Electronic Supplementary Information

Palladium-catalyzed decarboxylative heterocyclizations of [60]fullerene: preparation of novel vinyl-substituted [60]fullerene-fused tetrahydrofurans/pyrans/quinolines

Qingfeng Liu, Tong-Xin Liu,* Yifei Ru, Xue Zhu and Guisheng Zhang*

Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Henan Key Laboratory of Organic Functional Molecule and Drug Innovation, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China.

E-mail: liutongxin_0912@126.com and zgs6668@yahoo.com

Table of Contents

1. General Information S2

2. Experimental Procedures S2-S3

3. DEPT-135 Spectra of Compound **4c** S4

4. UV–vis Spectra of Representative Compounds S5-S15

5. CVs of Selected Compounds S16-S25

6. Spectral Data for Compounds **2**, **4** and **6** S26-S41

7. ^{1}H NMR and ^{13}C NMR Spectra of Compounds **2**, **4** and **6** S42-S83

1. General Information

Reagents were purchased as reagent grade and used without further purification. 1,2-Dichlorobenzene (ODCB) were treated with CaH_2. ^1H NMR (400 and 600 MHz) and ^{13}C NMR (100 and 150 MHz) were registered on Bruker 400 and 600 M spectrometers with tetramethylsilane (TMS) as internal standard. 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. Fluorescence properties of all obtained [60]fullerene adducts in present work were investigated, and no obvious fluorescence phenomenon was detected.

2. Experimental Procedures

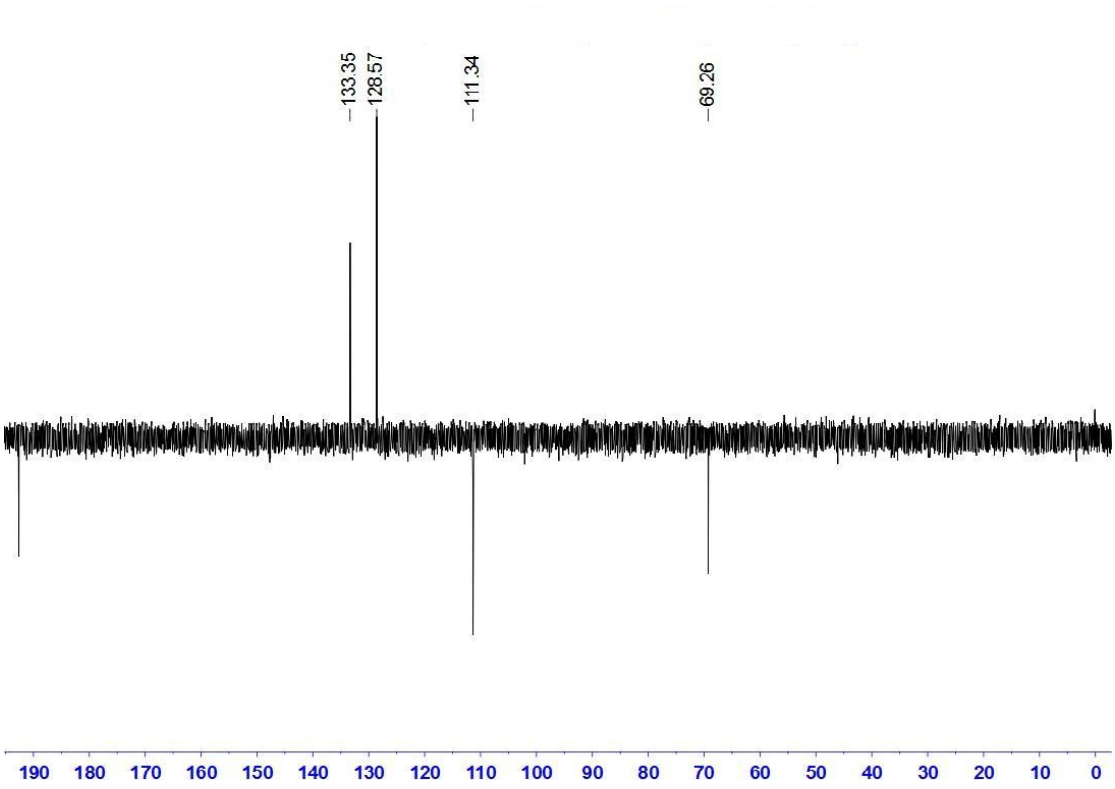
*General Procedure for the Synthesis of Products **2*** and ***4**:* A dry 15-mL tube equipped with a magnetic stirrer was charged with C_{60} (36.0 mg, 0.05 mmol), **1a** (**1b**−**l** and **3a**−**e**, 0.15 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol). After dissolving the solids in anhydrous ODCB (4 mL) by sonication, the sealed tube was stirred in an oil bath preset at a designated temperature for a desired time (monitored by TLC) in air. The reaction mixture was filtered through a silica gel plug to remove any insoluble material. After the solvent had been evaporated under vacuum, the residue was separated on a silica gel column with CS_2 as the eluent to recover unreacted C_{60} and the corresponding product **2a** (**2b**−**l** and **4a**−**e**).

*General Procedure for the Synthesis of Products **6**:* A dry 15-mL tube equipped with a magnetic stirrer was charged with C_{60} (36.0 mg, 0.05 mmol), **5a** (**5b**−**g**, 0.15 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol). After dissolving the solids in a mixture of anhydrous ODCB (4 mL) and CH_3CN (1 mL) by sonication, the sealed tube was stirred in an oil bath preset at a designated temperature for a desired time (monitored

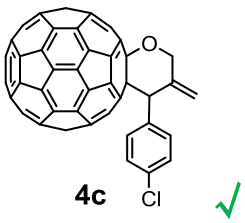
by TLC) under a nitrogen atmosphere. The reaction mixture was filtered through a silica gel plug to remove any insoluble material. After the solvent had been evaporated under vacuum, the residue was separated on a silica gel column with CS_2 as the eluent to recover unreacted C_{60}, and then the eluent was switched to CS_2/DCM to give the corresponding product **6a** (**6b-e**).

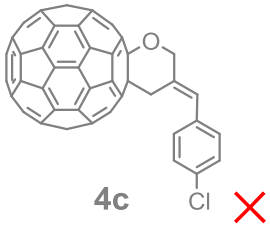
Scale-up Synthetic Experiments: A dry 200-mL tube equipped with a magnetic stirrer was charged with C_{60} (1.0 g, 1.39 mmol), **1a** or **3a** (0.792 g, 4.17 mmol) and $Pd(PPh_3)_4$ (0.161 g, 0.005 mmol). After dissolving the solids in anhydrous ODCB (100 mL) by sonication, the sealed tube was stirred in an oil bath preset (**1a:** 80 ^oC; **3a**: 130 ^oC) for 4 h in air. The reaction mixture was filtered through a silica gel plug to remove any insoluble material. After the solvent had been evaporated under vacuum, the residue was separated on a silica gel column with CS_2 as the eluent to recover unreacted C_{60} (0.420 g for the reaction with **1a**; 0.271 g for the reaction with **1b**) and the corresponding product (**2a**: 0.637 g, 53%; **4a**: 0.736 g, 61%).

3. DEPT-135 Spectra of Compound 4c



DEPT-135 Spectra of 4c (150 MHz, $CDCl_3/CS_2$)





4. UV–vis Spectra of Compounds

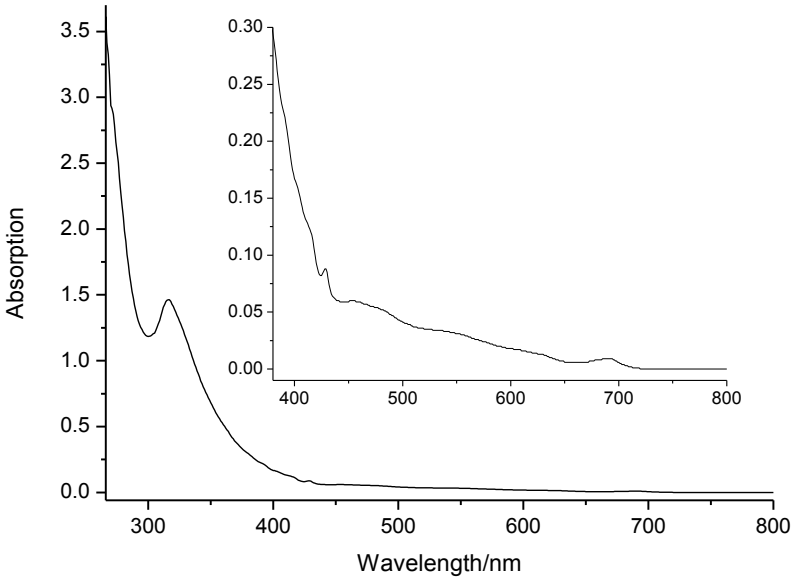


Figure S1. UV–vis spectrum of compound **2a** in $CHCl_3$

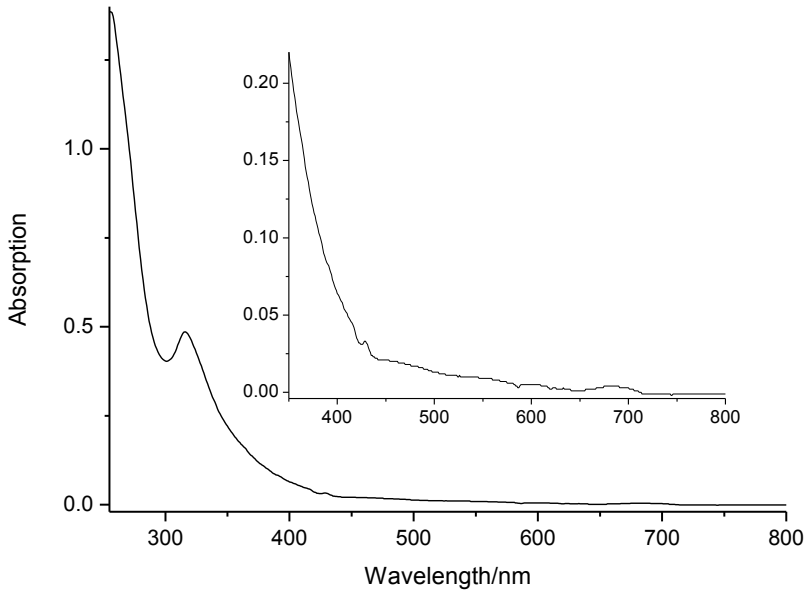


Figure S2. UV–vis spectrum of compound **2b** in $CHCl_3$

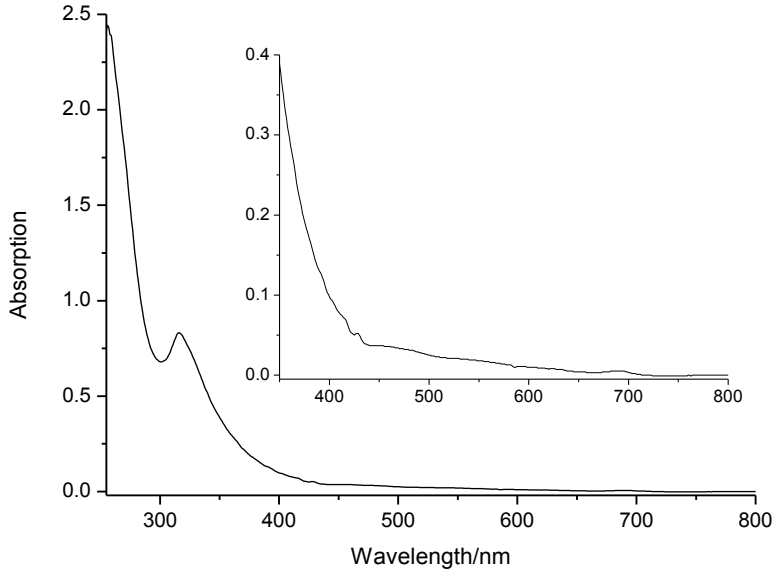


Figure S3. UV–vis spectrum of compound **2c** in $CHCl_3$

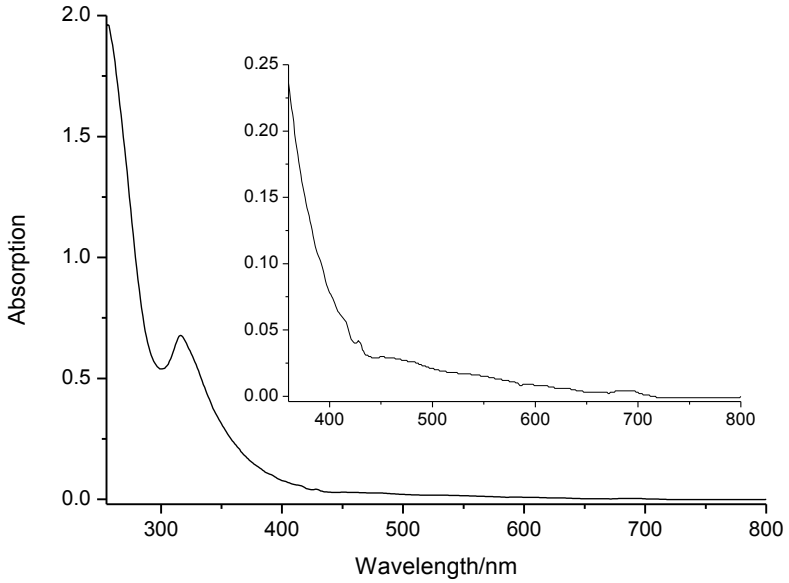


Figure S4. UV–vis spectrum of compound **2d** in $CHCl_3$

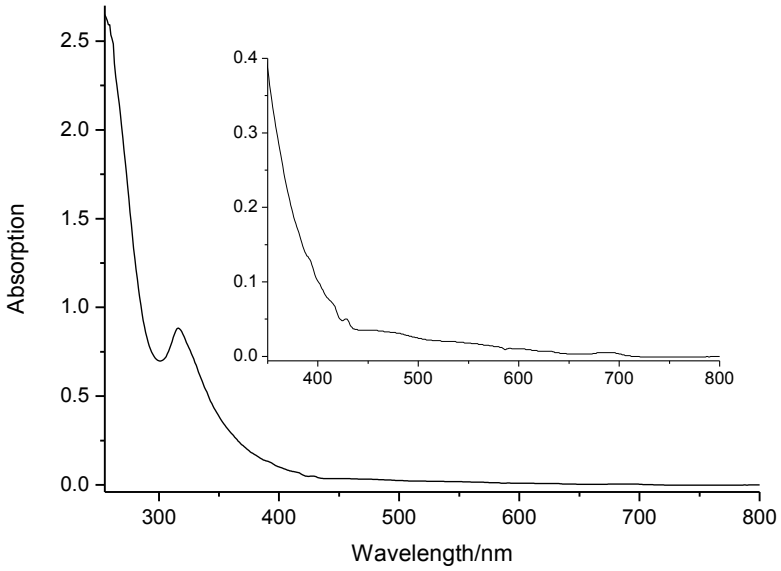


Figure S5. UV–vis spectrum of compound **2e** in $CHCl_3$

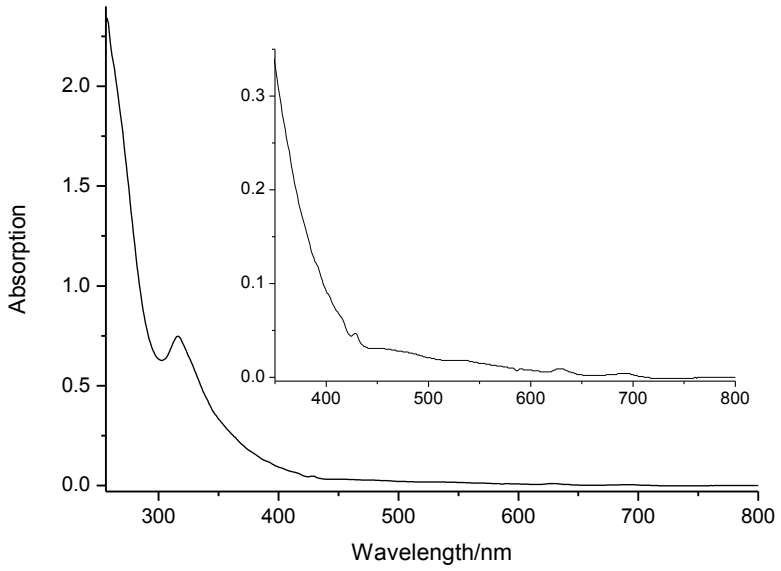


Figure S6. UV–vis spectrum of compound **2f** in $CHCl_3$

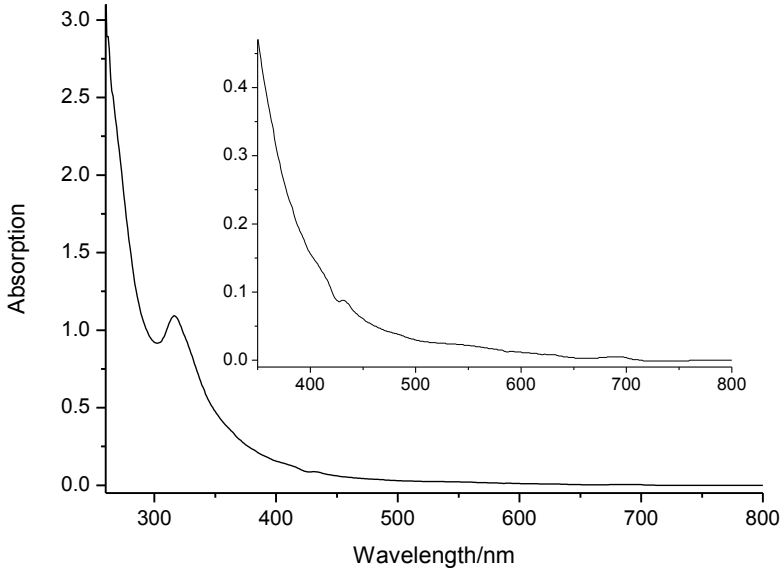


Figure S7. UV–vis spectrum of compound **2g** in $CHCl_3$

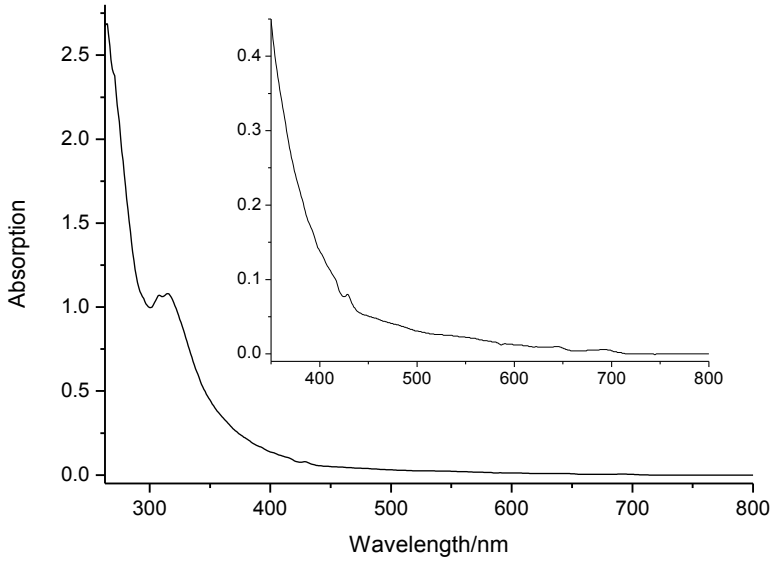


Figure S8. UV–vis spectrum of compound **2h** in $CHCl_3$

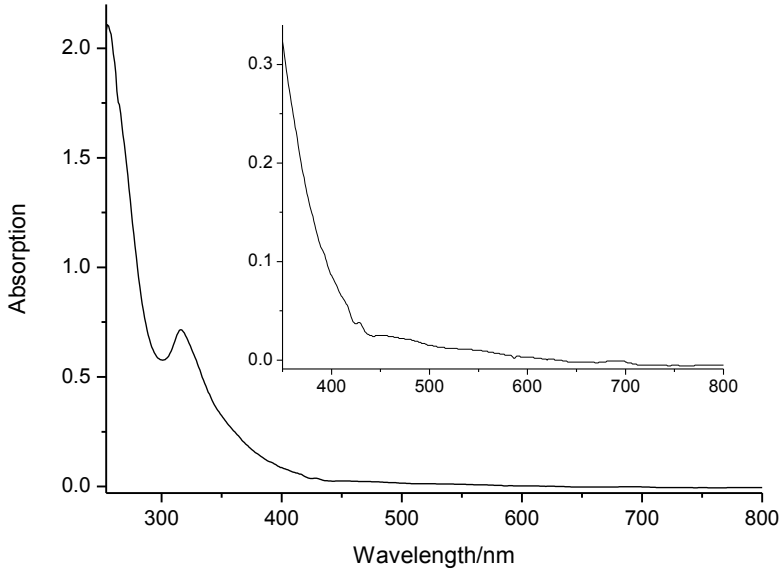


Figure S9. UV–vis spectrum of compound **2i** in $CHCl_3$

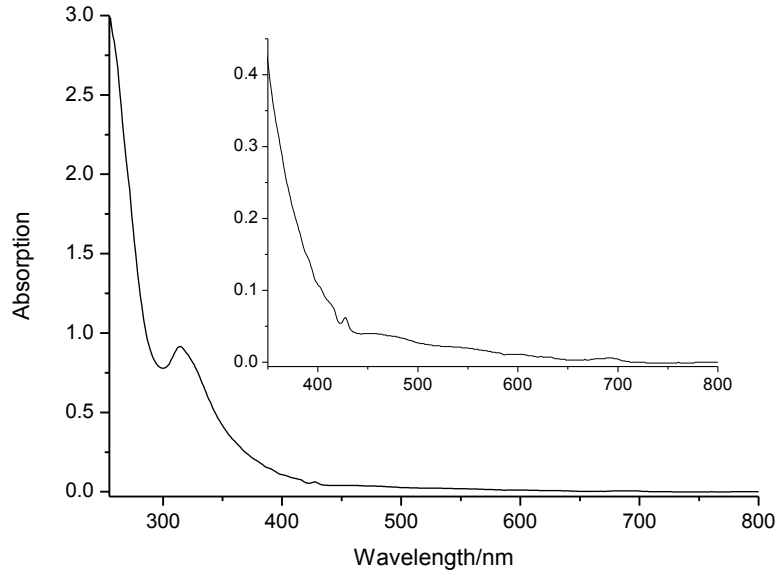


Figure S10. UV–vis spectrum of compound **2j** in $CHCl_3$

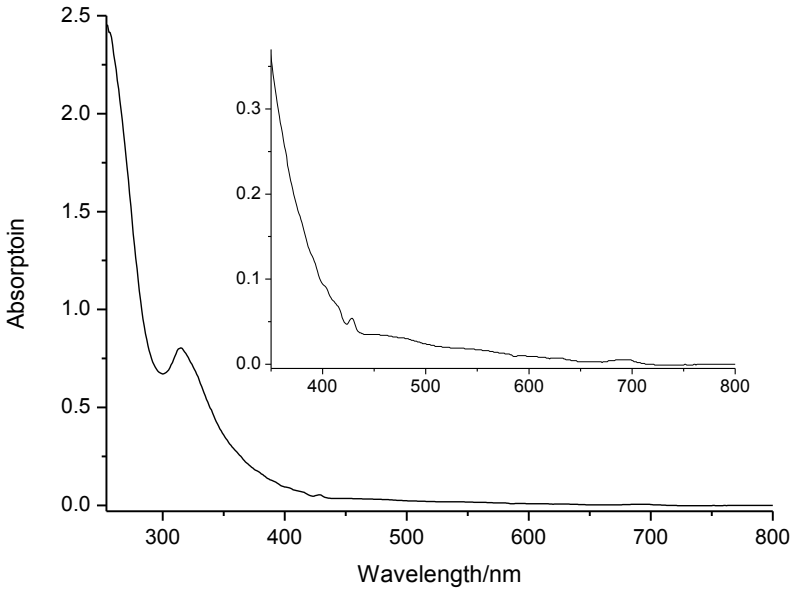


Figure S11. UV–vis spectrum of compound **2k** in $CHCl_3$

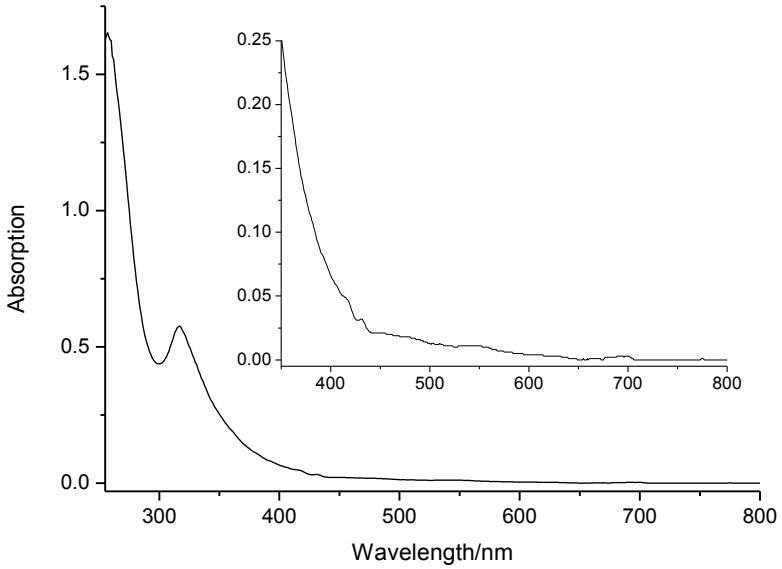


Figure S12. UV–vis spectrum of compound **4a** in $CHCl_3$

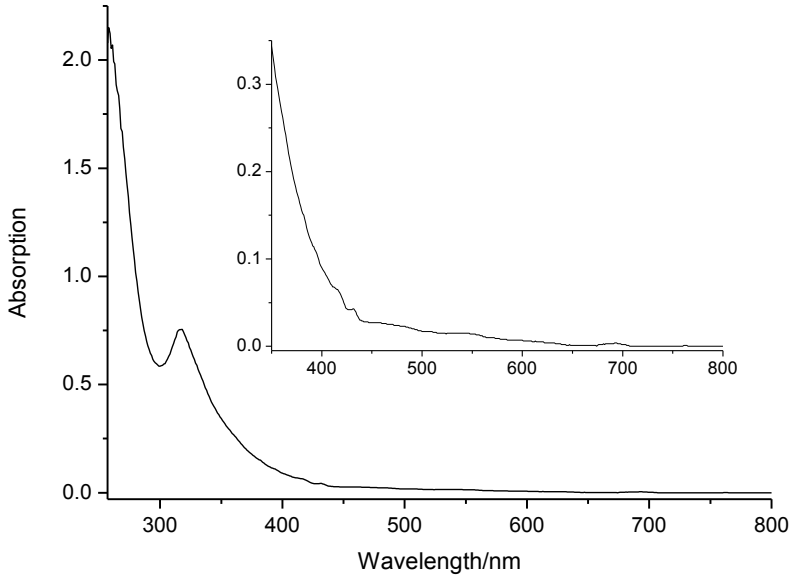


Figure S13. UV–vis spectrum of compound **4b** in $CHCl_3$

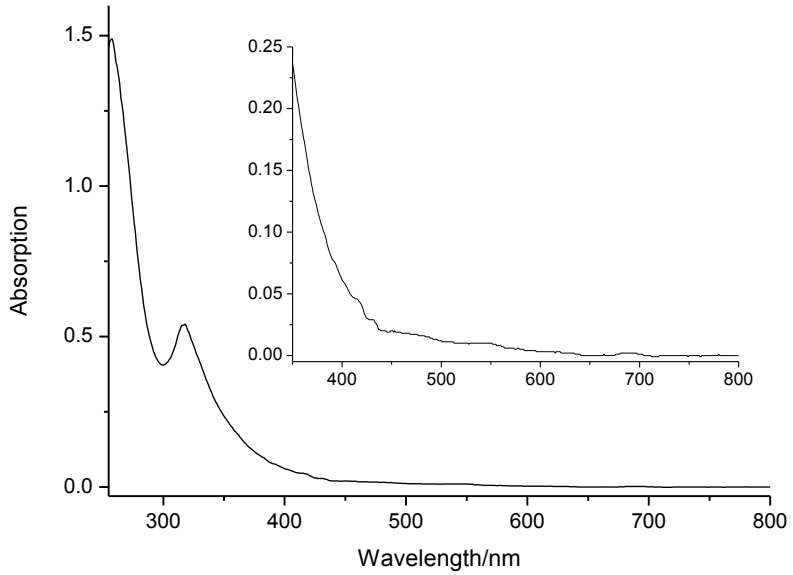


Figure S14. UV–vis spectrum of compound **4c** in $CHCl_3$

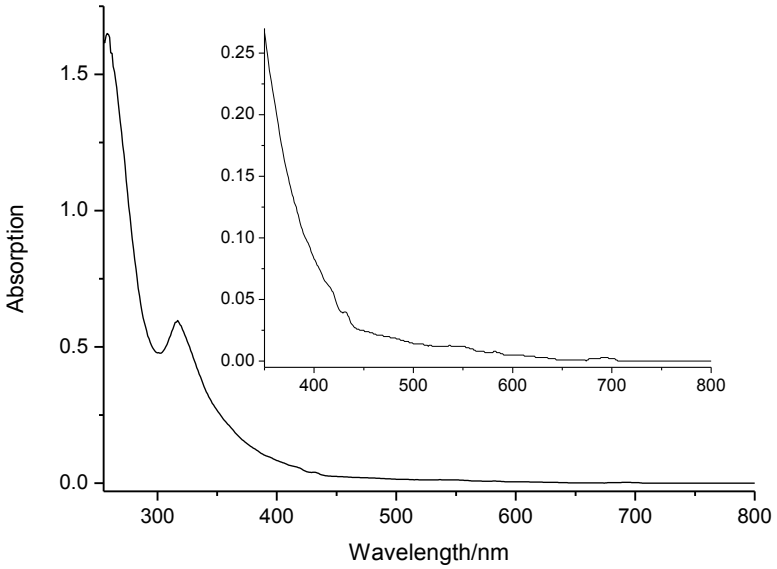


Figure S15. UV–vis spectrum of compound **4d** in $CHCl_3$

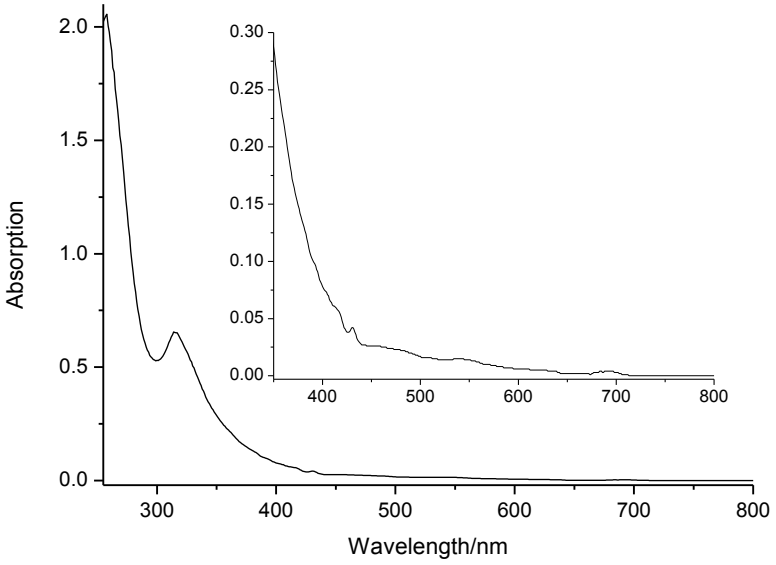


Figure S16. UV–vis spectrum of compound **4e** in $CHCl_3$

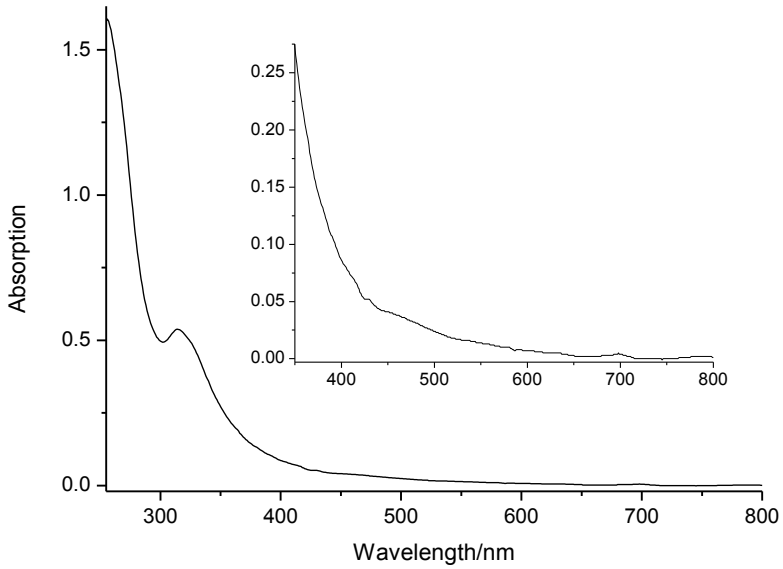


Figure S17. UV–vis spectrum of compound **6a** in $CHCl_3$

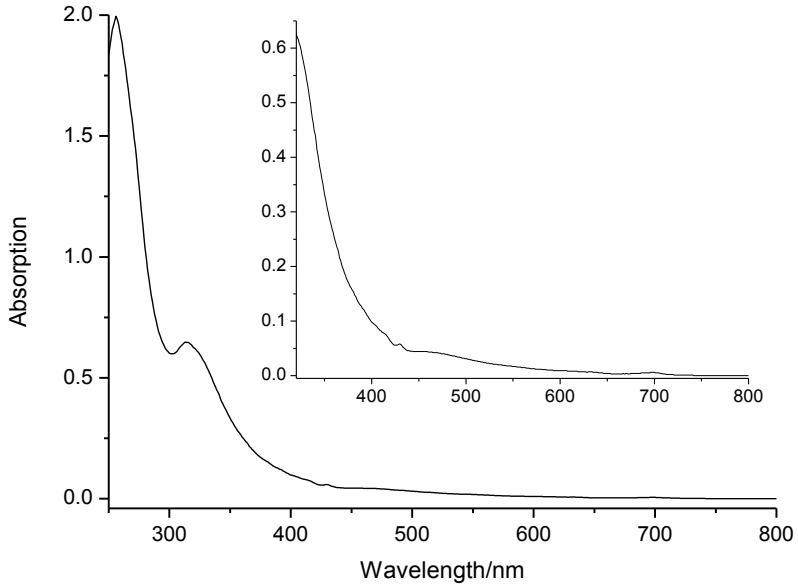


Figure S18. UV–vis spectrum of compound **6b** in $CHCl_3$

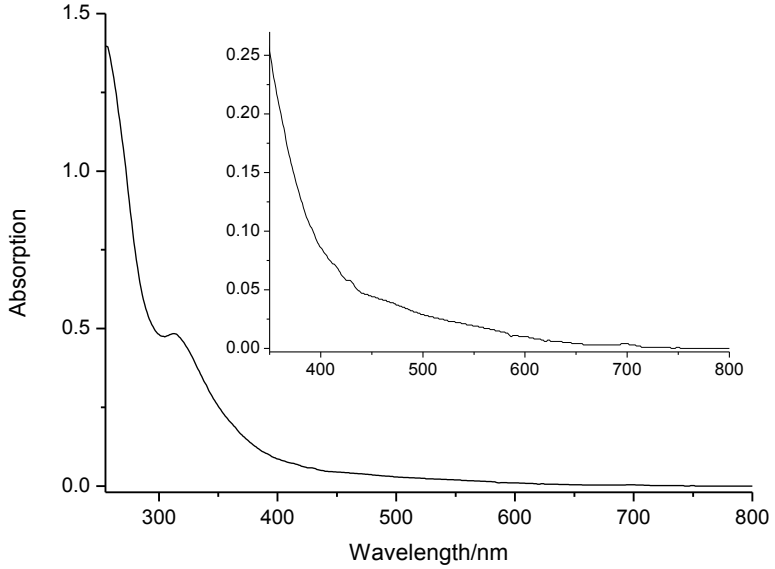


Figure S19 UV–vis spectrum of compound **6c** in $CHCl_3$

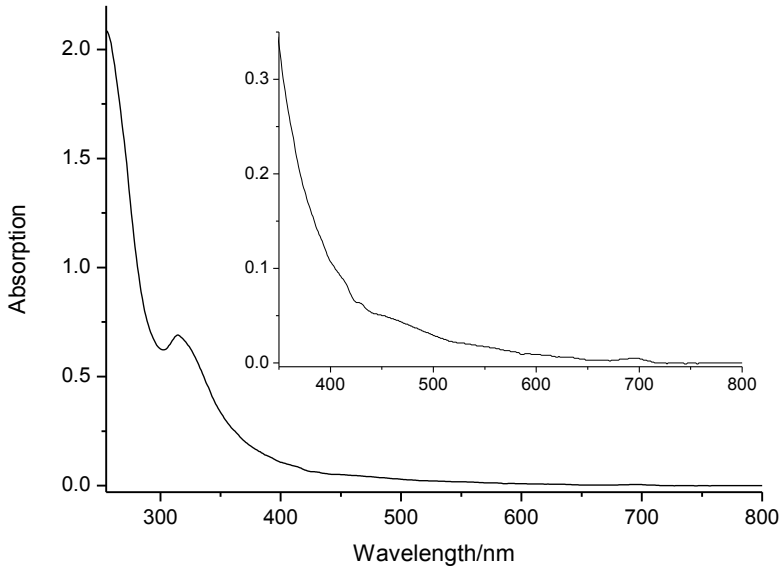


Figure S20. UV–vis spectrum of compound **6d** in $CHCl_3$

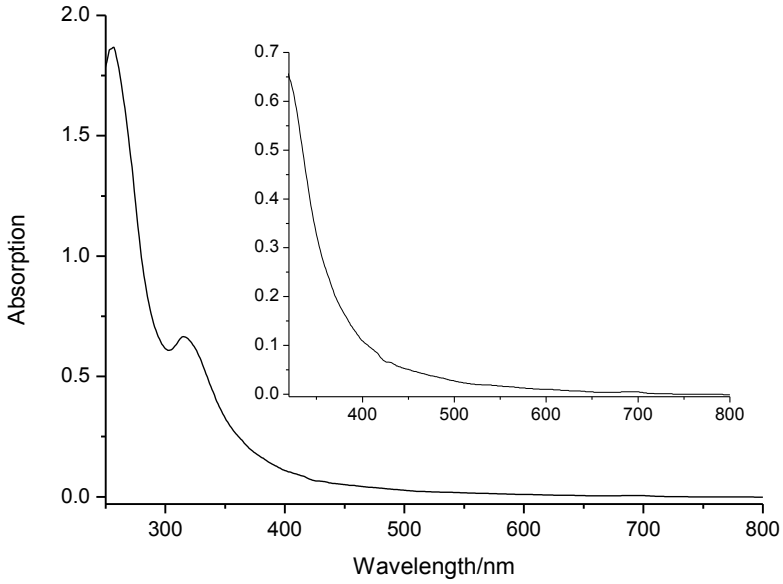


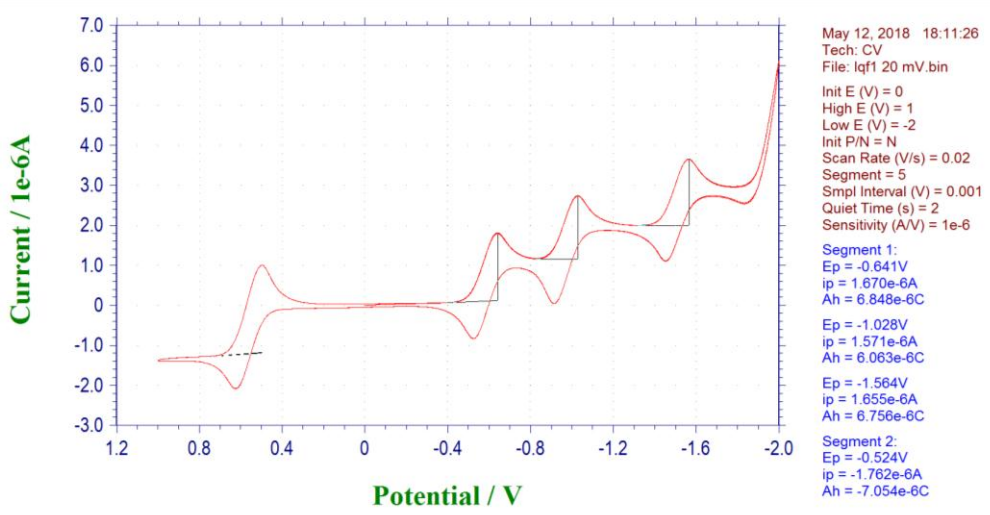
Figure S21. UV–vis spectrum of compound **6e** in $CHCl_3$

5. CVs of Selected Compounds

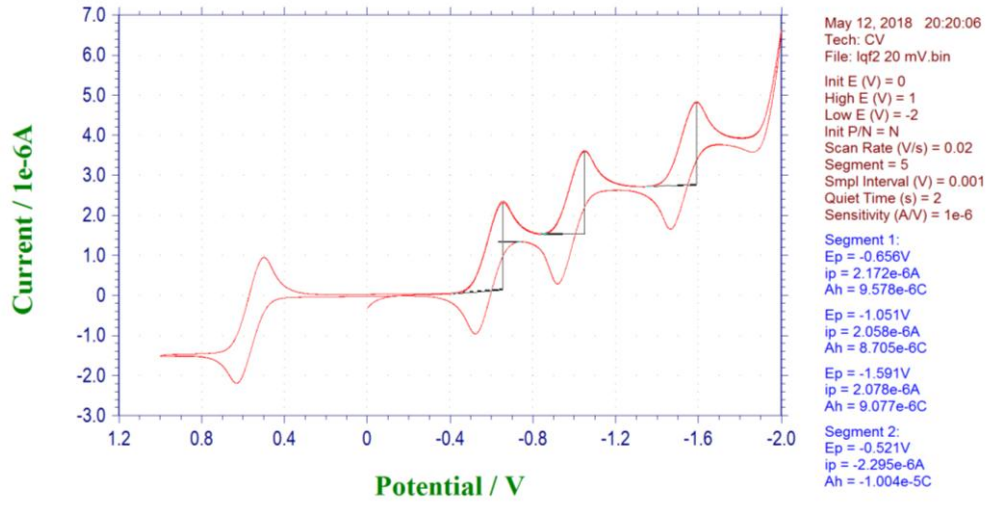
Table 1 Half-wave reduction potentials (V) of selected products, PCBM and C_{60}[a]

Compound	E_1	E_2	E_3	LUMO level[b] (ev)
2a	-1.148	-1.536	-2.071	-3.652
2b	-1.153	-1.548	-2.093	-3.647
2e	-1.142	-1.549	-2.100	-3.658
2f	-1.162	-1.571	-2.128	-3.638
2g	-1.158	-1.549	-2.089	-3.642
2h[c]	-1.173	-1.580	-2.135	-3.627
2i	-1.157	-1.559	-2.114	-3.643
2j	-1.158	-1.560	-2.108	-3.642
2k[d]	-1.173	-1.601	-2.177	-3.627
4a	-1.157	-1.538	-2.062	-3.643
4d	-1.153	-1.536	-2.064	-3.647
4f	-1.146	-1.525	-2.045	-3.654
6a	-1.178	-1.576	-2.115	-3.622
6c	-1.165	-1.551	-2.089	-3.635
6d	-1.163	-1.559	-2.090	-3.637
PCBM	-1.175	-1.576	-2.103	-3.625
C_{60}	-1.075	-1.463	-1.932	-3.725

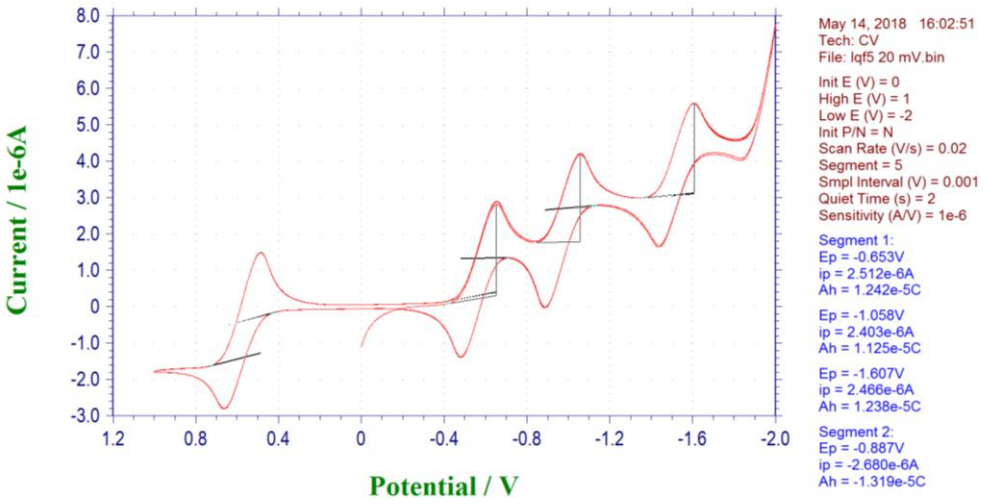
[a]Versus ferrocene/ferrocenium; *experimental conditions*: 1 mM of compound **2**, **4** or **6** and 0.1 M of $(n\text{-Bu})_4NClO_4$ in anhydrous *o*-dichlorobenzene; reference electrode: SCE; working electrode: Pt; auxiliary electrode: Pt wire; scanning rate: 20 mV s^{-1}. [b]Estimated using the following equation: LUMO level = $-(4.8 + E_1)$ eV. [c]Scanning rate: 50 mV s^{-1}. [d]Scanning rate: 10 mV s^{-1}.



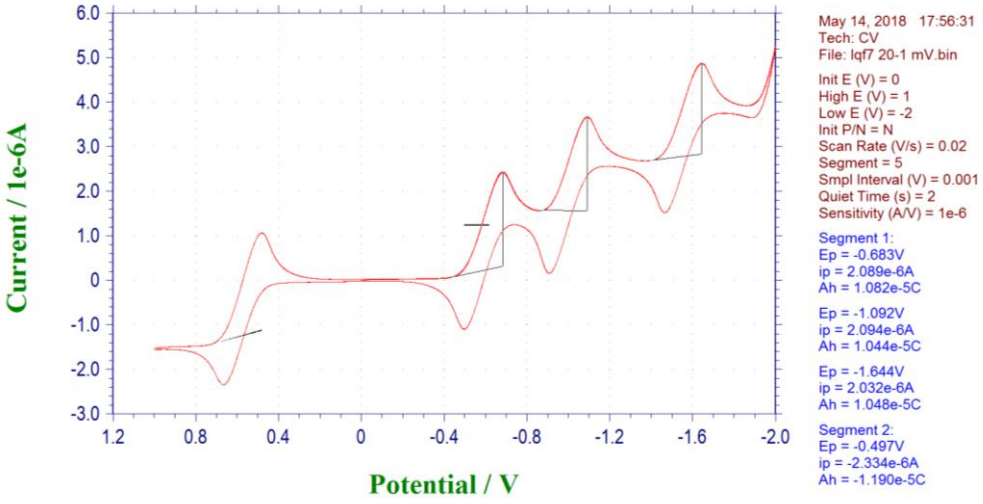
Cyclic voltammogram of compound **2a** (scanning rate: 20 mV s^{-1})



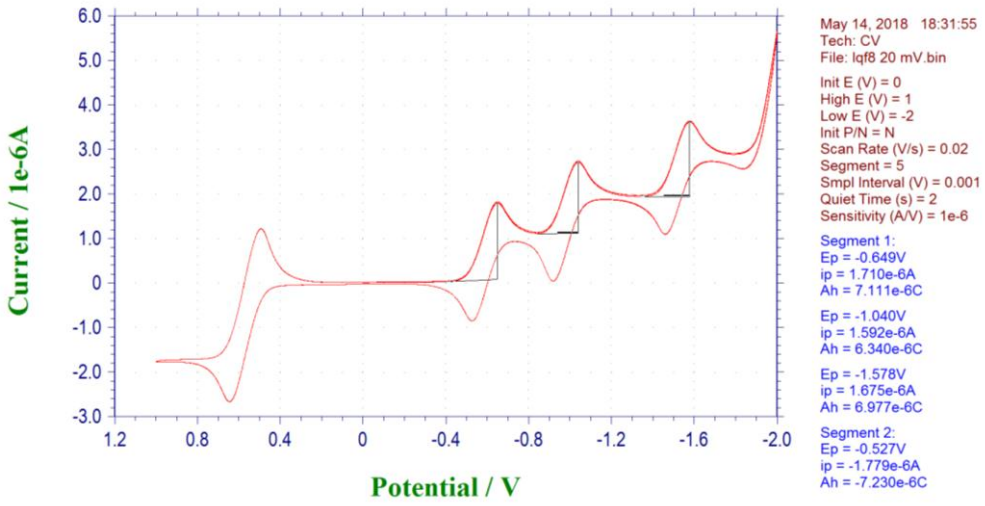
Cyclic voltammogram of compound **2b** (scanning rate: 20 mV s^{-1})



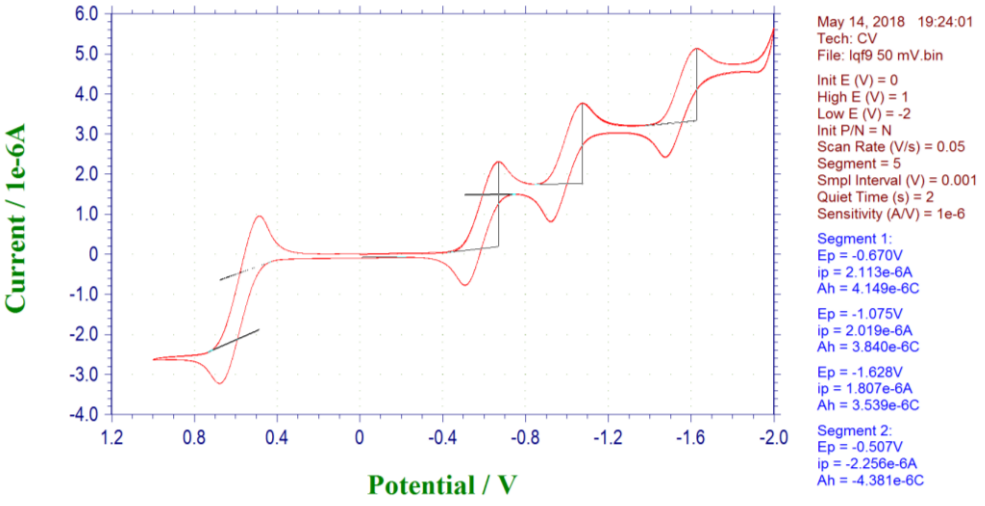
Cyclic voltammogram of compound **2e** (scanning rate: 20 mV s^{-1})



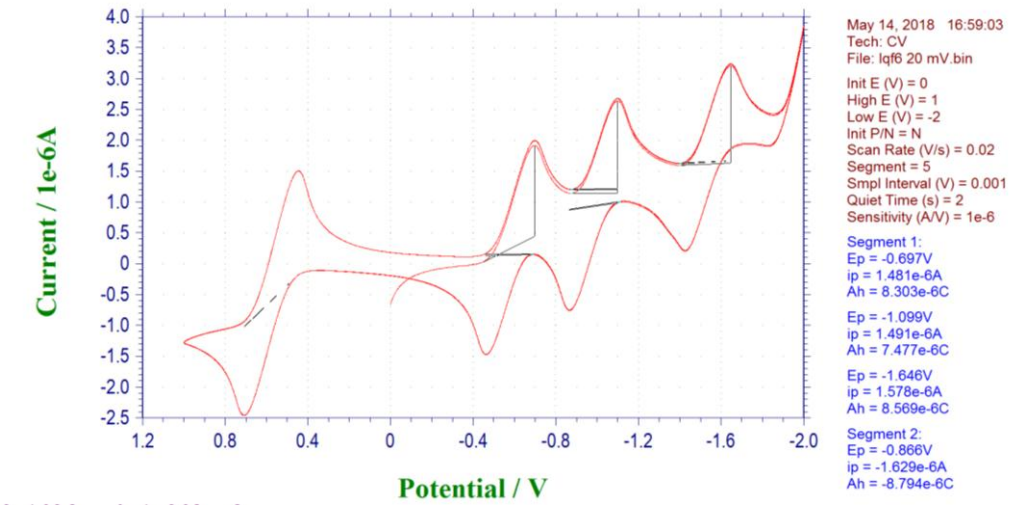
Cyclic voltammogram of compound **2f** (scanning rate: 20 mV s^{-1})



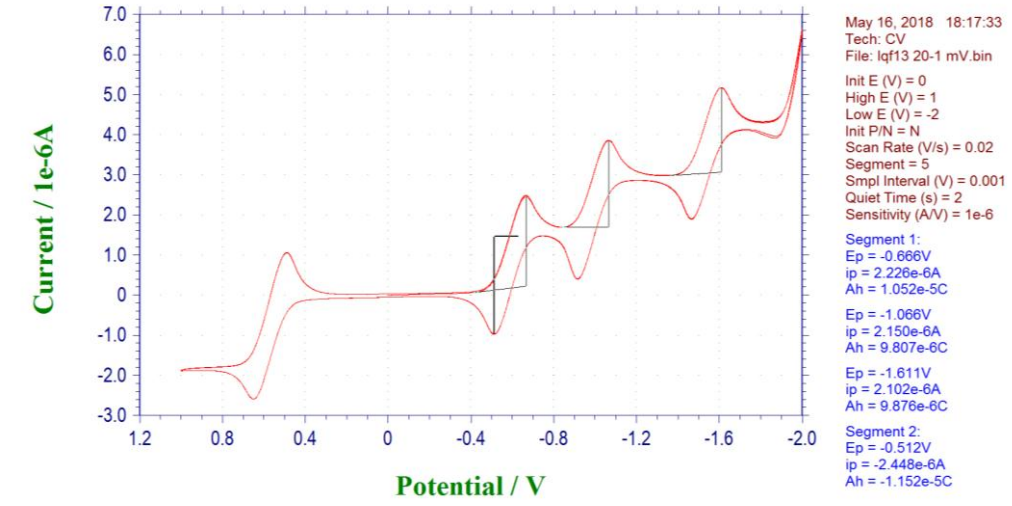
Cyclic voltammogram of compound **2g** (scanning rate: 20 mV s^{-1})



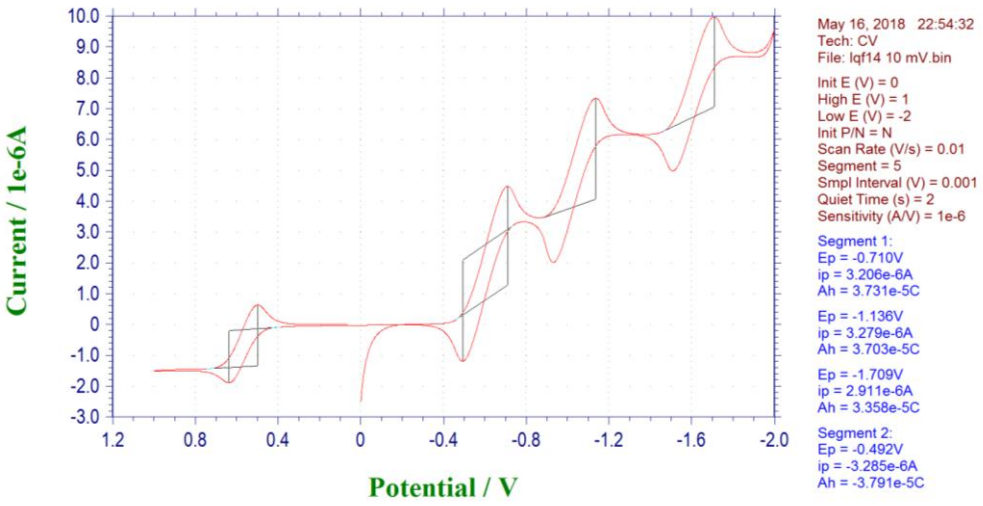
Cyclic voltammogram of compound **2h** (scanning rate: 50 mV s^{-1})



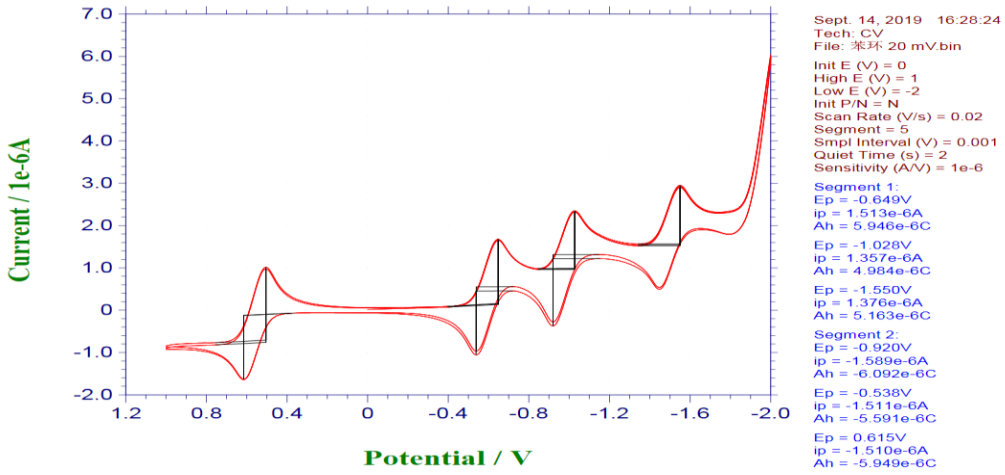
Cyclic voltammogram of compound **2i** (scanning rate: 20 mV s^{-1})



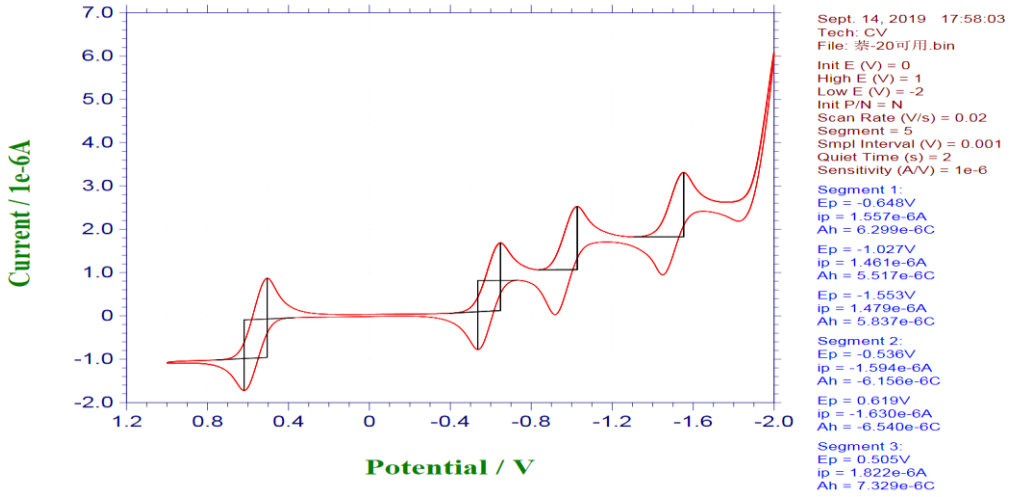
Cyclic voltammogram of compound **2j** (scanning rate: 20 mV s^{-1})



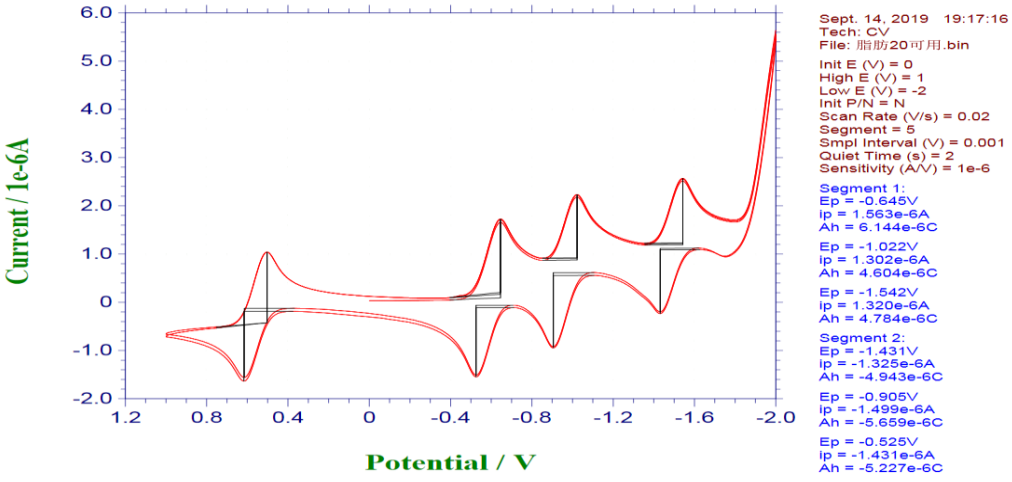
Cyclic voltammogram of compound **2k** (scanning rate: 10 mV s^{-1})



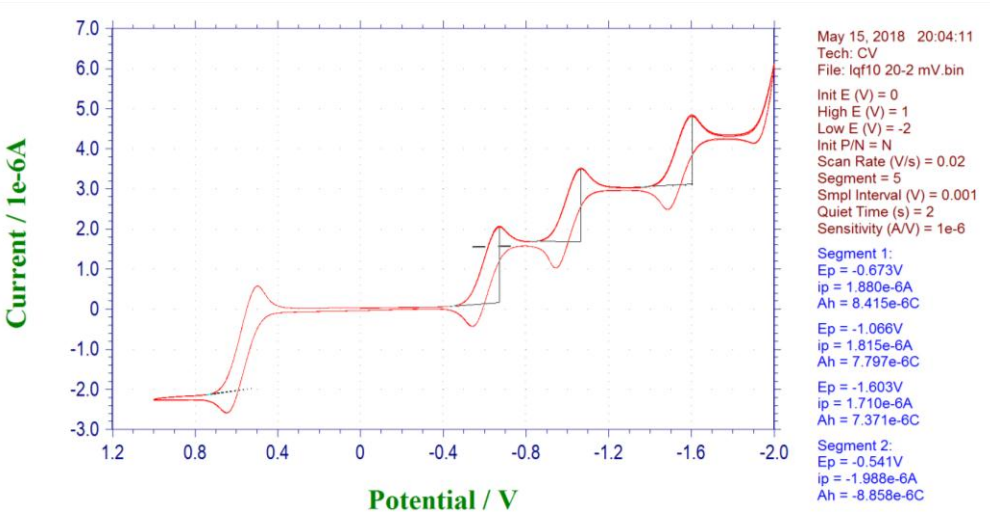
Cyclic voltammogram of compound **4a** (scanning rate: 20 mV s^{-1})



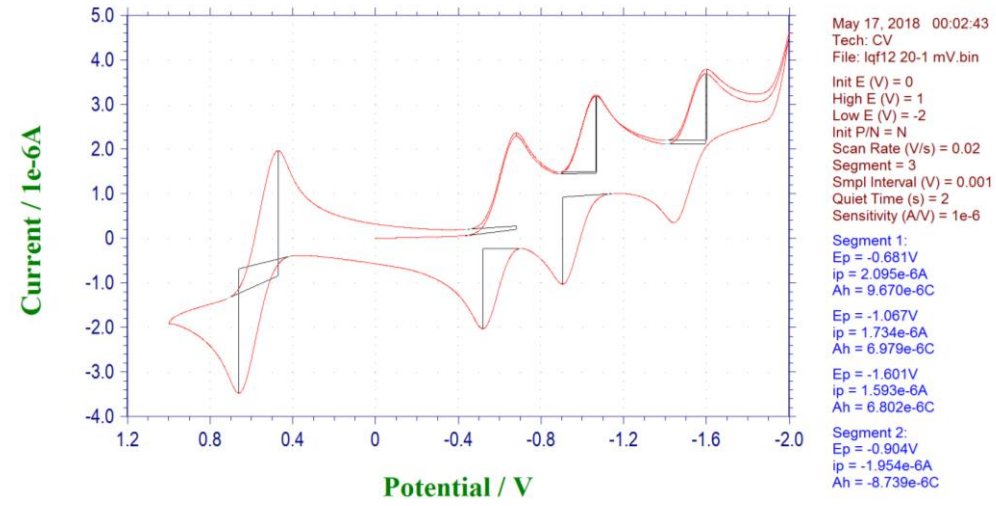
Cyclic voltammogram of compound **4d** (scanning rate: 20 mV s^{-1})



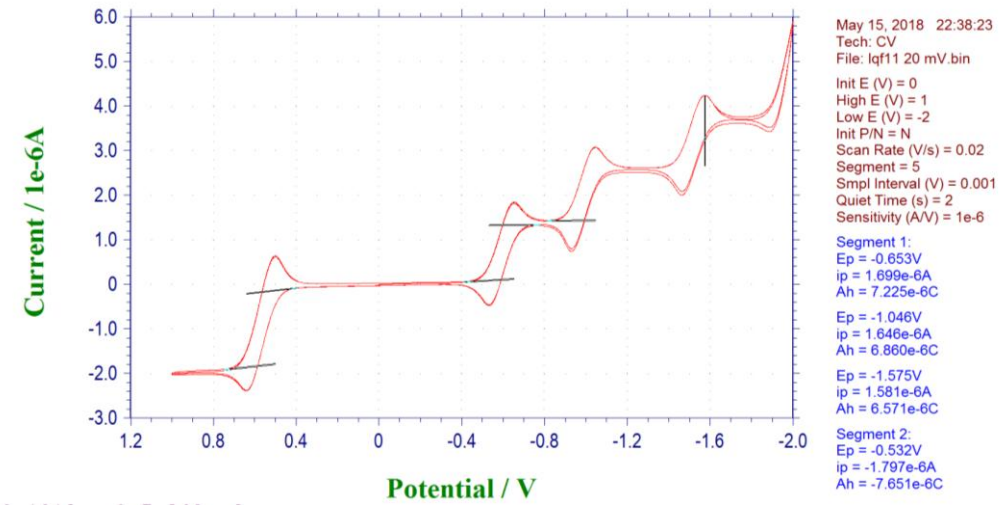
Cyclic voltammogram of compound **4e** (scanning rate: 20 mV s^{-1})



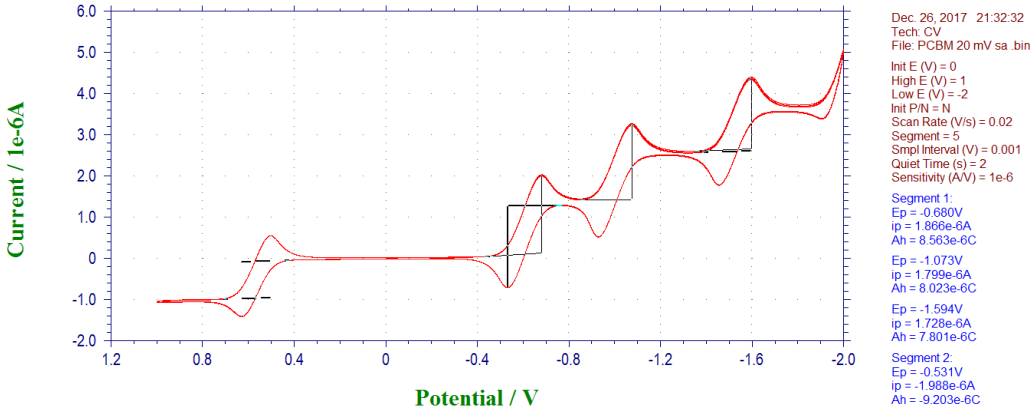
Cyclic voltammogram of compound **6a** (scanning rate: 20 mV s^{-1})



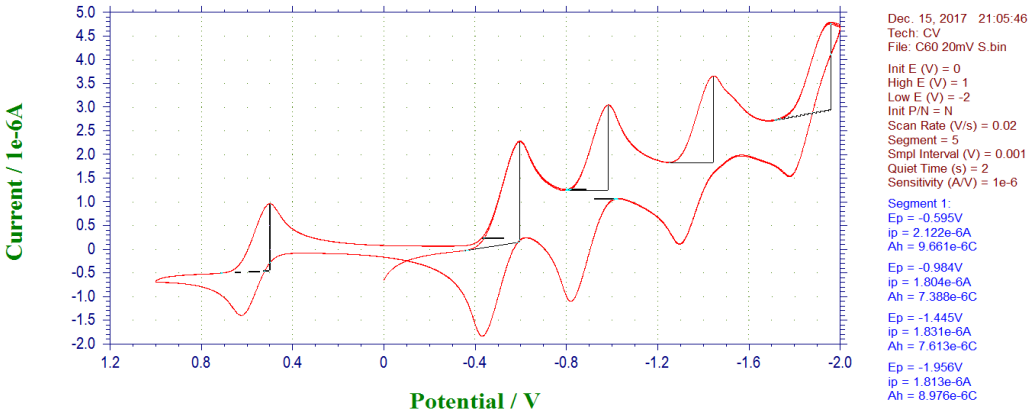
Cyclic voltammogram of compound **6c** (scanning rate: 20 mV s^{-1})



Cyclic voltammogram of compound **6d** (scanning rate: 20 mV s^{-1})

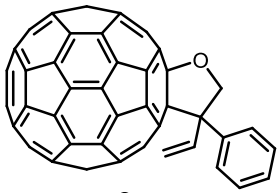


Cyclic voltammogram of compound **PCBM** (scanning rate: 20 mV s^{-1})



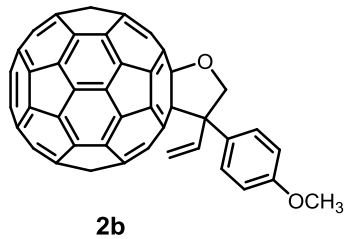
Cyclic voltammogram of compound **C_{60}** (scanning rate: 20 mV s^{-1})

6. Spectral Data for Compounds 2, 4 and 6



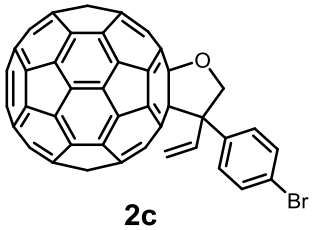
2a

Spectral data of **2a**: 28.6 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.50 (dd, J = 17.2, 10.8 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 5.73 (d, J = 8.8 Hz, 1H), 5.60 (d, J = 10.8 Hz, 1H), 5.42 (d, J = 17.2 Hz, 1H), 5.19 (d, J = 8.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.31, 153.26, 150.12, 149.08, 148.19, 147.64, 146.66, 146.60, 146.45, 146.44, 146.36, 146.27, 146.23, 146.20, 146.18, 146.12, 146.08, 145.89, 145.56, 145.50, 145.39, 145.32, 145.31, 145.28, 145.26, 144.85, 144.83, 144.76, 144.65, 144.62, 143.08, 143.00, 142.90, 142.89, 142.85, 142.56, 142.52, 142.50, 142.42, 142.36, 142.34, 142.21, 142.07, 141.83, 141.63, 141.61, 140.25, 140.00, 139.96, 139.64, 139.21, 138.84, 137.85, 137.78, 136.56, 128.86, 128.80, 127.95, 117.02, 99.82, 74.03, 64.22; FT-IR ν/cm^{-1} (KBr) 2850, 1511, 1434, 1187, 1105, 1046, 996, 953, 923, 752, 699, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 249 (5.19), 316 (4.80), 429 (3.58), 451 (3.40), 691 (2.57); MALDI-TOF MS *m/z* calcd for $C_{70}H_{10}O$ $[M]^-$ 866.0737, found 866.0712.



2b

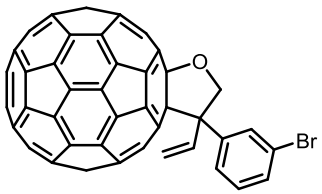
Spectral data of **2b**: 26.8 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.8 Hz, 2H), 7.50 (dd, J = 16.8, 10.8 Hz, 1H), 6.97 (d, J = 8.4 Hz, 2H), 5.68 (d, J = 9.0 Hz, 1H), 5.58 (d, J = 10.8 Hz, 1H), 5.41 (d, J = 16.8 Hz, 1H), 5.15 (d, J = 9.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.93, 153.55, 153.39, 150.21, 149.06, 148.19, 147.63, 146.65, 146.60, 146.45, 146.41, 146.34, 146.27, 146.21, 146.19, 146.12, 146.07, 145.92, 145.57, 145.48, 145.40, 145.38, 145.31, 145.26, 145.25, 144.85, 144.81, 144.75, 144.65, 143.07, 143.00, 142.89, 142.87, 142.84, 142.61, 142.56, 142.51, 142.49, 142.43, 142.41, 142.37, 142.34, 142.27, 142.07, 141.82, 141.65, 141.61, 139.99, 139.92, 139.65, 139.31, 138.86, 137.91, 137.69, 136.51, 132.23, 129.98, 116.76, 114.08, 99.77, 74.20, 63.82, 55.38; FT-IR ν/cm^{-1} (KBr) 2921, 2850, 1608, 1511, 1456, 1434, 1297, 1250, 1184, 1104, 1033, 995, 953, 924, 813, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.03), 316 (4.57), 591 (2.60), 680 (2.46); MALDI-TOF MS m/z calcd for $C_{71}H_{12}O_2$ $[M]^-$ 896.0843, found 896.0824.



2c

Spectral data of **2c**: 34.4 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.45 (dd, J = 17.4, 10.8 Hz, 1H), 5.63 (d, J = 9.6 Hz, 1H), 5.61 (d, J = 10.8 Hz, 1H), 5.38 (d, J = 17.4 Hz, 1H), 5.17 (d, J = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) δ 152.79, 152.75, 149.68, 148.96, 148.10, 147.56, 146.56, 146.52, 146.36, 146.35, 146.28, 146.20,

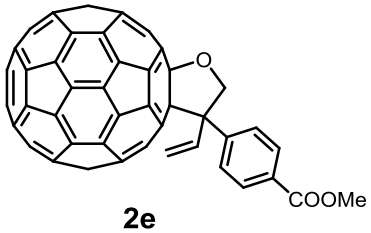
146.14, 146.08, 146.01, 145.84, 145.72, 145.61, 145.41, 145.36, 145.31, 145.29, 145.27, 145.24, 145.20, 144.76, 144.72, 144.62, 144.59, 144.52, 143.00, 142.93, 142.84, 142.82, 142.79, 142.78, 142.46, 142.42, 142.37, 142.35, 142.33, 142.29, 142.20, 142.10, 141.92, 141.76, 141.57, 139.96, 139.92, 139.61, 139.46, 139.36, 138.53, 137.75, 137.68, 136.68, 131.86, 130.48, 122.25, 117.21, 99.67, 76.83, 73.87, 63.77; FT-IR ν/cm^{-1} (KBr) 2919, 2850, 1487, 1455, 1431, 1181, 1102, 1079, 1049, 1008, 995, 952, 923, 796, 746, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.18), 316 (4.71), 590 (2.82), 689 (2.48); MALDI-TOF MS *m/z* calcd for $C_{70}H_9BrO$ $[M]^-$ 943.9842, found 943.9822.



2d

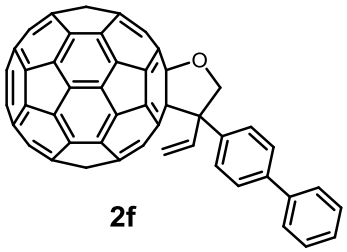
Spectral data of **2d**: 31.6 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.49−7.42 (m, 2H), 7.33 (t, J = 7.8 Hz, 1H), 5.63 (d, J = 9.6 Hz, 2H), 5.41 (d, J = 17.4 Hz, 1H), 5.18 (d, J = 9.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) δ 152.72, 149.69, 148.97, 148.15, 147.62, 146.61, 146.56, 146.41, 146.39, 146.34, 146.24, 146.18, 146.12, 146.06, 145.86, 145.73, 145.65, 145.46, 145.41, 145.35, 145.34, 145.31, 145.29, 145.24, 144.81, 144.77, 144.67, 144.63, 144.56, 143.04, 142.96, 142.86, 142.83, 142.82, 142.50, 142.47, 142.42, 142.39, 142.37, 142.34, 142.23, 142.12, 141.95, 141.80, 141.65, 141.62, 140.00, 139.96, 139.65, 139.32, 138.59, 137.81, 137.73, 136.74, 131.67, 131.05, 130.19, 127.70, 123.12, 117.40, 99.73, 76.90, 73.80, 63.79; FT-IR ν/cm^{-1}

(KBr) 2919, 2850, 1559, 1473, 1419, 1167, 1102, 1049, 995, 952, 926, 902, 779, 722, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.12), 316 (4.66), 590 (2.78), 688 (2.43); MALDI-TOF MS *m/z* calcd for $C_{71}H_{12}O_2$ $[M]^-$ 943.9842, found 943.9827.



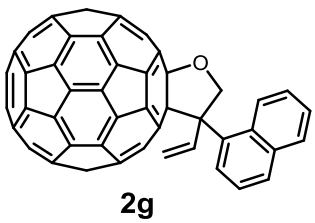
2e

Spectral data of **2e**: 30.5 mg, amorphous brown solid; mp >300 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, J = 7.8 Hz, 2H), 8.96 (d, J = 7.8 Hz, 2H), 7.49 (dd, J = 16.8, 10.8 Hz, 1H), 5.70 (d, J = 9.6 Hz, 1H), 5.62 (d, J = 10.8 Hz, 1H), 5.39 (d, J = 16.8 Hz, 1H), 5.22 (d, J = 9.0 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.85, 152.74, 149.68, 149.01, 148.20, 147.66, 146.65, 146.60, 146.46, 146.43, 146.36, 146.28, 146.23, 146.22, 146.15, 146.10, 145.96, 145.78, 145.68, 145.66, 145.46, 145.38, 145.33, 145.32, 145.29, 144.84, 144.79, 144.71, 144.67, 144.57, 143.09, 143.00, 142.91, 142.90, 142.86, 142.85, 142.53, 142.50, 142.47, 142.41, 142.37, 142.28, 142.13, 142.00, 141.83, 141.74, 141.64, 141.63, 140.03, 140.00, 139.67, 139.35, 138.66, 137.81, 136.68, 129.97, 129.63, 128.97, 117.57, 99.81, 73.89, 64.21, 52.37; FT-IR ν/cm^{-1} (KBr) 2849, 1722, 1607, 1431, 1278, 1188, 1106, 1049, 1019, 995, 953, 925, 766, 707, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 254 (5.19), 316 (4.72), 428 (3.55), 590 (2.81), 689 (2.42); MALDI-TOF MS *m/z* calcd for $C_{72}H_{12}O_3$ $[M]^-$ 924.0792, found 924.0760.



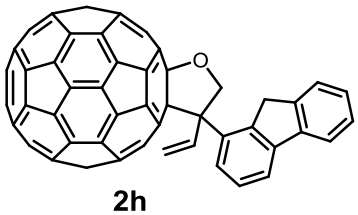
2f

Spectral data of **2f**: 32.9 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.52 (dd, J = 20.0, 8.0 Hz), 7.44 (t, J = 8.0 Hz, 2H), 7.35 (t, J = 8.0 Hz, 1H), 5.75 (d, J = 8.0 Hz, 1H), 5.63 (d, J = 8.0 Hz, 1H), 5.48 (d, J = 20.0 Hz, 1H), 5.23 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.23, 150.03, 149.03, 148.16, 147.61, 146.63, 146.58, 146.43, 146.41, 146.32, 146.25, 146.20, 146.17, 146.11, 146.05, 145.84, 145.53, 145.46, 145.37, 145.35, 145.29, 145.23, 144.82, 144.79, 144.73, 144.63, 144.59, 143.05, 142.97, 142.88, 142.86, 142.82, 142.81, 142.53, 142.49, 142.47, 142.41, 142.39, 142.33, 142.32, 142.29, 142.21, 142.04, 141.82, 141.62, 141.59, 140.36, 140.28, 139.98, 139.94, 139.64, 139.29, 139.27, 138.82, 137.89, 137.75, 136.64, 129.24, 128.98, 127.68, 127.28, 127.15, 117.04, 99.81, 77.37, 74.02, 64.02; FT-IR v/cm^{-1} (KBr) 2920, 2848, 1486, 1428, 1180, 1104, 1049, 995, 952, 923, 763, 730, 694, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.19), 316 (4.69), 429 (3.54), 590 (2.78), 689 (2.43); MALDI-TOF MS m/z calcd for $C_{76}H_{14}O$ $[M]^-$ 942.1050, found 942.1080.



2g

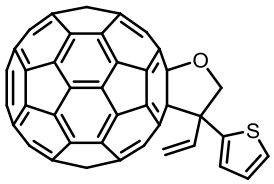
Spectral data of **2g**: 19.2 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 6.6 Hz, 1H), 7.87−7.83 (m, 2H), 7.79 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 5.89 (d, J = 9.0 Hz, 1H), 5.61 (d, J = 10.8 Hz, 1H), 5.29 (d, J = 17.4 Hz, 1H), 5.17 (d, J = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) δ 153.67, 153.04, 149.86, 149.50, 148.11, 147.67, 147.26, 146.66, 146.57, 146.49, 146.39, 146.31, 146.23, 146.22, 146.12, 146.07, 145.96, 145.88, 145.55, 145.40, 145.39, 145.34, 145.31, 145.25, 145.10, 145.09, 144.70, 144.66, 144.62, 144.49, 142.96, 142.91, 142.86, 142.83, 142.59, 142.52, 142.45, 142.36, 142.22, 142.10, 141.88, 141.68, 141.56, 140.23, 139.98, 138.64, 138.57, 138.27, 138.03, 137.76, 137.30, 135.82, 135.22, 131.65, 131.40, 129.71, 129.14, 126.88, 125.58, 125.45, 124.16, 118.52, 100.76, 77.50, 65.60; FT-IR ν/cm^{-1} (KBr) 2851, 1510, 1426, 1169, 1111, 1049, 999, 953, 919, 772, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 259 (5.17), 316 (4.70), 431 (3.52), 590 (2.77), 691 (2.36); MALDI-TOF MS *m/z* calcd for $C_{74}H_{12}O$ $[M]^-$ 916.0894, found 916.0874.



2h

Spectral data of **2h**: 33.3 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.89−7.78 (m, 3H), 7.59−7.52 (m, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 5.79 (d, J = 9.2 Hz, 1H), 5.62 (d, J = 10.8 Hz, 1H), 5.46 (d, J = 17.6 Hz, 1H), 5.24 (d, J = 9.2 Hz, 1H), 3.95 (q, J = 21.6 Hz, 2H); ^{13}C

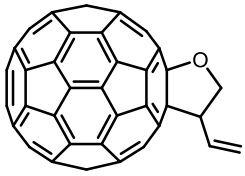
NMR (150 MHz, $CDCl_3/CS_2$) δ 153.10, 153.07, 150.04, 148.94, 147.91, 147.36, 146.40, 146.35, 146.22, 146.21, 146.07, 146.04, 146.02, 145.98, 145.94, 145.88, 145.80, 145.69, 145.33, 145.26, 145.13, 145.11, 145.06, 145.00, 144.61, 144.59, 144.50, 144.43, 144.39, 143.42, 143.23, 142.84, 142.75, 142.68, 142.66, 142.62, 142.60, 142.45, 142.34, 142.30, 142.25, 142.19, 142.18, 142.13, 142.10, 141.95, 141.87, 141.58, 141.42, 141.36, 141.24, 141.06, 139.80, 139.76, 139.40, 139.02, 138.52, 138.38, 137.62, 137.58, 136.42, 127.81, 127.08, 126.95, 125.07, 124.91, 120.10, 119.95, 116.65, 99.52, 74.08, 64.31, 37.25; FT-IR ν/cm^{-1} (KBr) 2853, 1464, 1423, 1399, 1181, 1102, 1051, 996, 953, 924, 904, 766, 733, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 253 (5.15), 315 (4.71), 429 (3.57), 643 (2.70), 690 (2.46); MALDI-TOF MS *m/z* calcd for $C_{77}H_{14}O$ $[M]^-$ 954.1050, found 954.1080.



2i

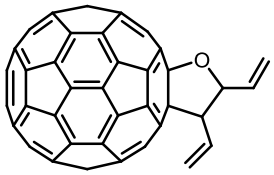
Spectral data of **2i**: 28.3 mg, amorphous brown solid; mp >300 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 3.6 Hz, 1H), 7.37 (d, J = 5.2 Hz, 1H), 7.32 (dd, J = 17.6, 11.2 Hz, 1H), 7.12 (t, J = 4.4 Hz, 1H), 5.72-5.65 (m, 2H), 5.46 (d, J = 9.2 Hz, 1H), 5.34 (d, J = 9.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.09, 152.67, 149.23, 149.21, 148.23, 147.67, 146.67, 146.61, 146.40, 146.38, 146.36, 146.26, 146.24, 146.15, 146.10, 145.95, 145.91, 145.54, 145.47, 145.45, 145.41, 145.39, 145.30, 145.28, 145.26, 144.74, 144.71, 144.71, 144.67, 143.07, 142.86, 142.48, 142.45, 142.43, 142.38, 142.37, 142.17, 141.91, 141.86, 141.81, 141.71, 140.09, 140.01,

139.81, 139.73, 139.59, 138.78, 138.45, 137.11, 136.90, 127.09, 126.71, 125.27, 116.79, 99.41, 77.82, 75.98, 74.52, 62.59; FT-IR ν/cm^{-1} (KBr) 2919, 2848, 1511, 1463, 1429, 1244, 1181, 1101, 1049, 995, 952, 925, 730, 696, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 255 (5.00), 316 (4.53), 590 (2.28), 692 (2.03); MALDI-TOF MS *m/z* calcd for $C_{68}H_8OS$ $[M]^-$ 872.0301, found 872.0321.



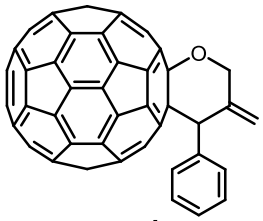
2j

Spectral data of **2j**: 14.2 mg, amorphous brown solid; mp >300 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 6.47−6.38 (m, 1H), 5.67 (d, J = 17.2 Hz, 1H), 5.52 (d, J = 10.4 Hz, 1H), 5.01 (dd, J = 9.2, 6.0 Hz, 1H), 4.87 (t, J = 9.2 Hz, 1H), 4.66−4.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ 154.79, 151.68, 149.86, 148.62, 147.88, 147.27, 146.32, 146.26, 146.23, 146.17, 146.15, 146.01, 146.00, 145.94, 145.84, 145.50, 145.47, 145.35, 145.27, 145.18, 145.13, 145.10, 145.09, 144.93, 144.91, 144.59, 144.48, 144.45, 144.28, 142.84, 142.76, 142.64, 142.61, 142.58, 142.53, 142.52, 142.23, 142.20, 142.16, 142.12, 142.08, 142.04, 141.98, 141.68, 141.62, 141.42, 140.12, 139.74, 139.63, 139.49, 137.78, 137.57, 137.28, 135.80, 133.86, 120.27, 99.06, 72.54, 70.13, 59.70; FT-IR ν/cm^{-1} (KBr) 3073, 2920, 2839, 1512, 1423, 1172, 1106, 1027, 986, 951, 921, 729, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 253 (5.10), 314 (4.71), 428 (3.53), 590 (2.75), 691 (2.53); MALDI-TOF MS *m/z* calcd for $C_{64}H_6O$ $[M]^-$ 790.0424, found 790.0439.



2k

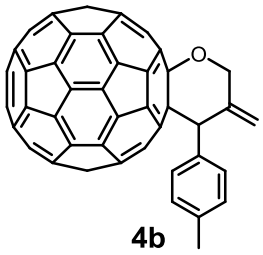
Spectral data of **2k**: 14.7 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76−6.67 (m, 1H), 6.59−6.50 (m, 1H), 5.88−5.83 (m, 2H), 5.64 (d, *J* = 10.0 Hz, 1H), 5.55−5.49 (m, 2H), 4.57 (dd, *J* = 10.0, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ 155.11, 153.37, 149.39, 149.27, 148.00, 147.42, 146.40, 146.36, 146.24, 146.22, 146.10, 146.07, 145.98, 145.95, 145.72, 145.64, 145.43, 145.26, 145.24, 145.22, 145.20, 145.19, 145.13, 145.11, 145.06, 144.61, 144.56, 144.43, 142.91, 142.88, 142.72, 142.64, 142.49, 142.29, 142.28, 142.22, 142.20, 142.18, 142.14, 142.12, 141.86, 141.75, 141.70, 141.54, 139.99, 139.97, 139.85, 139.59, 138.35, 137.41, 137.34, 136.00, 135.02, 133.29, 120.05, 119.94, 98.01, 82.14, 73.17, 62.25; FT-IR ν/cm^{-1} (KBr) 3076, 2919, 2847, 1420, 1179, 1104, 1019, 978, 918, 767, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 254 (5.09), 315 (4.60), 428 (3.42), 590 (2.70), 693 (2.40); MALDI-TOF MS *m/z* calcd for $C_{66}H_8O$ $[M]^-$ 816.0581, found 816.0555.



4a

Spectral data of **4a**: 19.9 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 5.84 (s, 1H), 5.79 (d, *J* = 16.0 Hz, 1H), 5.56 (d, *J* = 16.0 Hz, 1H), 5.52 (s, 1H), 5.39 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) δ 155.05, 152.40, 149.95, 148.94,

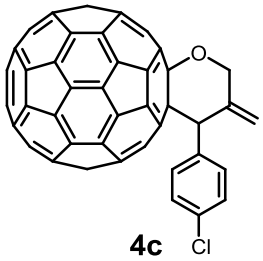
148.34, 147.71, 147.10, 146.68, 146.67, 146.46, 146.40, 146.26, 146.22, 146.21, 145.68, 145.62, 145.60, 145.50, 145.44, 145.37, 145.23, 145.19, 145.14, 144.76, 144.72, 144.70, 144.65, 142.90, 142.86, 142.75, 142.72, 142.67, 142.41, 142.39, 142.29, 142.26, 142.18, 142.12, 142.06, 141.44, 141.38, 141.26, 140.81, 140.05, 139.83, 139.19, 138.64, 138.40, 137.15, 136.67, 134.94, 132.18, 128.32, 127.96, 111.20, 93.78, 69.36, 66.39, 56.16; FT-IR ν/cm^{-1} (KBr) 3027, 2844, 1512, 1428, 1182, 1102, 1065, 900, 740, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.00), 318 (4.60), 431 (3.38), 691 (2.34); MALDI-TOF MS *m/z* calcd for $C_{70}H_{10}O$ $[M]^-$ 866.0726, found 866.0727.



4b

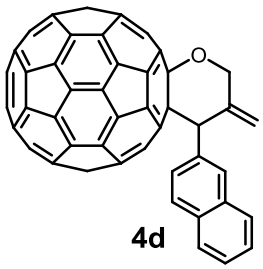
Spectral data of **4b**: 25.5 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.54 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 5.80−5.75 (m, 2H), 5.56−5.50 (m, 2H), 5.38 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) δ 154.83, 152.21, 149.72, 148.66, 147.99, 147.35, 146.84, 146.33, 146.11, 146.05, 145.91, 145.87, 145.35, 145.31, 145.27, 145.17, 145.09, 145.08, 145.02, 144.96, 144.88, 144.83, 144.54, 144.41, 144.39, 144.38, 144.30, 142.56, 142.52, 142.41, 142.38, 142.33, 142.08, 142.06, 141.96, 141.93, 141.83, 141.78, 141.72, 141.12, 141.06, 140.92, 140.48, 139.70, 139.47, 138.90, 138.32, 138.10, 137.13, 136.78, 136.30, 134.58, 131.74, 128.77, 110.78, 93.42, 69.06, 66.17, 55.44, 21.12; FT-IR ν/cm^{-1} (KBr) 2917, 2846, 1512, 1427, 1183, 1102, 1065, 890, 772, 526; UV-vis

($CHCl_3$) λ_{max}/nm (log ε) 256 (5.07), 317 (4.62), 431 (3.38), 692 (2.35); MALDI-TOF MS *m/z* calcd for $C_{71}H_{12}O$ $[M]^-$ 880.0883, found 880.0882.



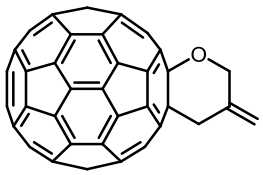
4c

Spectral data of **4c**: 25.6 mg, amorphous brown solid; mp >300 ^oC; ^1H NMR (600 MHz, $CDCl_3/CS_2$) δ 7.64 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 5.81 (s, 1H), 5.78 (d, J = 15.6 Hz, 1H), 5.56 (d, J = 16.2 Hz, 1H), 5.20 (s, 1H), 5.34 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) δ 154.76, 152.04, 149.78, 148.81, 148.45, 147.82, 146.78, 146.76, 146.56, 146.50, 146.34, 146.32, 146.29, 145.71, 145.62, 145.59, 145.55, 145.53, 145.48, 145.35, 145.32, 145.01, 144.85, 144.79, 144.75, 144.73, 144.49, 143.01, 142.96, 142.85, 142.82, 142.77, 142.49, 142.47, 142.36, 142.31, 142.25, 142.17, 142.14, 141.49, 141.40, 140.88, 140.15, 139.93, 139.41, 138.67, 138.60, 137.23, 136.85, 135.15, 134.00, 133.40, 128.62, 111.38, 93.83, 69.30, 66.24, 55.73; FT-IR ν/cm^{-1} (KBr) 2920, 2846, 1512, 1489, 1428, 1262, 1181, 1102, 1065, 1014, 902, 789, 731, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 255 (5.12), 317 (4.67), 431 (3.41), 691 (2.37); MALDI-TOF MS *m/z* calcd for $C_{70}H_9ClO$ $[M]^-$ 900.0336, found 900.0337.



4d

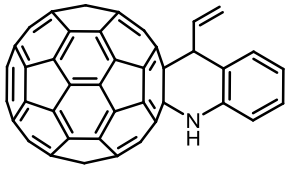
Spectral data of **4d**: 26.1 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.13 (s, 1H), 7.83−7.78 (m, 4H), 7.46−7.44 (m, 2H), 6.01 (s, 1H), 5.83 (d, J = 16.0 Hz, 1H), 5.58 (d, J = 16.0 Hz, 1H), 5.55 (s, 1H), 5.40 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) δ 154.60, 152.06, 149.64, 148.51, 147.92, 147.29, 146.59, 146.28, 146.05, 145.98, 145.87, 145.82, 145.27, 145.19, 145.11, 145.07, 145.03, 144.99, 144.96, 144.83, 144.80, 144.64, 144.44, 144.36, 144.30, 144.24, 142.73, 142.51, 142.45, 142.37, 142.33, 142.31, 142.25, 142.02, 142.00, 141.87, 141.84, 141.81, 141.72, 141.67, 141.07, 140.99, 140.84, 140.42, 139.70, 139.46, 138.89, 138.26, 138.07, 136.73, 136.26, 134.57, 132.87, 132.49, 131.27, 129.22, 127.82, 127.46, 127.31, 126.13, 125.98, 111.13, 93.44, 68.97, 65.99, 55.92; FT-IR ν/cm^{-1} (KBr) 2920, 2845, 1511, 1427, 1181, 1102, 1065, 897, 817, 740, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.04), 316 (4.59), 431 (3.41), 691 (2.30); MALDI-TOF MS m/z calcd for $C_{74}H_{12}O$ $[M]^-$ 916.0888, found 916.0889.



4e

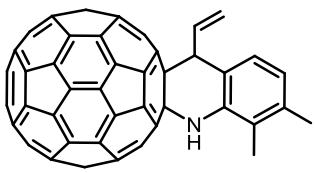
Spectral data of **4e**: 24.1 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 5.52 (s, 2H), 5.47 (s, 2H), 4.26 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) δ 155.36, 149.00, 148.38, 147.67, 146.62, 146.37, 146.25, 146.23, 146.17, 145.71, 145.56, 145.43, 145.32, 145.29, 144.90, 144.77, 144.65, 143.30, 142.91, 142.68, 142.65, 142.53, 142.31, 142.18, 141.97, 141.54, 141.24, 140.19, 139.78, 138.06, 136.02, 110.42, 92.46, 69.64, 63.17, 43.24; FT-IR ν/cm^{-1} (KBr) 2921, 2849,

1562, 1510, 1427, 1181, 1101, 1063, 975, 890, 767, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.01), 316 (4.52), 431 (3.32), 693 (2.18); MALDI-TOF MS *m/z* calcd for $C_{64}H_6O$ $[M]^-$ 790.0413, found 790.0414.



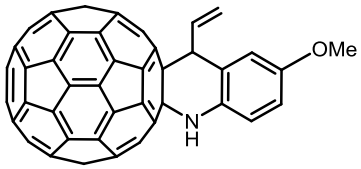
6a

Spectral data of **6a**: 11.5 mg, amorphous brown solid; mp >300 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, J = 7.2 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.24−7.17 (m, 2H), 6.95 (br, 1H), 5.64−5.58 (m, 3H), 5.15 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ 148.08, 147.63, 146.58, 146.51, 146.48, 146.46, 146.16, 145.99, 145.75, 145.73, 145.60, 145.41, 145.34, 145.32, 145.27, 145.04, 144.82, 144.76, 144.68, 144.54, 144.20, 142.99, 142.96, 142.67, 142.66, 142.63, 142.59, 142.30, 142.25, 142.23, 142.18, 142.16, 142.07, 142.05, 141.89, 141.83, 141.43, 141.41, 140.00, 139.82, 139.46, 139.27, 137.03, 136.54, 136.33, 135.85, 131.95, 128.68, 126.94, 122.56, 117.68, 78.22, 71.61; FT-IR v/cm^{-1} (KBr) 3333, 2919, 1606, 1592, 1511, 1462, 1423, 1254, 1182, 927, 750, 574, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.01), 314 (4.63), 590 (2.70), 698 (2.41); MALDI-TOF MS *m/z* calcd for $C_{69}H_9N$ $[M]^-$ 851.0740, found 851.0720.



6b

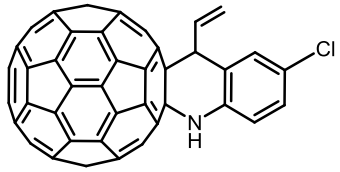
Spectral data of **6b**: 12.3 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, J = 7.8 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 6.97 (br, 1H), 5.82 (s, 1H), 5.65−5.59 (m, 2H), 5.15 (d, J = 10.2 Hz, 1H), 2.49 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 148.01, 147.54, 146.50, 146.41, 146.38, 146.36, 146.07, 145.90, 145.89, 145.67, 145.50, 145.32, 145.25, 145.21, 145.19, 144.77, 144.72, 144.60, 144.47, 143.04, 142.90, 142.86, 142.58, 142.57, 142.55, 142.50, 142.24, 142.18, 142.10, 141.96, 141.82, 141.75, 141.36, 141.32, 140.04, 139.77, 139.39, 136.95, 136.40, 135.76, 129.62, 124.01, 123.64, 123.43, 78.21, 71.76, 20.84, 12.95; FT-IR ν/cm^{-1} (KBr) 3368, 2920, 1587, 1512, 1455, 1278, 1182, 1096, 997, 926, 796, 787, 767, 737, 707, 574, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.07), 313 (4.66), 429 (3.45), 698 (2.50); MALDI-TOF MS m/z calcd for $C_{71}H_{13}N$ $[M]^-$ 879.1053, found 879.1068.



6c

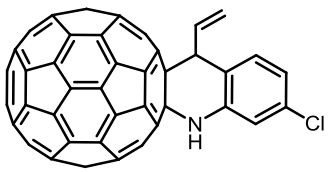
Spectral data of **6c**: 11.0 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.4 Hz, 1H), 7.15 (d, J = 2.4 Hz, 1H), 6.95 (br, 1H), 7.02 (dd, J = 8.4, 2.8 Hz, 1H), 5.69−5.62 (m, 2H), 5.51 (s, 1H), 5.18 (d, J = 9.6 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) δ 155.51, 148.11, 147.68, 146.61, 146.54, 146.51, 146.20, 145.78, 145.64, 145.46, 145.39, 145.37, 145.33, 144.86, 144.80, 144.75, 144.61, 143.02, 142.99, 142.70, 142.68, 142.64, 142.35, 142.29, 142.23, 142.11, 141.93, 141.87, 141.48, 141.45, 140.05, 139.87, 139.47, 138.37,

133.44, 118.53, 113.49, 113.25, 55.56; FT-IR ν/cm^{-1} (KBr) 3334, 2920, 2849, 1611, 1497, 1455, 1434, 1281, 1228, 1037, 927, 809, 739, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.02), 312 (4.60), 589 (2.74), 697 (2.35); MALDI-TOF MS *m/z* calcd for $C_{70}H_{11}NO$ $[M]^-$ 881.0846, found 881.0832.



6d

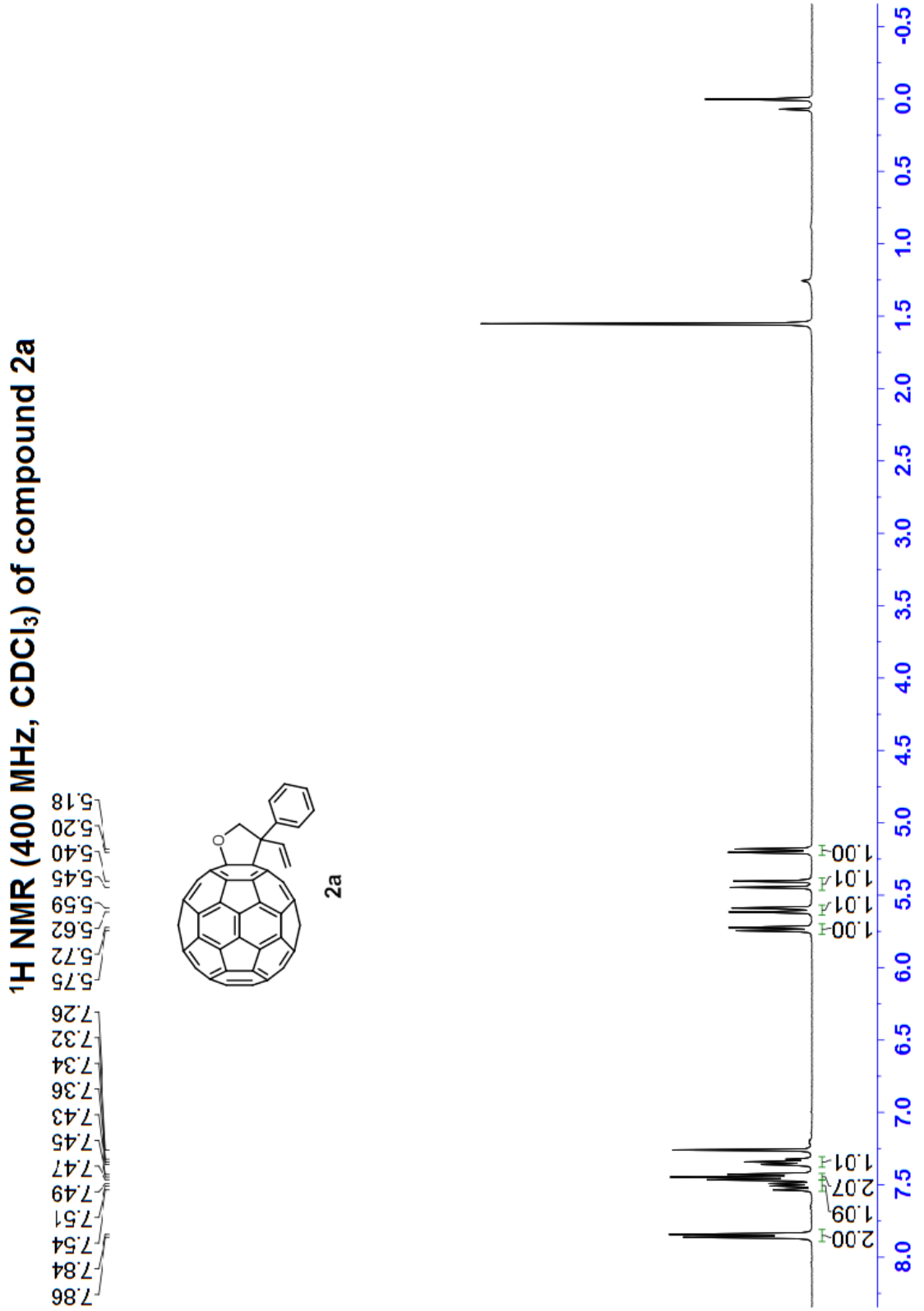
Spectral data of **6d**: 9.3 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 6.91 (br, 1H), 5.71−5.68 (m, 2H), 5.63 (s, 1H), 5.15 (d, J = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ 148.02, 147.57, 146.54, 146.47, 146.46, 146.41, 146.11, 146.08, 145.99, 145.87, 145.68, 145.65, 145.51, 145.41, 145.37, 145.27, 145.22, 144.74, 144.67, 144.59, 144.43, 144.01, 143.88, 143.48, 142.94, 142.90, 142.63, 142.60, 142.55, 142.25, 142.18, 142.08, 142.05, 142.02, 141.99, 141.83, 141.78, 141.37, 139.98, 139.78, 139.43, 137.03, 135.74, 133.55, 128.44, 127.84, 127.05, 118.63, 78.13, 71.23; FT-IR ν/cm^{-1} (KBr) 3335, 2919, 2849, 1511, 1484, 1436, 1259, 1188, 931, 814, 769, 715, 574, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.11), 315 (4.63), 590 (2.80), 697 (2.48); MALDI-TOF MS *m/z* calcd for $C_{69}H_8ClN$ $[M]^-$ 885.0351, found 885.0335.

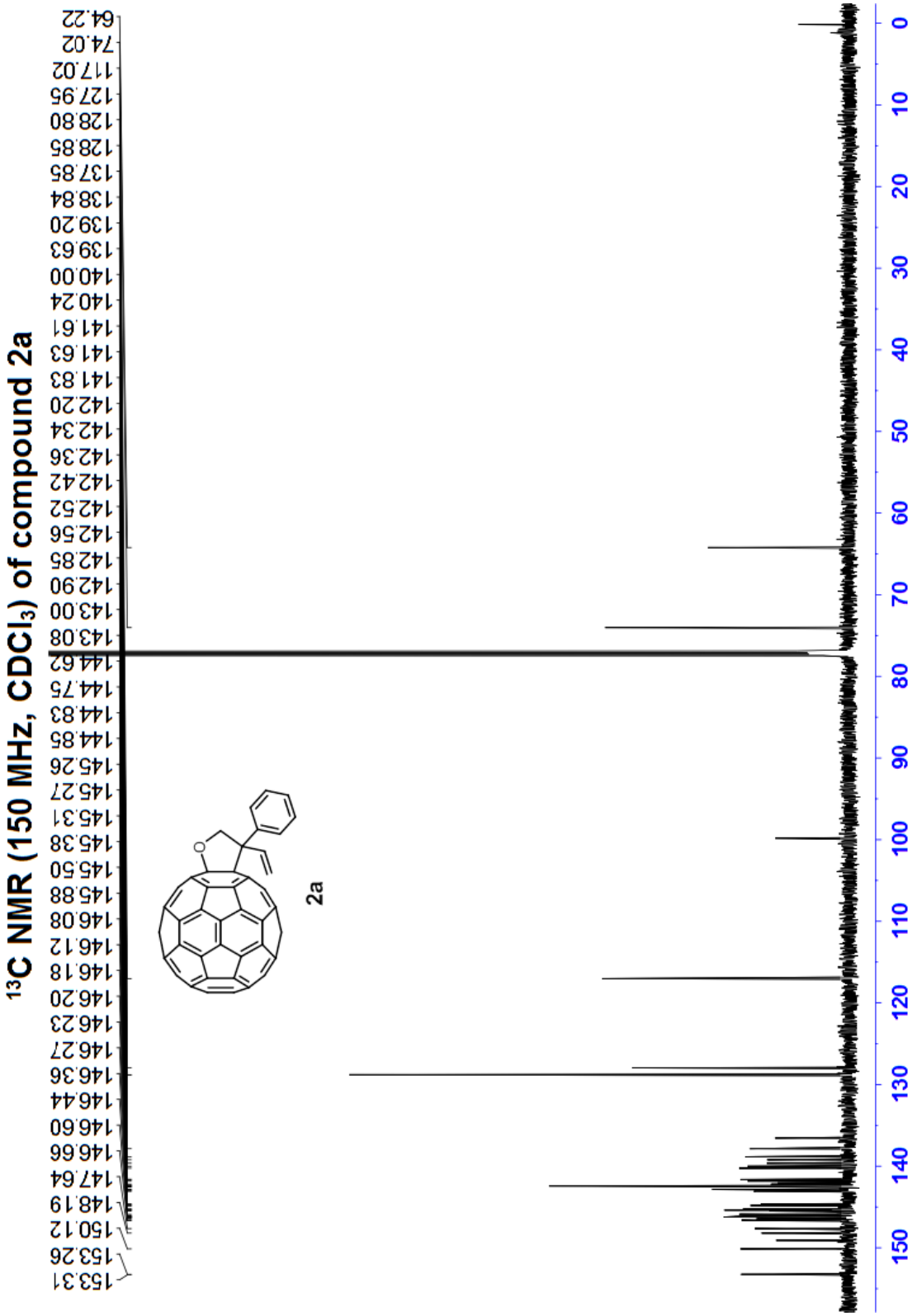


6e

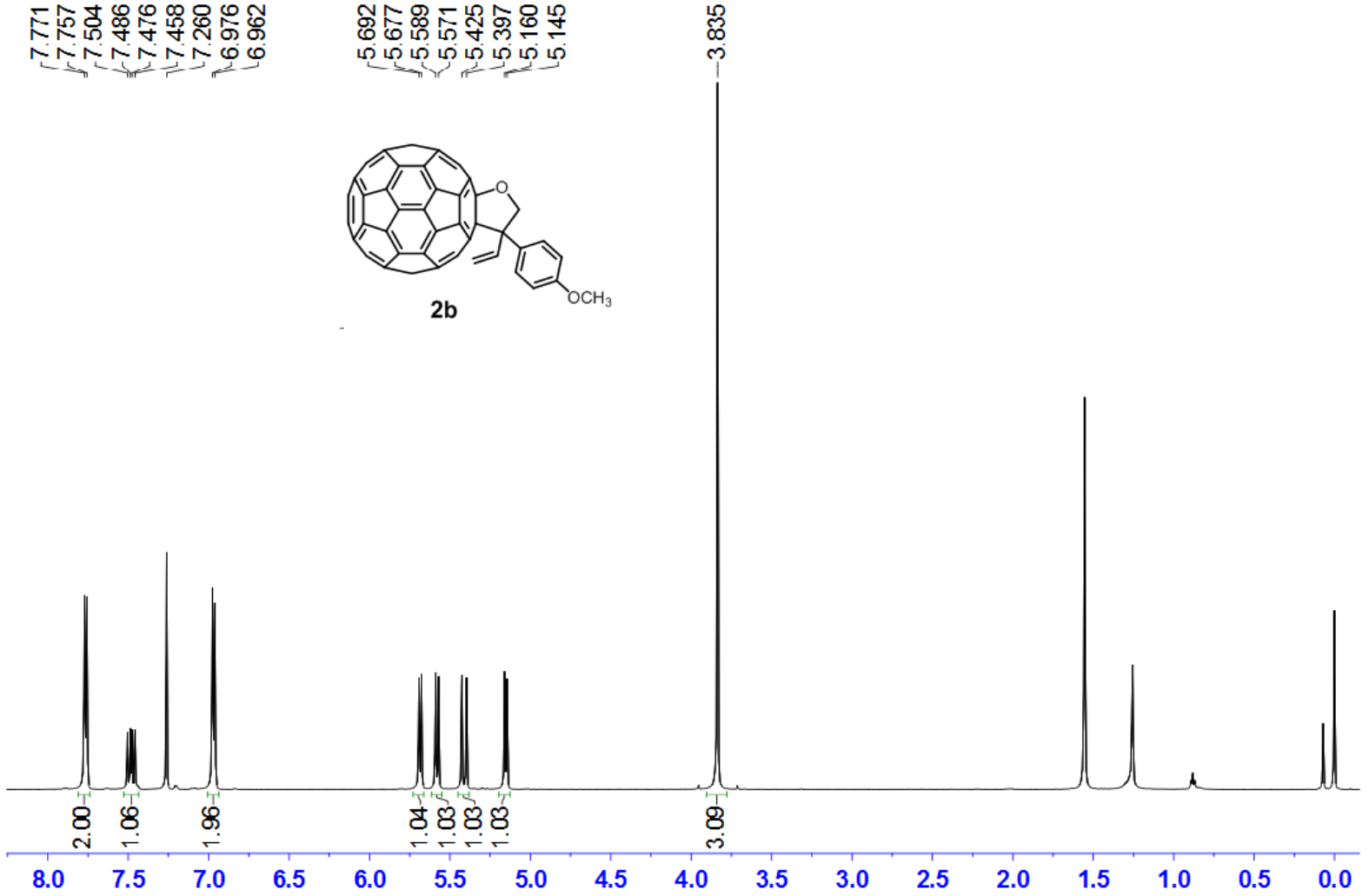
Spectral data of **6e**: 9.3 mg, amorphous brown solid; mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 2.0 Hz, 1H), 7.29 (dd, J = 8.0, 2.0 Hz, 1H), 6.94 (br, 1H), 5.68−5.63 (m, 3H), 5.14 (d, J = 9.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$) δ 148.25, 147.80, 146.73, 146.67, 146.64, 146.60, 146.32, 146.26, 146.16, 146.05, 145.91, 145.84, 145.70, 145.55, 145.48, 145.44, 145.42, 144.93, 144.87, 144.80, 144.66, 144.15, 144.14, 143.13, 143.12, 142.81, 142.78, 142.74, 142.42, 142.38, 142.33, 142.30, 142.28, 142.23, 142.21, 142.19, 142.04, 141.97, 141.56, 141.53, 140.16, 139.97, 139.60, 137.06, 135.88, 134.26, 130.54, 128.17, 122.58, 117.88, 78.23, 71.52; FT-IR ν/cm^{-1} (KBr) 3333, 2918, 1600, 1589, 1512, 1491, 1446, 1432, 1278, 1182, 1091, 1028, 931, 908, 848, 769, 715, 574, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.01), 315 (4.57), 694 (2.52); MALDI-TOF MS *m/z* calcd for $C_{69}H_8ClN$ $[M]^-$ 885.0921, found 885.0920.

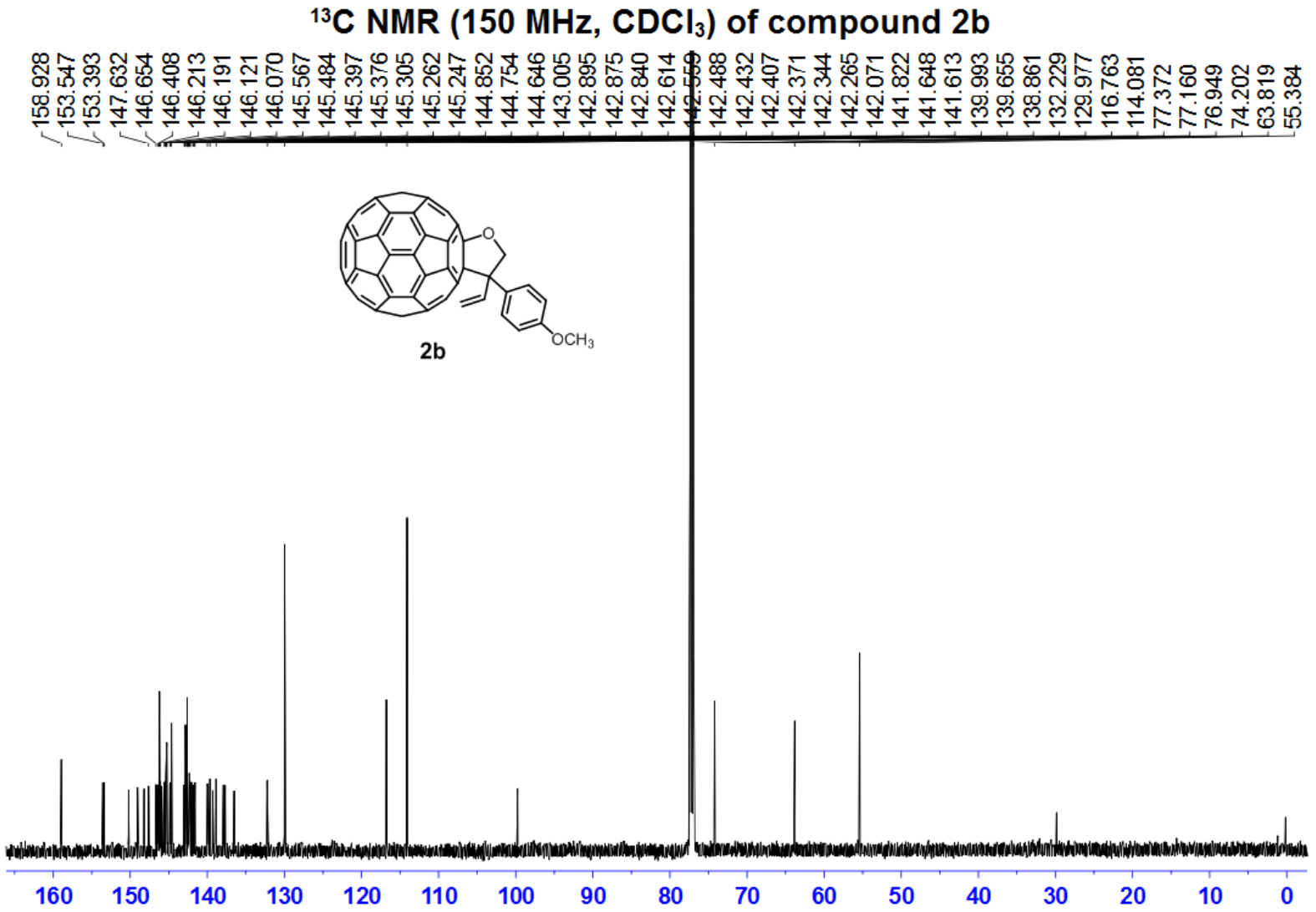
7. ^{1}H NMR and ^{13}C NMR Spectra of Compounds 2, 4 and 6



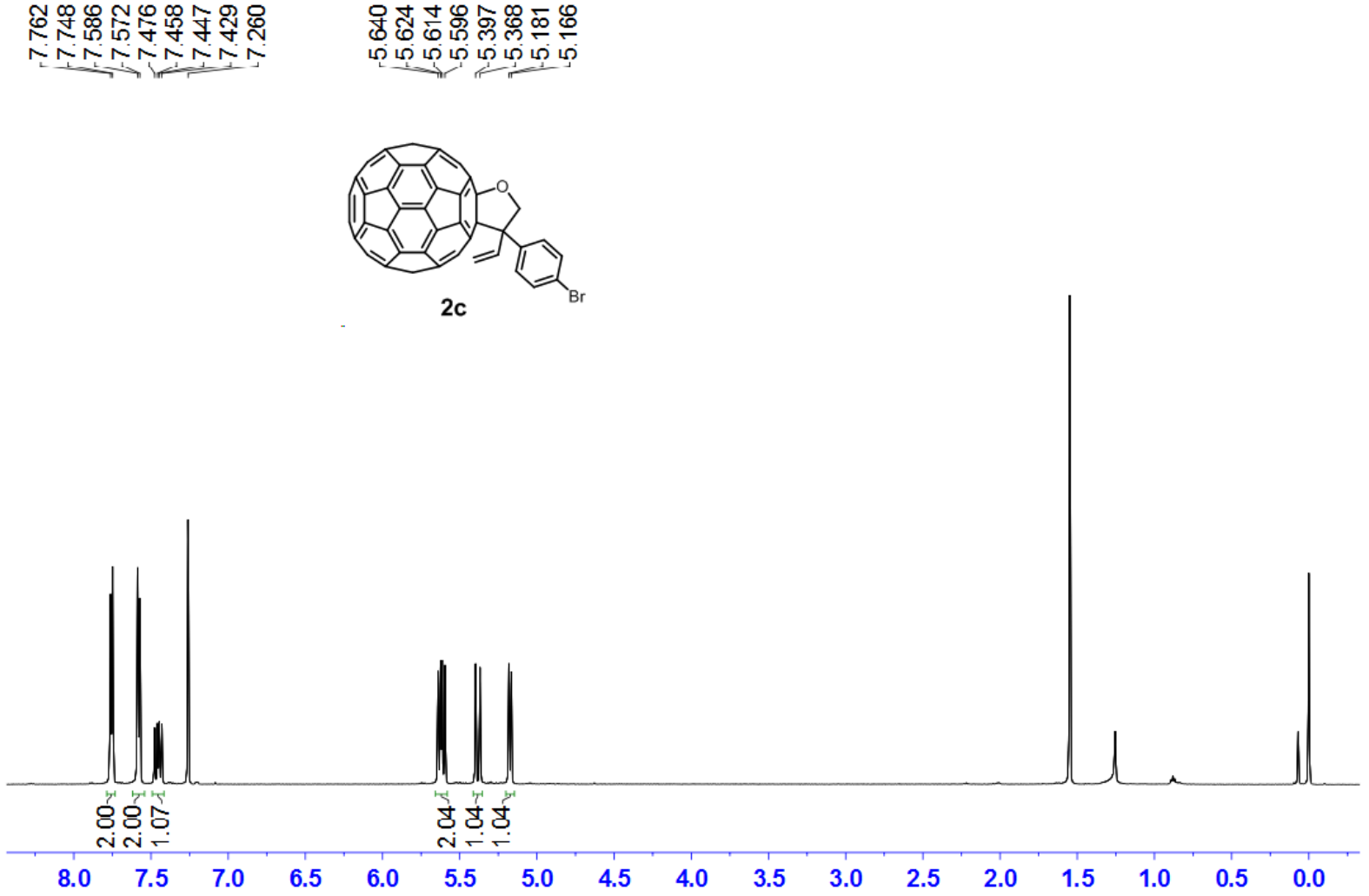

^{13}C NMR (150 MHz, $CDCl_3$) of compound 2a
2a
64.22
74.02
117.02
127.95
128.80
128.85
137.85
138.84
139.20
139.63
140.00
140.24
141.61
141.63
141.83
142.20
142.34
142.36
142.42
142.52
142.56
142.85
142.90
143.00
143.08
144.62
144.75
144.83
144.85
145.26
145.27
145.31
145.38
145.50
145.88
146.08
146.12
146.18
146.20
146.23
146.27
146.36
146.44
146.60
146.66
147.64
148.19
150.12
153.26
153.31
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

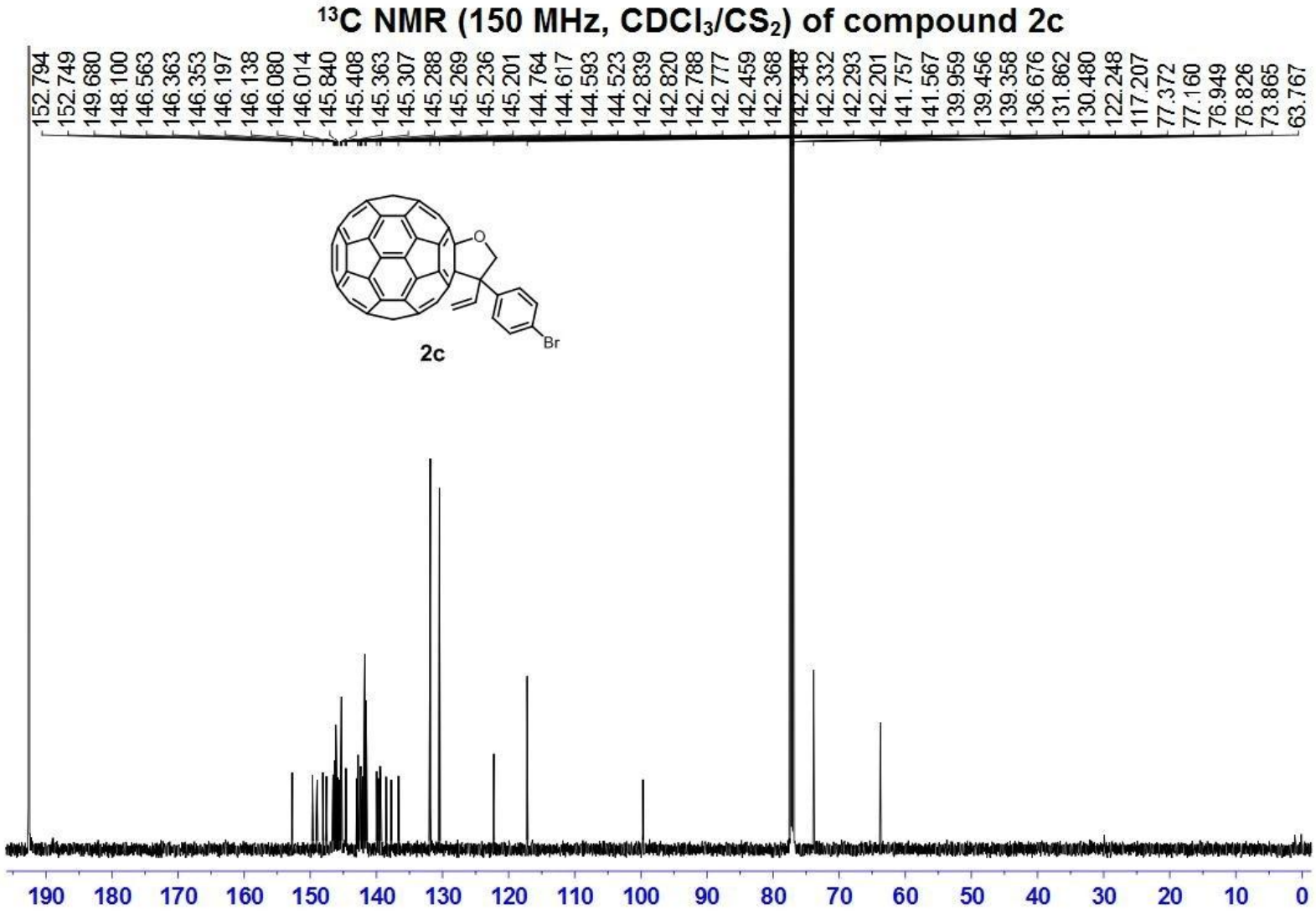
^{1}H NMR (600 MHz, $CDCl_3$) of compound 2b



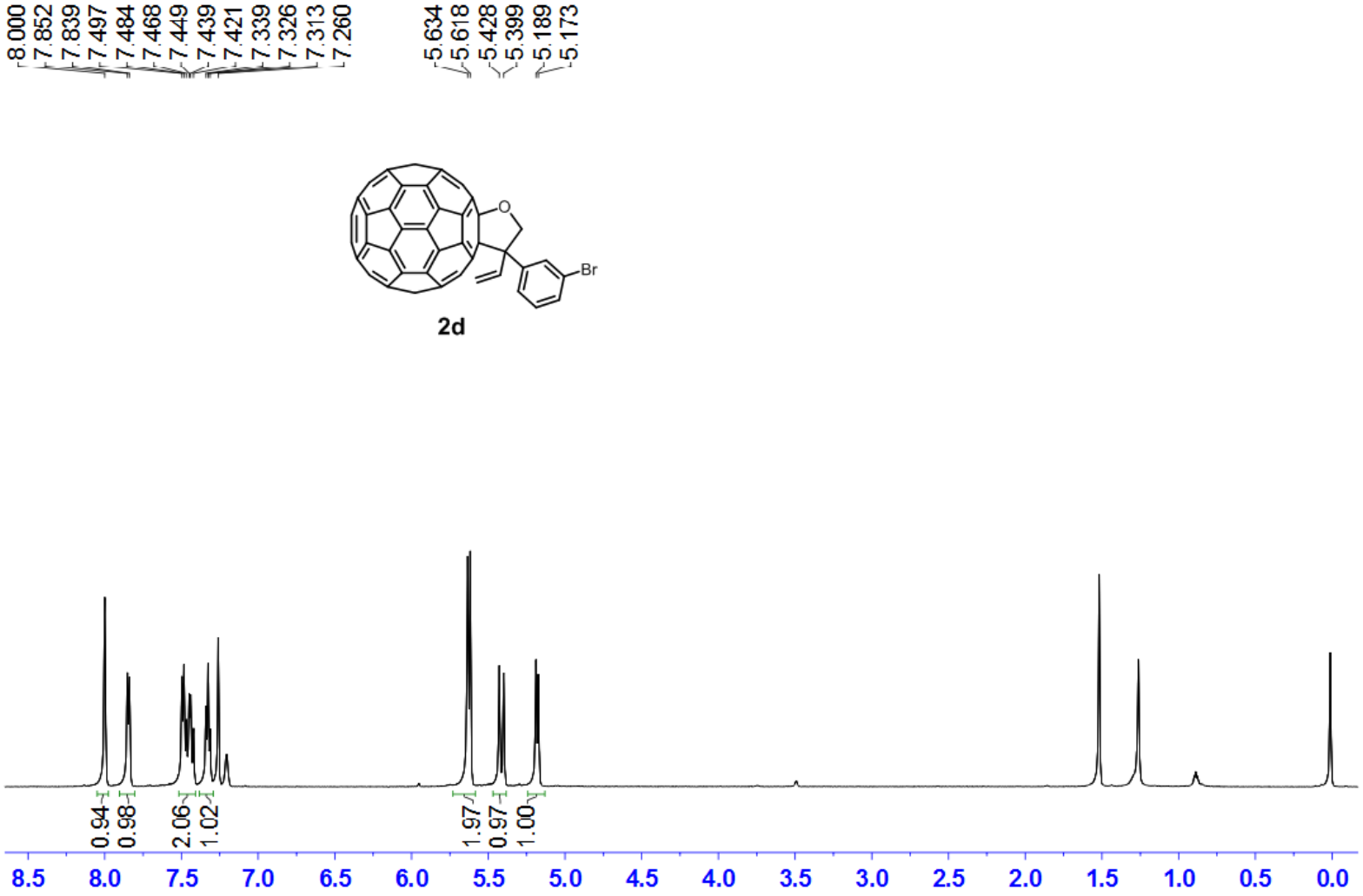

^{13}C NMR (150 MHz, $CDCl_3$) of compound 2b
158.928
153.547
153.393
147.632
146.654
146.408
146.213
146.191
146.121
146.070
145.567
145.484
145.397
145.376
145.305
145.262
145.247
144.852
144.754
144.646
143.005
142.895
142.875
142.840
142.614
142.559
142.488
142.432
142.407
142.371
142.344
142.265
142.071
141.822
141.648
141.613
139.993
139.655
138.861
132.229
129.977
116.763
114.081
77.372
77.160
76.949
74.202
63.819
55.384
O
OCH3
2b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

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



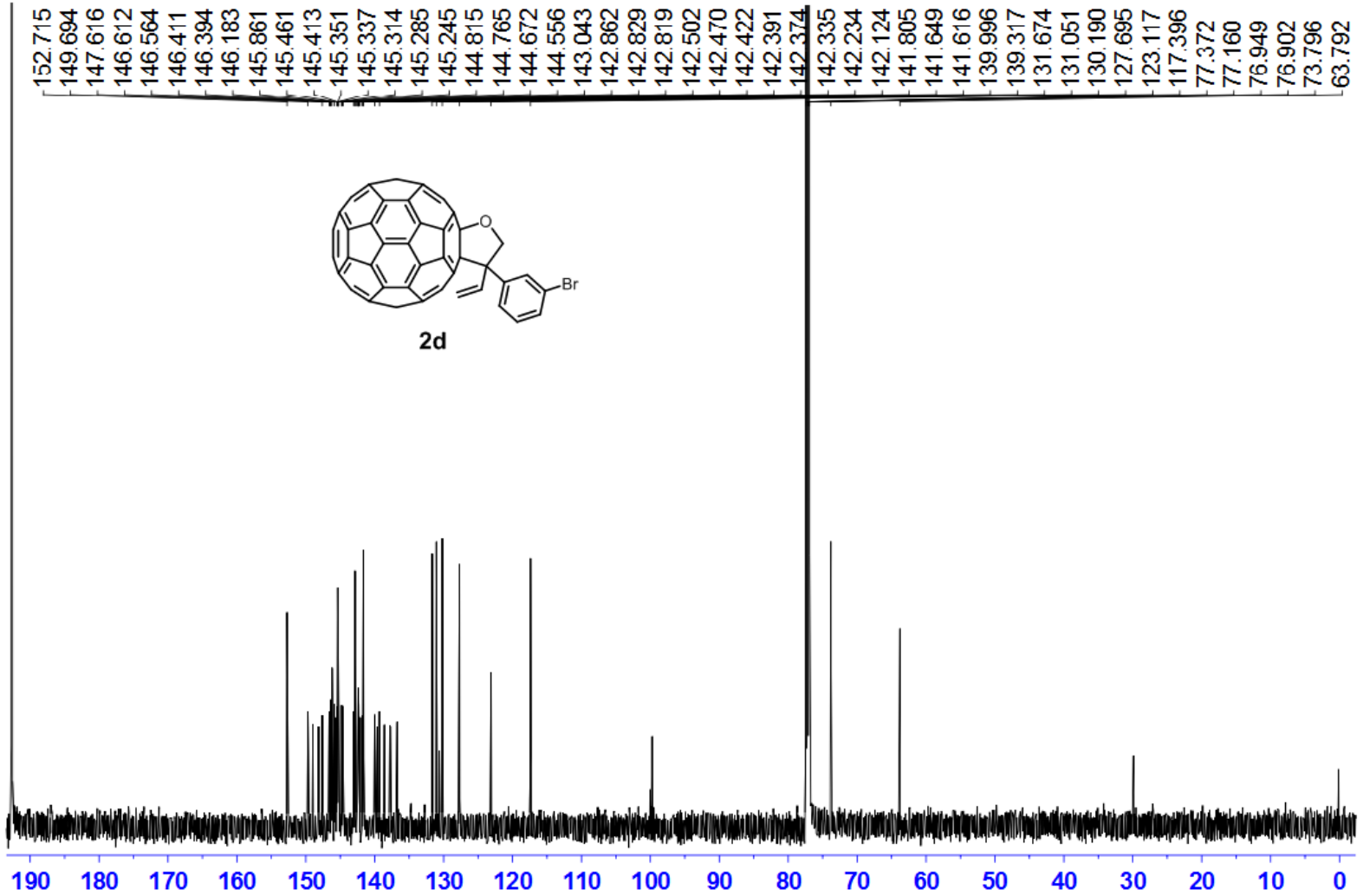

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2c
152.794
152.749
149.680
148.100
146.563
146.363
146.353
146.197
146.138
146.080
146.014
145.840
145.408
145.363
145.307
145.288
145.269
145.236
145.201
144.764
144.617
144.593
144.523
142.839
142.820
142.788
142.777
142.459
142.368
142.348
142.332
142.293
142.201
141.757
141.567
139.959
139.456
139.358
136.676
131.862
130.480
122.248
117.207
77.372
77.160
76.949
76.826
73.865
63.767
O
Br
2c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

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

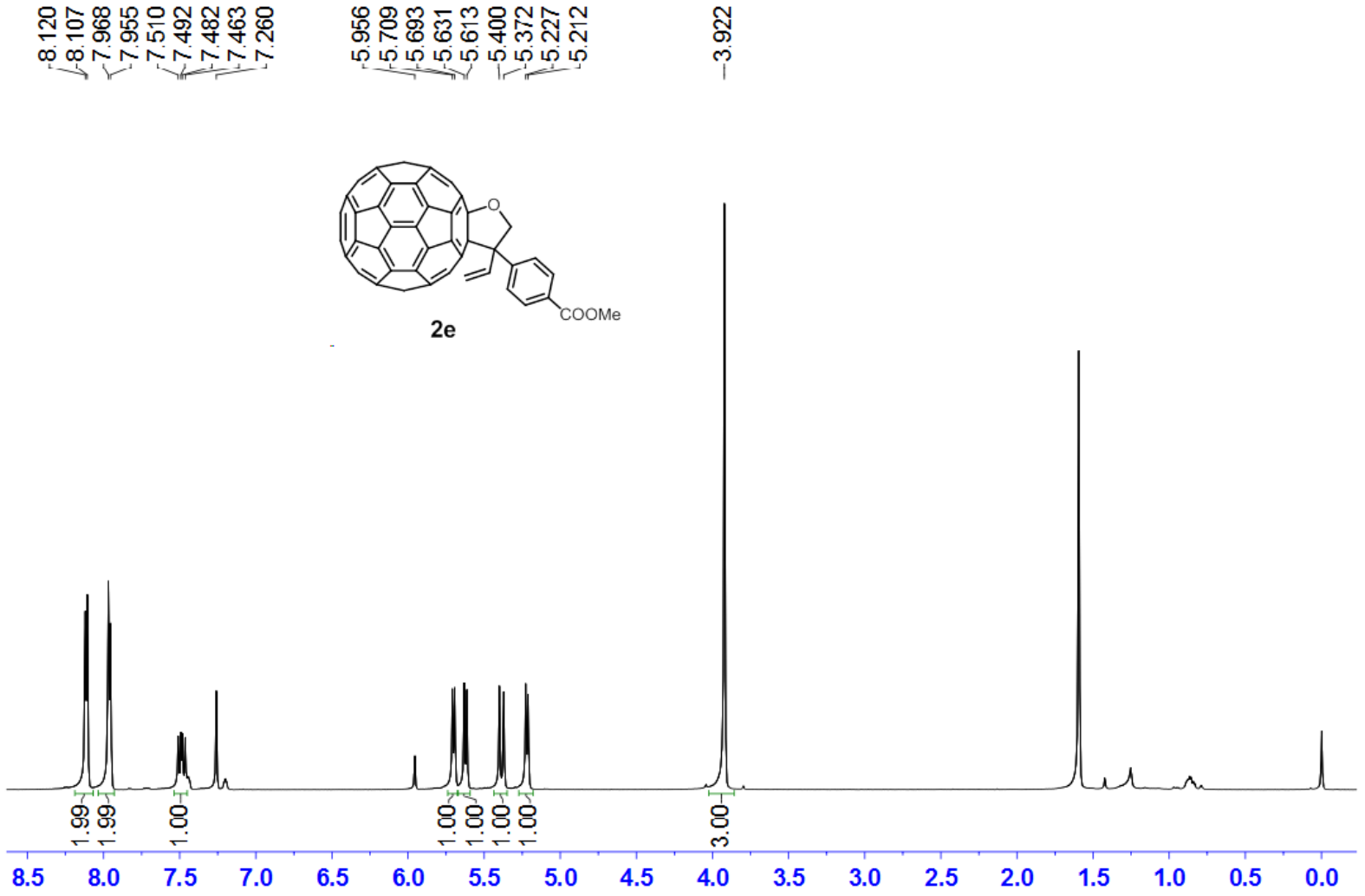


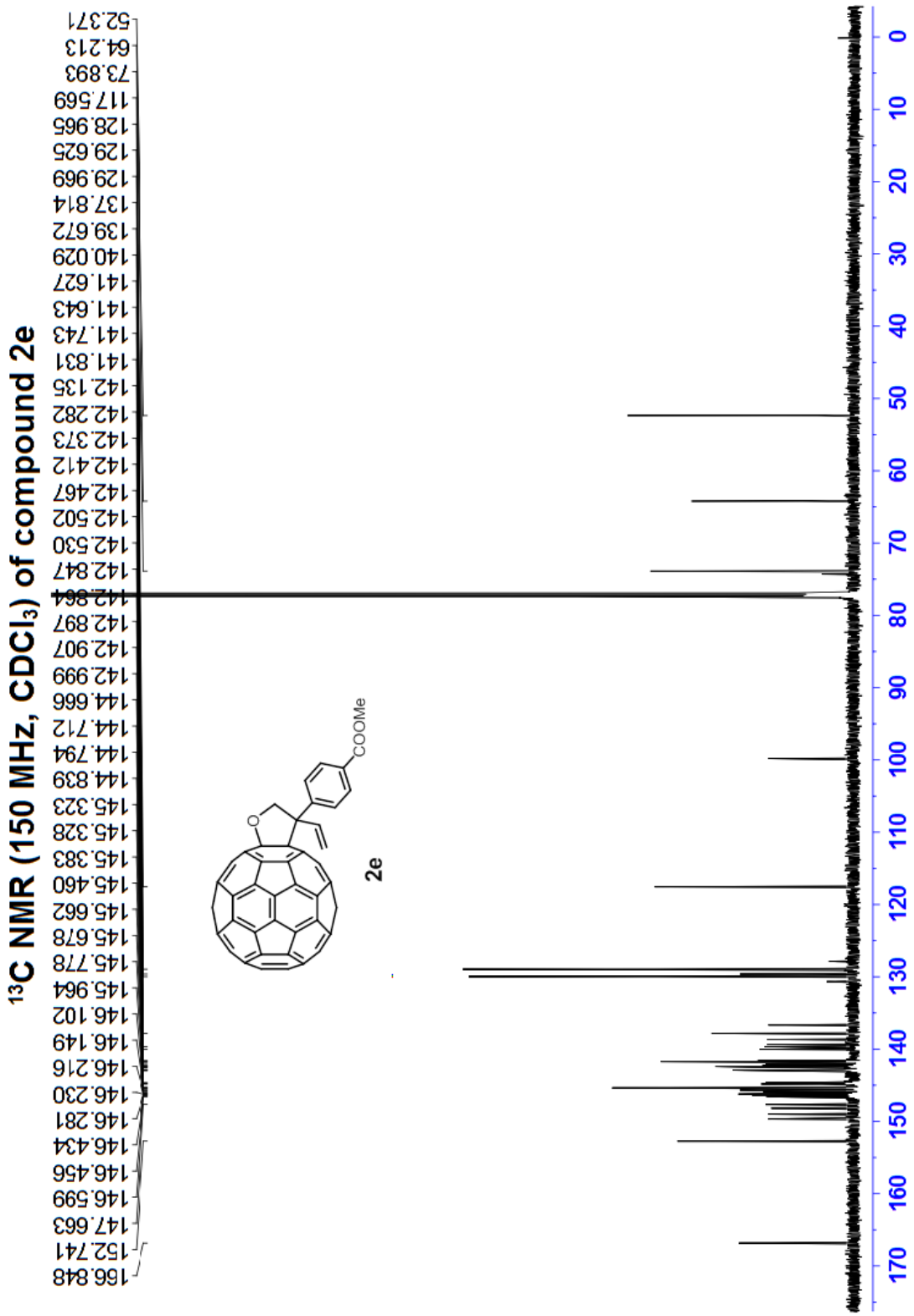
2d

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

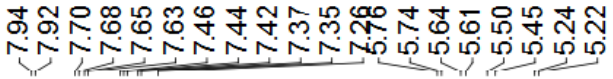


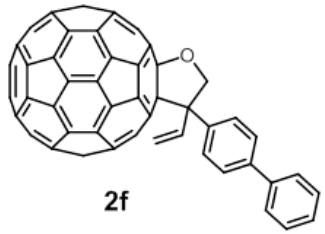
^{1}H NMR (600 MHz, $CDCl_3$) of compound 2e



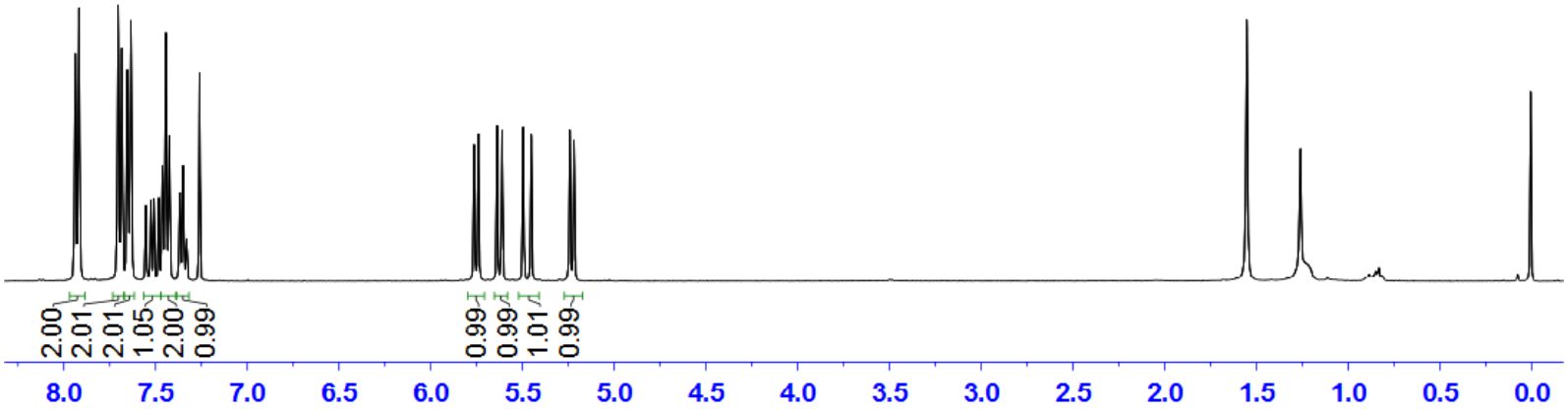

^{13}C NMR (150 MHz, $CDCl_3$) of compound 2e
COOMe
2e

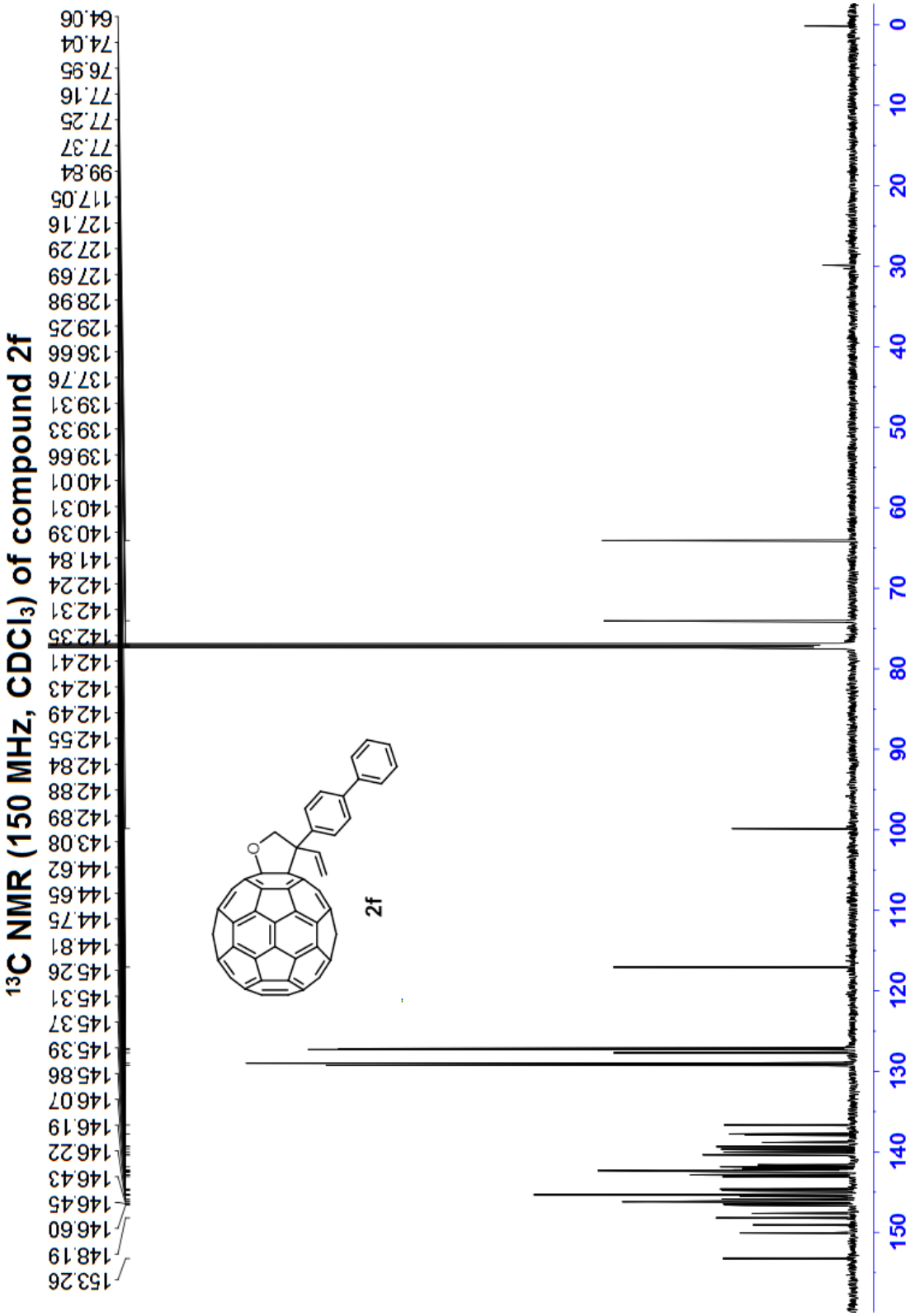
^{1}H NMR (400 MHz, $CDCl_3$) of compound 2f



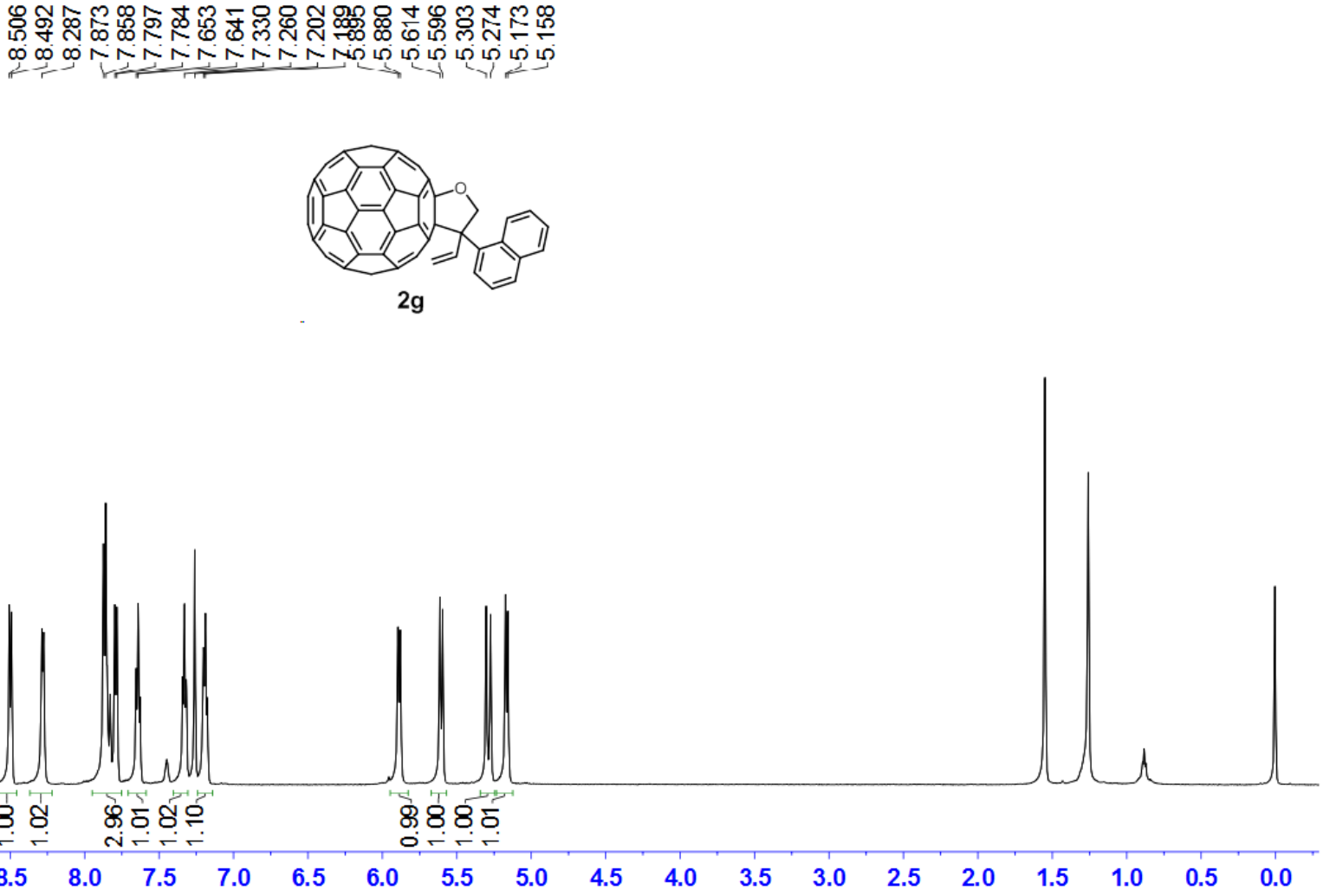


2f

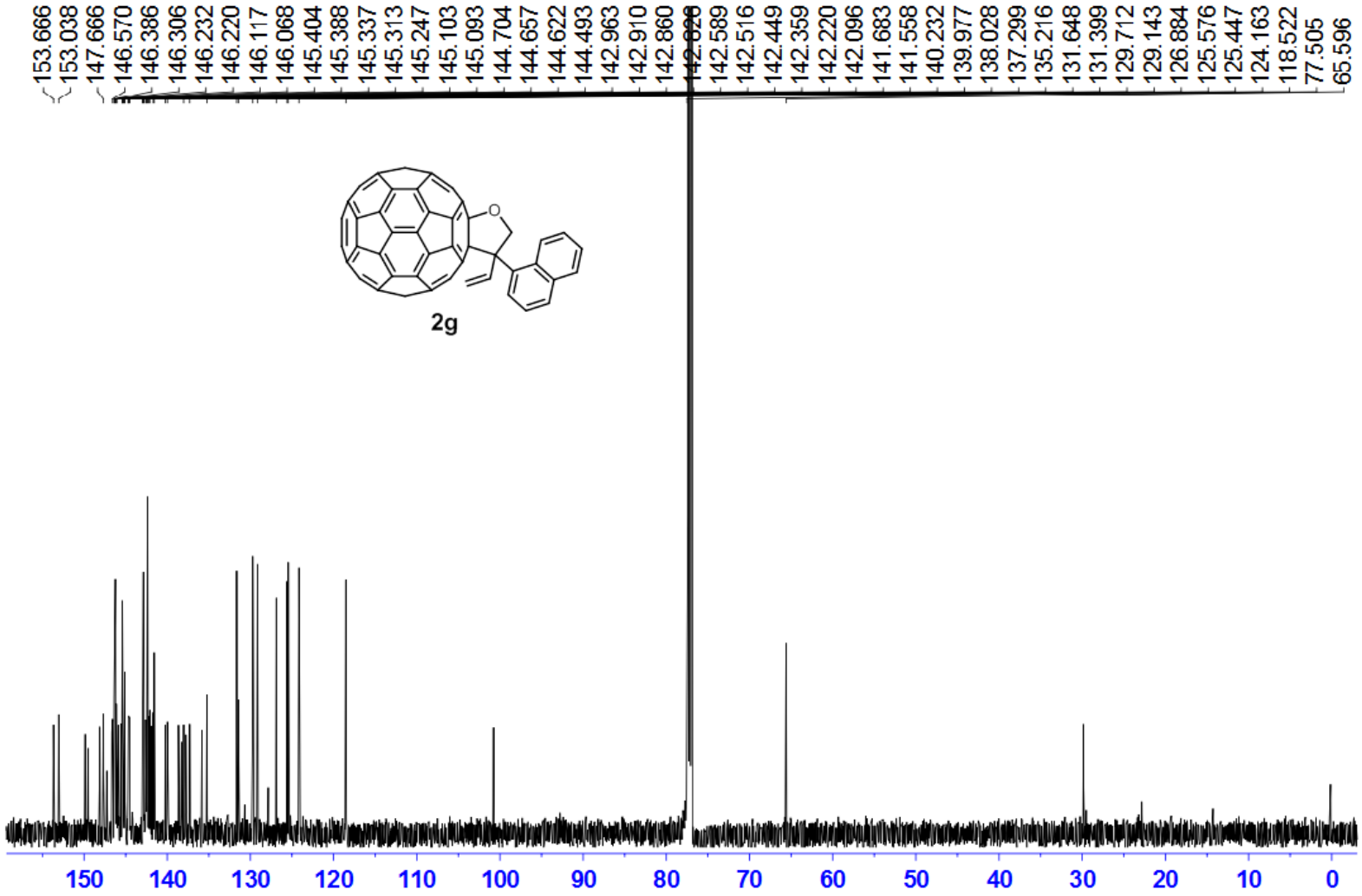



^{13}C NMR (150 MHz, $CDCl_3$) of compound 2f
2f

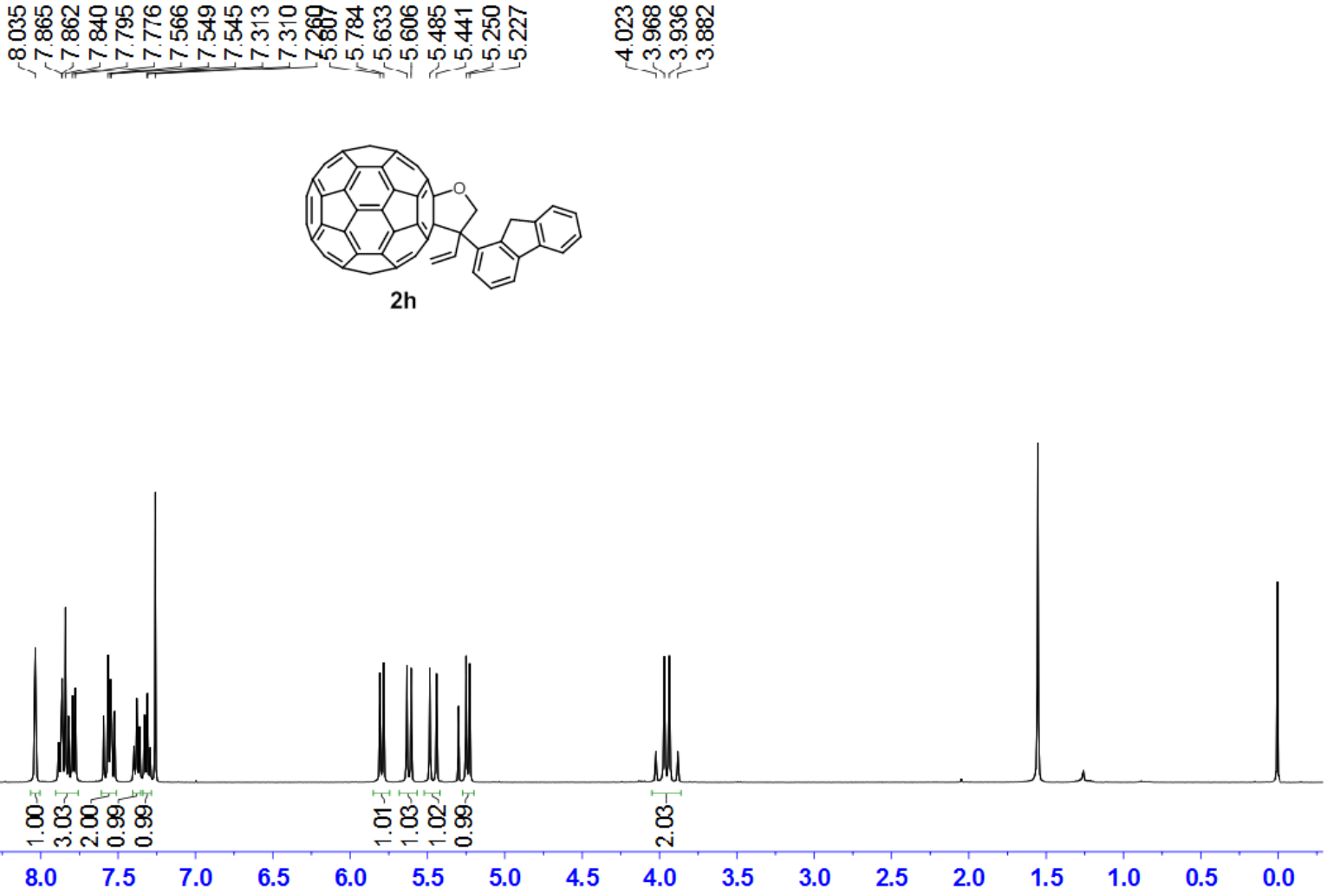
^{1}H NMR (600 MHz, $CDCl_3$) of compound 2g

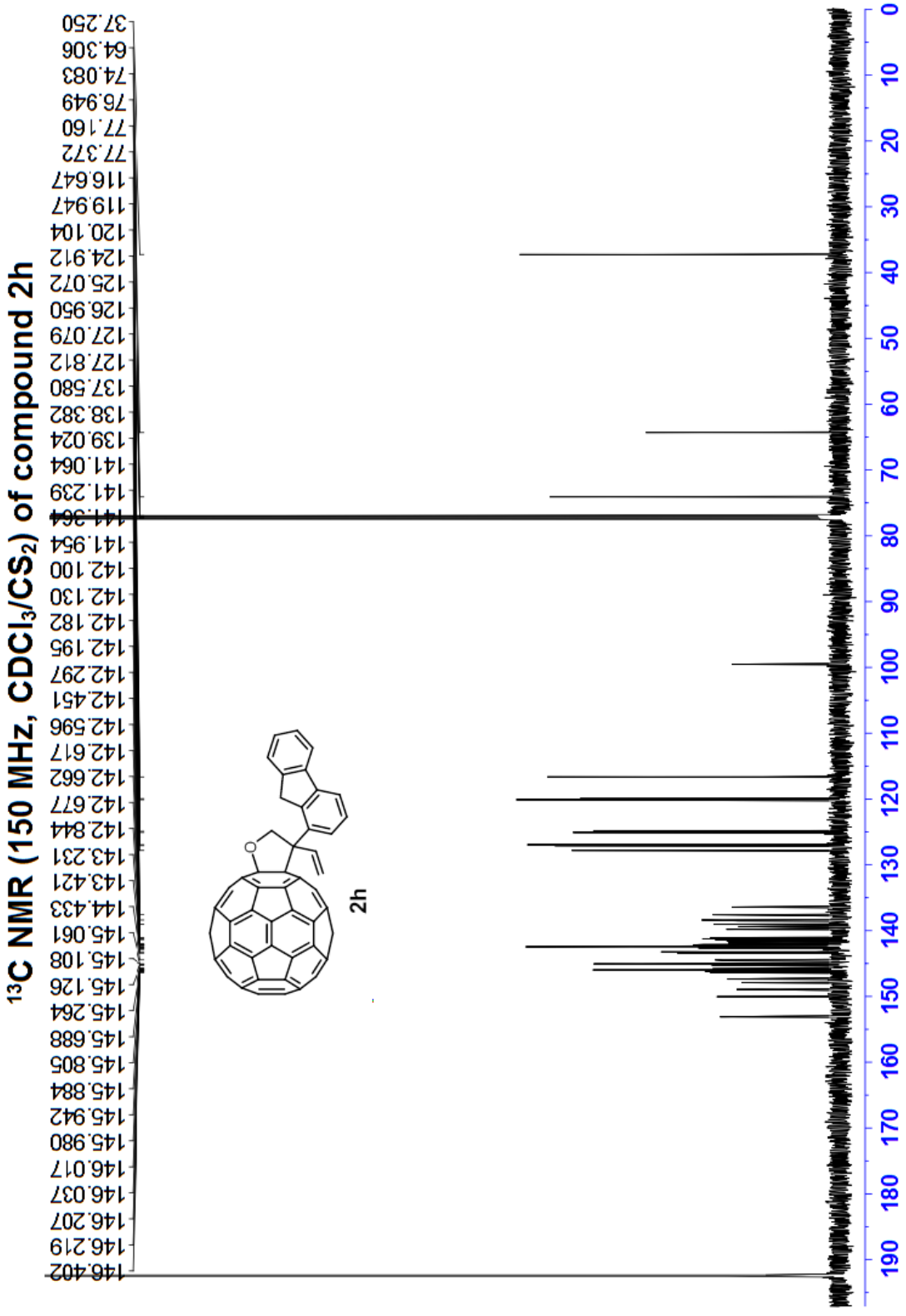


^{13}C NMR (150 MHz, $CDCl_3$) of compound 2g

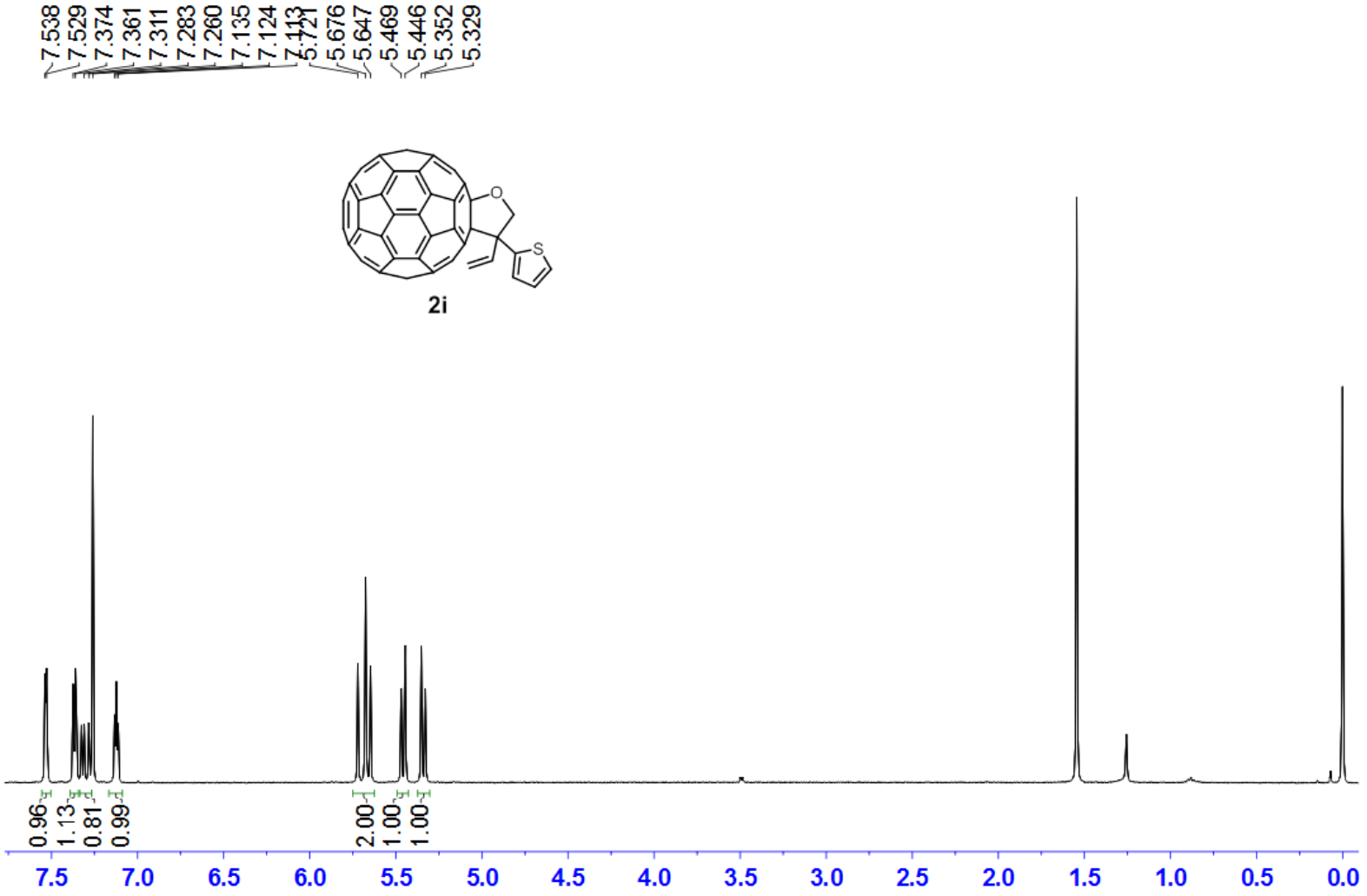


^{1}H NMR (400 MHz, $CDCl_3$) of compound 2h

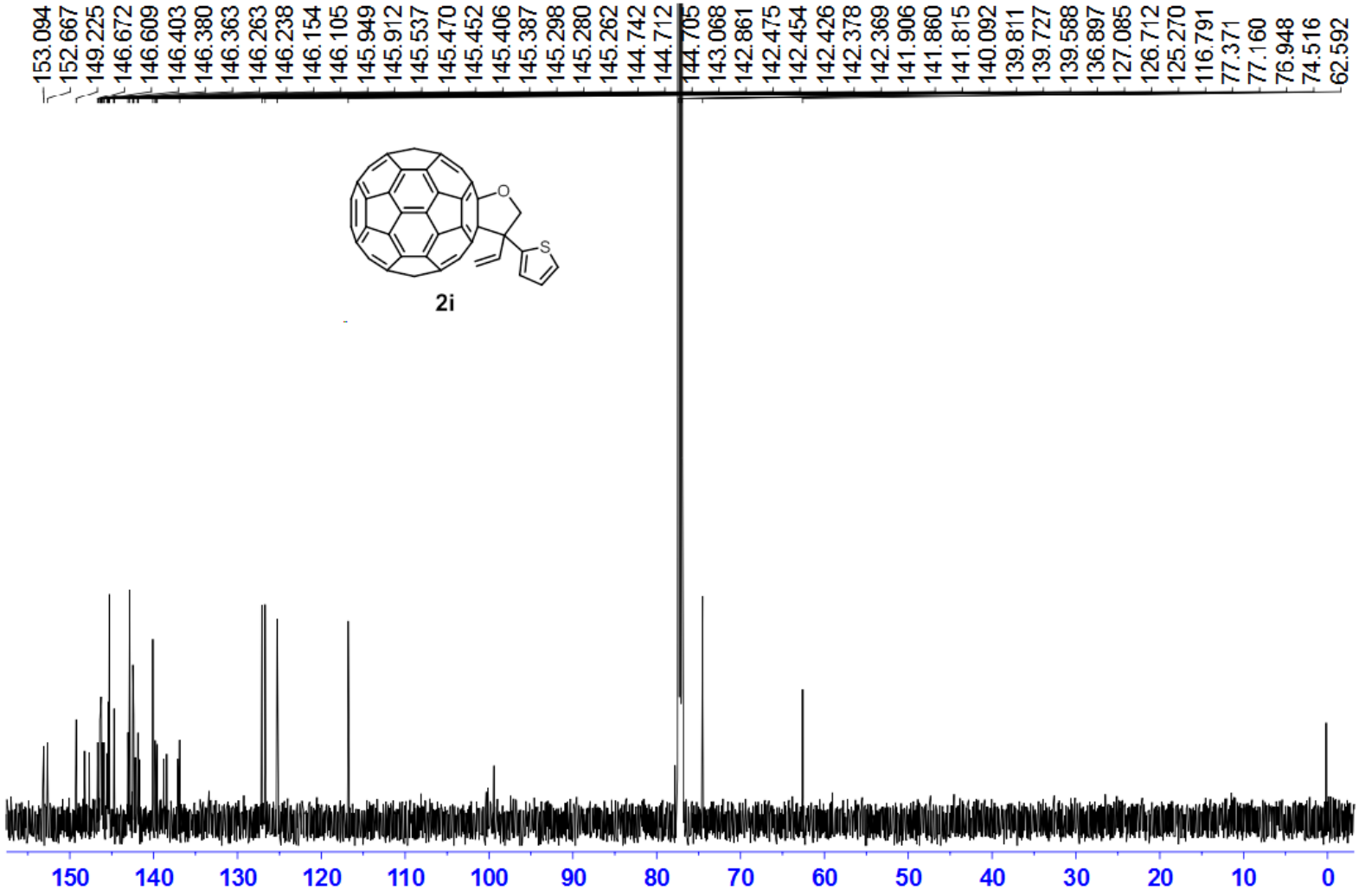



^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 2h
2h

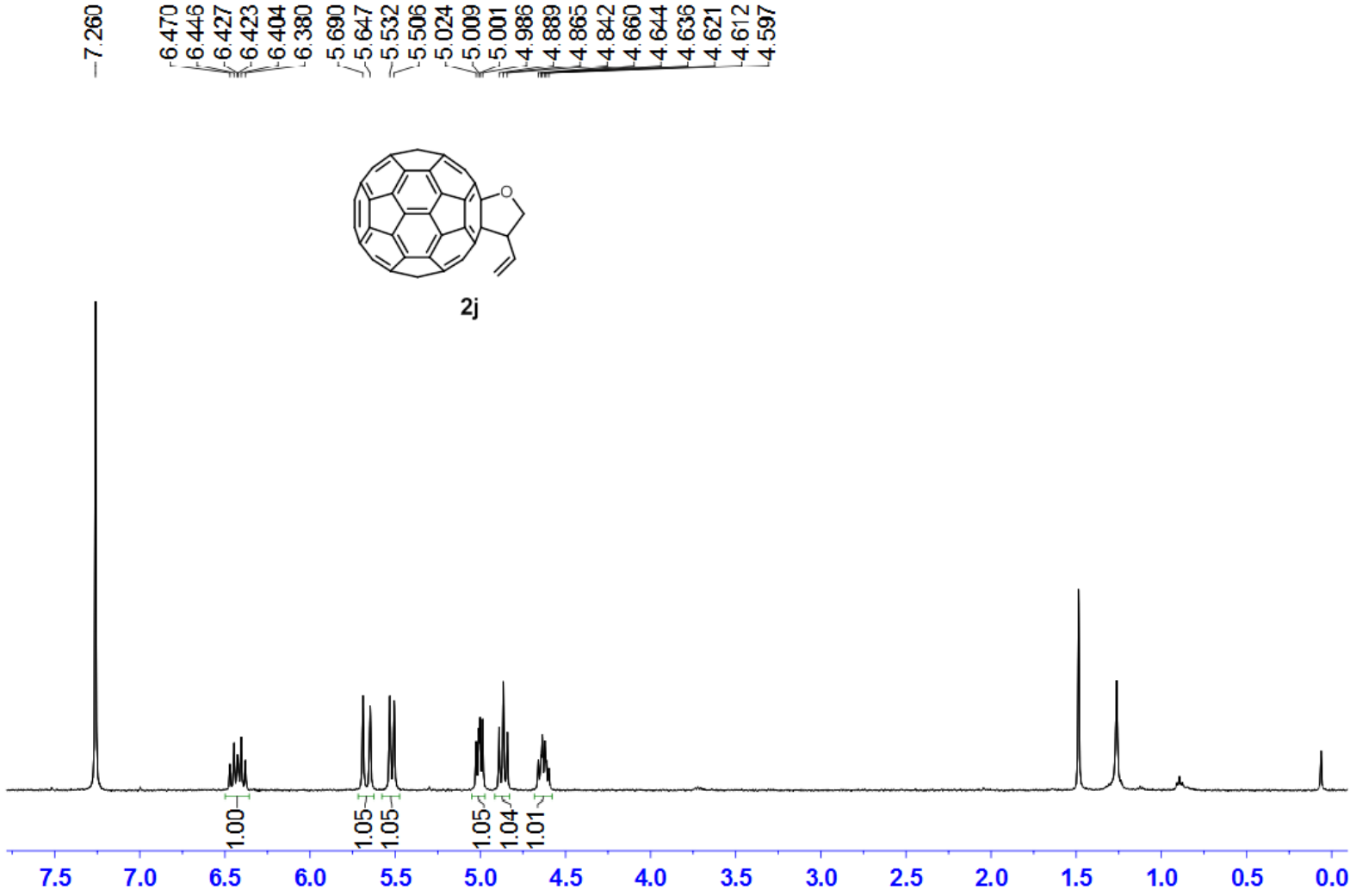
^{1}H NMR (400 MHz, $CDCl_3$) of compound 2i



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

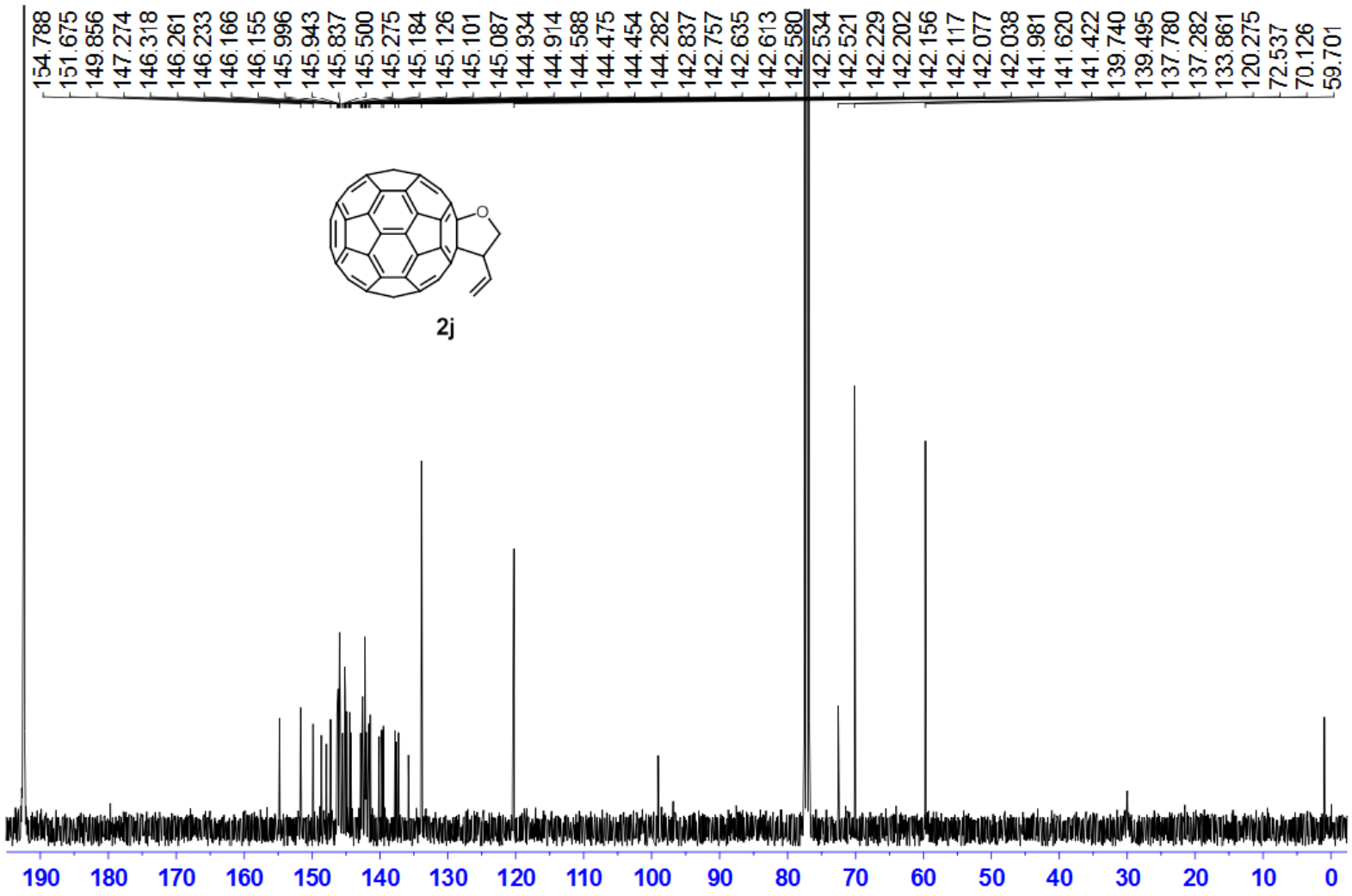


^{1}H NMR (400 MHz, $CDCl_3$) of compound 2j

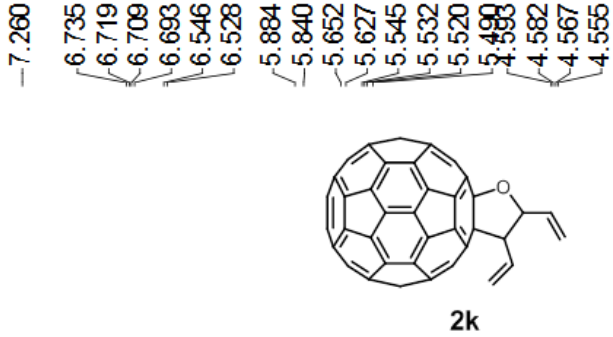


2j

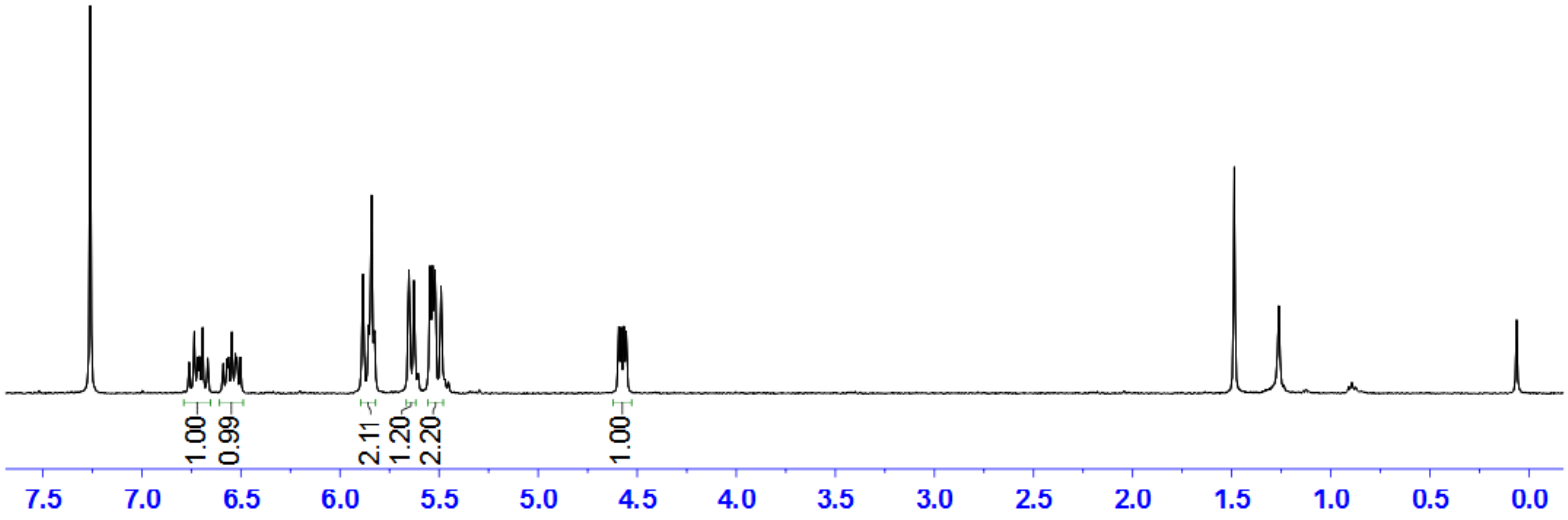
^{13}C NMR (100 MHz, $CDCl_3/CS_2$) of compound 2j

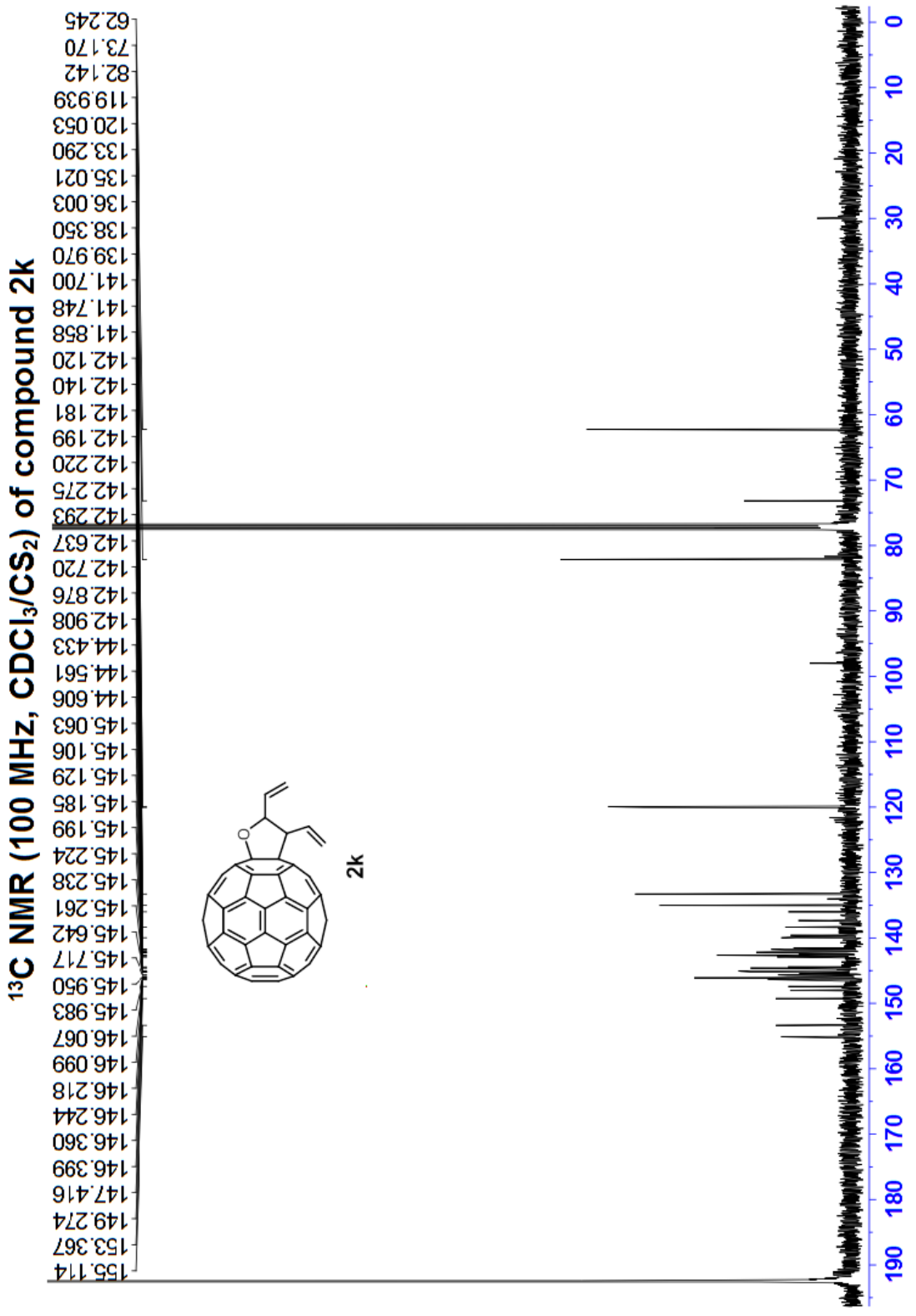


^{1}H NMR (400 MHz, $CDCl_3$) of compound 2k

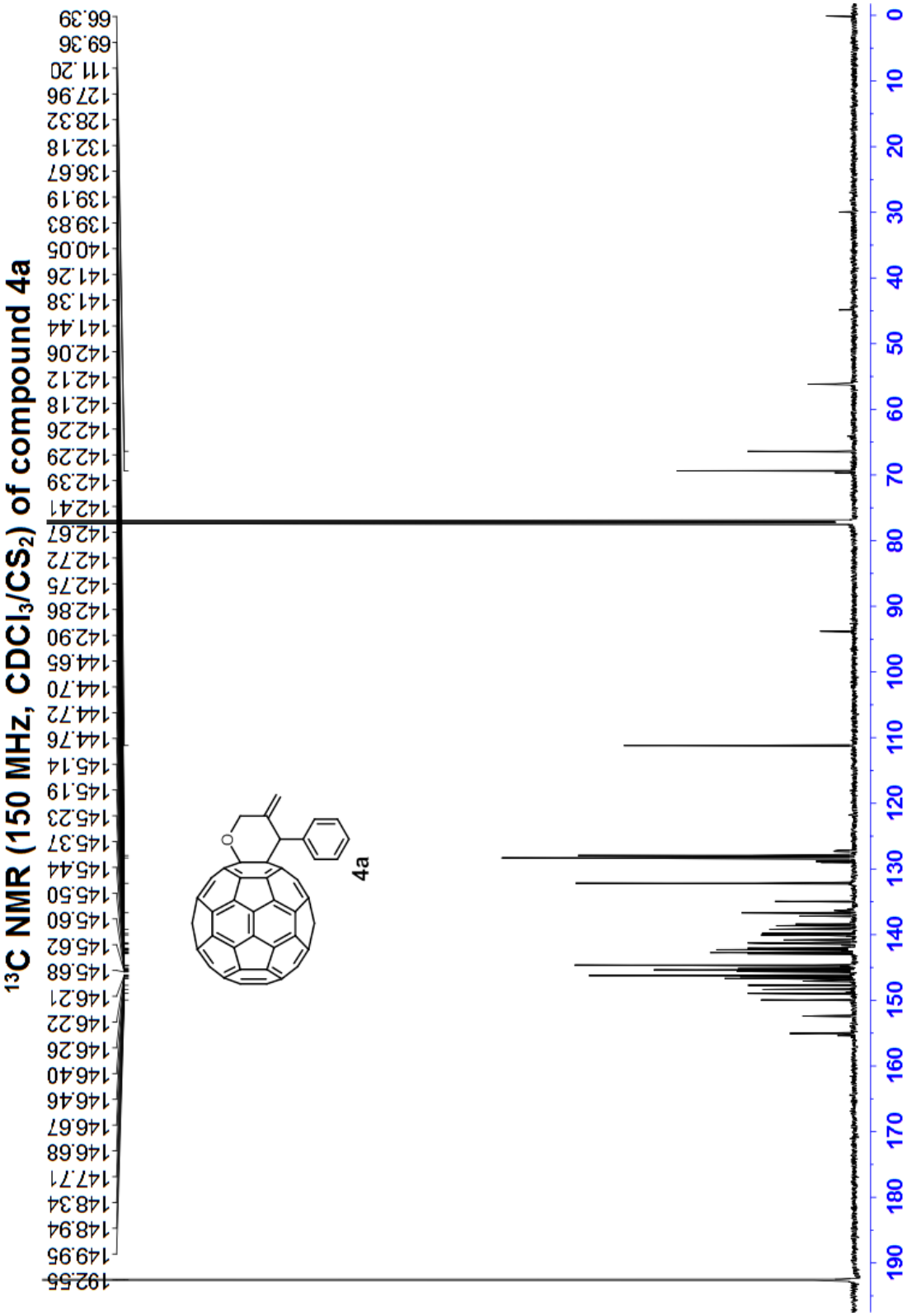


2k

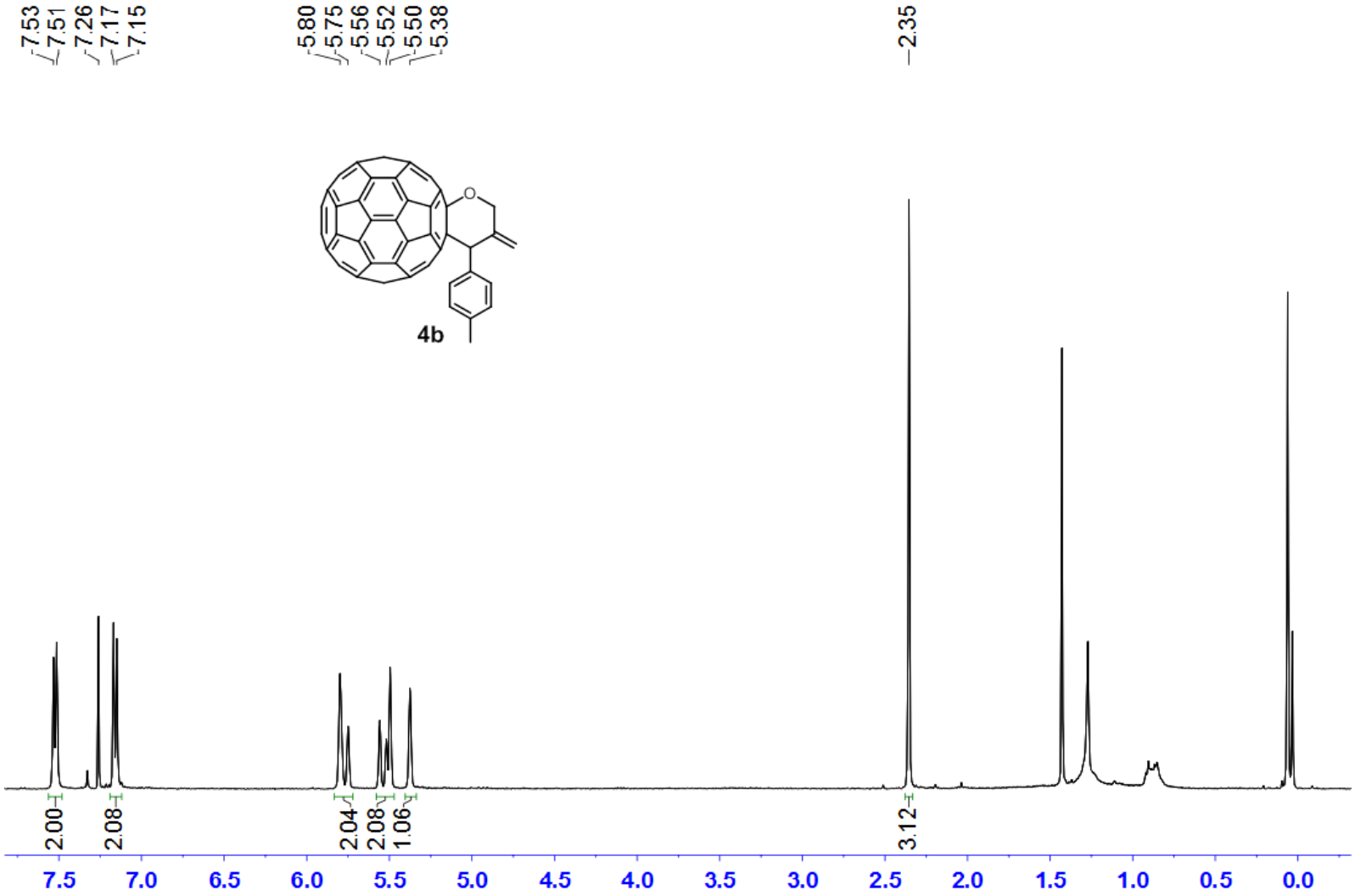


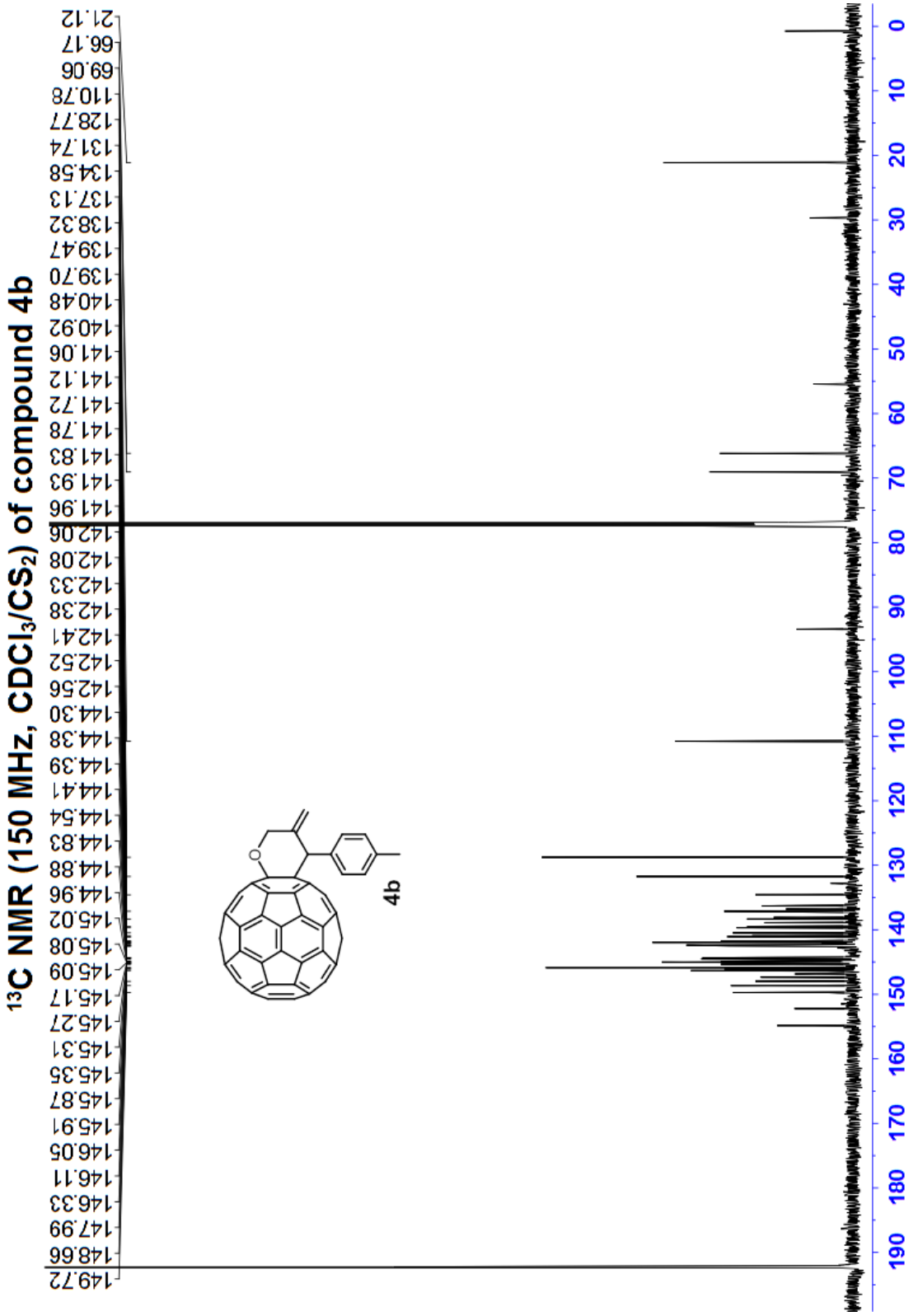

^{13}C NMR (100 MHz, $CDCl_3/CS_2$) of compound 2k
2k

^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 4a

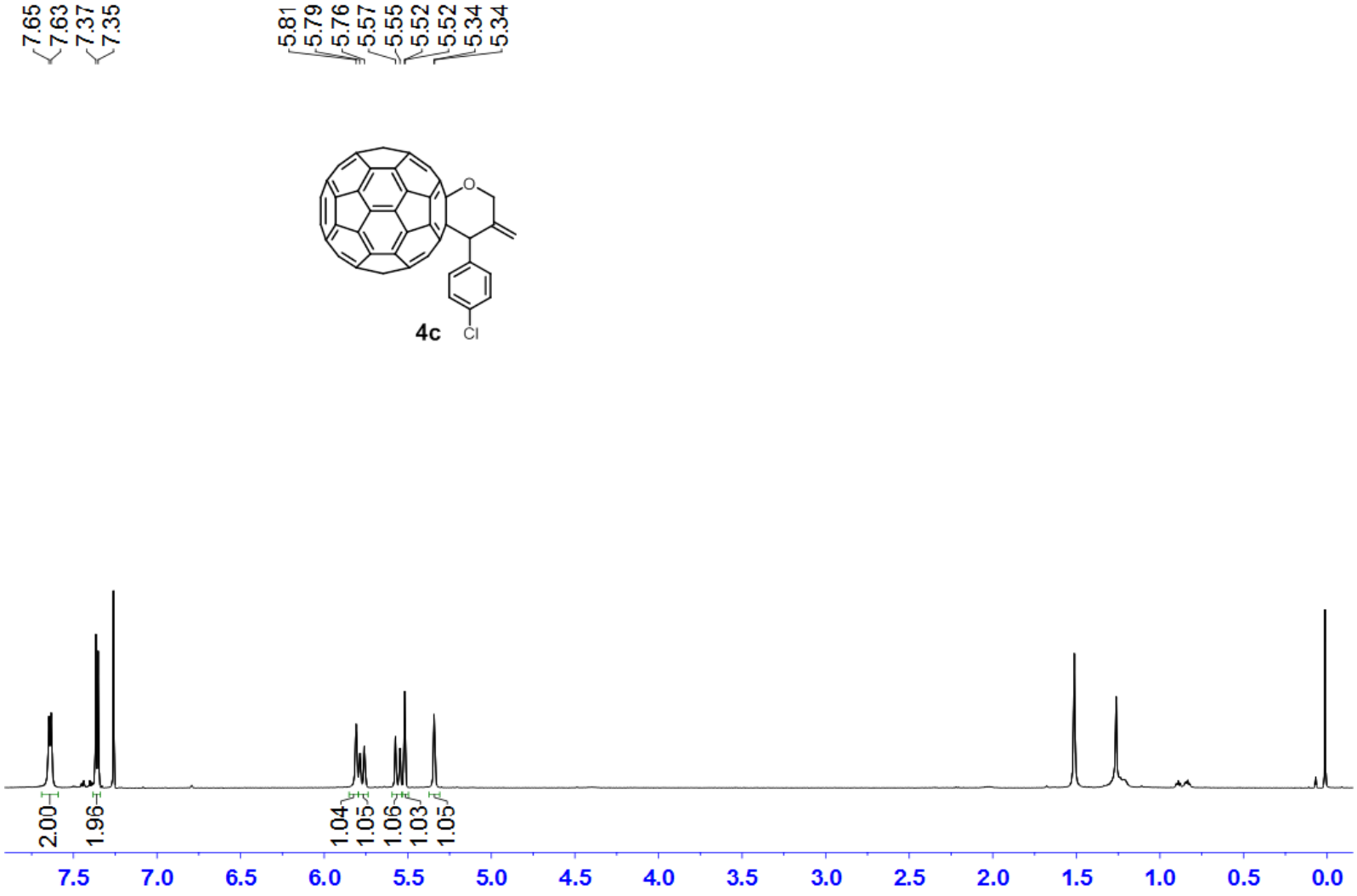

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 4a
4a

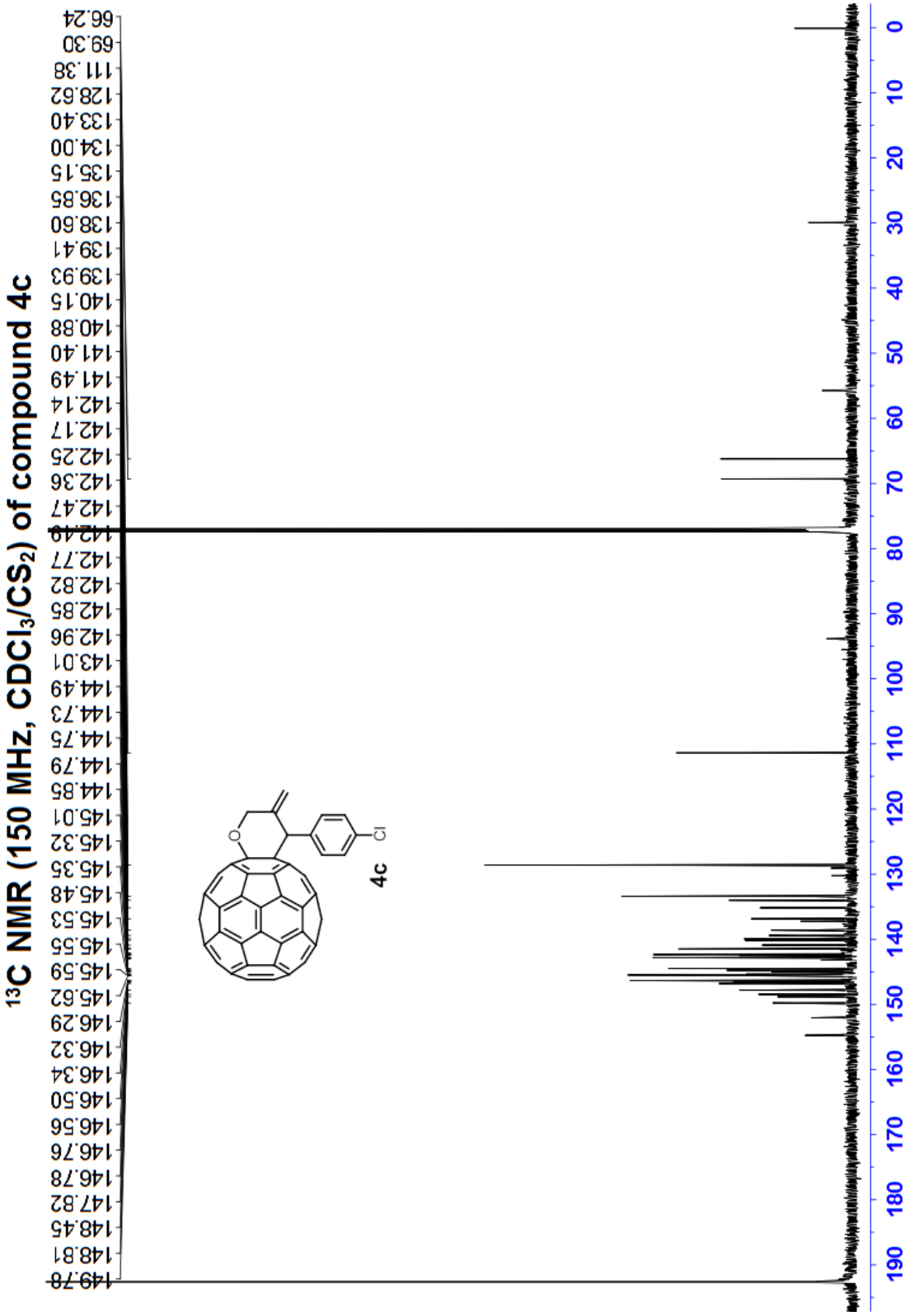
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 4b



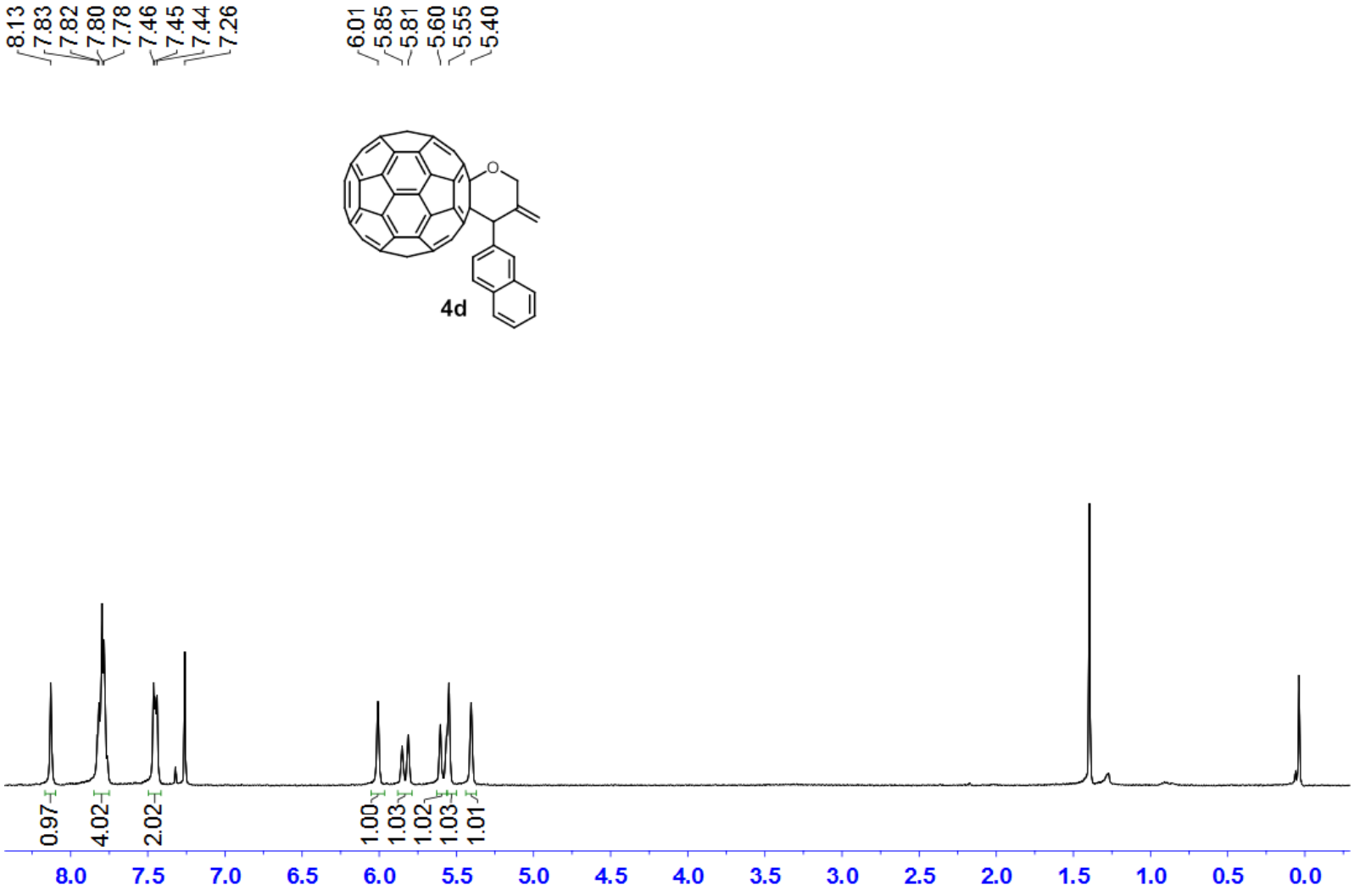

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 4b
4b

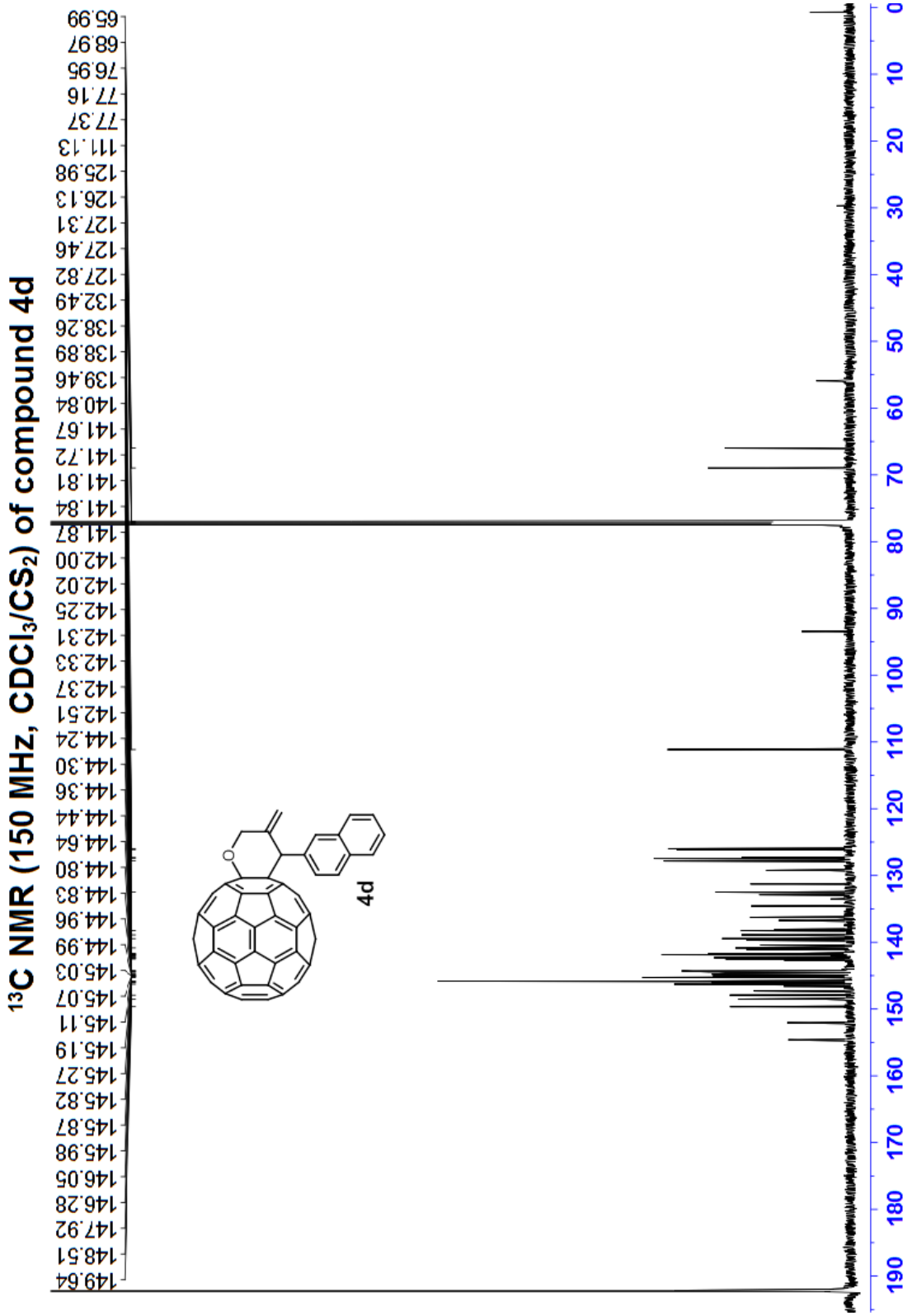
^{1}H NMR (600 MHz, $CDCl_3/CS_2$) of compound 4c



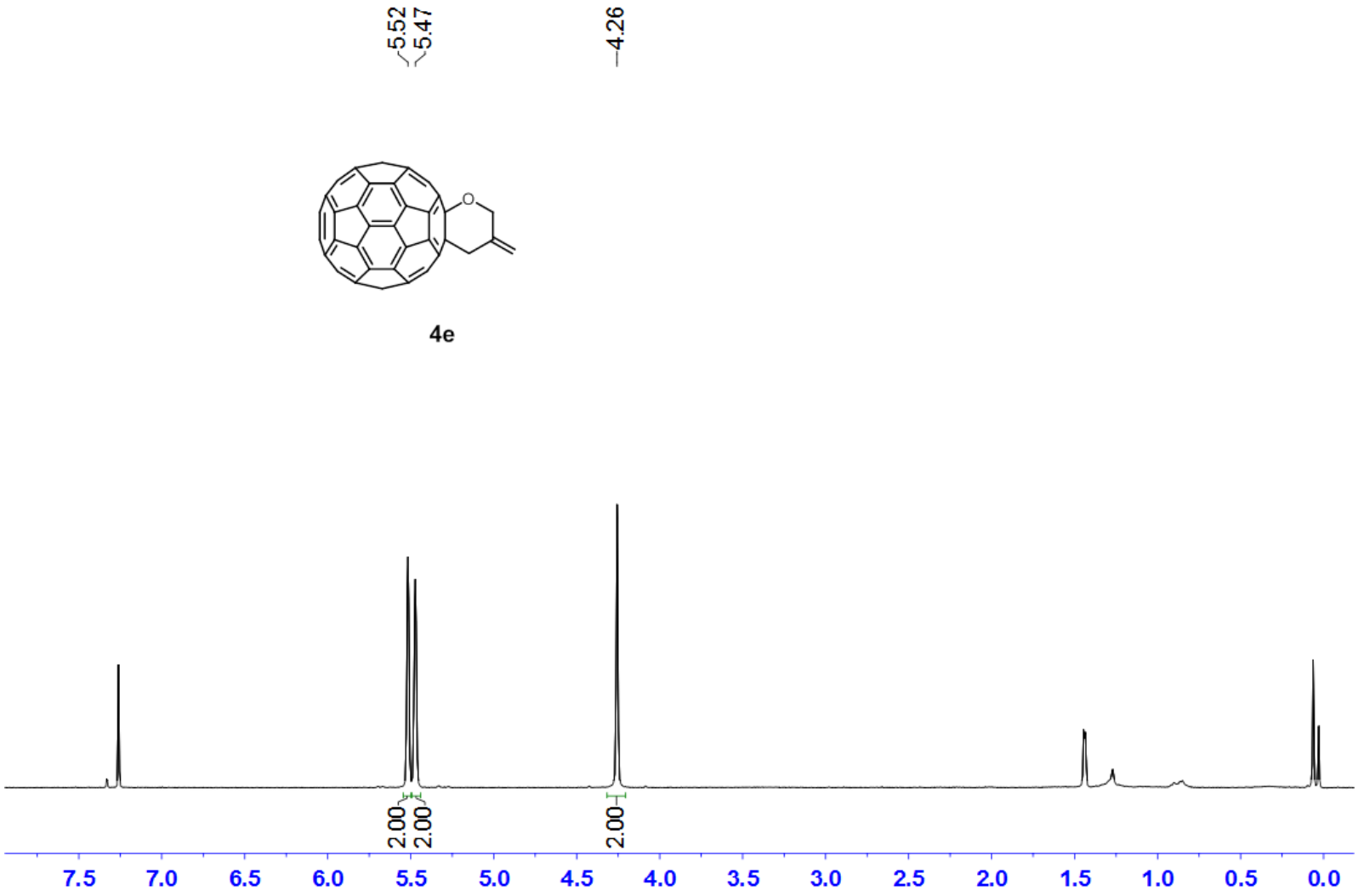

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 4c
4c
Cl
O

^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 4d

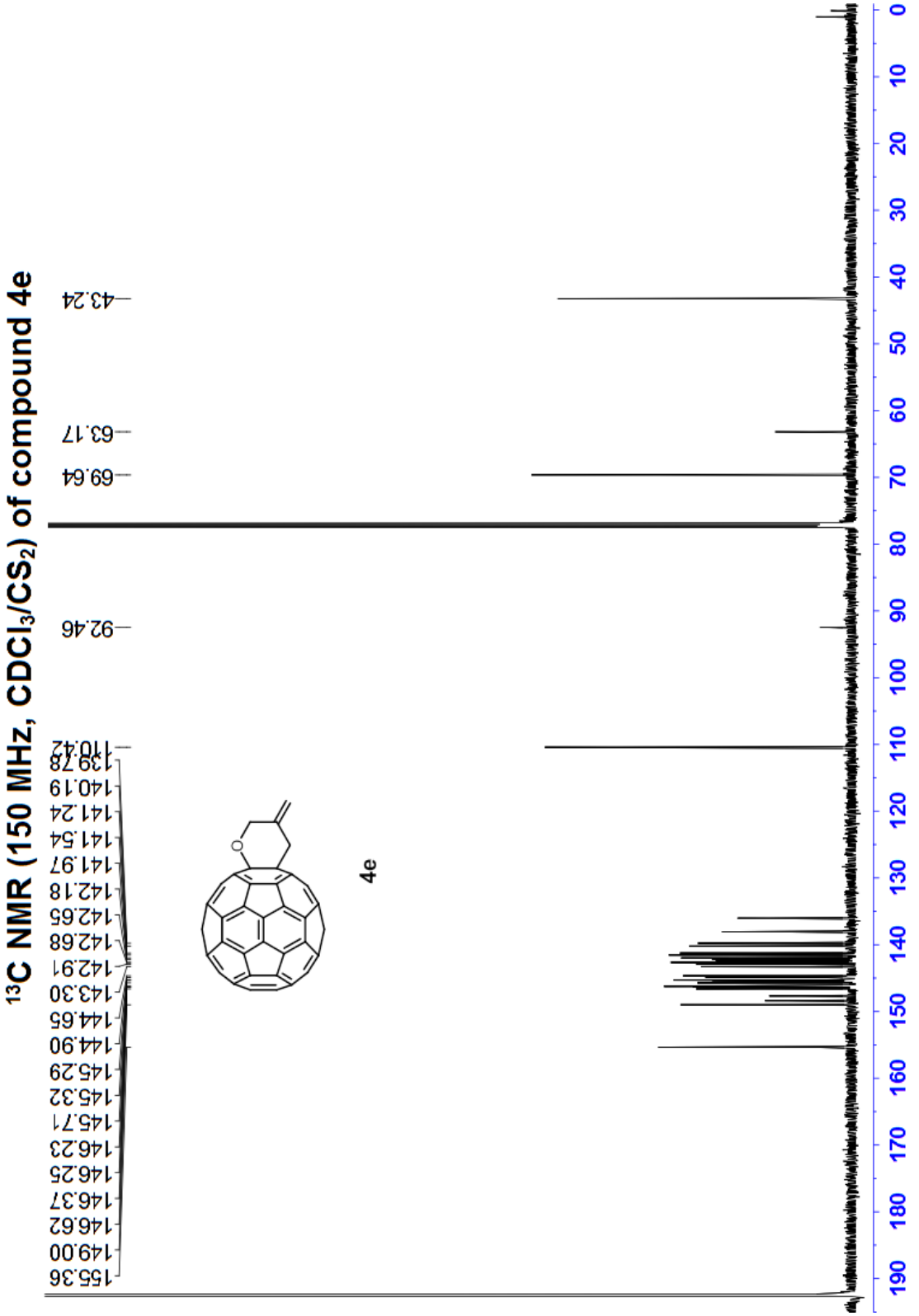



^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 4d
4d
149.64
148.51
147.92
146.28
146.05
145.98
145.87
145.82
145.27
145.19
145.11
145.07
145.03
144.99
144.96
144.83
144.80
144.64
144.44
144.36
144.30
144.24
142.51
142.37
142.33
142.31
142.25
142.02
142.00
141.87
141.84
141.81
141.72
141.67
140.84
139.46
138.89
138.26
132.49
127.82
127.46
127.31
126.13
125.98
111.13
77.37
77.16
76.95
68.97
65.99
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

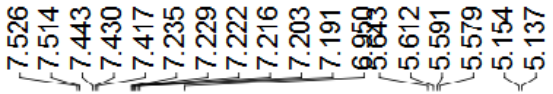
^{1}H NMR (400 MHz, $CDCl_3/CS_2$) of compound 4e

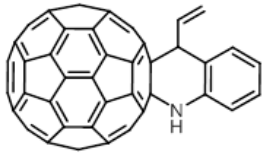


4e

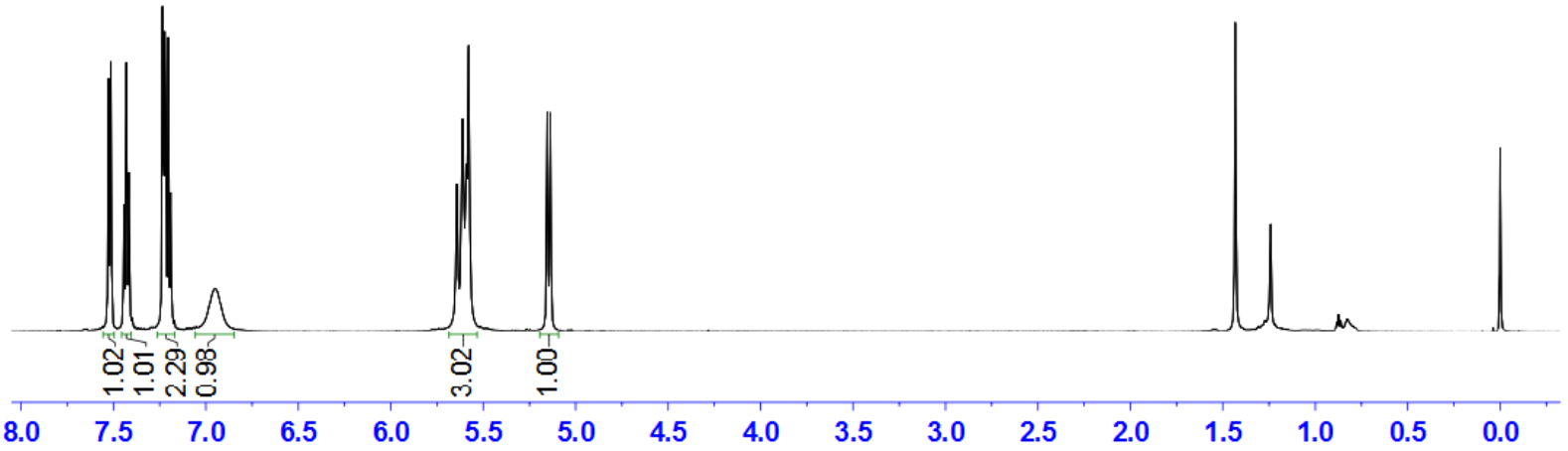

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 4e
4e
43.24
63.17
69.64
92.46
110.42
139.78
140.19
141.24
141.54
141.97
142.18
142.65
142.68
142.91
143.30
144.65
144.90
145.29
145.32
145.71
146.23
146.25
146.37
146.62
149.00
155.36
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

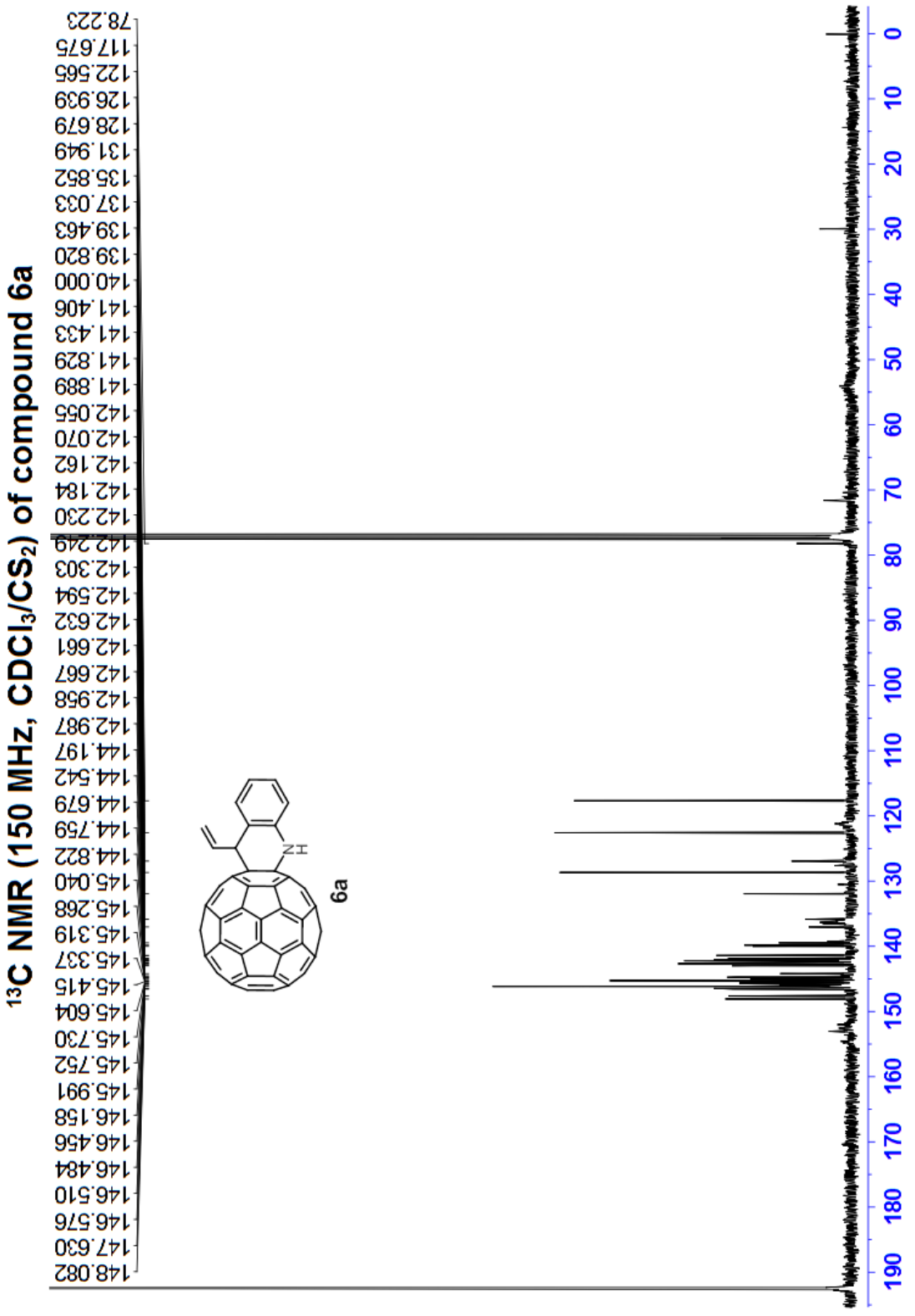
^{1}H NMR (600 MHz, $CDCl_3$) of compound 6a



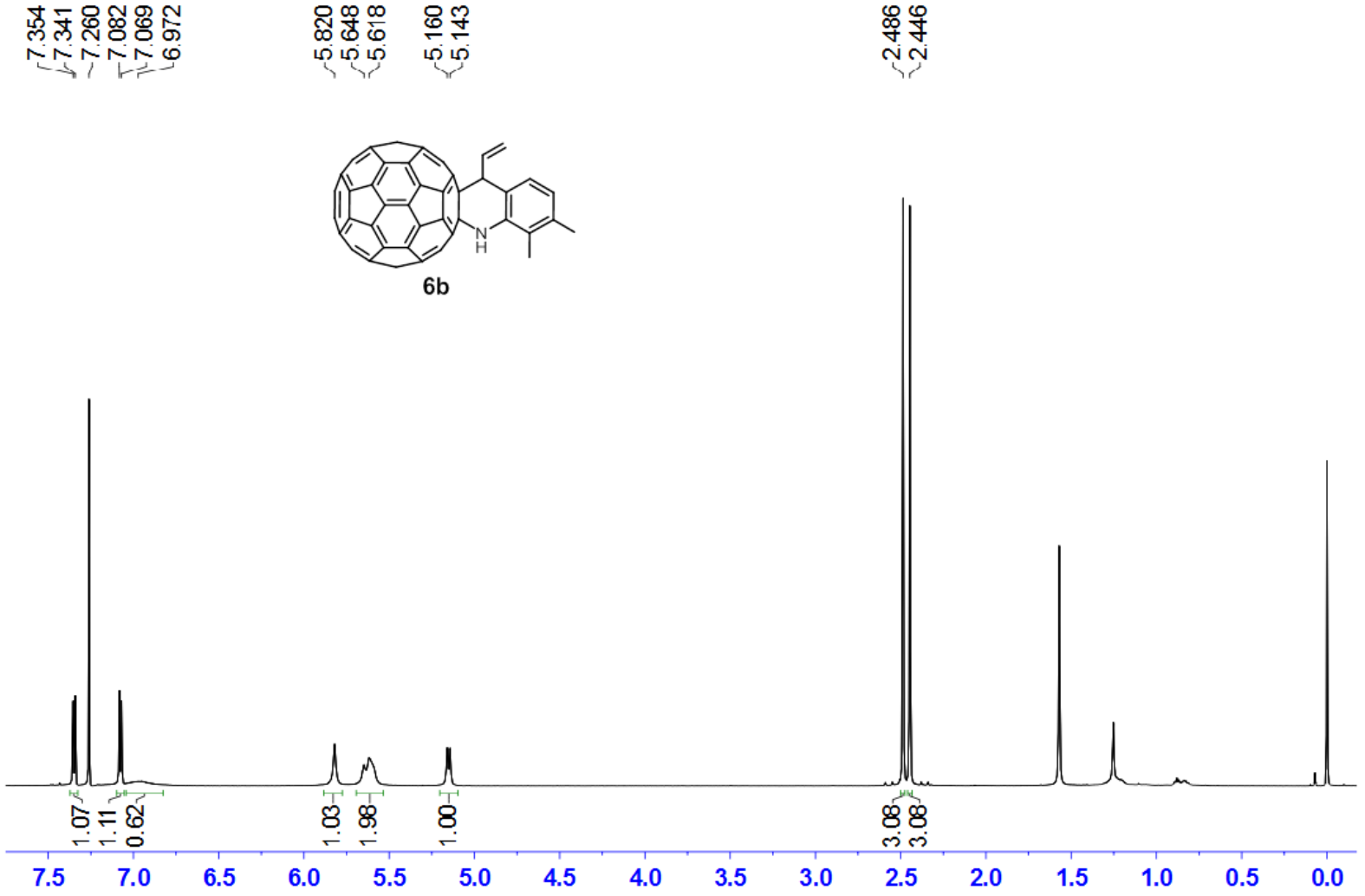


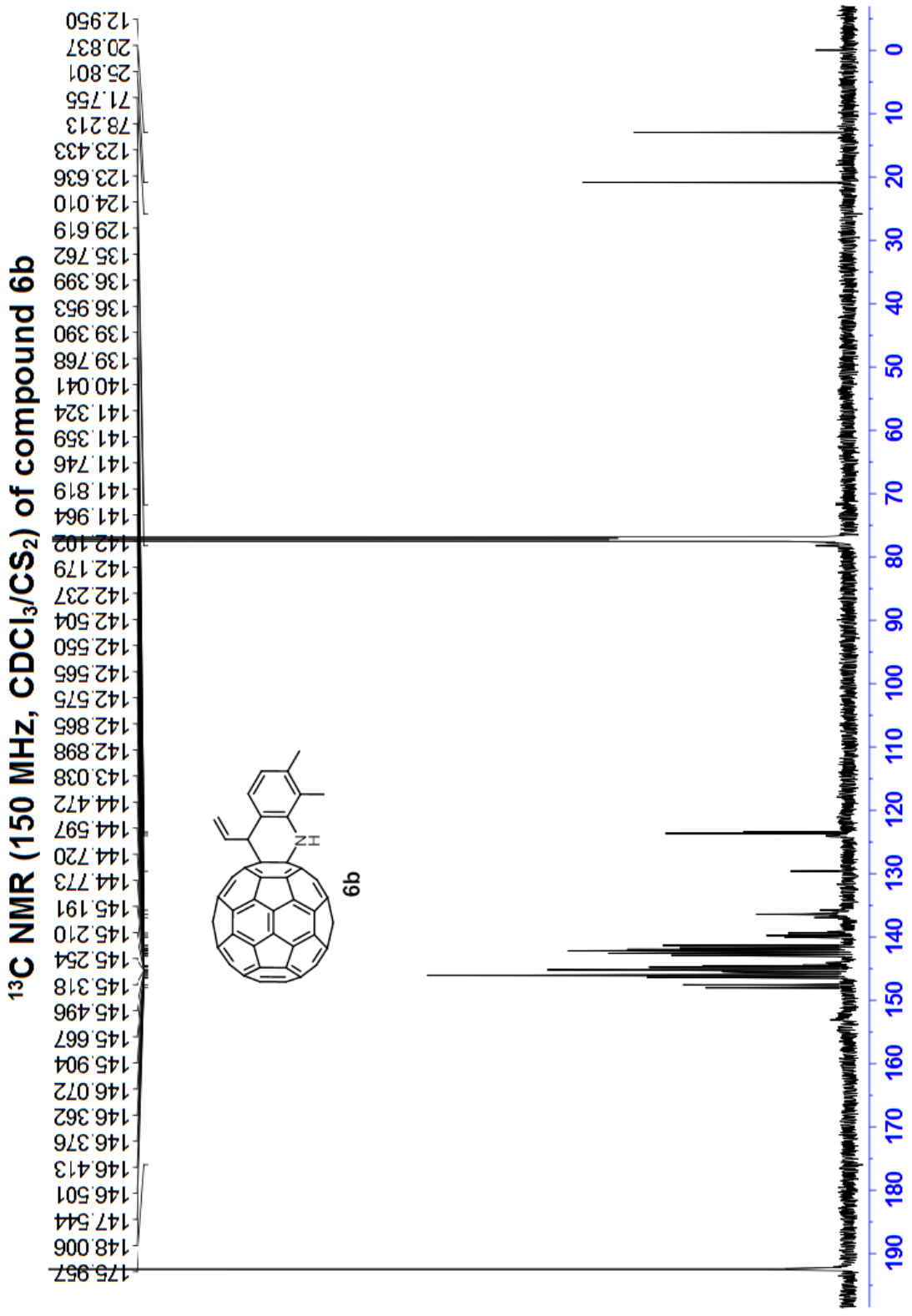
6a



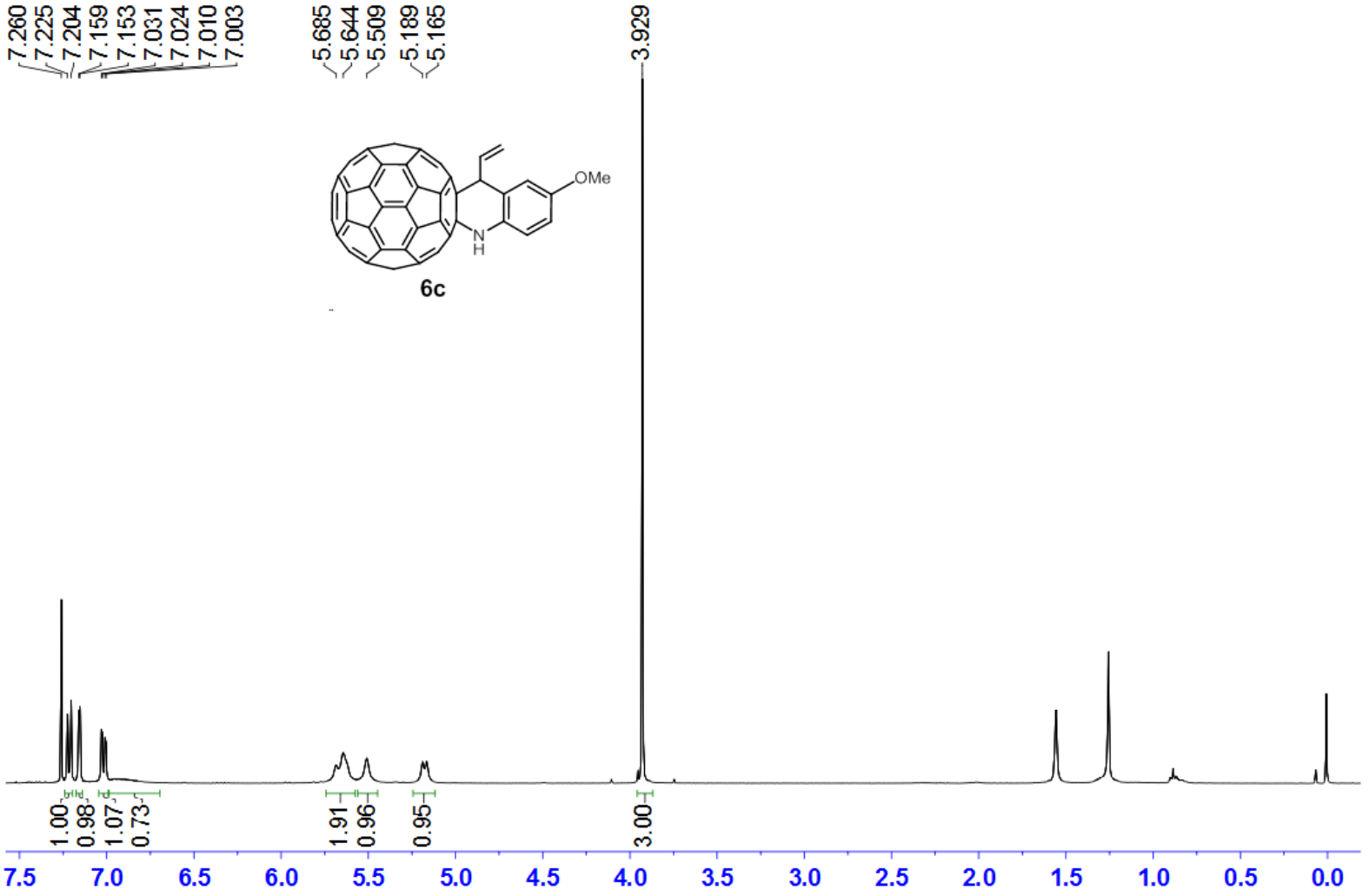

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 6a
6a
148.082
147.630
146.576
146.510
146.484
146.456
146.158
145.991
145.752
145.730
145.604
145.415
145.337
145.319
145.268
145.040
144.822
144.759
144.679
144.542
144.197
142.987
142.958
142.667
142.661
142.632
142.594
142.303
142.249
142.230
142.184
142.162
142.070
142.055
141.889
141.829
141.433
141.406
140.000
139.820
139.463
137.033
135.852
131.949
128.679
126.939
122.565
117.675
78.223
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

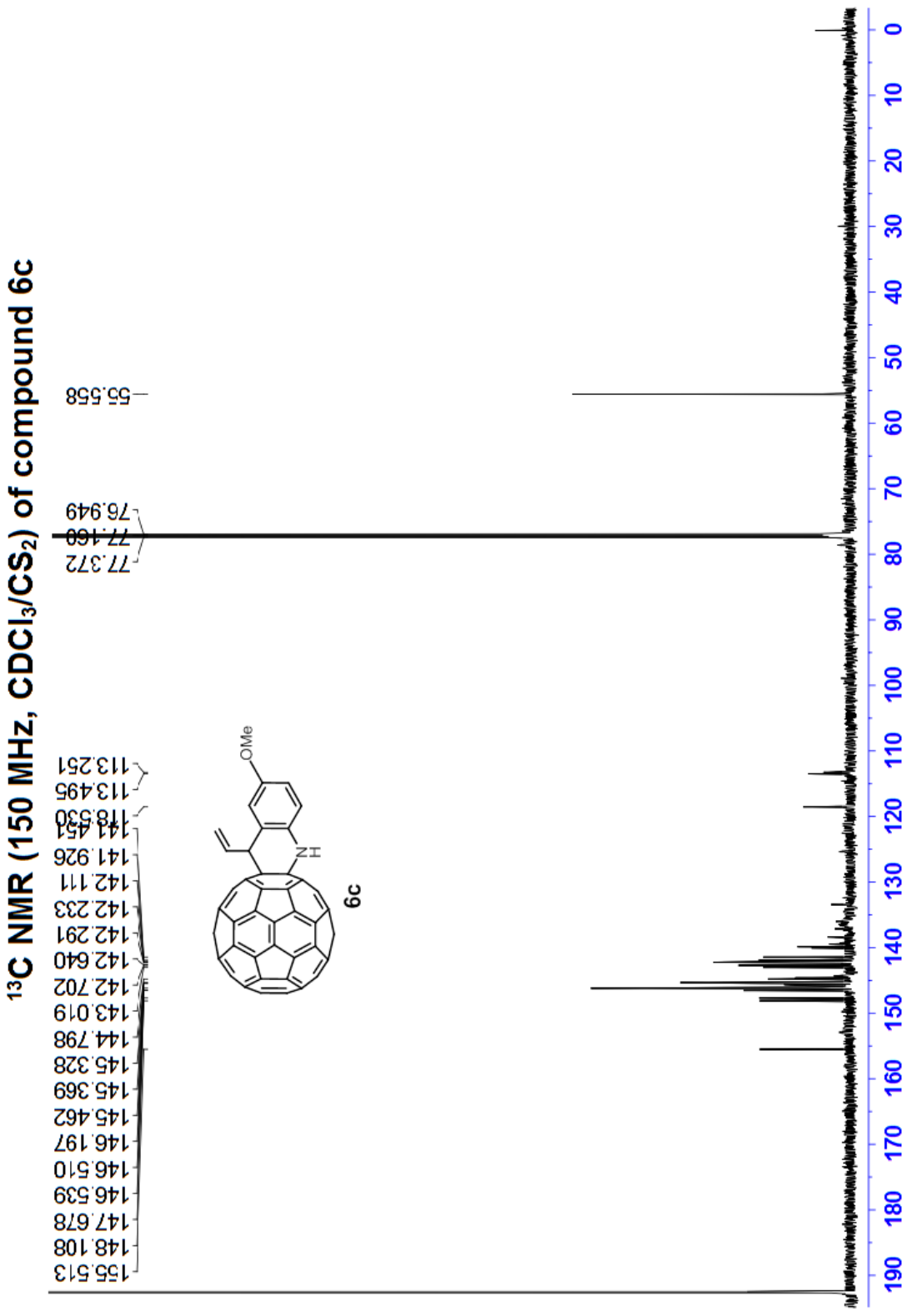
^{1}H NMR (600 MHz, $CDCl_3$) of compound 6b



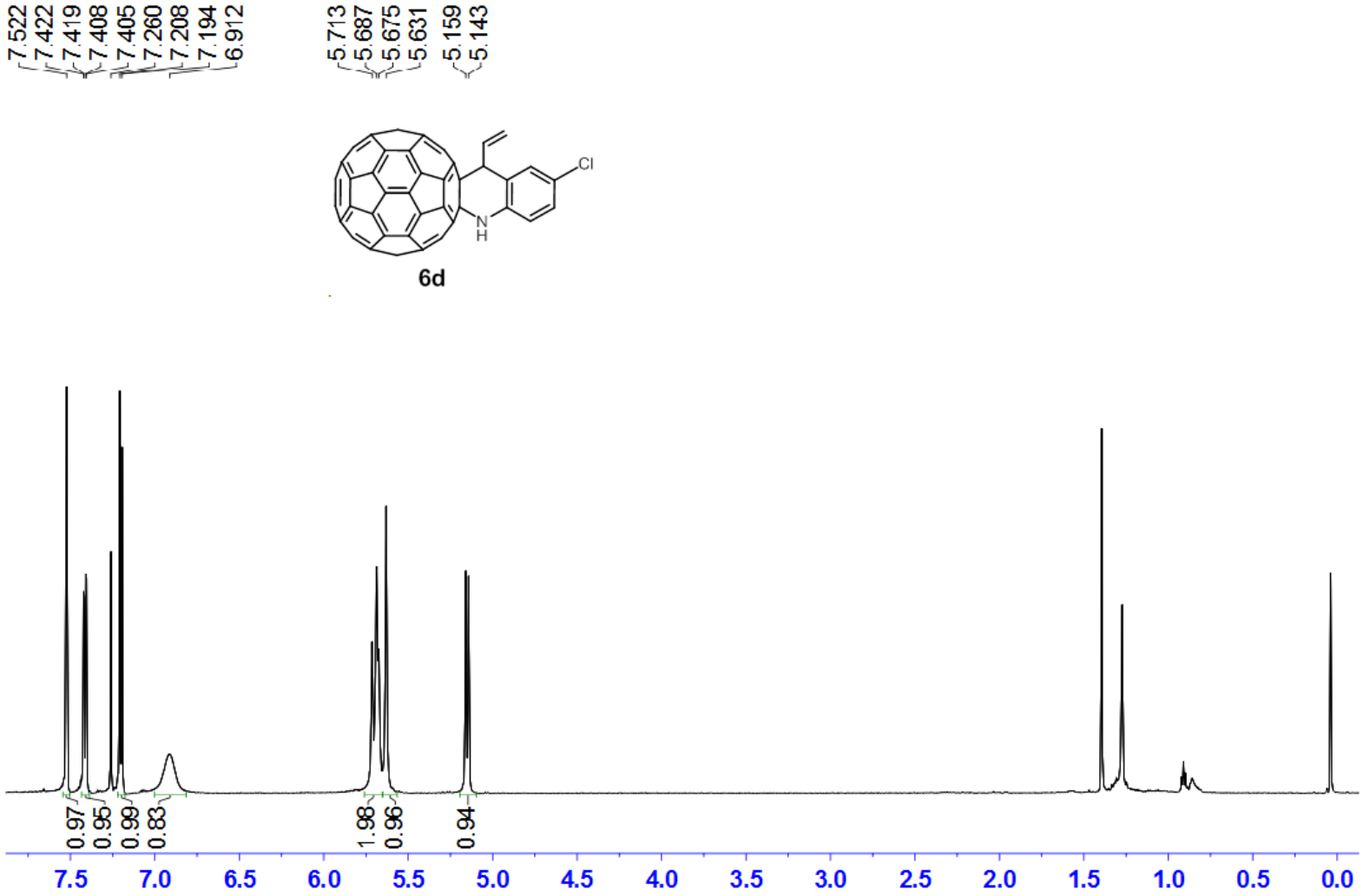

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 6b
6b
NH

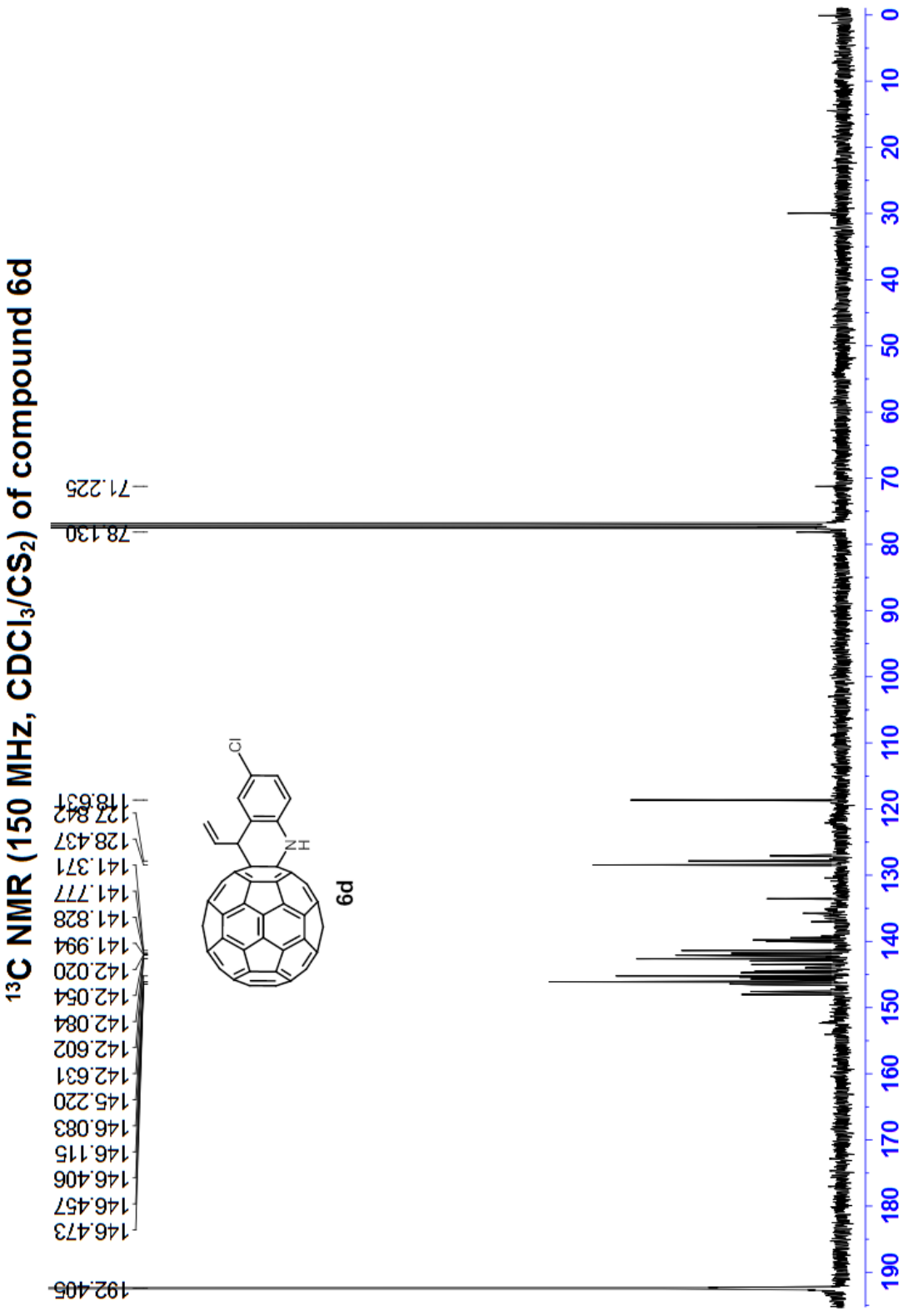
^{1}H NMR (400 MHz, $CDCl_3$) of compound 6c



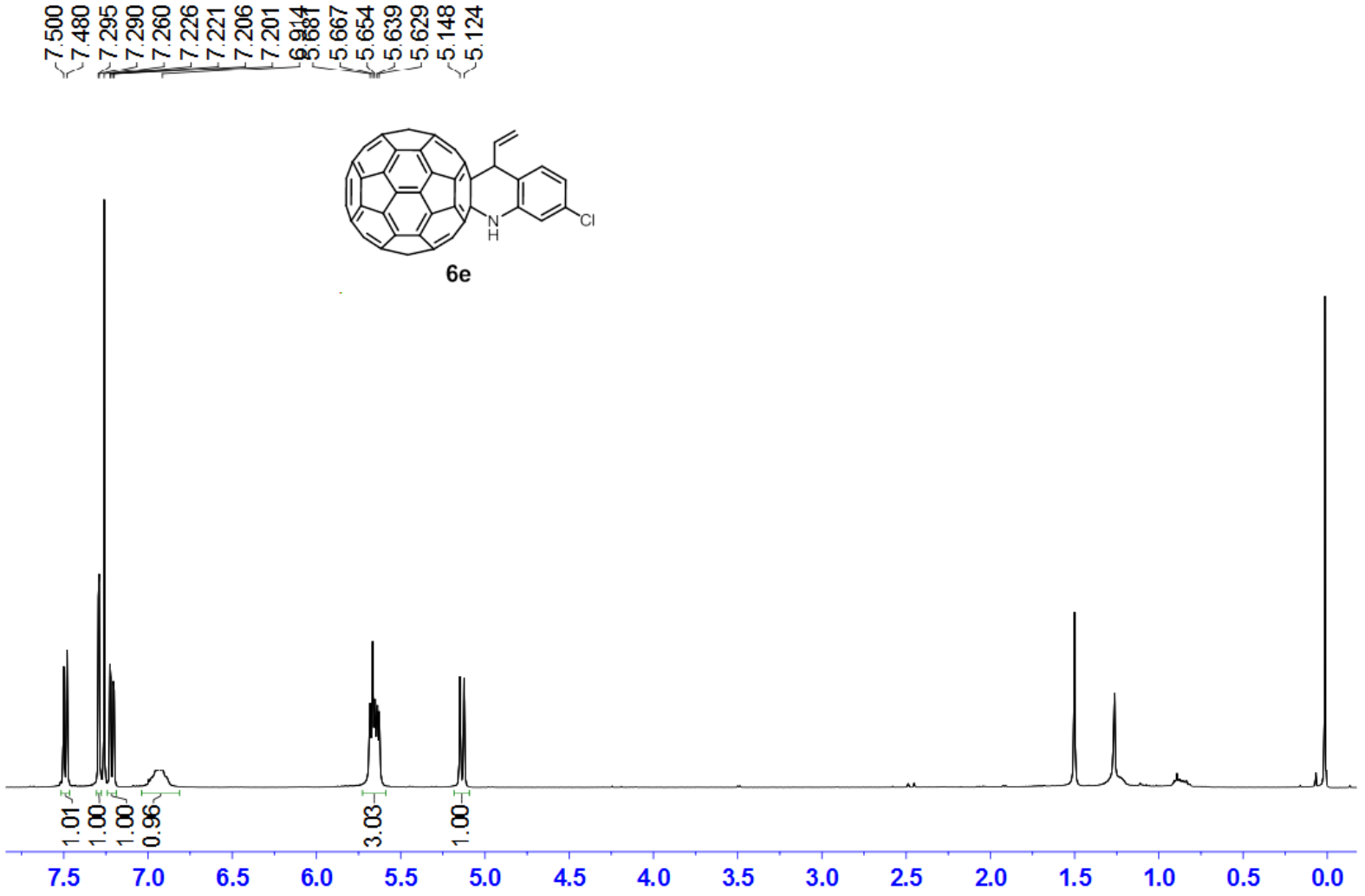

^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 6c
155.513
148.108
147.678
146.539
146.510
146.197
145.462
145.369
145.328
144.798
143.019
142.702
142.640
142.291
142.233
142.111
141.926
141.451
118.530
113.495
113.251
77.372
77.160
76.949
55.558
OMe
NH
6c

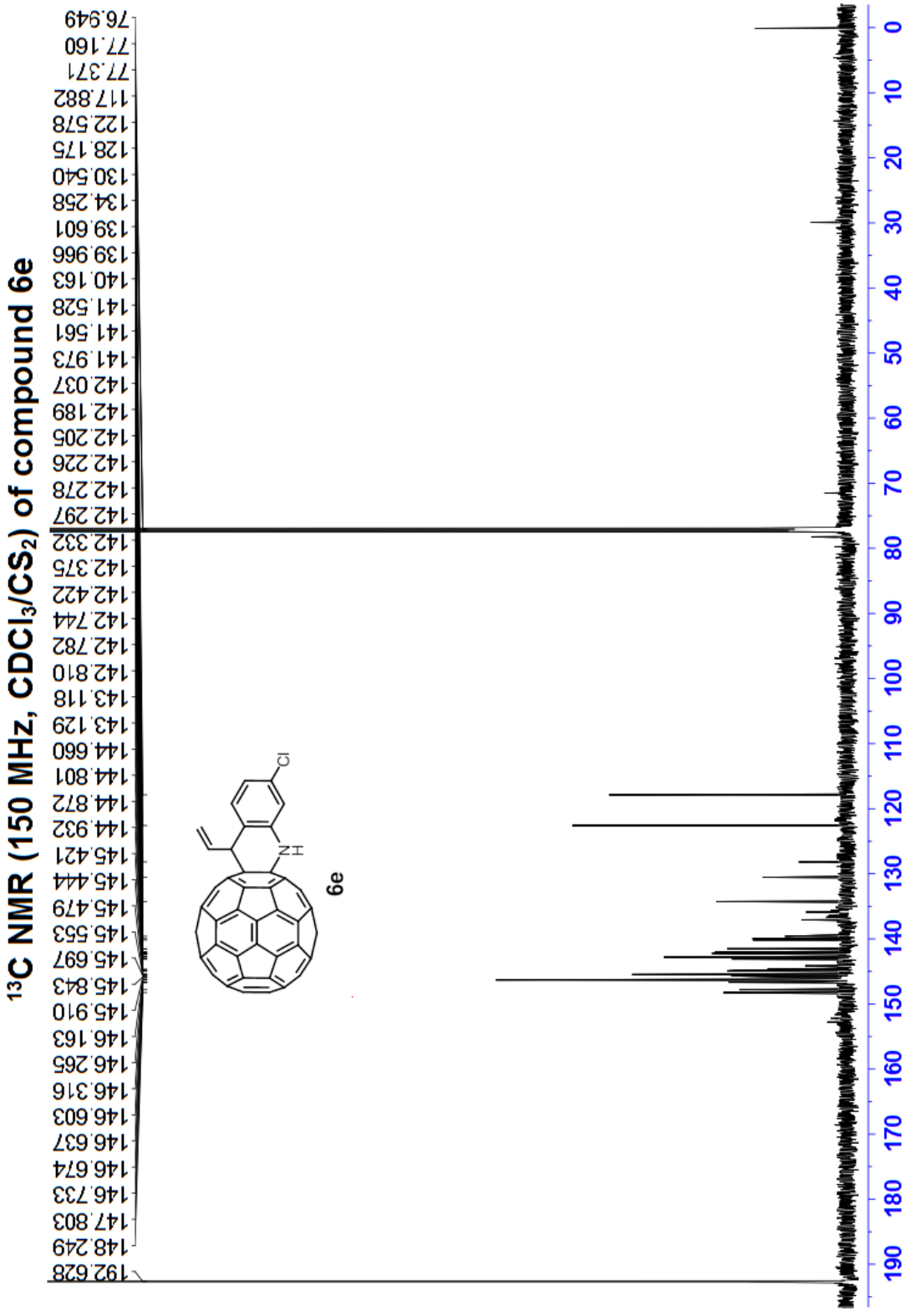
^{1}H NMR (600 MHz, $CDCl_3$) of compound 6d




^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 6d
192.405
146.473
146.457
146.406
146.115
146.083
145.220
142.631
142.602
142.084
142.054
142.020
141.994
141.828
141.777
141.371
128.437
127.842
118.631
78.130
71.225
Cl
NH
6d
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

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




^{13}C NMR (150 MHz, $CDCl_3/CS_2$) of compound 6e
6e
Cl
N
H