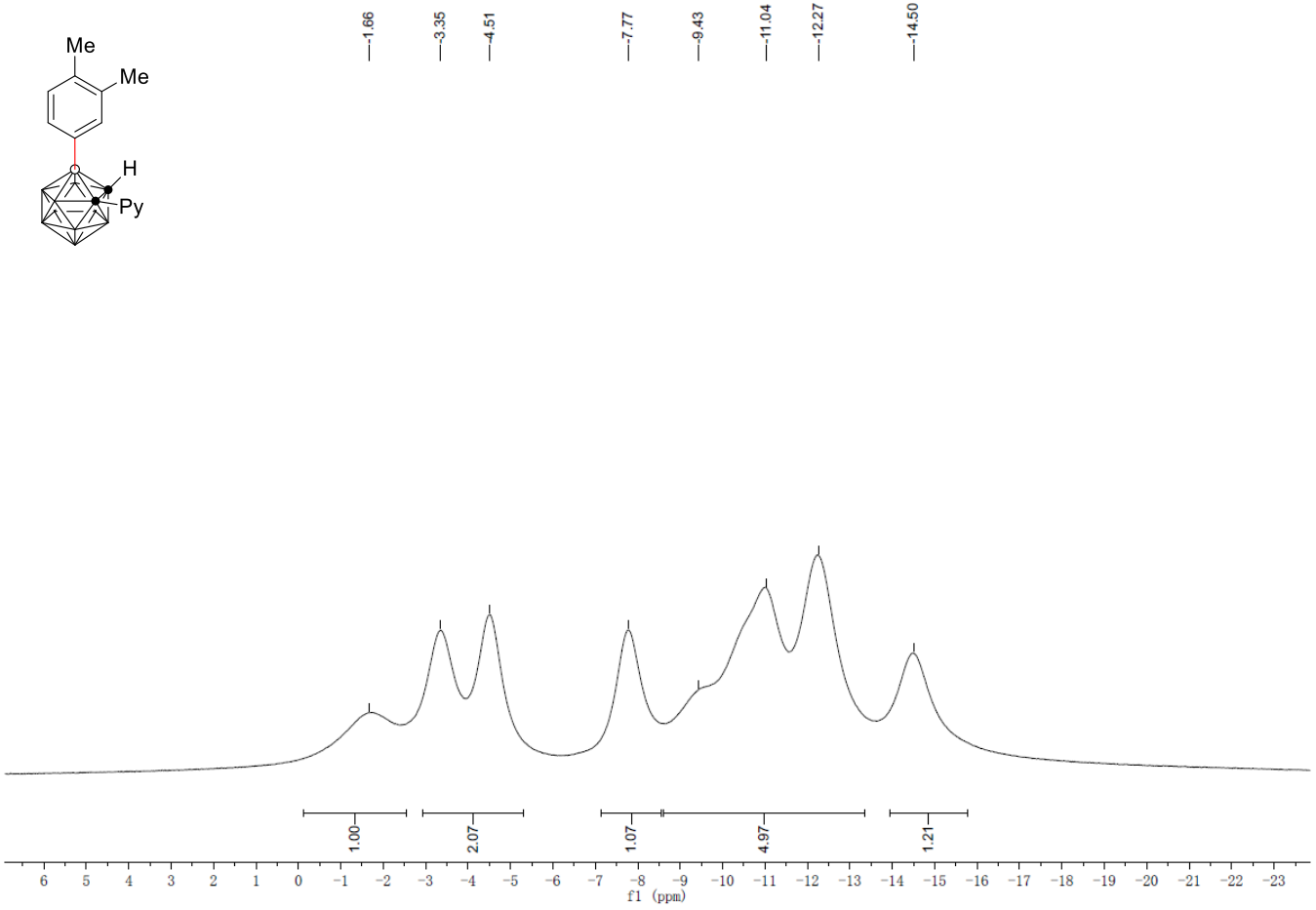
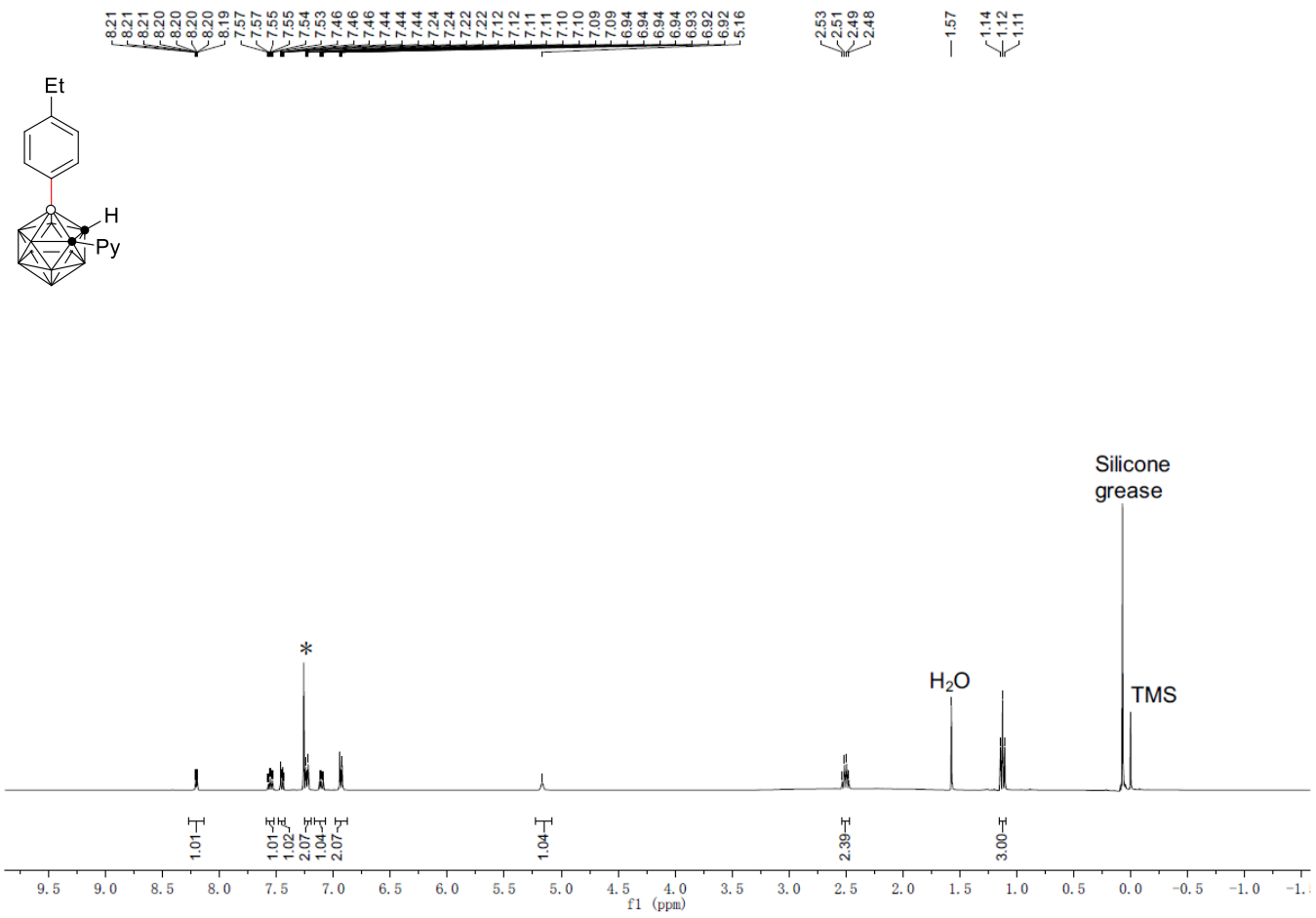
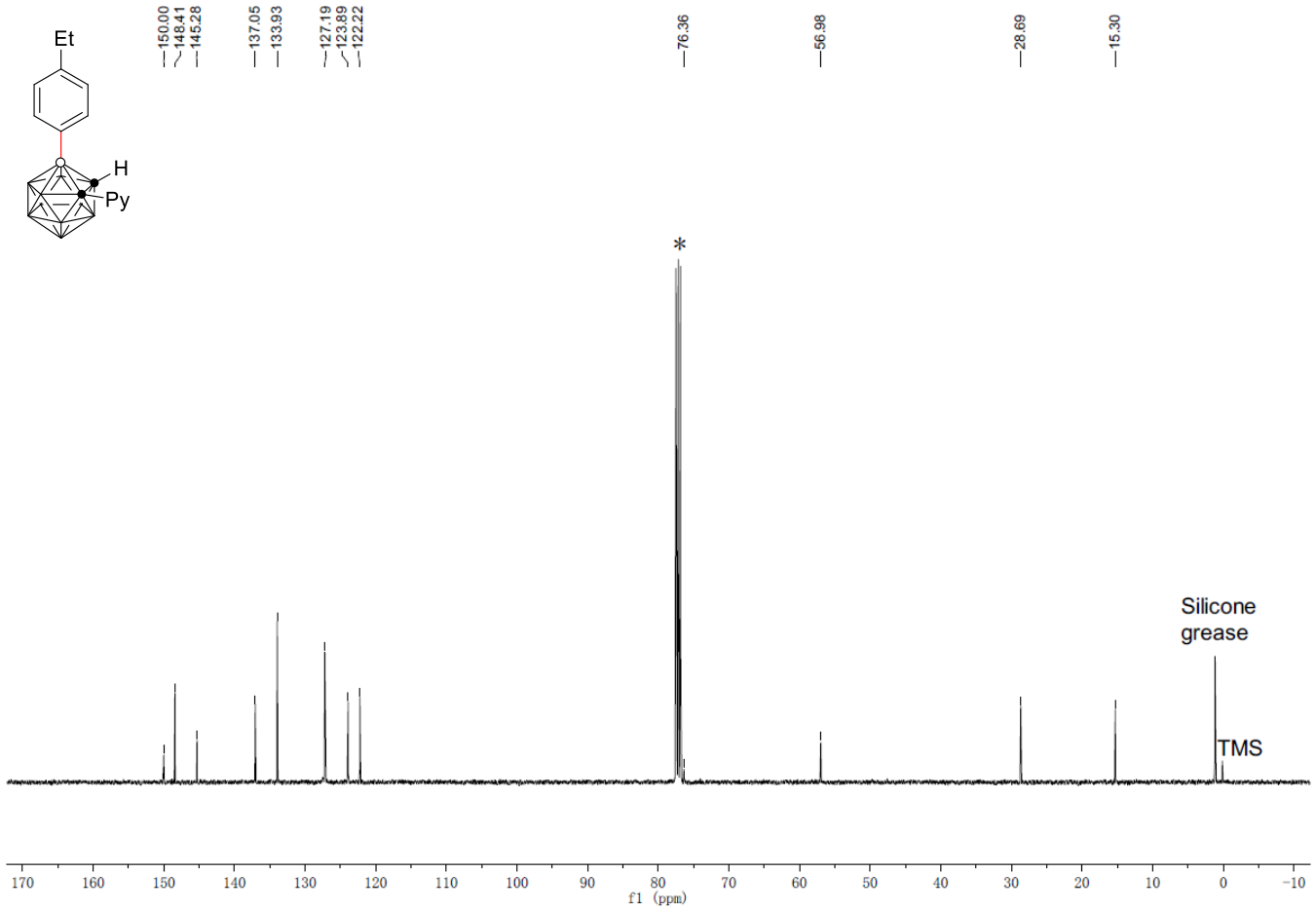


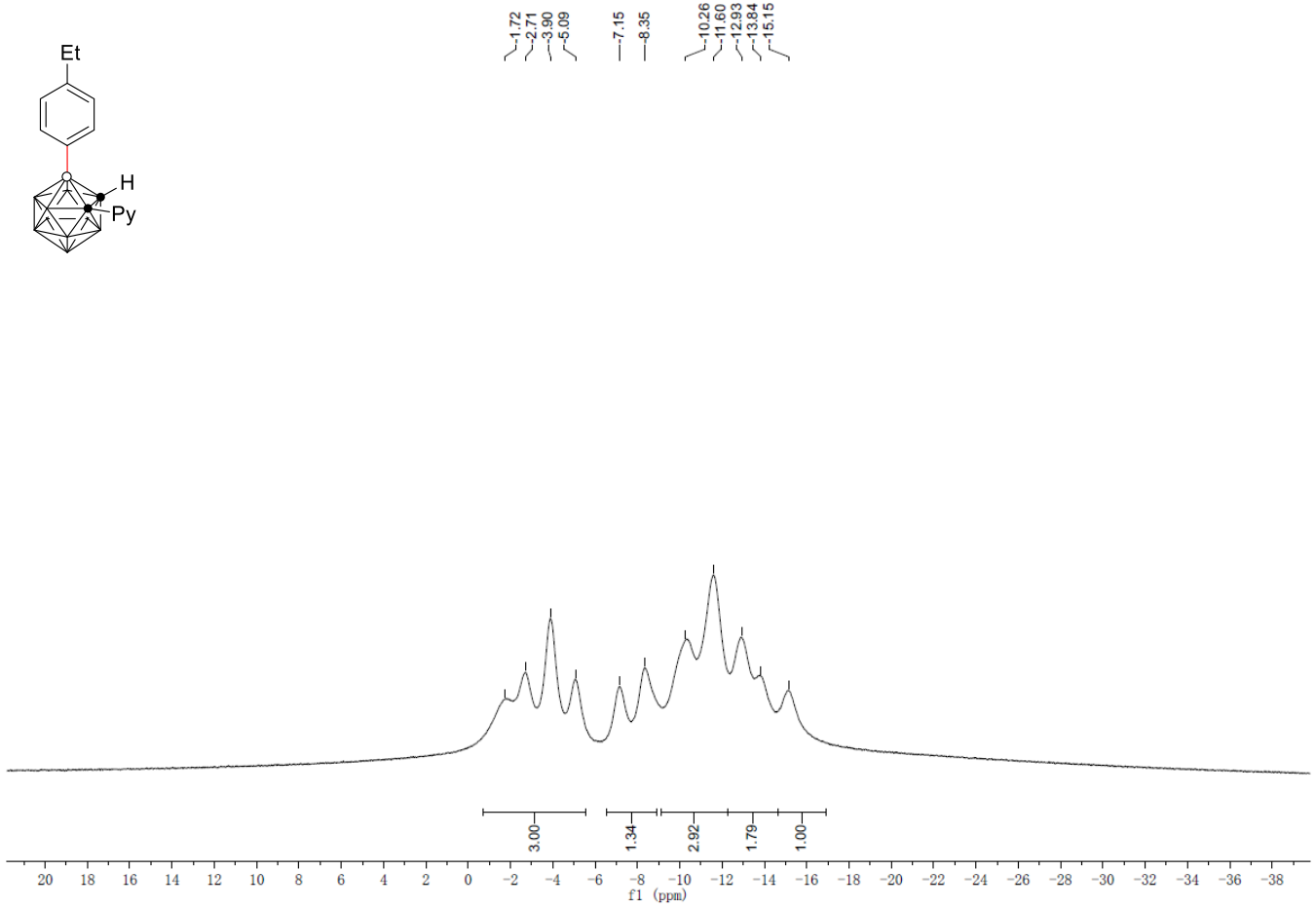
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3q**



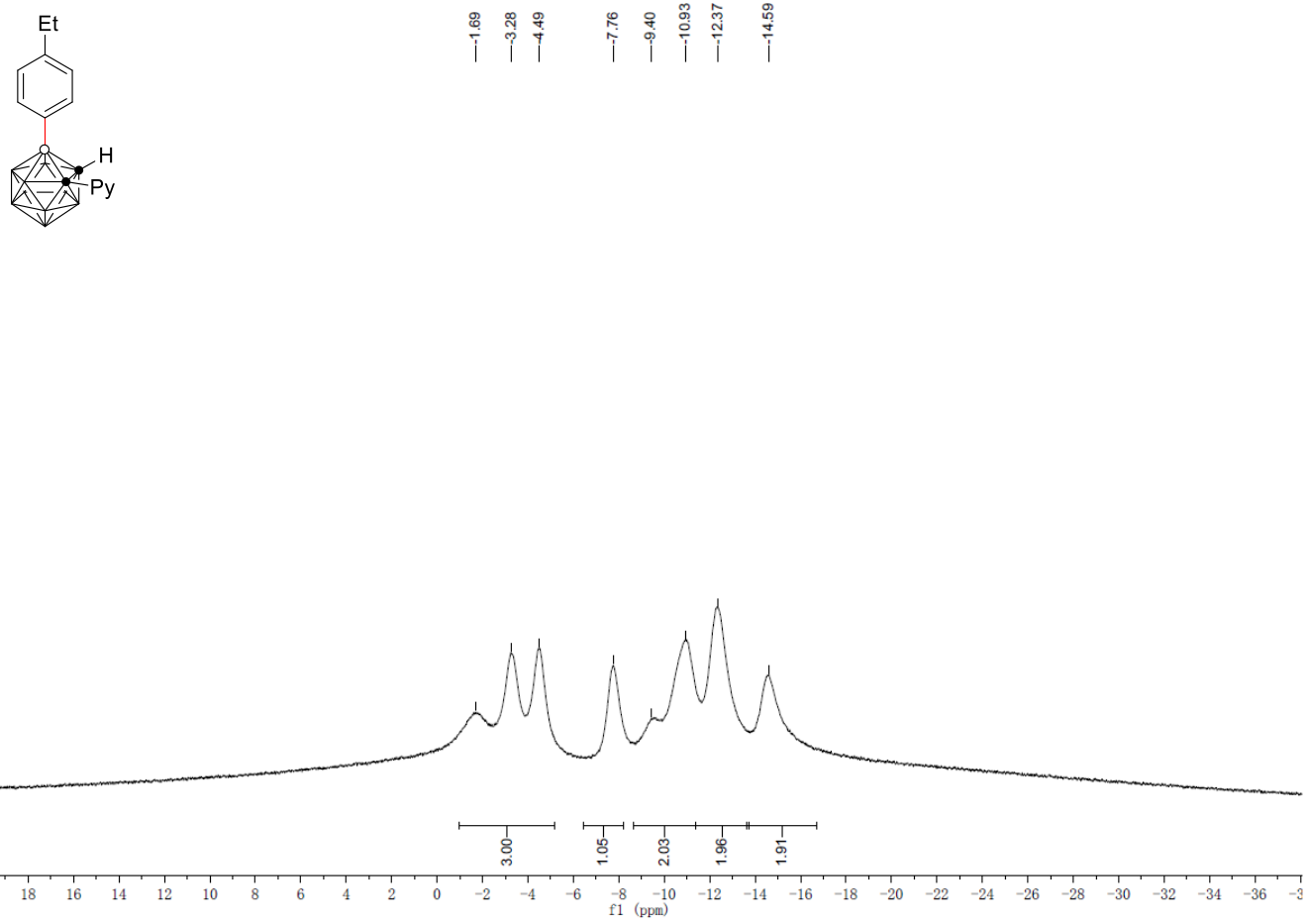
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3q**



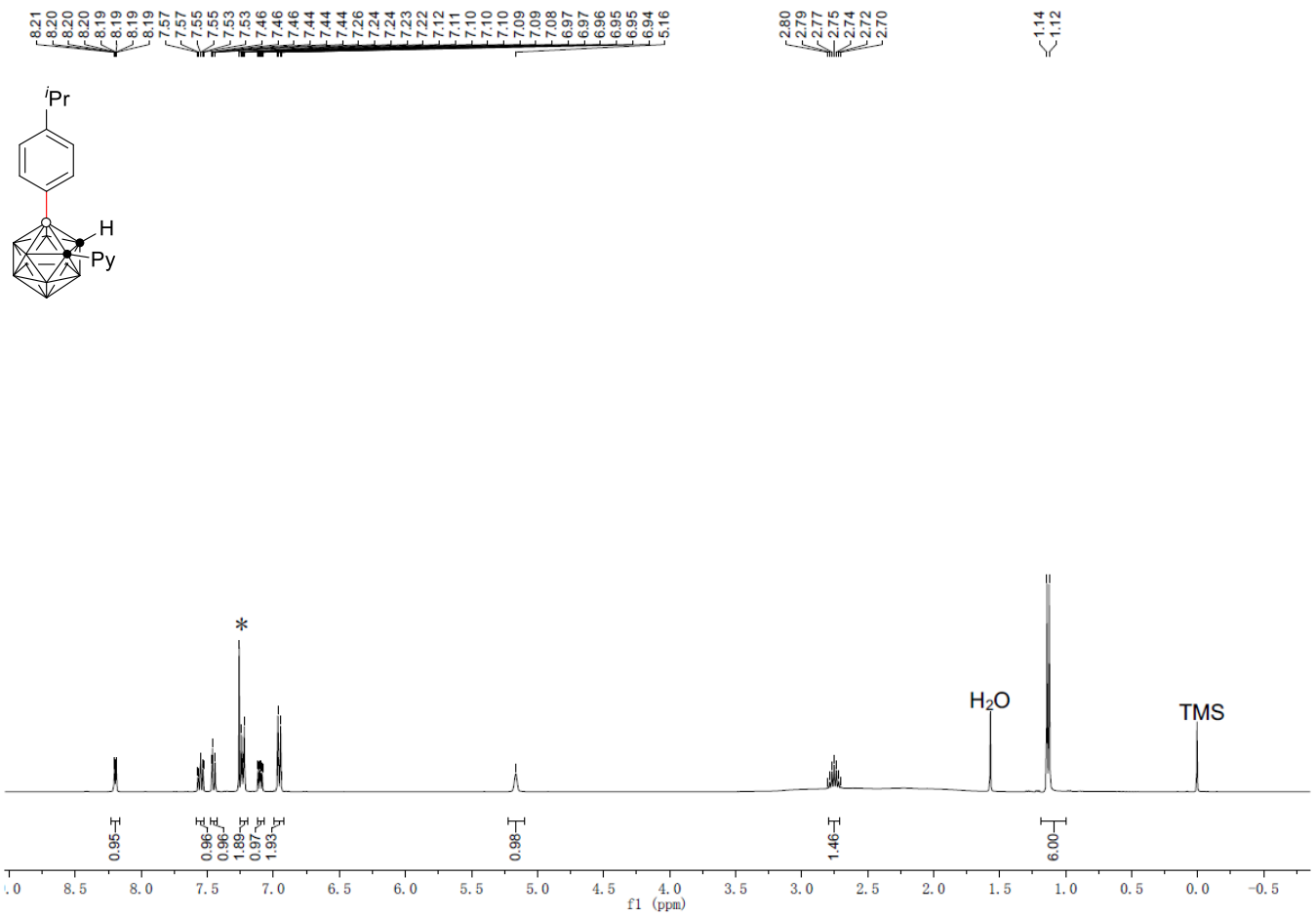
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3q**



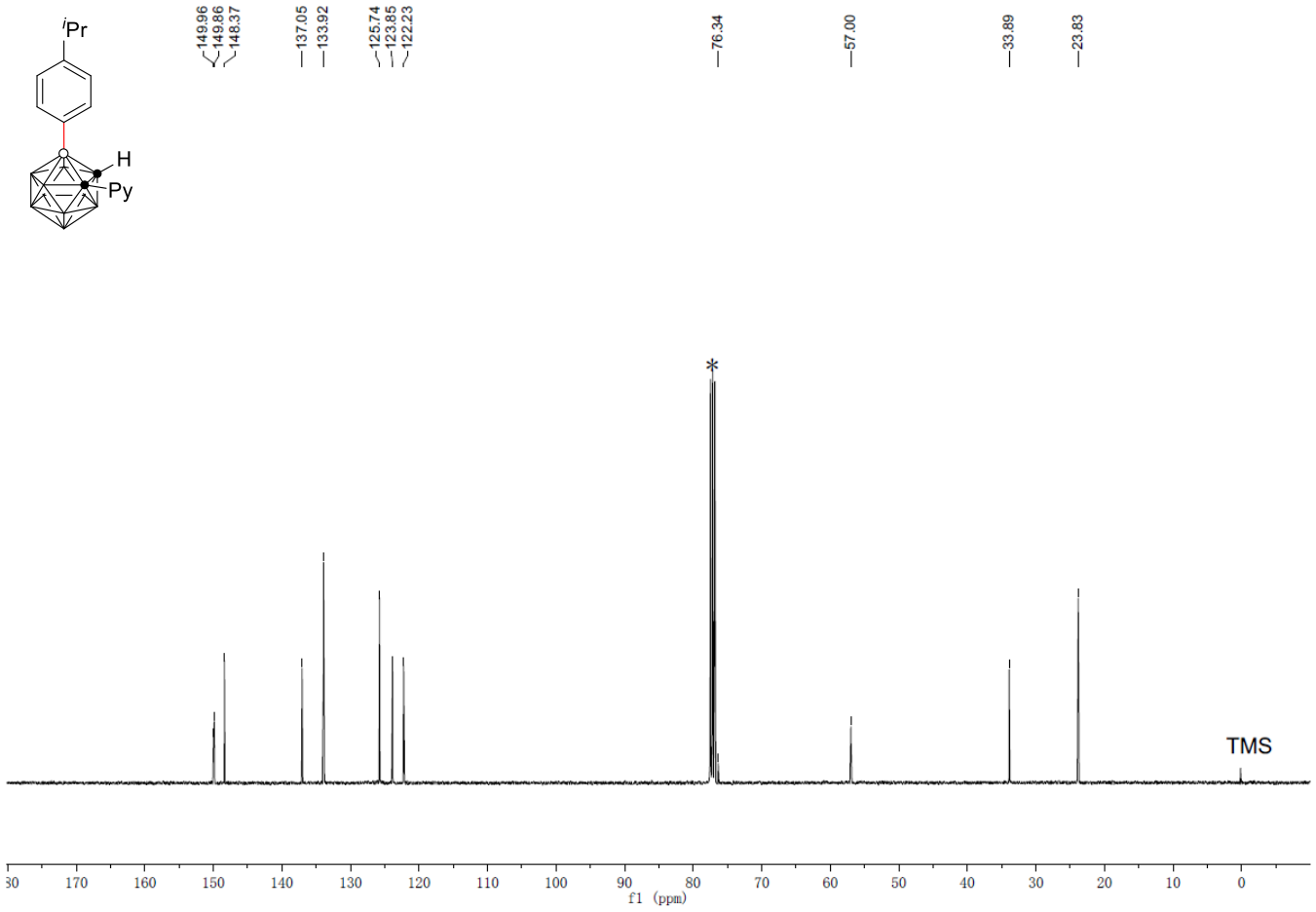
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3q**



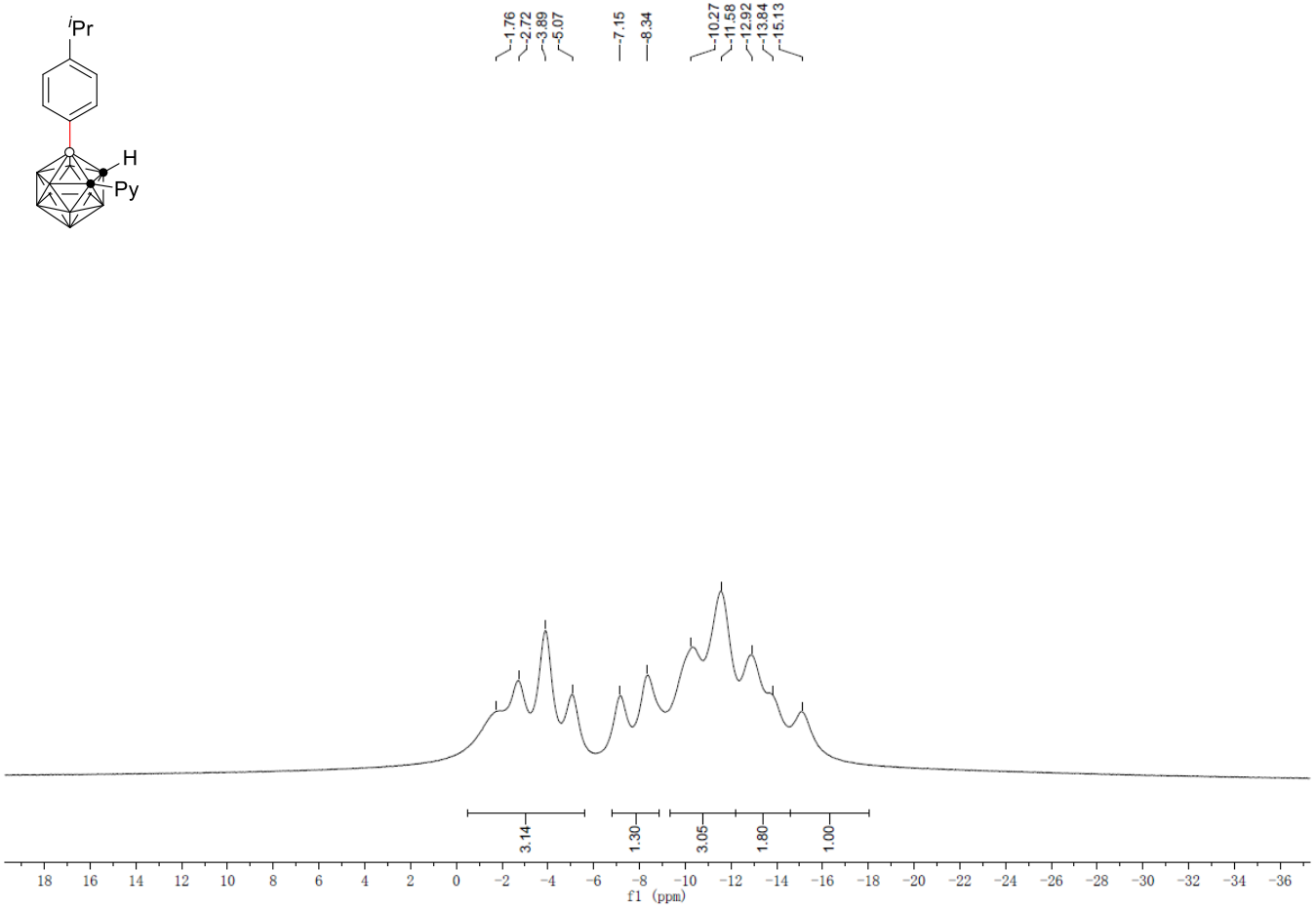
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3r**



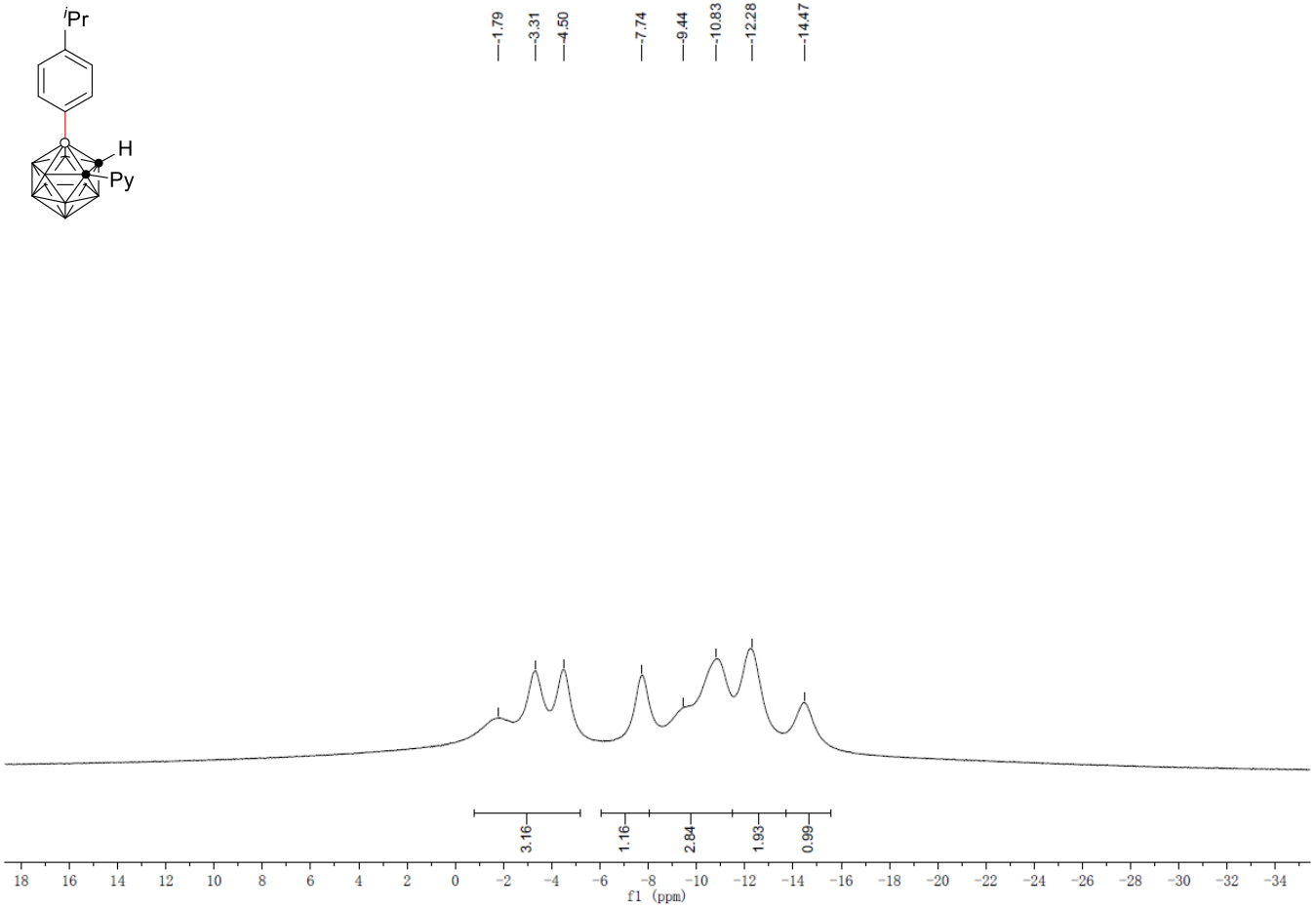
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3r**



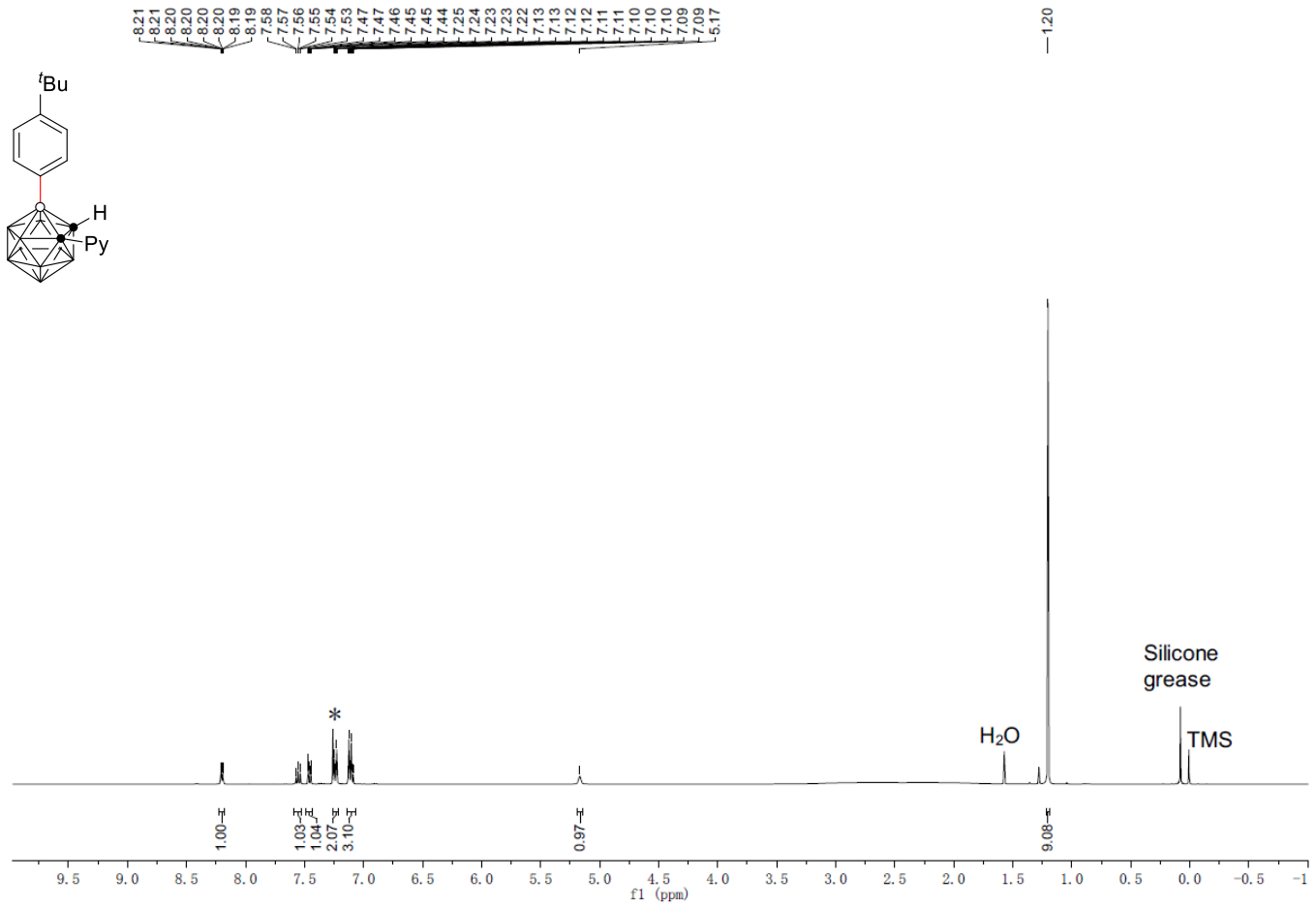
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3r**



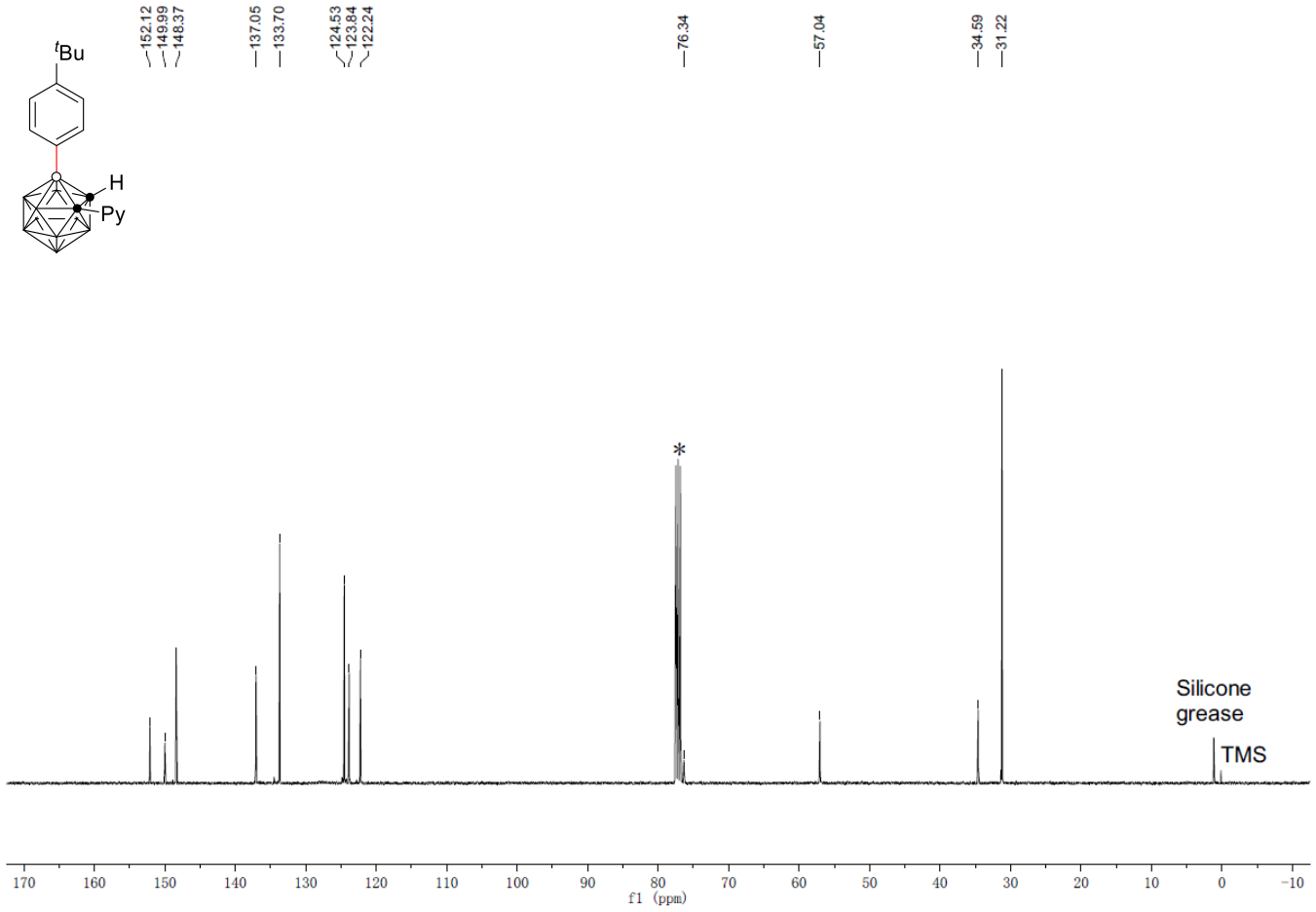
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3r**



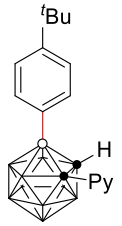
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3s**



^{13}C NMR (101 MHz, $CDCl_3$ *) of **3s**



^{11}B NMR (128 MHz, $CDCl_3$ *) of **3s**



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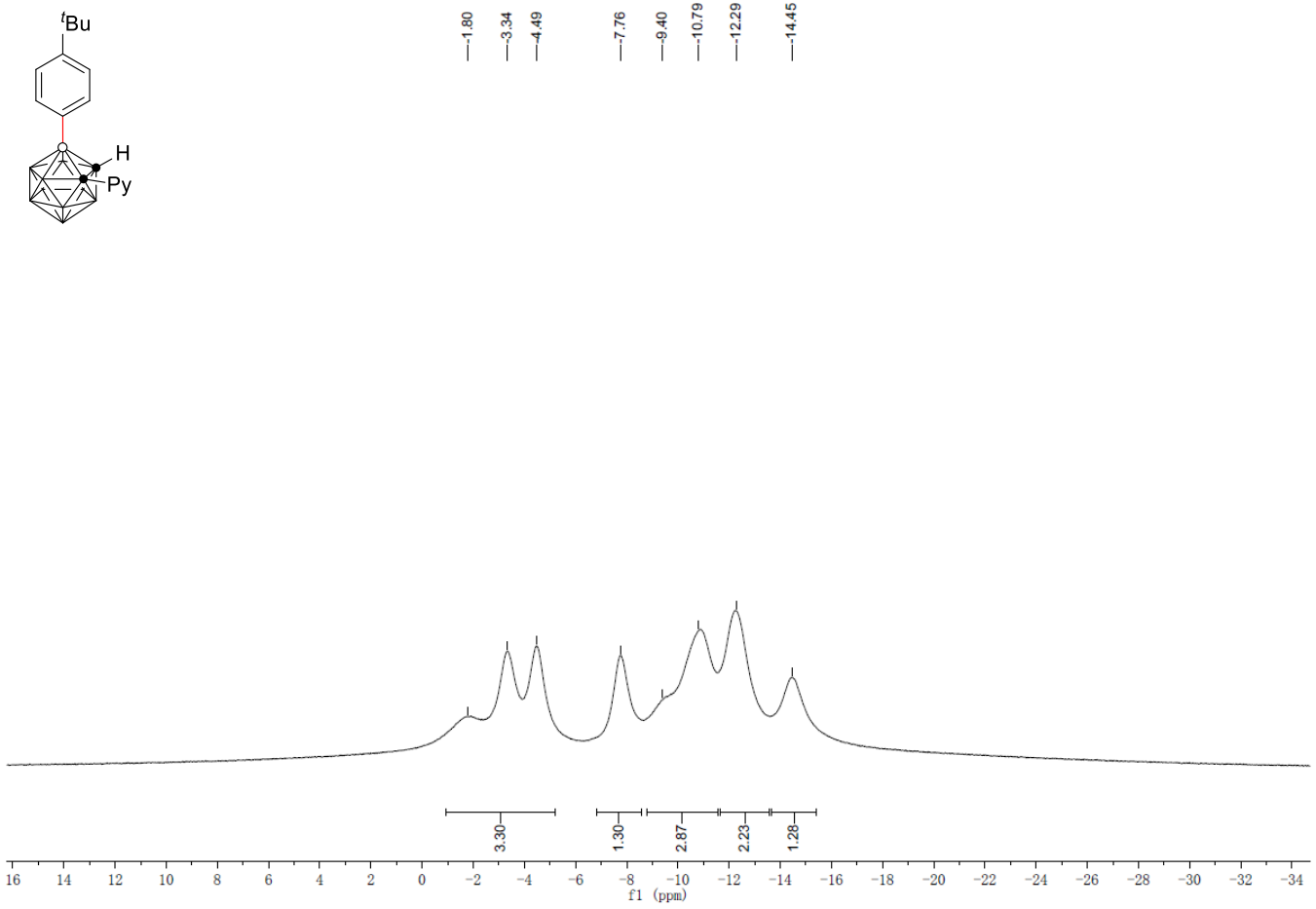
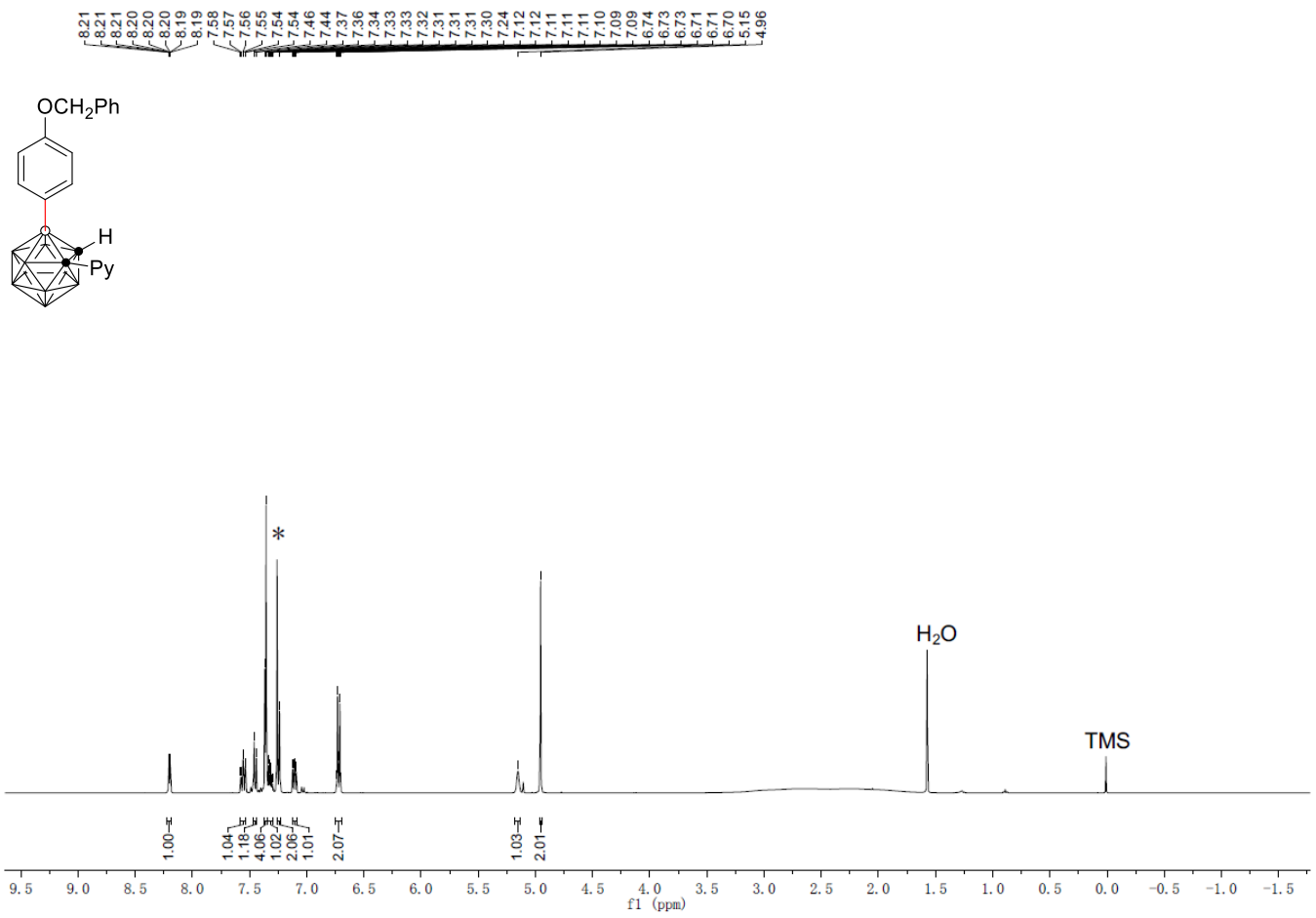
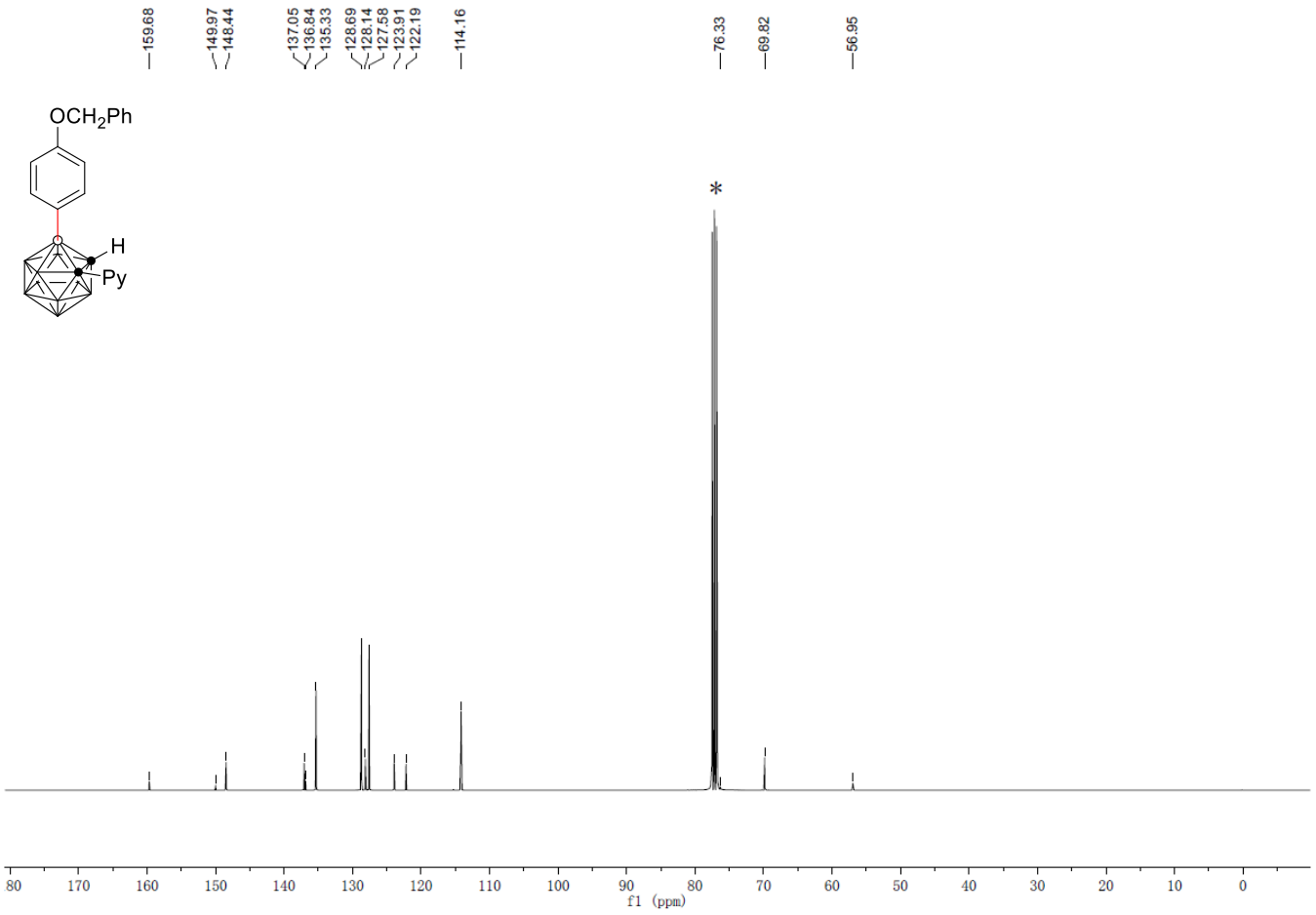


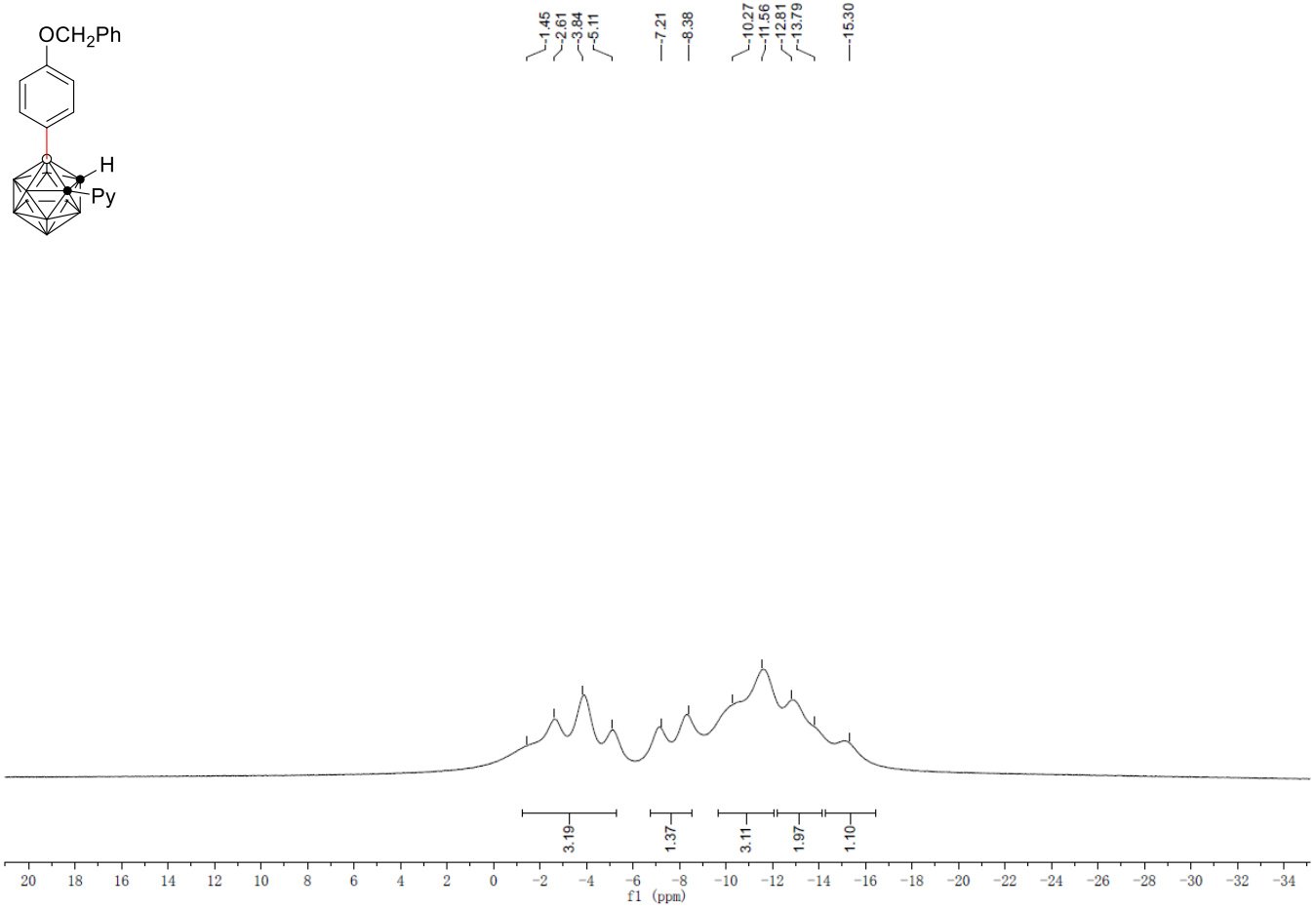
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3t**



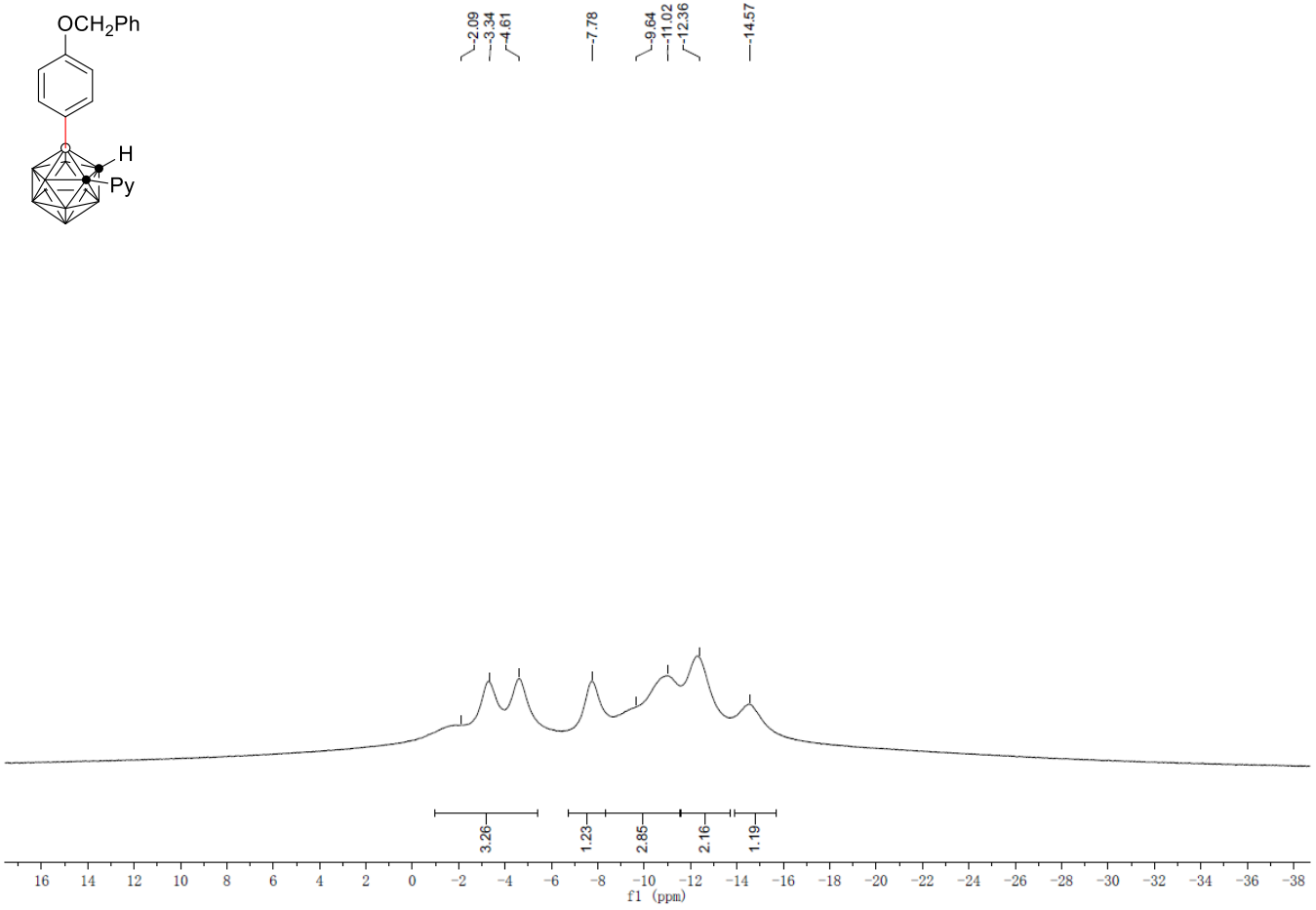
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3t**



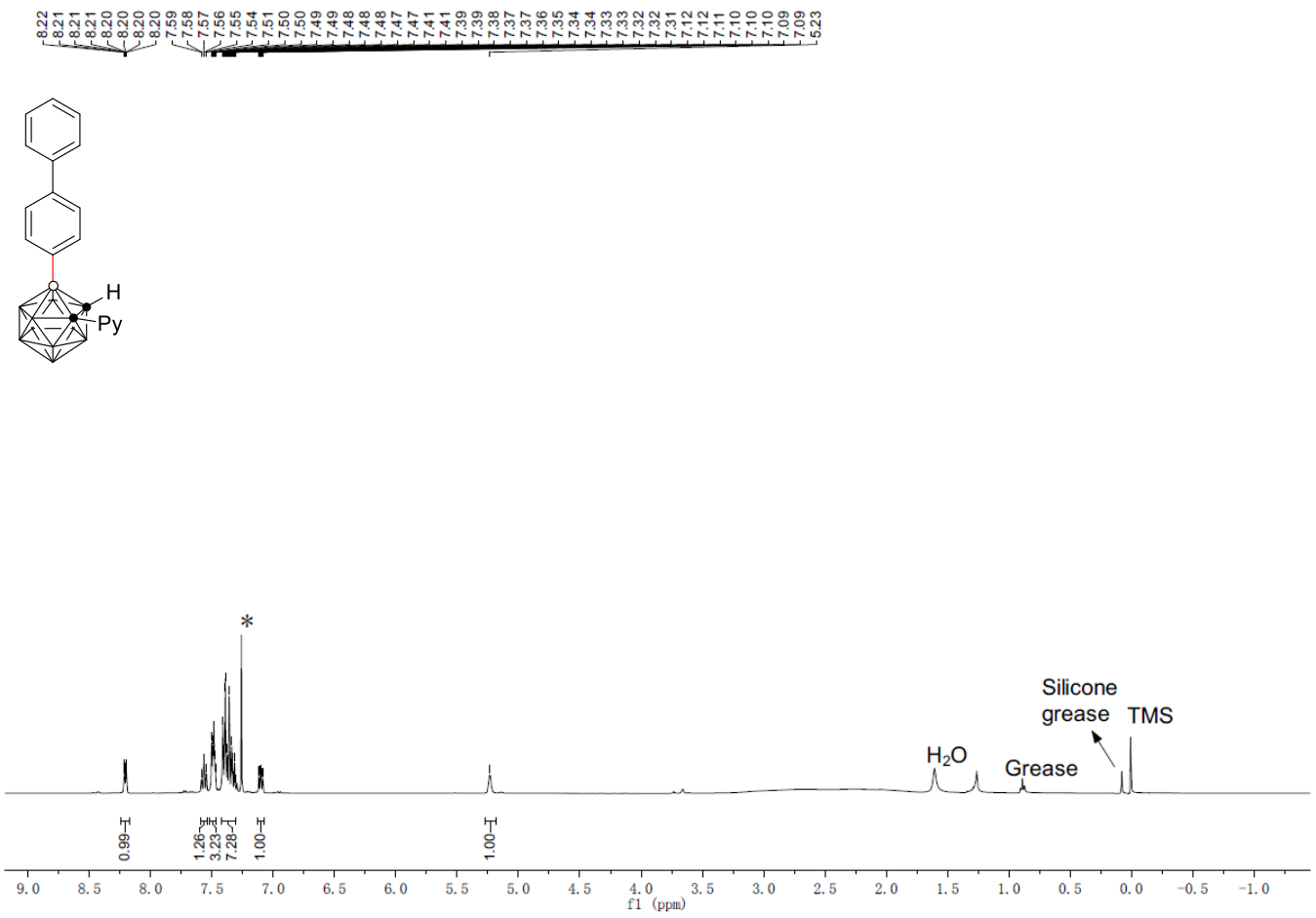
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3t**



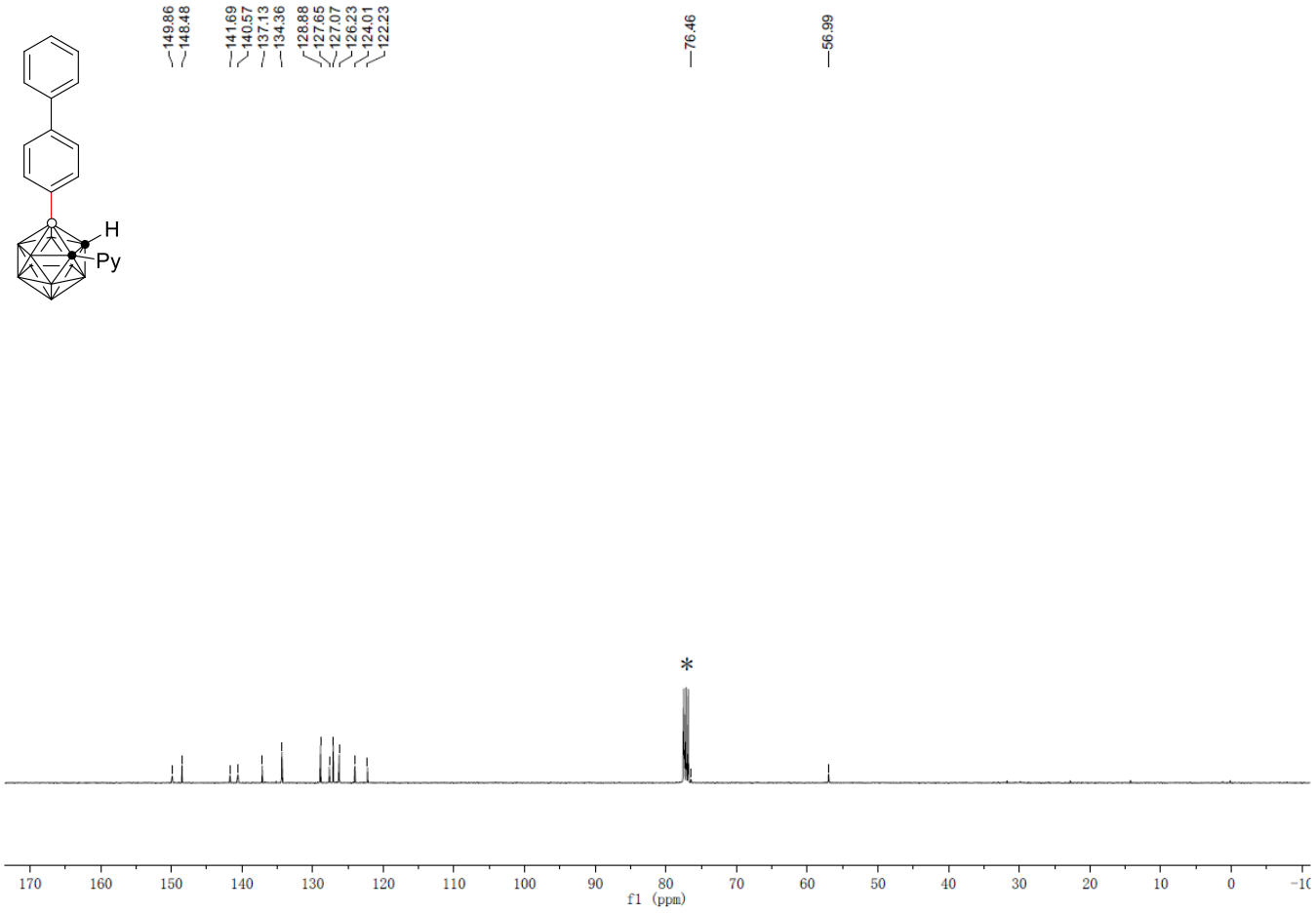
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3t**



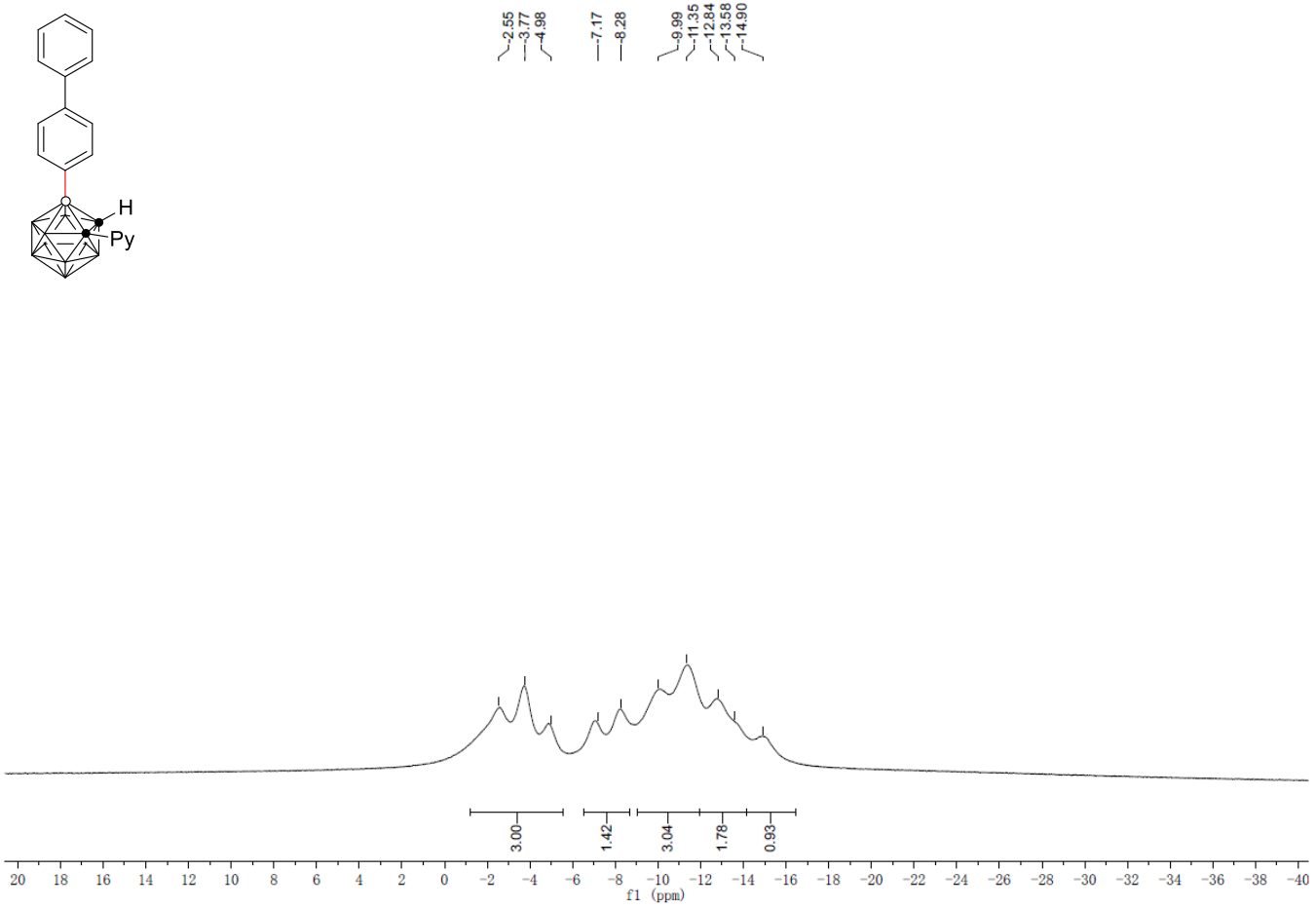
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3u**



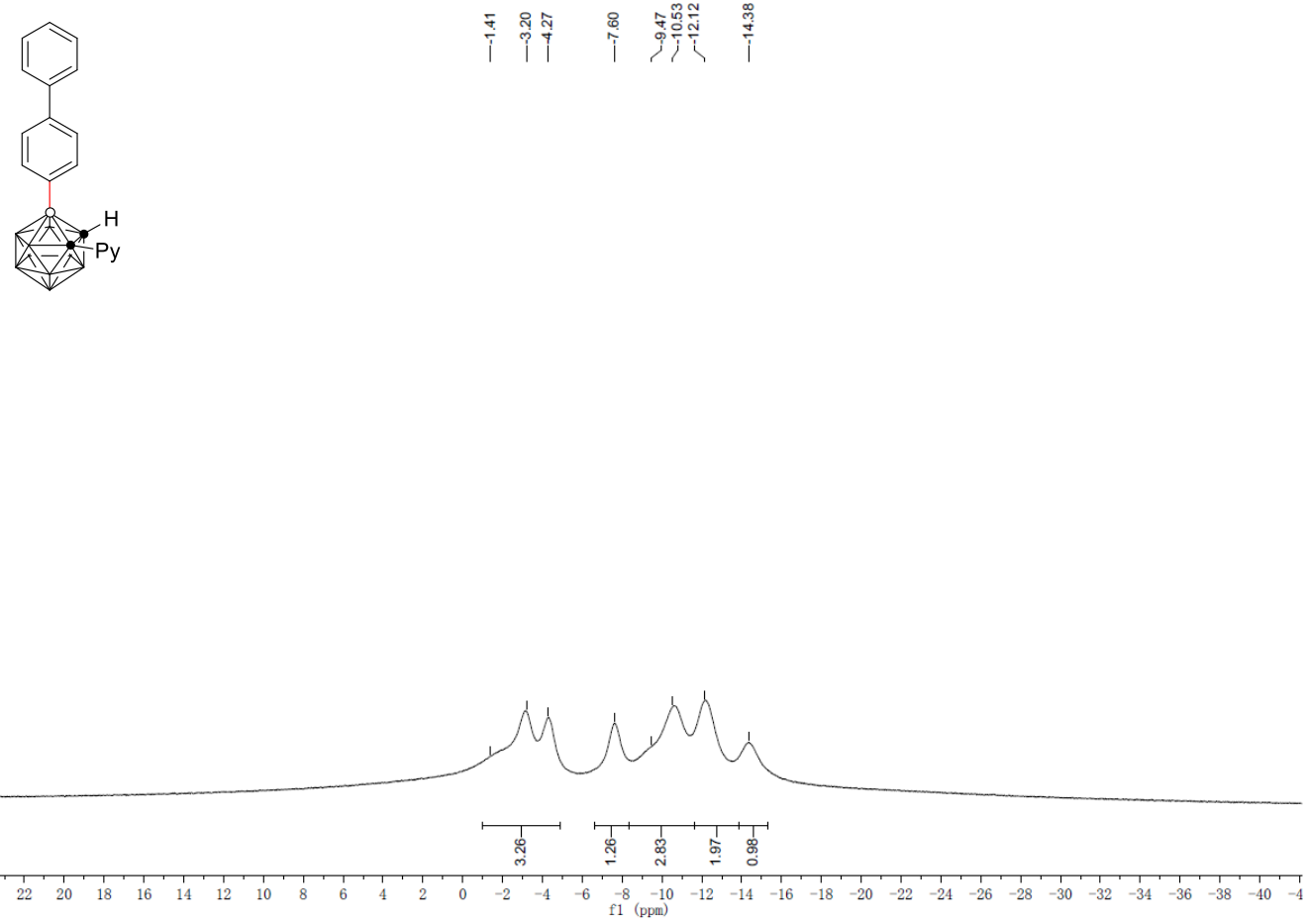
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3u**



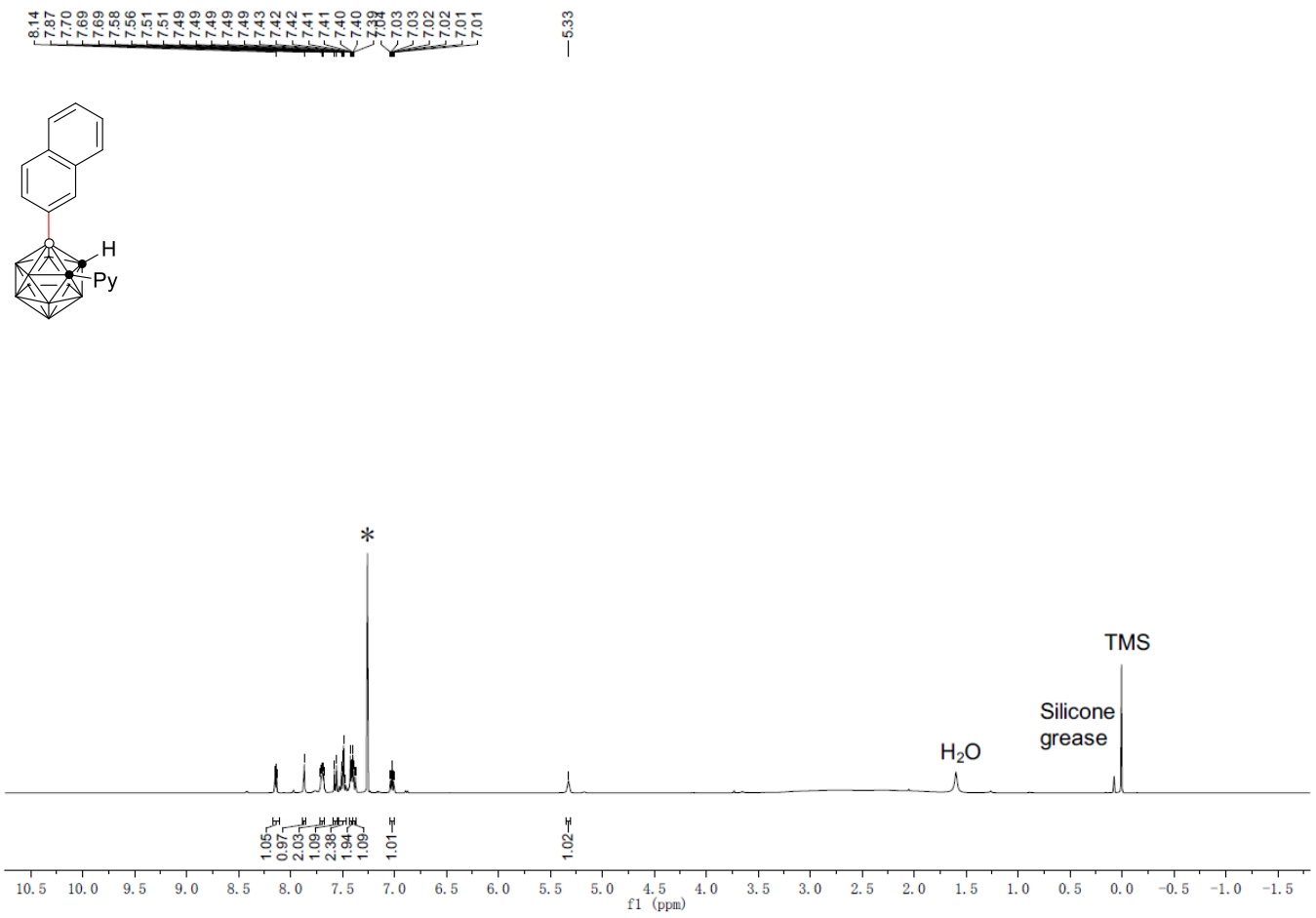
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3u**



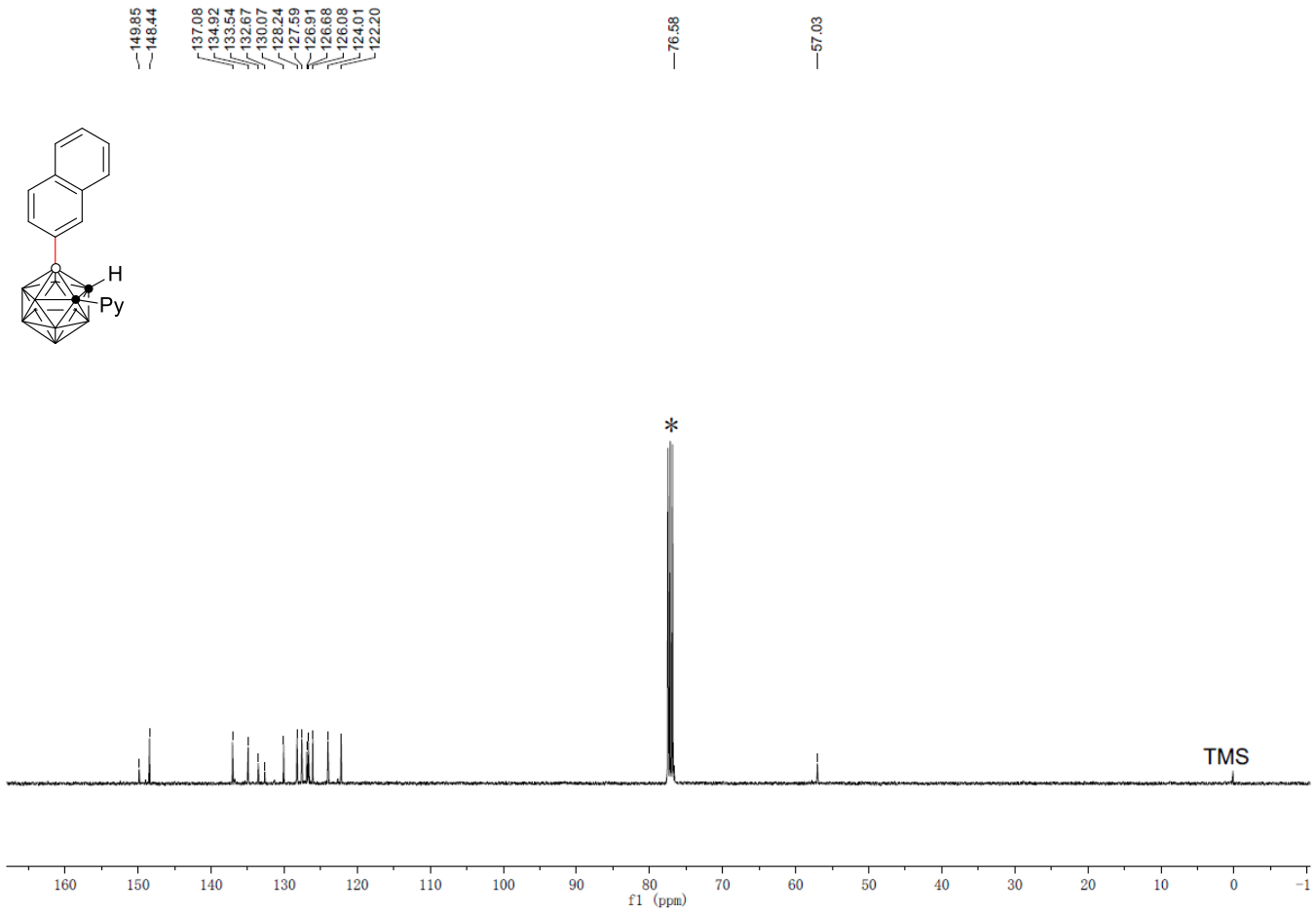
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3u**



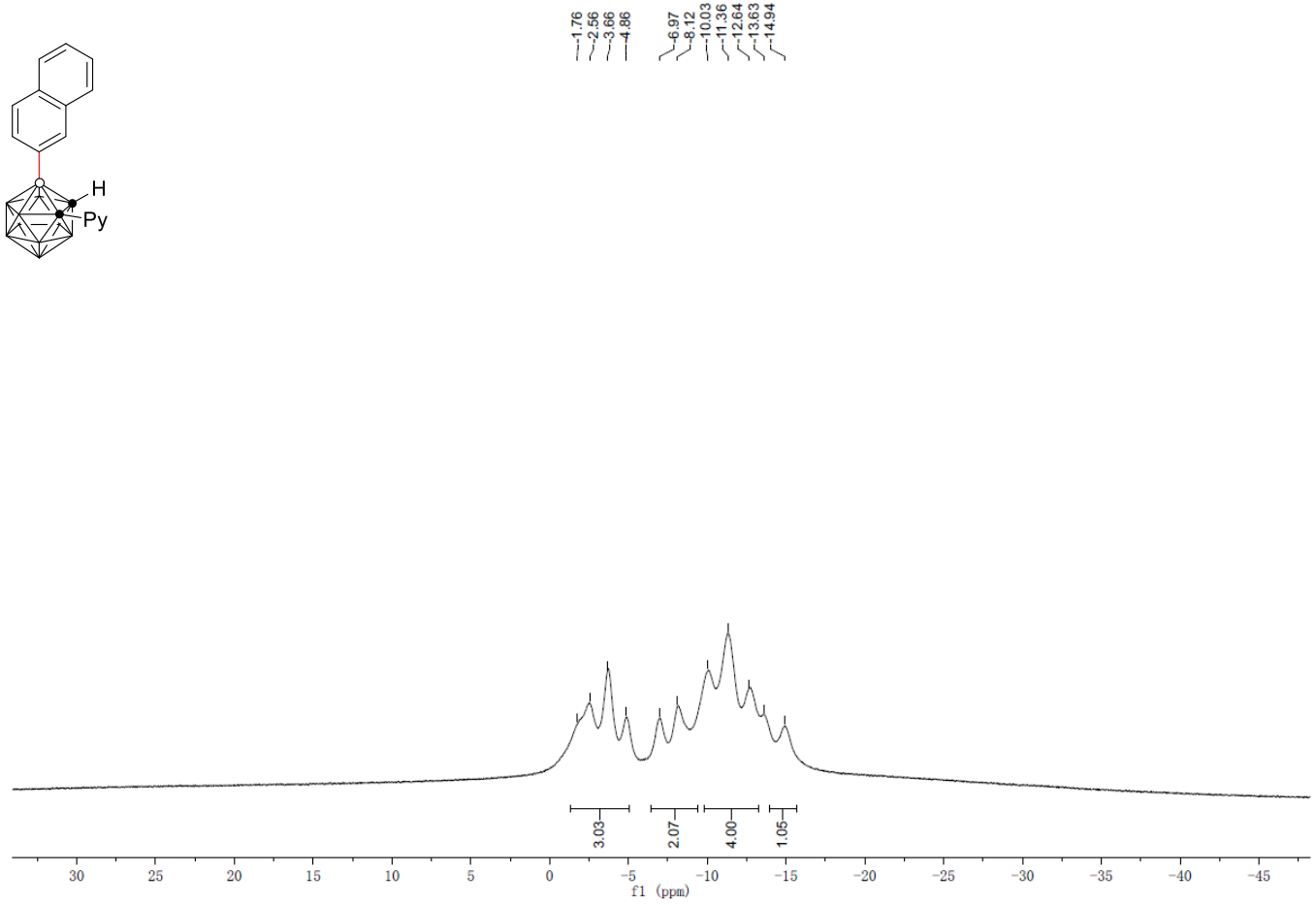
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3v**



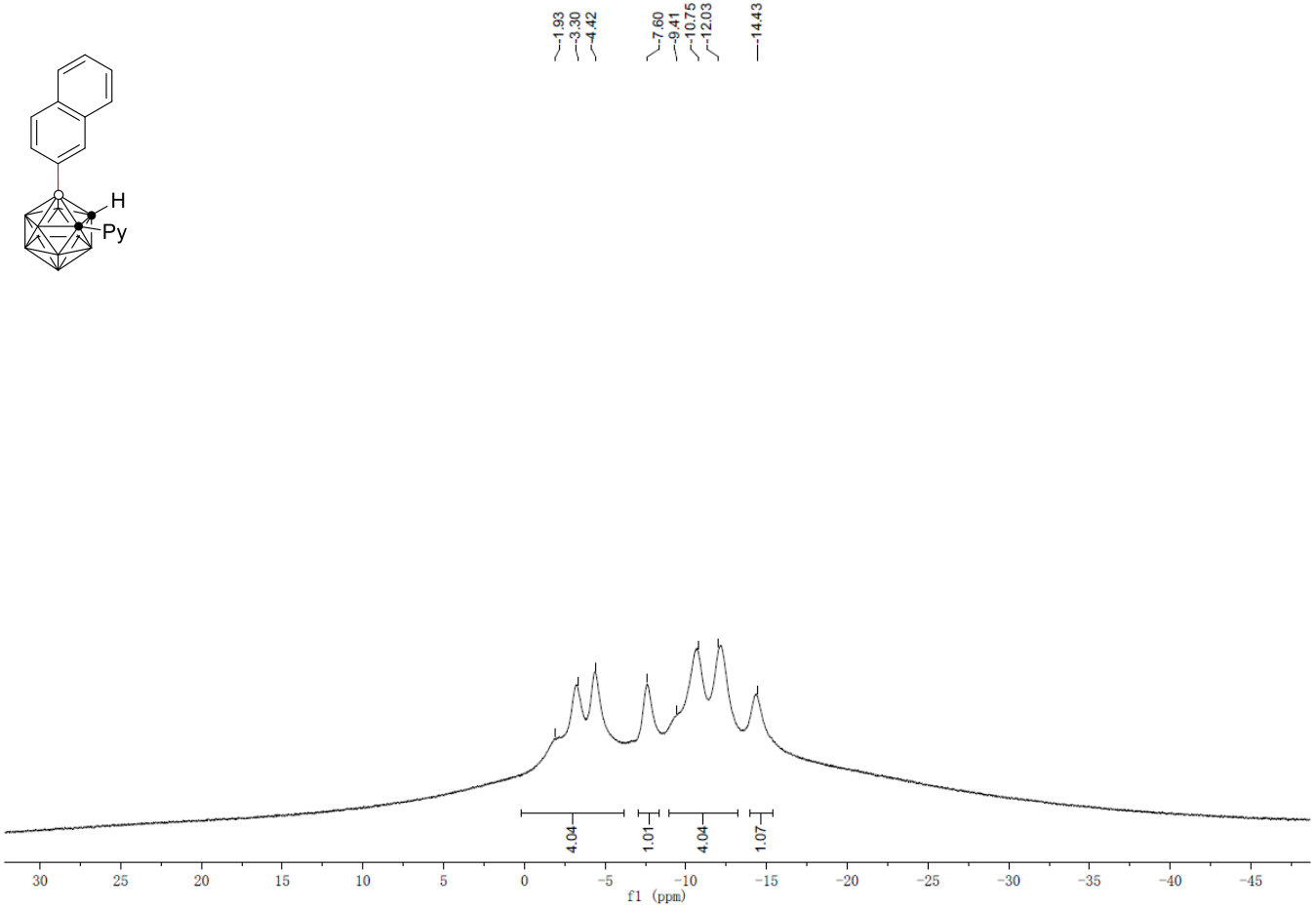
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3v**



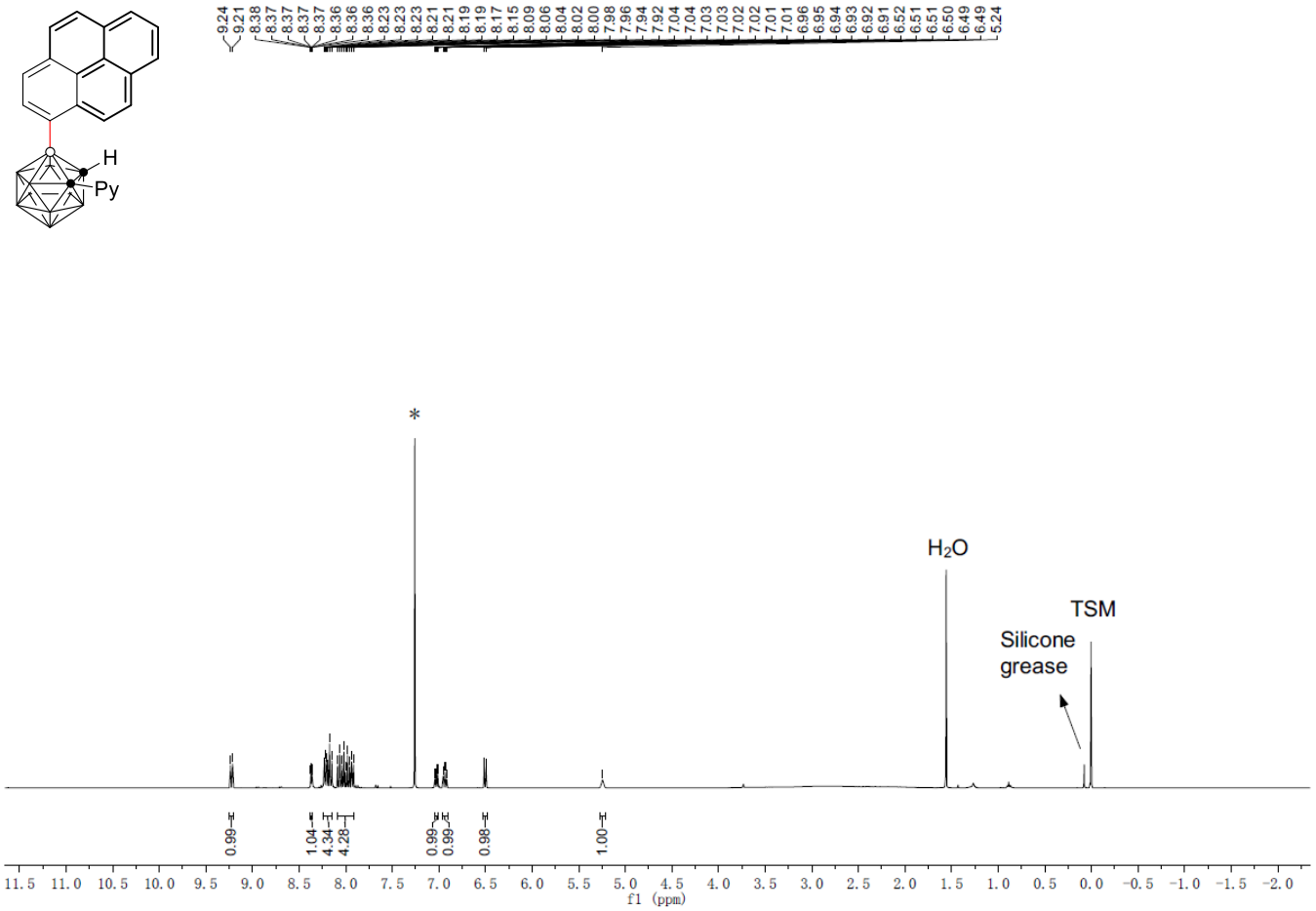
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3v**



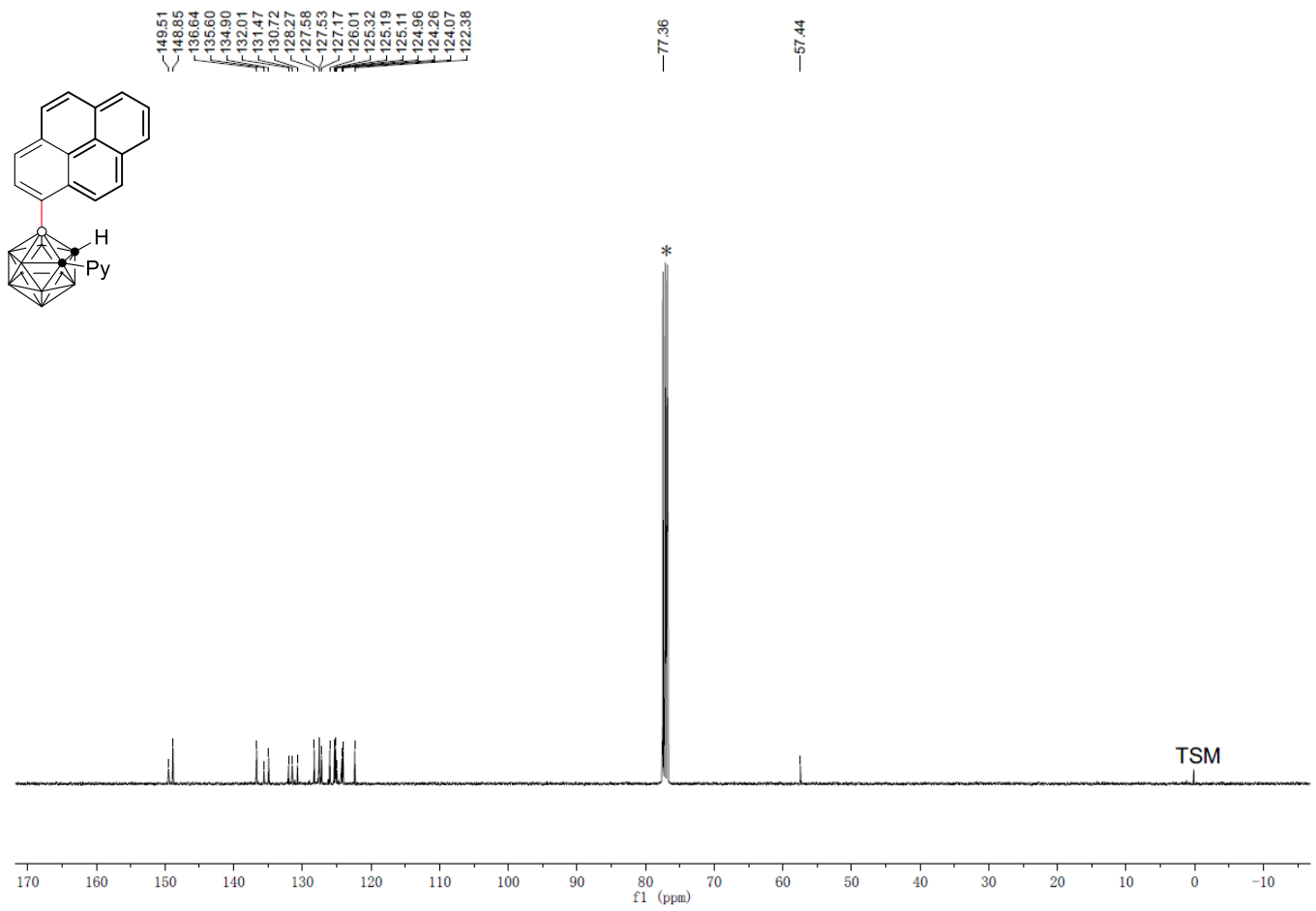
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3v**



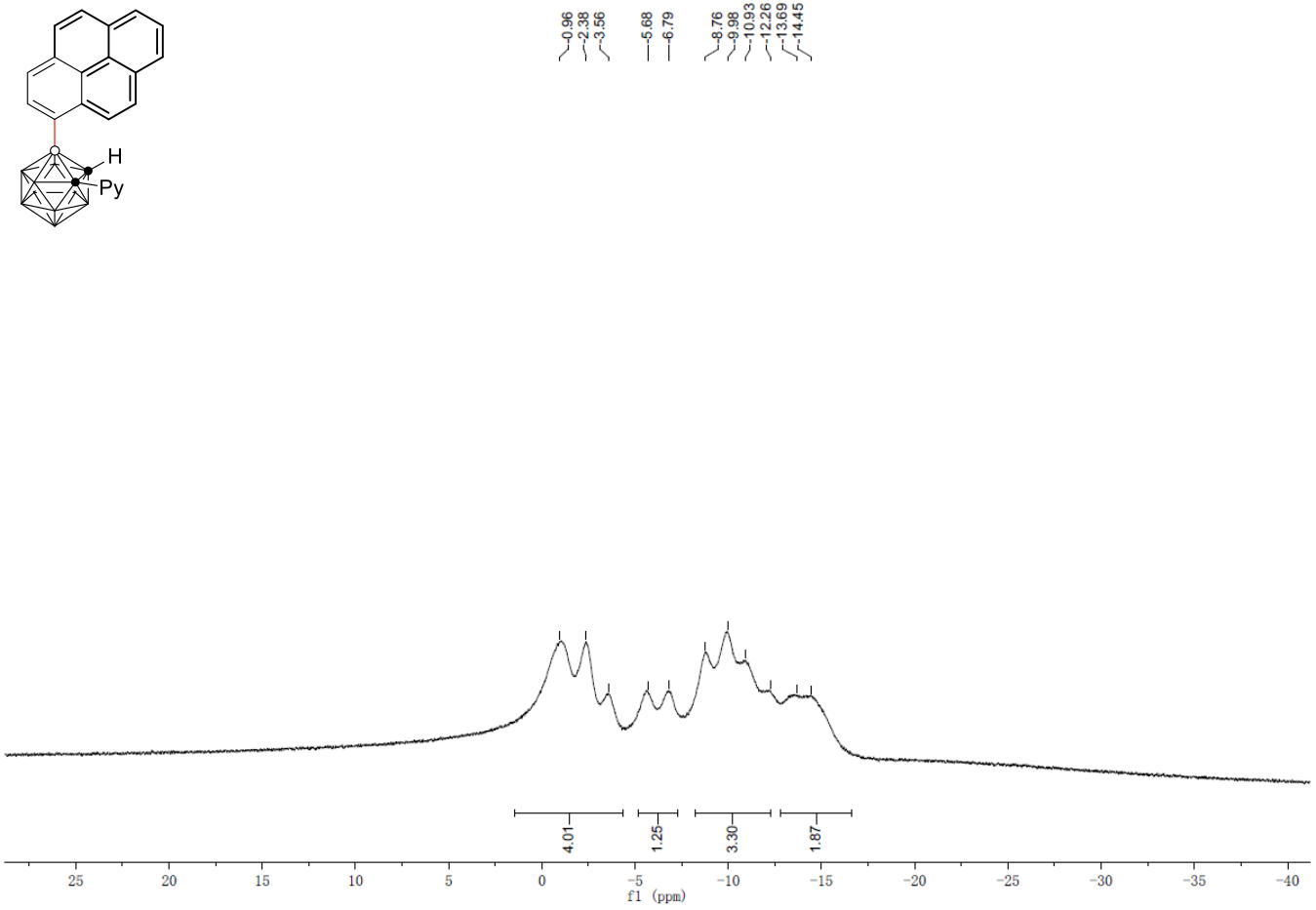
^{1}H NMR (400 MHz, $CDCl_3$ *) of **3w**



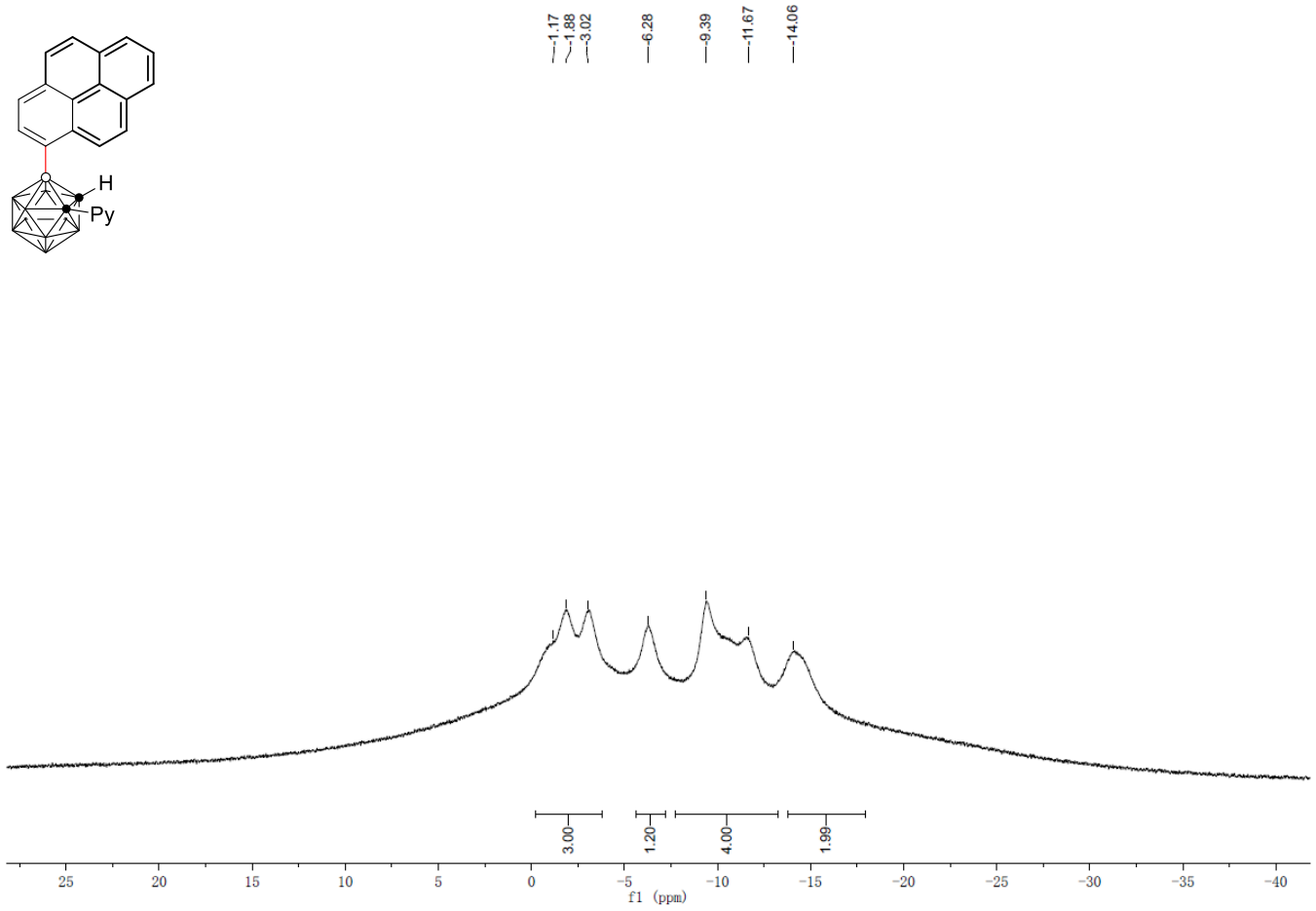
^{13}C NMR (101 MHz, $CDCl_3$ *) of **3w**



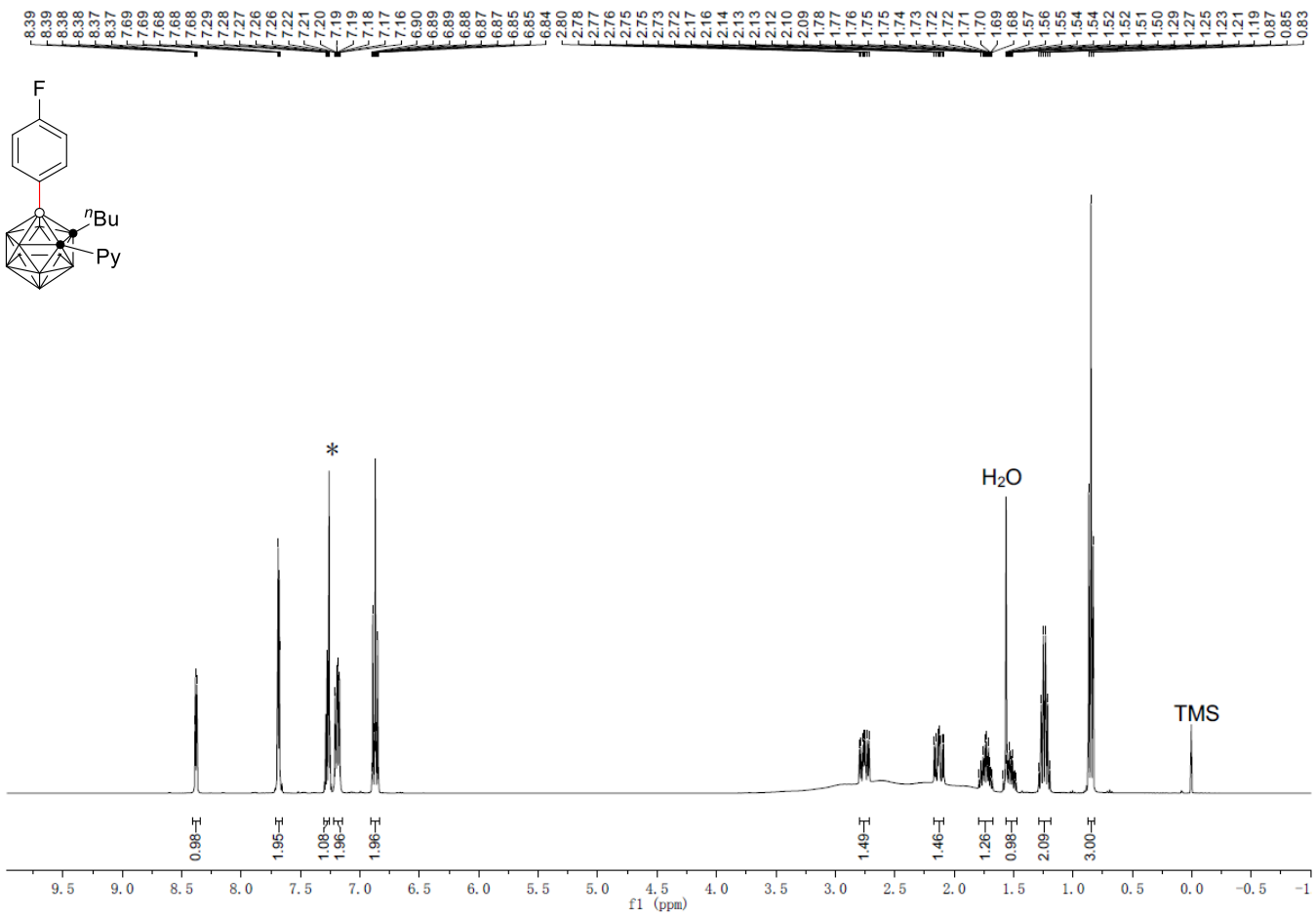
^{11}B NMR (128 MHz, $CDCl_3$ *) of **3w**



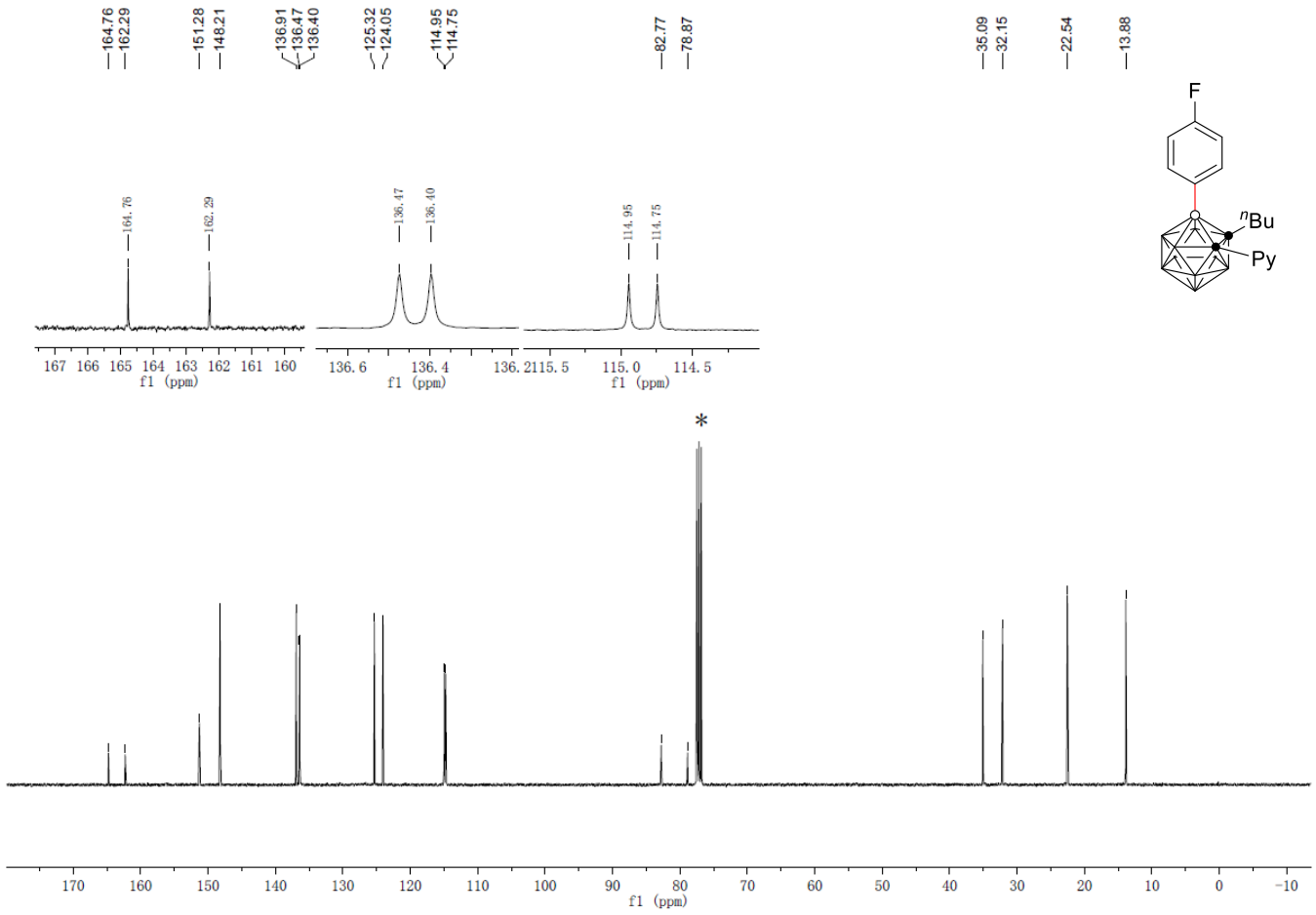
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **3w**



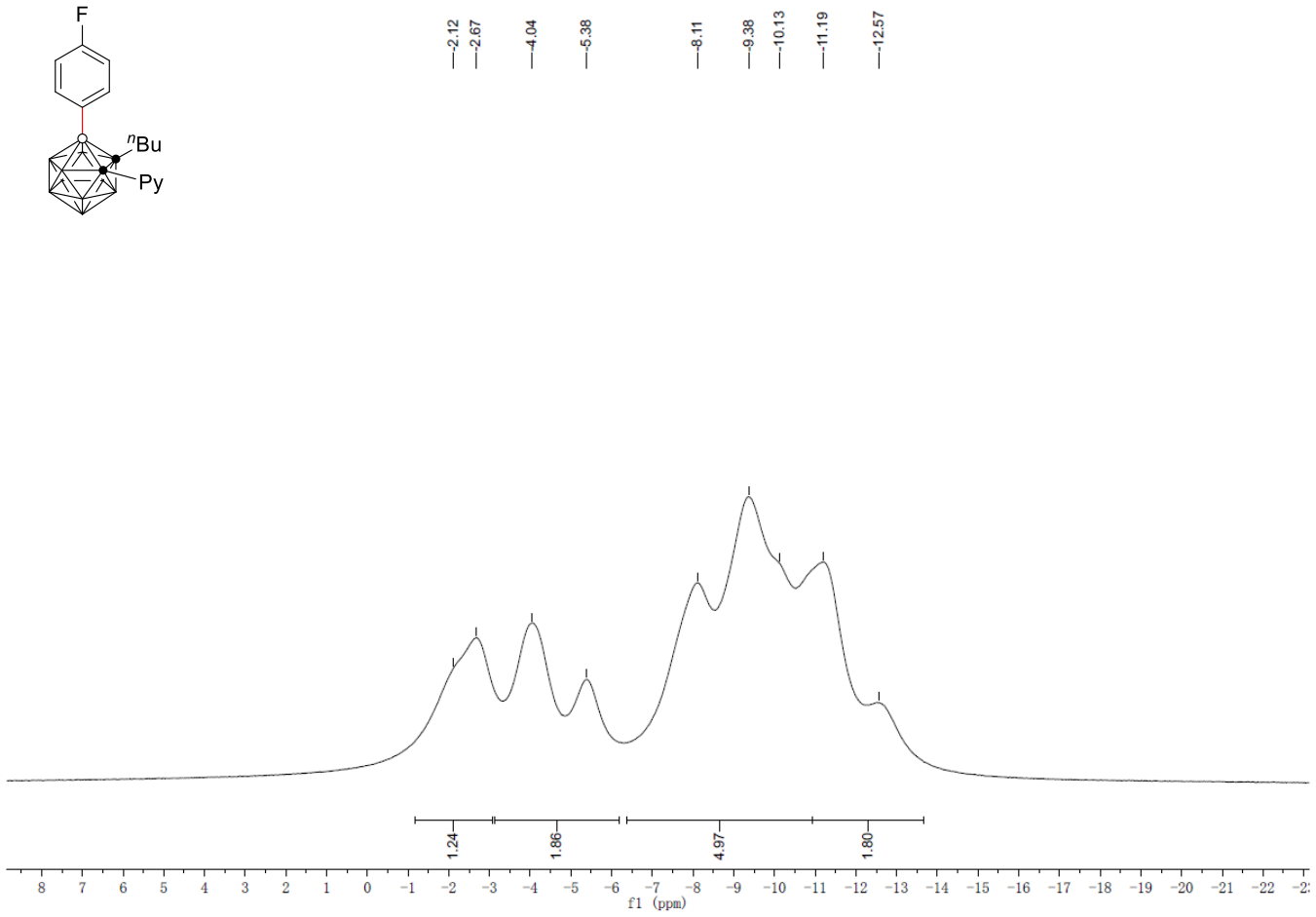
^{1}H NMR (400 MHz, $CDCl_3$ *) of **4a**



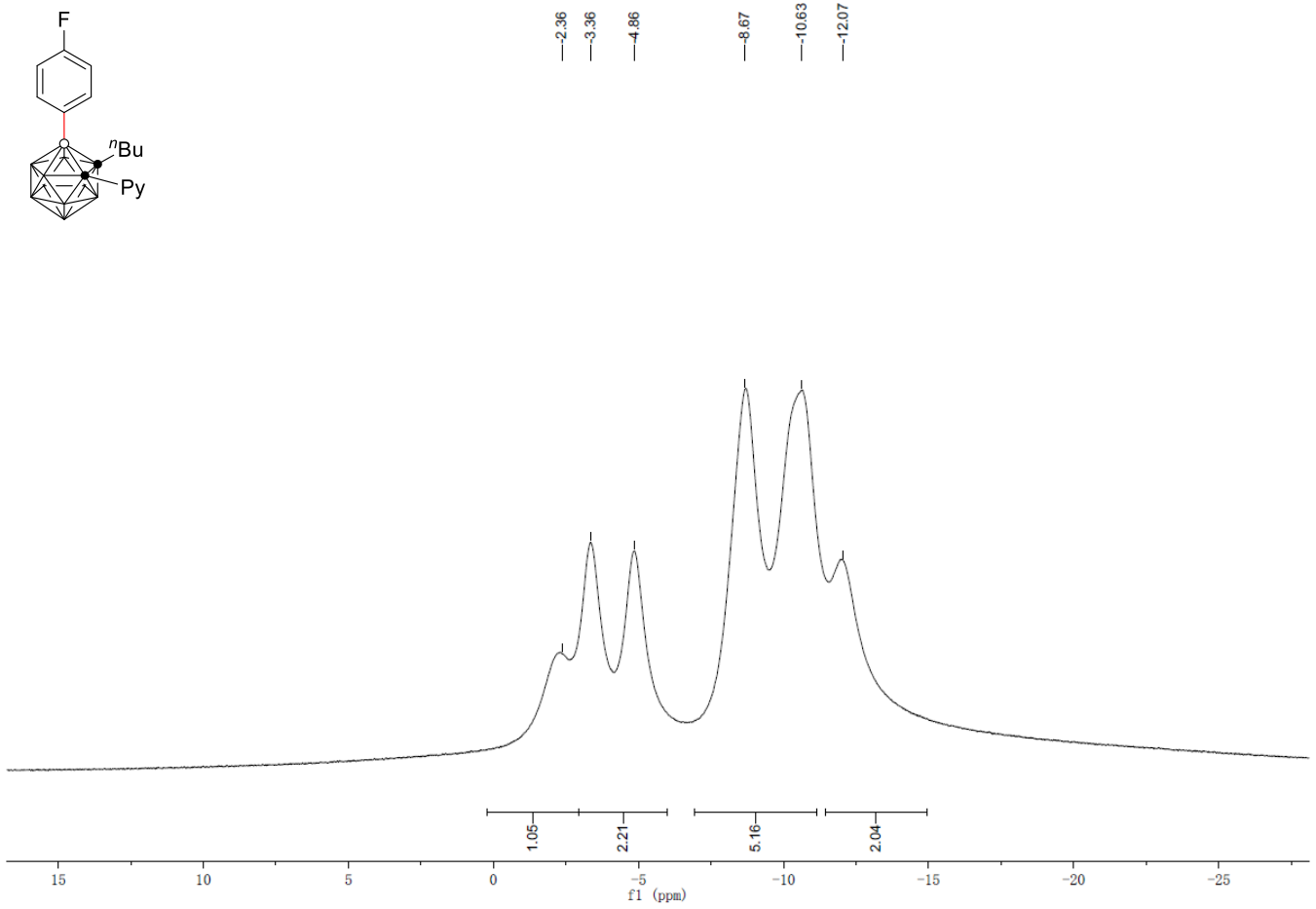
^{13}C NMR (101 MHz, $CDCl_3$ *) of **4a**



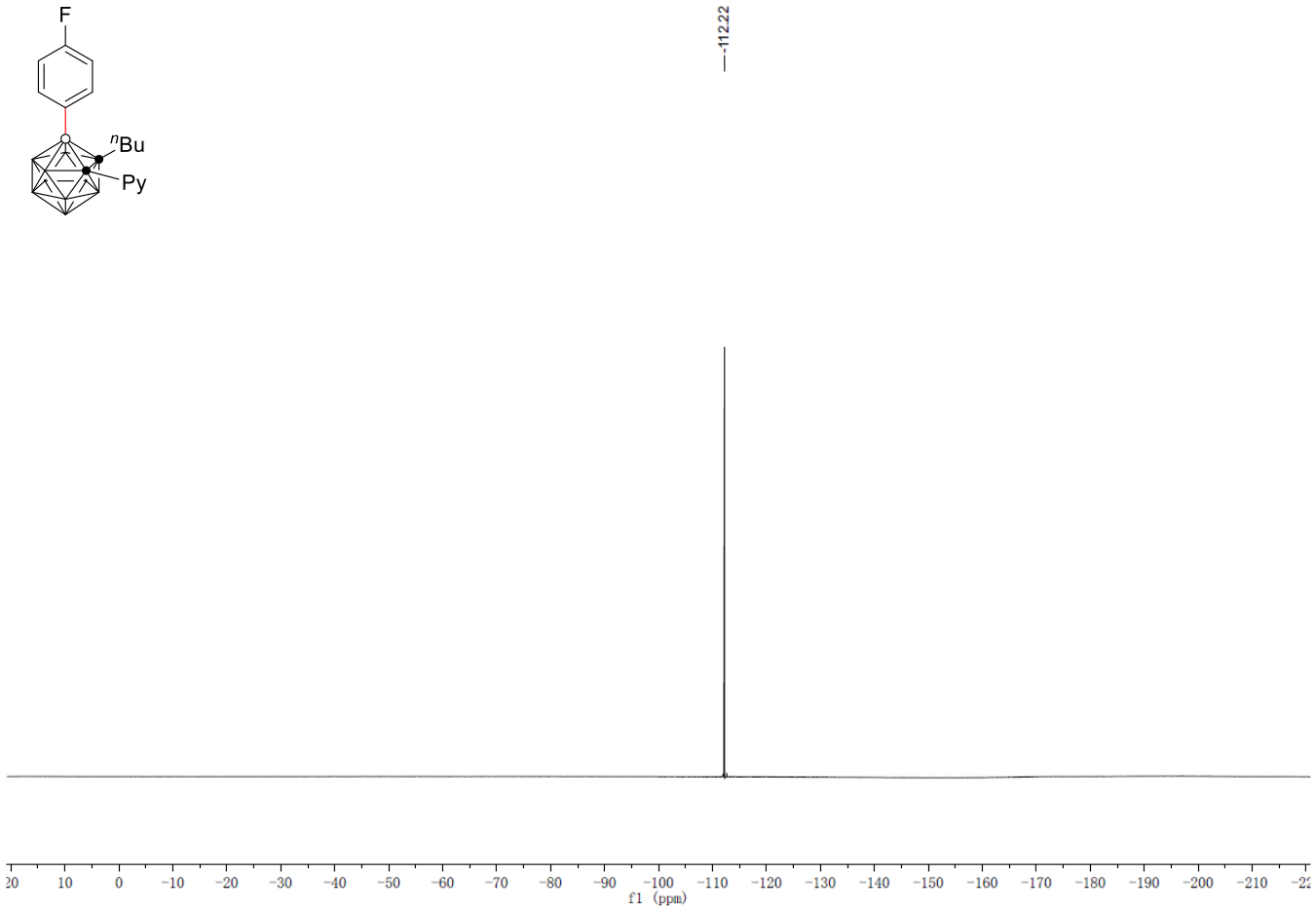
^{11}B NMR (128 MHz, $CDCl_3$ *) of **4a**



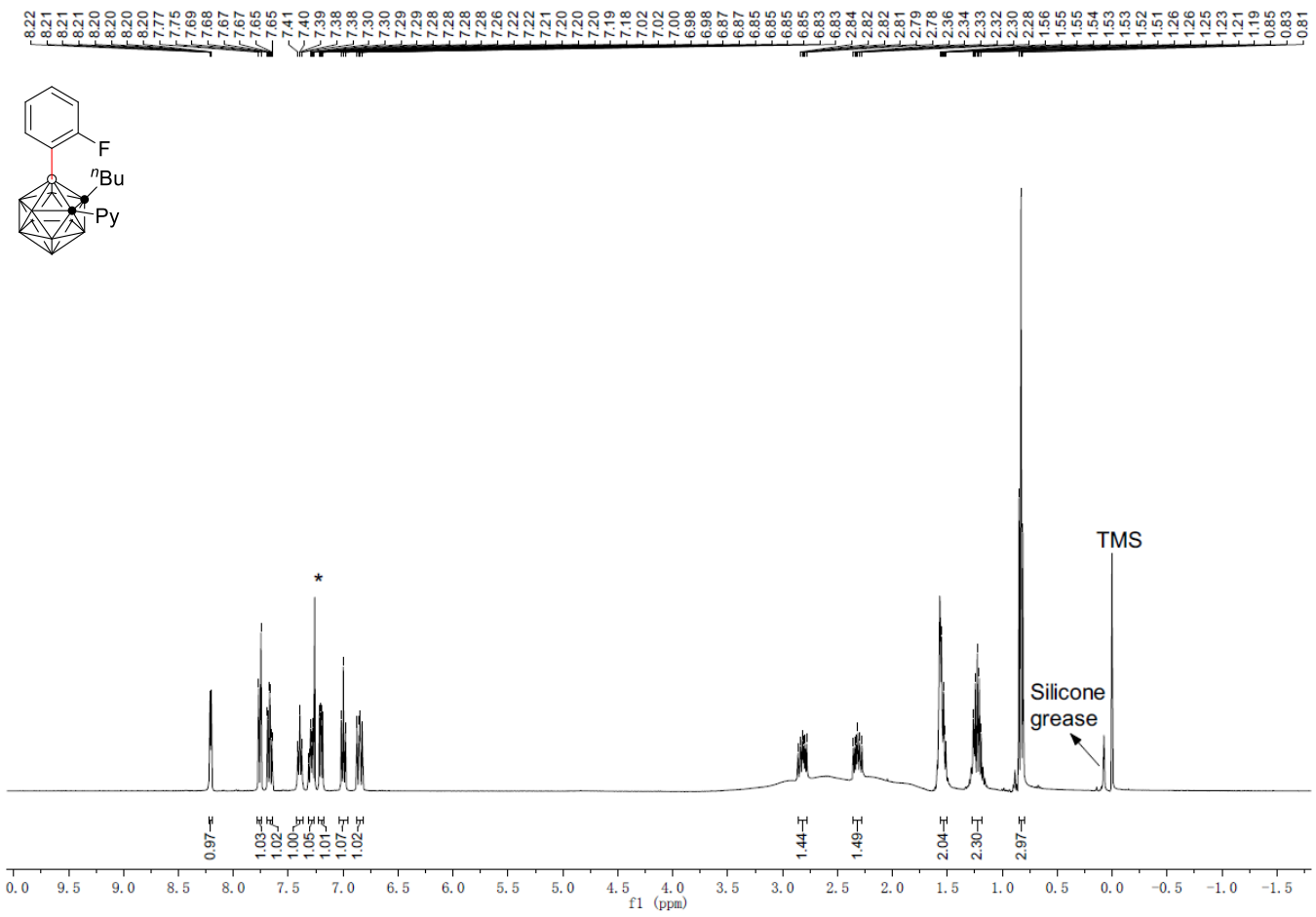
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **4a**



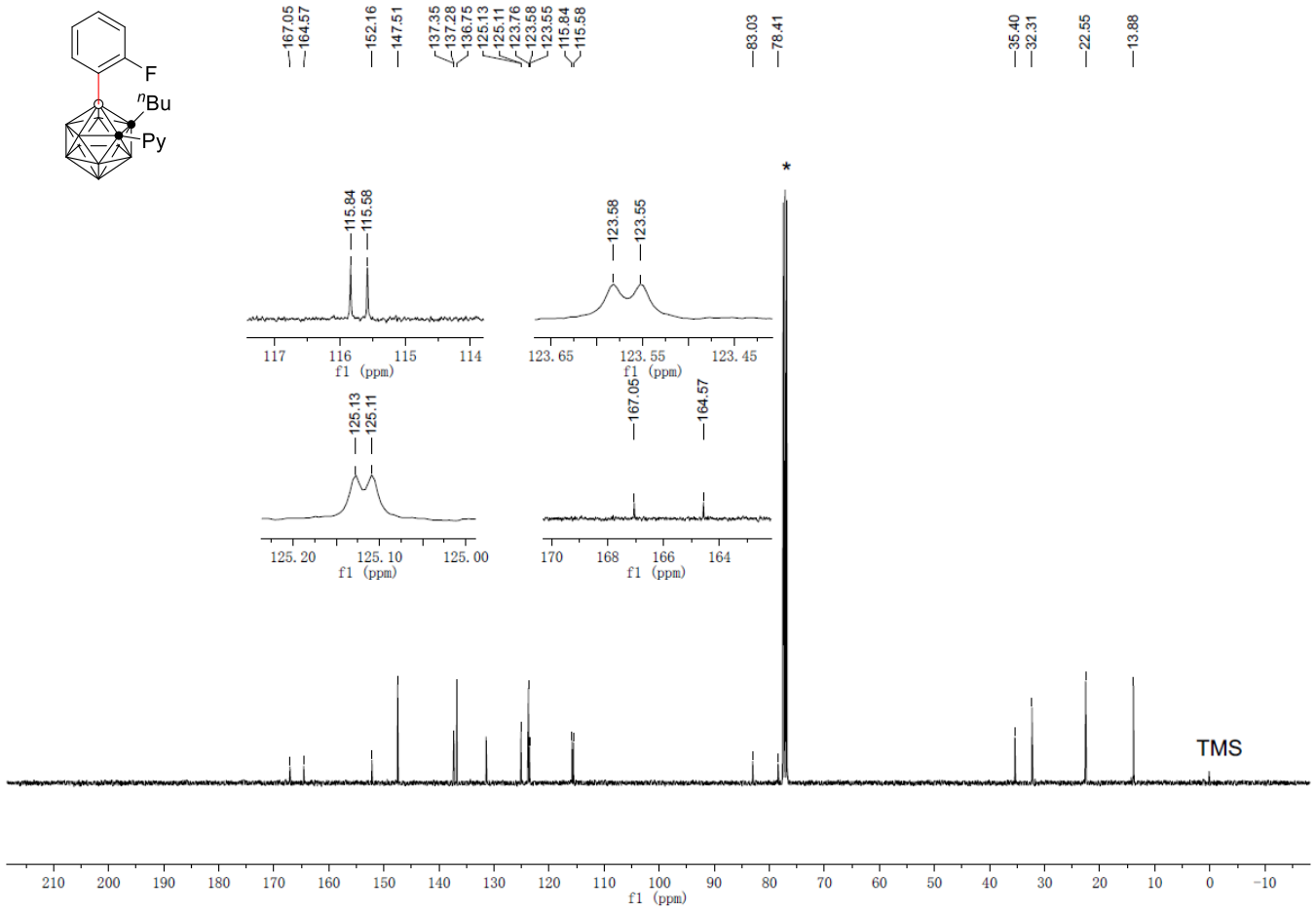
^{19}F NMR (376 MHz, $CDCl_3$ *) of **4a**



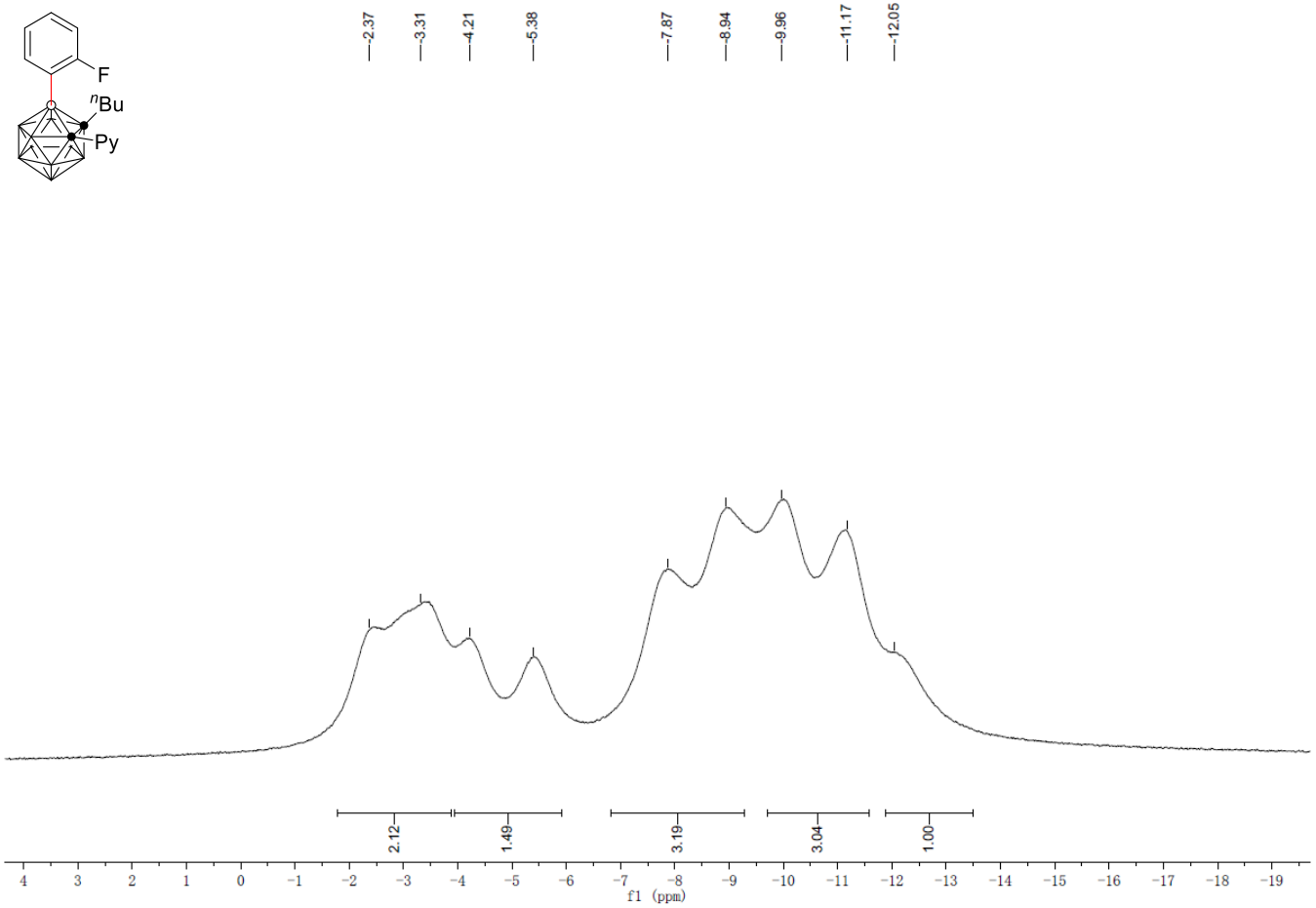
^{1}H NMR (400 MHz, $CDCl_3$ *) of **4b**



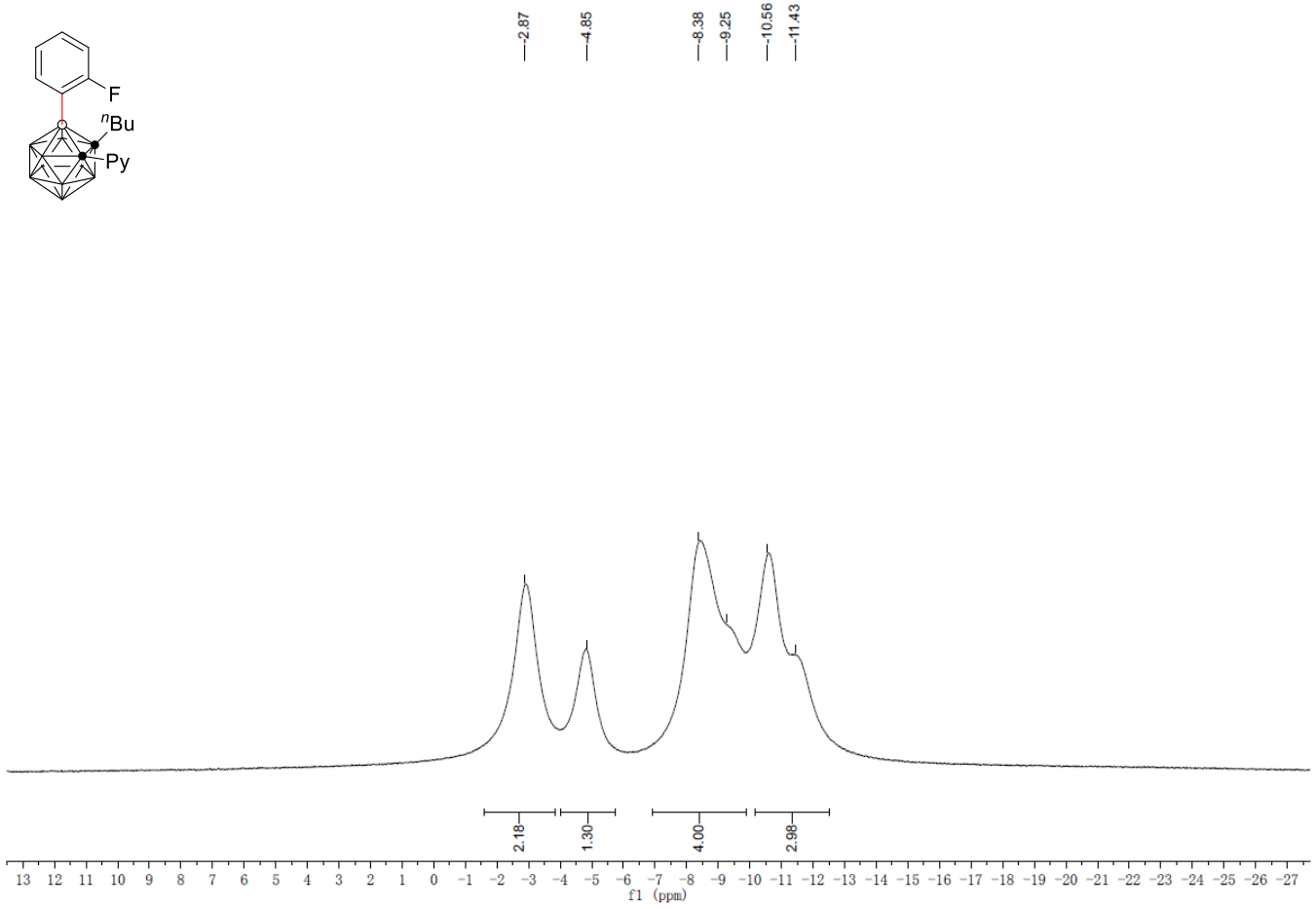
^{13}C NMR (101 MHz, $CDCl_3$ *) of **4b**



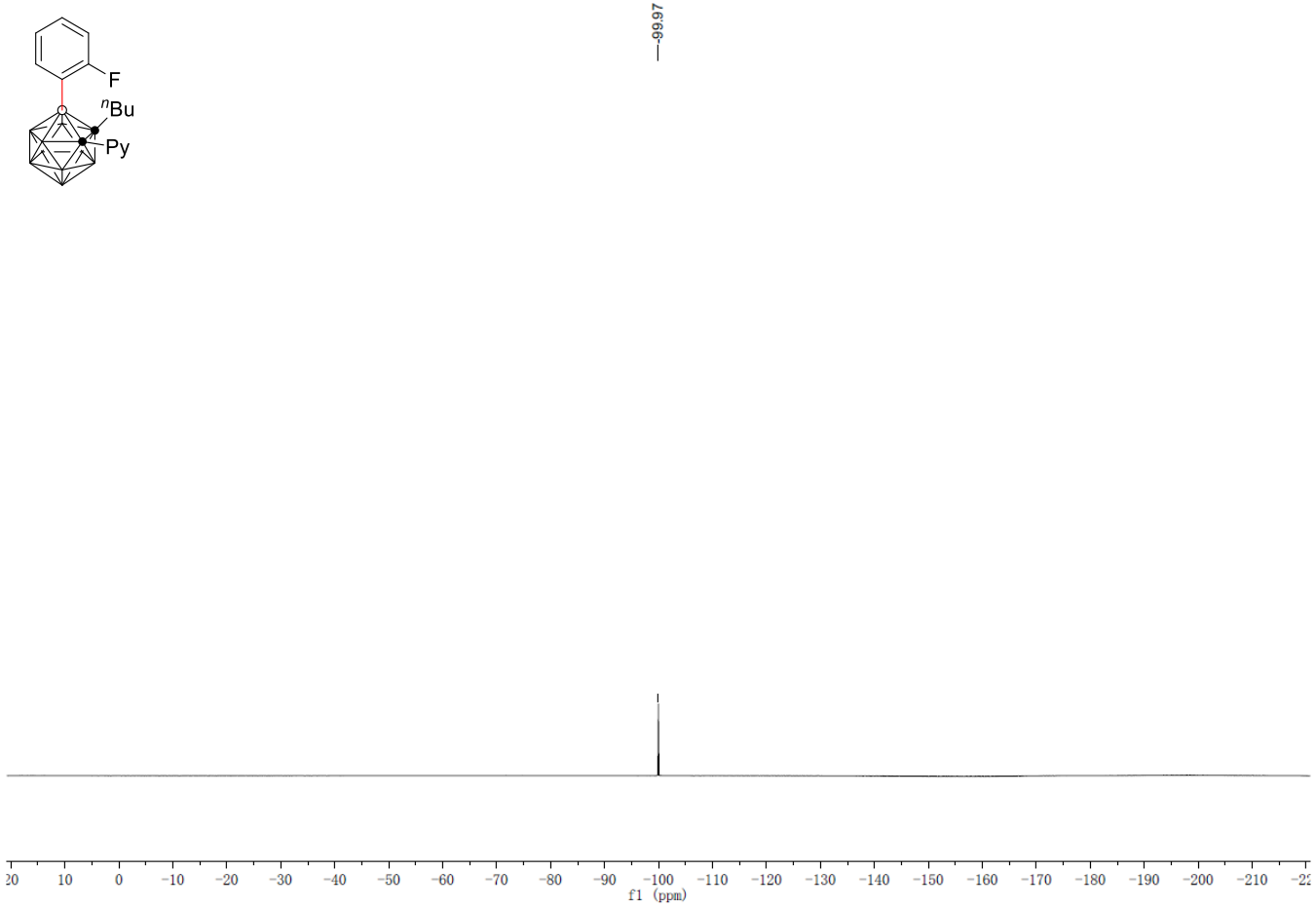
^{11}B NMR (128 MHz, $CDCl_3$ *) of **4b**



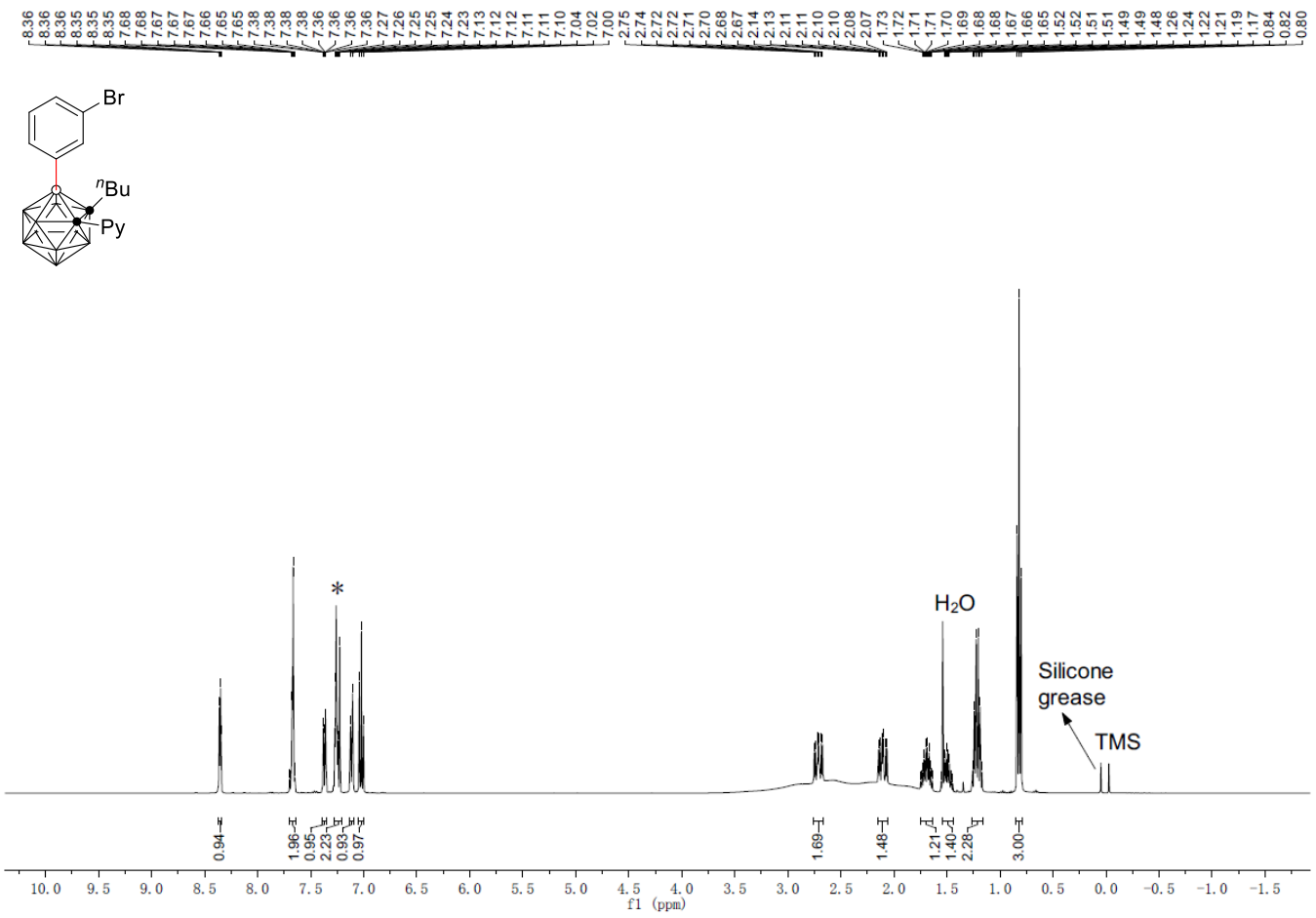
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **4b**



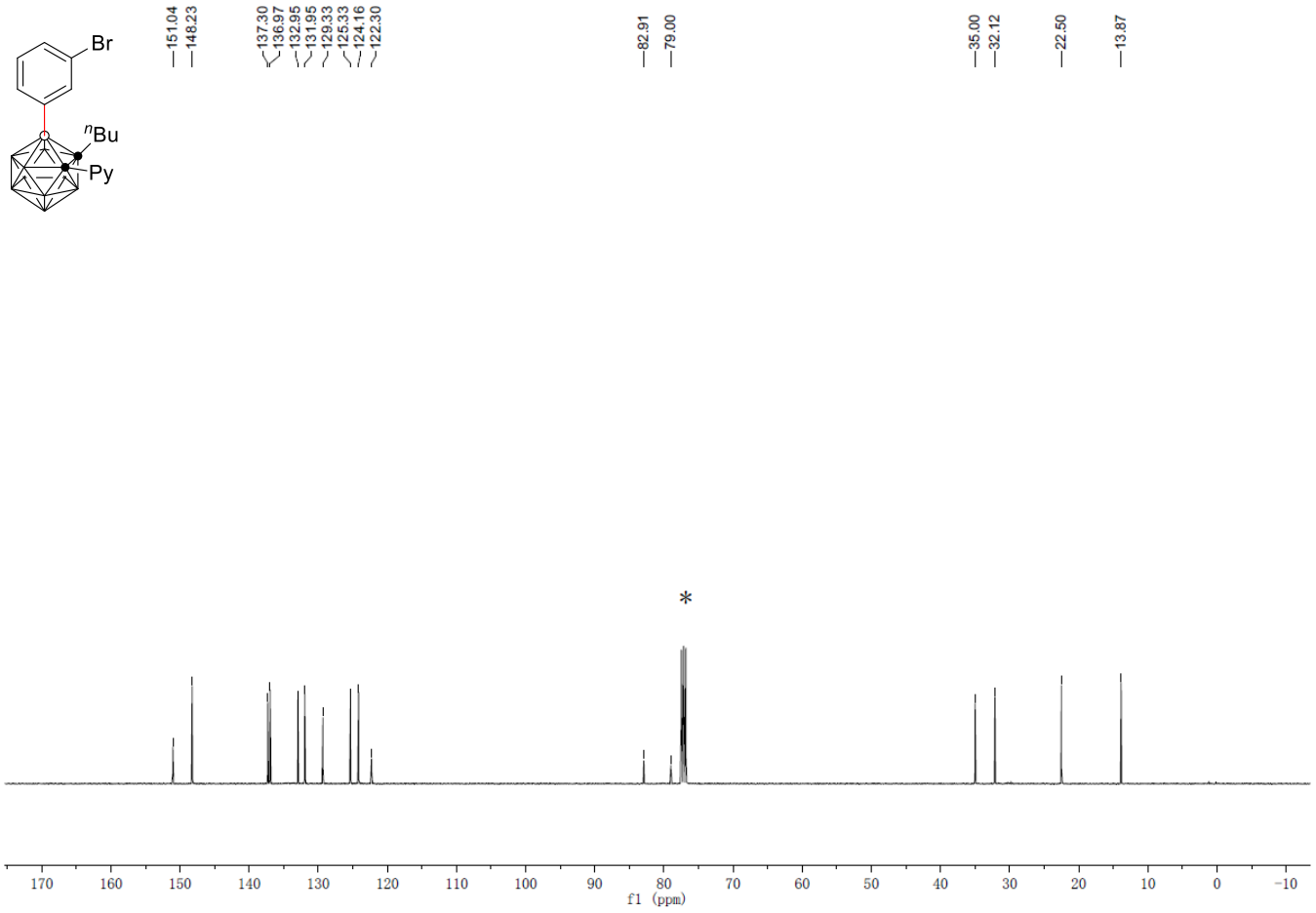
^{19}F NMR (376 MHz, $CDCl_3$*) of **4b**



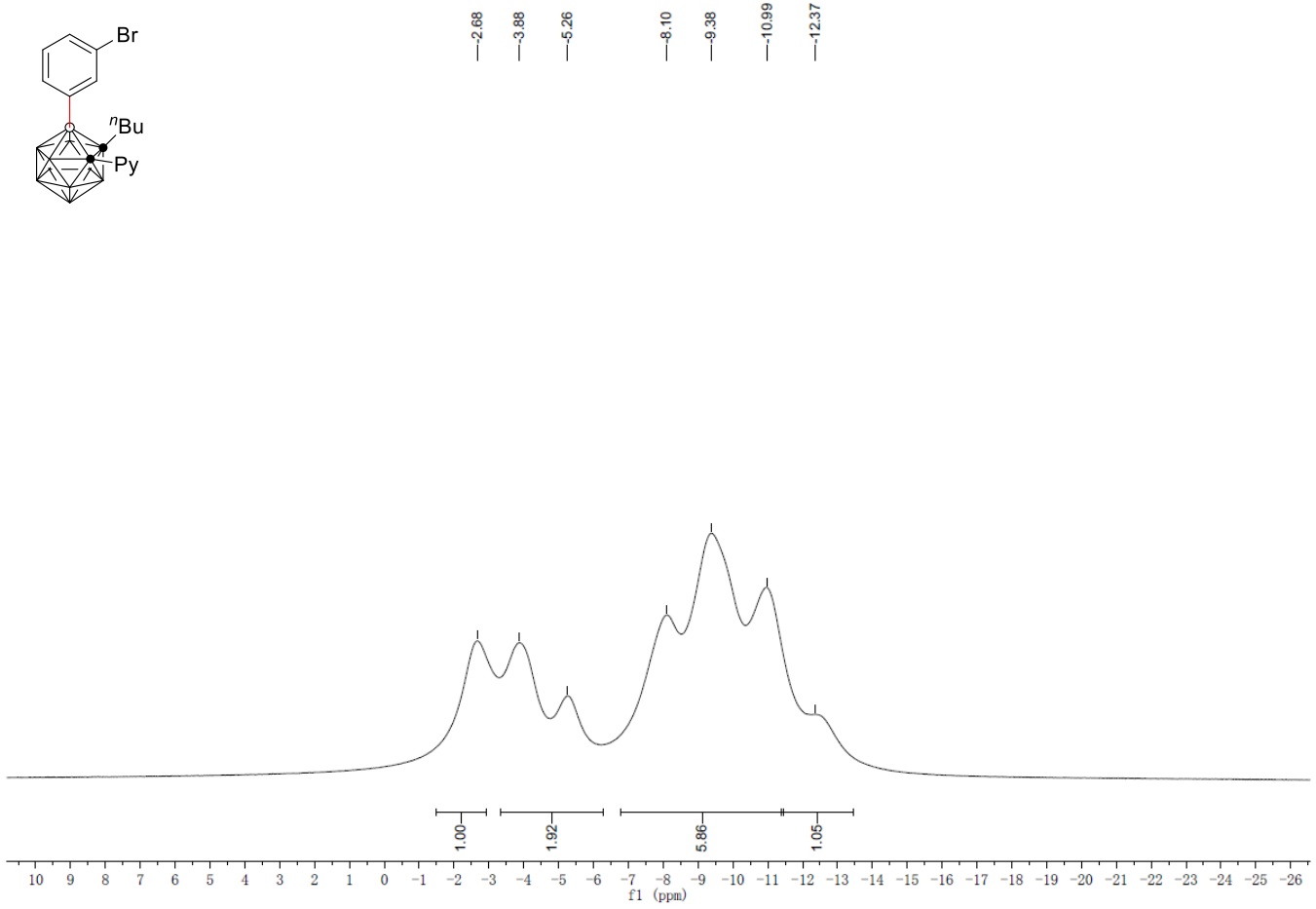
^{1}H NMR (400 MHz, $CDCl_3$ *) of **4c**



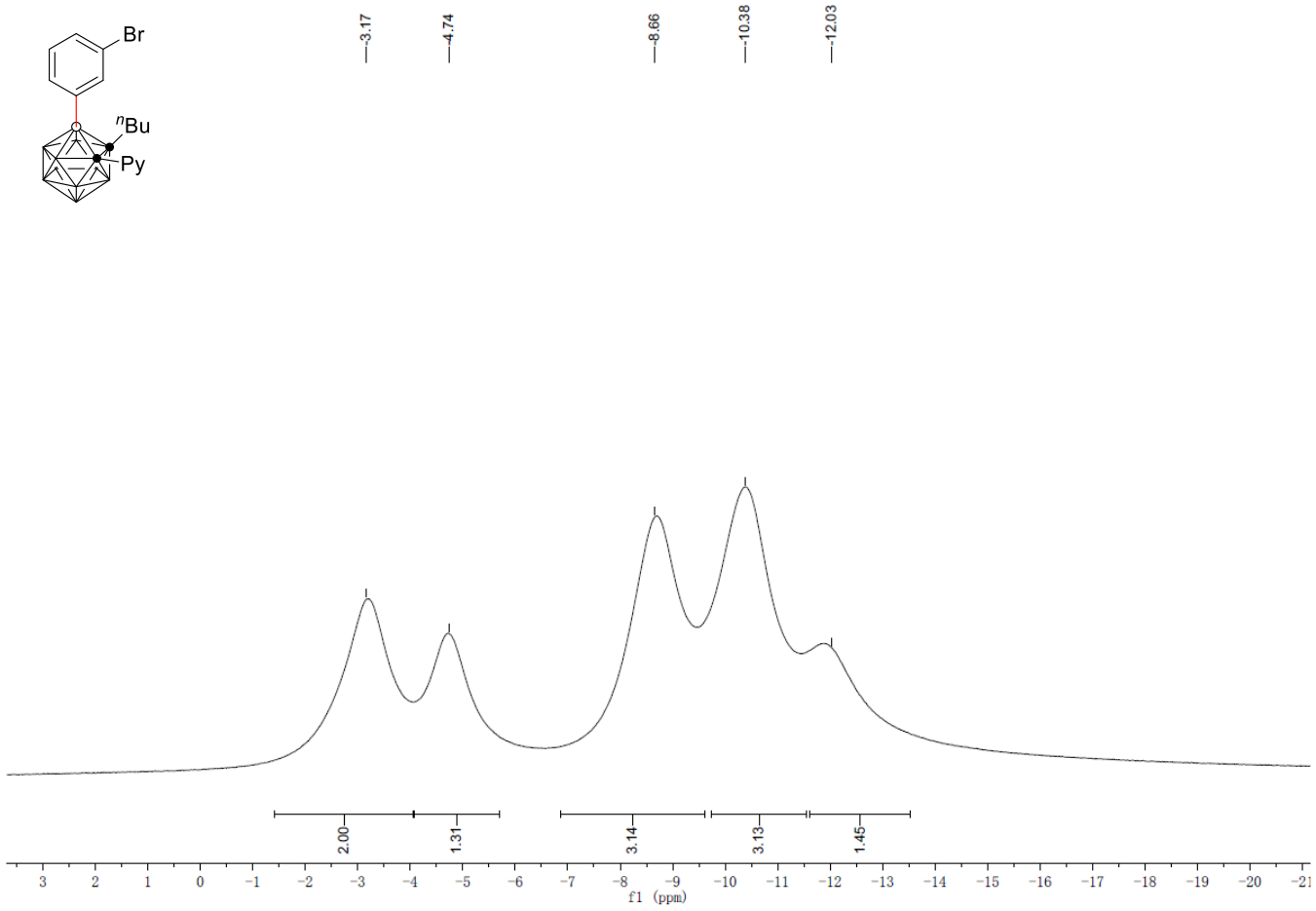
^{13}C NMR (101 MHz, $CDCl_3$ *) of **4c**



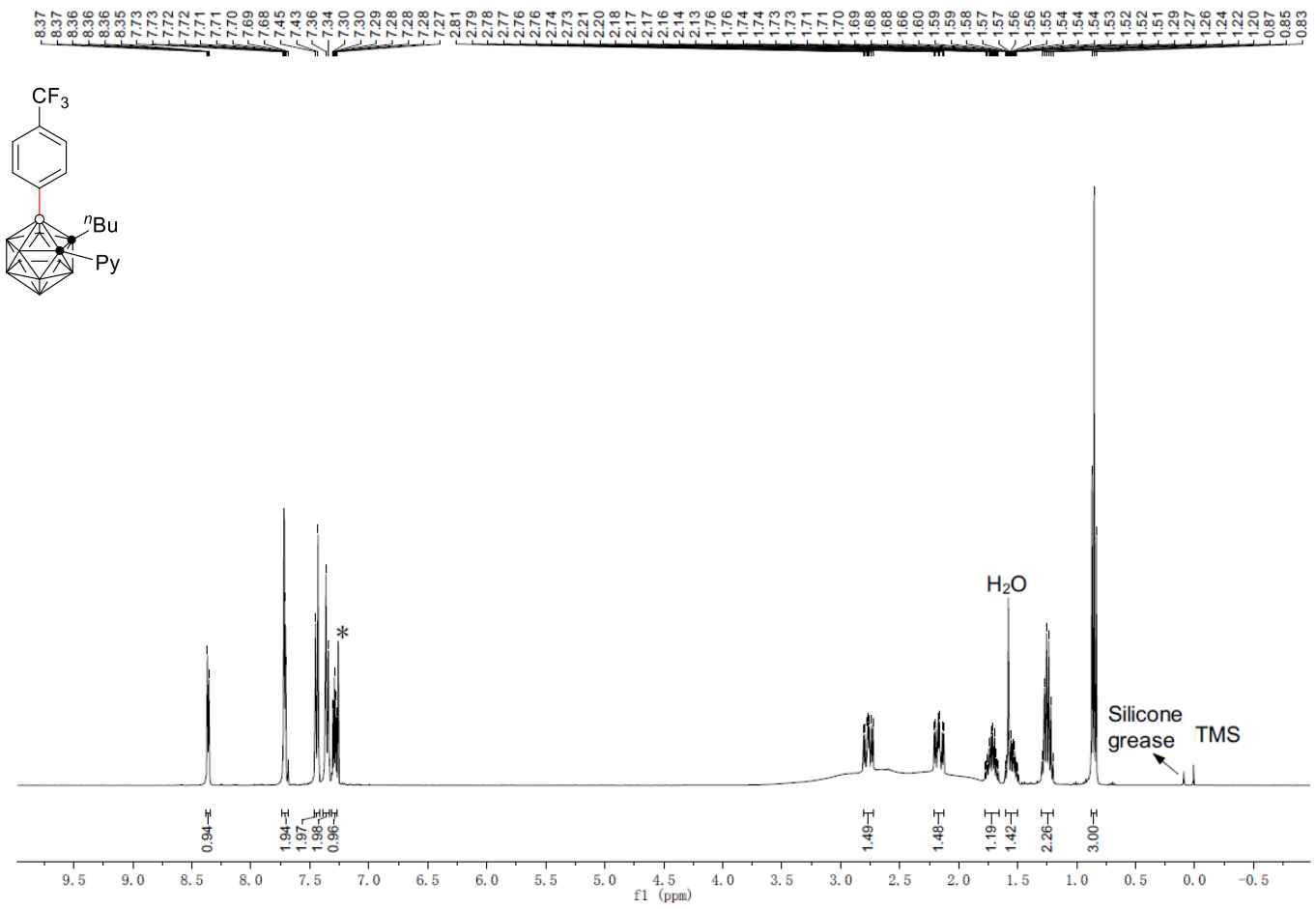
^{11}B NMR (128 MHz, $CDCl_3$ *) of **4c**



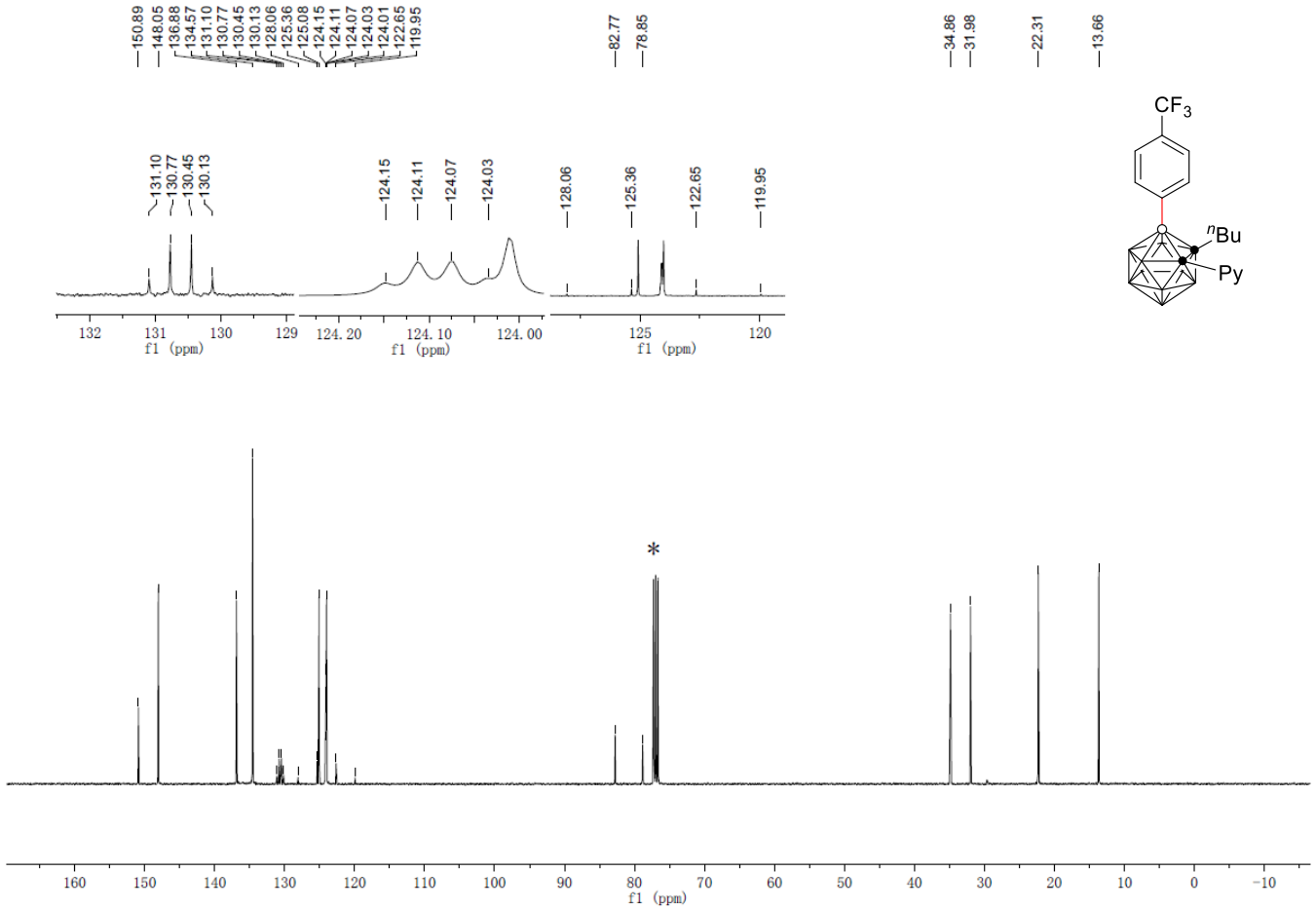
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **4c**



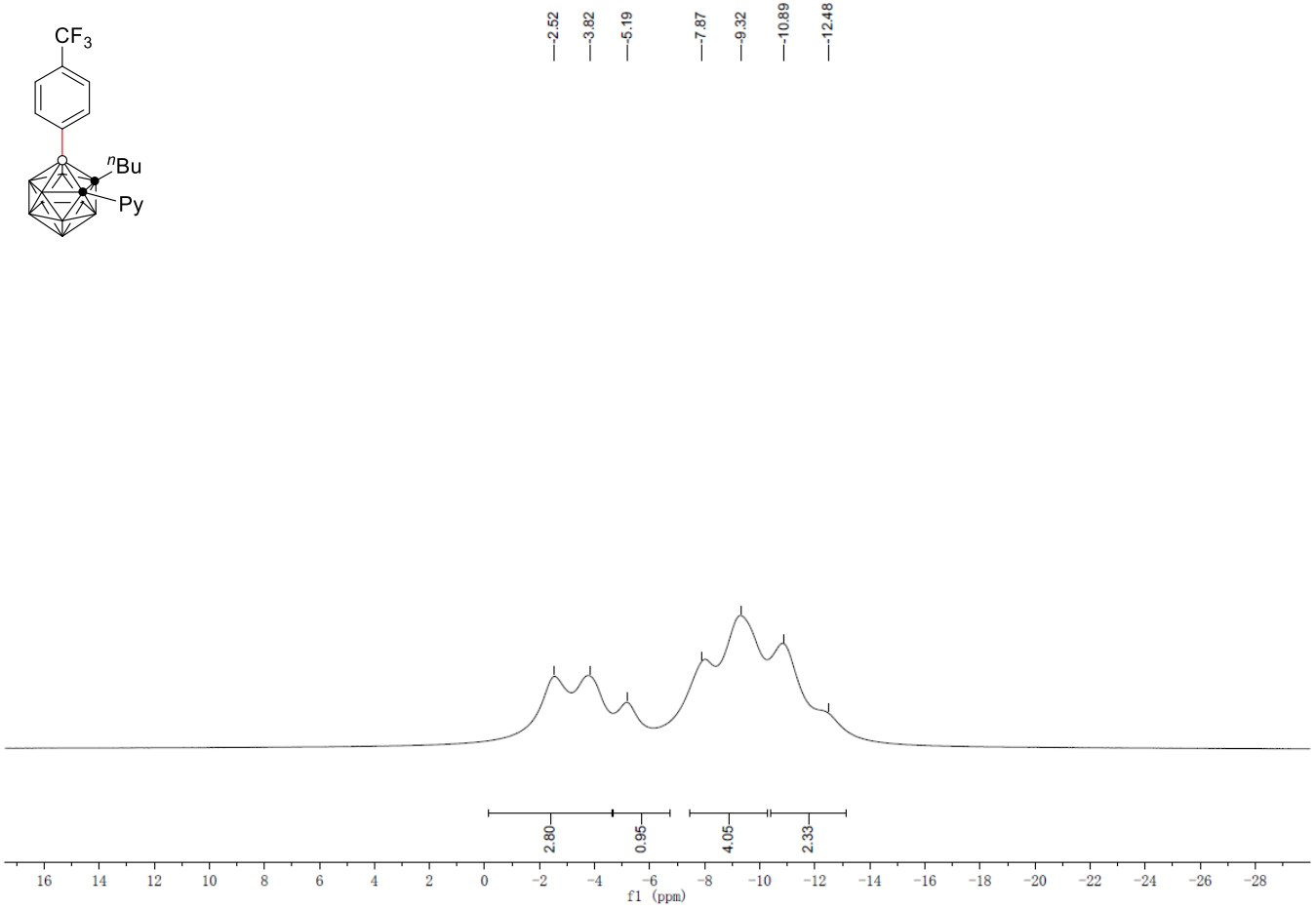
^{1}H NMR (400 MHz, $CDCl_3$ *) of **4d**



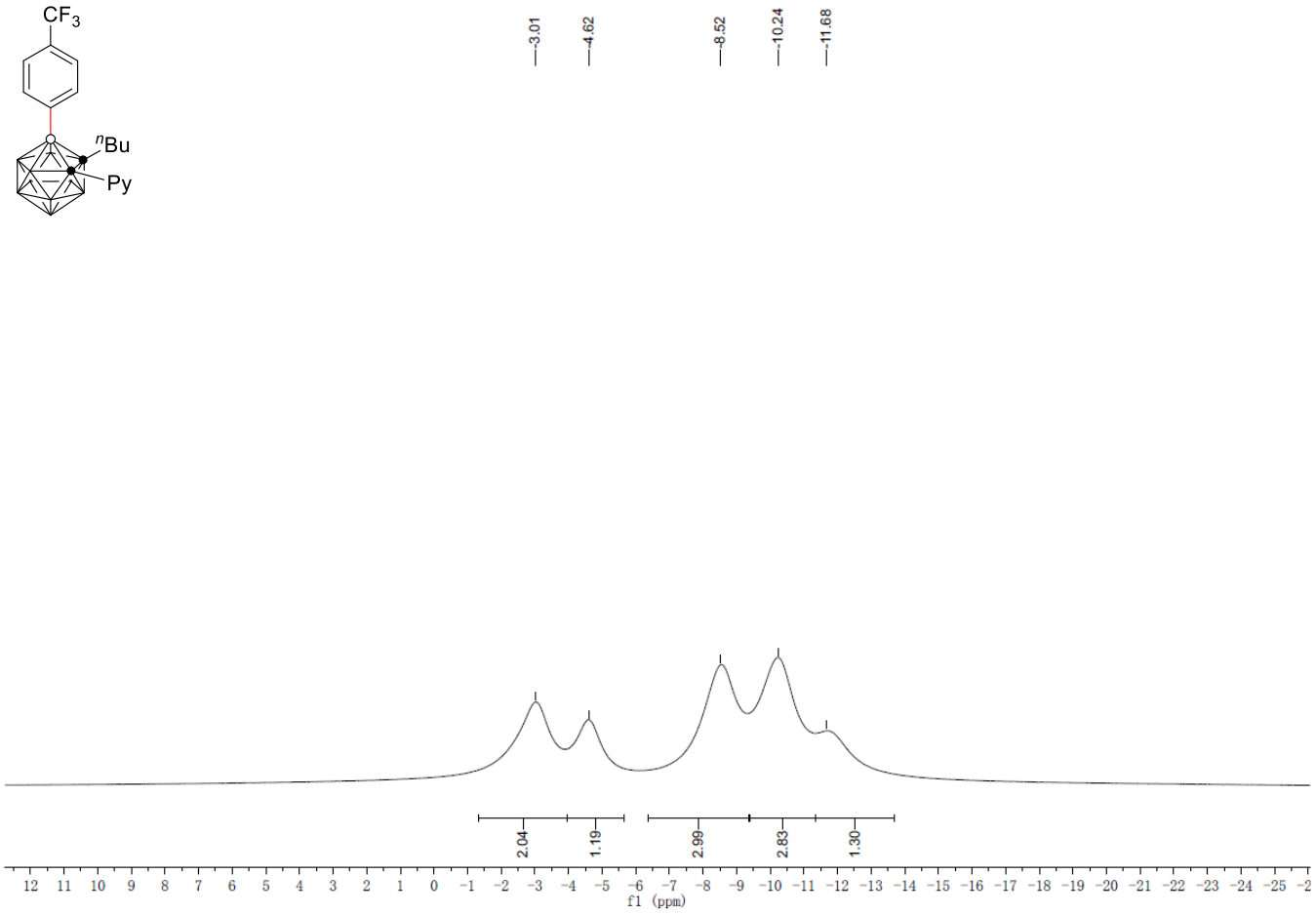
^{13}C NMR (101 MHz, $CDCl_3$ *) of **4d**



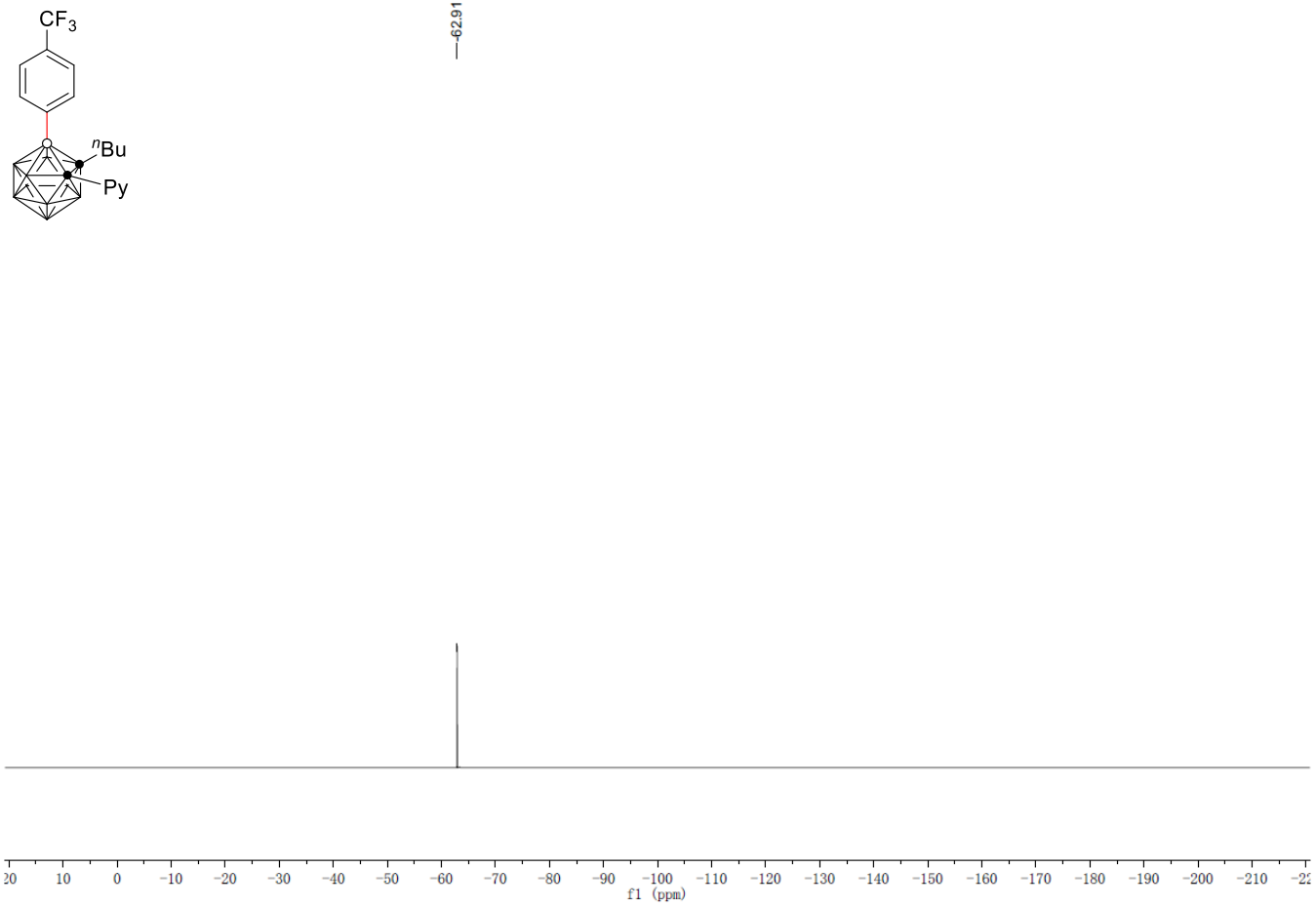
^{11}B NMR (128 MHz, $CDCl_3$ *) of **4d**



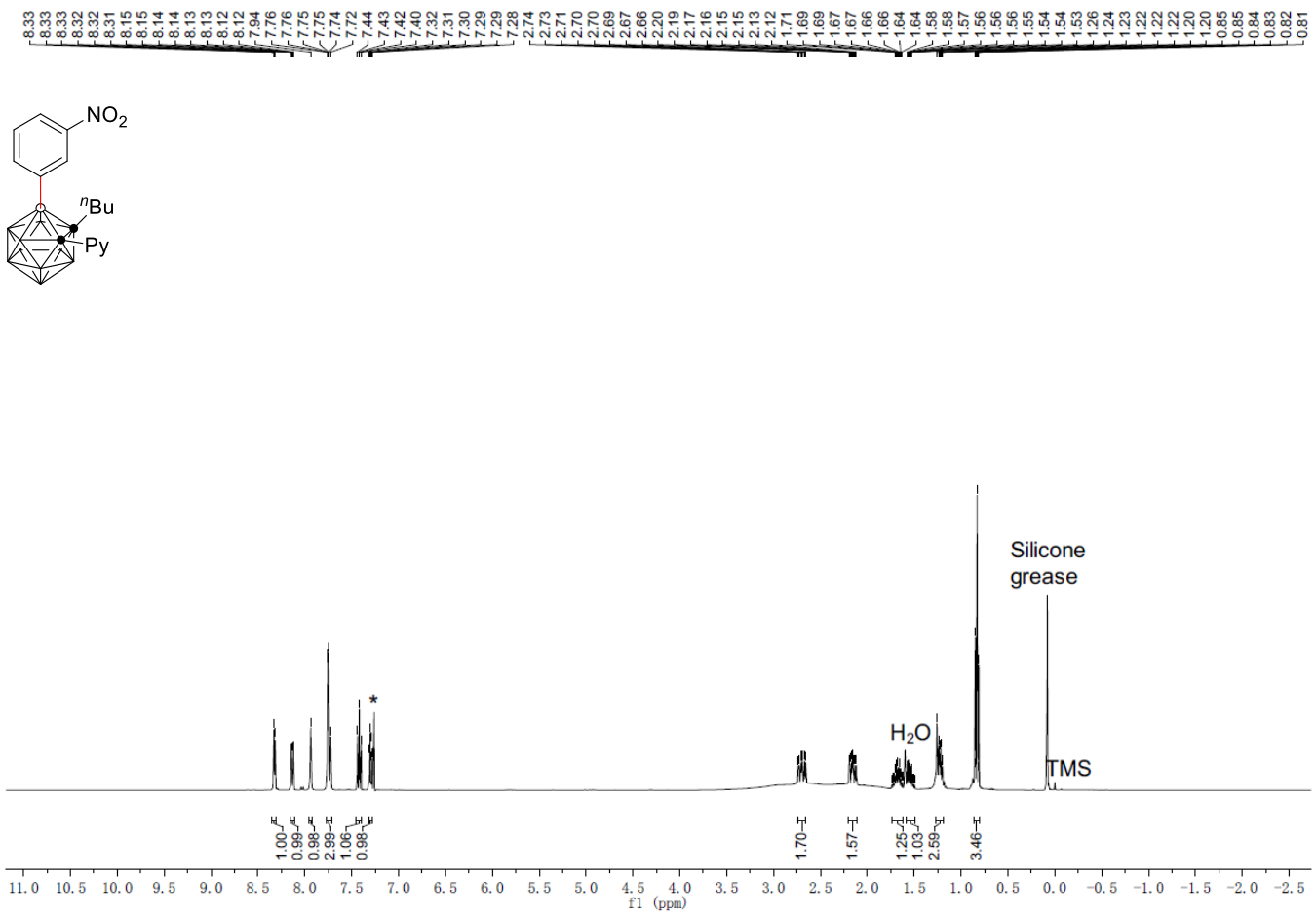
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **4d**



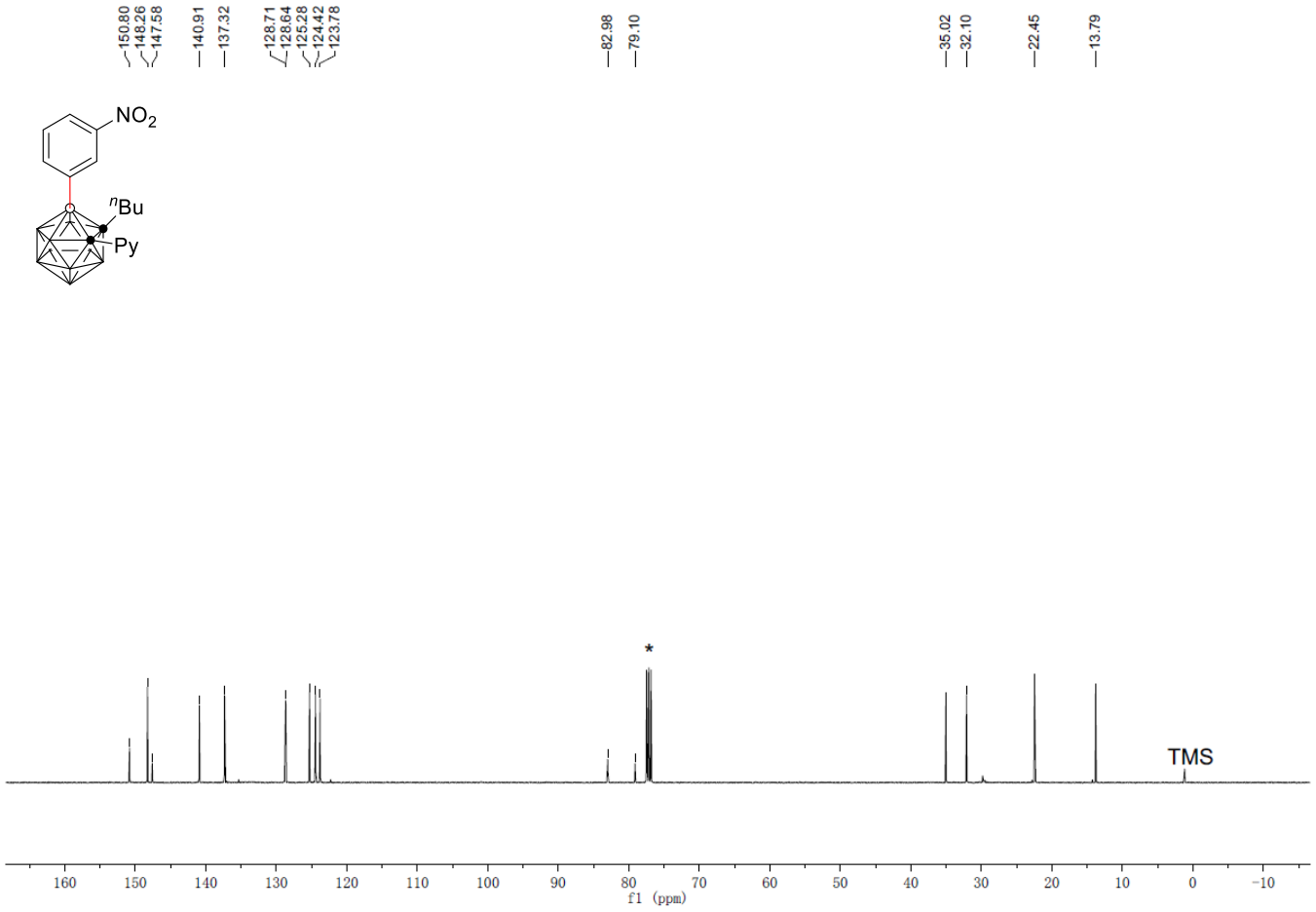
^{19}F NMR (376 MHz, $CDCl_3$ *) of **4d**



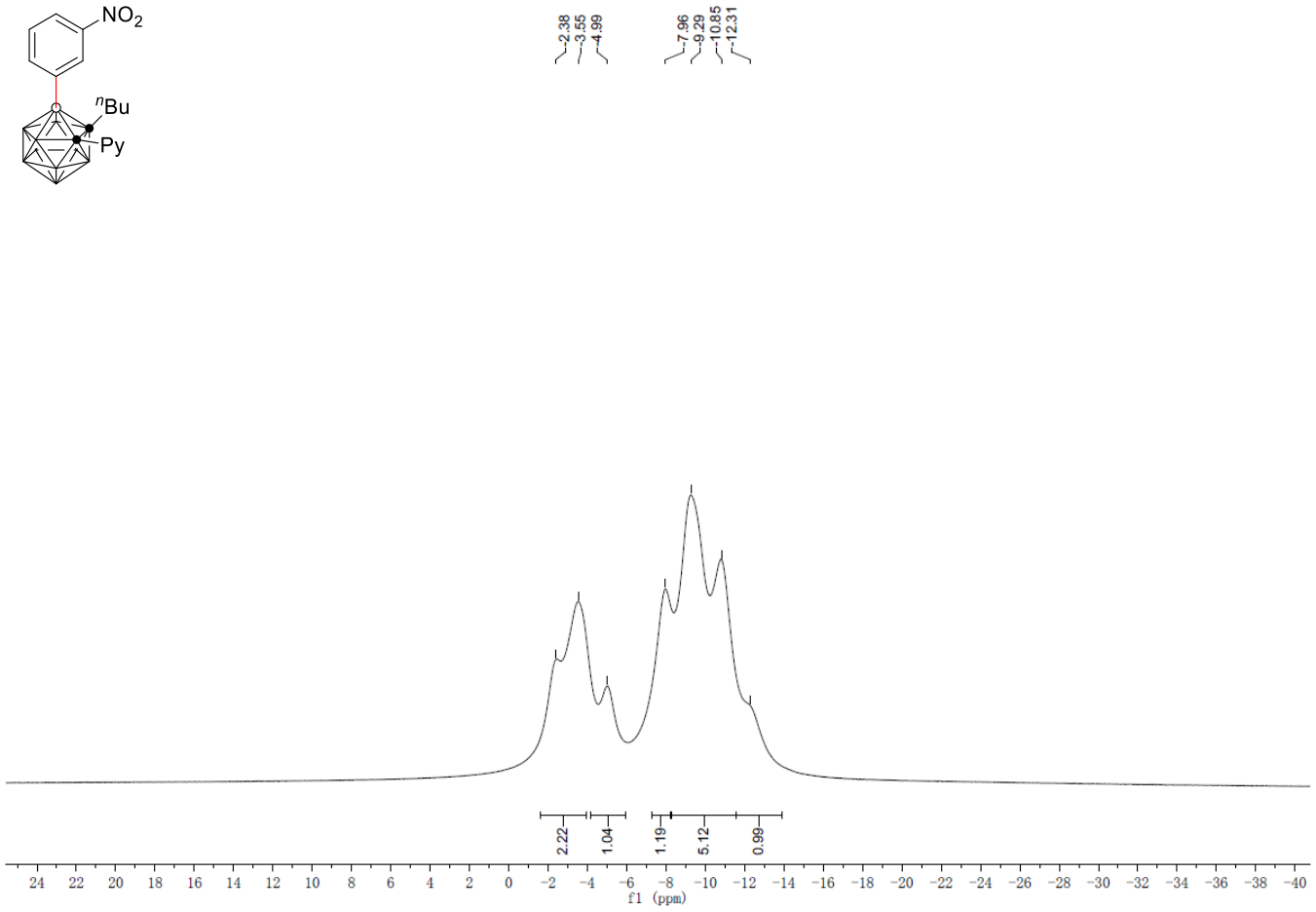
^{1}H NMR (400 MHz, $CDCl_3$ *) of **4e**



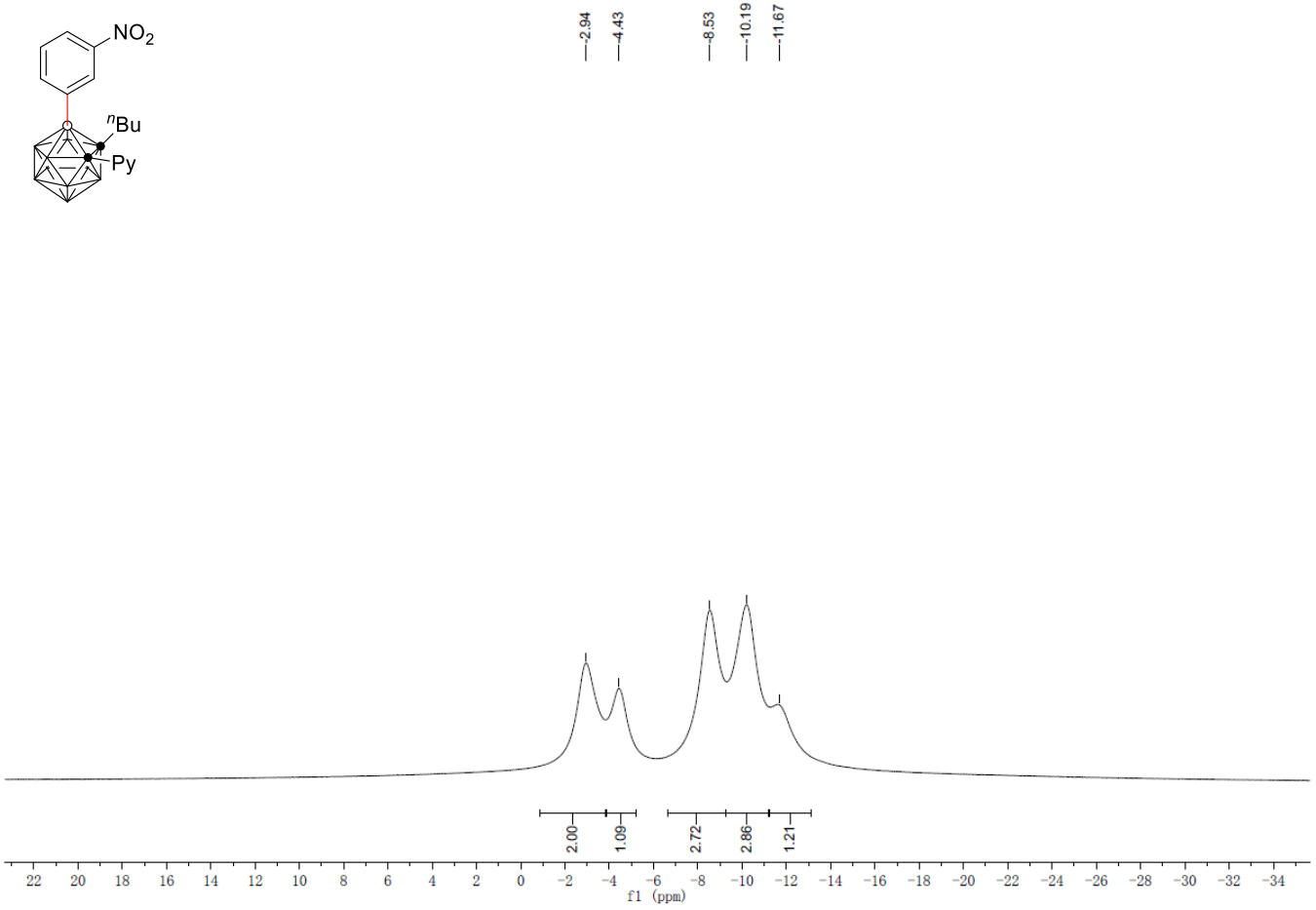
^{13}C NMR (101 MHz, $CDCl_3$ *) of **4e**



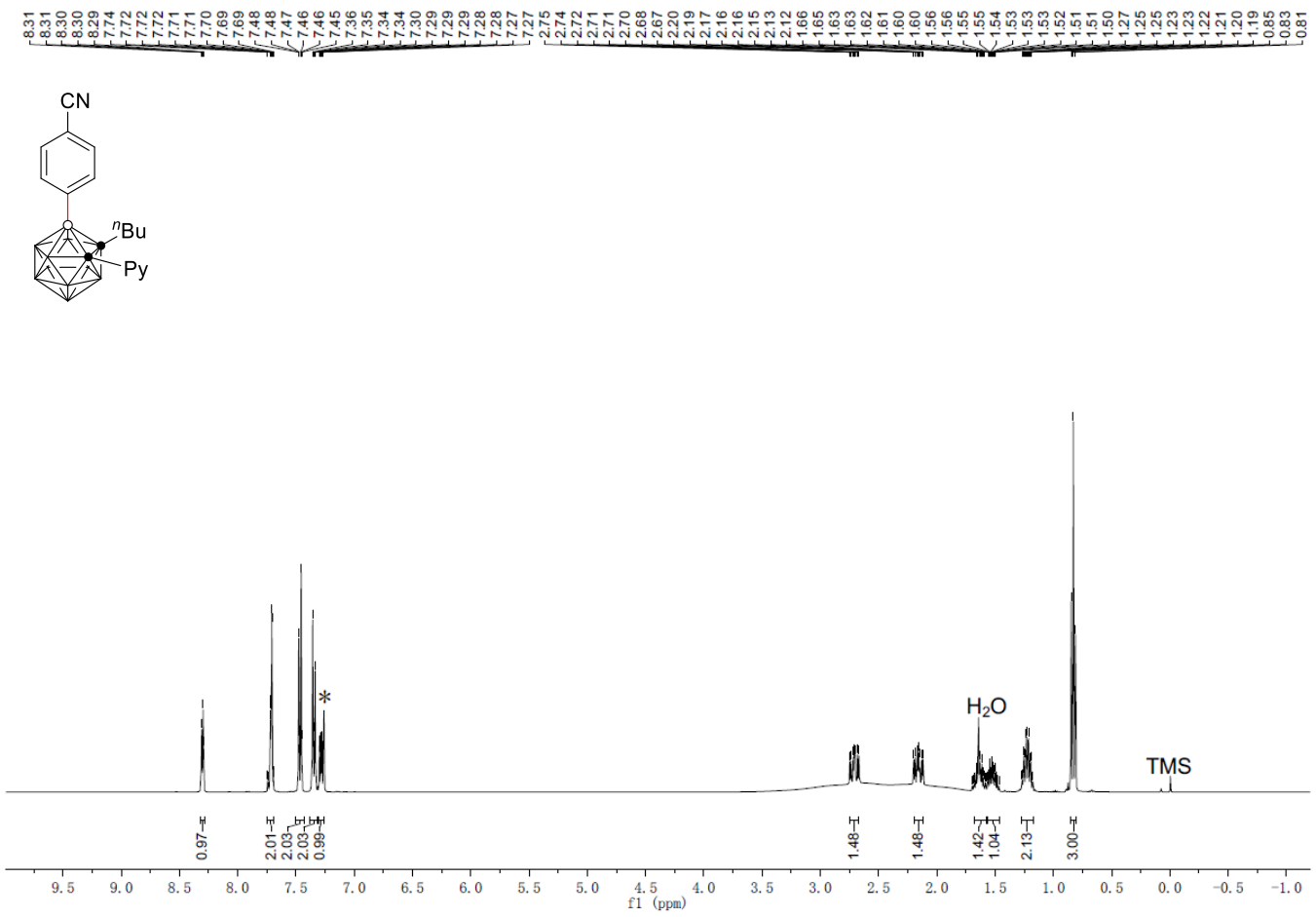
^{11}B NMR (128 MHz, $CDCl_3$ *) of **4e**



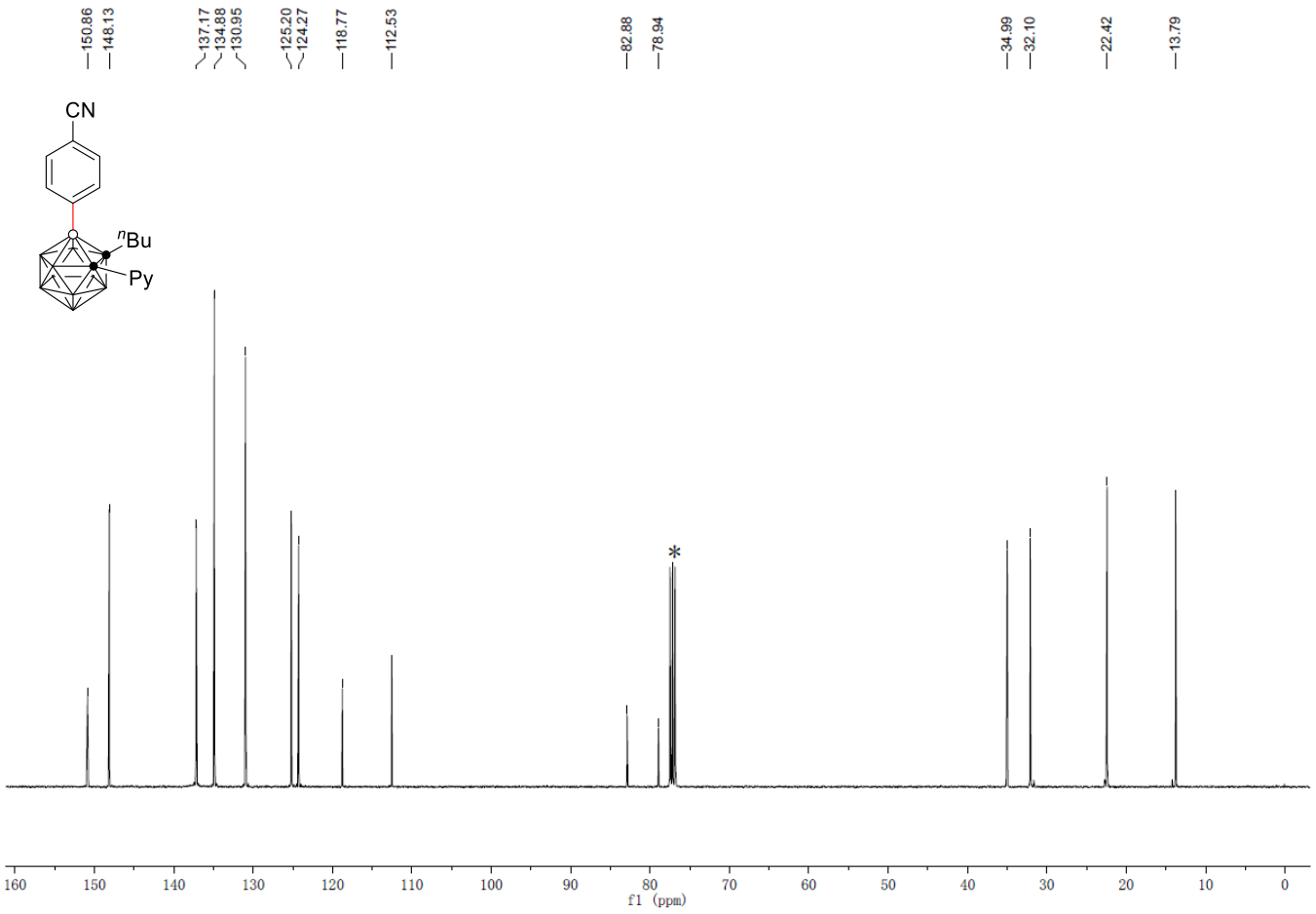
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **4e**



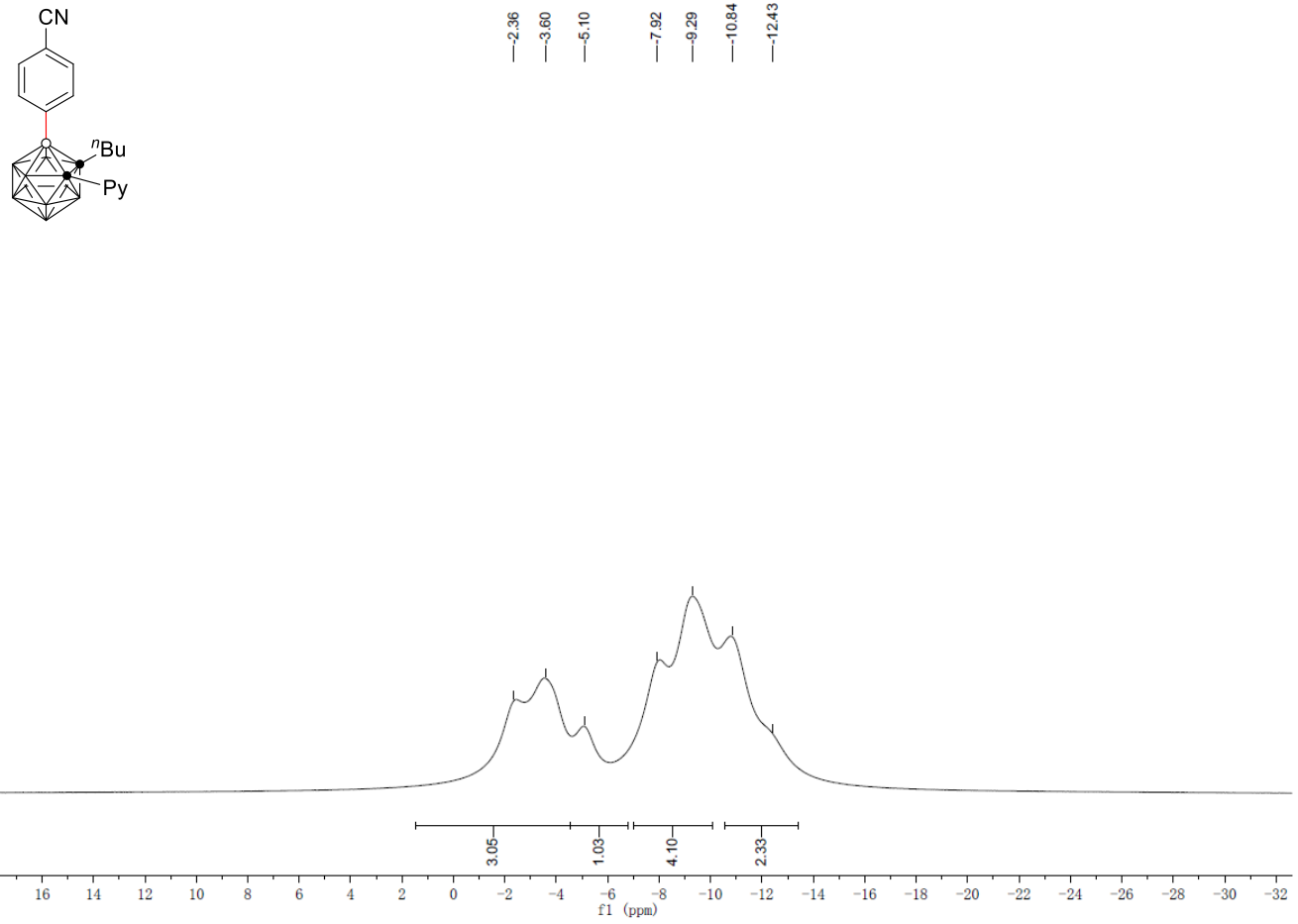
^{1}H NMR (400 MHz, $CDCl_3$ *) of **4f**



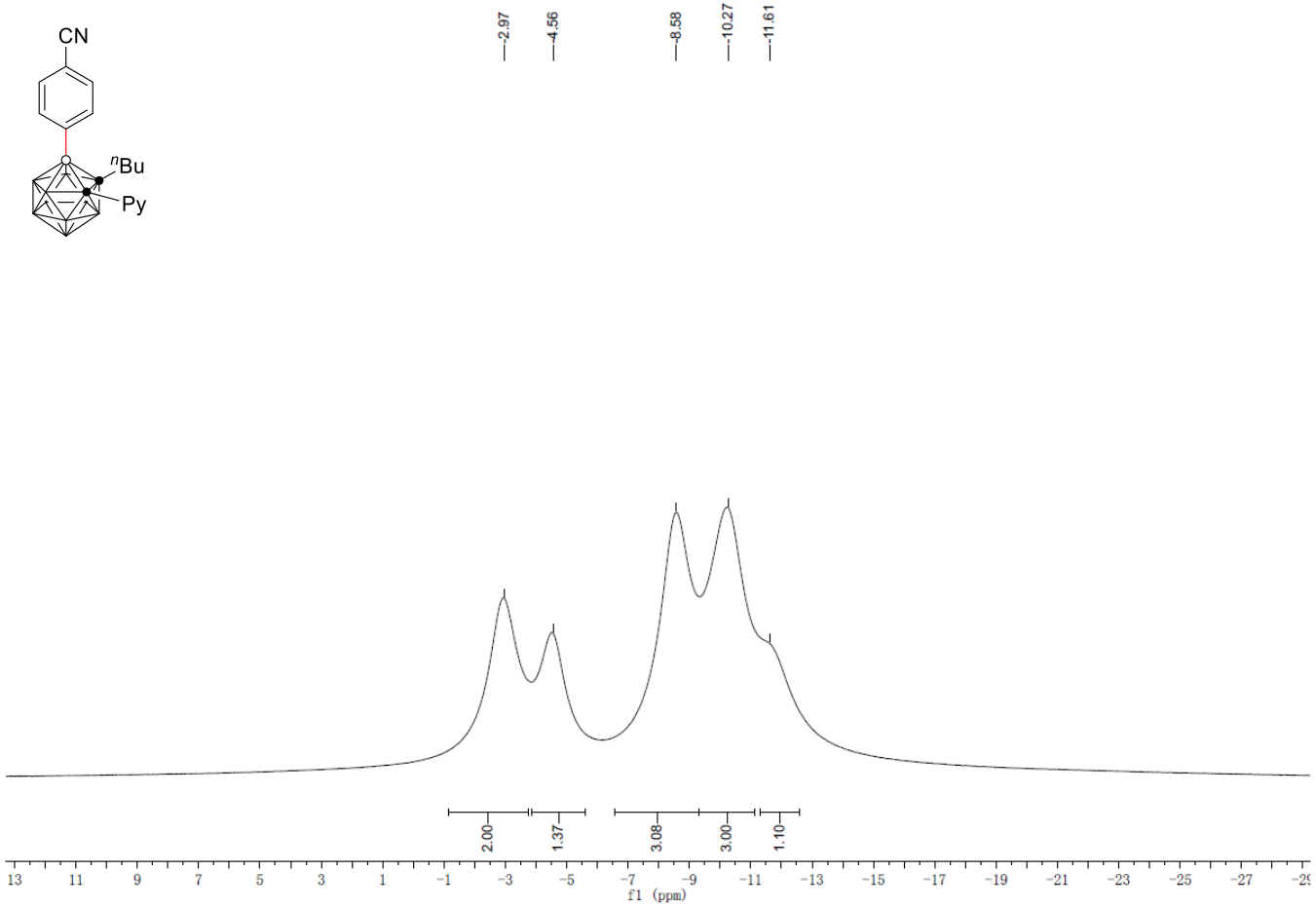
^{13}C NMR (101 MHz, $CDCl_3$ *) of **4f**



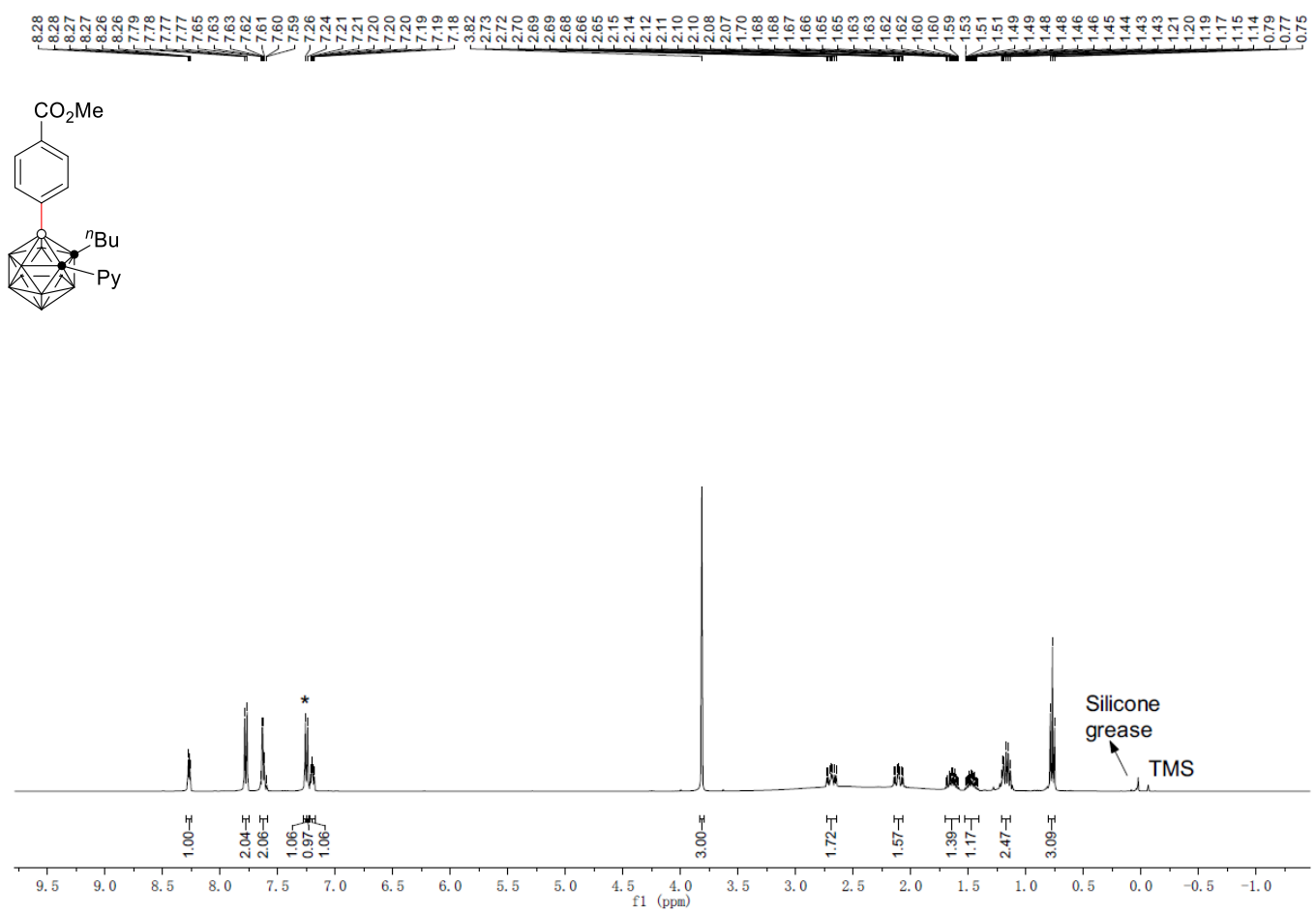
^{11}B NMR (128 MHz, $CDCl_3$ *) of **4f**



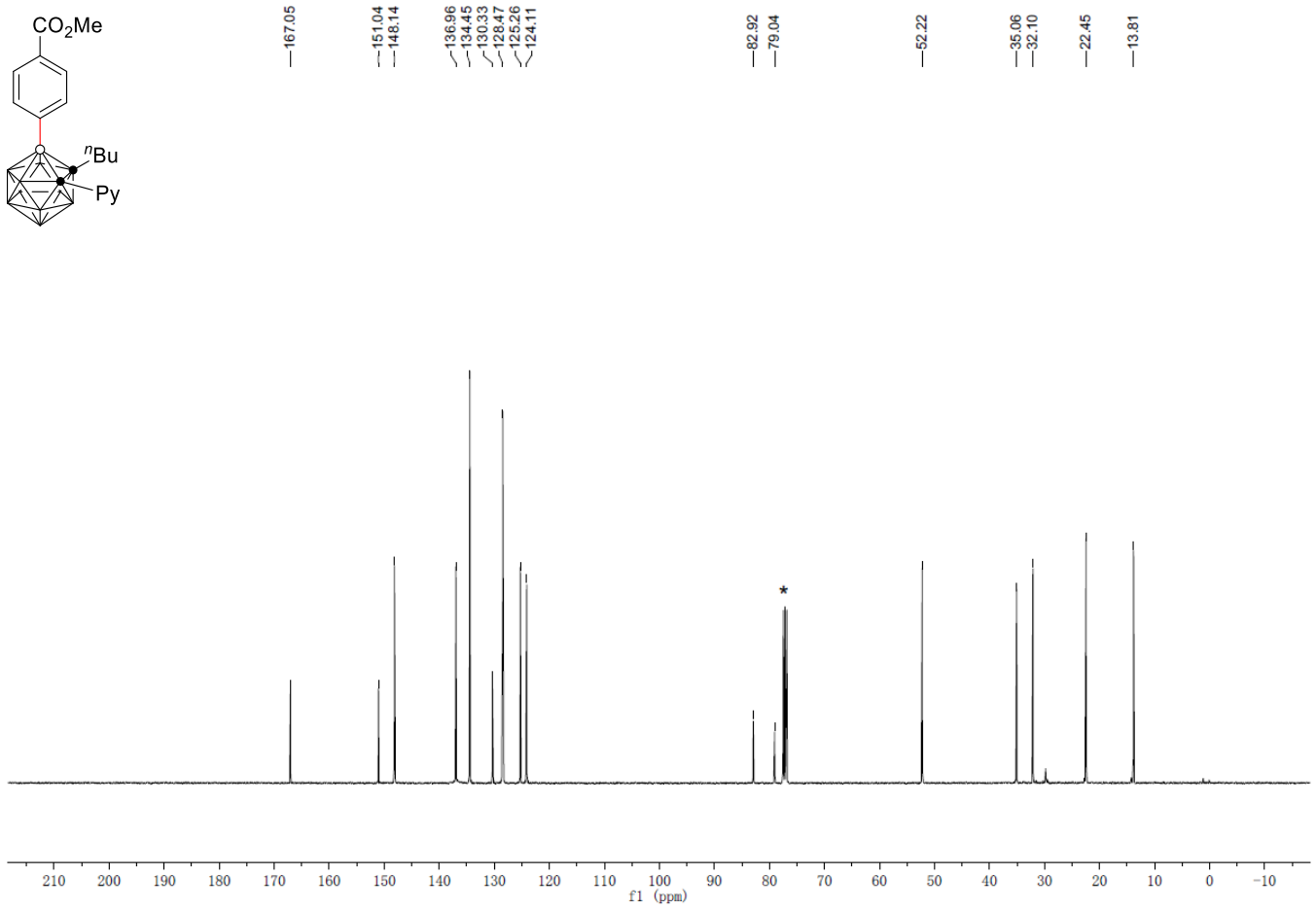
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **4f**



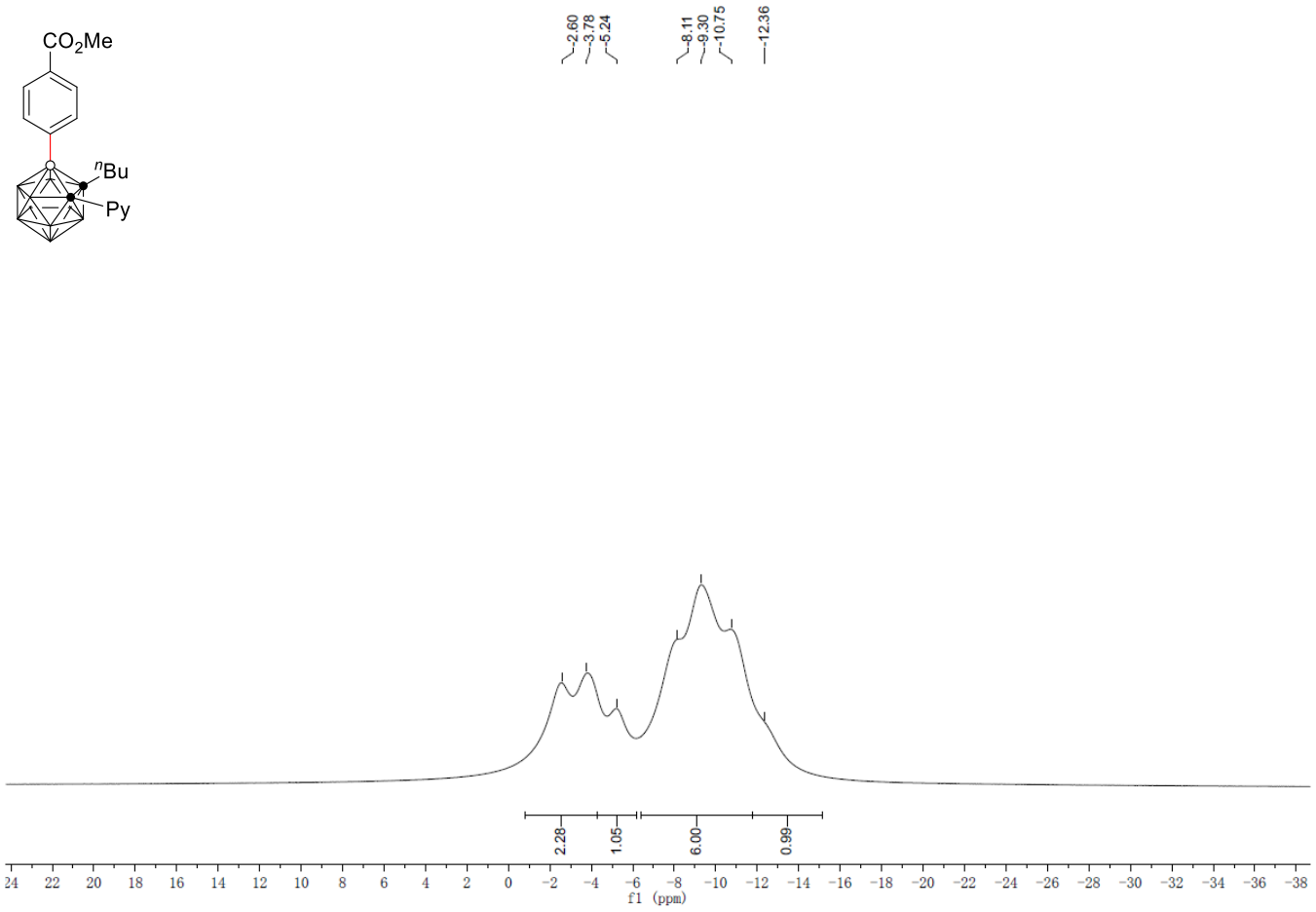
^{1}H NMR (400 MHz, $CDCl_3$ *) of **4g**



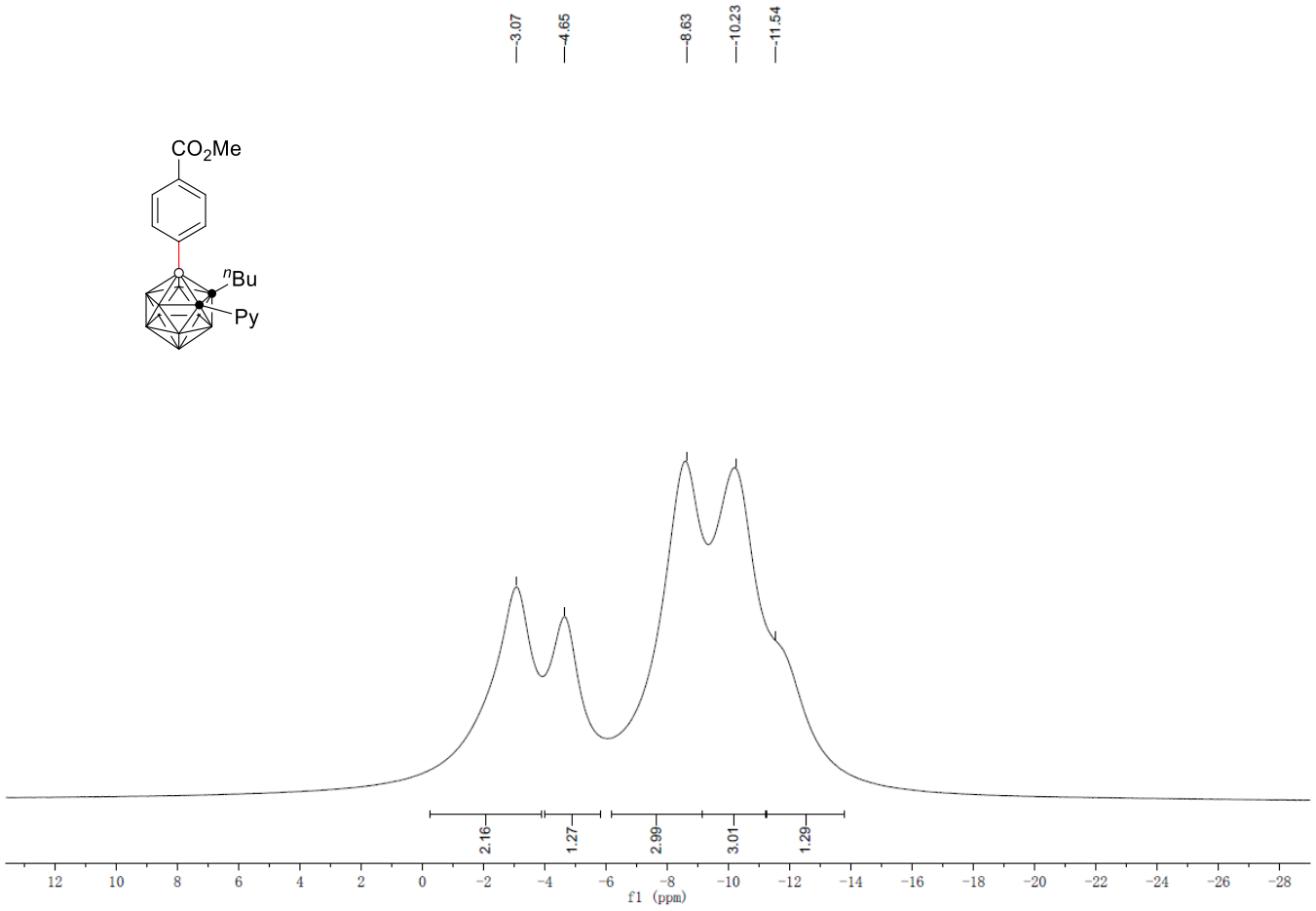
^{13}C NMR (101 MHz, $CDCl_3$ *) of **4g**



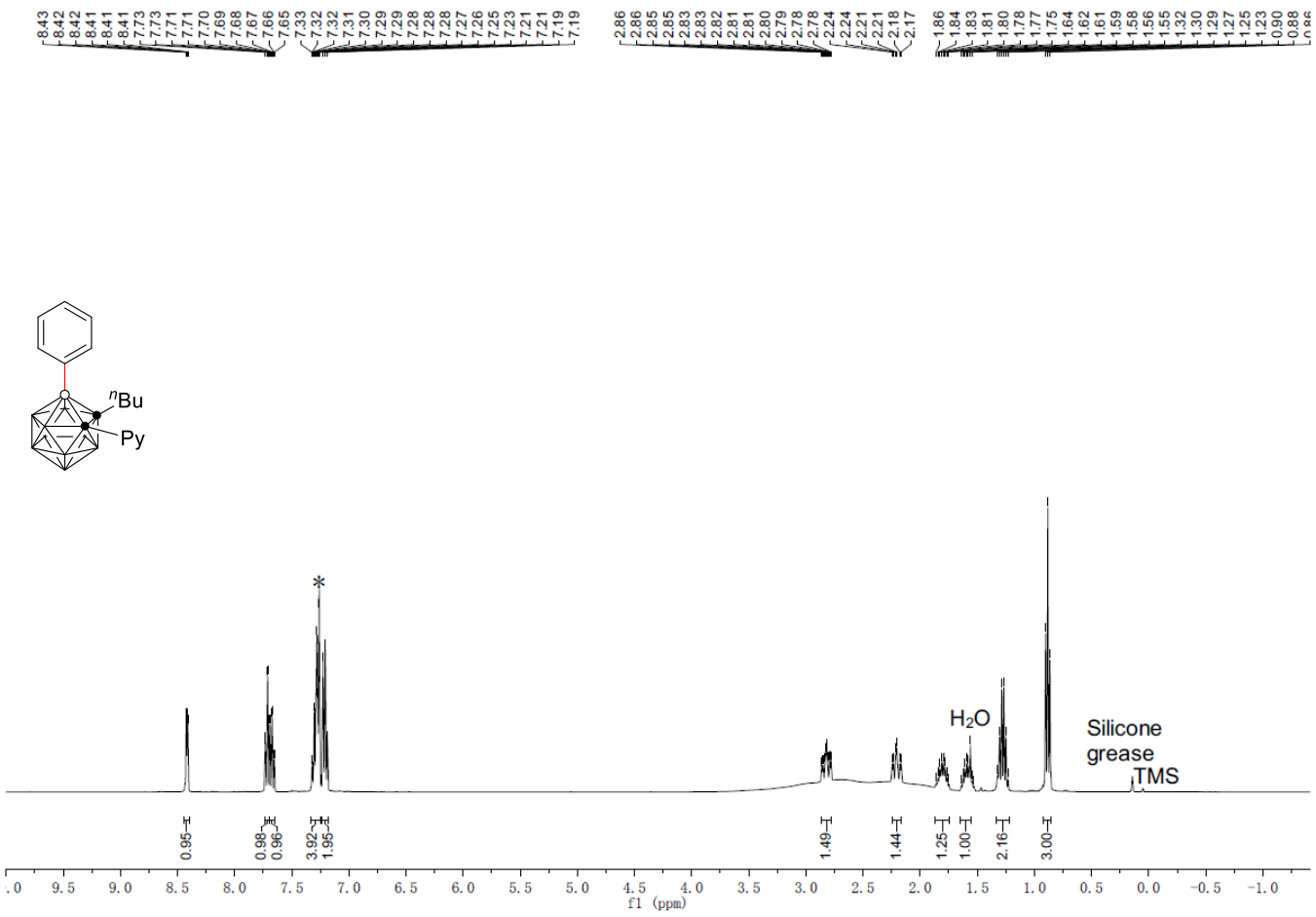
^{11}B NMR (128 MHz, $CDCl_3$ *) of **4g**



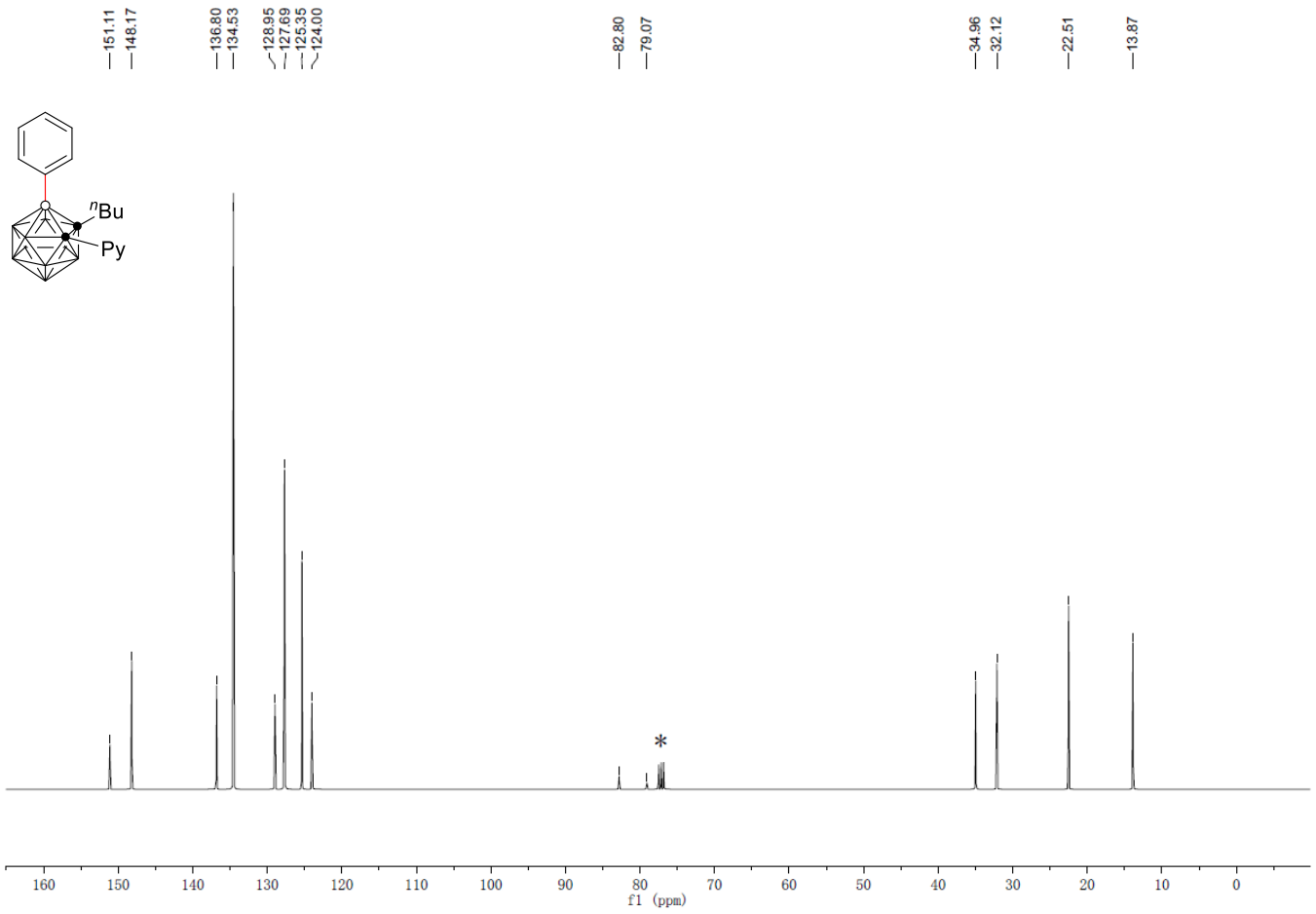
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **4g**



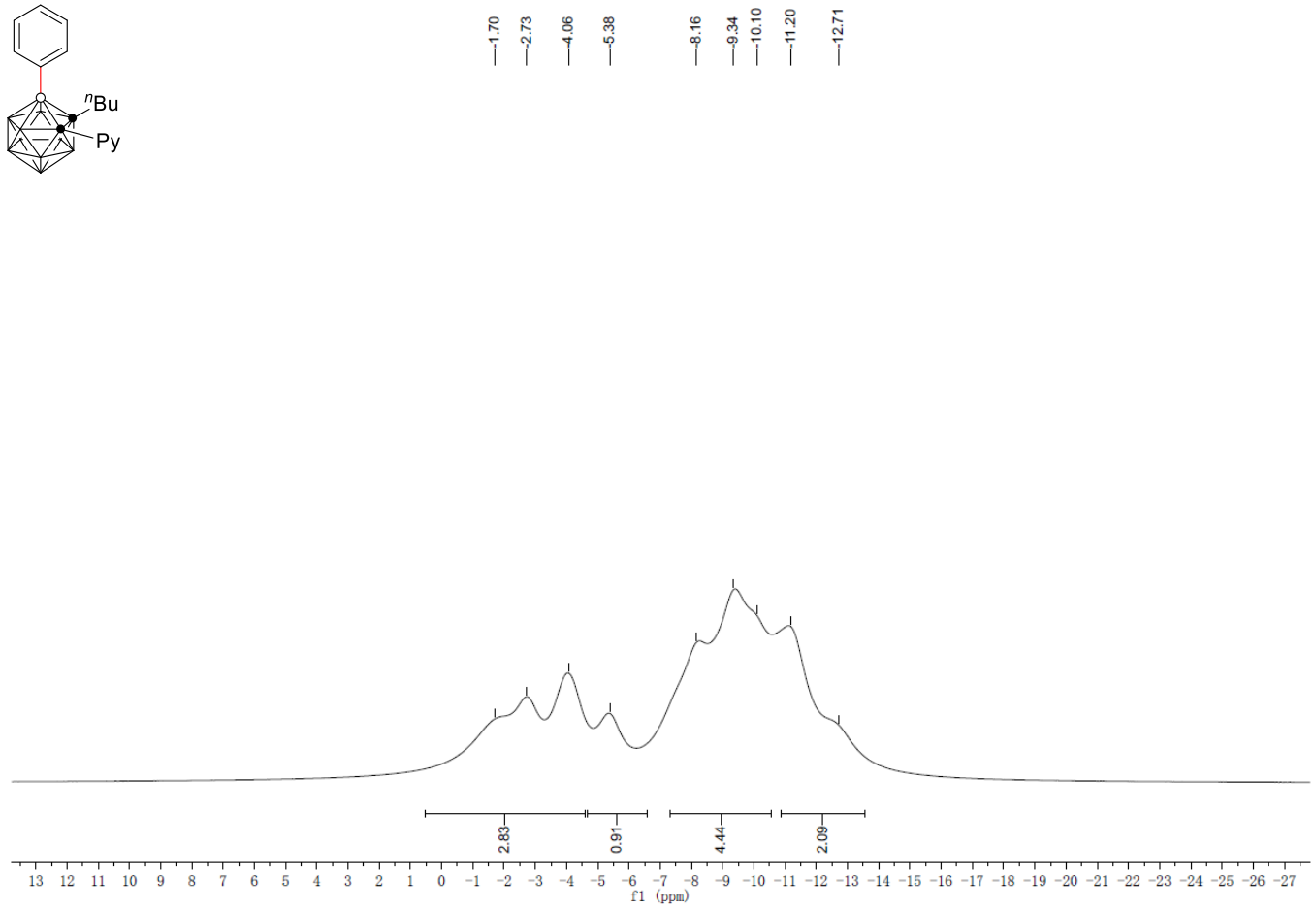
^{1}H NMR (400 MHz, $CDCl_3$ *) of **4h**



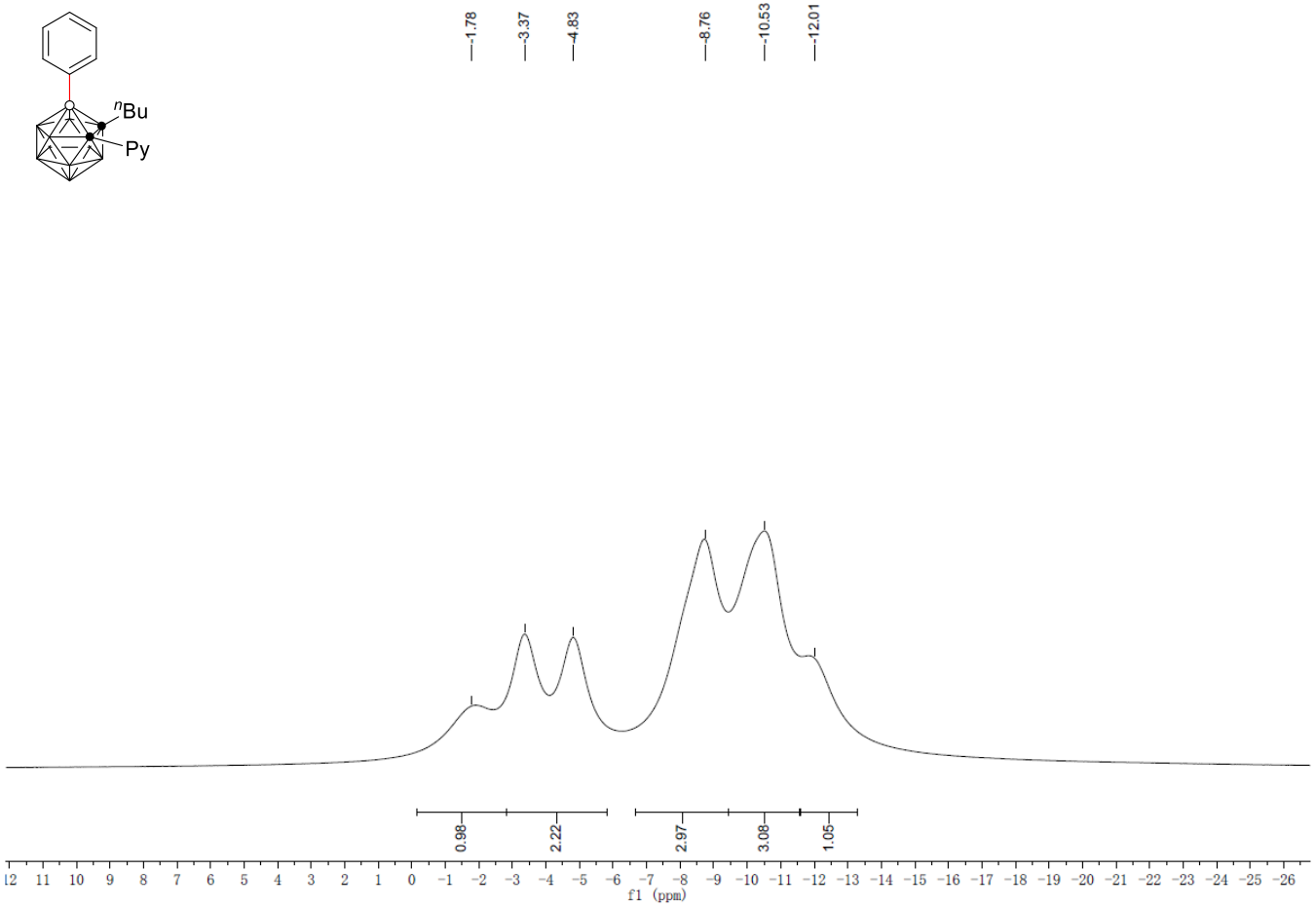
^{13}C NMR (101 MHz, $CDCl_3$ *) of **4h**



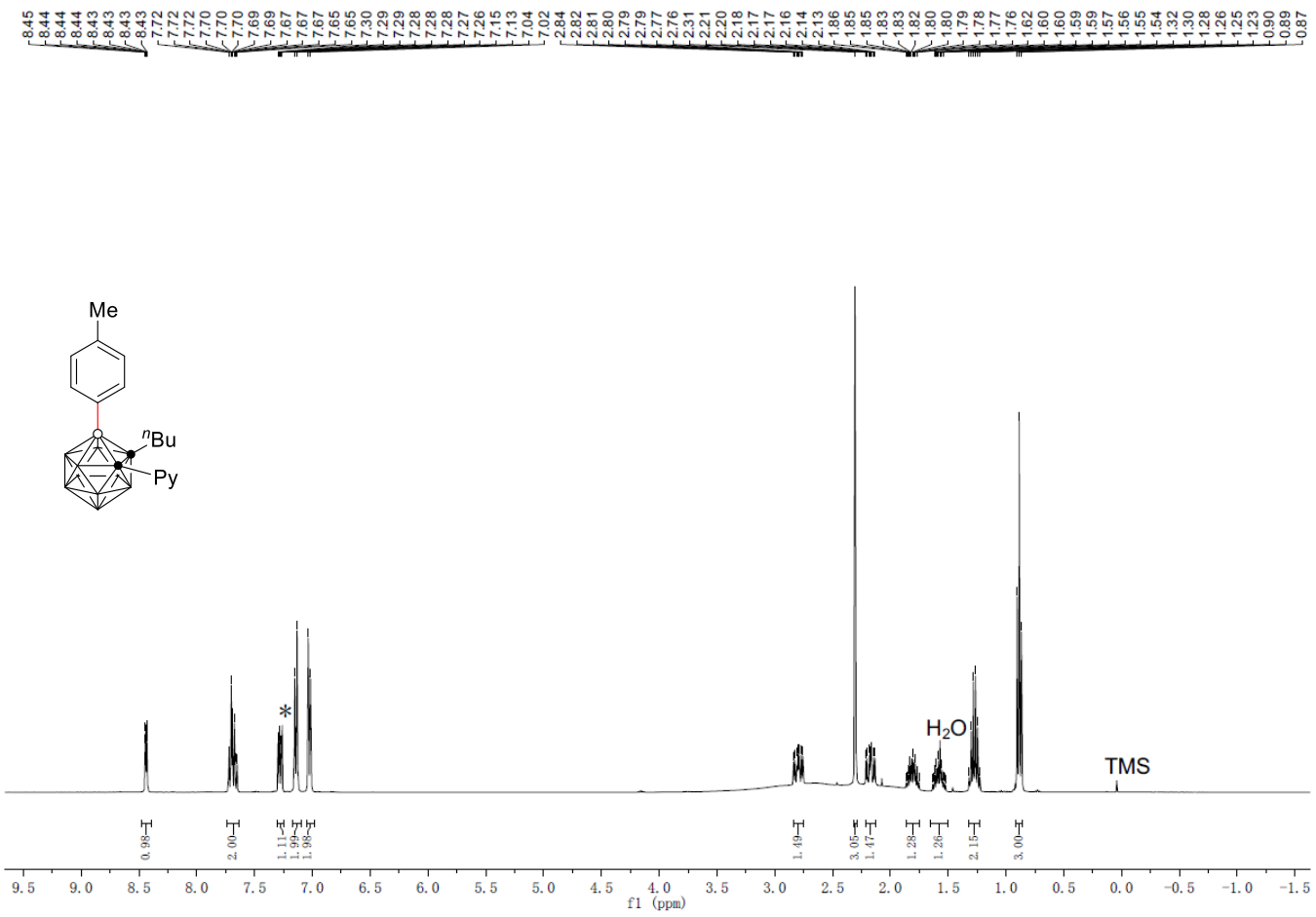
^{11}B NMR (128 MHz, $CDCl_3$ *) of **4h**



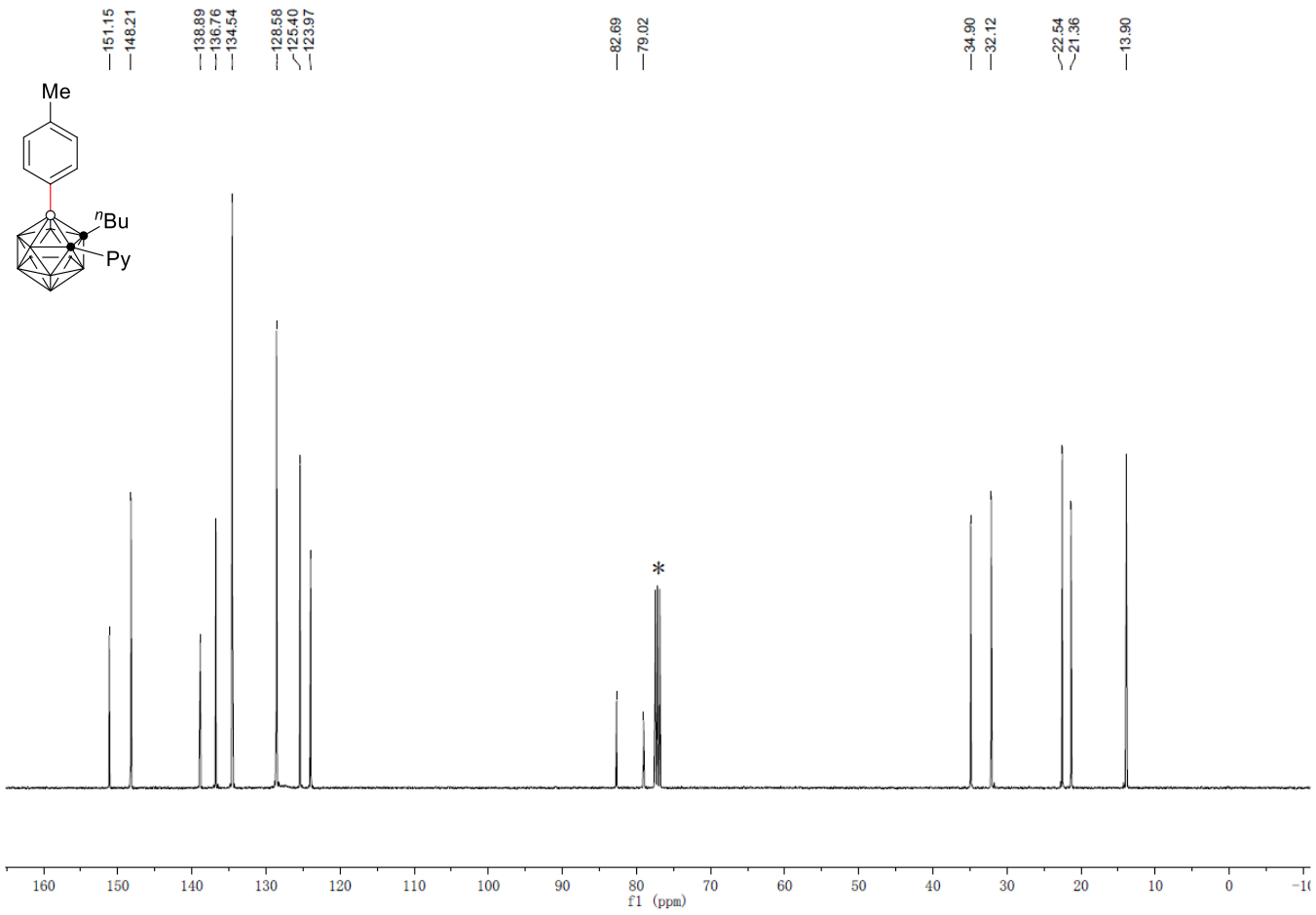
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **4h**



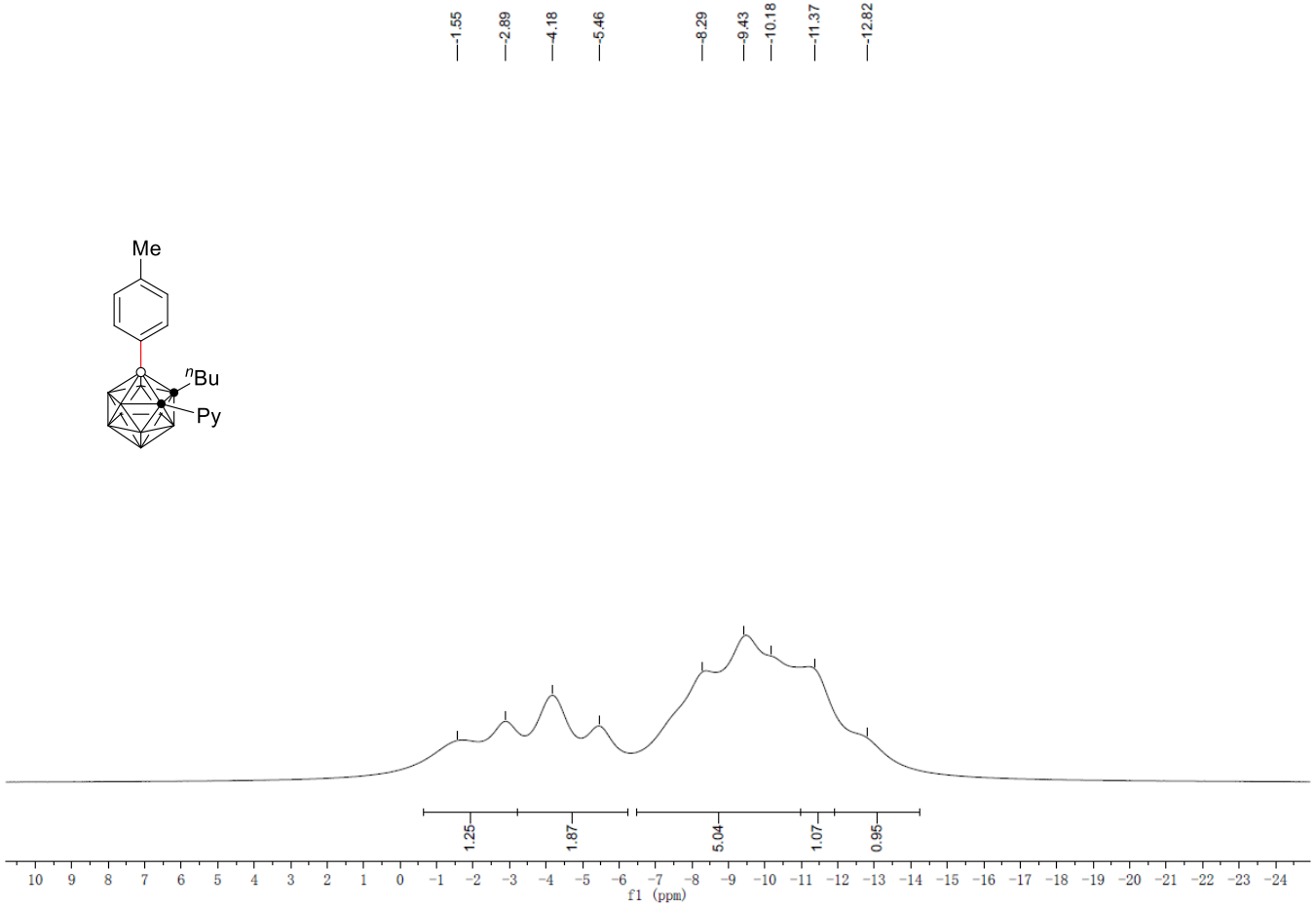
^{1}H NMR (400 MHz, $CDCl_3$ *) of **4i**



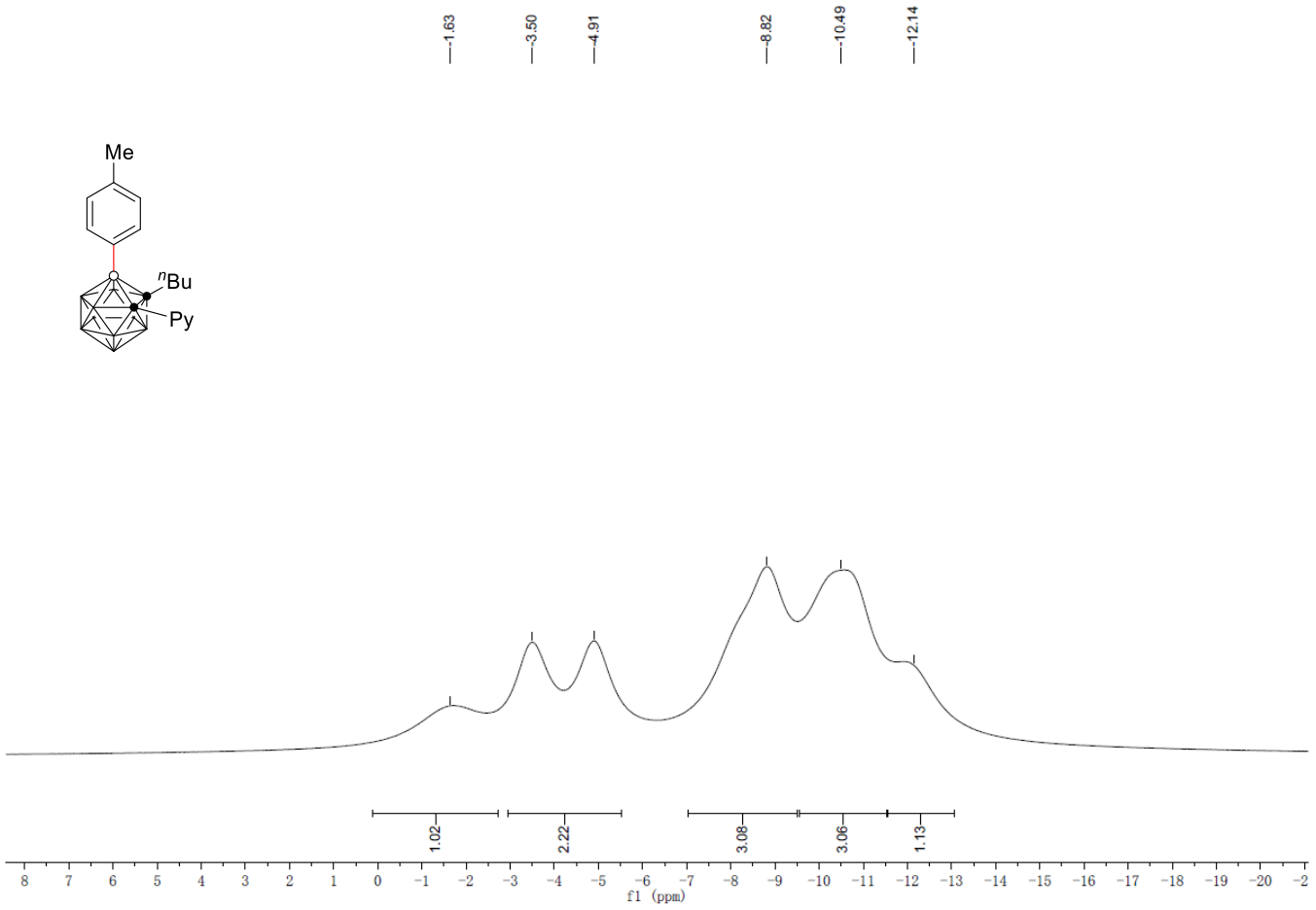
^{13}C NMR (101 MHz, $CDCl_3$ *) of **4i**



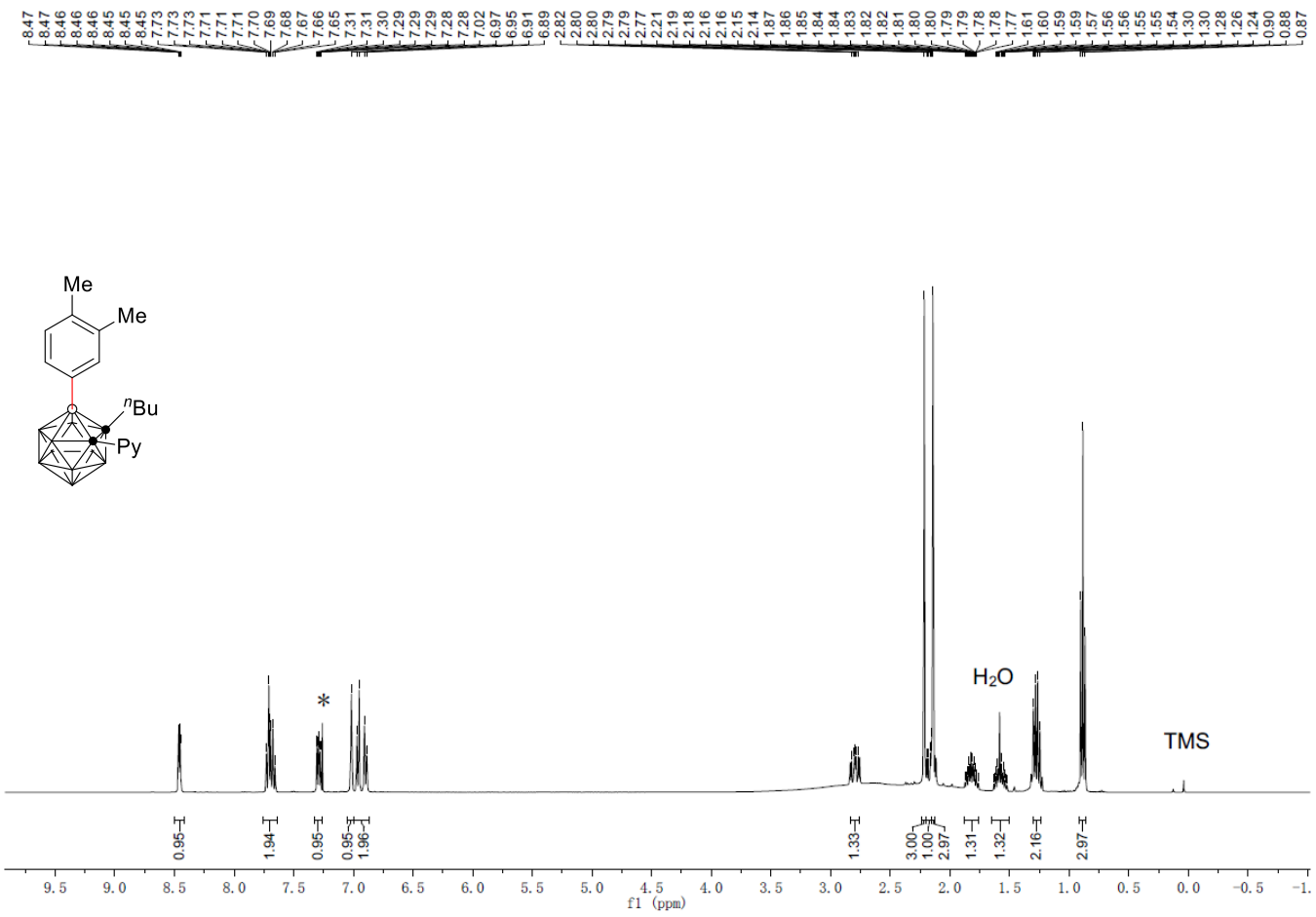
^{11}B NMR (128 MHz, $CDCl_3$ *) of **4i**



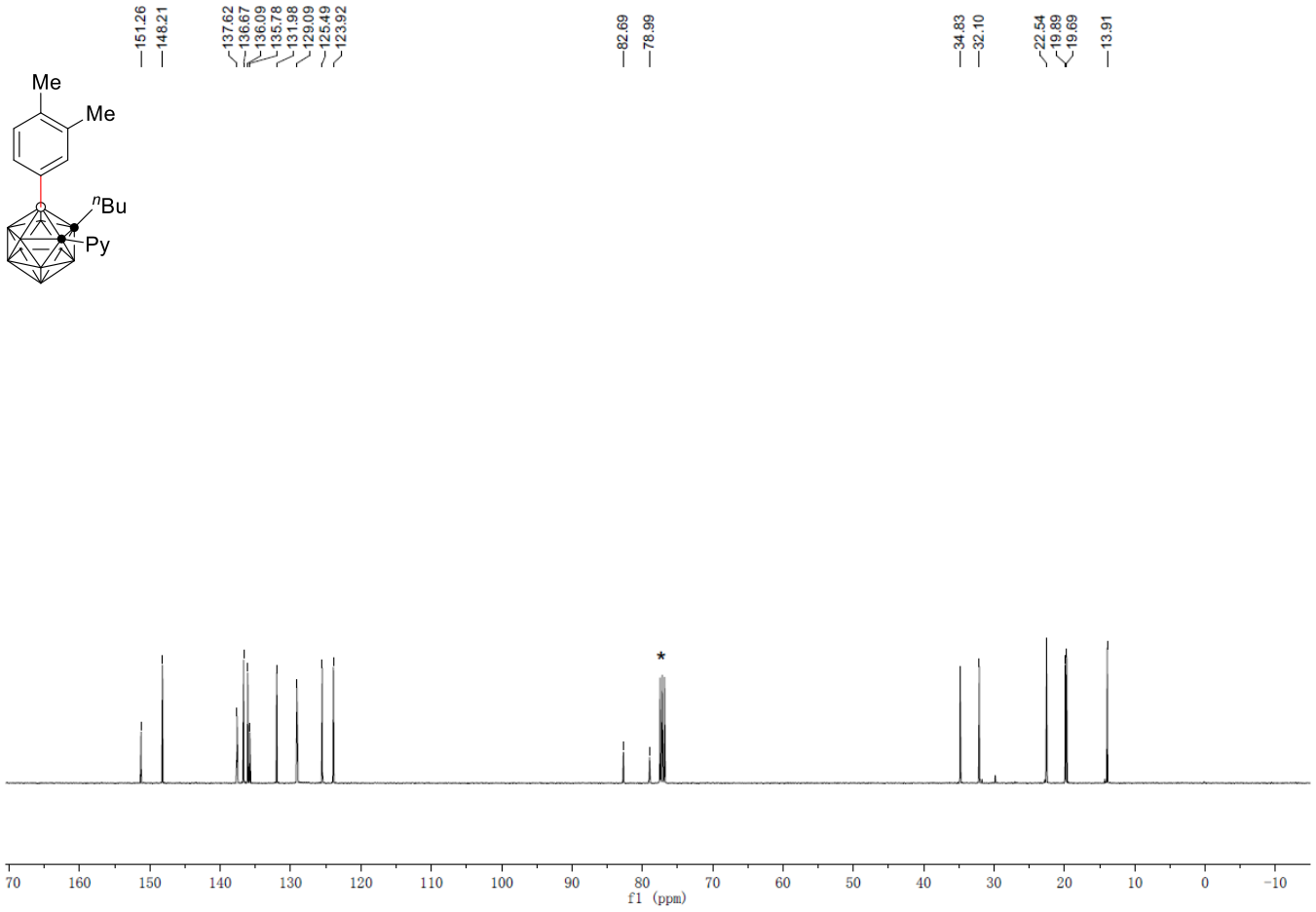
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **4i**



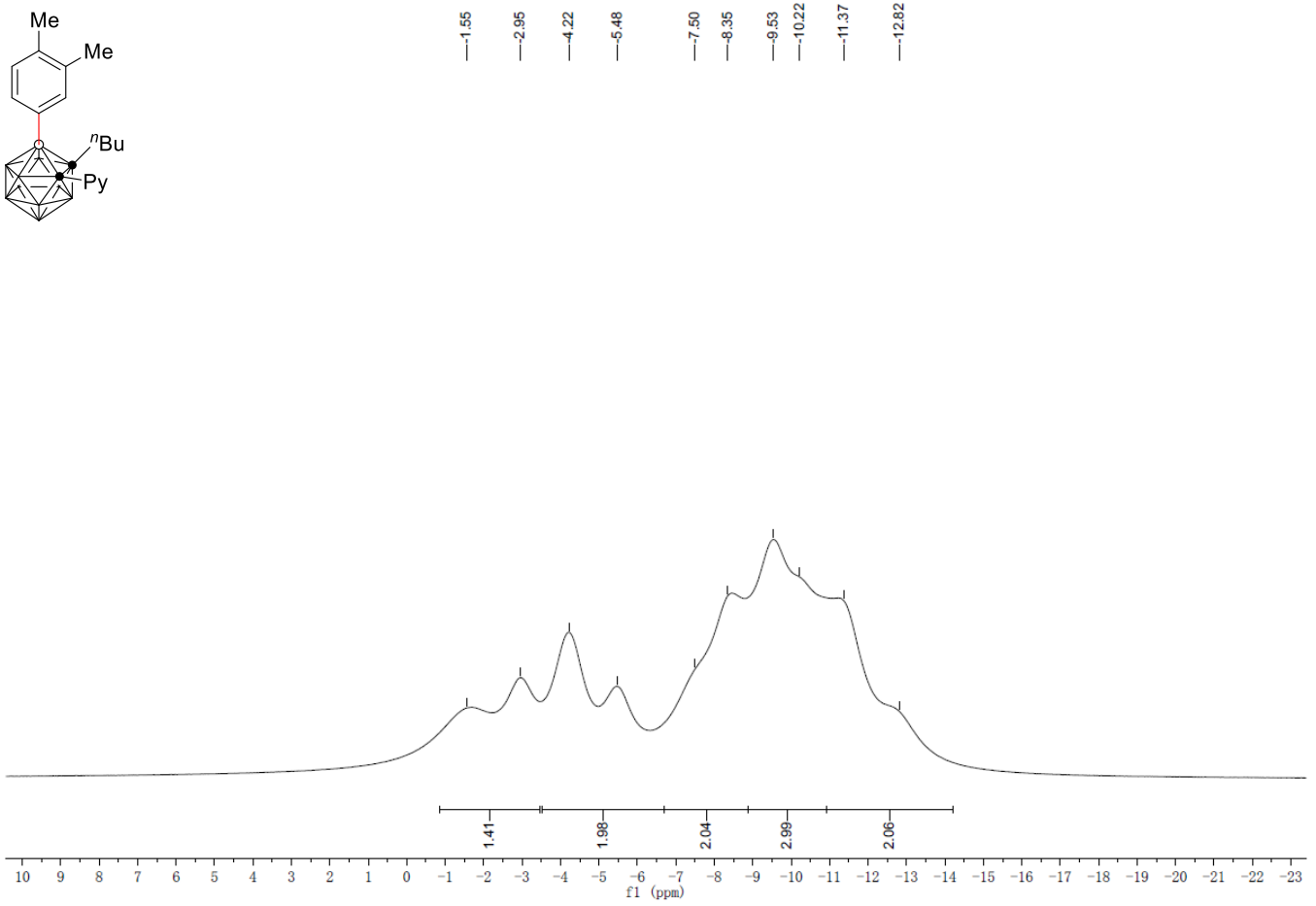
^{1}H NMR (400 MHz, $CDCl_3$ *) of **4j**



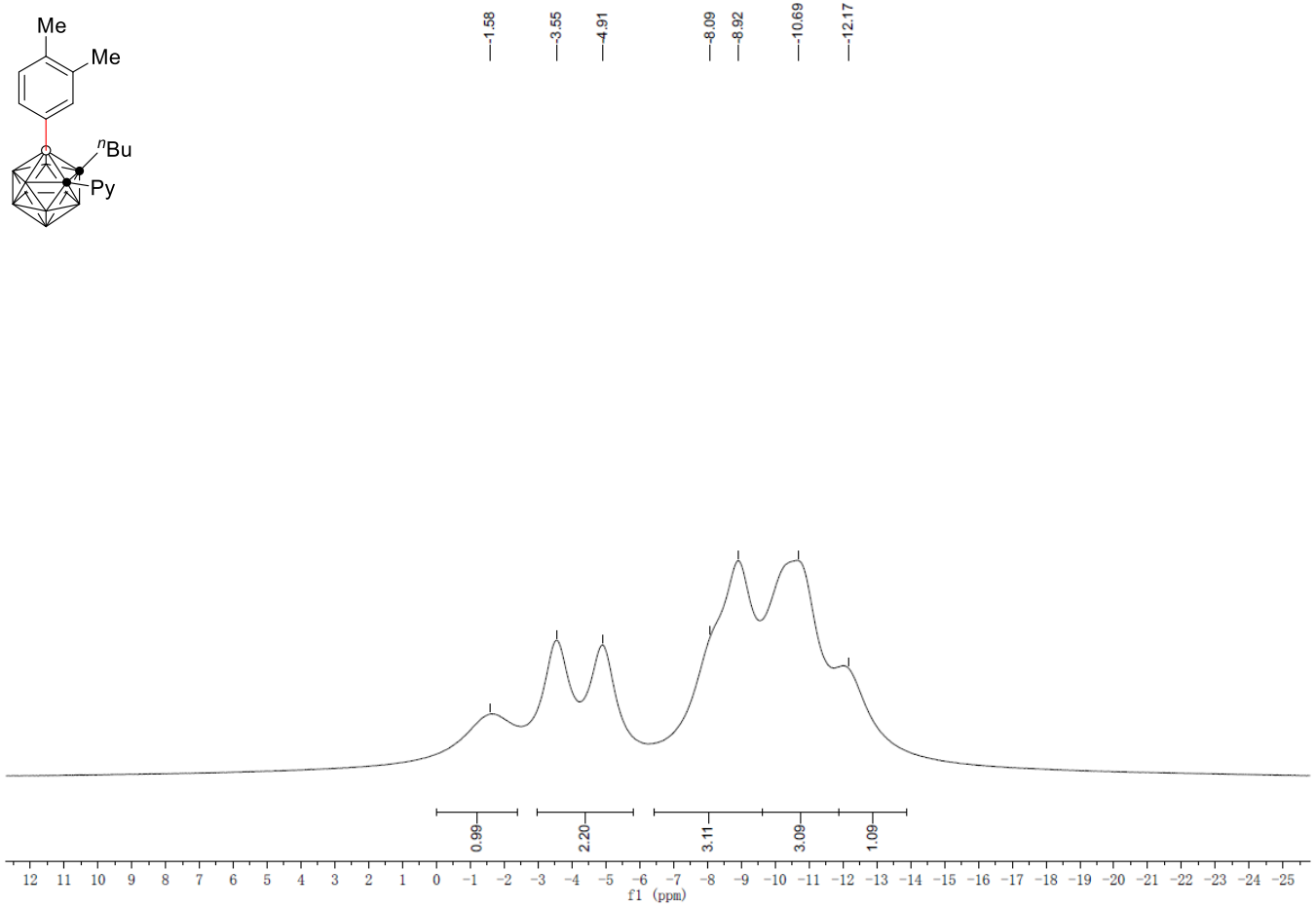
^{13}C NMR (101 MHz, $CDCl_3$ *) of **4j**



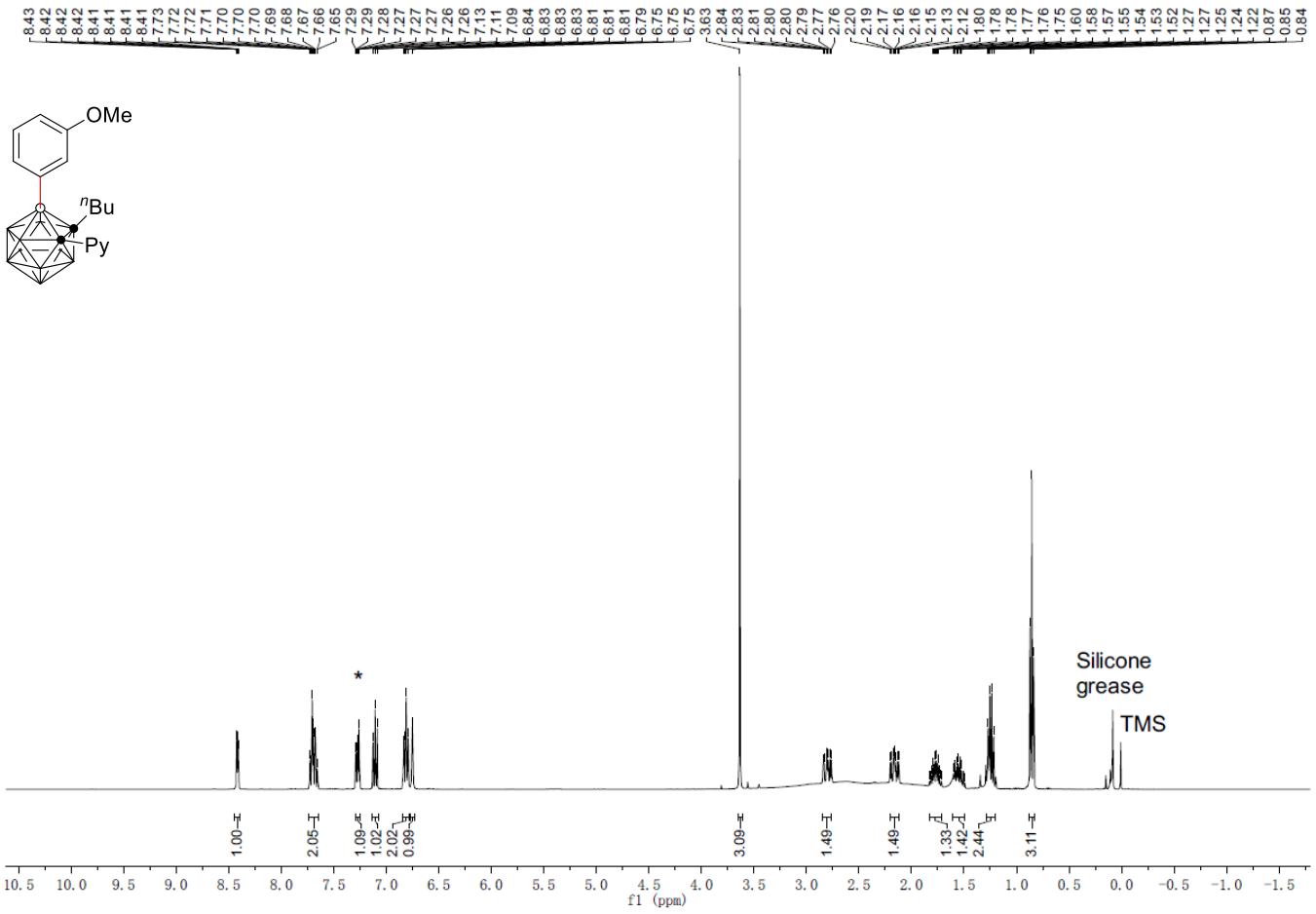
^{11}B NMR (128 MHz, $CDCl_3$ *) of **4j**



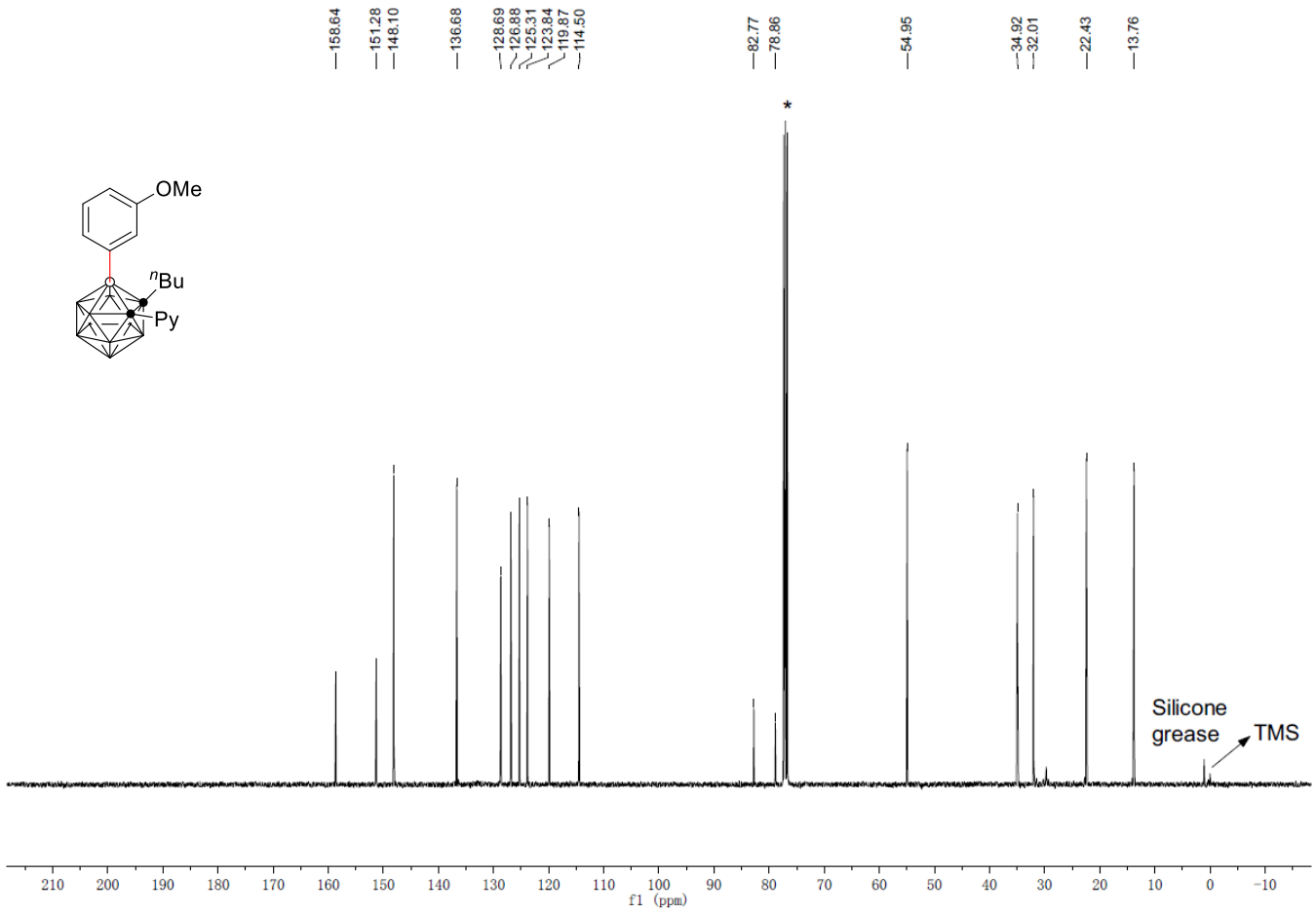
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **4j**



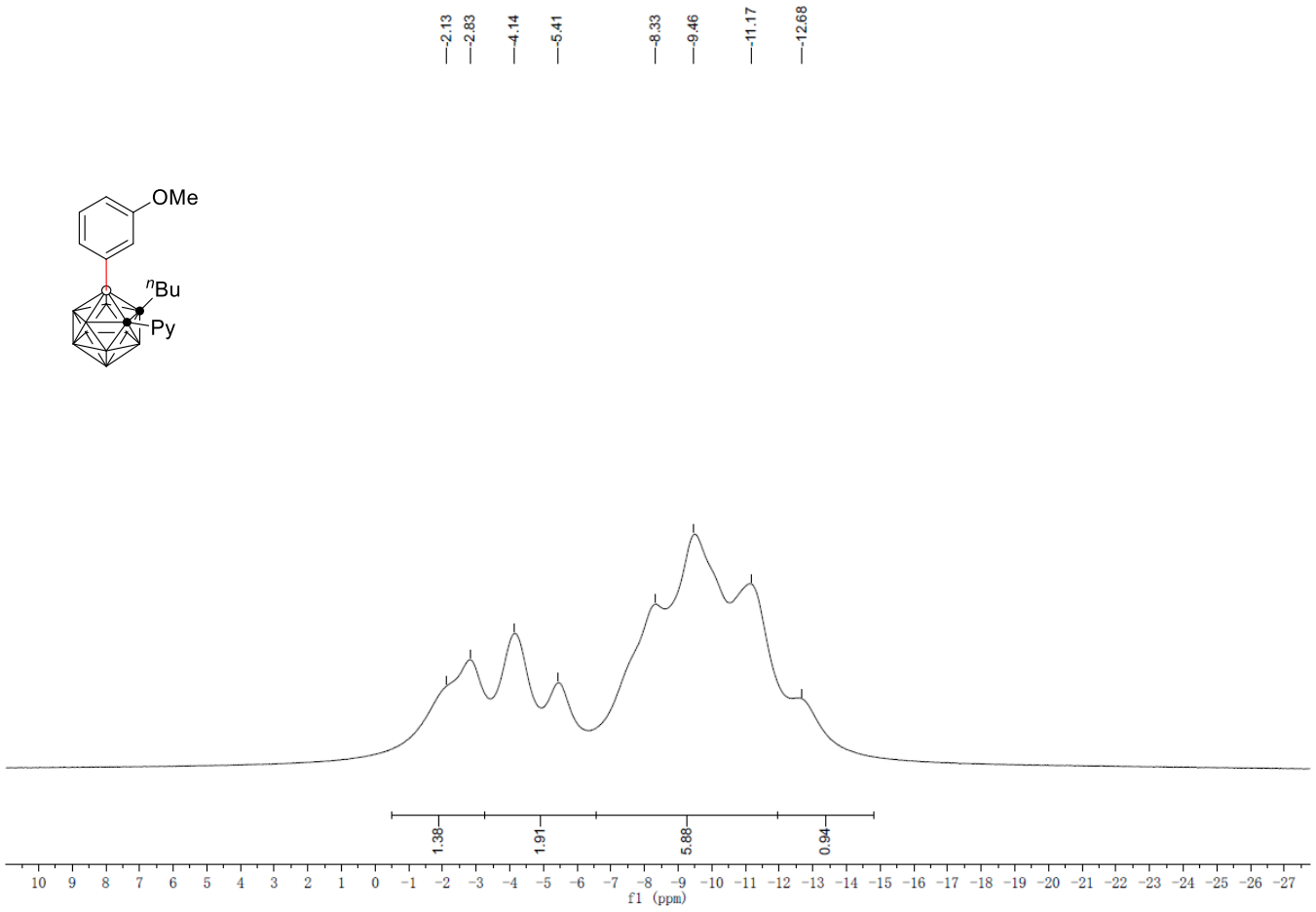
^{1}H NMR (400 MHz, $CDCl_3$ *) of **4k**



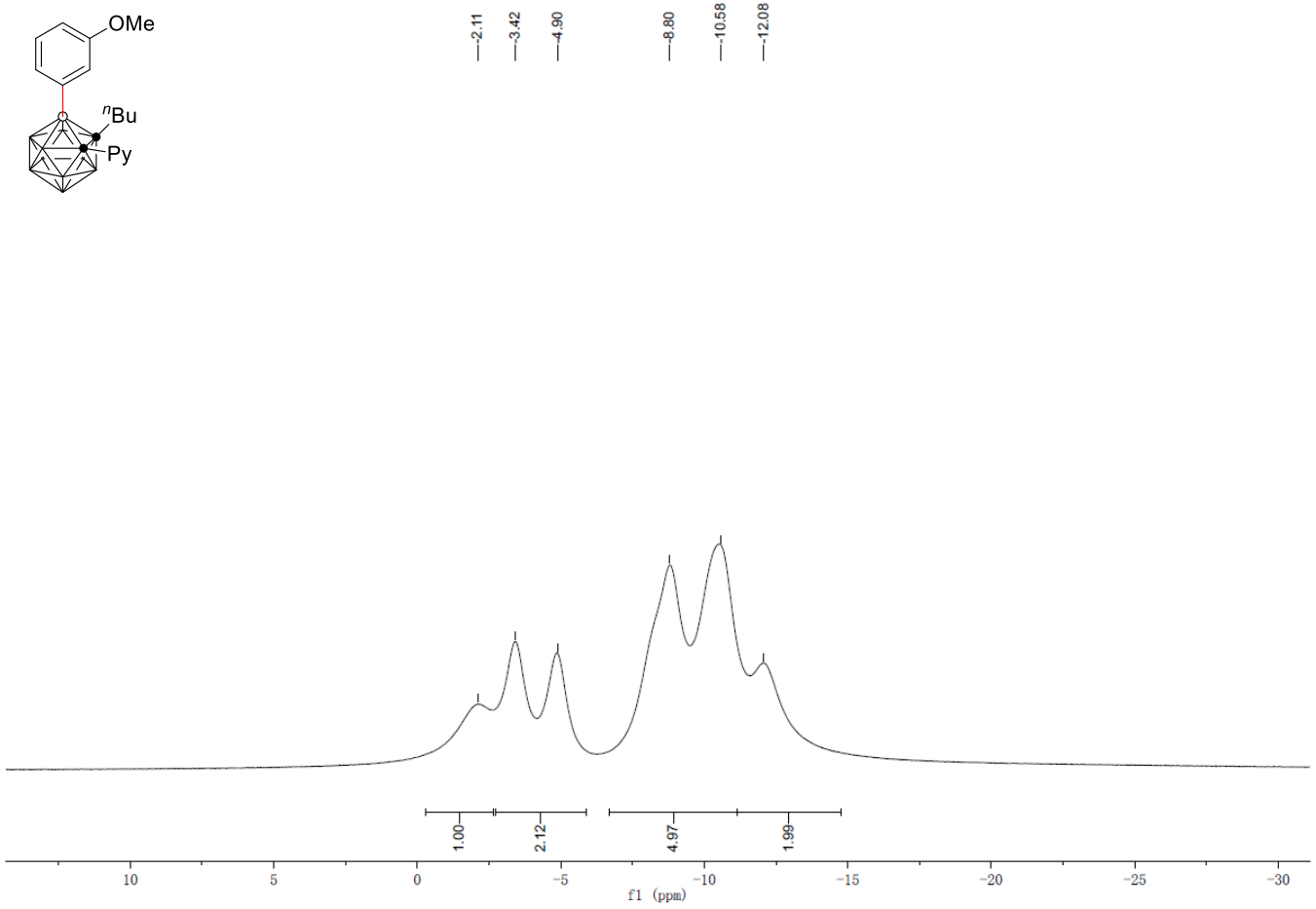
^{13}C NMR (101 MHz, $CDCl_3$*) of **4k**



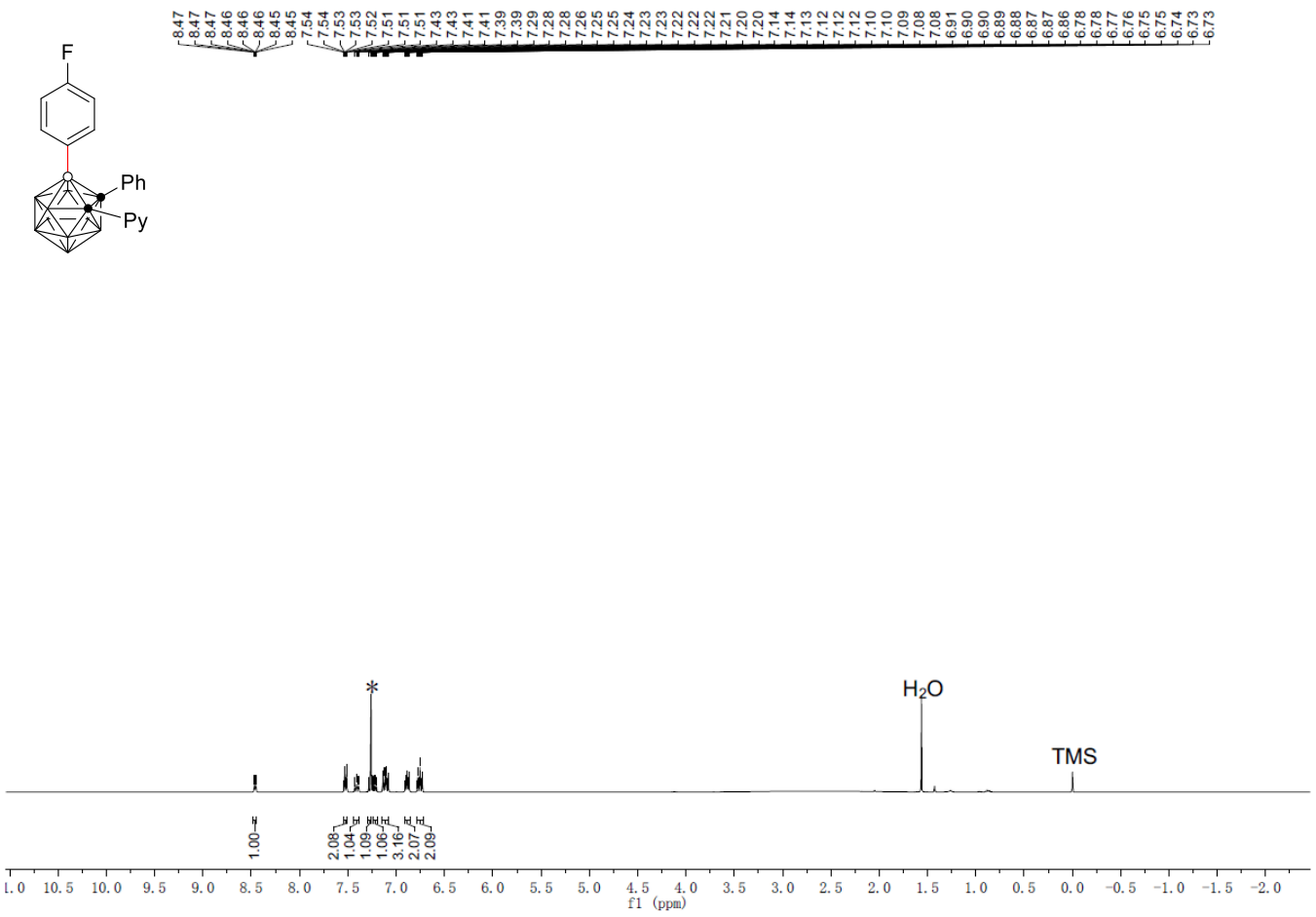
^{11}B NMR (128 MHz, $CDCl_3$ *) of **4k**



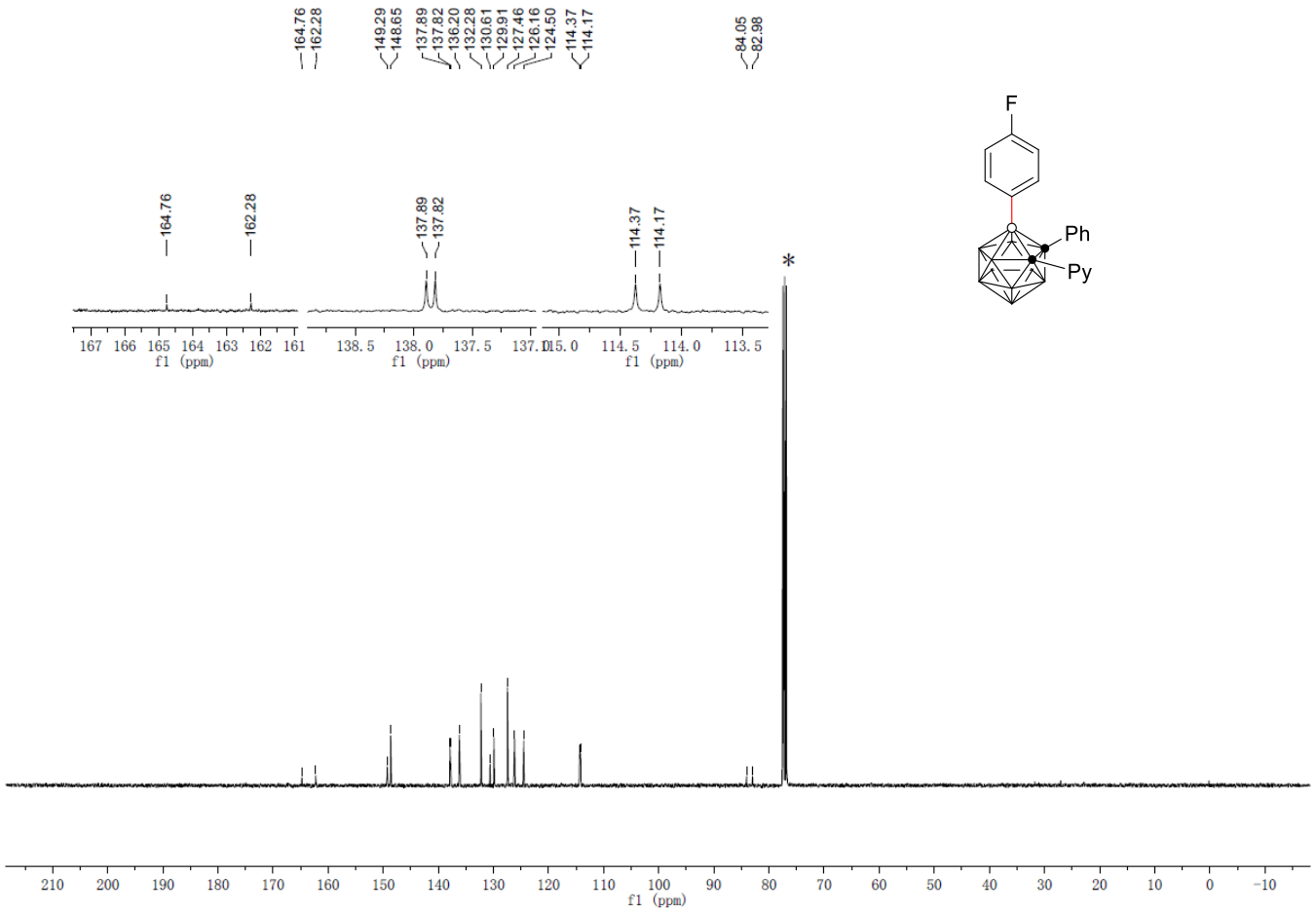
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **4k**



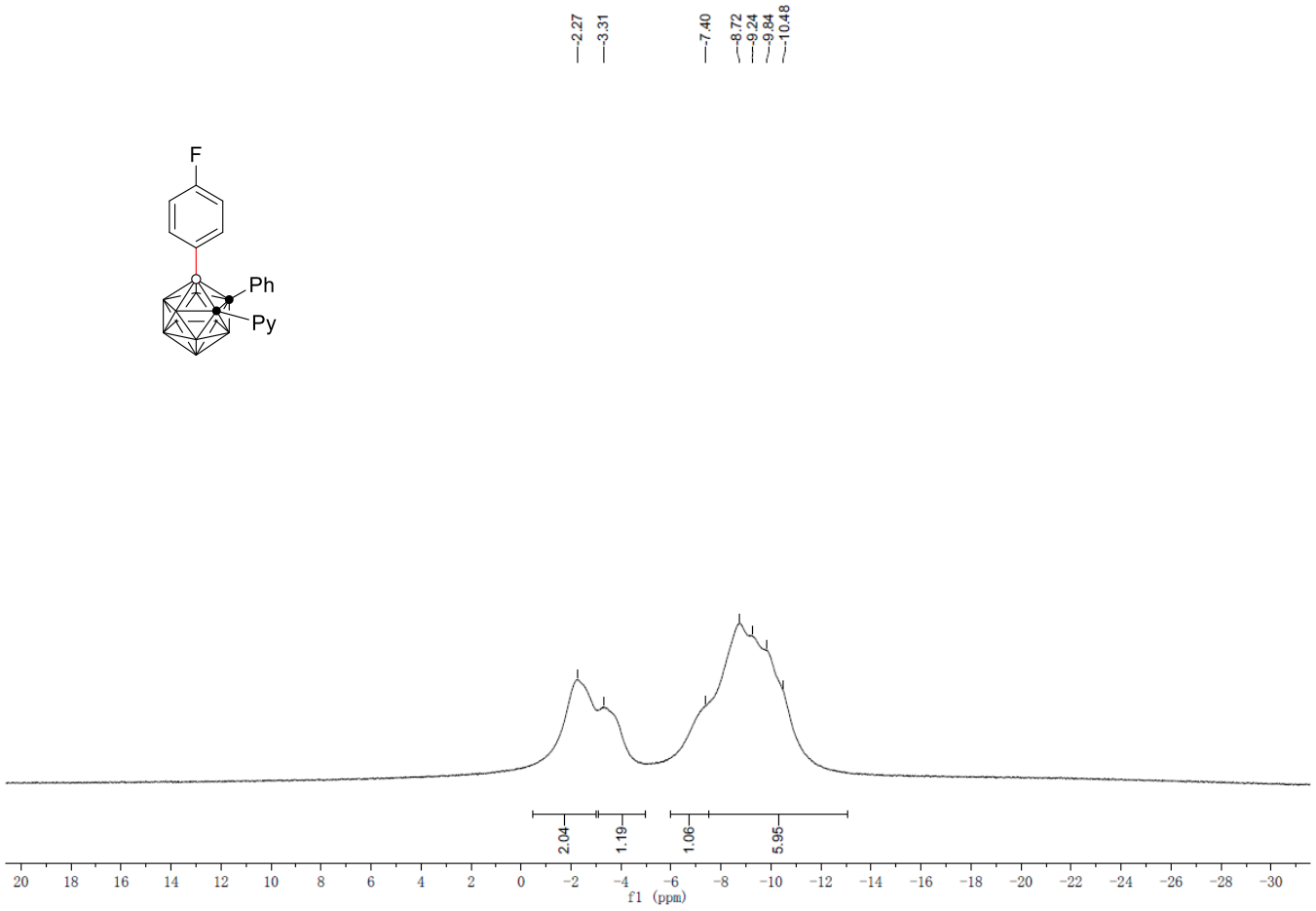
^{1}H NMR (400 MHz, $CDCl_3$ *) of **4l**



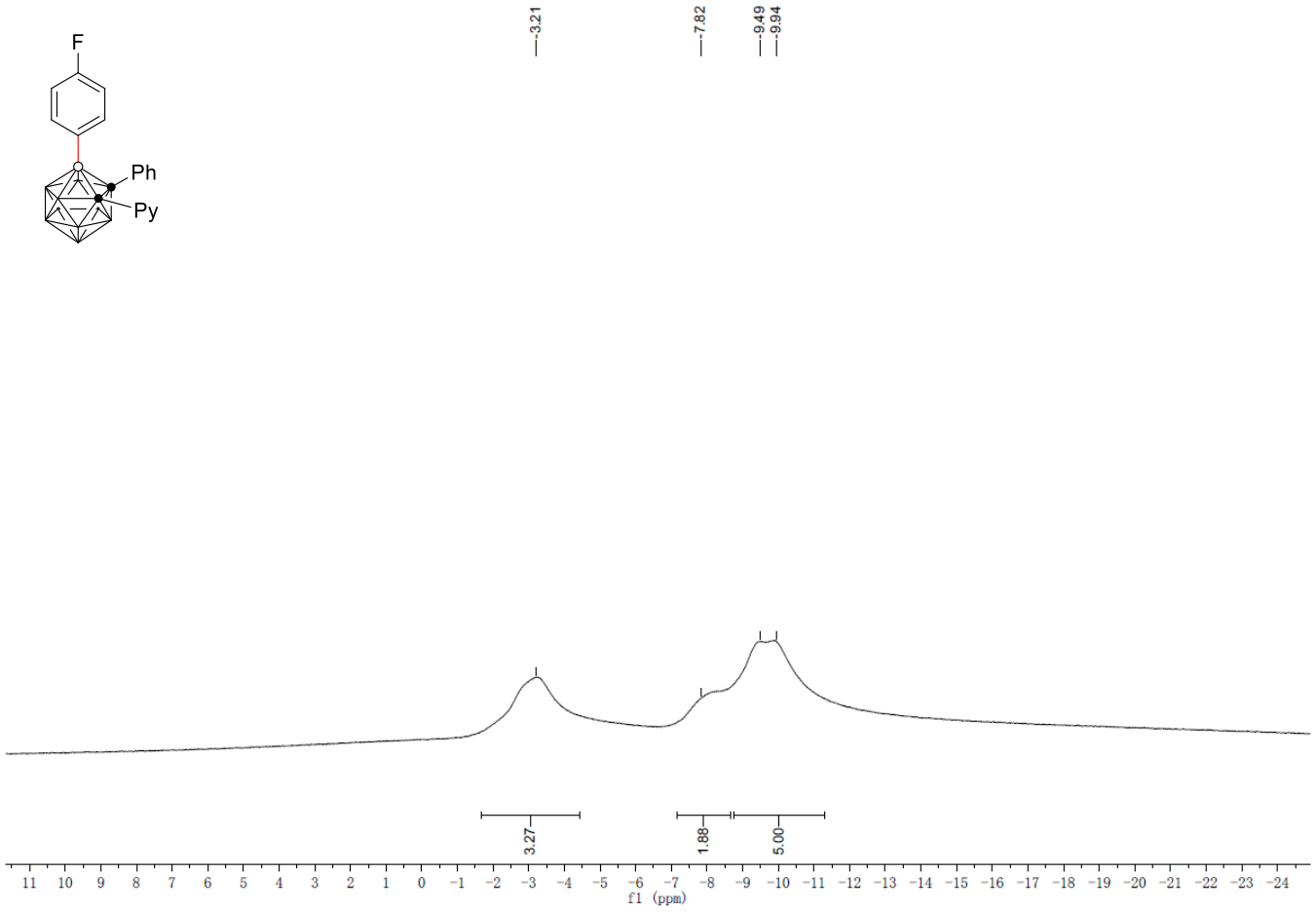
^{13}C NMR (101 MHz, $CDCl_3$ *) of **4l**



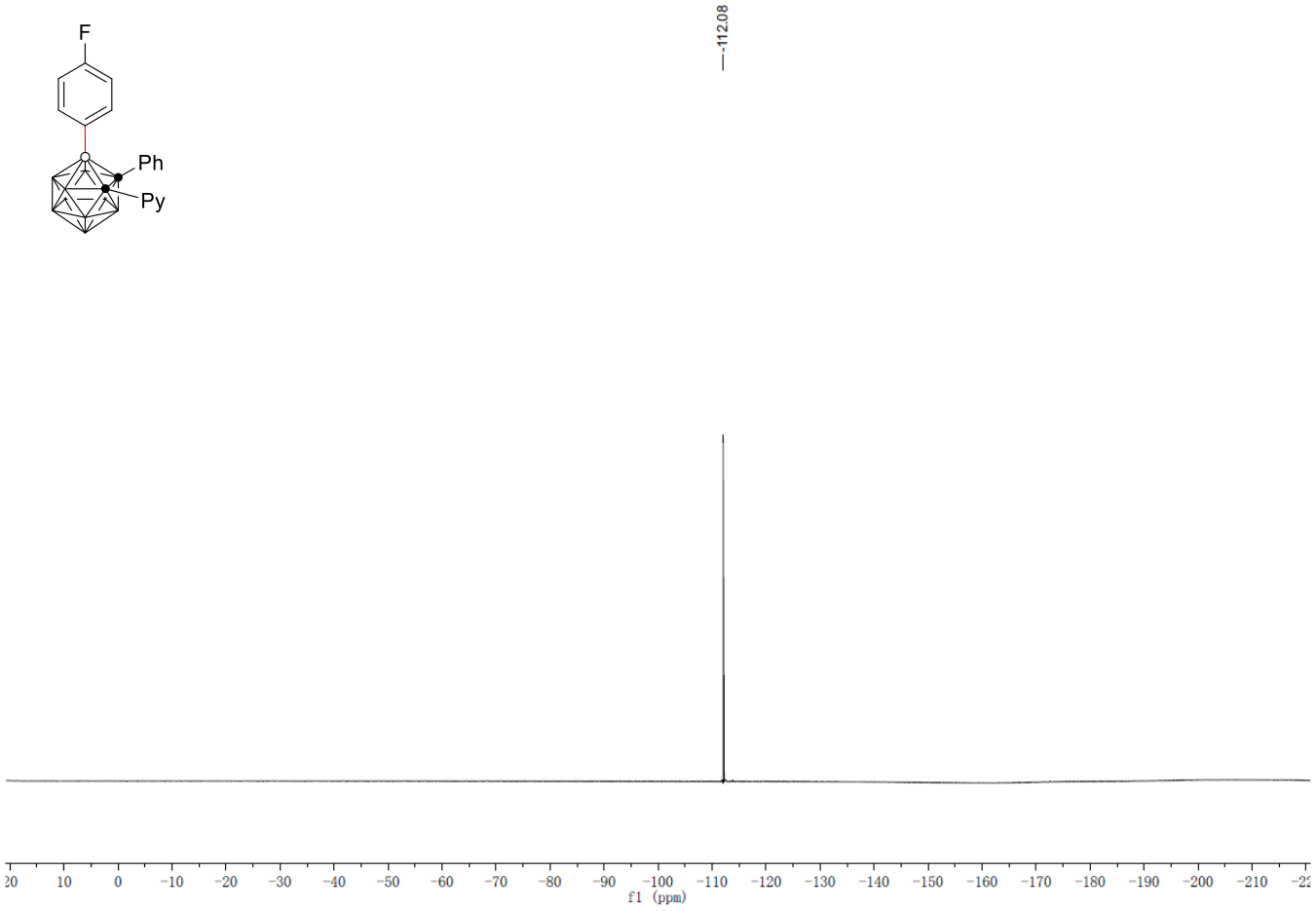
^{11}B NMR (128 MHz, $CDCl_3$ *) of **4l**



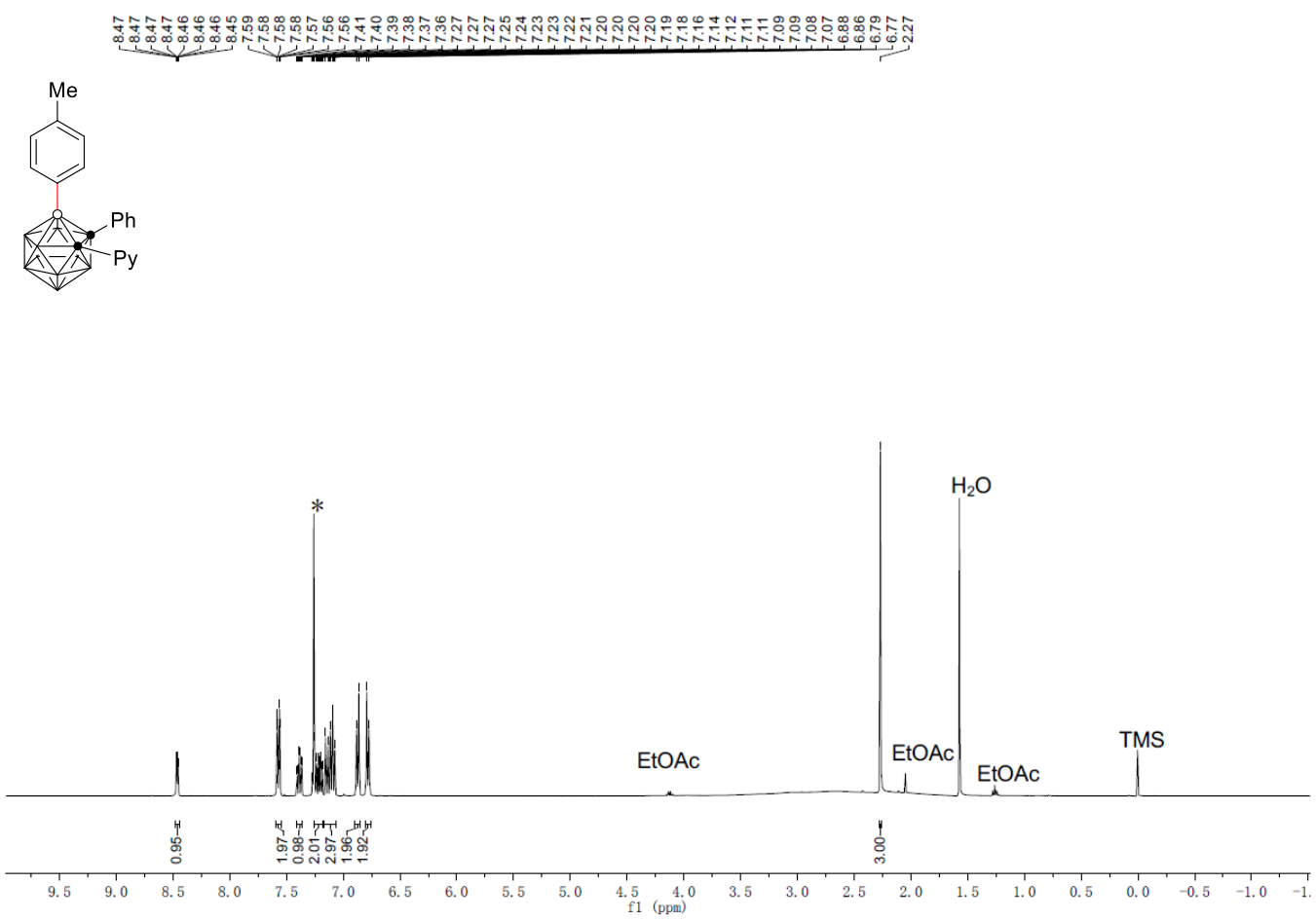
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **4l**



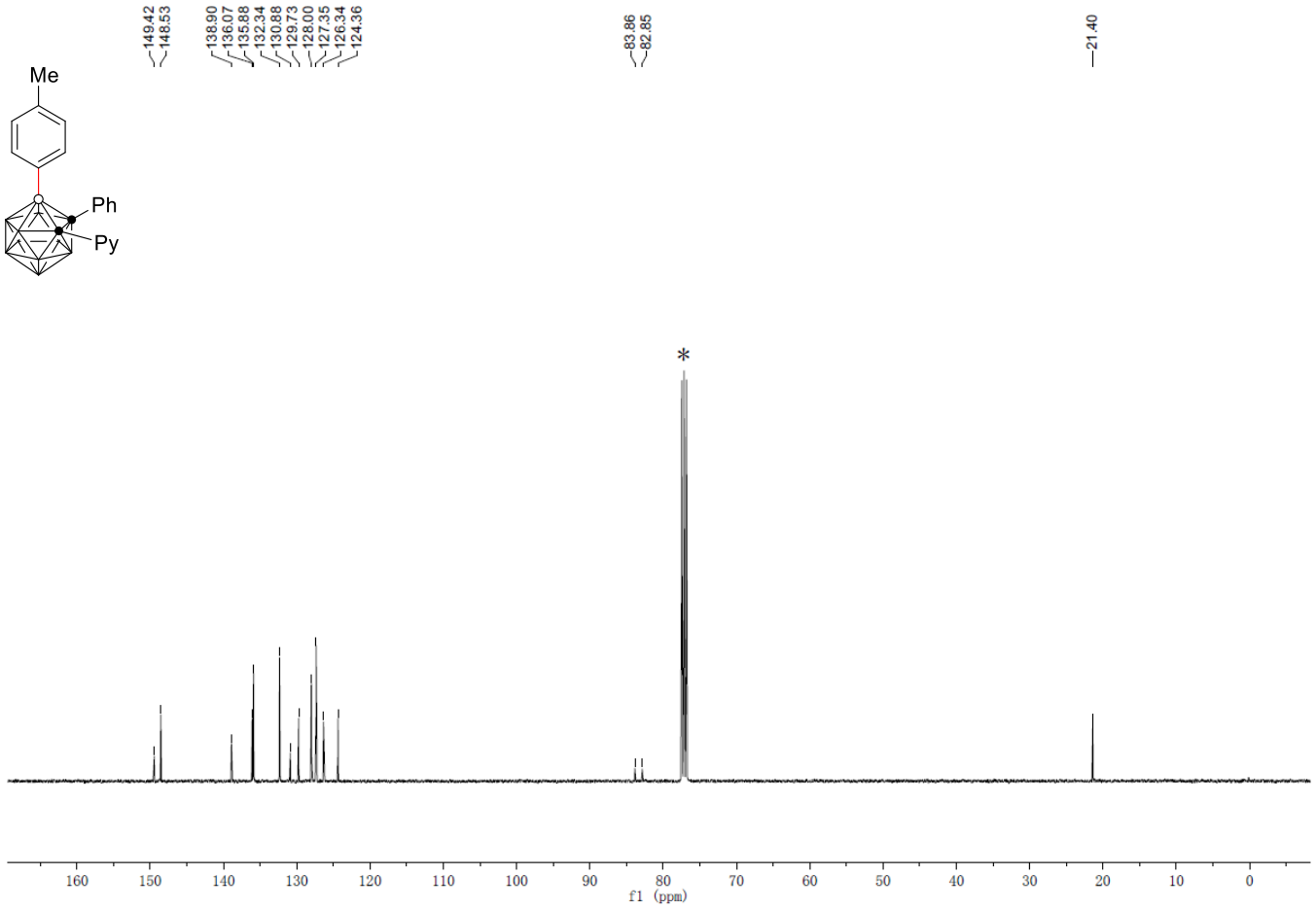
^{19}F NMR (376 MHz, $CDCl_3$ *) of **4l**



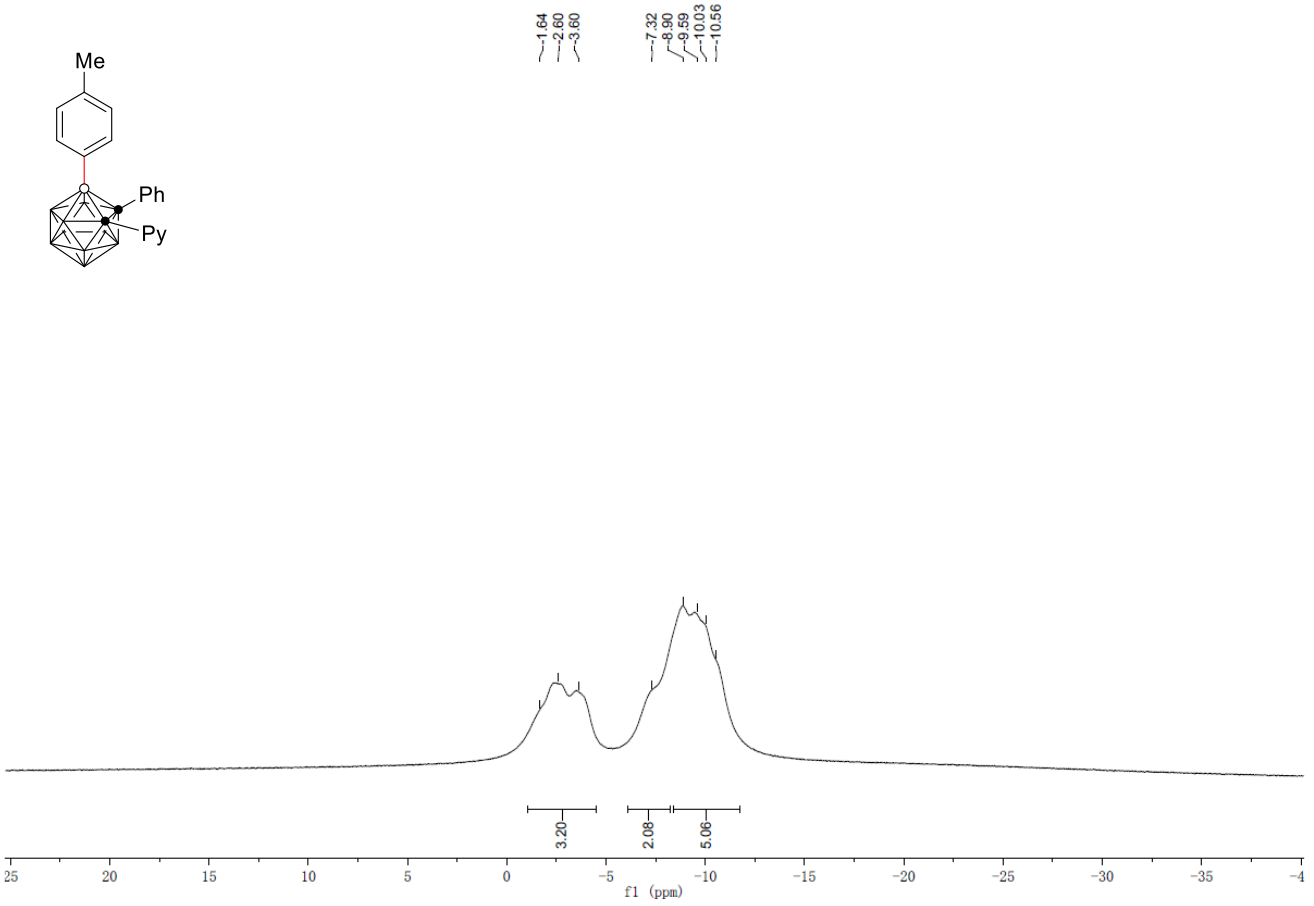
^{1}H NMR (400 MHz, $CDCl_3$ *) of **4m**



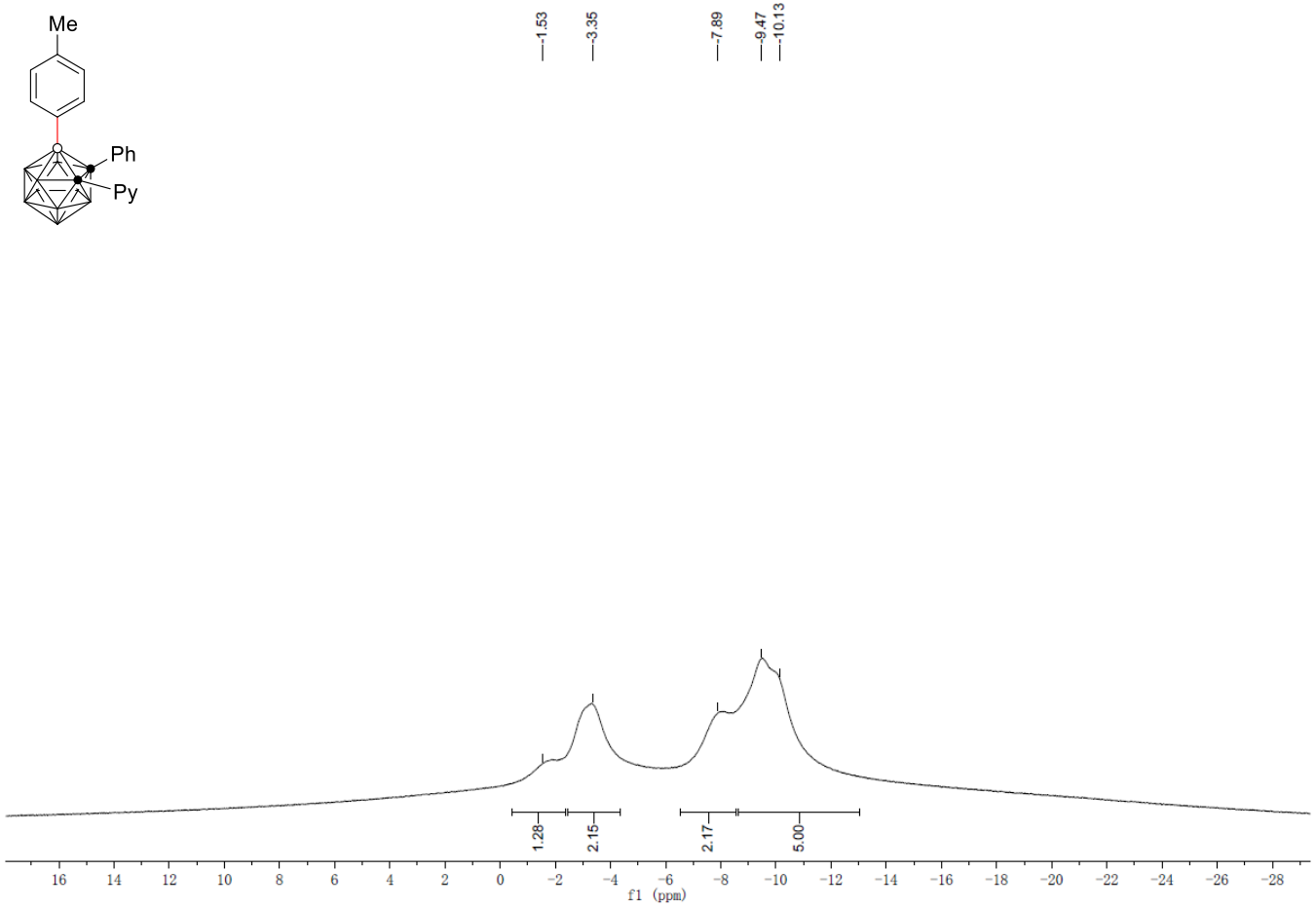
^{13}C NMR (101 MHz, $CDCl_3$ *) of **4m**



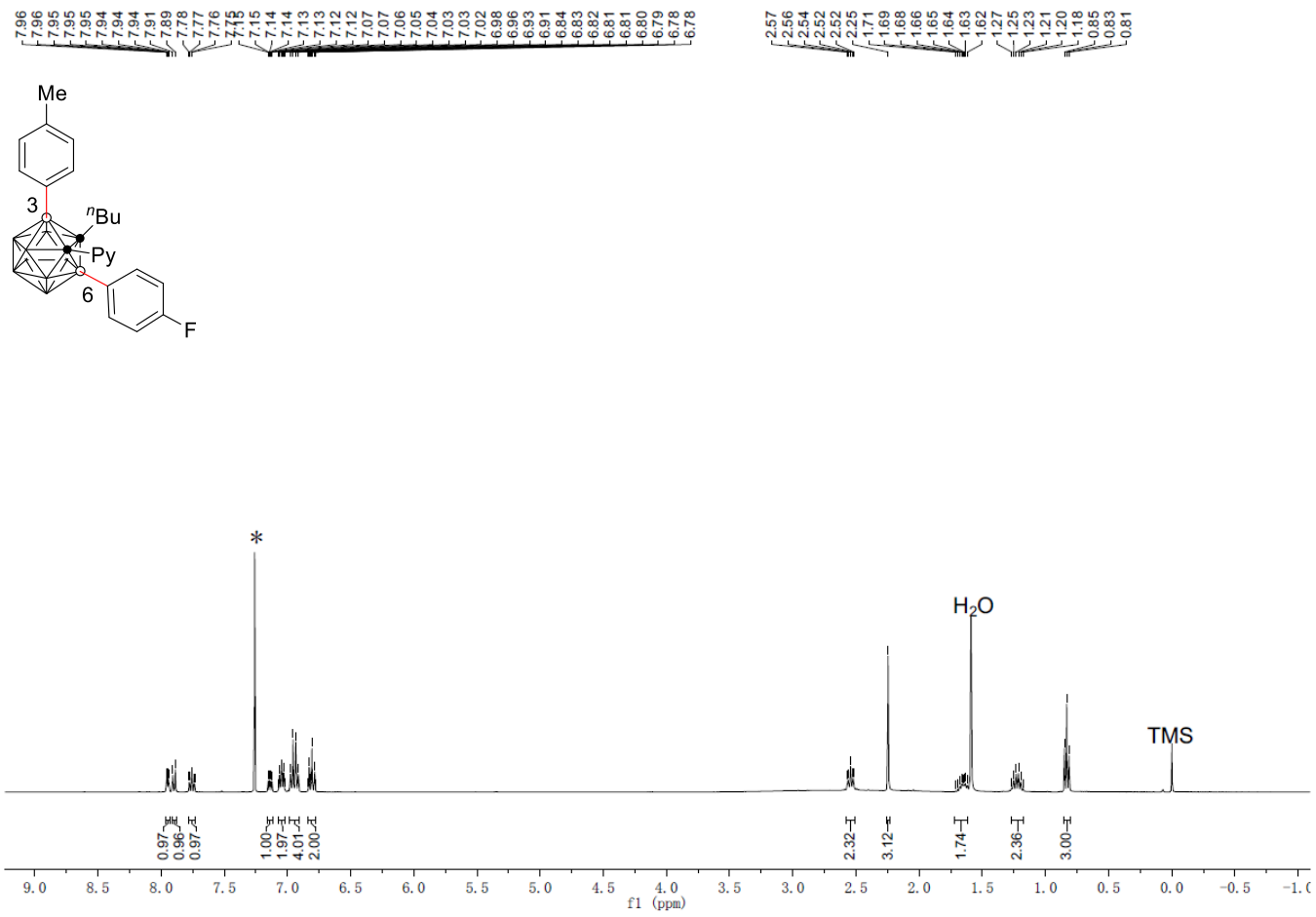
^{11}B NMR (128 MHz, $CDCl_3$ *) of **4m**



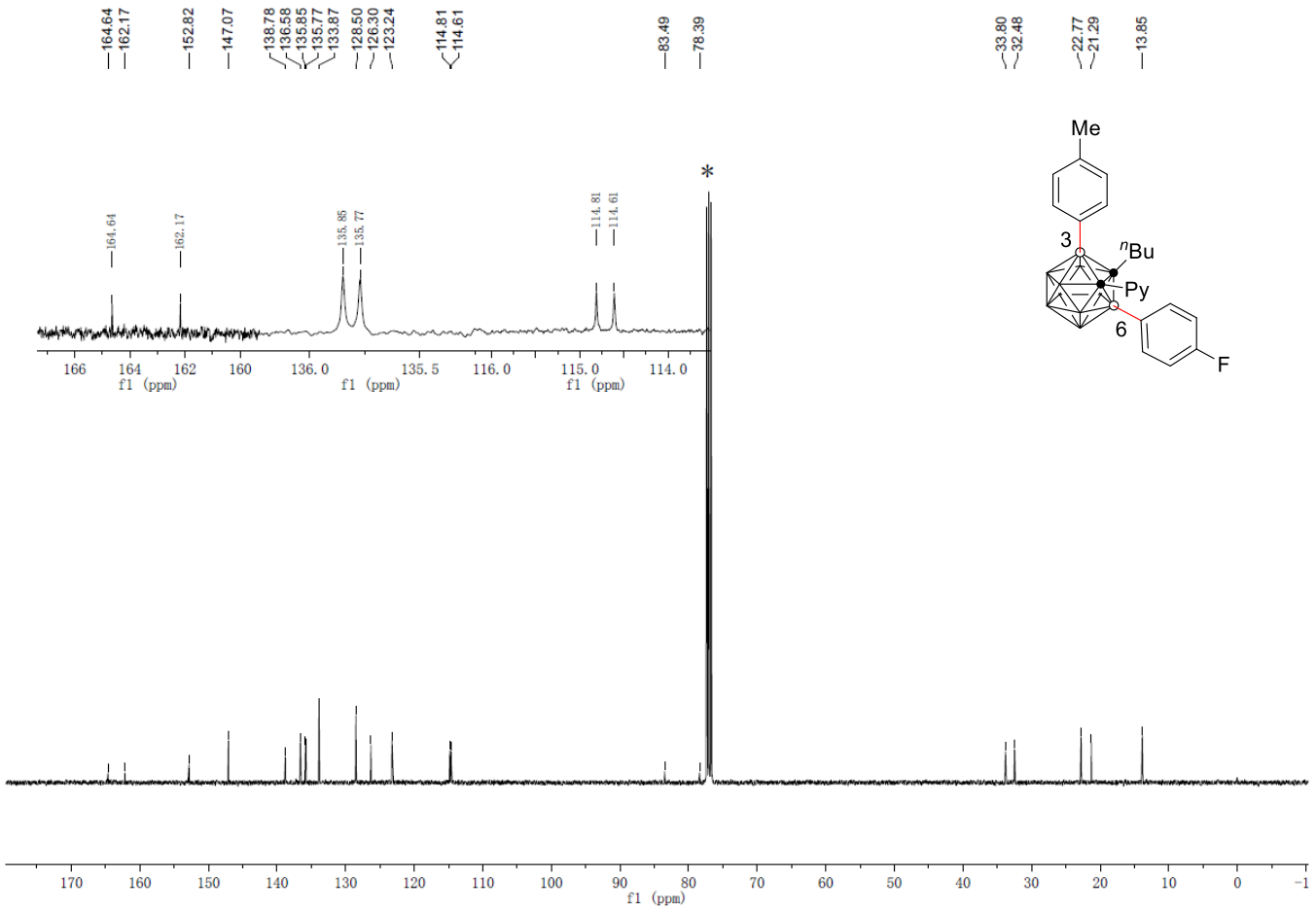
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **4m**



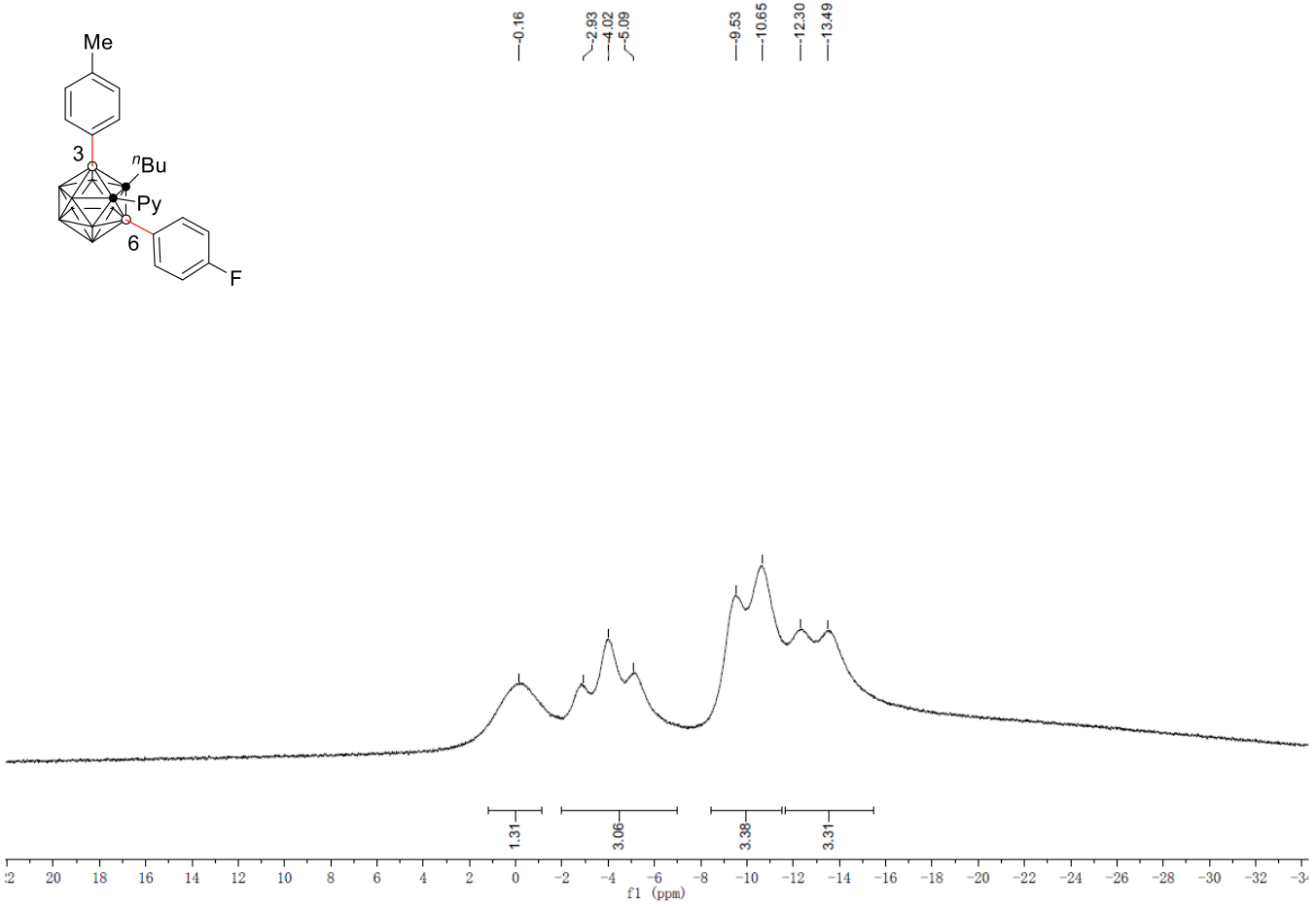
^{1}H NMR (400 MHz, $CDCl_3$ *) of **5**



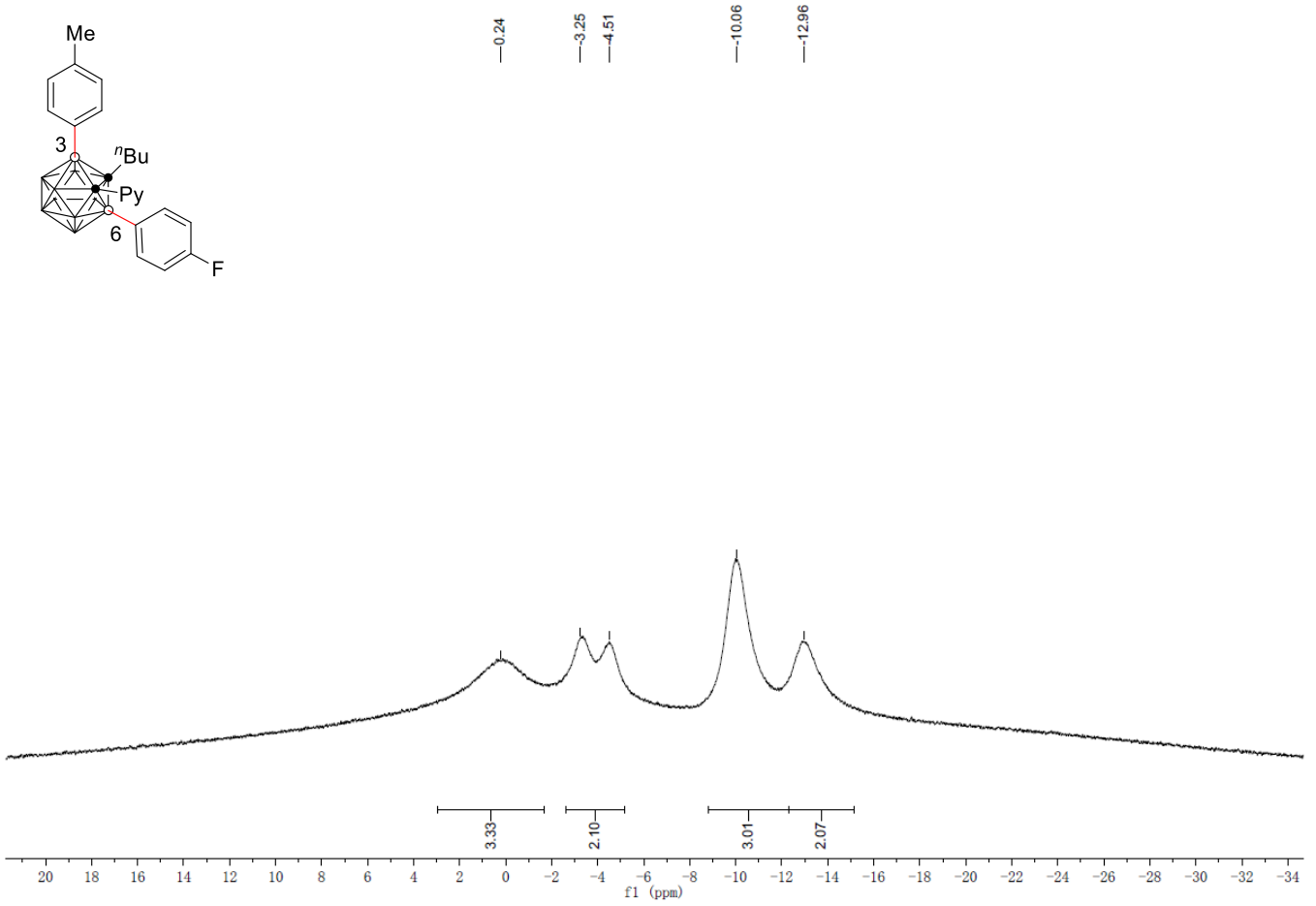
^{13}C NMR (101 MHz, $CDCl_3$ *) of **5**



^{11}B NMR (128 MHz, $CDCl_3$ *) of **5**



$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$ *) of **5**



^{19}F NMR (376 MHz, $CDCl_3$ *) of **5**