Supporting Info

Synthesis and reactivity of 5-heterotruxenes containing sulfur or nitrogen as heteroatom

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1 Crystallographic data

The X-ray diffraction data were collected at 100 K on an Agilent SuperNova diffractometer equipped with a Cu$K\alpha$ (using for **NCC**, **SCC**, (**SO)CC**) and Mo$K\alpha$ (using for (**SO2)CC**) micro-focus X-ray source and an Oxford Cryosystems open-flow nitrogen cryostat. Structures were solved by direct methods with SHELXS-97 [1] and refined against F^2 with full-matrix least-squares using SHELXL-2018 [2]. All non-H atoms were refined with anisotropic atomic

displacement parameters. Hydrogen atoms were located on Fourier difference maps and refined with positional parameters or included in geometric positions and refined as riding atoms with isotropic thermal parameters based upon the corresponding bonding carbon atom (U_{iso} = 1.5U_{eq} for methyl groups and U_{iso} = 1.2U_{eq} for the rest). The oxygen atom in the **SOCC** structure was found as disordered. The components of disorder were located on a difference Fourier map and refined in two positions with site occupation factors (s.o.f.) = 0.9 and 0.1.

[1] Sheldrick, G. M. SHELX-97: *Program for Crystal Structure Solution*; University of Göttingen, Germany, 1997.
[2] Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem*. 2015, 71, 3−8.

Crystal data for the structure NCC $C_{36}H_{37}N$, M = 483.67, colourless, 0.15 × 0.15 × 0.15 mm, monoclinic, space group $P2_1/n$, a = 10.1994(4), b = 13.3386(5), c = 19.9210(7) Å, β = 96.989(3) °, V = 2690.0(2) Å^3, T = 100.0(1) K, Z = 4, d_{calc}= 1.194 g/cm^3, μ (Cu$K\alpha$) = 0.511 mm^{-1}, θ_{max} = 72.19°, 5230 independent reflections, 4709 with $I > 2\sigma(I)$. R = 0.045, wR = 0.126 (R = 0.049, wR = 0.130 for all data), *GOOF* = 0.95.

Crystal data for the structure SCC $C_{34}H_{32}S$, M = 472.66, colourless, 0.6 × 0.1 × 0.1 mm, monoclinic, space group $P2_1/n$, a = 17.2366(3), b = 7.2333(1), c = 41.0092(8) Å, β = 95.052(2) °, V = 5093.06(15) Å^3, T = 99.9(2) K, Z = 8, d_{calc}= 1.233 g/cm^3, μ (Cu$K\alpha$) = 1.264 mm^{-1}, θ_{max} = 66.59°, 8974 independent reflections, 7872 with $I > 2\sigma(I)$. R = 0.074, wR = 0.193 (R = 0.082, wR = 0.196 for all data), *GOOF* = 1.01.

Crystal data for the structure (SO)CC $C_{34}H_{32}SO$, M = 488.66, colourless, 0.25 × 0.15 × 0.15 mm, orthorhombic, space group *Pbca*, a = 14.4446(2), b = 16.2063(2), c = 21.8323(3) Å, V = 5110.80(12) Å^3, T = 99.9(2) K, Z = 8, d_{calc}= 1.270 g/cm^3, μ (Cu$K\alpha$) = 1.307 mm^{-1}, θ_{max} = 66.57°, 4489 independent reflections, 4288 with $I > 2\sigma(I)$. R = 0.067, wR = 0.162 (R = 0.069, wR = 0.164 for all data), *GOOF* = 1.06.

Crystal data for the structure (SO2)CC $C_{34}H_{32}SO_2$, M = 504.66, colourless, 0.35 × 0.2 × 0.1 mm, monoclinic, space group $P2_1/c$, a = 7.1863(2), b = 21.7963(7), c = 17.2689(4) Å, β = 101.827(2) °, V = 2647.49(13) Å^3, T = 100.0(1) K, Z = 4, d_{calc}= 1.266 g/cm^3, μ (Mo$K\alpha$) = 0.152 mm^{-1}, θ_{max} = 26.37°, 5376 independent reflections, 4118 with $I > 2\sigma(I)$. R = 0.043, wR = 0.096 (R = 0.065, wR = 0.104 for all data), *GOOF* = 0.97.

2 SCC crystal structure and thermal ellipsoid plot

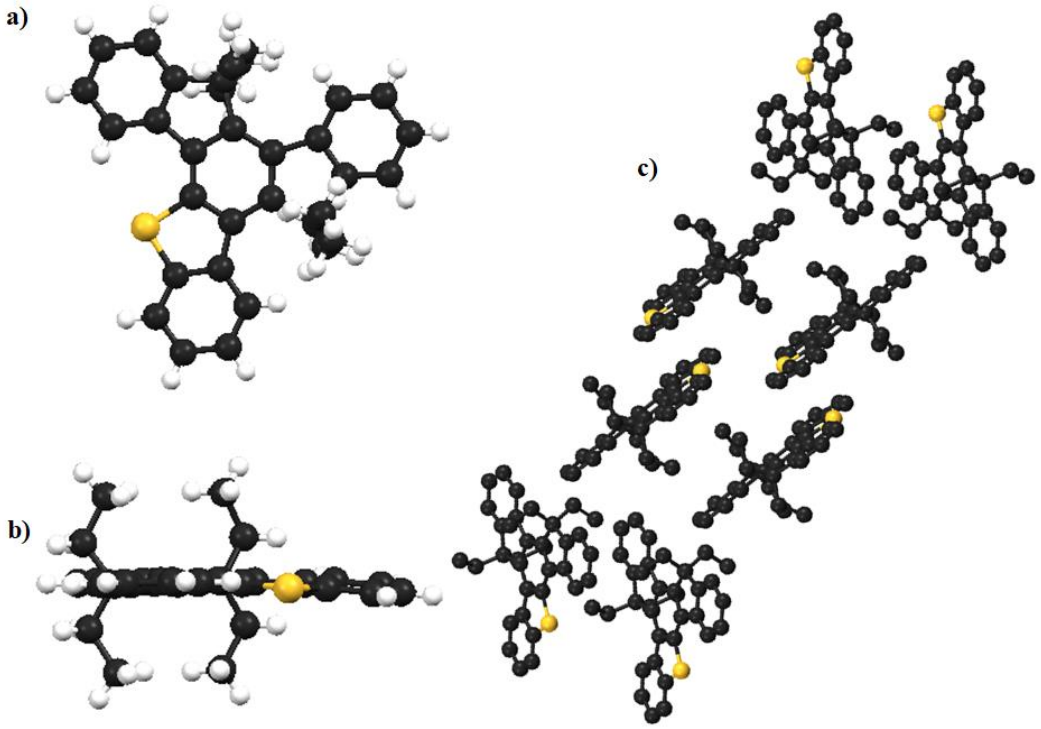


Figure S1a. SCC crystal structure a) top view, b) side view, c) packing.

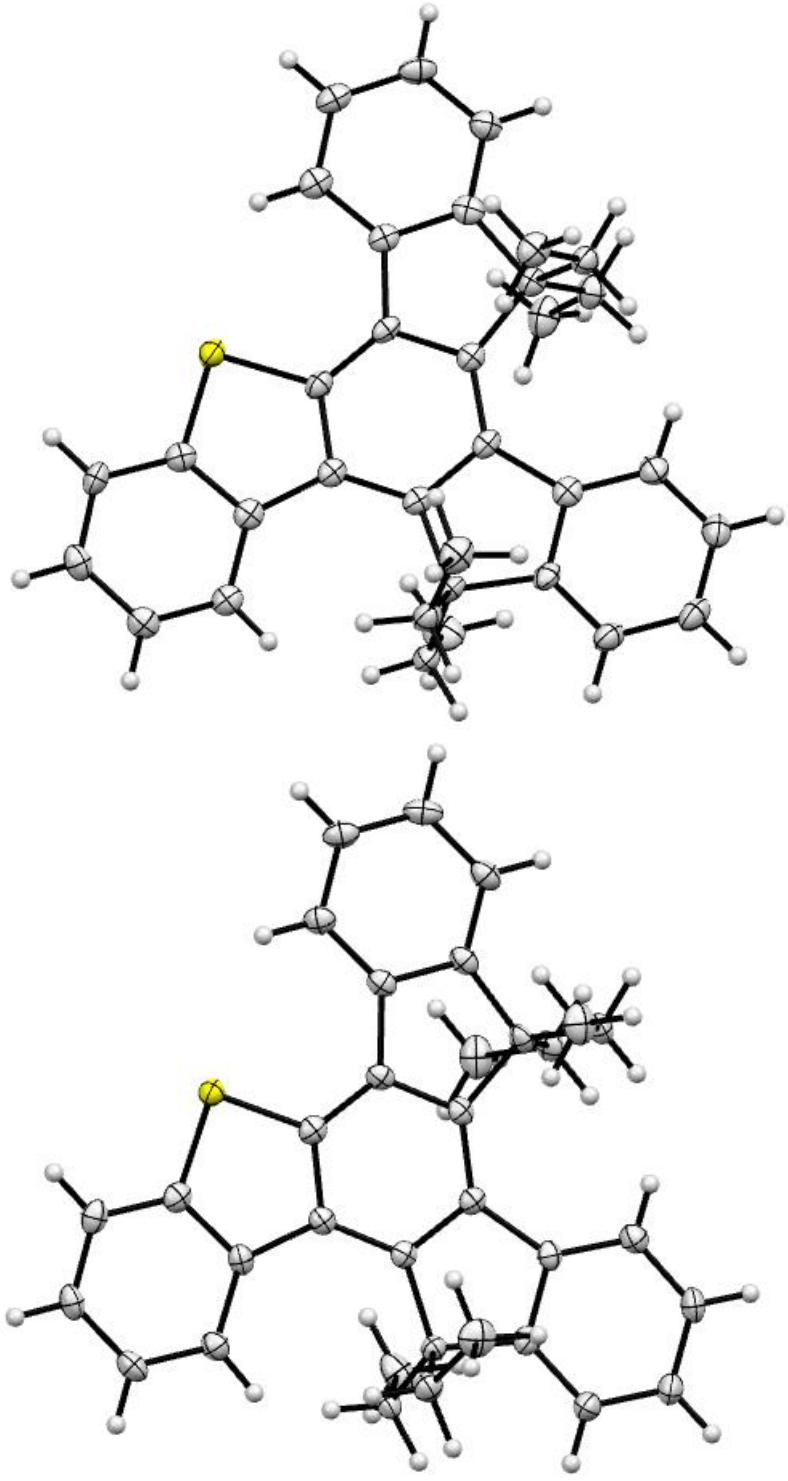


Figure S1b. Crystal structures of two independent molecules of SCC at 100 K. Thermal ellipsoids with 50% probability.

SCC crystal for X-ray diffraction were grown by slow evaporation of solvent (ACN) during several days at 20°C.

3 (SO)CC structure and thermal ellipsoid plot

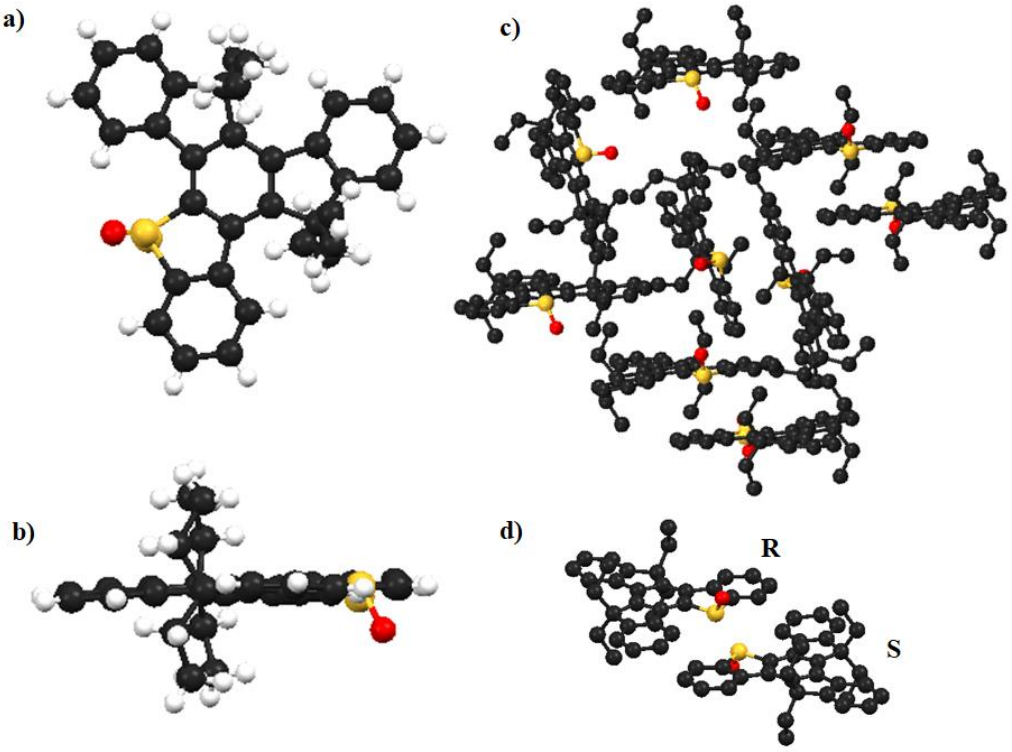


Figure S2a. (SO)CC crystal structure a) top view, b) side view, c) packing, d) enantiomers – stereogenic center are present at sulfur atom.

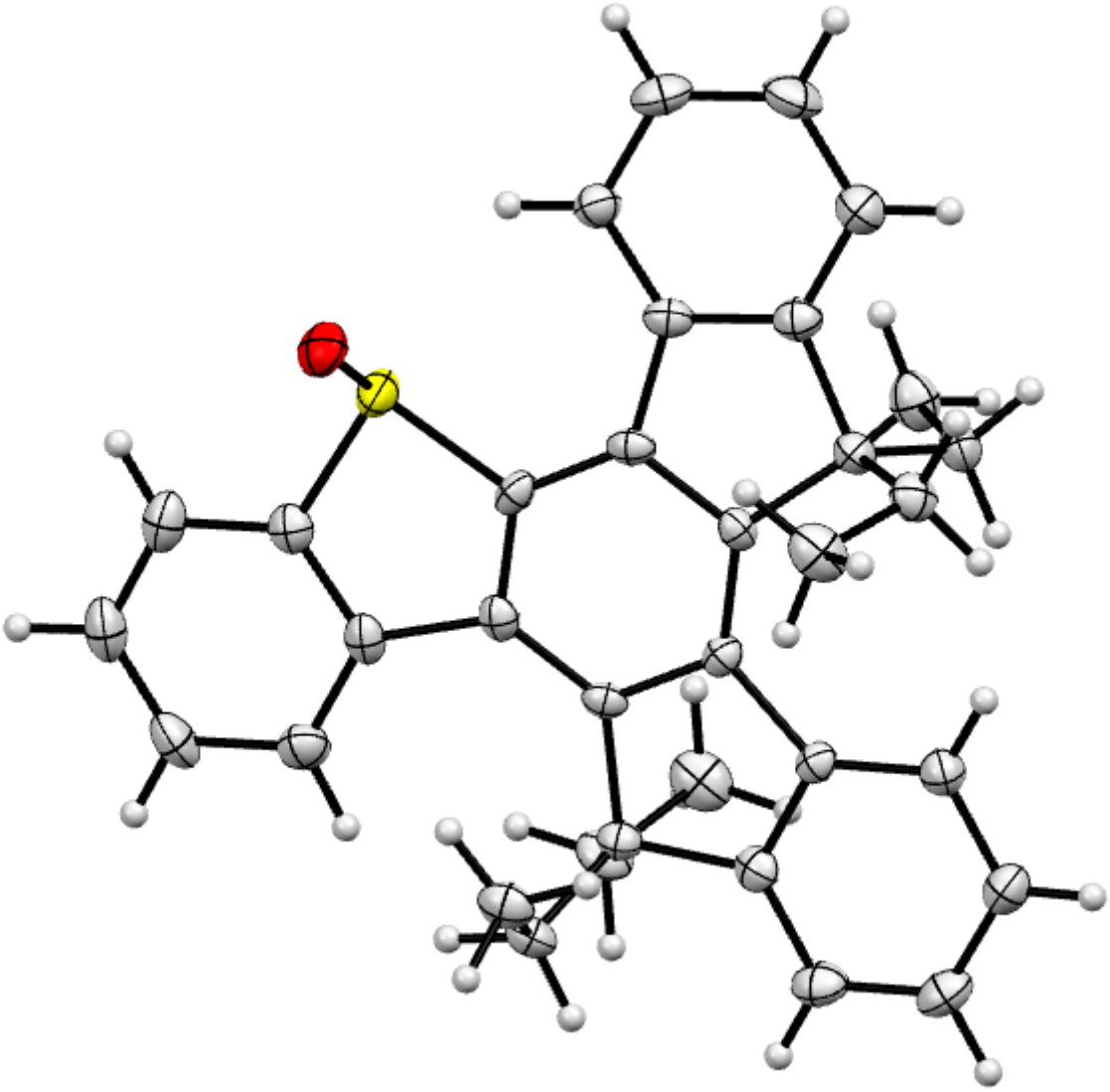


Figure S2b. Crystal structure of (SO)CC at 100 K. Thermal ellipsoids with 50% probability.

(SO)CC crystal for X-ray diffraction were grown by slow evaporation of solvent (ACN) during several days at 20°C.

4 $(SO_2)CC$ structure and thermal ellipsoid plot

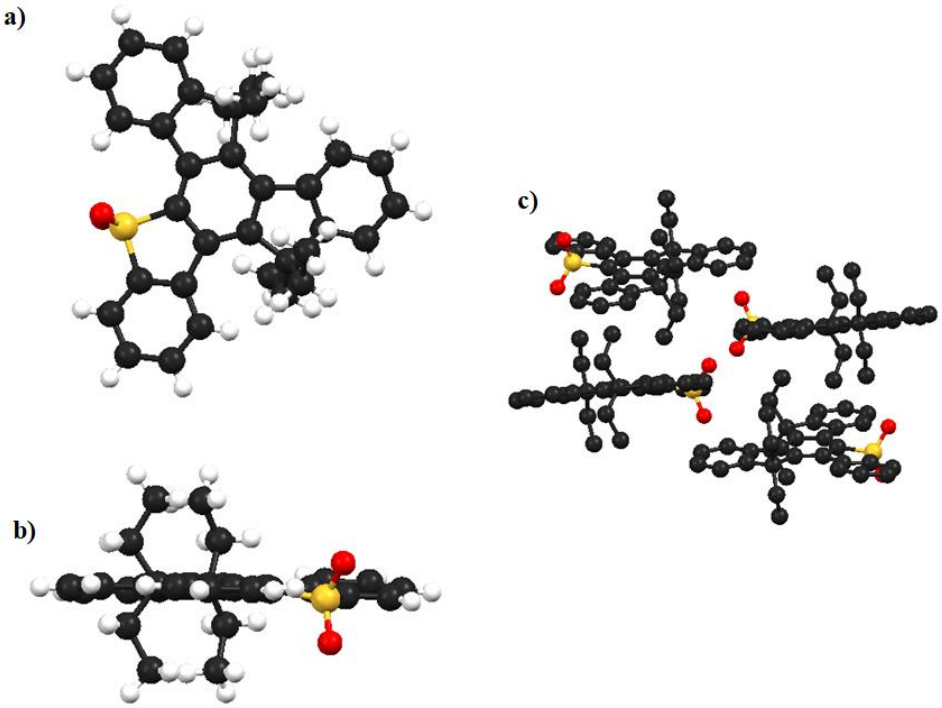


Figure S3a. (SO2)CC crystal structure a) top view, b) side view, c) packing.

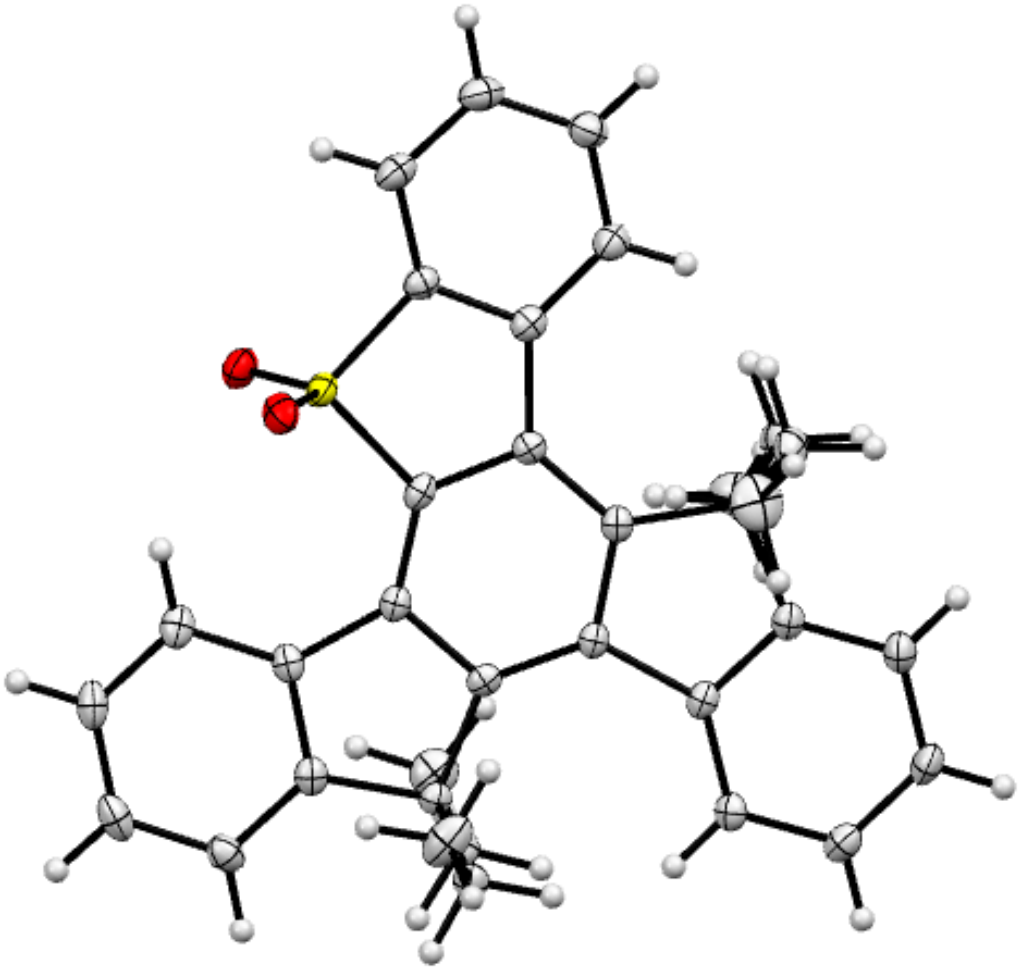


Figure S3b. Crystal structure of (SO2)CC at 100 K. Thermal ellipsoids with 50% probability.

(SO2)CC crystal for X-ray diffraction were grown by slow evaporation of solvent (ACN) during several days at 20°C.

5 NCC structure and thermal ellipsoid plot

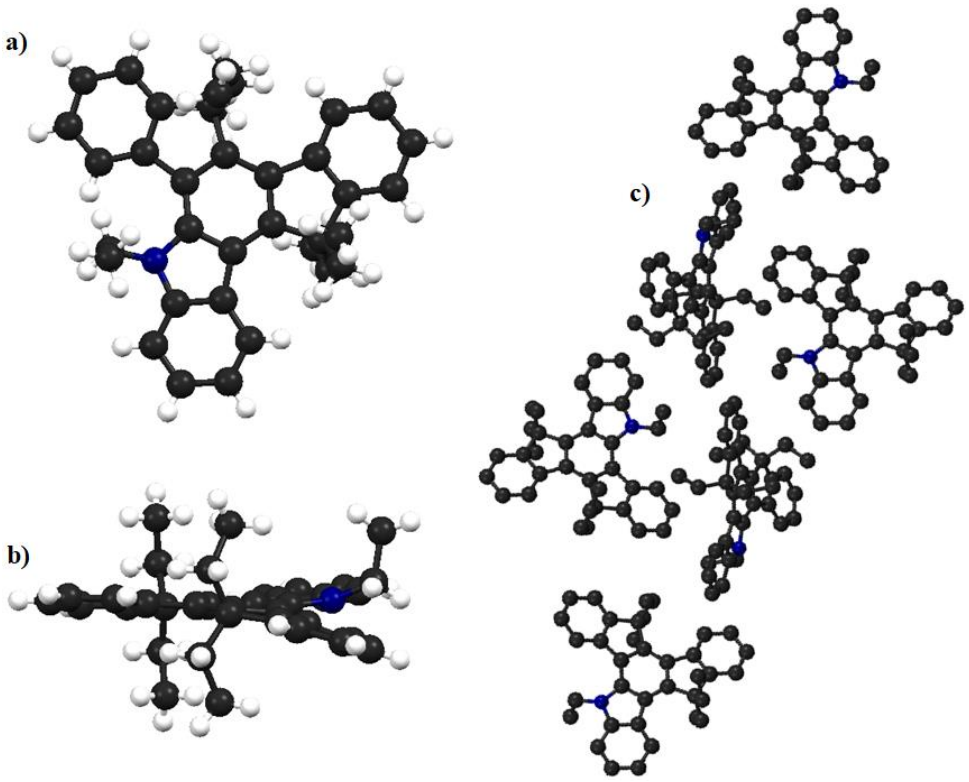


Figure S4a. NCC crystal structure a) top view, b) side view, c) packing.

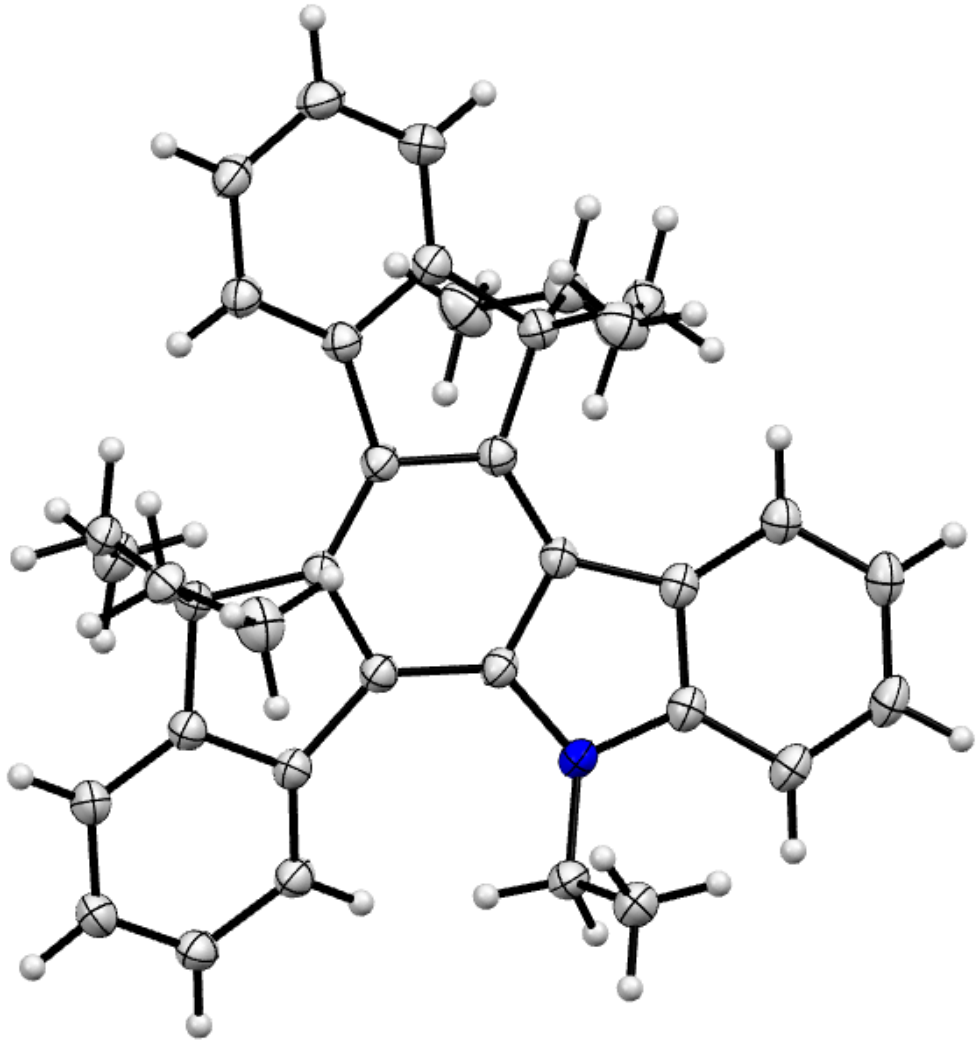


Figure S4b. Crystal structure of NCC at 100 K. Thermal ellipsoids with 50% probability.

NCC crystal for X-ray diffraction were grown by slow evaporation of solvent (ACN) during several days at 20°C.

6 ^{1}H NMR of 6a in CD_2Cl_2

Figure S5a. ^{1}H NMR of 6a in CD_2Cl_2

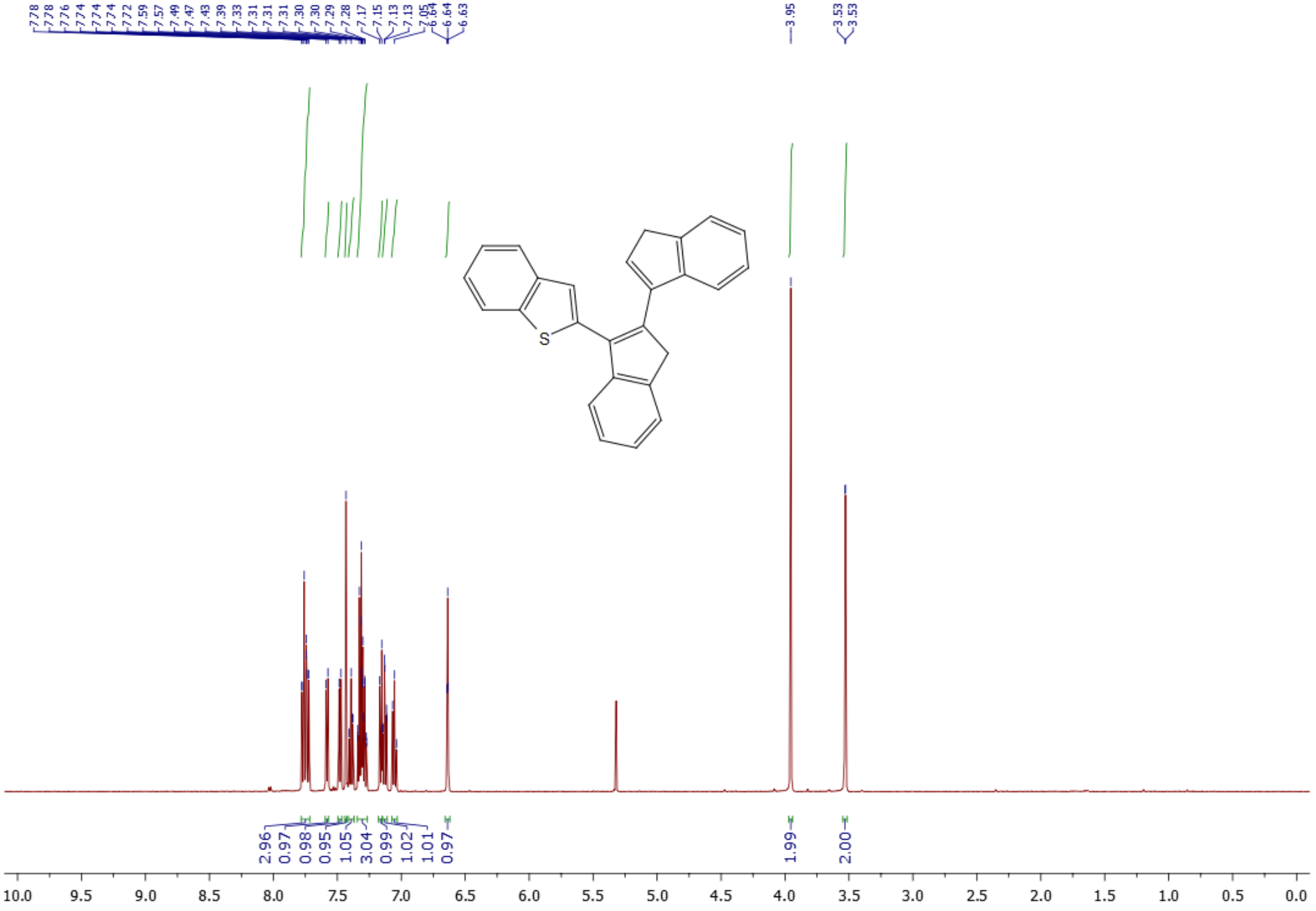
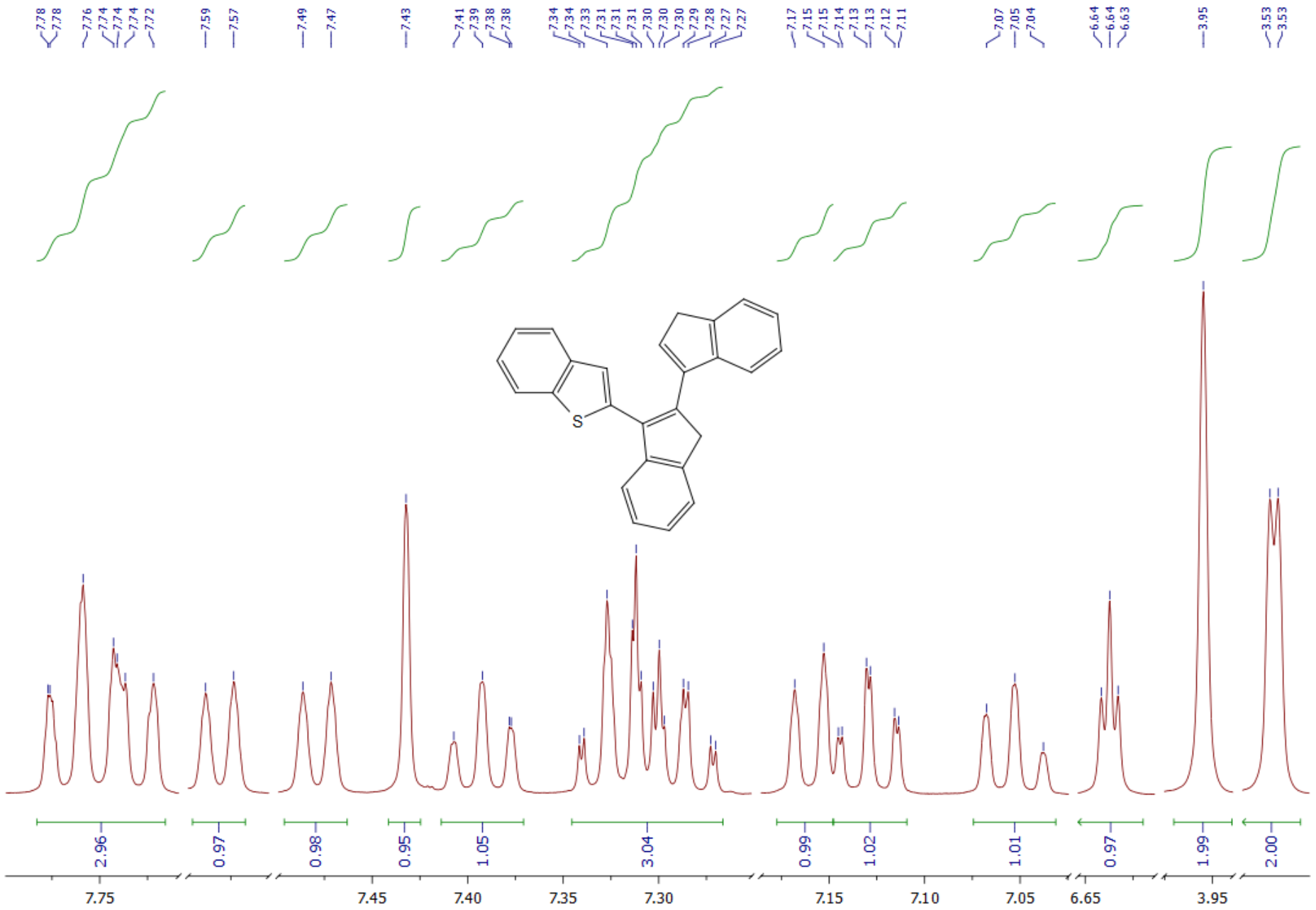


Figure S5b. ^{1}H NMR of 6a in CD_2Cl_2



7 $^{13}C\{^{1}H\}$ NMR of 6a in CD_2Cl_2

Figure S6a. $^{13}C\{^{1}H\}$NMR of 6a in CD_2Cl_2

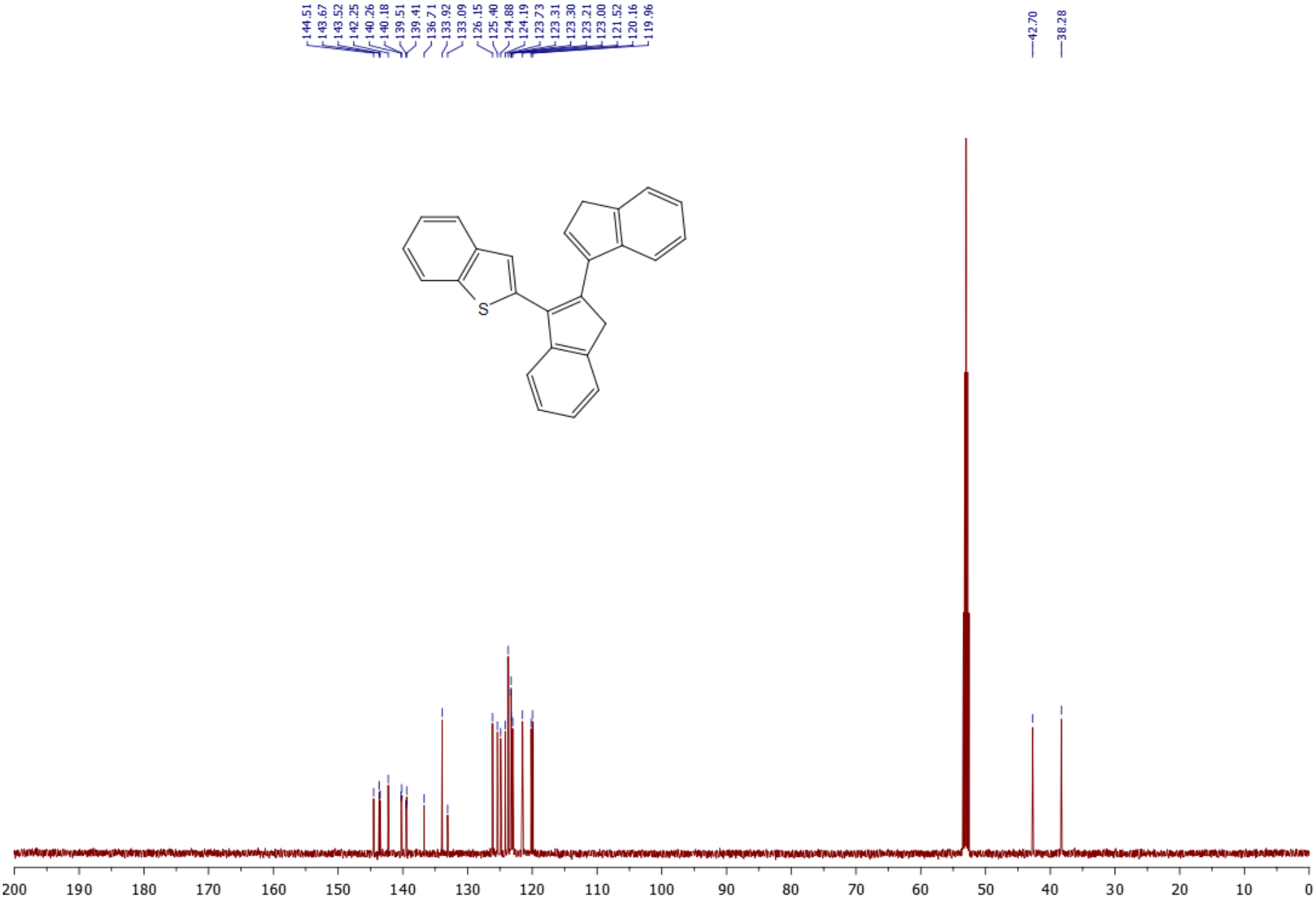
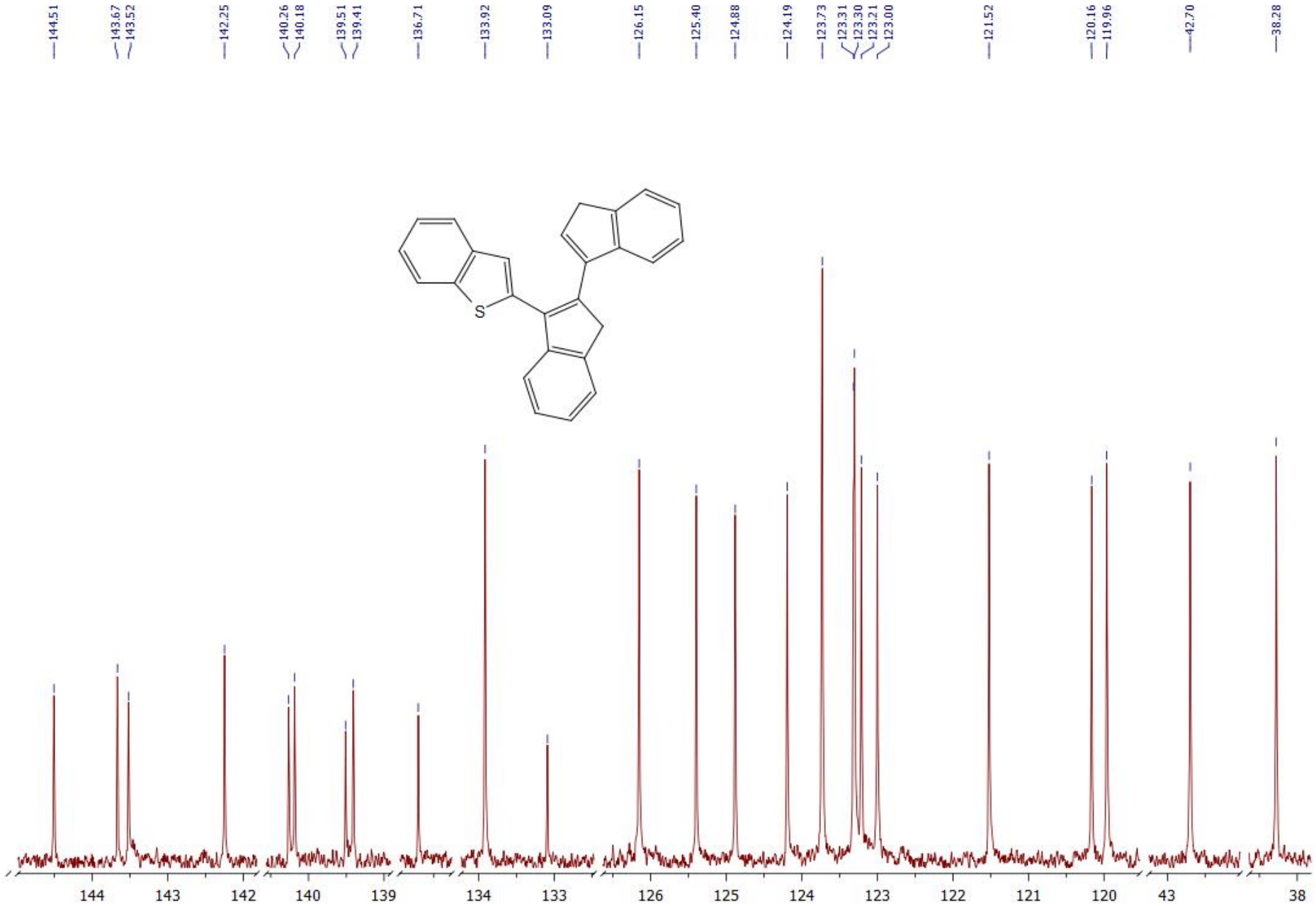


Figure S6b. $^{13}C\{^{1}H\}$ NMR of 6a in CD_2Cl_2



8 ^{1}H NMR of SCC in CD_2Cl_2

Figure S7a. ^{1}H NMR of SCC in CD_2Cl_2

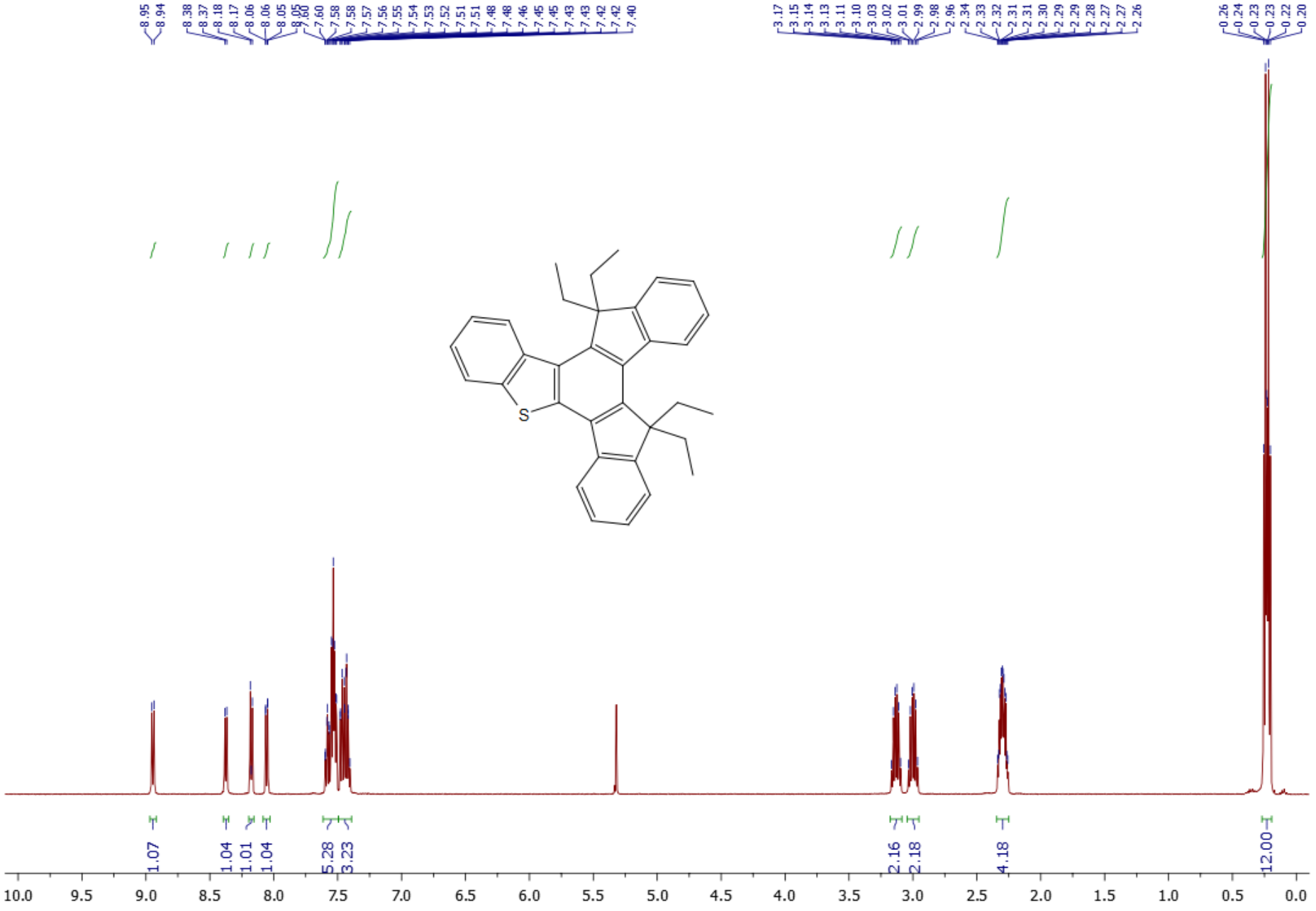
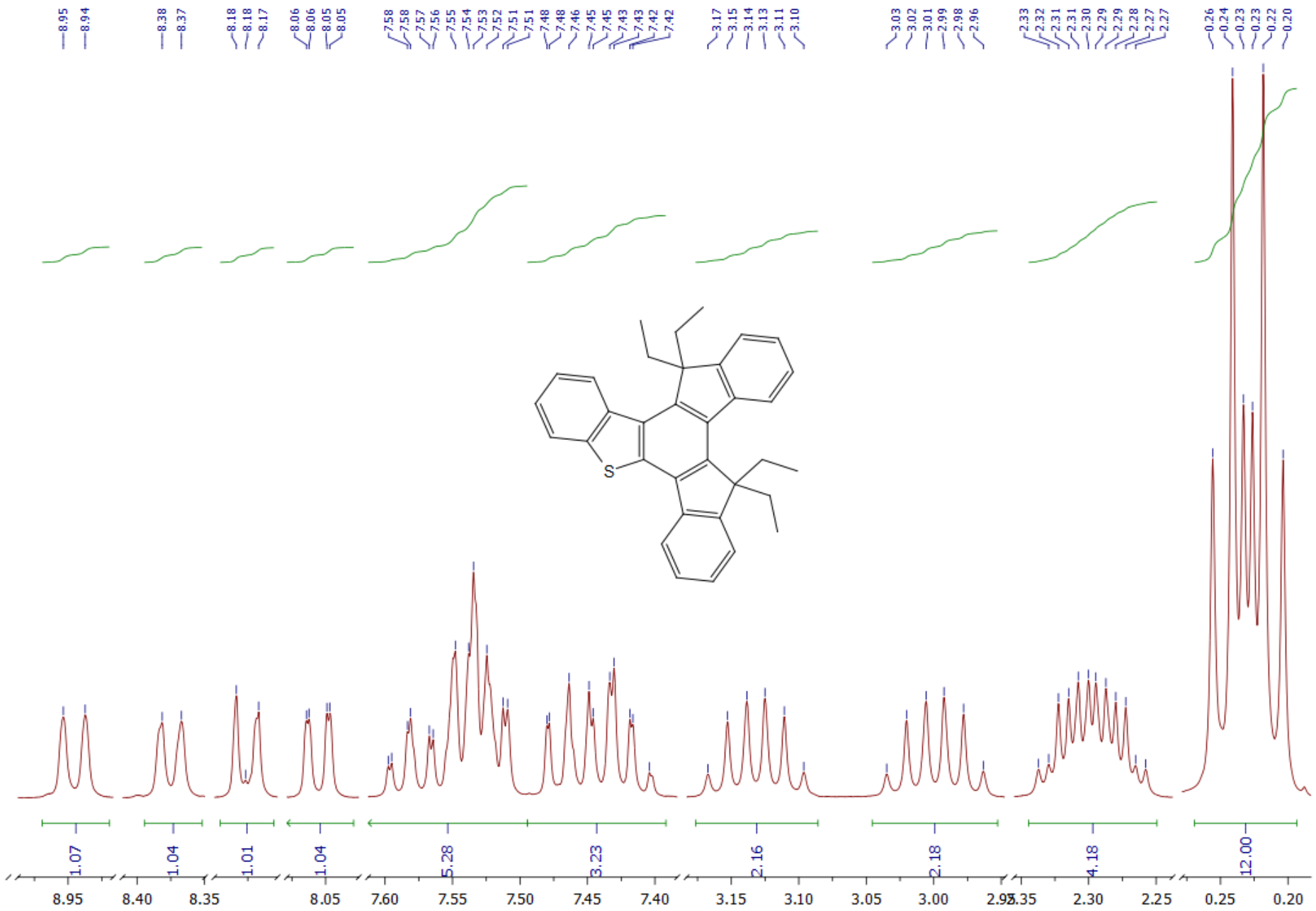


Figure S7b. ^{1}H NMR of SCC in CD_2Cl_2



9 $^{13}C\{^{1}H\}$ NMR of SCC in CD_2Cl_2

Figure S8a. . $^{13}C\{^{1}H\}$ NMR of SCC in CD_2Cl_2

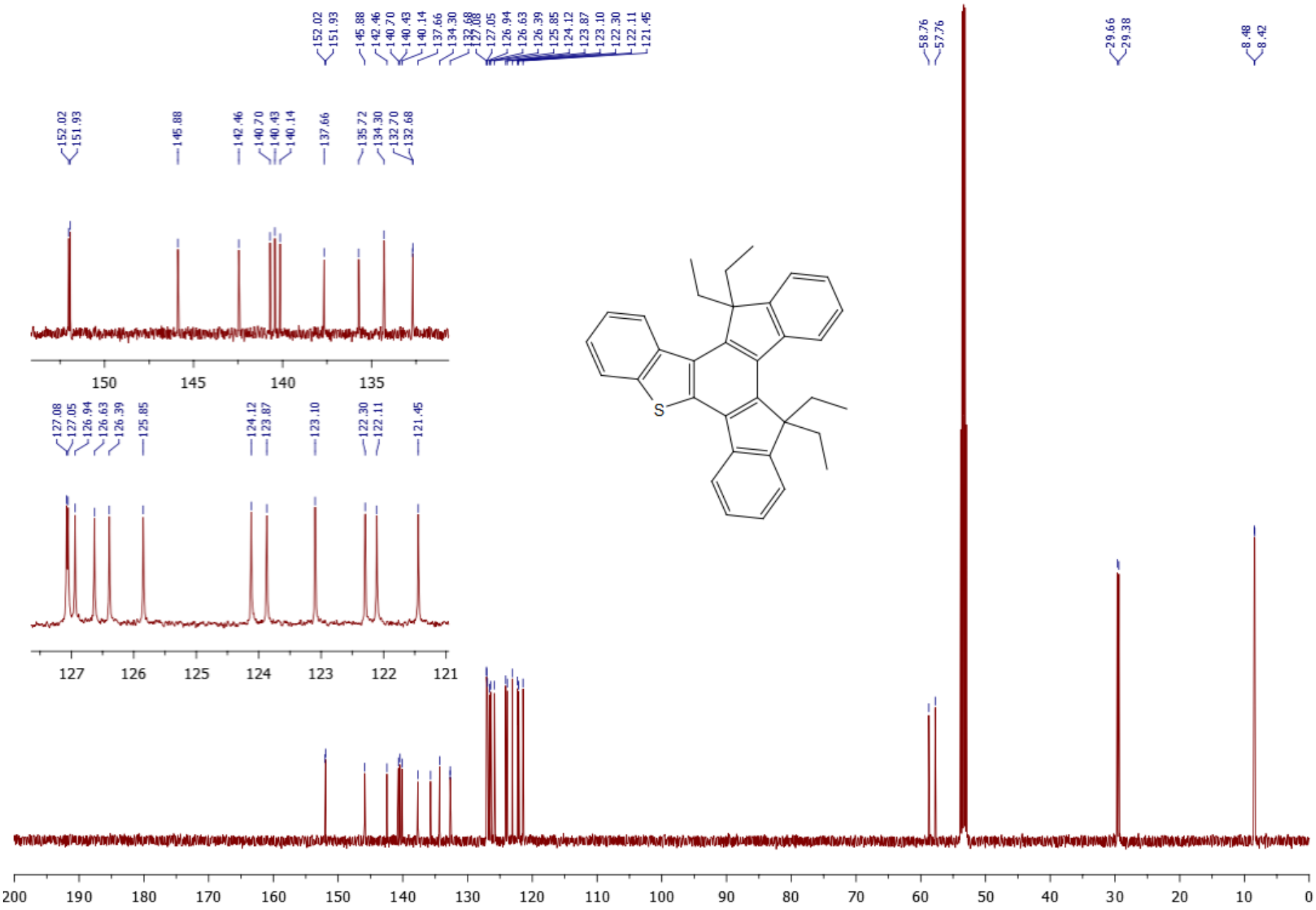
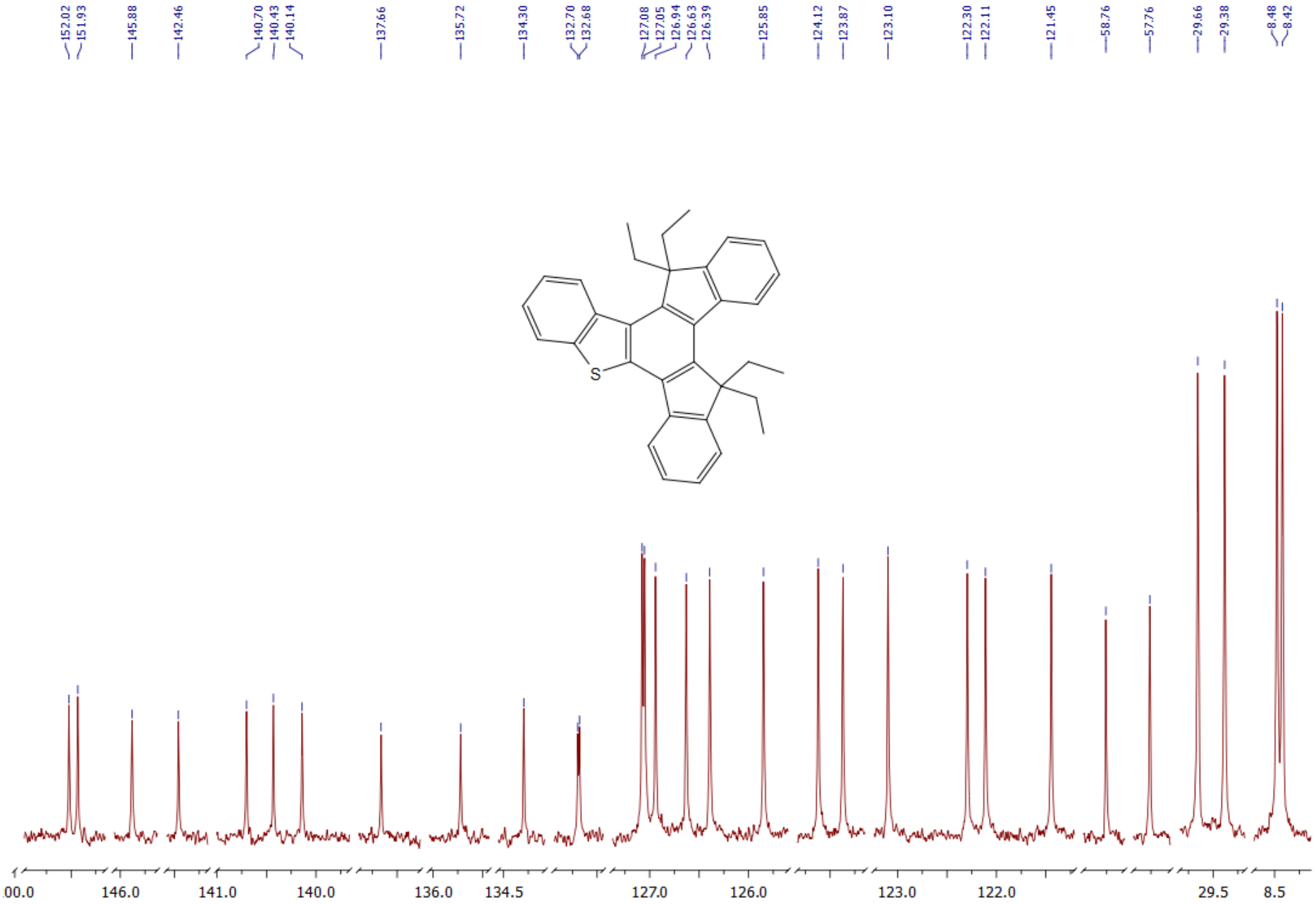


Figure S8b. $^{13}C\{^{1}H\}$ NMR of SCC in CD_2Cl_2



10 ^{1}H NMR of (SO)CC in CD_2Cl_2

Figure S9a. ^{1}H NMR of (SO)CC in CD_2Cl_2

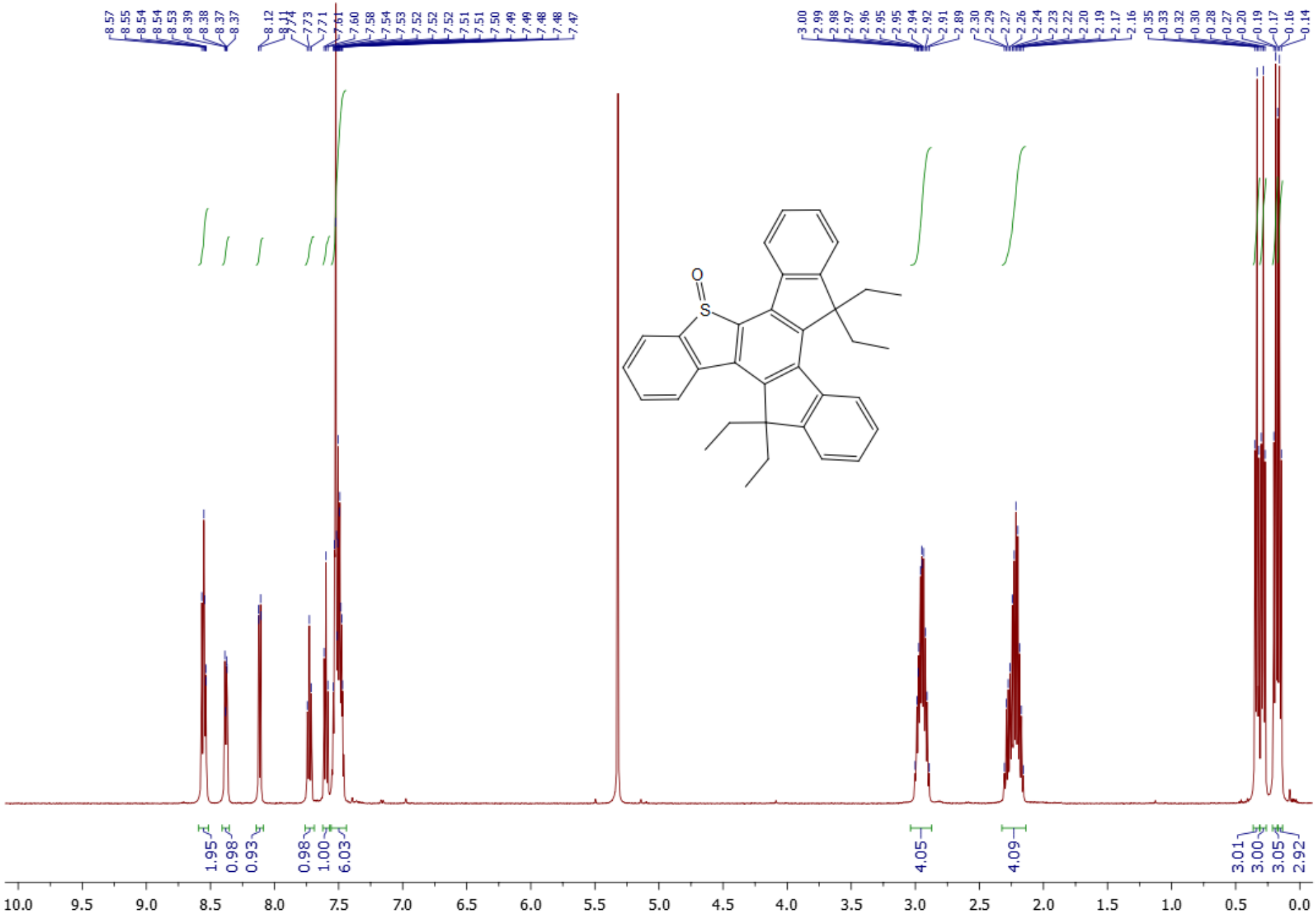
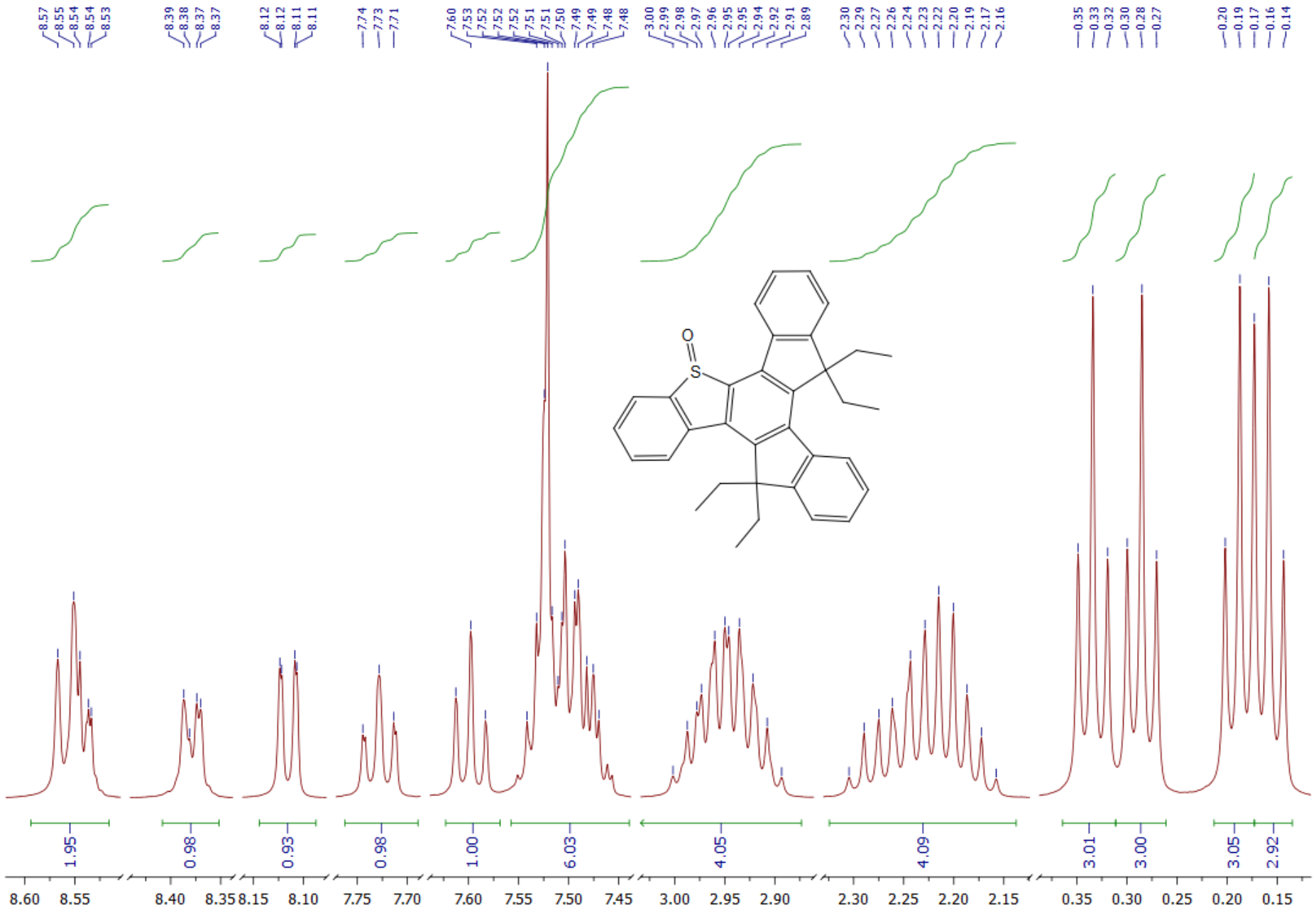


Figure S9b. ^{1}H NMR of (SO)CC in CD_2Cl_2



11 $^{13}C\{^{1}H\}$ NMR of (SO)CC in CD_2Cl_2

Figure S 10a. $^{13}C\{^{1}H\}$ NMR of (SO)CC in CD_2Cl_2

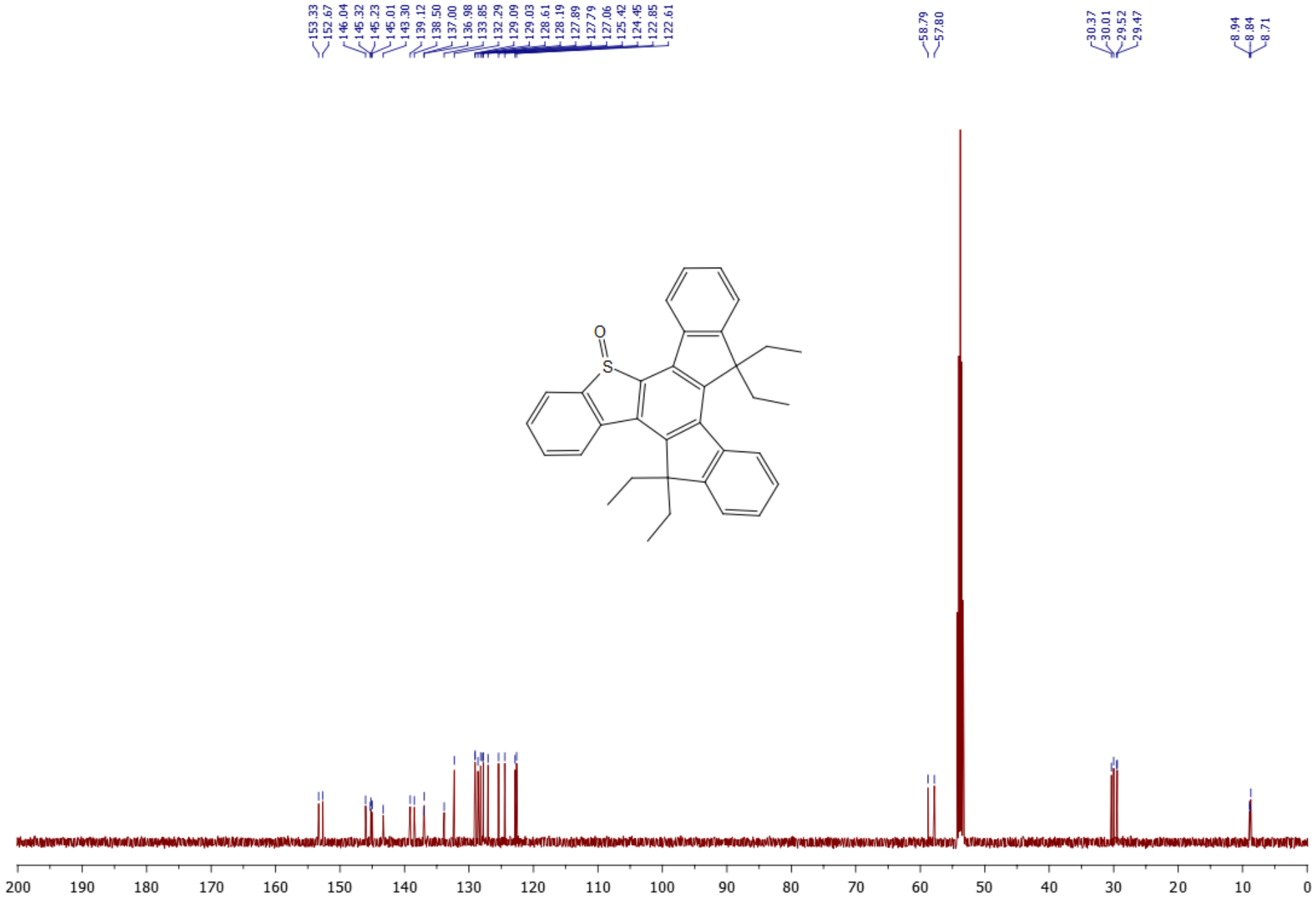


Figure S10b. $^{13}C\{^{1}H\}$ NMR of (SO)CC in CD_2Cl_2

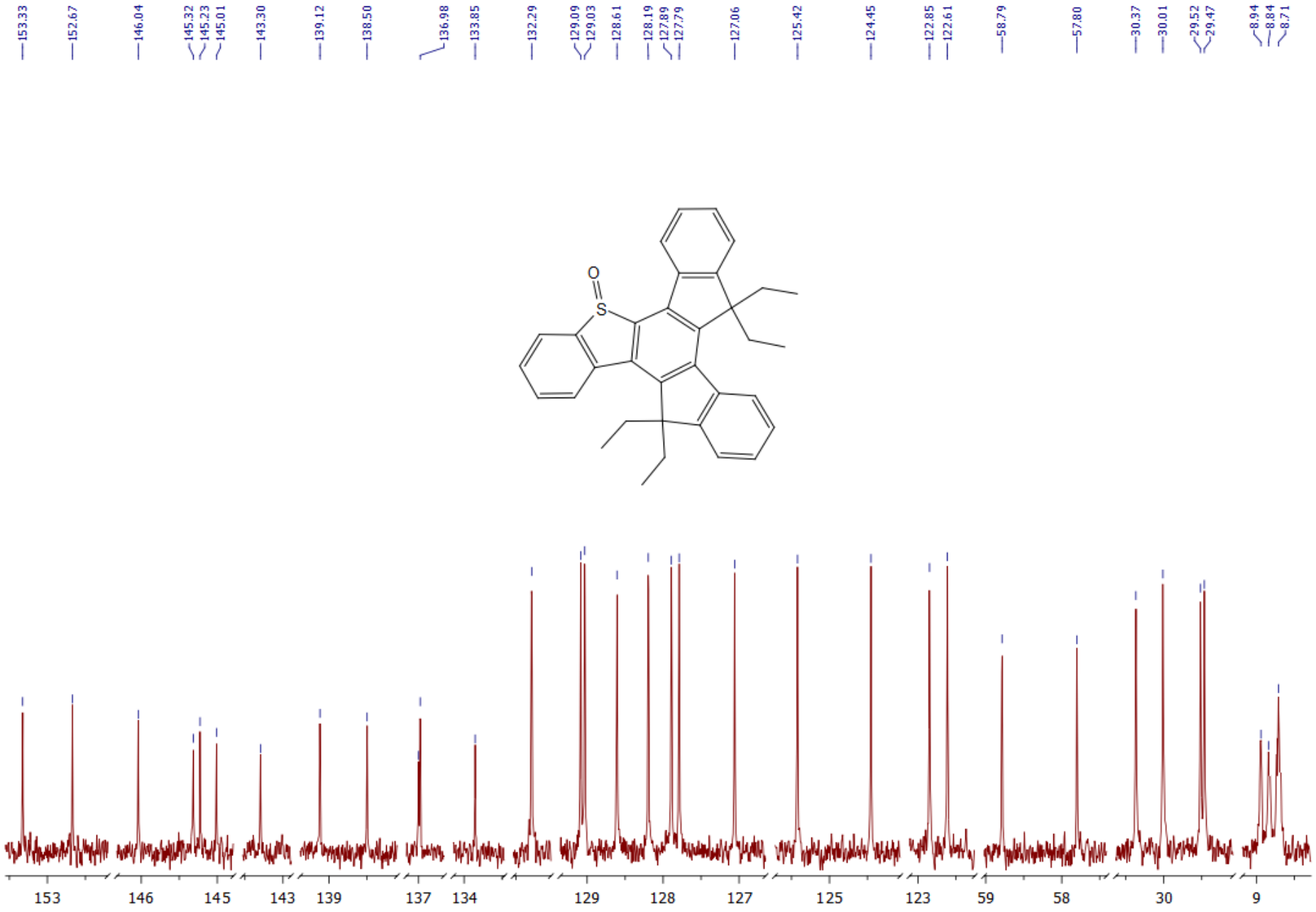


Figure S11a. ^{1}H NMR of 10 in CD_2Cl_2

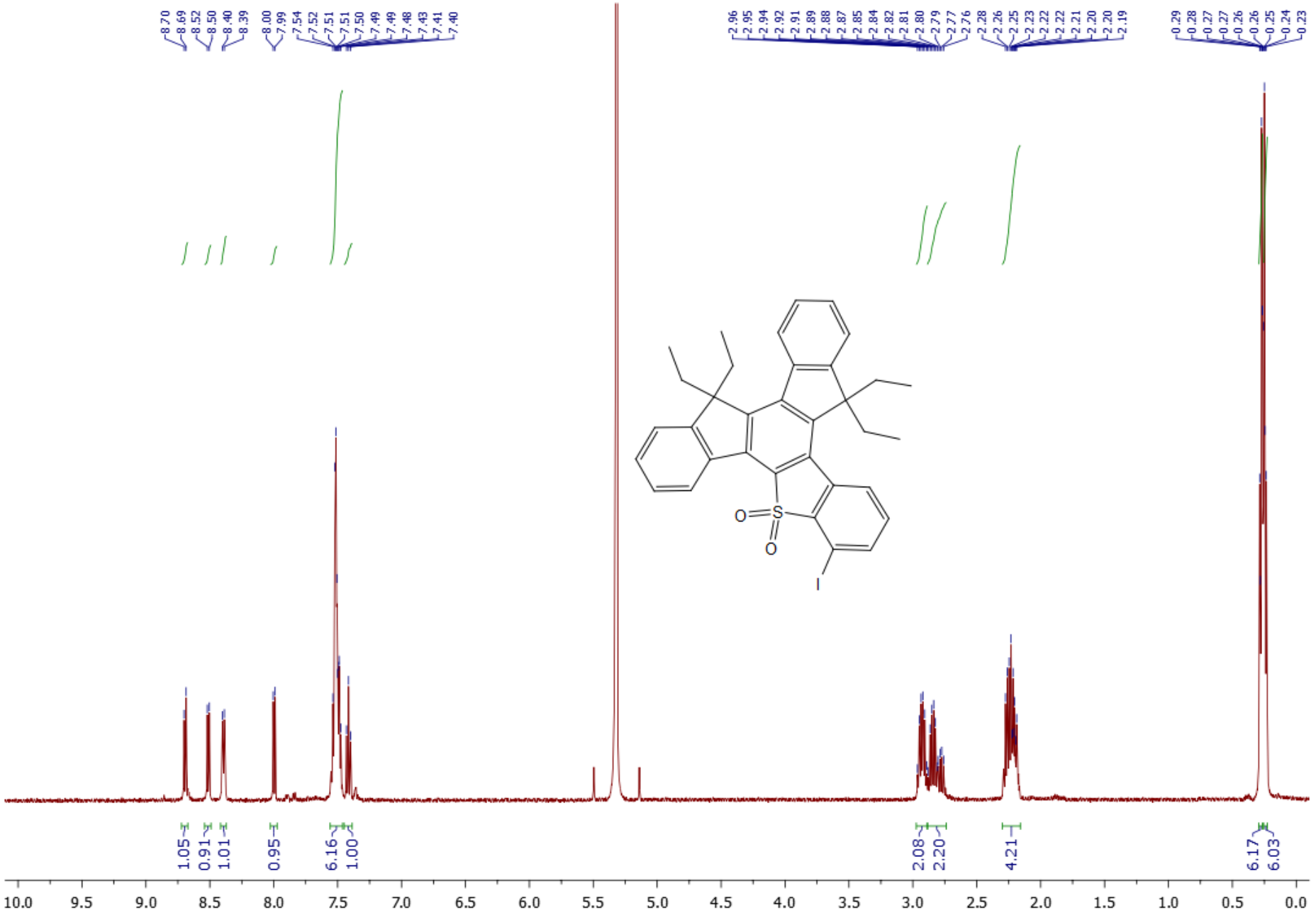
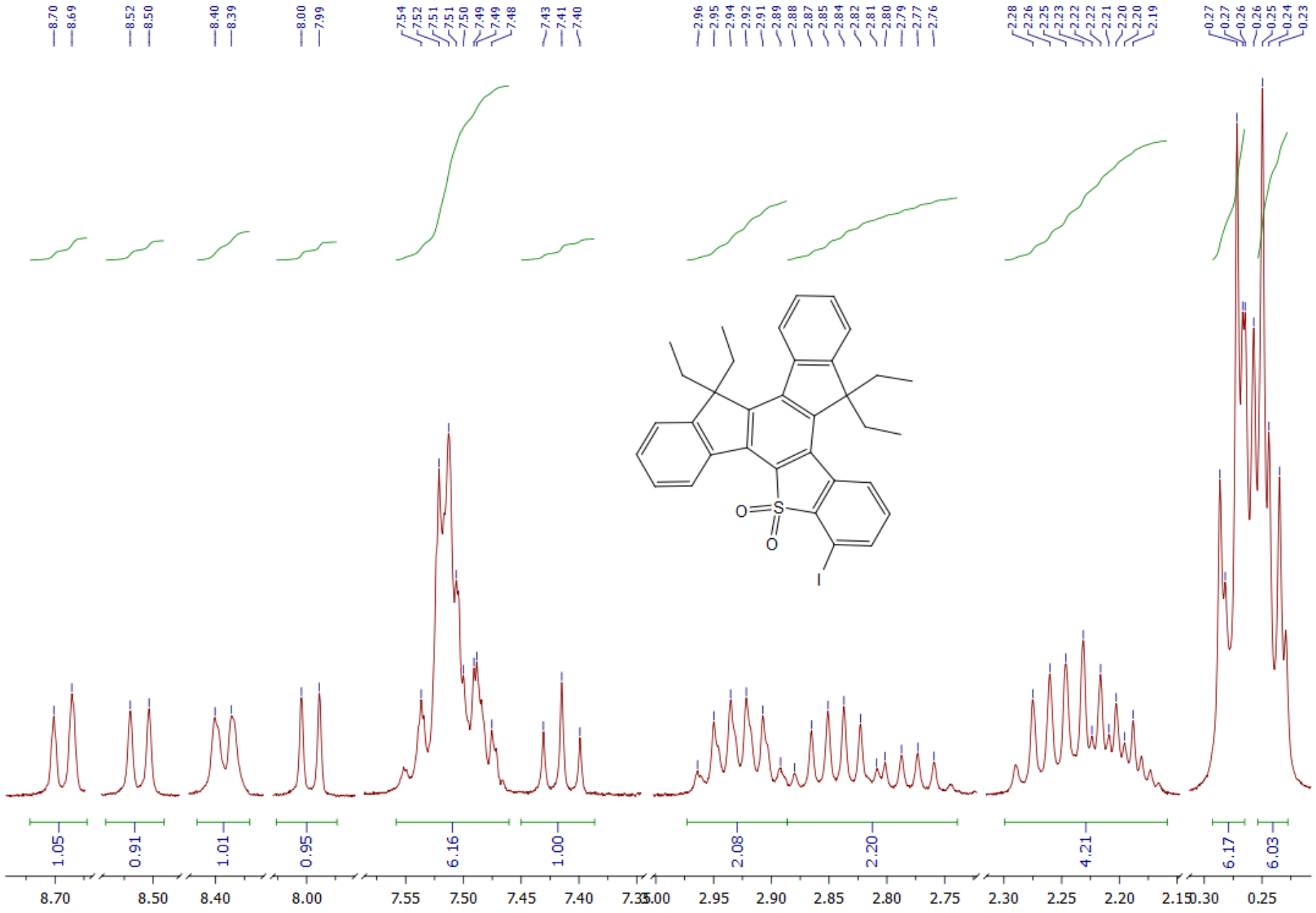


Figure S11b. ^{1}H NMR of 10 in CD_2Cl_2



13 $^{13}C\{^{1}H\}$ NMR of 10 in CD_2Cl_2

Figure S12a. $^{13}C\{^{1}H\}$ NMR of 10 in CD_2Cl_2

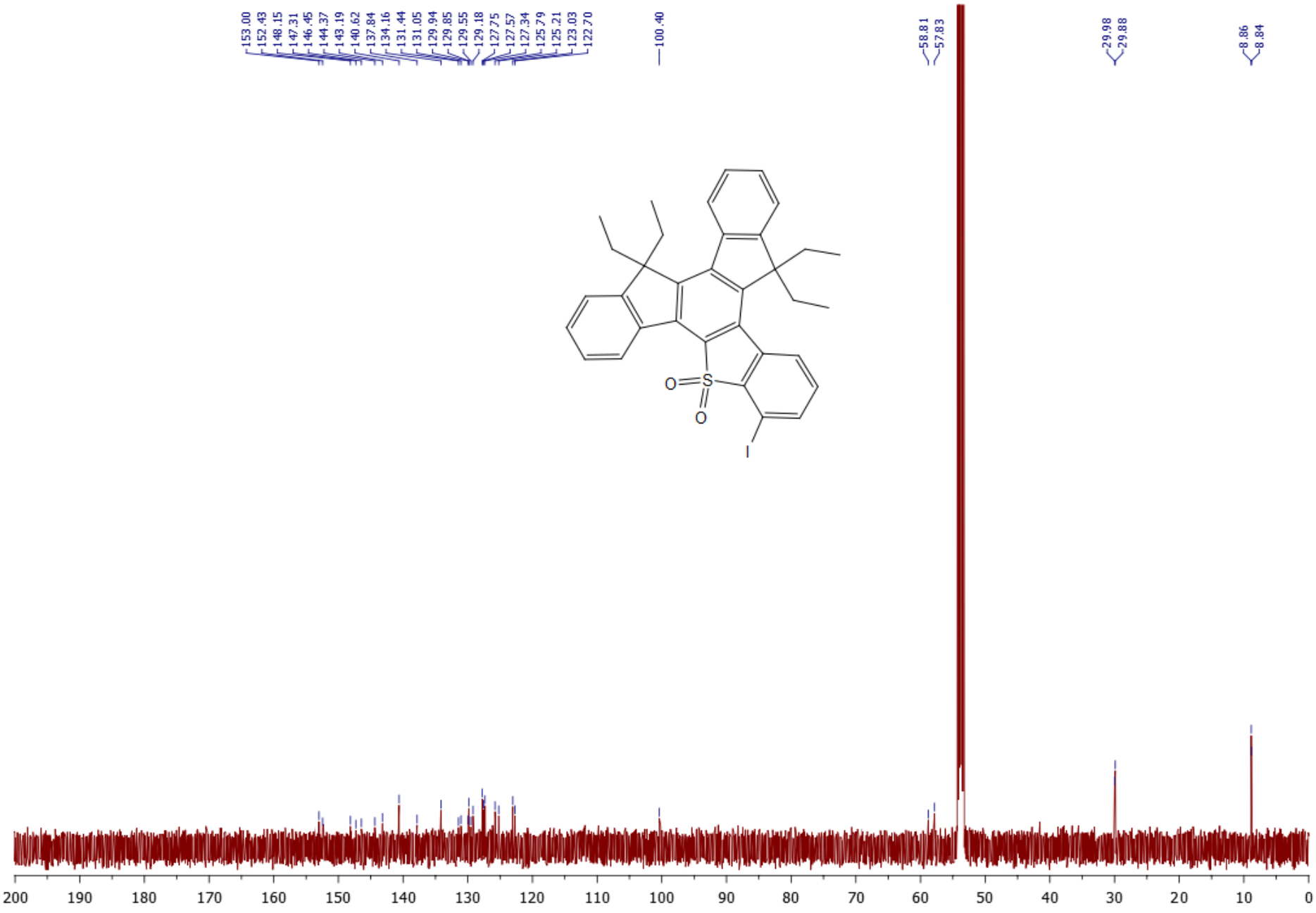
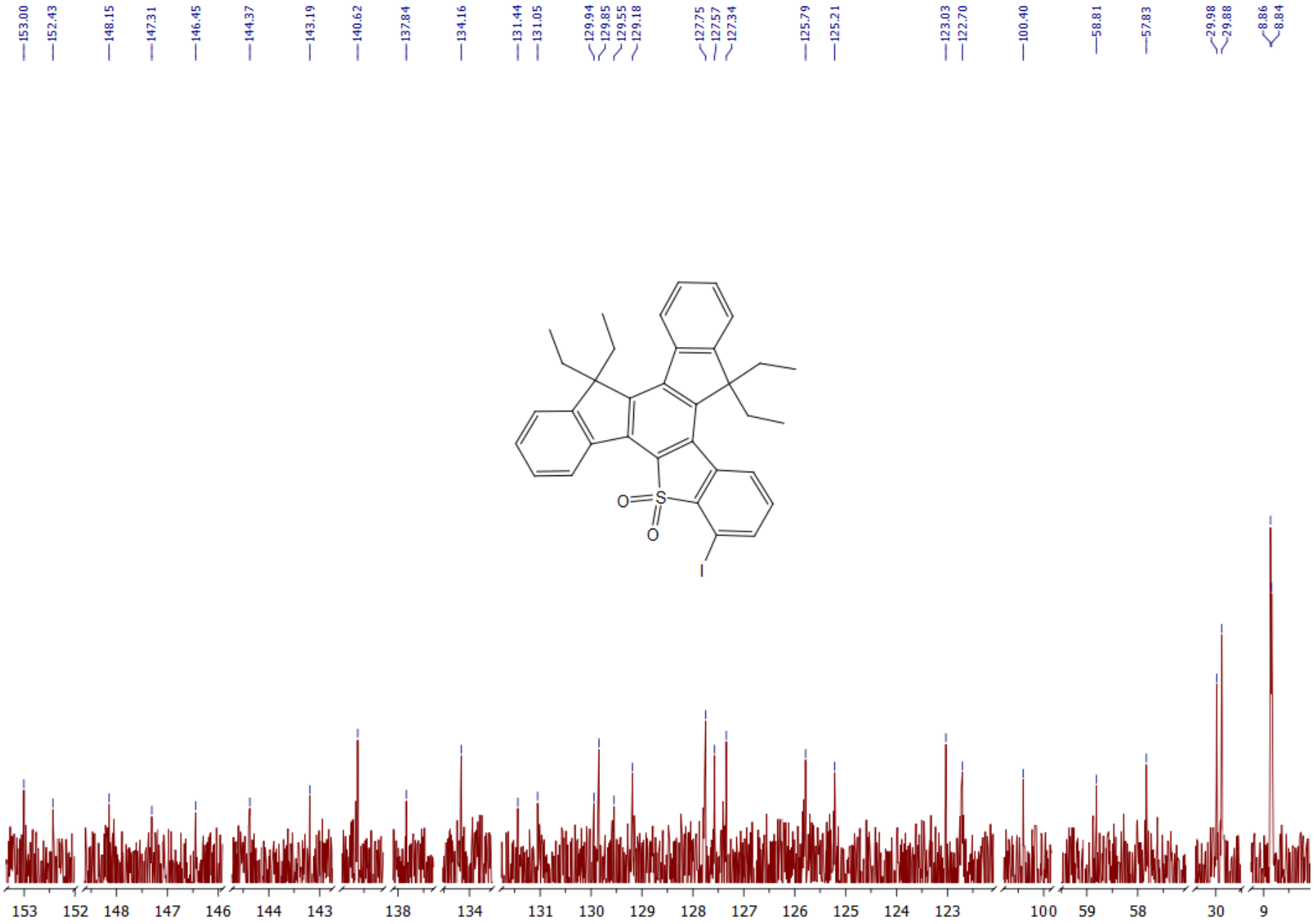


Figure S12b. $^{13}C\{^{1}H\}$ NMR of 10 in CD_2Cl_2



14 ^{1}H NMR of 24 in CD_2Cl_2

Figure S13a. ^{1}H NMR of 24 in CD_2Cl_2

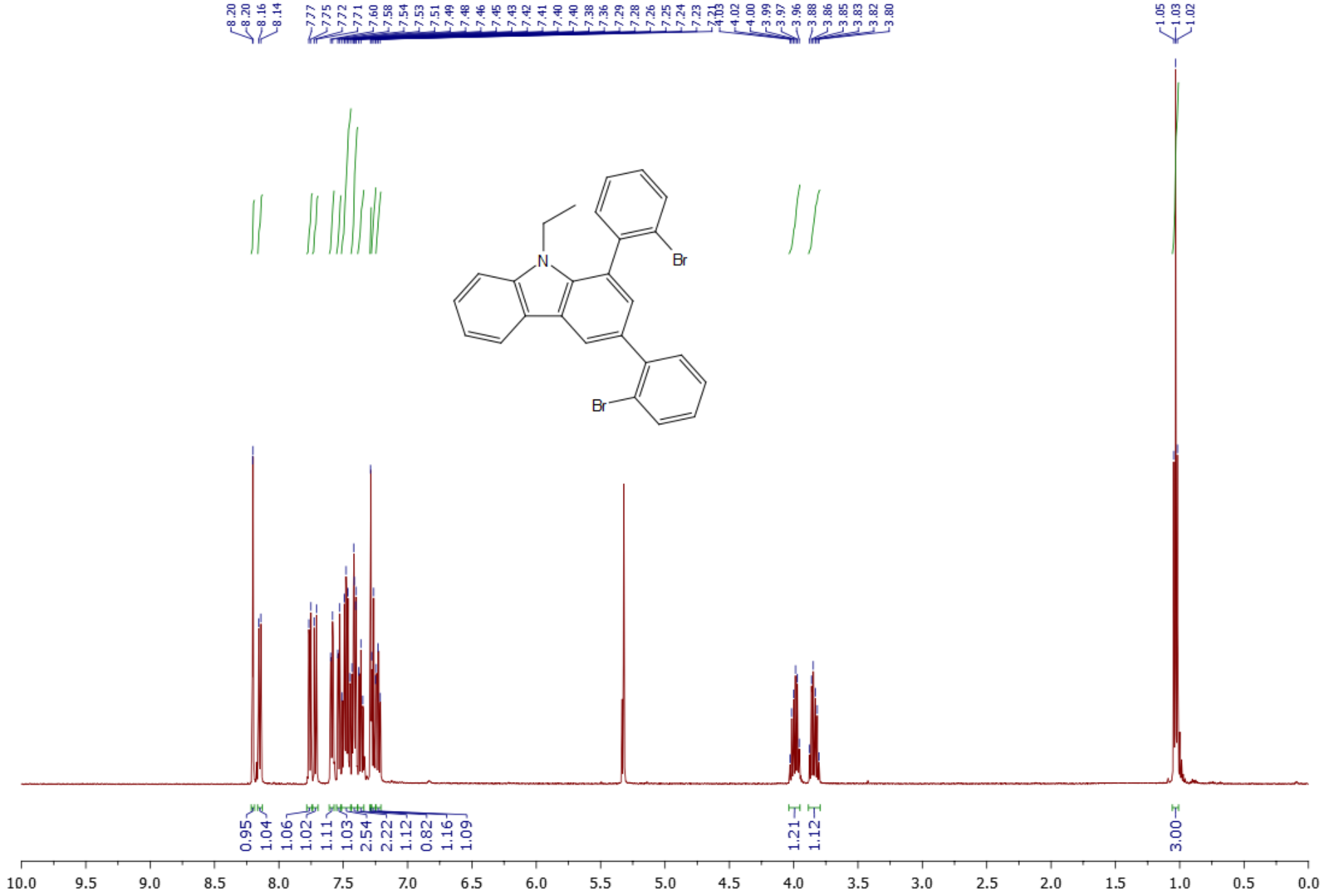
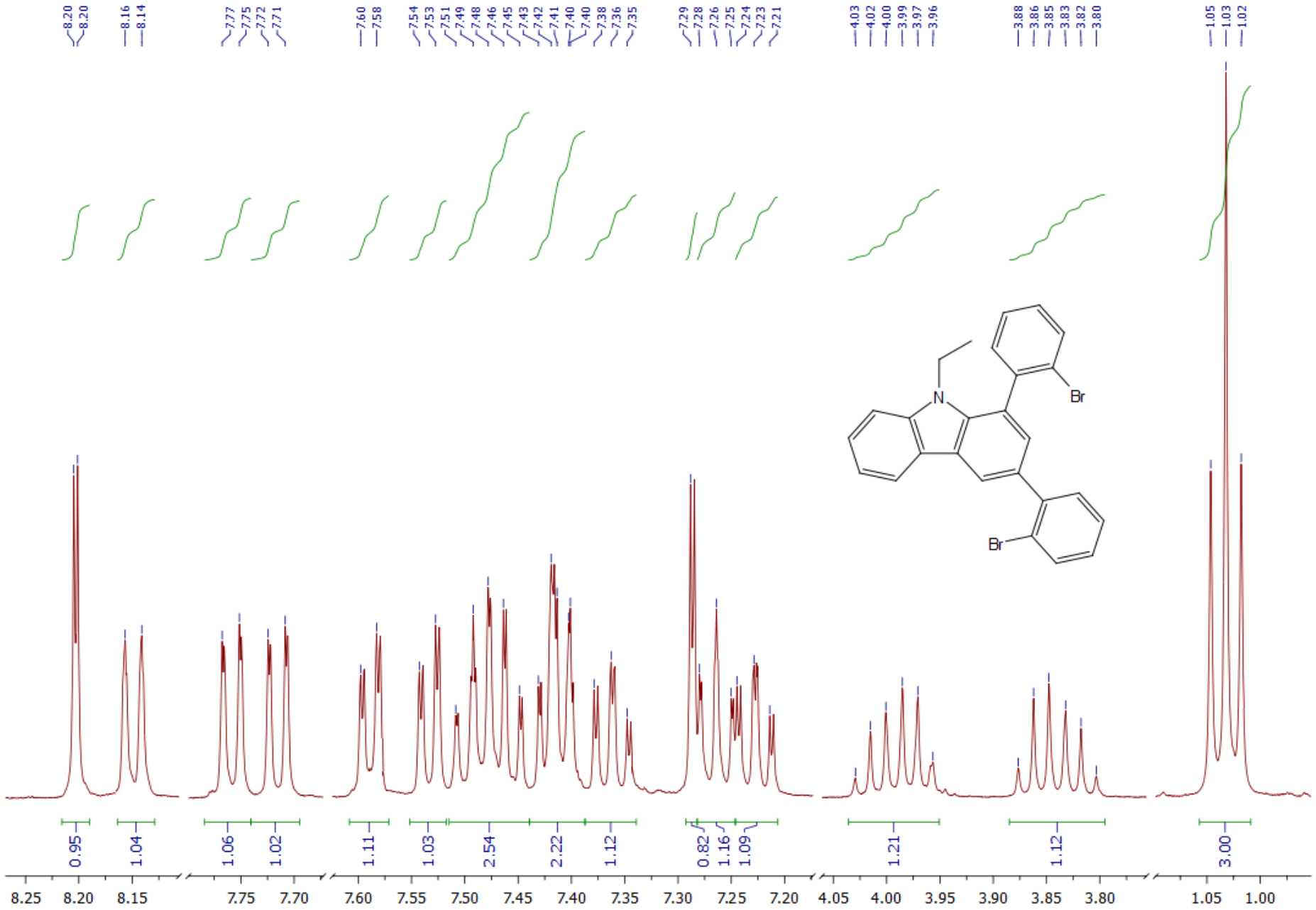


Figure S13b. ^{1}H NMR of 24 in CD_2Cl_2



15 $^{13}C\{^{1}H\}$ NMR of 24 in CD_2Cl_2

Figure S14a. $^{13}C\{^{1}H\}$ NMR of 24 in CD_2Cl_2

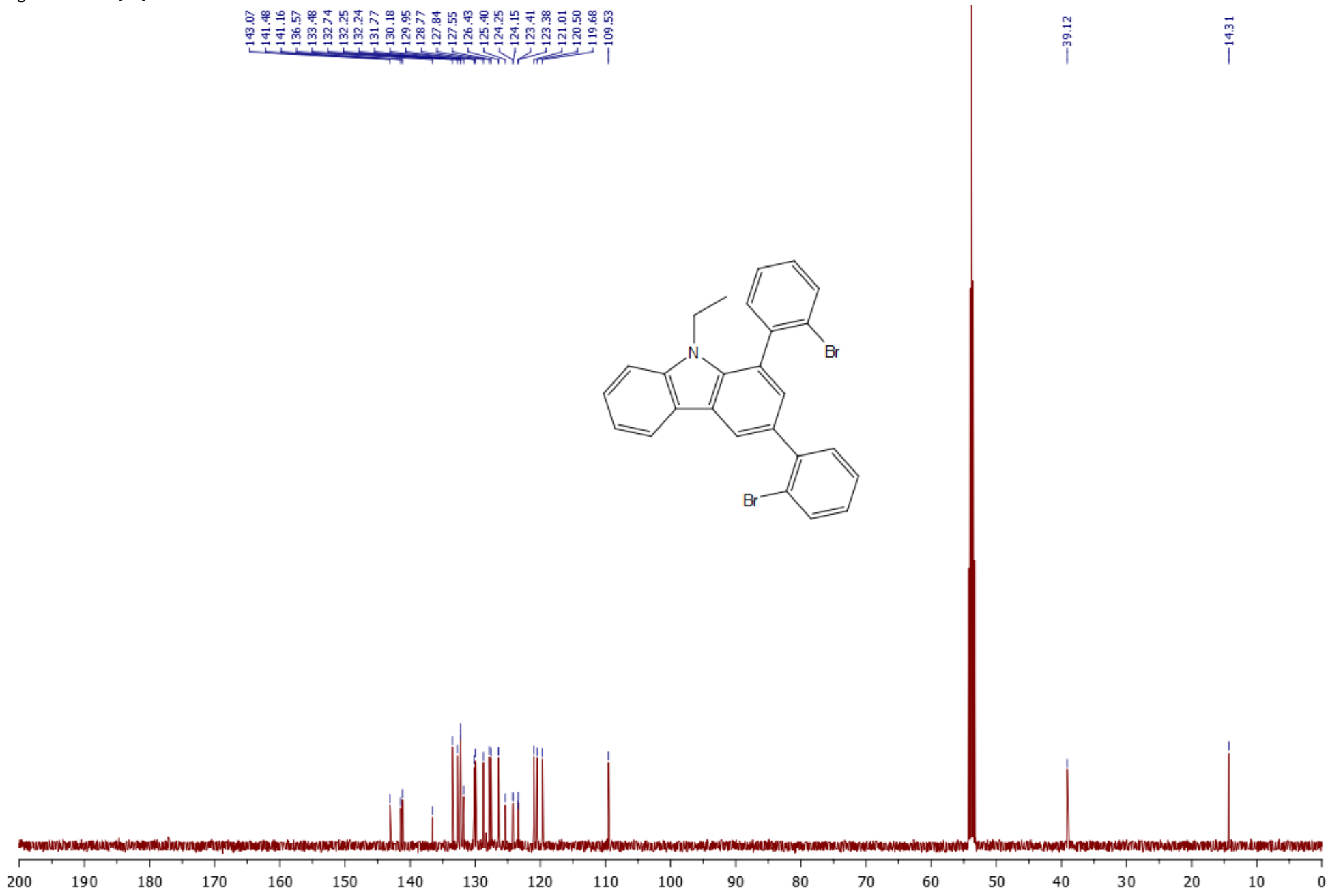
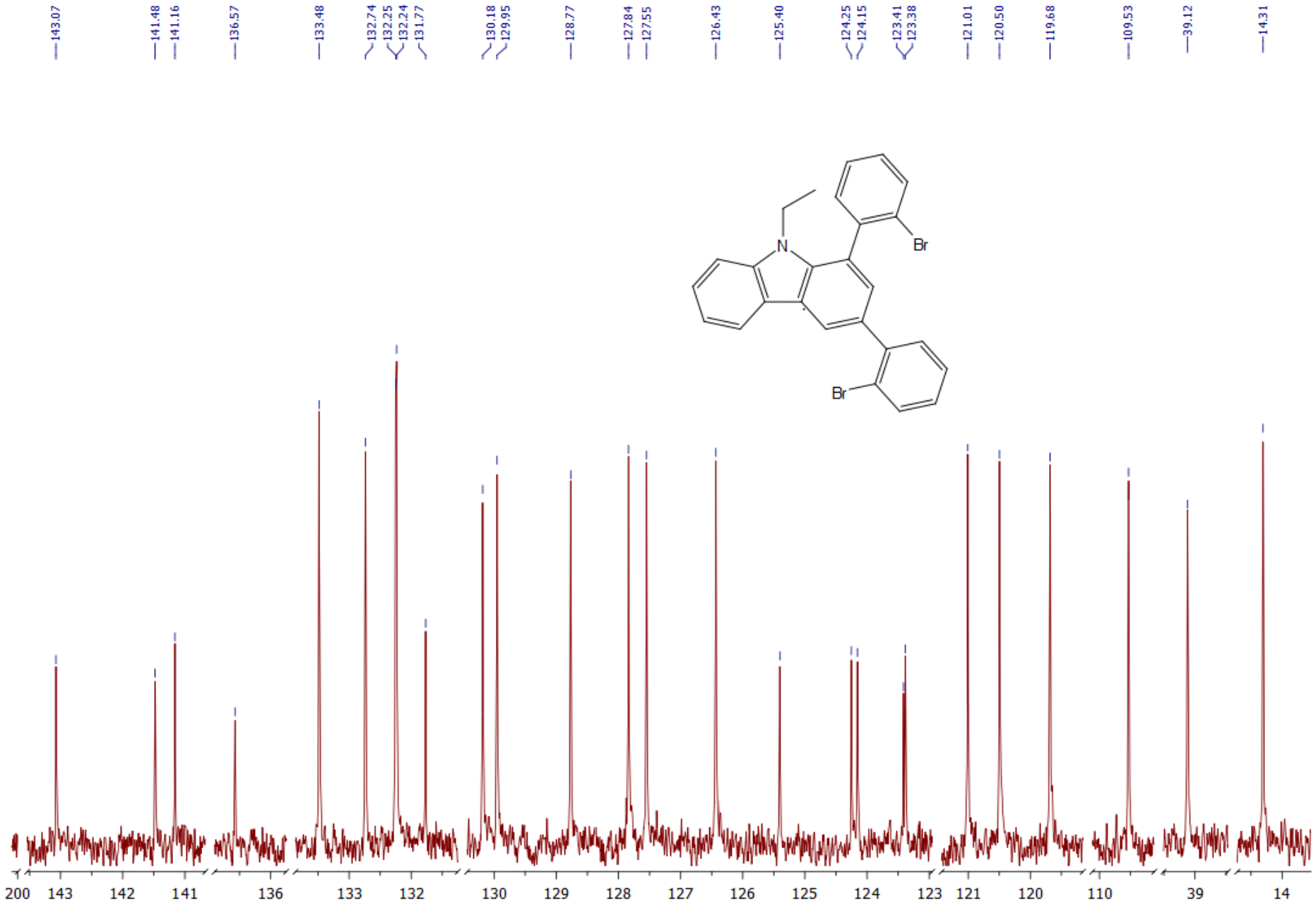


Figure S14b. $^{13}C\{^{1}H\}$ NMR of 24 in CD_2Cl_2



16 ^{1}H NMR of NCC in C_6D_6

Figure S15a. ^{1}H NMR of NCC in C_6D_6

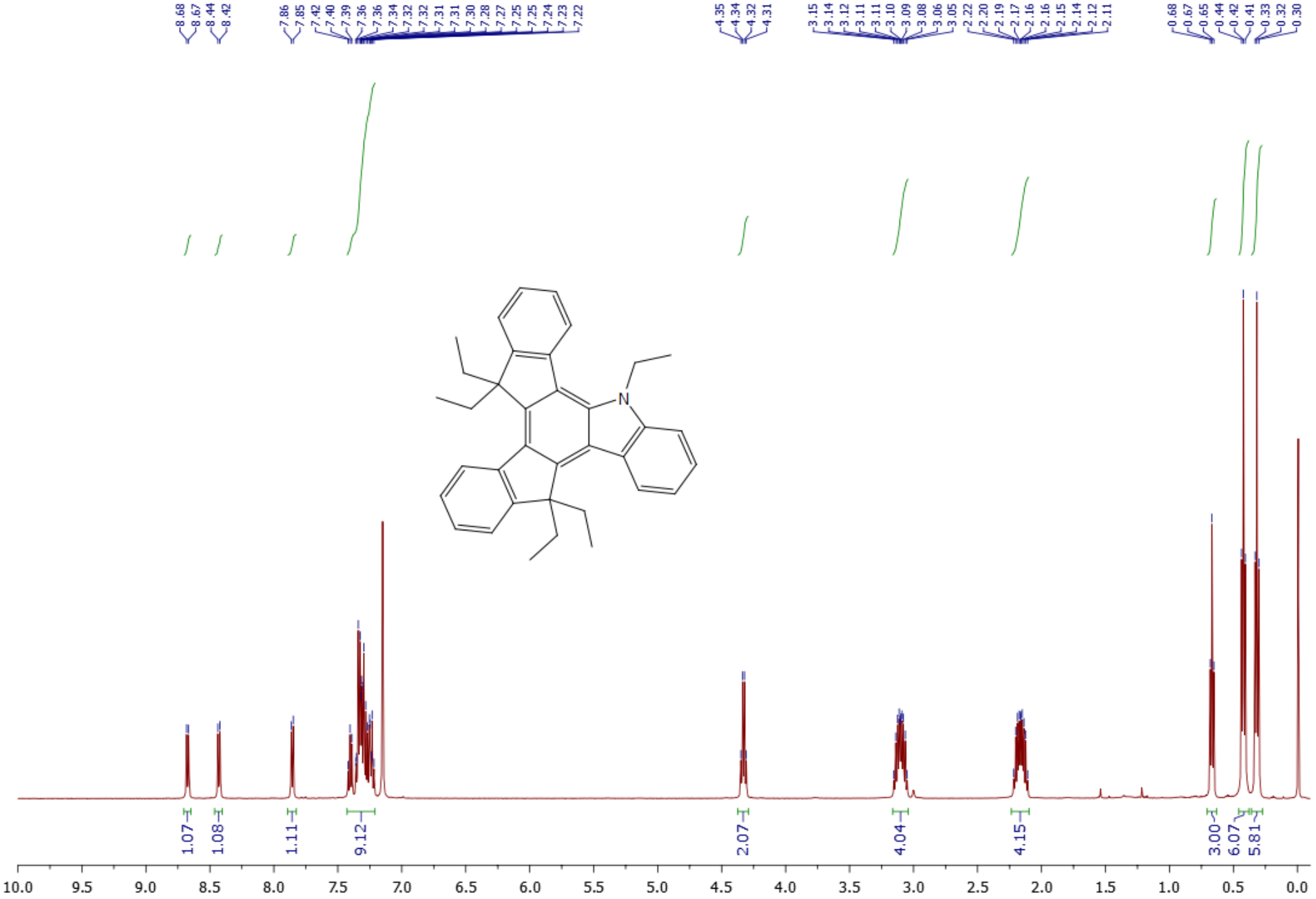
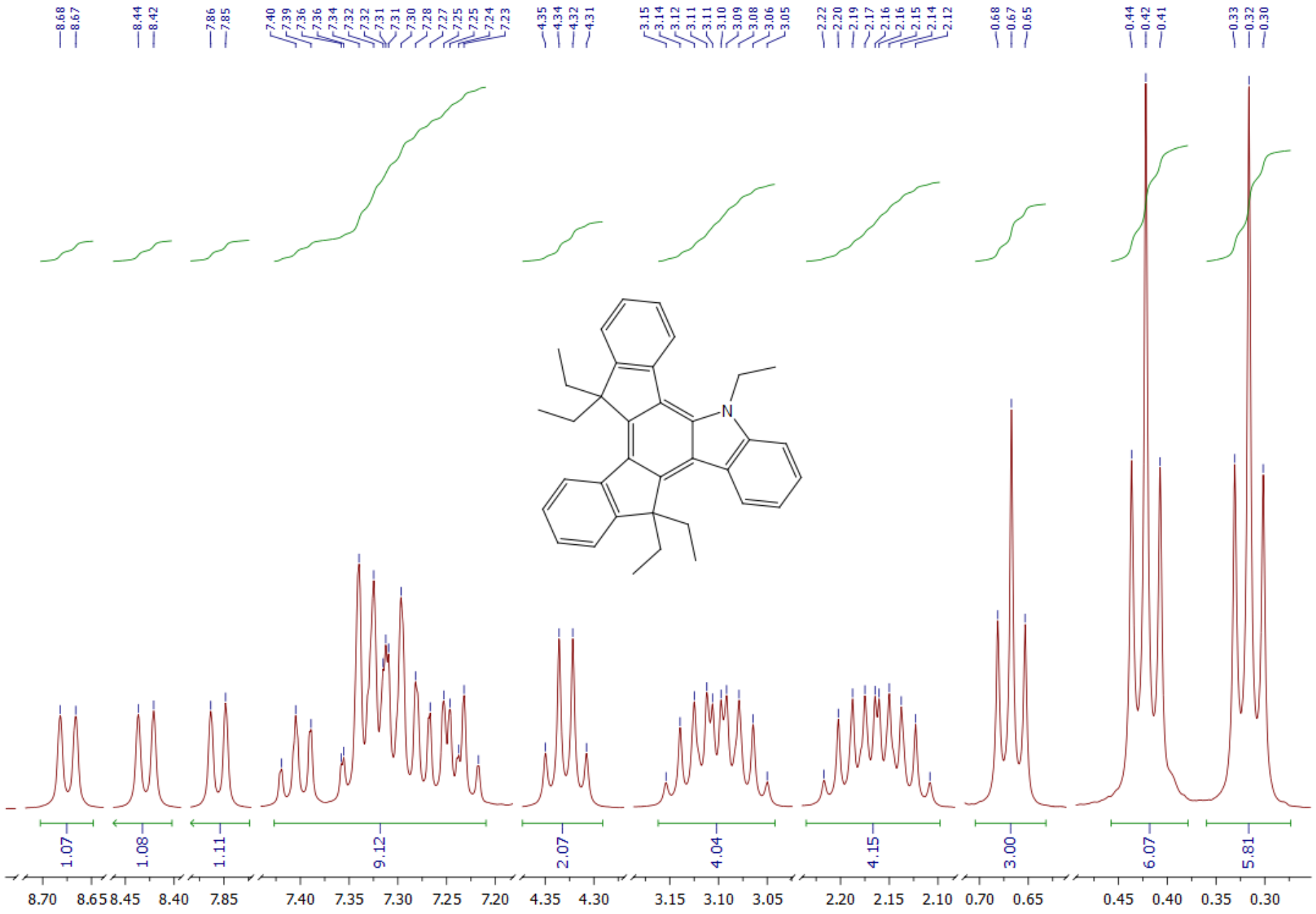


Figure S15b. ^{1}H NMR of NCC in C_6D_6



17 $^{13}C\{^{1}H\}$ NMR of NCC in C_6D_6

Figure S16a. $^{13}C\{^{1}H\}$ NMR of NCC in C_6D_6

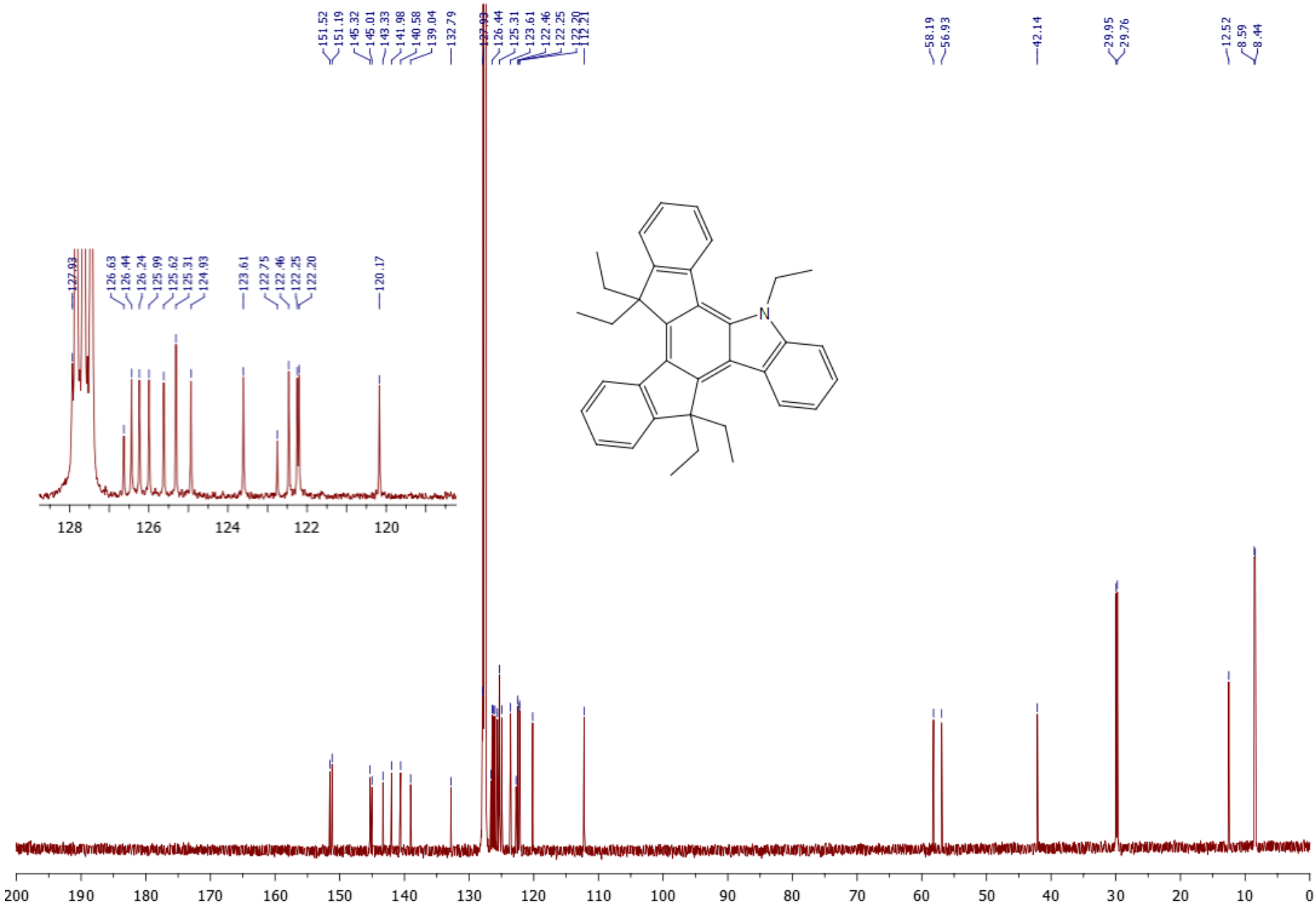
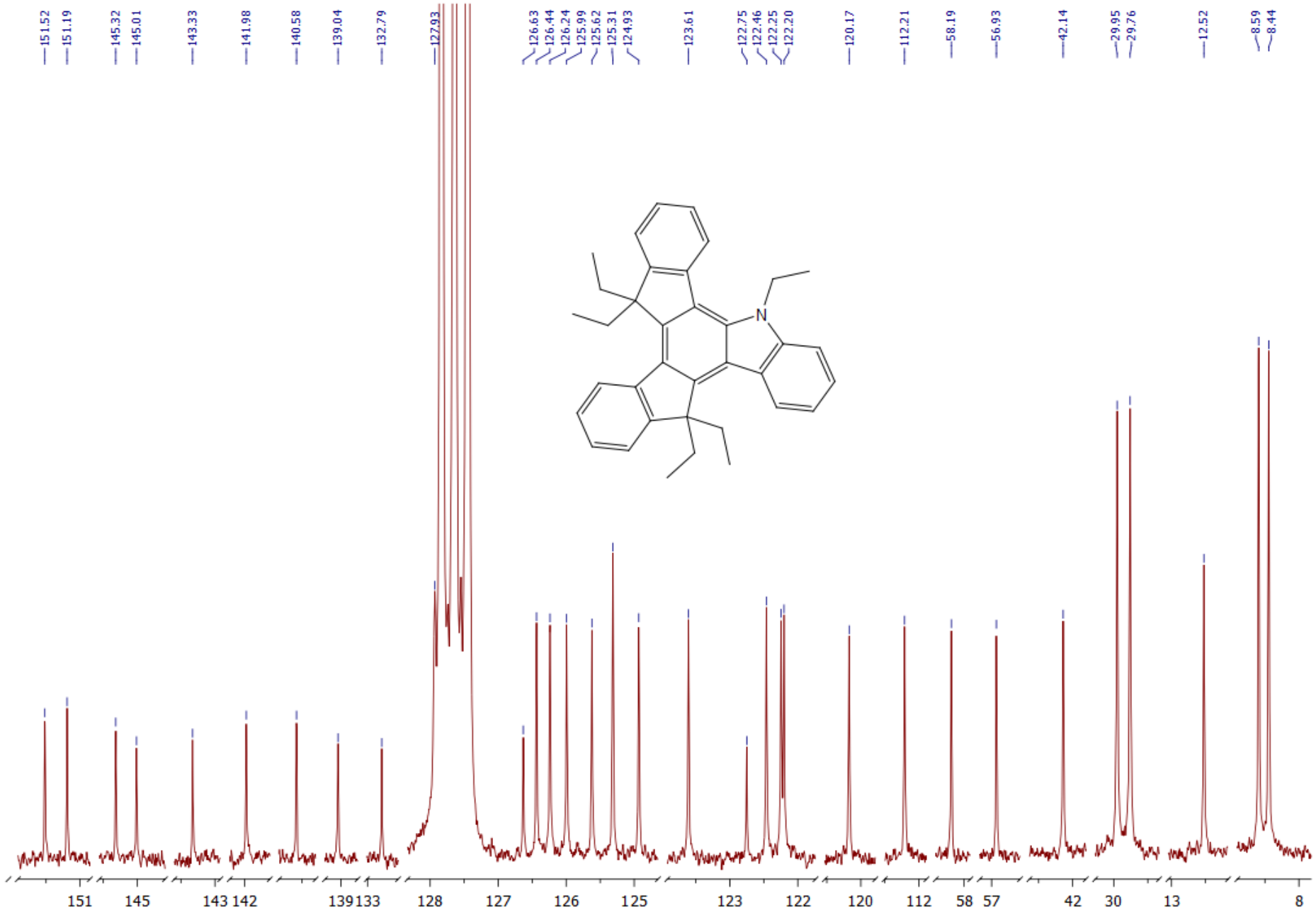


Figure S16a. $^{13}C\{^{1}H\}$ NMR of NCC in C_6D_6



18 ^{1}H NMR of 27 in CD_2Cl_2

Figure S17a. ^{1}H NMR of 27 in CD_2Cl_2

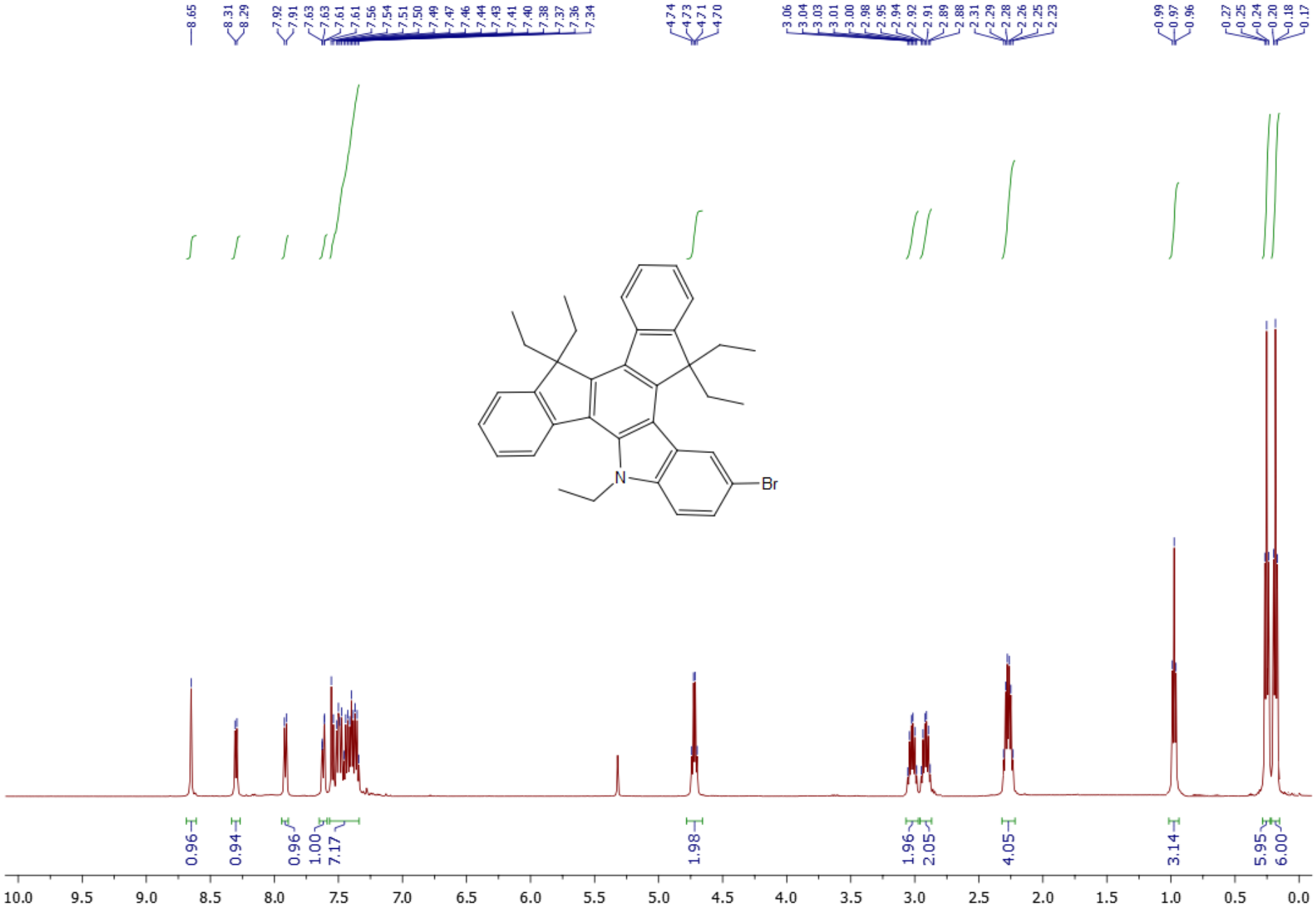
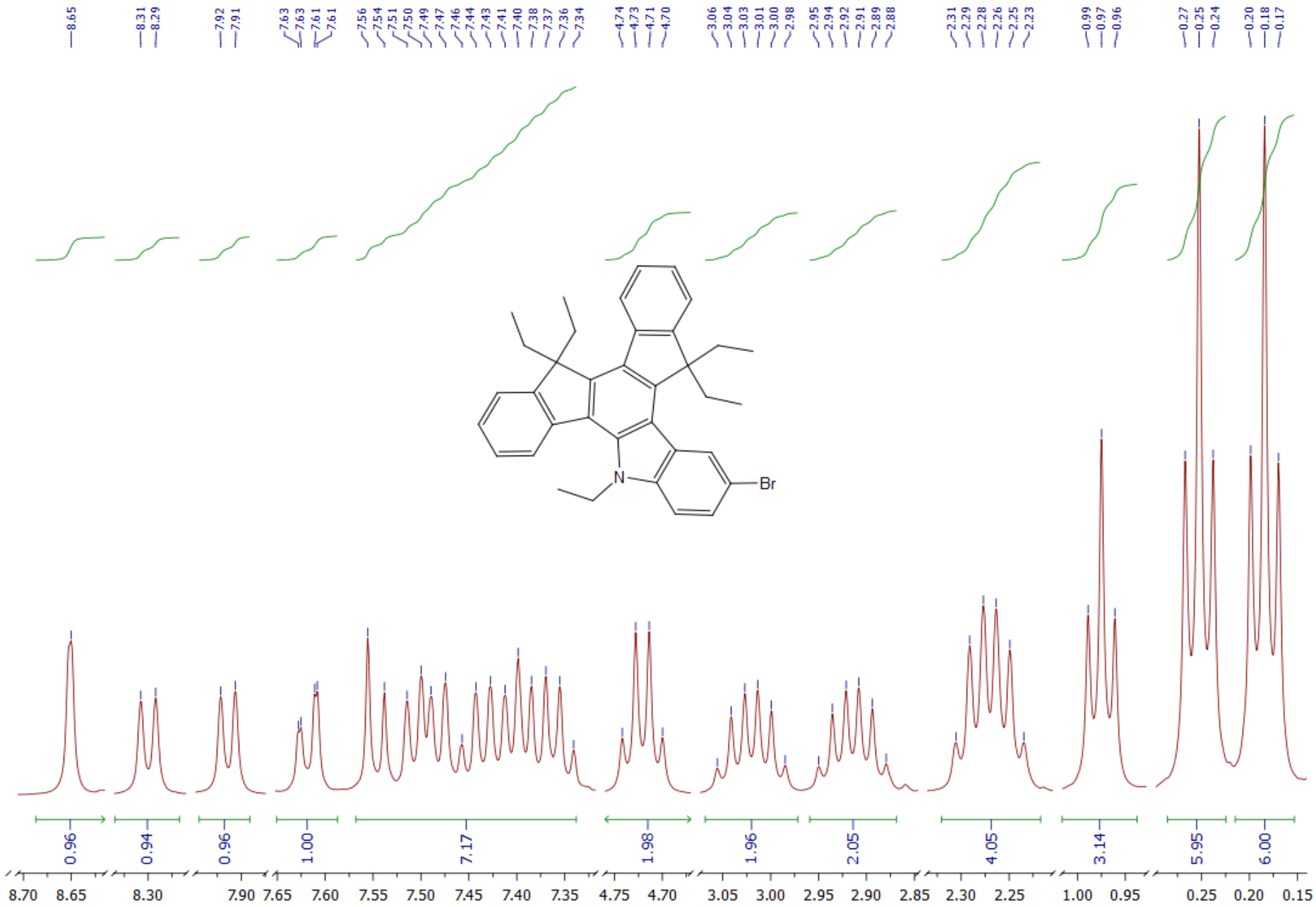


Figure S17b. ^{1}H NMR of 27 in CD_2Cl_2



19 $^{13}C\{^{1}H\}$ NMR of 27 in CD_2Cl_2

Figure S18a. $^{13}C\{^{1}H\}$ NMR of 27 in CD_2Cl_2

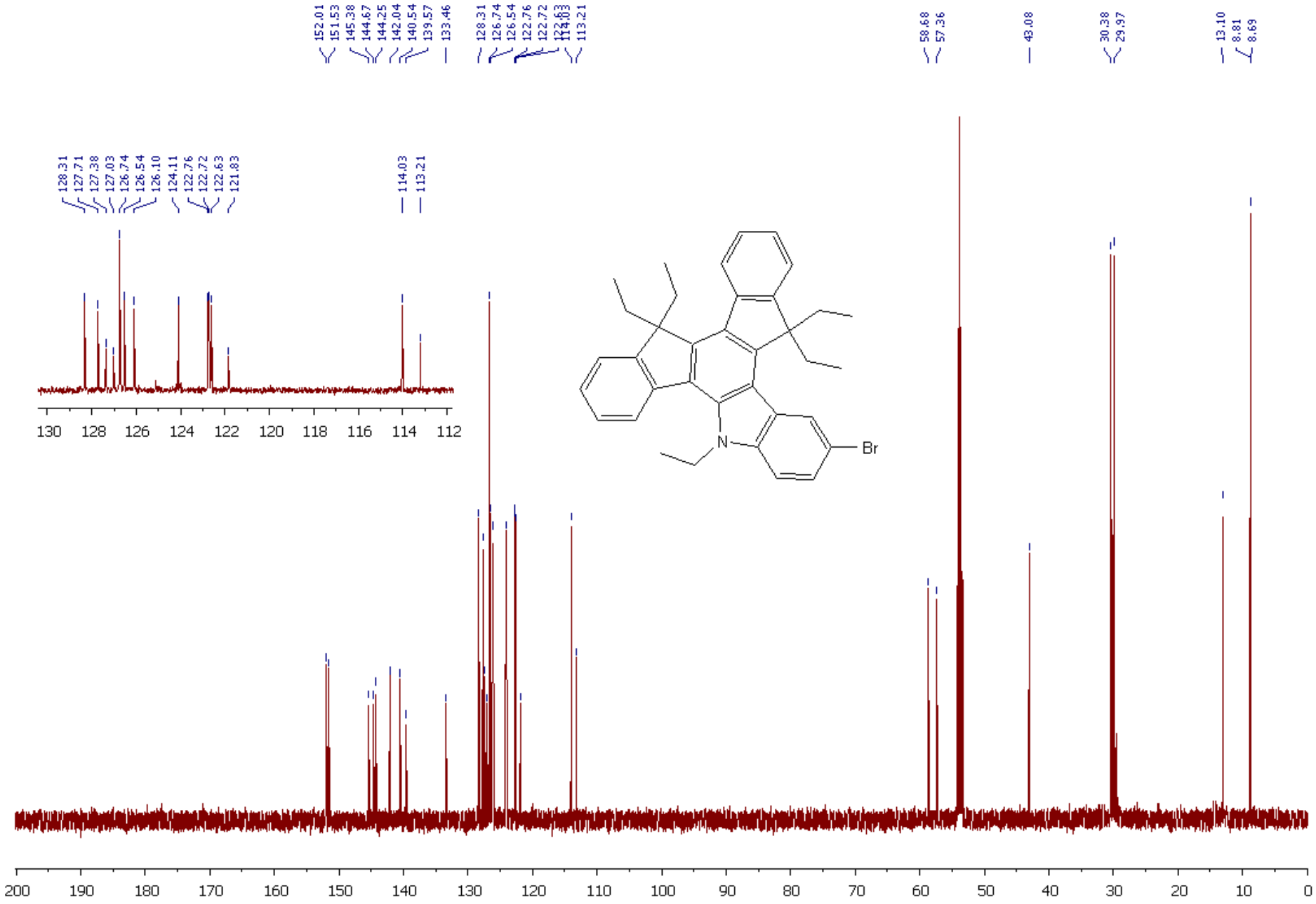


Figure S18b. $^{13}C\{^{1}H\}$ NMR of 27 in CD_2Cl_2