

Supplementary Data

Super critical water assisted preparation of recyclable gold nanoparticles and their catalytic utility in cross-coupling reactions under sustainable conditions

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I. General methods

Materials, methods and instruments

The formation of AuNPs from $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ by SCF processing was confirmed using Powder X-ray diffraction (PXRD) analysis, which was recorded in the BRUKER D8 ADVANCE X-ray Diffractometer with $\text{Cu K}\alpha$ radiation ($\alpha = 1.5418 \text{ \AA}$) from $2\theta = 10$ to 80° in steps of 0.02° and a count time of 0.2s. UV-visible absorption spectra were measured using VARIAN (Cary 500 Scan) UV-vis-NIR spectrophotometer system. The surface morphology of SCF assisted synthesis of AuNPs was characterized by field emission scanning electron microscopy (FE-SEM) and High Resolution Transmission Electron Microscopy (HR-TEM) analysis. SEM and HR-TEM images were captured at different locations of the AuNPs coated substrate using Carl Zeiss AG, Supra 55VP with an accelerating voltage of 0.1–30 kV and Tecnai G2 F20 S-Twin working at an accelerating voltage of 200 kV, respectively. The formation of AuNPs was further confirmed by X-ray photoelectron spectroscopy (XPS) analysis using Thermo Scientific MULTILAB 2000 base system with X-ray, Auger and ISS attachments using $\text{Mg K}\alpha$ (1253.6 eV) as X-ray source. All reactions were carried out in ultra clean glass vials and stir bars. Analytical TLC was performed on precoated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness (Macherey-Nagel, Germany) using analytical grade solvents and visualized with iodine spray (10% w/w I_2 in silica gel), UV light ($\lambda = 254$ and 365 nm) and alkaline KMnO_4 solution. Column chromatography was performed using thick-walled glass columns along with a mixture of petroleum ether and ethyl acetate on silica gel (100-200 mesh, SRL, India). The relative proportions of solvents in chromatography solvent mixtures refer to the volume to volume ratio. FT-IR spectra were recorded on a Bruker TENSOR 27 spectrometer in the frequency range from 400 to 4000 cm^{-1} using KBr pellet technique. ^1H and ^{13}C NMR spectra were obtained in and CDCl_3 on a BRUKER spectrometer

at 400 and 100 MHz respectively. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, $\delta = 0.00$) as internal standard and expressed in parts per million (ppm). The number of protons (n) for a given resonance was indicated as nH . Spin multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet). Coupling constants (J) are given in hertz (Hz). High resolution mass spectra (HRMS) were obtained using a Q-TOF and JEOL-GCMate II mass spectrometer. GC-MS spectra were obtained using a PerkinElmer instrument. ICP measurements were done using Agilent technologies 5110-ICP-OES equipped with auto sampler capacity of 240 tubes. UV-visible spectra for all solution and the thin film phase were recorded in chloroform solution and a thin film on a SHIMADZU UV-3600 plus UV-VIS-NIR spectrometer. Photoluminescence spectra were recorded on a Jasco spectrofluorometer FP-8500. Cyclic voltammetry (CV) experiments were performed with an Autolab potentiostat galvanostat (Model PGSTAT-30). All CV measurements were carried out at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, silver wire as the pseudo-reference electrode and a Pt wire as the counter electrode. Tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte was used in argon-purged acetonitrile at a scan rate 50 mV s^{-1} . A thermal evaporator with a sputtering unit (model no.: VRSU04D) and thickness monitor (model no.: CTM-200) was used for chemical vapour deposition. The OPV device performance was measured by recording the current voltage characteristics using a potentiostat (Keithley 2400) under illumination from a Solar Simulator (Science-Tech) with an AM 1.5G filter set and an illumination intensity of 100 mW cm^{-2} .

II. Experimental

Typical experimental procedure for Suzuki / Sonogashira / Heck coupling and catalyst recycling

In a screw cap vial containing 5 mL of demineralized water/EtOH (1:1 v/v) were added aryl halide (0.01 mol, 1.0 eq), arylboronic acid (0.01 mol, 1.0 eq) or terminal alkyne (0.01 mol, 1.0 eq) or styrene (0.01 mol, 1.0 eq), K₂CO₃ (0.02 mol, 2.0 eq) and AuNPs (0.1 mol%). The vial was capped and heated at reflux for 1 h, after which the solvents were distilled-off at reduced pressure. To the resulting crude mixture was added 5 mL of EtOH, centrifuged at 1000 rpm and filtered on a membrane filter (0.2 μM) to remove AuNPs. Further washing with portions of EtOH, pure water and acetone in a sequential manner affords the recycled AuNPs. The filtrate which contains crude product was distilled-off and traces of starting materials were removed by a short pad of silica gel flash chromatography using EtOAc/cyclohexane to obtain the pure product.

Biphenyl (3a)¹

White solid; ¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.32 (t, 2H, *J* = 8.0 Hz), 7.39 (t, 4H, *J* = 8.0 Hz), 7.58 (d, 4H, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 127.3, 127.4, 128.9, 141.3.

4-Methyl biphenyl (3b)¹

White solid; ¹H NMR (400 MHz, CDCl₃, δ in ppm): 2.38 (s, 3 H), 7.24 (d, 2 H, *J* = 8.0 Hz), 7.32 (d, 1 H, *J* = 8.0 Hz), 7.42 (t, 2 H, *J* = 8.0 Hz), 7.48 (d, 2 H, *J* = 8.0 Hz), 7.57 (d, 2 H, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 21.2, 127.0, 127.1, 128.8, 129.5, 129.6, 137.1, 138.4, 141.2.

4-Acetylbiphenyl (3c)²

White solid; ¹H NMR (400 MHz, CDCl₃, δ in ppm): 2.63 (s, 3H), 7.39 (t, 1H, *J* = 8.0 Hz), 7.46 (t, 2H, *J* = 8.0 Hz), 7.62 (d, 2H, *J* = 8.0 Hz), 7.67 (d, 2H, *J* = 8.0 Hz), 8.02 (d, 2H, *J* = 8.0 Hz); ¹³C

NMR (100 MHz, CDCl₃, δ in ppm): 26.6, 127.2, 127.3, 128.2, 128.9, 129.0, 135.9, 139.9, 145.8, 197.7.

2-Methoxyl biphenyl (3d)³

Colourless liquid; ¹H NMR (400 MHz, CDCl₃, δ in ppm): 3.79 (s, 3H), 7.02-6.96 (m, 2H), 7.33-7.29 (m, 3H), 7.40 (t, 2H, $J = 8.0$ Hz), 7.52 (d, 2H, $J = 8.0$ Hz); ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 55.6, 111.3, 120.9, 127.0, 128.0, 128.7, 129.6, 130.8, 130.9, 138.6, 156.5.

4-Methoxyl biphenyl (3e)¹

White solid; ¹H NMR (400 MHz, CDCl₃, δ in ppm): 3.83 (s, 3H), 6.97 (d, 2H, $J = 8.0$ Hz), 7.30 (d, 1H, $J = 8.0$ Hz), 7.40 (t, 2H, $J = 8.0$ Hz), 7.53 (t, 4H, $J = 8.0$ Hz); ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 55.4, 114.2, 126.7, 126.8, 128.2, 128.8, 133.8, 140.9, 159.2.

4-Fluorobiphenyl (3f)⁴

White solid; ¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.12-7.06 (m, 2H), 7.31 (t, 1H), 7.40 (t, 2H, $J = 8.0$ Hz), 7.53-7.49 (m, 4H); ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 115.6, 127.1, 127.3, 128.8, 137.4, 140.3, 161.4, 163.8.

Diphenylacetylene (5a)⁵

¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.35-7.29 (m, 6H), 7.58-7.53 (m, 4H); ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 89.5, 123.2, 128.2, 128.5, 131.7.

(4-Methoxyphenyl)phenylacetylene (5b)⁶

¹H NMR (400 MHz, CDCl₃, δ in ppm): 3.83 (s, 3H), 6.89 (d, 2H, $J = 8.0$ Hz), 7.38-7.32 (m, 3H), 7.54-7.44 (m, 4H), ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 55.4, 88.1, 89.2, 113.9, 115.4, 123.4, 127.9, 128.4, 133.1, 131.4, 159.6,

(4-Nitrophenyl)phenylacetylene (5c)⁷

¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.39-7.35 (m, 3H), 7.58-7.54 (m, 2H), 7.66 (d, 2H, *J* = 8.0 Hz), 8.21 (d, 2H, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 87.7, 94.8, 122.0, 123.7, 128.6, 129.3, 130.1, 131.9, 132.1, 146.9.

Phenyl-*p*-tolylacetylene (5d)⁸

¹H NMR (400 MHz, CDCl₃, δ in ppm): 2.31 (s, 3H), 7.15 (d, 2H, *J* = 8.0 Hz), 7.28-7.22 (m, 3H), 7.44 (d, 2H, *J* = 8.0 Hz), 7.50-7.45 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 21.5, 88.5, 89.8, 120.0, 123.5, 128.0, 128.1, 129.0, 131.6, 138.2.

(4-Cyanophenyl)phenylacetylene (5e)⁹

¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.44-7.40 (m, 3H), 7.58-7.55 (m, 2H), 7.68-7.61 (m, 4H); ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 87.7, 93.7, 111.4, 118.5, 122.2, 128.2, 128.5, 129.1, 131.8, 132.0.

(*E*)-1,2-Diphenylethene (5a')¹⁰

¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.15 (s, 2H), 7.27-7.31 (t, 2H, *J* = 7.6 Hz); 7.35-7.43 (t, 4H, *J* = 7.6 Hz), 7.57 (d, 4H, *J* = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 126.5, 127.6, 128.7, 137.4.

4'-(Diphenylamino)-[1,1'-biphenyl]-4-carbaldehyde (3h)

Bright green solid; Mp: 74.2-77.0 °C; R_f = 0.23 (5% EA / PE); FT-IR (KBr): 3032, 2924, 2854, 1703, 1594, 1491, 1328, 1282, 1182, 1086, 965, 822, 756, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.10 (t, 2H, *J* = 8.0 Hz), 7.14 – 7.19 (m, 6H), 7.32 (t, 4H, *J* = 8.0 Hz), 7.53 (d, 2H, *J* = 12.0 Hz), 7.74 (d, 2H, *J* = 8.0 Hz), 7.94 (d, 2H, *J* = 8.0 Hz), 10.05 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 123.1, 123.4, 124.9, 126.9, 128.0, 129.4, 130.3, 132.7, 134.6, 146.6, 147.3, 148.4, 191.9; HRMS: *m/z* calcd for C₂₅H₁₉NO [M]⁺: 349.1467, found: 349.1459.

5-(4-(Diphenylamino)phenyl)thiophene-2-carbaldehyde (3i)

Bright green solid; Mp: 80.6 - 83.1°C; $R_f = 0.22$ (5% EA / PE); FT-IR (KBr): 3040, 2938, 2871, 1729, 1666, 1595, 1495, 1453, 1281, 1228, 1056, 812, 754, 695 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , δ in ppm): 7.07-7.17 (m, 6H), 7.29 – 7.35 (m, 6H), 7.53 (d, 3H, $J = 12.0$ Hz), 7.72 (d, 1H, $J = 4.0$ Hz), 9.88 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , δ in ppm): 122.3, 122.8, 123.9, 125.0, 126.1, 127.2, 129.5, 137.7, 141.3, 146.9, 149.1, 154.6, 182.6; HRMS: m/z calcd for $\text{C}_{23}\text{H}_{17}\text{NOS}$ $[\text{M}]^+$: 355.1031, found: 355.1026.

4'-(Dimethylamino)-[1,1'-biphenyl]-4-carbaldehyde (3j)

Bright green solid; Mp: 178.0 – 179.0°C; $R_f = 0.52$ (DCM); FT-IR (KBr): 3087, 2935, 2870, 1694, 1602, 1370, 1293, 1208, 1172, 950, 811, 692 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , δ in ppm): 3.03 (s, 6H), 6.79 (d, 2H, $J = 8.0$ Hz), 7.57 (d, 2H, $J = 8.0$ Hz), 7.70 (d, 2H, $J = 8.0$ Hz), 7.88 (d, 2H, $J = 8.0$ Hz), 10.00 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , δ in ppm): 40.3, 112.5, 126.2, 126.9, 128.0, 130.3, 134.0, 147.2, 150.7, 191.9; HRMS: m/z calcd for $\text{C}_{15}\text{H}_{15}\text{NO}$ $[\text{M}]^+$: 225.1154, found: 225.1148.

4'-(Diethylamino)-[1,1'-biphenyl]-4-carbaldehyde (3k)

Bright green solid; Mp: 97.0 – 98.2°C; $R_f = 0.31$ (5% EA / PE); FT-IR (KBr): 3097, 2989, 2915, 2838, 1696, 1596, 1536, 1369, 1279, 1204, 1167, 926, 812, 749, 680 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , δ in ppm): 1.21 (t, 6H, $J = 8.0$ Hz), 3.41 (q, 4H, $J = 8.0$ Hz), 6.74 (d, 2H, $J = 8.0$ Hz), 7.54 (d, 2H, $J = 12.0$ Hz), 7.69 (d, 2H, $J = 8.0$ Hz), 7.87 (d, 2H, $J = 8.0$ Hz), 9.99 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , δ in ppm): 12.6, 44.4, 111.7, 125.7, 126.0, 128.3, 130.3, 133.8, 147.3, 148.0, 191.9; HRMS: m/z calcd for $\text{C}_{17}\text{H}_{19}\text{NO}$ $[\text{M}]^+$: 253.1467, found: 253.1461.

2-((4'-(Diphenylamino)-[1,1'-biphenyl]-4-yl)methylene)malononitrile (6a)

Yellowish red semi solid; $R_f = 0.36$ (5% EA / PE); FT-IR (KBr): 3030, 2924, 2857, 2225, 1579, 1488, 1331, 1277, 1196, 1081, 824, 753, 697 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , δ in ppm): 7.10 – 7.21 (m, 8H), 7.31 – 7.36 (m, 4H), 7.54 (d, 2H, $J = 12.0$ Hz), 7.74 (s, 1H), 7.77 (d, 2H, $J = 4.0$ Hz), 7.98 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3 , δ in ppm): 80.9, 113.0, 114.1, 122.6, 123.8, 125.1, 127.0, 127.9, 129.1, 129.5, 131.5, 131.6, 146.8, 147.1, 149.0, 159.1; HRMS: m/z calcd for $\text{C}_{28}\text{H}_{19}\text{N}_3$ $[\text{M}]^+$: 397.1579, found: 397.1574.

2-((5-(4-(Diphenylamino)phenyl)thiophen-2-yl)methylene)malononitrile (6b)

Brown semi solid; $R_f = 0.11$ (10% EA / PE); FT-IR (KBr): 3044, 2939, 2865, 2227, 1578, 1496, 1436, 1330, 1200, 1077, 819, 760, 700 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , δ in ppm): 7.06 (d, 2H, $J = 10.0$ Hz), 7.12 – 7.18 (m, 5H), 7.54 (d, 2H, $J = 10.0$ Hz), 7.69 (d, 1H, $J = 5.0$ Hz), 7.76 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3 , δ in ppm): 75.1, 113.6, 114.5, 121.7, 123.3, 124.3, 124.8, 125.5, 127.5, 129.6, 133.1, 140.3, 146.6, 149.9, 150.2, 157.1; HRMS: m/z calcd for $\text{C}_{26}\text{H}_{17}\text{N}_3\text{S}$ $[\text{M}]^+$: 403.1143, found: 403.1141.

2-((4'-(Dimethylamino)-[1,1'-biphenyl]-4-yl)methylene)malononitrile (6c)

Dark red semi solid; $R_f = 0.26$ (10% EA / PE); FT-IR (KBr): 3079, 2937, 2872, 2236, 1608, 1467, 1379, 1265, 1183, 1105, 813, 725 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , δ in ppm): 3.03 (s, 6H), 6.59 (d, 1H, $J = 5.0$ Hz), 6.79 (d, 2H, $J = 10.0$ Hz), 7.56 (d, 2H, $J = 10.0$ Hz), 7.62 (d, 3H, $J = 10.0$ Hz), 7.71 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3 , δ in ppm): 40.3, 81.4, 112.0, 112.5, 114.0, 126.4, 127.7, 129.7, 131.6, 136.1, 139.2, 150.4, 160.0; HRMS: m/z calcd for $\text{C}_{18}\text{H}_{15}\text{N}_3$ $[\text{M}]^+$: 273.1266, found: 273.1260.

2-((4'-(Diethylamino)-[1,1'-biphenyl]-4-yl)methylene)malononitrile (6d)

Red semi solid; $R_f = 0.27$ (10% EA / PE); FT-IR (KBr): 3062, 2936, 2873, 2226, 1632, 1406, 1277, 1196, 1134, 660 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , δ in ppm): 1.23 (t, 6H, $J = 5.0$ Hz), 3.45 (q, 4H, $J = 5.0$ Hz), 6.77 (d, 2H, $J = 10.0$ Hz), 7.56 (d, 2H, $J = 10.0$ Hz), 7.62 (d, 2H, $J = 10.0$ Hz), 7.66 (d, 2H, $J = 10.0$ Hz), 7.72 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3 , δ in ppm): 12.6, 44.4, 81.1, 111.8, 113.9, 121.0, 126.0, 126.2, 128.0, 128.3, 129.7, 131.7, 150.5, 160.1; HRMS: m/z calcd for $\text{C}_{20}\text{H}_{19}\text{N}_3$ $[\text{M}]^+$: 301.1579, found: 301.1573.

5''-((4-(Dimethylamino)phenyl)ethynyl)-[2,2':5',2''-terthiophene]-5-carbaldehyde (5f)

brown solid; ^1H NMR (500 MHz, CDCl_3 , δ in ppm): 3.01 (s, 6H), 6.62 (d, 2H, $J = 10.0$ Hz), 6.98 (d, 1H, $J = 5.0$ Hz), 7.02 (d, 1H, $J = 5.0$ Hz), 7.08 (d, 1H, $J = 5.0$ Hz), 7.25 (d, 1H, $J = 5.0$ Hz), 7.27 (d, 1H, $J = 5.0$ Hz), 7.40 (d, 2H, $J = 10.0$ Hz), 7.69 (d, 1H, $J = 5.0$ Hz), 9.89 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3 , δ in ppm): 40.1, 72.6, 82.3, 111.7, 112.1, 124.2, 124.5, 124.9, 126.8, 130.9, 131.7, 132.6, 133.6, 134.9, 137.2, 141.8, 146.4, 150.3, 182.4; HRMS: m/z calcd for $\text{C}_{23}\text{H}_{17}\text{NOS}_3$ $[\text{M}]^+$: 419.0472, found: 419.0466.

5-((4-(Dimethylamino)phenyl)ethynyl)thieno[3,2-b]thiophene-2-carbaldehyde (5g)

dark brown solid; ^1H NMR (500 MHz, CDCl_3 , δ in ppm): 3.04 (s, 6H), 6.67 (d, 2H, $J = 5.0$ Hz), 7.38 (s, 1H), 7.43 (d, 2H, $J = 5.0$ Hz), 7.86 (s, 1H), 9.97 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3 , δ in ppm): 40.1, 80.9, 99.3, 108.3, 111.7, 122.9, 128.8, 132.7, 132.8, 138.7, 145.3, 145.7, 150.6, 183.1; HRMS: m/z calcd for $\text{C}_{17}\text{H}_{13}\text{NOS}_2$ $[\text{M}]^+$: 311.0439, found: 311.0436.

2,6-bis(3-Hexylthiophen-2-yl)dithieno[3,2-b:2',3'-d]thiophene (3g)

Yellow solid; ^1H NMR (500 MHz, CDCl_3 , δ in ppm): 0.9 (t, 6H, $J = 5.0$ Hz), 1.32-1.42 (m, 12H), 1.69 (p, 4H, $J = 5.0$ Hz), 2.83 (t, 4H, $J = 10.0$ Hz), 6.99 (d, 2H, $J = 5.0$ Hz), 7.24 (d, 2H, $J = 5.0$ Hz), 7.31 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3 , δ in ppm): 14.0, 22.6, 29.2, 29.2, 30.7, 31.6, 119.2,

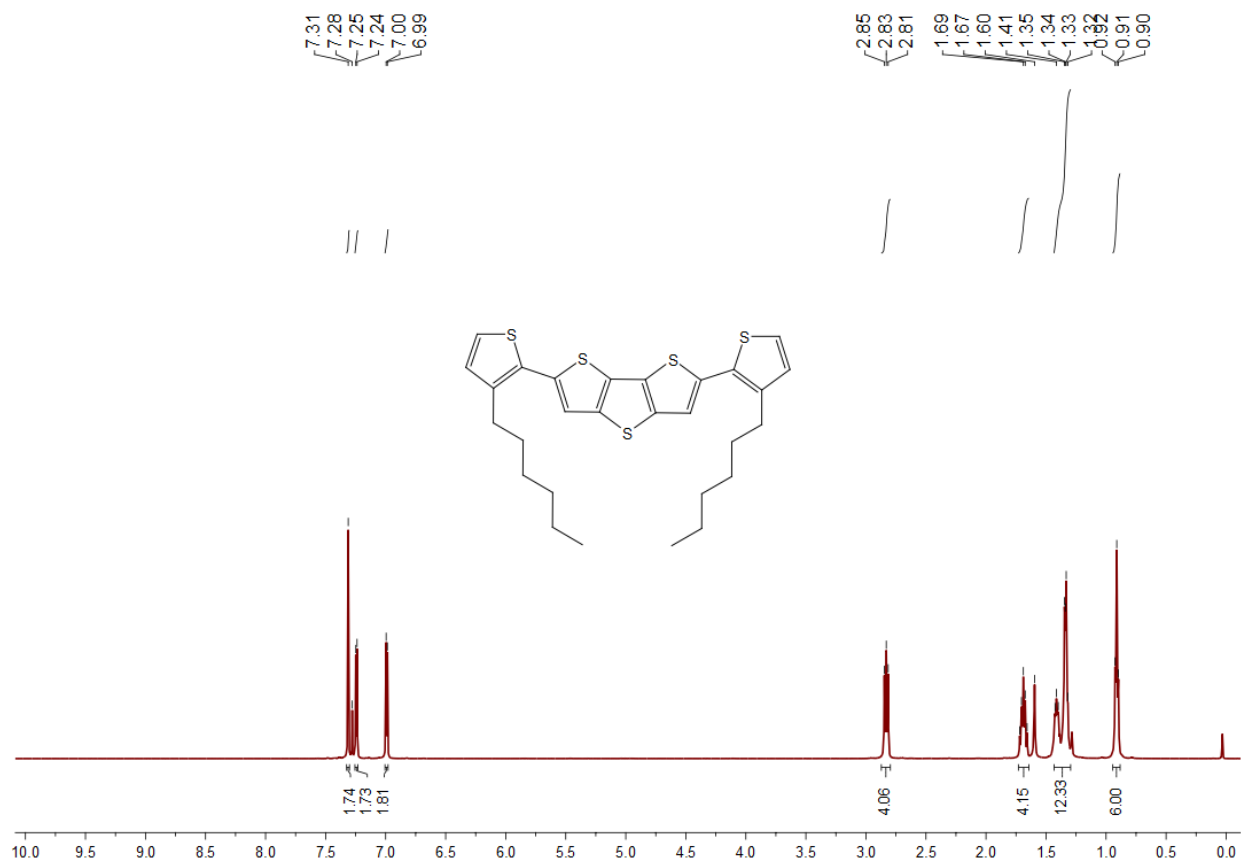
124.4, 130.1, 130.5, 130.6, 136.9, 140.3, 140.9; HRMS: m/z calcd for $C_{28}H_{32}S_5 [M]^+$: 528.1108, found: 528.1101.

References

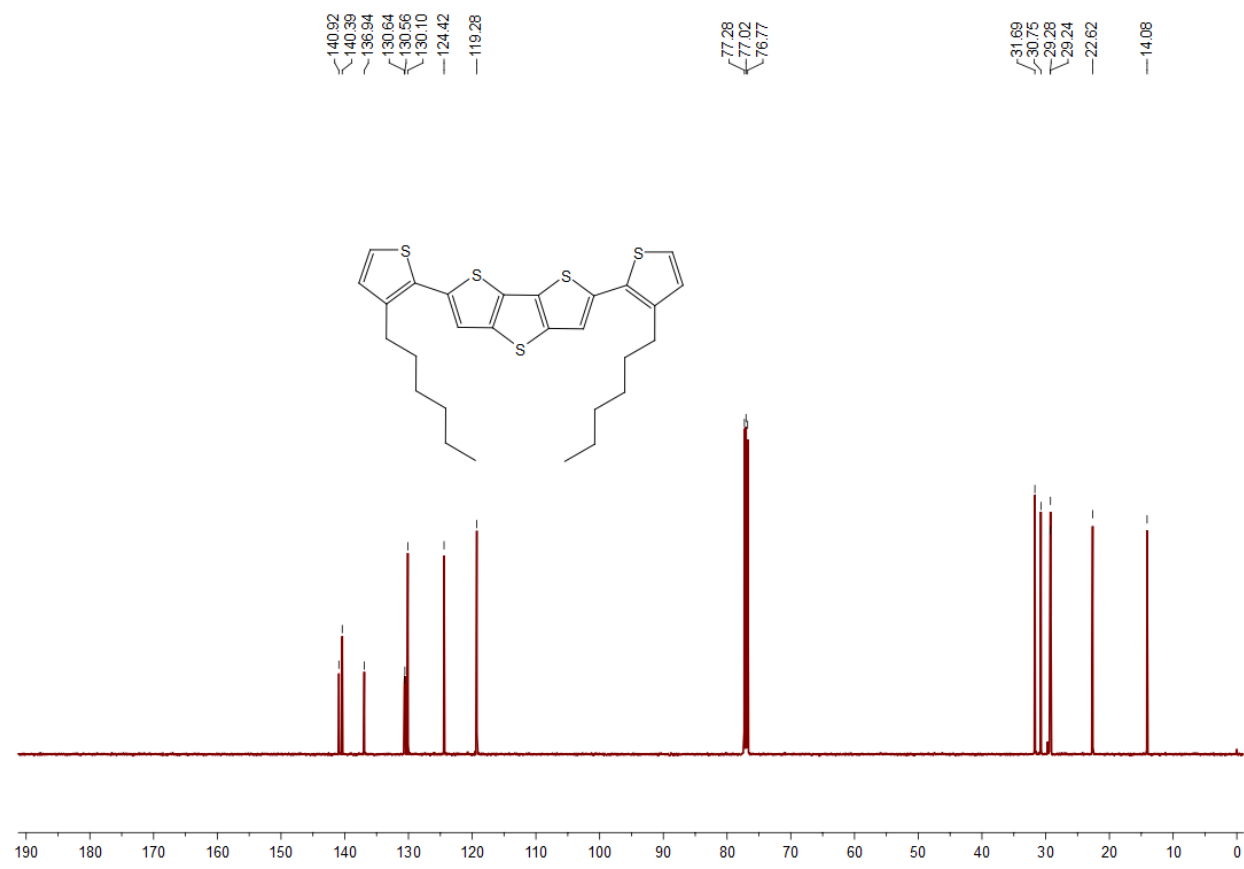
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III. ^1H NMR & ^{13}C NMR of **3g**, **5f**, **5g**, **3h-3k** and **6a-6d**

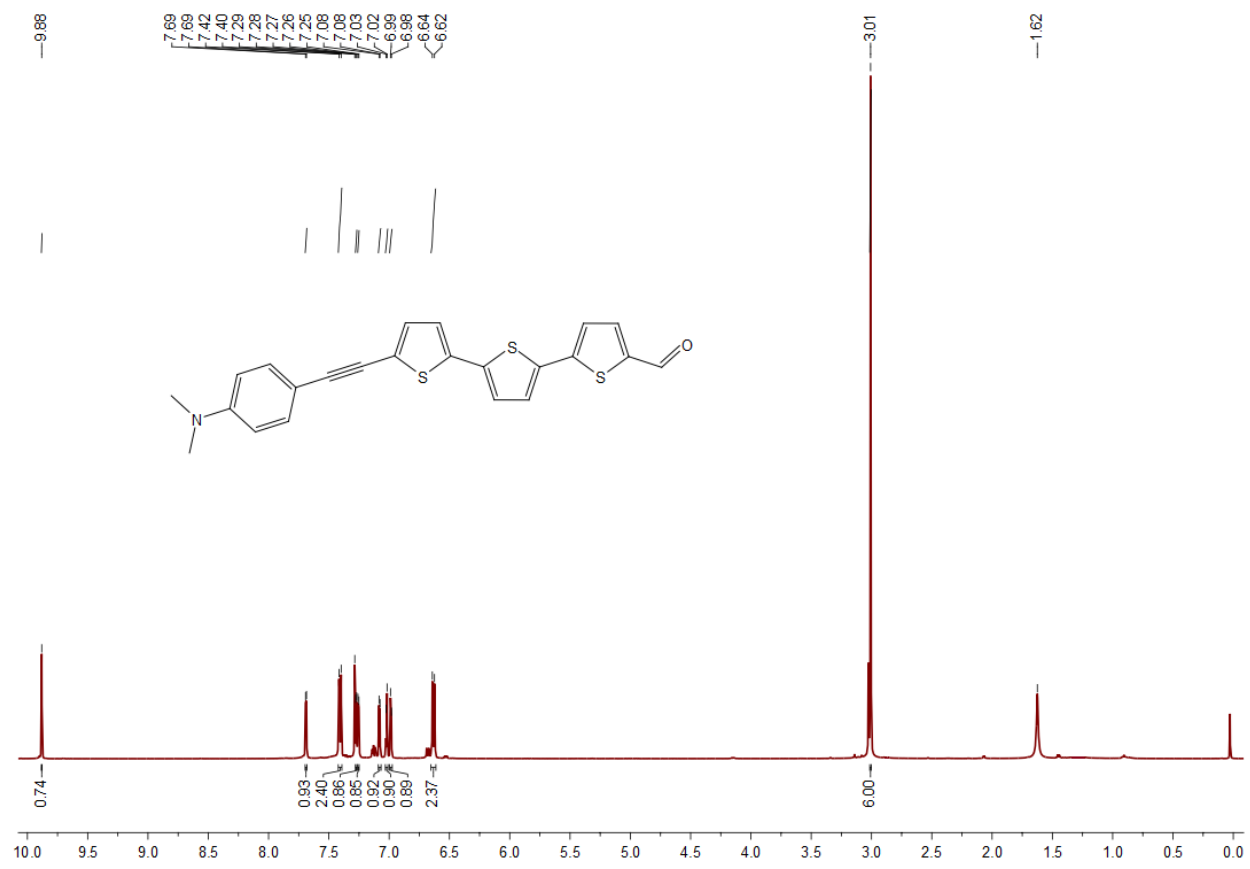
^1H NMR spectrum of compound **3g** in CDCl_3



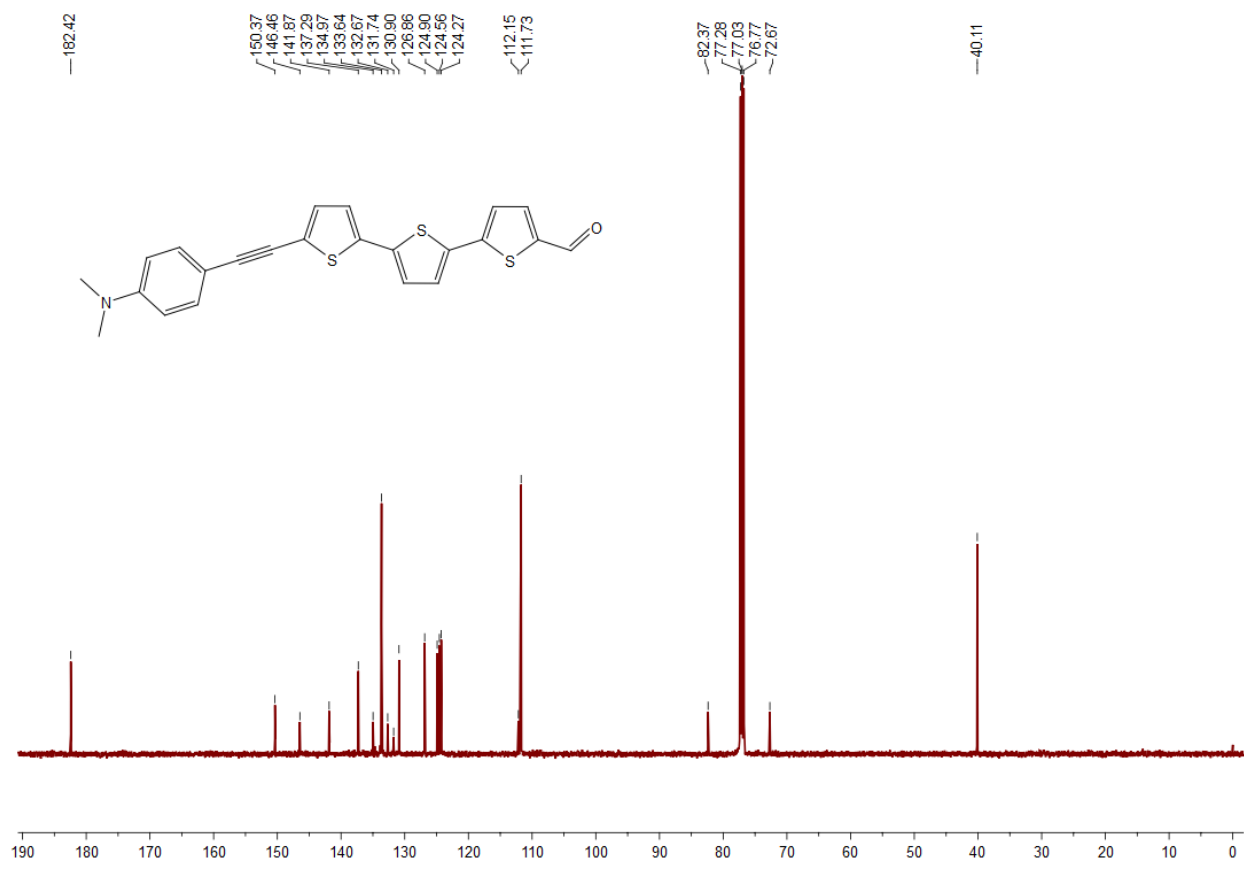
^{13}C NMR spectrum of compound **3g** in CDCl_3



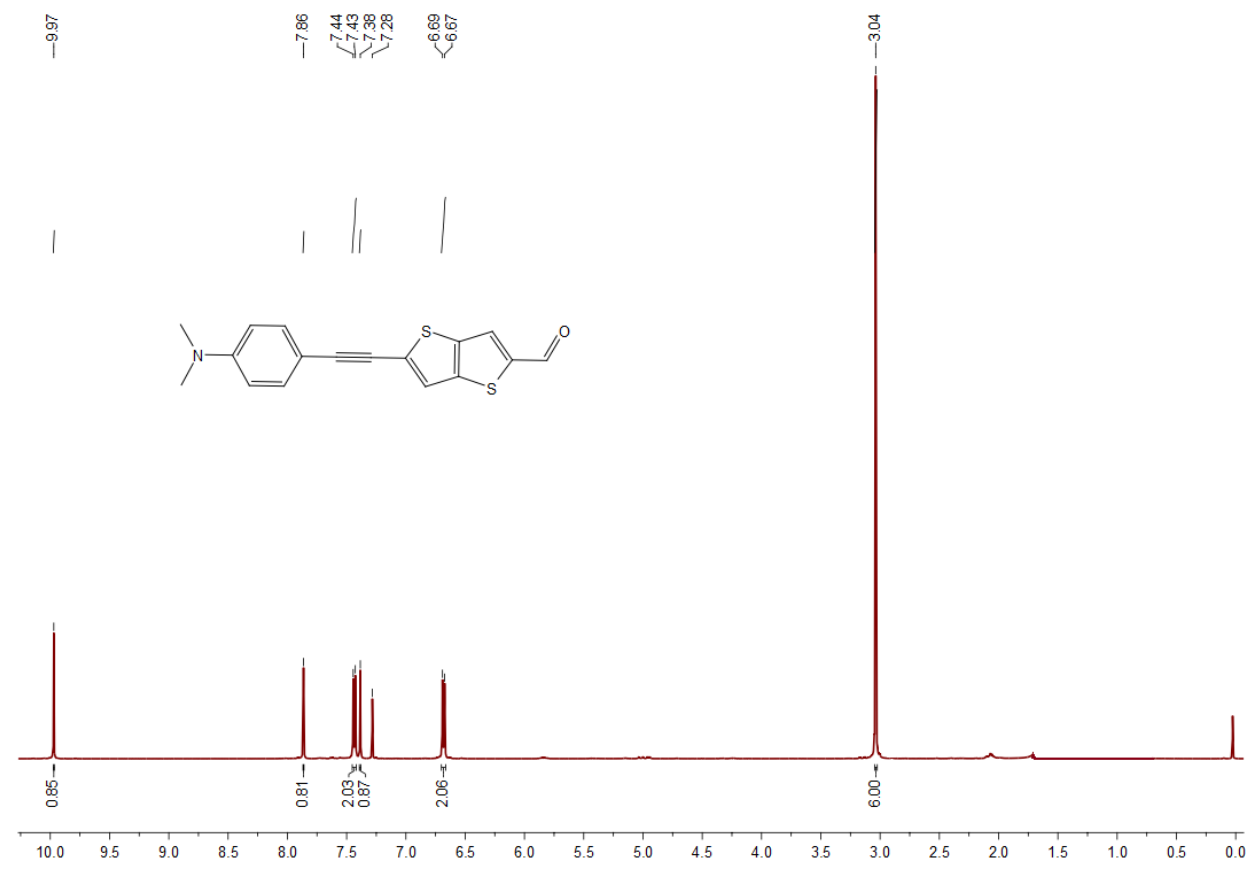
^1H NMR spectrum of compound **5f** in CDCl_3



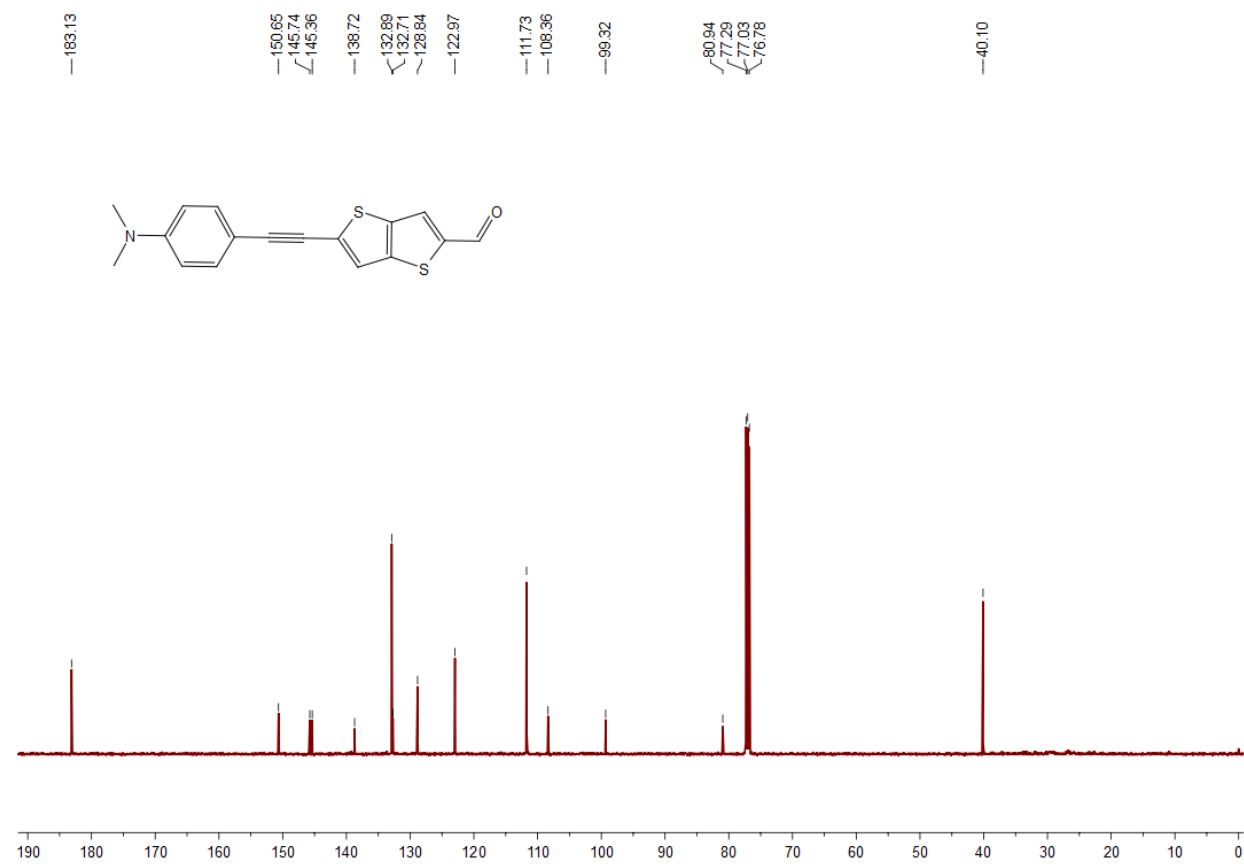
^{13}C NMR spectrum of compound **5f** in CDCl_3



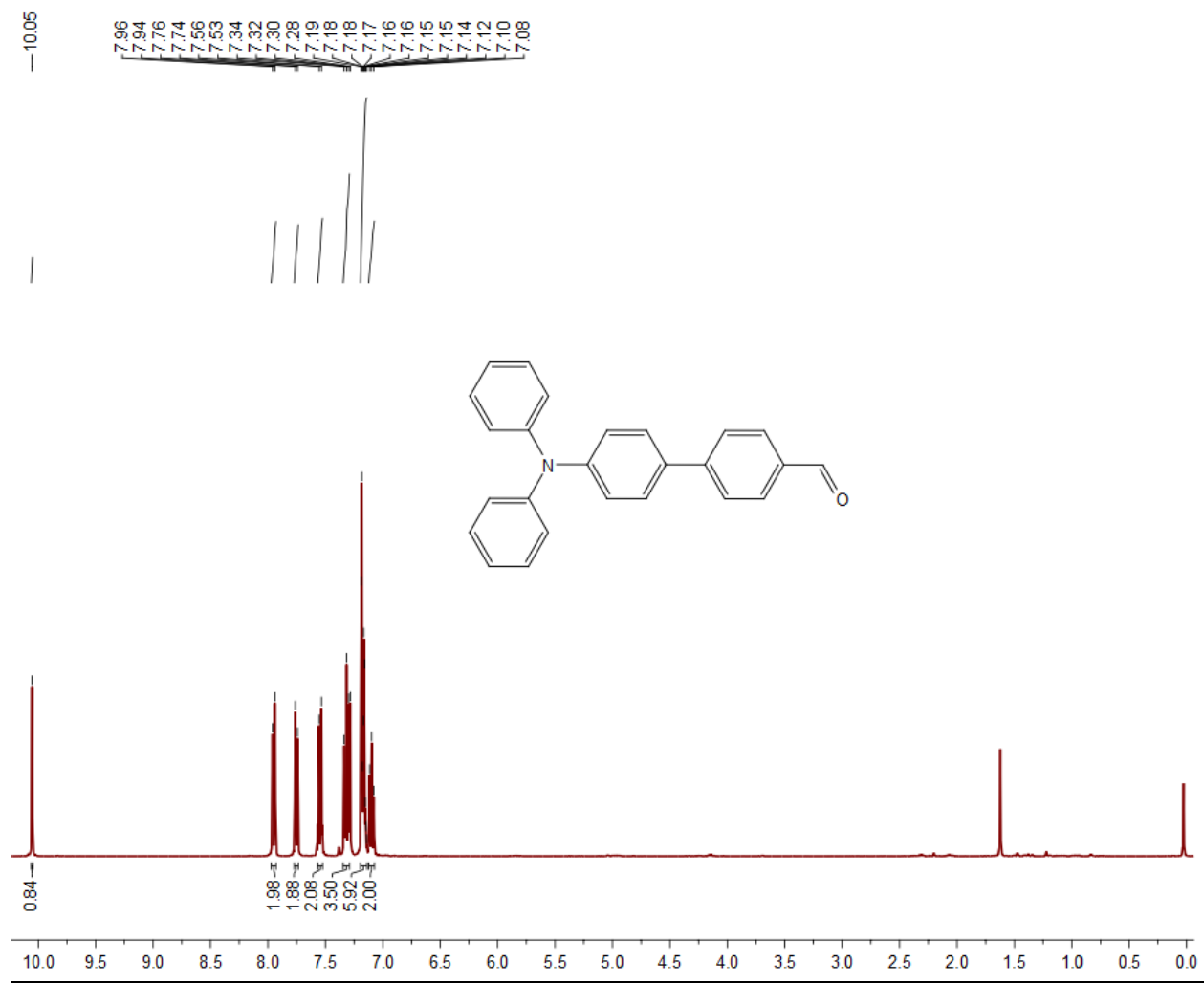
^1H NMR spectrum of compound **5g** in CDCl_3



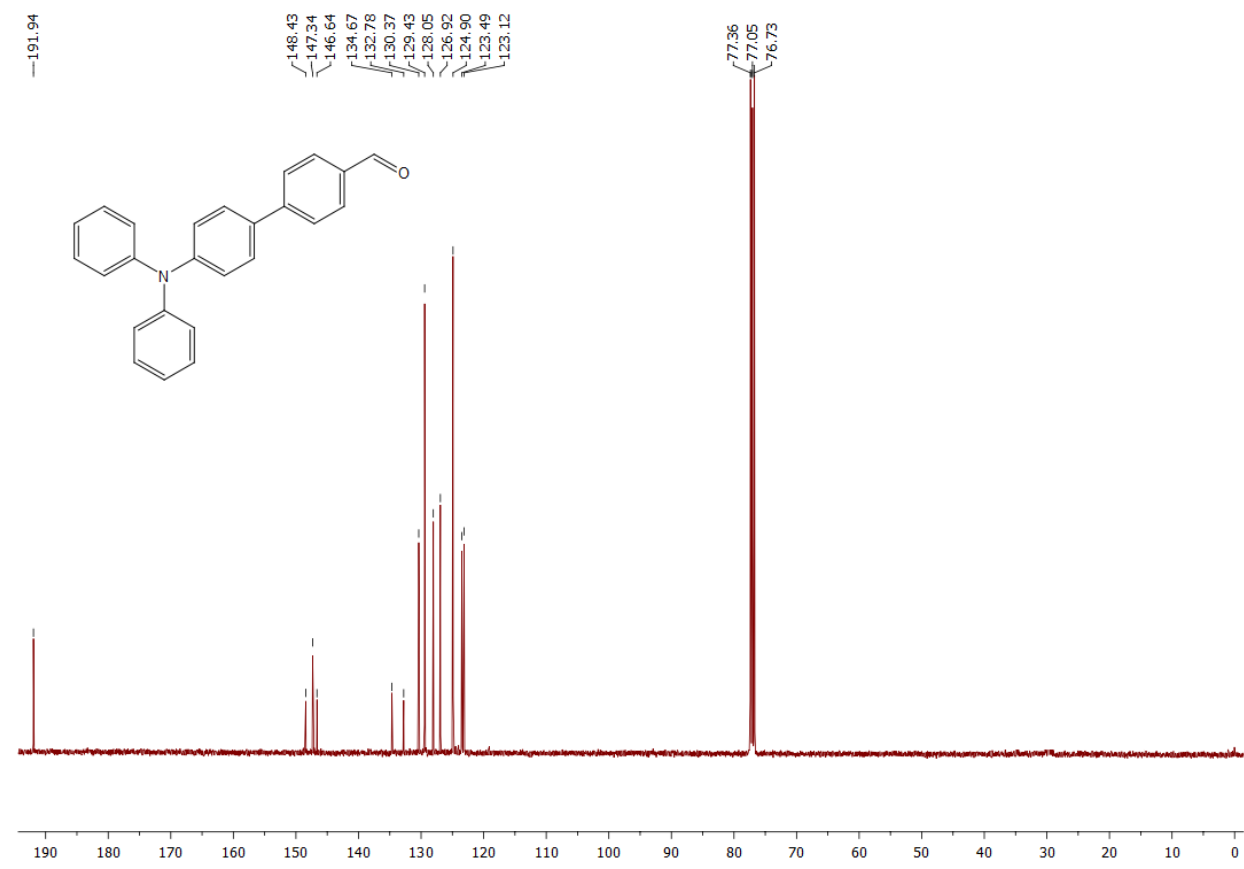
^{13}C NMR spectrum of compound **5g** in CDCl_3



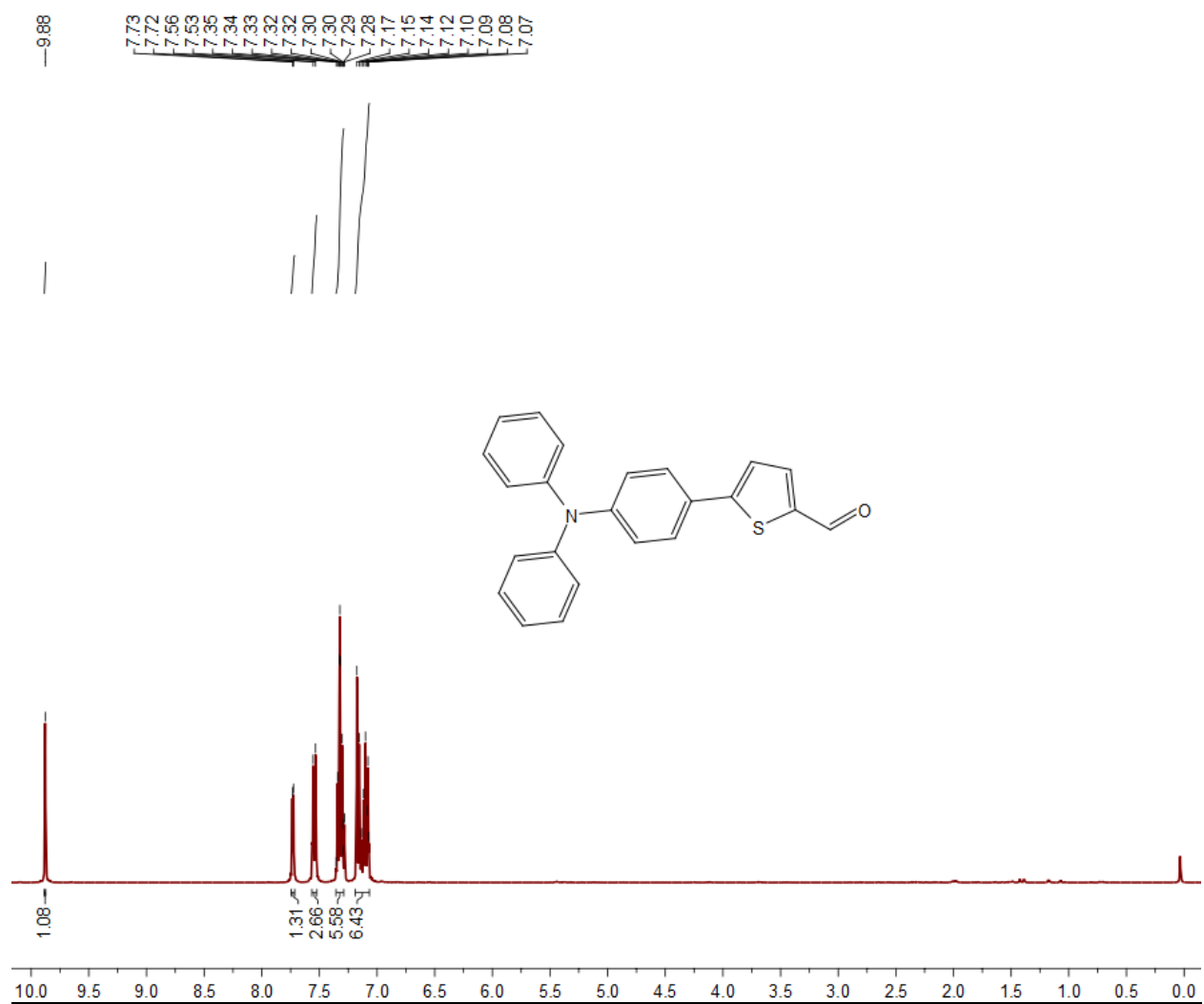
^1H NMR spectrum of compound **3h** in CDCl_3



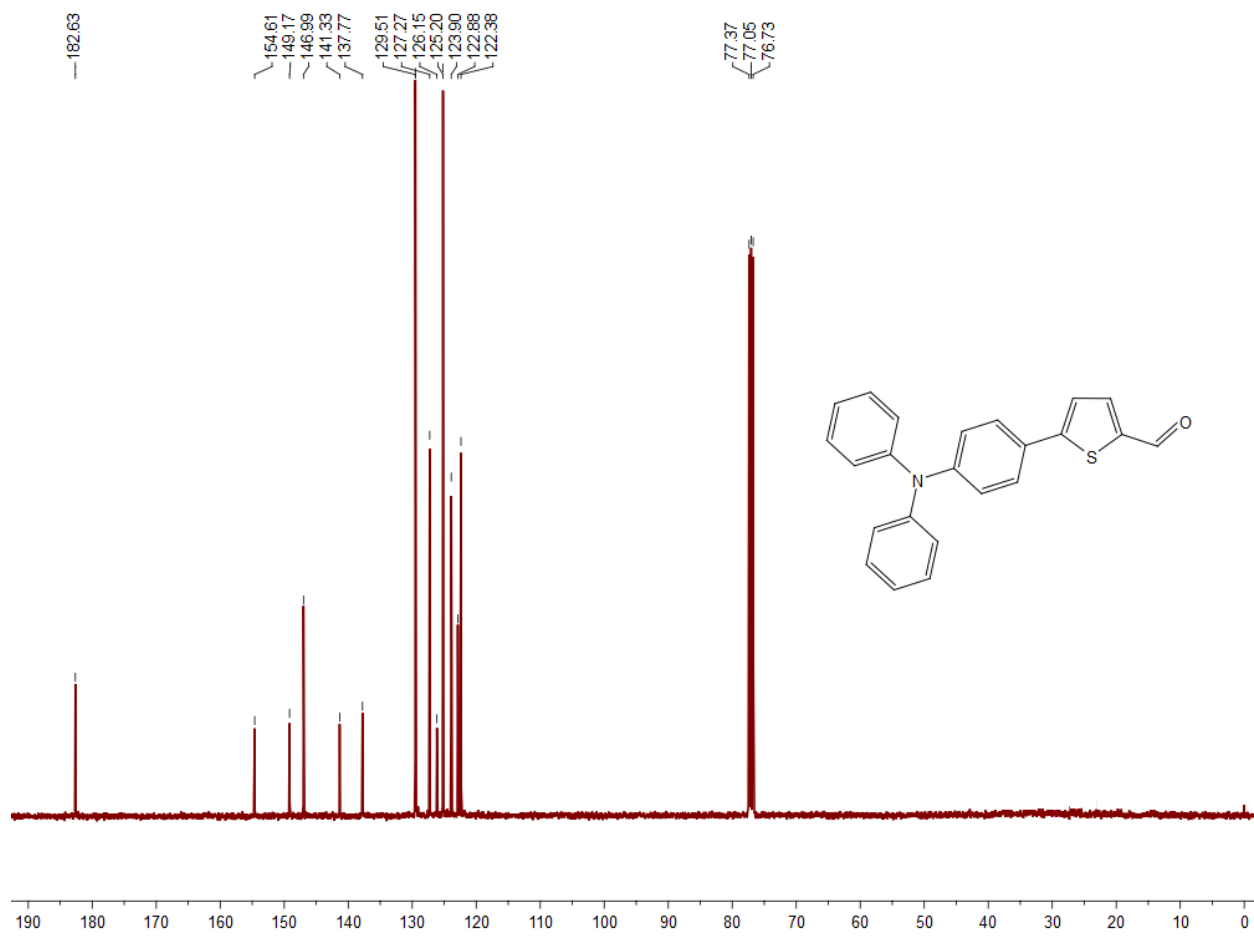
^{13}C NMR spectrum of compound **3h** in CDCl_3



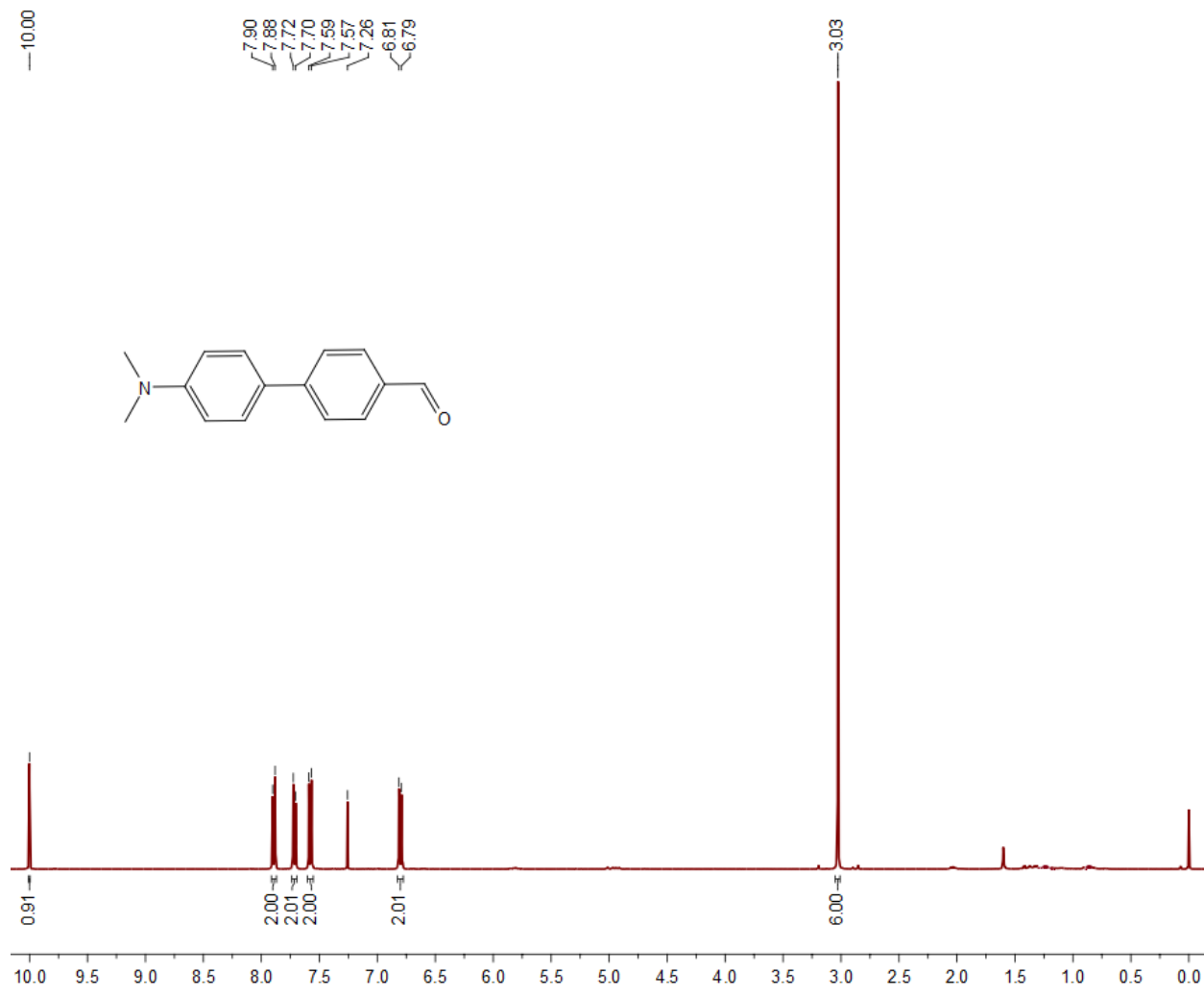
^1H NMR spectrum of compound **3i** in CDCl_3



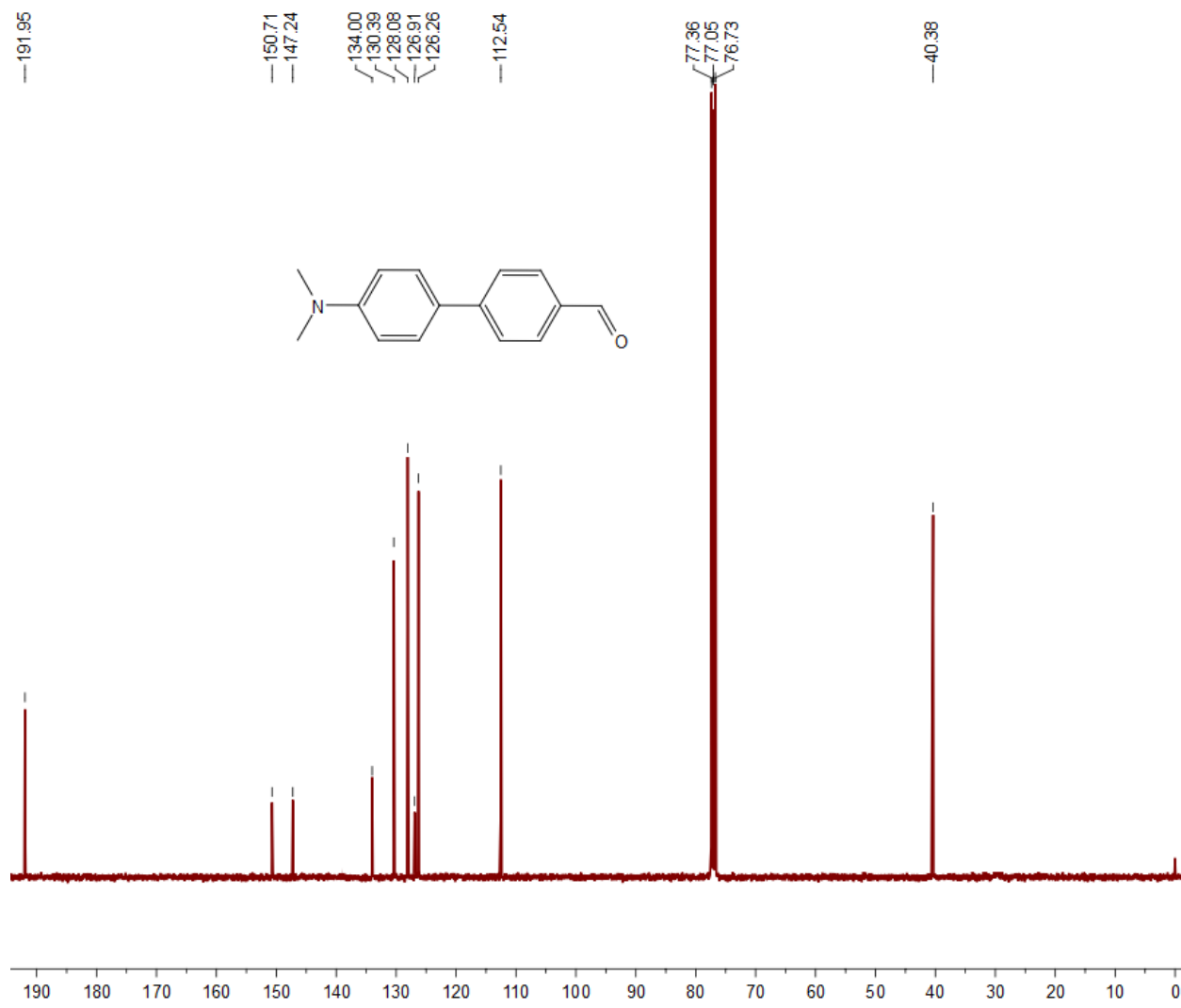
^{13}C NMR spectrum of compound **3i** in CDCl_3



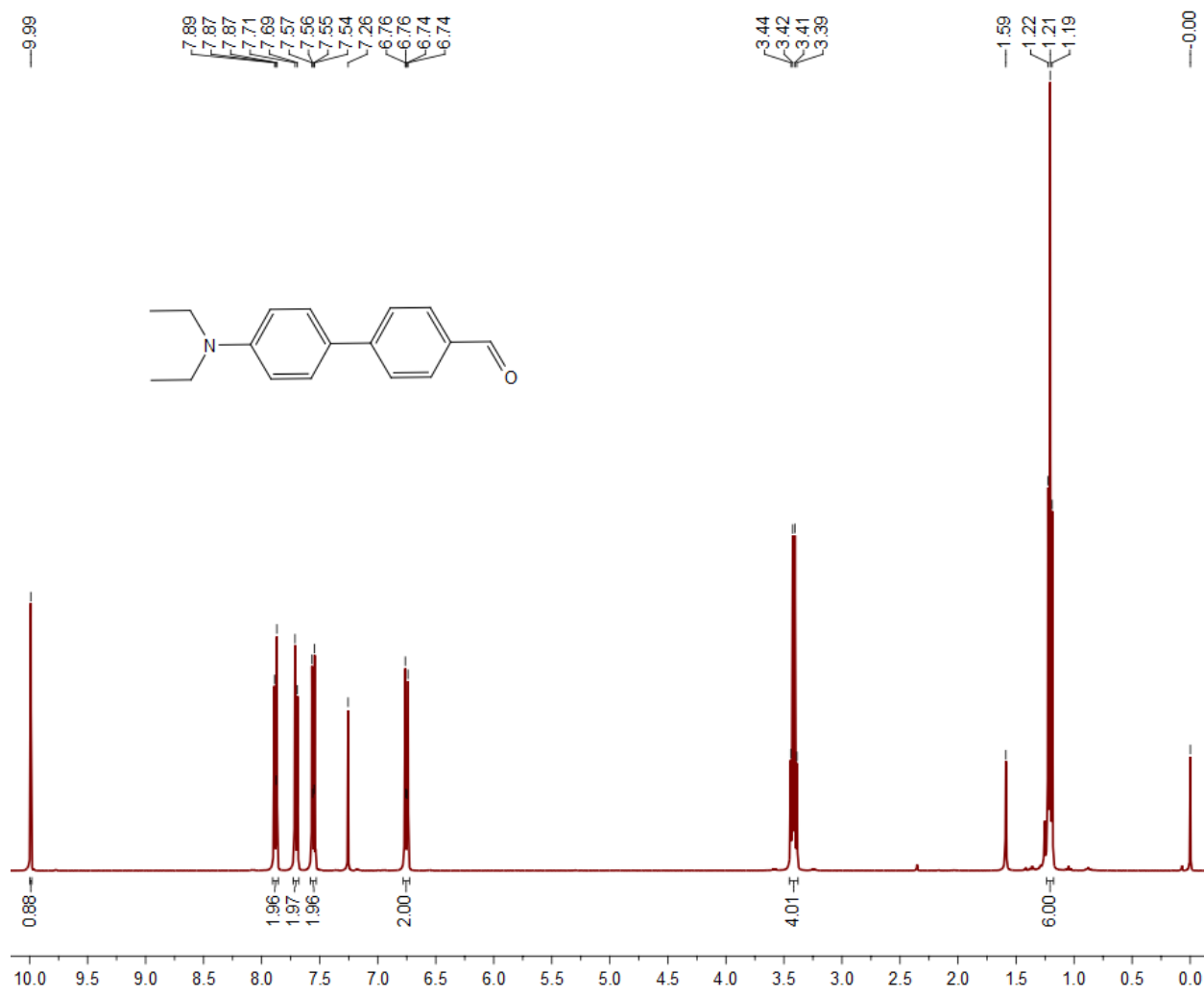
^1H NMR spectrum of compound **3j** in CDCl_3



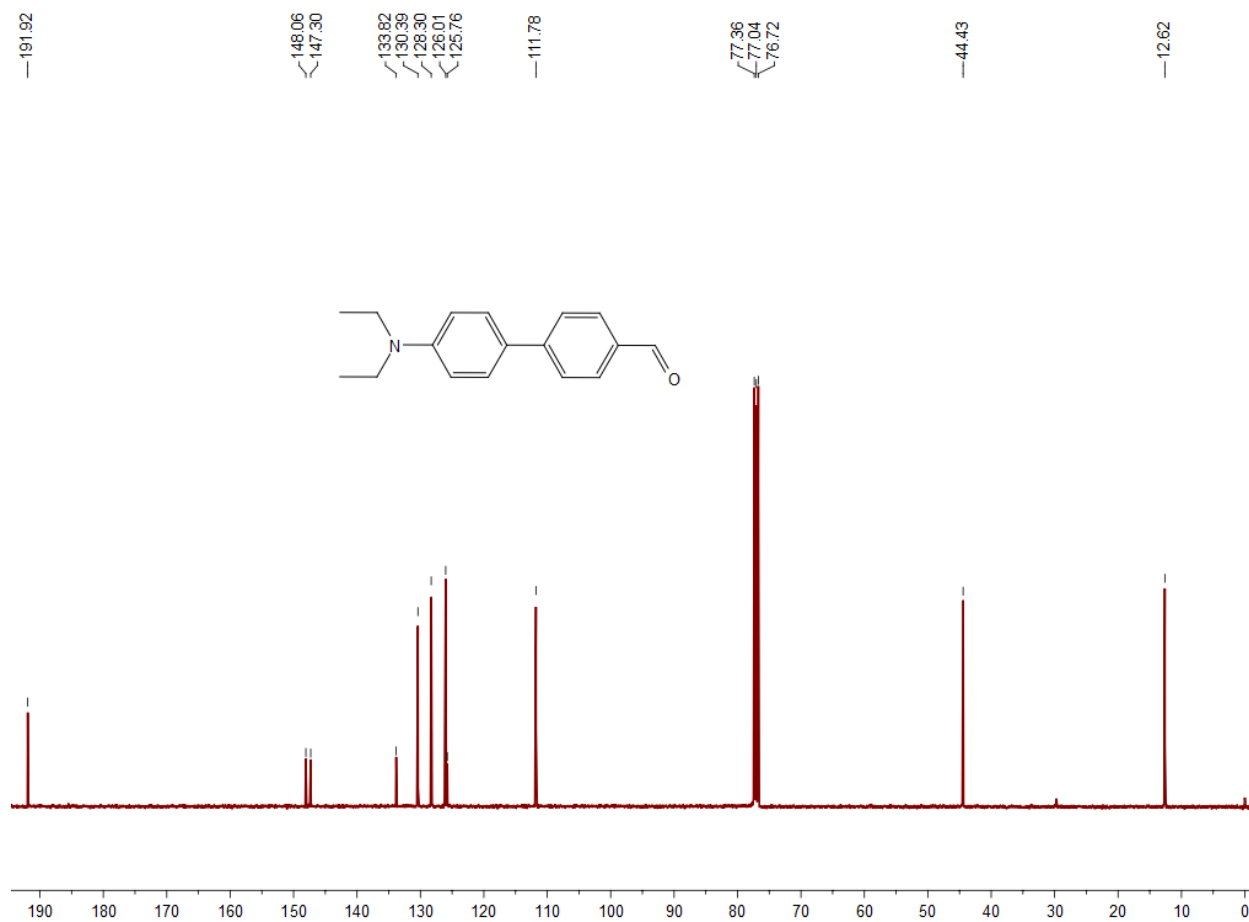
^{13}C NMR spectrum of compound **3j** in CDCl_3



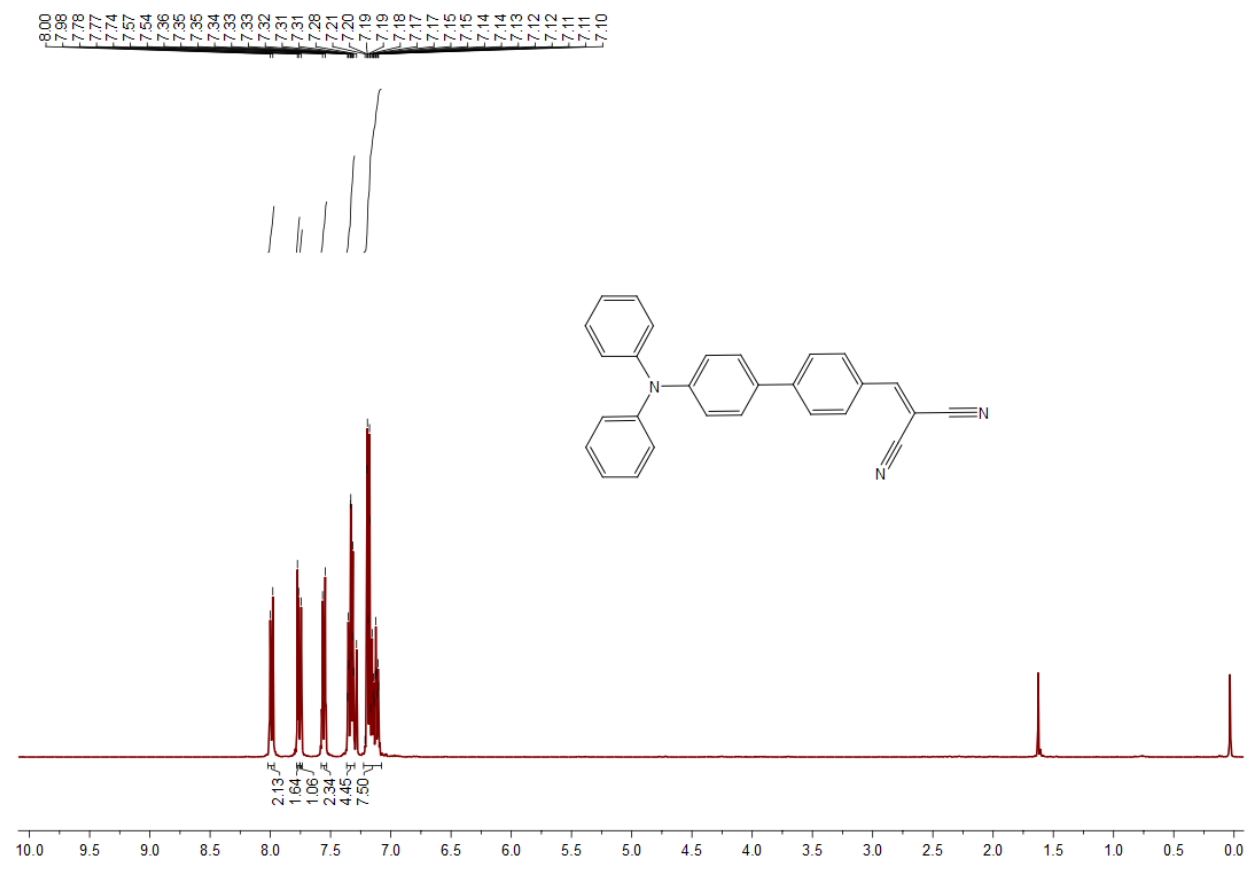
^1H NMR spectrum of compound **3k** in CDCl_3



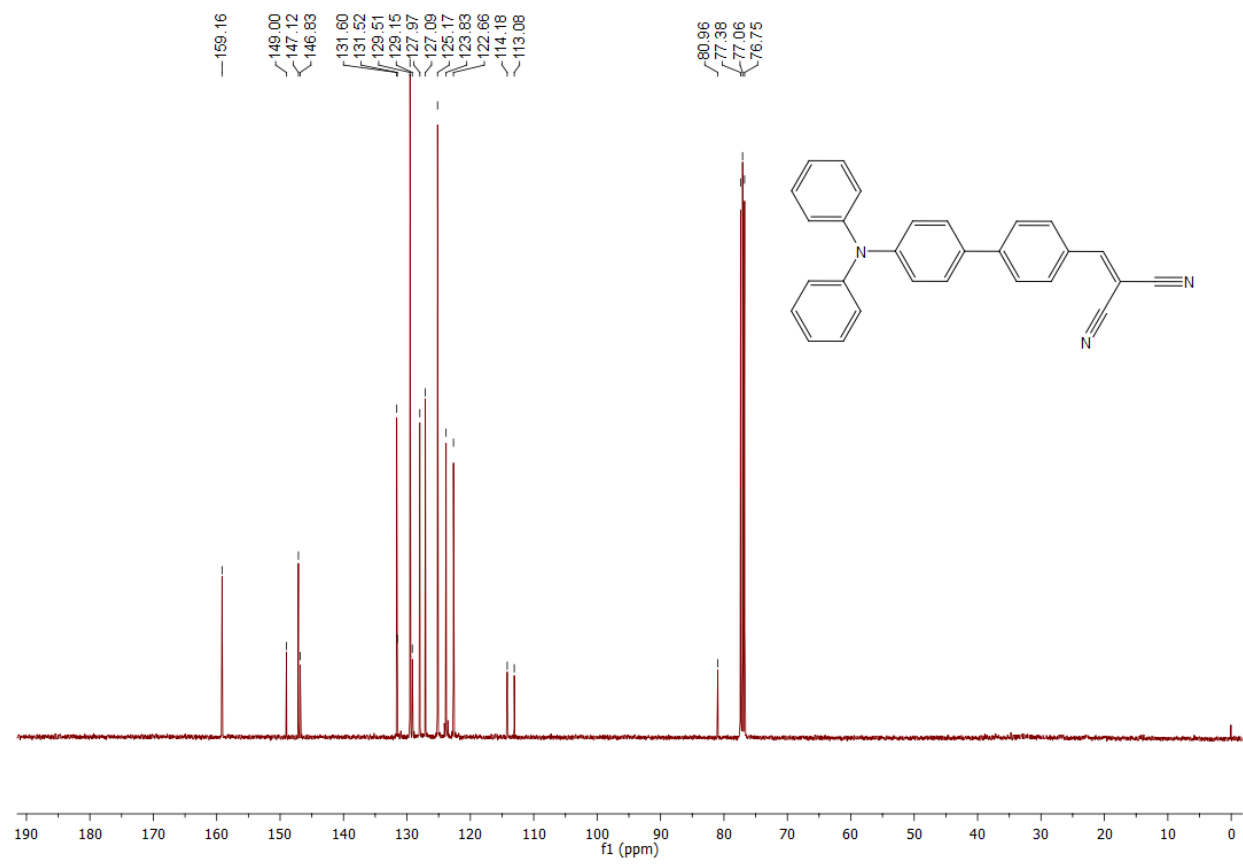
^{13}C NMR spectrum of compound **3j** in CDCl_3



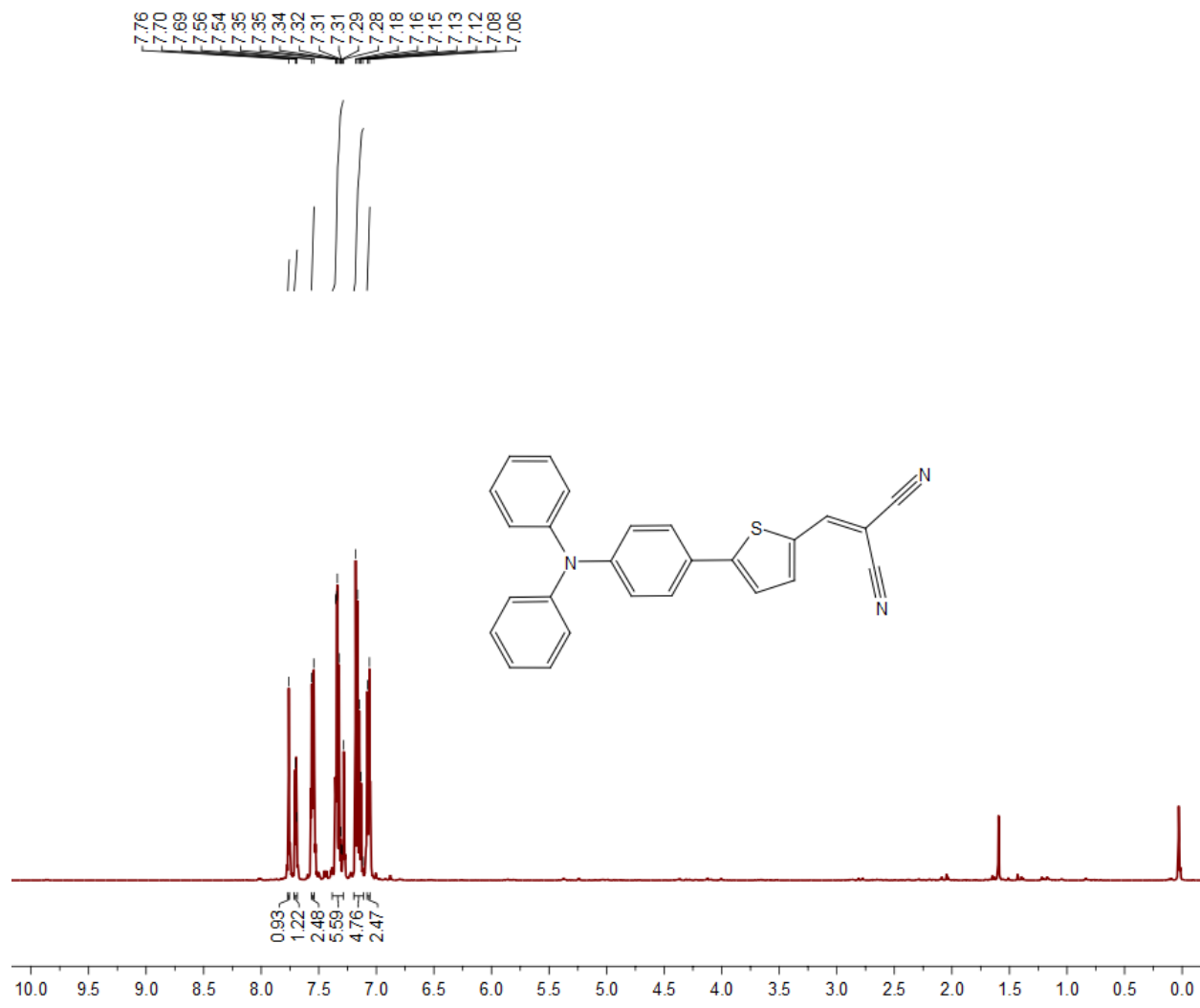
¹H NMR spectrum of compound **6a** in CDCl₃



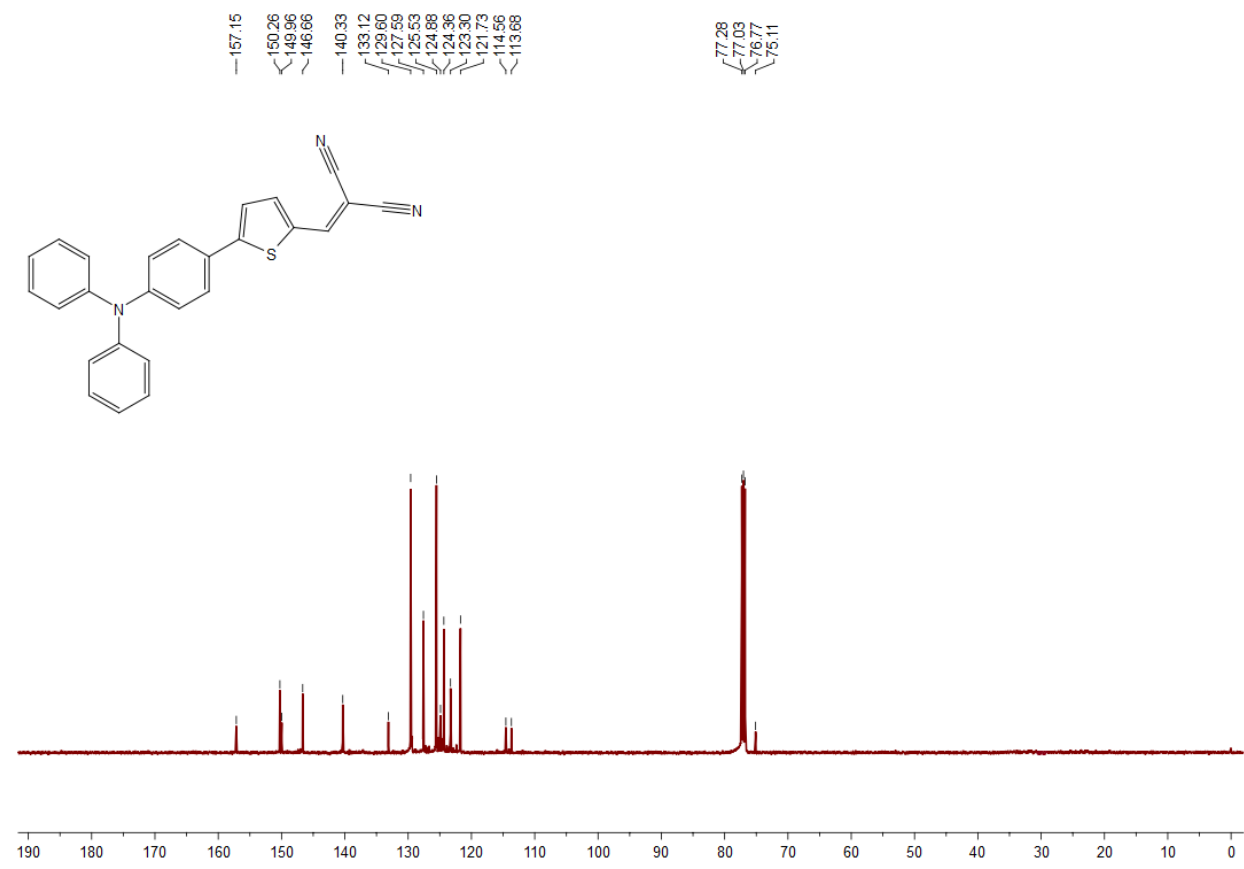
^{13}C NMR spectrum of compound **6a** in CDCl_3



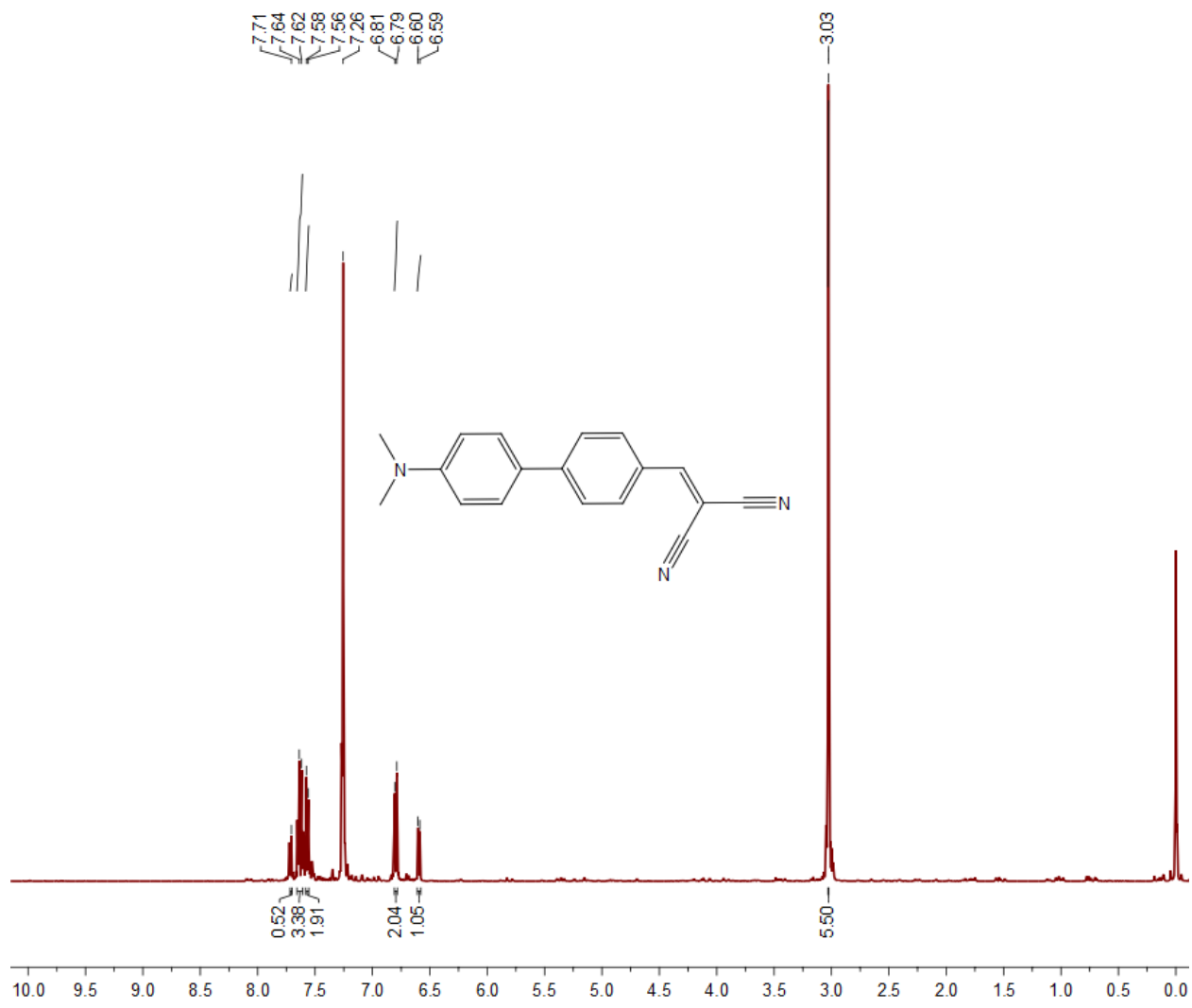
^1H NMR spectrum of compound **6b** in CDCl_3



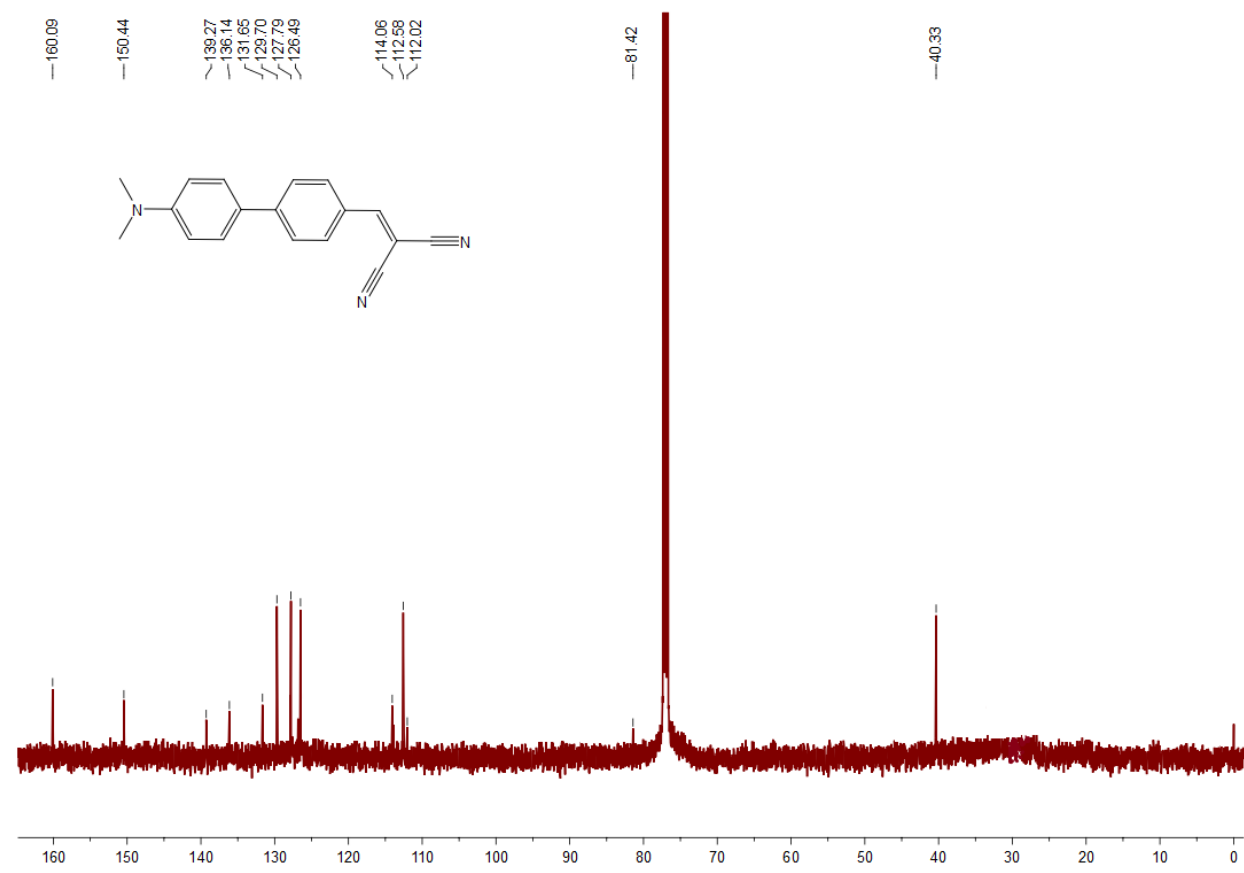
^{13}C NMR spectrum of compound **6b** in CDCl_3



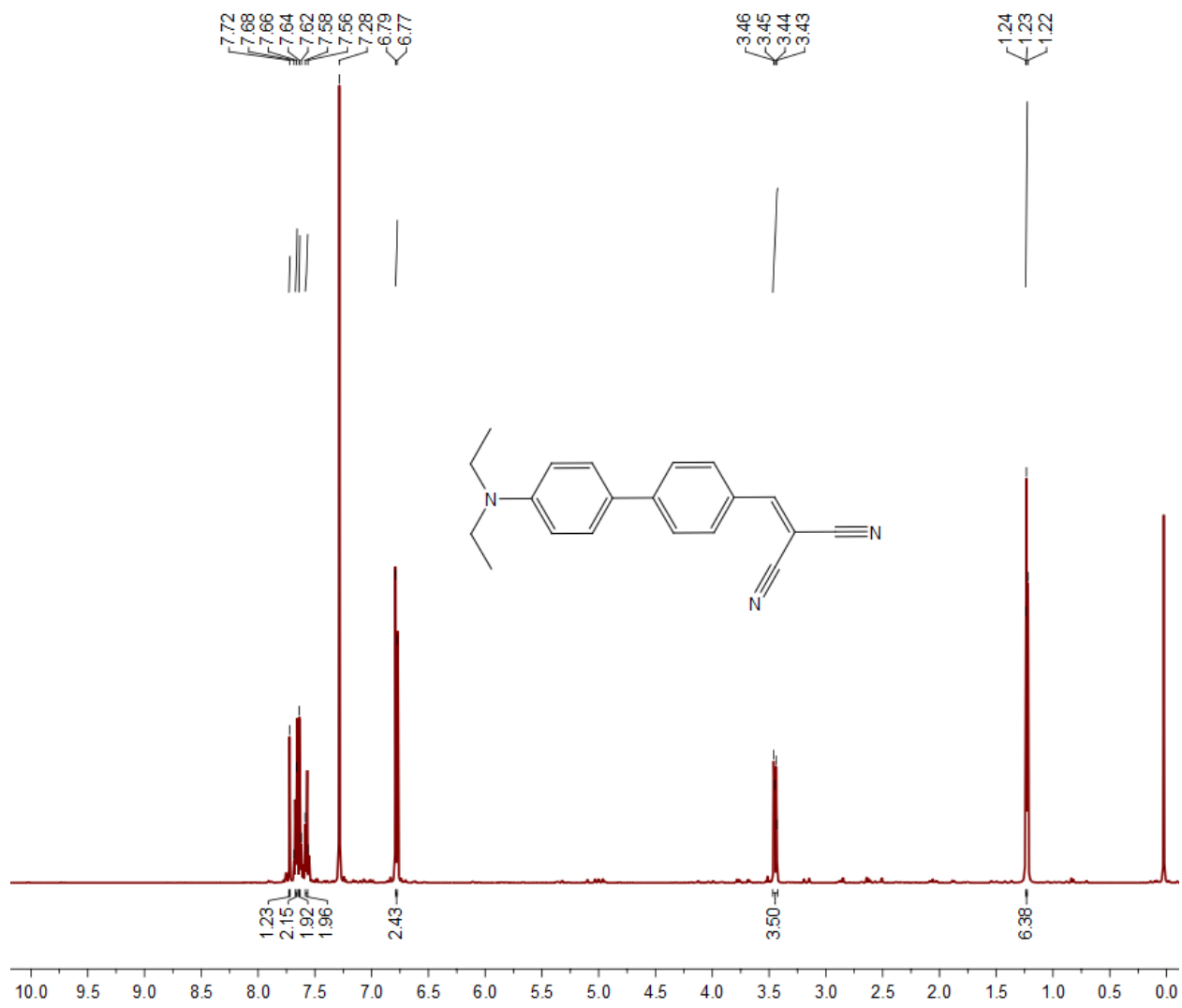
^1H NMR spectrum of compound **6c** in CDCl_3



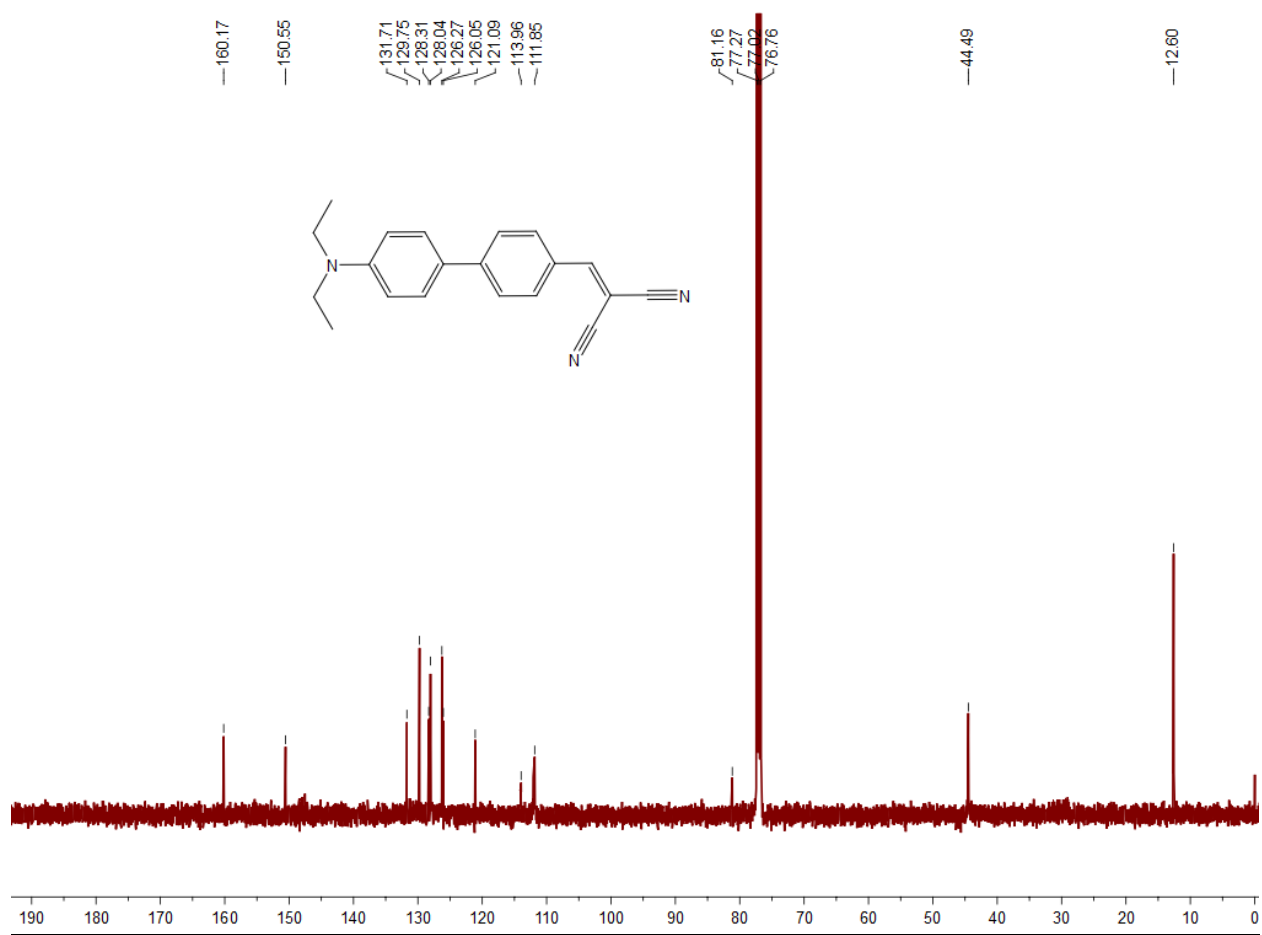
^{13}C NMR spectrum of compound **6c** in CDCl_3



^1H NMR spectrum of compound **6d** in CDCl_3



^{13}C NMR spectrum of compound **6d** in CDCl_3



IV. UV-vis spectra of **6a-6d** as thin film

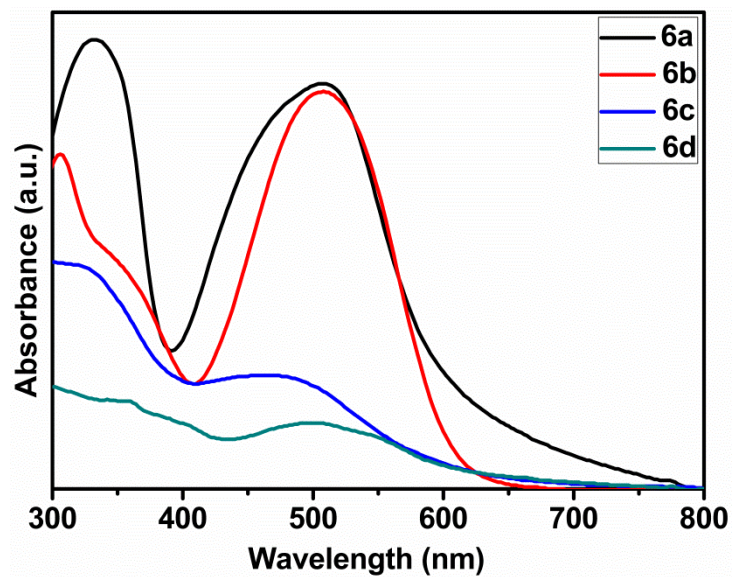


Fig. S1 Thin film UV-vis spectra of **6a-6d** recorded in quartz plate

V. UV-vis spectra of **6a-6d** in different solvents

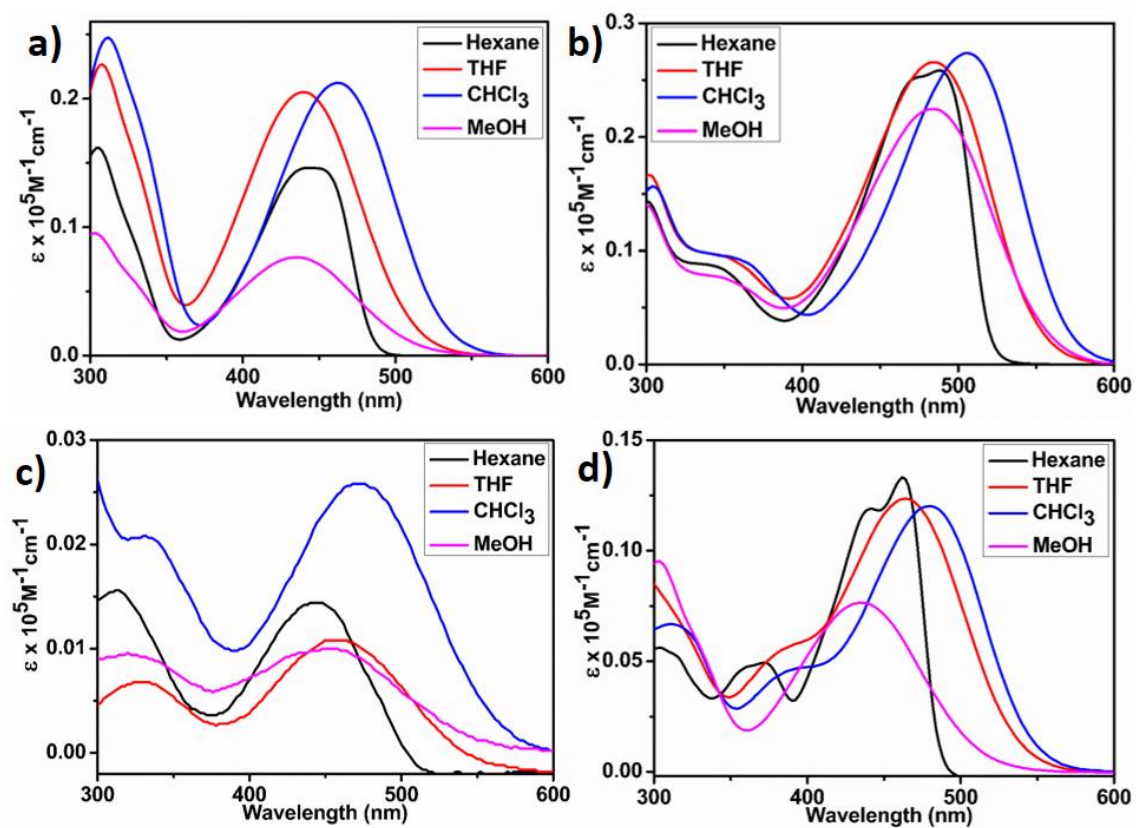


Fig. S2 UV-vis spectra of compound **6a-6d** recorded in different solvents (5×10^{-5} M)

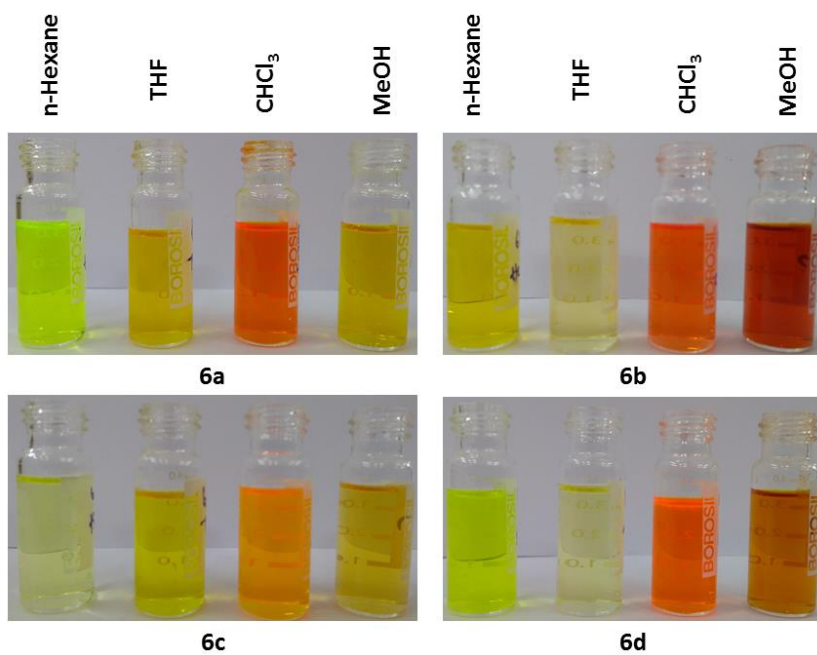


Fig. S3 Solvatochromic behaviour of **6a-6d** in different solvents (5×10^{-5} M)

VI. Photoluminescence spectra of **6a-6d**

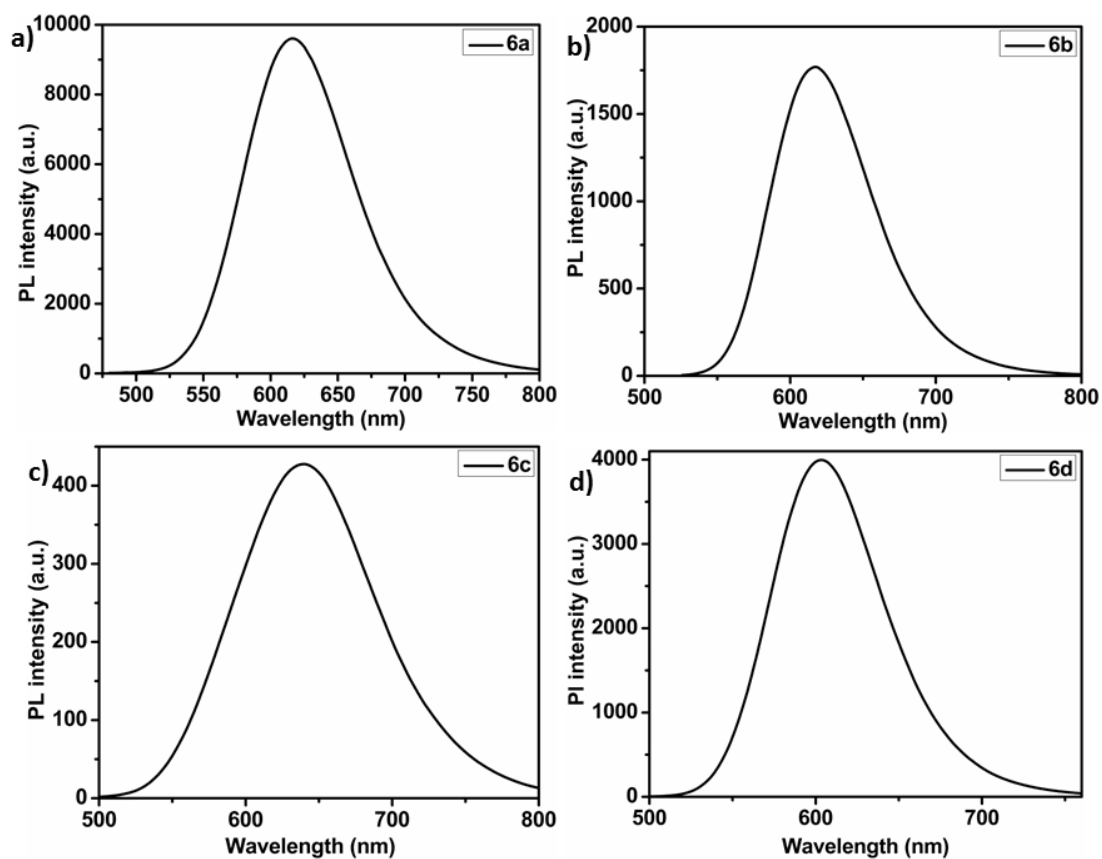


Fig S4 Photoluminescence of **6a-6d** in CHCl_3 (**6a** in 5×10^{-6} M and **6b-6d** in 5×10^{-5} M)

Table S1 Photoluminescence data of **6a-6d**

6a-6d	λ_{em} (nm)	Stokes shift (cm^{-1})
6a	616	64900
6b	622	89300
6c	667	60200
6d	623	80000

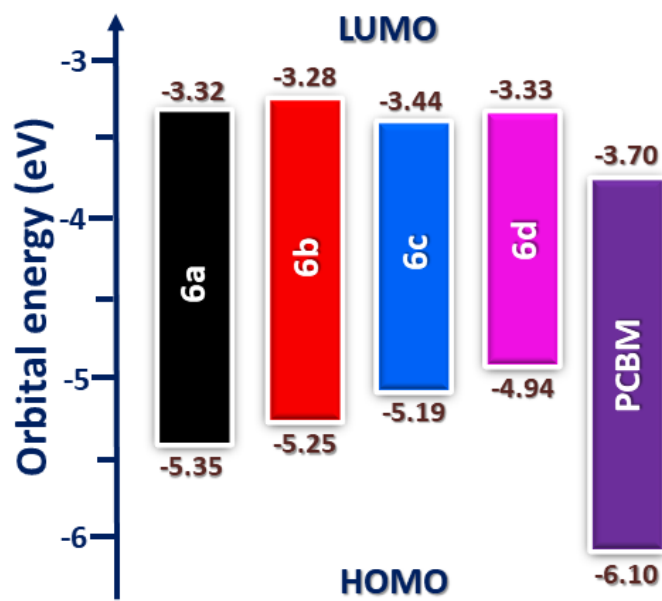


Fig S5 Energy band diagram of **6a-6d** against standard n-type material (PCBM)