Electronic Supplementary Material (ESI) for RSC Advances.

Influence of the heteroatom introduction on the physicochemical properties of 5-heterotruxenes containing nitrogen, oxygen and sulfur atom

Krzysztof Górski*, Krzysztof Noworyta, Justyna Mech-Piskorz*

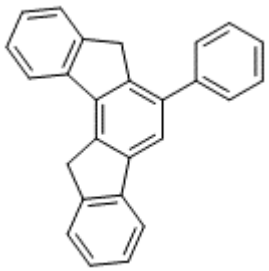
Institute of Physical Chemistry, Polish Academy of Sciences; Kasprzaka 44/52, 01-224 Warsaw, Poland

KEYWORDS: truxene, heterotruxene, thiatruxene, azatruxene, oxatruxene, sulfoxide, sulfone, NMR spectra, hot chromatography,

Table of contents

1. Synthesis of NCC

Acetophenone, triphenylphosphine, methanesulfonic acid, and tetraethoxysilane were purchased at Sigma Aldrich and ABCR. 2-(Indan-1-ylidene)indan-1-one was synthesized according to literature data.[1] For reactions at higher temperatures, a heating mantle was used. Solvents used for the synthesis were analytical grade. In NMR measurement, the standard residual solvent peak was taken as an internal NMR chemical shift.



6-phenyl-7,12-dihydroindeno[1,2-a]fluorene, ***5*** – 2-(Indan-1-ylidene)indan-1-one **1** (246 mg, 1 mmol) and acetophenone **2** (132 mg, 1.1 mmol) were dissolved in 3 ml of dichloromethane. Next methanesulfonic acid (130 µL, 2 mmol, 1,484 g/mL) and tetraethoxysilane (0.9 mL, 4 mmol, 0.933 g/mL) were added. Then the temperature of obtained mixture was increased to 50 °C. After 72 h mixture was adsorbed at 1 g of silica gel and the crude product was purified via "hot" chromatography (see page S7 SI) using 1 g of silica gel, as stationary phase, and boiling hexane, as eluent. After evaporation of the majority of the solvent, the precipitate was filtered off and washed two times with 2 mL of cooled methanol to obtain 198 mg of **5,** as pale yellow solid, with the reaction yield of 60%.

Procedure without orthosilicate: 2-(Indan-1-ylidene)indan-1-one **1** (246 mg, 1 mmol) and acetophenone **2** (132 mg, 1.1 mmol) were dissolved in 0.5 mL of 1,2-dichloroethane. After the addition of methanesulfonic acid (130 µL, 2 mmol, 1,484 g/mL) temperature of the obtained mixture was increased to 100 °C. After 72 h mixture was adsorbed at 1 g of silica gel and the crude product was purified via "hot" chromatography (see page S7 SI) using 1 g of silica gel, as stationary phase, and boiling hexane, as eluent. After evaporation of the majority of the solvent obtained precipitate was filtered off and washed two times with 2 mL of cooled methanol to obtain 185 mg of **5,** as pale yellow solid, with the reaction yield of 56%.

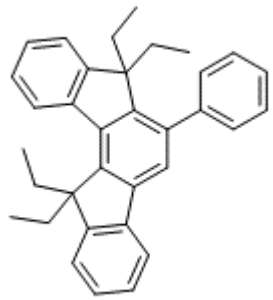
^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.96 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.79 (s, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.65 (d, *J* = 1.2 Hz, 1H), 7.64 (s, 1H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.43 (dd, *J* = 14.6, 7.3 Hz, 2H), 7.36 (t, *J* = 7.1 Hz, 2H), 4.25 (s, 2H), 4.03 (s, 2H)

7.43 (dd, *J* = 14.6, 7.3 Hz, 2H), 7.36 (t, *J* = 7.1 Hz, 2H), 4.25 (s, 2H), 4.03 (s, 2H)

^{13}C {^{1}H} NMR (126 MHz, CD_2Cl_2) δ: 144.4, 143.9, 142.2, 141.9, 141.9, 141.8, 140.4, 138.6, 138.3, 135.9, 129.1, 128.9, 127.6, 127.2, 127.2, 127.1, 127.0, 125.6, 125.4, 122.5, 120.2, 119.2, 37.7, 36.5

HRMS (EI–TOF) m/z (M+): calcd for $C_{26}H_{18}$, 330.1409; found, 330.1410;

elemental analysis (%): calcd for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.55; H, 5.45.



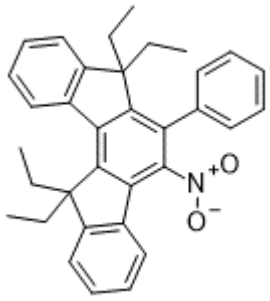
7,7,12,12-tetraethyl-6-phenyl-7,12-dihydroindeno[1,2-a]fluorene, ***6*** – 6-phenyl-7,12-dihydroindeno[1,2-a]fluorene **5** (990 mg, 3 mmol) was dispersed in the mixture of 15 mL of tetrahydrofuran and 15 mL of N-methylpirolidone. Then the obtained solution was deaerated two times, using a vacuum/argon procedure. After that the mixture was cooled to -78 °C, under an argon atmosphere, and sodium hydride was added (1.06 g, 26.4 mmol, 60% in mineral oil). The reaction temperature was slowly elevated and kept between -10 – 0 °C. After all gas was relased, the dropwise addition of bromoethane (1.96 mL, 26.4 mmol, d = 1.47 g/mL) to the dark red solution was started. After 16 h, 15 mL of hexane and 15 mL of water were added to the reaction mixture. Then the organic layer was separated, dried over $MgSO_4$ and evaporated. The crude product was purified via column chromatography using silica gel, as a stationary phase, and hexane, as eluent, to obtain 1.3 g of **6,** as a white solid, with the reaction yield of 98%.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.25 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.45 – 7.42 (m, 4H), 7.41 – 7.37 (m, 4H), 7.36 – 7.30 (m, 3H), 7.28 (d, *J* = 7.4 Hz, 1H), 2.92 – 2.83 (m, 2H), 2.23 (dq, *J* = 14.7, 7.4 Hz, 2H), 1.85 – 1.79 (m, 2H), 1.77 – 1.72 (m, 2H), 0.32 (t, *J* = 7.3 Hz, 6H), 0.26 (t, *J* = 7.3 Hz, 6H).

^{13}C {^{1}H } NMR (126 MHz, $CDCl_3$) δ: 151.9, 151.1, 144.6, 142.3, 142.1, 141.4, 141.4, 140.8, 139.5, 138.4, 129.1, 127.5, 127.1, 127.1, 126.8, 126.7, 126.3, 124.1, 122.9, 122.0, 121.1, 118.8, 58.1, 57.4, 32.4, 30,0, 8.8, 8.1.

HRMS (EI–TOF) m/z (M+): calcd for $C_{34}H_{34}$, 442.2661; found, 442.2663;

elemental analysis (%): calcd for $C_{34}H_{34}$: C, 92.26; H, 7.74. Found: C, 92.31; H, 7.69.



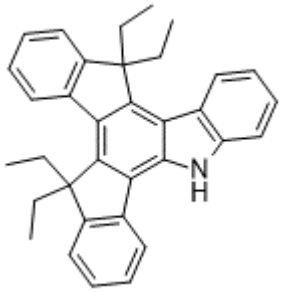
5-nitro-7,7,12,12-tetraethyl-6-phenyl-7,12-dihydroindeno[1,2-a]fluorene, ***7*** – 7,7,12,12-tetraethyl-6-phenyl-7,12-dihydroindeno[1,2-a]fluorene **6** (1.33 g, 3 mmol) was dissolved in 30 mL of dichloromethane. Then 1 mL of concentrated nitric acid (65% aqua solution) was added. After 30 min in room temperature, the reaction was completed (monitored by TLC, SiO_2/10% solution of dichloromethane in hexane). 30 mL of water was added to the obtained mixture. Next the organic layer was separated, washed with 10 mL of 10% aqua solution of NaOH, and dried over $MgSO_4$. After evaporation of the solvent, 1.46 g of **7**, as a yellow solid, was obtained with the reaction yield of ~ 100%.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.28 (d, *J* = 7.4 Hz, 1H), 7.46 – 7.34 (m, 10H), 7.32 – 7.26 (m, 2H), 2.89 (dq, *J* = 14.5, 7.2 Hz, 2H), 2.22 (dq, *J* = 14.7, 7.4 Hz, 2H), 1.72 (q, *J* = 7.3 Hz, 4H), 0.30 (t, *J* = 7.3 Hz, 6H), 0.24 (t, *J* = 7.4 Hz, 6H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ: 152.5, 151.6, 145.8, 145.1, 144.5, 140.8, 139.1, 136.1, 133.0, 131.5, 129.9, 129.4, 128.7, 128.7, 127.9, 127.7, 127.5, 126.8, 124.9, 122.4, 122.2, 120.6, 58.2, 57.9, 32.2, 29.7, 8.8, 8.0.

HRMS (EI–TOF) m/z (M+): calcd for $C_{34}H_{33}NO_2$, 487.2511; found, 487.2512;

elemental analysis (%): calcd for $C_{34}H_{33}NO_2$: C, 83.74; H, 6.82; N, 2.87. Found: C, 83.79; H, 6.85; N, 2.89.



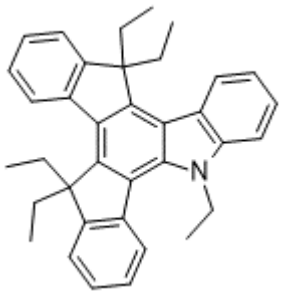
10,10,15,15-tetraethyl-5-azatruxene, ***8*** – To the 5-nitro-7,7,12,12-tetraethyl-6-phenyl-7,12-dihydroindeno[1,2-a]fluorene **7** (852.7 mg, 1.75 mmol) triphenylphosphine (1.84 g, 7 mmol) was added, and the mixture was heated up to 270-280 °C, in an argon atmosphere. After 1 h a dark solution was cooled to room temperature and then dissolved in 17.5 mL of dichloromethane. The crude product was adsorbed at silica gel and purified via column chromatography, using silica gel, as stationary phase, and 10% solution of dichloromethane in hexane→20% solution of dichloromethane in hexane, as eluent, to obtain 488 mg of **8,** as a white solid, with the reaction yield of 61%.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.68 (s, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.30 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.47 (m, 4H), 7.43 – 7.40 (m, *J* = 10.6, 4.3 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 3.06 – 2.96 (m, 4H), 2.32 – 2.23 (m, 4H), 0.27 (t, *J* = 7.3 Hz, 6H), 0.23 (t, *J* = 7.3 Hz, 6H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.6, 150.9, 145.6, 142.5, 142.1, 140.8, 140.7, 135.0, 132.0, 126.8, 126.3, 126.1, 125.4, 125.4, 124.9, 124.1, 123.3, 122.5, 122.3, 122.3, 119.8, 119.6, 119.6, 111.2, 58.7, 57.0, 30.0, 29.8, 8.7, 8.5.

HRMS (EI–TOF) m/z (M+): calcd for $C_{34}H_{33}N$, 455.2613; found, 455.2612;

elemental analysis (%): calcd for $C_{34}H_{33}N$: C, 89.63; H, 7.30; N, 3.07. Found: C, 89.67; H, 7.31; N, 3.02.

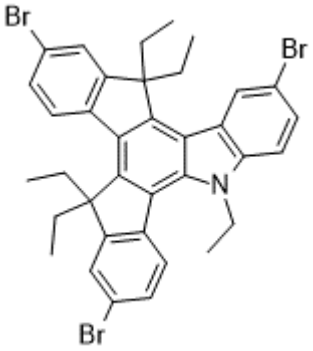


5,10,10,15,15-pentaethyl-5-azatruxene, ***NCC*** – *10,10,15,15-tetraethyl-5-azatruxene* **8** (455 mg, 1 mmol) was dissolved in 5 mL of dimethylformamide (purged with an argon for 1 h at 0 °C). Then shredded potassium hydroxide (122 mg, 2.2 mmol) was added, followed by dropwise addition of bromoethane (0.164 mL, 2.2 mmol, d = 1.46 g/mL). After 16 h, 10 mL of water was added and the obtained mixture was extracted 5 times with 5 mL of hexane. Combined extracts were dried over $MgSO_4$ and evaporated to obtain 483 mg of **NCC,** as white solid, with the reaction yield of ~100%. Analysis are in accordance with literature data.[2]

^{1}H NMR (500 MHz, C_6D_6) δ: 8.67 (d, *J* = 7.9 Hz, 1H), 8.43 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.20 (m, 9H), 4.33 (q, *J* = 7.0 Hz, 2H), 3.11 (m, 4H), 2.17 (m, 4H), 0.67 (t, *J* = 7.0 Hz, 3H), 0.42 (t, *J* = 7.3 Hz, 6H), 0.32 (t, *J* = 7.3 Hz, 6H)

^{13}C {^{1}H} NMR (126 MHz, C_6D_6) δ: 151.5, 151.2, 145.3, 145.0, 143.3, 142.0, 140.6, 139.0, 132.8, 127.9, 126.6, 126.4, 126.2, 126.0, 125.6, 125.3, 124.9, 123.6, 122.8, 122.5, 122.3, 122.2, 120.2, 112.2, 58.2, 56.9, 42.1, 30.0, 29.8, 12.5, 8.6, 8.4;

Elemental analysis (%). Calcd for $C_{36}H_{37}N$: C 89.39, H 7.71, N 2.90; Found: C 89.42, H 7.76. N 2.83.



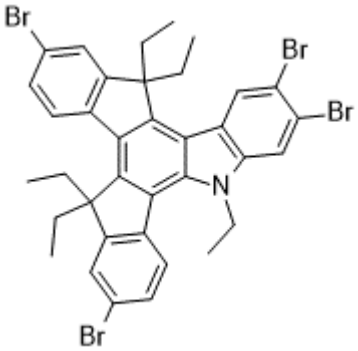
2,8,12–tribromo–5,10,10,15,15– pentaethyl–5–azatruxene, ***9a*** – 484 mg (1 mmol) of 5,10,10,15,15-pentaethyl-5-azatruxene **NCC** was dissolved in 1 mL of dichloromethane at 0 °C. At this step 0.16 mL (3.1 mmol, 3.1 equiv) of bromine and was slowly added. After 1 h, 10 mL of methanol was added dropwise and the formed white precipitate was filtrated, to get 626.4 mg (87%) of tribromoderivative. In the case of no precipitate, the obtained solution was cooled to 0 °C and obtained crystals were filtrated.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.57 (d, *J* = 1.6 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.62 – 7.46 (m, 6H), 4.63 (q, *J* = 7.0 Hz, 2H), 2.96 – 2.82 (m, 4H), 2.24 – 2.13 (m, 4H), 0.97 (t, *J* = 7.0 Hz, 3H), 0.24 (t, *J* = 7.3 Hz, 6H), 0.19 (t, *J* = 7.3 Hz, 6H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.8, 153.6, 145.2, 143.7, 143.6, 140.3, 139.1, 139.0, 131.9, 129.5, 129.5, 128.3, 127.4, 126.6, 125.7, 125.6, 125.5, 124.8, 123.6, 121.5, 120.3, 120.0, 113.5, 113.2, 58.5, 57.4, 42.6, 29.9, 29.6, 13.0, 8.6, 8.5.

HRMS (EI–TOF) m/z (M+): calcd for $C_{36}H_{34}NBr_3$: 717.0241; found: 717.0245;

Elemental analysis (%). Calcd for $C_{36}H_{34}NBr_3$: C 60.02, H 4.76, N 1.94; Found: C 60.09, H 4.80. N 1.99.



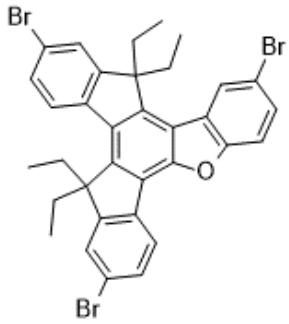
2,7,8,12–tetrabromo–5,10,10,15,15–pentaethyl–5–azatruxene, ***10*** – 484 mg (1 mmol) of 5,10,10,15,15-pentaethyl-5-azatruxene **NCC** was dissolved in 1 mL of dichloromethane at 0 °C and 0.21 mL (4.1 mmol, 4.1 equiv) of bromine was slowly added. After 1 h, 10 mL of methanol was added dropwise and the formed white precipitate was filtrated, to get 728 mg (91%) of tetrabromoderivative.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.67 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.51 (m, 5H), 4.76 (q, *J* = 6.9 Hz, 2H), 2.89 – 2.85 (m, 2H), 2.79 – 2.74 (m, 2H), 2.26 – 2.15 (m, 4H), 0.49 (t, *J* = 7.0 Hz, 3H), 0.24 (t, *J* = 7.2 Hz, 6H), 0.19 (t, *J* = 7.1 Hz, 6H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ: 153.2, 153.4, 145.1, 144.8, 144.6, 143.3, 139.9, 138.1, 133.7, 130.2, 129.9, 129.8, 127.5, 127.0, 125.6, 125.6, 125.5, 124.9, 123.9, 122.3, 120.9, 120.5, 117.7, 112.2, 58.9, 57.3, 45.2, 30.1, 29.6, 12.0, 8.6, 8.5.

HRMS (EI–TOF) m/z (M+): calcd for $C_{36}H_{33}NBr_4$: 794.9346; found: 794.9350;

Elemental analysis (%). Calcd for $C_{36}H_{33}NBr_4$: C 54.10, H 4.16, N 1.75; Found: C 54.12, H 4.21. N 1.74.



2,8,12–tribromo–10,10,15,15–tetraethyl–5–oxatruxene, ***9b*** – 456 mg (1 mmol) of 10,10,15,15-tetraethyl-5-oxatruxene **OCC** was dissolved in 1 mL of dichloromethane at 0 °C and 0.16 mL (3.1 mmol, 3.1 equiv) of bromine was slowly added. After 1 h, 10 mL of methanol was added dropwise, and the white precipitate was filtrated to get 631 mg (93%) of tribromoderivative.

^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.46 (s, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 0.8 Hz, 2H), 7.65 – 7.62 (m, 3H), 7.57 (dd, *J* = 8.4, 1.9 Hz, 1H), 2.87 (dq, *J* = 14.6, 7.3 Hz, 2H), 2.77 (dq, *J* = 14.3, 7.3 Hz, 2H), 2.25 (m, 4H), 0.27 (t, *J* = 7.3 Hz, 6H), 0.22 (t, *J* = 7.3 Hz, 6H).

^{13}C {^{1}H} NMR (126 MHz, CD_2Cl_2) δ: 155.9, 153.1, 153.1, 151.9, 145.3, 143.8, 140.0, 137.8, 133.8, 130.4, 129.8, 129.8, 127.0, 125.8, 125.6, 125.0, 125.0, 125.0, 123.5, 121.3, 120.5, 119.0, 115.7, 113.5, 59.8, 57.3, 30.4, 29.7, 8.4, 8.1.

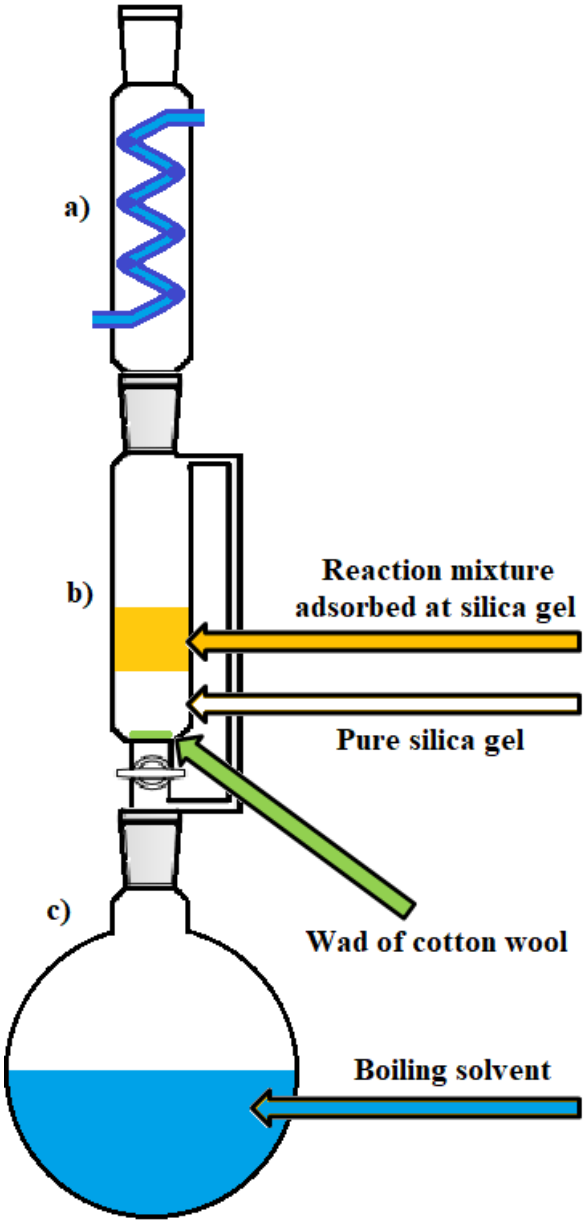
HRMS (EI–TOF) m/z (M+): calcd for $C_{34}H_{29}OBr_3$: 689.9768; found: 689.9753;

Elemental analysis (%). Calcd for $C_{34}H_{29}OBr_3$: C 58.90, H 4.22; Found: C 59.02, H 4.25.

1 K. Górski, J. Mech-Piskorz, K. Noworyta, B. Leśniewska and M. Pietraszkiewicz, *New J. Chem.*, 2018, **42**, 5844–5852.

2 K. Górski, J. Mech-Piskorz, B. Leśniewska, O. Pietraszkiewicz and M. Pietraszkiewicz, *J. Org. Chem.*, 2019, **84**, 11553–11561.

2. “Hot” chromatography apparatus



Scheme S1. „Hot” chromatography apparatus.

Apparatus for “hot” chromatography purification is presented on Scheme S1. It consists of three main parts: a) **condenser**, b) **dropping funnel with pressure equalizing tube**. The reaction mixture is adsorbed at silica gel before purification. Than pure silica is placed on a cotton wad inside the dropping funnel and the reaction mixture previously adsorbed at the silica gel is placed on top. c) **round-bottom flask** filled with boiling solvent, heated with a heating mantle. Such apparatus allows chromatographic purification by an eluent negligible dissolving product at room temperature (as in the case of compound **5** in hexane). What is more, the continuous nature of the process allows the minimization of the solvent used for chromatography, making the process cheaper, and more environmentally friendly. It is particularly important during syntheses on a larger scale. Comparative TLC analysis of the extract with the droplet from the funnel indicates the end of purification.

3. Scan rate of truxene and 5-hetrotruxenes.

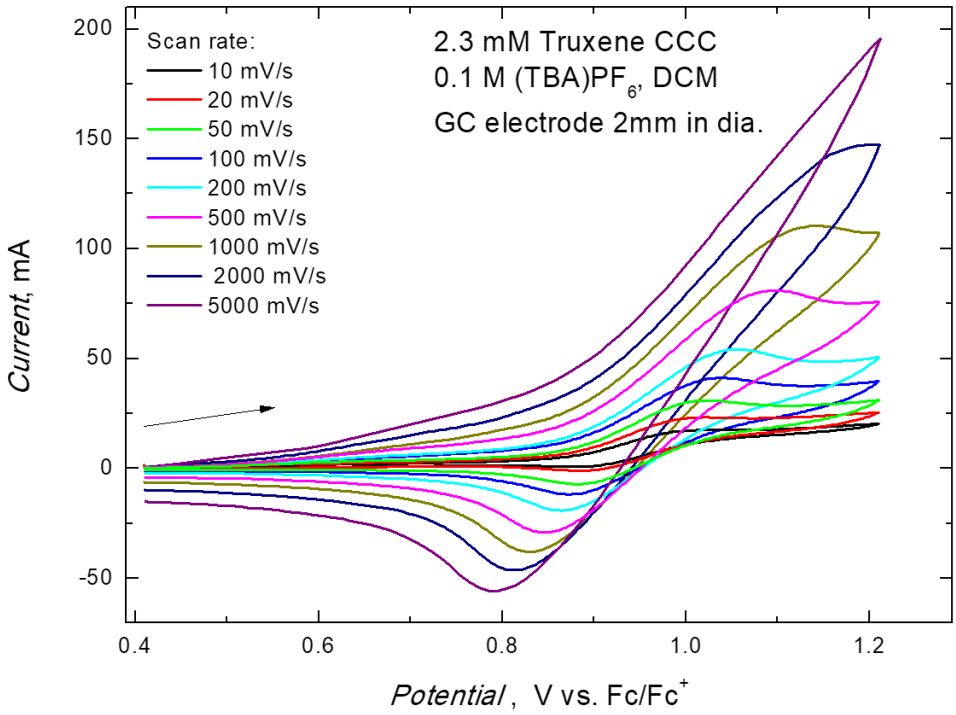


Figure S1 Cyclic voltammograms of **CCC** in 0.1 M (TBA)PF_6 in DCM, at different scan rates.

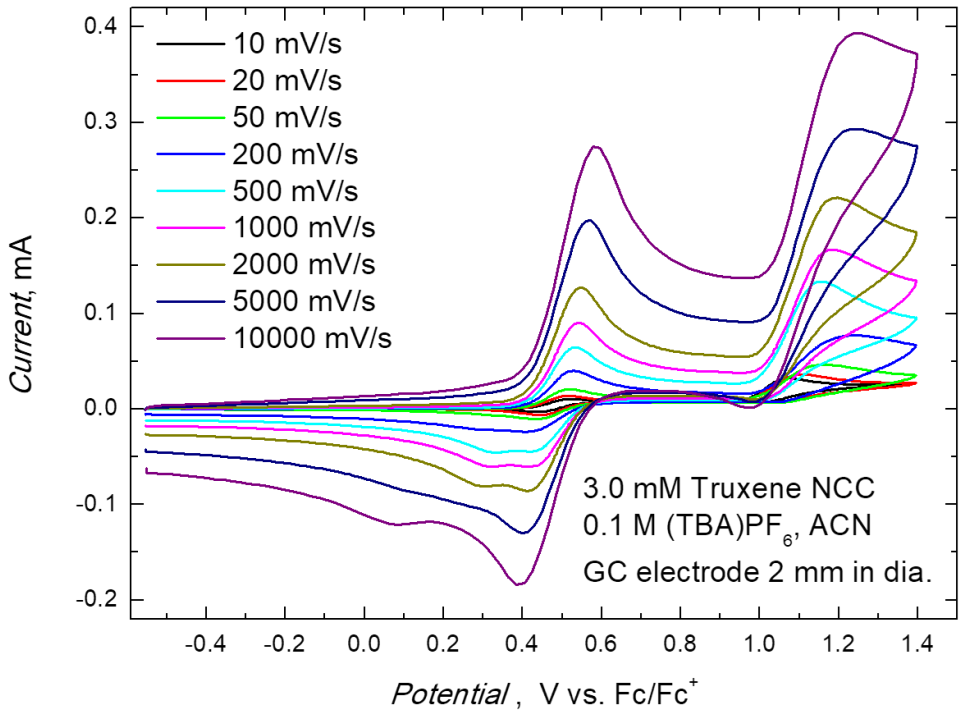


Figure S2. Cyclic voltammograms of **NCC** in 0.1 M (TBA)PF6 in ACN, at different scan rates.

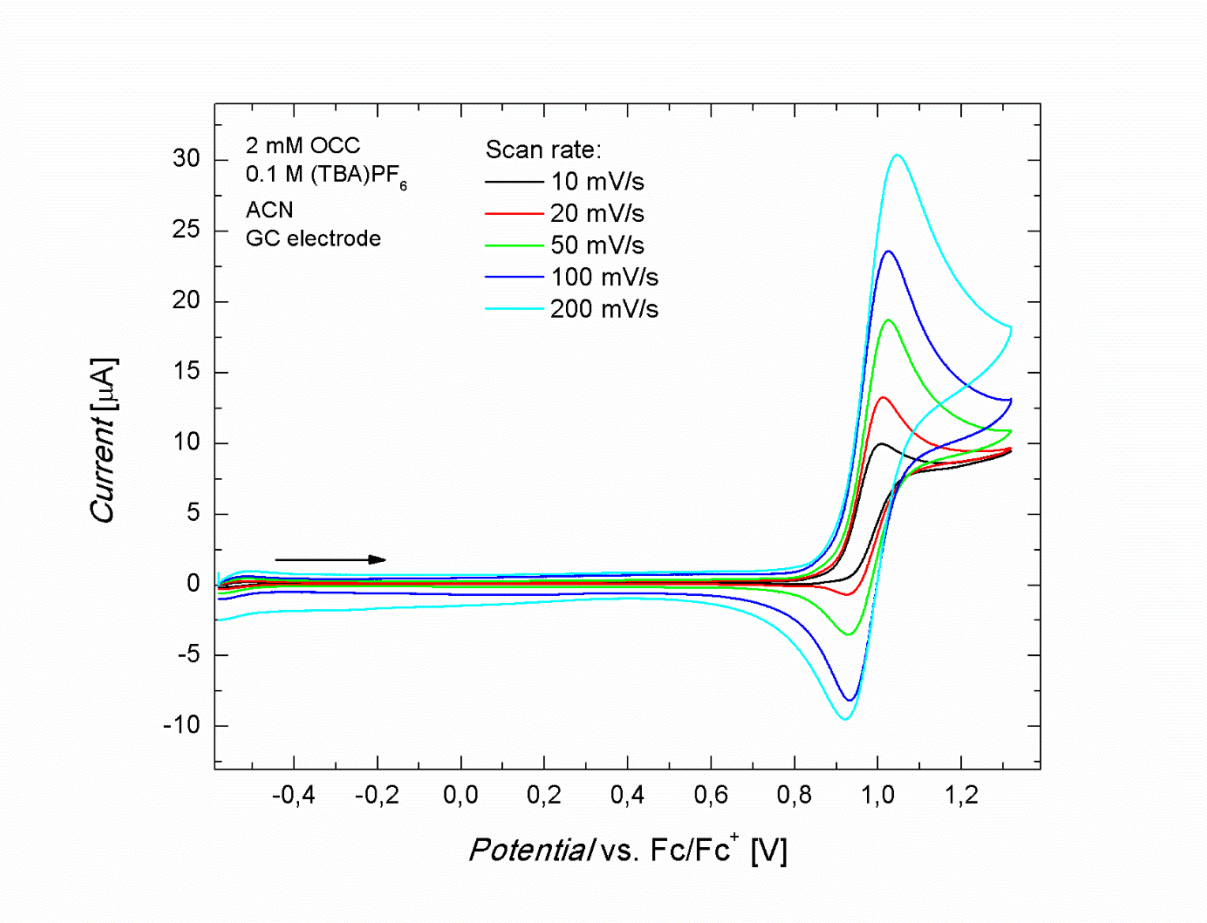


Figure S3. Cyclic voltammograms of **OCC** in 0.1 M (TBA)PF6 in ACN, at different scan rates.

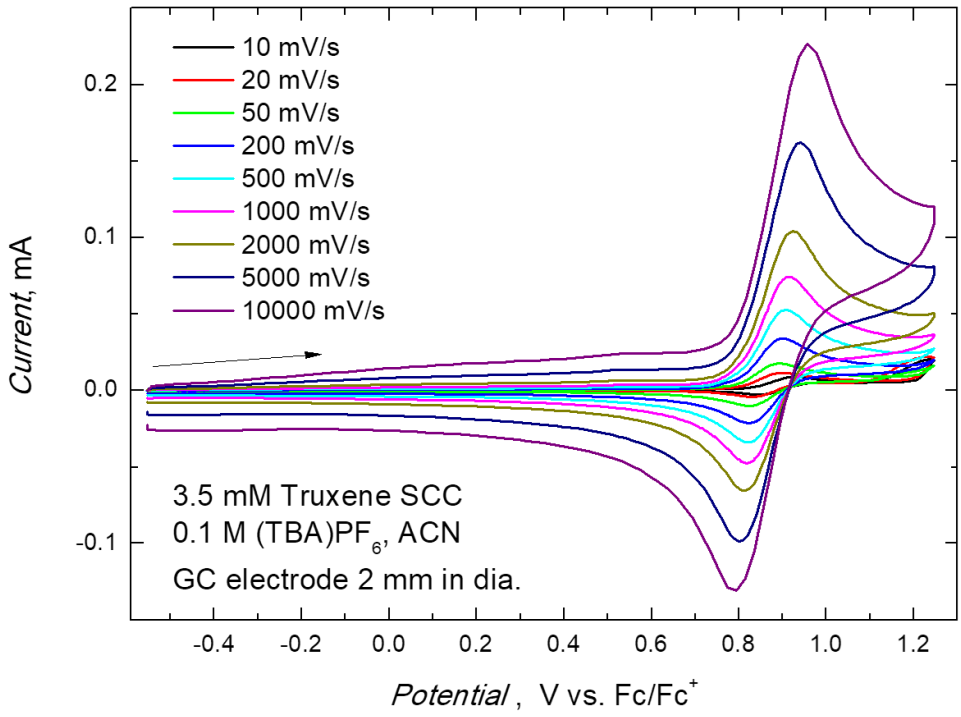


Figure S4. Cyclic voltammograms of **SCC** in 0.1 M (TBA)PF6 in ACN, at different scan rates.

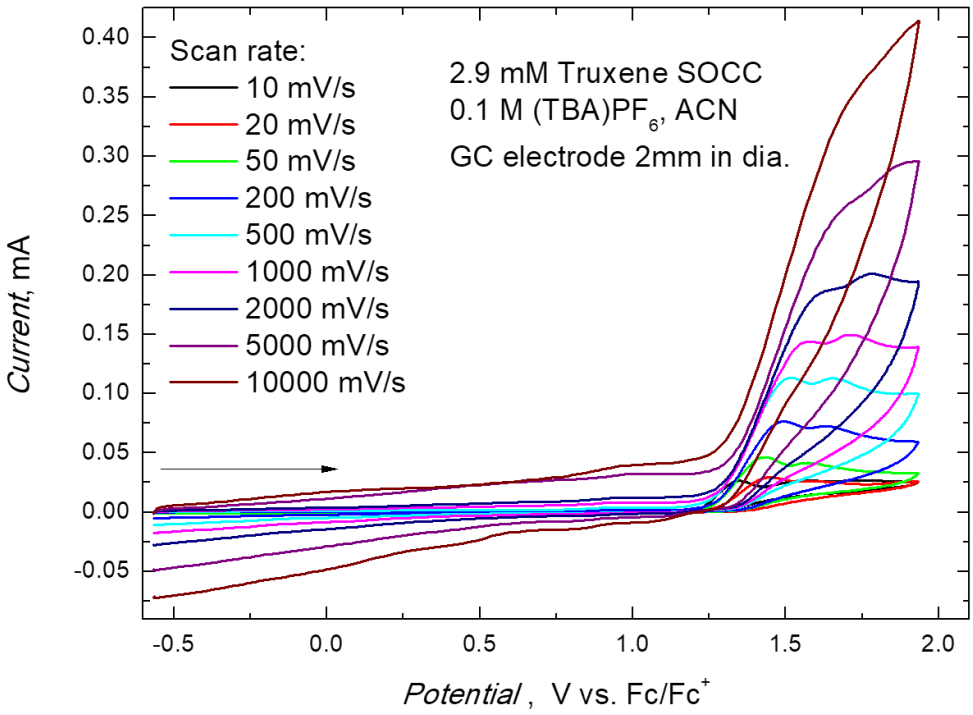


Figure S5. Cyclic voltammograms of **(OS)CC** in 0.1 M (TBA)PF6 in ACN, at different scan rates.

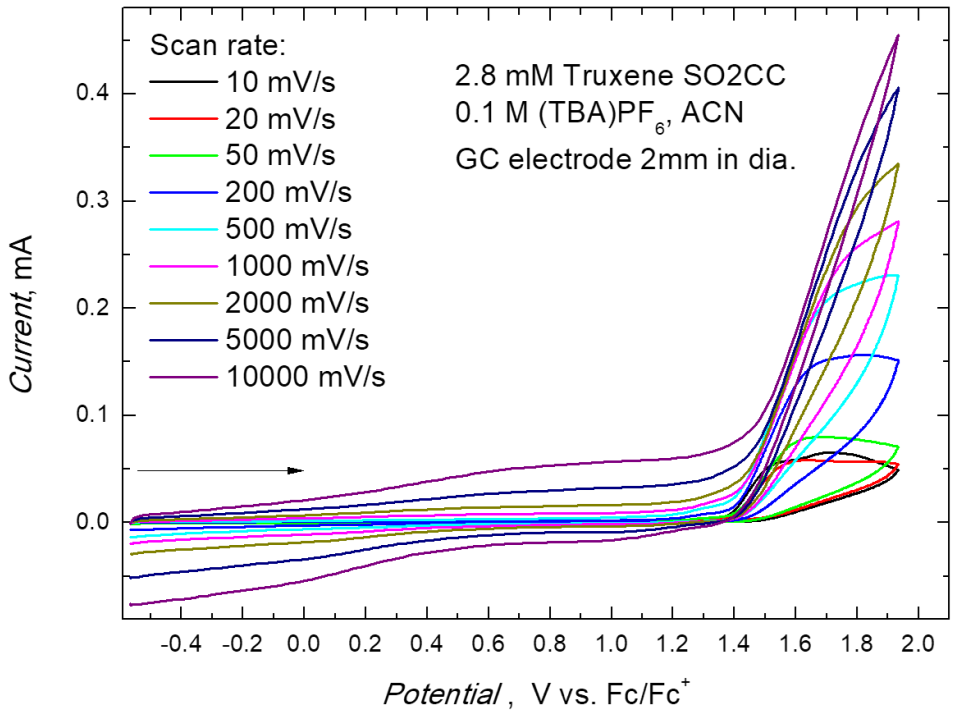


Figure S6. Cyclic voltammograms of **(O_2S)CC** in 0.1 M (TBA)PF6 in ACN, at different scan rates.

4. Reduction of (OS)CC.

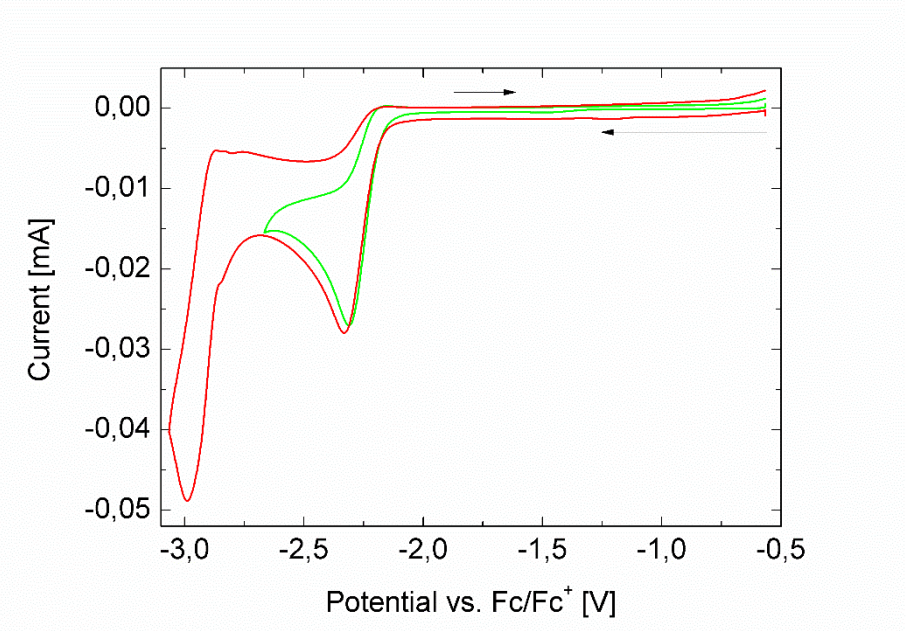


Figure S7 Cyclic voltammograms of **(OS)CC** in 0.1 M $(TBA)PF_6$ in ACN, scan rate 100 mV/s.

5. Spectral radiation distribution of the UV-C lamp

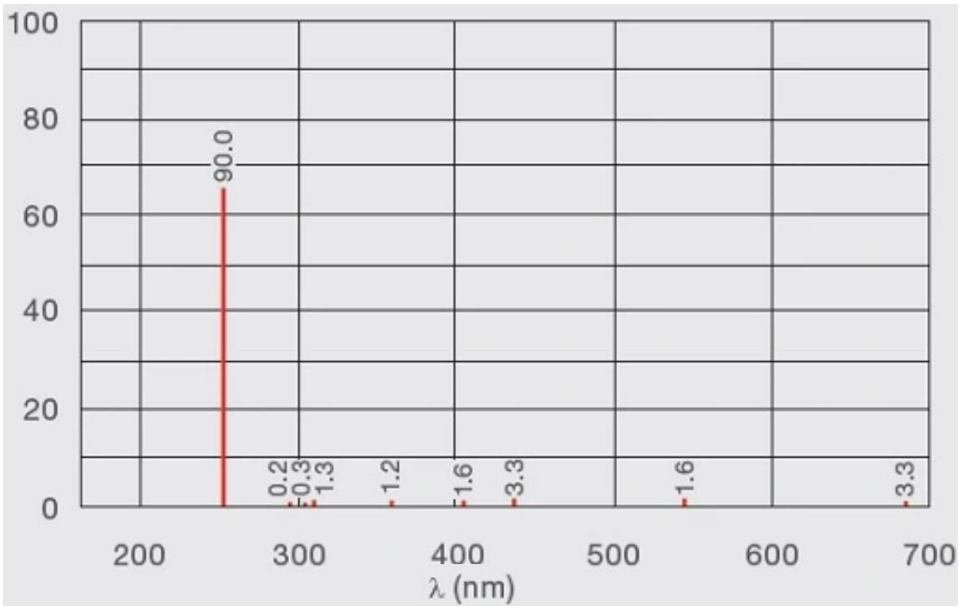
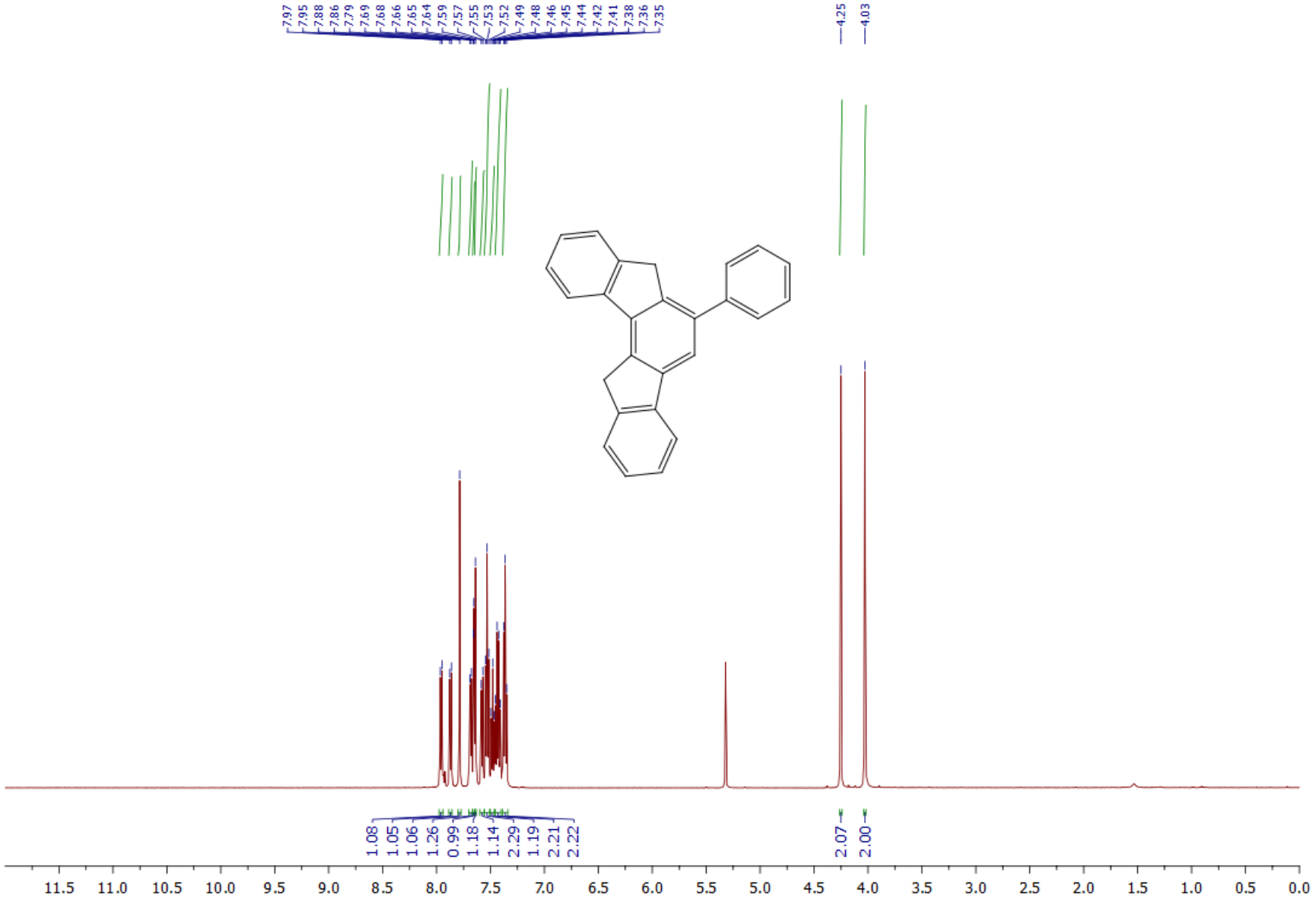
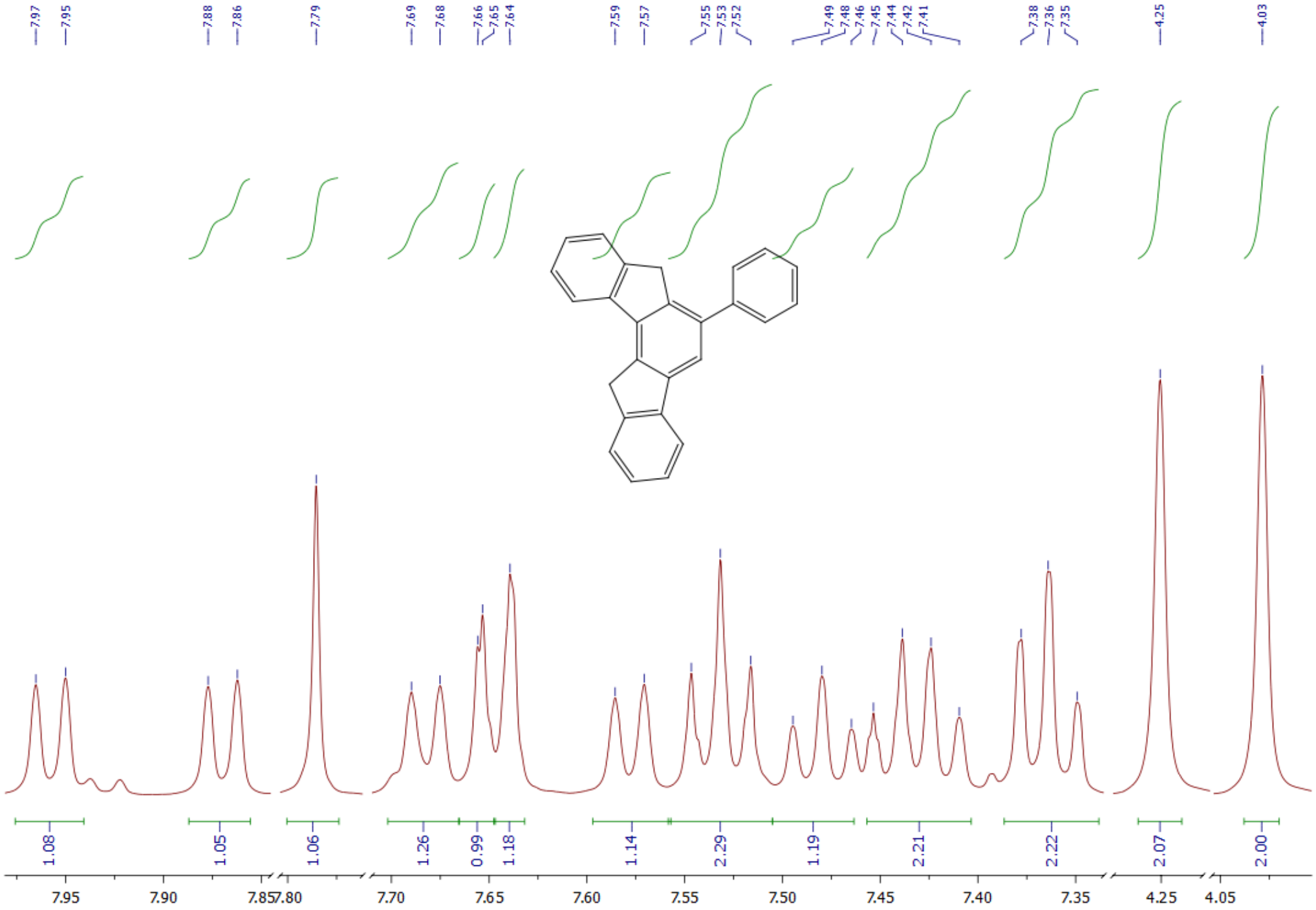


Figure S8 Spectral radiation distribution of the OSRAM UV-C lamp Puritec HNS L 2G11, 55.

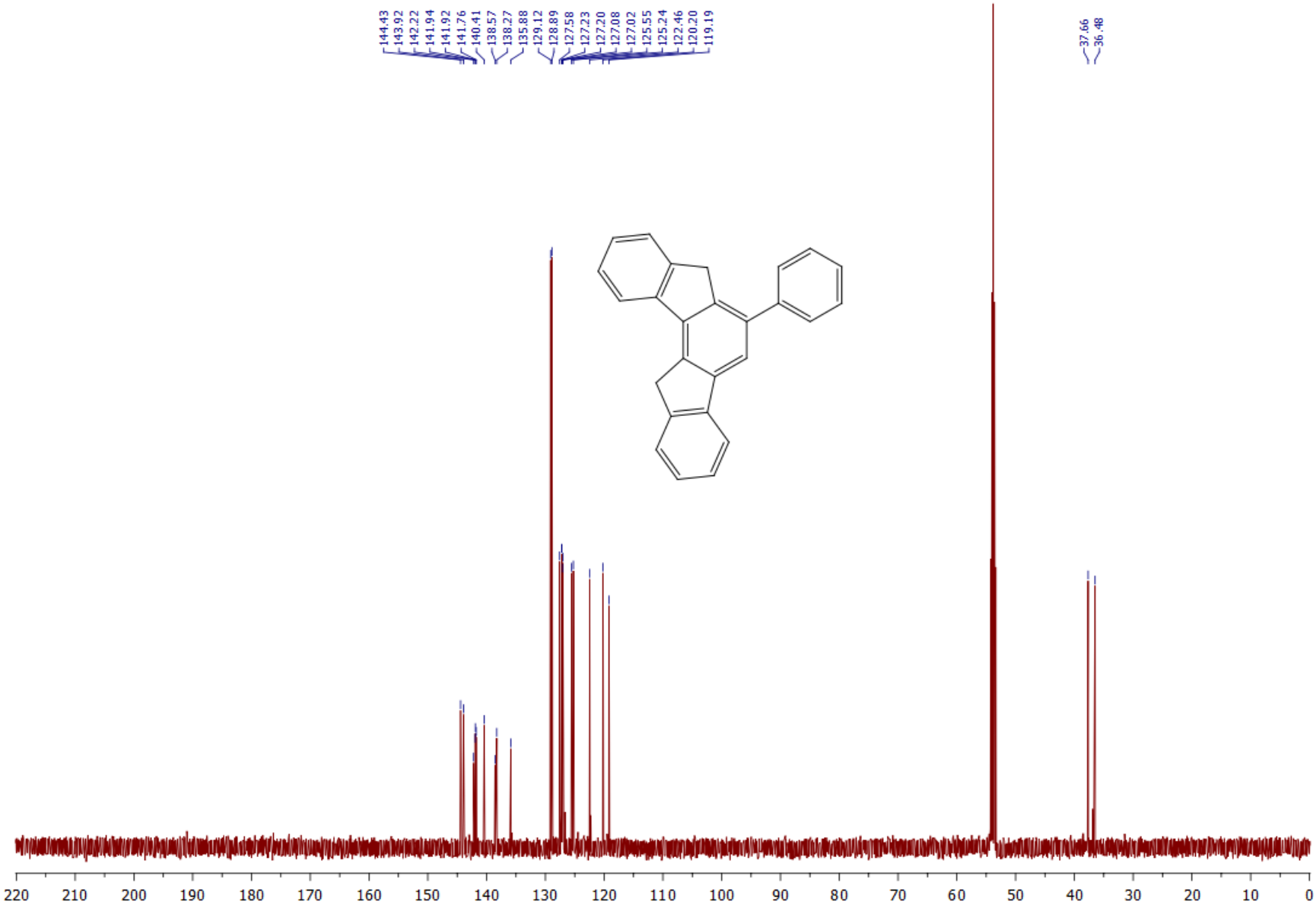
6. NMR spectra of 5 in CD_2Cl_2

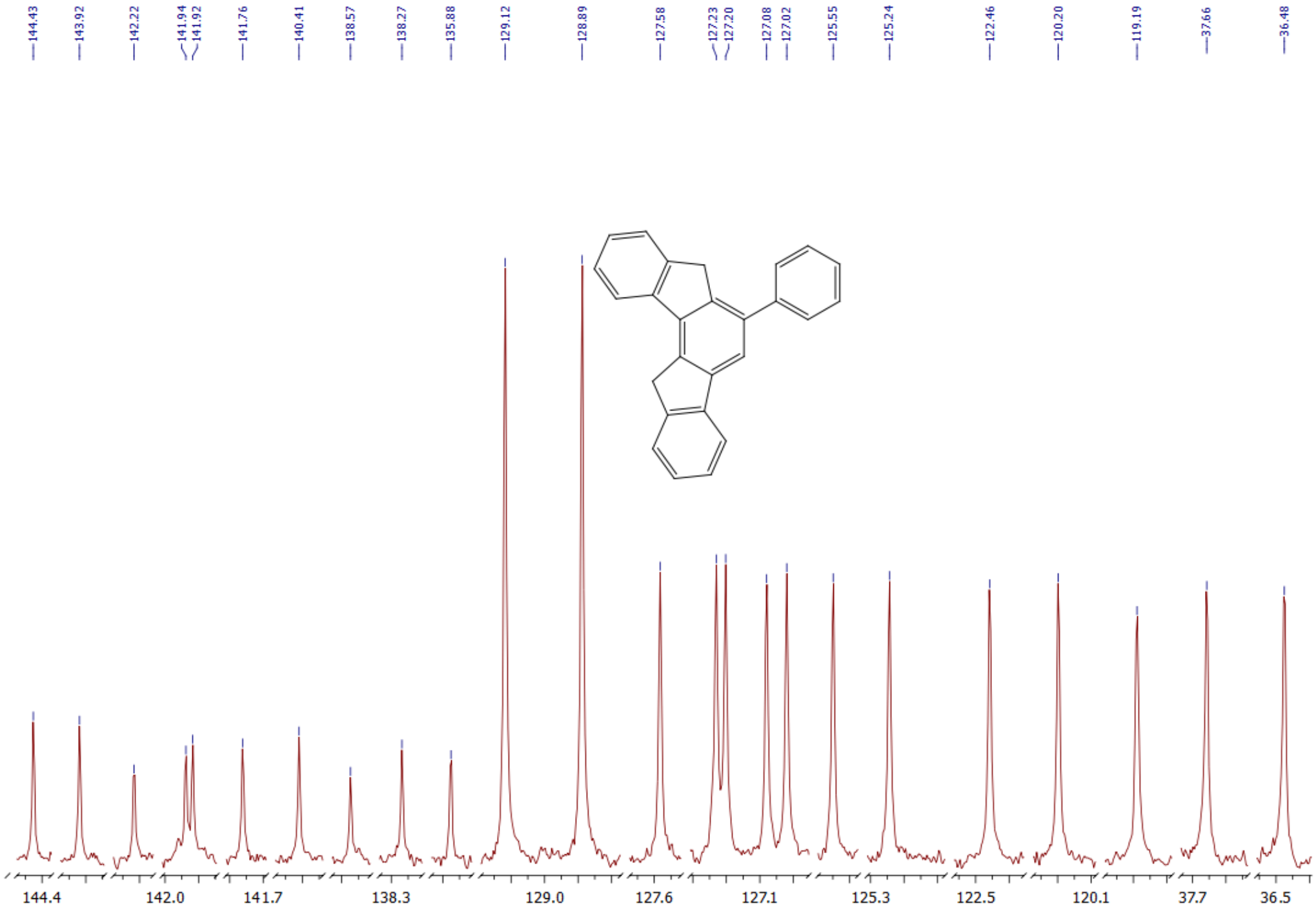
^1H NMR of **5** in CD_2Cl_2 500 MHz




7.97
7.95
7.88
7.86
7.79
7.69
7.68
7.66
7.65
7.64
7.59
7.57
7.55
7.53
7.52
7.49
7.48
7.46
7.45
7.44
7.42
7.41
7.38
7.36
7.35
4.25
4.03
1.08
1.05
1.06
1.26
0.99
1.18
1.14
2.29
1.19
2.21
2.22
2.07
2.00
7.95
7.90
7.85
7.80
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
4.25
4.05

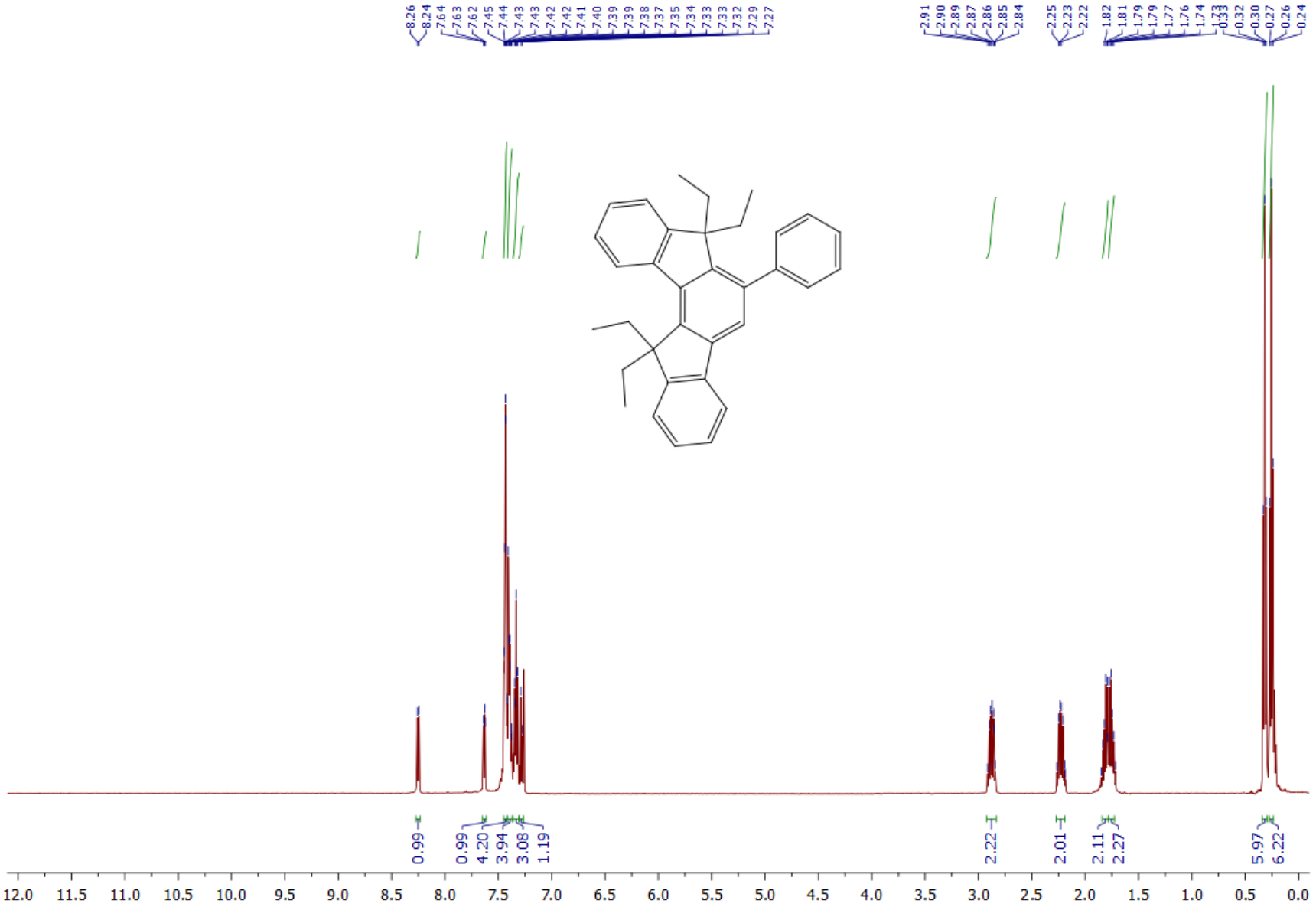
^{13}C {^{1}H} NMR spectra of **5** in CD_2Cl_2 126 MHz

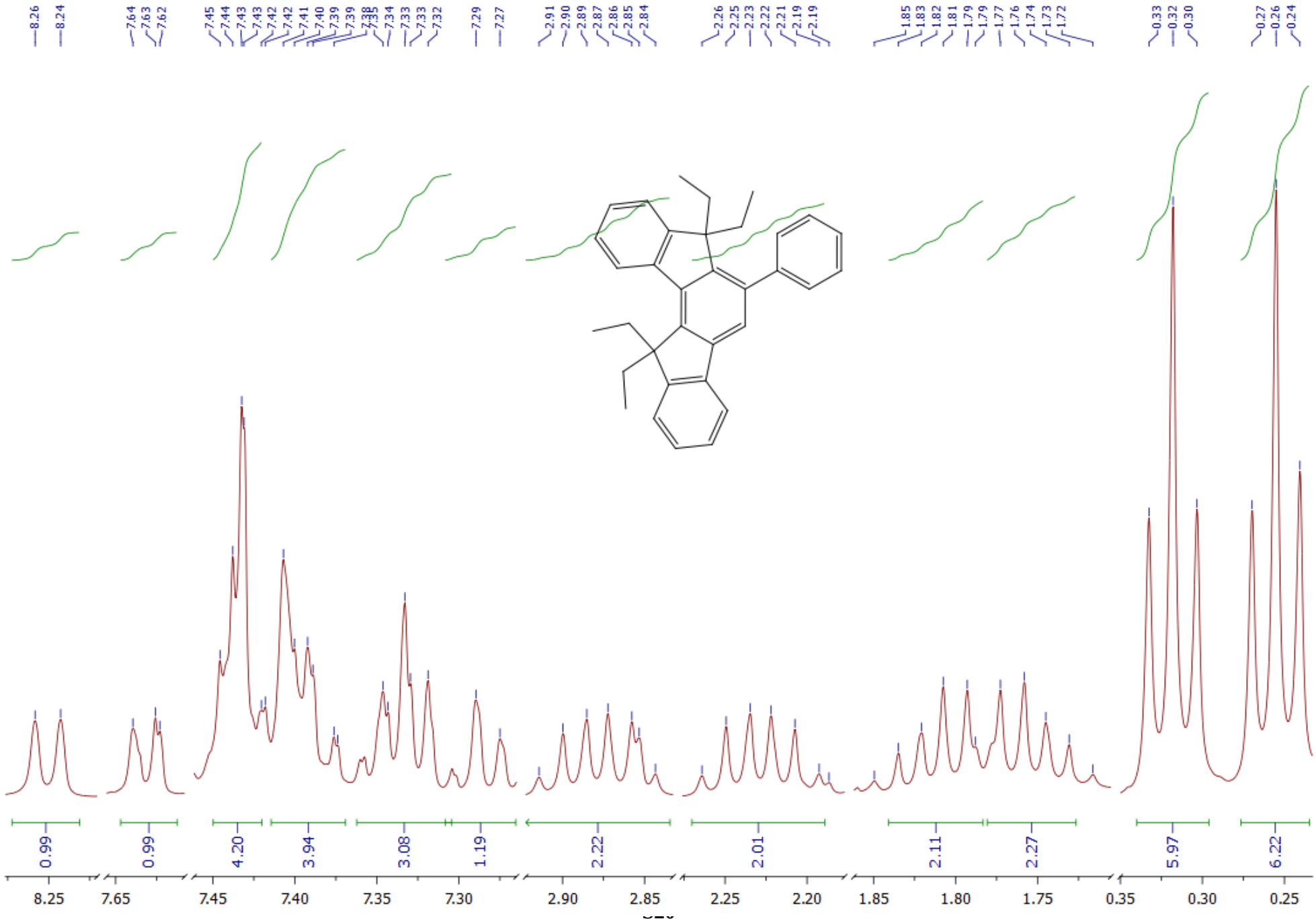



144.43
143.92
142.22
141.94
141.92
141.76
140.41
138.57
138.27
135.88
129.12
128.89
127.58
127.23
127.20
127.08
127.02
125.55
125.24
122.46
120.20
119.19
37.66
36.48
144.4
142.0
141.7
138.3
129.0
127.6
127.1
125.3
122.5
120.1
37.7
36.5

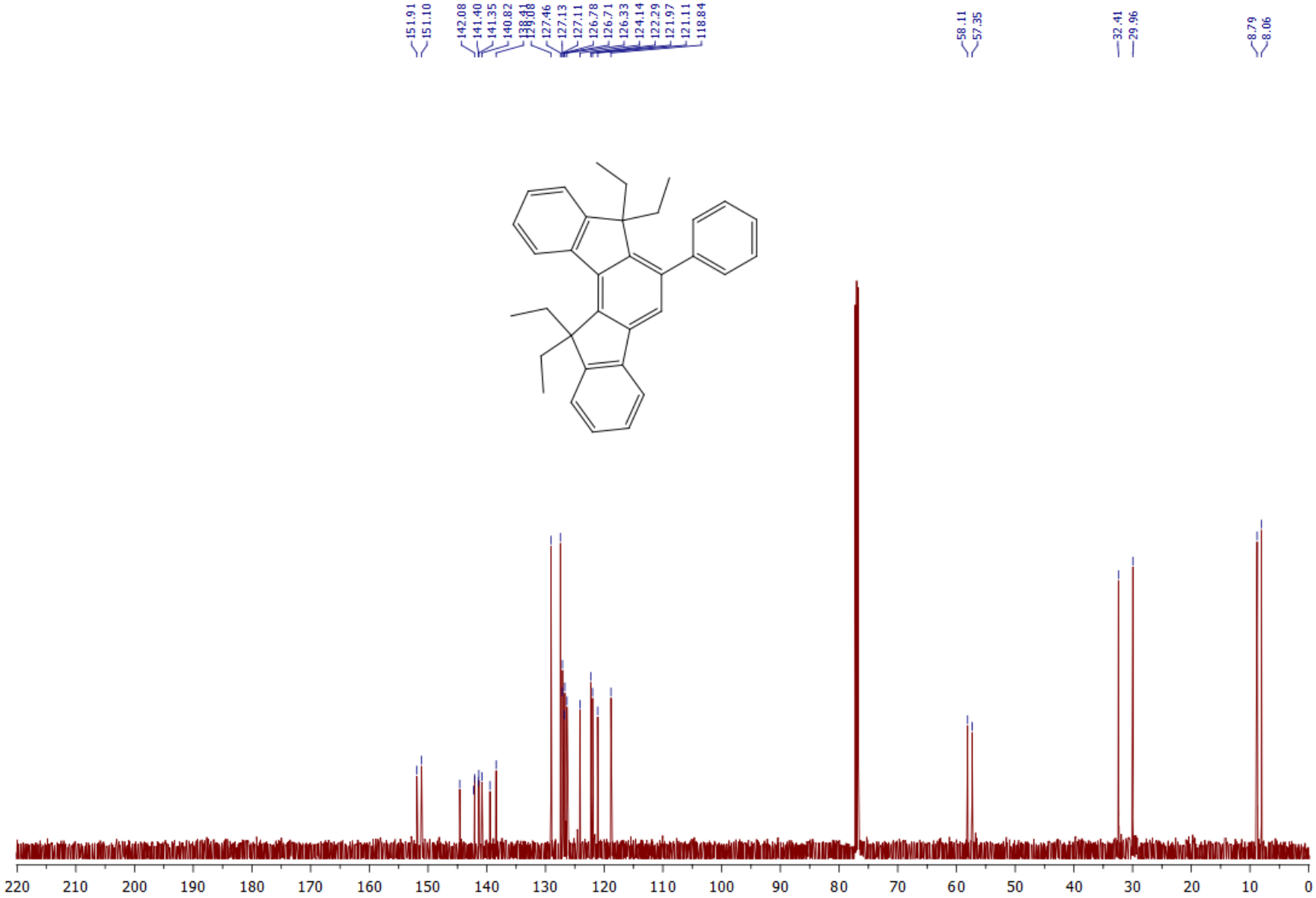
7. NMR spectra of 6 in $CDCl_3$

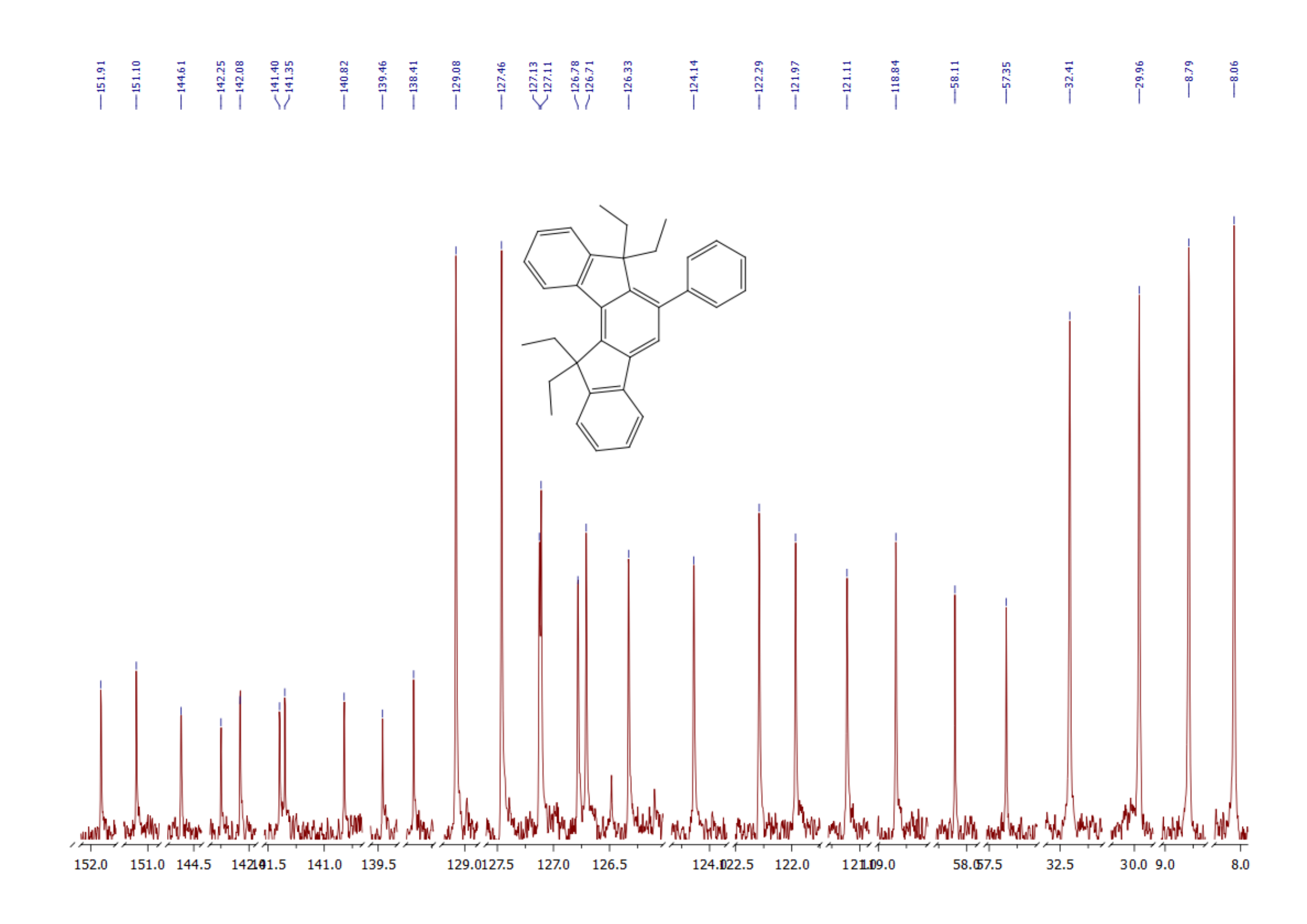
^1H NMR of **6** in $CDCl_3$ 500 MHz




8.26
8.24
7.64
7.63
7.62
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.39
7.39
7.38
7.35
7.34
7.33
7.33
7.32
7.29
7.27
2.91
2.90
2.89
2.87
2.86
2.85
2.84
2.26
2.25
2.23
2.22
2.21
2.19
2.19
1.85
1.83
1.82
1.81
1.79
1.79
1.77
1.76
1.74
1.73
1.72
0.33
0.32
0.30
0.27
0.26
0.24
0.99
0.99
4.20
3.94
3.08
1.19
2.22
2.01
2.11
2.27
5.97
6.22
8.25
7.65
7.45
7.40
7.35
7.30
2.90
2.85
2.25
2.20
1.85
1.80
1.75
0.35
0.30
0.25

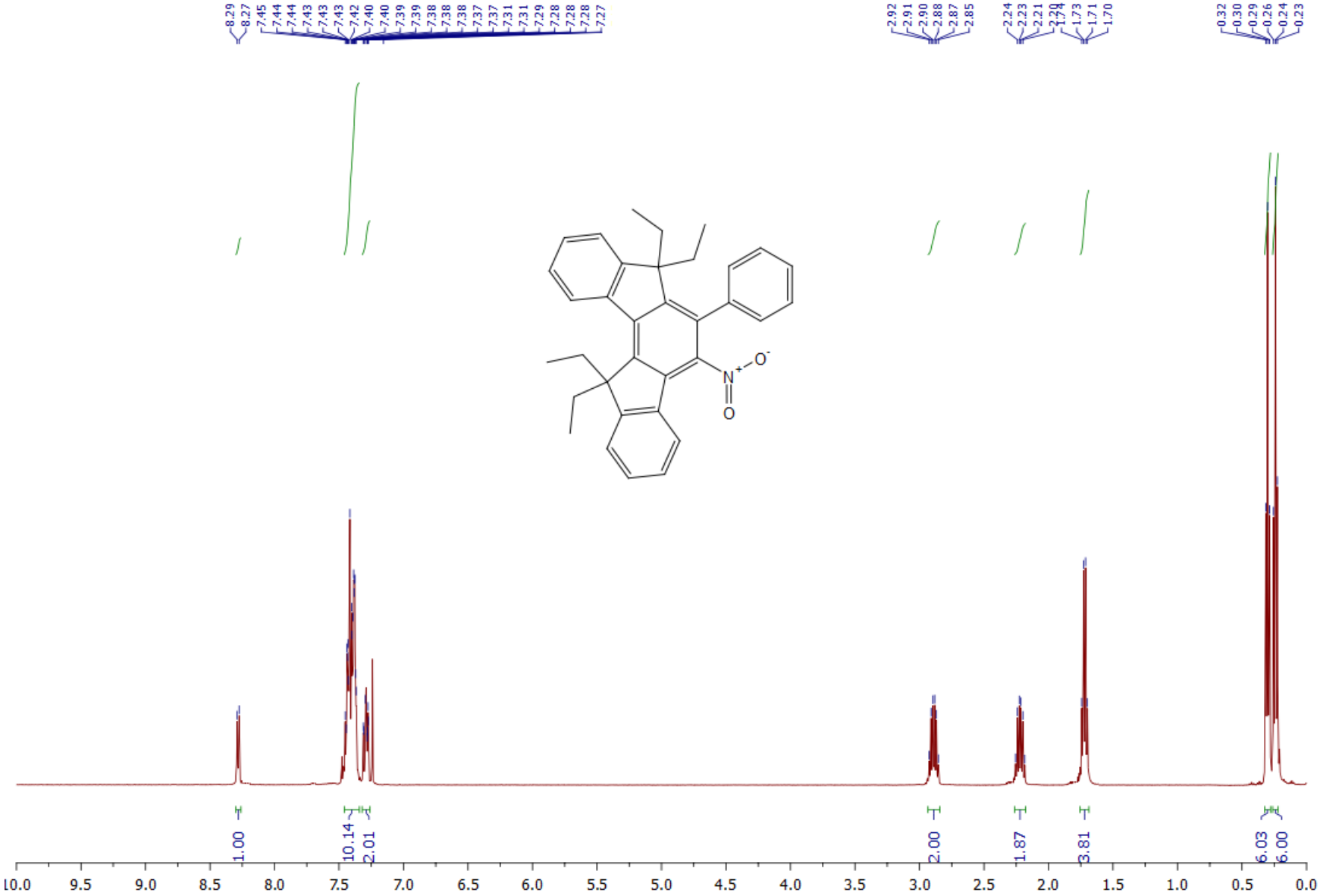
^{13}C {^{1}H} NMR spectra of **6** in $CDCl_3$ 126 MHz

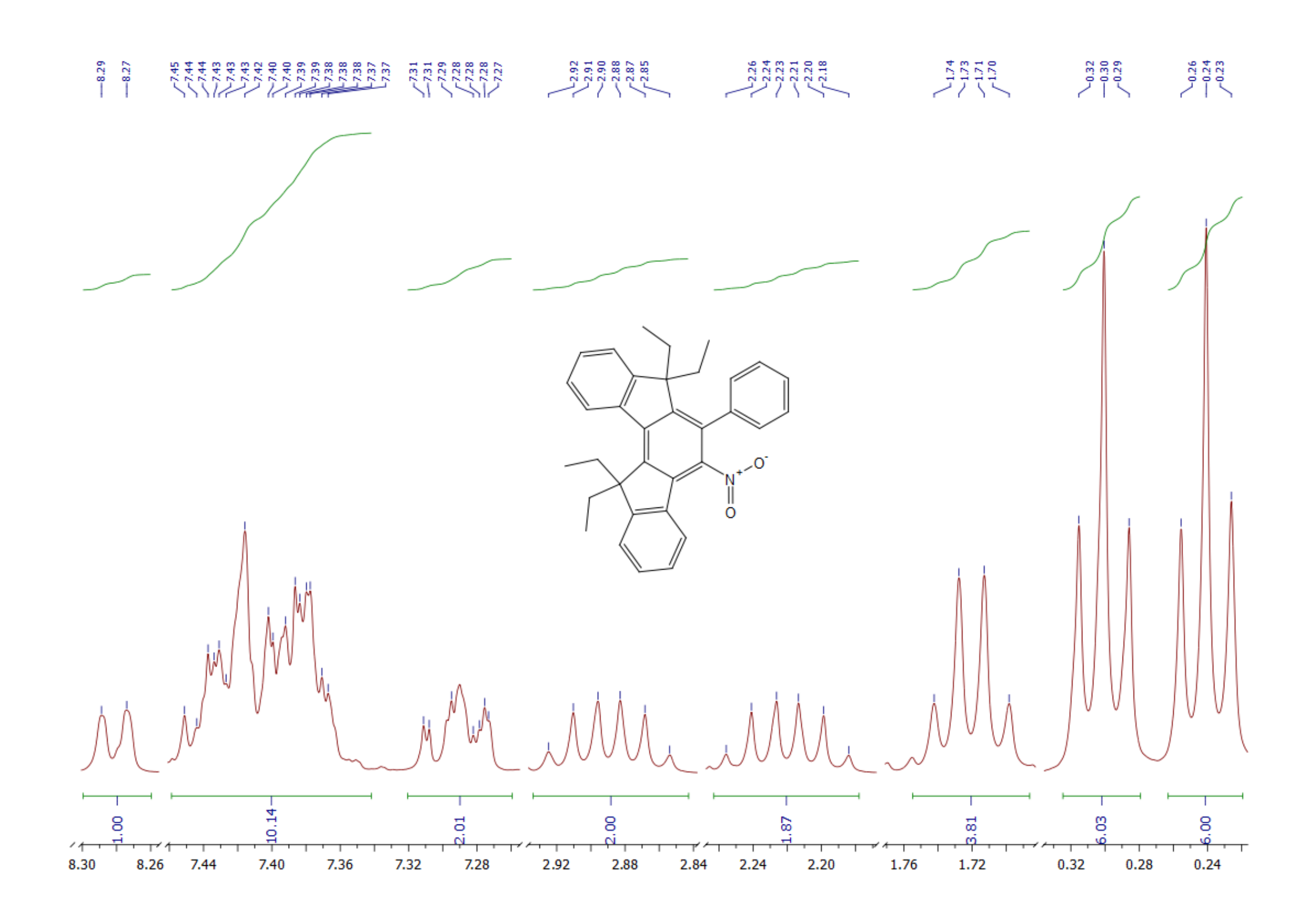



151.91
151.10
144.61
142.25
142.08
141.40
141.35
140.82
139.46
138.41
129.08
127.46
127.13
127.11
126.78
126.71
126.33
124.14
122.29
121.97
121.11
118.84
58.11
57.35
32.41
29.96
8.79
8.06
152.0
151.0
144.5
141.5
141.0
139.5
129.0
127.5
127.0
126.5
124.0
122.5
122.0
121.0
109.0
58.0
57.5
32.5
30.0
9.0
8.0

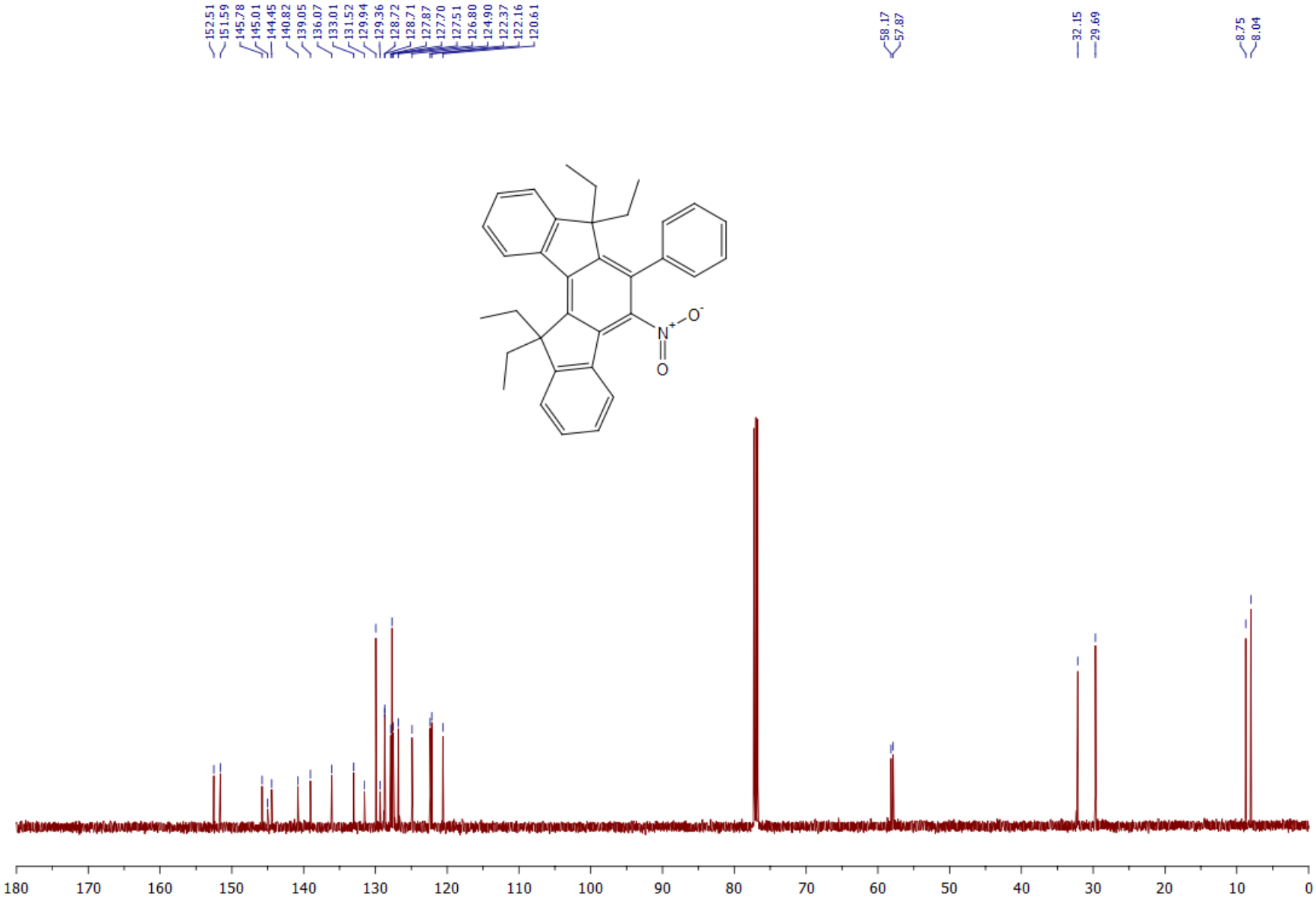
8. NMR spectra of 7 in $CDCl_3$

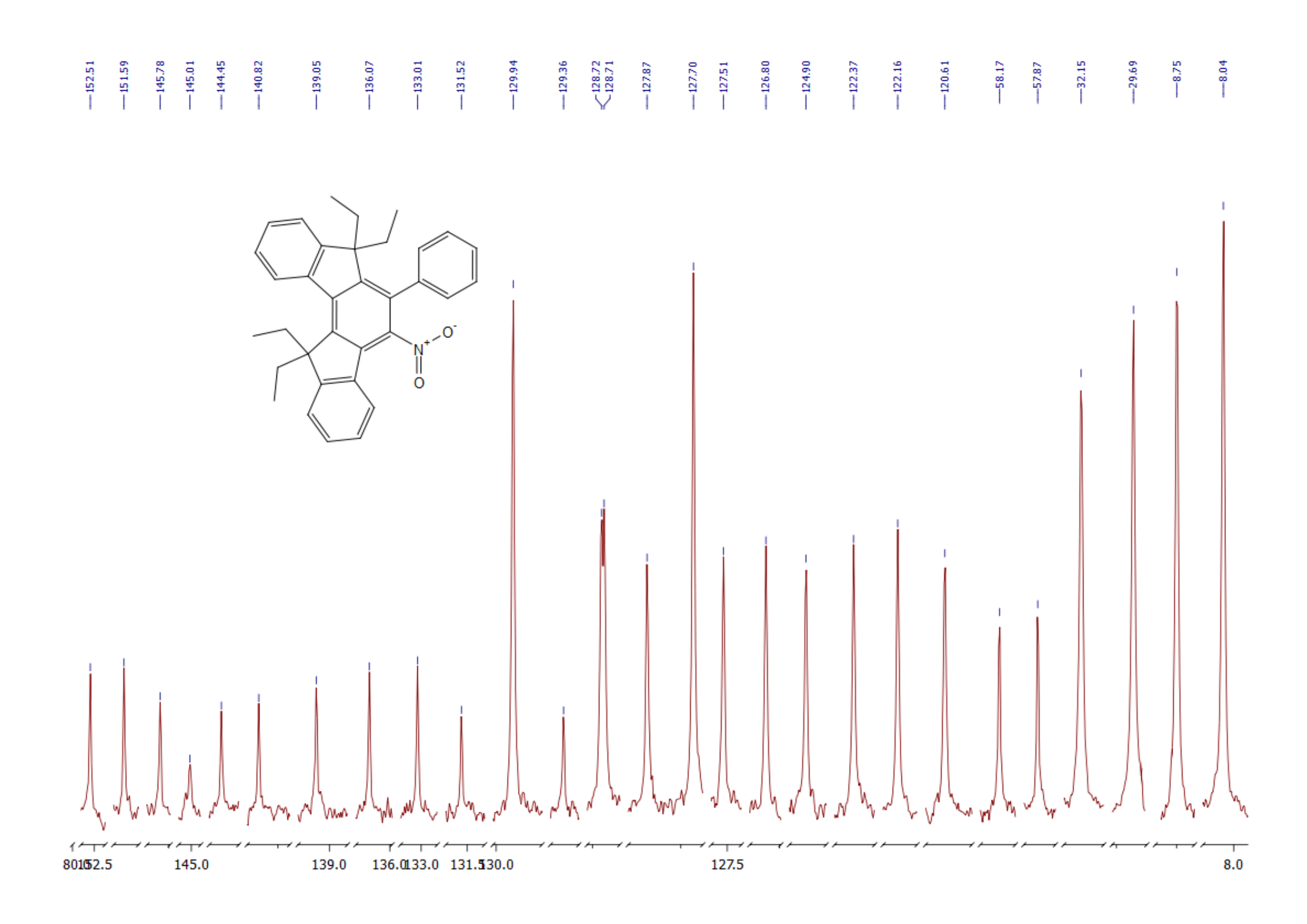
^1H NMR of **7** in $CDCl_3$ 500 MHz




8.29
8.27
7.45
7.44
7.44
7.43
7.43
7.43
7.42
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.31
7.31
7.29
7.28
7.28
7.28
7.27
2.92
2.91
2.90
2.88
2.87
2.85
2.26
2.24
2.23
2.21
2.20
2.18
1.74
1.73
1.71
1.70
0.32
0.30
0.29
0.26
0.24
0.23
N+
O-
O
1.00
10.14
2.01
2.00
1.87
3.81
6.03
6.00
8.30
8.26
7.44
7.40
7.36
7.32
7.28
2.92
2.88
2.84
2.24
2.20
1.76
1.72
0.32
0.28
0.24

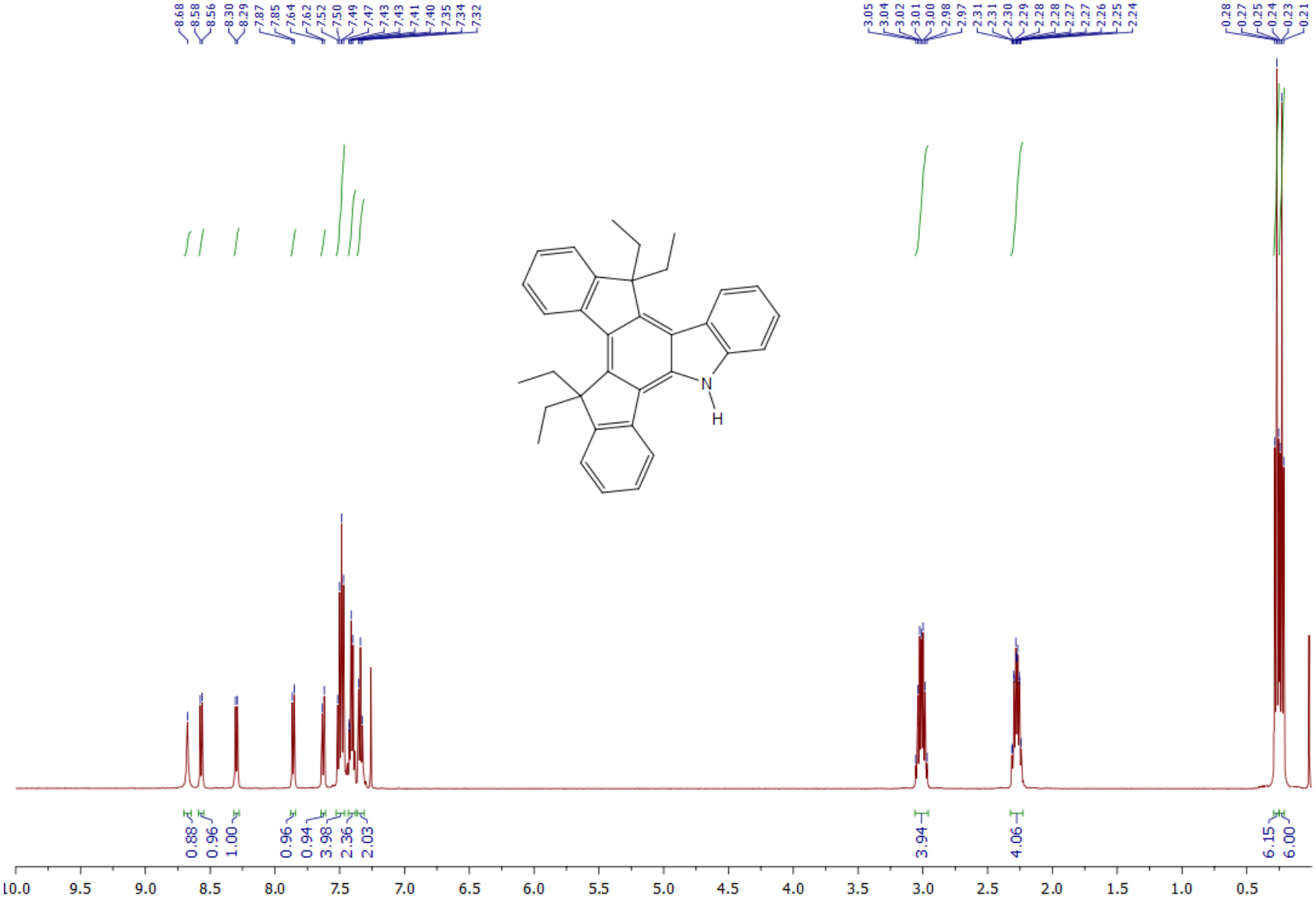
^{13}C {^{1}H} NMR spectra of **7** in $CDCl_3$ 126 MHz

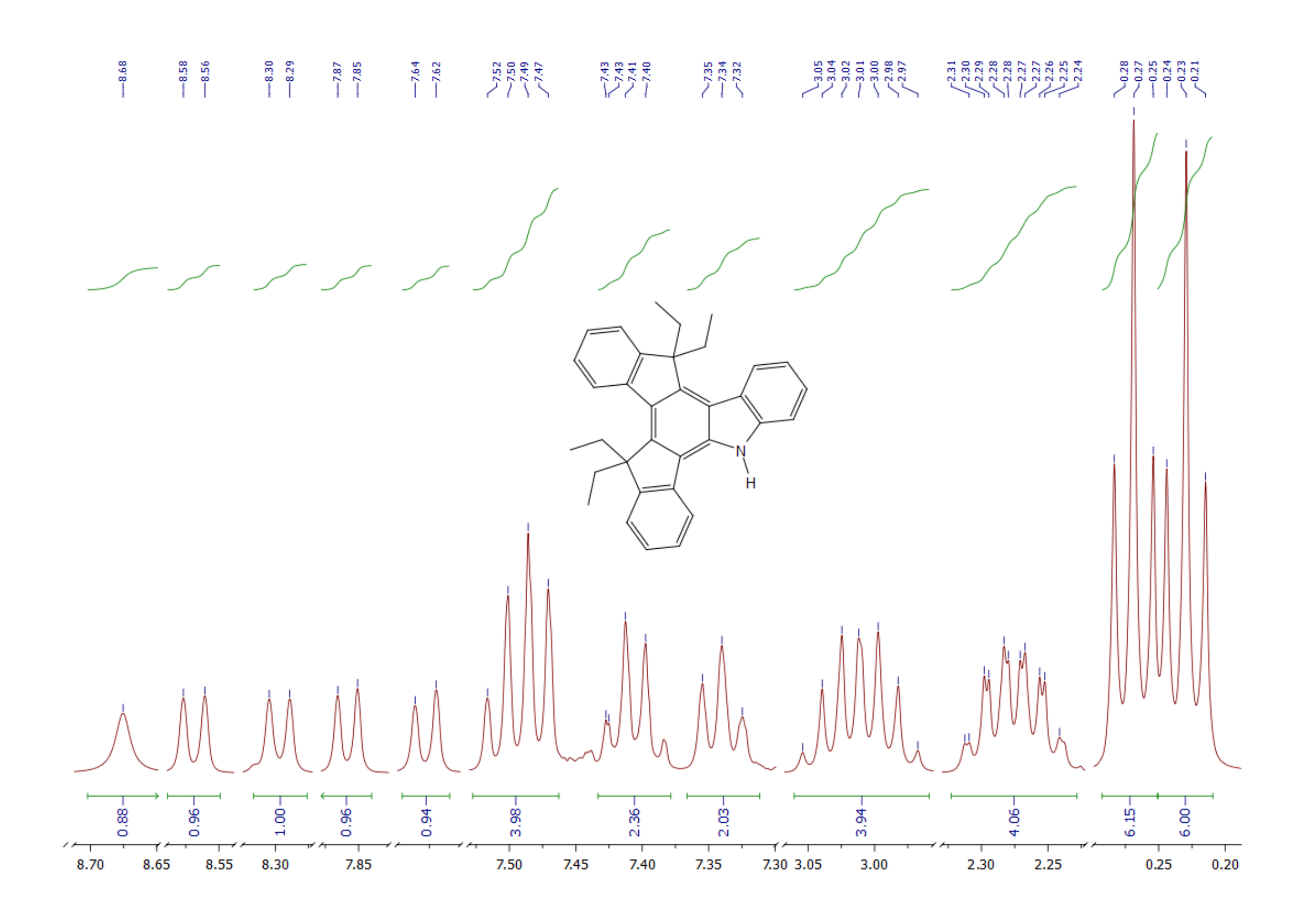



152.51
151.59
145.78
145.01
144.45
140.82
139.05
136.07
133.01
131.52
129.94
129.36
128.72
128.71
127.87
127.70
127.51
126.80
124.90
122.37
122.16
120.61
58.17
57.87
32.15
29.69
8.75
8.04
O
N+
O-
O
152.5
145.0
139.0
136.0
133.0
131.5
130.0
127.5
8.0

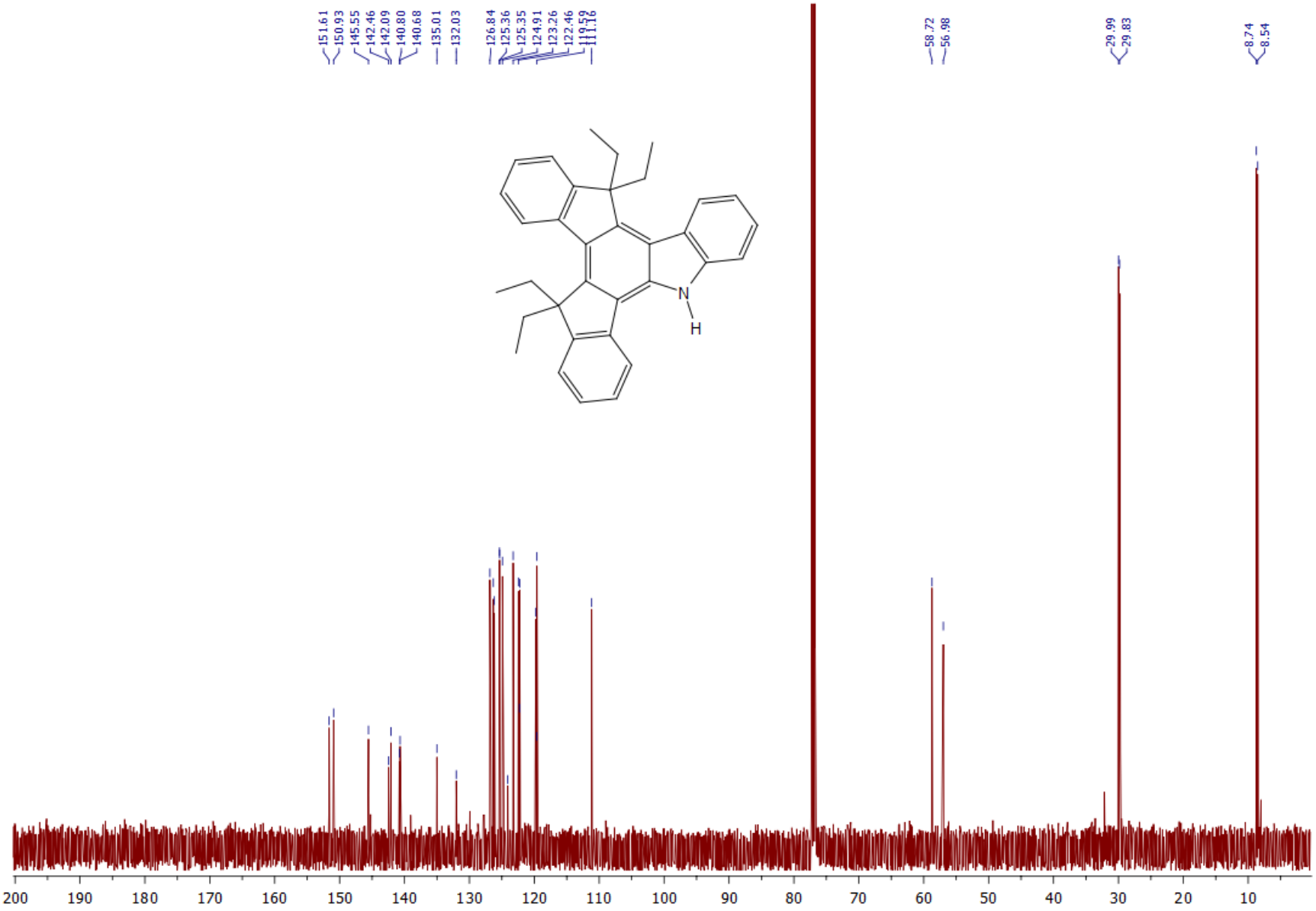
9. NMR spectra of 8 in $CDCl_3$

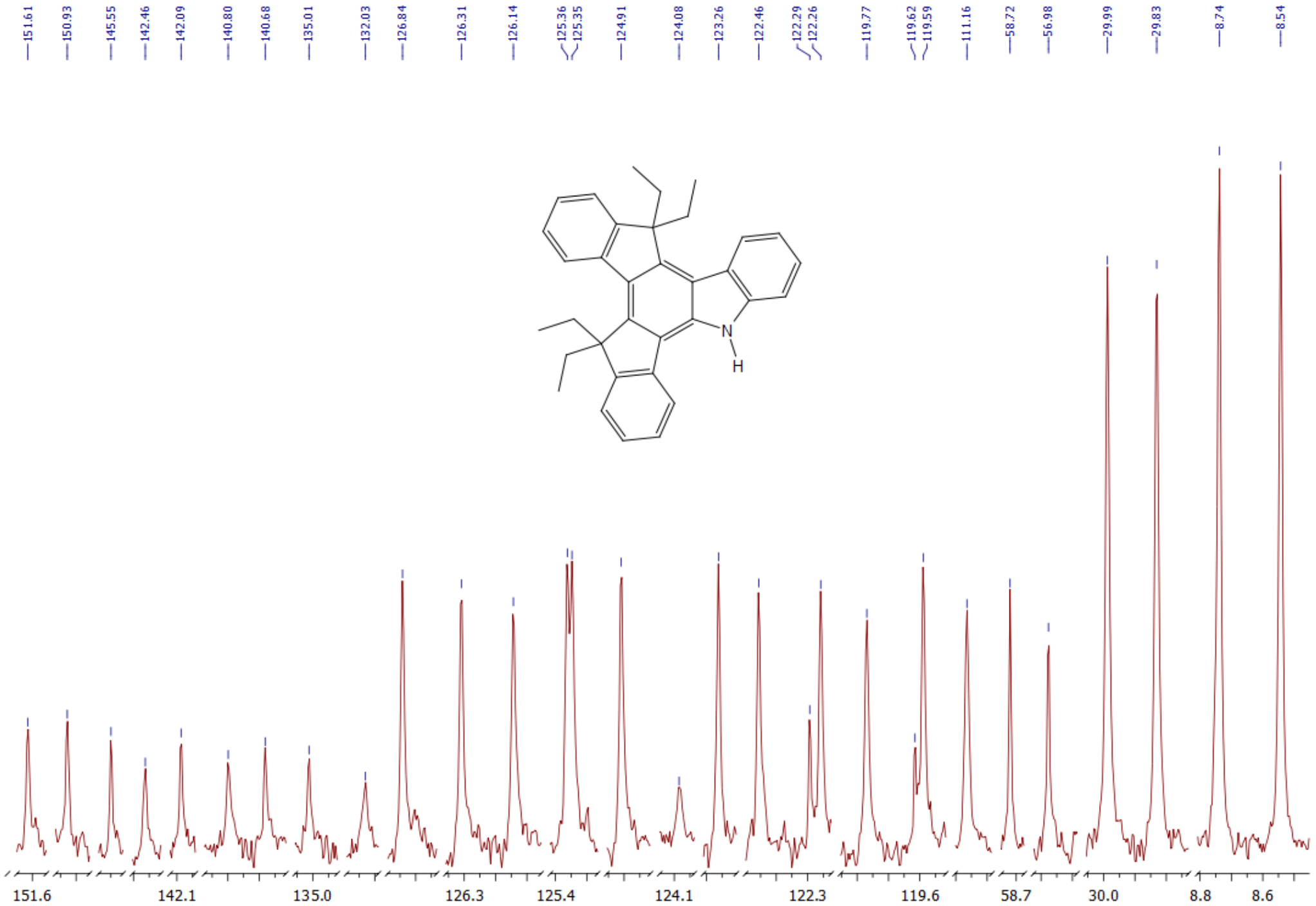
^1H NMR of **8** in $CDCl_3$ 500 MHz




8.68
8.58
8.56
8.30
8.29
7.87
7.85
7.64
7.62
7.52
7.50
7.49
7.47
7.43
7.43
7.41
7.40
7.35
7.34
7.32
3.05
3.04
3.02
3.01
3.00
2.98
2.97
2.31
2.30
2.29
2.28
2.28
2.27
2.27
2.26
2.25
2.24
0.28
0.27
0.25
0.24
0.23
0.21
N
H
0.88
0.96
1.00
0.96
0.94
3.98
2.36
2.03
3.94
4.06
6.15
6.00
8.70
8.65
8.55
8.30
7.85
7.50
7.45
7.40
7.35
7.30
3.05
3.00
2.30
2.25
0.25
0.20

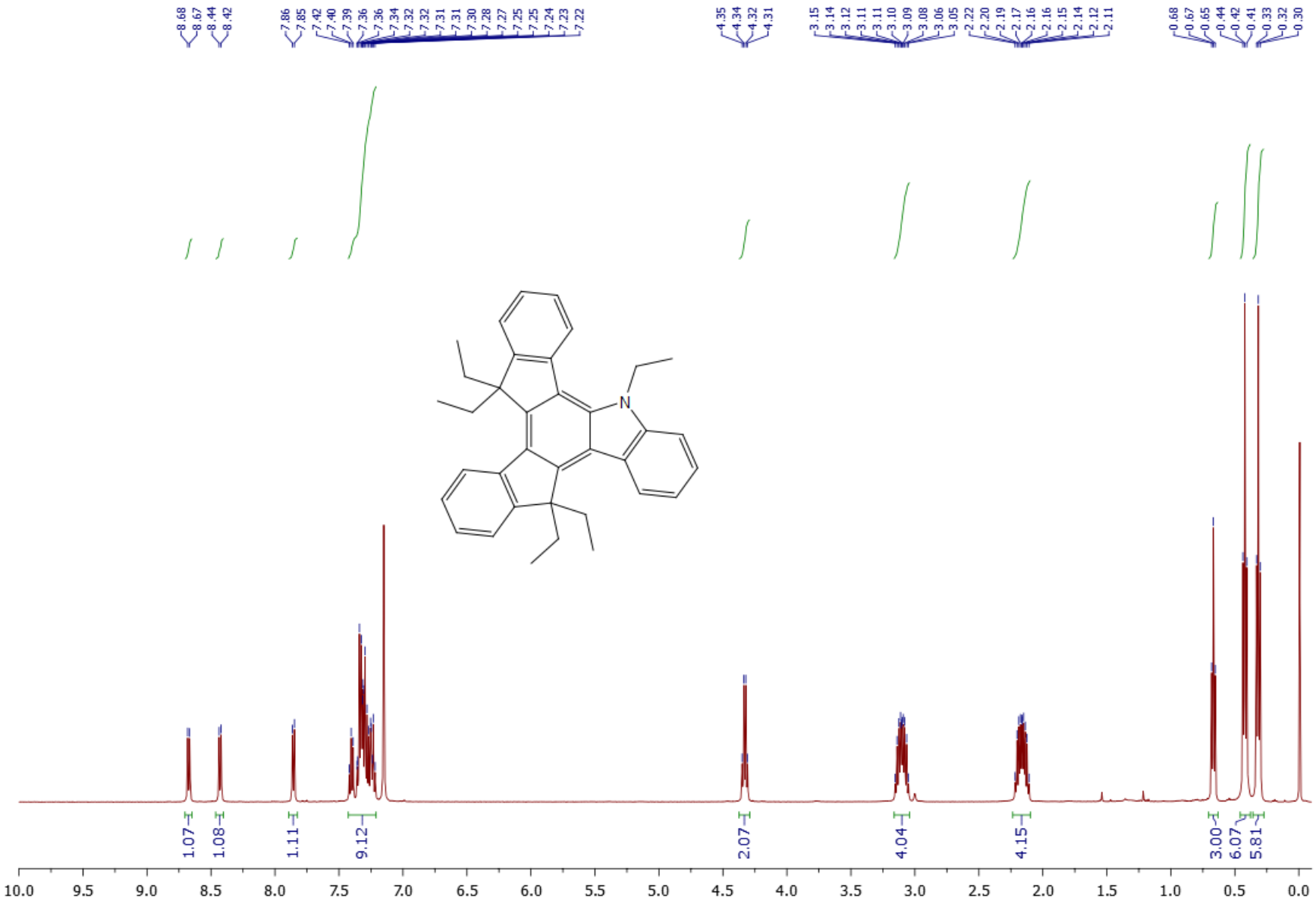
^{13}C {^{1}H} NMR spectra of **8** in $CDCl_3$ 126 MHz

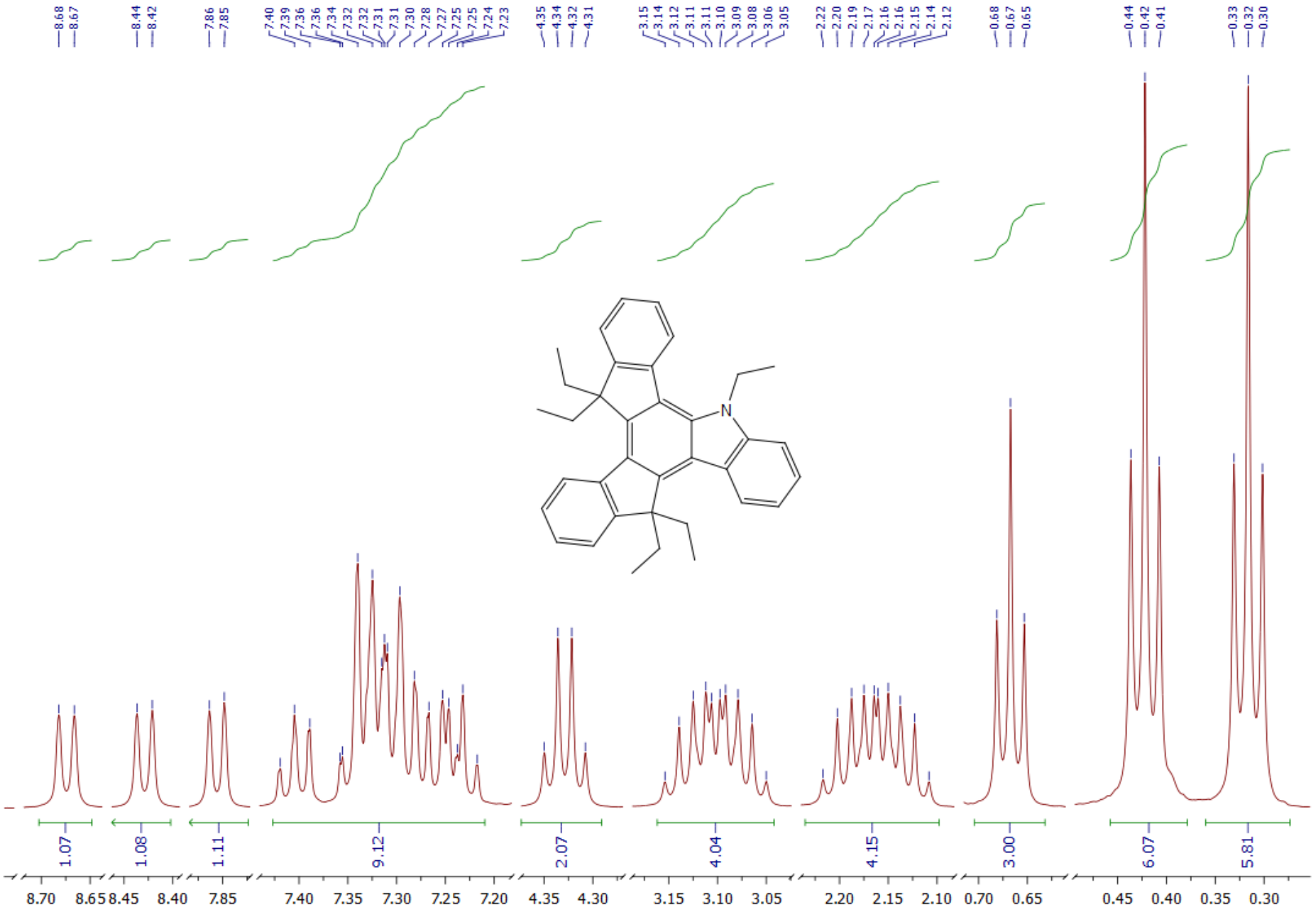



151.61
150.93
145.55
142.46
142.09
140.80
140.68
135.01
132.03
126.84
126.31
126.14
125.36
125.35
124.91
124.08
123.26
122.46
122.29
122.26
119.77
119.62
119.59
111.16
58.72
56.98
29.99
29.83
8.74
8.54
N
H
151.6
142.1
135.0
126.3
125.4
124.1
122.3
119.6
58.7
30.0
8.8
8.6

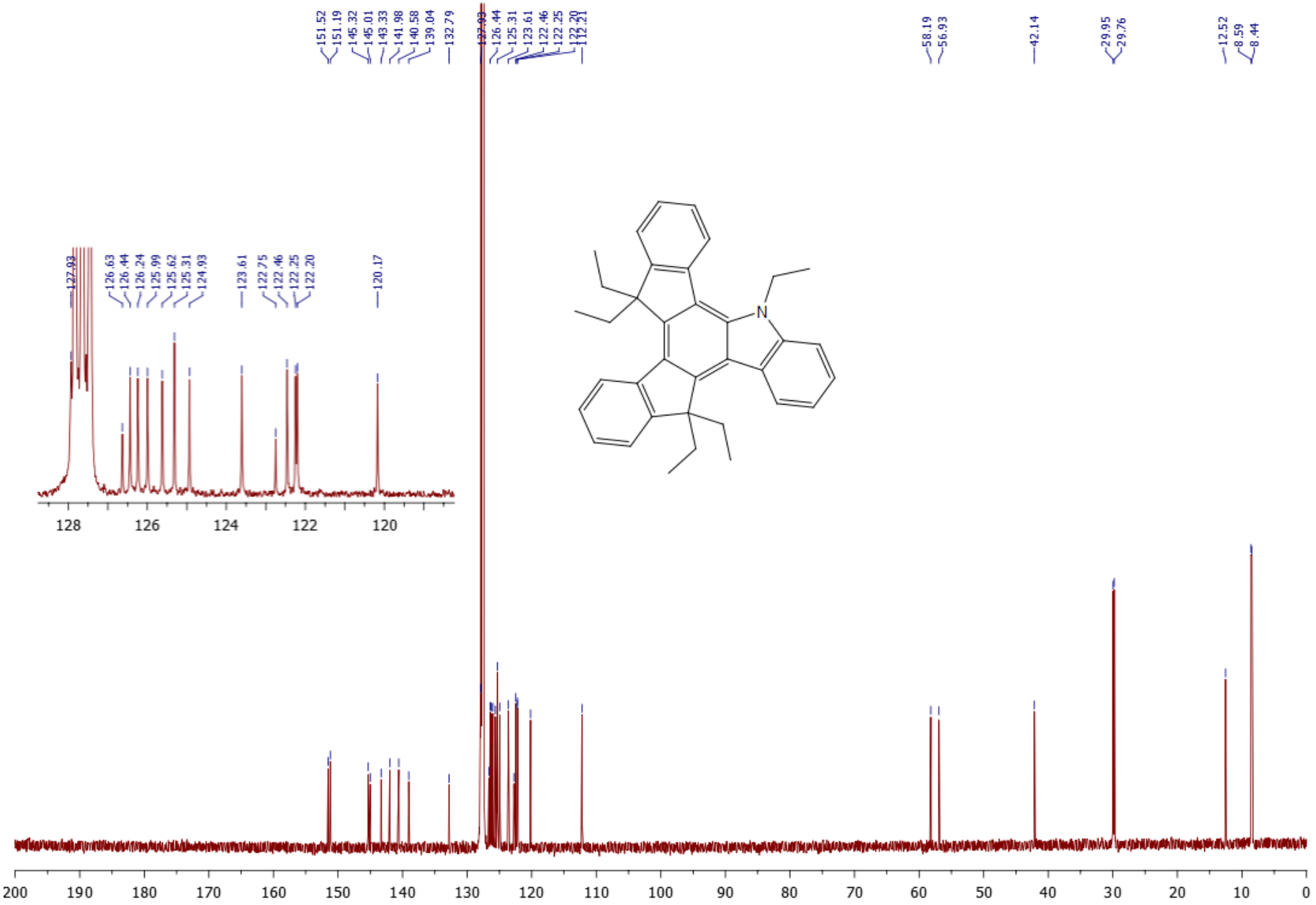
10. NMR spectra of NCC in C6D6

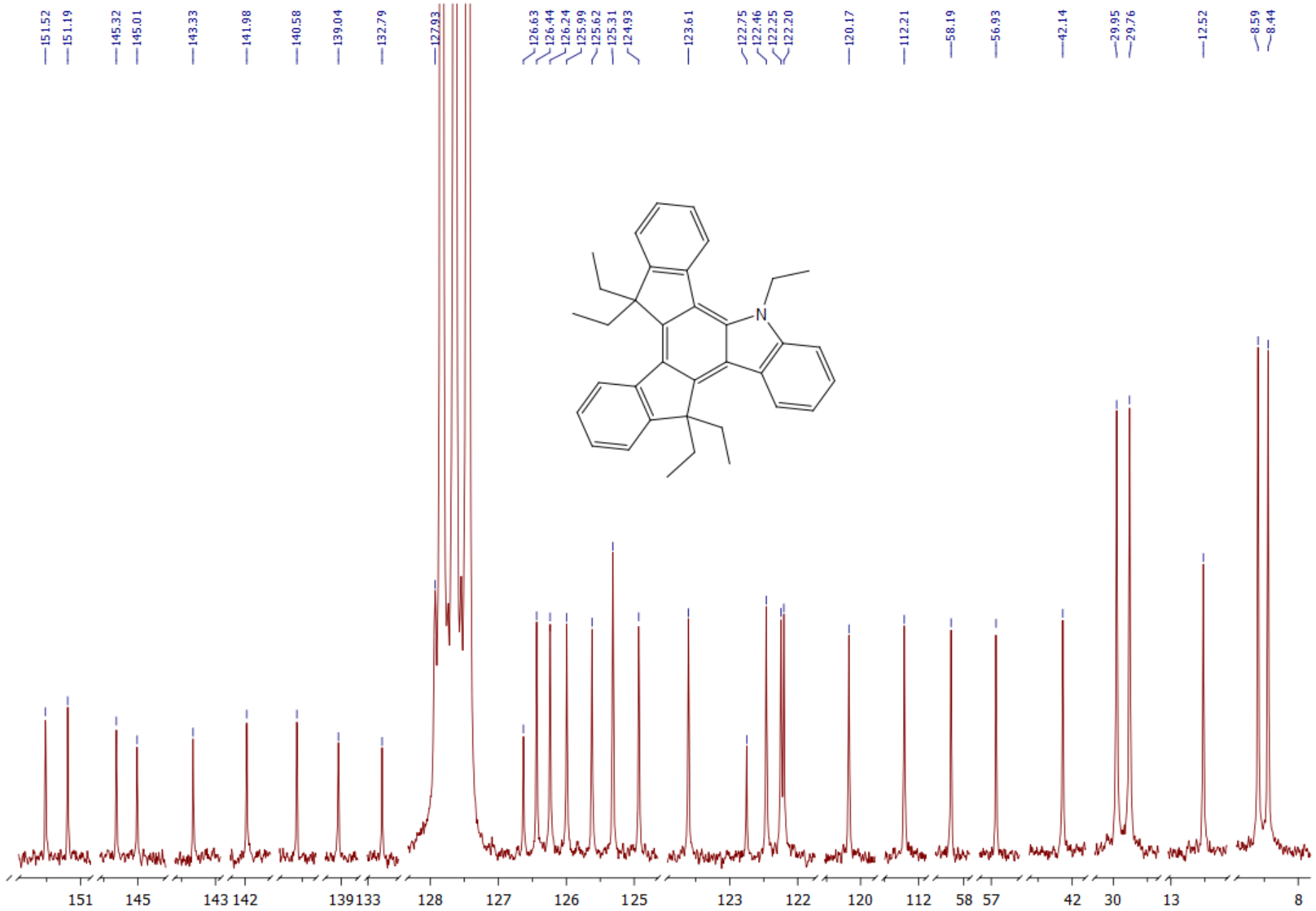
^{1}H NMR of NCC in C_6D_6, 500 MHz




8.68
8.67
8.44
8.42
7.86
7.85
7.40
7.39
7.36
7.36
7.34
7.32
7.32
7.31
7.31
7.30
7.28
7.27
7.25
7.25
7.24
7.23
4.35
4.34
4.32
4.31
3.15
3.14
3.12
3.11
3.11
3.10
3.09
3.08
3.06
3.05
2.22
2.20
2.19
2.17
2.16
2.16
2.15
2.14
2.12
0.68
0.67
0.65
0.44
0.42
0.41
0.33
0.32
0.30
N
1.07
1.08
1.11
9.12
2.07
4.04
4.15
3.00
6.07
5.81
8.70
8.65
8.45
8.40
7.85
7.40
7.35
7.30
7.25
7.20
4.35
4.30
3.15
3.10
3.05
2.20
2.15
2.10
0.70
0.65
0.45
0.40
0.35
0.30

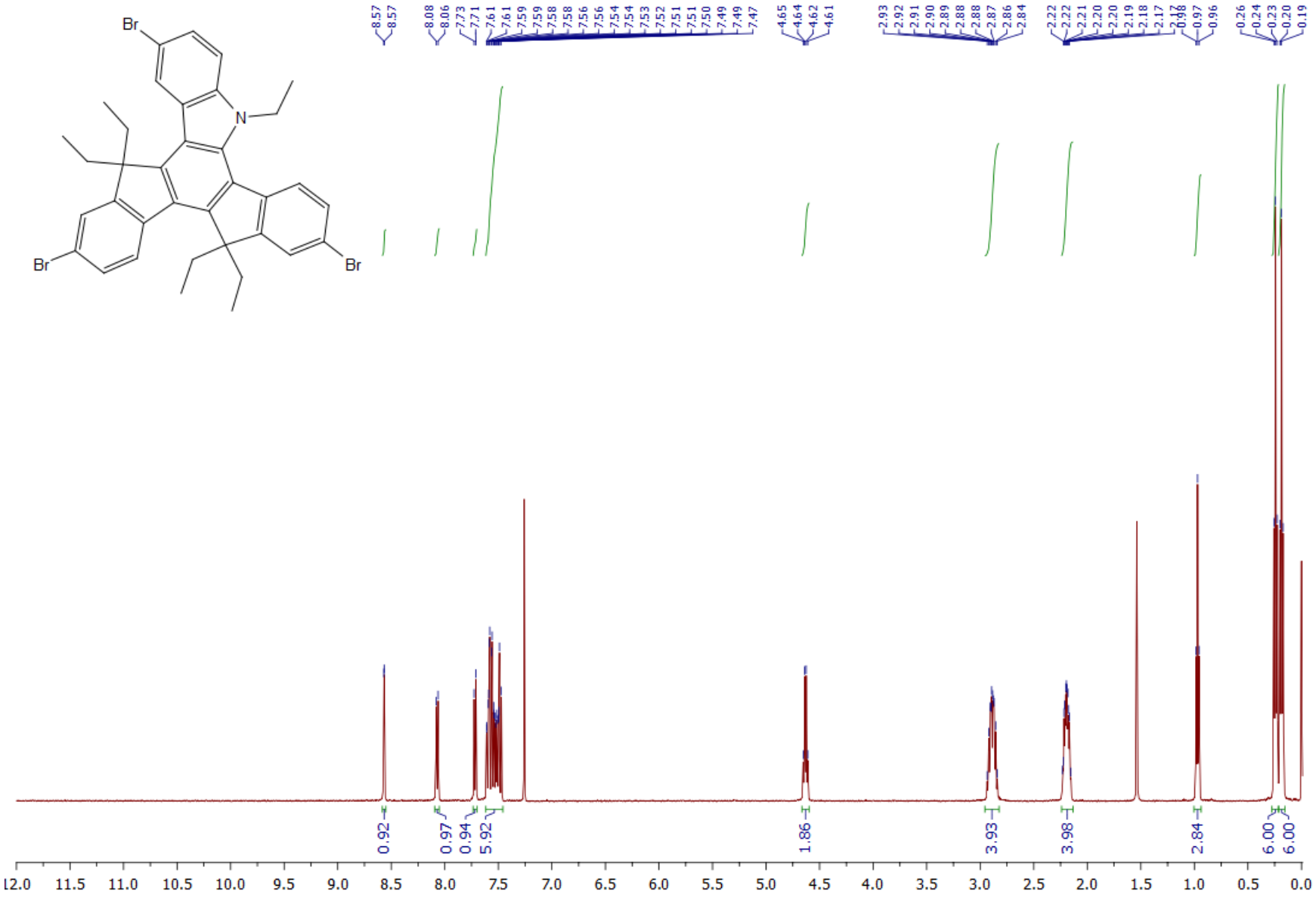
13C{1H} NMR of NCC in C6D6, 126 MHz

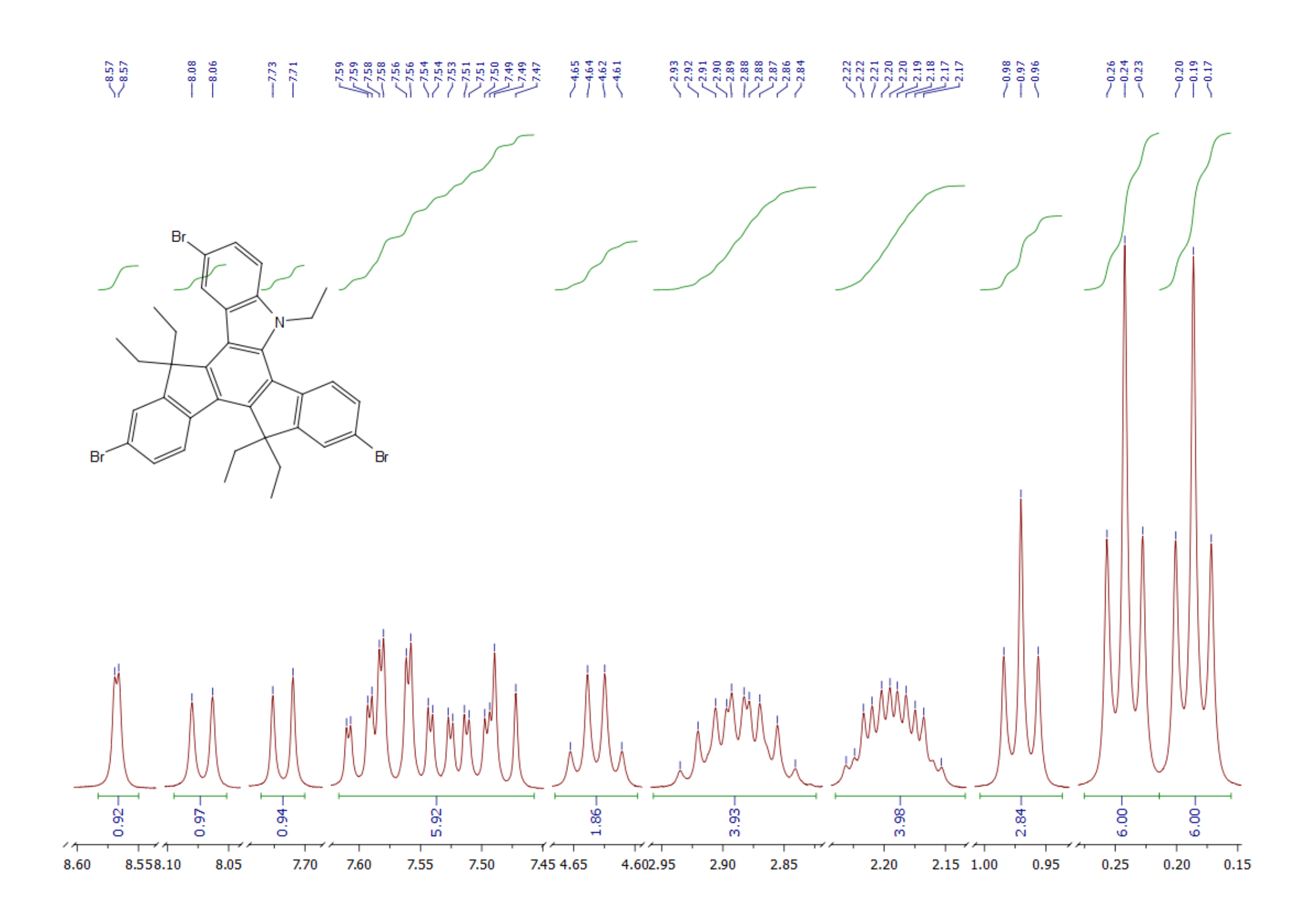



151.52
151.19
145.32
145.01
143.33
141.98
140.58
139.04
132.79
127.93
126.63
126.44
126.24
125.99
125.62
125.31
124.93
123.61
122.75
122.46
122.25
122.20
120.17
112.21
58.19
56.93
42.14
29.95
29.76
12.52
8.59
8.44
N
151
145
143
142
139
133
128
127
126
125
123
122
120
112
58
57
42
30
13
8

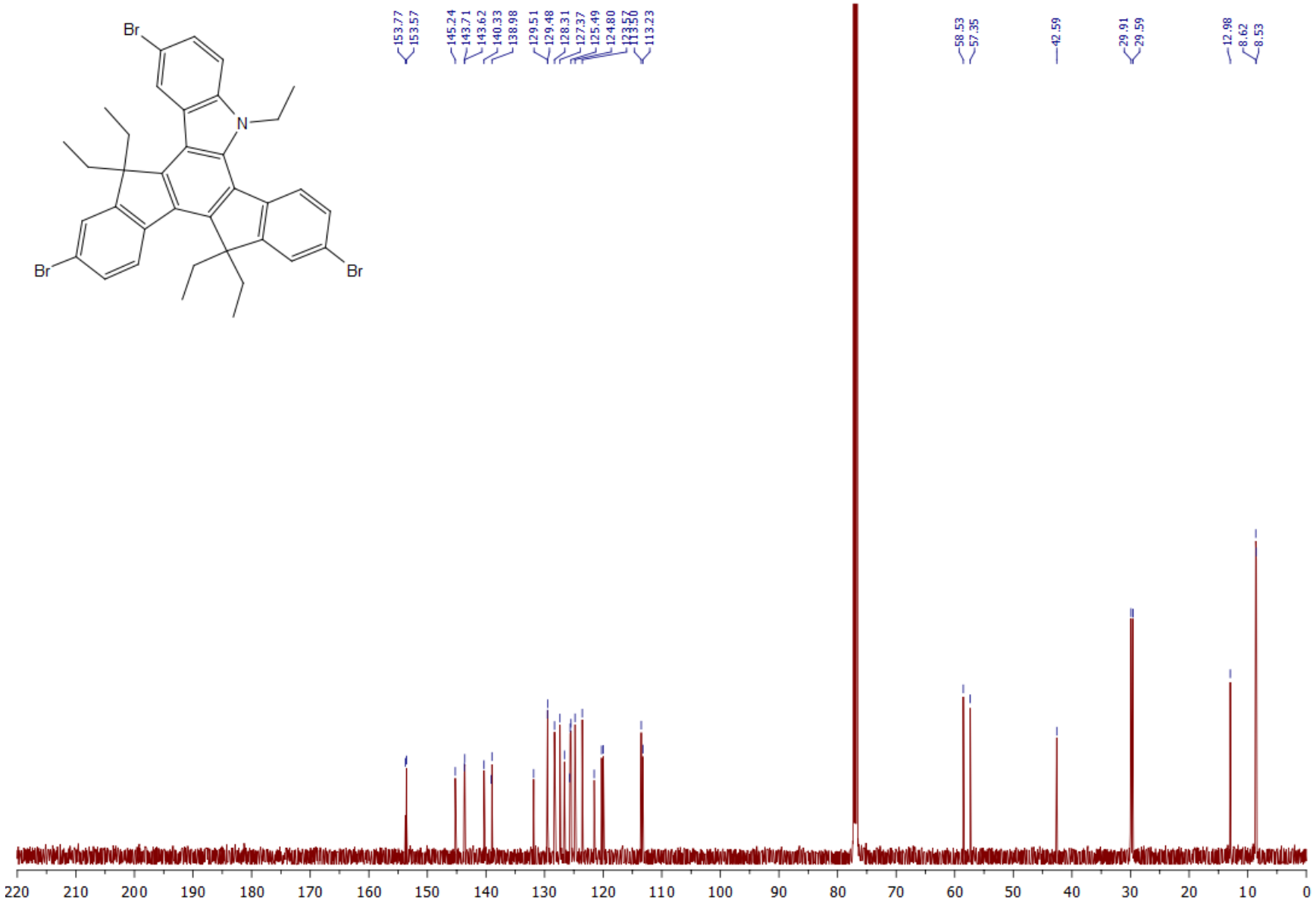
11. NMR spectra of 9a in $CDCl_3$

^1H NMR of 9a in $CDCl_3$ 500 MHz

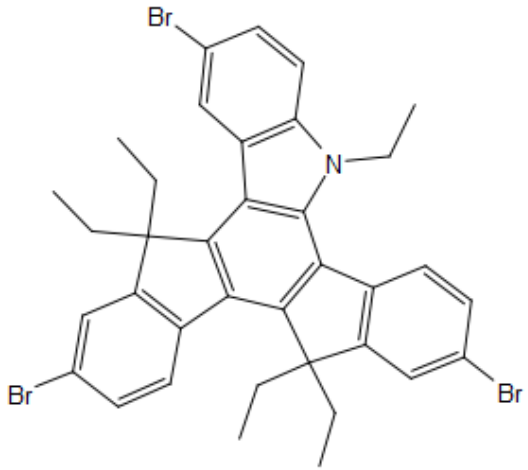


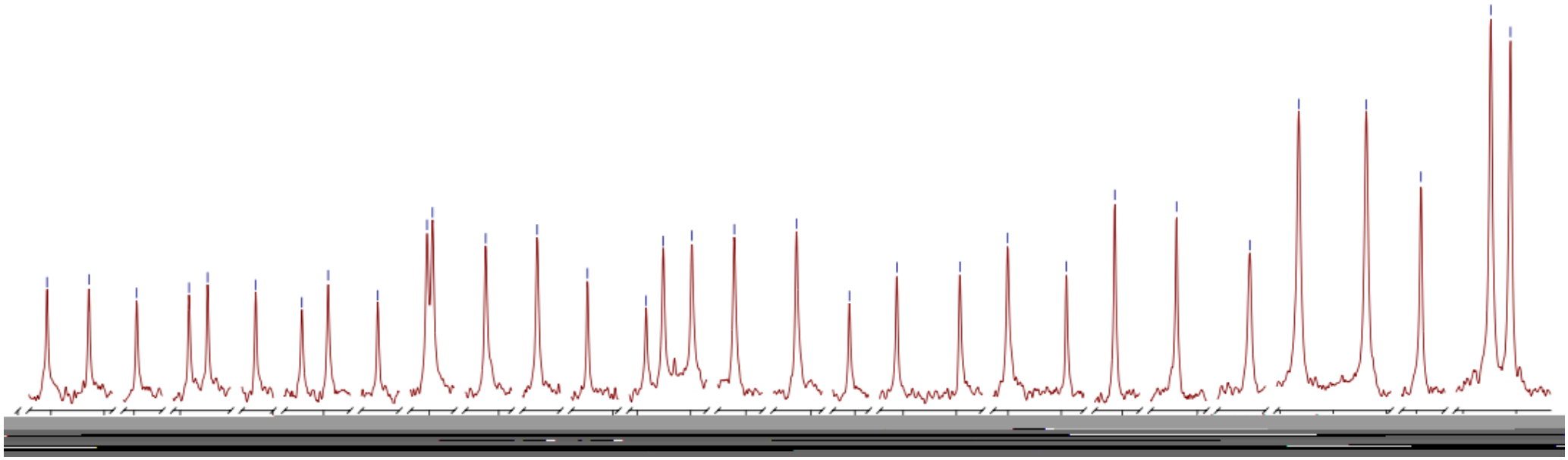

8.57
8.57
8.08
8.06
7.73
7.71
7.59
7.59
7.58
7.58
7.56
7.56
7.54
7.54
7.53
7.51
7.51
7.50
7.49
7.49
7.47
4.65
4.64
4.62
4.61
2.93
2.92
2.91
2.90
2.89
2.88
2.88
2.87
2.86
2.84
2.22
2.22
2.21
2.20
2.20
2.19
2.18
2.17
2.17
0.98
0.97
0.96
0.26
0.24
0.23
0.20
0.19
0.17
Br
N
Br
Br
0.92
0.97
0.94
5.92
1.86
3.93
3.98
2.84
6.00
6.00
8.60
8.55
8.10
8.05
7.70
7.60
7.55
7.50
7.45
4.65
4.60
2.95
2.90
2.85
2.20
2.15
1.00
0.95
0.25
0.20
0.15

^{13}C {^{1}H} NMR spectra of 9a in $CDCl_3$ 126 MHz



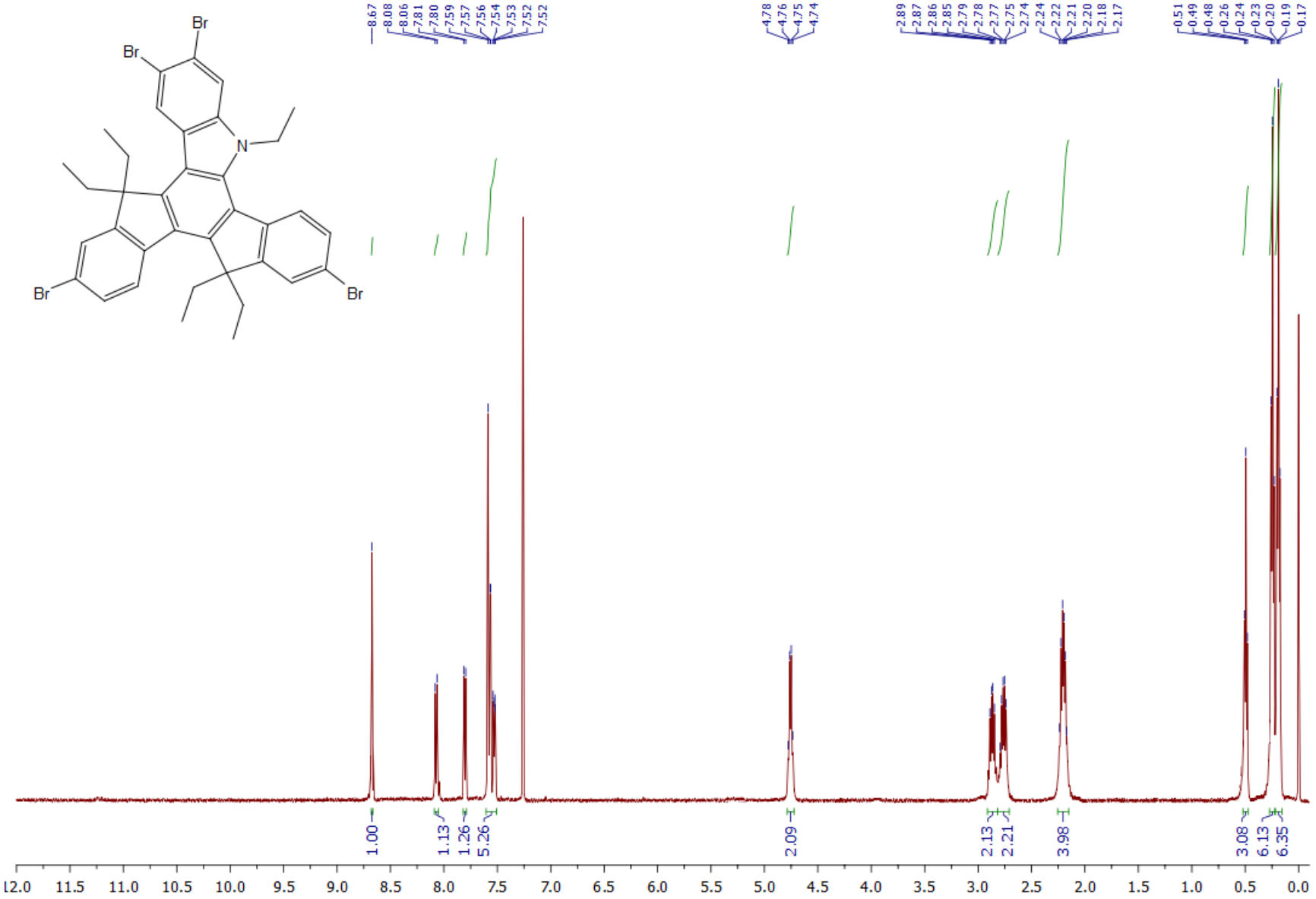
153.77
153.57
145.24
143.71
143.62
140.33
139.10
138.98
131.86
129.48
128.31
127.37
126.62
125.63
125.49
124.80
123.57
121.53
120.28
119.98
113.50
113.23
58.53
57.35
42.59
29.91
29.59
12.98
8.62
8.53

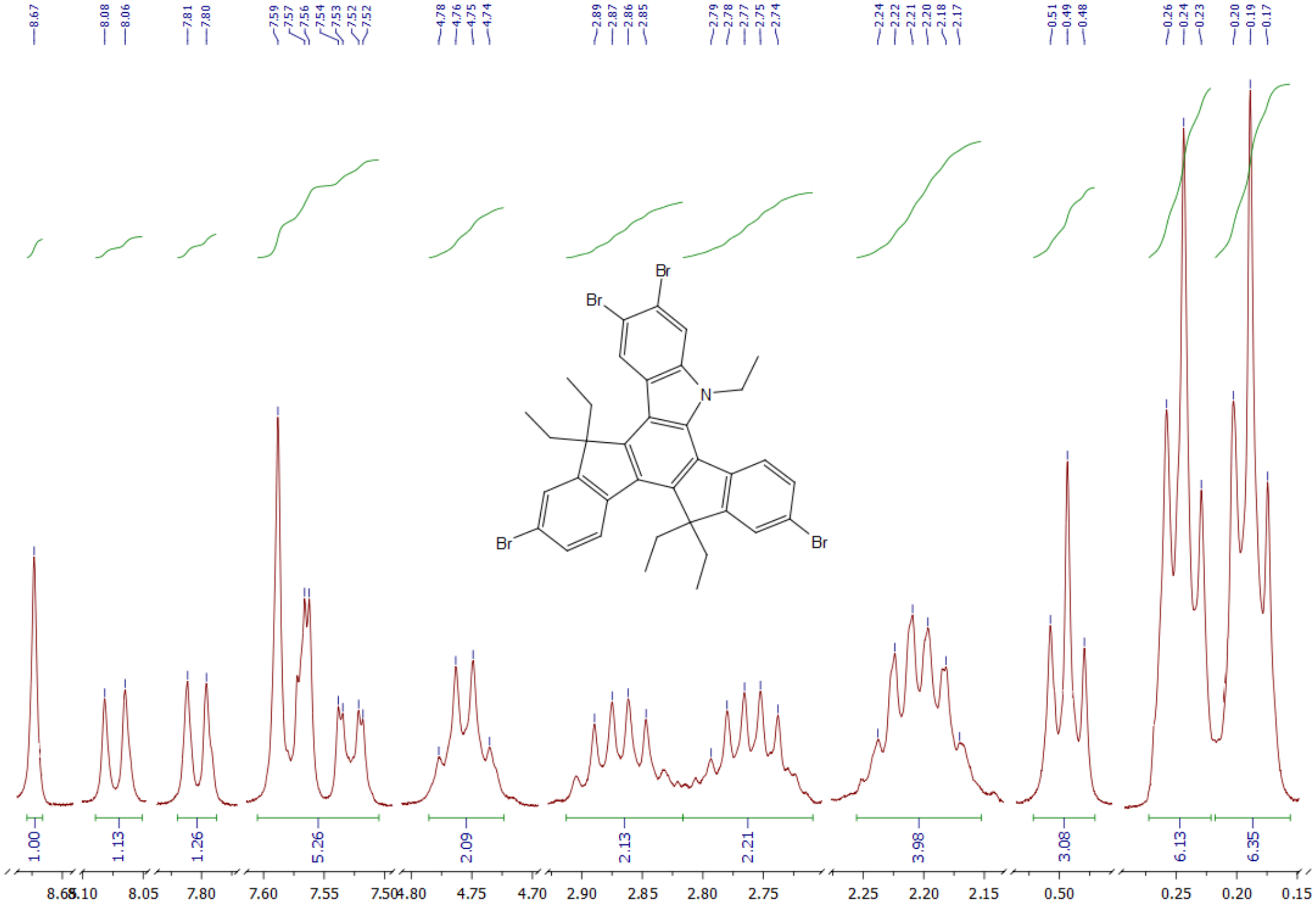




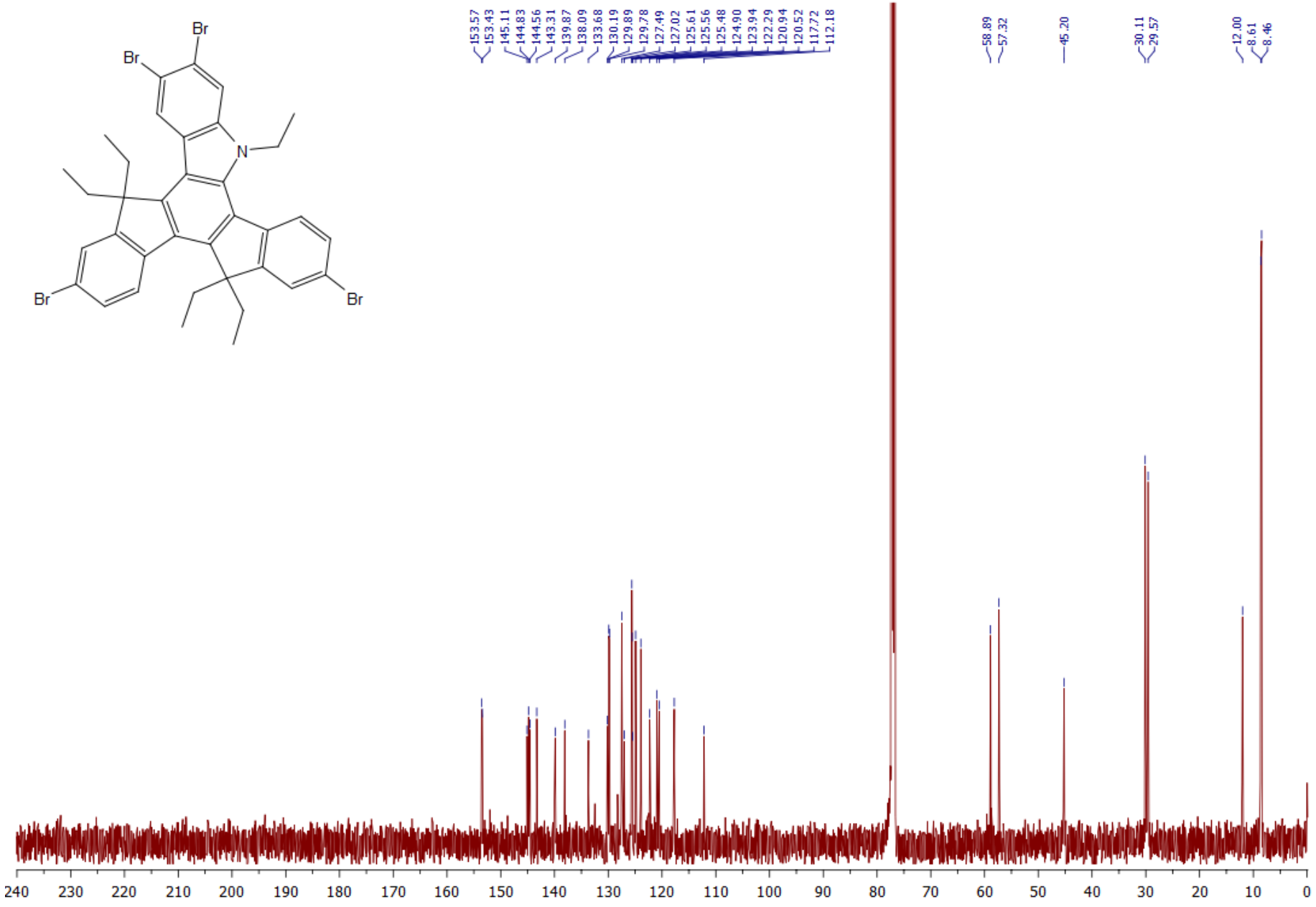
12. NMR spectra of 10 in $CDCl_3$

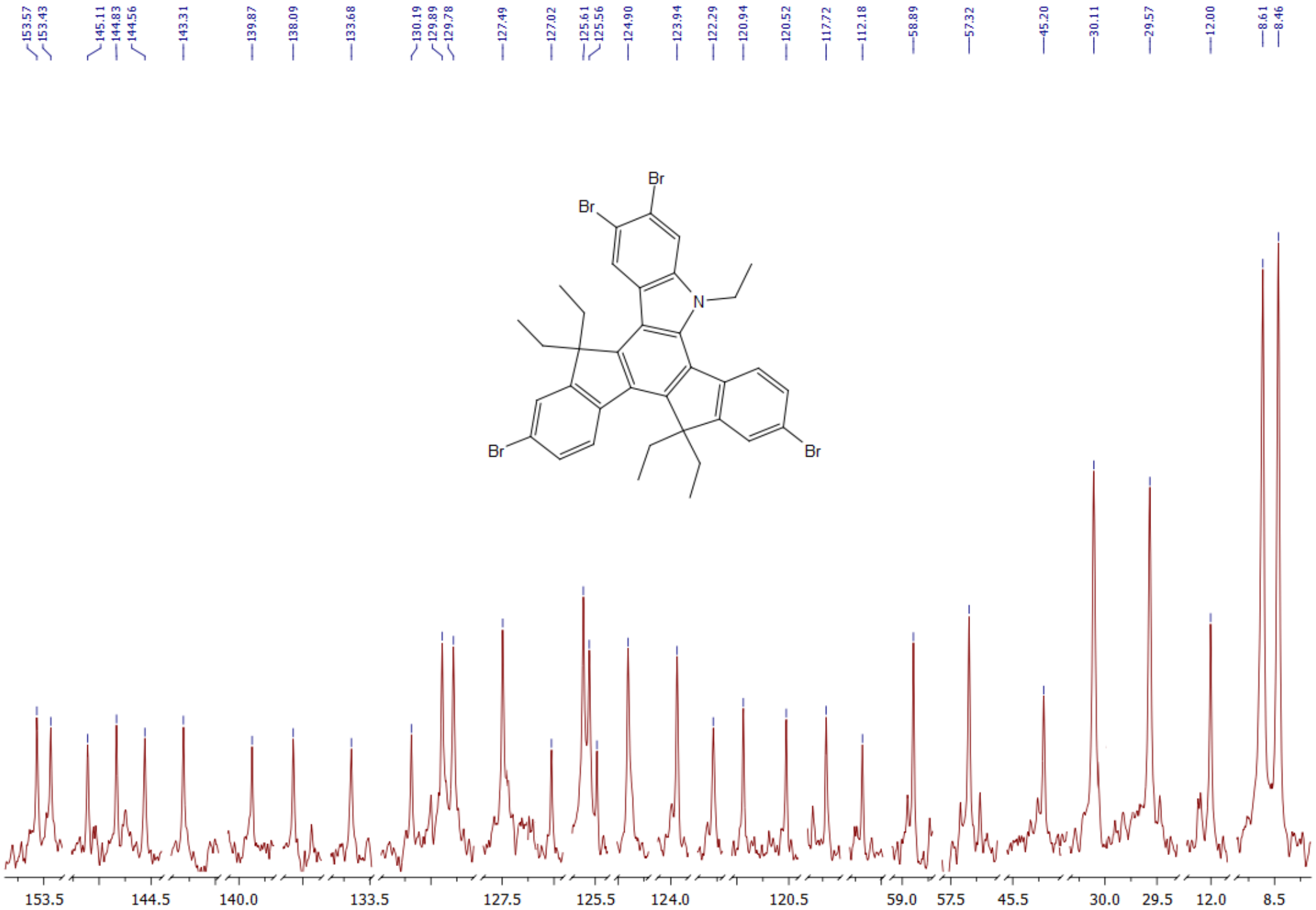
^1H NMR of 10 in $CDCl_3$ 500 MHz




8.67
8.08
8.06
7.81
7.80
7.59
7.57
7.56
7.54
7.53
7.52
7.52
4.78
4.76
4.75
4.74
2.89
2.87
2.86
2.85
2.79
2.78
2.77
2.75
2.74
2.24
2.22
2.21
2.20
2.18
2.17
0.51
0.49
0.48
0.26
0.24
0.23
0.20
0.19
0.17
Br
Br
N
Br
Br
1.00
1.13
1.26
5.26
2.09
2.13
2.21
3.98
3.08
6.13
6.35
8.65
8.10
8.05
7.80
7.60
7.55
7.50
4.80
4.75
4.70
2.90
2.85
2.80
2.75
2.25
2.20
2.15
0.50
0.25
0.20
0.15

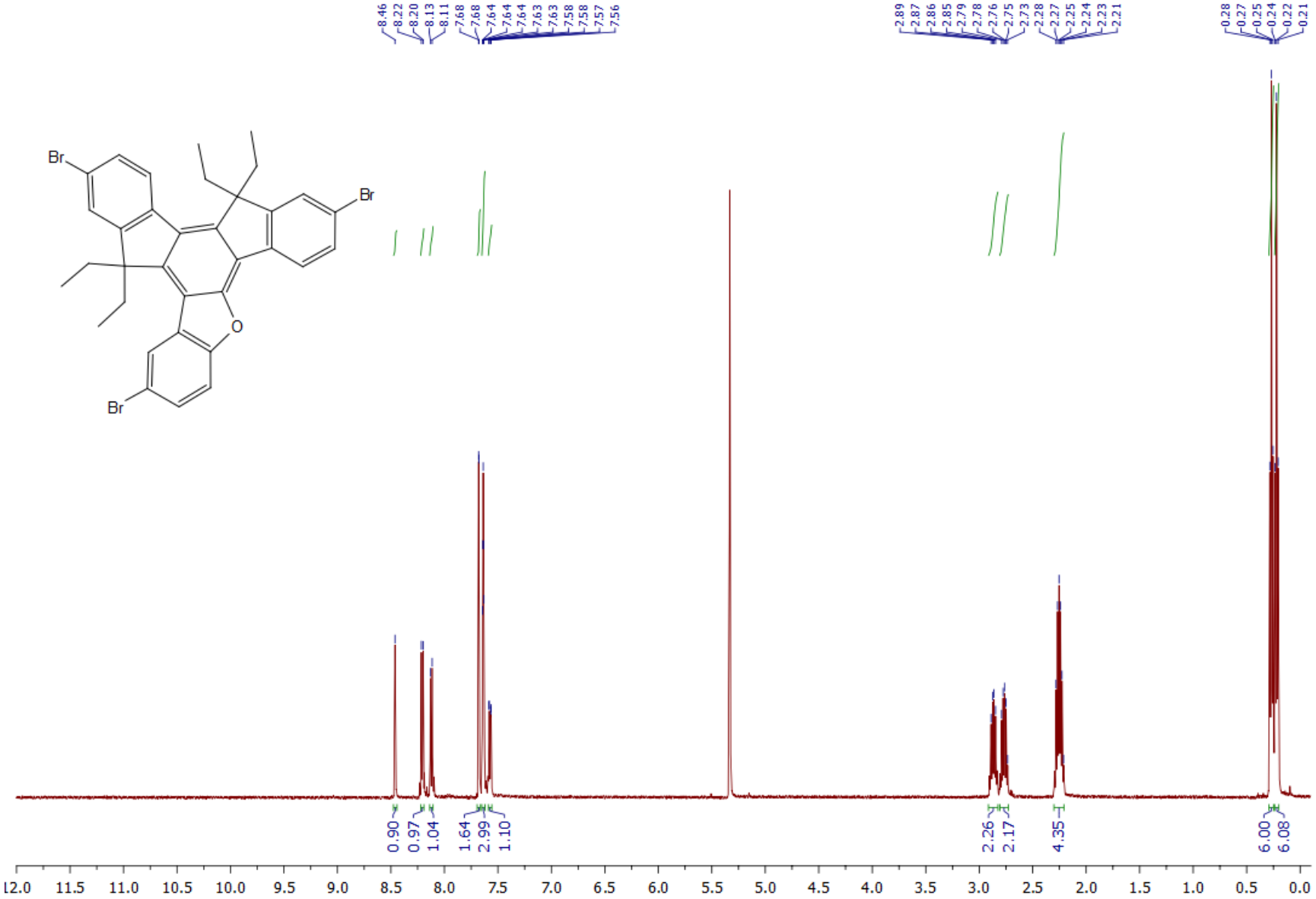
^{13}C {^{1}H} NMR spectra of 10 in $CDCl_3$ 126 MHz

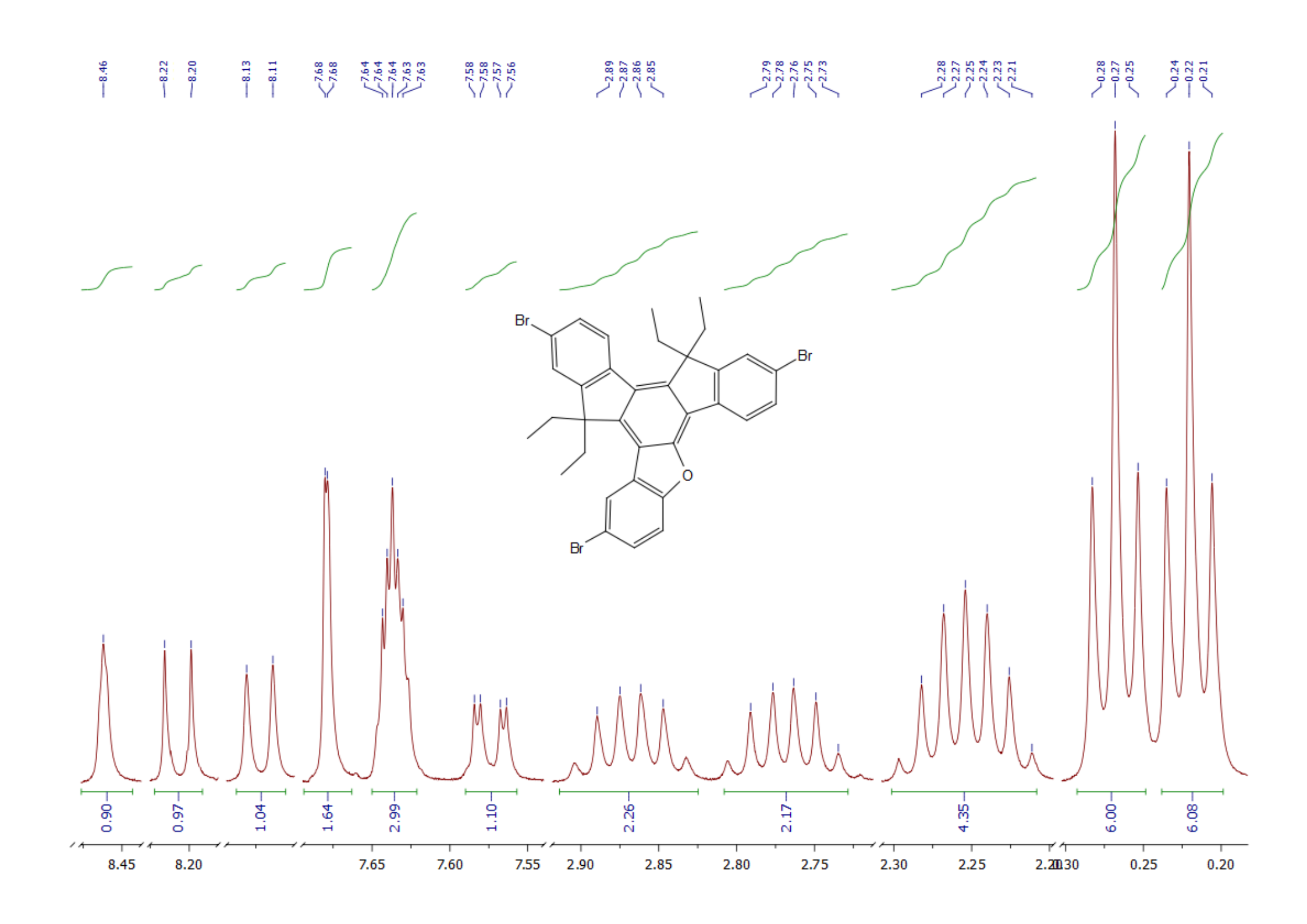



153.57
153.43
145.11
144.83
144.56
143.31
139.87
138.09
133.68
130.19
129.89
129.78
127.49
127.02
125.61
125.56
124.90
123.94
122.29
120.94
120.52
117.72
112.18
58.89
57.32
45.20
30.11
29.57
12.00
8.61
8.46
Br
Br
Br
Br
N
153.5
144.5
140.0
133.5
127.5
125.5
124.0
120.5
59.0
57.5
45.5
30.0
29.5
12.0
8.5

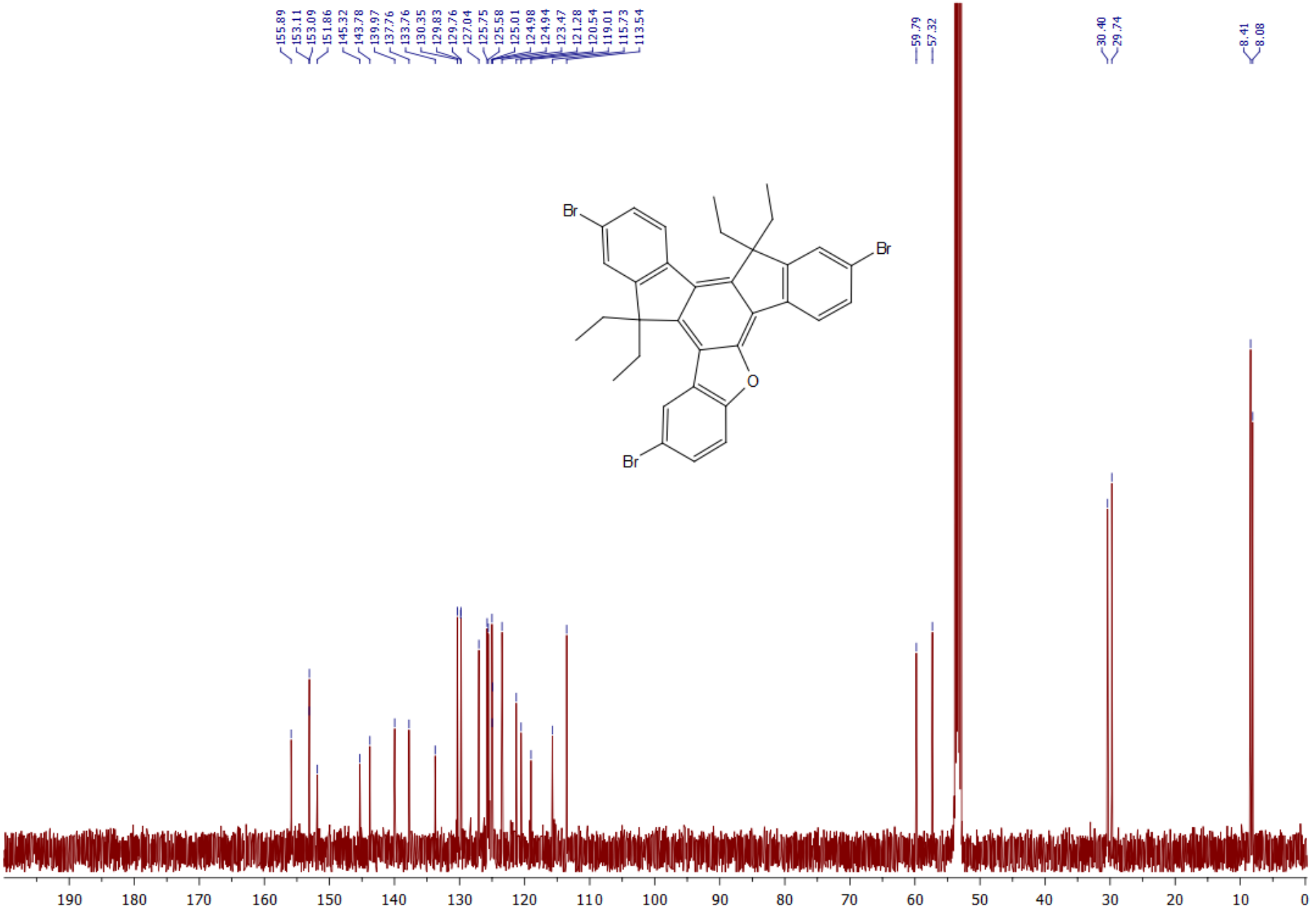
13. NMR spectra of 9b in CD_2Cl_2

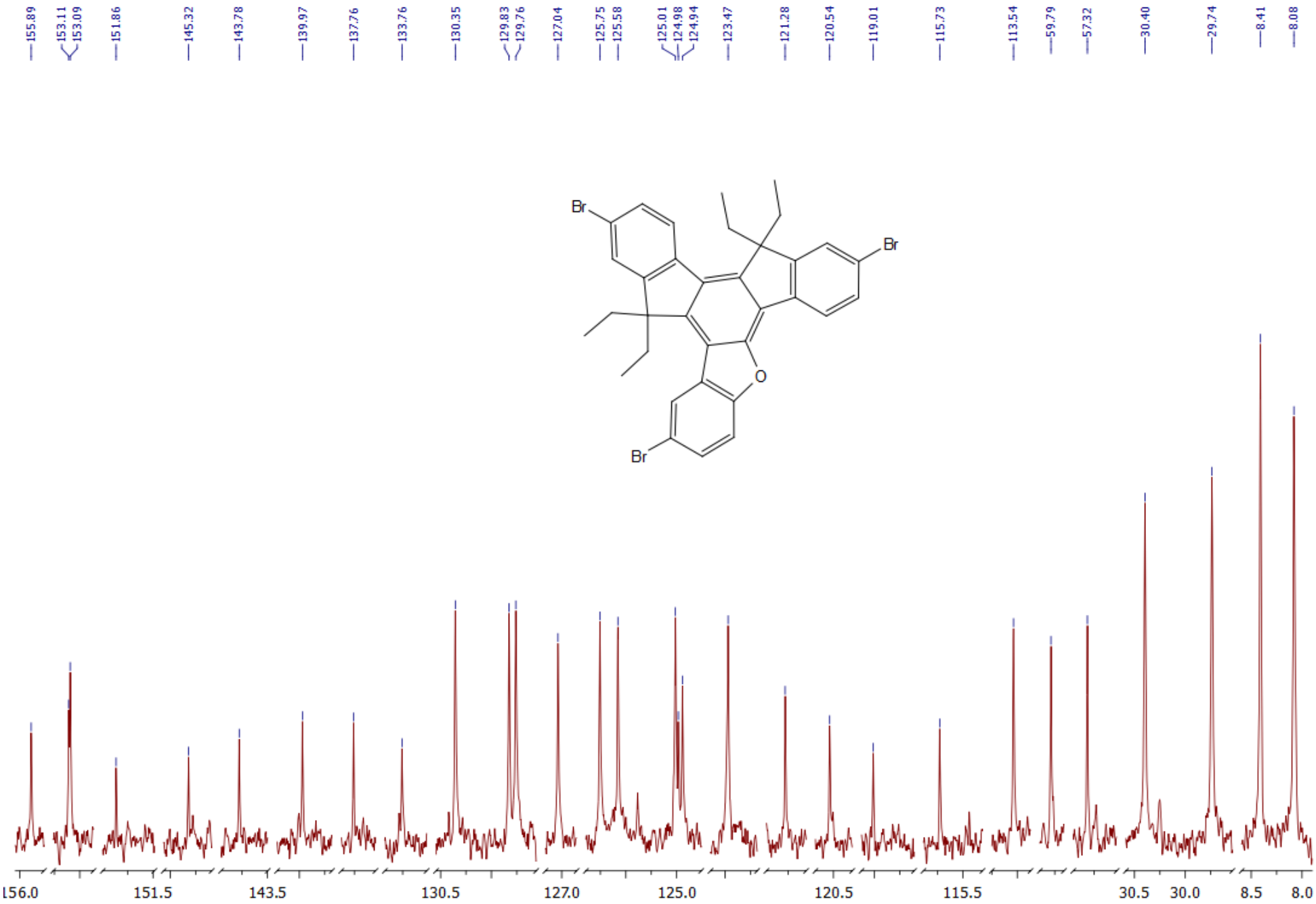
^1H NMR of 9b in CD_2Cl_2 500 MHz




8.46
8.22
8.20
8.13
8.11
7.68
7.68
7.64
7.64
7.64
7.63
7.63
7.58
7.58
7.57
7.56
2.89
2.87
2.86
2.85
2.79
2.78
2.76
2.75
2.73
2.28
2.27
2.25
2.24
2.23
2.21
0.28
0.27
0.25
0.24
0.22
0.21
Br
Br
Br
O
0.90
0.97
1.04
1.64
2.99
1.10
2.26
2.17
4.35
6.00
6.08
8.45
8.20
7.65
7.60
7.55
2.90
2.85
2.80
2.75
2.30
2.25
0.30
0.25
0.20

^{13}C {^{1}H} NMR spectra of 9b in CD_2Cl_2 126 MHz




155.89
153.11
153.09
151.86
145.32
143.78
139.97
137.76
133.76
130.35
129.83
129.76
127.04
125.75
125.58
125.01
124.98
124.94
123.47
121.28
120.54
119.01
115.73
113.54
59.79
57.32
30.40
29.74
8.41
8.08
Br
Br
Br
O
156.0
151.5
143.5
130.5
127.0
125.0
120.5
115.5
30.5
30.0
8.5
8.0