Metal-Free C-H Functionalization and Aromatization Sequence for the Synthesis of 1-(Indol-3-yl)carbazoles and Total Synthesis of 7-Bromo-1-(6-bromo-1*H*-indol-3-yl)-9*H*-carbazole

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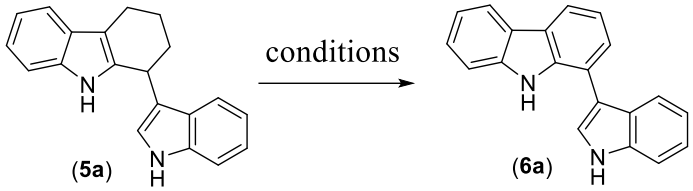
Supporting Information

Contents

General Experimental

All the reactions were monitored by thin layer chromatography using ethyl acetate/hexane system. All reaction solvents used were of GR grade and were distilled before using. All the other commercial reagents were used as received. Evaporation of solvents were performed using a rotary evaporator connected to a membrane pump at various temperatures. All new compounds were characterized by TLC, melting point (m.p.), ^{1}H NMR and ^{13}C NMR, IR, and HRMS (ESI). Analytical TLC was conducted using Merck aluminium sheets covered with silica gel. The plates were either visualized under UV-light and/or stained by dipping in Seebach's magic TLC stain. All the obtained products were purified by column chromatography using silica gel (100–200 mesh). Melting points were measured using a capillary melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded at Bruker 400 and 100 MHz, respectively, or at 500 and 125 MHz, respectively. Chemical shifts are calculated in ppm and the coupling constants (*J*) in Hz. DMSO-d_6, and $CDCl_3$ were used as the solvents and signal positions were measured relative to the signal for DMSO (δ 2.50 ppm for ^{1}H NMR and δ 39.52 ppm for ^{13}C NMR), and $CDCl_3$ (δ 7.26 ppm for 1H NMR and δ 77.16 ppm for ^{13}C NMR). Data are presented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, dd = doublet doublet, t = triplet, q = quartet, m = multiplet). IR spectra were recorded on FT/IR-5300 instrument and are reported in frequency of absorption (cm^{-1}). TOF and quadrupole mass analyser types are used for the HRMS measurements. Single crystal X-ray diffraction data were collected on a Rigaku Oxford XtaLAB Pro-Pilatus3 R 200K-A detector system equipped with a CuK_{α}(λ = 1.54184 Å) MicroMax-003 micro focus sealed tube operated at 50 kV and 0.6 mA or a Bruker D8 Quest-Photon II detector system equipped with a MoKα(λ = 0.71073 Å) micro focus sealed tube operated at 50 kV and 1 mA. Data was collected at 293 K, and the reduction performed using CrysAlisPro or Bruker SAINT Software; the structure was solved and refined using the Bruker SHELXL-2017/1 software.

Table S1: Reaction optimization for aromatization of compound **5a**[a]:



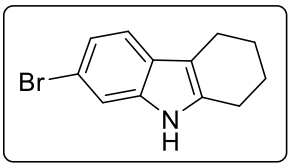
S. No	Reagent	Solvent	Temp	Time	Yield (6a)[b] (%)
1	O_2	Xylene	reflux	24 h	10
2	Chloranil	Xylene	reflux	2 h	50
3	DDQ	1,4-dioxane	rt	1 h	78
4	I_2 (25 mol %)	DMSO	100 ^{o}C	8 h	20
5	NCS	1,4-dioxane	rt	4 h	0
6	NCS, KO^{t}Bu (4.0 equiv)	1,4-dioxane	rt	2 h	5
7	IBX	DMSO	rt	2 h	0
8	DDQ	1,4-dioxane	rt	10 min	81%

[a]Reaction conditions: compound **5a** (0.3 mmol, 1.0 equiv), oxidizing reagent (0.6 mmol, 2.0 equiv), solvent (1.5 mL), [b] Isolated yields.

Synthesis of starting materials (3a-f):

All the tetrahydrocarbazoles other than **3a**[1a] and **3f**[1b] were prepared by refluxing phenylhydrazine hydrochloride (6.0 mmol, 1.0 equiv) with cyclohexanone (6.0 mmol, 1.0 equiv) in presence of 1 mL of con. HCl in ethanol solvent (5 mL) for 1 hour followed by quenching with H_2O, filtration, drying under vacuum and flash column chromatography on silica gel using 5 % ethyl acetate in hexanes (**3b-e**)[1c]

7-Bromo-2,3,4,9-tetrahydro-1*H*-carbazole (3e)[1]



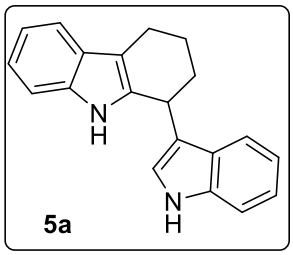
Colorless solid; R_f = 0.46, EtOAc/hexanes (0.5:9.5); ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] 7.60 (br, 1H), 7.36 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.17 (dd, *J* = 7.6, 1.2 Hz, 1H), 2.68 (q, *J* = 6.8 Hz, 4H), 1.93-1.85 (m, 4H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ [ppm] 136.4, 134.8, 126.7, 122.1, 118.9, 114.2, 113.2, 110.3, 23.1, 23.0, 22.9, 20.7.

Synthesis of 1-(1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5a-u)

General procedure:

Tetrahydrocarbazole (**3a-g**) (1.46 mmol) was dissolved in 4 mL of 1,4-dioxane in a RB flask and closed with a glass stopper. NCS (1.46 mmol) was added slowly for five minutes, after which indole (2.19 mmol) was added slowly. After 10 minutes, completion of the reaction was monitored by TLC and, the reaction mixture was quenched with water, extracted with ethyl acetate, the organic layer was washed with water, dried with sodium sulfate and concentrated under vaccum to afford the crude compound (**5a-u**). The crude compound thus obtained was further purified using column chromatography on silica gel. Note: It is difficult to remove residual solvents (ethyl acetate, hexanes) from these compounds. Chasing with appropriate amount of $CHCl_3$ and longer time of drying under high vacuum is needed to obtain pure compound.

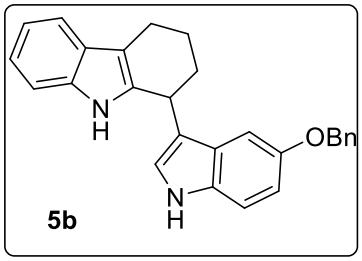
1-(1*H*-Indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5a)[2]



Colorless fluffy solid turns pale pink; Yield = 330 mg (79%); m.p. 154 °C; R_f = 0.46, EtOAc/hexanes (2:8); ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] 8.02 (br s, 1H), 7.64 (br s, 1H), 7.54 (dd, *J* = 5.84, 3.15 Hz, 1H), 7.46 (d, *J* = 7.96 Hz, 1H), 7.39 (d, *J* = 8.15 Hz, 1H), 7.21 (ddd, *J* = 7.82, 1.04 Hz, 1H), 7.17 (ddd, *J* = 3.26, 0.47 Hz, 1H), 7.11-7.04 (m, 3H), 6.96 (d, *J* = 2.35 Hz, 1H), 4.47 (q, *J* = 7.2, 5.8 Hz, 1H), 2.88-2.84 (m, 2H), 2.33-2.26 (m, 1H), 2.17-2.07 (m, 2H), 1.95-1.85 (m,

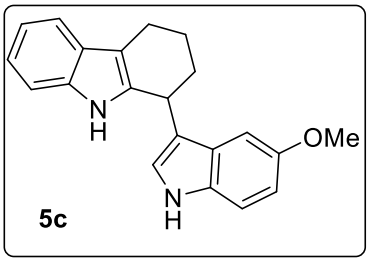
1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ [ppm] 136.6 (2C), 135.8, 127.9, 126.7, 122.4, 122.3, 121.2, 119.8, 119.2, 119.1, 118.6, 118.1, 111.4, 110.8, 110.6, 32.6, 32.2, 22.6, 21.3; IR (neat, cm^{-1}) 3407, 2931, 2851, 1640, 1457, 1299, 1234, 1093, 1009, 742; HRMS (ESI-TOF) Calcd for $C_{20}H_{18}N_2$ $[M+H]^+$ 287.1543, Found: 287.1542.

1-(5-(Benzyloxy)-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5b)[2]



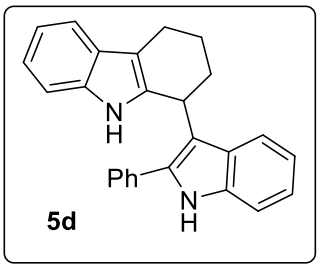
Pale pink solid; Yield = 412 mg, (90%); m.p. 242-244 ºC; R_f = 0.40, EtOAc/hexanes (2:8); ^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] 10.71 (br s, 1H), 10.39 (br s, 1H), 8.30 ($CHCl_3$ impurity), 7.44 (d, *J* = 7.59 Hz, 1H), 7.35-7.30 (m, 5H), 7.27 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 1.5 Hz, 1H), 6.84 (s, 1H), 6.79 (d, *J* = 9.9 Hz, 1H), 4.91 (s, 2H), 4.44 (t, *J* = 5.94 Hz, 1H), 2.79-2.72 (m, 2H), 2.21-2.16 (m, 1H), 1.98-1.89 (m, 2H), 1.80-1.71 (m, 1H); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6) δ [ppm] 151.7, 137.7, 136.6, 136.0, 131.8, 128.2 (2C), 127.5 (2C), 127.4, 127.0, 126.6, 123.8, 120.1, 117.9, 117.3, 117.2, 112.0, 111.5, 110.8, 108.8, 102.3, 79.2 ($CHCl_3$ impurity), 69.2, 32.1, 31.6, 21.3, 20.9; IR(neat, cm^{-1}) 3390, 3319, 3032, 2927, 2835, 1619, 1483, 1451, 1329, 1271, 1214, 1183, 1008; HRMS (ESI-TOF) Calcd for $C_{27}H_{24}N_2O$ $[M+H]^+$ 393.1961, Found: 393.1960.

1-(5-Methoxy-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-carbazole (5c)[3]



Colorless solid; Yield = 152 mg (83%); m.p. 274 ºC; R_f = 0.40, EtOAc/hexanes (2:8); ^{1}H NMR (400 MHz, DMSO-d_6) δ [ppm] 10.70 (br s, 1H), 10.39 (br s, 1H), 8.32 ($CHCl_3$ impurity), 7.40 (d, *J* = 7.1 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 6.99-6.90 (m, 2H), 6.85 (d, *J* = 2.40 Hz, 1H), 6.76 (d, *J* = 2.3 Hz, 1H), 6.70 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.43 (t, *J* = 5.6 Hz, 1H), 3.60 (s, 3H), 2.80-2.70 (m, 2H), 2.21-2.15 (m, 1H), 1.99-1.88 (m, 2H), 1.80-1.76 (m, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$+DMSO-d_6) δ [ppm] 153.6, 136.5, 135.7, 131.7, 127.5, 126.9, 123.3, 120.7, 118.5, 117.7 (2C), 112.1, 111.6, 110.6, 110.1, 100.6, 55.7, 32.1, 31.8, 22.0, 21.0; IR (neat, cm^{-1}) 3401, 2934, 2854, 1642, 1484, 1454, 1296, 1273, 1211, 1173, 798, 740; HRMS (ESI-TOF) Calcd for $C_{21}H_{20}N_2O$ $[M+H]^+$ 317.1648, Found: 317.1648.

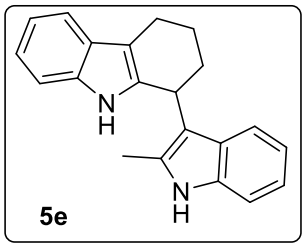
1-(2-Phenyl-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5d)[3]



Colorless solid; Yield = 340 mg (81%); m.p. 230 ºC; R_f = 0.50, EtOAc/hexanes (2:8); ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] 8.12 (br s, 1H), 7.61-7.55 (m, 4H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.14 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.12-7.06 (m, 3H), 7.03 (d, *J* = 7.94 Hz, 1H), 6.87 (t, *J* = 7.9 Hz, 1H), 4.61-4.58 (m, 1H), 2.98-2.87 (m, 2H), 2.38-2.30 (m, 1H), 2.29-2.20 (m, 2H), 1.92-1.88 (m, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ [ppm] 136.8, 136.2, 136.1, 135.9, 133.0, 129.1 (2C), 128.6 (3C), 128.3, 128.1,127.7,

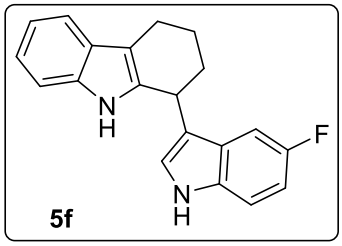
122.5, 121.0, 120.7, 120.1, 119.1, 118.1, 113.9, 110.9, 110.5, 32.9, 32.3, 24.0, 21.3; IR (neat, cm^{-1}) 3387, 2926, 2846, 1735, 1484, 1457, 1444, 1299, 1238; HRMS (ESI-TOF) Calcd for $C_{26}H_{22}N_2$ $[M+H]^+$ 363.1856, Found: 363.1860.

1-(2-Methyl-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5e) [2]



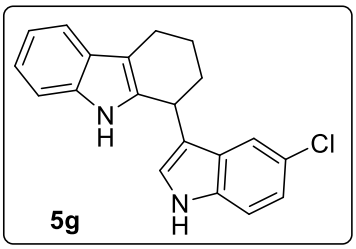
Yellow color fluffy solid; Yield = 267 mg (77%); m.p. 110 °C; R_f = 0.47, EtOAc/hexanes (2:8); ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] 7.80 (br s, 1H), 7.57 (br s, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.13 (dt, *J* = 6.3, 2.1 Hz, 2H), 7.10-7.06 (m, 3H), 6.88 (t, *J* = 7.4 Hz, 1H), 4.41 (d, *J* = 5.0 Hz, 1H), 2.96-2.83 (m, 2H), 2.32 (s, 3H), 2.21-2.16 (m, 2H), 2.14-2.07 (m, 1H), 1.98-1.90 (m, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ [ppm] 136.7, 135.9, 135.4, 131.9, 128.1, 127.9, 121.2, 121.1, 119.6, 119.1, 119.0, 118.1, 113.0, 110.8, 110.7, 110.3, 32.5, 32.2, 23.7, 21.3, 12.0; IR (neat, cm^{-1}) 3414, 2924, 2851, 1643, 1512, 1450, 1412, 1314, 1264, 1091, 731; HRMS (ESI-TOF) Calcd for $C_{21}H_{20}N_2$ $[M+H]^+$ 301.1699, Found: 301.1699.

1-(5-Fluoro-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5f)



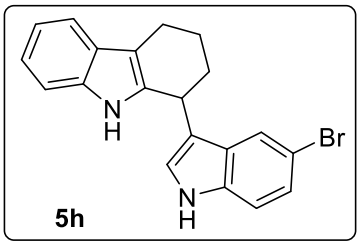
Pale brown solid; Yield = 261 mg (73%); m.p. 220 °C; R_f = 0.40, EtOAc/hexanes (2:8); ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] 8.01 (br s, 1H), 7.62 (br s, 1H), 7.55 (dd, *J* = 6.2, 3.9 Hz, 1H), 7.29 (dd, *J* = 8.8, 4.5 Hz, 1H), 7.21-7.16 (m, 1H), 7.12-7.08 (m, 3H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.90 (dt, *J* = 9.0, 2.5 Hz, 1H), 4.41 (q, *J* = 5.8, 2.1 Hz, 1H), 2.87-2.84 (m, 2H), 2.31-2.24 (m, 1H), 2.13-2.04 (m, 2H), 1.94 -1.84 (m, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ [ppm] 159.0, 156.7, 136.0 (d, *J* = 17.5 Hz), 133.1, 127.8, 127.0 (d, *J* = 9.5 Hz), 124.2, 121.4, 119.2, 118.8 (d, *J* = 4.5 Hz), 118.2, 112.0 (d, *J* = 9.5 Hz), 110.9 (d, *J* = 5.9 Hz), 110.7, 110.6, 104.2 (d, *J* = 23.9 Hz), 32.5, 32.0, 22.4, 21.2; IR (KBr, cm^{-1}) 3409, 2930, 2852, 1628, 1484, 1455, 1327, 1297, 1266, 1236, 1173, 1092, 1009, 744; HRMS (ESI-TOF) Calcd for $C_{20}H_{17}FN_2$ $[M+H]^+$ 305.1449, Found: 305.1451.

1-(5-Chloro-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5g) [2]



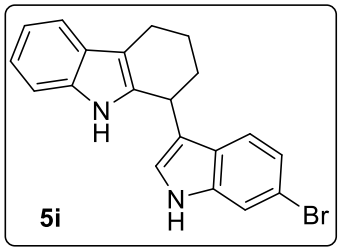
Pale pink solid; Yield = 120 mg (64%); m.p. 252 °C; R_f = 0.48, EtOAc/hexanes (2.5:7.5); ^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] 11.10 (br s, 1H), 10.38 (br s, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 9.0 Hz, 1H), 7.33 (s, 1H), 7.26 (d, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 9.3 Hz, 1H), 7.05 (s, 1H), 6.99 (t, *J* = 6.8 Hz, 1H), 6.95 (t, *J* = 6.6 Hz, 1H), 4.46 (s, 1H), 2.75 (br, 2H), 2.17 (br, 1H), 1.95 (br, 2H), 1.80 (br, 1H); ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ [ppm] 136.2, 135.9, 135.0, 127.3, 127.0, 125.0, 122.9, 120.8, 120.1, 117.9, 117.7, 117.4, 117.3, 113.0, 110.8, 108.7, 32.2, 31.5, 21.4, 20.9; IR (KBr, cm^{-1}) 3401, 2928, 2849, 1643, 1465, 1419, 1292, 1222, 1094, 746; HRMS (ESI-TOF) Calcd for $C_{20}H_{17}ClN_2$ $[M+H]^+$ 321.1153, Found: 321.1154.

1-(5-Bromo-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5h)[3]



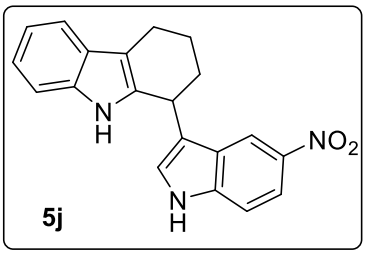
Colorless fluffy solid turn pink on standing; Yield = 140 mg (66%); m.p. 254 ºC; R_f = 0.40, EtOAc/hexanes (2:8); ^{1}H NMR (400 MHz, DMSO-d_6) δ [ppm] 9.68 (br s, 1H), 8.41 (br s, 1H), 7.23 (s, 1H), 7.12 (d, *J* = 5.8 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.84 (d, *J* = 1.8 Hz, 1H), 6.82 (d, *J* = 2.0 Hz, 1H), 6.68 (t, *J* = 3.6 Hz, 2H), 6.50 (d, *J* = 2.0 Hz, 1H), 4.05 (br, 1H), 2.45 (br, 2H), 1.88 (br, 1H), 1.72-1.64 (m, 2H), 1.50-1.47 (m, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$+DMSO-d_6) δ [ppm] 135.9, 135.7, 135.2, 128.1, 127.3, 124.1, 124.0, 120.9, 120.6, 118.4, 117.6, 117.5, 112.9, 111.8, 110.6, 109.9, 31.8, 31.76, 21.6, 20.9; IR (neat, cm^{-1}) 3412, 2933, 2851, 1644, 1461, 1299, 1221, 1094, 883, 737; HRMS (ESI-TOF) Calcd for $C_{20}H_{17}BrN_2$ $[M+H]^+$ 365.0648, Found: 365.0646.

1-(6-Bromo-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5i)[3]



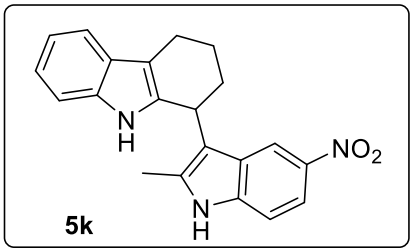
Pink fluffy solid; Yield = 300 mg (71%); m.p. 124 ºC; R_f = 0.50, EtOAc/hexanes (3:7); ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] 7.97 (br s, 1H), 7.57 (br s, 1H), 7.52 (d, *J* = 5.4 Hz, 1H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.24 (s, 1H), 7.17-7.15 (m, 1H), 7.12 (dd, *J* = 1.6, 8.5 Hz, 1H), 7.10-7.08 (m, 2H), 6.92 (d, *J* = 2.3 Hz, 1H), 4.42 (t, *J* = 6.1 Hz, 1H), 2.84-2.82 (m, 2H), 2.28-2.23 (m, 1H), 2.09-2.02 (m, 2H), 1.92-1.83 (m, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ [ppm] 137.4, 136.0, 135.8, 127.8, 125.6, 123.1, 122.9, 121.4, 120.6, 119.3, 118.9, 118.2, 115.9, 114.3, 110.9, 110.8, 32.5, 32.3, 22.5, 21.2; IR (neat, cm^{-1}) 3350, 2982, 1735, 1448, 1372, 1236, 1096, 1043, 914, 731. HRMS (ESI-TOF) Calcd for $C_{20}H_{17}BrN_2$ $[M+H]^+$ 365.0648, Found: 365.0647.

1-(5-Nitro-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5j)



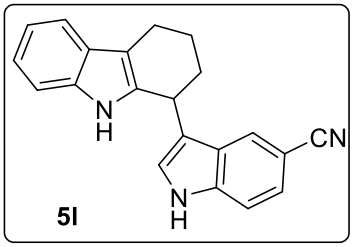
Yellow solid; Yield = 100 mg (52%); m.p. 210-214 ºC; R_f = 0.50, EtOAc/hexanes (3:7); ^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] 11.67 (br s, 1H), 10.40 (br s, 1H), 8.35 (d, *J* = 1.5 Hz, 1H), 7.98 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.55 (d, *J* = 8.9 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 1.6 Hz, 1H), 7.18 (d, *J* = 2.8 Hz, 1H), 6.98 (t, *J* = 6.98 Hz, 1H), 6.94 (t, *J* = 7.0 Hz, 1H), 4.8 (t, *J* = 6.0 Hz, 1H), 2.84-2.71 (m, 2H), 2.26-2.21 (m, 1H), 2.00-1.91 (m, 2H), 1.81 (br, 1H); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6) δ [ppm] 140.3, 139.7, 136.0, 135.9, 127.2, 127.0, 125.6, 120.6, 120.4, 118.1, 117.6, 116.5, 115.8, 112.1, 110.9, 109.1, 32.4, 31.3, 21.4, 20.9; IR (neat, cm^{-1}) 3379, 2927, 2843, 1699, 1576, 1514, 1464, 1419, 1322, 1231, 1092, 737; HRMS (ESI-TOF) Calcd for $C_{20}H_{17}N_3O_2$ $[M+H]^+$ 332.1394, Found: 332.1396.

1-(2-Methyl-5-nitro-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5k)



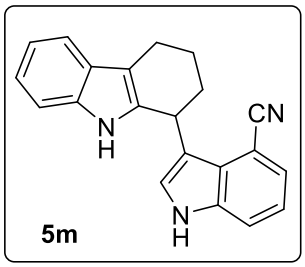
Yellow solid; Yield = 298 mg (74%); m.p. 298 °C; R_f = 0.40, EtOAc/hexanes (3.5:6.5); ^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] 11.60 (br s, 1H), 10.83 (br s, 1H), 7.87 (d, *J* = 8.9 Hz, 2H), 7.44-7.40 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.95 (t, *J* = 3.72 Hz, 2H), 4.51 (br, 1H), 2.82 (br, 2H), 2.24 (s, 3H), 2.24-2.18 (m, 1H), 2.05-2.02 (m, 1H), 1.99-1.92 (m, 1H), 1.89-1.82 (m, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$+DMSO-d_6) δ [ppm] 140.7, 138.6, 136.2, 135.8, 135.5, 127.5, 127.2, 120.7, 118.6, 117.8, 116.0, 115.0, 114.7, 110.6, 110.4, 110.2, 32.0, 31.6, 23.0, 20.9, 11.7; IR (neat, cm^{-1}) 3362, 2941, 1701, 1626, 1573, 1466, 1441, 1419, 1315, 1279, 1232, 1179, 1124, 1052, 1007, 730; HRMS (ESI-TOF) Calcd for $C_{21}H_{19}N_3O_2$ $[M+Na]^+$ 368.1369, Found: 368.1372.

3-(2,3,4,9-Tetrahydro-1*H*-carbazol-1-yl)-1*H*-indole-5-carbonitrile (5l)[3]



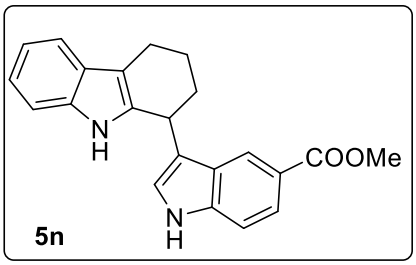
Colorless solid; Yield = 110 mg (61%); m.p. 280 °C; R_f = 0.44, EtOAc/hexanes (3.5:6.5); ^{1}H NMR (400 MHz, DMSO-d_6) δ [ppm] 11.5 (br s, 1H), 10.4 (br s, 1H), 7.87 (s, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.43 (d, *J* = 5.8 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.17 (s, 1H), 6.98 (t, *J* = 8.6 Hz, 2H), 4.55 (br, 1H), 2.90 (br, 1H), 2.78-2.74 (m, 1H), 2.21 (br, 1H), 1.95 (br, 2H), 1.81 (br, 1H); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6) δ [ppm] 138.2, 136.0 (2C), 127.0, 126.1, 125.9, 124.3, 123.6, 120.9, 120.3, 118.8, 118.0, 117.5, 112.8, 110.9, 109.0, 100.4, 79.2 ($CHCl_3$ impurity), 32.3, 31.3, 21.4, 20.8; IR (KBr, cm^{-1}) 3468, 3435, 3401, 2857, 2220, 1643, 1468, 1297, 805, 746; HRMS (ESI-TOF) Calcd for $C_{21}H_{17}N_3$ $[M+H]^+$ 312.1495, Found: 312.1493.

3-(2,3,4,9-Tetrahydro-1*H*-carbazol-1-yl)-1*H*-indole-4-carbonitrile (5m)



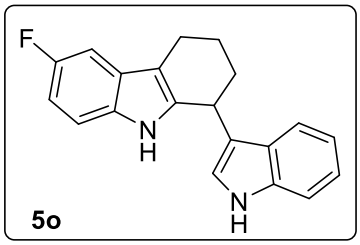
Colorless fluffy solid; Yield = 105 mg (58%); m.p. 230 °C; R_f = 0.60, EtOAc/hexanes (3:7); ^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] 11.5 (br s, 1H), 10.6 (br s, 1H), 8.31 ($CHCl_3$ impurity), 7.75 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 7.14 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.01 (t, *J* = 7.1 Hz, 1H), 6.95 (t, *J* = 7.1 Hz, 1H), 6.88 (s, 1H), 4.89 (br, 1H), 2.81-2.76 (m, 1H), 2.72-2.66 (m, 1H), 2.26 (br, 1H), 1.99 (br, 1H), 1.94 (br, 1H), 1.79 (br, 1H); ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ [ppm] 136.7, 136.0, 135.7, 127.1, 127.0, 125.6, 125.0, 120.9, 120.4, 119.4, 118.0, 117.7, 117.5, 117.2, 110.8, 109.4, 100.1, 79.2 ($CHCl_3$ impurity), 35.5, 30.2, 20.8, 19.9; IR (neat, cm^{-1}) 3410, 2928, 2854, 2214, 1643, 1465, 1429, 1347, 1297, 1264, 1234, 1110, 791, 745; HRMS (ESI-TOF) Calcd for $C_{21}H_{17}N_3$ $[M+H]^+$ 312.1495, Found: 312.1500.

Methyl 3-(2,3,4,9-tetrahydro-1*H*-carbazol-1-yl)-1*H*-indole-5-carboxylate (5n)



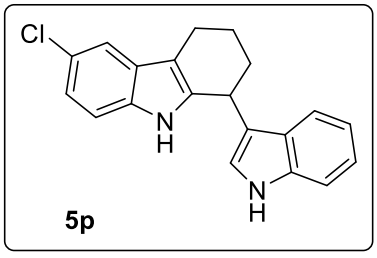
Brown solid; Yield = 234 mg (59%); m.p. 292 °C; R_f = 0.57, EtOAc/hexanes (3:7); ^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] 11.3 (br s, 1H), 10.4 (br s, 1H), 8.16 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.05 (s, 1H), 6.99 (t, *J* = 7.0 Hz, 1H), 6.95 (t, *J* = 7.0 Hz, 1H), 4.54 (t, *J* = 6.08 Hz, 1H), 3.80 (s, 3H), 2.80-2.73 (m, 2H), 2.24-2.22 (m, 1H), 2.04-1.98 (m, 1H), 1.93 (br, 1H), 1.82 (br, 1H); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6) δ [ppm] 167.7, 139.6, 136.6, 136.4, 127.5, 126.3, 125.6, 122.5, 121.7, 120.7, 120.3, 119.5, 118.4, 117.9, 112.0, 111.3, 109.3, 52.1, 32.5, 31.9, 21.7, 21.4; IR (neat, cm^{-1}) 3389, 3821, 2925, 2851, 1684, 1644, 1435, 1310, 1291, 1252, 1222, 1104, 747; HRMS (ESI-TOF) Calcd for $C_{22}H_{20}N_2O_2$ [M+Na]$^+$ 367.1417, Found: 367.1419.

6-Fluoro-1-(1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5o) [2]



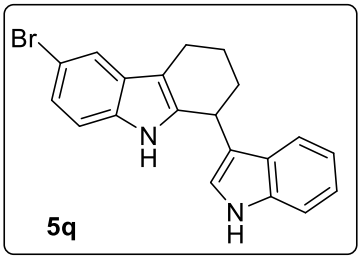
Pale brown solid; Yield = 230 mg (72%); m.p. 90 °C; R_f = 0.42, EtOAc/hexanes (2:8); ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] 7.84 (br s, 1H), 7.51 (br s, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.26 (s, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.93 (dd, *J* = 8.6, 4.5 Hz, 1H), 6.90 (d, *J* = 2.3 Hz, 1H), 6.86 (d, *J* = 2.1 Hz, 1H), 4.46 (t, *J* = 7.0 Hz, 1H), 2.88 (t, *J* = 5.4 Hz, 2H), 2.36-2.31 (m, 1H), 2.20-2.13 (m, 2H), 1.99-1.92 (m, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ [ppm] 158.7, 156.8, 138.7, 136.5, 132.2, 128.2 (d, *J* = 9.3 Hz), 126.6, 122.8 (d, *J* = 9.3 Hz), 119.8, 119.1, 118.2, 111.5, 111.2 (d, *J* = 9.6 Hz), 110.7 (d, *J* = 4.4 Hz), 109.0 (d, *J* = 26.5 Hz), 103.1 (d, *J* = 23.1 Hz), 32.6, 32.0, 22.5, 21.1; IR (neat, cm^{-1}) 3345, 2983, 1735, 1483, 1463, 1442, 1401, 1372, 1236, 1157, 1043, 938, 730; HRMS (ESI-TOF) Calcd for $C_{20}H_{17}FN_2$ [M+H]$^+$ 305.1449, Found: 305.1450.

6-Chloro-1-(1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5p)



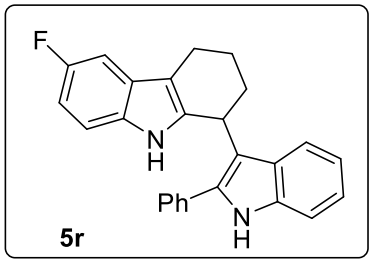
Brown solid; Yield = 73 mg (73%); m.p. 84-86 °C; R_f = 0.46, EtOAc/hexanes (2.5:7.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] 8.05 (br s, 1H), 7.65 (br s, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H) 7.40 (d, *J* = 8.6 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 1.9 Hz, 1H), 6.99 (d, *J* = 2.3 Hz, 1H), 4.45 (q, *J* = 6.5 Hz, 1H), 2.82-2.79 (m, 2H), 2.31-2.26 (m, 1H), 2.16-2.07 (m, 2H), 1.93-1.85 (m, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ [ppm] 138.3, 136.6, 134.1, 129.0, 126.6, 124.8, 122.4, 122.3, 121.3, 120.0, 119.2, 118.2, 117.7, 111.6, 111.5, 110.4, 32.7, 32.0, 22.6, 21.1; IR (neat, cm^{-1}) 3404, 2924, 2847, 1979, 1617, 1577, 1544, 1455, 1439, 1335, 1303, 1272, 1224, 1090, 1055, 993, 741; HRMS (ESI-TOF) Calcd for $C_{20}H_{17}ClN_2$ [M+H]$^+$ 321.1153, Found: 321.1153.

6-Bromo-1-(1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5q)[2]



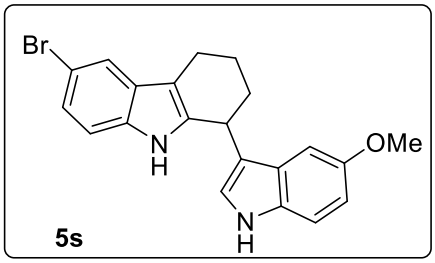
Brown solid; Yield = 225 mg (77%); m.p. 110 ºC; R_f = 0.54, EtOAc/hexanes (2.5:7.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] 8.05 (br s, 1H), 7.66 (br s, 1H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.40 (dd, *J* = 8.0, 3.4 Hz, 2H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.15 (dd, *J* = 1.85, 8.5 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 8.5 Hz, 1H), 6.99 (t, *J* = 2.3 Hz, 1H), 4.45 (t, *J* = 7.0 Hz, 1H), 2.82-2.79 (m, 2H), 2.31-2.26 (m, 1H), 2.16-2.08 (m, 2H), 1.93-1.85 (m, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ [ppm] 138.2, 136.7, 134.4, 129.7, 126.6, 122.9, 122.5, 122.4, 120.9, 119.9, 119.2, 118.2, 112.4, 112.1, 111.5, 110.4, 32.7, 32.1, 22.6, 21.1; IR (neat, cm^{-1}) 3415, 2928, 2854, 1640, 1465, 1435, 1304, 795, 747; HRMS (ESI-TOF) Calcd for $C_{20}H_{17}BrN_2$ $[M+H]^+$ 365.0648, Found: 365.0647.

6-Fluoro-1-(2-phenyl-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5r)



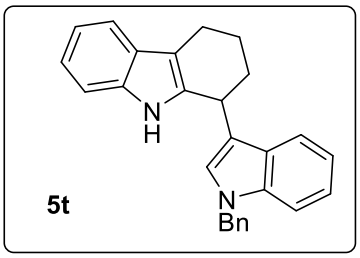
Colorless solid; Yield = 520 mg (86%); m.p. 128 ºC; R_f = 0.50, EtOAc/hexanes (3:7); ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] 8.11 (br s, 1H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.59 (br s, 1H), 7.54 (d, *J* = 3.2 Hz, 1H), 7.52 (s, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.21 (dd, *J* = 9.8, 2.3 Hz, 1H), 7.16 (dt, *J* = 7.60, 0.8 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.95 (dd, *J* = 8.8, 4.4 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.81 (dt, *J* = 9.2, 2.4 Hz, 1H), 4.62-4.59 (m, 1H), 2.91-2.88 (m, 2H), 2.39-2.23 (m, 3H), 1.98-1.89 (m, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ [ppm] 158.7, 156.9, 138.9, 136.2 (d, *J* = 5.2 Hz), 132.8, 132.2, 129.1 (2C), 128.6 (2C), 128.4, 128.3, 127.7, 122.5, 120.5, 120.1, 113.7, 111.2 (d, *J* = 9.5 Hz), 111.0, 110.7 (d, *J* = 4.4 Hz), 109.0 (d, *J* = 26.2 Hz), 103.2 (d, *J* = 23.9 Hz), 32.9, 32.1, 23.9, 21.2; IR (neat, cm^{-1}) 3395, 2928, 2848, 2360, 1735, 1481, 1443, 1421, 1307, 1282, 1230, 1124, 1107, 1068, 742; HRMS (ESI-TOF) Calcd for $C_{26}H_{21}FN_2$ $[M+H]^+$ 381.1762, Found: 381.1767.

6-Bromo-1-(5-methoxy-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5s)



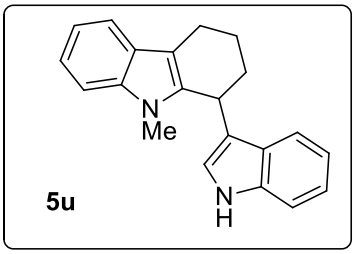
Colorless solid; Yield = 190 mg (80%); m.p. 262-264 ºC; R_f = 0.50, EtOAc/hexanes (3.5:6.5); ^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] 10.7 (br s, 1H), 10.6 (br s, 1H), 7.58 (s, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.09 (dd, *J* = 8.5, 1.4 Hz, 1H), 6.89 (d, *J* = 1.9 Hz, 1H), 6.75 (s, 1H), 6.72 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.45 (t, *J* = 5.6 Hz, 1H), 3.62 (s, 3H), 2.73 (q, *J* = 5.9 Hz, 2H), 2.18 (br, 1H), 2.0-1.90 (m, 2H), 1.79 (br, 1H); ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ [ppm] 152.8, 138.6, 134.6, 131.7, 128.9, 126.5, 123.7, 122.4, 119.6, 116.8, 112.7, 112.1, 110.7, 110.5, 108.7, 100.6, 55.2, 31.9, 31.5, 21.2, 20.7; IR (neat, cm^{-1}) 3409, 3281, 2940, 2842, 1717, 1575, 1483, 1436, 1302, 1276, 1205, 1037, 743; HRMS (ESI-TOF) Calcd for $C_{21}H_{19}BrN_2O$ $[M+H]^+$ 395.0754, Found: 395.0756.

1-(1-Benzyl-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5t)



Colorless fluffy solid; Yield = 329 mg (73%); m.p. 94-96 ^{o}C; R_f = 0.50, EtOAc/hexanes (0.5:9.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] 7.65 (br s, 1H), 7.55 (dd, *J* = 3.0, 5.5 Hz, 1H), 7.49 (d, *J* = 5.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 3H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.21 (t, *J* = 5.0 Hz, 1H), 7.18 (dd, *J* = 1.5, 3.5 Hz, 1H), 7.15 (d, *J* = 7.0 Hz, 2H), 7.11 (dd, *J* = 3.0, 6.0 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.92 (s, 1H), 5.27 (s, 2H), 4.49 (t, *J* = 5.0 Hz, 1H), 2.88-2.85 (m, 2H), 2.34-2.29 (m, 1H), 2.18-2.10 (m, 2H), 1.96-1.89 (m, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ [ppm] 137.6, 137.1, 136.6, 135.8, 128.9 (2C), 127.9, 127.8, 127.4, 127.0 (2C), 126.6, 122.1, 121.2, 119.5 (2C), 119.2, 118.2, 117.8, 110.8, 110.6, 110.0, 50.2, 32.6, 32.4, 22.7, 21.3; IR (neat, cm^{-1}) 3399, 3051, 2924, 2846, 1611, 1545, 1462, 1393, 1353, 1298, 1172, 1010, 735; HRMS (ESI-TOF) Calcd for $C_{27}H_{24}N_2$ $[M+H]^+$ 377.2012, Found: 377.2012.

1-(1H-indol-3-yl)-9-methyl-2,3,4,9-tetrahydro-1H-carbazole (5u)



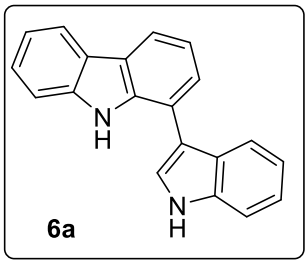
Colorless fluffy solid; Yield = 150 mg (50%); m.p. 200-202 ^{o}C; R_f = 0.50, EtOAc/hexanes (2:8); ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] 7.89 (br s, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.24-7.11 (m, 4H), 6.52 (s, 1H), 4.55 (br, 1H), 3.40 (s, 3H), 2.93-2.87 (m, 1H), 2.78-2.70 (m, 1H), 2.26-2.15 (m, 2H), 1.83-1.79 (m, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ [ppm] 137.2, 137.1, 136.6, 127.2, 126.3, 123.4, 122.2, 120.9, 119.5, 119.0, 118.9, 118.6, 118.2, 111.4, 110.4, 108.8, 31.0, 29.9, 29.3, 21.3, 19.2; IR (neat, cm^{-1}): 3402, 3049, 2839, 1615, 1564, 1472, 1451, 1418, 1377, 1334, 1307, 1272, 1245, 1224, 1188, 1127, 1088, 1034, 1008, 3399, 3051, 2924, 2846, 1611, 1545, 1462, 1393, 1353, 1298, 1172, 1010, 735; HRMS (ESI-TOF) Calcd for $C_{21}H_{20}N_2$ $[M+H]^+$ 323.1519, Found: 323.1516.

Synthesis of 1-(1*H*-indol-3-yl)-9*H*-carbazole (6a-u)

General procedure:

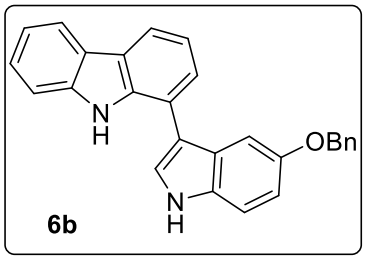
Compound **5a-5u** (0.3 g, 1.0 mmol) was dissolved in 5 mL of 1,4-dioxane in a RB flask and closed with a glass stopper. DDQ (2.0 mmol) was added slowly. After 10 minutes, completion of the reaction was monitored by TLC and the reaction mixture was quenched with water, extracted with ethyl acetate, the organic layer was washed with water, dried with anhydrous sodium sulfate and concentrated under vacuum to afford the crude compound (**6a-6u**). The crude compound thus obtained was further purified using column chromatography on silica gel. Note: It is difficult to remove residual solvents (ethyl acetate, hexanes) from some of the compounds. Chasing with appropriate amount of $CHCl_3$ and longer time of drying is needed to obtain pure compound.

1-(1*H*-Indol-3-yl)-9*H*-carbazole (6a)[4]



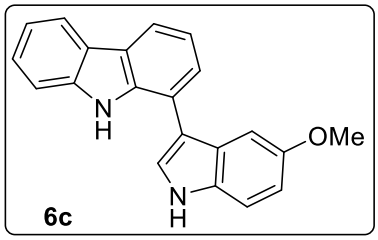
Pale yellow solid; Yield = 240 mg (81%); m.p. 228-230 ºC; R_f = 0.64, EtOAc/hexanes (3:7); ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] 8.34 (br, 1H), 8.20 (br, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 7.75 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 2.3 Hz, 1H), 7.42 (t, *J* = 7.15 Hz, 1H), 7.36-7.32 (m, 3H), 7.27 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ [ppm] 139.5, 138.4, 136.6, 126.41, 126.36, 125.9, 123.9, 123.6, 122.9, 122.7, 120.6 (2C), 120.2, 119.8, 119.5, 118.9, 118.5, 115.1, 111.8, 110.8; IR (neat, cm^{-1}) 3451, 3057, 2926, 1639, 1459, 1418, 1317, 1265, 739; HRMS (ESI-TOF) Calcd for $C_{20}H_{14}N_2$ $[M+Na]^+$ 305.1049, Found: 305.1048.

1-(5-(Benzyloxy)-1*H*-indol-3-yl)-9*H*-carbazole (6b)



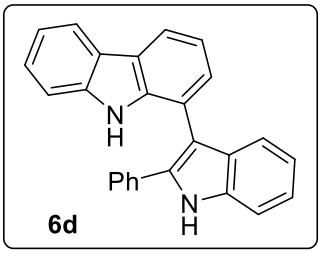
Colorless solid; Yield = 75 mg (76%); m.p. 264 ºC; R_f = 0.60, EtOAc/hexanes (3:7); ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ [ppm] 11.40 (br s, 1H), 10.91 (br s, 1H), 8.14 (d, *J* = 7.65 Hz, 1H), 8.04 (d, *J* = 7.65 Hz, 1H), 7.77 (d, *J* = 2.43 Hz, 1H), 7.56 (d, *J* = 8.30 Hz, 1H), 7.52 (d, *J* = 6.92 Hz, 1H), 7.46-7.43 (m, 3H), 7.37 (t, *J* = 7.73 Hz, 3H), 7.32-7.25 (m, 3H), 7.17 (t, *J* = 7.08 Hz, 1H), 6.94 (dd, *J* = 8.81, 2.32 Hz, 1H), 5.08 (s, 2H); ^{13}C {^{1}H} NMR (125 MHz, DMSO-*d*$_6$) δ [ppm] 153.0, 142.2, 137.9, 137.6, 130.1, 128.5 (2C), 127.8, 127.7 (2C), 126.4, 125.6, 125.13, 125.10, 123.2, 122.9, 120.2, 119.33, 119.27, 118.8, 117.9, 112.8, 112.7, 112.2, 111.8, 103.0, 70.2; IR (neat, cm^{-1}) 3725, 3391, 3054, 2916, 1703, 1618, 1575, 1477, 1453, 1425, 1409, 1383, 1319, 1296, 1264, 1232, 1202, 1179, 1012, 935, 739; HRMS (ESI-TOF) Calcd for $C_{27}H_{20}N_2O$ $[M+H]^+$ 389.1648, Found: 389.1647.

1-(5-Methoxy-1*H*-indol-3-yl)-9*H*-carbazole (6c)



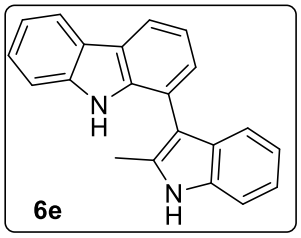
Brown solid; Yield = 48 mg (77%); m.p. 102 ºC; R_f = 0.60, EtOAc/hexanes (3:7); ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ [ppm] 11.37 (br, 1H), 10.87 (br, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 7.7 Hz, 1H), 7.75 (s, 1H), 7.56 (t, *J* = 7.3 Hz, 2H, doublet and triplet are merging), 7.43 (d, *J* = 8.8 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.15 Hz, 1H), 7.14 (s, 1H), 6.88 (d, *J* = 8.6 Hz, 1H), 3.75 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ [ppm] 153.7, 140.1, 137.5, 131.6, 126.2, 125.3, 125.0, 124.8, 122.9, 122.7, 120.0, 119.2, 119.0, 118.5, 117.6, 112.5, 112.0, 111.8, 111.6, 100.8, 55.2; IR (KBr, cm^{-1}) 3434, 2850, 1644, 1482, 1455, 1410, 1320, 1265, 1234, 1212, 1141, 1029, 796, 738; HRMS (ESI-TOF) Calcd for $C_{21}H_{16}N_2O$ $[M+H]^+$ 313.1335, Found: 313.1336.

1-(2-Phenyl-1*H*-indol-3-yl)-9*H*-carbazole (6d)



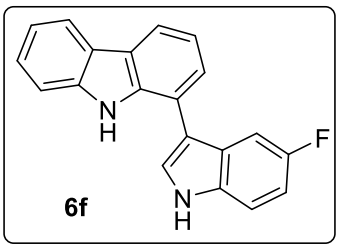
Colorless solid; Yield = 85 mg (86%); m.p. 180 °C; R_f = 0.50, EtOAc/hexanes (2:8); ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] 8.50 (br, 1H), 8.11 (dd, *J* = 12.7, 8.15 Hz, 2H), 7.88 (br, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.46-7.42 (m, 2H), 7.41 (dd, *J* = 1.5, 7.8 Hz, 2H), 7.36 (dt, *J* = 1.1, 7.2 Hz, 1H), 7.32-7.28 (m, 2H), 7.24-7.22 (m, 5H), 7.14 (dt, *J* = 0.8, 7.5 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ [ppm] 139.5, 138.8, 136.2, 134.8, 132.4, 129.1, 129.0 (3C), 128.1 (2C), 127.4 (2C), 125.8, 123.8, 123.6, 123.2, 120.8, 120.5, 120.2, 119.9, 119.4, 119.2, 117.9, 111.2, 110.7; IR (neat, cm^{-1}) 3409, 3051, 2920, 2850, 1754, 1718, 1487, 1452, 1413, 1387, 1370, 1311, 1258, 1231, 1154, 1072, 978, 799, 774, 737; HRMS (ESI-TOF) Calcd for $C_{26}H_{18}N_2$ $[M+H]^+$ 359.1543, Found: 359.1543.

1-(2-Methyl-1*H*-indol-3-yl)-9*H*-carbazole (6e)



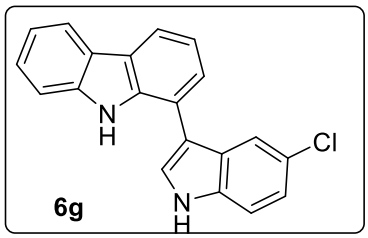
Pale brown solid; Yield = 92 mg (93%); m.p. 176 °C; R_f = 0.50, EtOAc/hexanes (1.5:8.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] 8.15 (d, *J* = 7.7 Hz, 1H), 8.11 (d, *J* = 7.7 Hz, 1H), 8.10 (br, 1H), 7.98 (br, 1H), 7.44 (dd, *J* = 0.95, 7.30 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.39 (dd, *J* = 1.09, 7.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.27-7.22 (m, 2H), 7.11 (t, *J* = 7.14 Hz, 1H), 2.47 (s, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ [ppm] 139.5, 139.0, 135.6, 132.8, 127.9, 127.5, 125.8, 123.8, 123.4, 121.8, 120.6, 120.3, 119.6, 119.4, 119.3, 118.9, 118.1, 110.9, 110.8, 110.7, 12.6; IR (neat, cm^{-1}) 3451, 2926, 1639, 1459, 1418, 1317, 1265, 739; HRMS (ESI-TOF) Calcd for $C_{21}H_{16}N_2$ $[M+Na]^+$ 319.1206, Found: 319.1205.

1-(5-Fluoro-1*H*-indol-3-yl)-9*H*-carbazole (6f)



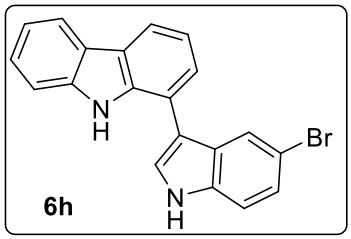
Colorless solid; Yield = 67 mg (74%); m.p. 118-122 °C (decomposition); R_f = 0.5, EtOAc/hexanes (3:7); ^{1}H NMR (400 MHz, DMSO-d_6) δ [ppm] 11.64 (br s, 1H), 10.93 (br s, 1H), 8.14 (d, *J* = 7.79 Hz, 1H), 8.06 (d, *J* = 7.62 Hz, 1H), 7.88 (d, *J* = 2.49 Hz, 1H), 7.53 (d, *J* = 7.62 Hz, 2H), 7.52 (d, *J* = 8.81 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.34 (dd, *J* = 10.25, 2.34 Hz, 1H), 7.26 (t, *J* = 7.53 Hz, 1H), 7.16 (dt, *J* = 7.50, 0.6 Hz, 1H), 7.05 (dt, *J* = 9.20, 2.46 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ [ppm] 158.5, 156.2, 140.01, 137.5, 133.2, 126.3, 126.2 (d, *J* = 9.9 Hz), 125.4, 125.1, 123.1, 122.7, 120.05, 119.0, 118.6 (d, *J* = 3.9 Hz), 118.0, 112.9 (d, *J* = 9.7 Hz), 112.5 (d, *J* = 4.7 Hz), 111.6, 109.8 (d, *J* = 26.0 Hz), 103.8 (d, *J* = 23.7 Hz); IR (neat, cm^{-1}) 3434, 2917, 2849, 1644, 1482, 1455, 1411, 1320, 1264, 1232, 795, 751; HRMS (ESI-TOF) Calcd for $C_{20}H_{13}FN_2$ $[M+Na]^+$ 323.0955, Found: 323.0956.

1-(5-Chloro-1*H*-indol-3-yl)-9*H*-carbazole (6g)



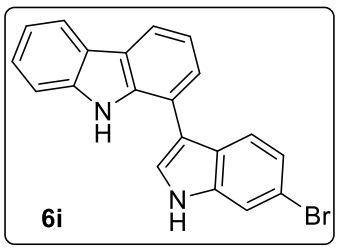
Light brown solid; Yield = 70 mg (74%); m.p. 82 °C; R_f = 0.50, EtOAc/hexanes (3:7); ^{1}H NMR (400 MHz, DMSO-d_6) δ [ppm] 11.74 (br, 1H), 10.96 (br, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 7.65 Hz, 1H), 7.89 (d, *J* = 2.4 Hz, 1H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.21 (dd, *J* = 1.9, 8.6 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ [ppm] 140.1, 137.6, 135.0, 127.1, 126.1, 125.4, 125.3, 124.1, 123.1, 122.7, 121.6, 120.1, 119.0, 118.6, 118.24, 118.21, 118.2, 113.5, 113.1, 111.6; IR (neat, cm^{-1}) 3468, 3436, 3401, 3370, 1643, 1492, 1456, 1409, 795, 753; HRMS (ESI-TOF) Calcd for $C_{20}H_{13}ClN_2$ $[M+Na]^+$ 339.0659, Found: 339.0652.

1-(5-Bromo-1*H*-indol-3-yl)-9*H*-carbazole (6h)



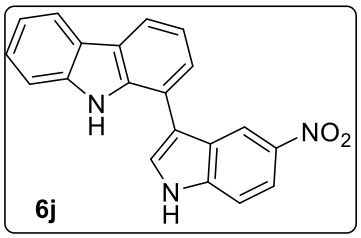
Light brown solid; Yield = 150 mg (84%); m.p. 78-82 °C; R_f = 0.50, EtOAc/hexanes (2:8); ^{1}H NMR (400 MHz, DMSO-d_6) δ [ppm] 11.7 (br, 1H), 10.9 (br, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 8.07 (d, *J* = 7.64 Hz, 1H), 7.86 (d, *J* = 2.5 Hz, 1H), 7.75 (d, *J* = 1.6 Hz, 1H), 7.54 (d, *J* = 2.1 Hz, 1H), 7.52 (d, *J* = 1.5 Hz, 1H), 7.50 (d, *J* = 5.8 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.31 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.1 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ [ppm] 140.1, 137.6, 135.2, 127.9, 125.9, 125.4, 125.3, 124.1, 123.0, 122.7, 121.2, 120.1, 119.0, 118.6, 118.2 (2C), 113.9, 112.0, 112.0, 111.5; IR (neat, cm^{-1}) 3414, 2924, 2851, 1643, 1512, 1450, 1412, 1314, 1264, 1091, 798, 762, 731; HRMS (ESI-TOF) Calcd for $C_{20}H_{13}BrN_2$ $[M+H]^+$ 361.0335, Found: 361.0335.

1-(6-Bromo-1*H*-indol-3-yl)-9*H*-carbazole (6i)



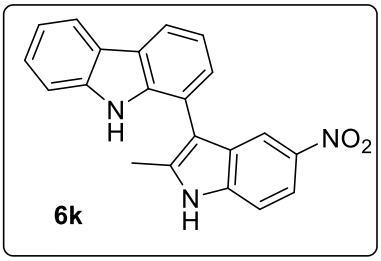
Light pink solid; Yield = 83 mg (85%); m.p. 186 °C; R_f = 0.60, EtOAc/hexanes (3:7); ^{1}H NMR (400 MHz, DMSO-d_6) δ [ppm] 11.70 (br, 1H), 10.9 (br, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 8.07 (d, *J* = 7.65 Hz, 1H), 7.84 (d, *J* = 2.4 Hz, 1H), 7.72 (d, *J* = 1.5 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.52 (s, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.22 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6) δ [ppm] 140.0, 137.6, 137.4, 125.3, 125.2, 125.1, 125.0, 123.0, 122.7, 122.2, 120.9, 120.0, 118.9, 118.6, 118.3, 118.1, 114.3, 114.2, 112.6, 111.5; IR (neat, cm^{-1}) 3418, 2918, 2849, 2360, 1700, 1585, 1490, 1438, 1419, 1384, 1371, 1304, 1256, 1225, 1101, 1049, 974, 789, 735, 715; HRMS (ESI-TOF) Calcd for $C_{20}H_{13}BrN_2$ $[M+H]^+$ 361.0335, Found: 361.0338.

1-(5-Nitro-1*H*-indol-3-yl)-9*H*-carbazole (6j)



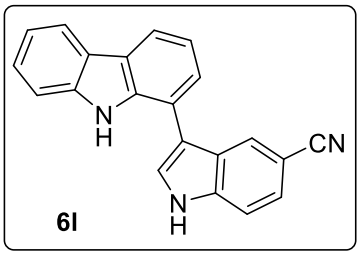
Orange solid; Yield = 80 mg (82%); m.p. 310-312 °C; R_f = 0.60, EtOAc/hexanes (3.5:6.5); ^{1}H NMR (400 MHz, DMSO-d_6) δ [ppm] 12.3 (br, 1H), 11.0 (br, 1H), 8.52 (s, 1H), 8.17 (d, J = 8.5 Hz, 2H), 8.12 (d, J = 10.6 Hz, 1H), 8.06 (s, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.57 (d, J = 7.0 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.32 (t, J = 7. 6 Hz, 1H), 7.18 (t, J = 7.18 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6) δ [ppm] 141.0, 140.1, 139.6, 137.7, 128.1, 125.6 (2C), 125.5, 123.2, 122.6, 120.1, 119.0, 118.8, 118.7, 117.2, 117.0, 116.3, 115.0, 112.4, 111.5; IR (neat, cm^{-1}) 3416, 1642, 1519, 1414, 1322, 1291, 1267, 1230, 1121, 1095, 1065, 750; HRMS (ESI-TOF) Calcd for $C_{20}H_{13}N_3O_2$ $[M+Na]^+$ 350.0900, Found: 350.0901.

1-(2-Methyl-5-nitro-1*H*-indol-3-yl)-9*H*-carbazole (6k)



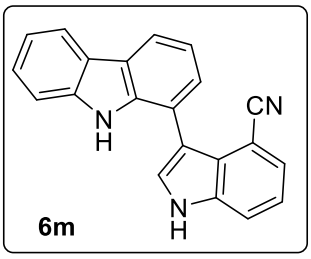
Yellow solid; Yield = 135 mg (98%); m.p. 330-336 °C; R_f = 0.60, EtOAc/hexanes (3.5:6.5); ^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] 12.13 (br s, 1H), 10.81 (br s, 1H), 8.17 (d, J = 7.79 Hz, 2H), 8.11 (s, 1H), 8.03 (d, J = 8.79 Hz, 1H), 7.59 (d, J = 8.91 Hz, 1H), 7.44 (d, J = 7.94 Hz, 1H), 7.41 (d, J = 7.06 Hz, 1H), 7.36 (t, J = 7.55 Hz, 1H), 7.31 (t, J = 7.45 Hz, 1H), 7.17 (t, J = 7.17 Hz, 1H), 2.41 (s, 3H); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6) δ 140.7, 140.0, 139.0, 138.5, 137.7, 127.4, 127.0, 125.5, 123.0, 122.6, 120.2, 119.1, 118.9, 118.6, 116.6, 116.2, 114.7, 111.8, 111.3, 111.1, 12.5; IR (neat, cm^{-1}) 3390, 2923, 2851, 1627, 1510, 1475, 1319, 1233, 1125, 1054, 890, 733; HRMS (ESI-TOF) Calcd for $C_{21}H_{15}N_3O_2$ $[M+H]^+$ 342.1237, Found: 342.1238.

3-(9*H*-Carbazol-1-yl)-1*H*-indole-5-carbonitrile (6l)



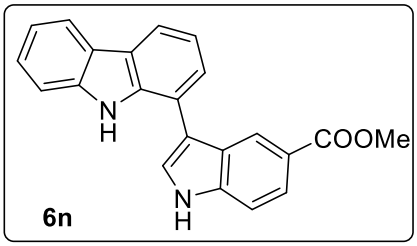
Colorless solid; Yield = 88 mg (96%); m.p. 222 °C; R_f = 0.60, EtOAc/hexanes (3:7); ^{1}H NMR (400 MHz, DMSO-d_6) δ [ppm] 12.08 (br, 1H), 10.96 (br, 1H), 8.30 ($CHCl_3$ impurity), 8.15 (d, J = 7.7 Hz, 1H), 8.10 (d, J = 6.8 Hz, 1H), 8.09 (s, 1H), 8.02 (d, J = 2.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 7.7 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ [ppm] 140.1, 138.3, 137.6, 126.9, 125.9, 125.6, 125.5, 124.8, 124.4, 123.1, 122.7, 120.7, 120.1, 119.1, 118.7, 118.5, 117.5, 113.3, 113.2, 111.5, 101.6; IR (neat, cm^{-1}) 3443, 2920, 2851, 2222, 1644, 1494, 1457, 1416, 1322, 1215, 1234, 1129, 798, 743. HRMS (ESI-TOF) Calcd for $C_{21}H_{13}N_3$ $[M+H]^+$ 308.1182, Found: 308.1182.

3-(9*H*-Carbazol-1-yl)-1*H*-indole-4-carbonitrile (6m)



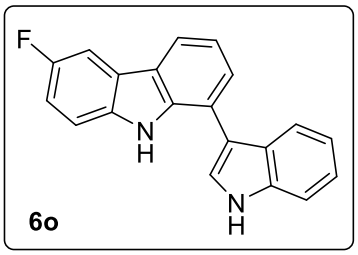
Colorless solid; Yield = 40 mg (82%); m.p. 320-324 ºC (decomposition); R_f = 0.40, EtOAc/hexanes (3.5:6.5); ^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] 12.06 (br s, 1H), 10.81 (br s, 1H), 8.13 (d, *J* = 7.75 Hz, 1H), 8.10 (d, *J* = 7.75 Hz, 1H), 7.88 (d, *J* = 8.12 Hz, 1H), 7.85 (d, *J* = 1.5 Hz, 1H), 7.52 (d, *J* = 7.14 Hz, 1H), 7.43 (d, *J* = 7.87 Hz, 1H), 7.39 (d, *J* = 7.12 Hz, 1H), 7.33 (dd, *J* = 8.10, 6.38 Hz, 2H), 7.22 (t, *J* = 7.49 Hz, 1H), 7.15 (t, *J* = 7.37 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ [ppm] 140.0, 139.6, 136.6, 128.3, 128.0, 126.5, 125.6, 125.2, 122.8, 122.2, 121.2, 120.1, 119.1, 118.4, 118.1, 118.0, 117.2, 116.8, 112.1, 111.3, 110.2; IR (neat, cm^{-1}) 3440, 2926, 2853, 2223, 1644, 1493, 1494, 1457, 1416, 1265, 1235, 1129, 741, 705; HRMS (ESI-TOF) Calcd for $C_{21}H_{13}N_3$ [M+Na]$^+$ 330.1002, Found: 330.1002.

Methyl 3-(9*H*-carbazol-1-yl)-1*H*-indole-5-carboxylate (6n)



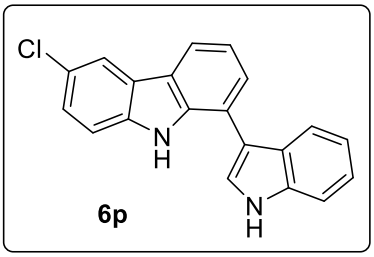
Colorless solid; Yield = 82 mg (83%); m.p. 220 ºC; R_f = 0.50, EtOAc/hexanes (3.5:6.5); ^{1}H NMR (500 MHz, $CDCl_3$+DMSO-d_6) δ [ppm] 10.6 (br, 1H), 9.08 (br, 1H), 8.33 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.52 (s, 1H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.24 (t, *J* = 8.7 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 3.72 (s, 3H); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6) δ [ppm] 167.2, 140.1, 139.1, 137.7, 126.1, 125.8, 125.5, 125.4, 123.1, 122.7, 122.5, 121.6, 120.9, 120.1, 118.9, 118.6, 118.3, 118.1, 113.6, 111.8, 111.5, 51.7; IR (KBr, cm^{-1}) 3455, 2917, 2849, 1642, 1495, 1451, 1433, 1323, 1278, 1246, 751; HRMS (ESI-TOF) Calcd for $C_{22}H_{16}N_2O_2$ [M+Na]$^+$ 363.1104, Found: 363.1105.

6-Fluoro-1-(1*H*-indol-3-yl)-9*H*-carbazole (6o)



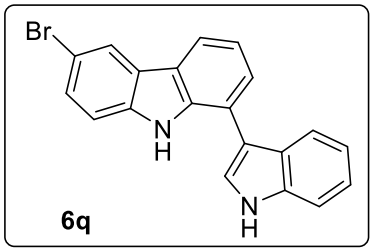
Light brown solid; Yield = 75 mg (83%); m.p. 196 ºC; R_f = 0.50, EtOAc/hexanes (3:7); ^{1}H NMR (400 MHz, DMSO-d_6) δ [ppm] 11.56 (br s, 1H), 10.97 (br s, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.99 (dd, *J* = 9.4, 2.5 Hz, 1H), 7.82 (d, *J* = 2.5 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.60 (dd, *J* = 7.2, 0.7 Hz, 1H), 7.55-7.51 (m, 2H), 7.29-7.19 (m, 3H), 7.10 (t, *J* = 7.2 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6) δ [ppm] 157.4, 155.6, 138.7, 136.6, 126.0, 125.7, 124.2, 123.2 (d, *J* = 9.5 Hz), 122.8, 121.6, 119.5, 119.4, 119.1, 118.9, 118.2, 113.0 (d, *J* = 25.1 Hz), 112.4 (d, *J* = 8.7 Hz), 112.1, 111.9, 105.5 (d, *J* = 23.8 Hz); IR (neat, cm^{-1}) 3412, 3051, 1720, 1590, 1543, 1493, 1452, 1420, 1333, 1305, 1267, 1232, 1170, 1119, 1051, 1013, 959, 928, 741, 725; HRMS (ESI-TOF) Calcd for $C_{20}H_{13}FN_2$ [M+H]$^+$ 301.1136, Found: 301.1139.

6-Chloro-1-(1*H*-indol-3-yl)-9*H*-carbazole (6p)



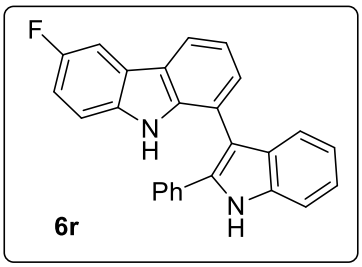
Yellow solid; Yield = 69 mg (70%); m.p. 260 °C; R_f = 0.60, EtOAc/hexanes (3:7); ^{1}H NMR (400 MHz, DMSO-d_6) δ [ppm] 11.5 (br, 1H), 11.10 (br, 1H), 8.24 (s, 1H), 8.10 (d, *J* = 7.7 Hz, 1H), 7.80 (s, 1H), 7.67 (d, *J* = 8.04 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ [ppm] 138.5, 138.2, 136.6, 125.9 (2C), 125.2, 124.3, 124.1, 122.9, 122.2, 121.6, 119.7, 119.5, 119.4, 119.3, 119.1, 118.3, 113.0, 112.0, 111.9; IR (neat, cm^{-1}) 3433, 3259, 3046, 2986, 2251, 2125, 1709, 1632, 1458, 1362, 1273, 1005, 820, 757, 728; HRMS (ESI-TOF) Calcd for $C_{20}H_{13}ClN_2$ $[M+H]^+$ 317.0840, Found: 317.0843.

6-Bromo-1-(1*H*-indol-3-yl)-9*H*-carbazole (6q)



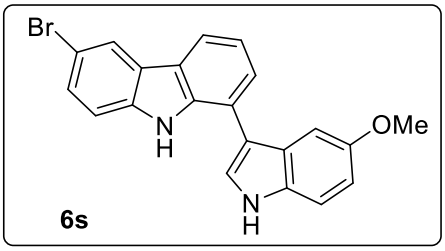
Light brown solid; Yield = 70 mg (71%); m.p. 232 °C; R_f = 0.60, EtOAc/hexanes (3:7); ^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] 11.55 (br s, 1H), 11.09 (br s, 1H), 8.39 (s, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 2.2 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.49 (s, 2H, a doublet and singlet merging), 7.29 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6) δ [ppm] 138.7, 138.0, 136.5, 127.7, 126.0, 125.9, 124.7, 124.3, 122.6, 122.0, 121.6, 119.5, 119.4, 119.3, 119.0, 118.3, 113.5, 111.9, 111.8, 110.6; IR (neat, cm^{-1}): 3364, 2918, 2849, 1711, 1626, 1574, 1460, 1419, 1260, 1234, 1088, 1052, 843, 743, 726: HRMS (ESI-TOF) Calcd for $C_{20}H_{13}BrN_2$ $[M+Na]^+$ 361.0335, Found: 361.0338.

6-Fluoro-1-(2-phenyl-1*H*-indol-3-yl)-9*H*-carbazole (6r)



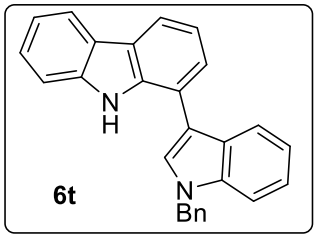
Colorless solid; Yield = 172 mg (76%); m.p. 234 °C; R_f = 0.50, EtOAc/hexanes (3:7); ^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] 11.75 (br, 1H), 10.66 (br, 1H), 8.15 (d, *J* = 10.0 Hz, 1H), 7.98 (dd, *J* = 2.5, 9.0 Hz, 1H), 7.55 (d, *J* = 10.0 Hz, 1H), 7.47 (d, *J* = 10.0 Hz, 2H), 7.34 (dd, *J* = 5.0, 10.0 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.23 (dt, *J* = 2.0, 10.7 Hz, 3H), 7.19-7.14 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 5.0 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ [ppm] 157.6, 155.3, 140.2, 136.3 (d, *J* = 17.1 Hz), 134.6, 132.4, 129.1, 128.4 (2C), 128.2, 127.3, 127.0 (2C), 123.1 (d, *J* = 9.4 Hz), 122.5 (d, *J* = 4.2 Hz), 122.1, 119.5 (d, *J* = 5.7 Hz), 119.0 (d, *J* = 3.9 Hz), 118.9, 113.2, 112.9, 112.3 (d, *J* = 8.7 Hz), 111.5, 109.7, 105.7, 105.5; IR (neat, cm^{-1}) 3405, 3360, 1718, 1483, 1456, 1410, 1131, 1277, 1236, 1209, 1116, 1055, 741; HRMS (ESI-TOF) Calcd for $C_{26}H_{17}FN_2$ $[M+H]^+$ 377.1449, Found: 377.1445.

6-Bromo-1-(5-methoxy-1*H*-indol-3-yl)-9*H*-carbazole (6s)



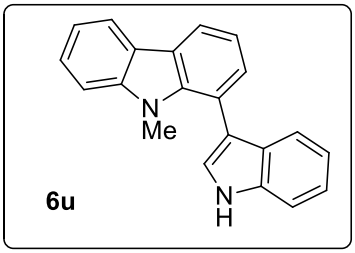
Colorless solid; Yield = 75 mg (77%); m.p. 244 ºC; R_f = 0.50, EtOAc/hexanes (3.5:6.5); ^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] 11.39 (br, 1H), 11.04 (br, 1H), 8.38 (d, *J* = 1.5 Hz, 1H), 8.10 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 2.5 Hz, 1H), 7.61 (dd, *J* = 0.7, 7.4 Hz, 1H), 7.52 (t, *J* = 8.5 Hz, 1H), 7.50 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 2.25 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.74 (s, 3H); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6) δ [ppm] 153.8, 138.7, 138.0, 131.6, 127.7, 126.2, 125.7, 124.9, 124.7, 122.5, 122.0, 119.5, 119.4, 118.1, 113.5, 112.5, 111.8, 111.7, 110.6, 100.8, 55.3; IR (neat, cm^{-1}) 3411, 3383, 3321, 2849, 2361, 2199, 1716, 1574, 1481, 1444, 1404, 1299, 1207, 1173, 1124, 1095, 1070, 798, 745; HRMS (ESI-TOF) Calcd for $C_{21}H_{15}BrN_2O$ $[M+H]^+$ 391.0441, Found: 391.0442.

1-(1-Benzyl-1*H*-indol-3-yl)-9*H*-carbazole (6t)



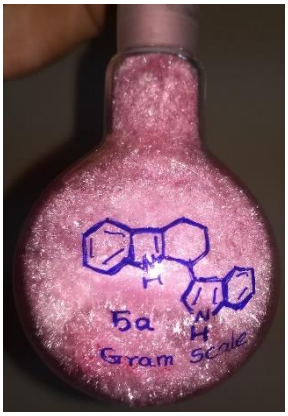
Colorless fluffy solid; Yield = 90 mg (91%); m.p. 200-204 ºC; R_f = 0.50, EtOAc/hexanes (0.5:9.5); ^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm] 10.9 (br s, 1H), 8.16 (d, *J* = 7.7 Hz, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 8.01 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.58-7.55 (m, 3H), 7.39 (dt, *J* = 7.14, 1.4 Hz, 3H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.30-7.27 (m, 2H), 7.23-7.16 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 5.57 (s, 2H); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6) δ [ppm] 140.1, 138.0, 137.6, 136.2, 128.6 (2C), 128.1, 127.4, 127.3 (2C), 126.7, 125.4, 123.1, 122.8, 121.8, 120.0, 119.8, 119.6, 119.0, 118.6, 118.5, 118.0, 112.1, 111.5, 110.9, 110.7, 49.5; IR (neat, cm^{-1}) 3412, 3051, 1720, 1590, 1543, 1493, 1452, 1420, 1333, 1305, 1267, 1232, 1170, 1119, 1051, 1013, 959, 928, 741, 725; HRMS (ESI-TOF) Calcd for $C_{27}H_{20}N_2$ $[M+H]^+$ 373.1699, Found: 373.1699.

1-(1H-indol-3-yl)-9-methyl-9H-carbazole (6u)



Colorless solid; Yield = 61 mg (68%); m.p. 162-164 ºC; R_f = 0.60, EtOAc/hexanes (2:8); ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] 8.30 (br s, 1H), 8.16 (d, *J* = 7.1 Hz, 1H), 8.14 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.48 (t, *J* = 8.2 Hz, 2H), 7.41 (t, *J* = 8.8 Hz, 2H), 7.34 (s, 1H), 7.32 (d, *J* = 5.1 Hz, 1H), 7.29 (d, *J* = 3.4 Hz, 1H), 7.27 (d, *J* = 3.7 Hz, 2H), 7.11 (t, *J* = 7.1 Hz, 1H), 3.41 (s, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ [ppm] 142.3, 140.0, 135.7, 130.2, 129.3, 125.8, 124.0, 123.2, 123.1, 122.6, 120.4, 120.3, 120.2, 119.4, 119.1, 118.9, 118.1, 116.4, 111.2, 109.0, 31.6; IR (neat, cm^{-1}) 3385, 3049, 2925, 2166, 1893, 1775, 1616, 1582, 1482, 1454, 1438, 1399, 1328, 1282, 1230, 1195, 1158, 1126, 1093, 1058, 1009; HRMS (ESI-TOF) Calcd for $C_{21}H_{16}N_2$ $[M+H]^+$ 297.1386, Found: 297.1388.

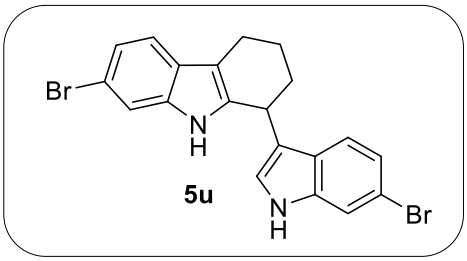
Gram scale synthesis of 5a:



Tetrahydrocarbazole (**3a**) (1.0 g, 5.8 mmol, 1.0 equiv) was dissolved in 10 mL of 1,4-dioxane in a RB flask and closed with a glass stopper. NCS (5.8 mmol, 1.0 equiv) was added in portions within five minutes, after which indole (8.7 mmol, 1.5 equiv) was added slowly. After 10 minutes, completion of the reaction was monitored by TLC and, the reaction mixture was quenched with water, extracted with ethyl acetate, the organic layer was washed with water, dried with sodium sulfate and concentrated under vacuum to afford the crude compound (**5a)**. The crude compound thus obtained was further purified using column chromatography on silica gel using ethyl acetate: hexanes (0.7:9.3)). Pale pink fluffy solid, Yield (1.24 g, 75%)

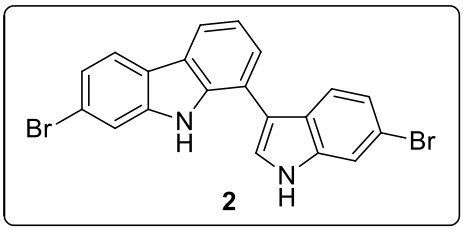
Total synthesis of 7-bromo-1-(6-bromo-1*H*-indol-3-yl)-9*H*-carbazole (2):

7-Bromo-1-(6-bromo-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (5v)



Pink fluffy solid; Yield = 200 mg (75%); m.p. 80 ^{o}C; R_f = 0.44, EtOAc/hexanes (2:8); ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] 8.01 (br s, 1H), 7.54 (br s, 1H), 7.52 (s, 1H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 1.9 Hz, 1H), 4.38 (t, *J* = 6.14 Hz, 1H), 2.81 (br, 2H), 2.27-2.22 (br, 1H), 2.09-2.00 (m, 2H), 1.92-1.83 (m, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ [ppm] 137.5, 136.8, 136.5, 126.7, 125.4, 123.2, 123.0, 122.4, 120.5, 119.4, 118.5, 116.0, 114.7, 114.4, 113.7, 111.0, 32.5, 32.1, 22.4, 21.1; IR (neat, cm^{-1}) 3401, 3057, 2923, 2852, 1585, 1538, 1490, 1438, 1417, 1308, 1230, 1187, 1095, 1050, 973, 889, 825, 787, 745; HRMS (ESI-TOF) Calcd for $C_{20}H_{16}Br_2N_2$ $[M+H]^+$ 442.9753, Found: 442.9751.

7-Bromo-1-(6-bromo-1*H*-indol-3-yl)-9*H*-carbazole (2)[5]

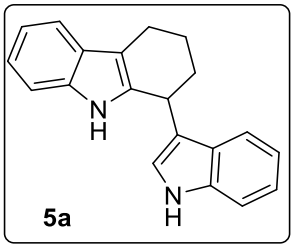


Colorless solid; Yield = 85 mg (86%); m.p. 294-296 ^{o}C (decomposition); R_f = 0.50, EtOAc/hexanes (2.5:7.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] 8.41 (br, 1H), 8.11 (br, 1H), 8.04 (d, *J* = 7.7 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.69 (d, *J* = 1.6 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 1.3 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H) 7.46 (d, *J* = 2.2 Hz, 1H), 7.36 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.30 (dd, *J* = 8.5, 1.6 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.2, 138.2, 137.3, 126.7, 115.2, 124.0, 123.2, 123.1, 122.9, 122.7, 121.8, 121.3, 120.4, 119.4, 119.1, 118.0, 116.6, 114.9, 114.7, 113.9; IR (neat, cm^{-1}) 3425, 2918, 1641, 1495, 1442, 1415, 1264, 789, 748; HRMS (ESI-TOF) Calcd for $C_{20}H_{12}Br_2N_2$ $[M+H]^+$ 438.9440, Found: 438.9440.

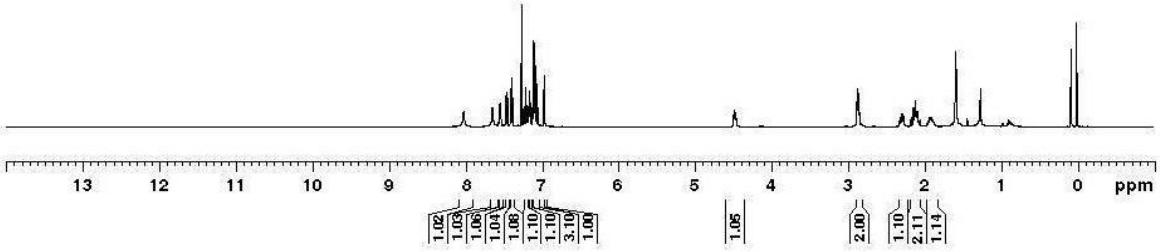
Comparison of spectral data of natural product 7-Bromo-1-(6-bromo-1*H*-indol-3-yl)-9*H*-carbazole (2) with that of the isolated compound:[5]

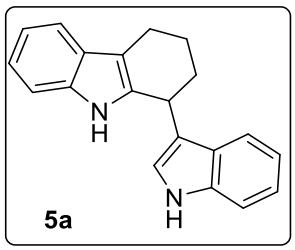
S. No	1H (Reported), $CDCl_3$	1H (Observed), 500 MHz, $CDCl_3$	^{13}C (Reported), $CDCl_3$	^{13}C (Observed), 100 MHz, $CDCl_3$
1	8.42 (br, 1H)	8.41 (br, 1H)	140.0	140.2
2	8.12 (br, 1H)	8.11 (br, 1H)	138.1	138.2
3	8.04 (br, d, *J* = 7.7 Hz, 1H)	8.04 (br, d, *J* = 7.7 Hz, 1H)	137.1	137.3
4	7.97 (d, *J* = 8.3 Hz, 1H)	7.97 (d, *J* = 8.3 Hz, 1H)	126.6	126.7
5	7.69 (d, *J* = 1.6 Hz, 1H)	7.69 (d, *J* = 1.6 Hz, 1H)	125.0	125.2
6	7.55 (dd, *J* = 7.3, 1.1 Hz, 1H)	7.55 (d, *J* = 7.3 Hz, 1H)	123.8	124.0
7	7.53 (d, *J* = 1.5 Hz, 1H)	7.53 (d, *J* = 1.3 Hz, 1H)	123.0	123.2
8	7.51 (d, *J* = 8.6 Hz, 1H)	7.50 (d, *J* = 8.5 Hz, 1H)	122.9	123.1
9	7.47 (d, *J* = 2.2 Hz, 1H)	7.46 (d, *J* = 2.2 Hz, 1H)	122.8	122.9
10	7.36 (dd, *J* = 8.3, 1.6 Hz, 1H)	7.36 (dd, *J* = 8.3, 1.6 Hz, 1H)	122.6	122.7
11	7.32 (t, *J* = 7.5 Hz, 1H)	7.34 (t, *J* = 7.6 Hz, 1H)	121.6	121.8
12	7.30 (dd, *J* = 8.5, 1.6 Hz, 1H)	7.30 (dd, *J* = 8.5, 1.6 Hz, 1H)	121.1	121.3
13			120.0	120.4
14			119.3	119.4
15			118.9	119.1
16			117.8	118.0
17			116.4	116.6
18			114.7	114.9
19			114.6	114.7
20			113.7	113.9

^{1}H and ^{13}C NMR Spectra

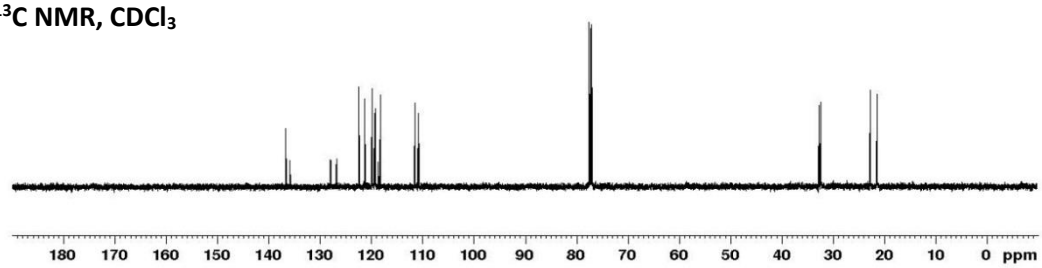


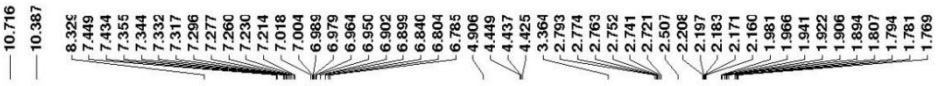
^{1}H NMR, $CDCl_3$

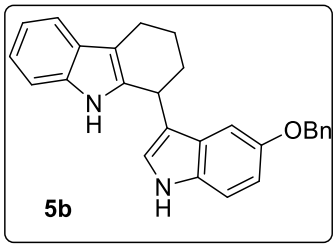




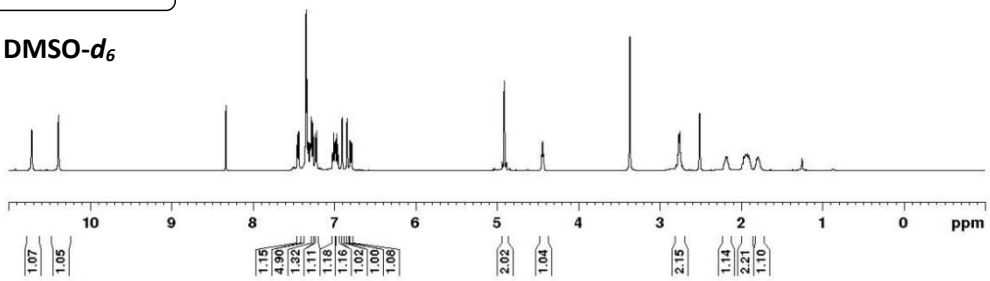
^{13}C NMR, $CDCl_3$

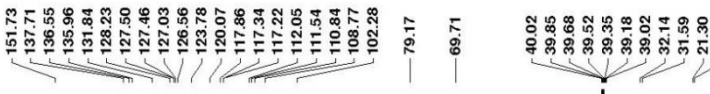


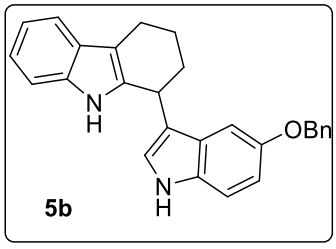




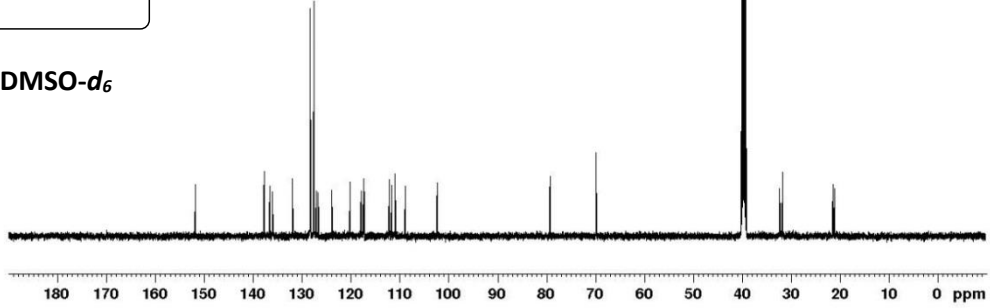
^{1}H NMR, DMSO-*d*$_6$

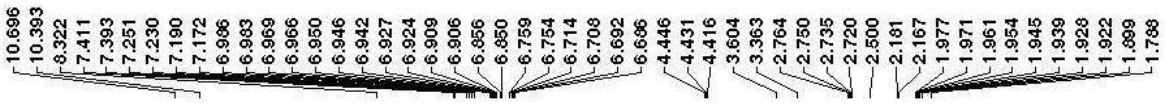


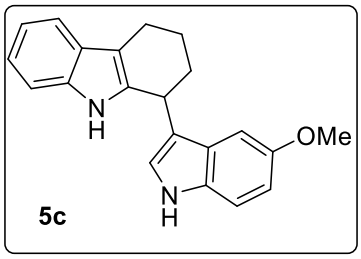




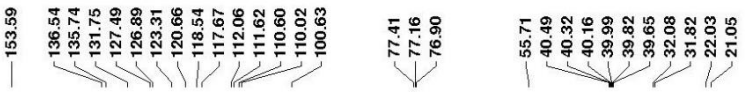
^{13}C NMR, DMSO-*d*$_6$

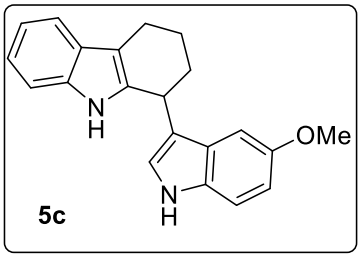




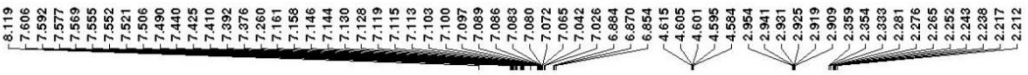


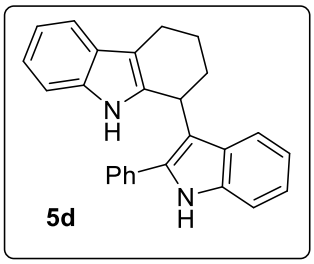
^{1}H NMR, DMSO-*d*$_6$



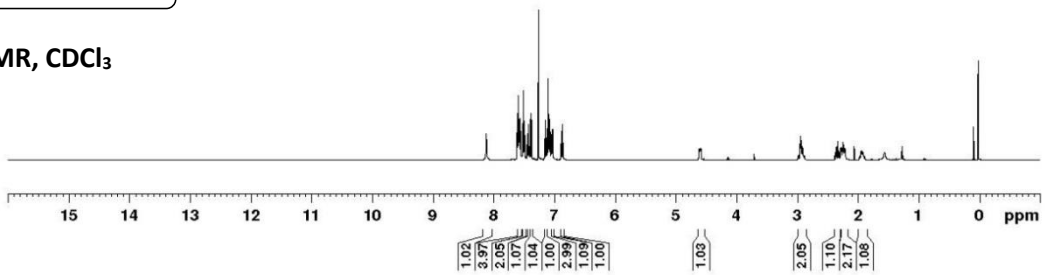


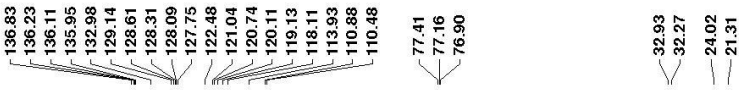
^{13}C NMR, CDCl$_3$+DMSO-*d*$_6$

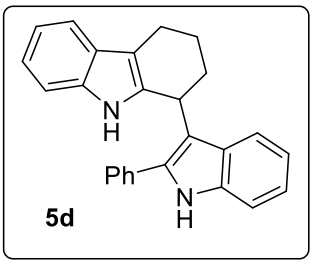




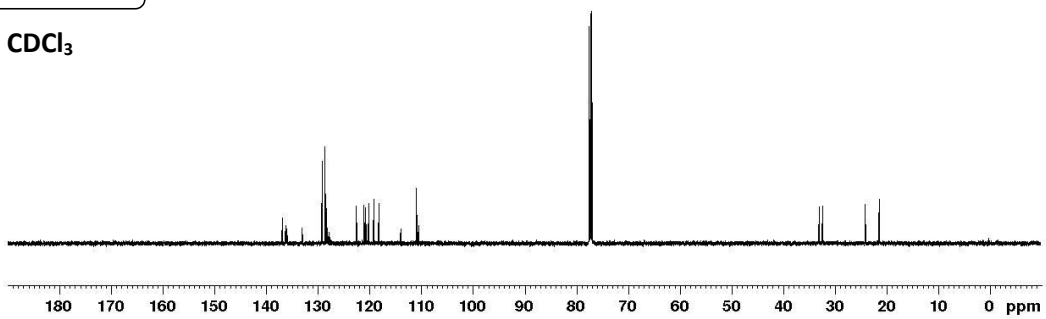
^{1}H NMR, $CDCl_3$

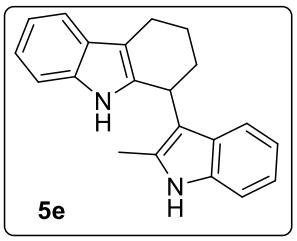




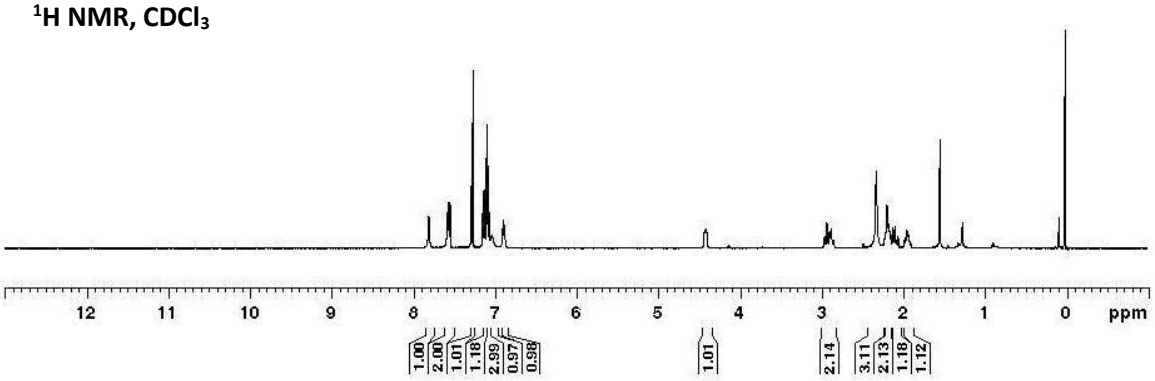


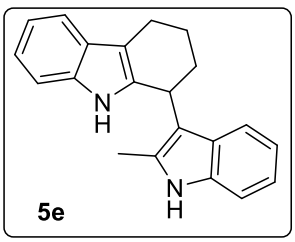
^{13}C NMR, $CDCl_3$



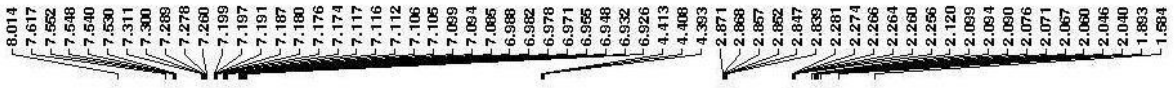


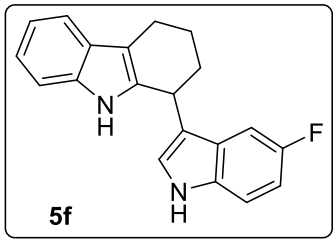
^{1}H NMR, $CDCl_3$



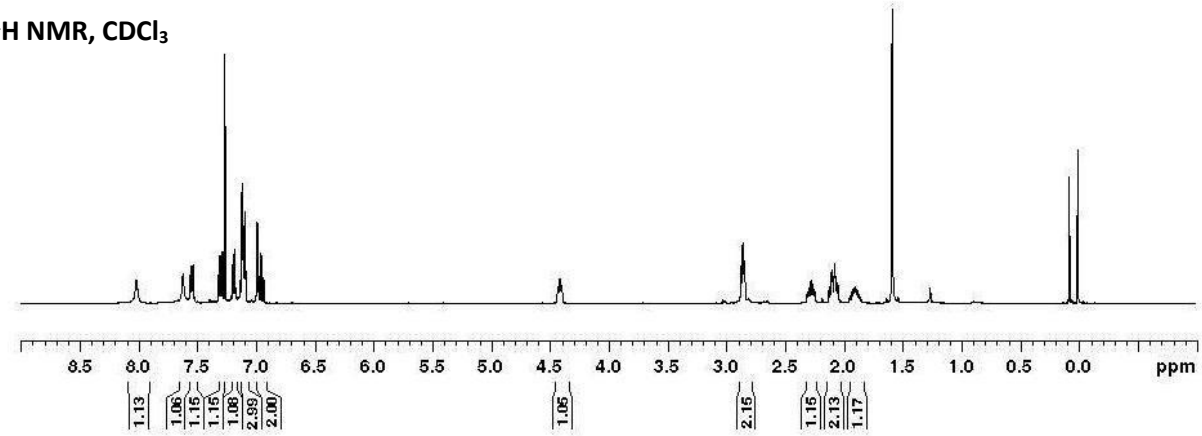


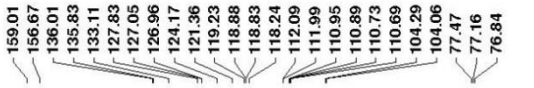
^{13}C NMR, $CDCl_3$

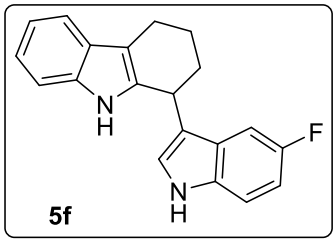




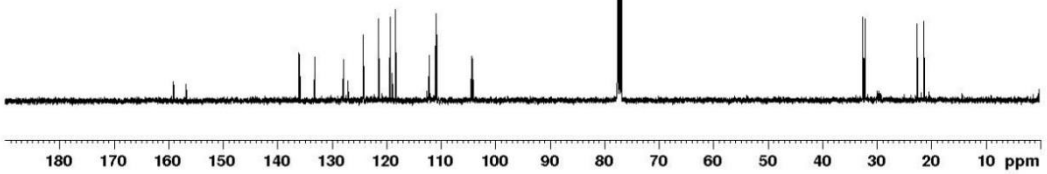
^{1}H NMR, $CDCl_3$

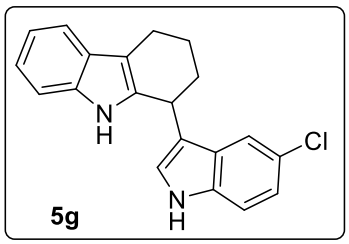




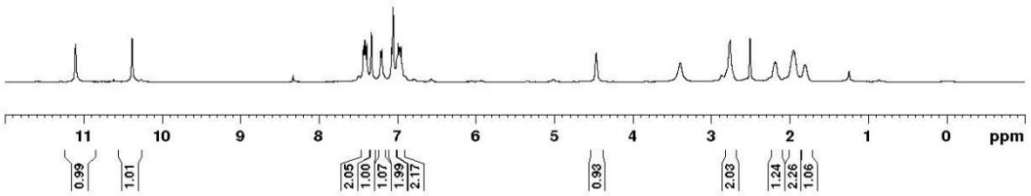


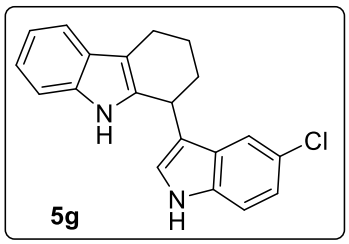
^{13}C NMR, $CDCl_3$



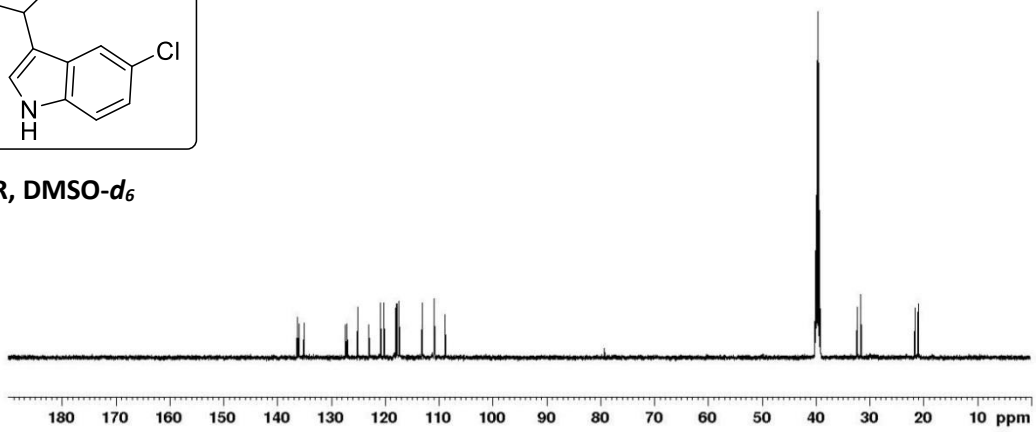


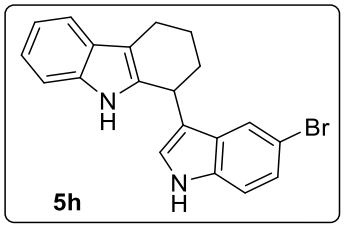
^{1}H NMR, DMSO-*d*$_6$



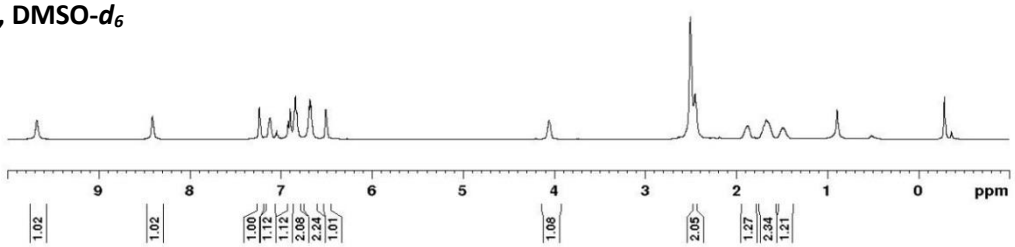


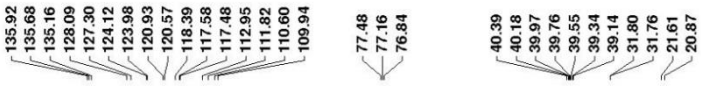
^{13}C NMR, DMSO-*d*$_6$

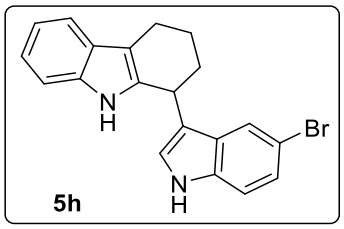




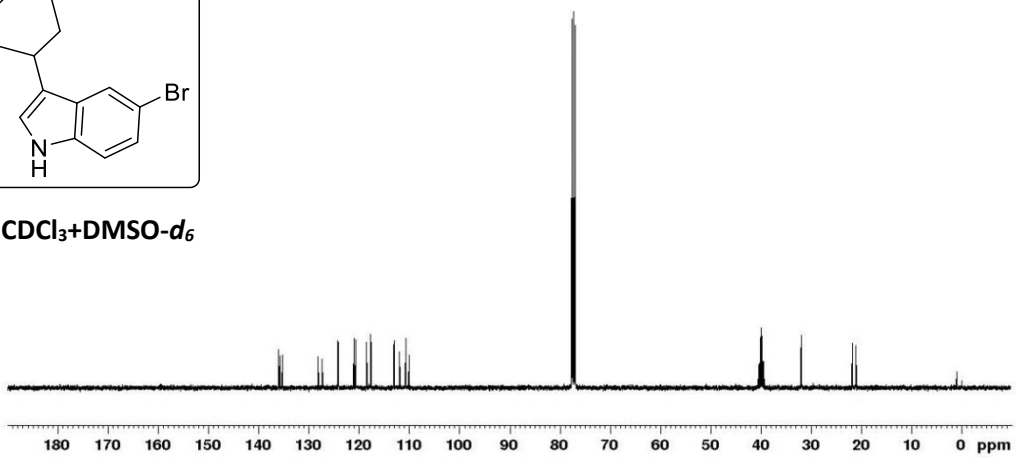
^{1}H NMR, DMSO-*d*$_6$

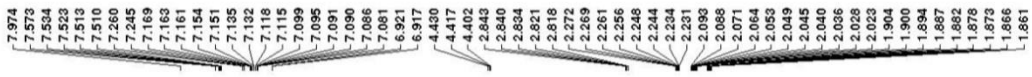


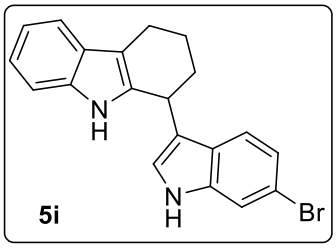




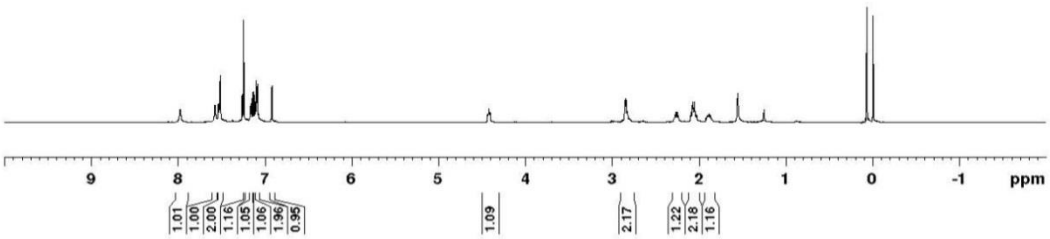
^{13}C NMR, CDCl$_3$+DMSO-*d*$_6$

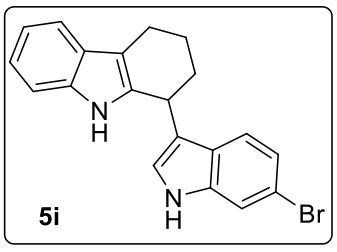




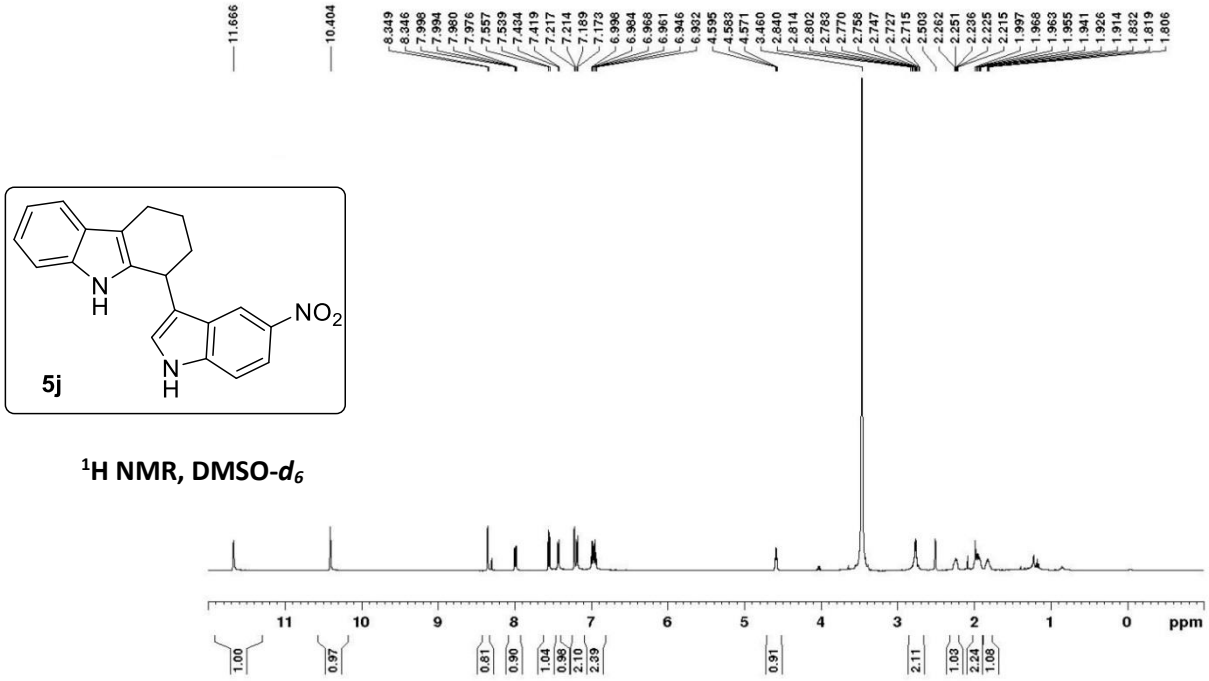


^{1}H NMR, $CDCl_3$

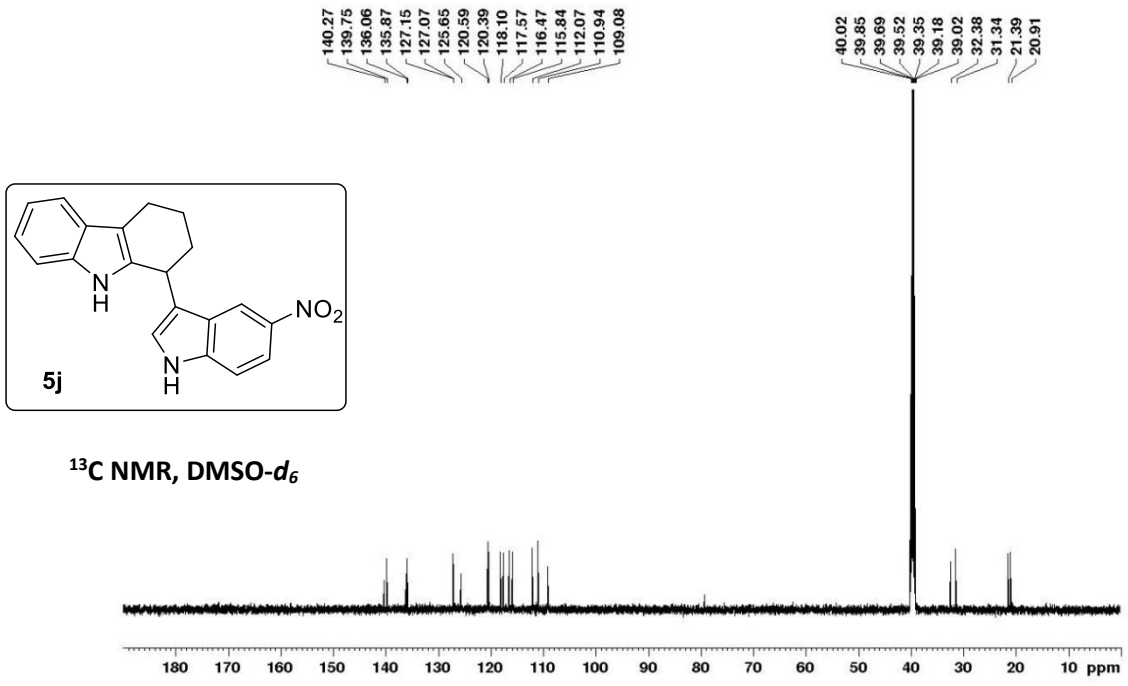




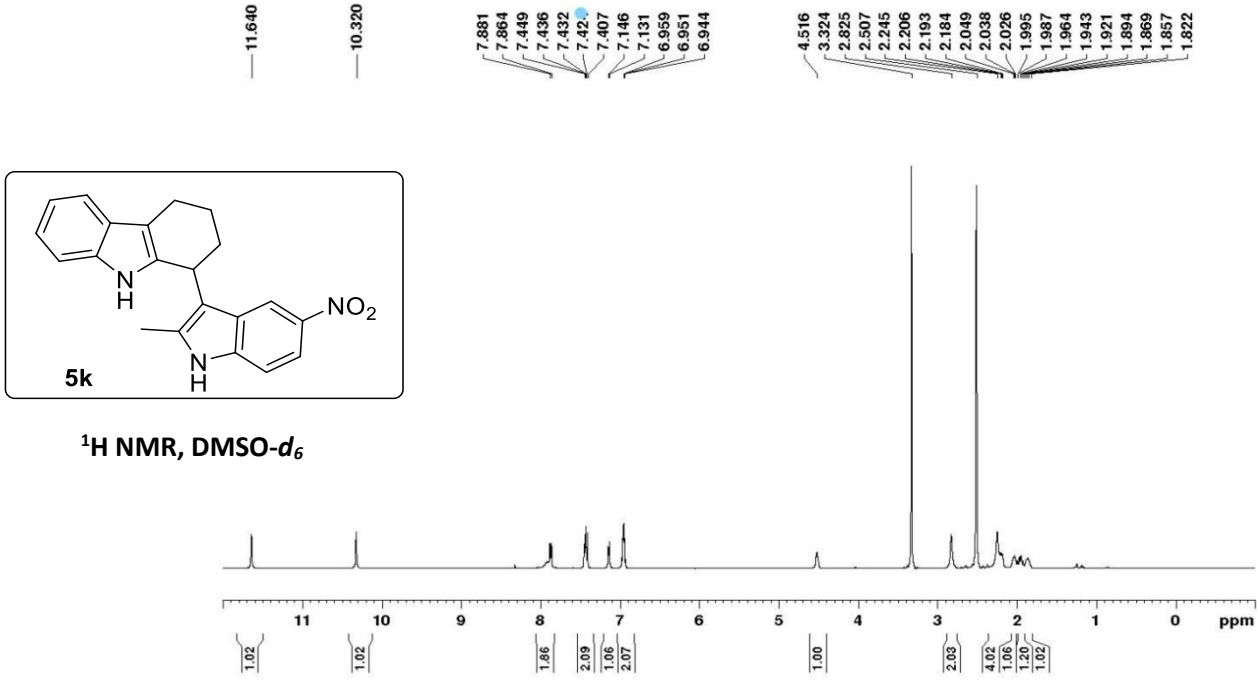
^{13}C NMR, $CDCl_3$



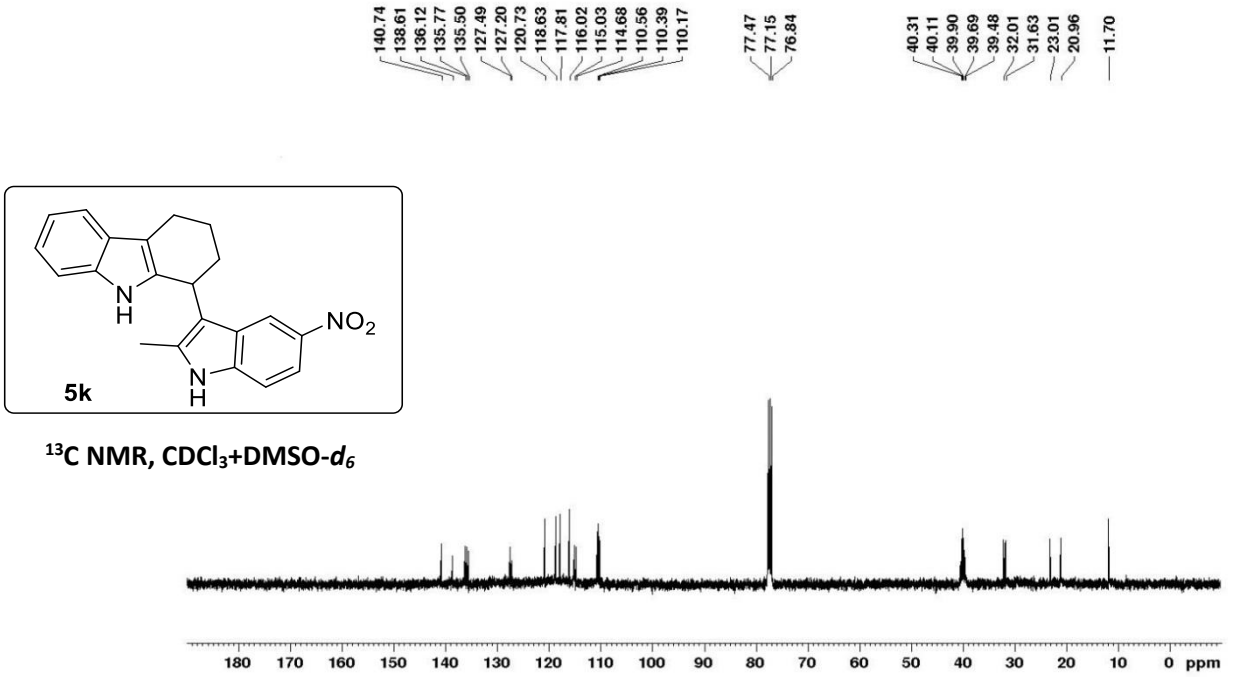
^{1}H NMR, DMSO-*d*$_6$



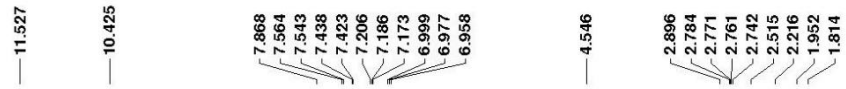
^{13}C NMR, DMSO-*d*$_6$

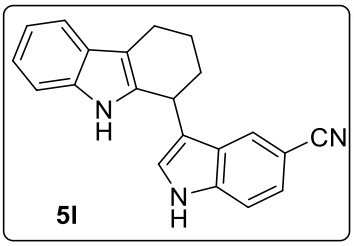


^{1}H NMR, DMSO-*d*$_6$

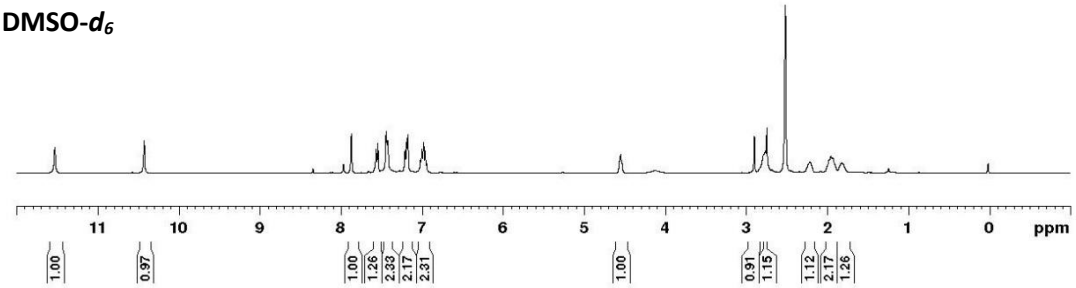


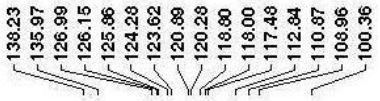
^{13}C NMR, CDCl$_3$+DMSO-*d*$_6$

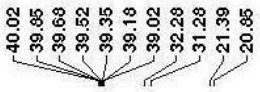


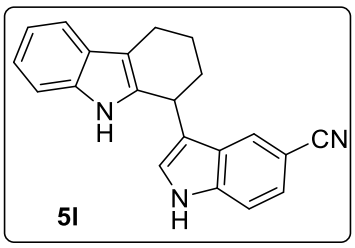


^{1}H NMR, DMSO-*d*$_6$

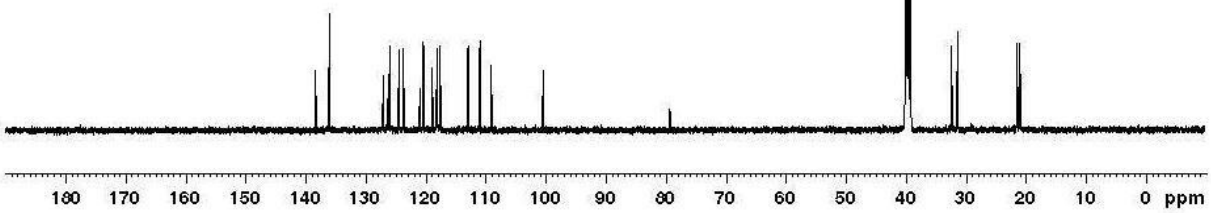


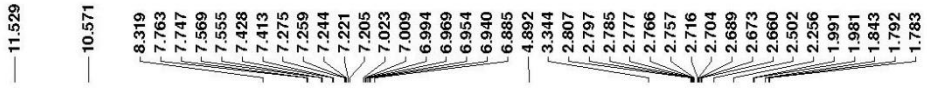


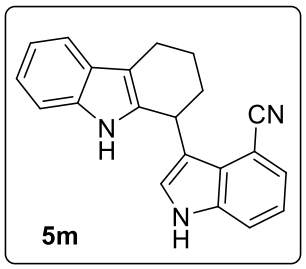




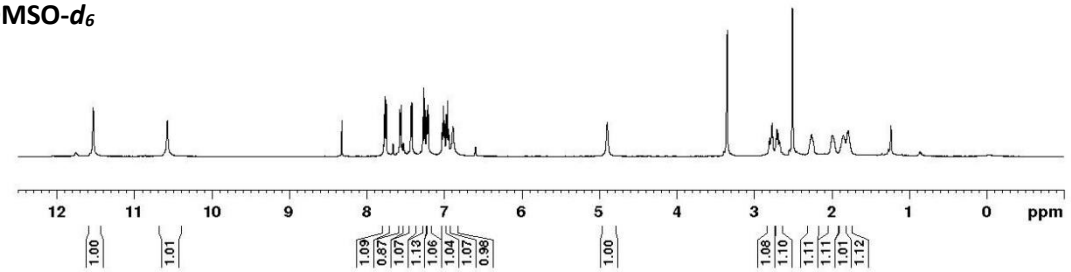
^{13}C NMR, DMSO-*d*$_6$

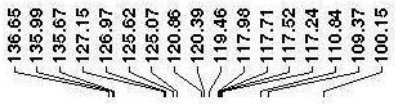


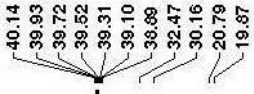


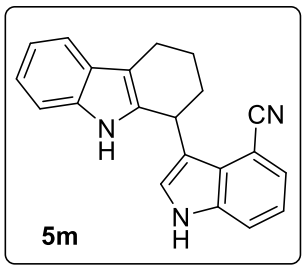


^{1}H NMR, DMSO-*d*$_6$

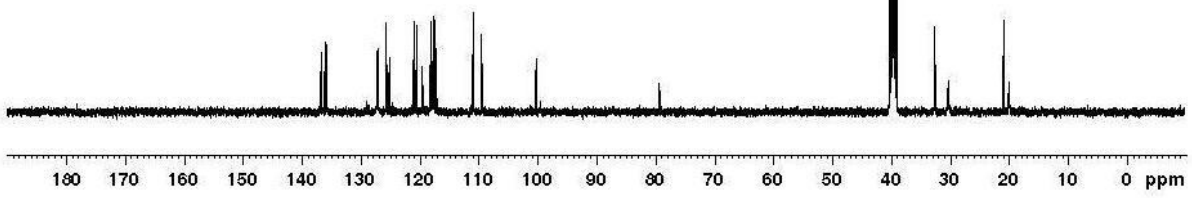


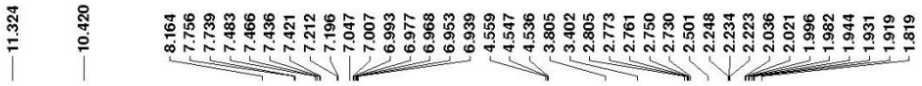


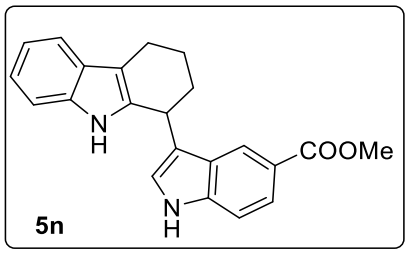




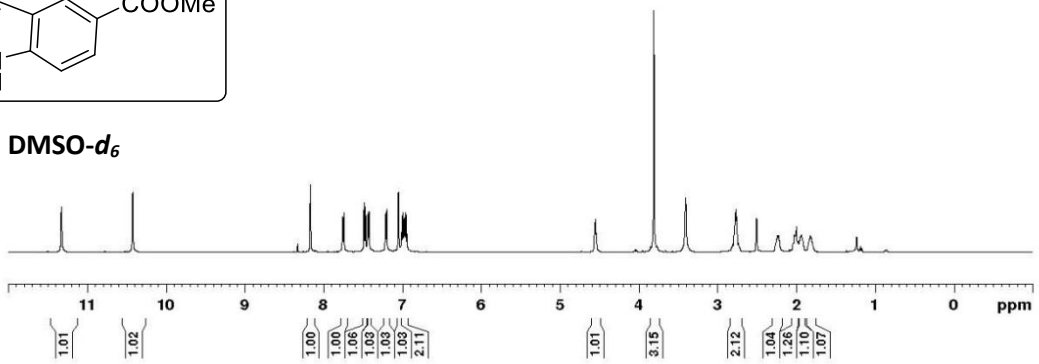
^{13}C NMR, DMSO-*d*$_6$

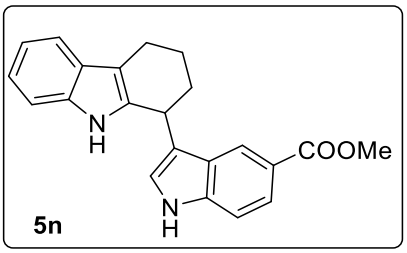




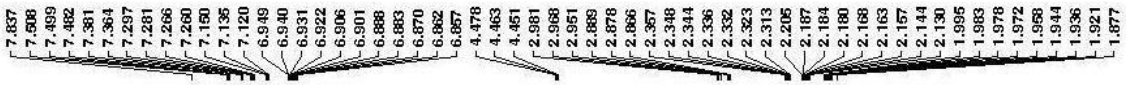


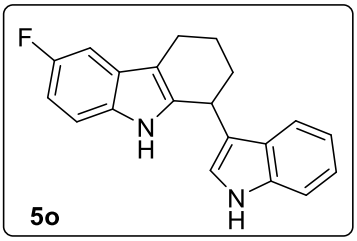
^{1}H NMR, DMSO-*d*$_6$



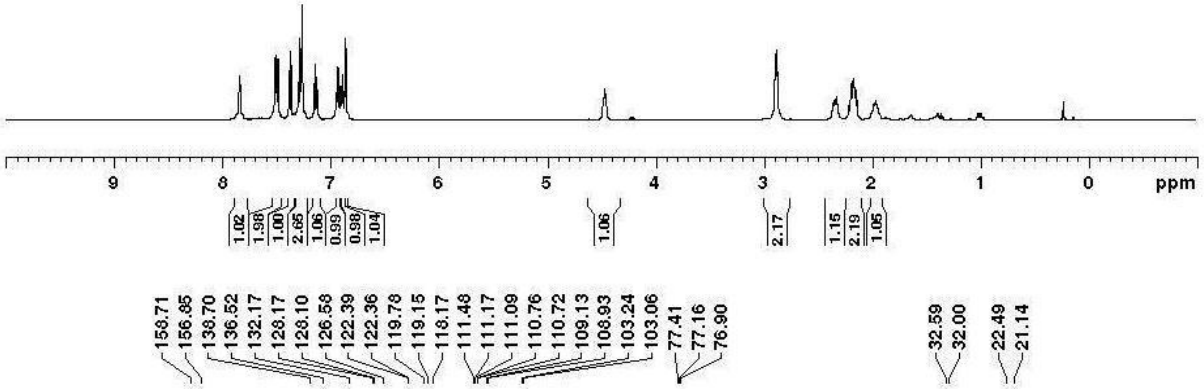


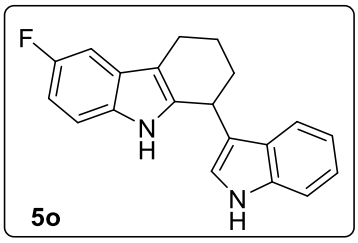
^{13}C NMR, DMSO-*d*$_6$



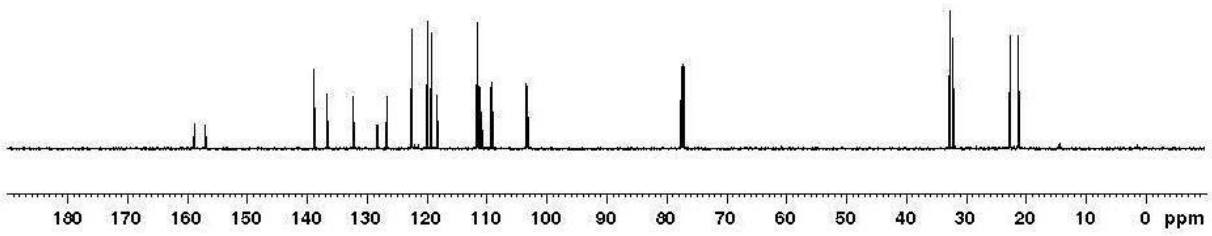


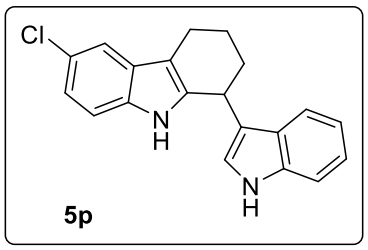
^{1}H NMR, $CDCl_3$





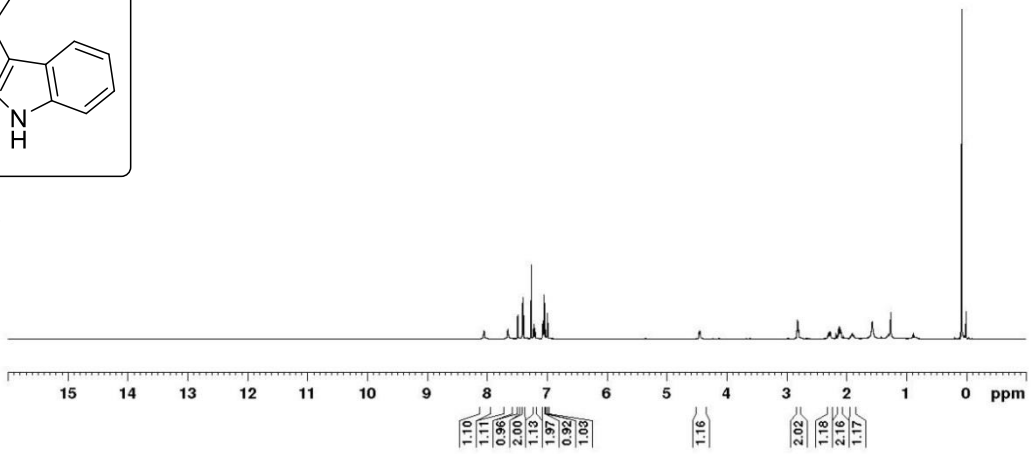
^{13}C NMR, $CDCl_3$

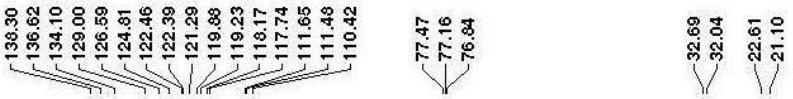


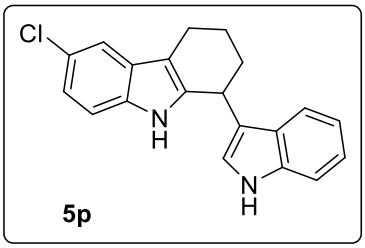


5p

^{1}H NMR, $CDCl_3$







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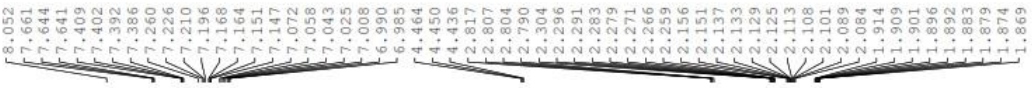
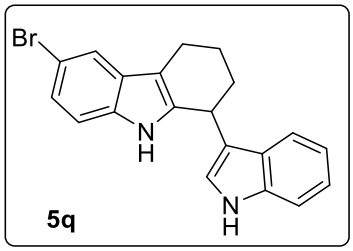
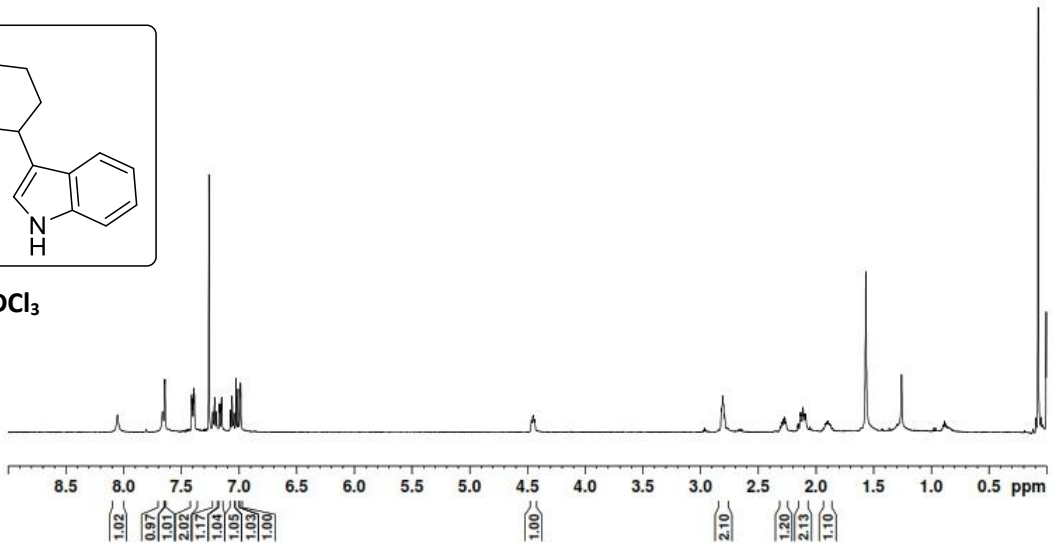
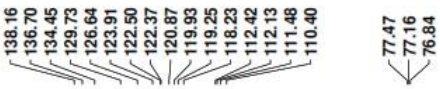
^{13}C NMR, $CDCl_3$

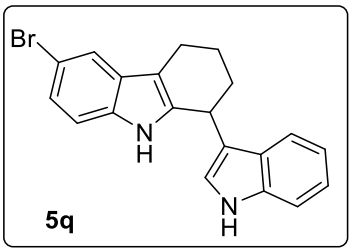




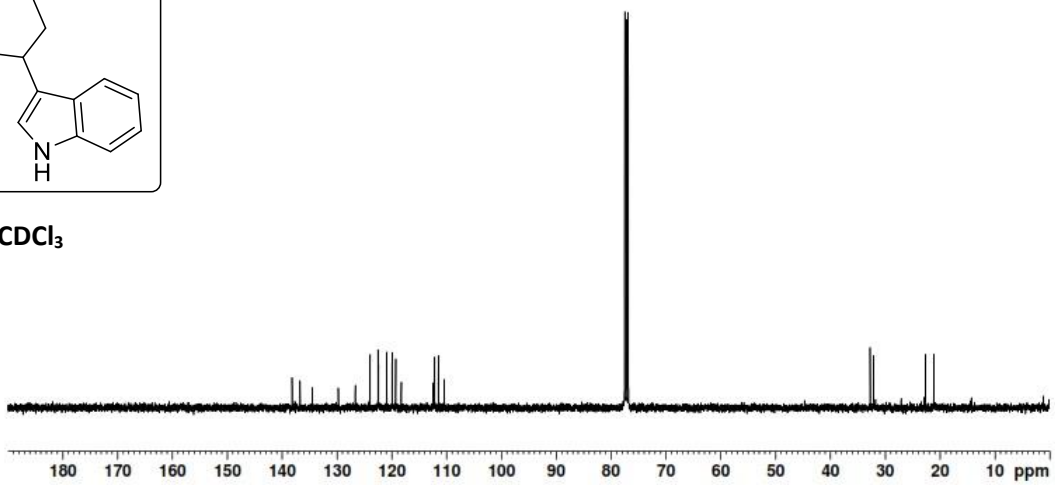
^{1}H NMR, $CDCl_3$

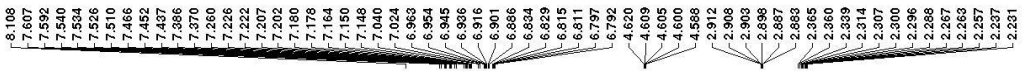


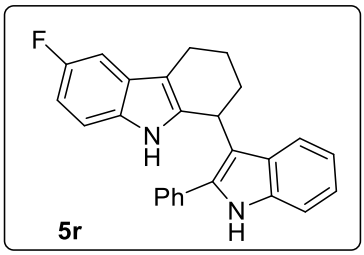




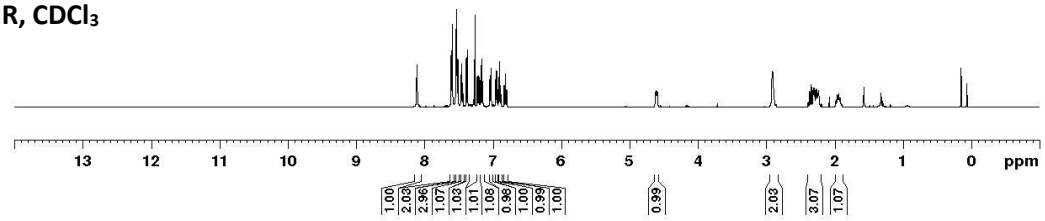
^{13}C NMR, $CDCl_3$

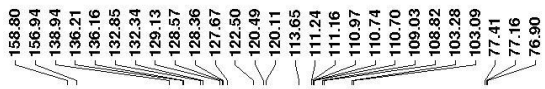


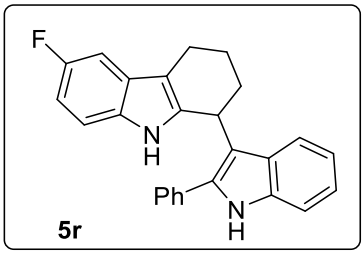




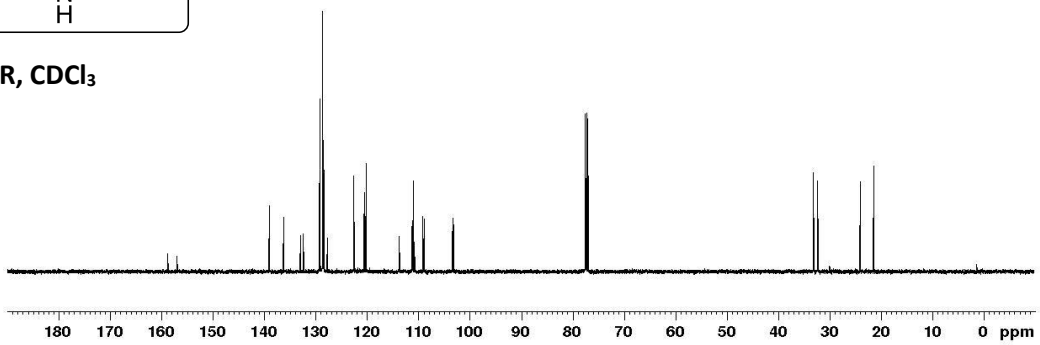
^{1}H NMR, $CDCl_3$

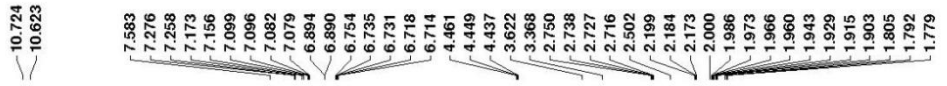


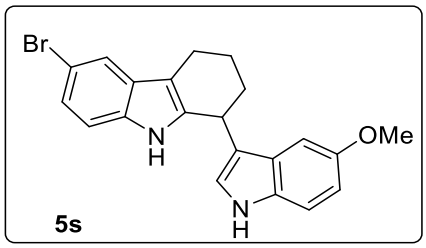




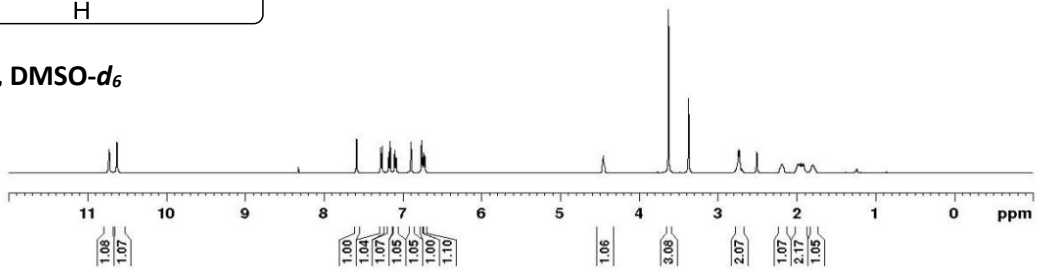
^{13}C NMR, $CDCl_3$

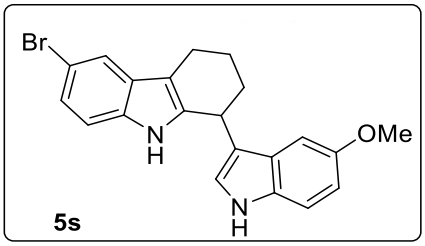




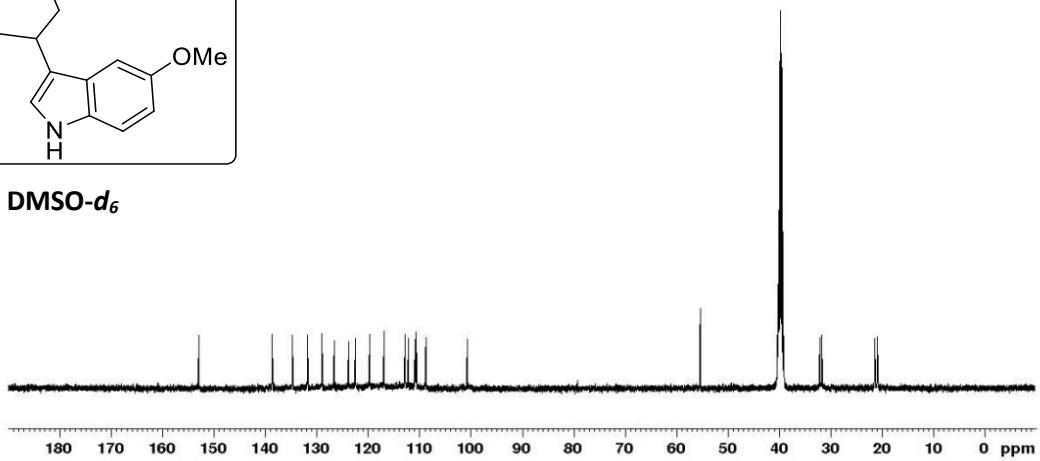


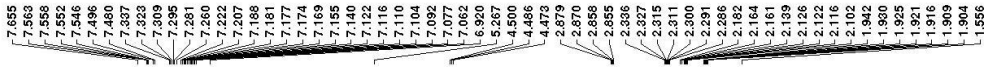
^{1}H NMR, DMSO-*d*$_6$

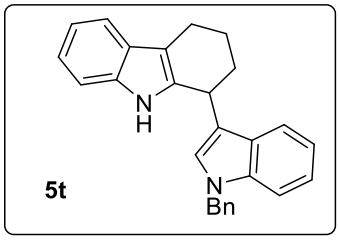




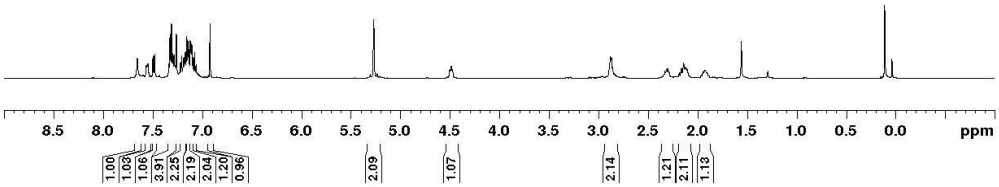
^{13}C NMR, DMSO-*d*$_6$

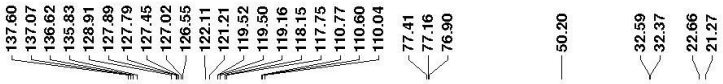


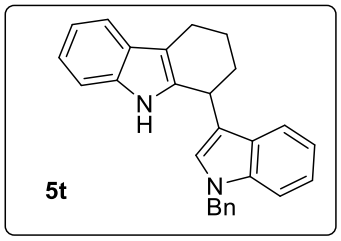




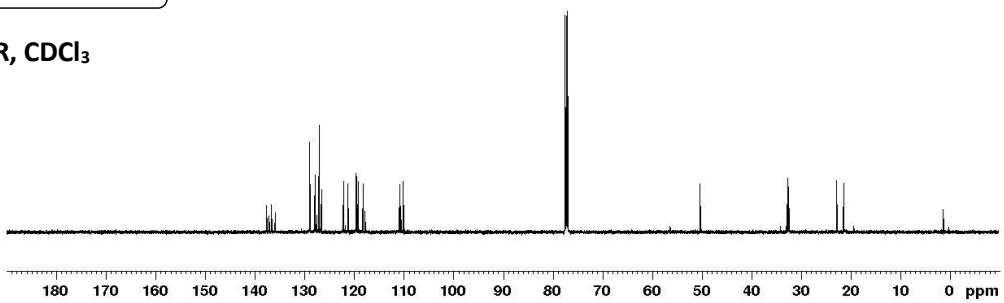
^{1}H NMR, $CDCl_3$

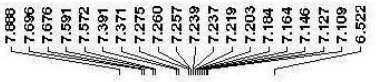


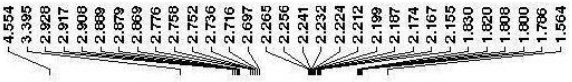


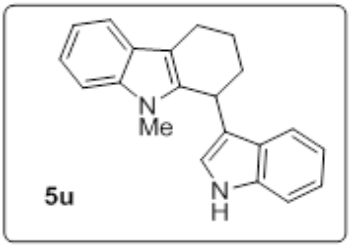


^{13}C NMR, $CDCl_3$

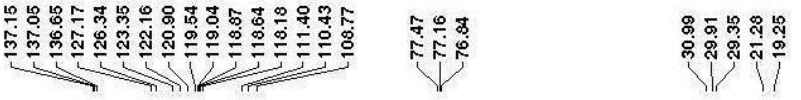


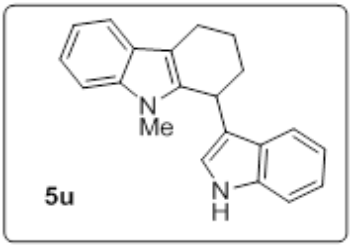




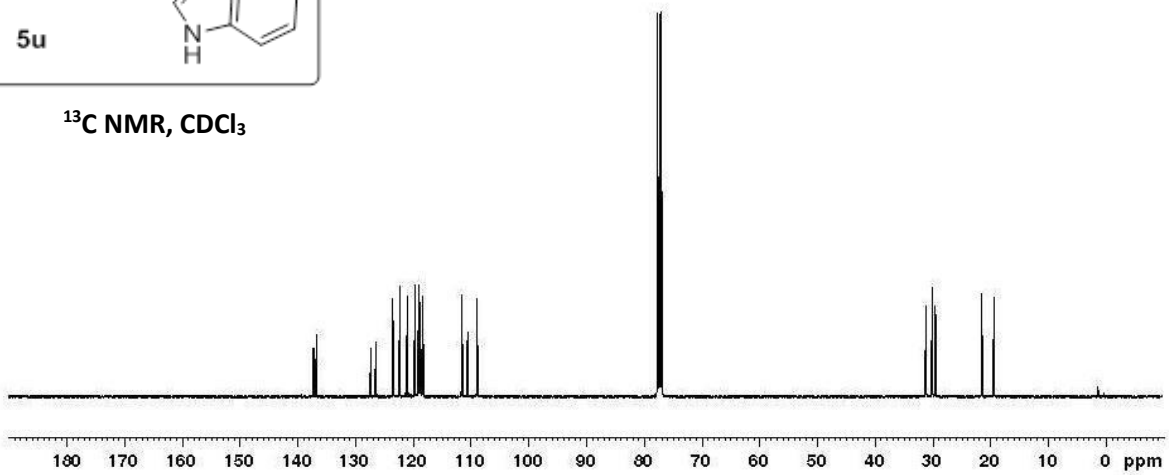


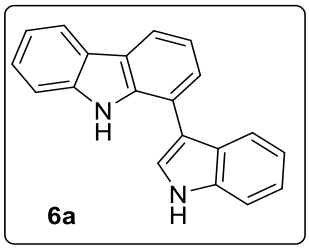
^{1}H NMR, $CDCl_3$



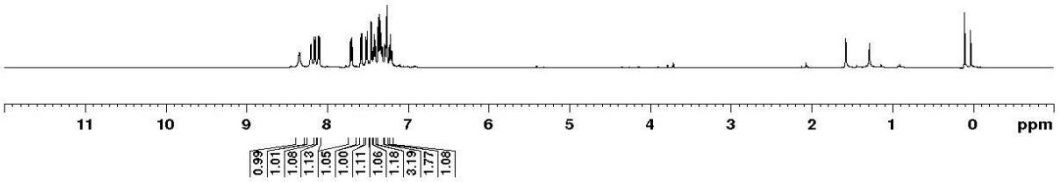


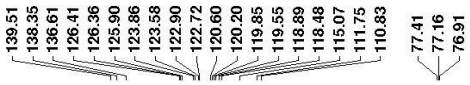
^{13}C NMR, $CDCl_3$

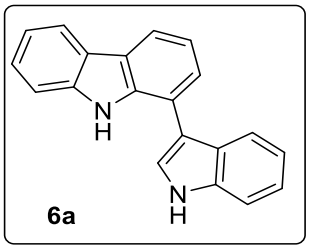




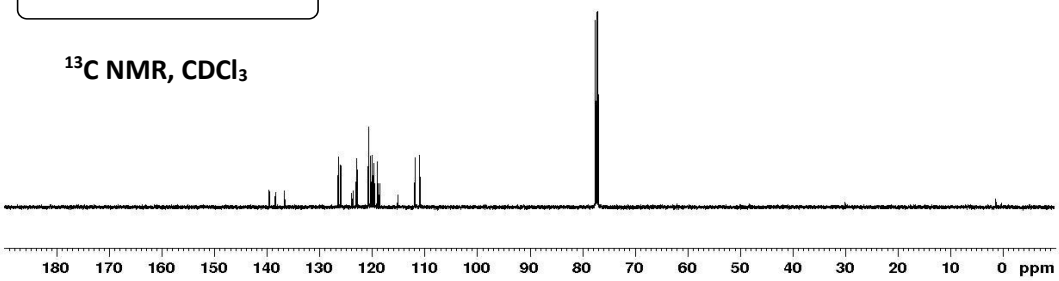
^{1}H NMR, $CDCl_3$

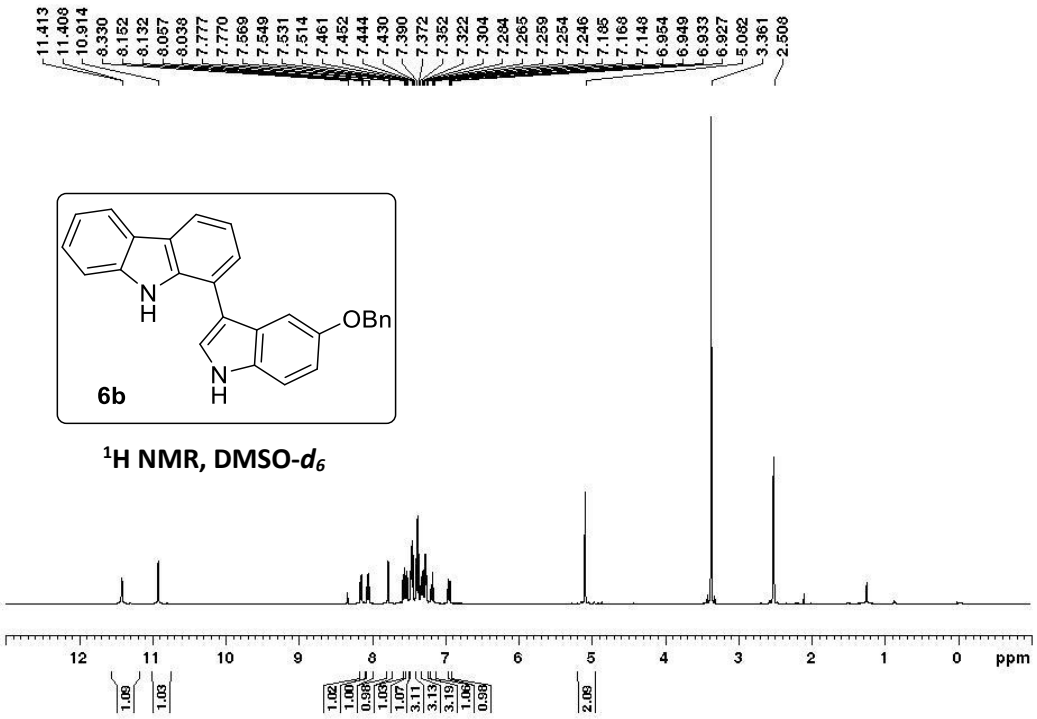




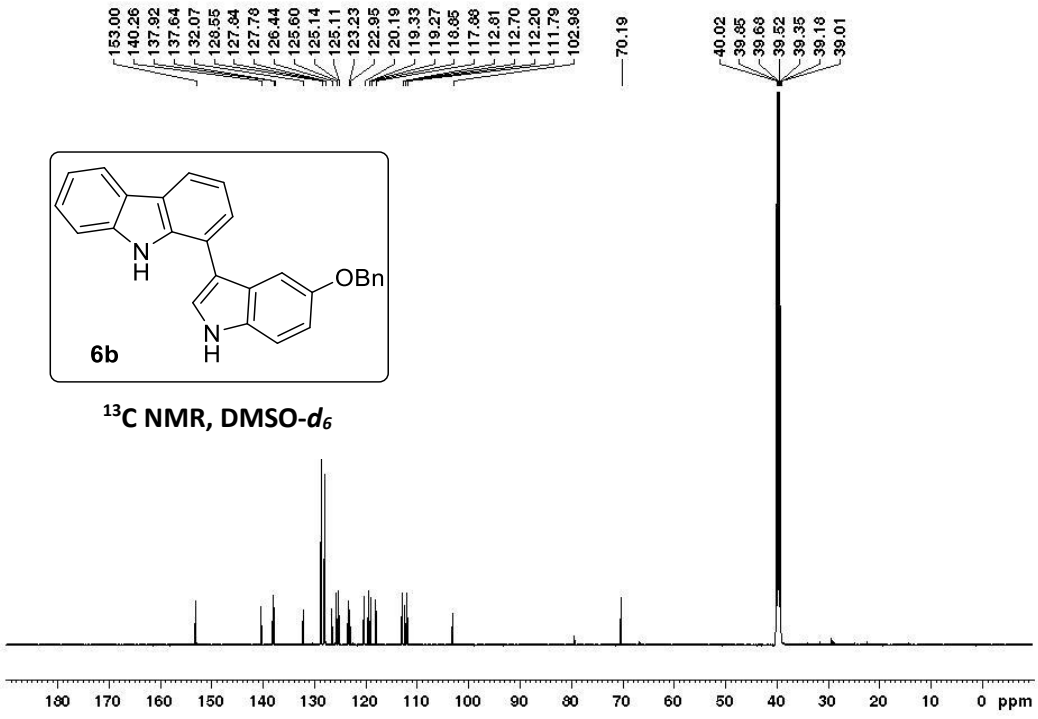


^{13}C NMR, $CDCl_3$

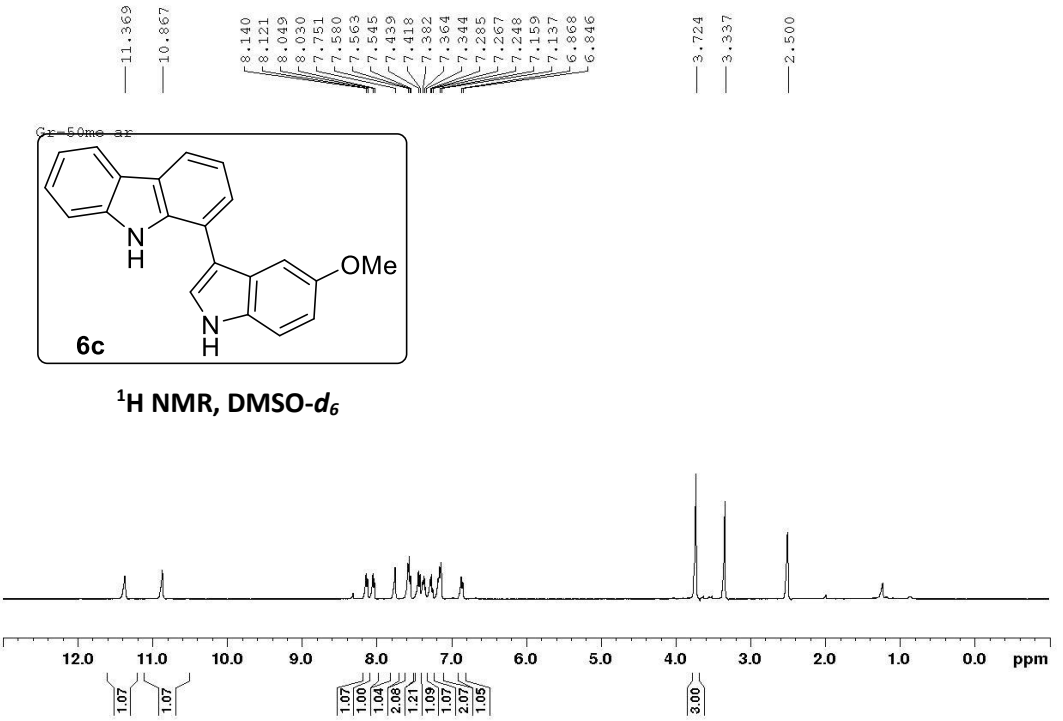




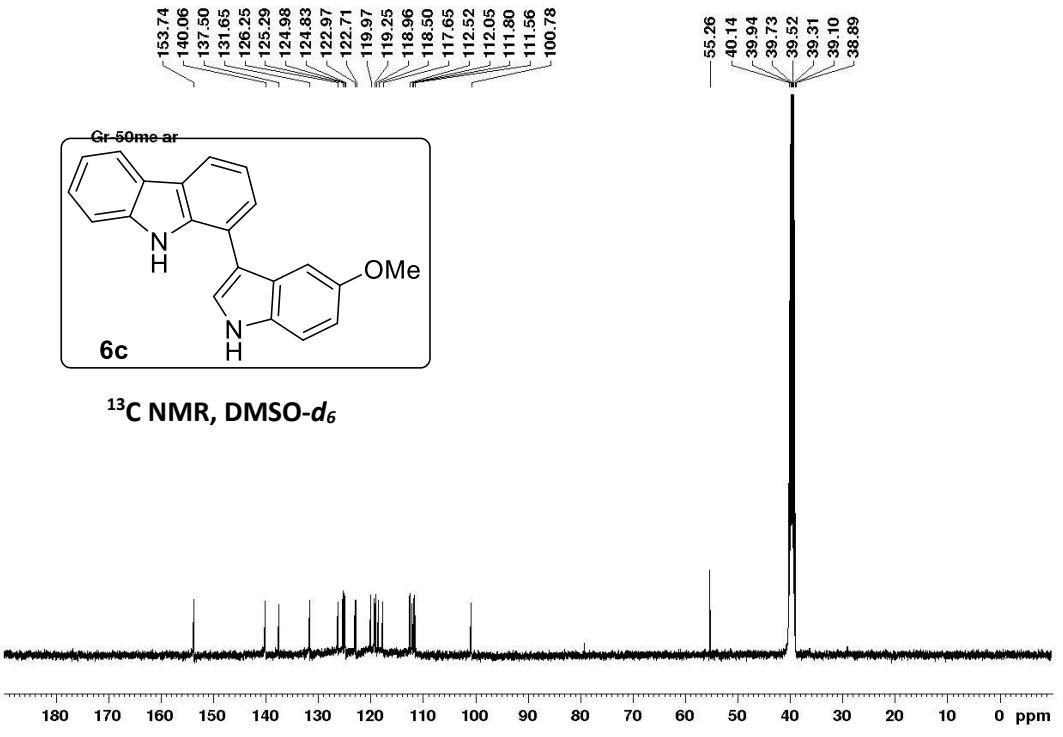
^{1}H NMR, DMSO-*d*$_6$



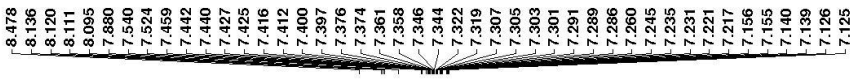
^{13}C NMR, DMSO-*d*$_6$

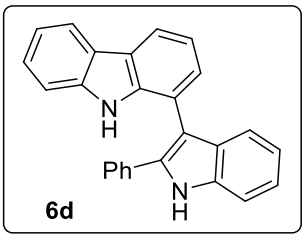


^{1}H NMR, DMSO-*d*$_6$

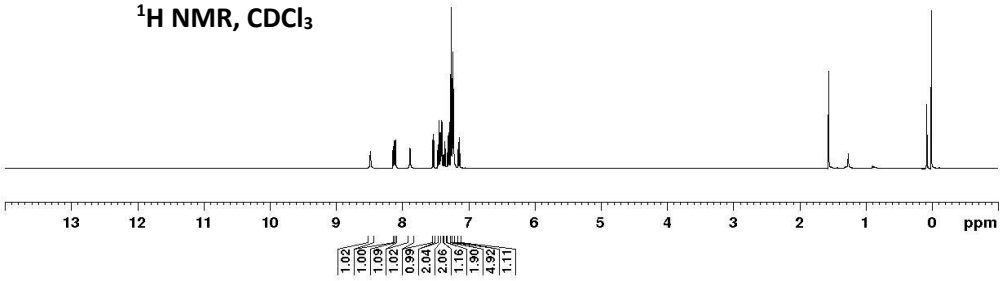


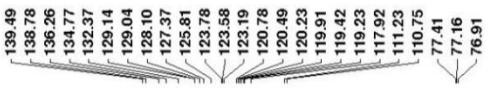
^{13}C NMR, DMSO-*d*$_6$

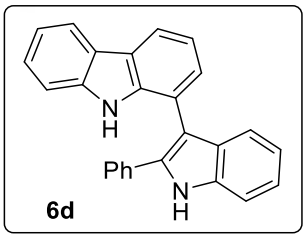




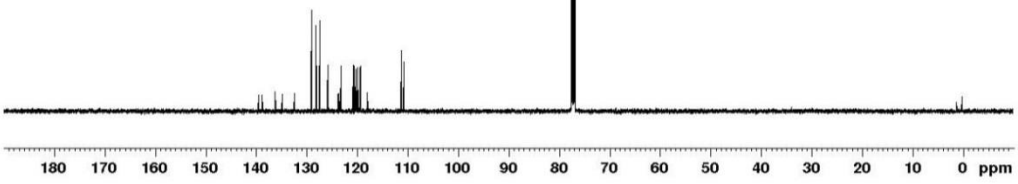
^{1}H NMR, $CDCl_3$

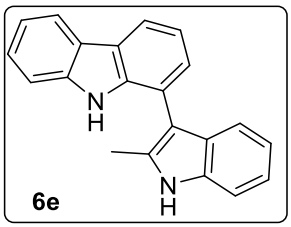




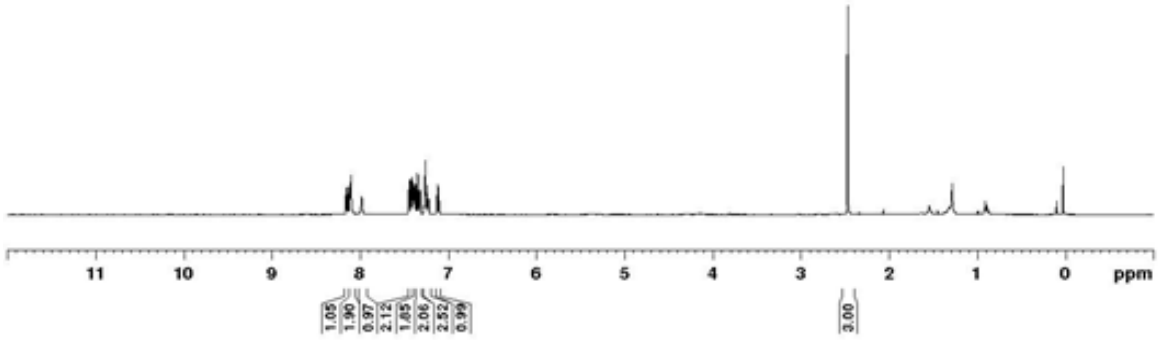


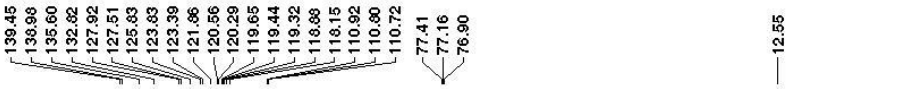
^{13}C NMR, $CDCl_3$

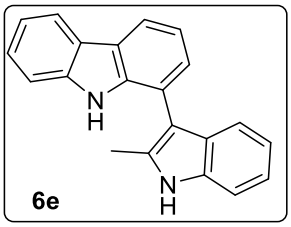




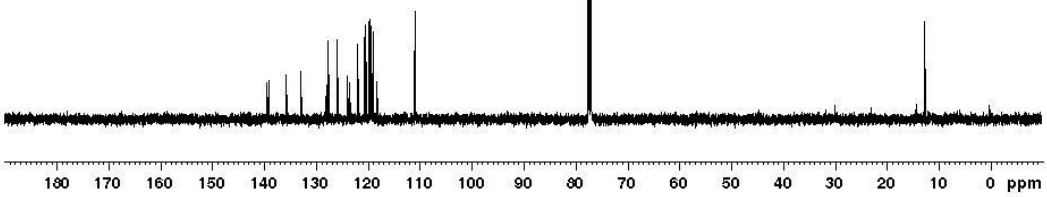
^{1}H NMR, $CDCl_3$

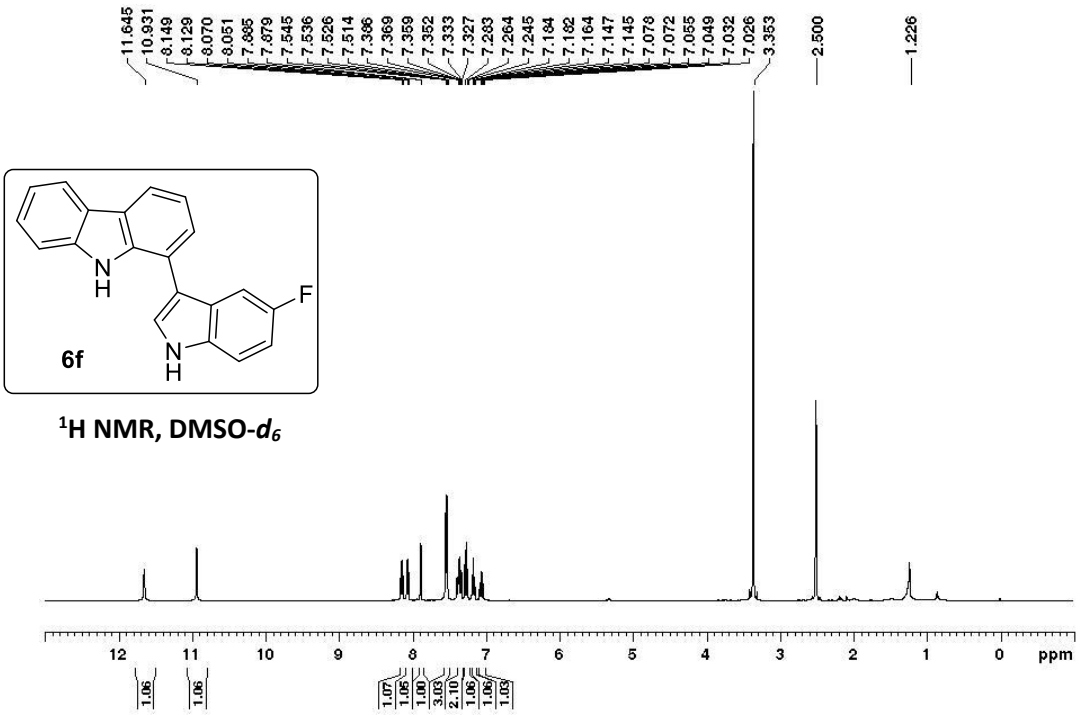




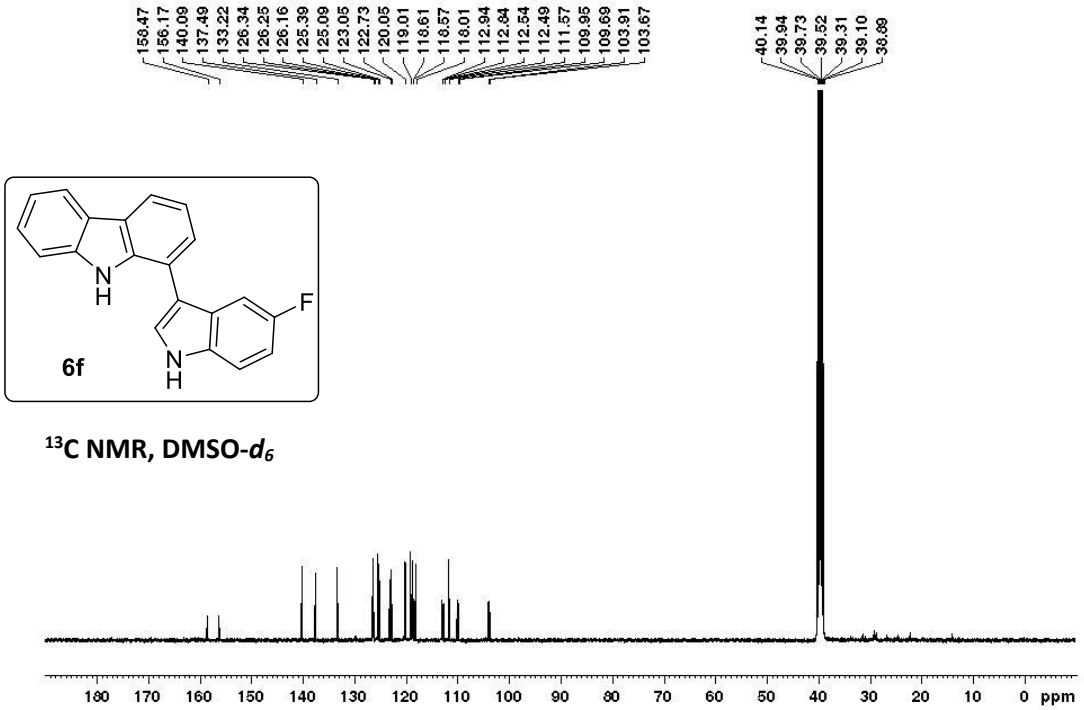


^{13}C NMR, $CDCl_3$

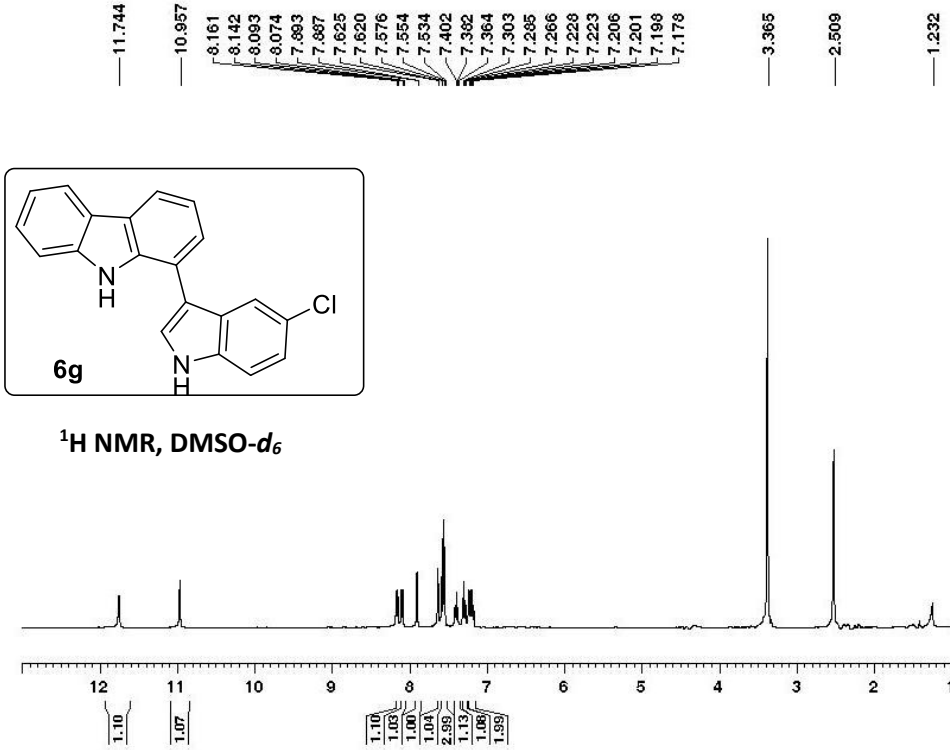




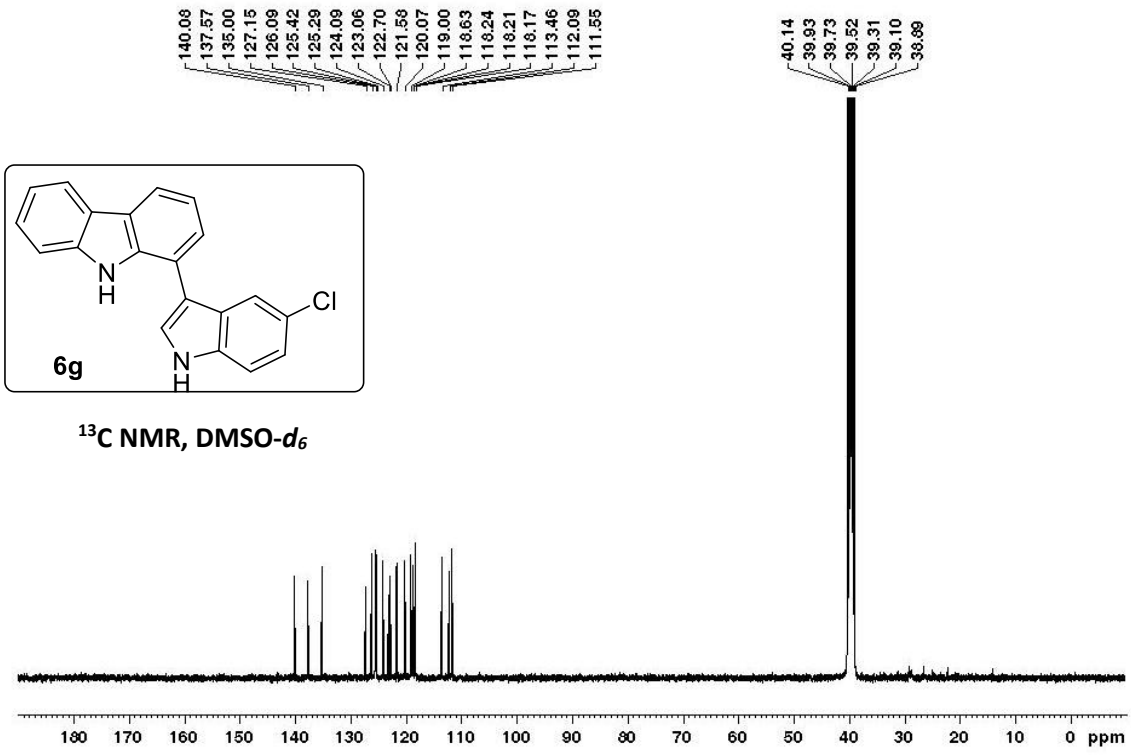
^{1}H NMR, DMSO-*d*$_6$



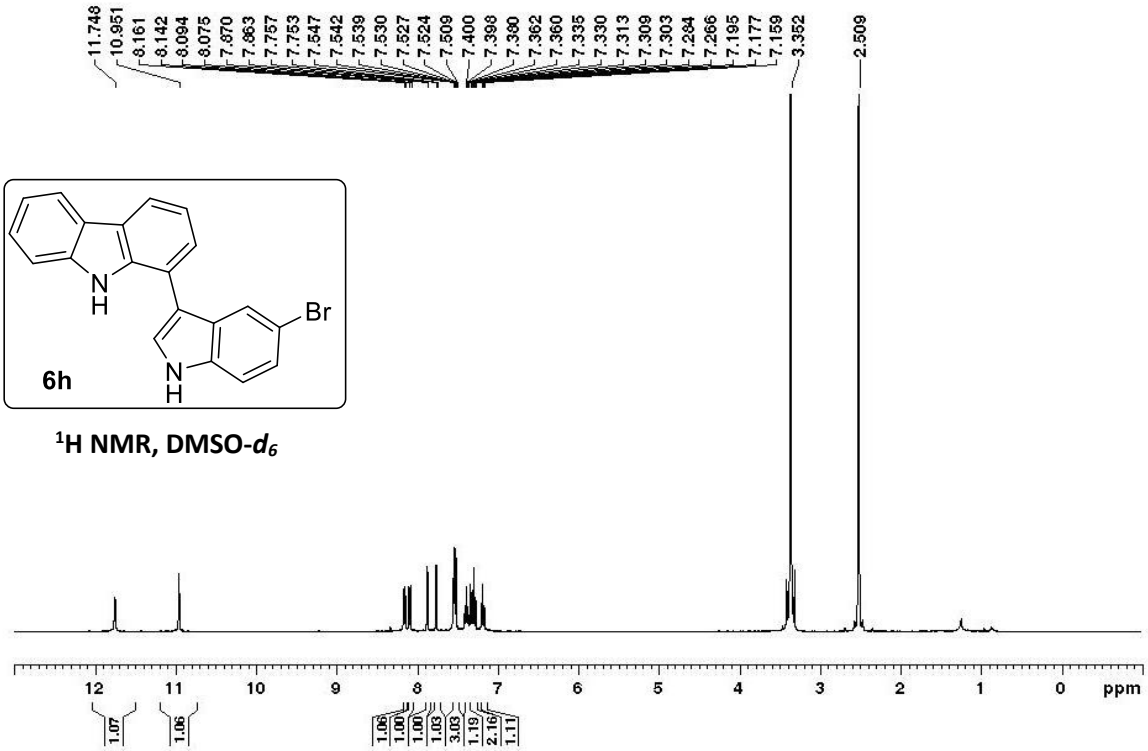
^{13}C NMR, DMSO-*d*$_6$



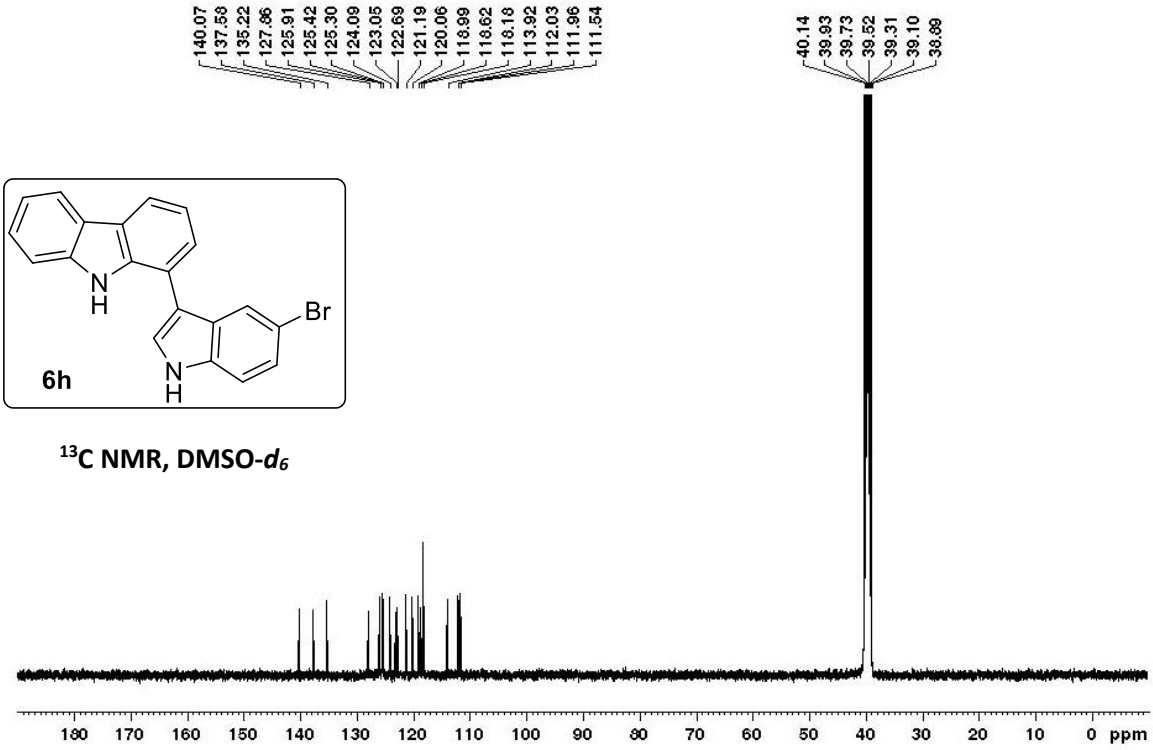
^{1}H NMR, DMSO-*d*$_6$



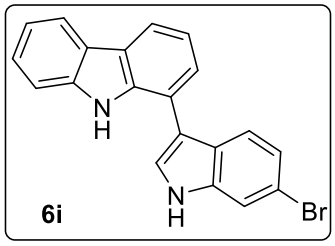
^{13}C NMR, DMSO-*d*$_6$



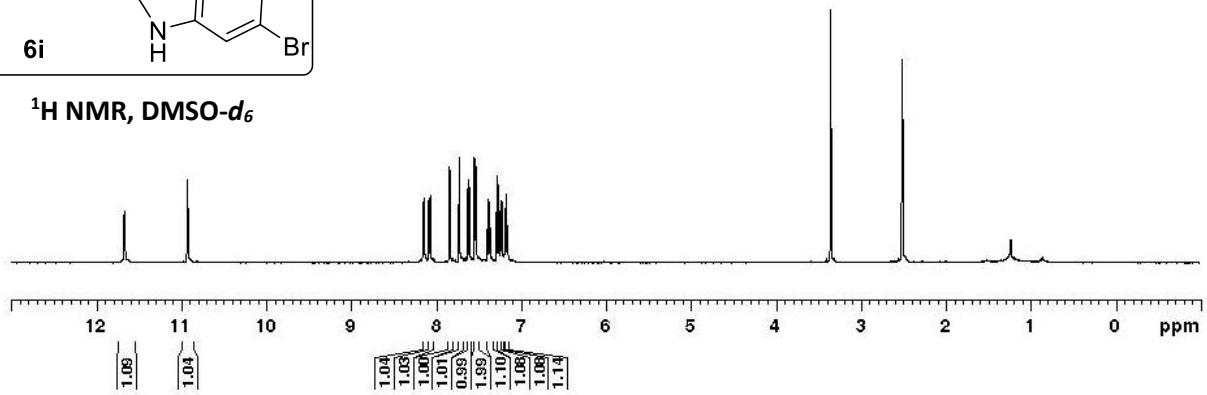
^{1}H NMR, DMSO-*d*$_6$

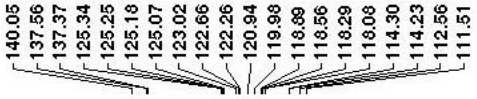


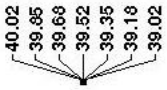
^{13}C NMR, DMSO-*d*$_6$

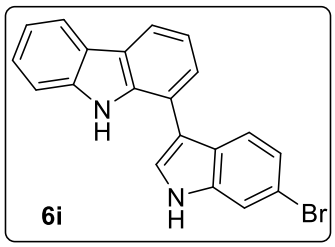


^{1}H NMR, DMSO-*d*$_6$

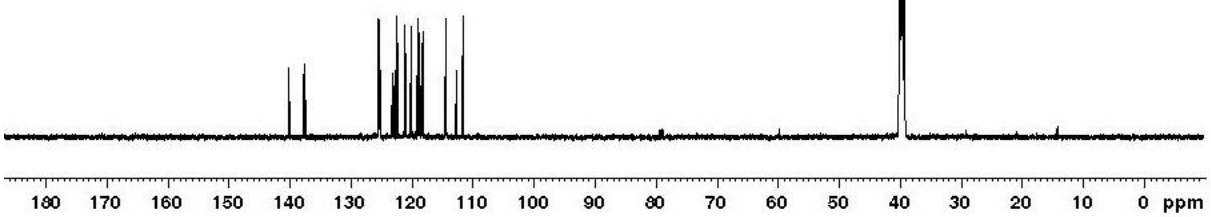


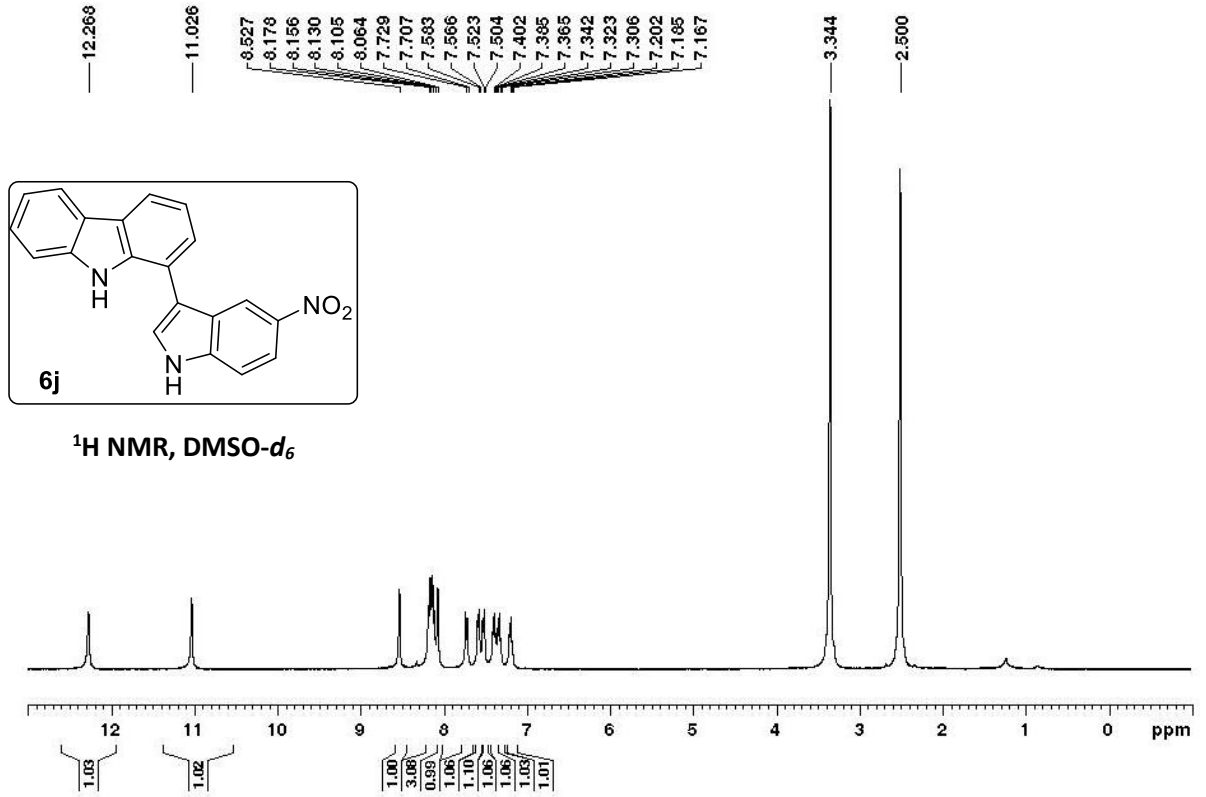




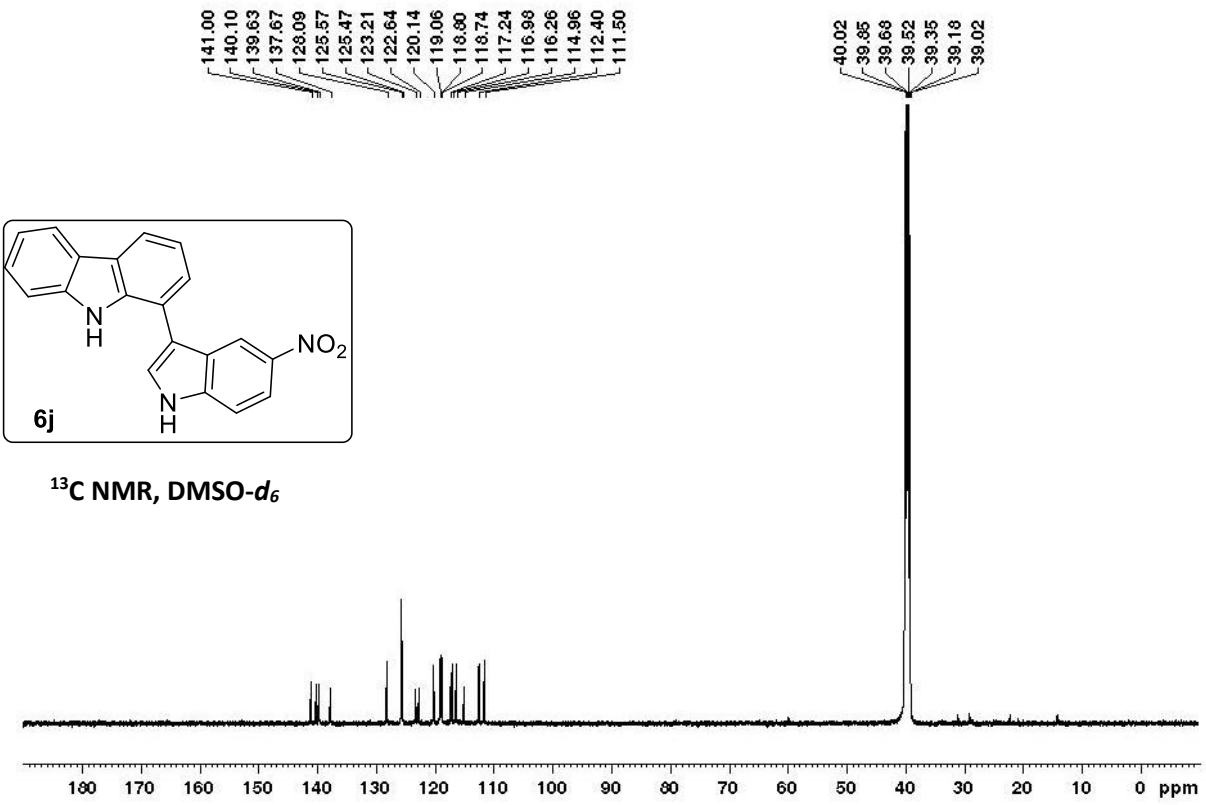


^{13}C NMR, DMSO-*d*$_6$

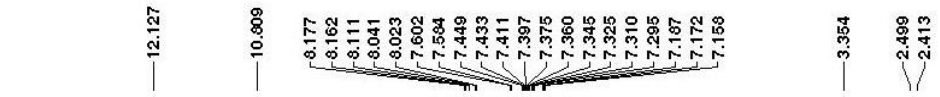


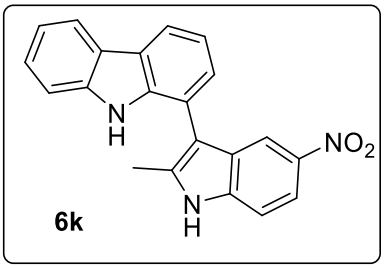


^{1}H NMR, DMSO-*d*$_6$

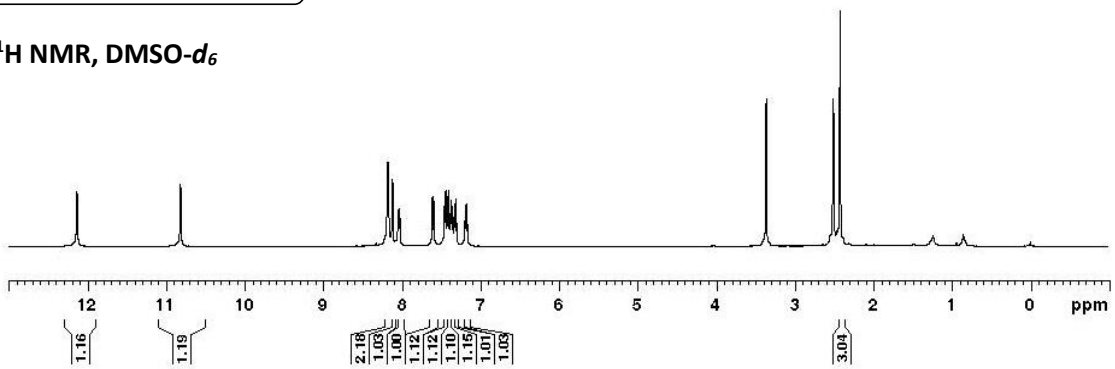


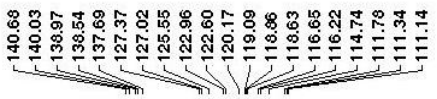
^{13}C NMR, DMSO-*d*$_6$

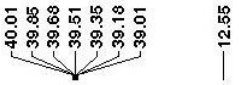


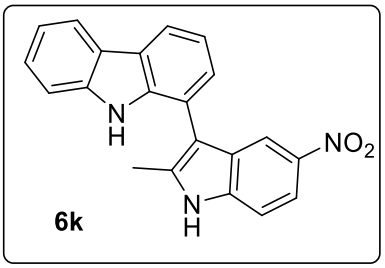


^{1}H NMR, DMSO-*d*$_6$

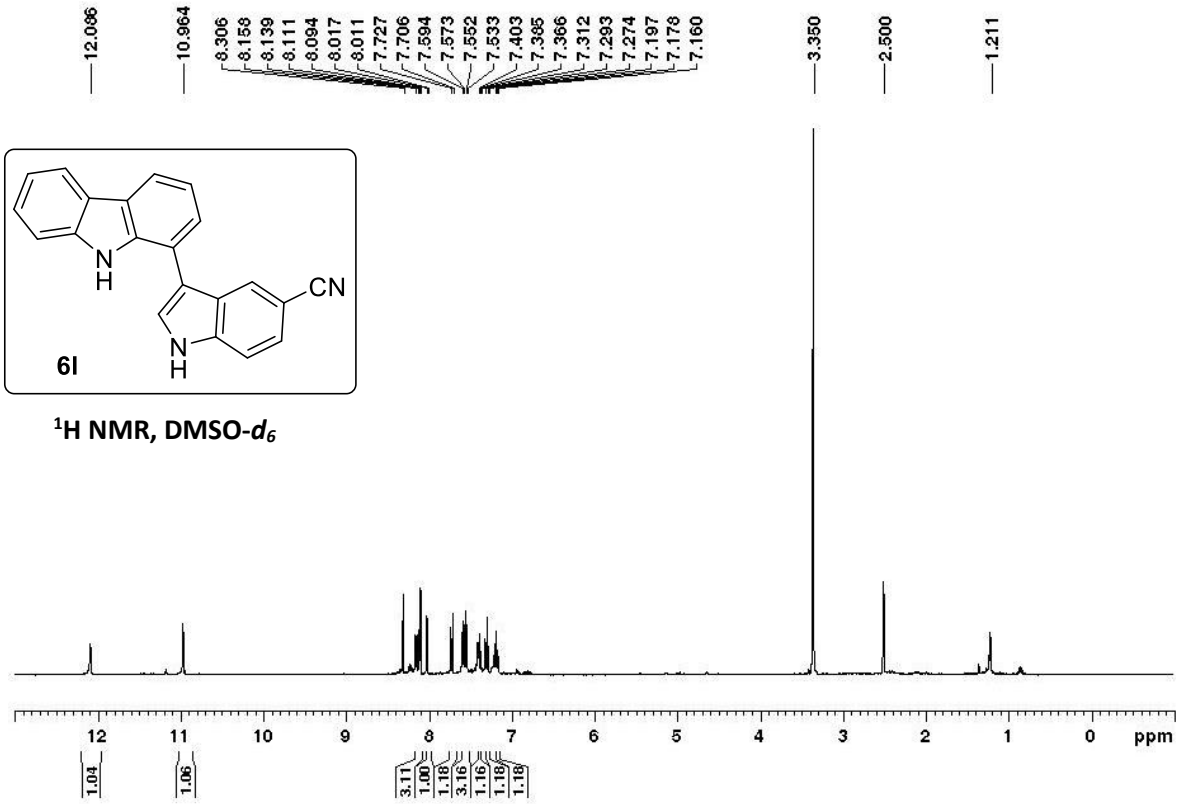




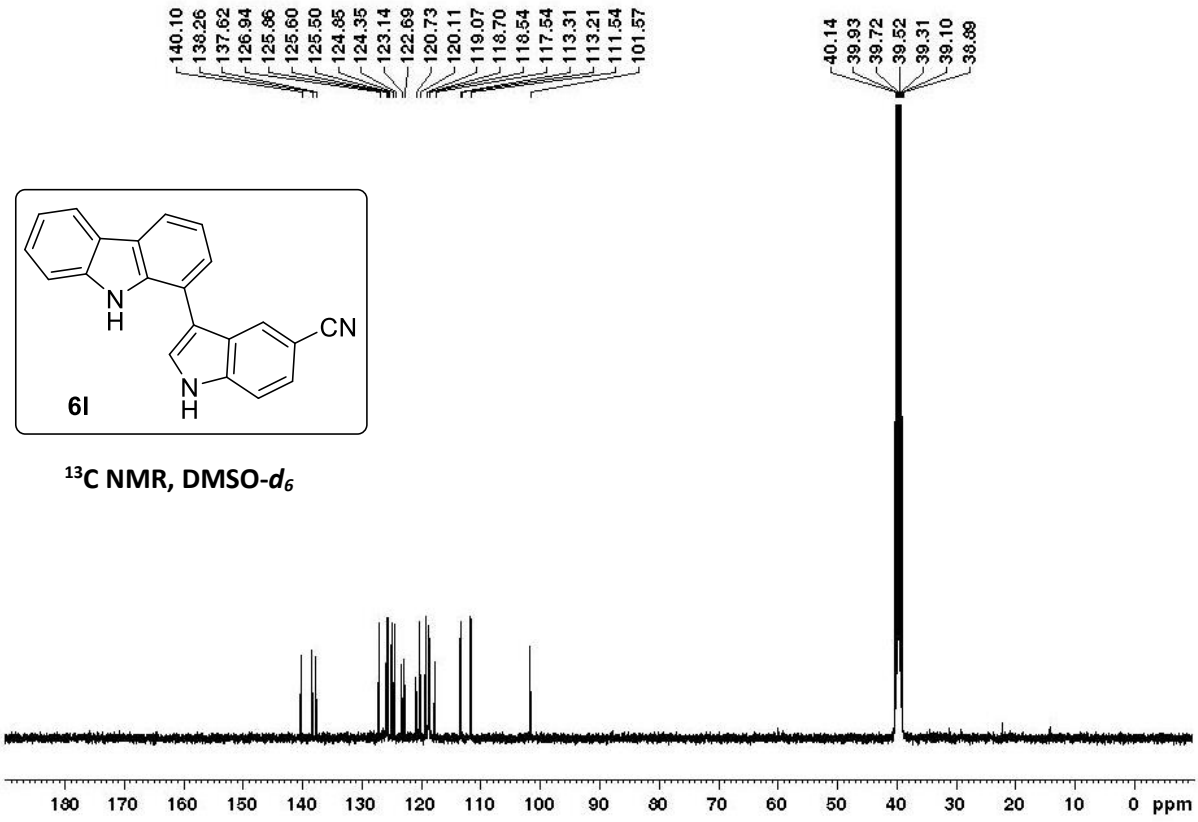




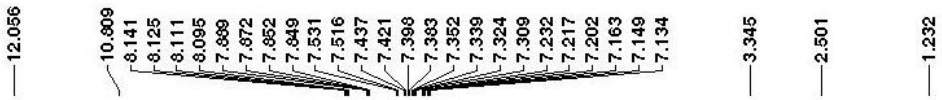
^{13}C NMR, DMSO-*d*$_6$

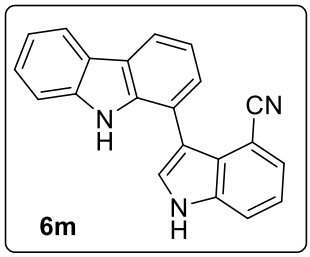


^{1}H NMR, DMSO-*d*$_6$

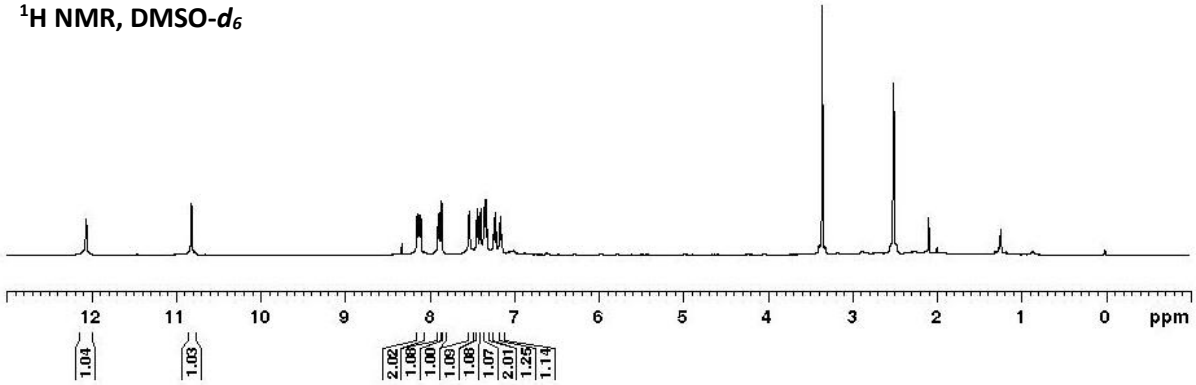


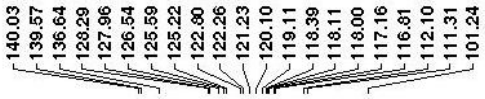
^{13}C NMR, DMSO-*d*$_6$

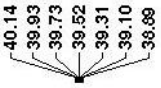


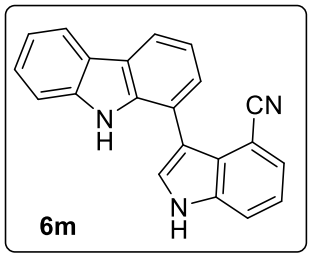


^{1}H NMR, DMSO-*d*$_6$

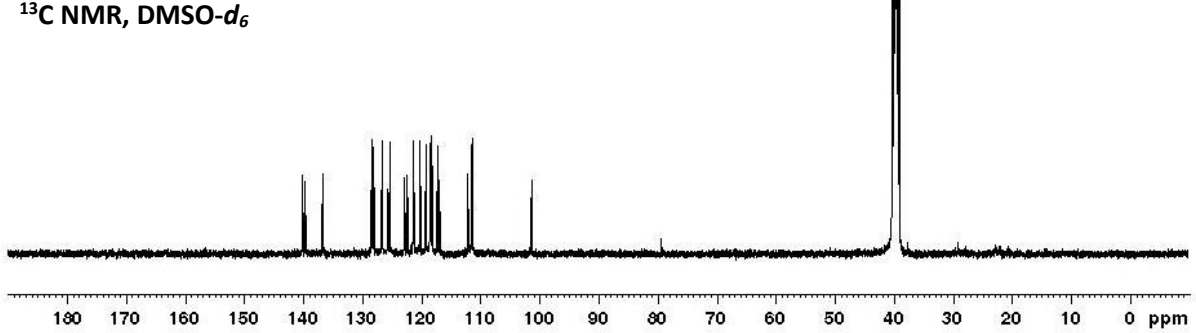


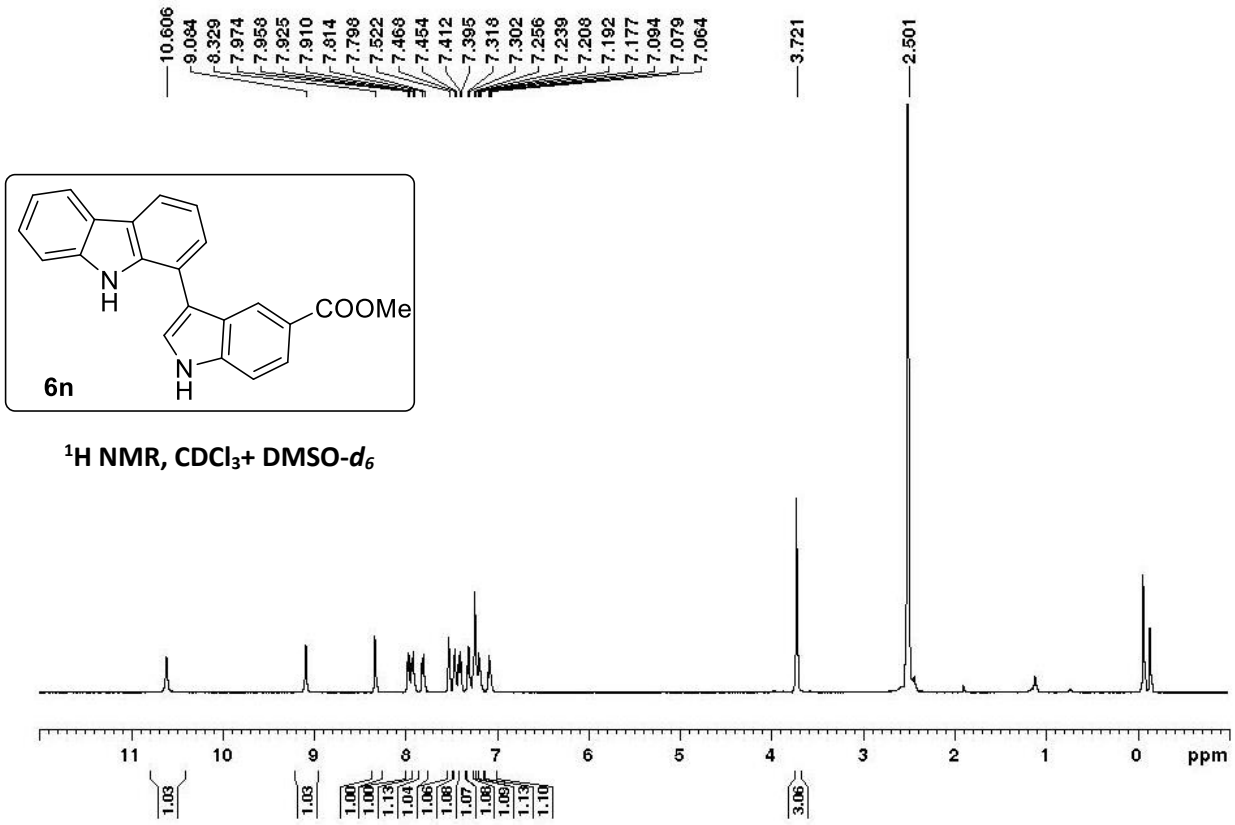




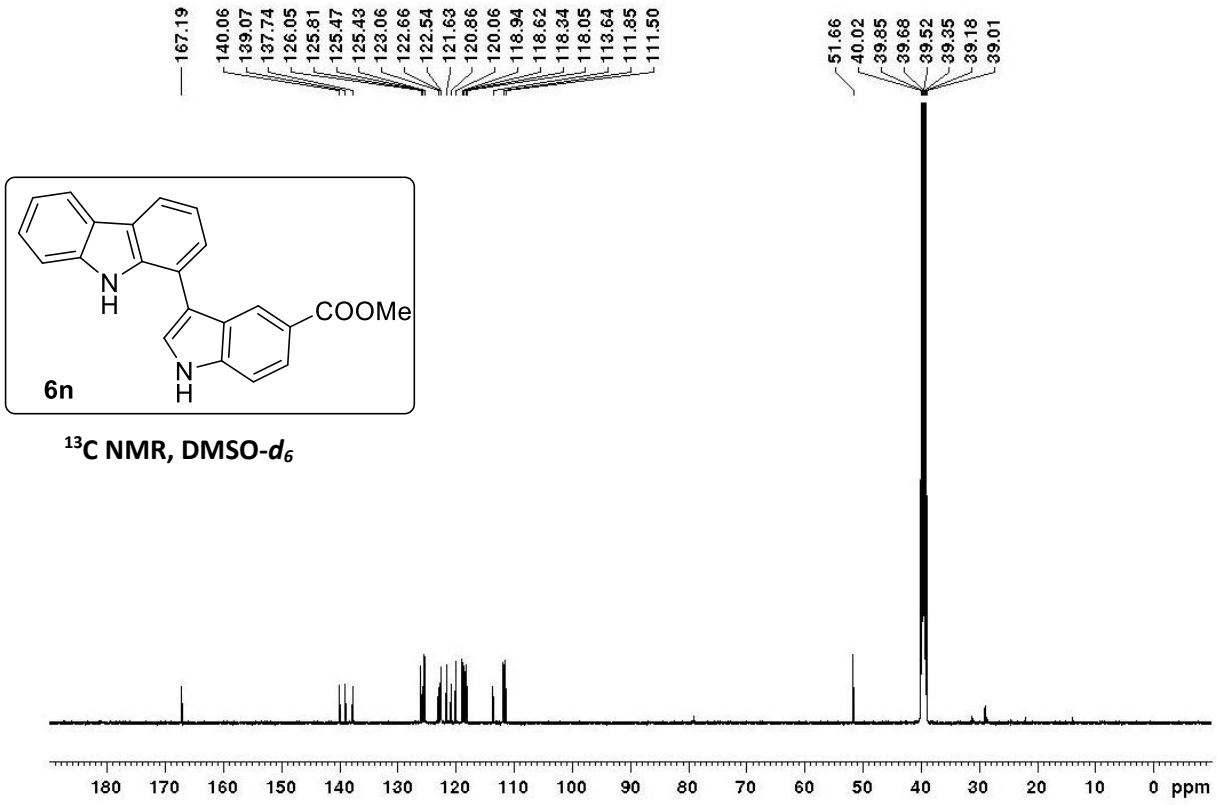


^{13}C NMR, DMSO-*d*$_6$

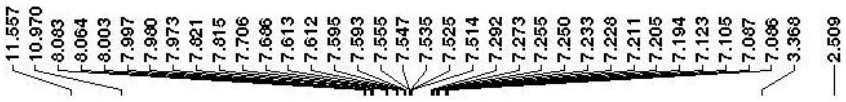


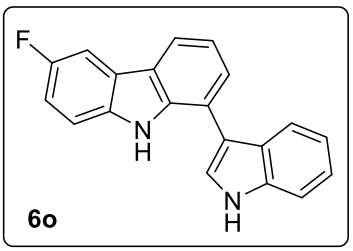


^{1}H NMR, $CDCl_3$+ DMSO-*d_6*

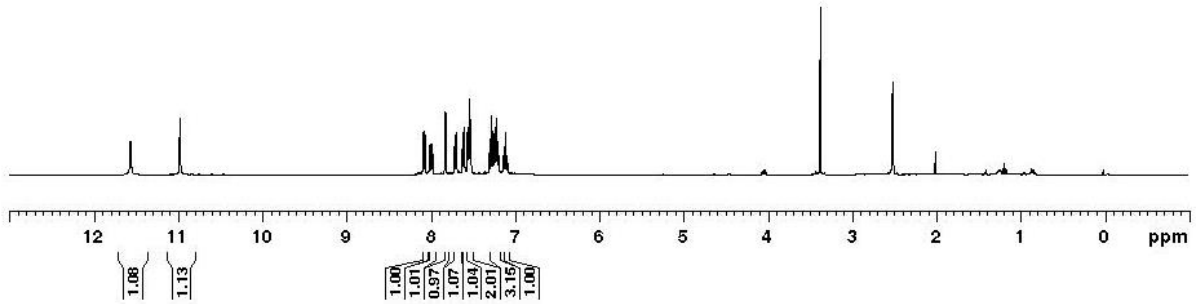


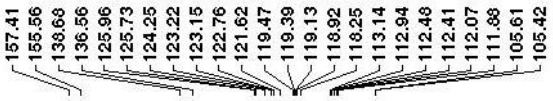
^{13}C NMR, DMSO-*d_6*

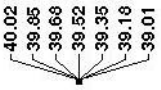


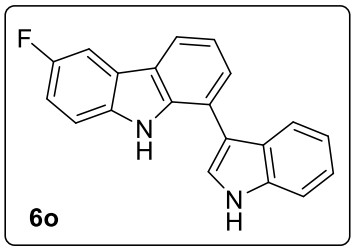


^{1}H NMR, DMSO-*d*$_6$

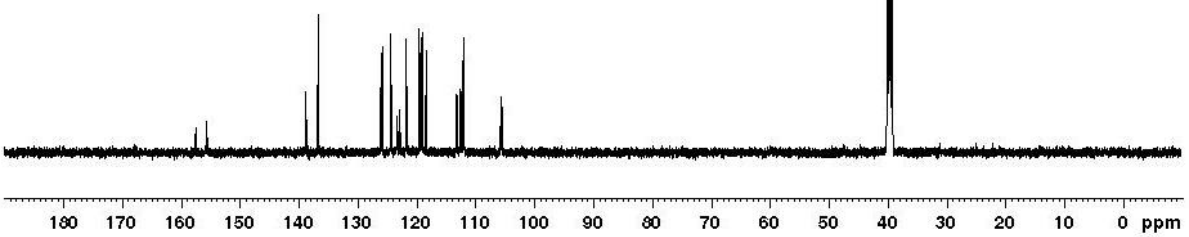


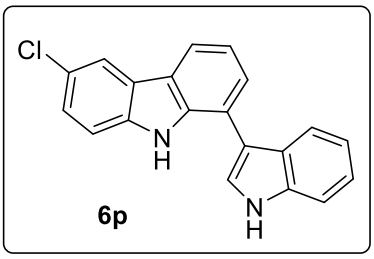




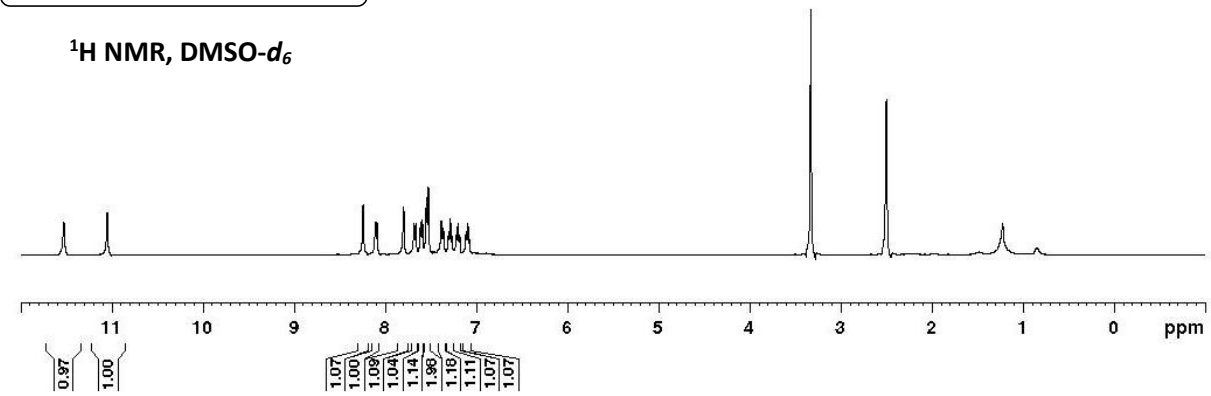


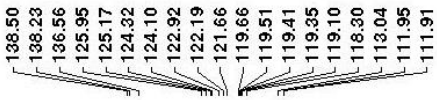
^{13}C NMR, DMSO-*d*$_6$

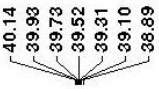


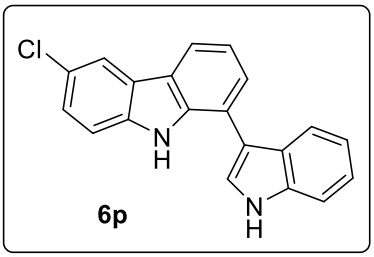


^{1}H NMR, DMSO-*d*$_6$

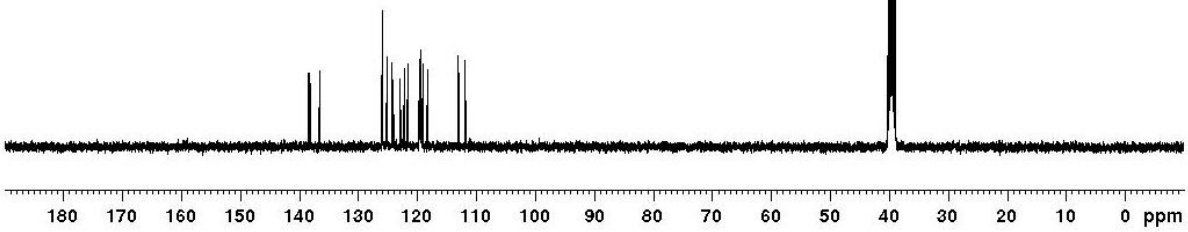


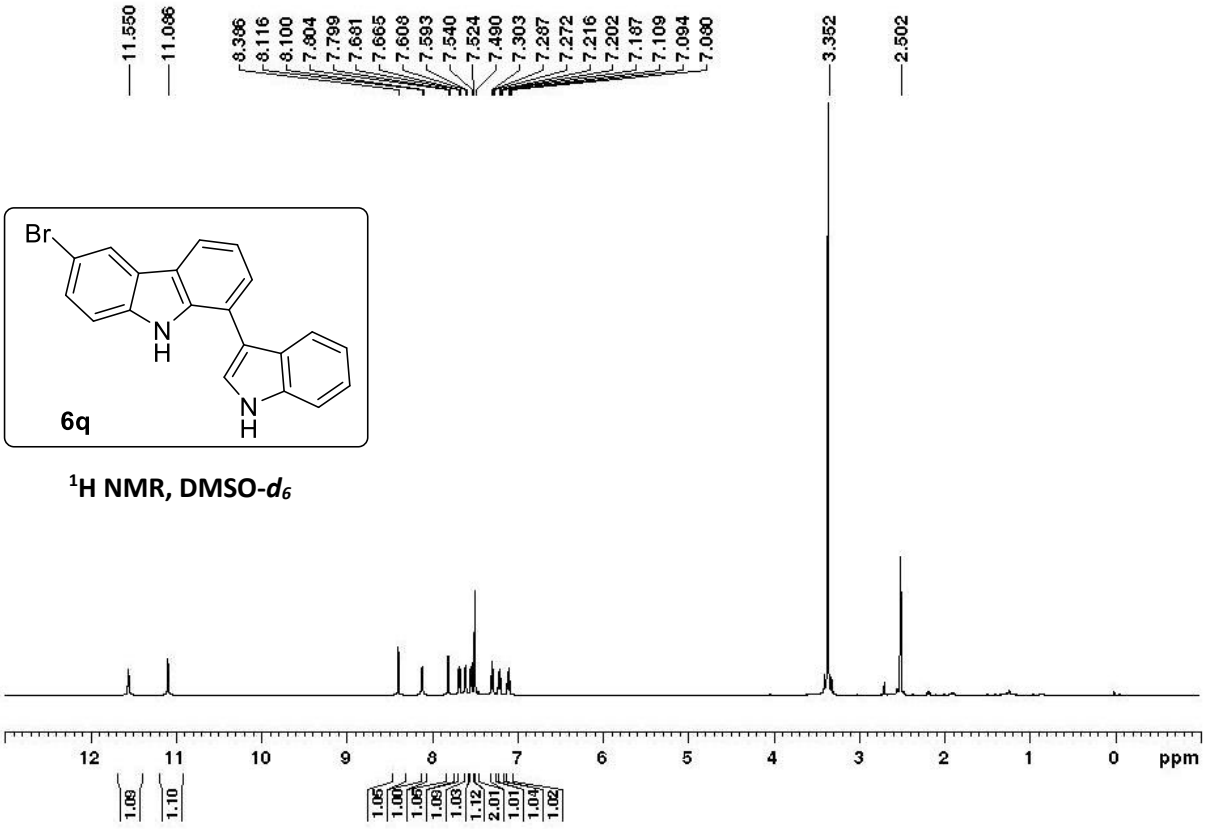




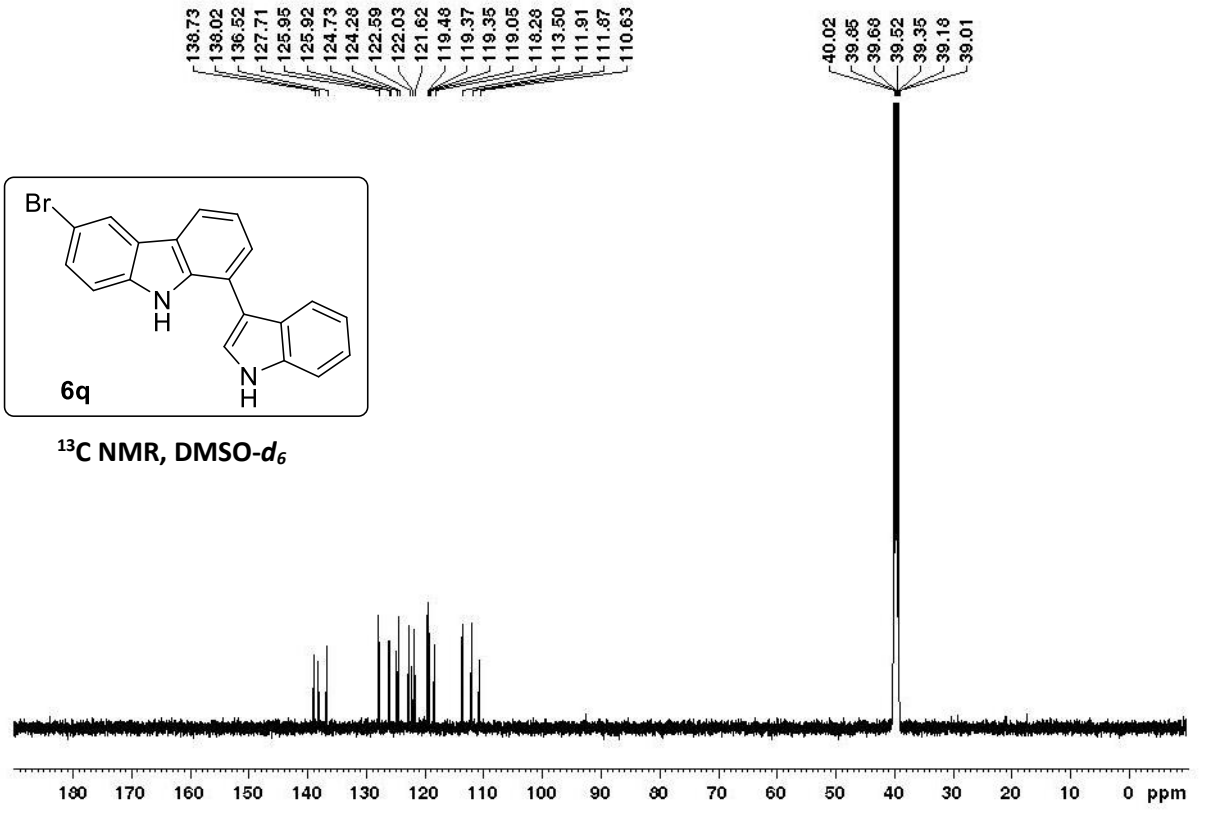


^{13}C NMR, DMSO-*d*$_6$





^{1}H NMR, DMSO-*d*$_6$



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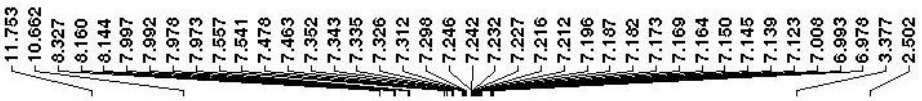
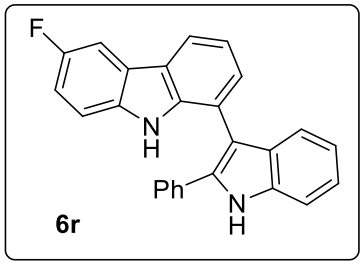
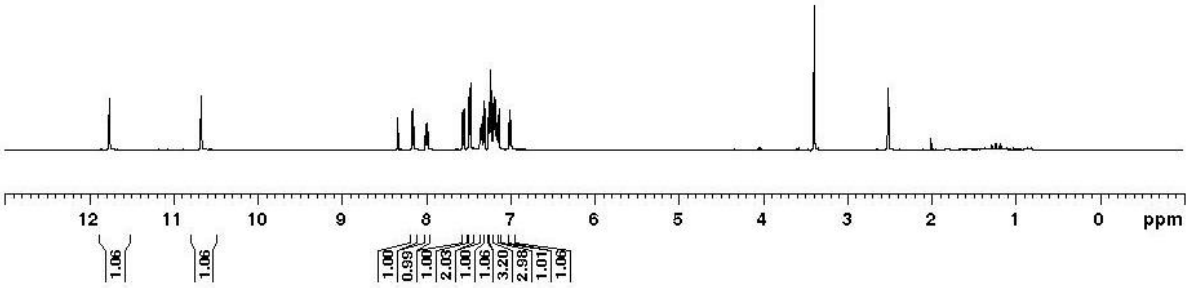
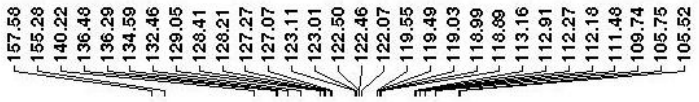
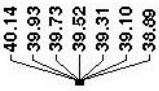


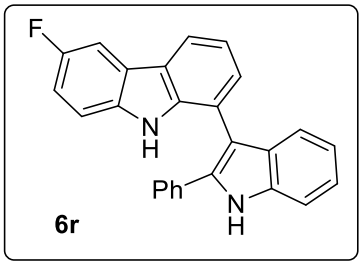


^{1}H NMR, DMSO-*d*$_6$

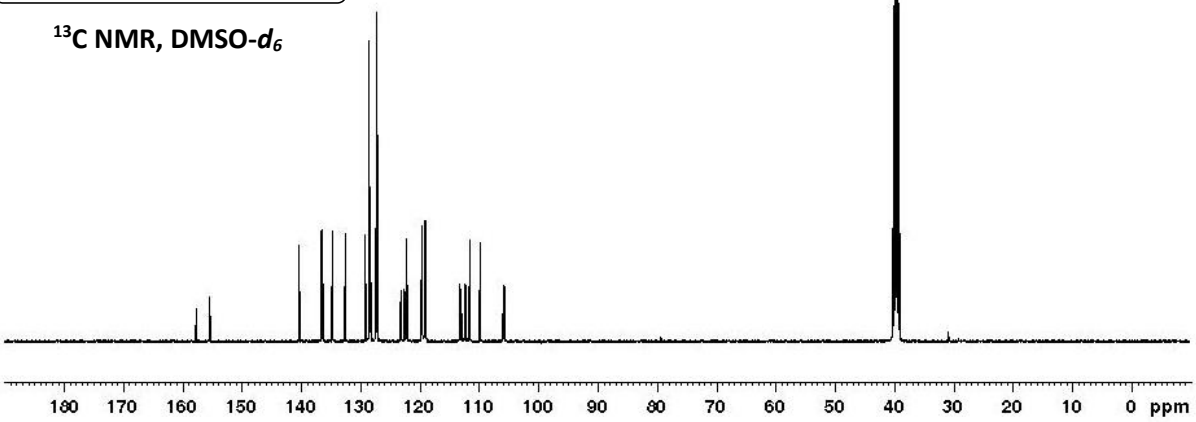


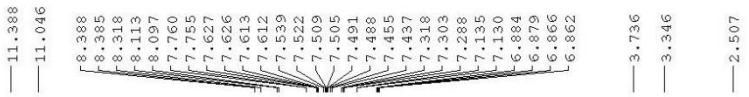


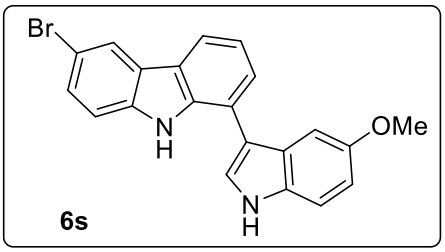




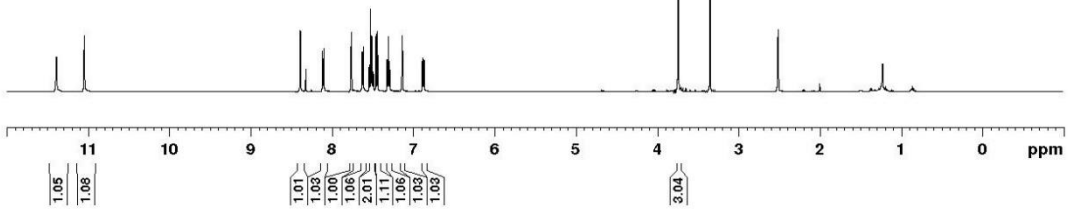
^{13}C NMR, DMSO-*d*$_6$

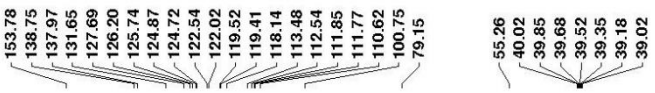


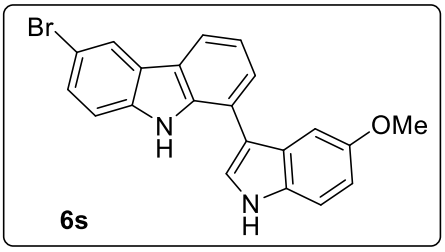




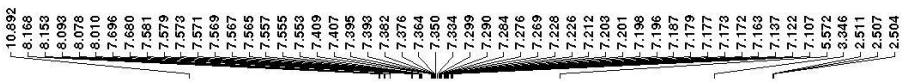
^{1}H NMR, DMSO-*d*$_6$

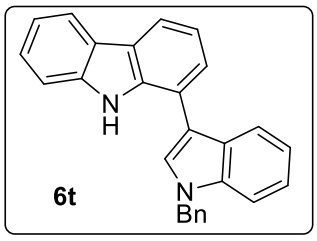




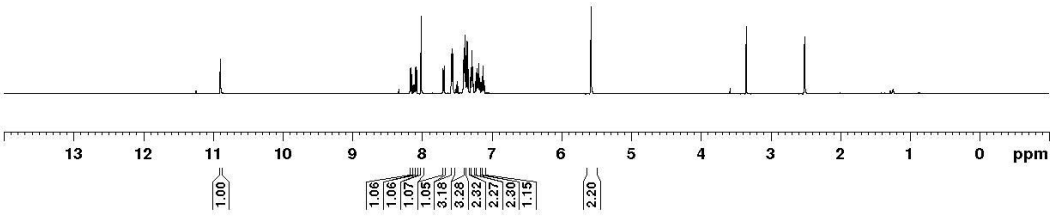


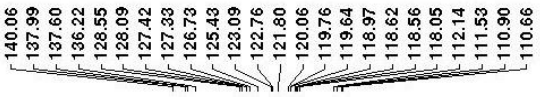
^{13}C NMR, DMSO-*d*$_6$

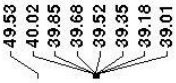


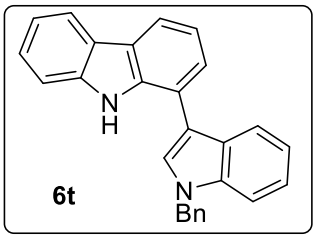


^{1}H NMR, DMSO-*d*$_6$

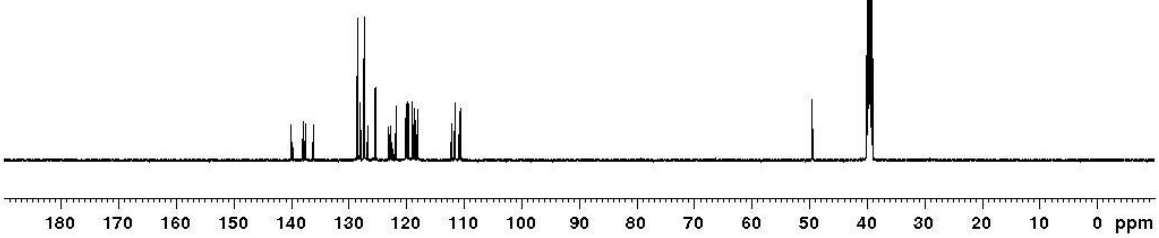


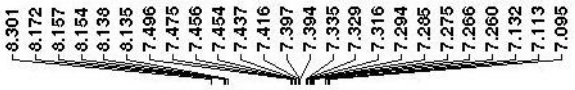


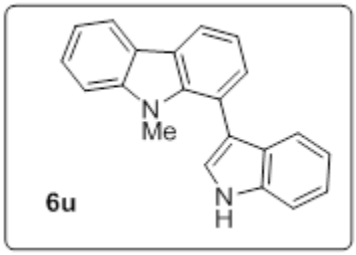




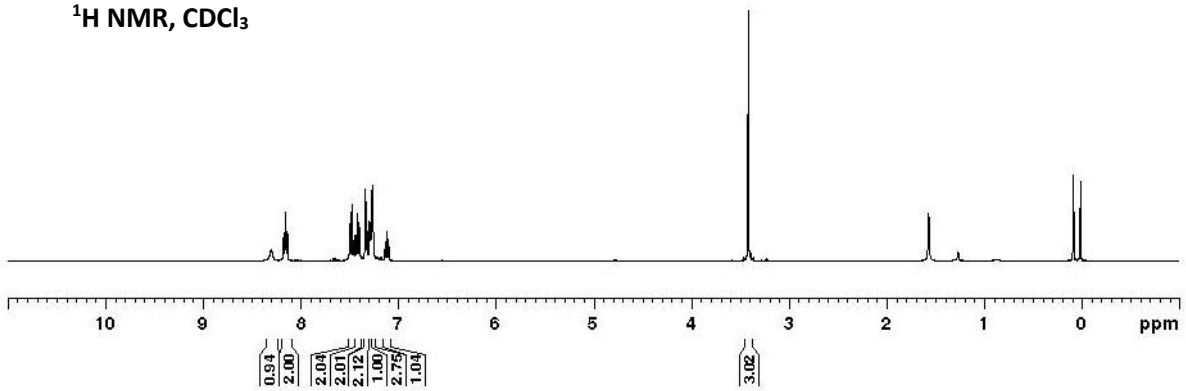
^{13}C NMR, DMSO-*d*$_6$

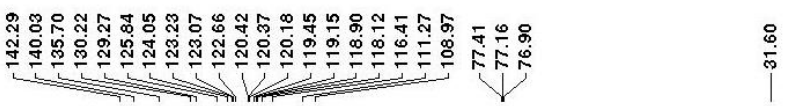


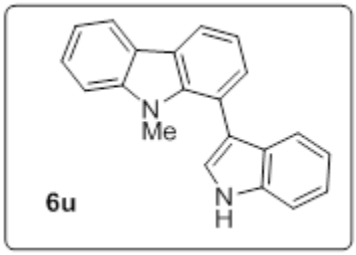




^{1}H NMR, $CDCl_3$







^{13}C NMR, $CDCl_3$

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1. a) Gore, S.; Baskaran, S.; König, B. *Org. Lett.* **2012**, *14*, 4568-4571. b) Pitts, M. R.; Harrison, J. R.; Moody, C. J. *J. Chem. Soc. Perkin Trans.* **2001**, 1, 955. c) Robinson, B. The Fischer Indole Synthesis, John Wiley & Sons Inc. 1982.
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