Supporting Information

Palladium-Catalyzed Three-Component Tandem Coupling-Carboannulation Reaction Leading to Polysubstituted [60]Fullerene-Fused Cyclopentanes

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1. General Information

Unless otherwise specified, all reagents were purchased as reagent grade and used without further purification. $Pd(PPh_3)_4$ and (hetero)aryliodides were purchased from Innochem. Rb_2CO_3 was purchased from Energy Chemical. 2-(buta-2,3-dien-1-yl)malonates **2a**,[1] **2b**,[1] **2c**,[2] **2d**,[3] **2e**,[1b,4] **2f**,[1b] and aryliodide **3o**[5] was prepared by following the literature procedure. 1,2-Dichlorobenzene (ODCB) were treated with CaH_2. ^{1}H NMR (400 and 600 MHz) and ^{13}C NMR (100 and 150 MHz) were registered on Bruker 400 and 600 M spectrometers with tetramethylsilane (TMS) as internal standard. UV–vis Spectra were recorded on Shimadzu UV-1700. CVs were recorded on CHI660E. FT-IR was registered on Thermo Nicolet NEXUS 670 FTIR. HRMS were measured on Bruker Ultraflextreme MALDI-TOF/TOF using *E*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix.

References:

(1) (a) Naidu, V. R.; Posevins, D.; Volla, C. M. R.; Bäckvall, J.-E. *Angew. Chem. Int. Ed.* **2017**, *56*, 1590. (b) Tsukamoto, H.; Ito, K.; Doi, T. *Chem. Commun.* **2018**, *54*, 5102.

(2) Cérat, P.; Gritsch, P. J.; Goudreau, S. R.; Charette, A. B. *Org. Lett.* **2016**, *18*, 1410.

(3) Meguro, M.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 694.

(4) Ahmar, M.; Cazes, B.; Gore, J. *Tetrahedron*, **1987**, *43*, 3453.

(5) Deng, R.; Huang, Y.; Ma, X.; Li, G.; Zhu, R.; Wang, B.; Kang, Y.-B.; Zhenhua Gu, Z. *J. Am. Chem. Soc.* **2014**, *136*, 4472.

2. Experimental Procedures

*General Procedure for the Synthesis of Products **4**:* A dry 15-mL tube equipped with a magnetic stirrer was charged with C_{60} (36.0 mg, 0.05 mmol), **2a** (0.1 mmol), **3a** (0.1 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol). After dissolving the solids in anhydrous ODCB (4 mL) and MeCN (1 mL) by sonication, the sealed tube was stirred in an oil bath preset at a designated temperature for a desired time (monitored by TLC) in air. The reaction mixture was filtered through a silica gel plug to remove any insoluble material. After the solvent had been evaporated under vacuum, the residue was separated on a silica gel column with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM to give product **4**.

*Typical Procedure for the Synthesis of Product **4aa** from $Pd(PPh_3)_4$−catalyzed Reaction of C_{60} with Substrates **2a** and **3a** at a minimum 1 mmol scale*: A dry 200-mL tube equipped with a magnetic stirrer was charged with C_{60} (720.0 mg, 1.0 mmol), **2a** (0.368 g, 2.0 mmol) and **3a** (0.408 g, 2.0 mmol) and $Pd(PPh_3)_4$ (0.116 g, 0.10 mmol). After dissolving the solids in anhydrous ODCB (80 mL) and MeCN (20 mL) by sonication, the sealed tube was stirred in an oil bath at 100 ^oC for 4 h in air. The reaction mixture was filtered through a silica gel plug to remove any insoluble material. After the solvent had been evaporated under vacuum, the residue was separated on a silica gel column with CS_2 as the eluent to recover unreacted C_{60} (0.360 g), and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give product **4aa**: (0.303 g, 31%).

*Transformations of C_{60}-Fused Cyclopentane **4aa*:** A 50-mL tube equipped with a magnetic stirrer was charged with **4aa** (49.0 mg, 0.05 mmol) and NaOH (20.0 mg, 0.50 mmol). After dissolving the solids in CB (16 mL) and MeOH (4 mL) by sonication, the sealed tube was stirred in an oil bath at 80 ^oC for 18 h in air, and then

acidified with 0.4 mL of acetic acid. The reaction mixture was filtered through a silica gel plug to remove any insoluble material. After the solvent had been evaporated under vacuum, the residue was separated on a silica gel column with CS_2/DCM/EtOAc (v/v/v = 10:5:2) as the eluent to give product **6** (30.0 mg, 66%).

Procedures for UV-Vis Spectra Recording: A dry 100-mL volumetric flask was charged with the product **4** (1.4×10^{-3}~1.6×10^{-3} mmol). After dissolving the solid with 100 mL of $CHCl_3$ by sonication, a small amount of sample solution is added to a cuvette and then placed in the UV-vis spectrophotometer to record the UV-vis spectrum of product **4**.

Procedures for Electrochemical Characterization Recording: In dry 15-mL electrolytic cup, 2.0×10^{-3} mmol of product **4**, 2 mL of the solution of $(n\text{-Bu})_4NClO_4$ in ODCB (0.1 M), and 18 μL of the solution of ferrocene in ODCB (0.054 M) was added, respectively. After sonication, three different electrodes (reference electrode: SCE; working electrode: Pt; auxiliary electrode: Pt wire) were placed in the sample solution, then running electrochemical workstation recorded the cyclic voltammogram (CV) of product **4** under argon atmosphere.

3. UV–vis Spectra of Compounds

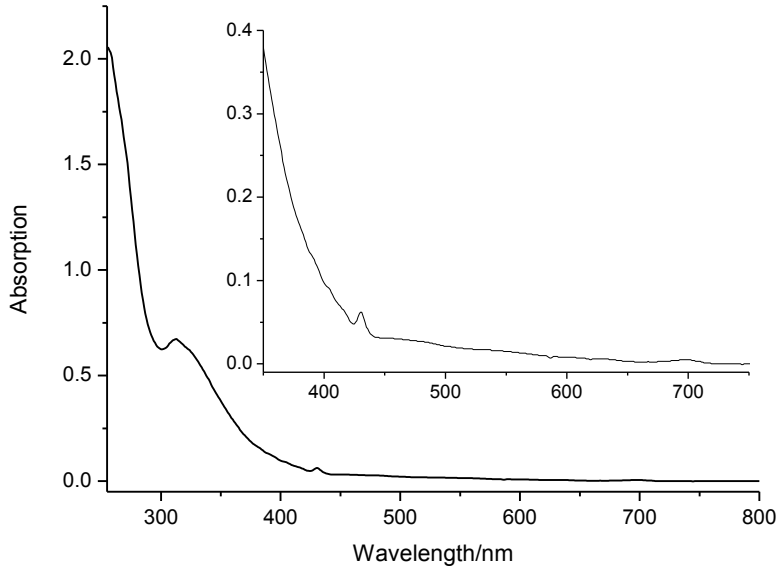


Figure S1. UV–vis spectrum of compound **4aa** in $CHCl_3$

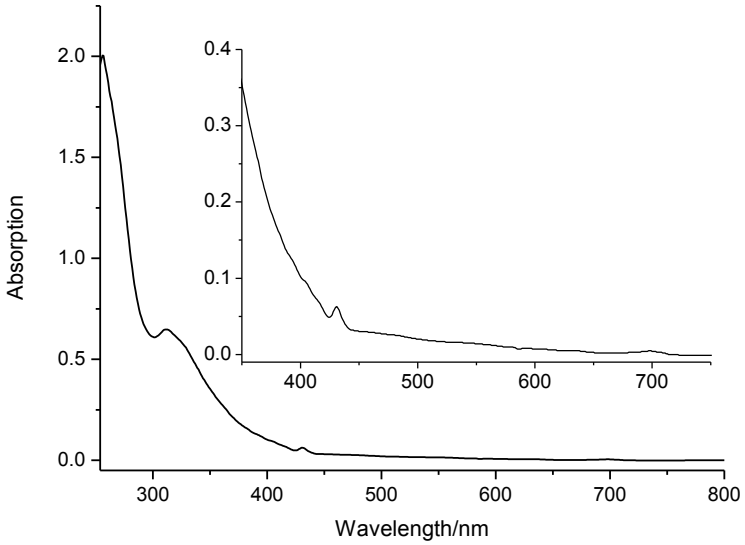


Figure S2. UV–vis spectrum of compound **4ab** in $CHCl_3$

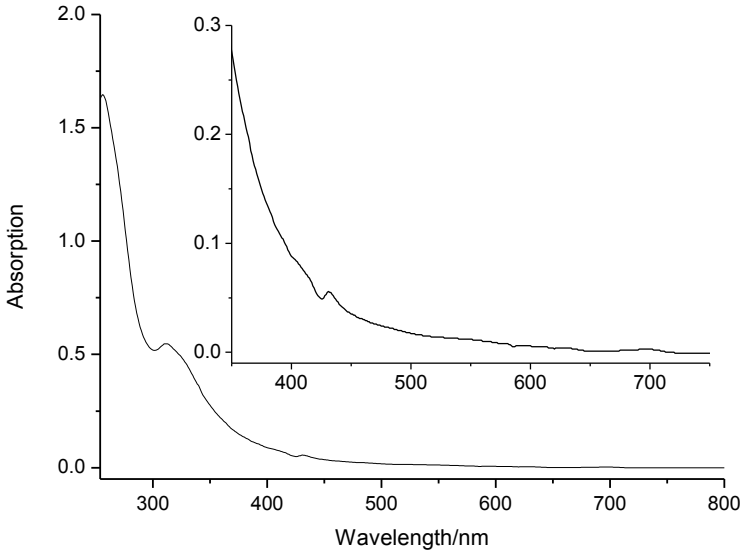


Figure S3. UV–vis spectrum of compound **4ac** in $CHCl_3$

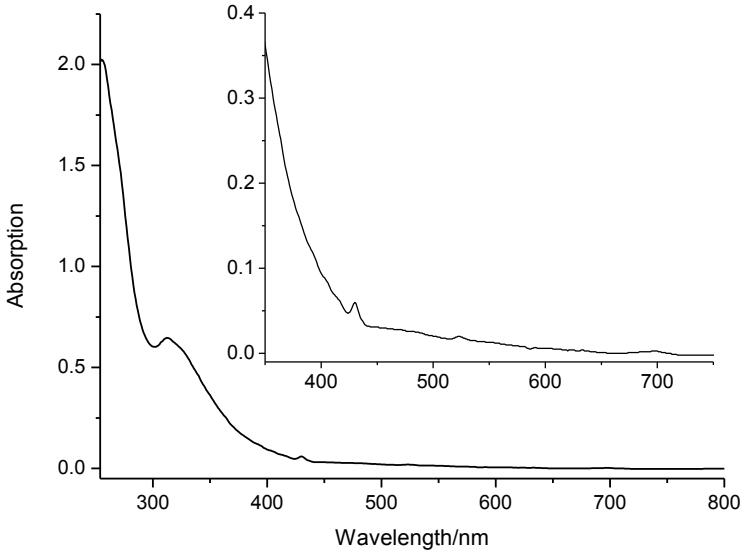


Figure S4. UV–vis spectrum of compound **4ad** in $CHCl_3$

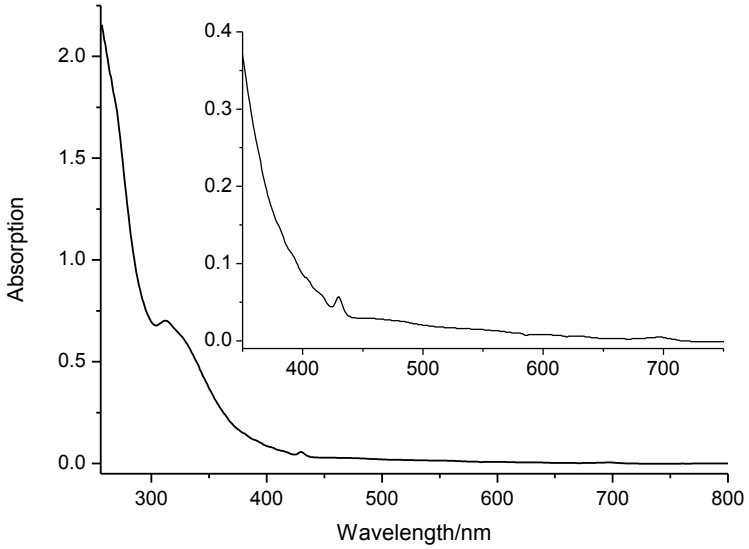


Figure S5. UV–vis spectrum of compound **4ae** in $CHCl_3$

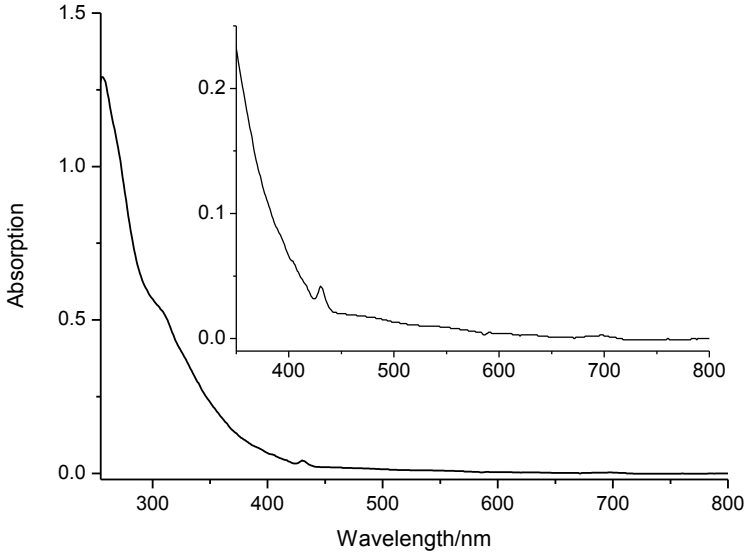


Figure S6. UV–vis spectrum of compound **4af** in $CHCl_3$

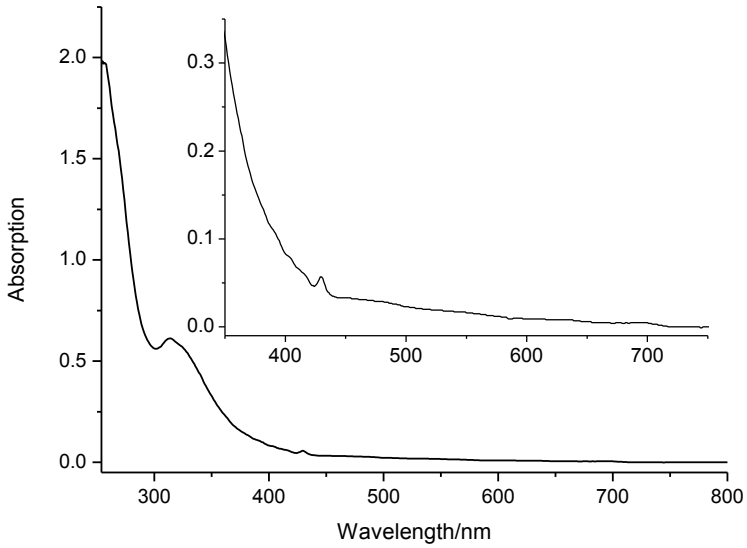


Figure S7. UV–vis spectrum of compound **4ag** in $CHCl_3$

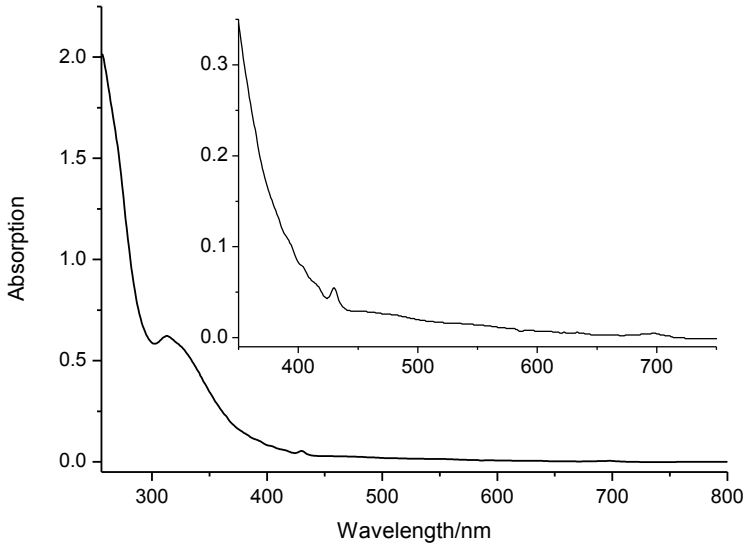


Figure S8. UV–vis spectrum of compound **4ah** in $CHCl_3$

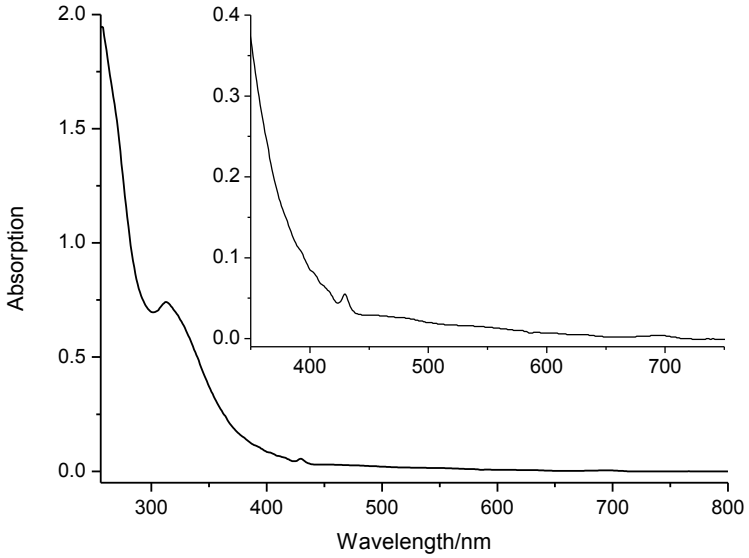


Figure S9. UV–vis spectrum of compound **4ai** in $CHCl_3$

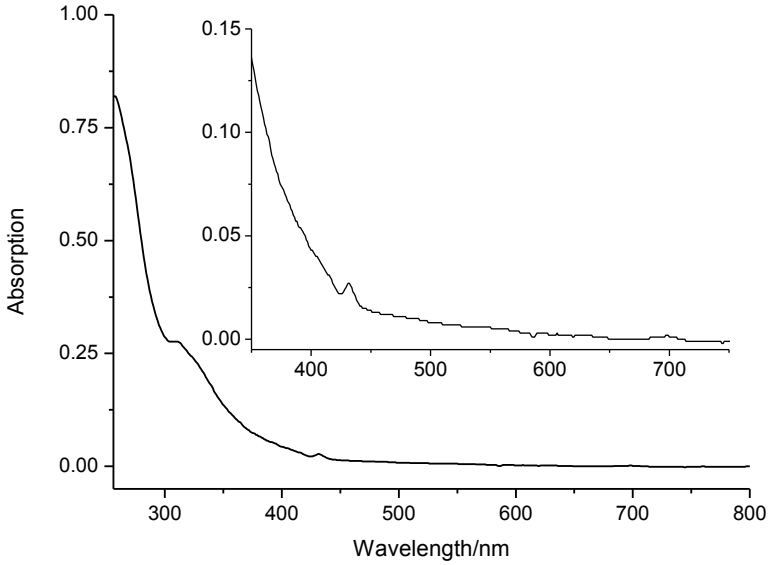


Figure S10. UV–vis spectrum of compound **4aj** in $CHCl_3$

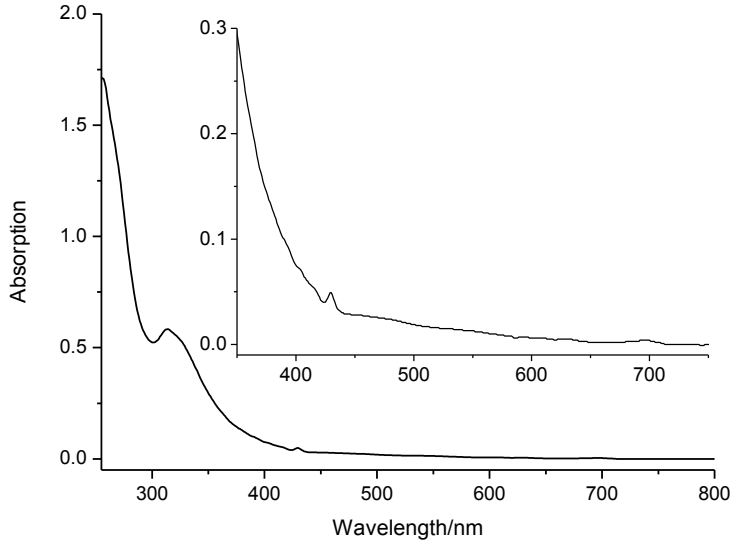


Figure S11. UV–vis spectrum of compound **4ak** in $CHCl_3$

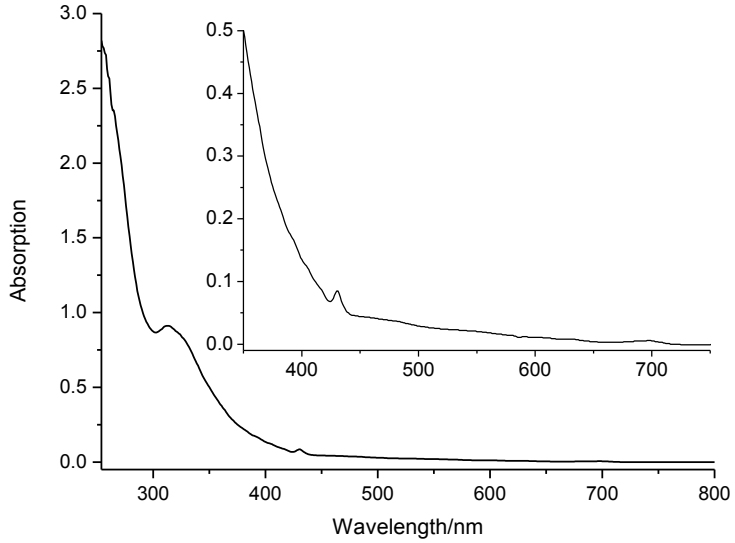


Figure S12. UV–vis spectrum of compound **4al** in $CHCl_3$

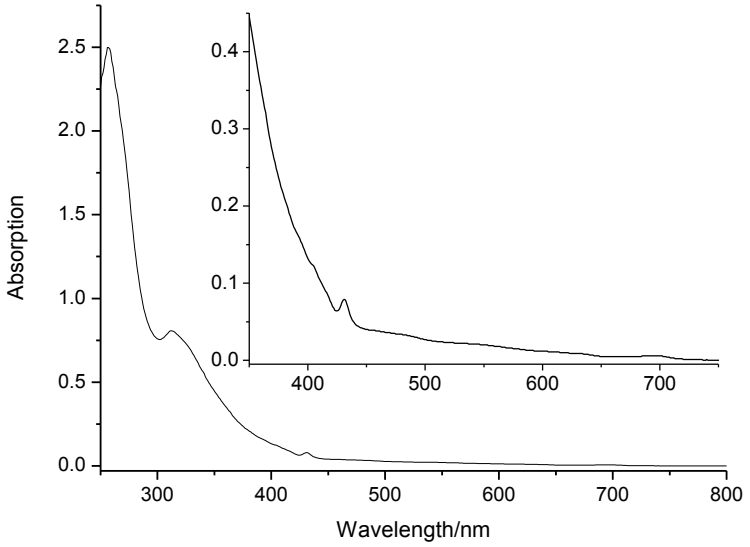


Figure S13. UV–vis spectrum of compound **4am** in $CHCl_3$

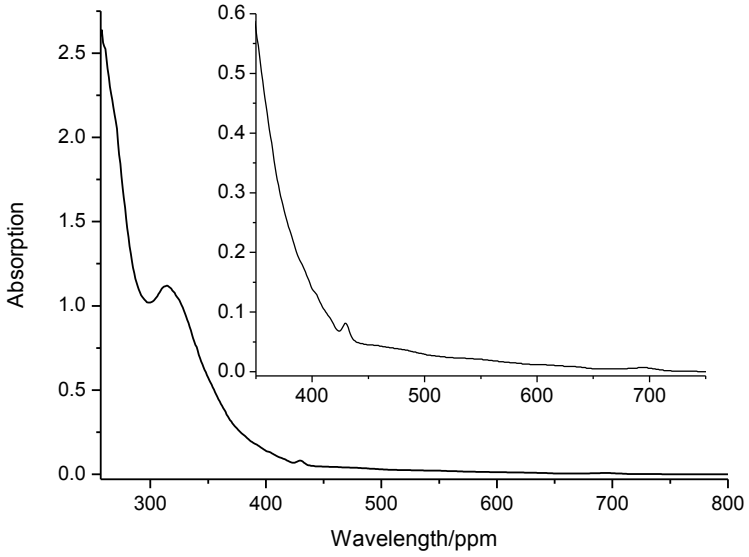


Figure S14. UV–vis spectrum of compound **4an** in $CHCl_3$

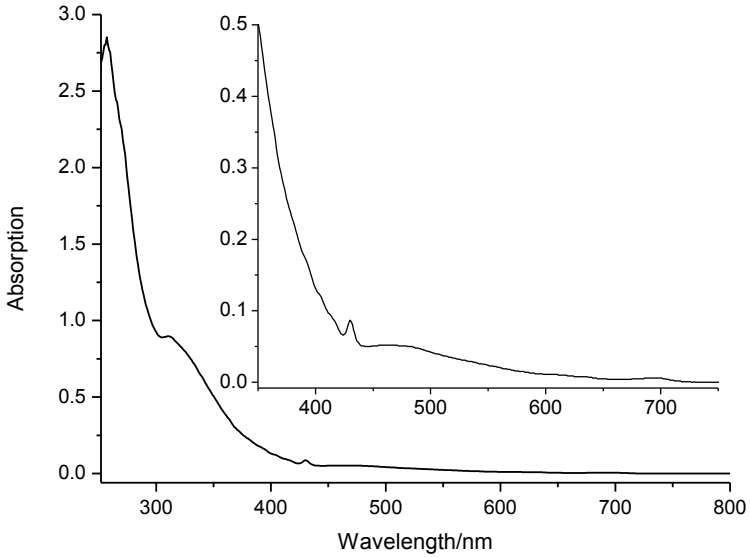


Figure S15. UV–vis spectrum of compound **4ao** in $CHCl_3$

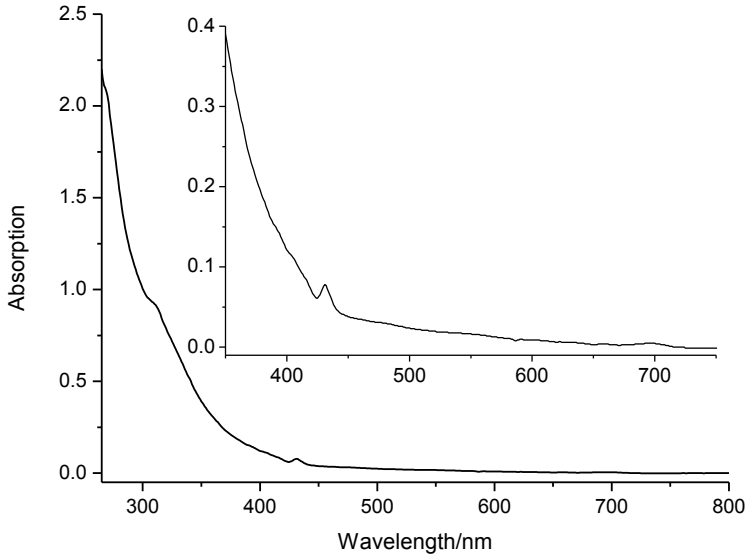


Figure S16. UV–vis spectrum of compound **4ap** in $CHCl_3$

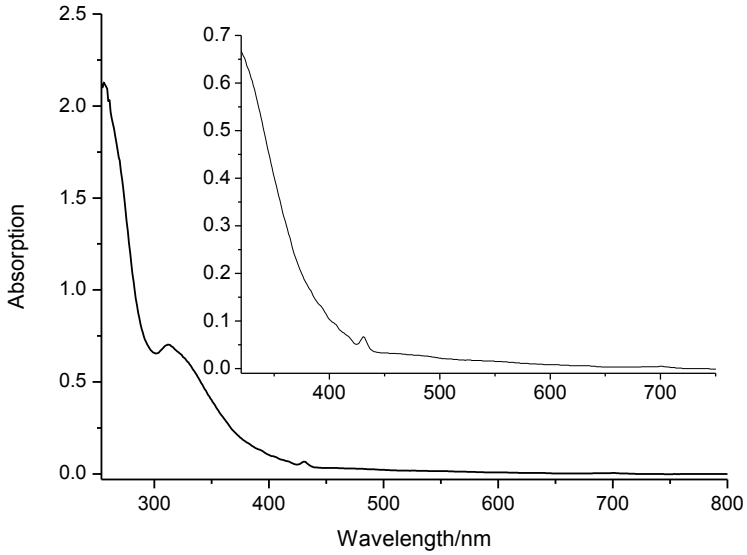


Figure S17. UV–vis spectrum of compound **4ba** in $CHCl_3$

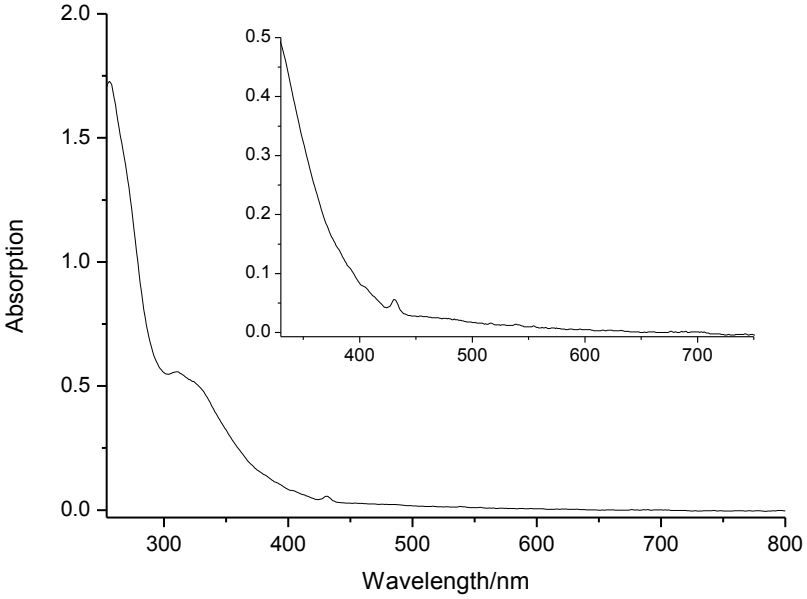
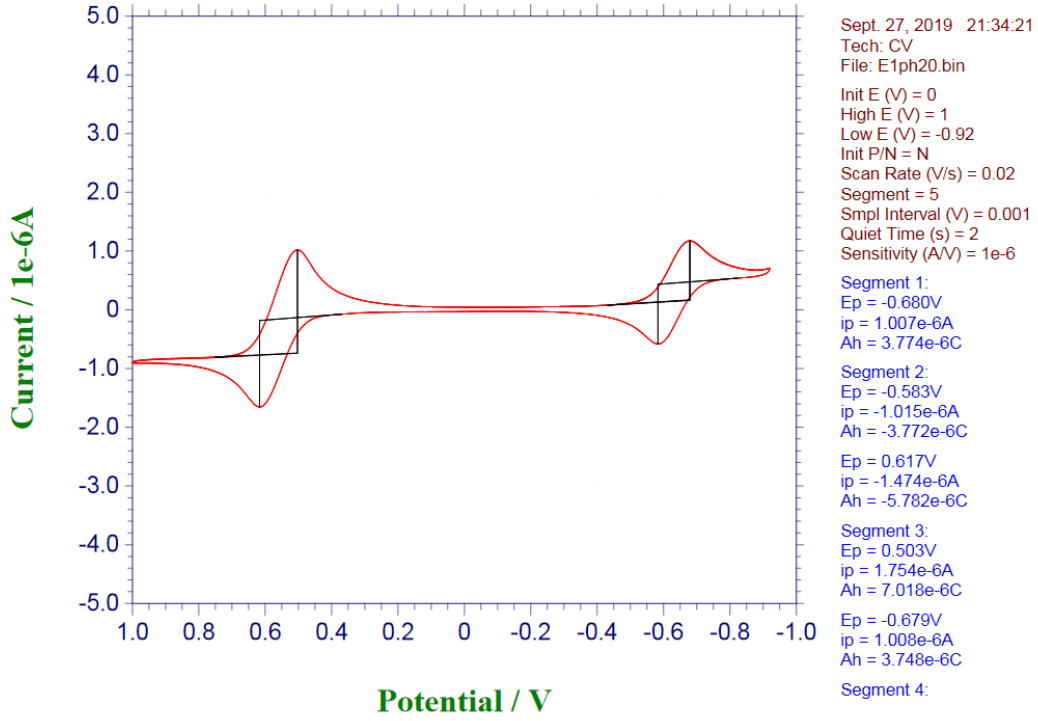
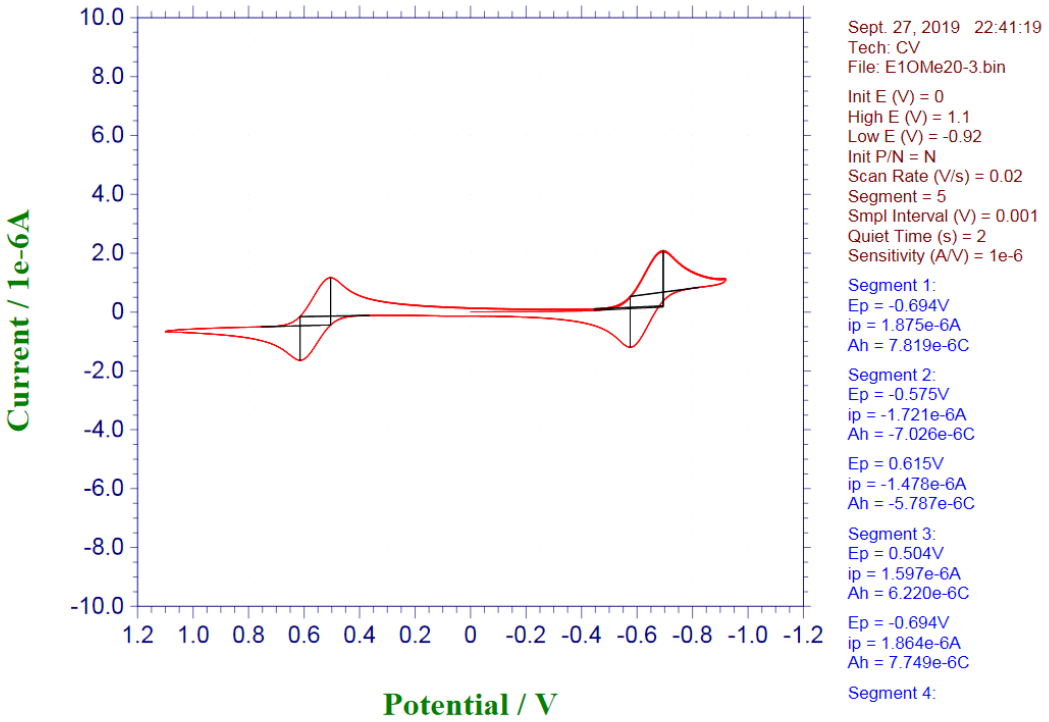


Figure S18. UV–vis spectrum of compound **6** in $CHCl_3$

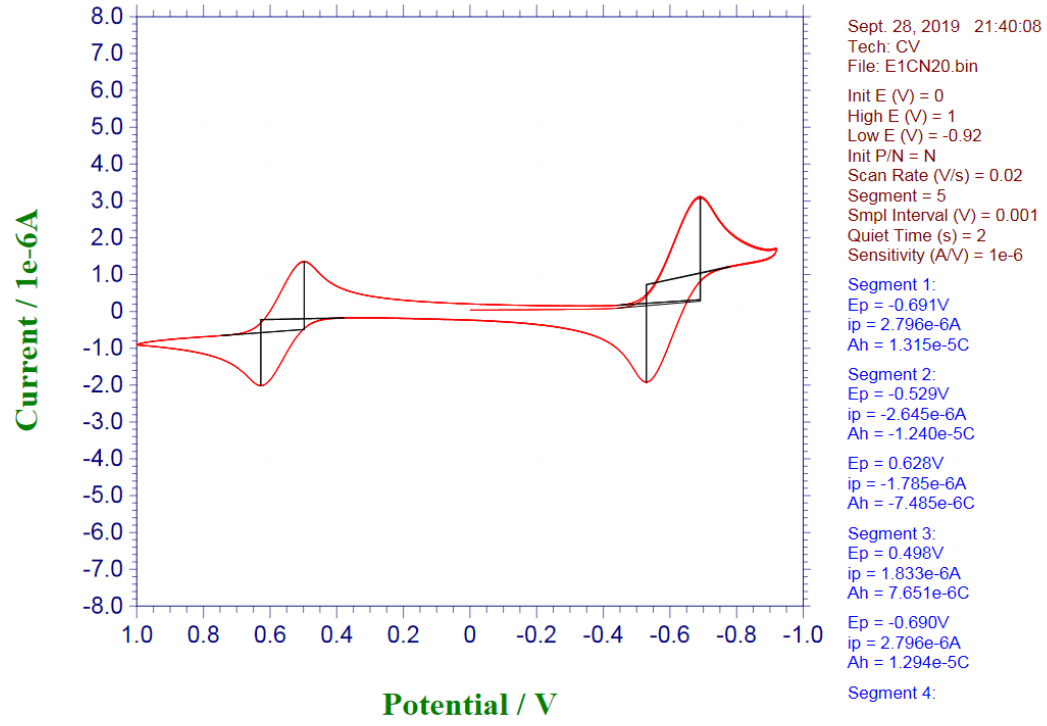
4. CVs of Selected Compounds



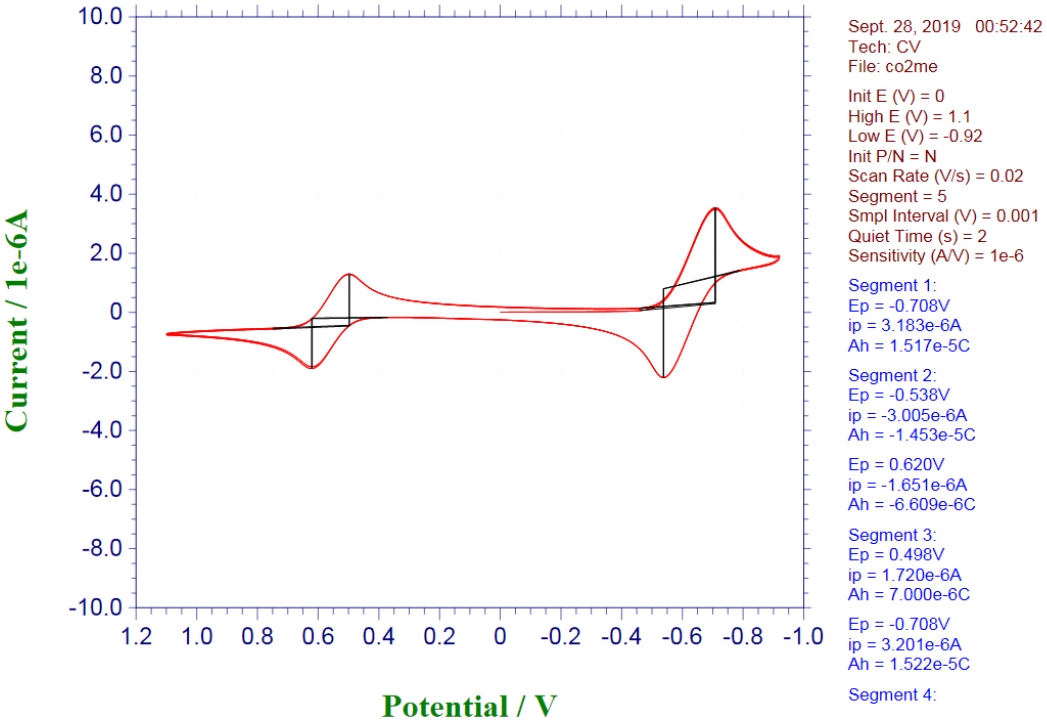
Cyclic voltammogram of compound **4aa** (scanning rate: 20 mV s^{-1})



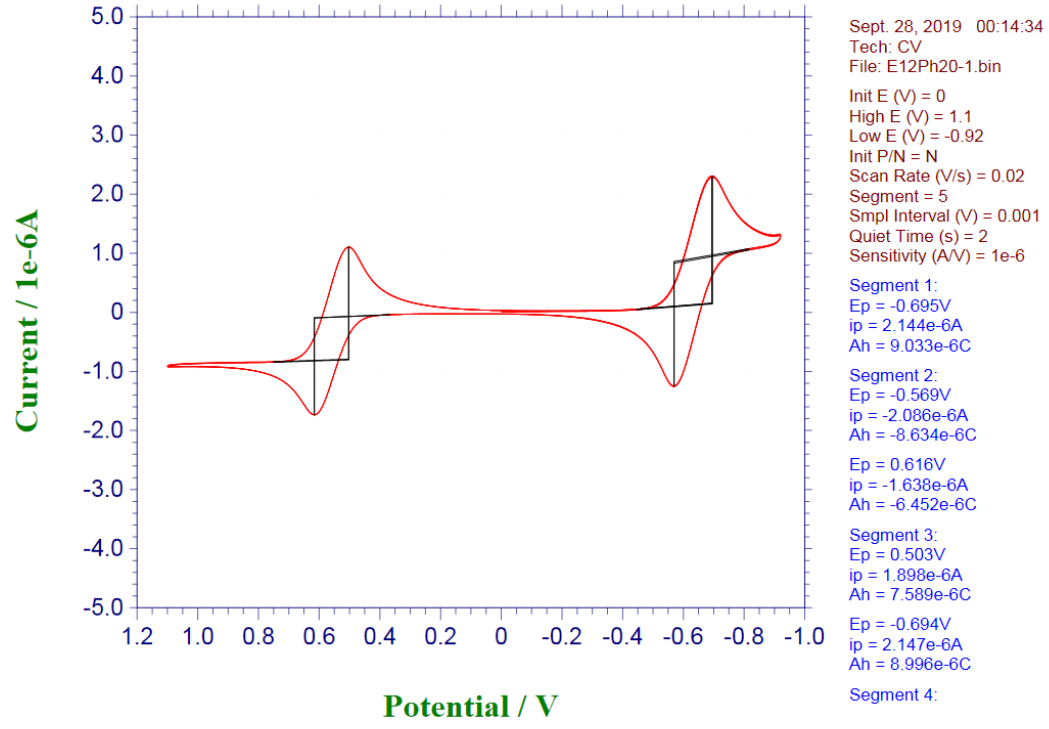
Cyclic voltammogram of compound **4ac** (scanning rate: 20 mV s^{-1})



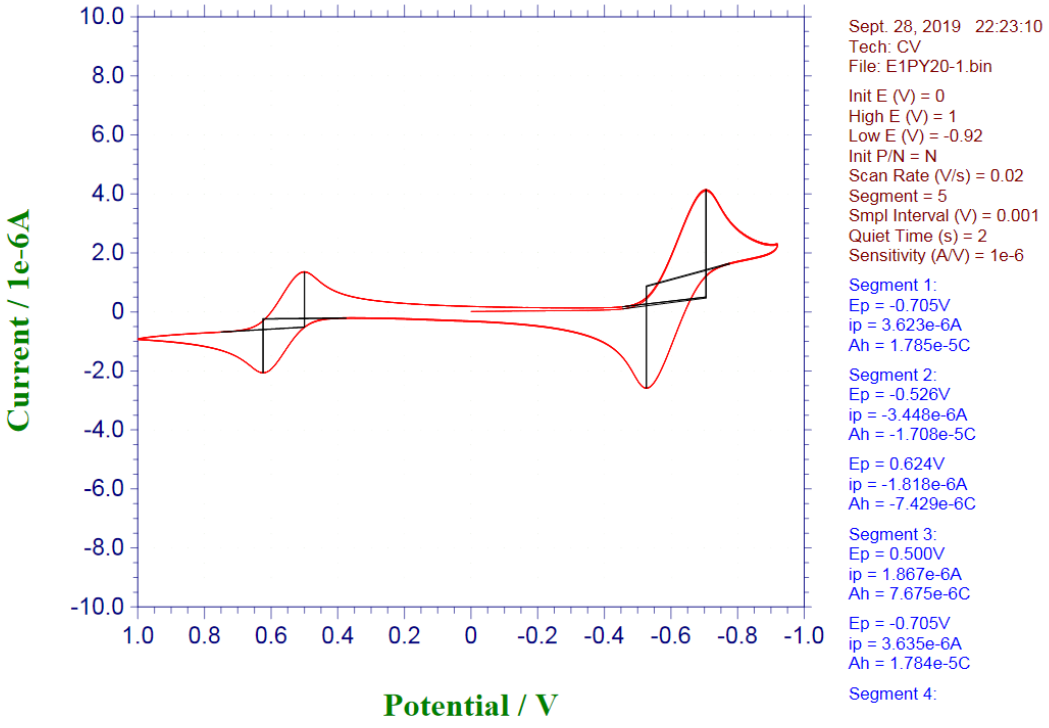
Cyclic voltammogram of compound **4ag** (scanning rate: 20 mV s^{-1})



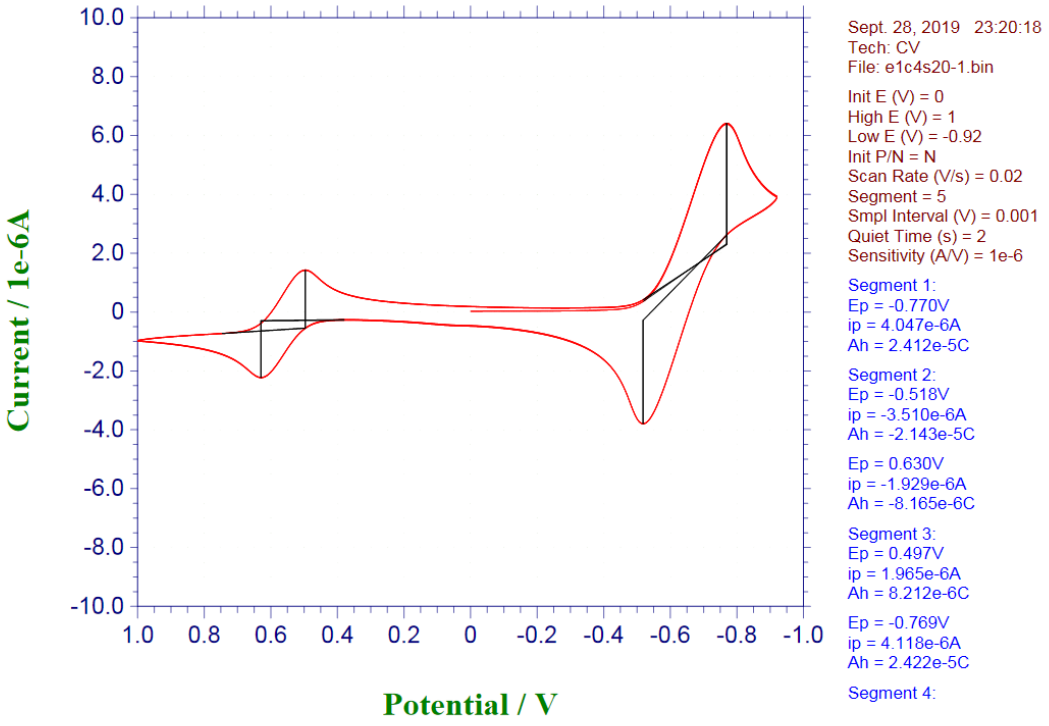
Cyclic voltammogram of compound **4ah** (scanning rate: 20 mV s^{-1})



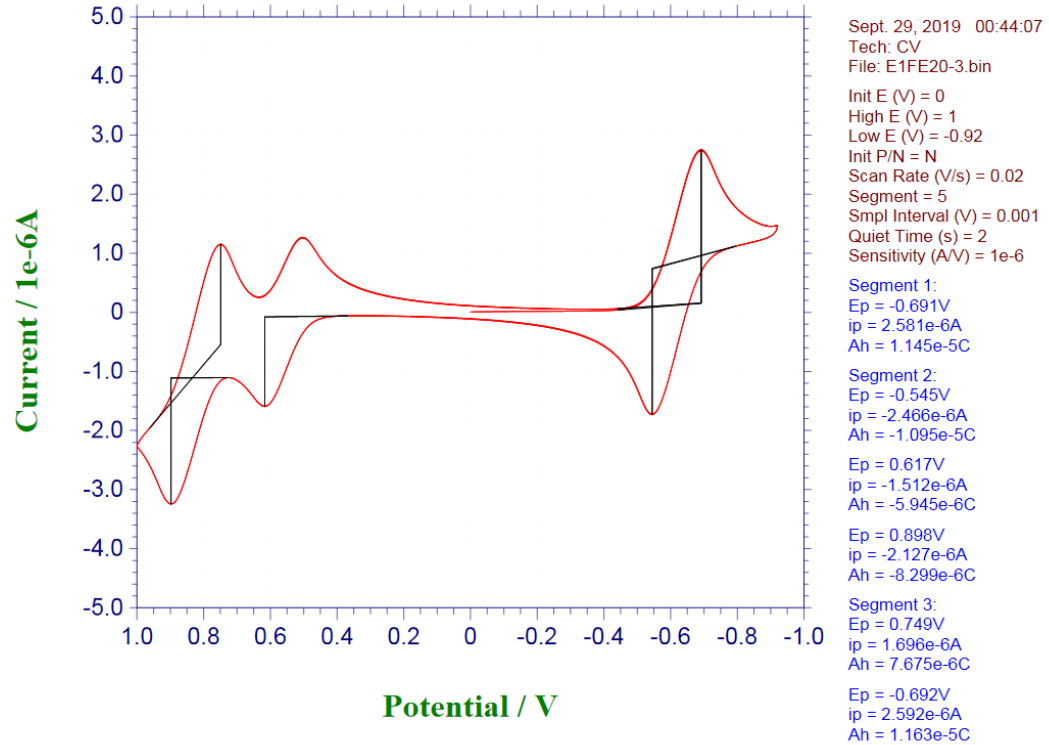
Cyclic voltammogram of compound **4aj** (scanning rate: 20 mV s^{-1})



Cyclic voltammogram of compound **4ak** (scanning rate: 20 mV s^{-1})

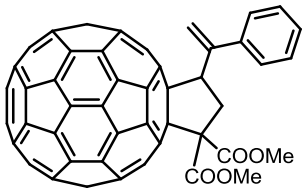


Cyclic voltammogram of compound **4am** (scanning rate: 20 mV s^{-1})



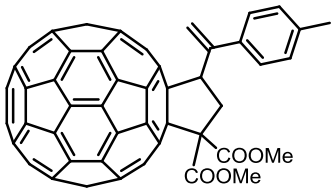
Cyclic voltammogram of compound **4ao** (scanning rate: 20 mV s^{-1})

5. Synthesis and Spectral Data for Compounds 4 and 6



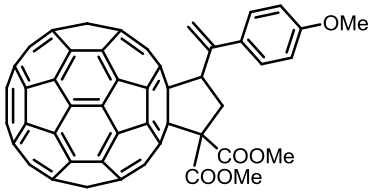
4aa

Compound **4aa**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) as the eluent to give **4aa** (16.7 mg, 34%), amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45–7.44 (m, 2H), 7.20–7.18 (m, 3H), 5.71 (s, 1H), 5.70 (s, 1H), 5.32 (dd, *J* = 14.4, 3.6 Hz, 1H), 4.16 (t, *J* = 14.4 Hz, 1H), 4.10 (s, 3H), 3.80 (s, 3H), 3.19 (dd, *J* =13.2, 4.2 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$) δ 171.1, 168.9, 154.7, 154.1, 152.1, 151.2, 147.3, 147.2, 146.9, 146.6, 146.5, 146.4, 146.39, 146.3, 146.2, 146.1, 146.0, 145.93, 145.91, 145.9, 145.8, 145.7, 145.6, 145.33, 145.3, 145.27, 145.24, 145.2, 145.1, 145.0, 144.7, 144.6, 144.5, 144.2, 143.1, 143.0, 142.7, 142.66, 142.5, 142.3, 142.2, 142.1, 141.9, 141.8, 141.7, 141.66, 141.53, 141.5, 141.2, 141.15, 141.1, 139.7, 138.9, 138.8, 138.7, 138.3, 137.0, 136.4, 134.7, 128.3, 128.2, 127.7, 117.3, 74.6, 74.0, 68.9, 53.6, 53.4, 52.9, 51.9, 37.6; FT-IR ν/cm^{-1} (KBr) 2946, 1735, 1430, 1266, 1243, 1192, 1173, 1138, 1113, 1080, 903, 775, 697, 527; UV-vis ($CHCl_3$) λ_{max}/nm 255, 313, 430, 590, 633, 697; MALDI-TOF MS *m/z* calcd for $C_{75}H_{16}O_4$ $[M]^-$ 980.1054, found 980.1052.



4ab

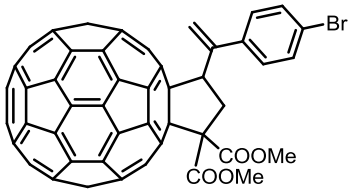
Compound **4ab**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **4ab** (13.4 mg, 27%), amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 5.69 (s, 1H), 5.66 (s, 1H), 5.31 (dd, *J* = 14.4, 3.6 Hz, 1H), 4.17 (t, *J* = 14.4 Hz, 1H), 4.10 (s, 3H), 3.81 (s, 3H), 3.21 (dd, *J* = 13.6, 4.0 Hz, 1H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 171.6, 169.4, 155.0, 154.4, 152.3, 151.4, 147.5, 147.4, 147.1, 146.9, 146.6, 146.5, 146.4, 146.3, 146.26, 146.2, 146.1, 146.08, 146.05, 146.0, 145.9, 145.89, 145.8, 145.7, 145.44, 145.42, 145.4, 145.38, 145.3, 145.2, 145.1, 144.8, 144.7, 144.6, 144.3, 143.2, 143.1, 142.9, 142.8, 142.76, 142.7, 142.5, 142.45, 142.3, 142.2, 142.1, 141.9, 141.8, 141.7, 141.3, 141.28, 139.7, 139.1, 138.9, 138.8, 138.4, 138.1, 137.1, 136.4, 134.7, 129.1, 127.7, 116.8, 74.8, 74.2, 69.1, 53.8, 53.3, 52.1, 37.7, 21.3; FT-IR *v*/cm^{-1} (KBr) 2946, 1739, 1430, 1262, 1189, 1170, 1137, 1078, 900, 821, 735, 526; UV-vis ($CHCl_3$) λ_{max}/nm 256, 312, 431, 590, 697; MALDI-TOF MS *m/z* calcd for $C_{76}H_{18}O_4$ [M]$^-$ 994.1211, found 994.1209.



4ac

Compound **4ac**: the product mixture was separated and purified by silica gel column

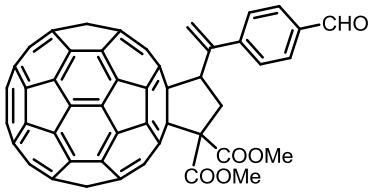
chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 6:1) to give **4ac** (9.9 mg, 20%), amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.38 (m, 2H), 6.76–6.72 (m, 2H), 5.64 (s, 1H), 5.63 (s, 1H), 5.29 (dd, *J* = 14.4, 3.6 Hz, 1H), 4.17 (t, *J* = 14.0 Hz, 1H), 4.10 (s, 3H), 3.81 (s, 3H), 3.73 (s, 3H), 3.20 (dd, *J* = 13.6, 3.6 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 171.6, 169.4, 159.7, 155.0, 154.4, 152.4, 151.4, 147.5, 147.4, 147.1, 146.9, 146.6, 146.5, 146.4, 146.35, 146.2, 146.15, 146.1, 146.05, 145.9, 145.86, 145.7, 145.5, 145.44, 145.4, 145.3, 145.25, 145.2, 144.9, 144.7, 144.6, 144.4, 143.2, 143.17, 142.9, 142.86, 142.8, 142.6, 142.5, 142.48, 142.4, 142.2, 142.1, 142.0, 141.84, 141.8, 141.7, 141.32, 141.3, 139.8, 139.1, 138.9, 138.8, 138.5, 137.1, 136.4, 134.8, 133.9, 129.0, 116.0, 113.8, 74.8, 74.2, 69.2, 55.5, 53.8, 53.3, 52.1, 37.7; FT-IR ν/cm^{-1} (KBr) 2947, 2831, 1735, 1605, 1509, 1452, 1430, 1247, 1177, 1138, 1114, 1078, 1031, 904, 833, 730, 526; UV-vis ($CHCl_3$) λ_{max}/nm 256, 312, 431, 590, 697; MALDI-TOF MS *m/z* calcd for $C_{76}H_{18}O_5$ $[M]^-$ 1010.1160, found 1010.1156.



4ad

Compound **4ad**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **4ad** (21.7 mg, 41%), amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (s, 4H), 5.73 (s, 1H), 5.71 (s, 1H), 5.27 (dd, *J* = 14.4, 3.6 Hz, 1H), 4.16 (t, *J* = 14.4 Hz, 1H), 4.10 (s, 3H), 3.81 (s, 3H), 3.20 (dd, *J*

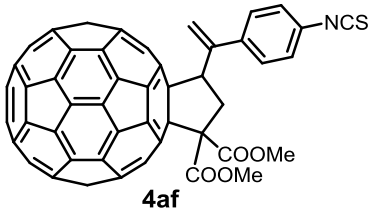
= 13.2, 4.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 171.5, 169.3, 154.6, 154.1, 152.2, 151.2, 147.5, 147.4, 147.0, 146.7, 146.6, 146.56, 146.5, 146.4, 146.23, 146.2, 146.12, 146.1, 145.9, 145.88, 145.85, 145.8, 145.75, 145.7, 145.6, 145.5, 145.48, 145.47, 145.4, 145.3, 145.29, 145.28, 144.9, 144.7, 144.6, 144.4, 143.3, 143.2, 142.9, 142.9, 142.8, 142.6, 142.5, 142.3, 142.25, 142.1, 142.06, 141.84, 141.8, 141.7, 141.4, 141.3, 140.3, 139.7, 139.2, 139.1, 138.8, 138.6, 137.1, 136.7, 134.9, 131.5, 129.4, 122.3, 118.3, 74.8, 74.2, 69.2, 53.8, 53.3, 52.1, 37.6; FT-IR ν/cm^{-1} (KBr) 2945, 1735, 1486, 1430, 1264, 1243, 1190, 1173, 1078, 1007, 907, 830, 764, 734, 575, 526; UV-vis ($CHCl_3$) λ_{max}/nm 254, 312, 430, 590, 633, 697; MALDI-TOF MS *m/z* calcd for $C_{75}H_{15}BrO_4$ $[M]^-$ 1058.0159, found 1058.0155.



4ae

Compound **4ae**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **4ae** (31.2 mg, 62%), amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 5.86 (s, 1H), 5.84 (s, 1H), 5.28 (dd, *J* = 14.4, 3.6 Hz, 1H), 4.19 (t, *J* = 14.0 Hz, 1H), 4.12 (s, 3H), 3.81 (s, 3H), 3.23 (d, *J* = 13.2, 4.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 191.8, 171.5, 169.3, 154.4, 153.9, 152.14, 151.1, 147.53, 147.5, 147.4, 146.9, 146.6, 146.56, 146.5, 146.4, 146.2, 146.18, 146.1, 145.9, 145.8, 145.7, 145.6, 145.5, 145.48, 145.46, 145.4, 145.36, 145.3, 145.2, 144.8, 144.6, 144.4, 143.3,

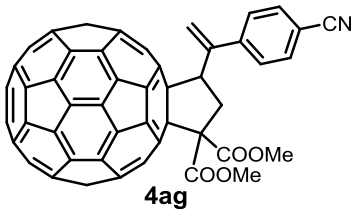
143.2, 142.9, 142.85, 142.7, 142.5, 142.4, 142.3, 142.26, 142.1, 142.0, 141.84, 141.8, 141.7, 141.4, 141.3, 139.6, 139.2, 139.1, 138.8, 138.6, 137.0, 136.7, 135.8, 135.0, 129.8, 128.4, 120.0, 74.8, 74.1, 69.1, 53.9, 53.4, 52.0, 37.6; FT-IR ν/cm^{-1} (KBr) 2947, 2834, 2728, 1735, 1702, 1602, 1430, 1267, 1243, 1172, 1079, 909, 837, 730, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 312, 430, 590, 633, 697; MALDI-TOF MS *m/z* calcd for $C_{76}H_{16}O_5$ $[M]^-$ 1008.1003, found 1008.1001.



4af

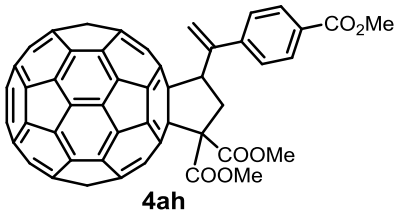
Compound **4af**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 6:1) to give **4af** (17.6 mg, 34%), amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 5.76 (s, 1H), 5.72 (s, 1H), 5.29 (dd, *J* = 14.4, 4.0 Hz, 1H), 4.17 (t, *J* = 14.0 Hz, 1H), 4.11 (s, 3H), 3.81 (s, 3H), 3.19 (dd, *J* = 13.6, 4.0 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 171.5, 169.3, 154.5, 154.0, 152.2, 151.2, 147.5, 147.4, 147.0, 146.6, 146.58, 146.56, 146.5, 146.4, 146.2, 146.19, 146.12, 146.1, 145.9, 145.85, 145.8, 145.7, 145.6, 145.5, 145.47, 145.43, 145.4, 145.3, 145.28, 144.8, 144.7, 144.6, 144.4, 143.3, 143.2, 142.93, 142.9, 142.85, 142.7, 142.5, 142.49, 142.3, 142.26, 142.1, 141.84, 141.8, 141.71, 141.7, 141.4, 141.3, 140.5, 139.7, 139.2, 139.1, 138.8, 138.6, 137.0, 136.7, 135.8, 134.9, 130.9, 128.9, 125.8, 118.6, 74.8, 74.1, 69.1, 53.9, 53.3, 51.9, 37.5; FT-IR ν/cm^{-1} (KBr) 2946, 2032, 1734, 1502, 1430, 1266, 1242, 1193, 1173, 1163,

1137, 1113, 1078, 906, 838, 730, 527; UV-vis ($CHCl_3$) λ_{max}/nm 256, 430, 590, 697; MALDI-TOF MS *m/z* calcd for $C_{76}H_{15}NO_4S$ $[M]^-$ 1037.0727, found 1037.0729.



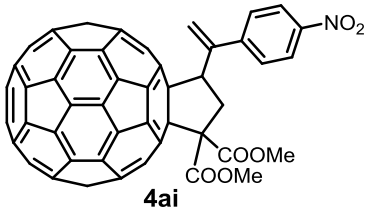
4ag

Compound **4ag**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 6:1) to give **4ag** (23.6 mg, 47%), amorphous brown solid; ^1H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 5.86 (s, 1H), 5.80 (s, 1H), 5.30 (dd, *J* = 14.4, 3.0 Hz, 1H), 4.17 (t, *J* = 13.8 Hz, 1H), 4.11 (s, 3H), 3.81 (s, 3H), 3.20 (dd, *J* = 13.8, 3.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 171.5, 169.2, 154.2, 153.8, 152.1, 151.0, 147.6, 147.4, 146.9, 146.6, 146.58, 146.5, 146.45, 146.3, 146.27, 146.2, 146.14, 146.1, 146.0, 145.84, 145.8, 145.77, 145.75, 145.6, 145.5, 145.43, 145.4, 145.36, 145.3, 145.28, 144.8, 144.7, 144.4, 143.3, 143.26, 143.0, 142.9, 142.7, 142.5, 142.46, 142.3, 142.04, 142.0, 141.9, 141.8, 141.7, 141.7, 141.4, 141.3, 139.6, 139.2, 139.1, 138.9, 138.6, 137.0, 136.8, 135.0, 132.2, 128.4, 120.3, 118.7, 111.8, 74.8, 74.1, 69.1, 53.9, 53.4, 51.9, 37.5; FT-IR *v*/cm^{-1} (KBr) 2947, 1735, 1431, 1267, 1243, 1194, 1174, 1079, 910, 844, 730, 527; UV-vis ($CHCl_3$) λ_{max}/nm 255, 314, 430, 590, 697; MALDI-TOF MS *m/z* calcd for $C_{76}H_{15}NO_4$ $[M]^-$ 1005.1007, found 1005.1006.



4ah

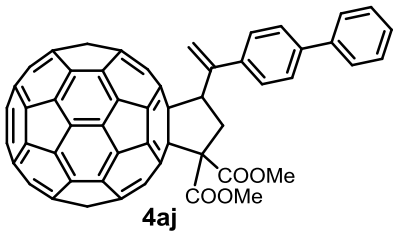
Compound **4ah**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 5:1) to give **4ah** (23.3 mg, 45%), amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 5.81 (s, 1H), 5.79 (s, 1H), 5.36 (dd, *J* = 14.4, 3.6 Hz, 1H), 4.19 (t, *J* = 14.0 Hz, 1H), 4.12 (s, 3H), 3.87 (s, 3H), 3.81 (s, 3H), 3.22 (dd, *J* = 13.6, 4.0 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 171.5, 169.3, 166.8, 154.5, 154.1, 152.2, 151.2, 147.5, 147.4, 147.0, 146.6, 146.57, 146.5, 146.4, 146.38, 146.2, 146.16, 146.1, 146.08, 145.9, 145.9, 145.86, 145.8, 145.7, 145.69, 145.5, 145.46, 145.4, 145.39, 145.35, 145.3, 145.2, 144.8, 144.64, 144.6, 144.4, 143.2, 143.19, 142.9, 142.8, 142.6, 142.5, 142.4, 142.3, 142.2, 142.1, 142.0, 141.8, 141.79, 141.7, 141.4, 141.3, 139.7, 139.1, 139.08, 138.8, 138.6, 137.0, 136.7, 134.9, 129.7, 129.69, 127.7, 119.4, 74.8, 74.2, 69.1, 53.8, 53.3, 52.3, 52.0, 37.6; FT-IR ν/cm^{-1} (KBr) 2946, 1734, 1606, 1432, 1276, 1243, 1190, 1175, 1108, 1079, 908, 859, 780, 730, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 313, 430, 590, 697; MALDI-TOF MS *m/z* calcd for $C_{77}H_{18}O_6$ $[M]^-$ 1038.1110, found 1038.1114.



4ai

Compound **4ai**: the product mixture was separated and purified by silica gel column

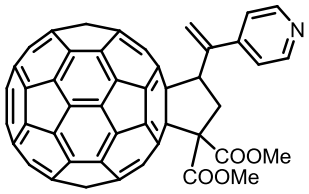
chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 7:1) to give **4ai** (20.5 mg, 40%), amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.0 Hz, 2H), 7.65 (d, *J* = 9.0 Hz, 2H), 5.90 (s, 1H), 5.85 (s, 1H), 5.35 (dd, *J* = 14.4, 3.6 Hz, 1H), 4.18 (t, *J* = 13.8 Hz, 1H), 4.12 (s, 3H), 3.82 (s, 3H), 3.23 (dd, *J* = 13.2, 4.2 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 171.5, 169.2, 154.1, 153.7, 152.0, 151.0, 148.0, 147.6, 147.5, 147.45, 146.9, 146.6, 146.58, 146.5, 146.45, 146.3, 146.25, 146.2, 146.1, 145.83, 145.82, 145.8, 145.6, 145.5, 145.4, 145.39, 145.32, 145.31, 145.3, 145.2, 144.8, 144.7, 144.6, 144.4, 143.3, 143.27, 143.0, 142.95, 142.9, 142.7, 142.6, 142.4, 142.3, 142.27, 142.04, 142.0, 141.9, 141.8, 141.7, 141.69, 141.4, 141.3, 139.6, 139.2, 139.19, 138.9, 138.7, 136.94, 136.9, 135.1, 128.6, 123.7, 121.0, 74.7, 74.1, 69.1, 53.9, 53.4, 52.1, 37.5; FT-IR ν/cm^{-1} (KBr) 2946, 2920, 2847, 1735, 1594, 1518, 1431, 1342, 1266, 1243, 1193, 1174, 1138, 1112, 1078, 910, 856, 763, 730, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 312, 430, 590, 633, 697; MALDI-TOF MS *m/z* calcd for $C_{75}H_{15}NO_6$ $[M]^-$ 1025.0905, found 1025.0901.



4aj

Compound **4aj**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **4aj** (14.3 mg, 27%), amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56–7.54 (m, 2H), 7.51–7.49 (m, 2H),

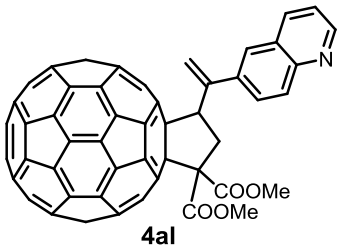
7.45–7.44 (m, 2H), 7.41–7.38 (m, 2H), 7.33–7.30 (m, 1H), 5.78 (s, 1H), 5.74 (s, 1H), 5.38 (dd, J = 14.4, 3.6 Hz, 1H), 4.21 (t, J = 14.4 Hz, 1H), 4.12 (s, 3H), 3.82 (s, 3H), 3.24 (dd, J = 13.2, 4.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 171.6, 169.4, 154.9, 154.3, 152.3, 151.4, 147.5, 147.4, 147.1, 146.9, 146.6, 146.5, 146.4, 146.3, 146.2, 146.16, 146.1, 146.05, 145.92, 145.9, 145.86, 145.7, 145.5, 145.46, 145.42, 145.4, 145.3, 145.25, 145.2, 144.9, 144.7, 144.6, 144.4, 143.2, 143.17, 142.9, 142.87, 142.8, 142.6, 142.5, 142.48, 142.4, 142.2, 142.1, 142.0, 141.8, 141.7, 141.69, 141.34, 141.3, 141.1, 140.6, 140.3, 139.8, 139.1, 138.9, 138.8, 138.4, 137.1, 136.5, 134.9, 128.9, 128.3, 127.6, 127.1, 127.05, 117.4, 74.8, 74.3, 69.2, 53.8, 53.3, 52.2, 37.7; FT-IR ν/cm^{-1} (KBr) 2946, 1735, 1485, 1430, 1264, 1242, 1190, 1173, 1078, 905, 842, 768, 659, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 431, 590, 698; MALDI-TOF MS *m/z* calcd for $C_{81}H_{20}O_4$ $[M]^-$ 1056.1367, found 1056.1365.



4ak

Compound **4ak**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 7:1) to give **4ak** (20.1 mg, 41%), amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (d, J = 4.8 Hz, 2H), 7.39 (d, J = 5.4 Hz, 2H), 5.89 (s, 1H), 5.87 (s, 1H), 5.32 (dd, J = 14.4, 3.6 Hz, 1H), 4.18 (t, J = 13.8 Hz, 1H), 4.11 (s, 3H), 3.81 (s, 3H), 3.20 (dd, J = 13.6, 3.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 171.5, 169.2, 154.3, 153.9, 152.1, 151.1, 150.1, 148.9, 147.6, 147.4, 146.9,

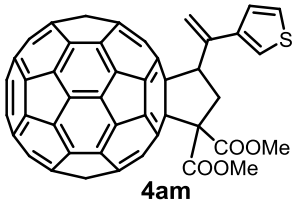
146.6, 146.57, 146.5, 146.4, 146.37, 146.3, 146.2, 146.14, 146.1, 145.9, 145.8, 145.77, 145.75, 145.6, 145.5, 145.45, 145.4, 145.38, 145.3, 144.8, 144.7, 144.66, 144.65, 144.4, 143.3, 143.2, 142.93, 142.9, 142.87, 142.7, 142.5, 142.48, 142.3, 142.26, 142.1, 141.9, 141.8, 141.7, 141.4, 141.3, 139.6, 139.2, 139.17, 138.9, 138.8, 137.0, 136.8, 135.0, 122.3, 120.5, 74.7, 74.1, 69.1, 53.9 53.4 51.5 37.5; FT-IR ν/cm^{-1} (KBr) 2946, 1734, 1591, 1431, 1268, 1242, 1194, 1174, 1078, 910, 831, 729, 527; UV-vis ($CHCl_3$) λ_{max}/nm 256, 314, 429, 590, 697; MALDI-TOF MS *m/z* calcd for $C_{74}H_{15}NO_4$ $[M]^-$ 981.1007, found 981.1005.



4al

Compound **4al**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 7:1) to give **4al** (28.9 mg, 56%), amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 7.84 (dd, *J* = 2.0 Hz, *J* = 8.8 Hz, 1H), 7.34 (q, *J* = 4.0 Hz, 1H), 5.88 (s, 1H), 5.86 (s, 1H), 5.47 (dd, *J* = 14.4, 4.0 Hz, 1H), 4.23 (t, *J* = 14.0 Hz, 1H), 4.14 (s, 3H), 3.82 (s, 3H), 3.28 (d, *J* = 13.6, 4.0 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 171.6 169.3, 154.6 154.1, 152.3 151.2, 150.9, 148.0, 147.5, 147.4, 147.0, 146.6, 146.53, 146.5, 146.4, 146.3, 146.2, 146.15, 146.1, 146.0, 145.9, 145.84, 145.8, 145.7, 145.5, 145.4, 145.38, 145.3, 145.25, 145.1, 144.8, 144.6, 144.58, 144.4, 143.2, 142.9, 142.86, 142.8, 142.6, 142.5, 142.4, 142.3,

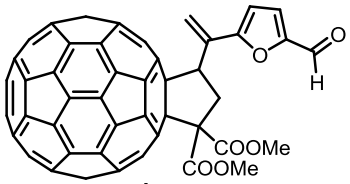
142.2, 142.0, 141.9, 141.8, 141.7, 141.68, 141.3, 141.26, 139.7, 139.5, 139.2, 139.0, 138.8, 138.3, 137.1, 136.6, 136.3, 134.9, 129.7, 129.5, 127.9, 126.8, 121.7, 118.9, 74.8, 74.2, 69.2, 53.9, 53.3, 52.2, 37.7; FT-IR ν/cm^{-1} (KBr) 2946, 1734, 1430, 1266, 1241, 1193, 1172, 1138, 1112, 1079, 906, 838, 729, 527; UV-vis ($CHCl_3$) λ_{max}/nm 254, 312, 430, 590, 697; MALDI-TOF MS *m/z* calcd for $C_{78}H_{17}NO_4$ $[M]^-$ 1031.1163, found 1031.1165.



4am

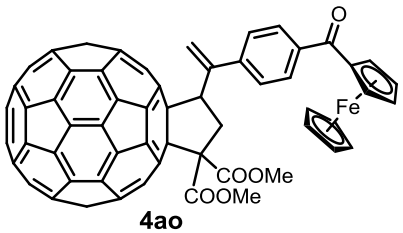
Compound **4am**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **4am** (16.3 mg, 33%), amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3/CS_2$, v/v = 10:1) δ 7.34–7.33 (m, 1H), 7.20–7.19 (m, 1H), 7.17–7.15 (m, 1H), 5.79 (s, 1H), 5.65 (s, 1H), 5.20 (dd, *J* = 15.0, 3.6 Hz, 1H), 4.16 (t, *J* = 14.4 Hz, 1H), 4.08 (s, 3H), 3.80 (s, 3H), 3.14 (dd, *J* = 13.2, 4.2 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$, v/v = 10:1) δ 171.0, 168.8, 154.9, 154.3, 152.0, 151.2, 147.3, 147.2, 146.9, 146.5, 146.4, 146.34, 146.3, 146.2, 146.1, 146.0, 145.9, 145.89, 145.74, 145.73, 145.7, 145.6, 145.32, 145.3, 145.25, 145.1, 145.0, 144.7, 144.6, 144.4, 144.2, 143.0, 143.0, 142.8, 142.7, 142.67, 142.6, 142.5, 142.4, 142.3, 142.2, 142.1, 141.9, 141.7, 141.6, 141.57, 141.5, 141.2, 141.1, 140.9, 139.7, 139.0, 138.97, 138.7, 138.5, 137.0, 136.3, 134.4, 126.8, 126.0, 123.2, 115.5, 74.5, 74.0, 68.8, 53.3, 52.9, 52.7, 37.3; FT-IR ν/cm^{-1} (KBr) 2946, 1732, 1626, 1431,

1268, 1239, 1174, 1138, 1113, 1079, 905, 788, 735, 575, 527; UV-vis ($CHCl_3$) λ_{max}/nm 256, 312, 431, 695; MALDI-TOF MS m/z calcd for $C_{73}H_{14}O_4S$ $[M]^-$ 986.0618, found 986.0793.



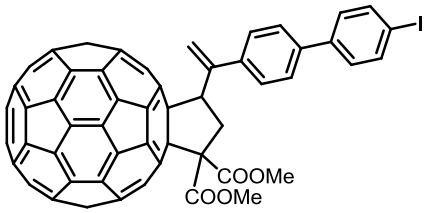
4an

Compound **4an**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **4an** (16.5 mg, 33%), amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.16 (d, *J* = 4.2 Hz, 1H), 6.77 (d, *J* = 4.2 Hz, 1H), 6.38 (s, 1H), 5.91 (s, 1H), 5.18 (dd, *J* = 13.8, 4.2 Hz, 1H), 4.21 (t, *J* = 14.4 Hz, 1H), 4.08 (s, 3H), 3.82 (s, 3H), 3.13 (dd, *J* = 13.8, 4.2 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 177.7, 171.3, 169.2, 159.1, 154.7, 154.0, 152.1, 152.0, 151.1, 147.6, 147.5, 146.9, 146.6, 146.5, 146.47, 146.4, 146.3, 146.26, 146.2, 146.19, 146.18, 145.9, 145.85, 145.8, 145.7, 145.6, 145.5, 145.47, 145.34, 145.3, 145.2, 145.1, 144.8, 144.7, 144.65, 144.4, 143.3, 143.2, 142.9, 142.7, 142.5, 142.48, 142.4, 142.3, 142.2, 142.1, 141.9, 141.8, 141.75, 141.7, 141.67, 141.4, 139.8, 139.7, 139.3, 139.2, 138.9, 137.0, 136.8, 134.7, 134.6, 119.6, 111.4, 74.5, 74.1, 69.1, 53.8, 53.4, 50.5, 37.2; FT-IR *v*/cm^{-1} (KBr) 2947, 1733, 1678, 1562, 1500, 1430, 1261, 1244, 1195, 1175, 1139, 1079, 1027, 968, 908, 796, 766, 728, 527; UV-vis ($CHCl_3$) λ_{max}/nm 258, 314, 430, 694; MALDI-TOF MS *m/z* calcd for $C_{74}H_{14}O_6$ $[M]^-$ 998.0796, found 998.0799.



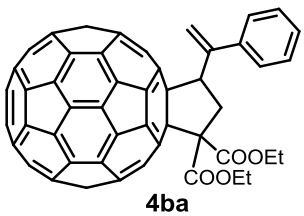
4ao

Compound **4ao**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 7:1) to give **4ao** (30.4 mg, 51%), amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 5.81 (s, 2H), 5.42 (dd, *J* = 14.4, 3.6 Hz, 1H), 4.74–4.73 (m, 1H), 4.71–4.70 (m, 1H), 4.54–4.52 (m, 2H), 4.22 (t, *J* = 14.0 Hz, 1H), 4.13 (s, 3H), 4.11 (s, 5H), 3.82 (s, 3H), 3.25 (dd, *J* = 13.6, 4.0 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 198.6, 171.6, 169.3, 154.7, 154.0, 152.3, 151.3, 147.5, 147.4, 147.0, 146.8, 146.6, 146.59, 146.5, 146.4, 146.3, 146.14, 146.12, 146.1, 145.94, 145.9, 145.87, 145.86, 145.7, 145.5, 145.44, 145.43, 145.4, 145.3, 145.0, 144.8, 144.7, 144.6, 144.4, 144.37, 143.3, 143.2, 142.94, 142.9, 142.7, 142.5, 142.4, 142.35, 142.3, 142.2, 141.9, 141.85, 141.8, 141.7, 141.67, 141.4, 141.3, 139.7, 139.5, 139.2, 138.9, 138.85, 138.2, 137.0, 136.7, 135.0, 128.0, 127.8, 118.4, 78.1, 74.9, 74.1, 72.9, 72.88, 71.7, 71.6, 70.5, 69.2, 53.9, 53.3, 52.0, 37.4; FT-IR ν/cm^{-1} (KBr) 3092, 2948, 1757, 1735, 1634, 1604, 1513, 1445, 1430, 1375, 1264, 1240, 1189, 1173, 1138, 1117, 1080, 1046, 1027, 857, 829, 779, 763, 575, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 310, 430, 695; MALDI-TOF MS *m/z* calcd for $C_{86}H_{24}FeO_5$ $[M]^+$ 1192.0979, found 1192.0981.



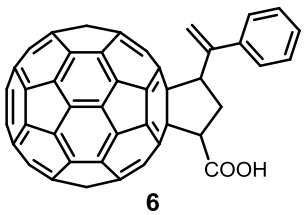
4ap

Compound **4ap**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **4ap** (11.8 mg, 20%), amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.78 (s, 1H), 5.75 (s, 1H), 5.36 (dd, *J* = 14.4, 4.0 Hz, 1H), 4.19 (t, *J* = 14.0 Hz, 1H), 4.12 (s, 3H), 3.81 (s, 3H), 3.24 (dd, *J* = 13.6, 4.0 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 171.6, 169.4, 154.9, 154.2, 152.3, 151.3, 147.5, 147.4, 147.0, 146.8, 146.6, 146.55, 146.4, 146.35, 146.2, 146.15, 146.1, 146.07, 146.06, 146.0, 145.9, 145.85, 145.7, 145.5, 145.47, 145.43, 145.4, 145.3, 145.25, 145.2, 144.8, 144.7, 144.6, 144.4, 143.2, 143.18, 142.9, 142.88, 142.8, 142.6, 142.5, 142.3, 142.2, 142.1, 141.9, 141.82, 141.8, 141.7, 141.4, 141.3, 140.8, 140.0, 139.9, 139.7, 139.1, 138.9, 138.8, 138.4, 138.0, 137.1, 136.5, 134.9, 128.9, 128.5, 126.8, 117.7, 93.4, 74.8, 74.3, 69.2, 53.8, 53.3, 52.2, 37.7; FT-IR *v*/cm^{-1} (KBr) 2946, 1735, 1478, 1431, 1266, 1243, 1192, 1173, 1079, 999, 905, 813, 731, 527; UV-vis ($CHCl_3$) λ_{max}/nm 256, 431, 591, 697; MALDI-TOF MS *m/z* calcd for $C_{81}H_{19}IO_4$ [M]$^-$ 1182.0334, found 1182.0336.



4ba

Compound **4ba**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **4ba** (13.5 mg, 27%), amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.46 (m, 2H), 7.22–7.19 (m, 3H), 5.72 (s, 2H), 5.36 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.66–4.50 (m, 2H), 4.45–4.38 (m, 1H), 4.21–4.11 (m, 2H), 3.22 (dd, *J* = 16.0, 4.0 Hz, 1H), 1.50 (t, *J* = 8.0 Hz, 3H), 1.22 (t, *J* = 8.0 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 171.2, 169.0, 155.1, 154.4, 152.6, 151.5, 147.5, 147.4, 147.3, 146.9, 146.7, 146.6, 146.55, 146.4, 146.36, 146.3, 146.2, 146.1, 146.08, 146.05, 145.94, 145.9, 145.7, 145.5, 145.45, 145.4, 145.39, 145.3, 145.25, 145.1, 144.9, 144.7, 144.6, 144.4, 143.2, 143.17, 142.9, 142.87, 142.8, 142.6, 142.5, 142.4, 142.2, 142.1, 141.9, 141.83, 141.8, 141.7, 141.66, 141.4, 141.36, 141.3, 139.7, 139.0, 138.88, 138.6, 138.4, 137.1, 136.5, 134.9, 128.4, 128.3, 127.9, 117.4, 74.8, 74.3, 69.0, 62.8, 62.6, 52.1, 37.7, 14.4, 14.1; FT-IR ν/cm^{-1} (KBr) 2976, 1731, 1462, 1440, 1264, 1238, 1180, 1137, 1112, 1079, 1010, 904, 776, 731, 698, 576, 527; UV-vis ($CHCl_3$) λ_{max}/nm 256, 312, 431, 699; MALDI-TOF MS *m/z* calcd for $C_{77}H_{20}O_4$ $[M]^-$ 1008.1367, found 1008.1369.

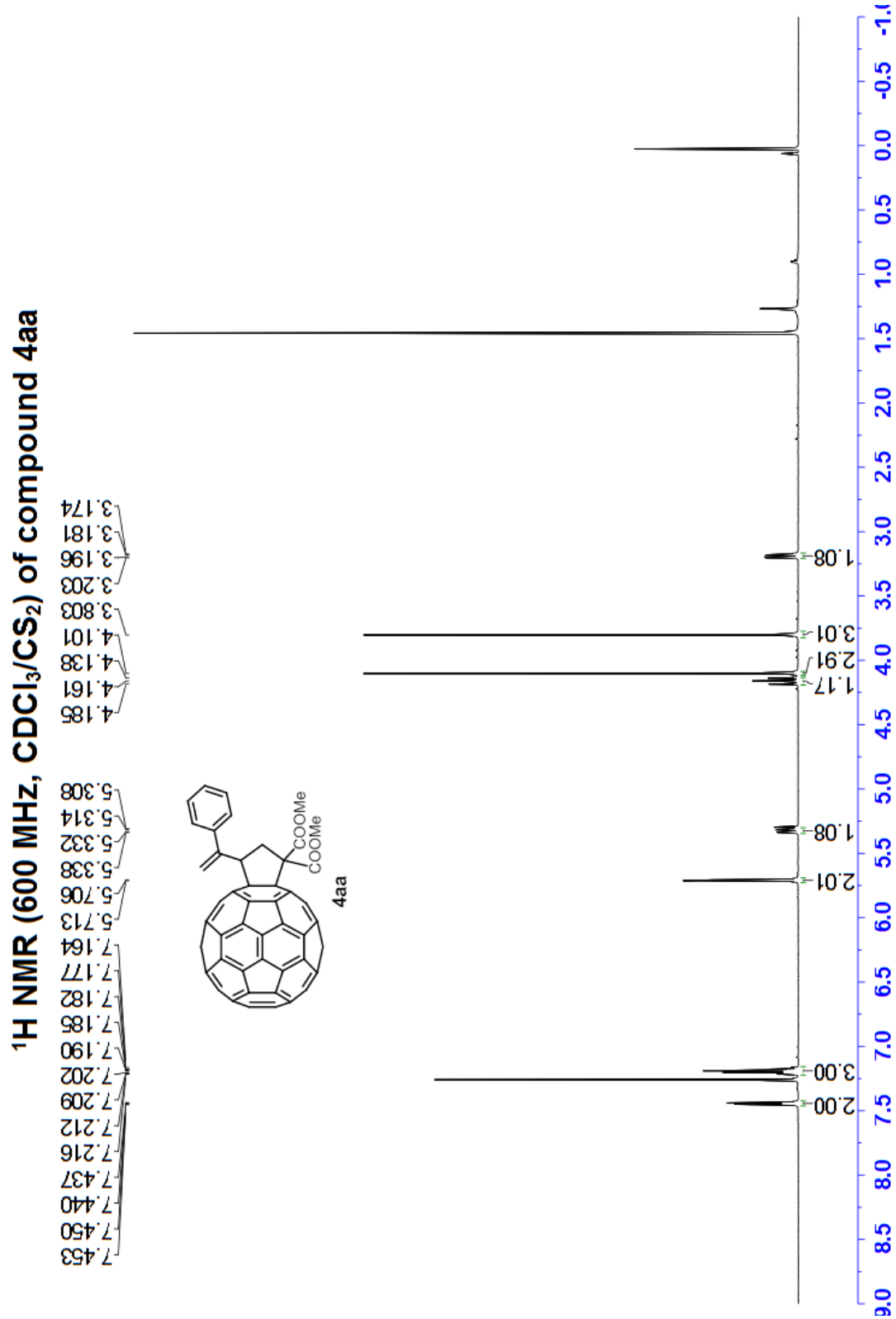


6

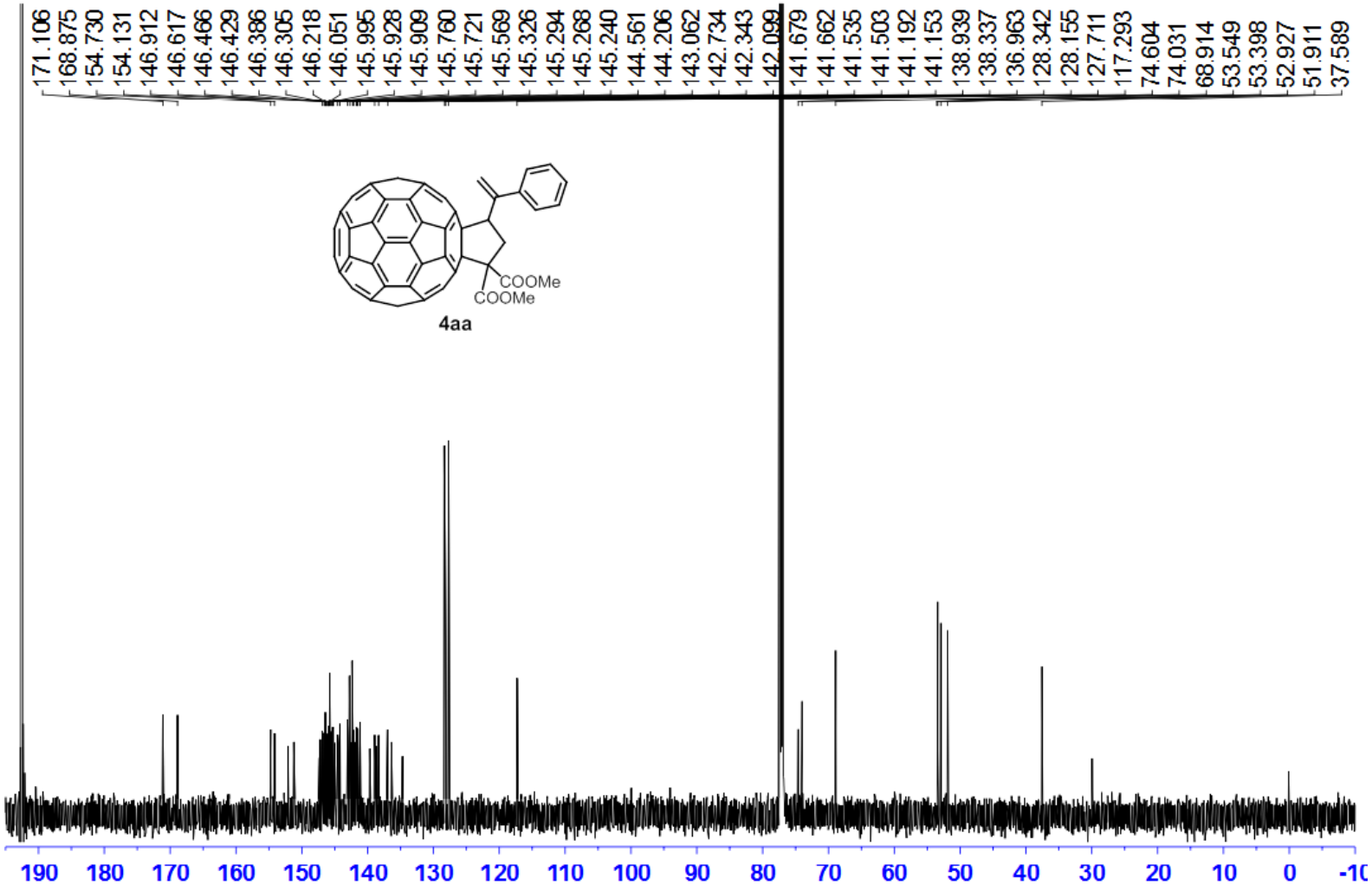
Compound **6**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM/EtOAc (v/v/v = 10:5:2) to give **6** (30.0 mg, 66%),

amorphous brown solid; ^{1}H NMR (600 MHz, DMSO-d_6/CS_2, v/v = 1:10) δ 12.79 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.16–7.11 (m, 3H), 5.70 (s, 1H), 5.63 (s, 1H), 5.11 (d, *J* = 12.6 Hz, 1H), 4.69 (d, *J* = 9.0 Hz, 1H), 3.54 (q, *J* = 13.2 Hz, 1H), 2.92 (d, *J* = 12.6 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6/CS_2, v/v = 1:10) δ 155.3, 155.2, 153.8, 153.5, 147.1, 147.0, 146.7, 146.0, 145.9, 145.6, 145.5, 145.2, 145.1, 145.06, 144.9, 144.82, 144.8, 144.7, 144.6, 144.1, 144.0, 143.98, 143.95, 143.9, 143.5, 143.4, 143.22, 143.2, 141. 9, 141.8, 141.5, 141.4, 141.39, 141.1, 141.0, 140.96, 140.9, 140.8, 140.6, 140.5, 140.4, 140.3, 138.2, 137.7, 137.4, 135.3, 135.0, 134.0, 133.2, 127.3, 126.8, 126.6, 116.2, 73.9, 72.1, 55.0, 33.3, 29.1; FT-IR ν/cm^{-1} (KBr) 2959, 2926, 1716, 1575, 1420, 1261, 1212, 1177, 1097, 1051, 1026, 905, 804, 776, 696, 527; UV-vis ($CHCl_3$) λ_{max}/nm 256, 311, 431, 689; MALDI-TOF MS *m/z* calcd for $C_{72}H_{12}O_2$ $[M]^+$ 908.0832, found 908.0836.

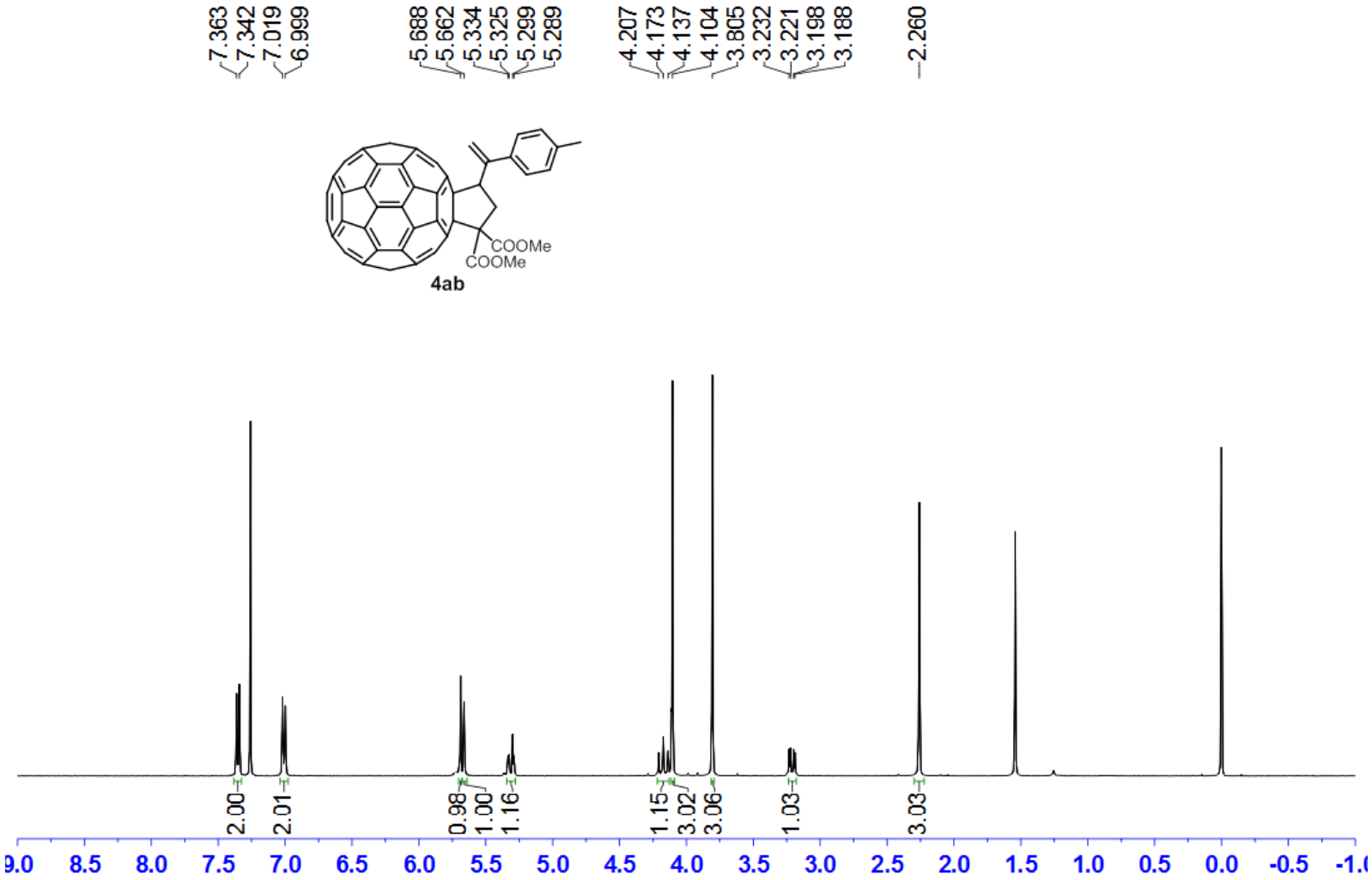
6. ^{1}H NMR and ^{13}C NMR Spectra of Compounds 4



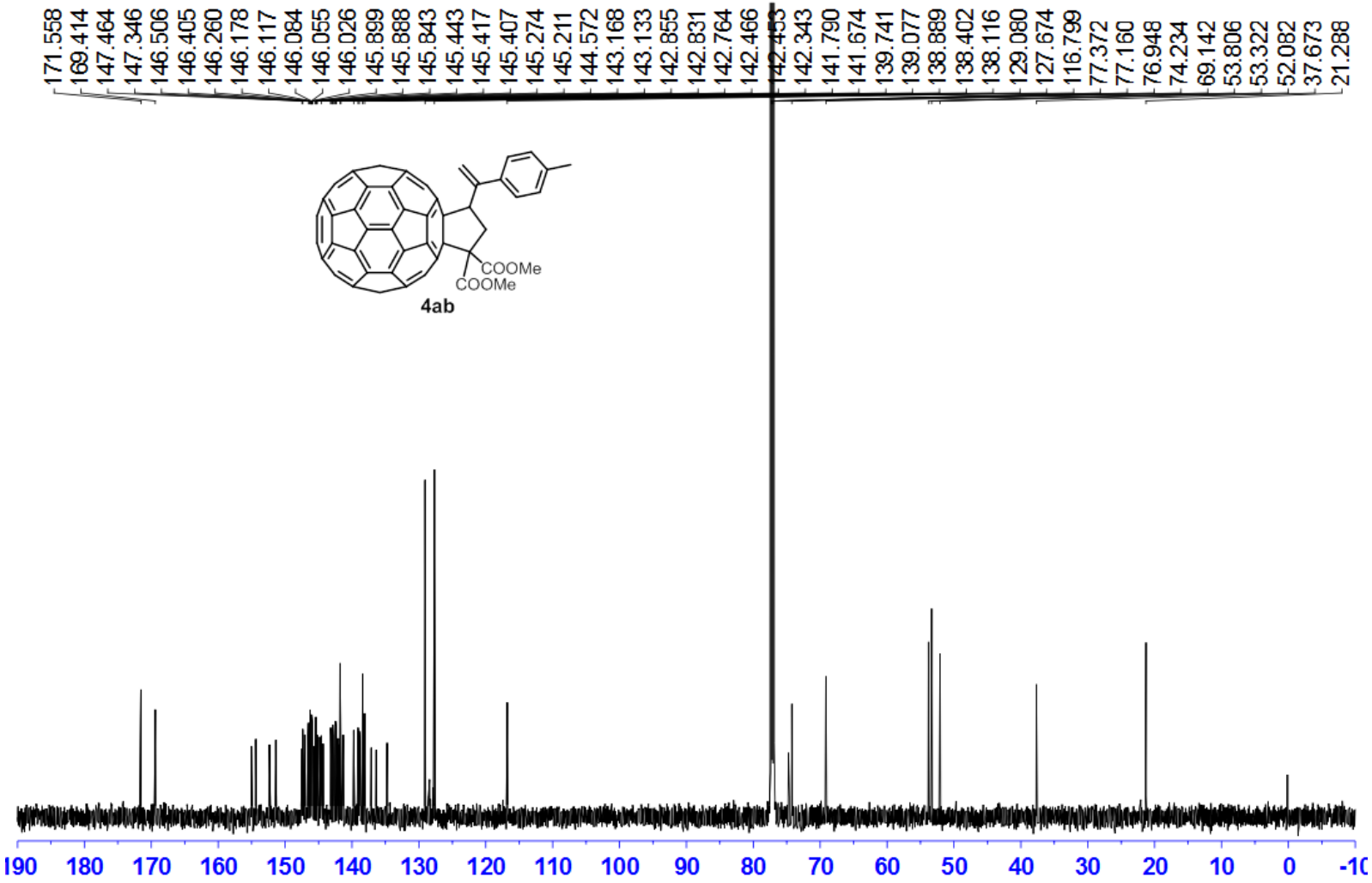
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 4aa



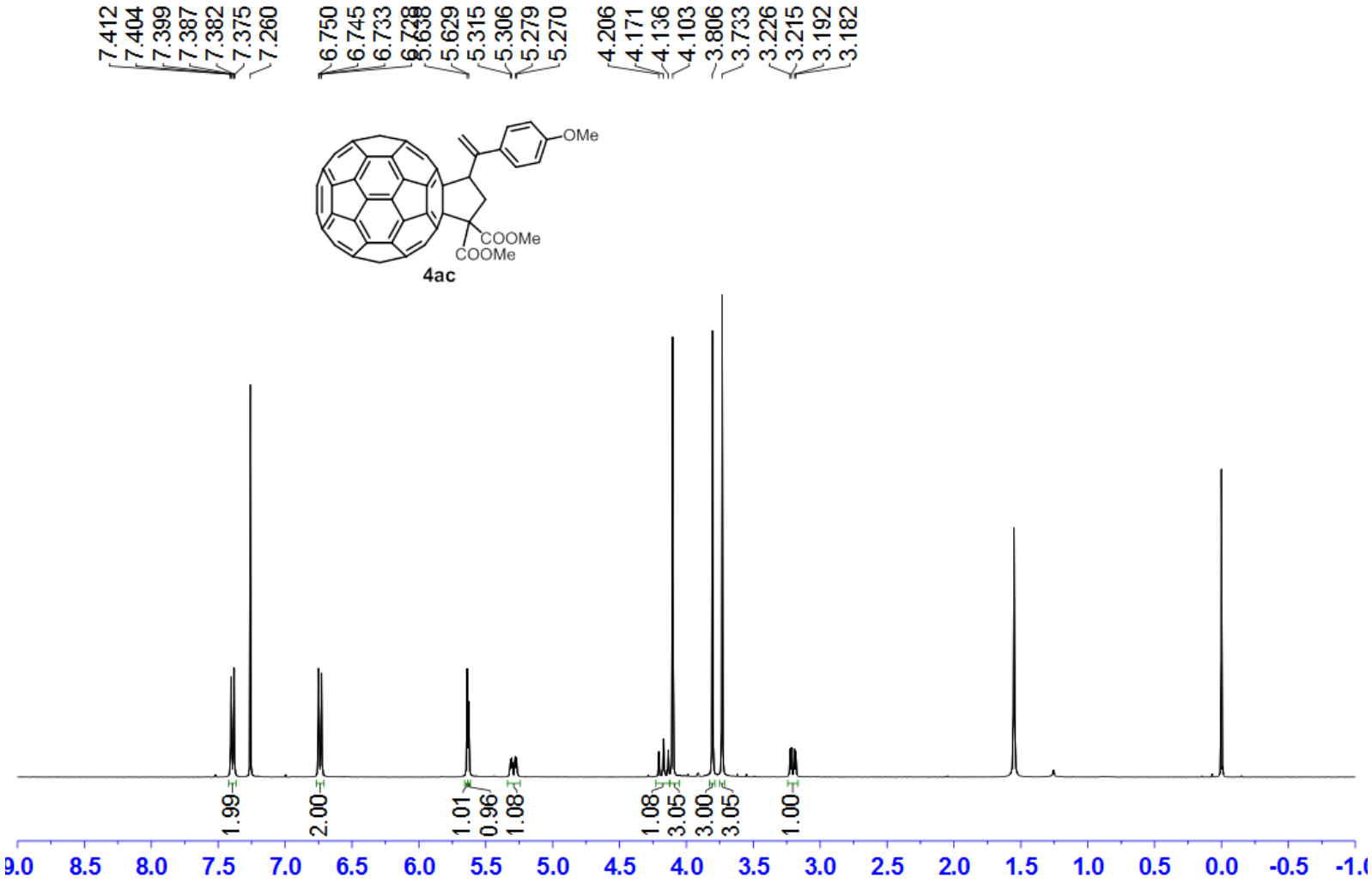
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4ab



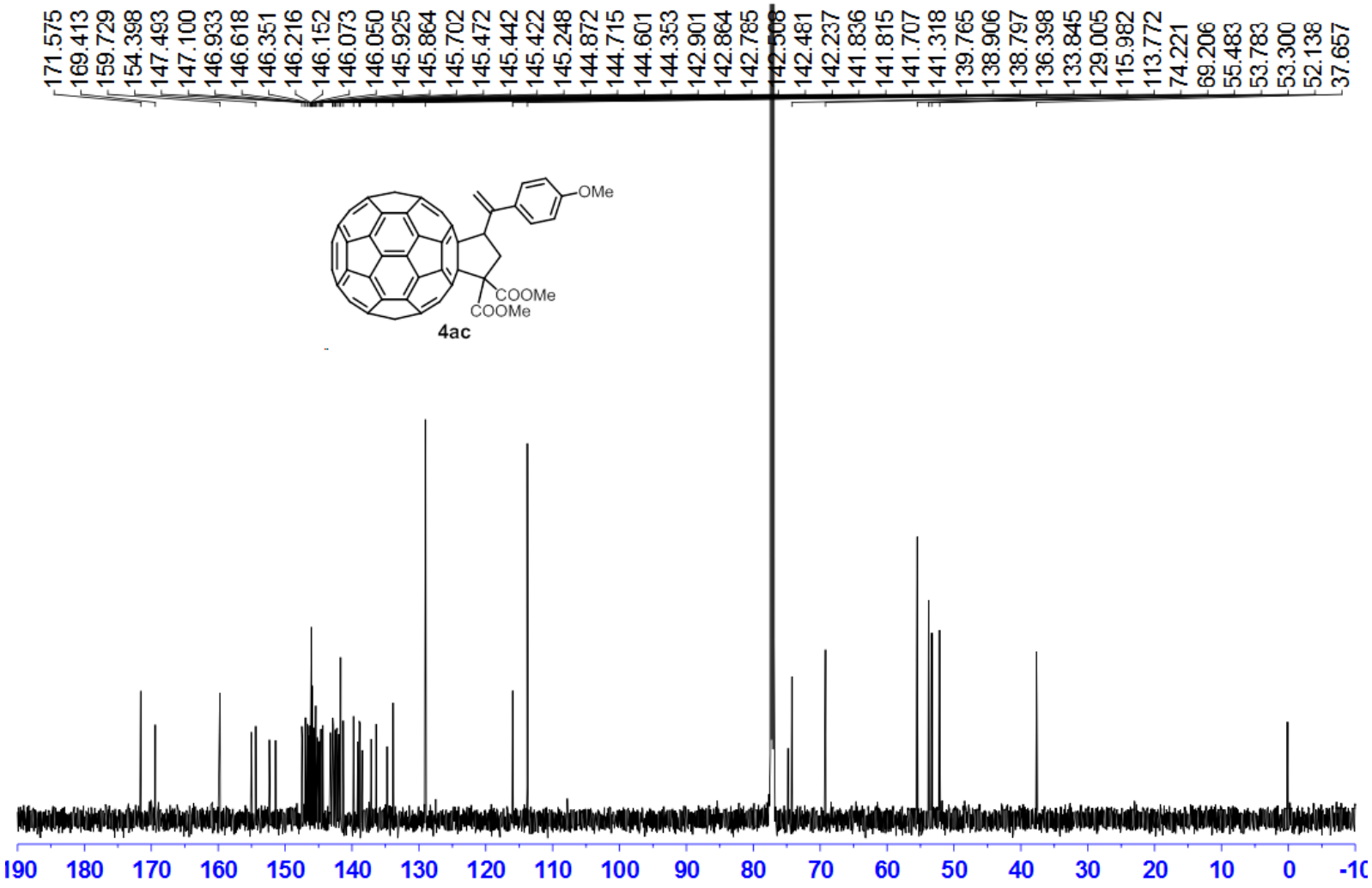
^{13}C NMR (150 MHz, $CDCl_3$) of compound 4ab



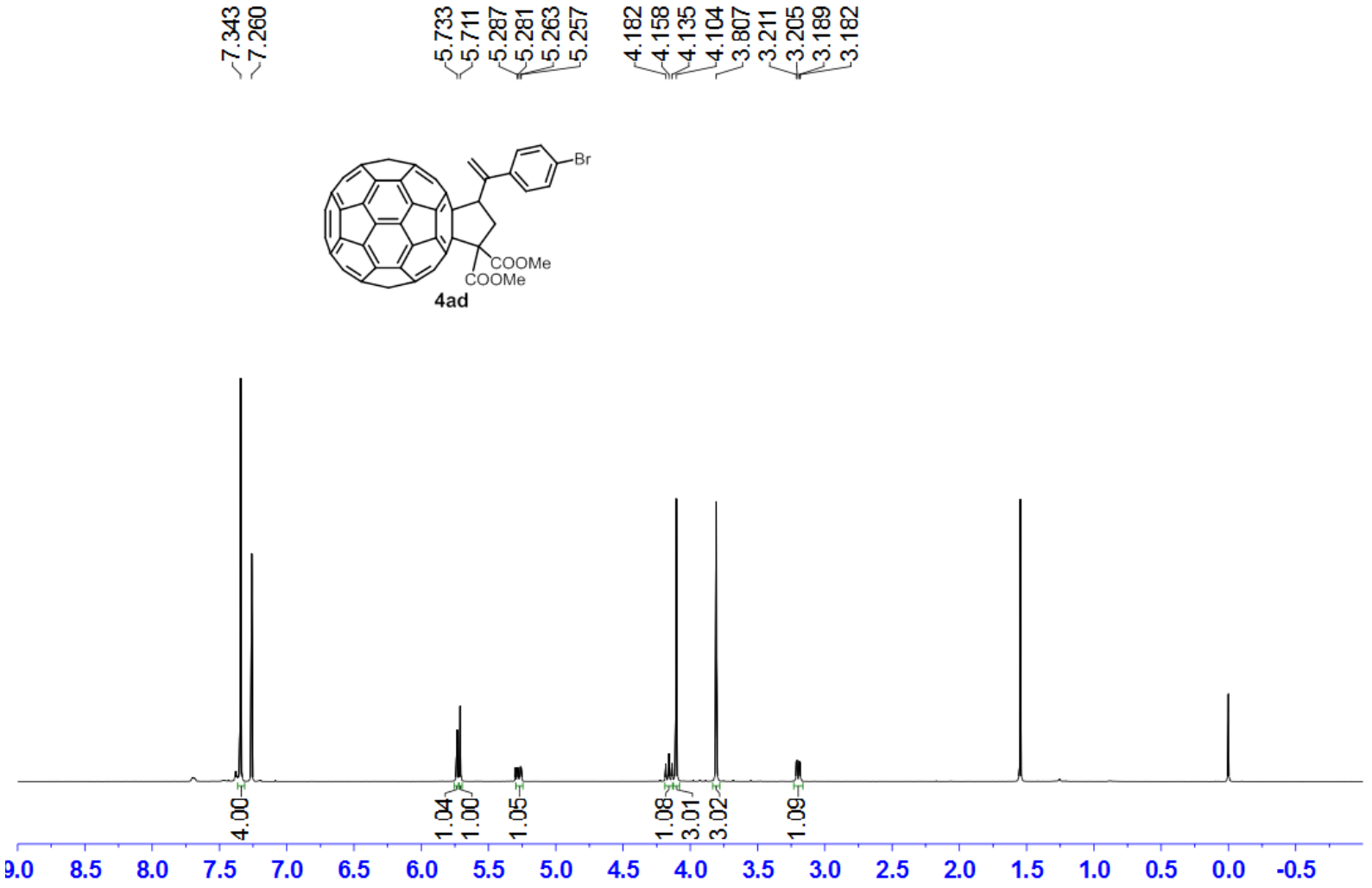
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4ac

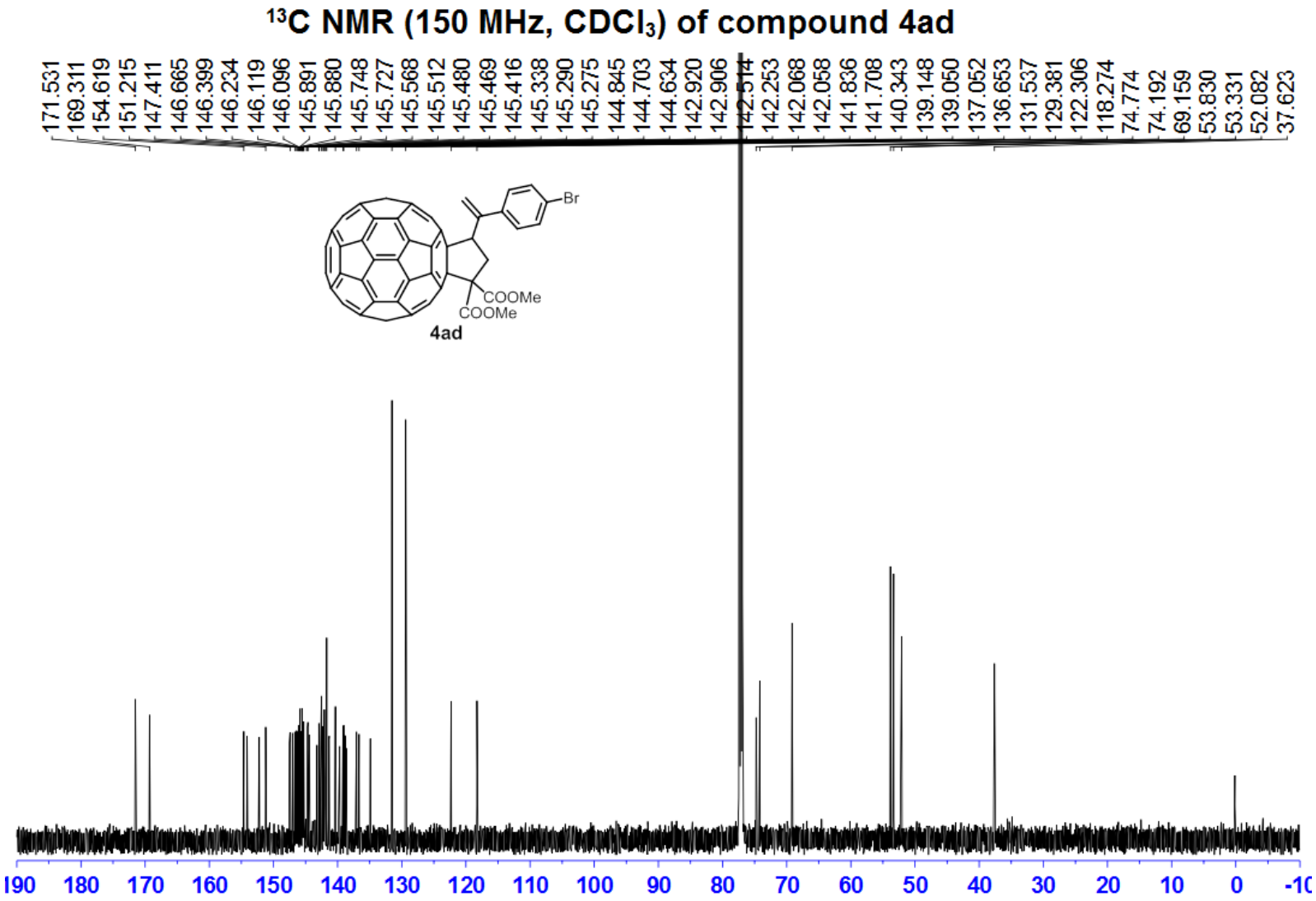


^{13}C NMR (150 MHz, $CDCl_3$) of compound 4ac

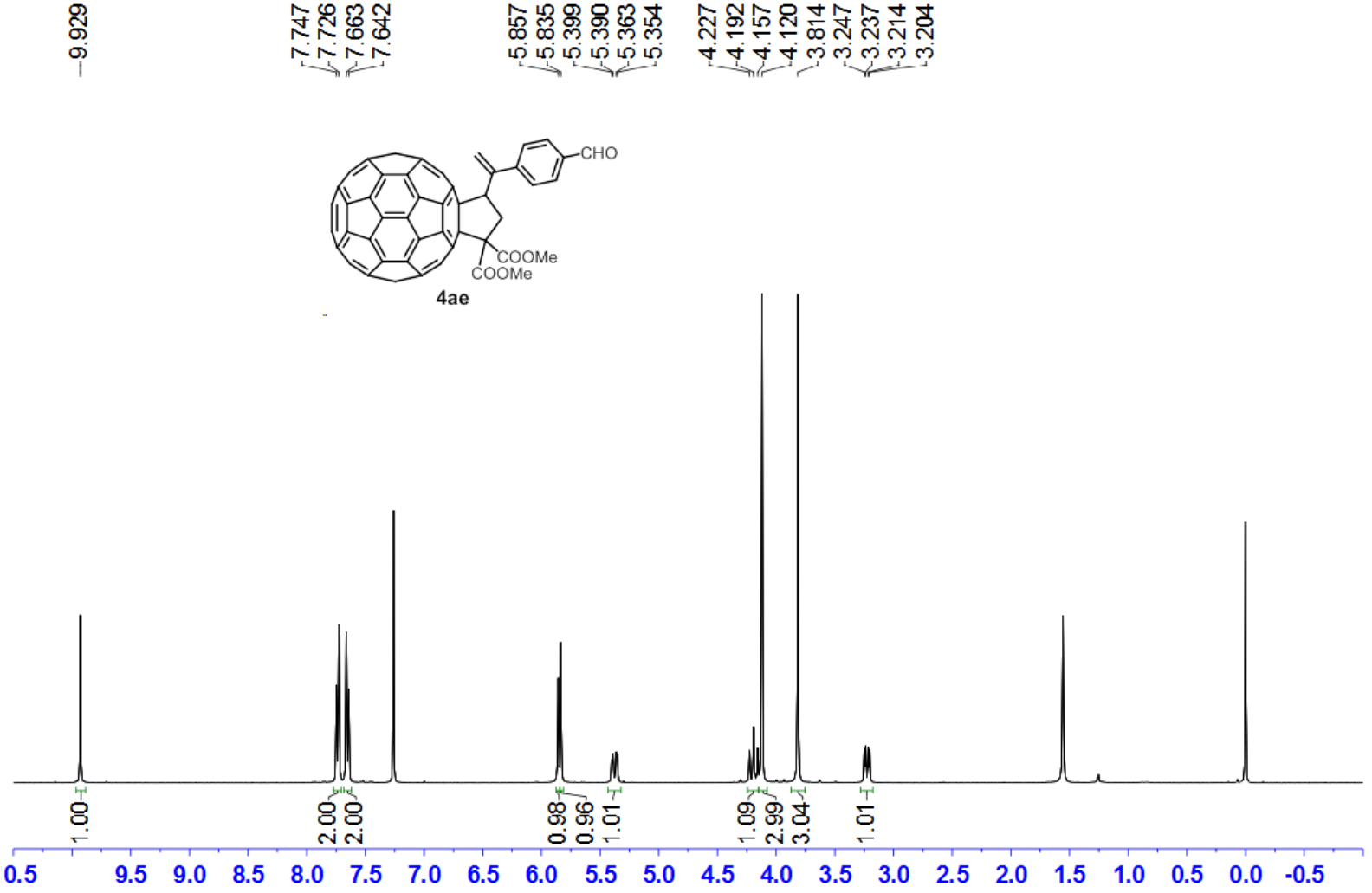


^{1}H NMR (600 MHz, $CDCl_3$) of compound 4ad

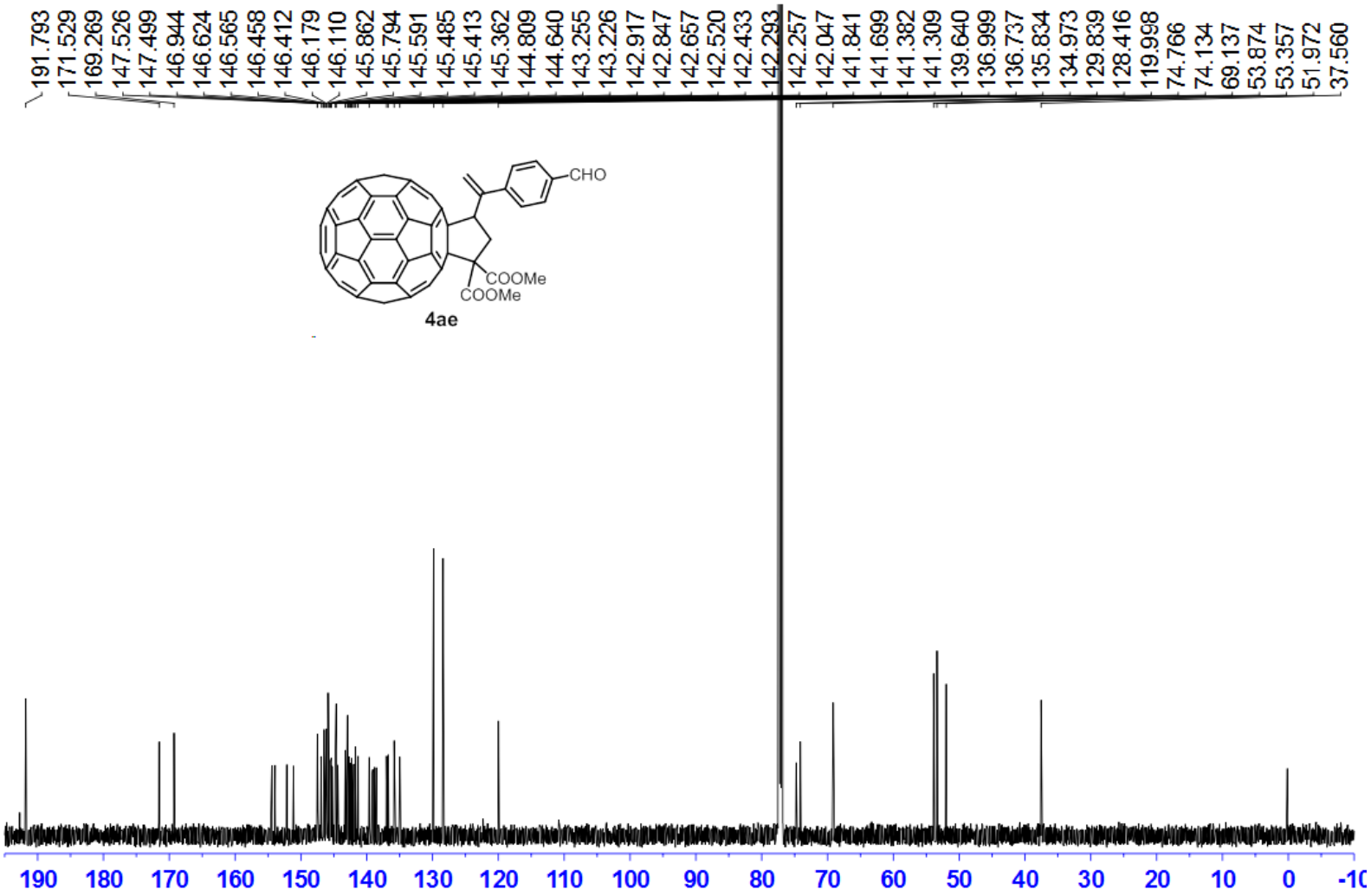



13C NMR (150 MHz, CDCl3) of compound 4ad
171.531
169.311
154.619
151.215
147.411
146.665
146.399
146.234
146.119
146.096
145.891
145.880
145.748
145.727
145.568
145.512
145.480
145.469
145.416
145.338
145.290
145.275
144.845
144.703
144.634
142.920
142.906
142.514
142.253
142.068
142.058
141.836
141.708
140.343
139.148
139.050
137.052
136.653
131.537
129.381
122.306
118.274
74.774
74.192
69.159
53.830
53.331
52.082
37.623
Br
COOMe
COOMe
4ad
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

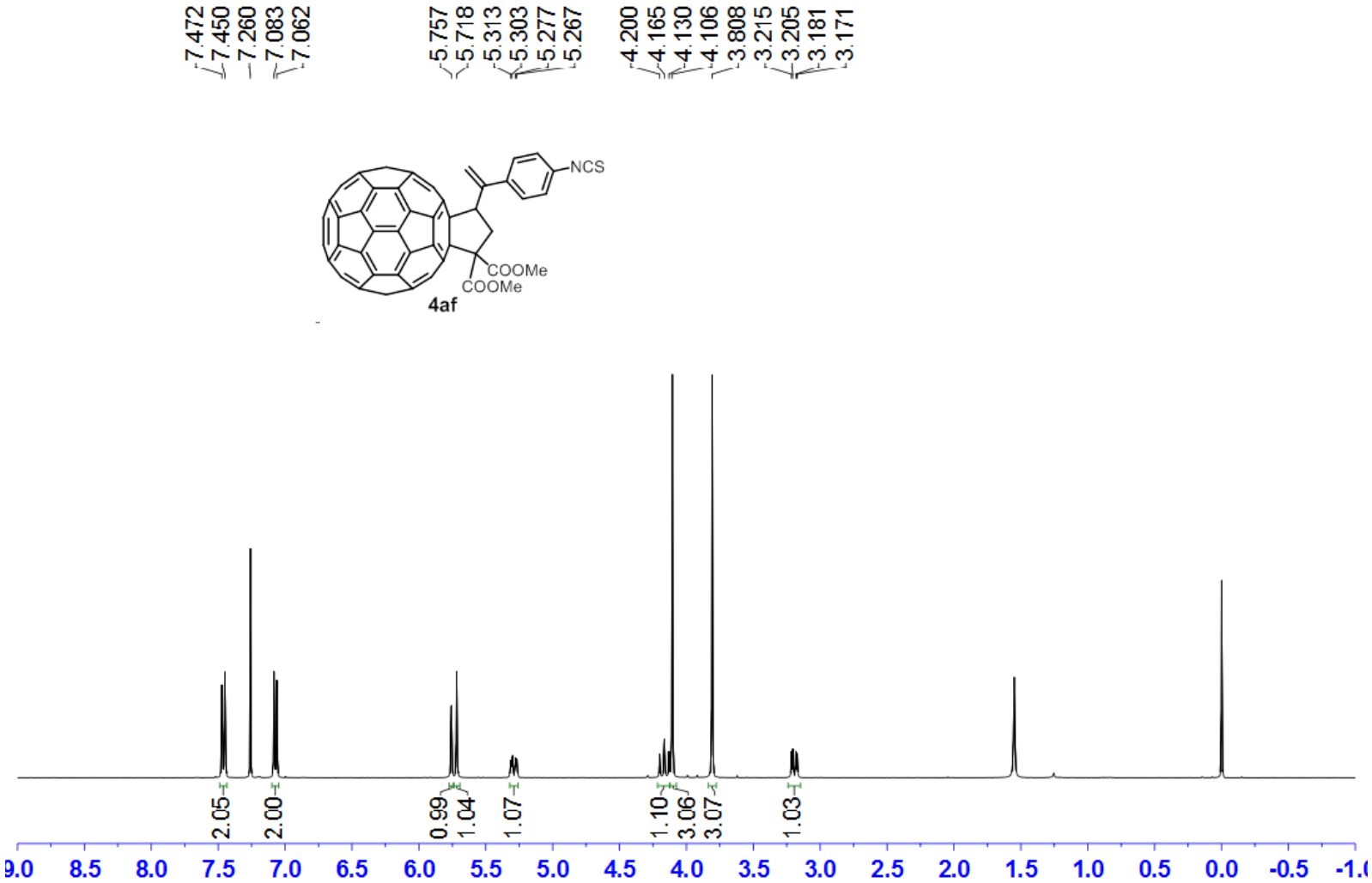
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4ae

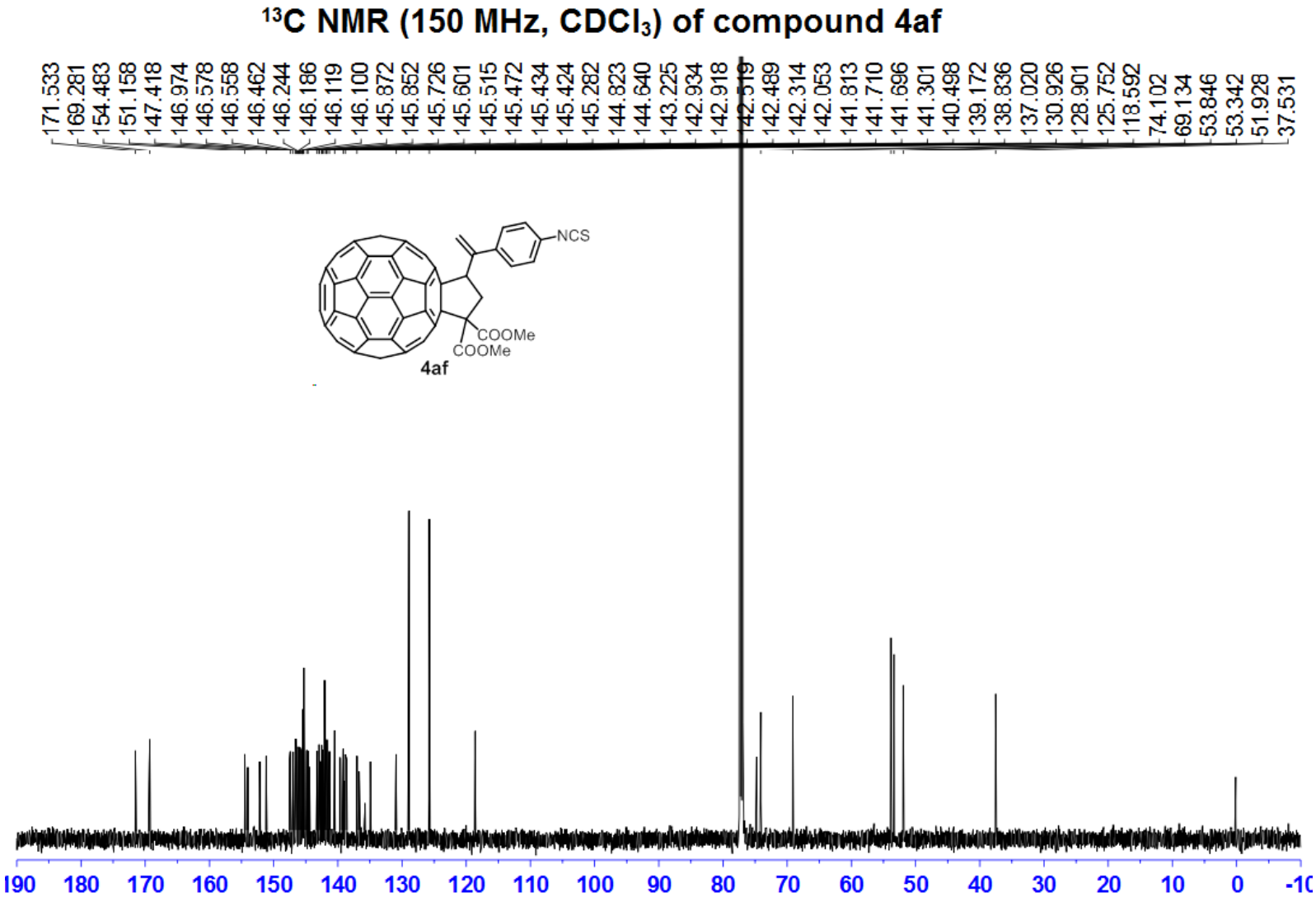


^{13}C NMR (150 MHz, $CDCl_3$) of compound 4ae

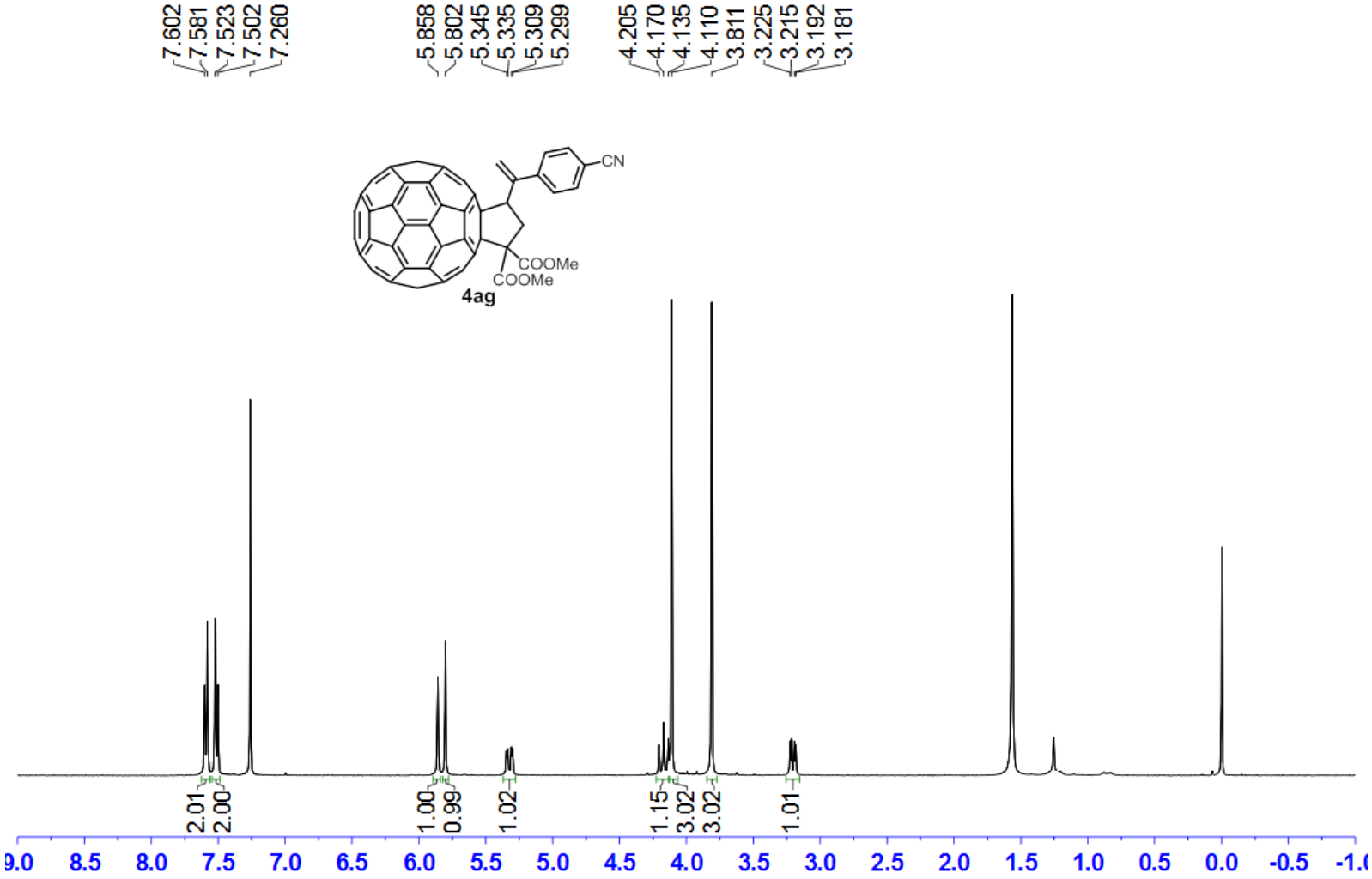


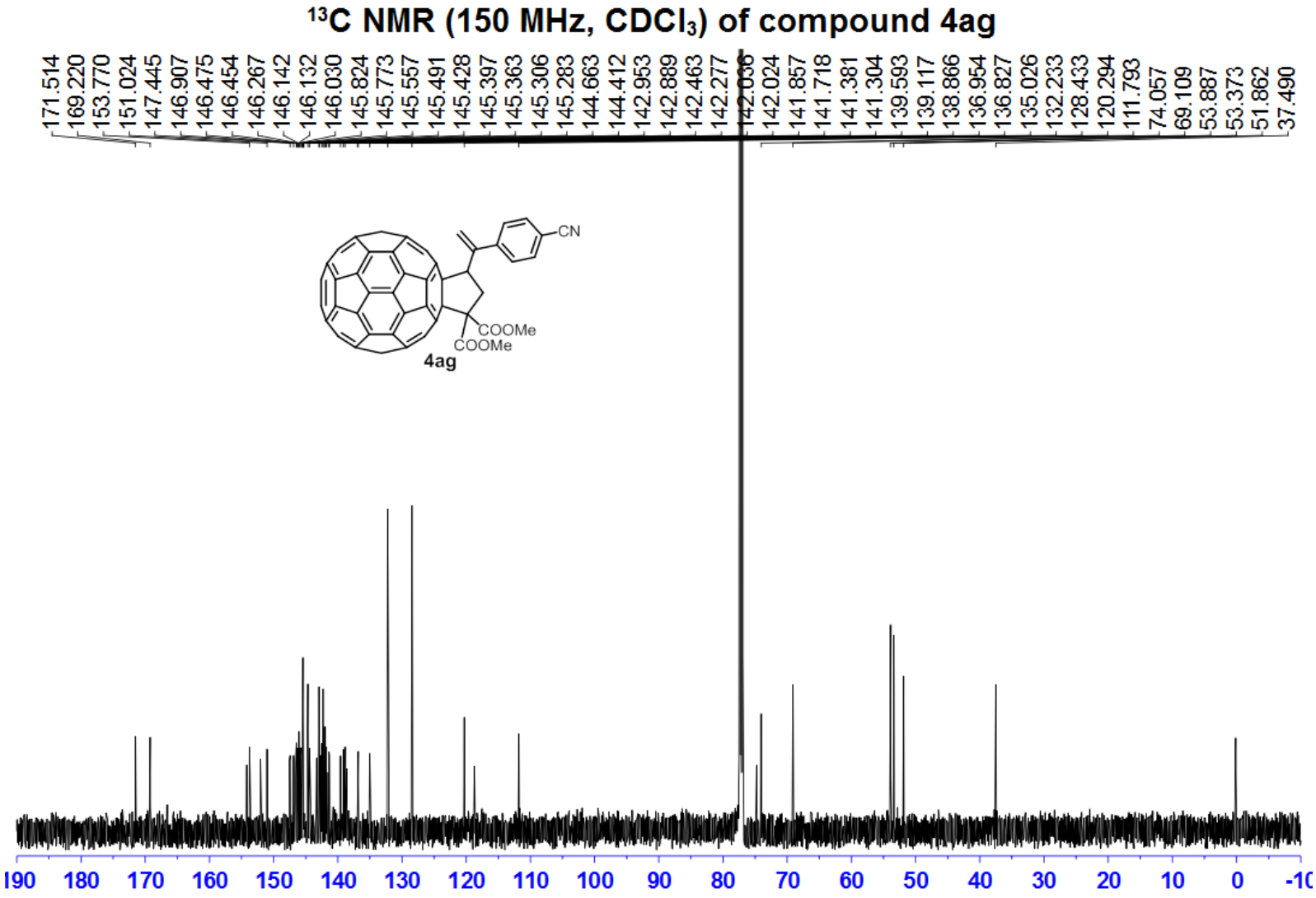
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4af



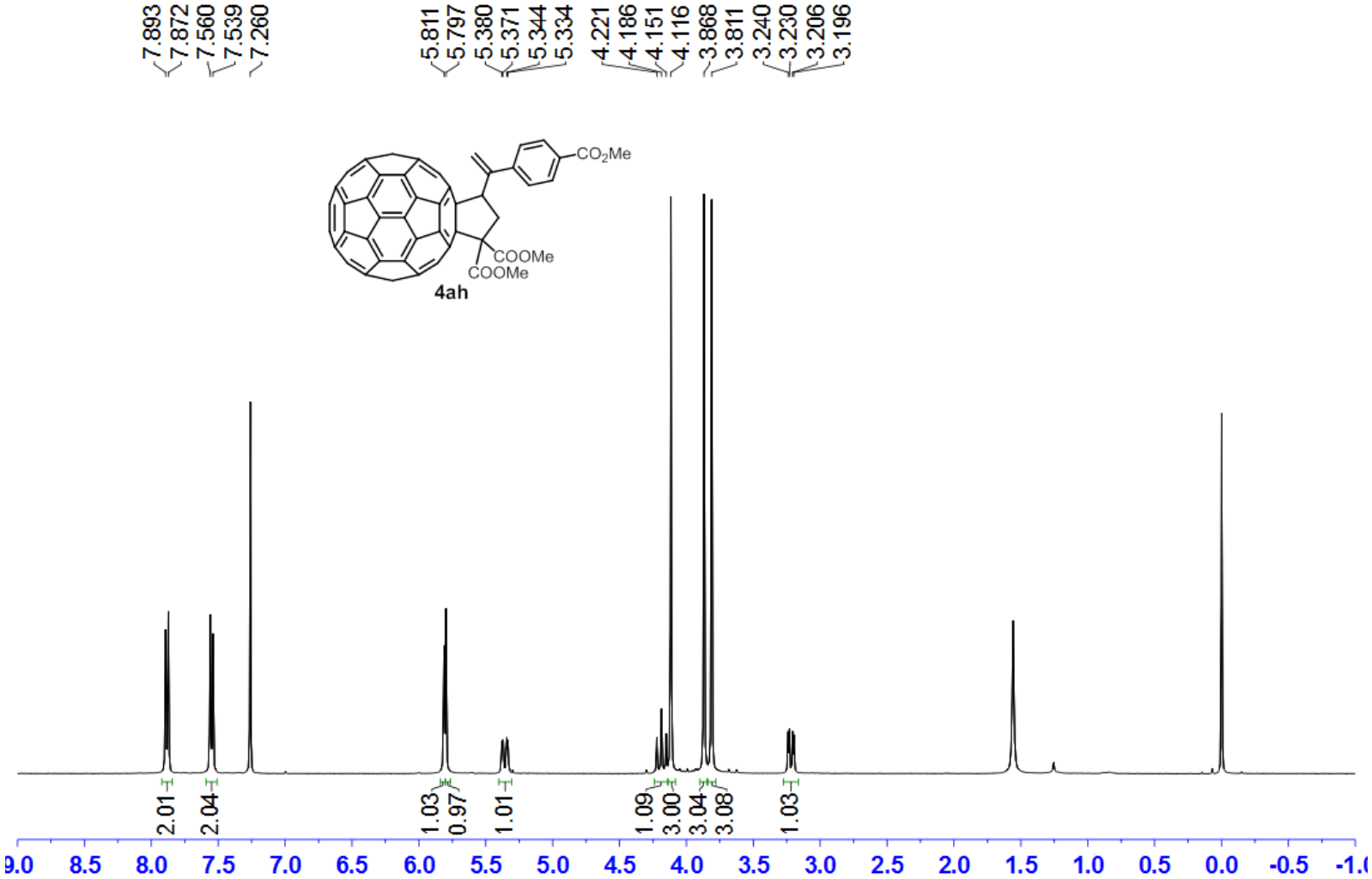

13C NMR (150 MHz, CDCl3) of compound 4af
171.533
169.281
154.483
151.158
147.418
146.974
146.578
146.558
146.462
146.244
146.186
146.119
146.100
145.872
145.852
145.726
145.601
145.515
145.472
145.434
145.424
145.282
144.823
144.640
143.225
142.934
142.918
142.519
142.489
142.314
142.053
141.813
141.710
141.696
141.301
140.498
139.172
138.836
137.020
130.926
128.901
125.752
118.592
74.102
69.134
53.846
53.342
51.928
37.531
NCS
COOMe
COOMe
4af
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

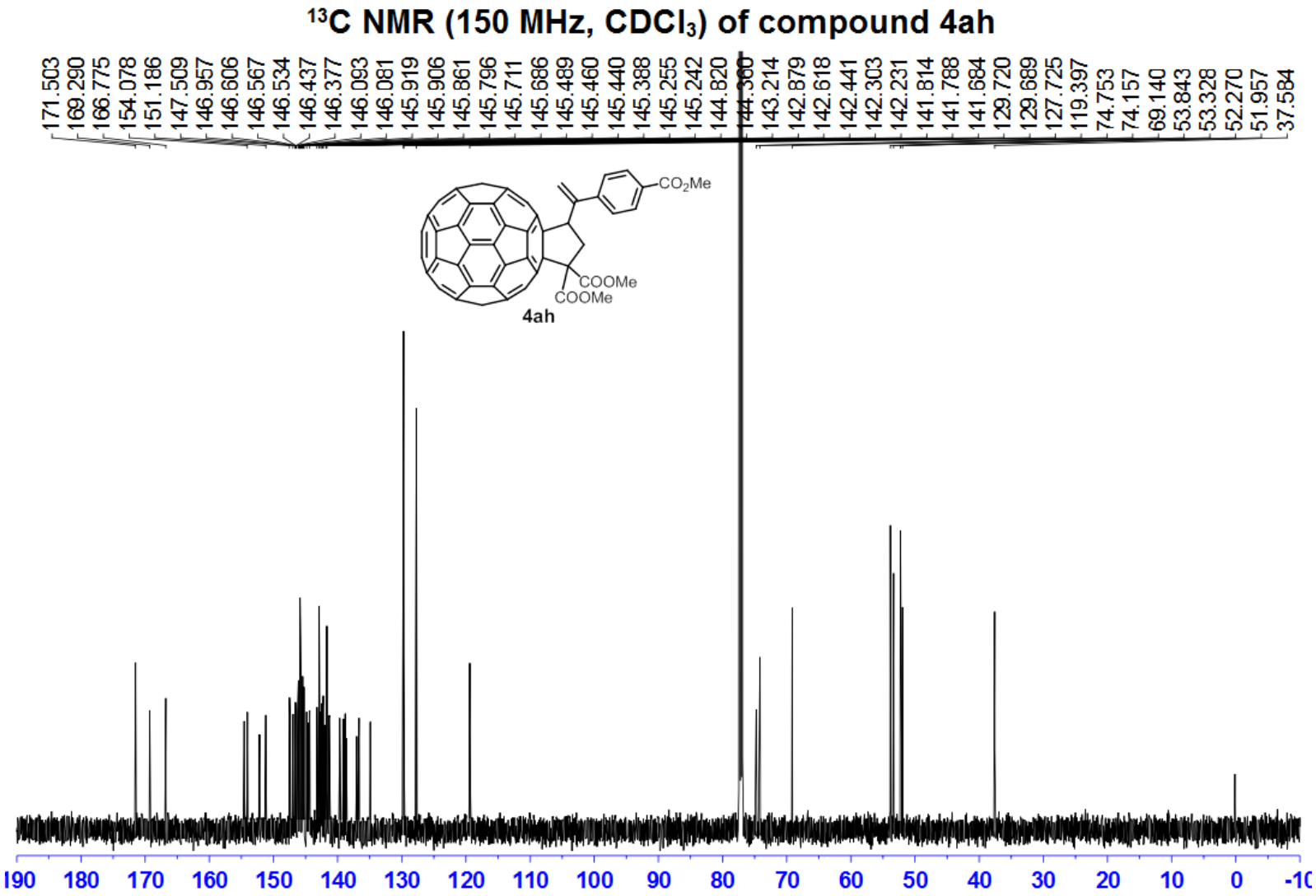
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4ag



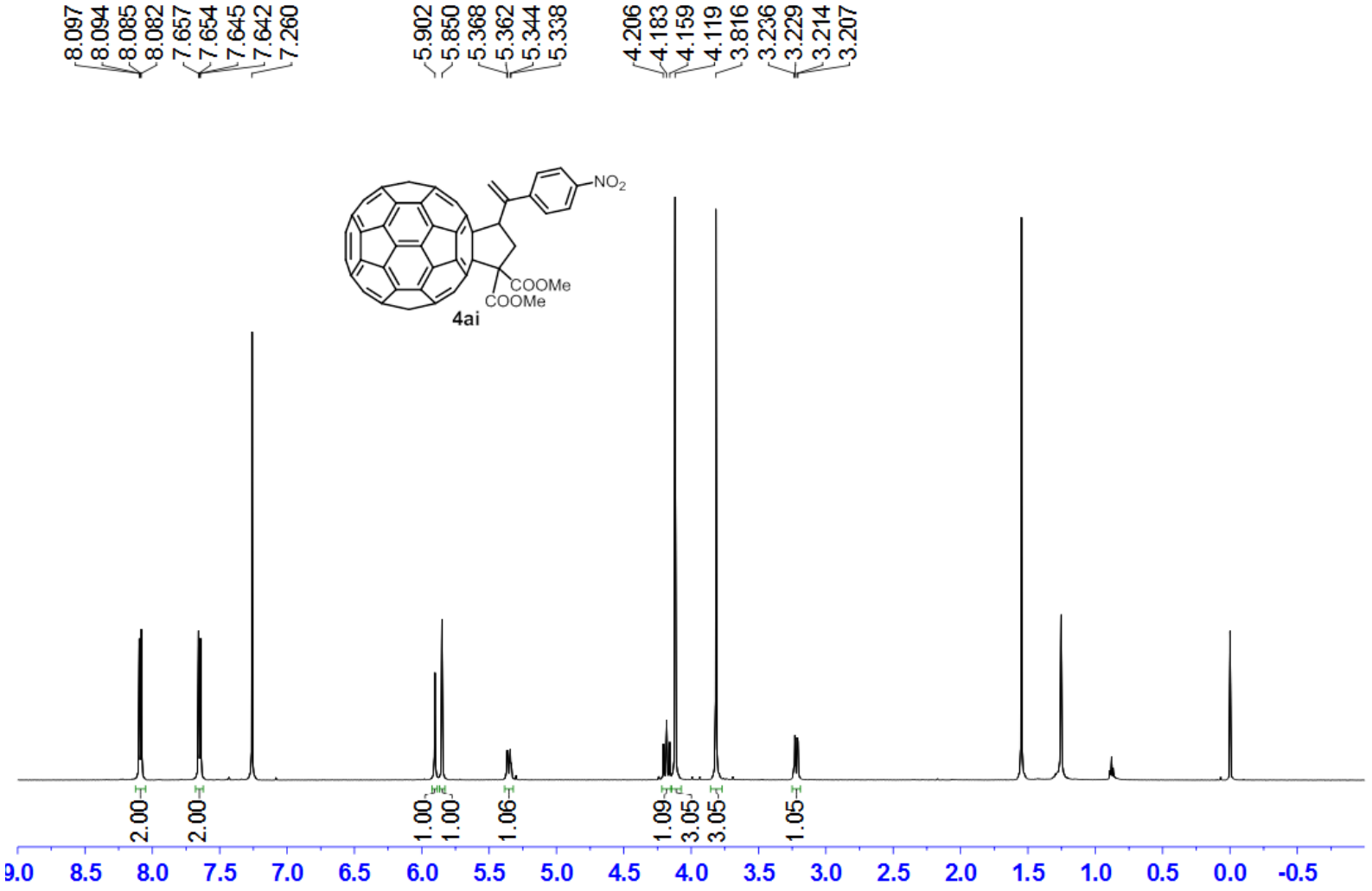

13C NMR (150 MHz, CDCl3) of compound 4ag
171.514
169.220
153.770
151.024
147.445
146.907
146.475
146.454
146.267
146.142
146.132
146.030
145.824
145.773
145.557
145.491
145.428
145.397
145.363
145.306
145.283
144.663
144.412
142.953
142.889
142.463
142.277
142.036
142.024
141.857
141.718
141.381
141.304
139.593
139.117
138.866
136.954
136.827
135.026
132.233
128.433
120.294
111.793
74.057
69.109
53.887
53.373
51.862
37.490
CN
COOMe
COOMe
4ag
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

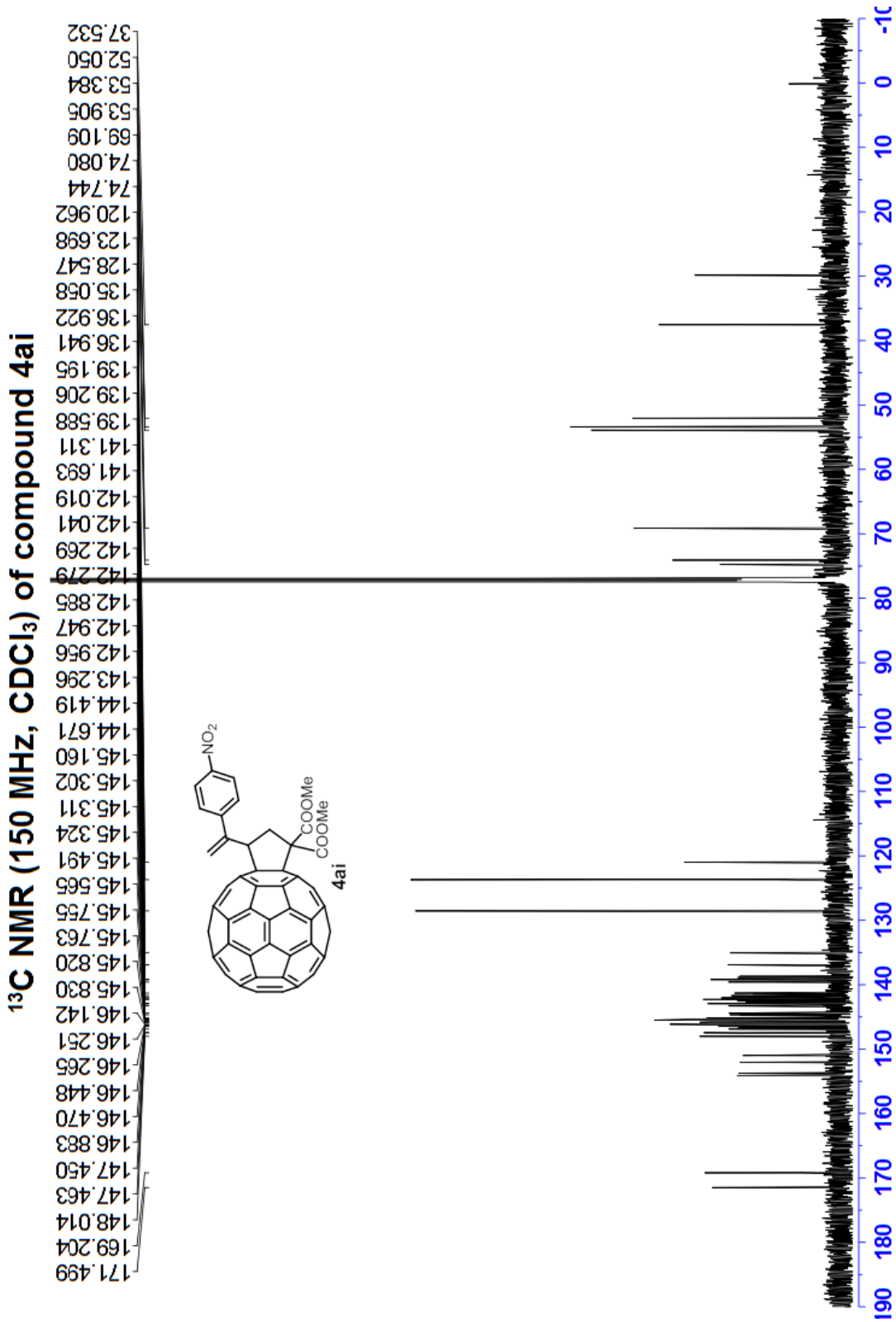
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4ah

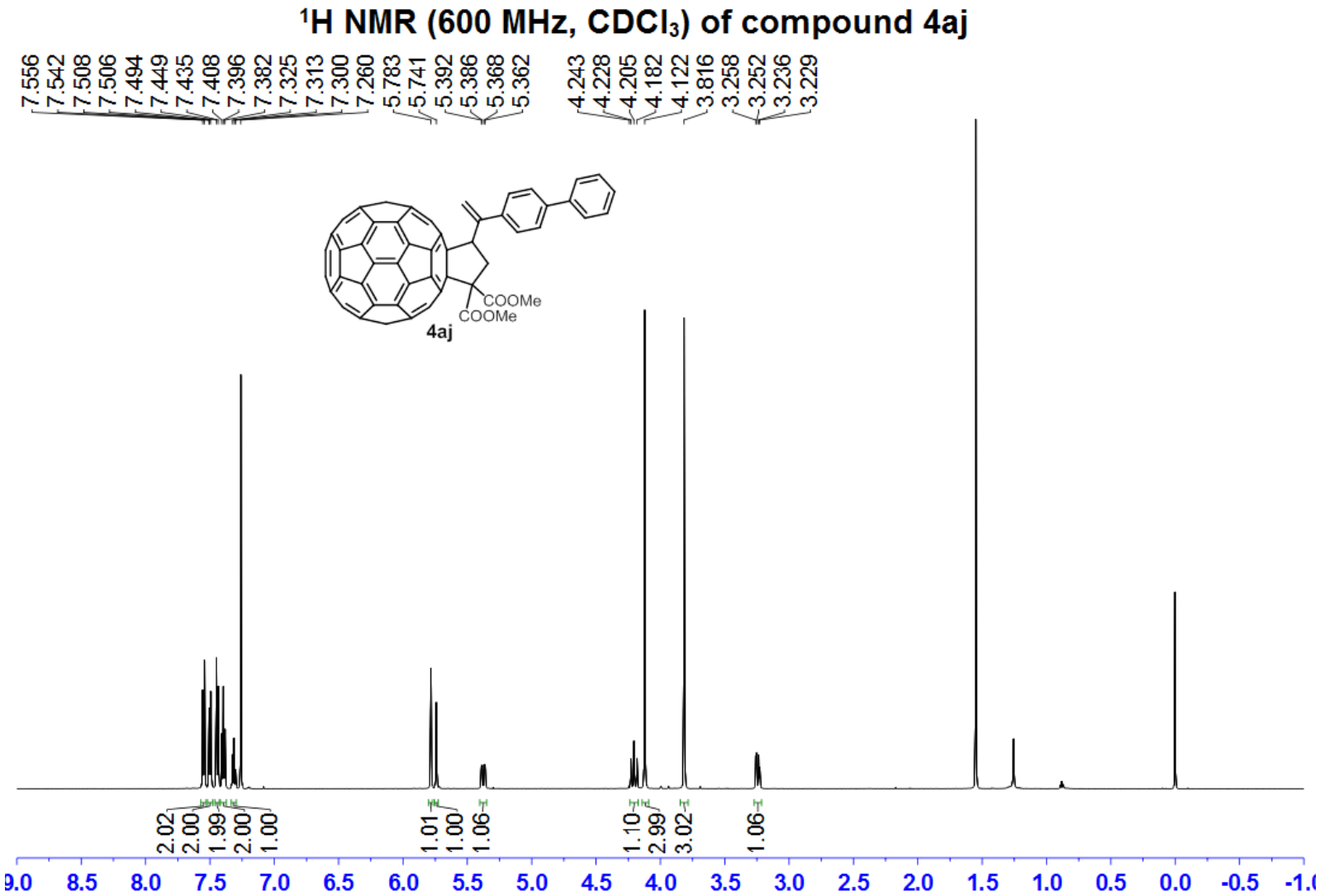



13C NMR (150 MHz, CDCl3) of compound 4ah
171.503
169.290
166.775
154.078
151.186
147.509
146.957
146.606
146.567
146.534
146.437
146.377
146.093
146.081
145.919
145.906
145.861
145.796
145.711
145.686
145.489
145.460
145.440
145.388
145.255
145.242
144.820
144.360
143.214
142.879
142.618
142.441
142.303
142.231
141.814
141.788
141.684
129.720
129.689
127.725
119.397
74.753
74.157
69.140
53.843
53.328
52.270
51.957
37.584
CO2Me
COOMe
COOMe
4ah
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

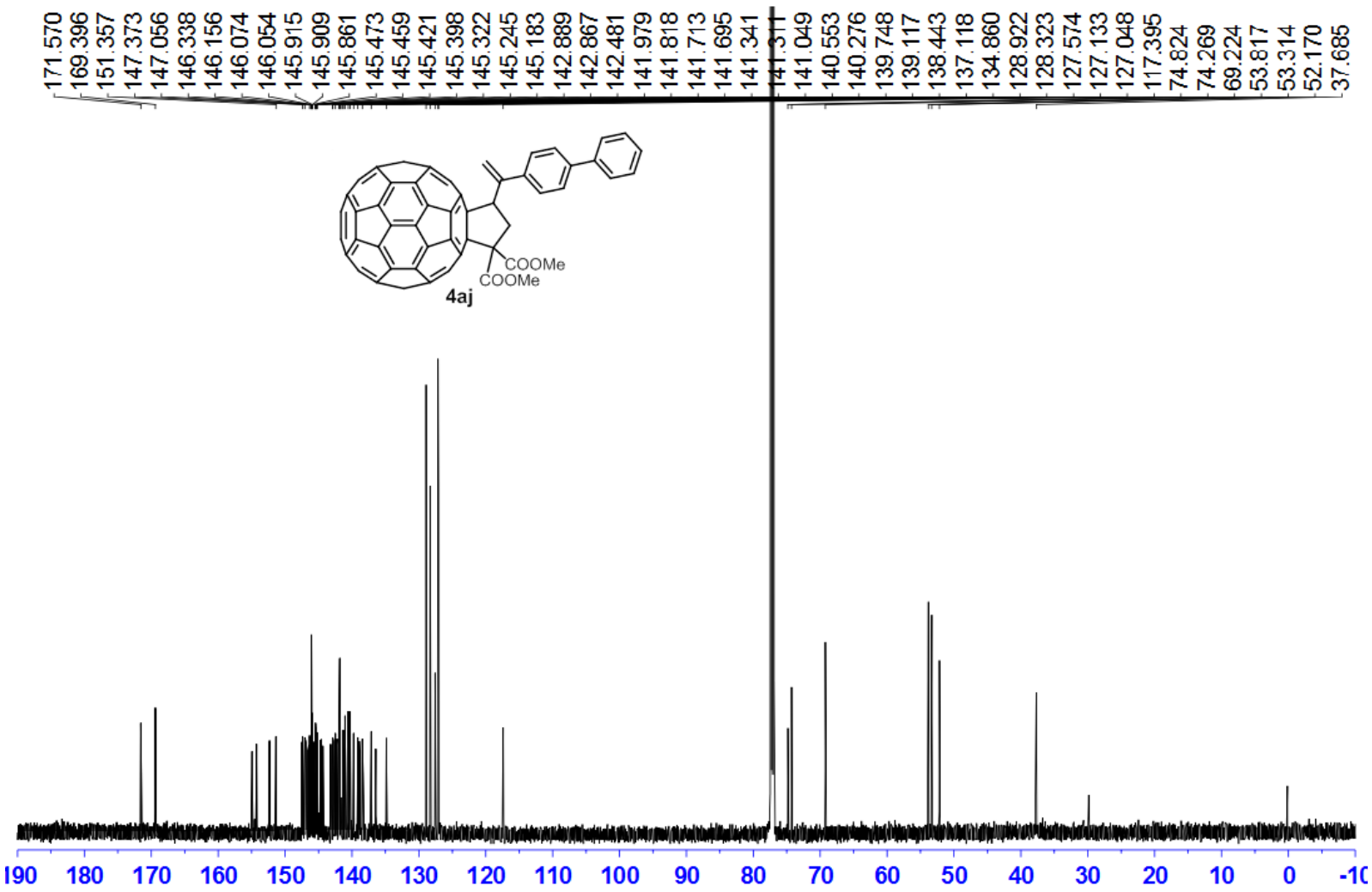
^{1}H NMR (600 MHz, $CDCl_3$) of compound 4ai



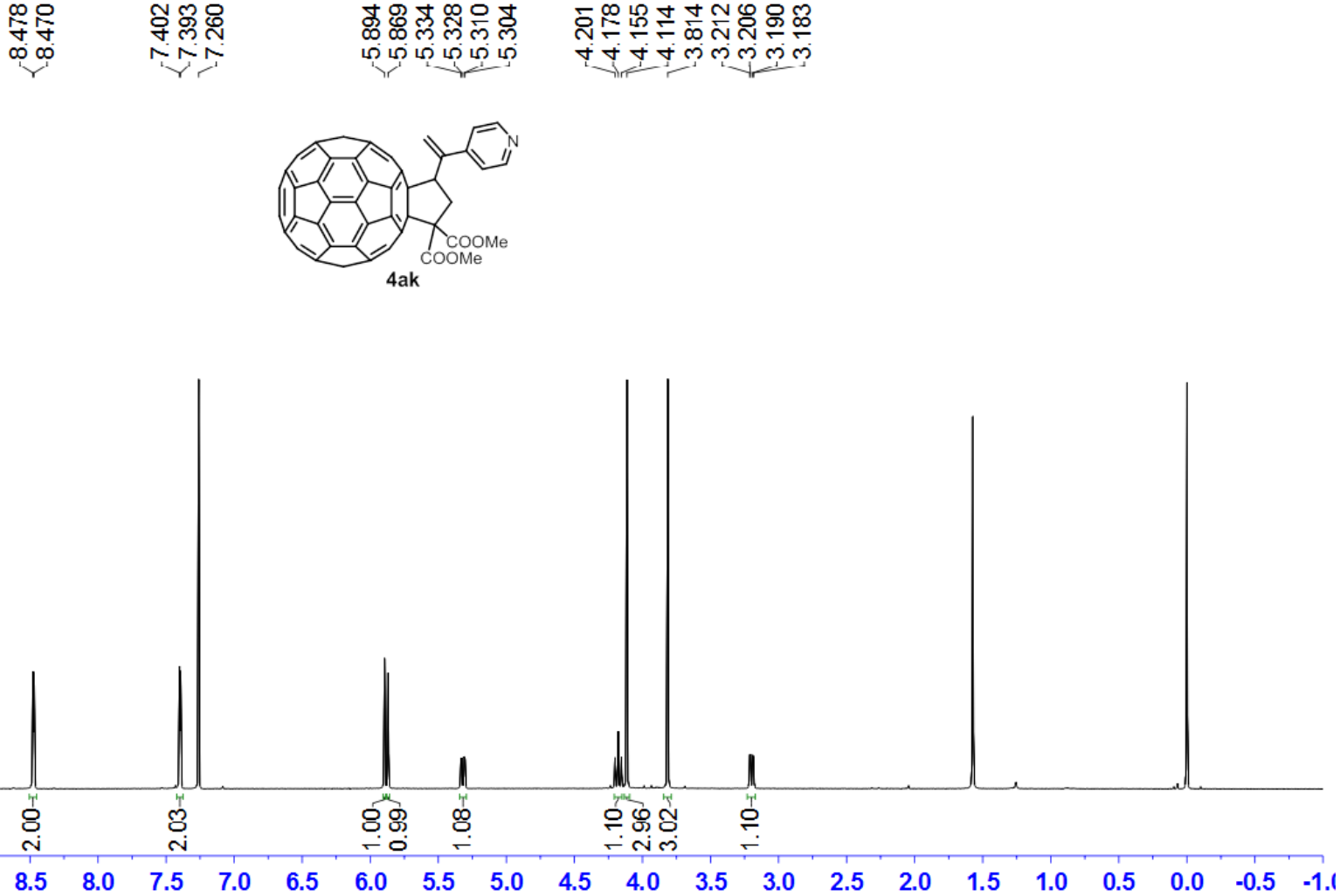

^{13}C NMR (150 MHz, $CDCl_3$) of compound 4ai
171.499
169.204
148.014
147.463
147.450
146.883
146.470
146.448
146.265
146.251
146.142
145.830
145.820
145.763
145.755
145.565
145.491
145.324
145.311
145.302
145.160
144.671
144.419
143.296
142.956
142.947
142.885
142.279
142.269
142.041
142.019
141.693
141.311
139.588
139.206
139.195
136.941
136.922
135.058
128.547
123.698
120.962
74.744
74.080
69.109
53.905
53.384
52.050
37.532
NO_2
COOMe
COOMe
4ai
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


¹H NMR (600 MHz, CDCl₃) of compound 4aj
7.556
7.542
7.508
7.506
7.494
7.449
7.435
7.408
7.396
7.382
7.325
7.313
7.300
7.260
5.783
5.741
5.392
5.386
5.368
5.362
4.243
4.228
4.205
4.182
4.122
3.816
3.258
3.252
3.236
3.229
COOMe
COOMe
4aj
2.02
2.00
1.99
2.00
1.00
1.01
1.00
1.06
1.10
2.99
3.02
1.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

^{13}C NMR (150 MHz, $CDCl_3$) of compound 4aj

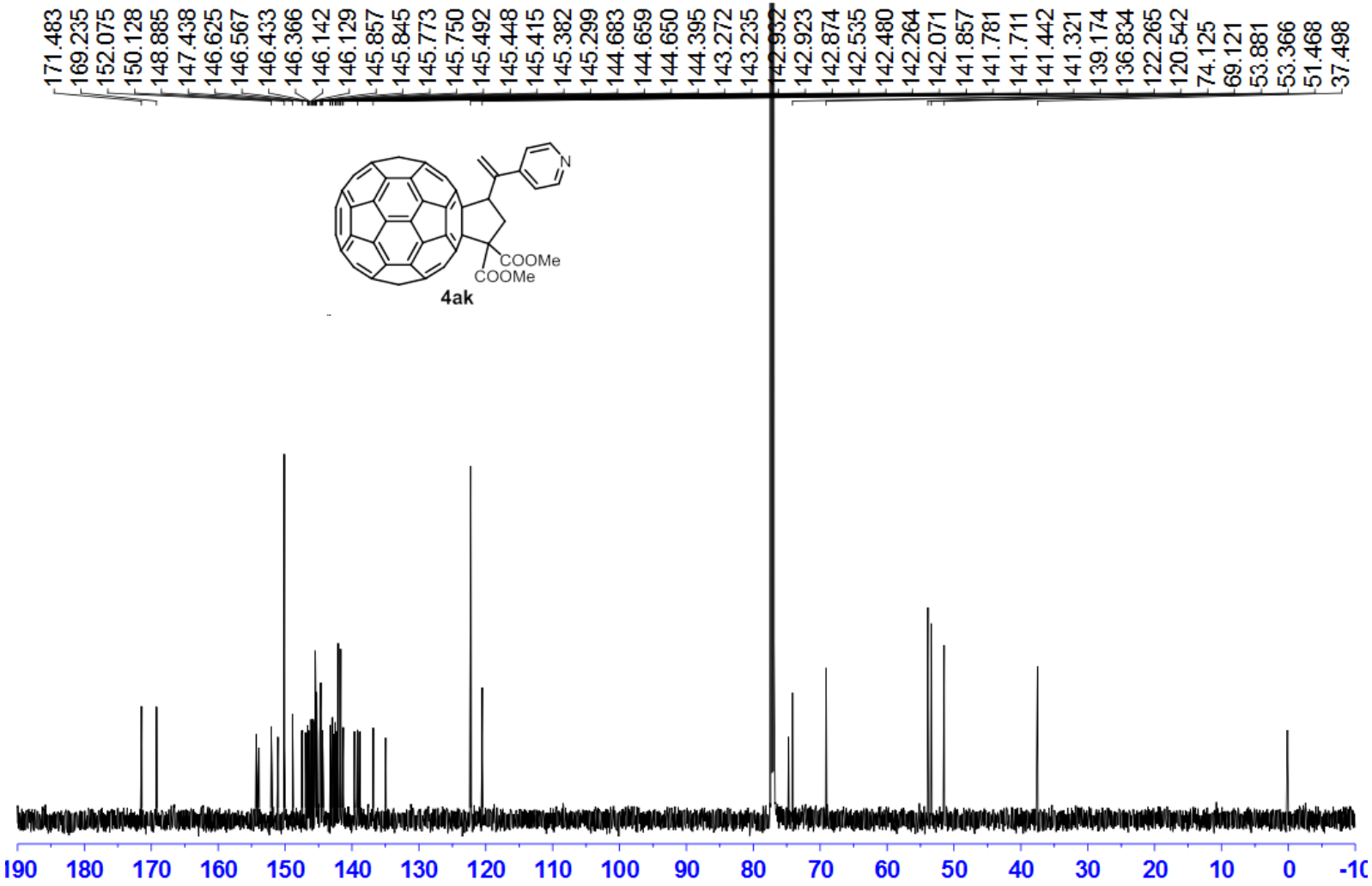


^{1}H NMR (600 MHz, $CDCl_3$) of compound 4ak

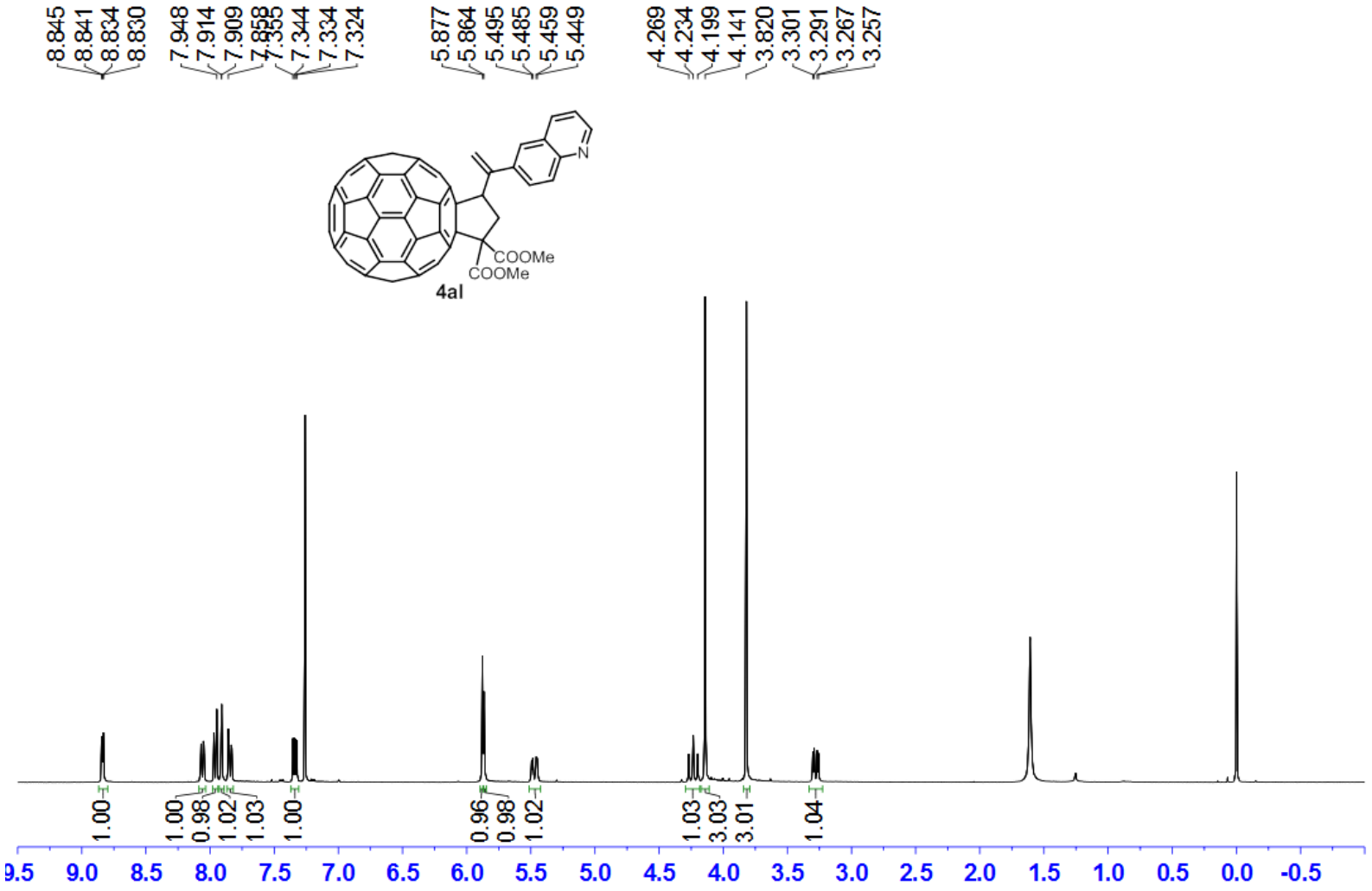


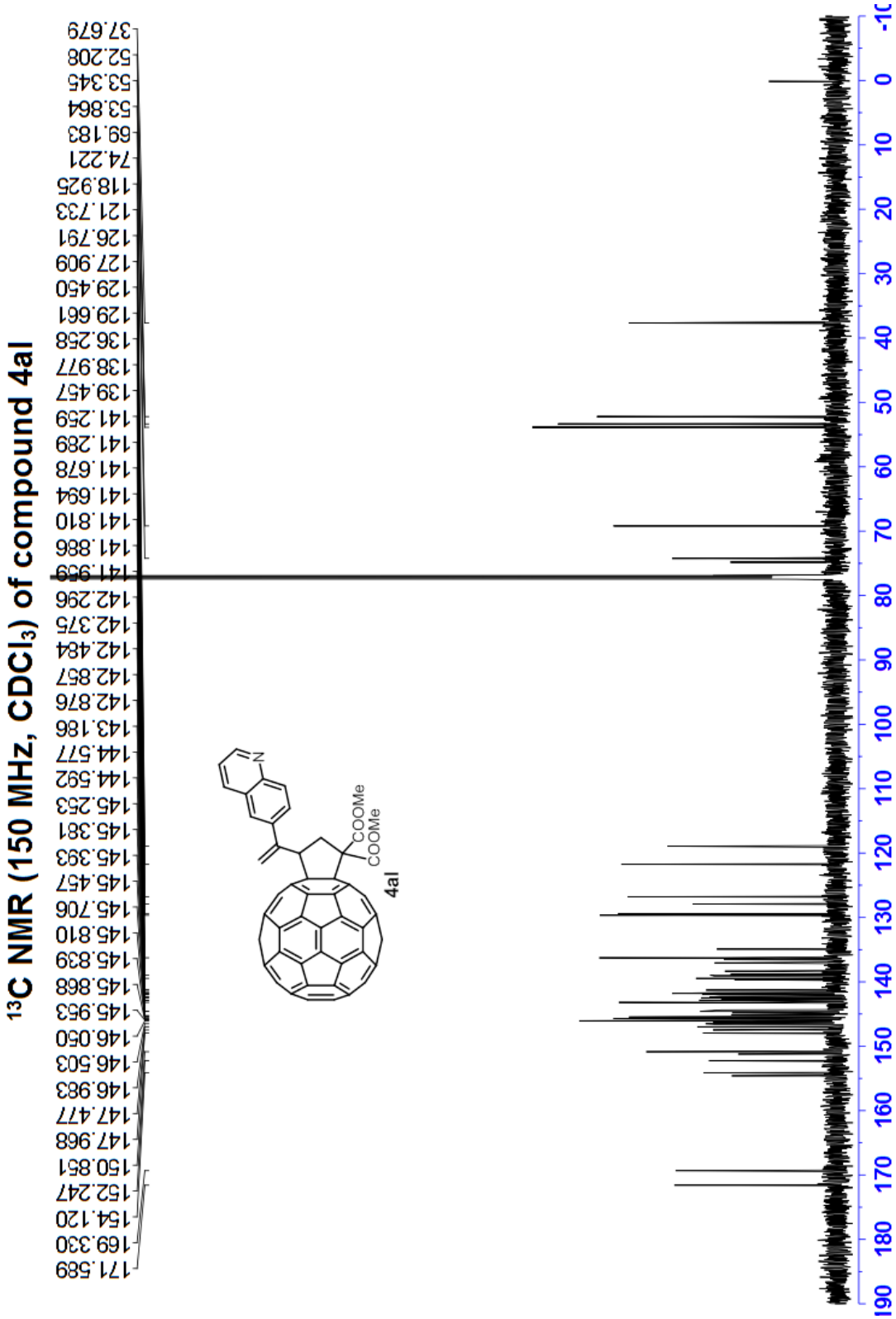
4ak

^{13}C NMR (150 MHz, $CDCl_3$) of compound 4ak

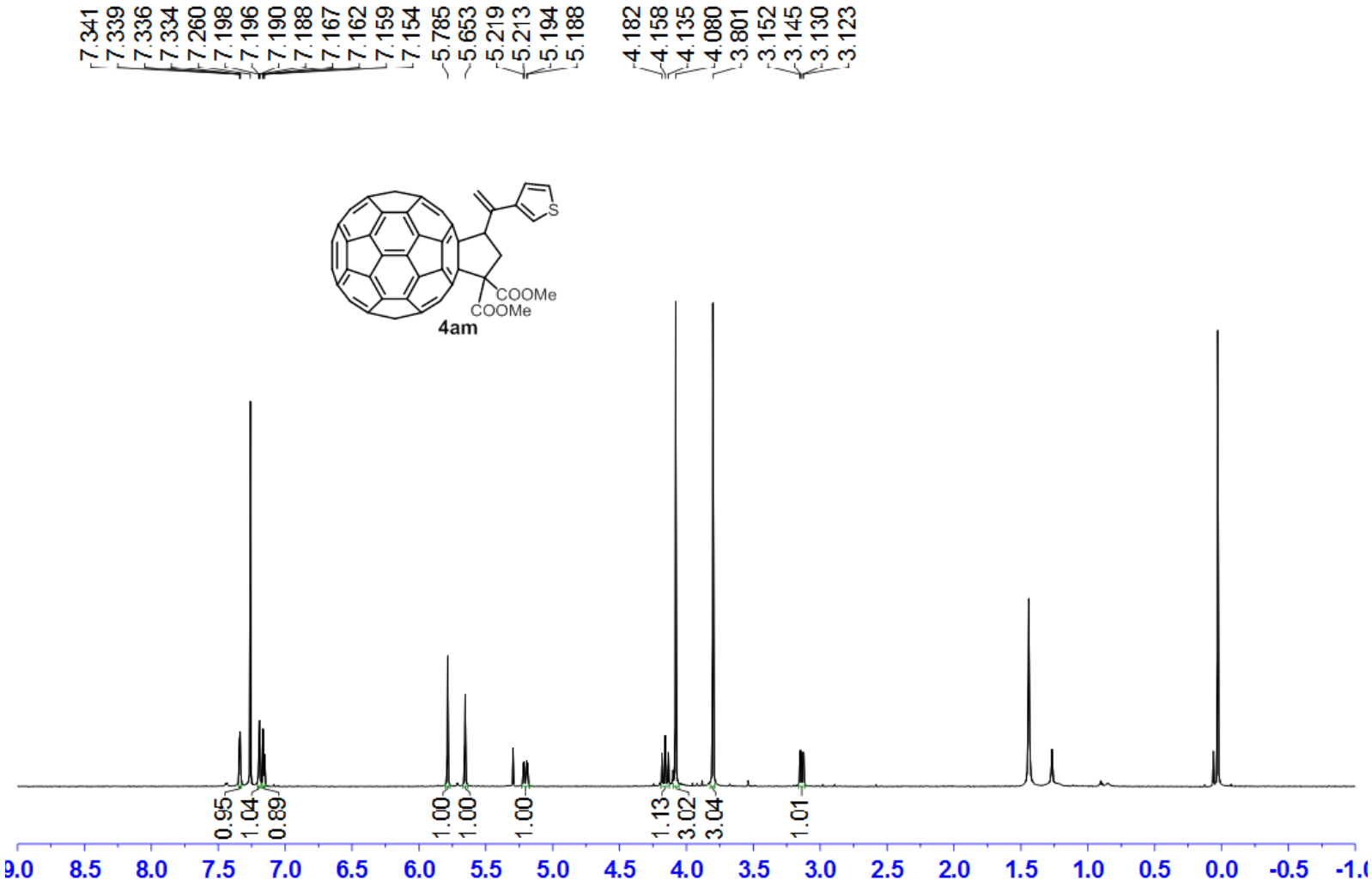


^{1}H NMR (400 MHz, $CDCl_3$) of compound 4al

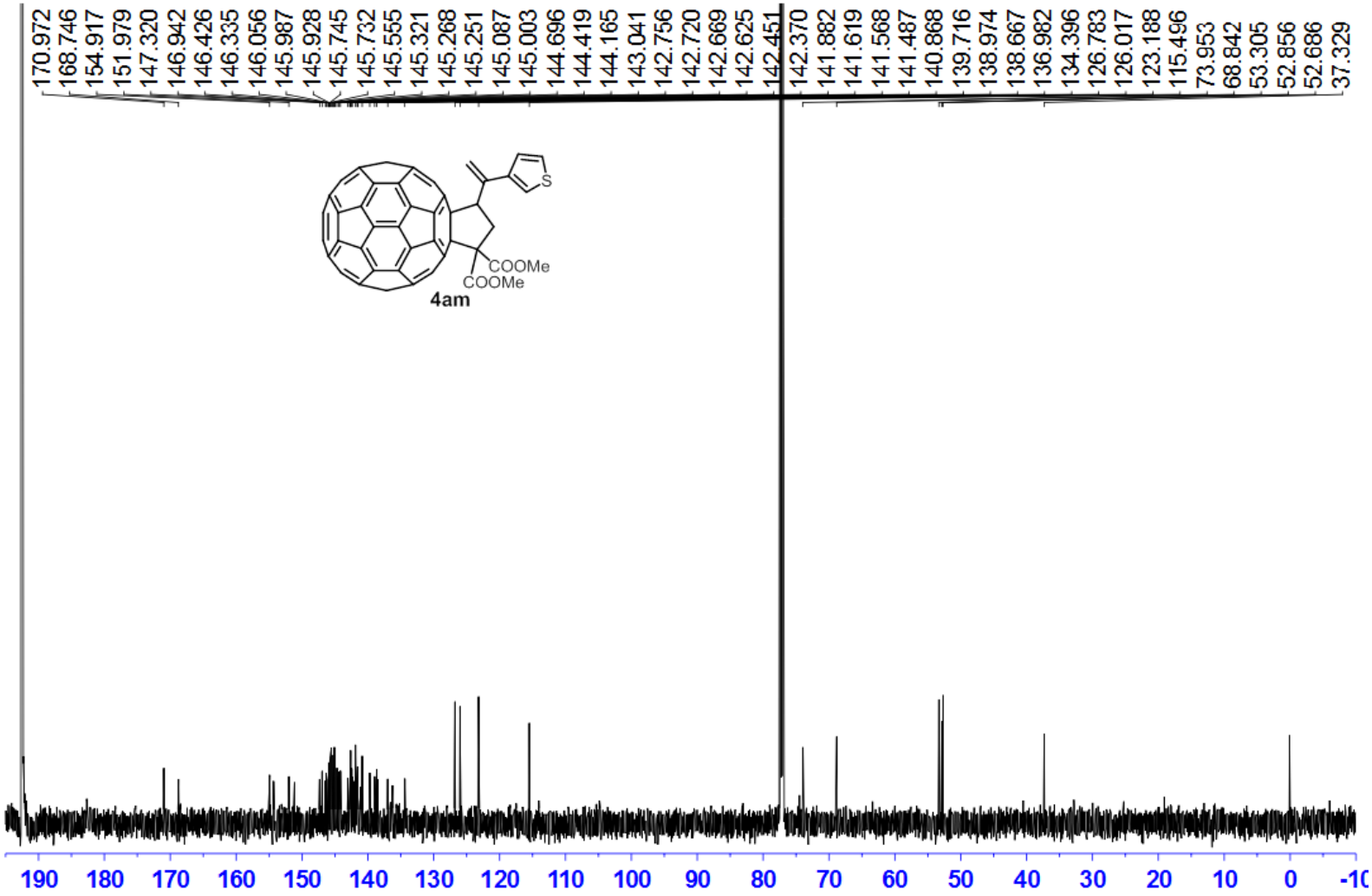



^{13}C NMR (150 MHz, $CDCl_3$) of compound 4al
COOMe
COOMe
4al

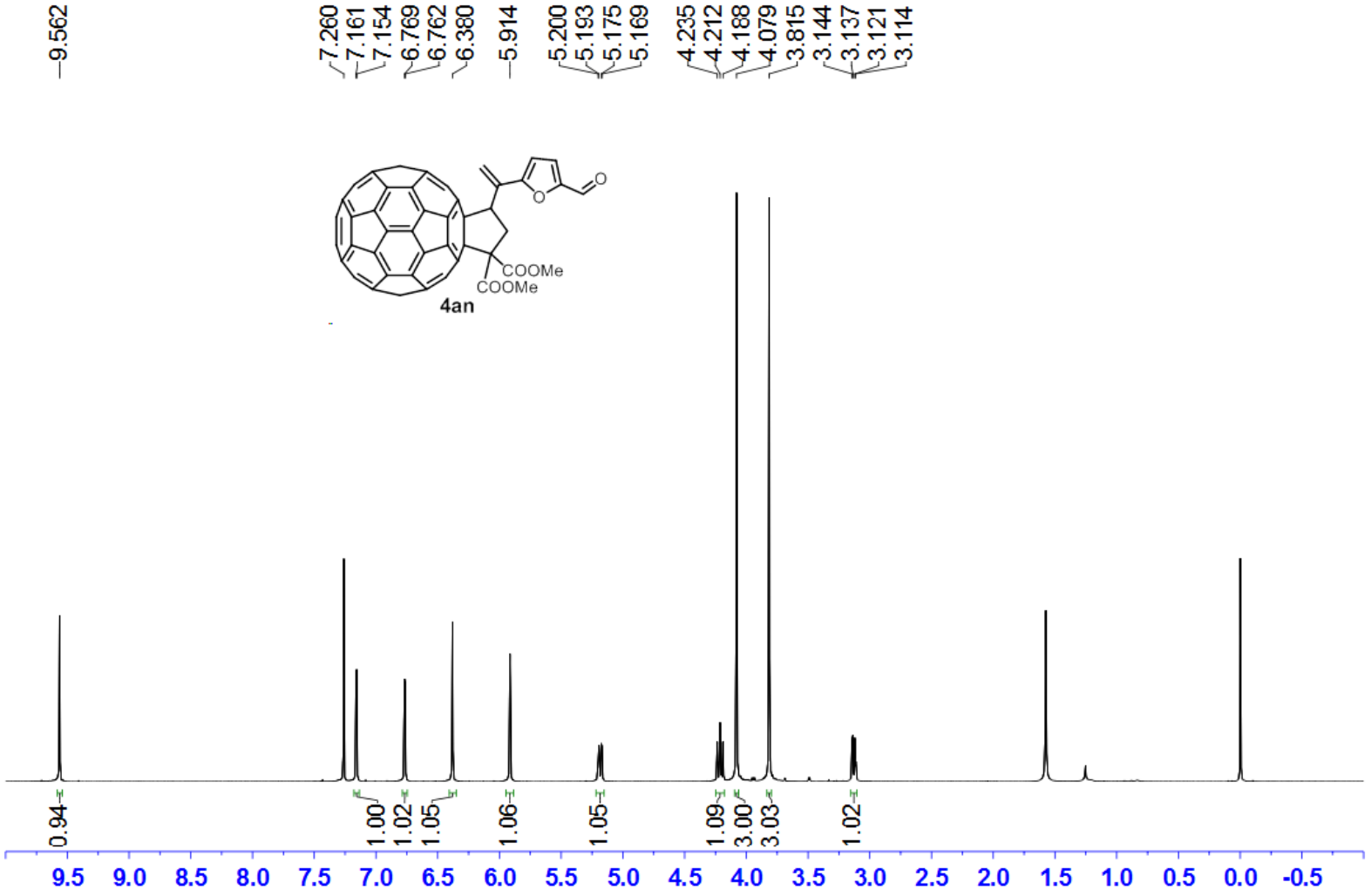
^{1}H NMR (600 MHz, $CDCl_3/CS_2$) of compound 4am

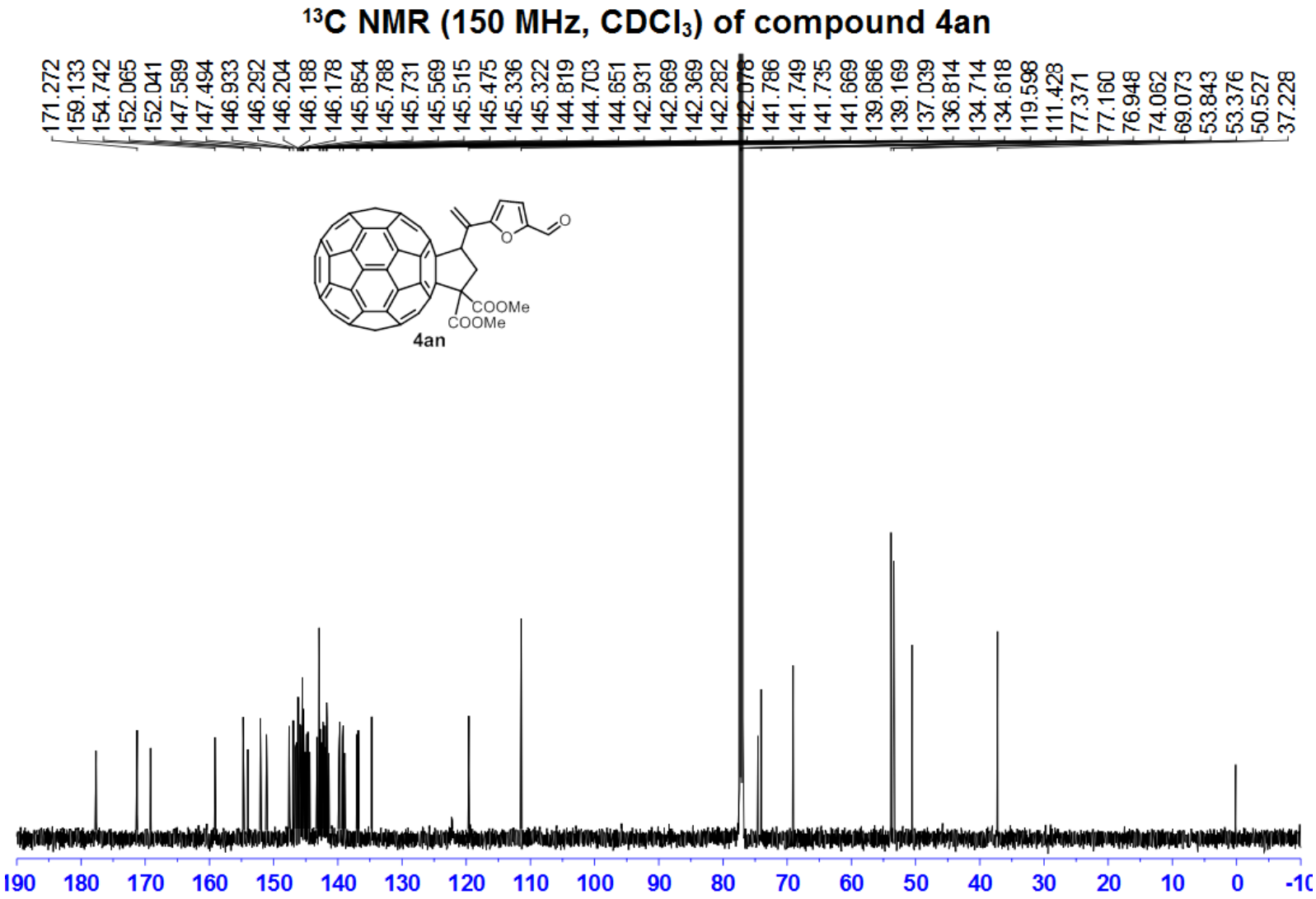


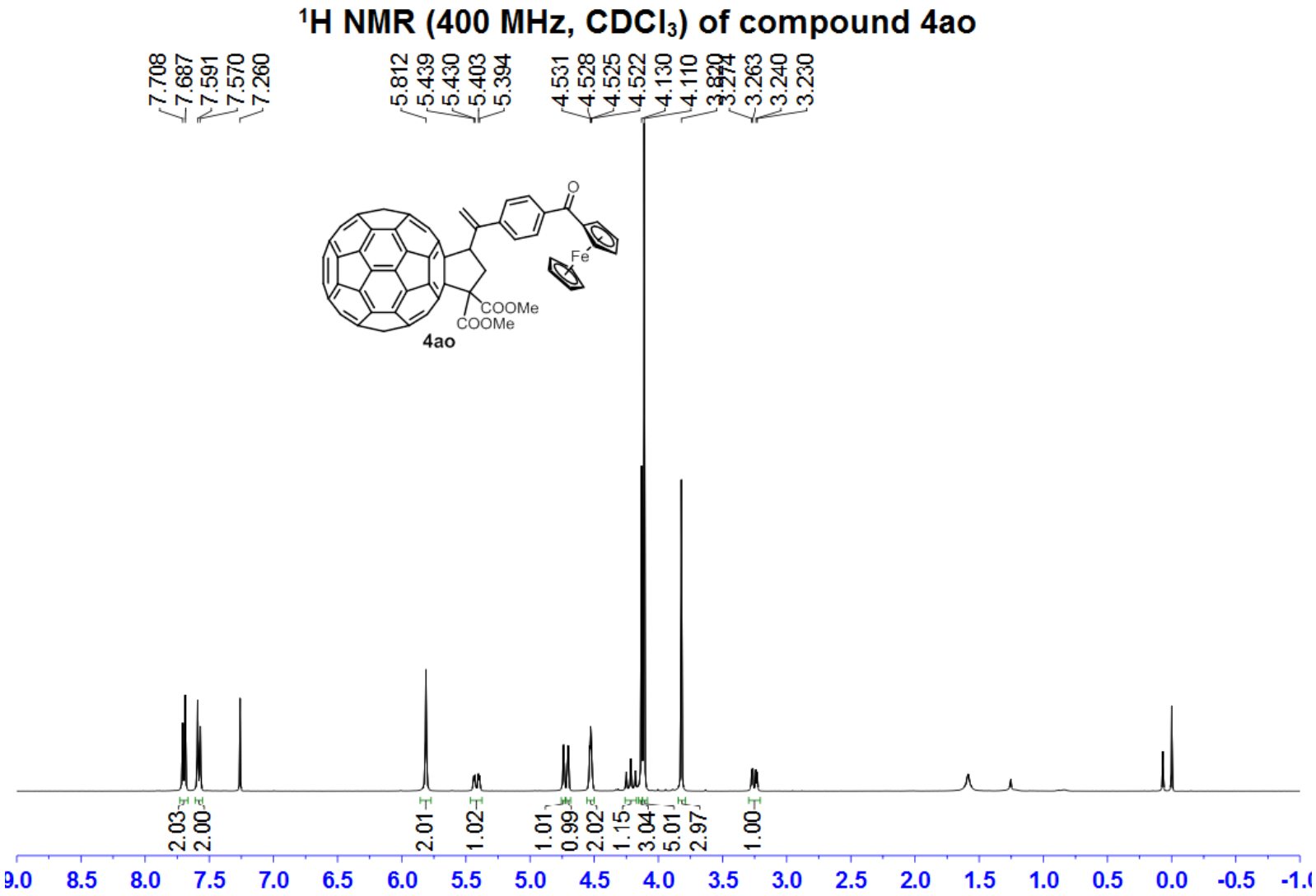
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 4am



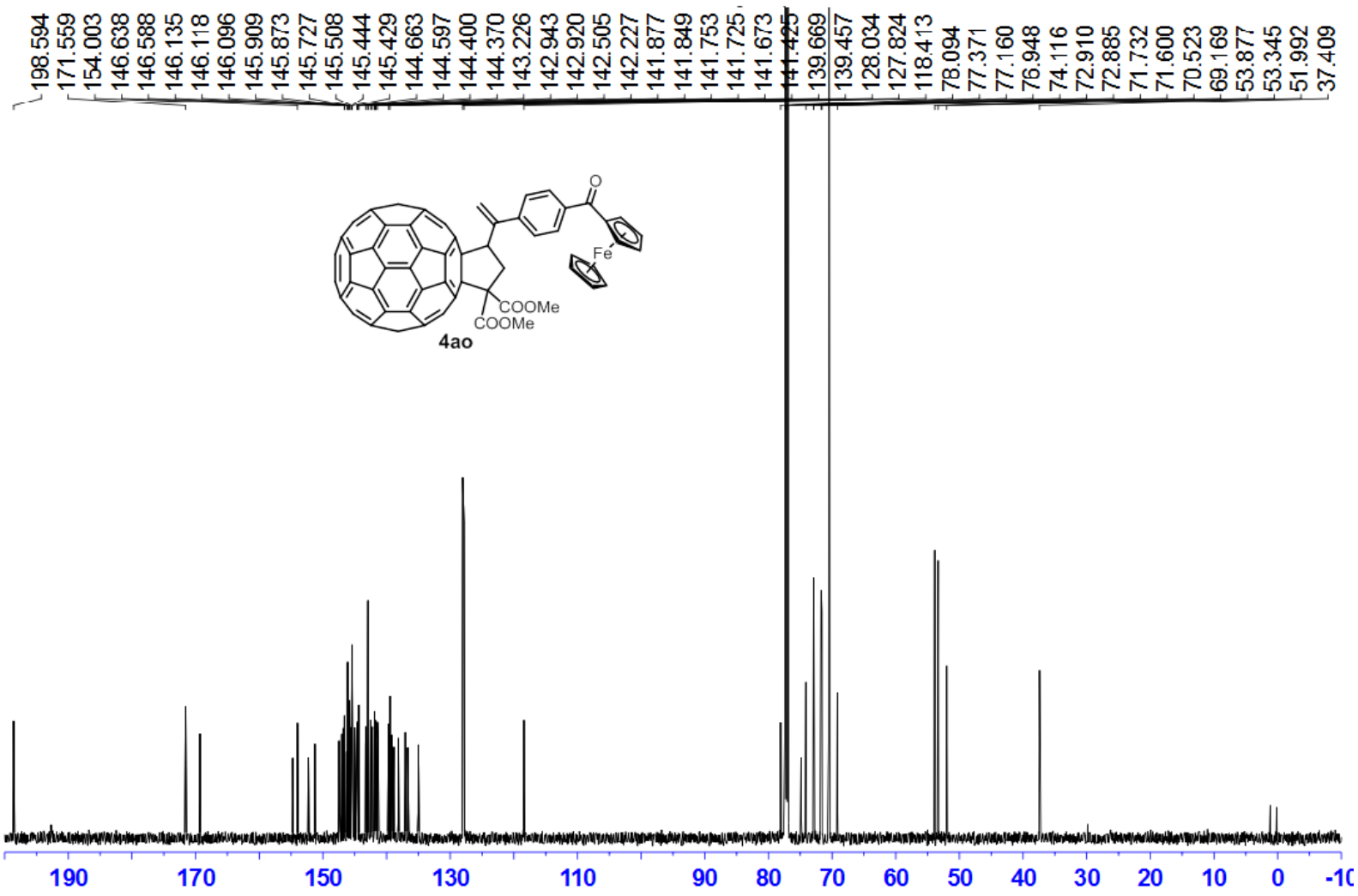
^{1}H NMR (600 MHz, $CDCl_3$) of compound 4an



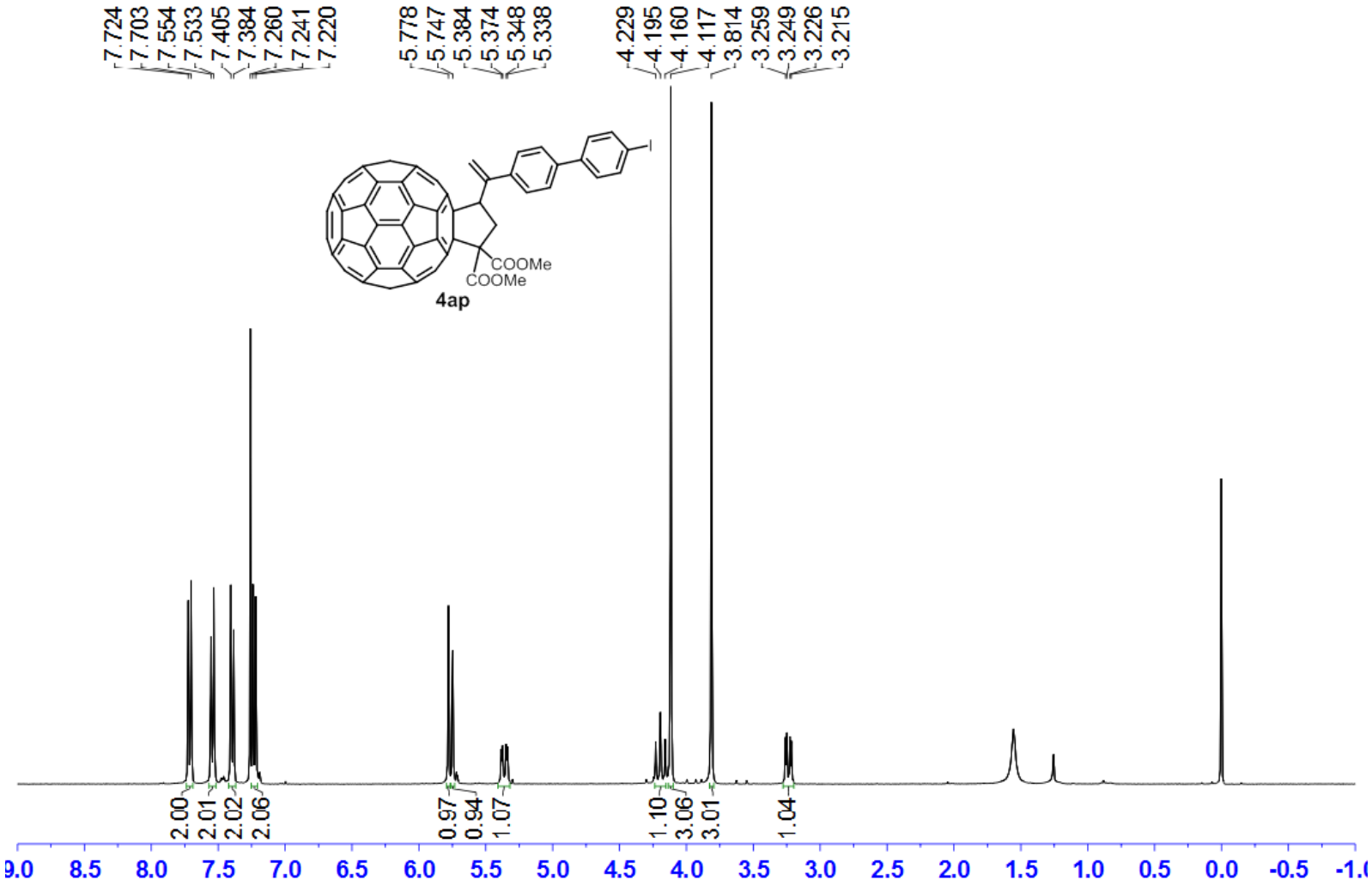

13C NMR (150 MHz, CDCl3) of compound 4an
171.272
159.133
154.742
152.065
152.041
147.589
147.494
146.933
146.292
146.204
146.188
146.178
145.854
145.788
145.731
145.569
145.515
145.475
145.336
145.322
144.819
144.703
144.651
142.931
142.669
142.369
142.282
142.078
141.786
141.749
141.735
141.669
139.686
139.169
137.039
136.814
134.714
134.618
119.598
111.428
77.371
77.160
76.948
74.062
69.073
53.843
53.376
50.527
37.228
O
O
COOMe
COOMe
4an
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


¹H NMR (400 MHz, CDCl₃) of compound 4ao
7.708
7.687
7.591
7.570
7.260
5.812
5.439
5.430
5.403
5.394
4.531
4.528
4.525
4.522
4.130
4.110
3.263
3.240
3.230
O
Fe
COOMe
COOMe
4ao
2.03
2.00
2.01
1.02
1.01
0.99
2.02
1.15
3.04
5.01
2.97
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

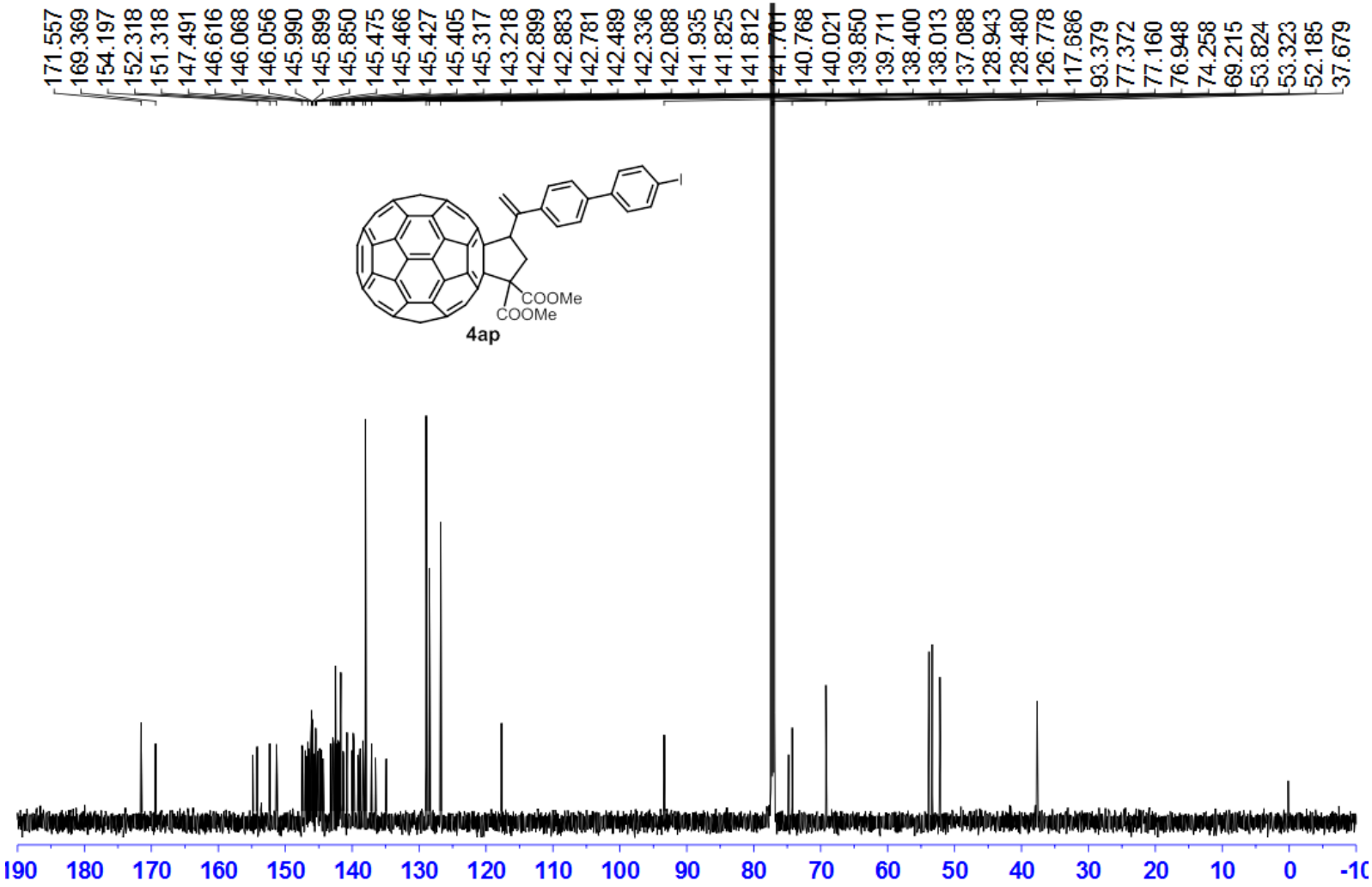
^{13}C NMR (150 MHz, $CDCl_3$) of compound 4ao

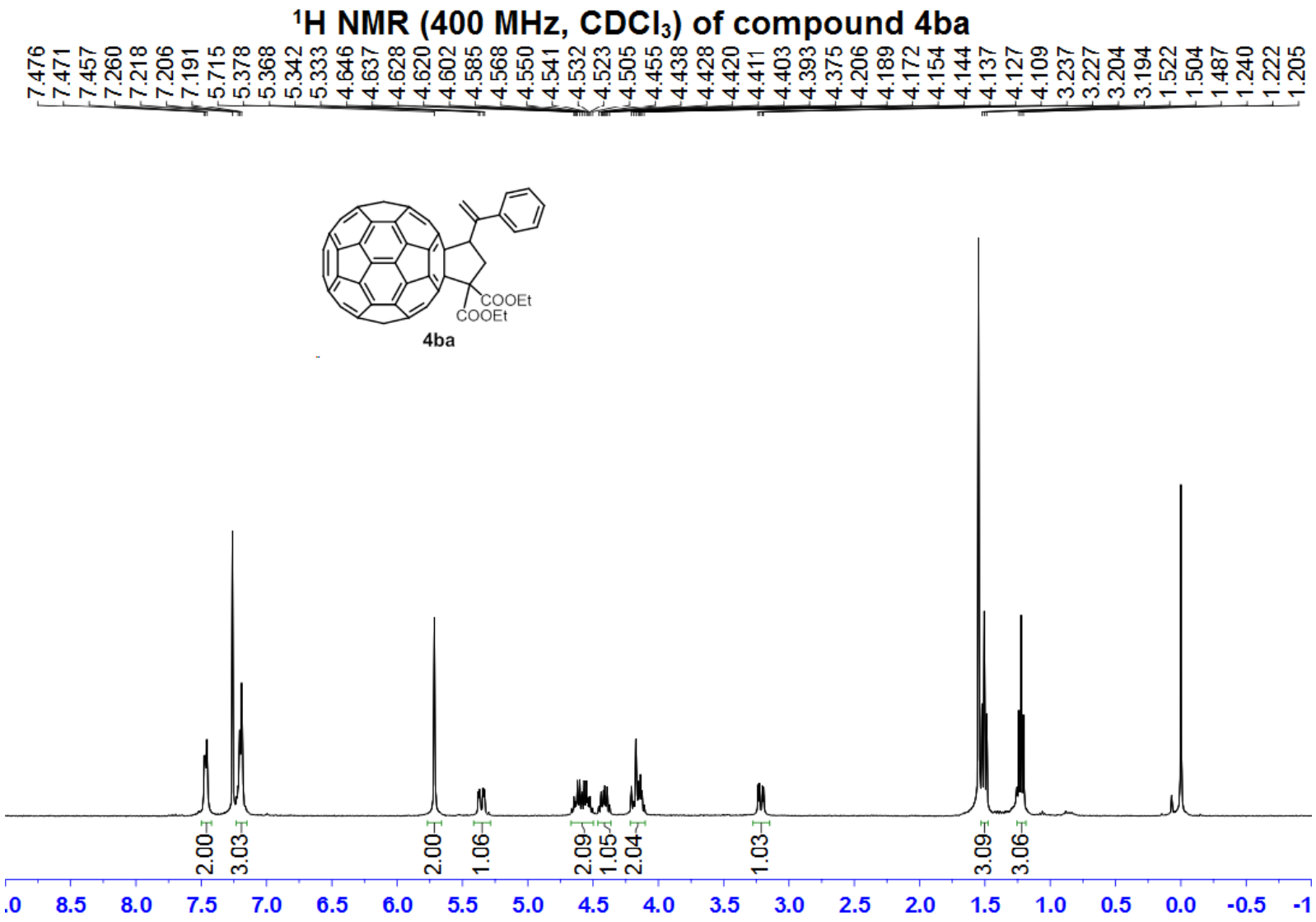


^{1}H NMR (400 MHz, $CDCl_3$) of compound 4ap

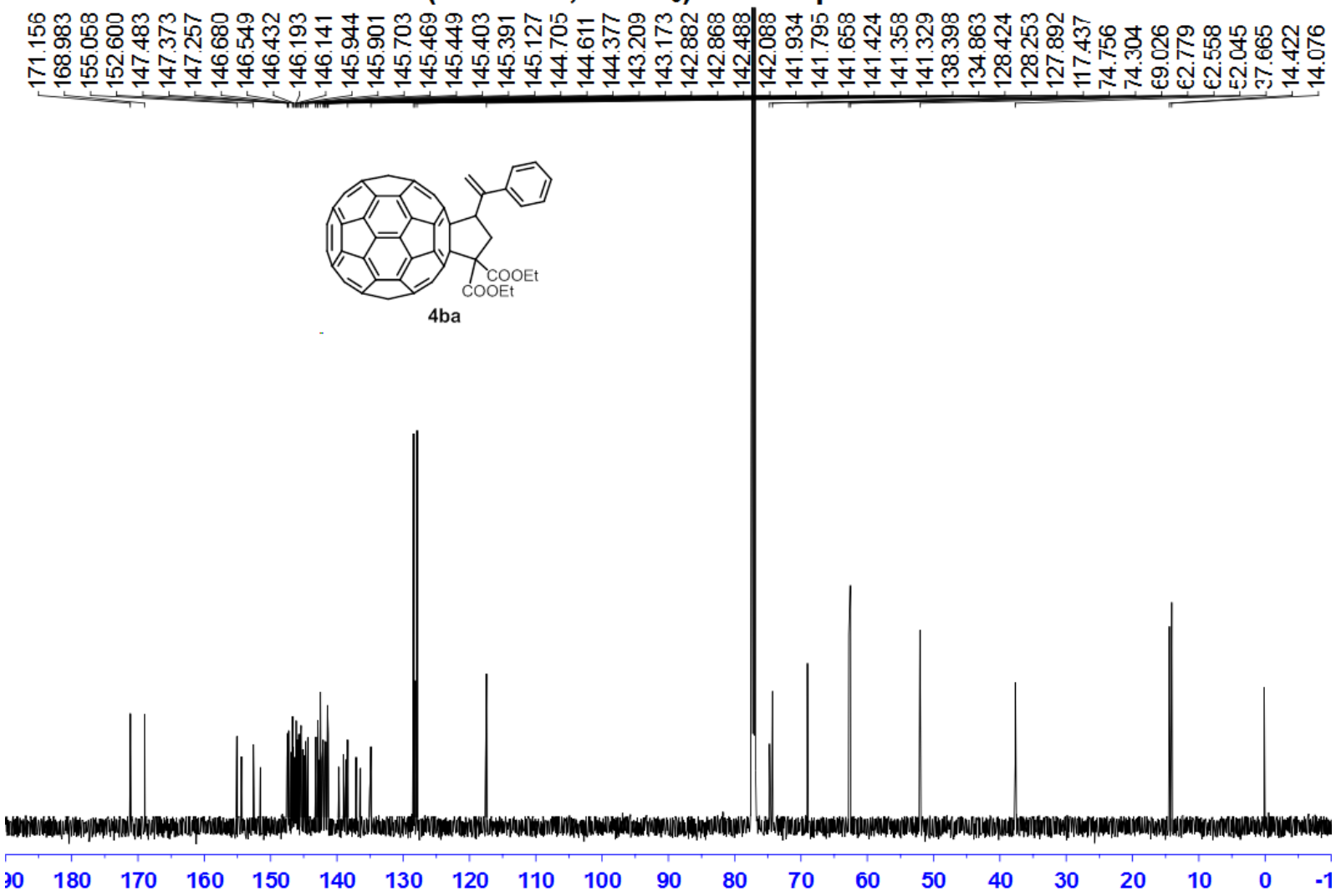


^{13}C NMR (150 MHz, $CDCl_3$) of compound 4ap



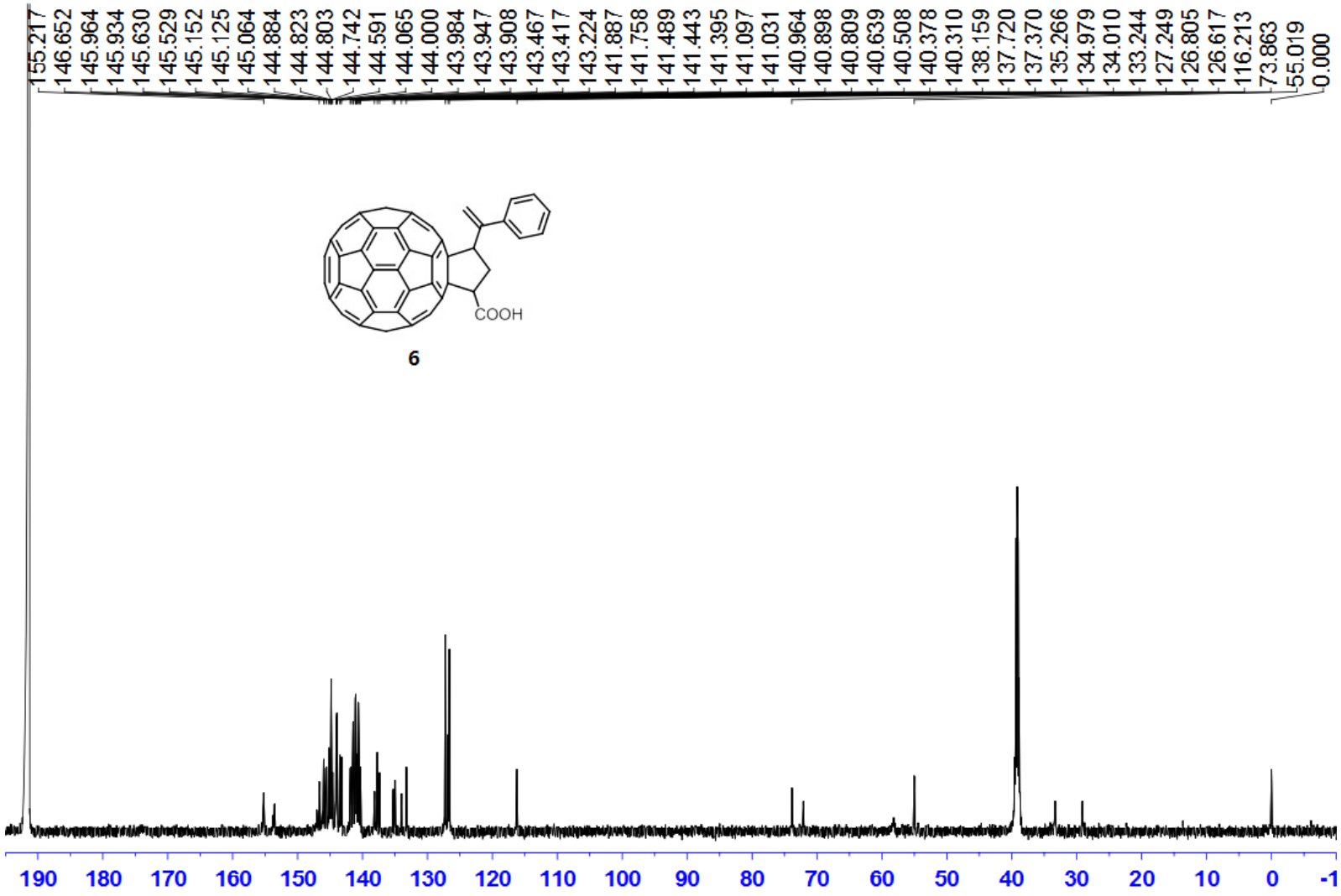

¹H NMR (400 MHz, CDCl₃) of compound 4ba
7.476
7.471
7.457
7.260
7.218
7.206
7.191
5.715
5.378
5.368
5.342
5.333
4.646
4.637
4.628
4.620
4.602
4.585
4.568
4.550
4.541
4.532
4.523
4.505
4.455
4.438
4.428
4.420
4.411
4.403
4.393
4.375
4.206
4.189
4.172
4.154
4.144
4.137
4.127
4.109
3.237
3.227
3.204
3.194
1.522
1.504
1.487
1.240
1.222
1.205
COOEt
COOEt
4ba
2.00
3.03
2.00
1.06
2.09
1.05
2.04
1.03
3.09
3.06
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1

^{13}C NMR (150 MHz, $CDCl_3$) of compound 4ba



^{1}H NMR (600 MHz, DMSO-d_6/CS_2) of compound 6
12.791
7.442
7.429
7.162
7.150
7.137
7.125
7.113
5.696
5.627
5.116
5.095
4.695
4.680
3.570
3.547
3.526
3.504
2.931
2.910
COOH
6
0.92
2.00
3.07
0.97
1.06
0.90
0.98
0.96
0.93
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

^{13}C NMR (150 MHz, DMSO-d_6/CS_2) of compound 6



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