Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Beyond PCBM: Methoxylated 1,4-Bisbenzyl [60]Fullerene Adducts for Efficient Organic Solar Cells

Shaohua Huang,‡[a] Guangye Zhang,‡[a] Nicholas S. Knutson,[a] Matthew T. Fontana,[a] Rachel C. Huber,[a] Amy S. Ferreira,[a] Sarah H. Tolbert,*[,a,b] Benjamin J. Schwartz*[,a] and Yves Rubin*[,a]

[a]*Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Drive East, Los Angeles, California 90095-1569, United States.*

E-mail: *schwartz@chem.ucla.edu* *(BJS);* *rubin@chem.ucla.edu* *(YR)*

[b]*Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California 90095-1569, United States.*

E-mail: *tolbert@chem.ucla.edu* *(SHT)*

‡Contributed equally to this work.

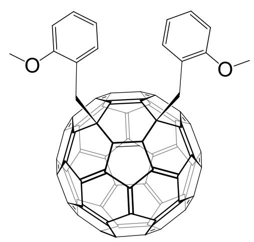
I. Synthesis of the Fullerene Derivatives

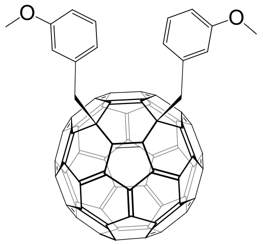
Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. All reactions were performed with dry solvents under an argon atmosphere in flame-dried glassware with standard vacuum-line techniques, unless specified otherwise. All work-up and purification procedures were carried out with reagent-grade solvents in air.

General procedure for the preparation of symmetric 1,4-bisbenzyl fullerene adducts 1a-f:

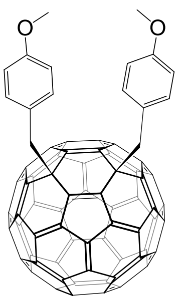
Trimethylhydroquinone (246 mg, 1.6 mmol, 5.4 eq) in 25 mL of benzonitrile and a suspension of C_{60} (216 mg, 0.3 mmol, 1.0 eq) in 25 mL of benzonitrile were both degassed under reduced pressure over 30 minutes. Tetrabutylammonium hydroxide (1 M in methanol, 3.3 mL, 11.0 equiv.) was added to the solution of trimethylhydroquinone at room temperature. The color of the solution immediately changed from colorless to red. After stirring for 30 minutes at this temperature, the resulting red solution was transferred to the purple suspension of C_{60} in benzonitrile *via* a cannula over a 30-minute time period and stirred for an additional 30 minutes, giving a dark solution. To this solution, benzyl bromide was added (6.0 mmol, 20 eq) and the resulting solution stirred overnight at room temperature. The reaction mixture was treated with 1 mL of aqueous HCl (*ca*. 1 M), dried over anhydrous $MgSO_4$, and filtered through a pad of silica gel (eluted with toluene). The filtrate was concentrated under reduced pressure. Chromatography of the residue gave the desired 1,4-bisadduct.

1,4-Bis(2-methoxybenzyl)-1,4-dihydro[60]fullerene (1a): The synthesis of **1a** follows the general procedure (35%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, J = 7.4, 1.7 Hz, 2H), 7.34 (td, J = 7.4, 1.7 Hz, 2H), 7.08 (td, J = 7.4, 1.0 Hz, 2H), 7.01 (d, J = 7.4 Hz, 2H), 4.07 (AB-q, J = 12.7 Hz, 2H), 3.88 (AB-q, J = 12.7 Hz, 2H), 3.82 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.57, 158.11, 152.01, 148.76, 148.57, 147.14, 146.97, 146.86, 146.29, 145.45, 144.88, 144.86, 144.84, 144.79, 144.46, 144.28, 144.22, 144.20, 143.78, 143.75, 143.17, 143.12, 142.93, 142.70, 142.57, 142.09, 141.93, 140.46, 138.90, 137.41, 132.56, 129.05, 124.99, 120.76, 111.27, 60.11, 55.09, 42.34. FAB-HRMS m/z calculated for $C_{76}H_{19}O_2$ $[M+H]^+$: 963.1380, found 963.1390.

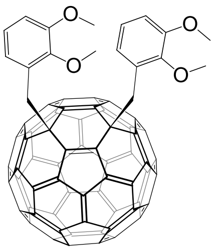




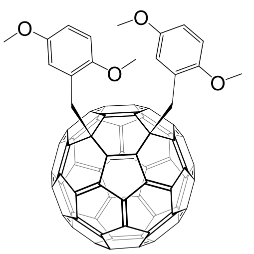
1,4-Bis(3-methoxybenzyl)-1,4-dihydro[60]fullerene (1b): The synthesis of **1b** follows the general procedure (40%). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) 7.39 (t, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.13 (s, 2H), 6.90 (dd, *J* = 8.2, 1.7 Hz, 2H), 3.86 (s, 6H), 3.77 (AB-q, *J* = 12.8 Hz, 2H), 3.72 (AB-q, *J* = 12.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.58, 157.99, 151.84, 148.67, 148.64, 147.21, 147.00, 146.93, 146.20, 145.51, 145.02, 144.79, 144.75, 144.71, 144.39, 144.31, 144.26, 144.15, 143.94, 143.76, 143.20, 143.11, 142.99, 142.66, 142.51, 142.02, 140.54, 138.80, 137.86, 137.80, 130.56, 129.47, 127.73, 123.60, 117.57, 112.32, 60.44, 55.35, 48.61. FAB-HRMS m/z calculated for $C_{76}H_{19}O_2$ $[M+H]^+$: 963.1380, found 963.1403.



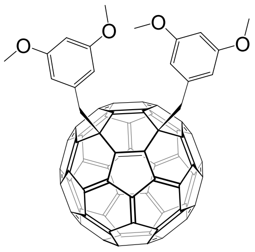
1,4-Bis(4-methoxybenzyl)-1,4-dihydro[60]fullerene (1c): The synthesis of **1c** follows the general procedure (30%). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) 7.50 (d, *J* = 8.2 Hz, 4H), 7.00 (d, *J* = 8.2 Hz, 4H), 3.80 – 3.70 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.00, 158.07, 151.91, 148.76, 148.66, 147.20, 147.09, 146.99, 146.93, 146.28, 145.50, 145.34, 145.01, 144.85, 144.78, 144.72, 144.40, 144.31, 144.27, 144.17, 143.94, 143.75, 143.19, 143.11, 142.97, 142.67, 142.56, 142.51, 142.01, 140.51, 138.87, 137.92, 133.27, 132.10, 128.32, 113.89, 113.53, 60.89, 55.36, 47.85. FAB-HRMS m/z calculated for $C_{76}H_{19}O_2$ $[M+H]^+$: 963.1380, found 963.1390.



1,4-Bis(2,3-dimethoxybenzyl)-1,4-dihydro[60]fullerene (1d): The synthesis of **1d** follows the general procedure (35%). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) 7.23 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.14 (t, *J* = 7.9 Hz, 2H), 6.91 (dd, *J* = 8.2, 1.5 Hz, 2H), 4.10 (AB-q, *J* = 12.7 Hz, 2H), 3.94 (s, 6H), 3.90 (AB-q, *J* = 15.4 Hz, 2H), 3.88 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.17, 152.92, 152.07, 148.76, 148.59, 148.11, 147.25, 147.11, 146.97, 146.86, 146.40, 145.41, 145.03, 144.95, 144.91, 144.75, 144.42, 144.24, 144.23, 144.18, 143.79, 143.77, 143.12, 143.09, 142.88, 142.60, 142.53, 142.04, 141.96, 140.42, 138.80, 137.85, 129.86, 124.48, 123.46, 111.86, 60.89, 60.08, 55.75, 42.08. FAB-HRMS m/z calculated for $C_{78}H_{23}O_4$ $[M+H]^+$: 1023.1591, found 1023.1587.



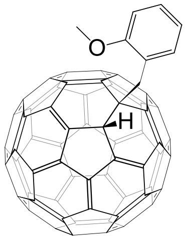
1,4-Bis(2,5-dimethoxybenzyl)-1,4-dihydro[60]fullerene (1e): The synthesis of **1e** follows the general procedure (32%). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) 7.14 (d, *J* = 3.1 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.85 (dd, *J* = 8.9, 3.1 Hz, 2H), 4.00 (AB-q, *J* = 12.7 Hz, 2H), 3.83 (s, 6H), 3.82 (AB-q, *J* = 12.7 Hz, 2H), 3.77 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.65, 153.45, 152.44, 151.99, 148.74, 148.56, 147.10, 147.08, 146.97, 146.83, 146.27, 145.40, 144.90, 144.81, 144.79, 144.77, 144.41, 144.25, 144.19, 144.17, 143.74, 143.69, 143.12, 143.07, 142.87, 142.63, 142.53, 142.49, 142.08, 141.84, 140.36, 138.84, 137.29, 126.13, 119.20, 112.69, 112.06, 60.02, 55.84, 55.71, 42.44. FAB-HRMS m/z calculated for $C_{76}H_{19}O_2$ $[M+H]^+$: 1023.1591, found 1023.1576.



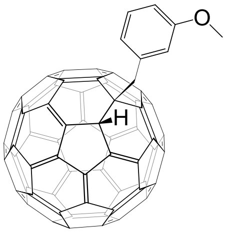
1,4-Bis(3,5-dimethoxybenzyl)-1,4-dihydro[60]fullerene (1f): The synthesis of **1f** follows the general procedure (40%). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) 6.73 (s, 4H), 6.45 (s, 2H), 3.84 (s, 12H), 3.78 (AB-q, *J* = 14.4 Hz, 2H), 3.74 (AB-q, *J* = 14.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.75, 160.72, 157.96, 151.86, 148.67, 148.67, 147.20, 147.00, 146.94, 146.22, 145.51, 145.02, 144.76, 144.71, 144.39, 144.30, 144.26, 144.16, 143.89, 143.76, 143.19, 143.11, 142.97, 142.66, 142.59, 142.51, 142.05, 142.01, 140.57, 138.81, 138.51, 137.81, 109.74, 98.85, 60.35, 55.46, 48.90. FAB-HRMS m/z calculated for $C_{78}H_{23}O_4$ $[M+H]^+$: 1023.1591, found 1023.1581.

Synthesis of the Asymmetric 1,4-Bisbenzyl Fullerene C_{60} Adducts 1g–k via Monobenzylated Adducts 2a,b,e.

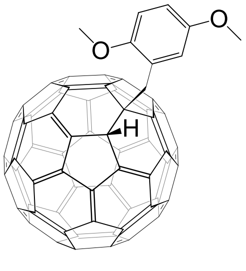
1-(2-Methoxybenzyl)-1,2-dihydro[60]fullerene (2a): A suspension of C_{60} (144 mg, 0.2 mmol) and Cs_2CO_3 (196 mg, 0.6 mmol) in dry DMSO (25 mL) was prepared and 1-propanethiol (45 μL, 0.5 mmol) was added to the suspension. The resulting mixture was stirred for 2 hours under argon at room temperature. 2-Methoxybenzyl chloride (250 mg, 1.6 mmol) was added to the resulting dark-red solution. Stirring continued for another 2 hours and the color of the solution turned green, indicative of an alkylated C_{60} monoanion. Following this, acetic acid (0.5 mL) was added, and after 5 minutes, the solution was poured into 100 mL of methanol. The solids were collected by centrifugation and then dissolved in a minimum volume of CS_2. Chromatography, using a mixture of cyclohexane and toluene (2:1 by volume), gave 1-(2-methoxybenzyl)-1,2-dihydro[60]fullerene **2a** (93 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.40 (ddd, *J* = 8.2, 7.6, 1.7 Hz, 1H), 7.11 (td, *J* = 7.5, 1.1 Hz, 1H), 7.06 (dd, *J* = 8.3, 0.6 Hz, 1H), 6.73 (s, 1H), 4.82 (s, 2H), 3.92 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.21, 156.18, 154.25, 147.50, 147.36, 147.17, 146.47, 146.45, 146.39, 146.26, 146.22, 145.93, 145.50, 145.44, 145.39, 145.35, 144.76, 144.69, 143.32, 143.16, 142.62, 142.61, 142.30, 142.09, 142.03, 141.71, 141.60, 140.21, 139.90, 136.56, 135.48, 133.19, 129.36, 124.64, 121.00, 111.36, 66.01, 59.41, 55.22, 46.74. MALDI-TOF-MS m/z calculated for $C_{68}H_{11}O$ [M+H$^+$]: 843, found 843.



1-(3-Methoxybenzyl)-1,2-dihydro[60]fullerene (2b): To a suspension of C_{60} (144 mg, 0.2 mmol) and Cs_2CO_3 (196 mg, 0.6 mmol) in dry DMSO (25 mL) was added 1-propanethiol (45 μL, 0.5 mmol). The mixture was stirred for 2 hours under argon at room temperature. 3-methoxybenzyl bromide (42 μL, 0.3 mmol) was added to the resulting dark red solution and the stirring continued for 20 minutes. The color of the solution turned green, indicative of a substituted C_{60} monoanion. Acetic acid (0.5 mL) was added, and after 5 minutes the solution was poured into 100 mL of methanol. The solids were collected by centrifugation and then dissolved in a minimum volume of CS_2. Chromatography using a mixed solvent of cyclohexane and toluene (2:1 by volume) gave 1-(3-methoxybenzyl)-1,2-dihydro[60]fullerene **2b** (64 mg, 38%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.49 – 7.38 (m, 2H), 7.34 (s, 1H), 6.96 (d, J = 7.1 Hz, 1H), 6.65 (s, 1H), 4.74 (s, 2H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.82, 155.41, 153.91, 147.55, 147.39, 147.05, 146.51, 146.48, 146.35, 146.27, 145.88, 145.60, 145.53, 145.49, 145.48, 144.81, 144.67, 143.33, 142.67, 142.30, 142.14, 142.09, 141.99, 141.75, 141.70, 140.33, 140.09, 137.32, 136.43, 136.13, 129.94, 123.89, 117.59, 112.93, 65.82, 59.12, 55.19, 53.16. MALDI-TOF-MS m/z calculated for $C_{68}H_{11}O$ [M+H$^+$]: 843, found 843.

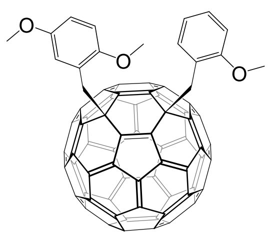


1-(2,5-Dimethoxybenzyl)-1,2-dihydro[60]fullerene (2e): To a suspension of C_{60} (144 mg, 0.2 mmol) and Cs_2CO_3 (196 mg, 0.6 mmol) in dry DMSO (25 mL) 1-propanethiol (45 μL, 0.5 mmol) was added. The mixture was stirred for 2 hours under argon at room temperature. 2,5-dimethoxybenzyl chloride (298 mg, 1.6 mmol) was added to the resulting dark-red solution and stirring continued for another 1.5 hours. Following this, the color of the solution turned green, indicating the presence of a C_{60} monoanion. Acetic acid (0.5 mL) was added and five minutes later the solution was poured into 100 mL of methanol. The solids were collected by centrifugation and then dissolved into a minimum volume of CS_2. Chromatography, using a mixed solvent of cyclohexane and toluene (1:1 by volume), gave 1-(2,5-dimethoxybenzyl)-1,2-dihydro[60]fullerene **2e** (98 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.26 (d, J = 2.2



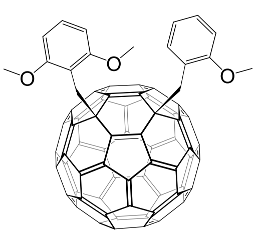
Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 1H), 6.89 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.72 (s, 1H), 4.77 (s, 2H), 3.89 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.06, 154.25, 153.53, 152.37, 147.51, 147.36, 147.17, 146.48, 146.42, 146.39, 146.28, 146.23, 145.94, 145.52, 145.45, 145.41, 145.39, 144.77, 144.70, 143.33, 142.64, 142.63, 142.31, 142.11, 142.02, 141.72, 141.64, 140.25, 139.95, 136.55, 135.57, 129.12, 128.37, 125.64, 119.49, 113.31, 112.11, 65.90, 59.31, 55.69, 55.57, 46.75. MALDI-TOF-MS m/z calcd for $C_{69}H_{13}O_2$ [M+H$^+$]: 873, found 873.

1-(2,5-Dimethoxybenzyl)-4-(2-methoxybenzyl)-1,4-dihydro[60]fullerene (1g): To a de-gased solution of 1-(2-methoxybenzyl)-1,2-dihydro[60]fullerene **2a** (0.05 mmol, 1 eq) in 10 mL dry benzonitrile, a 1 M THF solution of *t*-BuOK (75 μL, 0.075 mmol, 1.5 eq) was added via syringe with stirring. After 10 min, 2,5-dimethoxybenzyl chloride (77 mg, 0.5 mmol, 10 eq) (prepared from the reaction of 2,5-dimethoxybenzyl alcohol with $SOCl_2$) was added to the solution. The solution was then heated to 70 °C and stirred for 7 hours. An aqueous solution of NH_4Cl (0.1 mL) was added after the solution was cooled to room temperature. The solution was then poured into 100 mL methanol. The solids were collected by centrifuging and then redissolved in 1 mL CS_2. Chromatography gave 1-(2,5-dimethoxybenzyl)-4-(2-methoxybenzyl)-1,4-dihydro[60]fullerene (**1g**) (20 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) 7.54 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.35 (ddd, *J* = 8.1, 7.6, 1.6 Hz, 1H), 7.12 (d, *J* = 3.1 Hz, 1H), 7.09 (td, *J* = 7.4, 1.0 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 1H), 6.85 (dd, *J* = 8.9, 3.1 Hz, 1H), 4.07 (AB-q, *J* = 12.7 Hz, 1H), 4.00 (AB-q, *J* = 12.7 Hz, 1H), 3.89 (AB-q, *J* = 12.7 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.77 (s, 3H), 3.70 (AB-q, *J* = 12.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* (ppm) 158.75, 158.63, 158.22, 153.37, 152.45, 152.07, 151.99, 148.75, 148.55, 147.10, 146.97, 146.82, 146.37, 146.22, 145.40, 144.90, 144.82, 144.78, 144.76, 144.41, 144.25, 144.19, 144.17, 143.76, 143.73, 143.69,



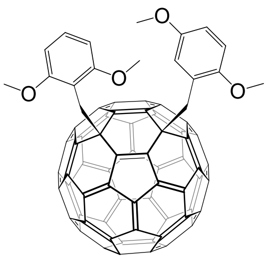
143.68, 143.11, 143.07, 142.86, 142.63, 142.53, 142.49, 142.07, 141.85, 141.83, 138.84, 138.83, 137.32, 137.27, 132.53, 129.00, 126.13, 125.06, 120.61, 119.30, 112.57, 112.01, 111.34, 60.14, 60.00, 55.87, 55.70, 55.20, 42.40, 42.35. MALDI-TOF-MS m/z calculated for $C_{77}H_{21}O_3$ [$M+H^+$]: 993, found 993.

1-(2,6-Dimethoxybenzyl)-4-(2-methoxybenzyl)-1,4-dihydro[60]fullerene (1h): To a de-gased solution of 1-(2-methoxybenzyl)-2-H-dihydro[60]fullerene **2a** (0.05 mmol, 1 eq) in 10 mL dry benzonitrile, a 1.0 M THF solution of *t*-BuOK (75 µL, 0.075 mmol, 1.5 eq) was added through syringe with stirring. After 10 minutes, 2,6-dimethoxybenzyl chloride (77 mg, 0.5 mmol, 10eq) (prepared from the reaction of 2,6-dimethoxybenzyl alcohol with $SOCl_2$) was added. The solution was heated to 70 °C and stirred for 6 hours. An aqueous solution of NH_4Cl (0.1 mL) was added after the solution was cooled to room temperature. The solution was then poured into 100 mL methanol. The solids were collected by centrifuging and then redissolved in 1 mL CS_2. Chromatography gave 1-(2,6-dimethoxybenzyl)-4-(2-methoxybenzyl)-1,4-dihydro[60]fullerene (**1h**) (18 mg, 36%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.46 (d, J = 6.8 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.01 (t, J = 7.3 Hz, 1H), 6.94 (d, J = 8.2 Hz, 1H), 6.75 (d, J = 8.3 Hz, 2H), 4.48 (AB-q, J = 12.7 Hz, 2H), 4.43 (AB-q, J = 12.7 Hz, 1H), 3.96 (AB-q, J = 12.5 Hz, 1H), 3.90 (s, 4H), 3.83 (AB-q, J = 12.5 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.53, 159.23, 158.33, 157.94, 152.54, 151.88, 148.99, 148.63, 148.99, 148.48, 147.31, 147.25, 147.07, 147.04, 147.02, 146.97, 146.93, 146.75, 145.75, 145.33, 145.30, 145.09, 145.00, 144.84, 144.79, 144.74, 144.70, 144.65, 144.45, 144.43, 144.23, 144.21, 144.17, 144.16, 144.10, 143.87, 143.65, 143.63, 143.34, 143.16, 143.11, 143.02, 142.92, 142.84, 142.66, 142.62, 142.58, 142.50, 142.46, 142.06, 141.83, 141.70, 140.27, 139.01, 138.70, 137.46, 137.03, 132.31, 129.05, 128.82, 128.70, 124.93, 120.30,

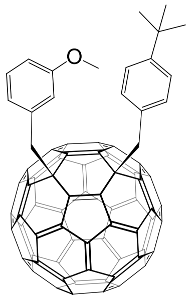


113.71, 111.18, 104.39, 59.90, 55.68, 55.07, 42.41, 35.39. MALDI-TOF-MS m/z calculated for $C_{77}H_{21}O_3$ [M+H$^+$]: 993, found 993.

1-(2,5-Dimethoxybenzyl)-4-(2,6-dimethoxybenzyl)-1,4-dihydro[60]fullerene (1i): To a degased solution of 1-(2,5-dimethoxybenzyl)-2-H-dihydro[60]fullerene **2e** (0.05 mmol, 1 eq) in 10 mL dry benzonitrile, a 1 M THF solution of *t*-BuOK (75 μL, 0.075 mmol, 1.5 eq) was added via syringe with stirring. After 10 min, 2,6-dimethoxybenzyl chloride (77 mg, 0.5 mmol, 10 eq) (prepared from the reaction of 2,6-dimethoxybenzyl alcohol with $SOCl_2$) was added to the solution. The solution was then heated to 70 ℃ and stirred for 6 hours. An aqueous solution of NH_4Cl (0.1 mL) was added after the solution was cooled to room temperature. The solution was then poured into 100 mL methanol. The solids were collected by centrifuging and then redissolved in 1 mL CS_2. Flash chromatography gave 1-(2,5-dimethoxybenzyl)-4-(2,6-dimethoxybenzyl)-1,4-dihydro[60]fullerene (**1i**) (20 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm) 7.32 (t, *J* = 8.3 Hz, 1H), 7.05 (d, *J* = 2.7 Hz, 1H), 6.89 – 6.79 (m, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 4.50 (AB-q, *J* = 12.6 Hz, 1H), 4.44 (AB-q, *J* = 12.6 Hz, 1H), 3.91 (s, 6H), 3.87 (AB-q, *J* = 12.6 Hz, 1H), 3.80 (s, 3H), 3.74 (AB-q, *J* = 12.6 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.54, 159.27, 158.24, 153.23, 152.57, 152.18, 151.81, 149.00, 148.59, 148.50, 147.32, 147.26, 147.08, 147.04, 147.03, 146.97, 146.93, 146.76, 145.66, 145.34, 145.31, 145.09, 145.02, 144.84, 144.80, 144.75, 144.72, 144.66, 144.45, 144.43, 144.24, 144.22, 144.17, 144.10, 143.88, 143.67, 143.62, 143.52, 143.34, 143.16, 143.10, 143.03, 142.93, 142.85, 142.67, 142.62, 142.59, 142.50, 142.46, 142.07, 141.85, 141.68, 140.28, 139.00, 138.71, 137.48, 137.04, 129.05, 128.84, 128.24, 126.03, 125.31, 121.26, 119.34, 115.50, 113.76, 112.30, 111.78,

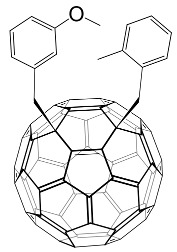


104.44, 59.92, 59.74, 55.95, 55.72, 55.57, 42.54, 35.41. MALDI-TOF-MS m/z calculated for $C_{78}H_{23}O_4$ [M+H$^+$]: 1023, found 1023.



1-(3-Methoxybenzyl)-4-(4-*t*-butylbenzyl)-1,4-dihydro[60]fullerene (1j): To a de-gased solution of 1-(3-methoxybenzyl)-2-H-dihydro[60]fullerene (**2b**, 0.05 mmol, 1 eq) in 10 mL of dry benzonitrile, a 1 M THF solution of *t*-BuOK (75 µL, 0.075 mmol, 1.5 eq) was added through a syringe. After 10 minutes, 4-*t*-butylbenzyl bromide (mg, 0.5 mmol, 10 eq) was added. The solution was stirred at room temperature for 4 hours. An aqueous solution of NH_4Cl (0.1 mL) was added and the solution was poured into 100 mL methanol. The solids were collected by centrifuge and then redissolved in 1 mL CS_2. Chromatography gave 1-(3-methoxybenzyl)-4-(p-*t*-butylbenzyl)-1,4-dihydro[60]fullerene (**1j**, 20 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.61 (AB-q, J = 7.9 Hz, 2H), 7.56 (AB-q, J = 7.9 Hz, 2H), 7.31 (t, J = 7.8 Hz, 1H), 7.04 (d, J = 7.4 Hz, 1H), 7.00 (s, 1H), 6.85 (d, J = 7.9 Hz, 1H), 4.06 (AB-q, J = 13.1 Hz, 1H), 3.96 (AB-q, J = 13.1 Hz, 1H), 3.84 (s, 3H), 3.30 (s, 2H), 1.28 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.26, 158.64, 157.93, 152.34, 151.56, 150.71, 148.78, 148.67, 148.65, 148.63, 147.22, 147.20, 147.00, 146.99, 146.97, 146.93, 146.87, 145.66, 145.50, 145.05, 144.98, 144.84, 144.81, 144.75, 144.73, 144.71, 144.40, 144.33, 144.31, 144.26, 144.18, 144.13, 143.98, 143.86, 143.71, 143.20, 143.17, 143.13, 143.07, 143.04, 142.93, 142.68, 142.66, 142.57, 142.46, 142.15, 142.06, 141.91, 140.49, 138.83, 138.81, 137.87, 137.61, 133.56, 130.91, 129.15, 125.72, 123.61, 117.36, 112.22, 60.94, 60.34, 55.33, 48.27, 48.07, 34.62, 31.33. FAB-HRMS m/z calculated for $C_{79}H_{25}O$ [M+H]$^+$: 989.1900, found 989.1909.

1-(3-Methoxybenzyl)-4-(2-methylbenzyl)-1,4-dihydro[60]fullerene (1k): To a de-gased solution of 1-(3-methoxybenzyl)-2-H-dihydro[60]fullerene (**2b**) (0.05 mmol, 1 eq) in 10 mL dry benzonitrile, a 1 M THF solution of *t*-BuOK (75 μL, 0.075 mmol, 1.5 eq) was added through a syringe. After 10 minutes, 2-methylbenzyl bromide (92 mg, 0.5 mmol, 10 eq) was added and the solution was stirred at room temperature for 4 hours. An aqueous solution of NH_4Cl (0.1 mL) was then added and the solution was poured into 100 mL methanol. The solids were collected by centrifuge and then redissolved in 1 mL CS_2. Chromatography gave 1-(3-methoxybenzyl)-4-(2-methylbenzyl)-1,4-dihydro[60]fullerene (**1k**, 19 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.62 (d, J = 7.3 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.31 – 7.27 (m, 2H), 6.99 (d, J = 7.5 Hz, 1H), 6.94 (s, 1H), 6.80 (dd, J = 8.3, 1.7 Hz, 1H), 4.20 (AB-q, J = 13.3 Hz, 1H), 4.07 (AB-q, J = 13.3 Hz, 1H), 3.82 (s, 3H), 3.41 (s, 2H), 2.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.36, 158.30, 157.58, 152.12, 151.54, 148.77, 148.71, 148.68, 148.43, 147.26, 147.24, 147.02, 147.00, 146.97, 146.82, 146.71, 145.65, 145.57, 145.14, 145.08, 144.84, 144.75, 144.64, 144.43, 144.35, 144.30, 144.19, 144.15, 144.11, 143.93, 143.84, 143.73, 143.27, 143.25, 143.19, 143.16, 143.10, 143.02, 142.75, 142.71, 142.65, 142.61, 142.47, 142.22, 142.08, 141.99, 140.67, 138.89, 138.86, 138.03, 137.55, 137.52, 137.46, 134.84, 132.43, 131.43, 129.31, 128.08, 126.41, 123.52, 117.32, 112.32, 60.68, 60.29, 55.07, 48.64, 45.37, 20.98. FAB-HRMS m/z calculated for $C_{76}H_{19}O$ $[M+H]^+$: 947.1430, found 947.1433



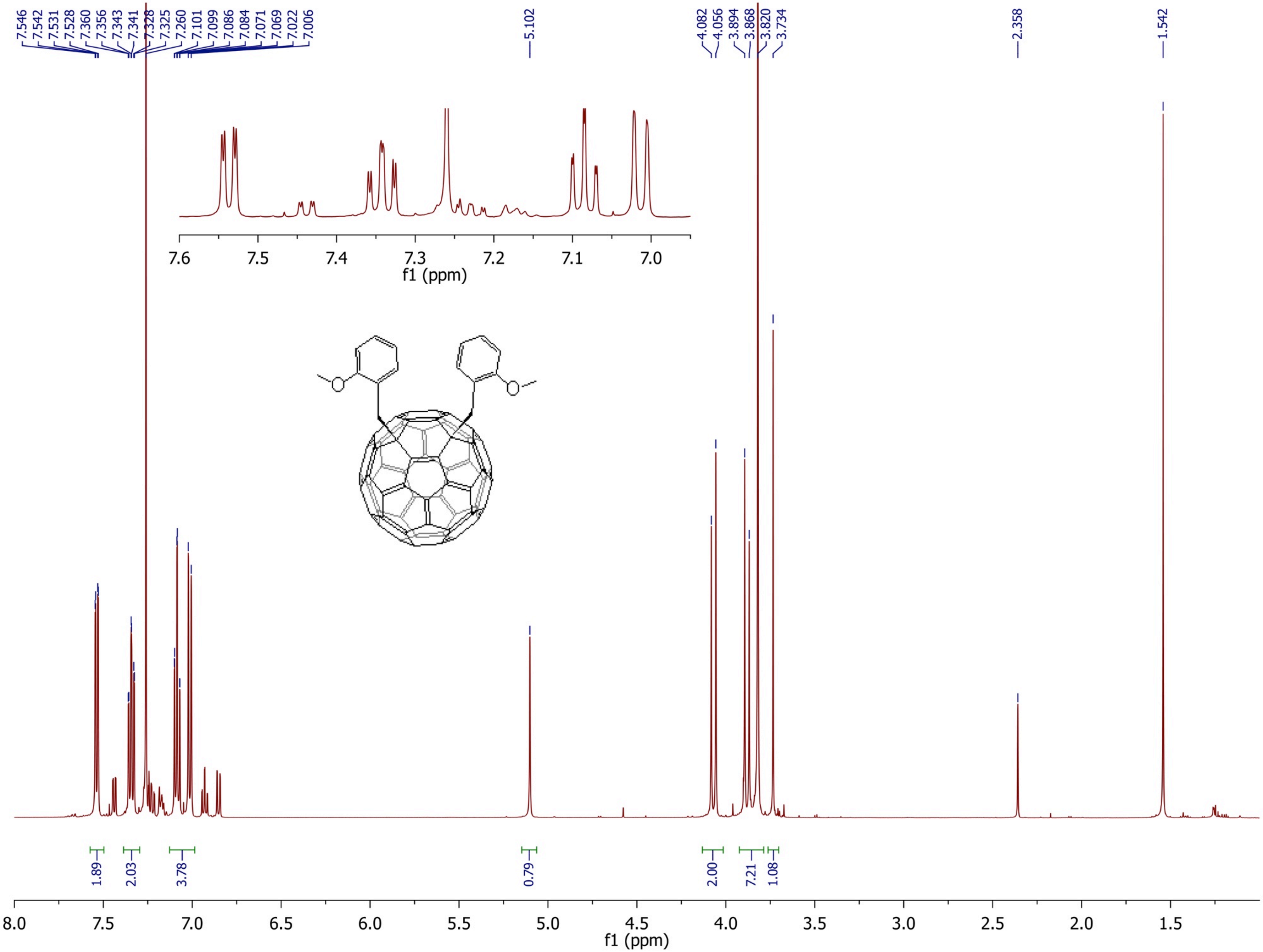


Figure S1. ^{1}H NMR spectrum of compound **1a** (500 MHz, $CDCl_3/CS_2$ (1:1)).

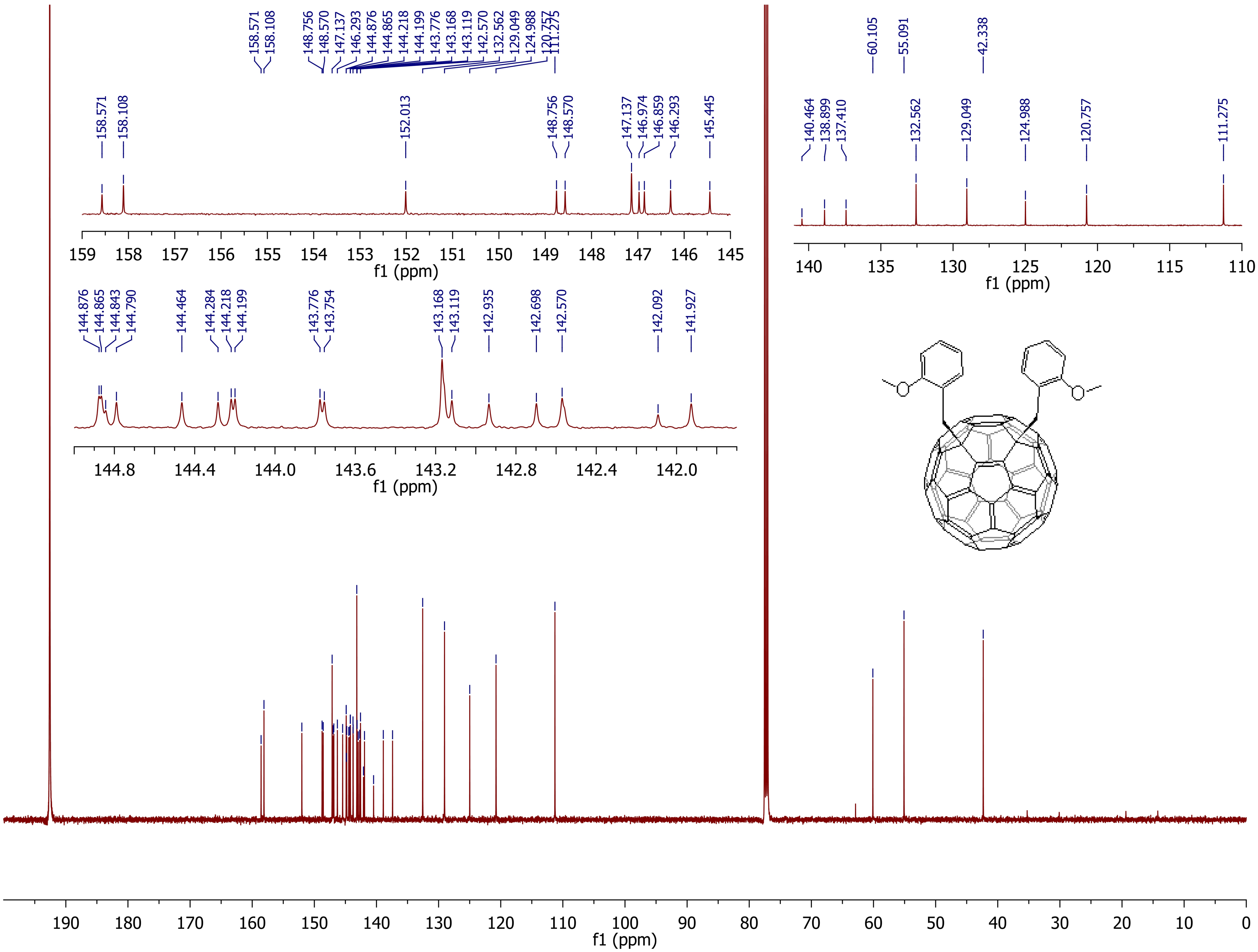


Figure S2. ^{13}C NMR spectrum of compound **1a** (125 MHz, $CDCl_3/CS_2$ (1:1)).

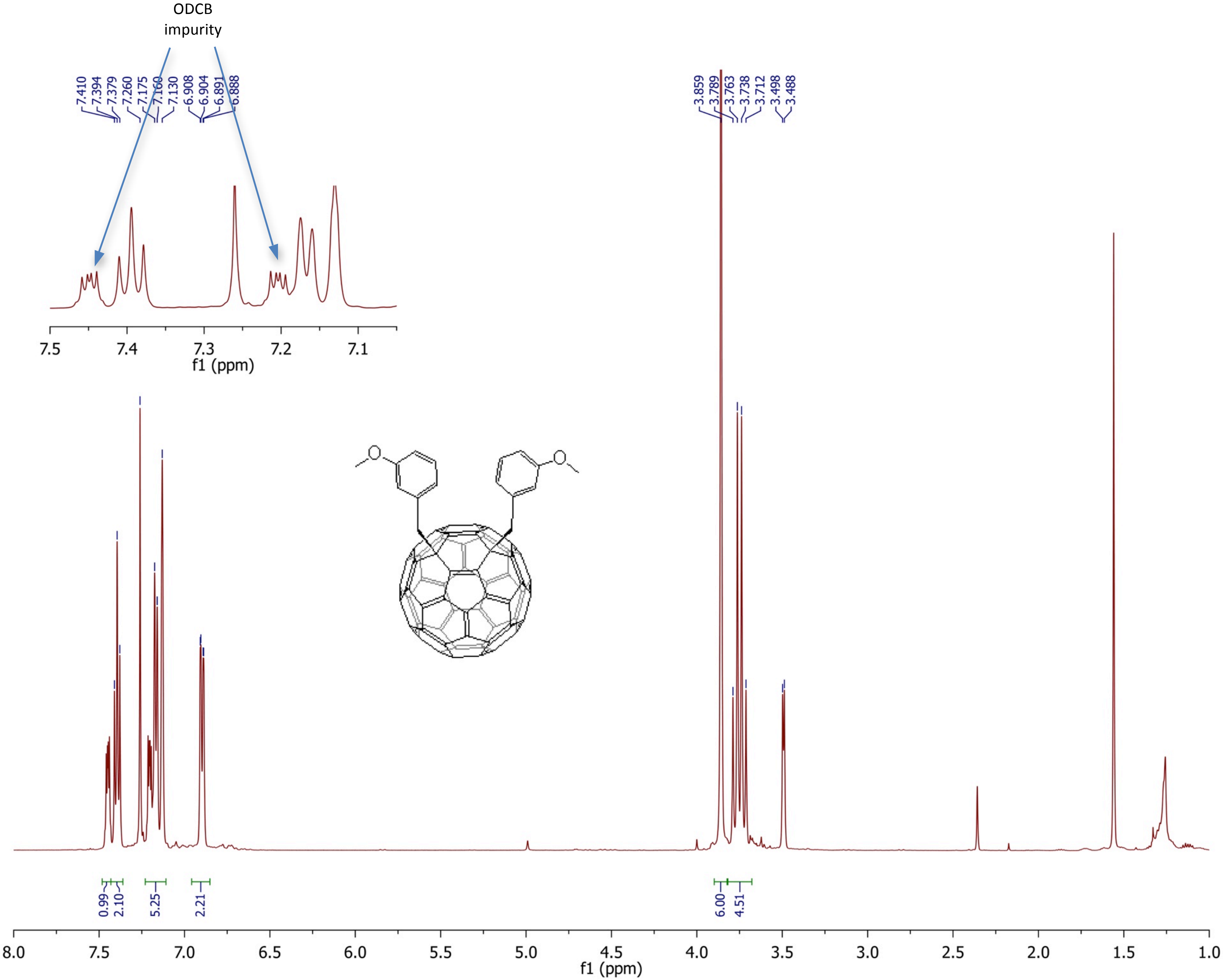


Figure S3. ^{1}H NMR spectrum of compound **1b** (500 MHz, $CDCl_3/CS_2$ (1:1)).

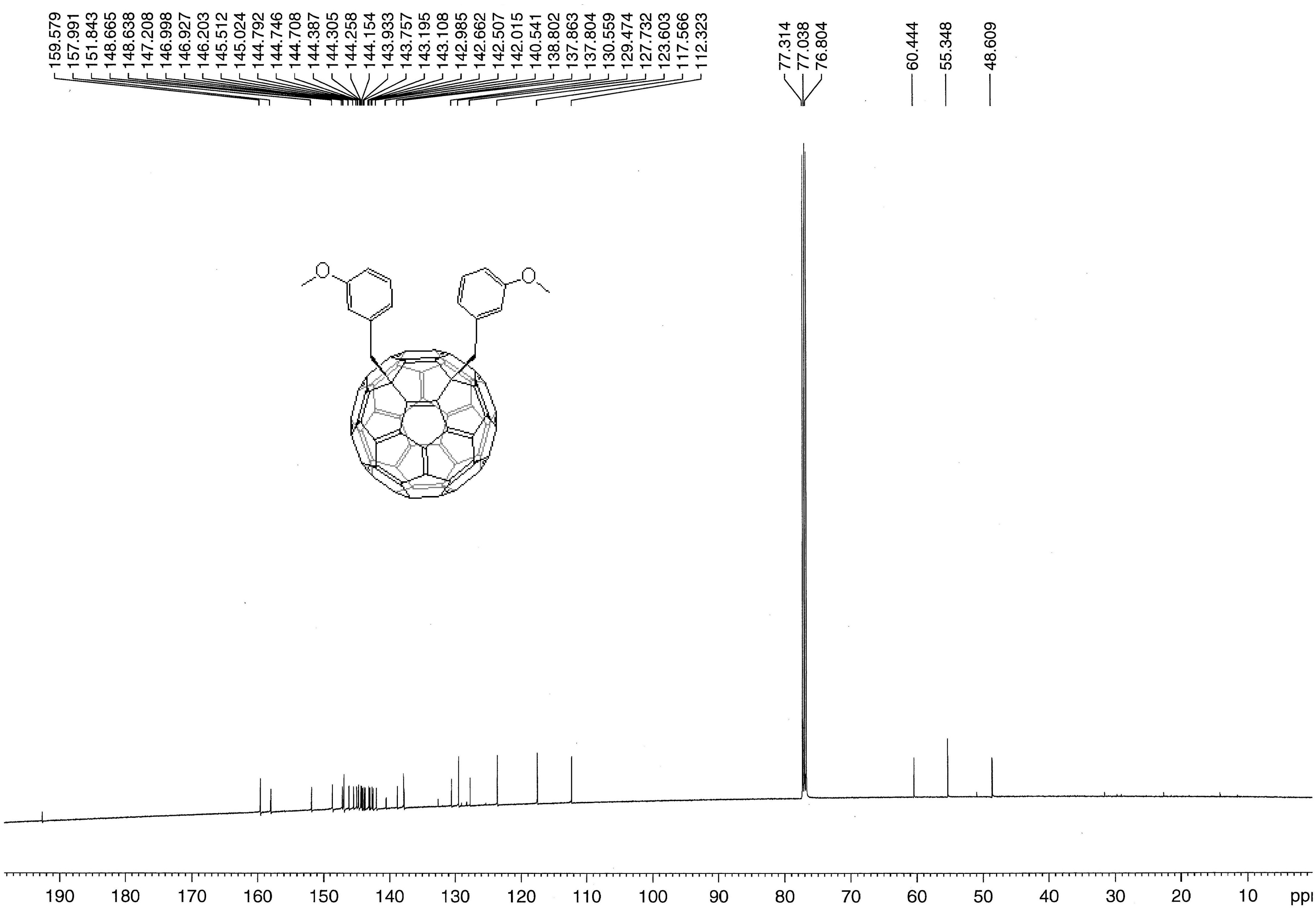


Figure S4. ^{13}C NMR spectrum of compound **1b** (125 MHz, $CDCl_3/CS_2$ (1:1)).

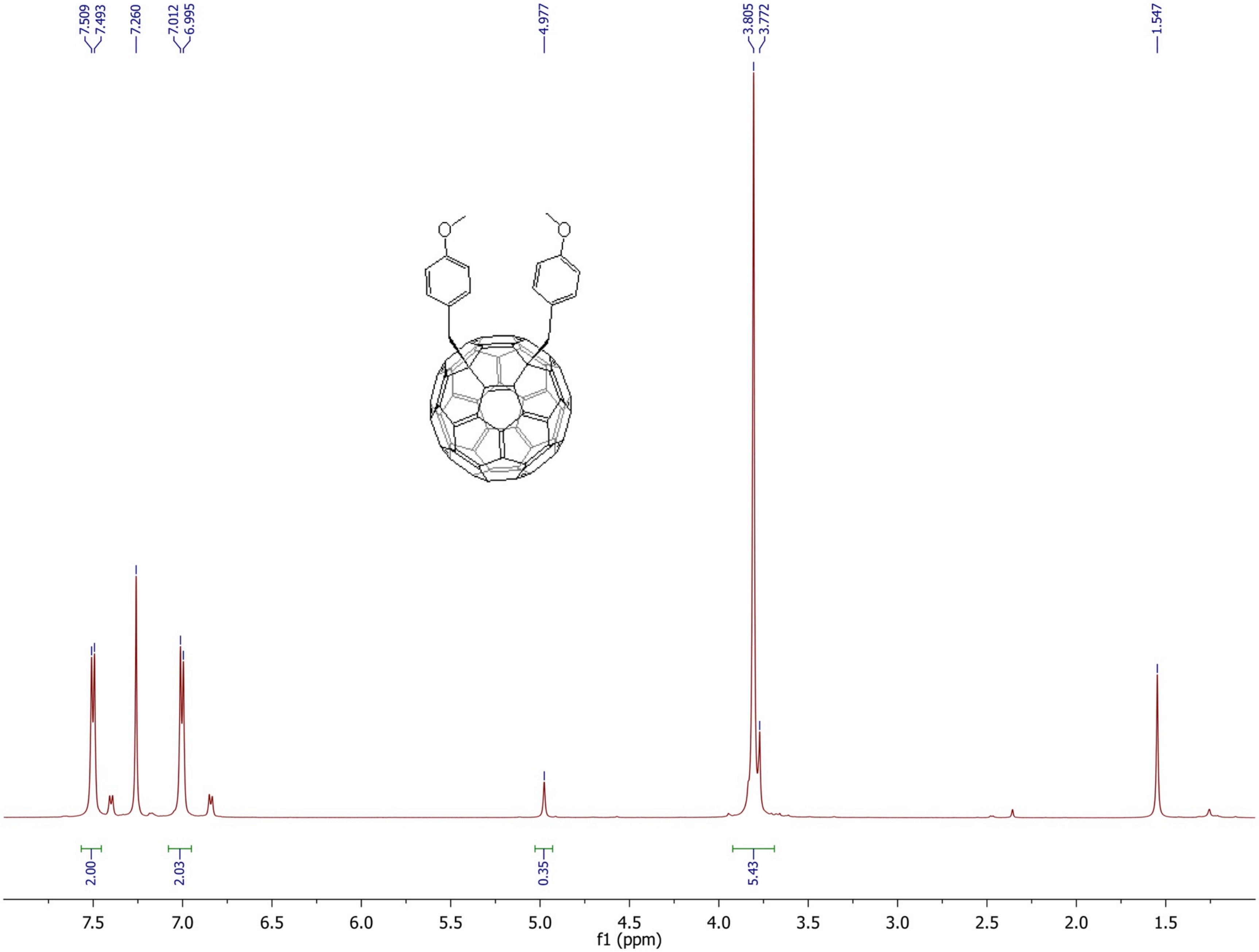


Figure S5. ^{1}H NMR spectrum of compound **1c** (500 MHz, $CDCl_3$).

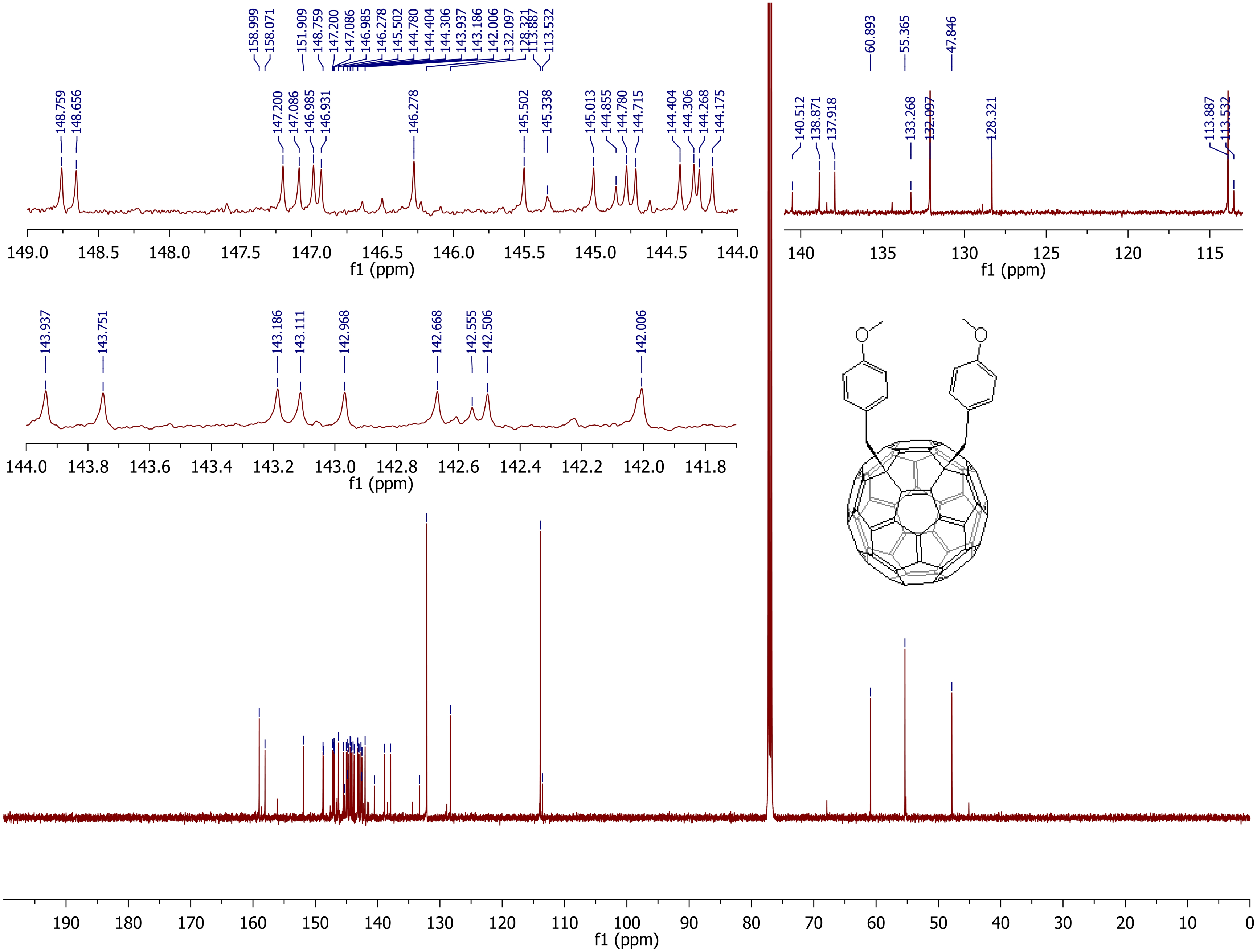


Figure S6. ^{13}C NMR spectrum of compound **1c** (125 MHz, CDCl$_3$).

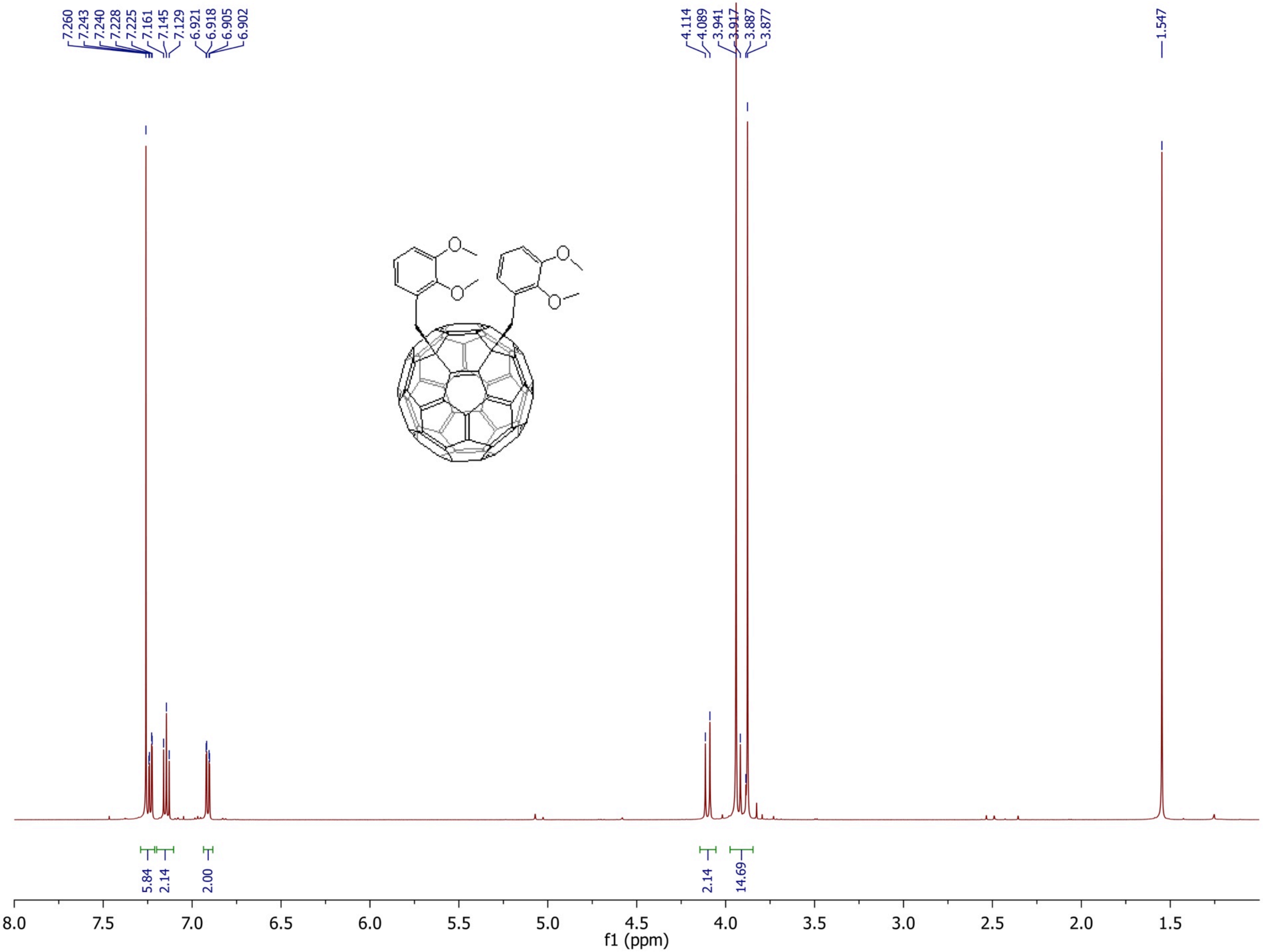


Figure S7. ^{1}H NMR spectrum of compound **1d** (500 MHz, $CDCl_3/CS_2$ (1:1)).

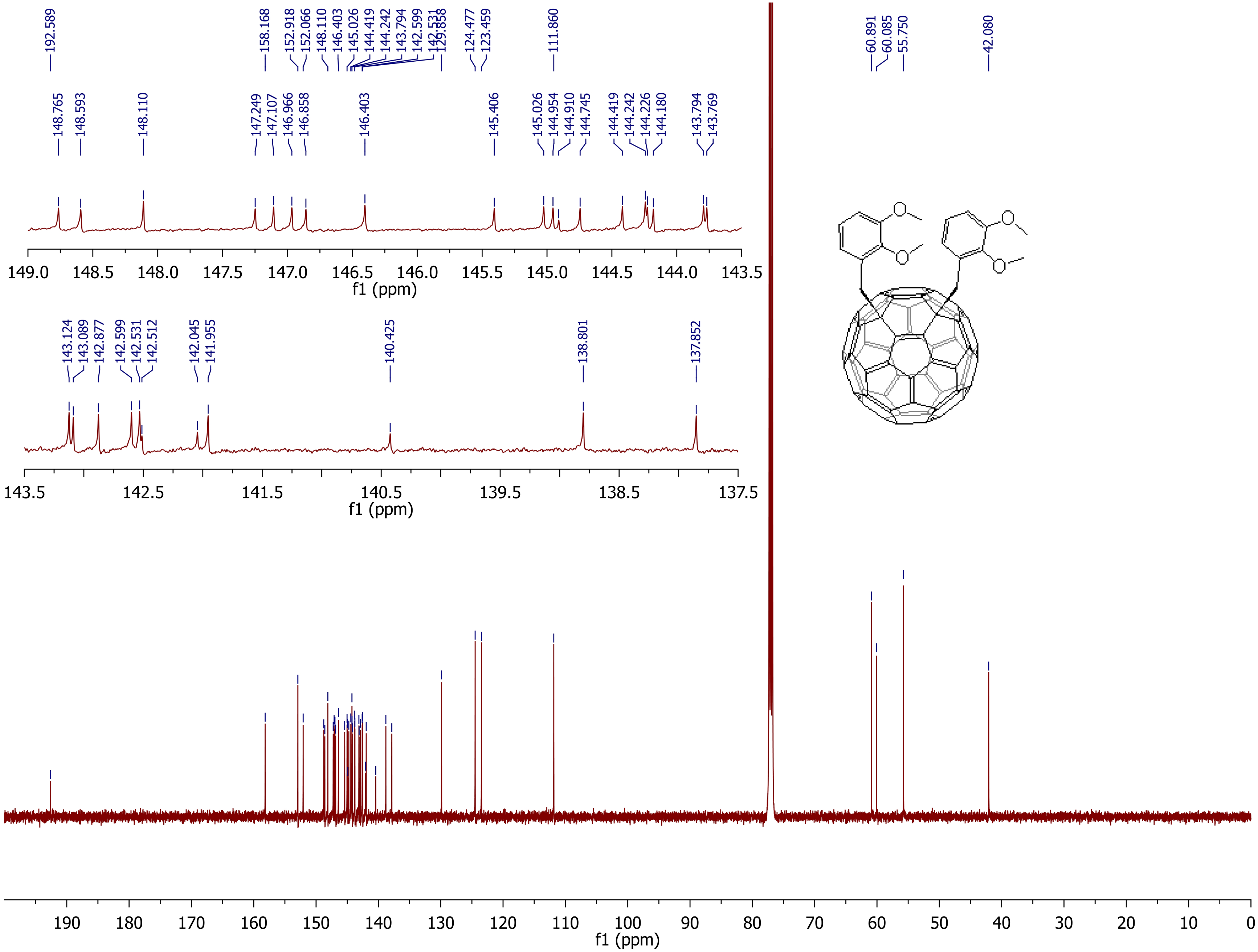


Figure S8. ^{13}C NMR spectrum of compound **1d** (125 MHz, $CDCl_3/CS_2$ (1:1)).

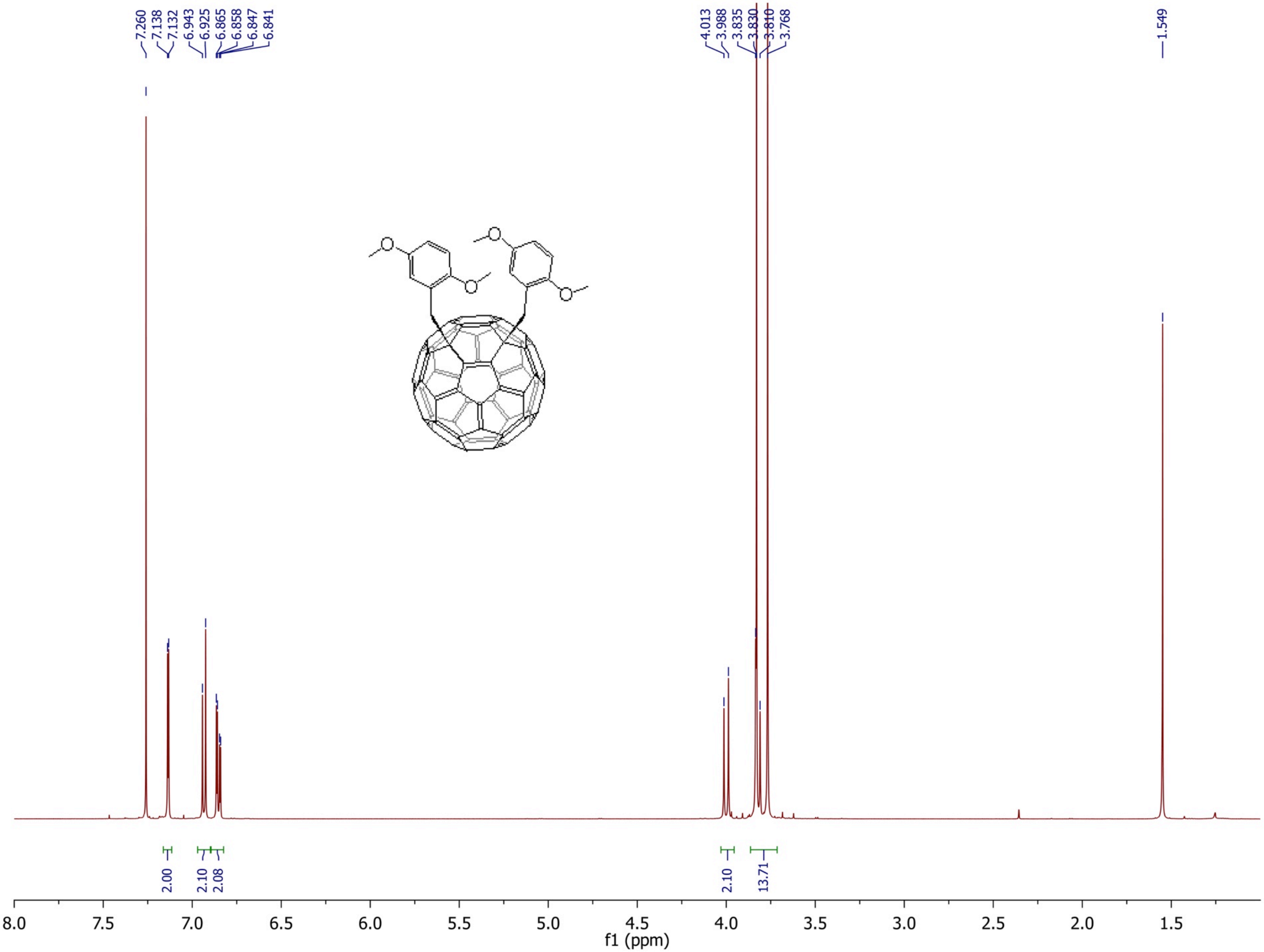


Figure S9. ^{1}H NMR spectrum of compound **1e** (500 MHz, $CDCl_3$).

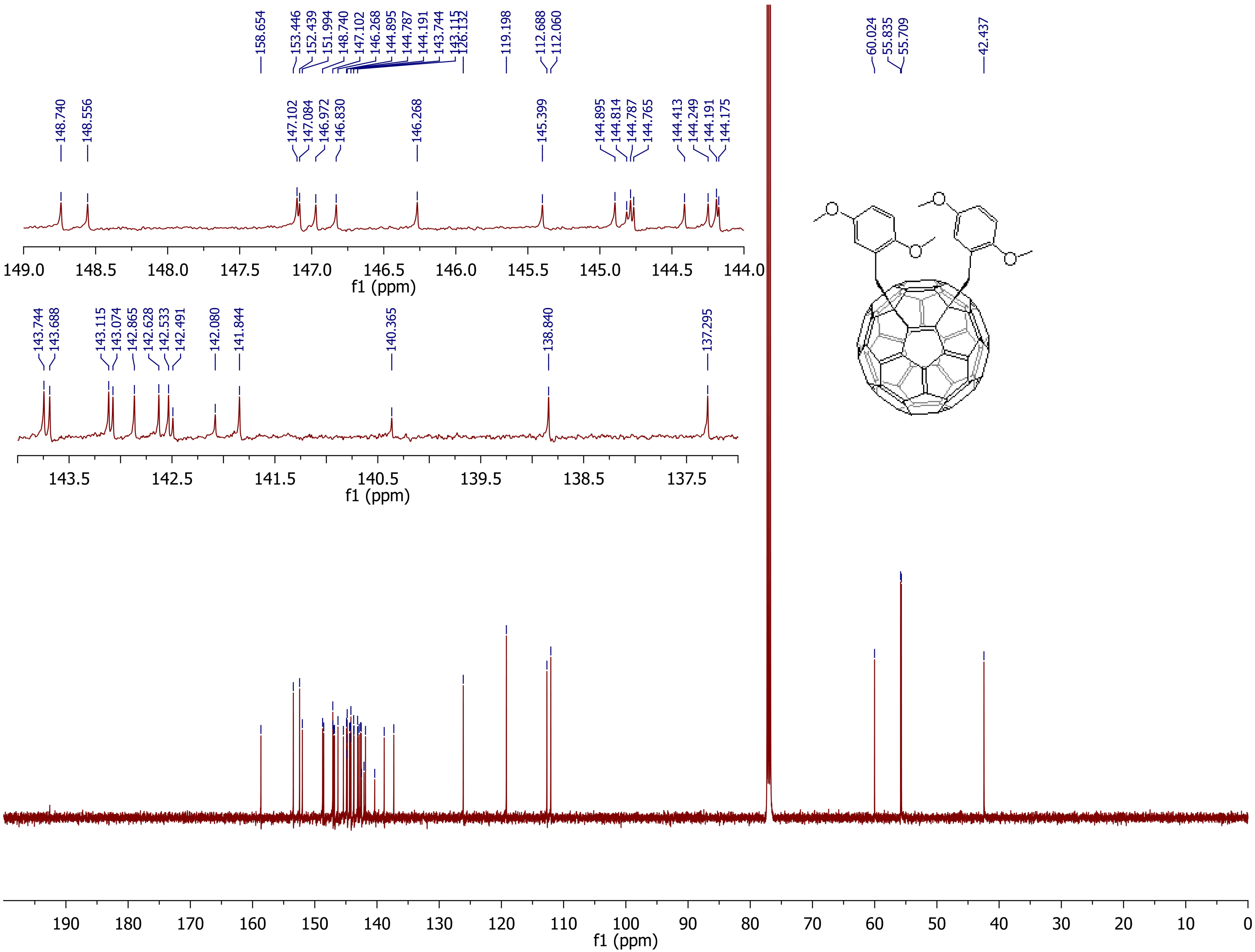


Figure S10. ^{13}C NMR spectrum of compound **1e** (125 MHz, CDCl$_3$).

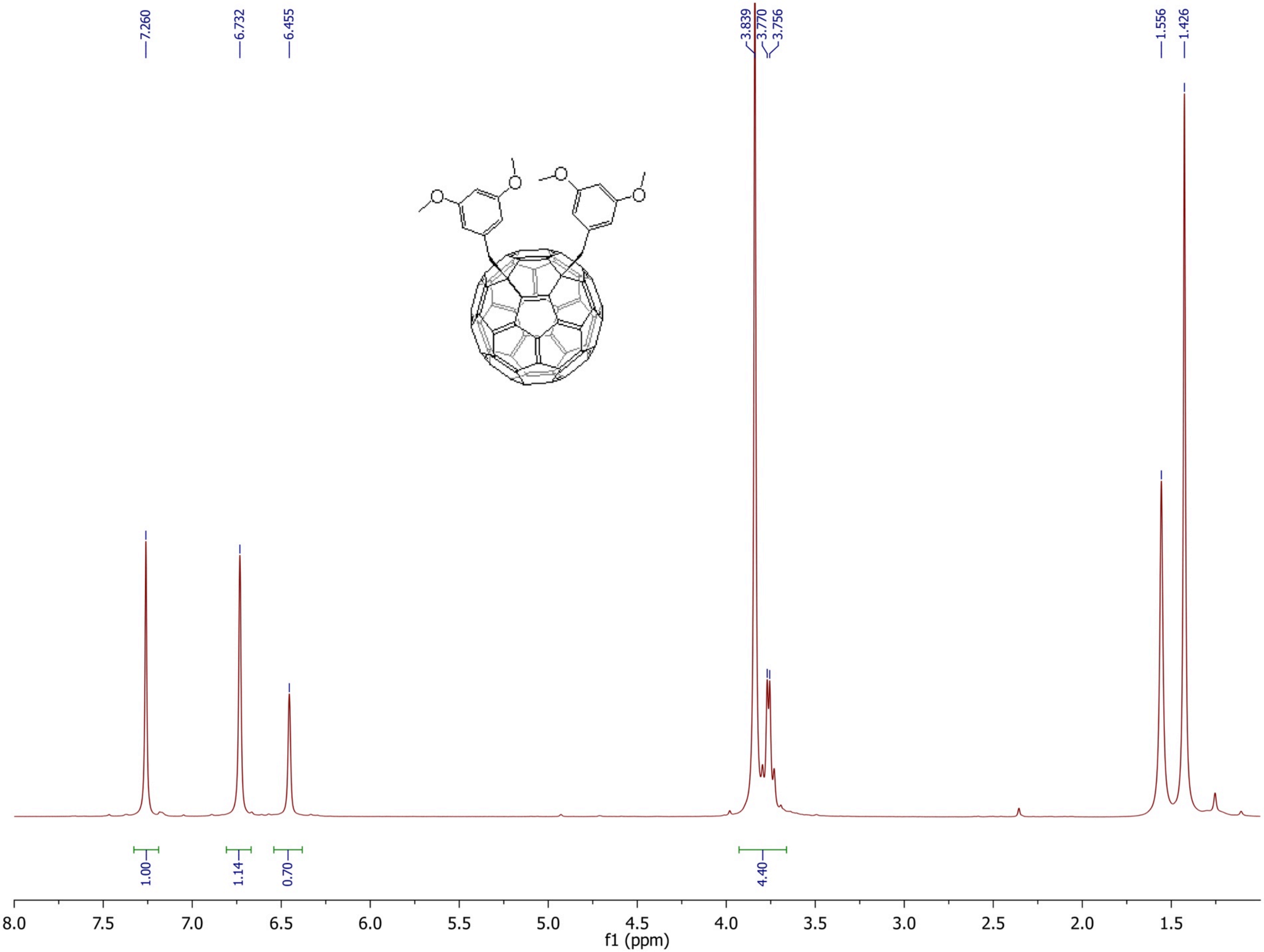


Figure S11. ^{1}H NMR spectrum of compound **1f** (500 MHz, $CDCl_3$).

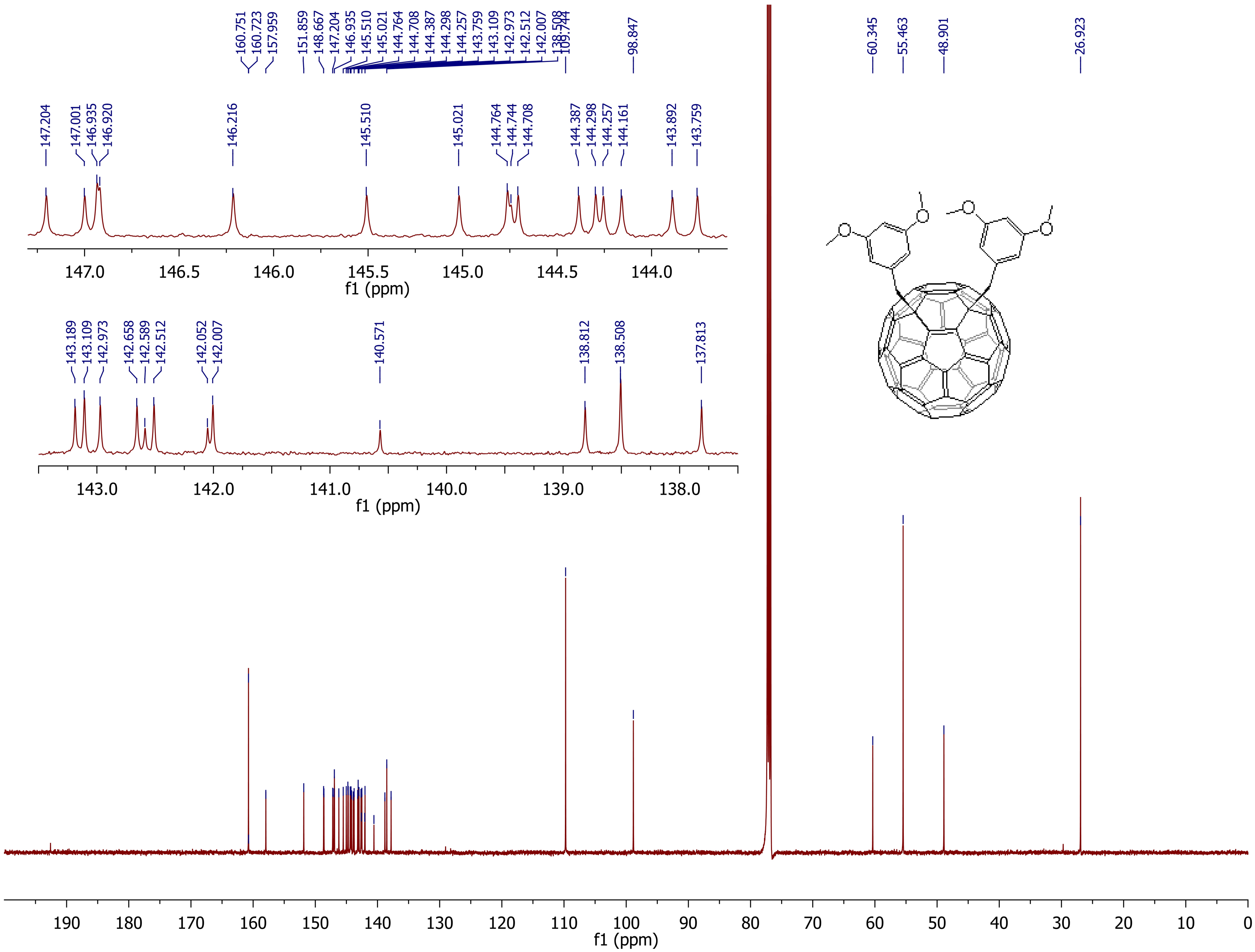


Figure S12. ^{13}C NMR spectrum of compound **1f** (125 MHz, $CDCl_3$).

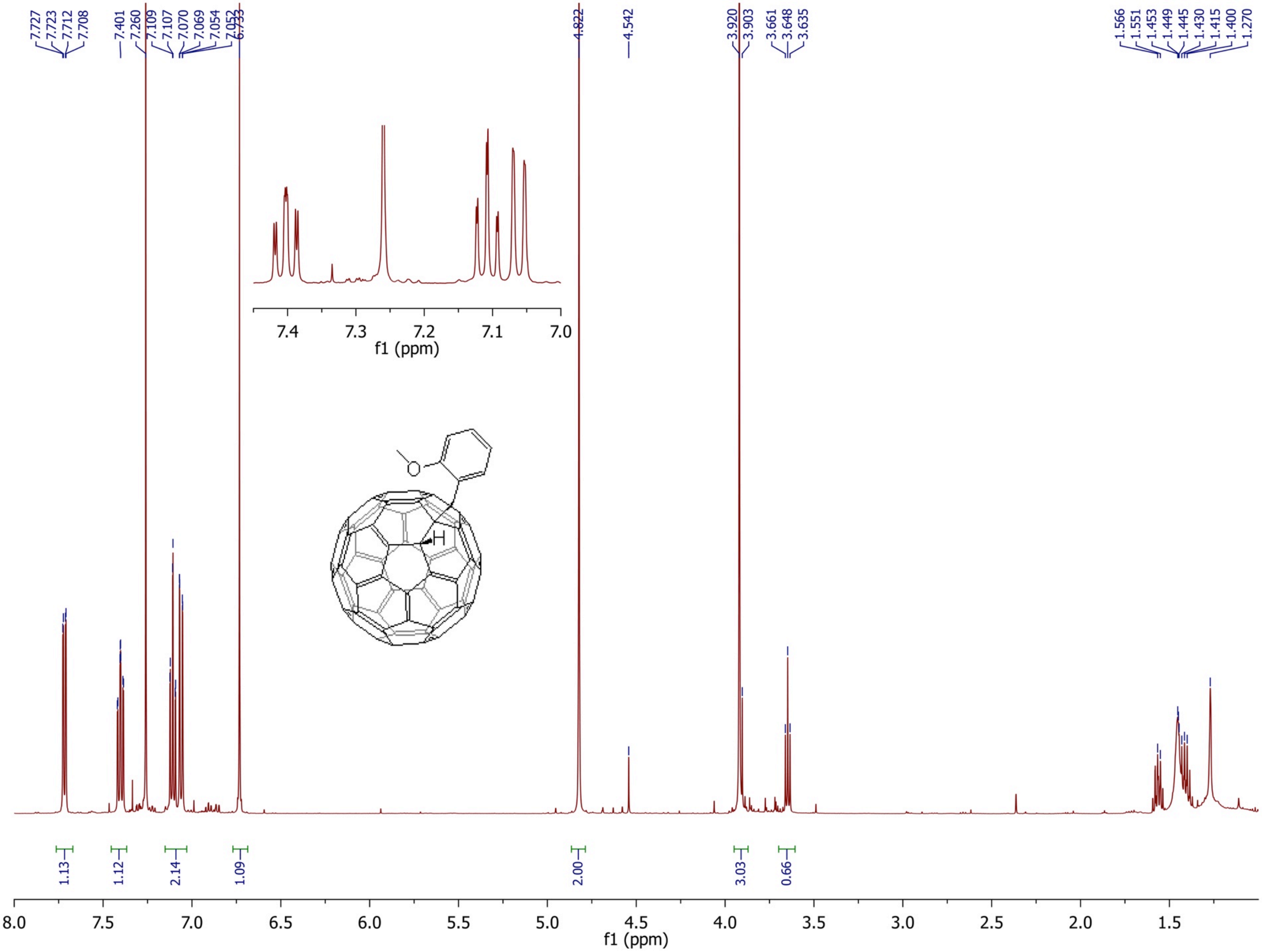


Figure S13. ^{1}H NMR spectrum of compound **2a** (500 MHz, $CDCl_3/CS_2$ (1:1)).

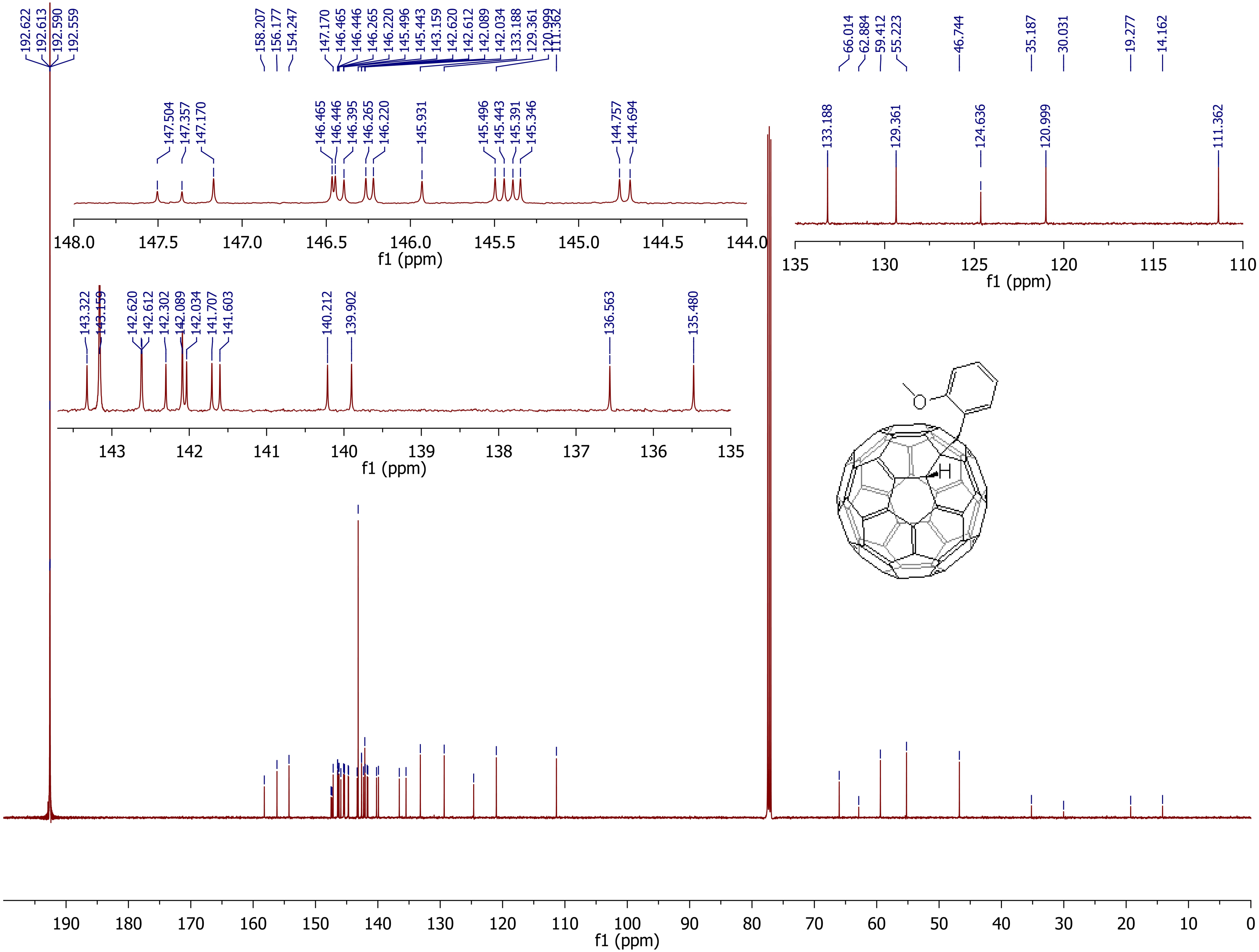


Figure S14. ^{13}C NMR spectrum of compound **2a** (125 MHz, $CDCl_3/CS_2$ (1:1)).

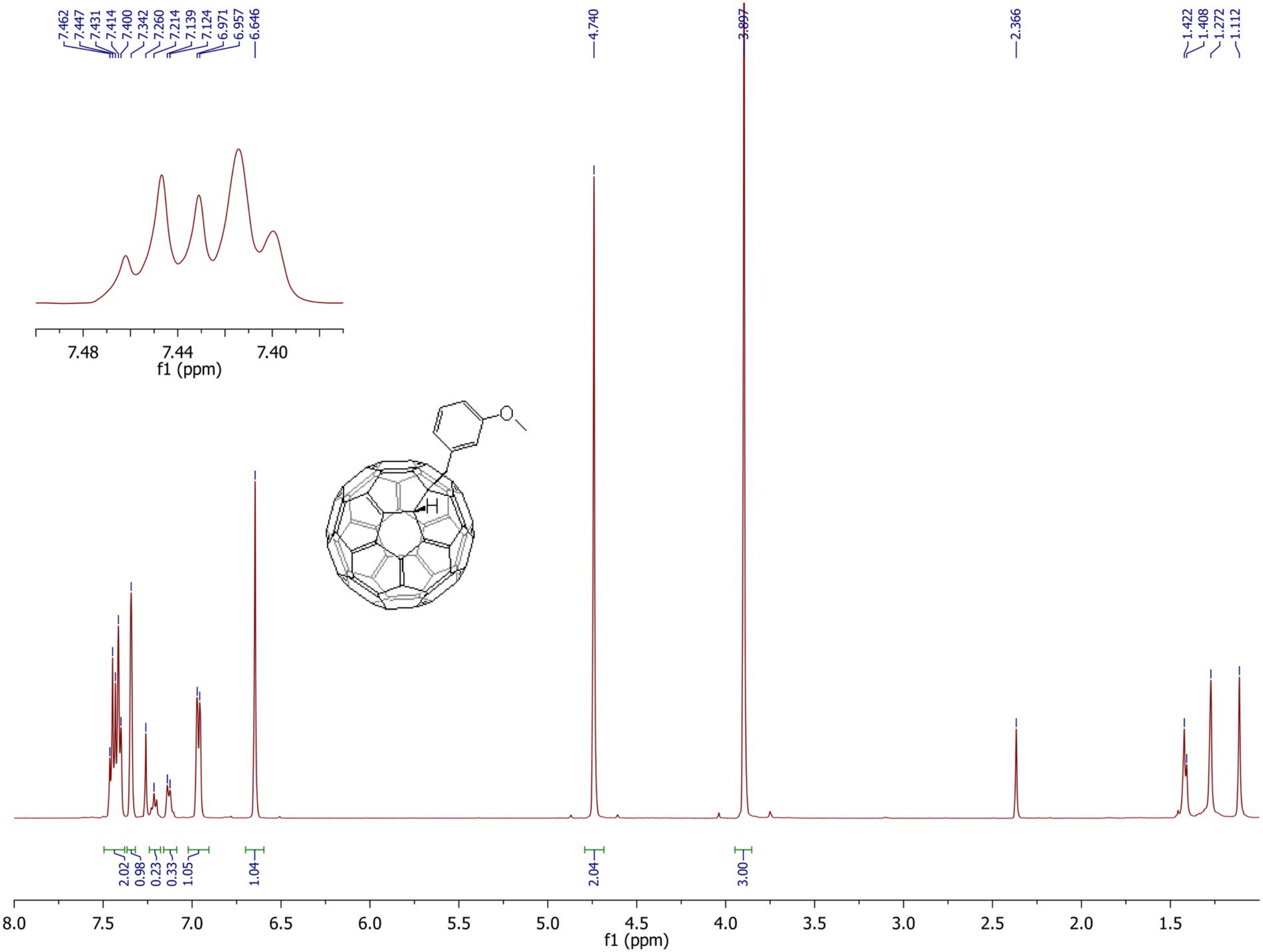


Figure S15. ^{1}H NMR spectrum of compound **2b** (500 MHz, $CDCl_3/CS_2$ (1:1)).

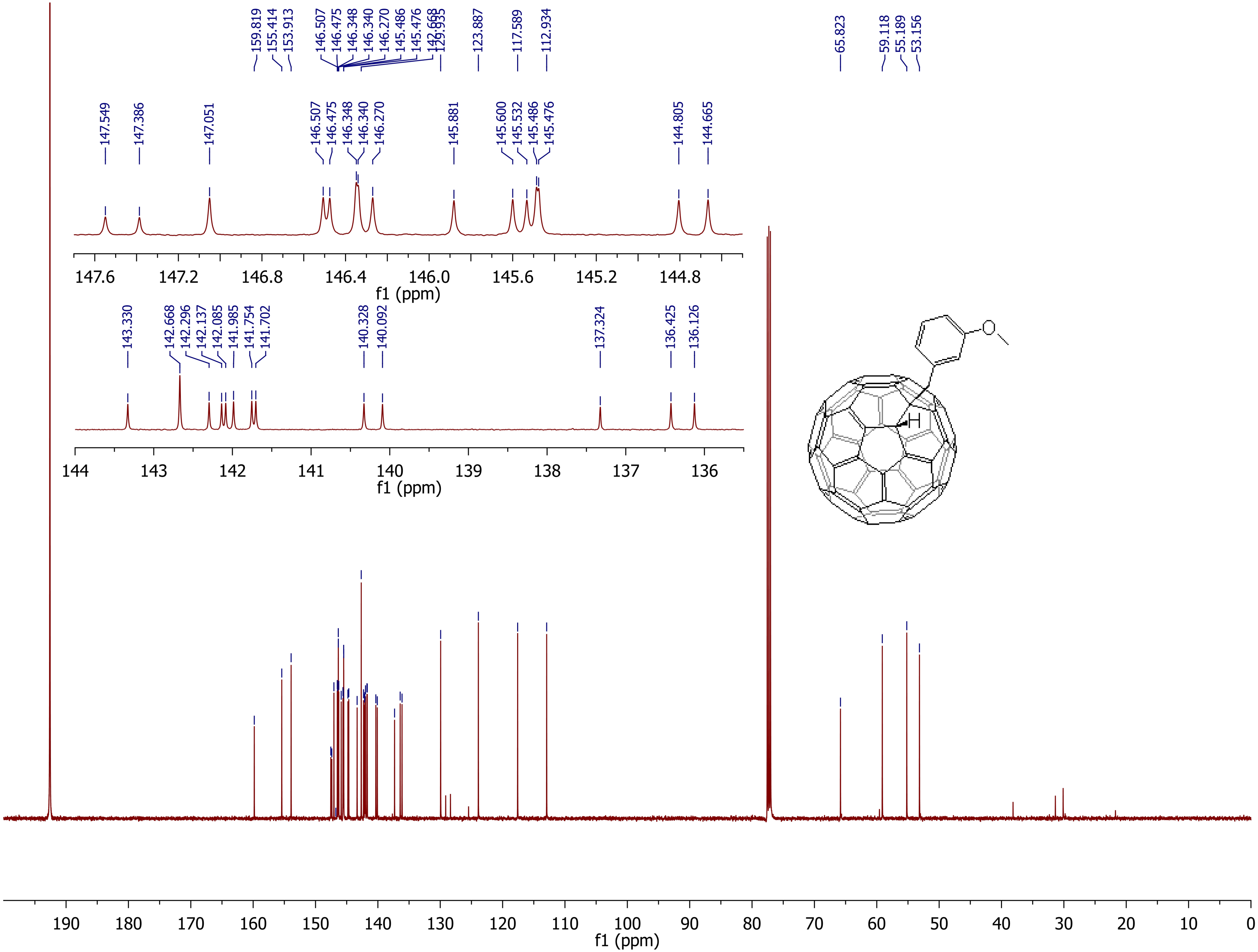


Figure S16. ^{13}C NMR spectrum of compound **2b** (125 MHz, $CDCl_3/CS_2$ (1:1)).

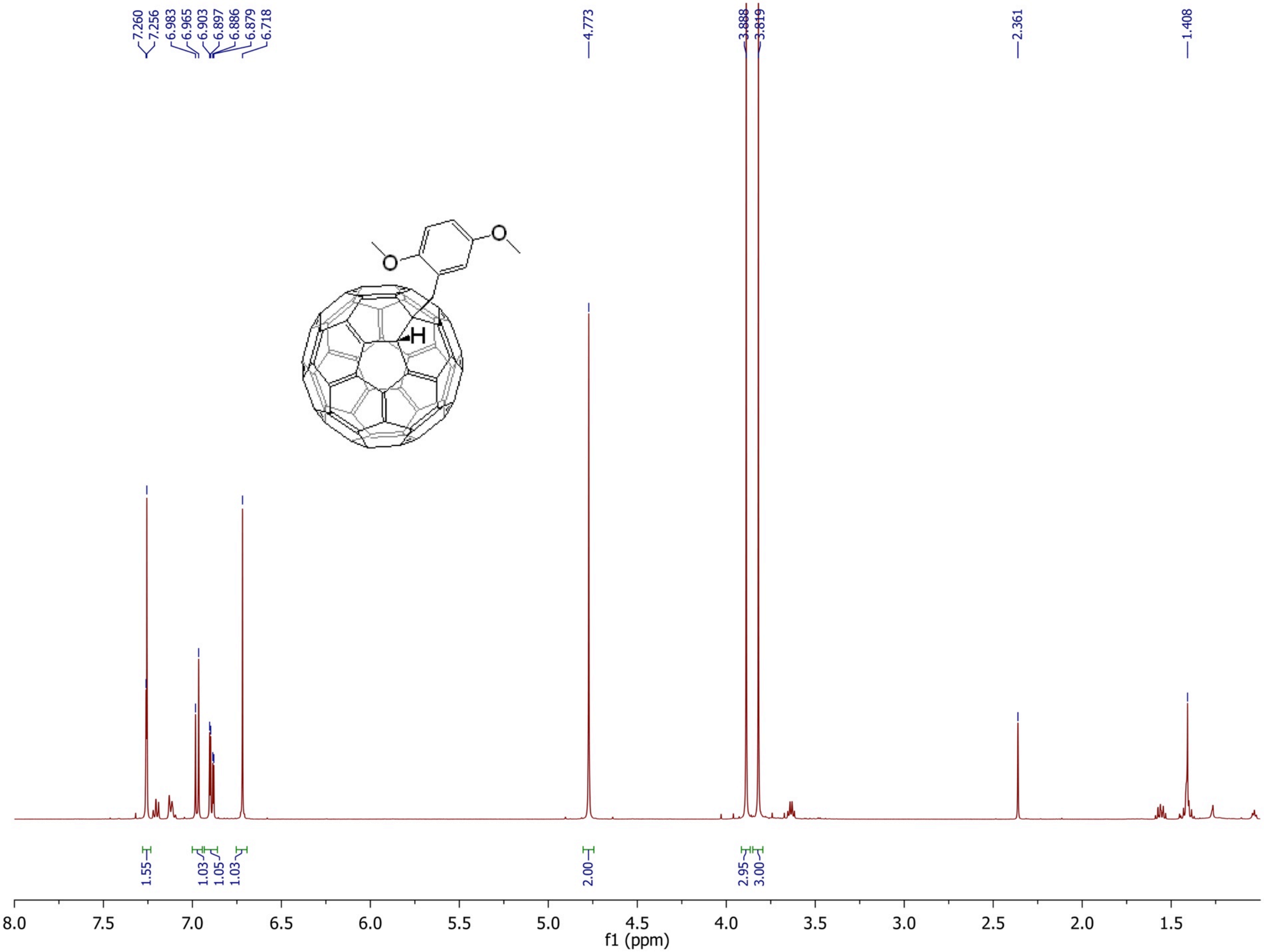


Figure S17. ^{1}H NMR spectrum of compound **2e** (500 MHz, $CDCl_3/CS_2$ (1:1)).

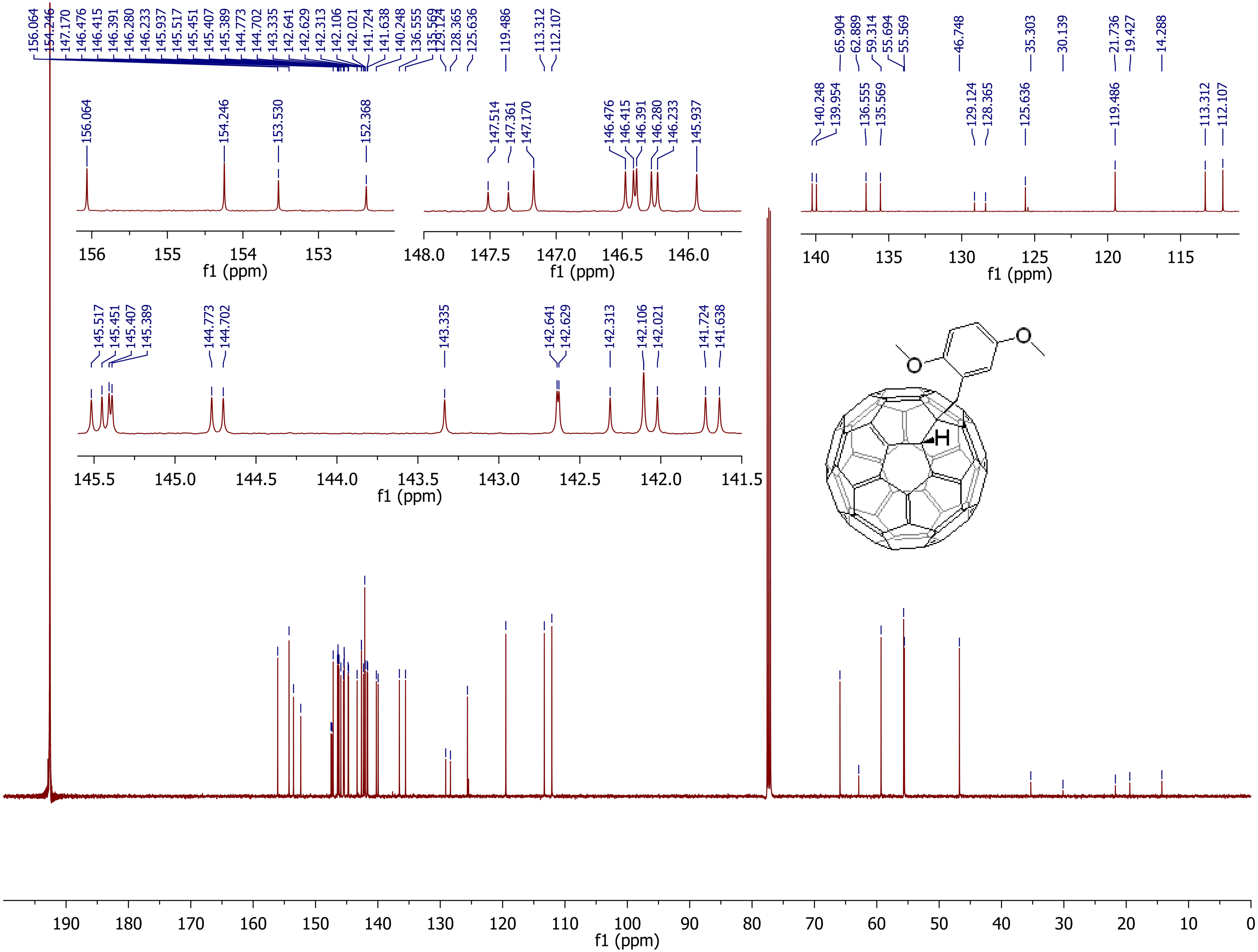


Figure S18. ^{13}C NMR spectrum of compound **2e** (125 MHz, $CDCl_3/CS_2$ (1:1)).

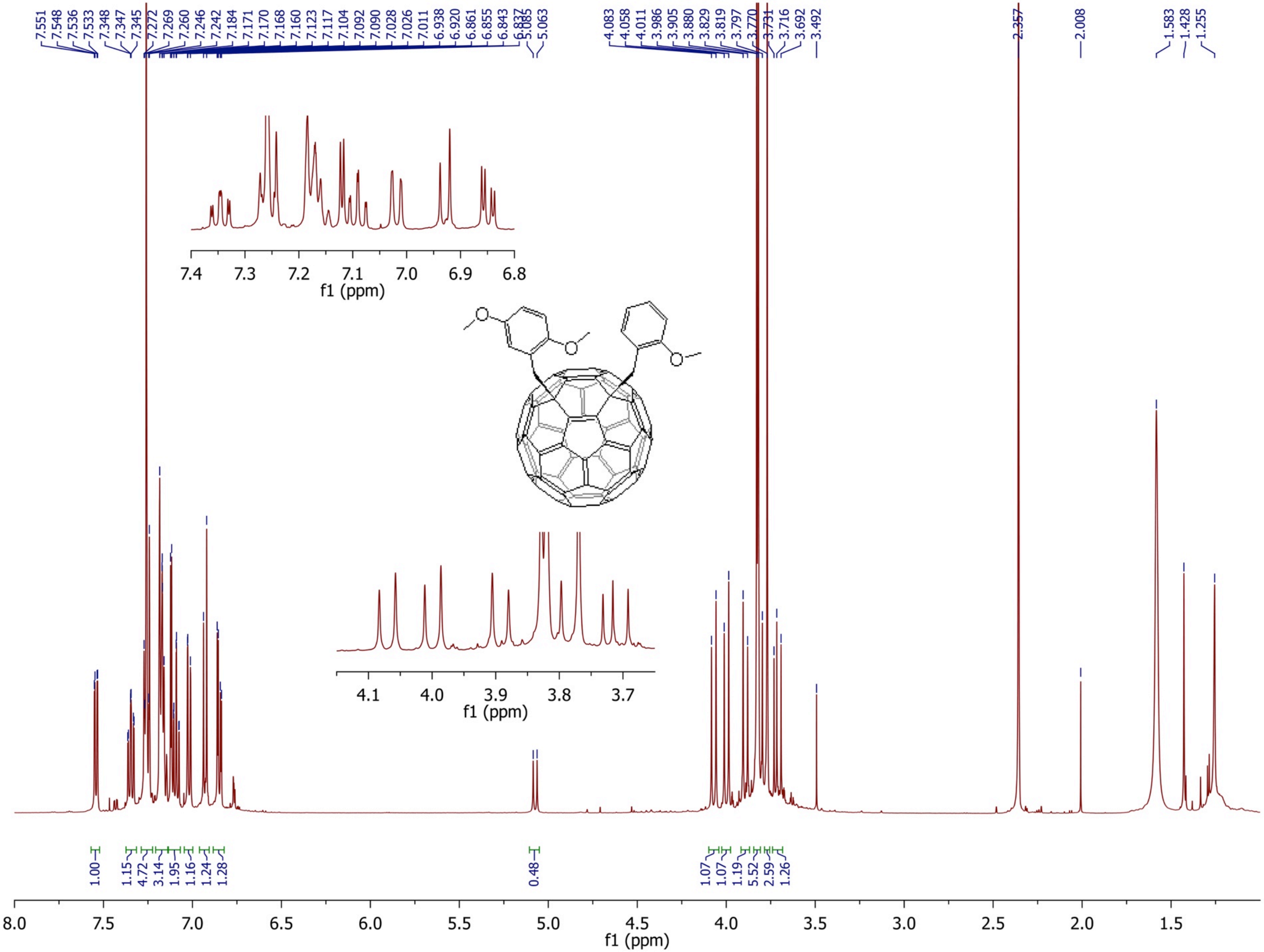


Figure S19. ^{1}H NMR spectrum of compound **1g** (500 MHz, $CDCl_3/CS_2$ (1:1)).

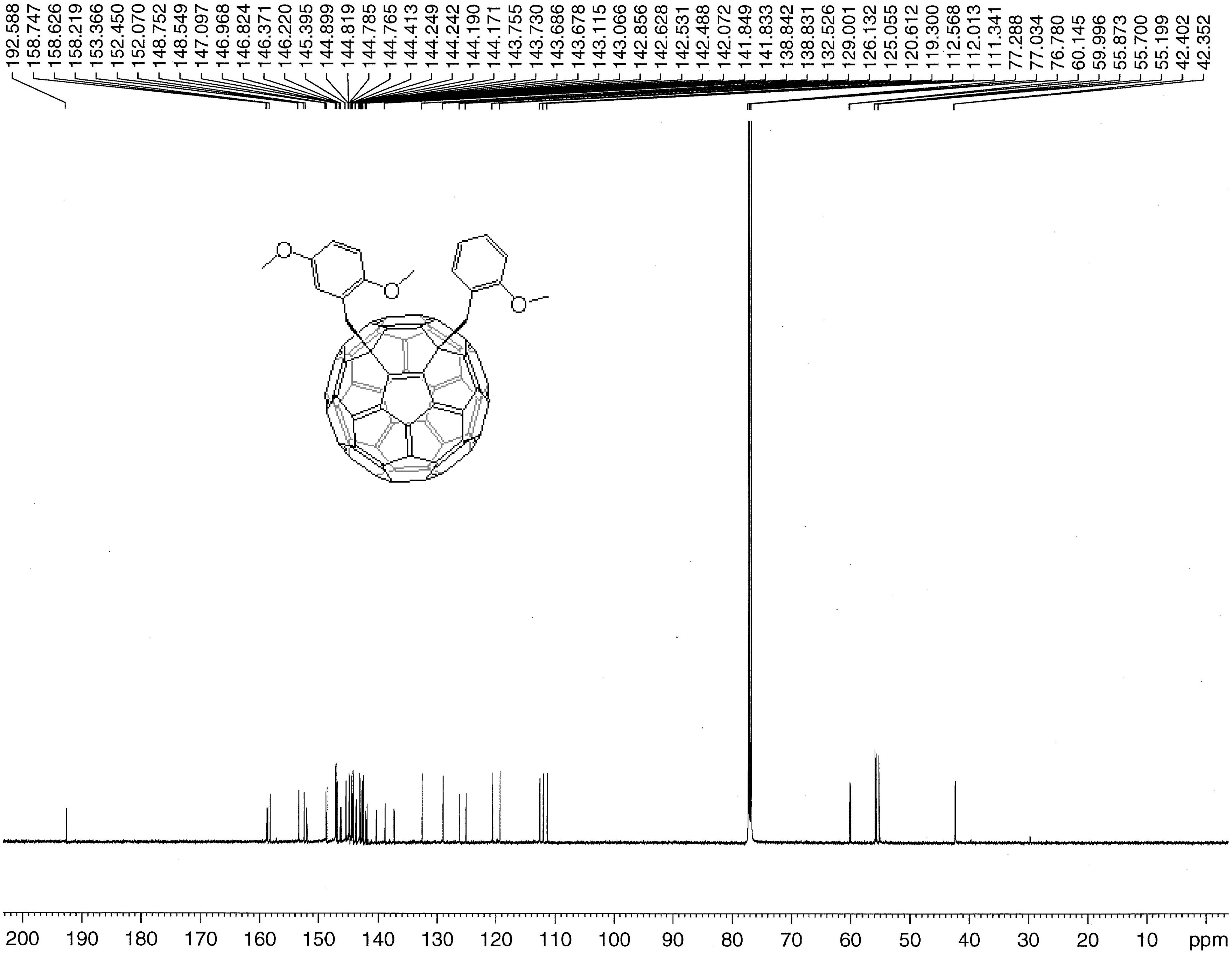


Figure S19.1. ^{13}C NMR Spectrum of compound **1g** (125 MHz, $CDCl_3/CS_2$ (1:1)).

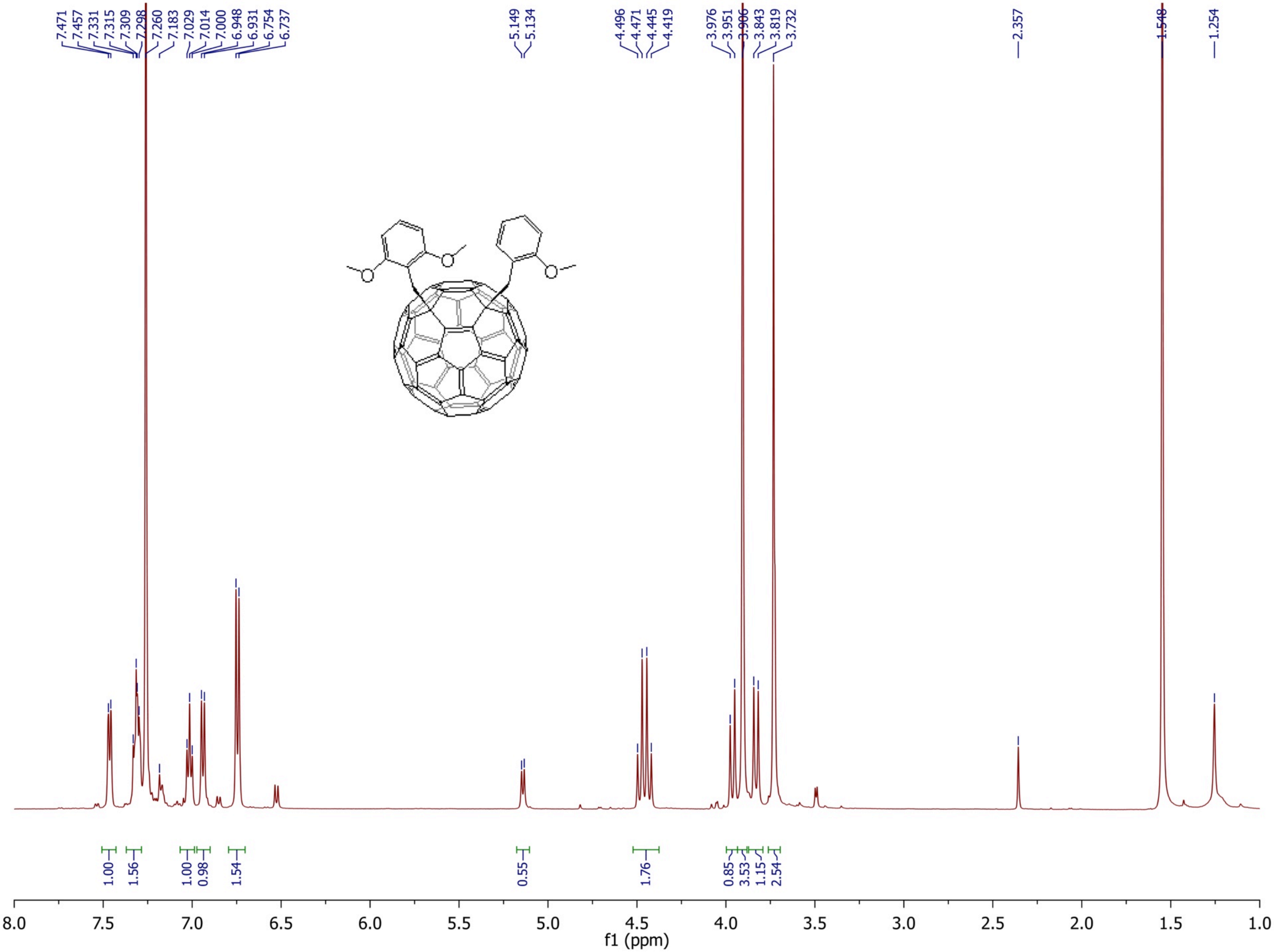


Figure S20. ^{1}H NMR spectrum of compound **1h** (500 MHz, $CDCl_3$).

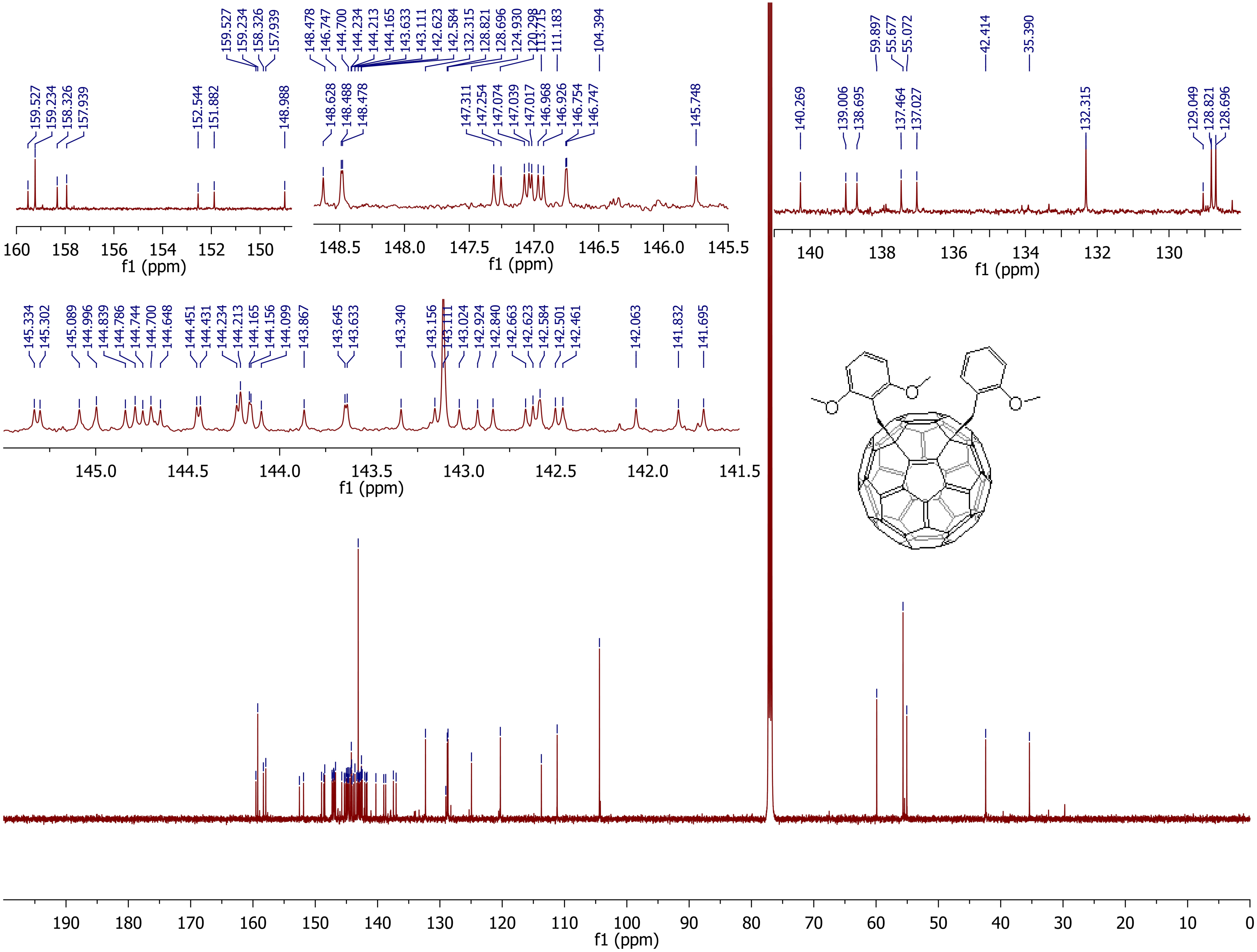


Figure S21. ^{13}C NMR spectrum of compound **1h** (125 MHz, $CDCl_3$).

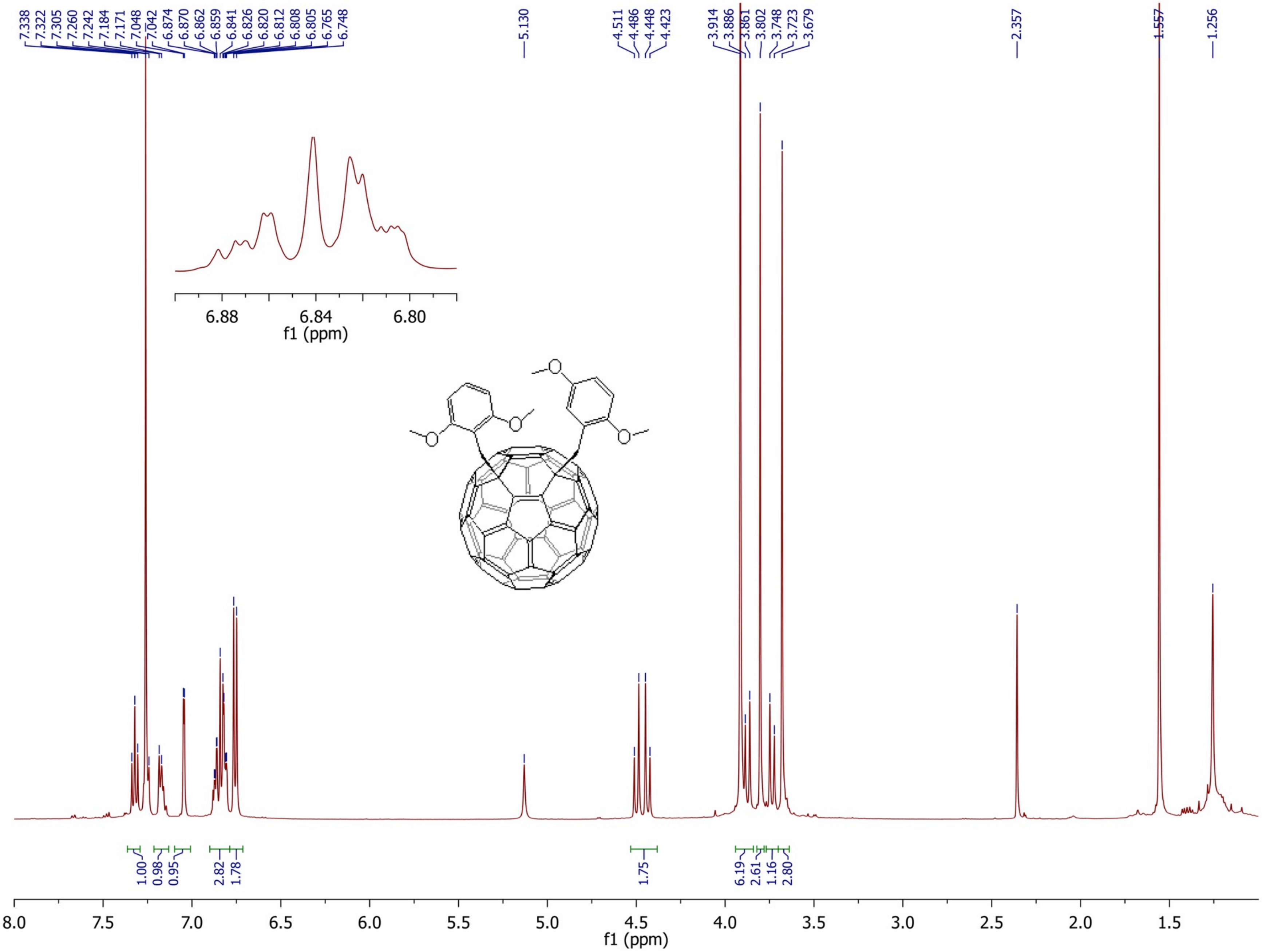


Figure S22. ^{1}H NMR spectrum of compound **1i** (500 MHz, $CDCl_3/CS_2$ (1:1)).

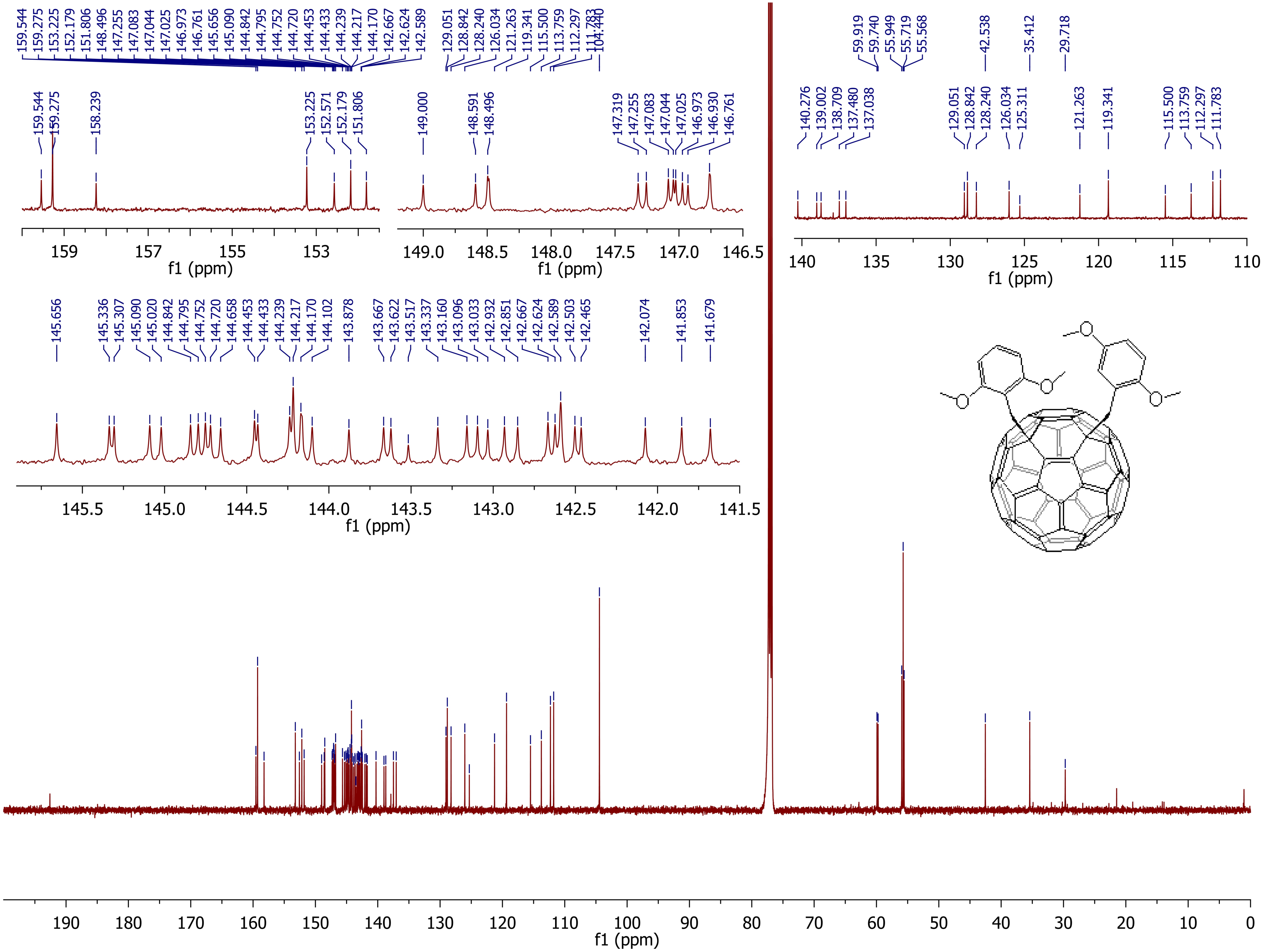


Figure S23. ^{13}C NMR spectrum of compound **1i** (125 MHz, $CDCl_3/CS_2$ (1:1)).

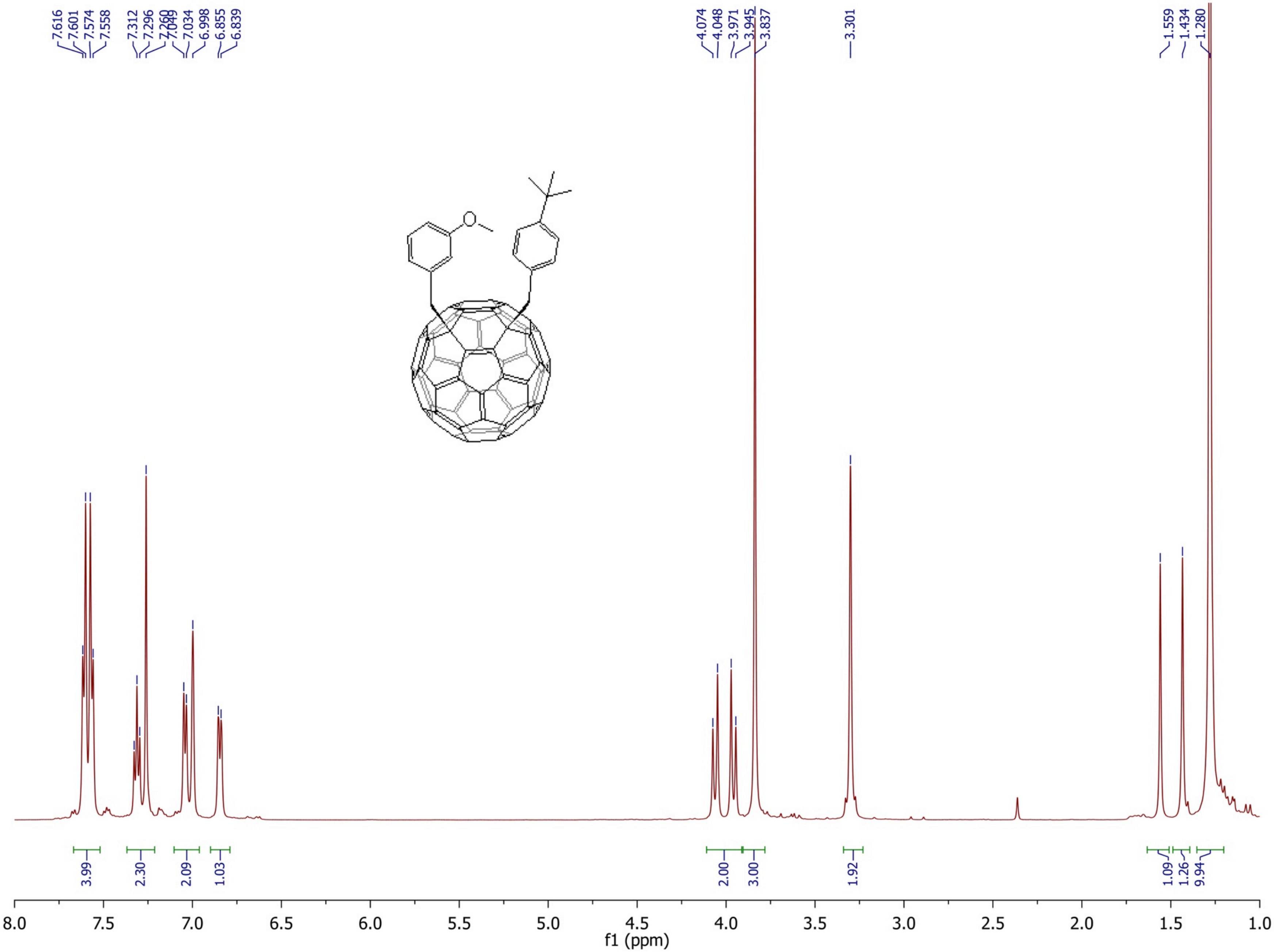


Figure S24. ^{1}H NMR spectrum of compound **1j** (500 MHz, $CDCl_3$).

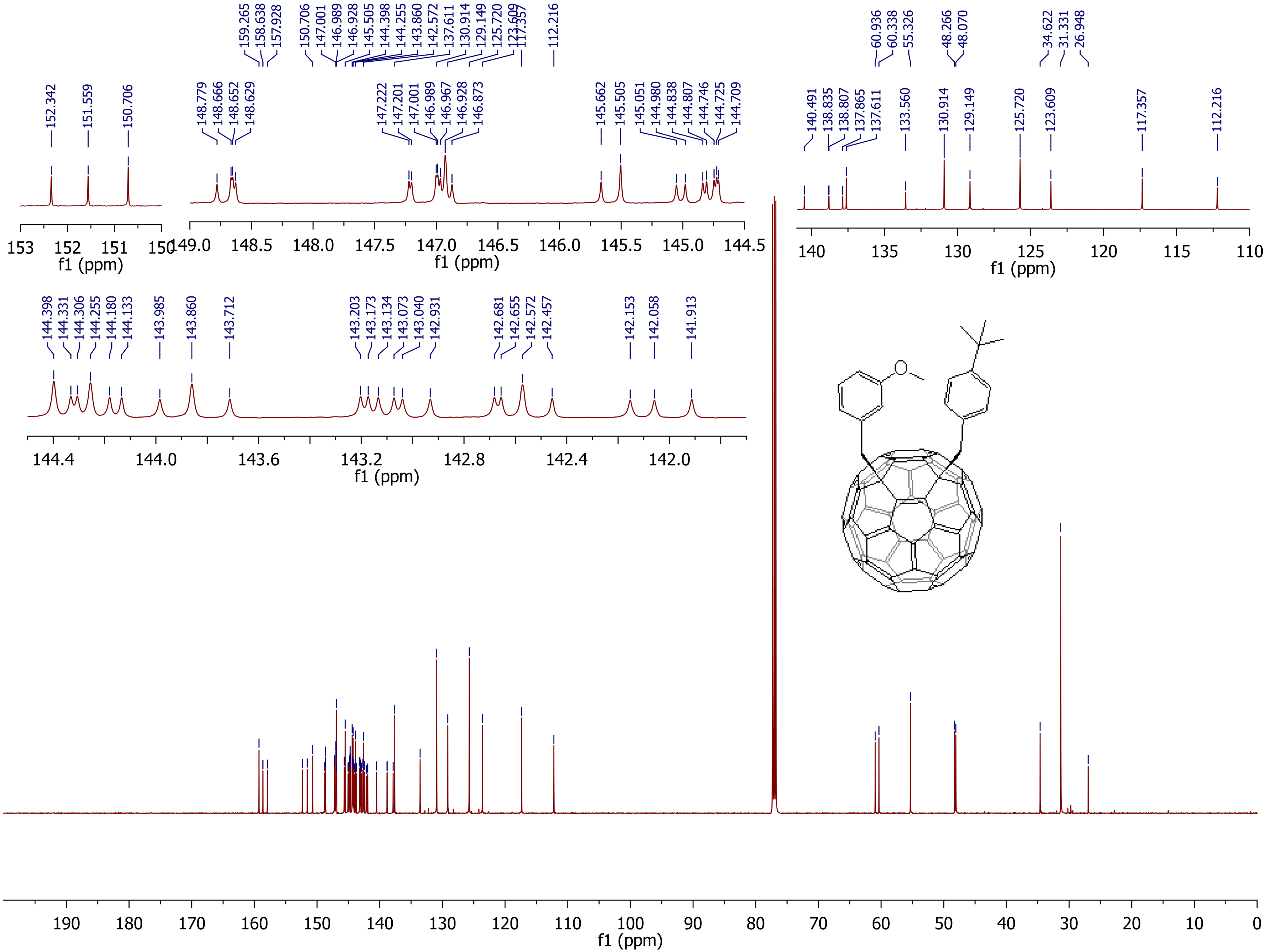


Figure S25. ^{13}C NMR spectrum of compound **1j** (125 MHz, $CDCl_3$).

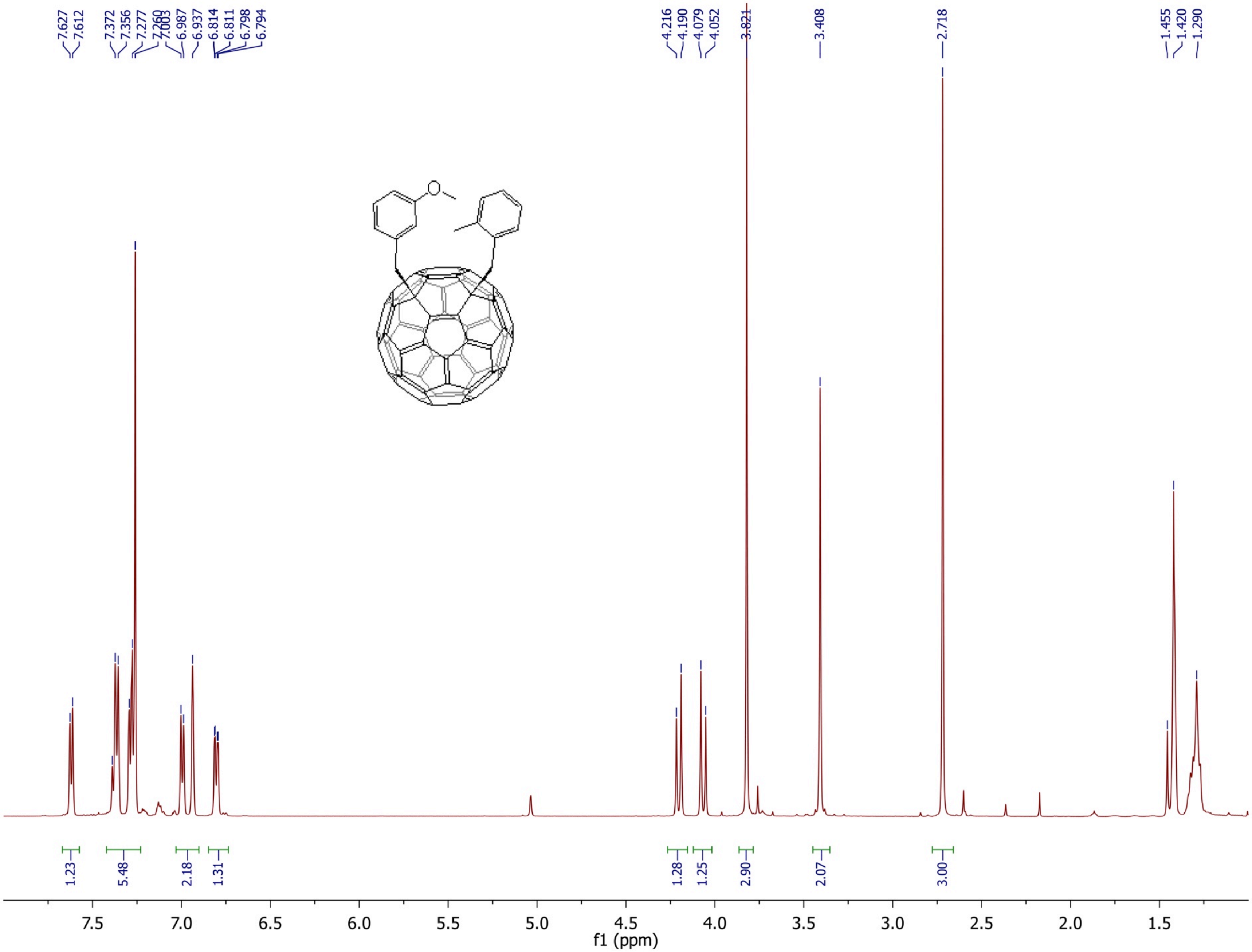


Figure S26. ^{1}H NMR spectrum of compound **1k** (500 MHz, $CDCl_3/CS_2$ (1:1)).

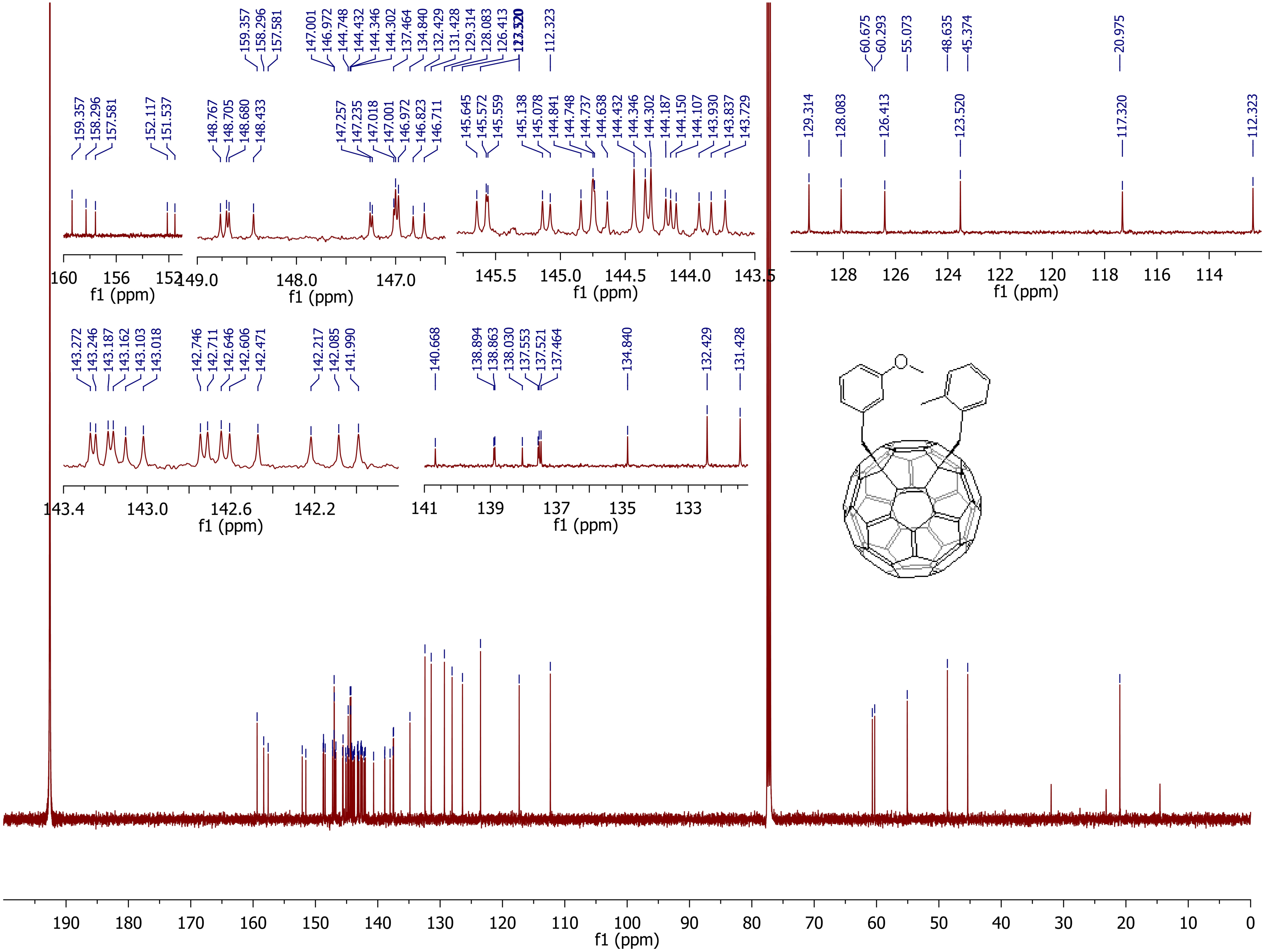


Figure S27. ^{13}C NMR spectrum of compound **1k** (125 MHz, $CDCl_3/CS_2$ (1:1)).

II. UV-Visible Absorption and External Quantum Efficiency (EQE)

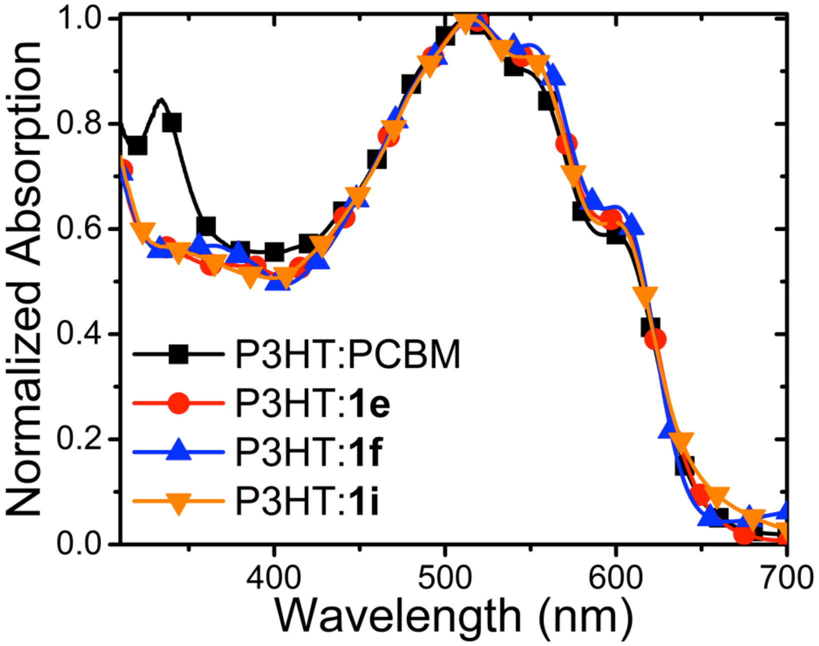


Figure S28. Typical UV-visible absorption spectra for P3HT:fullerene bis-adduct films.

In Figure S28, together with P3HT:PCBM, we plot the UV-visible absorption spectra of films made with P3HT:**1e**, P3HT:**1f** and P3HT:**1i**. These examples show that the absorption profile of the MeO-BBF does not display a well-defined absorption peak near 340 nm, unlike PCBM. Instead, the bis-adduct peaks are slightly shifted to the red compared to PCBM. The same trend is observed in the EQE measurements over the same wavelength range, as shown below in Figure S29 for P3HT:**1e** and P3HT:PCBM. The current densities obtained by integrating the EQE spectra for P3HT:PCBM and P3HT:**1e** are 8.38 mA/cm^2 and 8.57 mA/cm^2, respectively, which confirm the J_{sc}'s we obtained directly from the *J*-*V* measurements.

Figure S30 is the EQE spectra for PTB7:PCBM and PTB7:**1e**, which yield integrated current densities of 11.9 mA/cm^2 and 11.8 mA/cm^2, respectively, confirming the J_{sc}'s we measured directly from the *J*-*V* curves.

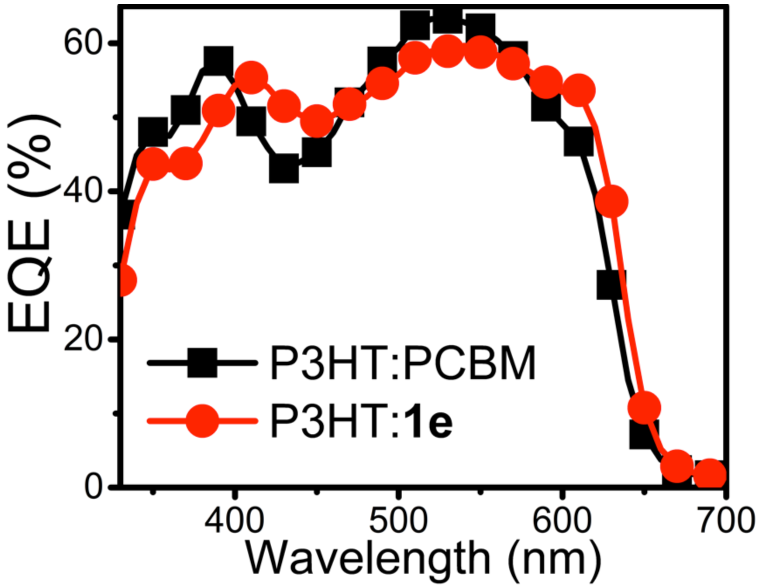


Figure S29. EQE spectra taken on the same P3HT:fullerene devices used in Figure 3 of the main text.

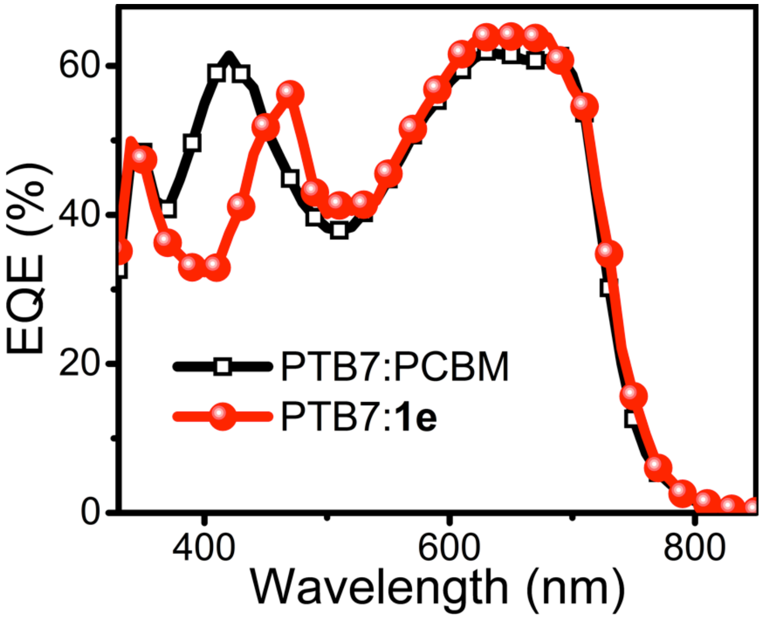


Figure S30. EQE spectra taken on the same PTB7:fullerene devices used in Figure 3 of the main text.

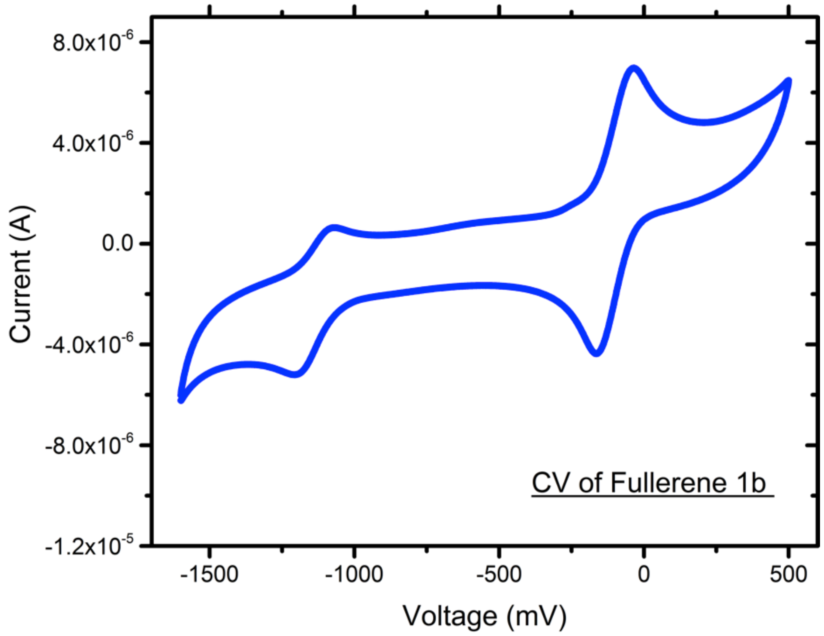
III. Parameters Summarized from 2D-GIWAXS Measurements

Table S1. Summary of GIWAXS Parameters

	(200) Peak Position ($Å^{-1}$)	(200) Peak Area (A.U.)	(200) Peak FWHM (A.U.)	Fullerene Peak Position ($Å^{-1}$)	Fullerene Peak Area (A.U.)	Fullerene FWHM (A.U.)
P3HT:PCBM	0.774	15.9	5.1	1.401	112	28.7
P3HT:**1b**	0.776	14.1	5.2	1.404	98	29.2
P3HT:**1k**	0.772	12.9	4.9	1.405	114	29.6
P3HT:**1j**	0.774	12.8	4.6	1.392	111	30.9

IV. Electrochemical Properties

V. Two cyclic voltammograms are displayed in Figure S31 to show the typical electrochemical properties of MeO-BBFs. The peaks located at more negative voltages are for the fullerenes and the peaks at more positive voltages come from the oxidation/reduction of ferrocene/ferrocenium (Fc/Fc$^+$). Table S2 summarizes the results on more MeO-BBFs as well as PCBM.



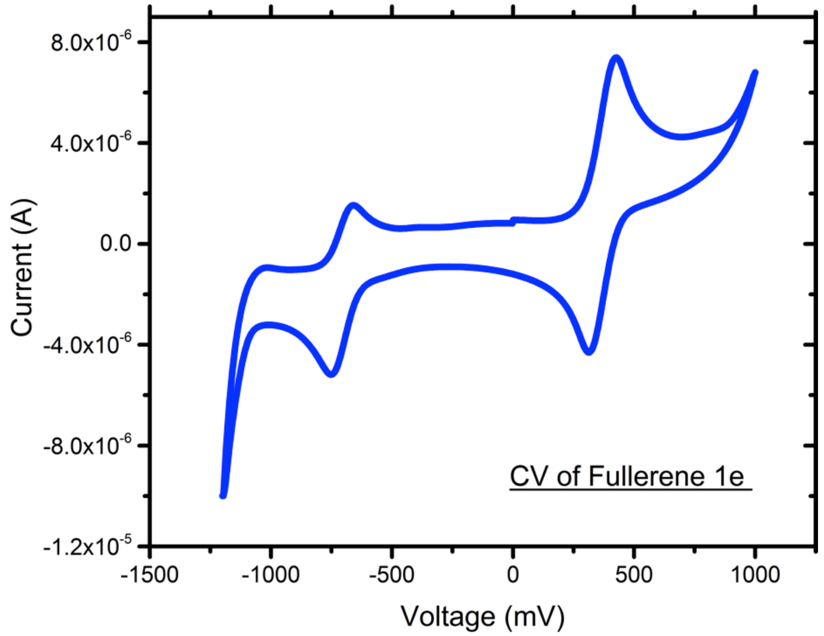


Figure S31. Cyclic voltammogram of fullerene **1b** and **1e**.

Table S2. Fullerene LUMO Levels Calculated Using Density Functional Theory and Determined by Cyclic Voltammetry

Method:	*Theory (DFT)*		*Experimental (CV)*	
Compound	*HOMO (eV)*	*LUMO (eV)*	*$E_{1/2}$ vs Fc/Fc$^+$ (V)*[b]	*LUMO (eV)*[c]
PCBM	–5.66	–3.09	–0.98	–3.81
1,4-bisbenzyl	–5.62	–3.06		
2-(OMe) (**1a**)[a]	–5.46	–2.93	–1.07	–3.73
3-(OMe) (**1b**)[a]	–5.55	–2.99	–1.04	–3.76
4-(OMe) (**1c**)[a]	–5.55	–3.01	–1.05	–3.75
2,3-$(OMe)_2$ (**1d**)[a]	–5.38	–2.84		
2,5-$(OMe)_2$ (**1e**)[a]	–5.36	–2.87	–1.07	–3.73
3,5-$(OMe)_2$ (**1f**)[a]	–5.47	–2.92		
2,6-$(OMe)_2$[a]	–5.31	–2.79		
2,3,6-$(OMe)_3$[a]	–5.23	–2.72		
1j			–1.03	–3.77
1k			–1.04	–3.76

[a] Substituent positions of the corresponding 1,4-bisbenzyl derivatives

[b] The first reduction potential ($E_{1/2}$) are listed relative to Fc/Fc$^+$.

[c] The energy level of Fc/Fc$^+$ was assumed to be –4.8 eV relative to vacuum.[1]

References

1 J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch and J. Daub, *Adv. Mater.*, 1995, **7**, 551–554.