

Supporting information

Bis-indolylation of aldehydes and ketones using silica supported FeCl₃: A Molecular docking studies of bisindoles by targeting SARS-CoV-2 main protease binding site

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General Information	S2
General experimental procedure for the synthesis of 1-2	S2
Spectral data of bis-indolyl methane derivatives	S2-S6
N-(4-(di(1H-indol-3-yl)methyl)phenyl)dodecanamide (1t) from 1q	S7
Physical and Spectral Data for Compound 1t	S7
¹ H and ¹³ C NMR Spectra	S8-34
SEM images and EDX spectra of SiO ₂ -FeCl ₃ of different aging	S35
References	S36

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General method

The starting materials indole or substituted indoles, various types of aldehydes (aromatic, aliphatic, heterocyclic etc.), anhydrous ferric chloride and silica gel 230-400 meshes has been purchased either from Sigma Aldrich chemical Co., USA or Across Organics or SRL India and were used as received. All the solvents were distilled prior to use. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature using Bruker Ascend 400 MHz spectrometers (400 MHz for ^1H and 100 MHz for ^{13}C). Chemical shifts were reported in parts per million from the tetramethyl silane internal reference, and coupling constants were reported in Hertz. Proton multiplicities were represented as s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on a Fourier transform infrared (FT-IR, Model: Spectrum 100) spectrometer KBr pellets or in thin films. Surface morphology of the silica gel supported material was estimated by Field Emission Scanning Electron Microscope Model – Sigma 300, Carl Zeiss instrument.

General experimental procedure for the synthesis of 1-2:

A mixture of indoles (2.0 mmol), corresponding aldehydes or ketones (1.0 mmol) and $\text{FeCl}_3\text{-SiO}_2$ (20 mg, 2 mol% FeCl_3) were taken in a cone shaped flask and mix thoroughly using wide thick glass rod or spatula. Then the flask was immersed onto a preheated water bath of temperature 80°C with continuous grinding of the mixture. After completion of the reaction (monitored by TLC), the catalyst was recovered by dissolving the product in a suitable solvent like ethyl acetate or dichloromethane or methanol. The residue (catalyst) was collected, dried under vacuum and recycled. The filtrate containing the product was concentrated by distillation and distillated was collected for recycling purpose. In most cases pure product was crystallized out form the residual filtrate. Only few cases the product was purified by column chromatography (ethyl acetate –hexane). Synthesized products were characterized by melting point, IR data, ^1H NMR, and ^{13}C NMR spectral analysis.

3,3'-(Phenylmethylene)bis(1H-indole) (1a): Yield: 96%; light pink solid, m. p. 148-150°C, lit.¹ m. p. 152°C; FT-IR (KBr) ν_{max} 3420, 3050, 1595, 1510, 1457, 1340 cm⁻¹; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.37 (m, 4H), 7.31 (t, J = 7.6 Hz, 2H), 7.25-7.18 (m, 3H), 7.03 (t, J = 7.6 Hz, 2H), 5.92 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.0, 136.7, 128.7, 128.3, 127.1, 126.2, 123.7, 121.9, 119.9, 119.7, 119.2, 111.1, 40.2.

3, 3'-(4-Methylphenyl)methylene)bis(1H-indole) (1b): Yield: 94%; pink solid, m. p. 96°C, lit.¹ m. p. 97-98°C; FT-IR (KBr) ν_{max} 3421, 1635, 1510, 1454, 1415, 1339 cm⁻¹; ^1H NMR (400 MHz, CDCl_3) δ 7.88 (s, 2H), 7.42 (d, J = 8 Hz, 2H), 7.36 (d, J = 8 Hz, 2H), 7.28-7.25 (m, 2H), 7.19 (t, J = 7.2 Hz, 2H), 7.11 (d, J = 8 Hz, 2H), 7.03 (t, J = 7.6 Hz, 2H), 6.67 (s, 2H), 5.88 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.0, 136.7, 135.5, 128.9, 128.6, 127.1, 123.6, 121.9, 120.0, 119.9, 119.2, 111.0, 39.8, 21.1.

3,3'-(4-Hydroxylphenyl)methylene)bis(1H-indole) (1c): Yield: 95%; light orange solid, m. p. 198°C, lit m. p.² 195-196°C; FT-IR (KBr) ν_{max} 3416, 1617, 1510, 1454, 1415, 1337, 1217, 1166, 1096, 744 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 10.74 (s, 2H), 9.11 (s, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 7.6 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 7.0 (t, J = 7.2 Hz, 2H), 6.82 (t, J = 7.2 Hz, 2H), 6.75 (s, 2H), 6.63 (d, J = 8.4Hz, 2H), 5.68 (s, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ 155.7, 137.0, 135.6, 129.6, 127.1, 123.8, 121.2, 119.6, 119.1, 118.5, 115.2, 111.8, 39.9.

3, 3'-(4-Methoxylphenyl)methylene)bis(1H-indole) 1d: Yield: 94%; off-white solid, m. p. 190°C, lit.² m. p. 190-192°C; FT-IR (KBr) ν_{max} 3412, 1636, 1564, 1509, 1455, 1340, 1250, 1175, 1095, 1028, 744 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 8 Hz, 2H), 7.25 (t, J = 6 Hz, 2H), 7.18 (t, J = 6.8 Hz, 2H), 7.0 (t, J = 6.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 6.63 (q, 2H), 5.84 (s, 1H), 5.29 (s, 1H), 3.78 (s, 3H); ¹³C (100 MHz, CDCl₃) δ 157.9, 136.7, 136.2, 129.6, 127.0, 123.5, 121.9, 120.1, 120.0, 119.2, 113.5, 111.0, 55.2, 39.3.

3,3'-(4-hydroxy 3-methoxyphenyl)methylene)bis(1H-indole) (1e): Yield: 75%; red solid, m. p. 95°C, lit.³ m. p. 99°C; FT-IR (KBr) ν_{max} 3403, 2984, 2891, 2309, 1596, 1507, 1414, 1257, 1036, 739 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 10.76 (s, 2H), 8.70 (s, 1H), 7.33 (d, J = 8 Hz, 2H), 7.28 (d, J = 8 Hz, 2H), 7.02 (t, J = 7.2 Hz, 2H), 6.95 (s, 1H), 6.85 (t, J = 7.2 Hz, 2H), 6.80 (s, 2H), 6.67 (t, J = 8 Hz, 2H), 5.71 (s., 1H), 3.66 (s, 3H) ¹³C NMR (100 MHz, DMSO-d₆) d 147.6, 144.9, 137.0, 136.4, 127.1, 123.8, 121.2, 120.9, 119.6, 119.1, 118.5, 115.5, 113.3, 111.8, 56.0.

3,3'-(3,4-dihydroxylphenyl)methylene)bis(1H-indole) (1f)

Yield: 95%; red solid, m. p. 202-203°C, lit.⁴ m. p. 204-206°C; FT-IR (KBr) ν_{max} 3772, 3621, 2309, 1596, 1510, 1338, 1267, 1097, 741 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 10.76 (s, 2H), 8.66 (s, 1H), 8.58 (s, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8 Hz, 2H), 7.03 (t, J = 7.2 Hz, 2H), 6.86 (t, J = 7.2 Hz, 2H), 6.78 (s, 2H), 6.71 (s, 1H), 6.62 (s, 2H), 5.64 (s, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ 145.1, 143.6, 137.0, 136.4, 127.2, 123.8, 121.2, 119.7, 119.5, 119.1, 118.5, 116.2, 115.5, 111.8, 39.4

3,3'-(4-N,N-dimethylbenzenamine)bis(1H-indole) (1g): Yield: 75%, colourless solid, m. p. 208°C, lit.² m. p. 210-212°C; FT-IR (KBr) ν_{max} 3421, 3026, 1610, 1437, 1328, 1099 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 10.77 (s, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.03 (t, J = 7.2 Hz, 2H), 6.85 (t, J = 7.6 Hz, 2H), 6.79 (s, 2H), 6.62 (d, J = 8.8 Hz, 2H), 5.70 (s, 1H), 2.83 (s, 6H); ¹³C NMR (100 MHz, DMSO-d₆) δ 149.1, 137.0, 133.2, 129.2, 127.1, 123.8, 121.2, 119.7, 119.2, 118.4, 112.7, 111.8, 40.8, 39.2.

3,3'-(phenylmethylene)bis(2-methyl-1H-indole) (1h): Yield: 93%, pinkish solid, m. p. 255°C, lit.⁵ m. p. 257-258°C; FT-IR (KBr) ν_{max} 2929, 1597, 1487, 1460, 1426, 1341, 1298, 1221, 1132, 1010 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 10.72 (s, 2H), 7.24-7.15 (m, 7H), 6.85 (t, J = 6.8 Hz, 2H), 6.77 (d, J = 8.0 Hz, 2H), 6.64 (t, J = 8.0 Hz, 2H), 5.89 (s, 1H), 2.04 (s, 6H); ¹³C NMR (100 MHz, DMSO-d₆) δ 144.7, 135.5, 132.4, 129.1, 128.7, 128.3, 126.2, 119.9, 118.9, 118.3, 112.6, 110.7, 39.9, 12.4.

3,3'-(phenylmethylene)bis(5-bromo-1H-indole) (1i): Yield: 99%; orange solid, m. p. 252°C, lit.⁶ m. p. 253-255°C; FT-IR (KBr) ν_{max} 1598, 1559, 1455, 1415, 1333, 1216 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 11.09 (s, 2H), 7.44 (s, 2H), 7.35-7.27 (m, 6H), 7.20 (d, J = 7.2 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 6.89 (s, 2H), 5.86 (s, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ 144.7, 135.7, 128.8, 128.7, 128.6, 126.5, 125.6, 123.9, 121.6, 118.1, 114.0, 111.3, 39.7.

3,3'-(phenylmethylene)bis(N-methyl-1H-indole) (1j): Yield: 94%, red solid, m. p. 200°C, lit.⁵ m. p. 200-201°C; FT-IR (KBr) ν_{max} 2933, 1615, 1549, 1474, 1424, 1367, 1328, 1228, 1200, 1152, 1120 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.34 (m, 4H), 7.28 (t, J = 8.4 Hz, 4H), 7.20 (t, J = 7.6 Hz, 3H), 7.00 (t, J = 8.0 Hz, 2H), 6.53 (s, 2H), 5.88 (s, 1H), 3.68 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 144.4, 137.4, 128.7, 128.2, 128.2, 127.4, 126.0, 121.4, 120.0, 118.6, 118.2, 109.0, 40.1, 32.7.

3,3'-(phenylmethylene)bis(5-nitro-1H-indole) (1k): Yield: 70%; pale yellow solid, m. p. >250°C, lit.⁶ m. p. >300°C; FT-IR (KBr) ν_{max} 3368, 1622, 1580, 1514, 1470, 1424, 1378, 1325, 1239, 1090 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 11.69 (s, 2H), 8.33 (s, 2H), 7.99-7.96 (dd, J = 8.8, 1.6 Hz, 2H), 7.55 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 7.22 (t, J = 7.2 Hz, 2H), 7.14 (s, 2H), 6.21 (s, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ 144.2, 140.6, 140.2, 128.9, 128.7, 128.1, 126.8, 126.2, 121.0, 117.1, 116.7, 112.6, 38.9.

3,3'-(pyridin-2-ylmethylene)bis(1H-indole) (1l): Yield: 84%, white solid, m. p. 226-228°C, lit.⁶ m. p. 232-235°C; FT-IR (KBr) ν_{max} 3450, 3144, 2922, 1588, 1567, 1470, 1456, 1436, 1340, 1214, 1090 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 10.86 (s, 2H), 8.50 (s, 1H), 7.67 (t, J = 6.0 Hz, 1H), 7.39-7.30 (m, 5H), 7.19 (t, J = 5.2 Hz, 1H), 7.03 (t, J = 7.2 Hz, 2H), 6.94 (s, 2H), 6.87 (t, J = 7.2 Hz, 2H), 5.92 (s, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ 164.4, 149.1, 136.8, 130.0, 127.1, 124.0, 122.9, 121.7, 121.3, 119.4, 118.7, 117.3, 111.9, 43.0.

3,3'-(pyridin-3-ylmethylene)bis(1H-indole) (1m): Yield: 89%; white solid, m. p. 142°C, lit.⁶ m. p. 145-147°C; FT-IR (KBr) ν_{max} 3405, 2920, 2853, 1671, 1580, 1456, 1420, 1337, 1218, 1103 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 10.90 (s, 2H), 8.62 (s, 1H), 8.40 (s, 1H), 7.70 (d, J = 8 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8 Hz, 3H), 7.05 (t, J = 7.6 Hz, 2H), 6.87 (t, J = 8.0 Hz, 4H), 5.91 (s, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ 150.0, 147.5, 137.0, 136.1, 126.8, 124.1, 121.5, 119.4, 118.7, 117.5, 112.0, 37.5.

Tri(1H-indol-3-yl)methane (1n): Yield: 93%; yellow solid, m. p. 248°C, lit.⁷ m. p. 244-245°C; FT-IR (KBr) ν_{max} 3258, 3052, 2923, 2588, 1618, 1485, 1456, 1337, 1216, 1093, 1003 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 10.74 (s, 3H), 7.41 (d, *J* = 6.8 Hz, 3H), 7.34 (d, *J* = 7.2 Hz, 3H), 7.02-6.86 (m, 9H), 6.07 (s, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ 137.0, 127.2, 123.6, 121.0, 119.7, 118.7, 118.3, 111.8, 31.3.

3, 3'-(2-chlorophenyl)methylenebis(1H-indole) (1o): Yield: 96%; white solid, m. p. 72°C, lit.⁸ m. p. 71-73°C; FT-IR (KBr) ν_{max} 3414, 1628, 1458, 1417, 1338, 1094 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 2H), 7.45 (t, *J* = 8.0 Hz, 3H), 7.36 (d, *J* = 8 Hz, 2H), 7.28-7.17 (m, 4H), 7.15-7.05 (m, 3H), 6.59 (s, 2H), 6.38 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 141.3, 136.7, 133.9, 130.3, 129.5, 127.5, 127.0, 126.7, 123.8, 122.0, 119.8, 119.3, 118.3, 111.1, 36.6.

3,3'-(4-chlorophenyl)methylenebis(1H-indole) (1p): Yield: 92%; brown solid, m. p. 78°C, lit.⁷ m. p. 75-76°C; FT-IR (KBr) ν_{max} 3417, 1638, 1486, 1455, 1416, 1337, 1092 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 2H), 7.40 (d, *J* = 4.4 Hz, 2H), 7.37 (d, *J* = 4.4 Hz, 2H), 7.30-7.25 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.65 (s, 2H), 5.89 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 142.5, 136.6, 131.7, 130.1, 128.3, 126.8, 123.6, 122.1, 119.8, 119.3, 119.1, 111.1, 39.6.

3, 3'-(4-nitrophenyl)methylenebis(1H-indole) (1q): Yield: 98%; yellow solid, m. p. 220°C, lit.² m. p. 219-220°C; FT-IR (KBr) ν_{max} 3455, 1638, 1506, 1456, 1415, 1341, 1100 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 10.93 (s, 2H), 8.13 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.86 (t, *J* = 8.0 Hz, 4H), 6.01 (s, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ 153.6, 146.2, 137.0, 129.9, 126.8, 124.3, 123.9, 121.5, 119.4, 118.9, 117.1, 112.0, 40.6.

3,3'-(4-(octadecyloxy)phenyl)bis(1H-indole) (1r): Yield: 93%; light orange solid, m. p. 98-100°C; FT-IR (KBr) ν_{max} 3410, 2978, 2310, 1594, 1511, 1391, 1236, 1059, 740 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.28-7.25 (m, 2H), 7.19 (t, *J* = 6.8 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.66 (s, 2H), 5.86 (s, 1H), 3.94 (t, *J* = 6.4 Hz, 2H), 1.78-1.76 (m, 2H), 1.28 (s, 30H), 0.91 (t, *J* = 6.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 157.5, 136.7, 136.0, 129.6, 127.1, 123.5, 121.9, 120.1, 120.0, 19.2, 114.1, 111.0, 68.0, 39.3, 31.9, 29.7, 29.6, 29.5, 29.4, 26.1, 22.7, 14.2. HRMS calcd. for C₄₁H₅₄N₂O 590.4236 found 591.4314 (M+H⁺)

1,4-bis (di(1H-indol-3-yl)methyl)benzene (1s): Yield: 95%; white solid, m. p. 250°C, lit.⁹ m. p. 246-248°C; FT-IR (KBr) ν_{max} 3408, 3052, 1615, 1456, 1418, 1338, 1215, 1092, 1010, 738 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.45 (s, 4H), 7.41 (d, *J* = 7.6 Hz, 4H), 7.29 (s, 2H), 7.28 (s, 2H), 7.24 (s, 4H), 7.17 (t, *J* = 7.6 Hz, 4H), 7.03 (t, *J* = 8 Hz, 4H), 6.33 (s, 4H), 5.79 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 141.5, 136.6, 128.5, 127.0, 123.6, 121.7, 119.9, 119.6, 118.9, 111.1, 39.9.

3,3'-(methyl methylene)bis(1H-indole) (vibrindole A) (1u): Yield: 95%, colourless solid, m. p. 145°C, lit.¹⁰ m. p. 150°C; FT-IR (KBr) ν_{max} 2958, 2866, 2836, 1624, 1548, 1454, 1337, 1220, 1124, 1095, 1013 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (bs, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 2H), 6.93 (s, 2H), 4.71 (q, *J* = 7.2 Hz, 1H), 1.84 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 136.6, 126.9, 121.8, 121.6, 121.2, 119.7, 119.0, 111.1, 28.2, 21.8.

3,3'-(propylmethylen)bis(1H-indole) (1v): Yield: 95%, colourless solid, m. p. 148°C; lit.¹¹ m. p. 150-152°C; FT-IR (KBr) ν_{max} 2954, 2857, 1617, 1521, 1480, 1455.68, 1337, 1219, 1151, 1093, 1010 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (s, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 2H), 6.98 (s, 2H), 4.52-4.46 (m, 1H), 2.24-2.13 (m, 2H), 1.49-1.34 (m, 2H), 1.47-1.34 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 136.6, 127.2, 121.7, 121.4, 120.6, 119.7, 119.0, 111.0, 38.1, 33.7, 21.4, 14.3.

3-(1, 2, 2-tri(1H-indol-3-yl)ethyl)-1H-indole (1w): Yield: 41% (along with 40% of **1n**), white solid, m. p. >250°C; FT-IR (KBr) ν_{max} 3249, 3050, 2923, 1618, 1480, 1456, 1345, 1216, 1090 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 10.47 (s, 4H), 7.82 (d, *J* = 7.6 Hz, 4H), 7.34 (s, 4H), 7.11 (d, *J* = 7.6 Hz, 4H), 6.90-6.83 (m, 8H), 5.77 (s, 2H); ¹³C NMR (100MHz, DMSO-d₆) δ 136.2, 127.4, 122.8, 120.5, 119.7, 119.5, 118.1, 111.4, 38.1; HRMS calcd for C₃₄H₂₆N₄ 490.2157 found 492.2246 (M+2H⁺).

3-(2-(1H-indol-3-yl)propan-2-yl)-1H-indole (2a): Yield: 88%; white solid, m. p. 155°C, lit.^{3, 11} m. p. 160°C; FT-IR (KBr) ν_{max} 3399, 2200, 1452, 1097, 1010, 739 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.13 – 7.08 (m, 4H), 6.92 (t, *J* = 7.6 Hz, 2H), 1.95 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 137.1, 126.3, 125.5, 121.4, 121.3, 120.5, 118.7, 111.1, 34.9, 30.0.

3-(2-(1H-indol-3-yl)butan-2-yl)-1H-indole (2b): Yield: 94%; colourless solid, m. p. 62°C; lit.¹² sticky solid, FT-IR (KBr) ν_{max} 2922, 1626, 1540, 1451, 735 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (s, 2H), 7.37 (d, *J* = 8 Hz, 2H), 7.33 (d, *J* = 8 Hz, 2H), 7.11 – 7.05 (m, 4H), 6.86 (t, *J* = 7.6 Hz, 2H), 2.43 (q, *J* = 7.2 Hz, 1H), 1.83 (s, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 137.0, 126.5, 124.2, 121.3, 121.2, 121.2, 118.6, 110.9, 38.7, 32.7, 26.2, 9.1

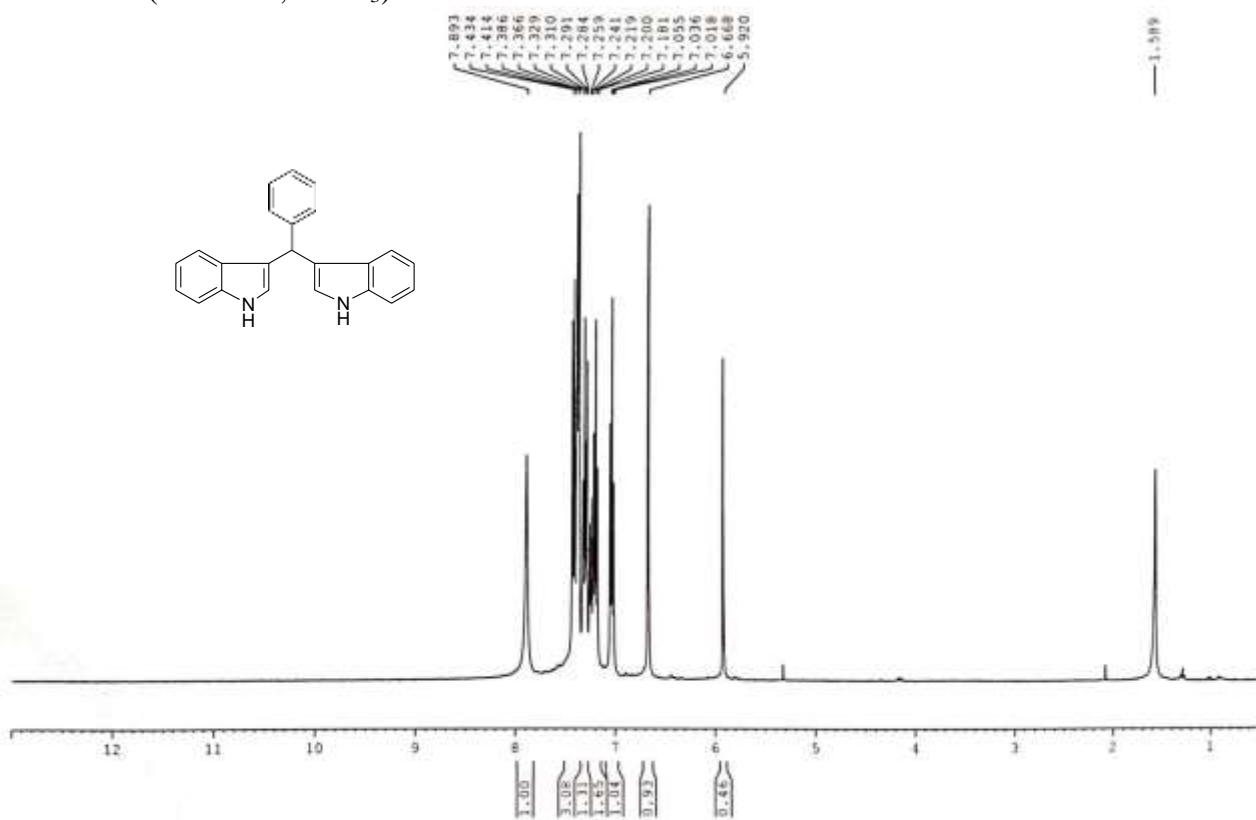
3-(1-(1H-indol-3-yl)-1-phenylethyl)-1H-indole (2c): Yield: 94%; white solid, m. p. 184°C, lit.¹³ m. p. 187-189°C; FT-IR (KBr) ν_{max} 3402, 2308, 1450, 1096, 1006, 740 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (s, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 4H), 7.30 – 7.15 (m, 5H), 6.97 (t, *J* = 8.0 Hz, 2H), 6.63 (s, 2H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 148.0, 137.1, 128.1, 127.8, 126.5, 125.8, 124.7, 123.4, 122.1, 121.5, 118.9, 111.2, 43.7, 28.8

3-(1-(1H-indol-3-yl)cyclohexyl)-1H-indole (2d): Yield: 92 %; white solid, m. p. 120°C; lit.¹³ 118-120°C; FT-IR (KBr) ν_{max} 3166, 2977, 2309, 1699, 1533, 1411, 1057, 738 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8 Hz, 2H), 7.09 (t, *J* = 8.8 Hz, 4H), 6.92 (t, *J* = 7.6 Hz, 2H), 2.57 (d, *J* = 6 Hz, 4H), 1.69-1.62 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 137.0, 126.3, 123.7, 122.0, 121.5, 121.2, 118.5, 111.1, 39.5, 36.8, 26.8, 23.0.

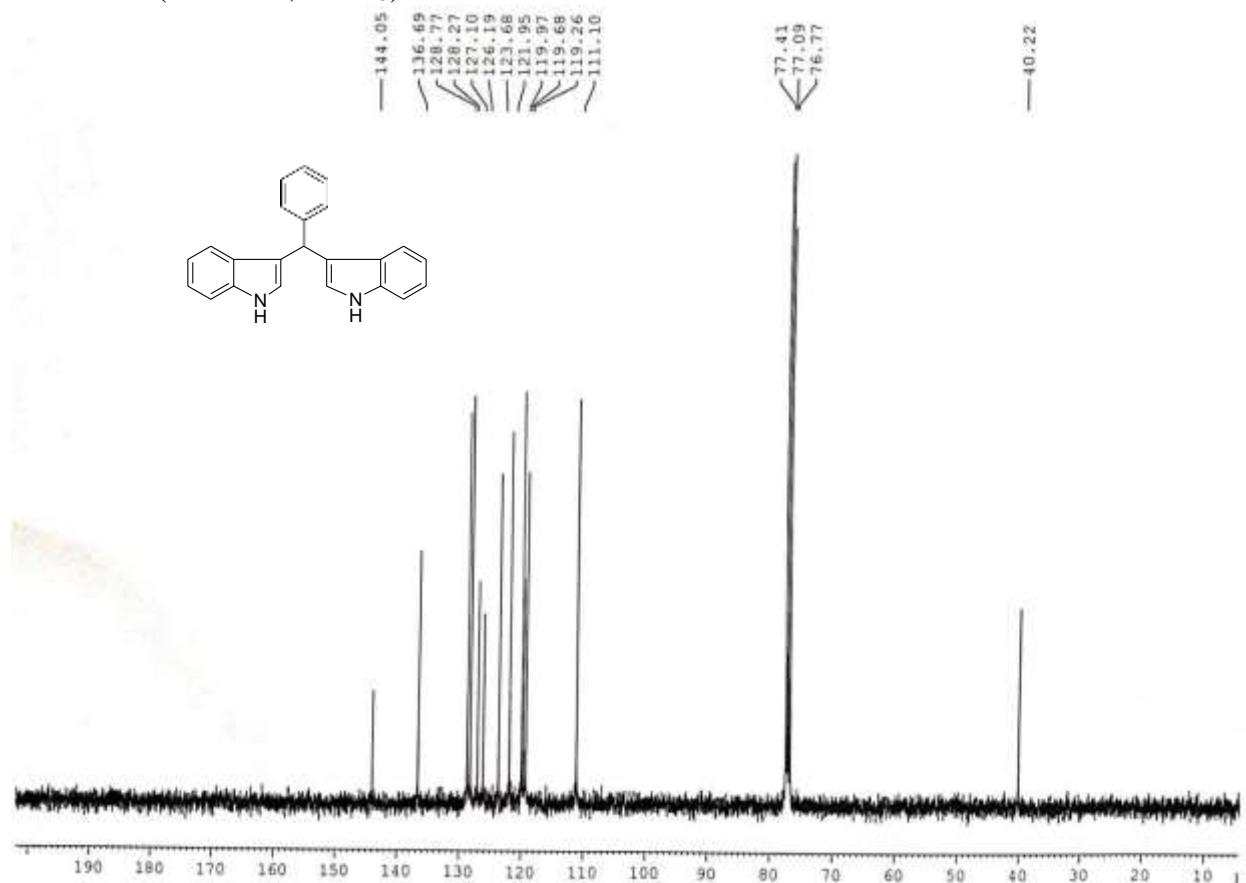
Experimental procedure for the synthesis of 1t from 1q: A mixture of **1q** (367 mg, 1mmol), Pd-C (10%, 40 mg) and hydrazine hydrate (1.5 mmol) in ethanol (10 mL) was reflux for 2 hrs. After cooling the mixture was filtered off, residue was washed with ethyl acetate (2x10 mL). The combined filtrate was evaporated under reduced pressure and the residue was used for next step without purification. To the stirred solution of the residue in dichloromethane (5 mL), triethyl amine (500μL) and lauroyl chloride (270 mg, 1.2 mmol) were added successively and stirred for 4hrs at room temperature. After completion of the reaction (TLC), water (10 mL) was added and extracted with dichloromethane (3x 10 mL), dried over anhydrous Na₂SO₄ and evaporated to residue. The purification of the crude product by column chromatography (1:1, ethyl acetate-hexane) afforded the title compound **1t**.

N-(4-(di(1H-indol-3-yl)methyl)phenyl)dodecanamide (1t): Yield: 49% (two steps); pinkish solid, m. p. 110-112°C; FT-IR (KBr) ν_{max} 3396, 2921, 1661, 1597, 1521, 1458, 1409, 1092 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 2H), 7.39 (d, *J* = 7.6 Hz, 4H), 7.34 (d, *J* = 8 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.16 (s, 1H), 7.01 (t, *J* = 7.6 Hz, 2H), 6.55 (s, 2H), 5.84 (s, 1H), 2.39-2.33 (m, 2H), 1.74-1.66 (m, 2H), 1.28 (bs, 16H), 0.90 (t, *J* = 5.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 140.1, 136.7, 135.9, 129.2, 127.0, 123.7, 121.9, 120.0, 119.9, 119.5, 119.2, 111.1, 39.6, 37.8, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 25.7, 24.8, 22.7, 14.1; HRMS calcd for C₃₅H₄₁N₃O 519.3250 found 520.3395 (M+H⁺)

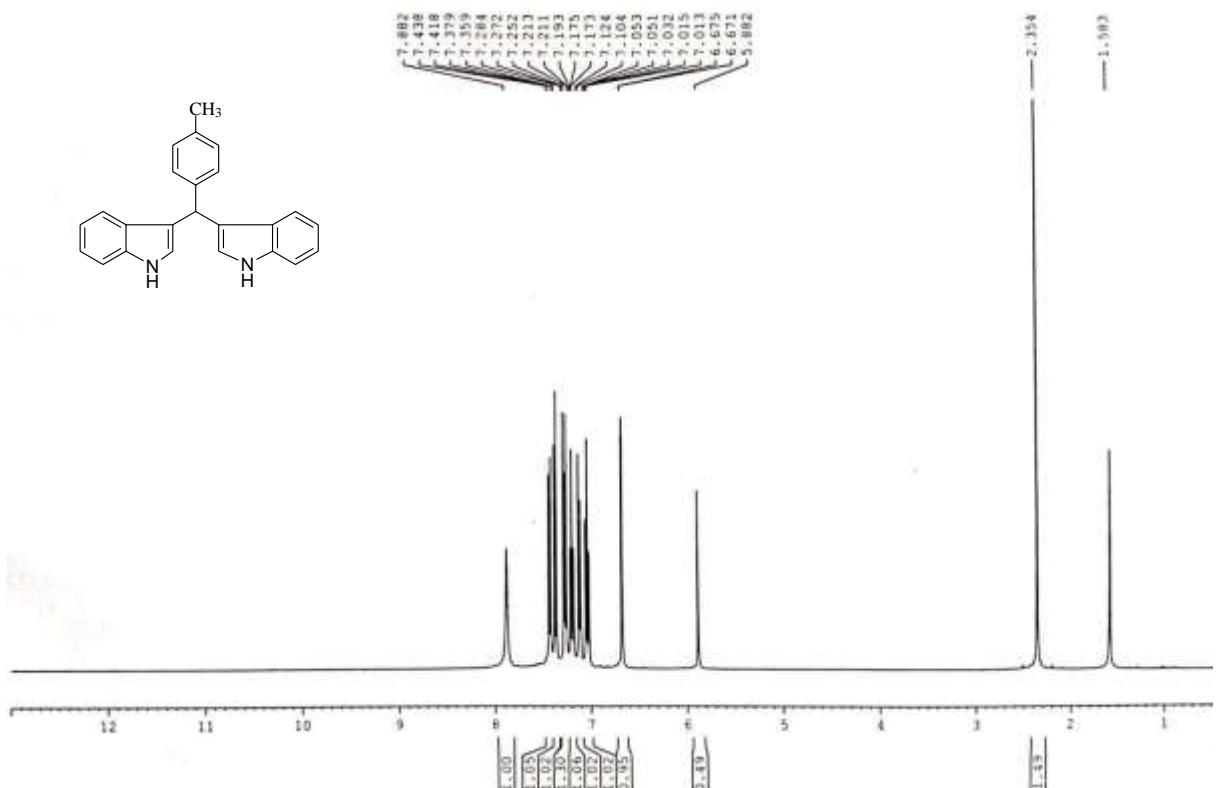
¹H NMR of **1a** (400 MHz, CDCl₃)



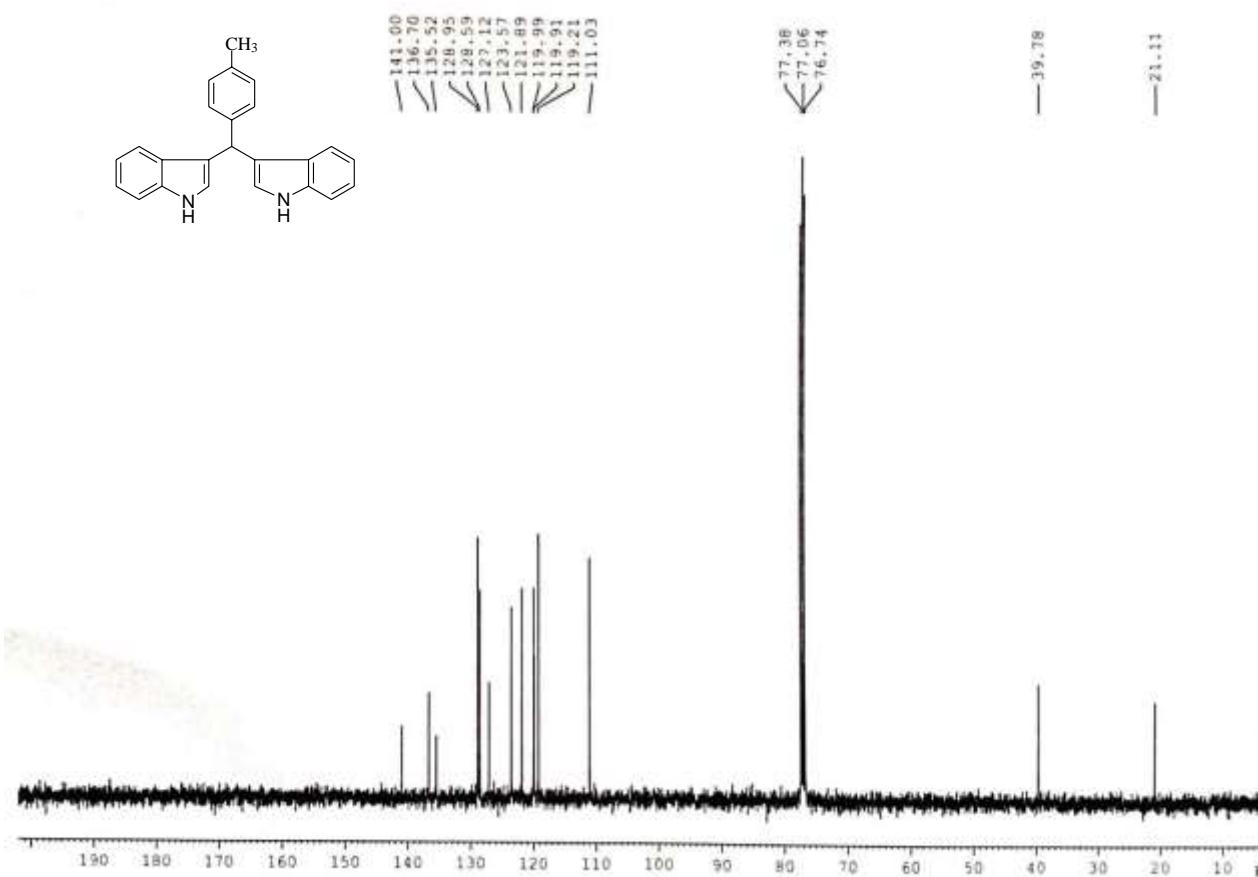
¹³C NMR of **1a** (100 MHz, CDCl₃)



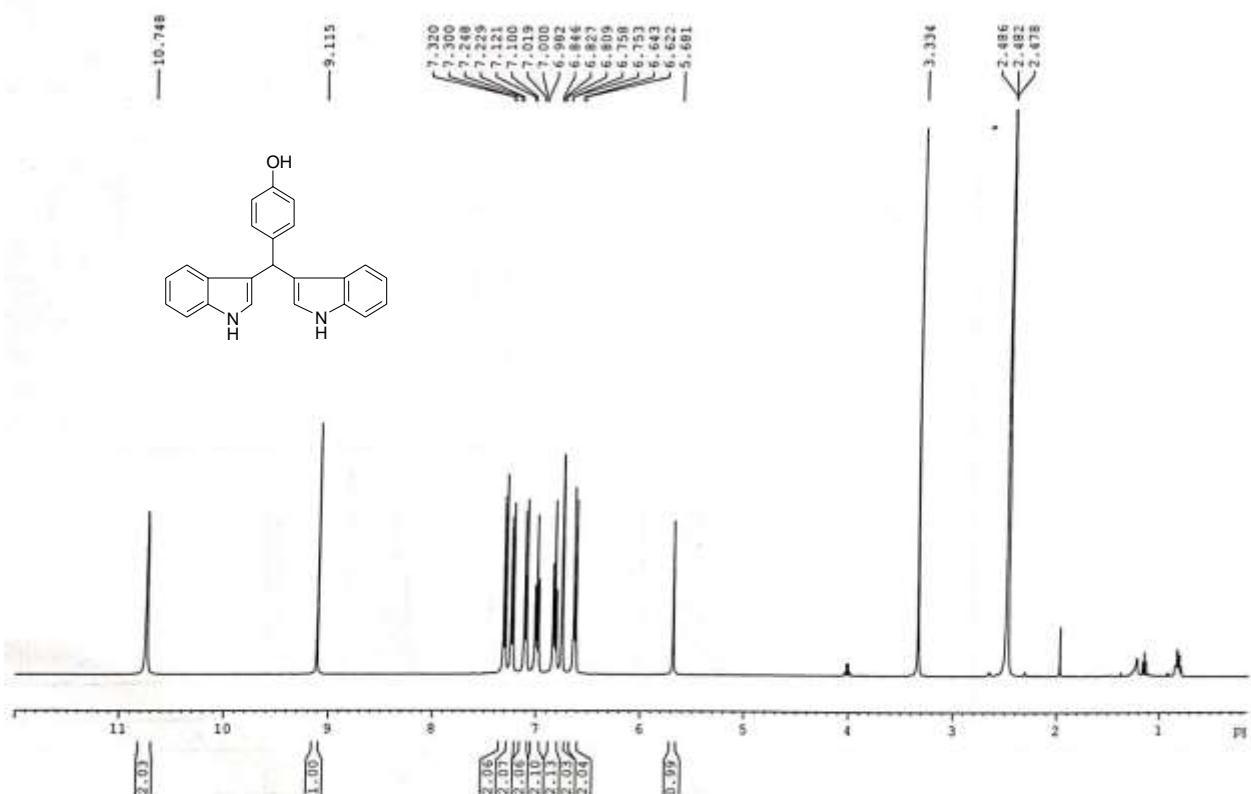
¹H NMR of **1b** (400 MHz, CDCl₃)



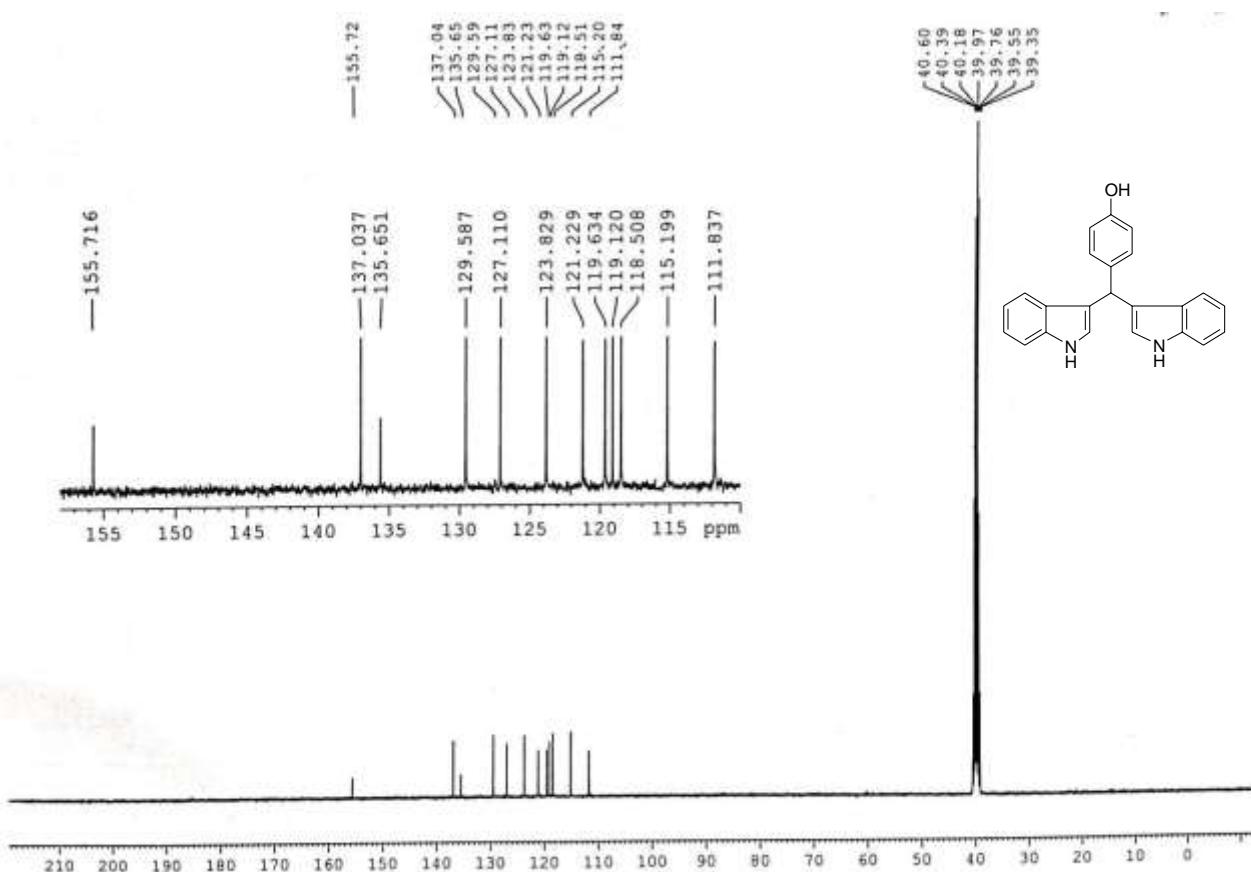
¹³C NMR of **1b** (100 MHz, CDCl₃)



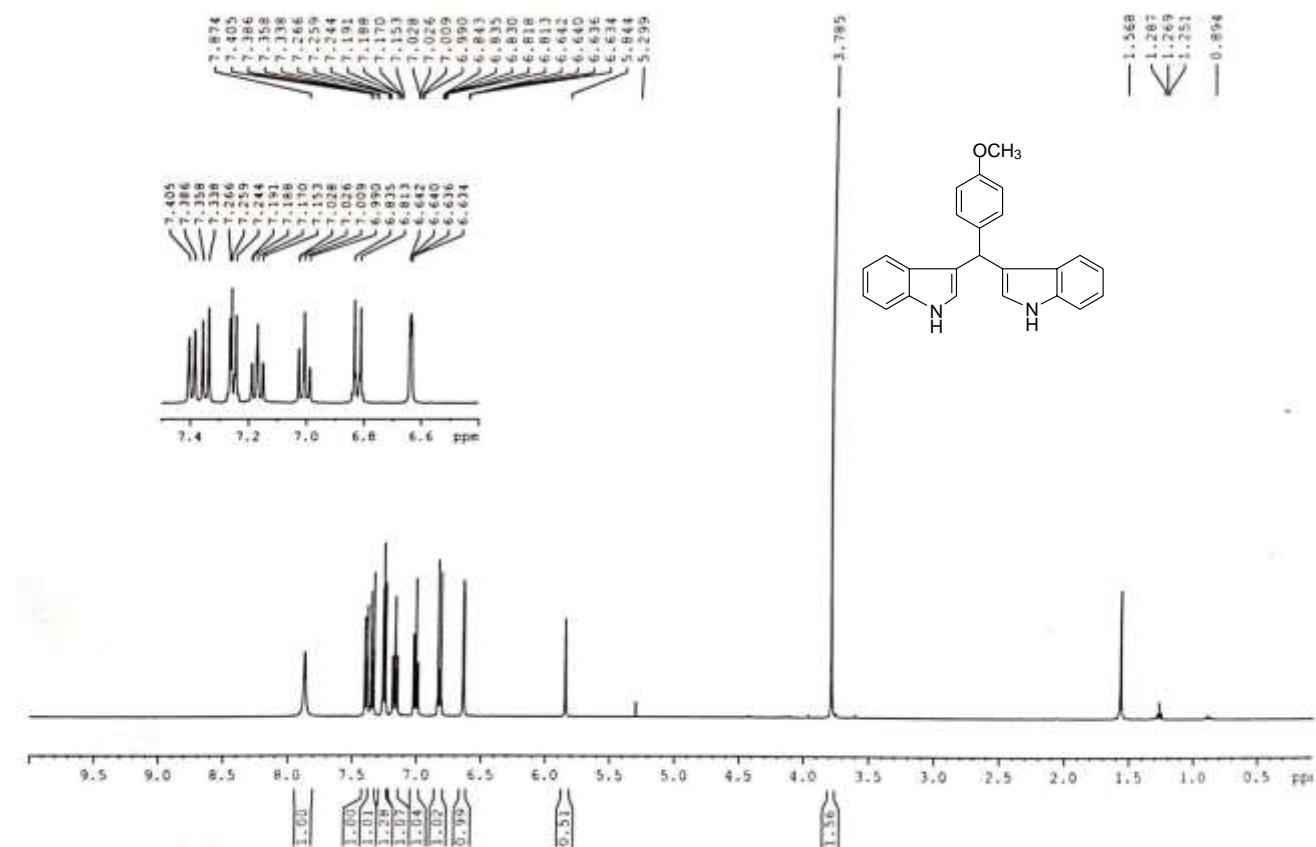
¹H NMR of **1c** (400 MHz, DMSO-d₆)



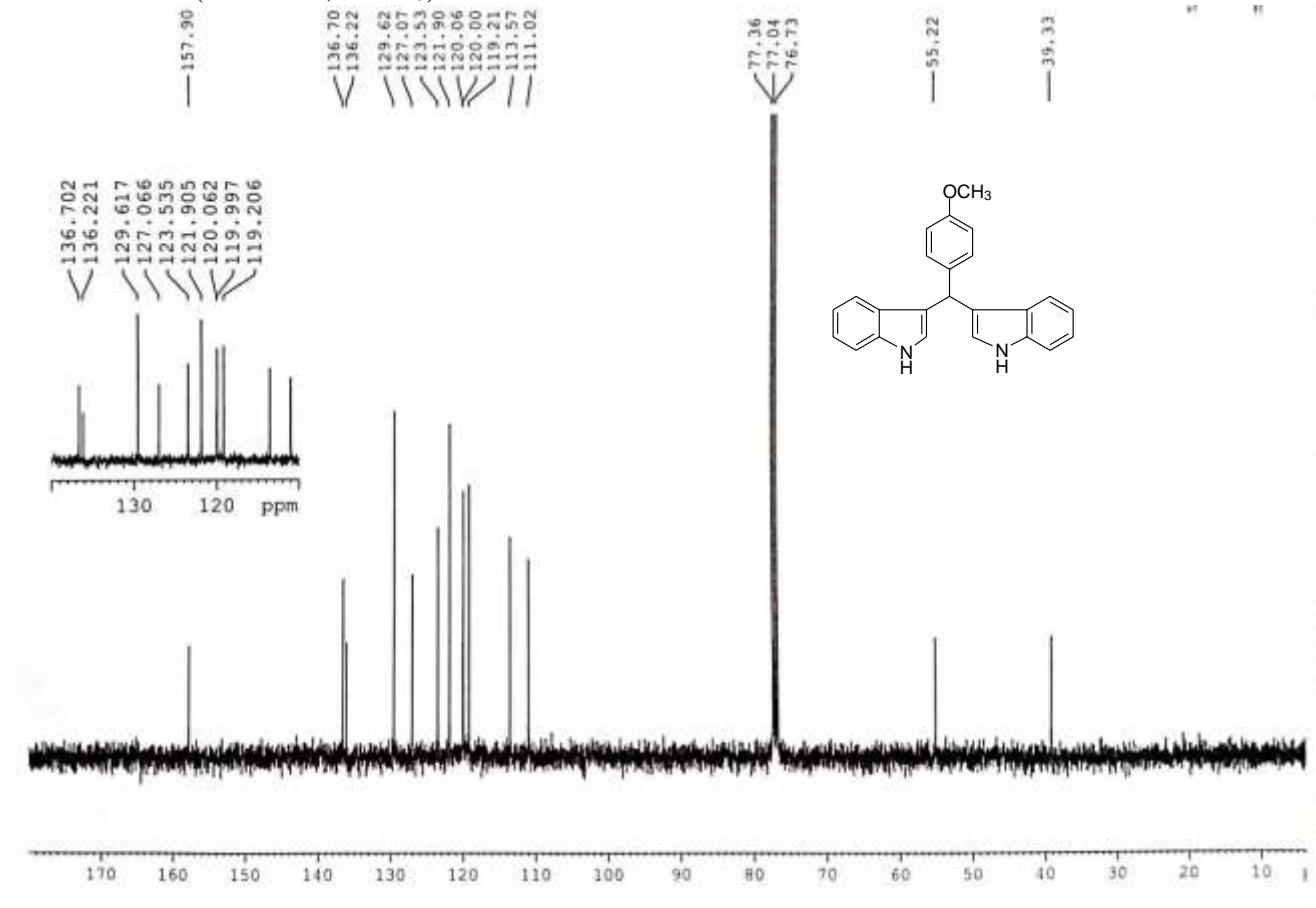
¹³C NMR of **1c** (100 MHz, DMSO-d₆)



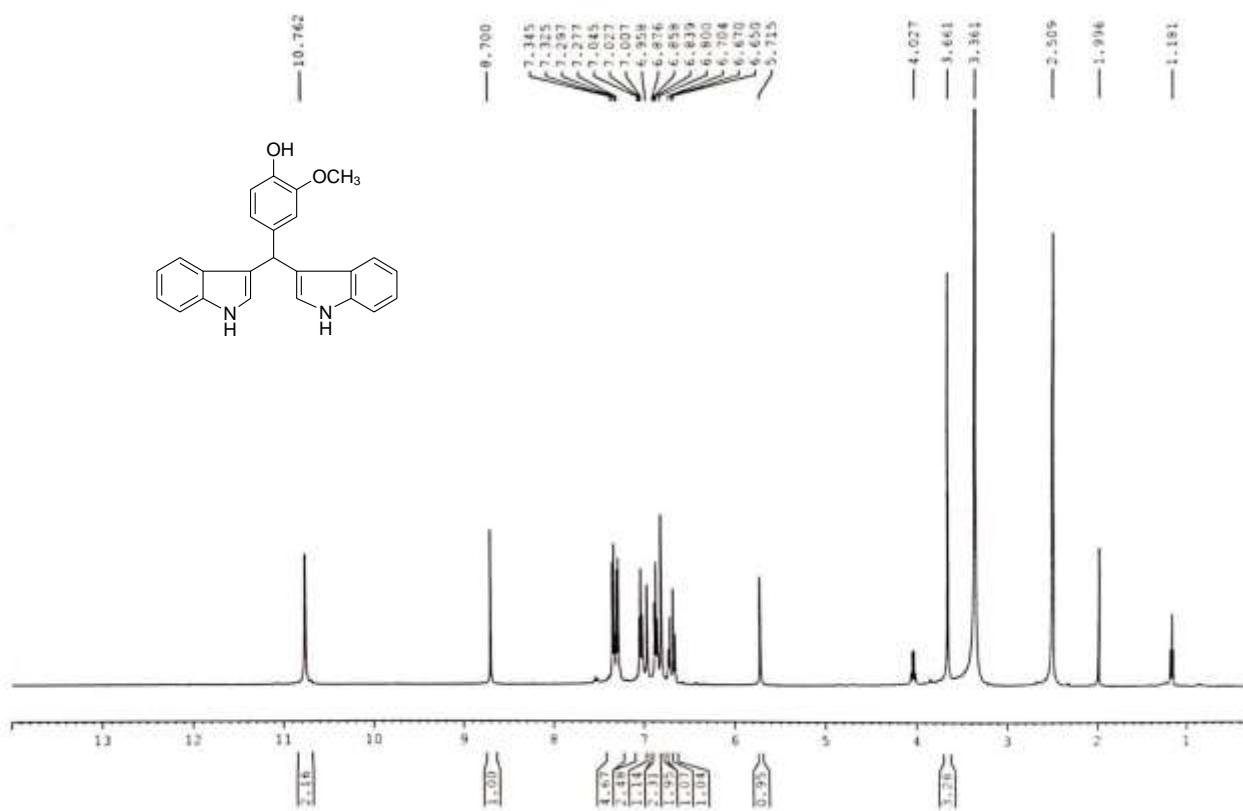
¹H NMR of **1d** (400 MHz, CDCl₃)



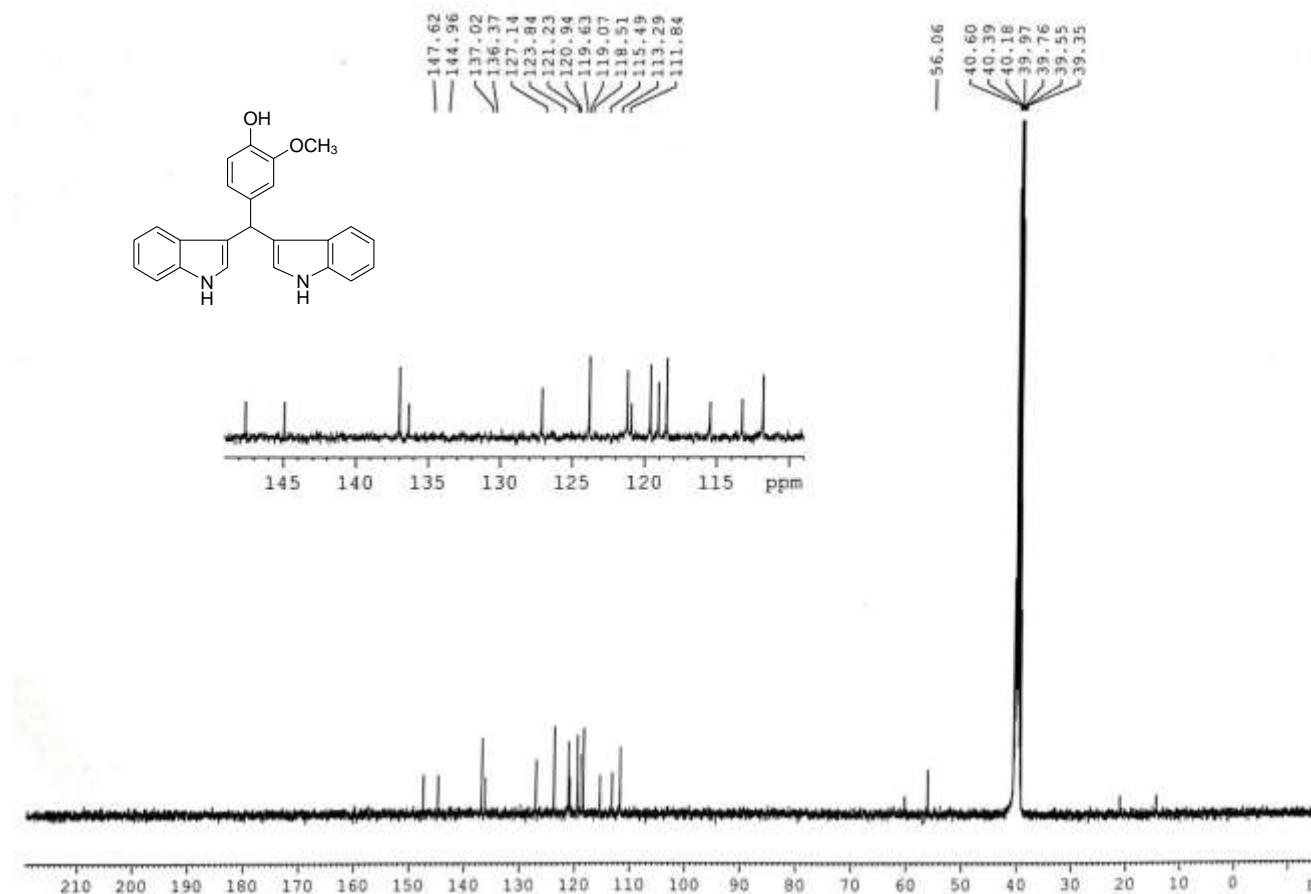
¹³C NMR of **1d** (100 MHz, CDCl₃)



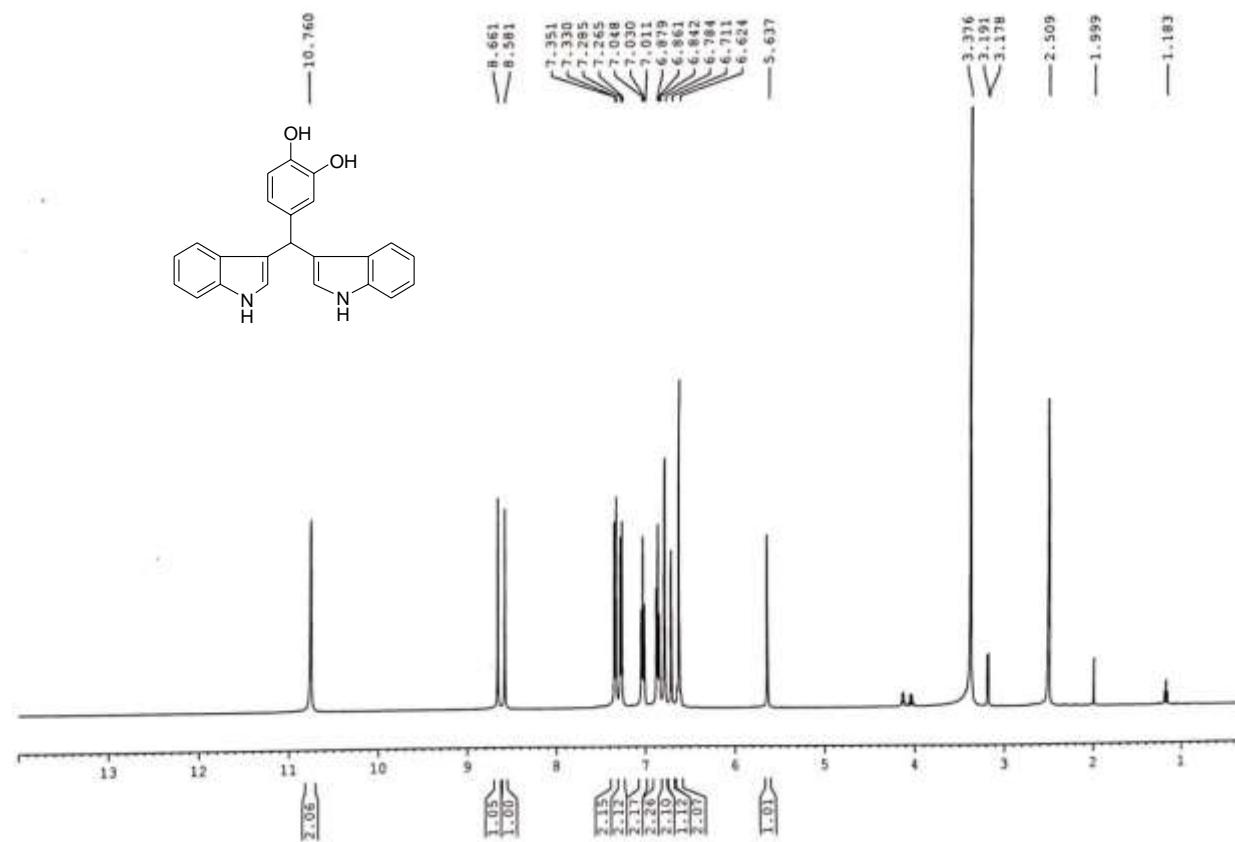
¹H NMR of **1e** (400 MHz, DMSO-d₆)



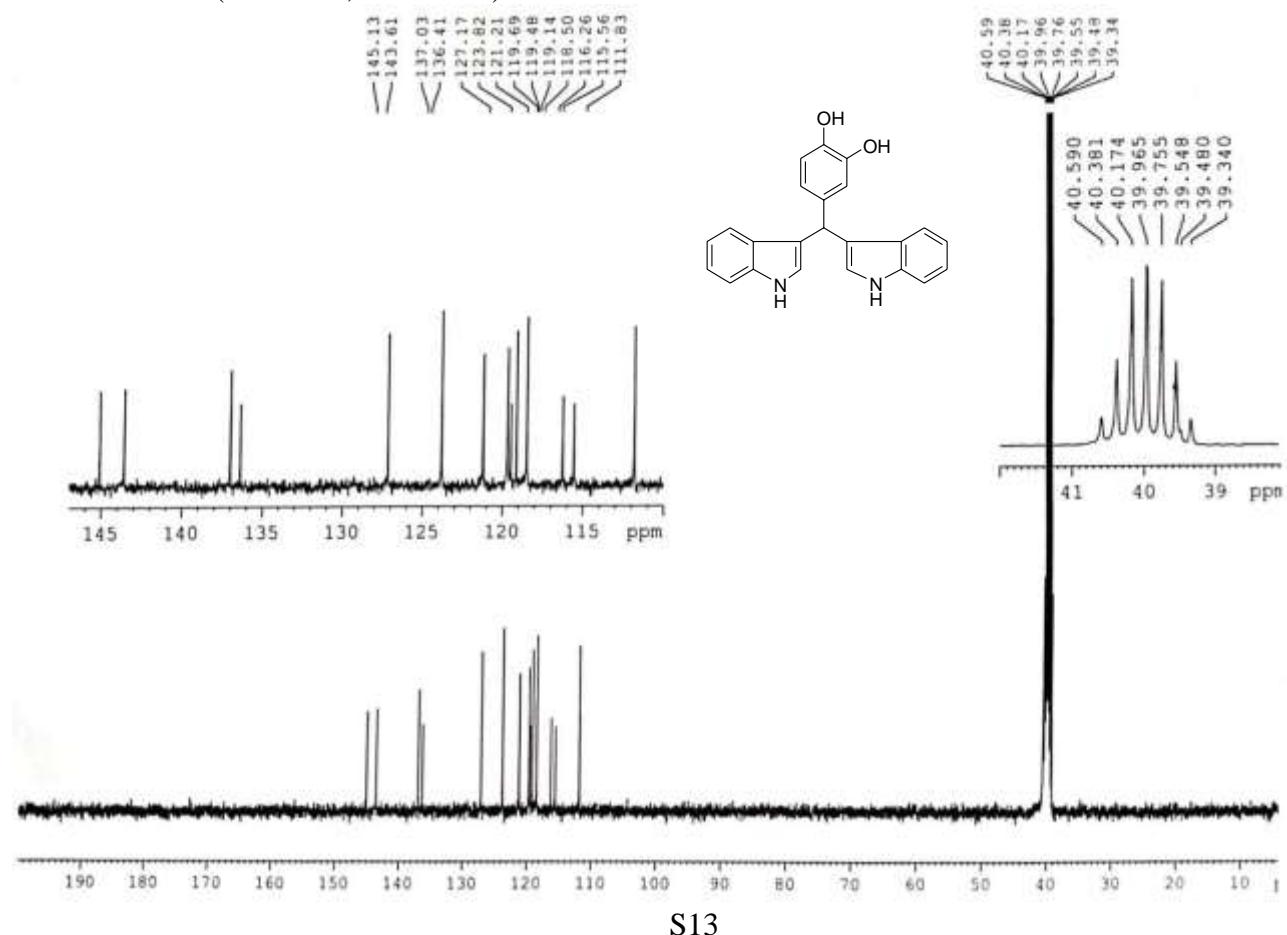
¹³C NMR of **1e** (100 MHz, DMSO-d₆)



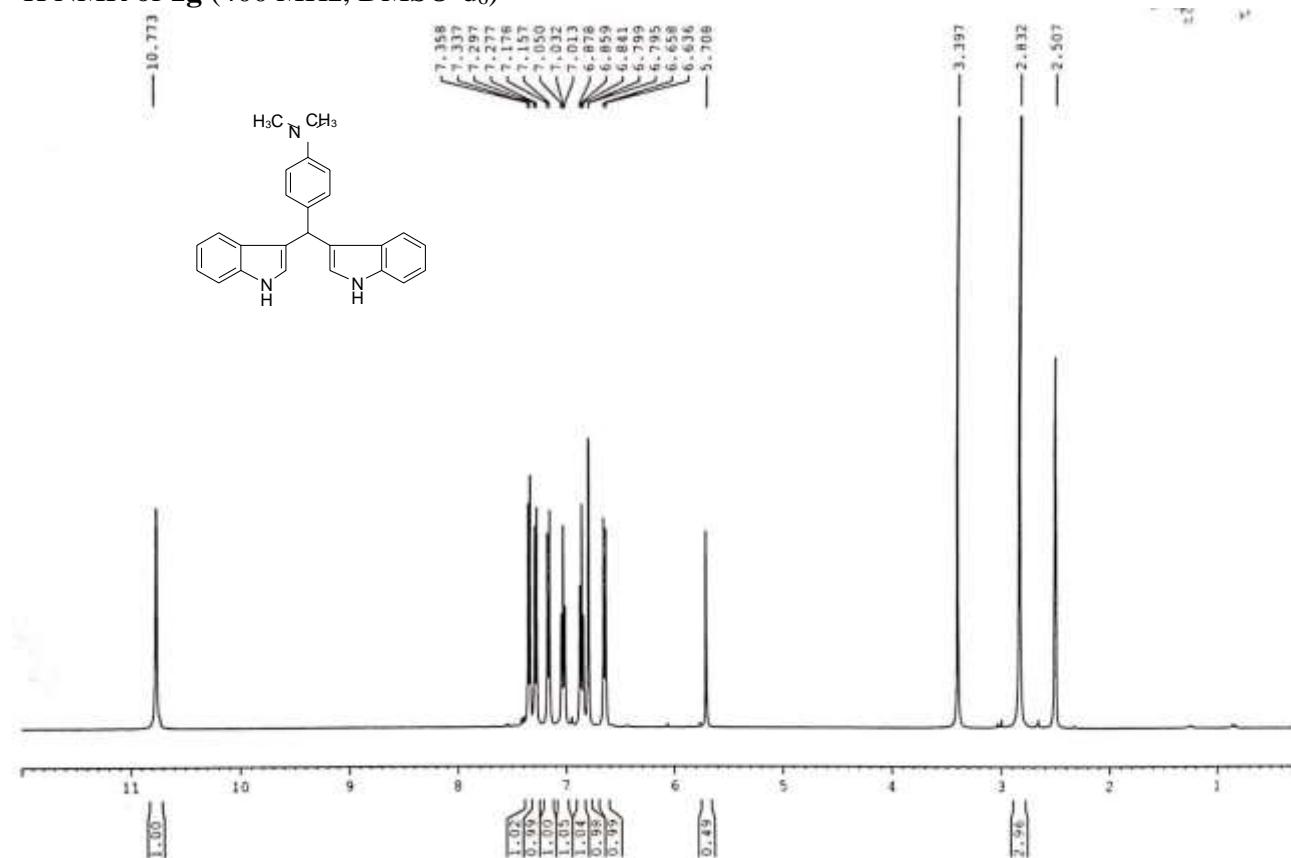
¹H NMR of **1f** (400 MHz, DMSO-d₆)



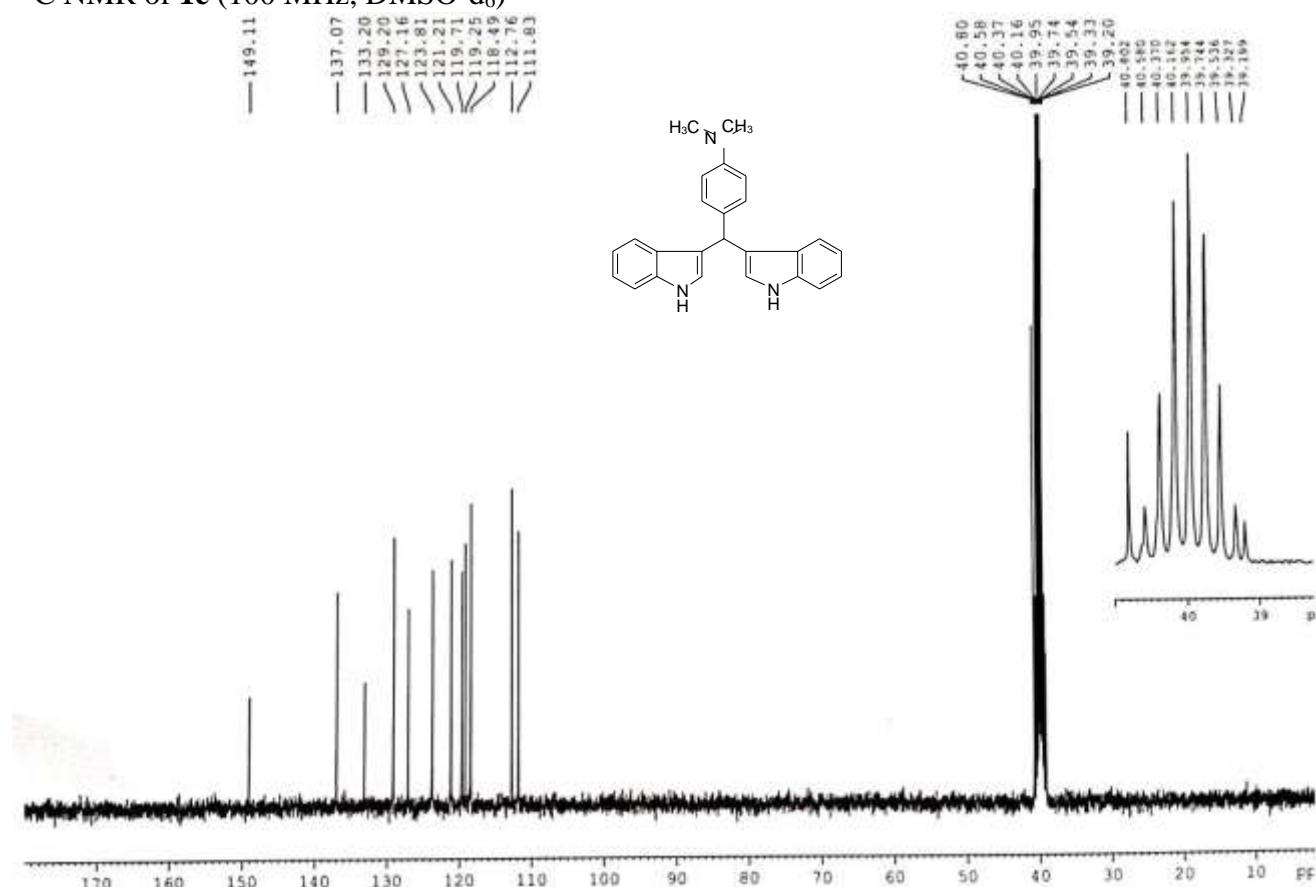
¹³C NMR of **1f** (100 MHz, DMSO-d₆)



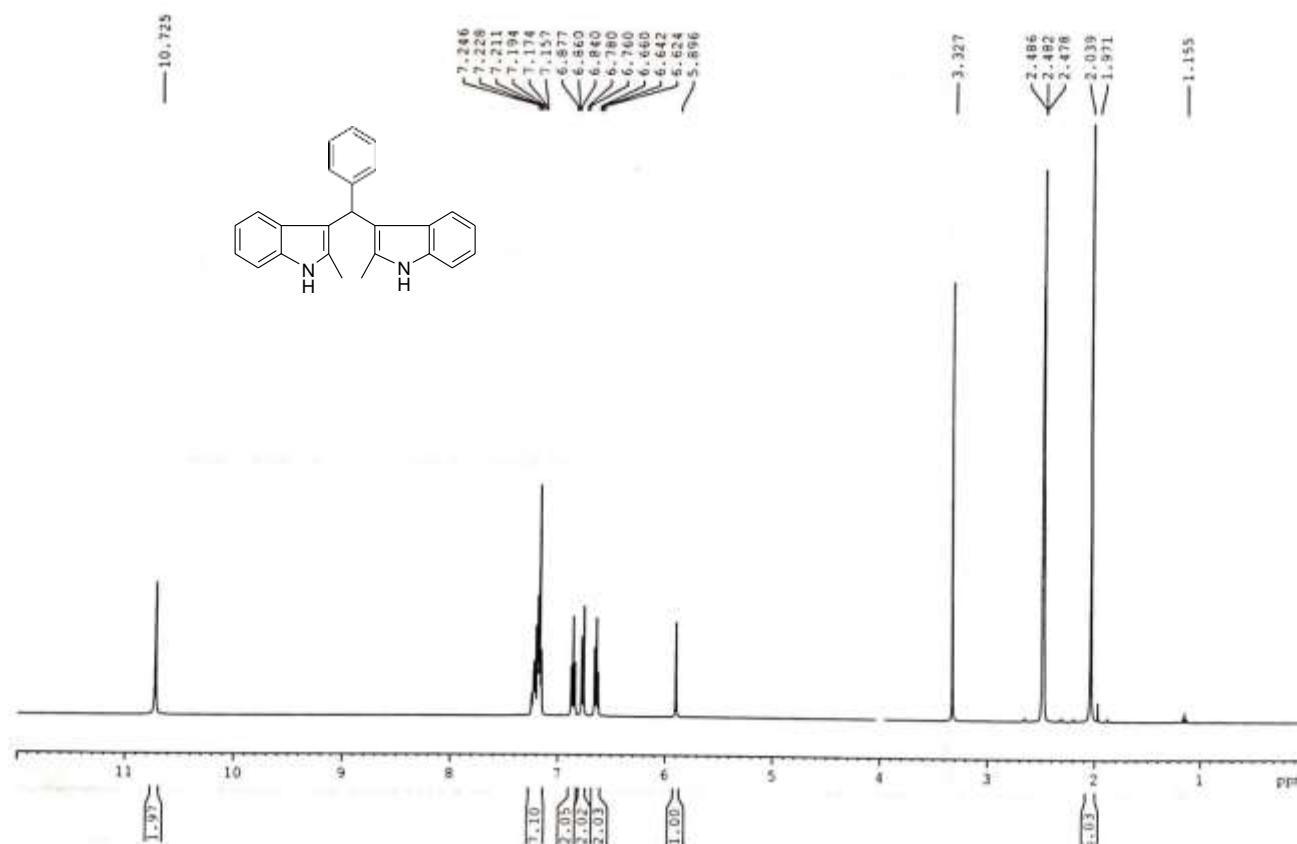
¹H NMR of **1g** (400 MHz, DMSO-d₆)



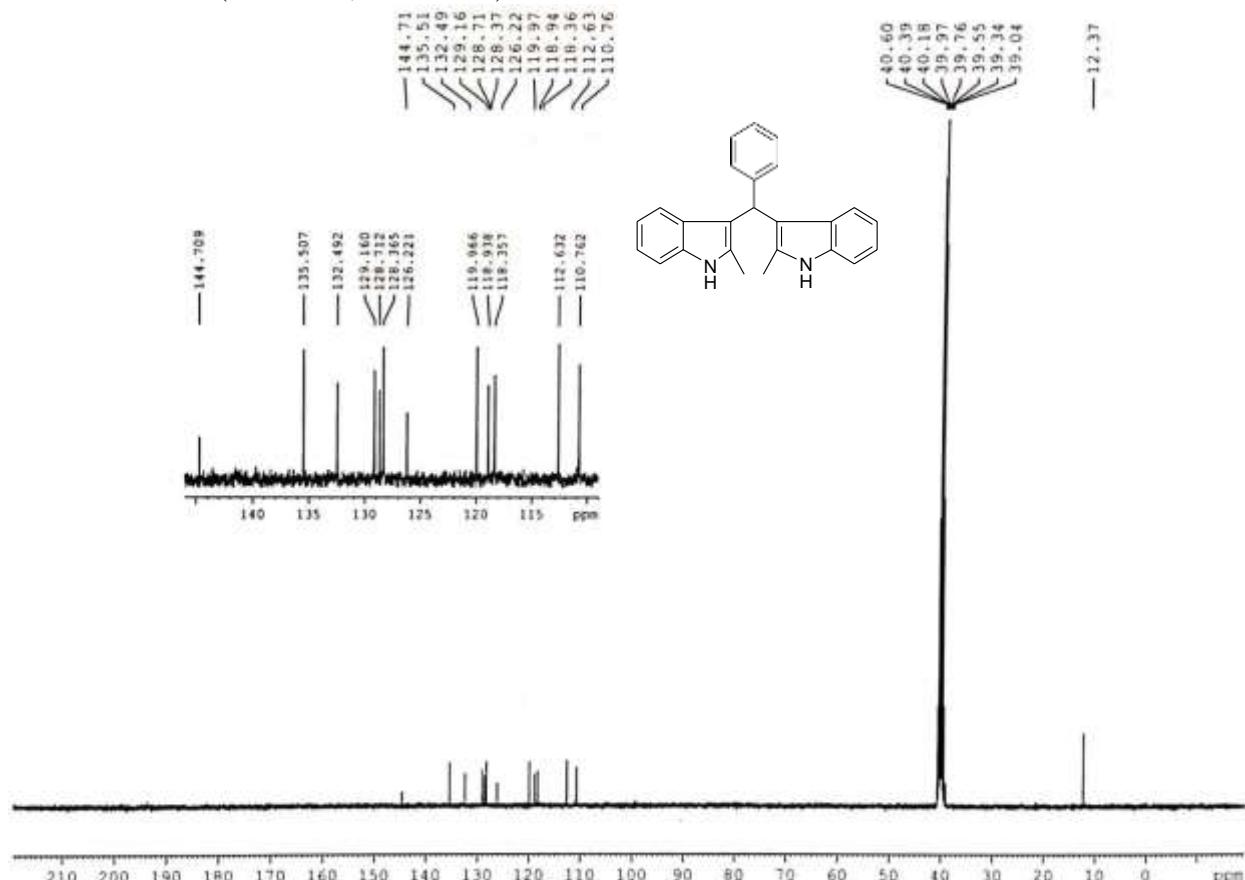
¹³C NMR of **1e** (100 MHz, DMSO-d₆)



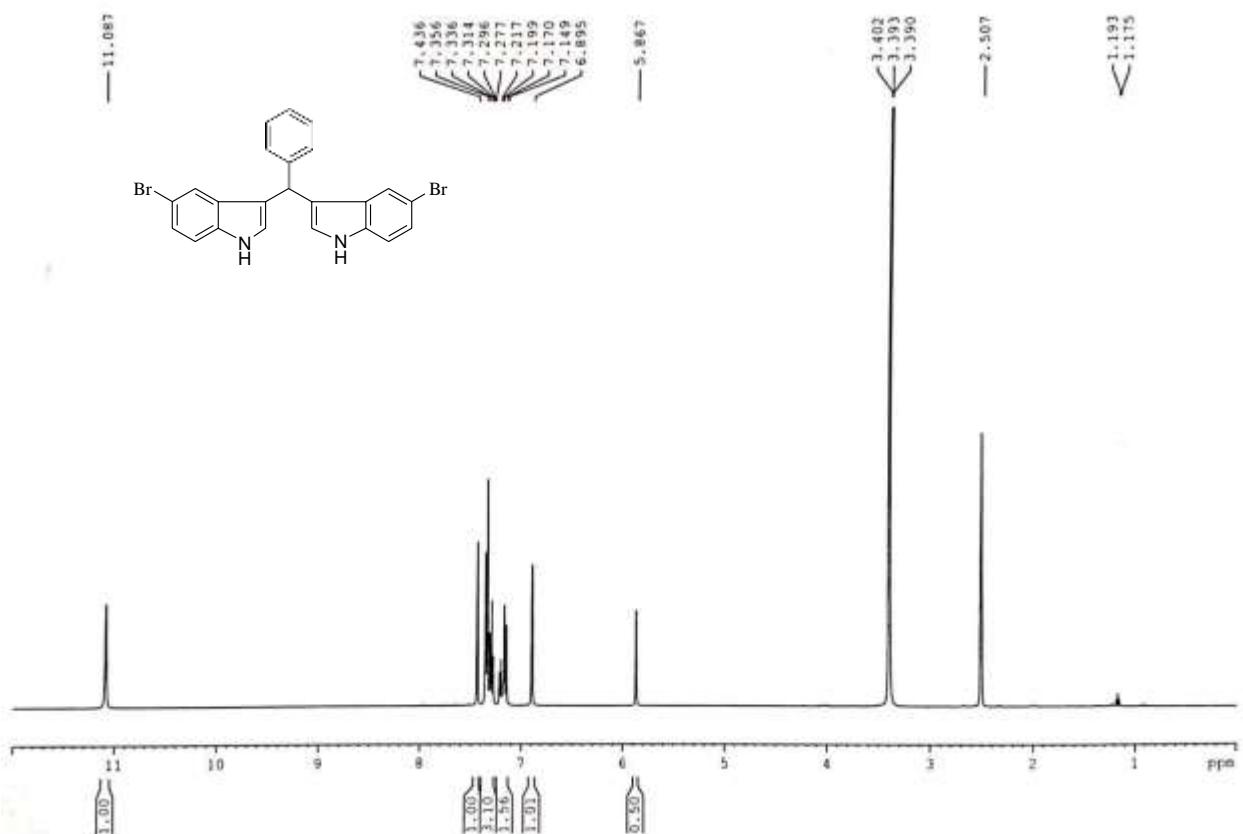
¹H NMR of **1h** (400 MHz, DMSO-d₆)



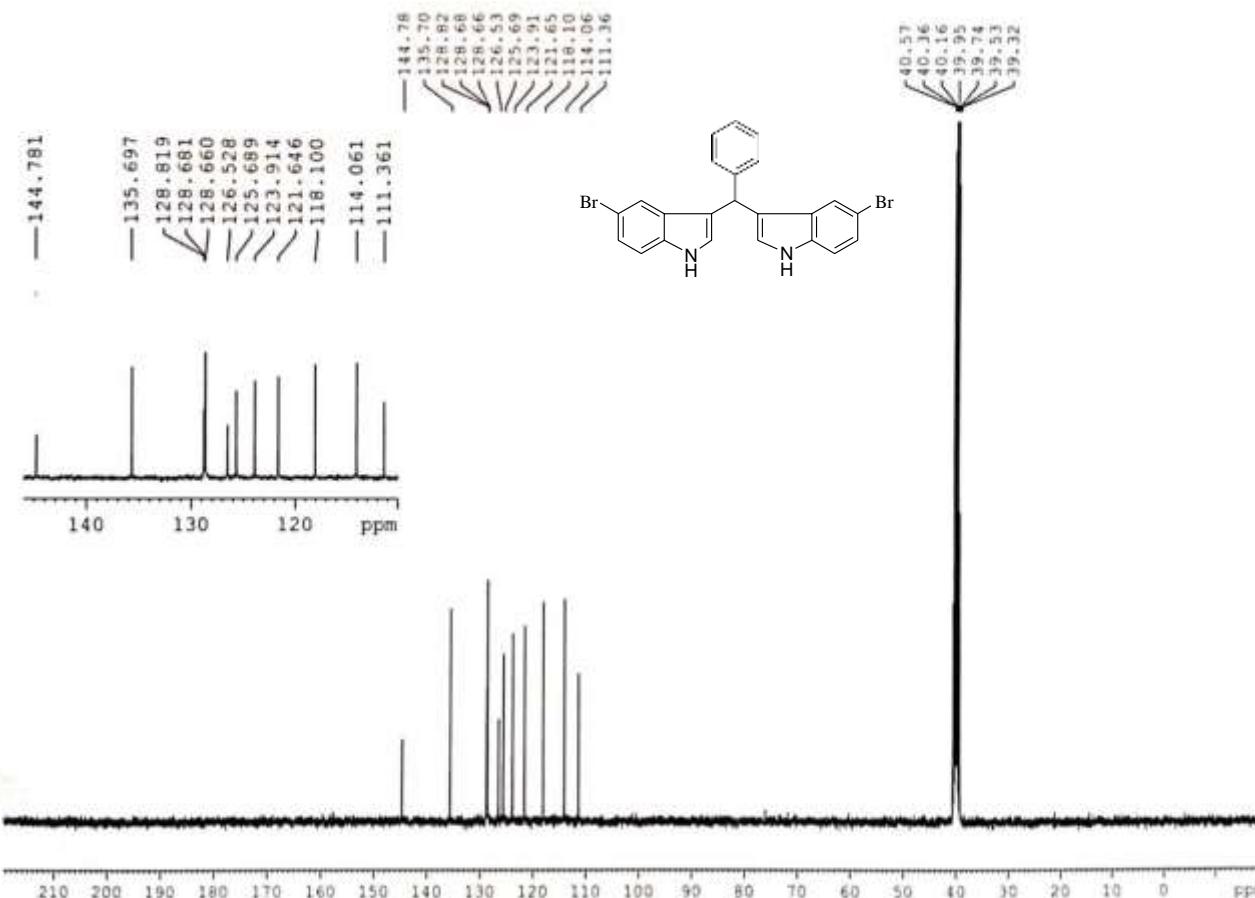
¹³C NMR of **1h** (100 MHz, DMSO-d₆)



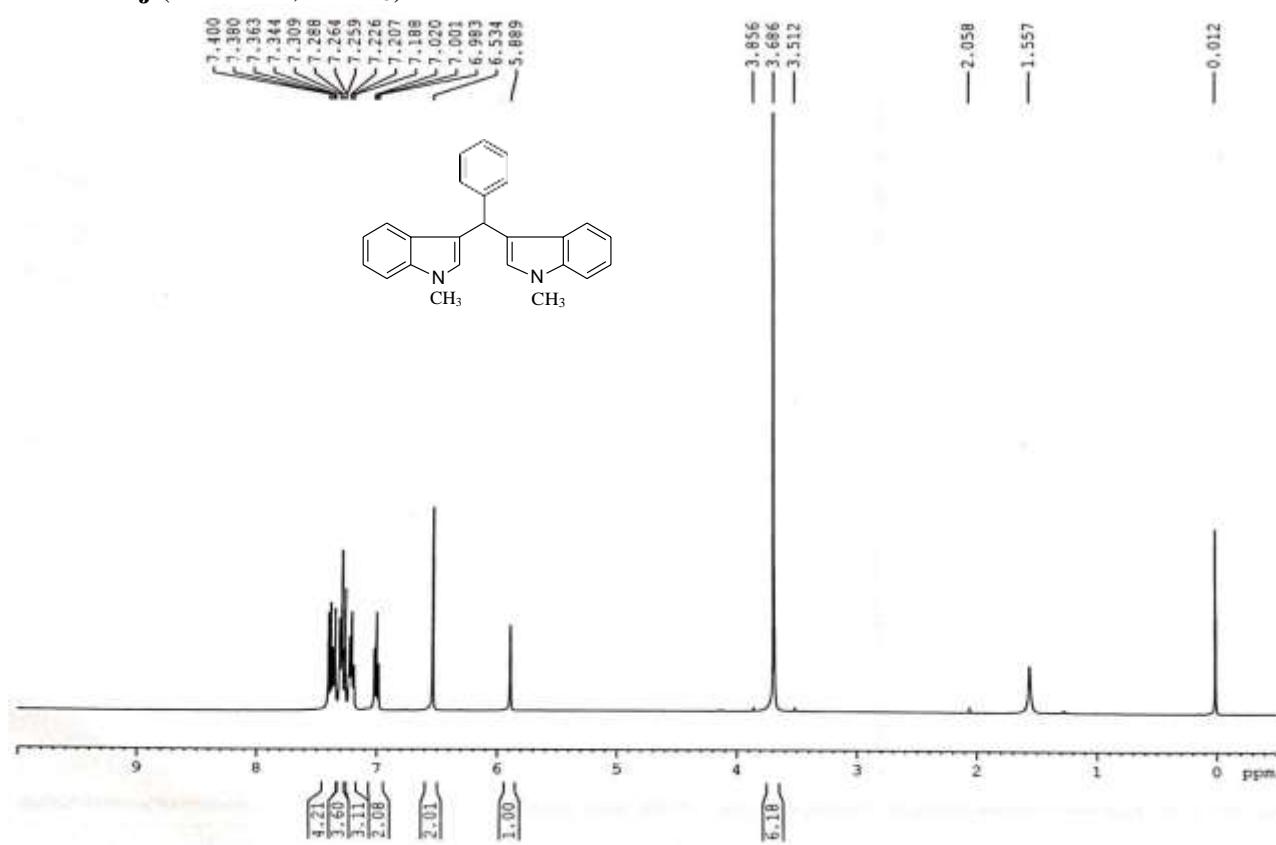
¹H NMR of **1i** (400 MHz, DMSO-d₆)



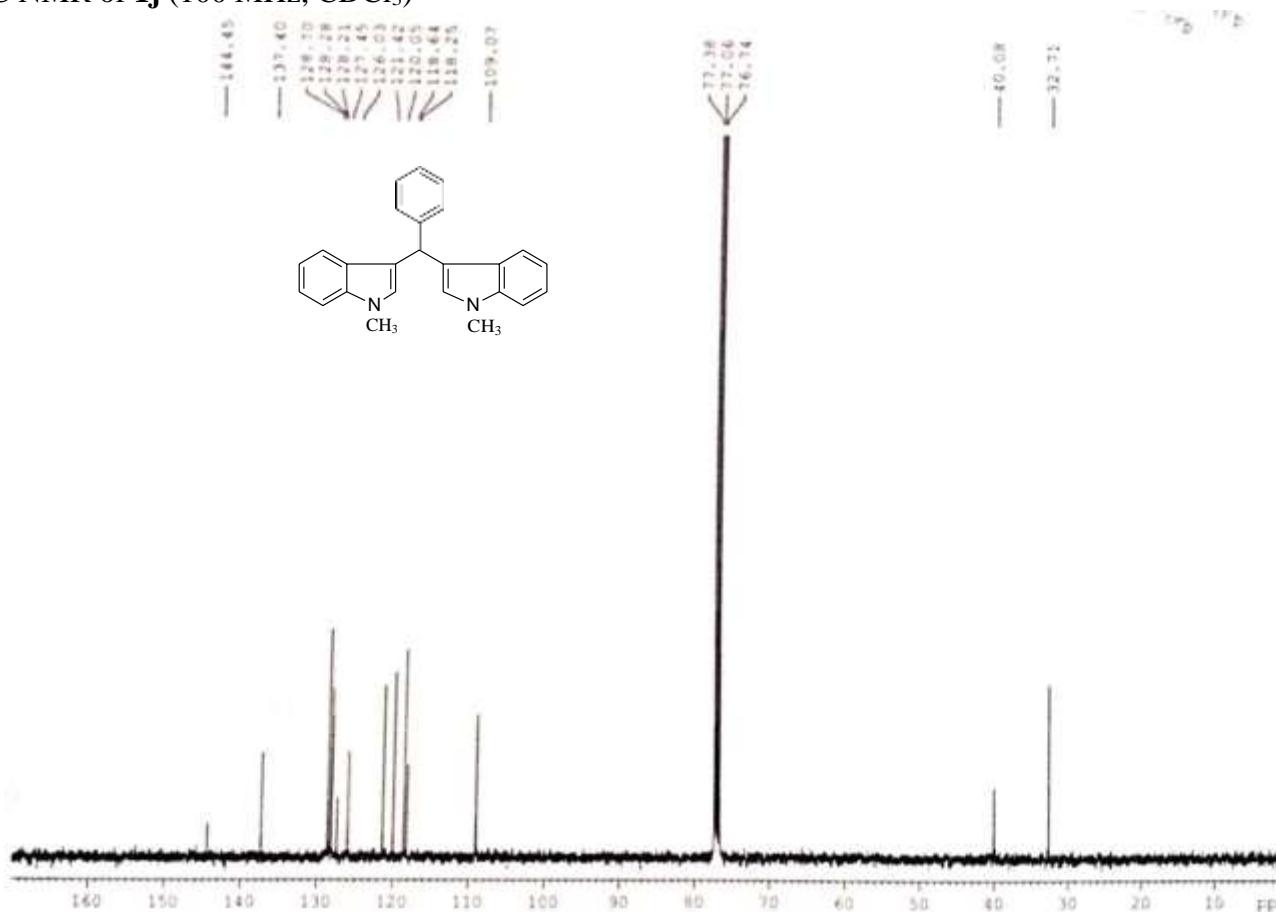
¹³C NMR of **1i** (100 MHz, DMSO-d₆)



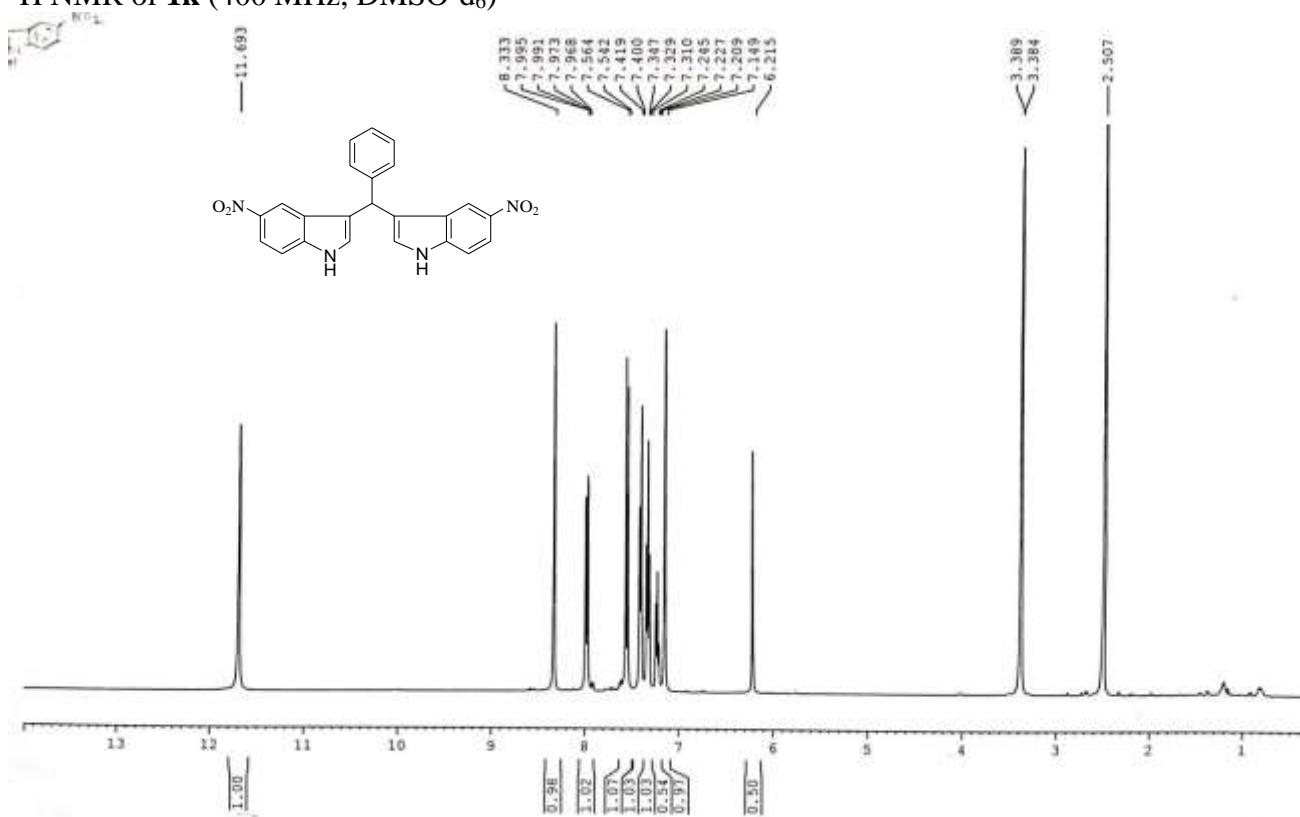
¹H NMR of **1j** (400 MHz, CDCl₃)



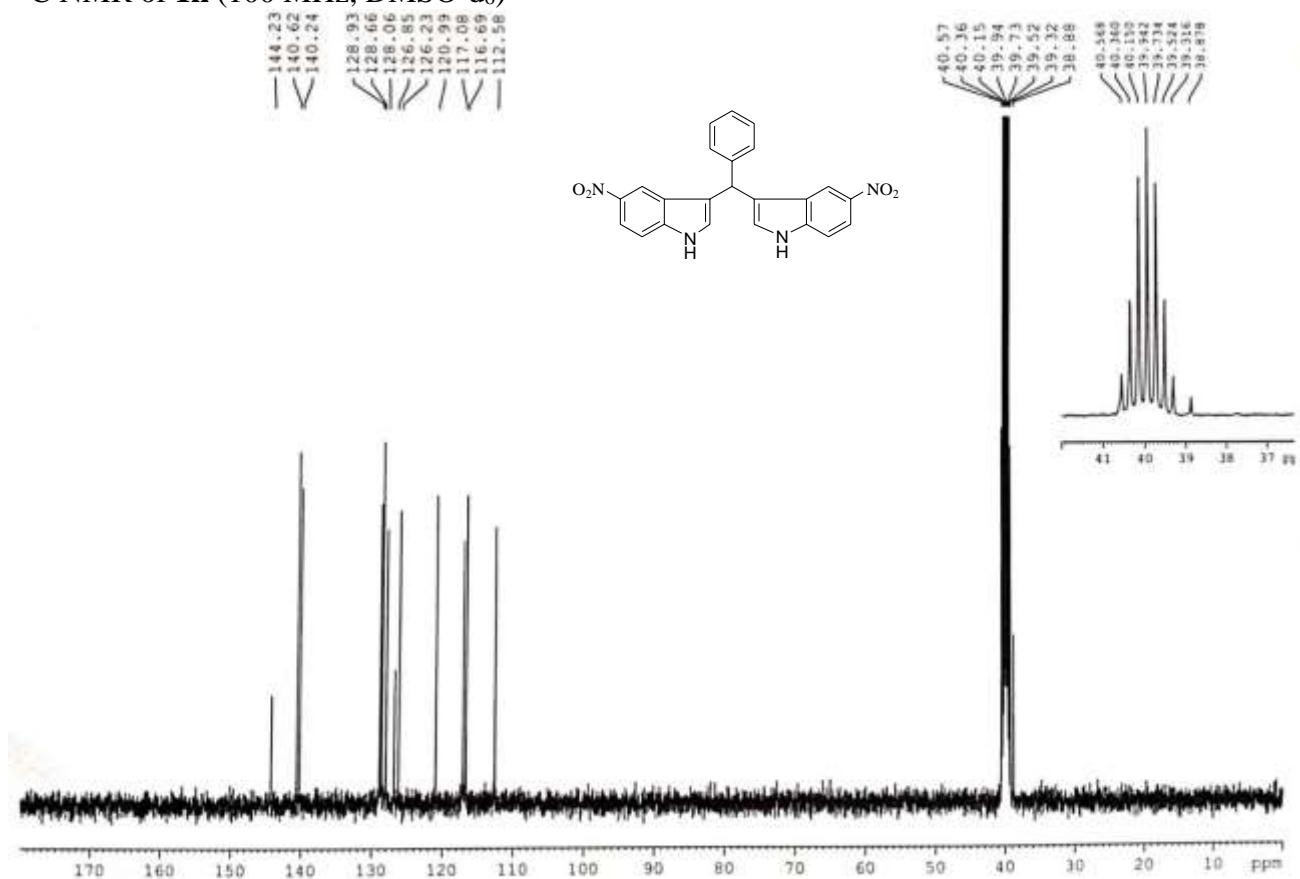
¹³C NMR of **1j** (100 MHz, CDCl₃)



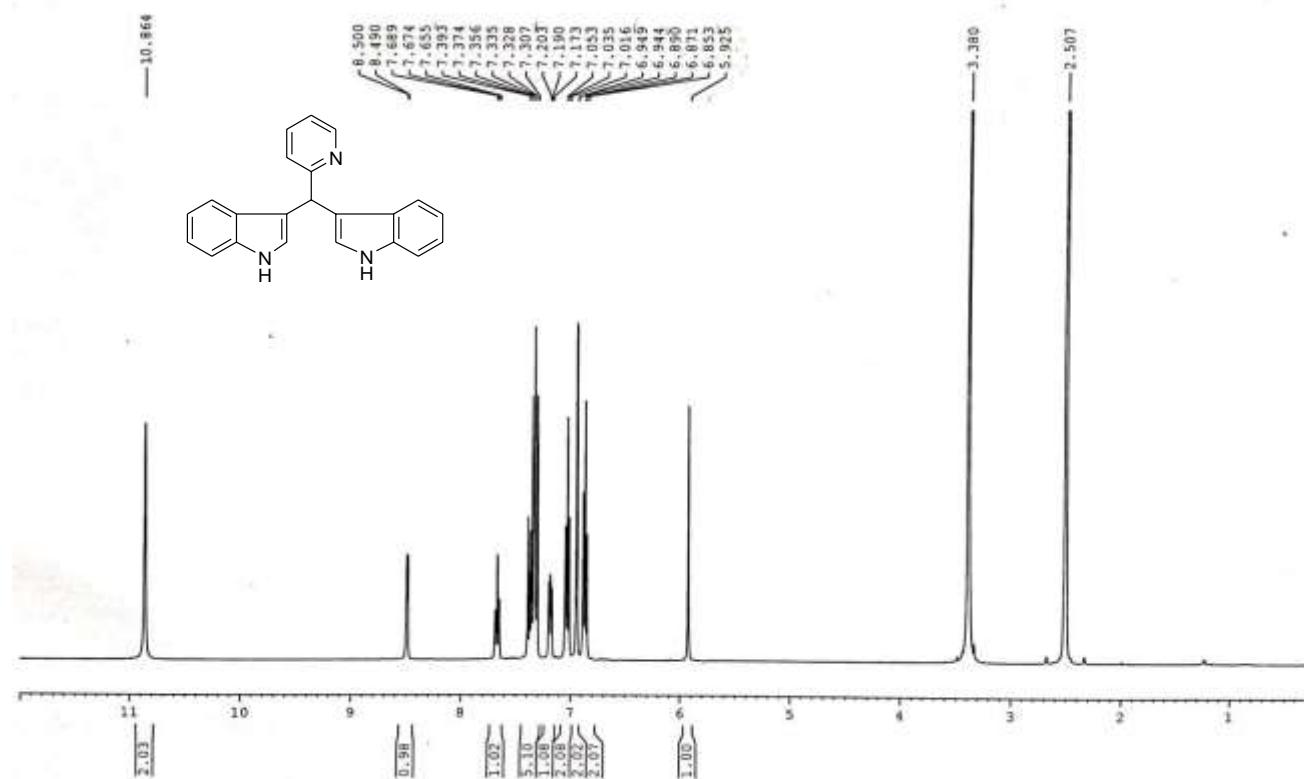
¹H NMR of **1k** (400 MHz, DMSO-d₆)



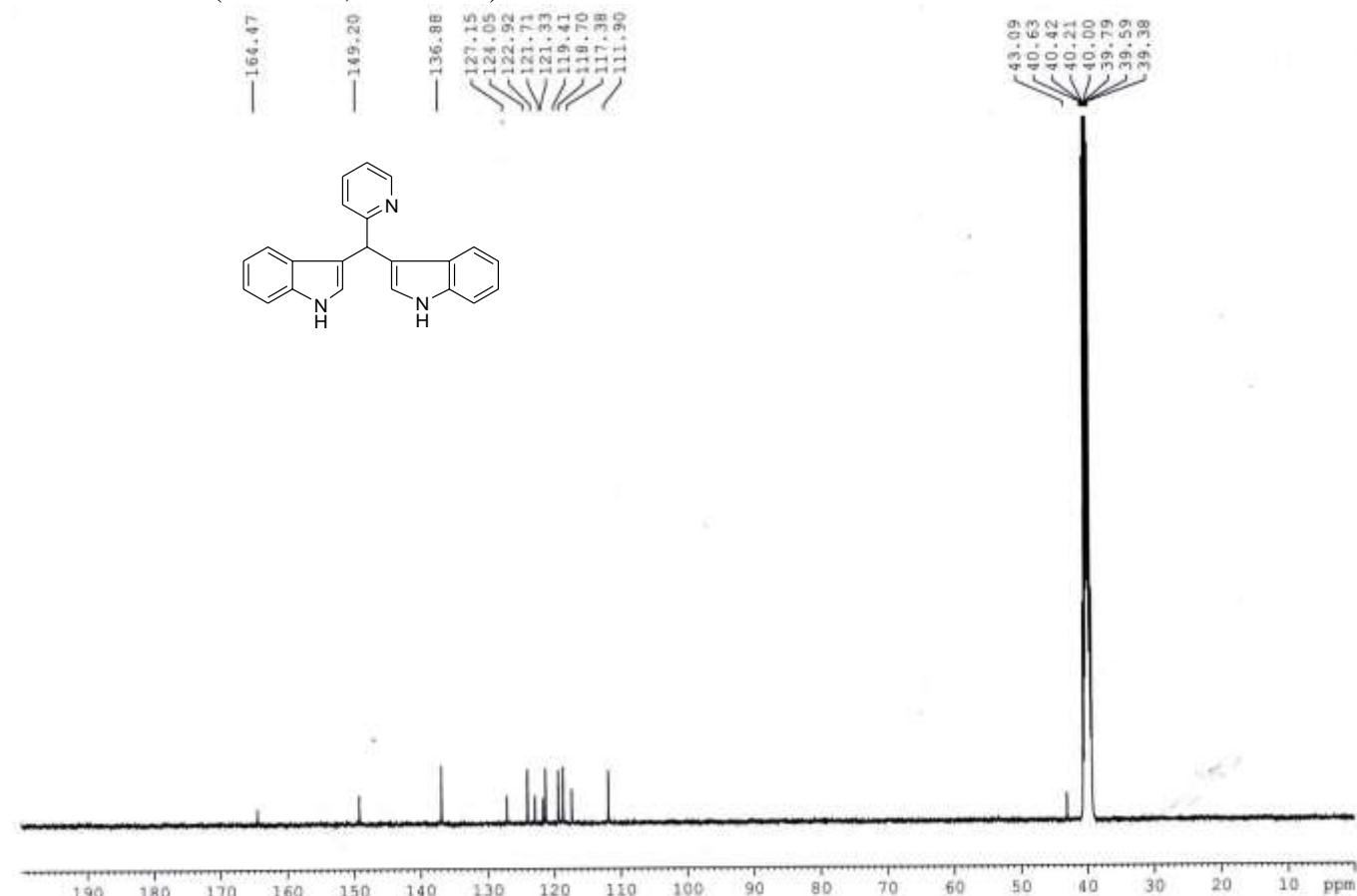
¹³C NMR of **1k** (100 MHz, DMSO-d₆)



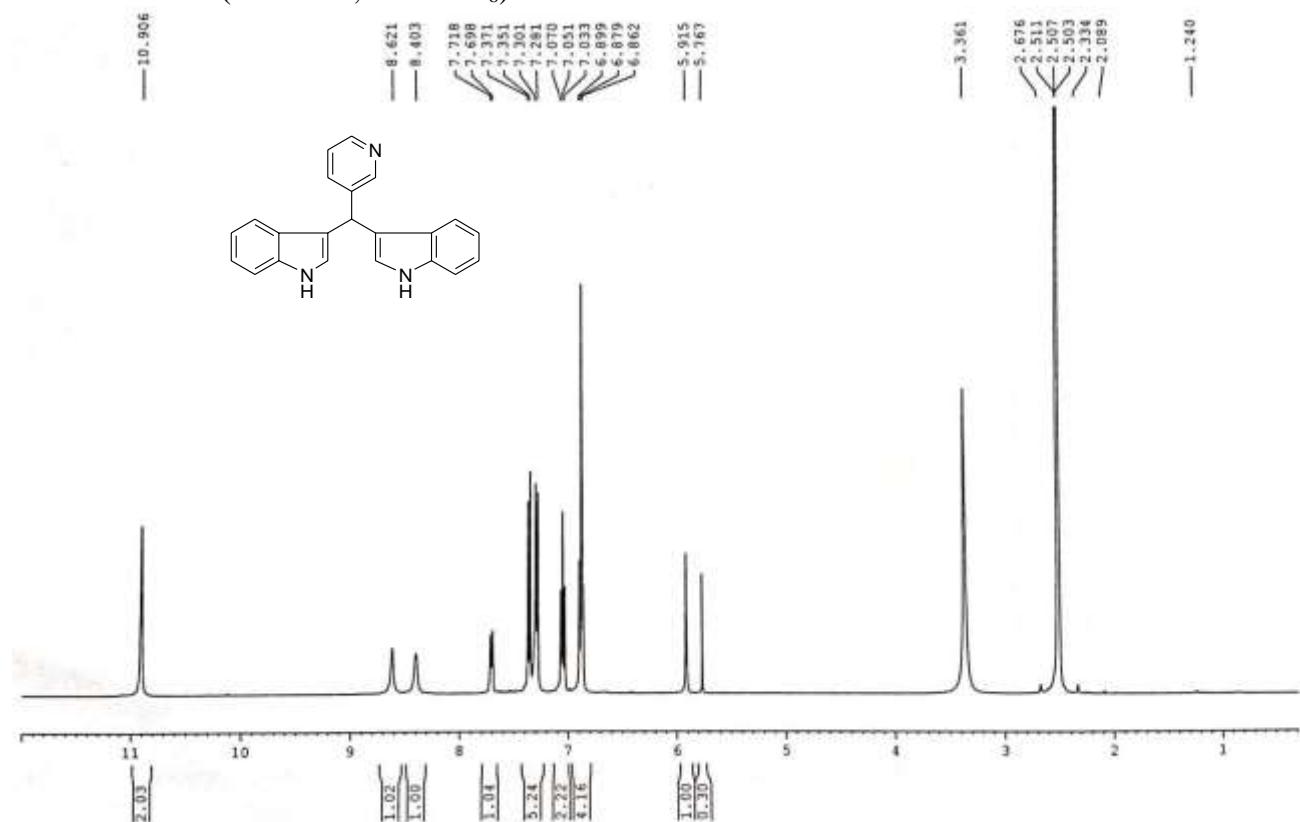
¹H NMR of **1I** (400 MHz, DMSO-d₆)



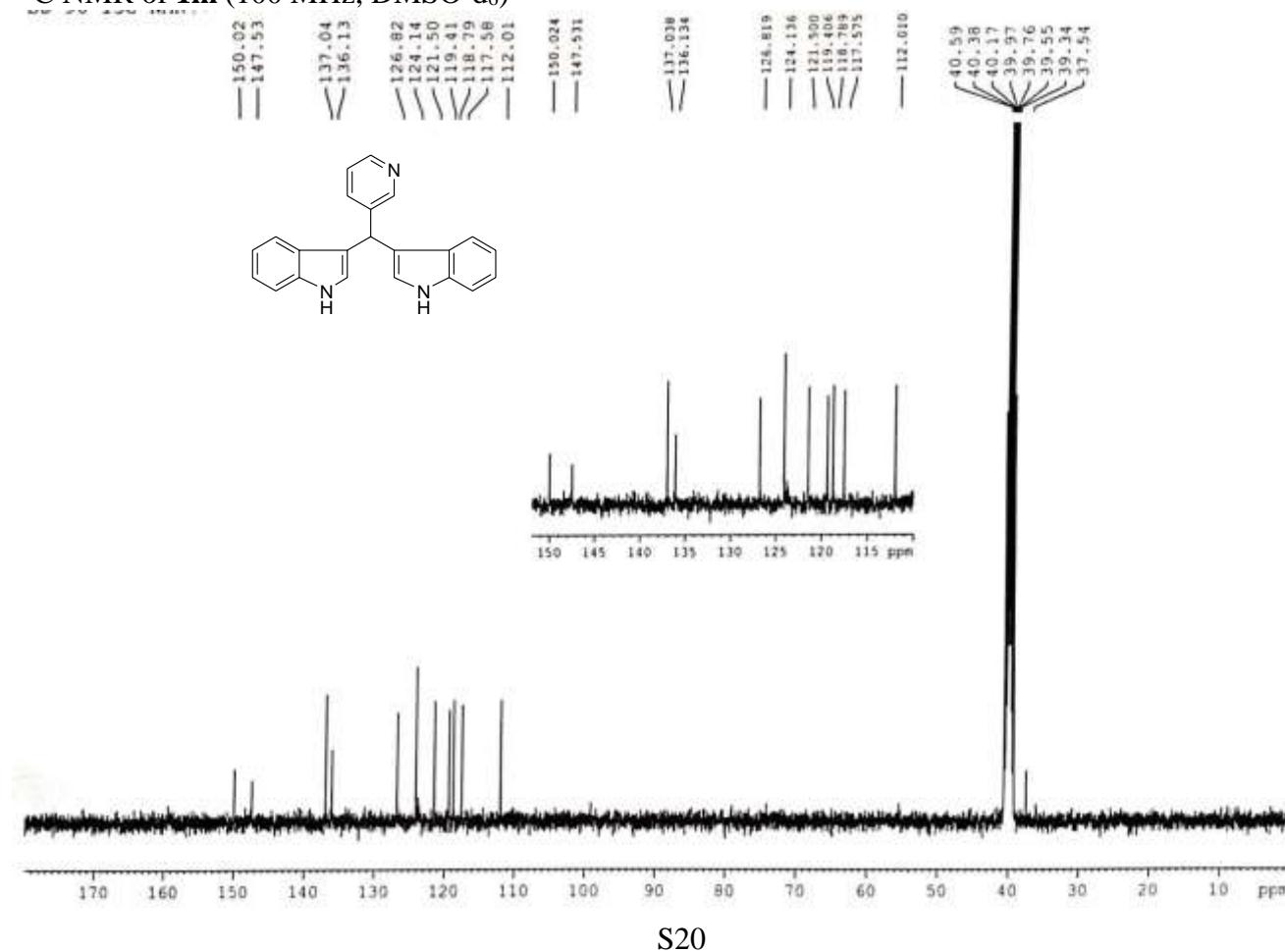
¹³C NMR of **1l** (100 MHz, DMSO-d₆)



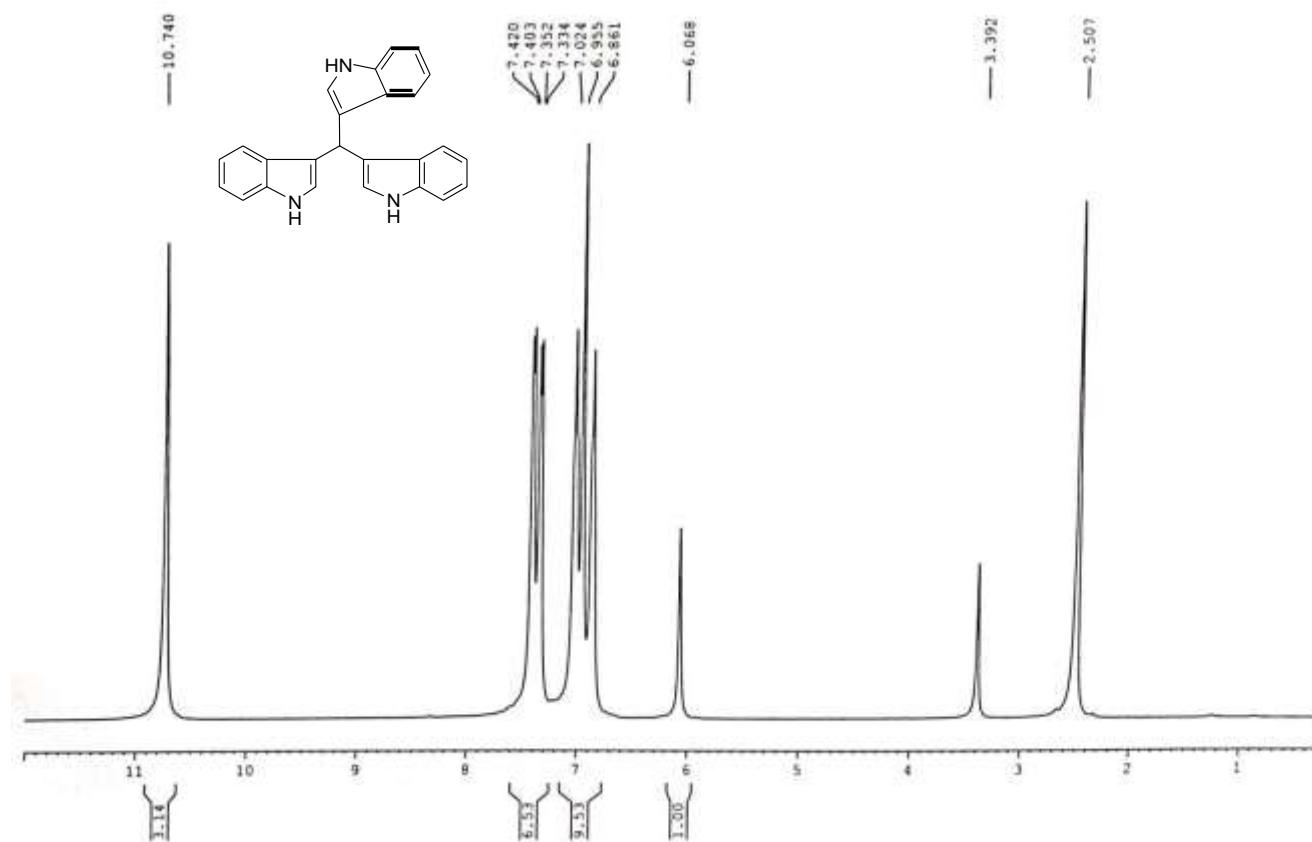
¹H NMR of **1m** (400 MHz, DMSO-d₆)



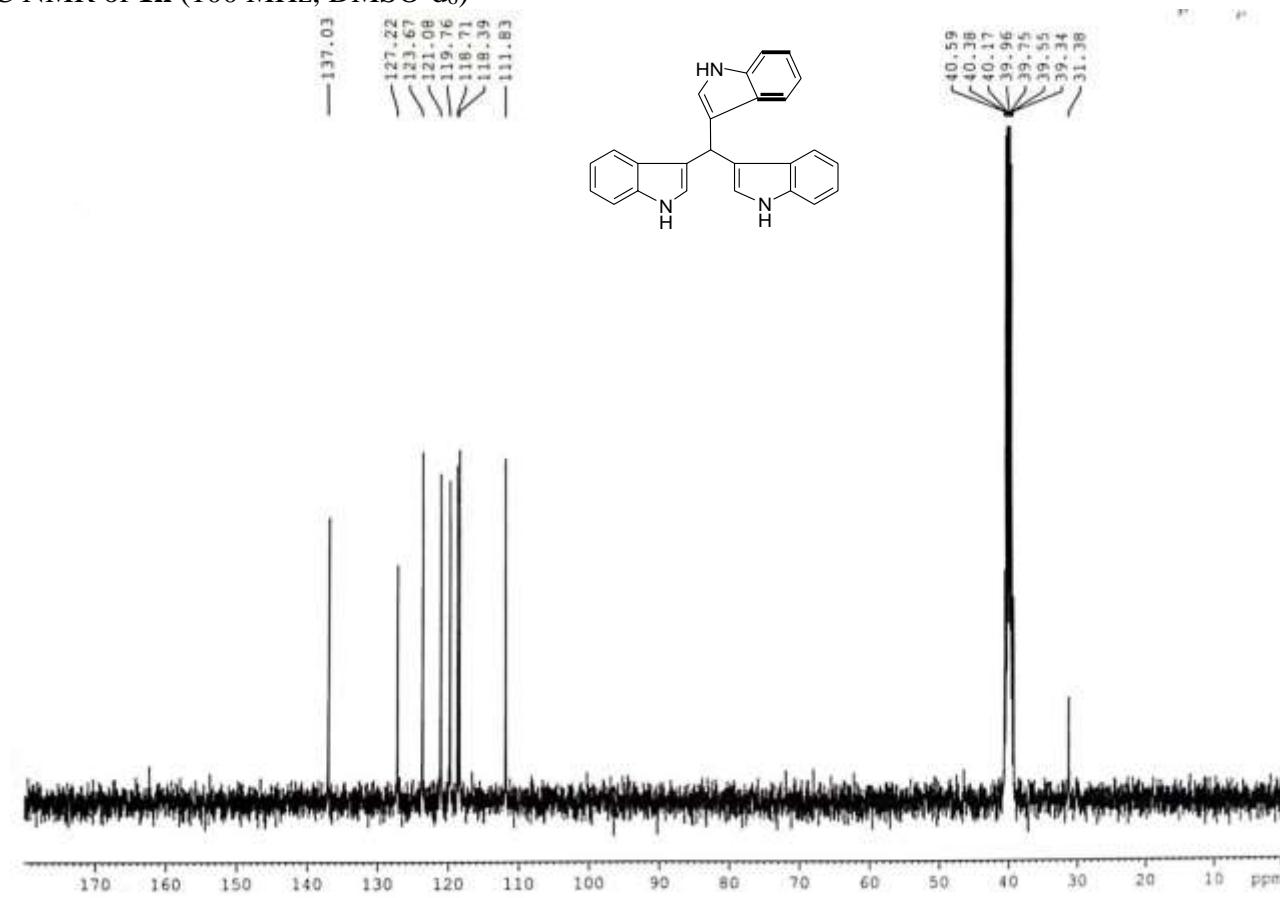
¹³C NMR of **1m** (100 MHz, DMSO-d₆)



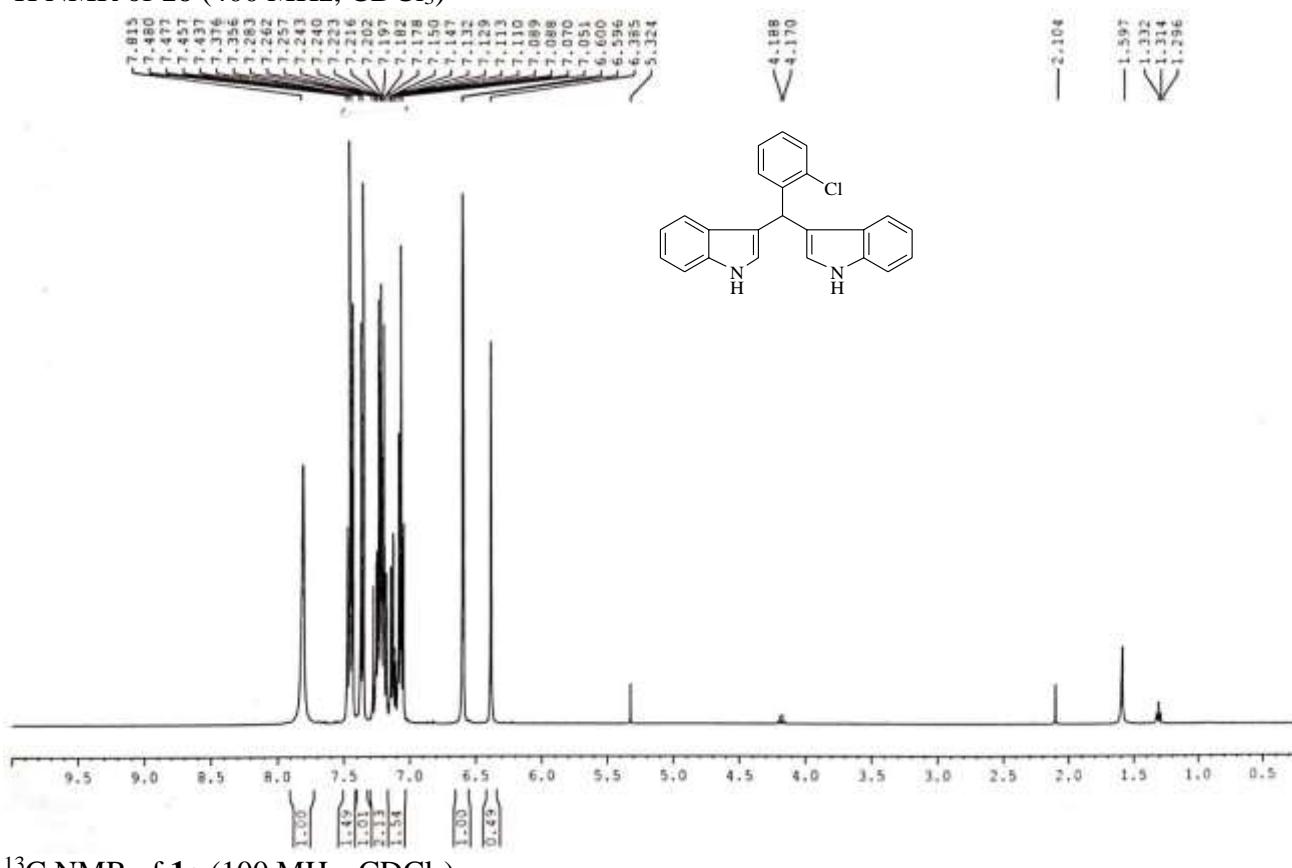
¹H NMR of **1n** (400 MHz, DMSO-d₆)



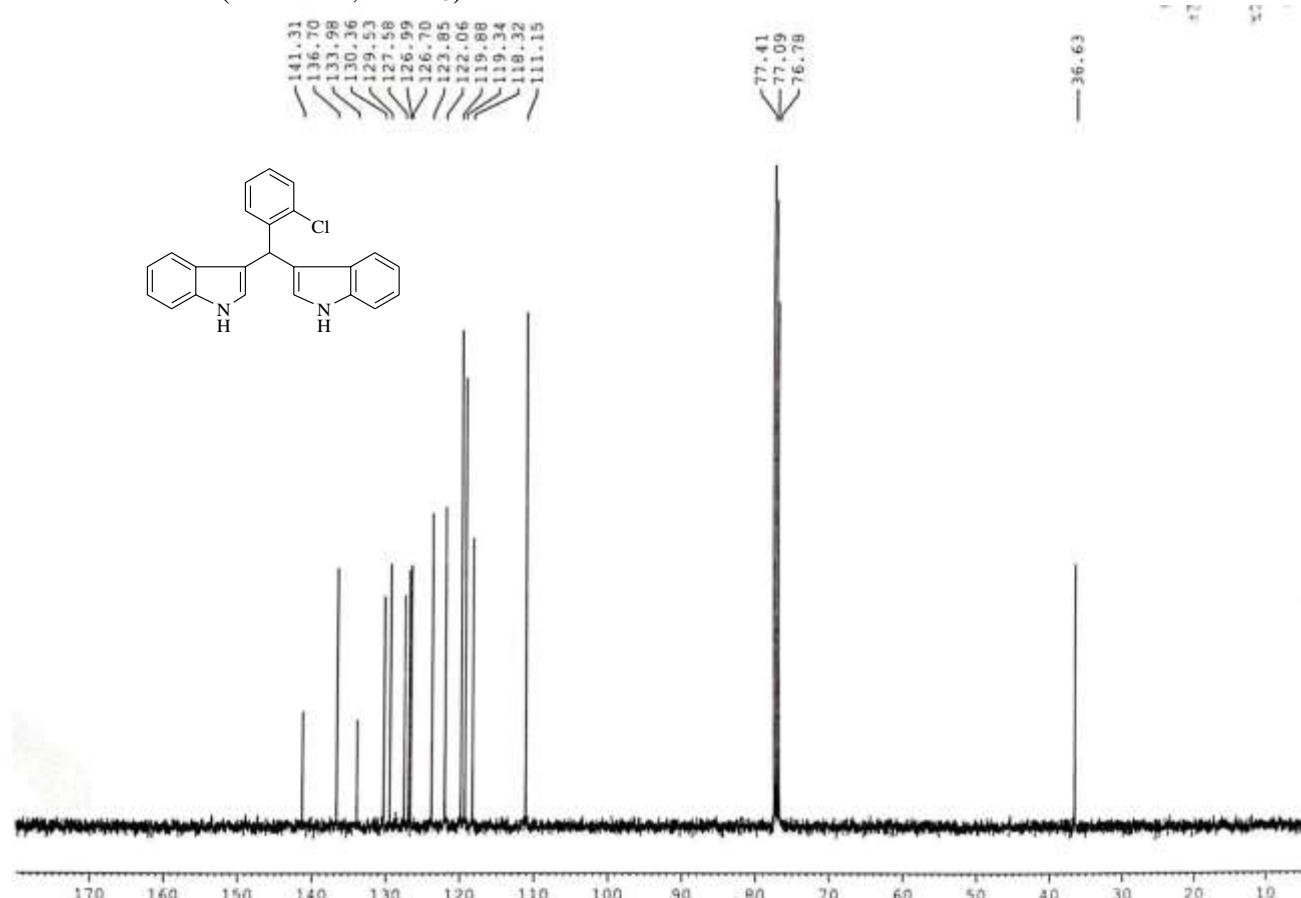
¹³C NMR of **1n** (100 MHz, DMSO-d₆)



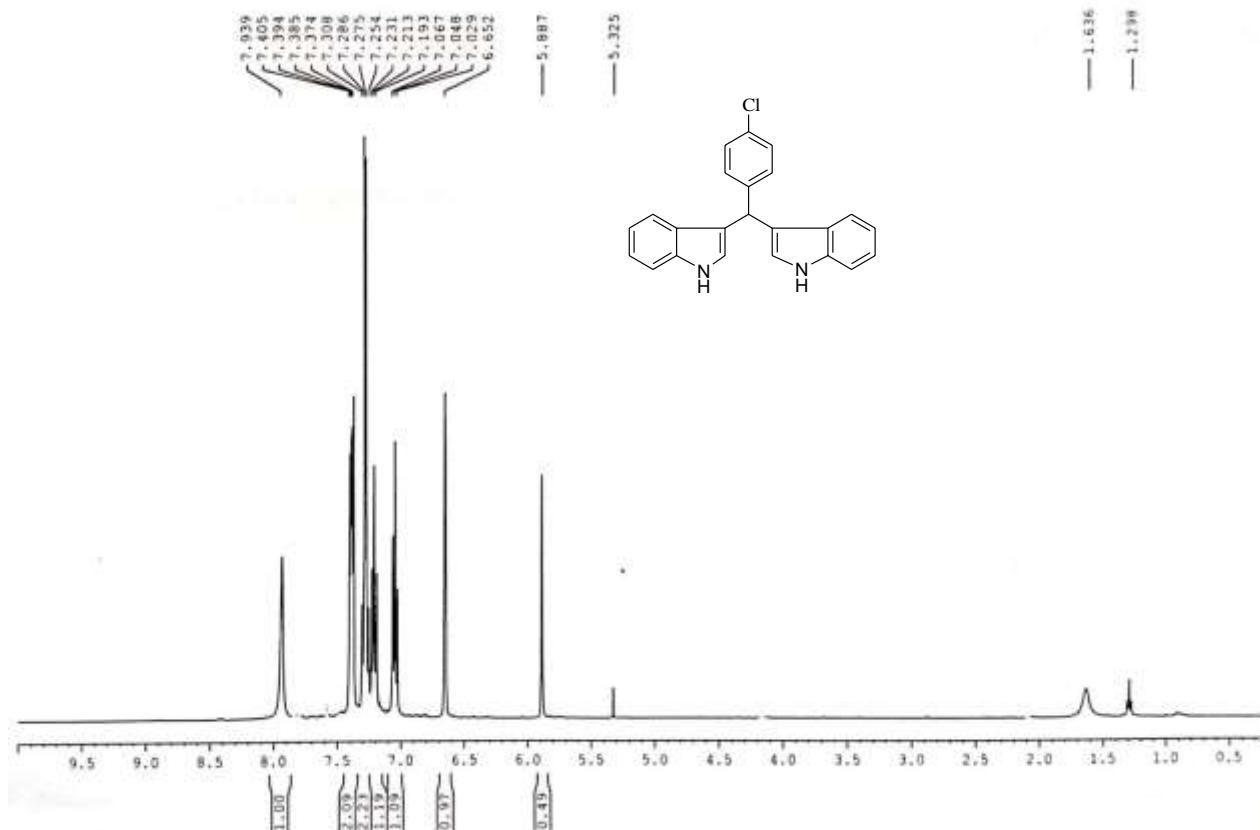
¹H NMR of **1o** (400 MHz, CDCl₃)



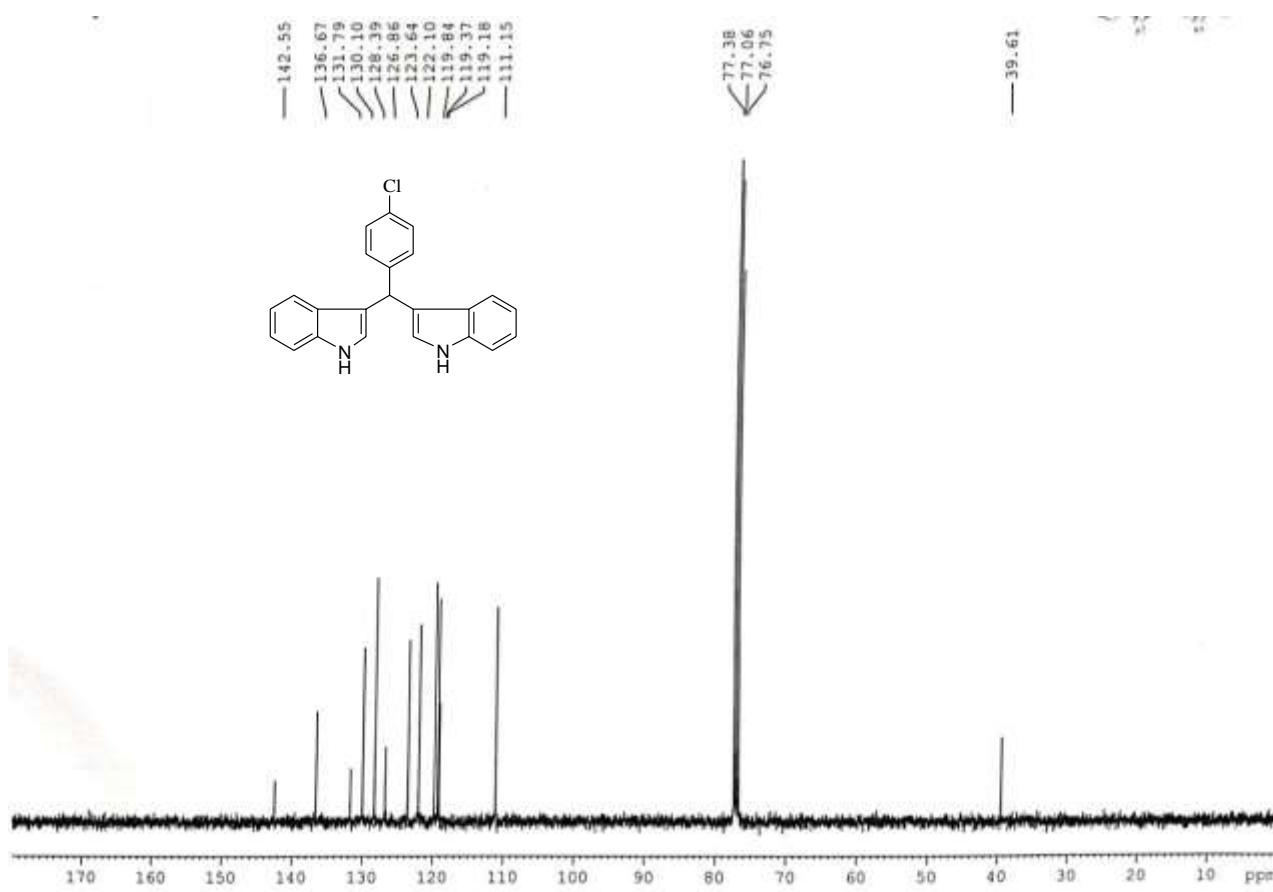
¹³C NMR of **1o** (100 MHz, CDCl₃)



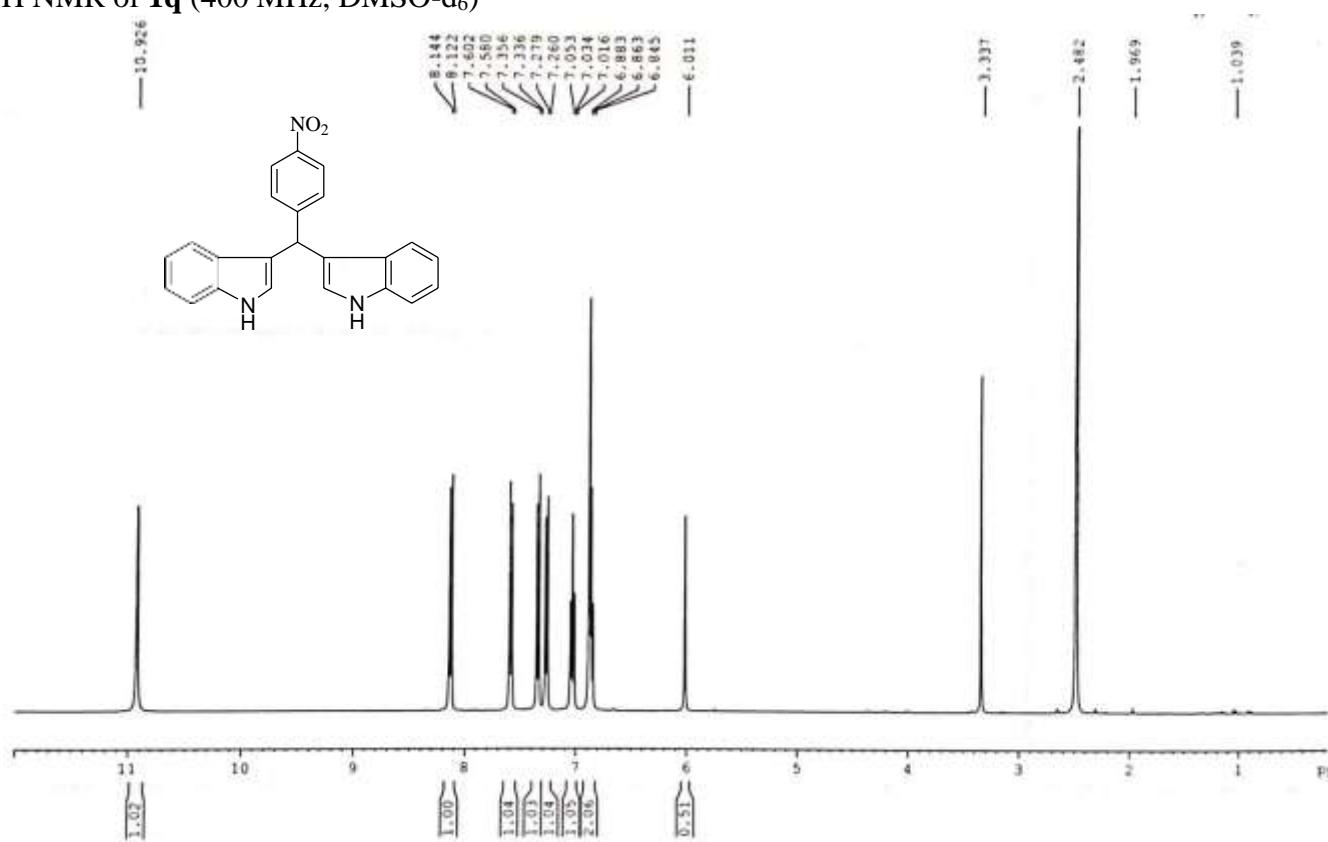
¹H NMR of **1p** (400 MHz, CDCl₃)



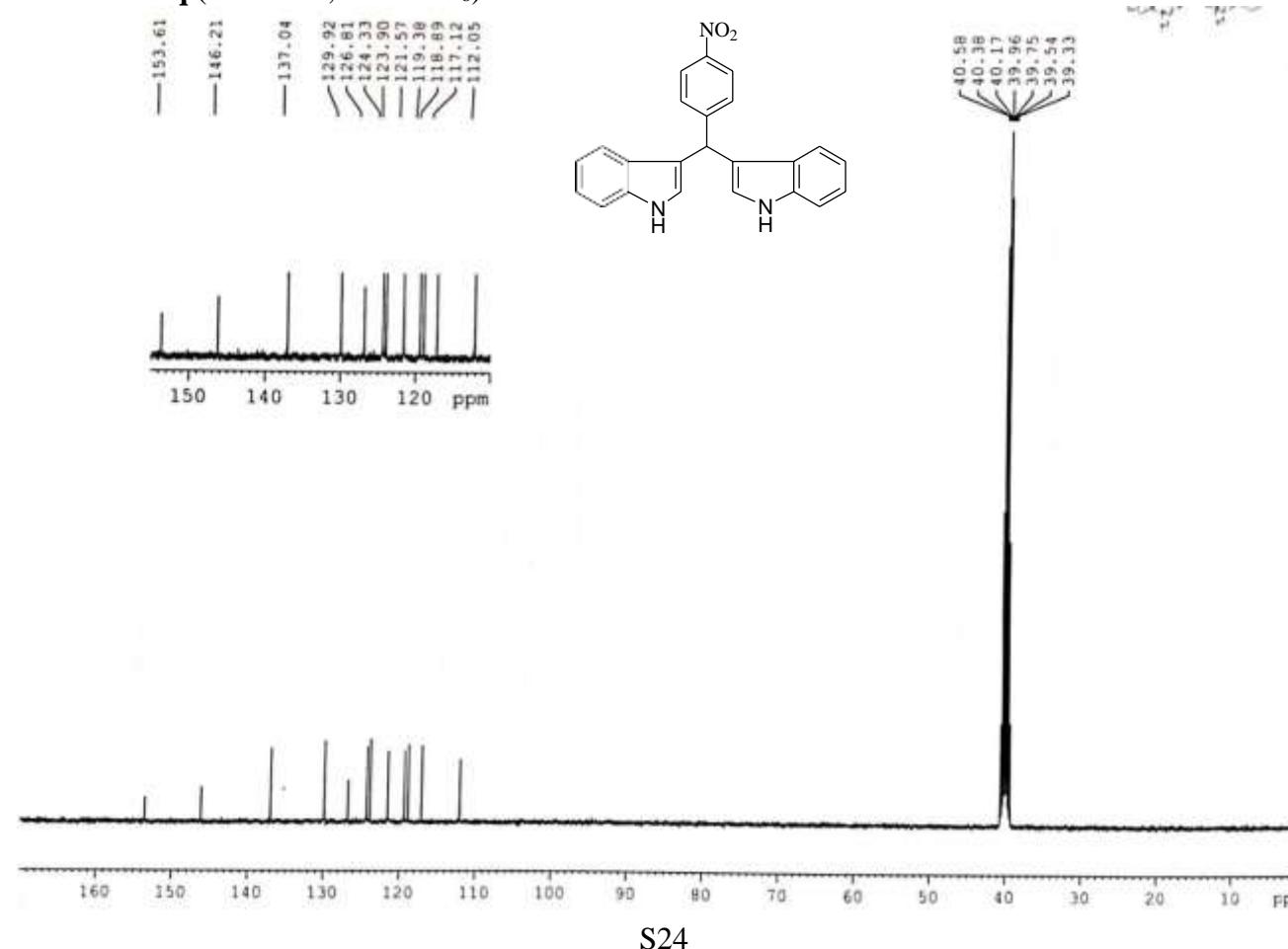
¹³C NMR of **1p** (100 MHz, CDCl₃)



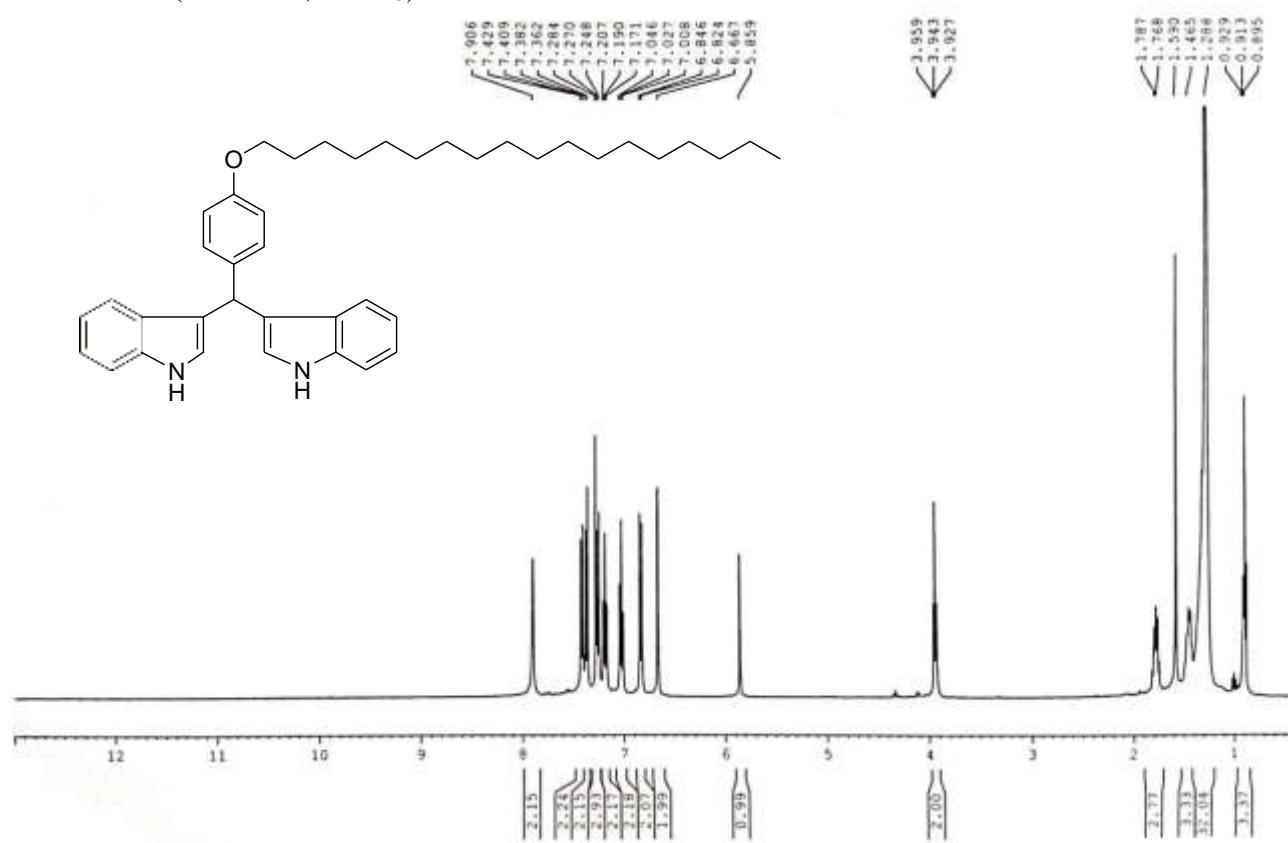
¹H NMR of **1q** (400 MHz, DMSO-d₆)



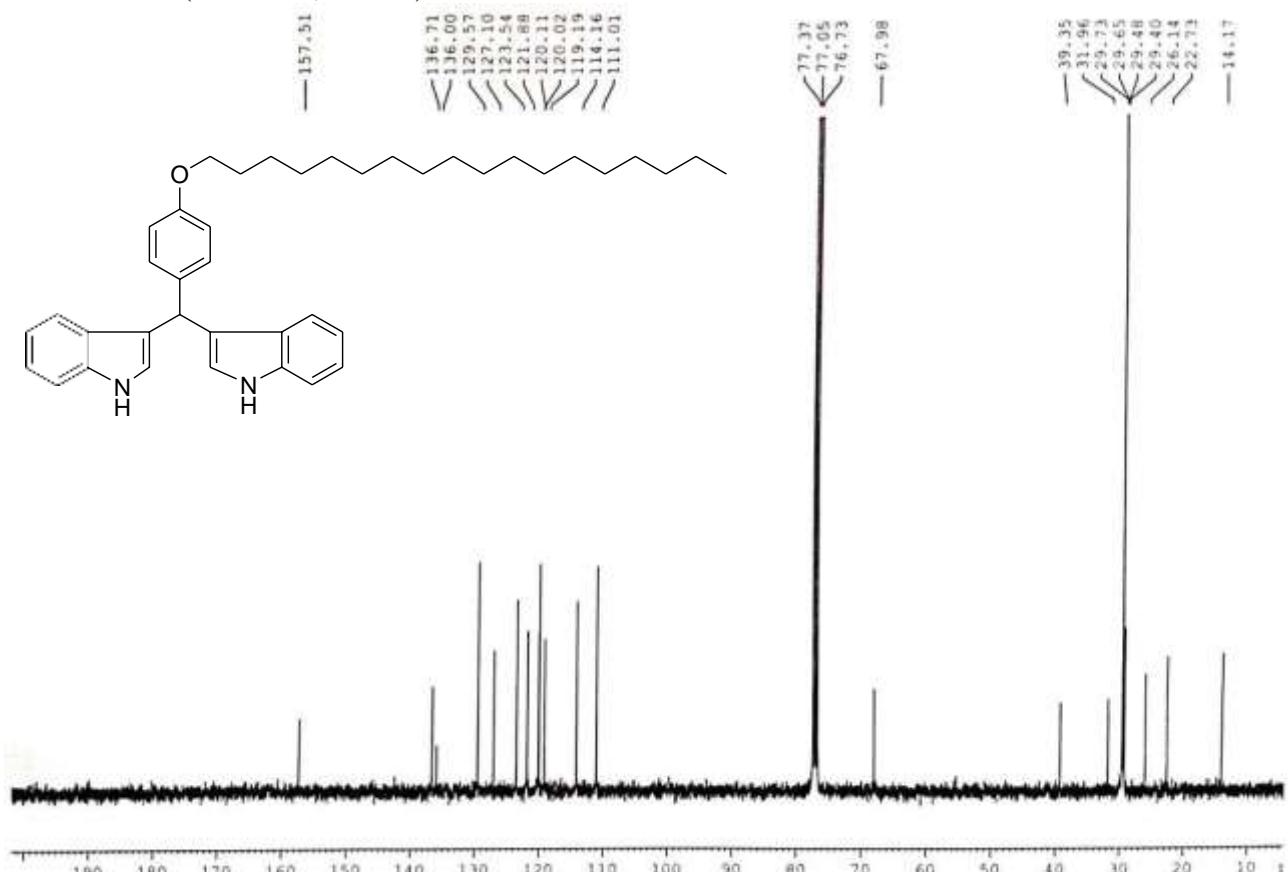
¹³C NMR of **1q** (100 MHz, DMSO-d₆)



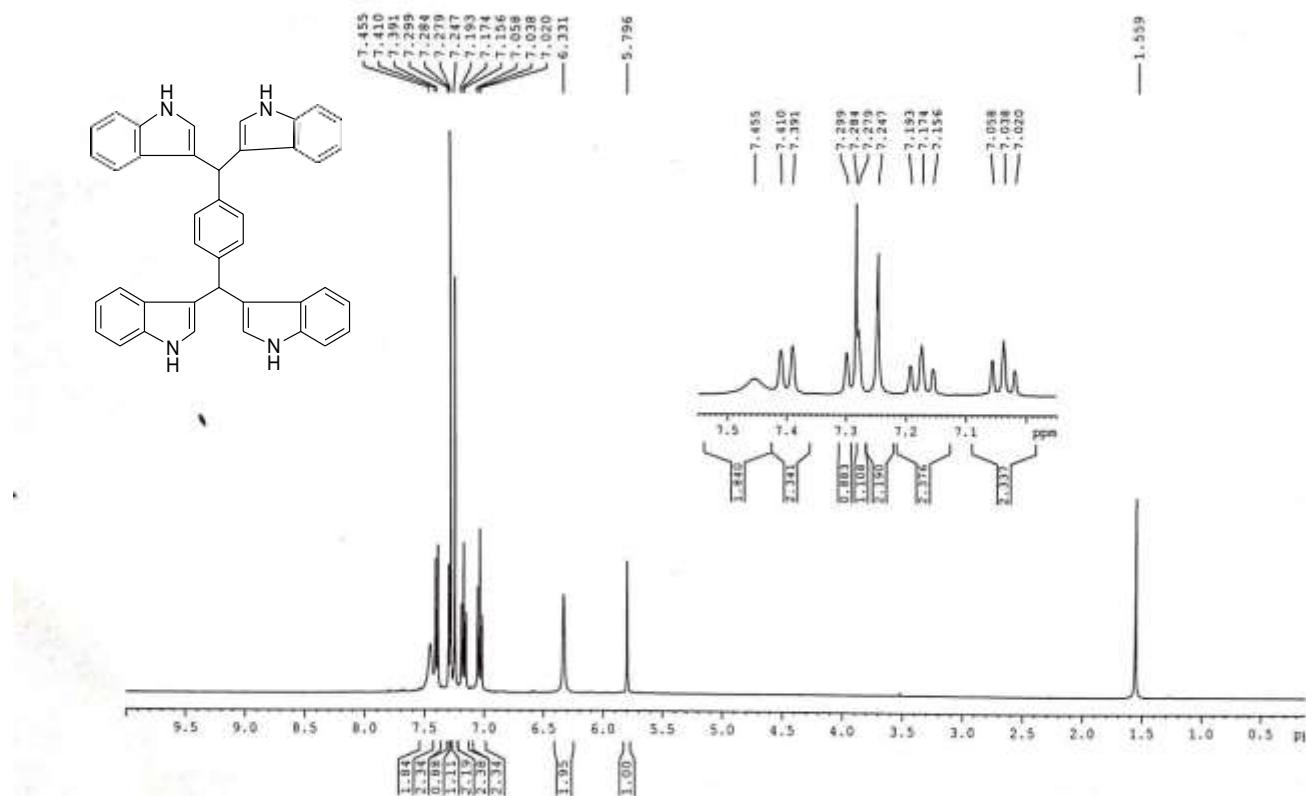
¹H NMR of **1r** (400 MHz, CDCl₃)



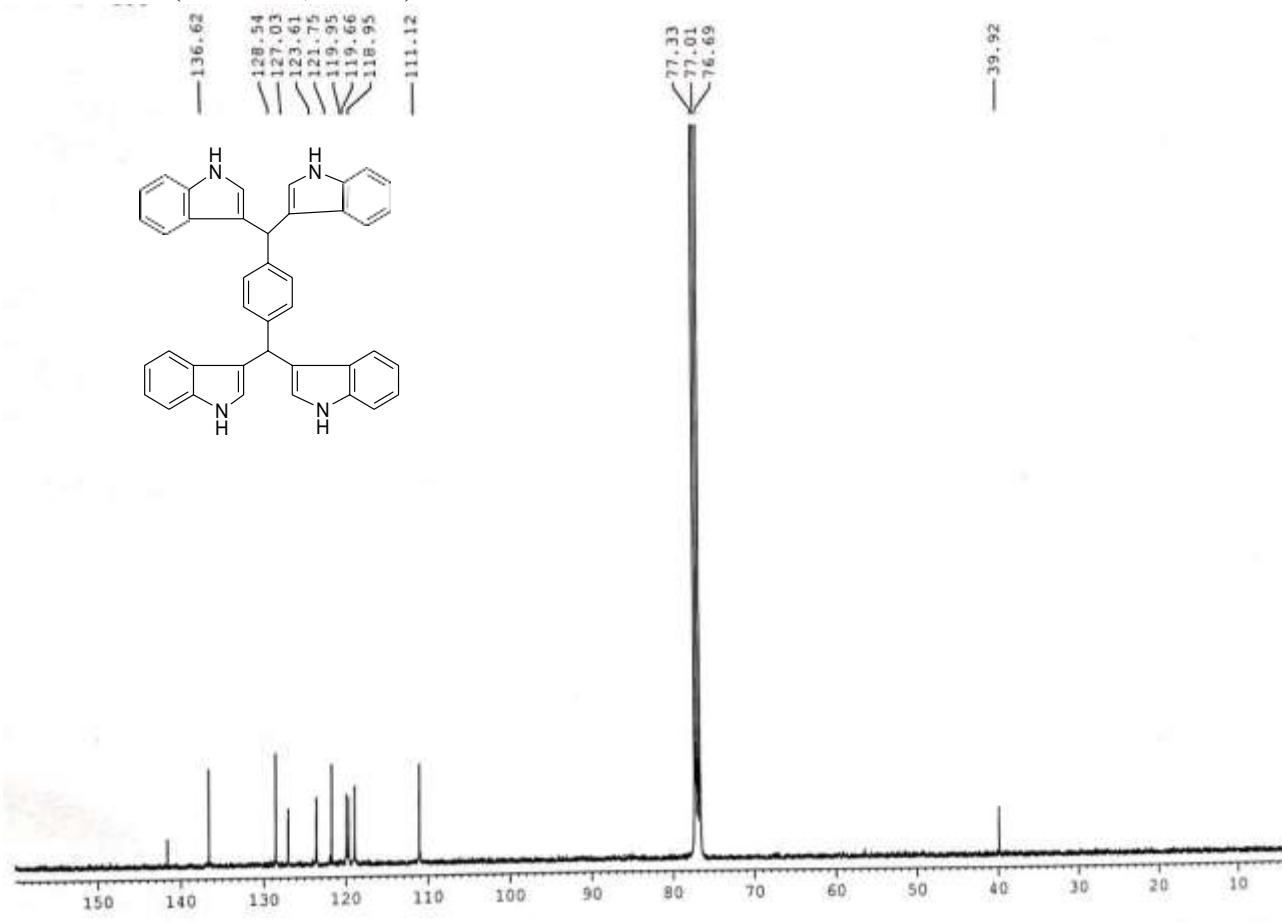
¹³C NMR of **1r** (100 MHz, CDCl₃)



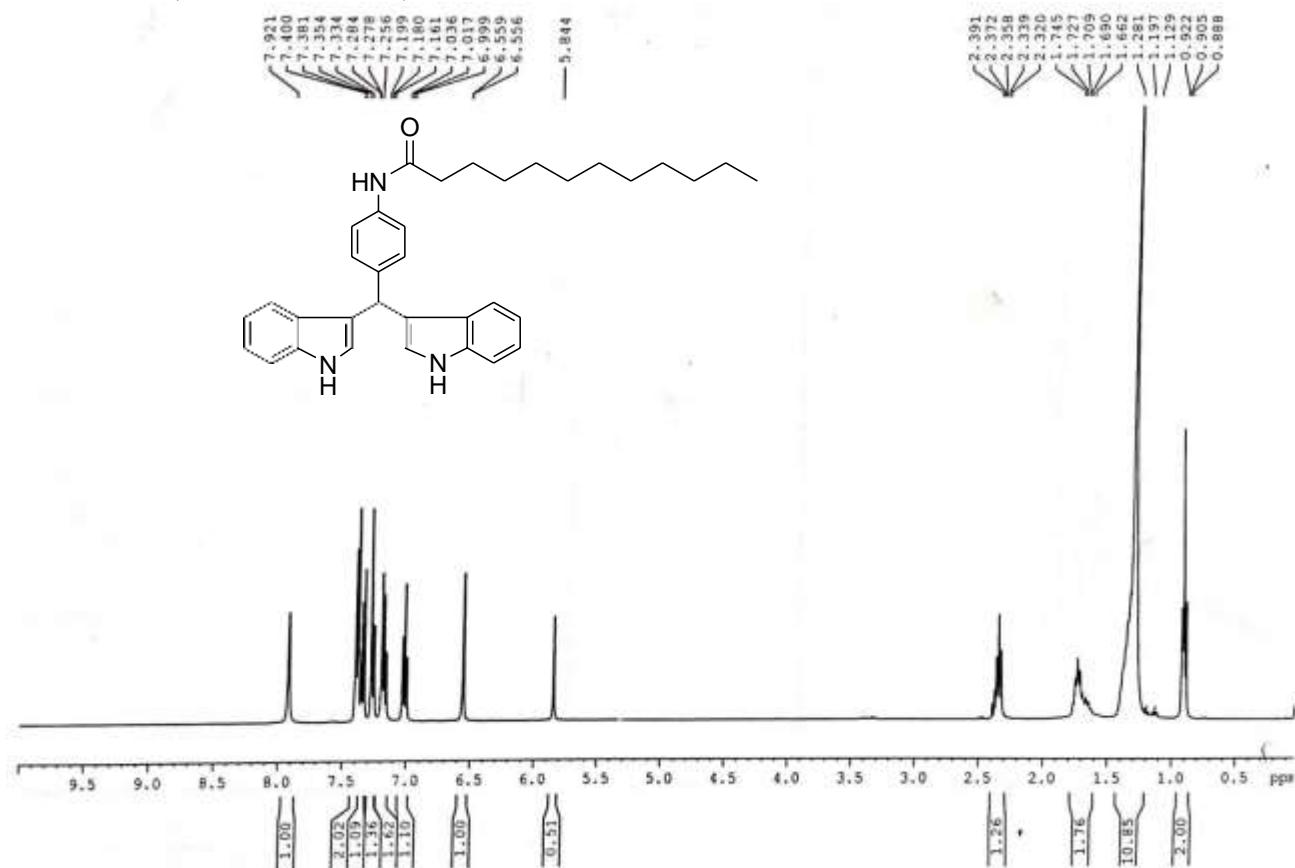
¹H NMR of **1s** (400 MHz, CDCl₃)



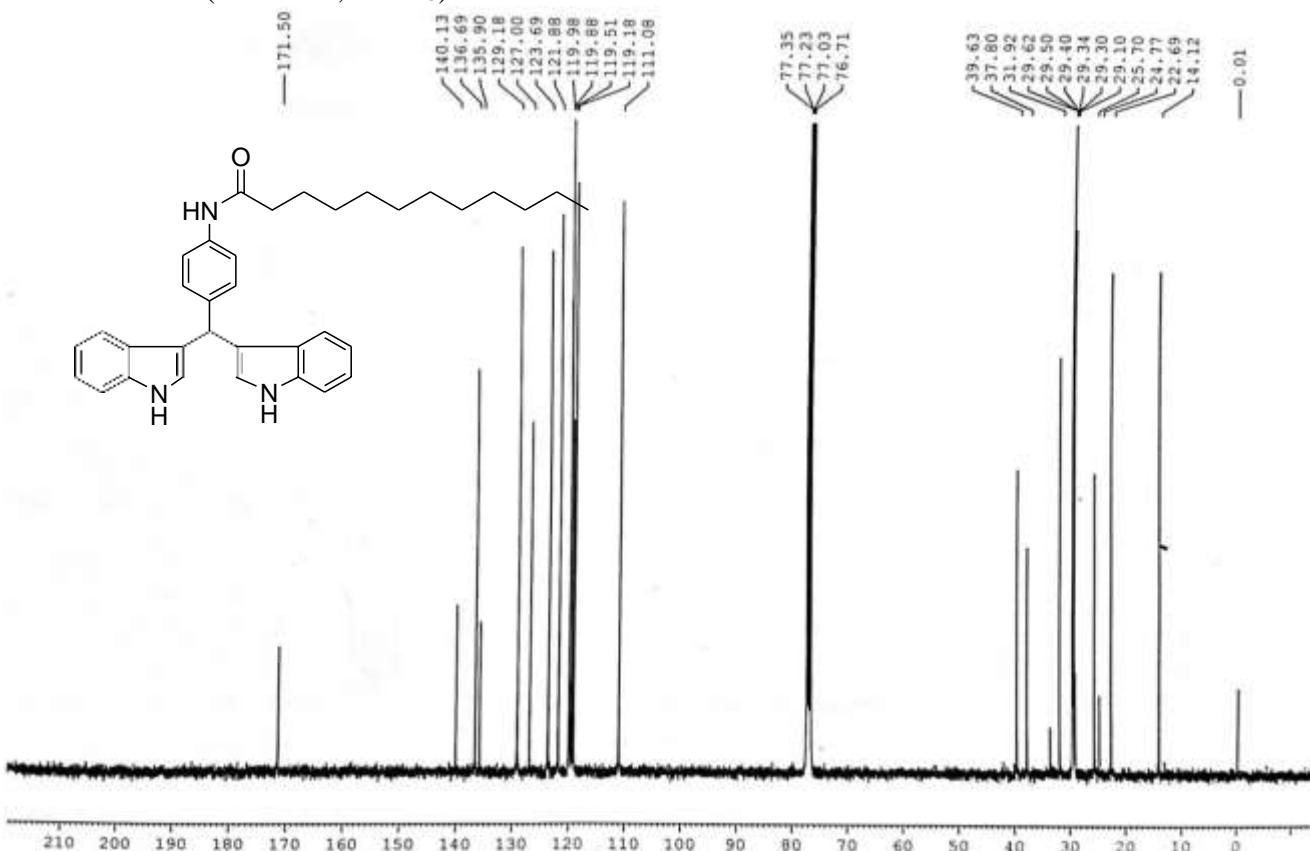
¹³C NMR of **1s** (100 MHz, CDCl₃)



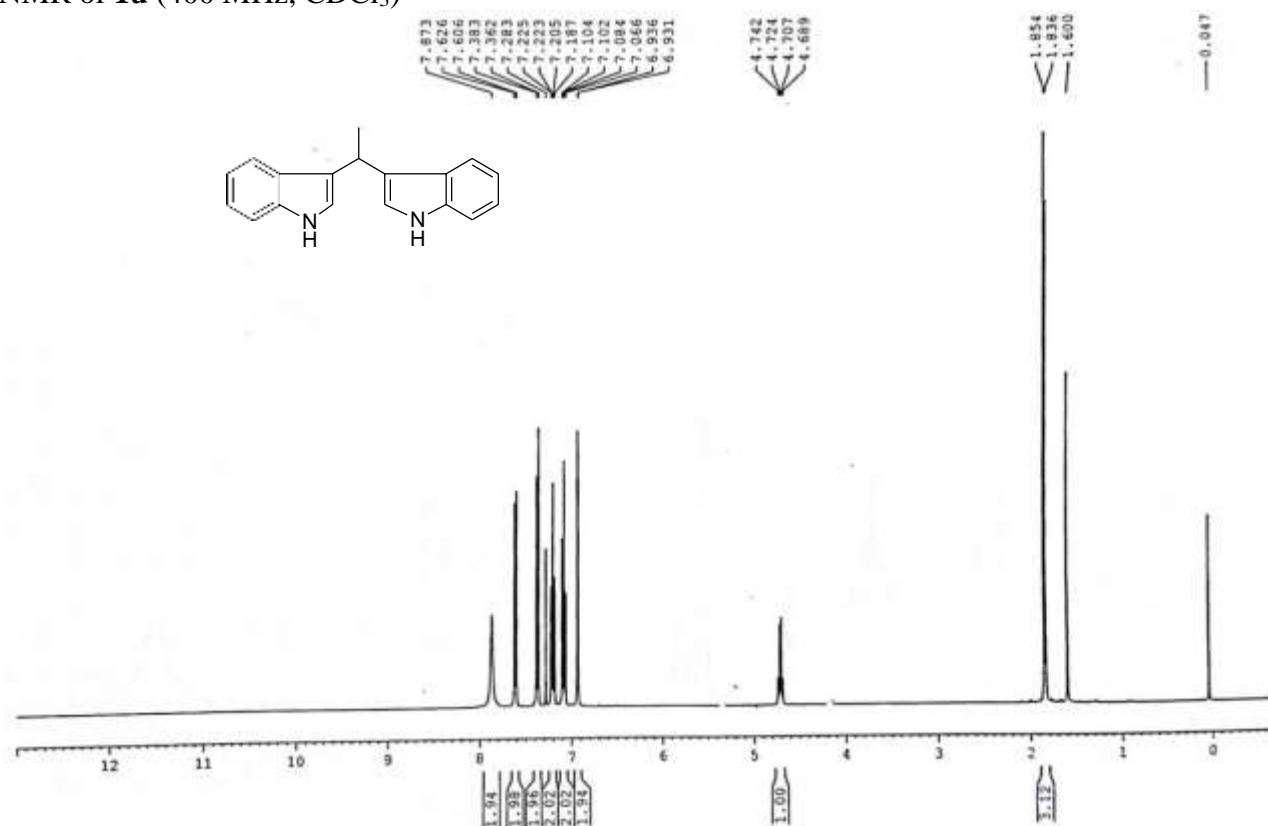
¹H NMR of **1t** (400 MHz, CDCl₃)



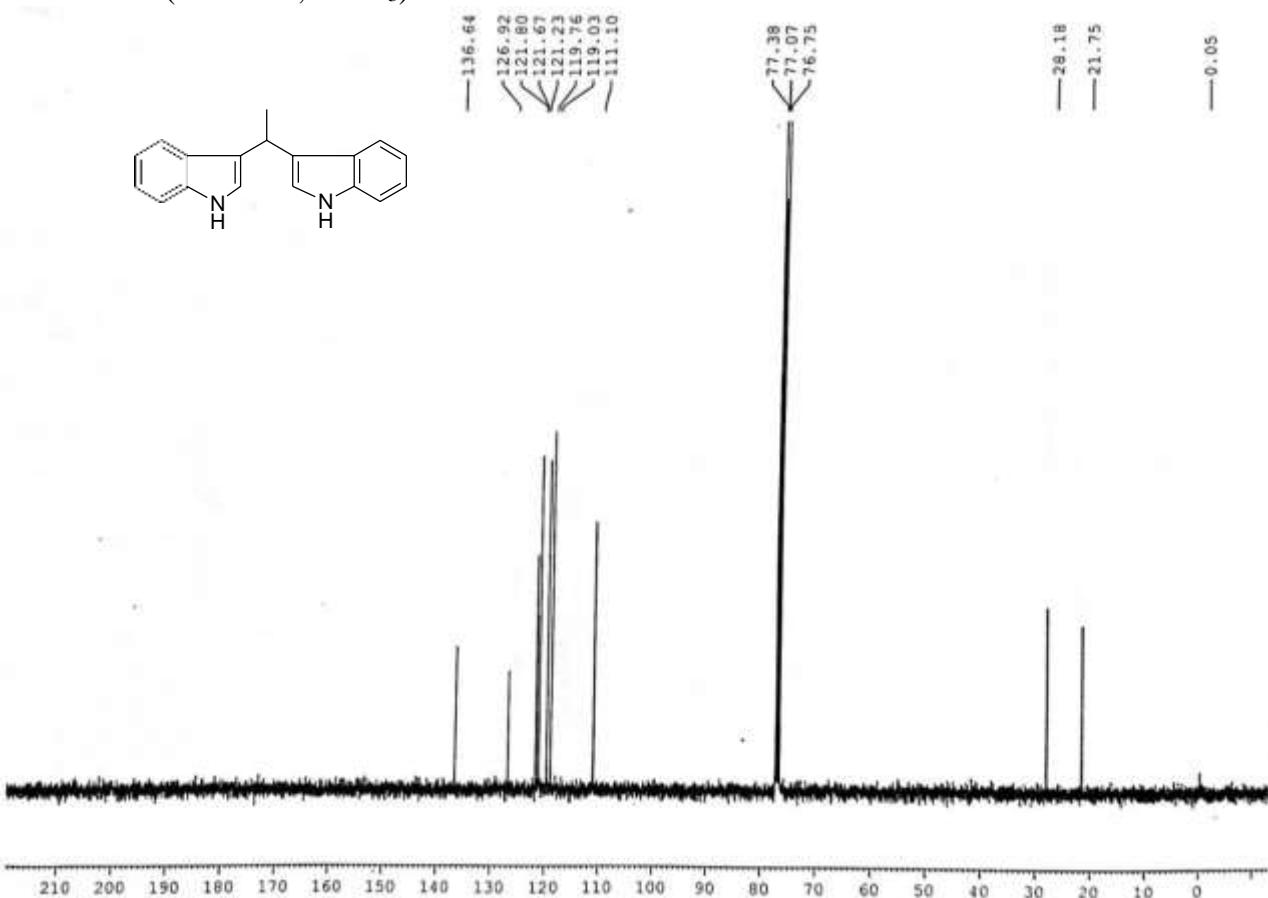
¹³C NMR of **1t** (100 MHz, CDCl₃)



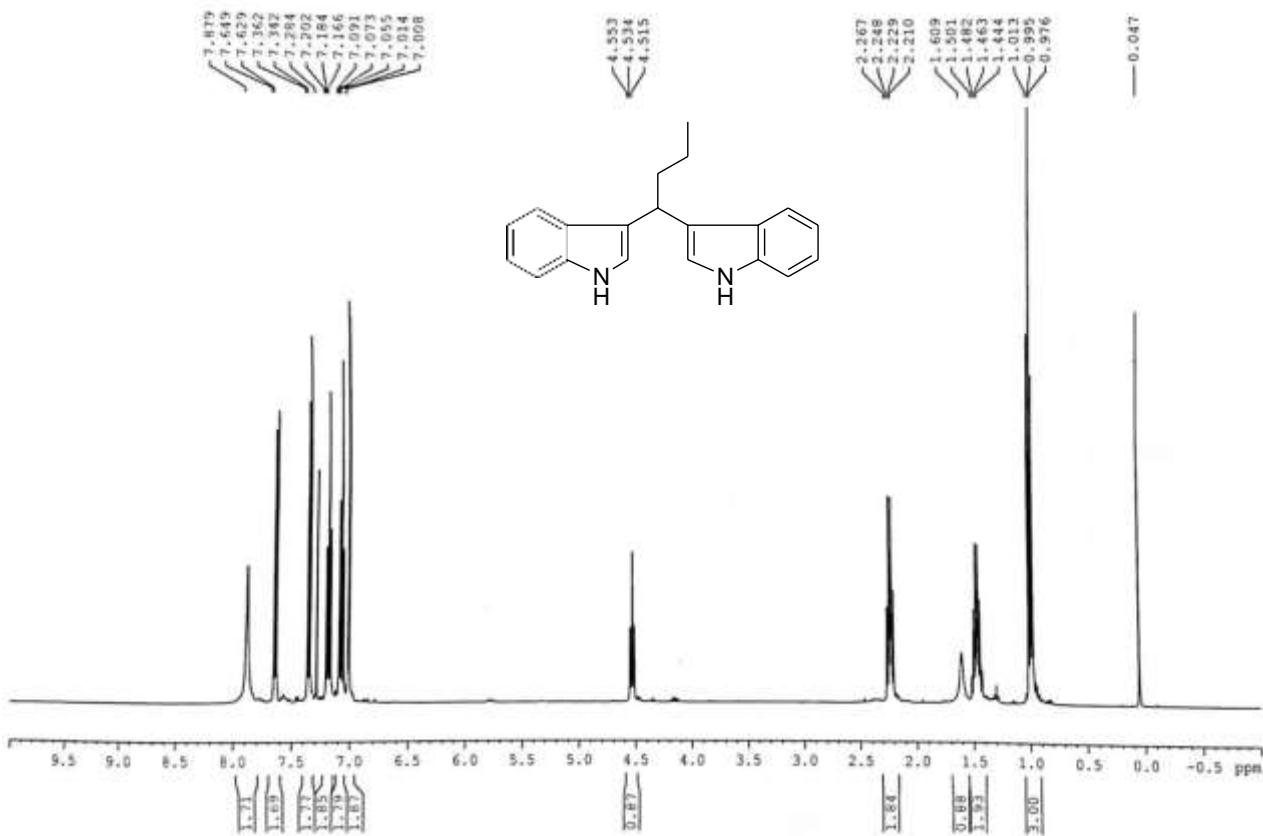
¹H NMR of **1u** (400 MHz, CDCl₃)



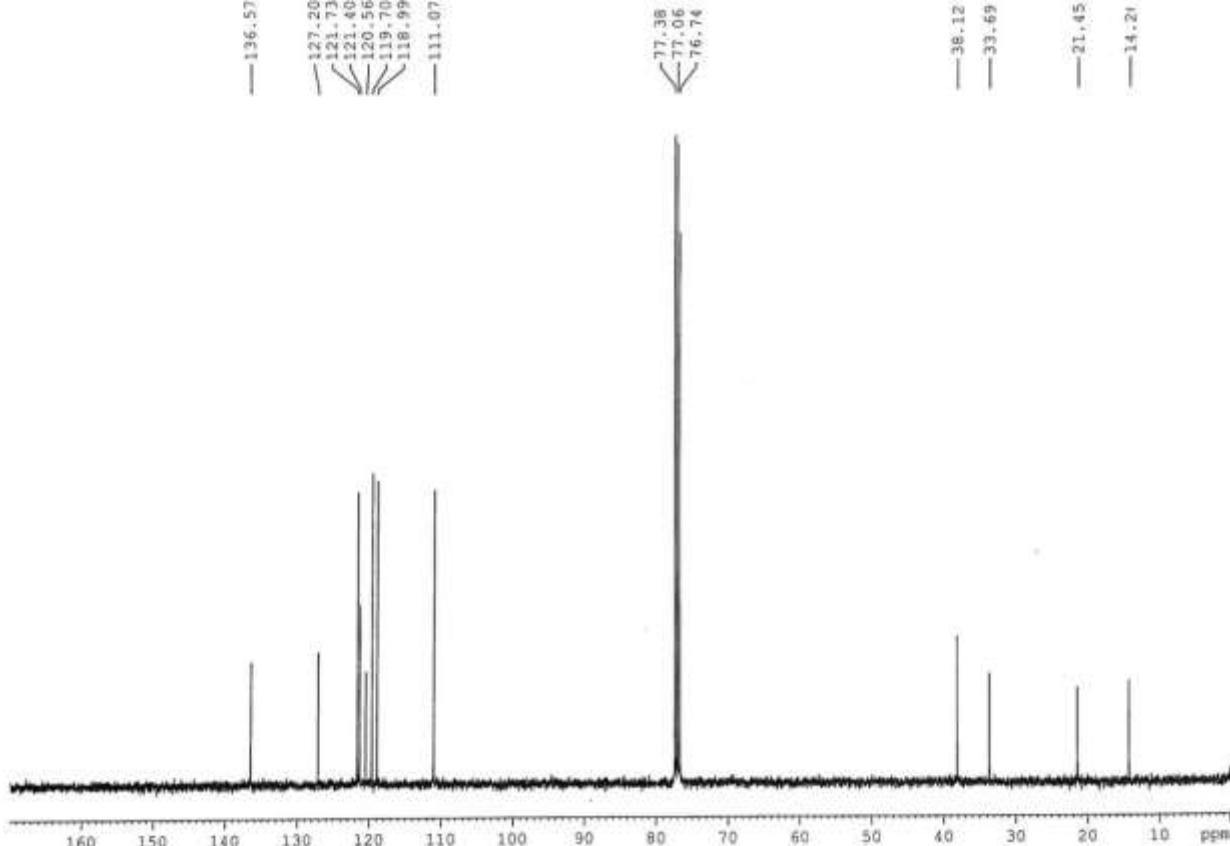
¹³C NMR of **1u** (100 MHz, CDCl₃)



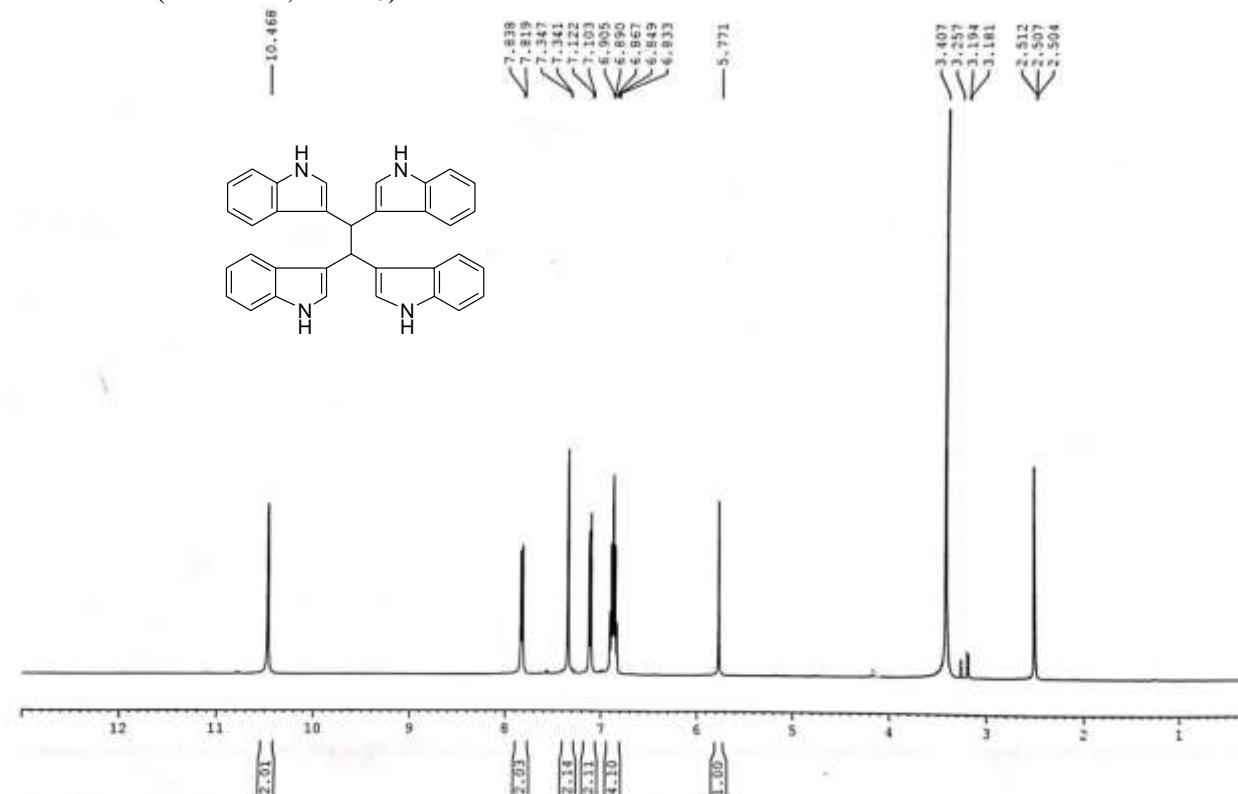
¹H NMR of **1v** (400 MHz, CDCl₃)



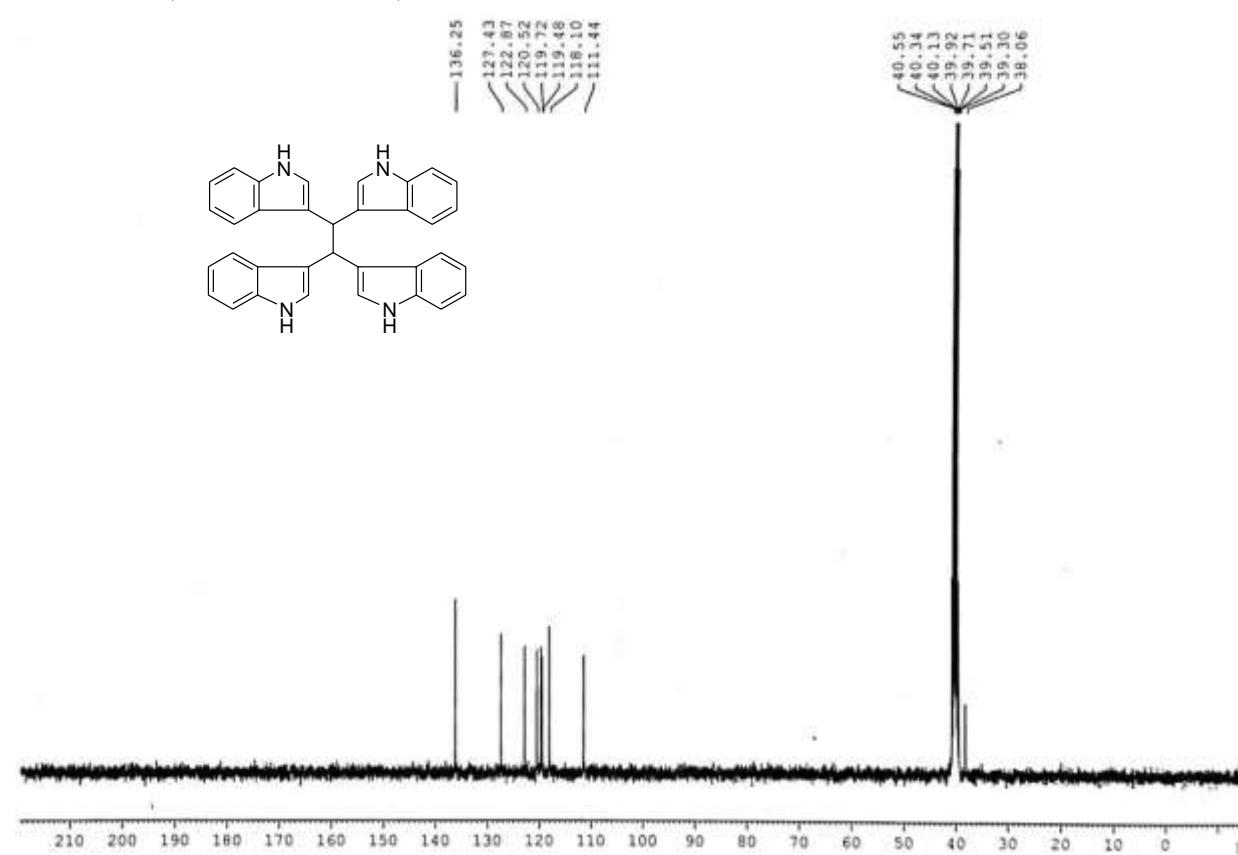
¹³C NMR of **1v** (100 MHz, CDCl₃)



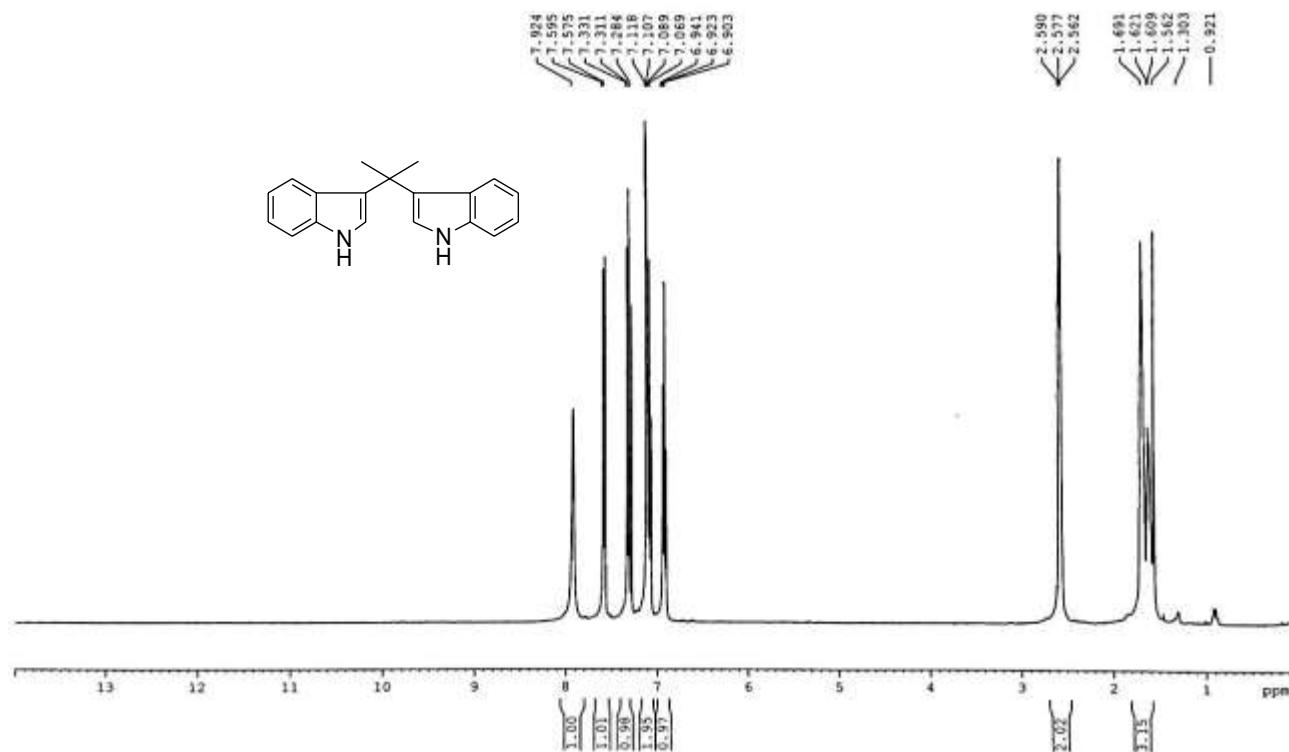
¹H NMR of **1w** (400 MHz, CDCl₃)



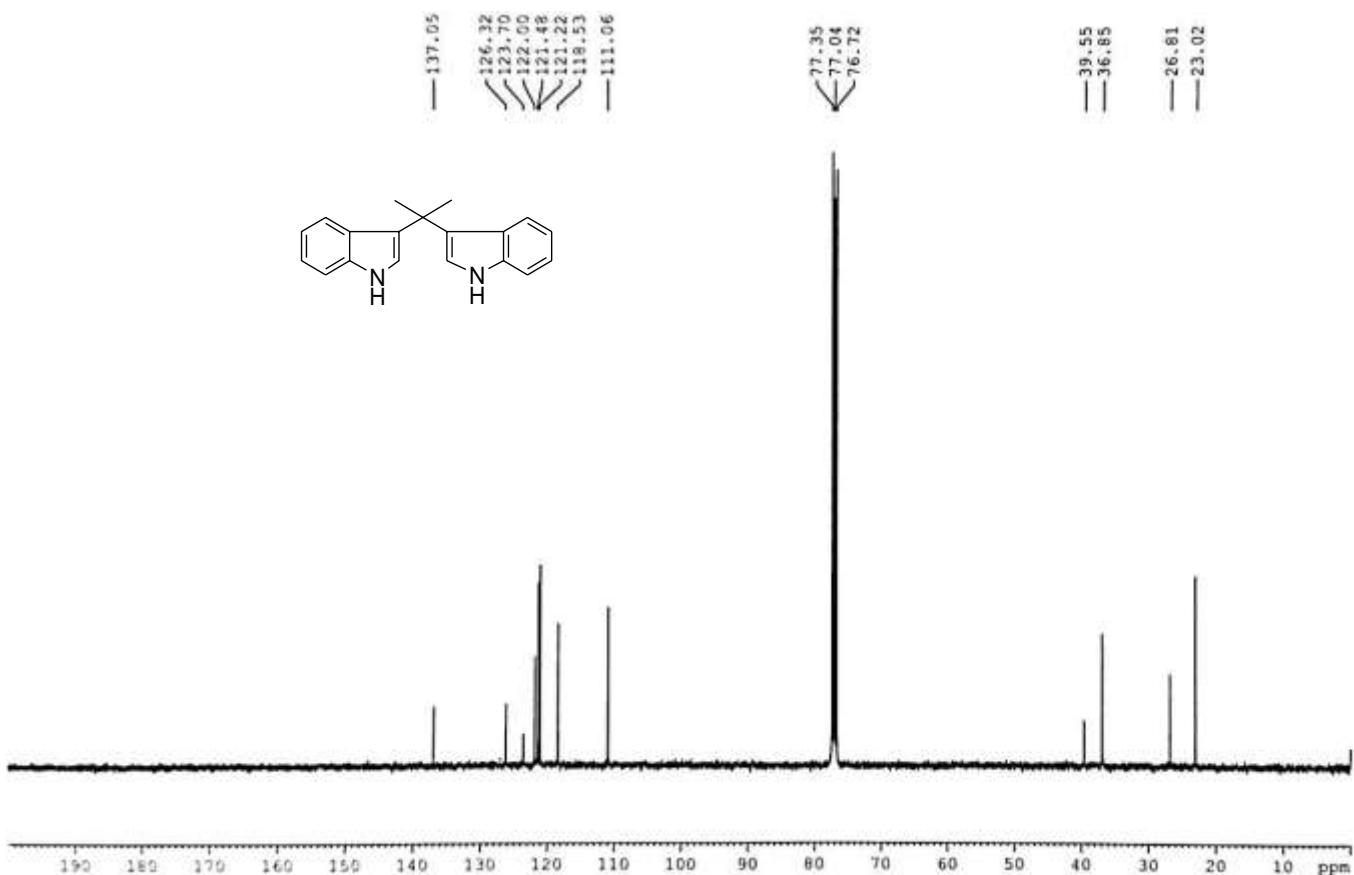
¹³C NMR of **1w** (100 MHz, CDCl₃)



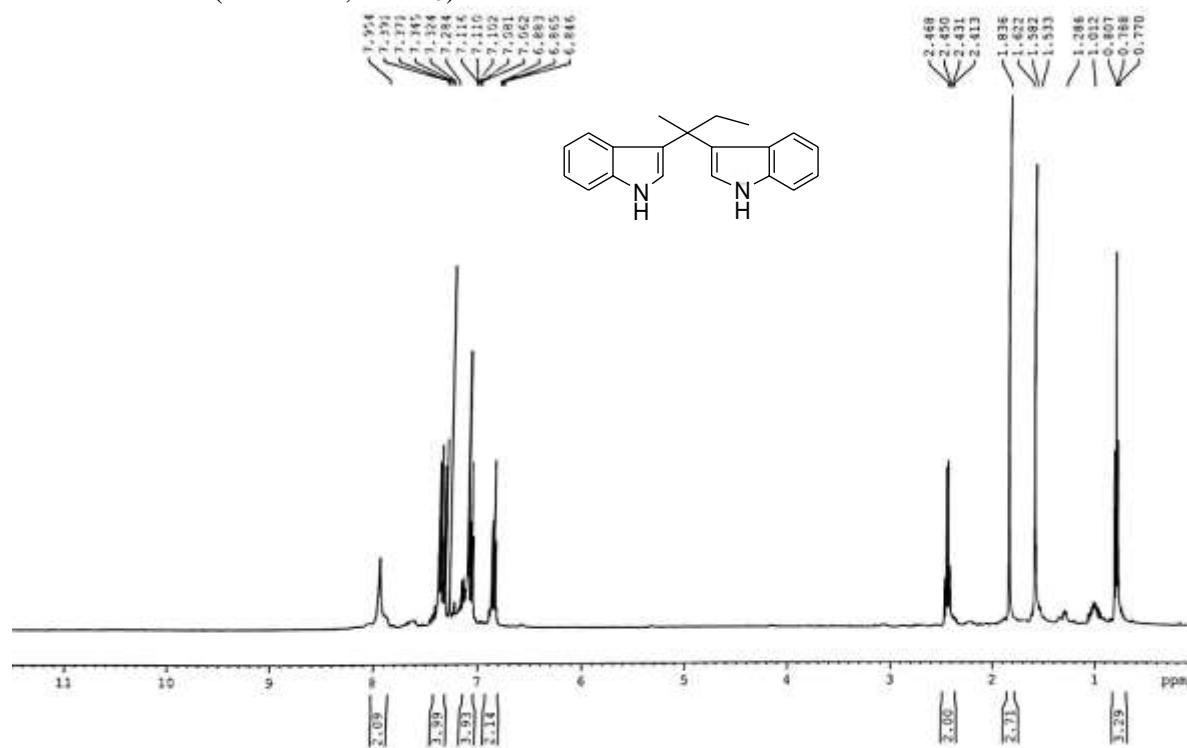
¹H NMR of **2a** (400 MHz, CDCl₃)



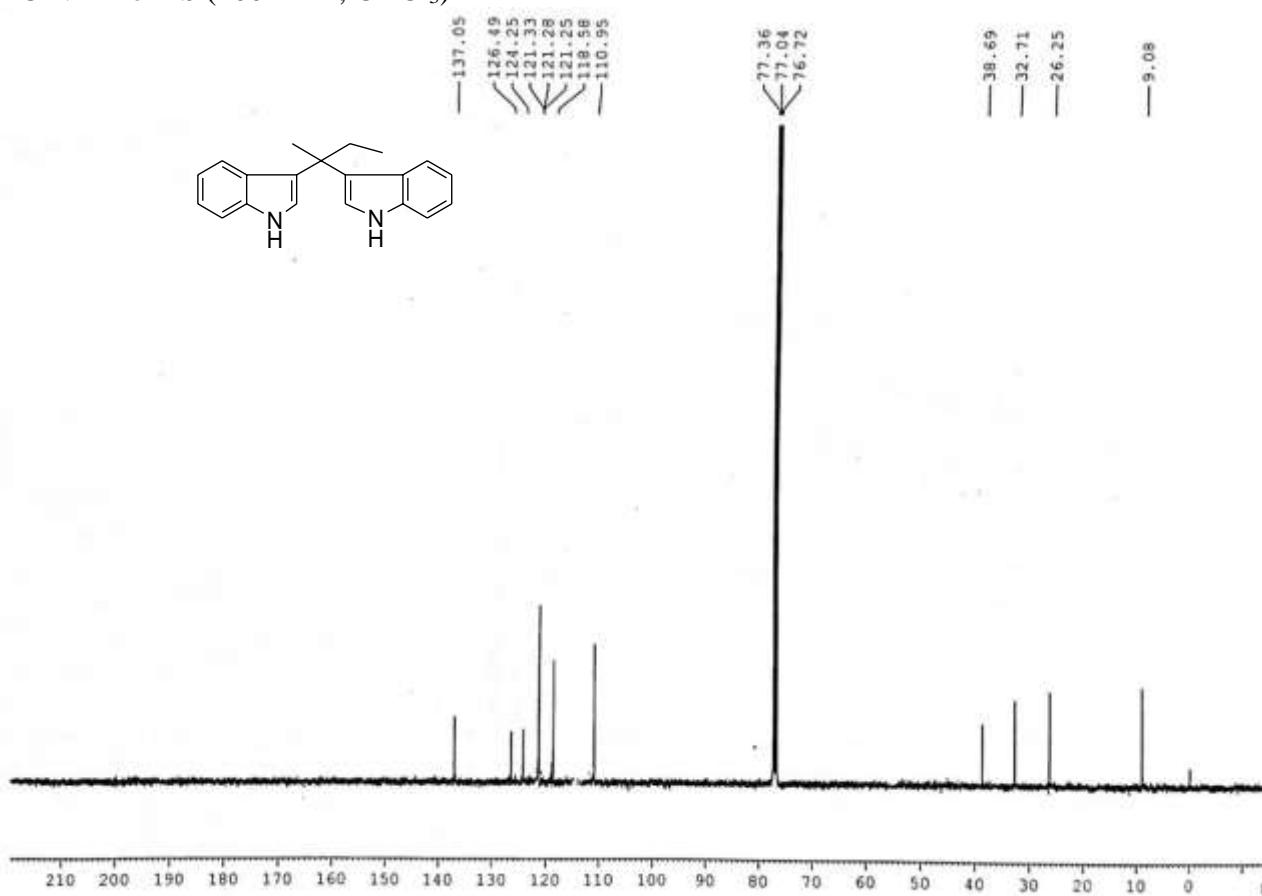
¹³C NMR of **2a** (100 MHz, CDCl₃)



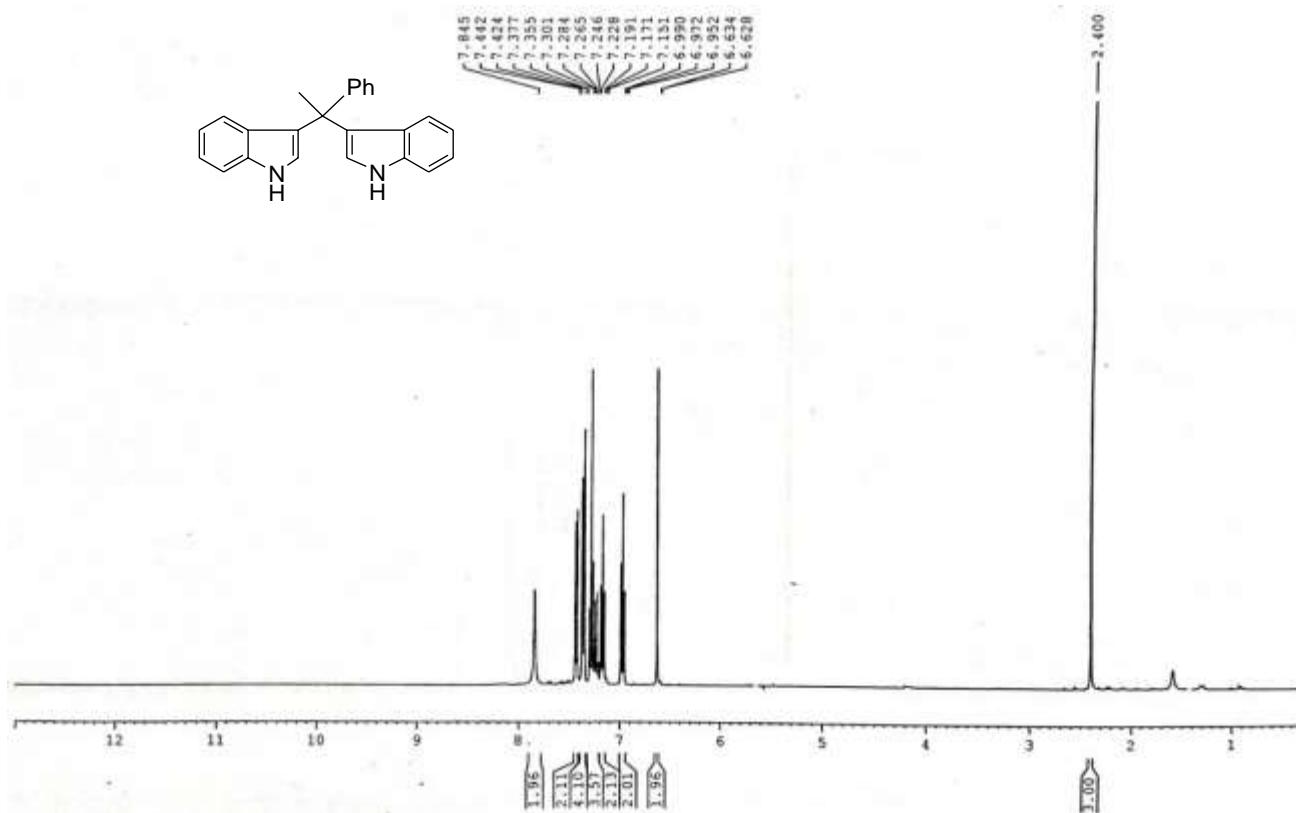
¹H NMR of **2b** (400 MHz, CDCl₃)



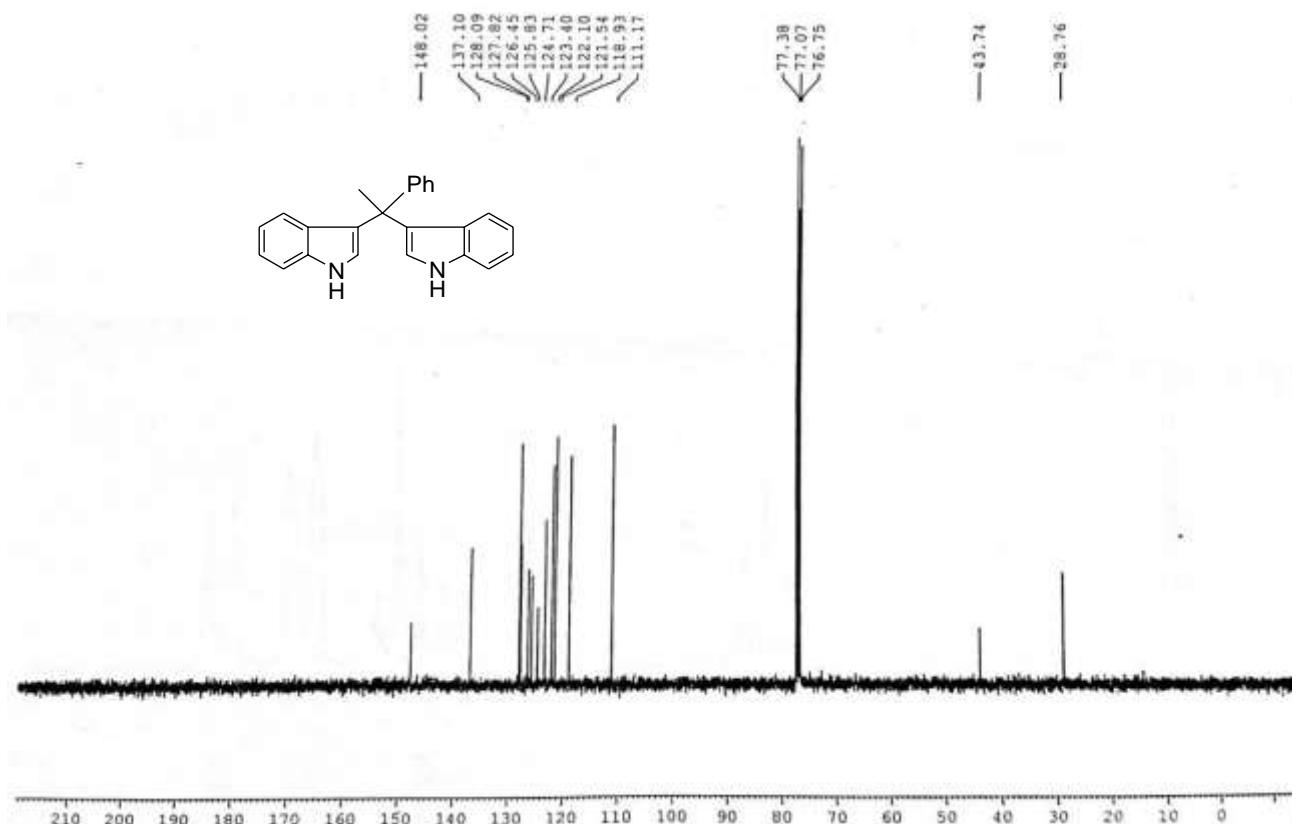
¹³C NMR of **2b** (100 MHz, CDCl₃)



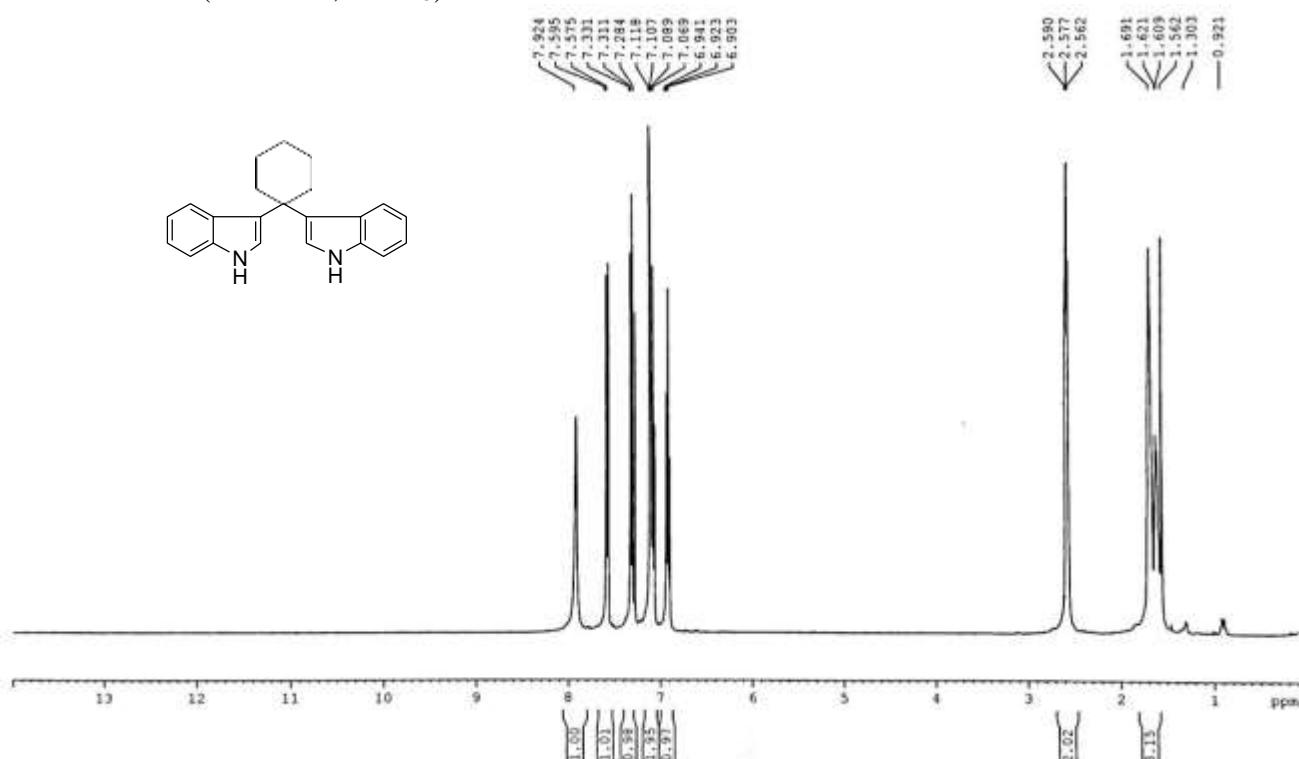
¹H NMR of **2c** (400 MHz, CDCl₃)



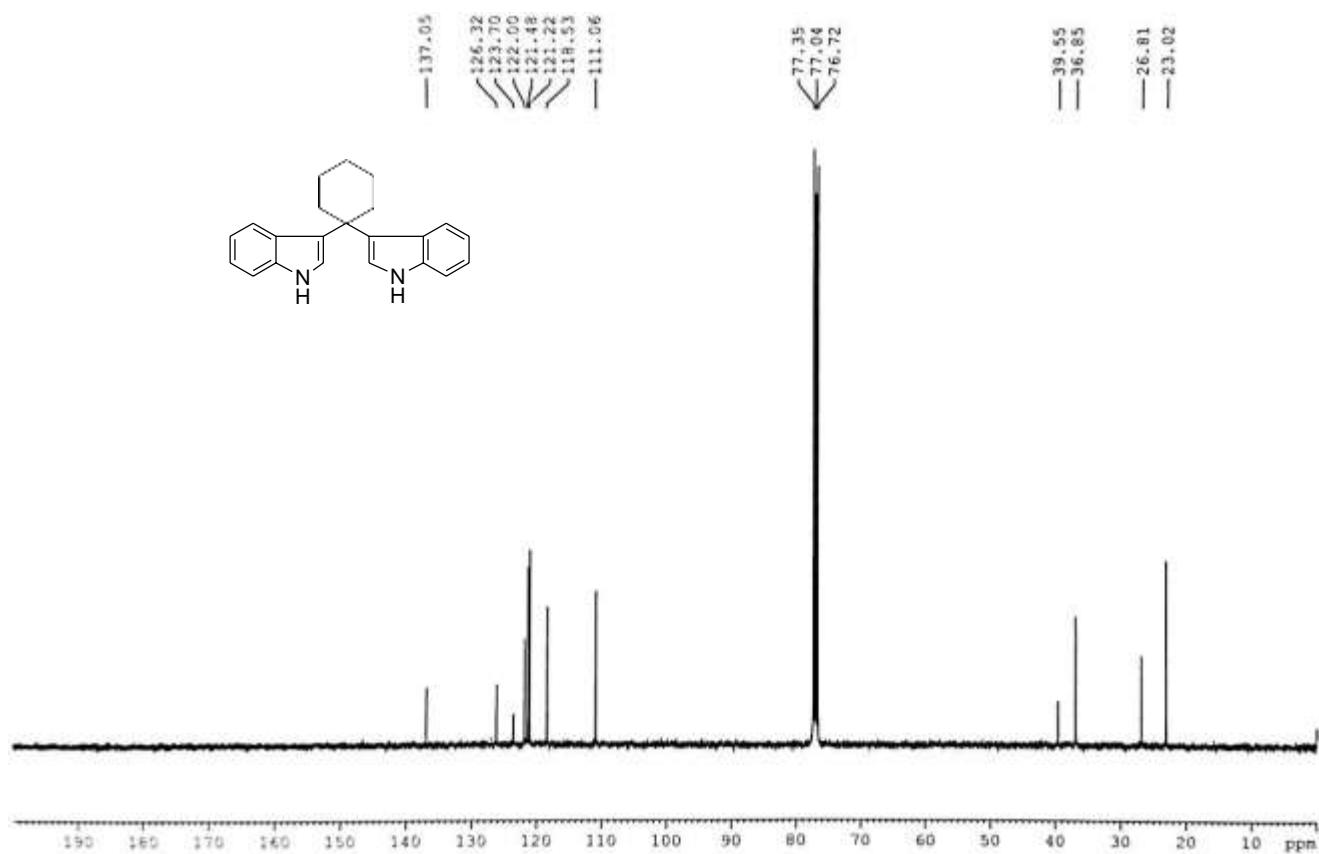
¹³C NMR of **2c** (100 MHz, CDCl₃)



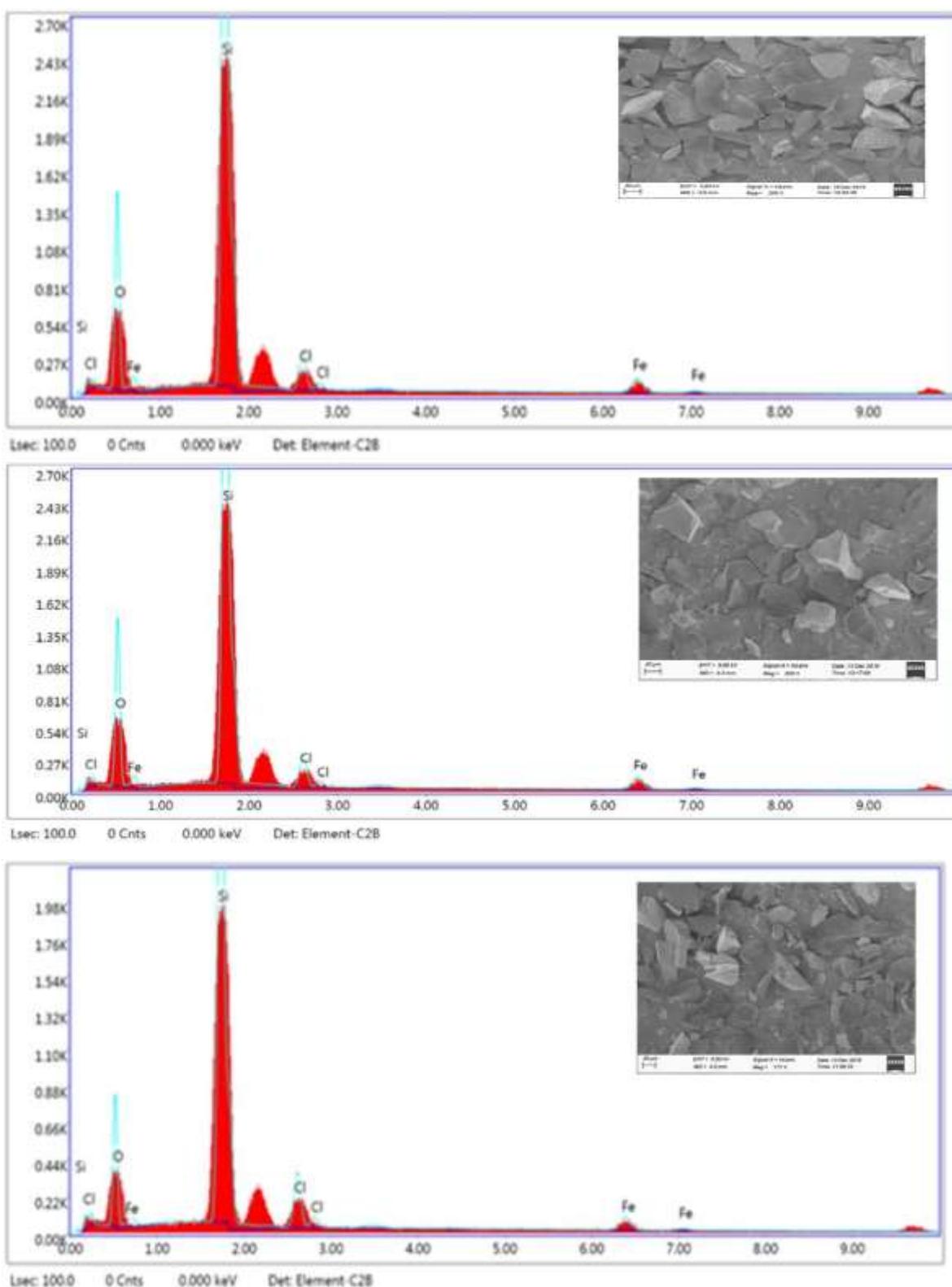
¹H NMR of **2d** (400 MHz, CDCl₃)



¹³C NMR of **2d** (100 MHz, CDCl₃)



Characterization of Silica-supported Ferric Chloride



SEM images and EDX spectra of [A] freshly prepared $\text{SiO}_2\text{-FeCl}_3$; [B] six months old $\text{SiO}_2\text{-FeCl}_3$ and [C] recycled $\text{SiO}_2\text{-FeCl}_3$ after 5th cycle

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