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Electronic Supplementary Information

Palladium-catalyzed domino spirocyclization of [60]fullerene: synthesis of diverse [60]fullerene-fused spiro[4,5]/[5,5] derivatives

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1. General Information

Unless otherwise specified, all reagents were purchased as reagent grade and used without further purification. Substrates **1** were prepared by following the literature procedure.[1] $Pd(PPh_3)_4$ and Cs_2CO_3 were purchased from Sigma-Aldrich. Chlorobenzene (CB) was treated with CaH_2. ^1H 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 Spectrum 400F. 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) C. Hollingworth, A. Hazari, M. N. Hopkinson, M. Tredwell, E. Benedetto, M. Huiban, A. D. Gee, J. M. Brown and V. Gouverneur, *Angew. Chem., Int. Ed.*, 2011, **50**, 2613; (b) J. Ye, Z. Shi, T. Sperger, Y. Yasukawa, C. Kingston, F. Schoenebeck and M. Lautens, *Nat. Chem.*, 2017, **9**, 361; (c) Q. Huang, A. Fazio, G. Dai, M. A. Campo and R. C. Larock, *J. Am. Chem. Soc.*, 2004, **126**, 7460; (d) X. Yang, H. Lu, X. Zhu, L. Zhou, G. Deng, Y. Yang and Y. Liang, *Org. Lett.*, 2019, **21**, 7284; (e) H. Yoon, M. Rödz, F. Landau and M. Lautens, *Angew. Chem., Int. Ed.*, 2017, **56**, 10920.

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2. Experimental Procedures

*General Procedure for the Synthesis of Products **2a**–**i**, **2k**–**n**, and **2p**–**z**:* A dry 15-mL tube equipped with a magnetic stirrer was charged with C_{60} (36.0 mg, 0.05 mmol), **1** (0.1 mmol for **1a**, **1c**–**e**, **1g**–**i**, **1k** and **1l**; 0.15 mmol for **1b**, **1f**, **1m**–**n**, and **1p**–**1z**), $Pd(PPh_3)_4$ (2.9 mg, 0.0025 mmol) and Cs_2CO_3 (32.6 mg, 0.1 mmol). After dissolving the solids in anhydrous CB (6 mL) by sonication, the sealed tube was stirred in an oil bath preset at a designated temperature for a desired time. 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 the product **2a**–**i**, **2k**–**n**, and **2p**–**z**.

*General Procedure for the Synthesis of Products **2aa**–**dd**:* A dry 15-mL tube equipped with a magnetic stirrer was charged with C_{60} (36.0 mg, 0.05 mmol), **1** (0.15 mmol for **1aa**–**cc**; 0.1 mmol for **1dd**), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol for **1aa** and **1cc**; 2.9 mg, 0.0025 mmol for **1bb** and **1dd**) and Cs_2CO_3 (32.6 mg, 0.1 mmol). After dissolving the solids in anhydrous CB (6 mL) by sonication, the sealed tube was stirred in an oil bath preset at a designated temperature (150 ^oC for **1aa** and **1dd**; 140 ^oC for **1bb** and **1cc**) for a desired time. 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 give unreacted C_{60} and the product **2aa**–**dd**.

*Typical Procedure for the Synthesis of Product **2a** from $Pd(PPh_3)_4$-catalyzed Reaction of C_{60} with Substrates **1a** at a minimum 1 mmol scale*: A dry 250-mL round-bottomed flask equipped with a magnetic stirrer was charged with C_{60} (720.2 mg, 1.0 mmol), **1a** (678 mg, 2.0 mmol), $Pd(PPh_3)_4$ (57.9 mg, 0.05 mmol) and Cs_2CO_3

(652 mg, 2.0 mmol, 0.1 mmol). After dissolving the solids in anhydrous CB (100 mL) by sonication, the round-bottomed flask was stirred in an oil bath at 130 ^{o}C for 24 h. 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 give unreacted C_{60} (326.3 mg) and the product **2a** (368.3 mg, 40%).

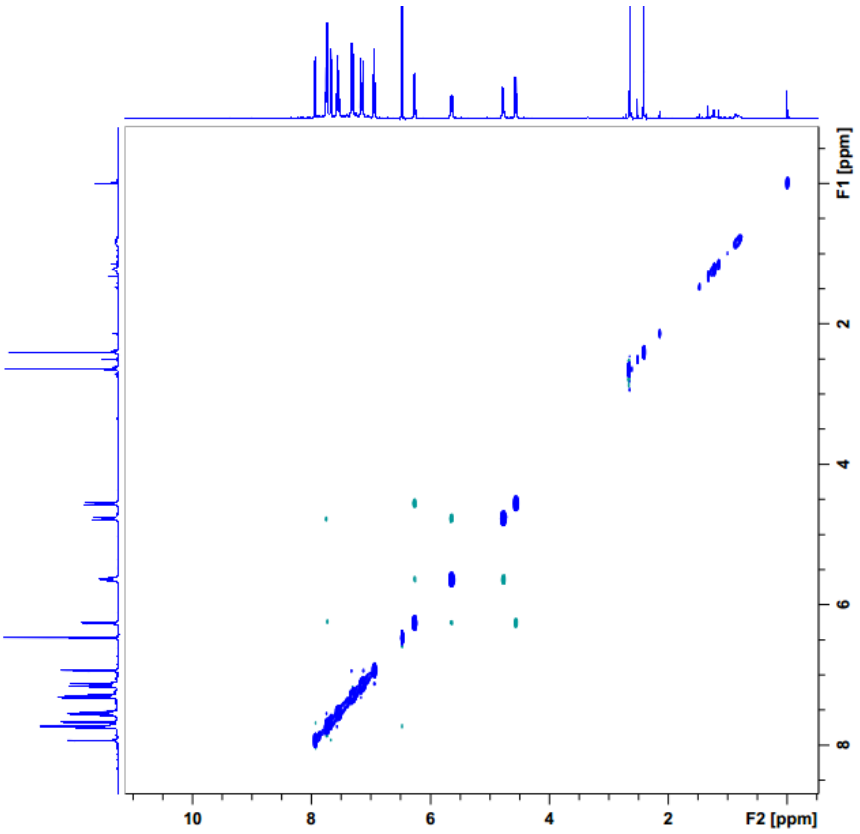
*Typical Procedure for the Synthesis of Product **2r** from $Pd(PPh_3)_4$-catalyzed Reaction of C_{60} with Substrates **1r** at a minimum 1 mmol scale*: A dry 250-mL round-bottomed flask equipped with a magnetic stirrer was charged with C_{60} (720.4 mg, 1.0 mmol), **1r** (1.23 g, 3.0 mmol), $Pd(PPh_3)_4$ (58.2 mg, 0.05 mmol) and Cs_2CO_3 (653.6 mg, 2.0 mmol). After dissolving the solids in anhydrous CB (100 mL) by sonication, the round-bottomed flask was stirred in an oil bath at 130 ^{o}C for 24 h. 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} (314.3 mg), and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give product **2r** (493.8 mg, 49%).

Procedures for UV-Vis Spectra Recording: A dry 100-mL volumetric flask was charged with the product **2** (1.3×10^{-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 **2**.

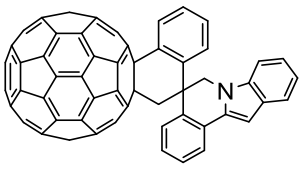
Procedures for Electrochemical Characterization Recording: In dry 15-mL electrolytic cup, 2.0×10^{-3} mmol of product **2**, 2 mL of the solution of (n-Bu)$_4$NClO$_4$ in ODCB (0.1 M), and 18 μL of the solution of ferrocene in ODCB (0.054 M) was

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 **2** under argon atmosphere.

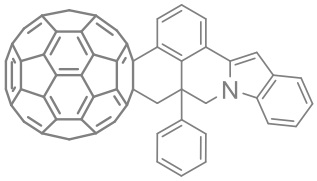
3. NOESY-1D ^{1}H NMR of 2aa



NOESY-1D ^{1}H NMR of **2aa** (600 MHz, DMSO-d_6/CS_2)

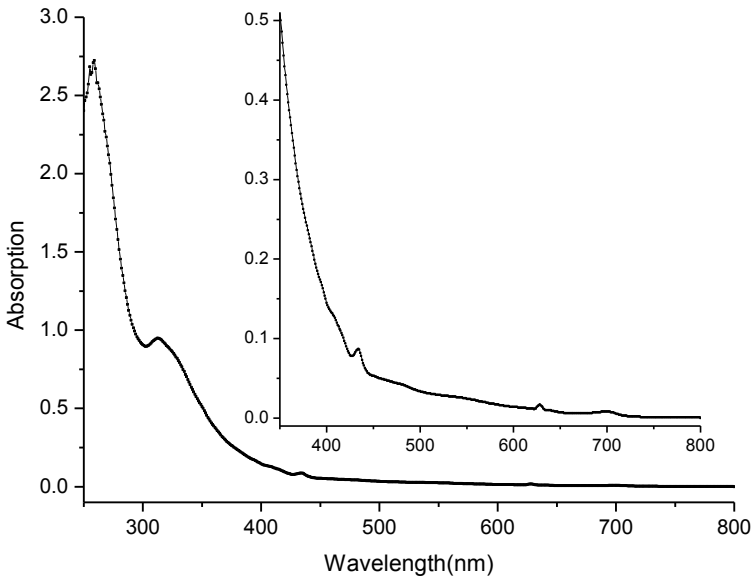


2aa √

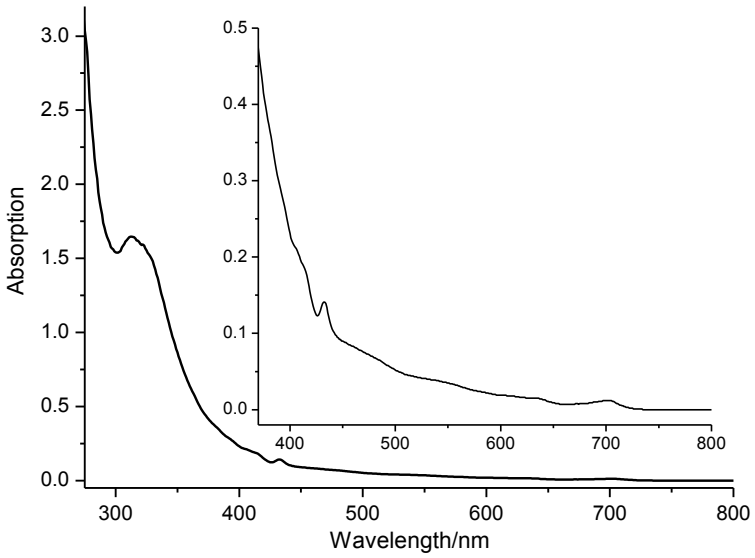


2aa ×

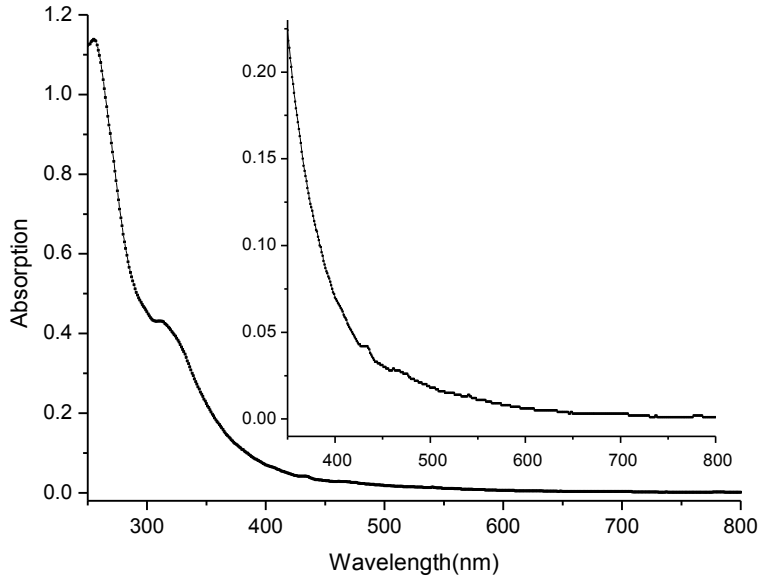
4. UV–vis Spectra of Compounds 2



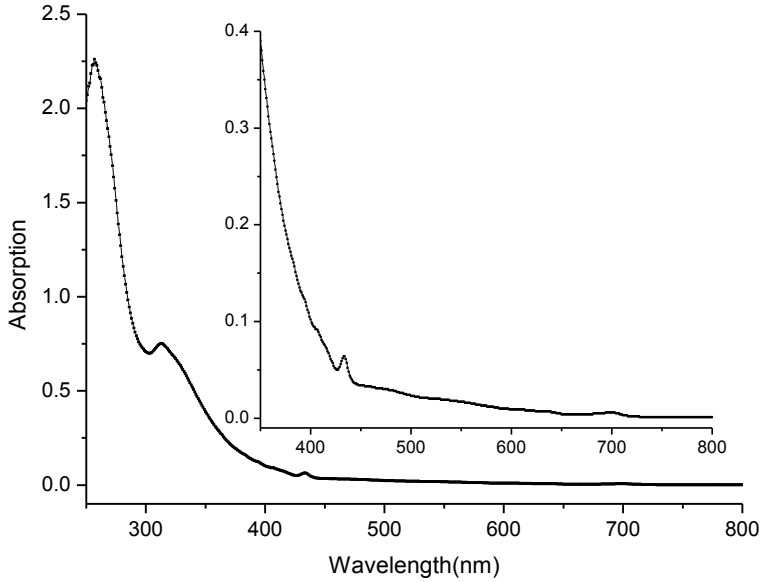
UV–vis spectrum of compound **2a** in $CHCl_3$



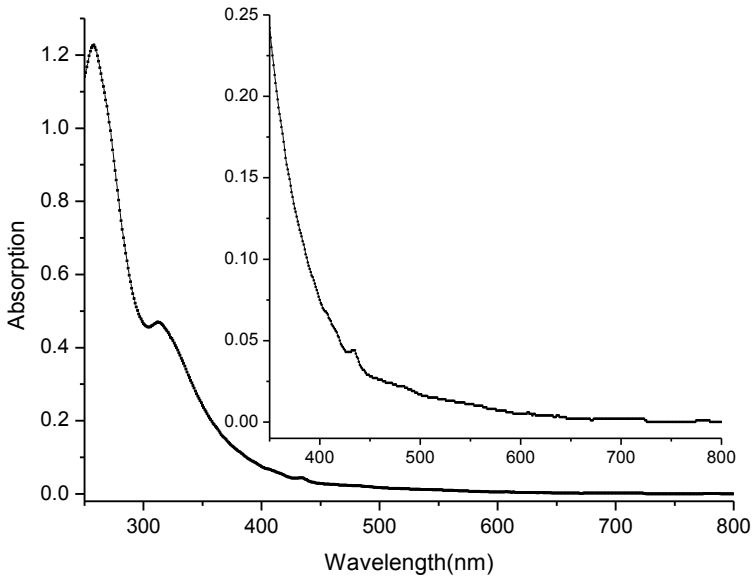
UV–vis spectrum of compound **2b** in $CHCl_3$



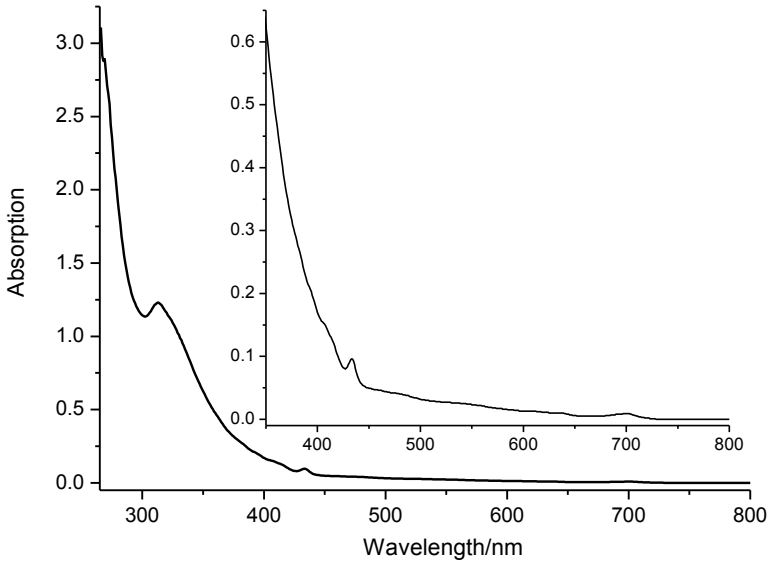
UV–vis spectrum of compound **2c** in $CHCl_3$



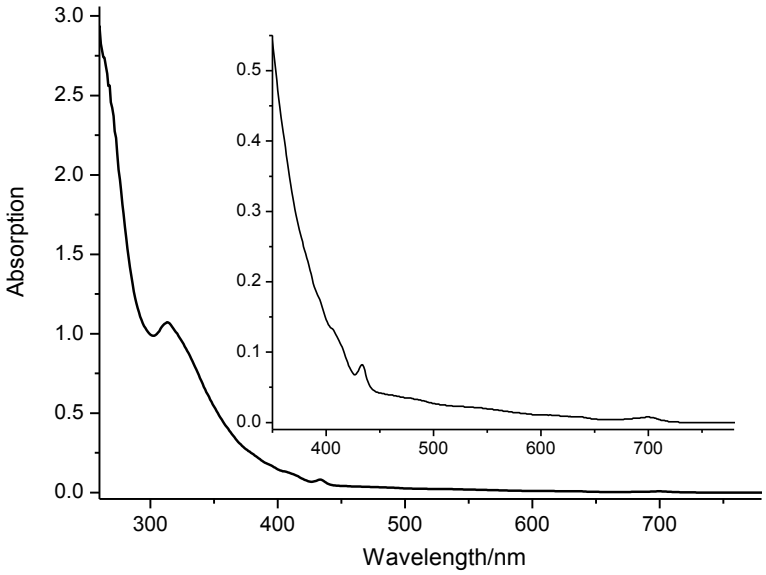
UV–vis spectrum of compound **2d** in $CHCl_3$



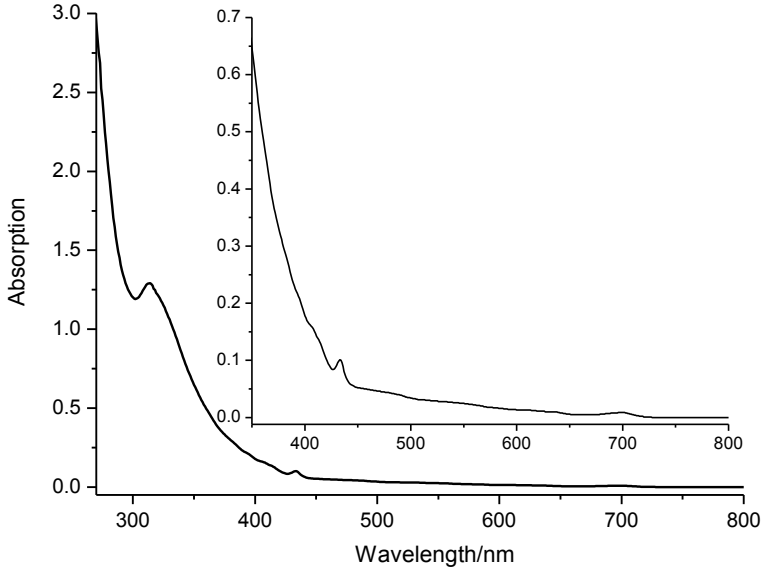
UV–vis spectrum of compound **2e** in $CHCl_3$



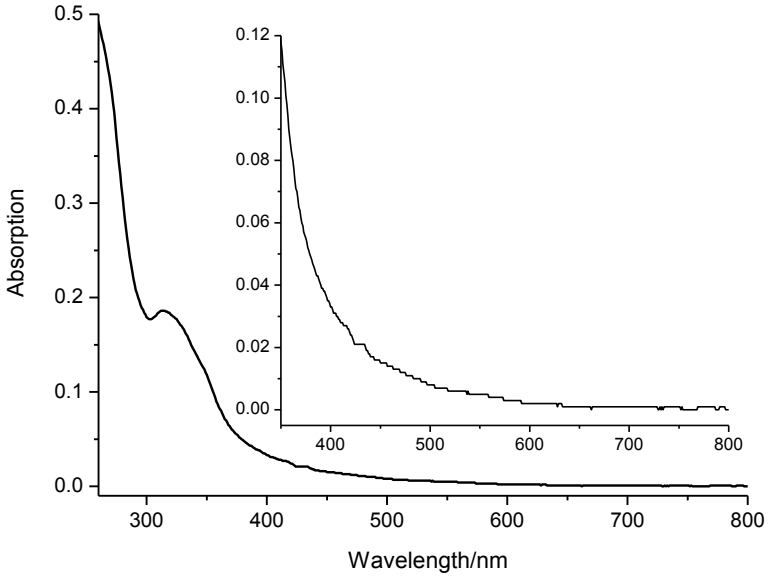
UV–vis spectrum of compound **2f** in $CHCl_3$



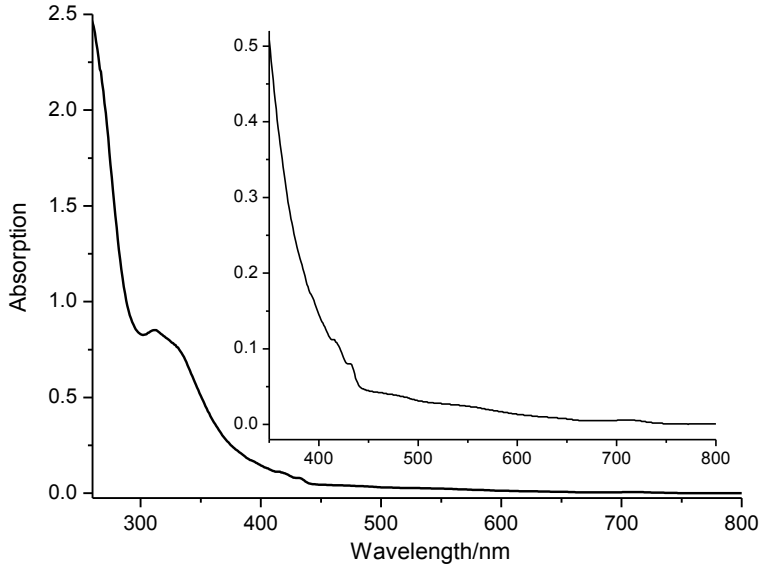
UV–vis spectrum of compound **2g** in $CHCl_3$



UV–vis spectrum of compound **2h** in $CHCl_3$



UV–vis spectrum of compound **2i** in $CHCl_3$



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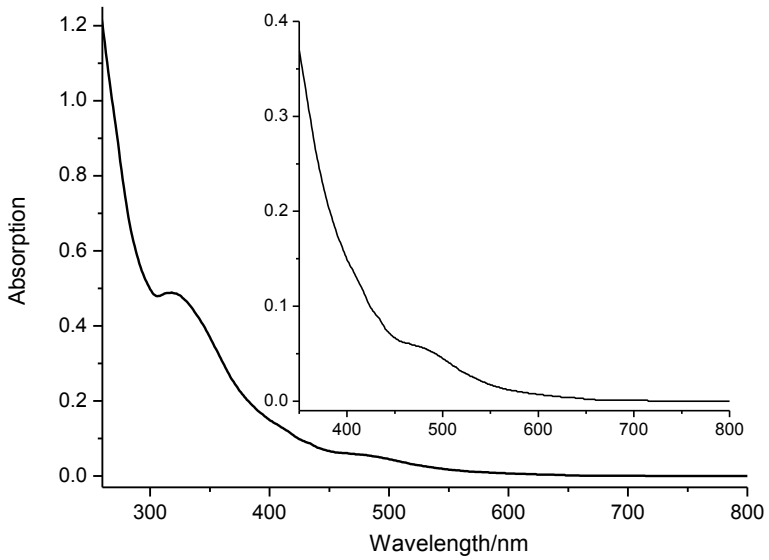
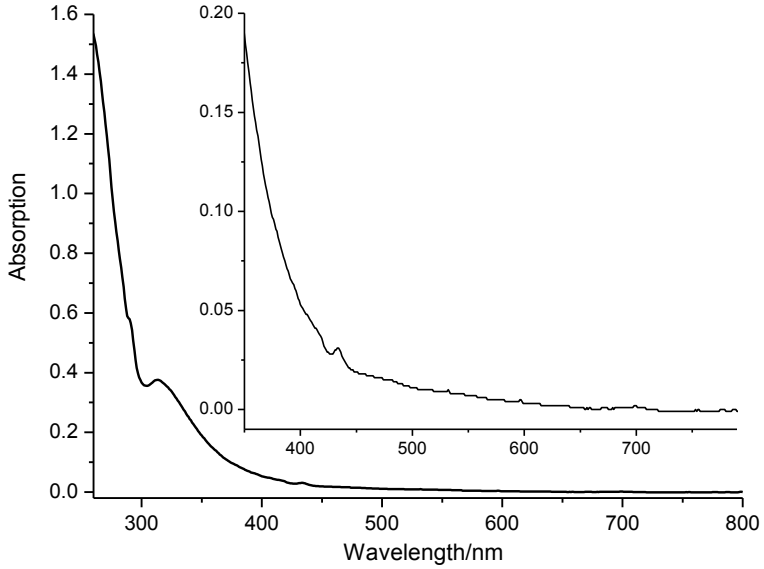
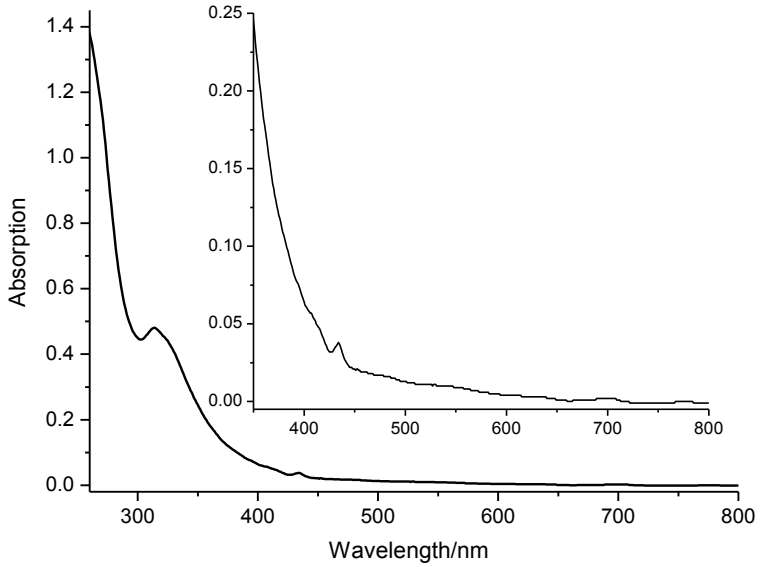


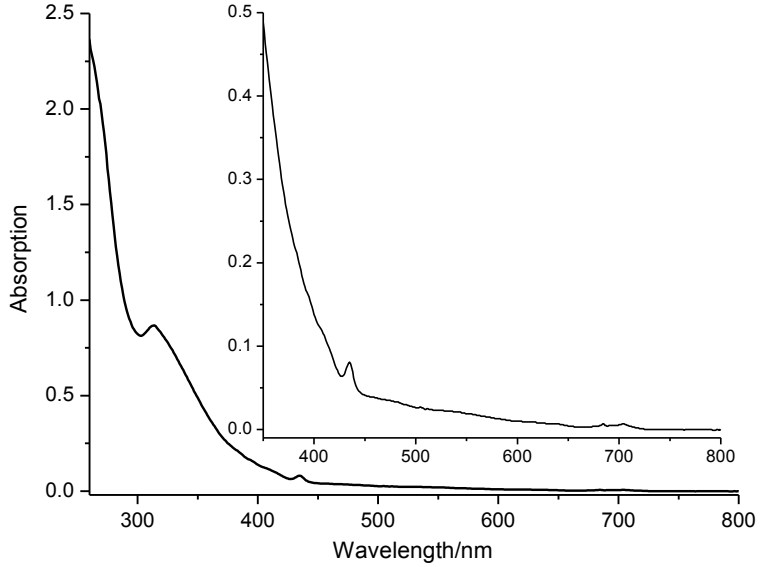
UV–vis spectrum of compound **2l** in $CHCl_3$



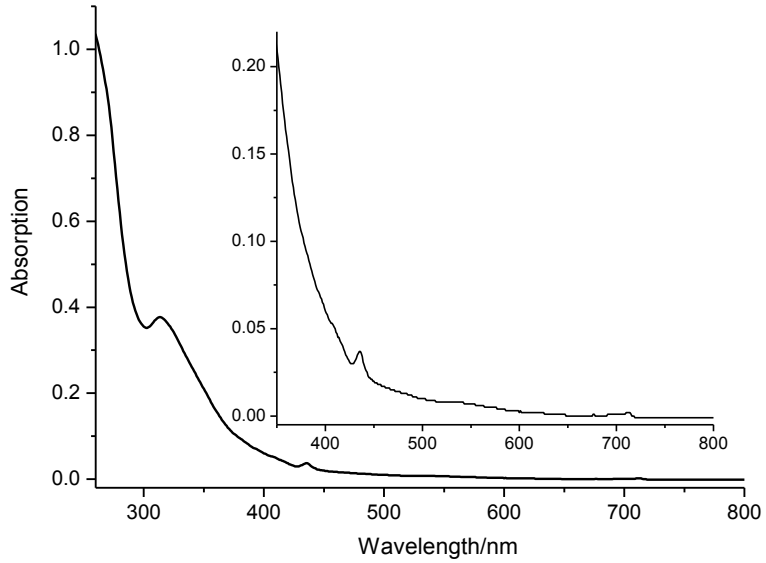
UV–vis spectrum of compound **2m** in $CHCl_3$



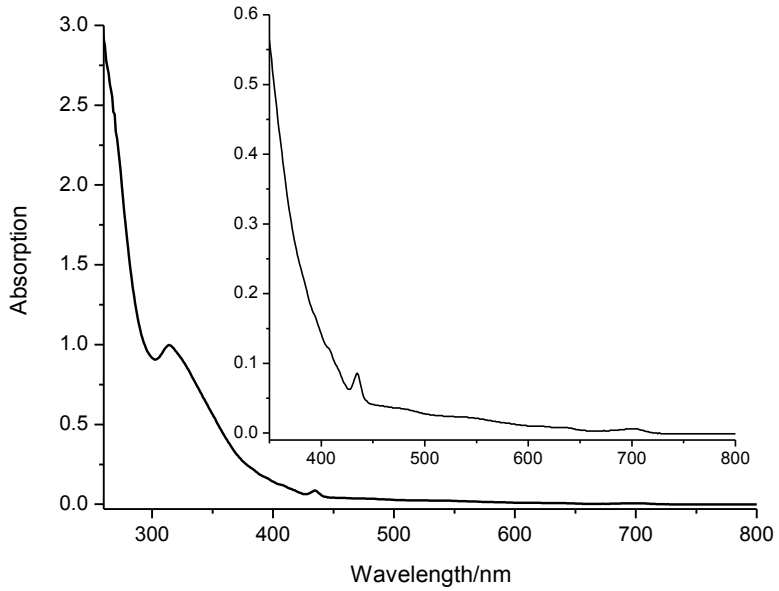
UV–vis spectrum of compound **2n** in $CHCl_3$



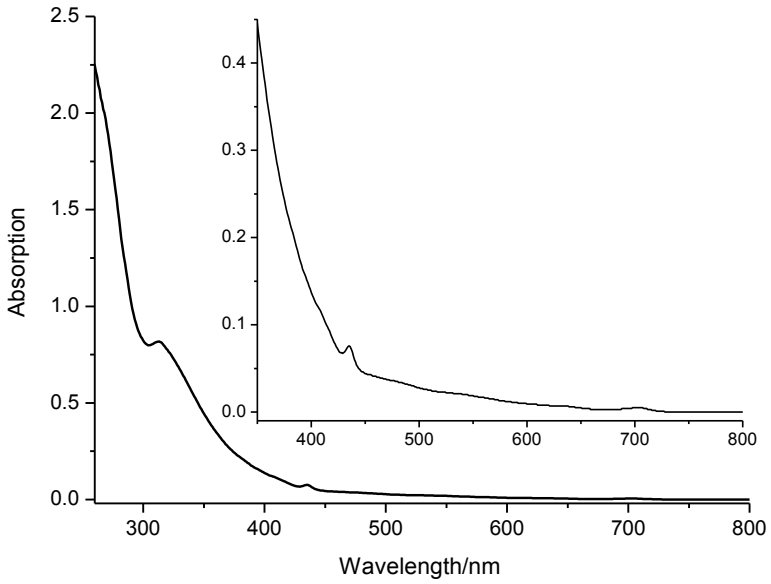
UV–vis spectrum of compound **2p** in $CHCl_3$



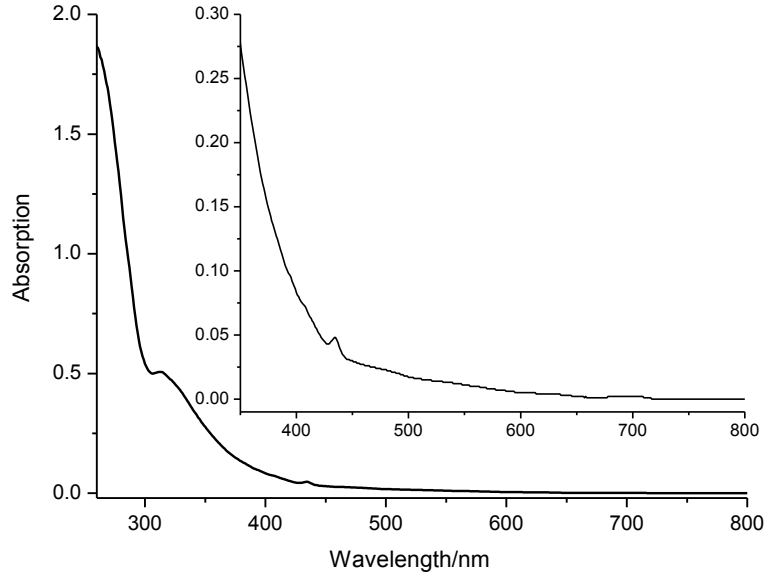
UV–vis spectrum of compound **2q** in $CHCl_3$



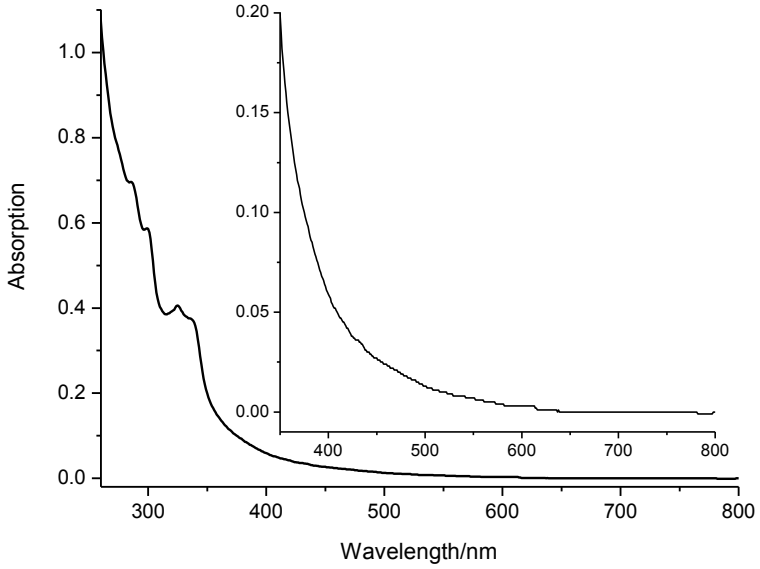
UV–vis spectrum of compound **2r** in $CHCl_3$



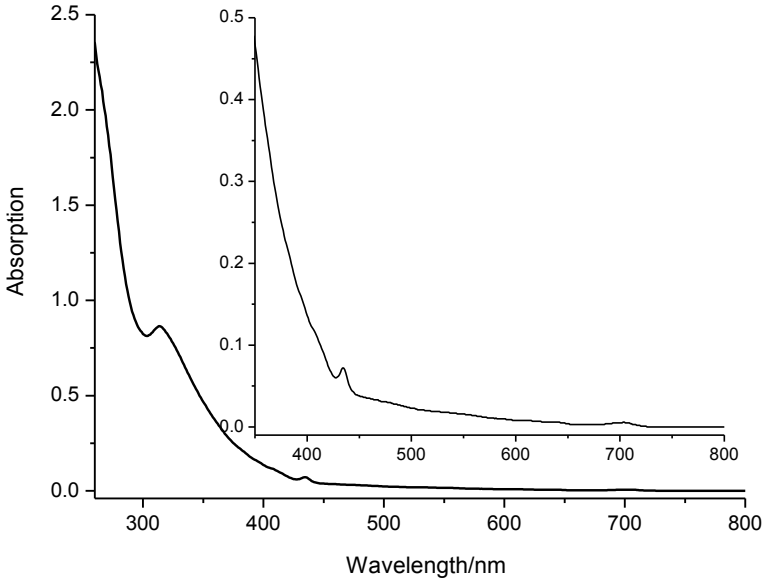
UV–vis spectrum of compound **2s** in $CHCl_3$



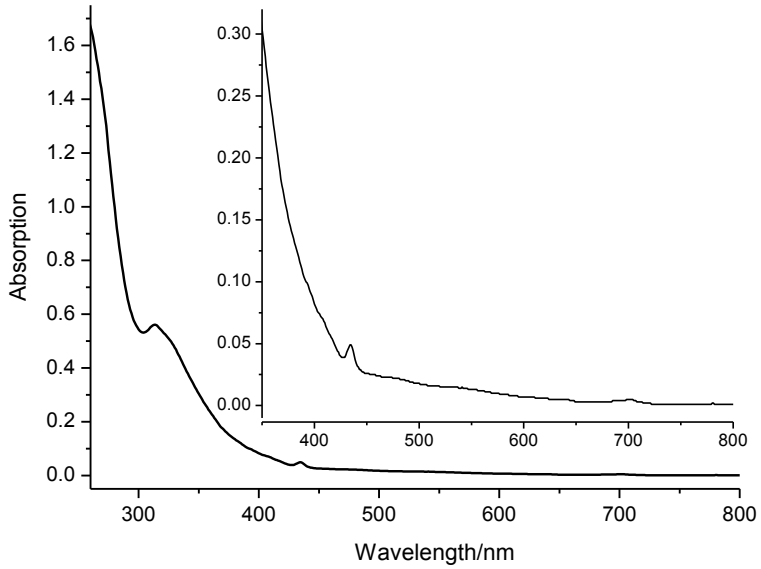
UV–vis spectrum of compound **2t** in $CHCl_3$



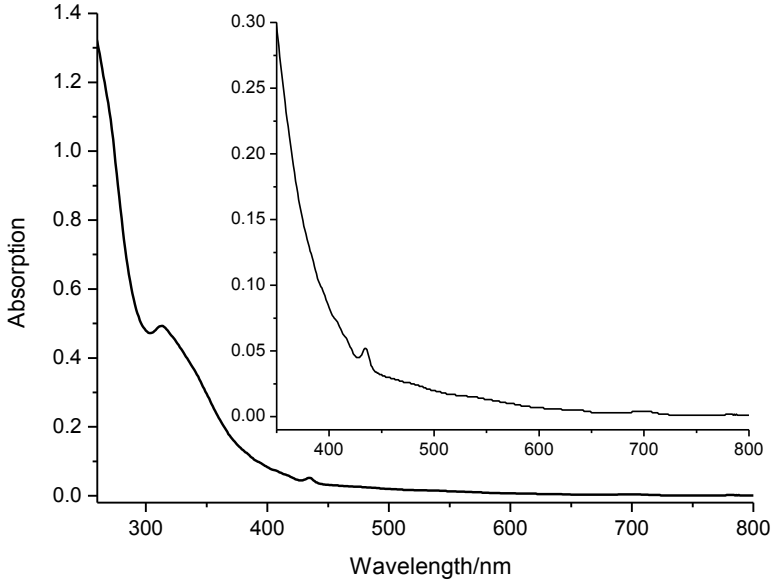
UV–vis spectrum of compound **2u** in $CHCl_3$



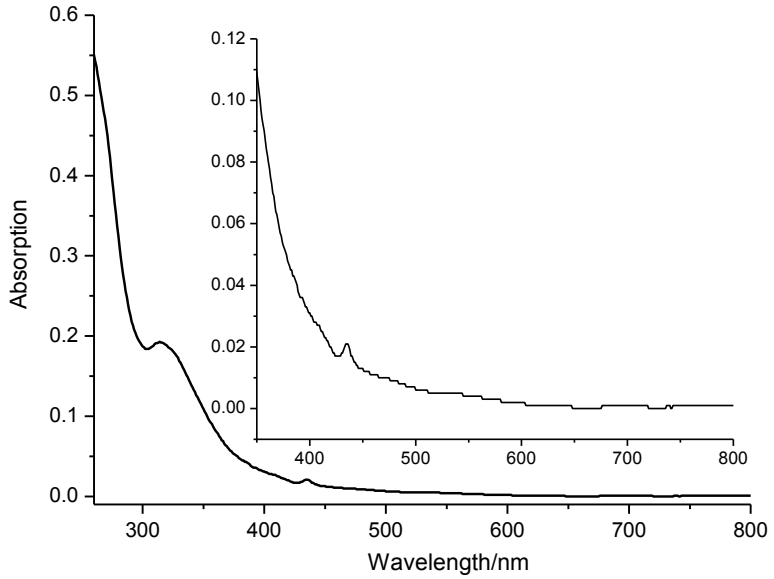
UV–vis spectrum of compound **2w** in $CHCl_3$



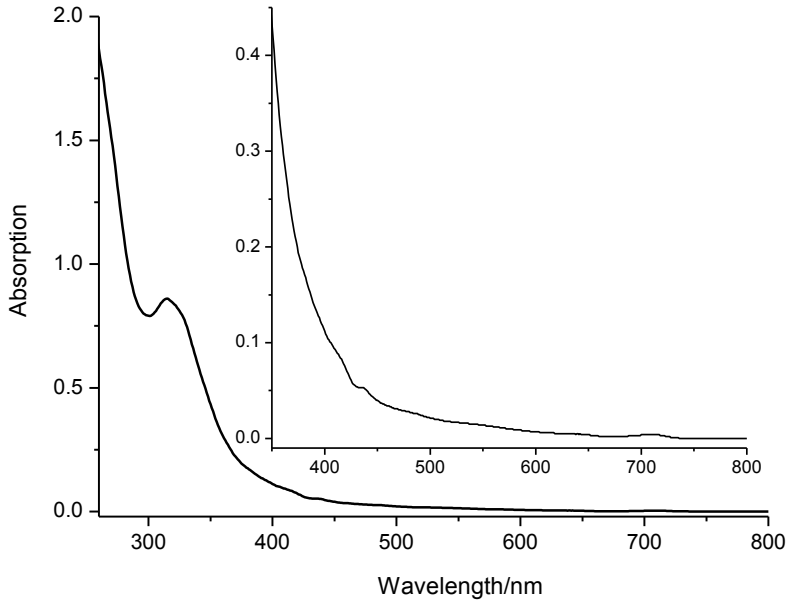
UV–vis spectrum of compound **2x** in $CHCl_3$



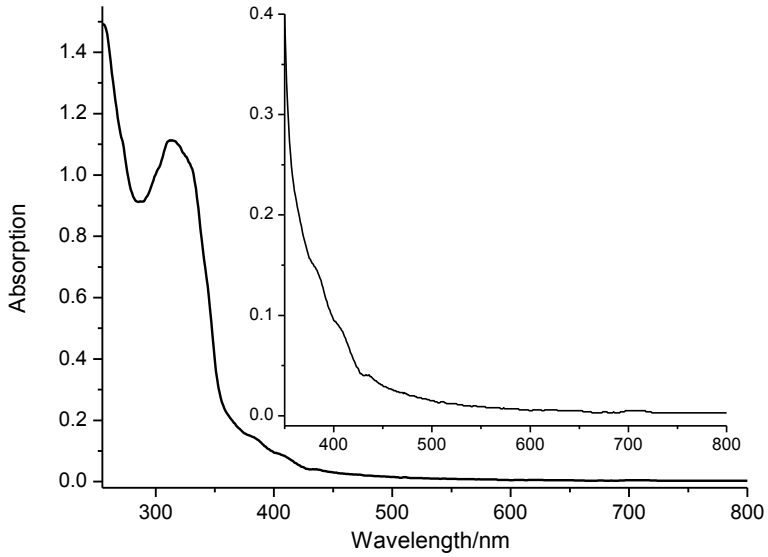
UV–vis spectrum of compound **2y** in $CHCl_3$



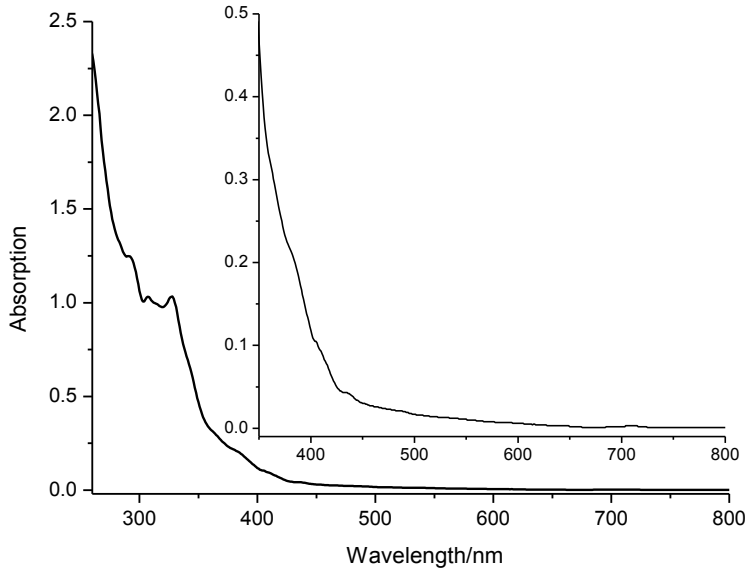
UV–vis spectrum of compound **2z** in $CHCl_3$



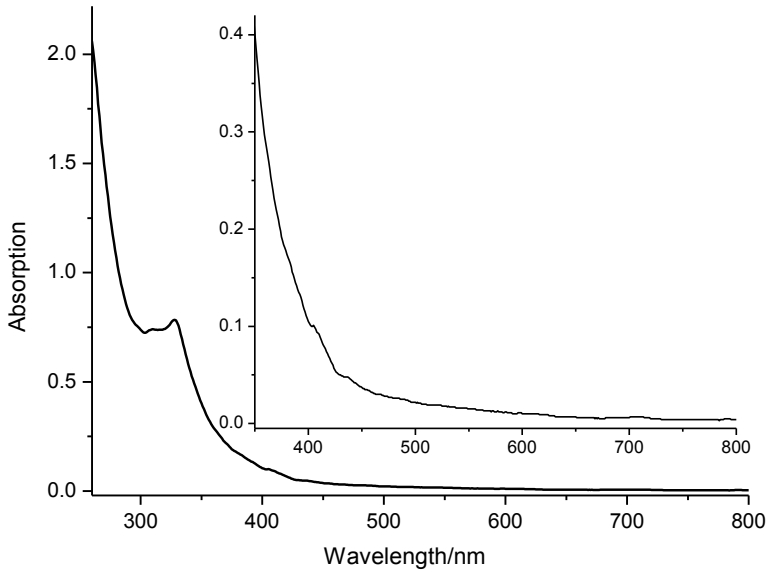
UV–vis spectrum of compound **2aa** in $CHCl_3$



UV–vis spectrum of compound **2bb** in $CHCl_3$

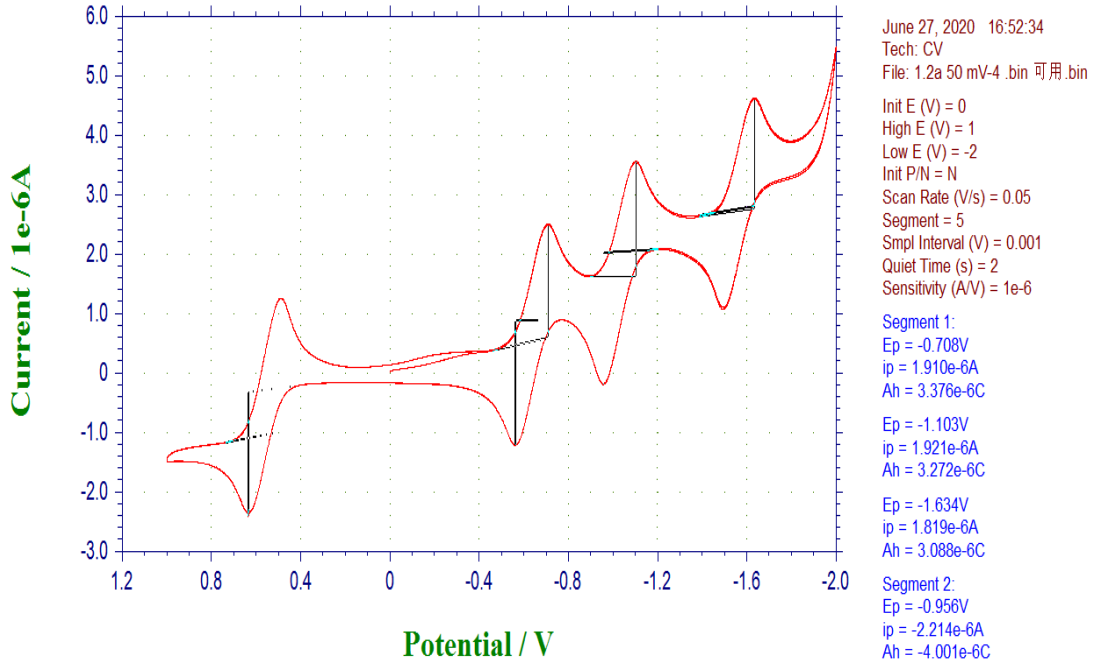


UV–vis spectrum of compound **2cc** in $CHCl_3$

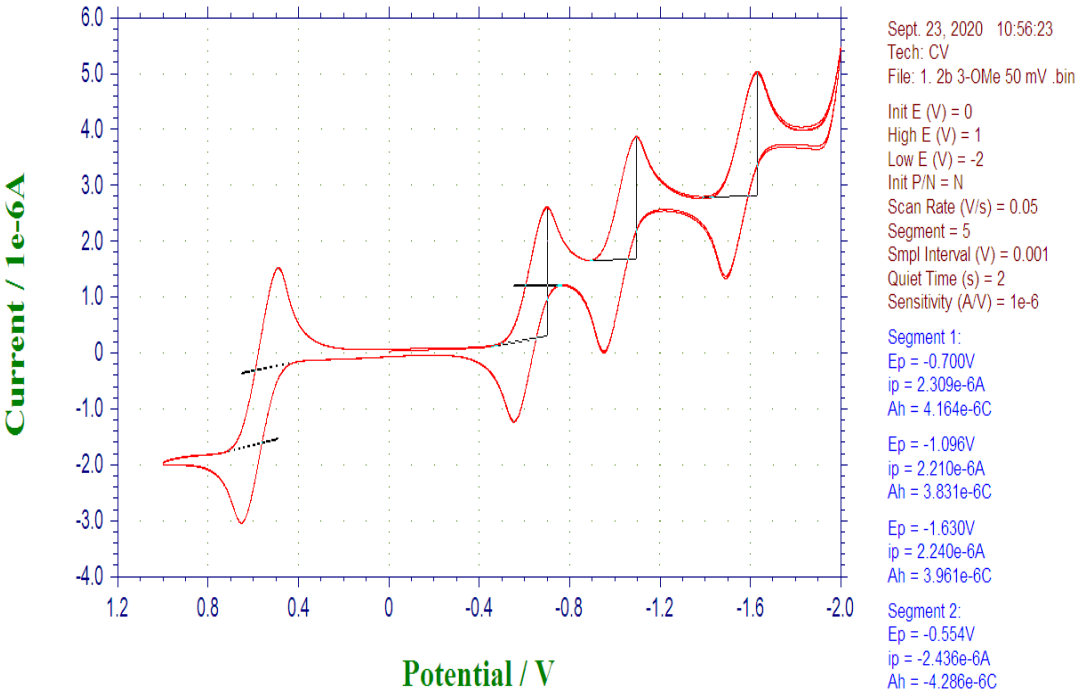


UV–vis spectrum of compound **2dd** in $CHCl_3$

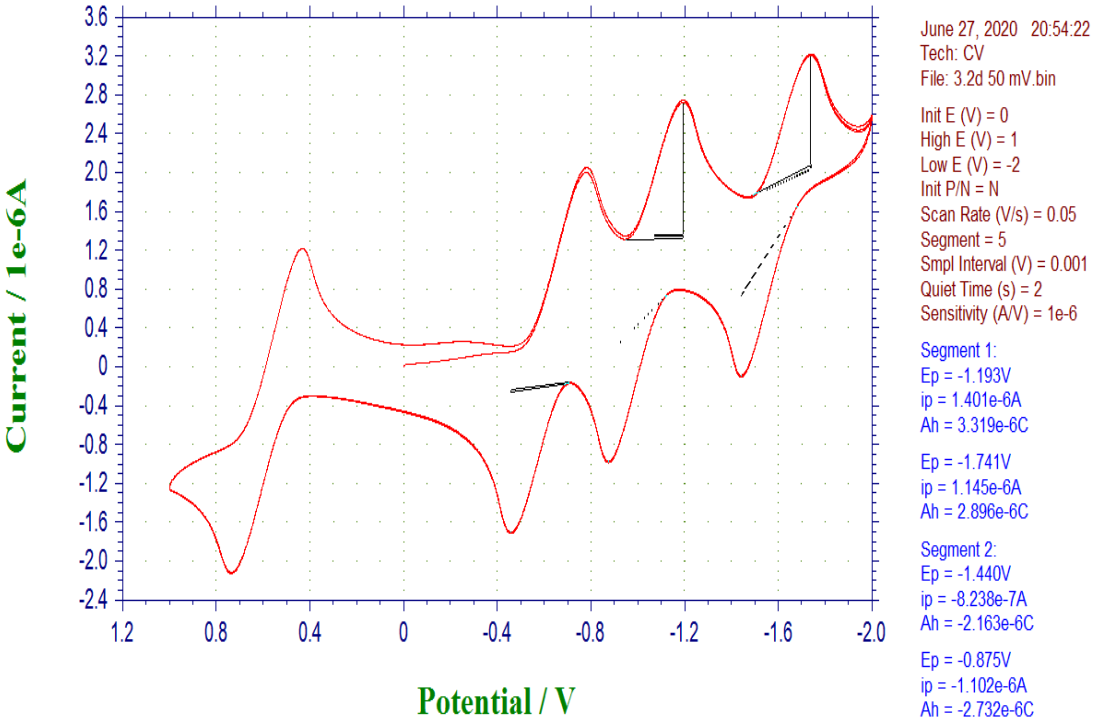
5. CVs of Selected Compounds



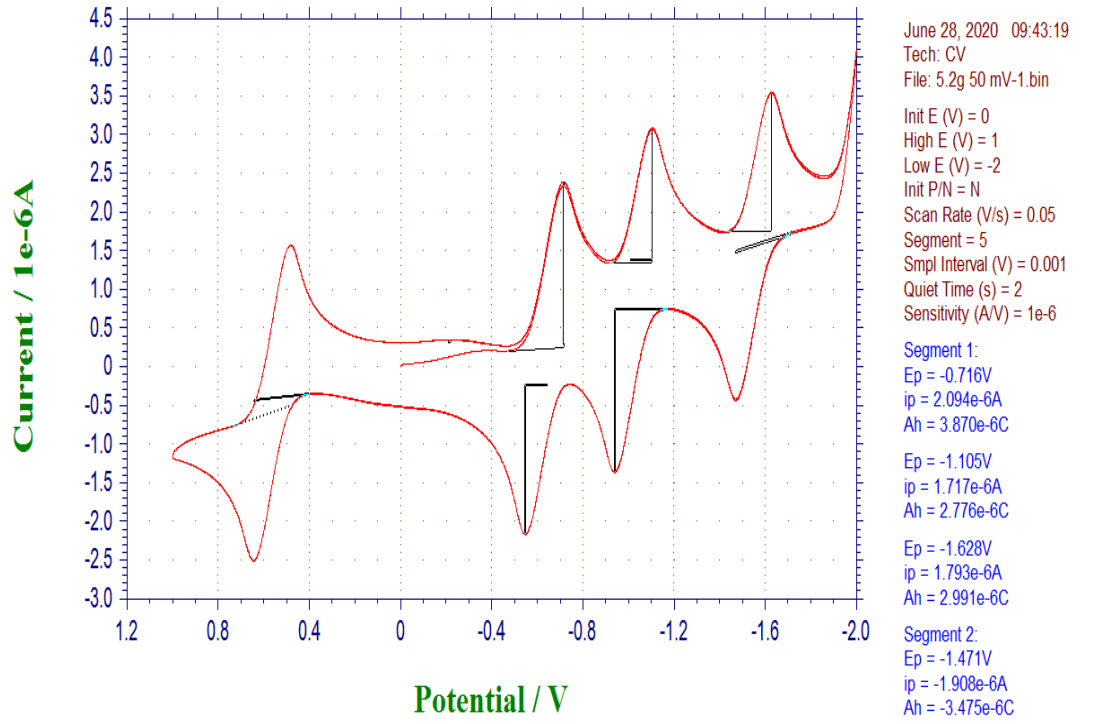
Cyclic voltammogram of compound **2a** (scanning rate: 50 mV s^{-1})



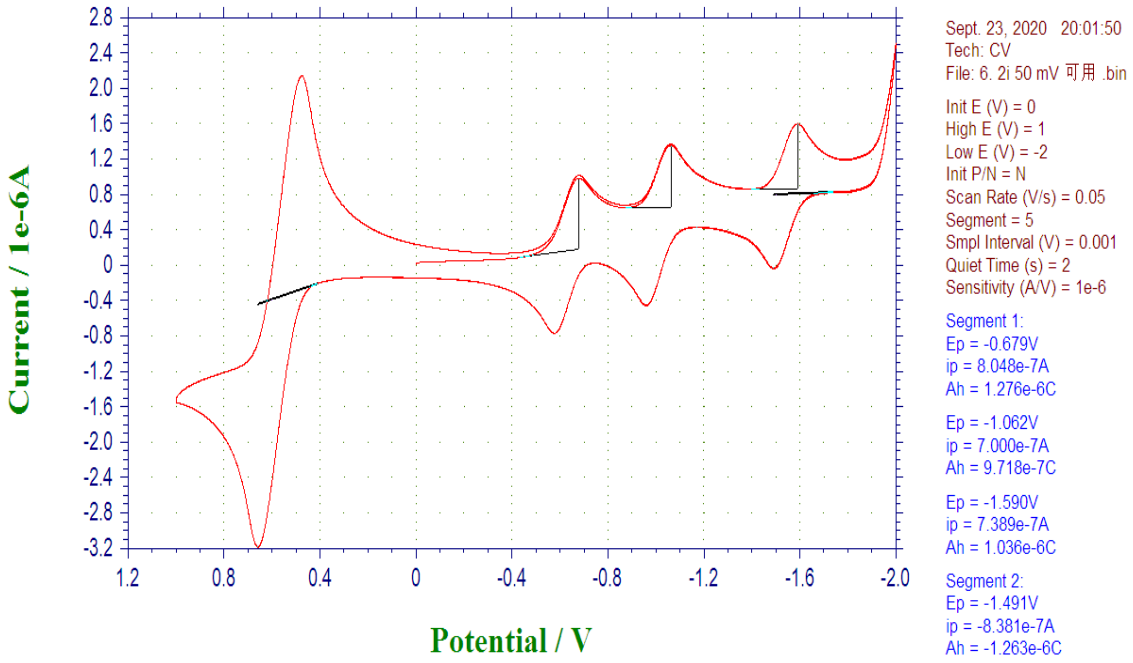
Cyclic voltammogram of compound **2b** (scanning rate: 50 mV s^{-1})



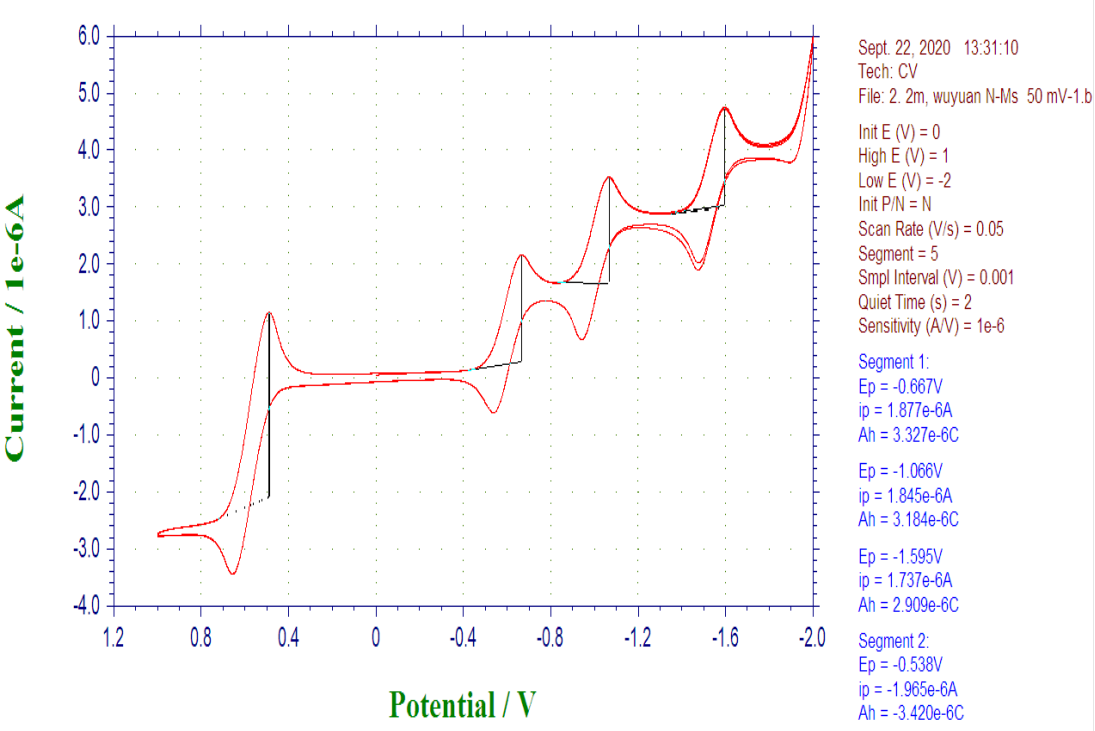
Cyclic voltammogram of compound **2d** (scanning rate: 50 mV s^{-1})



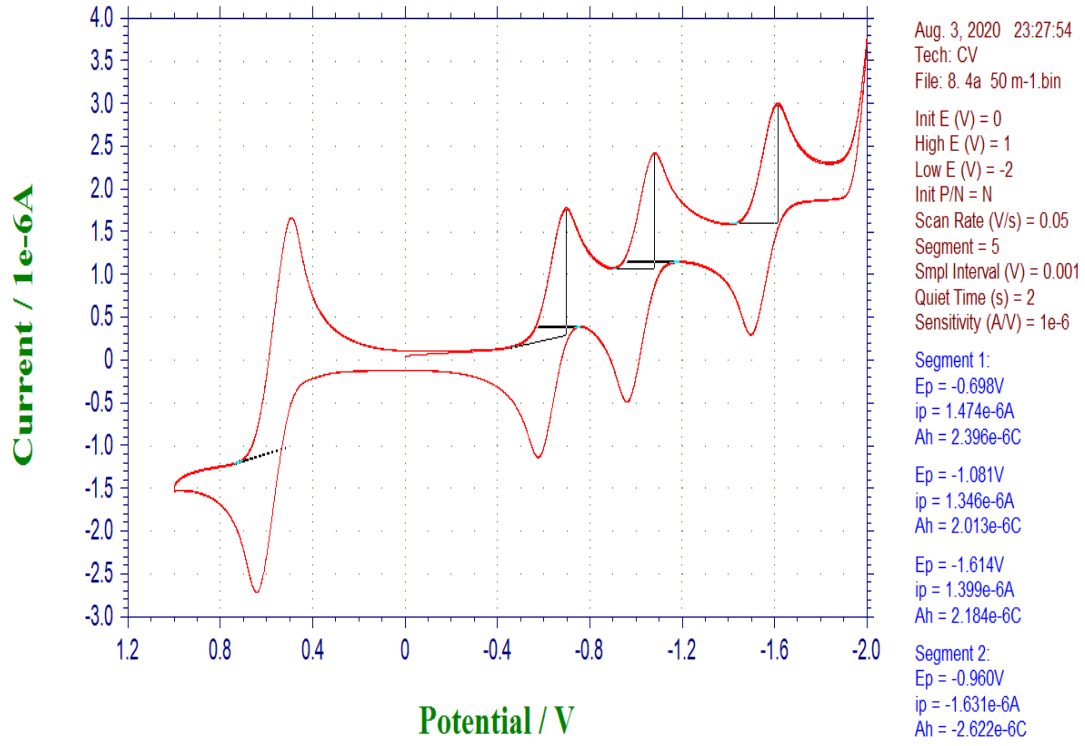
Cyclic voltammogram of compound **2e** (scanning rate: 50 mV s^{-1})



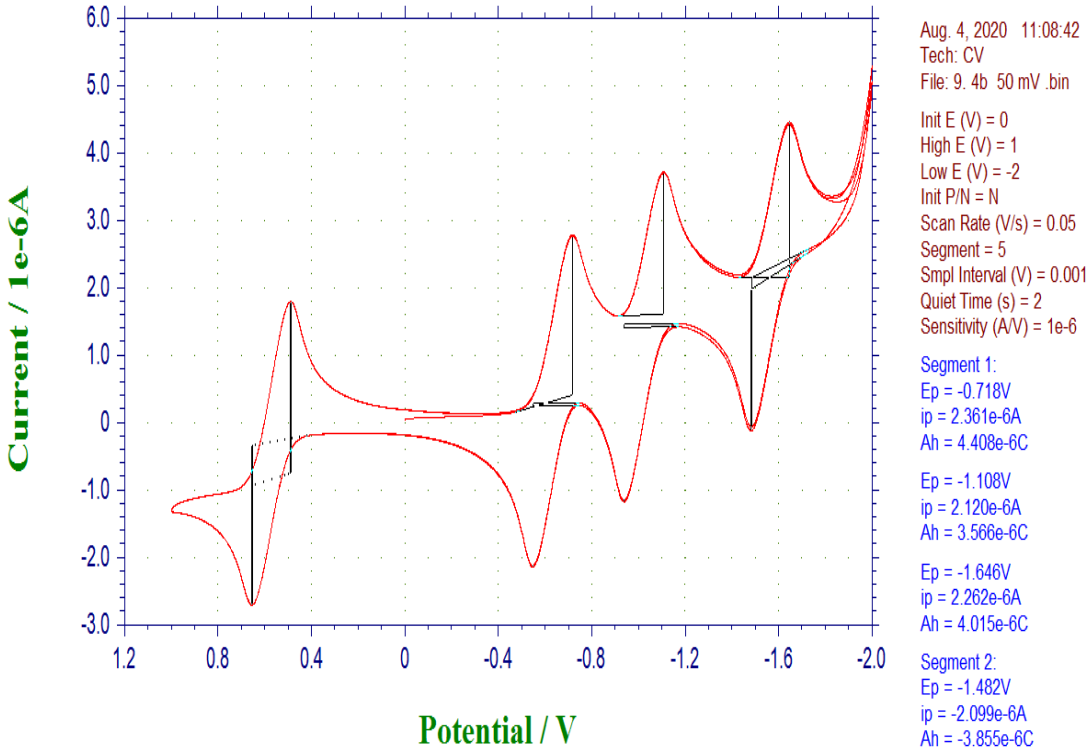
Cyclic voltammogram of compound **2i** (scanning rate: 50 mV s^{-1})



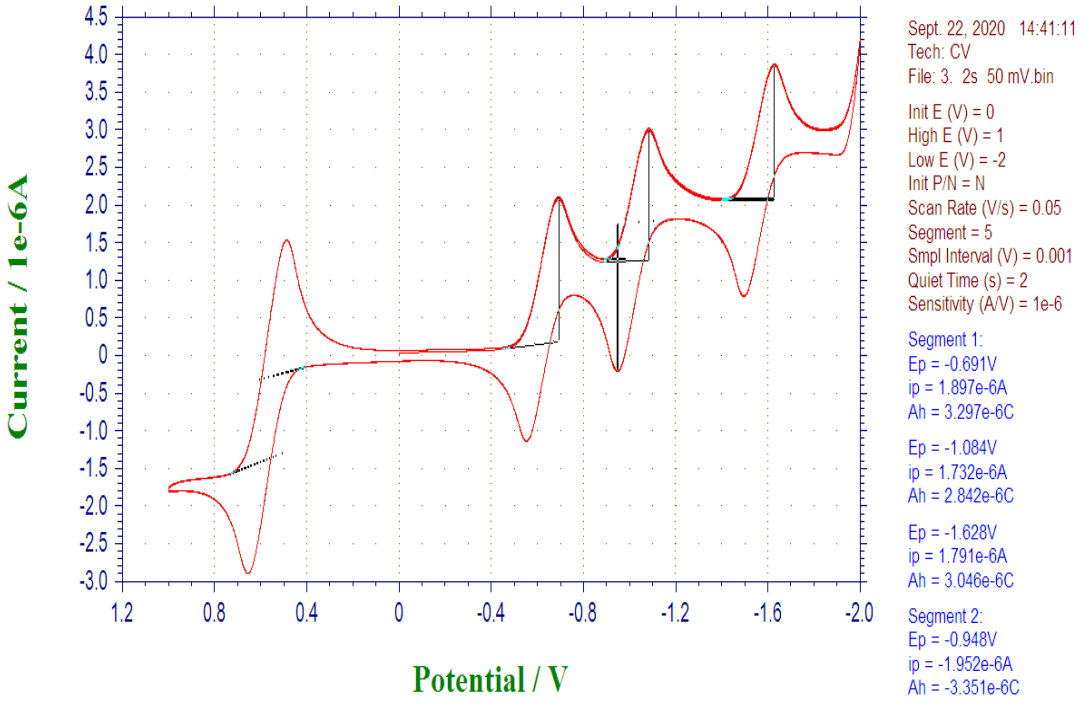
Cyclic voltammogram of compound **2m** (scanning rate: 50 mV s^{-1})



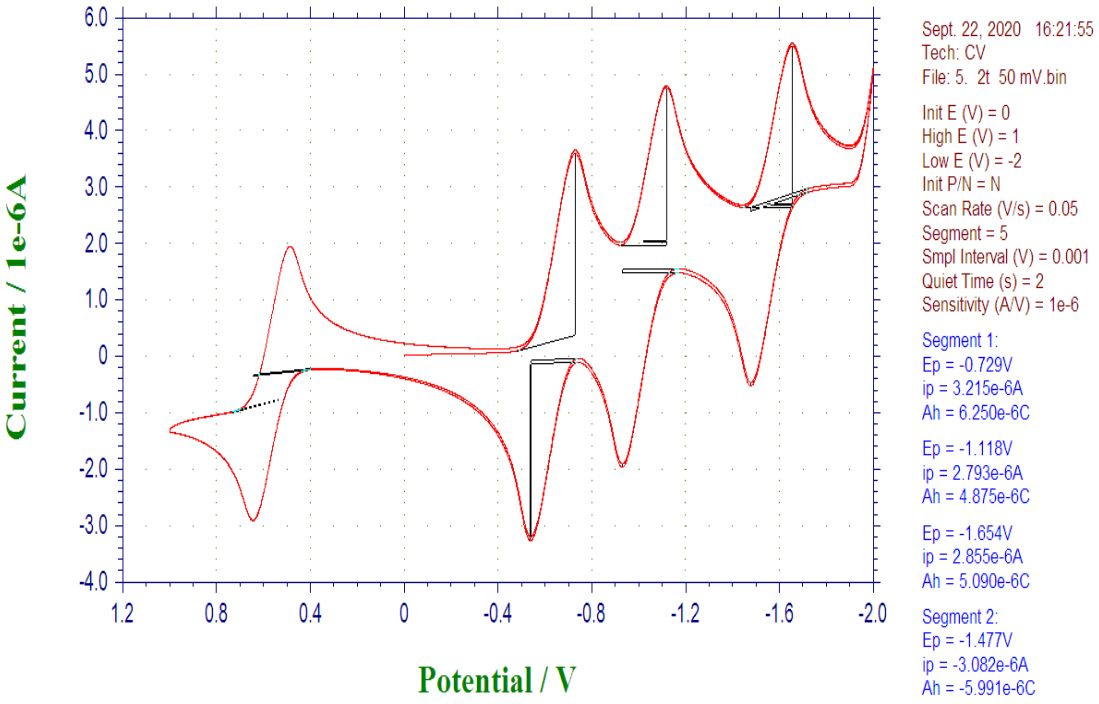
Cyclic voltammogram of compound **2p** (scanning rate: 50 mV s^{-1})



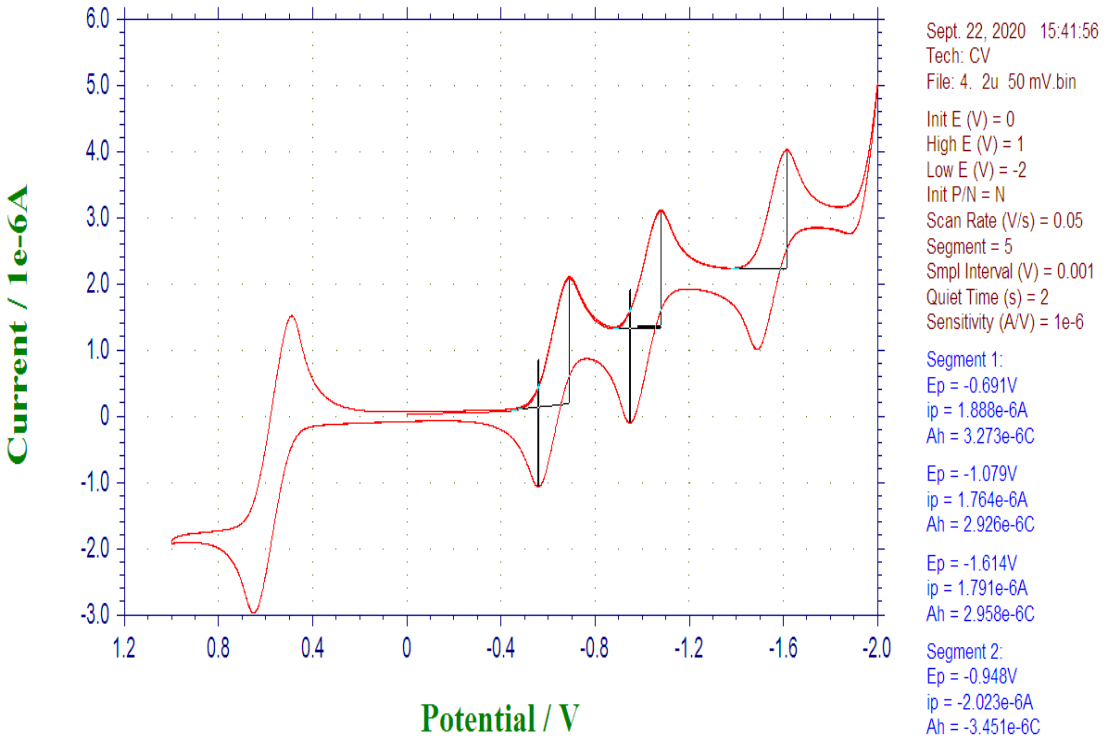
Cyclic voltammogram of compound **2q** (scanning rate: 50 mV s^{-1})



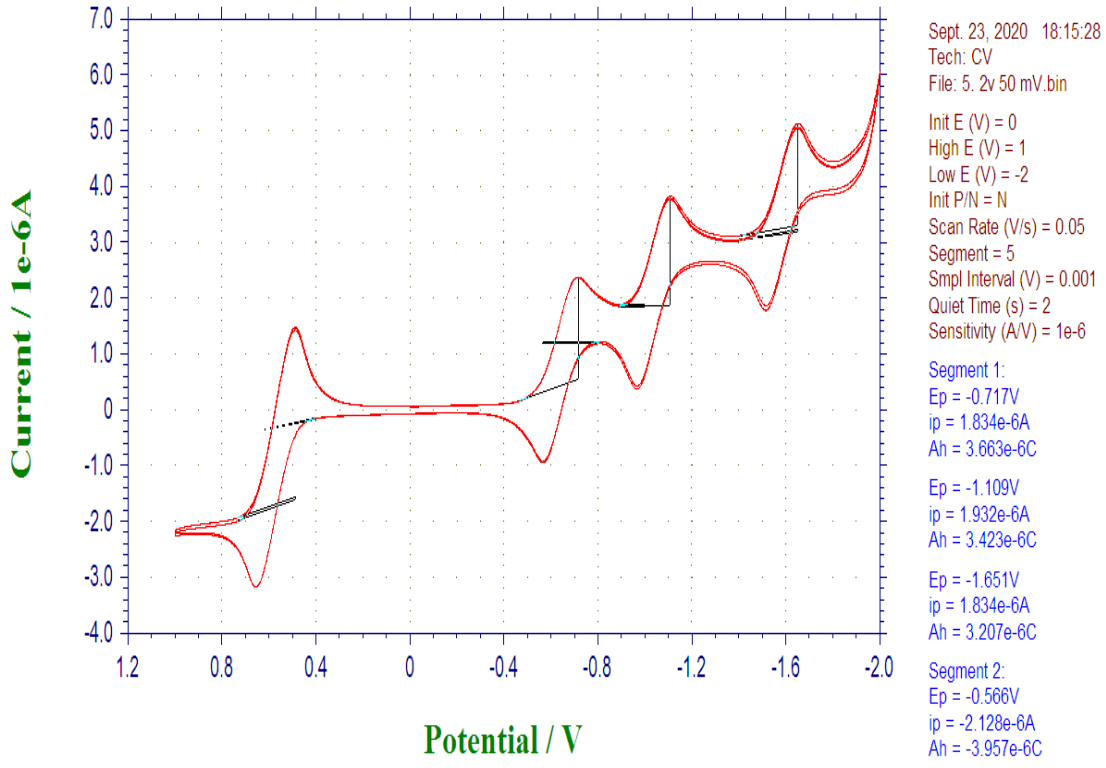
Cyclic voltammogram of compound **2r** (scanning rate: 50 mV s^{-1})



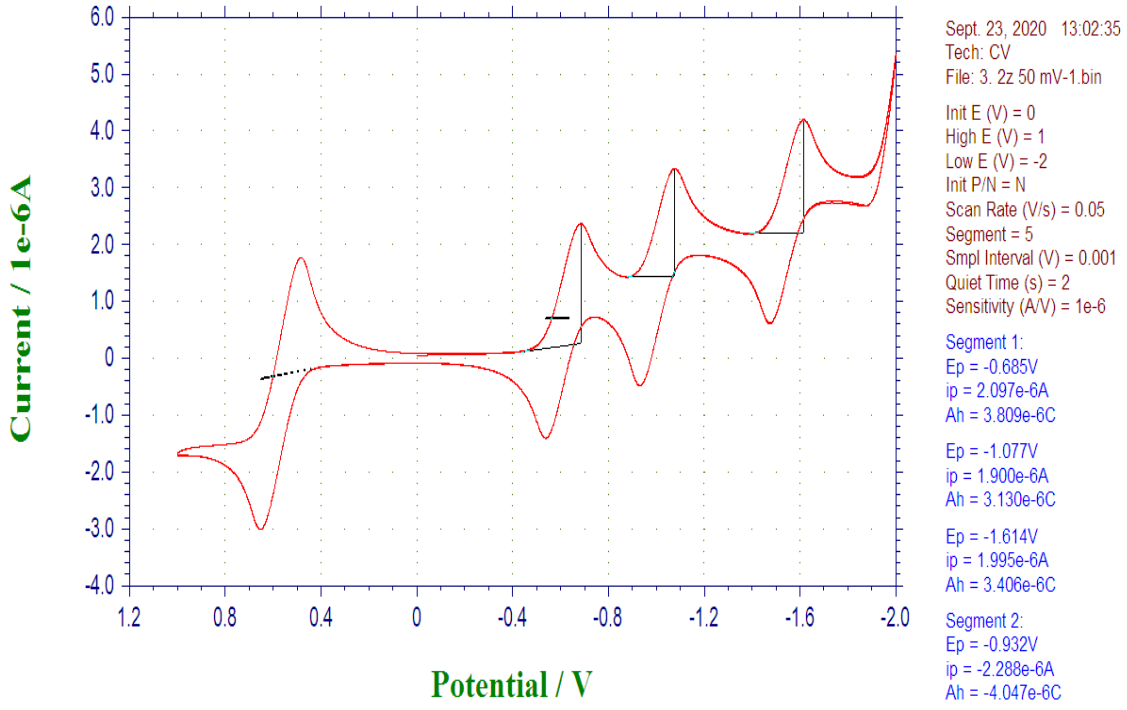
Cyclic voltammogram of compound **2s** (scanning rate: 50 mV s^{-1})



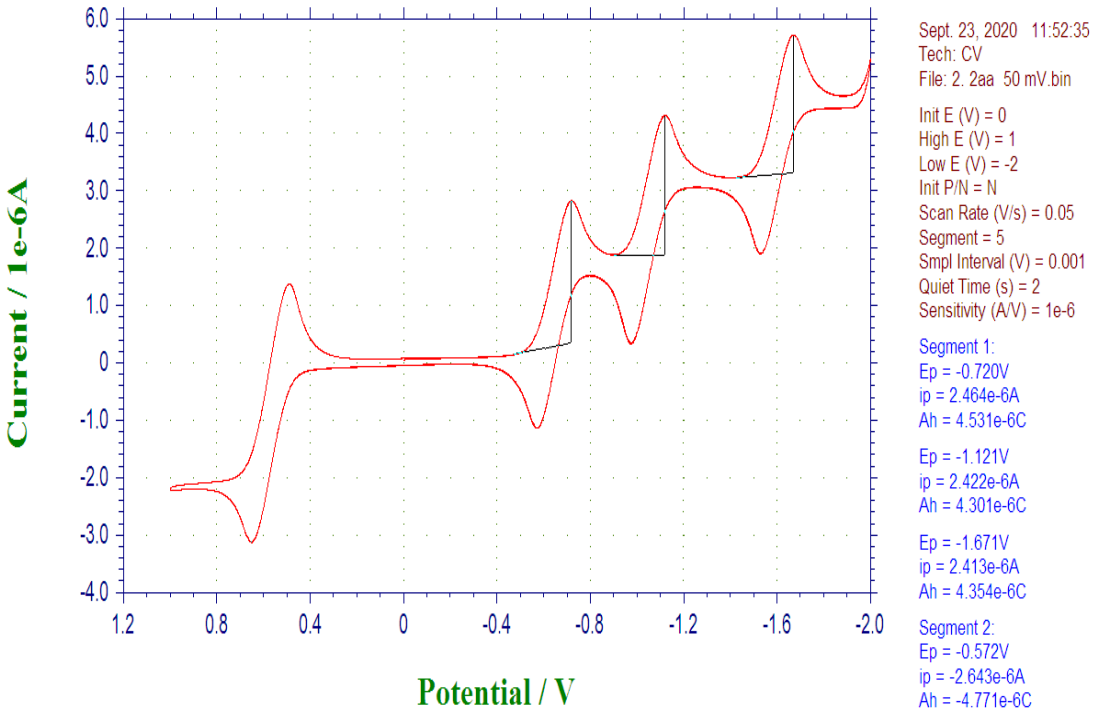
Cyclic voltammogram of compound **2t** (scanning rate: 50 mV s^{-1})



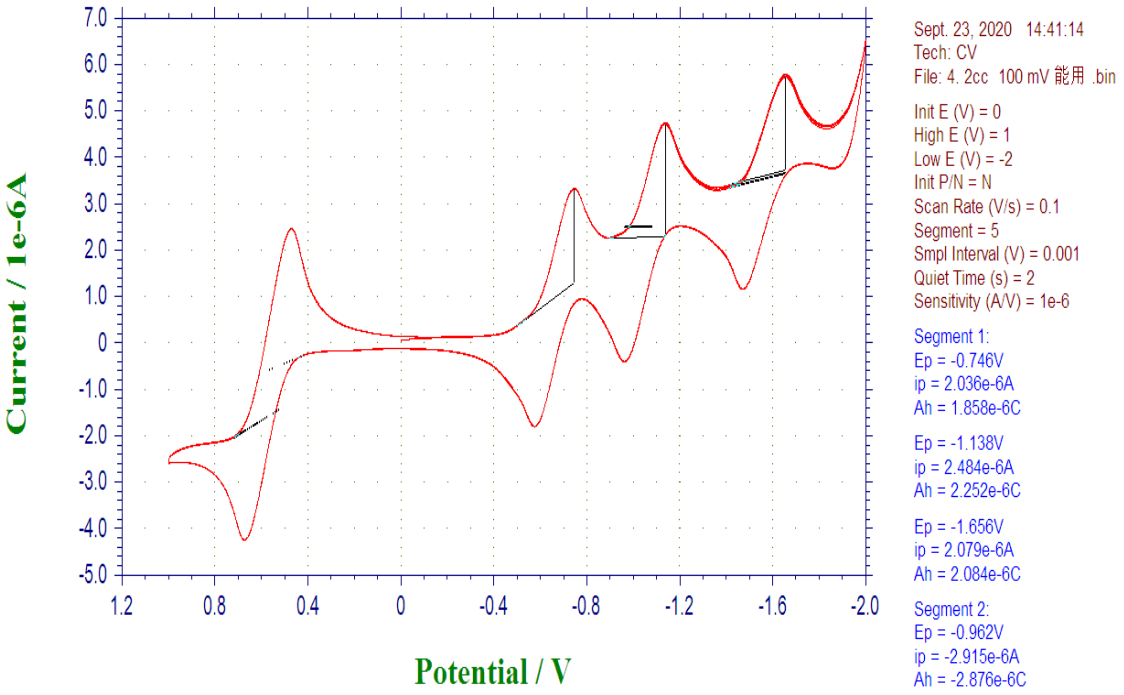
Cyclic voltammogram of compound **2u** (scanning rate: 50 mV s^{-1})



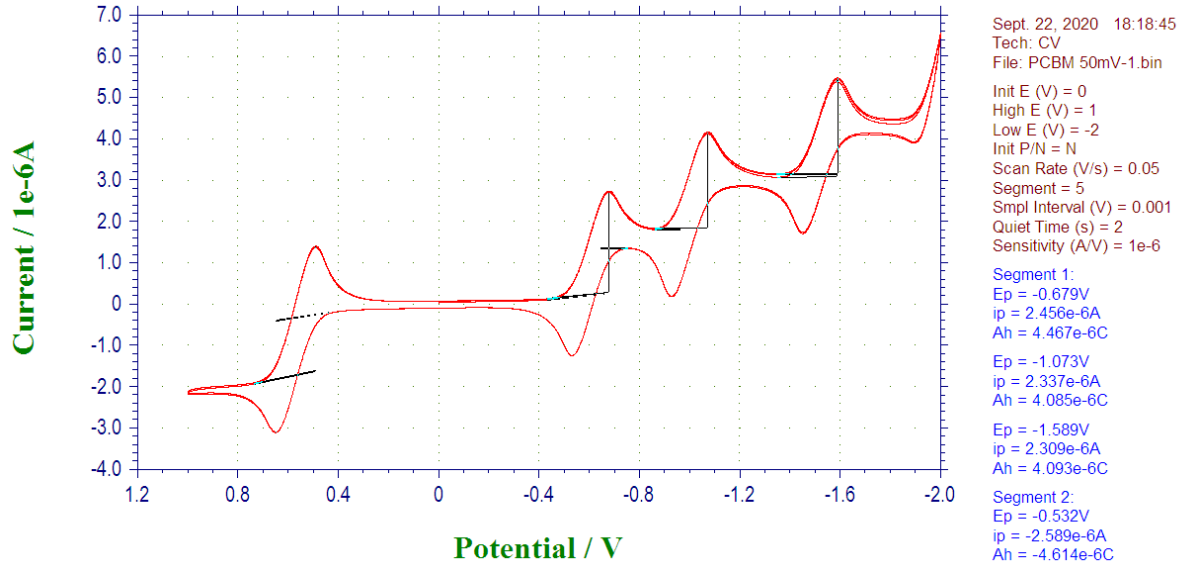
Cyclic voltammogram of compound **2x** (scanning rate: 50 mV s^{-1})



Cyclic voltammogram of compound **2y** (scanning rate: 50 mV s^{-1})

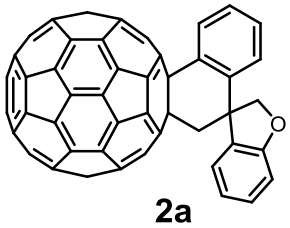


Cyclic voltammogram of compound **2aa** (scanning rate: 100 mV s^{-1})



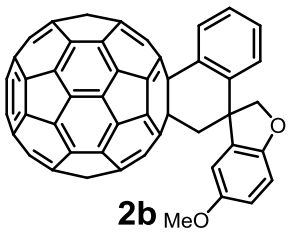
Cyclic voltammogram of compound **PCBM** (scanning rate: 50 mV s^{-1})

6. Spectral Data for Compounds 2



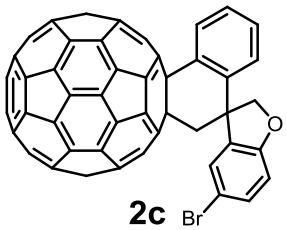
2a

Spectral data of **2a**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2a** (22.2 mg, 48%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.57–7.49 (m, 2H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 9.2 Hz, 1H), 5.02 (d, *J* = 9.2 Hz, 1H), 4.85 (d, *J* = 15.2 Hz, 1H), 4.55 (d, *J* = 14.8 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 161.7, 158.2, 157.4, 152.9, 152.4, 148.0, 147.5, 147.4, 146.5, 146.4, 146.35, 16.3, 146.15, 146.1, 146.07, 145.9, 145.7, 145.6, 145.4, 145.37, 145.3, 145.2, 145.1, 145.0, 144.9, 144.5, 144.43, 144.4, 144.37, 144.2, 142.9, 142.8, 142.5, 142.47, 142.44, 142.4, 142.2, 142.1, 142.05, 142.0, 141.9, 141.88, 141.6, 141.5, 141.3, 141.28, 140.9, 140.15, 140.1, 138.7, 137.0, 136.1, 136.0, 135.8, 135.1, 134.9, 130.8, 130.2, 129.0, 128.5, 128.0, 127.1, 125.3, 119.4, 110.5, 81.1, 73.3, 65.2, 62.4, 45.8; FT-IR *v*/cm^{-1} 2934, 1592, 1481, 1460, 1221, 1099, 1024, 1002, 845, 751, 696, 575, 552, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 312, 433, 699; MALDI-TOF MS *m/z* calcd for $C_{75}H_{12}O$ $[M]^-$ 928.0894, found 928.0888.



2b MeO

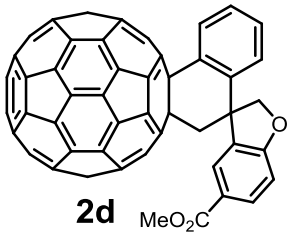
Spectral data of **2b**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **2b** (19.2 mg, 40%); amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3/CS_2$) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 6.92 (s, 1H), 6.81–6.78 (m, 2H), 6.60 (d, *J* = 9.0 Hz, 1H), 5.01 (d, *J* = 9.0 Hz, 1H), 4.85 (d, *J* = 15.0 Hz, 1H), 4.55 (d, *J* = 15.0 Hz, 1H), 3.65 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 158.3, 157.4, 156.2, 153.1, 152.7, 152.5, 148.1, 147.5, 147.4, 146.6, 146.45, 146.4, 146.36, 146.2, 146.17, 146.1, 145.9, 145.7, 145.6, 145.57, 145.5, 145.4, 145.37, 145.2, 145.1, 145.07, 145.0, 144.6, 144.5, 144.44, 144.42, 144.3, 143.0, 142.9, 142.6, 142.5, 142.48, 142.2, 142.12, 142.1, 142.0, 141.9, 141.87, 141.7, 141.6, 141.4, 141.37, 141.0, 140.22, 140.2, 138.7, 136.9, 136.2, 135.9, 135.8, 135.1, 135.0, 129.1, 128.6, 128.1, 127.1, 126.1, 116.4, 116.3, 110.6, 81.4, 73.2, 65.3, 62.9, 55.9, 45.8; FT-IR ν/cm^{-1} 2923, 1709, 1511, 1486, 1423, 1354, 1263, 1197, 1031, 1004, 865, 805, 753, 696, 575, 552, 524; UV-vis ($CHCl_3$) λ_{max}/nm 252, 312, 432, 701; MALDI-TOF MS *m/z* calcd for $C_{76}H_{14}O_2$ $[M]^-$ 958.0999, found 958.0995.



2c

Spectral data of **2c**: the product mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2c** (22.8 mg, 45%); amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3/CS_2$) δ 7.72 (d, *J* = 7.2 Hz,

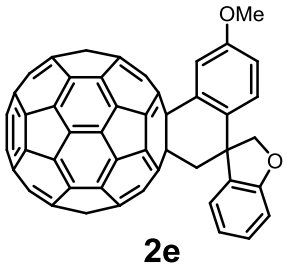
1H), 7.68 (d, *J* = 6.6 Hz, 1H), 7.58–7.53 (m, 2H), 7.44 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 9.6 Hz, 1H), 5.04 (d, *J* = 9.0 Hz, 1H), 4.80 (d, *J* = 14.4 Hz, 1H), 4.55 (d, *J* = 15.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 160.9, 157.8, 156.9, 152.4, 151.5, 147.4, 147.3, 146.4, 146.3, 146.1, 146.0, 145.8, 145.5, 145.45, 145.3, 145.28, 145.2, 145.1, 144.9, 144.8, 144.4, 144.3, 144.26, 142.83, 142.8, 142.5, 142.4, 142.38, 142.35, 142.1, 142.0, 141.8, 141.6, 141.4, 141.2, 138.7, 137.0, 136.2, 136.0, 135.6, 134.9, 134.7, 133.2, 132.9, 129.1, 128.7, 128.2, 127.8, 126.7, 111.9, 111.4, 81.6, 73.0, 65.0, 62.3, 45.7; FT-IR ν/cm^{-1} 1708, 1460, 1261, 1219, 1201, 1102, 1000, 964, 899, 868, 797, 757, 697, 676, 574, 550, 526; UV-vis ($CHCl_3$) λ_{max}/nm 255, 313, 461, 696; MALDI-TOF MS *m/z* calcd for $C_{74}H_{11}BrO$ $[M]^-$ 1005.9999, found 1005.9991.



2d

Spectral data of **2d**: the 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 **2d** (16.0 mg, 32%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.04 (s, 1H), 7.96 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.68 (t, *J* = 6.8 Hz, 2H), 7.59–7.51 (m, 2H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 9.2 Hz, 1H), 5.11 (d, *J* = 9.2 Hz, 1H), 4.81 (d, *J* = 14.8 Hz, 1H), 4.57 (d, *J* = 14.8 Hz, 1H), 3.79 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 166.1, 165.9, 158.1, 157.2, 152.6, 151.8, 147.7, 147.63, 147.6, 146.7, 146.6,

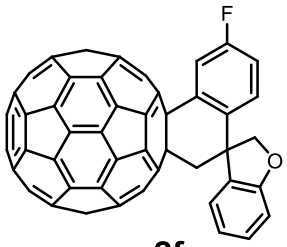
146.57, 146.4, 146.3, 146.28, 146.1, 145.8, 145.77, 145.75, 145.6, 145.59, 145.51, 145.5, 145.47, 145.4, 145.36, 145.2, 145.1, 144.8, 144.64, 144.6, 144.5, 144.2, 143.1, 143.06, 142.8, 142.7, 142.62, 142.6, 142.3, 142.28, 142.2, 142.1, 141.9, 141.65, 141.63, 141.6, 141.5, 141.4, 141.1, 140.4, 140.37, 138.9, 137.4, 136.5, 136.4, 135.9, 135.3, 135.0, 129.3, 128.9, 128.4, 127.1, 126.1, 122.0, 110.4, 82.5, 73.4, 65.4, 62.1, 51.9, 46.1; FT-IR ν/cm^{-1} 1712, 1607, 1510, 1437, 1286, 1229, 1114, 1019, 996, 797, 761, 733, 698, 676, 574, 552, 525; UV-vis ($CHCl_3$) λ_{max}/nm 257, 312, 434, 699; MALDI-TOF MS *m/z* calcd for $C_{77}H_{14}O_3$ $[M]^-$ 986.0948, found 986.0942.



2e

Spectral data of **2e**: the 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 **2e** (19.0 mg, 40%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.67 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.22 (m, 2H), 7.00 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.90 (t, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 9.2 Hz, 1H), 4.98 (d, *J* = 9.2 Hz, 1H), 4.84 (d, *J* = 14.8 Hz, 1H), 4.49 (d, *J* = 14.8 Hz, 1H), 3.95 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 162.0, 159.7, 158.3, 157.5, 153.2, 152.8, 148.2, 147.6, 147.57, 146.7, 146.6, 146.5, 146.3, 146.27, 146.2, 146.0, 145.9, 145.8, 145.78, 145.5, 145.46, 145.3, 145.27, 145.2, 145.1, 144.7, 144.6, 144.5, 144.4, 143.1, 143.0, 142.7, 142.63, 142.6, 142.58, 142.3, 142.25, 142.2, 142.17, 142.0, 141.8, 141.6, 141.5, 141.49, 141.45, 141.1, 140.3,

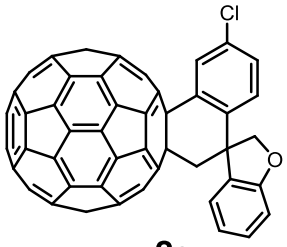
138.8, 137.3, 137.2, 136.2, 136.17, 135.4, 135.1, 134.2, 130.8, 130.2, 128.6, 125.8, 119.5, 114.9, 112.8, 110.7, 81.6, 73.6, 65.4, 62.1, 55.3, 46.2; FT-IR ν/cm^{-1} 2829, 1607, 1591, 1495, 1478, 1458, 1422, 1315, 1251, 1215, 1158, 1097, 1024, 900, 813, 751, 725, 575, 551, 525; UV-vis ($CHCl_3$) λ_{max}/nm 258, 312, 434, 721; MALDI-TOF MS *m/z* calcd for $C_{76}H_{14}O_2$ $[M]^-$ 958.0999, found 958.0994.



2f

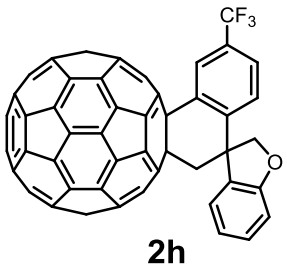
Spectral data of **2f**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2f** (14.2 mg, 30%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.75 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.41 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.18 (td, *J* = 8.4, 2.4 Hz, 1H), 6.92–6.87 (m, 2H), 6.60 (d, *J* = 9.2 Hz, 1H), 4.98 (d, *J* = 9.2 Hz, 1H), 4.83 (d, *J* = 14.8 Hz, 1H), 4.53 (d, *J* = 15.2 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 163.3, 161.9, 161.6, 157.7, 156.9, 152.6, 152.2, 147.9, 147.5, 147.4, 146.5, 146.45, 146.4, 146.2, 146.15, 146.1, 145.9, 145.7, 145.6, 145.5, 145.44, 145.4, 145.3, 145.2, 145.14, 145.1, 144.8, 144.5, 144.4, 144.37, 144.0, 143.0, 142.9, 142.6, 142.5, 142.49, 142.46, 142.2, 142.1, 142.0, 141.96, 141.9, 141.7, 141.5, 141.34, 141.3, 141.29, 141.0, 140.2, 140.18, 138.7, 138.2, 138.1, 137.8, 137.1, 136.1, 135.9, 135.1, 135.0, 130.5, 130.4, 129.2, 129.1, 125.2, 119.6, 116.2, 116.0, 114.6, 114.5, 110.7, 81.1, 73.2, 65.0, 62.0, 45.7; FT-IR ν/cm^{-1} 2918, 1710, 1597, 1479, 1454, 1427, 1247, 1197, 1147, 1096, 1024, 1003, 862,

819, 750, 696, 574, 551, 525; UV-vis ($CHCl_3$) λ_{max}/nm 256, 313, 433, 700; MALDI-TOF MS *m/z* calcd for $C_{75}H_{11}FO$ $[M]^-$ 946.0799, found 946.0795.



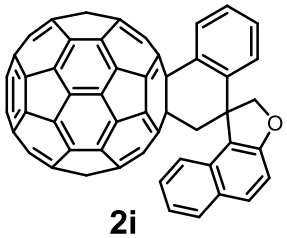
2g

Spectral data of **2g**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2g** (19.0 mg, 40%); amorphous brown solid; ^1H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.47 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.24 (t, *J* = 8.0 Hz, 1H), 6.93–6.88 (m, 2H), 6.60 (d, *J* = 9.2 Hz, 1H), 4.98 (d, *J* = 9.2 Hz, 1H), 4.81 (d, *J* = 15.2 Hz, 1H), 4.52 (d, *J* = 14.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 162.0, 157.8, 157.0, 152.7, 152.2, 147.9, 147.6, 147.5, 146.6, 146.5, 146.49, 146.48, 146.3, 146.24, 146.2, 146.0, 145.8, 145.7, 145.6, 145.53, 145.5, 145.4, 145.3, 145.2, 145.18, 144.9, 144.6, 144.5, 144.49, 144.4, 144.1, 143.0, 142.96, 142.7, 142.6, 142.58, 142.5, 142.3, 142.2, 142.1, 142.09, 142.07, 142.0, 141.8, 141.6, 141.4, 141.38, 141.0, 140.6, 140.3, 140.26, 138.8, 137.9, 137.1, 136.2, 136.0, 135.2, 135.0, 134.5, 130.6, 130.5, 129.1, 128.8, 128.1, 125.1, 119.7, 110.7, 81.0, 73.7, 65.0, 62.2, 45.5; FT-IR *v*/cm^{-1} 2973, 2879, 1592, 1510, 1478, 1450, 1379, 1318, 1087, 1046, 879, 821, 795, 744, 573, 551, 525; UV-vis ($CHCl_3$) λ_{max}/nm 260, 314, 434, 698; MALDI-TOF MS *m/z* calcd for $C_{75}H_{11}ClO$ $[M]^-$ 962.0504, found 962.0500.



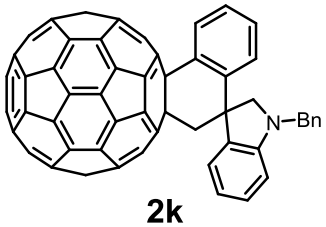
2h

Spectral data of **2h**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2h** (18.3 mg, 37%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.97 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 6.96–6.92 (m, 2H), 6.64 (d, *J* = 9.2 Hz, 1H), 4.99 (d, *J* = 9.2 Hz, 1H), 4.87 (d, *J* = 15.2 Hz, 1H), 4.63 (d, *J* = 15.2 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 162.0, 157.6, 156.9, 152.5, 151.9, 147.9, 147.7, 147.6, 146.7, 146.6, 146.54, 146.5, 146.3, 146.29, 146.2, 146.1, 146.0, 145.8, 145.7, 145.6, 145.57, 145.5, 145.48, 145.4, 145.3, 145.2, 144.9, 144.7, 144.6, 144.5, 144.47, 144.1, 143.1, 143.0, 142.7, 142.64, 142.6, 142.58, 142.3, 142.2, 142.13, 142.1, 142.08, 142.0, 141.8, 141.7, 141.4, 141.37, 141.1, 140.4, 140.3, 138.8, 137.2, 137.1, 136.3, 136.0, 135.1, 135.0, 130.7, 130.65, 127.9, 125.9, 125.0, 124.9, 119.8, 110.8, 80.8, 73.1, 64.9, 62.6, 45.7; FT-IR ν/cm^{-1} 2926, 1612, 1584, 1480, 1451, 1429, 1327, 1220, 1161, 1118, 1081, 964, 884, 838, 743, 698, 575, 552, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 312, 433, 697; MALDI-TOF MS *m/z* calcd for $C_{76}H_{11}F_3O$ $[M]^-$ 996.0767, found 996.0764.



2i

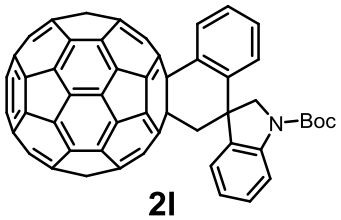
Spectral data of **2i**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2i (**20.7 mg, 42%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.82 (d, *J* = 7.2 Hz, 1H), 7.77–7.72 (m, 3H), 7.70–7.68 (m, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.16–7.13 (m, 3H), 6.73 (d, *J* = 9.2 Hz, 1H), 5.02 (d, *J* = 9.2 Hz, 1H), 4.97 (d, *J* = 15.2 Hz, 1H), 4.65 (d, *J* = 15.2, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 161.0, 158.8, 158.6, 154.5, 153.6, 147.7, 147.6, 146.9, 146.6, 146.55, 146.35, 146.3, 146.2, 146.1, 146.0, 145.8, 145.6, 145.55, 145.5, 145.4, 145.3, 145.26, 144.9, 144.7, 144.6, 144.56, 144.5, 143.1, 143.08, 142.8, 142.7, 142.6, 142.5, 142.4, 142.3, 142.25, 142.1, 142.08, 141.9, 141.7, 141.5, 141.3, 141.25, 141.2, 140.9, 140.4, 140.3, 138.3, 137.3, 136.1, 135.6, 135.5, 135.1, 134.8, 133.1, 132.6, 130.1, 129.8, 129.3, 129.0, 128.8, 128.1, 127.0, 125.8, 122.8, 117.9, 112.7, 81.5, 73.2, 65.1, 65.08, 45.8; FT-IR *v*/cm^{-1} 1620, 1579, 1516, 1430, 1377, 1257, 1204, 1093, 1019, 810, 742, 553, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 314, 431, 695; MALDI-TOF MS *m/z* calcd for $C_{79}H_{14}O$ $[M]^-$ 978.1050, found 978.1052.



2k

Spectral data of **2k**: the mixture was separated and purified by silica gel column

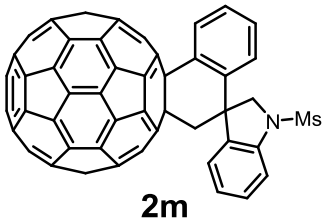
chromatography with CS_2 as the eluent to give unreacted C_{60} and **2k** (14.1 mg, 28%); amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3/CS_2$) δ 7.85 (d, *J* = 7.2 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.53–7.49 (m, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 6.6 Hz, 1H), 7.26–7.23 (m, 4H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.68 (t, *J* = 7.8 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 1H), 5.56 (d, *J* = 10.2 Hz, 1H), 4.92 (d, *J* = 15.0 Hz, 1H), 4.62 (d, *J* = 15.0 Hz, 1H), 4.48 (d, *J* = 15.0 Hz, 1H), 4.27 (d, *J* = 15.0 Hz, 1H), 3.96 (d, *J* = 10.2 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 159.3, 157.7, 154.3, 153.5, 153.4, 149.0, 147.6, 147.56, 146.6, 146.5, 146.46, 146.4, 146.3, 146.2, 146.1, 145.9, 145.8, 145.76, 145.5, 145.47, 145.4, 145.3, 145.2, 145.1, 145.08, 145.0, 144.7, 144.6, 144.57, 144.56, 144.4, 143.1, 143.0, 142.9, 142.7, 142.6, 142.5, 142.4, 142.39, 142.2, 142.18, 142.17, 142.1, 142.0, 141.7, 141.5, 141.45, 141.4, 141.0, 140.2, 140.1, 138.6, 137.5, 137.0, 136.1, 135.7, 135.2, 135.19, 135.17, 131.6, 129.9, 129.0, 128.7, 128.2, 128.1, 127.9, 127.6, 127.4, 126.9, 116.2, 107.3, 73.0, 65.4, 64.4, 61.0, 52.4, 45.5; FT-IR *v*/cm^{-1} 2920, 1711, 1598, 1488, 1449, 1429, 1352, 1274, 1217, 1155, 1083, 1027, 840, 801, 732, 693, 666, 575, 552, 525; UV-vis ($CHCl_3$) λ_{max}/nm 257, 311, 430, 707; MALDI-TOF MS *m/z* calcd for $C_{82}H_{19}N$ [M]$^-$ 1017.1523, found 1017.1521.



2l

Spectral data of **2l**: the 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

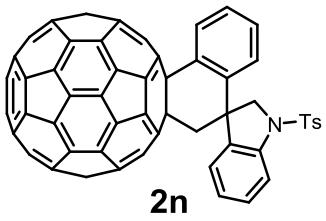
was switched to CS_2/DCM (v/v = 7:1) to give **2l** (16.9 mg, 33%); amorphous brown solid; ^{1}H NMR (600 MHz, DMSO-d_6/CS_2) δ 7.84 (br, 1H), 7.71–7.68 (m, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.21 (br, 1H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.13 (s, 1H), 5.02 (br, 1H), 4.60 (d, *J* = 15.0 Hz, 1H), 4.33 (br, 1H), 1.55 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6/CS_2 with $Cr(acac)_3$ as relaxation reagent) δ 153.1, 152.8, 148.4, 147.7, 147.68, 146.8, 146.7, 146.5, 146.4, 146.3, 146.1, 146.0, 145.7, 145.6, 145.45, 145.4, 145.36, 144.8, 144.7, 143.2, 143.1, 142.9, 142.8, 142.7, 142.5, 142.4, 142.3, 142.2, 142.0, 141.8, 141.6, 141.55, 141.14, 140.5, 137.2, 136.3, 135.4, 129.6, 128.9, 128.4, 127.7, 121.1, 116.1, 65.4, 60.1, 28.7; FT-IR *v*/cm^{-1} 2851, 1711, 1603, 1575, 1485, 1430, 1310, 1254, 1216, 1120, 1009, 947, 851, 818, 755, 704, 669, 651, 575, 552, 526; UV-vis ($CHCl_3$) λ_{max}/nm 253, 317, 432, 693; MALDI-TOF MS *m/z* calcd for $C_{80}H_{21}NO_2$ $[M]^-$ 1027.1578, found 1027.1574.



2m

Spectral data of **2m**: the 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 = 3:1) to give **2m** (20.4 mg, 40%); amorphous brown solid; ^{1}H NMR (600 MHz, DMSO-d_6/CS_2) δ 7.70 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.10 (d, *J* = 11.4 Hz, 1H), 5.03 (d, *J* = 14.4 Hz, 1H), 4.60 (d, *J* = 15.0 Hz, 1H), 4.48 (d, *J* = 11.4

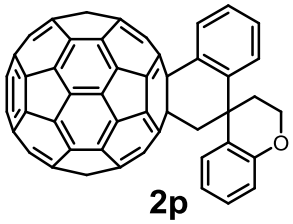
Hz, 1H), 2.88 (s, 3H); the ^{13}C NMR spectrum of **2m** could not be obtained because of poor solubility of the product; FT-IR ν/cm^{-1} 2924, 1701, 1598, 1482, 1435, 1365, 1338, 1151, 1092, 1017, 957, 743, 691, 637, 575, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 314, 433, 698; MALDI-TOF MS m/z calcd for $C_{76}H_{15}NO_2S$ $[M]^-$ 1005.0829, found 1005.0821.



2n

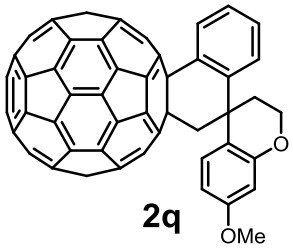
Spectral data of **2n**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **2n** (20.2 mg, 38%); amorphous brown solid; ^1H NMR (600 MHz, $CDCl_3/CS_2$) δ 7.70 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 7.2 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.27–7.24 (m, 2H), 7.19 (d, J = 7.8 Hz, 2H), 6.93 (t, J = 7.8 Hz, 1H), 6.01 (d, J = 10.8 Hz, 1H), 5.02 (d, J = 15.0 Hz, 1H), 4.56 (d, J = 15.0 Hz, 1H), 4.36 (d, J = 11.4 Hz, 1H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 159.0, 157.7, 152.6, 152.4, 148.2, 147.7, 147.6, 146.8, 146.6, 146.43, 146.4, 146.3, 146.1, 145.9, 145.72, 145.7, 145.6, 145.58, 145.43, 145.4, 145.3, 144.8, 144.78, 144.75, 144.6, 144.56, 144.5, 144.3, 143.1, 143.06, 142.8, 142.74, 142.7, 142.6, 142.5, 142.4, 142.3, 142.26, 142.2, 142.17, 141.9, 141.8, 141.5, 141.46, 141.2, 140.45, 140.4, 138.7, 137.0, 136.3, 136.2, 136.16, 135.3, 135.26, 135.2, 131.9, 130.4, 130.3, 129.7, 128.9, 128.8, 128.3, 127.5, 127.4, 121.6, 113.8, 73.9, 65.4, 61.5,

59.7, 45.6, 22.0; FT-IR ν/cm^{-1} 2924, 1602, 1482, 1446, 1362, 1234, 1154, 1126, 1016, 956, 762, 744, 636, 596, 575, 539, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 314, 434, 699; MALDI-TOF MS *m/z* calcd for $C_{82}H_{19}NO_2S$ $[M]^-$ 1081.1142, found 1081.1136.



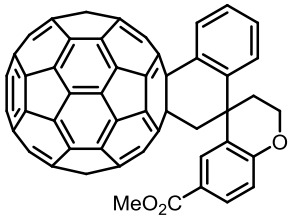
2p

Spectral data of **2p**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2p** (22.1 mg, 47%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.71 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.50–7.45 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.79 (t, *J* = 7.6 Hz, 1H), 5.26 (d, *J* = 15.2 Hz, 1H), 4.69 (d, *J* = 15.2 Hz, 1H), 4.60–4.54 (m, 2H), 4.19–4.13 (m, 1H), 3.01–2.97 (m, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 160.4, 160.2, 158.2, 154.5, 153.9, 147.74, 147.7, 147.6, 146.6, 146.5, 146.49, 146.4, 146.3, 146.2, 146.0, 145.8, 145.6, 145.5, 145.4, 145.35, 145.3, 145.2, 145.19, 145.1, 144.8, 144.6, 144.53, 144.5, 144.2, 143.0, 142.7, 142.69, 142.6, 142.59, 142.5, 142.3, 142.26, 142.2, 142.1, 142.0, 141.9, 141.65, 141.6, 141.5, 141.1, 141.0, 140.4, 140.37, 138.6, 136.6, 136.5, 135.5, 135.0, 134.98, 134.7, 129.6, 129.3, 129.1, 127.9, 127.8, 121.9, 119.0, 118.3, 75.4, 65.0, 64.5, 53.3, 45.8, 39.1; FT-IR ν/cm^{-1} 2861, 1610, 1573, 1498, 1436, 1327, 1274, 1258, 1237, 1196, 1163, 1107, 1023, 968, 901, 829, 795, 753, 727, 708, 691, 658, 574, 551, 524; UV-vis ($CHCl_3$) λ_{max}/nm 257, 313, 435, 504, 704; MALDI-TOF MS *m/z* calcd for $C_{76}H_{14}O$ $[M]^-$ 942.1050, found 942.1045.



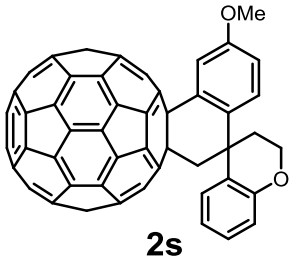
2q

Spectral data of **2q**: the 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 **2q** (20.0 mg, 41%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.65 (d, *J* = 7.2 Hz, 1H), 7.50–7.42 (m, 3H), 7.25 (d, *J* = 8.8 Hz, 1H), 6.38 (d, *J* = 2.4 Hz, 1H), 6.35 (dd, *J* = 8.8, 2.8 Hz, 1H), 5.22 (d, *J* = 15.6 Hz, 1H), 4.63 (d, *J* = 15.6 Hz, 1H), 4.54–4.43 (m, 2H), 4.16–4.11 (m, 1H), 3.70 (s, 3H), 2.95–2.90 (m, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 161.0, 160.4, 159.8, 158.3, 154.8, 154.2, 147.9, 147.7, 147.6, 146.6, 146.56, 146.5, 146.45, 146.3, 146.2, 146.0, 145.8, 145.6, 145.56, 145.5, 145.48, 145.4, 145.38, 145.3, 145.26, 145.2, 145.19, 144.8, 144.6, 144.56, 144.5, 144.2, 143.1, 143.07, 142.8, 142.7, 142.6, 142.5, 142.3, 142.27, 142.2, 142.1, 142.0, 141.9, 141.65, 141.6, 141.1, 141.09, 140.4, 140.35, 138.8, 137.2, 136.8, 136.4, 135.5, 135.0, 134.97, 134.7, 129.5, 129.2, 127.9, 127.8, 113.8, 106.7, 102.1, 75.5, 65.0, 64.6, 55.1, 52.9, 45.8, 38.6; FT-IR ν/cm^{-1} 2941, 1715, 1592, 1488, 1431, 1245, 1192, 1114, 1039, 904, 801, 762, 701, 682, 640, 574, 548, 525; UV-vis ($CHCl_3$) λ_{max}/nm 259, 313, 435, 711; MALDI-TOF MS *m/z* calcd for $C_{77}H_{16}O_2$ $[M]^-$ 972.1156, found 972.1154.



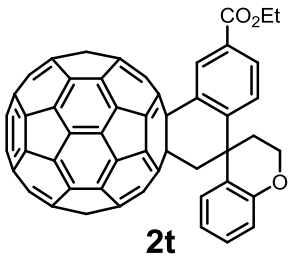
2r

Spectral data of **2r**: the 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 **2r** (25.2 mg, 50%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.15 (d, *J* = 2.0 Hz, 1H), 7.76 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.70 (d, *J* = 7. 2 Hz, 1H), 7.53 (td, *J* = 7.2, 2.0 Hz, 1H), 7.49–7.43 (m, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.23 (d, *J* = 15.6 Hz, 1H), 4.69 (d, *J* = 15.2 Hz, 1H), 4.64–4.58 (m, 1H), 4.51–4.44 (m, 1H), 4.23–4.17 (m, 1H), 3.70 (s, 3H), 3.07–3.01 (m, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 165.8, 163.5, 160.0, 157.8, 153.8, 153.4, 147.7, 147.2, 147.0, 146.6, 146.5, 146.43, 146.4, 146.3, 147.1, 145.9, 145.7, 145.5, 145.4, 145.4, 145.37, 145.2, 145.19, 145.16, 145.1, 144.7, 144.65, 144.6, 144.5, 144.4, 144.1, 143.0, 142.7, 142.6, 142.56, 142.5, 142.4, 142.3, 142.2, 142.15, 142.0, 141.95, 141.9, 141.6, 141.55, 141.5, 141.0, 140.9, 140.4, 140.36, 138.7, 138.66, 136.6, 136.5, 135.4, 135.2, 135.0, 134.5, 130.2, 129.7, 129.1, 128.2, 128.1, 121.2, 120.7, 118.2, 74.9, 64.9, 64.6, 53.3, 51.6, 45.8, 38.3; FT-IR ν/cm^{-1} 2892, 1715, 1619, 1591, 1498, 1448, 1427, 1344, 1329, 1264, 1239, 1149, 1113, 1065, 1021, 906, 858, 797, 762, 748, 705, 641, 572, 525; UV-vis ($CHCl_3$) λ_{max}/nm 256, 313, 434, 701; MALDI-TOF MS *m/z* calcd for $C_{78}H_{16}O_3$ $[M]^-$ 1000.1105, found 1000.1101.



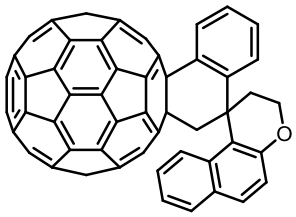
2s

Spectral data of **2s**: the 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 **2s** (22.0 mg, 45%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.44 (d, *J* = 8.4 Hz, 1H), 7. 40 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.19 (d, *J* = 2.4 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.74 (t, *J* = 8.0 Hz, 1H), 5.20 (d, *J* = 15.2 Hz, 1H), 4.58 (d, *J* = 15.2 Hz, 1H), 4.55–4.44 (m, 2H), 4.14–4.09 (m, 1H), 3.93 (s, 3H), 2.96–2.90 (m, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 160.3, 160.1, 159.1, 158.2, 154.7, 154.0, 147.7, 147.5, 146.6, 146.5, 146.45, 146.4, 146.3, 146.2, 145.9, 145.8, 145.79, 145.6, 145.5, 145.4, 145.3, 145.27, 145.2, 145.19, 145.17, 145.1, 144.8, 144.6, 144.5, 144.49, 144.2, 143.0, 142.7, 142.66, 142.6, 142.56, 142.5, 142.3, 142.24, 142.2, 142.0, 141.98, 141.9, 141.6, 141.59, 141.5, 141.1, 141.0, 140.4, 140.3, 138.6, 137.3, 136.7, 136.5, 136.47, 136.4, 135.0, 134.96, 134.7, 130.5, 129.0, 122.0, 118.9, 118.3, 115.0, 112.6, 75.5, 64.9, 64.5, 55.3, 52.9, 46.0, 39.4; FT-IR *v*/cm^{-1} 2924, 1712, 1591, 1427, 1265, 1240, 1019, 907, 797, 762, 747, 706, 642, 573, 551, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 313, 435, 704; MALDI-TOF MS *m/z* calcd for $C_{77}H_{16}O_2$ $[M]^-$ 972.1156, found 972.1148.



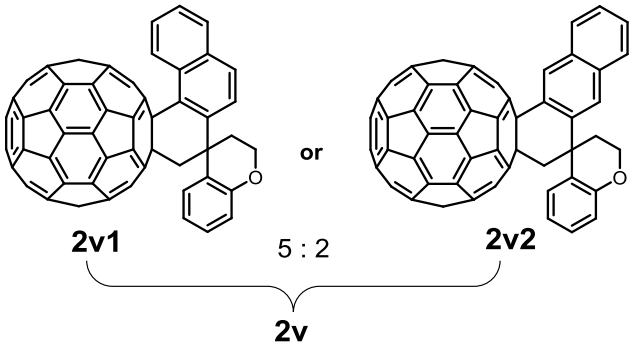
2t

Spectral data of **2t**: the 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 **2t** (16.8 mg, 33%); amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3/CS_2$) δ 8.37 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.79 (t, *J* = 7.8 Hz, 1H), 5.24 (d, *J* = 15.6 Hz, 1H), 4.75 (d, *J* = 15.6 Hz, 1H), 4.60–4.55 (m, 2H), 4.46–4.44 (m, 2H), 4.16–4.12 (m, 1H), 2.96–2.93 (m, 1H), 1.47 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 165.7, 156.0, 159.88, 157.6, 153.9, 153.2, 150.0, 147.6, 147.4, 147.3, 146.5, 146.36, 146.3, 146.26, 146.2, 146.0, 145.8, 145.6, 145.4, 145.3, 145.27, 145.2, 145.1, 145.0, 144.97, 144.7, 144.6, 144.3, 144.27, 143.8, 142.9, 142.6, 142.5, 142.4, 142.3, 142.0, 141.8, 141.76, 141.44, 141.4, 141.3, 140.9, 140.2, 138.4, 136.3, 136.2, 135.6, 134.7, 134.6, 134.58, 130.4, 129.8, 129.2, 129.1, 128.7, 121.3, 119.0, 118.3, 75.0, 64.5, 64.3, 61.1, 53.3, 45.4, 38.7, 14.4; FT-IR ν/cm^{-1} 2918, 1713, 1591, 1485, 1428, 1218, 1040, 907, 856, 800, 762, 744, 706, 574, 552, 525; UV-vis ($CHCl_3$) λ_{max}/nm 259, 312, 434, 697; MALDI-TOF MS *m/z* calcd for $C_{79}H_{18}O_3$ $[M]^-$ 1014.1261, found 1014.1256.

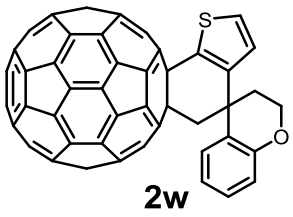


2u

Spectral data of **2u**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2u** (20.2 mg, 41%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.96 (d, *J* = 8.8 Hz, 1H), 7.77 (t, *J* = 6.8 Hz, 2H), 7.57–7.49 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.09–7.06 (m, 2H), 6.92 (t, *J* = 8.0 Hz, 1H), 5.23 (d, *J* = 16.0 Hz, 1H), 4.82 (d, *J* = 15.6 Hz, 1H), 4.74–4.70 (m, 1H), 4.63–4.59 (m, 1H), 4.25 (td, *J* = 11.6, 2.4 Hz, 1H), 3.11 (dt, *J* = 13.6, 2.4 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 160.2, 160.1, 159.3, 155.7, 154.3, 147.5, 147.3, 146.4, 146.2, 146.15, 146.1, 146.0, 145.99, 145.8, 145.7, 145.6, 145.5, 145.4, 145.3, 145.2, 145.0, 144.98, 144.8, 144.79, 144.6, 144.3, 144.2, 144.16, 144.1, 143.0, 142.8, 142.5, 142.4, 142.25, 142.2, 142.1, 141.9, 141.87, 141.8, 141.7, 141.66, 141.4, 141.3, 140.6, 140.5, 140.2, 140.1, 140.08, 137.8, 136.3, 136.26, 134.7, 134.6, 134.1, 133.9, 133.1, 131.2, 130.8, 130.7, 130.1, 129.6, 128.1, 127.7, 127.4, 123.5, 123.0, 119.8, 115.2, 75.0, 64.5, 63.6, 54.3, 45.5, 41.1; FT-IR ν/cm^{-1} 2936, 1714, 1591, 1498, 1447, 1427, 1262, 1240, 1190, 1149, 1113, 1065, 1021, 907, 797, 762, 705, 641, 574, 552, 526; UV-vis ($CHCl_3$) λ_{max}/nm 254, 325, 433, 699; MALDI-TOF MS *m/z* calcd for $C_{80}H_{16}O$ $[M]^-$ 992.1207, found 992.1200.

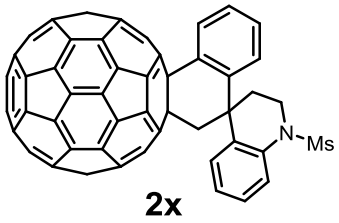


Spectral data of **2w**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2v** (14.8 mg, 30%); amorphous brown solid; **2v1** (major) ^{1}H NMR (400 MHz, $CDCl_3/CS_2$,) δ 8.45 (d, *J* = 8.4 Hz, 1H), 7. 98 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.57–7.52 (m, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.15–7.11 (m, 1H), 6.93–6.90 (m, 1H), 6.80 (t, *J* = 8.0 Hz, 1H), 5.63 (d, *J* = 15.6 Hz, 1H), 5.16 (d, *J* = 15.6 Hz, 1H), 4.69–4.57 (m, 2H), 4.21–4.15 (m, 1H), 3.08–3.03 (m, 1H); **2v2** (minor) ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.16 (s, 1H), 8.08 (s, 1H), 7. 96 (d, *J* = 9.2 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.57–7.52 (m, 1H), 7.15–7.11 (m, 1H), 6.93–6.90 (m, 1H), 6.80 (t, *J* = 8.0 Hz, 1H), 5.41 (d, *J* = 15.6 Hz, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 4.69–4.57 (m, 2H), 4.21–4.15 (m, 1H), 3.08–3.03 (m, 1H); MALDI-TOF MS *m/z* calcd for $C_{80}H_{16}O$ $[M]^-$ 992.1207, found 992.1205.



Spectral data of **2w**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2w** (20.9 mg, 44%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.50 (dd, *J* = 8.0, 2.0 Hz,

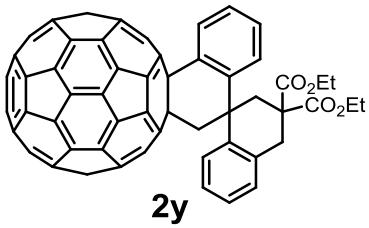
1H), 7. 29 (d, *J* = 5.2 Hz, 1H), 7.11 (t, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 5.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.78 (t, *J* = 8.0 Hz, 1H), 5.12 (d, *J* = 16.0 Hz, 1H), 4.88 (d, *J* = 15.6 Hz, 1H), 4.63–4.58 (m, 1H), 4.35–4.30 (m, 1H), 4.28–4.24 (m, 1H), 2.94–2.87 (m, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 159.7, 158.4, 157.5, 154.9, 153.8, 147.6, 147.5, 147.3, 146.7, 146.5, 146.4, 146.37, 146.3, 146.27, 146.2, 146.0, 145.8, 145.7, 145.5, 145.4, 145.3, 145.2, 145.1, 144.9, 144.6, 144.3, 143.9, 143.0, 142.6, 142.55, 142.5, 142.3, 142.2, 142.1, 141.9, 141.86, 141.8, 141.5, 141.4, 141.1, 140.2, 138.8, 137.0, 135.8, 135.3, 134.8, 134.7, 133.6, 129.2, 129.1, 122.1, 119.1, 117.9, 75.7, 66.2, 51.0, 40.7, 37.0; FT-IR ν/cm^{-1} 2922, 1720, 1447, 1343, 1260, 1039, 796, 762, 706, 542, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 313, 435, 701; MALDI-TOF MS *m/z* calcd for $C_{74}H_{12}OS$ $[M]^-$ 948.0614, found 948.0611.



2x

Spectral data of **2x**: the 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 = 3:1) to give **2x** (13.9 mg, 27%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.72 (d, *J* = 7.2 Hz, 1H), 7. 64–7.58 (m, 3H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 8.4 Hz, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 5.17 (d, *J* = 15.6 Hz, 1H), 4.69 (d, *J* = 15.6 Hz, 1H), 4.62–4.49 (m, 2H), 3.55 (td, *J* = 12.8, 2.8 Hz, 1H), 3.04 (dt, *J* = 13.2, 2.8 Hz, 1H), 2.92 (s, 3H); $^{13}C\{^{1}H\}$

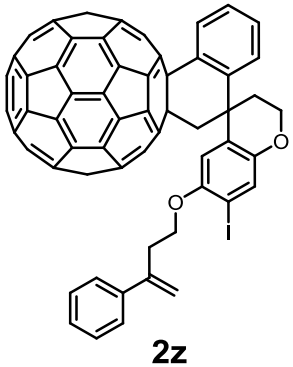
NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 160.5, 157.9, 154.3, 153.1, 147.9, 147.6, 147.2, 146.7, 146.61, 146.6, 146.5, 146.4, 146.3, 146.0, 145.9, 145.8, 145.7, 145.6, 145.5, 145.33, 145.3, 145.27, 145.2, 145.0, 144.9, 144.6, 144.54, 144.5, 144.0, 143.1, 142.9, 142.75, 142.7, 142.69, 142.5, 142.3, 142.28, 142.1, 142.0, 141.8, 141.70, 141.5, 141.2, 141.0, 140.6, 140.4, 138.4, 137.4, 137.3, 136.5, 135.4, 135.2, 134.8, 134.7, 130.0, 129.2, 128.8, 128.0, 127.7, 127.67, 121.9, 121.8, 75.4, 64.8, 55.5, 45.95, 44.4, 40.5, 40.4; FT-IR ν/cm^{-1} 2962, 1725, 1592, 1446, 1260, 1021, 907, 859, 797, 749, 701, 553, 526; UV-vis ($CHCl_3$) λ_{max}/nm 259, 314, 434, 701; MALDI-TOF MS *m/z* calcd for $C_{77}H_{17}NO_2S$ $[M]^-$ 1019.0985, found 1019.0984.



2y

Spectral data of **2y**: the 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 = 4:1) to give **2y** (24.3 mg, 45%); amorphous brown solid; ^1H NMR (600 MHz, $CDCl_3/CS_2$) δ 7.67 (d, *J* = 7.2 Hz, 1H), 7. 53 (d, *J* = 8.4 Hz, 1H), 7.50–7.46 (m, 2H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.11–7.10 (m, 2H), 7.06–7.03 (m, 1H), 5.29 (d, *J* = 15.0 Hz, 1H), 4.67 (d, *J* = 14.4 Hz, 1H), 4.63 (d, *J* = 15.0 Hz, 1H), 4.29–4.25 (m, 2H), 4.03–4.00 (m, 1H), 3.77–3.74 (m, 1H), 3.70 (dd, *J* = 14.4, 2.4 Hz, 1H), 3.40 (dd, *J* = 15.0, 2.4 Hz, 1H), 2.99 (d, *J* = 15.0 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 171.1, 169.4, 160.8, 158.2, 154.5, 153.2, 147.8, 147.5, 147.2,

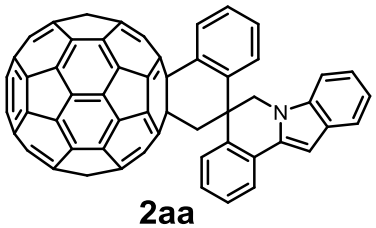
146.6, 146.53, 146.5, 146.4, 146.3, 146.2, 146.0, 146.9, 145.82, 145.8, 145.6, 145.45, 145.4, 145.3, 145.2, 145.1, 144.8, 144.6, 144.5, 144.4, 144.0, 143.0, 142.97, 142.8, 142.7, 142.62, 142.6, 142.4, 142.3, 142.27, 142.2, 142.1, 142.0, 141.7, 141.6, 141.5, 140.95, 140.9, 140.6, 140.3, 139.4, 137.6, 137.0, 136.4, 135.9, 135.5, 135.2, 134.9, 134.7, 133.8, 129.74, 129.7, 129.5, 128.0, 127.5, 126.6, 124.4, 64.9, 62.0, 61.2, 55.8, 55.3, 46.1, 43.1, 36.1, 14.2, 13.8; FT-IR ν/cm^{-1} 2920, 2851, 1714, 1591, 1452, 1360, 1259, 1181, 1022, 873, 745, 699, 573, 550, 523; UV-vis ($CHCl_3$) λ_{max}/nm 257, 313, 434, 699; MALDI-TOF MS *m/z* calcd for $C_{83}H_{24}O_4$ $[M]^-$ 1084.1680, found 1084.1670.



2z

Spectral data of **2z**: the 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 = 10:1) to give **2z** (16.8 mg, 28%); amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3/CS_2$) δ 7.67 (d, *J* = 7.2 Hz, 1H), 7. 50 (t, *J* = 6.6 Hz, 1H), 7.43 (d, *J* = 6.6 Hz, 2H), 7.33 (s, 1H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.15–7.11 (m, 3H), 6.76 (s, 1H), 5.27 (s, 1H), 5.19 (d, *J* = 15.0 Hz, 1H), 5.10 (s, 1H), 4.64 (d, *J* = 15.6 Hz, 1H), 4.49–4.47 (m, 1H), 4.42 (t, *J* = 10.8 Hz, 1H), 4.11 (t, *J* = 10.2 Hz, 1H), 3.70–3.66 (m, 1H), 3.43–3.39 (m, 1H), 2.90–2.89 (m, 3H); ^{13}C{^{1}H} NMR (150 MHz,

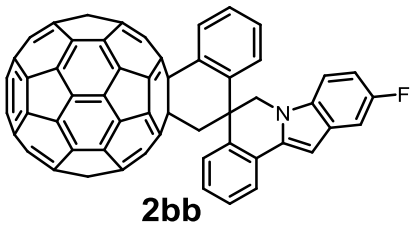
$CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 159.9, 157.8, 154.6, 154.2, 153.60, 149.6, 147.6, 147.4, 146.9, 146.3, 146.2, 146.0, 145.8, 145.6, 145.5, 145.4, 145.24, 145.2, 145.04, 145.0, 144.97, 144.9, 144.7, 144.6 144.56, 144.5, 144.4, 144.3, 144.0, 143.9, 142.9, 142.8, 142.6, 142.55, 142.5, 142.4, 142.3, 142.1, 142.05, 142.0, 141.9, 141.8, 141.77, 141.5, 141.4, 141.1, 140.9, 140.3, 139.9, 138.7, 136.5, 136.2, 135.3, 134.8, 134.5, 134.4, 129.5, 128.9, 128.5, 128.3, 128.0, 127.8, 127.6, 125.9, 122.0, 119.8, 114.9, 87.8, 74.6, 68.3, 64.7, 64.5, 53.3, 45.6, 38.2, 35.2; FT-IR ν/cm^{-1} 2929, 1619, 1592, 1485, 1434, 1332, 1251, 1179, 1153, 1084, 945, 929, 891, 767, 695, 628, 574, 524; UV-vis ($CHCl_3$) λ_{max}/nm 257, 314, 435, 698; MALDI-TOF MS *m/z* calcd for $C_{86}H_{23}IO_2$ $[M]^-$ 1214.0748, found 1214.0741.



2aa

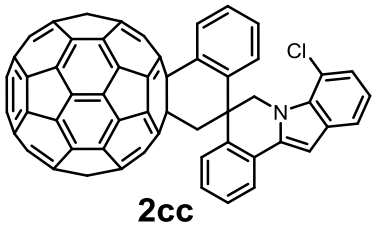
Spectral data of **2aa**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2aa** (12.9 mg, 25%); amorphous brown solid; ^{1}H NMR (400 MHz, DMSO-d_6/CS_2) δ 7.95 (d, J = 7.6 Hz, 1H), 7.72–7.33 (m, 3H), 7.69 (d, J = 8.0 Hz, 1H), 7.60–7.55 (m, 2H), 7.35–7.29 (m, 2H), 7.20–7.13 (m, 2H), 6.96 (d, J = 7.6 Hz, 1H), 6.49 (s, 1H), 6.27 (d, J = 14.4 Hz, 1H), 5.65 (d, J = 16.4 Hz, 1H), 4.79 (d, J = 16.0 Hz, 1H), 4.58 (d, J = 14.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6/CS_2 with $Cr(acac)_3$ as relaxation reagent) δ 150.7, 147.7, 147.6, 146.6, 146.5, 146.4, 146.3, 146.2, 146.17, 146.1, 146.06, 146.0, 145.6, 145.5, 145.3, 145.2, 145.1, 145.06, 144.5, 144.47, 144.4, 142.9, 142.88, 142.8,

142.6, 142.58, 142.5, 142.4, 142.3, 142.2, 142.0, 141.9, 141.7, 141.5, 141.2, 140.9, 140.86, 140.7, 140.3, 140.2, 136.8, 136.7, 136.4, 135.4, 134.9, 134.7, 132.8, 132.5, 130.5, 130.0, 129.6, 129.2, 128.9, 128.5, 125.8, 125.0, 122.7, 121.2, 121.1, 110.5, 98.7, 64.0, 58.2, 49.2, 45.3, 30.4; FT-IR ν/cm^{-1} 2919, 1712, 1603, 1510, 1444, 1357, 1318, 1054, 759, 742, 575, 552, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 314, 434, 707; MALDI-TOF MS *m/z* calcd for $C_{83}H_{17}N$ $[M]^-$ 1027.1366, found 1027.1362.



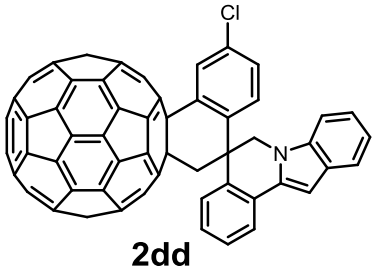
2bb

Spectral data of **2bb**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2bb** (16.5 mg, 32%); amorphous brown solid; ^{1}H NMR (400 MHz, DMSO-d_6/CS_2) δ 7.94 (d, J = 7.2 Hz, 1H), 7.80–7.68 (m, 4H), 7.58–7.55 (m, 2H), 7.32 (t, J = 8.0 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.89 (t, J = 8.8 Hz, 1H), 6.47 (s, 1H), 6.28 (d, J = 14.0 Hz, 1H), 5.70 (d, J = 15.6 Hz, 1H), 4.76 (d, J = 15.6 Hz, 1H), 4.56 (d, J = 14.4 Hz, 1H); the ^{13}C NMR spectrum of 2bb could not be obtained because of poor solubility of the product; FT-IR ν/cm^{-1} 2923, 1618, 1577, 1485, 1452, 1352, 1288, 1199, 1117, 1024, 952, 911, 860, 787, 756, 711, 575, 526; UV-vis ($CHCl_3$) λ_{max}/nm 256, 313, 436, 704; MALDI-TOF MS *m/z* calcd for $C_{83}H_{16}FN$ $[M]^-$ 1045.1272, found 1045.1271.



2cc

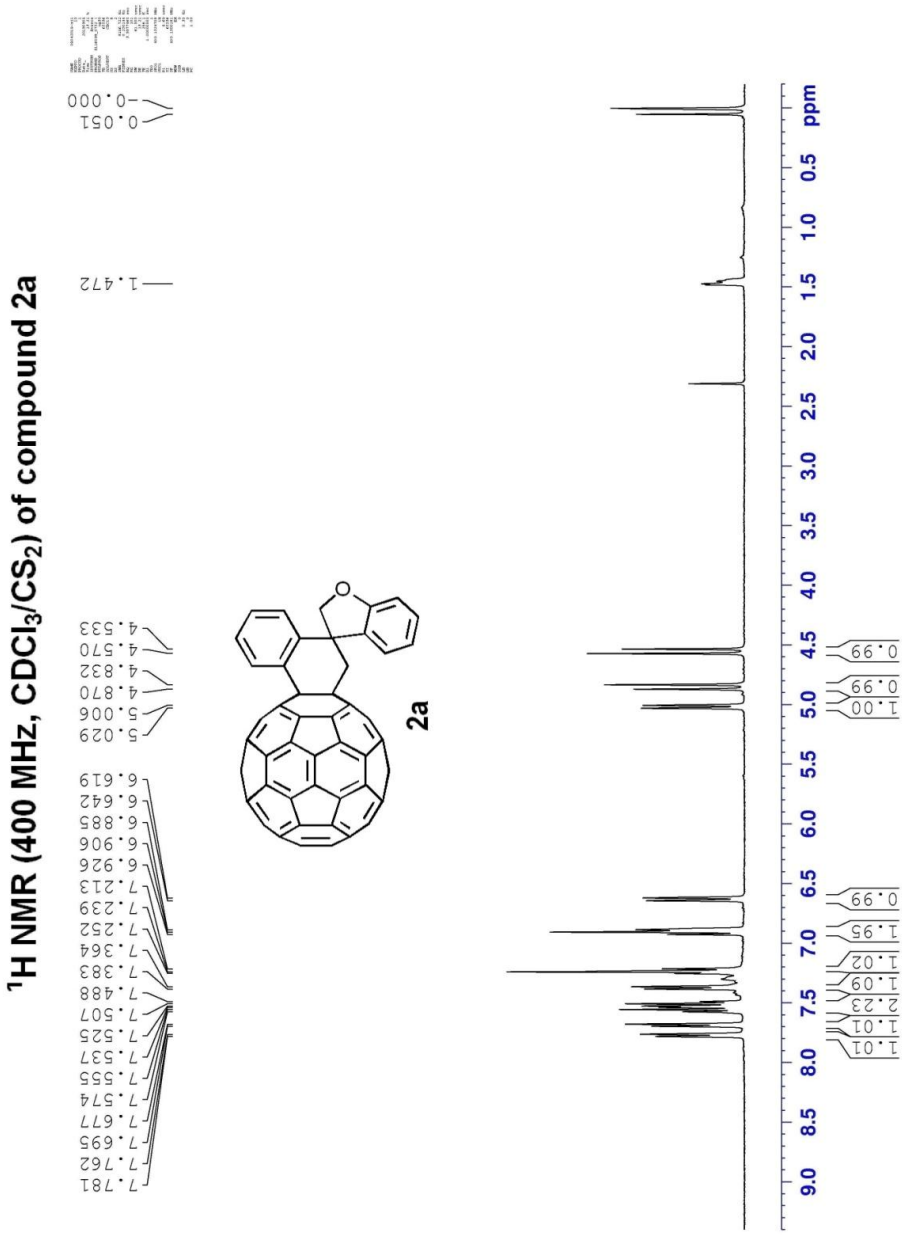
Spectral data of **2cc**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2cc** (17.2 mg, 32%); amorphous brown solid; ^{1}H NMR (400 MHz, DMSO-d_6/CS_2) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.61–7.54 (m, 2H), 7.36–7.30 (m, 3H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.55 (s, 1H), 5.46 (d, *J* = 16.0 Hz, 1H), 4.84 (d, *J* = 16.0 Hz, 1H), 4.70 (d, *J* = 14.4 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6/CS_2 with Cr(acac)$_3$ as relaxation reagent) δ 150.8, 147.8, 147.6, 147.0, 146.7, 146.5, 146.46, 146.3, 146.2, 146.15, 146.1, 145.6, 145.5, 145.4, 145.3, 145.26, 145.2, 145.1, 144.6, 144.5, 144.46, 144.4, 143.2, 143.0, 142.9, 142.8, 142.7, 142.5, 142.48, 142.4, 142.3, 142.2, 142.0, 141.9, 141.8, 141.6, 141.2, 140.9, 140.8, 140.3, 140.2, 140.16, 137.1, 136.8, 136.7, 136.65, 135.2, 134.9, 134.8, 134.4, 132.9, 132.6, 132.2, 131.4, 130.3, 129.3, 129.1, 128.6, 126.3, 125.4, 124.5, 121.6, 120.3, 117.1, 99.8, 64.3, 58.3, 50.9, 45.1, 2; FT-IR ν/cm^{-1} 2919, 1602, 1505, 1485, 1453, 1421, 1356, 1316, 1182, 1133, 943, 870, 789, 751, 722, 576, 525; UV-vis ($CHCl_3$) λ_{max}/nm 258, 307,432, 707; MALDI-TOF MS *m/z* calcd for $C_{83}H_{16}ClN$ $[M]^-$ 1061.0977, found 1061.0974.



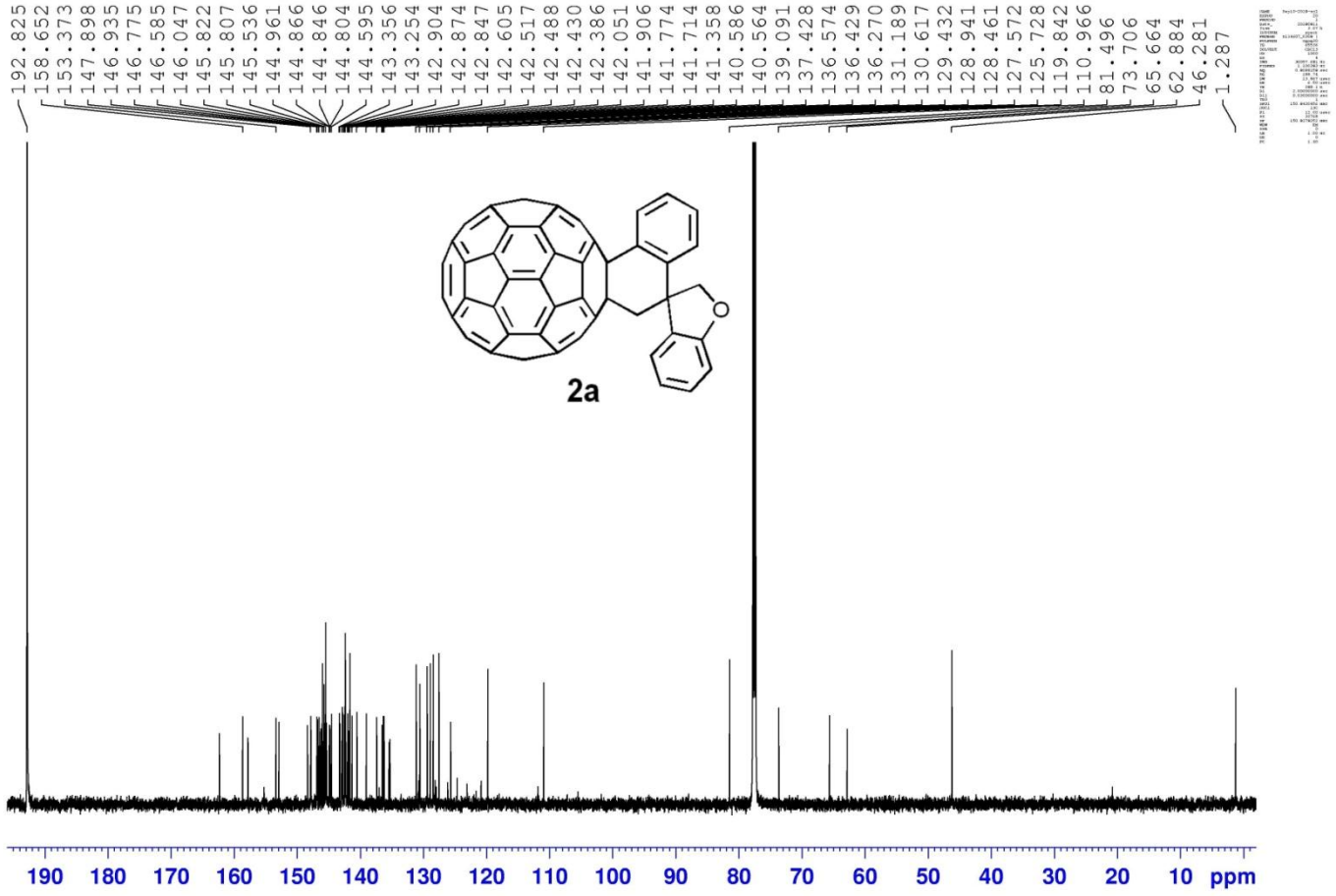
2dd

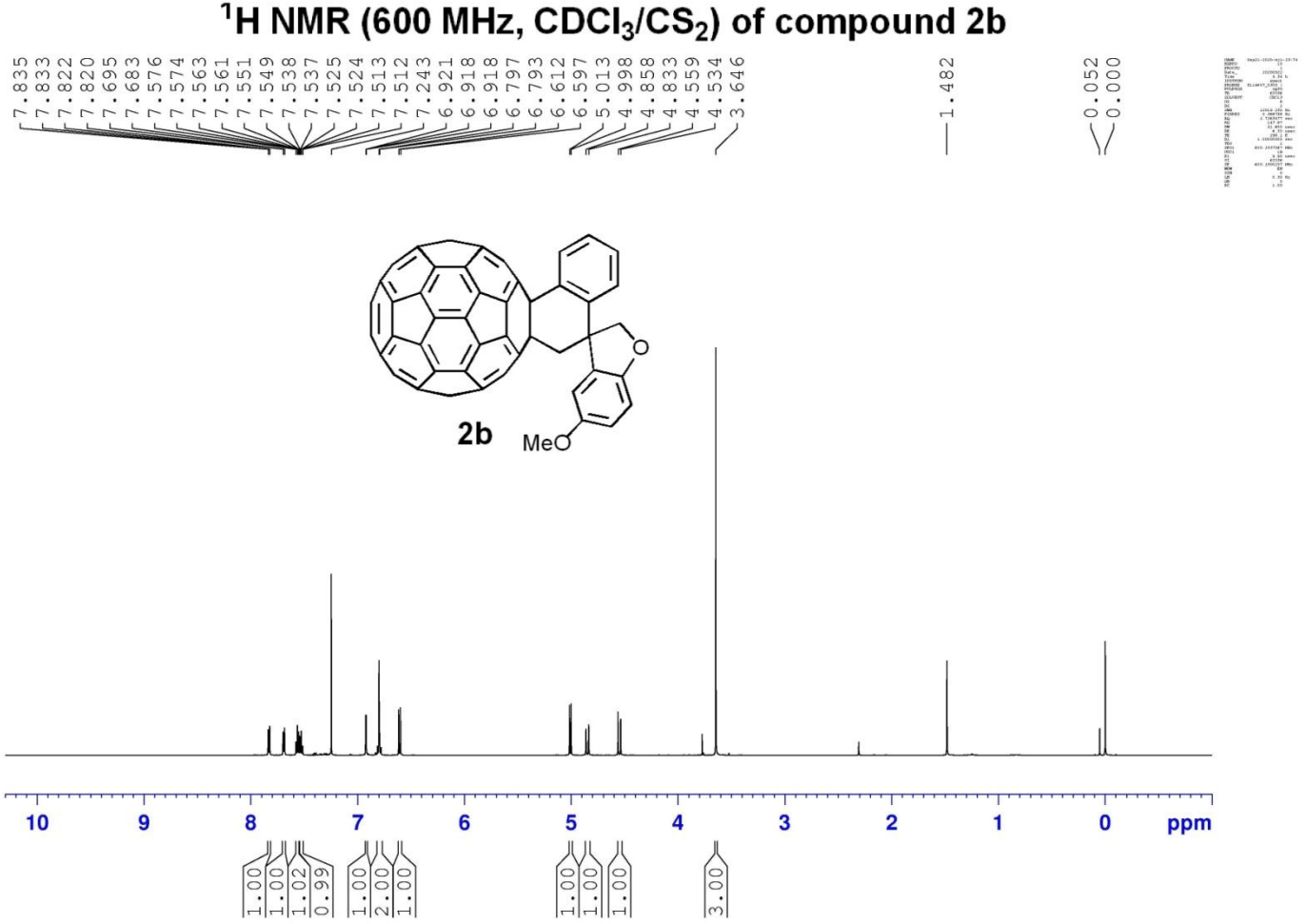
Spectral data of **2dd**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2dd** (10.7 mg, 20%); amorphous brown solid; ^{1}H NMR (600 MHz, DMSO-d_6/CS_2) δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.81 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.20–7.14 (m, 2H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.49 (s, 1H), 6.28 (d, *J* = 14.4 Hz, 1H), 5.68 (d, *J* = 16.2 Hz, 1H), 4.79 (d, *J* = 15.6 Hz, 1H), 4.56 (d, *J* = 14.4 Hz, 1H); the ^{13}C NMR spectrum of **2dd** could not be obtained because of poor solubility of the product; FT-IR ν/cm^{-1} 2918, 1597, 1507, 1455, 1353, 1319, 1173, 1096, 1043, 949, 924, 868, 825, 758, 742, 575, 553, 525; UV-vis ($CHCl_3$) λ_{max}/nm 258, 328, 433, 703; MALDI-TOF MS *m/z* calcd for $C_{83}H_{16}ClN$ $[M]^-$ 1061.0977, found 1061.0972.

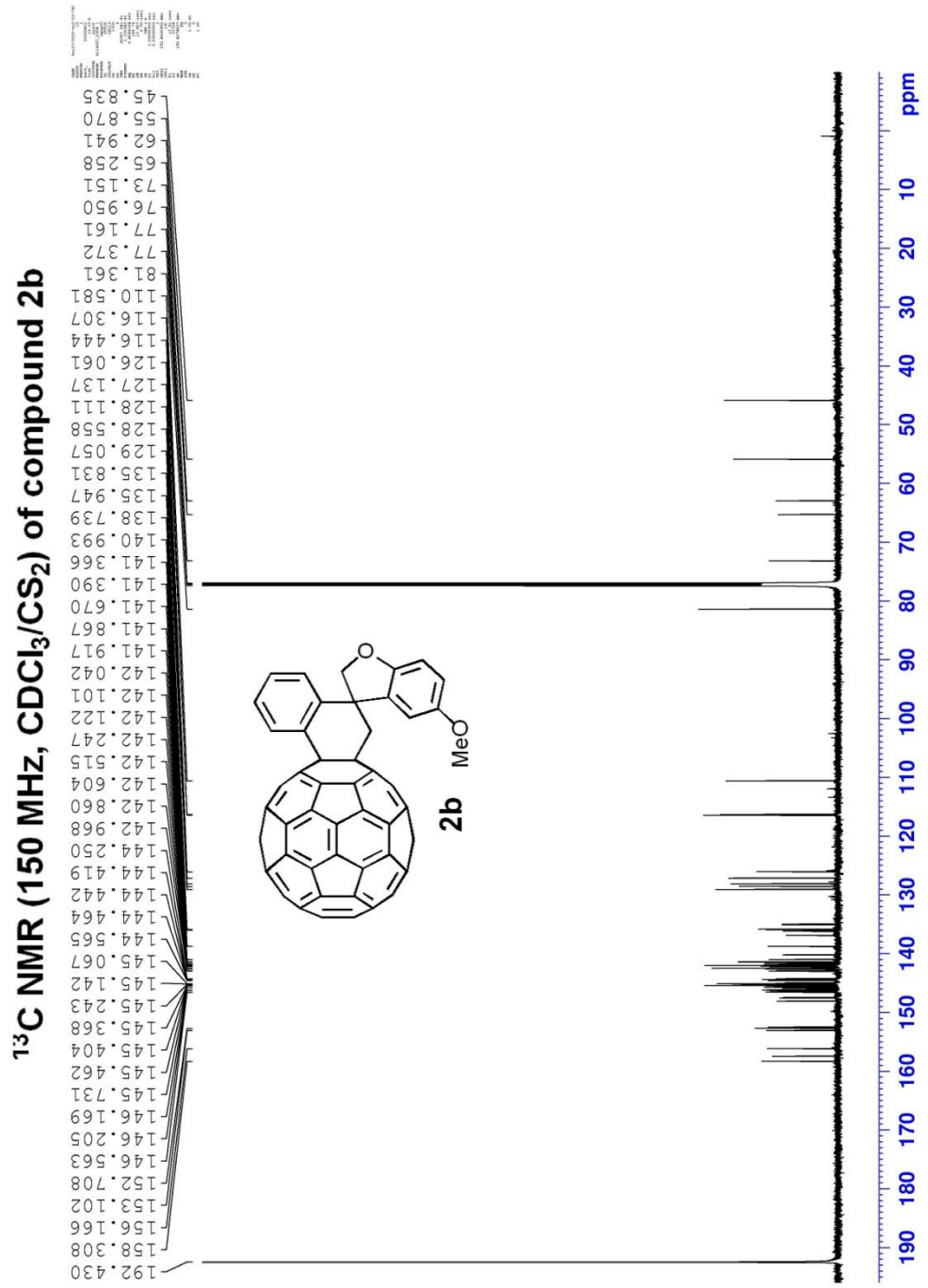
7. ^{1}H NMR and ^{13}C NMR Spectra of Compounds 2

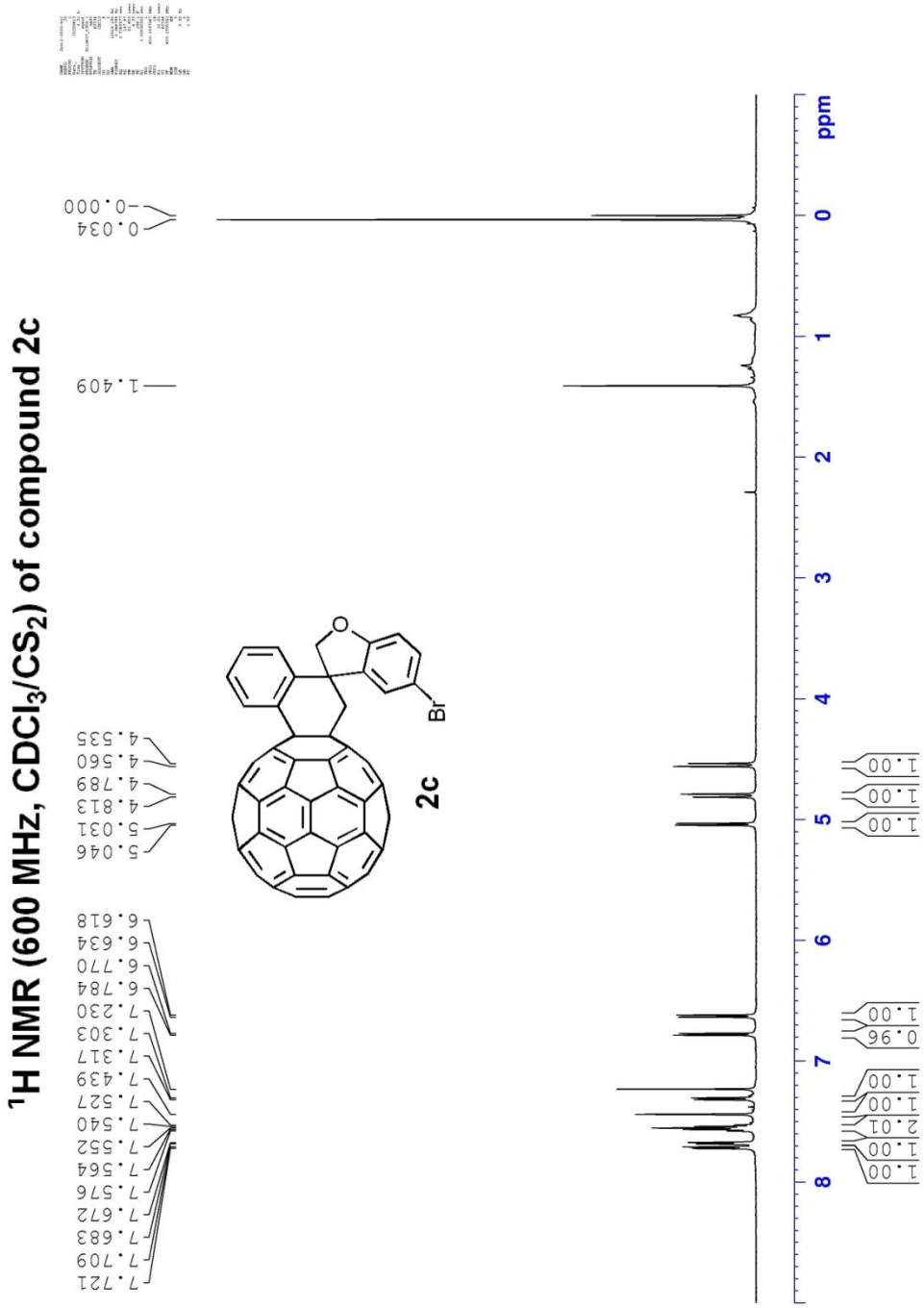


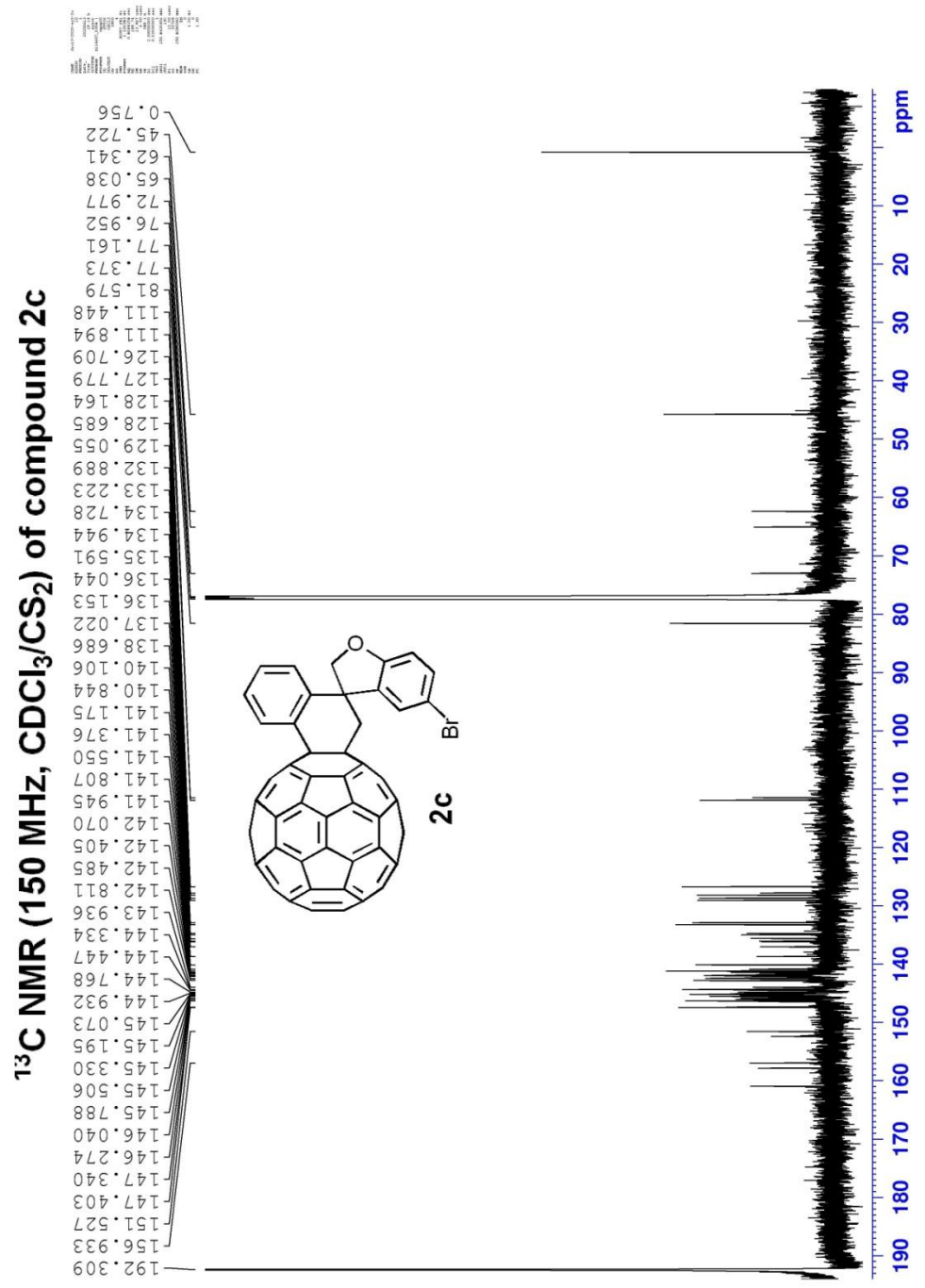
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2a

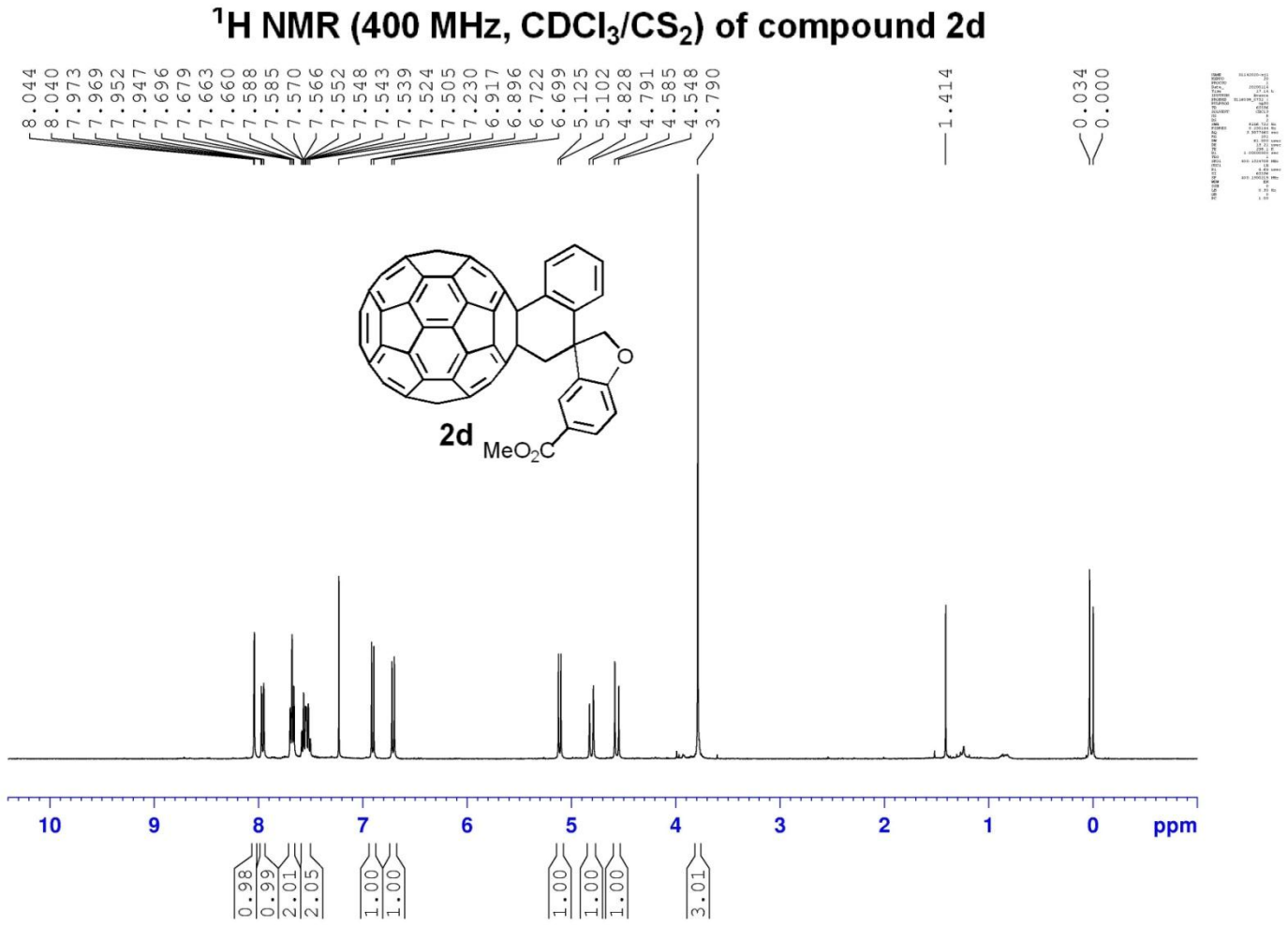


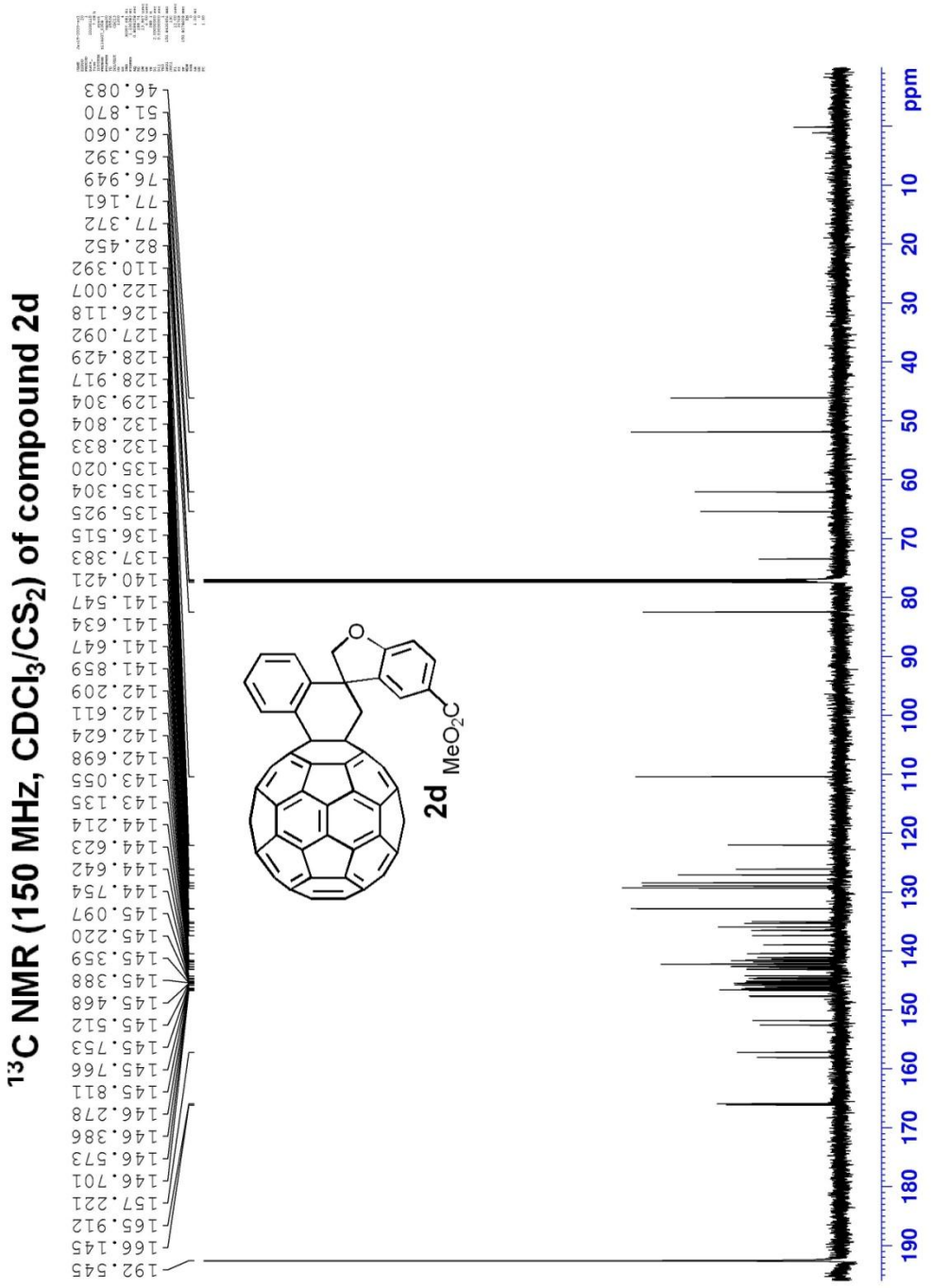

¹H NMR (600 MHz, CDCl3/CS2) of compound 2b
7.835
7.833
7.822
7.820
7.695
7.683
7.576
7.574
7.563
7.561
7.551
7.549
7.538
7.537
7.525
7.524
7.513
7.512
7.243
6.921
6.918
6.918
6.797
6.793
6.612
6.597
5.013
4.998
4.858
4.833
4.559
4.534
3.646
1.482
0.052
0.000
2b
MeO
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.02
0.99
1.00
2.00
1.00
1.00
1.00
1.00
3.00


^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2b
2b
MeO
ppm

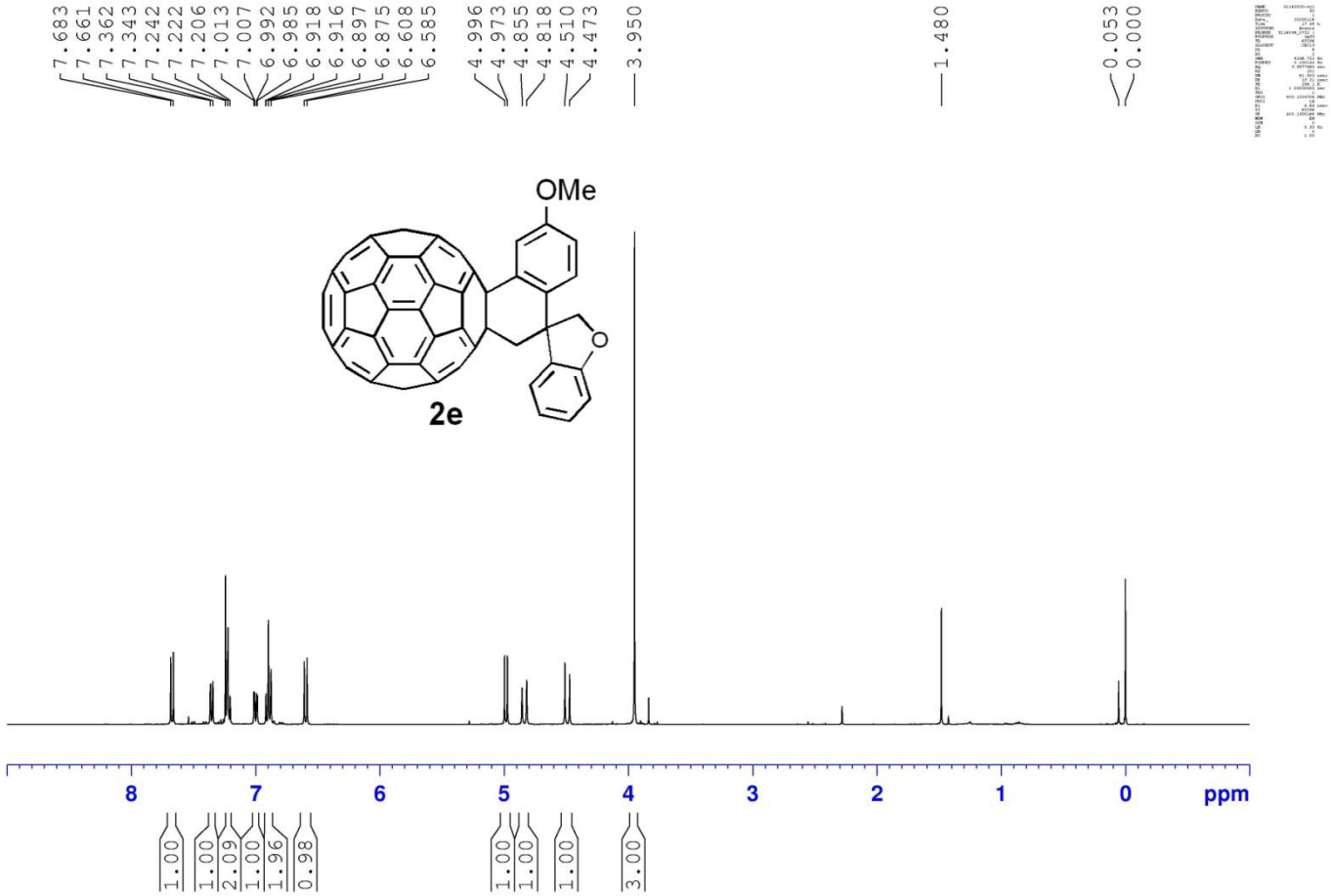

¹H NMR (600 MHz, CDCl3/CS2) of compound 2c
2c
Br
ppm

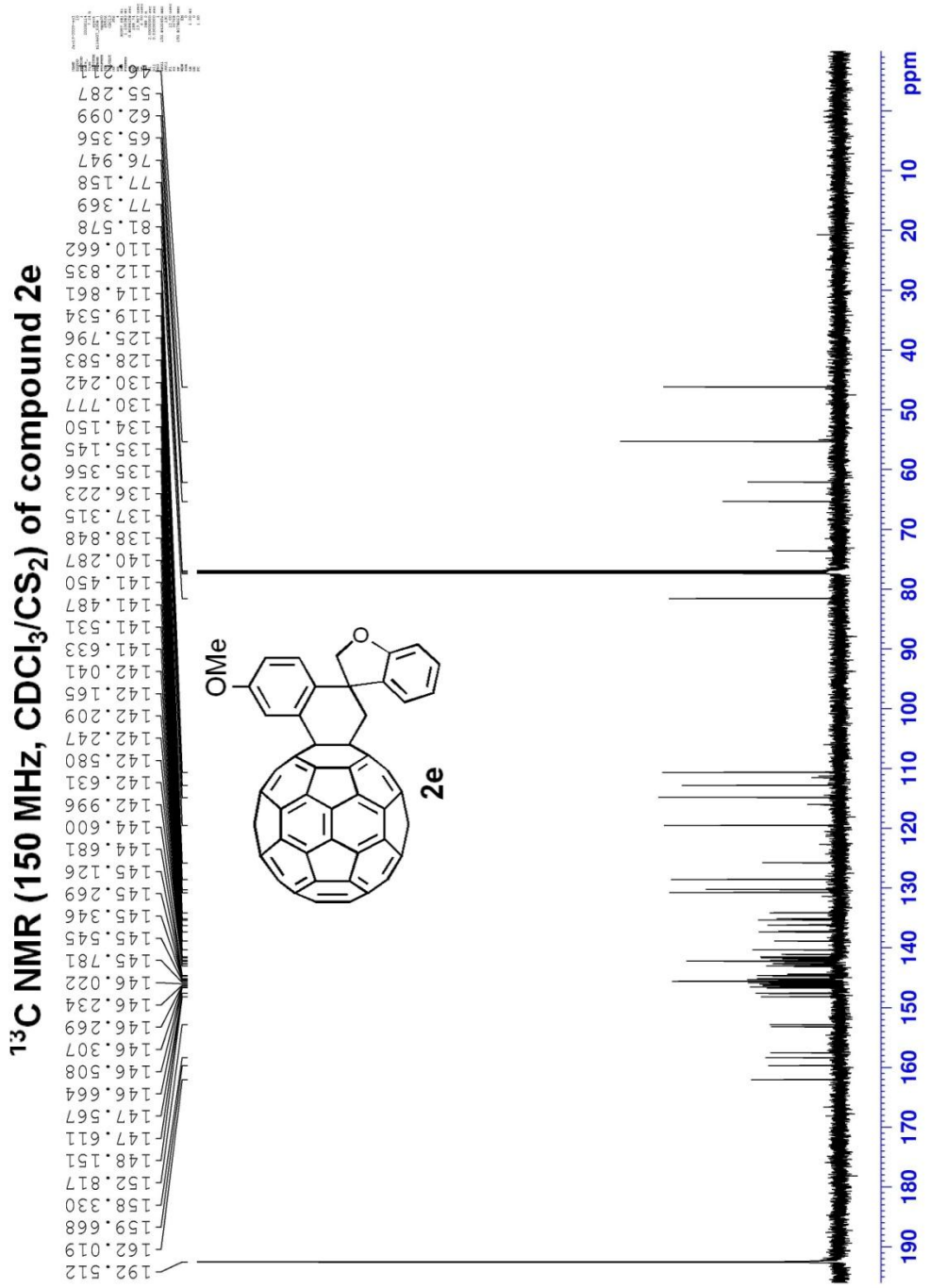

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2c
2c
Br
ppm


¹H NMR (400 MHz, CDCl3/CS2) of compound 2d
8.044
8.040
7.973
7.969
7.952
7.947
7.696
7.679
7.663
7.660
7.588
7.585
7.570
7.566
7.552
7.548
7.543
7.539
7.524
7.505
7.230
6.917
6.896
6.722
6.699
5.125
5.102
4.828
4.791
4.585
4.548
3.790
1.414
0.034
0.000
2d
MeO2C
10
9
8
7
6
5
4
3
2
1
0
ppm
0.98
0.99
2.01
2.05
1.00
1.00
1.00
1.00
1.00
3.01

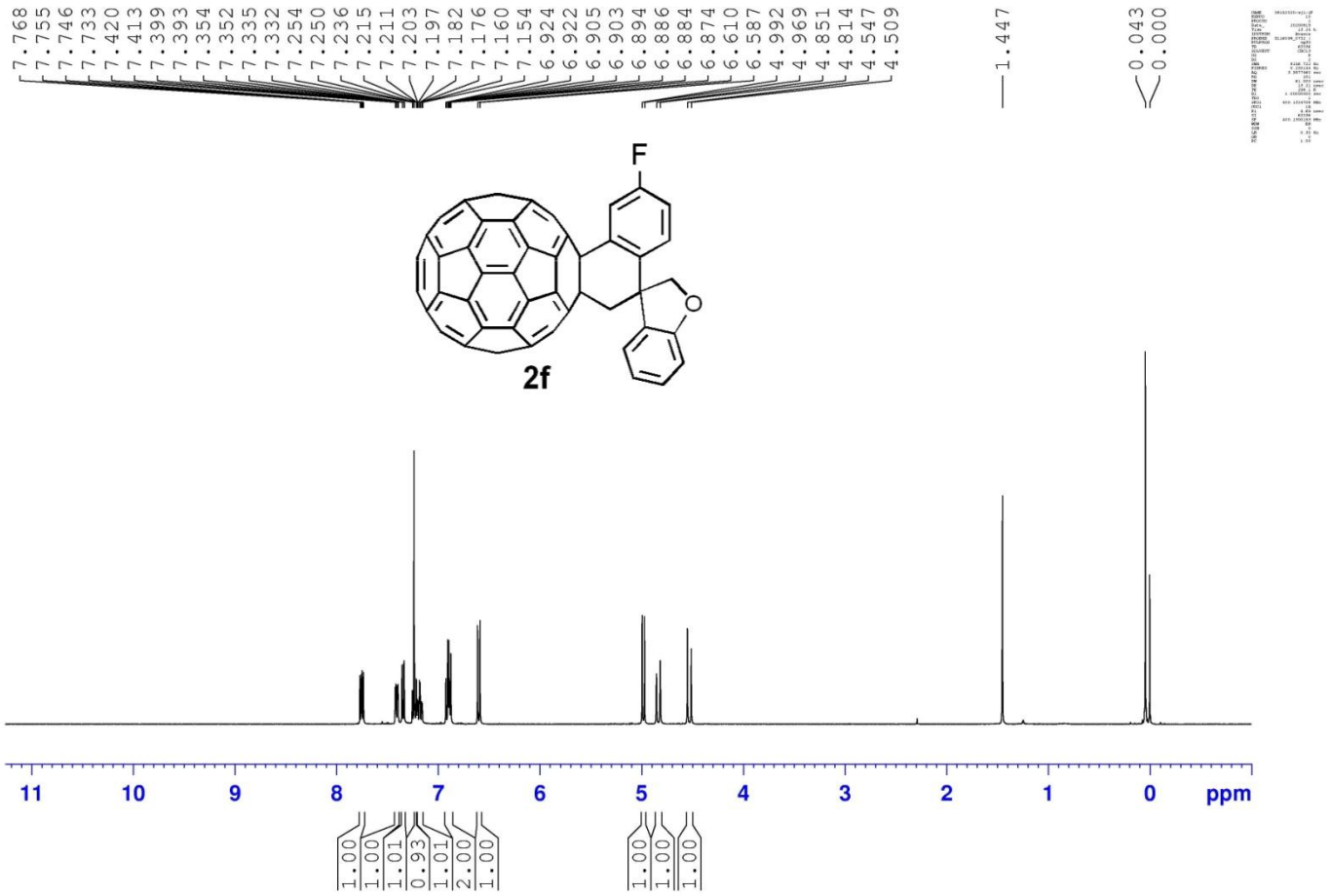

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2d
2d
MeO_2C
ppm

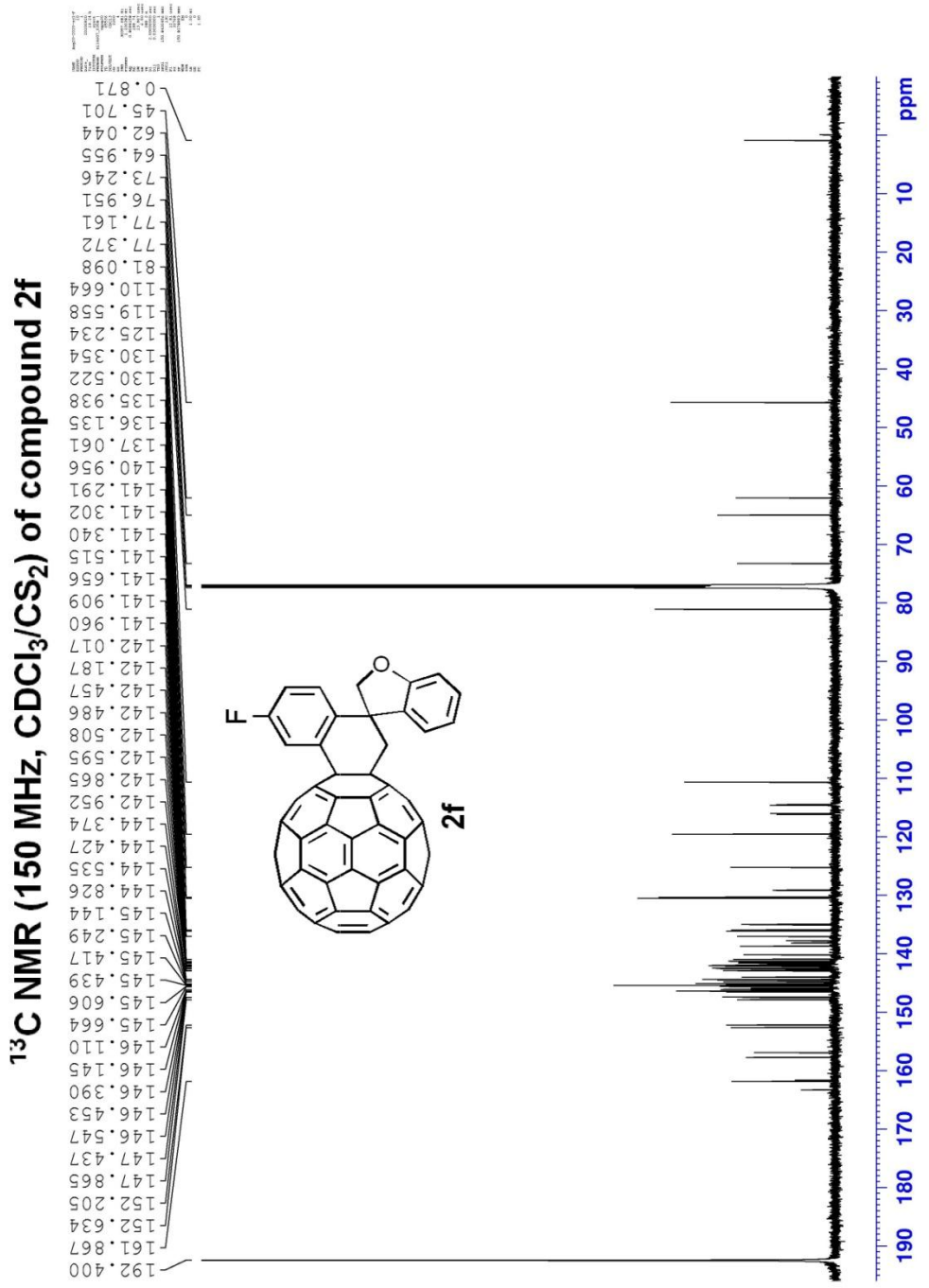
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2e



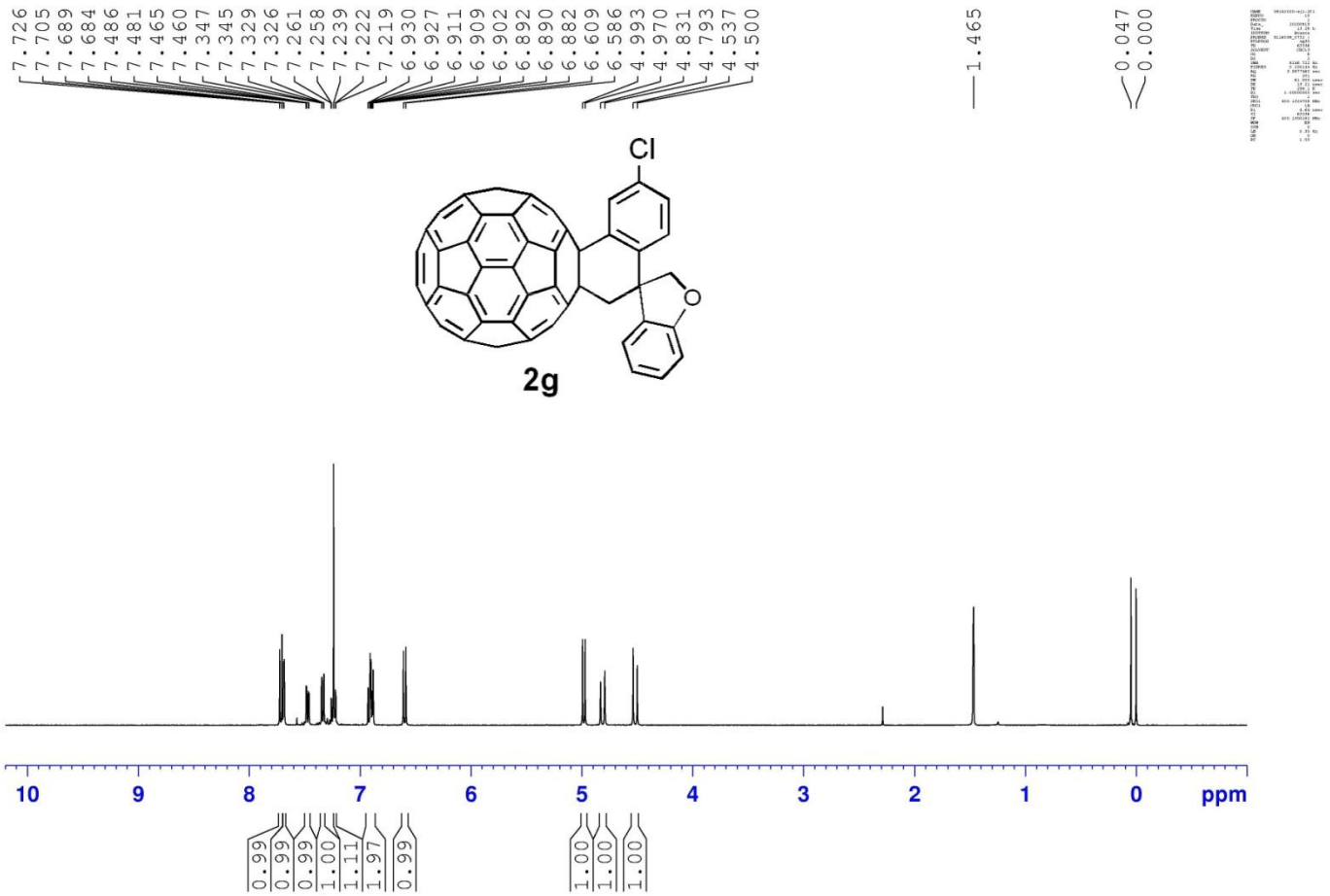

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2e
OMe
2e
ppm

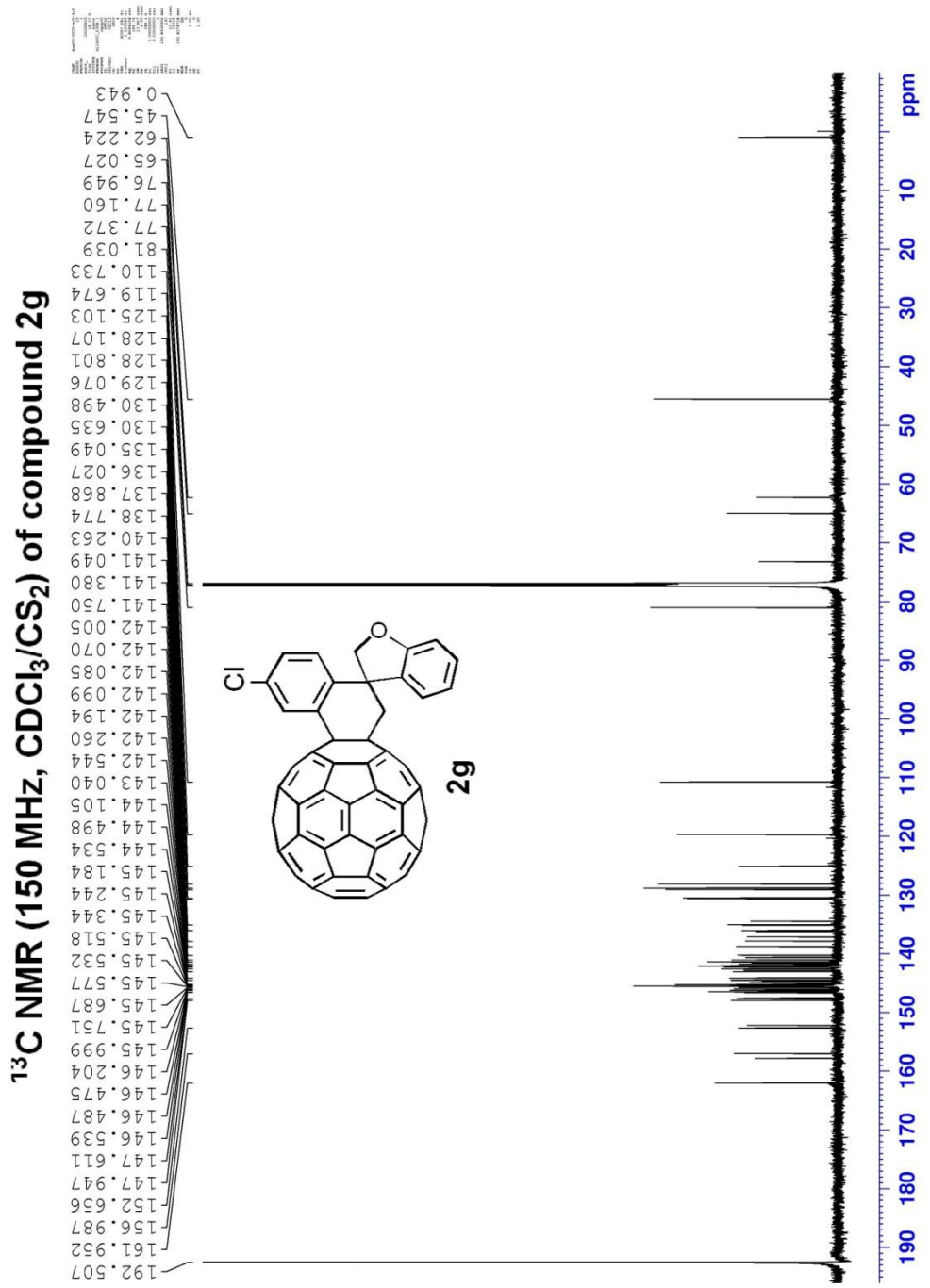
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2f



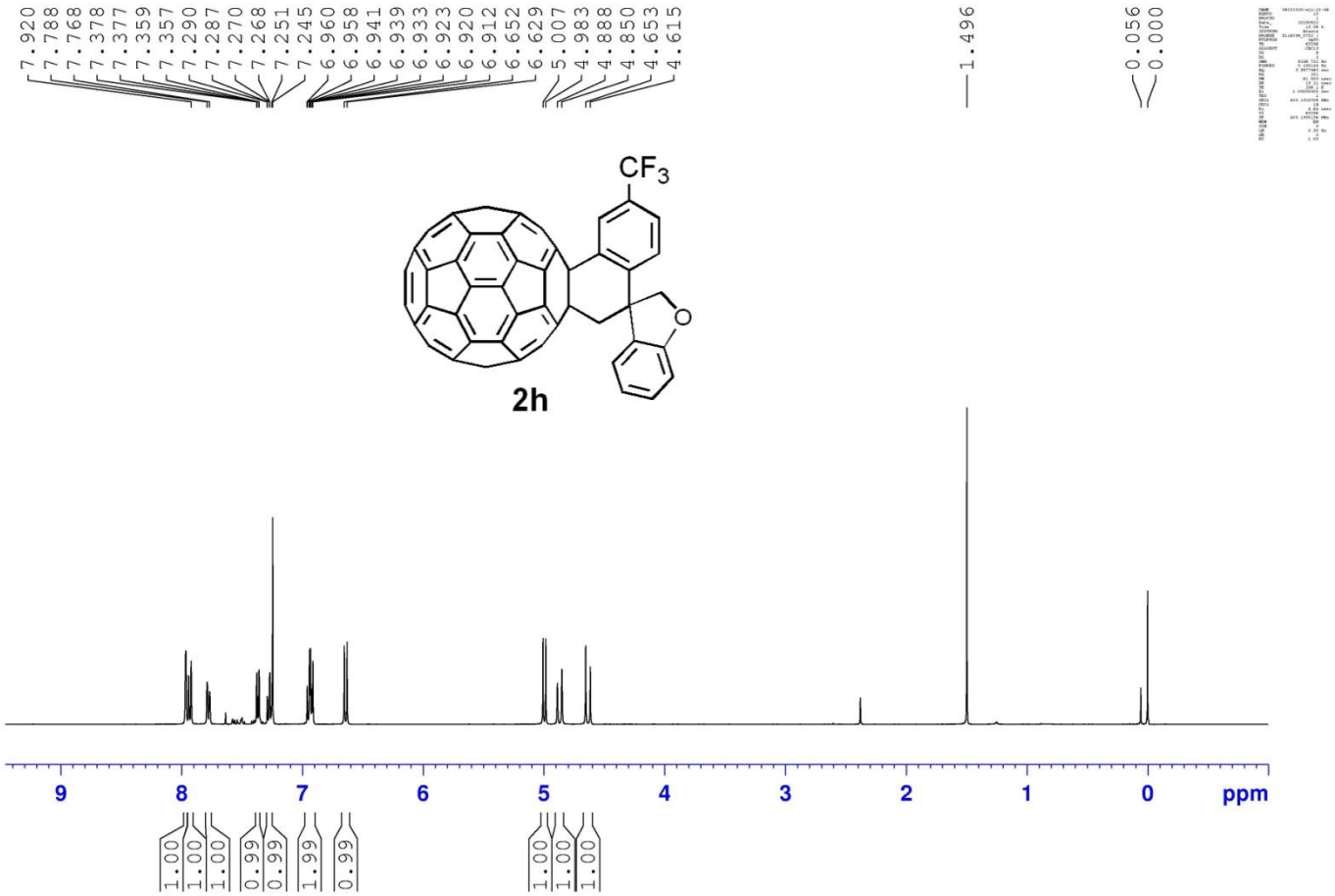

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2f
F
2f
ppm

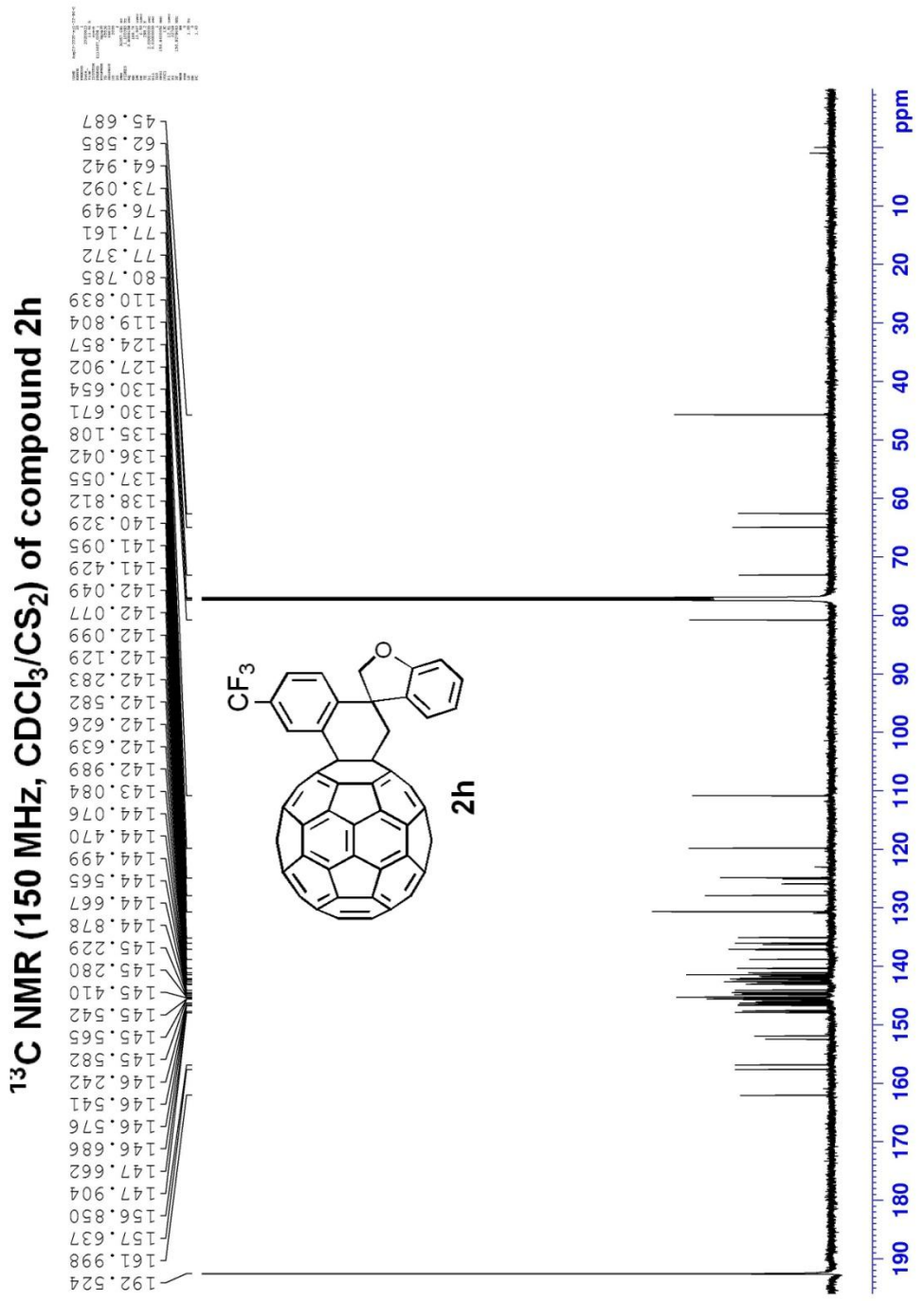
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2g



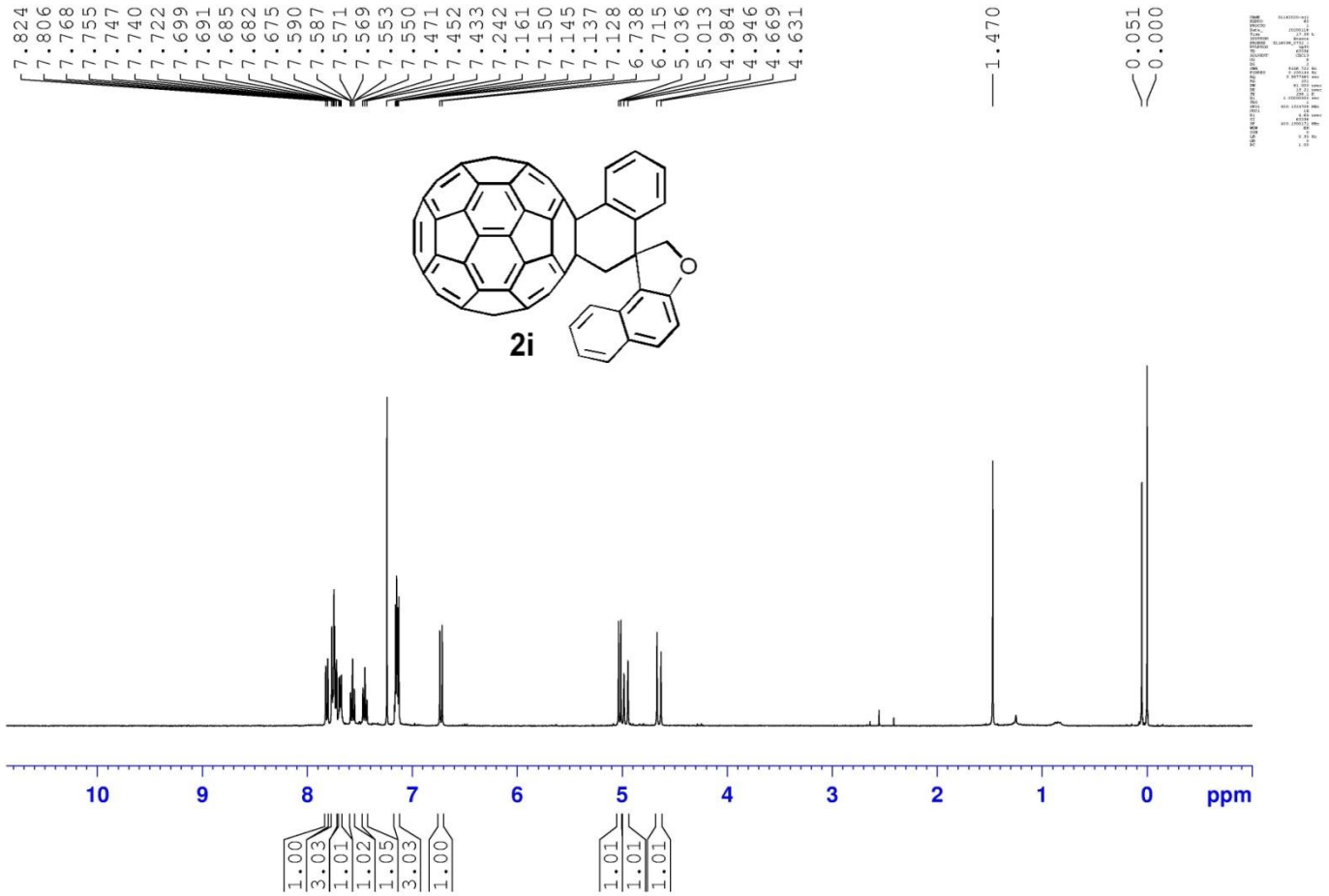

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2g
Cl
2g
ppm

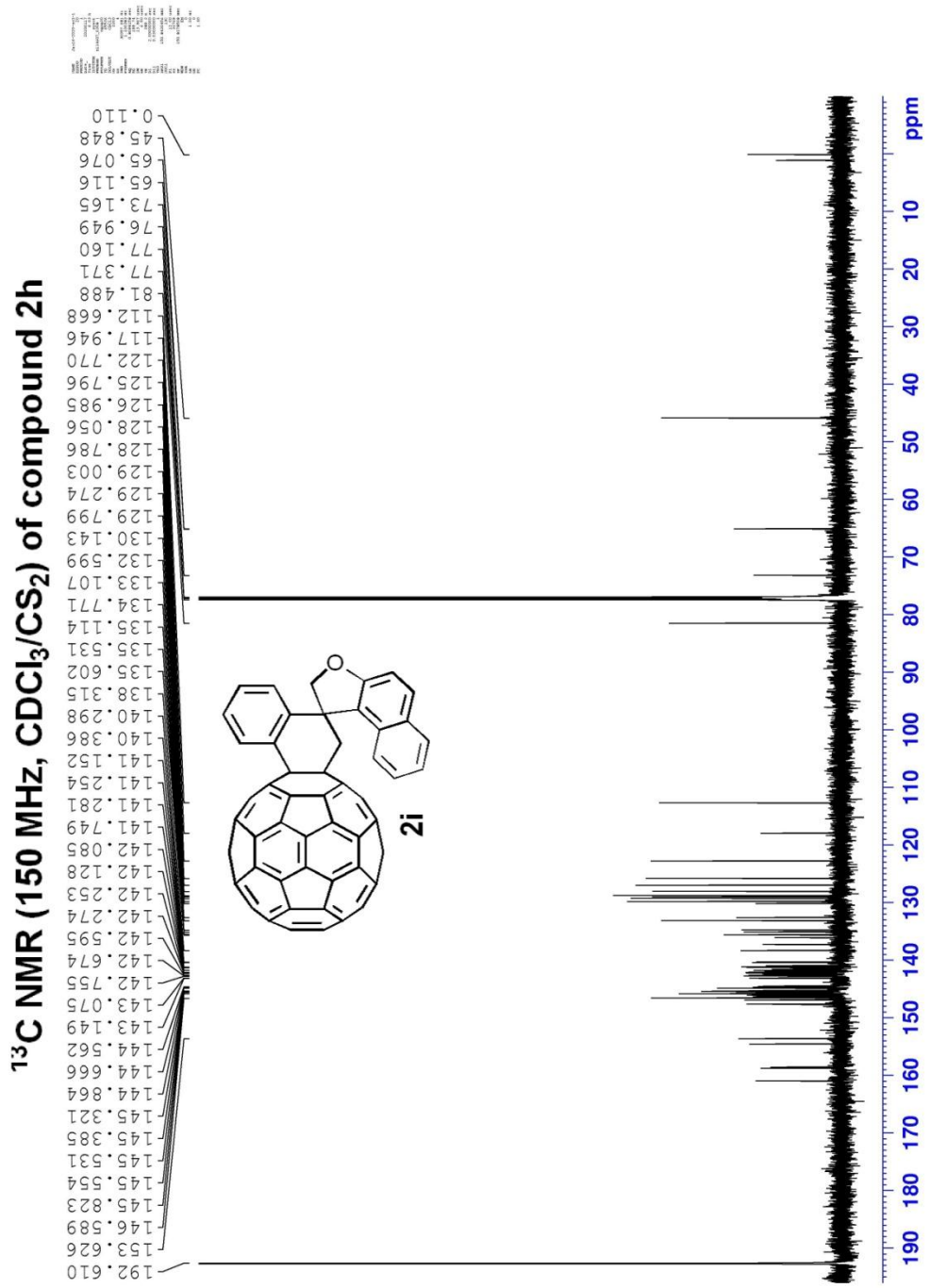
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2h



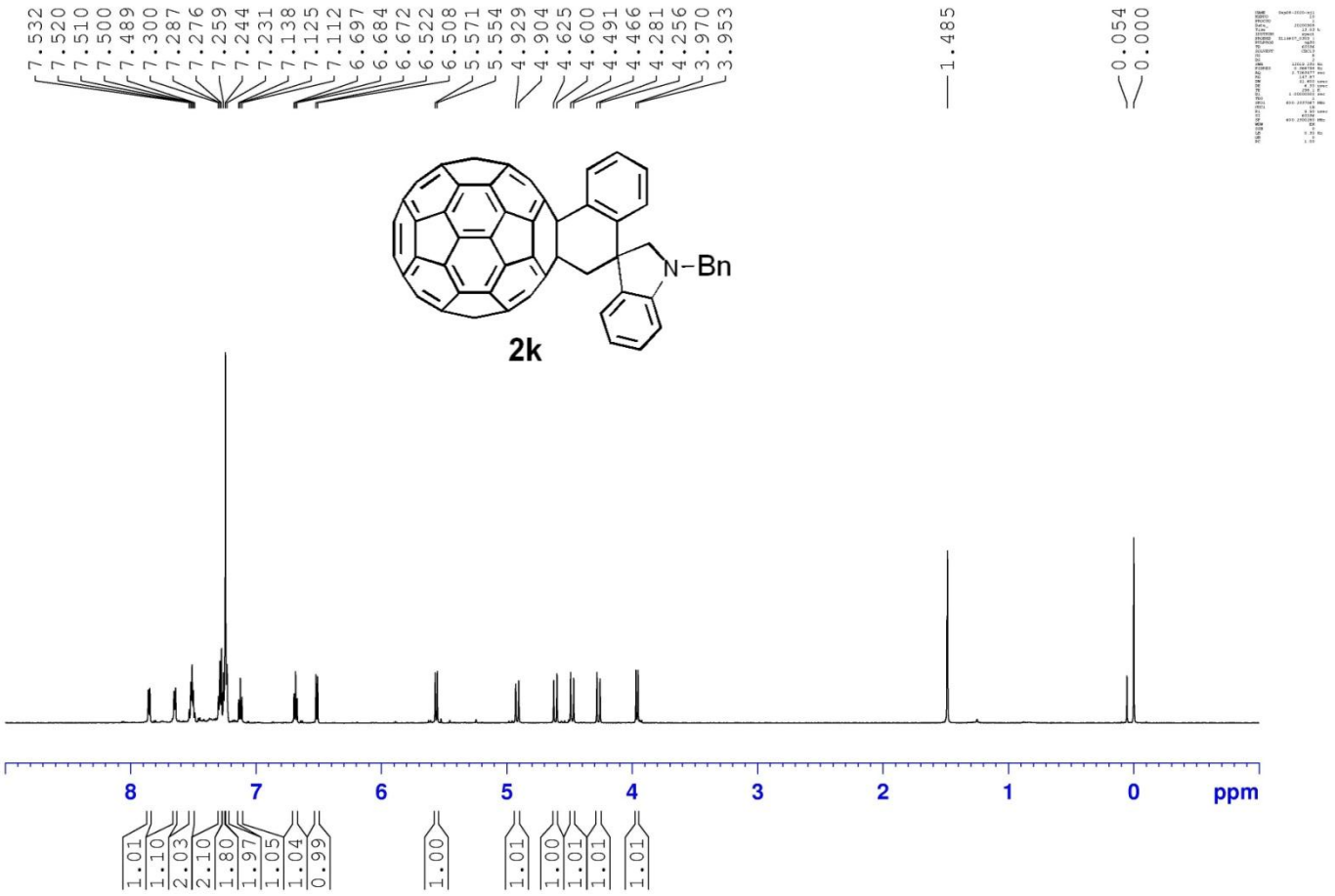

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2h
192.524
161.998
157.637
156.850
147.904
147.662
146.686
146.576
146.541
146.242
145.582
145.565
145.542
145.410
145.280
145.229
144.878
144.667
144.565
144.499
144.470
144.076
143.084
142.989
142.639
142.626
142.582
142.283
142.129
142.099
142.077
142.049
141.429
141.095
140.329
138.812
137.055
136.042
135.108
130.671
130.654
127.902
124.857
119.804
110.839
80.785
77.372
77.161
76.949
73.092
64.942
62.585
45.687
CF_3
2h
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

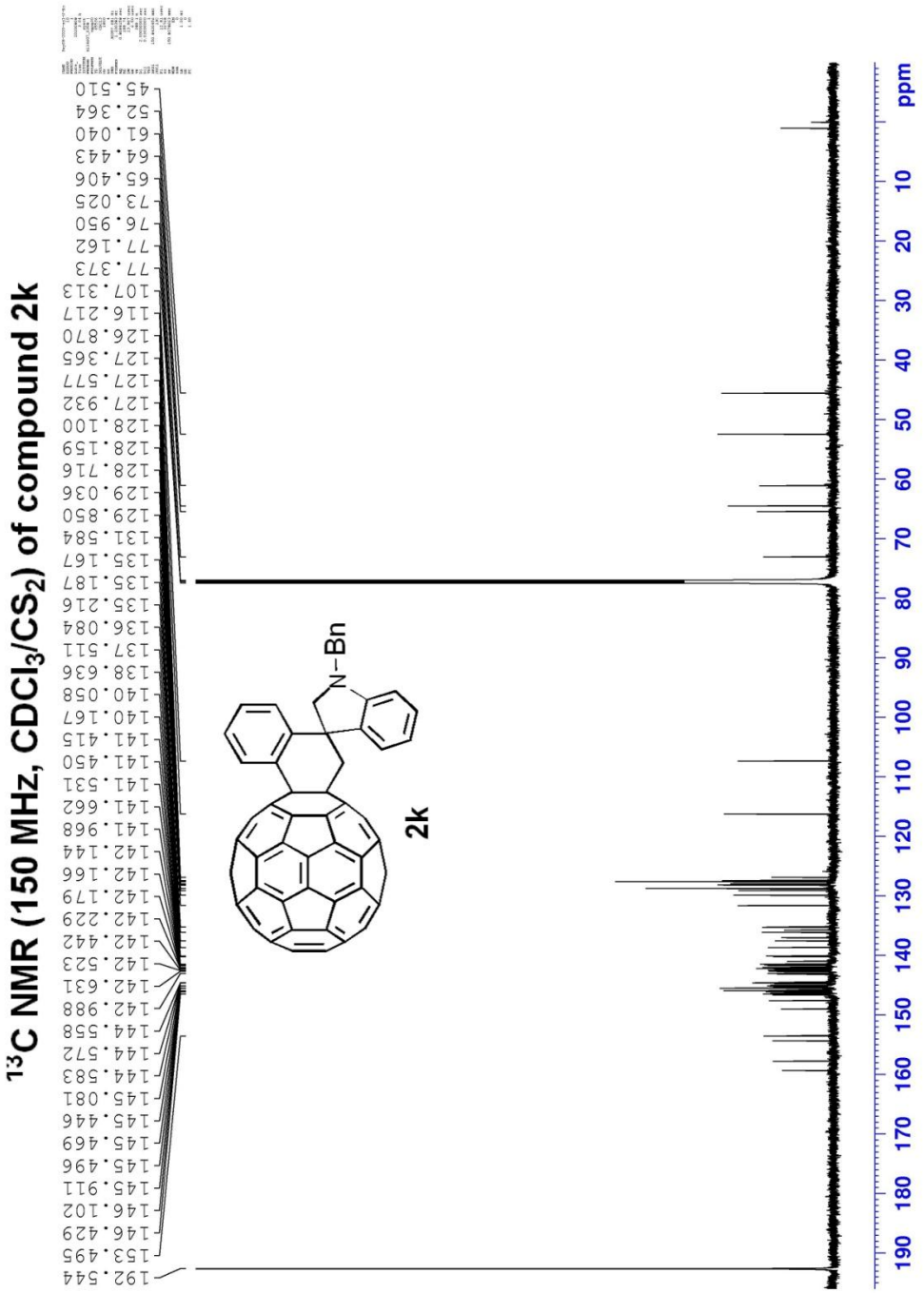
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2i



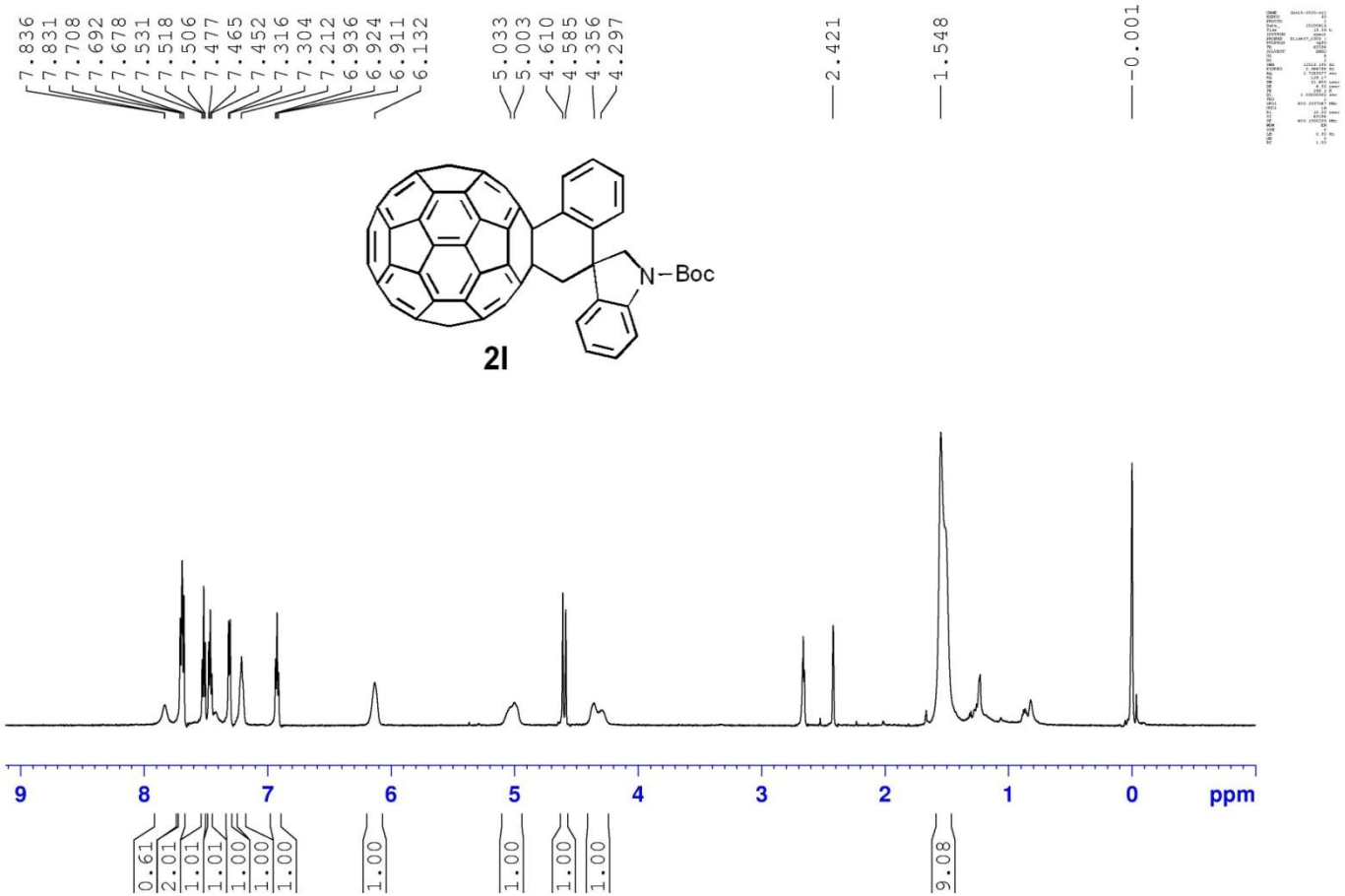

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2h
2i
ppm

^{1}H NMR (600 MHz, $CDCl_3/CS_2$) of compound 2k

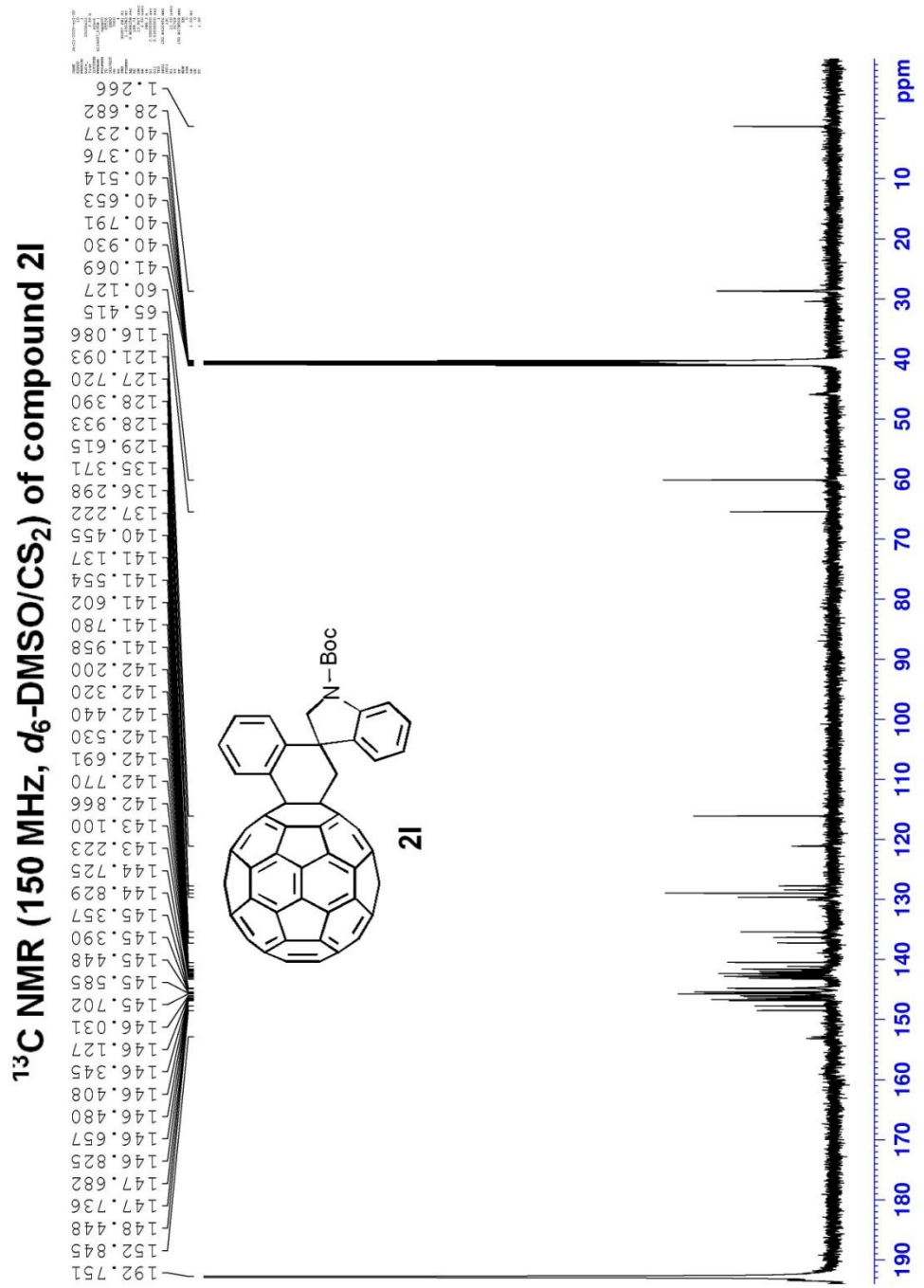


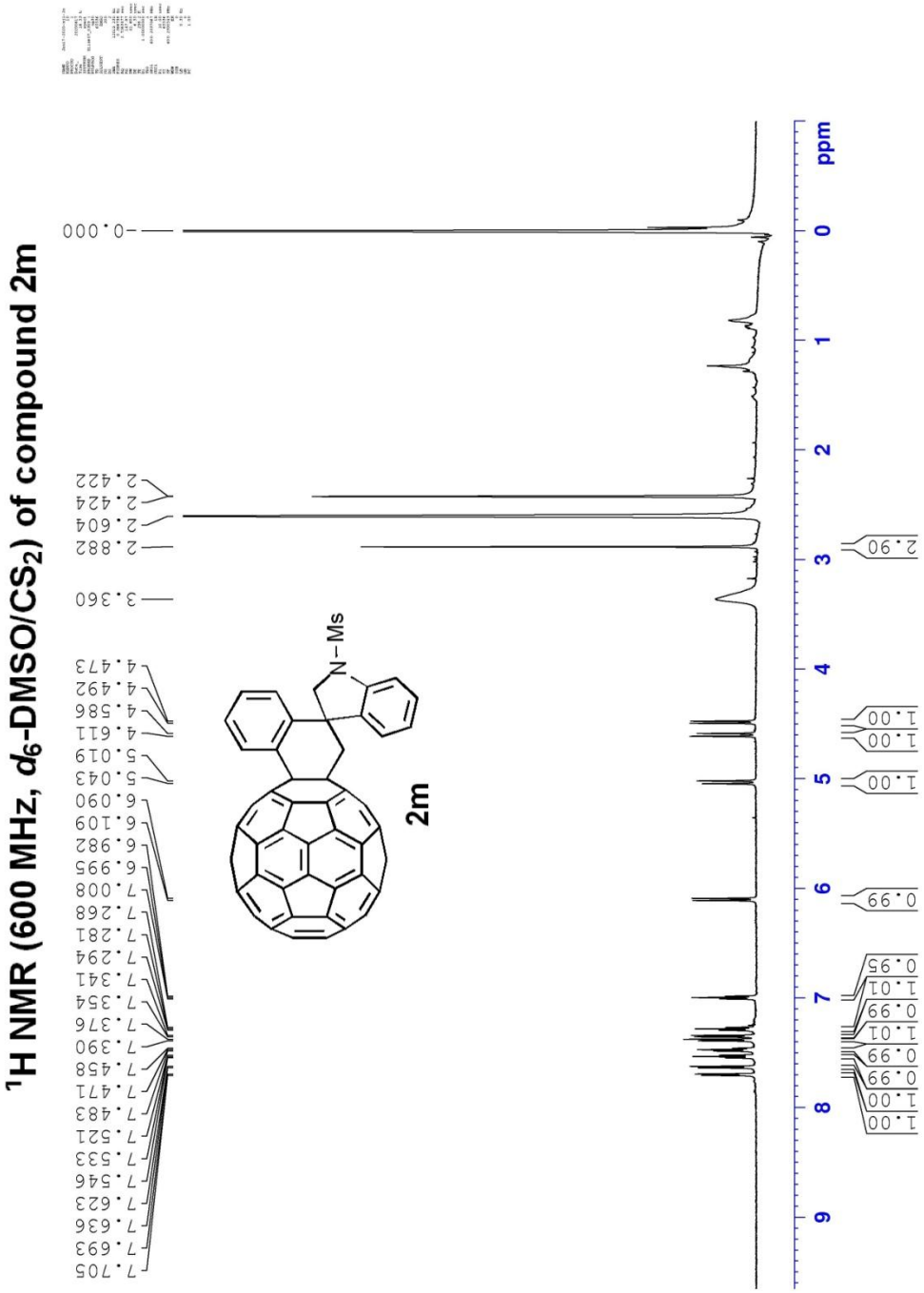

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2k
N–Bn
2k
ppm

^{1}H NMR (600 MHz, d_6-DMSO/CS_2) of compound 2l

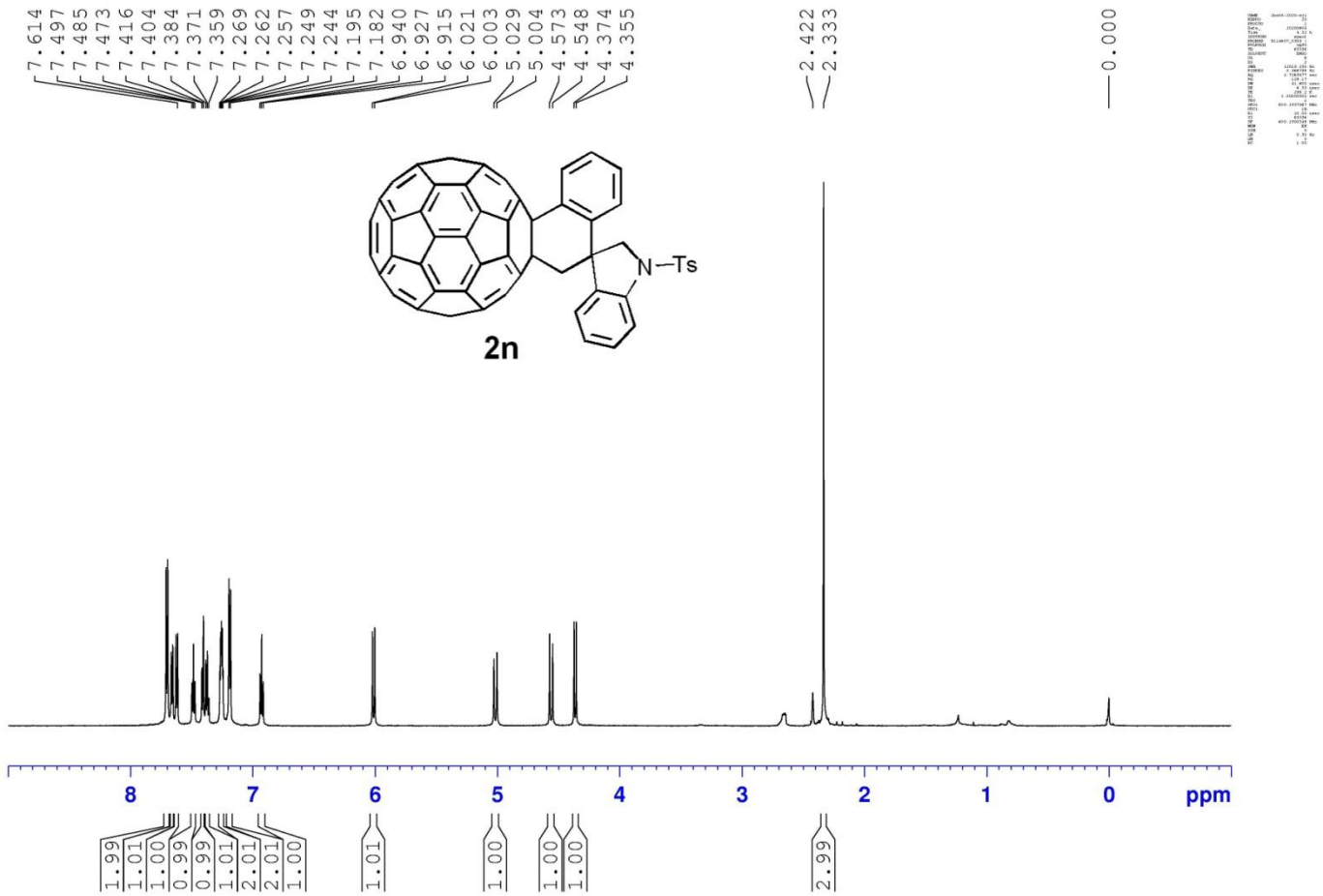


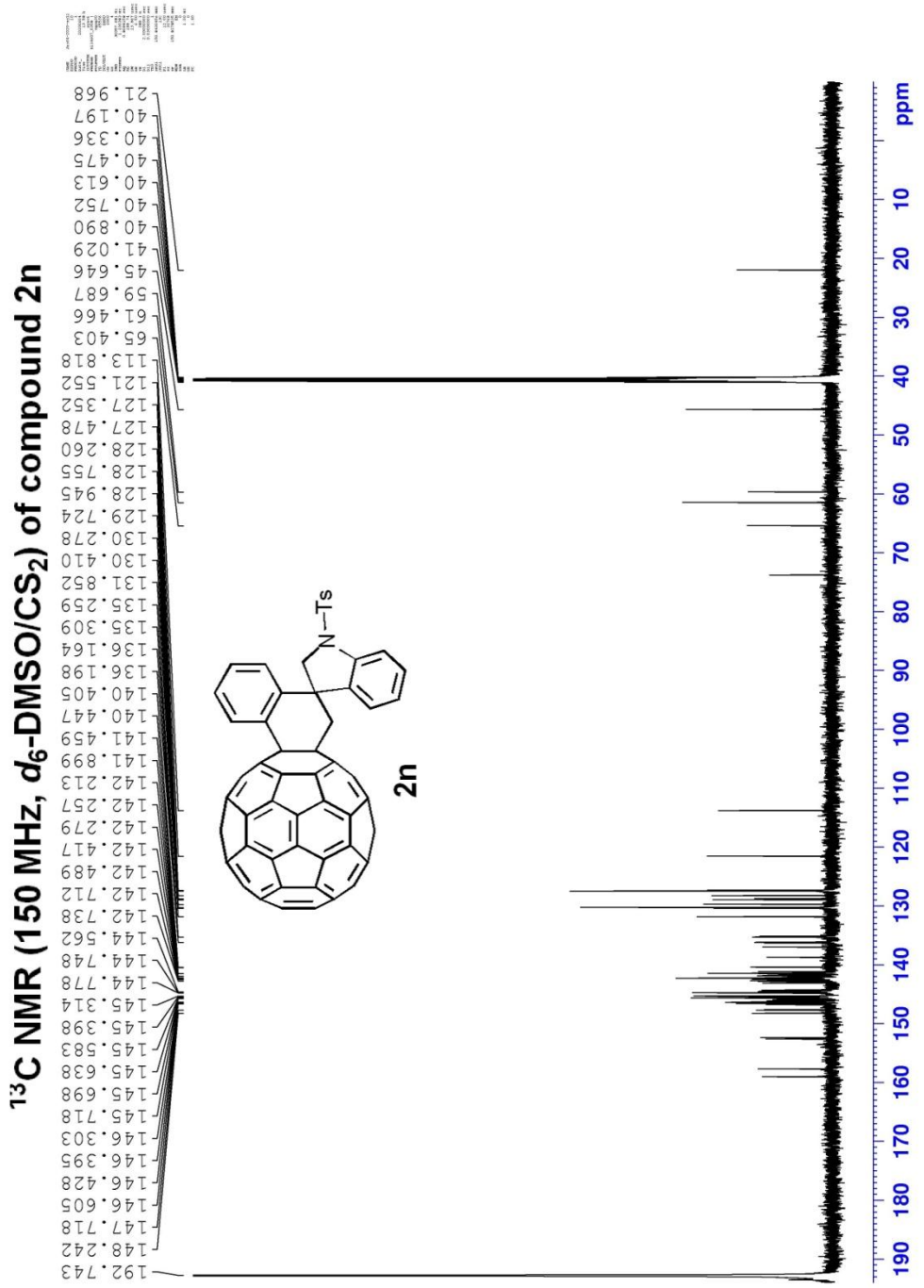
2l


^{13}C NMR (150 MHz, d_6-DMSO/CS_2) of compound 2l
N–Boc
2l
ppm

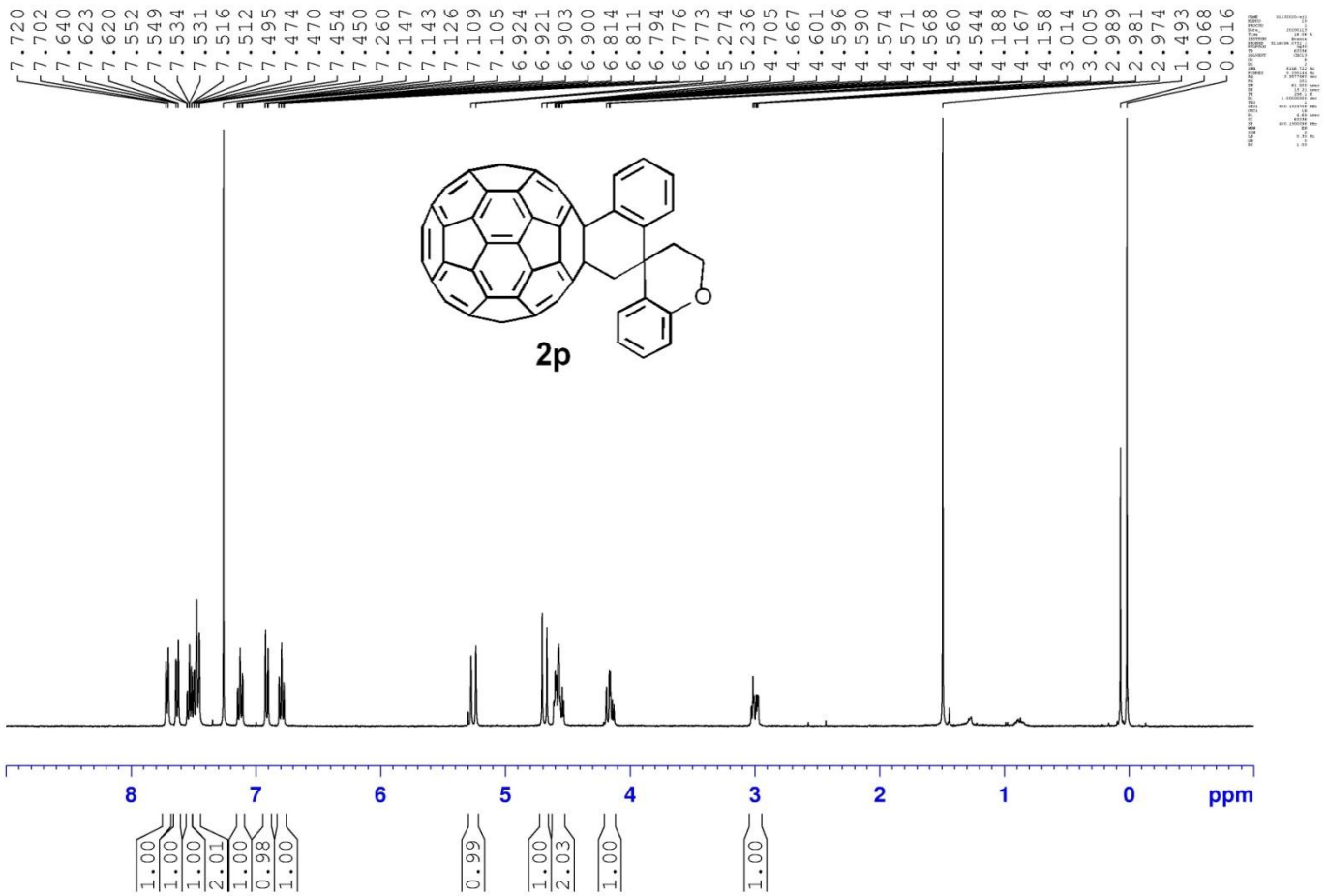

^{1}H NMR (600 MHz, d_6-DMSO/CS_2) of compound 2m
0.000
2.422
2.424
2.604
2.882
3.360
4.473
4.492
4.586
4.611
5.019
5.043
6.090
6.109
6.982
6.995
7.008
7.268
7.281
7.294
7.341
7.354
7.376
7.390
7.458
7.471
7.483
7.521
7.533
7.546
7.623
7.636
7.693
7.705
N–Ms
2m
ppm
0
1
2
3
4
5
6
7
8
9
2.90
1.00
1.00
1.00
0.99
0.95
1.01
0.99
1.01
0.99
0.99
1.00
1.00

^{1}H NMR (600 MHz, d_6-DMSO/CS_2) of compound 2n

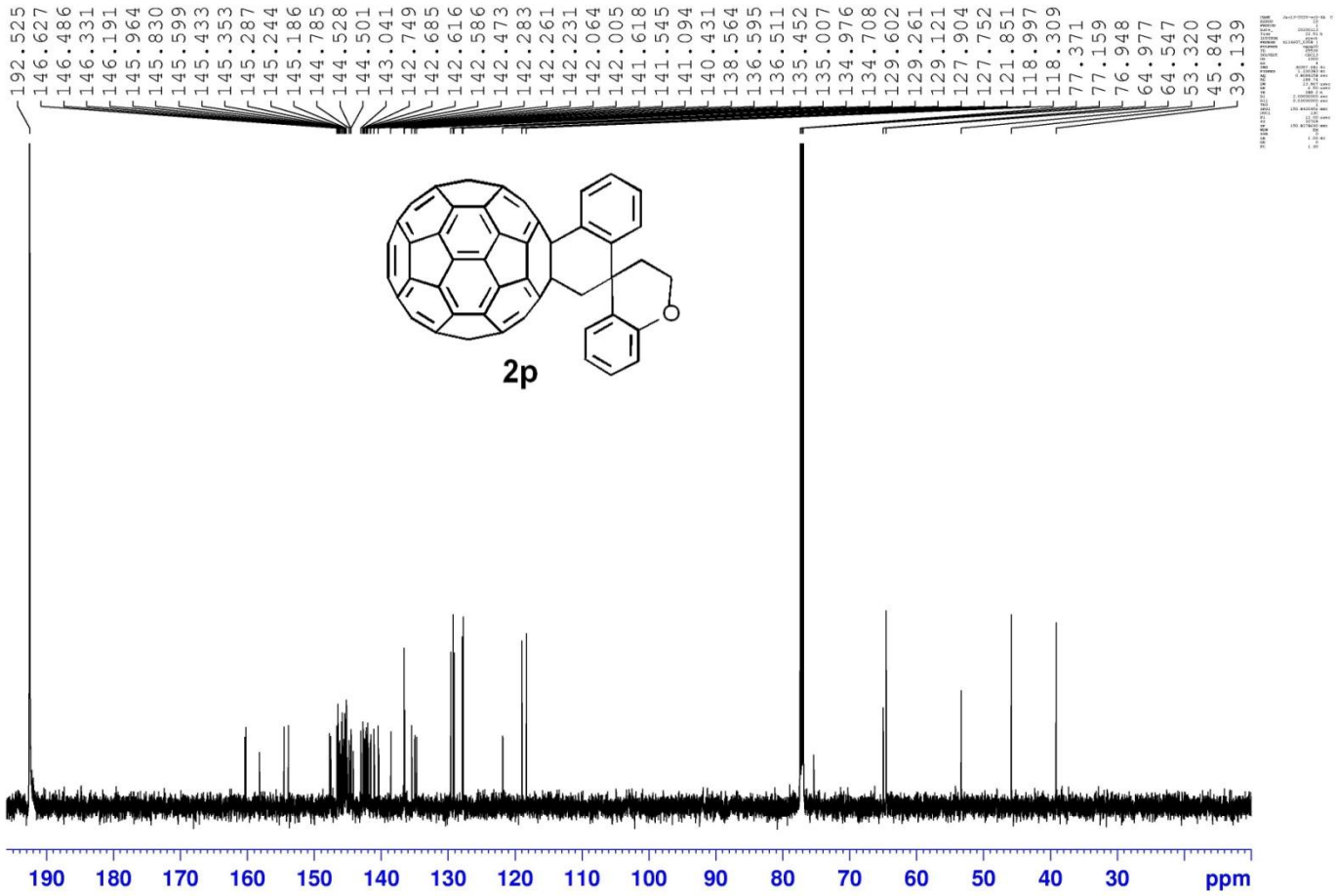


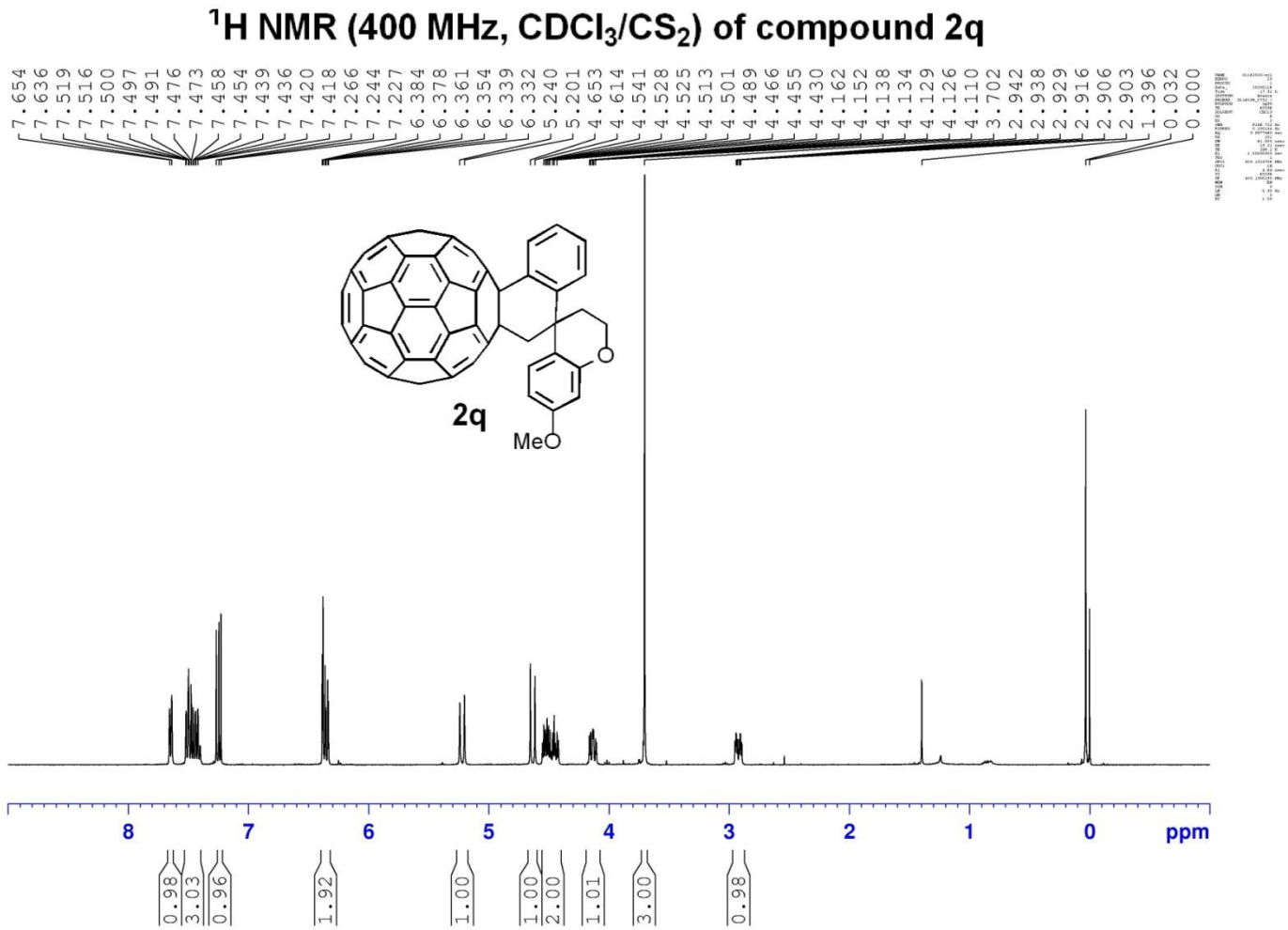

^{13}C NMR (150 MHz, d_6-DMSO/CS_2) of compound 2n
N—Ts
2n
ppm

^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2p

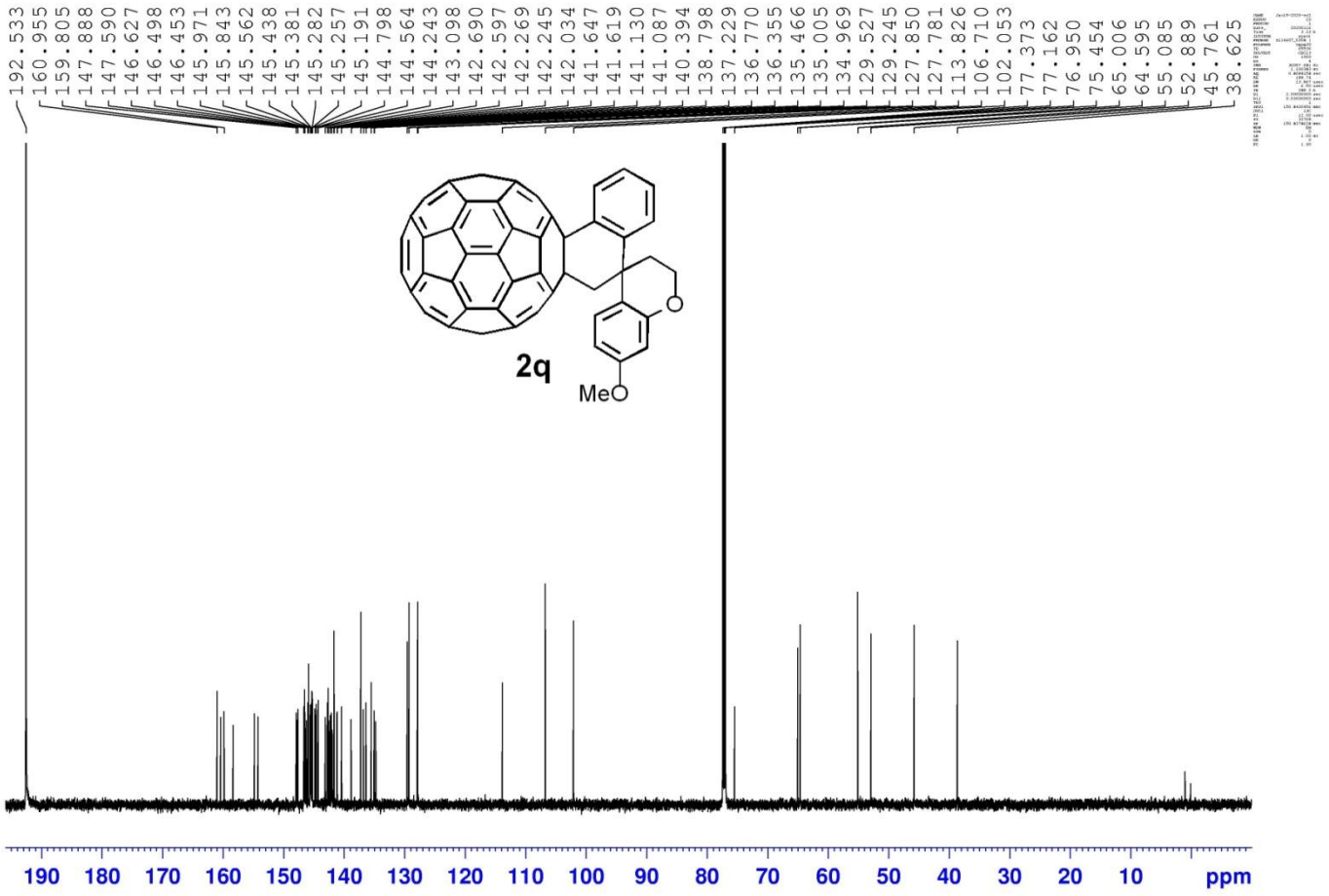


^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2p

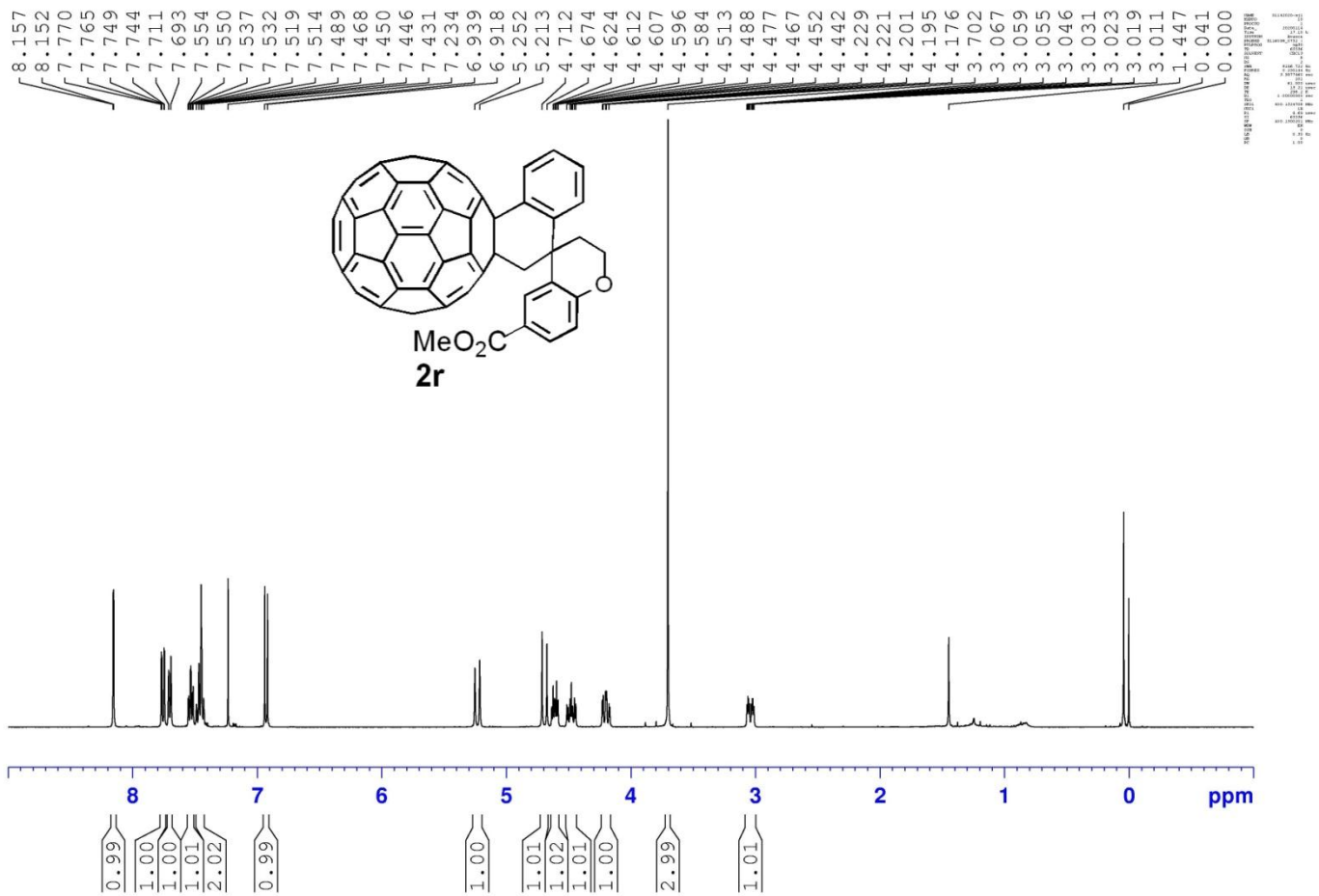


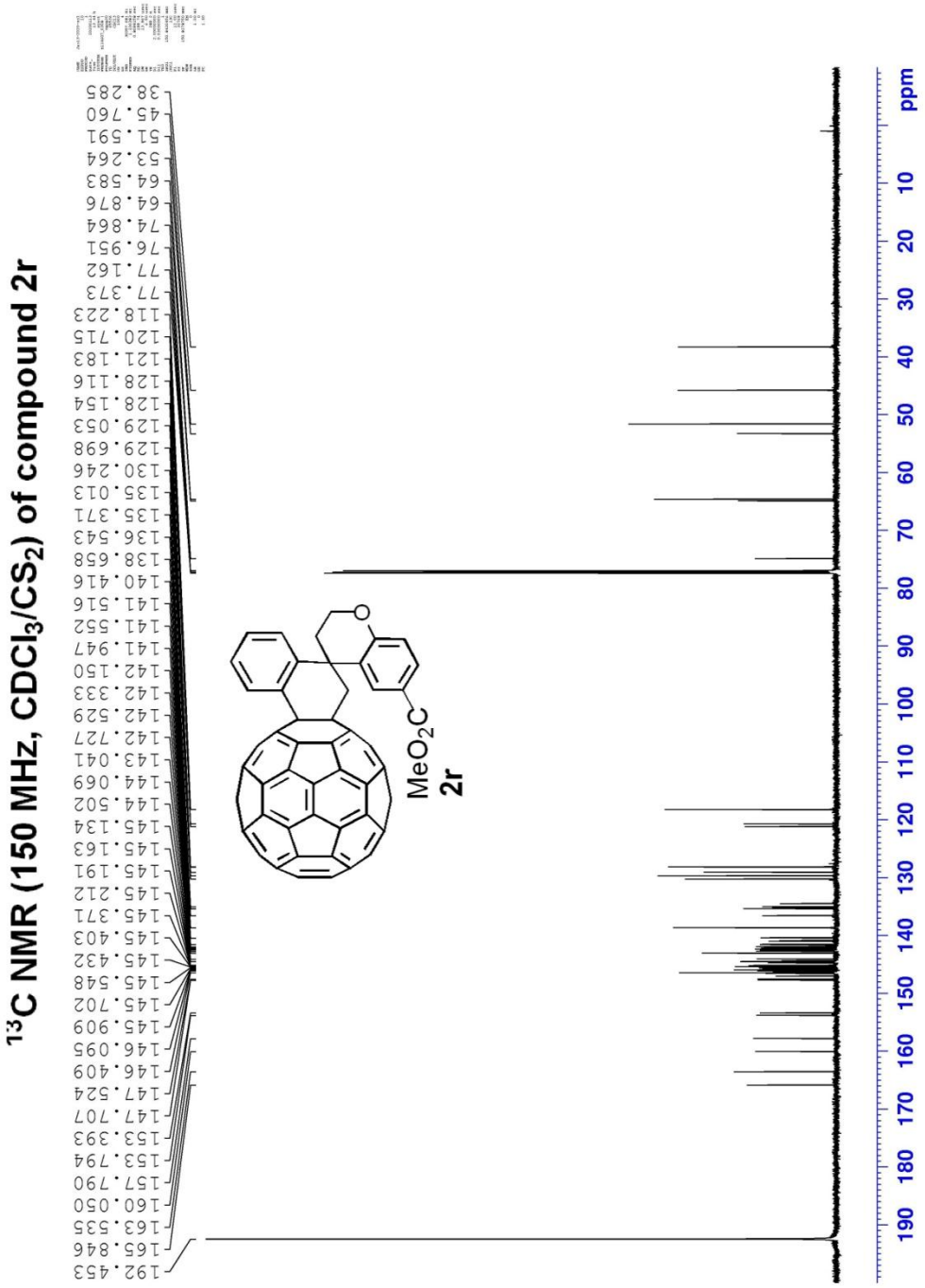

¹H NMR (400 MHz, CDCl3/CS2) of compound 2q
7.654
7.636
7.519
7.516
7.500
7.497
7.491
7.476
7.473
7.458
7.454
7.439
7.436
7.420
7.418
7.266
7.244
7.227
6.384
6.378
6.361
6.354
6.339
6.332
5.240
5.201
4.653
4.614
4.541
4.528
4.525
4.513
4.501
4.489
4.466
4.455
4.430
4.162
4.152
4.138
4.134
4.129
4.126
4.110
3.702
2.942
2.938
2.929
2.916
2.906
2.903
1.396
0.032
0.000
2q
MeO
8
7
6
5
4
3
2
1
0
ppm
0.98
3.03
0.96
1.92
1.00
1.00
2.00
1.01
3.00
0.98

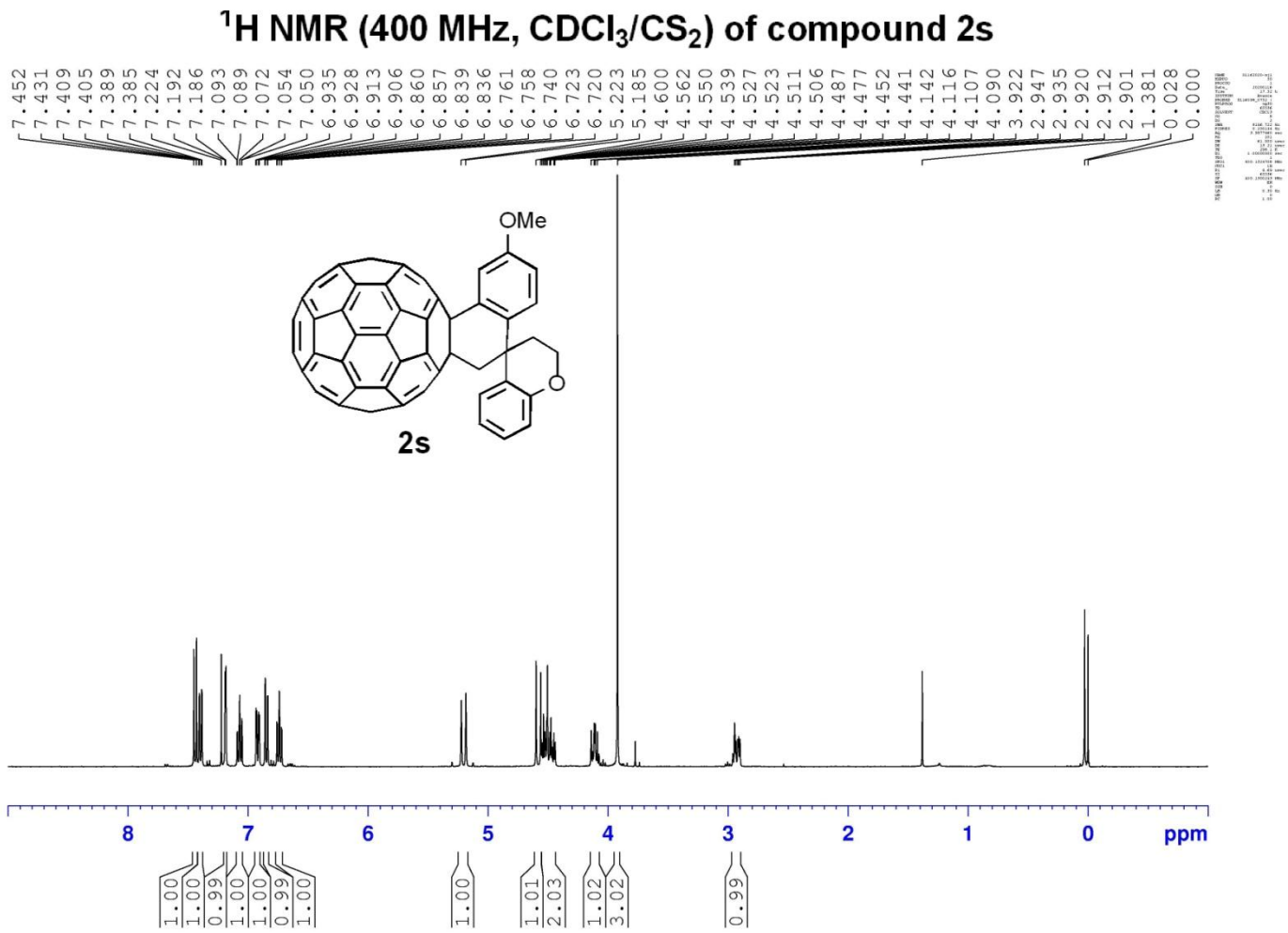
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2q

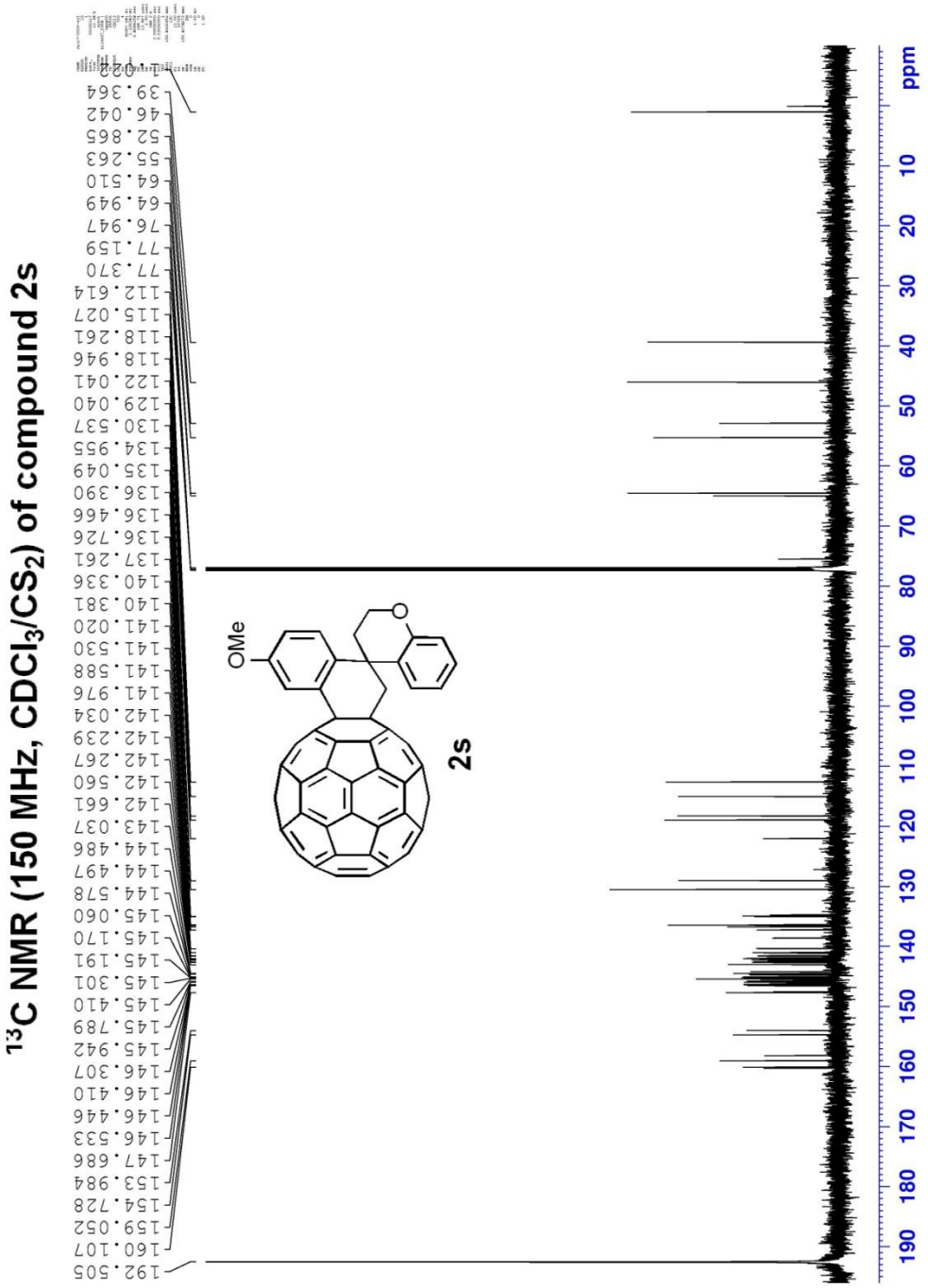


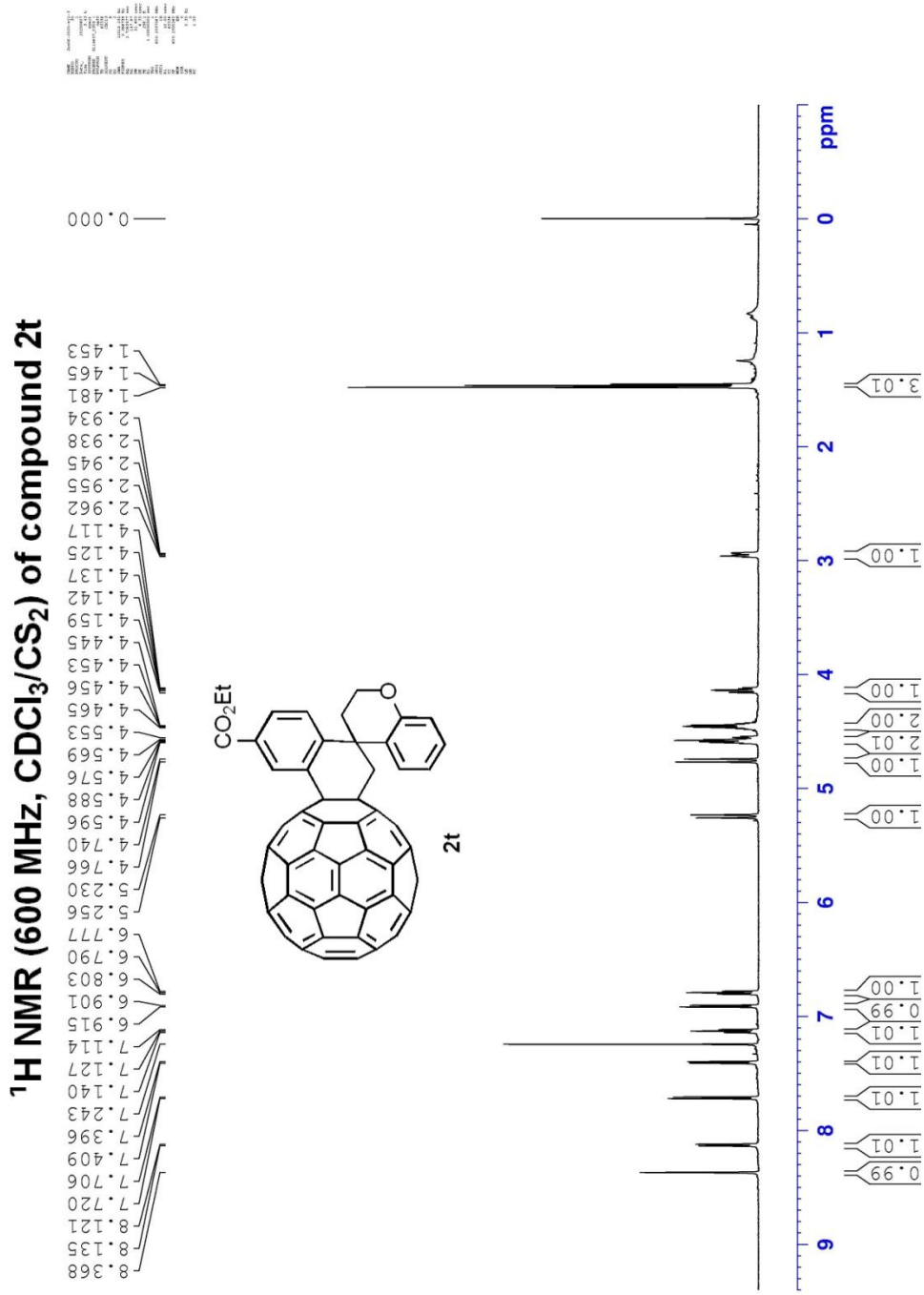
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2r

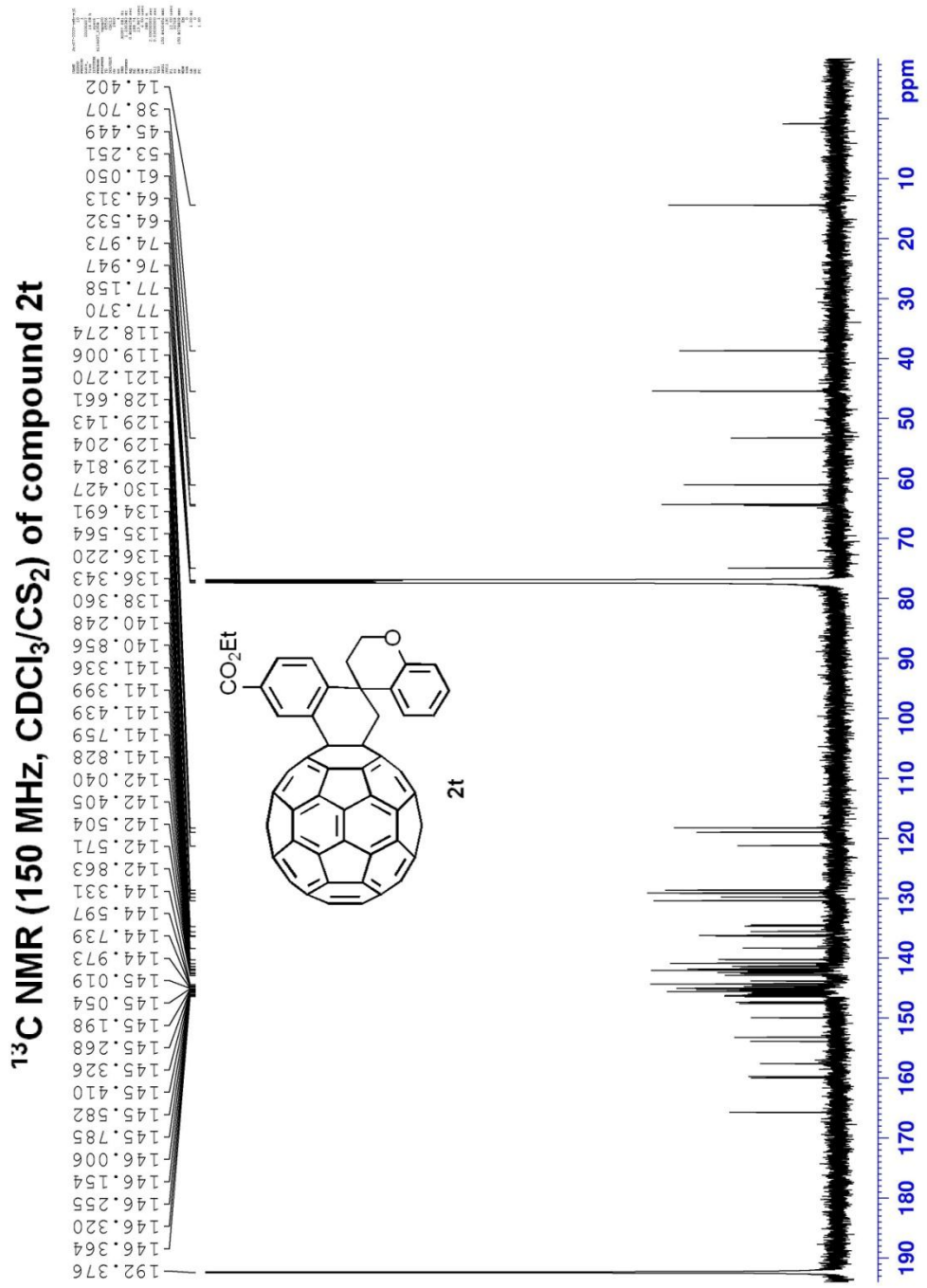



^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2r
MeO2C
2r
ppm

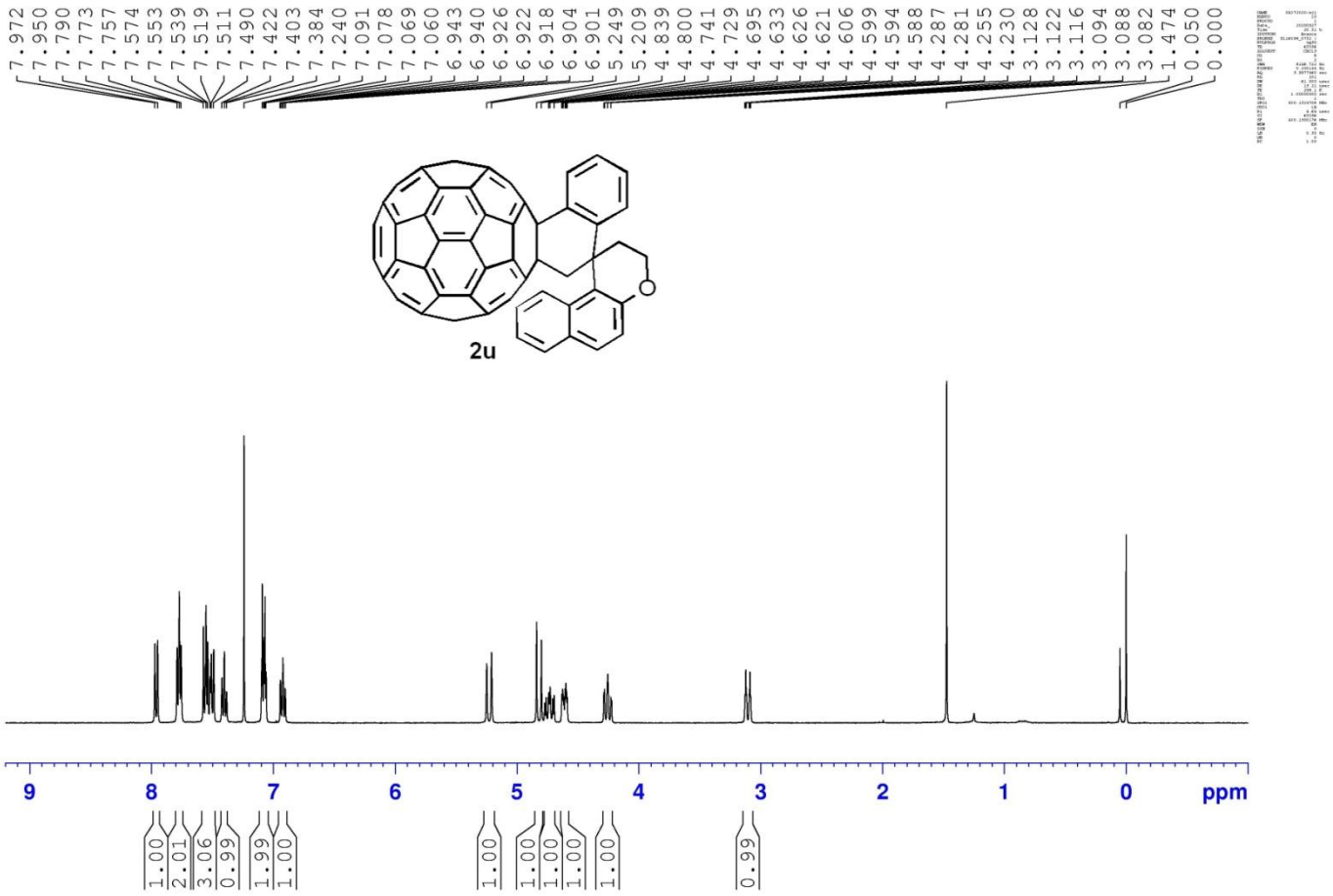

¹H NMR (400 MHz, CDCl3/CS2) of compound 2s
7.452
7.431
7.409
7.405
7.389
7.385
7.224
7.192
7.186
7.093
7.089
7.072
7.054
7.050
6.935
6.928
6.913
6.906
6.860
6.857
6.839
6.836
6.761
6.758
6.740
6.723
6.720
5.223
5.185
4.600
4.562
4.550
4.539
4.527
4.523
4.511
4.506
4.487
4.477
4.452
4.441
4.142
4.116
4.107
4.090
3.947
3.922
2.935
2.920
2.912
2.901
1.381
0.028
0.000
OMe
2s
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
0.99
1.00
1.00
0.99
1.00
1.00
1.01
2.03
1.02
3.02
0.99

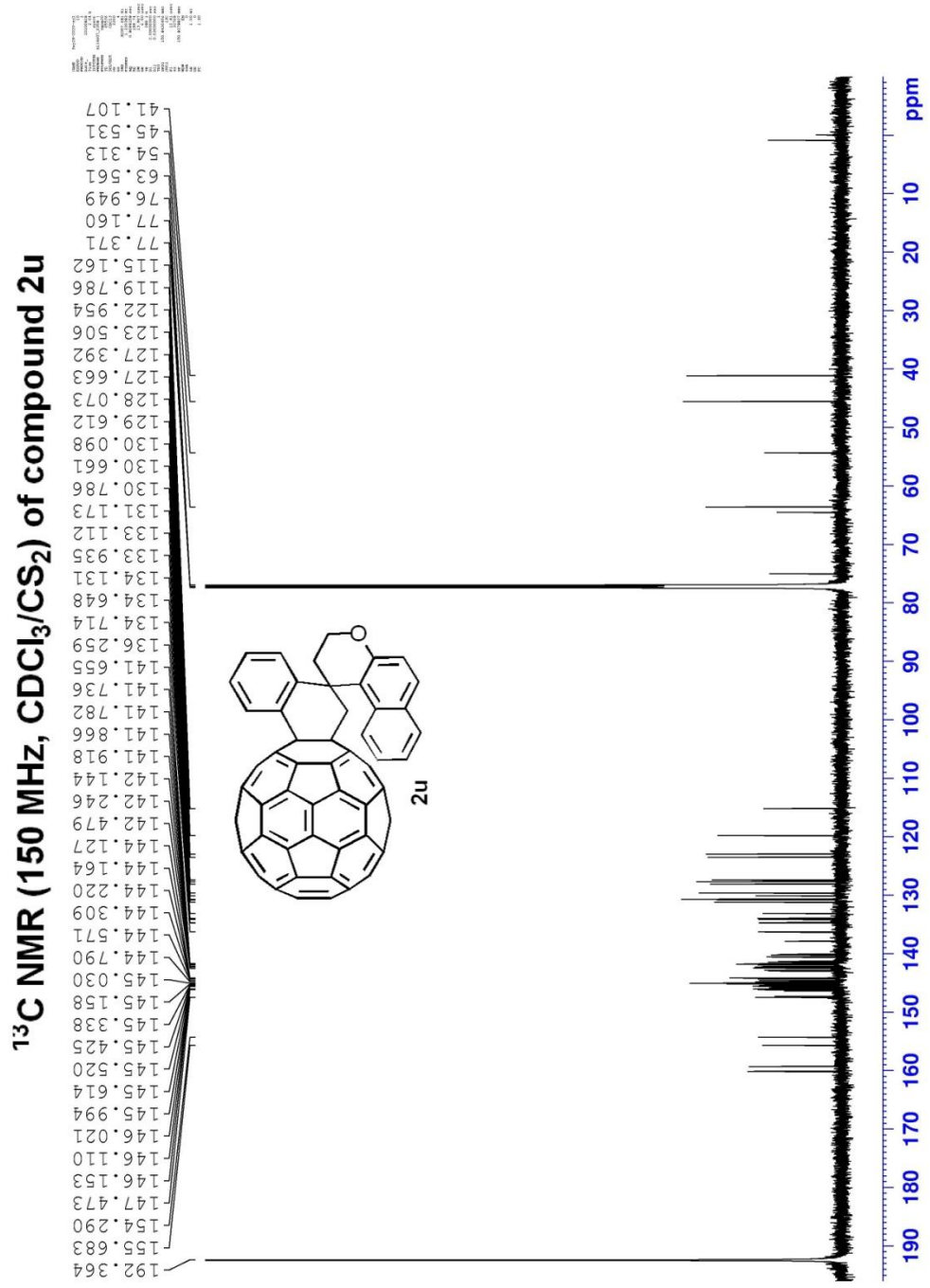

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2s
OMe
2s
ppm

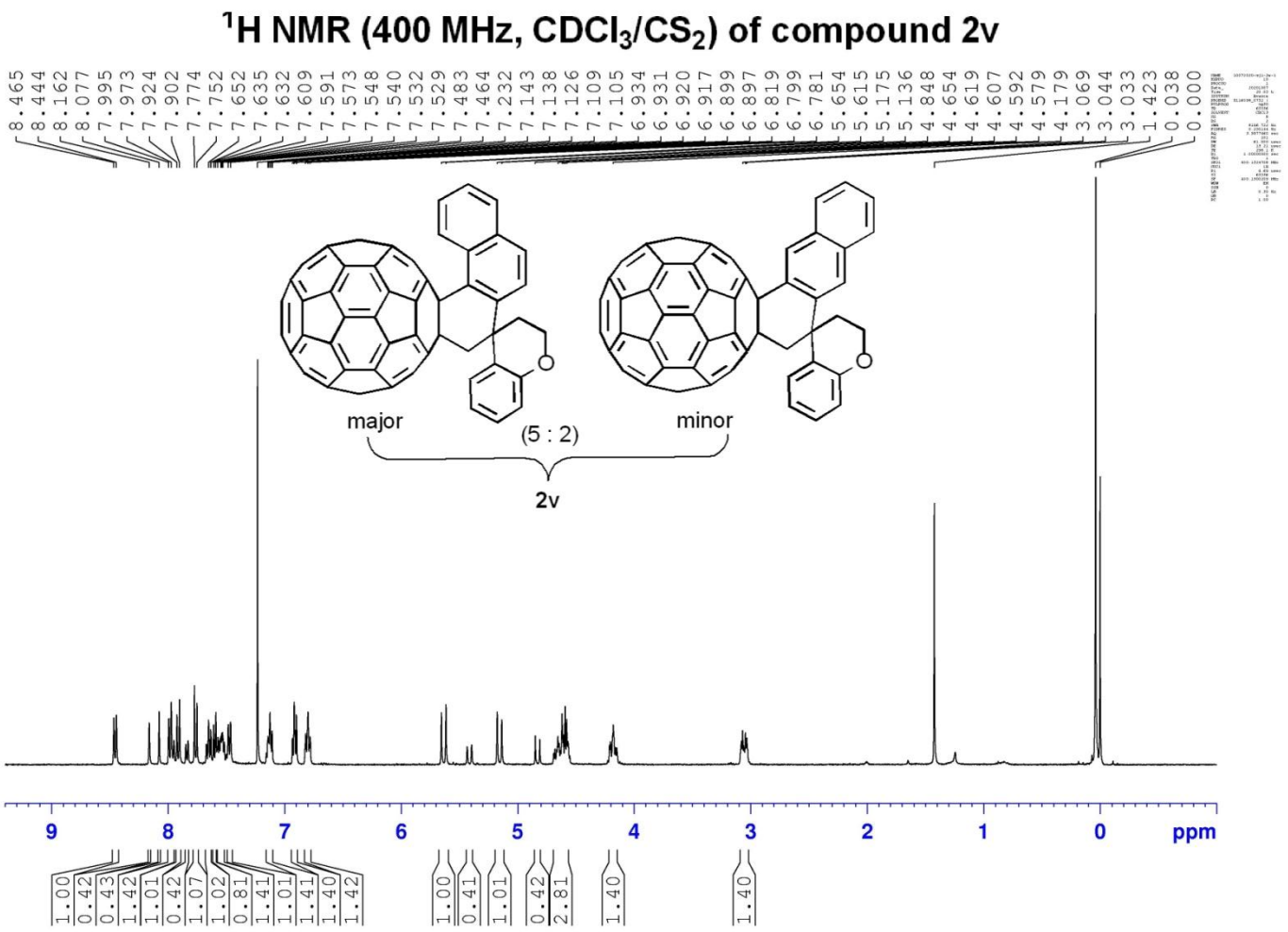

^{1}H NMR (600 MHz, $CDCl_3/CS_2$) of compound 2t
CO_2Et
2t
ppm


^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2t
CO_2Et
2t
ppm

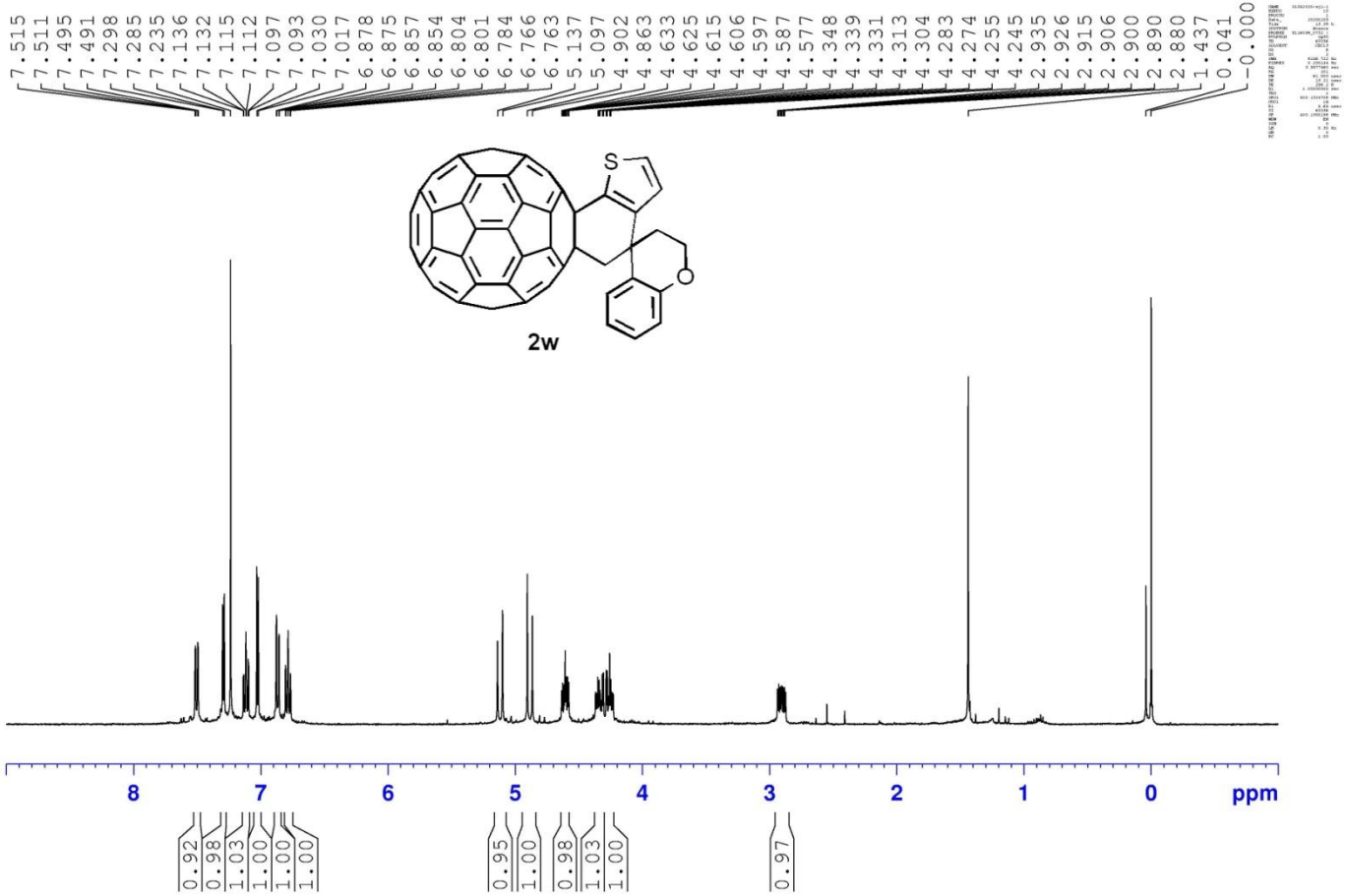
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2u

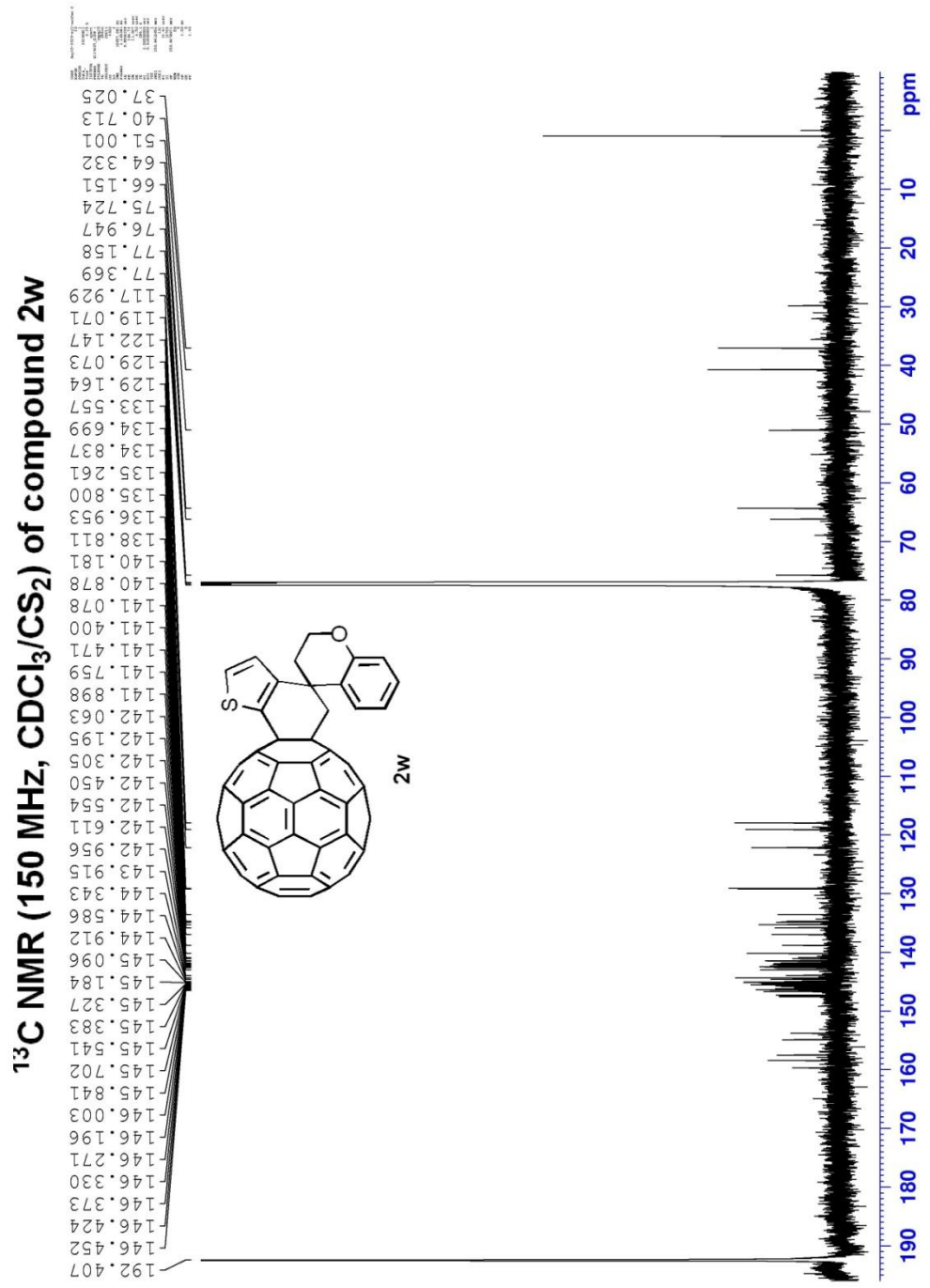



^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2u
2u
ppm

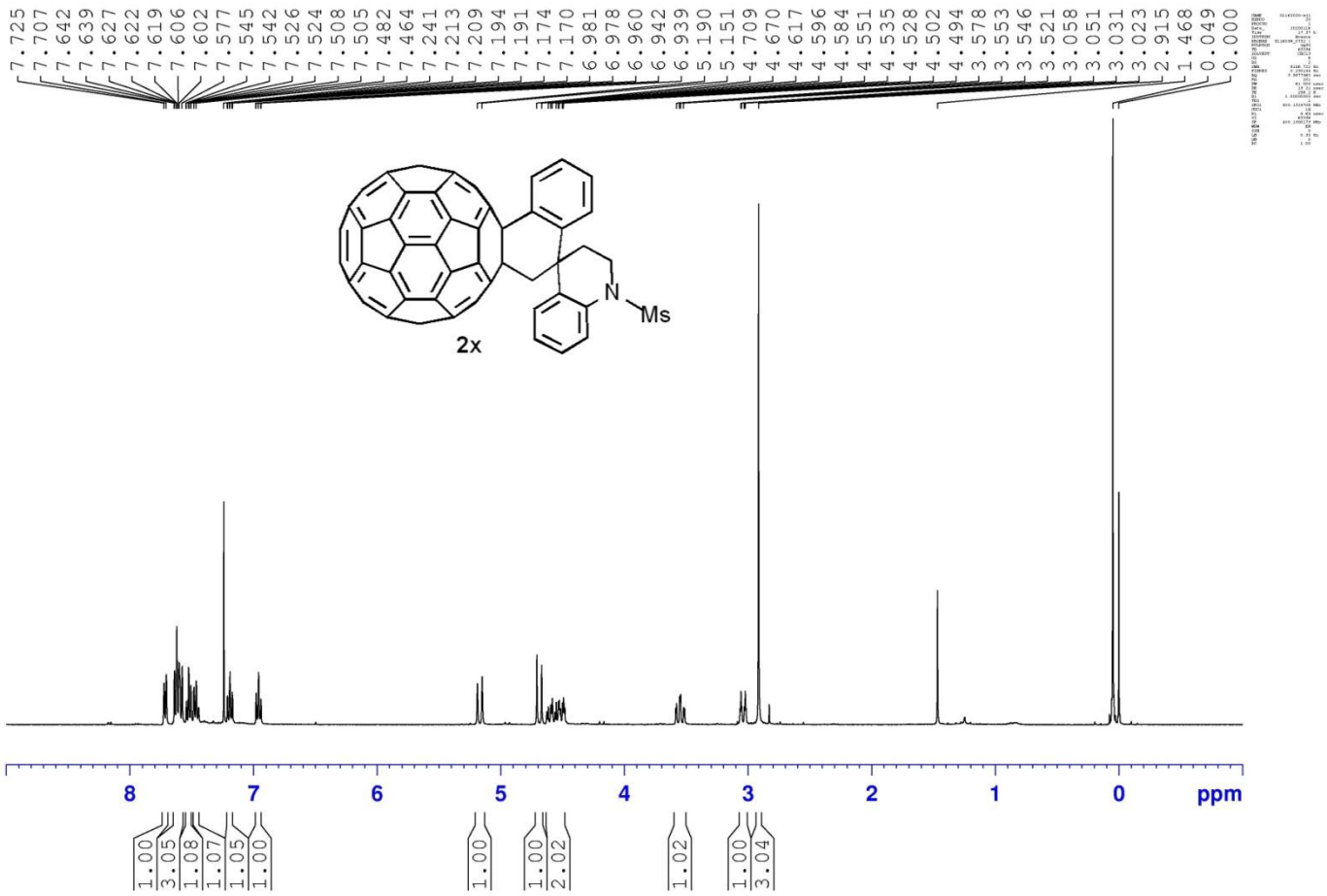

^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2v
major
(5 : 2)
minor
2v
ppm

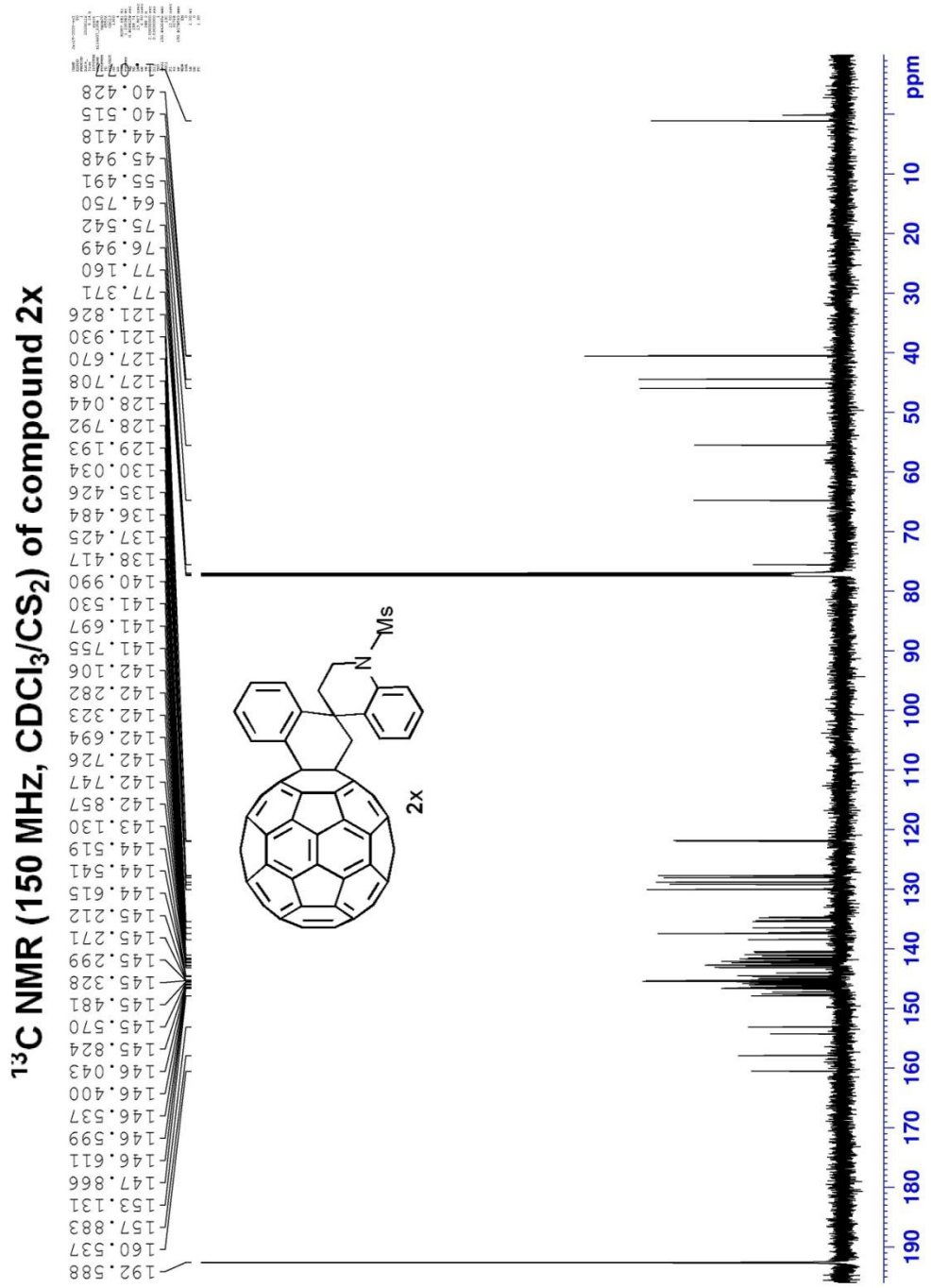
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2w



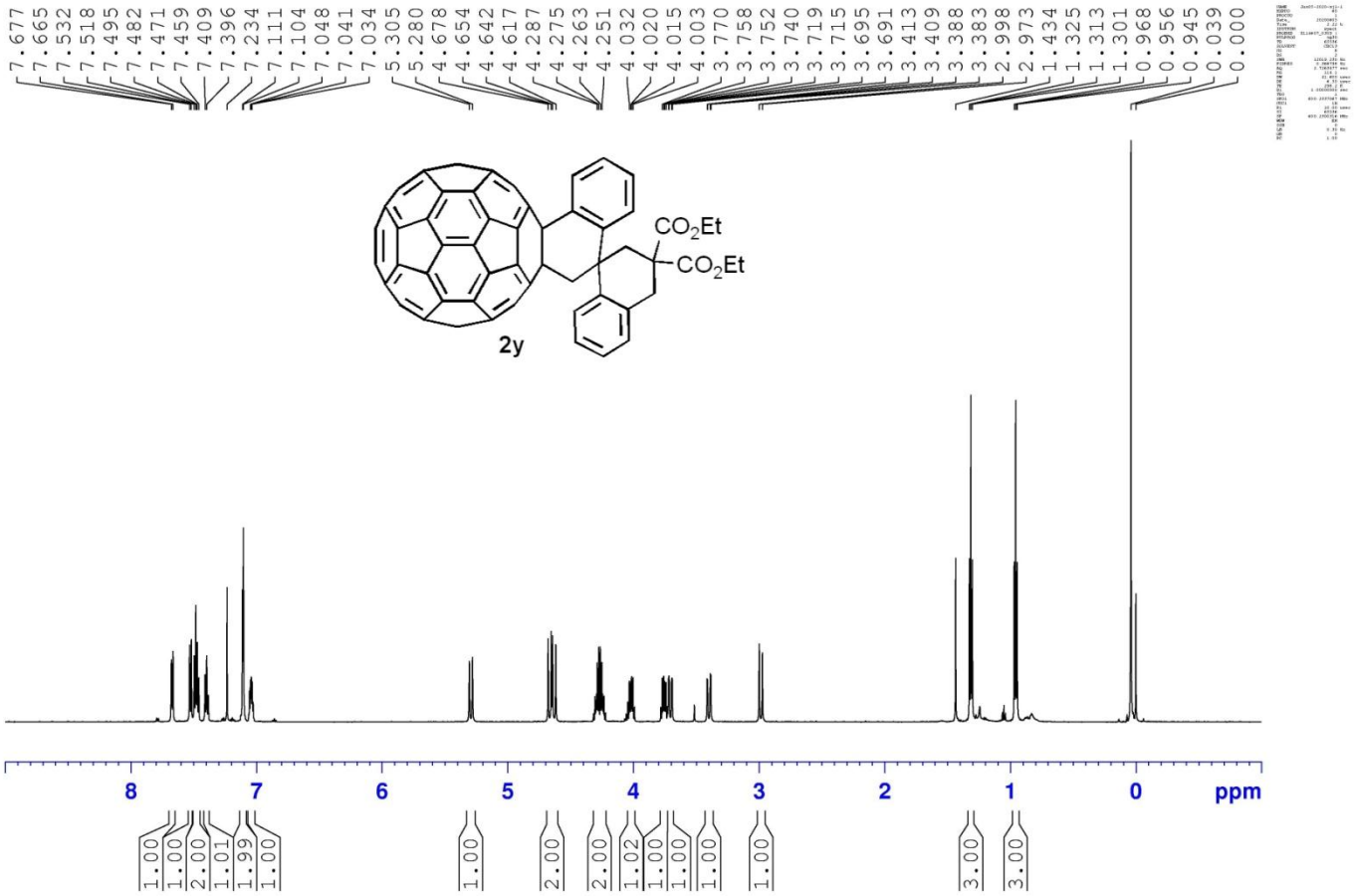

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2w
S
2w
ppm

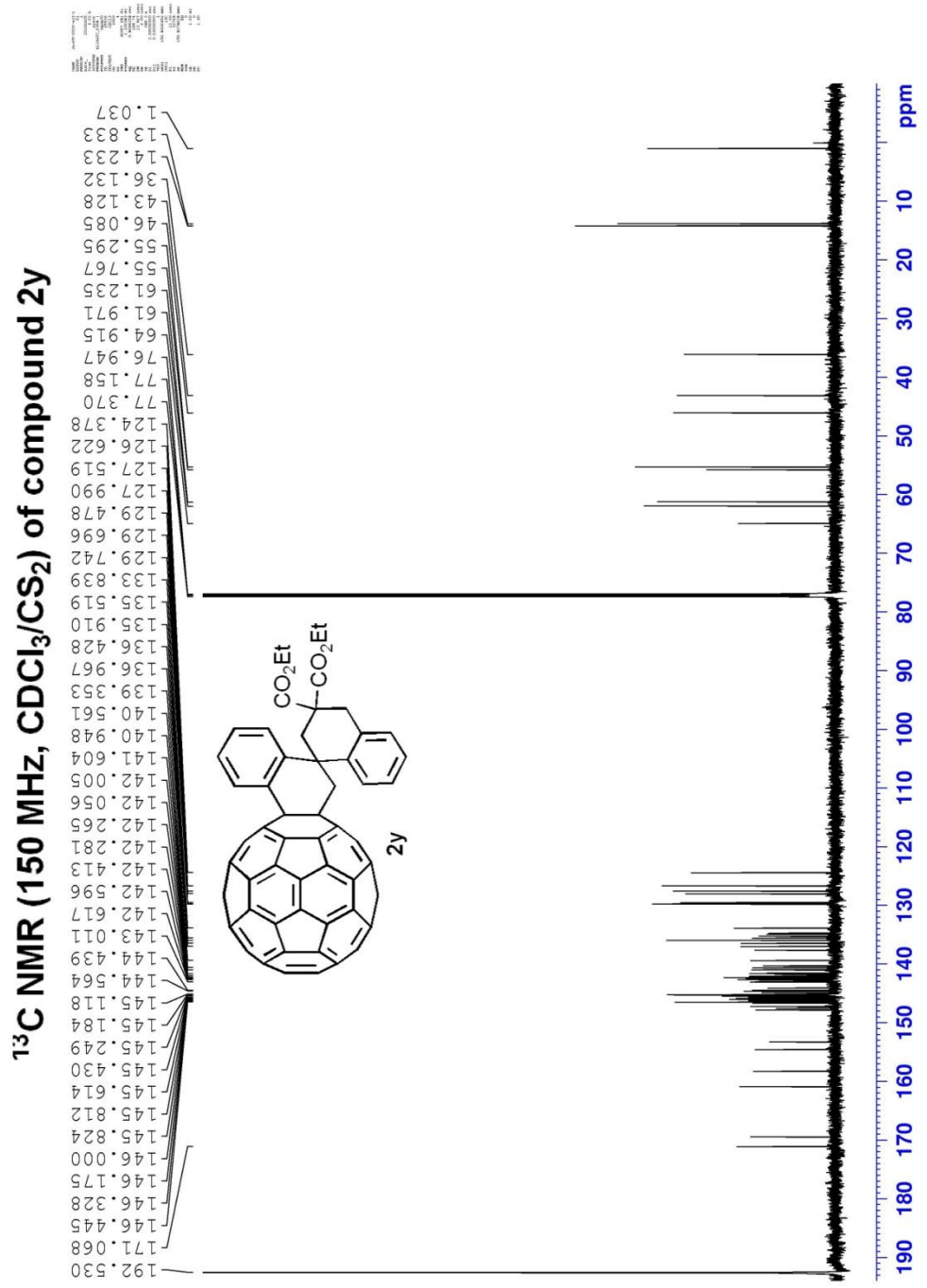
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2x

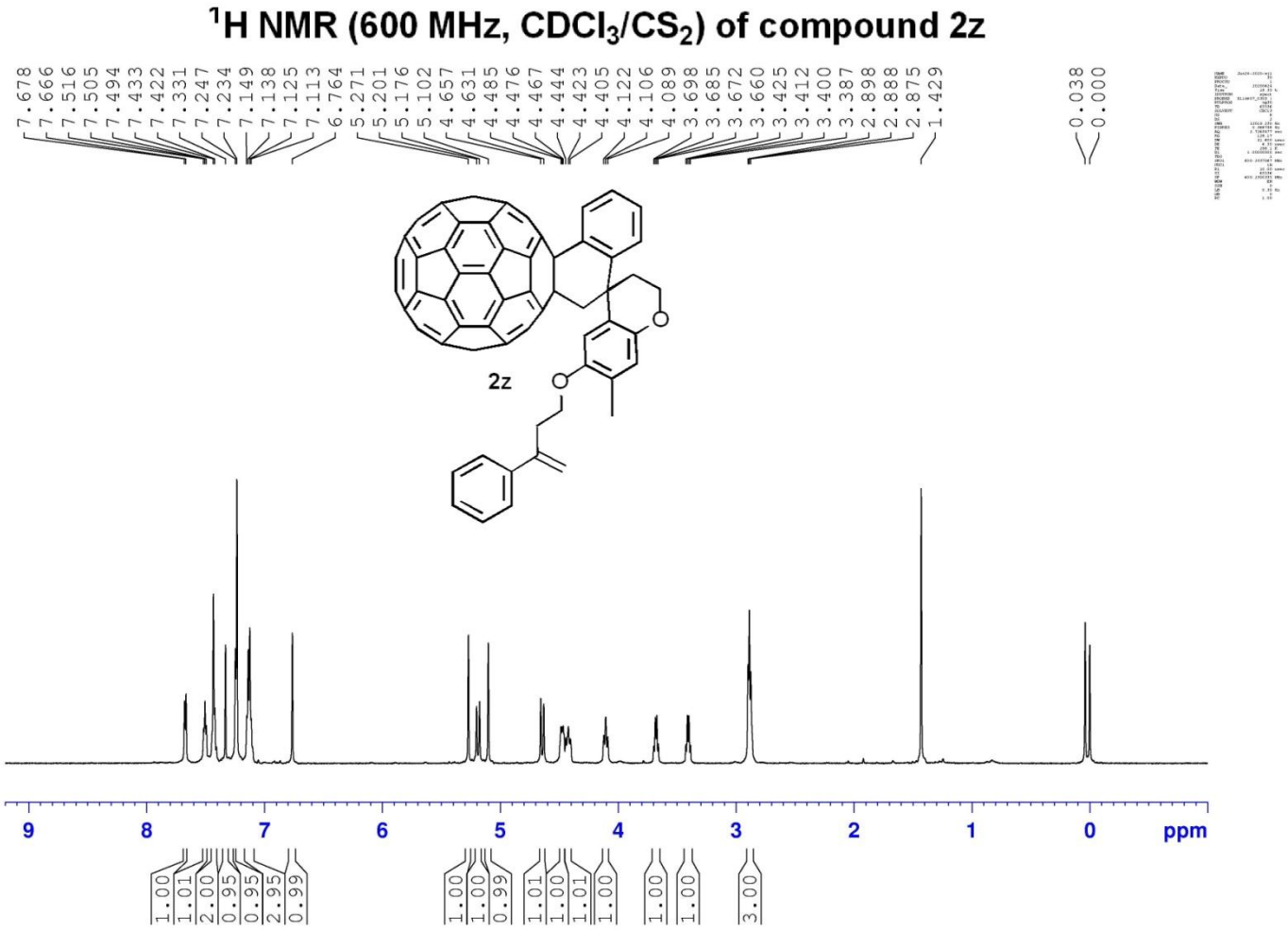


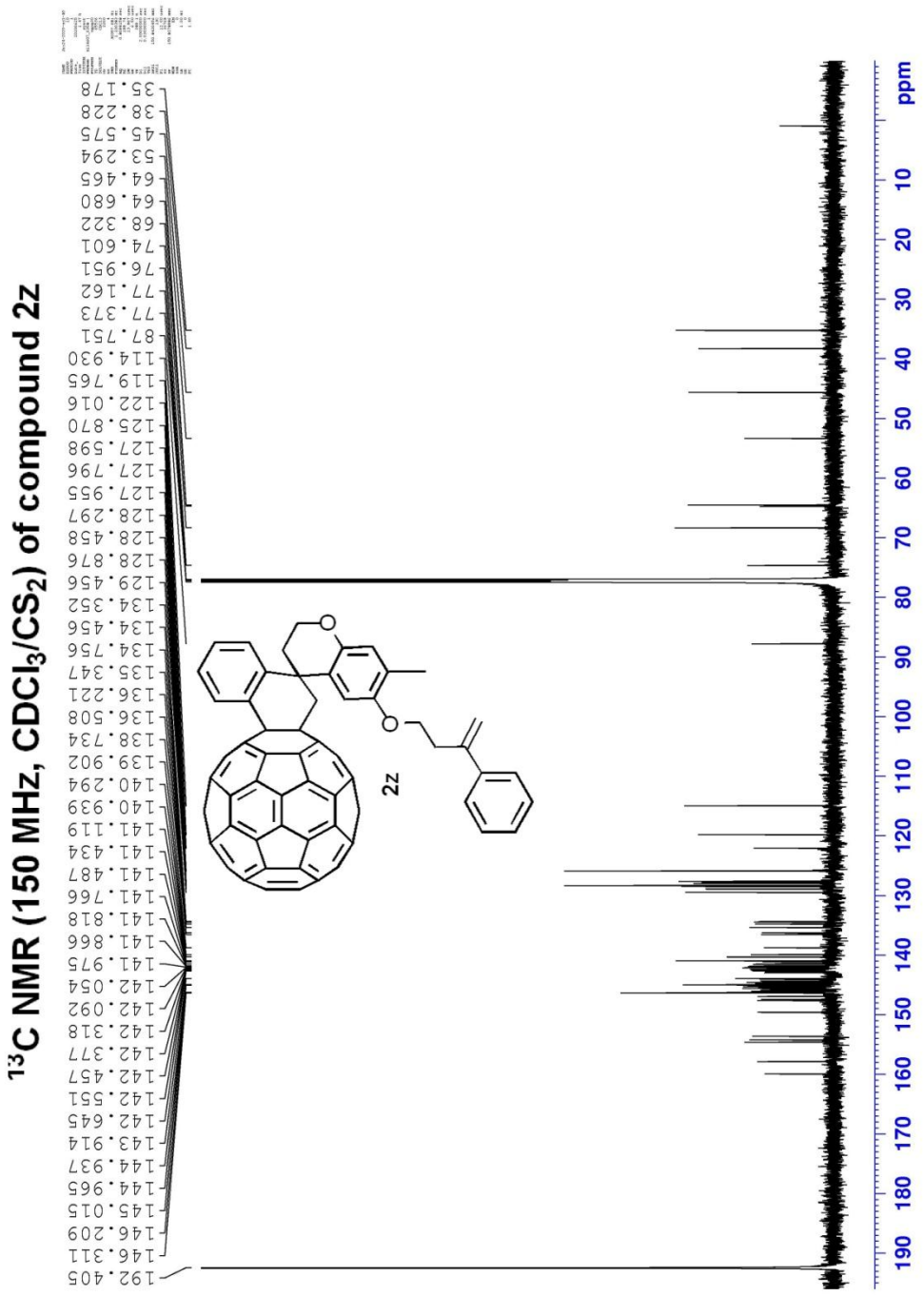

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2x
Ms
N
2x
ppm

^{1}H NMR (600 MHz, $CDCl_3/CS_2$) of compound 2y

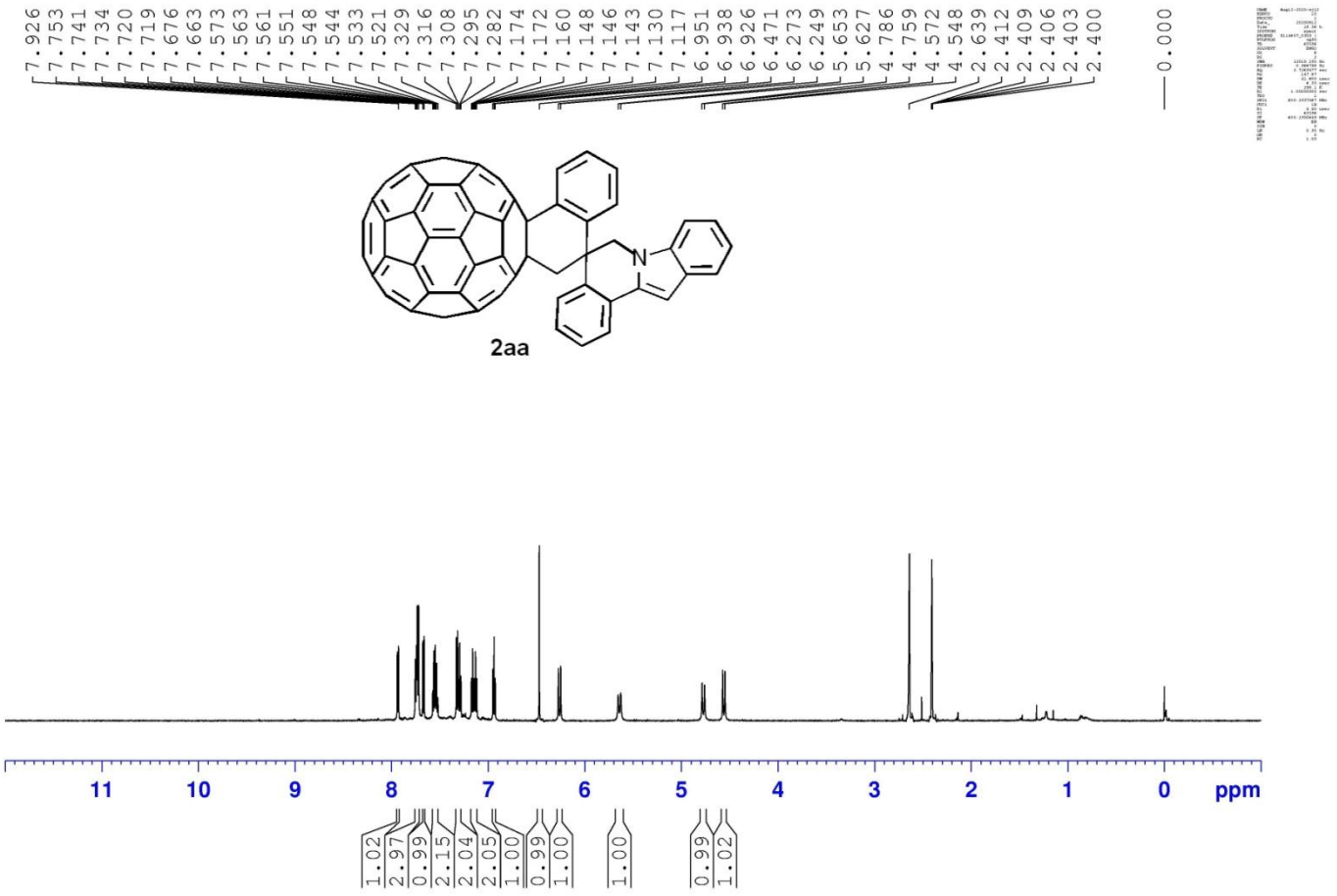


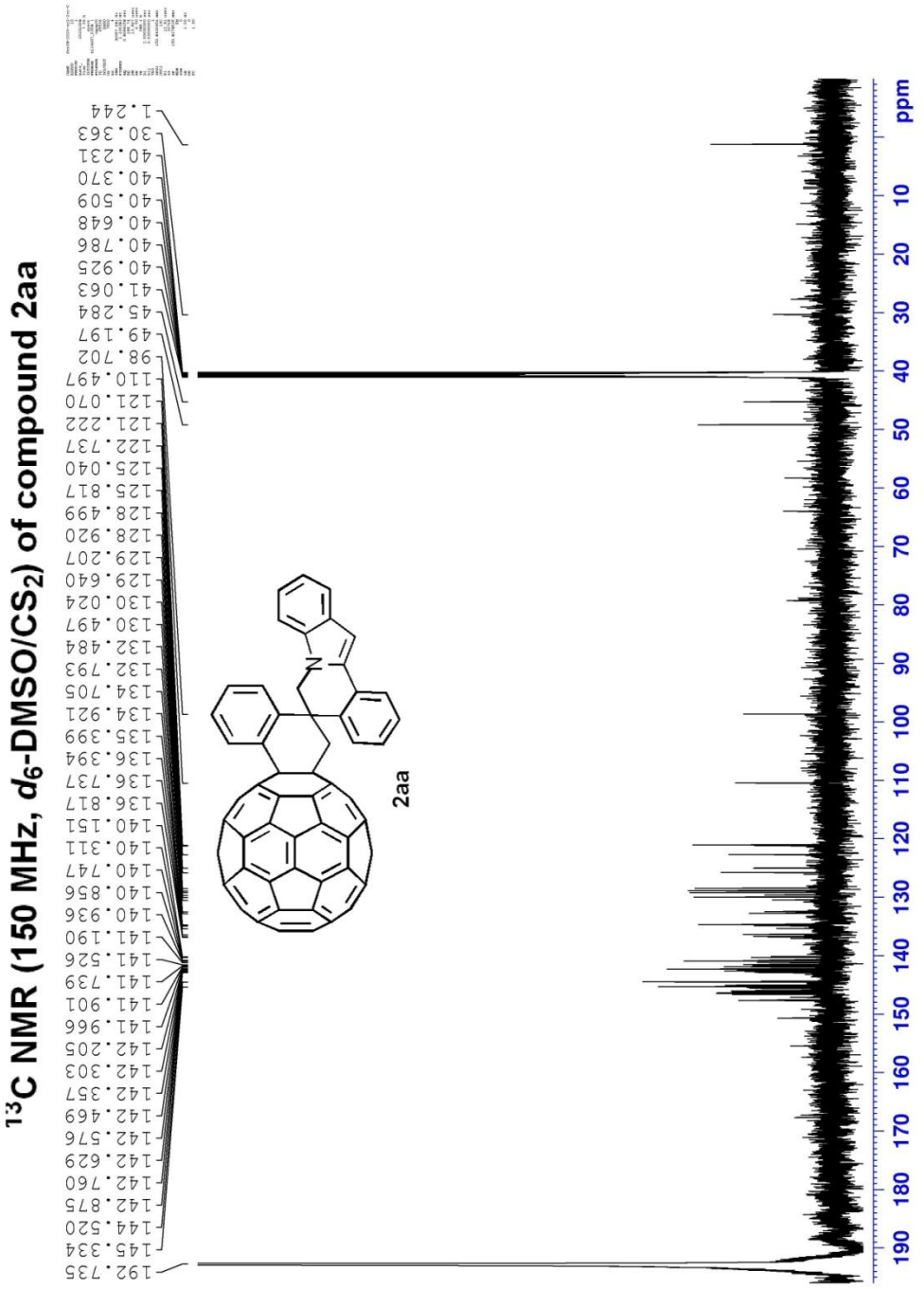

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2y
CO_2Et
CO_2Et
2y
ppm

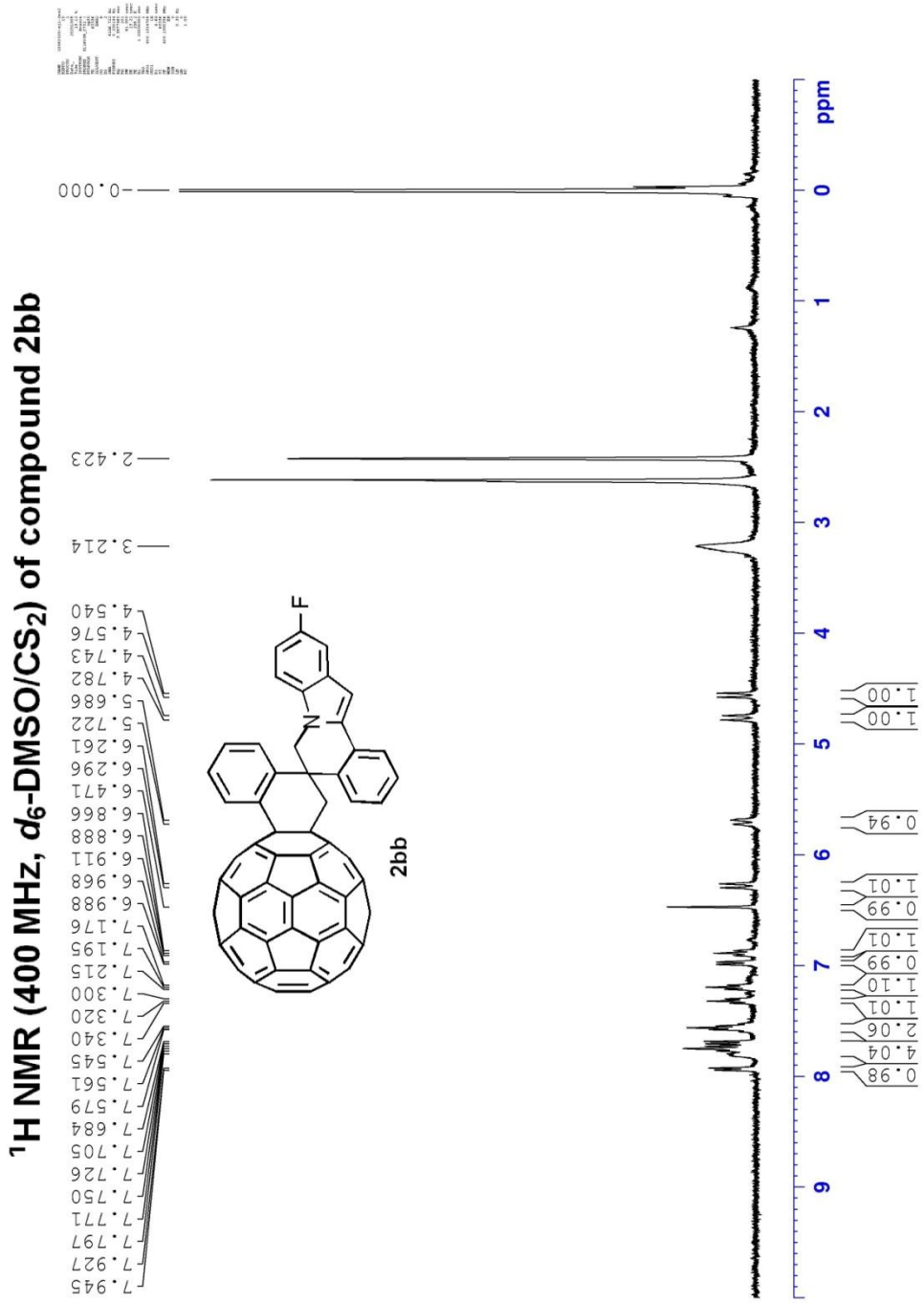

¹H NMR (600 MHz, CDCl3/CS2) of compound 2z
7.678
7.666
7.516
7.505
7.494
7.433
7.422
7.331
7.247
7.234
7.149
7.138
7.125
7.113
6.764
5.271
5.201
5.176
5.102
4.657
4.631
4.485
4.476
4.467
4.444
4.423
4.405
4.122
4.106
4.089
3.698
3.685
3.672
3.660
3.425
3.412
3.400
3.387
2.898
2.888
2.875
1.429
0.038
0.000
2z
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
2.00
0.95
0.95
2.95
0.99
1.00
1.00
0.99
1.01
1.00
1.01
1.00
1.00
1.00
3.00


^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2z
2z
ppm

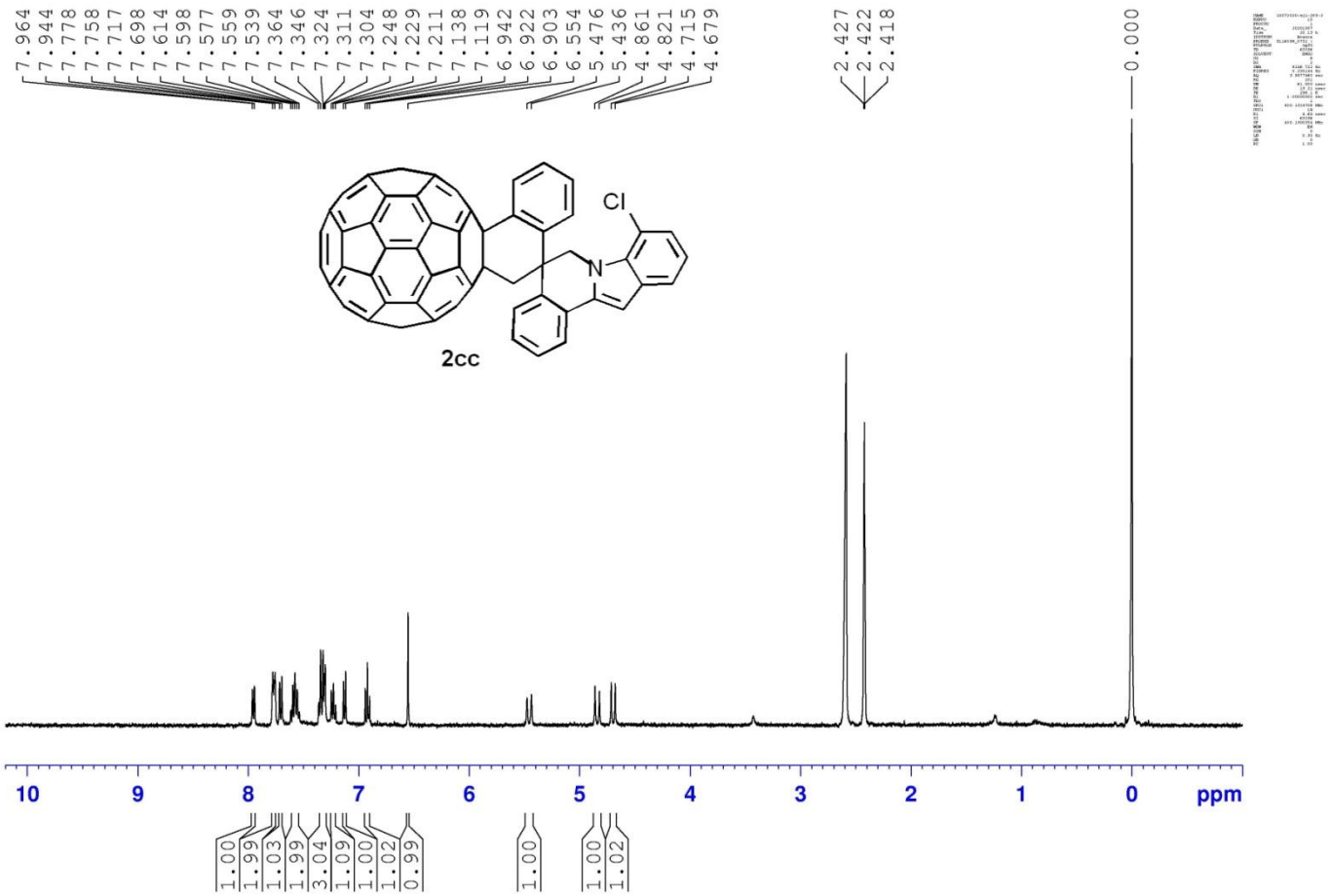
^{1}H NMR (600 MHz, d_6-DMSO/CS_2) of compound 2aa

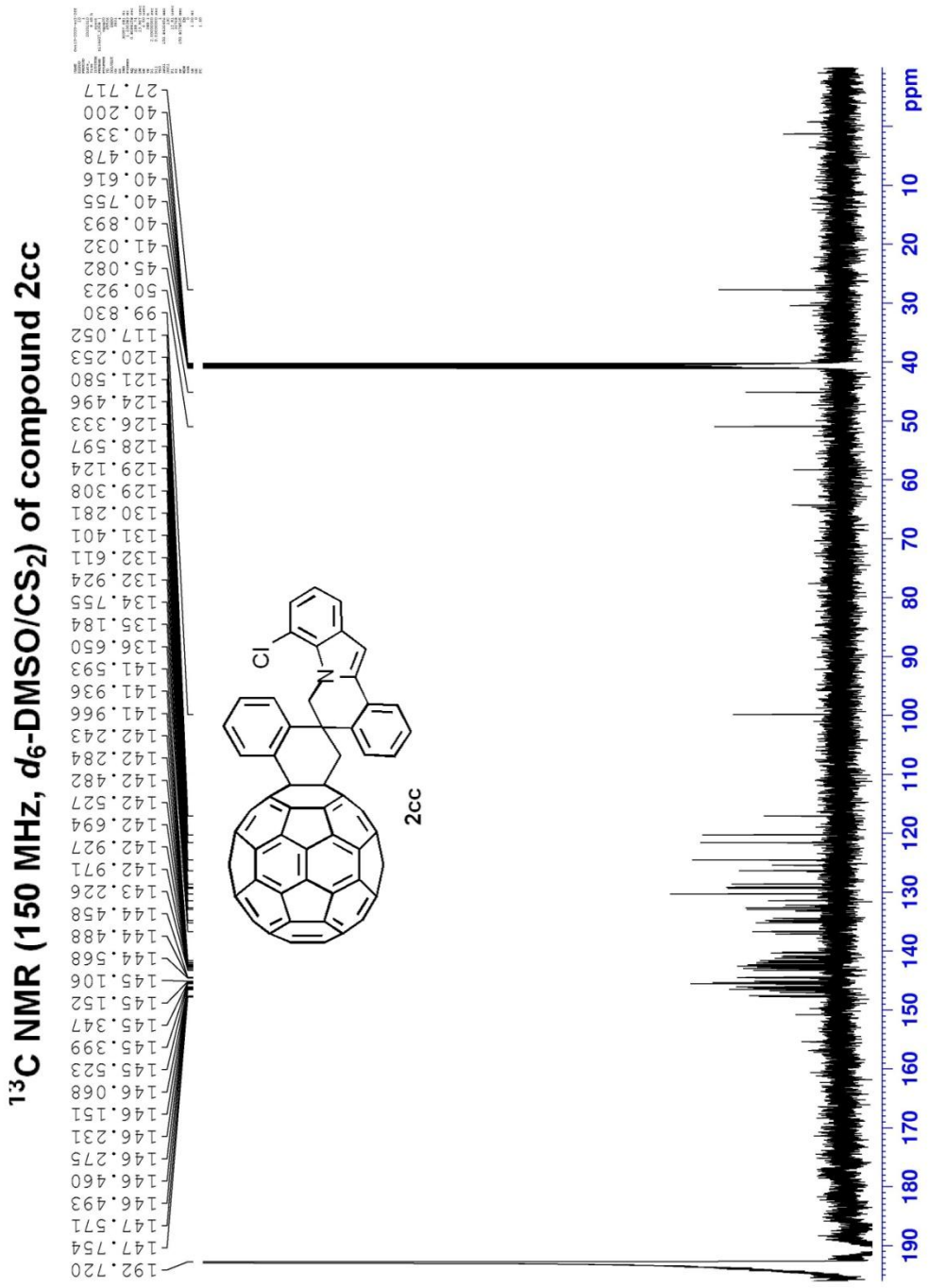


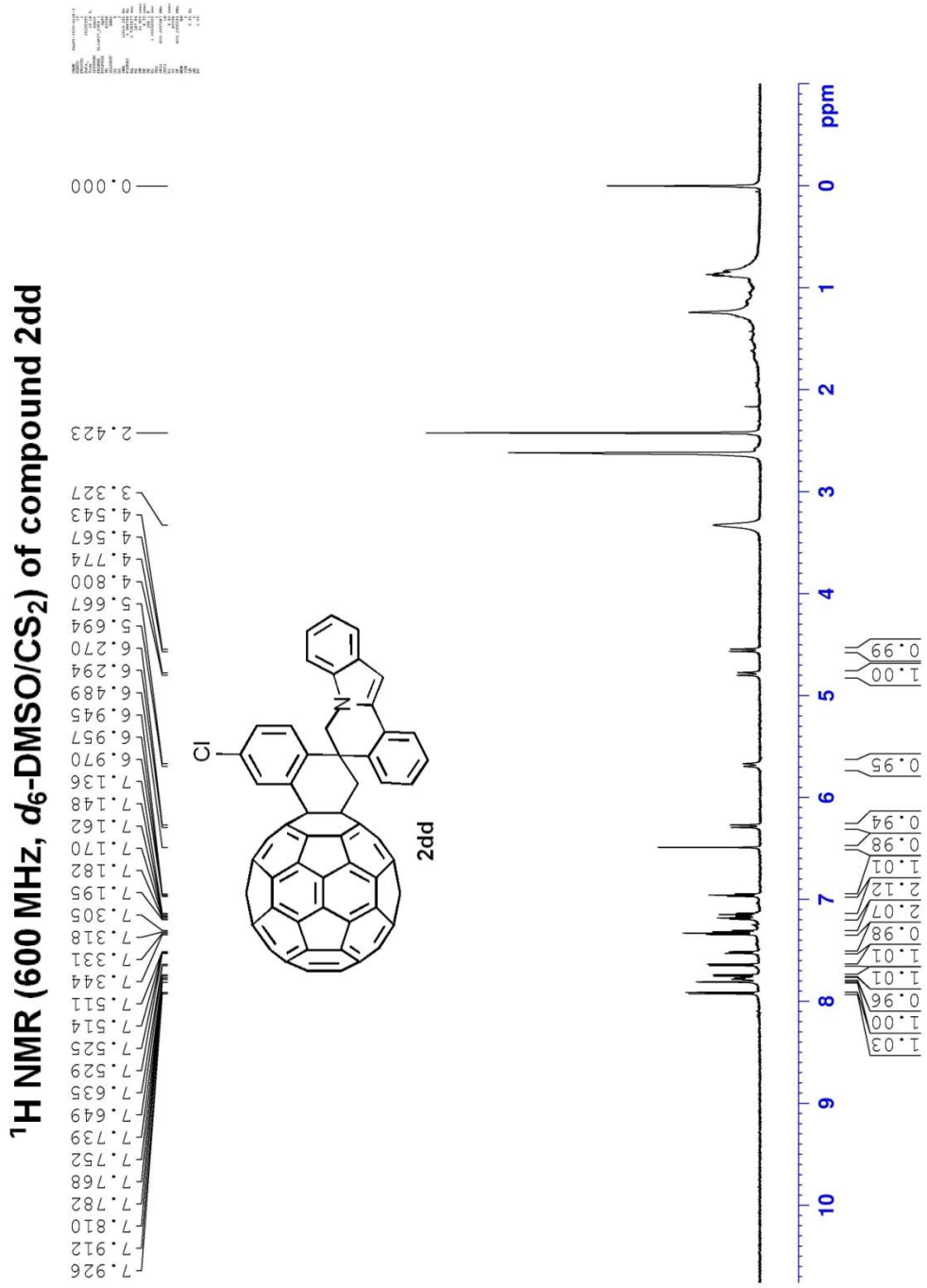

^{13}C NMR (150 MHz, d_6-DMSO/CS_2) of compound 2aa
2aa
ppm


^{1}H NMR (400 MHz, d_6-DMSO/CS_2) of compound 2bb
2bb
F
N
ppm
0
1
2
3
4
5
6
7
8
9
0.000
2.423
3.214
4.540
4.576
4.743
4.782
5.686
5.722
6.261
6.296
6.471
6.866
6.888
6.911
6.968
6.988
7.176
7.195
7.215
7.300
7.320
7.340
7.545
7.561
7.579
7.684
7.705
7.726
7.750
7.771
7.797
7.927
7.945
1.00
0.94
1.01
0.99
1.01
0.99
1.10
1.01
2.06
4.04
0.98

^{1}H NMR (400 MHz, d_6-DMSO/CS_2) of compound 2cc




^{13}C NMR (150 MHz, d_6-DMSO/CS_2) of compound 2cc
Cl
N
2cc
ppm


^{1}H NMR (600 MHz, d_6-DMSO/CS_2) of compound 2dd
Cl
2dd
ppm