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SUPPORTING INFORMATION

Title: Regioselective Synthesis of Novel *e*-Edge-[60]fullerenylmethanodihydropyrroles and 1,2-Dihydromethano[60]fullerenes

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General Remarks

All reactions were performed using dried glassware under a dry nitrogen or argon atmosphere. Toluene and THF were distilled over benzophenone-sodium. DCM was dried by distillation from calcium hydride and saturated with nitrogen gas. Flash column chromatography was performed using silica 60 (230-400 mesh, 0.040-0.063 mm). UV/*vis* spectra were recorded on a Shimadzu UV-1601. ^{1}H NMR and ^{13}C NMR spectra were run in $CDCl_3$ solution and acquired on a Varian Unity 300, 400 or 500 MHz spectrometer or a Bruker DMX-600 MHz spectrometer. The 2D INADEQUATE experiments on 20-30% ^{13}C-enriched samples were performed on a Bruker DMX 600 or Avance 800 MHz spectrometer. Mass spectra were determined on a ThermoFinnigan LTQ (Waltham, MA) fitted with a conventional IonMax electrospray ionization source. Spectra were obtained by infusion of a standard solution (2 : 1 chloroform : methanol). Typical settings were

spray voltages between 4 – 6 kV, capillary temperature 270 ^{0}C and sheath gas flow rates at 10 (arbitrary units).

Methyl 3-hydroxymethylphenylmethyl malonate (2)

A solution of methyl malonyl chloride (0.487 g, 0.24 mmol) in THF (24 mL) was added dropwise to a solution of 1,3-benzenedimethanol **1** (0.500 g, 3.60 mmol) and pyridine (0.285 g, 3.60 mmol) in THF (30 mL) over a 30 min period at 0 ºC. The solution was stirred for a further 3 h at r.t. and then diluted with DCM (150 mL) and washed with ammonium chloride solution (2 x 50 mL). The organic layer was then dried ($MgSO_4$) and concentrated in vacuo to yield the methyl malonate benzyl alcohol **2** (0.711 g, 83%) as a colorless oil. ^{1}H NMR (300 MHz): δ = 3.02 (bs, 1H), 3.41 (s, 2H), 3.81 (s, 3H), 4.66 (s, 2H), 5.16 (s, 2H), 7.32 (m, 4H). ^{13}C NMR (125 MHz): δ 40.9, 64.1, 66.5, 66.8, 127.5, 127.9, 128.3, 128.6, 135.1, 135.4, 166.2, 166.7. MS (EI): *m/z* 238 (M^{+}).

***3'-[Methoxycarbonyl(acetoxymethyl)]phenyl-1'-methyl-N-tert butoxycarbonyl glycinate* (3)**

To a solution of **2** (0.750 g, 2.98 mmol), *N*-Boc-glycine (0.955 g, 2.98 mmol) and DMAP (0.036 g, 0.298 mmol) in THF (10 mL) was added DCC (0.737 g, 3.57 mmol) and the mixture was stirred for 18 h, filtered and the filtrate was concentrated *in vacuo*. The crude product was redissolved in DCM (100 mL) and washed with 0.1 M HCl (20 mL), 0.1 M sodium carbonate solution (20 mL) and brine (20 mL). The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*, and the residue subjected to flash column chromatography. Elution with DCM/MeOH (98 : 2) provided **3** (0.766 g, 64%) as a pale

yellow oil. ^{1}H NMR (300 MHz): δ = 1.44 (s, 9H), 3.42 (s, 2H), 3.81 (s, 3H), 3.91 (d, 2H, *J* = 6.3 Hz), 5.17 (s, 2H), 5.18 (s, 2H), 5.40 (bs, 1H), 7.38 (m, 4H). ^{13}C NMR (75 MHz): δ = 13.7, 28.0, 41.2, 42.1, 61.3, 66.2, 66.4, 79.5, 127.6, 127.65. 127.7, 127.9, 135.5, 135.57, 135.6, 155.6, 166.1, 170.0. MS (ES +ve): *m/z* 418 ($M+Na^{+}$).

***3'-[Methoxycarbonyl(acetoxymethyl)]phenyl-1'-methyl-N-(diphenylmethylidene amino) glycinate* (5)**

The Boc-protected tether **3** (2.35 g, 5.95 mmol) was added to neat TFA (5.0 mL) and the reaction mixture was stirred for 1 h and then concentrated *in vacuo*. The reaction mixture was redissolved in distilled water (10 mL) and washed several times with diethyl ether (10 mL). The aqueous layer was retained and freeze-dried overnight to yield **4** (1.46 g, 60%) as a colorless oil. MS (CI): *m/z* 296 (RNH_2^{+}). To a suspension of the TFA salt **4** (1.45 g, 3.55 mmol) in DCM/MeCN (20 mL:10 mL) was added benzophenone imine (0.643 g, 3.55 mmol) and the reaction mixture was stirred vigorously for 24 h before being filtered and concentrated *in vacuo.* The yellow oil was then redissolved in diethyl ether (20 mL) and washed with brine (2 x 10 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo* to yield **5** as a viscous pale yellow oil (0.72 g, 44%). ^{1}H NMR (500 MHz): δ = 3.42 (s, 2H), 3.73 (s, 3H), 4.26 (s, 2H), 5.17 (s, 2H), 5.19 (s, 2H), 7.17 (m, 1H), 7.35 (s, 2H), 7.44 (m, 5H), 7.49 (m, 4H), 7.81 (d, 2H, *J* = 8.0 Hz). ^{13}C NMR (125 MHz): δ = 41.2, 52.5, 55.7, 66.1, 66.8, 127.6, 128.1, 128.3, 128.7, 130.5, 135.6, 135.9, 136.2, 137.5, 139.2, 166.2, 166.7, 170.4, 171.9. MS (CI): *m/z* 460 (M+1).

5',5''-Diphenyl-3''-methyl-2',3'(oxooxymethano[1,4]benzenomethanooxyoxo)-pyrrolo[3',4':1,9]-3''H-cyclopropa[16:17](C_{60}-I_h)[5,6]fullerene-3''-carboxylate **(6)**

A solution of DBU (0.122 mL, 0.868 mmol) in toluene (5 mL) was added to a stirred solution of **5** (0.100 g, 0.217 mmol), C_{60} (0.156 g, 0.217 mmol), and CBr_4 (0.144 g, 0.43 mmol) in toluene (250 mL), and the mixture was stirred for 18 h under an argon atmosphere. After evaporation of the solvent, the crude residue was subsequently subjected to flash silica gel chromatography using toluene as eluent to remove unreacted fullerene. Further elution with DCM afforded **6** as dark brown solid (0.075 g, 30%). ^{1}H NMR (500 MHz): δ = 4.03 (s, 3H); 5.37 (s, 2H); 5.52 (s, 2H); 7.22 (t, *J* = 7.5 Hz, 1H); 7.35 (d, *J* = 7.5 Hz, 1H); 7.38 (t, *J* = 8.0 Hz, 2H); 7.42 (d, *J* = 7.5 Hz, 1H); 7.49 (t, *J* = 8.0 Hz, 4H); 7.83 (s, 1H); 8.03 (d, *J* = 8.0 Hz, 4H). ^{13}C NMR (150 MHz): δ = 52.4; 53.9; 67.9; 68.1; 69.8; 81.2; 82.9; 95.9; 128.1; 128.3; 128.9; 129.5; 131.1; 131.2; 134.1; 134.8; 135.0; 137.5; 137.8; 139.4; 139.6; 141.3; 141.8; 142.0; 142.7; 142.93; 142.94; 143.0; 144.1; 144.2; 144.21; 144.3; 144.4; 144.9; 145.3; 145.4; 145.5; 146.1; 146.7; 146.8; 146.9; 147.1; 147.8; 148.5; 155.7; 161.6; 161.8; 162.8; 163.8. UV-*vis* (DCM): 424, 451 nm. MS (ES -ve): *m/z* 1175 (M^-).

3'-[Methoxycarbonyl(acetoxymethyl)]phenyl-1'-methyl-61[N-(diphenylmethylideneamino-1,2-methano[60]fullerene-61-carboxylate **(8)**

A solution of DBU (0.041 mL, 0.278 mmol) in toluene (3 mL) was added to a stirred solution of **5** (0.066 g, 0.139 mmol), C_{60} (0.100 g, 0.139 mmol), and CBr_4 (0.046 g, 0.139 mmol) in toluene (150 mL), and the mixture was stirred for 2 h under an argon atmosphere. Purification by flash silica gel chromatography (toluene then DCM as

eluent) afforded **8** as a dark brown solid (0.035 g, 20%). ^{1}H NMR (400 MHz): δ = 3.40 (s, 2H), 3.81 (s, 3H), 5.17 (s, 2H), 5.58 (s, 2H), 7.38 (m, 5H), 7.49 (m, 5H), 8.08 (d, 4H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz): δ = 41.8, 61.9, 67.0, 68.4, 83.0, 83.1, 96.3, 128.6, 128.7, 128.8, 128.9, 129.1, 129.3, 129.9, 134.8, 135.3, 136.1, 137.1, 139.4, 139.9, 141.2, 141.6, 142.0, 142.1, 142.11, 142.6, 142.7, 142.9, 143.0, 143.2 144.4, 145.1, 145.3, 145.4, 145.7, 146.1, 146.2, 146.7, 147.2, 147.4 147.6, 148.6, 153.4, 160.7, 162.4, 166.5, 166.6. MALDI-TOF (-ve ion mode): *m/z* 1177 (M^-), 720 (C_{60}^-).

61-Methyl-61-[3'-(t-butoxyamidoacetoxy)methyl]benzyl-61H-cyclopropa(C_{60}-I_h)[5,6]fullerene-61,61-dicarboxylate **(10)**

A solution of DBU (0.06 mL, 0.42 mmol) in toluene (5 mL) was added to a stirred solution of **3** (0.08 g, 0.27 mmol), C_{60} (0.150 g, 0.20 mmol), and CBr_4 (0.07 g, 0.21 mmol) in toluene (350 mL), and the mixture was stirred for overnight under an argon atmosphere. Purification by flash silica gel chromatography (toluene then toluene/ethyl acetate (80:20) as eluent) afforded **10** as dark brown solid (0.07 g, 32%). ^{1}H NMR (300 MHz): δ = 1.45 (s, 9H); 3.96 (d, *J* = 7.2 Hz, 2H); 4.03 (s, 3H); 5.04 (bs, 1H), 5.20 (s, 2H), 5.53 (s, 2H), 7.44 (m, 4H). ^{13}C NMR (75 MHz): δ = 28.6, 42.7, 54.3, 66.9, 68.8, 71.6, 128.9, 129.1, 129.2, 129.3, 135.4, 136.2, 138.9, 139.6, 141.1; 141.2, 142.0, 142.1, 142.42, 142.43, 143.1, 143.2, 143.3, 144.0, 144.1, 144.7, 144.8, 144.87, 144.9, 145.0, 145.1, 145.2, 145.3, 145.37, 145.40, 145.41, 145.48, 145.52, 163.6, 164.2. MS (ES -ve): *m/z* 1113 (M^-).

61-{3'-[N-(Diphenylmethylidene)aminoacetoxy]methyl}benzyl-61-methyl-61H-cyclopropa(C_{60}-I_h)[5,6]fullerene-61,61-dicarboxylate **(11)**

To a solution of **10** (0.090 g, 0.080 mmol) in freshly distilled and degassed DCM (5 mL) at r.t. was added dropwise TFA (0.1 mL). After stirring for 18 h the solvent was evaporated and the crude product was dried under high vacuum for several hours to give the TFA salt which was used without further purification in the subsequent conversion. The TFA salt was dissolved in freshly distilled THF/$CHCl_3$ (1:1, 10 mL) under nitrogen. Benzophenone imine (0.050 mmol, 0.015 mL) was added and the mixture was stirred for 30 min. The crude material was filtered through a short plug of silica gel using toluene/ethyl acetate (80 : 20) as eluent. Recrystallisation from $CHCl_3$/MeOH provided the title compound **11** (0.06 g, 62%). ^{1}H NMR (300 MHz): δ = 4.01 (s, 3H), 4.25 (s, 2H), 5.19 (s, 2H), 5.51 (s, 2H), 7.16 (m, 2H), 7.40 (m, 10H), 7.65 (m, 2H). ^{13}C NMR (75 MHz): δ = 51.9, 54.2, 55.8, 66.4, 68.8, 71.6, 127.9, 128.1, 128.4, 128.9, 129.00, 129.04, 129.1, 129.2, 130.8 135.3, 136.1, 136.6, 138.9, 139.4, 139.7, 141.15, 141.18, 142.07, 142.10, 142.4, 143.1, 143.2, 144.0, 144.1, 144.7, 144.8, 144.9, 145.0, 145.1, 145.2 145.4, 145.5, 163.6, 164.2, 170.7, 172.3. MS (ES -ve): *m/z* 1177 (M^-).

5',5'-Diphenyl-2',3'',3''-trimethylpyrrolo[3',4':1,9]-3''H-cyclopropa[16:17](C_{60}-I_h)[5,6]fullerene-2',3'',3''-tricarboxylate **(12)**

Solid potassium carbonate (0.18 g, 1.27 mmol) was added to a solution of the bis-adduct **6** (0.050 g, 4.25 x 10^{-2} mmol) in THF/MeOH (10:1, 5 mL) and the mixture was stirred at r.t. for 18 h. The mixture was then filtered and the solvent was removed *in vacuo*. The residue was subjected to flash column chromatography and elution with DCM/hexane

(90:10) followed by recrystallisation from chloroform/diethyl ether yielded the title compound **12** (0.02 g, 40%) as a brown amorphous solid. ^{1}H NMR (500 MHz): δ = 4.01 (s, 3H), 4.02 (s, 3H), 4.13 (s, 3H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 4H), 8.01 (d, *J* = 8.0 Hz, 4H). ^{13}C NMR (150 MHz): δ = 52.7, 53.4, 53.7, 53.9, 69.8, 81.9, 82.6, 95.2, 128.3 128.4, 129.7, 140.8, 137.5, 137.9, 138.42, 140.2, 140.8, 141.4, 141.7, 142.3, 142.8, 142.9 144.1, 144.2, 144.3, 144.4, 144.47, 144.49, 144.50, 144.9, 145.0, 145.1, 145.6, 145.8, 145.9, 146.9, 147.0, 147.1, 147.2 , 147.9, 148.5, 156.0, 160.3, 162.2, 164.2, 164.3. UV-*vis* (DCM): 424, 455 nm. MS (ES -ve): *m/z* 1001 (M^-).

General procedure for the ring-opening reactions

To a mixture of boron trifluoride-diethyl etherate, glacial acetic acid, and the appropriate starting material in freshly distilled DCM was added a solution of sodium cyanoborohydride in THF (1M) via syringe and under an atmosphere of argon. The mixture was stirred at RT and the progress of the reaction was followed by TLC. When TLC analysis showed total consumption of the starting material, the solvent was removed *in vacuo* and the residue purified by column chromatography.

Methyl-N-(diphenylmethyl)-2-[3',3'-dimethyl-3'H-cyclopropa[16:17](C_{60}-I_h)[5,6]fulleren-3',3'-dicarboxyl-1(9H)-yl]glycinate **(13)**

The title compound was prepared from **12** (0.026 g, 0.024 mmol) and 1 M $NaCNBH_3$ in THF (0.007 mL, 0.070 mmol) with boron trifluoride-diethyl etherate (0.04 mL), and glacial acetic acid (1 drop), in DCM (10 mL), and the mixture was stirred for 15 min.

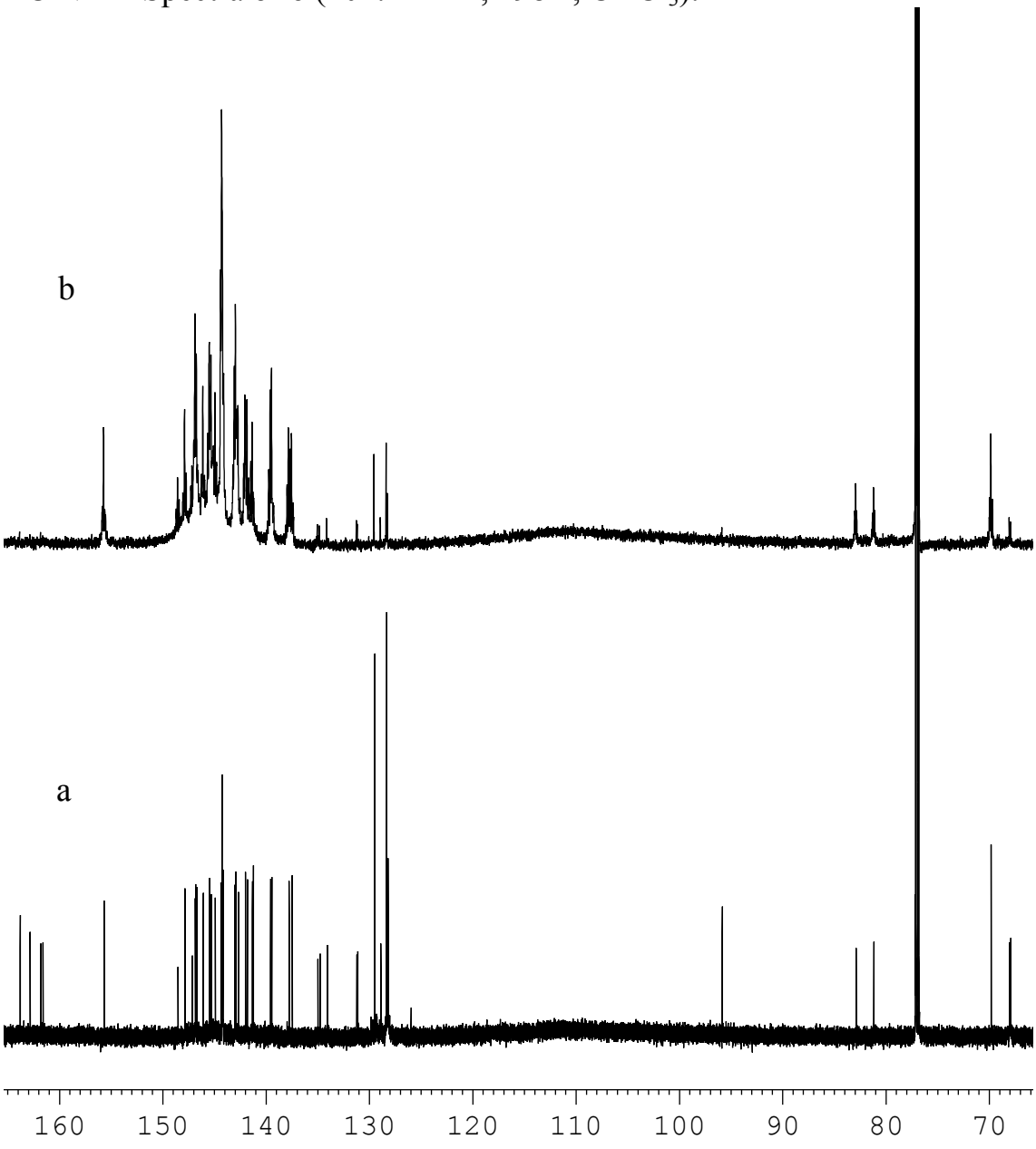
Purification using flash column chromatography (DCM/hexane, 30 : 20) gave **13** as a brown solid (0.010 g, 40%). ^{1}H NMR (500 MHz): δ = 3.42 (d, *J* = 12.0 Hz, 1H, NH), 3.86 (s, 3H) 3.88 (s, 3H), 3.98 (s, 3H), 4.67 (d, *J* = 12 Hz, 1H), 5.16 (s, 1H), 6.37 (s, 1H), 7.24 (m, 1H), 7.38 (m, 3H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (125 MHz): δ = 29.9, 52.7, 53.9, 54.1, 58.7, 66.5, 67.3, 69.9, 70.0, 71.3, 127.4, 127.8, 128.2, 128.4, 128.5, 129.1, 129.2, 130.3, 138.1, 138.2, 138.7, 138.8, 139.6, 139.9, 140.5, 141.6, 142.2, 142.4, 142.6, 142.8, 142.9, 143.0, 143.09, 143.10, 143.12, 143.25, 143.28, 143.3, 143.8, 144.0, 144.4, 144.5, 144.6, 144.9, 145.0, 145.1, 145.2, 145.4, 145.5, 145.6, 145.7, 145.78, 145.8, 146.2, 146.3, 147.2, 147.24, 147.4, 147.5, 148.0, 148.1, 148.2, 148.4, 148.5, 149.0, 149.9, 150.9, 156.2, 157.4, 164.0, 164.4, 172.9. MS (ES +ve): *m/z* 1106 (M^{+}).

15'-N-(Diphenylmethyl)amino-3'-methyl-40H-3,21-(oxooxymethano[1,4]benzenomethanooxyoxomethano)-3'H-cyclopropa[1,9](C$_{60}$, I$_h$)fullerene-3'-carboxylate **(14)**

The title compound was prepared from **6** (0.023 g, 0.020 mmol) and 1 M $NaCNBH_3$ in THF (0.630mL, 0.630mmol) with boron trifluoride-diethyl etherate (0.05 mL), and glacial acetic acid (1 drop), and the mixture was stirred for 18 h. Purification using flash column chromatography (DCM/hexane, 30 : 20) yielded **14** as a brown solid (0.013 g, 50%). ^{1}H NMR (500 MHz): δ = 3.38 (d, *J* = 13.5 Hz, 1H, NH), 3.99 (s, 3H), 4.54 (d, *J* = 13.5 Hz, 1H), 4.69 (d, *J* = 11.0 Hz, 1H), 4.81 (d, *J* = 11.0 Hz, 1H), 5.18 (s, 1H), 5.69 (d, *J* = 11.0 Hz, 1H), 5.75 (d, *J* = 11.0 Hz, 1H), 6.11 (s, 1H), 7.13 (m, 2H), 7.31 (m, 1H) 7.39

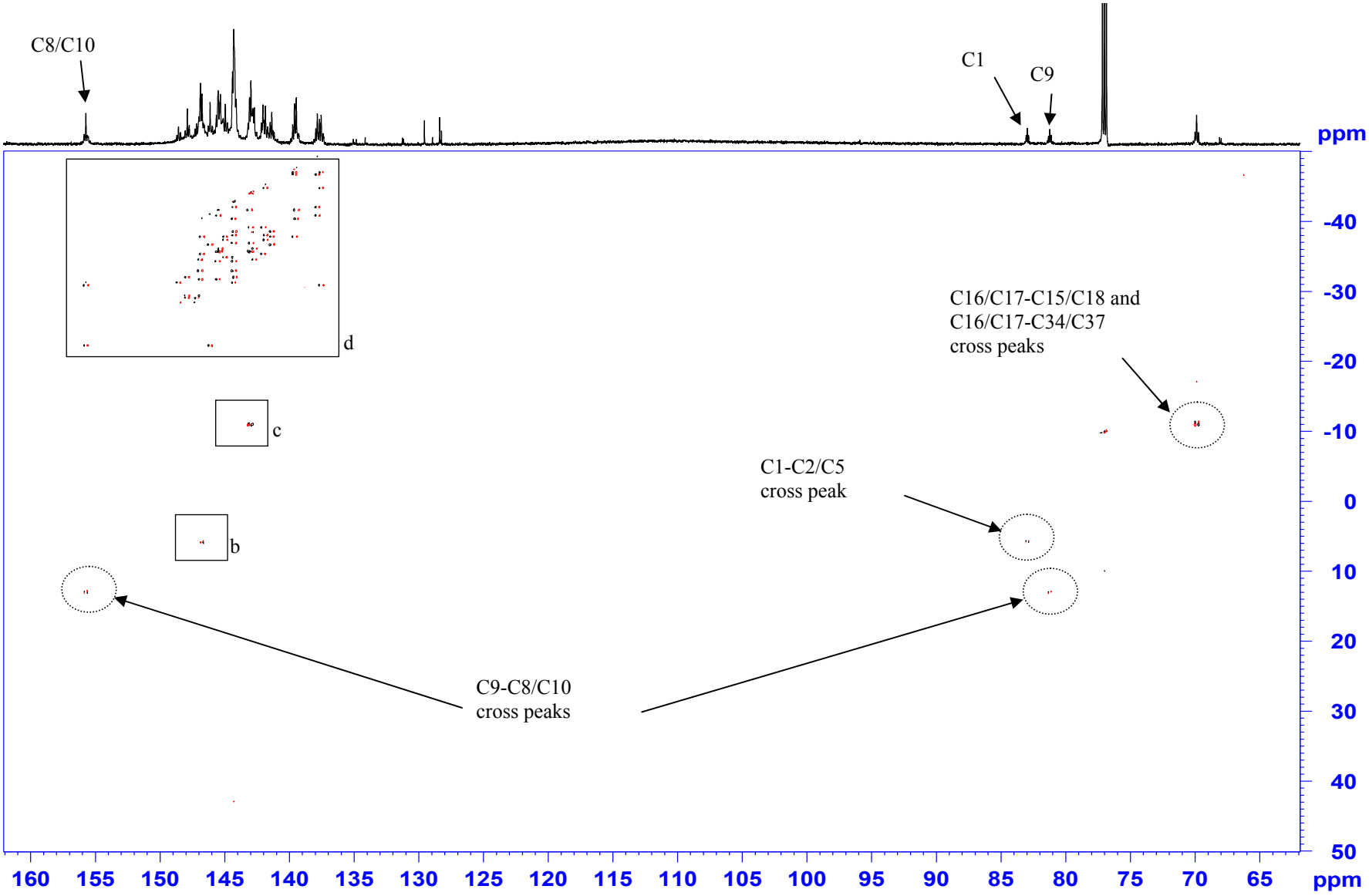
(t, *J* = 7.5 Hz), 7.54 (t, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.76 (s, 1H) 7.82 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (125 MHz): δ = 53.9, 60.8, 66.2, 66.7, 66.8, 68.2, 69.2, 69.3, 70.6, 127.2, 127.6, 128.1, 128.2, 128.8, 128.9, 129.1, 130.5, 130.6, 134.7, 134.8, 137.7, 137.8, 138.2, 138.5, 139.0, 139.9, 140.8, 140.9, 141.9, 142.0, 142.3, 142.5, 142.58, 142.6, 142.62, 142.7, 142.8, 142.9, 142.94, 143.2, 143.4, 143.5, 143.6, 143.7, 144.0, 144.1, 144.15, 144.16, 144.2, 144.3, 144.5, 144.6, 144.7, 144.72, 144.8, 144.9, 145.1, 145.2, 145.3, 145.6, 145.8, 146.1, 146.8, 146.9, 147.4, 147.6, 147.7, 147.8, 148.1, 148.2, 148.5, 148.7, 149.2, 155.6, 156.9, 161.2, 163.6, 171.7. MS (ES -ve): *m/z* 1179 (M^-).

^{13}C NMR Spectra of **6** (201.2 MHz, 298K, $CDCl_3$):

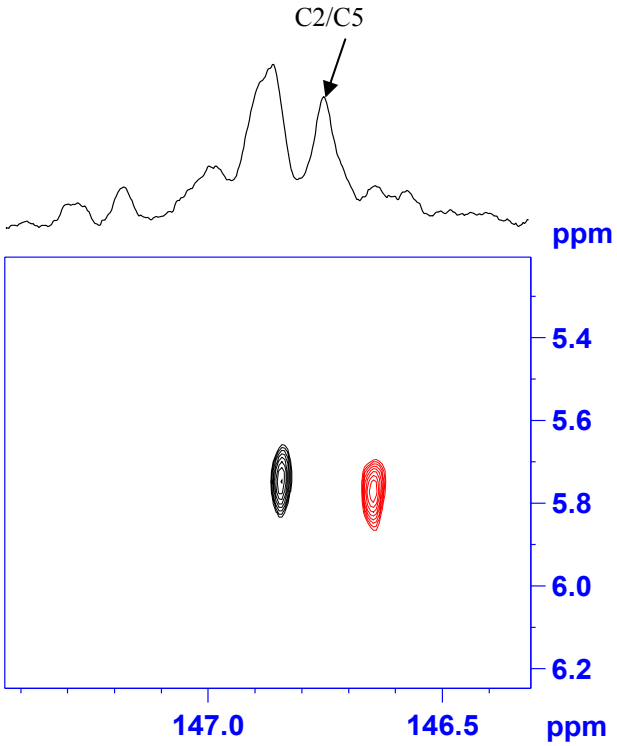


a: natural abundance
b: ^{13}C labeled

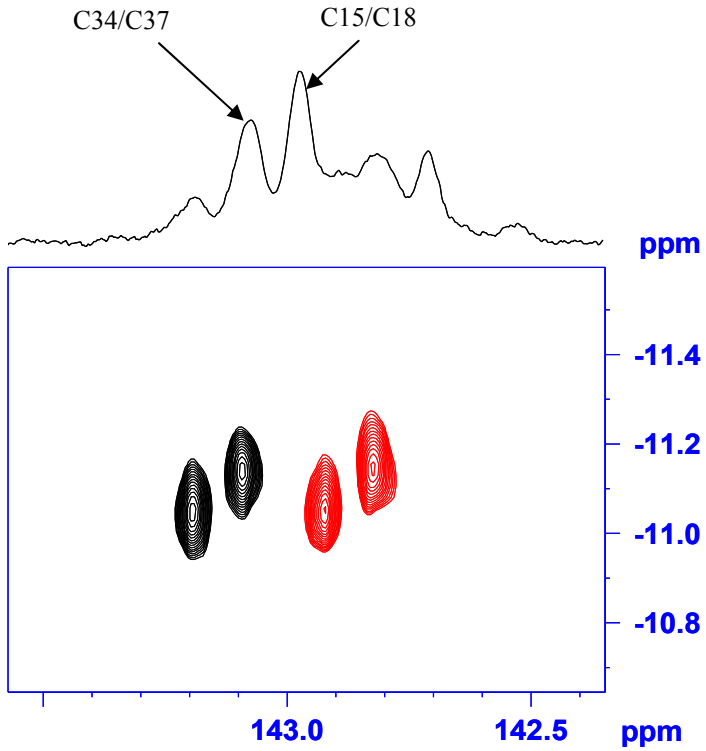
INADEQUATE full spectrum of **6** deliberately folded in F_1. 201.2 MHz, 298K, $CDCl_3$. Labels b, c and d outline areas of expansion below.



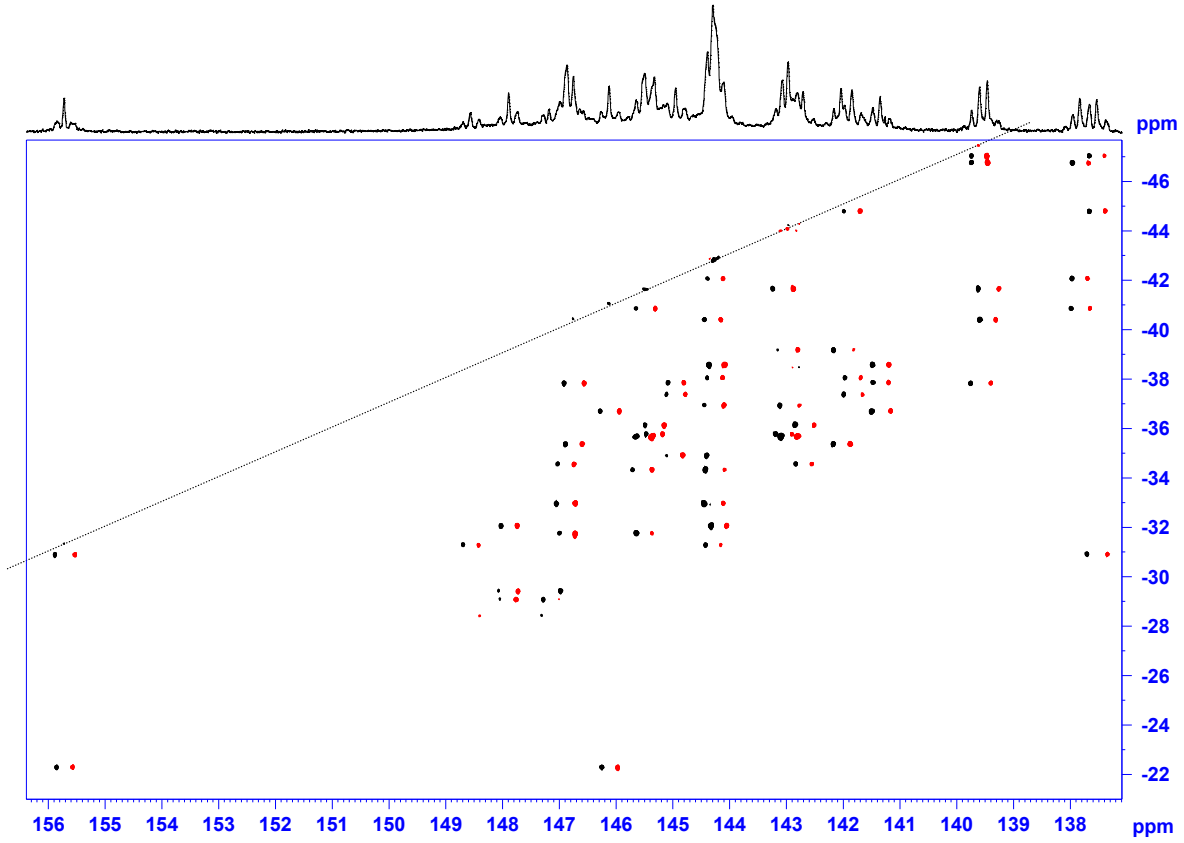
b) Expansion of C1-C2/C5 cross peak



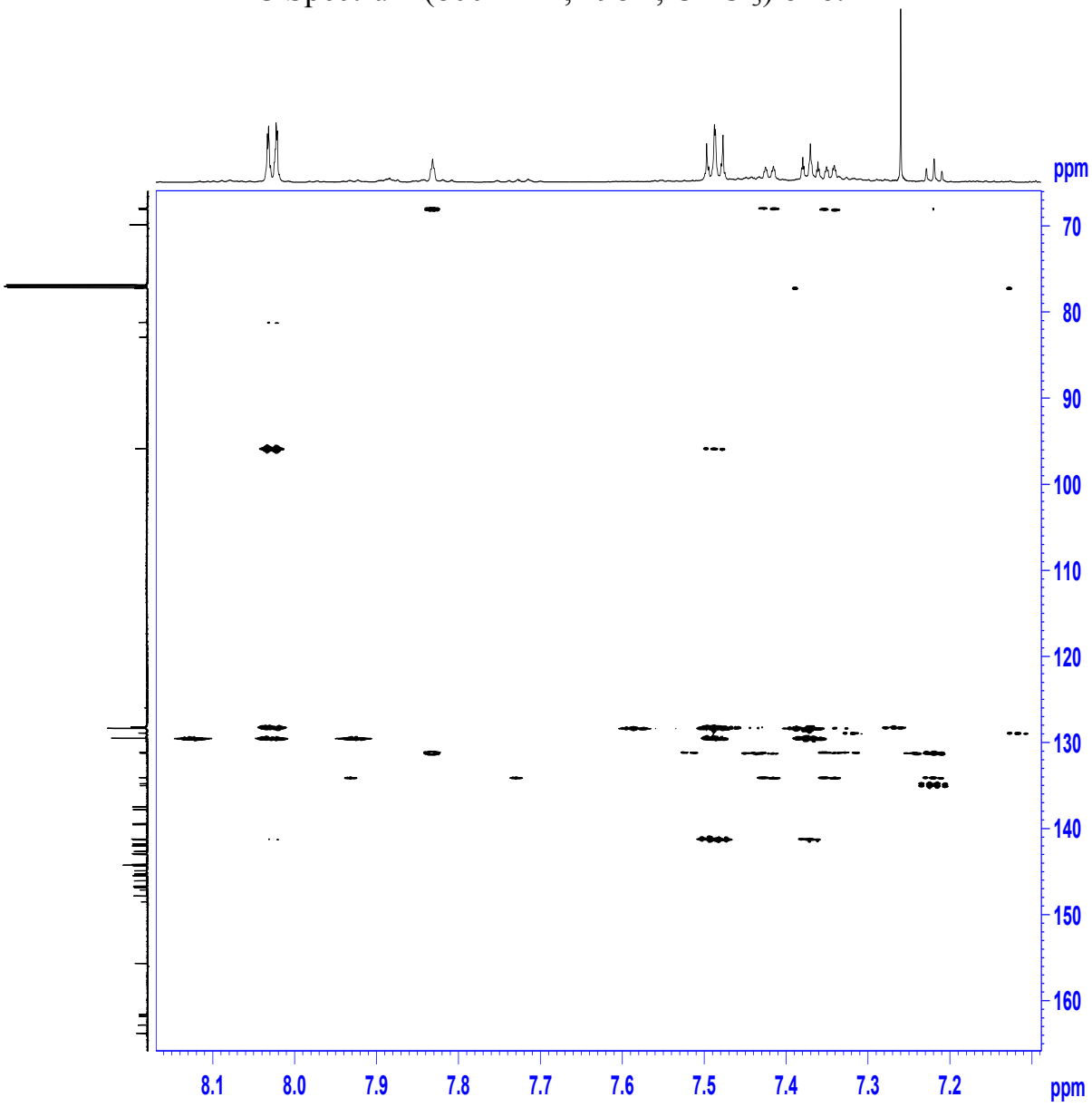
c) Expansion of C16/C17-C15/C18 and C16/C17-C34/C37 cross peak



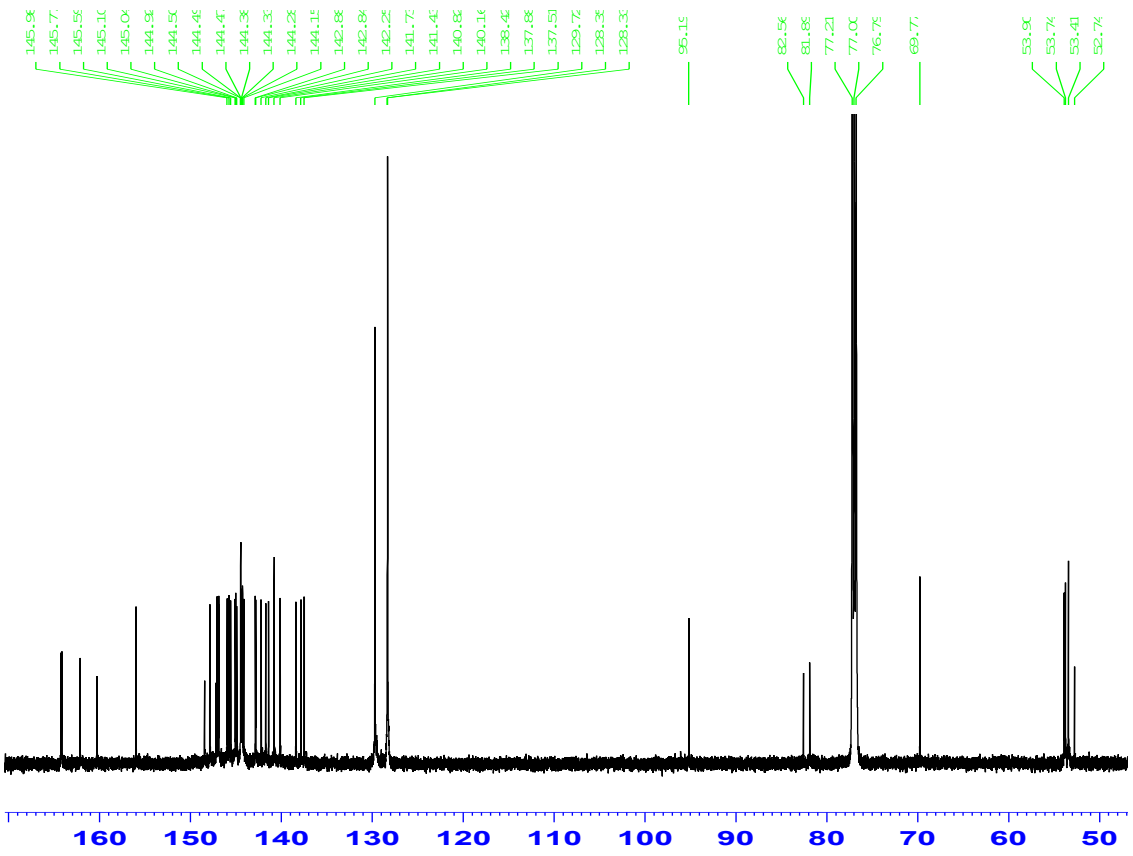
d) Expansion of the region containing sp^2 fullerenyl carbons. Artifact peaks are visible along the dotted line.



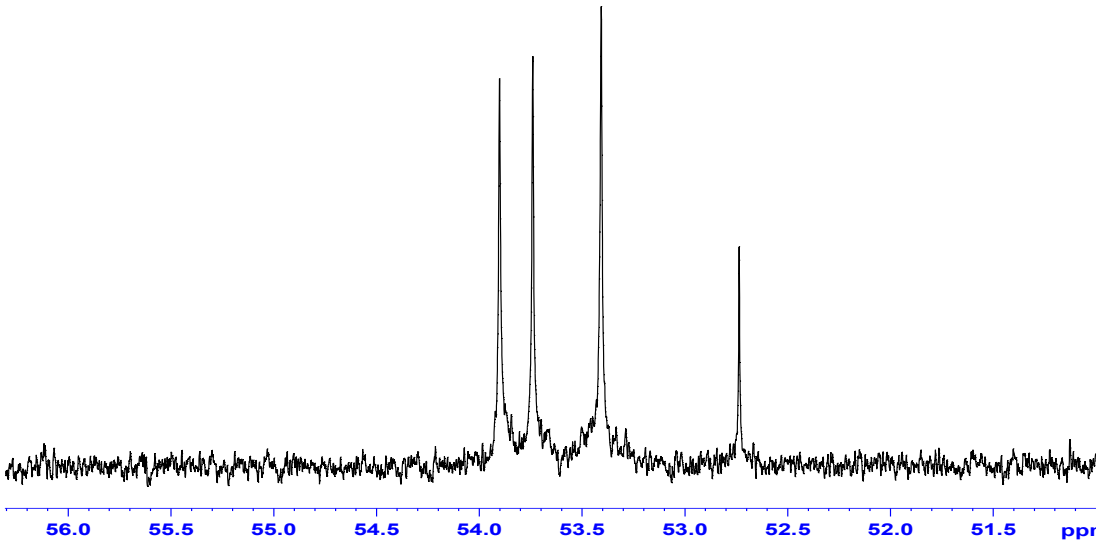
HMBC Spectrum (800 MHz, 298K, $CDCl_3$) of **6**:



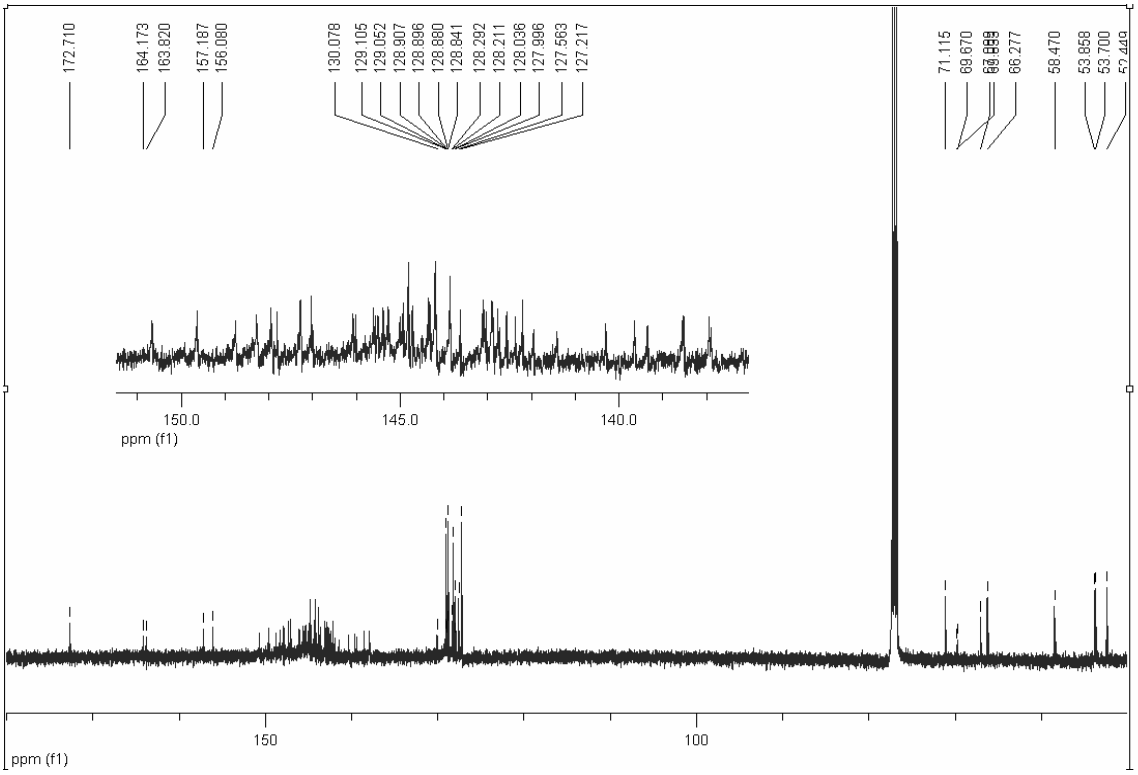
^{13}C NMR Spectrum of **12** (150.9MHz, 298K, $CDCl_3$):



^{13}C spectrum of **12** (expansion to show non equivalence of 3 methoxy groups):



^{13}C NMR Spectrum of **13** (100 MHz, 298K, $CDCl_3$): with expansion of fullerenyl sp^2 region:



^{13}C NMR Spectrum of **14** (150.9 MHz, 298K, $CDCl_3$):