

Supporting Information

Increasing the Open Circuit Voltage of Bulk-heterojunction Solar Cells by raising the LUMO level of the Acceptor

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Experimental procedure for fabrication of solar cells

As electron donor poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) from Covion (gift from Philips Research) is used.

The photovoltaic devices were prepared by spincoating EL grade PEDOT:PSS (Bayer EG) layers of ~ 60 nm onto pre-cleaned, patterned ITO substrates). The photoactive layer was deposited by spincoating from the appropriate solvent. The spin coating conditions were adjusted to give photoactive layers between 60 and 90 nm. Finally, a 1 nm layer of LiF (SigmaAldrich) and 80 nm of Al (5N, SigmaAldrich) were evaporated at $1 \cdot 10^{-6}$ mbar through a shadow mask. In this way, 4 cells were obtained with areas of 0.10 cm^2 , 0.15 cm^2 , 0.37 cm^2 and 1.0 cm^2 on the same substrate. Layer thickness measurements were performed with a Dektak 8 surface profilometer (Veeco).

For the complete series of PCBM compounds, ortho-dichlorobenzene (ODCB) was used as the processing solvent. Three series of devices were made by changing the weight ratio PCBMX/MDMOPPV (around 1:4) in such a way that molar ratio Fullerene/monomer MDMOPPV was kept constant at 1.1 (1) and 1.28 (2) and varied over a range (1.12-1.34). This resulted in some cases to large changes in the I-V characteristics of which the optimal results are presented.

Electrical device characterization was performed under a N_2 atmosphere. Current density-voltage (JV) were carried out using a home-built setup with a tungsten/halogen lamp (12V/50W) and a Keithley SMU 2400. For spectral response measurements the same setup was used in combination with a set of 22 interference filters, without bias light. The response of the samples was calculated relative to the response of a calibrated Si-diode. From the overlap of the spectral response of the sample with the standard AM1.5 (1000 W/m^2) spectrum we calculated the short circuit current density under AM1.5 conditions ($J_{sc,SR}$) assuming a linear relation between the illumination intensity and the short circuit current density. The $J_{sc,SR}$ is in this way largely insensitive to aging of Tungsten/halogen lamp, (long term) intensity variations and spectral mismatch errors.

General: All reagents and solvents were used as received or purified using standard procedures. [60]-Fullerene (99.5 %) was purchased from MTR, Ltd (Cleveland, Ohio) and used without further purification. Flash chromatography was performed using silica gel (Kieselgel Merck Type 9385 (230-400 mesh)). Melting points were determined with a Mettler FP1 melting point apparatus equipped with a Mettler FP2 microscope. ^1H NMR and ^{13}C NMR were performed on a Varian Unity Plus (500 MHz),

on a Varian VXR-300 (300 MHz) or on a Varian VXR-200 (200 MHz) instrument as indicated, at 298 K using TMS as an internal standard. IR measurements were performed on a Nicolet Nexus FT-IR instrument. UV/VIS were performed on a Perkin-Elmer Instruments Lambda 900 spectrometer. High Resolution Mass Spectroscopy (HRMS) was performed on a JEOL JMS 600 spectrometer. HPLC analyses were performed on a Hewlett Packard HP LC-Chemstation 3D (HP 1100 Series) using an analytical Cosmosil Buckyprep[®] column (4.6 x 250 mm). Cyclic Voltammetry and Differential Pulse Voltammetry were performed using an Autolab PGStat 100. Elemental analysis was performed by the Microanalytical Department of this laboratory.

Experimental details regarding the precursors for the methanofullerenes:

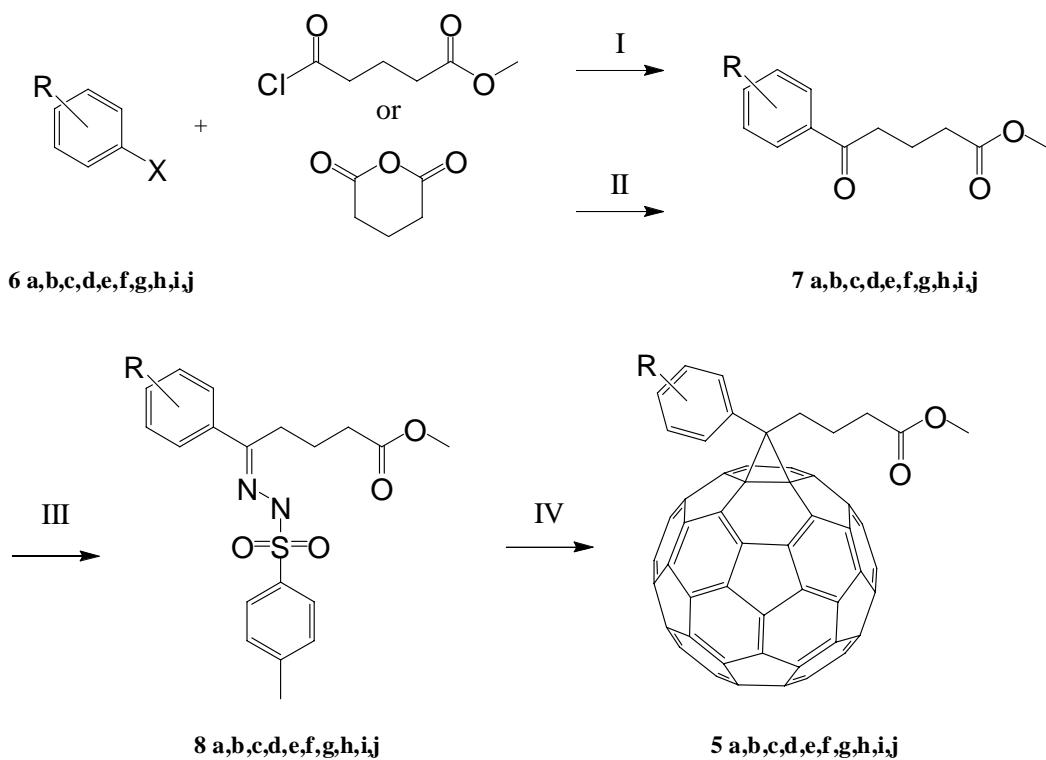


Figure 1: Synthetic route for the substituted-PCBM compounds

5-(4-Methoxy-phenyl)-5-oxo-pentanoic acid methyl ester (7a): A flame dried three-necked flask equipped with N₂ inlet and parafin bubbler was charged with AlCl₃ (15.32 g, 115 mmol, 2.3 eq.) and 1,1,2,2-tetrachloroethane (40 ml). The resulting suspension was cooled in ice and then anisole (8.11 g, 75 mmol, 1.5 eq.) was added. After stirring for a few minutes methyl 5-chloro-5-oxopentanoate (8.23 g, 50 mmol) was added in portions over 1 minute. A slow stream of N₂ was passed over the solution. The resulting orange-red solution was allowed to reach RT and was stirred overnight. The mixture was then poured onto crushed ice (500 g) and CH₂Cl₂ (150 ml) was added. The two-layer system was

separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 100 ml). The combined extracts were washed with dilute HCl (2N, 1 x 100 ml) and brine (1 x 100 ml) and then dried over Na_2SO_4 .

Evaporation of the solvents in vacuo yielded a pale yellow oil which crystallized upon standing. The solid was suspended in cold pentane (100 ml) and filtered through a glass funnel. The obtained solid was washed with cold pentane and dried in air. ^1H NMR (CDCl_3 , 300 MHz): δ (ppm): 7.94 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 9.0 Hz, 2H), 3.86 (s, 3H), 3.68 (s, 3H), 2.99 (t, J = 6.0 Hz, 2H), 2.43 (t, J = 6.0 Hz, 2H), 2.06 (m, 2H).

5-(3,4-Dimethoxy-phenyl)-5-oxo-pentanoic acid methyl ester (7b): Glutaric anhydride (5.0 g, 43.8 mmol) was dissolved in veratrole (100 ml, 785 mmol). The remaining solution was cooled in an ice-bath. While stirred, AlCl_3 (13.0 g, 97.5 mmol) was added at once resulting in a dark purple mixture. The mixture was stirred at 0 °C for 1h and thereafter at RT overnight. The mixture was poured onto concentrated HCl/ice. The remaining orange mixture was extracted with ether (2 x 150 ml) and dichloromethane (1 x 150 ml). The orange organic layers were combined and extracted with Na_2CO_3 (3 x 100 ml). The combined basic aqueous extracts were combined and acidified with cold concentrated HCl. The crude acid precipitates as a sticky white solid and was isolated by extraction with dichloromethane (2 x 150 ml). The organic layers were dried over Na_2SO_4 and concentrated in vacuo yielding a yellow sticky solid. This crude acid was dissolved in methanol (100 ml) and dry HCl was bubbled through the solution for ~ 15 min. The resulting clear solution was stirred overnight at RT. The mixture was evaporated to dryness and the resulting oil was redissolved in ether (150 ml). The resulting solution was washed with NaHCO_3 (10% solution, 150 ml), dried over Na_2SO_4 and concentrated in vacuo, yielding a yellow oil. The crude ester was purified by kugelrohr distillation (180–185 °C, 0.04 mm Hg) yielding a colorless oil which crystallizes (3.0 g, 11.3 mmol, 26%). ^1H NMR (CDCl_3 , 200 MHz): δ (ppm): 7.59 (dd, J = 8.5 Hz, J = 1.7 Hz, 1H), 7.53 (d, J = 1.7 Hz, 1H), 6.88 (d, J = 8.5 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 3.68 (s, 3H), 3.02 (t, J = 7.9 Hz, 2H), 2.42 (t, J = 7.9 Hz, 2H), 2.05 (m, 2H).

5-(2,3,4-Trimethoxy-phenyl)-5-oxo-pentanoic acid methyl ester (7c): To a stirred solution of AlCl_3 (20.0 g, 150 mmol) in nitrobenzene (80 ml) were added trimethyl pyragallol trimethyl ester (8.0 g, 47.6 mmol) and glutaric anhydride (8.0 g, 70.2 mmol). An exothermic reaction occurred with a color change from yellow to dark brown. The mixture was stirred for 48 h. at RT. The solidified mixture was poured onto concentrated HCl/ice. A pink-purple mixture is obtained which contains a lot of precipitated material. This solid is filtered through a glass funnel, dissolved in ether and extracted with aqueous Na_2CO_3 . Acidification with concentrated HCl yielded a light brown precipitate which was filtered and dried at 50 °C in vacuo. The original filtrate was also extracted with ether (2 x 100 ml). The combined extracts were then extracted with aqueous Na_2CO_3 . Acidification yielded a second batch of crude acid as a reddish powder after drying at 50 °C in vacuo. The crude acid was suspended in methanol (100 ml) and dry HCl gas was bubbled through the solution for ~ 15 min. After stirring the solution at RT overnight the methanol was removed and the residual oil was dissolved in ether (150 ml). The organic solution was washed with water (1 x 50 ml), dried over Na_2SO_4 and concentrated in vacuo. The obtained oil contained partly deprotected phenol(s). Therefore the oil was dissolved in dry acetone (100 ml). K_2CO_3 (40 mmol) and MeI (40 mmol) were added and the mixture was refluxed overnight. After

cooling to RT the mixture was filtered through Celite. The filtrate was evaporated to dryness. A SiO_2 column (5 x 10 cm) was prepared. Elution was started with a $\text{CHCl}_3/\text{Et}_2\text{O}$ (19/1) mixture. The product fractions were evaporated to dryness yielding a yellow oil (2.6 g, 8.8 mmol, 18%). ^1H NMR (CDCl_3 , 200 MHz): δ (ppm): 7.48 (d, J = 9.3 Hz, 1H), 6.70 (d, J = 9.3 Hz, 1H), 3.94 (s, 3H), 3.89 (s, 3H), 3.85 (s, 3H), 3.66 (s, 3H), 3.09 (t, J = 6.4 Hz, 2H), 2.41 (t, J = 6.4 Hz, 2H), 2.01 (m, 2H).

4-(2-methoxy-benzoyl)-butyric acid methyl ester (7d): A solution of o-bromoanisole (4.5 g, 24.06 mmol) in dry THF (100 ml) was placed under nitrogen. Under stirring, a solution of BuLi (15 ml, 1.6 N in hexane, 24 mmol) was added dropwise while the mixture was kept at -78 $^{\circ}\text{C}$. The resulting homogeneous solution was allowed to warm up to -55 $^{\circ}\text{C}$ in 30 min. Copper(I)iodide (2.38g, 12.49 mmol) was then added at once, resulting in a creamy brown solution. The mixture was allowed to warm up to -30 $^{\circ}\text{C}$ in 20 min. The obtained dark brown slurry was stirred for another 30 min, after which methyl 5-chloro-5-oxopentanoate (1.66 g, 10.09 mmol) was added, resulting in a green mixture. The mixture was allowed to warm up to 0 $^{\circ}\text{C}$ in 1 h. Dry MeOH (4 ml) was added, resulting in some precipitation. Aqueous NH_4Cl (50 ml) was added to the mixture. The mixture was then filtered through celite. The filtrate separated in a blue and a green layer, which were separated. The aqueous (blue) layer was extracted with ether (3x 50 ml). The combined organic extracts were washed with water (1x 100 ml) dried over Na_2SO_4 and concentrated in vacuo yielding a greenish liquid. To further purify the obtained product a SiO_2 column (7x 3 cm) was prepared. Mixture was brought on in toluene and worked in with toluene and 9:1 toluene:ether. Fractions containing product were concentrated in vacuo, yielding a yellow oil (1.92 g, 8.14 mmol, 80.6%). IR (neat) = ν (cm^{-1}): 2950 (m), 1737 (s), 1674 (m), 1597 (m), 1485 (m), 1437 (m), 1286 (m), 1246 (s), 1023 (m), 758 (m). ^1H NMR (CDCl_3 , 300 MHz): δ (ppm): 7.68 (dd, J = 7.7 Hz, J = 1.8 Hz, 1H), 7.46 (m, 1H), 6.93–7.04 (m, 2H), 3.90 (s, 3H), 3.67 (s, 3H), 3.04 (t, J = 7.3 Hz, 2H), 2.41 (t, J = 7.3 Hz, 2H), 2.08–2.01 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ (ppm): 201.7, 173.8, 158.4, 133.3, 130.1, 128.2, 120.5, 111.4, 97.9, 55.4, 51.4, 42.6, 33.3, 19.5. HRMS: Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_4$: 236.1047. Found: 236.1048.

5-(2,5-dimethoxyphenyl)-5-oxo-pentanoic acid methyl ester (7e) : Aluminum trichloride (9.04 g, 67.8 mmol) was suspended in dichloroethane (50 ml), placed under nitrogen and cooled to 0 $^{\circ}\text{C}$ while stirred. To the suspension p-dimethoxybenzene (6.29 g, 45.5 mmol) was added at once. Subsequently, methyl 5-chloro-5-oxopentanoate (5.05 g, 30.7 mmol) was added dropwise. The resulting mixture turned from green to brown and HCl gas formation was observed. The solution was allowed to warm up to RT and stirred for 20 h. The reaction mixture was poured out on ice (100 g). To the obtained yellow mixture 50 ml of dichloromethane was added and the mixture was stirred until all the ice had molten. The obtained mixture was then separated. The aqueous layer was extracted with dichloromethane (3x 50 ml). The organic layers were combined, washed with water (1x 75 ml) and brine (2x 75 ml) and dried over Na_2SO_4 . Evaporation of the solvents afforded a yellow oil. The oil was redissolved in ether (200 ml) and washed with a NaOH solution (0.5 M, 4x 50 ml). The ethereal layer was then washed with water (1x 100 ml) and dried over Na_2SO_4 . Concentration in vacuo afforded a light yellow liquid. The product was distilled using a kugelrohr apparatus (60 $^{\circ}\text{C}$, 0.5 mTorr). The obtained residue was a somewhat yellow oil that crystallized upon standing. The residue was suspended in n-pentane and sonicated. The suspension was filtered by suction yielding (3) as a white

powder (5.72 g, 21.5 mmol, 70%). IR (KBr) = ν (cm⁻¹): 2999 (m), 2951 (s), 2836 (s), 1737 (s), 1673 (s), 1609 (w), 1582 (w), 1495 (s), 1412 (m), 1279 (m), 1223 (m), 1048 (m), 1021 (m), 814 (m), 728 (m). ¹H NMR (CDCl₃, 300 MHz): δ (ppm): 7.24 (d, *J* = 3.3 Hz, 1H), 7.01 (dd, *J* = 9.2 Hz, *J* = 3.3 Hz, 1H), 6.89 (d, *J* = 9.2 Hz, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 3.66 (s, 3H), 3.04 (t, *J* = 7.0 Hz, 2H), 2.40 (t, *J* = 7.3 Hz, 2H), 2.01 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz): δ (ppm): 201.2, 177.4, 173.7, 153.3, 152.9, 128.2, 119.8, 113.7, 112.9, 55.9, 55.7, 51.4, 42.6, 33.2, 19.4. HRMS: Calcd for C₁₄H₁₈O₅: 266.1154. Found: 266.1161. Melting point: 50.0 – 50.5 (°C)

5-(2,4,6-trimethoxyphenyl)-5-oxo-pentanoic acid methyl ester (7f): A dried 250 ml flask was charged with AlCl₃ (9.2 g, 69 mmol) under N₂. Dichloroethane (50 ml) was added and the suspension was cooled on ice while stirred. 1,3,5-Trimethoxybenzene (7.57 g, 45 mmol) was added at once resulting in a homogeneous solution. After stirring for a few minutes methyl 5-chloro-5-oxopentanoate (4.94 g, 30 mmol) was added at once. The solution quickly turned dark brown. The cooling bath was removed and the mixture was stirred at RT for ~22 h. The reaction mixture was poured onto crushed ice and dichloromethane (50 ml) was added. The resulting mixture was separated. The aqueous layer was extracted with dichloromethane (3 x 50 ml). The combined organic layers were washed with H₂O (1 x 75 ml) and brine (2 x 75 ml), dried over Na₂SO₄ and concentrated in vacuo obtaining a purple oil. An SiO₂ column (5 x 11 cm) was prepared. Mixture was dissolved in toluene (50 ml) and brought on. Elution was started with toluene removing side products. Product was eluted with toluene:ether (9:1). Evaporation yielded a yellow viscous oil (7.58 g, 25.6 mmol, 85 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm): 6.08 (s, 2H), 3.71 (s, 3H), 3.66 (s, 6H), 3.57 (s, 3H), 2.69 (t, *J* = 6.7 Hz, 2H), 2.35 (t, *J* = 6.7 Hz, 2H), 1.98 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz): δ (ppm): 202.6, 173.7, 162.1, 161.3, 157.9, 113.2, 92.7, 90.4, 55.6, 55.2, 55.1, 51.3, 43.6, 33.0, 19.1.

5-(3,4-(methylenedioxy)phenyl)-5-oxo-pentanoic acid methyl ester (7g): A flame-dried three-necked flask, equipped with thermometer and stirr bar, was placed under a nitrogen atmosphere and charged with 1,2-(methylenedioxy)benzene (10 g, 81.88 mmol, 1.2 eq.) and methyl 5-chloro-5-oxopentanoate (1.2 g, 7.32 mmol). To this mixture was added 1,2-dichloroethane (40 ml). At 0 °C Sn(IV)Cl₄ (21 ml) was dropped to the solution. The mixture turned dark green and was stirred for 15 h, resulting in the formation of a deep purple suspension from which a deep purple solid had formed. The mixture was poured out on ice (100 g), the solid was transferred onto the ice using chloroform (50 ml). After all the ice had molten a green suspension was obtained. The aqueous layer was then extracted with chloroform (3 x 100 ml). The organic layers were collected and washed subsequently with NaHCO₃ (1 x 100 ml) and H₂O (1 x 100 ml), dried over Na₂SO₄ and concentrated in vacuo yielding a black oil. A SiO₂ column (2 x 20 cm) was prepared. The mixture was entered with a toluene : ether (1:1) mixture and eluted with a toluene : ether (1:1) mixture. An orange oil was obtained which solidified upon standing. ¹H NMR and ¹³C NMR showed the product to be a mixture of product and starting material (2:1). The mixture was not further purified but used in the next reaction step.

methyl 5-[2-(methylthio)phenyl]-5-oxopentanoate (7h):

magnesium turnings (6.11 g, 251 mmol) were mixed with some glasspearls and stirred under nitrogen atmosphere for 24 hours at room temperature THF (40 ml.) and an iodine crystal were added which resulted in a brown and then green/grey solution. A mixture of 2-bromo-thioanisole (10.00 g,

49.2mmol) in THF (40 ml.) was added over 70 minutes. The solution became grey/black and a temperature rise to 40°C was observed. The solution was stirred for 2,5 hours and then added by Canula-manner to a solution of glutaric anhydride (10.98 g, 96.2 mmol) in THF (50 ml.) at -40 °C. After 2 hours the mixture was allowed to warm up slowly to room temperature and was stirred overnight. The resulting mixture was poured onto a saturated solution of ammonium chloride (300 ml.). The aqueous layer was extracted with ether (3 x 100ml.) The combined colorless organic layers were washed with brine (2 x 200ml.), dried over sodium sulfate and concentrated in vacuo yielding a yellow/brownish powder. The powder was suspended in ether, filtered and dried in vacuo yielding a white powder. Yield: 6.95g (29.1 mmol, 60%). MP = 118 °C; IR (KBr); ν (cm⁻¹): 2933 (m), 1698 (s), 1669 (s), 1587 (m), 1556 (m), 1467 (m), 1430 (s), 1332 (m), 1275(m), 1219(m), 1147(m) 961 (s), 746 (s); ¹H-NMR (CDCl₃, 300 MHz): δ (ppm): 7.80 (d, J = 7.69 Hz, 1H), 7.45 (t, J = 7.69 Hz, 1H), 7.29 (d, J = 8.06 Hz, 1H), 7.16 (t, J = 7.69 Hz, 1H), 3.04 (t, J = 6.95 Hz, 2H), 2.48 (t, J = 7.33 Hz, 2H), 2.41 (s, 3H), 2.06 (m, 2H); ¹³C-NMR: (CDCl₃, 50 MHz): δ (ppm): 200.4, 179.0, 142.3, 134.4, 132.2, 130.0, 125.2, 123.5, 38.7, 33.0, 19.1, 16.0. HRMS: Calcd for C₁₂H₁₄O₃S: 238.0664. Found: 238.0677. The acid (6.37 g, 26.7mmol) was dissolved in of methanol (270 ml.). Some drops of concentrated hydrochloric acid were added. The resulting clear colorless mixture was stirred for 22 hours at room temperature. Subsequently the methanol was evaporated and the resulting brownish liquid was dissolved in ether (80 ml.), dried over sodium sulfate and concentrated in vacuo yielding a slightly yellow/golden solid. Yield: 5.56g (22.0 mmol, 82.4 %). MP = 28 °C; IR: (KBr); ν (cm⁻¹): 2950 (m), 1735 (s), 1671 (s), 1587 (m), 1558 (m), 1434 (s), 1370 (m), 1212 (s), 1048 (m), 982 (m), 884 (w), 749 (s); ¹H-NMR: (CDCl₃, 300 MHz): δ (ppm): 7.80 (d, J = 8.05 Hz, 1H), 7.44 (t, J = 8.05 Hz, 1H), 7.26 (d, J = 8.06 Hz, 1H), 7.15 (t, J = 7.69 Hz, 1H), 3.65 (s, 3H), 3.01 (t, J = 6.96 Hz, 2H), 2.43 (t, J = 7.32 Hz, 2H), 2.41 (s, 3H), 2.05 (q, J = 7.35 Hz, 2H); ¹³C-NMR. (CDCl₃, 50 MHz): δ (ppm): 200.7, 174.0, 142.6, 134.4, 132.4, 130.4, 125.3, 123.7, 51.8, 39.0, 33.3, 19.7, 16.2. HRMS: Calcd for C₁₃H₁₆O₃S: 252.0820. Found: 252.0834.

methyl 5-[4-(methylthio)phenyl]-5-oxopentanoate (7i):

A dry 3-neckled flask was charged with AlCl₃ (15.3 g, 115.0 mmol) and some glasspearls and was stirred for 2 hours. Subsequently, 1,1,2,2-tetrachloroethane (40 ml.) vwas added. The resulting suspension was cooled with ice and thioanisole (9.32 g, 75.0 mmol) was added. After stirring for a few minutes, methyl 4-(chloroformyl)butyrate (8.23 g, 50.0 mmol) was added slowly by using a dropping funnel. A small flow of nitrogen was left over the solution to get rid of hydrochloric acid. The resulting green solution was allowed to reach room temperature and was stirred overnight. After 19 hours, the mixture was poured onto crushed ice and 1,1,2,2-tetrachloroethane (150 ml.) was added. The two layer mixture was separated and the aqueous phase was extracted with 1,1,2,2-tetrachloroethane (2 x 100 ml.). The combined organic layers were washed with 2M hydrochloric acid (100 ml.) and brine (100 ml.), dried over sodium sulfate and evaporated in vacuo yielding 20.0g of a purple/orange bilayer liquid which crystallize after upon standing. Subsequently, pentane (100 ml.) was added and the mixture was kept in ultrasonic bath for 45 minutes. The mixture was filtered and washed with cold pentane yielding a white powder. Yield: 11.8g (46.7mmol), 93.3%; MP = 55°C; IR (KBr); ν (cm⁻¹): 2962 (s), 1738 (s), 1670 (s), 1588 (m), 1383 (m), 1275 (m), 1168 (m), 753 (w); ¹H-NMR (CDCl₃, 300 MHz): δ (ppm):

7.85 (d, $J = 8.79$ Hz, 2H), 7.24 (d, $J = 8.79$ Hz, 2H), 3.66 (s, 3H), 2.98 (t, $J = 7.33$ Hz, 2H), 2.49 (s, 3H), 2.41 (t, $J = 7.33$ Hz, 2H), 2.06 (m, 2H); ^{13}C -NMR (CDCl₃, 50 MHz): δ (ppm): 196.9, 172.2, 144.3, 131.6, 126.9, 123.5, 50.1, 35.7, 31.6, 17.9, 13.3. HRMS: Calcd for C₁₃H₁₆O₃S: 252.0820. Found: 252.0835.

5-oxo-5-pentafluorophenyl-pentanoic acid methyl ester (7j): A flame dried 3-necked flask equipped with: stirring egg, condensor, N₂-inlet, thermometer and dropping funnel, was charged with glutaric anhydride (5.63 g, 49.3 mmol, 2 eq.). The glutaric anhydride was dissolved in dry THF and brought to -35 °C with a cryostat apparatus, and ethanol as the cooling liquid. Then pentafluorobenzene magnesium bromide (50 ml, 0.5M in ether, 25 mmol) was dropped to the solution resulting in a brown reaction mixture which was allowed to warm up to RT and was stirred overnight. The reaction mixture was poured onto saturated aqueous NH₄Cl (40 ml). The layers were separated and the aqueous layer was extracted with Et₂O (1 x 150 ml). A thick gel formed and no separation was obtained (maybe NH₄Cl wasn't acidic enough?). The organic layer was dried over Na₂SO₄ and concentrated in vacuo yielding a brown oil. The thus obtained crude acid was esterified without further purification. The crude acid was dissolved in MeOH (200 ml) and a drop of fuming hydrochloric acid (37%) was added. This mixture was stirred at RT for 4 days. The resulting mixture was concentrated in vacuo and the obtained brown oil was redissolved in Et₂O (100 ml). The ethereal solution was washed with 1 M NaOH (3 x 50 ml), dried over Na₂SO₄ and concentrated in vacuo yielding a brown oil. Purification by Kugelrohr destillation (140 – 190 °C, 15 mTorr) yielded a colorless oil (1.29 g, 4.35 mmol, 17.4 %). IR (neat) = ν (cm⁻¹): 2956 (w), 1740 (s), 1650 (m), 1522 (m), 1497 (s), 1439 (w), 1404 (w), 1382 (w), 1314 (m), 1201 (w), 1140 (m), 983 (m), 860 (w). ^1H -NMR (CDCl₃, 300 MHz); δ (ppm): 3.67 (s, 3H), 2.96 (t, $J = 6.7$ Hz, 2H), 2.42 (t, $J = 7.3$ Hz, 2H), 2.05 (q, $J = 7.3$ Hz, 2H). ^{13}C -NMR (CDCl₃, 50 MHz); δ (ppm): 173.2, 51.7, 43.9, 32.6, 18.6. ^{19}F -NMR (CDCl₃, 200 MHz); δ (ppm): -142.18 (dd, $J = 6.9$ Hz, $J = 18.0$ Hz, 2F), -150.31 – -150.53 (m, 1H), -160.75 – -161.05 (m, 2H).

4-(methoxy-benzoyl)-methylbutyrate-p-tosylhydrazone (8a): 5-(4-Methoxy-phenyl)-5-oxo-pentanoic acid methyl ester (5.9 g, 25 mmol) and p-tosylhydrazide (5.6 g, 30 mmol) were solved in methanol (50 ml). The mixture was refluxed for 4 h. A yellow powder crystallized. This powder was then recrystallized from methanol obtaining pale-yellow crystals (7.8 g, 19.3 mmol, 77%) which were dried at 50 °C in vacuo. ^1H NMR (CDCl₃, 300 MHz): δ (ppm): 9.07 (s, 1H), 7.91 (d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 8.8$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 2.61 (t, $J = 8.1$ Hz, 2H), 2.40 (s, 3H), 2.32 (t, $J = 6.6$ Hz, 2H), 1.67 (m, 2H). ^{13}C NMR (CDCl₃, 75 MHz): δ (ppm): 174.6, 160.6, 153.6, 143.6, 135.8, 129.3, 128.6, 127.8, 127.5, 113.6, 55.2, 52.2, 32.0, 25.6, 21.4, 20.9.

3,4-(Dimethoxy-benzoyl)-methylbutyrate-p-tosylhydrazone (8b): 5-(3,4-Dimethoxy-phenyl)-5-oxo-pentanoic acid methyl ester (1.6 g, 6.0 mmol) and p-tosylhydrazide (7.2 mmol) were dissolved in methanol (5 m). The mixture was refluxed for 5 h. After slightly cooling a white precipitate formed. Mixture was left at RT overnight. The precipitated material was filtered through a glass filter and washed with cold methanol (2 x 2 ml). The resulting white solid was dried at 40 °C in vacuo. A two component mixture was obtained. The solid material was therefore recrystallized from boiling ethanol

(200 ml). A precipitate was formed. The mixture was cooled to RT and then put in fridge at -18°C overnight. A white solid was collected which was dried at 40°C in *vacuo*. The obtained solid was recrystallized from methanol (40 ml) obtaining a white solid which was dried at 40°C in *vacuo* (1.6 g, 3.68 mmol, 61 %). ^1H NMR (CDCl_3 , 300 MHz): δ (ppm): 9.02 (s, 1H), 7.91 (d, $J = 8.5$ Hz, 2H) 7.30 (m, 3H), 7.09 (dd, $J = 8.4$ Hz, $J = 2.2$ Hz, 1H), 6.79 (d, $J = 8.4$ Hz), 3.90 (s, 3H), 3.88 (s, 3H), 3.80 (s, 3H), 2.60 (t, $J = 7.7$ Hz, 2H), 2.40 (s, 3H), 2.33 (t, $J = 6.2$ Hz, 2H), 1.67 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ (ppm): 174.4, 153.7, 150.3, 148.7, 143.6, 135.7, 129.3, 129.2, 128.8, 127.8, 119.1, 110.1, 108.7, 55.7, 55.5, 52.0, 32.0, 25.5, 21.4, 20.9. HRMS: calcd for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_6\text{S}$: 434.15112. Found: 434.15329.

2,3,4-(Trimethoxy-benzoyl)-methylbutyrate-p-tosylhydrazone (8c): 5-(2,3,4-Trimethoxy-phenyl)-5-oxo-pentanoic acid methyl ester (2.6 g, 8.78 mmol) and p-tosylhydrazide (1.9 g, 10.2 mmol) were dissolved in toluene (40 ml). The resulting mixture was refluxed using a Dean-Stark setup. The first 20 ml. of the liquid which distilled over was removed. After 4 h. the mixture was allowed to cool to RT and was evaporated to dryness. The slightly yellow solid material that was obtained was recrystallized from methanol with stirring. A fine white precipitate was obtained while the solution was stirred in an ice-bath for 1 h. The solid was collected by filtration through a glass filter. The obtained solid was washed with cold methanol and dried at 50°C in *vacuo*. From the mother liquor a second fraction was obtained after storing at -18°C . (combined yield: 2.91 g, 6.27 mmol, 71 %). ^1H NMR (CDCl_3 , 300 MHz): δ (ppm): 7.81 (d, $J = 8.1$ Hz, 2H), 7.6 (s, 1H), 7.31 (d, $J = 8.1$ Hz, 2H), 6.69 (d, $J = 8.4$ Hz, 1H), 6.61 (d, $J = 8.4$ Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.63 (s, 3H), 3.53 (s, 3H), 2.48 (t, $J = 7.3$ Hz, 2H), 2.42 (s, 3H), 2.19 (t, $J = 7.3$ Hz, 2H), 1.74 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ (ppm): 173.5, 155.0, 154.7, 149.8, 143.7, 142.3, 135.3, 129.3, 127.8, 122.3, 119.0, 108.2, 97.8, 61.2, 60.9, 56.0, 51.4, 37.0, 32.8, 21.5, 21.2. HRMS: calcd for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_7\text{S}$: 464.16168. Found: 464.16031.

2-methoxy-benzoyl-methylbutyrate-p-tosylhydrazone (8d): 4-(2-methoxy-benzoyl)-butyric acid methyl ester (1.61 g, 6.82 mmol) was dissolved in methanol (25 ml). TsNHNH_2 (1.52 g, 8.16 mmol) was added at once and the mixture was brought to reflux for 12 h. The mixture was put in freezer for 48 h and crystallization was observed. The crystals were filtered by suction and dried in air. White crystals remained (1.69 g, 4.2 mmol, 61.3%). The filtrate was put in the freezer. A second fraction was obtained (0.38 g, 0.9 mmol, 13.8%). Combined yield: 2.17 g, 5.12 mmol, 75.1%. IR (KBr) = ν (cm^{-1}): 3177 (s), 2948 (s), 2830 (m), 1723 (s), 1598 (m), 1493 (m), 1336 (m), 1026 (m), 758 (m), 593 (m), 555 (m). ^1H NMR (CDCl_3 , 300 MHz); δ (ppm): 7.80 (d, $J = 8.1$ Hz, 2H), 7.28–7.42 (m, 4H), 6.99 (t, $J = 8.1$ Hz, 1H), 6.92 (d, $J = 8.8$ Hz, 2H), 3.62 (s, 6H), 2.49 (t, $J = 7.3$ Hz, 2H), 2.45 (s, 3H), 2.18 (t, $J = 7.3$ Hz, 2H), 1.73 (q, $J = 7.3$ Hz, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ (ppm): 117.4, 173.6, 155.0, 154.9, 143.7, 135.5, 131.2, 129.3, 128.0, 127.8, 121.5, 121.5, 111.4, 55.3, 51.3, 36.9, 32.7, 21.5, 20.9. HRMS: Calcd for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_5\text{S}$: 404.1406. Found: 404.1411. Melting point: $86.5 - 87.5^{\circ}\text{C}$. Elemental Analysis: Calcd for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_5\text{S}$: C: 59.39%, H: 5.98%, N: 6.93%, S: 7.93%. Found: C: 59.23%, H: 6.00%, N: 6.90%, S: 7.88%.

cis-2,5-(dimethoxy-benzoyl)-methylbutyrate-p-tosylhydrazone (8e): 5-(2,5-dimethoxy-phenyl)-5-oxo-pentanoic acid methyl ester (3.02 g, 11.35 mmol) was dissolved in methanol (25 ml). p-Tosylhydrazide (2.57 g, 13.8 mmol) was added at once. The remaining yellow solution was heated to

reflux for 12 h. The mixture was concentrated to ~10 ml and cooled to 0 °C resulting in crystallization. The obtained crystals were filtered by suction and a white powder remained (0.78 g, 1.73 mmol) with a cis:trans ratio of 1:13.5 (by ¹H NMR). The filtrate was left in the freezer overnight and filtered by suction. A white powder remained (2.76 g, 6.13 mmol) with a cis:trans ratio of 9.7:1. Combined yield 3.54 g (7.85 mmol), 69.2%. The cis product (2.76 g, 6.13 mmol) was recrystallized from a mixture of ethylether (50 ml) and t-butylmethyl-ether (3 ml). The obtained crystals were filtered by suction and dried in vacuo at 50 °C. White crystals were obtained (1.78 g, 3.95 mmol, 34.8%). IR (KBr) = ν (cm⁻¹): 3239 (s), 2973 (s), 2841 (m), 1728 (s), 1597 (w), 1501 (m), 1343 (m), 1172 (s), 1041 (s), 748 (m), 571 (m). ¹H NMR (CDCl₃, 300 MHz): δ (ppm): 7.82 (d, *J* = 8.4 Hz, 2H), 7.44 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.92 (dd, *J* = 9.2 Hz, *J* = 2.9 Hz, 1H), 6.85 (d, *J* = 9.2 Hz, 1H), 6.48 (d, *J* = 2.6 Hz, 1H), 3.75 (s, 3H), 3.64 (s, 3H), 3.58 (s, 3H), 2.49 (t, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 2.18 (t, *J* = 7.5 Hz, 2H), 1.73 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz): δ (ppm): 173.6, 154.6, 154.1, 148.9, 143.7, 135.5, 129.3, 127.8, 122.2, 115.9, 113.5, 112.7, 97.9, 55.8, 55.7, 51.4, 36.9, 32.7, 21.5, 21.0. HRMS: Calcd for C₂₂H₃₀N₂O₆S: 434.1511. Found: 434.1514. Melting point: 77.0 – 79.0 (°C). Element Analysis: Calcd for C₂₂H₃₀N₂O₆S: C: 58.65%, H: 6.71%, N: 6.22%, S: 7.12%. Found: C: 58.36%, H: 6.44%, N: 6.33%, S: 6.93%.

2,4,6-(Trimethoxy-benzoyl)-methylbutyrate-p-tosylhydrazone (8f): 5-(2,4,6-trimethoxyphenyl)-5-oxo-pentanoic acid methyl ester (4.45 g, 15 mmol) was dissolved in methanol (25 ml) and p-tosylhydrazide (3.36 g, 18 mmol, 1.2 eq.) was added at once. The resulting mixture was refluxed for 12 h. After cooling to RT no crystallization took place. Mixture was concentrated in vacuo. During concentration crystallization started. Mixture was left in the fridge (4 °C) overnight. The obtained crystals were filtered off yielding a white microcrystalline powder which was washed with cold methanol (2 x 2 ml). The obtained powder was dried in air. A second batch was obtained from the motherliquor. Combined yield: 5.81 g (12.5 mmol, 83 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm): 7.80 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.26 (s, 1H), 6.08 (s, 2H), 3.80 (s, 3H), 3.62 (s, 3H), 3.56 (s, 6H), 2.42 (m, 5H), 2.12 (t, *J* = 7.2 Hz, 2H), 1.66 (m, 2H).

3,4-(methylenedioxy)benzoyl-methylbutyrate-p-tosylhydrazone (8g): A 25 ml round bottom flask was placed under nitrogen and charged with crude 5-(3,4-(methylenedioxy)phenyl)-5-oxo-pentanoic acid methyl ester (0.52 g, 2.08 mmol), p-tosylhydrazide (0.465 g, 2.49 mmol, 1.2 eq.) and methanol (6 ml). The resulting yellow mixture was brought to reflux and allowed to react for 4 h. The reaction mixture was then cooled to RT and an off-white solid crystallized. The crystals were filtered off by suction. ¹H NMR analysis showed that this product was 1,2-(methylenedioxy)benzene. The filtrate was put in the freezer overnight and more crystallization was observed. White crystals were obtained. Yield: 130 mg (0.31 mmol, 15%). ¹H NMR (CDCl₃, 200 MHz): δ (ppm): 9.08 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.24 (m, 3H), 7.08 (dd, *J* = 8.3 Hz, 1.9 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 5.98 (s, 2H), 3.80 (s, 3H), 2.58 (m, 2H), 2.41 (s, 3H), 2.33 (m, 2H), 1.63 (m, 2H). ¹³C NMR (DMSO-d6, 75MHz); δ (ppm): 173.1, 154.8, 148.4, 147.6, 143.4, 136.2, 130.5, 129.6, 127.5, 120.7, 108.0, 105.8, 101.4, 51.4, 32.7, 25.9, 21.2, 21.1.

2-(methylthio)-benzoyl-methylbutyrate-p-tosylhydrazone (8h):

Compound 7h (2.50 g, 9.91 mmol) and toluene-4-sulfonohydrazide (2.32 g, 12.4 mmol) were dissolved in dry methanol (30 ml.) brought to reflux and stirred overnight. The reaction was followed by TLC using chloroform as the eluens. Subsequently, the mixture was cooled down slowly and placed in the refrigerator over the weekend resulting in crystallization. A white powder was obtained which was washed with cold methanol and dried in vacuo at 50 °C. Yield: 2.73 g (6.49 mmol, 65.5 %); MP = 85 °C; IR: (KBr): ν (cm⁻¹): 3257 (s), 3065 (m), 2983 (m), 2934 (m), 2891 (m), 1735 (s), 1595 (m), 1433 (m), 1378 (m), 1333 (m), 1164 (s), 1074 (w), 997 (w), 752 (m); ¹H-NMR: (CDCl₃, 200 MHz): δ (ppm): 9.05 (s, 1H), 7.85 (d, *J* = 8.05 Hz, 2H), 7.52 (d, *J* = 8.42 Hz, 2H), 7.24 (d, *J* = 8.06 Hz, 2H), 7.13 (d, *J* = 8.42 Hz, 2H), 3.74 (s, 3H), 2.54 (t, *J* = 7.68 Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 2.67 (t, *J* = 6.23 Hz, 2H), 1.61 (m, 2H); ¹³C-NMR: (CDCl₃, 50 MHz): δ (ppm): 173.7, 155.8, 143.9, 135.8, 135.4, 131.8, 130.3, 129.3, 128.1, 127.3, 126.2, 125.9, 51.4, 36.5, 33.1, 21.6, 20.8, 15.3. HRMS: Calcd for C₂₀H₂₄O₄S₂N₂: 420.1177. Found: 420.1198.

4-(methylthio)-benzoyl-methylbutyrate-p-tosylhydrazone (8i):

4.00 g. (15.9 mmol) of 7i, toluene-4-sulfonohydrazide (3.74 g, 20.0 mmol) and dry methanol (30 ml.) were mixed and refluxed for 4 hours. Subsequently, the mixture was cooled down and placed in the refrigerator over the weekend resulting in white crystals. The powder was washed with cold methanol and dried in vacuo at 50 °C. Yield: 5.50 g (13.1 mmol) 82.3%. MP = 135 °C; IR (KBr): ν (cm⁻¹): 3234 (s), 2947 (m), 1738 (s), 1595 (m), 1480 (m), 1390 (m), 1168 (s), 1060 (m), 815 (m); ¹H-NMR: (CDCl₃, 300 MHz): δ (ppm): 9.05 (s, 1H), 7.85 (d, *J* = 8.05 Hz, 2H), 7.52 (d, *J* = 8.42 Hz, 2H), 7.24 (d, *J* = 8.06 Hz, 2H), 7.13 (d, *J* = 8.42 Hz, 2H), 3.74 (s, 3H), 2.54 (t, *J* = 7.68 Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 2.67 (t, *J* = 6.23 Hz, 2H), 1.61 (m, 2H); ¹³C-NMR: (CDCl₃, 50 MHz): δ (ppm): 174.7, 153.1, 143.7, 140.6, 136.0, 132.7, 129.4, 127.9, 126.5, 125.8, 52.4, 32.0, 25.6, 21.6, 20.9, 15.3. HRMS: Calcd for C₂₀H₂₄O₄S₂N₂: 420.1177. Found: 420.1195.

Pentafluorobenzoyl-methylbutyrate-p-tosylhydrazone (8j): A 25 ml roundflask, equiped with stirring egg, condensor and N₂-inlet was charged with pentafluorophenyl-5-oxo-pentanoic acid methyl ester (1.0 g, 3.38 mmol), p-tosylhydrazide (755 mg, 4.05 mmol, 1.2 eq.) and methanol (15 ml). The resulting mixture was refluxed for 17 h. Then cooled to RT, no crystals were observed and the mixture was put in the fridge. After no crystallization was observed the mixture was concentrated to 1/4 volume and crystallization commenced after 3 h in the fridge. Two fractions of white crystals were obtained. Total yield: 680 mg (1.46 mmol, 43.3 %). IR (KBr) = ν (cm⁻¹): 3077 (s), 1700 (s), 1655 (m), 1596 (m), 1500 (s), 1351 (s), 1288 (m), 1253 (m), 1171 (s), 1084 (s), 984 (s), 926 (m), 881 (m), 848 (m), 817 (m), 668 (m), 549 (s). ¹H-NMR (CDCl₃, 200 MHz): δ (ppm): 9.83 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 3.79 (s, 3H), 2.51 (t, *J* = 7.3 Hz, 2H), 2.47 (s, 3H), 2.26 (t, *J* = 6.4 Hz, 2H), 1.66 (m, 2H). ¹³C-NMR (CDCl₃, 50 MHz): δ (ppm): 173.4, 142.6, 134.2, 128.0, 126.3, 51.1, 30.1, 28.1, 20.1, 18.1. ¹⁹F-NMR (CDCl₃, 200 MHz): δ (ppm): -142.43 (dd, *J* = 6.7 Hz, *J* = 16.0 Hz, 2H), -153.81 (t, *J* = 21.4 Hz, 1F), -162.32 (dt, *J* = 6.7 Hz, *J* = 21.4 Hz, 2H). HRMS: Calcd. for C₁₉H₁₇O₄N₂SiF₅: 464.0828. Found: 464.0829.

General method for a diazomethane addition to C₆₀: A mixture of methoxy-substituted benzoyl-methylbutyrate-p-tosylhydrazone (449 mg, 1.11 mmol), sodium methoxide (60 mg, 1.07 mmol) and

dry pyridine (15 ml) was placed under nitrogen and stirred at RT for 30 min. To the mixture a solution of C₆₀ (735 mg, 1.02 mmol) in 1,2-dichlorobenzene (75 ml) was added. The mixture was deoxygenated using ultrasound and three vacuum/N₂ purge cycles. Irradiation was started using a 150 W Na-lamp, no cooling was applied. The mixture was stirred and allowed to reach thermal equilibrium (T~86 °C). The reaction was allowed to continue for 12 h during which the color turned from purple to brown. The obtained mixture was concentrated in vacuo to 25 ml. An SiO₂ column was prepared (2.5x 20 cm) with 1,2-dichlorobenzene. The mixture was admitted and eluted with 1,2-dichlorobenzene. The fraction containing mono-adduct was collected and concentrated in vacuo, redissolved in a minimal amount of 1,2-dichlorobenzene and transferred to a centrifugal tube (100 ml). The product was precipitated with MeOH, centrifuged and decanted. The remaining pellet was washed twice with methanol. The obtained pellet was dried under vacuo at 40 °C for 24 h.

4-methoxy-[6,6]-PCBM (5a): IR (KBr) = ν (cm⁻¹): 2946 (m), 2828 (m), 2323 (w), 1731 (s), 1610 (m), 1512 (s), 1456 (m), 1431 (s). 1302 (w), 1247 (s), 1174 (s), 1109 (m), 1032 (m), 832 (m), 744 (w), 525 (s), 428 (m). UV-vis (toluene); λ_{max} (nm): 330, 433, 498, 697. ¹H NMR (CS₂/D₂O, 500 MHz); δ (ppm): 7.89 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.02 (s, 3H), 3.75 (s, 3H), 2.99 (br.t, *J* = 8.1 Hz, 2H), 2.59 (t, *J* = 7.3 Hz, 2H), 2.27 (m, 2H). ¹³C NMR (CS₂/D₂O); δ (ppm): 171.2, 159.2, 148.5, 147.6, 145.6, 145.0, 145.0, 144.9, 144.6, 144.5, 144.3, 143.9, 143.6, 142.9, 142.9, 142.8, 142.8, 142.1, 142.0, 141.9, 140.8, 140.6, 137.9, 137.6, 132.9, 128.0, 113.8, 79.9, 54.8, 51.2, 50.9, 33.6, 33.5, 22.5. Elemental Analysis: Calcd for C₇₃H₁₆O₃: C: 92.78%, H: 1.71%. Found: C: 92.94%, H: 1.65%.

3,4-dimethoxy-[6,6]-PCBM (5b): IR (KBr) = ν (cm⁻¹): 2946 (s), 2832 (m), 2326 (w), 1737 (s), 1589 (m), 1516 (s), 1462 (s), 1430 (s), 1251 (s), 1187 (s), 1140 (s), 1028 (s), 853 (w), 742 (m), 526 (s). UV (cyclohexane); λ_{max} (nm): 215, 262, 333. VIS (toluene); λ_{max} (nm): 433, 493, 698. ¹H NMR (CS₂/D₂O, 500 MHz); δ (ppm): (dd, *J* = 8.2, 2.2 Hz, 1H), 7.43 (d, *J* = 2.2 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 4.02 (s, 6H), 3.75 (s, 3H), 3.00 (m, 2H), 2.60 (t, *J* = 2.60 Hz, 2H), 2.27 (m, 2H). ¹³C NMR (CS₂/D₂O, 125 MHz); δ (ppm): 171.3, 149.4, 149.2, 148.5, 147.6, 145.6, 145.0, 144.98, 144.95, 144.9, 144.8, 144.6, 144.4, 144.3, 143.9, 143.6, 142.9, 142.84, 142.82, 142.75, 142.74, 142.0, 141.94, 137.91, 137.7, 128.4, 125.0, 115.6, 111.3, 78.0, 55.8, 55.4, 53.6, 51.0, 33.7, 33.5, 22.7. Elemental Analysis: Calcd for C₇₄H₁₈O₄: C: 91.54%, H: 1.87%. Found: C: 91.35%, H: 1.93%.

2,3,4-trimethoxy-[6,6]-PCBM (5c): IR (KBr) = ν (cm⁻¹): 2939 (s), 1738 (s), 1599 (w), 1494 (m), 1463 (m), 1412 (m), 1303 (w), 1235 (w), 1103 (m), 1017 (m), 526 (s). VIS (toluene); λ_{max} (nm): 434, 497, 698. ¹H NMR (CDCl₃, 500 MHz); δ (ppm): 6.75 (d, *J* = 8.6 Hz), 4.31 (s, 3H), 4.07 (s, 3H), 4.02 (s, 3H), 3.75 (s, 3H), 3.03 (m, 1H), 2.89 (m, 1H), 2.58 (m, 2H), 2.20 (m, 2H). ¹³C NMR (CS₂/D₂O, 125 MHz); δ (ppm): 171.4, 154.2, 152.4, 149.5, 149.4, 148.1, 145.9, 145.8, 145.3, 145.0, 144.93, 144.89, 144.85, 144.62, 144.60, 144.54, 144.51, 144.4, 144.3, 144.2, 143.9, 143.7, 143.6, 143.5, 142.9, 142.84, 142.81, 142.76, 142.71, 142.1, 142.0, 140.9, 140.8, 140.7, 140.4, 138.0, 137.9, 137.7, 136.3, 128.1, 120.3, 105.5, 81.2, 78.1, 61.3, 60.1, 55.5, 50.9, 48.3, 33.6, 31.8, 22.8. Elemental Analysis: Calcd for C₇₅H₂₀O₅: C: 89.99%, H: 2.01%. Found: C: 89.93%, H: 2.14%.

2-methoxy-[6,6]-PCBM (5d): IR (KBr) = ν (cm⁻¹): 2945 (m), 2328 (w), 1739 (s), 1599 (w), 1492 (m), 1430 (s), 1246 (s), 1186 (m), 1159 (m), 1026 (m), 758 (m), 574 (w), 527 (s). UV-vis (chloroform); λ_{max} (nm): 260 (ϵ = 127410), 328 (ϵ = 38648), 432 (ϵ = 2626), 495 (ϵ = 1498), 697 (ϵ = 261). ¹H NMR

(CS₂/D₂O, 500 MHz); δ (ppm): 7.89 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.60 (dt, J = 8.2 Hz, J = 1.6 Hz, 1H), 7.25 (m, 2H), 4.19 (s, 3H), 3.76 (s, 3H), 3.06–2.97 (m, 2H), 2.61 (t, J = 7.6 Hz, 2H), 2.29–2.24 (m, 2H). ¹³C NMR (CS₂, 125 MHz): δ (ppm): 171.6, 158.1, 150.0, 149.4, 148.3, 148.1, 146.3, 146.2, 145.5, 145.3, 145.1, 144.9, 144.8, 144.7, 144.6, 144.5, 144.2, 144.0, 143.98, 143.94, 143.90, 143.8, 143.12, 143.06, 143.0, 142.42, 142.38, 142.31, 142.26, 142.21, 142.15, 141.2, 141.1, 141.0, 140.7, 138.3, 138.2, 138.0, 136.3, 134.3, 130.0, 124.0, 120.7, 111.7, 81.0, 78.1, 55.6, 51.1, 47.9, 33.9, 31.6, 30.4, 23.1. Melting Point: > 300 °C. Elemental Analysis: Calcd for C₇₃H₁₆O₃: C: 93.18%, H: 1.71%. Found: C: 92.78%, H: 1.63%.

2,5-dimethoxy-[6,6]-PCBM (5e): IR (KBr) = ν (cm⁻¹): 2945 (m), 2328 (w), 1737 (s), 1613 (w), 1498 (s), 1463 (m), 1427 (s), 1218 (s), 1186 (m), 1047 (m), 1025 (m), 808 (m), 735 (w), 573 (w), 526 (s). UV-vis (chloroform); λ_{max} (nm): 260 (ϵ = 132106), 328 (ϵ = 41385), 433 (ϵ = 2795), 495 (ϵ = 1611), 697 (ϵ = 262). ¹H NMR (CS₂/D₂O, 500 MHz): δ (ppm): 7.38 (br. s, 1H), 7.11 (d, J = 8.8 Hz, 1H), 7.04 (br. d, J = 8.1 Hz, 1H), 4.09 (s, 3H), 3.95 (s, 3H), 3.74 (s, 3H), 2.98 (m, 2H), 2.59 (t, J = 7.3 Hz, 2H), 2.25 (m, 2H). ¹³C-NMR (CS₂, 125 MHz): δ (ppm): 171.4, 152.8, 151.8, 149.8, 149.0, 148.0, 147.8, 146.1, 145.9, 145.2, 145.0, 144.90, 144.87, 144.8, 144.61, 144.55, 144.51, 144.45, 144.4, 144.3, 144.2, 144.0, 143.7, 143.6, 143.5, 142.9, 142.8, 142.8, 142.7, 142.11, 142.05, 142.0, 141.93, 141.86, 140.9, 140.8, 140.7, 140.4, 138.0, 137.9, 137.8, 136.0, 124.6, 120.6, 113.3, 112.0, 80.7, 77.8, 55.6, 55.1, 50.9, 47.7, 33.6, 31.3, 22.7. Melting Point: > 300 °C. Elemental Analysis: Calcd for C₇₄H₁₈O₄: C: 91.54%, H: 1.87%. Found: C: 90.84%, 1.80%.

2,4,6-trimethoxy-[6,6]-PCBM (5f): IR (KBr) = ν (cm⁻¹): 2928 (s), 2835 (m), 1729 (s), 1611 (s), 1588 (m), 1457 (s), 1429 (m), 1340 (m), 1276 (w), 1226 (s), 1207 (s), 1159 (s), 1128 (s), 1037 (m), 811 (m), 526 (s). UV-vis (toluene); λ_{max} (nm): 329, 435, 498, 701. ¹H NMR (CS₂/D₂O, 300 MHz); δ (ppm): 6.39 (s, 2H), 4.06 (s, 6H), 4.04 (s, 3H), 3.75 (s, 3H), 2.96 (t, J = 7.7 Hz, 2H), 2.63 (t, J = 7.3 Hz, 2H), 2.27 (m, 2H). ¹³C-NMR (CS₂, 75 MHz): δ (ppm): 170.0, 159.4, 157.4, 149.3, 146.4, 144.3, 142.82, 142.79, 142.7, 142.6, 142.50, 142.45, 142.3, 142.19, 142.16, 142.0, 141.6, 141.4, 140.64, 140.61, 140.51, 140.48, 140.3, 140.1, 139.8, 139.6, 138.6, 138.3, 135.9, 133.3, 102.9, 89.1, 77.0, 53.3, 52.6, 48.6, 40.3, 31.7, 29.3, 20.5. Elemental Analysis: Calcd for C₇₅H₂₀O₅: C: 89.99%, H: 2.01%. Found: C: 89.86%, H: 1.91%.

3,4-methylenedioxy-[6,6]-PCBM (5g): IR (KBr) = ν (cm⁻¹): 2942.60 (s), 2772.38 (w), 2328.35 (m), 1738.08 (s), 1607.12 (w), 1501.06 (s), 1487.00 (s), 1346.29 (w), 1240.51 (s), 1187.53 (s), 1039.54 (s), 938.07 (m), 812.02 (m), 742.35 (m), 585.83 (w), 526.25 (s), 441.97 (w). UV-vis (toluene); λ_{max} (nm): 330, 432, 496, 696. ¹H NMR (CS₂/D₂O, 300 MHz); δ (ppm): 7.45 – 7.41 (m, 2H), 7.02 (d, J = 7.7 Hz, 1H), 6.18 (s, 2H), 3.74 (s, 3H), 2.99 – 2.94 (m, 2H), 2.56 (t, J = 7.3 Hz, 2H), 2.29 – 2.24 (m, 2H). ¹³C NMR (CS₂, 75 MHz); δ (ppm): 170.9, 148.0, 147.1, 147.0, 145.3, 144.7, 144.6, 144.5, 144.31, 144.28, 144.0, 143.7, 143.3, 142.6, 142.50, 142.45, 141.7, 141.61, 141.59, 140.5, 140.3, 137.6, 137.3, 129.5, 125.4, 111.7, 107.8, 101.0, 79.4, 51.1, 50.6, 33.4, 33.2, 29.8, 22.2. Melting Point: > 300 °C. Elemental Analysis: Calcd for C₇₃H₁₄O₃: C: 91.82%, H: 1.48%. Found: C: 92.01%, H: 1.44%.

2-methyl-thioether-[6,6]-PCBM (5h):

IR: (KBr) = ν (cm⁻¹): 2943 (w), 2859 (w), 1733 (s), 1583 (w), 1464 (m), 1431 (m), 1360 (w), 1247 (w), 1187 (m), 1155 (m), 737 (m), 526 (s); UV-VIS (toluene); λ_{max} (nm): 331 (ϵ = 43793), 435 (ϵ = 3063),

493 ($\varepsilon = 1732$), 697 ($\varepsilon = 290$); $^1\text{H-NMR}$: (CDCl_3 , 300 MHz): δ (ppm): 7.97 (d, $J = 7.69$ Hz, H), 7.63 (d, $J = 6.96$ Hz, H), 7.46 (d, $J = 7.69$ Hz, H), 3.78 (s, 3H), 3.11 (m, 2H), 2.82 (s, 3H), 2.60 (t, $J = 7.33$ Hz, 2H), 2.22 (m, 2H); $^{13}\text{C-NMR}$: (CDCl_3 , 50 MHz): δ (ppm): 173.5, 150.2, 150.0, 148.7, 148.6, 147.2, 146.7, 146.0, 145.89, 145.85, 145.82, 145.78, 145.6, 145.4, 145.3, 145.23, 145.20, 144.88, 144.87, 144.7, 144.6, 144.5, 144.4, 143.8, 143.8, 143.7, 143.7, 143.6, 143.0, 142.9, 142.8, 141.9, 141.7, 141.5, 141.3, 141.1, 139.2, 138.80, 138.76, 136.75, 135.0, 125.0, 111.0, 81.9, 78.4, 52.1, 51.4, 34.6, 30.8, 24.0, 16.7. Melting Point: > 295 °C. Elemental Analysis: Calcd for $\text{C}_{73}\text{H}_{16}\text{O}_2\text{S}$: C: 91.6 %, H: 1.69%. Found: C: 91.20, H: 1.51%.

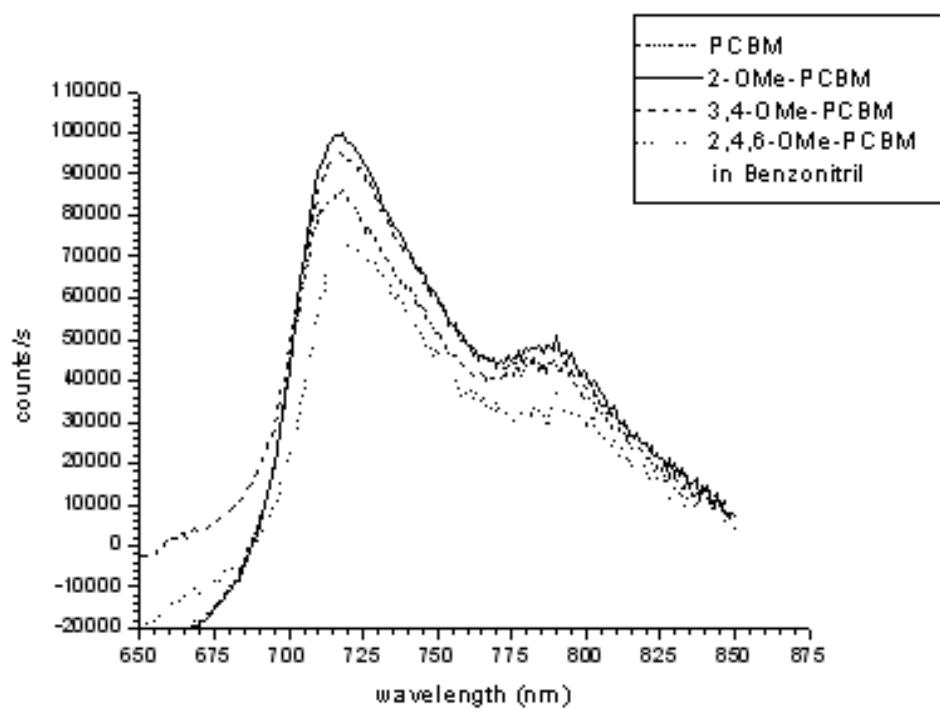
4-methyl-thioether-[6,6]-PCBM (5i):

IR (KBr) = ν (cm^{-1}): 2947 (m), 2912(m), 1730 (s), 1431 (s), 1187(m), 819(m), 742 (m), 548 (m), 525 (s); UV-VIS (toluene); λ_{max} (nm): 334 ($\varepsilon = 43538$), 433 ($\varepsilon = 2835$), 497 ($\varepsilon = 1700$), 696 ($\varepsilon = 282$); $^1\text{H-NMR}$: (CDCl_3 , 300 MHz): δ (ppm): 7.78 (d, $J = 8.05$ Hz, 2H), 7.34 (d, $J = 8.42$ Hz, 2H), 3.63 (s, 3H), 2.83 (m, 2H), 2.52 (s, 3H), 2.48 (t, $J = 7.69$ Hz, 2H), 2.12 (m, 2H); $^{13}\text{C-NMR}$: (CDCl_3 , 75 MHz): δ (ppm): 173.5, 148.6, 147.7, 145.82, 145.20, 145.15, 145.1, 143.8, 143.04, 143.00, 142.9, 142.20, 142.17, 142.11, 140.99, 138.8, 138.0, 137.7, 133.2, 132.4, 125.9, 51.7, 51.3, 33.9, 33.6, 22.4, 15.4. Melting Point: > 295 °C. Elemental Analysis: Calcd for $\text{C}_{73}\text{H}_{16}\text{O}_2\text{S}$: C: 91.62%, H: 1.69%. Found: C: 91.4%, H: 1.47%.

pentafluoro-[6,6]-PCBM (5j):

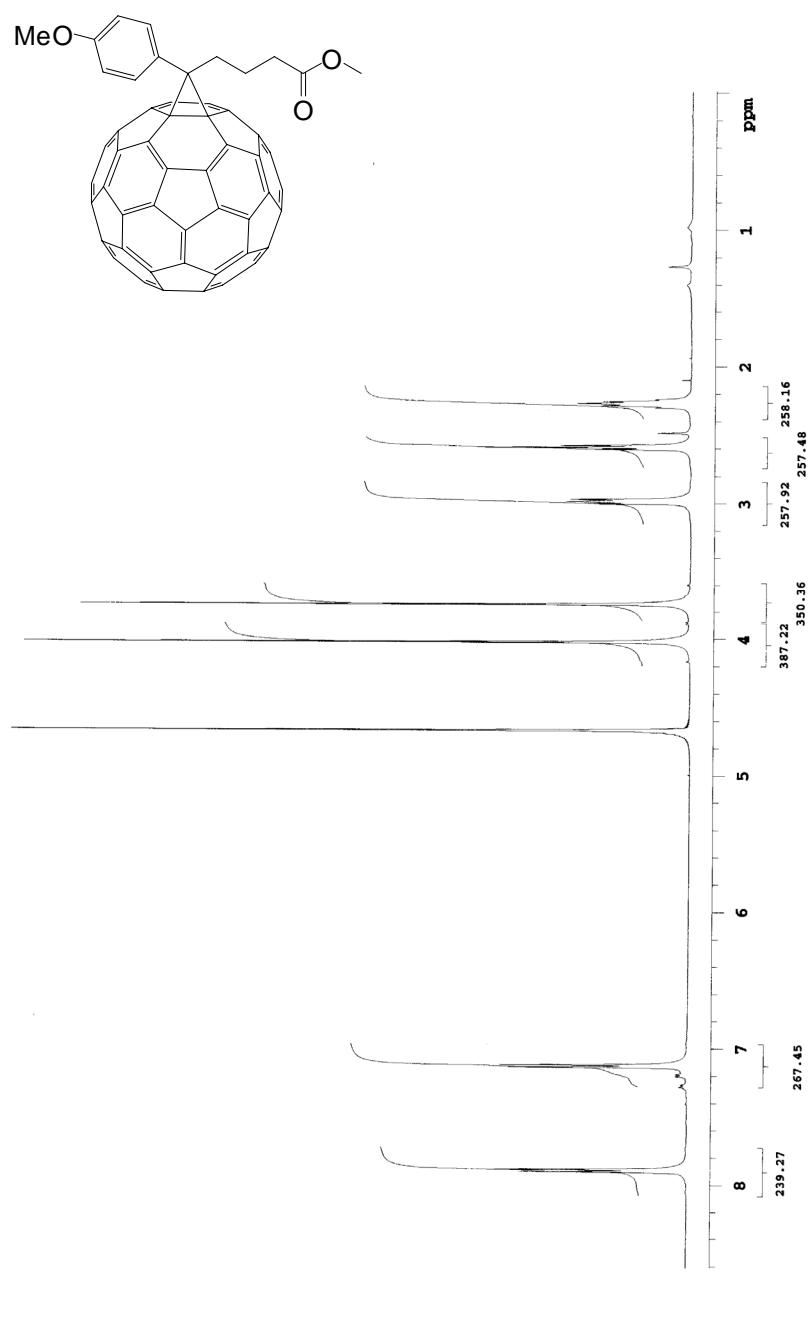
IR (KBr) = ν (cm^{-1}): 2946 (m), 2330 (w), 1738 (s), 1652 (w), 1514 (s), 1495 (s), 1464 (m), 1430 (m), 1350 (w), 1324 (w), 1254 (w), 1187 (m), 1070 (w), 995 (m), 986 (m), 956 (w), 915 (w), 838 (w), 791 (w), 775 (w), 743 (w), 711 (w), 678 (w), 581 (w), 573 (w), 553 (w), 527 (s). $^1\text{H NMR}$ (D_2O , 400 MHz); δ (ppm): 3.70 (s, 3H), 2.97 (t, $J = 8.4$ Hz, 2H), 2.59 (t, $J = 7.0$ Hz, 2H), 2.24 (m, 2H). $^{19}\text{F NMR}$ (D_2O , 400 MHz); δ (ppm): -137.54 (dd, $J = 16.8$ Hz, $J = 6.9$ Hz, 2F), -151.79 (t, $J = 22.1$ Hz, 1F), -159.79 (m, 2F). $^{13}\text{C NMR}$ (CS_2 , 100 MHz); δ (ppm): 170.8, 147.3, 146.7, 145.7, 144.9, 144.83, 144.80, 144.5, 144.29, 144.27, 144.24, 144.15, 144.04, 143.97, 143.4, 143.3, 142.59, 142.56, 142.54, 142.52, 141.7, 141.64, 141.60, 141.58, 140.7, 140.6, 138.9, 138.1, 136.4, 135.8, 75.0, 50.8, 32.8, 31.4, 21.8.

Fluorescence Spectra:

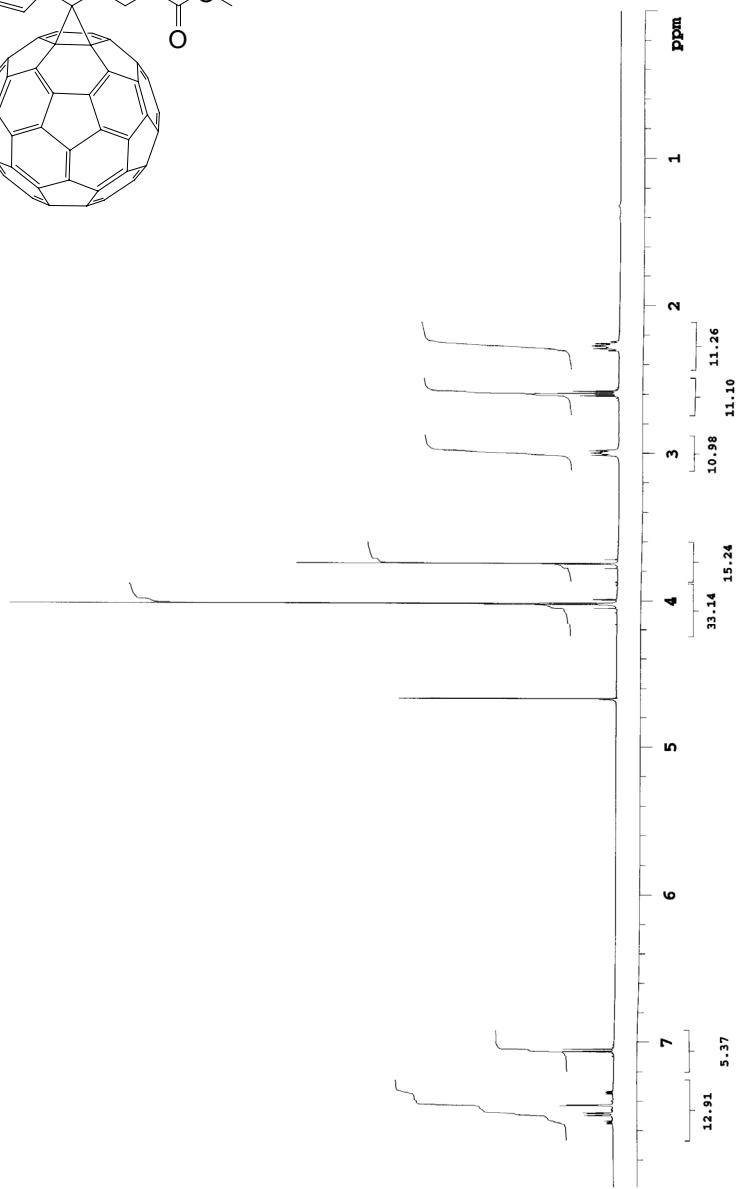
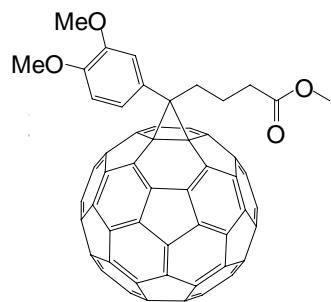


¹H-NMR Spectra of Fullerene Compounds

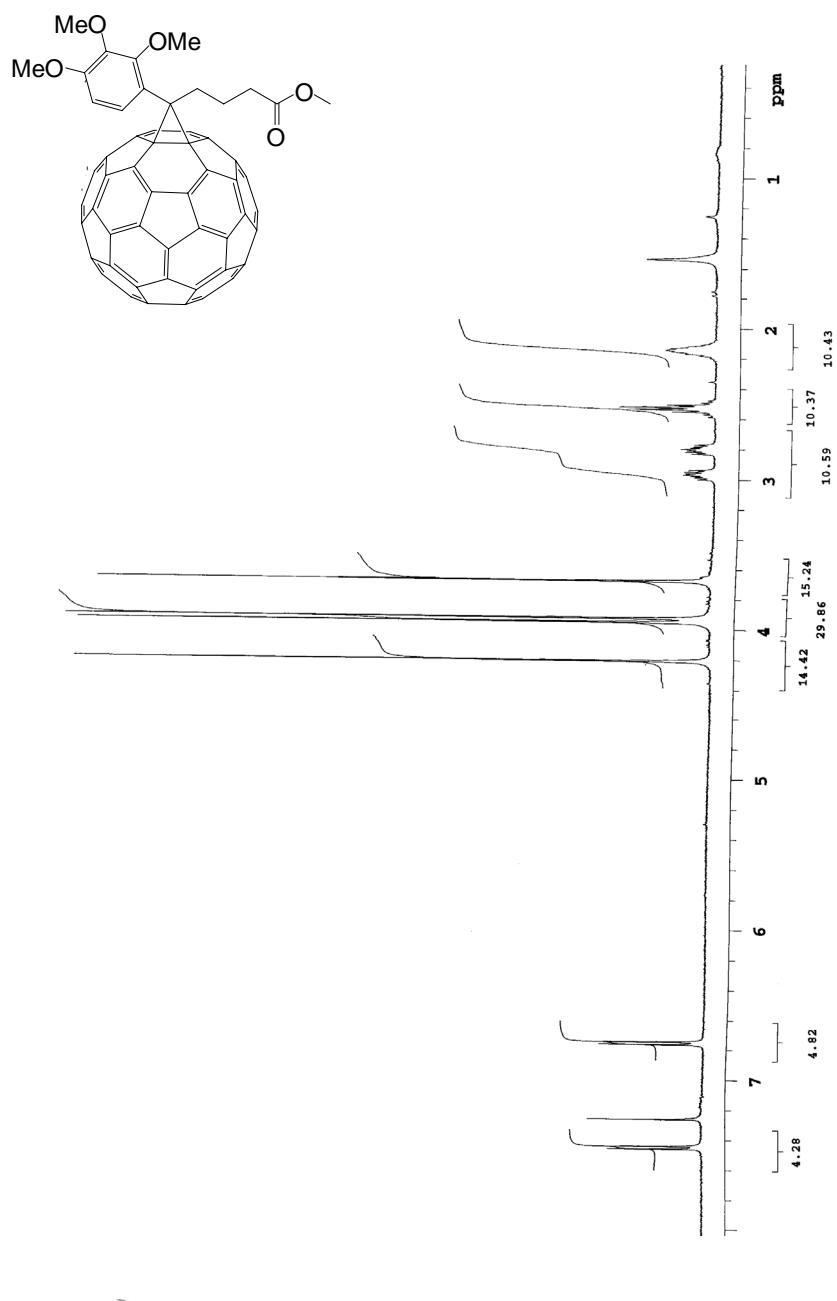
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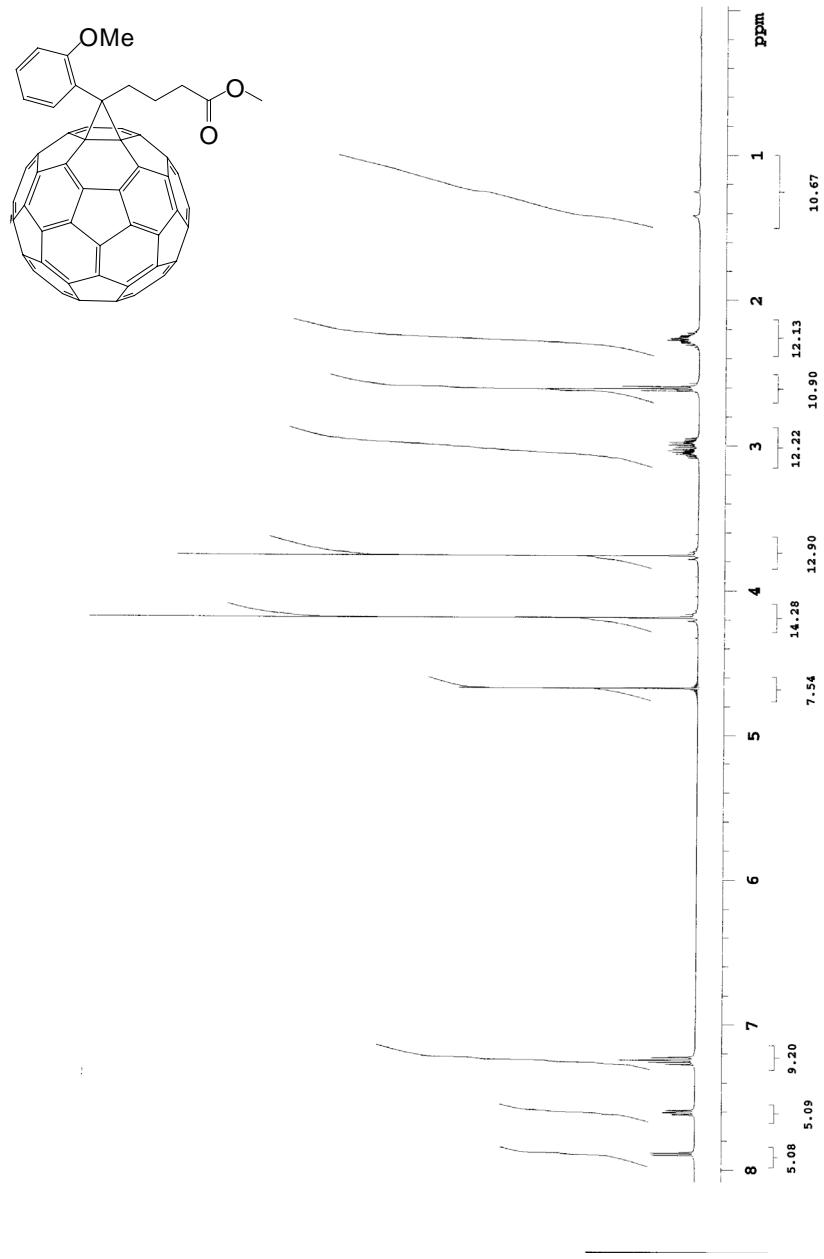
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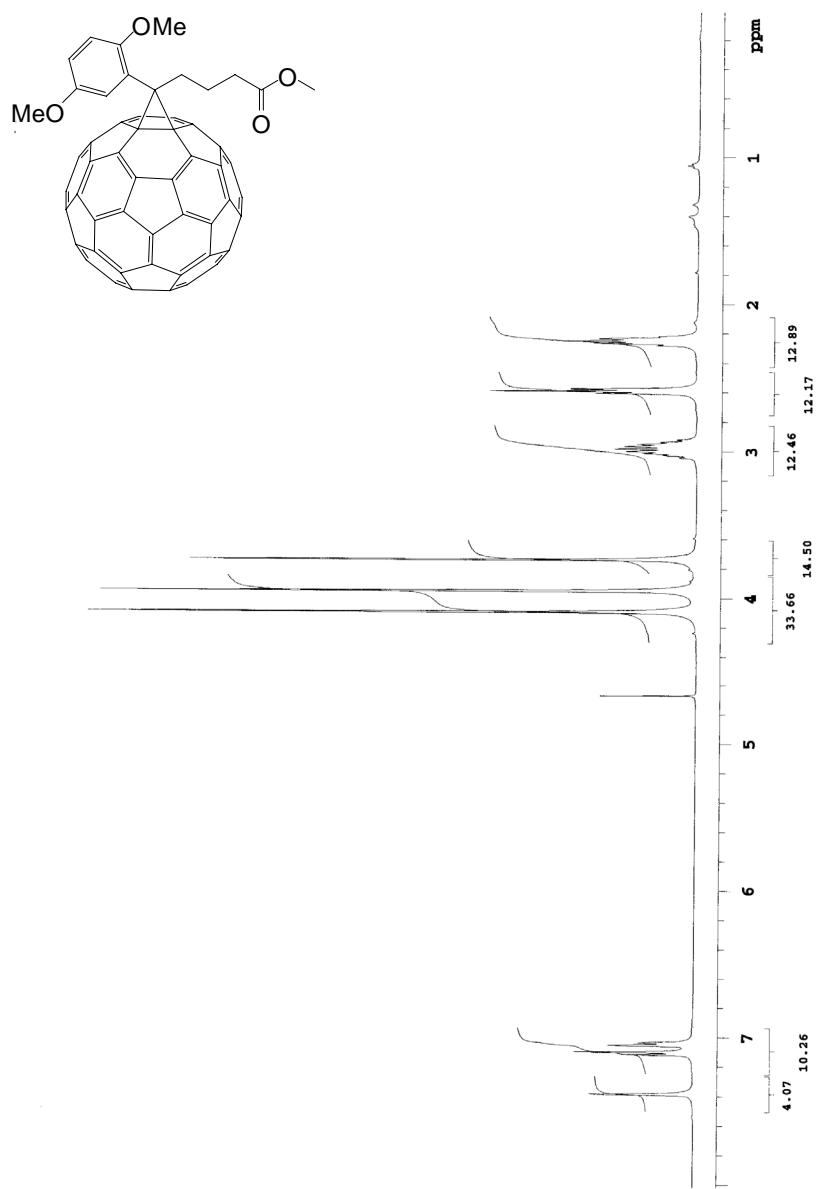
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5d

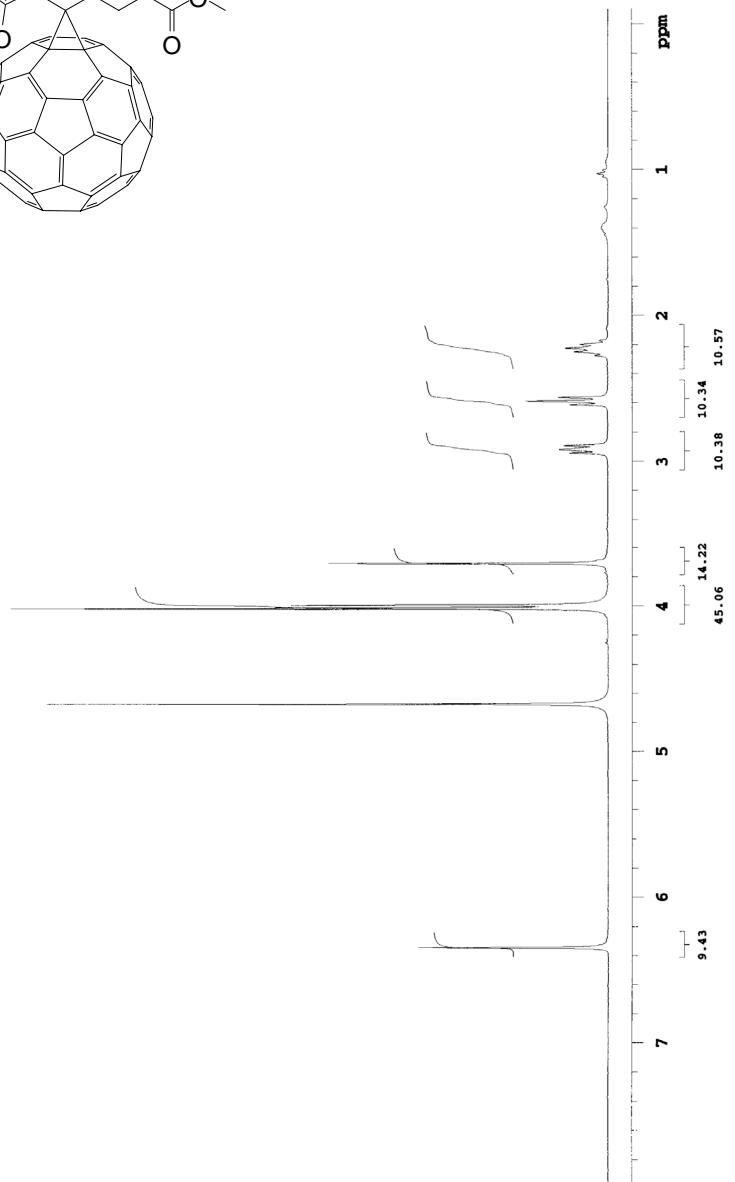
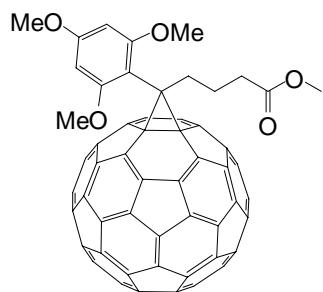


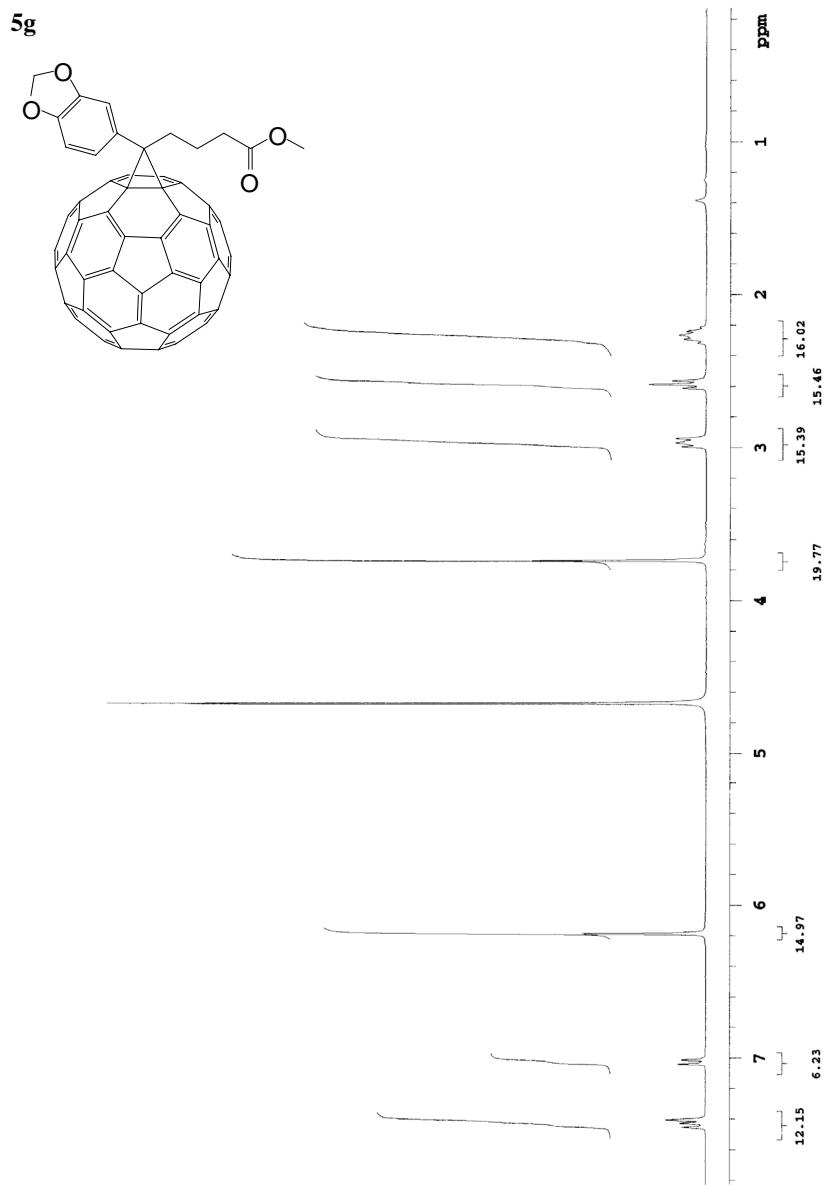
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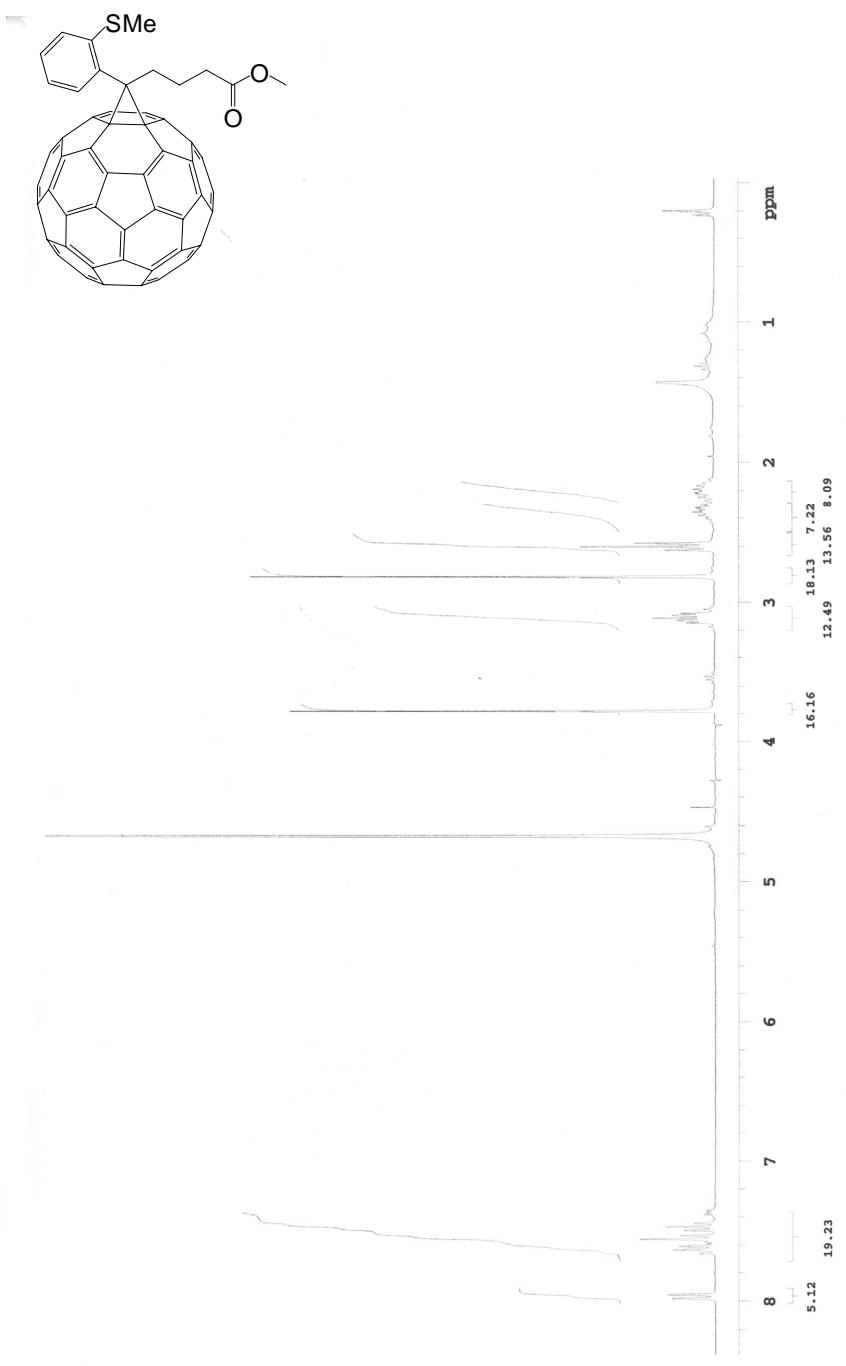
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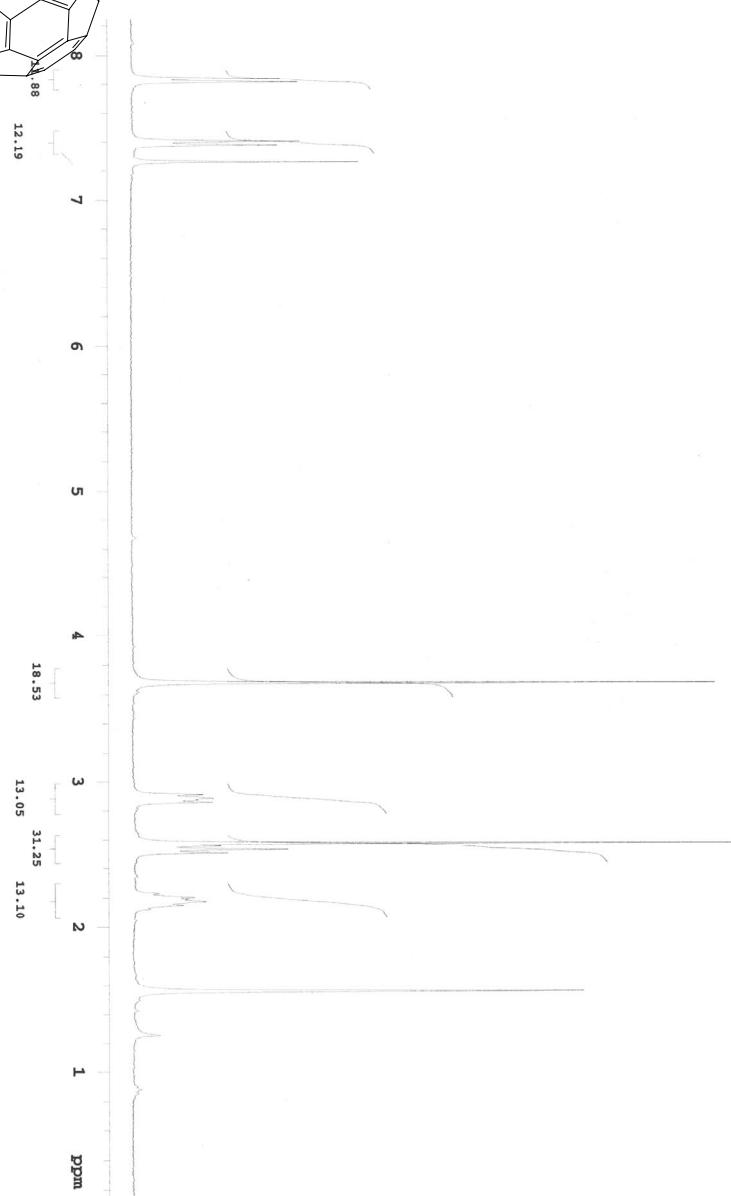




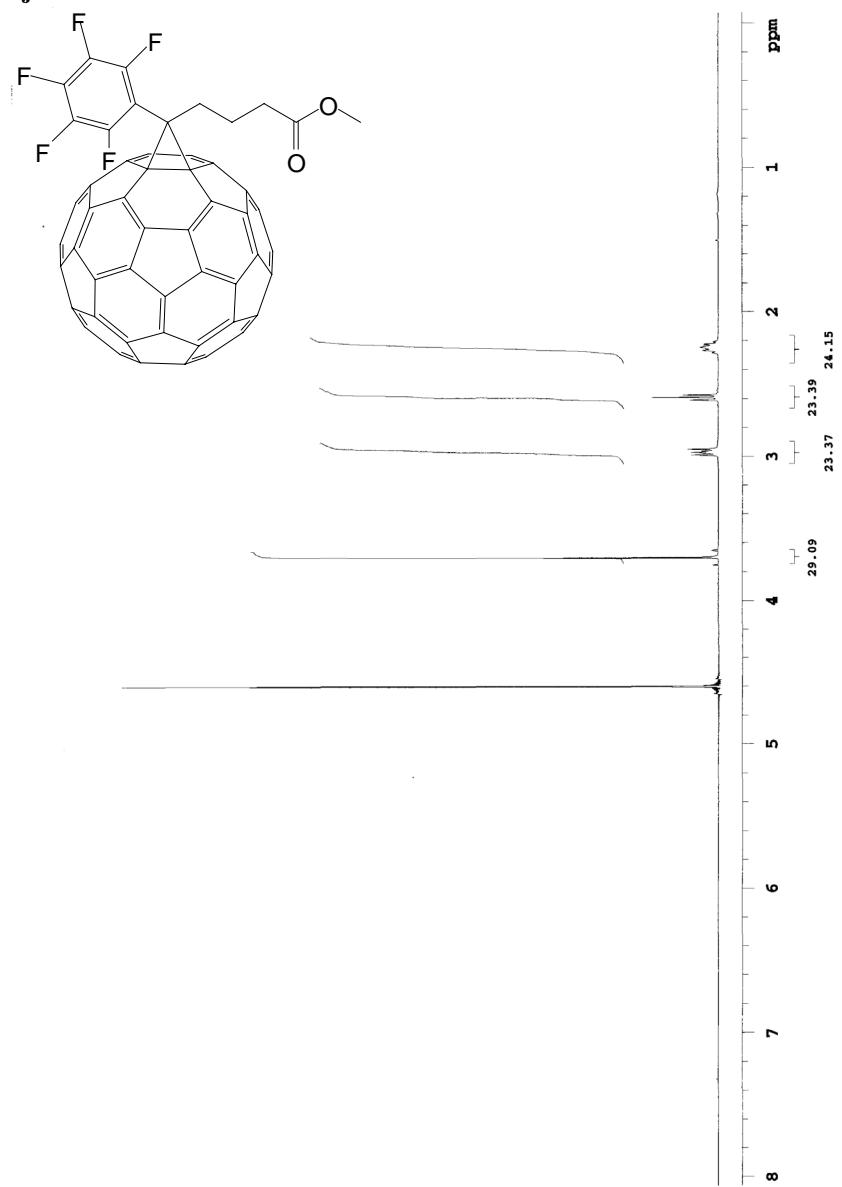
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5i

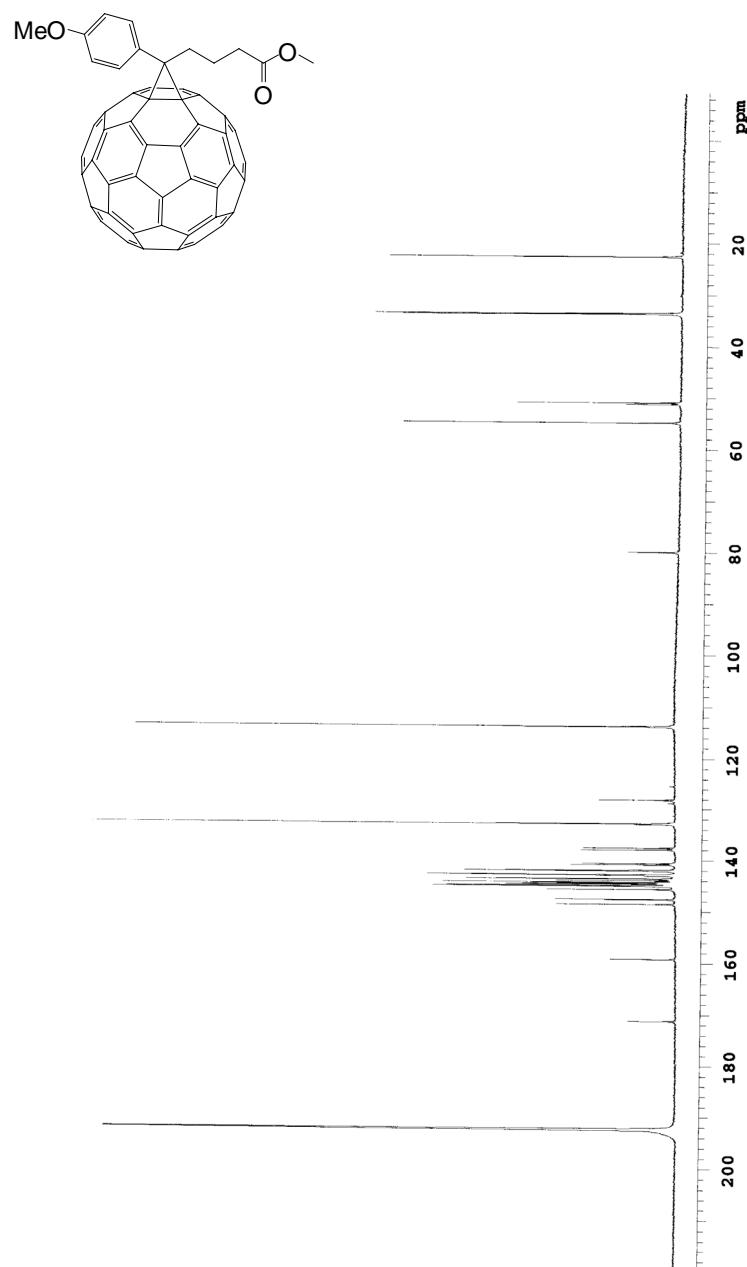


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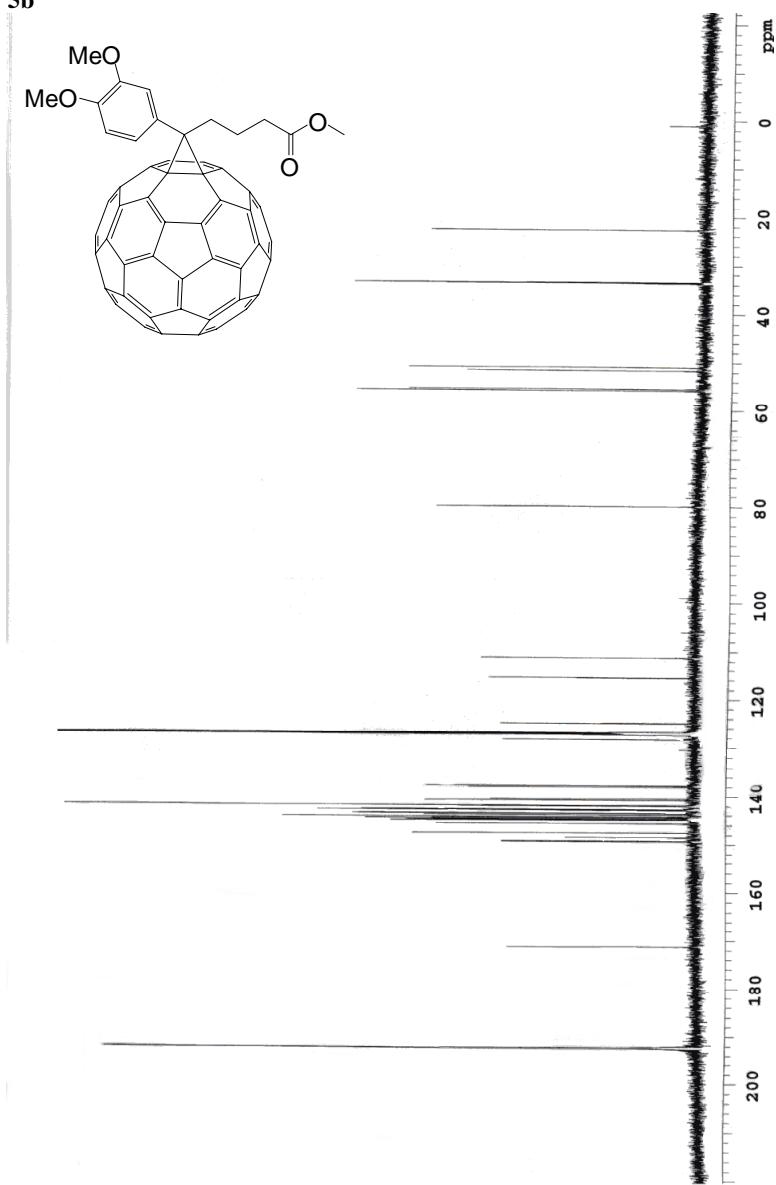
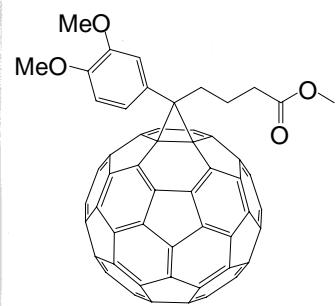


¹³C-NMR Spectra of Fullerene Compounds

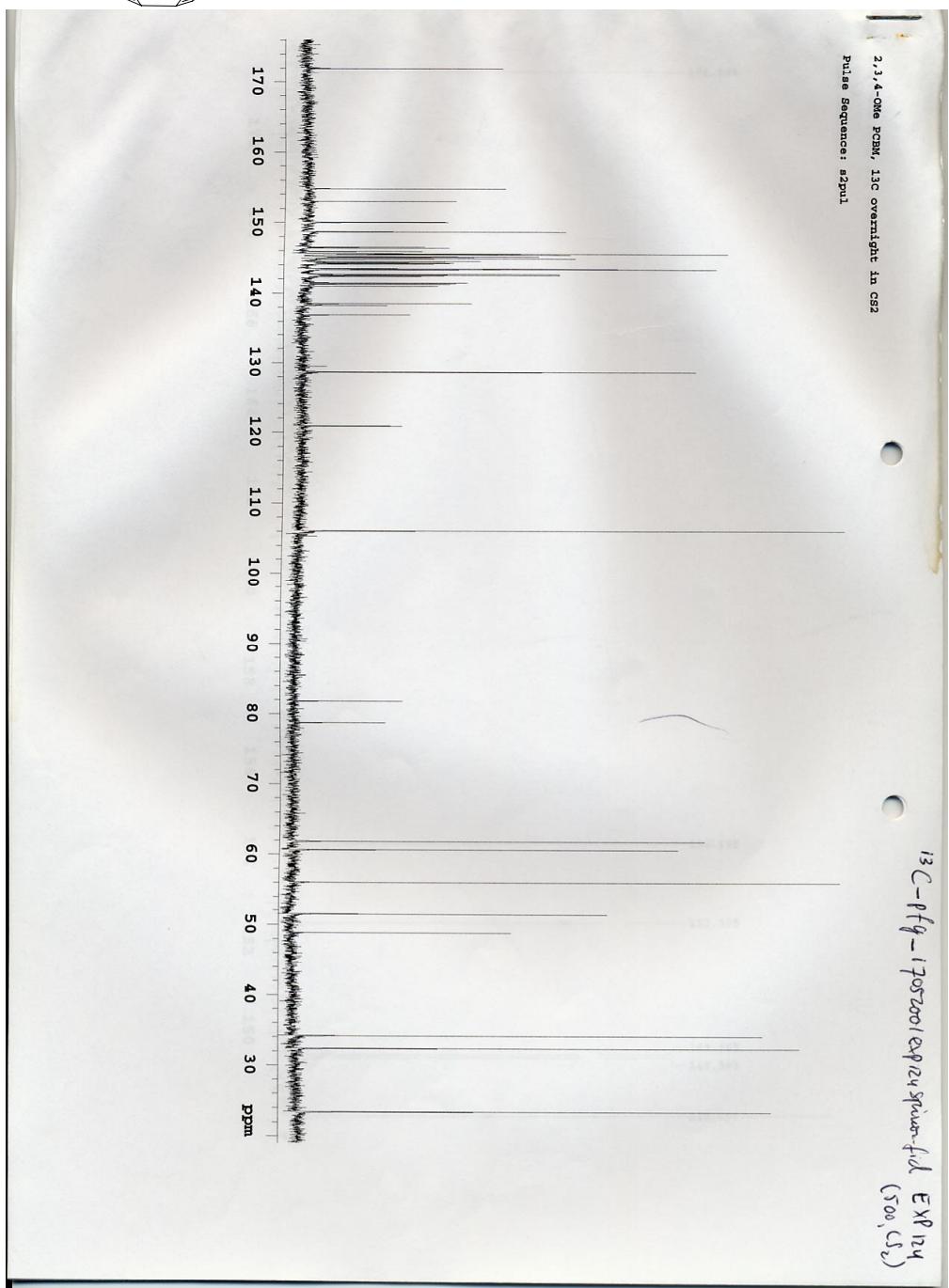
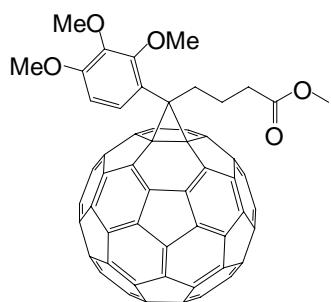
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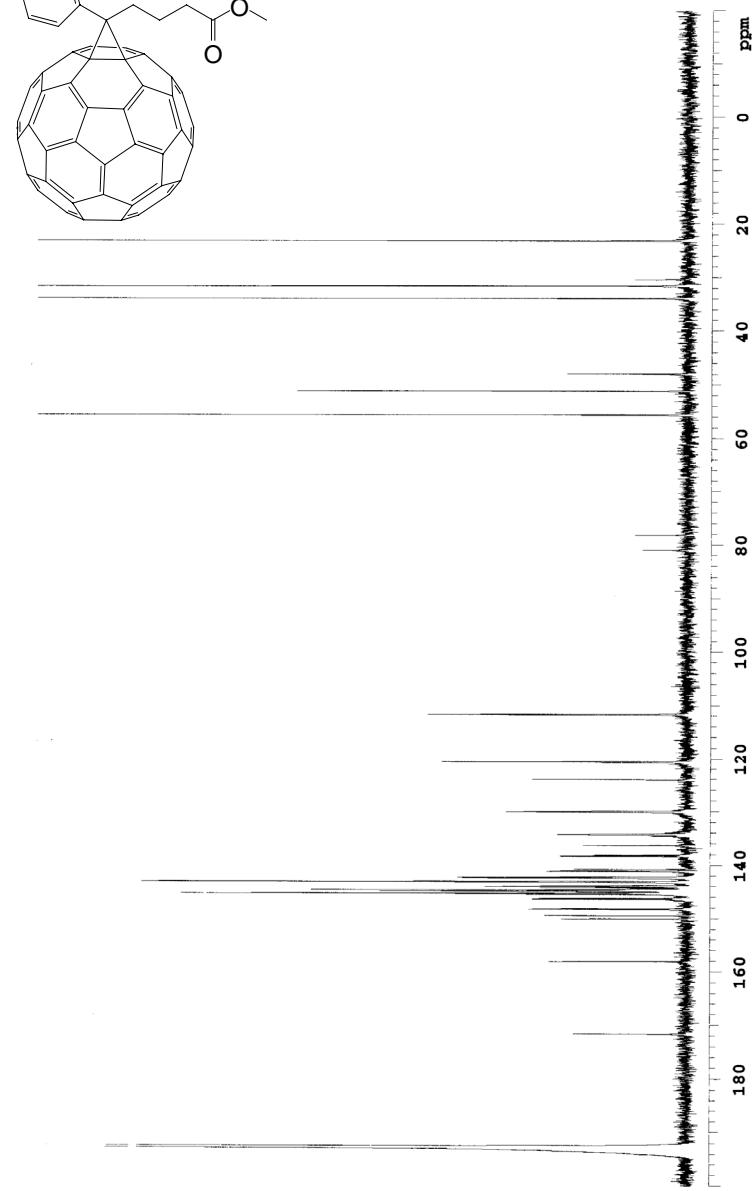
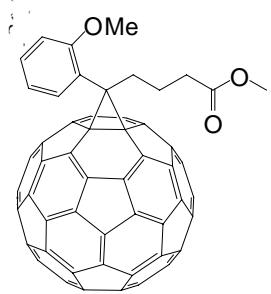


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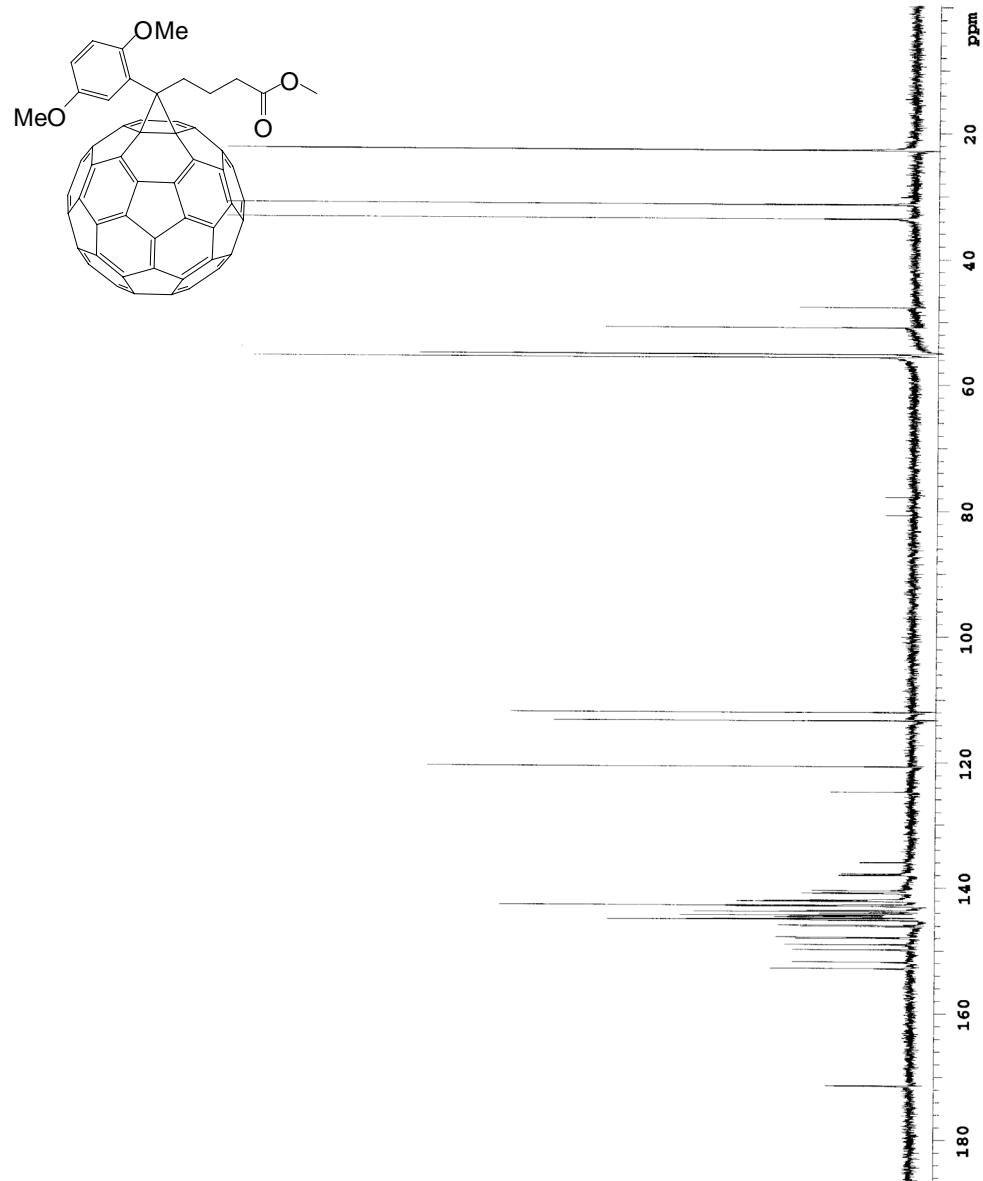


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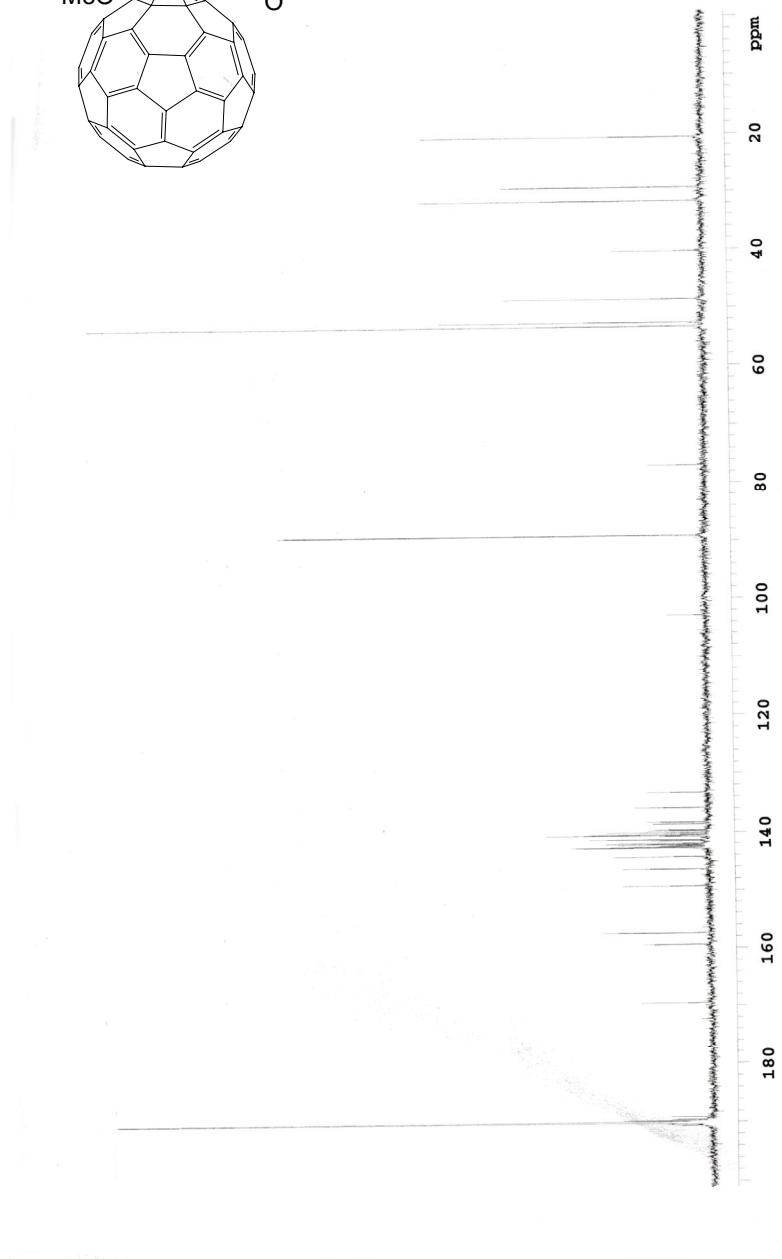
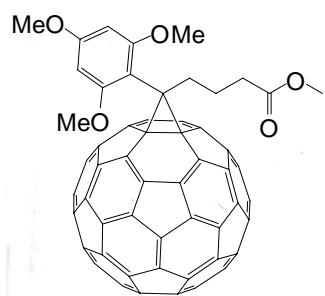




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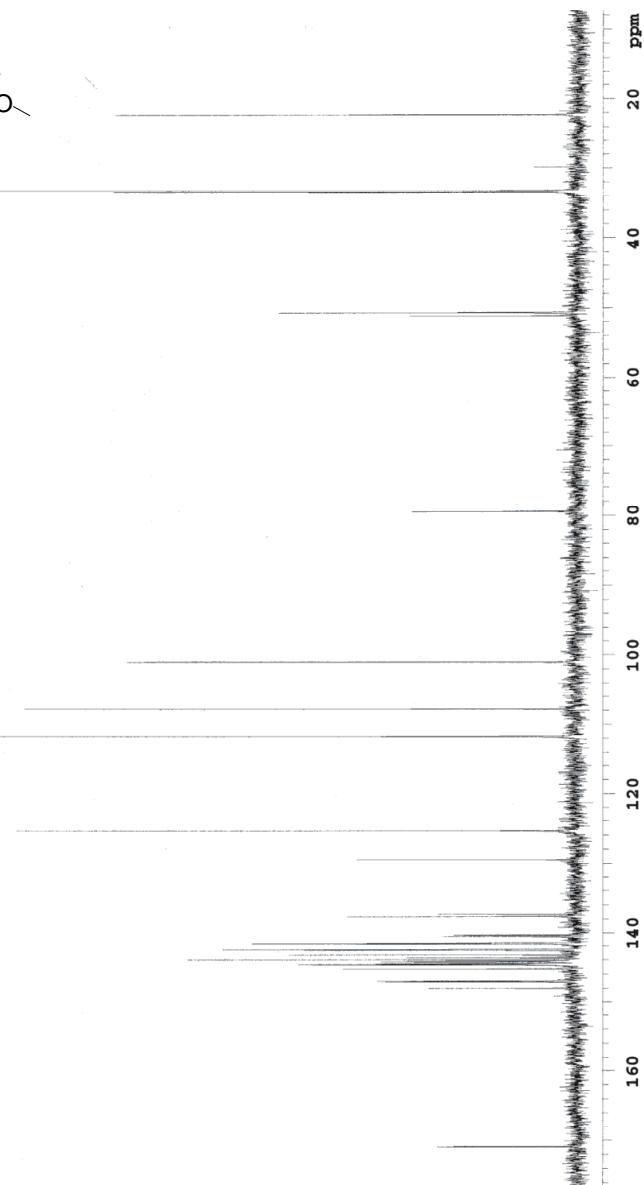
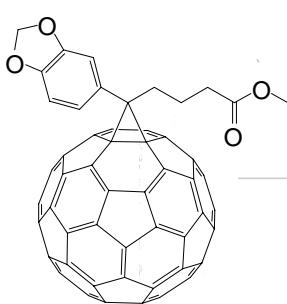


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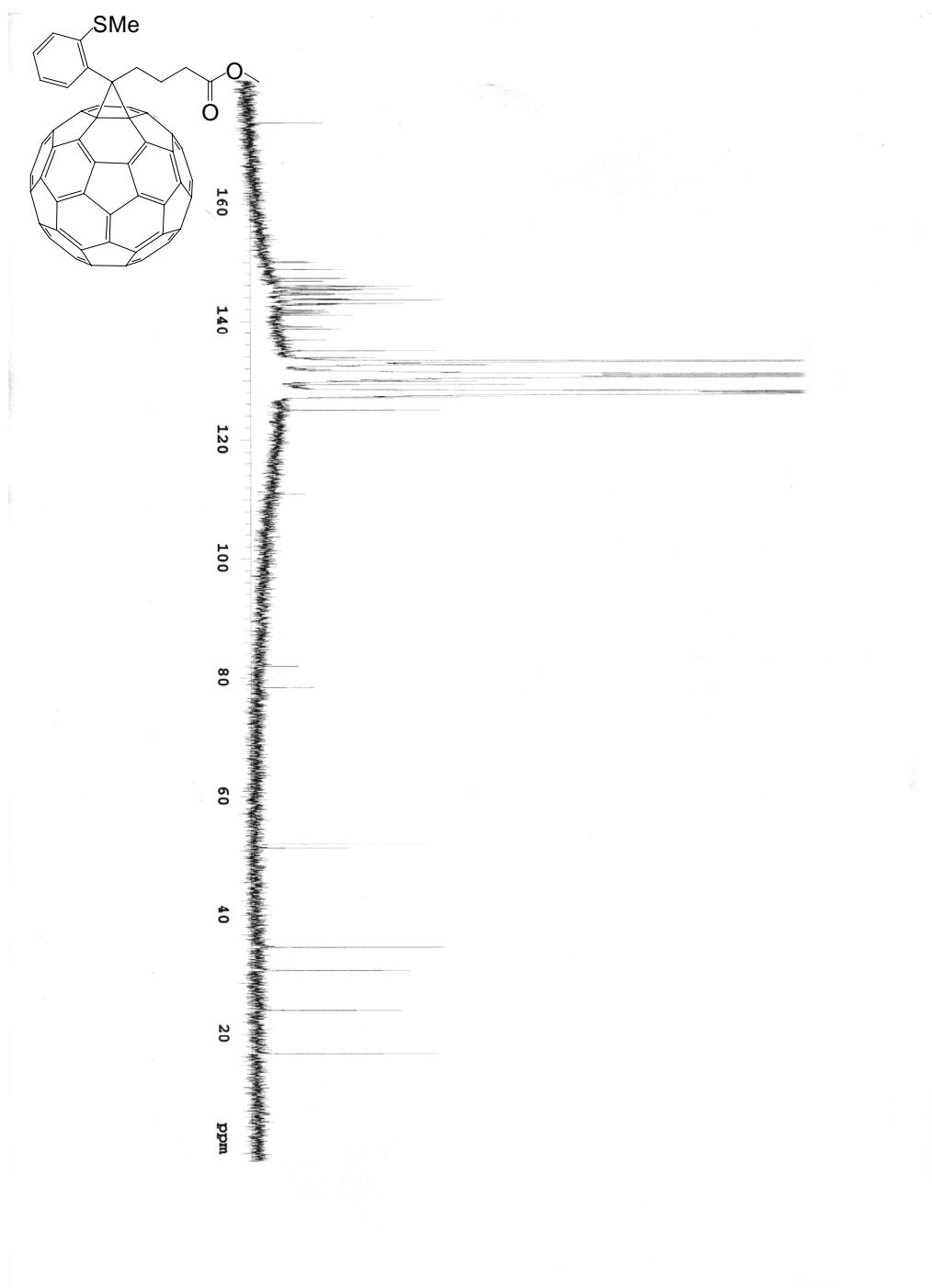


5g

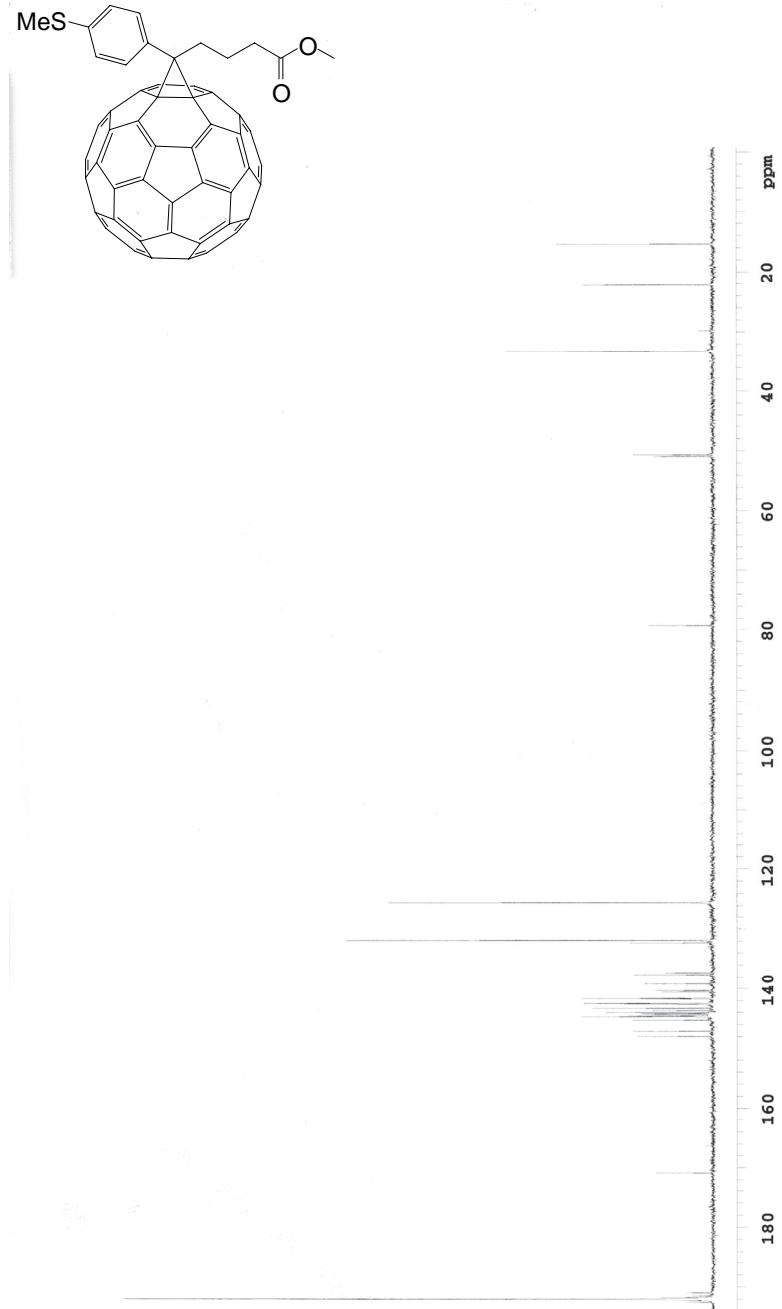
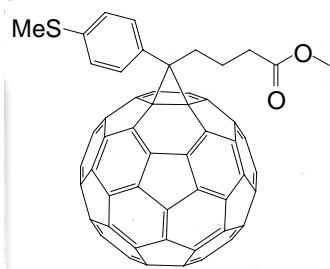
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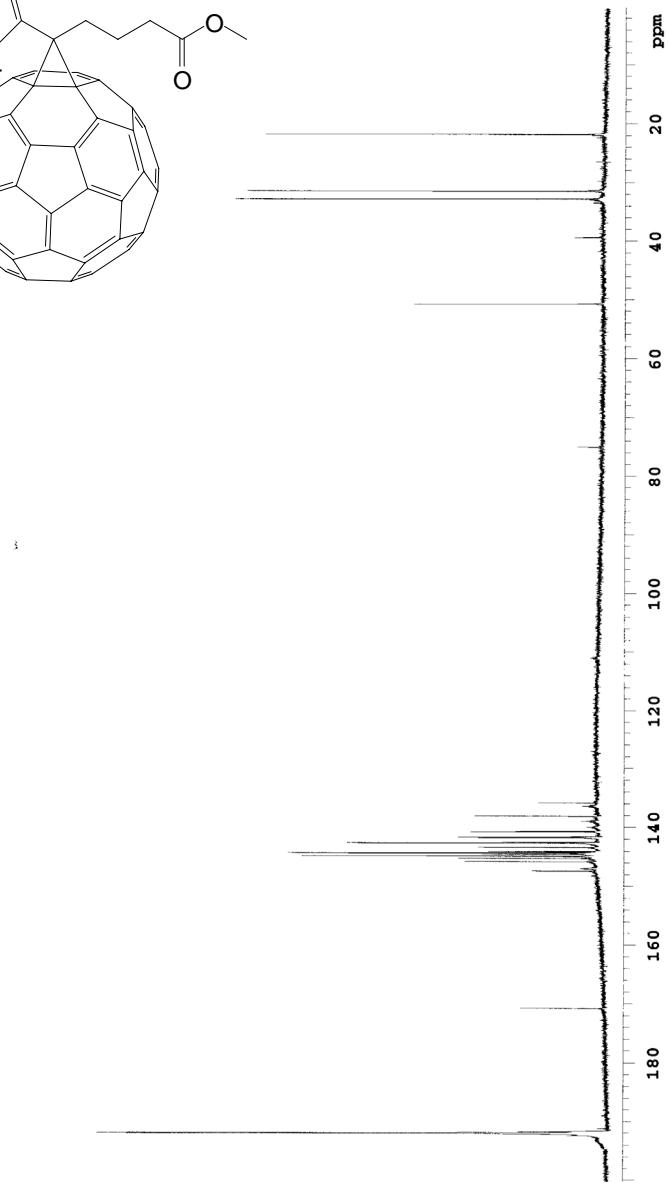
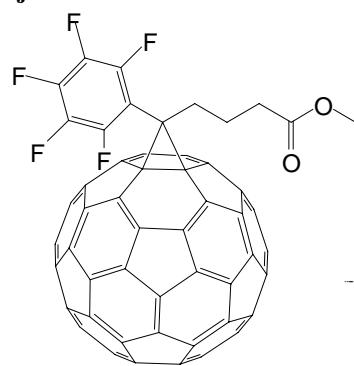
5h



5i



5j



¹⁹F-NMR Spectra of Fullerene Compounds

5j

