Electronic Supplementary Information

Palladium-catalyzed decarboxylative [2 + 3] cyclocarbonylation reactions of [60]fullerene: selective synthesis of [60]fullerene-fused 3-vinylcyclopentan-4-ones and cyclopentane-4-carbaldehydes

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1. General Information

All reagents were purchased as reagent grade and used without further purification unless otherwise specified. $Pd(PPh_3)_4$ and $Pd(OAc)_2$/bis-sulfoxide (White's catalyst) were purchased from Sigma-Aldrich. Chlorobenzene (PhCl) and 1,2-Dichlorobenzene (ODCB) was treated with CaH_2. Substrates **1**[1] and **4**[2] were prepared by following the literature procedure. ^{1}H NMR (400 and 600 MHz) and ^{13}C NMR (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 CHI 660E. FT-IR was registered on Perkin Elmer 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) B. Yan, L. Zuo, X. Chang, T. Liu, M. Cui, Y. Liu, H. Sun, W. Chen and W. Guo, Kinetically controllable Pd-catalyzed decarboxylation enabled [5+2] and [3+2] cycloaddition toward carbocycles featuring quaternary carbons. *Org. Lett.*, 2021, **23**, 351.

(2) R. Shintani, K. Moriya and T. Hayashi, Guiding the nitrogen nucleophile to the middle: palladium-catalyzed decarboxylative cyclopropanation of 2-alkylidenetrimethylene carbonates ith isocyanates, *Chem. Commun.*, 2011**,** **47**, 3057.

2. Experimental Procedures

*General Procedure for the Synthesis of Products **2a–m**:* A dry 15-mL tube equipped with a magnetic stirrer was charged with C_{60} (36.0 mg, 0.05 mmol), **1** (0.10 mmol), $Pd(PPh_3)_4$ (2.9 mg, 0.005 mmol). After dissolving the solids in anhydrous PhCl (6 mL) and DCM (1 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 give product **2** (for **2b**, **2h**, **2m** and **2m'** with CS_2/DCM as the eluent).

*General Procedure for the Synthesis of Products **2m'**:* A dry 15-mL tube equipped with a magnetic stirrer was charged with C_{60} (36.0 mg, 0.05 mmol), **1m** (0.025 mmol, 10.1 mg), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol). After dissolving the solids in anhydrous PhCl (6 mL) and DCM (1 mL) by sonication, an oil bath at 70 ^oC for 9 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/DCM as the eluent to give unreacted C_{60} (3.9 mg, 11%) and the product **2m'** (7.3 mg, 17%).

*General Procedure for the Synthesis of Products **5a–l**:* A dry 15-mL tube equipped with a magnetic stirrer was charged with C_{60} (36.0 mg, 0.05 mmol), **4** (0.15 mmol), $Pd(OAc)_2$/bis-sulfoxide (0.005 mmol; 0.0075 mmol for **4b** and **4k**) and dppbz (0.01 mmol; 0.015 mmol for **4b** and **4k**). After dissolving the solids in anhydrous ODCB (4 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 **5a–l**.

*Large-scale Synthesis of **2g***: A dry 250-mL round-bottomed flask equipped with a magnetic stirrer was charged with C_{60} (720.0 mg, 1.0 mmol), **1g** (540.4 mg, 2.0 mmol), $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol). After dissolving the solids in anhydrous PhCl (120 mL) and DCM (20 mL) by sonication, the round-bottomed flask was stirred in an oil bath at 50 ^oC for 11 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} (204.3 mg) and the product **2g** (520.2 mg, 55%).

*Large-scale Synthesis of **5a***: A dry 250-mL round-bottomed flask equipped with a magnetic stirrer was charged with C_{60} (720.0 mg, 1.0 mmol), **4a** (570.6 mg, 3.0 mmol), $Pd(OAc)_2$/bis-sulfoxide (50.3 mg, 0.1 mmol) and dppbz (89.3 mg, 0.2 mmol). After dissolving the solids in anhydrous ODCB (70 mL) by sonication, the round-bottomed flask was stirred in an oil bath at 110 ^oC for 20 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} (276.5 mg) and the product **5a** (424.2 mg, 49%).

*Synthetic Application for **7g**:* A dry 15-mL tube equipped with a magnetic stirrer was charged with **2g** (38.4 mg, 0.04 mmol), $BH_3{\cdot}NH_3$ (4.9 mg, 0.16 mmol). After dissolving the solids in anhydrous PhCl (6 mL) and EtOH (6 mL) by sonication, the

round-bottomed flask was stirred in an oil bath at 0 ^{o}C for 20 min 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 to give the product **7g** (*cis*-isomer: 10.4 mg, 27%; *trans*-isomer: 25.4 mg, 66%).

*Synthetic Application for **8a**:* A dry 15-mL tube equipped with a magnetic stirrer was charged with **5a** (34.7 mg, 0.04 mmol), $BH_3{\cdot}NH_3$ (4.9 mg, 0.16 mmol). After dissolving the solids in anhydrous CB (6 mL) and EtOH (6 mL) by sonication, the round-bottomed flask was stirred in an oil bath at 0 ^{o}C for 20 min 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 to give the quantitative product **8a**.

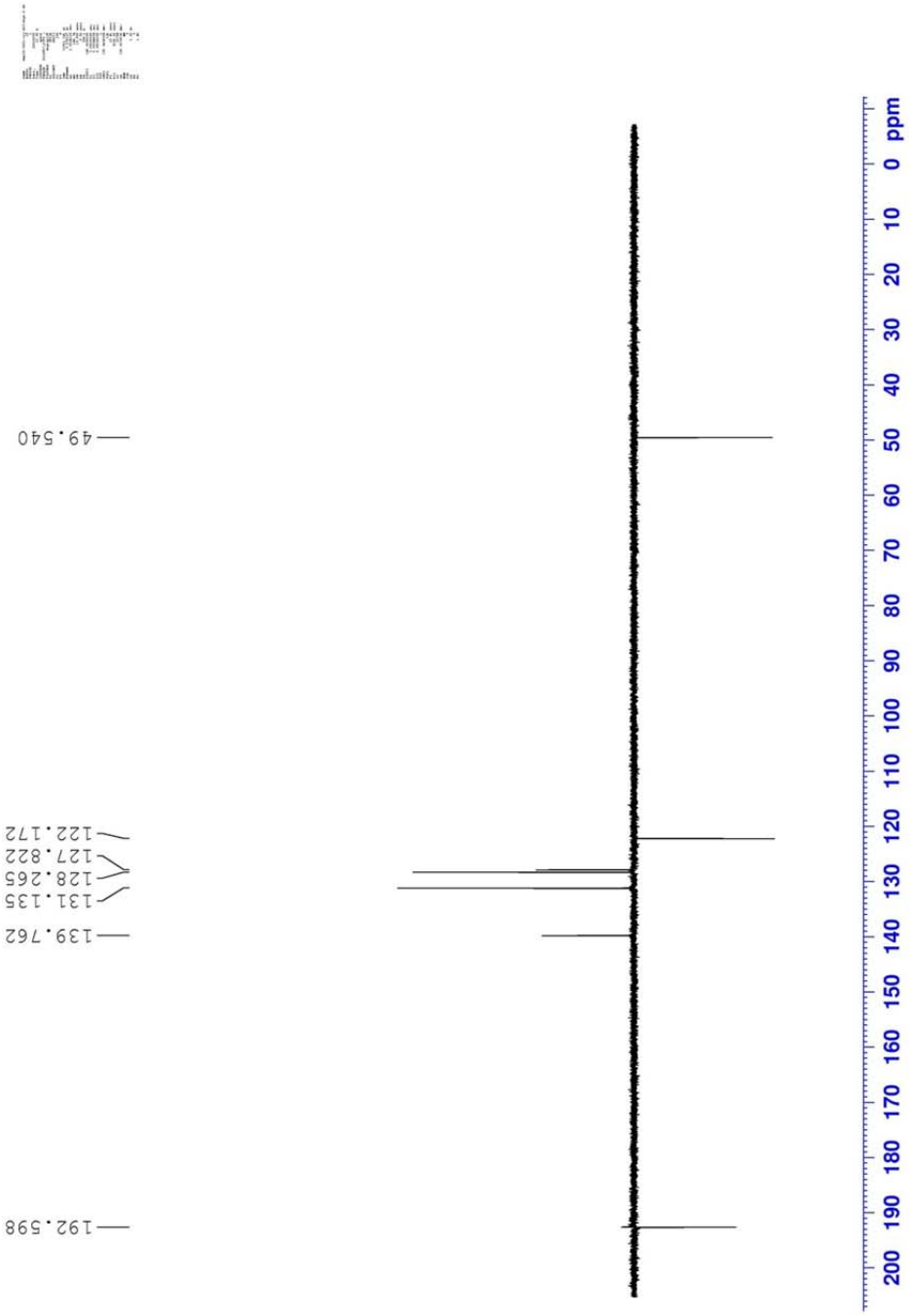
*Synthetic Application for **9a***: A dry 15-mL tube equipped with a magnetic stirrer was charged with **5a** (35.0 mg, 0.04 mmol), Dess-Martin periodinane (86.8 mg, 0.20 mmol). After dissolving the solids in anhydrous PhCl (6 mL) by sonication, the round-bottomed flask was stirred in an oil bath at 80 ^{o}C for 4 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 **5a** (3.3 mg, 9%), and then the eluent was switched to CS_2/DCM/EA to give the product **9a** (30.0 mg, 85%).

Procedures for Electrochemical Characterization Recording: In a dry 15-mL electrolytic cup, 2.0×10^{-3} mmol of product **2** (**5**), 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

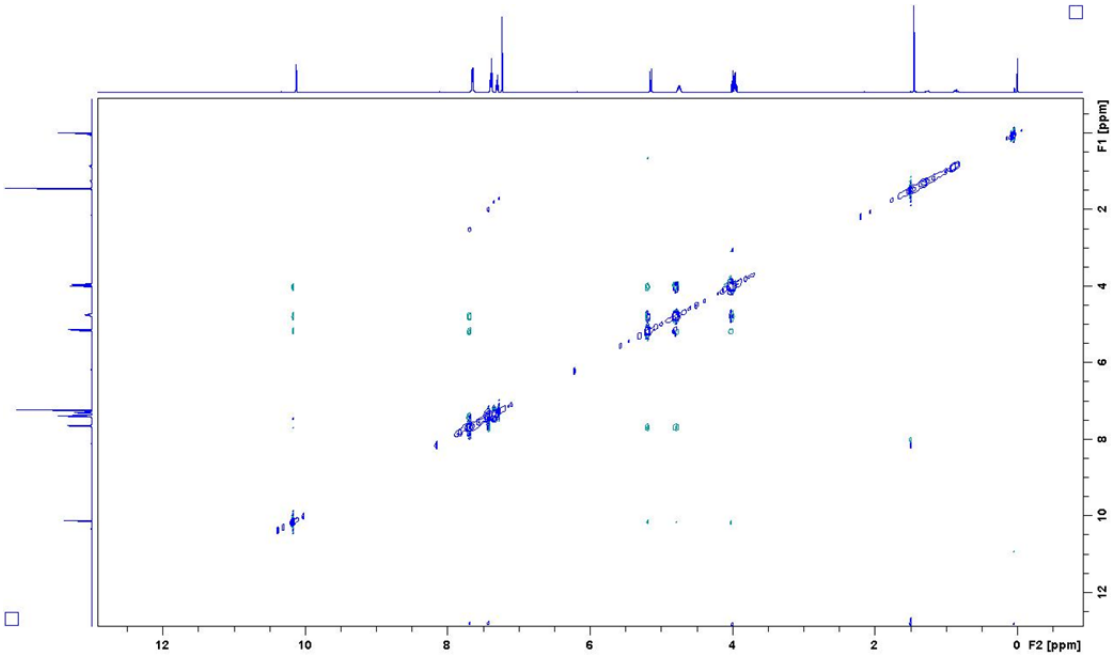
(reference electrode: SCE; working electrode: Pt; auxiliary electrode: Pt wire) were placed in the sample solution, then running electrochemical workstation recorded the cyclic voltammogram (CV) of product **2** (**5**) under an argon atmosphere.

Procedures for UV-vis Spectra Recording: A dry 100-mL volumetric flask was charged with the product **2** (**5**) (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 **2** (**5**).

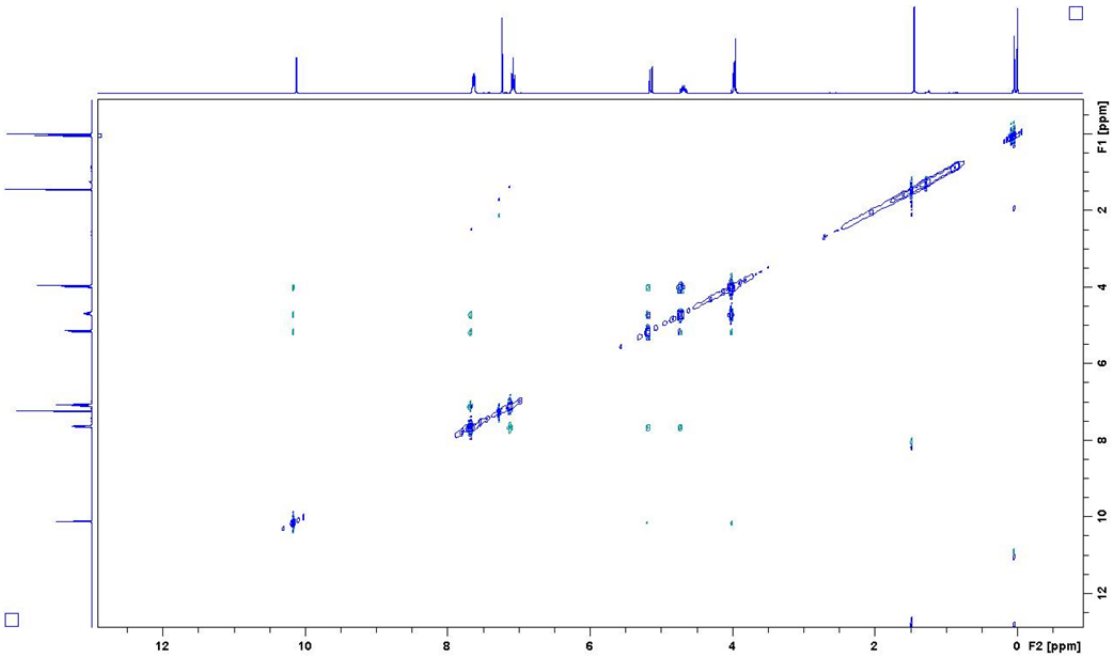
3. DEPT-135 Spectra of Compound 2a



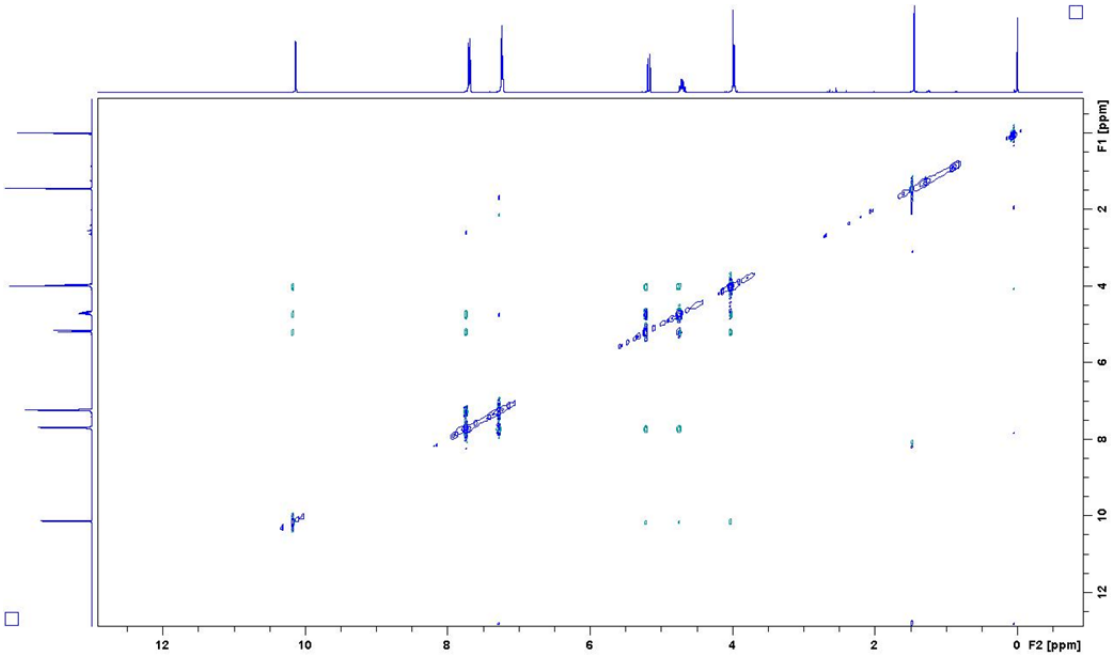
4. 2D-NOESY Spectra of Compounds 5a, 5d, 5i, *cis*- and *trans*-7g



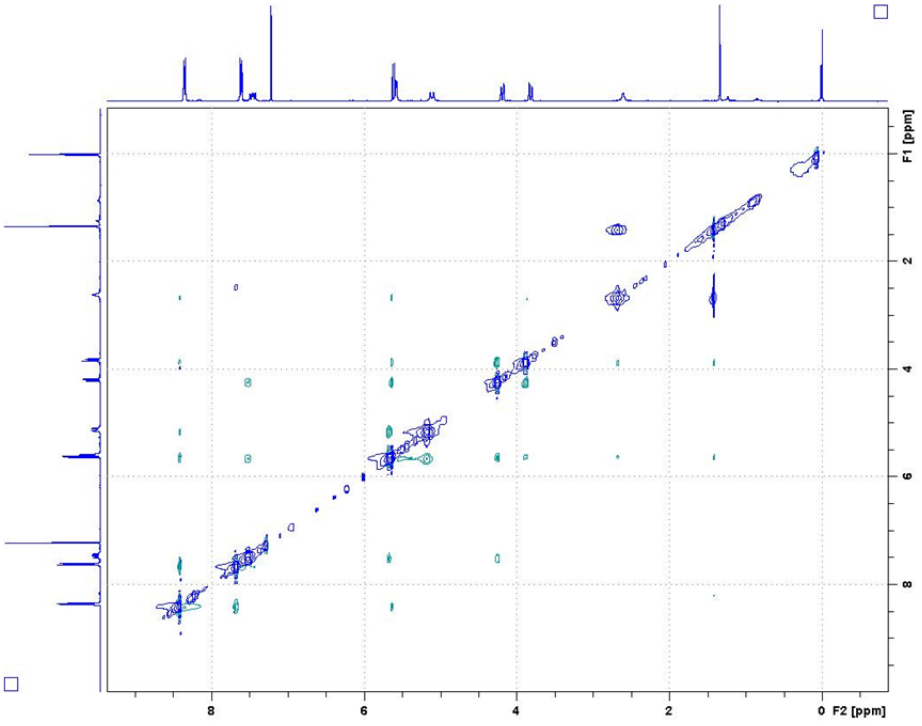
2D-NOESY Spectra of **5a** ($CDCl_3/CS_2$)



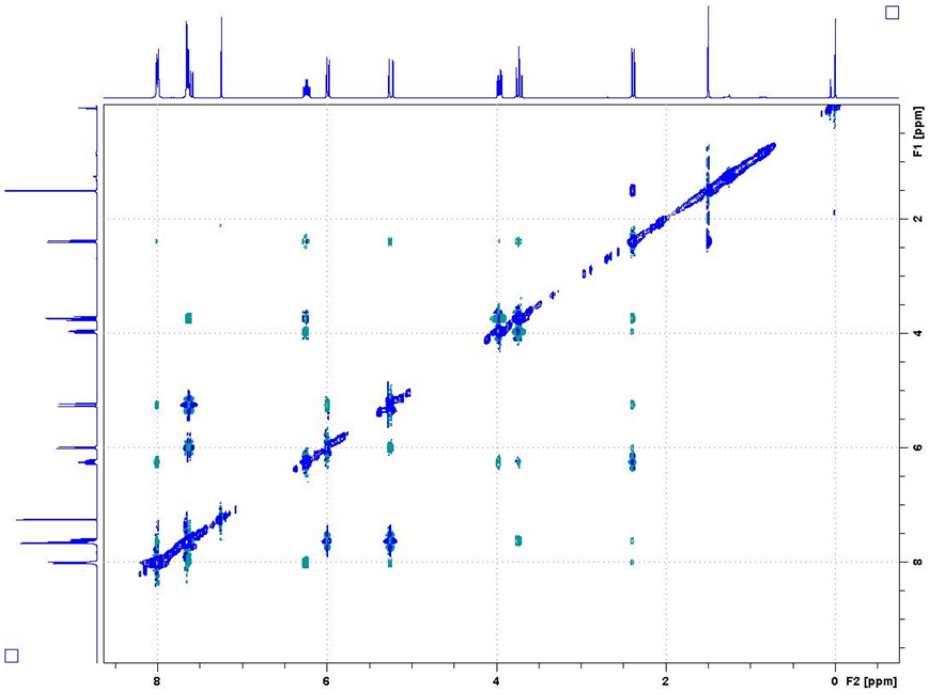
2D-NOESY Spectra of **5d** ($CDCl_3/CS_2$)



2D-NOESY Spectra of **5i** ($CDCl_3/CS_2$)

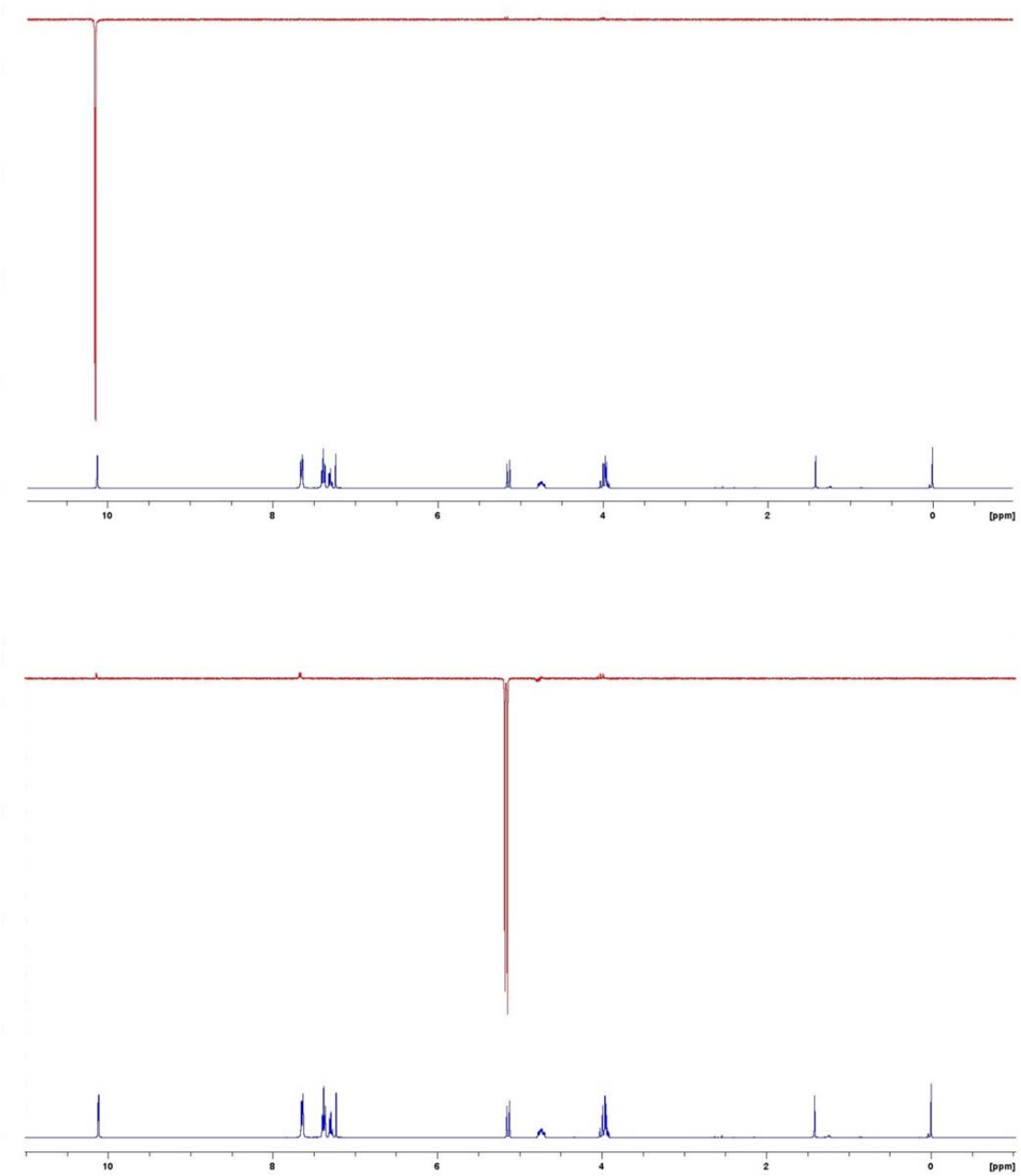


2D-NOESY Spectra of *cis*-**7g** ($CDCl_3/CS_2$)

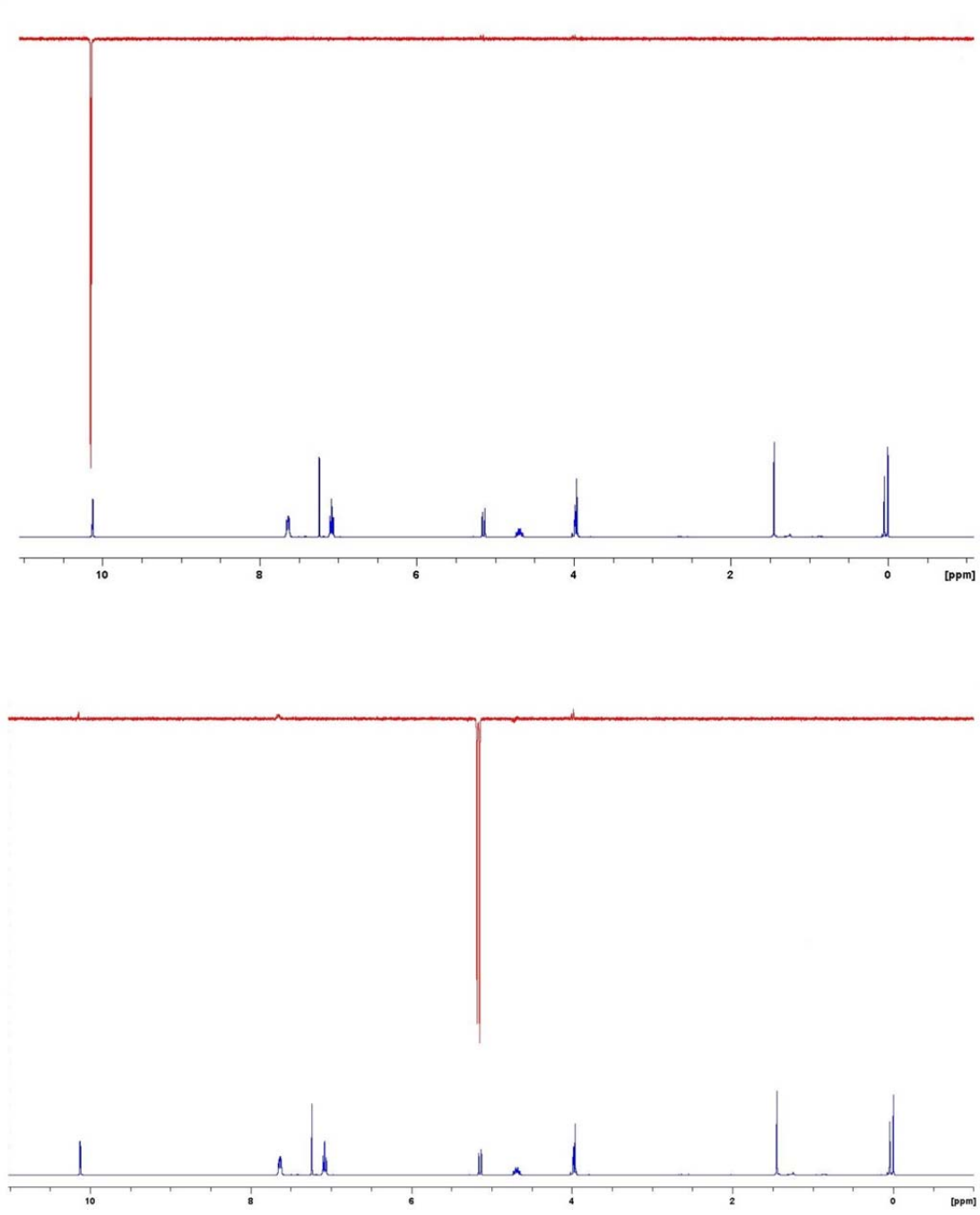


2D-NOESY Spectra of *trans*-**7g** ($CDCl_3/CS_2$)

5. 1D-NOESY ^{1}H NMR of 5a, 5d, 5i, 8a and 9a



1D-NOESY ^{1}H NMR of **5a** (600 MHz, $CDCl_3/CS_2$)



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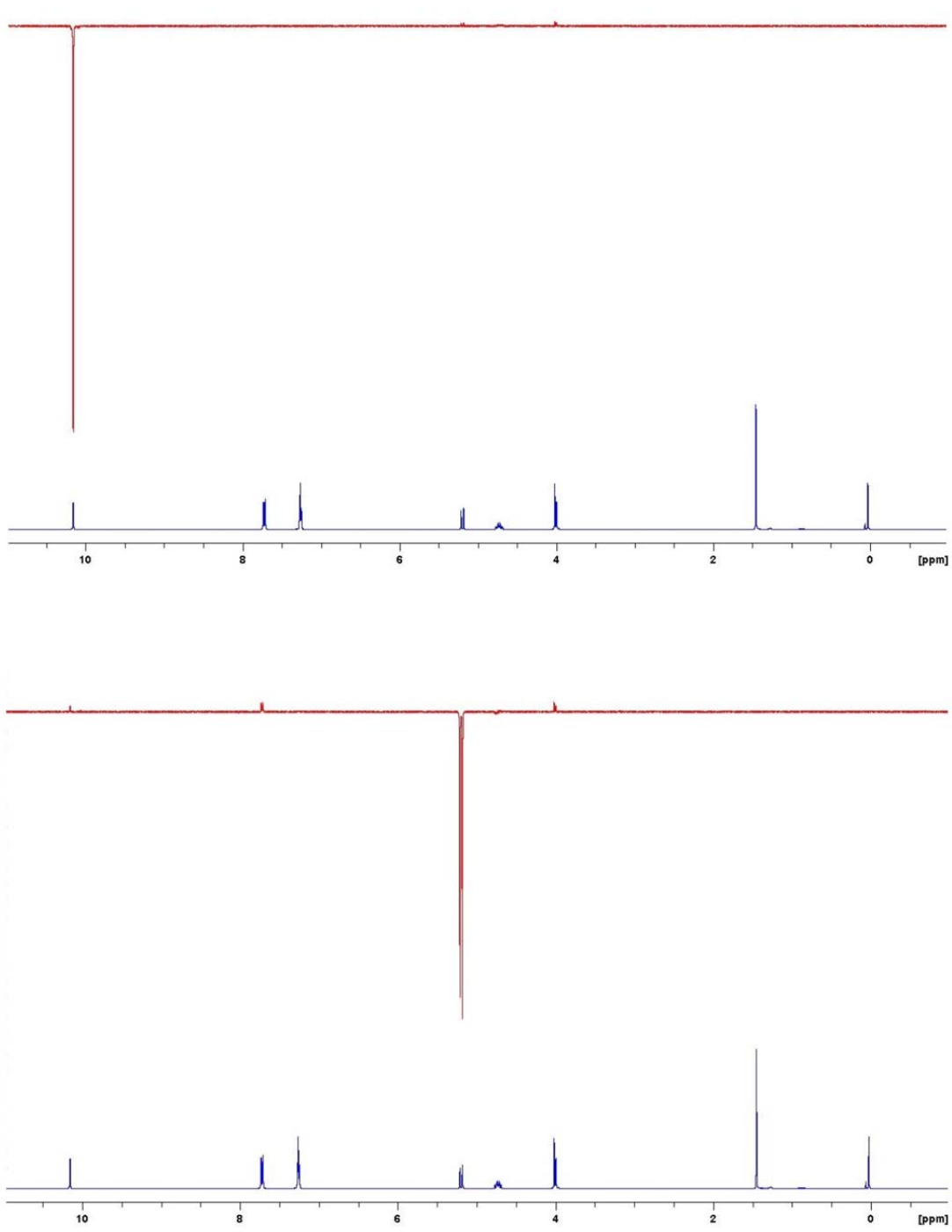
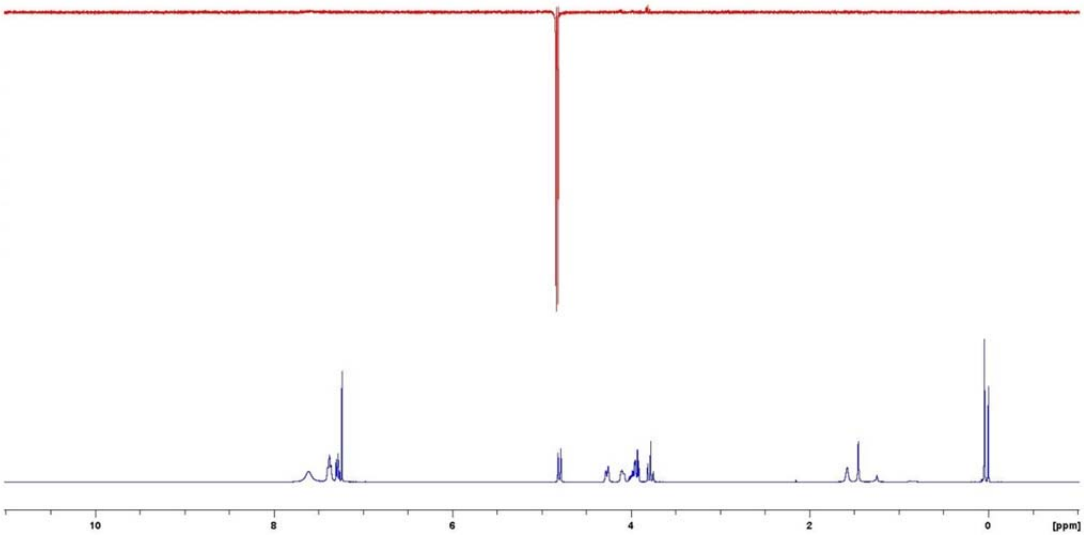
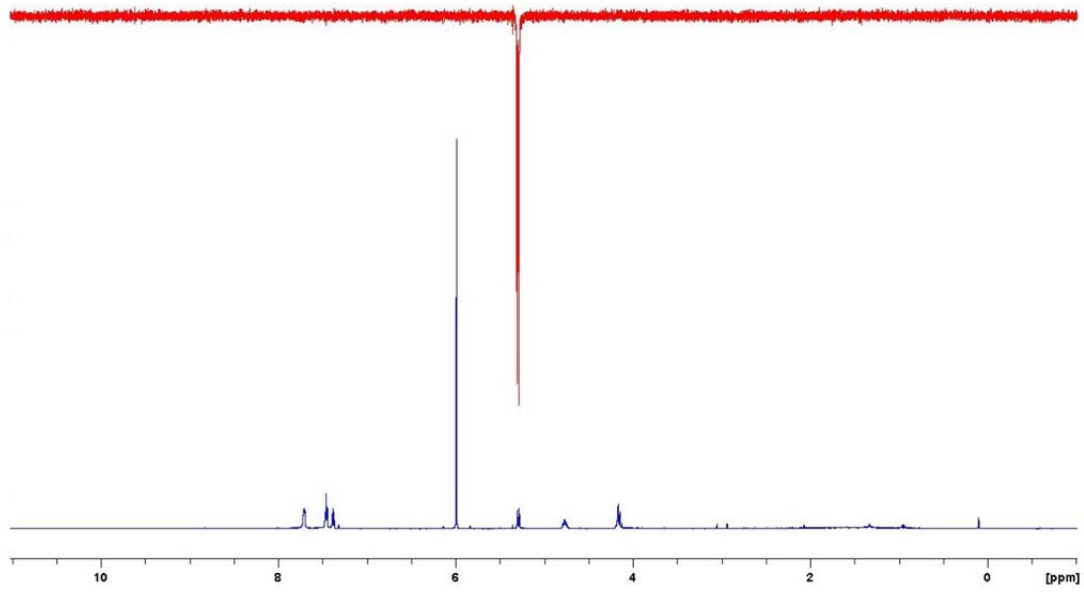


1D-NOESY ^{1}H NMR of **5i** (600 MHz, $CDCl_3/CS_2$)

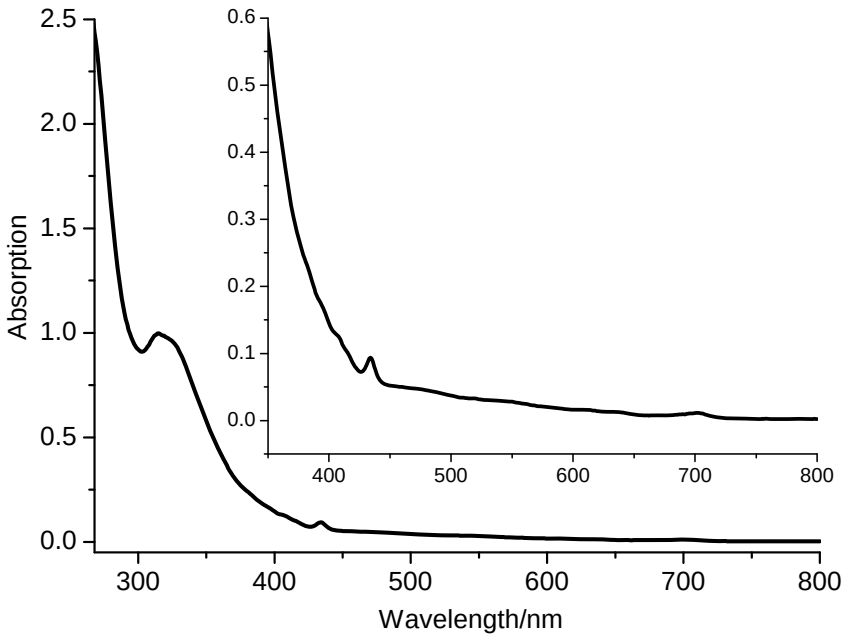


1D-NOESY ^{1}H NMR of **8a** (600 MHz, $CDCl_3/CS_2$)

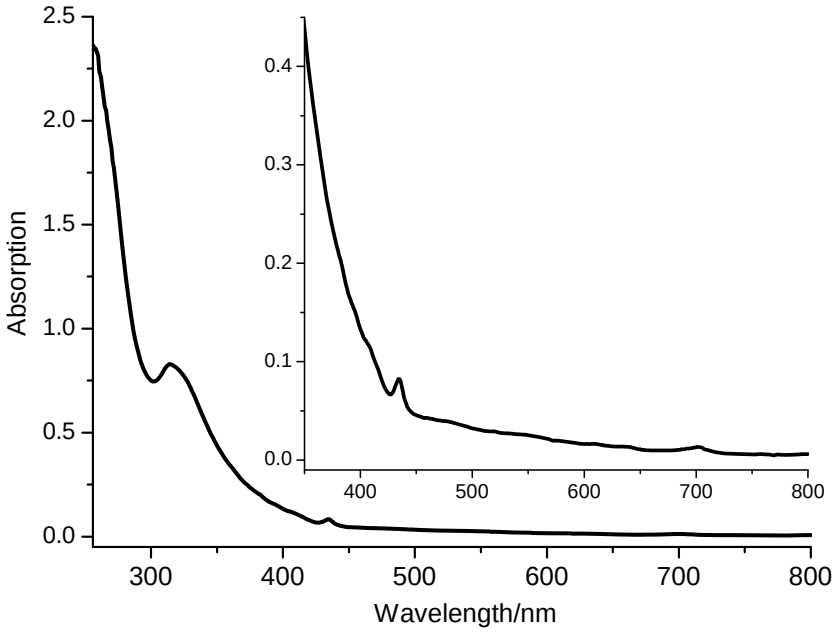


1D-NOESY ^{1}H NMR of **9a** (600 MHz, CD_2Cl_4/CS_2)

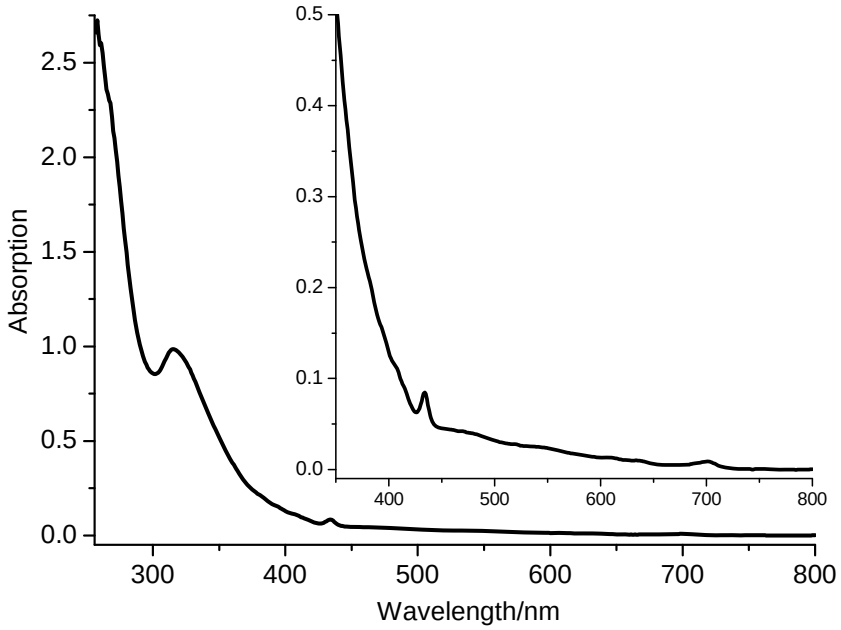
6. UV–vis Spectra of Compounds 2 and 5



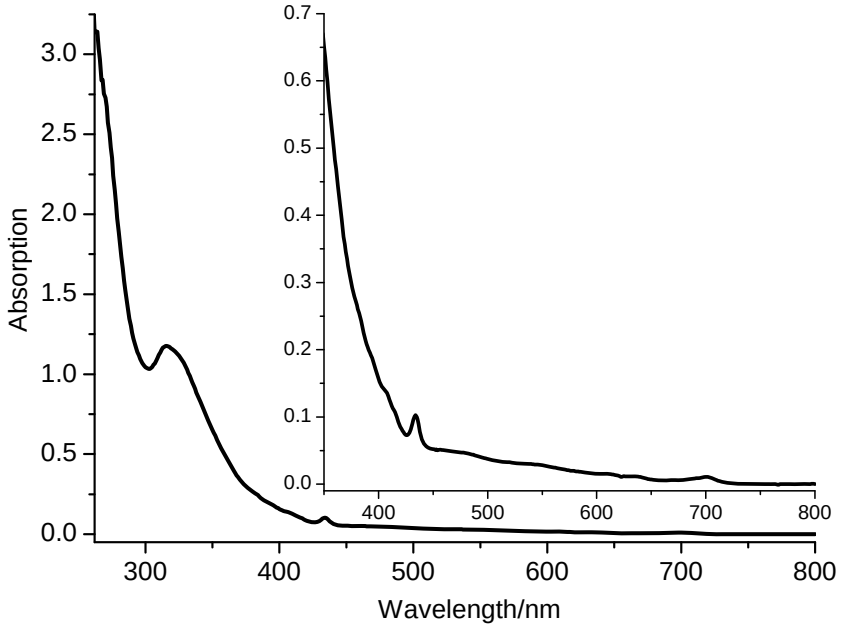
UV–vis spectrum of compound **2a** in $CHCl_3$



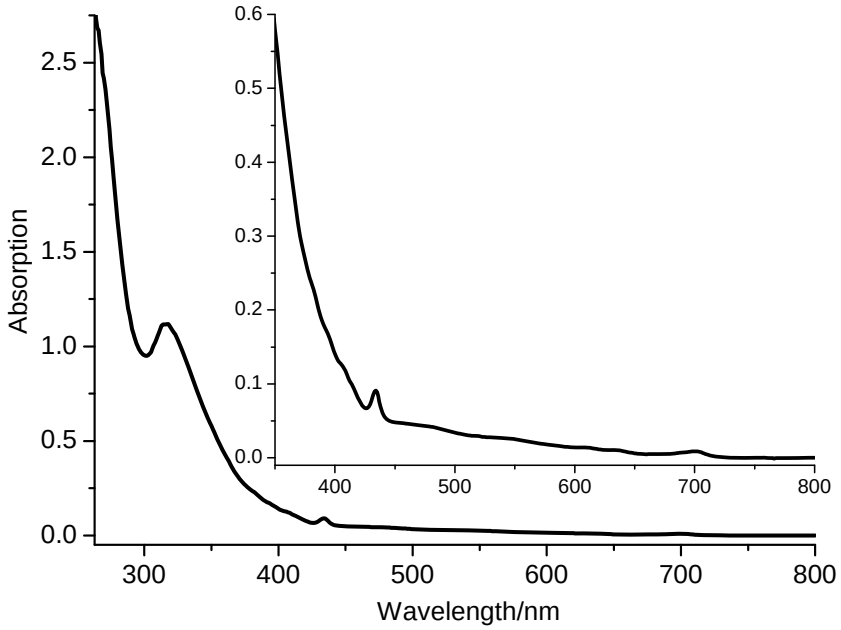
UV–vis spectrum of compound **2b** in $CHCl_3$



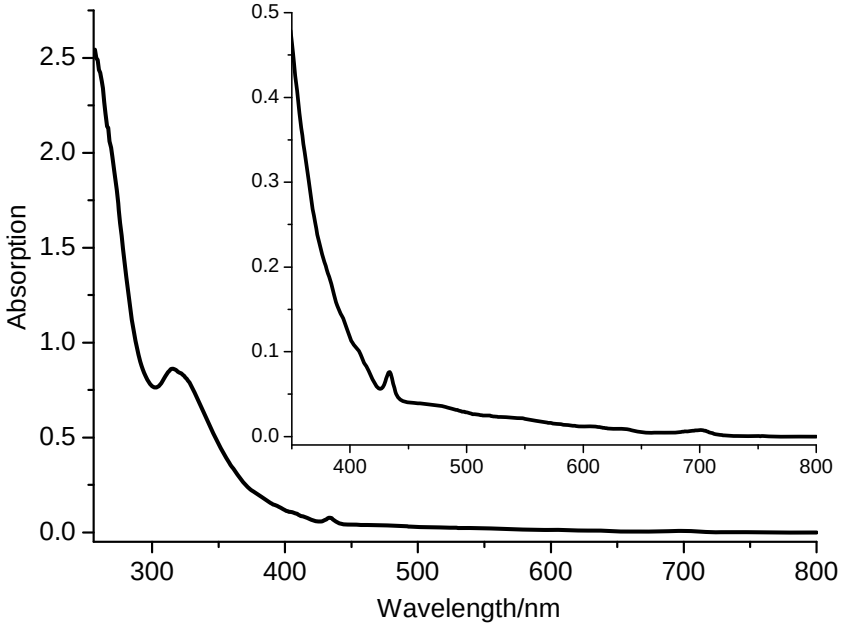
UV–vis spectrum of compound **2c** in $CHCl_3$



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



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



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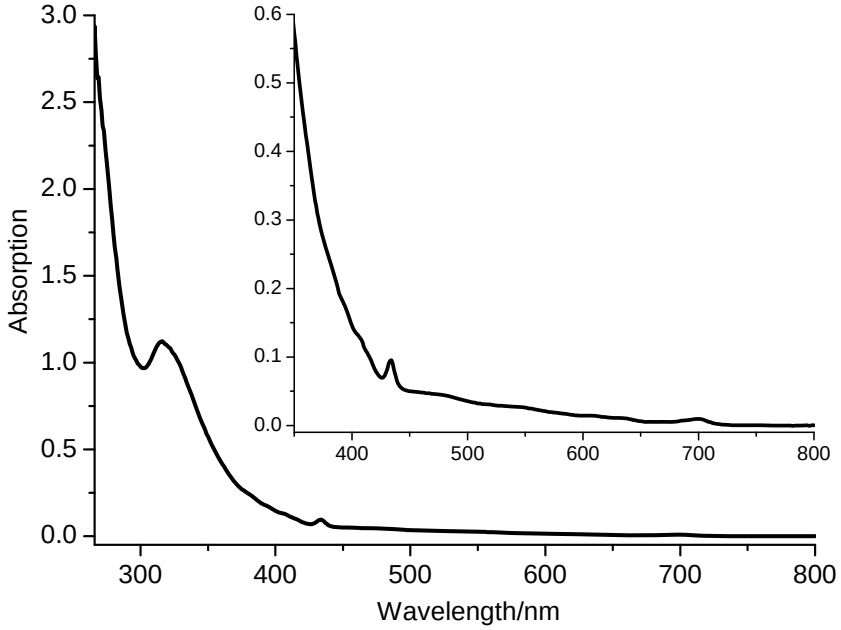
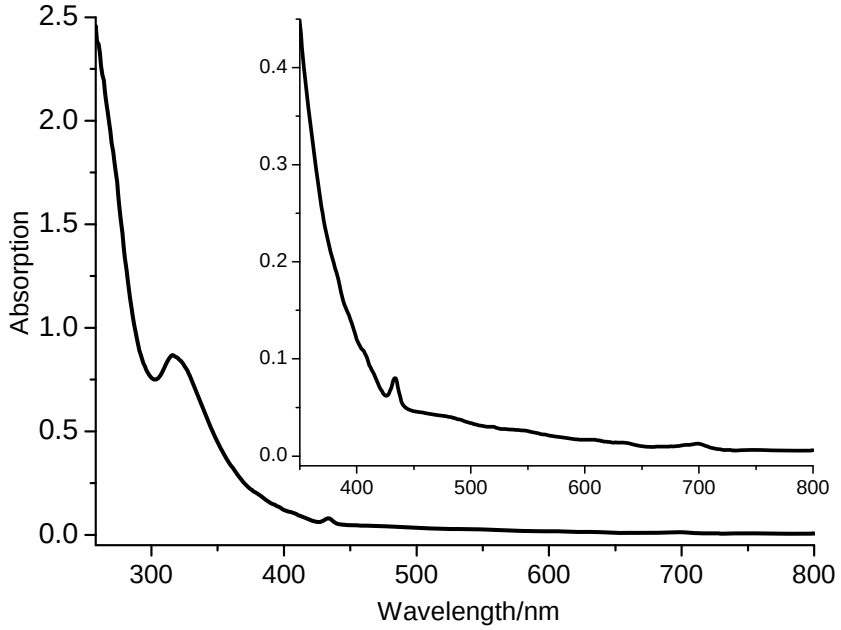
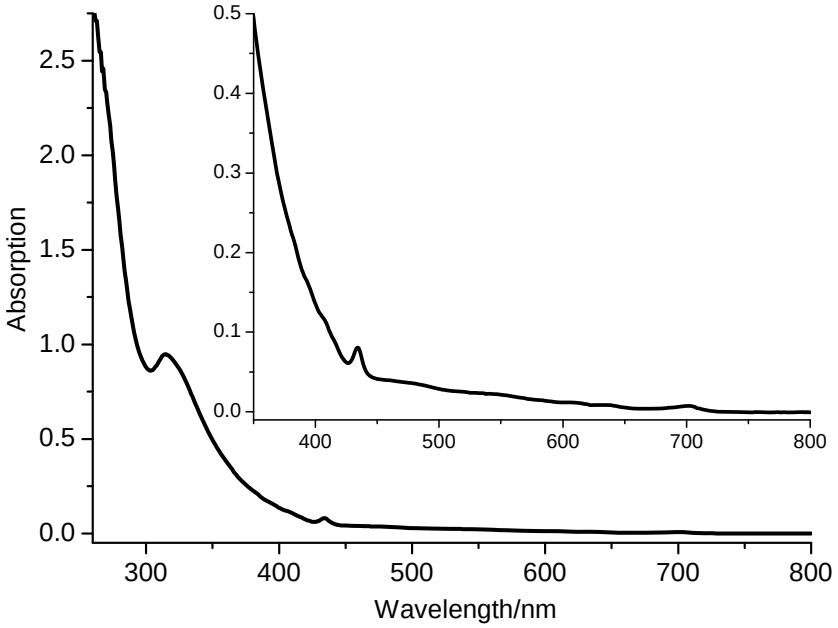


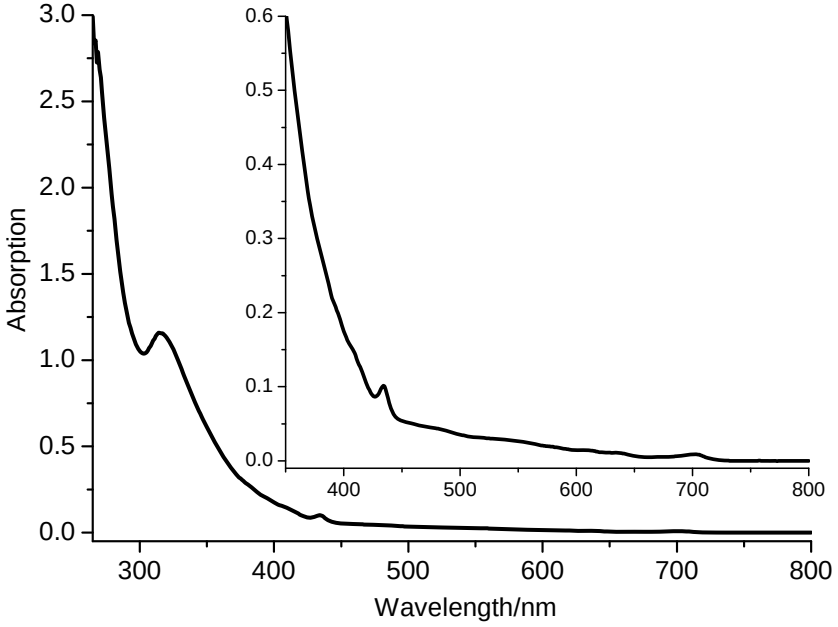
UV–vis spectrum of compound **2g** in $CHCl_3$



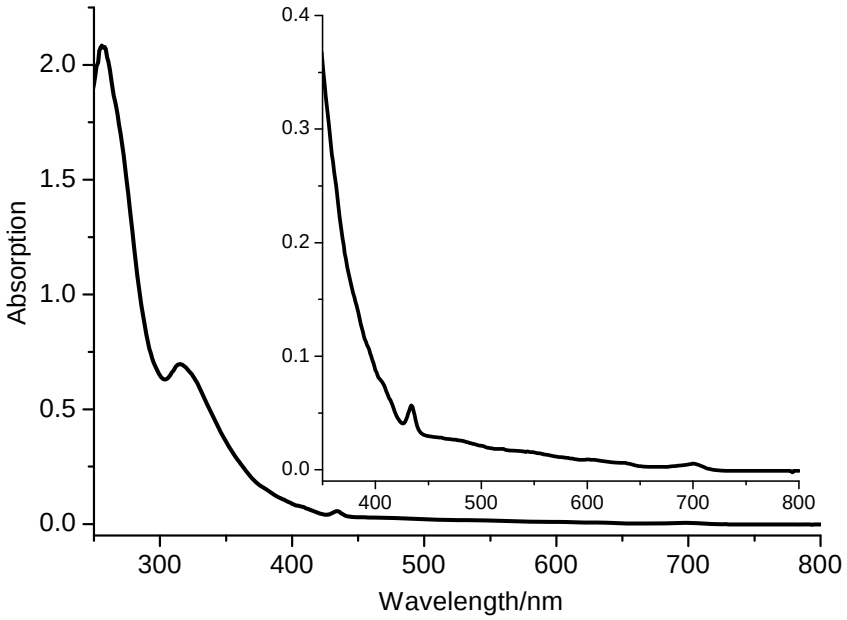
UV–vis spectrum of compound **2h** in $CHCl_3$



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



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



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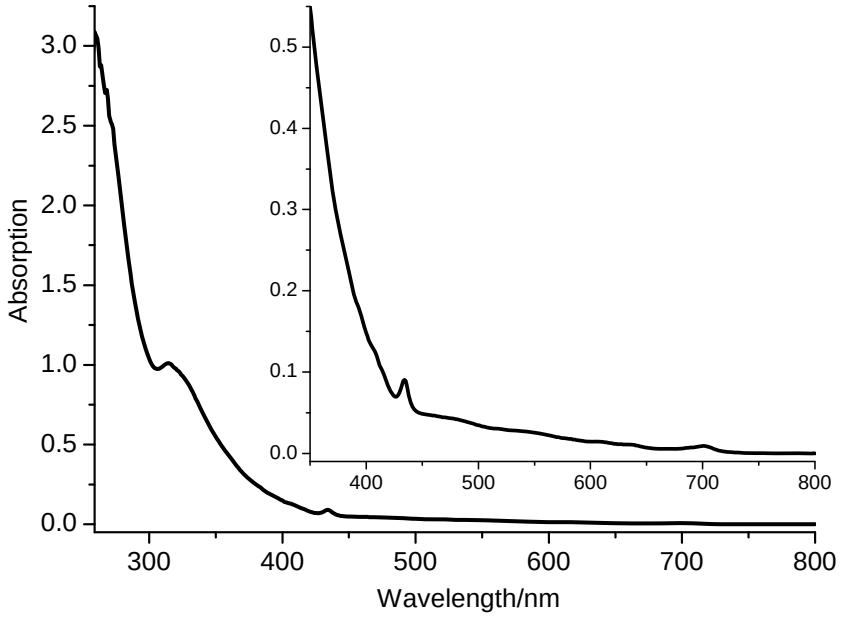
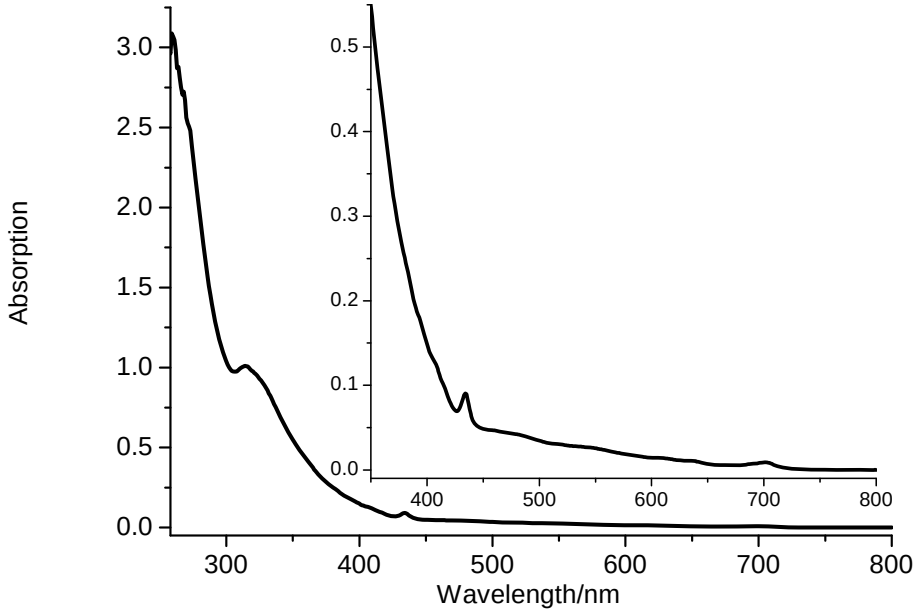
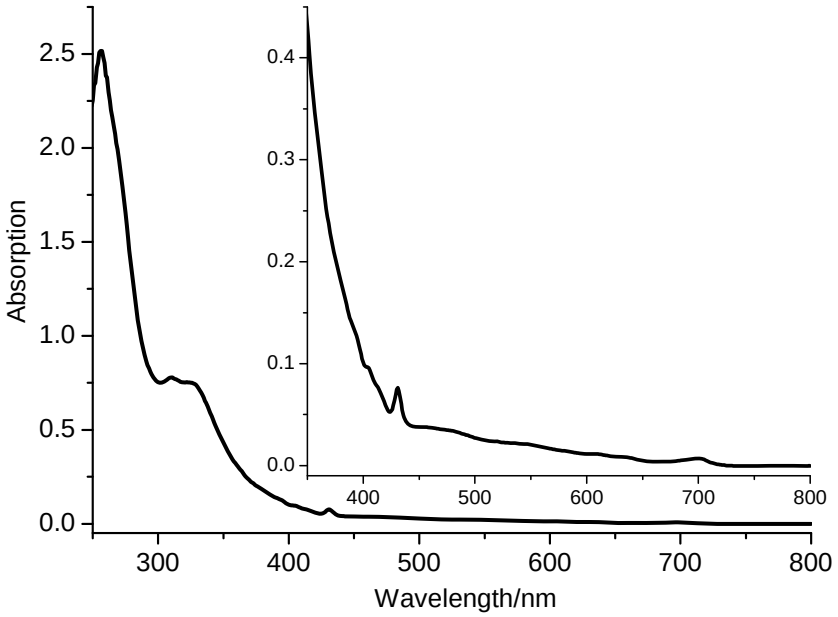


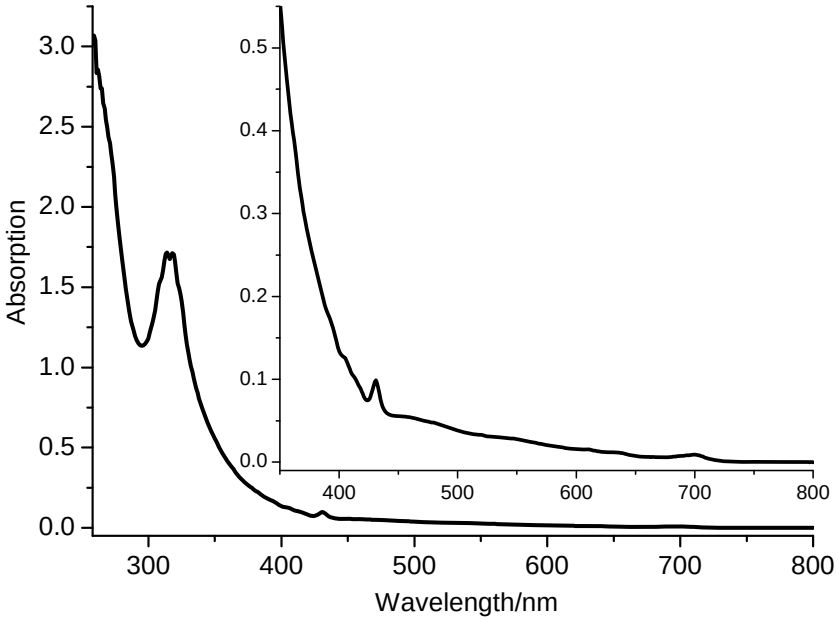
UV–vis spectrum of compound **2m** in $CHCl_3$



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



UV–vis spectrum of compound **5a** in $CHCl_3$



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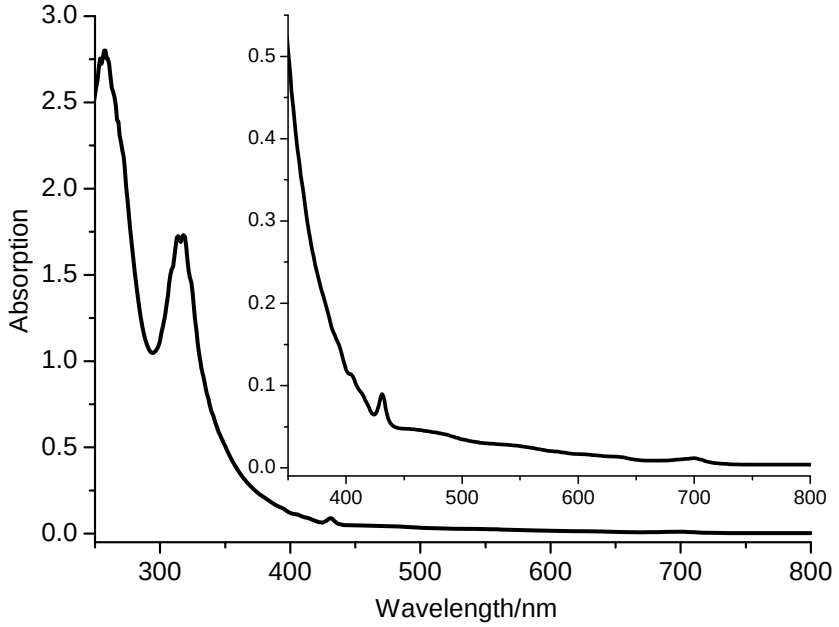
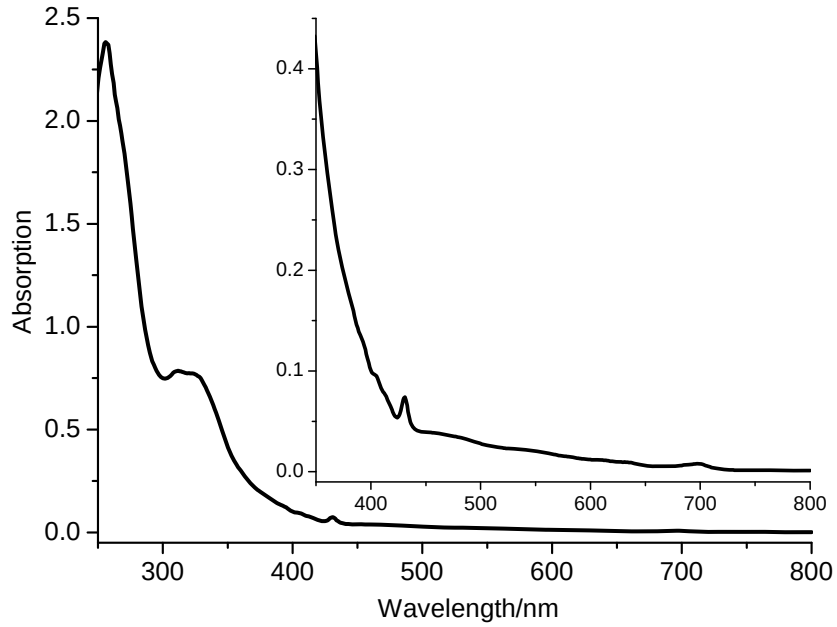
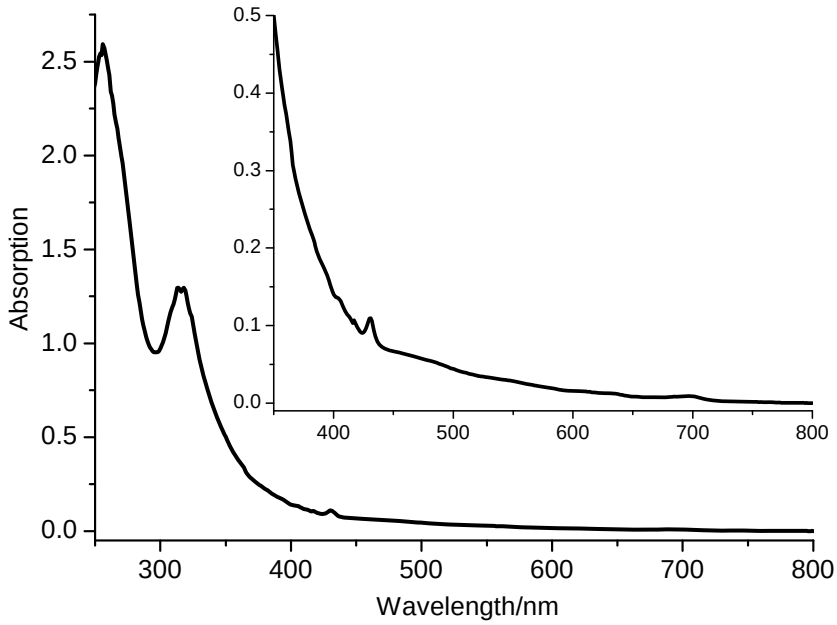


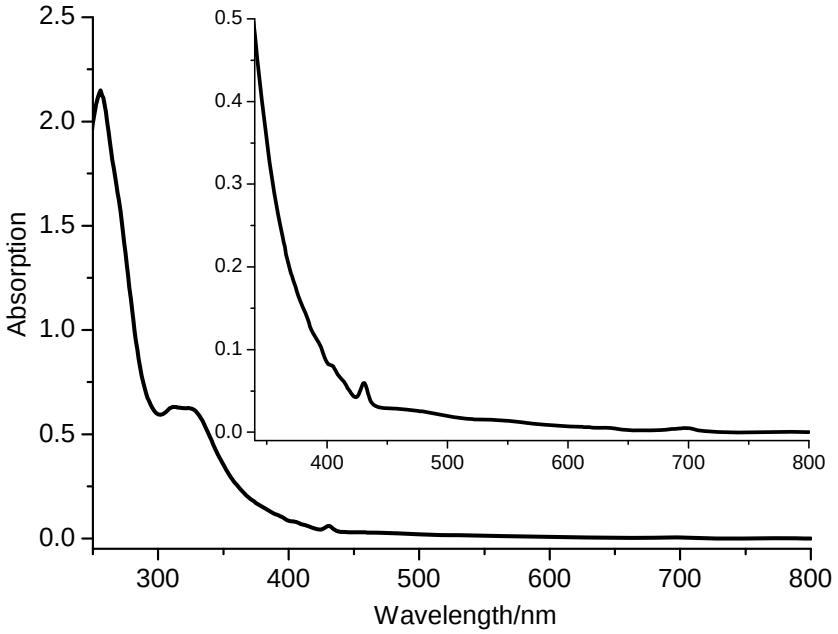
UV–vis spectrum of compound **5c** in $CHCl_3$



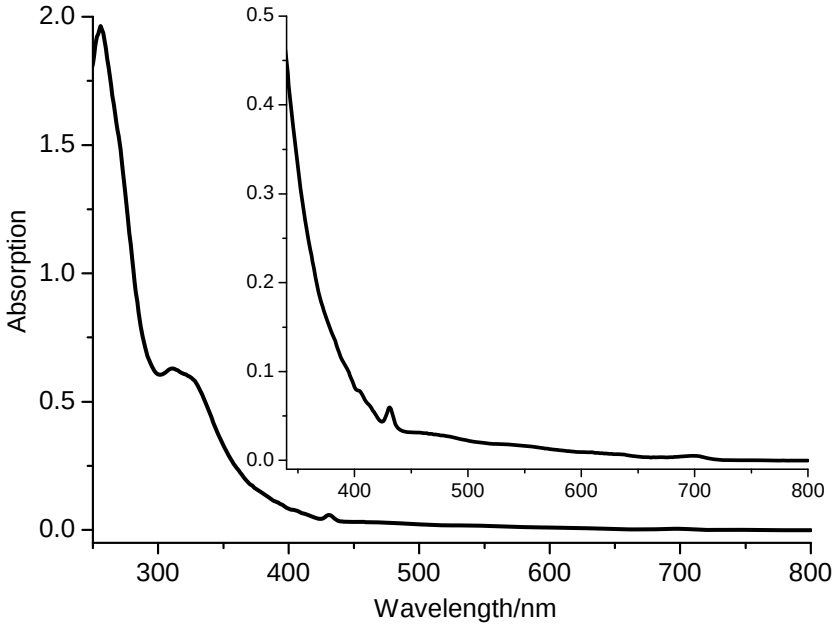
UV–vis spectrum of compound **5d** in $CHCl_3$



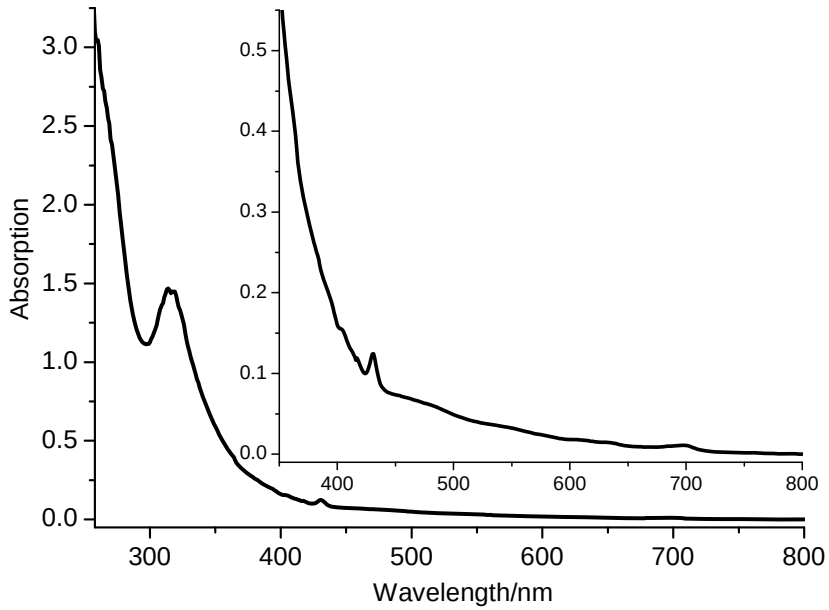
UV–vis spectrum of compound **5e** in $CHCl_3$



UV–vis spectrum of compound **5f** in $CHCl_3$



UV–vis spectrum of compound **5g** in $CHCl_3$



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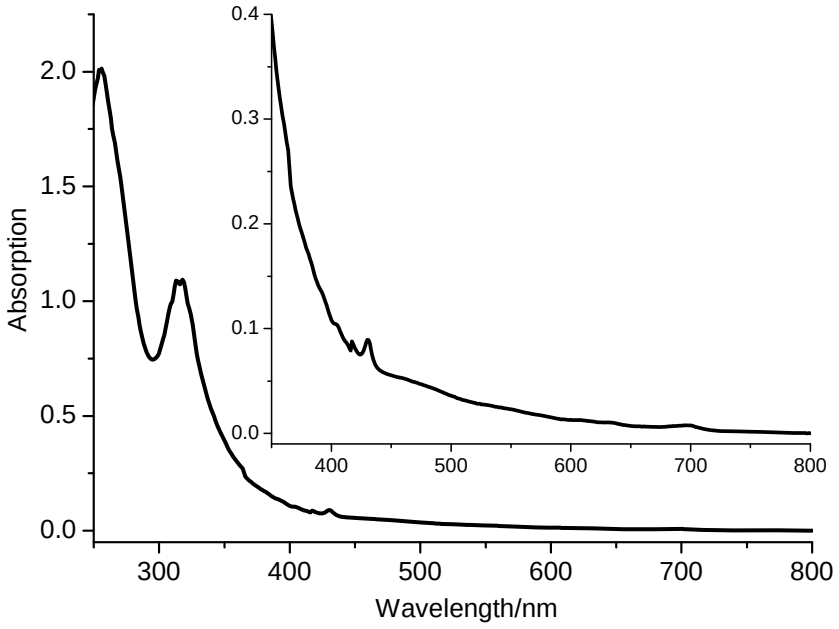

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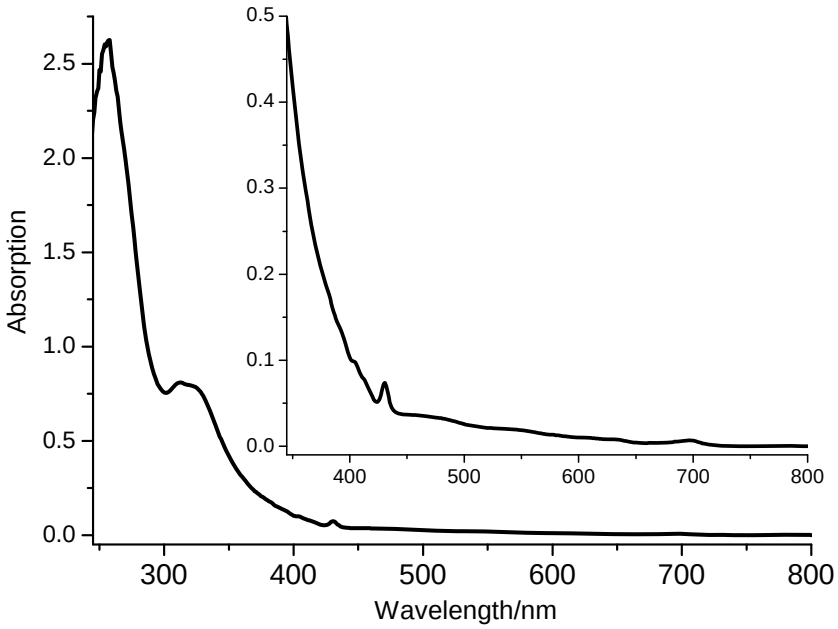

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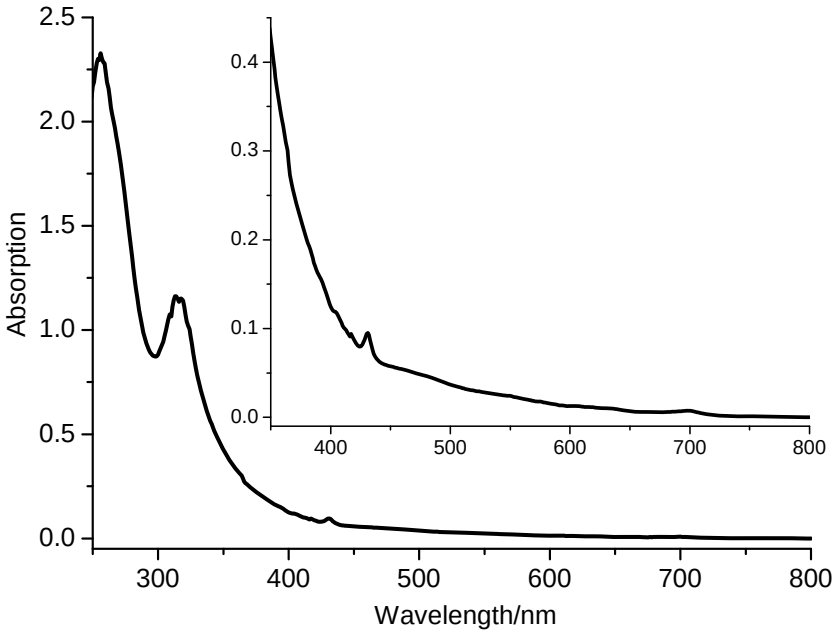

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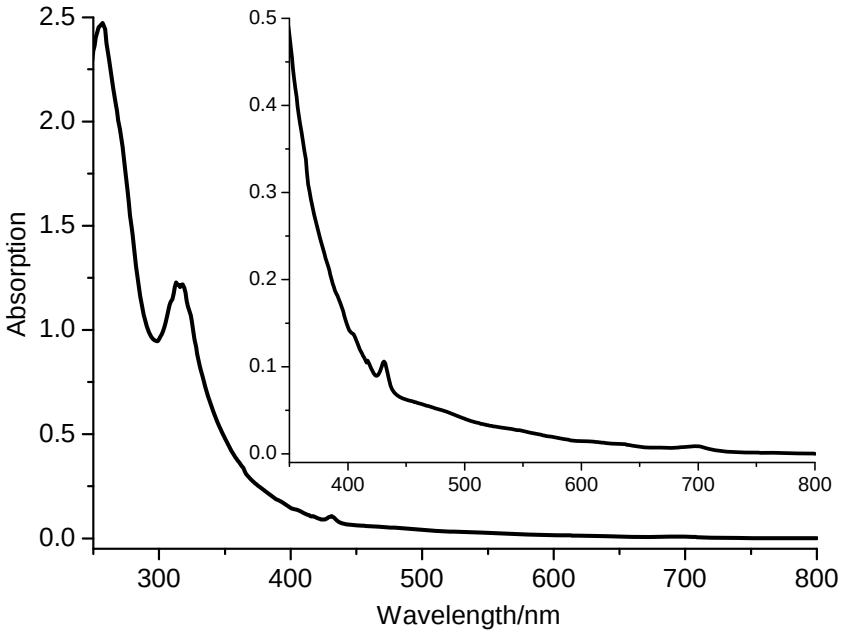
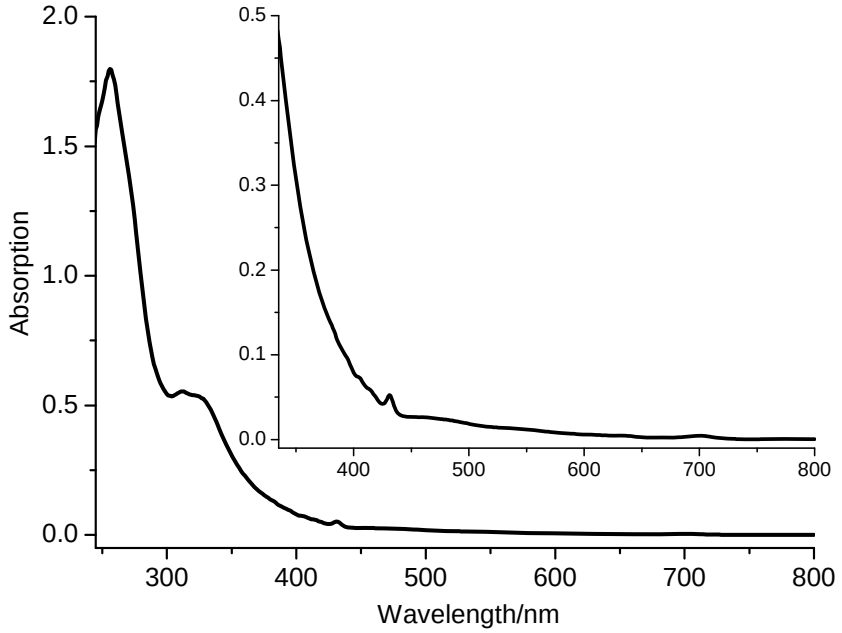
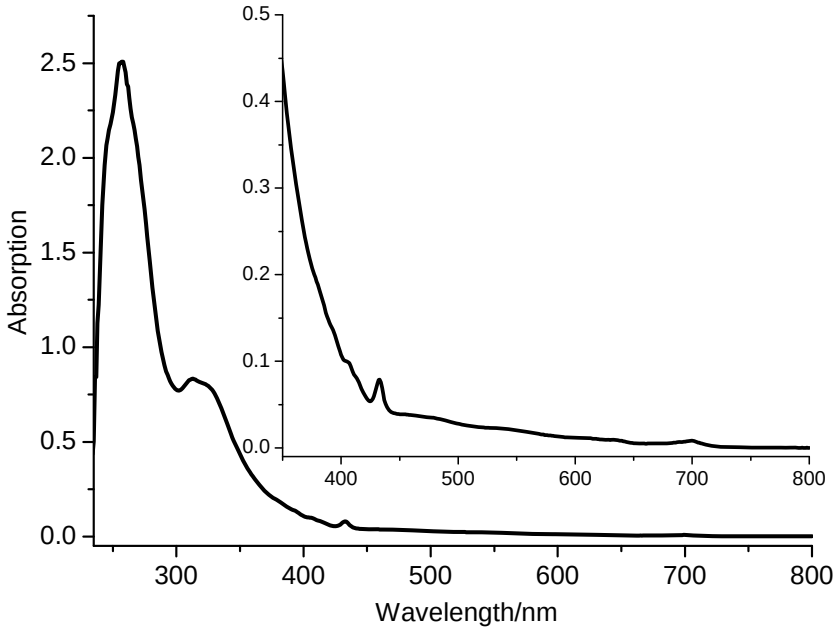


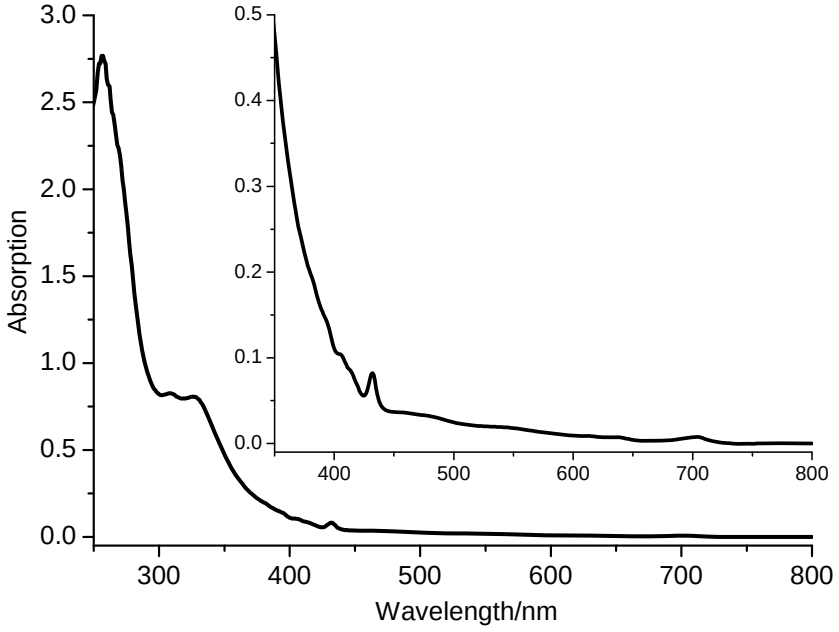
UV–vis spectrum of compound **5l** in $CHCl_3$



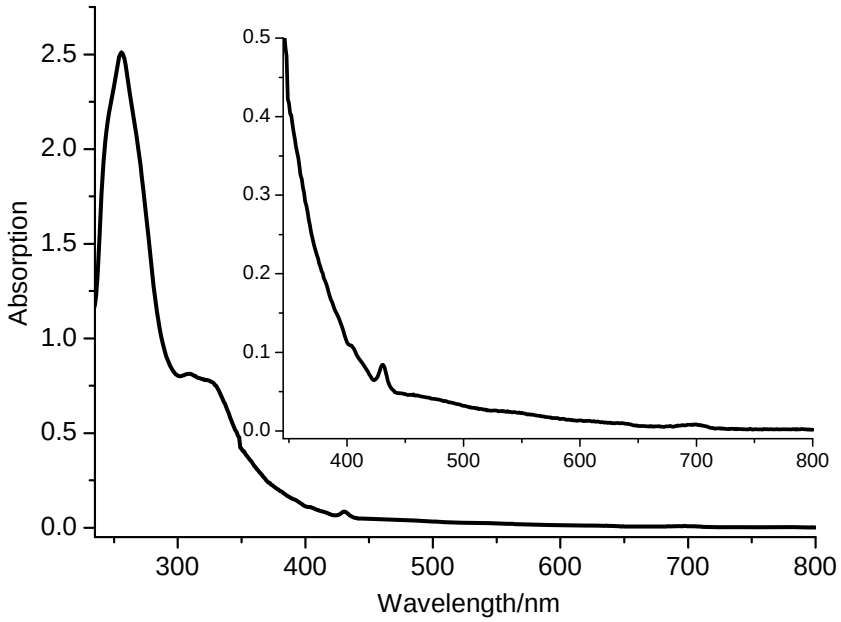
UV–vis spectrum of compound *cis*-**7g** in $CHCl_3$



UV–vis spectrum of compound *trans*-**7g** in $CHCl_3$



UV–vis spectrum of compound **8a** in $CHCl_3$



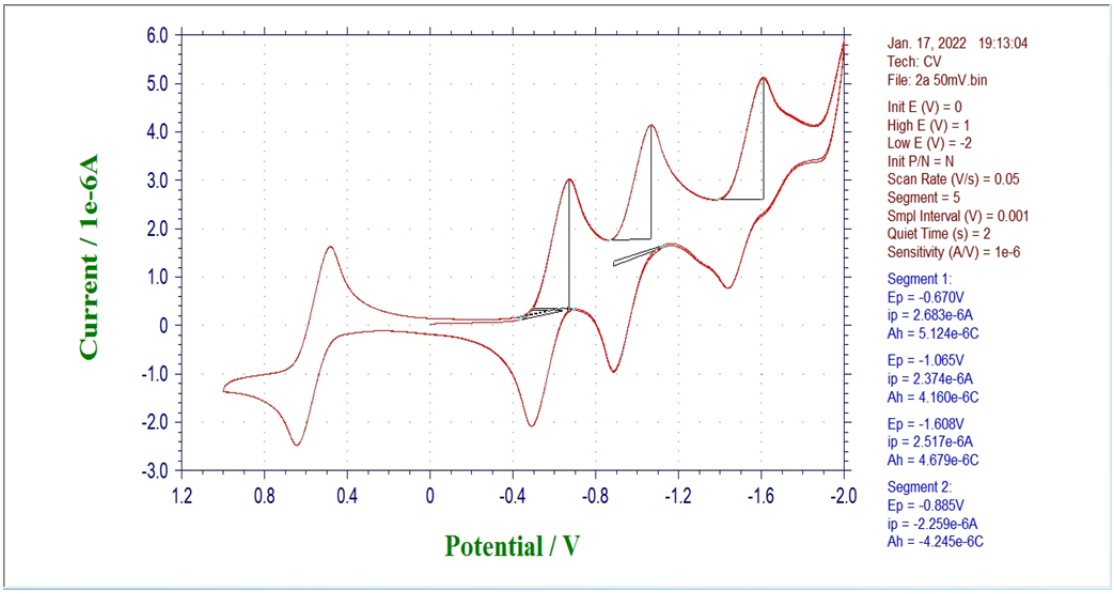
UV–vis spectrum of compound **9a** in $CHCl_3$

7. CVs of Selected Compounds 2 and 5

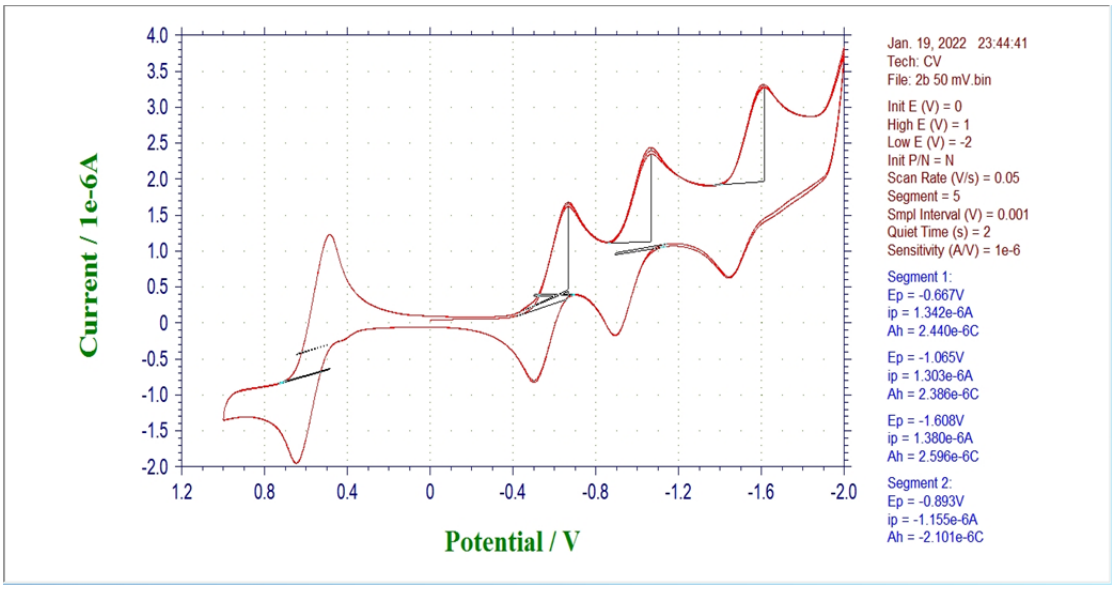
Table S1. Half-Wave Reduction Potentials of compounds 2, 5, PCBM and C_{60}[a]

Compound	E_1	E_2	E_3	*LUMO*
2a	–1.145	–1.543	–2.087	–3.655
2b	–1.151	–1.547	–2.093	–3.650
2c	–1.149	–1.555	–2.103	–3.651
2d	–1.152	–1.574	–2.136	–3.648
2e	–1.132	–1.524	–2.062	–3.668
2f	–1.154	–1.569	–2.121	–3.647
2g	–1.130	–1.518	–2.051	–3.670
2h	–1.134	–1.557	–2.118	–3.666
2i	–1.153	–1.560	–2.112	–3.647
2j	–1.145	–1.535	–2.080	–3.655
2k	–1.141	–1.551	–2.091	–3.660
5a	–1.171	–1.565	–2.110	–3.629
5b	–1.184	–1.593	–2.145	–3.616
5c	–1.180	–1.578	–2.124	–3.620
5d	–1.169	–1.574	–2.120	–3.631
5e	–1.174	–1.583	–2.136	–3.626
5f	–1.173	–1.573	–2.112	–3.627
5g	–1.164	–1.564	–2.107	–3.636
5h	–1.171	–1.583	–2.137	–3.629
5i	–1.159	–1.560	–2.109	–3.641
5j	–1.154	–1.548	–2.078	–3.646
5k	–1.169	–1.567	–2.112	–3.631
5l	–1.166	–1.551	–2.090	–3.634
PCBM	–1.180	–1.581	–2.110	–3.620
C_{60}	–1.088	–1.490	–1.973	–3.712

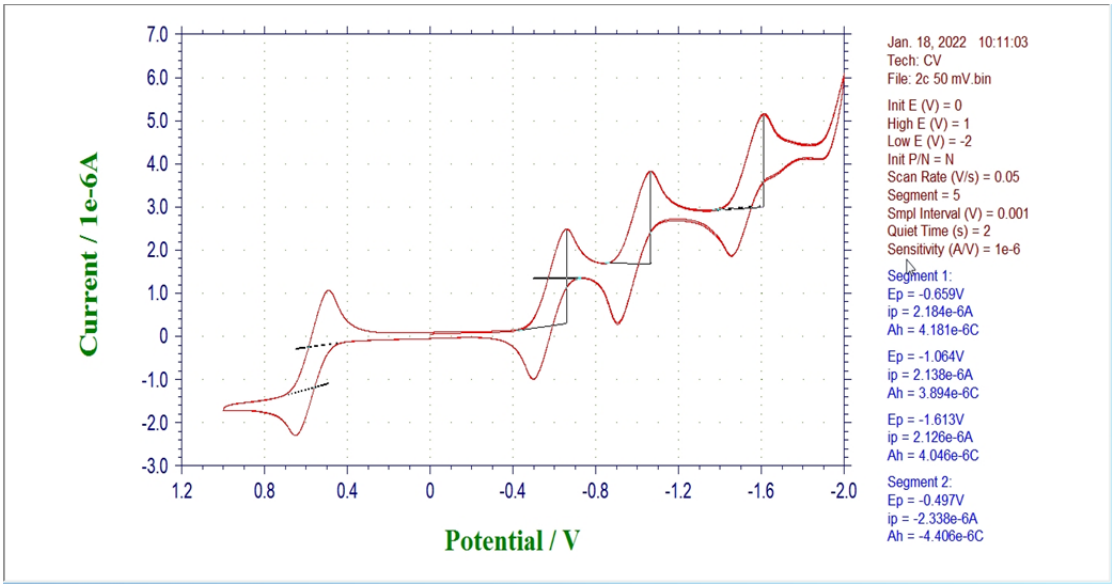
[a]Versus ferrocene/ferrocenium; experimental conditions: 1 mM of compounds **2** (**5**) and 0.1 M of $(n\text{-Bu})_4NClO_4$ in anhydrous *o*-dichlorobrnzene; referene electrode: SCE; working electrode: Pt; auxiliary electrode: Pt wire; scanning rate: 50 mV s^{-1}.



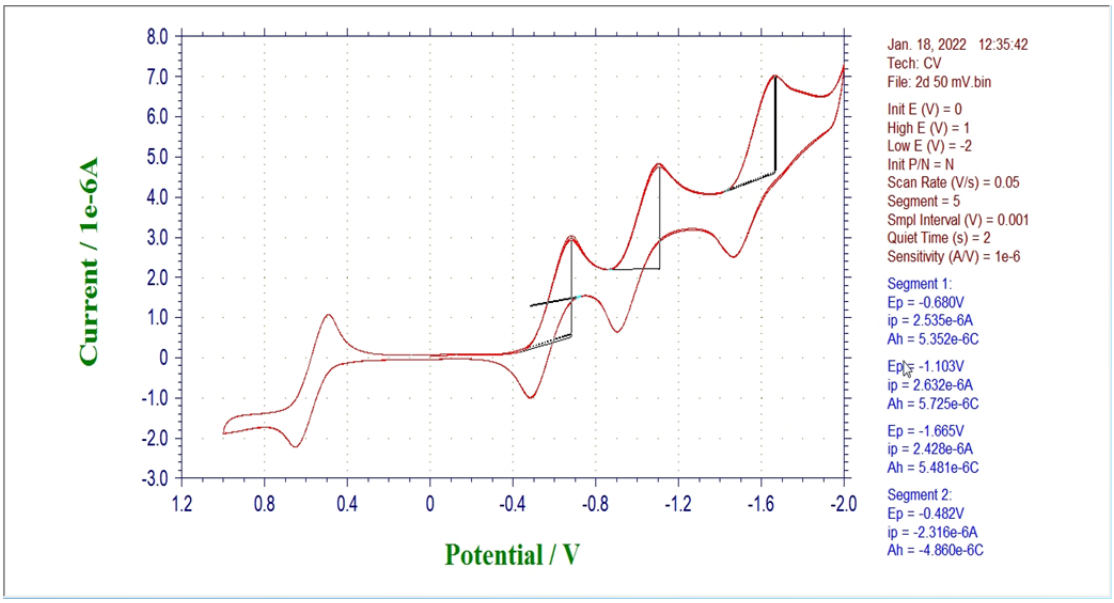
Cyclic voltammogram of compound **2a** (scanning rate: 50 mV s^{-1})



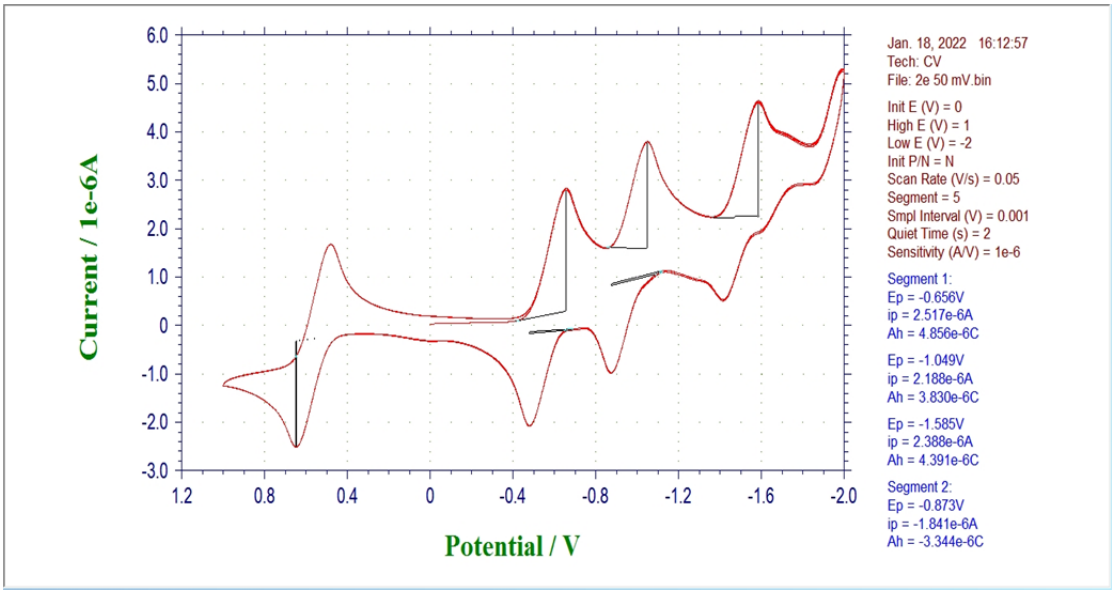
Cyclic voltammogram of compound **2b** (scanning rate: 50 mV s^{-1})



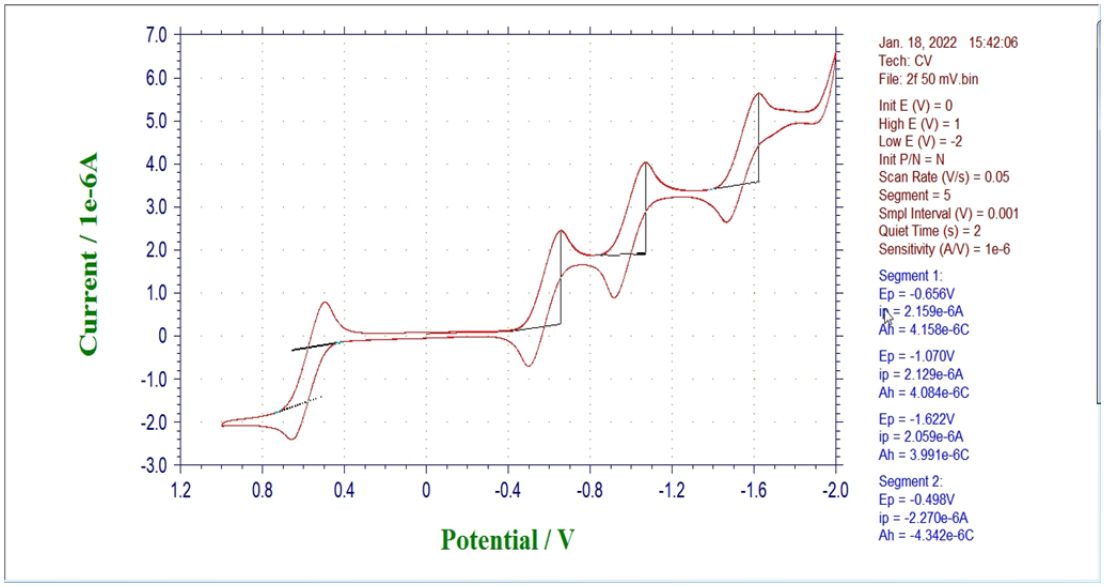
Cyclic voltammogram of compound **2c** (scanning rate: 50 mV s^{-1})



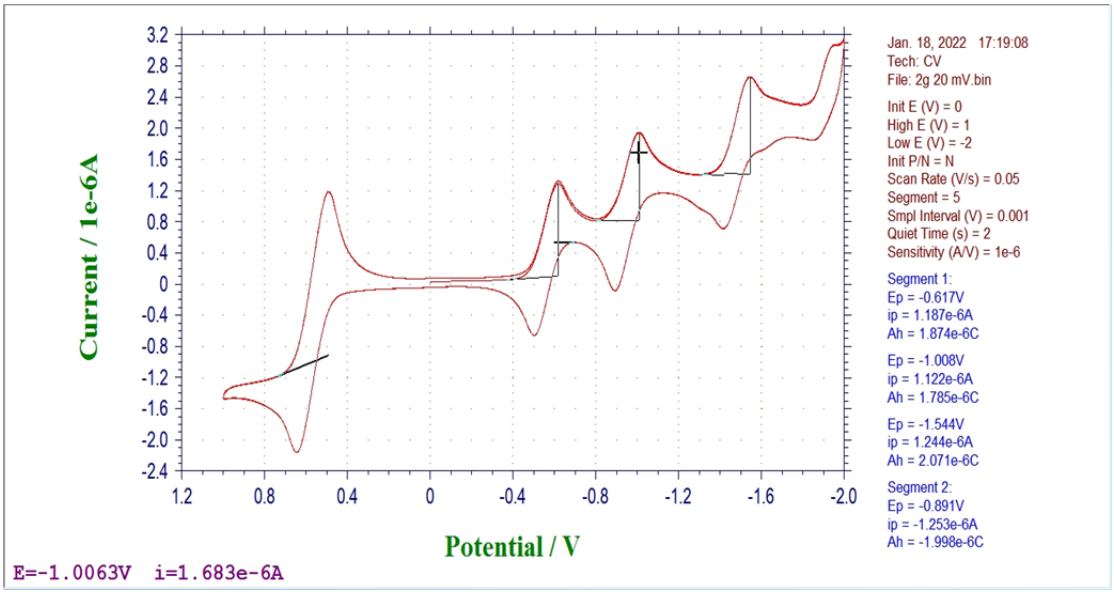
Cyclic voltammogram of compound **2d** (scanning rate: 50 mV s^{-1})



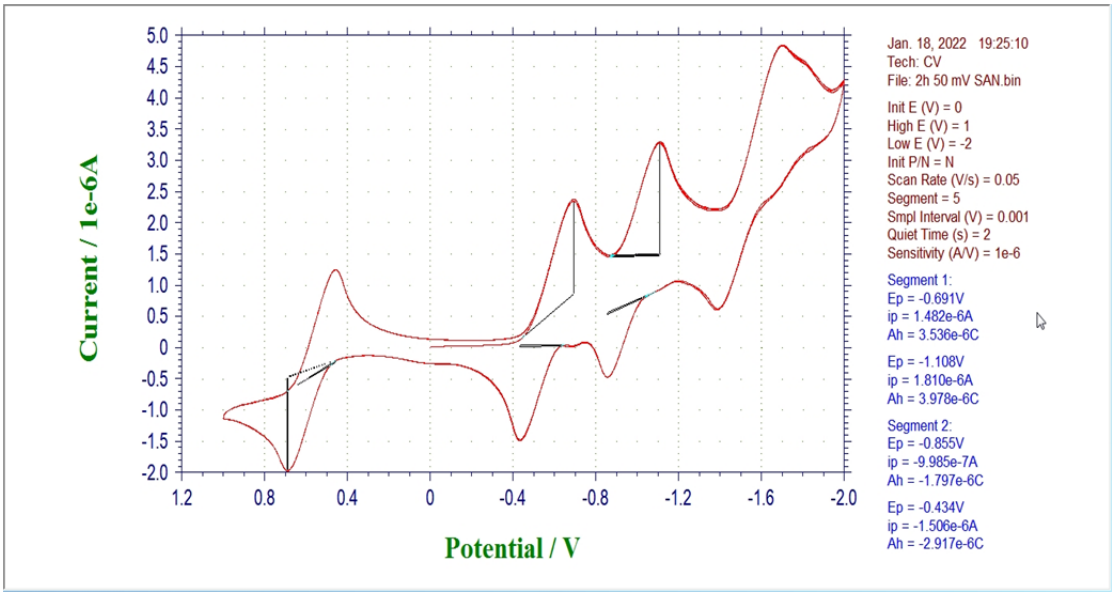
Cyclic voltammogram of compound **2e** (scanning rate: 50 mV s^{-1})



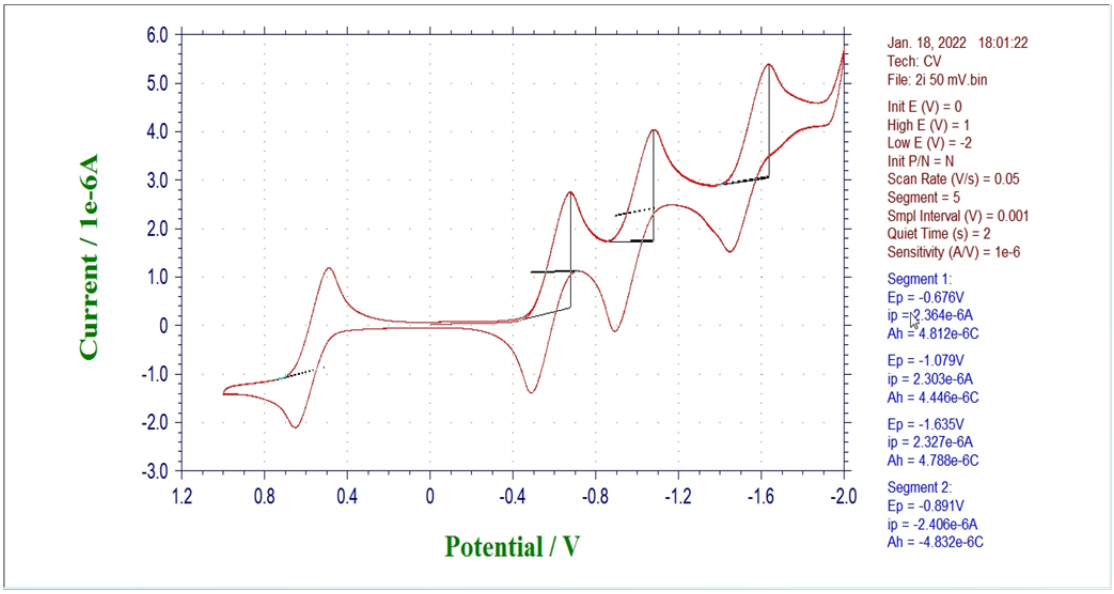
Cyclic voltammogram of compound **2f** (scanning rate: 50 mV s^{-1})



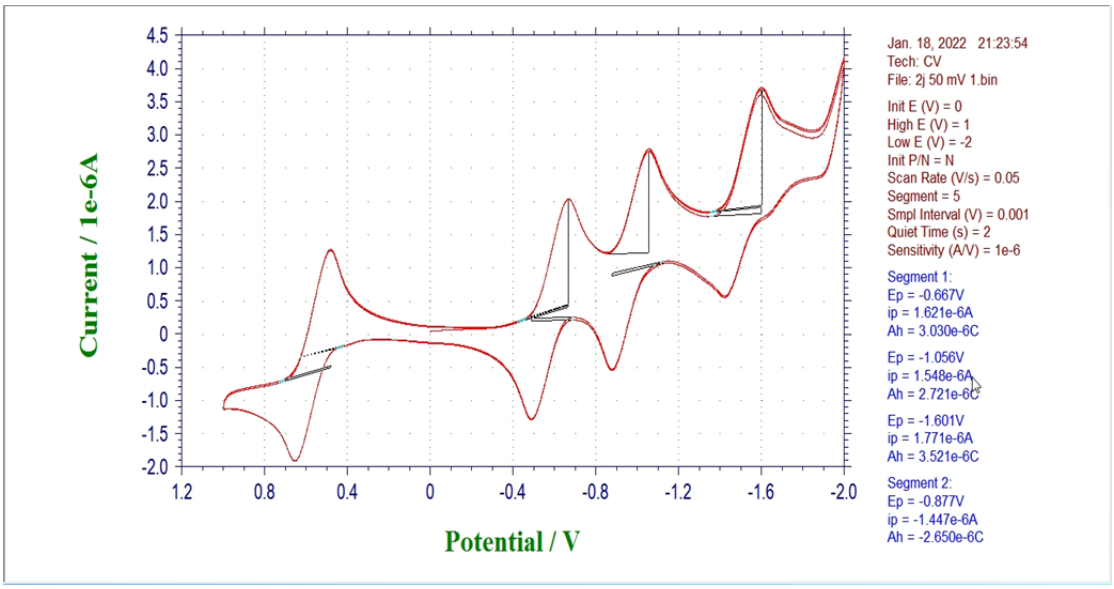
Cyclic voltammogram of compound **2g** (scanning rate: 50 mV s^{-1})



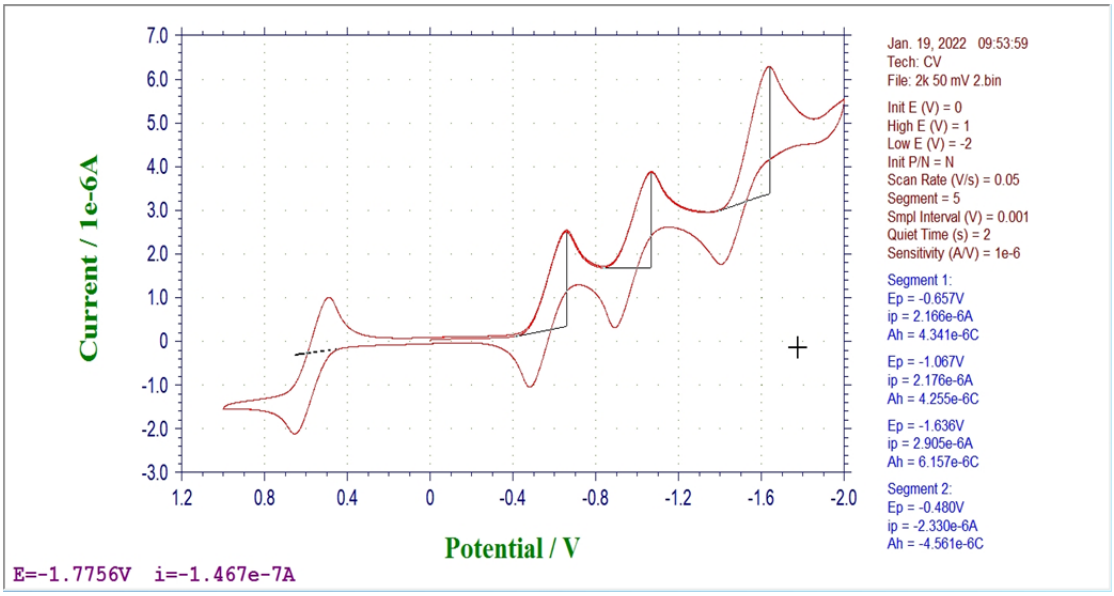
Cyclic voltammogram of compound **2h** (scanning rate: 50 mV s^{-1})



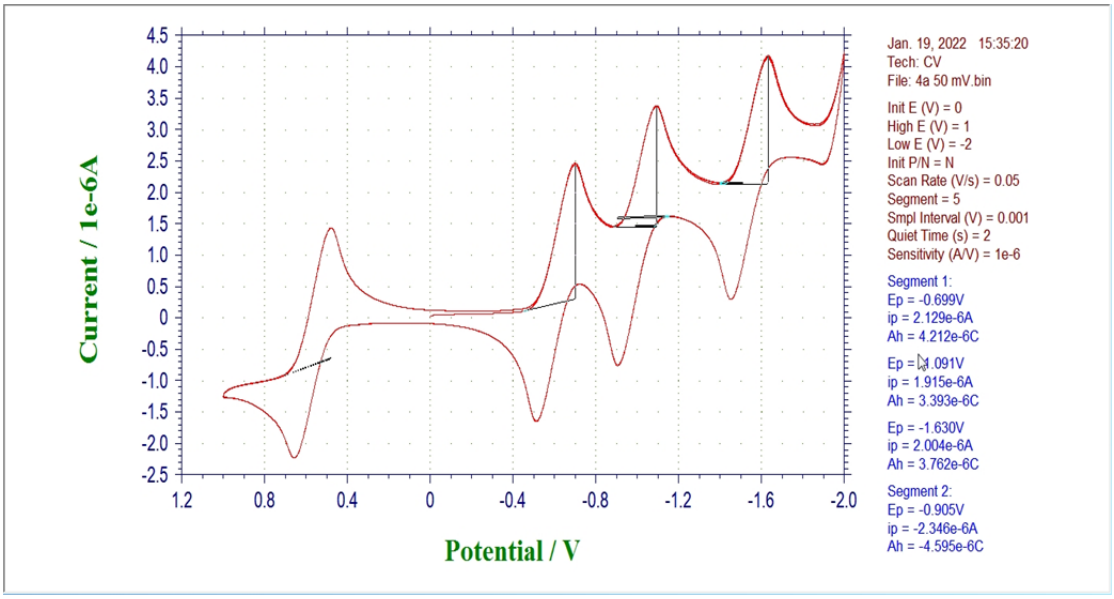
Cyclic voltammogram of compound **2i** (scanning rate: 50 mV s^{-1})



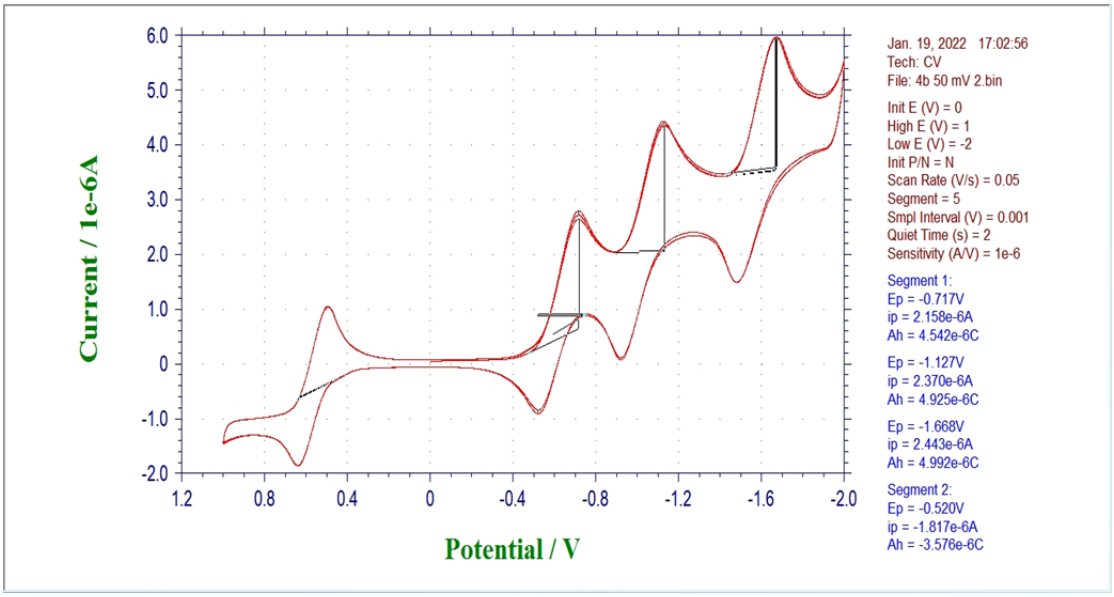
Cyclic voltammogram of compound **2j** (scanning rate: 50 mV s^{-1})



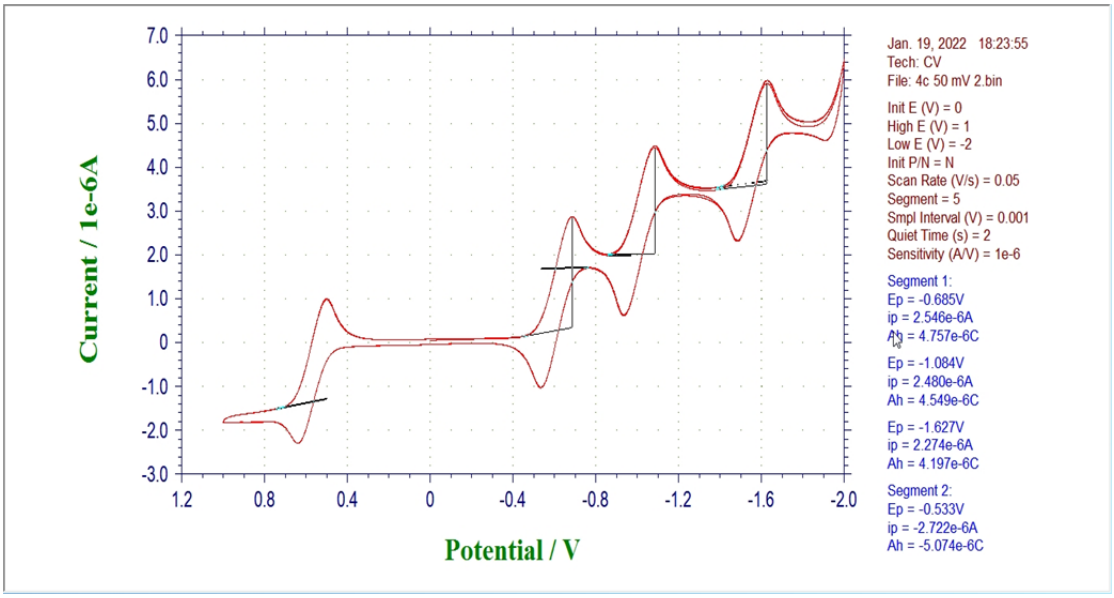
Cyclic voltammogram of compound **2k** (scanning rate: 50 mV s^{-1})



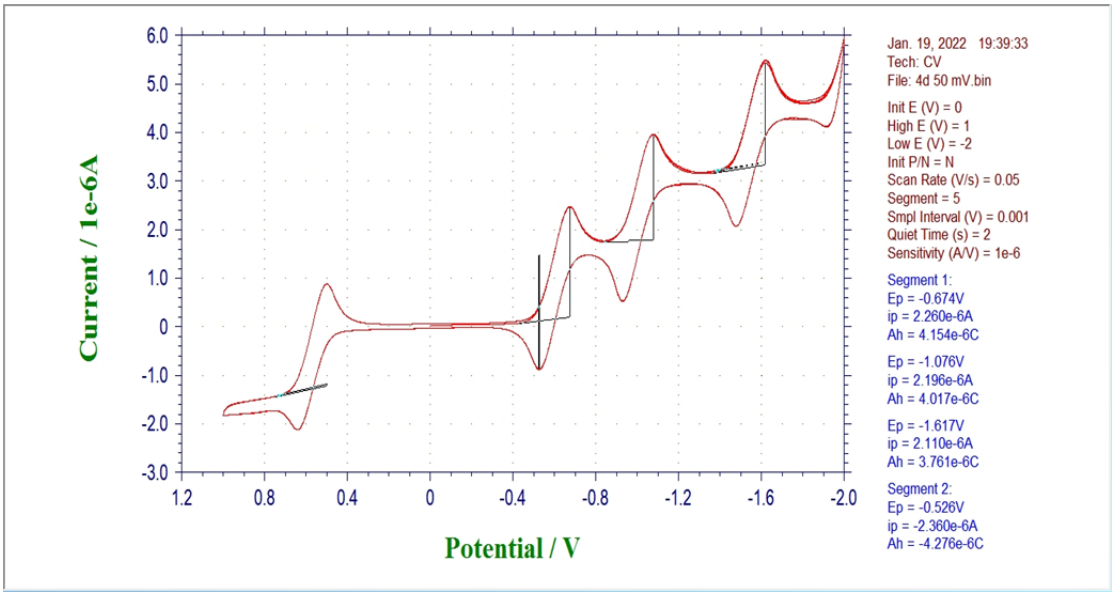
Cyclic voltammogram of compound **5a** (scanning rate: 50 mV s^{-1})



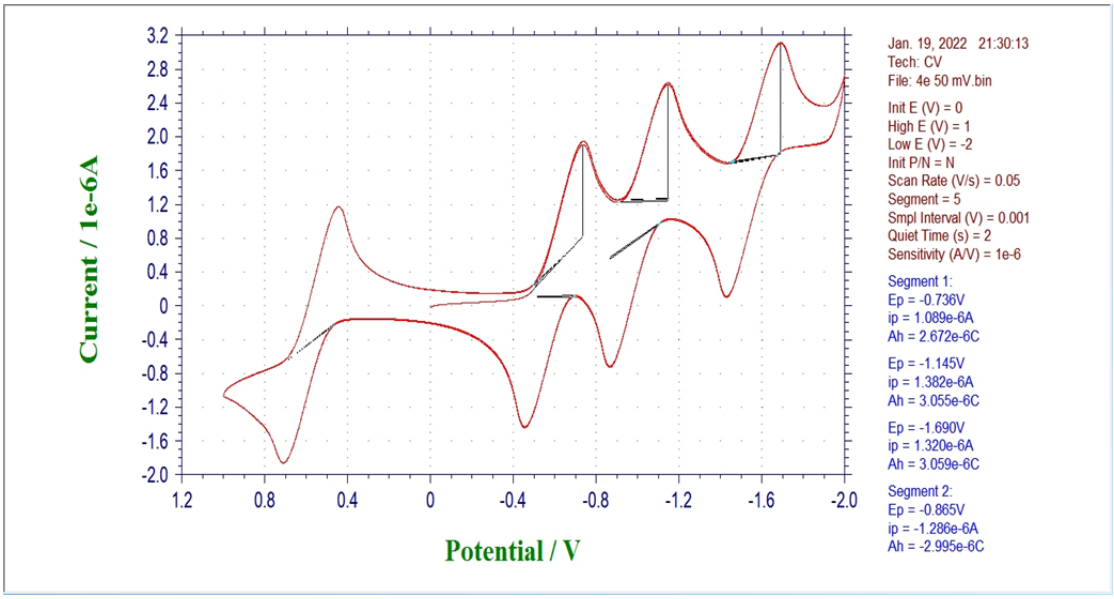
Cyclic voltammogram of compound **5b** (scanning rate: 50 mV s^{-1})



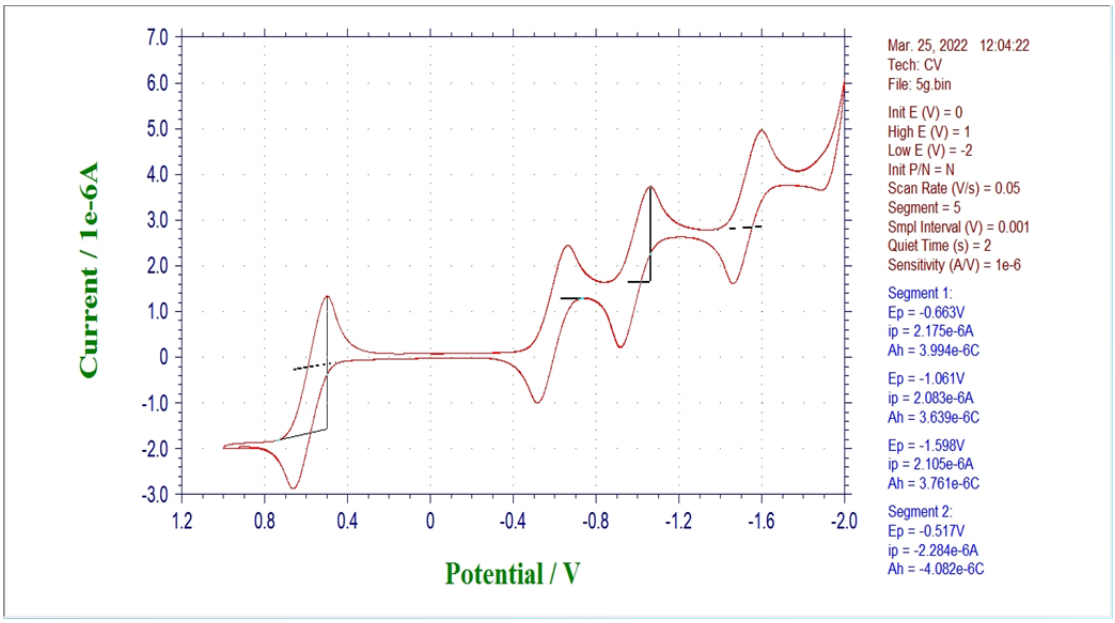
Cyclic voltammogram of compound **5c** (scanning rate: 50 mV s^{-1})



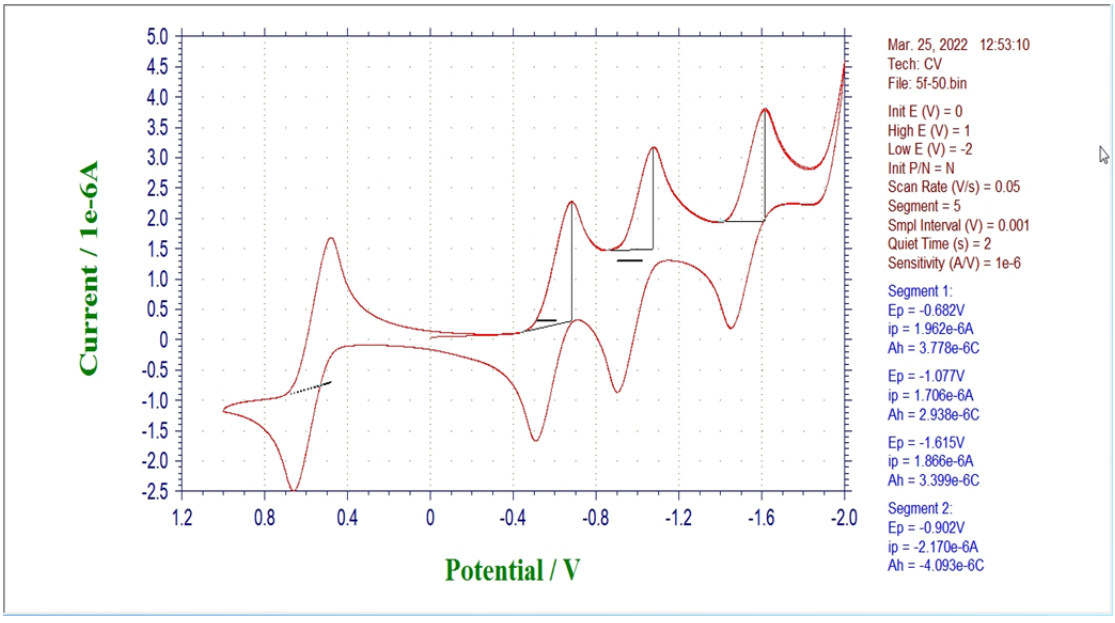
Cyclic voltammogram of compound **5d** (scanning rate: 50 mV s^{-1})



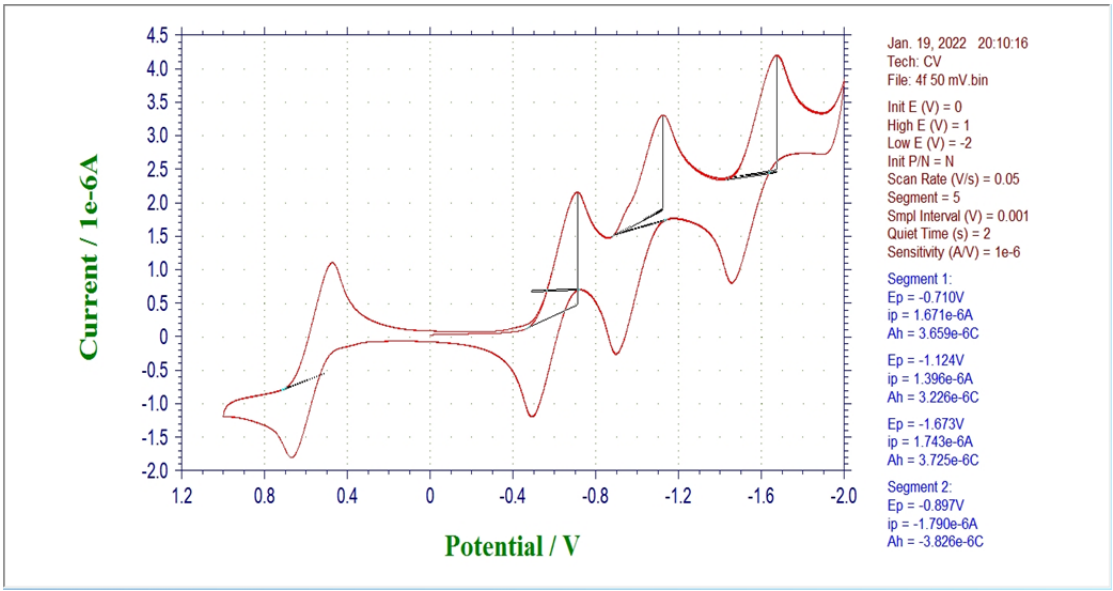
Cyclic voltammogram of compound **5e** (scanning rate: 50 mV s^{-1})



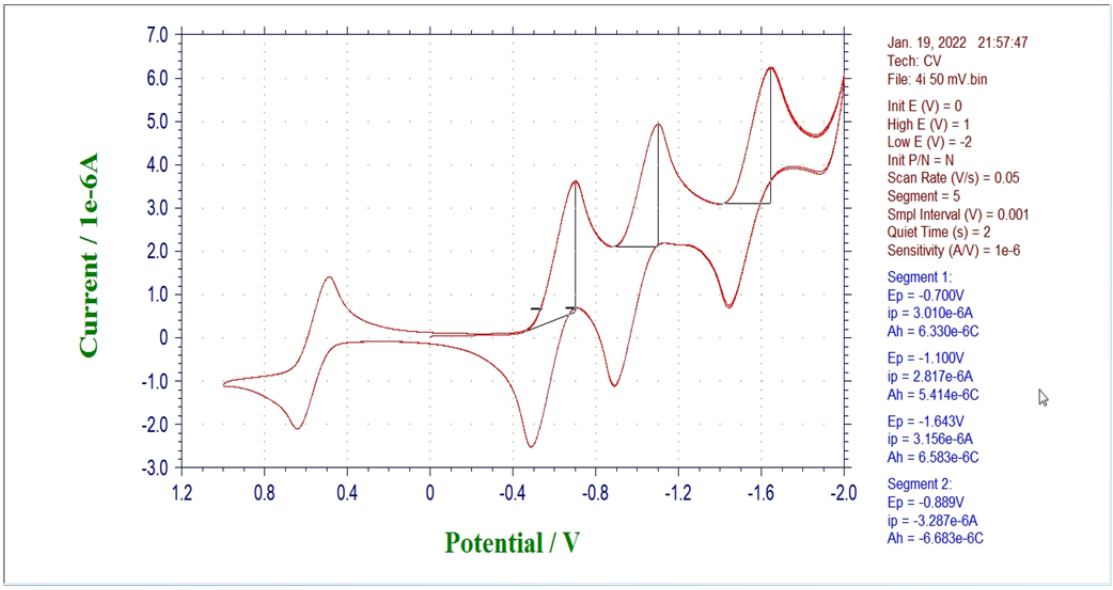
Cyclic voltammogram of compound **5f** (scanning rate: 50 mV s^{-1})



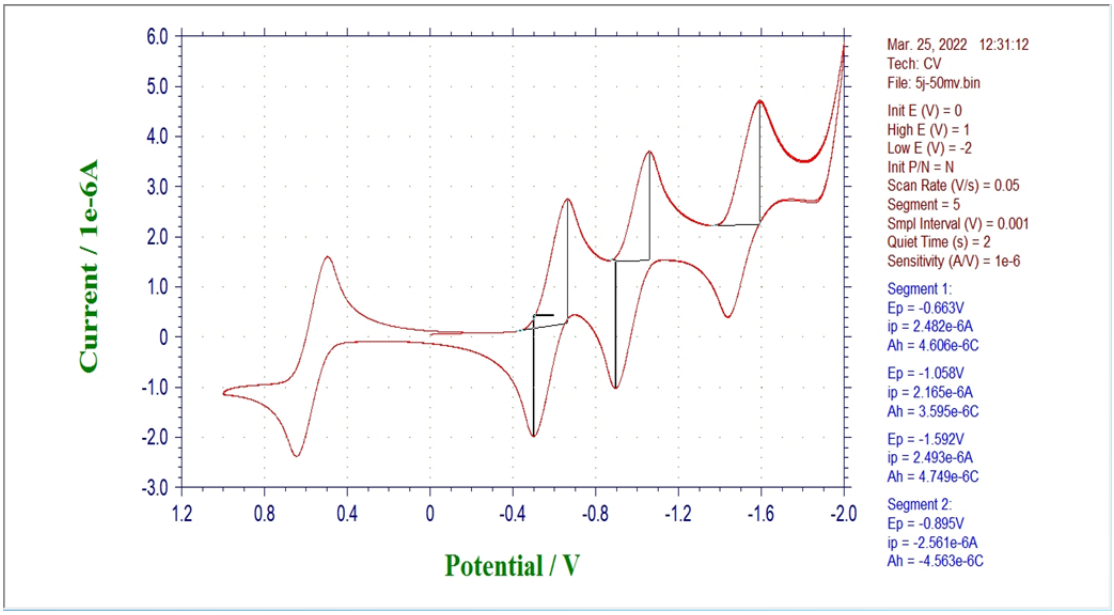
Cyclic voltammogram of compound **5g** (scanning rate: 50 mV s^{-1})



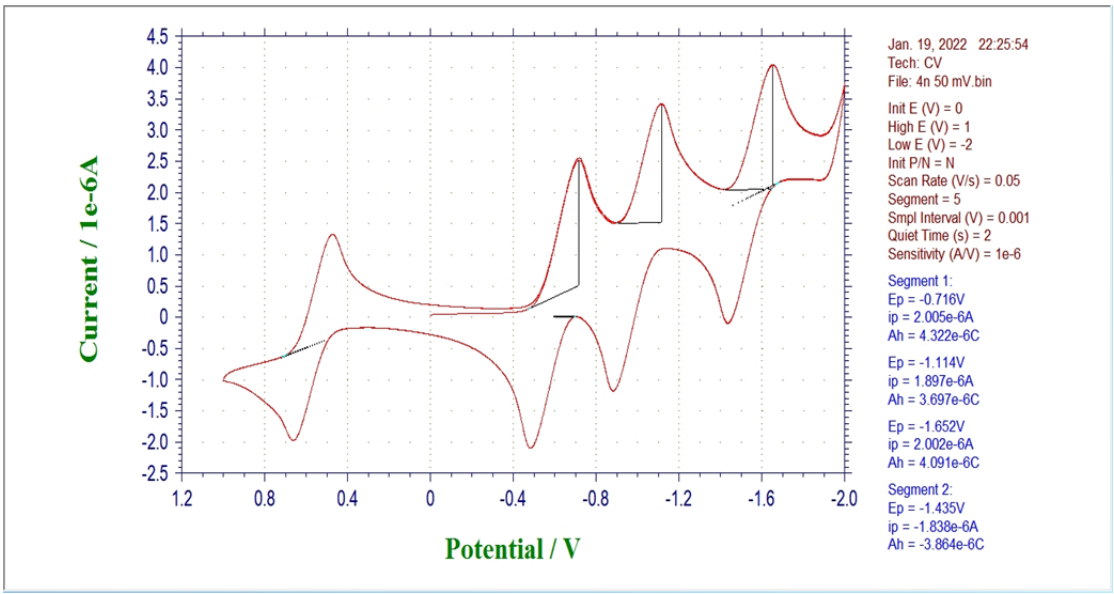
Cyclic voltammogram of compound **5h** (scanning rate: 50 mV s^{-1})



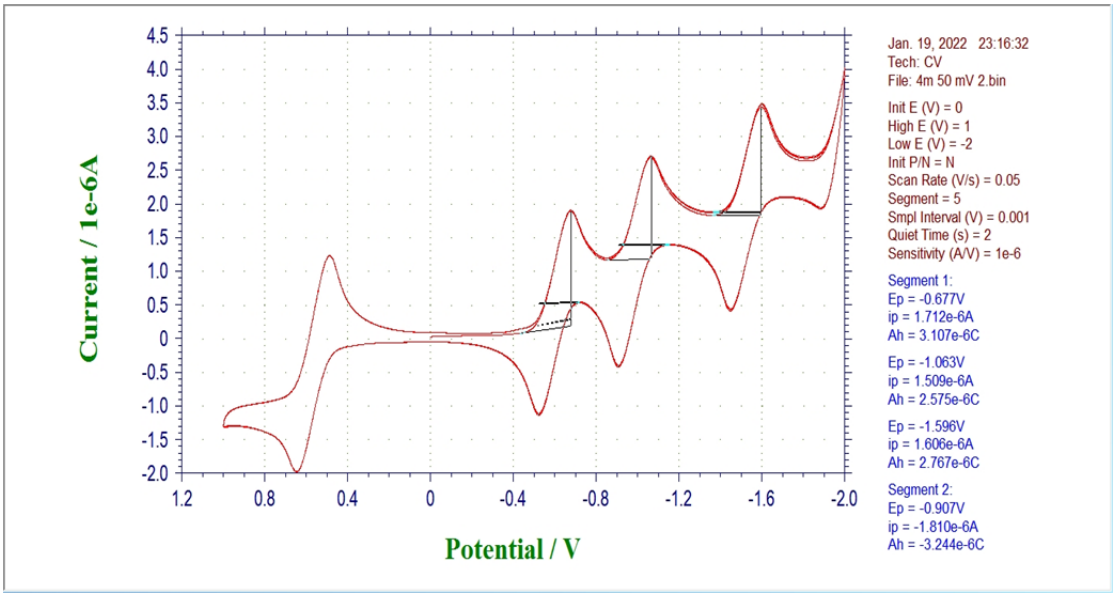
Cyclic voltammogram of compound **5i** (scanning rate: 50 mV s^{-1})



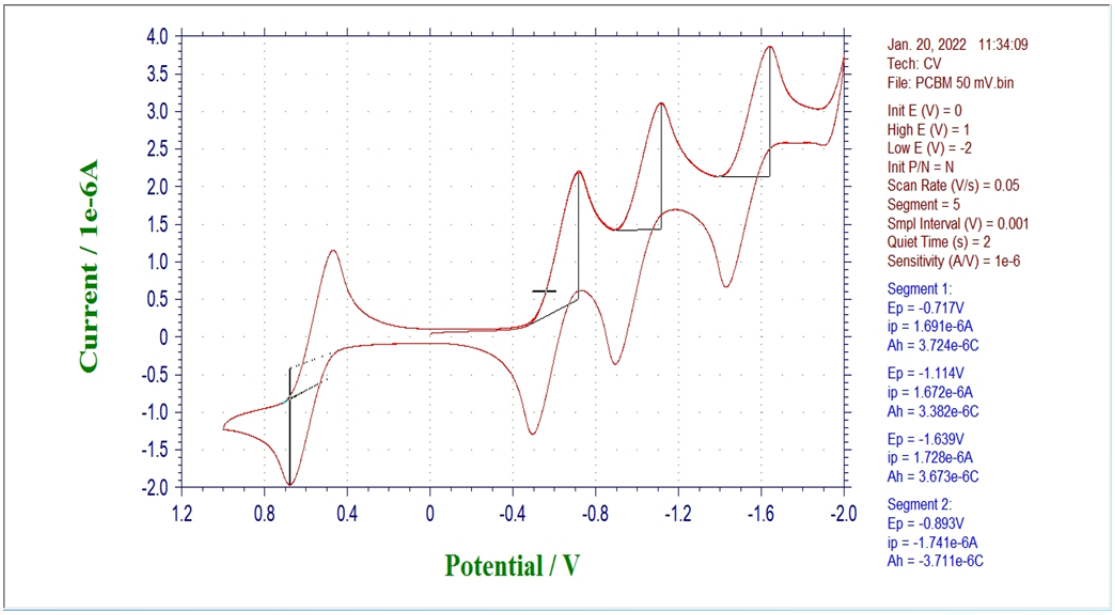
Cyclic voltammogram of compound **5j** (scanning rate: 50 mV s^{-1})



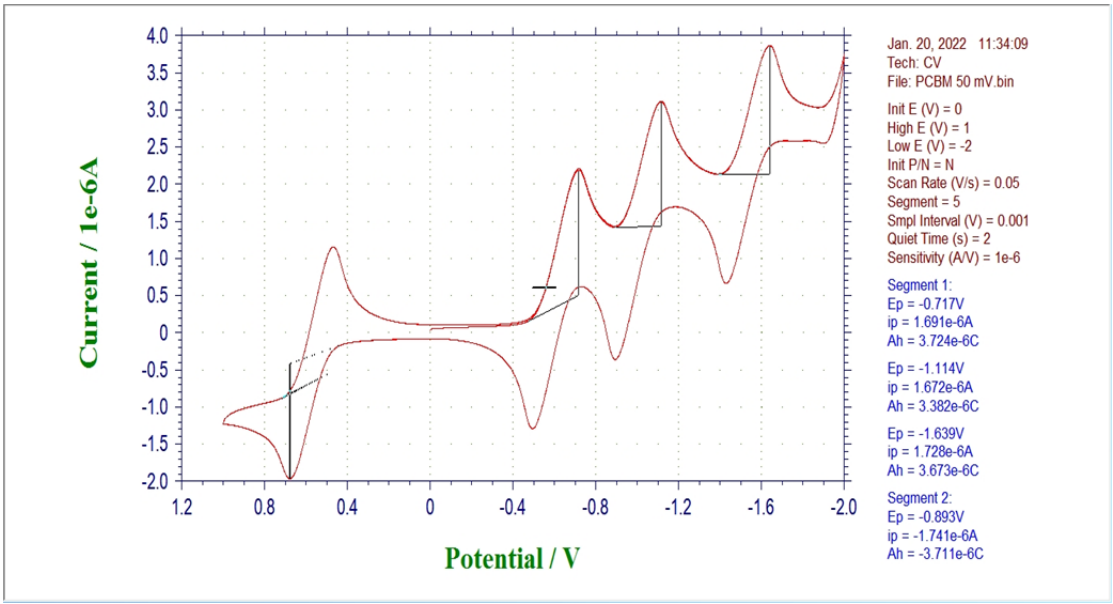
Cyclic voltammogram of compound **5k** (scanning rate: 50 mV s^{-1})



Cyclic voltammogram of compound **5l** (scanning rate: 50 mV s^{-1})

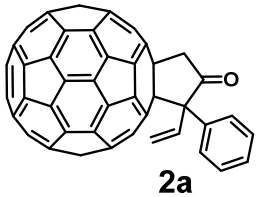


Cyclic voltammogram of compound **PCBM** (scanning rate: 50 mV s^{-1})



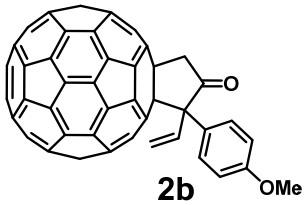
Cyclic voltammogram of compound **C_{60}** (scanning rate: 50 mV s^{-1})

8. Spectral Data for All Compounds



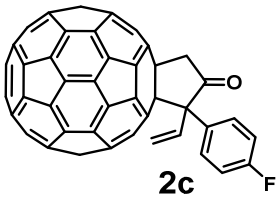
2a

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** (25.5 mg, 58%); amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3/CS_2$) 7.75 (dd, J = 17.4, 10.8 Hz, 1H), 7.67 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.8 Hz, 2H), 7.24–7.22 (m, 1H), 5.90 (d, J = 10.2 Hz, 1H), 5.70 (d, J = 17.4 Hz, 1H), 4.91 (d, J = 17.4 Hz, 1H), 4.26 (d, J = 17.4 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 207.8, 156.6, 155.3, 153.5, 151.9, 147.64, 147.59, 146.41, 146.37, 146.31, 146.29, 146.26, 146.12, 146.07, 146.01, 145.97, 145.7, 145.61, 145.58, 145.5, 145.4, 145.3, 145.2, 144.8, 144.6, 144.5, 144.4, 143.9, 143.2, 142.70, 142.66, 142.5, 142.13, 142.10, 142.0, 141.99, 141.98, 141.82, 141.79, 141.7, 141.5, 141.4, 141.1, 140.5, 140.1, 139.6, 139.2, 139.1, 137.1, 135.6, 134.7, 134.1, 131.0, 128.1, 127.7, 122.0, 76.3, 68.5, 61.5, 49.4; FT-IR ν/cm^{-1} 1744, 1509, 1259, 1092, 1014, 793, 688, 524; UV-vis ($CHCl_3$) λ_{max}/nm 255, 315, 434, 701; MALDI-TOF MS m/z calcd for $C_{71}H_{10}O$ $[M]^-$ 878.0737, found 878.0736.



2b

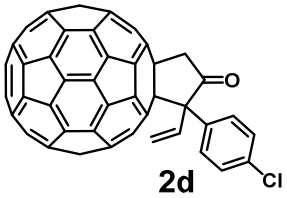
Spectral data of **2b**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 5:1) to give **2b** (18.4 mg, 40%); amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3/CS_2$) δ 7.72 (dd, *J* = 17.4, 10.2 Hz, 1H), 7.58 (d, *J* = 6.6, 1.8 Hz, 2H), 6.84 (d, *J* = 7.2, 1.8 Hz, 2H), 5.87 (d, *J* = 10.8 Hz, 1H), 5.68 (d, *J* = 17.4 Hz, 1H), 4.89 (d, *J* = 17.4 Hz, 1H), 4.25 (d, *J* = 17.4 Hz, 1H), 3.76 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 208.4, 158.6, 156.7, 155.1, 153.6, 152.0, 147.6, 147.5, 146.31, 146.28, 146.22, 146.20, 146.18, 146.02, 145.98, 145.9, 145.6, 145.58, 145.57, 145.5, 145.32, 145.28, 145.22, 145.18, 145.1, 144.7, 144.5, 144.40, 144.36, 143.8, 143.1, 142.6, 142.58, 142.56, 142.4, 142.04, 142.02, 141.92, 141.89, 141.7, 141.69, 141.66, 141.4, 141.3, 141.1, 140.4, 140.0, 139.8, 139.6, 139.1, 137.0, 135.5, 134.5, 134.1, 132.1, 131.0, 121.8, 113.4, 76.5, 68.1, 61.3, 55.0, 49.3; FT-IR ν/cm^{-1} 1736, 1508, 1247, 1179, 1005, 791, 523; UV-vis ($CHCl_3$) λ_{max}/nm 257, 315, 435, 702; MALDI-TOF MS m/z calcd for $C_{72}H_{12}O_2$ $[M]^-$ 908.0843, found 908.0840.



2c

Spectral data of **2c**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2c** (25.5 mg, 57%); amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3/CS_2$) δ 7.77 (dd, *J* = 17.4, 10.2 Hz, 1H), 7.68 (dd, *J* = 9.0, 5.4 Hz, 2H), 7.03 (t, *J* = 9.0 Hz, 2H), 5.92 (d, *J* = 10.2 Hz,

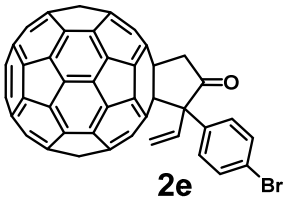
1H), 5.69 (d, J = 17.4 Hz, 1H), 4.91 (d, J = 17.4 Hz, 1H), 4.26 (d, J = 17.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 207.0, 161.7 (J_{C-F} = 248.0 Hz), 156.3, 154.9, 153.0, 151.5, 147.52, 147.46, 146.3, 146.23, 146.2, 146.16, 146.15, 146.0, 145.9, 145.8, 145.7, 145.6, 145.5, 145.4, 145.33, 145.25, 145.22, 145.20, 145.15, 144.6, 144.4, 144.34, 144.28, 143.6, 143.1, 142.58, 142.57, 142.5, 142.4, 142.0, 141.9, 141.88, 141.86, 141.8, 141.7, 141.6, 141.32, 141.28, 141.0, 140.4, 140.1, 139.6, 139.5, 139.1, 137.1, 135.4, 134.8, 134.6, 133.9, 132.7, 132.6, 122.2, 115.0, 114.8, 76.0, 67.7, 61.2, 49.1; ^{19}F NMR (377 MHz, $CDCl_3/CS_2$) δ: -112.4; FT-IR ν/cm^{-1} 1742, 1506, 1221, 1163, 979, 932, 801, 764, 524; UV-vis ($CHCl_3$) λ_{max}/nm 258, 315, 434, 700; MALDI-TOF MS m/z calcd for $C_{71}H_9OF$ $[M]^-$ 896.0643, found 896.0641.



2d

Spectral data of **2d**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2d** (22.7 mg, 49%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.75 (dd, J = 17.2, 10.4 Hz, 1H), 7.63 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.8 Hz, 2H), 5.91 (d, J = 10.4 Hz, 1H), 5.68 (d, J = 17.2 Hz, 1H), 4.90 (d, J = 17.6 Hz, 1H), 4.25 (d, J = 17.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 207.4, 156.2, 154.8, 152.8, 151.4, 147.5, 147.4, 146.24, 146.20, 146.17, 146.1, 146.0, 145.9, 145.7, 145.6, 145.5, 145.44, 145.39, 145.3, 145.23, 145.20, 145.16, 145.1, 114.6, 144.4,

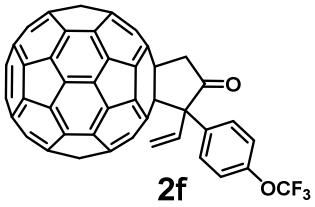
144.3, 144.2, 143.6, 143.1, 142.54, 142.53, 142.5, 142.4, 141.94, 141.9, 141.84, 141.81, 141.78, 141.63, 141.61, 141.26, 141.25, 140.9, 140.4, 140.0, 139.5, 139.3, 139.1, 137.5, 137.1, 135.3, 134.6, 133.8, 132.2, 128.1, 122.3, 75.9, 67.8, 61.3, 49.1; FT-IR ν/cm^{-1} 1745, 1489, 1400, 1186, 1092, 1014, 989, 935, 796, 525; UV-vis ($CHCl_3$) λ_{max}/nm 259, 316, 434, 700; MALDI-TOF MS m/z calcd for $C_{71}H_9OCl$ $[M]^-$ 912.0347, found 912.0342.



2e

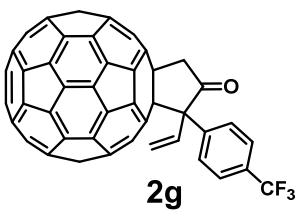
Spectral data of **2e**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2e** (26.0 mg, 54%); amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3/CS_2$) δ 7.76 (dd, *J* = 17.2, 10.8 Hz, 1H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 5.92 (d, *J* = 10.8 Hz, 1H), 5.68 (d, *J* = 17.4 Hz, 1H), 4.91 (d, *J* = 17.4 Hz, 1H), 4.26 (d, *J* = 17.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 208.0, 156.4, 155.0, 153.0, 151.5, 147.7, 147.6, 146.41, 146.37, 146.34, 146.31, 146.13, 146.11, 145.9, 145.7, 145.64, 145.60, 145.56, 145.5, 145.4, 145.38, 145.37, 145.33, 145.28, 145.25, 144.8, 144.6, 144.5, 144.4, 143.8, 143.2, 142.71, 142.69, 142.67, 142.5, 142.11, 142.07, 142.01, 141.97, 141.9, 141.8, 141.76, 141.43, 141.41, 141.1, 140.5, 140.11, 139.7, 139.4, 139.3, 138.2, 137.2, 135.5, 134.8, 133.9, 132.7, 131.2, 122.5, 122.2, 76.0, 68.0, 61.5, 49.3; FT-IR ν/cm^{-1} 1745, 1485, 1185, 1009, 936, 795, 525;

UV-vis ($CHCl_3$) λ_{max}/nm 256, 318, 434, 699; MALDI-TOF MS m/z calcd for $C_{71}H_9OBr$ $[M]^-$ 955.9842, found 957.9825.



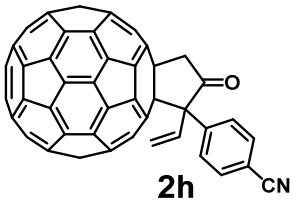
2f

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** (23.7 mg, 49%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.82–7.75 (m, 3H), 7.22 (d, J = 8.4 Hz, 2H), 5.95 (d, J = 10.4 Hz, 1H), 5.72 (d, J = 17.2 Hz, 1H), 4.95 (d, J = 17.6 Hz, 1H), 4.29 (d, J = 17.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 207.8, 156.3, 154.9, 152.9, 151.4, 148.4, 147.7, 147.6, 146.39, 146.36, 146.32, 146.29, 146.12, 146.09, 145.9, 145.64, 145.57, 145.54, 145.46, 145.37, 145.35, 145.34, 145.26, 145.2, 144.7, 144.54, 144.47, 144.4, 143.8, 143.2, 142.7, 142.68, 142.66, 142.5, 142.09, 142.08, 142.04, 142.00, 141.97, 141.9, 141.79, 141.76, 141.4, 141.1, 140.5, 140.2, 139.7, 139.4, 139.1, 137.7, 137.3, 135.5, 134.8, 133.9, 132.5, 122.6, 120.24 (J_{C-F} = 256.2 Hz), 120.21, 76.0, 67.9, 61.5, 49.3; ^{19}F NMR (565 MHz, $CDCl_3/CS_2$) δ: -57.5; FT-IR ν/cm^{-1} 1744, 1506, 1248, 1207, 1156, 935, 796, 524; UV-vis ($CHCl_3$) λ_{max}/nm 257, 316, 434, 701; MALDI-TOF MS m/z calcd for $C_{72}H_9O_2F_3$ $[M]^-$ 962.0560, found 962.0569.



2g

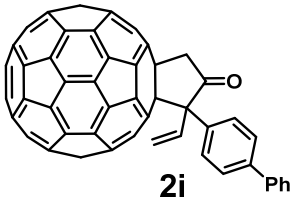
Spectral data of **2g**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2g** (23.7 mg, 50%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.81 (dd, *J* = 17.2, 10.4 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 5.96 (d, *J* = 10.4 Hz, 1H), 5.68 (d, *J* = 17.2 Hz, 1H), 4.94 (d, *J* = 17.6 Hz, 1H), 4.29 (d, *J* = 17.6 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 207.6, 156.2, 154.9, 152.6, 151.2, 147.7, 147.6, 146.40, 146.36, 146.34, 146.31, 146.13, 146.11, 145.8, 145.7, 145.6, 145.54, 145.49, 145.4, 145.37, 145.35, 145.29, 145.26, 145.1, 144.8, 144.54, 144.48, 144.3, 143.7, 143.24, 143.22, 143.17, 142.72, 142.69, 142.68, 142.5, 142.10, 142.07, 142.04, 142.01, 141.96, 141.9, 141.8, 141.78, 141.75, 141.41, 141.38, 141.0, 140.5, 140.2, 139.7, 139.3, 139.2, 137.3, 135.5, 134.9, 133.9, 131.5, 129.7 ($J_{C\text{-}F}$ = 32.6 Hz), 124.91, 124.89, 123.8 ($J_{C\text{-}F}$ = 270.8 Hz), 122.8, 75.8, 68.1, 61.6, 49.3; ^{19}F NMR (565 MHz, $CDCl_3/CS_2$) δ: -62.3; FT-IR ν/cm^{-1} 1745, 1512, 1323, 1162, 1118, 1069, 812, 525; UV-vis ($CHCl_3$) λ_{max}/nm 256, 316, 434, 699; MALDI-TOF MS m/z calcd for $C_{72}H_9OF_3$ $[M]^-$ 946.0611, found 962.0617.



2h

Spectral data of **2h**: 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 **2h** (23.5 mg, 52%); amorphous brown solid; ^{1}H NMR (600 MHz, $CDCl_3/CS_2$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.80 (dd, *J* = 17.4,

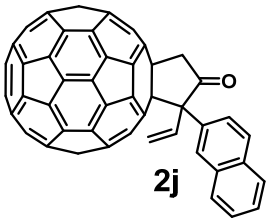
10.8 Hz 1H), 7.66 (d, J = 8.4 Hz, 2H), 5.97 (d, J = 10.8 Hz, 1H), 5.68 (d, J = 17.4 Hz, 1H), 4.94 (d, J = 17.4 Hz, 1H), 4.29 (d, J = 17.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 206.7, 155.9, 154.6, 152.1, 150.8, 147.6, 147.5, 146.33, 146.28, 146.25, 146.1, 146.0, 145.7, 145.6, 145.44, 145.43, 145.36, 145.34, 145.31, 145.30, 145.27, 145.23, 145.21, 144.8, 144.7, 144.43, 144.40, 144.3, 144.2, 143.6, 143.2, 142.7, 142.65, 142.62, 142.5, 142.03, 141.98, 141.94, 141.93, 141.9, 141.8, 141.74, 141.68, 141.66, 141.4, 141.3, 140.9, 140.5, 140.2, 139.7, 139.1, 138.9, 137.3, 135.3, 134.9, 133.7, 131.7, 131.6, 123.0, 118.0, 111.7, 75.5, 67.9, 61.4, 49.2; FT-IR ν/cm^{-1} 1742, 1501, 1261, 1093, 1004, 935, 806, 524; UV-vis ($CHCl_3$) λ_{max}/nm 256, 316, 433, 605, 699; MALDI-TOF MS m/z calcd for $C_{72}H_9ON$ $[M]^-$ 903.0690, found 903.0684.



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** (28.5 mg, 58%); amorphous brown solid; ^1H NMR (600 MHz, $CDCl_3/CS_2$) δ 7.78 (dd, J = 17.4, 10.8 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.52 (dd, J = 8.4, 1.2 Hz, 2H), 7.36 (t, J = 7.8 Hz, 2H), 7.27 (t, J = 7.8 Hz, 1H), 5.92 (d, J = 10.8 Hz, 1H), 5.72 (d, J = 17.4 Hz, 1H), 4.92 (d, J = 17.4 Hz, 1H), 4.28 (d, J = 17.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 208.1, 156.5, 155.1, 153.3, 151.8, 147.53, 147.48, 146.29, 146.26, 146.19, 146.17, 146.1, 145.99,

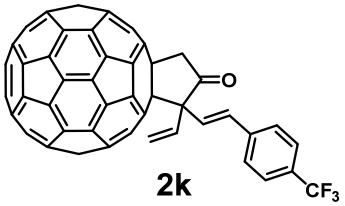
145.96, 145.8, 145.54, 145.51, 145.49, 145.3, 145.20, 145.15, 145.13, 144.6, 144.5, 144.4, 144.3, 143.8, 143.11, 143.09, 142.6, 142.5, 142.4, 141.99, 141.97, 141.90, 141.87, 141.7, 141.67, 141.66, 141.4, 141.3, 141.0, 140.4, 140.1, 140.03, 140.02, 139.6, 139.5, 139.1, 138.1, 137.0, 135.5, 134.7, 134.0, 131.3, 128.7, 127.4, 126.9, 126.6, 122.0, 76.3, 68.2, 61.4, 49.3; FT-IR ν/cm^{-1} 1742, 1484, 1181, 1142, 934, 901, 812, 759, 724, 693, 524; UV-vis ($CHCl_3$) λ_{max}/nm 259, 315, 435, 701; MALDI-TOF MS m/z calcd for $C_{77}H_{14}O$ $[M]^-$ 954.1050, found 954.1048.



2j

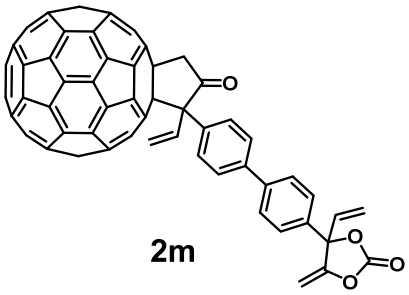
Spectral data of **2j**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give unreacted C_{60} and **2j** (26.4 mg, 57%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.21 (s, 1H), 7.89–7.75 (m, 5H), 7.46–7.42 (m, 2H), 5.96 (d, J = 10.4 Hz, 1H), 5.73 (d, J = 17.2 Hz, 1H), 4.98 (d, J = 17.6 Hz, 1H), 4.35 (d, J = 17.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 208.4, 156.5, 155.3, 153.3, 152.0, 147.61, 147.56, 146.37, 146.35, 146.27, 146.25, 146.2, 146.1, 146.03, 145.97, 145.9, 145.64, 145.61, 145.6, 145.5, 145.4, 145.34, 145.31, 145.26, 145.2, 144.7, 144.6, 144.5, 144.3, 143.9, 143.20, 143.16, 142.7, 142.63, 142.60, 142.5, 142.1, 142.04, 141.99, 141.95, 141.8, 141.7, 141.4, 141.3, 141.1, 140.5, 140.1, 139.7, 139.6, 139.1, 137.1, 136.6, 135.5, 134.8, 134.1, 132.7, 132.3, 130.5, 128.6, 128.4, 127.6, 127.5, 126.6, 126.1,

122.2, 76.4, 68.6, 61.6, 49.5; FT-IR ν/cm^{-1} 1742, 1501, 1143, 933, 798, 735, 525; UV-vis ($CHCl_3$) λ_{max}/nm 254, 315, 434, 702; MALDI-TOF MS m/z calcd for $C_{75}H_{12}O$ $[M]^-$ 928.0894, found 928.0895.



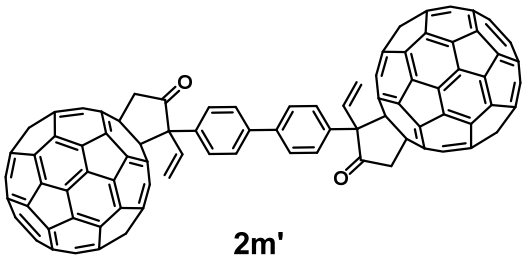
2k

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** (26.8 mg, 55%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.60–7.55 (m, 4H), 7.29 (d, J = 16.4 Hz, 1H), 7.08 (dd, J = 17.2, 10.4 Hz, 1H), 7.04 (d, J = 16.0 Hz, 1H), 5.83 (d, J = 10.4 Hz, 1H), 5.74 (d, J = 17.6 Hz, 1H), 4.61 (d, J = 17.2 Hz, 1H) , 4.47 (d, J = 17.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 208.5, 155.5, 155.3, 152.21, 152.20, 147.72, 147.65, 146.40, 146.38, 146.31, 148.28, 145.9, 145.68, 145.66, 145.54, 145.51, 145.47, 145.46, 145.43, 145.40, 145.1, 144.74, 144.68, 144.64, 144.58, 144.5, 143.29, 143.27, 142.74, 142.68, 142.2, 142.11, 142.09, 141.9, 141.8, 141.7, 141.5, 141.4, 140.4, 139.83, 139.81, 139.7, 137.6, 136.3, 135.9, 135.0, 134.6, 134.0, 131.1, 130.2 (J_{C-F} = 31.7 Hz), 126.9, 125.73, 125.71, 123.9 (J_{C-F} = 270.4 Hz), 121.0, 74.6, 65.2, 62.1, 48.8; ^{19}F NMR (565 MHz, $CDCl_3/CS_2$) δ: -62.3; FT-IR ν/cm^{-1} 1745, 1509, 1410, 1319, 1160, 1119, 1065, 524; UV-vis ($CHCl_3$) λ_{max}/nm 256, 315, 434, 700; MALDI-TOF MS m/z calcd for $C_{74}H_{11}OF_3$ $[M]^-$ 972.0767, found 972.0751.



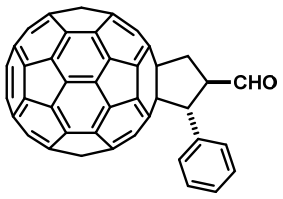
2m

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 = 2:1) to give **2m** (16.4 mg, 30%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.79 (dd, *J* = 17.2, 10.4 Hz, 1H), 7.78 (d, , *J* = 8.4 Hz, 2H), 7.59 (t, *J* = 8.4 Hz, 4H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.18 (dd, *J* = 17.2 Hz, 10.4 Hz, 1H), 5.94 (d, *J* = 10.8 Hz, 1H), 5.73 (d, *J* = 17.2 Hz, 1H), 5.54 (d, *J* = 3.6 Hz, 1H), 5.50 (d, *J* = 3.2 Hz, 1H), 5.06 (d, *J* = 3.6 Hz, 1H), 4.94 (d, *J* = 17.6 Hz, 1H) , 4.39 (d, *J* = 3.6 Hz, 1H), 4.29 (d, *J* = 18.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 207.1, 155.4, 154.0, 153.3, 152.2, 150.7, 149.3, 146.53, 146.46, 145.3, 145.24, 145.17, 145.15, 144.99, 144.95, 144.8, 144.7, 144.53, 144.49 144.46, 144.4, 144.32, 144.26, 144.24, 144.22, 144.20, 144.14, 144.1, 143.6, 143.4, 143.37, 143.2, 142.7, 142.11, 142.09, 141.6, 141.5, 141.4, 141.0, 140.94, 140.88, 140.8, 140.67, 140.66, 140.6, 140.33, 140.32, 140.27, 140.0, 139.4, 139.0, 138.6, 138.5, 138.0, 137.84, 137.77, 136.1, 134.8, 134.4, 134.0, 133.7, 132.9, 130.5, 126.3, 125.7, 125.6, 121.1, 117.4, 89.2, 87.7, 76.2, 75.2, 67.2, 60.4, 48.3; FT-IR ν/cm^{-1} 1821, 1742, 1677, 1496, 1399, 1260, 1094, 1014, 802, 524; UV-vis ($CHCl_3$) λ_{max}/nm 256, 314, 434, 700; MALDI-TOF MS m/z calcd for $C_{83}H_{18}O_4$ $[M]^-$ 1078.1211, found 1078.1206.



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 = 4:1) to give **2m'** (7.8 mg, 17%); amorphous brown solid; ^{1}H NMR (400 MHz, DMSO-d_6/CS_2) δ 7.73 (dd, *J* = 17.2 Hz, 10.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 4H), 7.55 (d, *J* = 8.4 Hz, 4H), 5.87 (d, *J* = 10.8 Hz, 2H), 5.62 (d, *J* = 17.2 Hz, 2H), 4.94 (dd, *J* = 17.6, 1.6 Hz, 2H), 4.25 (d, *J* = 17.6 Hz, 2H); the ^{13}C NMR spectrum of **2m'** could not be obtained because of poor solubility of the product; FT-IR ν/cm^{-1} 1742, 1497, 1424, 1144, 1024, 1003, 797, 764, 668, 525; UV-vis ($CHCl_3$) λ_{max}/nm 258, 315, 435, 702; MALDI-TOF MS m/z calcd for $C_{142}H_{18}O_2$ $[M]^-$ 1755.1346, found 1755.1324.

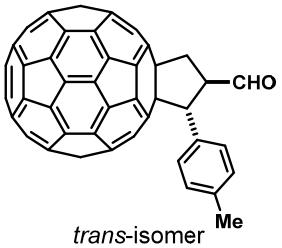


trans-isomer

5a

Spectral data of **5a**: 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 **5a** (19.2 mg, 44%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3$/CS_2) δ 10.12 (d, *J* = 2.8 Hz, 1H), 7.64 (d, *J* = 7.6

Hz, 2H) , 7.38 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 5.14 (d, J = 12.8 Hz, 1H), 4.78–4.70 (m, 1H), 4.02–3.92 (m, 2H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 199.9, 156.0, 155.6, 154.6, 152.4, 147.2, 146.2, 146.17, 146.15, 146.12, 146.02, 145.97, 145.9, 145.8, 145.7, 145.6, 145.4, 145.32, 145.3, 145.24, 145.21, 145.1, 145.0, 144.6, 144.5, 144.29, 144.28, 143.0, 142.9, 142.6, 142.52, 142.49, 142.4, 142.3, 142.1, 142.04, 142.98, 141.92, 141.85, 141.8, 141.6, 141.53, 141.49, 140.2, 140.1, 139.6, 139.4, 135.9, 135.6, 135.34, 135.26, 135.2, 129.3, 128.9, 128.3, 75.2, 68.9, 62.3, 53.2, 43.7; FT-IR ν/cm^{-1} 3307, 2973, 2879, 1718, 1426, 1379, 1087, 1046, 880, 524; UV-vis ($CHCl_3$) λ_{max}/nm 256, 310, 431, 700; MALDI-TOF MS m/z calcd for $C_{70}H_{10}O$ $[M]^-$ 866.0737, found 866.0716.

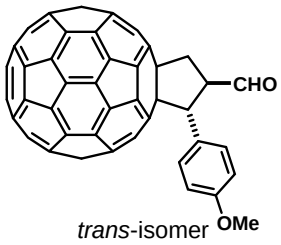


trans-isomer

5b

Spectral data of **5b**: 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 **5b** (13.2 mg, 30%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 10.10 (d, J = 2.8 Hz, 1H), 7.52 (d, J = 7.6 Hz, 2H) , 7.18 (d, J = 8.0 Hz, 2H), 5.10 (d, J = 12.8 Hz, 1H), 4.75–4.66 (m, 1H), 4.01–3.90 (m, 2H), 2.33 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 200.2, 156.2, 155.8, 154.8, 152.7, 147.3, 146.3, 146.28, 146.25, 146.19, 146.18, 146.1, 146.04, 146.01, 145.97, 145.8, 145.7, 145.42, 145.41,

145.35, 145.31, 145.28, 145.2, 145.1, 144.7, 144.5, 144.38, 144.35, 143.1, 143.0, 142.7, 142.59, 142.55, 142.5, 142.3, 142.2, 142.1, 142.0, 141.9, 141.8, 141.7, 141.63, 141.59, 140.3, 140.2, 139.7, 139.5, 138.0, 136.0, 135.4, 135.3, 132.6, 129.7, 129.3, 75.4, 69.0, 62.1, 53.4, 43.7, 21.3; FT-IR ν/cm^{-1} 3308, 2972, 2874, 1720, 1509, 1087, 1045, 879, 527; UV-vis ($CHCl_3$) λ_{max}/nm 258, 314, 431, 700; MALDI-TOF MS m/z calcd for $C_{71}H_{12}O$ $[M]^-$ 880.0894, found 880.0872.

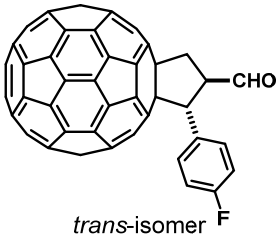


trans-isomer

5c

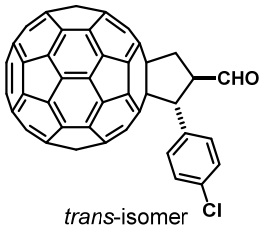
Spectral data of **5c**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 4:1) to give **5c** (6.9 mg, 15%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 10.10 (d, *J* = 2.8 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H) , 6.89 (d, *J* = 8.8 Hz, 2H), 5.10 (d, *J* = 12.8 Hz, 1H), 4.72–4.63 (m, 1H), 4.01–3.90 (m, 2H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 200.1, 159.3, 156.2, 155.7, 154.8, 152.7, 147.24, 147.22, 146.23, 146.22, 146.21, 146.15, 146.13, 146.06, 146.0, 145.93, 145.92, 145.7, 145.6, 145.38, 145.36, 145.3, 145.28, 145.27, 145.25, 145.13, 145.07, 144.6, 144.5, 144.4, 144.3, 143.1, 142.98, 142.96, 142.63, 142.56, 142.51, 142.46, 142.3, 142.1, 142.02, 141.96, 141.9, 141.8, 141.7, 141.58, 141.55, 140.2, 140.1, 139.7, 139.5, 135.9, 135.4, 135.24, 135.23, 130.4, 127.5, 114.3, 75.5, 68.9, 61.7, 55.0, 53.5, 43.6; FT-IR ν/cm^{-1}

1724, 1512, 1427, 1249, 1178, 1032, 828, 668, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 319, 431, 699; MALDI-TOF MS m/z calcd for $C_{71}H_{12}O_2$ $[M]^-$ 896.0843, found 896.0821.



trans-isomer
5d

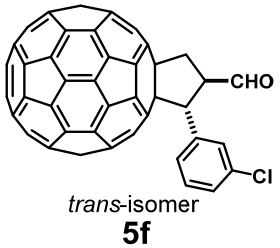
Spectral data of **5d**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **5d** (14.9 mg, 33%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 10.13 (d, J = 3.2 Hz, 1H), 7.64 (d, J = 8.4, 5.2 Hz, 1H), 7.08 (t, J = 8.4 Hz, 2H), 5.15 (d, J = 12.8 Hz, 1H), 4.73–4.65 (m, 1H), 4.02–3.95 (m, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 199.8, 162.4 (J_{C-F} = 247.0 Hz), 155.9, 155.5, 154.4, 152.1, 147.3, 146.23, 146.15, 146.1, 146.0, 145.97, 145.95, 145.9, 145.6, 145.5, 145.39, 145.35, 145.31, 145.3, 145.28, 145.25, 145.13, 145.1, 144.6, 144.5, 144.3, 143.1, 143.0, 142.7, 142.6, 142.53, 142.47, 142.3, 142.1, 142.04, 142.0, 141.95, 141.88, 141.86, 141.8, 141.7, 141.6, 141.5, 140.3, 140.2, 139.7, 139.5, 136.0, 135.4, 135.3, 135.2, 131.5, 130.9, 116.0, 115.8, 75.1, 68.9, 61.4, 53.5, 43.7; ^{19}F NMR (377 MHz, $CDCl_3/CS_2$) δ: -111.1; FT-IR ν/cm^{-1} 1718, 1508, 1425, 1230, 1095, 840, 525; UV-vis ($CHCl_3$) λ_{max}/nm 256, 312, 431, 697; MALDI-TOF MS m/z calcd for $C_{70}H_9FO$ $[M]^-$ 884.0643, found 884.0621.



trans-isomer

5e

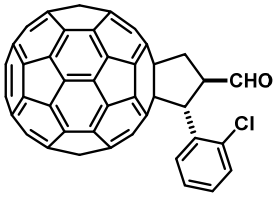
Spectral data of **5e**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **5e** (23.6 mg, 52%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 10.12 (d, *J* = 2.8 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H) , 7.36 (d, *J* = 8.4 Hz, 2H), 5.13 (d, *J* = 12.4 Hz, 1H), 4.74–4.65 (m, 1H), 3.97 (d, *J* = 8.8 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 199.5, 155.8, 155.4, 154.2, 151.9, 147.3, 146.25, 146.24, 146.16, 146.1, 146.0, 145.96, 145.94, 145.92, 145.60, 145.58, 145.5, 145.4, 145.38, 145.32, 145.29, 145.25, 145.14, 145.11, 144.6, 144.5, 144.3, 143.1, 143.0, 142.7, 142.59, 142.55, 142.5, 142.3, 142.1, 142.03, 142.00, 141.96, 141.89, 141.86, 141.8, 141.7, 141.6, 141.5, 140.3, 140.2, 139.7, 139.6, 136.1, 135.4, 135.3, 135.2, 134.4, 134.3, 130.6, 129.1, 75.0, 68.9, 61.5, 53.3, 43.7; FT-IR ν/cm^{-1} 1721, 1508, 1091, 1013, 827, 668, 524; UV-vis ($CHCl_3$) λ_{max}/nm 256, 318, 431, 697; MALDI-TOF MS m/z calcd for $C_{70}H_9ClO$ $[M]^-$ 900.0347, found 900.0326.



trans-isomer

5f

Spectral data of **5f**: 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 **5f** (26.1 mg, 58%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 10.14 (s, 1H), 7.63 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 5.11 (d, *J* = 12.4 Hz, 1H), 4.74–4.67 (m, 1H), 3.98–3.92 (m, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 199.3, 155.7, 155.3, 154.1, 151.7, 147.2, 146.20, 146.18, 146.11, 146.03, 145.98, 145.91, 145.90, 145.8, 145.53, 145.50, 145.42, 145.38, 145.35, 145.27, 145.24, 145.14, 145.09, 145.06, 144.5, 144.46, 144.3, 143.0, 142.9, 142.6, 142.53, 142.49, 142.4, 142.2, 142.1, 142.0, 141.91, 141.84, 141.82, 141.75, 141.7, 141.6, 141.5, 140.3, 140.1, 139.7, 139.5, 137.9, 136.0, 135.4, 135.3, 135.1, 134.9, 130.1, 128.5, 74.8, 68.9, 61.5, 53.2, 43.7; FT-IR ν/cm^{-1} 2963, 1722, 1507, 1428, 1259, 1082, 1015, 791, 524; UV-vis ($CHCl_3$) λ_{max}/nm 256, 312, 431, 697; MALDI-TOF MS m/z calcd for $C_{70}H_9ClO$ $[M]^-$ 900.0347, found 900.0339.

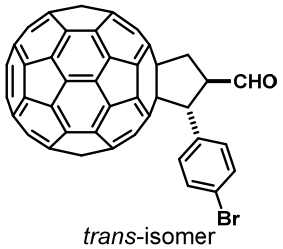


trans-isomer

5g

Spectral data of **5g**: 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 **5g** (14.4 mg, 32%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 10.03 (d, *J* = 3.2 Hz, 1H), 7.79 (d, *J* = 7.6

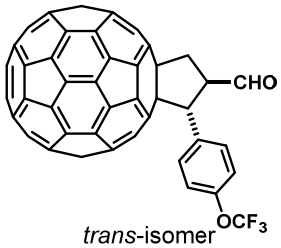
Hz, 1H) , 7.42 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.24 (t, J = 8.0 Hz, 1H), 5.87 (d, J = 12.8 Hz, 1H), 4.69–4.61 (m, 1H), 4.06–3.93 (m, 2H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 198.8, 156.1, 155.0, 154.9, 152.1, 147.12, 146.07, 146.04, 145.97, 145.90, 145.87, 145.8, 145.6, 145.51, 145.46, 145.4, 145.3, 145.24, 145.18, 145.14, 145.09, 145.0, 144.9, 144.5, 144.3, 144.1, 142.9, 142.5, 142.4, 142.3, 142.2, 142.1, 141.9, 141.81, 141.77, 141.7, 141.6, 141.5, 141.2, 140.2, 140.0, 139.6, 139.4, 135.8, 135.6, 135.5, 135.1, 134.5, 133.7, 130.3, 130.1, 129.2, 127.2, 74.5, 69.0, 56.6, 53.9, 43.3; FT-IR ν/cm^{-1} 2929, 1718, 1513, 1428, 1262, 1035, 802, 747, 526; UV-vis ($CHCl_3$) λ_{max}/nm 256, 311, 431, 698; MALDI-TOF MS m/z calcd for $C_{70}H_9ClO$ $[M]^-$ 900.0347, found 900.0354.



trans-isomer
5h

Spectral data of **5h**: 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 **5h** (22.5 mg, 47%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 10.11 (d, J = 2.8 Hz, 1H), 7.53 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 9.2 Hz, 2H), 5.10 (d, J = 12.4 Hz, 1H), 4.72–4.63 (m, 1H), 3.969 (d, J = 8.8 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 199.4, 155.8, 155.4, 154.2, 151.9, 147.2, 146.24, 146.22, 146.14, 146.10, 146.02, 145.95, 145.93, 145.90, 145.58, 145.56, 145.5, 145.39, 145.37,

145.33, 145.31, 145.29, 145.28, 145.2, 145.13, 145.10, 144.53, 144.49, 144.3, 143.1, 143.0, 142.7, 142.6, 142.54, 142.47, 142.3, 142.1, 142.02, 141.99, 141.95, 141.88, 141.85, 141.8, 141.7, 141.6, 141.5, 140.3, 140.2, 139.7, 139.6, 136.1, 135.4, 135.3, 135.2, 134.8, 132.1, 130.9, 122.7, 74.9, 68.9, 61.5, 53.3, 43.7; FT-IR ν/cm^{-1} 1722, 1508, 1010, 668, 524; UV-vis ($CHCl_3$) λ_{max}/nm 256, 313, 431, 697; MALDI-TOF MS m/z calcd for $C_{70}H_9BrO$ $[M]^-$ 943.9842, found 943.9821.

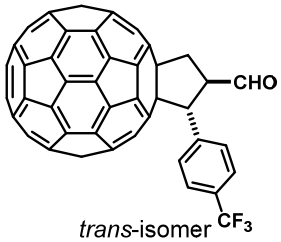


trans-isomer

5i

Spectral data of **5i**: 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 **5i** (19.4 mg, 41%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 10.13 (d, J = 2.8 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 5.17 (d, J = 12.4 Hz, 1H), 4.75–4.67 (m, 1H), 3.98 (d, J = 8.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 199.5, 155.8, 155.4, 154.1, 151.8, 149.0, 147.3, 146.24, 146.17, 146.1, 146.04, 145.97, 145.95, 145.9, 145.6, 145.52, 145.48, 145.40, 145.39, 145.35, 145.33, 145.31, 145.3, 145.26, 145.14, 145.12, 144.54, 144.51, 144.32, 144.31, 144.29, 143.1, 143.0, 142.7, 142.59, 142.55, 142.5, 142.3, 142.11, 142.03, 142.00, 141.96, 141.87, 141.85, 141.8, 141.7, 141.6, 141.5, 140.3, 140.2, 139.7, 139.5, 136.1, 135.4, 135.3, 135.2, 134.4, 130.7, 121.0, 120.7 (J_{C-F} = 257.2 Hz), 74.9, 68.9, 61.3,

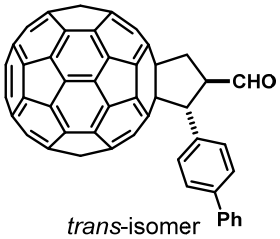
53.4, 43.7; ^{19}F NMR (565 MHz, $CDCl_3/CS_2$) δ: -57.5; FT-IR ν/cm^{-1} 1719, 1508, 1248, 1205, 1160, 524; UV-vis ($CHCl_3$) λ_{max}/nm 255, 318, 431, 697; MALDI-TOF MS m/z calcd for $C_{71}H_9F_3O_2$ $[M]^-$ 950.0560, found 950.0539.



trans-isomer

5j

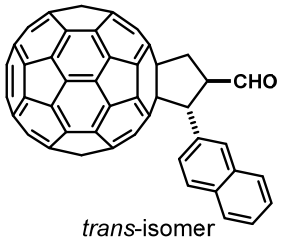
Spectral data of **5j**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **5j** (30.3 mg, 64%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 10.14 (d, J = 2.8 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 5.22 (d, J = 12.8 Hz, 1H), 4.81–4.73 (m, 1H), 4.05–3.95 (m, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 199.2, 155.6, 155.2, 153.9, 151.5, 147.2, 146.21, 146.20, 146.13, 146.05, 146.0, 145.93, 145.91, 145.7, 145.48, 145.46, 145.37, 145.36, 145.32, 145.29, 145.26, 145.2, 145.1, 144.5, 144.28, 144.25, 144.2, 143.03, 142.95, 142.63, 142.55, 142.5, 142.4, 142.2, 142.1, 142.0, 141.94, 141.91, 141.82, 141.79, 141.76, 141.7, 141.5, 141.4, 140.3, 140.2, 139.9, 139.7, 139.5, 136.1, 135.4, 135.2, 135.1, 130.4 (J_{C-F} = 32.4 Hz), 129.7, 125.7, 123.6 (J_{C-F} = 247.0 Hz), 74.7, 68.9, 61.5, 53.3, 43.7; ^{19}F NMR (377 MHz, $CDCl_3/CS_2$) δ: -62.4; FT-IR ν/cm^{-1} 1724, 1512, 1422, 1323, 1164, 1120, 1068, 1017, 841, 527; UV-vis ($CHCl_3$) λ_{max}/nm 258, 313, 431, 697; MALDI-TOF MS m/z calcd for $C_{71}H_9F_3O$ $[M]^-$ 934.0611, found 934.0619.



trans-isomer

5k

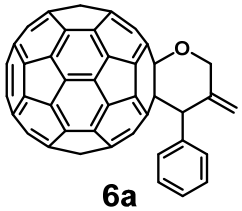
Spectral data of **5k**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **5k** (12.3 mg, 26%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 10.16 (d, *J* = 3.2 Hz, 1H),7.73 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 5.20 (d, *J* = 12.8 Hz, 1H), 4.82–4.74 (m, 1H), 4.05–3.95 (m, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 200.0, 156.1, 155.7, 154.7, 152.5, 147.3, 146.31, 146.27, 146.24, 146.22, 146.21, 146.14, 146.08, 146.00, 145.99, 145.9, 145.8, 145.7, 145.5, 145.43, 145.36, 145.3, 145.2, 145.1, 144.7, 144.6, 144.41, 144.39, 144.38, 143.1, 143.0, 142.7, 142.62, 142.59, 142.5, 142.4, 142.18, 142.15, 142.1, 142.02, 141.96, 141.9, 141.8, 141.6, 141.0, 140.3, 140.2, 140.1, 139.8, 139.6, 136.1, 135.5, 135.4, 135.3, 134.7, 129.9, 128.8, 127.5, 127.0, 75.4, 69.1, 62.1, 53.5, 43.8; FT-IR ν/cm^{-1} 3310, 2973, 2880, 1725, 1510, 1087, 1046, 880, 525; UV-vis ($CHCl_3$) λ_{max}/nm 256, 313, 431, 700; MALDI-TOF MS m/z calcd for $C_{76}H_{14}O$ $[M]^-$ 942.1050, found 942.1029.



trans-isomer

5l

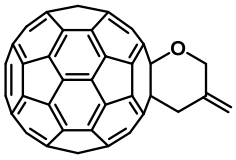
Spectral data of **5l**: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM (v/v = 8:1) to give **5l** (10.2 mg, 21%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 10.15 (d, *J* = 2.8 Hz, 1H), 8.08 (s, 1H), 7.87–7.77 (m, 4H), 7.48–7.43 (m, 2H), 5.31 (d, *J* = 12.4 Hz, 1H), 4.91–4.83 (m, 1H), 4.08–3.97 (m, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 199.9, 156.1, 155.8, 154.7, 152.4, 147.3, 146.3, 146.24, 146.22, 146.20, 146.11, 146.06, 146.0, 145.8, 145.6, 145.5, 145.43, 145.35, 145.31, 145.28, 145.2, 145.1, 144.7, 144.6, 144.39, 144.36, 143.1, 143.0, 142.7, 142.6, 142.5, 142.4, 142.2, 142.1, 142.04, 142.02, 141.96, 141.92, 141.86, 141.7, 141.61, 141.59, 140.3, 140.2, 139.7, 139.6, 136.1, 135.5, 135.4, 135.3, 133.2, 133.0, 128.8, 128.1, 127.8, 126.6, 126.5, 75.4, 69.1, 62.6, 53.5, 43.8; FT-IR ν/cm^{-1} 1723, 1510, 746, 574, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 313, 431, 698; MALDI-TOF MS m/z calcd for $C_{74}H_{12}O$ $[M]^-$ 916.0894, found 916.0878.



6a

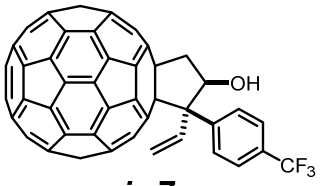
Spectral data of **6a**[3]: ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) *δ* 7.63 (d, *J* = 7.6 Hz, 2H),

7.34 (t, *J* = 7.2 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 1H), 5.80 (s, 1H), 5.75 (d, *J* = 15.6 Hz, 1H), 5.54–5.49 (m, 2H), 5.36 (s, 1H).



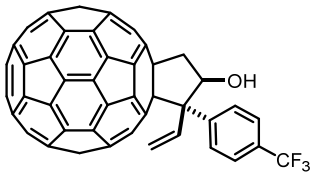
6m

Spectral data of **6m**[3]: the mixture was separated and purified by silica gel column chromatography with CS_2 as the eluent to give C_{60} and **6m** (12.7 mg, 32%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 5.50 (s, 2H), 5.45 (s, 2H), 4.24 (s, 2H).



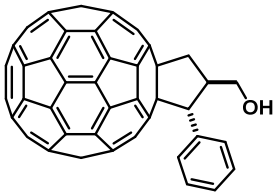
***cis*-7g**

Spectral data of ***cis*-7g**: the mixture was separated and purified by silica gel column chromatography with CS_2/DCM (v/v = 10:1) as the eluent to give ***cis*-7g** (10.2 mg, 27%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.38 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.50-7.43 (m, 1H), 5.62 (d, *J* = 10.8 Hz, 2H), 5.11 (d, *J* = 17.6 Hz, 1H), 4.20 (dd, *J* = 14.0, 3.2 Hz, 1H), 3.85 (dd, *J* = 14.0, 2.4 Hz, 1H), 2.71 (br, 1H); the ^{13}C NMR spectrum of ***cis*-7g** could not be obtained because of poor solubility of the product; FT-IR ν/cm^{-1} 3284, 2923, 1571, 1456, 1324, 1164, 1120, 1072, 1016, 927, 835, 526; UV-vis ($CHCl_3$) λ_{max}/nm 256, 312, 431, 701; MALDI-TOF MS m/z calcd for $C_{72}H_{11}F_3O$ $[M]^-$ 948.0767, found 948.0746.



***trans*-7g**

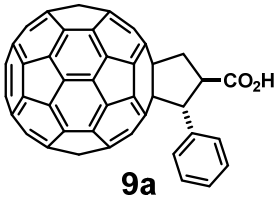
Spectral data of ***trans*-7g**: the mixture was separated and purified by silica gel column chromatography with CS_2/DCM (v/v = 4:1) as the eluent to give ***trans*-7g** (25.1 mg, 66%); amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.00 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.62 (dd, J = 17.6, 10.8 Hz, 1 H), 6.24 (td, J = 12.0, 6.4 Hz, 1 H), 5.99 (d, J = 11.2 Hz, 1H), 5.25 (d, J = 17.2 Hz, 1H), 3.96 (dd, J = 12.4, 6.4 Hz, 1 H), 3.73 (t, J = 12.4 Hz, 1H), 2.39 (d, J = 11.6 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 157.7, 156.0, 152.8, 152.5, 147.6, 147.5, 146.8, 146.49, 146.45, 146.4, 146.3, 146.2, 146.17, 145.8, 145.7, 145.61, 145.55, 145.52, 145.50, 145.48, 145.42, 145.41, 145.2, 144.9, 144.6, 144.4, 144.3, 143.9, 143.33, 143.28, 142.90, 142.86, 142.8, 142.7, 142.34, 142.27, 142.23, 142.20, 142.16, 142.0, 141.97, 141.89, 141.62, 141.57, 141.5, 140.7, 140.5, 139.7, 139.5, 139.1, 137.6, 135.9, 135.7, 134.5, 130.7, 129.9 (J_{C-F} = 32.4 Hz), 125.33, 125.31, 124.0 (J_{C-F} = 271.0 Hz), 123.3, 76.4, 71.2, 65.1, 64.9, 46.4; FT-IR ν/cm^{-1} 3373, 2854, 1616, 1413, 1321, 1164, 1112, 1068, 1016, 936, 808, 524; UV-vis ($CHCl_3$) λ_{max}/nm 257, 313, 433, 699; MALDI-TOF MS m/z calcd for $C_{72}H_{11}F_3O$ $[M]^-$ 948.0767, found 948.0746.



trans-isomer

8a

Spectral data of **8a**: the mixture was separated and purified by silica gel column chromatography with CS_2/DCM (v/v = 4:1) to give the quantitative product **8a**; amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.61 (s, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 4.27 (d, *J* = 10.0 Hz, 1H), 4.09 (d, *J* = 9.6 Hz, 1H), 4.03–3.92 (m, 2H), 3.78 (t, *J* = 12.0 Hz, 1H), 1.58 (s, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 157.4, 156.9, 155.8, 153.7, 147.2, 146.4, 146.2, 146.18, 146.15, 146.1, 146.04, 146.00, 145.93, 145.91, 145.7, 145.5, 145.29, 145.27, 145.24, 145.17, 145.11, 145.05, 144.6, 144.4, 143.1, 143.0, 142.6, 142.51, 142.48, 142.42, 142.39, 142.2 142.1, 142.02, 142.00, 141.95, 141.93, 141.89, 141.8, 141.7, 141.6, 141.5, 140.2, 140.1, 139.6, 139.3, 137.2, 136.1, 135.4, 135.1, 135.0, 128.8, 127.8, 76.0, 69.2, 62.9, 62.4, 46.0, 43.7; FT-IR ν/cm^{-1} 1704, 1428, 1357, 1218, 1185, 1085, 1041, 698, 526; UV-vis ($CHCl_3$) λ_{max}/nm 256, 326, 432, 702; MALDI-TOF MS m/z calcd for $C_{70}H_{12}O$ $[M]^-$ 868.0894, found 868.0872.



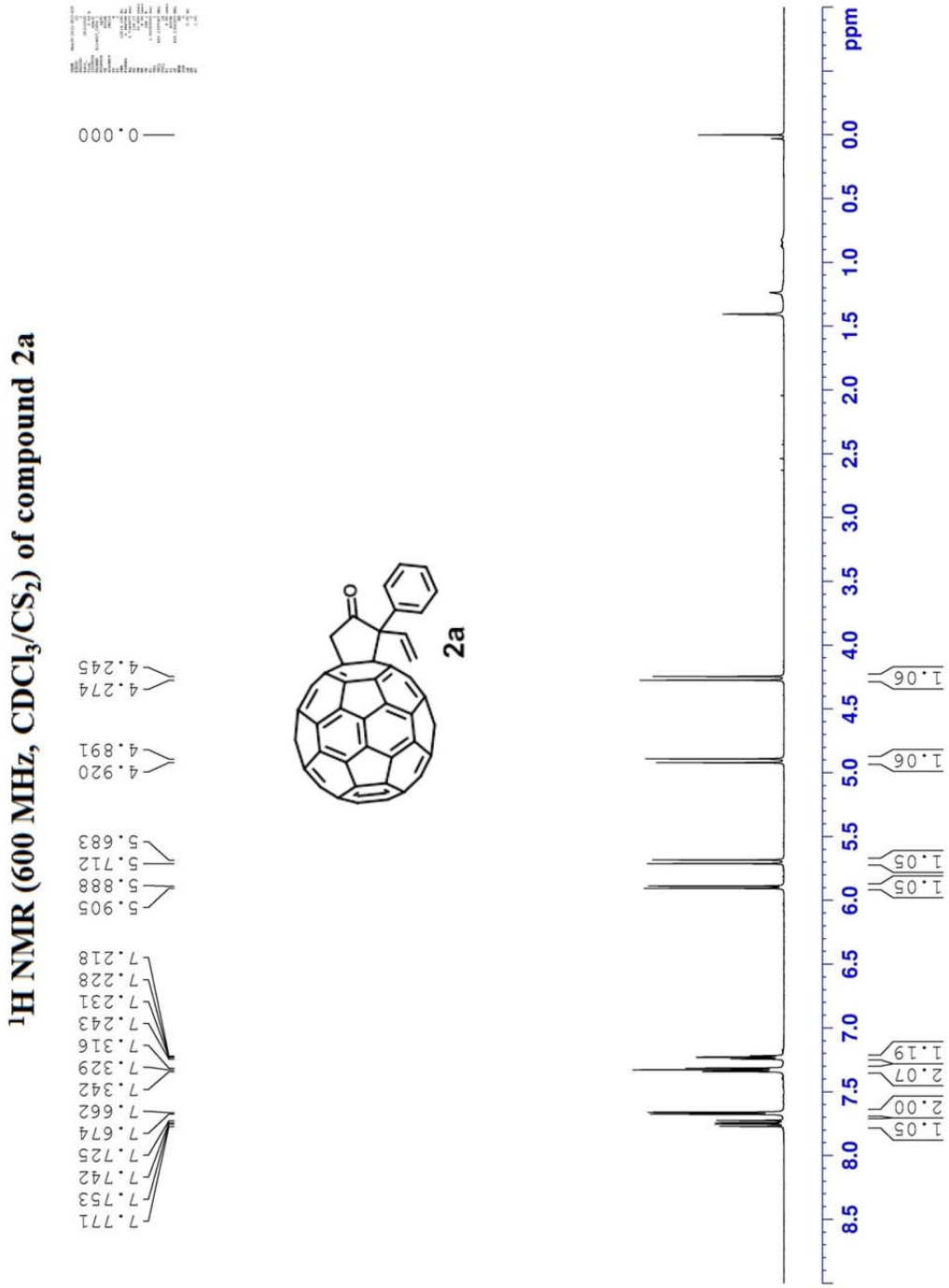
9a

Spectral data of **9a**: the mixture was separated and purified by silica gel column chromatography with CS_2/DCM/EA (v/v/v = 4:1:1) to give **9a** (30.0 mg, 85%); amorphous brown solid; ^{1}H NMR (400 MHz, DMSO-d_6/CS_2) δ 12.9 (br, 1 H), 7.63 (d, J = 7.2 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 5.17 (d, J = 12.4 Hz, 1H), 4.65–4.57 (m, 1H), 4.07–4.03 (m, 1 H), 3.95 (t, J = 12.4 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6/CS_2 with $Cr(acac)_3$ as relaxation reagent) δ 172.6, 156.3, 156, 155.1, 146.8, 146.1, 145.81, 145.76, 145.75, 145.72, 145.63, 145.59, 145.5, 145.4, 145.08, 145.97, 144.89, 144.85, 144.81, 144.76, 144.71, 144.65, 144.58, 144.17, 144.0, 143.96, 142.65, 142.59, 142.2, 142.14, 142.09, 142.03, 141.8, 141.7, 141.65, 141.6, 141.58, 141.53, 141.4, 141.27, 141.25, 141.1, 139.8, 139.7, 139.2, 139.0, 136.42, 135.7, 135.2, 135.0, 134.97, 128.3, 127.5, 74.8, 69.1, 63.5, 46.5, 46.1; FT-IR ν/cm^{-1} 3456, 1711, 1427, 1262, 1183, 1022, 697, 527; UV-vis ($CHCl_3$) λ_{max}/nm 256, 309, 430, 697; MALDI-TOF MS m/z calcd for $C_{70}H_{10}O_2$ $[M]^-$ 882.0686, found 882.0672.

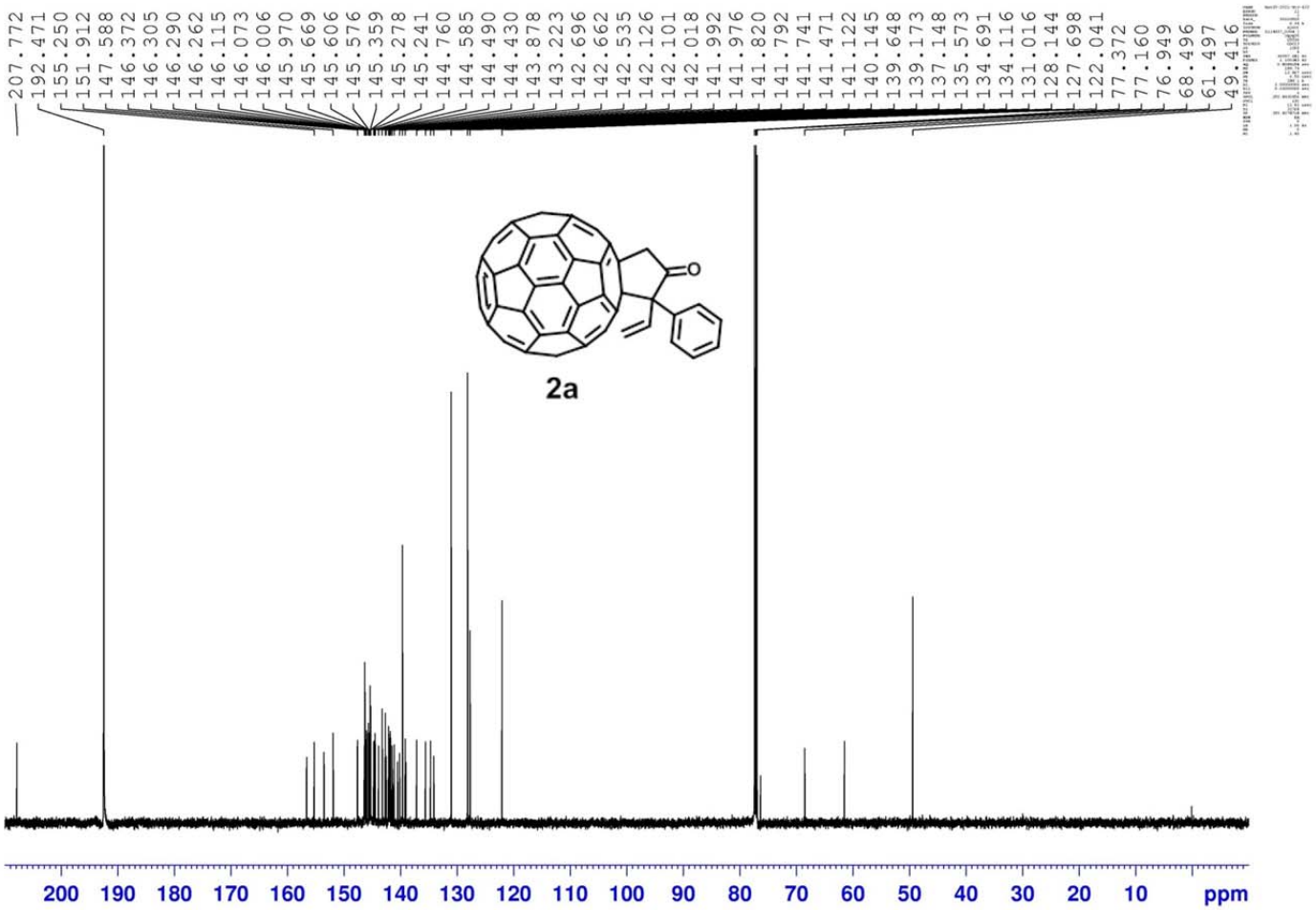
References:

(3) Liu, Q.; Liu, T.-X.; Ru, Y.; Zhu, X.; Zhang, G. Palladium-catalyzed decarboxylative heterocyclizations of [60]fullerene: preparation of novel vinyl-substituted [60]fullerene-fused tetrahydrofurans/pyrans/quinolines. *Chem. Commun.* **2019**, *55*, 14498.

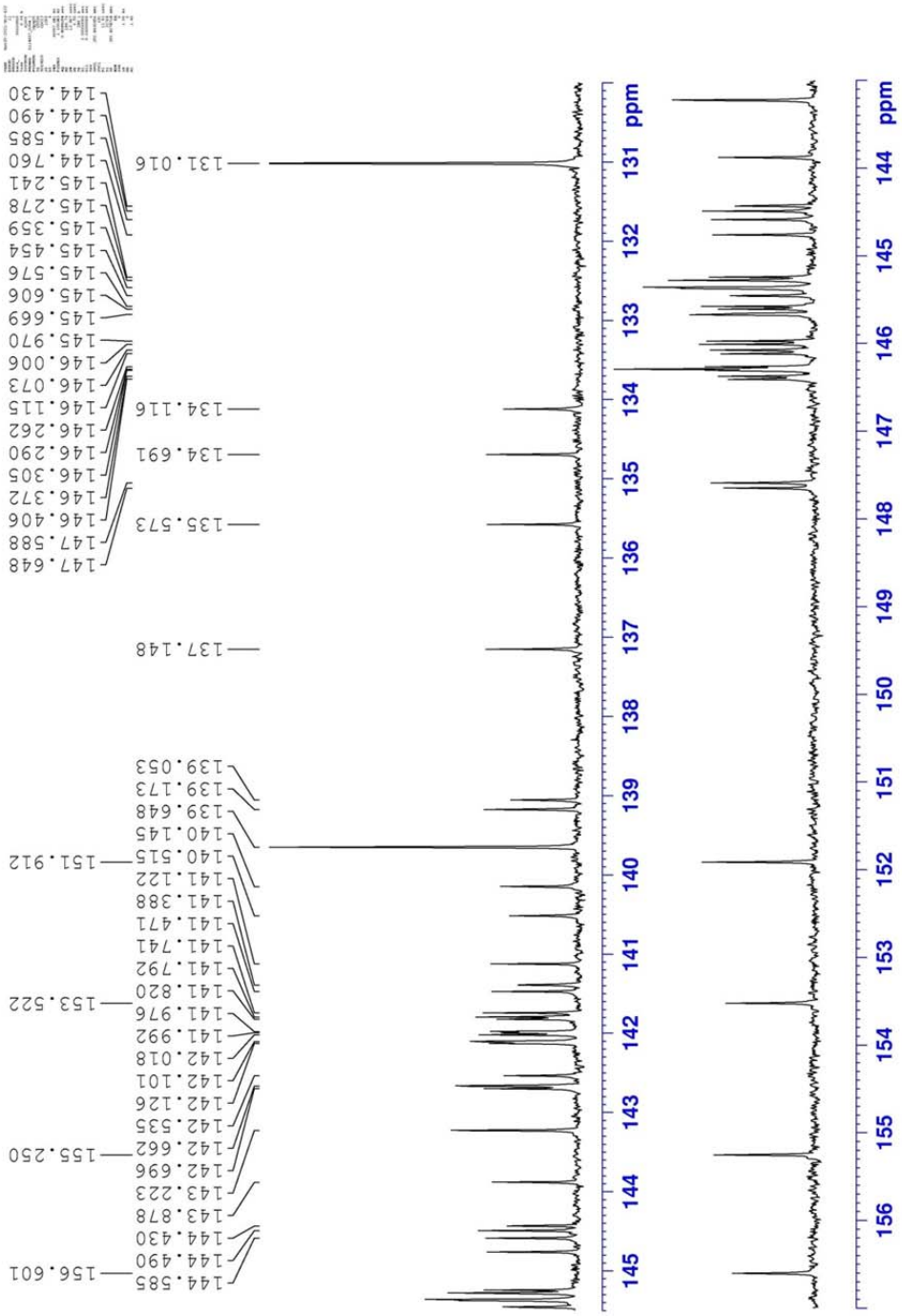
9. ^{1}H, ^{13}C and ^{19}F NMR Spectra of All Compounds



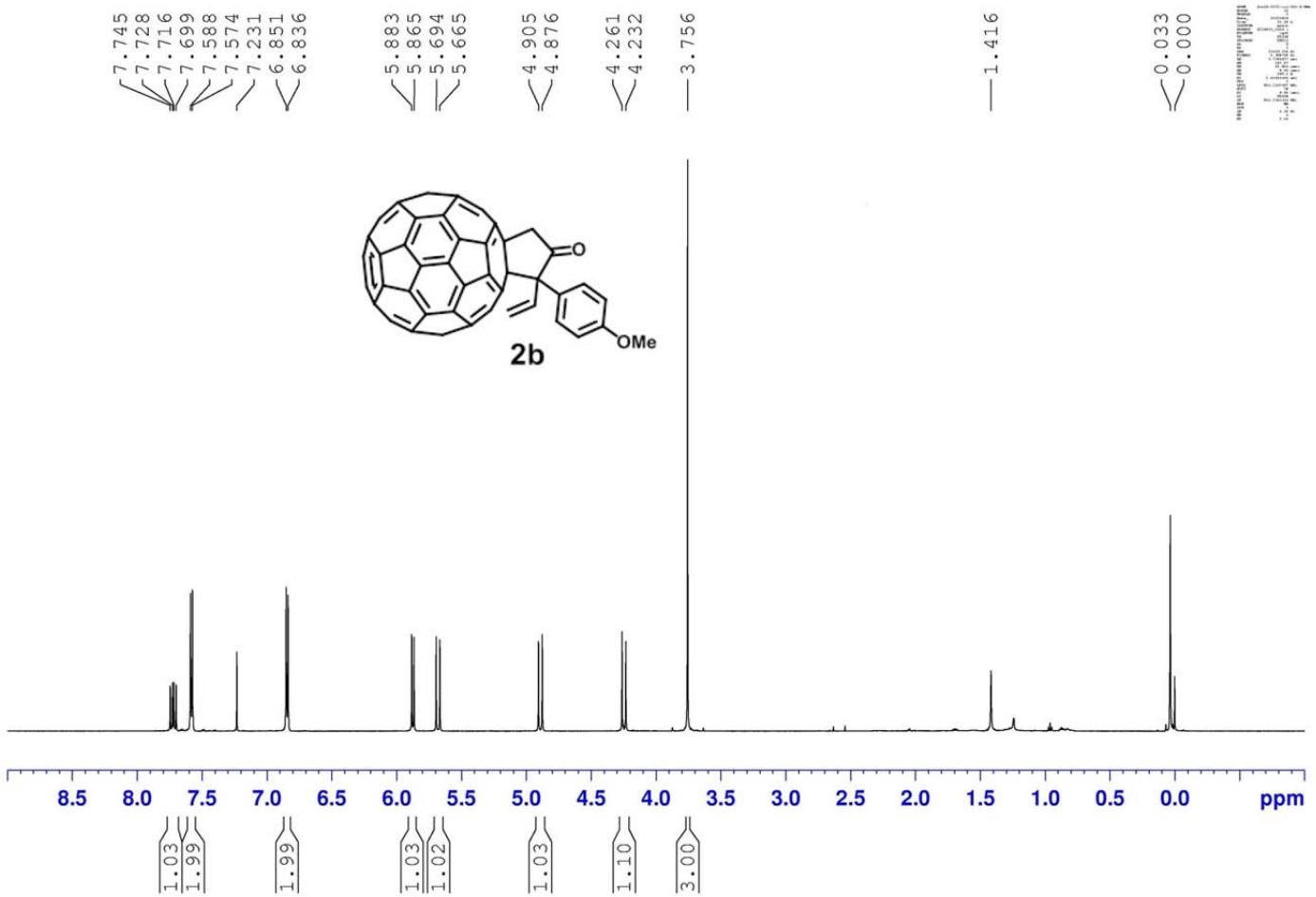
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2a



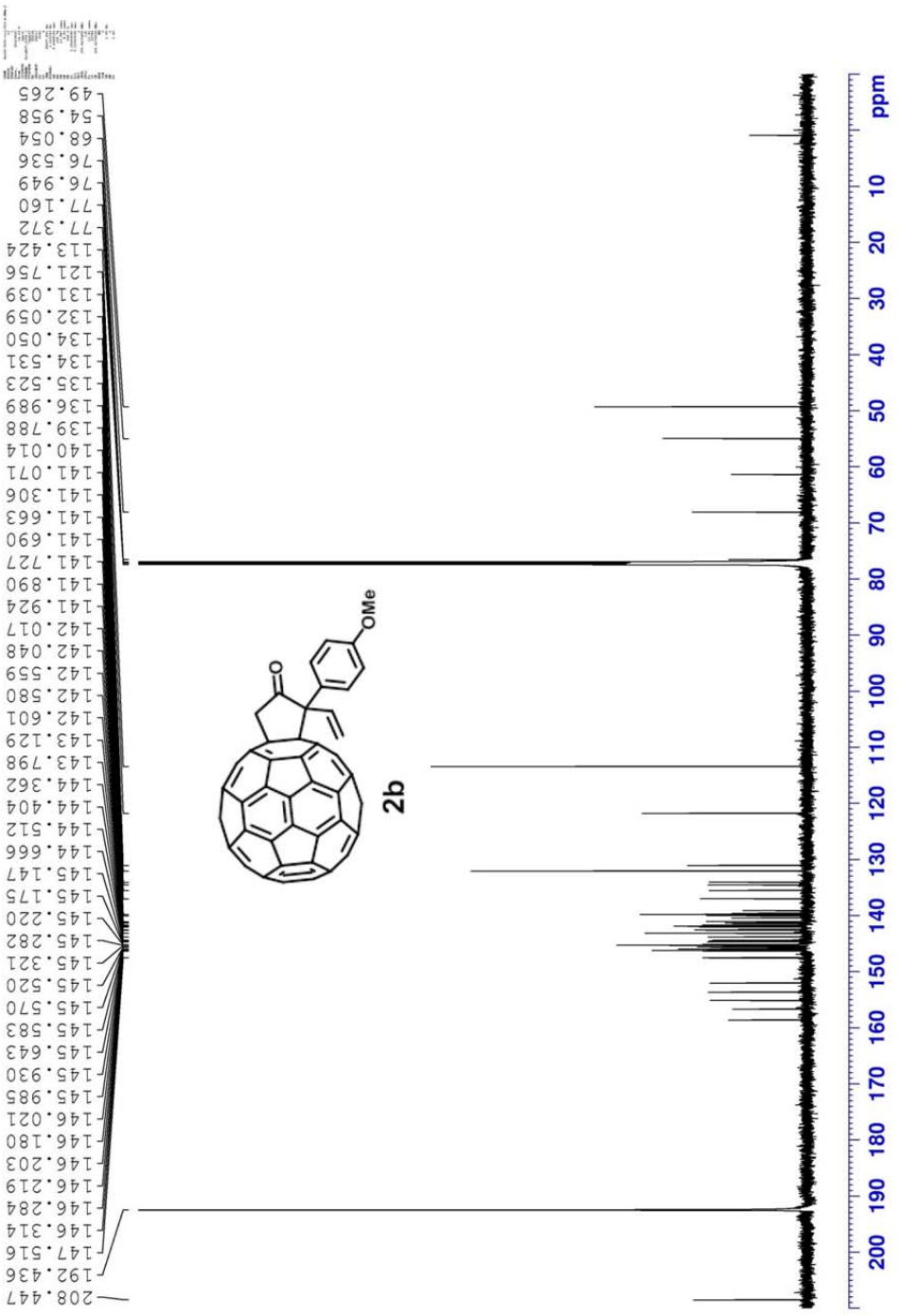
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2a



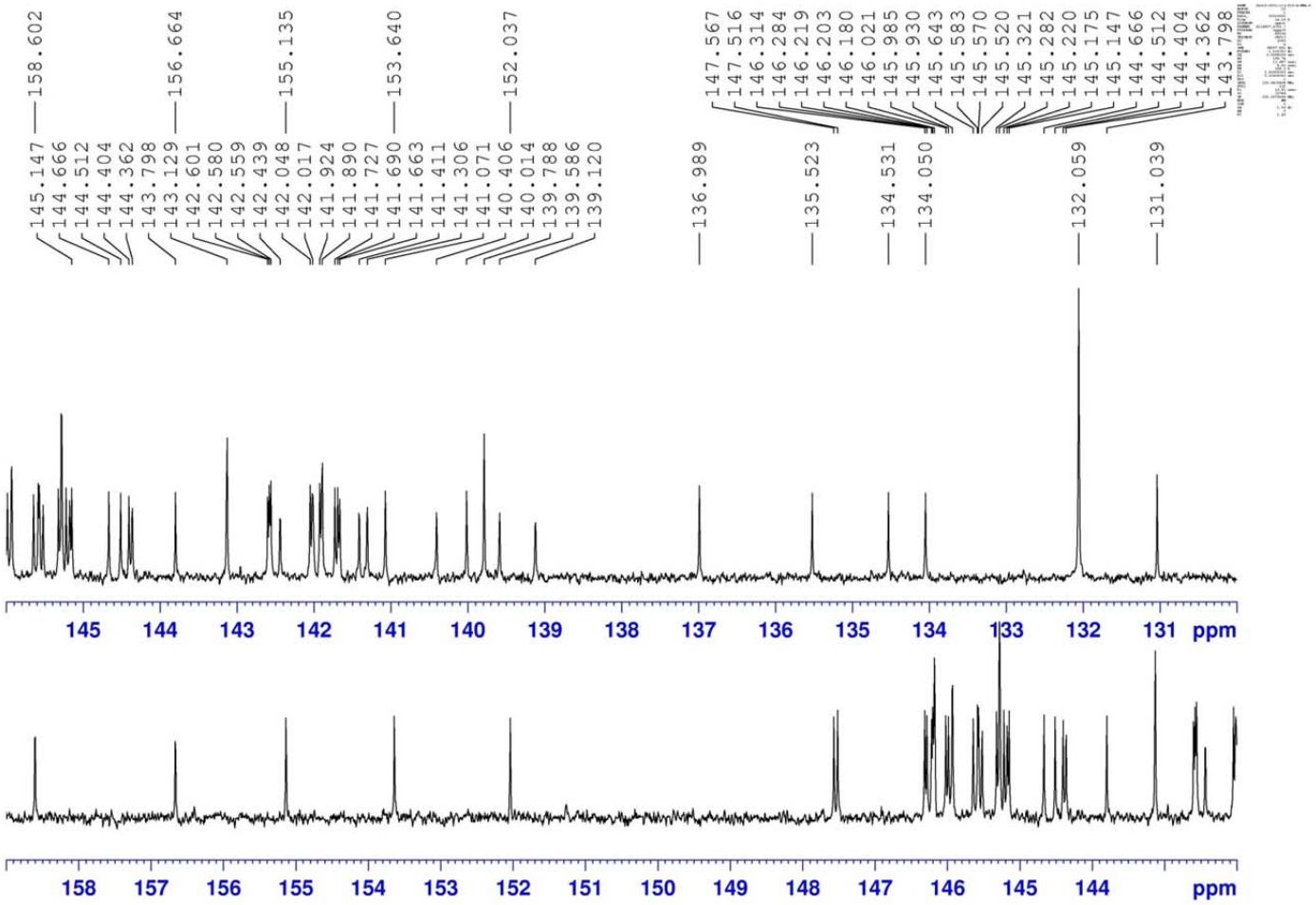
^{1}H NMR (600 MHz, $CDCl_3/CS_2$) of compound 2b



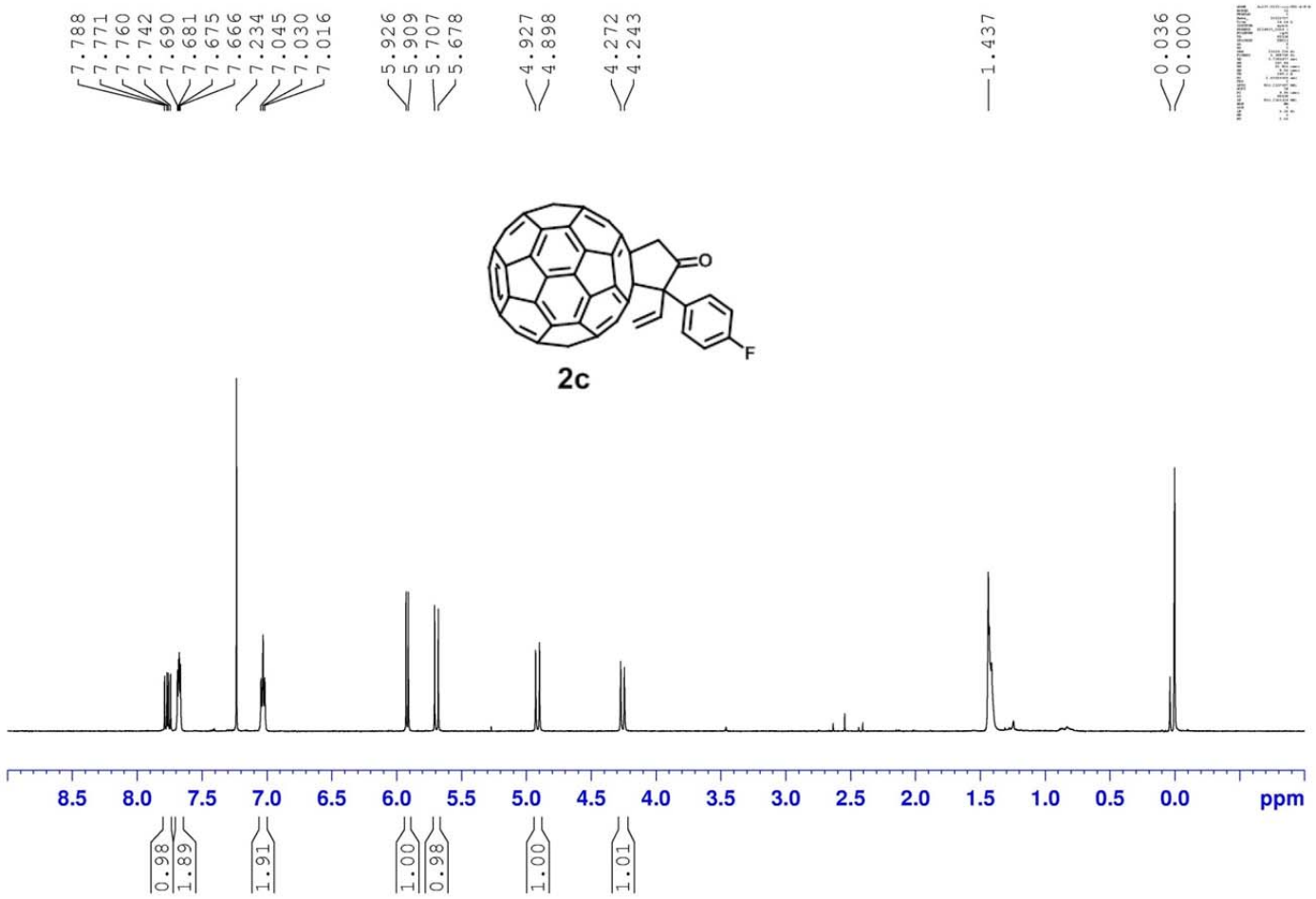
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2b



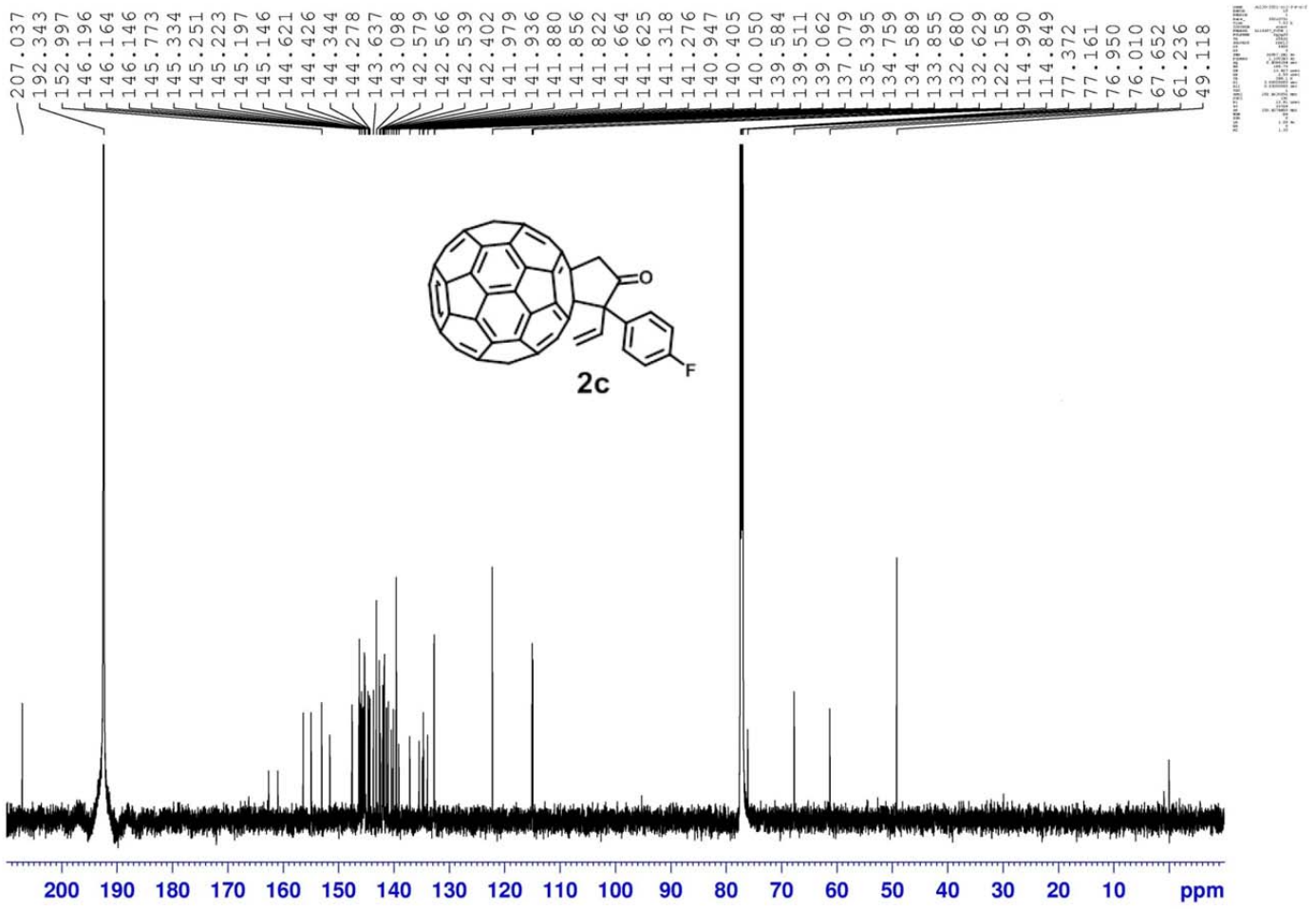
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2b



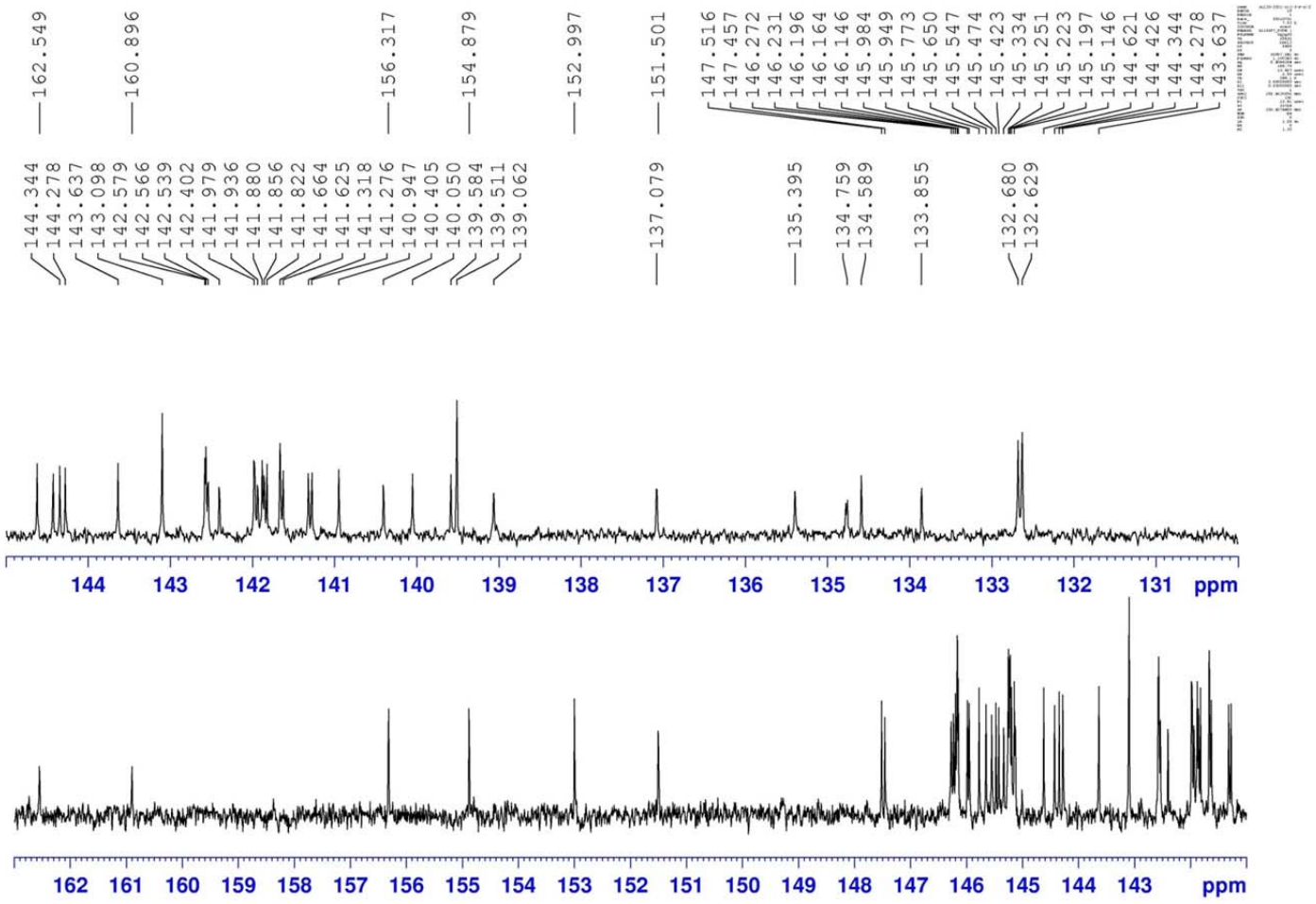
^{1}H NMR (600 MHz, $CDCl_3/CS_2$) of compound 2c



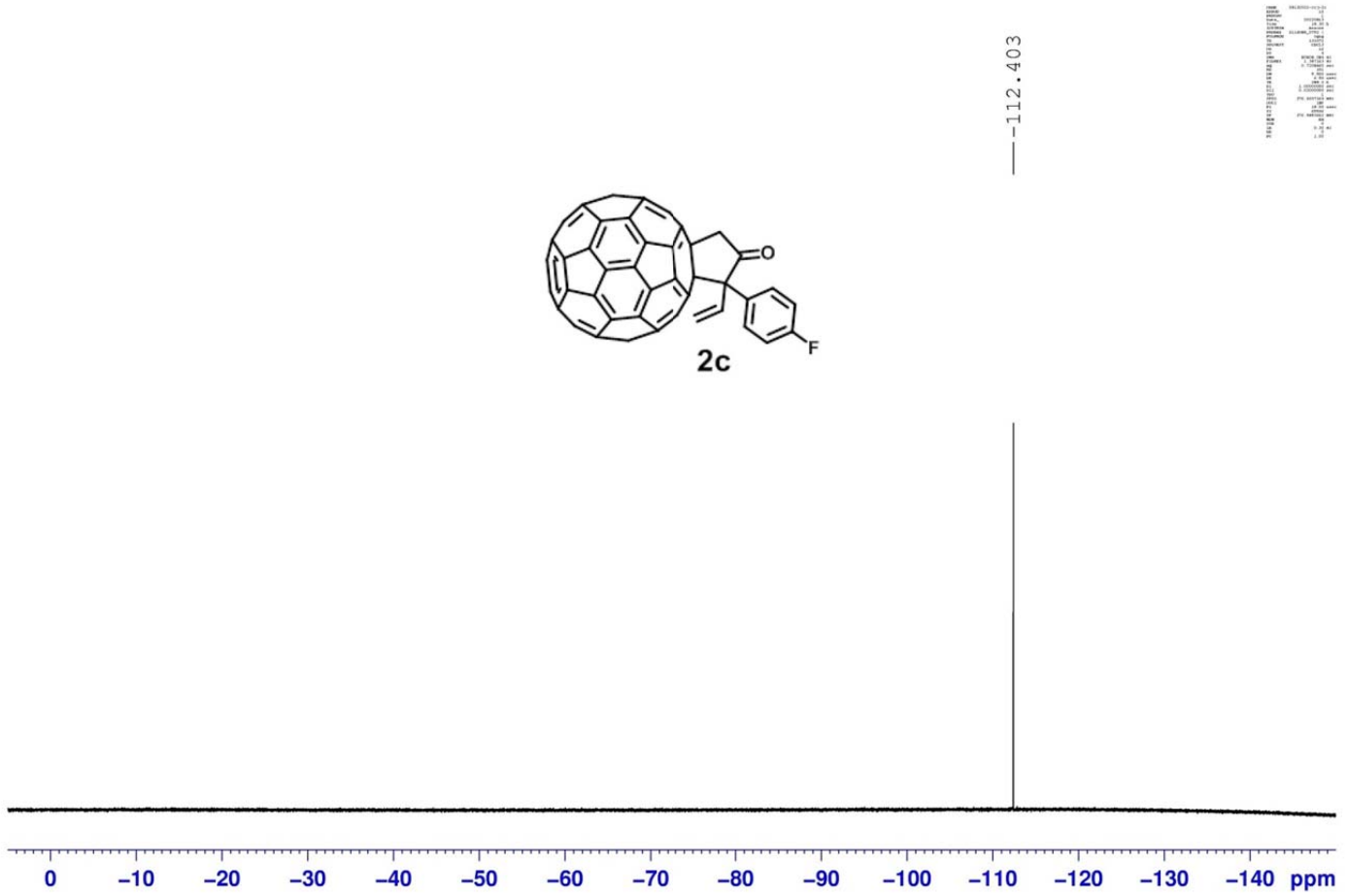
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2c



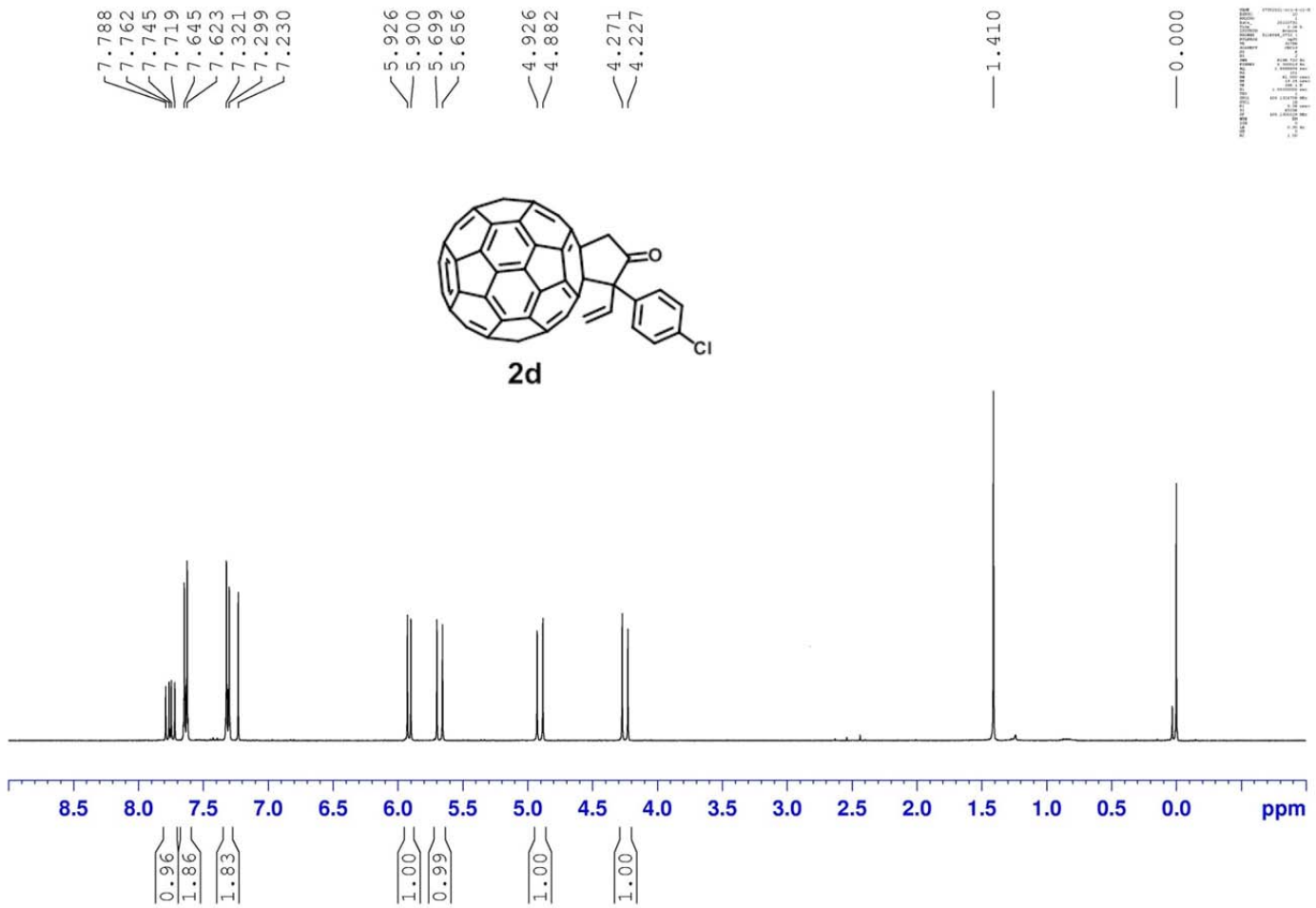
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2c

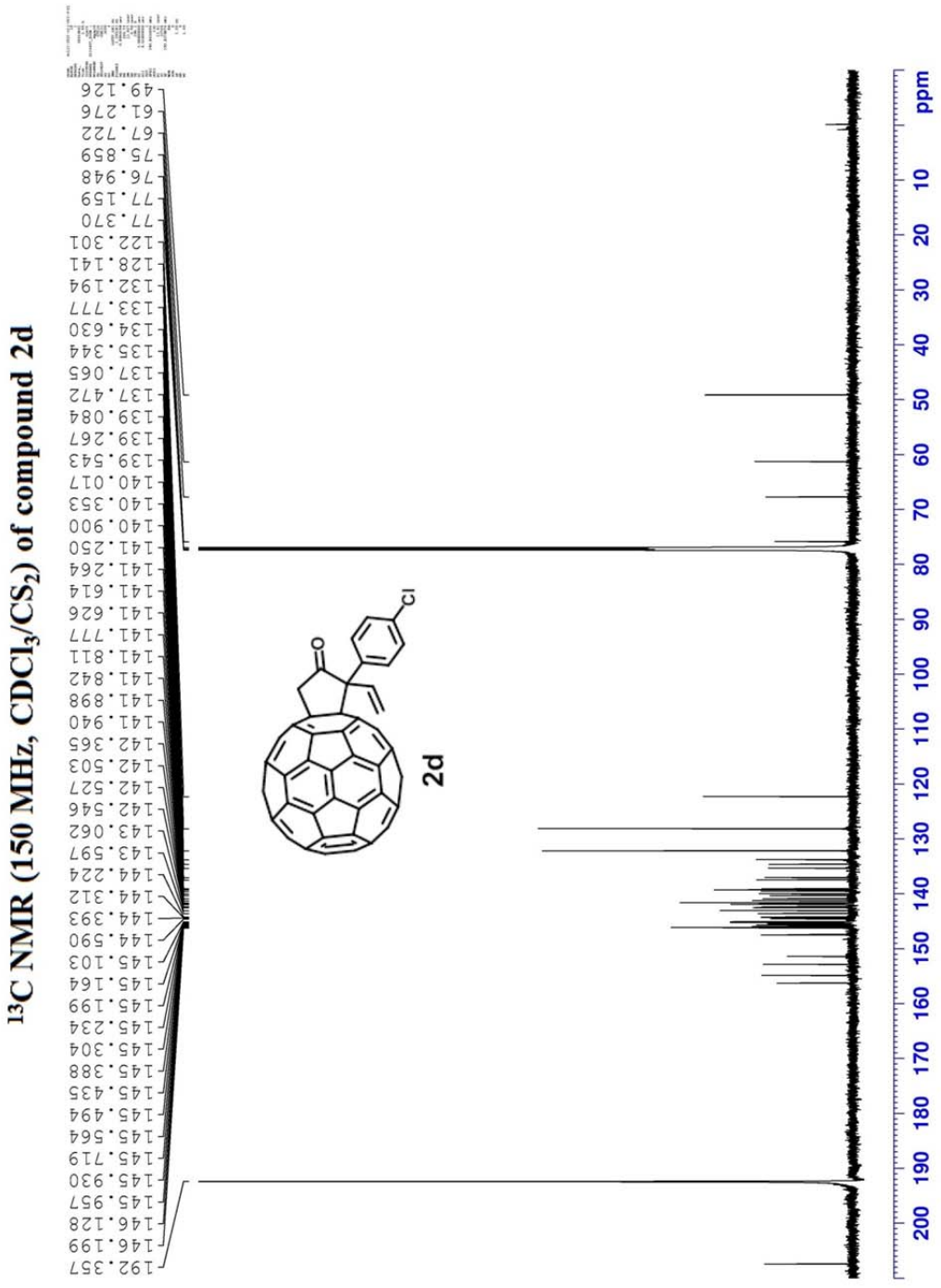


^{19}F NMR (377 MHz, $CDCl_3/CS_2$) of compound 2c

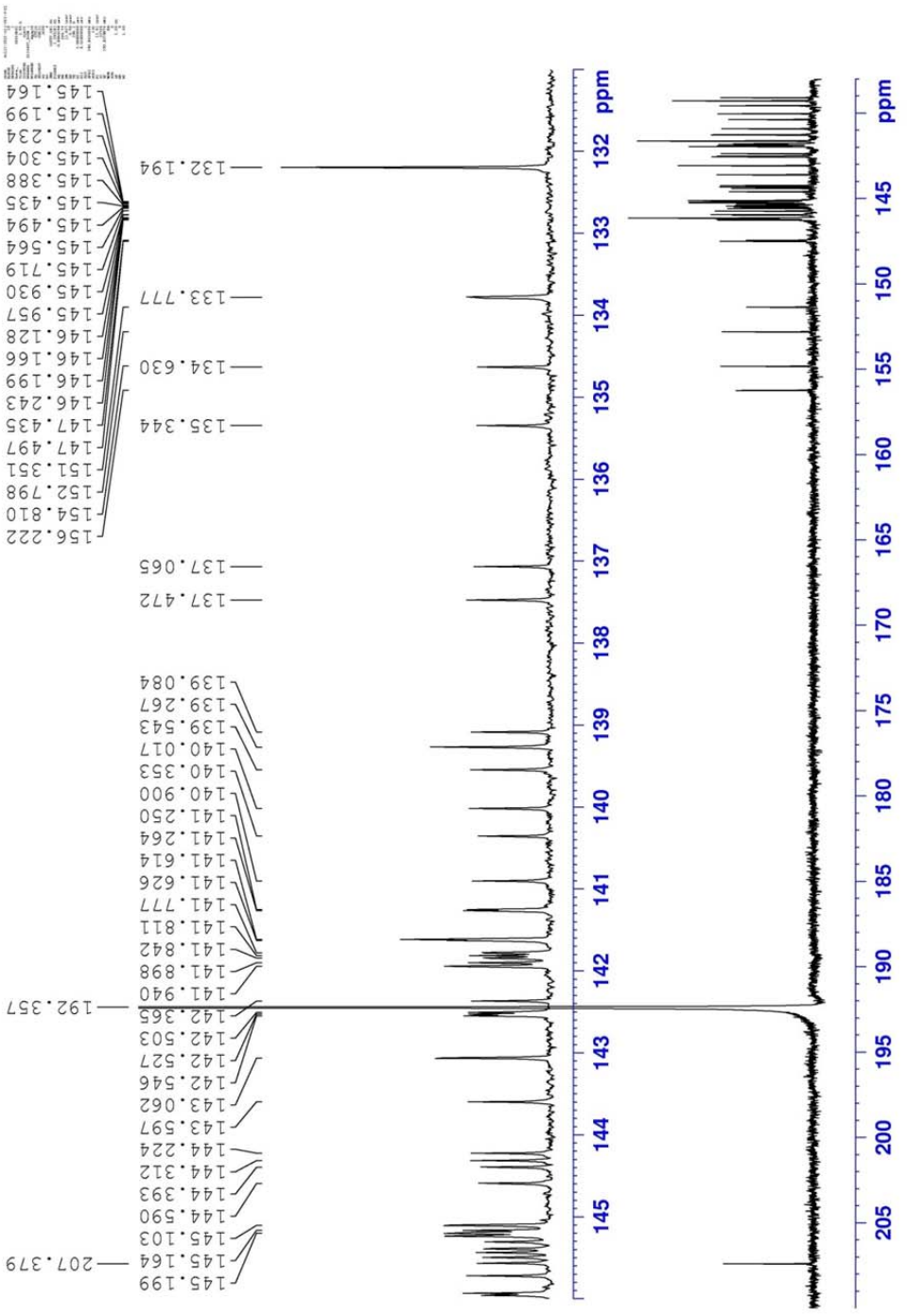


^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2d

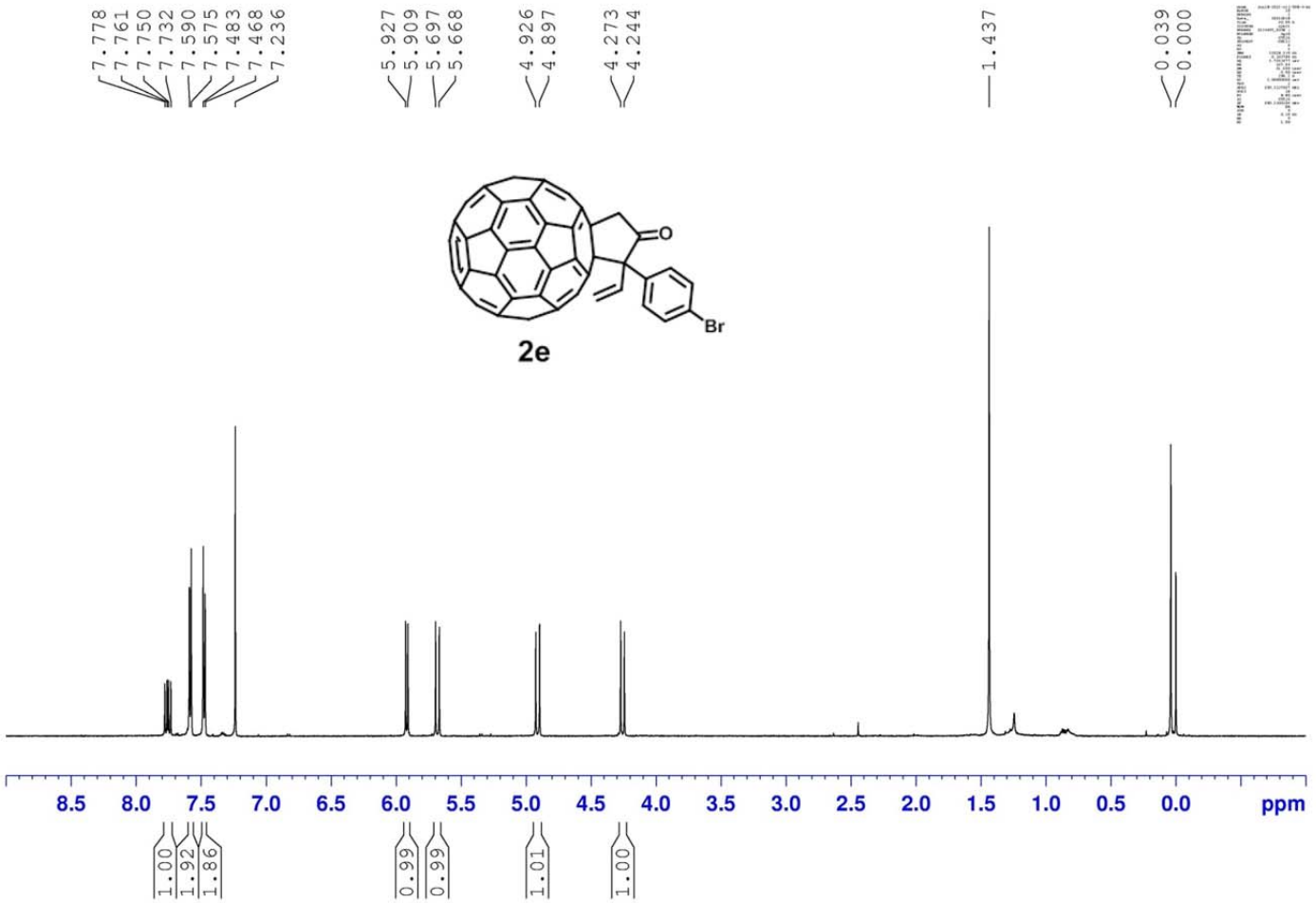


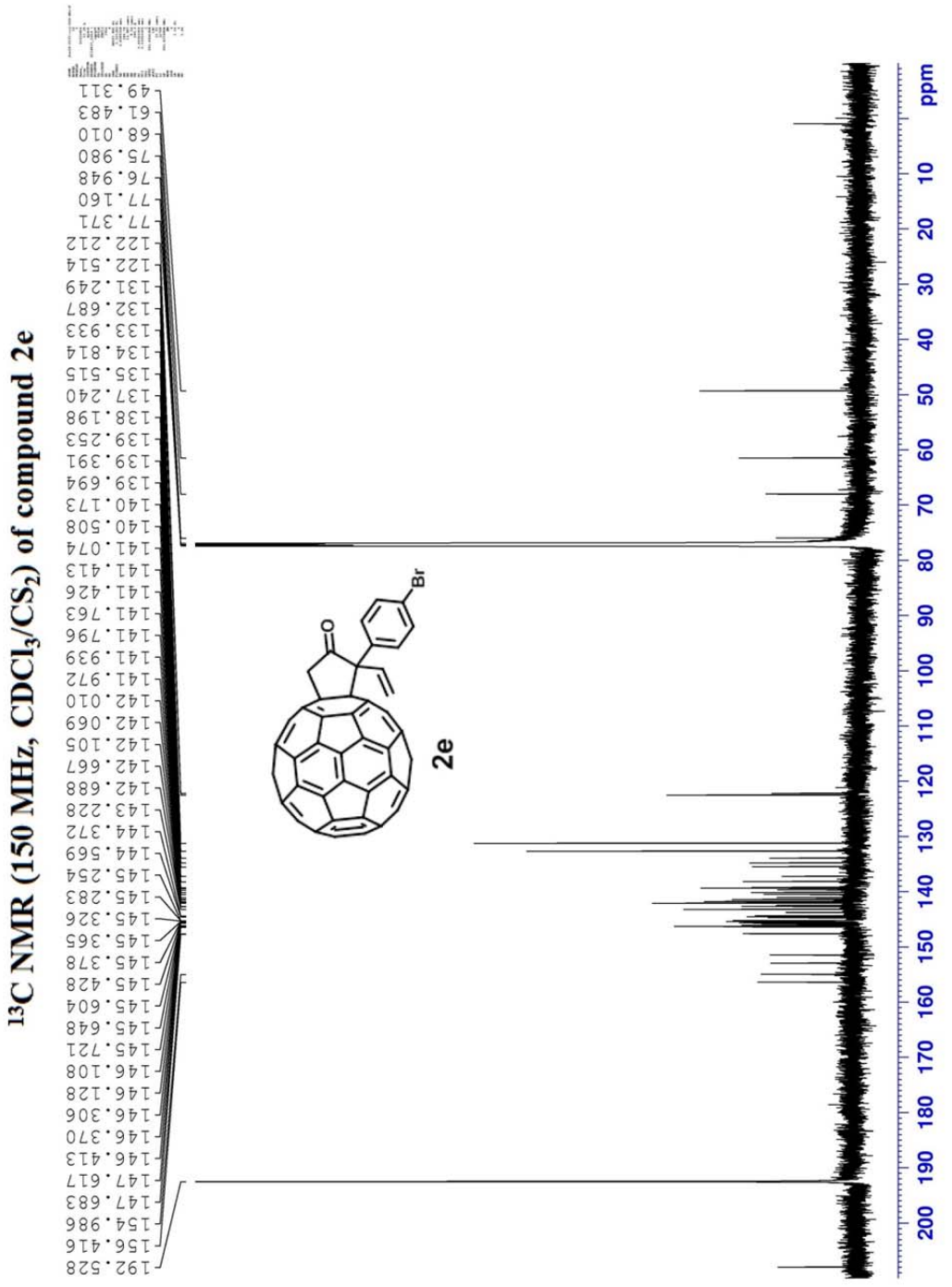

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2d
192.357
146.199
146.128
145.957
145.930
145.719
145.564
145.494
145.435
145.388
145.304
145.234
145.199
145.164
145.103
144.590
144.393
144.312
144.224
143.597
143.062
142.546
142.527
142.503
142.365
141.940
141.898
141.842
141.811
141.777
141.626
141.614
141.264
141.250
140.900
140.353
140.017
139.543
139.267
139.084
137.472
137.065
135.344
134.630
133.777
132.194
128.141
122.301
77.370
77.159
76.948
75.859
67.722
61.276
49.126
O
Cl
2d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

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

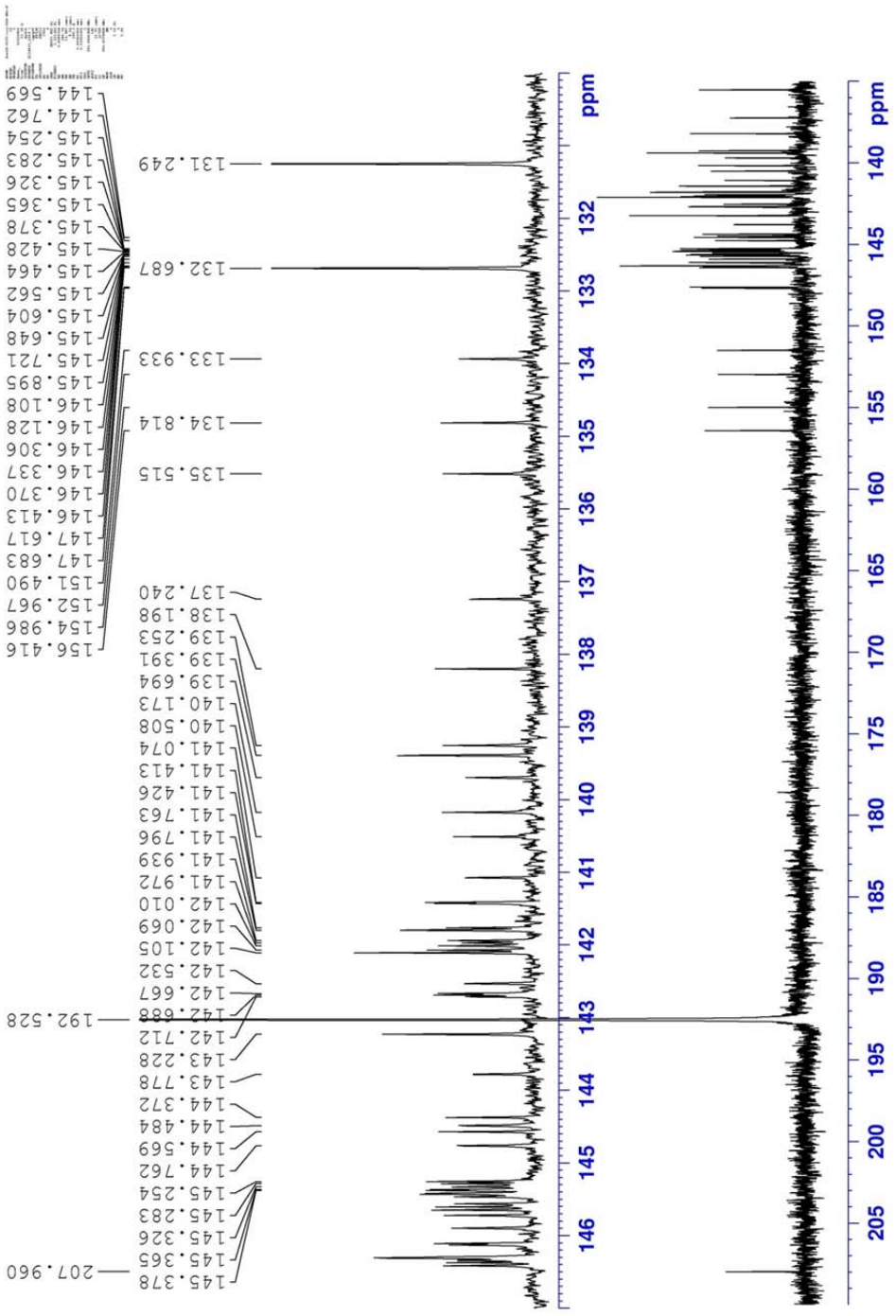


^{1}H NMR (600 MHz, $CDCl_3/CS_2$) of compound 2e

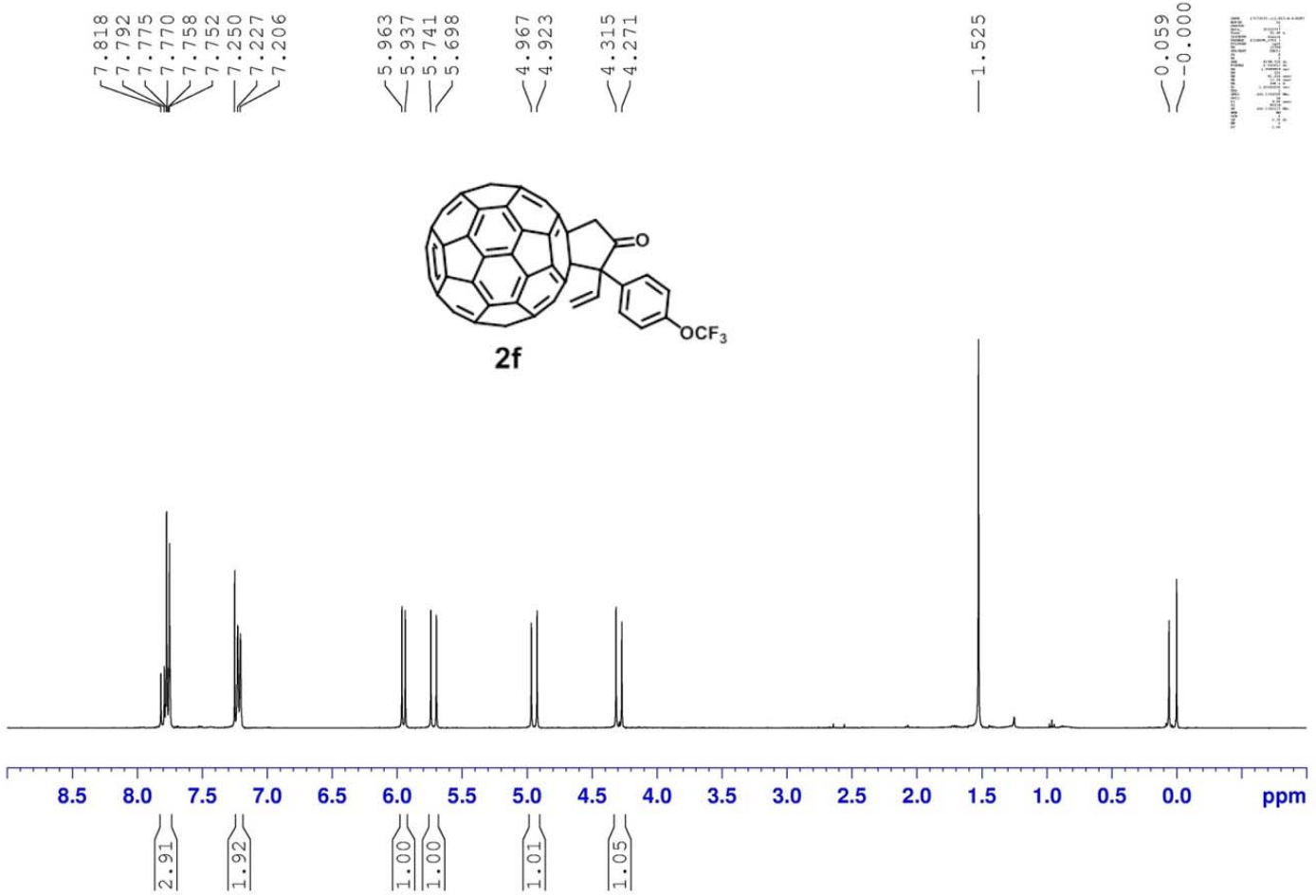


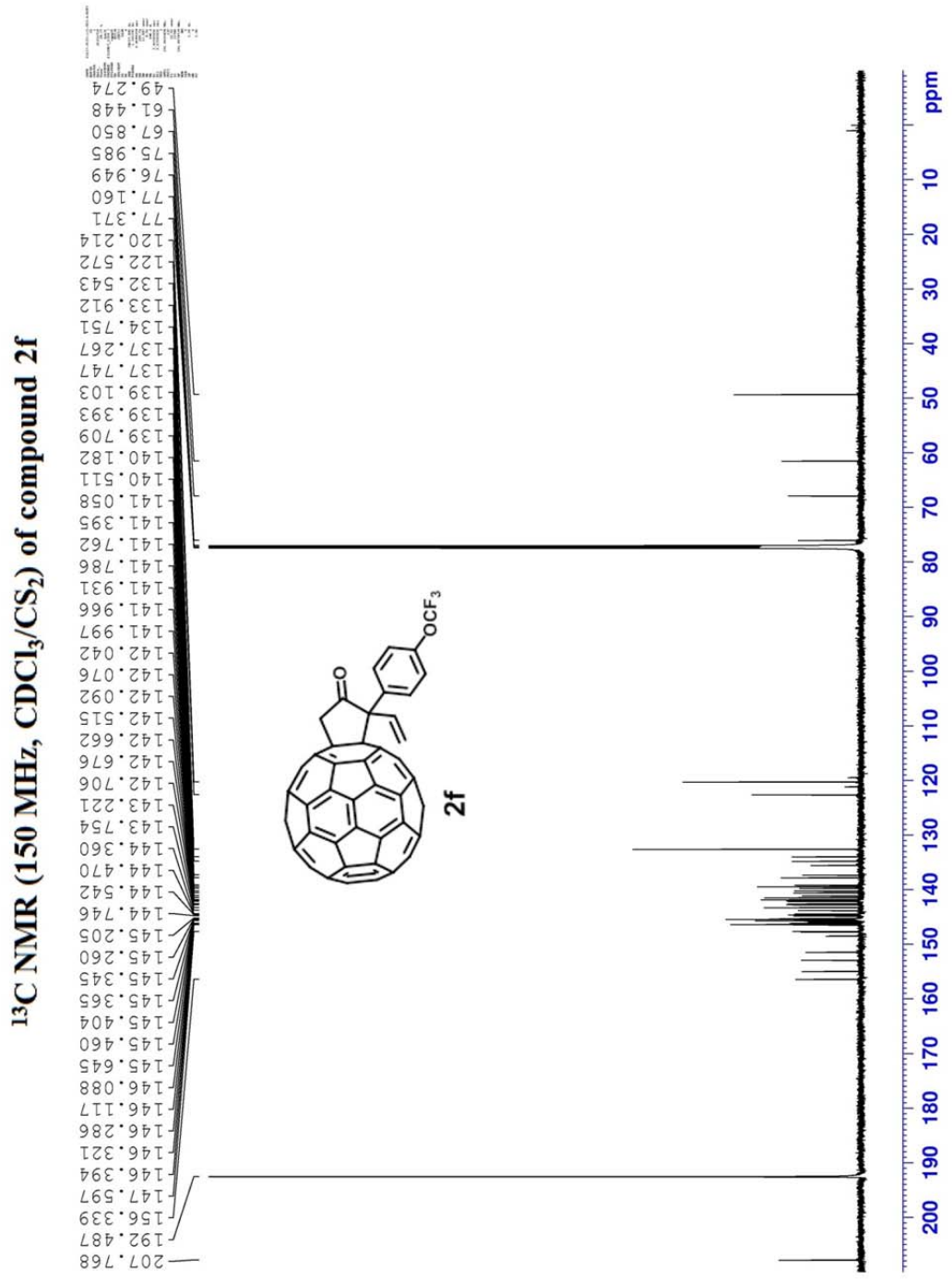

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2e
Br
2e
ppm

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

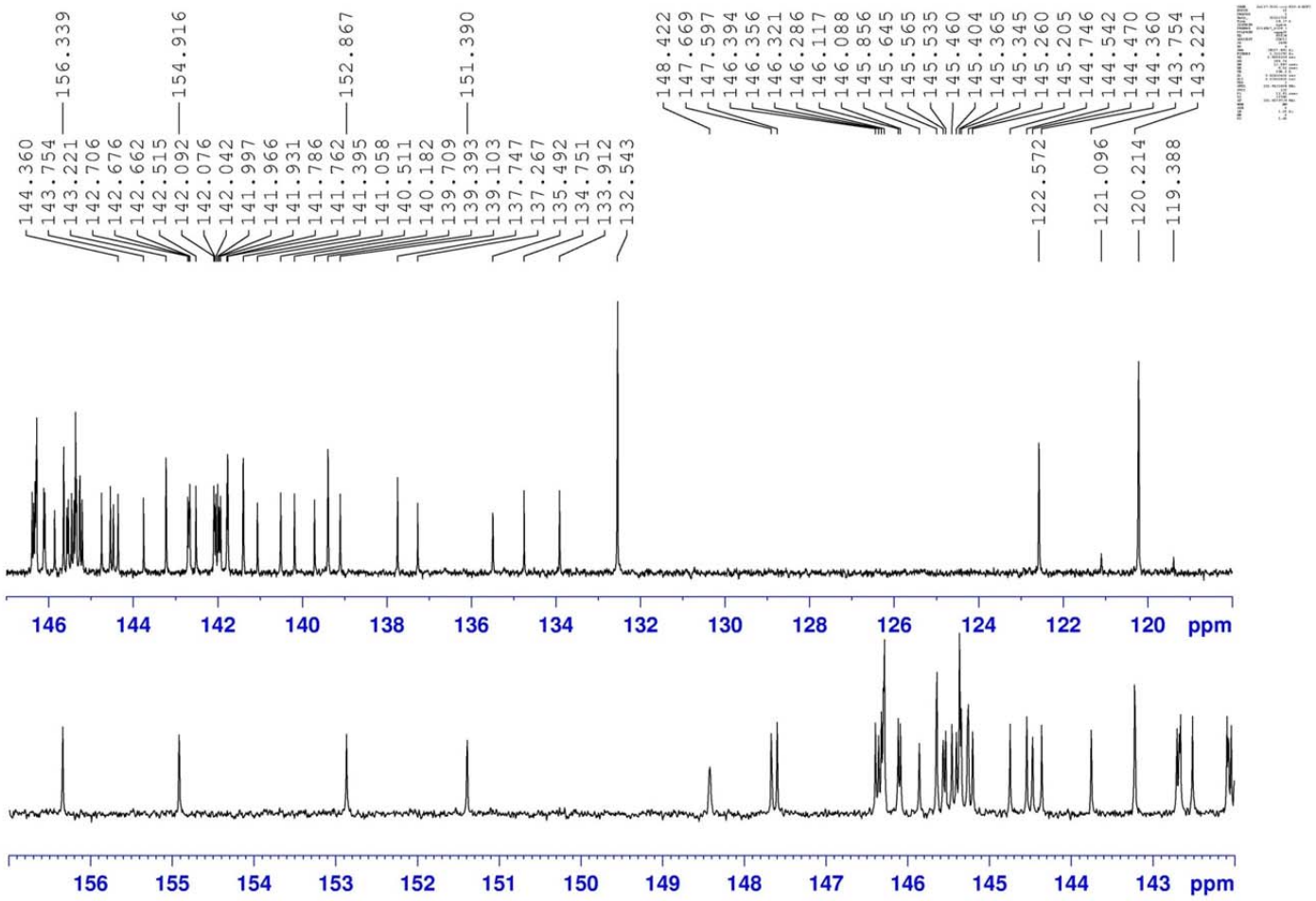


^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2f

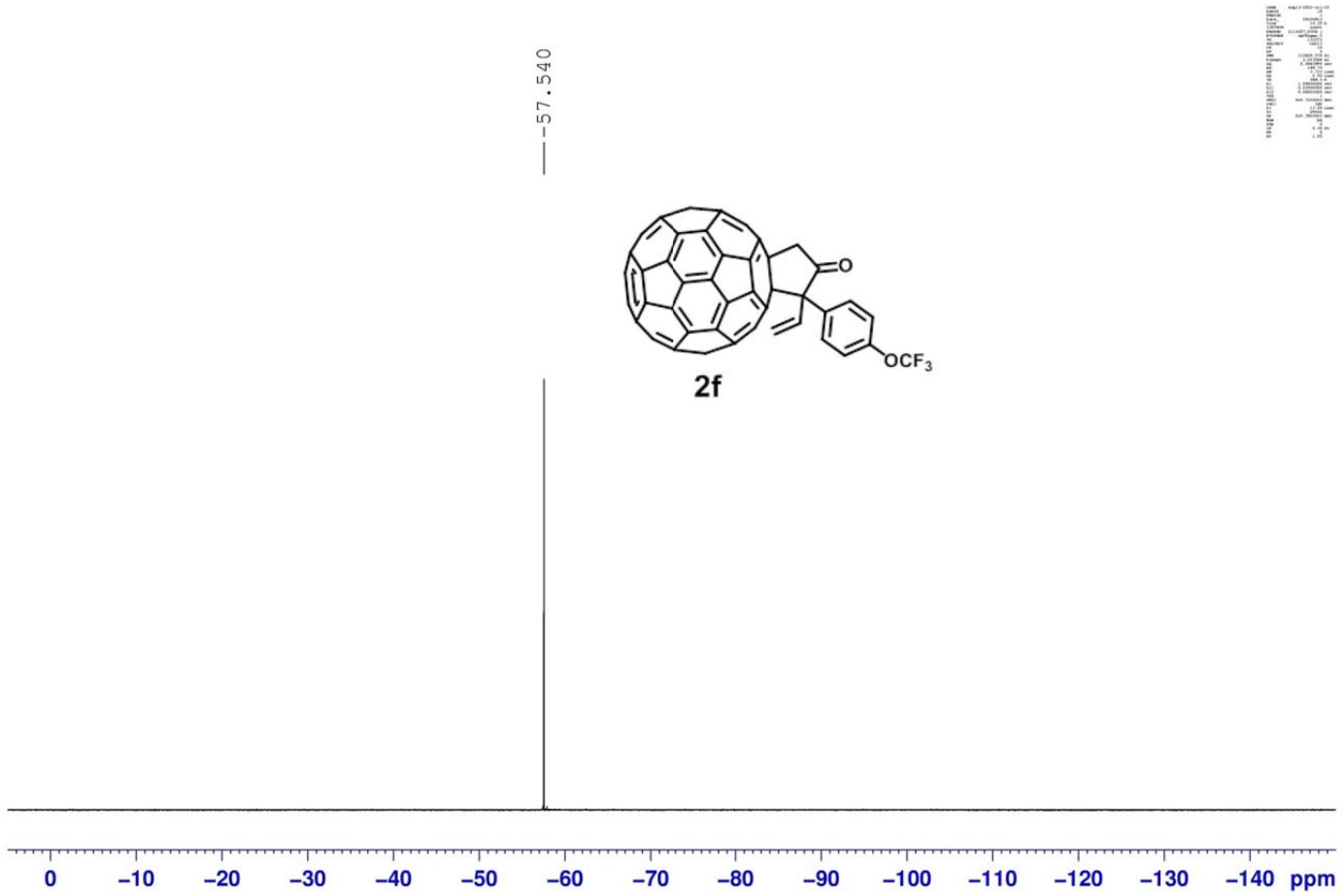



^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2f
207.768
192.487
156.339
147.597
146.394
146.321
146.286
146.117
146.088
145.645
145.460
145.404
145.365
145.345
145.260
145.205
144.746
144.542
144.470
144.360
143.754
143.221
142.706
142.676
142.662
142.515
142.092
142.076
142.042
141.997
141.966
141.931
141.786
141.762
141.395
141.058
140.511
140.182
139.709
139.393
139.103
137.747
137.267
134.751
133.912
132.543
122.572
120.214
77.371
77.160
76.949
75.985
67.850
61.448
49.274
O
OCF_3
2f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

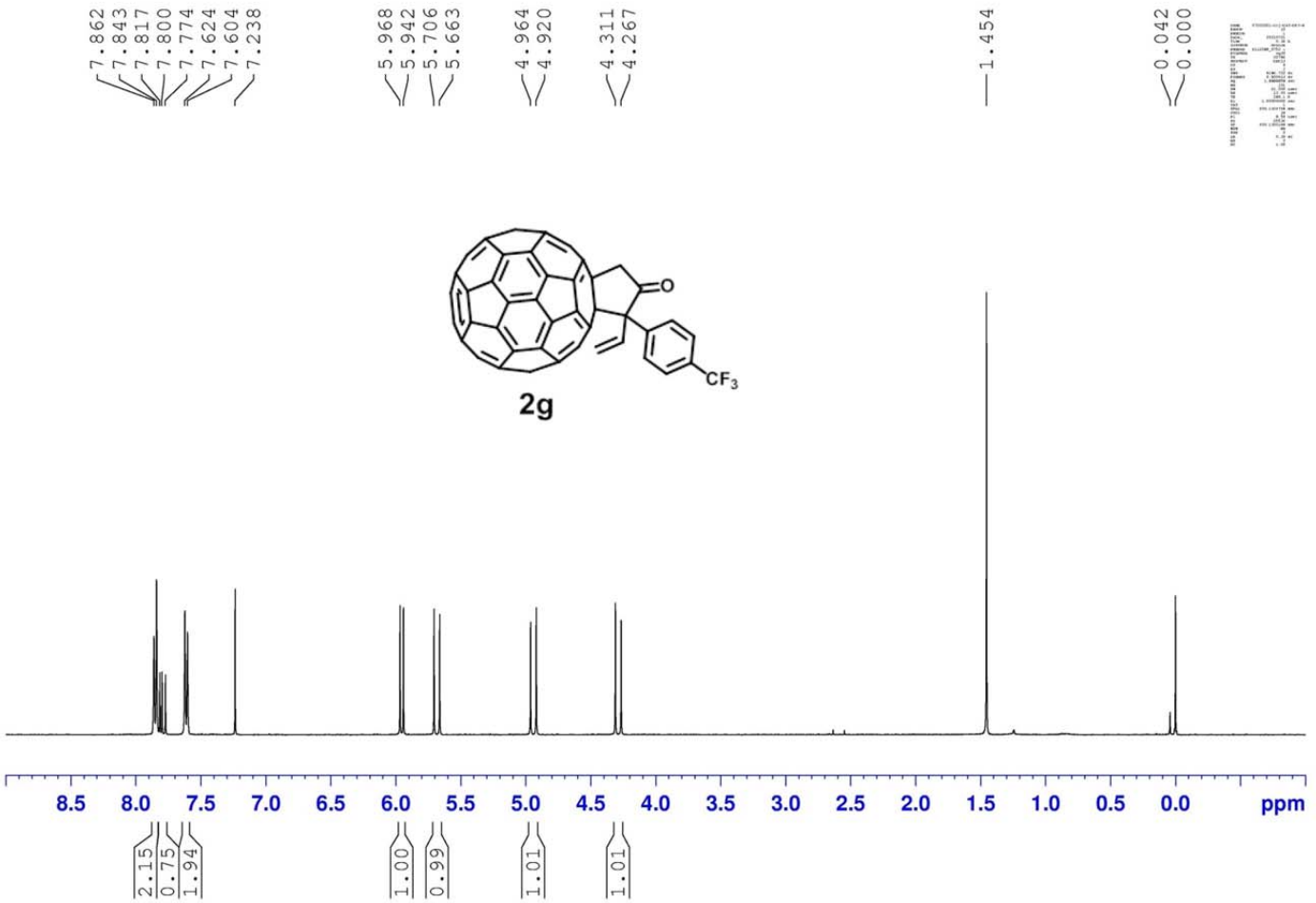
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2f



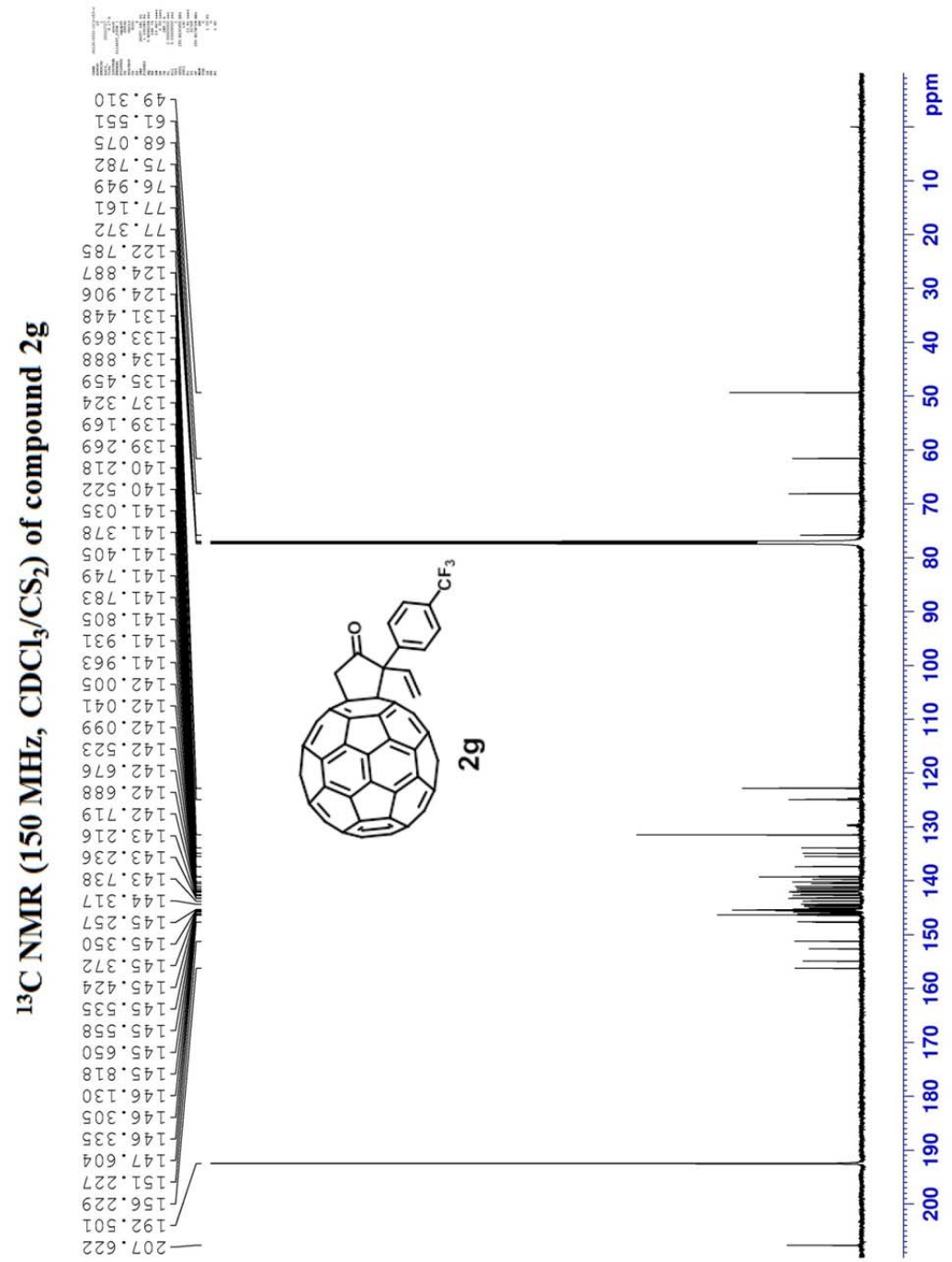
^{19}F NMR (565 MHz, $CDCl_3/CS_2$) of compound 2f



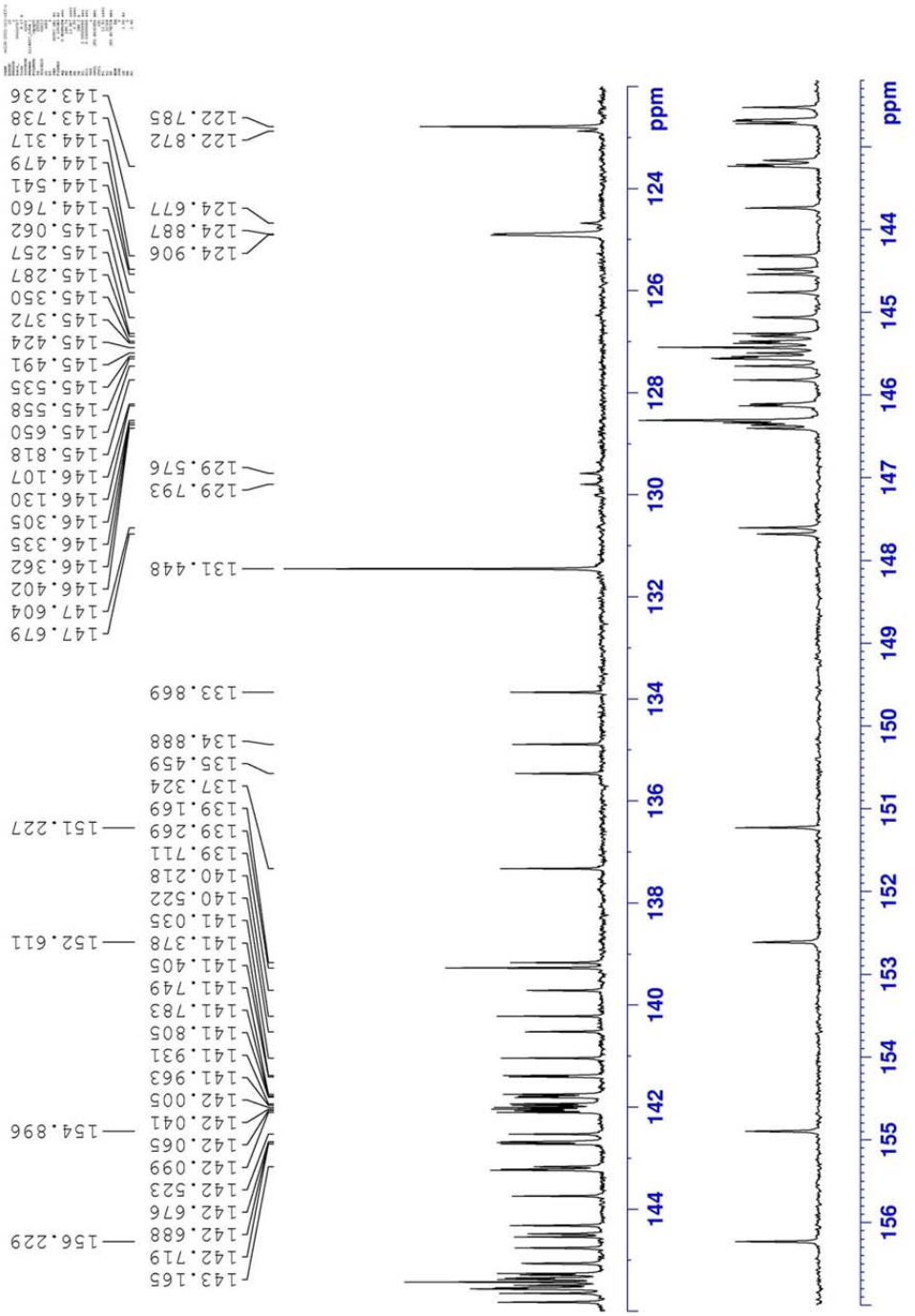
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2g



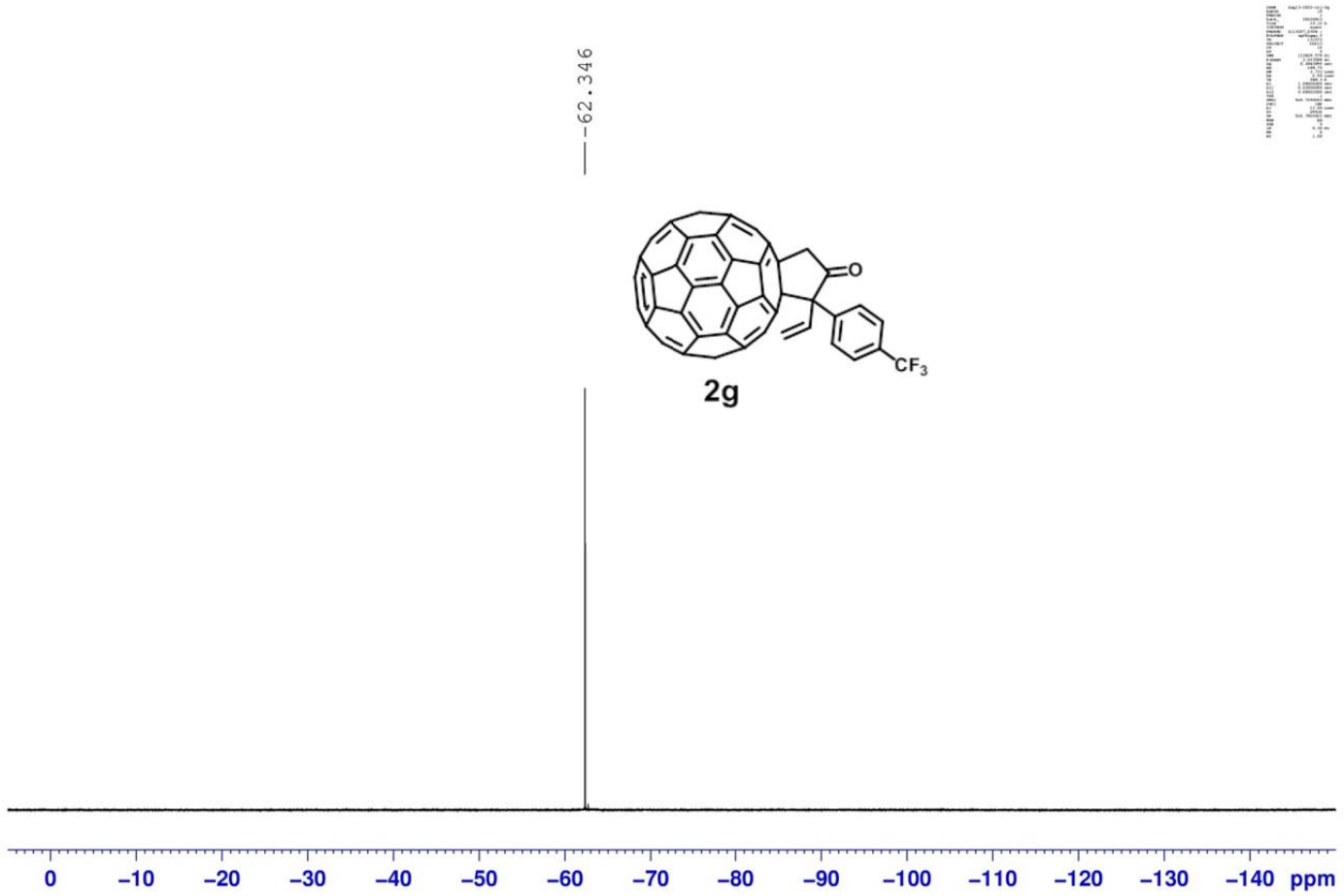
2g


^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2g
207.622
192.501
156.229
151.227
147.604
146.335
146.305
146.130
145.818
145.650
145.558
145.535
145.424
145.372
145.350
145.257
144.317
143.738
143.236
143.216
142.719
142.688
142.676
142.523
142.099
142.041
142.005
141.963
141.931
141.805
141.783
141.749
141.405
141.378
141.035
140.522
140.218
139.269
139.169
137.324
135.459
134.888
133.869
131.448
124.906
124.887
122.785
77.372
77.161
76.949
75.782
68.075
61.551
49.310
O
CF3
2g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

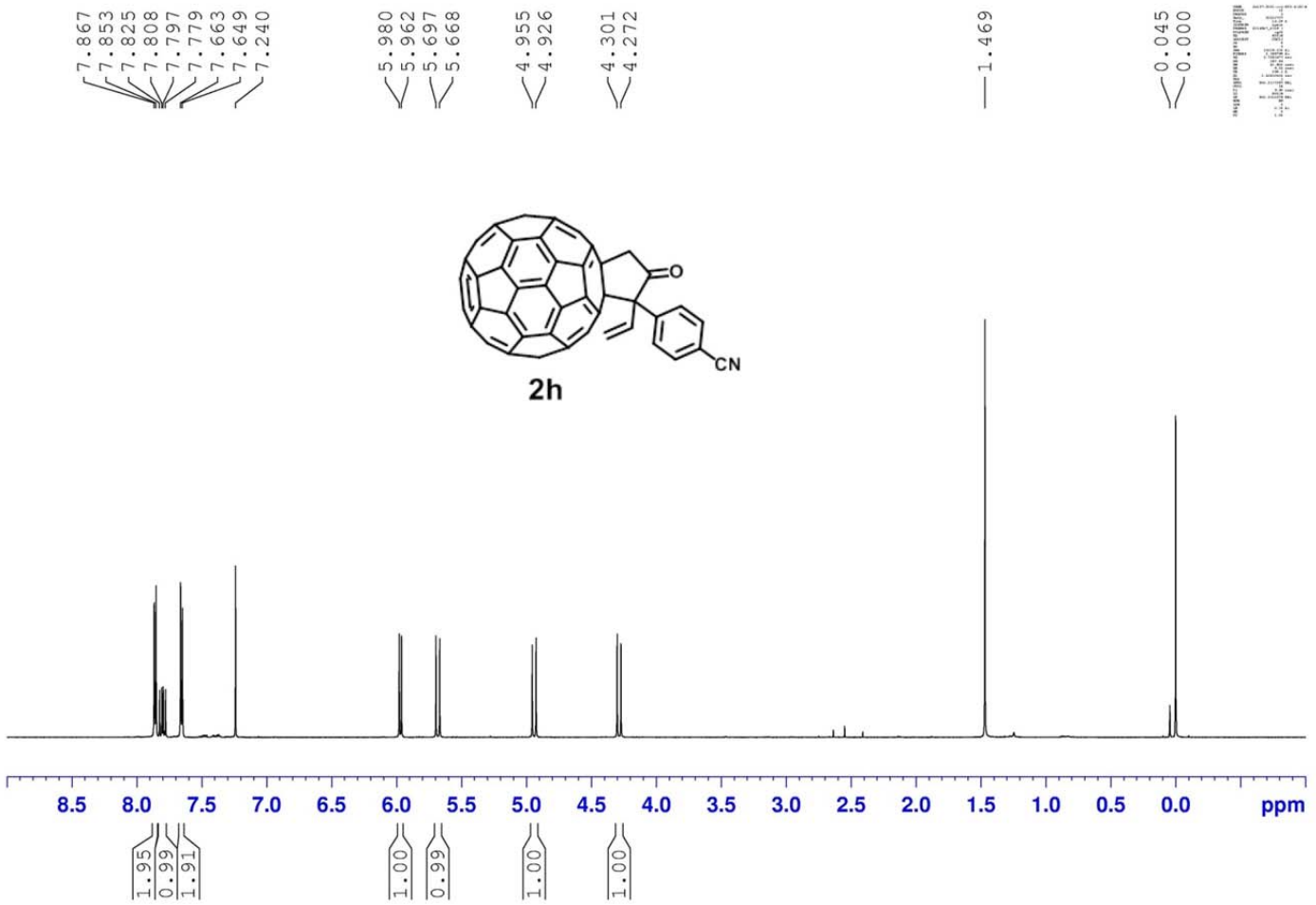
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2g



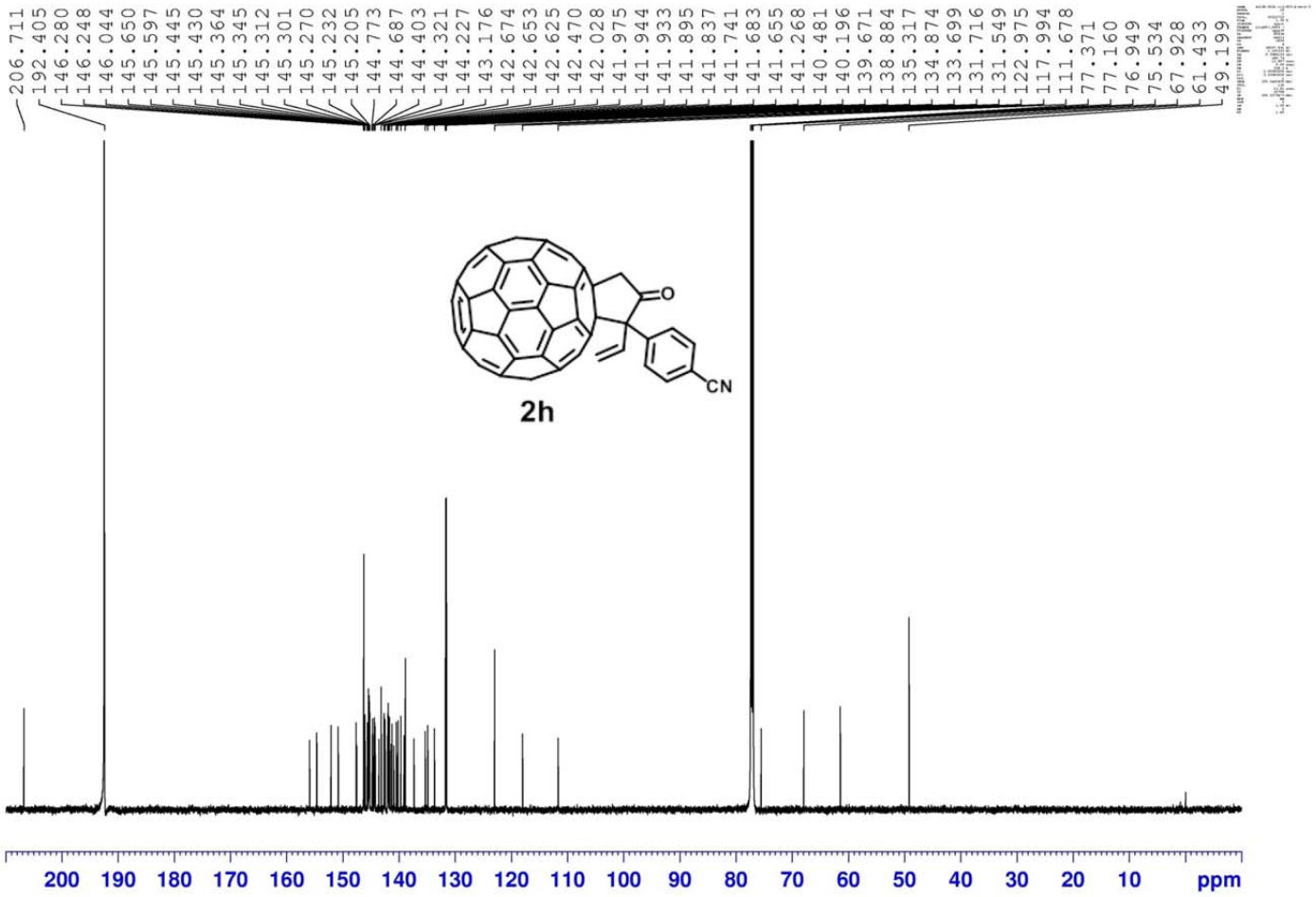
^{19}F NMR (565 MHz, $CDCl_3/CS_2$) of compound 2g



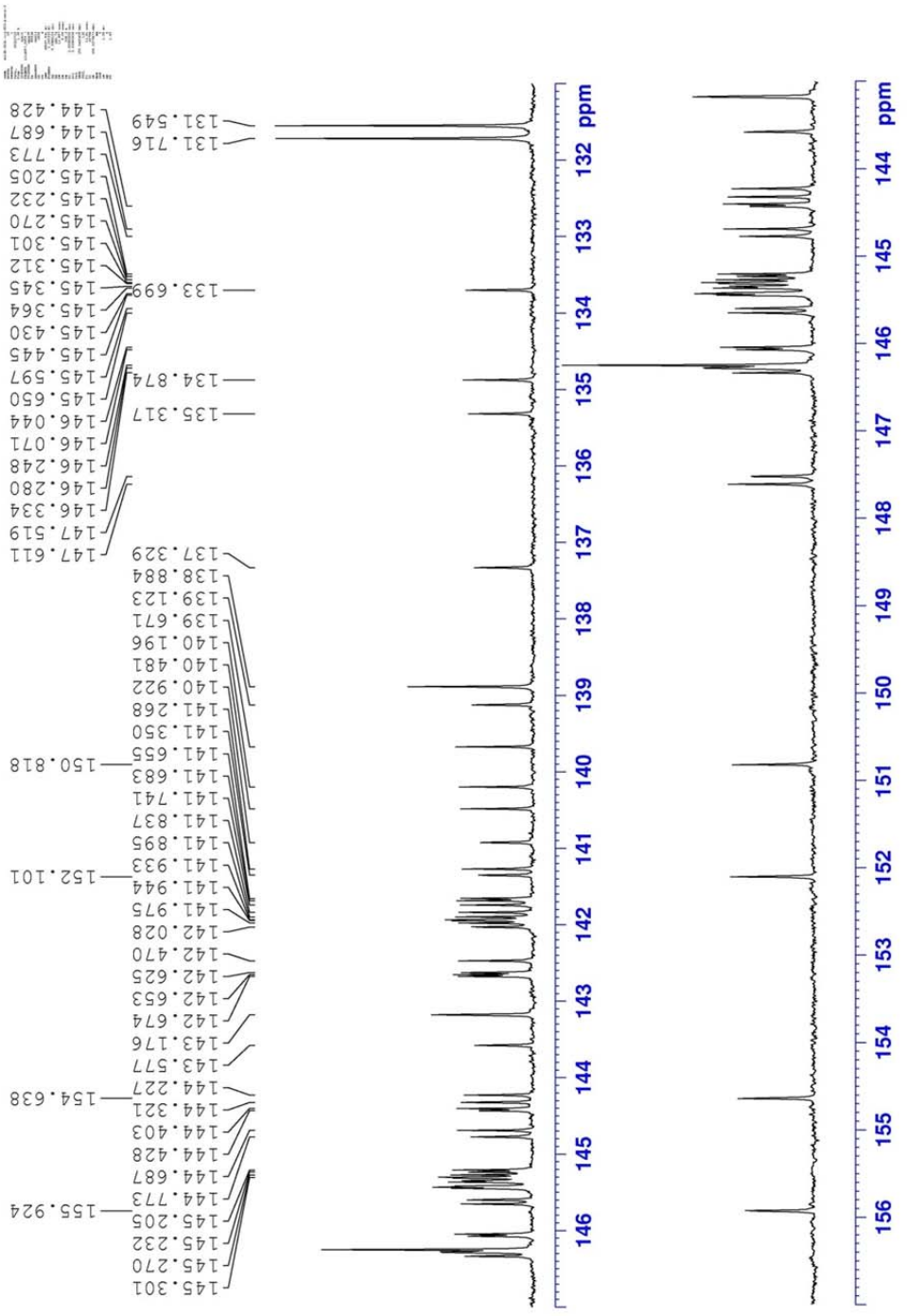
^{1}H NMR (600 MHz, $CDCl_3/CS_2$) of compound 2h



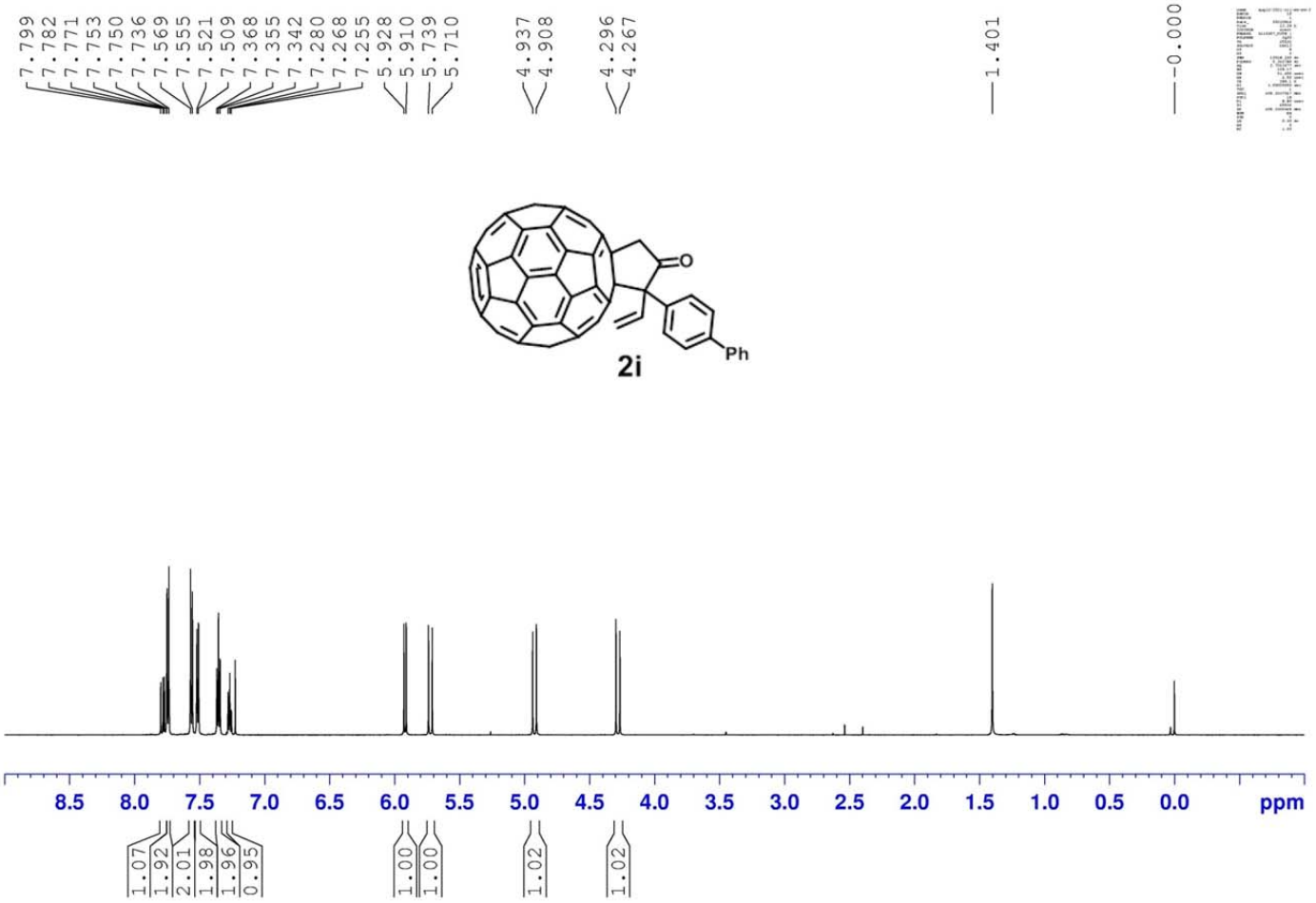
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2h



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

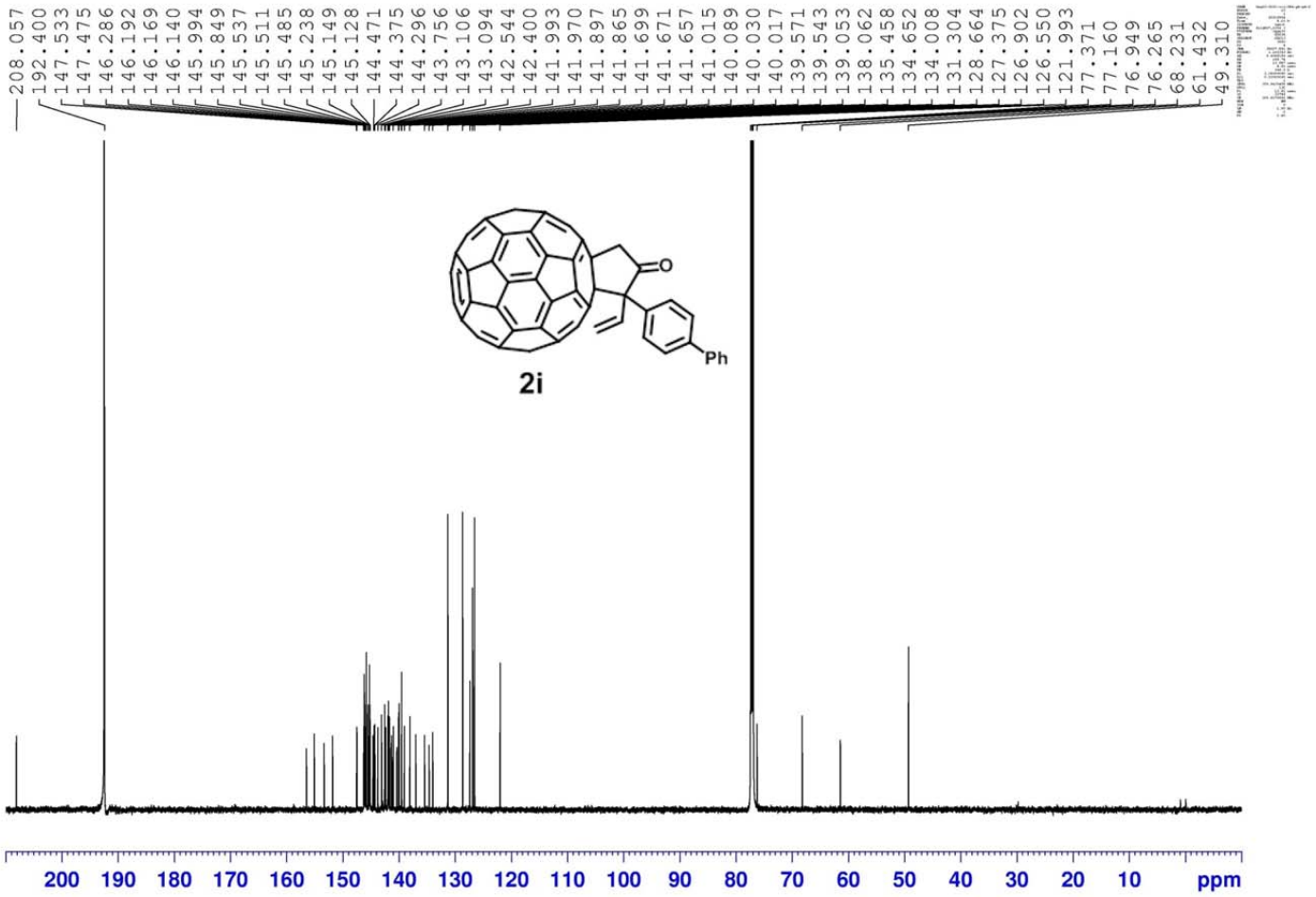


^{1}H NMR (600 MHz, $CDCl_3/CS_2$) of compound 2i

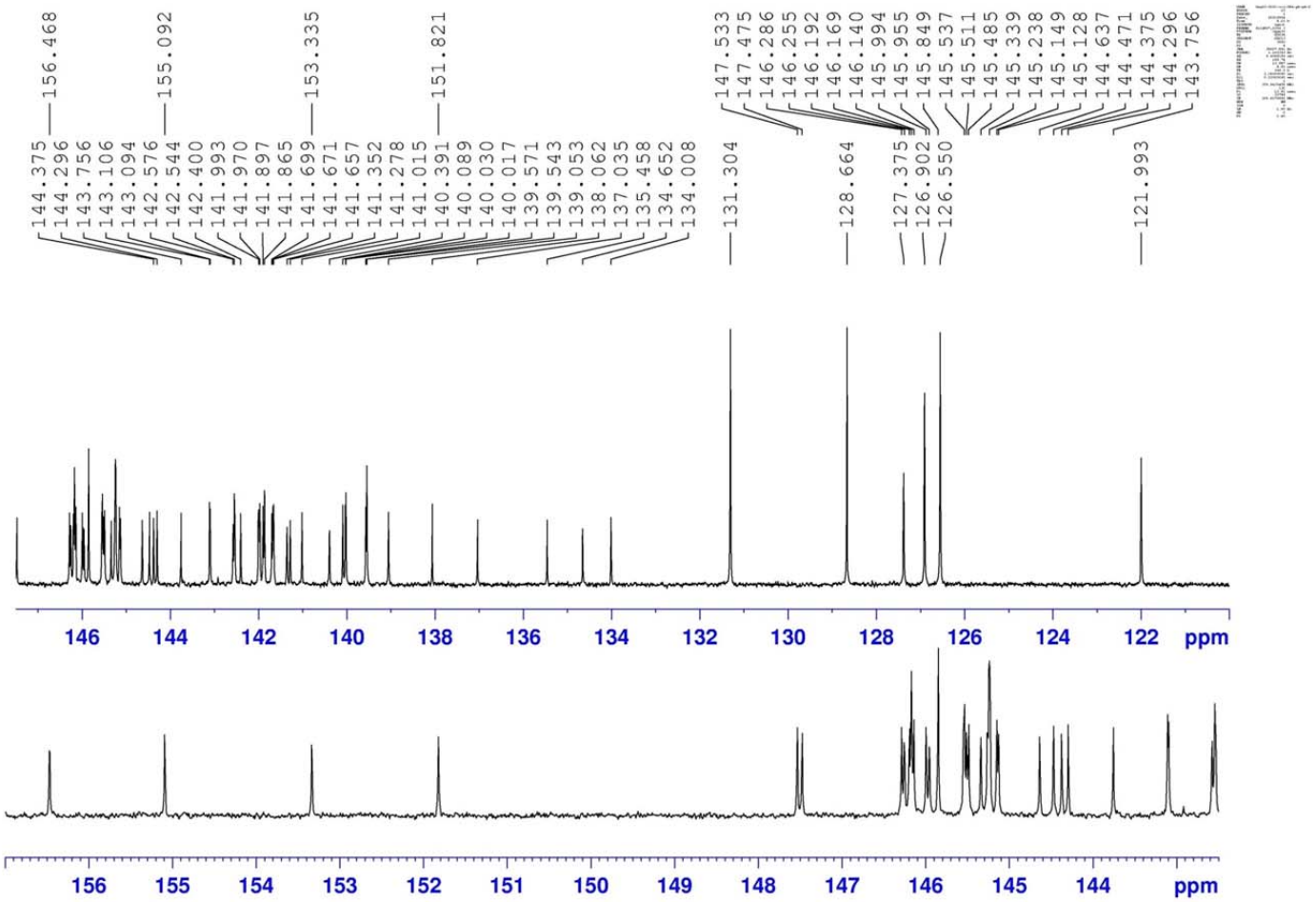


2i

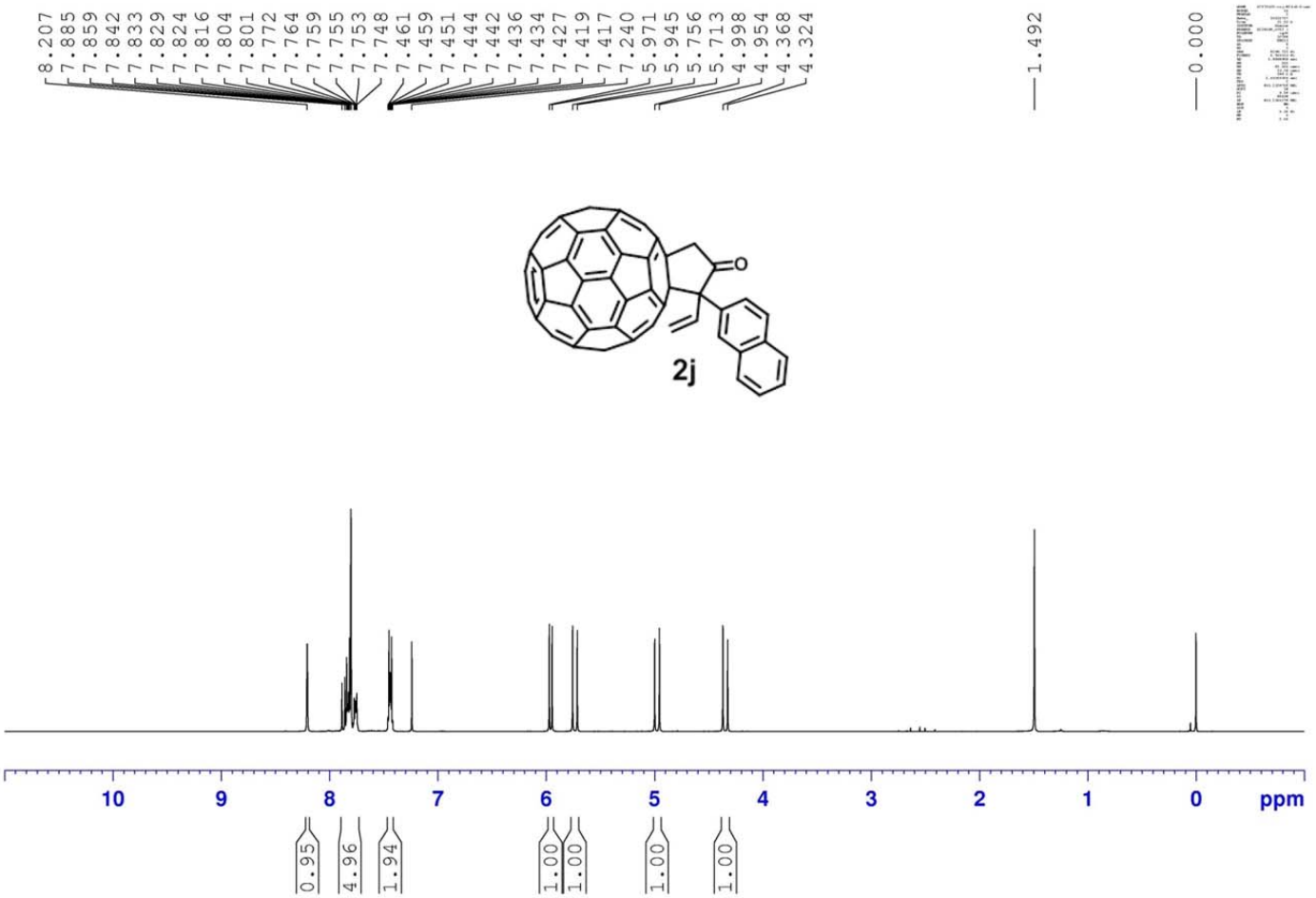
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2i



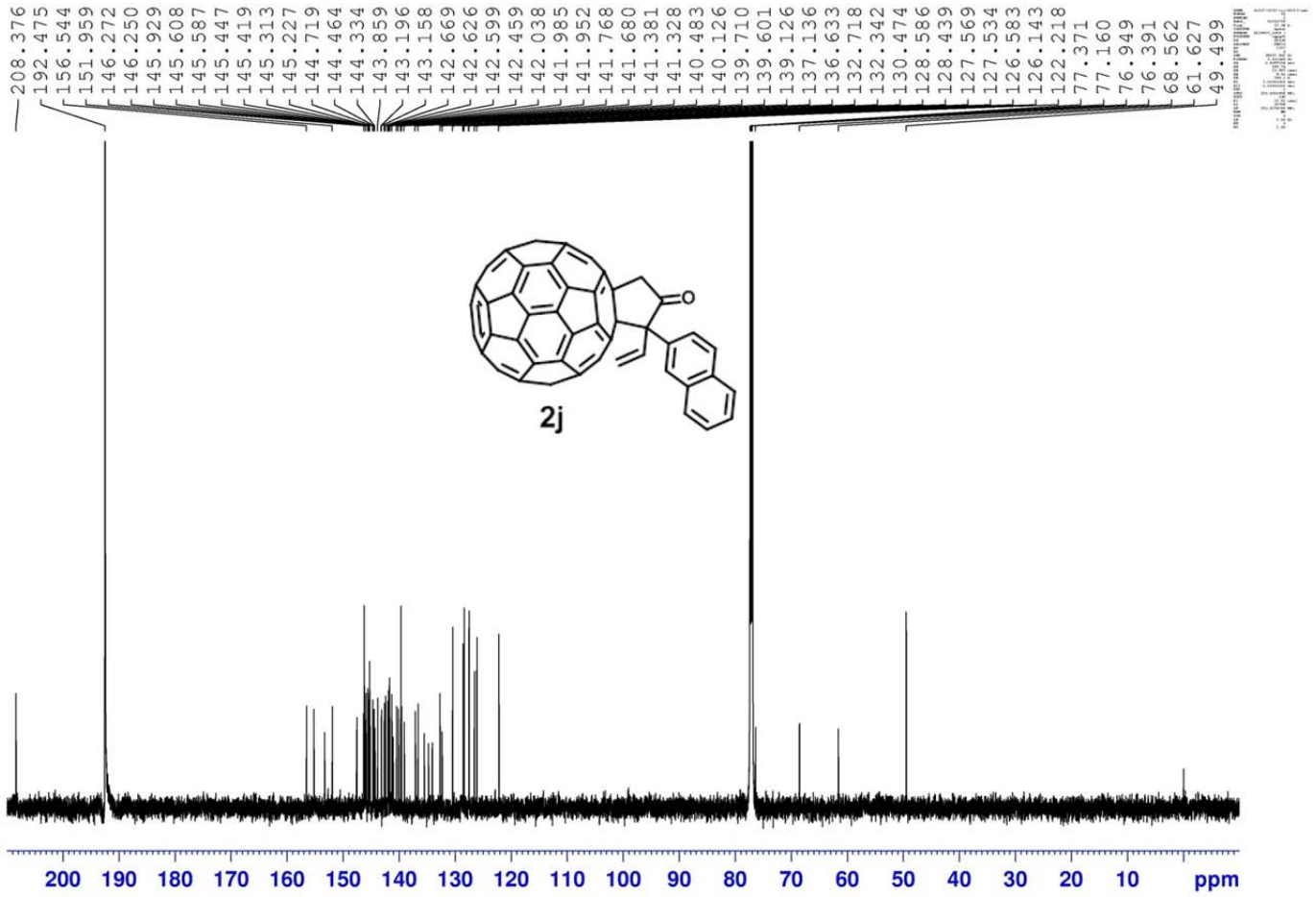
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2i



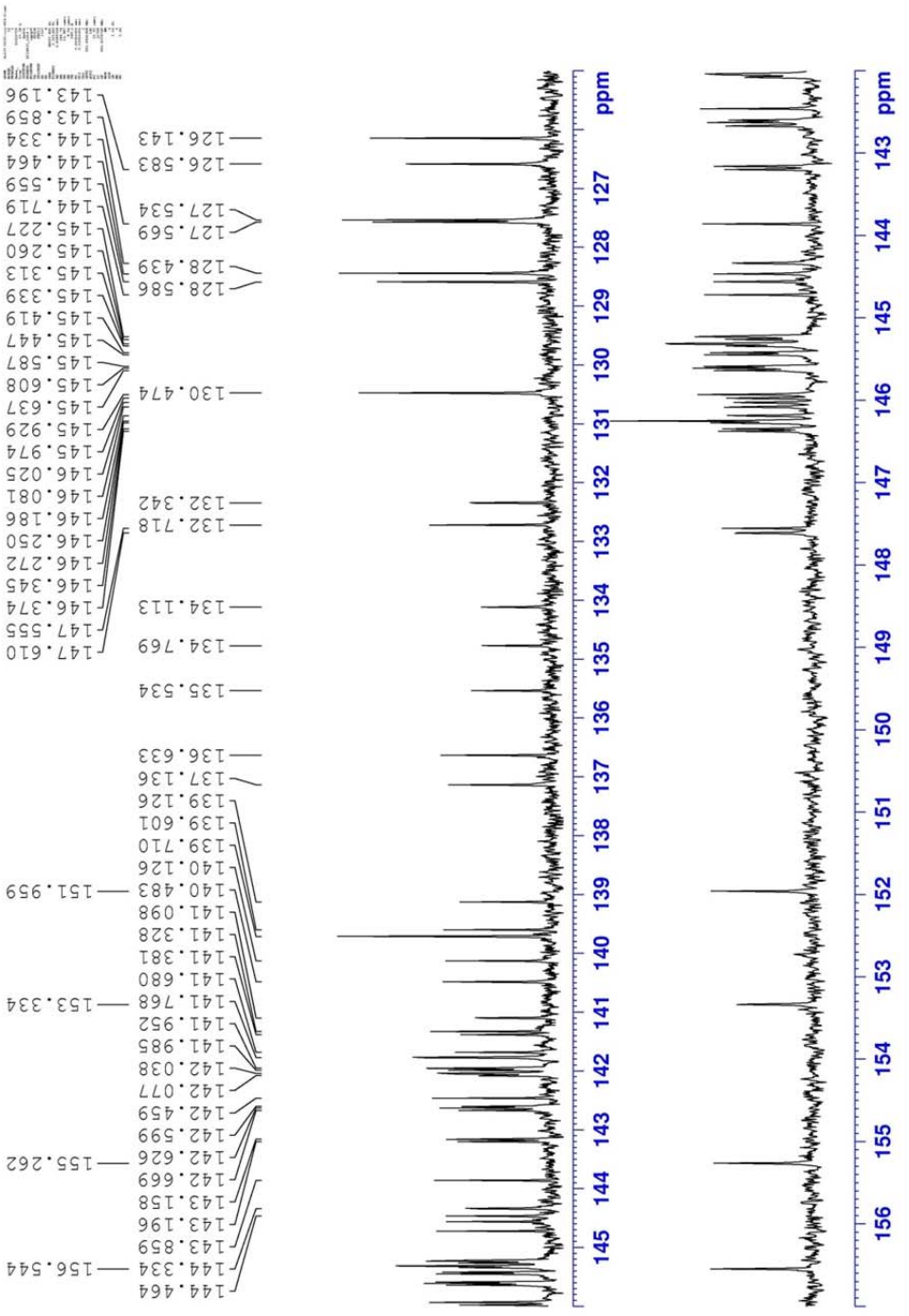
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2j



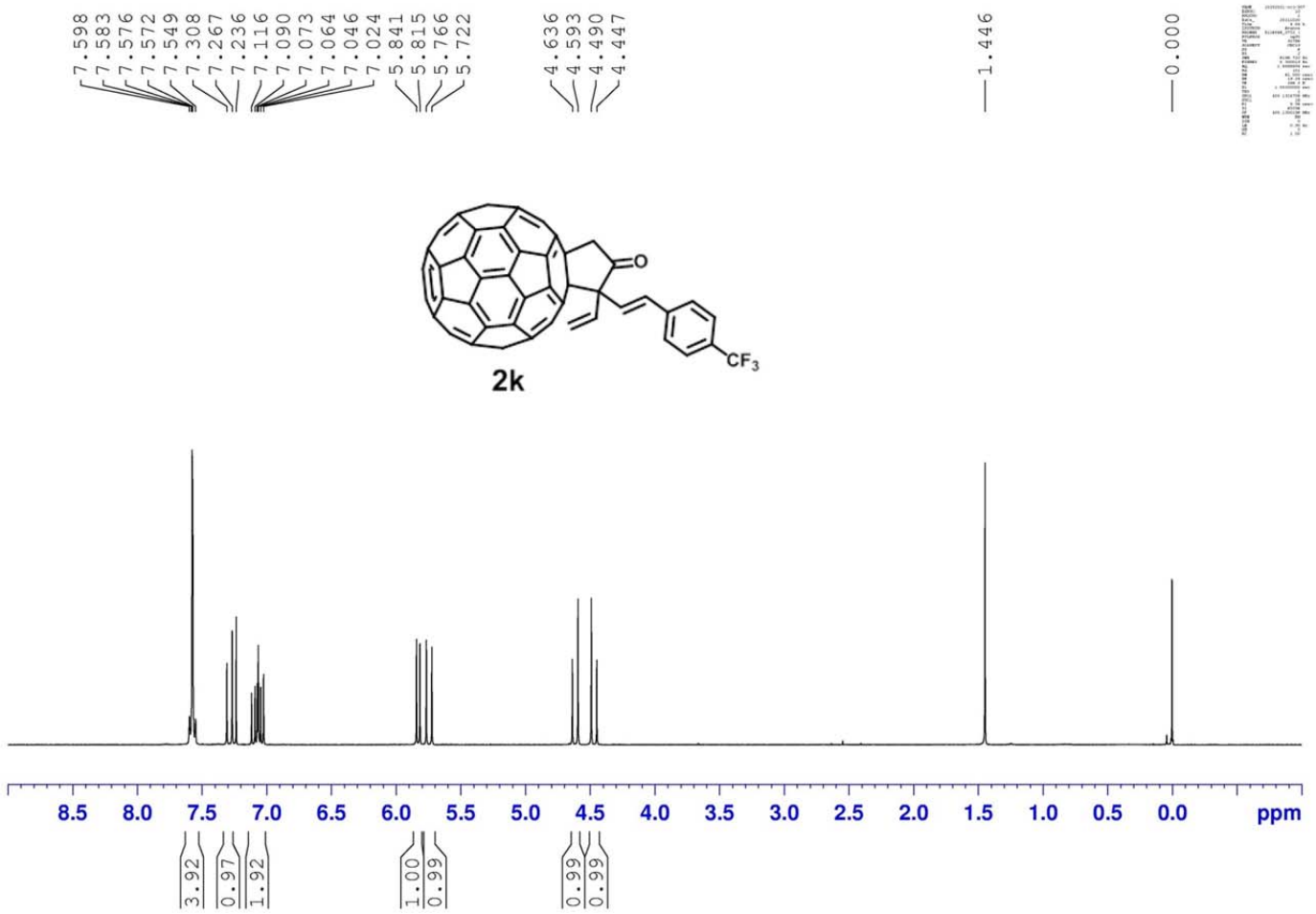
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2j



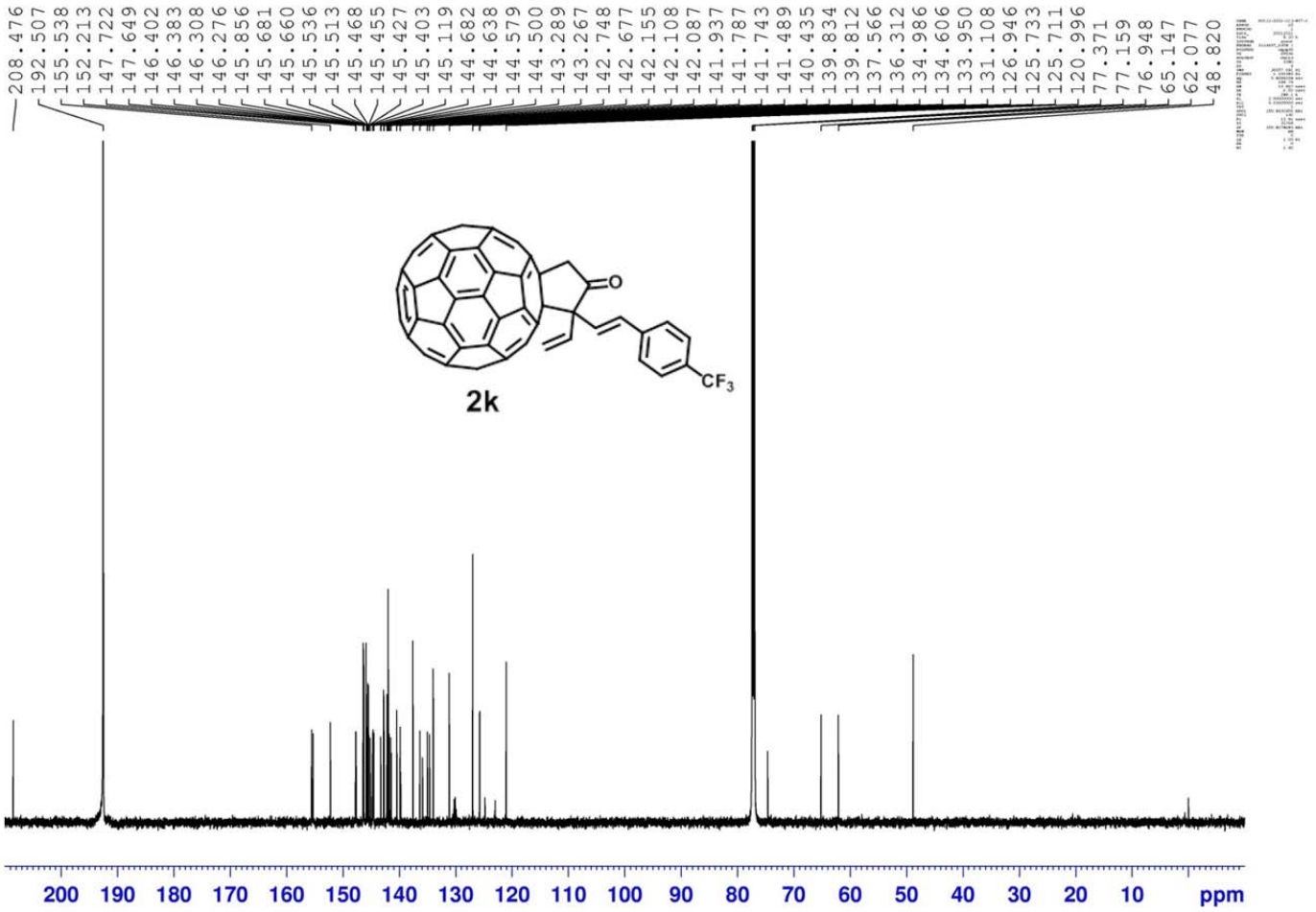
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2j



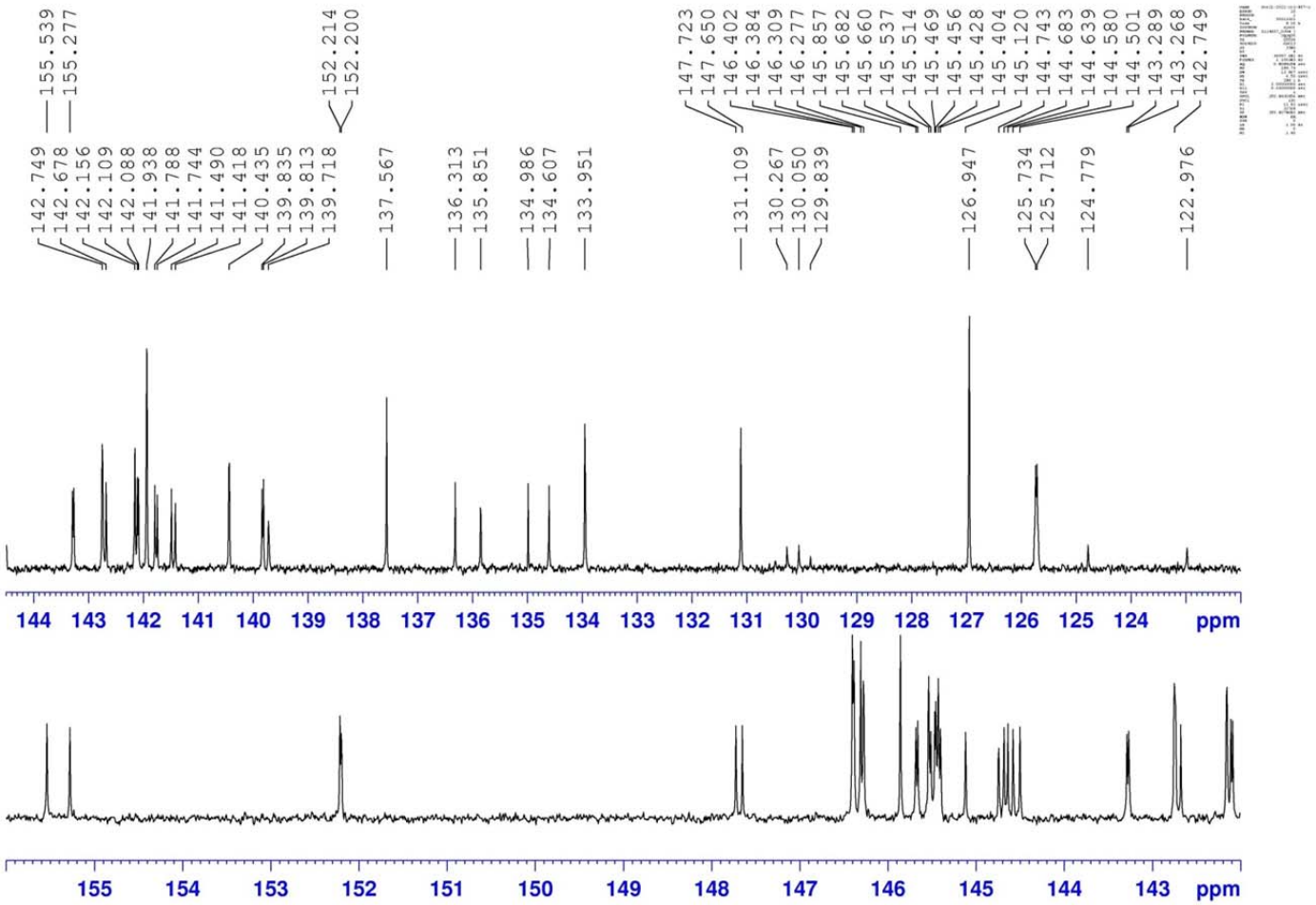
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2k



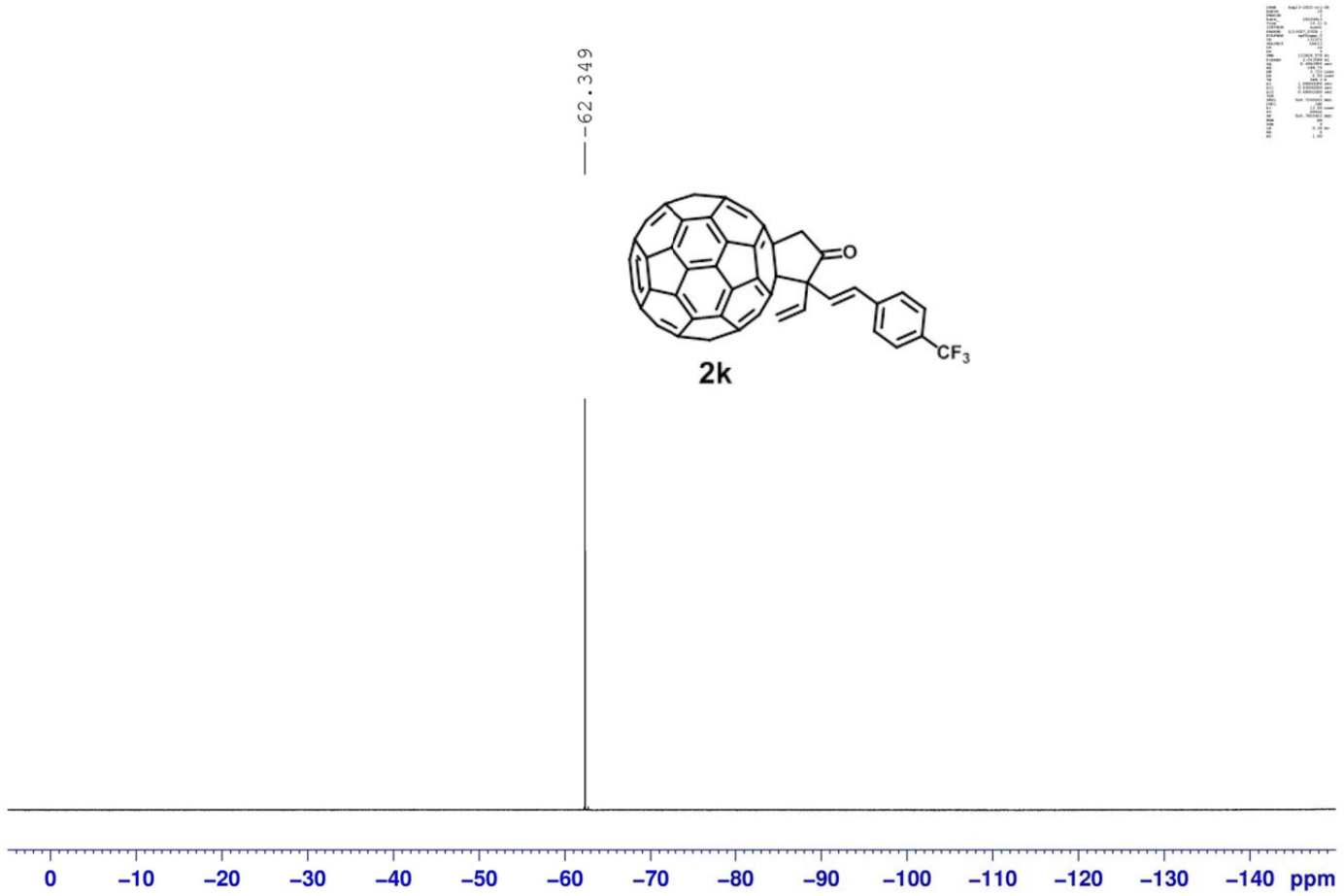
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2k



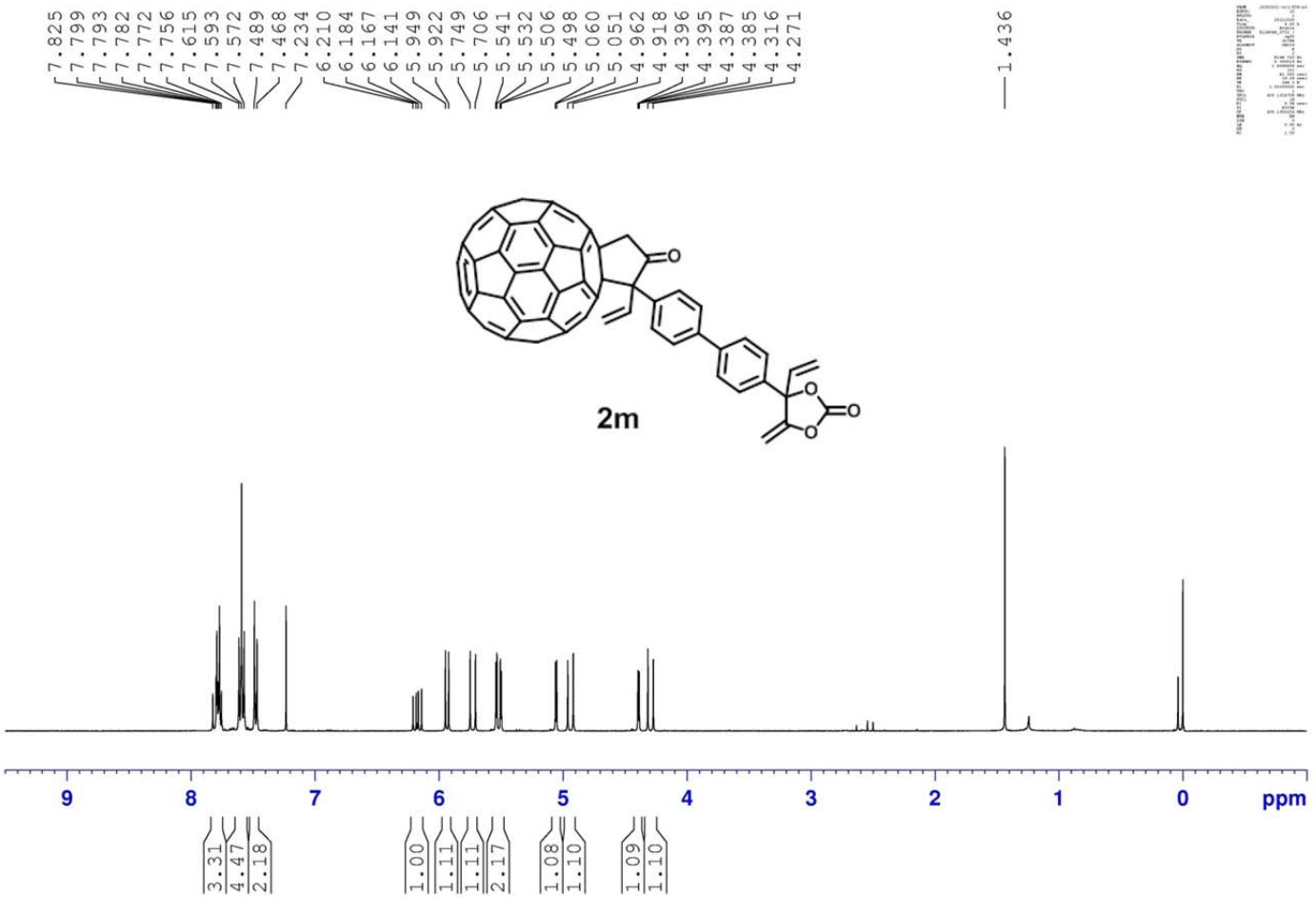
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2k

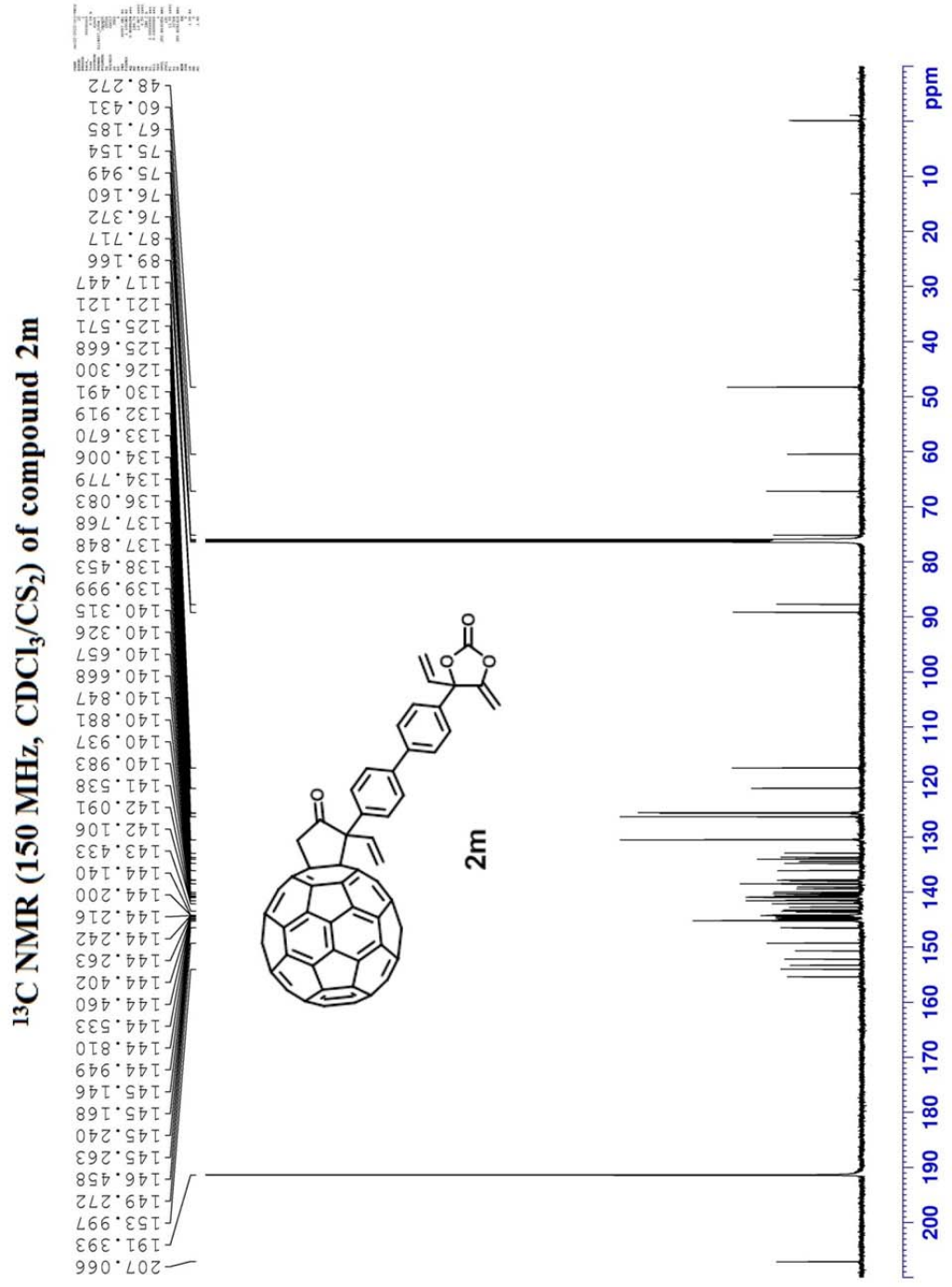


^{19}F NMR (565 MHz, $CDCl_3/CS_2$) of compound 2k

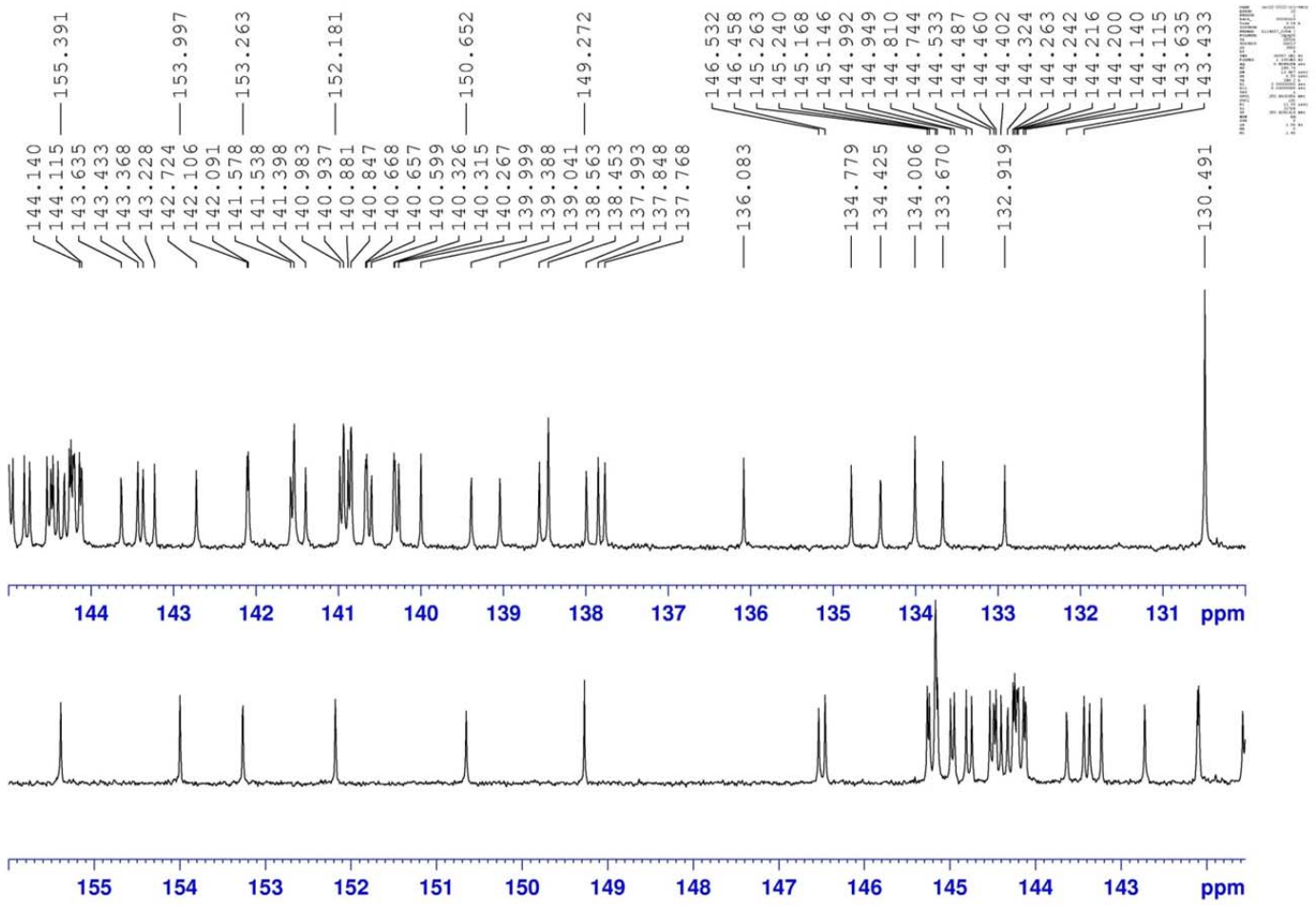


^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 2m

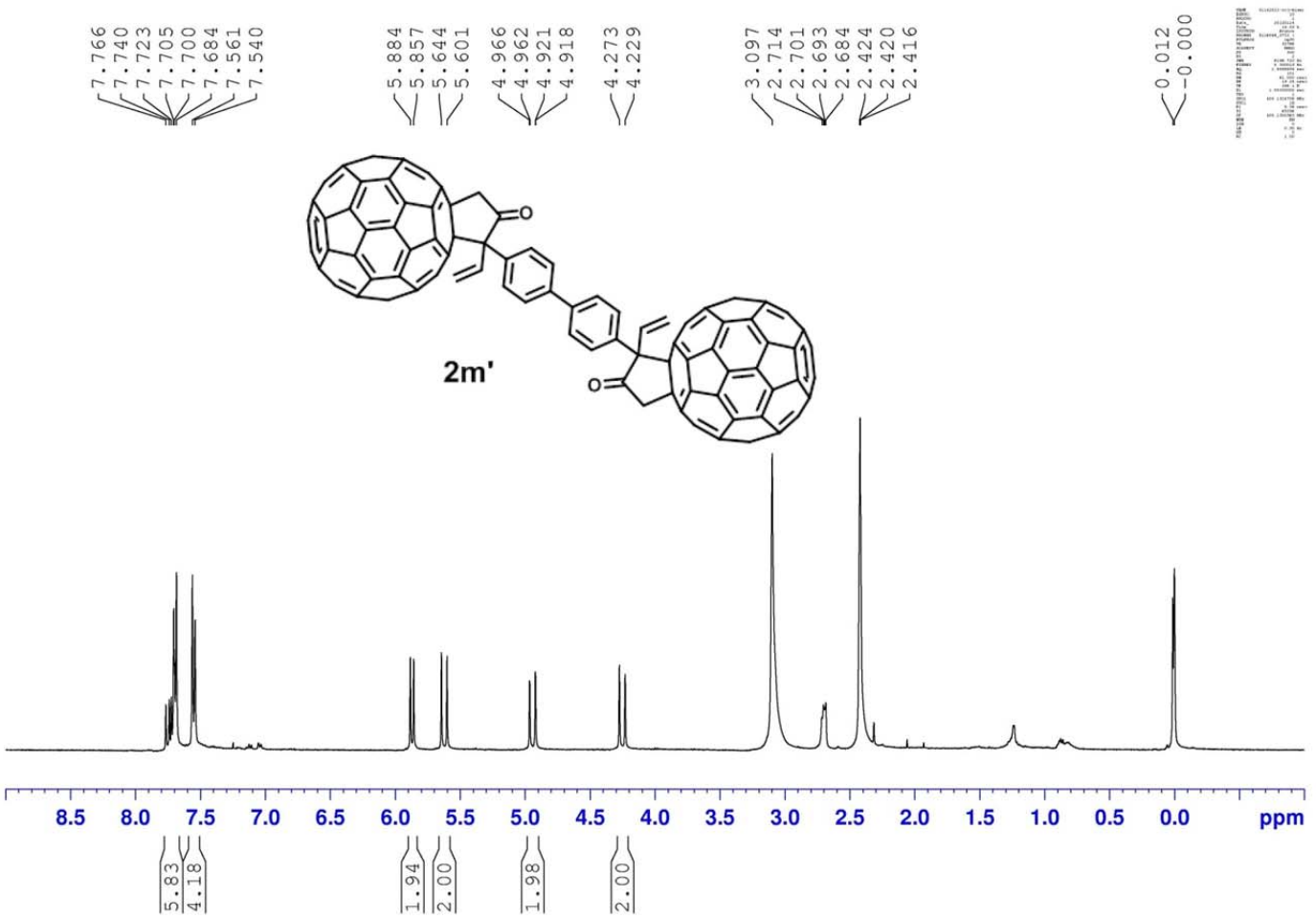



^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2m
2m
ppm

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

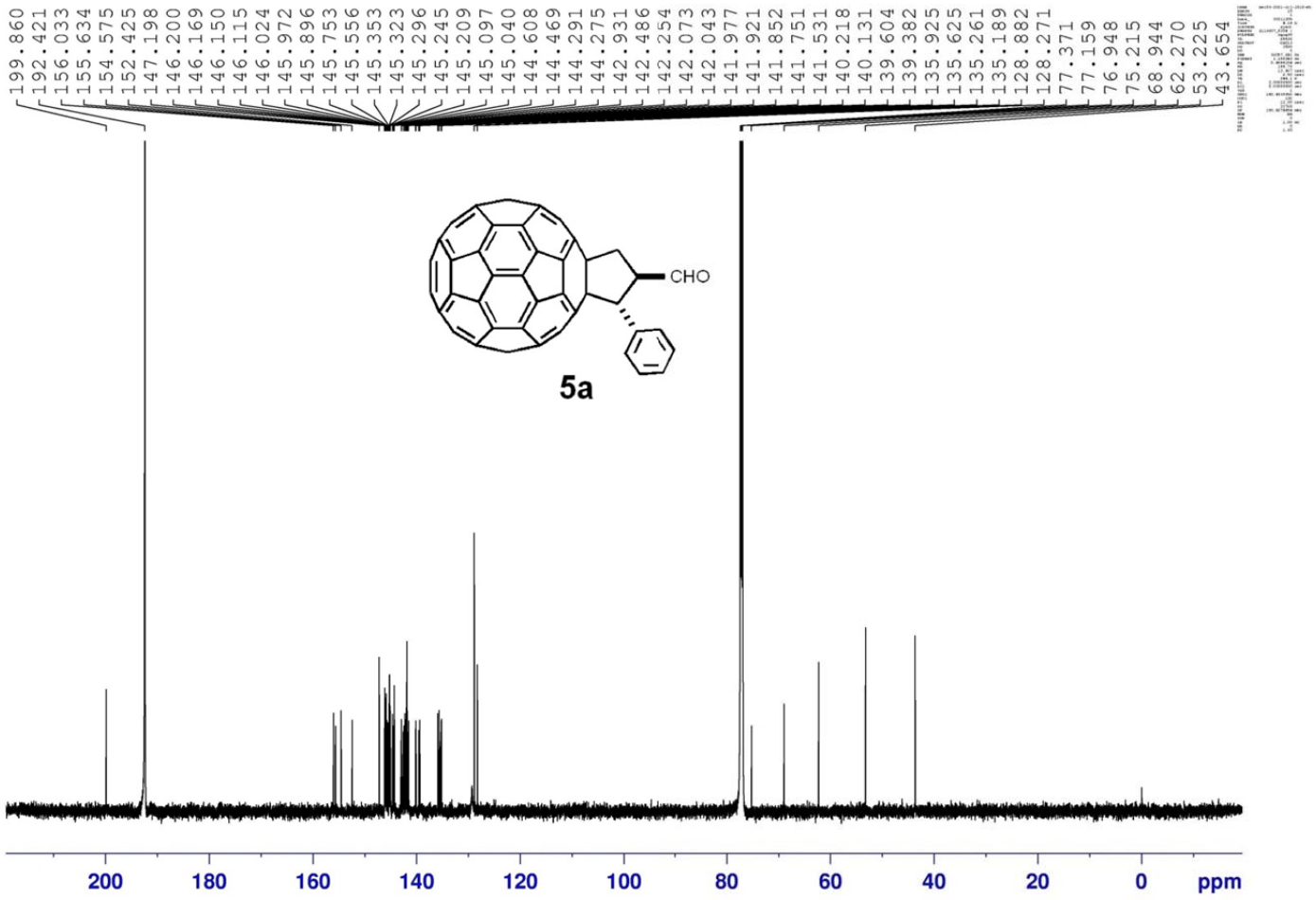


^{1}H NMR (400 MHz, DMSO-d_6/CS_2) of compound 2m'



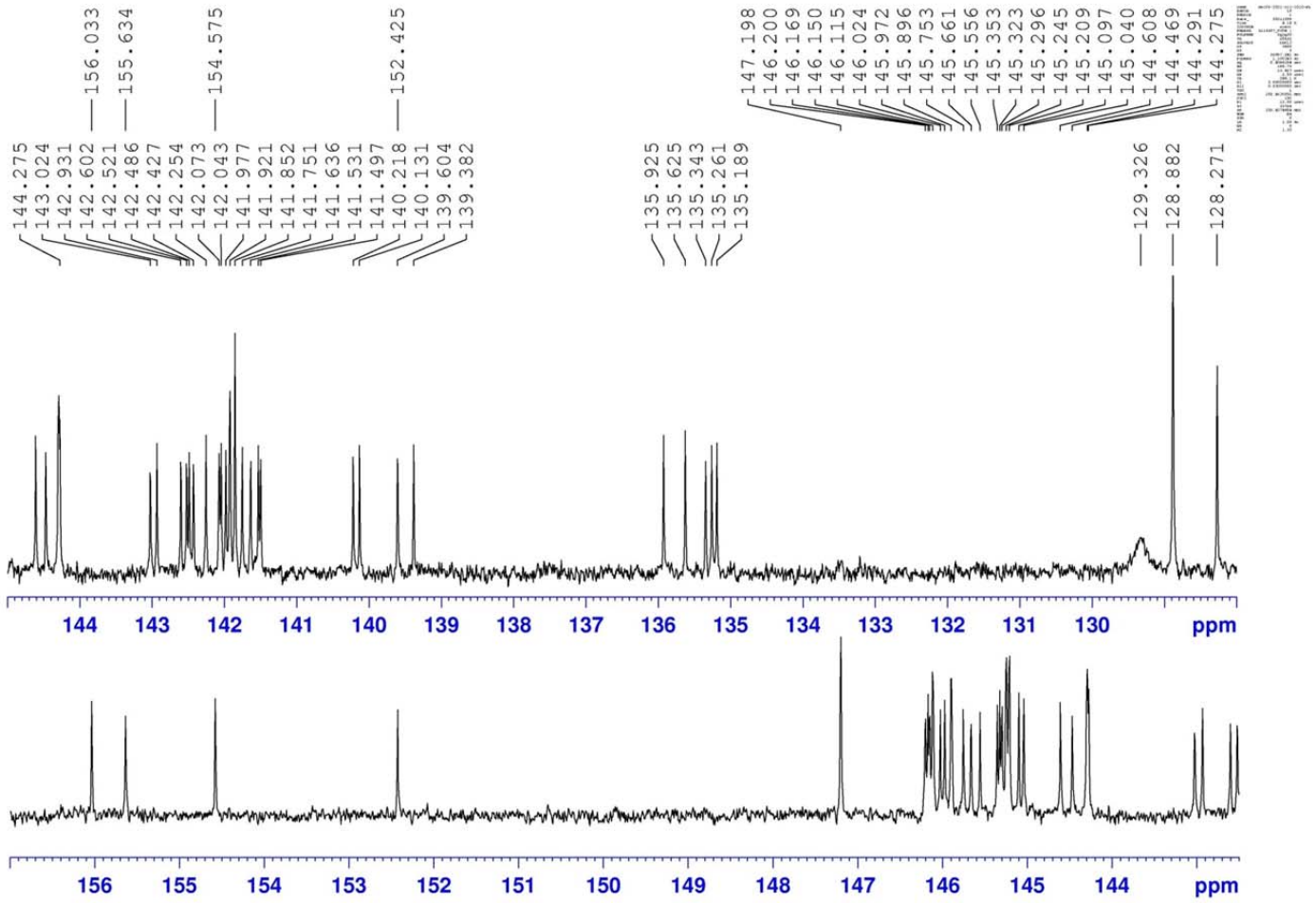
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 5a

^{1}H NMR (400 MHz, DMSO/CS_2) of compound 5a

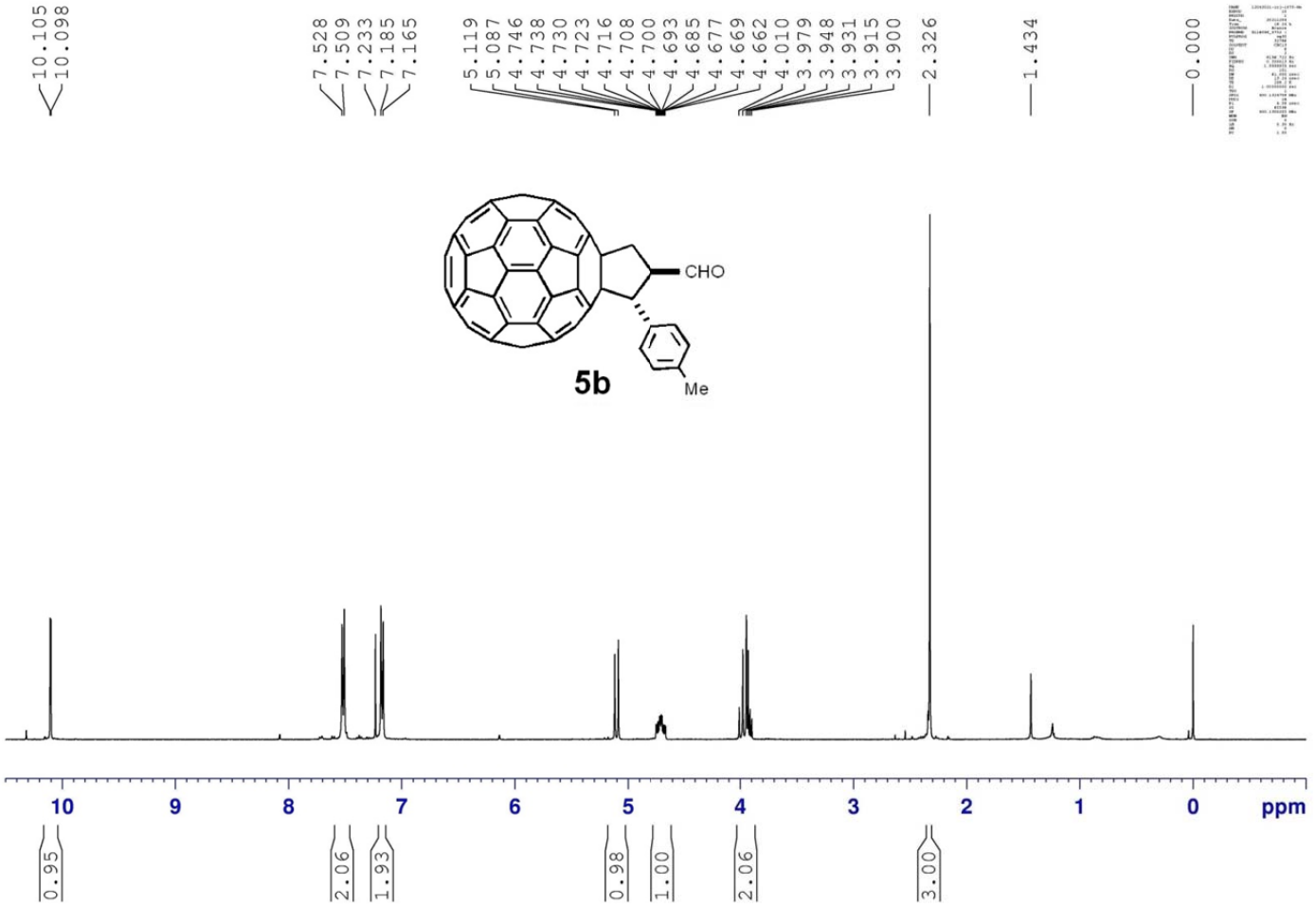


5a

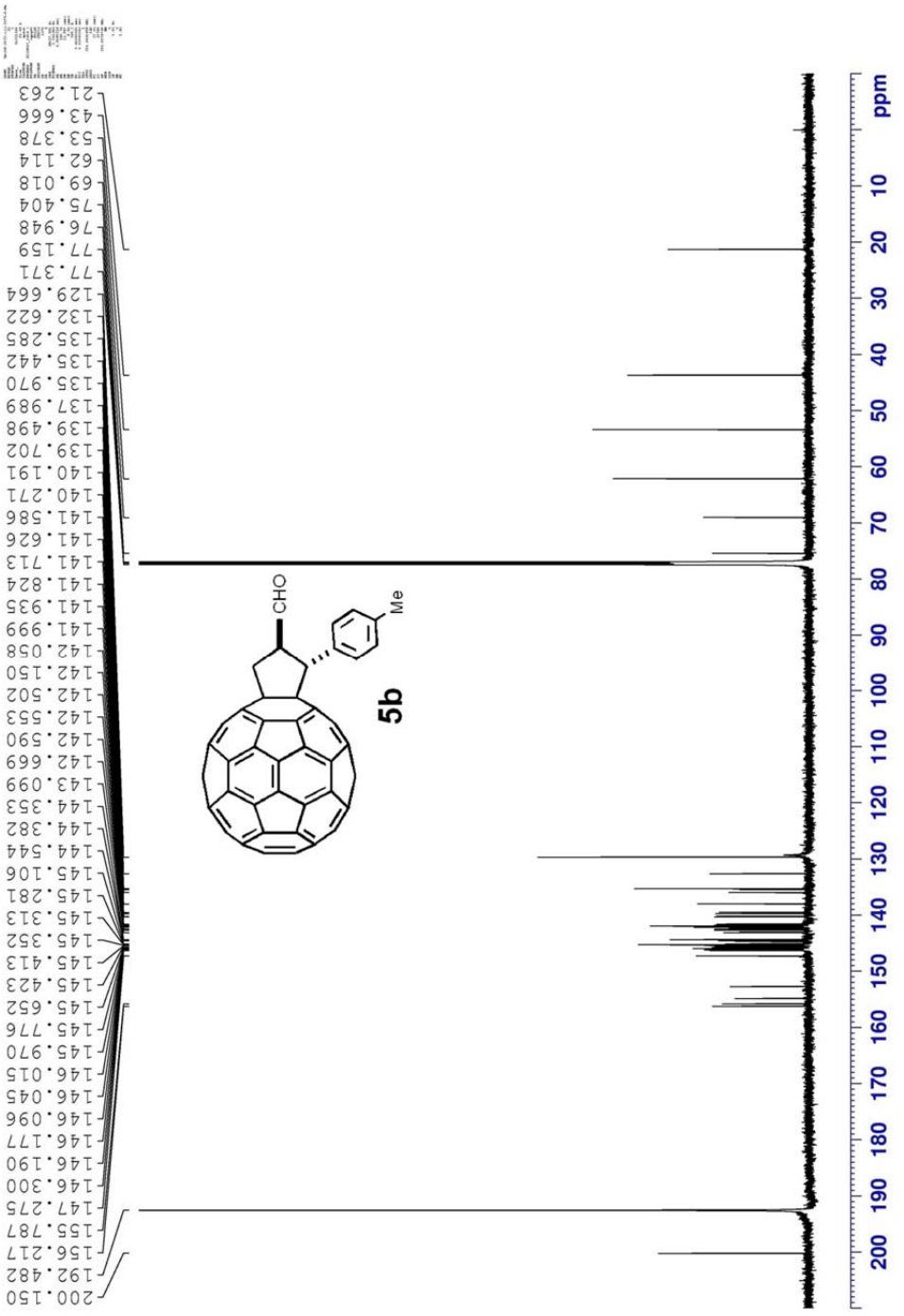
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5a



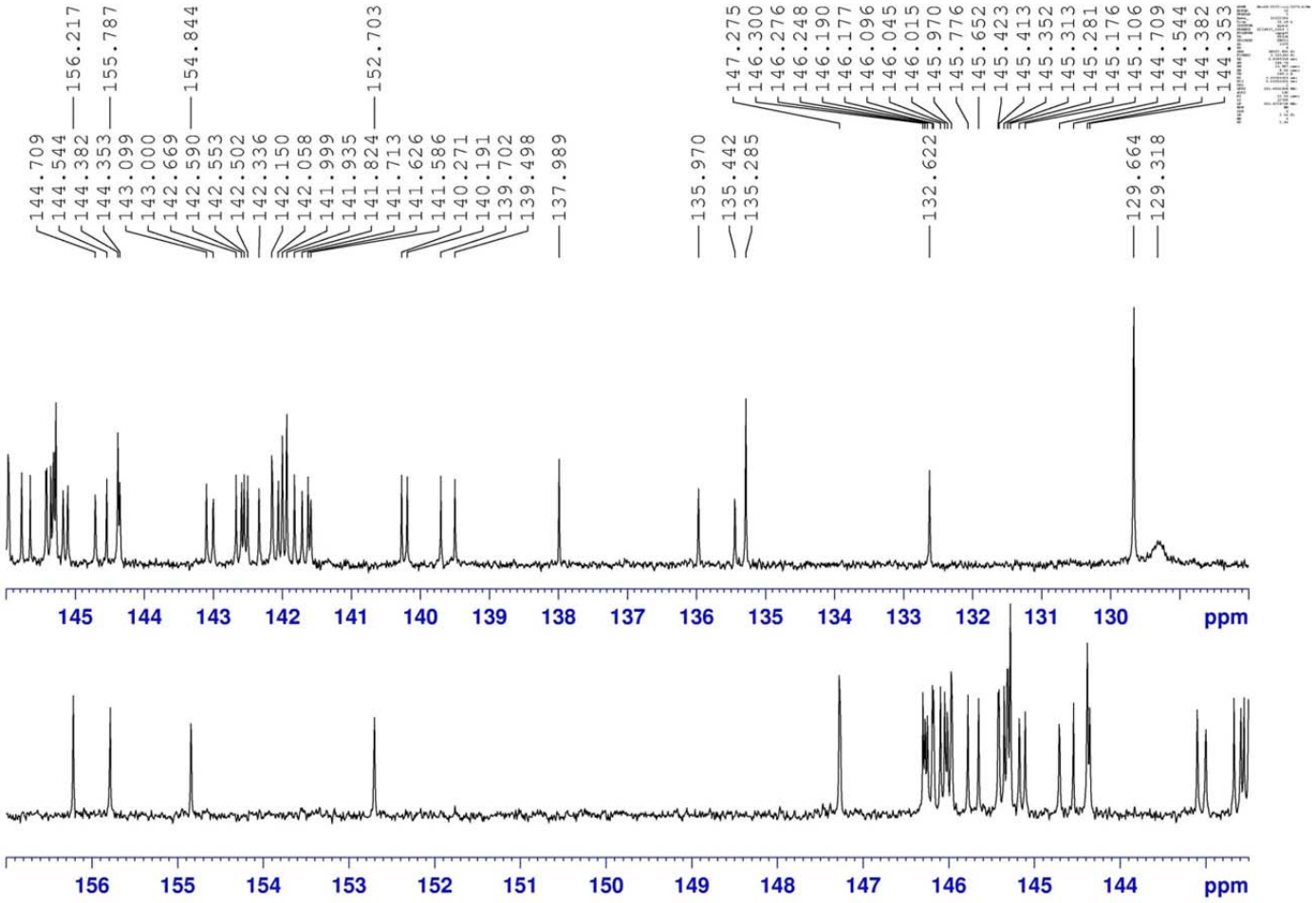
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 5b



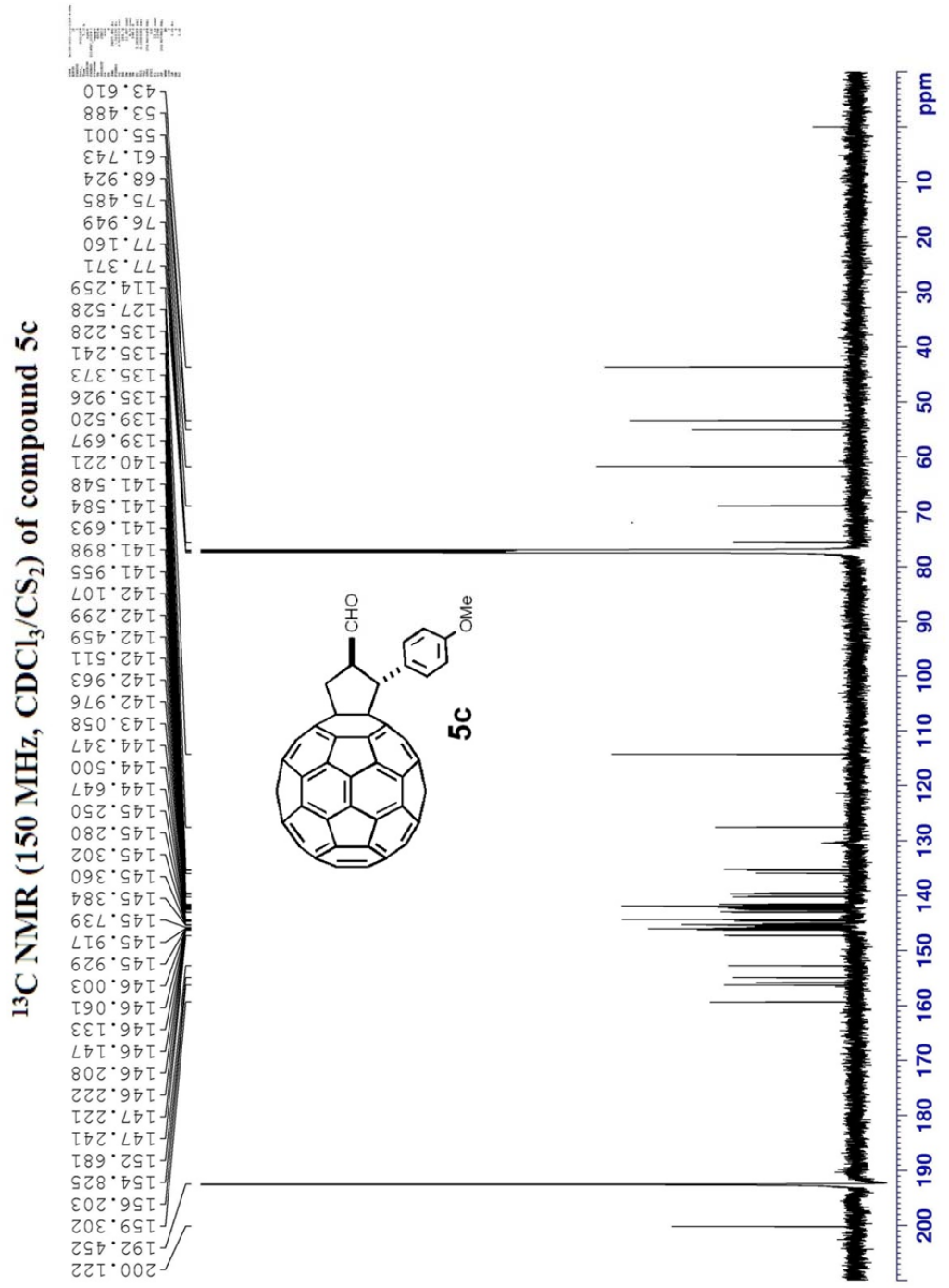
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5b



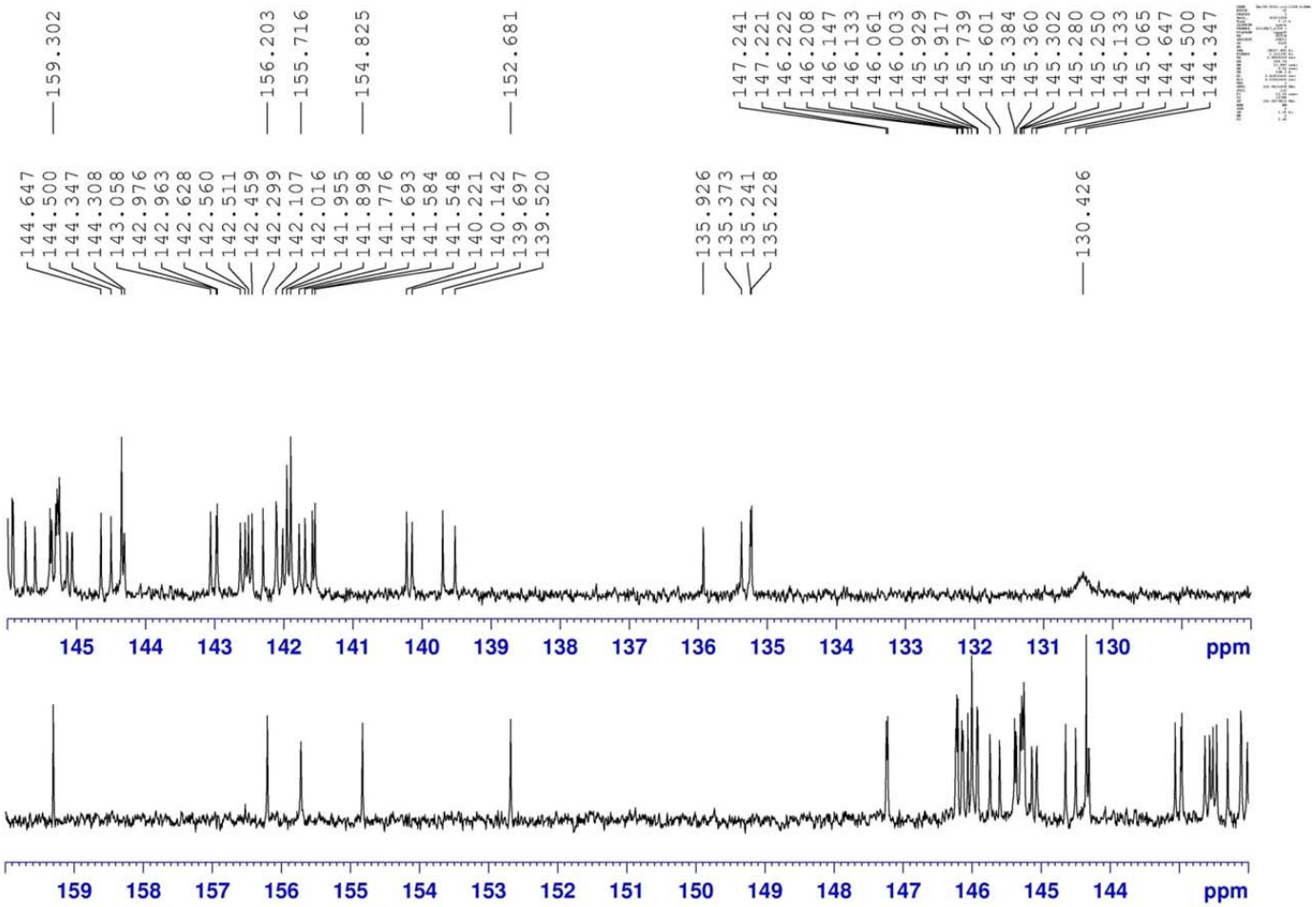
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5b



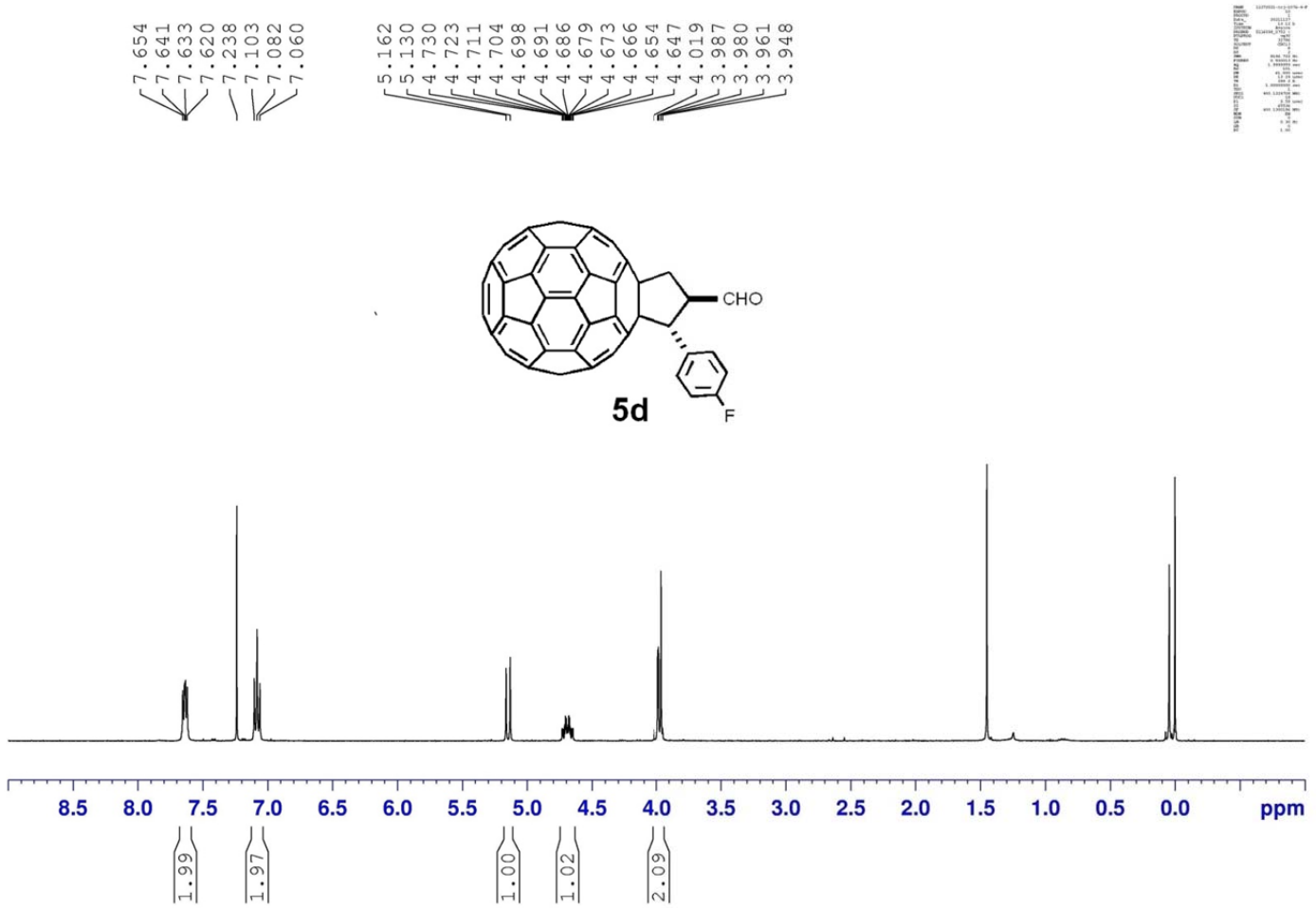
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 5c


^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5c
CHO
OMe
5c
ppm

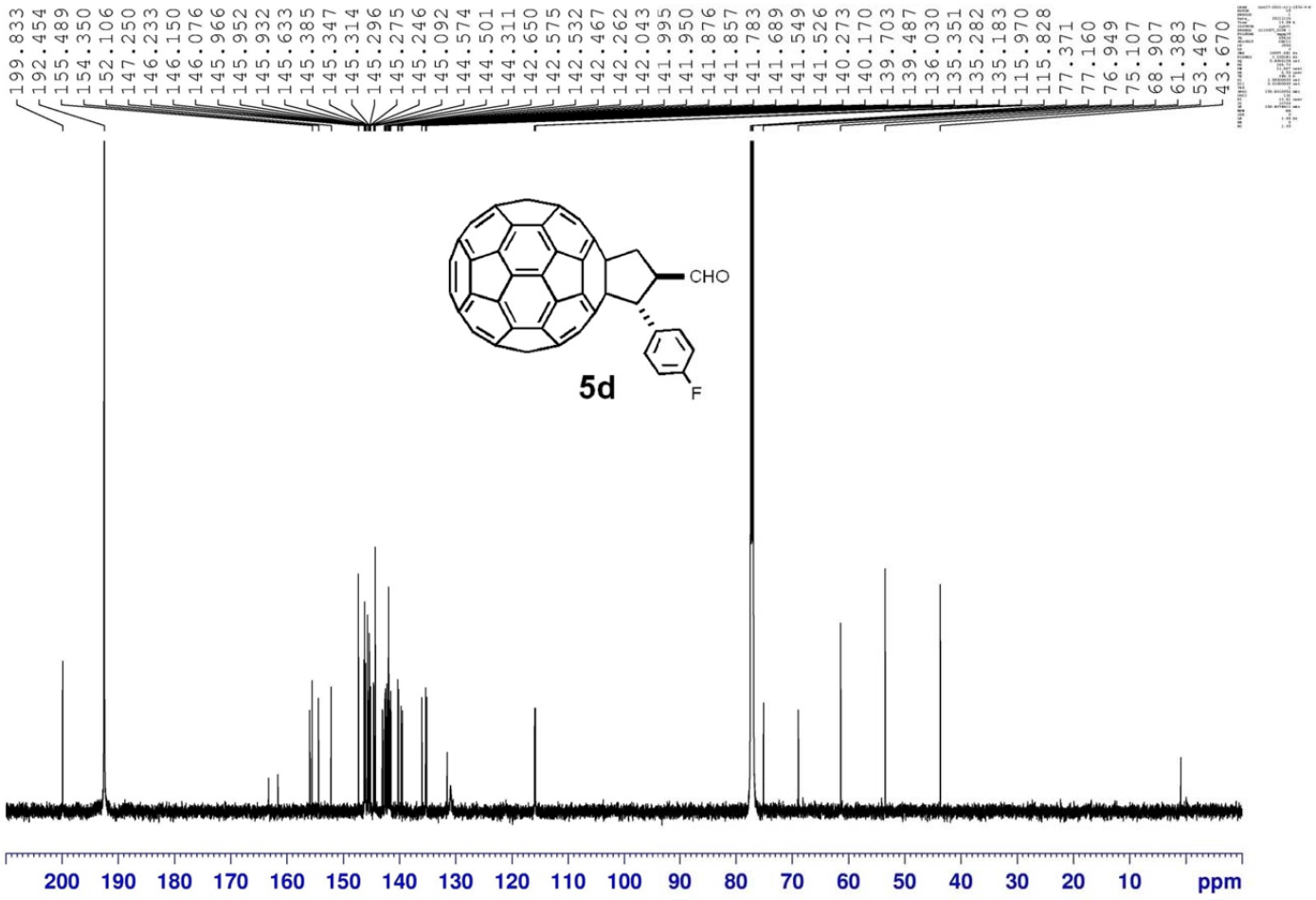
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5c



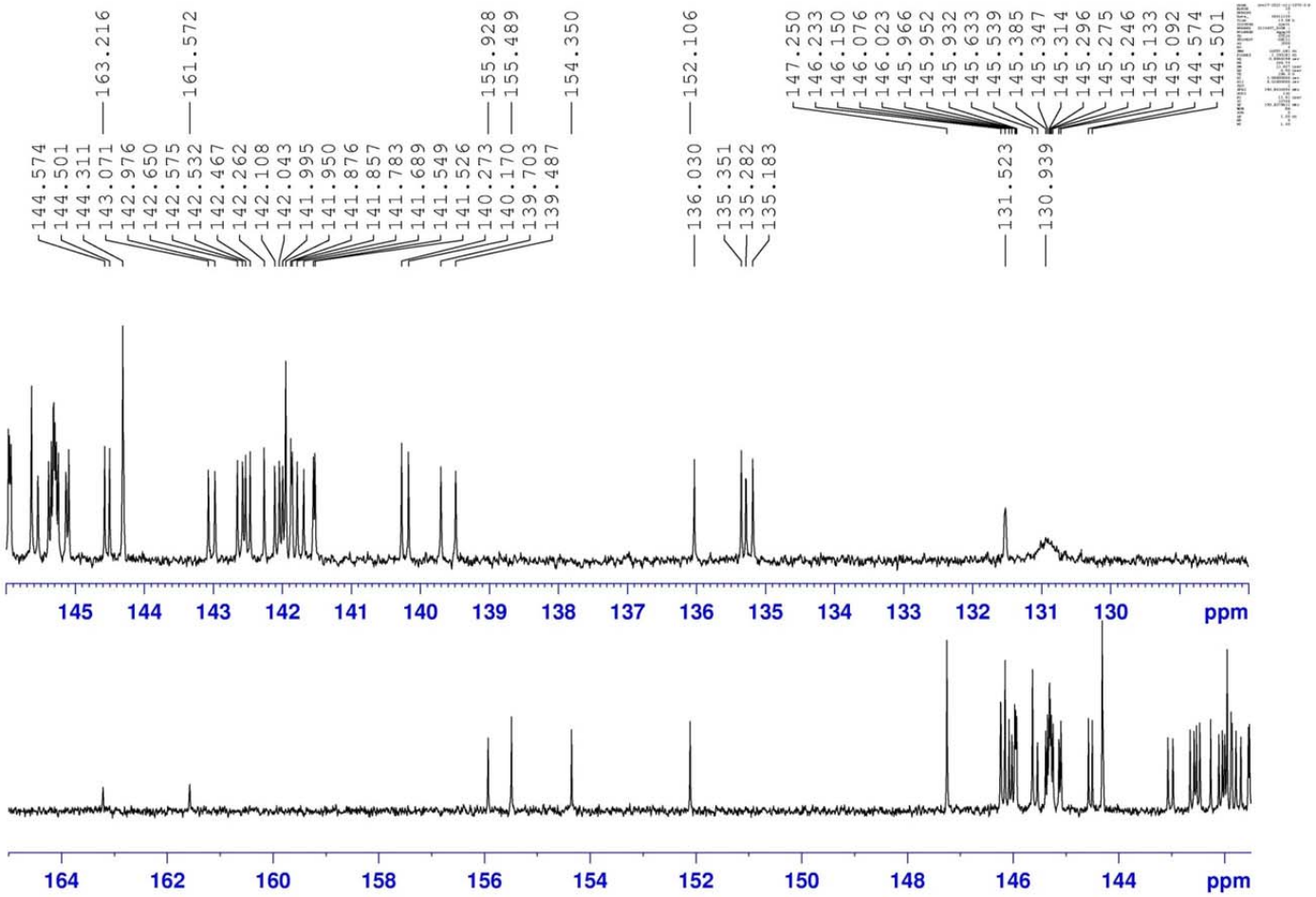
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 5d



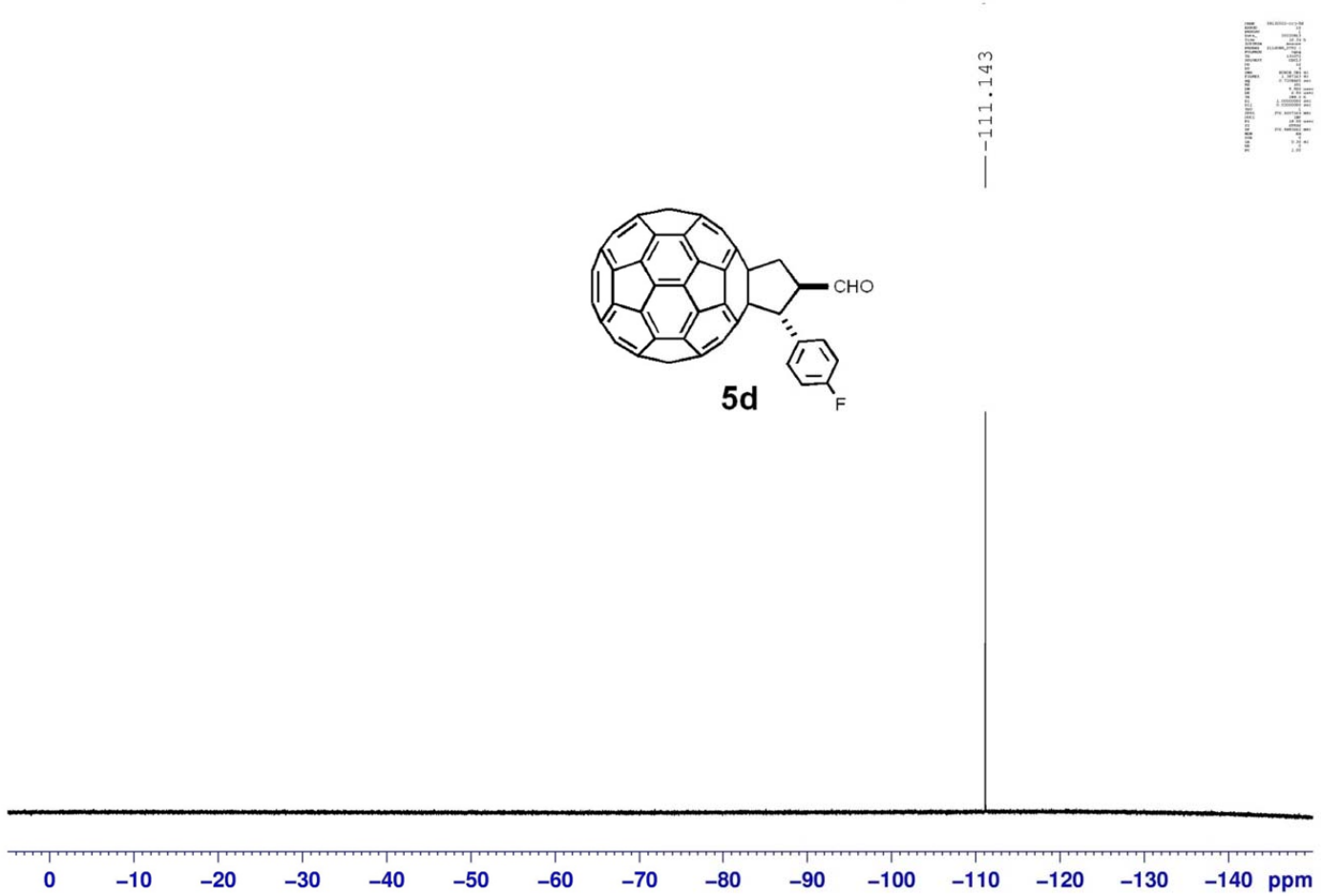
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5d



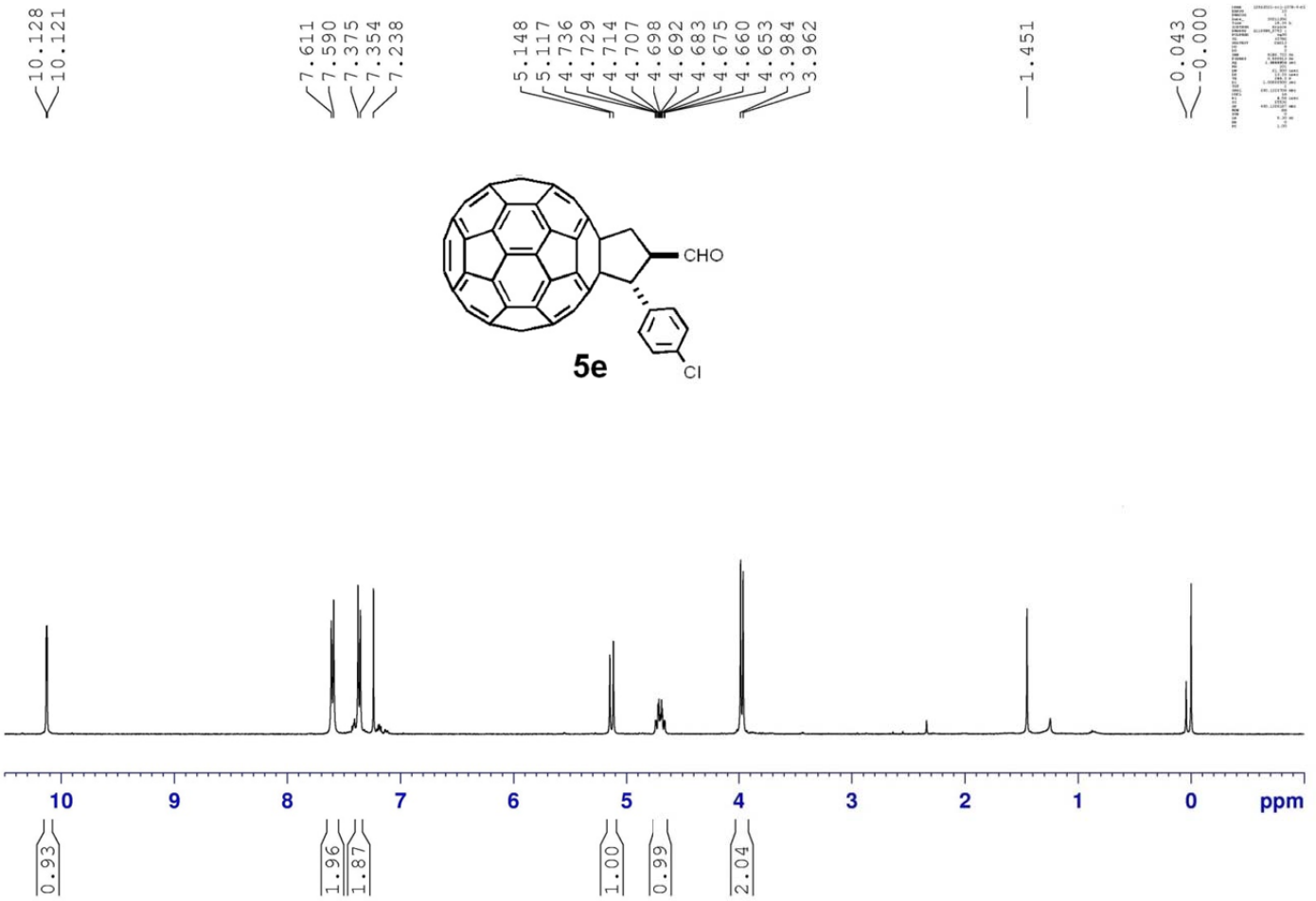
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5d



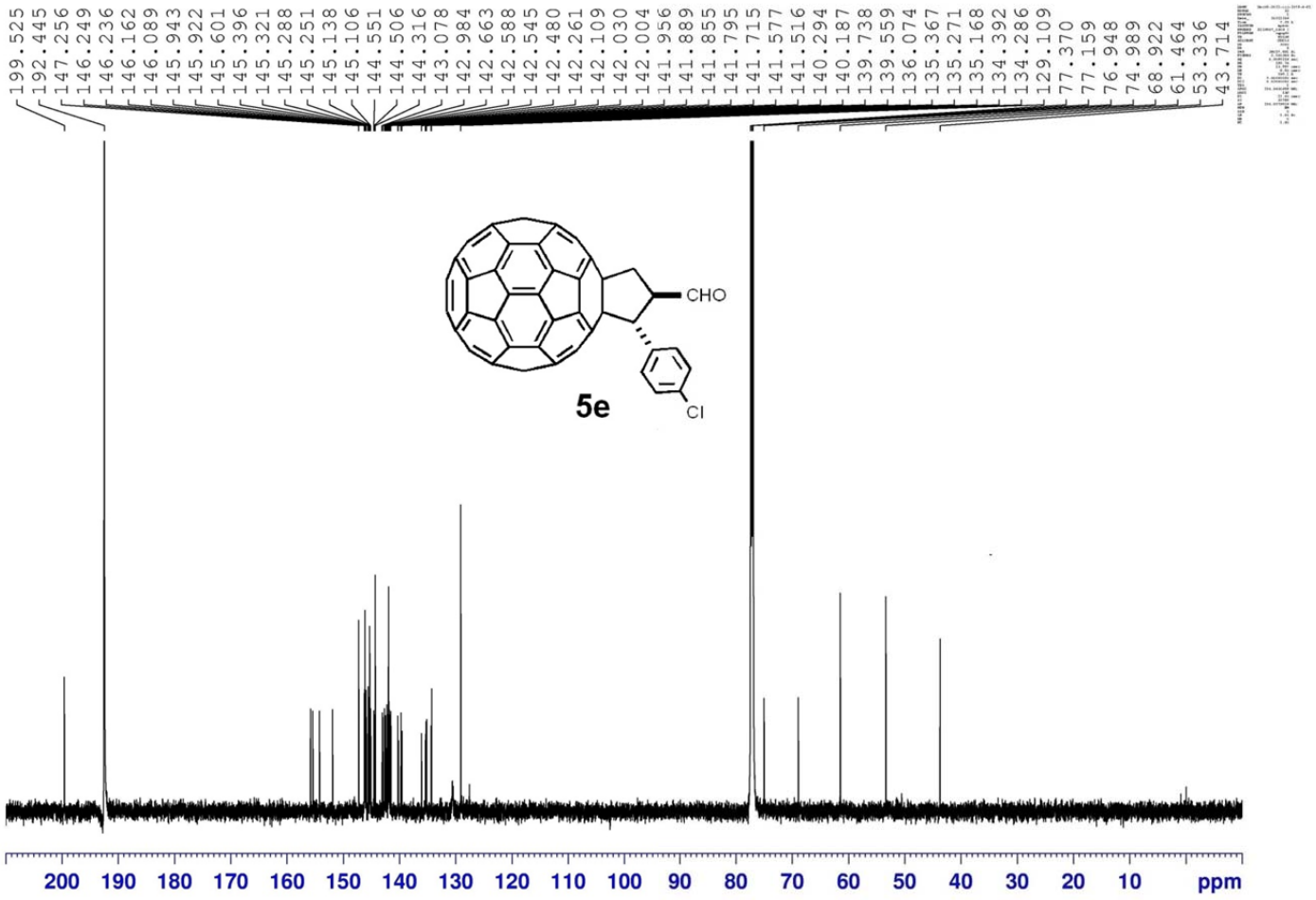
^{19}F NMR (377 MHz, $CDCl_3/CS_2$) of compound 5d



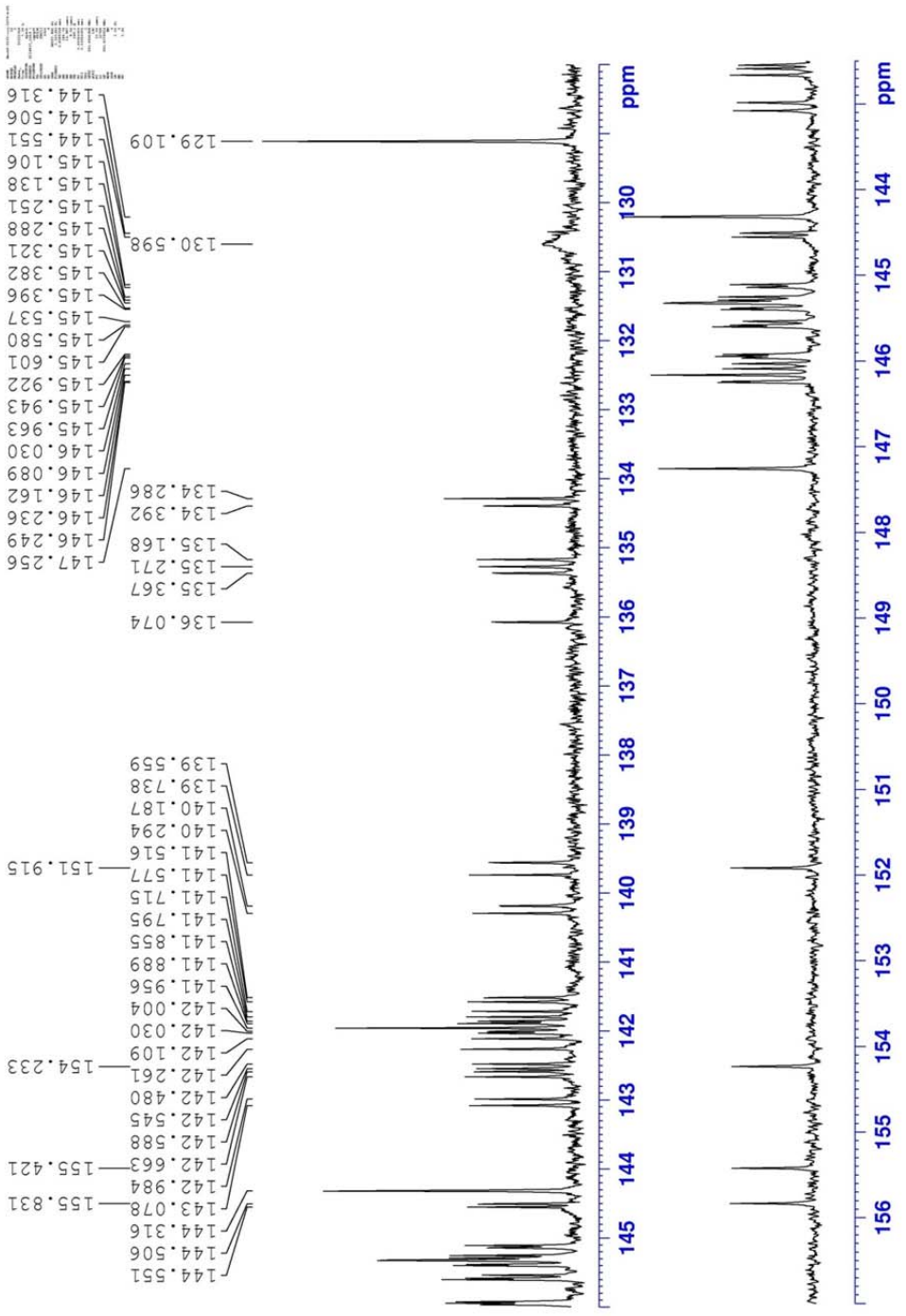
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 5e



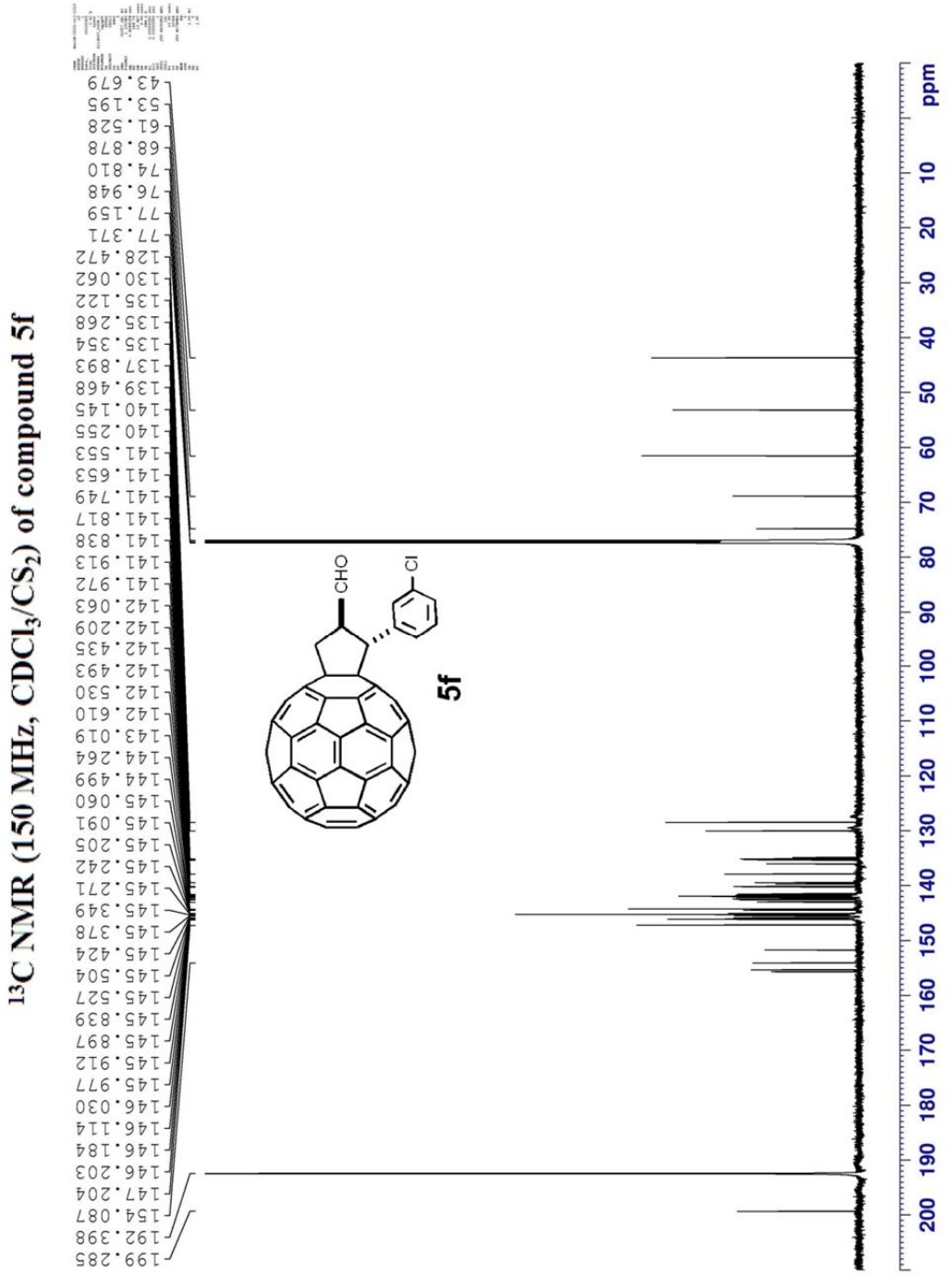
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5e



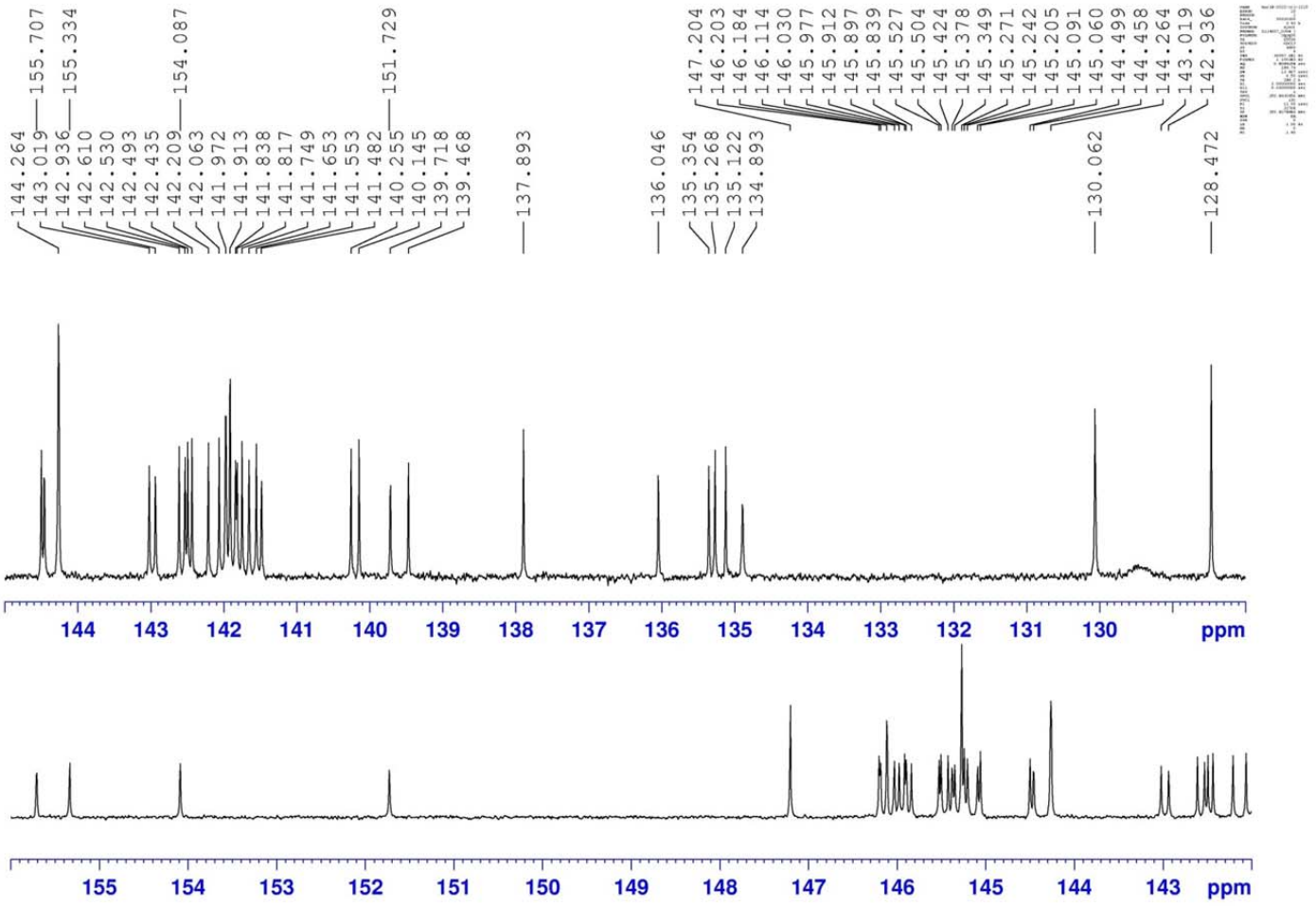
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5e



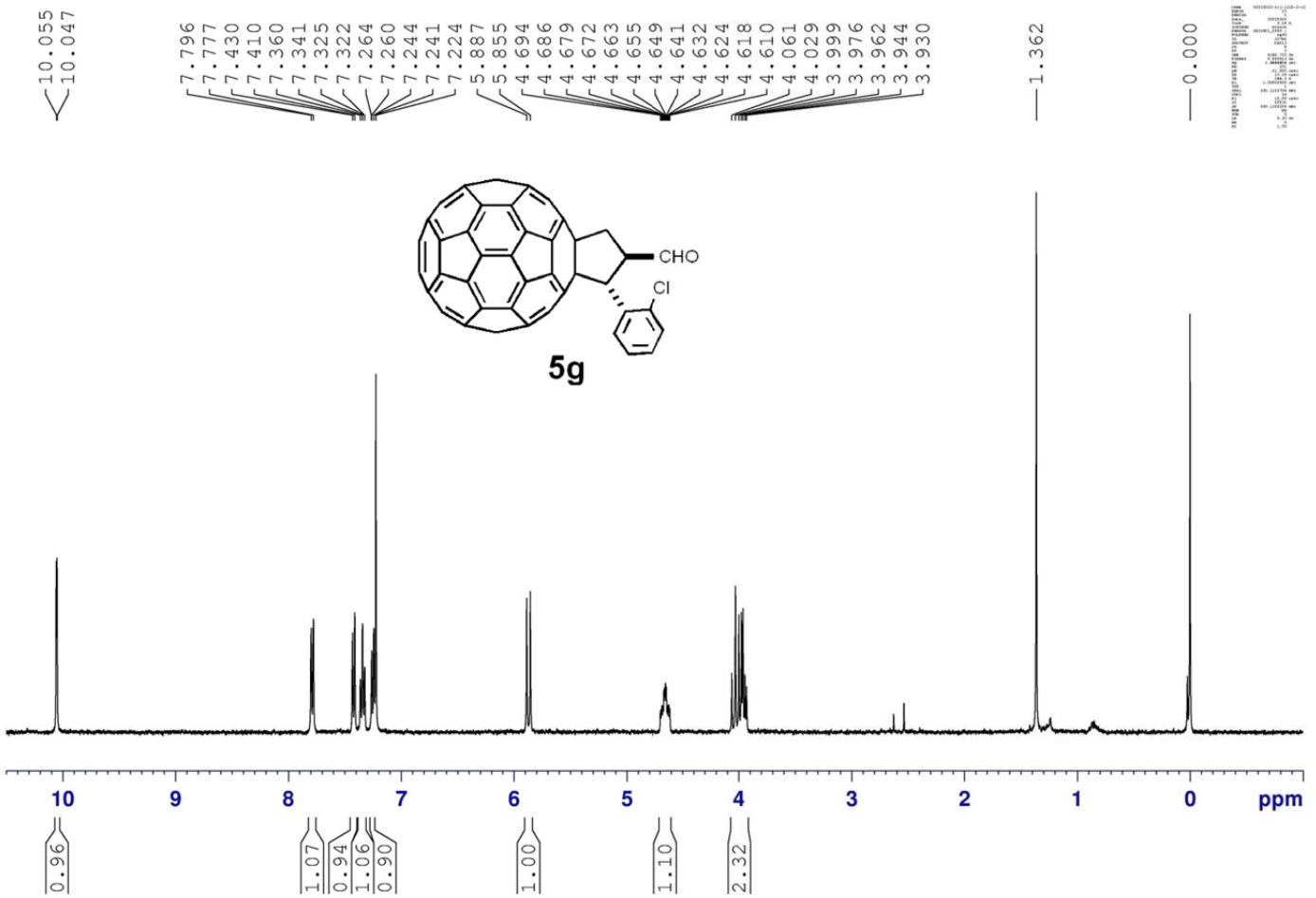
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 5f


13C NMR (150 MHz, CDCl3/CS2) of compound 5f
199.285
192.398
154.087
147.204
146.203
146.184
146.114
146.030
145.977
145.912
145.897
145.839
145.527
145.504
145.424
145.378
145.349
145.271
145.242
145.205
145.091
145.060
144.499
144.264
143.019
142.610
142.530
142.493
142.435
142.209
142.063
141.972
141.913
141.838
141.817
141.749
141.653
141.553
140.255
140.145
139.468
137.893
135.354
135.268
135.122
130.062
128.472
77.371
77.159
76.948
74.810
68.878
61.528
53.195
43.679
CHO
Cl
5f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

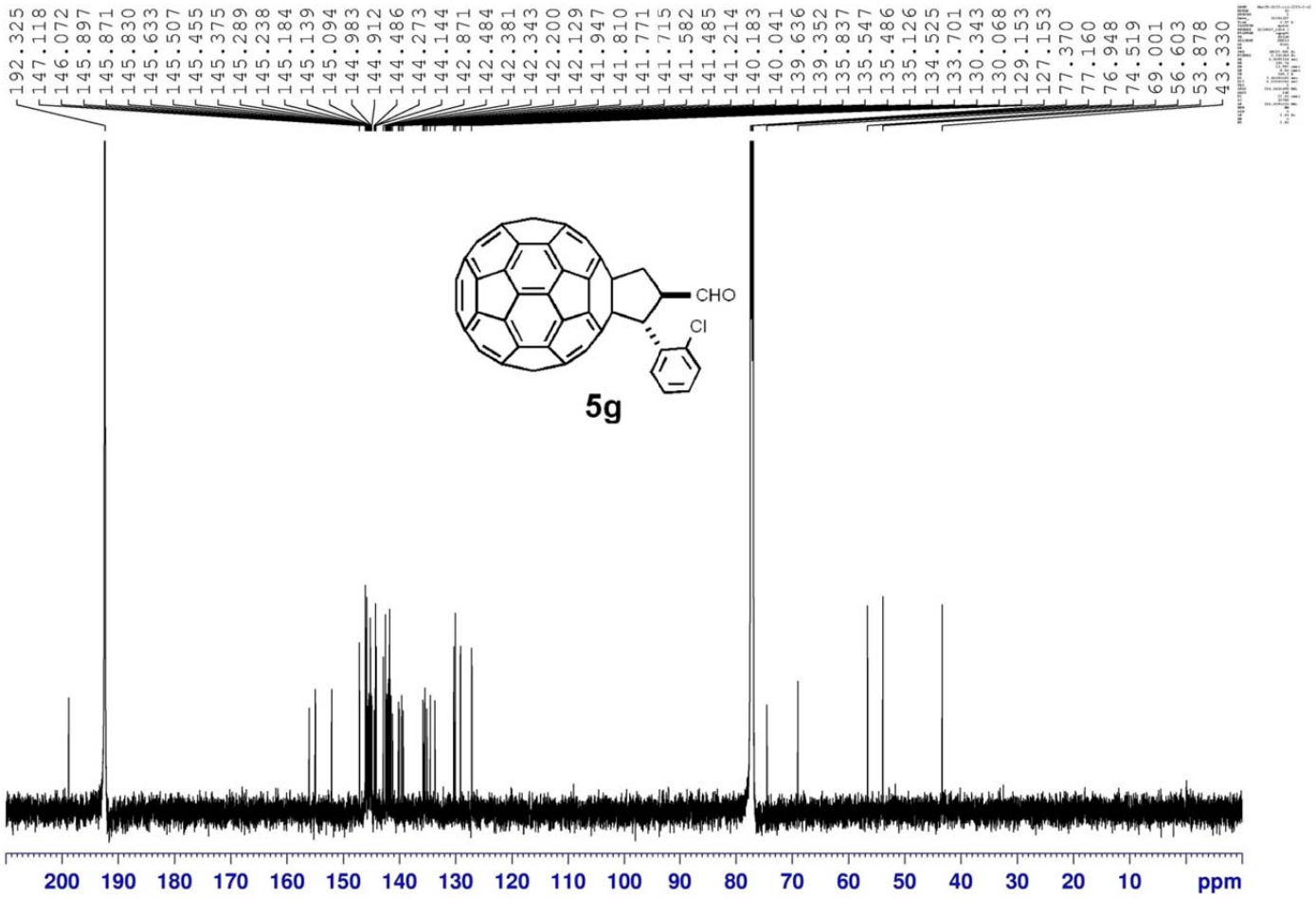
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5f



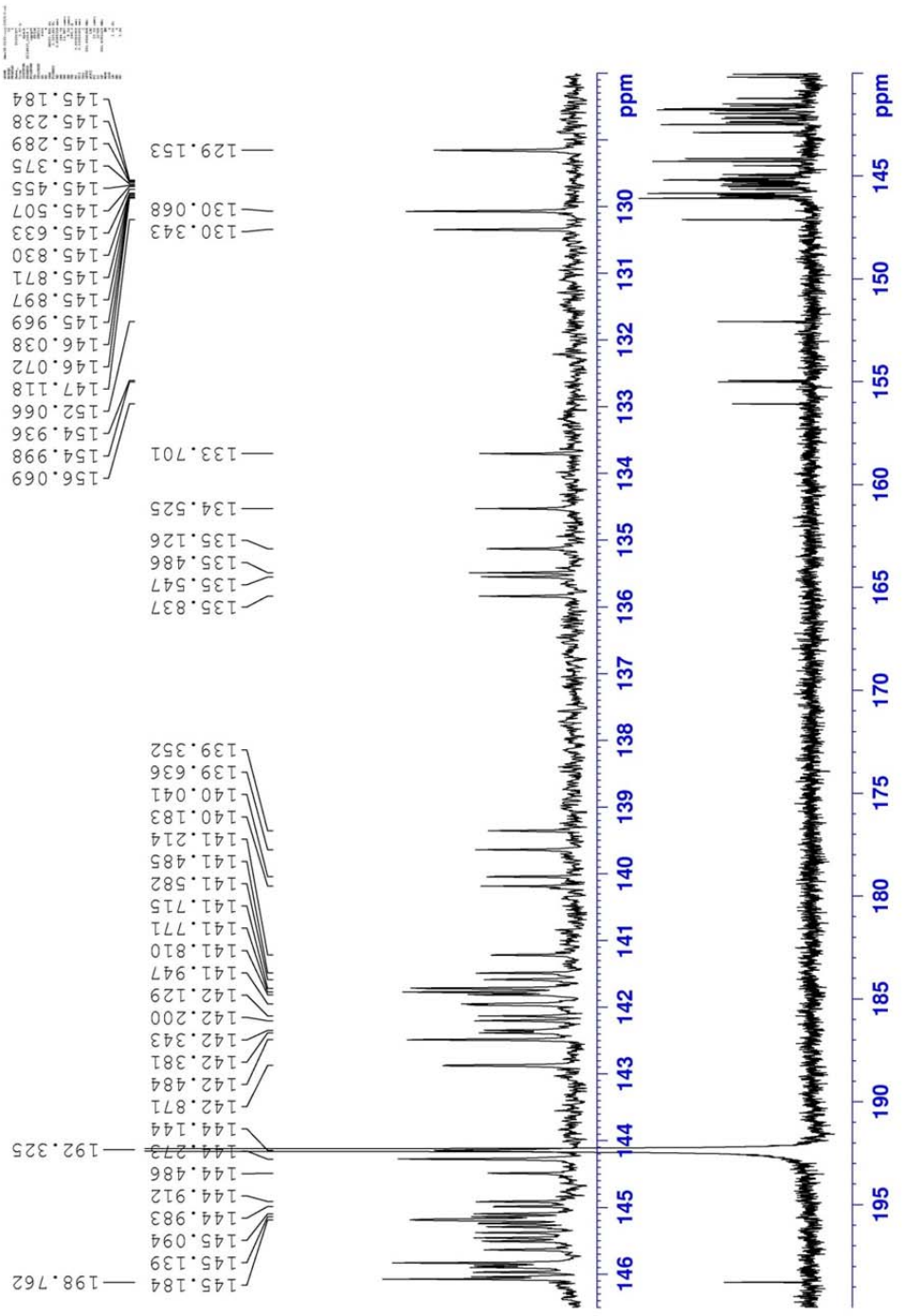
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 5g



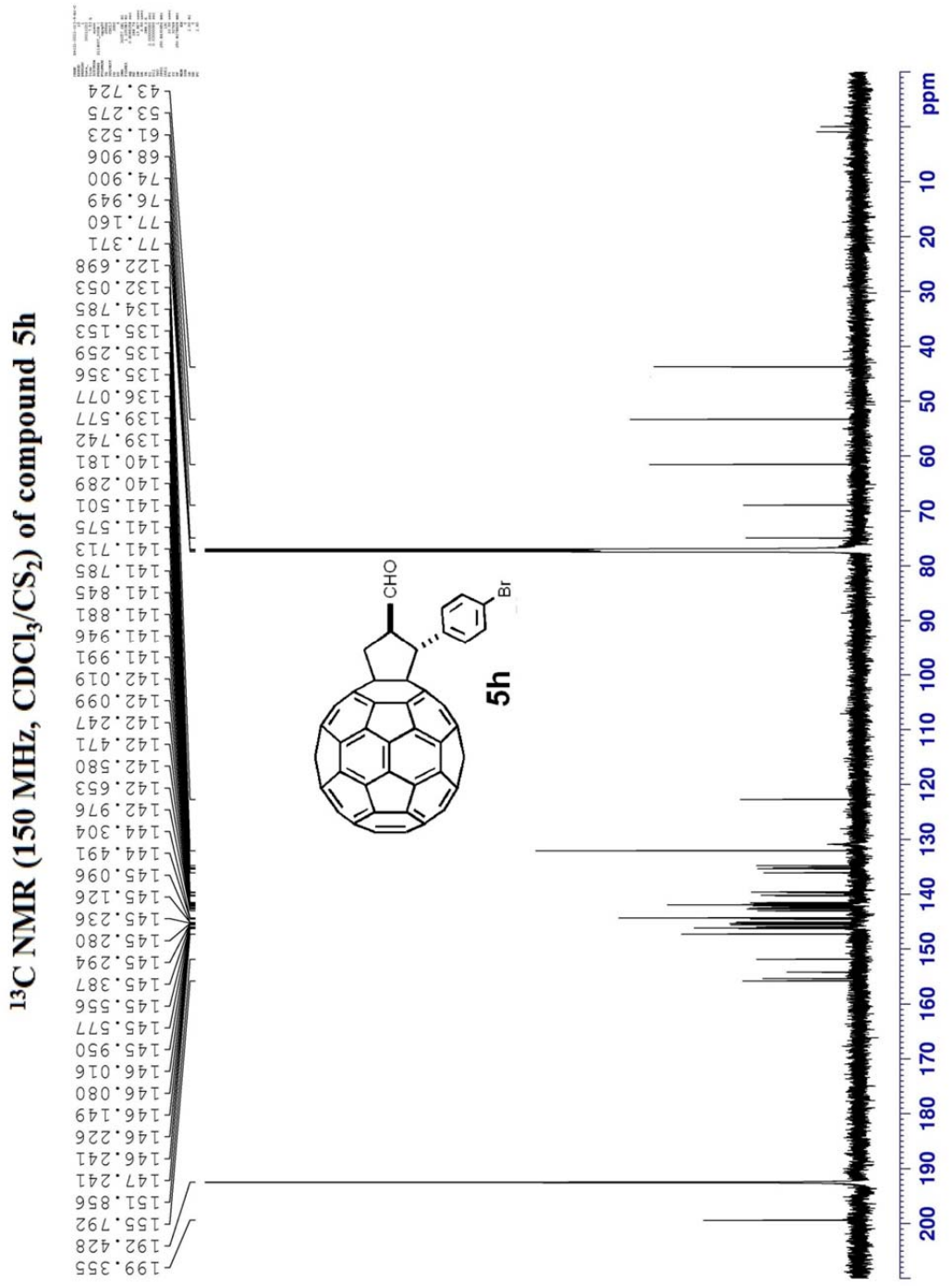
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5g



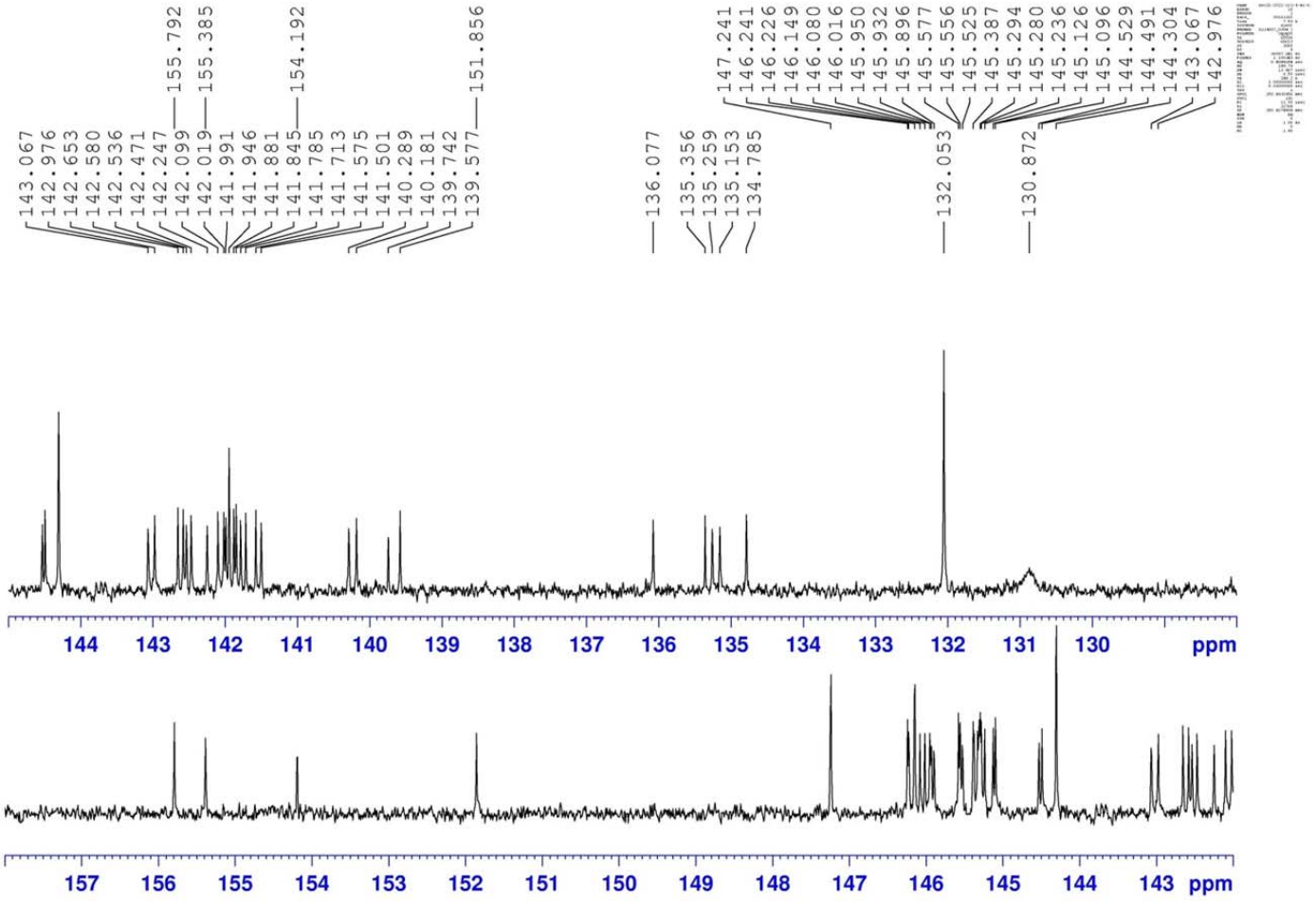
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5g



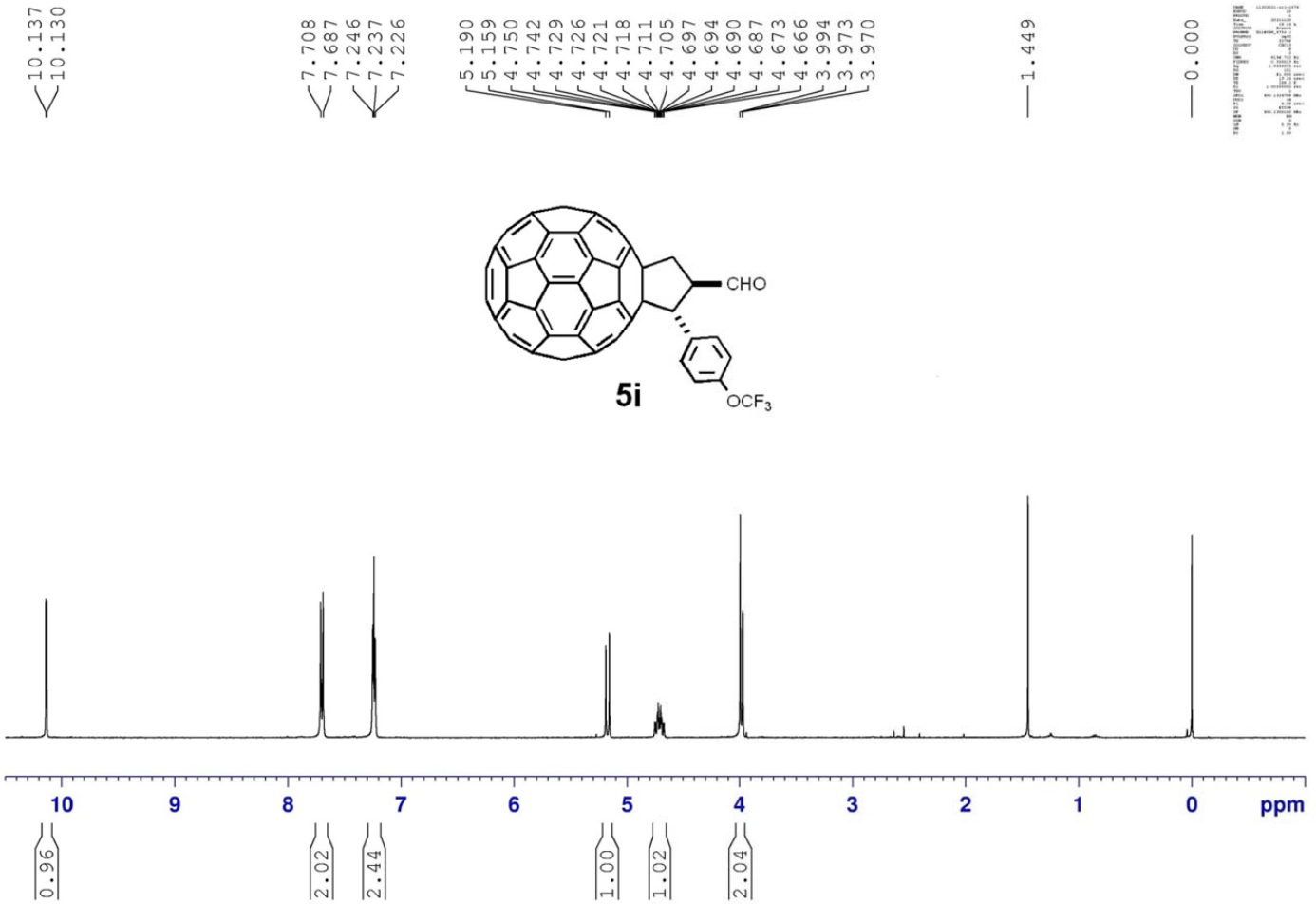
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 5h


13C NMR (150 MHz, CDCl3/CS2) of compound 5h
199.355
192.428
155.792
151.856
147.241
146.241
146.226
146.149
146.080
146.016
145.950
145.577
145.556
145.387
145.294
145.280
145.236
145.126
145.096
144.491
144.304
142.976
142.653
142.580
142.471
142.247
142.099
142.019
141.991
141.946
141.881
141.845
141.785
141.713
141.575
141.501
140.289
140.181
139.742
139.577
136.077
135.356
135.259
135.153
134.785
132.053
122.698
77.371
77.160
76.949
74.900
68.906
61.523
53.275
43.724
CHO
Br
5h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

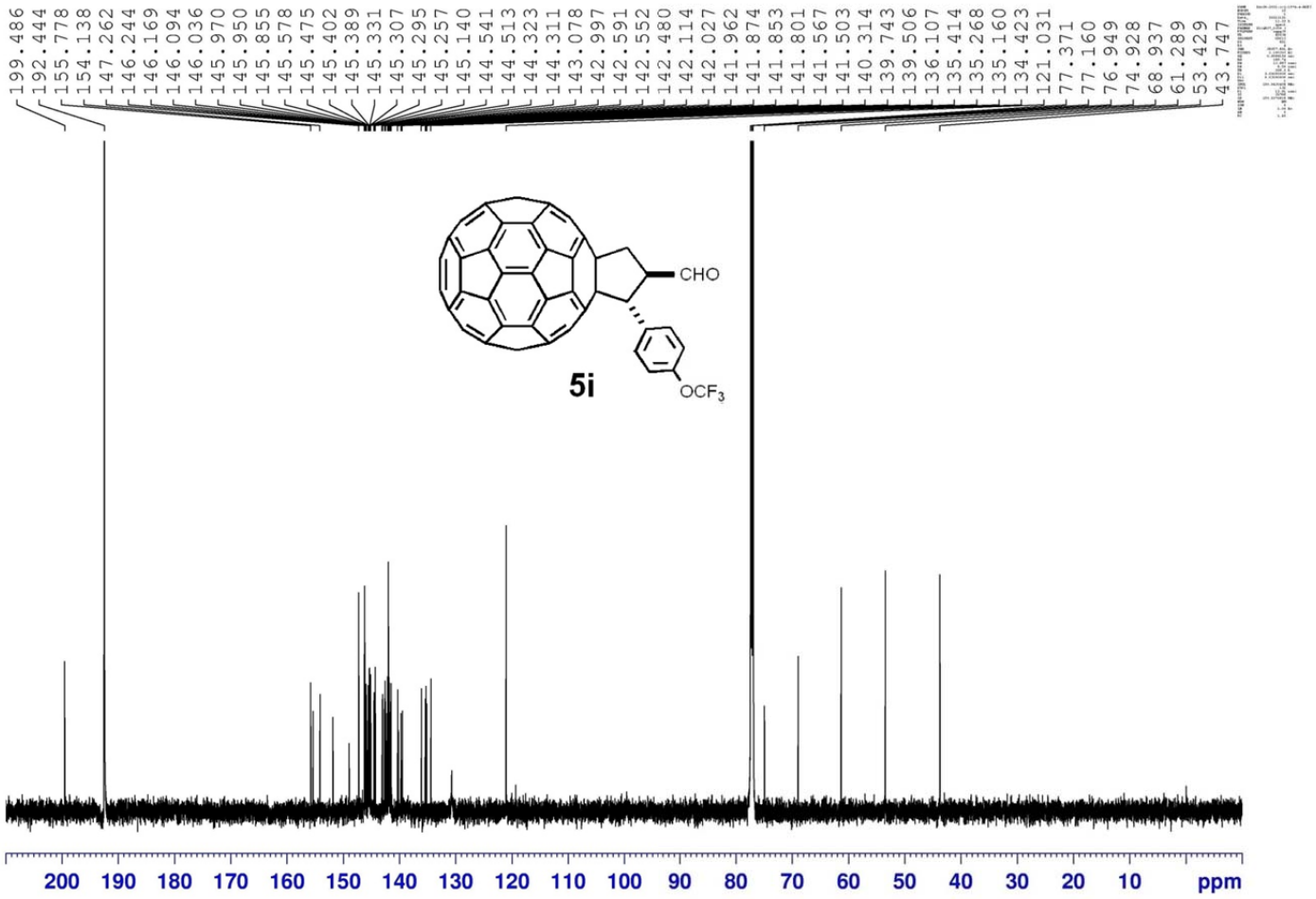
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5h



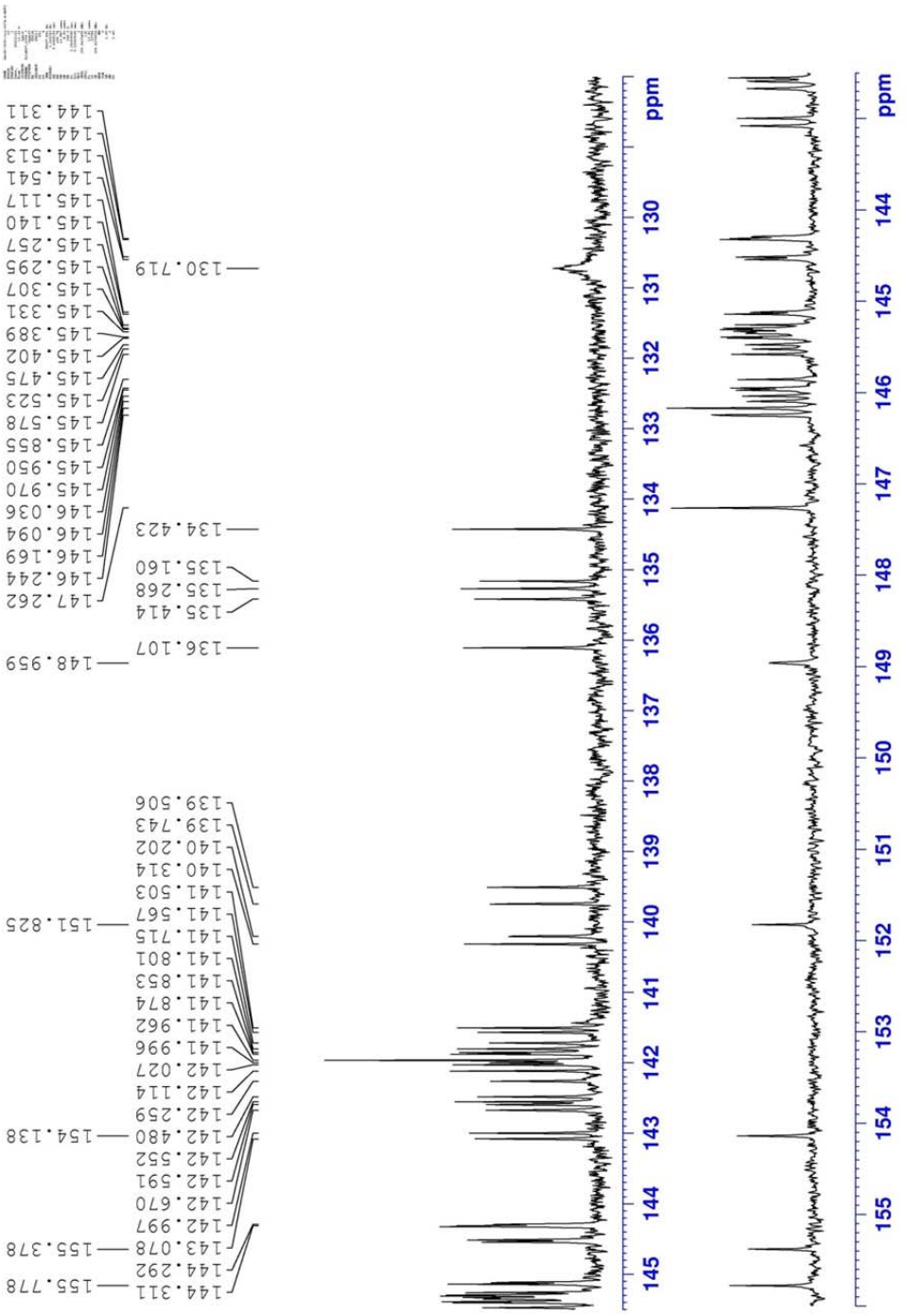
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 5i



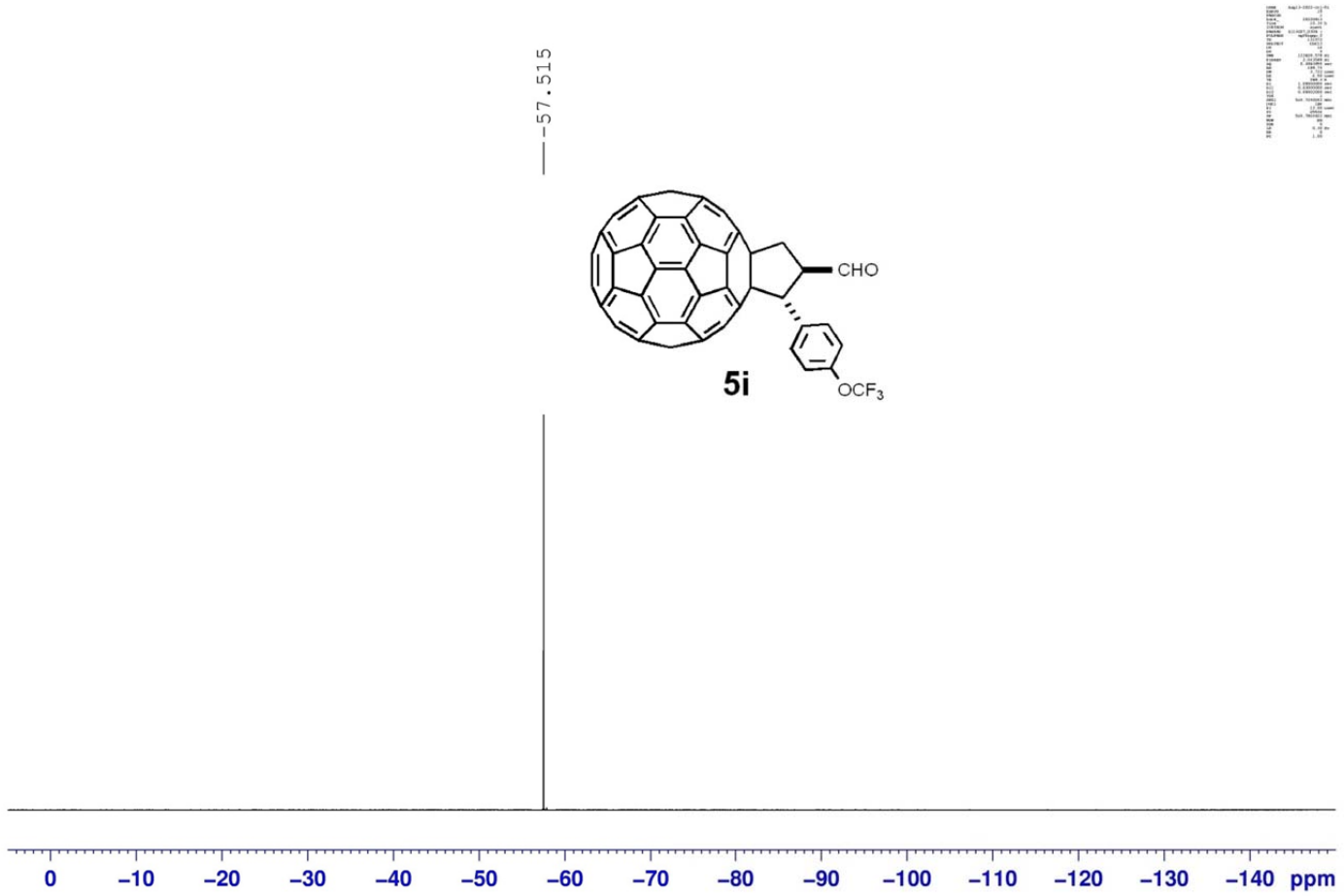
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5i



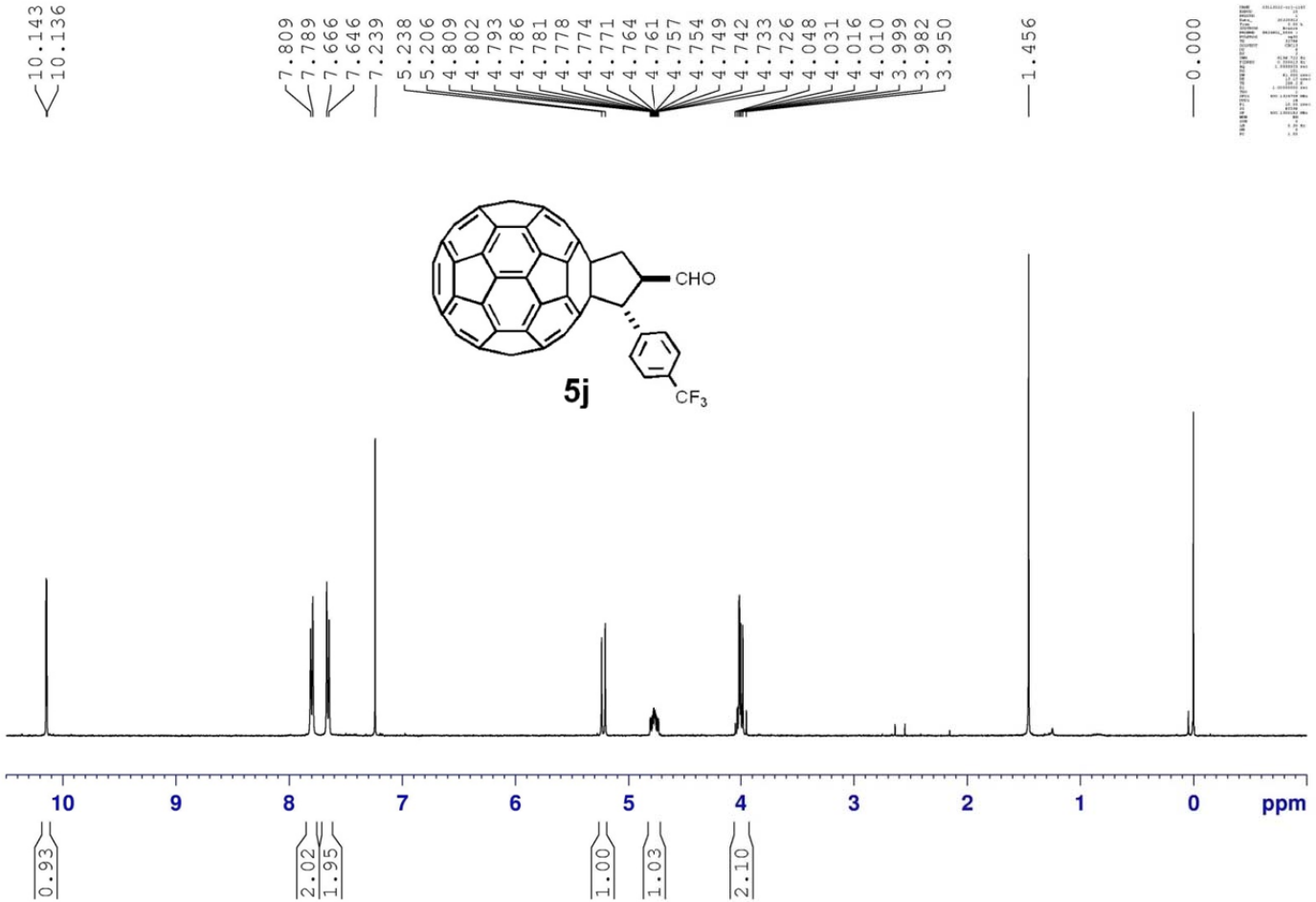
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5i

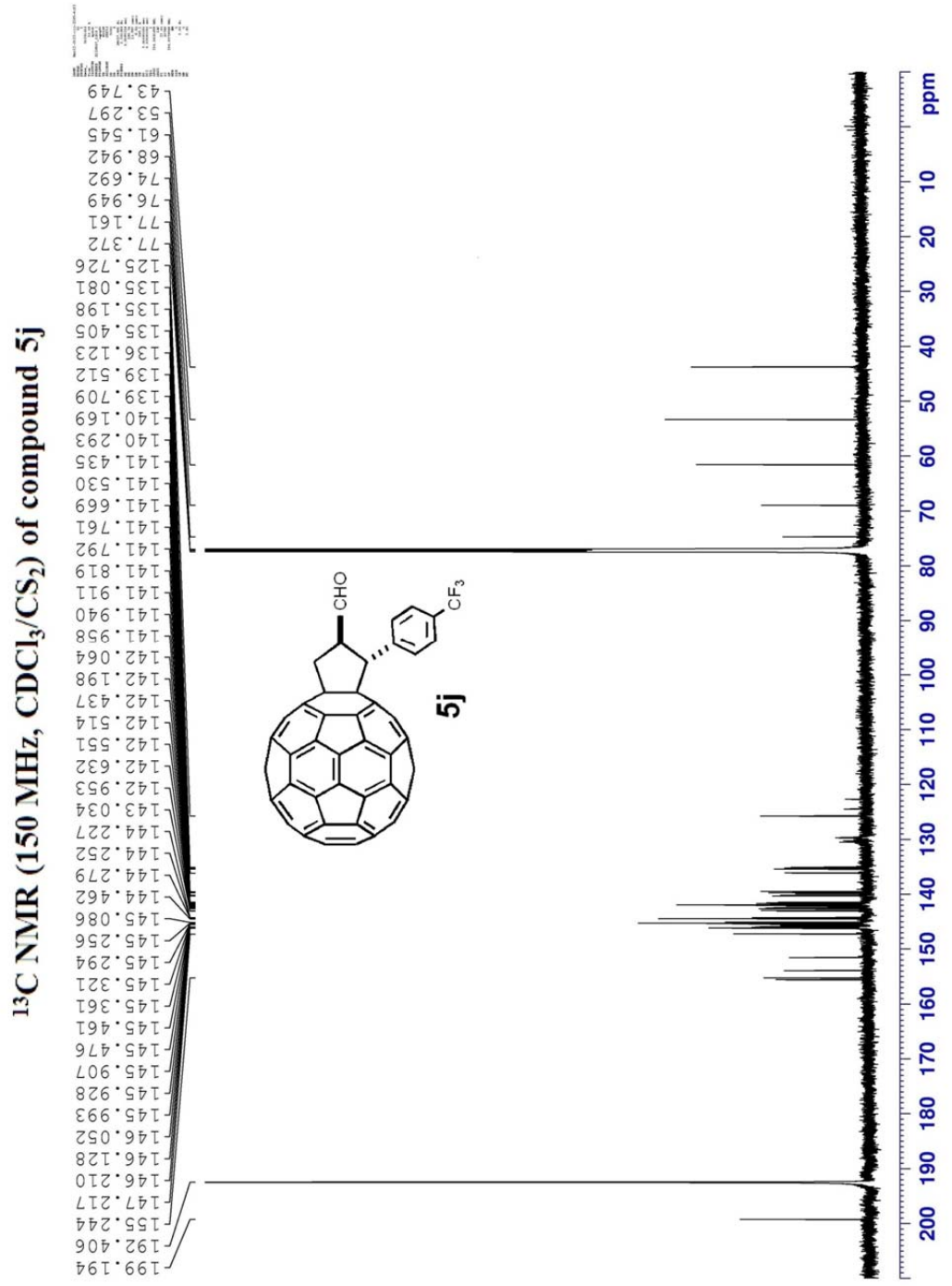


^{19}F NMR (565 MHz, $CDCl_3/CS_2$) of compound 5i

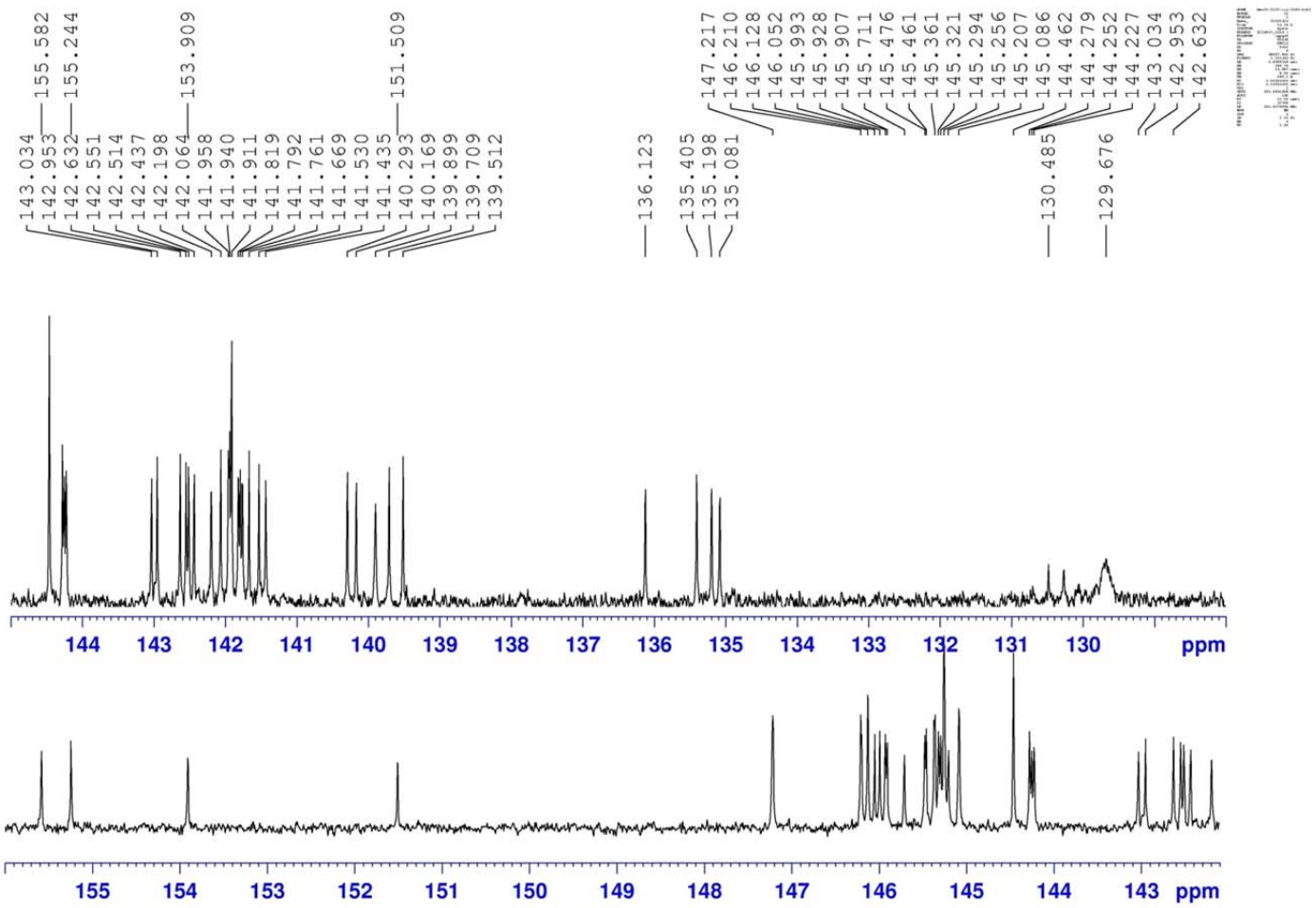


^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 5j

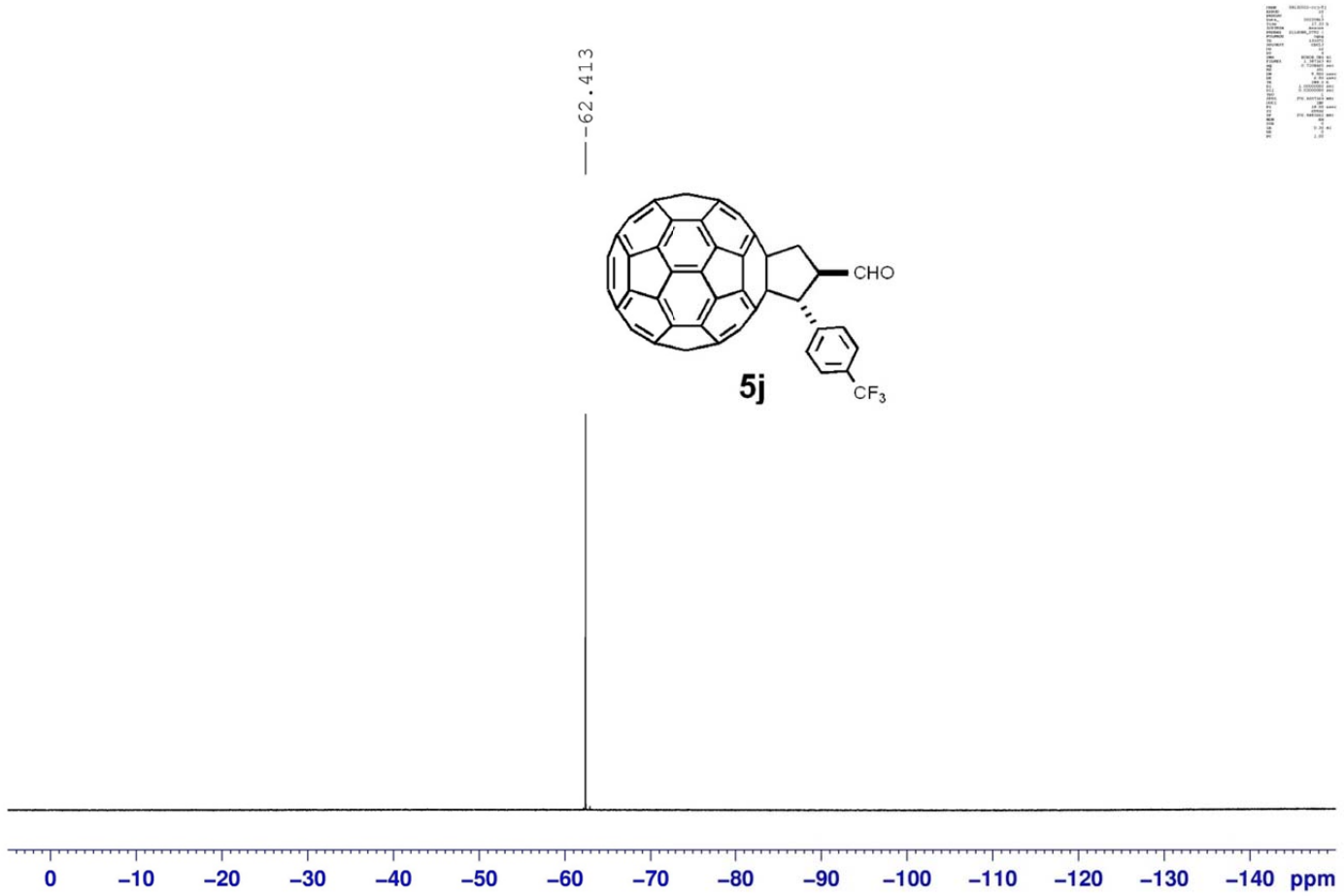



^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5j
199.194
192.406
155.244
147.217
146.210
146.128
146.052
145.993
145.928
145.907
145.476
145.461
145.361
145.321
145.294
145.256
145.086
144.462
144.279
144.252
144.227
143.034
142.953
142.632
142.551
142.514
142.437
142.198
142.064
141.958
141.940
141.911
141.819
141.792
141.761
141.669
141.530
141.435
140.293
140.169
139.709
139.512
136.123
135.405
135.198
135.081
125.726
77.372
77.161
76.949
74.692
68.942
61.545
53.297
43.749
CHO
CF_3
5j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

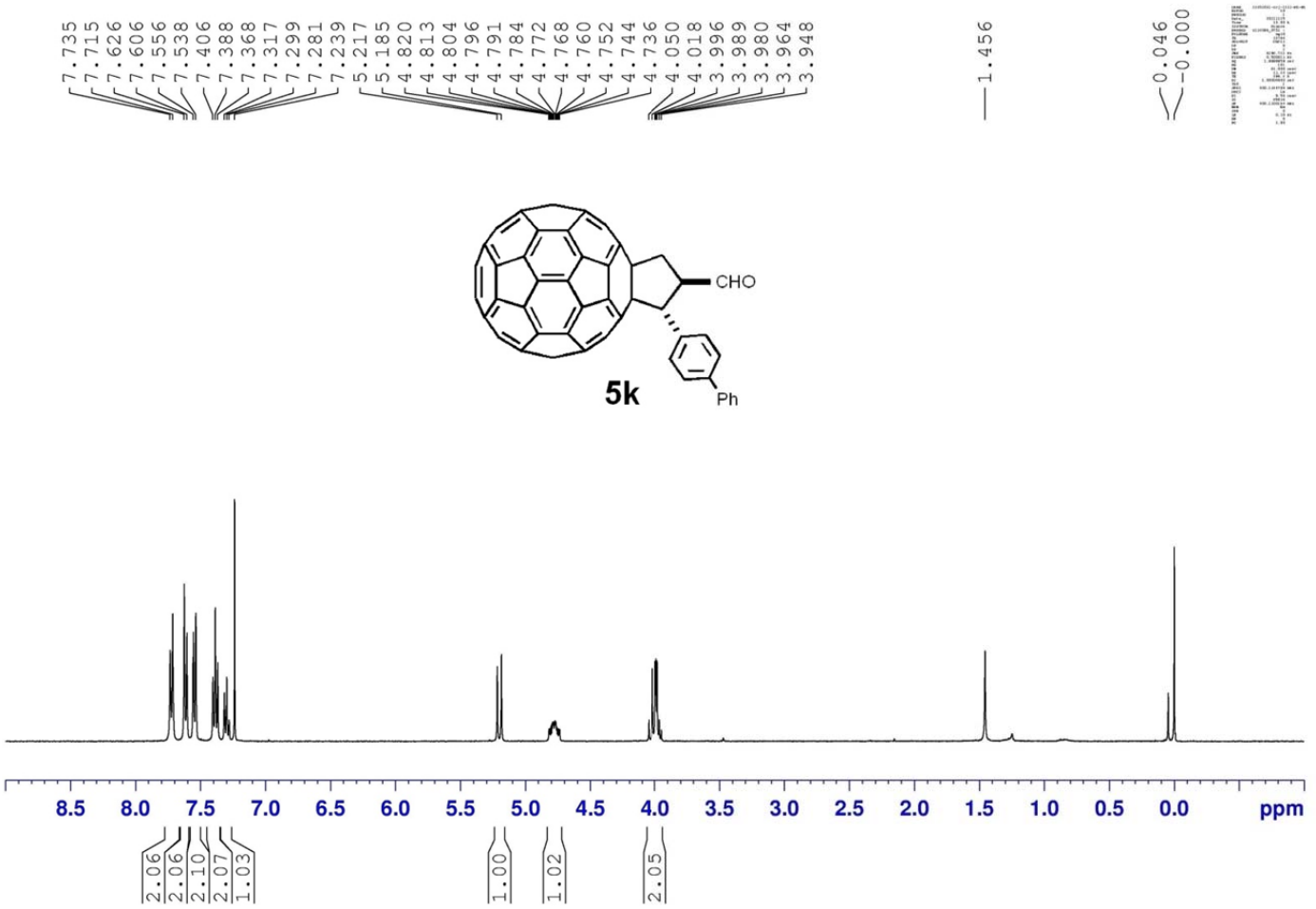
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5j

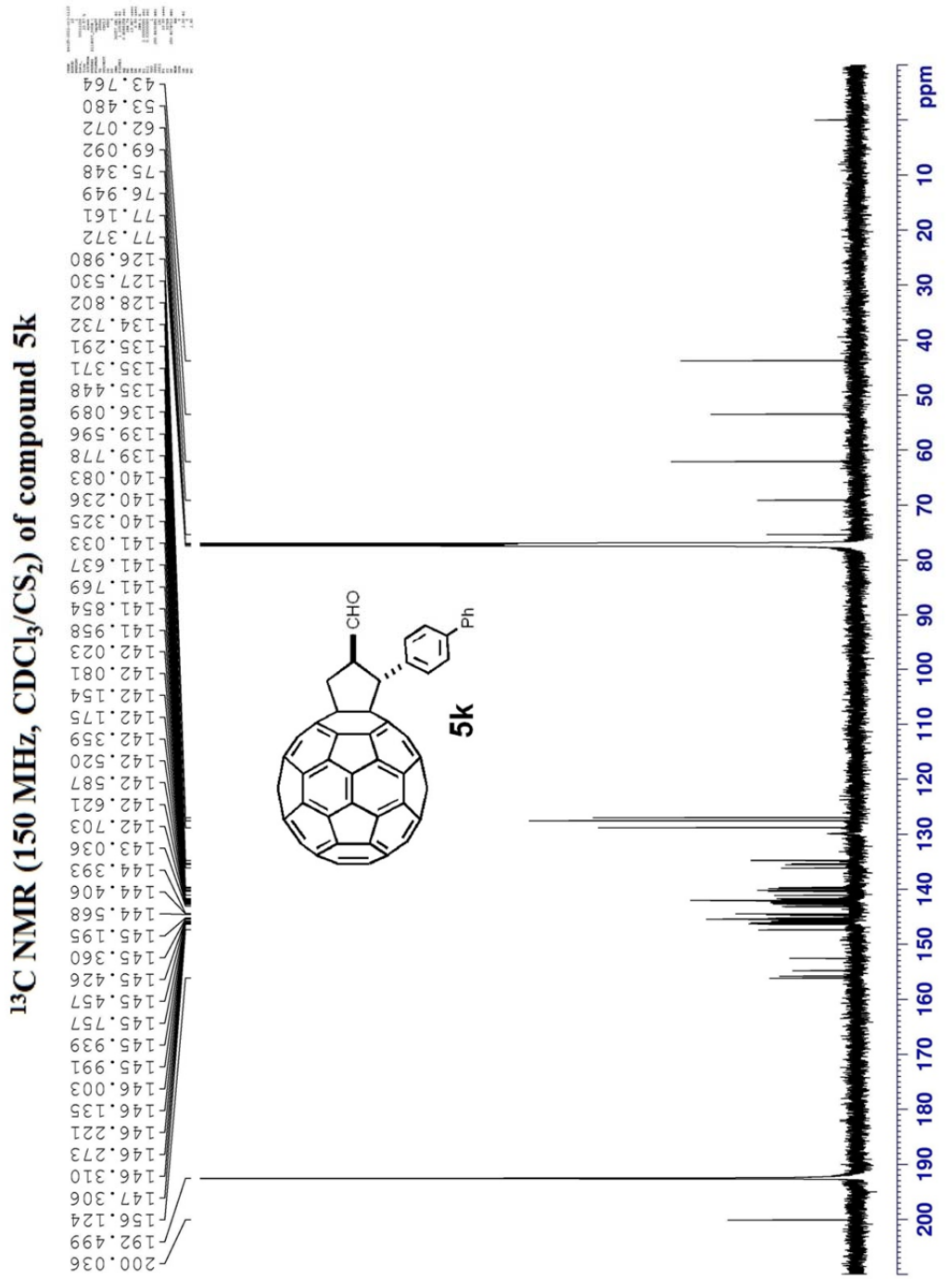


^{19}F NMR (377 MHz, $CDCl_3/CS_2$) of compound 5j

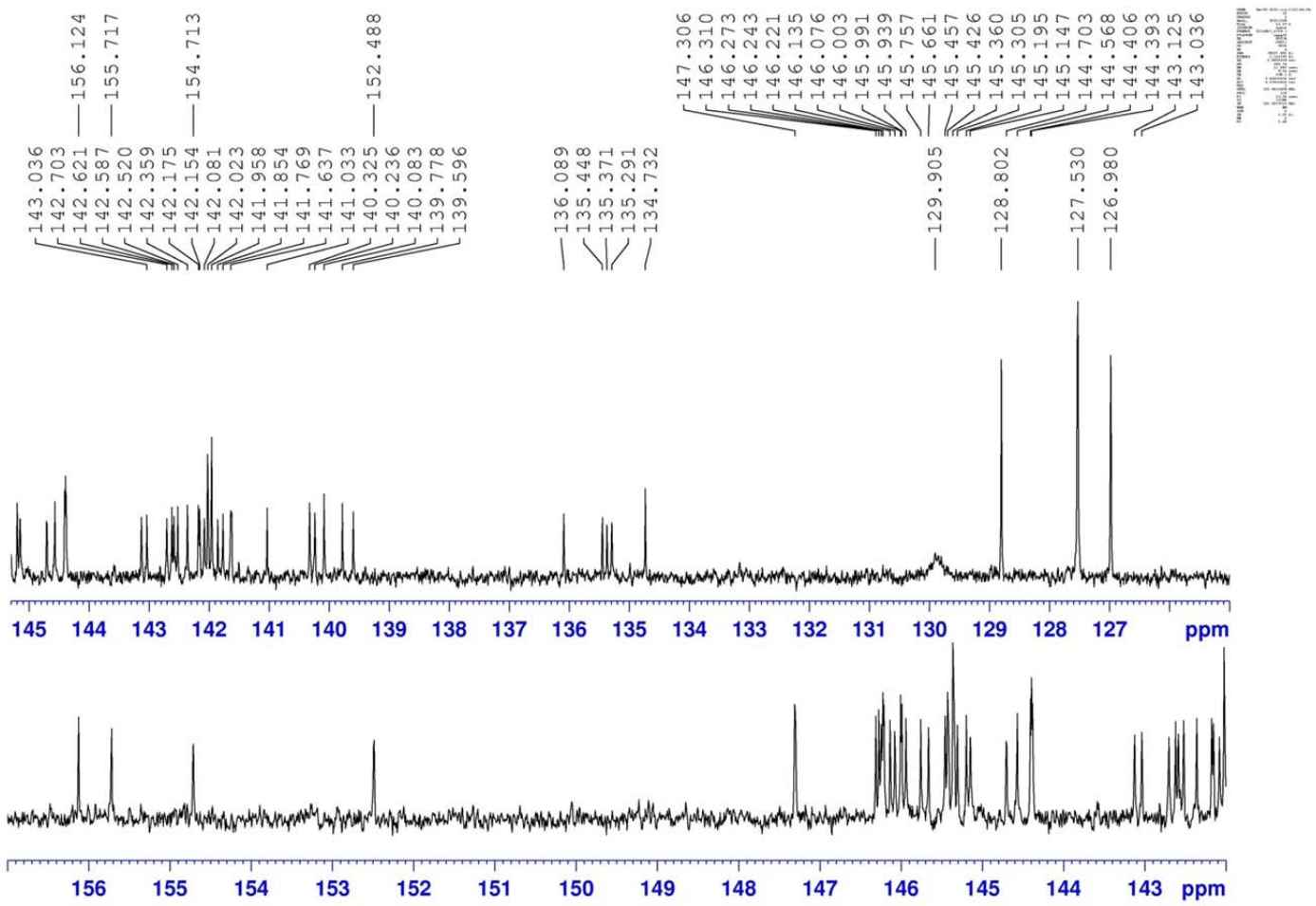


^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 5k



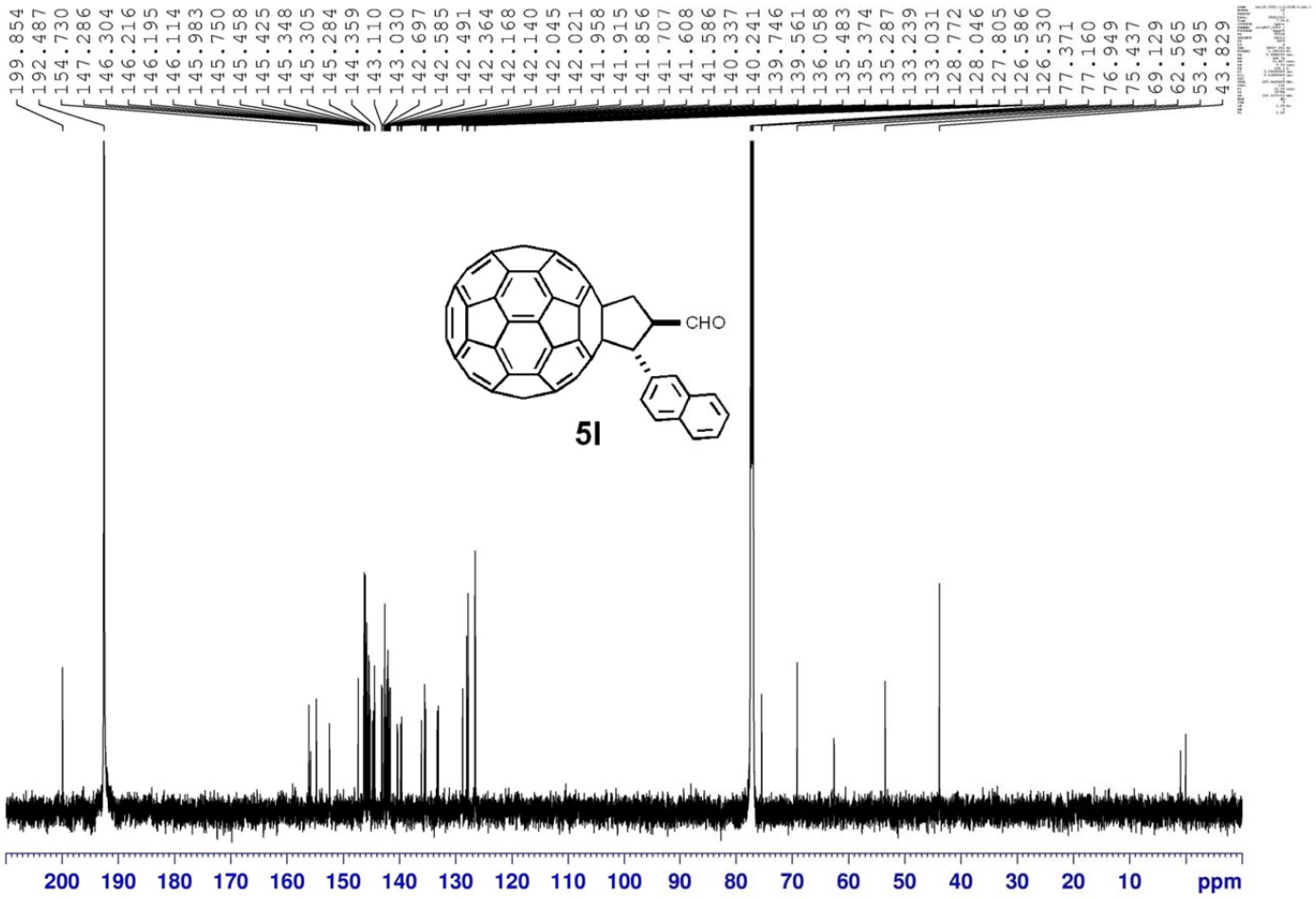

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5k
CHO
Ph
5k
ppm

Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5k

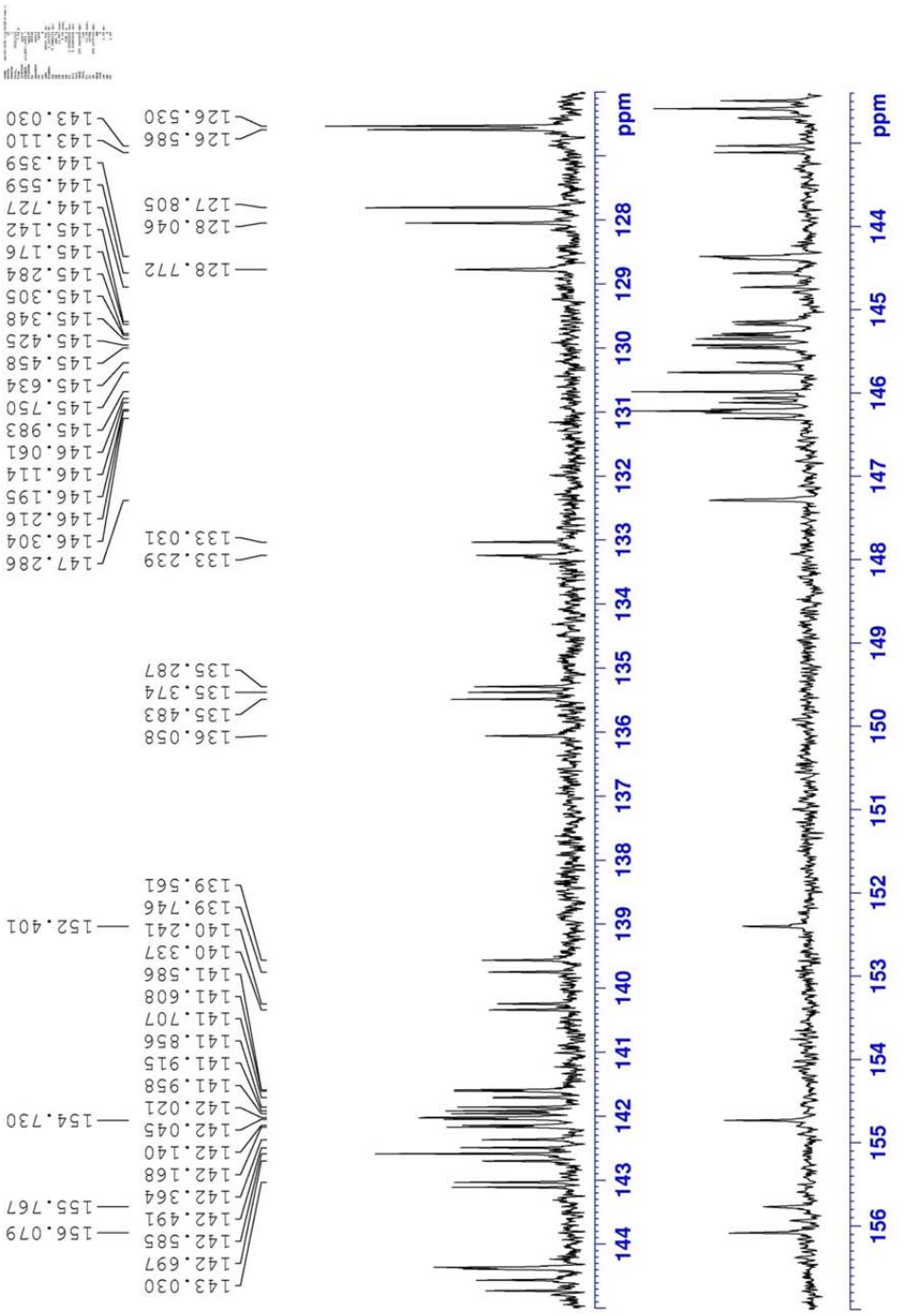


^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 5l

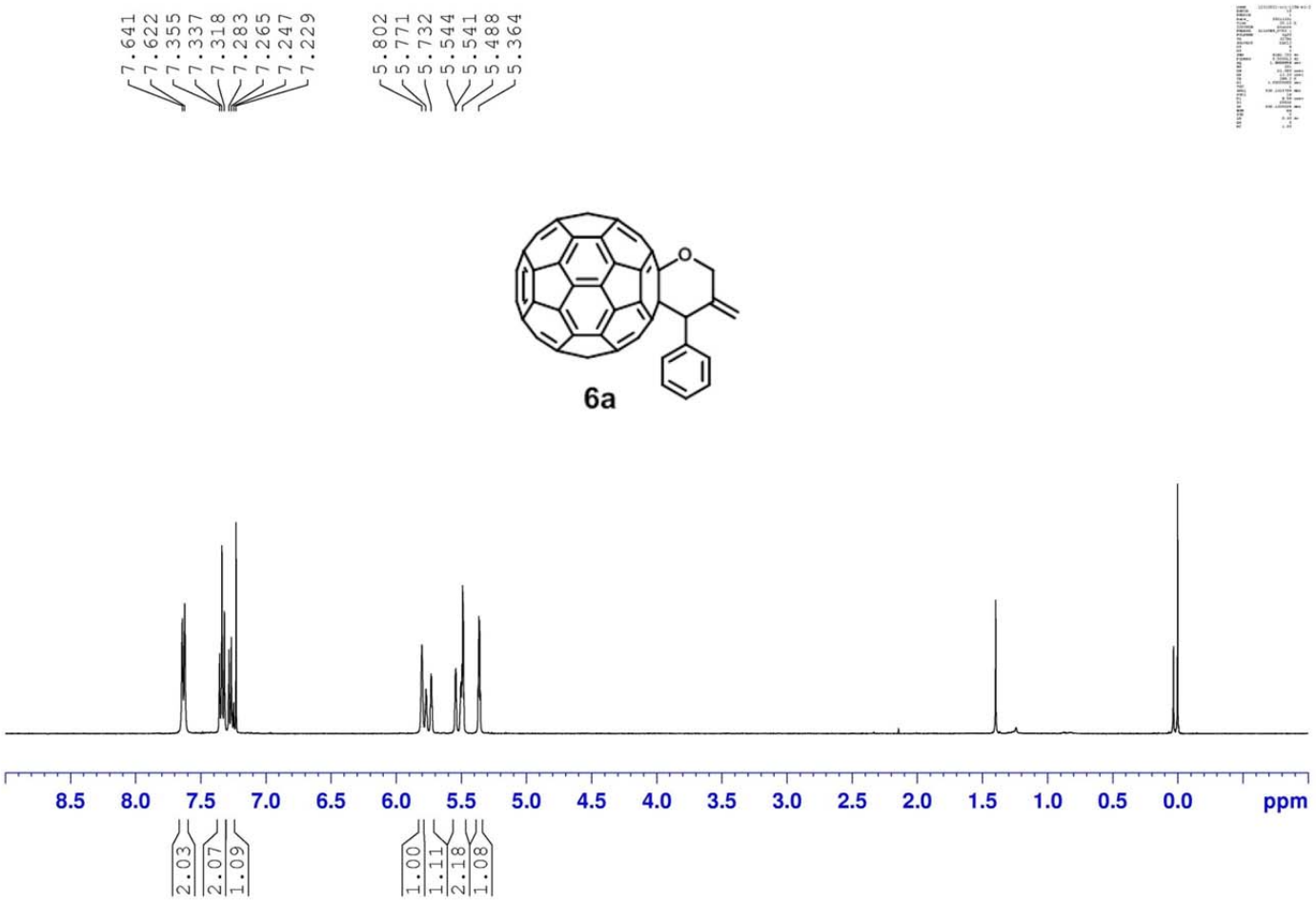
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5l



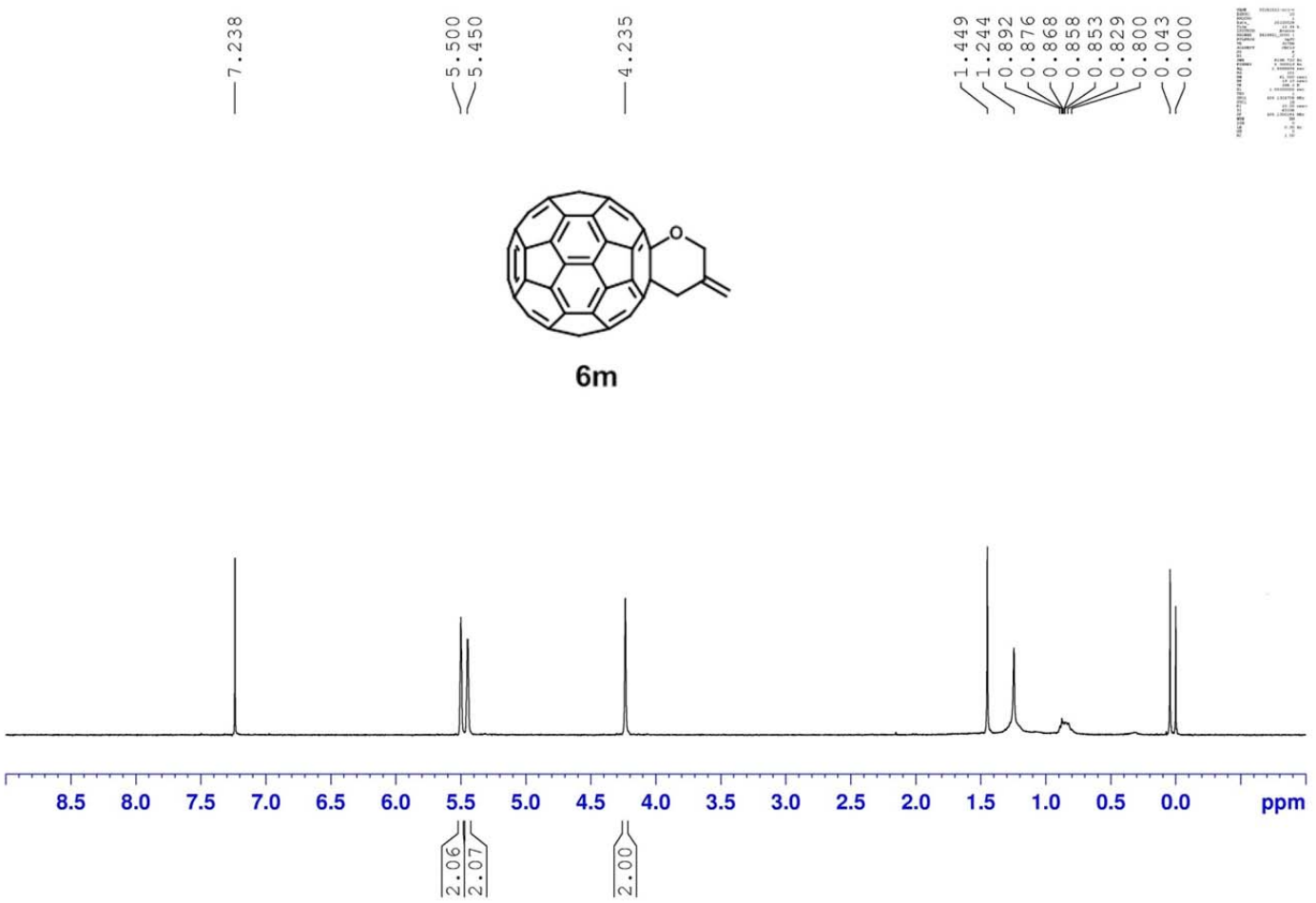
Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 5l



^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 6a

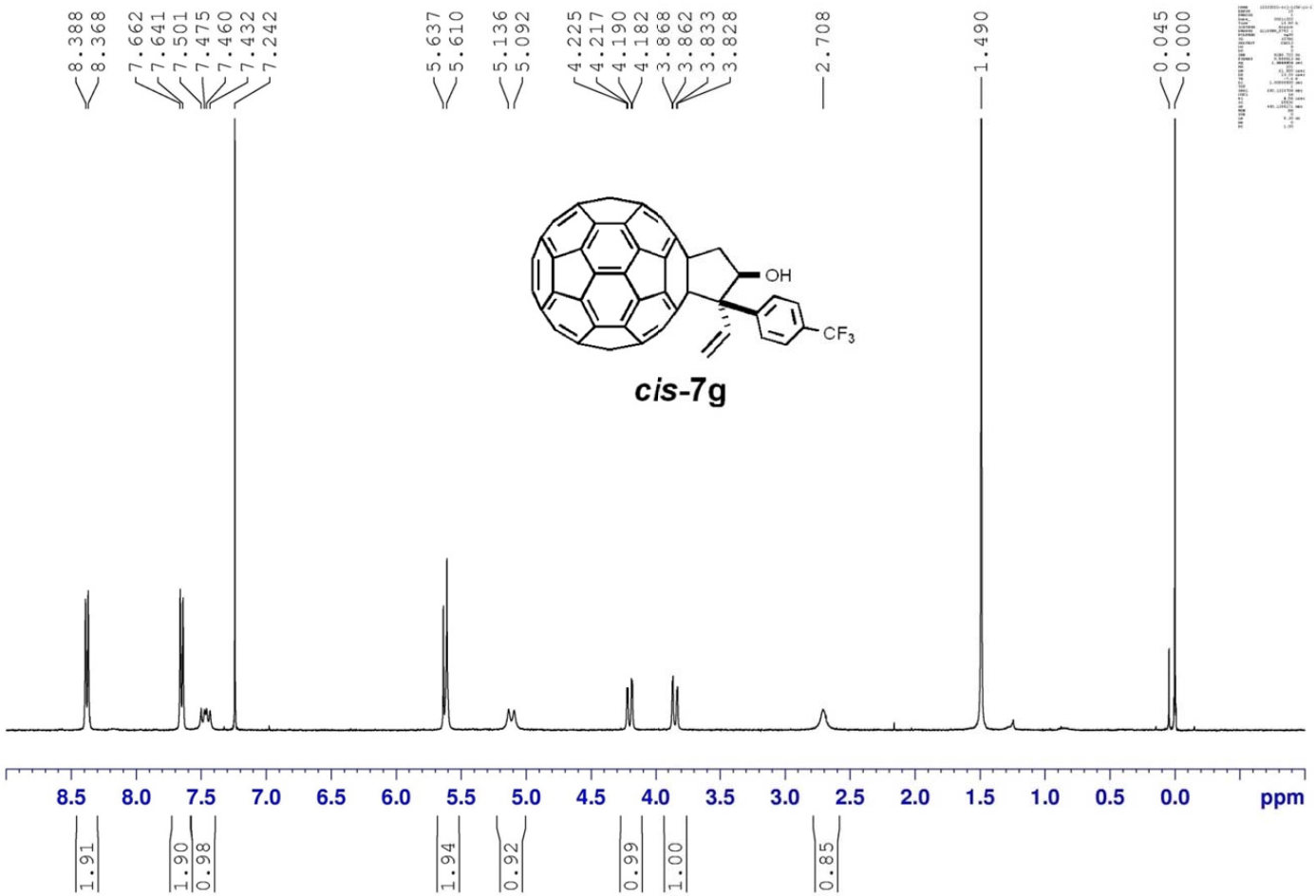


^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 6m



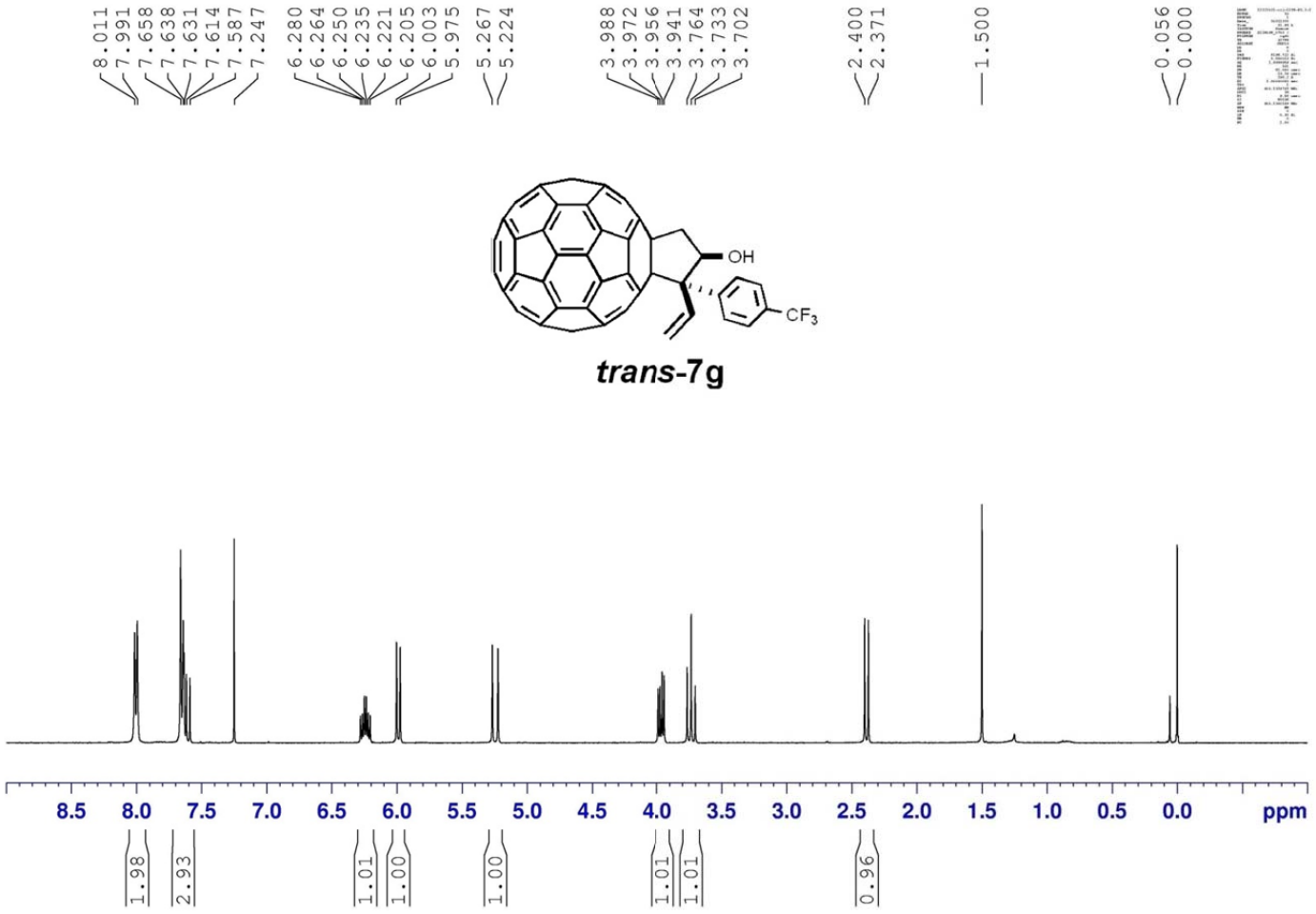
6m

^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound *cis*-7g



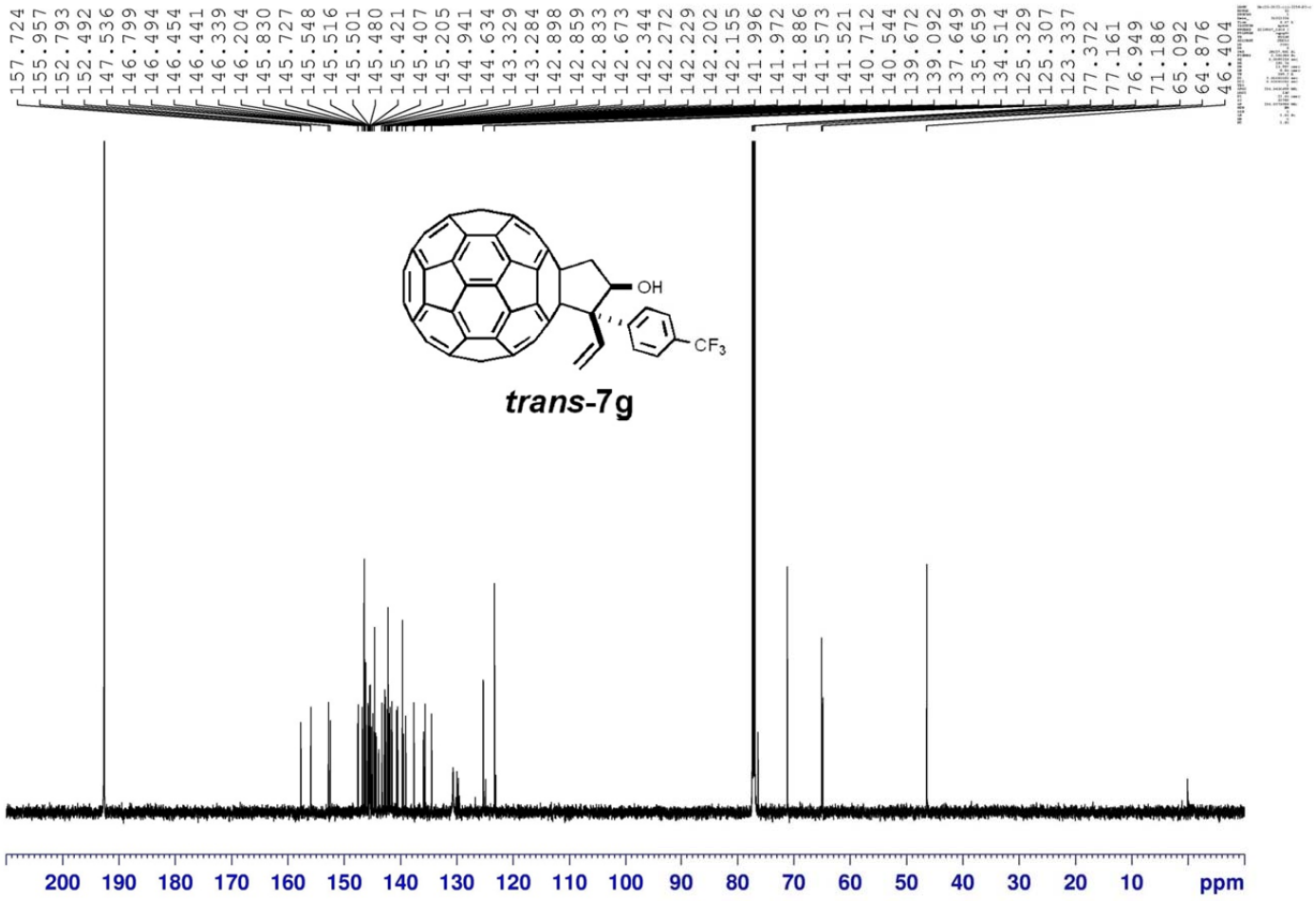
***cis*-7g**

^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound *trans*-7g

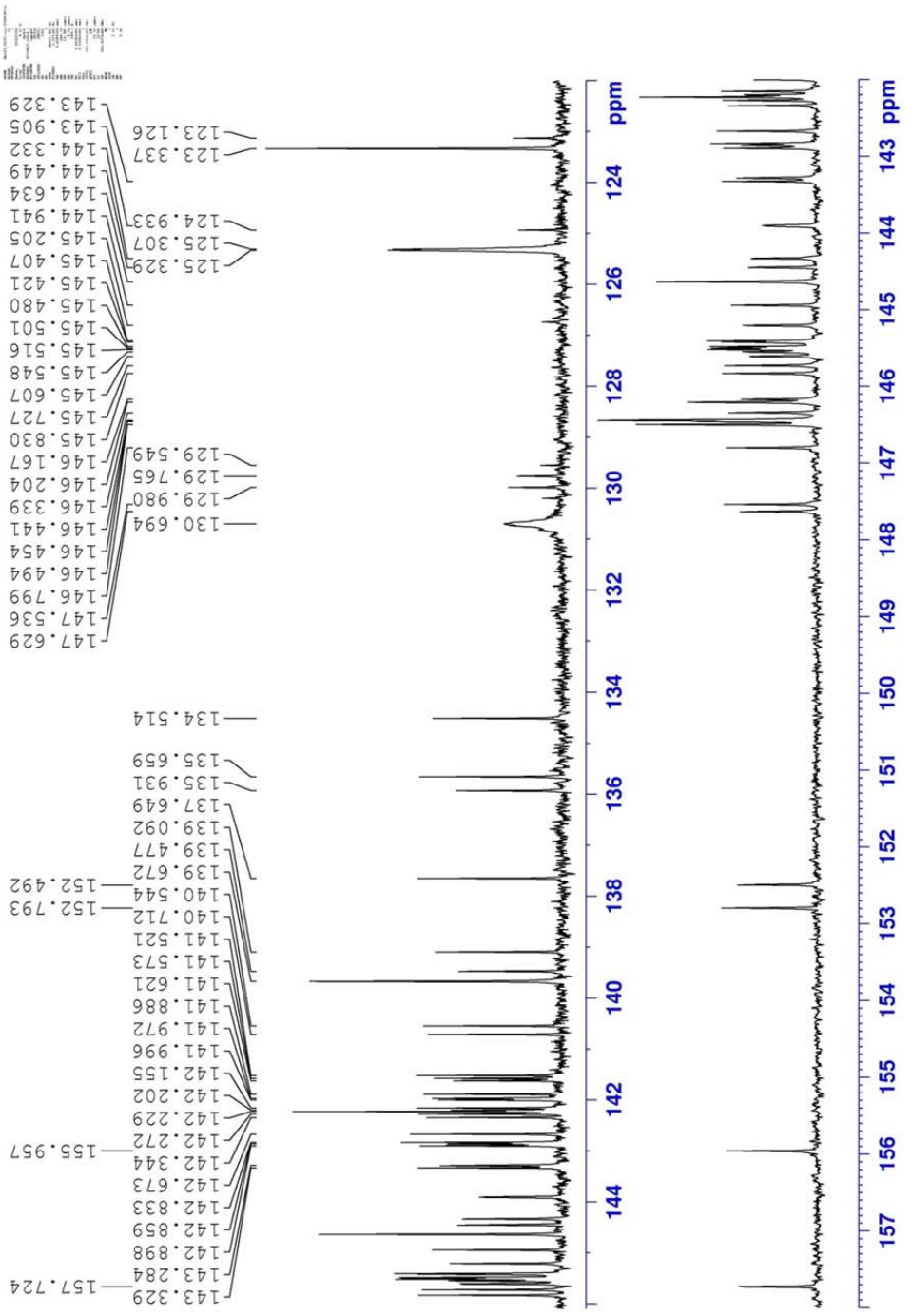


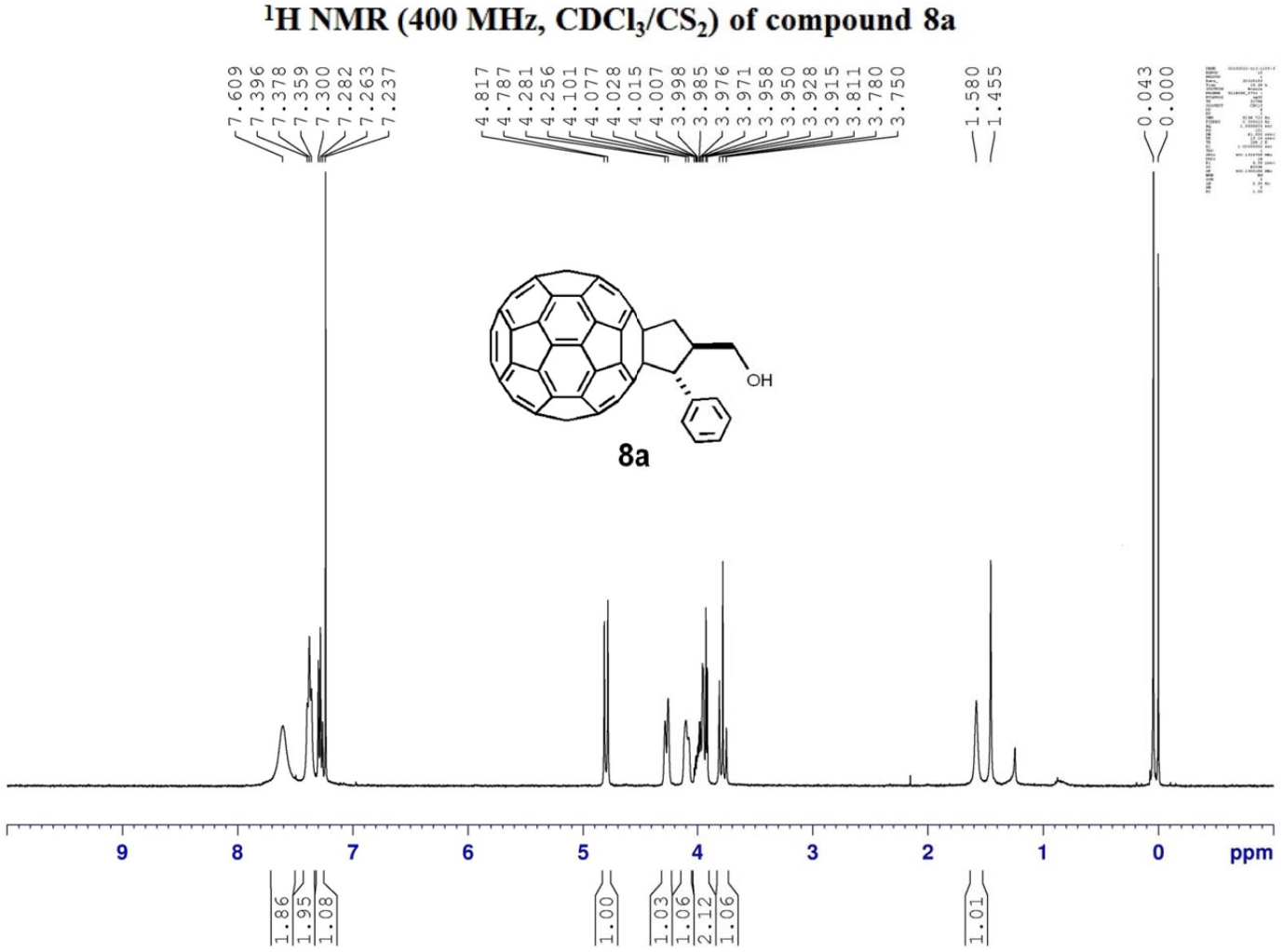
***trans*-7g**

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound *trans*-7g

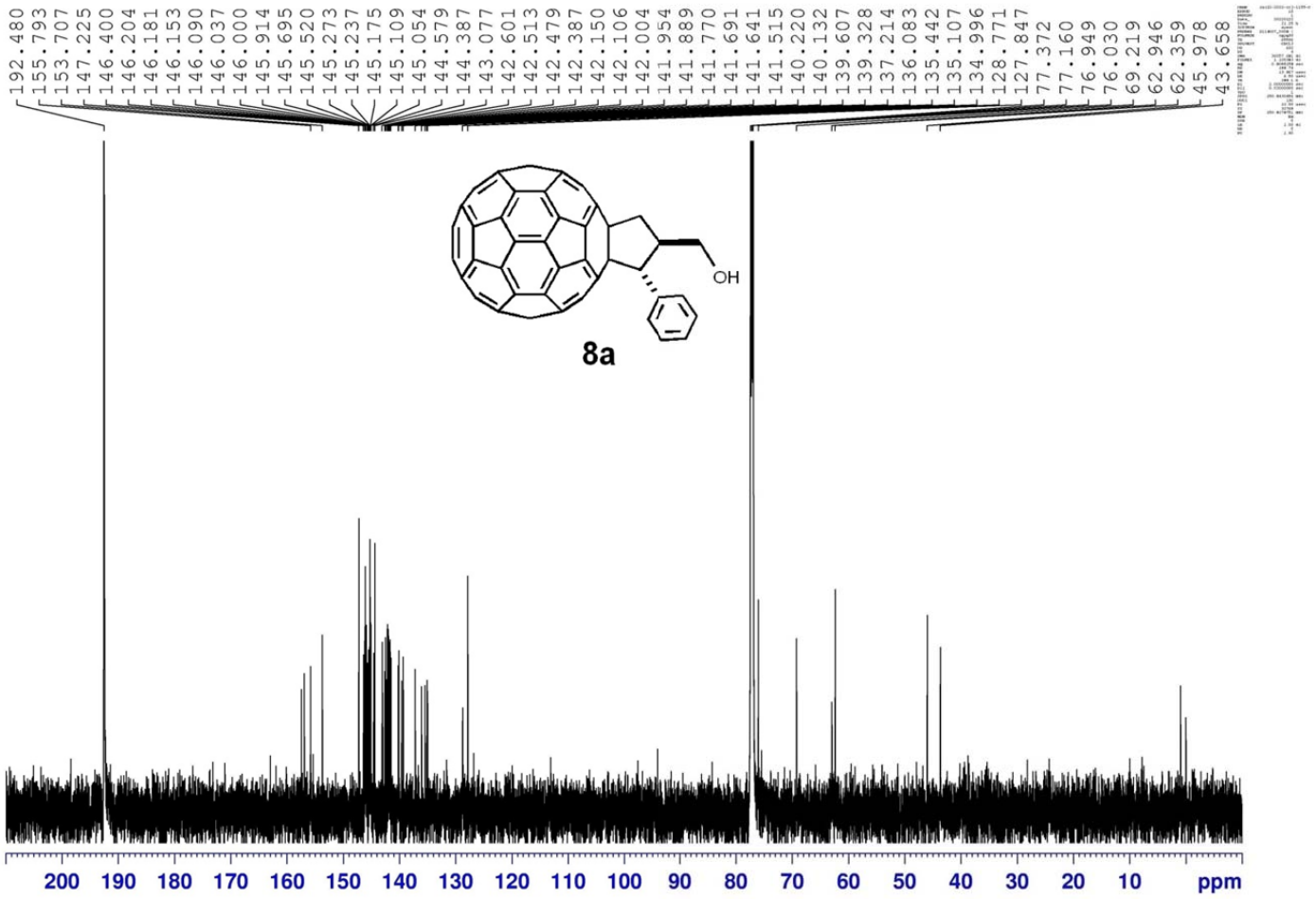


Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound *trans*-7g

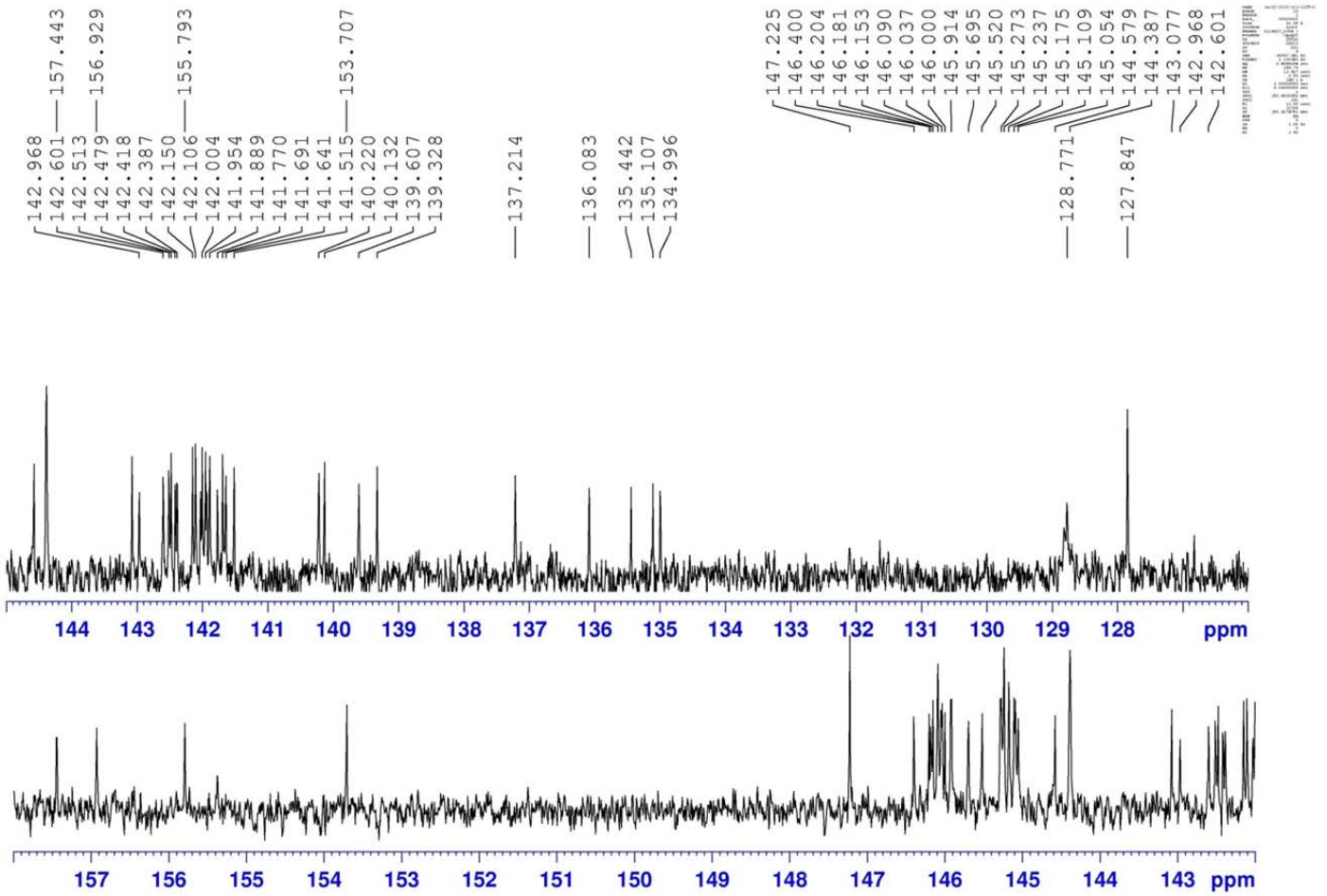



¹H NMR (400 MHz, CDCl₃/CS₂) of compound 8a
7.609
7.396
7.378
7.359
7.300
7.282
7.263
7.237
4.817
4.787
4.281
4.256
4.101
4.077
4.028
4.015
4.007
3.998
3.985
3.976
3.971
3.958
3.950
3.928
3.915
3.811
3.780
3.750
1.580
1.455
0.043
0.000
OH
8a
9
8
7
6
5
4
3
2
1
0
ppm
1.86
1.95
1.08
1.00
1.03
1.06
2.12
1.06
1.01

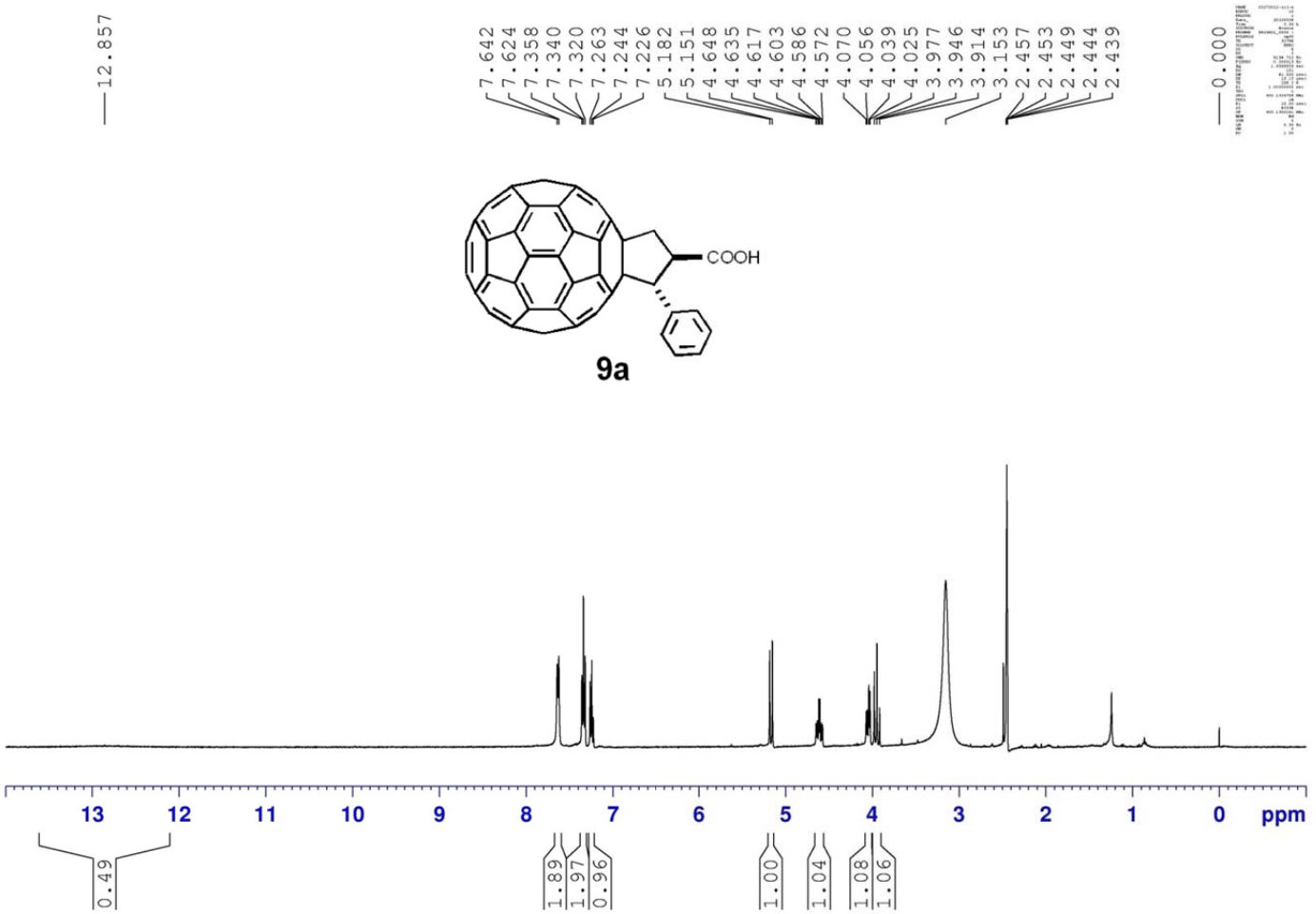
^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 8a



Expanded ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 8a

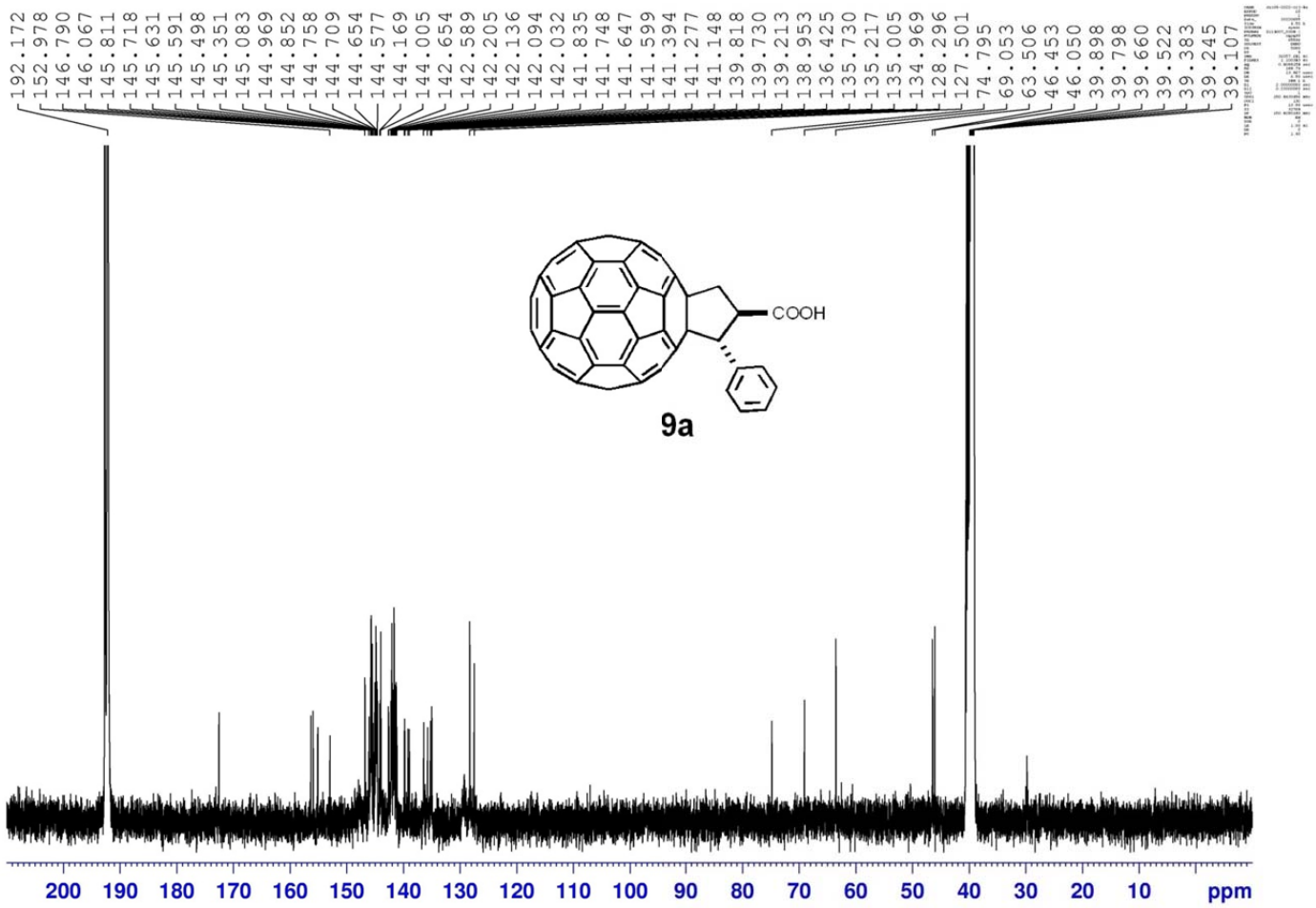


^{1}H NMR (400 MHz, DMSO-d_6/CS_2) of compound 9a



9a

^{13}C NMR (150 MHz, DMSO-d_6/CS_2) of compound 9a



Expanded ^{13}C NMR (150 MHz, DMSO-d_6/CS_2) of compound 9a