Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

An Exceptionally High Boron Content Supramolecular Cuboctahedron

*Daniel J. Clingerman, Robert D. Kennedy, Joseph E. Mondloch, Amy A. Sarjeant, Joseph T. Hupp, Omar K. Farha, Chad A, Mirkin**

[1]Department of Chemistry and the International Institute for Nanotechnology

Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA

*Corresponding Author:
Chad A. Mirkin
Email: chadnano@northwestern.edu
Phone: (+1) 847-467-7302; Fax: (+1) 847-467-5123

Contents

1. Synthetic procedures and characterization

General considerations: 1,7-dicarba-*closo*-dodecaborane (*m*-carborane) was purchased from Katchem (Czech Republic) and used as received. Diethyl 5-iodoisophthalate was prepared according to previously published literature procedures.[1] All other solvents and chemicals were obtained from Aldrich Chemical Co. (Milwaukee, USA). Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. For all air-sensitive manipulations either a Vacuum Atmospheres Nexus II N_2-filled glove box or Schlenk techniques were employed. Analytical thin layer chromatography (TLC) was performed using plastic plates pre-coated with silica gel (0.25 mm, 60 Å pore size) with a fluorescent indicator (254 nm). Visualization was accomplished with UV light and/or palladium chloride ($PdCl_2$) in hydrochloric acid (0.6 M in EtOH) as a stain. All NMR spectra were recorded Bruker Avance 400 MHz equipped with a broadband probe at 300 K. ^1H and $^1H\{^{11}B\}$ NMR spectra were referenced internally to residual protons in the deuterated solvents (dichloromethane-d_2 = δ 5.32; acetone-d_6 = δ 2.05). $^{13}C\{^1H\}$ NMR spectra were referenced internally to carbons in the deuterated solvents (dichloromethane-d_2 = δ 53.84; acetone-d_6 = δ 29.84). ^{11}B and $^{11}B\{^1H\}$ NMR spectra were referenced to a neat $BF_3\cdot Et_2O$ standard at 0.0 ppm. Electrospray ionization (ESI) mass spectra were recorded on an Agilent 6120 LC–TOF instrument in positive ion mode. Elemental analyses (C, H, N) were performed by Quantitative Technologies (Intertek), Whitehouse, NJ.

Compound 1

Compound **1** was prepared following a procedure analogous to that reported by Schörbel et al.[2] To a solution of *m*-carborane (1.00 g, 6.9 mmol) in diethyl ether (25 mL) was added *n*-BuLi (1.6 M solution in hexane, 4.3 mL, 6.9 mmol) at 0 °C. After 1.5 hours of stirring at room temperature, a slurry of CuCl (0.69 g, 6.9 mmol) in 20 mL THF was added at –30 °C under nitrogen. The mixture was allowed to stir for 1 hour at room temperature and then refluxed for 30 minutes. After the solvent was removed under reduced pressure, *N*-methylpyrrolidone (25 mL), diethyl 5-iodoisophthalate (2.72 g, 7.8 mmol), and $PdCl_2(PPh_3)_2$ (276 mg, 0.39 mmol) were added. The mixture was stirred at 100 °C for 48 hours, cooled and poured into 30 mL of brine. Additional NaCl (1 g) was added and the mixture was filtered and the filtrate was then discarded. The retentate was stirred in acetone and then filtered. The filtrate was then collected, solvent removed and the mixture was purified by column chromatography using a solvent gradient of 2:1–2:3 hexanes/DCM: 1.22 g (48 %). $^{1}H\{^{11}B\}$ NMR (400 MHz, CD_2Cl_2) δ 1.41 (t, 6 H, alkyl), 2.23 (s, 2 H, BH), 2.32 (s, 3 H, BH), 2.55 (s, 2 H, BH), 2.71 (s, 1 H, BH), 3.05 (s, 2 H, BH), 3.24 (s, 1 H, CH), 4.40 (q, 4 H, CH_2) 8.28 (s, 2 H, aromatic), 8.57 (s, 1 H, aromatic); $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CD_2Cl_2) δ 14.53 (CH_3), 56.22 ($C_{carborane}H$), 62.11 (CH_2), 77.34 ($C_{carborane}C_{ar}$), 130.91 (C_{ar}), 132.00 (C_{ar}), 133.04 (C_{ar}), 136.51 (C_{ar}), 165.28 (C_{ester}); ^{11}B NMR (128.4 MHz, CD_2Cl_2) δ –15.54 (d, $^{1}J_{B–H}$ = 187 Hz), –13.70 (d, $^{1}J_{B–H}$ = 170 Hz), –10.91 (d, $^{1}J_{B–H}$ = 156 Hz), –8.90 (d), –4.63 (d, $^{1}J_{B–H}$ = 160 Hz). HRMS (ESI+): *m*/*z* calcd for **1**: 367.2678. Found: 367.2715. Anal. Calcd for **1**: C 46.14, H 6.64. Found: C 46.13, H 6.57.

Compound 2

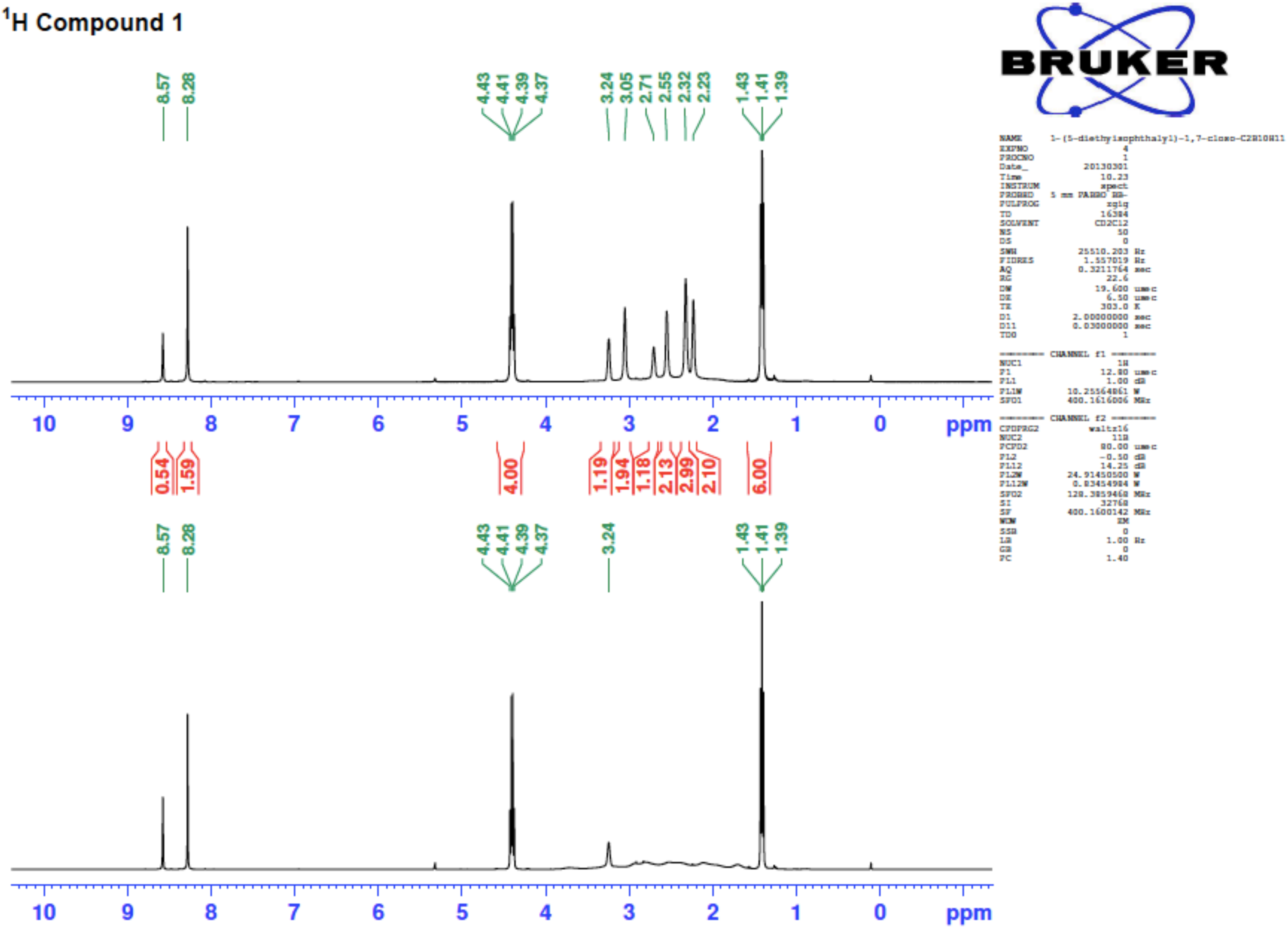
To a solution of **1** (1.12 g, 3.07 mmol) in EtOH (65 mL) was added a LiOH (4.8 g, 200 mmol) in H_2O (65 mL). After 2 days of stirring H_2O (100 mL) was added and the mixture was filtered. The filtrate was then acidified to pH 1 with conc. HCl producing a white precipitate. This was then filtered and washed with copious amounts of water and dried under dynamic vacuum overnight to obtain **2** in quantitative yield. $^{1}H\{^{11}B\}$ NMR (400 MHz, Acetone-d_6) δ 2.21 (s, 2 H, BH), 2.31 (s, 3 H, BH), 2.53 (s, 2 H, BH), 2.69 (s, 1 H, BH), 3.06 (s, 2 H, BH), 3.82 (s, 1 H, CH), 8.33 (s, 2 H, aromatic), 8.63 (s, 1 H, aromatic); $^{13}C\{^1H\}$ NMR (100.6 MHz, Acetone-d_6) δ 57.18 ($C_{carborane}H$), 77.67 ($C_{carborane}C_{ar}$), 131.69 (C_{ar}), 132.48 (C_{ar}), 133.34 (C_{ar}), 136.80 (C_{ar}), 166.05 (C_{acid}); ^{11}B NMR (128.4 MHz, Acetone-d_6) δ –14.58 (d), –12.82 (d, $^1J_{B–H}$ = 171 Hz), –10.18 (d, $^1J_{B–H}$ = 154 Hz), –8.10 (d), –4.06 (d, $^1J_{B–H}$ = 161 Hz). HRMS (ESI+): *m*/*z* calcd for **2**: 311.2052. Found: 311.2071. Anal. Calcd for **2**: C 38.95, H 5.23. Found: C 38.64, H 5.10.

Compound 3

To a solution of $Cu_2(OAc)_4 \cdot 2H_2O$ (86.1 mg, 0.23 mmol) in DMF (17 mL) was added **2** (138.8 mg, 0.45 mmol) in DMF (17 mL). The resulting blue solution was fractioned out into 17 × 2 mL portions and allowed to stand for 4 d at rt, after which the supernatant was removed and replaced with MeOH. The MeOH was replaced once a day for three days. The methanolic supernatant was removed and the residual solvent removed by heating under dynamic vacuum: 70.3 mg (42%). Anal. Calcd for **3·30 H_2O**: C 30.61, H 4.24. Found: C 30.68, H 4.23. The water found in elemental analysis is most likely due to exposure of the material to ambient moisture during sample preparation.

NMR Spectra for Compounds 1 and 2

^{1}H Compound 1

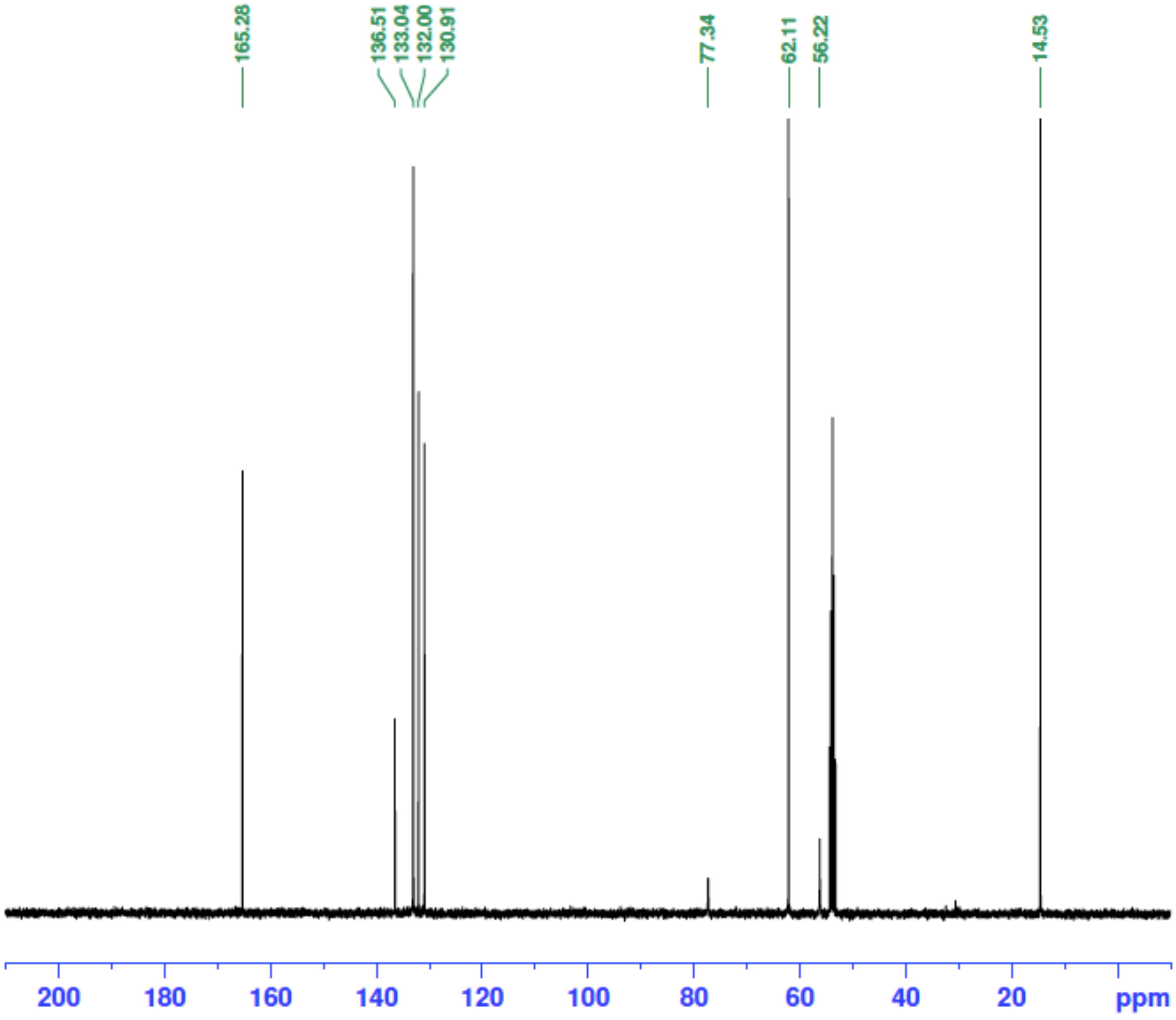


```
NAME      1-(5-diethyisophthalyl)-1,7-closo-C2B10H11
EXPNO                  4
PROCNO                 1
Date_           20130301
Time               10.23
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG             zgig
TD                 16384
SOLVENT          CD2Cl2
NS                    50
DS                     0
SWH            25510.203 Hz
FIDRES          1.557019 Hz
AQ             0.3211764 sec
RG                  22.6
DW                19.600 usec
DE                  6.50 usec
TE                 303.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.80 usec
PL1                 1.00 dB
PL1W         10.25564861 W
SFO1         400.1616006 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 11B
PCPD2              80.00 usec
PL2                -0.50 dB
PL12               14.25 dB
PL2W         24.91450500 W
PL12W         0.83454984 W
SFO2         128.3859468 MHz
SI                 32768
SF           400.1600142 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C Compound 1

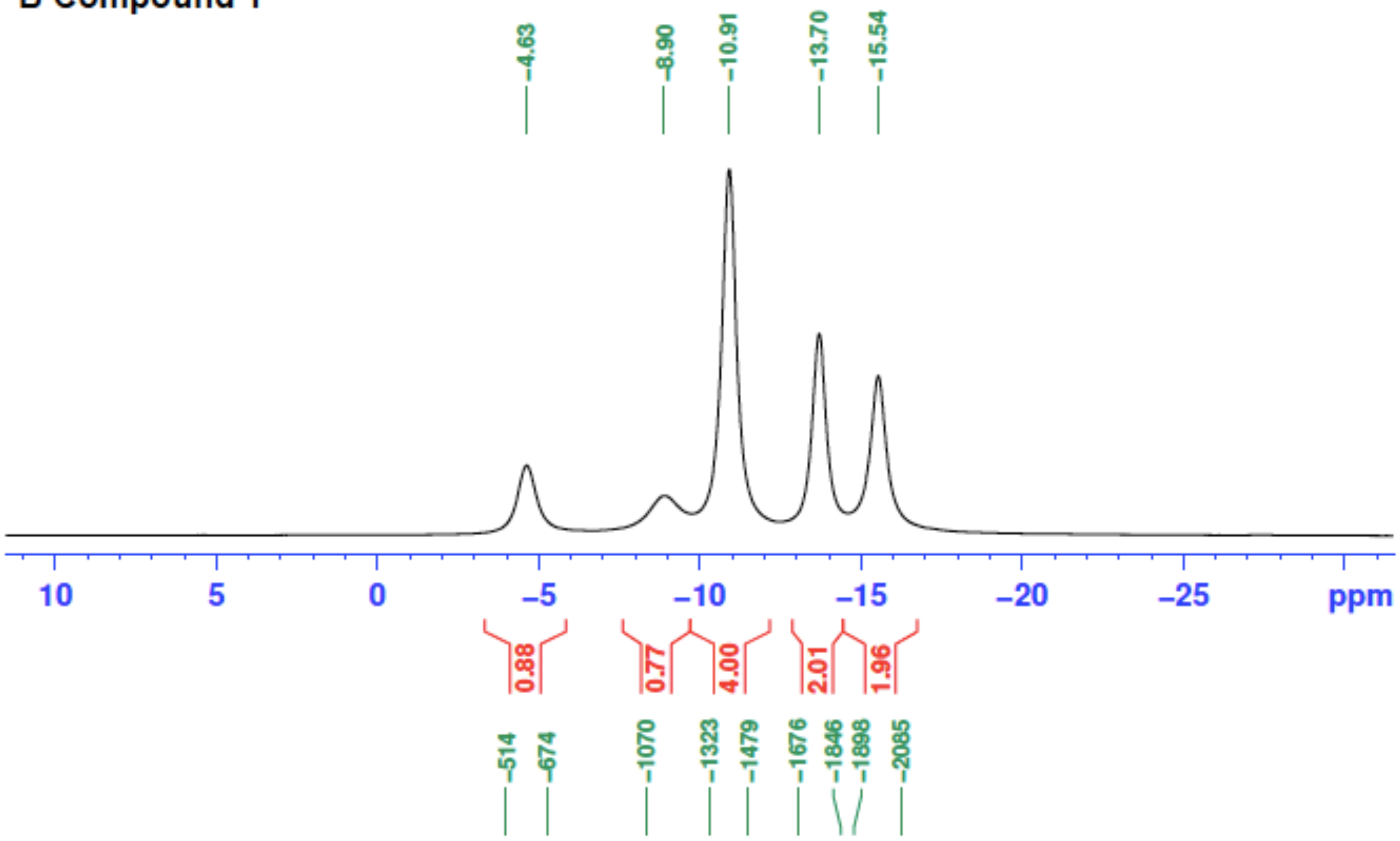


```
NAME       1-(5-diethylisophthalyl)-1,7-closo-C2B10H11
EXPNO                 5
PROCNO                1
Date_          20130301
Time              10.29
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT          CD2Cl2
NS                  146
DS                    0
SWH           27573.529 Hz
FIDRES         0.420739 Hz
AQ            1.1884362 sec
RG                  512
DW               18.133 usec
DE                 6.50 usec
TE                303.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.90 usec
PL1               -3.35 dB
PL1W        83.66055298 W
SFO1        100.6303741 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -0.50 dB
PL12              14.25 dB
PL13              16.25 dB
PL2W        14.48648834 W
PL12W        0.48524728 W
PL13W        0.30617034 W
SFO2        400.1616006 MHz
SI                32768
SF          100.6202642 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

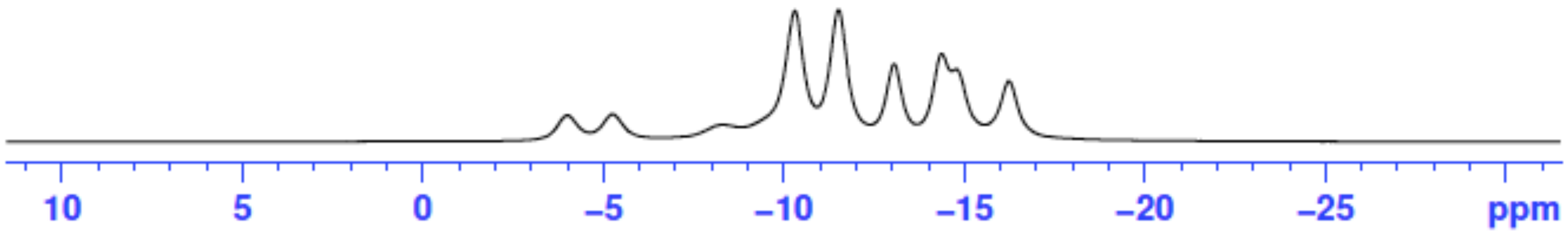
^{11}B Compound 1



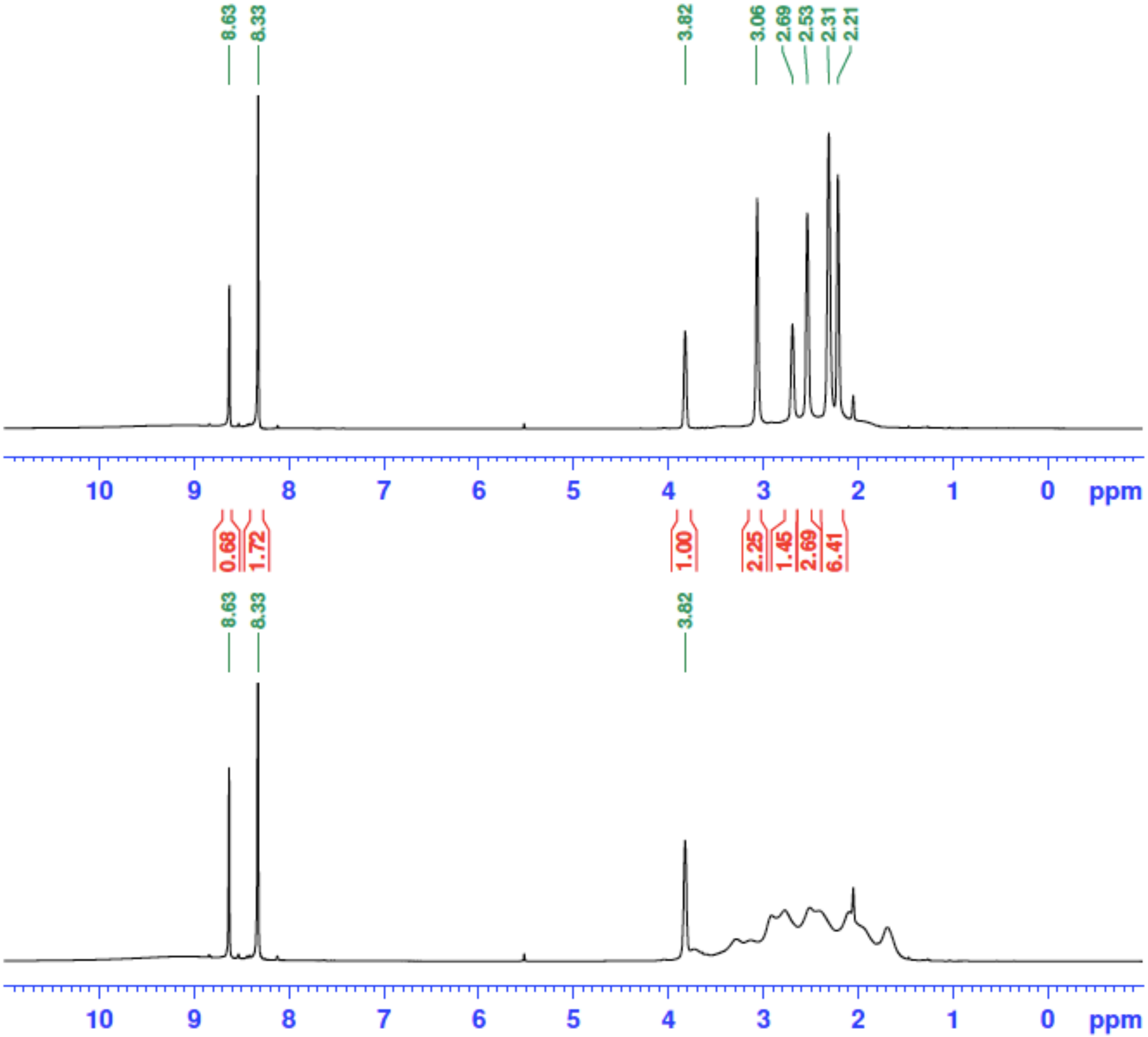
```
NAME      1-(5-diethyisophthalyl)-1,7-closo-C2B10H11
EXPNO                  1
PROCNO                 1
Date_           20130301
Time               10.06
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG             zgig
TD                 16384
SOLVENT          CD2Cl2
NS                   100
DS                     0
SWH            25510.203 Hz
FIDRES          1.557019 Hz
AQ             0.3211764 sec
RG                  90.5
DW                19.600 usec
DE                  6.50 usec
TE                 303.0 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 11B
P1                 12.80 usec
PL1                 1.00 dB
PL1W         17.63811874 W
SFO1         128.3859468 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -0.50 dB
PL12               14.25 dB
PL2W         14.48648834 W
PL12W         0.48524728 W
SFO2         400.1616006 MHz
SI                 32768
SF           128.3873152 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



^{1}H Compound 2

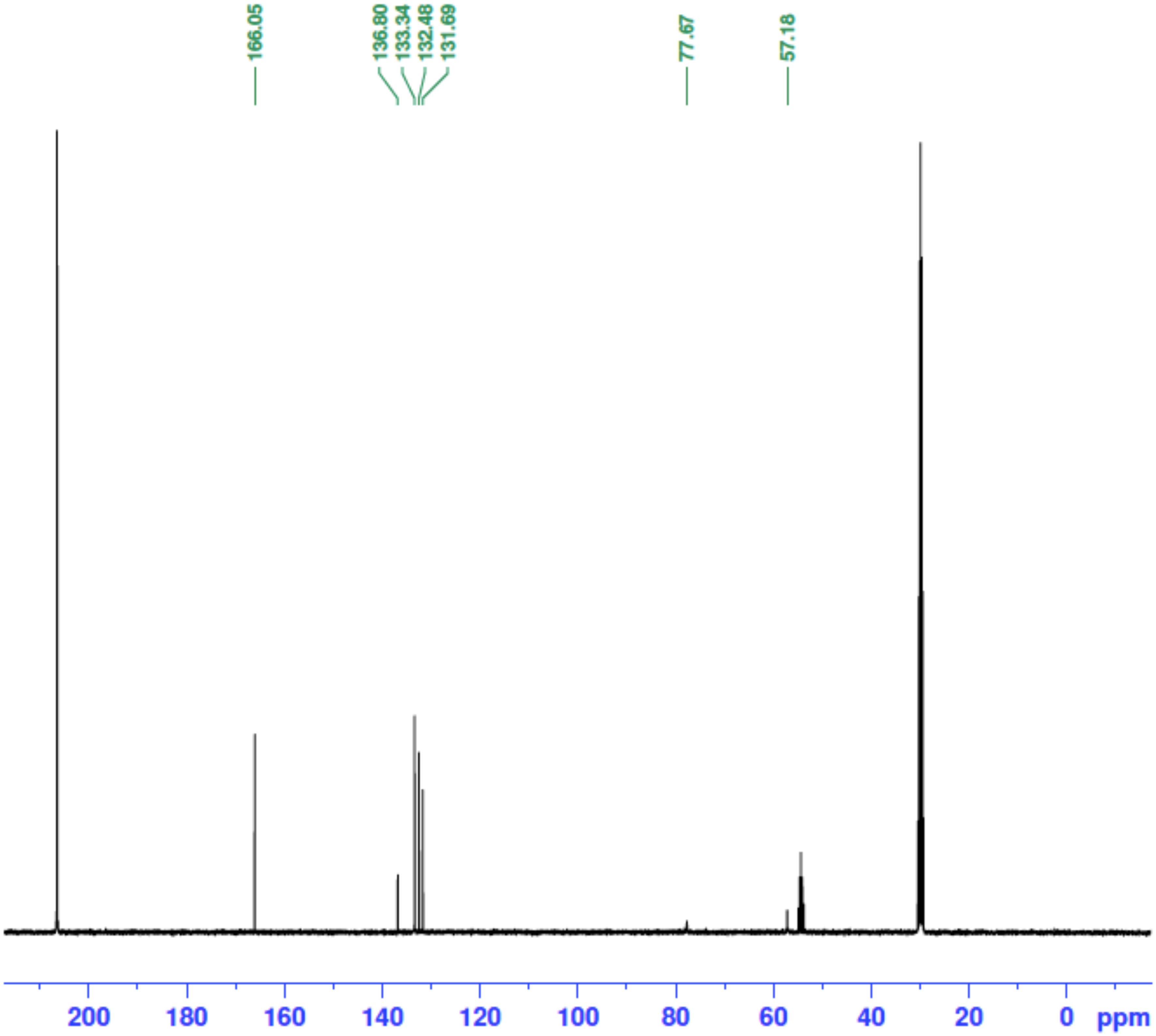


```
NAME      1-(5-isophthalic acid)-1,7-closo-C2B10H11
EXPNO                  7
PROCNO                 1
Date_           20130301
Time               12.07
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zgig
TD                 16384
SOLVENT          Acetone
NS                   100
DS                     0
SWH            25510.203 Hz
FIDRES          1.557019 Hz
AQ             0.3211764 sec
RG                    57
DW                19.600 usec
DE                  6.50 usec
TE                 303.2 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.80 usec
PL1                 1.00 dB
PL1W         10.25564861 W
SFO1         400.1616006 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 11B
PCPD2              80.00 usec
PL2                -0.50 dB
PL12               14.25 dB
PL2W         24.91450500 W
PL12W         0.83454984 W
SFO2         128.3859468 MHz
SI                 32768
SF           400.1600060 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C Compound 2

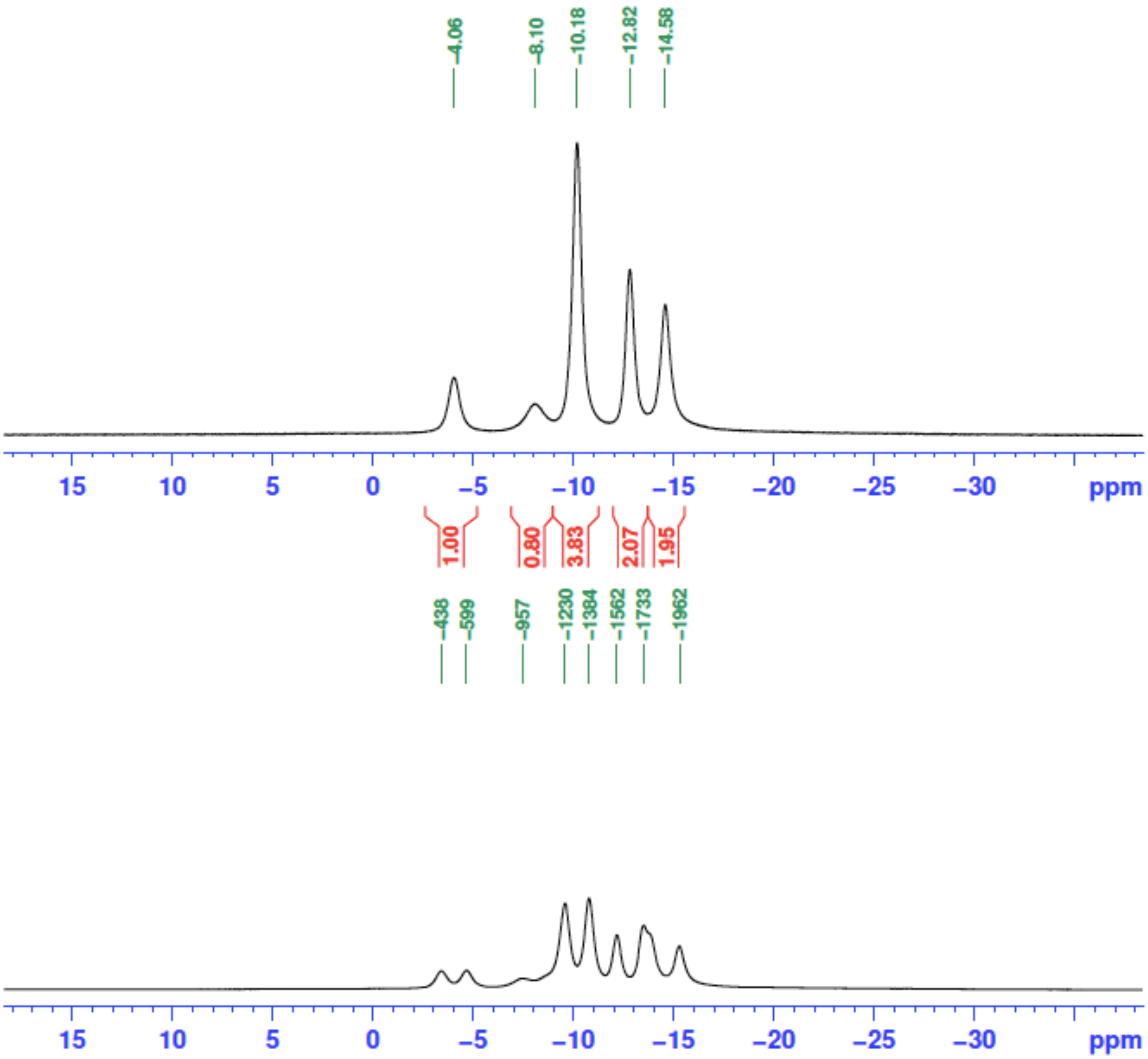


```
NAME       1-(5-isophthalic acid)-1,7-closo-C2B10H11
EXPNO                    9
PROCNO                   1
Date_             20130301
Time                 12.21
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT             Acetone
NS                     314
DS                       0
SWH            27573.529 Hz
FIDRES          0.420739 Hz
AQ             1.1884362 sec
RG                     512
DW                  18.133 usec
DE                    6.50 usec
TE                   303.2 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.98 usec
PL1                  -3.35 dB
PL1W           83.66055298 W
SFO1          100.6303741 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -0.50 dB
PL12                 14.25 dB
PL13                 16.25 dB
PL2W           14.48648834 W
PL12W           0.48524728 W
PL13W           0.30617034 W
SFO2          400.1616006 MHz
SI                   32768
SF            100.6202346 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

^{11}B Compound 2



```
NAME       1-(5-isophthalic acid)-1,7-closo-C2B10H11
EXPNO                    4
PROCNO                   1
Date_             20130301
Time                 11.59
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG               zgig
TD                   16384
SOLVENT            Acetone
NS                     100
DS                       0
SWH              25510.203 Hz
FIDRES            1.557019 Hz
AQ               0.3211764 sec
RG                     228
DW                  19.600 usec
DE                    6.50 usec
TE                   303.0 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   11B
P1                   12.80 usec
PL1                   1.00 dB
PL1W           17.63811874 W
SFO1           128.3859468 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -0.50 dB
PL12                 14.25 dB
PL2W           14.48648834 W
PL12W           0.48524728 W
SFO2           400.1616006 MHz
SI                   32768
SF             128.3872052 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

3. Crystallographic Structure Determination and Refinement Details.

Single crystals of **3** were mounted in inert oil and transferred to the cold gas stream of a Bruker Kappa APEX CCD area detector equipped with a CuKα microsource with Quazar optics. TWINABS-2012/1 (Bruker, 2012) was used for absorption correction. For twin component 1: *w*R2(int) was 0.0574 before and 0.0464 after correction. For twin component 2: *w*R2(int) was 0.0661 before and 0.0493 after correction. The ratio of minimum to maximum transmission is 0.85. All B–B and B–C distances in the carborane moieties were refined with similar distance restraints (SADI). The location of the carbon atom not attached to the phenyl ring was determined by examining the displacement parameters of the atoms in the carborane. The elongated displacement parameters of all B and C atoms indicate that these moieties are rotating about the C(Ph)–C bonds. The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of non-coordinated solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 43982.1 Å^3 [63.1%], total electron count / cell = 9643.9.[3–6]

Table S1 Crystal data and structural refinement for **3**; for atomic coordinates, equivalent isotropic displacement parameters, bond lengths, angles, and anisotropic displacement parameters please see the CIF (CCDC code *942360*)

Empirical formula	$C_{258}H_{414}B_{240}Cu_{24}N_6O_{120}$
Formula weight	9639.29
Temperature (K)	100.02
Crystal system	trigonal
Space group	$R\bar{3}$
a (Å), b (Å), c (Å)	31.498(4), 31.498(4), 81.077(12)

a (°), β (°), γ (°)	90, 90, 120
Volume (Å^3)	69662(24)
Z	3
Calculated Density (mg/mm^3)	0.689
Absorption coefficient (mm^{-1})	0.871
F(000)	14580
Crystal size (mm^3)	0.117 × 0.091 × 0.056
2θ range for data collection	7.82 to 117.86°
Index ranges	$-34 \leq h \leq 17$, $0 \leq k \leq 34$, $0 \leq l \leq 90$
Reflections collected	103596
Independent reflections	22202[R(int) = 0.0534]
Data/restraints/parameters	22202/5193/976
Goodness-of-fit on F^2	1.119
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0870$, $wR_2 = 0.2878$
Final R indices [all data]	$R_1 = 0.1088$, $wR_2 = 0.3009$
Largest diff. peak and hole (e Å^{-3})	0.913/–0.358

4. Powder X-ray Diffraction (PXRD)

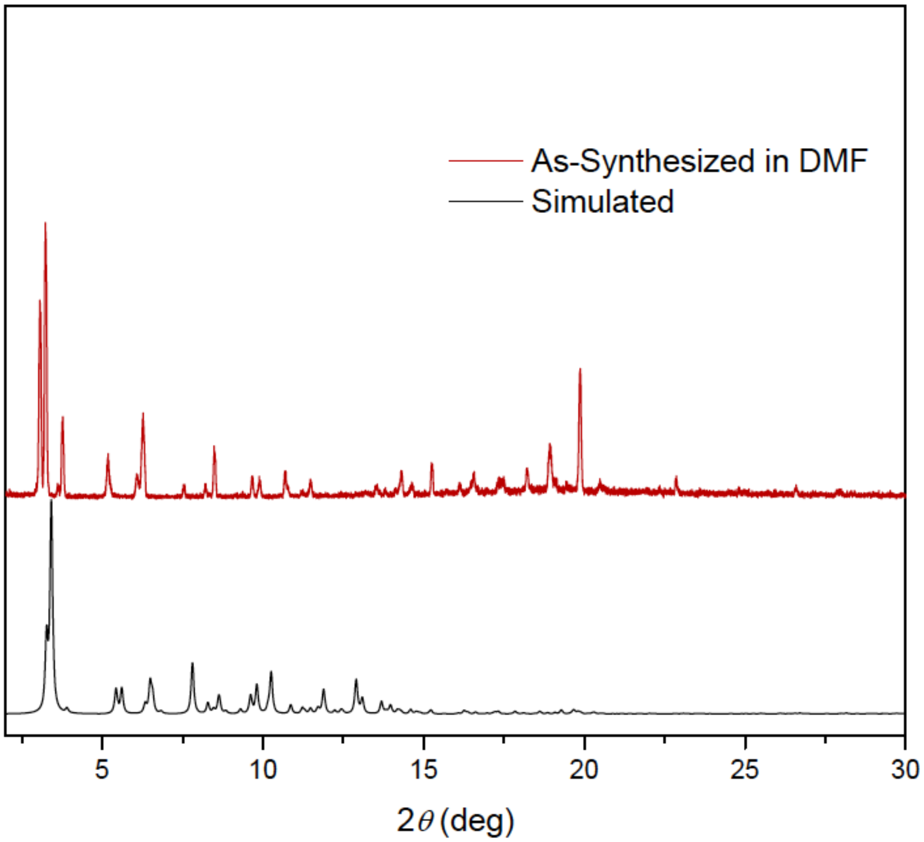


Figure S1. Powder X-ray diffraction (PXRD) patterns of **3**: pattern simulated from single-crystal structure in black, experimental pattern for the as-synthesized sample in red.

5. Thermogravimetric Analysis (TGA)

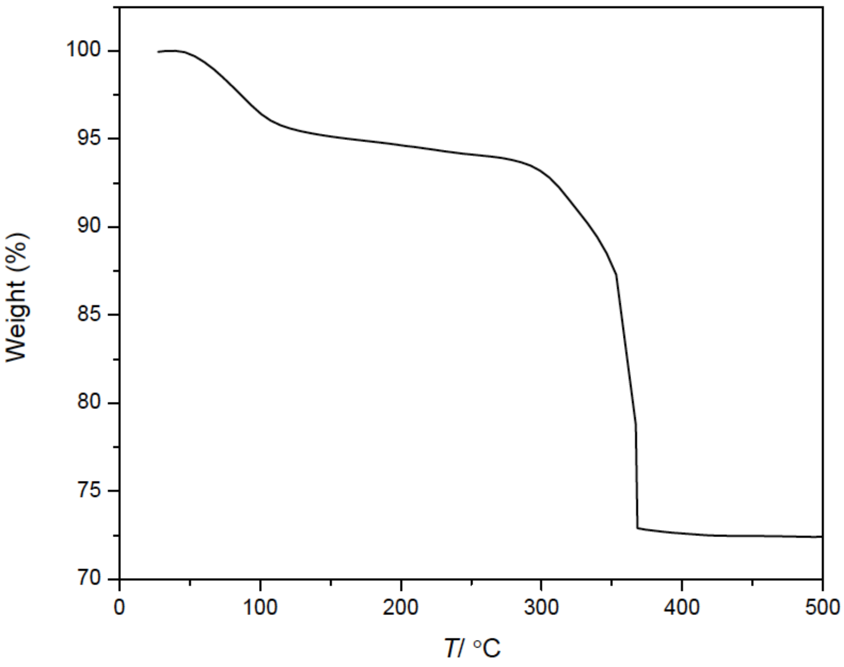


Figure S2. TGA curve of **3** (activated). The first step in the TGA is most likely due to residual moisture of the sample.

6. Gas Adsorption

The activation of **3**: an as-synthesized sample of **3** was soaked in methanol for 3 days, refreshing the methanol once per day. The methanol from the final soak was decanted and replaced with supercritical CO_2. Before adsorption measurement, the sample was further activated by heating under vacuum. Finally, 73.9 mg sample was used in gas adsorption measurement. Isotherms of N_2 at 77 K are shown below (Fig S3).

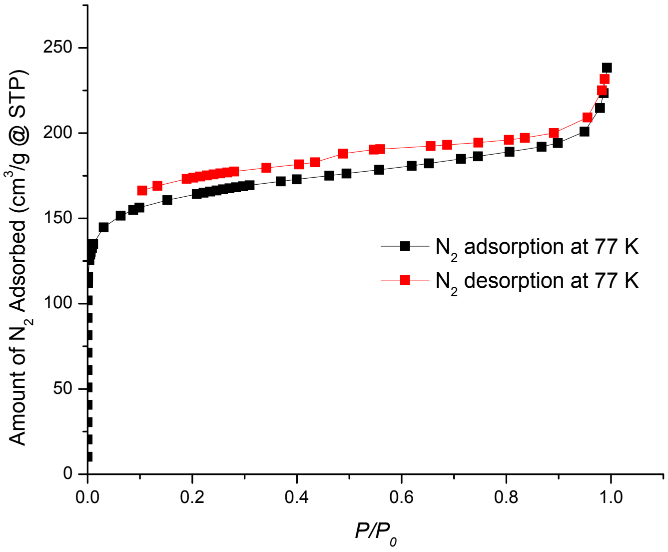


Figure S3. Adsorption and desorption isotherms of N_2 on activated **3**.

7. References

1. Farha, O. K.; Özgür Yazaydın, A.; Eryazici, I.; Malliakas, C. D.; Hauser, B. G.; Kanatzidis, M. G.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T., De novo synthesis of a metal–organic framework material featuring ultrahigh surface area and gas storage capacities. *Nat Chem* **2010**, *2*, 944–948.
2. Schöberl, U.; Magnera, T. F.; Harrison, R. M.; Fleischer, F.; Pflug, J. L.; Schwab, P. F. H.; Meng, X.; Lipiak, D.; Noll, B. C.; Allured, V. S.; Rudalevige, T.; Lee, S.; Michl, J., Toward a Hexagonal Grid Polymer: Synthesis, Coupling, and Chemically Reversible Surface-Pinning of the Star Connectors, 1,3,5-$C_6H_3(CB_{10}H_{10}CX)_3$. *J. Am. Chem. Soc.* **1997**, *119*, 3907–3917.
3. APEX2 V2.1–4 (Bruker, 2007)
4. olex2.solve (L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, in preparation, 2011)

5. SHELXL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112–122

6. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339–341.