# Supporting Information

## Diaryl-substituted ortho-carboranes as a new class of hypoxia inducible factor-1α Inhibitors

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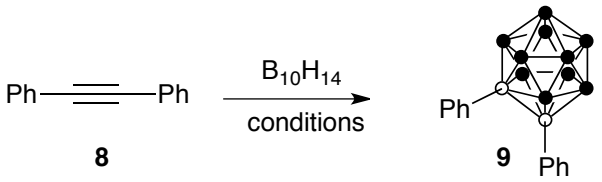
**General Information.** Analytical thin layer chromatography (TLC) was performed on a glass plates of silica gel 60 $GF_{254}$ (Merck), which were visualized by the quenching of UV fluorescence (254 nm), and/or by an aqueous alkaline $KMnO_4$ solution followed by heating. Column chromatography was conducted on silica gel (Merck Kieselgel 70-230 mesh). Most commercially supplied chemicals were used without further purification. $^1H$ and $^{13}C$ NMR spectra were recorded on a JEOL JNM-AL 300 (300 MHz) or a VARIAN UNITY-INOVA 400 (400 MHz) spectrometer. The chemical shifts are reported in δ units relative to internal tetramethylsilane. IR spectra were recorded on a Shimadzu FTIR-8200A spectrometer. Liquid chromatogram mass spectrometer was recorded on Shimadzu LCMS-2010EV. High-resolution mass spectra (ESI) were recorded on a Bruker Daltonics micro TOF-15 focus. *Decaborane* was purchased from Katchem spol. s r. o. (Praha, Czech Republic). Most commercially supplied chemicals were used without further purification. Alkynes **3a**-**g** were prepared from 5-ethynyl-1,2,3-trimethoxybenzene **2a** or 4-ethynyl-1,2-dimethoxybenzene **2b** according to the literature procedure.[1]

**The Optimization of Reaction Conditions for Decaborane Coupling.**

The reaction conditions of the decaborane coupling were optimized using 1,2-diphenylethyne **8** as the starting material. The results are shown in Table S1. The reaction of **8** with decaborane proceeded in the presence of acetonitrile for 8 h under toluene reflux conditions to give 1,2-diphenyl-*ortho*-carborane **9** in 30% yield (entry 1). Prolonging the reaction time did not increase the yield (entry 2). Next, the reaction was carried out by microwave irradiation in a sealed tube. Although the reaction time was reduced by the microwave irradiation, the yields of **9** did not increase (entries 3 and 4). A higher reaction temperature also did not increase the reaction yield (entry 5). Then, we examined the effects of Lewis bases on the coupling. Whereas propionitrile, which was efficient in our previous experiments,[2] was not effective for this reaction (entry 6), the combination of *N,N*-dimethylaniline and chlorobenzene, a protocol developed by Nagasawa *et al.*,[3] worked effectively. Indeed, the coupling of decaborane with **8** proceeded smoothly in the presence of three equivalents of *N,N*-dimethylaniline as the Lewis base in chlorobenzene by microwave irradiation for

15 min, giving 1,2-diphenyl-*ortho*-carborane **9** in 75% yield (entry 7).

**Table S1.** Optimization of reaction conditions for decaborane coupling




| entry | base | solvent | temp/°C | time | yield/% |
|---|---|---|---|---|---|
| 1 | $CH_3CN$ | toluene | 110 [a] | 8 h | 30 |
| 2 | $CH_3CN$ | toluene | 110 [a] | 22 h | 30 |
| 3 | $CH_3CN$ | toluene | 110 [b] | 30 min | 7 |
| 4 | $CH_3CN$ | toluene | 110 [b] | 1 h | 35 |
| 5 | $CH_3CN$ | toluene | 150 [b] | 1 h | 31 |
| 6 | $CH_3CH_2CN$ | toluene | 110 [b] | 1 h | 30 |
| 7 | *N,N*-dimethylaniline | chlorobenzene | 150 [b] | 15 min | 75 |

[a] Reactions were carried out under toluene reflux conditions. [b] Reactions were carried out under microwave-irradiated conditions in a sealed tube.

**Typical procedure for synthesis of 1-(3-Hydroxy-4-methoxyphenyl)-2-(3,4,5-trimethoxyphenyl) -*ortho*-carborane (1a)**

A mixture of decaborane (17.5 mg, 0.14 mmol), **3a** (30 mg, 0.095 mmol), *N,N*-dimethylaniline (22.2 μL, 0.28 mmol) was dissolved in chlorobenzene (1 mL) and microwave irradiation was carried out at 120 ºC for 15 min under nitrogen. The reaction mixture was extracted with EtOAc three times and combined organic layers were washed with water, 0.5 N HCl aq., and brine, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (Hexane/EtOAc = 10:1 to 1:1) to give **1a** as a white solid (25.5 mg, 61%). M.p. 152-153 ºC; $^1$H NMR (400 MHz; $CDCl_3$) δ 7.08 (m, 1H), 6.94 (m, 1H), 6.63 (s, 2H), 6.60 (s, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 5.50 (s, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.73 (s, 3H); $^{13}$C NMR (75 MHz; $CDCl_3$) δ 152.2, 148.0, 144.9, 125.9, 124.0, 123.1, 117.3, 109.7, 108.5, 85.8, 85.5, 77.4, 77.2, 77.0, 76.6, 60.8, 56.2, 55.9; $^{11}$B NMR (96.3 MHz; $CDCl_3$) δ -15.42, -7.71; IR (KBr) 2548, 1589, 1508, 1337, 1130, 835 cm$^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{27}B_{10}O_5$ [$M^-$] 431.2871; found 431.2876.

**1-(4-Methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1b)**

White solid; m.p. 100-102 ºC; $^1$H NMR (400 MHz; $CDCl_3$) δ 7.36 (d, *J* = 9.2 Hz, 2H), 6.67 (d, *J* = 9.2 Hz, 2H), 6.60 (s, 2H), 3.77 (s, 3H), 3.74 (s, 3H), 3.71 (s, 6H); $^{13}$C NMR (100 MHz; $CDCl_3$) δ 161.0, 152.3, 139.6, 132.1, 126.0, 123.1, 113.6, 108.5, 85.9, 85.4, 60.8, 56.2, 55.3; $^{11}$B NMR (96.3 MHz; $CDCl_3$) δ -14.74, -7.22; IR (KBr) 2548, 1589, 1508, 1337, 1130, 835 cm$^{-1}$; HRMS (ESI-TOF)

*m/z* calcd for $C_{18}H_{28}B_{10}O_4Na$ [M + $Na^+$] 439.2893; found 439.2892.

**1-(3-Methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1c)**

White solid; m.p. 128-129 ºC; $^1$H NMR (400 MHz; $CDCl_3$) δ 7.04-7.12 (m, 2H), 6.98 (s, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.61 (s, 2H), 3.77 (s, 3H), 3.70 (s, 9H); $^{13}$C NMR (75 MHz; $CDCl_3$) δ 161.0, 152.3, 139.6, 132.1, 126.0, 123.1, 113.6, 108.5, 85.9, 85.4, 60.8, 56.2, 55.3; $^{11}$B NMR (96.3 MHz; $CDCl_3$) δ -15.24, -7.22; IR (KBr) 2592, 1586, 1509, 1455, 1415, 1335, 1249, 1130, 1000 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{28}B_{10}O_4Na$ [M + $Na^+$] 439.2887; found 439.2892.

**1-(2-Methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1d)**

White solid; m.p. 137-140 ºC; $^1$H NMR (400 MHz; $CDCl_3$) δ 7.53 (d, *J* = 9.6 Hz, 1H), 7.23-7.28 (m, 1H), 6.74-6.81 (m, 2H), 6.65 (s, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 3.69 (s, 6H); $^{13}$C NMR (100 MHz; $CDCl_3$) δ 159.0, 152.2, 139.4, 134.6, 132.1, 126.7, 120.6, 118.6, 112.6, 108.1, 86.6, 83.8, 60.8, 56.1, 55.4; $^{11}$B NMR (96.3 MHz; $CDCl_3$) δ -15.04, -8.40, -6.57; IR (KBr) 2563, 1585, 1508, 1128, 754, 628 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{28}B_{10}O_4Na$ [M + $Na^+$] 439.2888; found 439.2892.

**1-(4-Methoxyphenyl)-2-(3,4-dimethoxyphenyl)-*ortho*-carborane (1e)**

White solid; m.p. 119-120 ºC; $^1$H NMR (400 MHz; $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 2.0 Hz, 1H), 6.65-6.60 (m, 3H), 3.80 (s, 3H), 3.73 (s, 6H); $^{13}$C NMR (100 MHz; $CDCl_3$) δ 160.9, 150.4, 148.0, 132.1, 124.0, 123.3, 123.1, 113.6, 113.5, 110.2, 85.9, 55.8, 55.3; $^{11}$B NMR (96.3 MHz; $CDCl_3$) δ -15.44, -13.86, -7.51; IR (KBr) 2960, 2636, 1518, 1332, 1022, 862, 615 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{26}B_{10}O_3Na$ [M + $Na^+$] 409.2783; found 409.2784.

**1-(3-Methoxyphenyl)-2-(3,4-dimethoxyphenyl)-*ortho*-carborane (1f)**

White solid; m.p. 95-98 ºC; $^1$H NMR (400 MHz; $CDCl_3$) δ 7.02-7.09 (m, 3H), 6.98 (s, 1H), 6.86 (s, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 8.8 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 3.70 (s, 3H); $^{13}$C NMR (100 MHz; $CDCl_3$) δ 159.0, 150.5, 148.0, 132.1, 129.2, 124.0, 123.1, 117.2, 115.1, 113.5, 110.2, 85.6, 85.0, 55.9, 55.3; $^{11}$B NMR (96.3 MHz; $CDCl_3$) δ -15.21, -13.67, -7.22; IR (KBr) 2567, 1601, 1520, 1414, 1271, 1153, 1024, 854 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{26}B_{10}O_3Na$ [M + $Na^+$] 409.2783; found 409.2784.

**1-(2-Methoxyphenyl)-2-(3,4-dimethoxyphenyl)-*ortho*-carborane (1g)**

White solid; m.p. 132-134 ºC; $^1$H NMR (400 MHz; $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 1H), 7.23 (t, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.90 (s, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.73 (t, *J* = 8.0, 1H), 6.60 (d, *J* = 8.8, 1H), 3.79 (s, 6H), 3.68 (s, 3H); $^{13}$C NMR (100 MHz; $CDCl_3$) δ 159.0, 150.2, 147.8, 134.5, 132.0, 124.0, 123.7, 120.5, 113.3, 112.6, 110.1, 87.1, 83.8, 55.8, 55.4; $^{11}$B NMR (96.3 MHz; $CDCl_3$) δ -15.21, -8.59, -6.54; IR (KBr) 2554, 1599, 1518, 1267, 1155, 1024, 758 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{26}B_{10}O_3Na$ [M + $Na^+$] 409.2783; found 409.2785.

**1-(4-(Benzyloxybenzoyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (6)**

White solid; m.p. 142-144 ºC; $^{1}$H NMR (400 MHz; $CDCl_3$) δ 7.68 (d, *J* = 8.8 Hz, 2H), 7.58-7.54(m, 4H), 7.40-7.42 (m, 5H), 7.05 (d, *J* = 9.2 Hz, 2H), 6.62 (s, 2H), 5.14 (s, 2H), 3.77 (s, 3H), 3.71 (s, 6H); $^{13}$C NMR (100 MHz; $CDCl_3$) δ 194.0, 162.8, 152.4, 140.0, 136.0, 134.0, 132.5, 130.6, 129.4, 128.7, 128.3, 127.5, 125.5, 114.6, 108.5, 85.5, 84.2, 70.2, 60.8, 56.2; $^{11}$B NMR (96.3 MHz; $CDCl_3$) δ -14.74, -7.22; IR (KBr) 2571, 1655, 1585, 1501, 1252, 1128, 1005, 841 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{31}H_{36}B_{10}O_5Na$ [M + $Na^+$] 620.3443; found 620.3445.

**1-(4-(Propargyloxybenzoyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (7)**

To mixture of **6** (34.1 mg, 0.057 mmol) in MeOH/THF (1:1 v/v, 1.5 mL) was added Pd/C (12 mg) and the mixture was stirred under $H_2$ gas for 1 h at room temperature. The reaction mixture was filtered with a celite pad and the solvent was removed under reduced pressure. The residue was dissolved in acetone (1.2 mL) and propargyl bromide (5.2μL, 0.068 mmol) and $K_2CO_3$ (78.7 mg, 0.57 mmol) were added with stirring. The reaction was quenched with water and the mixture was extracted with EtOAc three times. The combined organic layers washed with water, 0.5 N HCl aq., and brine, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (hexane:EtOAc = 20:1 to 3:2) to give **7** as a white solid (14.6 mg, 2 steps 47%). M.p. 158-159 ºC; $^{1}$H NMR (400 MHz; $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 2H), 7.58-7.56 (m, 4H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.23 (s, 2H), 4.77 (s, 2H), 3.77 (s, 3H), 3.71 (s, 6H), 2.56 (s, 1H); $^{13}$C NMR (75 MHz; $CDCl_3$) δ 194.0, 161.4, 152.4, 140.0, 139.6, 134.1, 132.3, 130.6, 130.1, 129.4, 125.5, 114.6, 108.5, 85.5, 84.1, 77.6, 77.2, 76.3, 60.8, 56.2, 55.9; $^{11}$B NMR (96.3 MHz; $CDCl_3$) δ -14.85, -7.19; IR (KBr) 3296, 2552, 1599, 1252, 847, 633 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{27}H_{32}B_{10}O_5Na$ [M + $Na^+$] 567.3158; found 567.3161.

**Cell culture**

The human cervical carcinoma cell line HeLa cells were obtained the Cell Resource Center for Biomedical Research, Institute of Development, Aging and Cancer, Tohoku University (Sendai, Japan). The cells were cultured under 5% $CO_2$ at 37 ºC in RPMI 1640 medium (Wako pure Chemical, Osaka, Japan) supplemented with 10% fetal bovine serum (FBS, HyClone, Logan, UT), 100 U/ml penicillin and 100 μg/ml streptomycin (Invitrogen, Carlsbad, CA). For subsequent experiments, the cells were seeded at a density of 2.5 x $10^5$ cells/ml/well in a 12-well TC plate (Greiner Japan, Tokyo, Japan), and incubated at 37 ºC for 12h. Hypoxic condition was achieved by replacing cells to 1% $O_2$, 95% $N_2$ and 5% $CO_2$ in a multigas incubator (Astec, Fukuoka, Japan).

**Reporter-gene assay**

**Hypoxia-induced HIF-1 transcriptional activity (Luciferase) Assay:**

HeLa cells expressing HRE-dependent firefly luciferase reporter construct (HRE-Luc) and constitutively expressing CMV-driven Renilla luciferase reporter with SureFECT Transfection Reagent were established with Cignal™ Lenti Reporter (SABiosciences, Frederick, MD) according to the manufacturer's instructions. The consensus sequence of HRE was 5'-TACGTGCT-3' from the erythropoietin gene. Cells stably expressing the HRE-reporter gene were selected with puromycin. The cells were incubated for 12 h with or without compounds under the normoxic or hypoxic condition. After removal of the supernatant, the luciferase assay was performed using a Luciferase Assay System (Promega, Madison, WI) according to the manufacturer's instructions. The drug concentration required to inhibit the relative light units by 50% ($IC_{50}$) was determined from semi-logarithmic dose–response plots.

**Western blotting**

HeLa cells were treated with compounds and incubated for 4 h under hypoxic condition. The cells were washed with PBS (Ca/Mg-free) three times, dipped in 100 μL of ice-cold lysis buffer (20 mM HEPES, pH = 7.4, 1% triton X-100, 10% glycerol, 1 mM EDTA, 5 mM sodium fluoride, 2.5 mM *p*-nitrophenylene phosphate, 10 μg/mL phenylmethylsulfonylfluoride, 1 mM sodium vanadate, and 10 μg/mL leupeptin) for 15 min, and disrupted with a Handy Sonic Disrupter, and the lysate was boiled for 5 min in a sample buffer (50 mM Tris, pH 7.4, 4% SDS, 10% glycerol, 4% 2-thioethanol, and 50 μg/mL bromophenol blue) at a ratio of 4:1. The cell lysates were subjected to SDS-polyacrylamide gel electrophoresis (PAGE), transferred to polyvinylidene difluoride (PVDF) membrane (GE Healthcare Buckinghamshire, UK), and immunoblotted with anti-HIF-1α antibody (BD Transduction Laboratories, Lexington, KY) and anti-Tubulin antibody (Santa Cruz Biotechnology, Santa Cruz, CA). After further incubation with horseradish peroxidase (HRP)-conjugated secondary antibody, the blot was treated with ECL kit (GE Healthcare) and protein expression was visualized with a Molecular Imager ChemiDoc XRS System (Bio-Rad, Hercules, CA)

**Reverse transcription polymerase chain reaction (RT-PCR)**

HeLa cells were treated with compounds and incubated for 4 h under hypoxic condition. Total RNA was extracted with an ISOGEN II (Wako Pure Chemicals, Osaka, Japan) according to the manufacturer's instructions. The extracted RNA (1 μg) was reverse transcribed at 40 ºC for 50 min by adding 5 μM random hexamer oligonucleotides (Promega, Madison, WI), and 2.5 mM dNTP (Bioline, London, UK). The PCR primers used were 5'-CTC AAA GTC GGA CAG CCT CA-3' (sense) and 5'-CCC TGC AGT AGG TTT CTG CT-3' (antisense) for HIF-1α and 5'-ACC ACA GTC CAT GCC ATC AC-3' (sense) and 5'- TCC CCA CCC TGT TGC TGT A -3' (antisense) for glyceraldehyde 3-phosphate dehydrogenase (GAPDH). PCR was carried out with 10 μL of template DNA and 40 μL of PCR buffer (10 mM Tris-HCl, pH 8.3, 50 mM KCl, and 1.5 mM MgCl2) containing each primer (0.2 μM), dNTP (0.2 mM), and BIOTAQTM DNA polymerase (1.25 units)

(Bioline). The PCR conditions for the primer sets were as follows: initial denaturation at 94 ºC for 5 min, 25 cycles of amplification consisting of a denaturation step at 94 ºC for 0.5 min, an annealing step at 58 ºC for 0.5 min, an extension step at 72 ºC for 1 min, and a final extension at 72 ºC for 7 min using PCR thermal cycler (Astec, Fukuoka, Japan). After the PCR, 10 μL of the reaction mixture was subjected to electrophoresis on 2% agarose gel. The PCR products were stained with ethidium bromide and HIF-1α and GAPDH mRNA expression was visualized with the Molecular Imager ChemiDoc XRS System.

**Target protein identification by a pull-down method**

HeLa cells were plated on ø100 dishes (5 x $10^6$ cells) and incubated at 37ºC for 24 hr. After treatment with compound **7** (10 μM) for 1 h, the cells were suspended in 100 μL of PBS and then irradiated with 360 nm UV radiation (UVP, Upland, CA, USA) on ice for 20 min. Click reactions of the probe and azide linked biotin were established with the Click-iT Protein Reaction Buffer Kit (Invitrogen) according to the manufacturer's instructions. The mixture was incubated for 1 h in 400 μL binding buffer (50 mM Tris (pH 7.5), 150 mM NaCl) in Streptavidin HP SpinTrap (GE Healthcare). After three washings with PBS, proteins were eluted in an elution buffer (1.2% SDS in PBS) followed by boiling for 5 min in a sample buffer (50 mM Tris, pH 7.4, 4% SDS, 10% glycerol, 4% 2-thioethanol, and 50 μg/mL bromophenol blue) at a ratio of 4:1 and then separated by SDS/PAGE.

**Reference**

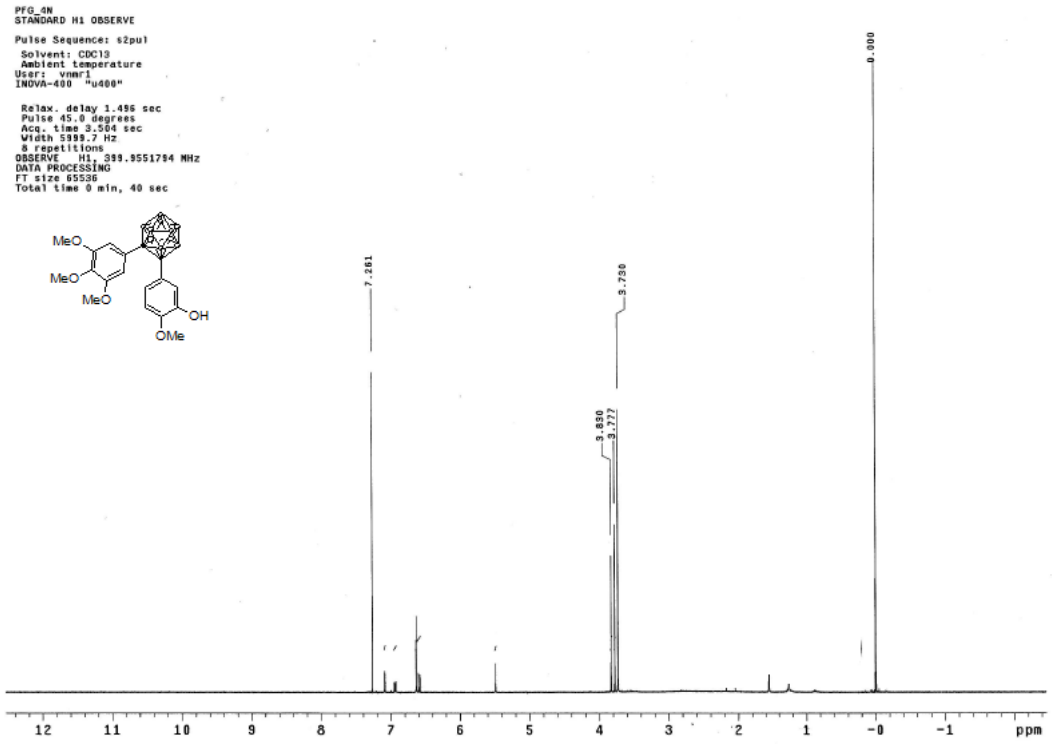
(1) N. J. Lawrence, F. A. Ghani, L. A. Hepworth, J. A. Hadfield, A. T. McGown, R. G. Pritchard, *Synthesis* **1999**, 1656–1660.

(2) Y. Yamamoto, T. Seko, H. Nakamura, H. Nemoto, H. Hojo, N. Mukai and Y. Hashmioto, *J. Chem. Soc., Chem. Commun.*, 1992, 157-158.

(3) H. Nagasawa et al. Unpublished results.

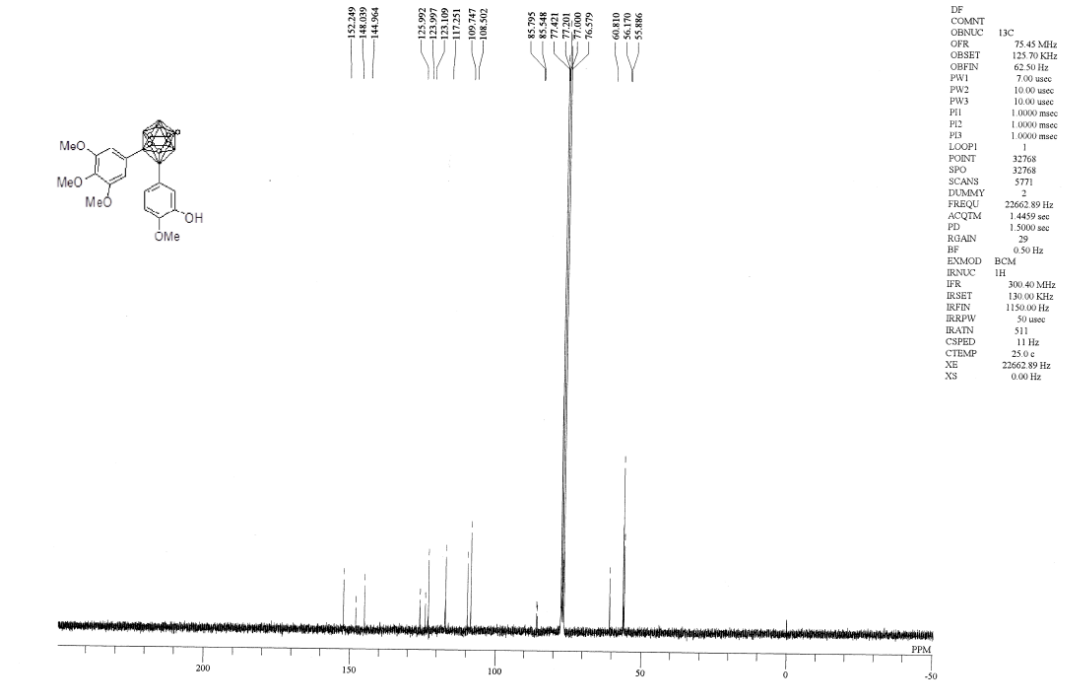
**1-(3-Hydroxy-4-methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1a)**

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



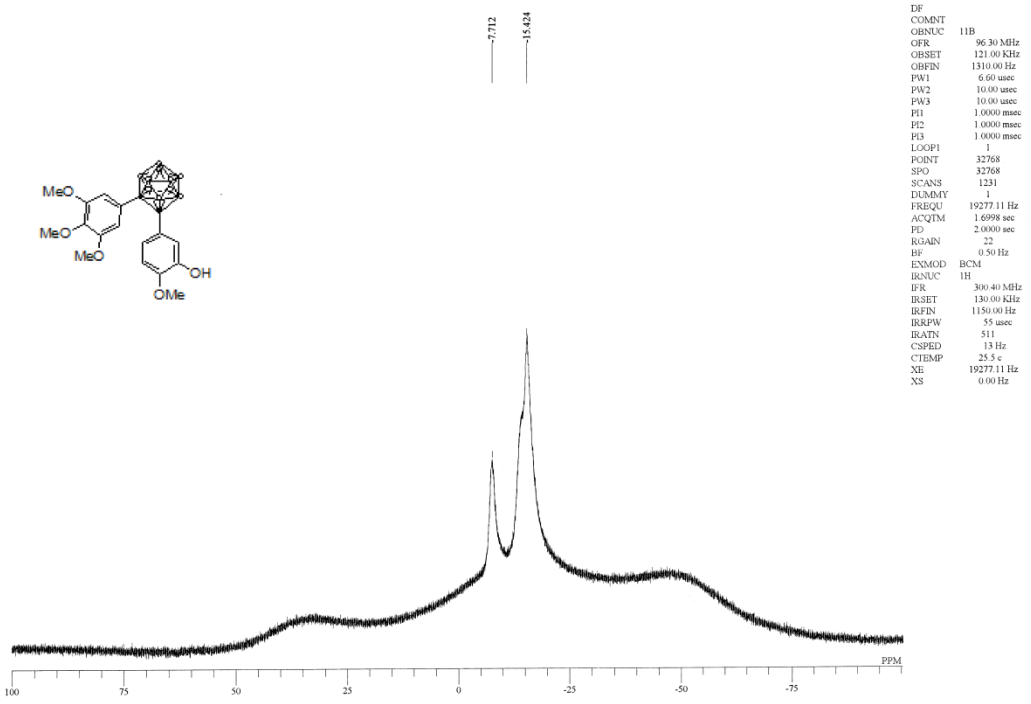

**1-(3-Hydroxy-4-methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1a)**

**$^{13}$C NMR ($CDCl_3$, 75MHz)**



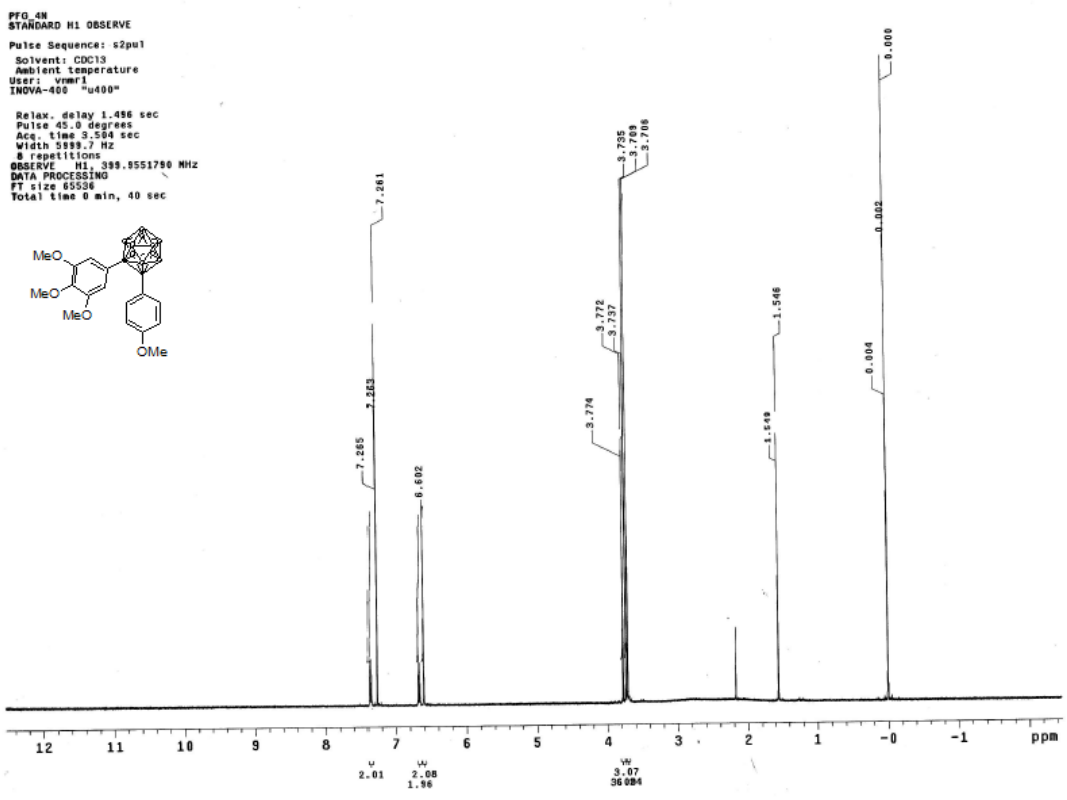
**1-(3-Hydroxy-4-methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1a)**

**$^{11}$B NMR ($CDCl_3$, 96.3MHz)**



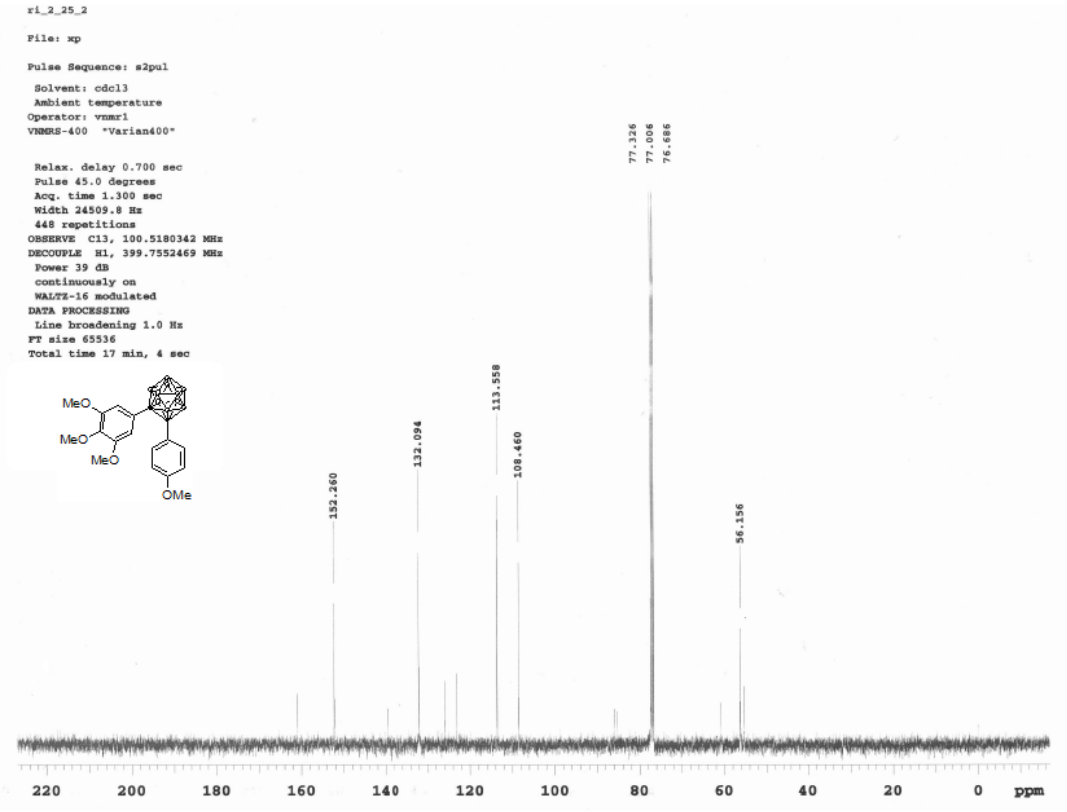

**1-(4-Methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1b)**

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



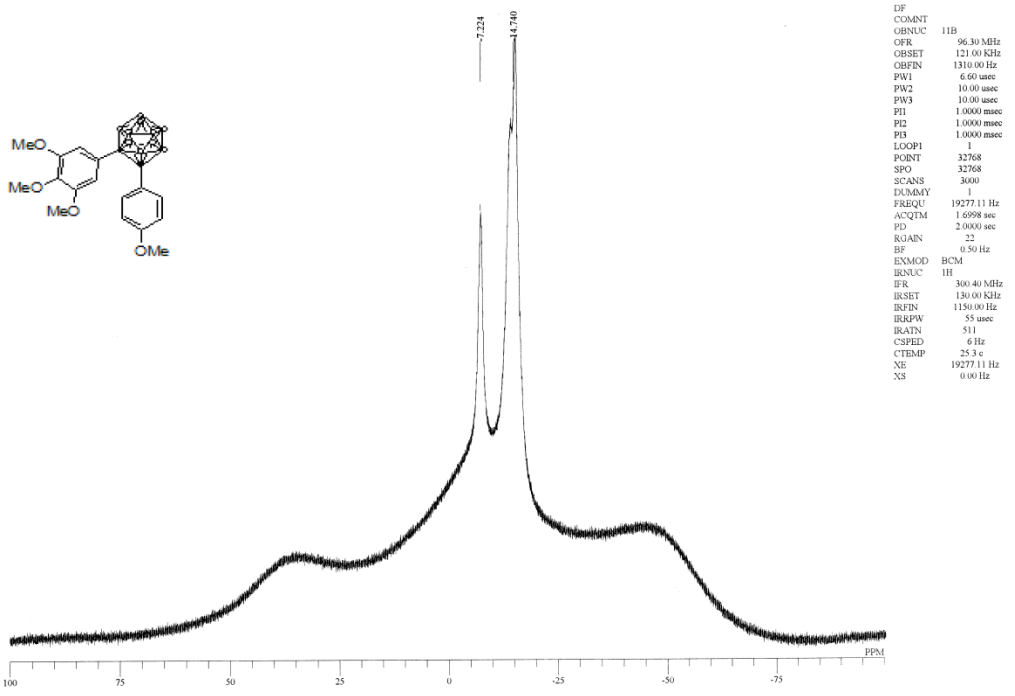
**1-(4-Methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1b)**

**$^{13}$C NMR ($CDCl_3$, 100MHz)**



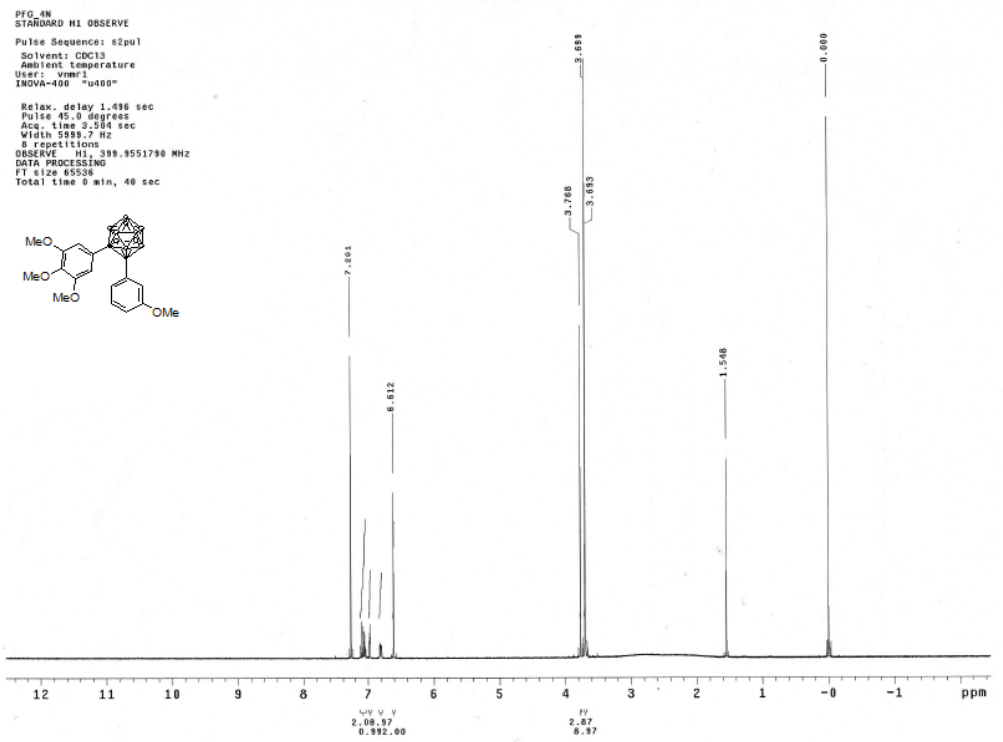

**1-(4-Methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1b)**

**$^{11}$B NMR ($CDCl_3$, 96.3MHz)**



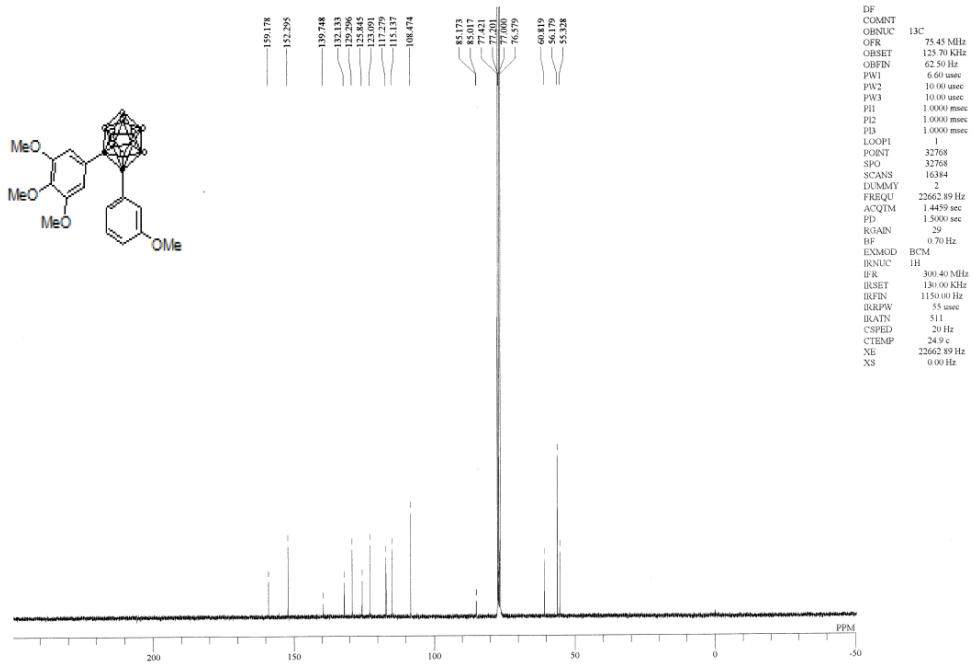
**1-(3-Methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1c)**

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



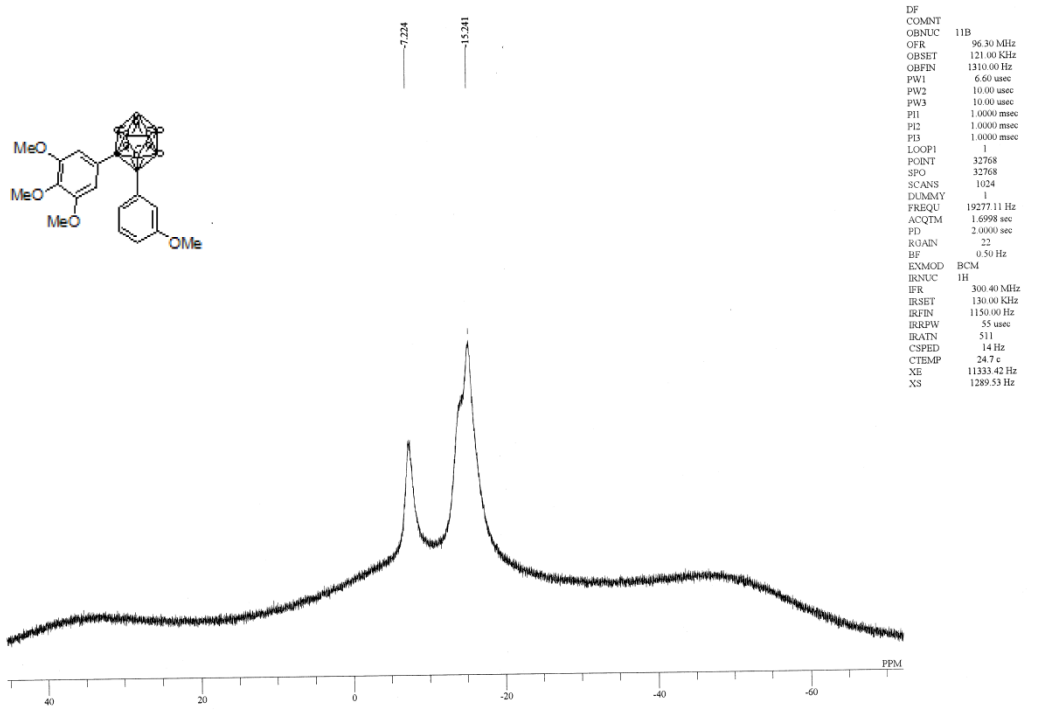

**1-(3-Methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1c)**

**$^{13}$C NMR ($CDCl_3$, 75MHz)**



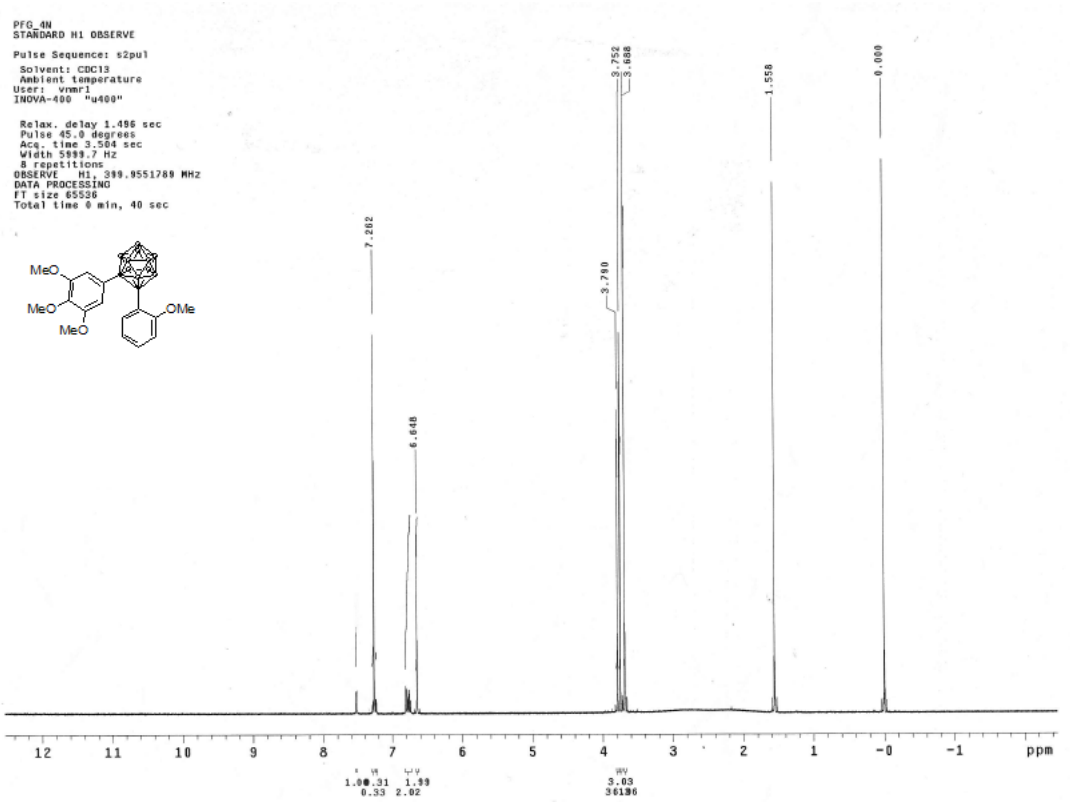

**1-(3-Methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1c)**

**$^{11}$B NMR ($CDCl_3$, 96.3MHz)**



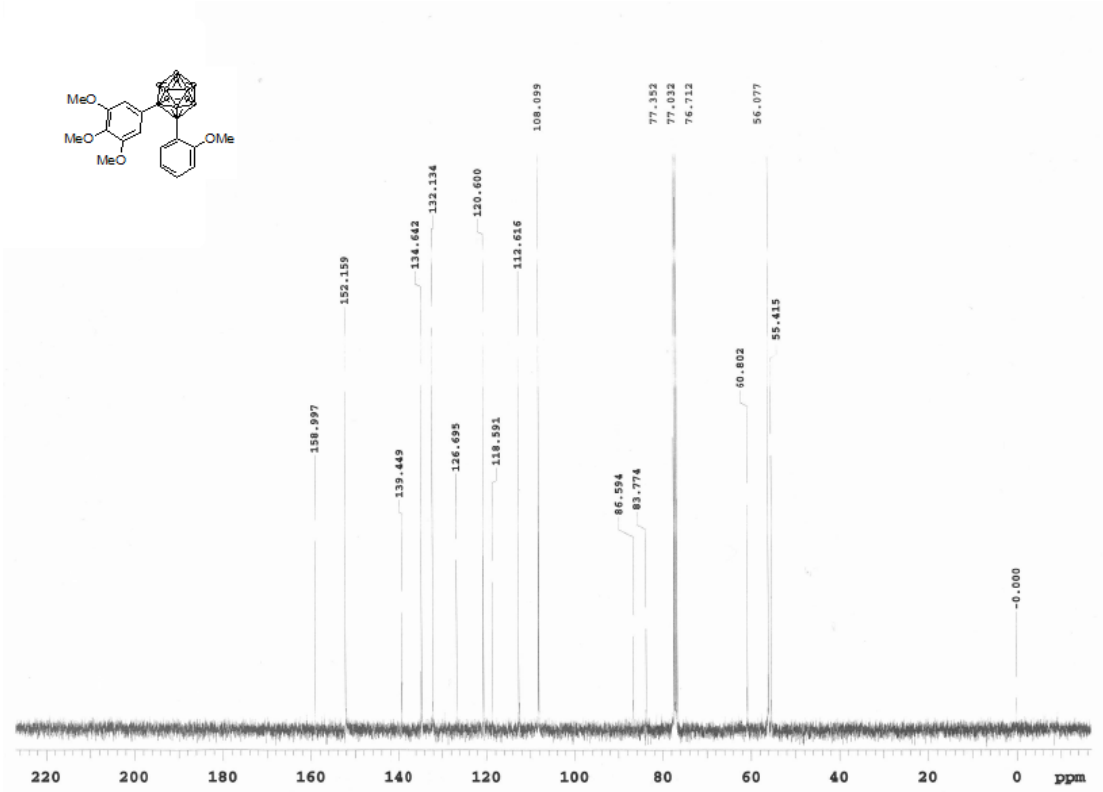

**1-(2-Methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1d)**

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



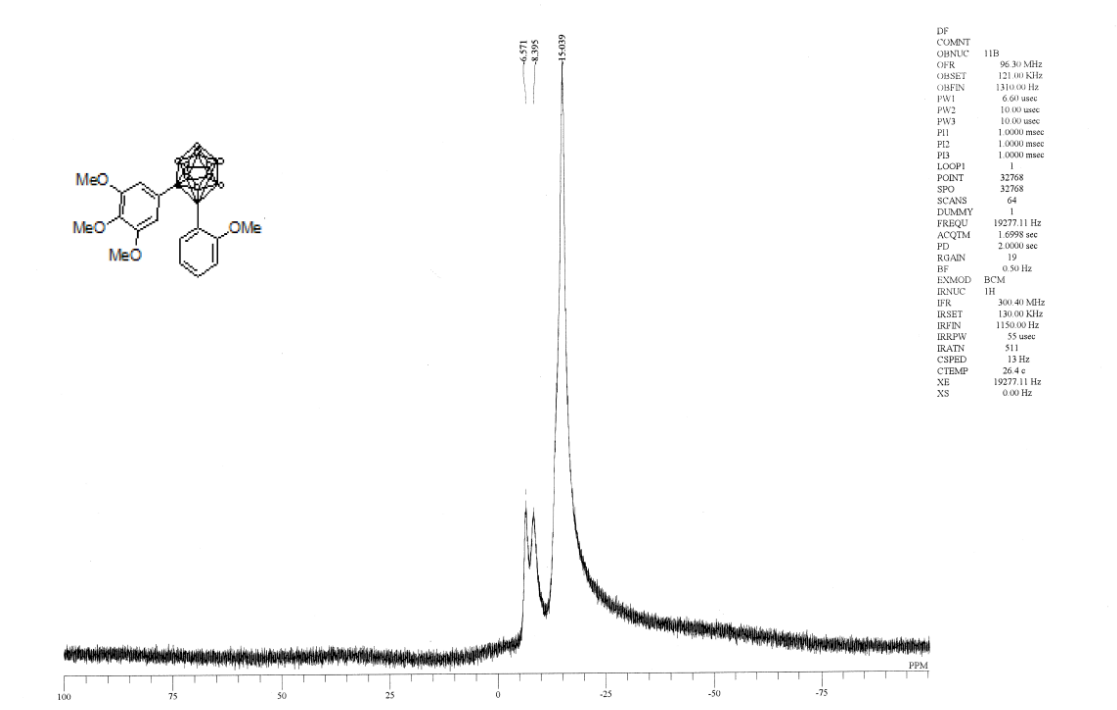
**1-(2-Methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1d)**

**$^{13}$C NMR ($CDCl_3$, 100MHz)**



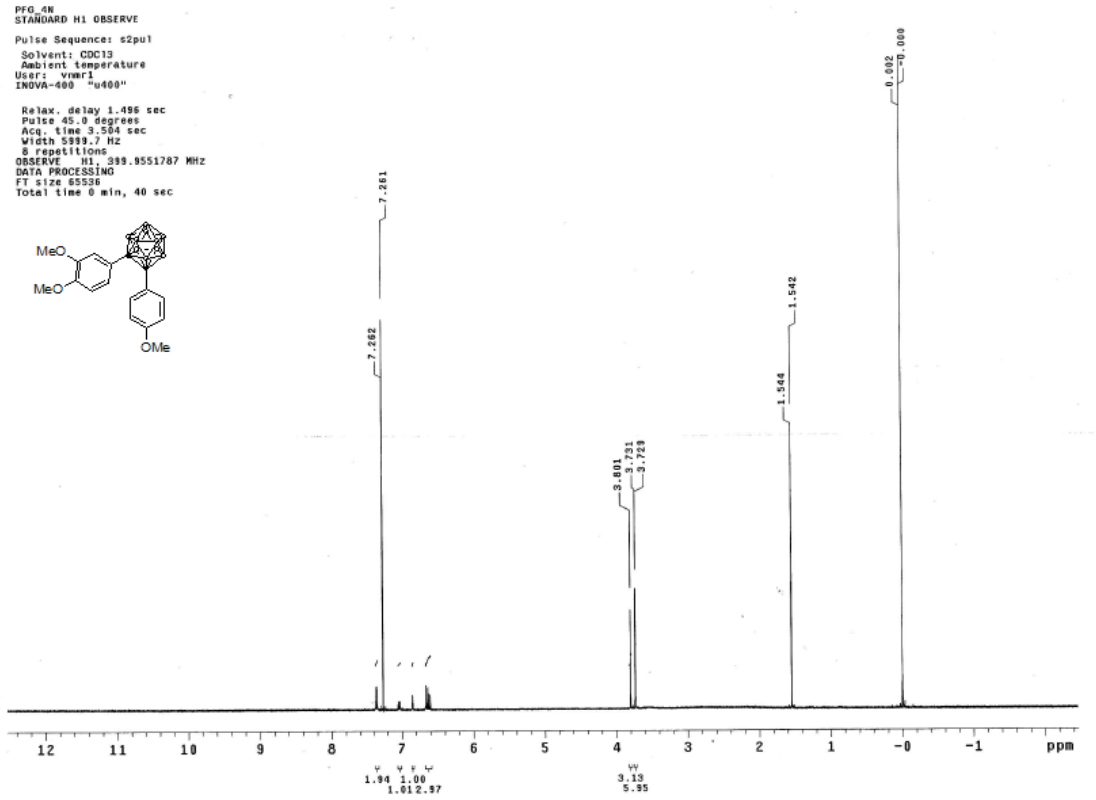

**1-(2-Methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (1d)**

**$^{11}$B NMR ($CDCl_3$, 96.3MHz)**



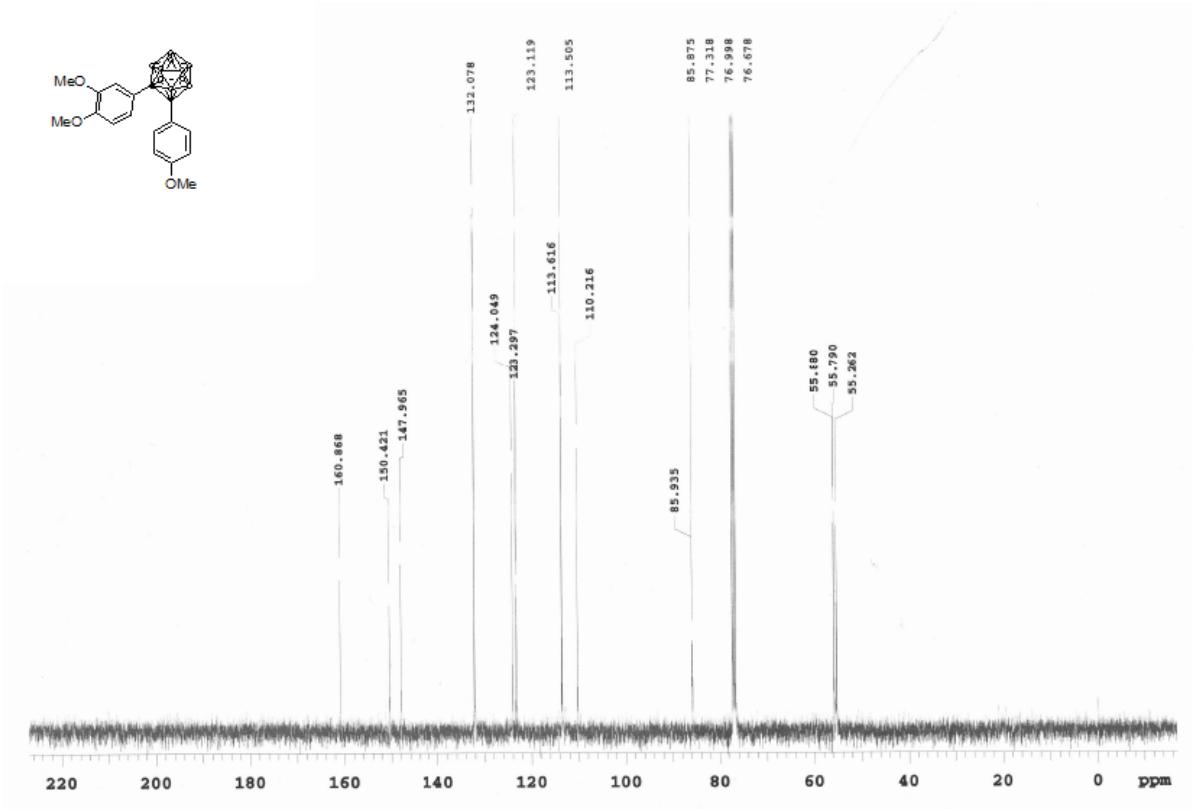
**1-(4-Methoxyphenyl)-2-(3,4-dimethoxyphenyl)-*ortho*-carborane (1e)**

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



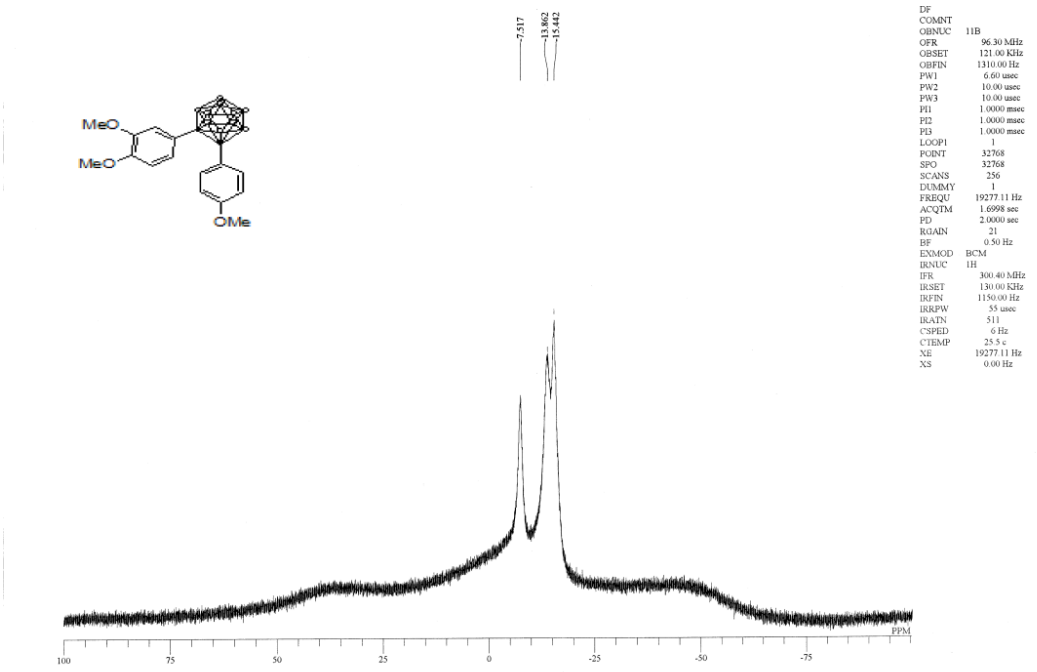

**1-(4-Methoxyphenyl)-2-(3,4-dimethoxyphenyl)-*ortho*-carborane (1e)**

**$^{13}$C NMR ($CDCl_3$, 100MHz)**



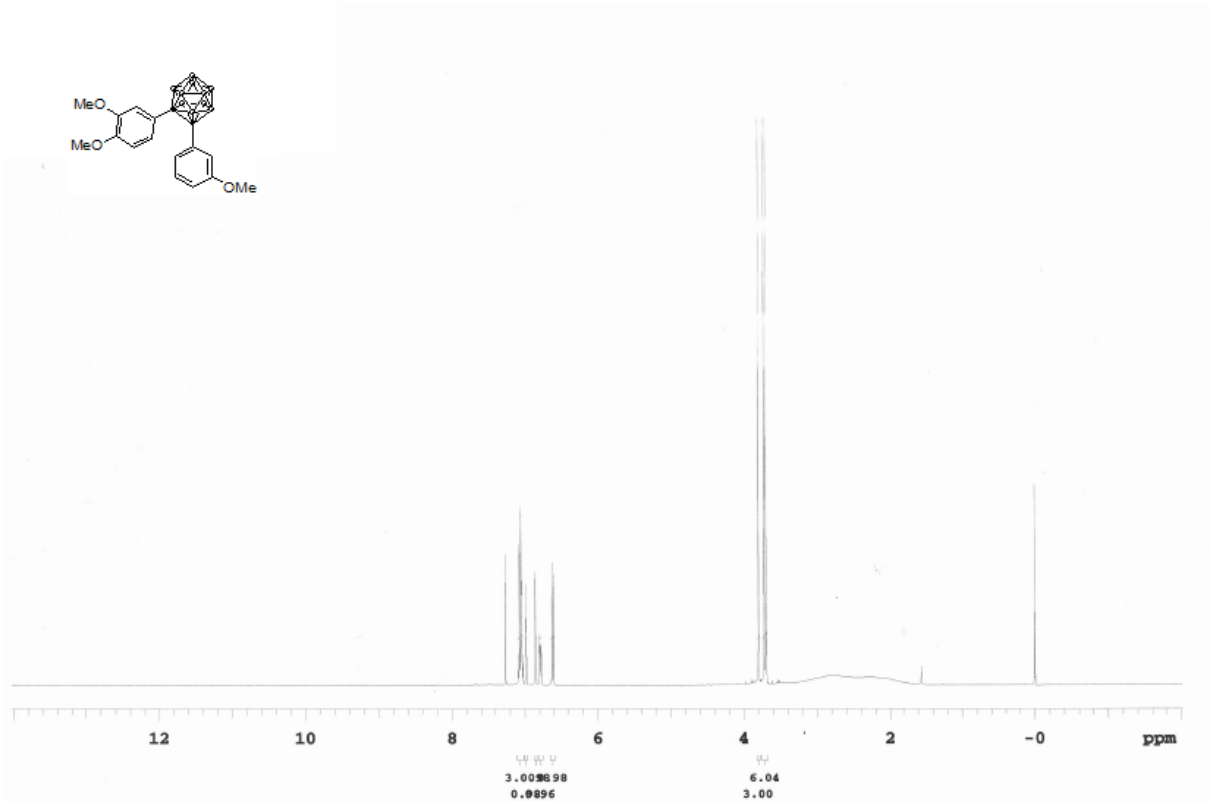
**1-(4-Methoxyphenyl)-2-(3,4-dimethoxyphenyl)-*ortho*-carborane (1e)**

**$^{11}$B NMR ($CDCl_3$, 96.3MHz)**



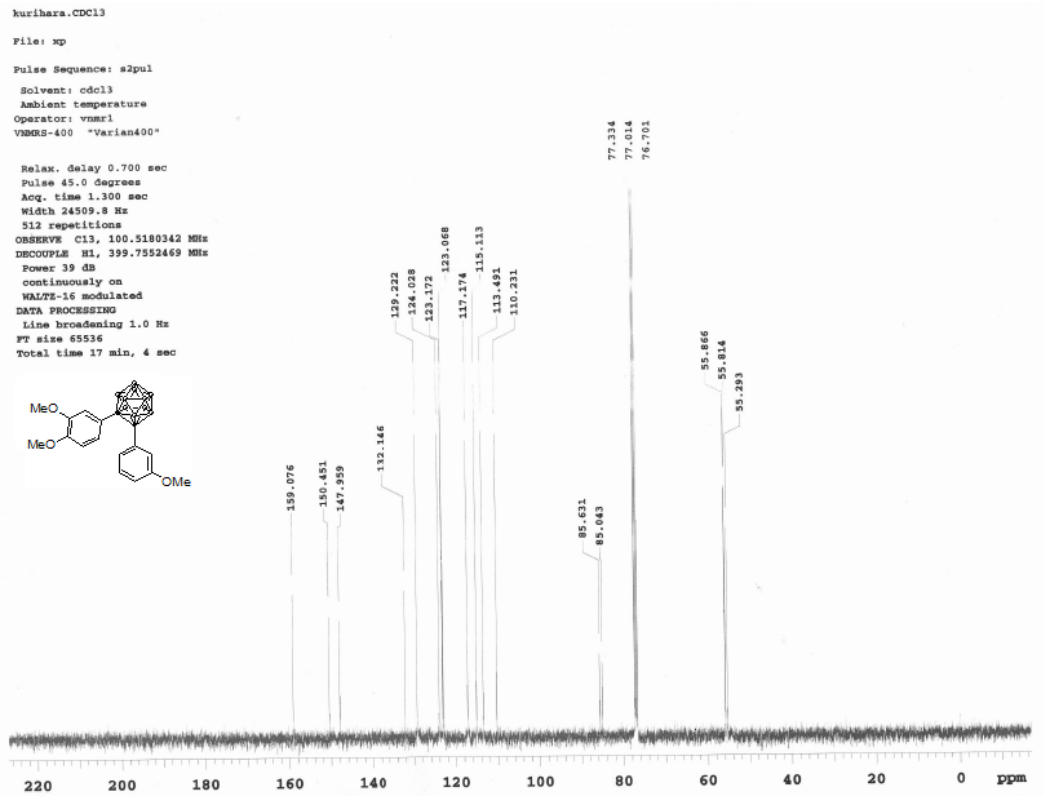

**1-(3-Methoxyphenyl)-2-(3,4-dimethoxyphenyl)-*ortho*-carborane (1f)**

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



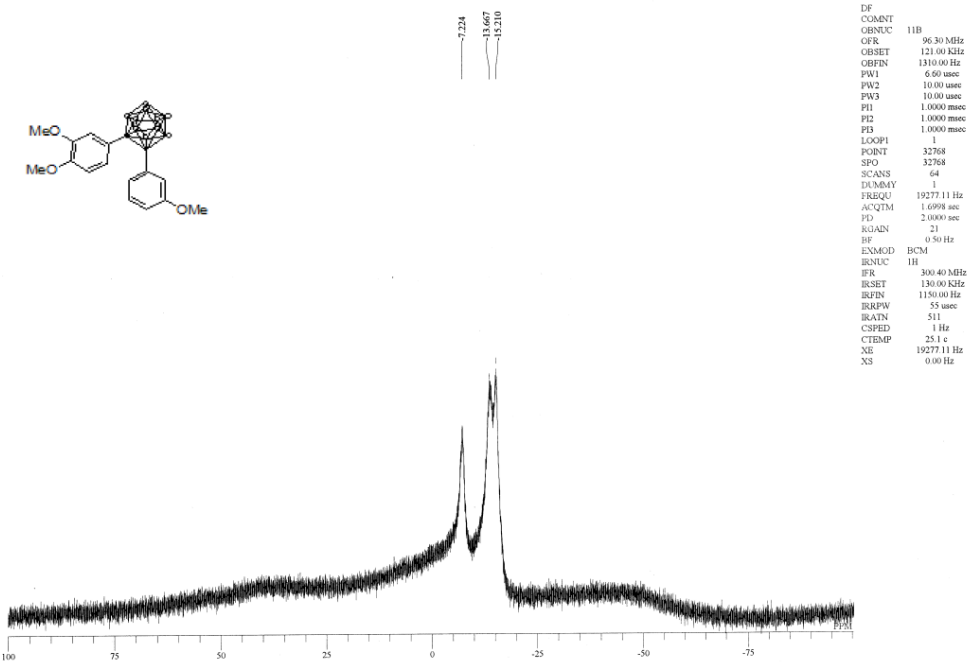
**1-(3-Methoxyphenyl)-2-(3,4-dimethoxyphenyl)-*ortho*-carborane (1f)**

**$^{13}$C NMR ($CDCl_3$, 100MHz)**



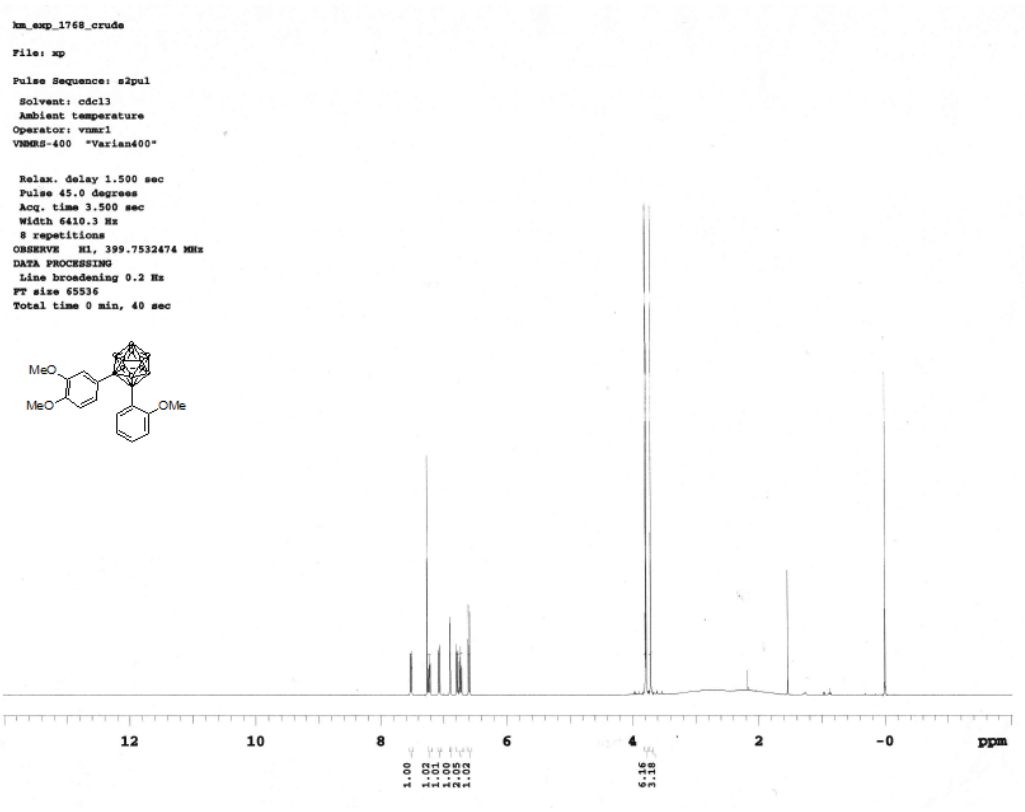

**1-(3-Methoxyphenyl)-2-(3,4-dimethoxyphenyl)-*ortho*-carborane (1f)**

**$^{11}$B NMR ($CDCl_3$, 96.3MHz)**



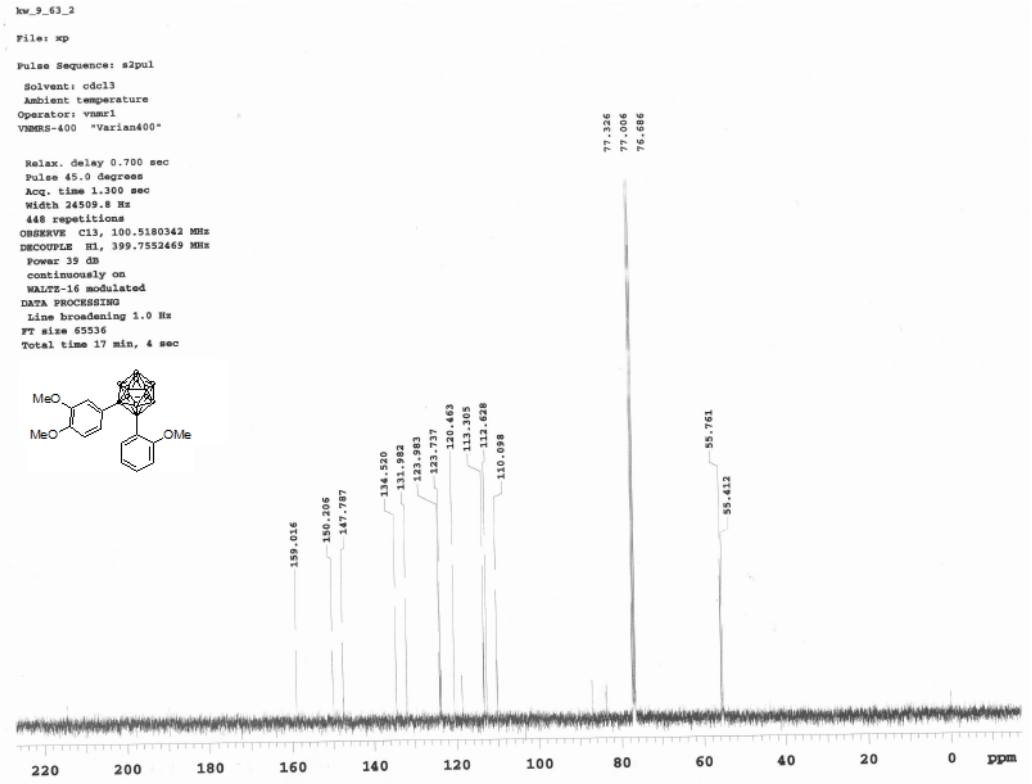
**1-(2-Methoxyphenyl)-2-(3,4-dimethoxyphenyl)-*ortho*-carborane (1g)**

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



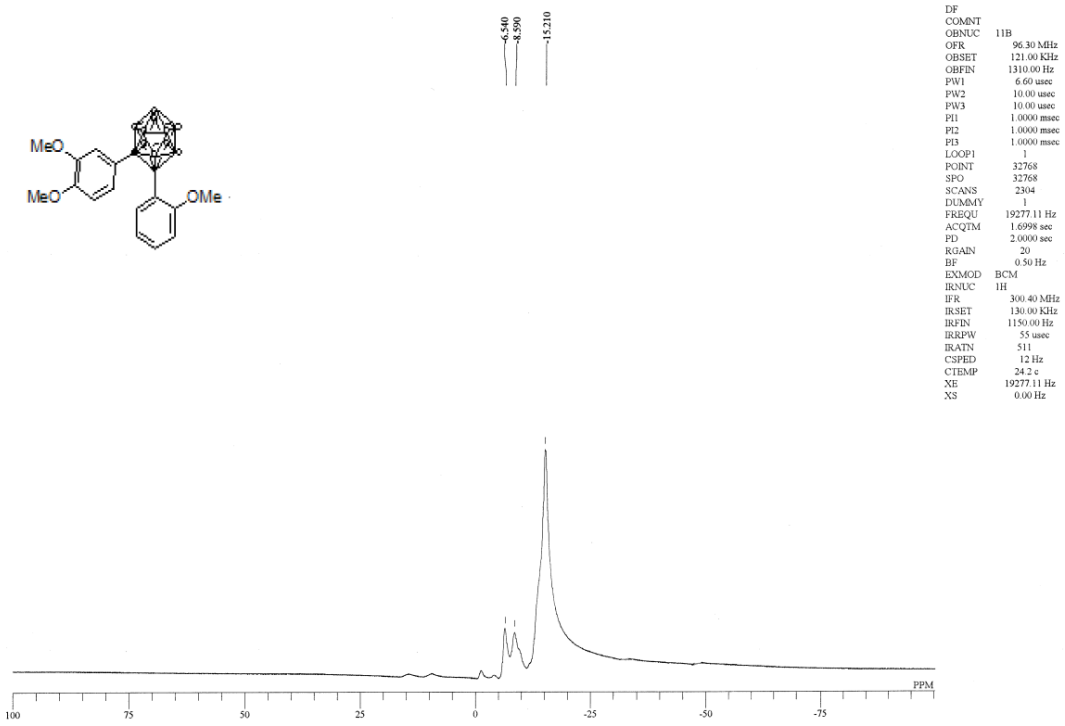

**1-(2-Methoxyphenyl)-2-(3,4-dimethoxyphenyl)-*ortho*-carborane (1g)**

**$^{13}$C NMR ($CDCl_3$, 100MHz)**



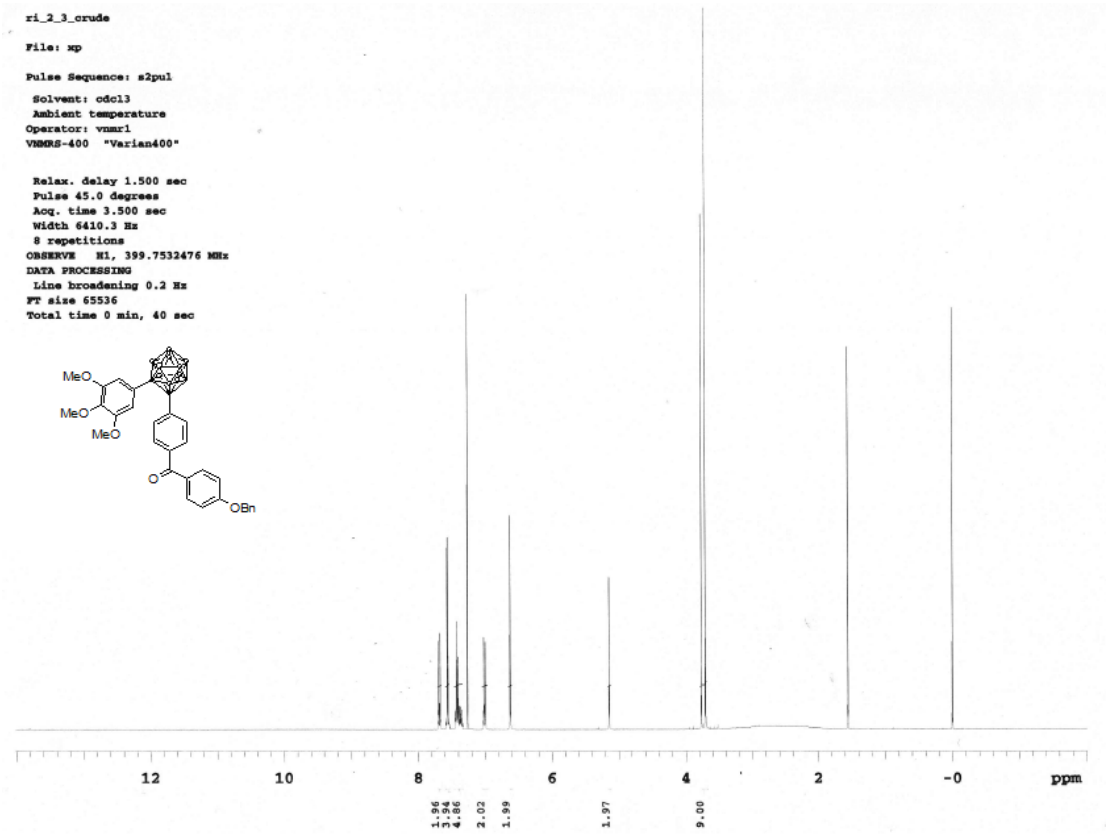
## 1-(2-Methoxyphenyl)-2-(3,4-dimethoxyphenyl)-*ortho*-carborane (1g)

## $^{11}$B NMR ($CDCl_3$, 96.3MHz)

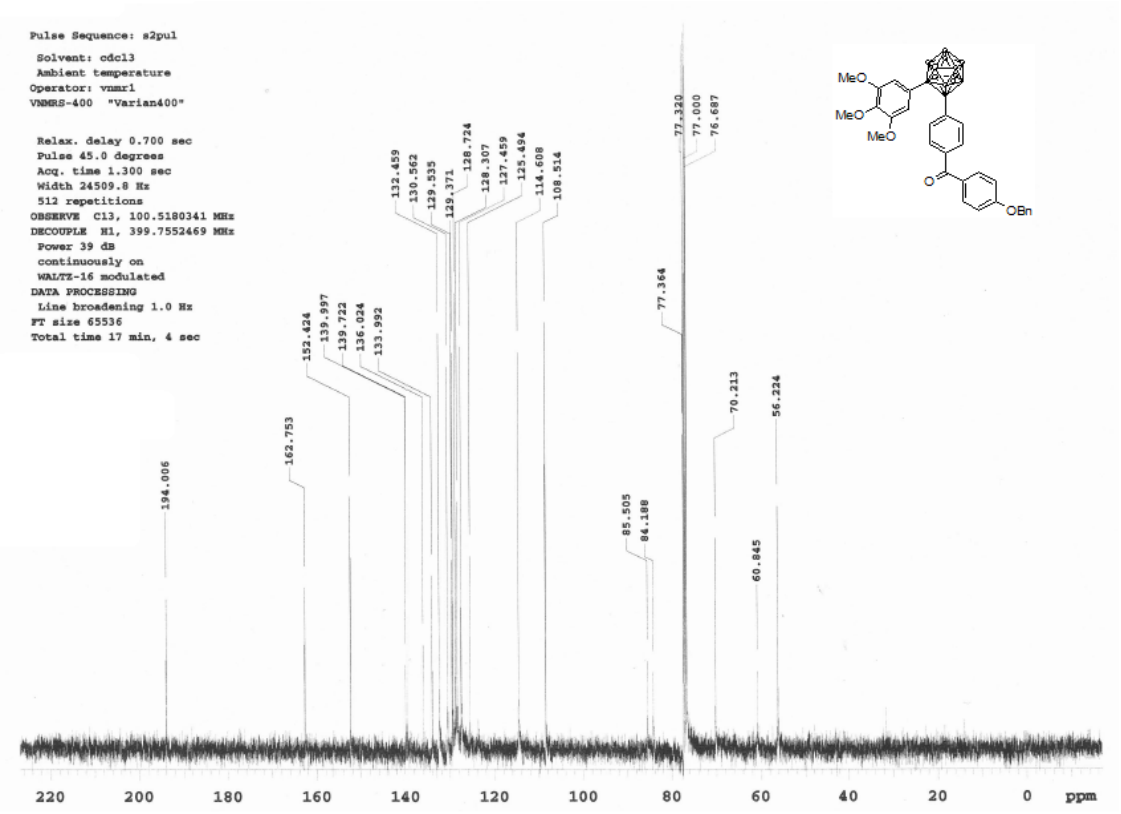



## 1-(4-(Benzyloxybenzoyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (6)

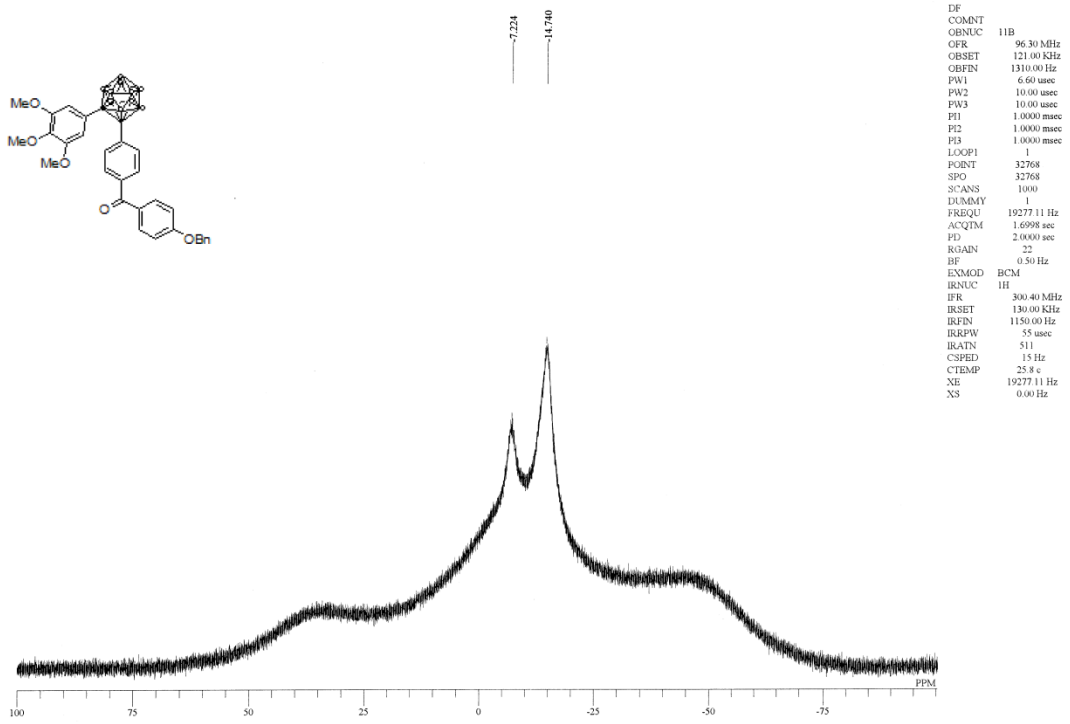
## $^{1}$H NMR ($CDCl_3$, 400MHz)



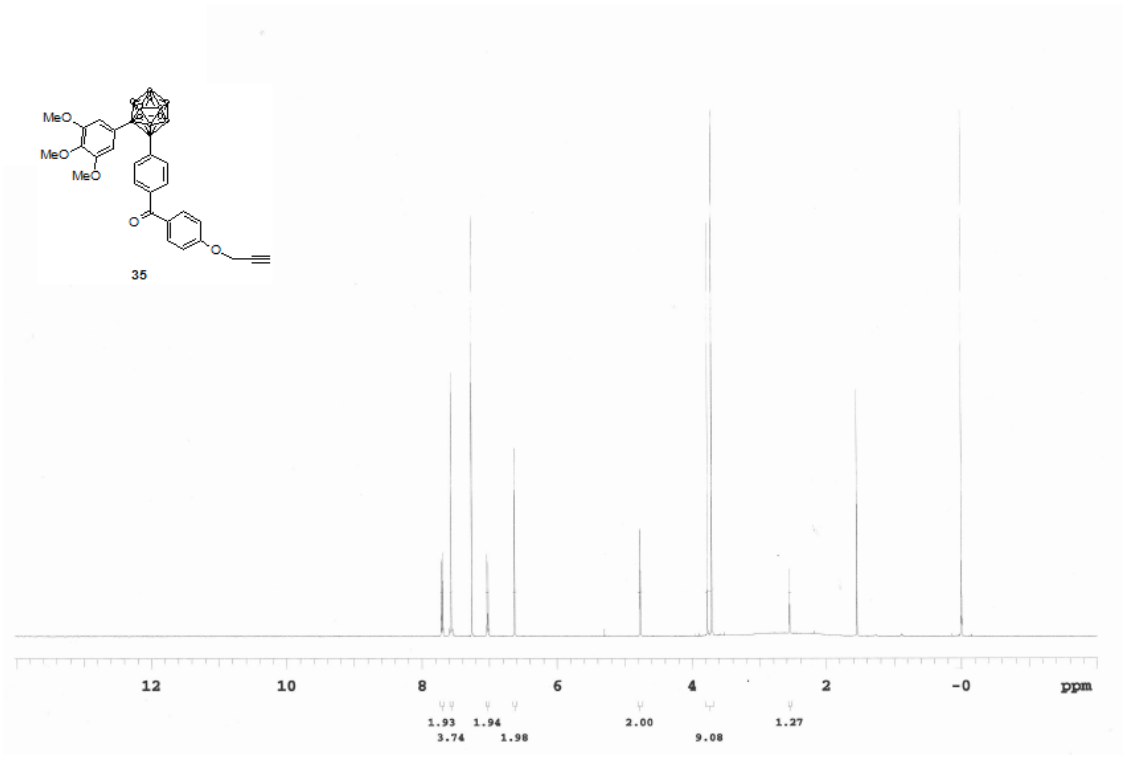
**1-(4-(Benzyloxybenzoyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (6)**
**$^{13}$C NMR ($CDCl_3$, 100MHz)**



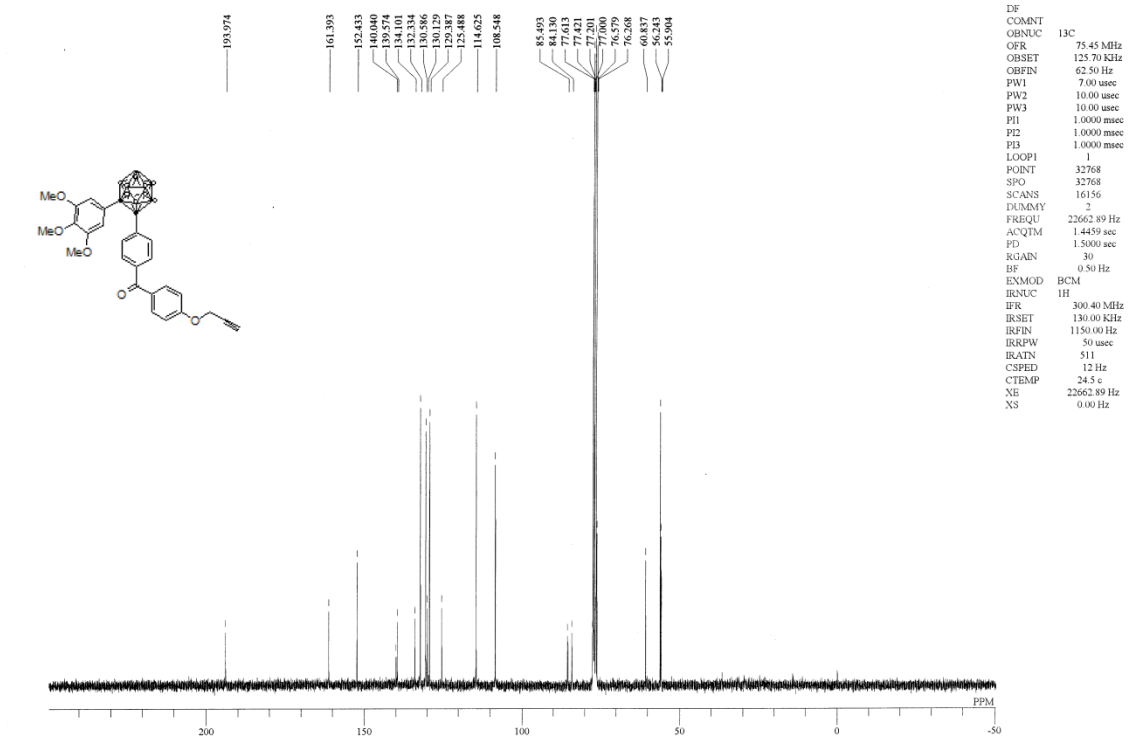

**1-(4-(Benzyloxybenzoyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (6)**
**$^{11}$B NMR ($CDCl_3$, 96.3MHz)**



**1-(4-(Propargyloxybenzoyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (7)**
**$^{1}$H NMR ($CDCl_3$, 400MHz)**




**1-(4-(Propargyloxybenzoyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (7)**
**$^{13}$C NMR ($CDCl_3$, 75MHz)**



**1-(4-(Propargyloxybenzoyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-*ortho*-carborane (7)**

**$^{11}$B NMR ($CDCl_3$, 96.3MHz)**