Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Sunlight-mediated [3+2] cycloaddtion of azobenzenes with arynes: An approach to carbazole skeleton

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1. General considerations

All ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 600 MHz Bruker FT-NMR spectrometer. All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI) and a Thermo Scientific Q Exactive HF Orbitrap-FTMS instrument. Melting points were determined in open capillary tube using WRS-1B digital melting point apparatus.

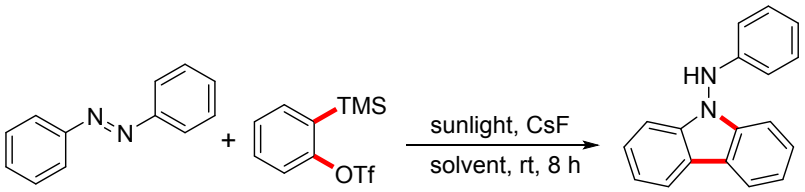
All of the starting materials, such as azobenzenes and 2-(trimethylsilyl)phenyl trifluoromethanesulfonates, were prepared according to the reported methods.[1-2] All the solvents were dried and freshly distilled prior to use. Products were purified by flash chromatography on silica gels, eluting with petroleum ether/ethyl acetate (3:1 to 50:1).

2. Typical procedure for the [3+2] cyclization of azobenzene with aryne

In a 10 mL oven-dried quartz photoreactor equipped with a magnetic stirrer bar was charged with azobenzene (**1a**, 36.4 mg, 0.20 mmol), 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (**2a**, 89.5 mg, 0.30 mmol), CsF (91.1 mg, 0.60 mmol) and freshly distilled acetonitrile (1.0 mL). The reaction was stirred under sunlight for 8 h. After that, the mixture in reaction tube was detected by TLC. Then the solvent was removed under vacuum to obtain the crude product. The mixture was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1 to 50:1), and afforded the desired product **3a** as a white solid (38.2 mg, 74% yield).

3. Further optimization of the reaction conditions

Table S1: Optimization of the solvent[a]



1a **2a** **3a**[b]

entry	solvent	yield (%)[b]
1	DCE	19
2	DCM	37
3	DMF	trace
4	DMSO	0
5	THF	7
6	PhMe	trace

[a] Reaction conditions: **1** (0.20 mmol), **2a** (0.30 mmol) and CsF (0.60 mmol) in anhydrous CH_3CN (1.0 mL) at room temperature under sunlight irradiation for 8 h. [b]Isolated yield.

4. Mechanistic studies

4.1 Absorption spectra of the starting materials

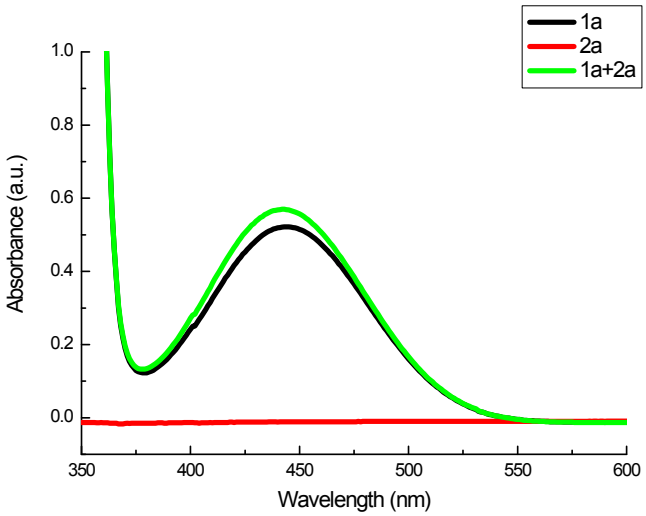
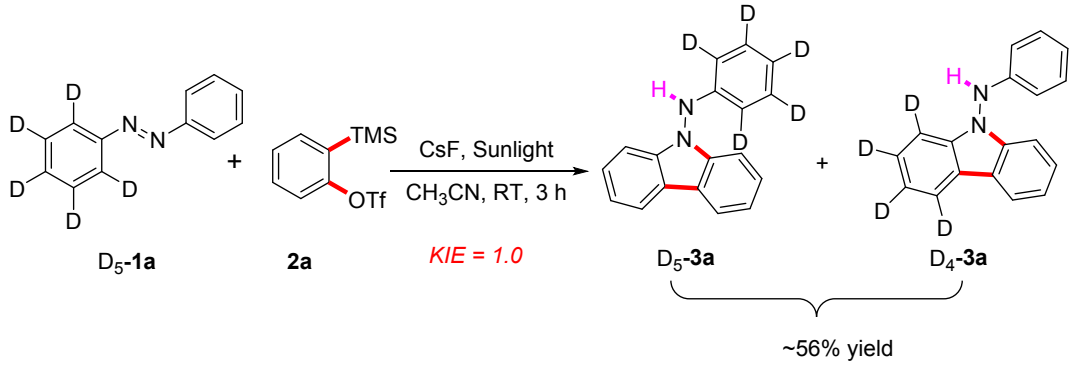
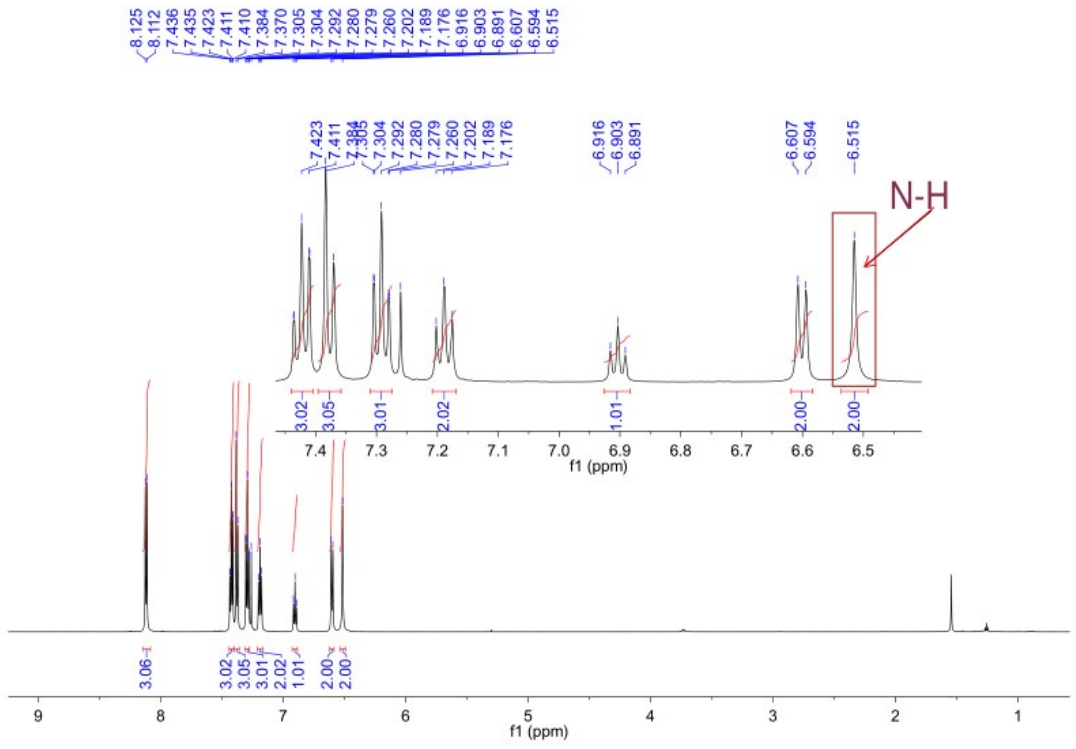


Figure S1. UV-vis absorption spectra of **1a** (1/128 M) and **2a** (1/85 M) in CH_3CN

4.2 Kinetic isotope effect experiment

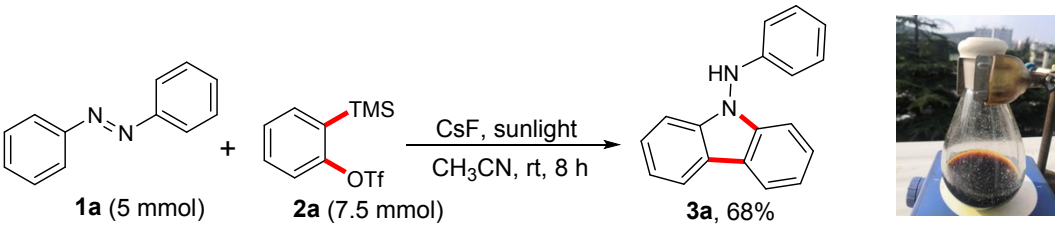


In a 10 mL oven-dried quartz photoreactor equipped with a magnetic stirrer bar was charged with azobenzene (**D_5-1a**, 37.4 mg, 0.20 mmol), CsF (91.1 mg, 0.60 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**, 89.5 mg, 0.30 mmol). Then freshly distilled Acetonitrile (1.0 mL) was added to the resulted mixture. The reaction was stirred under sunlight for 3 h. Then the solvent was removed under vacuum to obtain the crude product. The mixture was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 50:1), and afforded the mixed product (**D_5-3a** + **D_4-3a**) as a white solid (29.4 mg, 56 % yield). The KIE value (KIE = 1.0) was determined by ^{1}H NMR analysis.



5. Procedure for the gram-scale synthesis and transformation of 3a

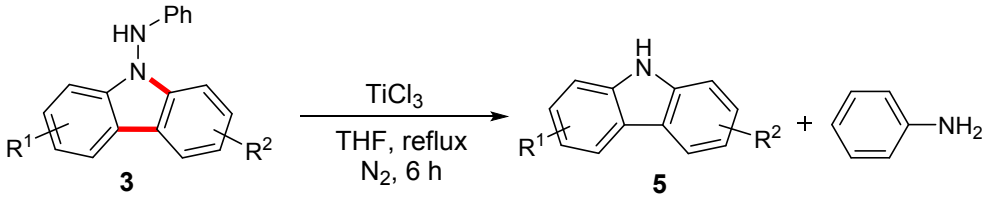
5.1 Gram-scale synthesis of 3a

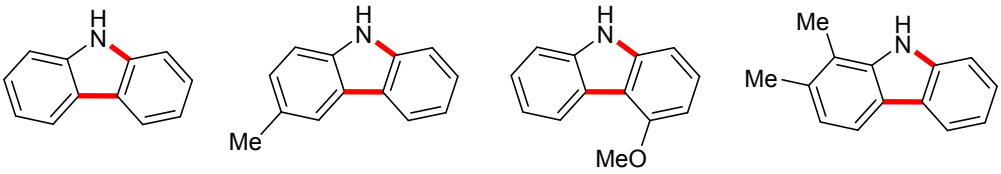


1a (5 mmol) **2a** (7.5 mmol) **3a**, 68%

In a 100 mL oven-dried round flask equipped with a magnetic stirrer bar was charged with azobenzene (**1a**, 0.91 g, 5.0 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**, 2.23 g, 7.5 mmol), CsF (2.28 g, 15.0 mmol) and freshly distilled acetonitrile (30 mL). The reaction was stirred under sunlight for 8 h. After that, the mixture in reaction tube was detected by TLC. Then the solvent was removed under vacuum to obtain the crude product. The mixture was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 50:1), and afforded the desired product **3a** as a white solid (0.877 g, 68% yield).

5.2 The transformation of 3 into carbazole 5





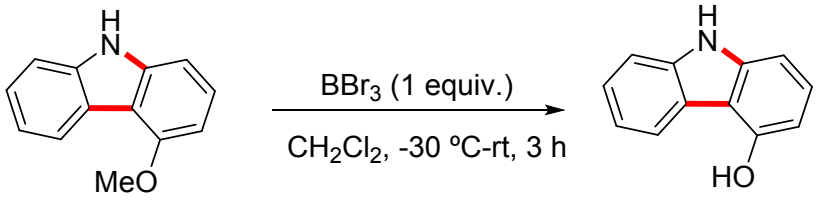
5a, 92% **5b**, 88% **5c**, 83% **5d**, 93%

Typical procedure for the transformation of **3a** into **5a**

Compound **3a** (0.20 mmol) was dissolved in THF (0.60 mL) according to its solubility in a 10 mL oven-dried reaction tube with a magnetic stirrer bar. Then an aqueous solution of titanium (III) trichloride (0.80 mmol, 0.80 mL, 15.0–20.0% $TiCl_3$

basis in 30% HCl) was added and the mixture was refluxed in an oil bath for 6 h under nitrogen with stirring. After cooling to room temperature, the reaction mixture was basified, while cooling in an ice-bath, with an aqueous solution of NaOH (20%) to pH >10. The residue was extracted with CH_2Cl_2, repeatedly.[3] The organic phases were combined. The solvent was evaporated and the residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1), and afforded carbazole **5a** as a white solid (30.7 mg, 92% yield), as well as amine was recovered after easy handling performance.

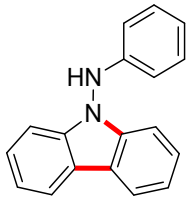
5.3 Typical procedure for the synthesis of 9*H*-carbazol-4-ol (6) from 5c[4]



5c **6**, 82%

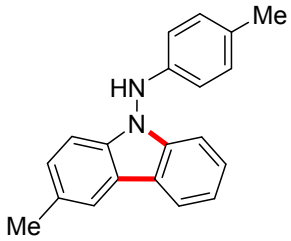
Under a N_2 atmosphere, the 4-methoxy-9*H*-carbazole (**5c**, 39.4 mg, 0.20 mmol), BBr_3 (1 equiv., 0.20 mL), and anhydrous CH_2Cl_2 were added into a dry Schlenk tube (15 mL) at -30 ºC. The resulted mixture was stirred for 3 h. After that, the mixture was allowed to warm to room temperature and quenched with water. The solvent was evaporated and the residue was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1), affording compound **6** (30.0 mg, 82% yield) as an off-white solid.

6. Characterization data for the products



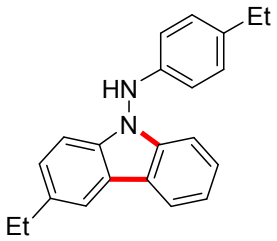
***N*-Phenyl-9*H*-carbazol-9-amine (3a)**[5]

Eluent: petroleum ether/ethyl acetate (50:1). White solid (38.2 mg, 74% yield); mp: 170–171 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.12 (d, *J* = 7.8 Hz, 2H), 7.43–7.41 (m, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 8.4 Hz, 2H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 2H), 6.57 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 146.5, 140.2, 129.50, 126.2, 121.4, 121.1, 120.4, 120.2, 112.7, 109.1. HRMS (ESI) $[M+H]^+$ Calcd for $C_{18}H_{15}N_2$ 259.1230; Found 259.1232.



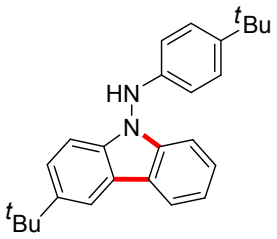
3-Methyl-*N*-(*p*-tolyl)-9*H*-carbazol-9-amine (3b)

Eluent: petroleum ether/ethyl acetate (50:1). White solid (45.7 mg, 80% yield); mp: 167–168 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.15 (s, 1H), 8.14 (d, *J* = 7.2 Hz, 1H), 7.98 (s, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.22–7.20 (m, 3H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.31 (d, *J* = 7.8 Hz, 2H), 2.47 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 145.9, 140.6, 138.6, 130.1, 129.1, 129. 0, 127.8, 126.4, 121.1, 120.9, 120.83, 120.76, 120.0, 112.9, 109.5, 109.4, 21.6, 20.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}N_2$ 287.1543; Found 287.1541.



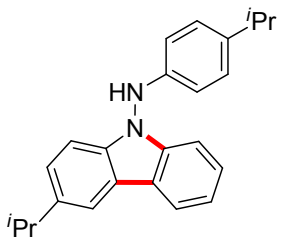
3-Ethyl-*N*-(4-ethylphenyl)-9*H*-carbazol-9-amine (3c)

Eluent: petroleum ether/ethyl acetate (50:1). White solid (52.1 mg, 83% yield); mp: 163–164 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.19 (s, 1H), 8.16 (d, J = 7.8 Hz, 1H), 8.02 (s, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.26 (s, 2H), 7.21 (t, J = 7.2 Hz, 1H), 6.94 (d, J = 8.4 Hz, 2H), 6.36–6.34 (m, 2H), 2.77 (q, J = 7.8 Hz, 2H), 2.46–2.42 (m, 2H), 1.28 (t, J = 7.8 Hz, 3H), 1.08 (t, J = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 146.1, 140.6, 138.8, 135.8, 135.5, 128.9, 126.7, 126.3, 121.0, 120.8, 119.9, 119.6, 112.8, 109.5, 109.4, 28.8, 27.8, 16.9, 16.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{23}N_2$ 315.1856; Found 315.1855.



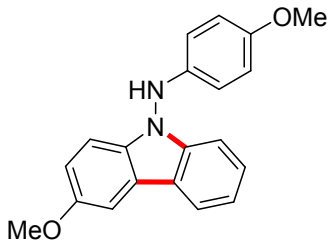
3-Butyl-*N*-(4-butylphenyl)-9*H*-carbazol-9-amine (3d)

Eluent: petroleum ether/ethyl acetate (50:1). White solid (59.9 mg, 81% yield); mp: 174–176 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.19 (s, 1H), 8.21 (d, J = 7.8 Hz, 1H), 8.20 (d, J = 1.8 Hz, 1H), 7.49 (dd, J = 8.4, 1.8 Hz, 1H), 7.41–7.36 (m, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 7.23–7.19 (m, 1H), 7.13 (d, J = 9.0 Hz, 2H), 6.34 (d, J = 9.0 Hz, 2H), 1.40 (s, 9H), 1.18 (s, 9H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 145.7, 142.8, 142.4, 140.6, 138.5, 126.3, 126.2, 124.3, 121.1, 120.8, 120.7, 119.9, 117.0, 112.4, 109.4, 109.1, 34.9, 34.1, 32.3, 31.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{31}N_2$ 371.2482; Found 371.2483.



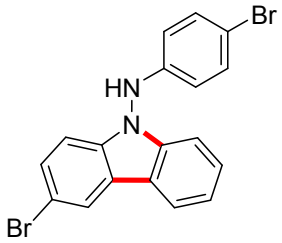
3-*iso*-Propyl-*N*-(4-*iso*-propylphenyl)-9*H*-carbazol-9-amine (3e)

Eluent: petroleum ether/ethyl acetate (50:1). White solid (54.0 mg, 79% yield); mp: 168–170 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, acetone-d_6) δ: 8.28 (s, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.92 (s, 1H), 7.26–7.23 (m, 2H), 7.18 (d, J = 0.6 Hz, 2H), 7.10–7.06 (m, 1H), 6.89 (d, J = 8.5 Hz, 2H), 6.36 (d, J = 8.5 Hz, 2H), 3.00–2.90 (m, 1H), 2.68–2.60 (m, 1H), 1.19 (d, J = 6.6 Hz, 6H), 1.01 (d, J = 7.2 Hz, 6H); ^{13}C NMR (150 MHz, acetone-d_6) δ: 145.8, 140.7, 140.6, 140.5, 138.9, 127.0, 125.8, 124.9, 121.2, 121.1, 120.2, 119.6, 117.5, 112.7, 109.0, 108.9, 34.1, 33.2, 24.2, 23.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{27}N_2$ 343.2169; Found 343.2169.



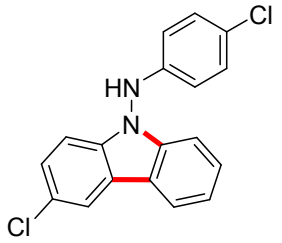
3-Methoxy-*N*-(4-methoxyphenyl)-9*H*-carbazol-9-amine (3f)

Eluent: petroleum ether/EtOAc (30:1). White solid (54.1 mg, 85% yield); mp: 159–161 ºC; R_f = 0.3 (petroleum ether/ethyl acetate = 15:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.02 (s, 1H), 8.17 (d, J = 7.8 Hz, 1H), 7.77 (s, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 6.72 (d, J = 8.4 Hz, 2H), 6.38 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 154.4, 153.8, 141.9, 140.9, 135.1, 126.4, 121.4, 121.1, 120.8, 119.6, 115.4, 115.1, 114.1, 110.4, 109.6, 104.1, 56.2, 55.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}N_2O_2$ 319.1441; Found 319.1442.



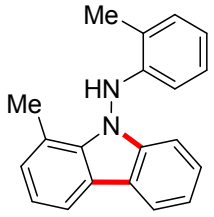
3-Bromo-*N*-(4-bromophenyl)-9*H*-carbazol-9-amine (3g)

Eluent: petroleum ether/ethyl acetate (30:1). White solid (63.7 mg, 77% yield); mp: 188–190 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 15:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.59 (s, 1H), 8.48 (d, J = 1.8 Hz, 1H), 8.27 (d, J = 7.8 Hz, 1H), 7.57–7.55 (m, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.32–7.26 (m, 4H), 6.37 (d, J = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 147.1, 140.3, 138.8, 132.5, 129.2, 127.6, 123.7, 123.0, 121.7, 120.9, 120.1, 114.8, 112.6, 111.6, 111.4, 109.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}Br_2N_2$: 414.9440; Found 414.9439.



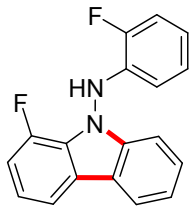
3-Chloro-*N*-(4-chlorophenyl)-9*H*-carbazol-9-amine (3h)

Eluent: petroleum ether/ethyl acetate (30:1). White solid (46.2 mg, 71% yield); mp: 179–181 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 15:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.57 (s, 1H), 8.34 (d, J = 1.8 Hz, 1H), 8.26 (d, J = 7.8 Hz, 1H), 7.48–7.44 (m, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.29–7.26 (m, 1H), 7.18 (d, J = 8.4 Hz, 2H), 6.43–6.40 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 146.8, 140.5, 138.5, 129.6, 127.5, 126.5, 124.9, 124.0, 122.4, 121.7, 120.8, 120.2, 114.3, 110.9, 109.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}Cl_2N_2$ 327.0450; Found 327.0451.



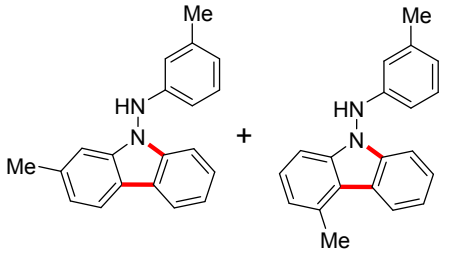
1-Methyl-*N*-(*o*-tolyl)-9*H*-carbazol-9-amine (3i)

Eluent: petroleum ether/ethyl acetate (50:1). White solid (38.3 mg, 67% yield); mp: 158–160 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.97 (s, 1H), 8.18 (d, J = 7.8 Hz, 1H), 8.08–8.01 (m, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.23 (t, J = 7.2 Hz, 1H), 7.17–7.11 (m, 3H), 6.78 (t, J = 7.8 Hz, 1H), 6.66 (t, J = 7.2 Hz, 1H), 5.57 (d, J = 5.9 Hz, 1H), 2.49 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 146.6, 140.7, 138.4, 131.0, 129.0, 127.3, 126.4, 121.5, 121.2, 121.0, 120.7, 120.3, 119.4, 118.7, 110.2, 109.6, 18.0, 17.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}N_2$ 287.1543; Found 287.1542.



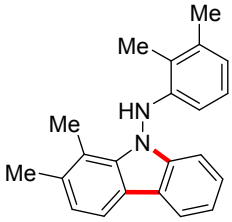
1-Fluoro-*N*-(2-fluorophenyl)-9*H*-carbazol-9-amine (3j)

Eluent: petroleum ether/ethyl acetate (50:1). White solid (34.6 mg, 59% yield); mp: 149–151 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.56 (s, 1H), 8.24 (d, J = 7.8 Hz, 1H), 8.07–8.04 (m, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.25–7.21 (m, 3H), 6.84–6.77 (m, 2H), 5.97–5.92 (m, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 150.5 (d, J = 238.4 Hz), 148.9 (d, J = 243.0 Hz), 141.2, 136.4 (d, J = 10.7 Hz), 127.2 (d, J = 8.9 Hz), 125.4, 121.3, 121.1, 121.1 (d, J = 6.2 Hz), 120.7, 120.5 (d, J = 6.3 Hz), 117.1, 115.9 (d, J = 17.4 Hz), 113.4, 112.8 (d, J = 17.3 Hz), 109.6. ^{19}F NMR (565 MHz, DMSO-d_6) δ: –133.1, –138.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}F_2N_2$ 295.1041; Found 295.1042.



2-Methyl-*N*-(*m*-tolyl)-9*H*-carbazol-9-amine (3k) and 4-Methyl-*N*-(*m*-tolyl)-9*H*-carbazol-9-amine (3k')

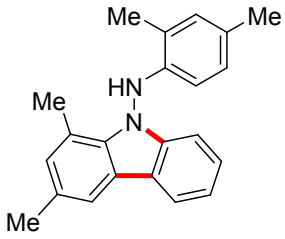
Eluent: petroleum ether/ethyl acetate (50:1). White solid (39.8 mg, 70% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.10 (d, J = 1.2 Hz, 1H), 9.05 (d, J = 1.2 Hz, 0.86H), 7.98 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 7.8 Hz, 0.88H), 7.83 (d, J = 7.8 Hz, 0.88H), 7.22–7.20 (m, 1H), 7.18 (d, J = 8.4 Hz, 0.86H), 7.17–7.14 (m, 0.86H), 7.11–7.08 (m, 2H), 7.06–7.03 (m, 1H), 7.02–6.99 (m, 1.76H), 6.98–6.97 (m, 1H), 6.85 (d, J = 8.4 Hz, 0.86H), 6.82 (d, J = 7.2 Hz, 1H), 6.78–6.75 (m, 2H), 6.37 (d, J = 7.2 Hz, 2H), 6.16 (s, 1.72H), 5.98 (s, 1.74H), 2.63 (s, 3H), 2.21 (s, 2.54H), 1.90 (d, J = 4.8 Hz, 5.57H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 148.2, 140.8, 140.4, 140.3, 140.2, 139.0, 136.3, 133.4, 129.61, 129.58, 126.3, 126.0, 125.9, 122.8, 121.8, 121.7, 121.4, 121.2, 121.11, 121.09, 120.7, 120.6, 120.3, 120.2, 119.4, 118.7, 113.2, 113.1, 109.9, 109.8, 109.43, 109.41, 109.3, 107.2, 22.2, 21.65, 21.63, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}N_2$ 287.1543; Found 287.1545.



***N*-(2,3-Dimethylphenyl)-1,2-dimethyl-9*H*-carbazol-9-amine (3l)**

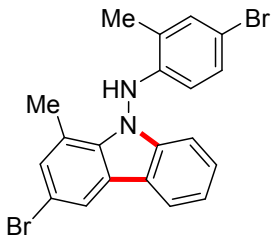
Eluent: petroleum ether/ethyl acetate (50:1).White solid (40.1 mg, 64% yield); mp: 166–168 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.89 (s, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.18 (t, J = 7.8 Hz, 2H), 7.07 (d, J = 7.8 Hz, 1H), 6.65 (d, J = 7.8 Hz,

1H), 6.57 (d, J = 7.2 Hz, 1H), 5.45 (d, J = 8.4 Hz, 1H), 2.44 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 146.3, 141.0, 138.8, 137.2, 135.2, 126.4, 125.9, 122.9, 121.5, 121.0, 120.21, 120.17, 120.0, 119.7, 119.4, 117.8, 109.7, 108.7, 20.55, 20.52, 13.2, 12.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{23}N_2$ 315.1856; Found 315.1856.



***N*-(2,4-Dimethylphenyl)-1,3-dimethyl-9*H*-carbazol-9-amine (3m)**

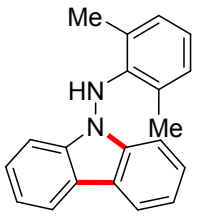
Eluent: petroleum ether/ethyl acetate (50:1). White solid (43.3 mg, 69% yield); mp: 157–159 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.77 (s, 1H), 8.11 (d, J = 7.8 Hz, 1H), 7.82 (s, 1H), 7.37–7.32 (m, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.21–7.16 (m, 1H), 6.95 (d, J = 5.4 Hz, 2H), 6.57 (d, J = 8.4 Hz, 1H), 5.44 (d, J = 7.8 Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 2.34 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 144.4, 141.01, 136.7, 131.7, 130.4, 129.0, 127.9, 127.5, 126.2, 121.7, 121.2, 120.8, 120.7, 120.5, 120.0, 118.4, 110.4, 109.6, 21.3, 20.5, 17.9, 17.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{23}N_2$ 315.1856; Found 315.1858.



3-Bromo-*N*-(4-bromo-2-methylphenyl)-1-methyl-*9H*-carbazol-9-amine (3n)

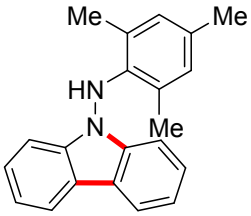
Eluent: petroleum ether/ethyl acetate (40:1). White solid (56.5 mg, 64% yield); mp: 196–198 ºC; R_f = 0.3 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, acetone-d_6) δ: 8.42 (s, 1H), 8.20 (d, J = 8.4 Hz, 2H), 7.43 (t, J = 7.8 Hz, 1H), 7.38 (s, 1H), 7.32 (d, J = 7.2 Hz, 2H), 7.28 (t, J = 7.2 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 5.73 (d, J = 8.4 Hz, 1H), 2.57 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (150 MHz, acetone-d_6) δ:

146.1, 141.7, 138.1, 134.1, 131.8, 130.6, 127.8, 124.8, 124.4, 124.3, 121.7, 121.6, 121.5, 121.3, 113.3, 113.2, 112.1, 110.3, 17.5, 17.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}Br_2N_2$ 442.9753; Found 442.9758.



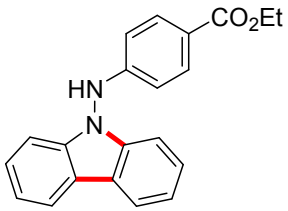
***N*-(2,6-Dimethylphenyl)-9*H*-carbazol-9-amine (3o)**

Eluent: petroleum ether/ethyl acetate (50:1). White solid (29.7 mg, 52% yield); mp: 141–143 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.33 (s, 1H), 8.17 (d, J = 7.8 Hz, 2H), 7.38 (t, J = 7.8 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 7.20 (t, J = 7.2 Hz, 2H), 6.95 (d, J = 7.2 Hz, 2H), 6.79 (t, J = 7.8 Hz, 1H), 1.93 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 143.5, 141.2, 129.9, 126.3, 126.0, 121.9, 120.9, 120.5, 119.8, 109.6, 19.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}N_2$ 287.1543; Found 287.1543.



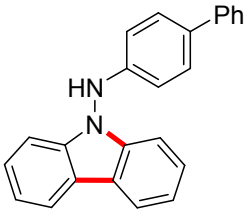
***N*-Mesityl-9*H*-carbazol-9-amine (3p)**

Eluent: petroleum ether/ethyl acetate (50:1). White solid (33.6 mg, 56% yield); mp: 132–134 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.19 (s, 1H), 8.15 (d, J = 7.8 Hz, 2H), 7.38 (t, J = 7.8 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.19 (t, J = 7.4 Hz, 2H), 6.76 (s, 2H), 2.16 (s, 3H), 1.90 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 141.2, 140.9, 130.6, 130.5, 126.3, 126.2, 120.8, 120.5, 119.7, 109.6, 20.5, 19.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{21}N_2$ 301.1699; Found 301.1699.



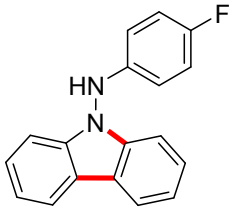
Ethyl 4-((9*H*-carbazol-9-yl)amino)benzoate (3q)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (49.5 mg, 75% yield); mp: 159–161 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.00 (s, 1H), 8.22 (d, J = 7.2 Hz, 2H), 7.77 (d, J = 7.8 Hz, 2H), 7.43 (t, J = 7.2 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 7.27 (t, J = 6.6 Hz, 2H), 6.50 (s, 2H), 4.21 (d, J = 6.6 Hz, 2H), 1.23 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 166.0, 152.2, 139.8, 131.6, 126.8, 121.3, 121.2, 121.1, 120.6, 111.8, 109.3, 60.5, 14.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}N_2O_2$ 331.1441; Found 331.1437.



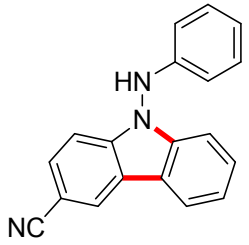
***N*-([1,1'-Biphenyl]-4-yl)-9*H*-carbazol-9-amine (3r)**

Eluent: petroleum ether/ethyl acetate (30:1). White solid (45.3 mg, 68% yield); mp: 184–186 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 15:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.55 (s, 1H), 8.23 (d, J = 7.8 Hz, 2H), 7.52 (d, J = 7.8 Hz, 2H), 7.44 (t, J = 7.2 Hz, 4H), 7.40–7.36 (m, 4H), 7.28–7.23 (m, 3H), 6.50 (d, J = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 147.6, 140.5, 140.2, 132.3, 129.3, 128.1, 126.9, 126.7, 126.4, 121.1, 121.0, 120.4, 113.1, 109.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{19}N_2$ 335.1543; Found 335.1540.



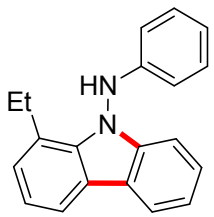
***N*-(4-Fluorophenyl)-9*H*-carbazol-9-amine (3s)**

Eluent: petroleum ether/ethyl acetate (50:1). White solid (34.2 mg, 62% yield); mp: 153–155 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.39 (s, 1H), 8.21 (d, J = 7.8 Hz, 2H), 7.44–7.42 (m, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.26–7.24 (m, 2H), 6.98 (t, J = 9.0 Hz, 2H), 6.45–6.42 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 156.9 (d, J = 233.2 Hz), 144.5, 140.1, 126.6, 121.04, 120.98, 120.3, 116.3 (d, J = 22.5 Hz), 114.0 (d, J = 7.8 Hz), 109.5. ^{19}F NMR (565 MHz, DMSO-d_6) δ: –119.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{14}FN_2$ 277.1136; Found 277.1138.



9-(Phenylamino)-9*H*-carbazole-3-carbonitrile (3t)

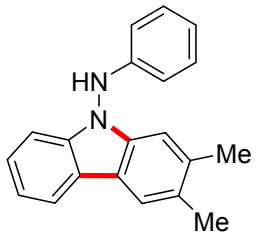
Eluent: petroleum ether/ethyl acetate (10:1). Pale yellow solid (26.6 mg, 47% yield); mp: 176–178 ºC; R_f = 0.5 (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.57 (s, 1H), 8.82 (s, 1H), 8.34 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.54–7.50 (m, 2H), 7.41 (d, J = 8.4 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.14 (t, J = 7.8 Hz, 2H), 6.81 (t, J = 7.8 Hz, 1H), 6.44 (d, J = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 147.5, 142.2, 140.7, 129.9, 129.9, 128.1, 126.4, 121.9, 121.6, 121.2, 120.8, 120.7, 120.3, 112.8, 110.6, 110.1, 102.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{14}N_3$ 284.1182; Found 284.1180.



1-Ethyl-*N*-phenyl-9*H*-carbazol-9-amine (3u)

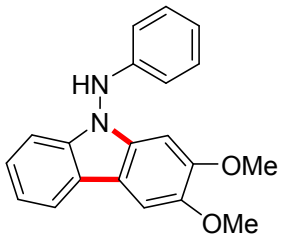
Eluent: petroleum ether/ethyl acetate (50:1). White solid (37.1 mg, 65% yield); mp:

153–154 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 7.8 Hz, 1H), 7.96–7.95 (m, 1H), 7.35–7.33 (m, 1H), 7.25–7.21 (m, 4H), 7.18–7.16 (m, 2H), 6.88–6.85 (m, 1H), 6.58 (s, 1H), 6.55 (d, *J* = 7.8 Hz, 2H), 3.05 (d, *J* = 108.6 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 147.3, 140.4, 137.9, 129.6, 127.8, 127.3, 126.0, 122.0, 121.9, 120.8, 120.5, 120.4, 120.2, 118.0, 112.4, 109.2, 24.3, 16.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}N_2$ 287.1543; Found 287.1540.



2, 3-Dimethyl-*N*-phenyl-9*H*-carbazol-9-amine (4a)

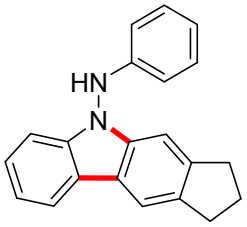
Eluent: petroleum ether/ethyl acetate (50:1). White solid (41.1 mg, 72% yield); mp: 181–183 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 7.8 Hz, 1H), 7.72 (s, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.15–7.11 (m, 2H), 7.04 (t, *J* = 7.8 Hz, 2H), 6.94 (s, 1H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.41 (d, *J* = 7.8 Hz, 2H), 6.15–6.11 (m, 1H), 2.31 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 146.7, 140.1, 139.0, 135.5, 129.5, 128.8, 125.4, 121.3, 120.8, 120.0, 119.9, 119.3, 112.6, 112.5, 109.6, 109.0, 20.9, 20.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}N_2$ 287.1543; Found 287.1545.



2, 3-Dimethoxy-*N*-phenyl-9*H*-carbazol-9-amine (4b)

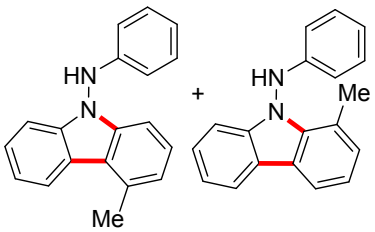
Eluent: petroleum ether/ethyl acetate (15:1). White solid (47.7 mg, 75% yield); mp: 157–159 ºC; R_f = 0.2 (petroleum ether/ethyl acetate = 10:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.28 (s, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.77 (s, 1H), 7.27 (t, *J* = 7.2 Hz,

1H), 7.21 (d, J = 7.8 Hz, 1H), 7.16 (t, J = 7.2 Hz, 1H), 7.12 (t, J = 7.8 Hz, 2H), 6.91 (s, 1H), 6.76 (t, J = 7.2 Hz, 1H), 6.40 (d, J = 7.8 Hz, 2H), 3.88 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 150.1, 148.2, 145.0, 139.6, 135.5, 129.7, 124.6, 121.4, 120.2, 120.1, 119.8, 112.7, 112.5, 109.4, 104.3, 93.0, 56.8, 56.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}N_2O_2$ 319.1441; Found 319.1443.



_N_-Phenyl-2, 3-dihydrocyclopenta[_b_]carbazol-5(1_H_)-amine (4c)

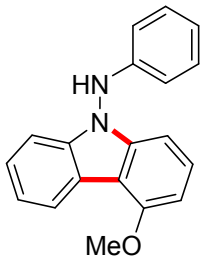
Eluent: petroleum ether/ethyl acetate (50:1). White solid (39.9 mg, 67% yield); mp: 177–179 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.01 (d, J = 7.8 Hz, 1H), 7.88 (s, 1H), 7.34–7.31 (m, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.15–7.12 (m, 2H), 7.10 (s, 1H), 6.84 (t, J = 7.2 Hz, 1H), 6.52 (d, J = 7.8 Hz, 2H), 6.27 (s, 1H), 3.03 (t, J = 7.2 Hz, 2H), 2.95 (t, J = 7.2 Hz, 2H), 2.15–2.10 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 146.7, 143.5, 140.4, 139.8, 136.7, 129.5, 125.4, 121.5, 120.8, 120.3, 119.93, 119.87, 115.5, 112.6, 108.9, 104.7, 33.3, 32.5, 26.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}N_2$ 299.1543; Found 299.1542.



4-Methyl-_N_-phenyl-9_H_-carbazol-9-amine (4d) and 1-Methyl-_N_-phenyl-9_H_-carbazol-9-amine (4d')

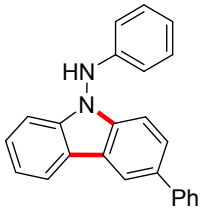
Eluent: petroleum ether/ethyl acetate (50:1). White solid (33.1 mg, 61% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.41 (s, 0.14H), 9.39 (s, 1H), 8.20 (d, J = 7.8 Hz, 1H), 8.17 (d, J = 7.8 Hz, 0.16H), 8.04 (d, J =

7.2 Hz, 0.14H), 7.43 (t, J = 7.8 Hz, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 7.23 (d, J = 7.2 Hz, 0.13H), 7.21 (d, J = 8.1 Hz, 1H), 7.15–7.10 (m, 2.6H), 7.04 (d, J = 6.6 Hz, 1H), 6.77 (t, J = 7.2 Hz, 1H), 6.74 (d, J = 7.2 Hz, 0.14H), 6.41 (d, J = 7.8 Hz, 2H), 6.36 (d, J = 6.0 Hz, 0.29H), 2.85 (s, 3H), 2.54 (s, 0.42H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 149.1, 148.1, 140.7, 140.3, 140.1, 138.5, 133.4, 129.8, 129.7, 129.1, 126.5, 126.4, 126.0, 122.9, 121.8, 121.5, 121.4, 121.1, 120.9, 120.7, 120.4, 120.3, 120.2, 119.7, 119.4, 118.7, 112.7, 111.7, 109.6, 109.3, 107.1, 20.8, 18.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{17}N_2$ 273.1386; Found 273.1385.



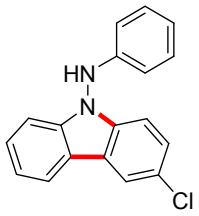
4-Methoxy-*N*-phenyl-9*H*-carbazol-9-amine (4e)

Eluent: petroleum ether/ethyl acetate (20:1). White solid (37.4 mg, 65% yield); mp: 156–158 ºC; R_f = 0.3 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.33 (d, J = 8.4 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.30–7.25 (m, 3H), 7.13 (t, J = 7.2 Hz, 2H), 6.91 (d, J = 7.8 Hz, 1H), 6.85 (d, J = 7.2 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 6.51 (d, J = 7.8 Hz, 2H), 6.35 (s, 1H), 4.06 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 156.2, 146.6, 141.7, 139.4, 129.5, 127.0, 125.3, 123.1, 121.0, 120.6, 120.4, 112.7, 110.4, 108.5, 102.0, 101.3, 55.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O$ 289.1335; Found 289.1340.



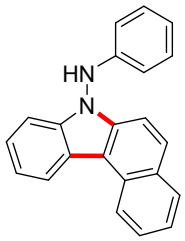
***N*-Phenyl-4-phenyl-9*H*-carbazol-9-amine (4f)**

Eluent: petroleum ether/ethyl acetate (30:1). White solid (40.0 mg, 60% yield); mp: 153–155 ºC; R_f = 0.3 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.12–8.05 (m, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.55 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.43–7.36 (m, 3H), 7.34–7.25 (m, 3H), 7.15 (t, *J* = 7.8 Hz, 2H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 2H), 6.43 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 146.5, 141.7, 140.9, 140.6, 139.7, 129.5, 128.8, 127.6, 127.2, 126.2, 121.3, 121.1, 120.7, 120.52, 120.46, 120.4, 119.9, 112.7, 109.2, 107.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{19}N_2$ 335.1543; Found 335.1541.



3-Chloro-*N*-phenyl-9*H*-carbazol-9-amine (4g)

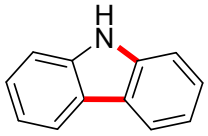
Eluent: petroleum ether/ethyl acetate (50:1). White solid (42.0 mg, 72% yield); mp: 136–138 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.05 (d, *J* = 5.4 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.30–7.28 (m, 2H), 7.19 (t, *J* = 7.8 Hz, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 2H), 6.52 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 146.2, 140.6, 138.6, 129.6, 126.9, 126.3, 125.8, 122.4, 121.3, 120.6, 120.5, 120.2, 112.7, 110.1, 109.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{14}ClN_2$ 293.0840; Found 293.0840.



***N*-Phenyl-7*H*-benzo[*c*]carbazol-7-amine (4h)**

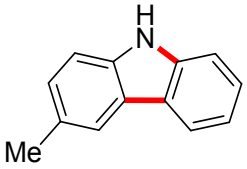
Eluent: petroleum ether/ethyl acetate (40:1). White solid (42.5 mg, 69% yield); mp: 166–168 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.62 (s, 1H), 8.84 (d, *J* = 8.4 Hz, 1H), 8.67 (d, *J* = 7.8 Hz, 1H), 8.07 (d,

J = 7.8 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.76 (t, *J* = 7.2 Hz, 1H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 148.3, 139.1, 138.2, 129.8, 129.7, 129.6, 128.1, 127.8, 125.2, 123.7, 123.5, 122.4, 121.4, 121.3, 120.5, 112.8, 112.7, 111.4, 110.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}N_2$ 309.1386; Found 309.1383.



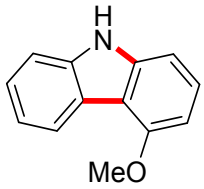
***9H*-Carbazole (5a)** [6]

Eluent: petroleum ether/ethyl acetate (20:1). White solid (30.7 mg, 92% yield); mp: 223–225 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 10:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 11.24 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 140.2, 126.0, 122.8, 120.6, 119.0, 111.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}N$ 168.0808; Found 168.0805.



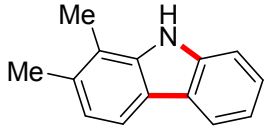
3-Methyl-*9H*-carbazole (5b)[6]

Eluent: petroleum ether/ethyl acetate (20:1). White solid (31.9 mg, 88% yield); mp: 215–217 ºC; R_f = 0.5 (petroleum ether/ethyl acetate = 10:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 11.07 (s, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.89 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.37–7.33 (m, 2H), 7.21–7.19 (m, 1H), 7.12–7.10 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 140.4, 138.4, 127.5, 127.3, 125.8, 123.0, 122.7, 120.5, 120.4, 118.7, 111.3, 111.1, 21.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}N$ 182.0964; Found 182.0965.



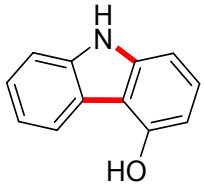
4-Methoxy-9*H*-carbazole (5c)[4]

Eluent: petroleum ether/ethyl acetate (15:1). Off-white solid (32.7 mg, 83% yield); mp: 132–134 ºC; R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.32 (d, *J* = 7.8 Hz, 1H), 7.99 (s, 1H), 7.39–7.35 (m, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 6.6 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 4.06 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 156.3, 140.9, 138.6, 126.7, 124.9, 123.1, 122.7, 119.6, 112.6, 110.0, 103.5, 100.4, 55.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}NO$ 198.0913; Found 198.0915.



1,2-Dimethyl-*9H*-carbazole (5d)[7]

Eluent: petroleum ether/ethyl acetate (20:1). White solid (36.2 mg, 93% yield); mp: 126–128 ºC; R_f = 0.4 (petroleum ether/ethyl acetate = 10:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 11.00 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.35–7.28 (m, 1H), 7.13–7.06 (m, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 2.45 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 140.4, 140.2, 133.3, 125.3, 123.5, 121.5, 120.8, 120.3, 118.8, 118.5, 117.5, 111.3, 20.0, 13.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}N$ 196.1121; Found 196.1120.



9*H*-Carbazol-4-ol (6)[8]

Eluent: petroleum ether/ethyl acetate (10:1). White solid (30.0 mg, 82% yield); mp:

169–172 ºC; R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.27 (d, *J* = 7.2 Hz, 1H), 8.06 (s, 1H), 7.41–7.38 (m, 2H), 7.26–7.23 (m, 3H), 7.02 (d, *J* =7.8 Hz, 1H), 6.58 (d, *J* = 7.2 Hz, 1H), 5.37 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 151.9, 141.4, 138.9, 126.6, 125.2, 122.8, 122.3, 119.7, 111.8, 110.1, 105.2, 103.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}N$ 184.0757; Found 184.0759.

7. References

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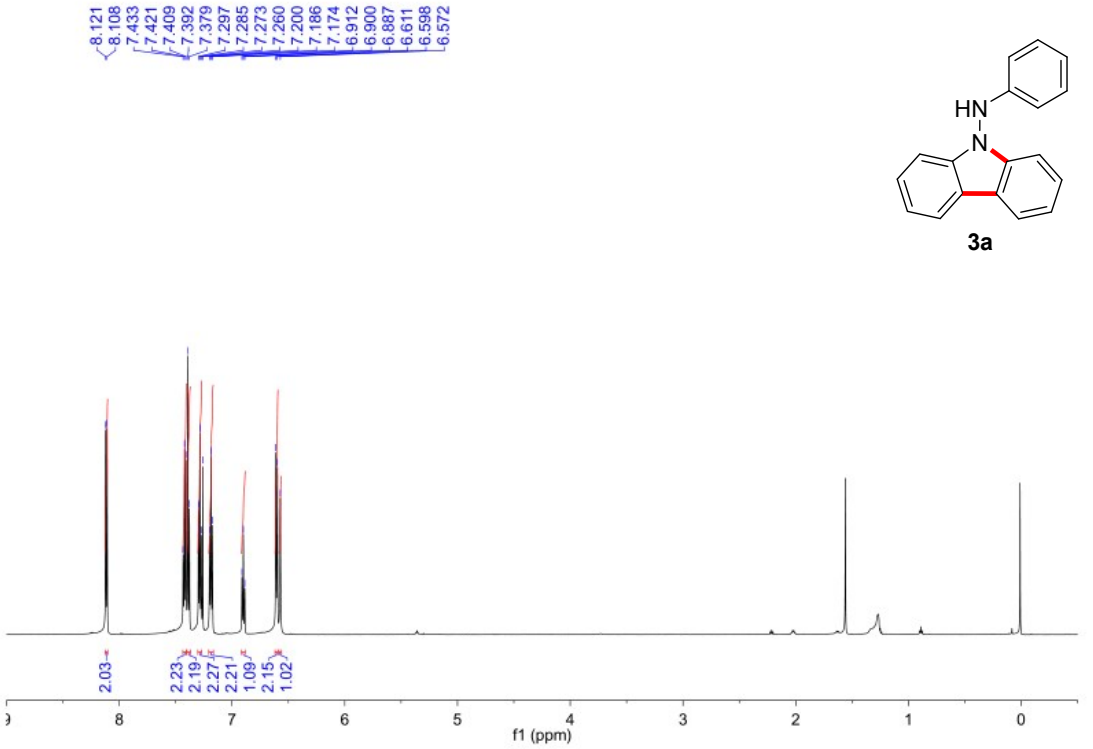
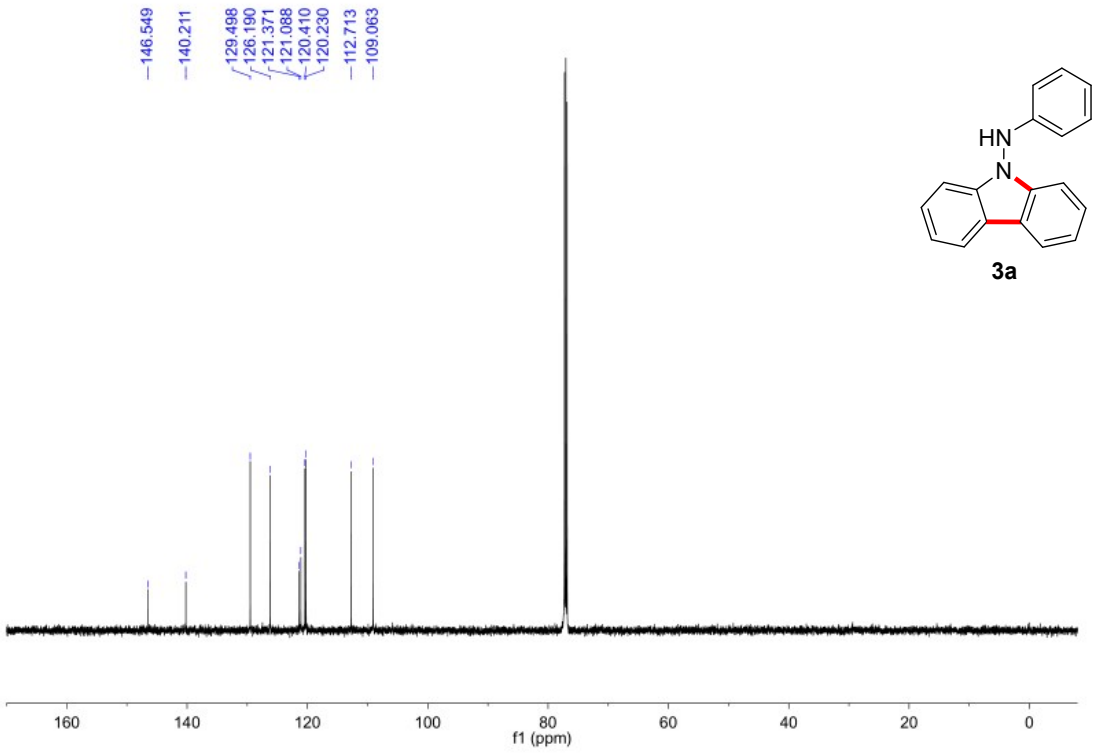
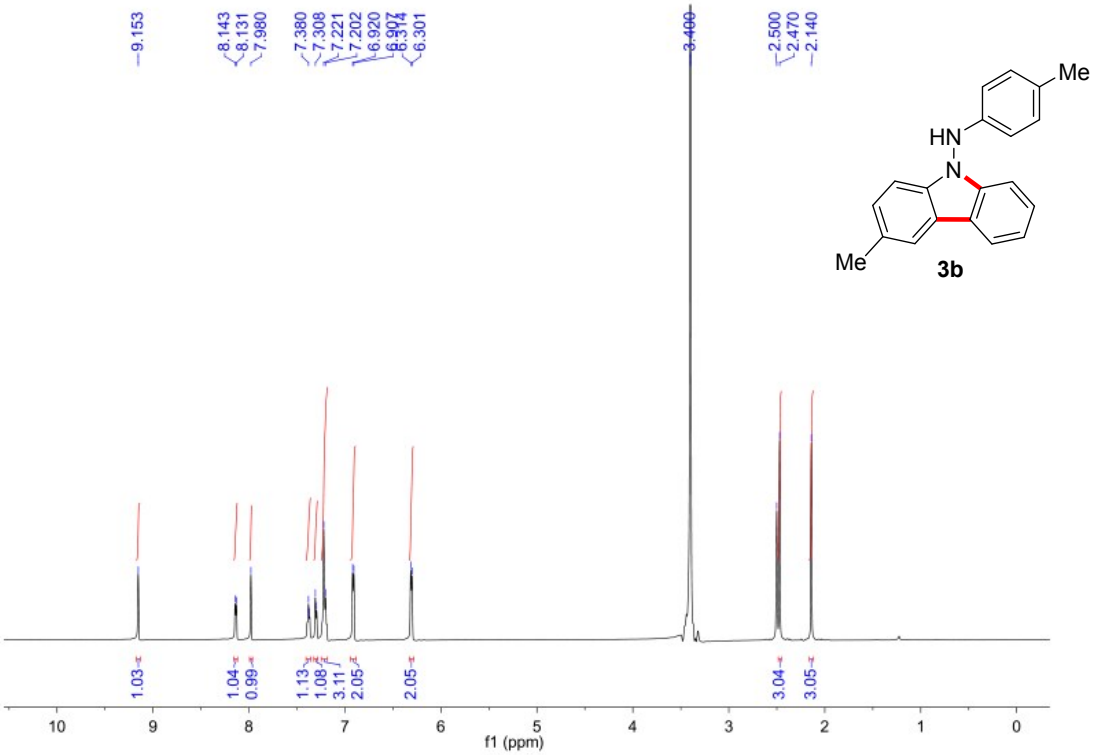
8. ^{1}H, ^{13}C and ^{19}F NMR spectra of the products

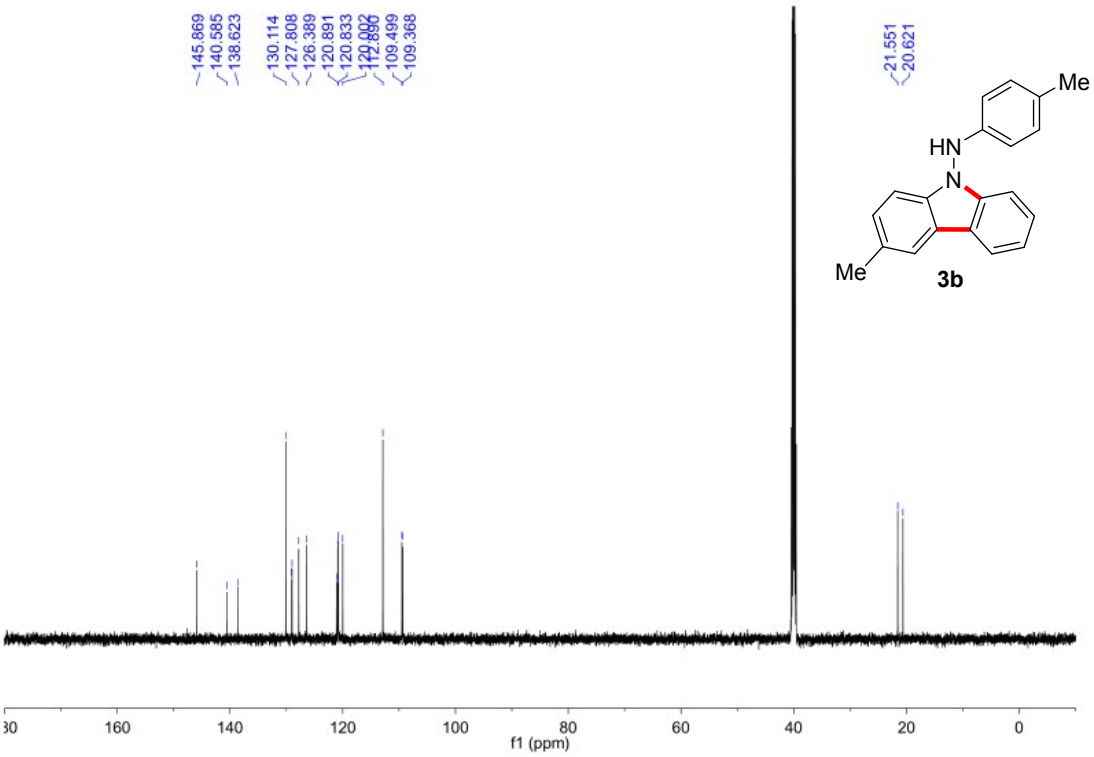
3a: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), $CDCl_3$



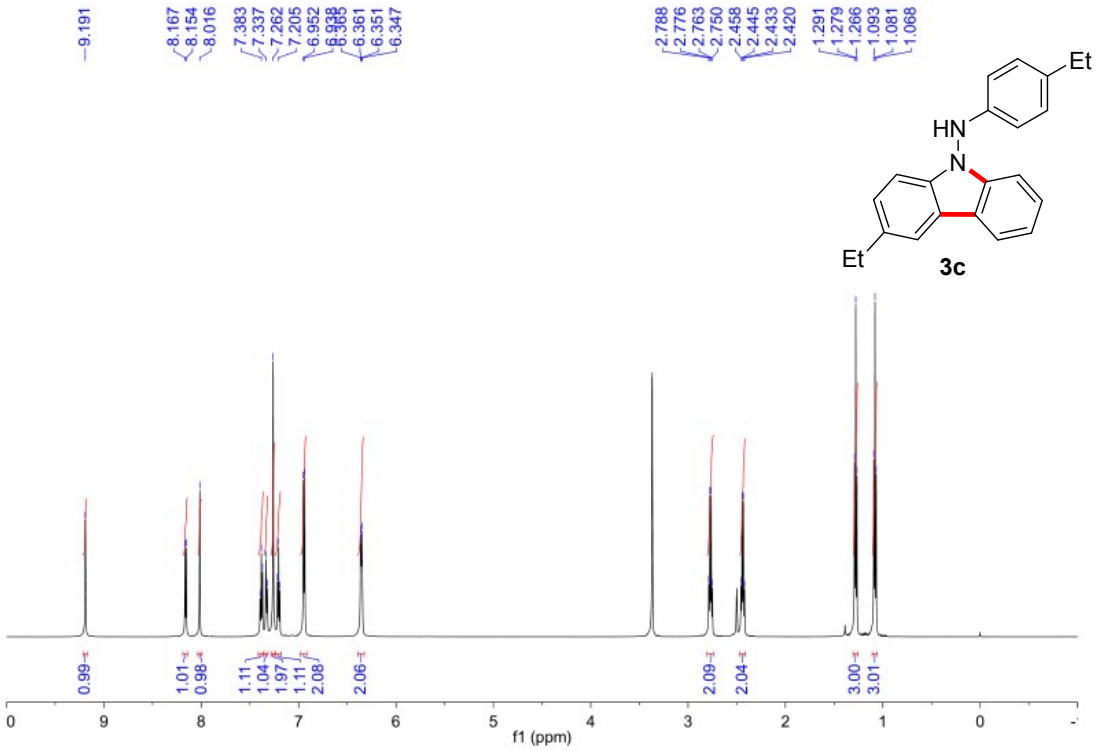


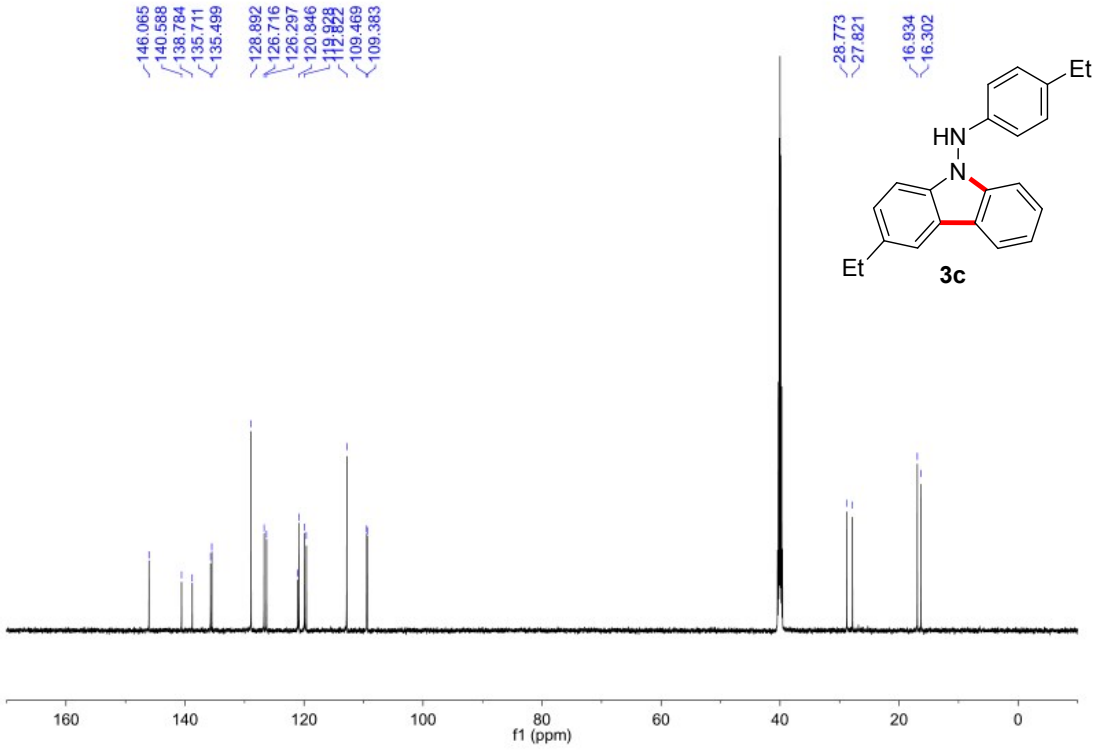
3b: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6



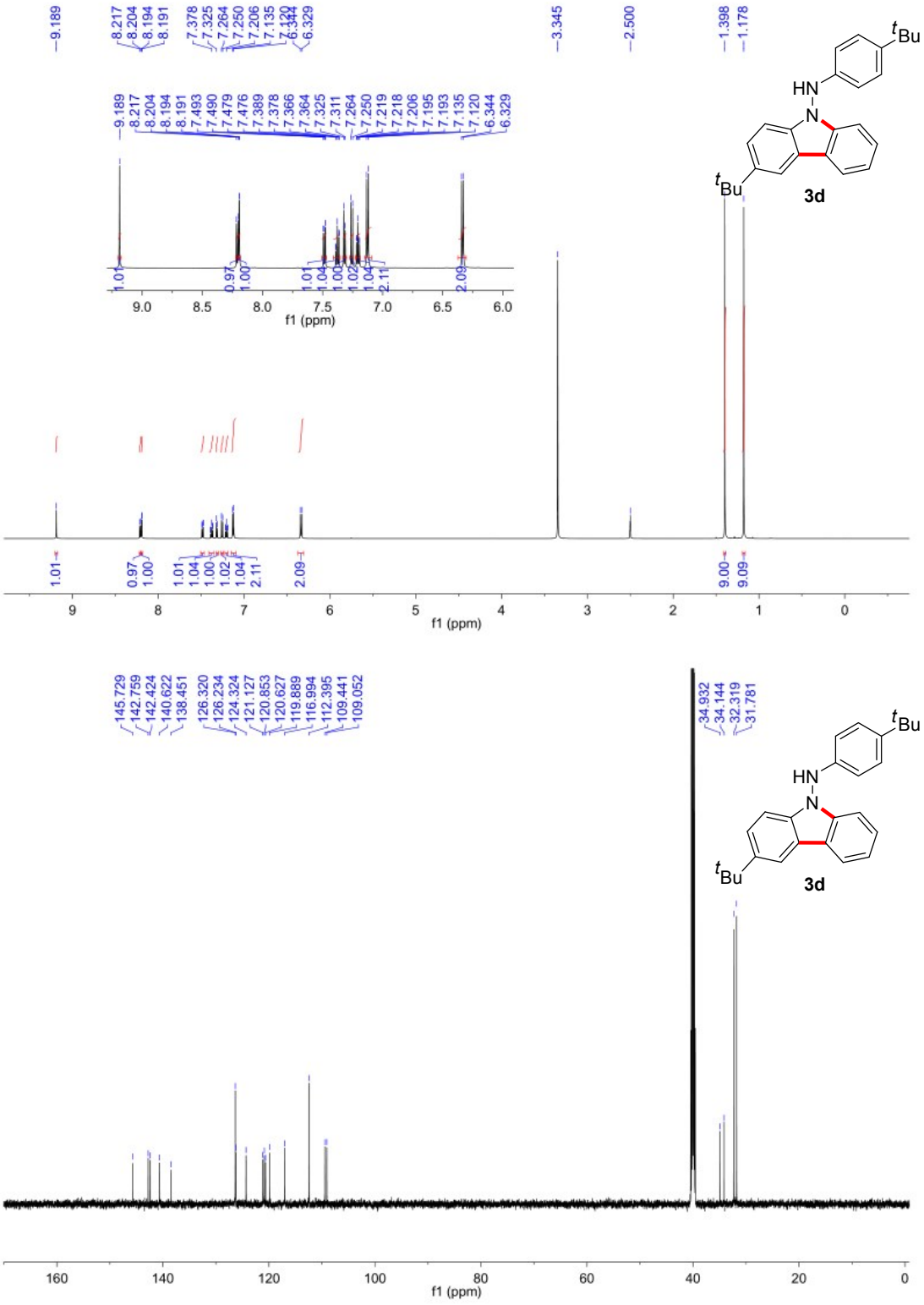


3c: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6

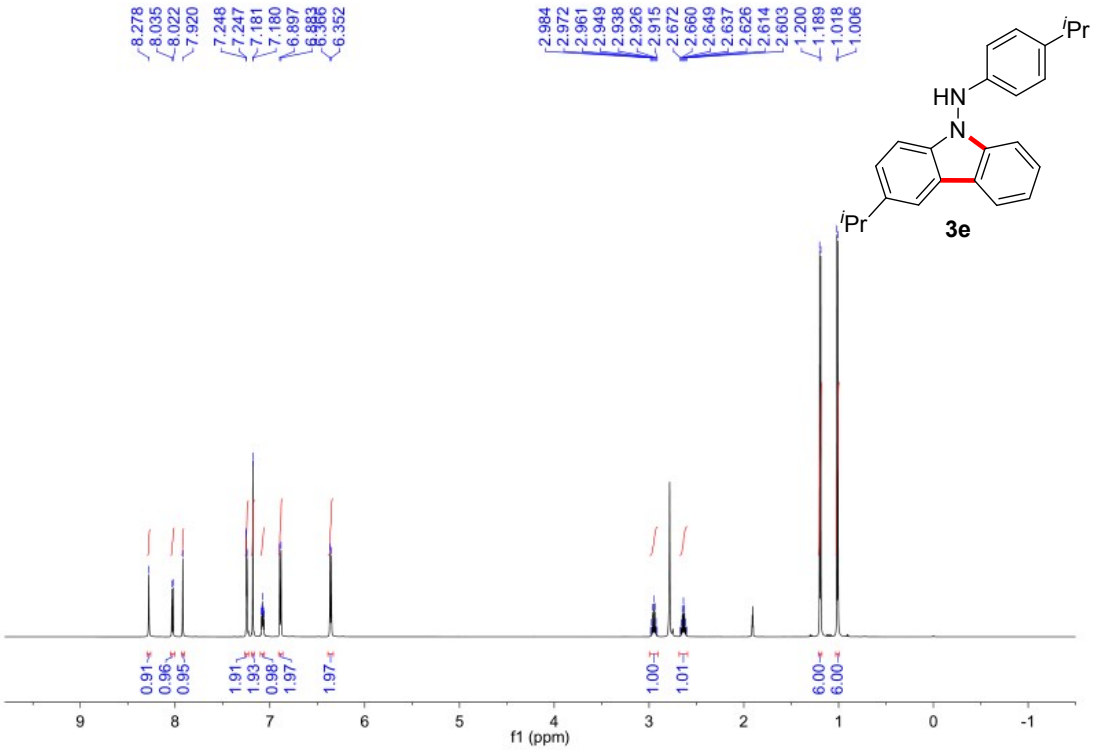


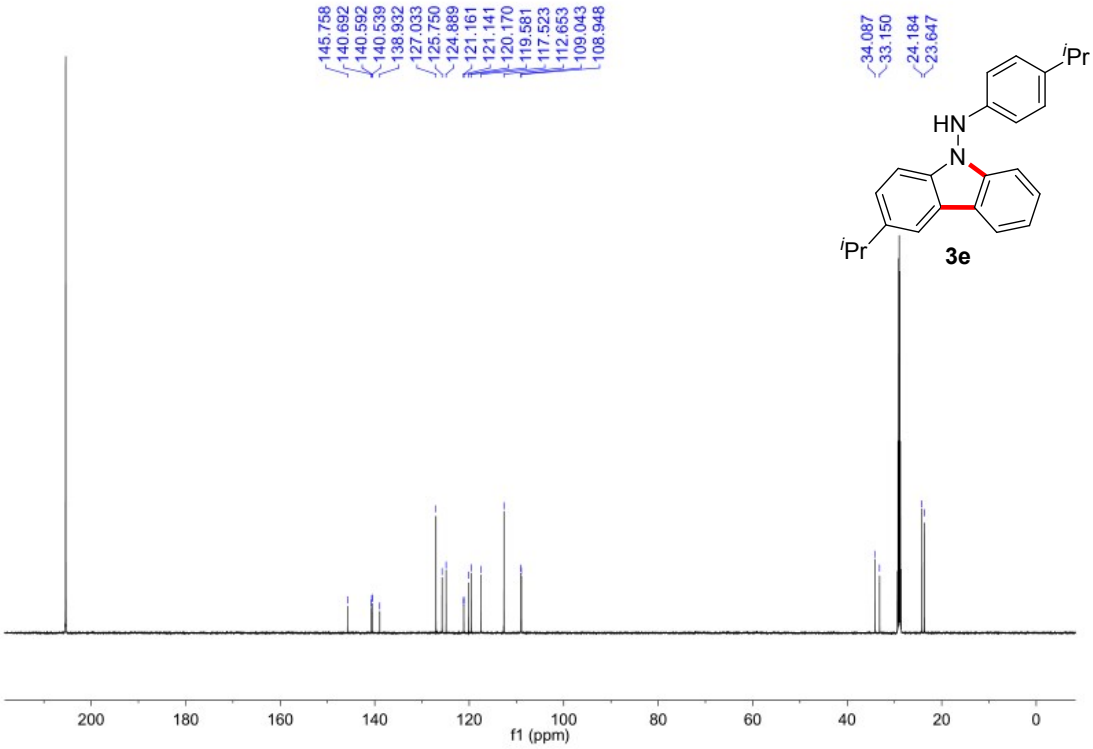


3d: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6

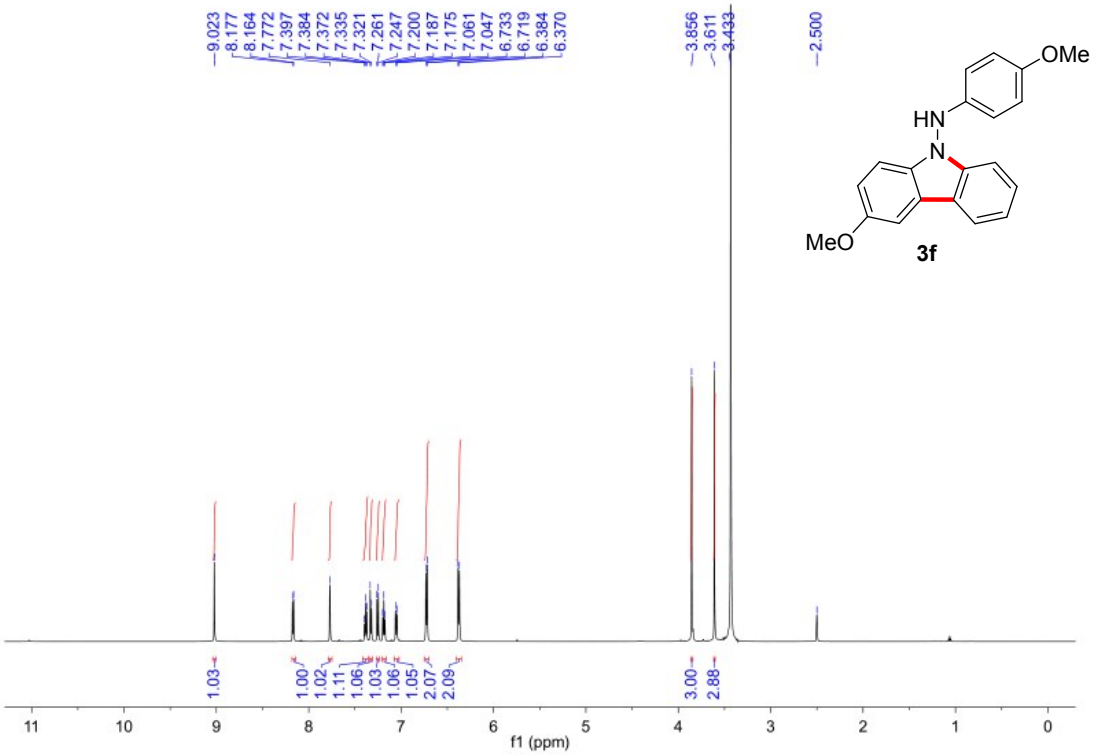


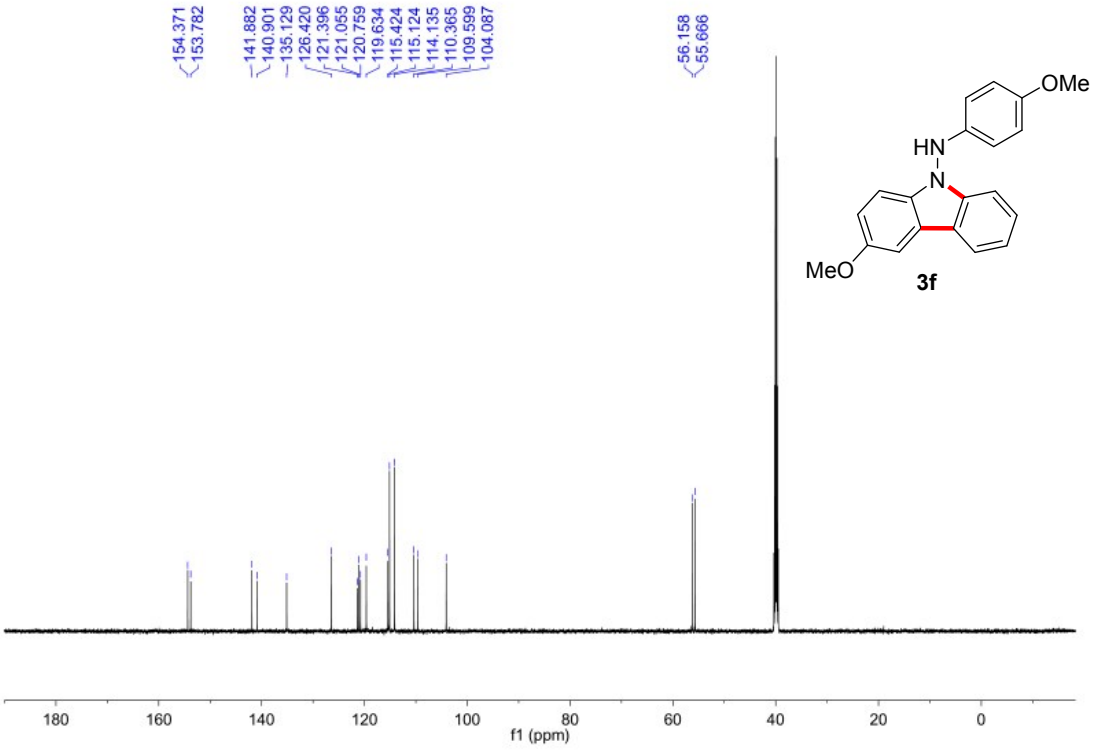
3e: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), acetone-d_6



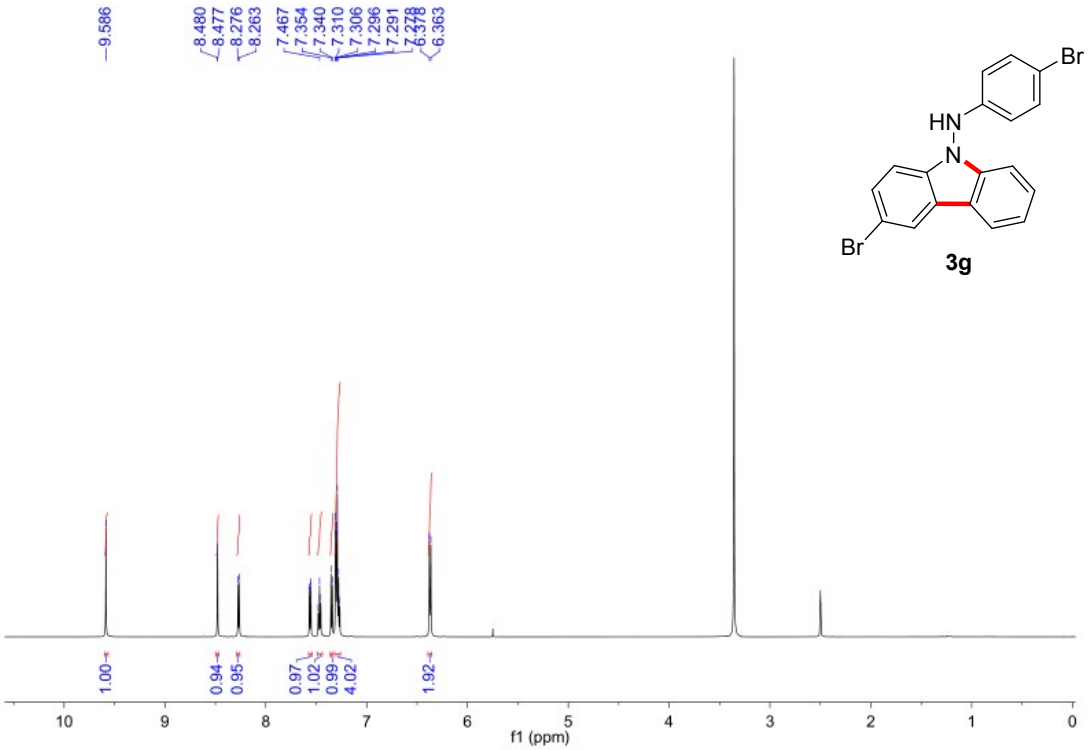


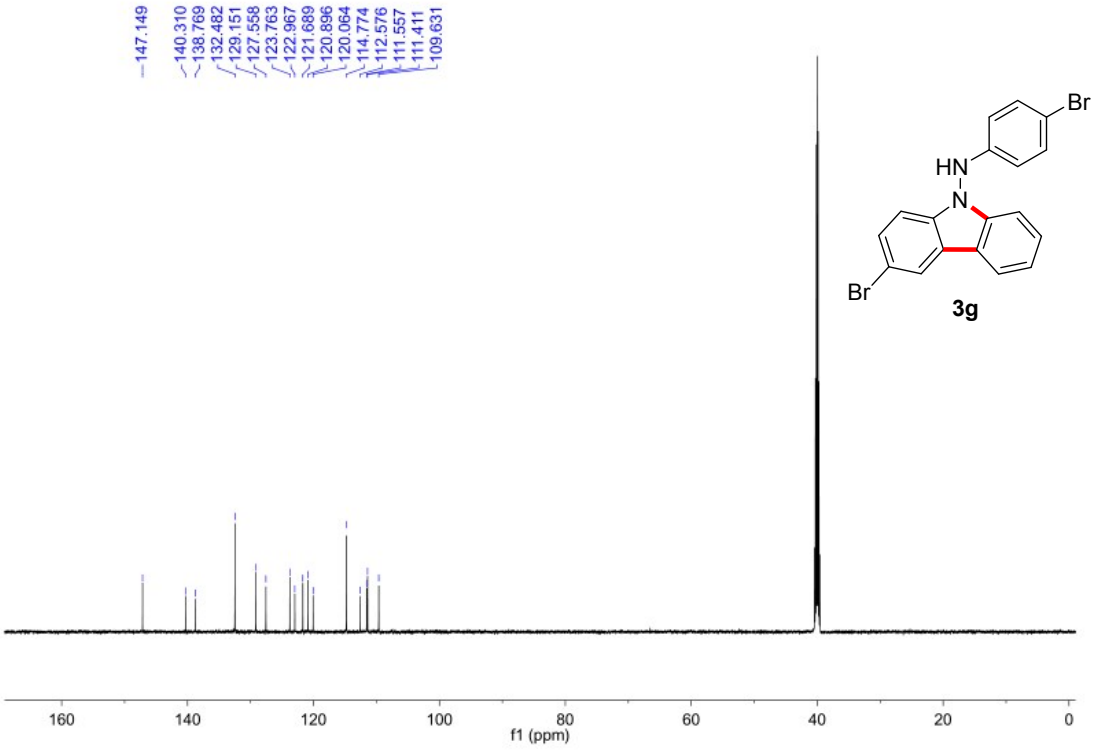
3f: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6



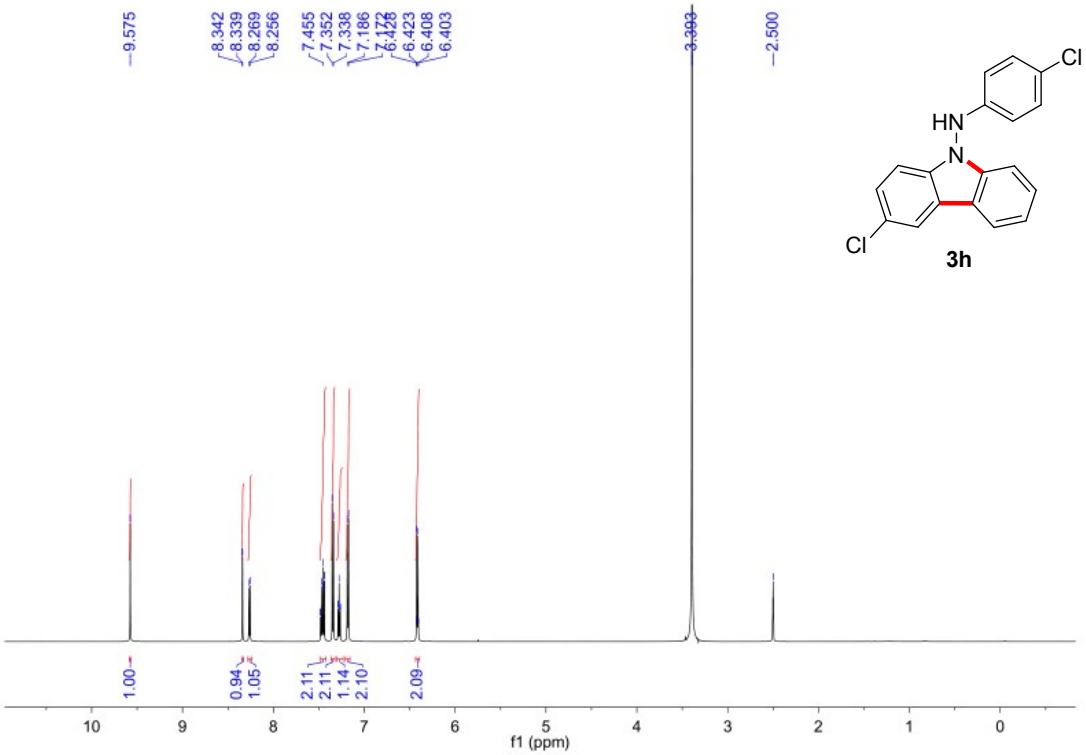


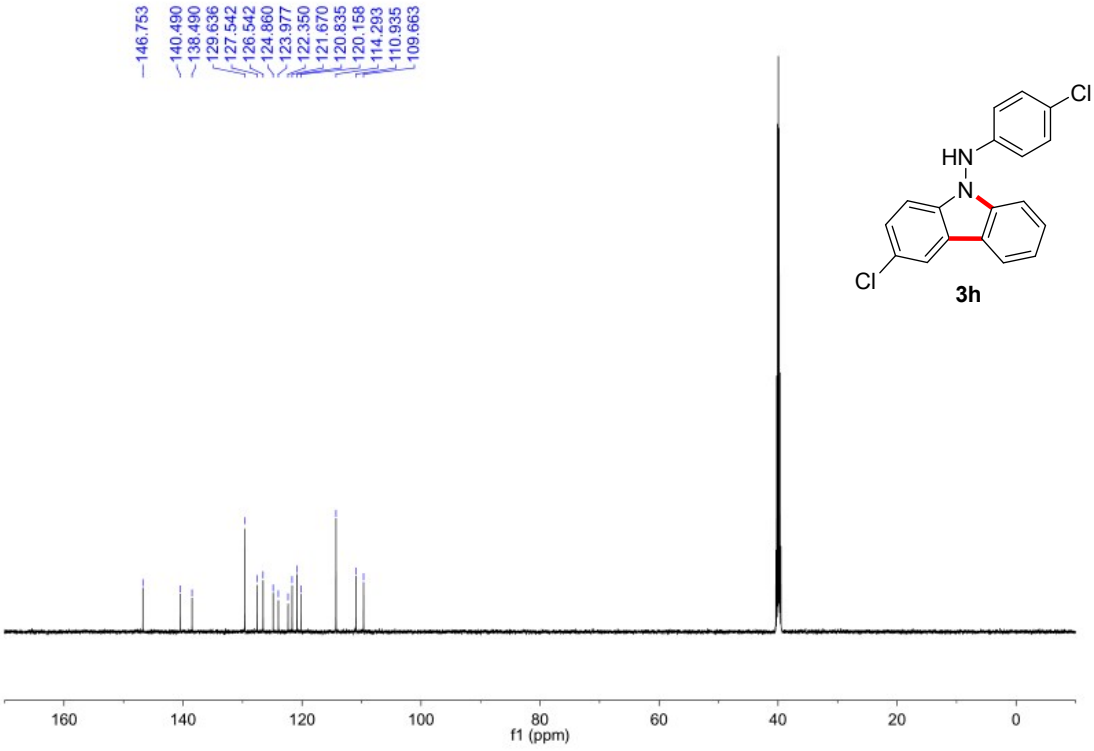
3g: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6



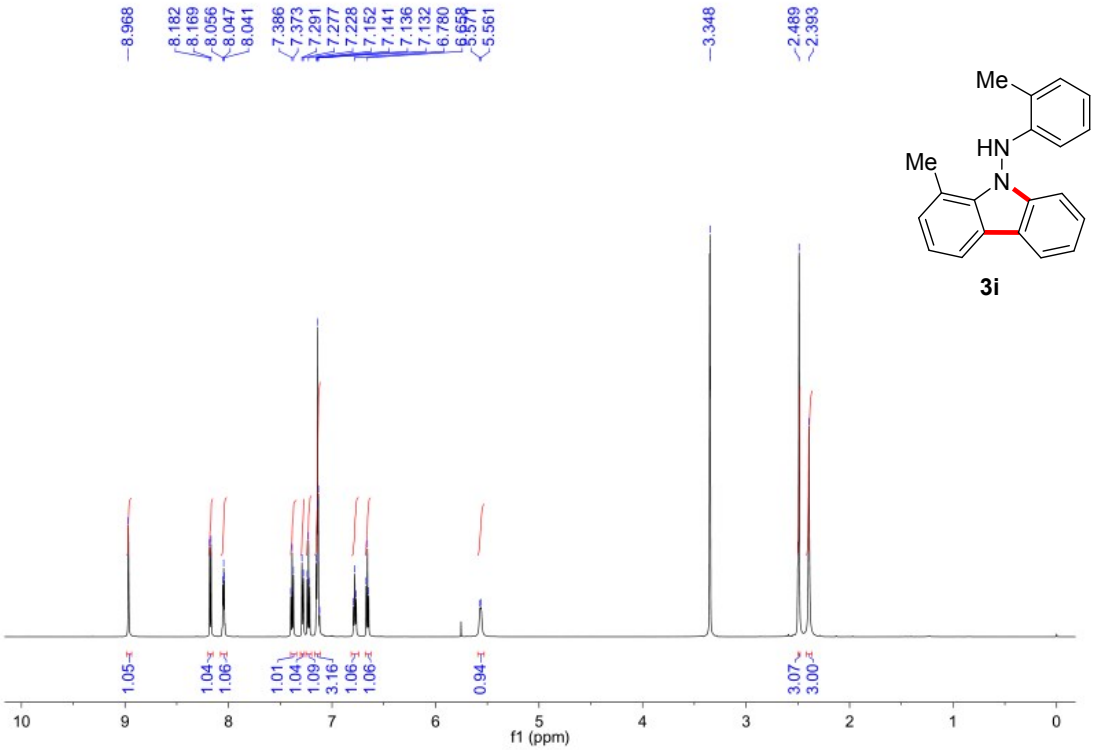


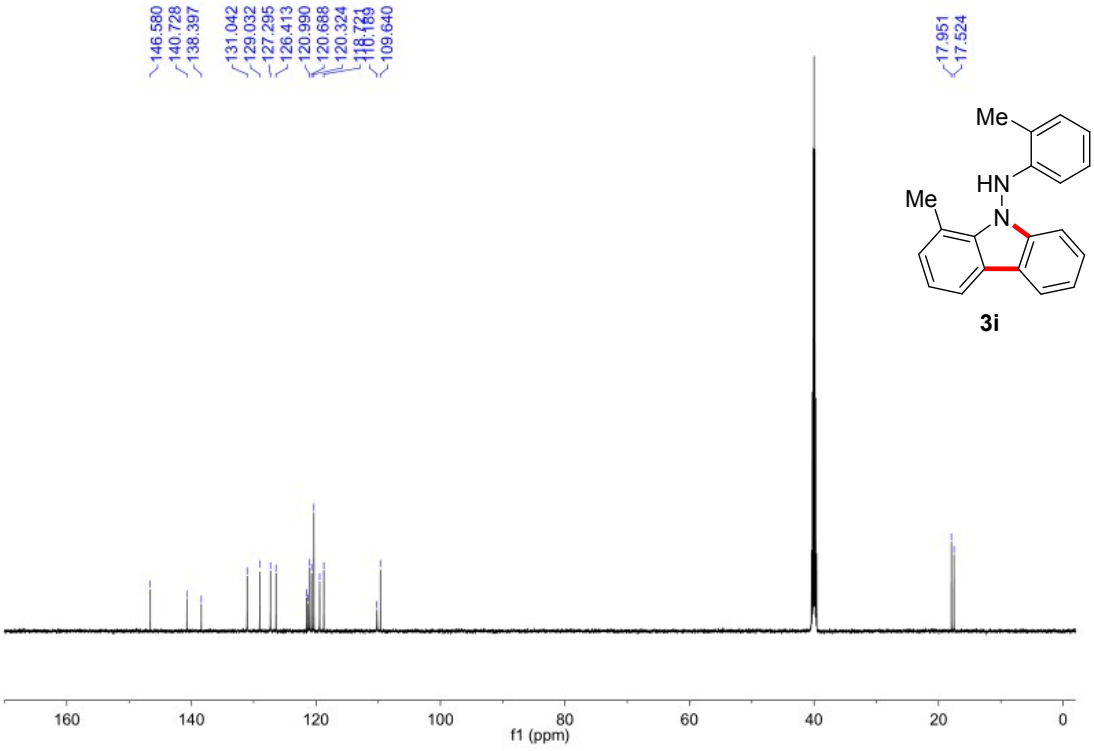
3h: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6



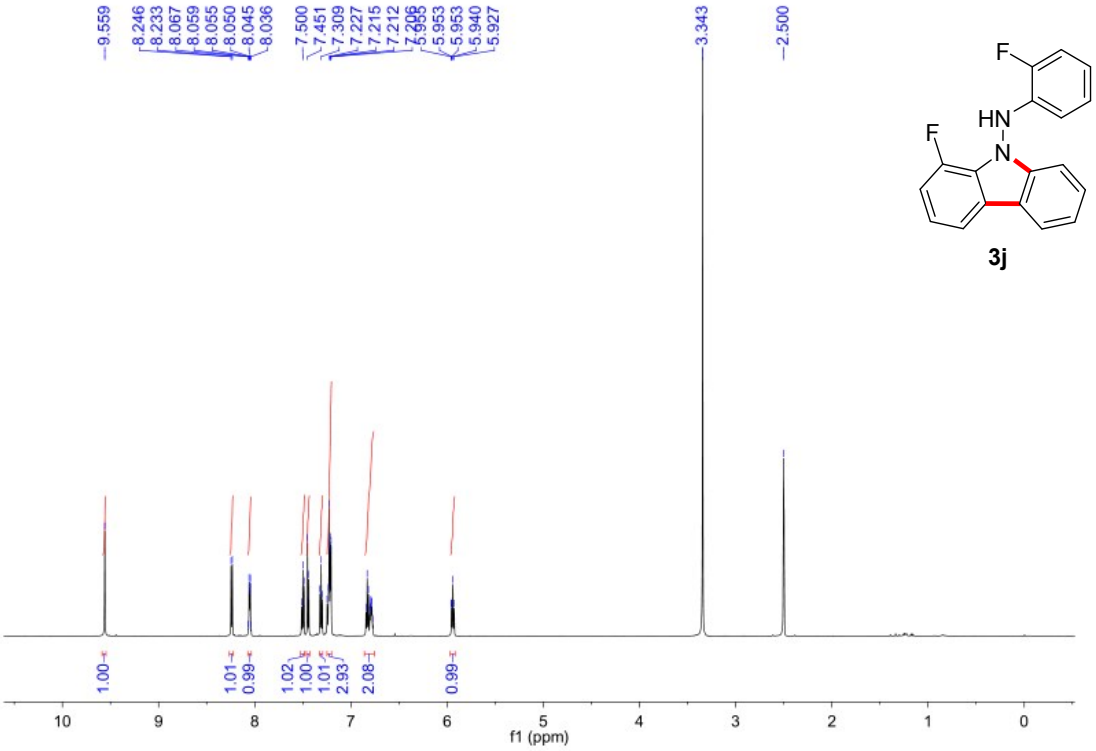


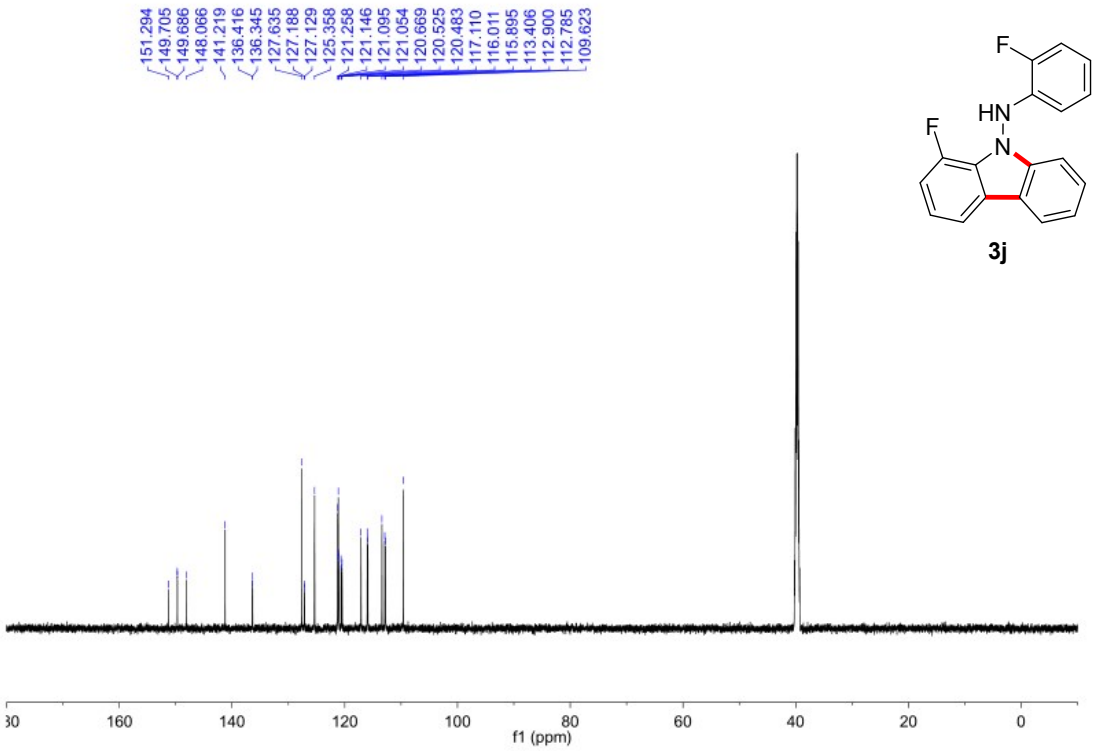
3i: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6

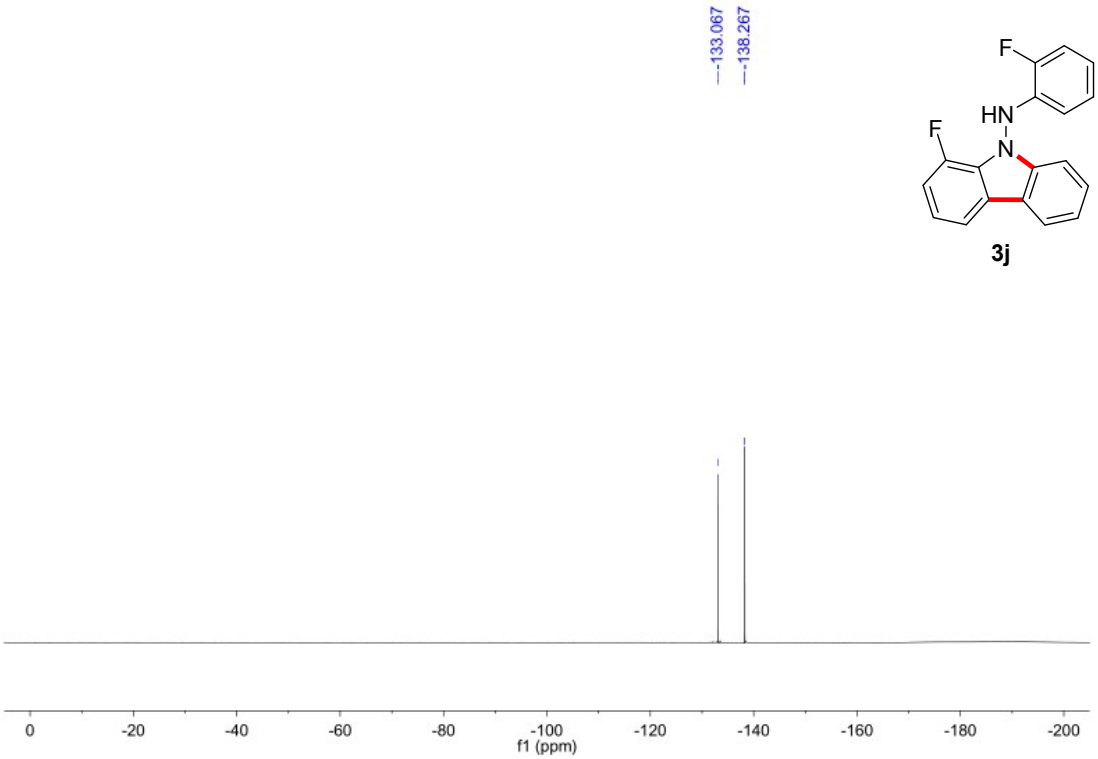




3j: ^{1}H NMR (600 MHz), ^{13}C NMR (150 MHz) and ^{19}F NMR (565 MHz), DMSO-d_6

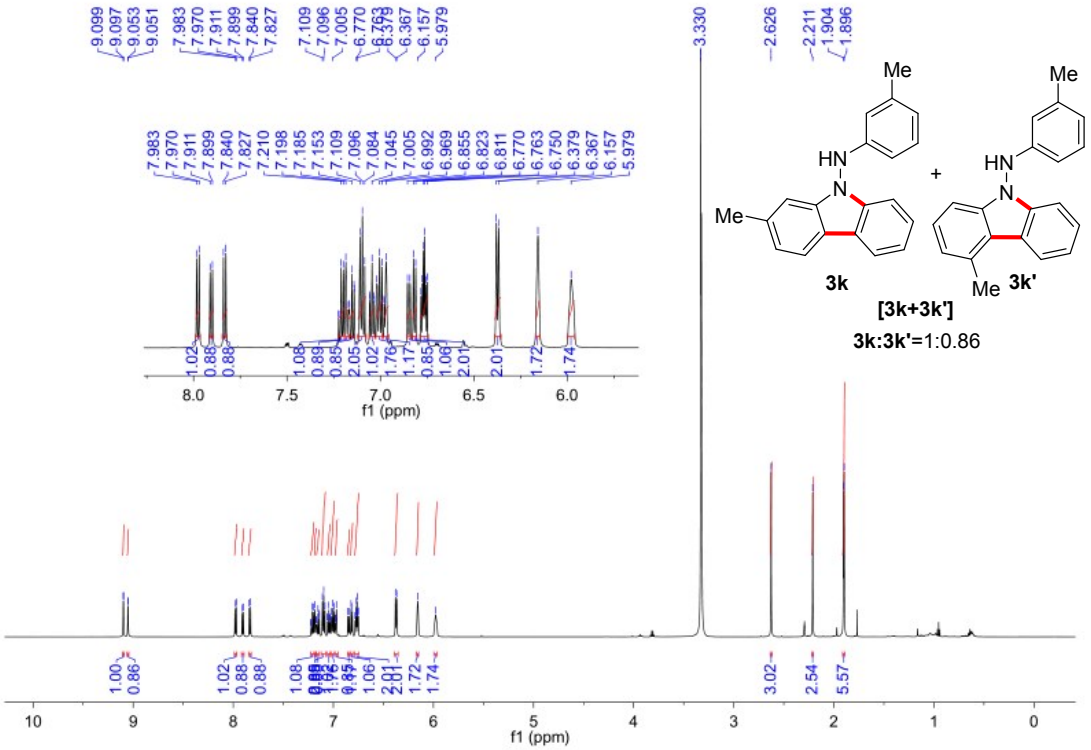


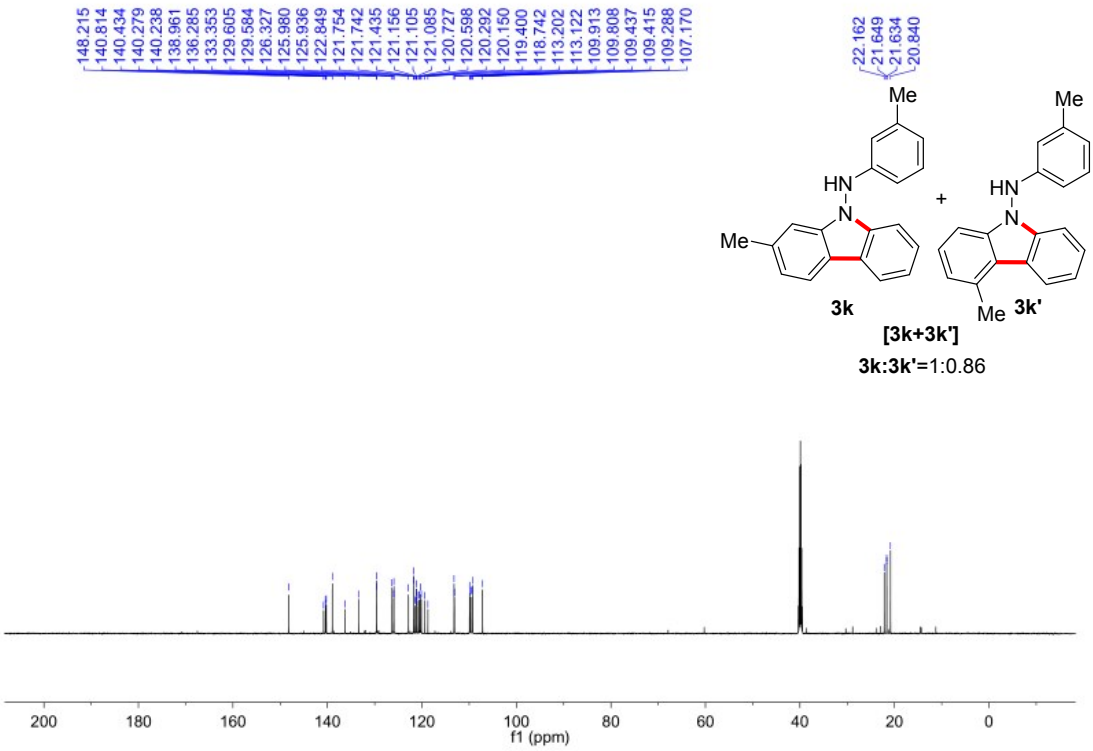




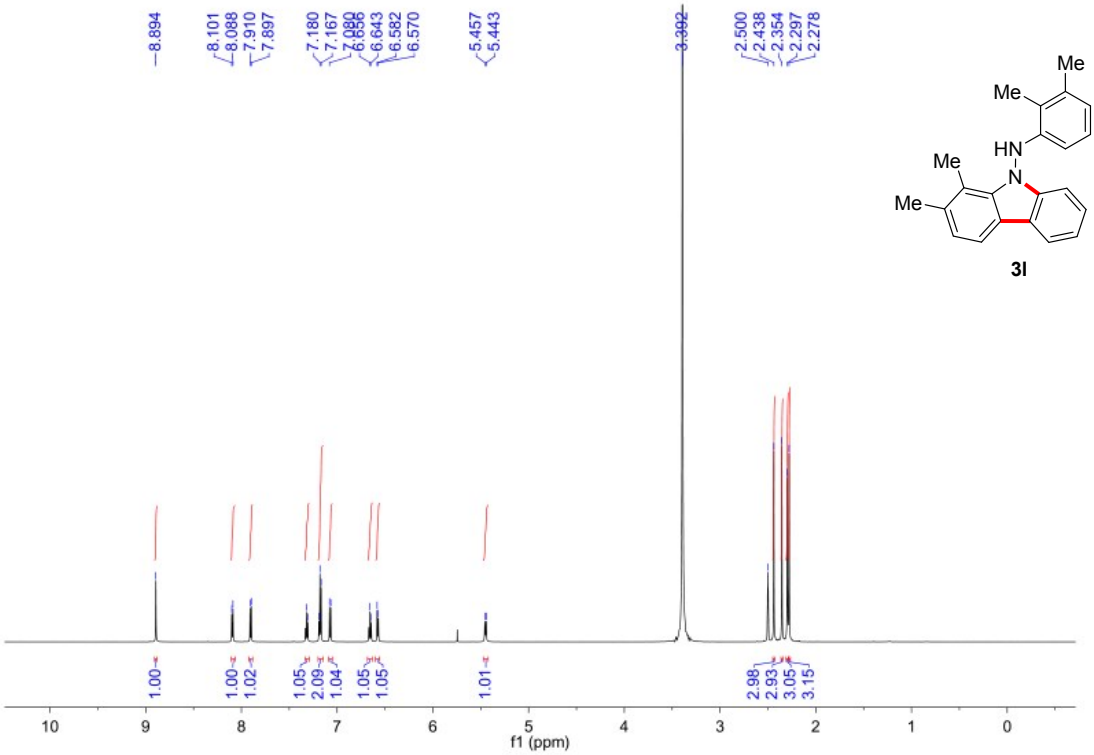
3j

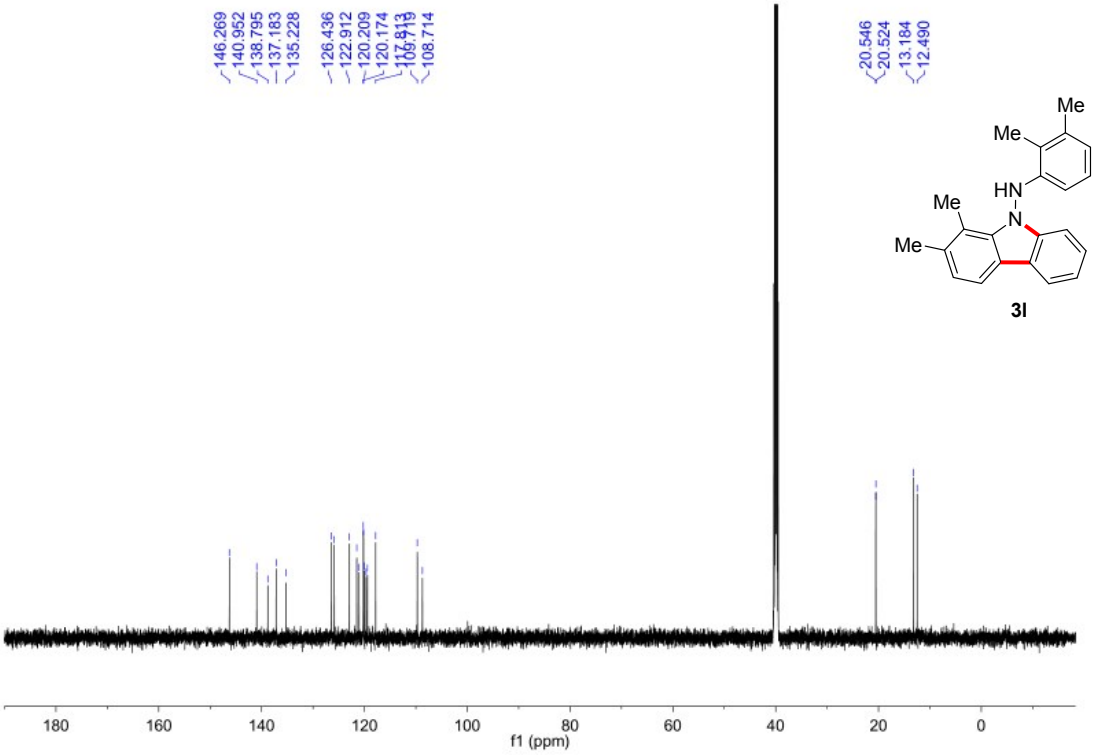
3k: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6



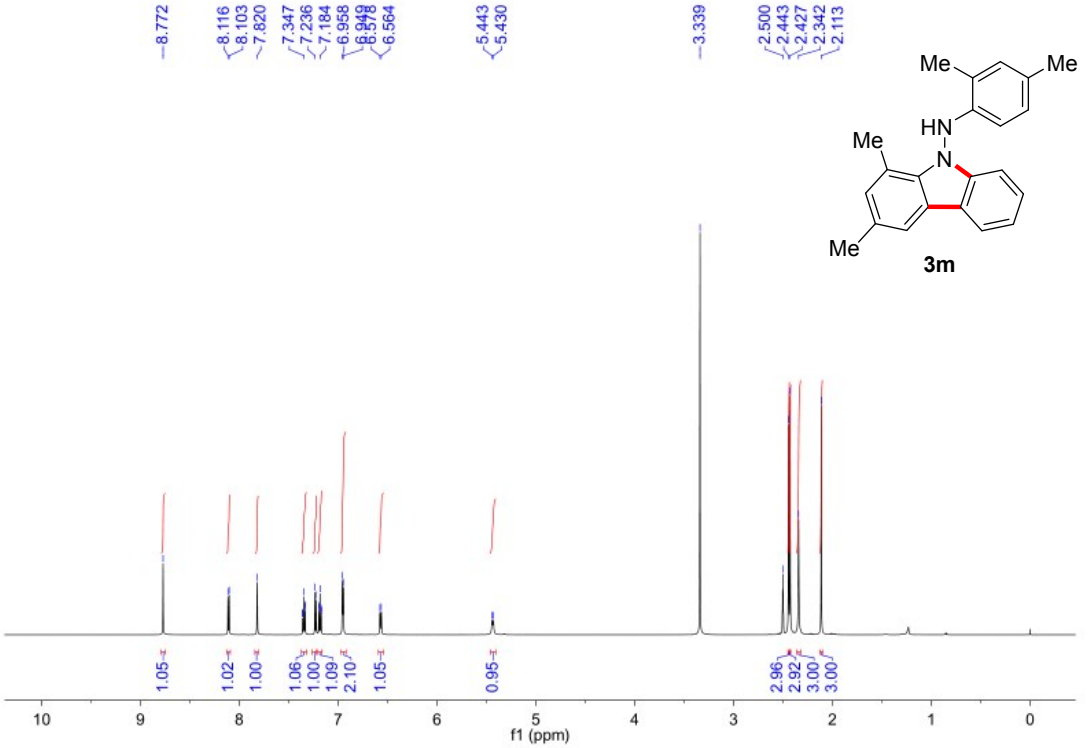


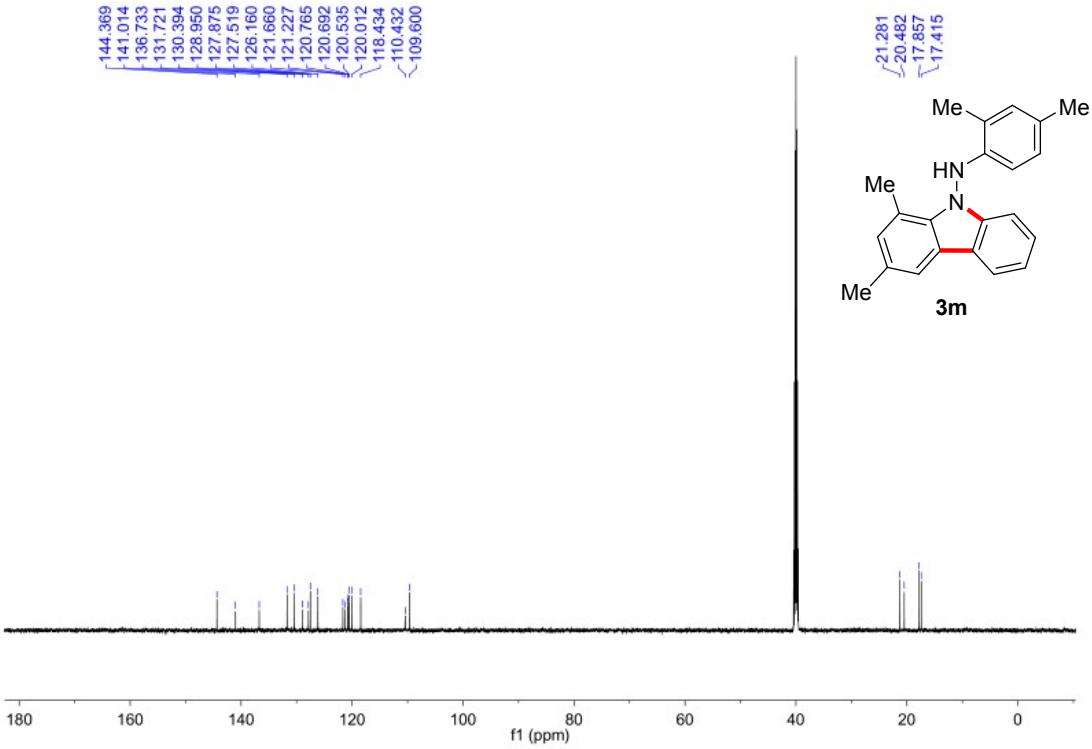
3l: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6



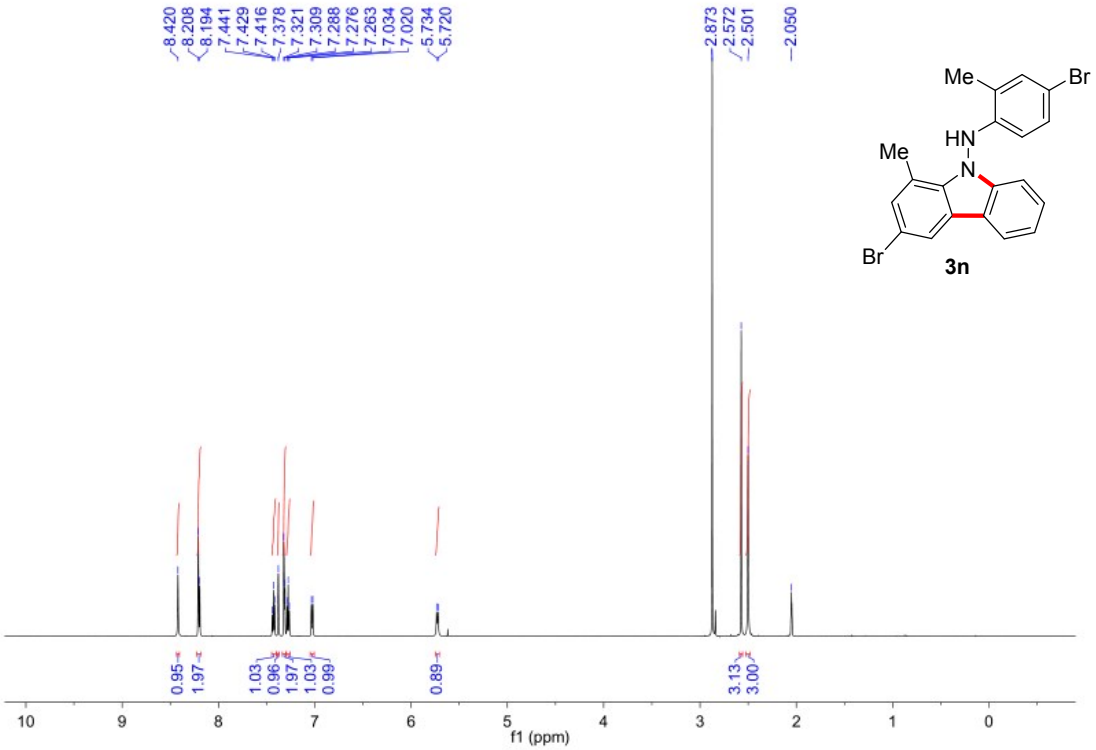


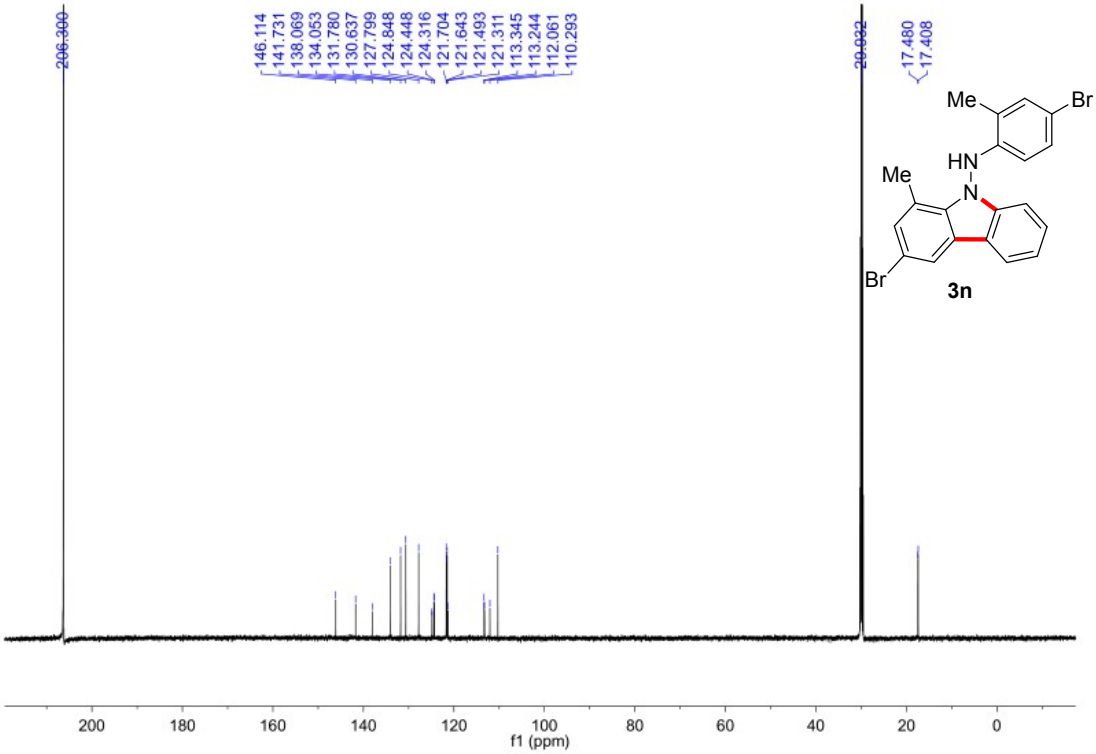
3m: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6



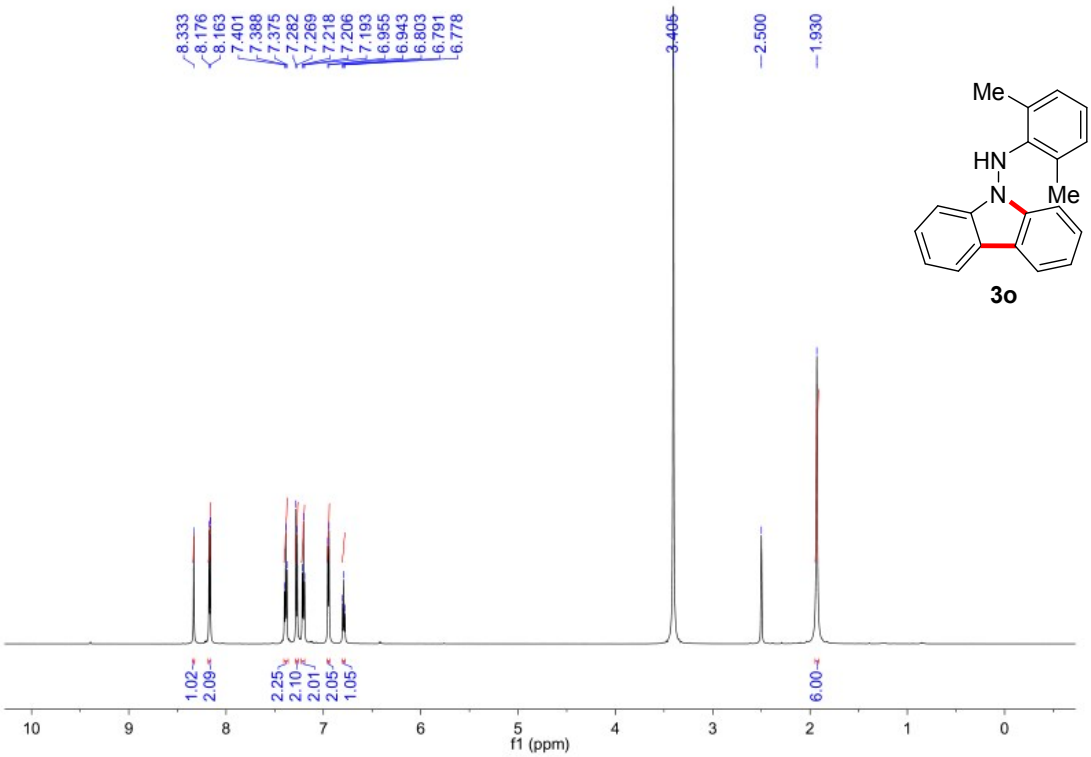


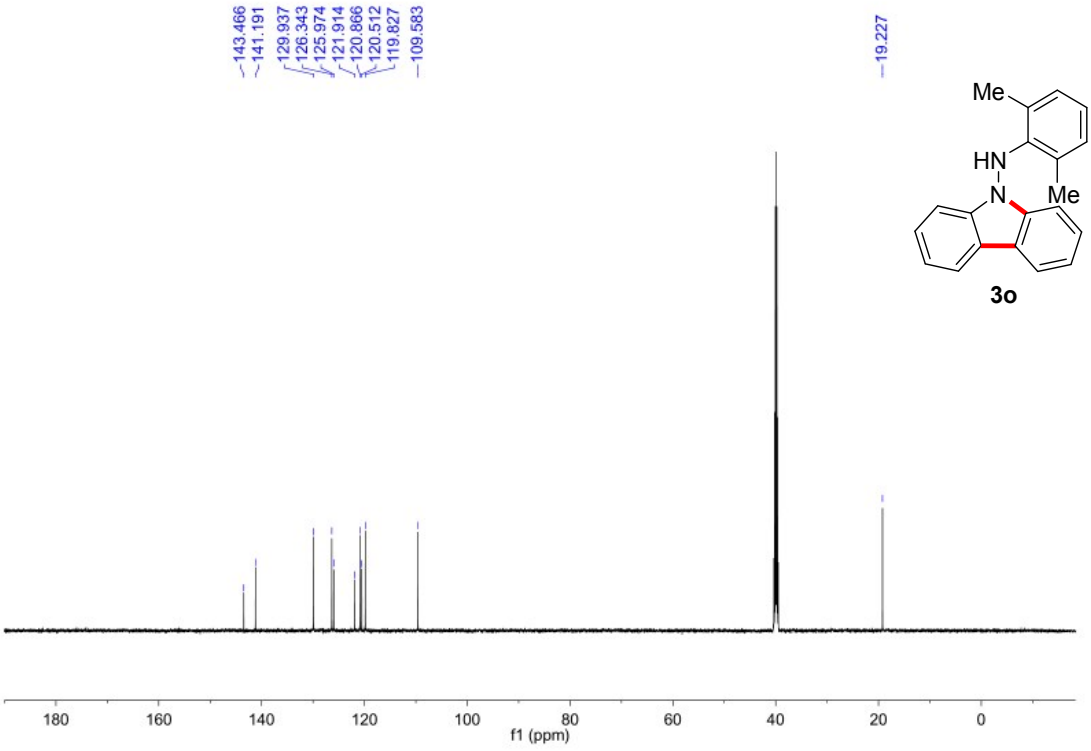
3n: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), acetone-d_6



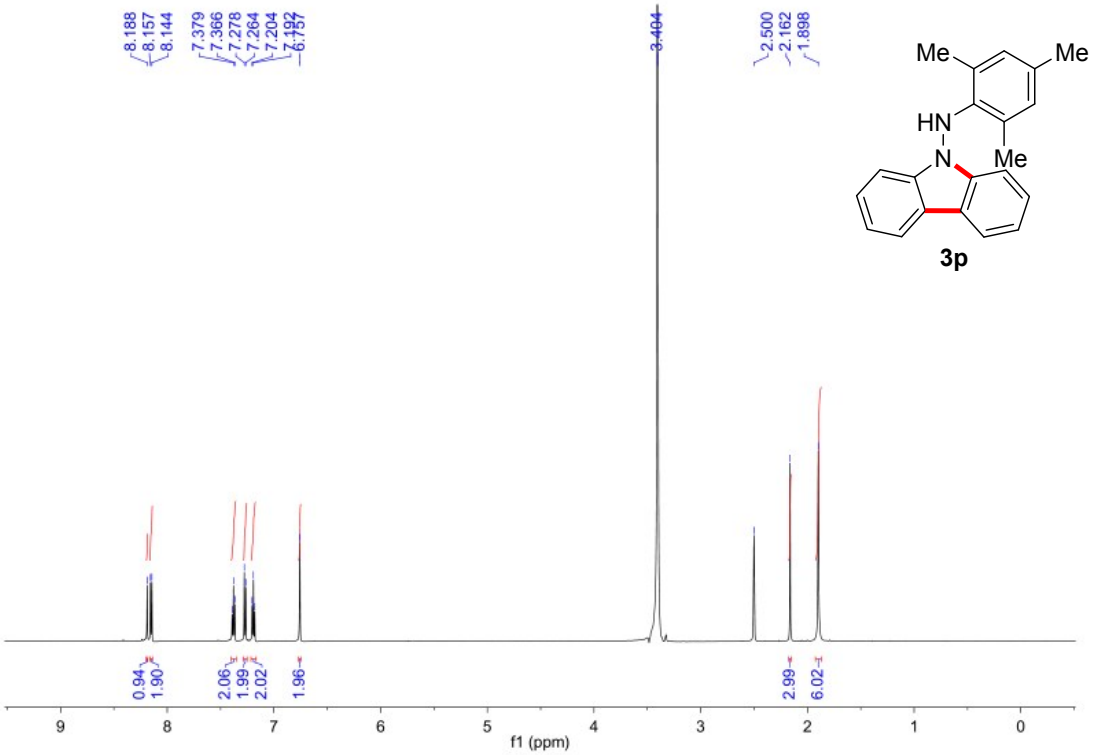


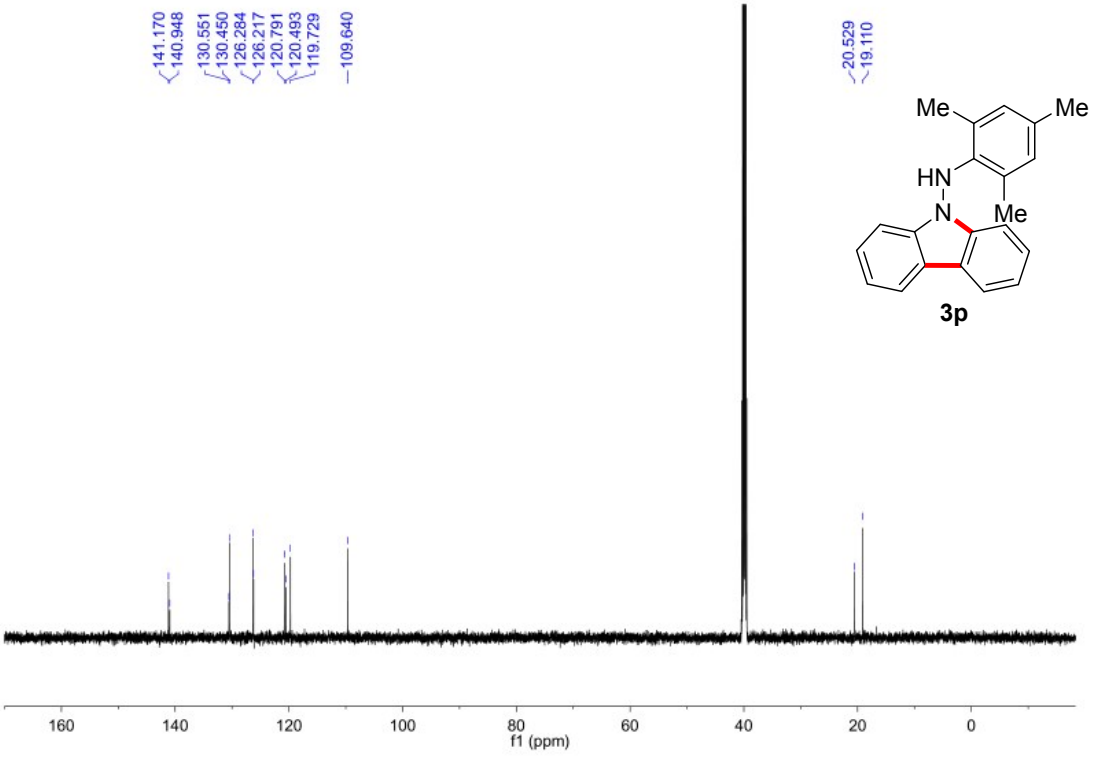
3o: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6



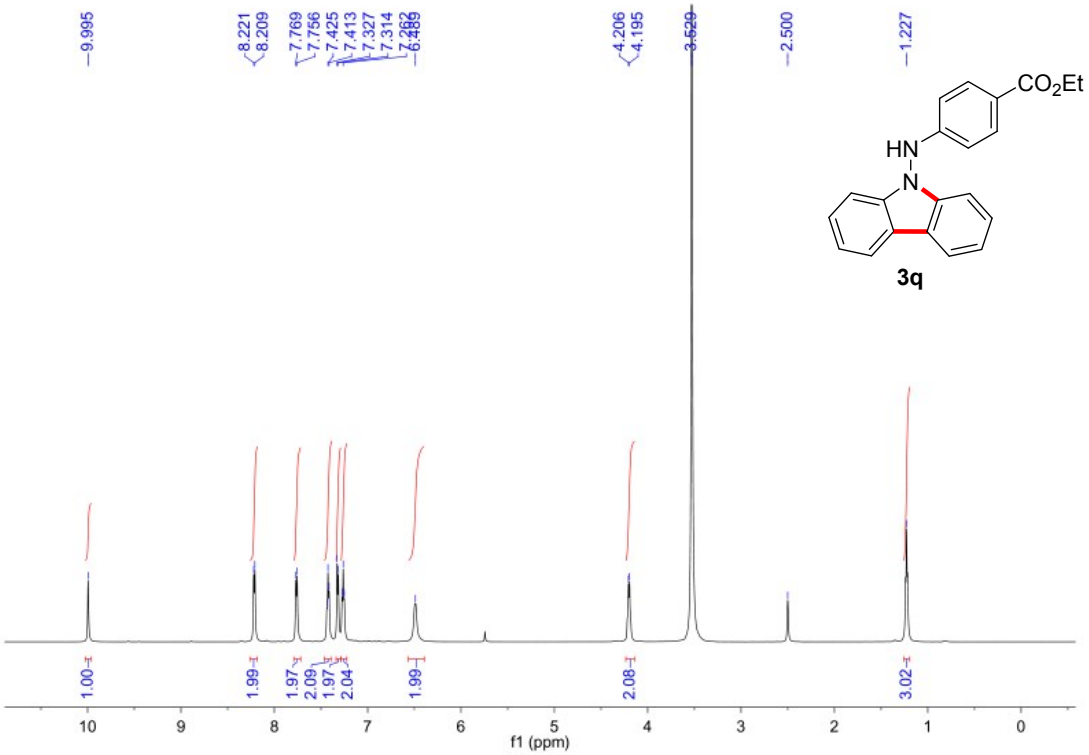


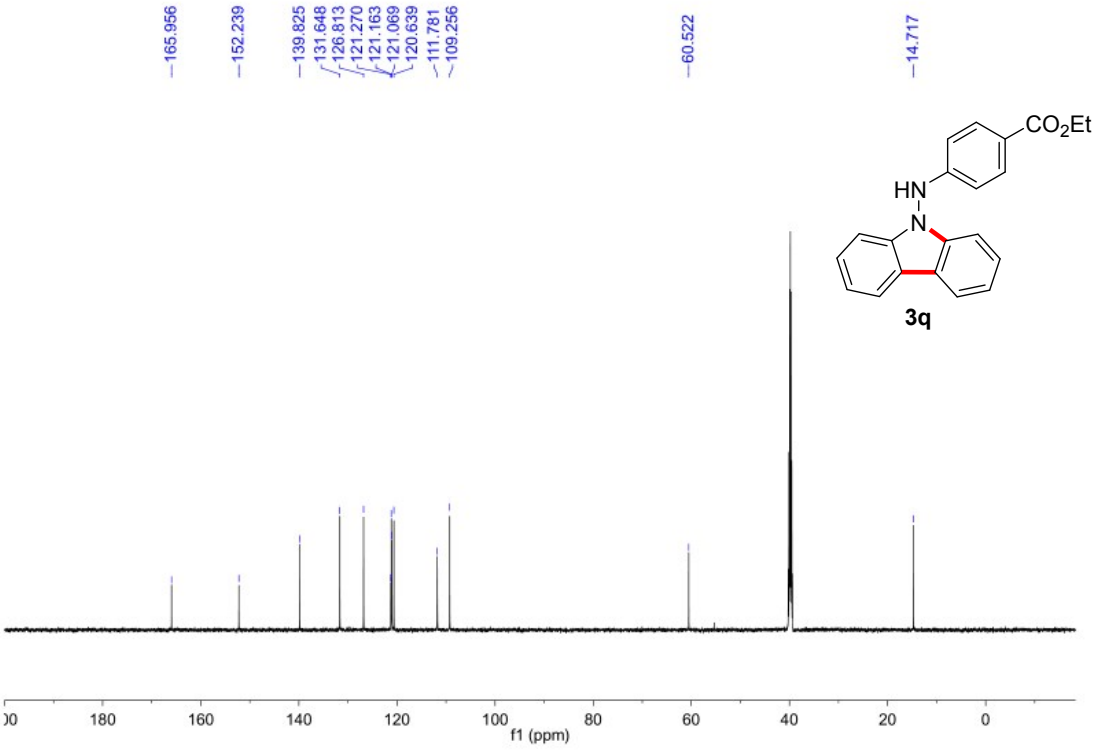
3p: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6



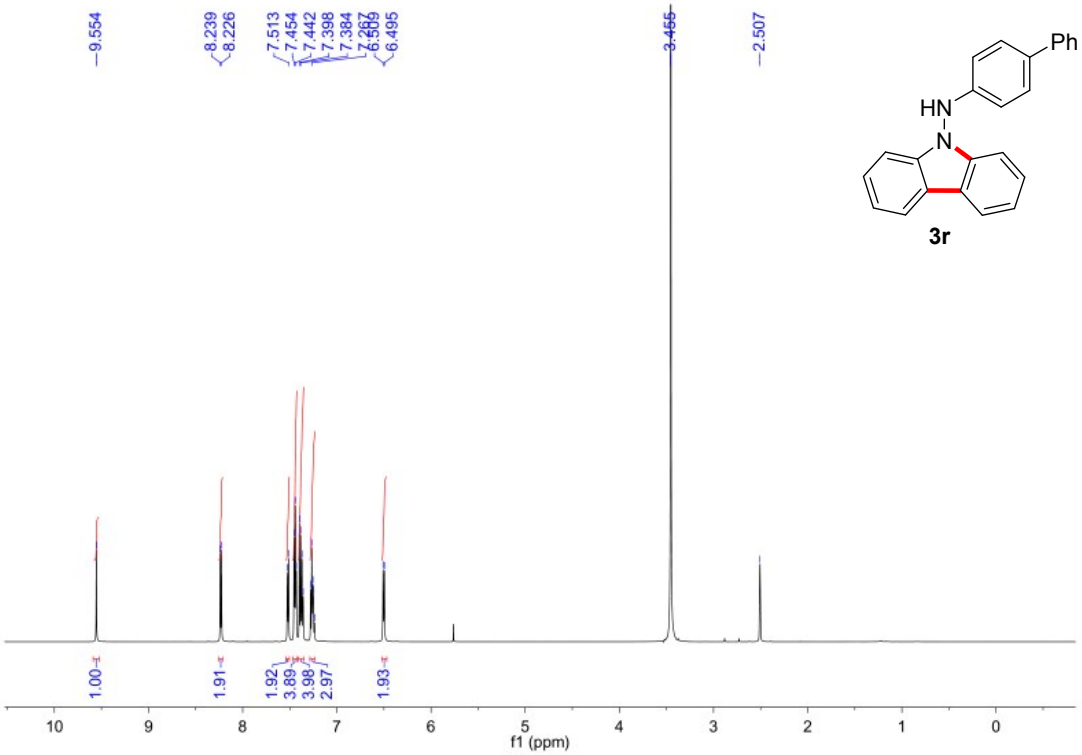


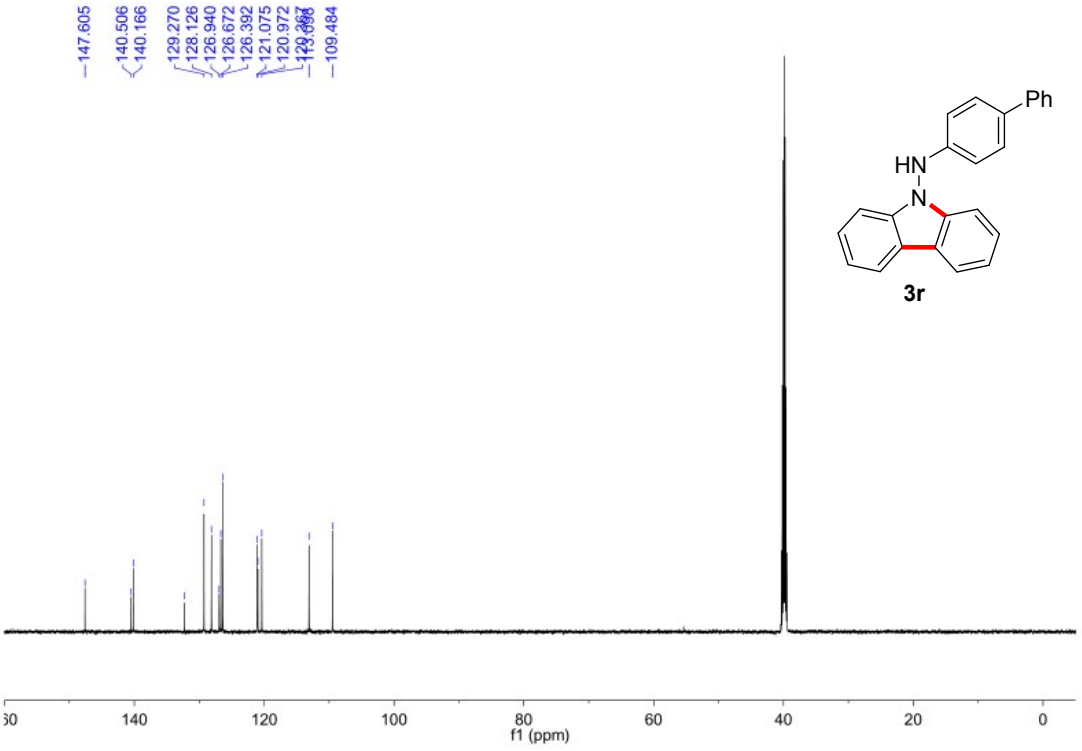
3q: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6



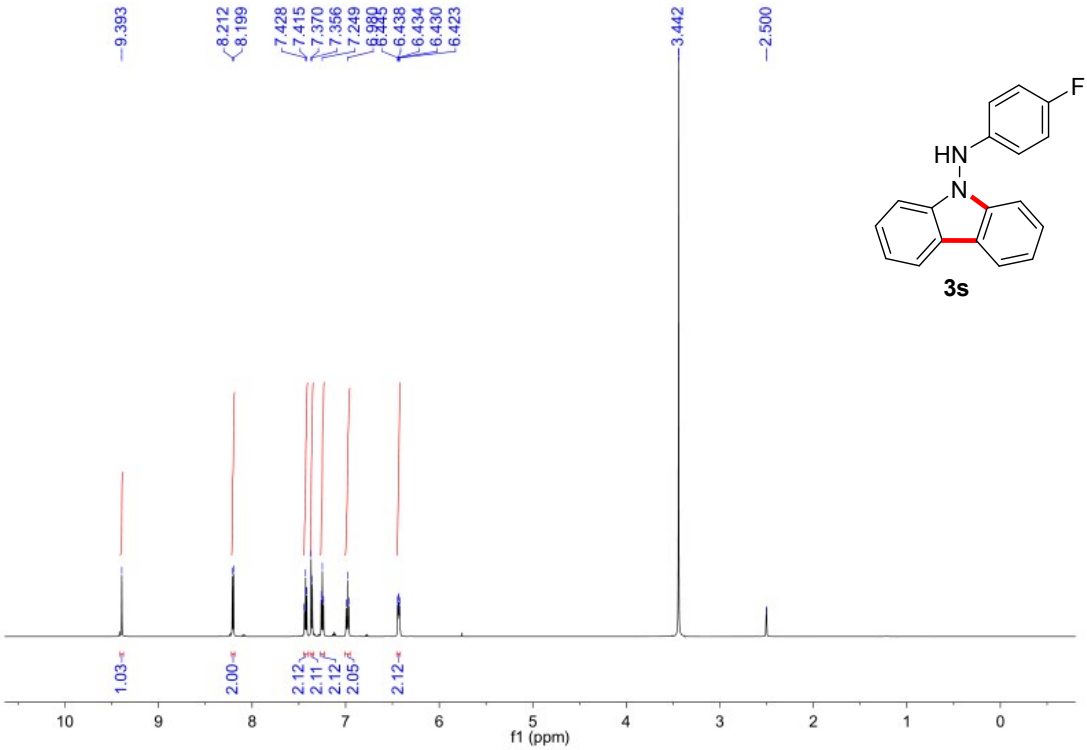


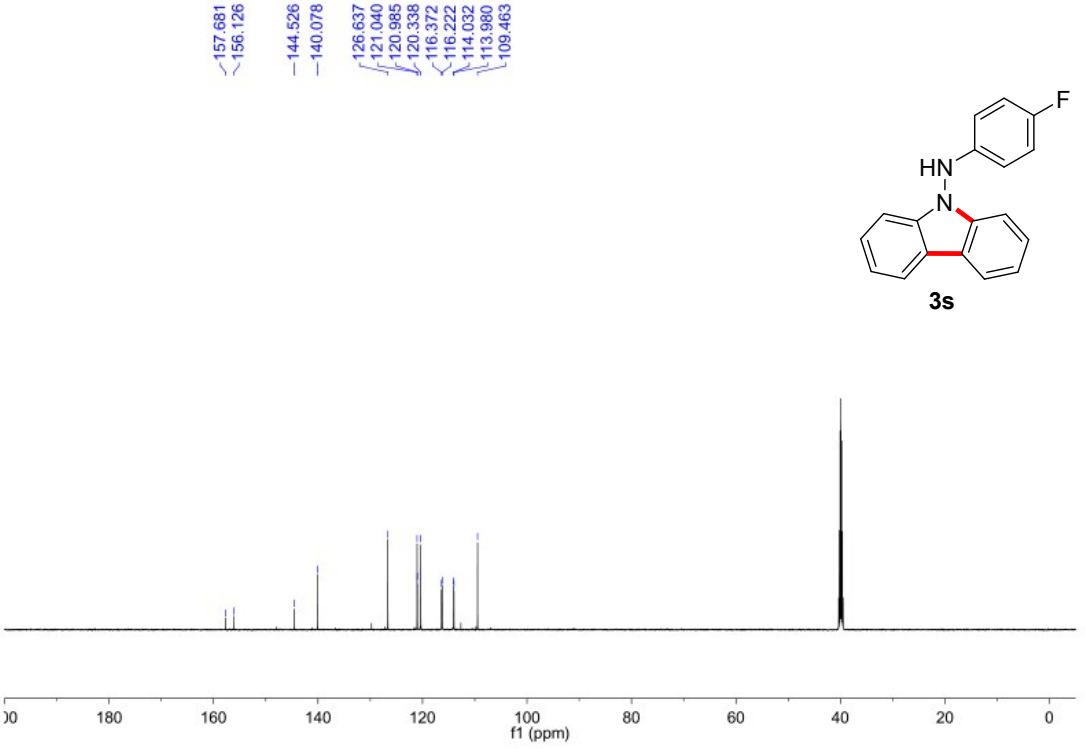
3r: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6

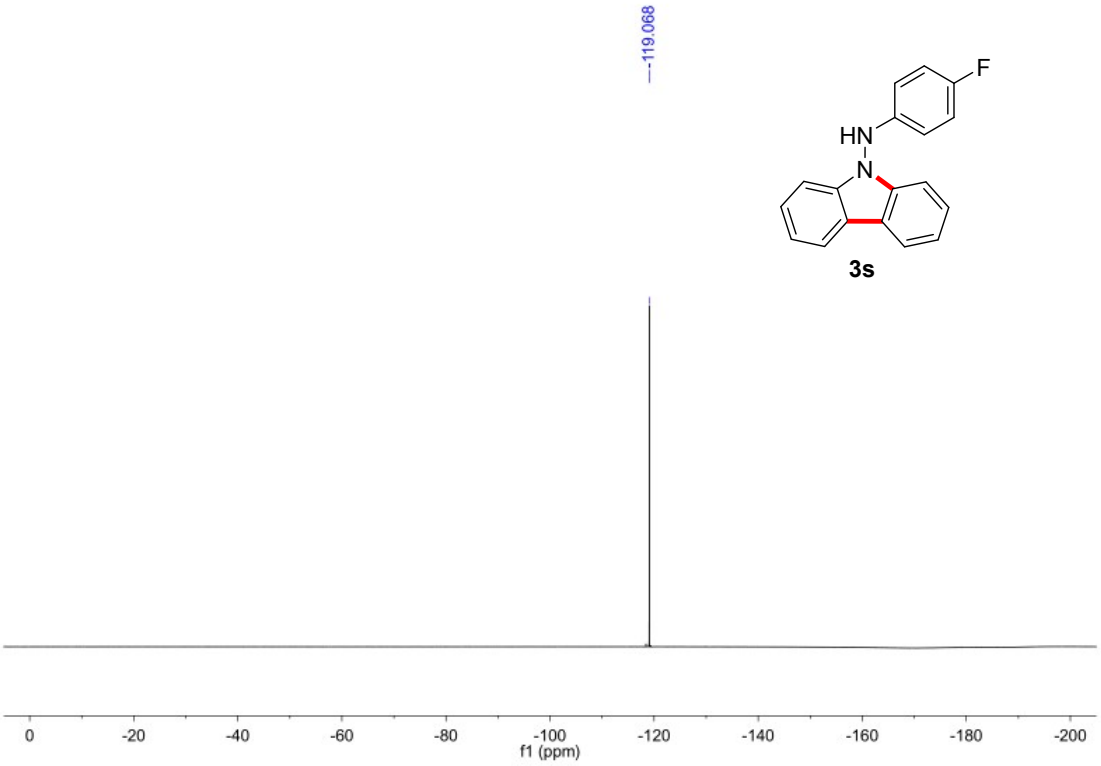




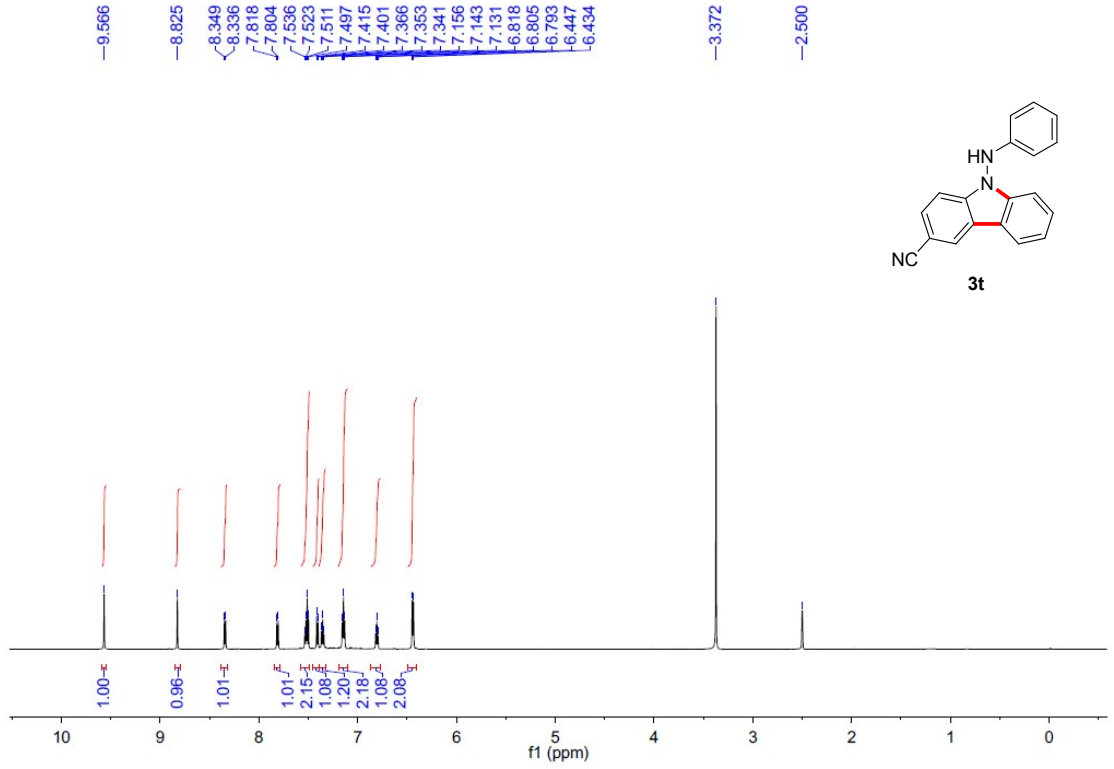
3s: ^{1}H NMR (600 MHz), ^{13}C NMR (150 MHz) and ^{19}F NMR (565 MHz), DMSO-d_6

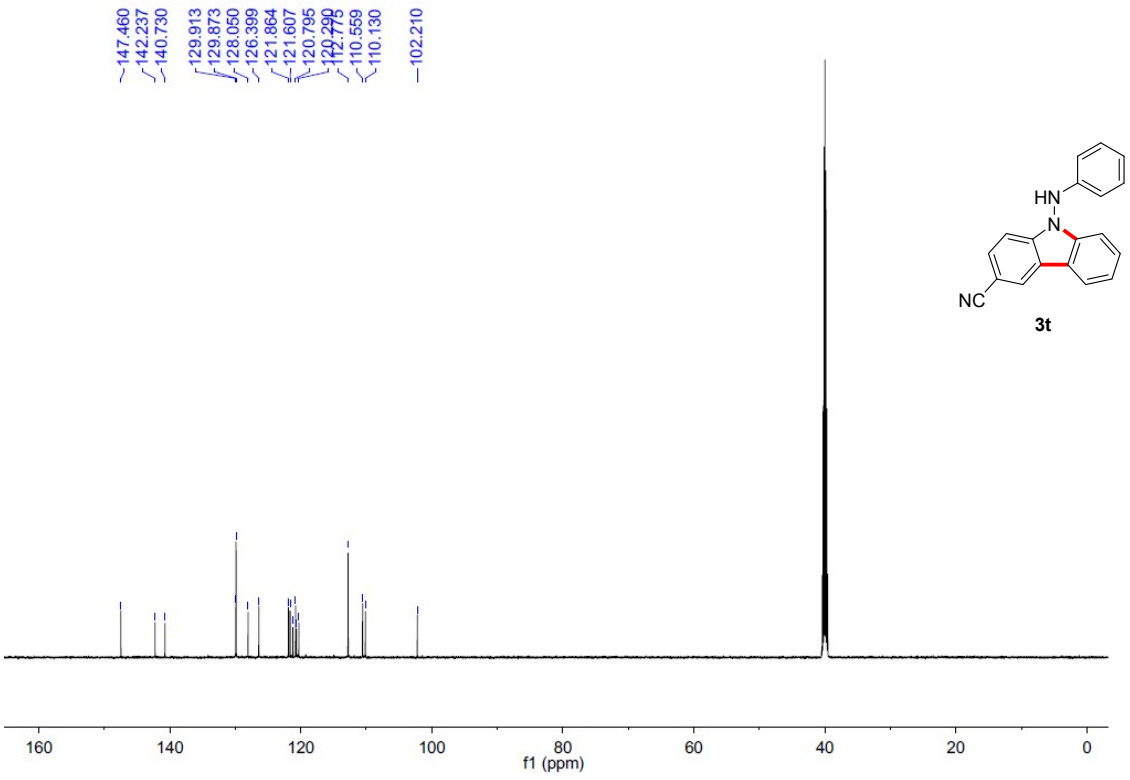




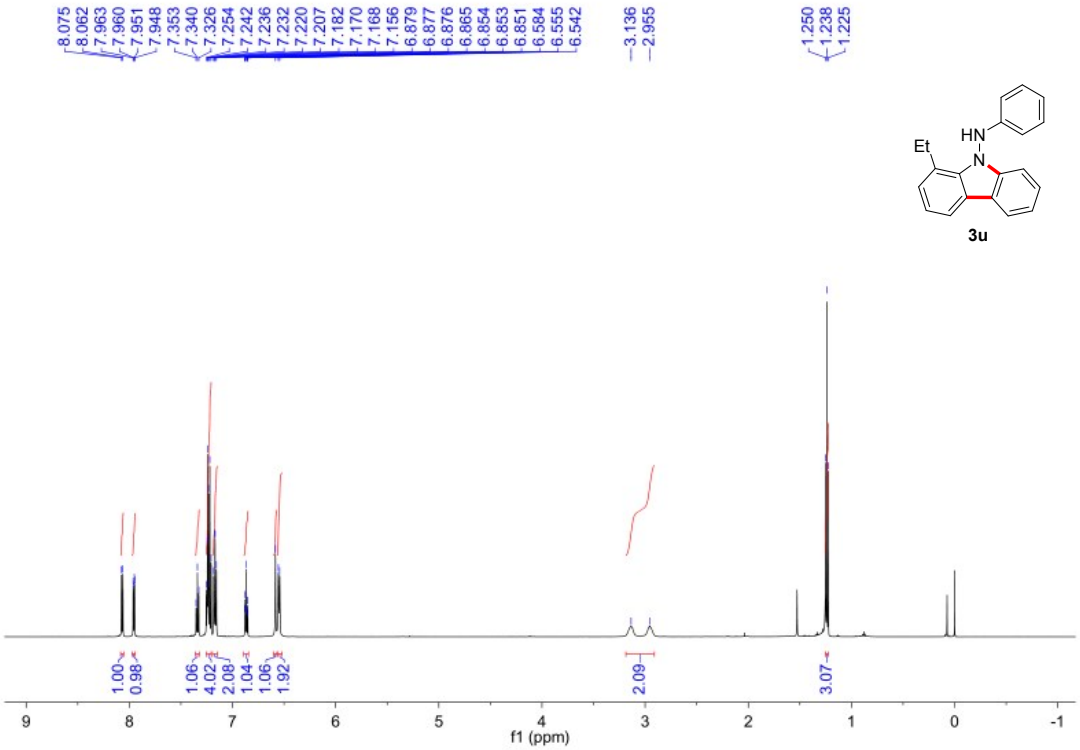

-119.068
F
HN
N
3s
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

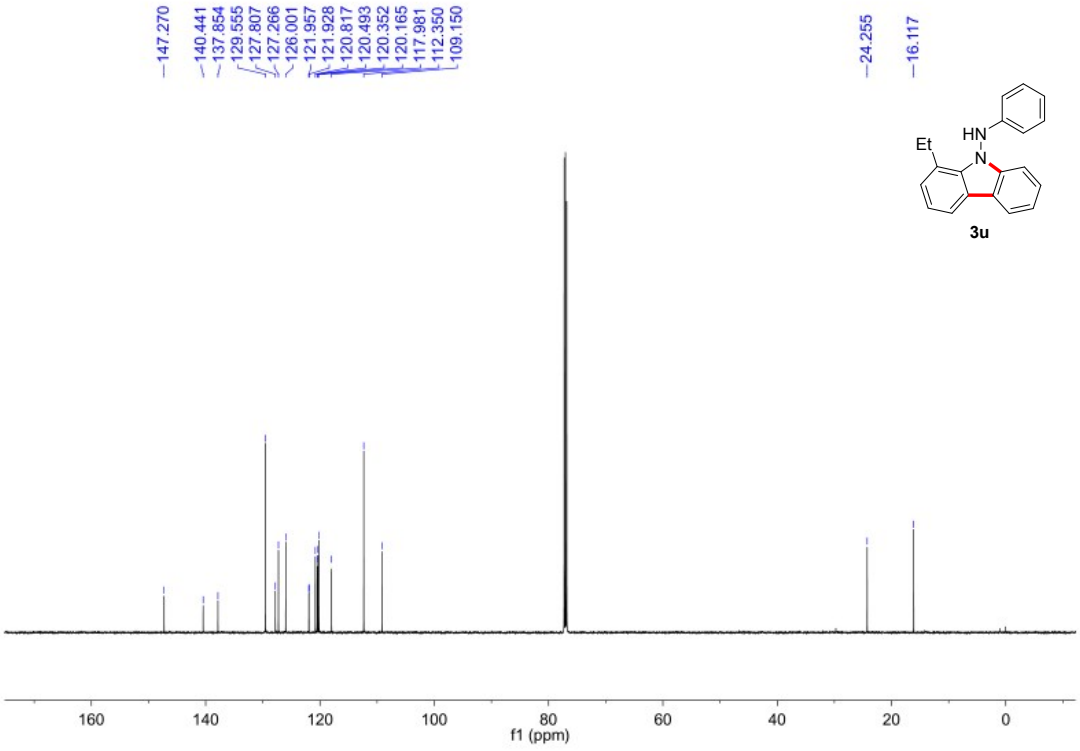
3t: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), $CDCl_3$



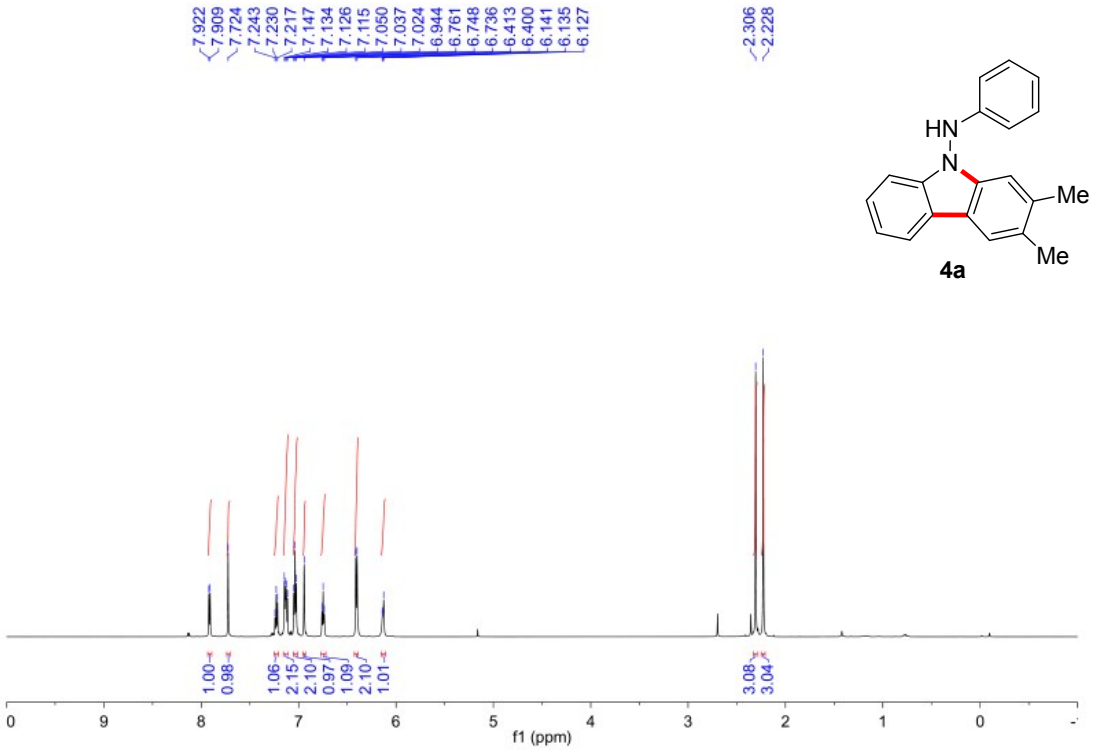


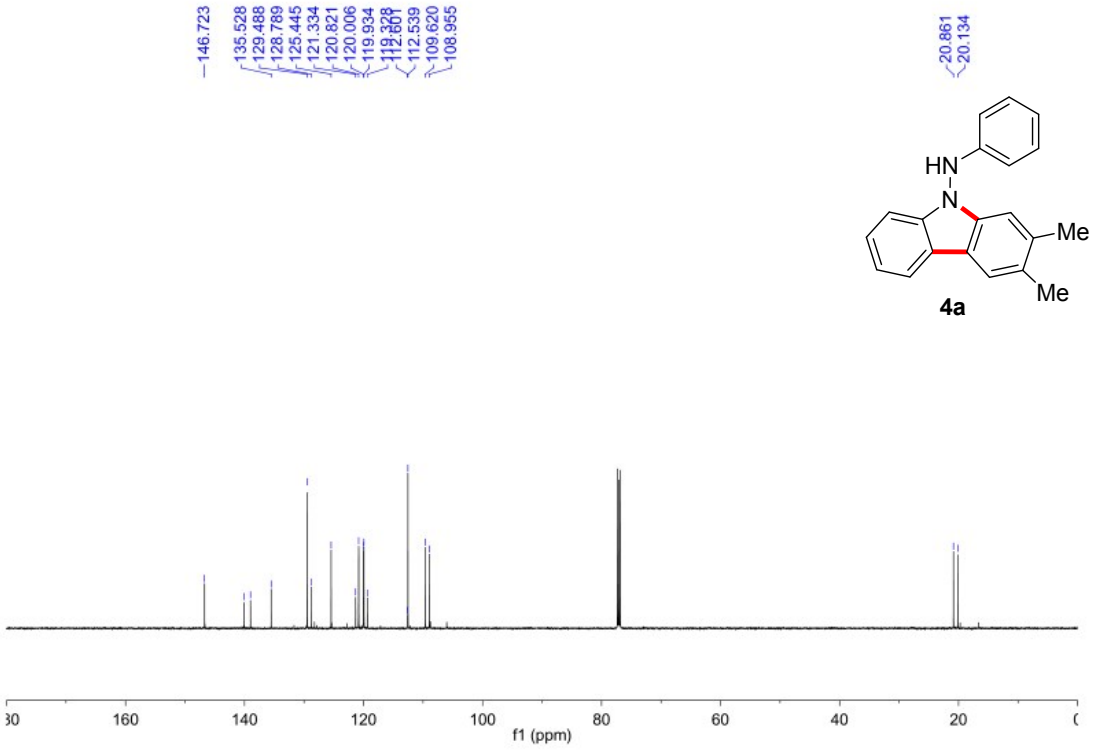
3u: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), $CDCl_3$



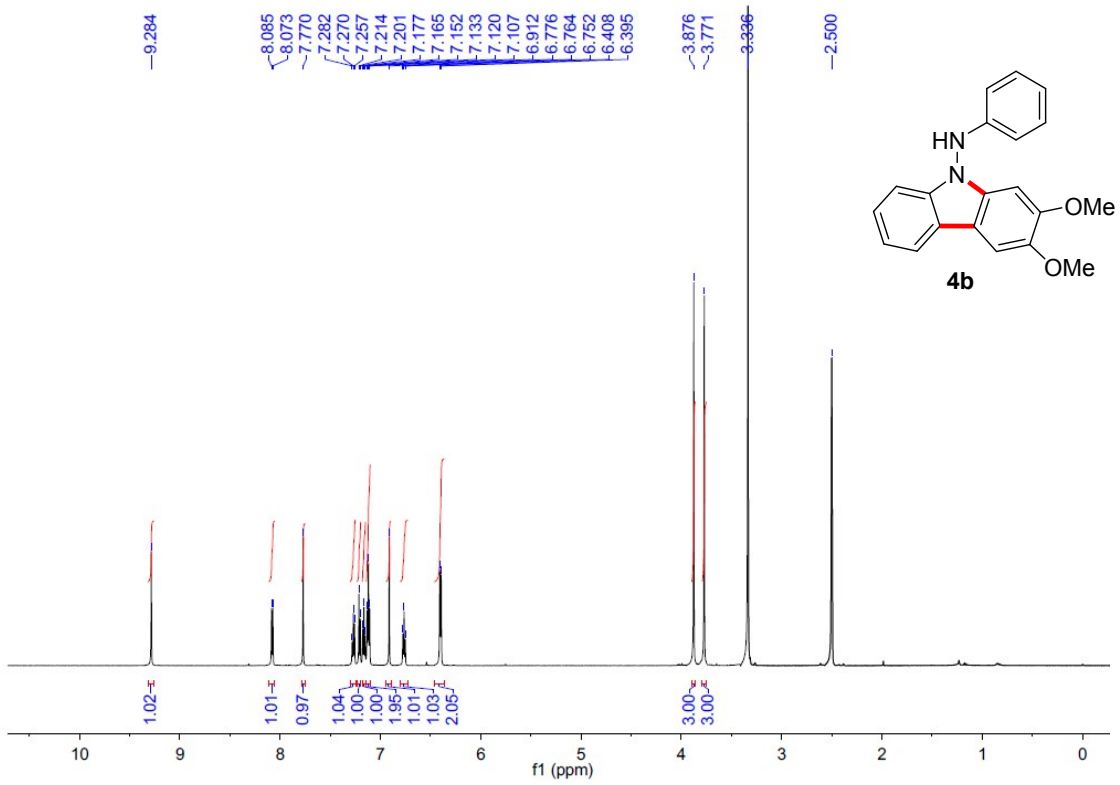


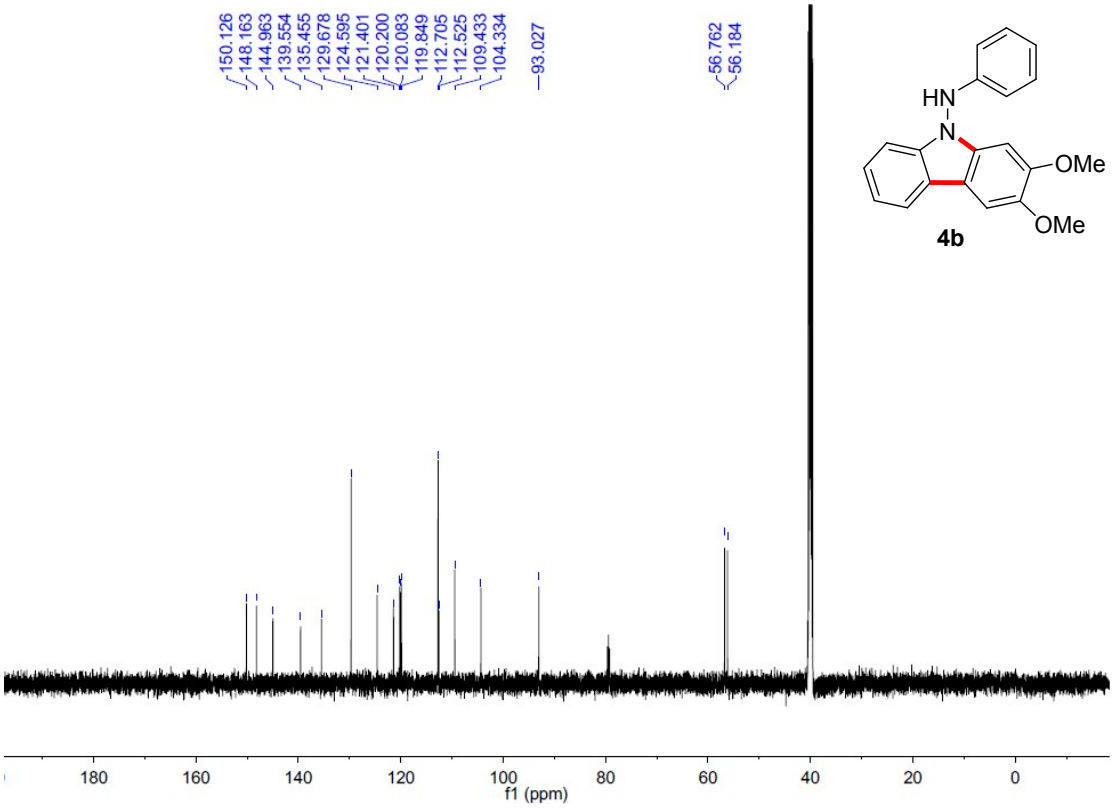
4a: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), $CDCl_3$



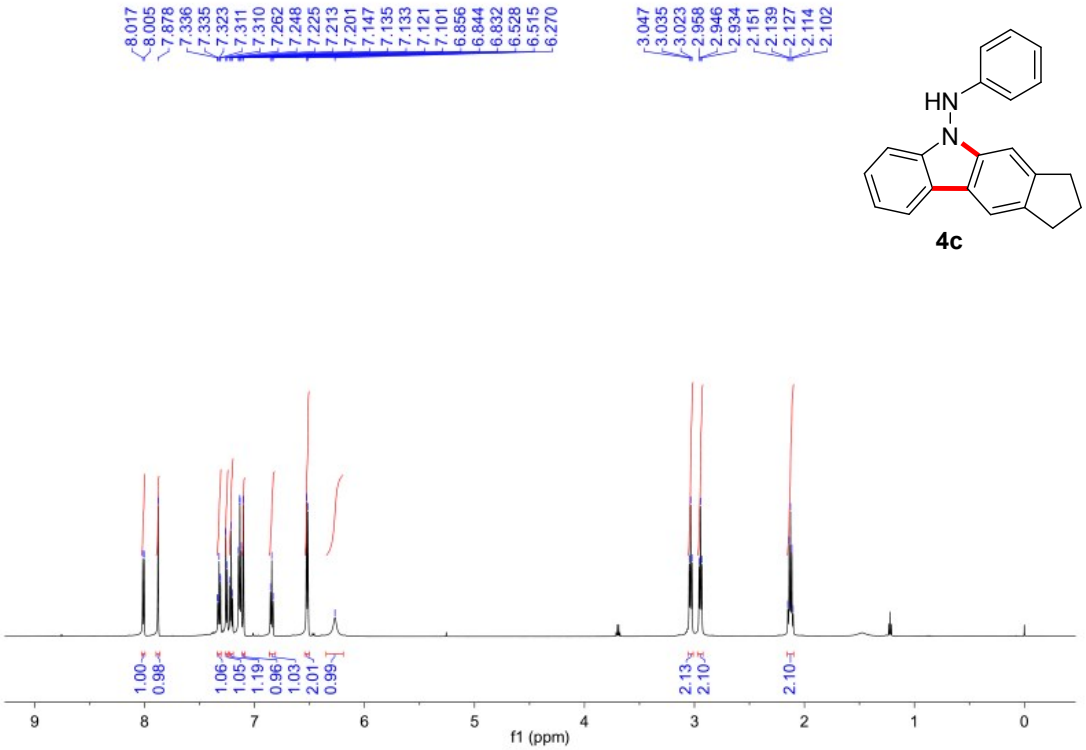


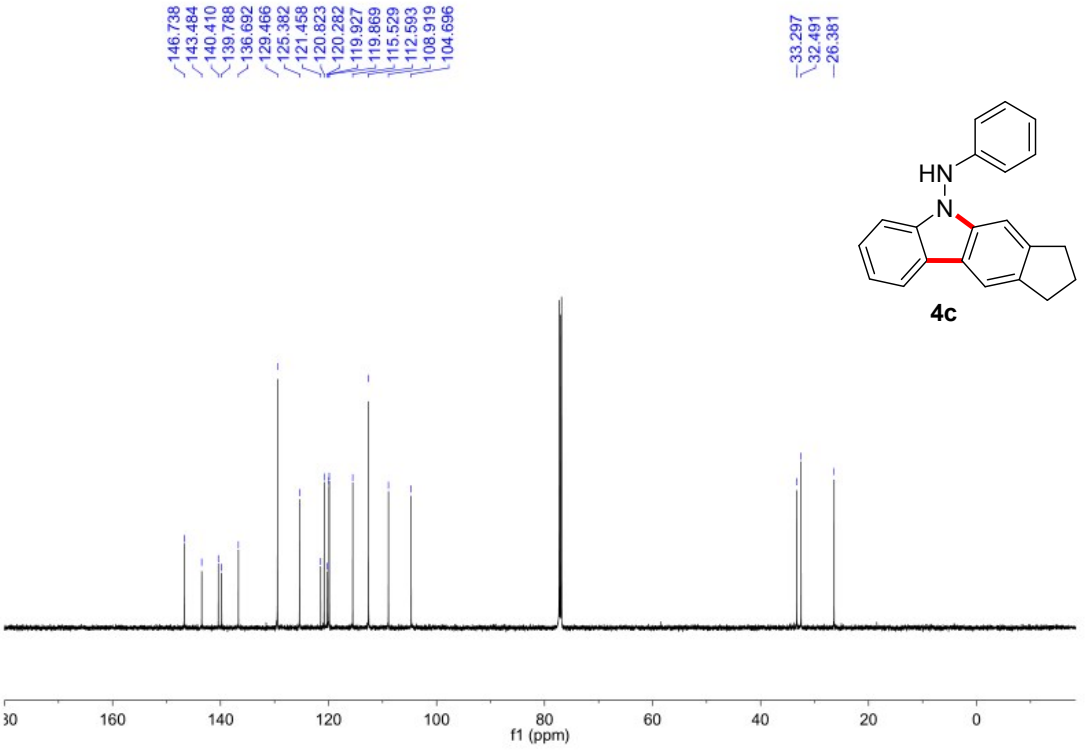
4b: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6



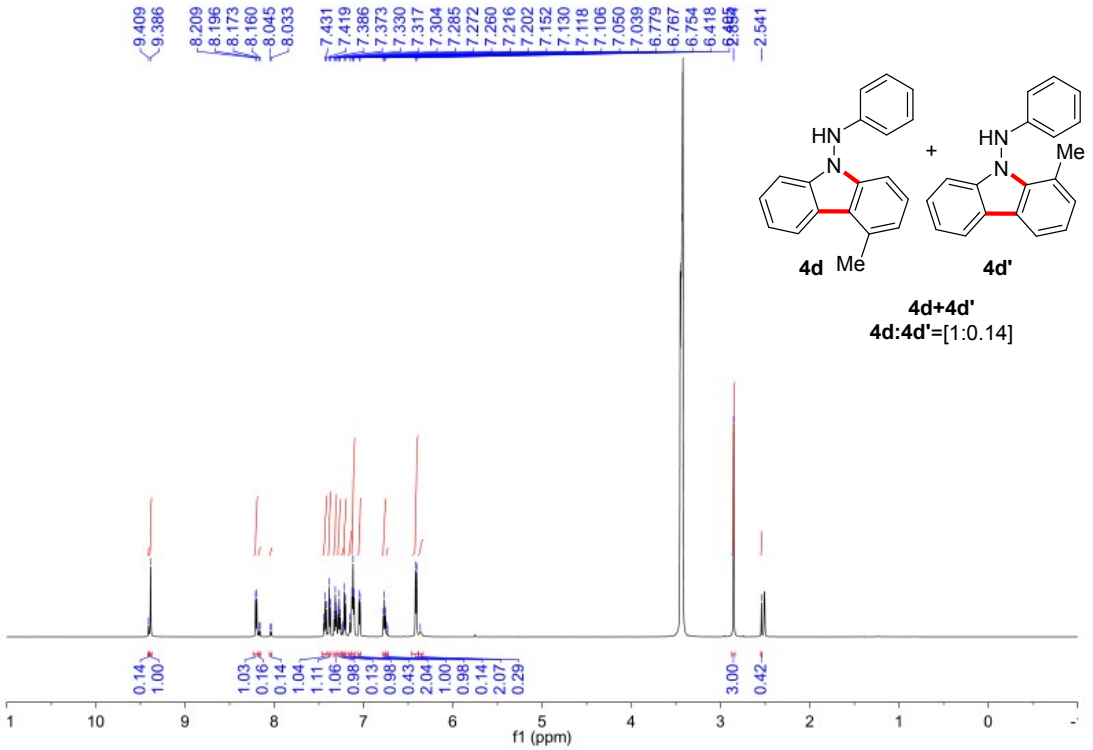


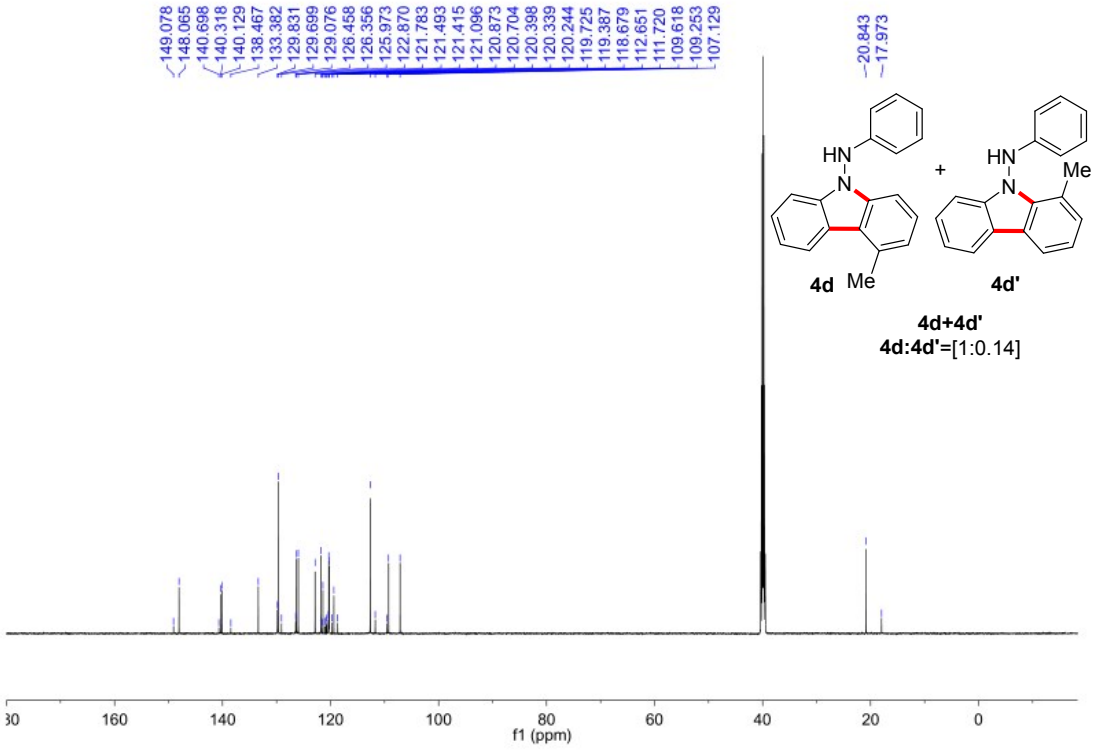
4c: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), $CDCl_3$



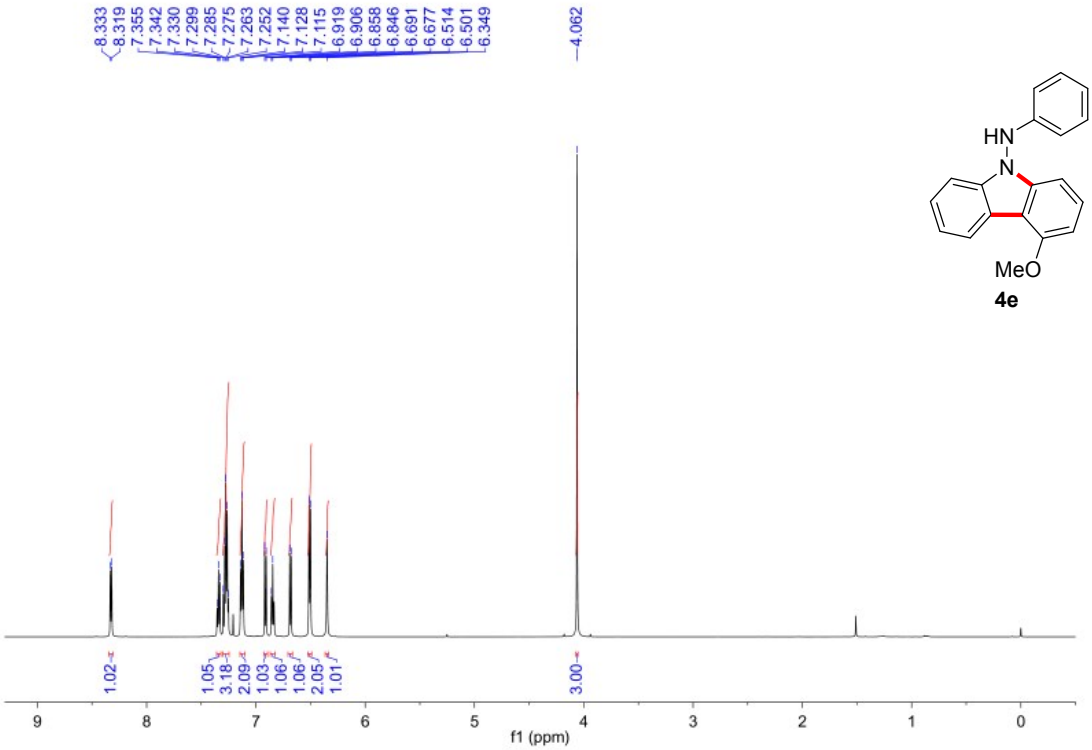


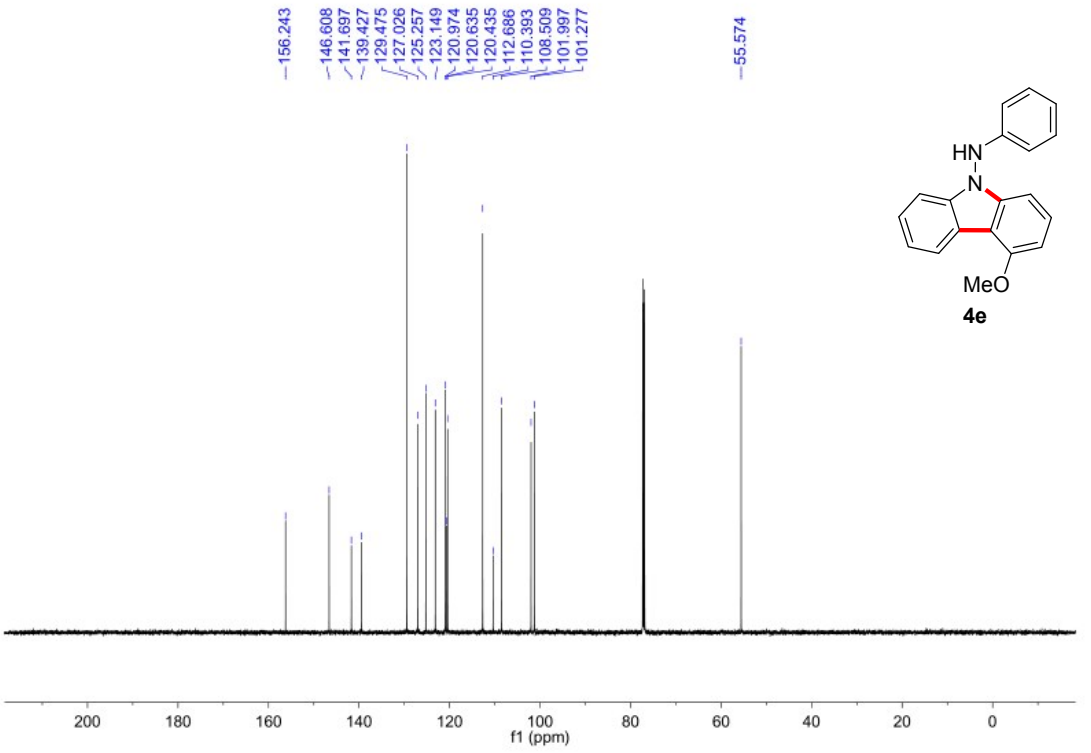
4d: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6



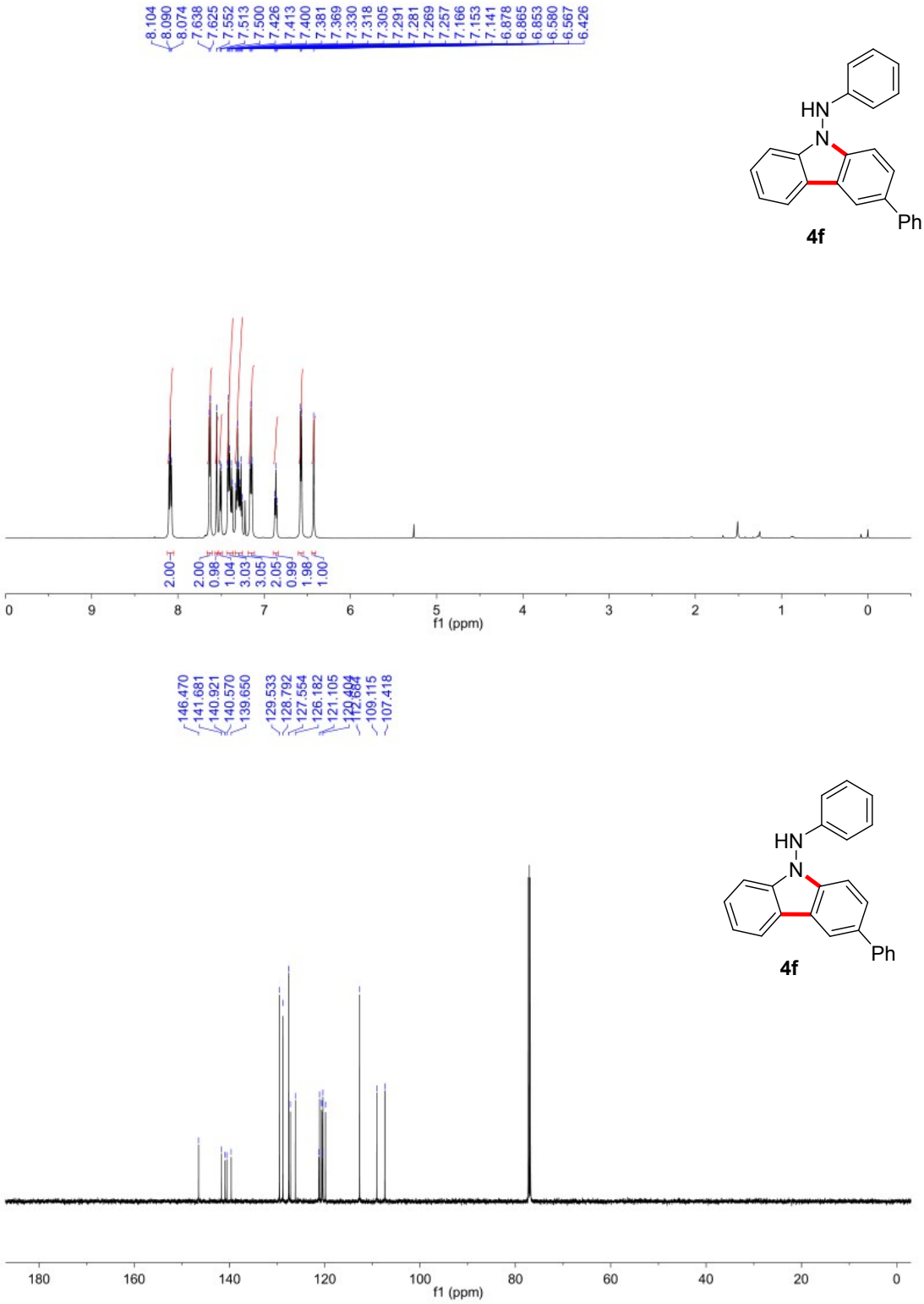


4e: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), $CDCl_3$

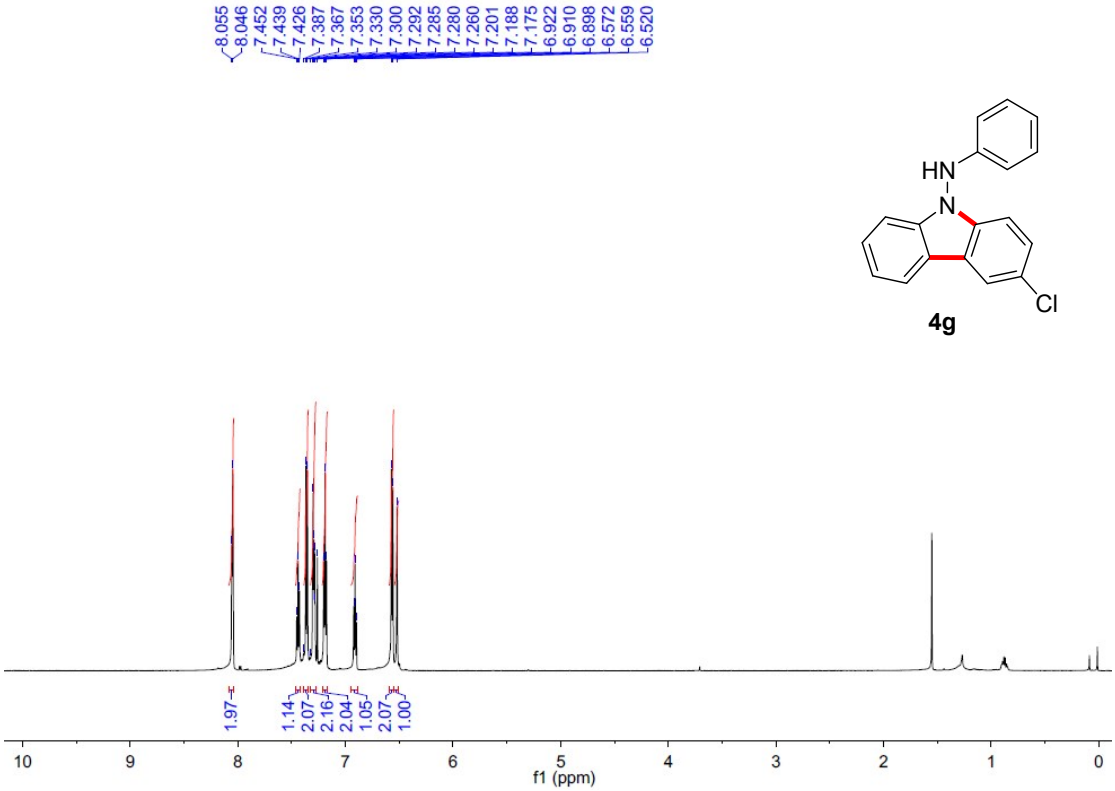


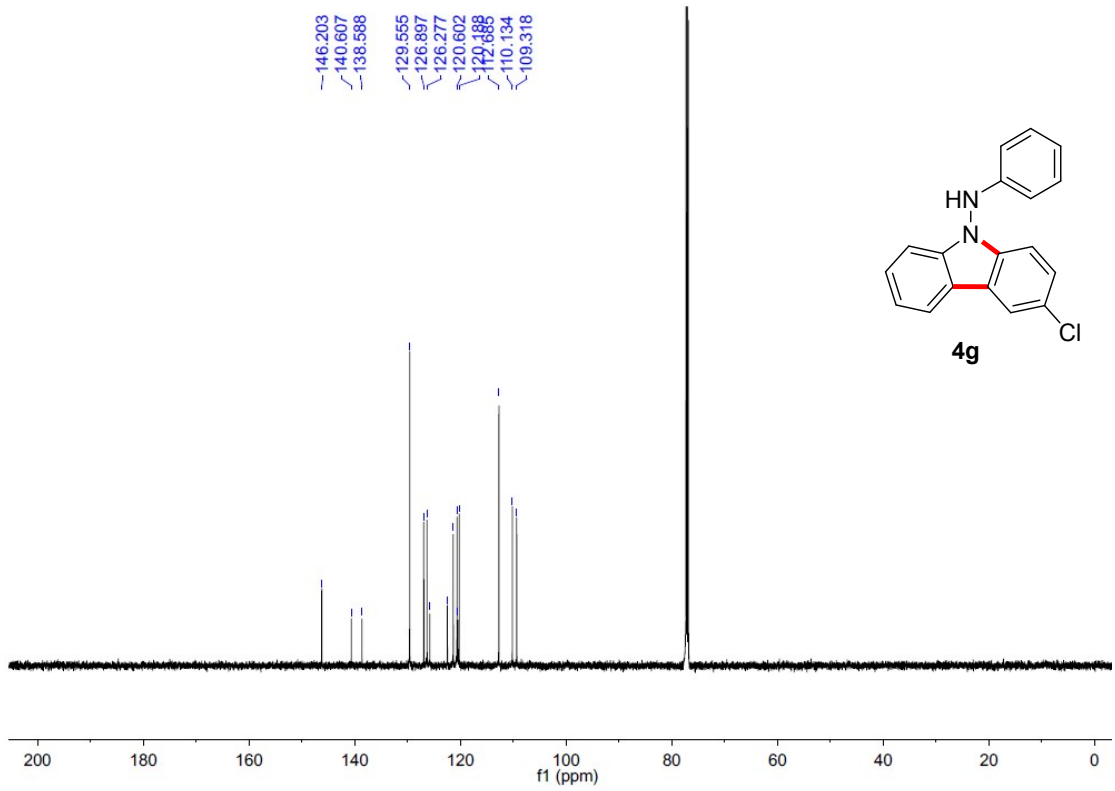


4f: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), $CDCl_3$

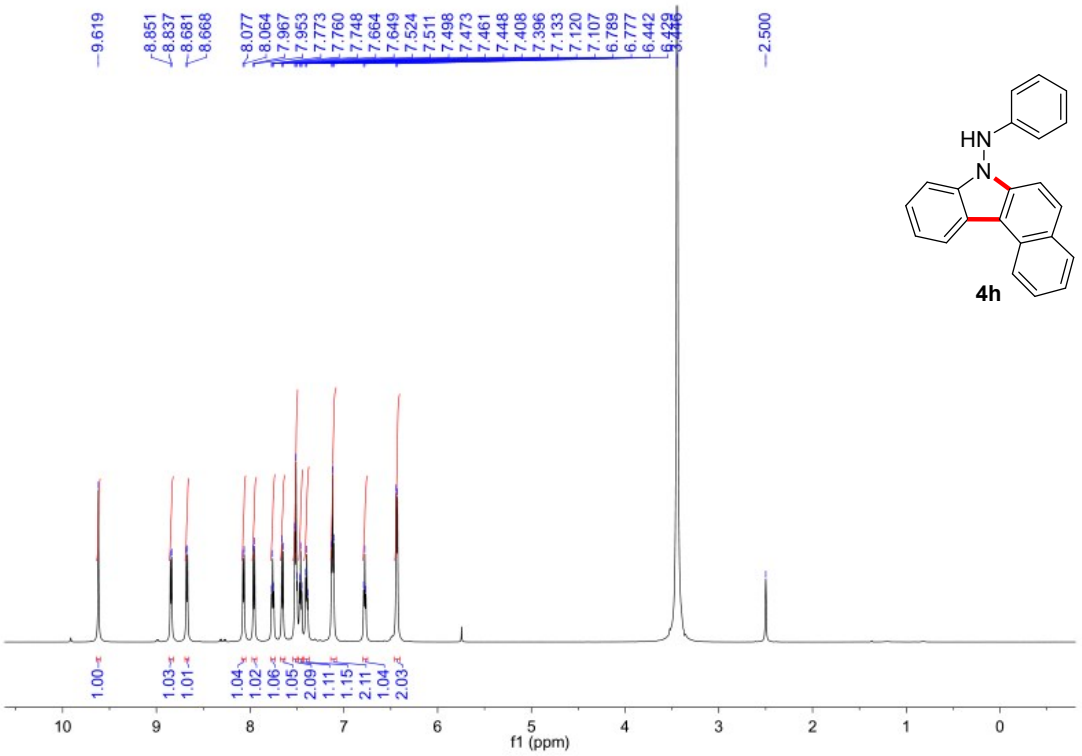


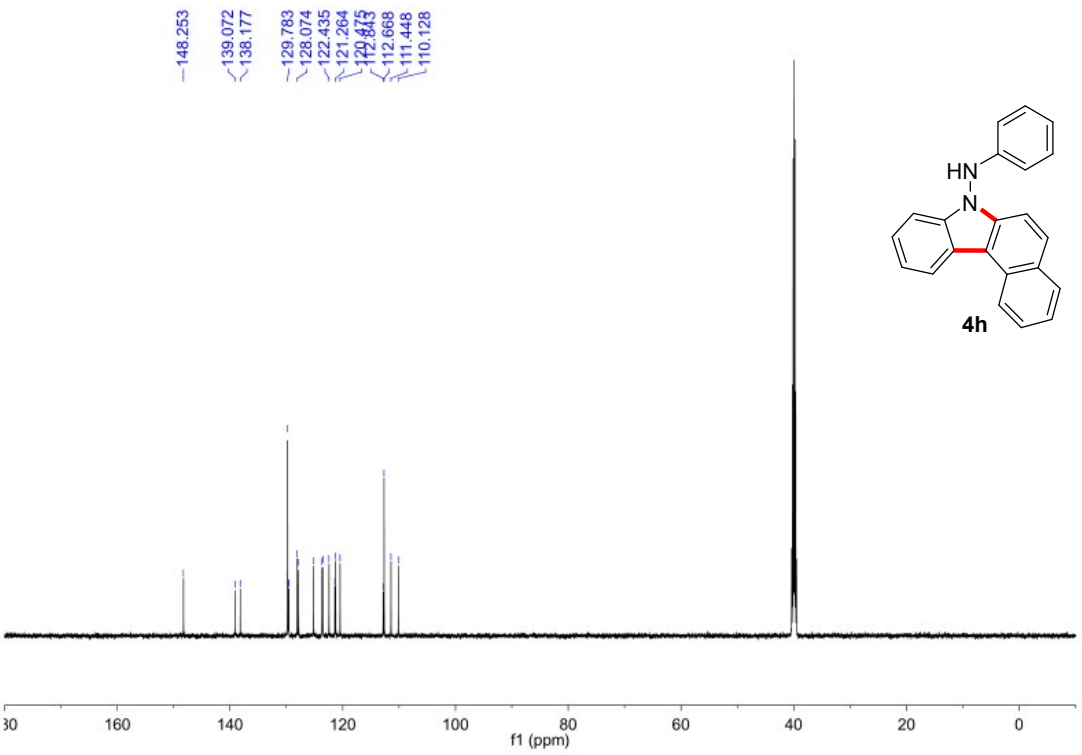
4g: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), $CDCl_3$



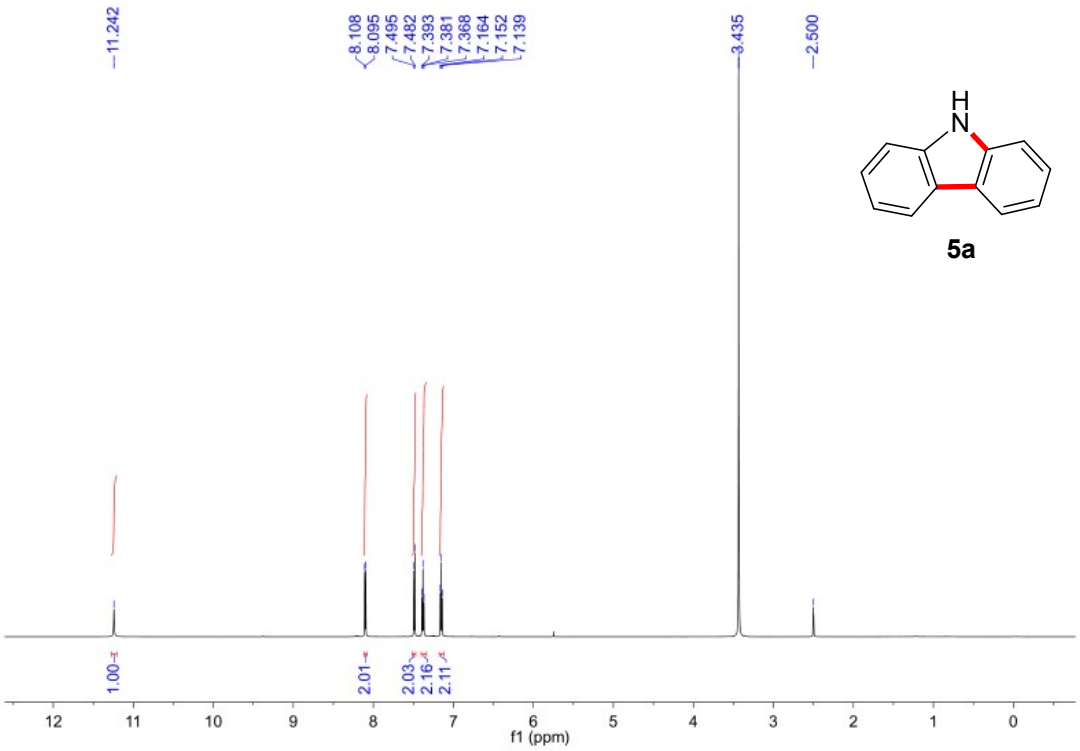


4h: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6

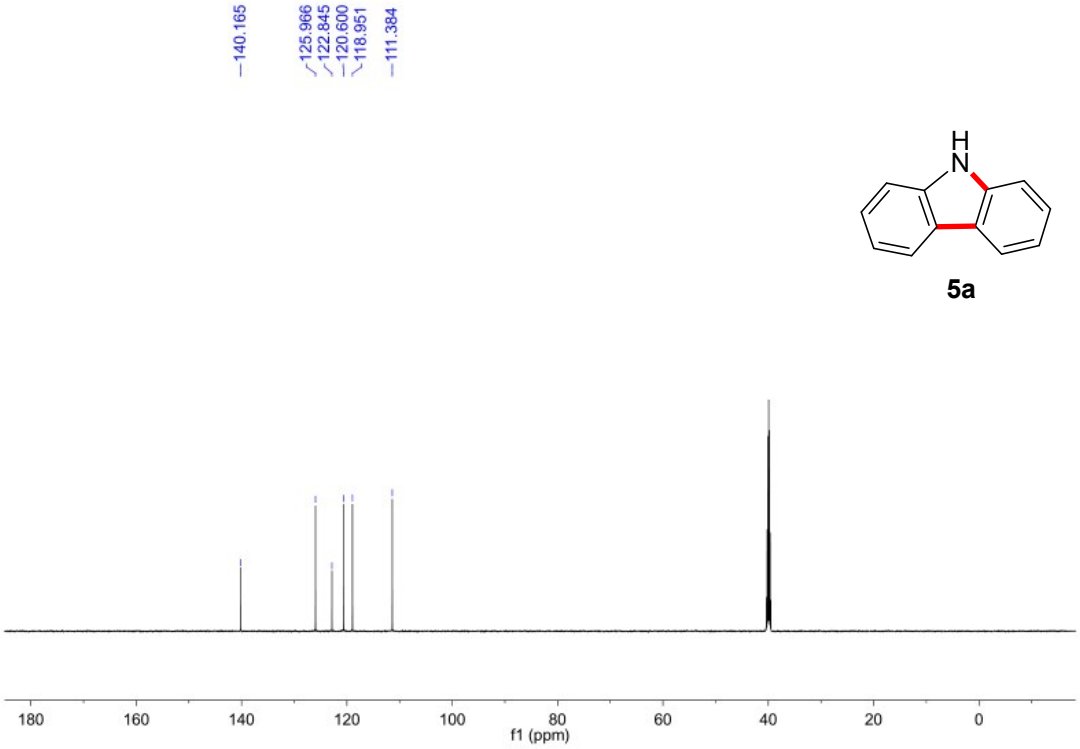




5a: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6

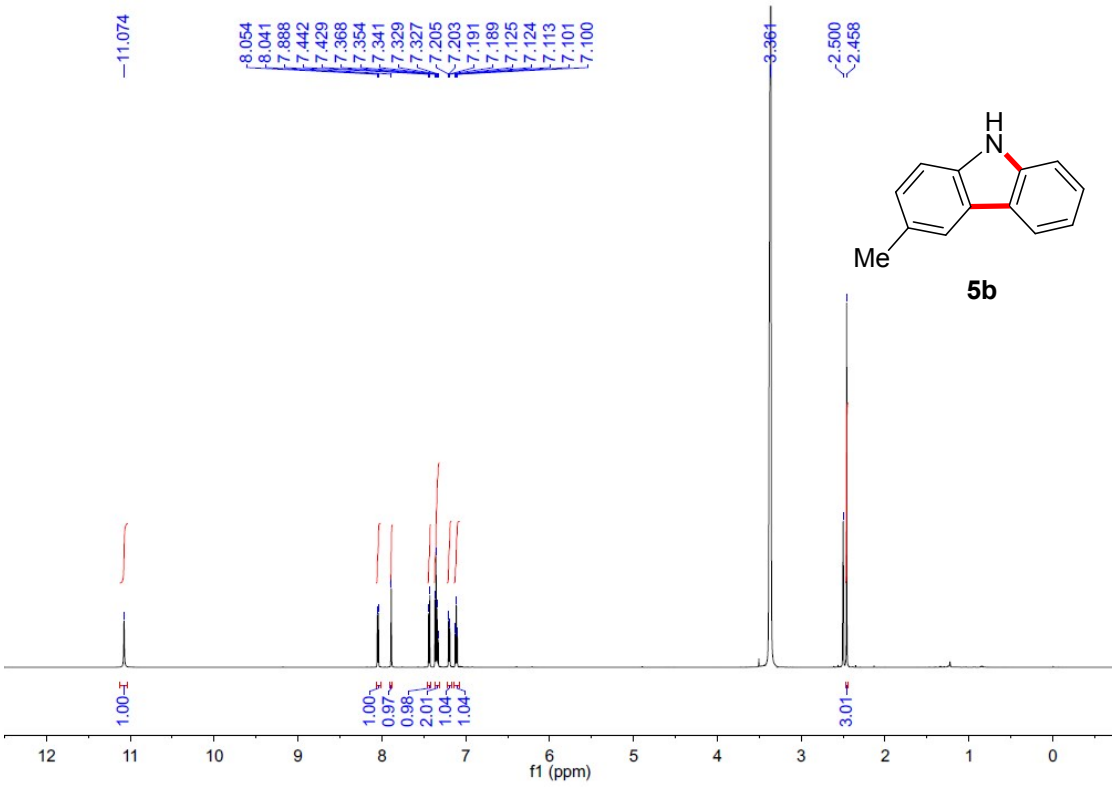


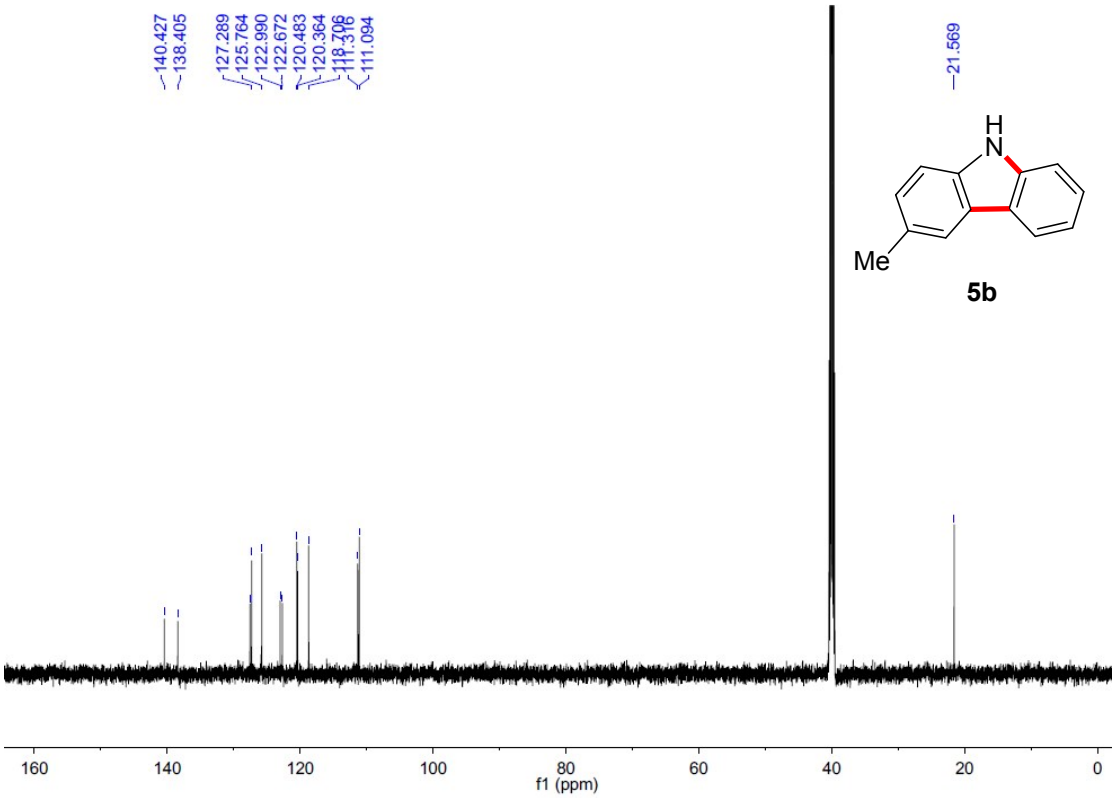
5a



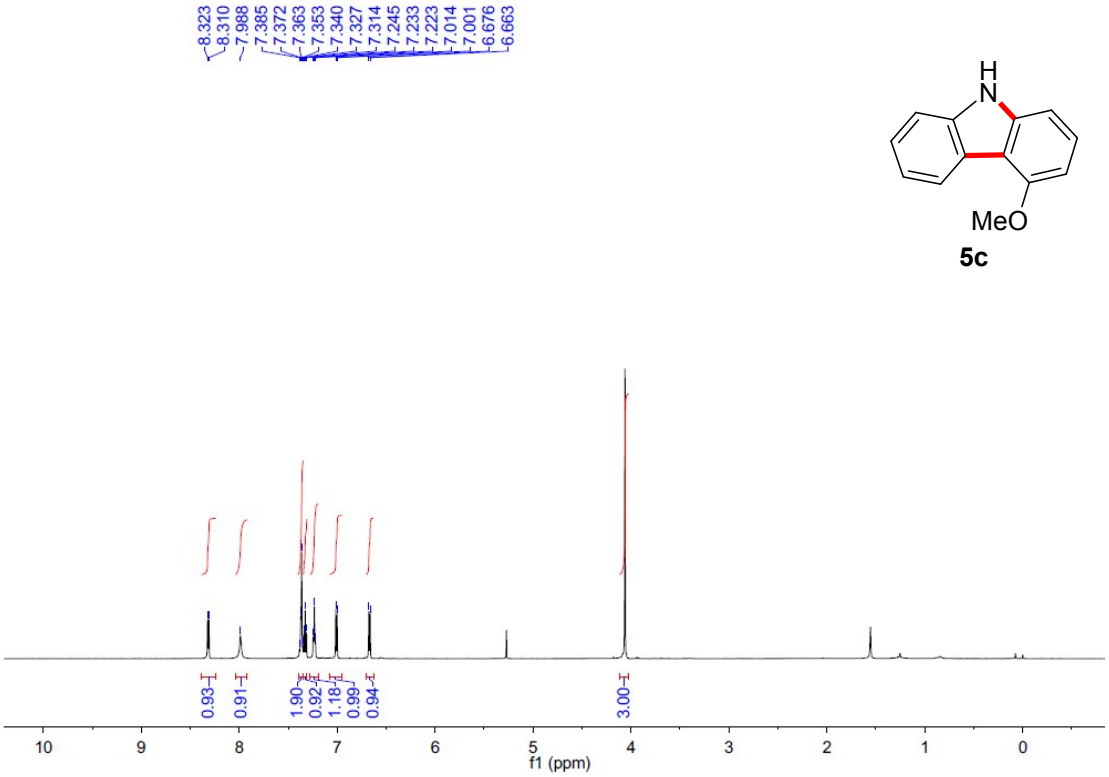
5a

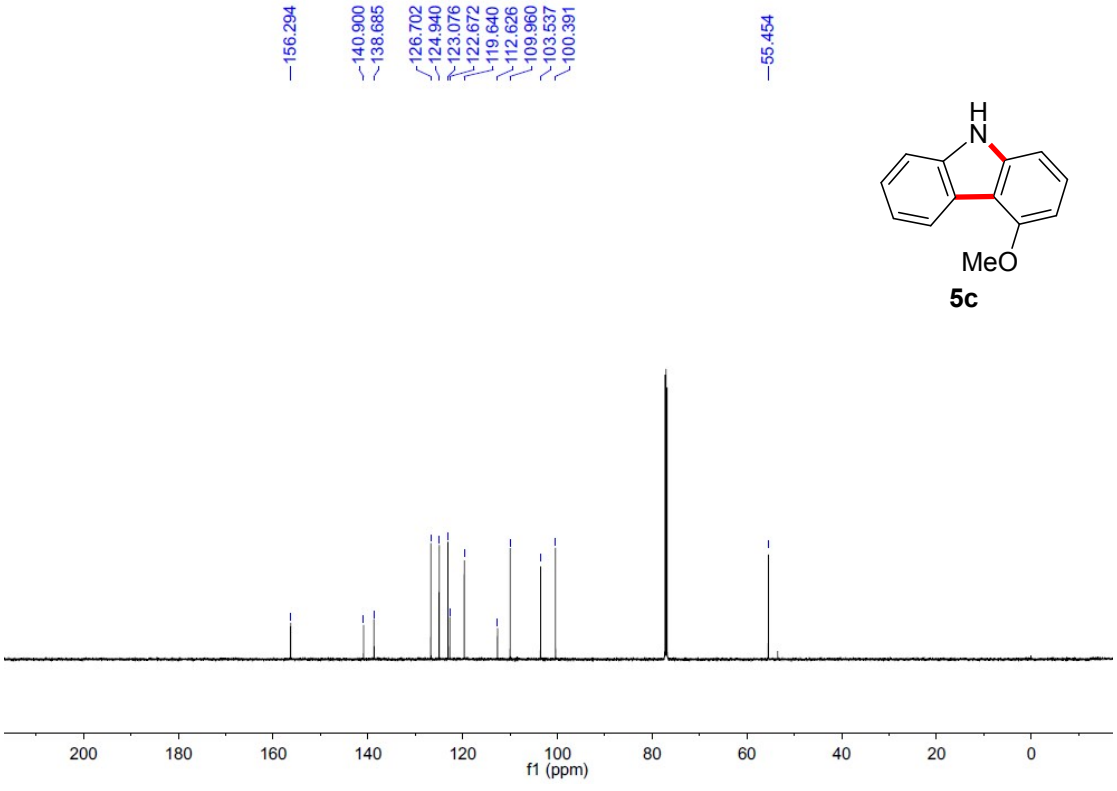
5b: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6



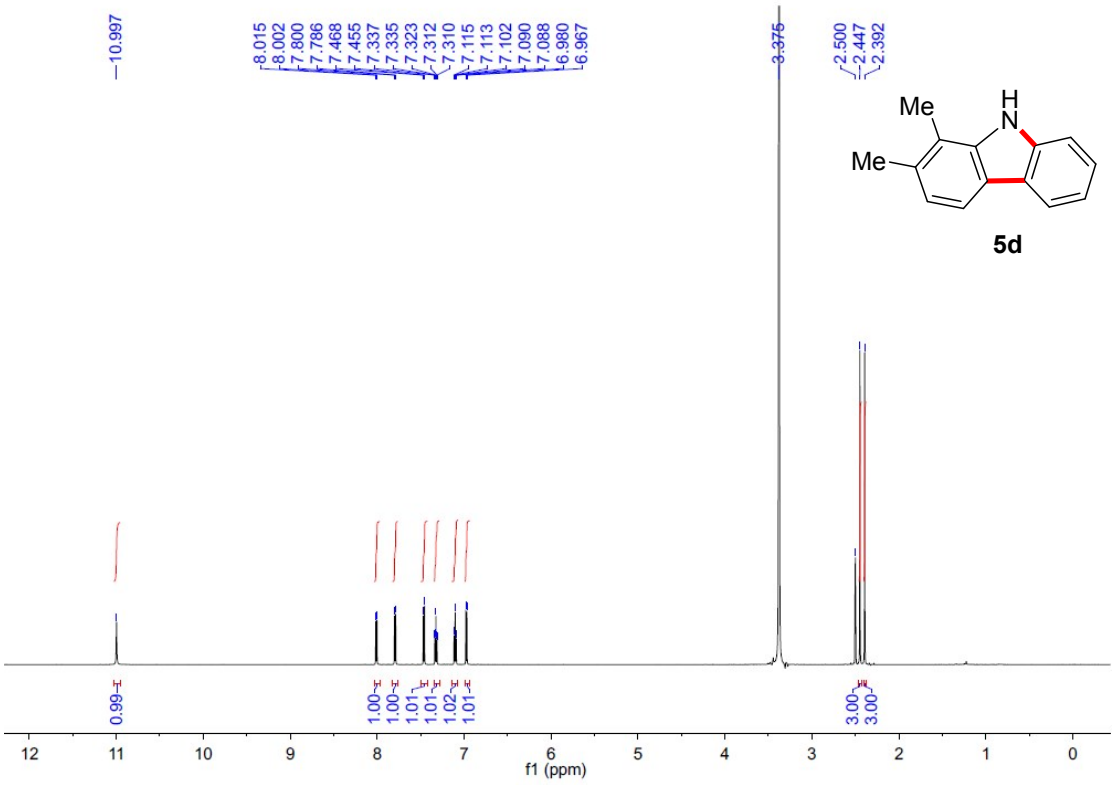


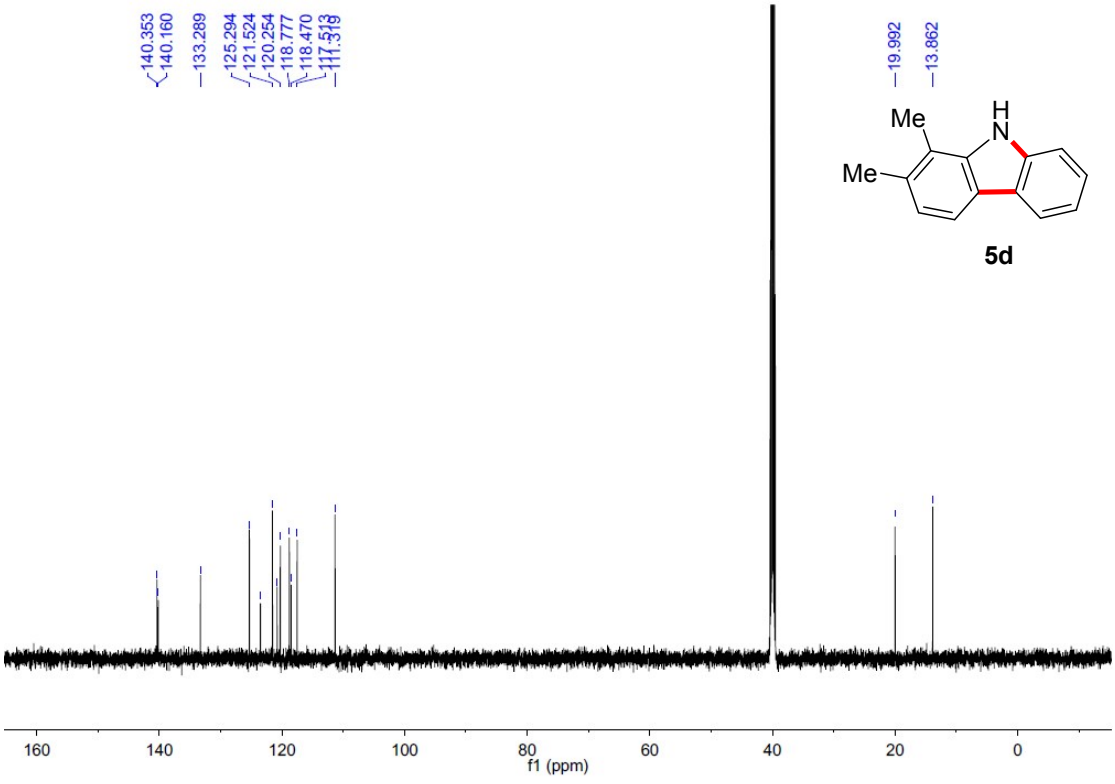
5c: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), $CDCl_3$



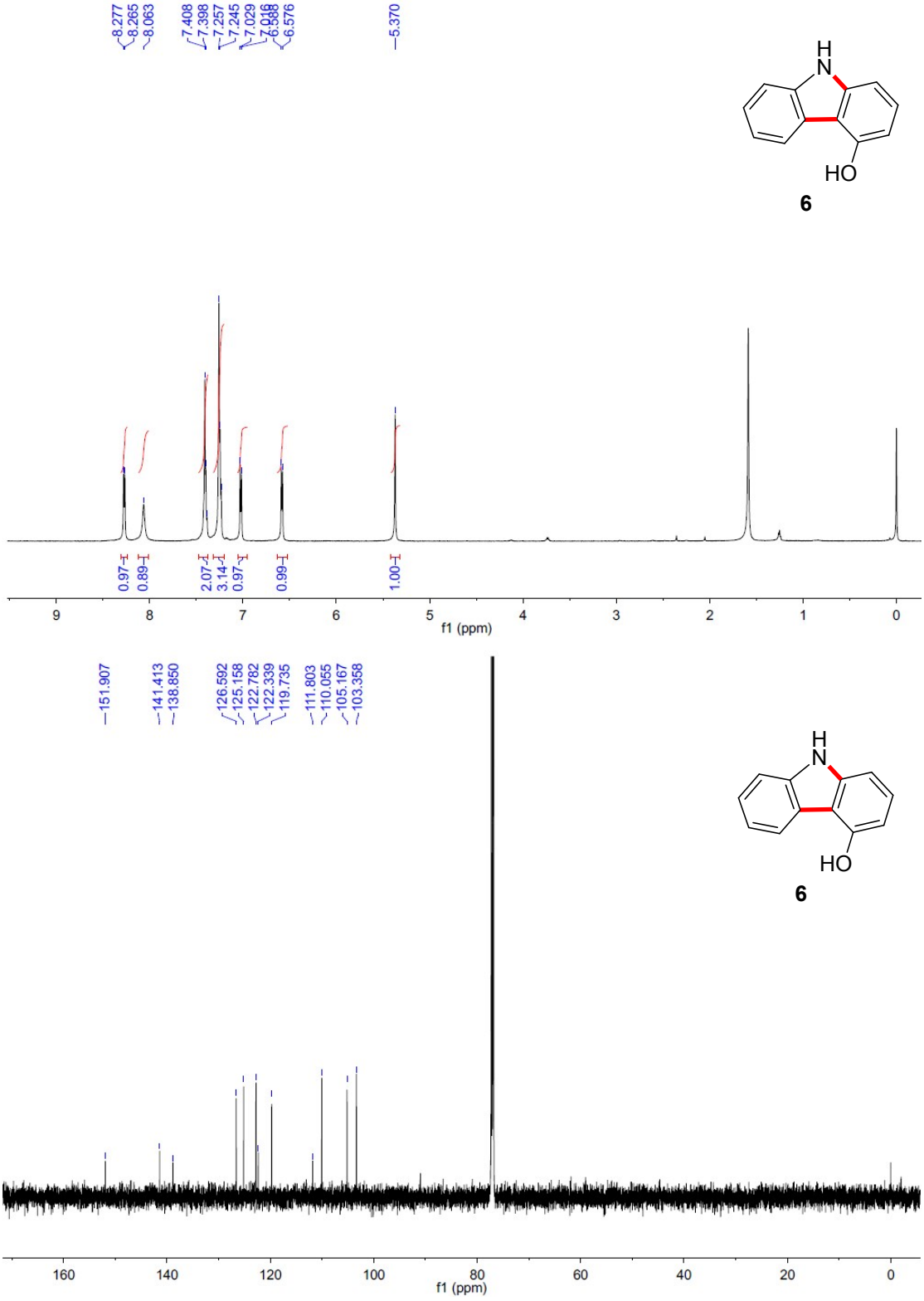


5d: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), DMSO-d_6

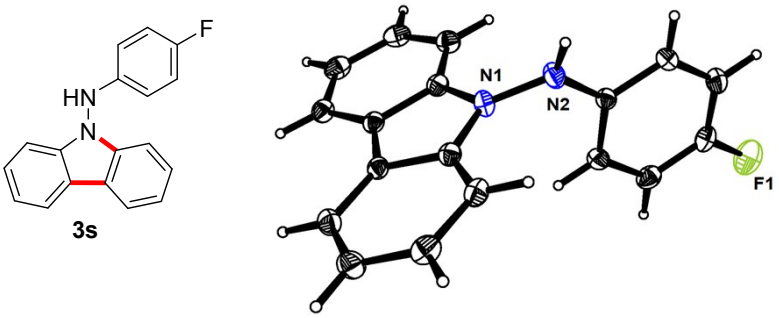


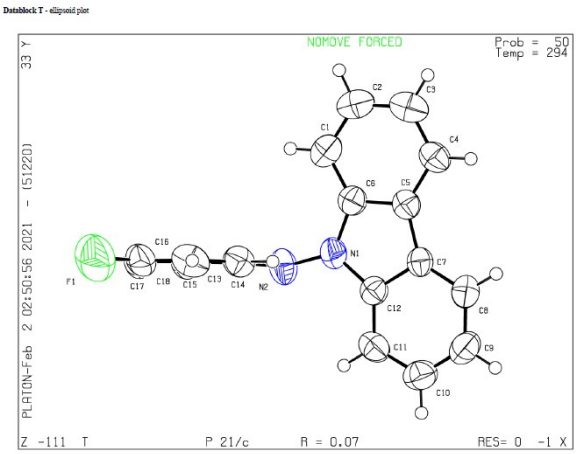


6: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), $CDCl_3$



9. Crystallographic data for 3s (CCDC: 2059983)





An ellipsoid plot (50% probability) view of the title compound.

The single crystal of **3s** was cultivated from the mixed solvents of ethyl acetate and petroleum ether with a volume ratio of 1:10 via solvent volatilization under air. Single-crystal X-ray diffraction data was collected at room Temperature on a SMART APEXII CCD X diffractometer.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) T

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: T

```
Bond precision:  C-C = 0.0044 A          Wavelength=0.71073

Cell:            a=11.661(2)     b=11.744(2)         c=10.481(2)
                 alpha=90        beta=102.40(3)      gamma=90
Temperature:     294 K

                Calculated                Reported
Volume          1401.9(5)                 1401.9(5)
Space group     P 21/c                    P 21/c
Hall group      -P 2ybc                   -P 2ybc
Moiety formula  C18 H13 F N2              C18 H13 F N2
Sum formula     C18 H13 F N2              C18 H13 F N2
Mr              276.30                    276.30
Dx,g cm-3       1.309                     1.309
Z               4                         4
Mu (mm-1)       0.087                     0.087
F000            576.0                     576.0
F000'           576.25
h,k,lmax        13,13,12                  13,13,12
Nref            2482                      2477
Tmin,Tmax       0.991,0.994               0.989,0.999
Tmin'           0.990

Correction method= # Reported T Limits: Tmin=0.989 Tmax=0.999
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 25.048

R(reflections)= 0.0669( 1702)     wR2(reflections)= 0.2282( 2477)

S = 1.053                 Npar= 191
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

10. DFT calculations

Computational methods: All the calculations were performed with the GAUSSIAN 16 programs.[1] The geometrical optimizations of the reactants, intermediates, transition states (TSs) and products were performed with the density functional exchange correlation (B3LYP) method,[2,3] including the empirical dispersion corrections developed by Grimme et al.[4,5], and the augmented correlation consistent basis set 6-311+G(d) for all nonmetal atoms.[6] Vibrational frequency calculations at the same level were performed to confirm stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency). In several cases where the TSs could not be easily confirmed by the animation of their vibrations, intrinsic reaction coordinate (IRC)[7,8] calculations were performed to establish the connection of each TS to its corresponding reactant and product. The relative energies of all optimized structures were refined by performing single-point energy calculations with the PCM solvation model[9,10] using acetonitrile as solvent.

Mechanistic studies are examined thoroughly with DFT calculation, the profile of the reaction pathway is depicted in Figure S2. Firstly, interaction of 2-(trimethylsilyl)phenyl triflates **2a** with CsF in situ generates the benzyne. Then azobenzene **1a** approaches to benzene by nucleophilic attacking via transition state $\mathbf{TS_{C\text{-}N}}$ with energy barrier of 19.1 kcal/mol, producing intermediate $\mathbf{I^1}$. Further, a sunlight irradiation results into the formation of intermediate $\mathbf{II^3}$ with the C1–C2 distance of 3.04 Å, herein, involving two steps: (1) intersystem crossing (ISC) between $\mathbf{I^1}$ and $\mathbf{I^3}$, and (2) the transformation from $\mathbf{I^3}$ to $\mathbf{II^3}$ through a rotation of benzene group. Next, a stable five-membered heterocycle carbazole is quickly obtained through the formation of C1–C2 bond via transition state $\mathbf{TS_{C\text{-}C}}$ with low energy barrier of only 9.0 kcal/mol. Finally, the H1 transfer from C to N is required for obtaining target product. However, we found that it is very difficult for a direct H1 transfer from C to N. As shown the direct H1 transfer transition state $\mathbf{TS'_{N\text{-}H}}$ (without H_2O) in Figure S3, its energy barrier is up to 61.2 kcal/mol due to high deformation cost. Here, an alternative stratagem is proposed to perform the H1 transfer from C to N with H_2O. We found that, with the assistance of one H_2O molecule, the energy barrier of the H1 transfer from C to N is observably decreased to be 20.1 kcal/mol.

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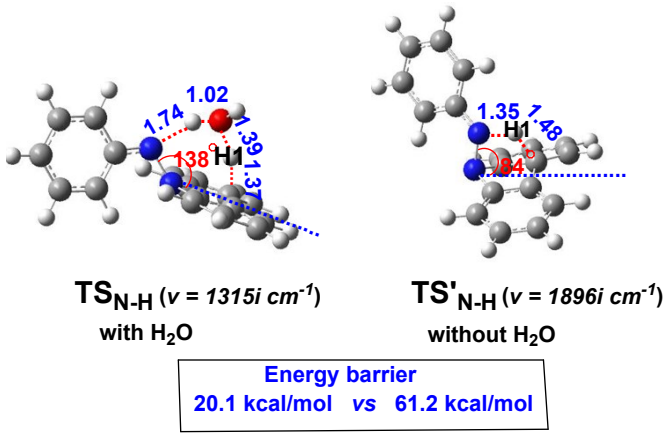


Figure S2. Comparison between two the transition states with H_2O and without H_2O

Atomic coordinates of key transition states and intermediates

TS$_{C-N}$ (v = 160i cm^{-1})

C	2.296548653095	-2.358826594022	-0.641669986485
C	1.563244054570	-1.460768656169	0.150129419117

C	2.219076846214	-0.660459238095	1.102225610510
C	3.601015197438	-0.742083603792	1.222926569663
C	4.335006963124	-1.603644936863	0.402370491795
C	3.681038800406	-2.410919807256	-0.530387927769
H	1.767713576523	-2.991984796087	-1.345115976053
H	1.645175551871	-0.009462261688	1.747782402182
H	4.109957753185	-0.137737131476	1.965956188374
H	5.413526763770	-1.658271984000	0.504282057410
H	4.248162458473	-3.089889042961	-1.157413462541
C	-3.904902646625	-1.780334967881	-0.623773006819
C	-4.703563176301	-0.827331662035	0.017239903607
C	-4.109859301115	0.218739034363	0.721856809317
C	-2.722176886462	0.322082159315	0.783587820899
C	-1.927160318390	-0.640903642860	0.151748478358
C	-2.520499781837	-1.696816149949	-0.556282248003
H	-4.366364086890	-2.588904957352	-1.180396782529
H	-5.784311616838	-0.900448657419	-0.038958615512
H	-4.725374373161	0.958964495757	1.220955186382
H	-2.251126089765	1.132850366398	1.323876583345
H	-1.895531463533	-2.429939969934	-1.049514089372
N	0.169445754311	-1.505901793408	-0.018500356896
N	-0.512389889130	-0.498644467621	0.274212787525
C	0.117053239964	1.461770617120	0.058018683826
C	0.155491045286	1.618136589369	-1.309783491983
C	0.537447564521	2.920811398706	-1.667998223663
C	0.817237099909	3.876746458965	-0.680615366199
C	0.725568831653	3.556644517594	0.680795114150
C	0.345257725162	2.247954742570	1.059524847595
H	-0.070132498073	0.859438242294	-2.049694116452
H	0.612609235389	3.178762461124	-2.719767466627
H	1.109018937408	4.879619669032	-0.981450480282
H	0.949177075847	4.324091568262	1.419793643128

I[1]

C	-2.2816017857	-2.473859155	-0.6885702851
C	-1.6672235806	-1.3241181829	-0.1513835491
C	-2.4628196514	-0.3399604665	0.4751907347
C	-3.8354926423	-0.517754778	0.5406445814
C	-4.4421925699	-1.637291178	-0.0420076986
C	-3.6624892288	-2.6139526271	-0.6610209212
H	-1.6515414336	-3.2379765736	-1.1283577325
H	-2.0150373742	0.5345227686	0.9218977312
H	-4.4445799227	0.2272366681	1.0402448426
H	-5.520073932	-1.7494714118	0.000533026

H	-4.1265953545	-3.4902935915	-1.0986757773
C	3.5929721907	-2.2649407329	0.8707124715
C	4.5786877411	-1.4338566528	0.3342153345
C	4.2184507732	-0.2601429685	-0.328586601
C	2.8784907334	0.092674013	-0.4561651832
C	1.9004969862	-0.7526588335	0.0753947066
C	2.2499345165	-1.9311270552	0.7423028746
H	3.8706379896	-3.1700946517	1.3989125478
H	5.6253202635	-1.6981156956	0.4378715244
H	4.9812057579	0.3833317828	-0.7520728676
H	2.5936185592	0.9950245549	-0.9802390285
H	1.4779987583	-2.5602578614	1.166274658
N	-0.2766056558	-1.3927575862	-0.2009010222
N	0.5064079307	-0.410295652	-0.0691515291
C	0.1472629899	1.0248065842	-0.1449286843
C	0.5108955497	1.8011176725	0.9652323341
C	0.1955234116	3.1539848141	0.9316795599
C	-0.4220729389	3.6748561059	-0.2126719472
C	-0.7182516913	2.8438246731	-1.2983357671
C	-0.4683560316	1.4496070589	-1.3231917185
H	1.0053467591	1.3680463627	1.8302199565
H	0.4338710026	3.7927701711	1.7757258317
H	-0.6640589417	4.7348354661	-0.2524895072
H	-1.176251078	3.3162318582	-2.1690411957

I^3

C	-2.5721070624	-1.839563913	-1.0137451492
C	-1.6797686331	-1.1036950865	-0.2011330346
C	-2.2103860246	-0.3926119552	0.9013564774
C	-3.5764205546	-0.4119407909	1.1564747491
C	-4.4512167481	-1.1202735874	0.3278456469
C	-3.9365964715	-1.8360274503	-0.7576916315
H	-2.1668521565	-2.4035025746	-1.8471842037
H	-1.549371882	0.145801735	1.5690593671
H	-3.9628393051	0.1276530428	2.015486289
H	-5.5164877269	-1.123554005	0.5320436696
H	-4.6034592033	-2.3989242981	-1.4029315207
C	3.4641973698	-2.3756298953	0.7334162806
C	4.5190622679	-1.5850944764	0.2748888427
C	4.2452865143	-0.3486557588	-0.311329818
C	2.9331353716	0.0991191127	-0.4409956623
C	1.8775960637	-0.6926477851	0.028846865
C	2.1491478293	-1.9349979465	0.6158948564

H	3.6643998625	-3.3373394643	1.194054953
H	5.5431403461	-1.9290016536	0.3721263054
H	5.0558063869	0.2690713793	-0.6835145548
H	2.7328871316	1.0515177628	-0.9160149707
H	1.3285673057	-2.5413155203	0.978344457
N	-0.3336794317	-1.2477730529	-0.4980136584
N	0.5198123443	-0.2779510557	-0.1037841143
C	0.189992681	1.1091863964	-0.145631677
C	0.7392626149	2.0271047102	0.7683820508
C	0.3917985386	3.3743160811	0.7011378277
C	-0.5133326802	3.8396698833	-0.2557758771
C	-1.0852568069	2.9367477158	-1.1664565148
C	-0.6977698992	1.6250725136	-1.0705327615
H	1.4285807047	1.6776717252	1.5296772685
H	0.8256172445	4.0669871811	1.414064321
H	-0.7805582392	4.8904169847	-0.2967037996
H	-1.7948587522	3.2737520459	-1.915445279

II[3]

C	-2.4842332807	-2.0891654147	0.8415862338
C	-1.6386218579	-1.2382901942	0.0927957042
C	-2.2118814471	-0.482332855	-0.9563632134
C	-3.5738628567	-0.5715867817	-1.2220117217
C	-4.4027632476	-1.3956973614	-0.4564795971
C	-3.8449440305	-2.156012636	0.5764889496
H	-2.0450169954	-2.685181824	1.6345464717
H	-1.5882297746	0.1457294945	-1.5788948216
H	-3.9923470016	0.0052436031	-2.0408968466
H	-5.4649572993	-1.4529799541	-0.6685472021
H	-4.4748889742	-2.8083384175	1.1727885247
C	0.1034280635	3.3285404728	-0.785164928
C	-0.5968048316	3.7835702007	0.3326254834
C	-0.9332407584	2.8898468803	1.3503080591
C	-0.5716180249	1.5479507881	1.2567602632
C	0.1247671022	1.0981571621	0.1330716958
C	0.4623498947	1.9864659367	-0.890987594
H	0.3626501944	4.0155602311	-1.5835391028
H	-0.8790720225	4.8279863927	0.4101865476
H	-1.4707883364	3.2382257178	2.2257664482
H	-0.8211898212	0.8536468103	2.0504644247
H	0.9857199882	1.6267170667	-1.7693405082
N	-0.2917963868	-1.3088926457	0.4075656815
N	0.5120654235	-0.2888325304	0.042398444

C	1.8863527242	-0.5906545525	-0.0486954479
C	2.3472929224	-1.9070149595	-0.2544978183
C	3.714404362	-2.1619339509	-0.3298683947
C	4.6552249008	-1.1347006712	-0.2183898176
C	4.2153790211	0.1851475129	-0.0233353372
C	2.8625420524	0.3877381373	0.0592191087
H	1.6254265362	-2.7080342105	-0.3533830049
H	4.0499242725	-3.1813647352	-0.4883851466
H	5.7170405268	-1.3474531008	-0.2849573473
H	4.9243599626	1.0023413885	0.0662858098

$TS_{C\text{-}C}$ (ν = 384i cm^{-1})

C	3.061992236744	-1.524021020325	0.831729536053
C	2.036983993380	-0.904376189805	0.077775193992
C	2.411033432760	-0.054385424482	-0.990598526294
C	3.754138251508	0.176781271848	-1.264363501501
C	4.755965223790	-0.417265324103	-0.492031025674
C	4.397930500586	-1.272841296025	0.556034252218
H	2.778045441065	-2.192016976375	1.637955561979
H	1.652226824975	0.391093454959	-1.621746496887
H	4.022936504102	0.820361498067	-2.096102882615
H	5.801030612336	-0.227950122879	-0.712225641451
H	5.167311424990	-1.749186140326	1.155136173949
C	0.019453192701	3.051904550989	1.187543353434
C	-0.965539636350	3.648139111485	0.391656056135
C	-1.596411443336	2.918476330185	-0.607355898130
C	-1.282863140589	1.549696861635	-0.804564101688
C	-0.282291978747	0.967302025299	0.028464990131
C	0.345739119896	1.698363993143	1.020373116852
H	0.521017527026	3.628981462973	1.956487557890
H	-1.214643203488	4.694091972476	0.536386551988
H	-2.314731369244	3.395366099458	-1.265089959634
H	-1.463768328582	1.123571802661	-1.786035262834
H	1.057584524029	1.221637159298	1.683468555558
N	0.745017985531	-1.259689255276	0.411800699928
N	-0.249915979002	-0.469883411616	-0.024568778577
C	-1.567906829218	-0.990984607809	-0.018819898012
C	-1.900131128999	-2.337826278590	0.166252284613
C	-3.248993882241	-2.698573790489	0.137094031721
C	-4.252304117159	-1.750160330746	-0.079070486520
C	-3.913321123941	-0.399052188473	-0.273237354730
C	-2.581225060096	-0.062438928197	-0.224996503431
H	-1.124568821176	-3.075681614865	0.330767732877

H	-3.518899081330	-3.739463552279	0.282101797980
H	-5.293966398790	-2.054275872828	-0.103568735725
H	-4.685684273131	0.343535731011	-0.450504393595

III

C	-3.5174198276	-0.0361537315	0.7587779375
C	-2.2030172328	-0.0938110743	0.2306591589
C	-1.9809305539	0.5309258863	-1.0209619385
C	-3.0119358977	1.1950728517	-1.6824095388
C	-4.2969237207	1.2558411802	-1.1407890116
C	-4.5359418292	0.624637897	0.0864770668
H	-3.71219474	-0.5216008614	1.7104249519
H	-1.0012039791	0.4814142175	-1.483777456
H	-2.8065596512	1.6632481767	-2.6412178234
H	-5.0949165185	1.7731040041	-1.6627994866
H	-5.5297875602	0.6518379896	0.5244888115
C	1.5467436816	-3.6854873391	-0.6142745051
C	2.8357148007	-3.1111537009	-0.959258967
C	3.1930936694	-1.8756878145	-0.5550035619
C	2.2952023538	-1.1289683632	0.3863073092
C	0.8810288767	-1.619673876	0.3575774825
C	0.5751114941	-2.9629977964	0.0163430422
H	1.3321492366	-4.6983981289	-0.9369084573
H	3.5127222904	-3.7005460161	-1.5683212697
H	4.1644243421	-1.4572720249	-0.7938670893
H	2.6886852129	-1.3861183194	1.394655656
H	-0.4240596557	-3.3512230036	0.1661557685
N	-1.273524746	-0.8258026769	0.9447193023
N	0.0262163602	-0.6277686054	0.6005026857
C	0.2686436229	1.8865411002	0.9490341774
C	0.7562272288	0.6187116913	0.6618669931
C	2.1129864097	0.3692262215	0.4409372146
C	3.0239401717	1.416130648	0.4641723013
C	2.5464198355	2.7091697166	0.6981564187
C	1.189543829	2.9358376307	0.9520190637
H	-0.7784639819	2.0580003507	1.1585029217
H	4.0833253461	1.2401368239	0.3108308897
H	3.2382948866	3.544298027	0.6982318222
H	0.8436321459	3.9430583193	1.1569122301

$TS_{N\text{-}H}$ (ν = 1315i cm^{-1})

C	2.605933143934	-0.221521361828	-1.124245581833
C	2.219720376422	-0.514629409772	0.208239091525
C	3.261869345412	-0.794703000128	1.132964460654

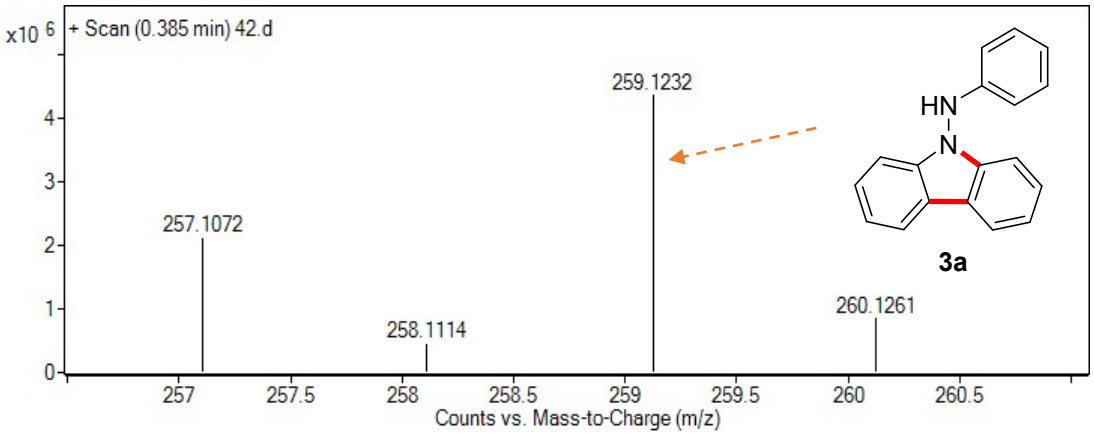
C	4.594175078347	-0.774596461784	0.745490734667
C	4.961658000228	-0.477040816467	-0.573717187700
C	3.948879346206	-0.204245766961	-1.495374105277
H	1.840545516311	-0.016362244311	-1.865127902365
H	2.994845199945	-1.026210816693	2.160254628708
H	5.361264322270	-0.993352027604	1.483723477600
H	6.004917046588	-0.461407204995	-0.870808465386
H	4.204743686229	0.024590874226	-2.526770961178
C	-2.464789384024	-2.981845107435	-0.394697305215
C	-3.672186919805	-2.223860134705	-0.360643713345
C	-3.644285390530	-0.856870623468	-0.271078603303
C	-2.370301683161	-0.204553908298	-0.138374251268
C	-1.168007420888	-0.987139635716	-0.331681814963
C	-1.219248200326	-2.389666088993	-0.368602539789
H	-2.532570085653	-4.062773950700	-0.455741911706
H	-4.620975289764	-2.745365722093	-0.415211808782
H	-4.560516396286	-0.277108723815	-0.259649688853
H	-2.011177766536	-0.306174329268	1.177675223171
H	-0.308220897505	-2.973238411271	-0.415238156379
N	0.930927298367	-0.571842288972	0.670849021085
N	-0.074814771428	-0.172709005140	-0.252790964745
C	-0.531227229117	1.173885511265	-0.291294529049
C	0.225119153385	2.341826476497	-0.272517796830
C	-0.464274307210	3.552931825126	-0.314314941958
C	-1.866202668436	3.593175519249	-0.354295756221
C	-2.616069647781	2.417973335575	-0.326703187958
C	-1.938115681831	1.201140295769	-0.291781040199
H	1.307124708493	2.310602881944	-0.237246917456
H	0.095789232658	4.482026939330	-0.319303325232
H	-2.372164454771	4.551589672396	-0.398172702317
H	-3.700351889430	2.454883356212	-0.330199090178
O	-1.189565182534	-0.384462083329	2.295555265376
H	-0.225021925825	-0.469667852815	1.967819440891
H	-1.259796781956	0.387581208972	2.872859785805

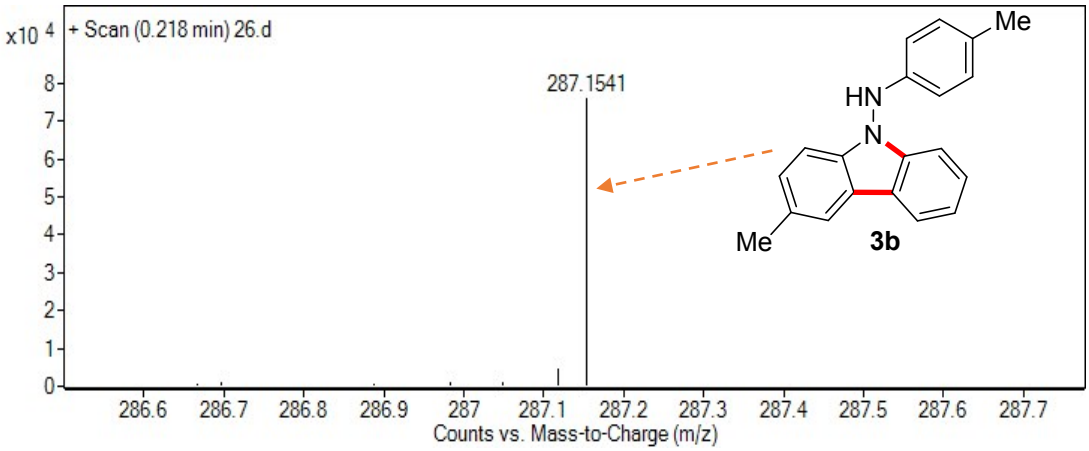
TS'$_{\mathbf{N\text{-}H}}$ (ν = 1896i cm^{-1})

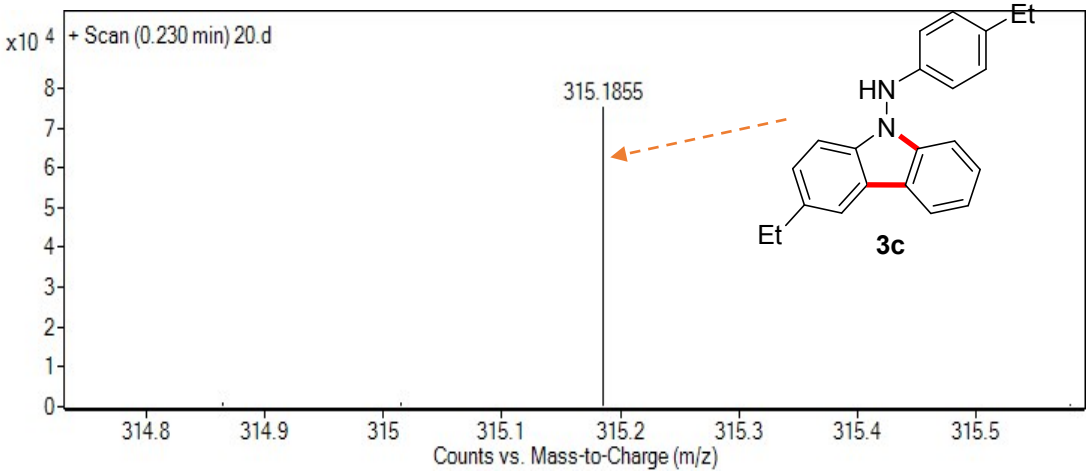
C	2.683028522136	0.368357824154	-0.966625582451
C	1.961626025330	0.453626591724	0.249466116558
C	2.671493421429	0.405151281077	1.477072857643
C	4.049250036790	0.265877915493	1.480866517231
C	4.755021783873	0.181615543628	0.274173900465
C	4.063156202354	0.238137979333	-0.941753086450
H	2.146498910568	0.425506622591	-1.904090008682
H	2.116666410008	0.477383061517	2.406220385914

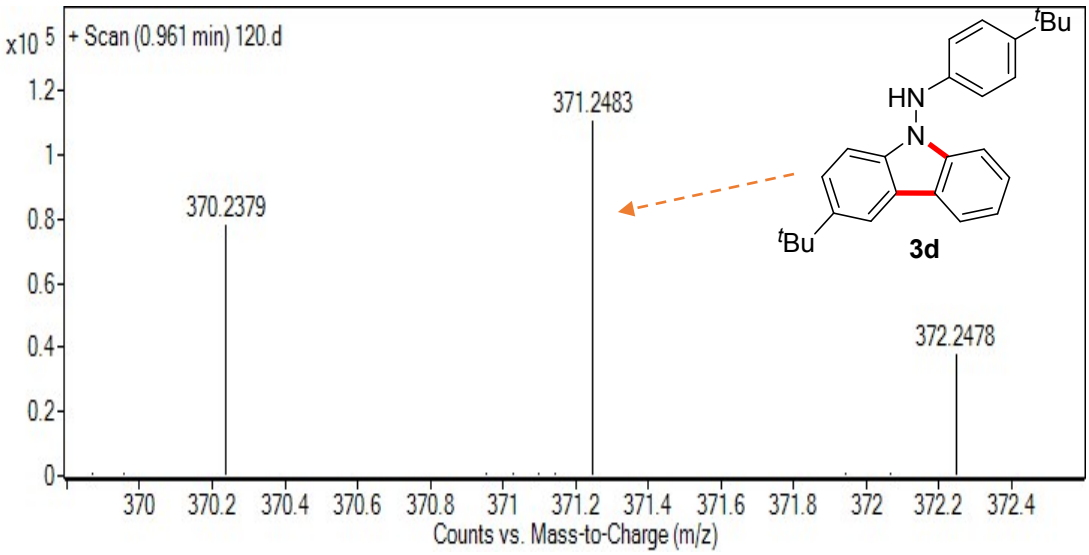
H	4.582157233296	0.226194634552	2.424839994740
H	5.834515820130	0.078724141139	0.281346957534
H	4.610690389292	0.183359979991	-1.876824187736
C	-0.542180245130	-3.279084096082	-0.798936735786
C	-1.399038727892	-3.305032941844	0.348876263520
C	-1.842970436851	-2.169188450609	0.973340971222
C	-1.408185667365	-0.873170996779	0.463367585043
C	-0.562945583548	-0.902978381330	-0.763469989077
C	-0.109097305005	-2.047347446444	-1.346166411429
H	-0.234182950490	-4.211386403641	-1.257014998209
H	-1.711876156411	-4.272909672524	0.730379044595
H	-2.501190405779	-2.230923314088	1.833830545797
H	-0.234796475141	-0.164131825281	1.020028977100
H	0.558046259880	-2.018485468660	-2.201386609257
N	0.606789556980	0.629948702441	0.326993396808
N	-0.163618805947	0.483761029404	-0.928246657270
C	-1.388616364699	1.191910583518	-0.553120990503
C	-1.750318669412	2.481622271370	-0.888780666403
C	-2.937753331065	2.982008144940	-0.339471705181
C	-3.704243454792	2.201751298806	0.537685259035
C	-3.320363308055	0.905621632498	0.888668554768
C	-2.151723215858	0.385162258306	0.327159154357
H	-1.140952565851	3.079726672879	-1.557602405811
H	-3.267907680490	3.982923470931	-0.595186242384
H	-4.620493041938	2.613659725193	0.948566420494
H	-3.926699180348	0.318338631796	1.570393373806

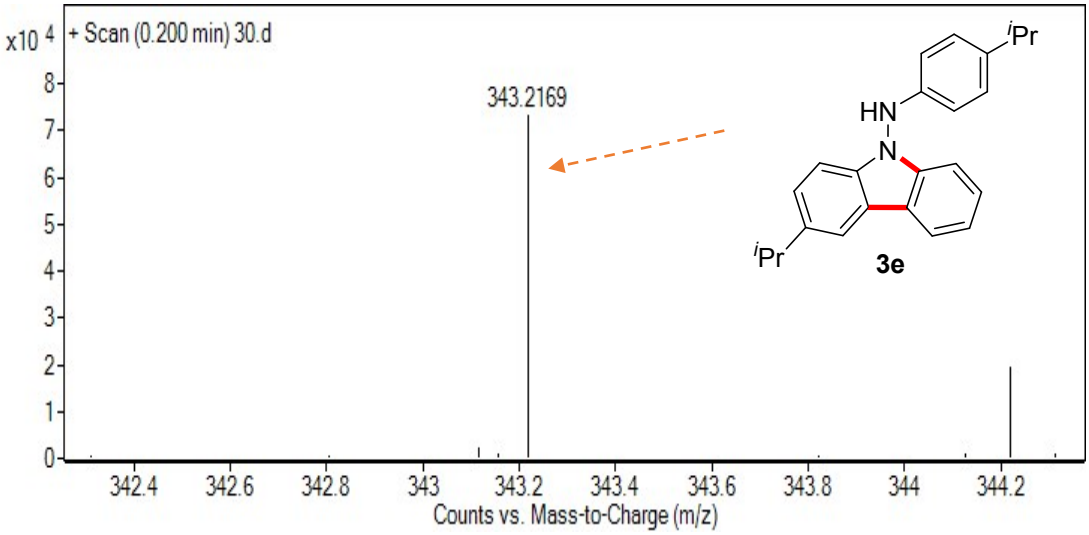
11. HRMS analysis reports for new compounds

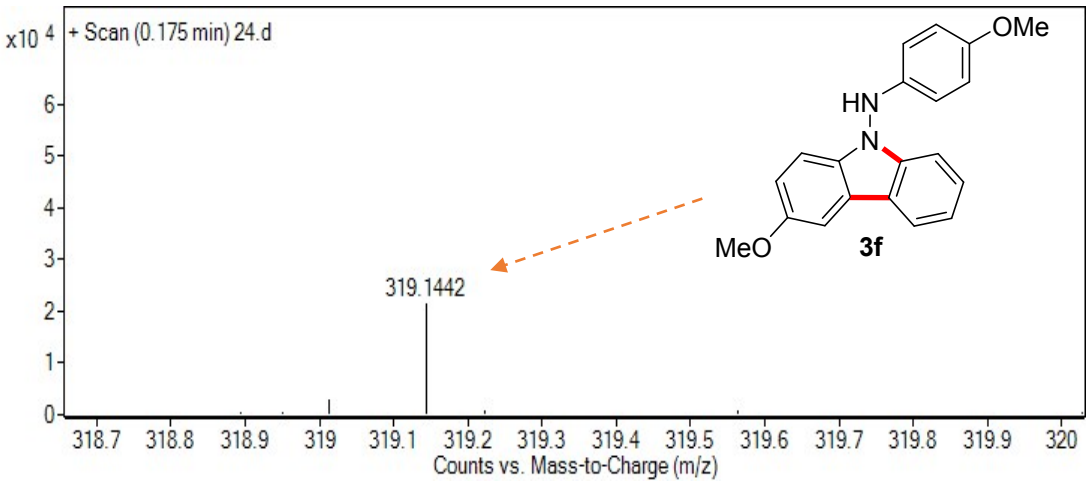







x10 5
+ Scan (0.961 min) 120.d
371.2483
370.2379
372.2478
tBu
HN
N
tBu
3d
Counts vs. Mass-to-Charge (m/z)


x10 4
+ Scan (0.200 min) 30.d
343.2169
iPr
HN
N
iPr
3e
Counts vs. Mass-to-Charge (m/z)

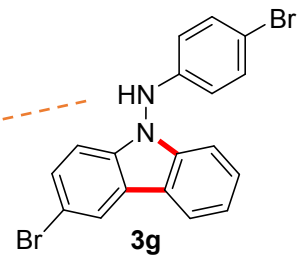

x10 4
+ Scan (0.175 min) 24.d
319.1442
OMe
HN
N
MeO
3f
Counts vs. Mass-to-Charge (m/z)

Operation Mode: ESI Positive Ion Mode

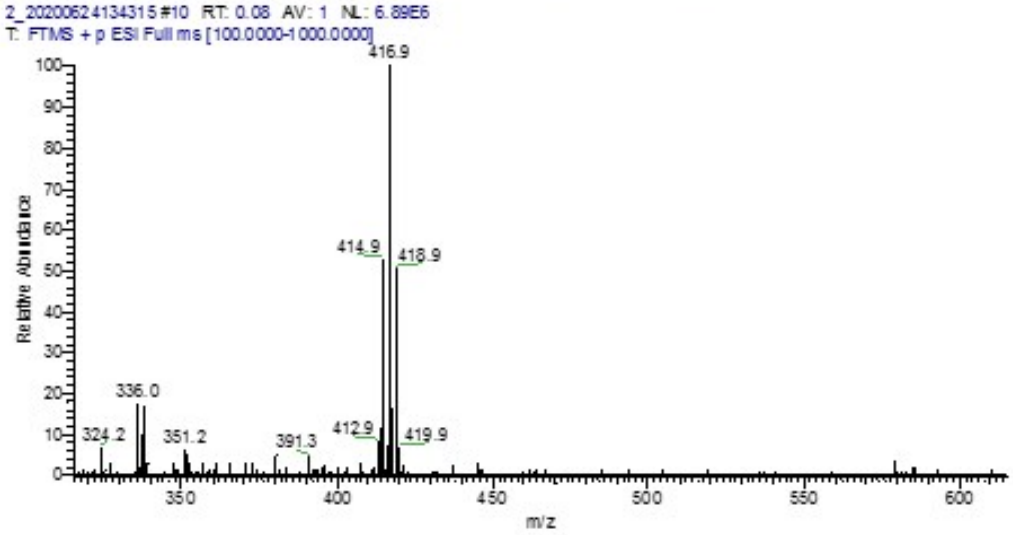
Elemental composition search on mass 414.94

m/z= 409.94-419.94

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
414.9439	414.9440	-0.29	12.5	$C_{18}H_{13}N_2Br_2$
	414.9434	1.04	15.0	$C_{16}H_6O_6N_3Br$
	414.9448	-2.20	14.5	$C_{18}H_8O_7Br$
	414.9421	4.27	15.5	$C_{14}H_4O_5N_6Br$
	414.9459	-4.75	-0.5	$C_6H_{17}O_7N_4Br_2$



3g

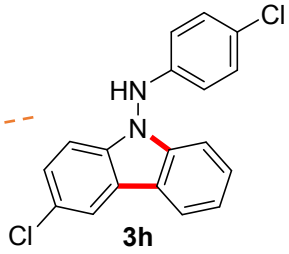


Operation Mode: ESI Positive Ion Mode

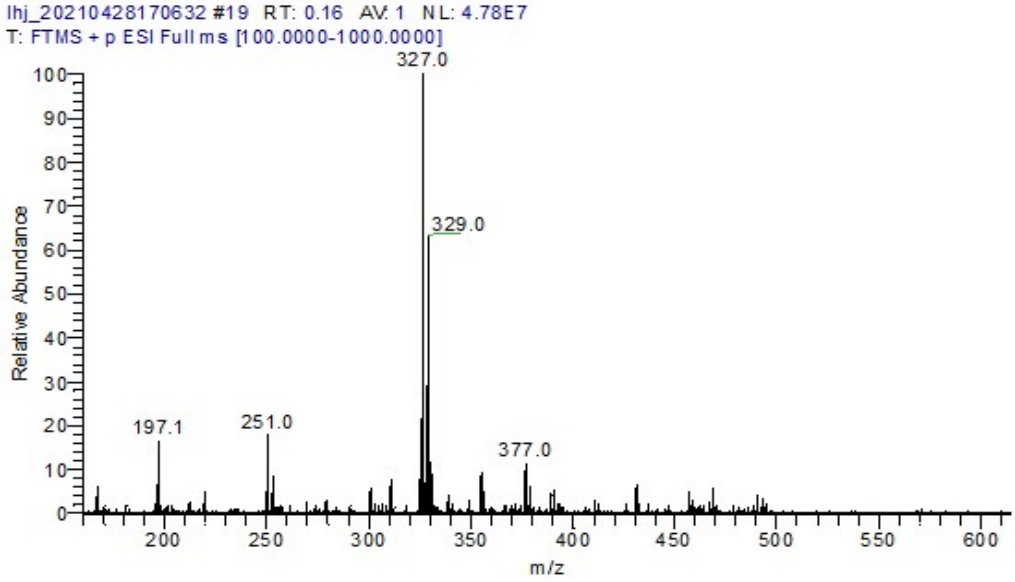
Elemental composition search on mass 327.0451

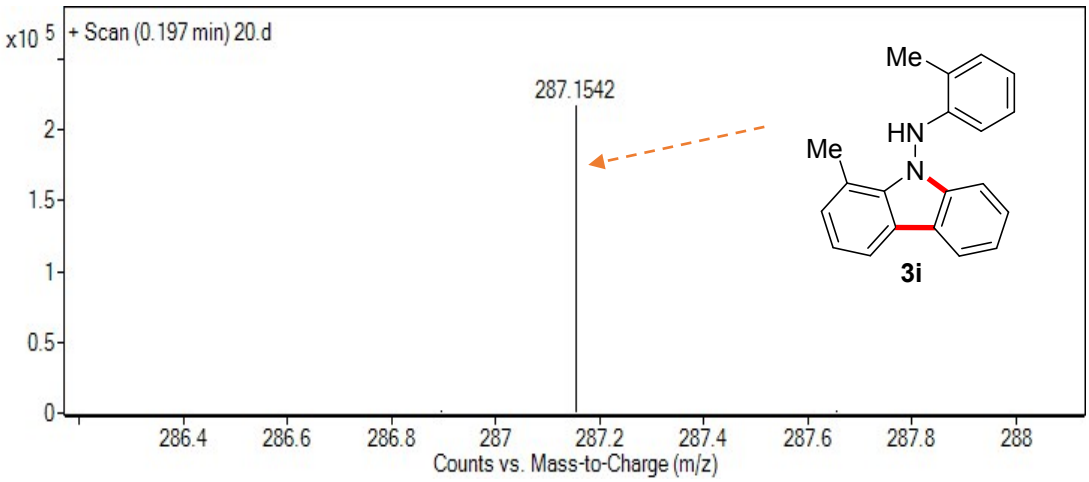
m/z= 322.0451-332.0451

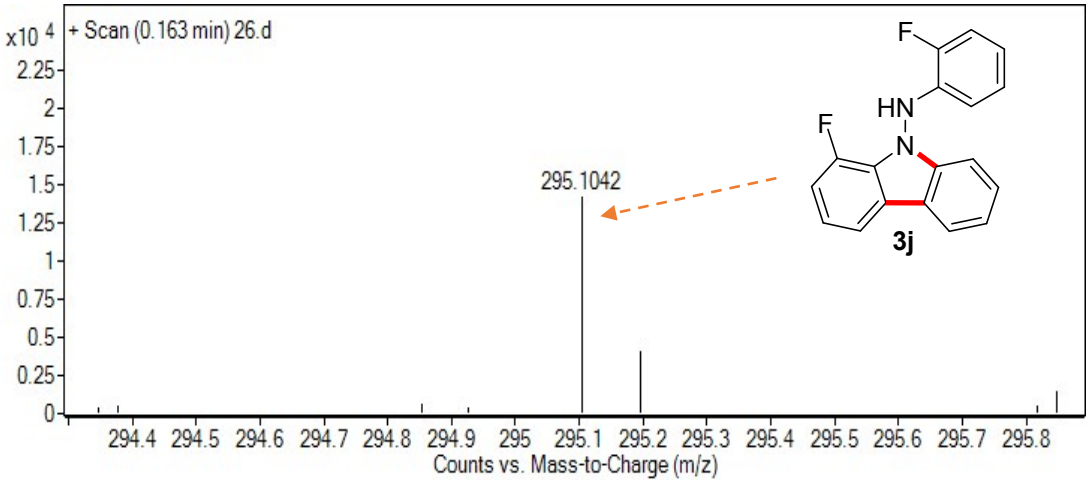
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
327.0451	327.0450	0.21	12.5	$C_{18}H_{13}N_2Cl_2$
	327.0445	1.70	17.0	$C_{21}H_{10}ONCl$
	327.0441	3.19	21.5	$C_{24}H_7O_2$

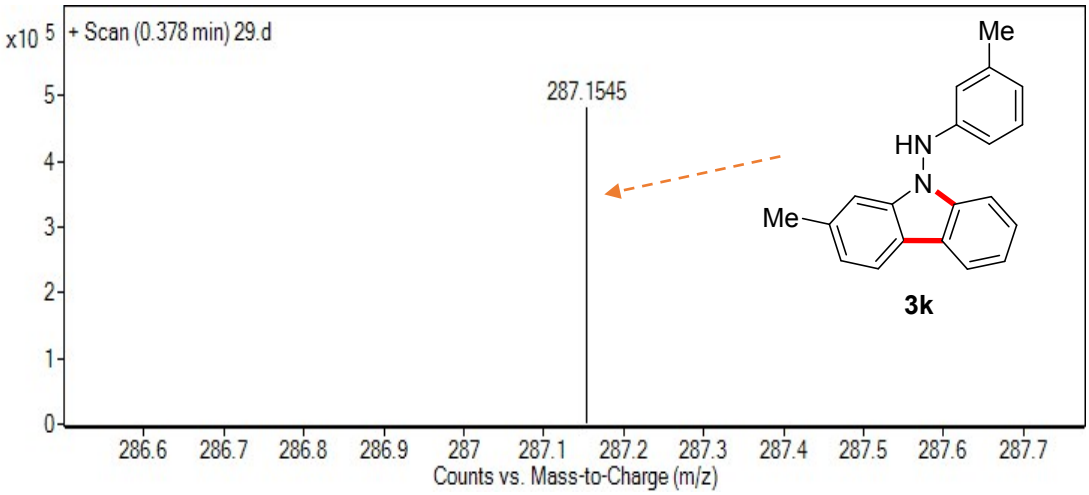


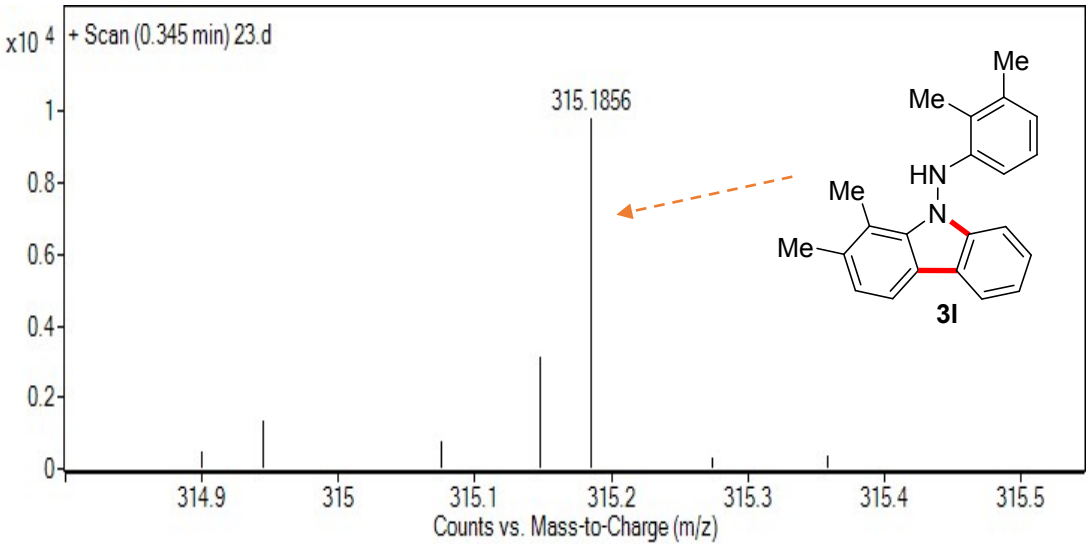
3h

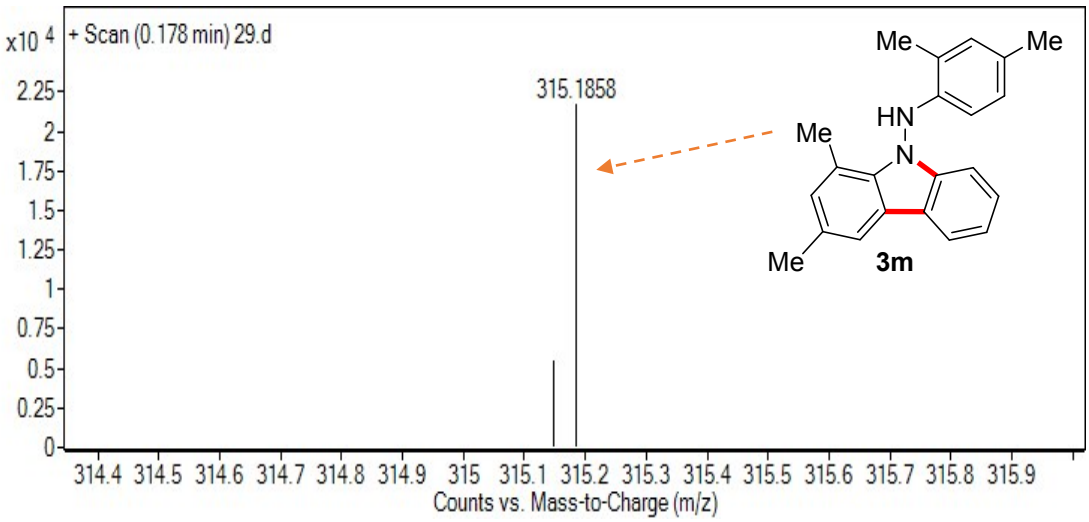


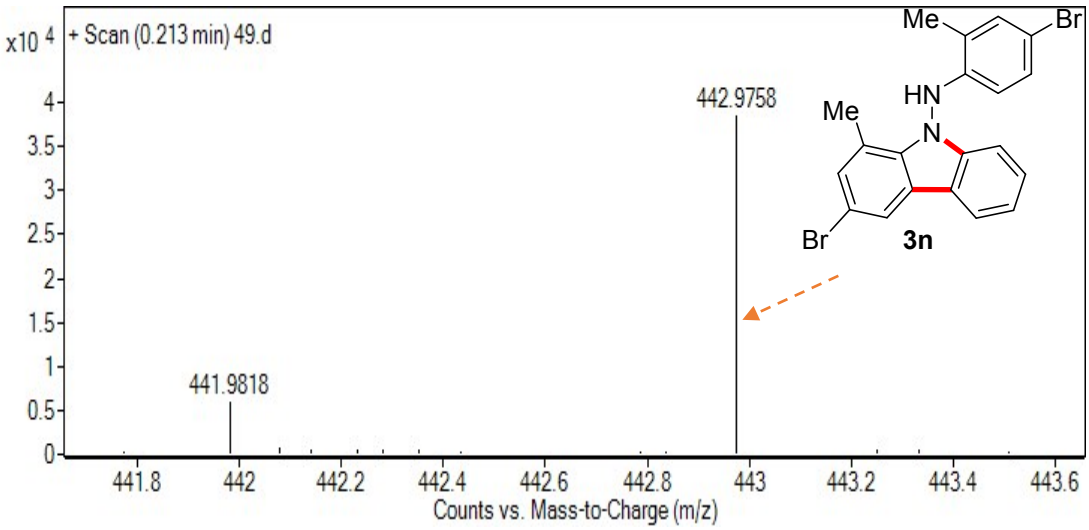

x10 5
+ Scan (0.197 min) 20.d
287.1542
Me
HN
Me
N
3i
2
1.5
1
0.5
0
286.4
286.6
286.8
287
287.2
287.4
287.6
287.8
288
Counts vs. Mass-to-Charge (m/z)

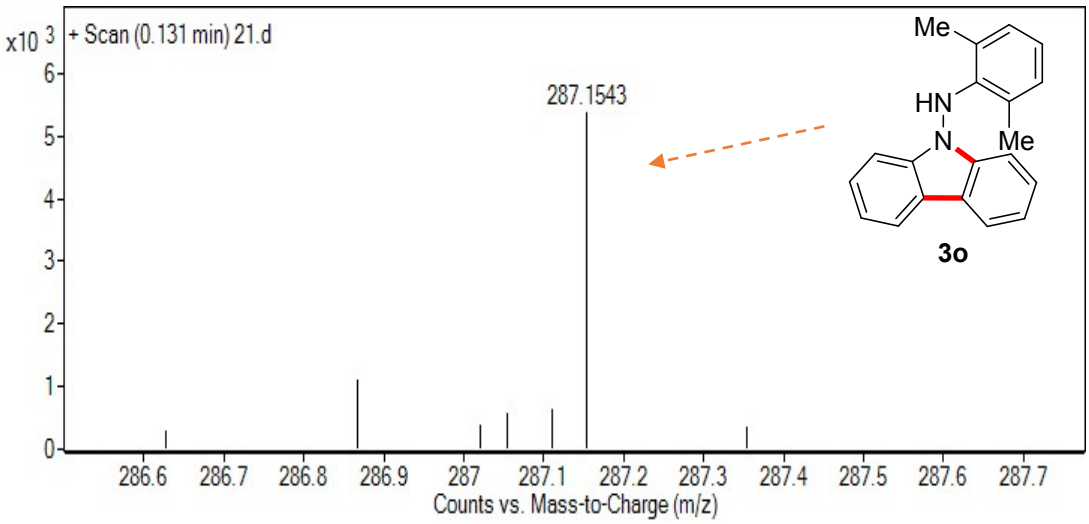

x10 4
+ Scan (0.163 min) 26.d
295.1042
F
HN
F
N
3j
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
294.4
294.5
294.6
294.7
294.8
294.9
295
295.1
295.2
295.3
295.4
295.5
295.6
295.7
295.8
Counts vs. Mass-to-Charge (m/z)

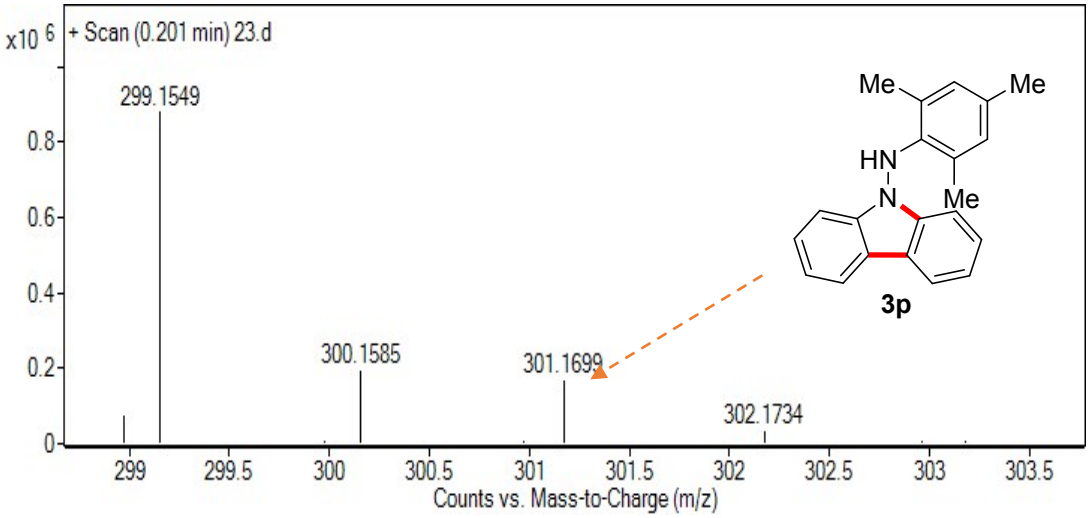

x10 5
+ Scan (0.378 min) 29.d
287.1545
Me
HN
N
Me
3k
5
4
3
2
1
0
286.6
286.7
286.8
286.9
287
287.1
287.2
287.3
287.4
287.5
287.6
287.7
Counts vs. Mass-to-Charge (m/z)


x10 4
+ Scan (0.345 min) 23.d
315.1856
Me
Me
HN
N
Me
Me
3l
Counts vs. Mass-to-Charge (m/z)


x10 4
+ Scan (0.178 min) 29.d
315.1858
Me
Me
HN
N
Me
Me
3m
Counts vs. Mass-to-Charge (m/z)


x10 4
+ Scan (0.213 min) 49.d
442.9758
441.9818
Me
Br
HN
N
Me
Br
3n
Counts vs. Mass-to-Charge (m/z)


x10 3
+ Scan (0.131 min) 21.d
287.1543
Me
HN
N
Me
3o
Counts vs. Mass-to-Charge (m/z)

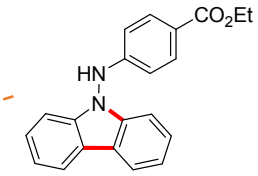

x10 6
+ Scan (0.201 min) 23.d
299.1549
300.1585
301.1699
302.1734
Me
Me
HN
N
Me
3p
Counts vs. Mass-to-Charge (m/z)

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 331.14

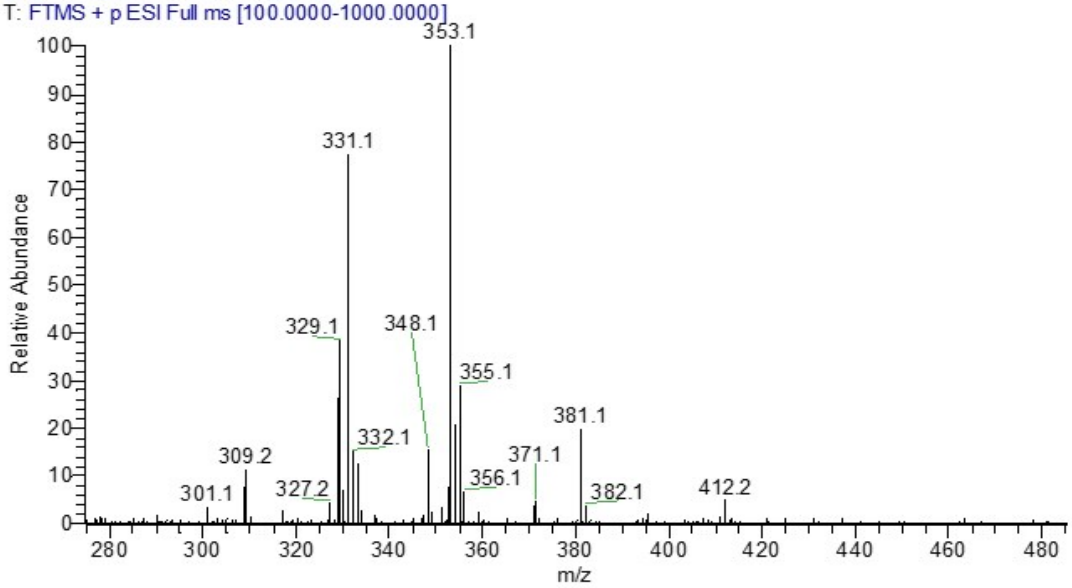
m/z= 326.14-336.14

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
331.1437	331.1441	-1.10	13.5	$C_{21}H_{19}O_2N_2$
	331.1428	2.95	14.0	$C_{19}H_{17}ON_5$



3q

3#8 RT: 0.06 AV: 1 NL: 2.39E7
T: FTMS + p ESI Full ms [100.0000-1000.0000]

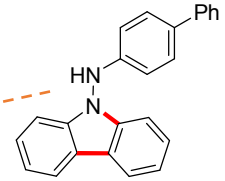


Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 335.15

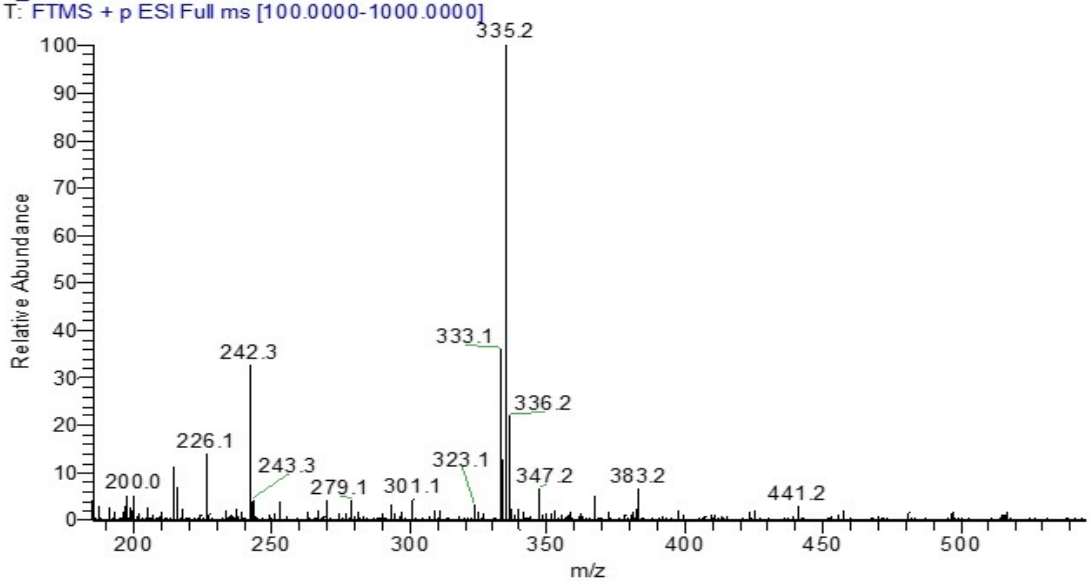
m/z= 330.15-340.15

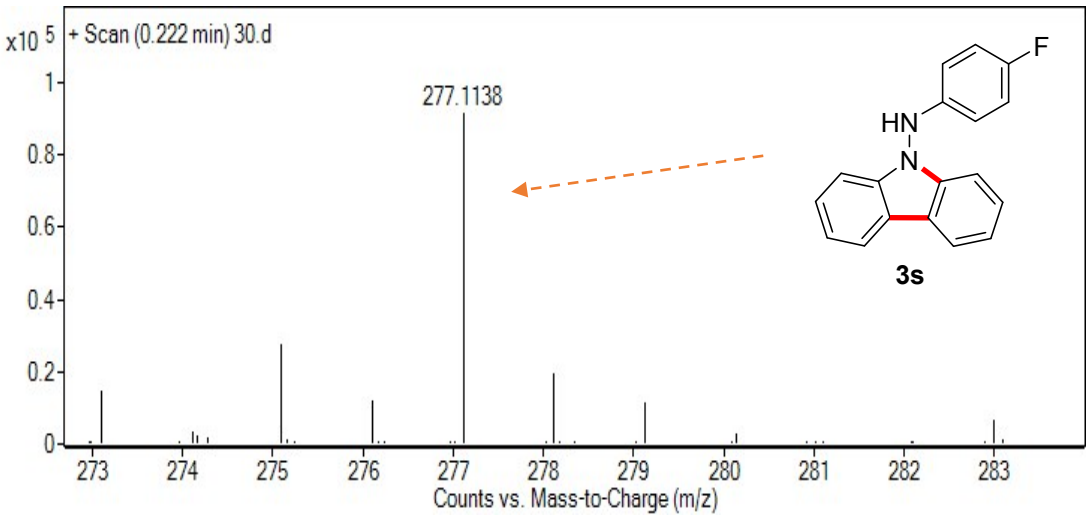
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
335.1540	335.1543	-0.67	16.5	$C_{24}H_{19}N_2$
	335.1553	-3.83	1.5	$C_{12}H_{28}N_6Br$

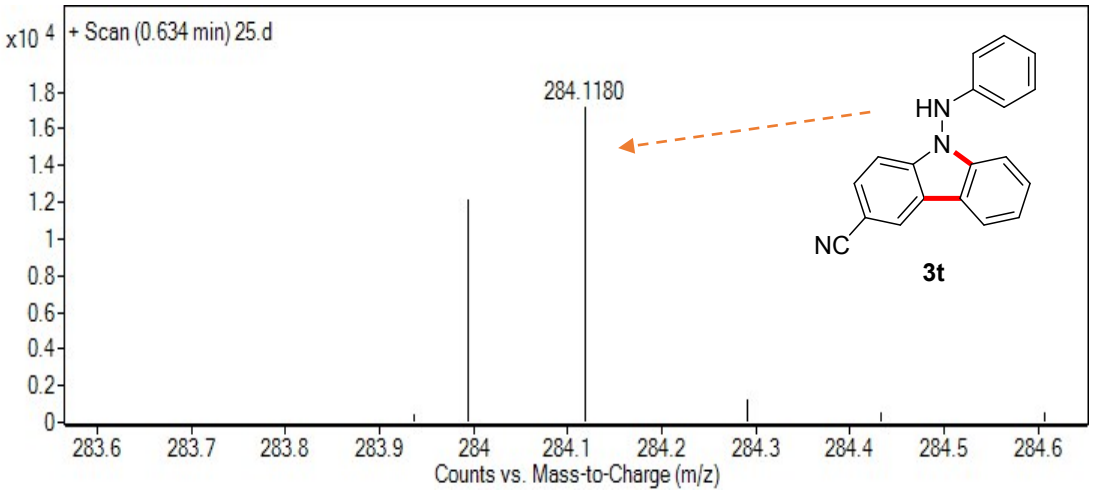


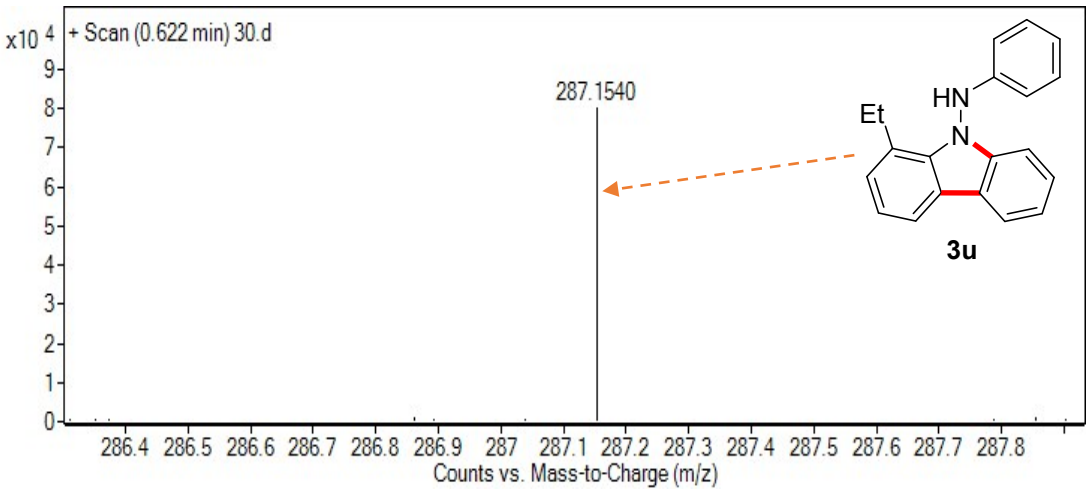
3r

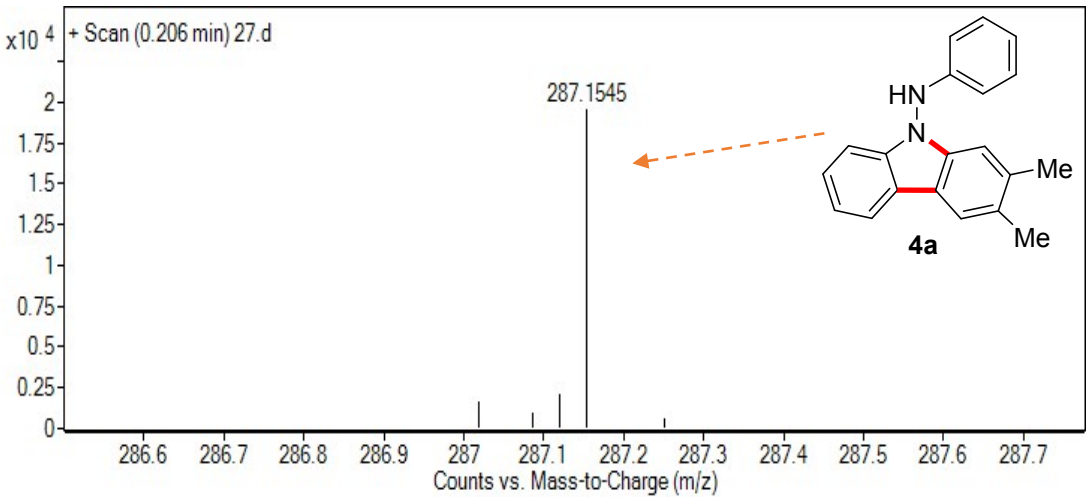
5_20200624132459#17 RT: 0.14 AV: 1 NL: 3.22E7
T: FTMS + p ESI Full ms [100.0000-1000.0000]

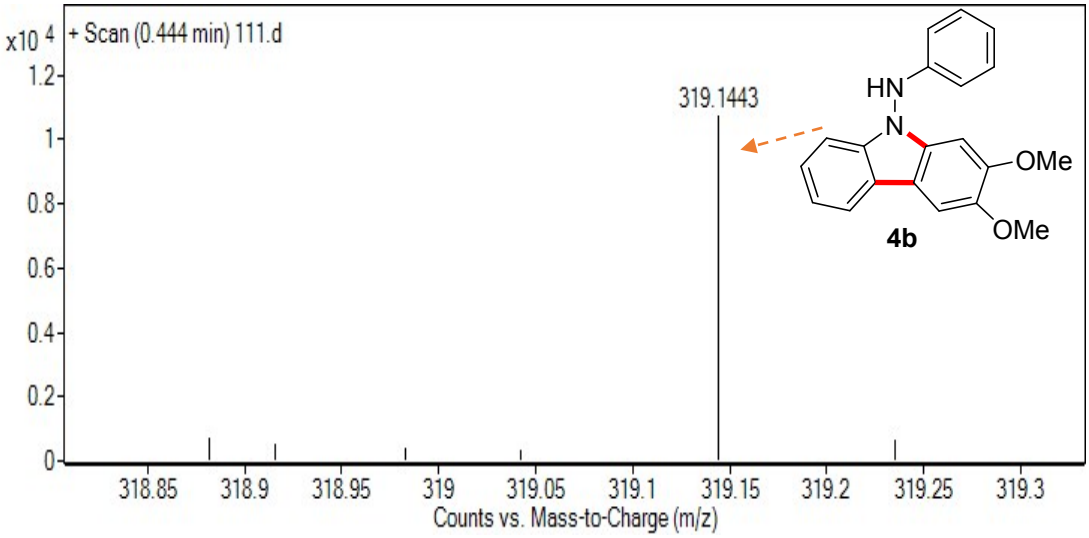


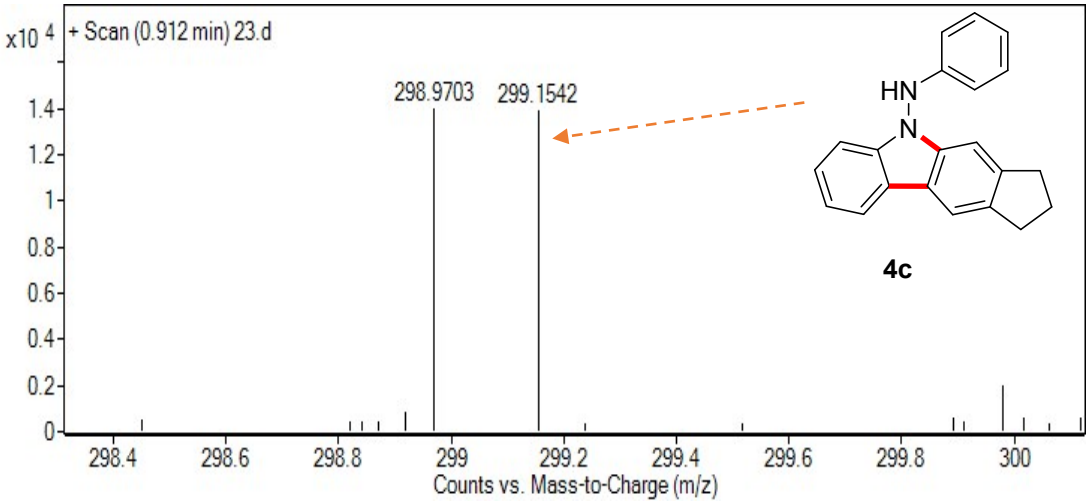

x10 5
+ Scan (0.222 min) 30.d
277.1138
HN
N
F
3s
Counts vs. Mass-to-Charge (m/z)

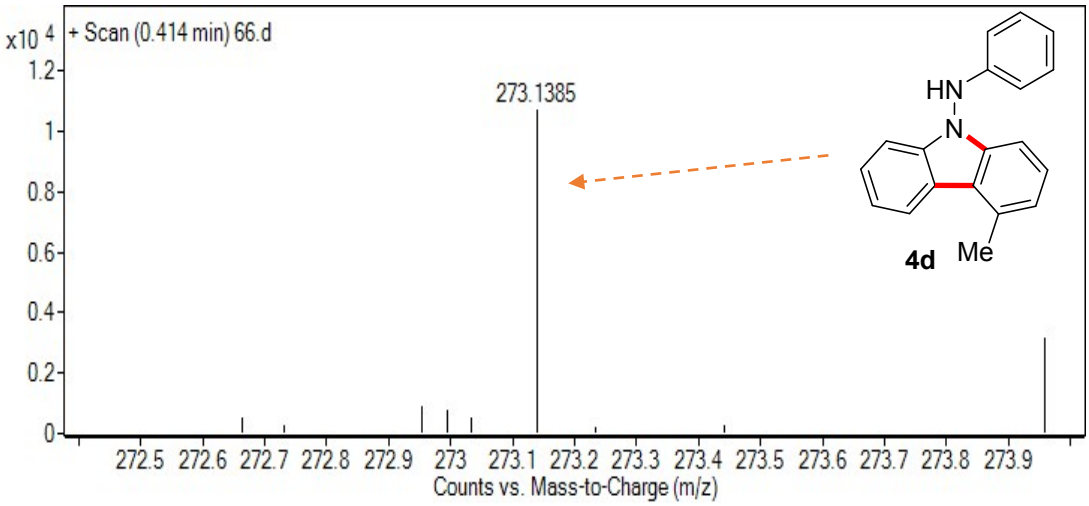

x10 4
+ Scan (0.634 min) 25.d
284.1180
HN
N
NC
3t
Counts vs. Mass-to-Charge (m/z)

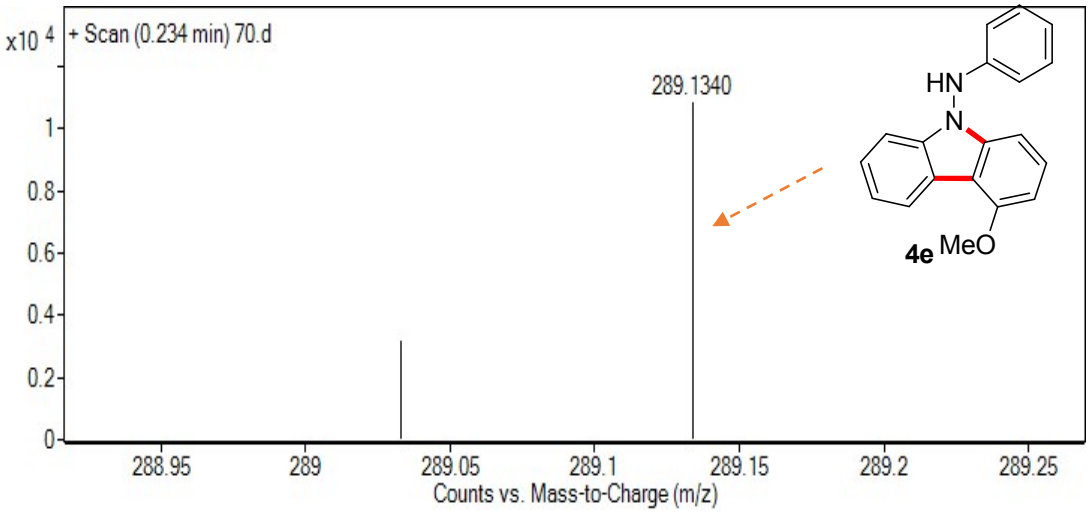

x10 4
+ Scan (0.622 min) 30.d
287.1540
HN
N
Et
3u
Counts vs. Mass-to-Charge (m/z)


x10 4
+ Scan (0.206 min) 27.d
287.1545
HN
N
Me
Me
4a
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
286.6
286.7
286.8
286.9
287
287.1
287.2
287.3
287.4
287.5
287.6
287.7
Counts vs. Mass-to-Charge (m/z)


x10 4
+ Scan (0.444 min) 111.d
319.1443
HN
N
OMe
OMe
4b
1.2
1
0.8
0.6
0.4
0.2
0
318.85
318.9
318.95
319
319.05
319.1
319.15
319.2
319.25
319.3
Counts vs. Mass-to-Charge (m/z)


x10 4
+ Scan (0.912 min) 23.d
298.9703
299.1542
HN
N
4c
1.4
1.2
1
0.8
0.6
0.4
0.2
0
298.4
298.6
298.8
299
299.2
299.4
299.6
299.8
300
Counts vs. Mass-to-Charge (m/z)


x10 4
+ Scan (0.414 min) 66.d
1.2
1
0.8
0.6
0.4
0.2
0
273.1385
HN
N
Me
4d
272.5 272.6 272.7 272.8 272.9 273 273.1 273.2 273.3 273.4 273.5 273.6 273.7 273.8 273.9
Counts vs. Mass-to-Charge (m/z)

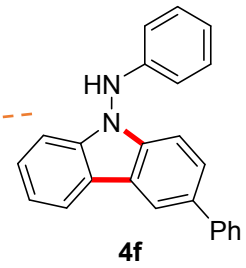

x10 4
+ Scan (0.234 min) 70.d
1
0.8
0.6
0.4
0.2
0
289.1340
HN
N
MeO
4e
288.95 289 289.05 289.1 289.15 289.2 289.25
Counts vs. Mass-to-Charge (m/z)

Operation Mode: ESI Positive Ion Mode

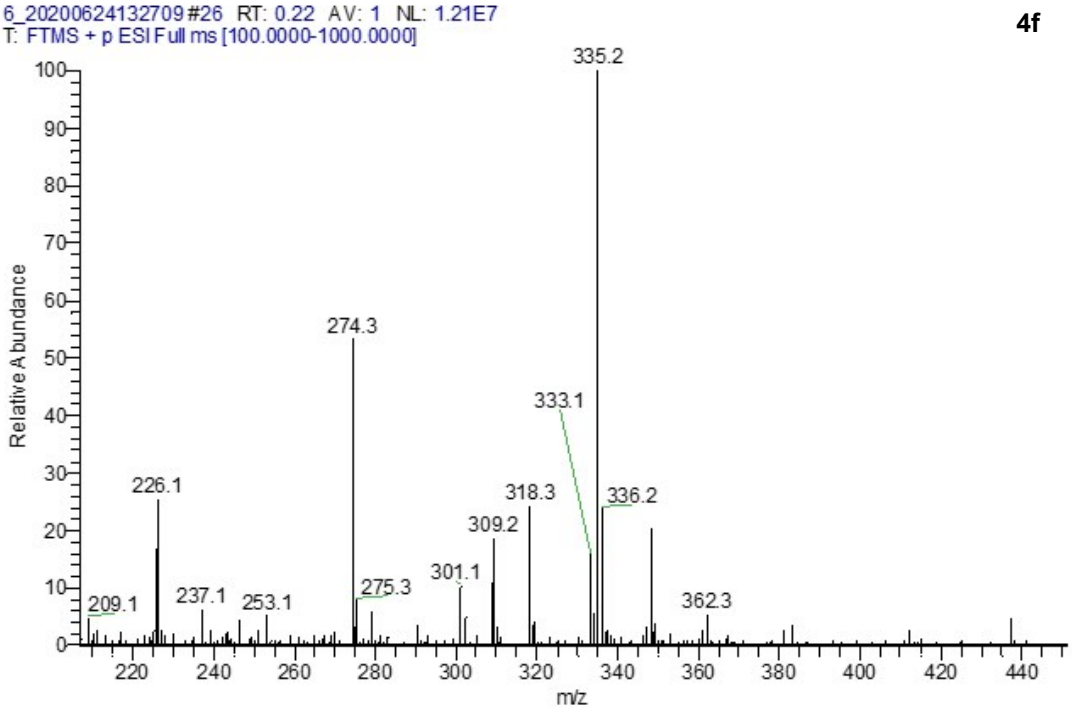
Elemental composition search on mass 335.15

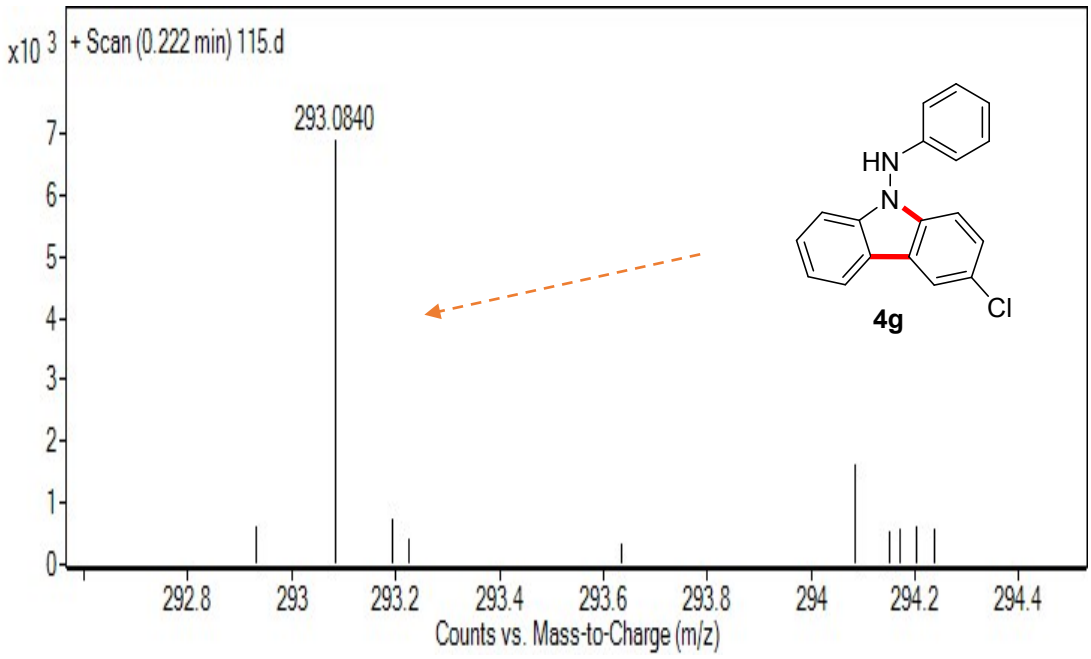
m/z= 330.15-340.15

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
335.1541	335.1543	-0.40	16.5	$C_{24}H_{19}N_2$
	335.1553	-3.56	1.5	$C_{12}H_{28}N_6Br$



4f





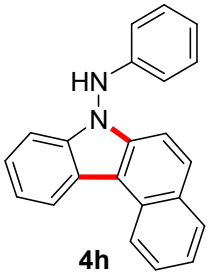
4g

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 309.14

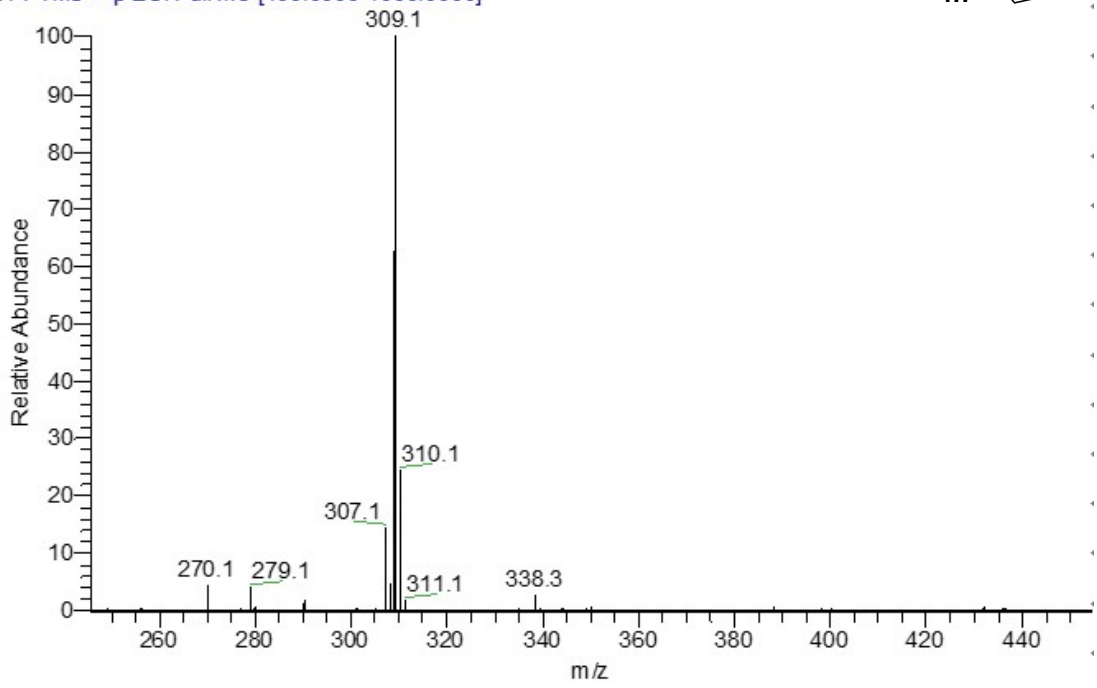
m/z= 304.14-314.14

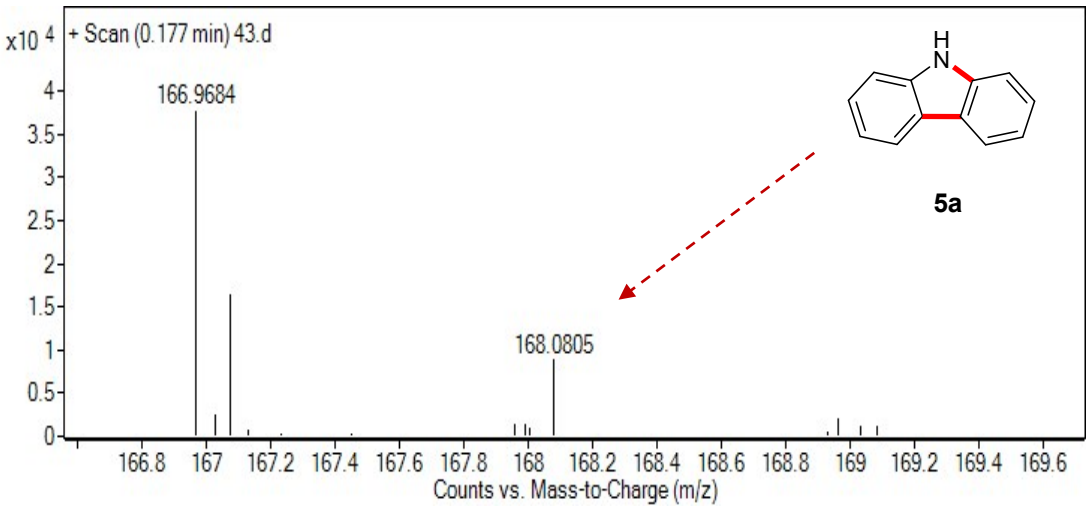
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
309.1383	309.1386	-0.92	15.5	$C_{22}H_{17}N_2$
	309.1397	-4.35	0.5	$C_{10}H_{26}N_6Br$



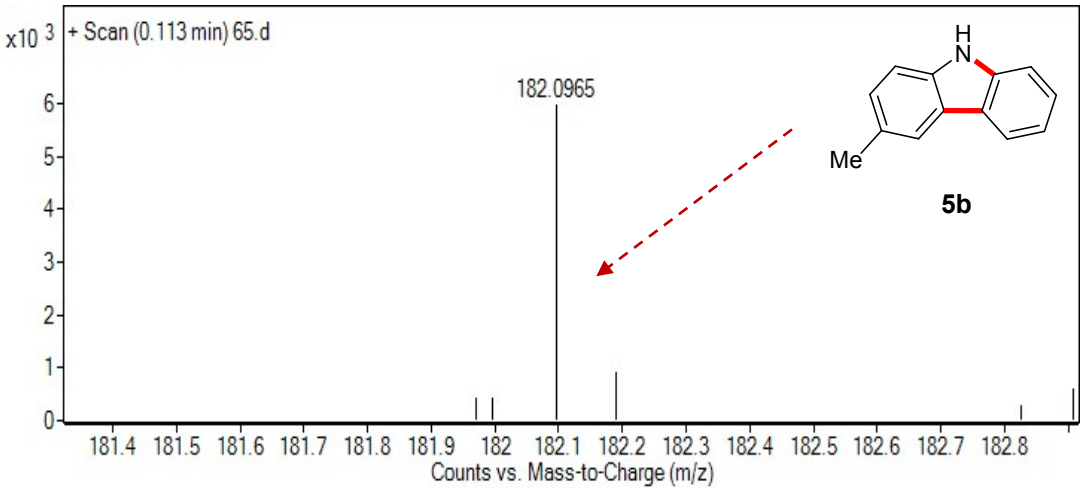
4h

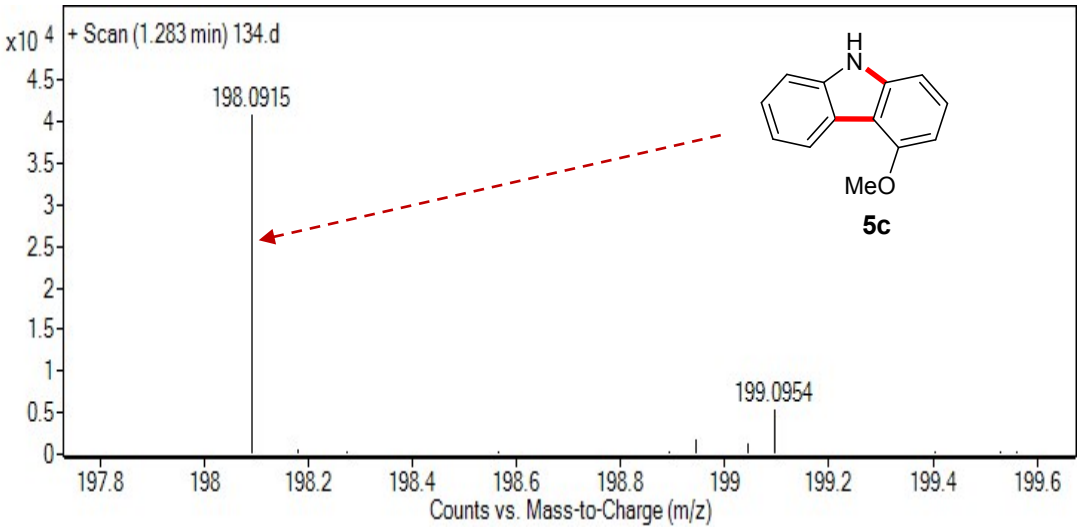
1_20200624133801 #21 RT: 0.18 AV: 1 NL: 5.74E7
T: FTMS + p ESI Full ms [100.0000-1000.0000]

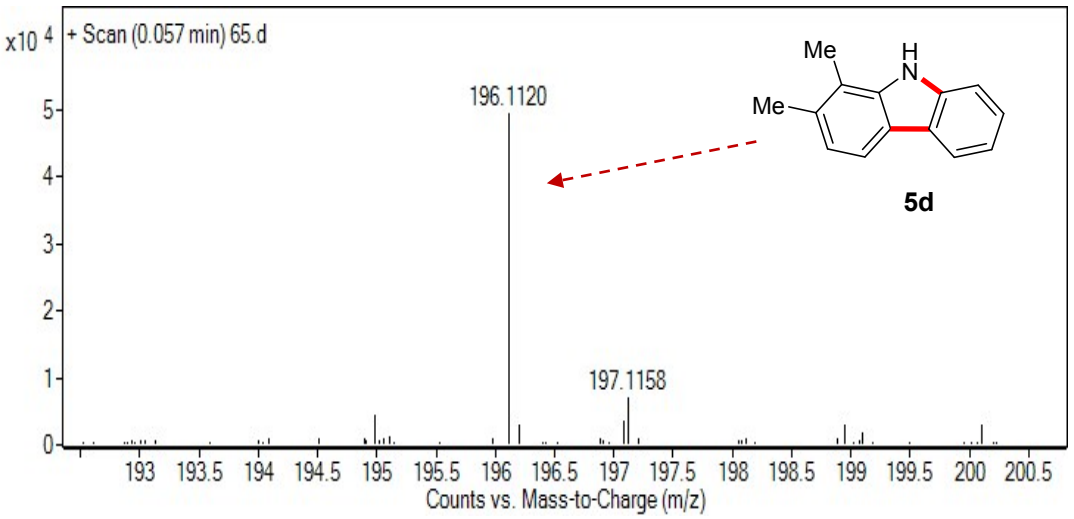


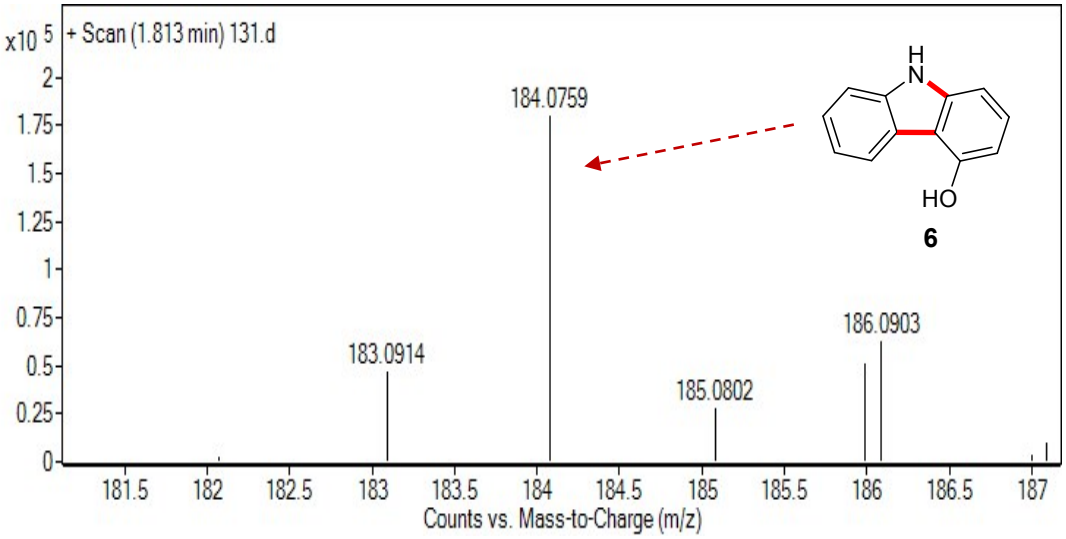


5a


x10 3
+ Scan (0.113 min) 65.d
182.0965
H
N
Me
5b
Counts vs. Mass-to-Charge (m/z)


x10 4
+ Scan (1.283 min) 134.d
198.0915
199.0954
H
N
MeO
5c
Counts vs. Mass-to-Charge (m/z)


x10 4
+ Scan (0.057 min) 65.d
196.1120
197.1158
Me
Me
H
N
5d
Counts vs. Mass-to-Charge (m/z)


x10 5
+ Scan (1.813 min) 131.d
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
184.0759
183.0914
185.0802
186.0903
181.5
182
182.5
183
183.5
184
184.5
185
185.5
186
186.5
187
Counts vs. Mass-to-Charge (m/z)
H
N
HO
6