Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Palladium catalyzed selective mono-arylation of *o*-carboranes via B-H activation

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Context

General information

Experimental

Spectroscopic data for products

Crystal Data and Summary of Data Collection and Refinement

Copies of ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR and $^{11}B\{^{1}H\}$ NMR

General information

1b[1], 1c[2], 1d[2], 1e[3] and 1f[2] were synthesized according to literature methods. 1,2-dichloroethane was dried and freshly distilled over CaH_2 before use. Other materials were purchased from J&K Scientific and used as received unless otherwise specified. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200-300 meshes) is used for column chromatography, and the distillation range of petroleum ether is 60-90^{o}C. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were recorded on the Bruker 400MHz or 600MHz instruments, $^{11}B\{^{1}H\}$ NMR spectra were recorded on the Bruker 600MHz instruments. All ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectral data are reported in *ppm* relative to tetramethylsilane (TMS) as internal standard, and $^{11}B\{^{1}H\}$ NMR spectral data are referenced to external BF_3•Et_2O. HRMS data were measured with ESI techniques.

Experiment

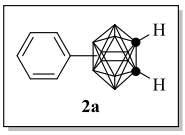
General procedure for palladium catalyzed arylation of *o*-carboranes:

To a 10 mL dried flask were sequentially added *o*-carborane (0.25 mmol), 1,2-dichloroethane (1 mL), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Ag_2CO_3 (138 mg, 0.5 mmol), iodobenzene (0.75 mmol) under argon atmosphere. After the reaction mixture was stirred at 60^{o}C for 48h, the reaction mixture was cooled to room temperature and filtered through a short silica gel column using CH_2Cl_2 as eluent. After evaporation of the solvent, the residue was purified by column chromatography on 200-300 mesh silica gel with petroleum ether as eluent.

Reference:

1. T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, S. I. Trotz, *Inorg. Chem.* 1963, **2**, 1097.
2. T. E. Paxson, M. K. Kaloustian, G. M. Tom, R. J. Wiersema, M. F. Hawthorne, *J. Am. Chem. Soc.* 1972, **94**, 4882.
3. A. F. Armstrong, J. F. Valliant, *Inorg. Chem.* 2007, **46**, 2148.

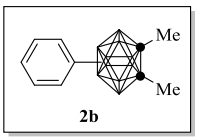
Spectroscopic data for products



2a

An inseparable mixture of B8 and B9 isomers was obtained. The ratio of B8/B9 is 1:8.

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.56-7.54 (d, *J* = 8Hz, 2H), 7.34-7.30 (m, 3H), 3.77 (s, 1H), 3.71(s, 1H); $^{13}C\{^{1}H\}$ NMR (150MHz, $CDCl_3$, *ppm*): δ 133.2, 133.1, 129.8, 128.6, 128.3, 127.9, 59.1, 55.0, 54.9; $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ -1.9 (1B, -*B(9)*Ph), -2.6 (1B), -3.6 (1B), -8.9 (1B), -9.8 (1B), -12.9 (1B), -14.3 (1B), -14,5 (1B), -15.0 (1B), -16.8 (1B); HRMS: calculated for $C_8B_{10}H_{17}$ (M^++H) 221.2328; found: 221.2333.



2b

An inseparable mixture of B8 and B9 isomers was obtained. The ratio of B8/B9 is 1:1.6.

^{1}H NMR (400MHz, $CDCl_3$, *ppm*): δ 7.49-7.48 (m, 1H), 7.37-7.36 (m, 1H), 7.25-7.19 (m, 3H), 2.04(s, 6H); $^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$, *ppm*): δ 133.0, 132.5, 127.5, 127.3, 127.2, 127.0, 72.2, 72.1, 67.8, 23.4, 23.2, 22.4; $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ 4.9 (1B, -*B(9)*Ph), 0.1 (1B, -*B(8)*Ph), -4.7 (2B), -9.0 (3B), -10.2 (7B), -11.3 (2B); HRMS: calculated for $C_{10}B_{10}H_{21}$ (M^++H) 249.2641; found: 249.2640.

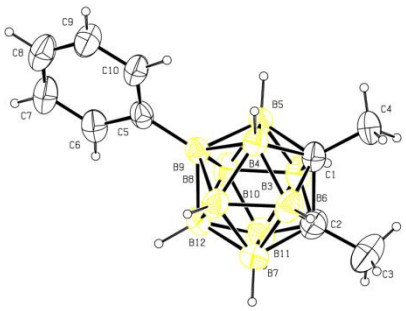
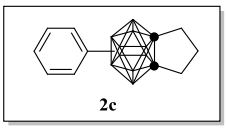
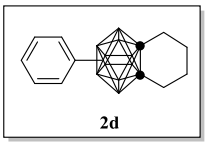


Figure S1. Crystal structure of **2b**-B9



An inseparable mixture of B8 and B9 isomers was obtained. The ratio of B8/B9 is 1:1.4.

^{1}H NMR (400MHz, $CDCl_3$, *ppm*): δ 7.51-7.50 (m, 1H), 7.38-7.37 (m, 1H), 7.26-7.25 (m, 2H), 7.22-7.20 (m, 1H), 2.57-2.43(m, 6H); $^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$, *ppm*): δ 133.0, 132.6, 127.5, 127.3, 126.9, 82.9, 82.6, 78.9, 34.8, 34.7, 33.9, 32.3, 32.0; $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ 3.5 (1B, *-B(9)*Ph), 2.5 (1B, *-B(8)*Ph), -6.3 (2B), -7.6 (2B), -9.1 (1B), -9.7 (2B), -11.9 (3B), -12.4 (3B); HRMS: calculated for $C_{11}B_{10}H_{21}$ (M^{+}+H) 261.2641; found: 261.2641.



An inseparable mixture of B8 and B9 isomers was obtained. The ratio of B8/B9 is 1:1.4.

^{1}H NMR (400MHz, $CDCl_3$, *ppm*): δ 7.38-7.37 (m, 2H), 7.23-7.19 (m, 3H), 2.49 (brs, 4H), 1.63-1.58 (m, 4H); $^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$, *ppm*): δ 133.0, 132.5, 127.5, 127.3, 127.2, 126.9, 71.9, 71.8, 67.5, 32.9, 32.8, 32.1, 19.8, 19.7, 19.6; $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ 4.3 (1B, *-B(9)*Ph), 1.2 (1B, *-B(8)*Ph), -5.3 (2B), -8.8 (2B), -9.8 (2B), -10.3 (2B), -12.4 (2B), HRMS: calculated for $C_{12}B_{10}H_{23}$ (M^{+}+H) 275.2797;

found: 275.2796.

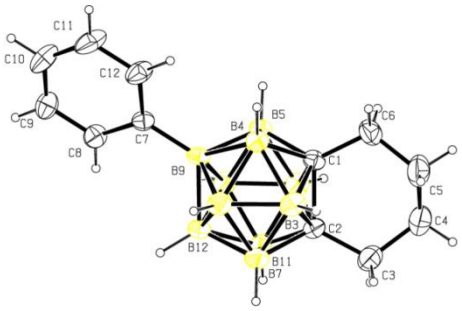
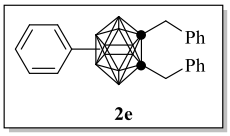
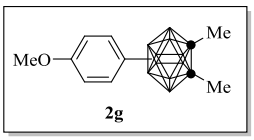


Figure S2. Crystal structure of **2d**-B9



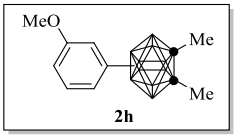
An inseparable mixture of B8 and B9 isomers was obtained. The ratio of B8/B9 is 1:1.6.

^{1}H NMR (400MHz, $CDCl_3$, *ppm*): δ 7.38-7.34 (m, 6H), 7.25-7.23 (m, 6H), 7.15-7.14 (m, 3H), 3.67 (s, 4H); $^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$, *ppm*): δ 135.1, 134.9, 132.4, 130.4, 130.3, 128.7, 128.6, 128.1, 127.2, 126.9, 78.3, 73.9, 41.4, 40.6; $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ 5.7 (1B, *-B(9)*Ph), 0.5 (1B, *-B(8)*Ph), -3.9 (3B), -9.7 (3B), -10.8 (8B); HRMS: calculated for $C_{22}B_{10}H_{29}$ (M^{+}+H) 401.3267; found: 401.3267.



An inseparable mixture of B8 and B9 isomers was obtained. The ratio of B8/B9 is 1:1.8.

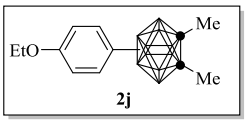
^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.30-7.29 (d, *J* = 6Hz, 2H), 6.80-6.79 (d, *J* = 6Hz, 2H), 3.77 (s, 3H), 2.07 (s, 6H); $^{13}C\{^{1}H\}$ NMR (150MHz, $CDCl_3$, *ppm*): δ 159.1, 135.9, 133.6, 113.0, 71.9, 67.2, 55.0, 23.4, 22.4; $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ 4.9 (1B, *-B(9)*Ar), -0.1(1B, *-B(8)*Ar), -5.1 (2B), -9.1 (2B), -10.0 (5B), -11.4(1B); HRMS: calculated for $C_{11}B_{10}H_{23}O_1$ (M^{+}+H) 279.2747; found: 279.2747.



2h

An inseparable mixture of B8 and B9 isomers was obtained. The ratio of B8/B9 is 1:1.7.

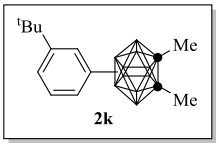
^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.25-7.14 (m, 1H), 7.14-7.10 (m, 1H), 7.06-6.94 (m, 1H), 6.82-6.76 (m, 1H), 3.80 (s, 3H), 2.07 (s, 6H); ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$, *ppm*): δ 158.7, 158.6, 140.5, 128.5, 128.4, 125.5, 125.0, 118.7, 118.2, 112.5, 112.3, 72.1, 72.0, 67.8, 55.0, 54.9, 23.4, 23.2, 22.4; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, *ppm*): δ 4.7 (1B, -*B(9)*Ar), -0.02 (1B, -*B(8)*Ar), -4.8 (1B), -5.0 (1B), -9.0 (4B), -10.1 (8B), -11.3 (1B); HRMS: calculated for $C_{11}B_{10}H_{23}O_1$ (M^++H) 279.2747; found: 279.2745.



2j

An inseparable mixture of B8 and B9 isomers was obtained. The ratio of B8/B9 is 1:1.5.

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.28-7.27 (d, *J* = 6Hz, 2H), 6.78-6.77 (d, *J* = 6Hz, 2H), 4.03-3.99 (m, 2H), 2.07 (s, 6H), 1.42-1.34 (m, 3H); ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$, *ppm*): δ 158.6, 158.4, 135.9, 134.1, 133.6, 113.7, 113.6, 72.1, 67.2, 63.1, 23.4, 23.2, 22.4, 14.9; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, *ppm*): δ 4.9 (1B, -*B(9)*Ar), 0.2 (1B, -*B(8)*Ar), -4.7 (1B), -4.9 (1B), -9.0 (3B), -10.1 (8B), -11.3 (1B); HRMS: calculated for $C_{12}B_{10}H_{25}O_1$ (M^++H) 293.2903; found: 293.2903.

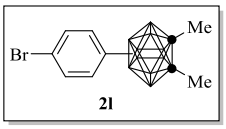


2k

An inseparable mixture of B8 and B9 isomers was obtained. The ratio of B8/B9 is 1:2.5.

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.42 (s, 1H), 7.31-7.28 (m, 2H), 7.25-7.24 (m, 1H), 2.06 (s, 6H), 1.28 (s, 9H); ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$, *ppm*): δ 149.9, 149.6. 132.8, 132.2, 124.5, 124.3, 72.0, 67.5, 34.4, 34.3, 31.3, 23.4, 23.2, 22.4;

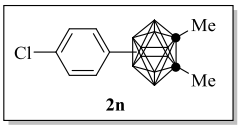
$^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ 5.7 (1B, *-B(9)*Ar), 0.9 (1B, *-B(8)*Ar), -4.0 (1B), -4.3 (1B), -8.3 (3B), -9.3 (8B), -10.7 (1B); HRMS: calculated for $C_{14}B_{10}H_{29}$ (M^++H) 305.3267; found: 305.3265



2l

An inseparable mixture of B8 and B9 isomers was obtained. The ratio of B8/B9 is 1:1.6.

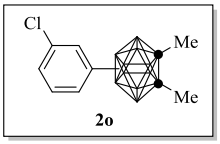
^{1}H NMR (400MHz, $CDCl_3$, *ppm*): δ 7.39-7.32 (m, 3H), 7.23-7.21 (m, 1H), 2.08 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$, *ppm*): δ 139.8, 134.7, 134.2, 130.5, 130.3, 72.4, 68.0, 23.4, 23.2, 22.4; $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ 4.4 (1B, *-B(9)*Ar), -0.4 (1B, *-B(8)*Ar), -4.8 (2B), -8.9 (2B), -10.1 (5B), -11.2 (1B); HRMS: calculated for $C_{10}B_{10}H_{20}Br_1$ (M^++H) 327.1746; found: 327.1749.



2n

An inseparable mixture of B8 and B9 isomers was obtained. The ratio of B8/B9 is 1:2.2.

^{1}H NMR (400MHz, $CDCl_3$, *ppm*): δ 7.41-7.39 (d, *J* = 8Hz, 1H), 7.29-7.27(d, *J* = 8Hz, 1H), 7.23-7.21 (d, *J* = 8Hz, 1H), 7.19-7.17 (d, *J* = 8Hz, 1H), 2.08 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$, *ppm*): δ 134.3, 133.8, 133.6, 133.3, 127.6, 127.4, 72.3, 72.2, 68.0, 23.4, 23.2, 22.4; $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ 4.4 (1B, *-B(9)*Ar), -0.4 (1B, *-B(8)*Ar), -4.7 (2B), -8.9 (2B), -10.1 (3B), -11.2 (1B); HRMS: calculated for $C_{10}B_{10}H_{20}Cl_1$ (M^++H) 283.2251; found: 283.2253.

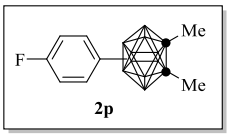


2o

An inseparable mixture of B8 and B9 isomers was obtained. The ratio of B8/B9 is 1:1.9.

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.32-7.13 (m, 4H), 2.07 (s, 6H); $^{13}C\{^{1}H\}$ NMR (150MHz, $CDCl_3$, *ppm*): δ 133.4, 132.8, 132.3, 131.1, 130.6, 128.8, 128.7, 127.3,

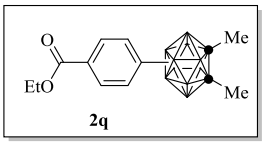
127.0, 72.4, 72.3, 68.3, 23.4, 23.2, 22.4; $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ 4.1 (1B, -*B(9)*Ar), -0.6 (1B, -*B(8)*Ar), -4.8 (1B), -5.0 (1B), -8.9 (2B), -10.1 (8B), -11.1 (1B); HRMS: calculated for $C_{10}B_{10}H_{20}Cl_1$ (M^++H) 283.2251; found: 283.2250.



2p

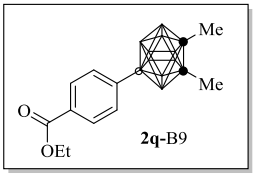
An inseparable mixture of B8 and B9 isomers was obtained. The ratio of B8/B9 is 1:1.8.

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.46-7.43 (m, 1H), 7.33-7.31 (m, 1H), 6.97 -6.94 (m, 1H), 6.92-6.89 (m, 1H), 2.08 (s, 6H); $^{13}C\{^{1}H\}$ NMR (150MHz, $CDCl_3$, *ppm*): δ 163.5-161.9 (d, *J* = 93Hz), 134.5, 134.0, 114.3, 114.1, 72.3, 72.2, 67.7, 23.4, 23.2, 22.4; $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ 4.9 (1B, -*B(9)*Ar), 0.1 (1B, -*B(8)*Ar), -4.4 (2B), -8.6 (3B), -9.7 (4B), -10.9 (1B); HRMS: calculated for $C_{10}B_{10}H_{20}F_1$ (M^++H) 267.2547; found: 267.2548.



2q

The isomers of B8 and B9 can be separated by column chromatography. The ratio of B8/B9 is 1:2.7.



2q-B9

^{1}H NMR (400MHz, $CDCl_3$, *ppm*): δ 7.88-7.86 (d, *J* = 8Hz, 2H), 7.44-7.42 (d, *J* = 8Hz, 2H), 4.37-4.32 (q, *J* = 8Hz, 2H), 2.09 (s, 3H), 2.07 (s, 3H), 1.38-1.34(t, *J* = 8Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$, *ppm*): δ 167.0, 142.7, 132.5, 129.0, 128.2, 72.3, 68.5, 60.6, 23.4, 22.5, 14.3; $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ 4.3 (1B, -*B*Ar), -5.0 (3B), -8.9 (2B), -10.1 (4B); HRMS: calculated for $C_{13}B_{10}H_{25}O_2$ (M^++H) 321.2852; found: 321.2857.

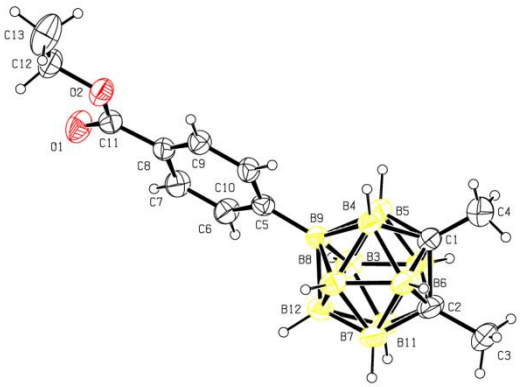
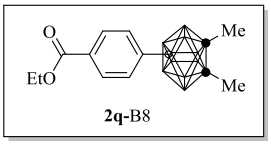


Figure S3. Crystal structure of **2q**-B9



^{1}H NMR (400MHz, $CDCl_3$, *ppm*): δ 7.92-7.90 (d, *J* = 8Hz, 2H), 7.56-7.54 (d, *J* = 8Hz, 2H), 4.39-4.35 (q, *J* = 8Hz, 2H), 2.09 (s, 6H), 1.39-1.36 (t, *J* = 8Hz, 3H); ^{13}C{^{1}H} NMR (100MHz, $CDCl_3$, *ppm*): δ 166.9, 147.2, 132.9, 129.3, 128.4, 72.5, 60.7, 23.2, 14.4; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, *ppm*): δ -0.5 (1B, -*B*Ar), -4.7 (2B), -8.9 (1B), -9.6 (1B), -10.1 (2B), -11.1 (3B); HRMS: calculated for $C_{13}B_{10}H_{25}O_2$ (M^++H) 321.2846; found: 321.2852.

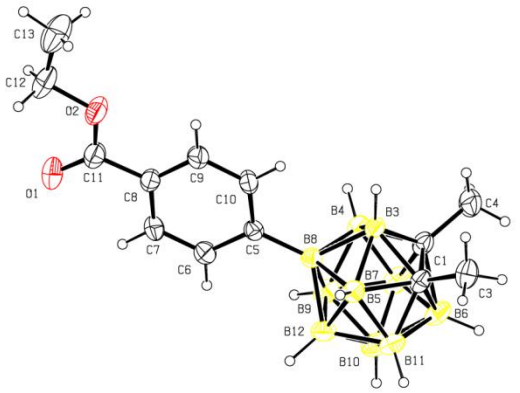
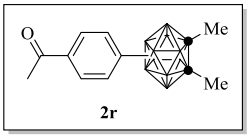
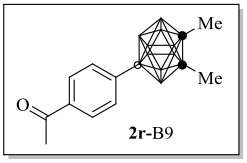


Figure S4. Crystal structure of **2q**-B8



2r

The isomers of B8 and B9 can be separated by column chromatography. The ratio of B8/B9 is 1:2.1.



2r-B9

^{1}H NMR (400MHz, $CDCl_3$, *ppm*): δ 7.80-7.78 (d, *J* = 8Hz, 2H), 7.47-7.45 (d, *J* = 8Hz, 2H), 2.56 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H); ^{13}C{^{1}H} NMR (100MHz, $CDCl_3$, *ppm*): δ 198.5, 144.5, 135.8, 132.7, 127.1, 72.4, 68.7, 26.6, 23.4, 22.5; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, *ppm*): δ 4.2 (1B, -*B*Ar), -5.0 (2B), -8.9 (2B), -10.1 (5B); HRMS: calculated for $C_{12}B_{10}H_{23}O_1$ (M^++H) 291.2747; found: 291.2749.

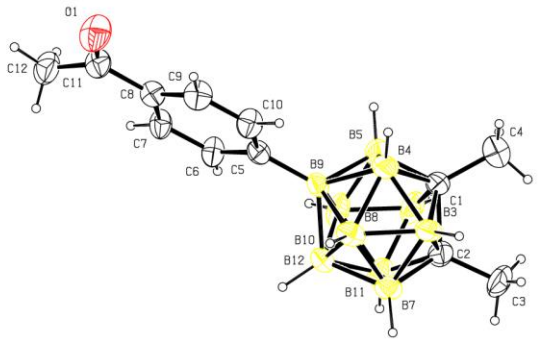
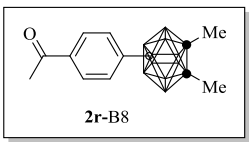


Figure S5. Crystal structure of **2r**-B9



2r-B8

^{1}H NMR (400MHz, $CDCl_3$, *ppm*): δ 7.85-7.83 (d, *J* = 8Hz, 2H), 7.59-7.57 (d, *J* = 8Hz, 2H), 2.58 (s, 3H), 2.09 (s, 6H); ^{13}C{^{1}H} NMR (100MHz, $CDCl_3$, *ppm*): δ 198.5, 145.2, 135.9, 133.2, 127.2, 72.5, 26.6, 23.2; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, *ppm*): δ -0.5 (1B, -*B*Ar), -4.7 (2B), -8.8 (1B), -9.6 (1B), -10.1 (2B), -11.1 (3B); HRMS: calculated for $C_{12}B_{10}H_{23}O_1$ (M^++H) 291.2744; found: 291.2747.

Explanation for assigning chemical shift of B(9)/B(8) without running proton-coupled ^{11}B NMR, and without exact numbering other nine boron atoms with 2D NMR:

The ^{11}B NMR of *o*-carboranes has been studied detailed by many chemists, and the ^{11}B NMR of B(9)/B(8) functionalized *o*-carboranes have also been reported. In our case, both isomers of **2q** could be separated completely and their exact structure was confirmed by X-ray analysis. Base on the ^{11}B NMR of 2q-B(8) and 2q-B(9), we then compared them to that of B(9,12) and B(8,10) substituted *o*-carboranes to assign which peak belongs to B(8) or B(9). (For selected examples, please see: *Inorg. Chem.* 1991, **30**, 4866; *Inorg. Chem.* 1995, **34**, 2095; *Chem. Commun.* 2011, **47**, 2252.)

For parent 1, 2-Me_2-*o*-carborane, the ^{11}B NMR of which displays four set peaks with a 2:2:4:2 pattern, which belong to B(9, 12)/δ = -5.5, B(8, 10)/δ = -8.6, B(4, 5, 7, 11)/δ = -9.8, B(3, 6)/δ = -10.7, respectively. (**Figure S6**) When one B atom was arylated, the ^{11}B NMR spectra has a distinct change due to the desymmetrical of icosahedron, and the peaks have some overlaps, thus led the assignment of exact numbering of other nine boron atoms very difficult, especially in our case with inseparable isomers to recording NMR spectra. So, assigning the functionalized B atom is reported. (For recent examples, please see: *J. Am. Chem. Soc.* 2013, **135**, 12192; *J. Am. Chem. Soc.* 2014, **136**, 15513.)

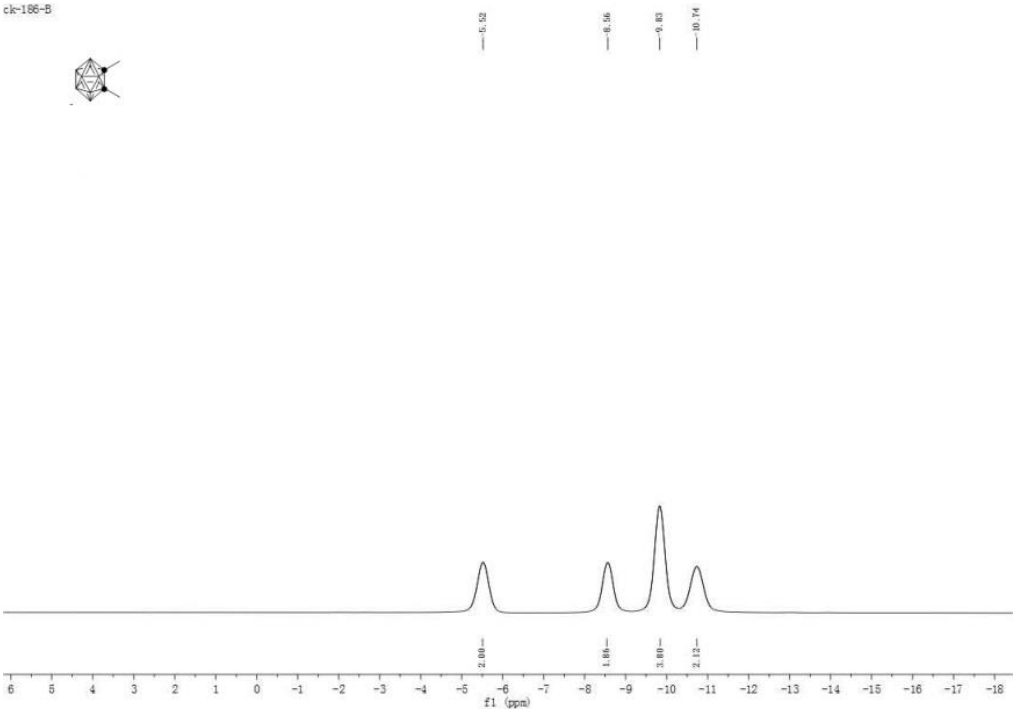


Figure S6. $^{11}B\{^{1}H\}$ NMR of 1, 2-Me_2-*o*-carborane

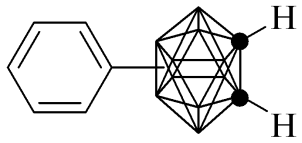
Table S1. Crystal data and Summary of Data Collection and Refinement for **2b**-B9, **2d**-B9 and **2r**-B9

	2b-B9	**2d**-B9	**2r**-B9
formula	$C_{10}H_{20}B_{10}$	$C_{12}H_{22}B_{10}$	$C_{12}H_{22}B_{10}O$
fw	248.36	274.39	290.39
Crystal system	orthorhombic	orthorhombic	monoclinic
space group	*Pbca*	*P21 21 21*	*C*2/c
a, Å	24.322(5)	9.0090(5)	24.2272(13)
b, Å	8.2628(8)	12.9189(8)	13.0711(6)
c, Å	15.382(3)	14.1739(10)	23.5734(10)
α, deg	90	90	90
β, deg	90	90	108.334(5)
γ, deg	90	90	90
V, $Å^3$	3091.4(9)	1649.65(18)	7086.2(6)
Z	8	4	16
D, $g·cm^{-3}$	1.067	1.105	1.089
μ, mm^{-1}	0.050	0.053	0.057
F(000)	1040.0	576.0	2432.0
no. of obsd reflns	3023	2909	6922
no. of params	184	199	421
R_1	0.1195	0.0736	0.1112
wR_2	0.4433	0.2079	0.3787
GOOF	1.044	1.068	1.035

Table S2. Crystal data and Summary of Data Collection and Refinement for **2q**-B9 and **2q**-B8

	2q-B9	**2q**-B8
formula	$C_{13}H_{24}B_{10}O_2$	$C_{13}H_{24}B_{10}O_2$
fw	320.42	320.42
Crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	7.0474(4)	7.3151(4)
b, Å	19.9445(12)	13.2180(6)
c, Å	13.4339(6)	19.6674(9)
α, deg	90	90
β, deg	94.295(5)	93.078(5)
γ, deg	90	90
V, Å^3	1882.92(18)	1898.90(15)
Z	4	4
D, g·cm^{-3}	1.130	1.121
μ, mm^{-1}	0.063	0.062
F(000)	672.0	672.0
no. of obsd reflns	3690	3723
no. of params	229	230
refnd		
R_1	0.0877	0.0694
wR_2	0.2999	0.2029
GOOF	1.040	1.058

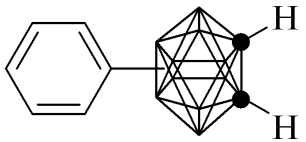
ck-246-H


H
H

2a

7.63
7.62
7.56
7.54
7.34
7.33
7.32
7.31
7.30
7.26
3.85
3.77
3.71
0.01
CH_2Cl_2
0.25
1.92
3.03
0.12
1.00
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

ck-246-C



2a

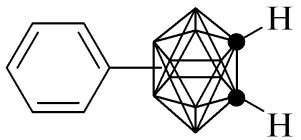
133.25
133.12
129.78
128.57
128.28
127.86
77.21
77.00
76.79
59.06
55.01
54.95
-0.02

CH_2Cl_2

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

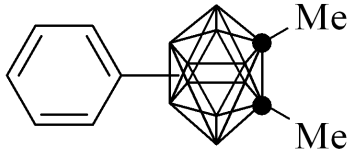
ck-246-B


H
H

2a

1.91
2.67
3.58
8.87
9.80
12.90
14.28
14.52
15.03
16.81
1.00
0.94
0.74
0.85
0.73
0.89
1.41
0.68
0.63
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
f1 (ppm)

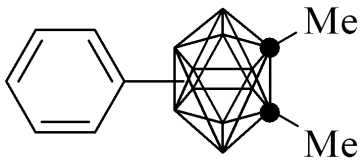
ck-200-H


Me
Me

2b

7.49
7.48
7.37
7.36
7.26
7.25
7.25
7.24
7.22
7.22
7.22
7.21
7.20
7.20
7.19
2.05
2.04
2.01
1.55
1.25
0.07
0.00
0.72
1.15
2.91
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

ck-200-C



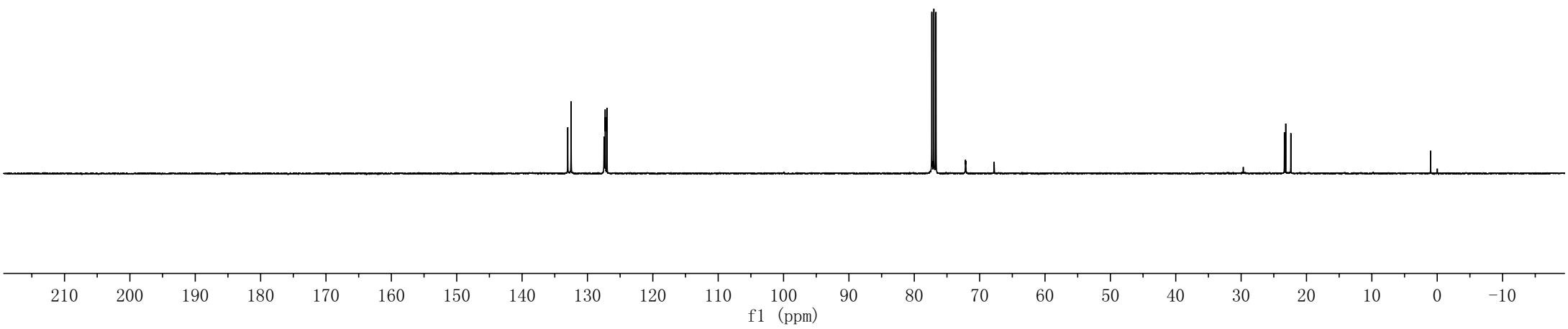
2b

133.01
132.50
127.46
127.28
127.25
127.00

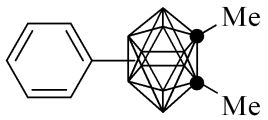
77.32
77.20
77.00
76.68
72.17
72.12
67.78

23.38
23.17
22.39

1.00



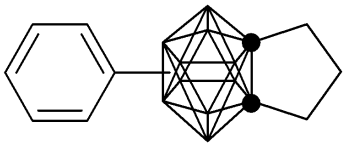
ck-200-B


Me
Me

2b

4.92
0.14
-4.72
-9.00
-10.18
-11.30
1.00
0.69
2.07
2.11
6.68
1.26
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
f1 (ppm)

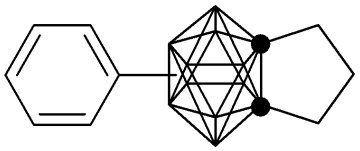
ck-208-H



2c

7.51
7.50
7.38
7.37
7.26
7.25
7.22
7.21
7.20
7.20
2.57
2.56
2.54
2.53
2.50
2.49
2.49
2.48
2.47
2.46
2.45
2.44
2.43
1.59
1.25
0.10
0.09
0.08
0.07
0.05
0.01
0.00
0.84
0.83
2.93
1.08
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

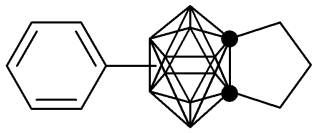
ck-238-C



2c

133.03
132.63
127.48
127.30
126.97
82.99
82.61
78.98
77.21
77.00
76.79
34.83
34.67
33.91
32.32
32.00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

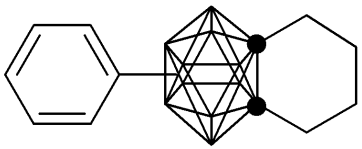
ck-238-B



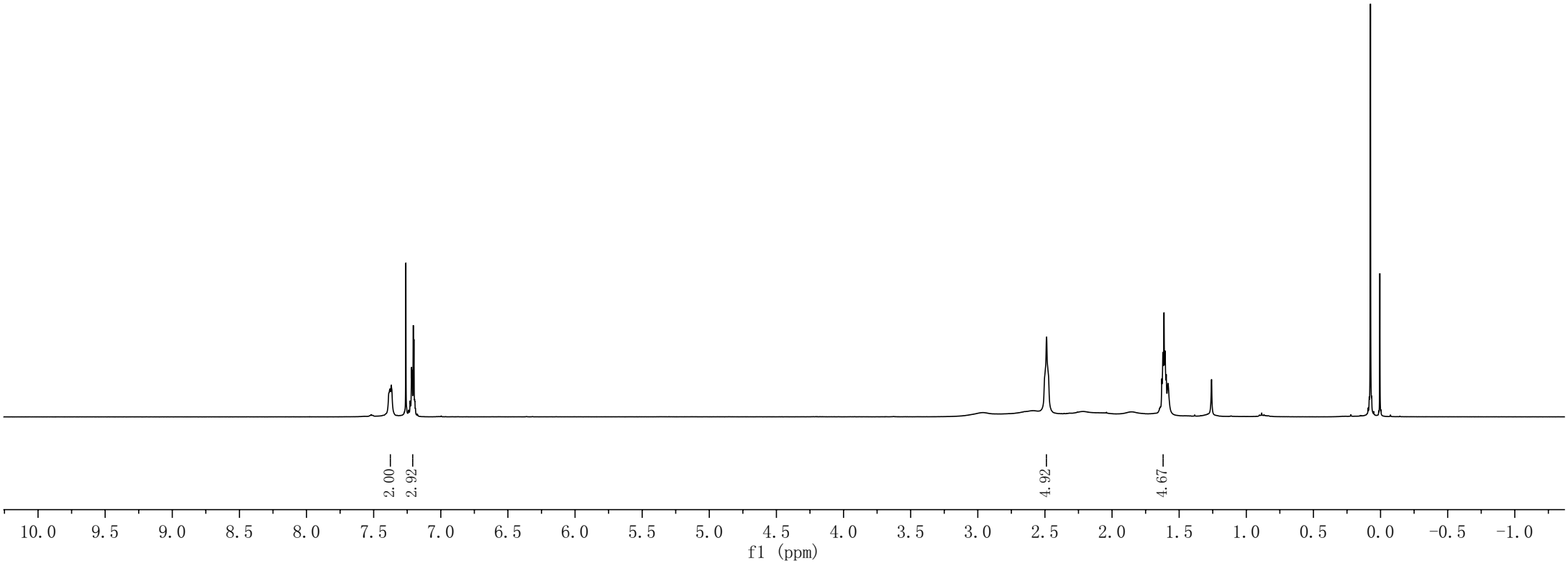
2c

3.46
2.51
6.30
7.62
9.13
9.73
11.93
12.40
1.00
0.67
2.11
1.92
0.93
1.94
3.09
2.82
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
f1 (ppm)

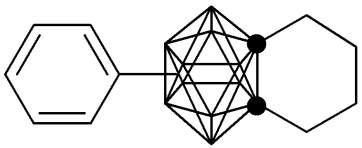
ck-209-H



2d


7.38
7.37
7.26
7.23
7.23
7.22
7.21
7.20
7.20
7.20
7.19
2.49
1.63
1.62
1.61
1.60
1.60
1.58
1.26
0.08
0.08
0.07
0.01
2.00
2.92
4.92
4.67
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

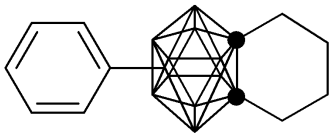
ck-209-C



2d

133.03
132.54
127.47
127.28
127.25
126.95
77.21
77.00
76.79
71.92
71.84
67.55
32.90
32.82
32.05
19.80
19.70
19.62
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

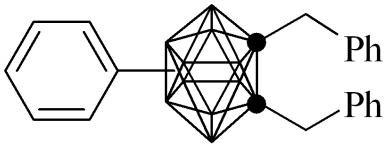
ck-209-B



2d

4.28
1.25
5.30
8.87
9.85
10.35
12.42
1.00
0.72
1.62
1.49
2.10
2.05
1.61
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
f1 (ppm)

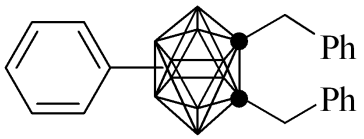
ck-207-H


Ph
Ph

2e

7.38
7.36
7.34
7.26
7.25
7.24
7.23
7.23
7.15
7.15
7.14
3.67
0.07
0.00
6.19
6.99
2.93
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

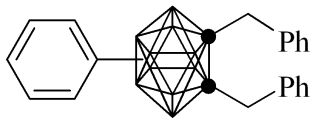
ck-207-C


Ph
Ph

2e

135.08
134.88
132.43
130.40
130.37
128.67
128.65
128.14
127.21
126.98
78.30
77.32
77.20
77.00
76.68
73.91
41.45
40.61
1.01
-0.01
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

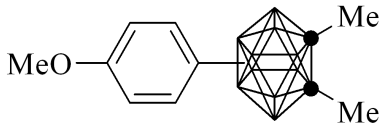
ck-239-B


Ph
Ph

2e

5.70
0.50
3.89
9.70
10.83
1.00
0.70
2.42
3.02
8.20
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
f1 (ppm)

ck-227-H

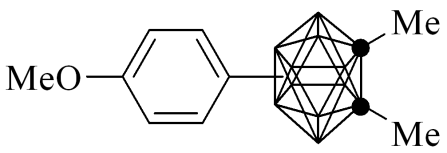

MeO
Me
Me

2g

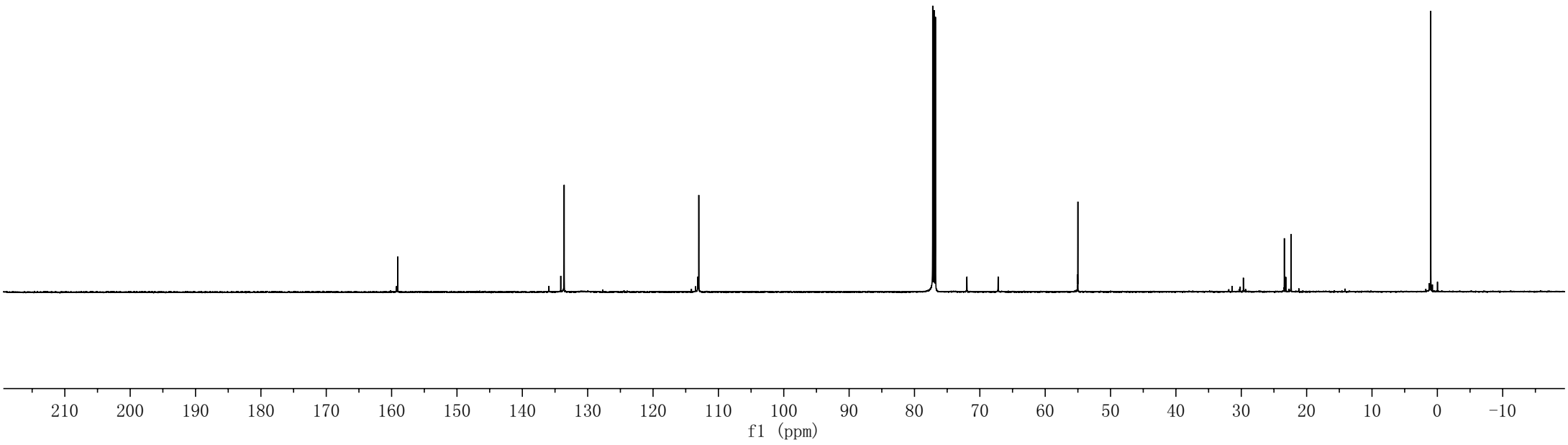
7.30
7.29
7.26
6.80
6.78
3.80
3.77
2.07
2.07
0.08
0.01
1.85
1.88
3.00
7.28
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

ck-227-C

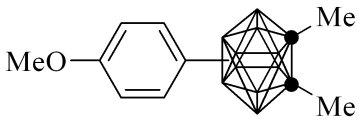
159.06
135.92
133.60
113.00
77.21
77.00
76.79
71.98
67.20
55.00
23.41
22.38
1.00



2g



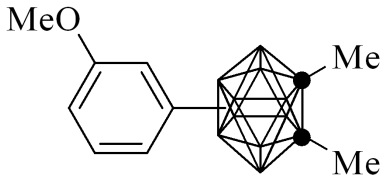
ck-227-B


MeO
Me
Me

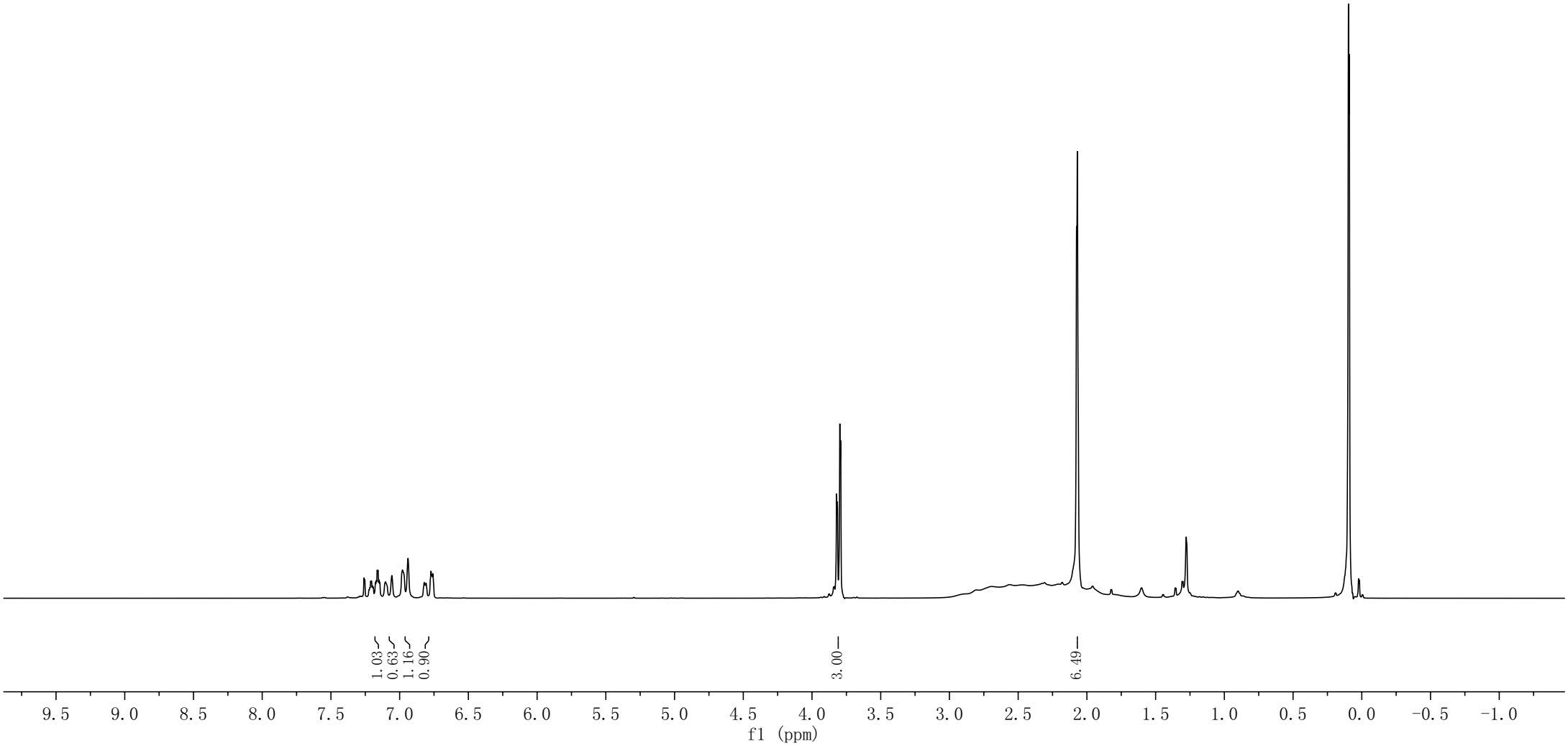
2g

4.96
0.15
5.07
9.06
10.03
11.41
1.00
0.42
1.31
1.54
4.53
0.59
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
f1 (ppm)

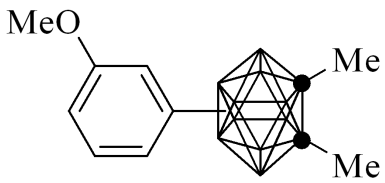
ck-226-H


MeO
Me
Me

2h


7.26
7.25
7.22
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.16
7.16
7.15
7.14
7.10
7.06
6.98
6.94
6.82
6.81
6.81
6.77
6.76
6.76
3.82
3.82
3.80
3.79
2.08
2.07
0.10
0.09
0.02
1.03
0.63
1.16
0.90
3.00
6.49
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

ck-226-C



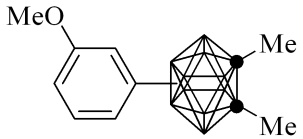
2h

158.73
158.60
140.54
128.53
128.35
125.50
125.02
118.73
118.19
112.48
112.25
77.21
77.00
76.79
72.13
72.06
67.80
55.01
54.96
23.37
23.16
22.38
1.00

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

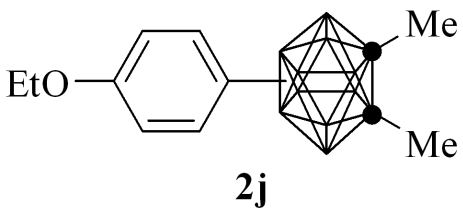
ck-226-B


MeO
Me
Me

2h

4.74
0.02
4.78
5.04
9.02
10.16
11.30
1.00
0.60
1.17
1.08
2.71
7.87
1.29
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
f1 (ppm)

ck-230-H

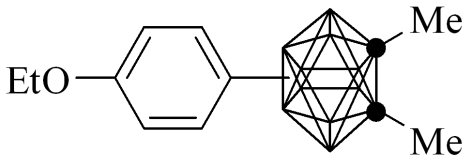

EtO
Me
Me

2j

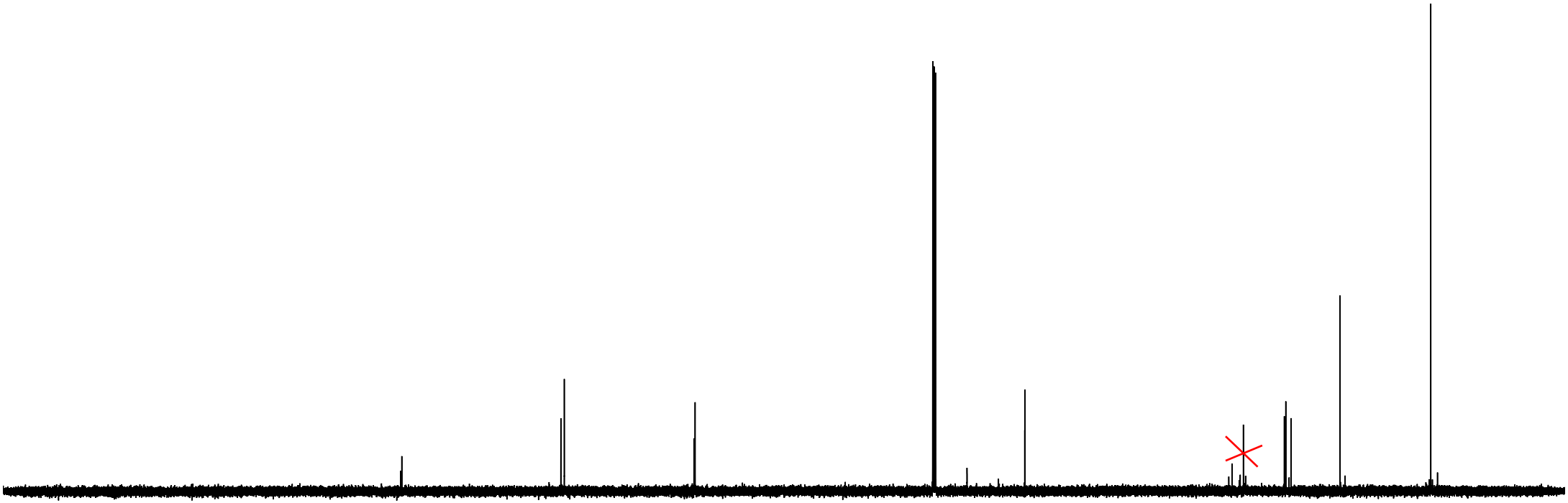
7.39
7.28
7.27
7.26
6.82
6.82
6.81
6.78
6.78
6.77
4.03
4.02
4.00
3.99
2.07
2.07
1.42
1.40
1.40
1.40
1.39
1.39
1.38
1.34
1.29
1.26
0.10
0.08
0.08
0.08
0.01
0.01
0.01
1.00
1.45
1.03
1.65
2.90
8.93
4.80
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

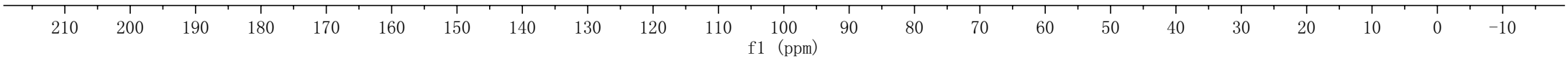
ck-230-C

158.63
158.44
135.92
134.11
133.58
113.74
113.57
77.21
77.00
76.79
72.09
67.24
63.09
23.42
23.19
22.38
14.89

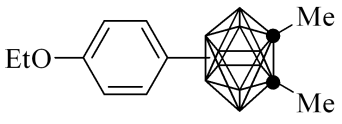


2j





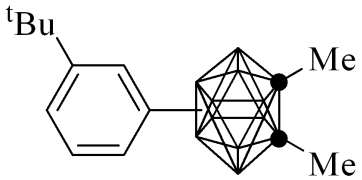
ck-230-B


EtO
Me
Me

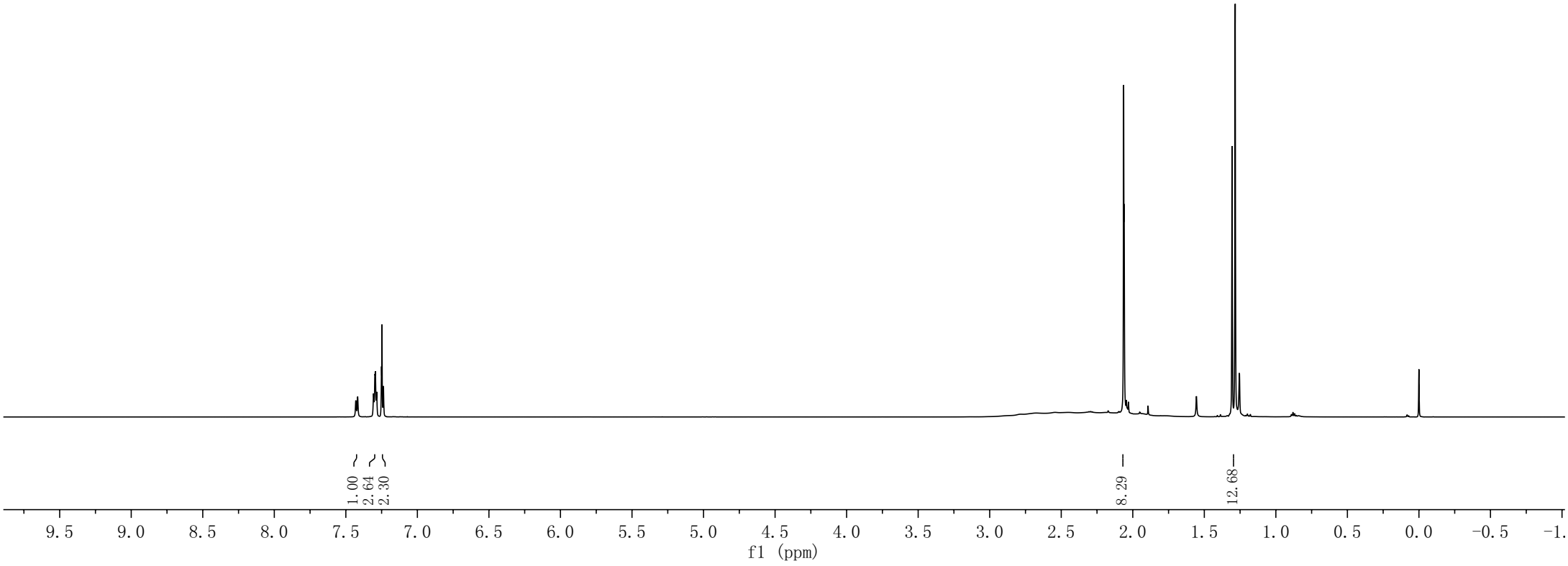
2j

4.97
0.19
4.73
4.98
9.01
10.09
11.33
1.00
0.65
2.21
2.76
8.18
1.30
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
f1 (ppm)

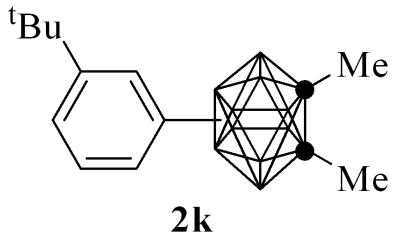
ck-229-H


tBu
Me
Me

2k

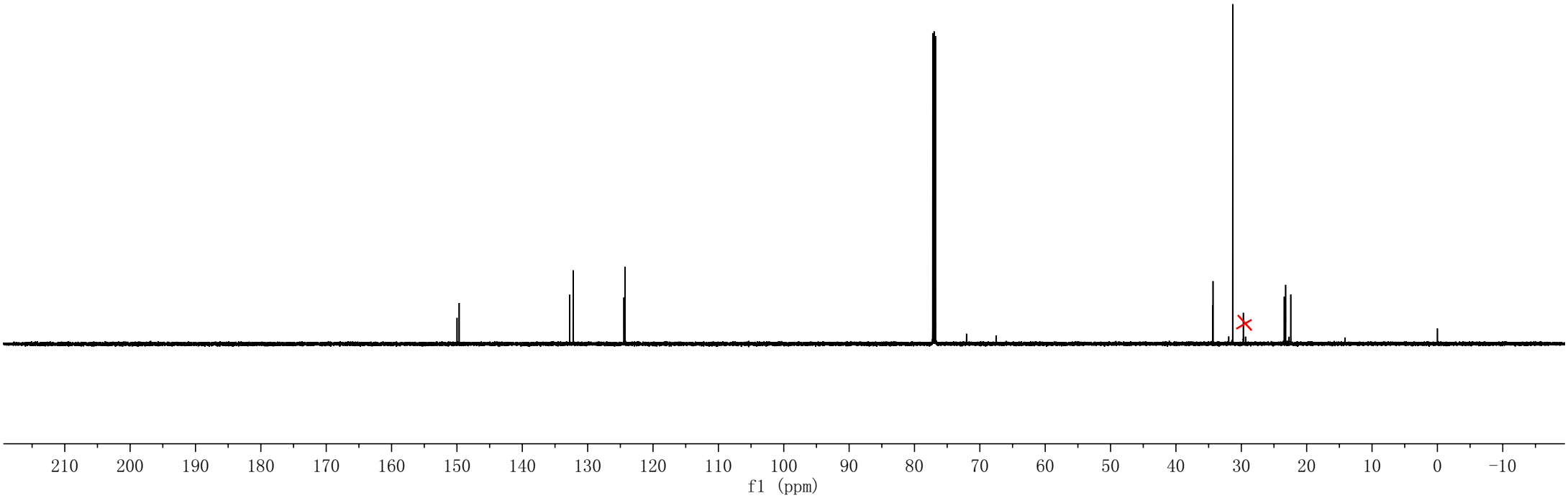

7.43
7.42
7.31
7.30
7.29
7.28
7.25
7.25
7.24
2.06
2.06
2.04
2.04
2.03
1.89
1.56
1.31
1.28
1.25
0.00
0.00
1.00
2.64
2.30
8.29
12.68
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

ck-229-C

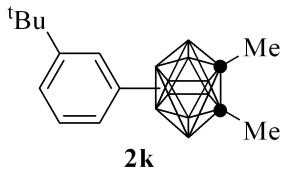


2k

149.98
149.66
132.76
132.23
124.46
124.28
77.21
77.00
76.79
72.04
72.01
67.54
34.38
34.32
31.32
23.43
23.21
22.43



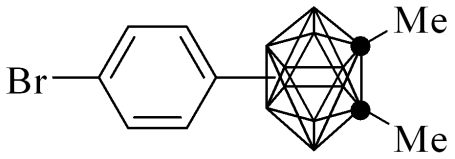
ck-229-B


tBu
Me
Me

2k

5.74
0.96
4.03
4.31
8.35
9.30
10.69
1.00
0.63
2.30
2.54
8.09
1.28
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
f1 (ppm)

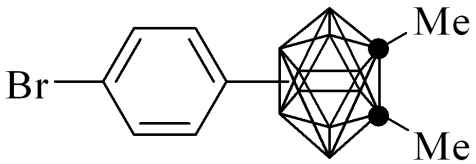
ck-215-H


Br
Me
Me

2l

7.39
7.37
7.35
7.34
7.32
7.26
7.23
7.21
2.08
2.04
3.24
1.00
6.59
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

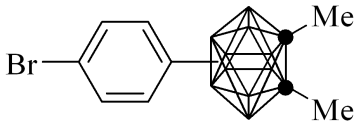
ck-215-C


Br
Me
Me

2l

139.82
134.68
134.21
130.52
130.34
121.99
121.72
77.32
77.00
76.68
72.36
68.04
23.41
23.21
22.45
1.01
-0.01
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

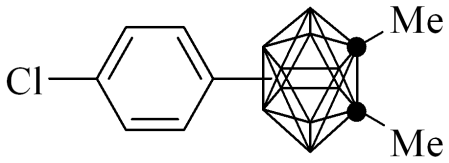
ck-215-B


Br
Me
Me

2l

4.37
0.42
4.80
8.97
10.14
11.17
1.00
0.64
0.90
0.69
1.85
4.89
1.11
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
f1 (ppm)

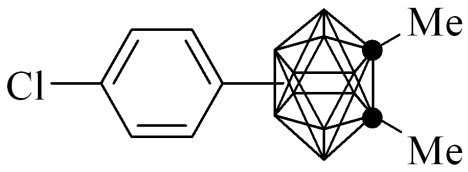
ck-216-H


Cl
Me
Me

2n

7.41
7.39
7.29
7.27
7.26
7.23
7.21
7.19
7.16
2.08
2.07
0.07
0.00
1.05
0.99
1.03
0.95
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

ck-216-C



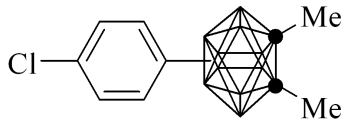
2n

134.33
133.85
133.59
133.30
127.59
127.41
77.32
77.20
77.00
76.68
72.34
72.25
68.04
23.41
23.21
22.44
1.01
-0.02

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

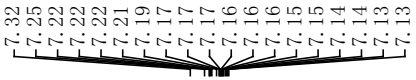
ck-216-B

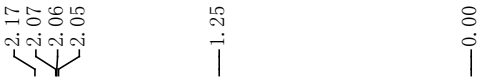

Cl
Me
Me

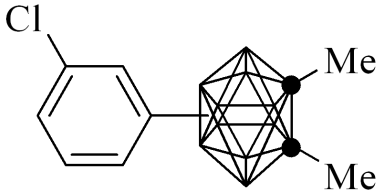
2n

4.38
0.41
4.74
8.95
10.13
11.20
1.00
0.83
1.67
1.36
2.88
0.85
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
−2
−4
−6
−8
−10
−12
−14
f1 (ppm)

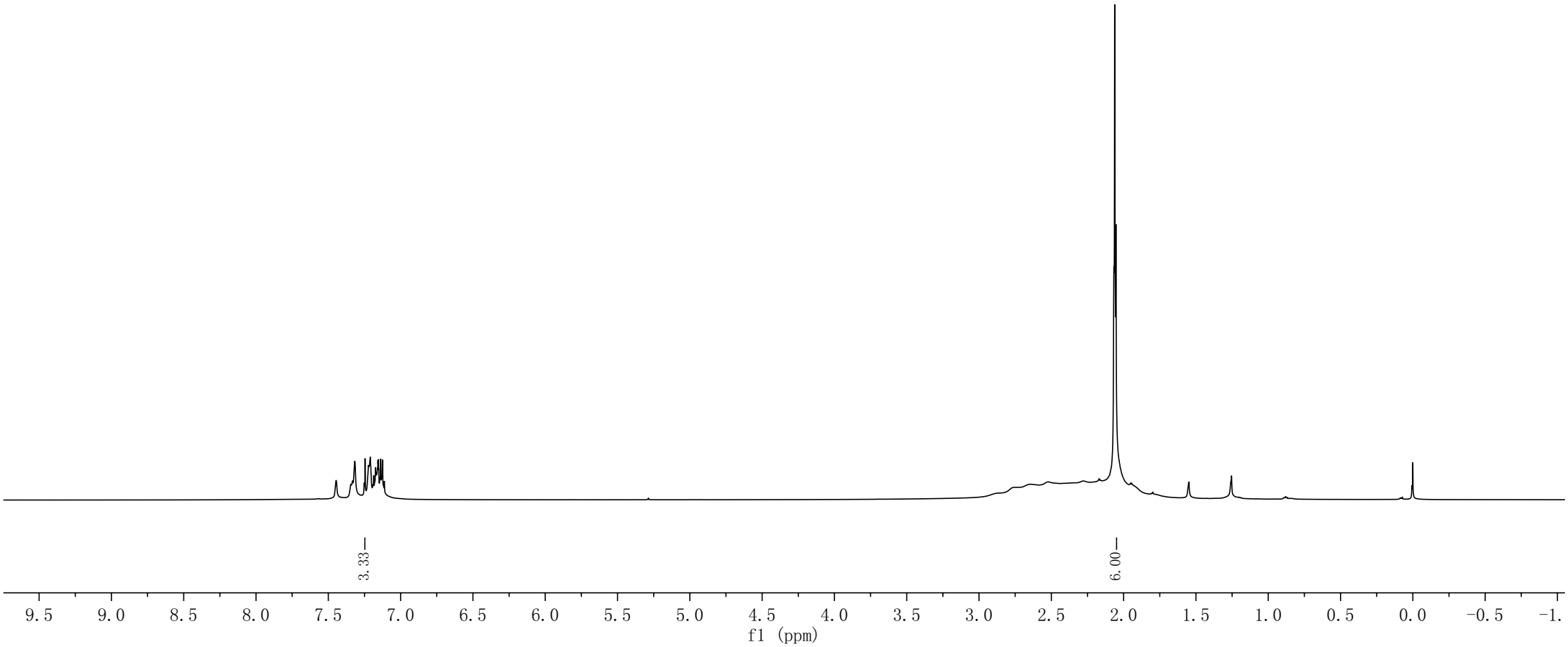
ck-218-H


7.32
7.25
7.22
7.22
7.22
7.21
7.19
7.17
7.17
7.17
7.16
7.16
7.16
7.15
7.15
7.14
7.14
7.13
7.13

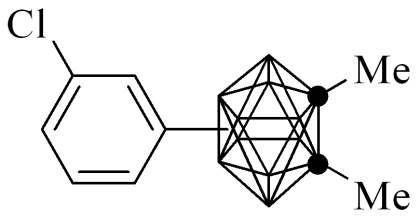

2.17
2.07
2.06
2.05
1.25
0.00


Cl
Me
Me

2o


3.33
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

ck-218-C

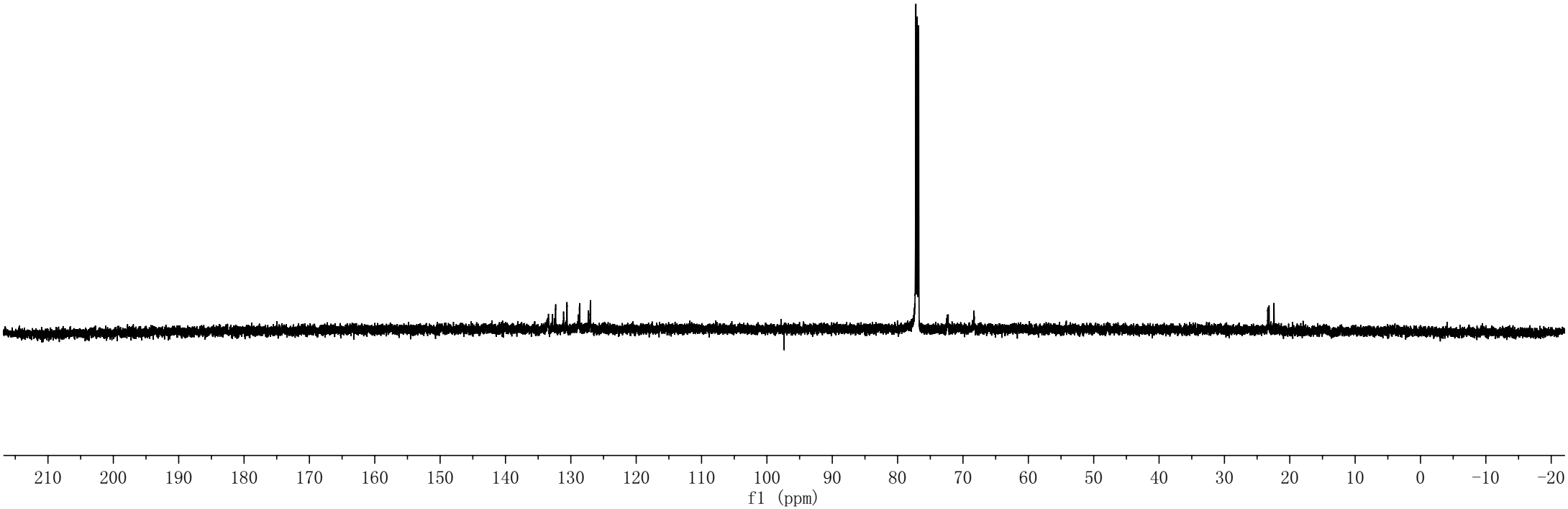


2o

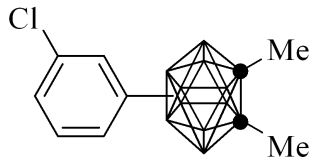
133.40
132.82
132.32
131.14
130.59
128.83
128.66
127.29
127.00

77.21
77.00
76.79
72.40
72.26
68.32

23.36
23.17
22.41



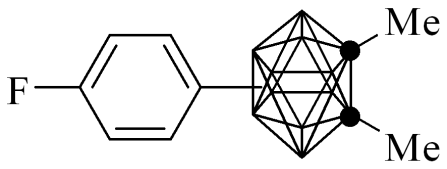
ck-218-B


Cl
Me
Me

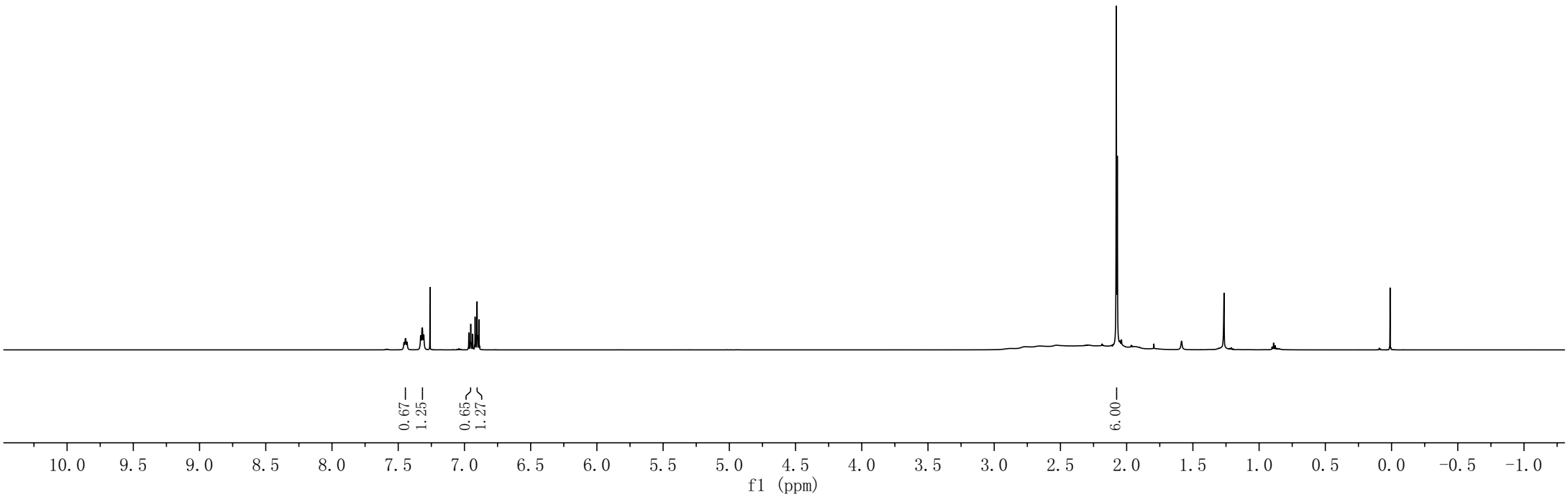
2o

4.10
0.63
4.78
5.05
8.94
10.12
11.12
1.00
0.53
1.09
1.13
2.23
7.93
1.31
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
f1 (ppm)

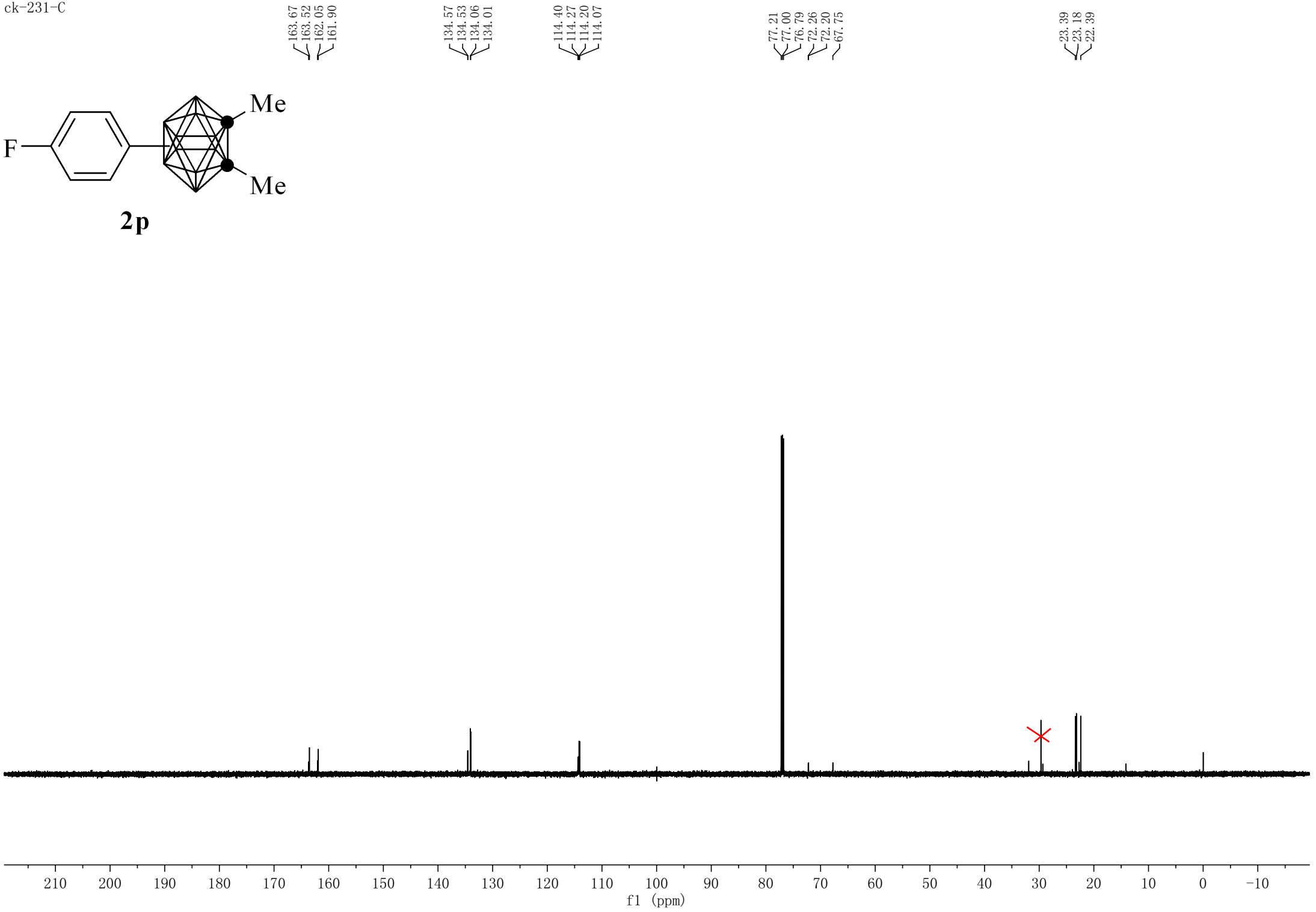
ck-231-H


F
Me
Me

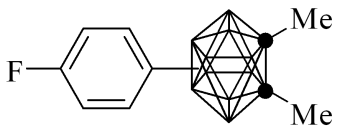
2p


7.46
7.45
7.44
7.43
7.33
7.32
7.32
7.31
7.26
6.97
6.96
6.96
6.95
6.95
6.94
6.94
6.92
6.92
6.91
6.90
6.90
6.89
6.89
2.08
2.07
0.01
0.67
1.25
0.65
1.27
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

ck-231-C


163.67
163.52
162.05
161.90
134.57
134.53
134.06
134.01
114.40
114.27
114.20
114.07
77.21
77.00
76.79
72.26
72.20
67.75
23.39
23.18
22.39
F
Me
Me
2p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

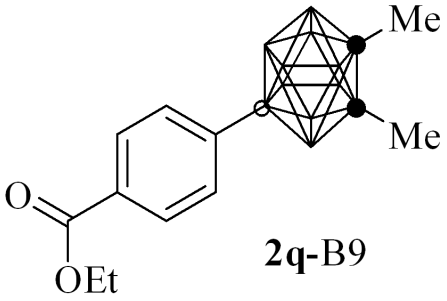
ck-231-B


F
Me
Me

2p

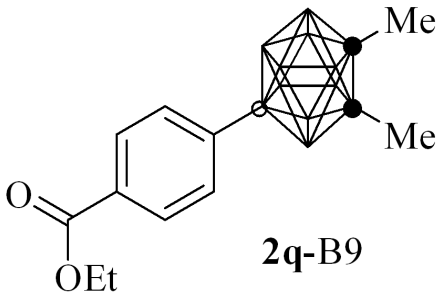
4.88
0.10
4.36
8.62
9.76
10.92
1.00
0.61
2.19
2.46
3.41
1.11
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
f1 (ppm)

ck-220-s-H



2q-B9

ck-220-s-C

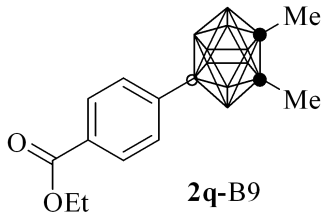


2q-B9

167.04
142.72
132.48
129.01
128.23
77.32
77.00
76.68
72.33
68.52
60.62
23.39
22.48
14.33
1.00
-0.02

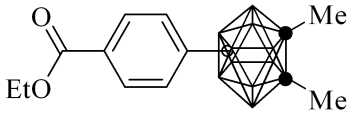
f1 (ppm)

ck-220-S-B



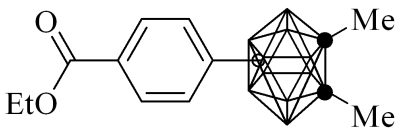
2q-B9

ck-220-x-H



2q-B8

ck-220-x-C

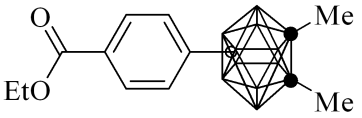


2q-B8

166.99
153.73
132.98
129.28
128.39
77.32
77.20
77.00
76.68
72.45
60.70
23.23
14.35
1.01

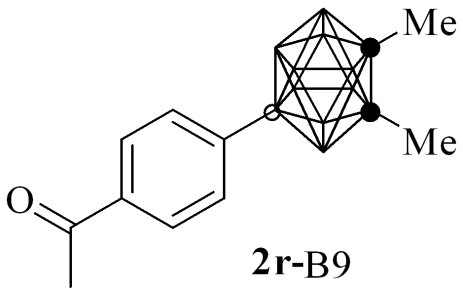
f1 (ppm)

ck-220-X-B



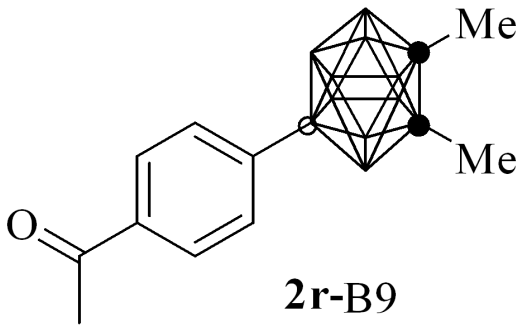
2q-B8

ck-222-s-H



2r-B9

ck-222-s-C



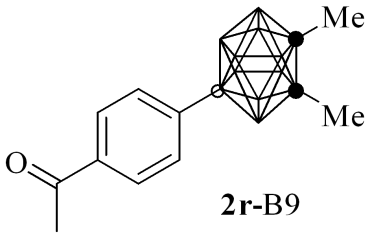
2r-B9

198.49
144.46
135.76
132.72
127.09
77.32
77.00
76.68
72.38
68.66
26.57
23.40
22.50
1.00
-0.02

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

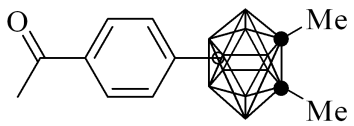
f1 (ppm)

ck-222-S-B



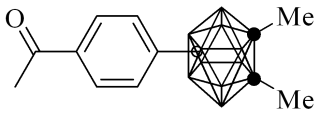
2r-B9

ck-222-x-H



2r-B8

ck-222-x-C



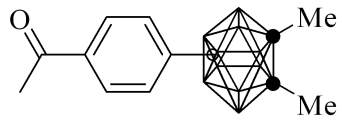
2r-B8

198.46
145.23
135.99
133.23
127.24
77.32
77.00
76.68
72.52
26.61
23.24
1.01
-0.02

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

ck-222-X-B



2r-B8