Supporting Information for

Phenanthroline-^fBuOK Promoted Intramolecular C-H Arylation of Indoles with Arl under Transition Metal-Free Conditions

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1. General information

Solvents were predried over activated 4 Å molecular sieves and further dried by refluxing and distilling over sodium (1,4-dioxane), CaH₂ (toluene, octane, CH₃CN, CH₂Cl₂ and DMF) or P₂O₅ (PhCl) under argon atmosphere. 1 H, 13 C{ 1 H} NMR spectra were recorded on a Bruker 400 spectrometer. Chemical shifts are reported in δ units relative to CDCl₃ [1 H δ = 7.26, 13 C δ = 77.16], DMSO- d_6 [1 H δ = 2.50, 13 C δ = 39.52].

2. General procedures

2.1. Intramolecular Cyclization

2.1.1. Screening reaction conditions (Table 1)

The starting material **1a** (0.5 mmol, 167 mg), 1,10-phenanthroline (0.05 mmol, 9 mg) and 7 BuOK (1.0 mmol, 112 mg) were weighed directly into a Schlenk tube and dried under high vacuum for 15 min. Solvent(10 mL) was added and stirred at 90 °C, monitored by TLC. The reaction mixture was directly examined by 1 H NMR spectrometer to determine the conversion and selectivity by using dibenzyl ether (24 μ L) as an internal standards.

2.2. General procedure

The starting material 1 (0.5 mmol), 1,10-phenanthroline (0.05 mmol, 9 mg) and 'BuOK (1.0 mmol, 112 mg) were weighed directly into a Schlenk tube and dried under high vacuum for 15 min. PhCl (10 mL) was added and stirred at 90 °C and the reaction was monitored by TLC. Upon completion, the reaction mixture was directly prified by silica gel column (EtOAc/CH₂Cl₂/petroleum ether as eluent) to give the target product.

6H-isoindolo[2,1-a]indole (2a)

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (50:5:1) to give the product, white solid, 85.2 mg, 83%, mp 184–185 °C. 1 H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.43-7.36 (m, 2H), 7.32 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.64 (s, 1H),

5.08 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl₃) δ 144.1, 141.8, 134.0, 133.2, 132.9, 128.3, 127.2, 123.7, 121.8, 121.6, 121.1, 119.7, 109.4, 91.4, 48.5.6

8-methyl-6*H*-isoindolo[2,1-*a*]indole (2b)

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (50:5:1) to give the product, white solid, 88.8 mg, 81%, mp 177–178 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.28 (s, 1H), 7.23-7.17 (m, 2H), 7.11 (t, J = 7.6 Hz, 1H), 6.58 (s, 1H), 5.02 (s, 2H), 2.44 (s, 3H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 144.3, 142.2, 137.3, 133.9, 133.0, 130.5, 129.0, 124.3, 121.6, 121.4, 120.8, 119.6, 109.2, 90.7, 48.4, 21.8. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₆H₁₄N 220.1121, found 220.1123.

5*H*-[1,3]dioxolo[4',5':5,6]isoindolo[2,1-*a*]indole (2c)

This compound was prepared according to the general procedure method. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (100:10:1) to give the product, white solid, 103.5 mg, 83%, mp 207–208 °C. ¹H NMR (400 MHz, DMSO- d_6) δ 7.55 (d, J = 8.0 Hz, 1H), 7.40-7.38 (m, 2H), 7.21 (s, 1H), 7.09 (t, J = 7.6 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.51 (s, 1H), 6.11 (s, 2H), 5.06 (s, 2H). 13 C{ 1 H} NMR (100 MHz, DMSO- d_6) δ 147.6, 147.3, 143.7, 136.0, 133.7, 132.2, 125.8, 121.0, 120.8, 119.2, 109.5, 105.1, 101.6, 101.5, 89.7, 48.4. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₆H₁₂NO₂ 250.0863, found 250.0869.

9-methoxy-6*H*-isoindolo[2,1-*a*]indole (2d)

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (50:5:1) to give the product, yellow solid, 71.8 mg, 61%, mp 168–169 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 7.6 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 2.4 Hz, 1H), 7.22-7.18 (m, 1H), 7.11 (t, J = 7.2 Hz, 1H), 6.87 (dd, J = 8.0, 2.4 Hz, 1H), 6.62 (s, 1H), 5.00 (s, 2H), 3.90 (s, 3H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 160.1, 144.0, 134.4, 134.1, 133.9, 132.8, 124.3, 121.8, 121.7, 119.7, 113.6, 109.3, 106.0, 91.4, 55.7, 48.1. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₆H₁₄NO 236.1070, found 236.1073.

13H-benzo[4,5]isoindolo[2,1-a]indole (2e)

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (50:5:1) to give the product, white solid, 53.6 mg, 42%, mp 98–99 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.88 (m, 2H), 7.82-7.79 (m, 2H), 7.69 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 6.66 (s, 1H), 5.34 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 145.1, 138.0, 134.5, 133.0, 132.8, 130.7, 129.3, 129.2, 129.1, 127.3, 125.9, 123.3, 121.9, 121.8, 119.7, 119.2, 109.2, 91.6, 48.0. HRMS (ESI–TOF) m/z: [M+H]+ calcd for C₁₉H₁₄N 256.1121, found 256.1126.

11-methyl-6H-isoindolo[2,1-a]indole (2f)

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (50:5:1) to give the product, white solid, 93.2 mg, 85%, mp 95–96 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 8.4 Hz, 2H), 7.23 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 7.2 Hz, 1H), 7.09 (t, J = 7.2 Hz, 1H), 4.89 (s, 2H), 2.51 (s, 3H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 141.8, 140.2, 133.8, 133.7, 133.2, 128.1, 126.4, 123.6, 121.5, 120.9, 119.7, 118.9, 109.1, 102.1, 48.1, 9.1. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₆H₁₄N 220.1121, found 220.1119.

12*H*-benzo[*g*]isoindolo[2,1-*a*]indole (2g)

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (50:5:1) to give the product, white solid, 111.1 mg, 87%, mp 145–146 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.62-7.54 (m, 3H), 7.48-7.38 (m, 3H), 7.24 (d, J = 2.4 Hz, 1H), 6.71 (d, J = 3.2 Hz, 1H), 5.21 (s, 2H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 141.1, 135.5, 133.7, 133.0, 132.5, 131.3, 128.8, 128.5, 128.0, 127.2, 126.5, 125.5, 124.0, 121.6, 121.3 (two peaks), 102.9, 54.1. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₉H₁₄N 256.1121, found 256.1123.

2-bromo-6*H*-isoindolo[2,1-*a*]indole (2h)

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (100:10:1) to give the product, white solid, 99.5 mg, 70%, mp 197–198 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (s, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 7.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 7.26-7.20 (m, 2H), 6.55 (s, 1H), 5.05 (s, 2H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 145.3, 141.8, 134.5, 132.7 (two peaks), 128.4, 127.6, 124.4, 124.1, 123.7, 121.3, 112.9, 110.7, 91.0, 48.7. HRMS (ESI–TOF) m/z: [M+H]+ calcd for C₁₅H₁₁BrN 284.0069, found 284.0070.

3-fluoro-6*H*-isoindolo[2,1-*a*]indole (2i)

This compound was prepared according to the general procedure method. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (100:10:1) to give the product, white solid, 105.0 mg, 90%, mp 172–173 °C. ¹H NMR (400 MHz, DMSO- d_6) δ 7.80 (d, J = 7.6 Hz, 1H), 7.62-7.58 (m, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.39-7.32 (m, 2H), 6.93-6.87 (m, 1H), 6.70 (s, 1H), 5.19 (s, 2H). ¹³C{¹H} NMR (100 MHz, DMSO- d_6) δ 158.7 (d, J = 234.0 Hz), 144.2 (d, J = 3.6 Hz), 142.0, 133.4 (d, J = 12.9 Hz), 131.9, 128.9, 128.1, 127.4, 124.1, 122.2 (d, J = 10.1Hz), 120.6, 107.8 (d, J = 24.4 Hz), 96.4 (d, J = 25.8 Hz), 91.2, 48.5. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₅H₁₁FN 224.0870, found 224.0872.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (50:5:1) to give the product, yellow solid, 185.3 mg, 83%, mp 248–249 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, J = 7.6 Hz, 2H), 7.99 (s, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 7.2 Hz, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.57-7.43 (m, 8H), 7.37-7.30 (m, 3H), 6.73 (s, 1H), 5.12 (s, 2H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 145.0, 141.9, 141.8, 141.3, 136.0, 133.7, 133.6, 133.0, 132.3, 128.7, 128.4, 127.4, 126.1, 123.7, 123.5, 121.4, 121.2, 120.4 (two peaks), 120.0, 110.1, 109.8, 91.9, 48.7. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₃₃H₂₃N₂ 447.1856, found 447.1861.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (50:5:1) to give the product, yellow solid, 210.3 mg, 70%, mp 252–253 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 1.2 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.62-7.59 (m, 6H), 7.54-7.51 (m, 4H), 7.49-7.40 (m, 8H), 7.34-7.29 (m, 3H), 7.27-7.24 (m, 6H), 6.67 (s, 1H), 5.10 (s, 2H). 13 C{¹H} NMR (100 MHz, CDCl₃) δ 147.2, 146.0, 144.8, 141.9, 140.8, 137.6, 135.4, 133.5, 133.4, 133.1, 132.7, 128.9, 128.3, 128.2, 128.0, 127.3, 127.0, 126.8, 125.1, 124.3, 123.7, 121.2, 121.1, 119.9, 109.6, 91.7, 48.6. HRMS (ESI–TOF) m/z: [M+H]+ calcd for C₄₅H₃₃N₂ 601.2638, found 601.2631.

1-chloro-6*H*-isoindolo[2,1-a]indole (2l)

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (50:5:1) to give the product, white solid, 95.9 mg, 80%, mp 142–143 °C. ¹H NMR (400 MHz, DMSO– d_6) δ 7.86 (d, J = 7.2 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.48-7.38 (m, 3H), 7.13 (d, J = 2.0 Hz, 1H), 7.12 (s, 1H), 6.74 (s, 1H), 5.19 (s, 2H). 13 C{ 1 H} NMR (100 MHz, DMSO– d_6) δ 144.3, 142.2, 134.2, 131.5, 130.4, 128.1, 127.7, 124.8, 124.0, 121.8, 121.1, 118.9, 109.0, 89.2, 48.8. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₅H₁₁NCl 240.0580; found 240.0579.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (50:5:1) to give the product, white solid, 87.5 mg, 73%, mp 182-183 °C. ¹H NMR (400 MHz, DMSO- d_6) δ 7.81 (d, J = 7.2 Hz, 1H), 7.61-7.59

(m, 3H), 7.45 (t, J = 6.8 Hz, 1H), 7.38 (t, J = 7.2 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.70 (s, 1H), 5.20 (s, 2H). ¹³C{¹H} NMR (100 MHz, DMSO- d_6) δ 144.4, 142.1, 133.8, 131.7, 130.9, 128.1, 127.6, 125.7, 124.1, 122.5, 120.9, 119.6, 109.9, 91.2, 48.6. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₅H₁₁NCl 240.0580; found 240.0580.

4-chloro-6*H*-isoindolo[2,1-a]indole (2n)

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (100:10:1) to give the product, white solid, 86.3 mg, 72%, mp 111–112 °C. ¹H NMR (400 MHz, DMSO– d_6) δ 7.80 (d, J = 7.6 Hz, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 7.2 Hz, 1H), 7.38 (td, J = 7.2, 1.2 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.73 (s, 1H), 5.45 (s, 2H). 13 C{ 1 H} NMR (100 MHz, DMSO– d_6) δ 144.9, 142.2, 134.4, 131.0, 130.1, 128.1, 127.7, 123.9, 121.1, 120.8, 120.3, 120.2, 115.4, 91.8, 51.0. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₅H₁₁NCl 240.0580; found 240.0582.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (100:10:1) to give the product, yellow solid, 77.9 mg, 65%, mp 180–181 °C. ¹H NMR (400 MHz, DMSO– d_6) δ 7.81 (d, J = 8.0 Hz, 1H), 7.70 (s, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 6.70 (s, 1H), 5.21 (s, 2H). 13 C{ 1 H} NMR (100 MHz, DMSO– d_6) δ 144.3, 142.2, 133.6, 132.1, 131.6, 131.1, 128.2, 124.4, 122.0, 121.4 (two peaks), 119.5, 110.0, 91.6, 48.3. HRMS (ESI–TOF) m/z: [M+H]+ calcd for C₁₅H₁₁NCl 240.0580; found 240.0576.

6*H*-isoindolo[2,1-*a*]indole-1-carbonitrile (2p)

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (50:5:1) to give the product, yellow solid, 54.1 mg, 47%, mp 181-182 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 7.6 Hz, 1H), 7.49-7.34 (m, 5H), 7.16 (t, J = 7.6 Hz, 1H), 6.75 (s, 1H), 5.00 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 146.6, 141.8, 134.2, 133.5, 132.0, 128.6, 128.3, 125.0, 123.7, 121.7, 120.9, 119.0, 113.7, 103.4, 90.5, 48.8. HRMS (ESI-TOF) m/z: [M+H]+ calcd for C₁₆H₁₁N₂ 231.0917, found 231.0925.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (100:10:1) to give the product, white solid, 59.7 mg, 42%, mp 87–88 °C. This compound was prepared according to the general procedure, white solid (1.85 g, 90%). ¹H NMR (400 MHz, DMSO– d_6) δ 7.83 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.62 (t, J = 7.2 Hz, 2H), 7.45 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H), 7.05 (t, J = 7.2 Hz, 1H), 6.71 (s, 1H), 5.21 (s, 2H). ¹³C{¹H} NMR (100 MHz, DMSO– d_6) δ 144.6, 142.2, 133.5, 132.1, 131.5, 131.0, 127.2, 122.3, 121.5, 121.4, 120.0, 119.5, 110.0, 91.7, 48.2. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₅H₁₁NBr 284.0075; found 284.0071.

6H-pyrido[2',3':4,5]pyrrolo[2,1-a]isoindole (2r)

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (10:5:1) to give the product, white solid, 65.0 mg, 63%, mp 173–174 °C. ¹H NMR (400 MHz, DMSO– d_6) δ 8.33 (dd, J = 4.8, 2.0 Hz, 1H), 7.88 (d, J = 7.2 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.2 Hz, 1H), 7.11 (dd, J = 8.4, 4.8 Hz, 1H), 6.82 (s, 1H), 5.25 (s, 2H). 13 C{ 1 H} NMR (100 MHz, DMSO– d_6) δ 149.8, 146.1, 142.5, 141.9, 131.7, 128.2 (two peaks), 127.0, 124.0, 121.5, 116.8, 115.9, 91.7, 49.1. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₄H₁₁N₂ 207.0922; found 207.0917.

6H-pyrido[3',4':4,5]pyrrolo[2,1-a]isoindole (2s)

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (10:5:1) to give the product, white solid, 84.5 mg, 82%, mp 188–189 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.92 (d, J = 0.8 Hz, 1H), 8.29 (d, J = 6.4 Hz, 1H), 7.71 (d, J = 7.2 Hz, 1H), 7.47-7.40 (m, 2H), 7.35 (td, J = 7.6, 1.2 Hz, 1H), 7.22 (d, J = 6.0 Hz, 1H), 6.64 (s, 1H), 5.01 (s, 2H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 145.0, 144.5, 141.6, 140.6, 137.1, 131.9, 129.7, 128.5, 128.0, 123.7, 121.5, 104.6, 90.5, 48.4. HRMS (ESITOF) m/z: [M+H]⁺ calcd for C₁₄H₁₁N₂ 207.0917, found 207.0919.

10*H*-pyrido[3',2':4,5]pyrrolo[2,1-*a*]isoindole (2t)

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (10:5:1) to give the product, yellow solid, 75.5 mg, 73%, mp 180–181 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, J = 4.8 Hz, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.06 (dd, J = 7.6, 4.8 Hz, 1H), 6.59 (s, 1H), 5.23 (s, 2H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 145.7, 144.4, 142.5, 142.1, 132.4, 129.4, 128.4, 128.0, 125.6, 124.0, 121.3, 116.0, 89.8, 48.0. HRMS (ESI–TOF) m/z: [M+H] $^{+}$ calcd for C₁₄H₁₁N₂ 207.0917, found 207.0920.

5*H*-[1,3]dioxolo[4,5-f]pyrido[3',2':4,5]pyrrolo[2,1-a]isoindole (2u)

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (10:5:1) to give the product, white solid, 105.1 mg, 84%, mp 193–194 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, J = 4.8 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.15 (s, 1H), 7.03 (dd, J = 7.6, 4.8 Hz, 1H), 6.97 (s, 1H), 6.41 (s, 1H), 6.04 (s, 2H), 5.09 (s, 2H). 13 C{¹H} NMR (CDCl₃, 100 MHz) δ 148.3 (two peaks), 145.9, 144.6, 142.0, 136.2, 129.0, 126.1, 125.6, 115.9, 104.9, 101.8, 88.4, 47.9. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C_{15} H₁₁N₂O₂ 251.0821; found 251.0820.

 $8\text{-chloro-}6H\text{-pyrido}[3',\!4'\text{:}4,\!5]pyrrolo[2,\!1\text{-}a]isoindole\ (2v)$

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (10:5:1) to give the product, white solid, 71.0 mg, 59%, mp 137–138 °C. ¹H NMR (400 MHz, DMSO– d_6) δ 8.89 (s, 1H), 8.22 (d, J = 6.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.72 (s, 1H), 7.51 (d, J = 7.6 Hz, 2H), 6.87 (s, 1H), 5.26 (s, 2H). 13 C{ 1 H} NMR (100 MHz, DMSO– d_6) δ 144.4, 143.7, 143.3, 139.3, 136.7, 132.6, 129.9, 129.0, 128.3, 124.5, 122.7, 105.6, 91.0, 48.6. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₄H₁₀N₂Cl 241.0533; found 241.0537.

2.3 Preparation of starting materials

2.3.1. General procedure for synthesis of S1

$$R^{1} \stackrel{\text{II}}{\longleftarrow} OH \xrightarrow{\text{NaBH}_4, \text{I}_2} R^{1} \stackrel{\text{II}}{\longleftarrow} OH \xrightarrow{\text{AcOH, 100 °C}} R^{1} \stackrel{\text{II}}{\longleftarrow} Br$$

A 100 mL round-bottom flask was charged with benzoic acid (8 mmol) and THF (20 mL, pre-dried over sodium). NaBH₄ (2.5 equiv) was added and cooled in an ice bath. A solution of I₂ (1.0 equiv) in THF (10 mL) was added dropwise over 30 min with vigorous evolution of hydrogen. After the flask was heated to reflux for 12 h and then cooled to room temperature, diluted with methanol until the solid disappeared. After stirring 30 min, the solvent was removed by rotary evaporation leaving a white paste which was dissolved by addition of 20% aqueous KOH (20 mL). The solution was stirred for 4 h and extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under vacuum. The residue benzyl alcohol was used in the next step without purification. ¹

A solution of 40% W/V hydrogen bromide- H_2O (10 equiv, 6.5 mL) was added dropwise to the cooled benzyl alcohol (5 mmol) over 15 min. The mixture was heated reflux for 2 h and then cooled to room temperature, after which it was added to 30% aqueous NaOH to make the PH > 10. The solution was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 , filtered, and concentrated under vacuum. The residue benzyl bromide was used in the next step without purification.⁵

OH
$$CF_3COOH$$
, $AgNO_3$ OH PBr_3 OH CH_2CI_2 S2

A 100 mL round-bottom flask was charged with benzyl alcohol (10 mmol), CF₃COOH (13 mmol) and AgNO₃ (13 mmol). Then MeOH (15 mL) was added and cooled in an ice bath. A solution of I₂ (1.0 equiv) in MeOH (25 mL) was added dropwise over 30 min. The resulting reaction mixture was monitored by TLC. Then filtered and concentrated under vacuum. The residue benzyl alcohol was used in the next step without purification. PBr₃ (1.5 mL, 16 mmol) was added over a solution of alcohols (8 mmol) in dry CH₂Cl₂ (100 mL), and the reaction mixture was stirred at rt for 16 h. Solvent was evaporated, and the resulting oil was treated with saturated NaHCO₃. The resulting aqueous phase was extracted with CH₂Cl₂. The combined organic extracts were dried Na₂SO₄ and concentrated in vacuo, yielding bromides, which were crystallised from Et₂O. White solid, 2.25g, 82%, mp 73–74 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.24 (s, 1H), 6.96 (s, 1H), 5.99 (s, 2H), 4.55 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 148.8 (two peaks), 133.5, 119.2, 110.1, 102.1, 88.9, 39.7.²

To a cold -78°C stirred solution of n-BuLi (30 mmol) in dry Et₂O was added TMEDA (30 mmol) followed 10 min later by a solution of 1-naphthalenemethanol (12 mmol) in dry Et₂O (50 mL). The pale green mixture was warmed to rt, becoming deep blue, and was stirred for 4 h. The reaction mixture was treated with a solution of resublimed iodine (14.4 mmol) in dry Et₂O (50 mL), becoming colorless. To the mixture was

added 75 mL of saturated aqueous Na₂S₂O₃. The aqueous phase was extracted with Et₂O (75 mL). The combined organic extracts were dried Na₂SO₄ and concentrated. Purified on silica gel chromatography using petroleum ether/EtOAc (10:1) to give the product. White solid, 1.23g, 36%, mp 134–135 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.58-7.48 (m, 3H), 5.28 (s, 2H), 2.03 (s, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 138.5, 136.1, 133.6, 132.7, 130.4, 128.7, 127.5, 126.6, 124.6, 99.9, 67.4.³

A 100 mL round-bottom flask was charged with 1-nitronaphthalene (10 mmol) under Ar. Then THF (70 mL) was added in -40 °C. Vinylmagnesium bromide (30 mmol) was added dropwise over 30 min. The resulting reaction mixture was monitored by TLC. After which it was added to saturated NH₄Cl. The solution was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered, concentrated and purified on silica gel chromatography using petroleum ether/EtOAc (20:1) to give the product. Yellow solid, 650 mg, 39%, mp 158–159 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.78 (s, 1H), 7.92 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 8.4 Hz, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.23-7.21 (m, 1H), 6.69 (t, J = 2.4 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 130.5, 129.0, 125.6, 124.0, 123.9, 122.4, 121.8, 120.9, 120.8, 119.5, 104.4.⁴

2.3.2. General procedure for the synthesis of 1

$$R_1 \stackrel{\text{II}}{\underset{\text{H}}{||}} + R_2 \stackrel{\text{II}}{\underset{\text{II}}{||}} + R_2 \stackrel{\text{II}}{\underset{\text{DMSO, rt}}{||}} R_1 \stackrel{\text{ROH}}{\underset{\text{DMSO, rt}}{||}} R_1 \stackrel{\text{ROH}}{\underset{\text{II}}{||}} R_2 \stackrel{\text{II}}{\underset{\text{II}}{||}} R_$$

KOH (2 equiv) was weighed directly into a schlenk tube and dried under vacuum for 15 min. Then DMSO (10 mL) was added and stirred for 5 minutes, indole (5 mmol) was slowly added. After stirring for 30 min, S1 or S2 (1.2 equiv) was added. The resulting reaction mixture was monitored by TLC. The reaction was quenched by H₂O and extracted with Et₂O. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered, concentrated and purified on silica gel chromatography (EtOAc/CH₂Cl₂/petroleum ether as eluent) to give the product.⁵

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/EtOAc (30:1) to give the product, white solid (1.23 g, 74%), mp 75–76 °C. 1 H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.22-7.10 (m, 5H), 6.94 (t, J = 7.6 Hz, 1H), 6.59 (d, J = 2.8 Hz, 1H), 6.45 (d, J = 8.0 Hz, 1H), 5.28 (s, 2H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 139.6, 139.5, 136.3, 129.4, 128.8 (two peaks), 128.4, 127.7, 122.0, 121.2, 119.9, 109.8, 102.2, 97.2, 55.2. 6

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/EtOAc (30:1) to give the product, white solid (1.74 g, 100%), mp 83–84 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.18 (td, J = 7.2, 1.2 Hz, 1H), 7.16 (td, J = 7.6, 1.2 Hz, 1H), 7.13 (d, J = 2.8 Hz, 1H), 6.82 (d, J = 8.8 Hz, 1H), 6.61 (d, J = 2.8 Hz, 1H), 6.42 (s, 1H), 5.29 (s, 2H), 2.13 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 139.3, 139.2, 139.0, 136.4, 130.4, 128.7, 128.6, 128.4, 122.0, 121.1, 119.8, 109.8, 102.1, 93.4, 55.1, 21.2. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₆H₁₅IN 348.0244, found 348.0245.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/EtOAc (20:1) to give the product, white solid (1.62 g, 86%), mp 128–129 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 7.6 Hz, 1H), 7.29 (s, 1H), 7.25-7.10 (m, 4H), 6.58 (s, 1H), 6.03 (s, 1H), 5.88 (s, 2H), 5.22 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 149.0, 148.0, 136.2, 133.1, 128.8, 128.2, 122.1, 121.21, 119.9, 118.7, 109.8, 108.1, 102.3, 101.8, 85.0, 55.1. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₆H₁₃INO₂ 377.9985, found 377.9991.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/EtOAc (20:1) to give the product, white solid (1.36 g, 77%), mp 85–86 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 7.6 Hz, 1H), 7.43 (d, J = 2.8 Hz, 1H), 7.24 (s, 1H), 7.19 (td, J = 7.6, 1.2 Hz, 1H), 7.17-7.11 (m, 1H), 7.09 (d, J = 3.2 Hz, 1H), 6.71 (dd, J = 8.8, 2.4 Hz, 1H), 6.57 (d, J = 3.2 Hz, 1H), 6.46 (d, J = 8.8 Hz, 1H), 5.25 (s, 2H), 3.74 (s, 3H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 159.3, 136.3, 131.5, 128.8, 128.4, 128.3, 124.8, 121.9, 121.1, 119.8, 114.6, 109.9, 102.0, 97.5, 55.6, 54.4. HRMS (ESI–TOF) m/z: [M+H] $^{+}$ calcd for C₁₆H₁₅INO 364.0193, found 364.0196.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/EtOAc (30:1) to give the product, white solid (1.65 g, 86%), mp 108-109 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J=8.8 Hz, 1H), 7.86 (d, J=8.0 Hz, 1H),

7.83 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.42-7.33 (m, 2H), 7.20 (t, J = 7.6 Hz, 1H), 6.66 (d, J = 2.8 Hz, 1H), 6.40 (d, J = 3.2 Hz, 1H), 5.86 (s, 2H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 136.4 (two peaks), 134.2, 133.5, 133.2, 130.8, 128.9 (two peaks), 128.1, 126.8, 126.4, 124.0, 121.8, 121.2, 119.9, 109.4, 102.5, 101.7, 52.3. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₉H₁₅IN 384.0244, found 384.0248.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/EtOAc (30:1) to give the product, white solid (1.5 g, 86%), mp 103–104 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.22-7.15 (m, 4H), 6.98 (t, J = 7.6 Hz, 1H), 6.90 (s, 1H), 6.51 (d, J = 7.6 Hz, 1H), 5.26 (s, 2H), 2.40 (s, 3H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 139.9, 139.4, 136.7, 129.3, 129.0, 128.8, 127.7, 125.9, 122.0, 119.2, 119.1, 111.4, 109.6, 97.2, 54.9, 9.8. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₆H₁₅IN 348.0244, found 348.0246.

This compound was prepared according to the general procedure from **S4**. Purified on silica gel chromatography using petroleum ether/EtOAc (30:1) to give the product, white solid (1.63 g, 85%), mp 138–139 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.8 Hz, 1H), 7.30-7.28 (m, 2H), 7.04 (d, J = 2.8 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 6.70 (d, J = 2.8 Hz, 1H), 6.33 (d, J = 7.6 Hz, 1H), 5.59 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 139.6, 139.4, 131.5, 129.4, 129.2, 129.0, 128.9, 127.5, 126.2, 125.6, 123.5, 122.6, 121.7, 121.1, 120.5, 103.6, 96.4, 59.1. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₉H₁₅IN 384.0244, found 384.0246.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (30:2:1) to give the product, white solid (1.69 g, 82%), mp 91–92 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.0 Hz, 1H), 7.78 (s, 1H), 7.24 (t, J = 4.4 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.09-7.05 (m, 2H), 6.96 (t, J = 7.6 Hz, 1H), 6.51 (d, J = 2.8 Hz, 1H), 6.42 (d, J = 7.6 Hz, 1H), 5.25 (s, 2H). 13 C{¹H} NMR (100 MHz, CDCl₃) δ 139.6, 139.1, 135.1, 130.4, 129.6, 128.8, 127.6, 124.9, 123.7, 113.2, 111.3, 101.8, 97.3, 55.4. HRMS (ESI–TOF) m/z: [M+H]+ calcd for C₁₅H₁₂BrIN 411.9192, found 411.09201.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/EtOAc (30:1) to

give the product, white solid (1.55 g, 88%), mp 71–72 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 7.6 Hz, 1H), 7.59 (dd, J = 9.2, 5.6 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 3.2 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.92 (t, J = 8.4 Hz, 2H), 6.59 (d, J = 3.2 Hz, 1H), 6.49 (d, J = 7.6 Hz, 1H), 5.25 (s, 2H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 160.0 (d, J = 236.4 Hz), 139.6, 139.1, 136.4 (d, J = 12.0 Hz), 129.5, 128.8, (d, J = 3.7 Hz), 127.6, 126.8, 125.2, 121.9 (d, J = 9.1 Hz), 108.7 (d, J = 24.2 Hz), 102.4, 97.3, 96.3 (d, J = 26.2 Hz), 55.4. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₅H₁₂FIN 351.9993, found 351.9998.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (30:2:1) to give the product, white solid (1.31 g, 71%), mp 109–110 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (dd, J = 8.0, 1.2 Hz, 1H), 7.11-6.99 (m, 5H), 6.89 (td, J = 8.8, 1.6 Hz, 1H), 6.66 (dd, J = 3.2, 0.8 Hz, 1H), 6.38 (d, J = 7.6 Hz, 1H), 5.18 (s, 2H). ¹³C{ ¹H} NMR (CDCl₃, 100 MHz) δ 139.7, 139.1, 137.2, 129.6, 129.0, 128.9, 127.7, 127.6, 126.5, 122.7, 119.7, 108.6, 101.0, 97.3, 55.6. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₅H₁₂NClI 367.9703; found 367.9707.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (30:2:1) to give the product, white solid (1.47 g, 80%), mp 71–72 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (dd, J = 8.0, 0.8 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.19 (s, 1H), 7.12 (td, J = 8.0, 0.8 Hz, 1H), 7.07 (dd, J = 8.4, 2.0 Hz, 1H), 7.04 (d, J = 3.2 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 6.54 (d, J = 3.2 Hz, 1H), 6.42 (d, J = 7.6 Hz, 1H), 5.19 (s, 2H). 13 C{¹H} NMR (CDCl₃, 100 MHz) δ 139.7, 139.1, 136.9, 129.6, 129.1, 128.9, 128.2, 127.7, 127.3, 122.1, 120.7, 109.9, 102.5, 97.4, 55.4. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₅H₁₂NClI 367.9703; found 367.9707.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (30:2:1) to give the product, white solid (1.71 g, 93%), mp 98–99 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (dd, J = 8.0, 1.2 Hz, 1H), 7.53 (dd, J = 8.0, 1.2 Hz, 1H), 7.11-7.07 (m, 2H), 7.02-6.98 (m, 2H), 6.90 (td, J = 8.8, 1.6 Hz, 1H), 6.58 (d, J = 3.2 Hz, 1H), 6.24 (d, J = 7.6 Hz, 1H), 5.63 (s, 2H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 141.3, 139.4, 131.9, 131.6, 131.1, 129.1, 128.8, 127.0, 123.8, 120.8, 120.1, 117.0, 102.9, 96.2, 57.5. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₅H₁₂NClI 367.9703; found 367.9707.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (30:2:1) to give the product, white solid (1.75 g, 95%), mp 57–58 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 8.4 Hz, 1H), 7.67 (dt, J = 7.6, 1.2 Hz, 1H), 7.19-7.12 (m, 3H), 7.07 (d, J = 3.2 Hz, 1H), 6.94 (dd, J = 8.4, 2.8 Hz, 1H), 6.60 (dd, J = 3.2, 0.4 Hz, 1H), 6.47 (d, J = 2.4 Hz, 1H), 5.22 (s, 2H). 13 C{ 1 H} NMR (CDCl₃, 100 MHz) δ 141.5, 140.5, 136.3, 135.5, 129.7, 128.8, 128.1, 127.8, 122.3, 121.3, 120.1, 109.6, 102.8, 94.1, 55.0. HRMS (ESI–TOF) m/z: [M+H] $^{+}$ calcd for C₁₅H₁₂NClI 367.9703; found 367.9700.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (20:2:1) to give the product, white solid (1.41 g, 79%), mp 103–104 °C . ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.0 Hz, 1H), 7.47 (dd, J = 11.6, 7.6 Hz, 2H), 7.28 (d, J = 3.2 Hz, 1H), 7.23-7.17 (m, 2H), 7.00 (t, J = 8.0 Hz, 1H), 6.80 (d, J = 3.2 Hz, 1H), 6.48 (d, J = 7.6 Hz, 1H), 5.34 (s, 2H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 139.7, 138.5, 136.0, 131.0, 129.9, 129.8, 128.9, 127.6, 125.3, 121.6, 118.7, 114.6, 103.5, 101.2, 97.4, 55.4. HRMS (ESI–TOF) m/z: [M+H] $^{+}$ calcd for C₁₅H₁₂IN₂ 359.0040, found 359.0045.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (30:2:1) to give the product, white solid (1.85 g, 90%), mp 86–87 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.69-7.66 (m, 2H), 7.21-7.16 (m, 2H), 7.15-7.11 (m, 1H), 7.08-7.04 (m, 2H), 6.63 (d, J = 2.4 Hz, 1H), 6.60 (d, J = 3.2 Hz, 1H), 5.21 (s, 2H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 141.7, 140.8, 136.3, 132.6, 130.7, 128.8, 128.1, 123.4, 122.3, 121.3, 120.1, 109.6, 102.8, 95.1, 54.9. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₅H₁₂NBrI 411.9198; found 411.9200.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (10:2:1) to give the product, brown solid (0.84 g, 50%), mp 132–133 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.48 (dd, J = 4.8, 1.6 Hz, 1H), 7.88 (dd, J = 8.0, 1.2 Hz, 1H), 7.51 (dt, J = 8.4, 1.2 Hz, 1H), 7.34 (d, J = 3.2 Hz, 1H), 7.17 (td, J = 7.6, 1.2 Hz, 1H), 7.08 (dd, J = 8.4, 4.8 Hz, 1H), 6.98

(td, J = 8.0, 1.6 Hz, 1H), 6.79 (dd, J = 3.2, 0.8 Hz, 1H), 6.49 (d, J = 8.0 Hz, 1H), 5.30 (s, 2H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 147.1, 143.7, 139.8, 138.9, 131.6, 129.7, 129.4, 128.9, 127.8, 117.1, 116.8, 103.5, 97.4, 55.5. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₄H₁₂N₂I 335.0045; found 335.0048.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (10:2:1) to give the product, yellow solid (1.42 g, 85%), mp 124–125 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.95 (s, 1H), 8.28 (d, J = 6.0 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.18-7.10 (m, 3H), 6.97 (t, J = 7.6 Hz, 1H), 6.66 (d, J = 1.2 Hz, 1H), 6.49 (d, J = 7.6 Hz, 1H), 5.28 (s, 2H)). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 144.1, 141.1, 140.0, 139.7, 138.6, 129.7, 129.2, 128.8, 127.7, 125.5, 105.1, 102.0, 97.4, 55.0. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₄H₁₂IN₂ 335.0040, found 335.0045.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (10:2:1) to give the product, white solid (1.62 g, 97%), mp 81–82 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.35 (dd, J = 4.8, 1.2 Hz, 1H), 7.96 (dd, J = 7.6, 1.6 Hz, 1H), 7.87 (dd, J = 8.0, 0.8 Hz, 1H), 7.21 (d, J = 3.6 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.10 (dd, J = 8.0, 4.4 Hz, 1H), 6.95 (t, J = 7.6 Hz, 1H), 6.69 (d, J = 7.6 Hz, 1H), 6.53 (d, J = 3.6 Hz, 1H), 5.53 (s, 2H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 147.8, 143.3, 140.0, 139.6, 129.3, 129.0, 128.7, 128.3, 128.1, 120.5, 116.2, 100.5, 98.0, 52.8. HRMS (ESI–TOF) m/z: [M+H]+ calcd for C₁₄H₁₂IN₂ 335.0040, found 335.0044.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (10:2:1) to give the product, white solid (1.51 g, 80%), mp 106-107 °C. 1 H NMR (400 MHz, CDCl₃) δ 8.34 (dd, J = 4.4, 1.6 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.25 (s, 1H), 7.21 (d, J = 3.2 Hz, 1H), 7.09-7.06 (m, 1H), 6.49-6.48 (m, 1H), 6.34 (s, 1H), 5.86-5.84 (m, 2H), 5.43 (s, 2H). 13 C{ 1 H} NMR (CDCl₃, 100 MHz) δ 148.9, 148.1, 147.8, 143.3, 133.6, 129.1, 127.9, 120.6, 118.8, 116.2, 109.0, 101.8, 100.6, 86.0, 52.6. HRMS (ESITOF) m/z: [M+H]⁺ calcd for C₁₅H₁₂N₂O₂I 378.9943; found 378.9945.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (10:2:1) to give the product, yellow solid (1.29 g, 70%), mp 124–125 °C. 1 H NMR (400 MHz, CDCl₃) δ 8.98 (d, J = 0.8 Hz, 1H), 8.33 (d, J =

6.0 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.15 (td, J = 6.4, 1.2 Hz, 1H), 7.12 (d, J = 3.2 Hz, 1H), 7.00 (dd, J = 8.4, 2.4 Hz, 1H), 6.71 (dd, J = 3.2, 1.2 Hz, 1H), 6.47 (d, J = 2.4 Hz, 1H), 5.26 (s, 2H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 144.4, 141.4, 140.8, 140.6, 140.0, 135.6, 130.0, 129.0, 127.8, 125.6, 105.0, 102.6, 94.3, 54.7. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₄H₁₁N₂CII 368.9655; found 368.9659.

General procedure for 1j and 1k

To tube were added CuI (0.3 mmol), carbazole (20 mmol), K₃PO₄ (60 mmol), followed by Ar for 15 min. 1-bromo-4-iodobenzene (21 mmol) and trans-1,2-diaminocyclohexane (5 mmol) were added. Then toluene (60 mL) was added. The reaction tube was sealed and the contents stirred while being heating in an oil bath at 115 °C for 24 h. The reaction mixture was cooled to ambient temperature, diluted with ethyl acetate and filtered through a plug of celites, eluting with additional ethyl acetate. The filtrate was concentrated and the resulting residue purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (30:2:1) to give the product. White solid, 5.35 g, 83%, mp 138–139 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.41 (t, J = 7.6 Hz, 3H), 7.36 (t, J = 7.6 Hz, 3H), 7.28 (t, J = 7.6 Hz, 2H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 140.7, 136.9, 133.2, 128.8, 126.2, 123.6, 121.0, 120.5, 120.3, 109.7.

Bis(biphenyl-4-yl)amine (30 mmol), 1-bromo-4-iodobenzene (30 mmol), CuI (0.3 mmol), 'BuOK (45 mmol), trans-1,2-cyclohexanediamine (3 mmol) were added to 1,4-dioxane (50 mL). The mixture was stirred at 100° C for 12 h, then cooled to room temperature. Water (100 mL) and toluene (100 mL) were added to the mixture. The organic later was separated, dried NaSO4 and concentrated. The residue was washed with methanol and then purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (30:2:1) to give the product. White solid, 10.3 g, 72%, mp 169-170 °C. 1 H NMR (400 MHz, CDCl₃) δ 7.61 (d, J=7.6 Hz, 4H), 7.54 (d, J=8.4 Hz, 4H), 7.48 (t, J=8.0 Hz, 4H), 7.40 (d, J=8.4 Hz, 2H), 7.36 (t, J=7.2 Hz, 2H), 7.21 (d, J=8.4 Hz, 4H), 7.08 (d, J=8.8 Hz, 2H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 146.8, 146.6, 140.5, 136.1, 132.4, 128.9, 128.1, 127.1, 126.8, 125.7, 124.5, 115.4.6

n-BuLi (7.5 mL, 12 mmol) was added dropwise to a solution of Bromobenzene (10 mmol) in dry THF (40 mL) at -78°C in Ar. After 10 minutes, trimethyl borate (1.4 mL, 12 mmol) was added dropwise. The mixture was stirred for another 10 minutes at -78°C, and then allowed to warm to rt. The resulting mixture was neutralized with aqueous hydrochloric acid and stirred for 3 hours at room temperature. The product was extracted with chloroform, concentrated, washed with toluene, The residue product was used in the next step without purification.

 K_2CO_3 (2.76 g, 20 mmol) was added to a suspension of indole (5.5 mmol), phenylboronic acid (5 mmol) and Pd(PPh₃)₄ (0.25 mmol) at RT. Then THF/H₂O (30/5 mL) was added. After the mixture was stirred for 15 hours at 75°C, the solution was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered, concentrated and purified on silica gel chromatography (EtOAc/petroleum ether as eluent) to give the product. The residue product was used in the next step without purification.

KOH (2 equiv) was weighed directly into a Schlenk tube and dried under vacuum for 15 min. Then DMSO (10 mL) was added and stirred for 5 minutes, indole (5 mmol) was slowly added. After stirring for 30 min, 1-(bromomethyl)-2-iodobenzene (1.2 equiv) was added. The resulting reaction mixture was monitored by TLC. The reaction was quenched by H₂O and extracted with Et₂O. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered, concentrated and purified on silica gel chromatography (EtOAc/petroleum ether as eluent) to give the product.

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (20:2:1) to give the product, white solid (2.01 g, 70%), mp 219–220 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 1.2 Hz, 1H), 7.93 (dd, J = 7.6, 0.8 Hz, 1H), 7.90-7.86 (m, 2H), 7.65-7.63 (m, 2H), 7.56-7.51 (m, 3H), 7.46 (td, J = 7.2, 1.2 Hz, 2H), 7.37-7.31 (m, 3H), 7.23-7.19 (m, 2H), 7.01 (td, J = 8.0, 1.6 Hz, 1H), 6.72 (d, J = 2.4 Hz, 1H), 6.58 (dd, J = 8.0, 1.2 Hz, 1H), 5.37 (s, 2H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 141.7, 141.1, 139.6, 139.4, 136.1, 136.0, 132.5, 129.5, 129.4, 129.3, 128.9, 128.7, 127.7, 127.4, 126.0, 123.5, 121.8, 120.4, 120.0, 119.8, 110.3, 110.1, 102.8, 97.3, 55.4. HRMS (ESI–TOF) m/z: [M+H]+ calcd for C₃₃H₂₄IN₂ 575.0979, found 575.0989.

$N-([1,1'-biphenyl]-4-yl)-N-(4-(1-(2-iodobenzyl)-1H-indol-5-yl)phenyl)-[1,1'-biphenyl]-4-amine \ (1k)-(1,1'-biphenyl)-(1,1'-b$

This compound was prepared according to the general procedure. Purified on silica gel chromatography using petroleum ether/CH₂Cl₂/EtOAc (20:2:1) to give the product, white solid (2.37 g, 65%), mp 100–101 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 6.8 Hz, 2H), 7.57 (t, J = 8.0 Hz, 6H), 7.51 (d, J = 8.4 Hz, 4H), 7.41 (t, J = 7.6 Hz, 5H), 7.30 (t, J = 7.6 Hz, 2H), 7.26-7.22 (m, 7H), 7.17-7.11 (m, 2H), 6.95 (t, J = 7.6 Hz, 1H), 6.62 (d, J = 2.8 Hz, 1H), 6.51 (d, J = 7.6 Hz, 1H), 5.30 (s, 2H). 13 C{ 1 H} NMR (100 MHz, CDCl₃) δ 147.1, 146.1, 140.8, 139.6, 139.5, 137.4, 135.8, 135.5, 132.9, 129.5, 129.3, 129.1, 128.9 (two peaks), 128.2, 128.0, 127.8, 127.0, 126.8, 125.0, 124.3, 121.7, 119.3, 110.1, 102.6, 97.3, 55.4. HRMS (ESI–TOF) m/z: [M+H]+ calcd for C₄₅H₃₄IN₂ 729.1761, found 729.1749.

3. X-Ray Crystallographic Data

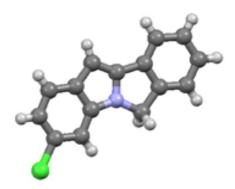


Table S1 Crystal data and structure refinement for 3-chloro-6*H*-isoindolo[2,1-a]indole

Empirical formula	C ₁₅ H ₁₀ ClN
Formula weight	239.69
Temperature/K	290(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	21.7792(5)
b/Å	5.94230(10)
c/Å	17.7812(4)
α/°	90
β/°	103.244(2)

γ/°	90
•	

Volume/ $Å^3$ 2240.01(8)

Z

 $\begin{array}{lll} \rho calcg/cm^{3} & 1.421 \\ \mu/mm^{-1} & 2.774 \\ F(000) & 992.0 \end{array}$

Crystal size/mm 3 0.250 × 0.240 × 0.200 Radiation CuK α (λ = 1.54184) 2 Θ range for data collection/ $^{\circ}$ 8.342 to 142.732

Index ranges $-19 \le h \le 26, -5 \le k \le 6, -21 \le 1 \le 21$

8

Reflections collected 7681

Independent reflections 4170 [Rint = 0.0258, Rsigma = 0.0309]

Data/restraints/parameters 4170/0/307Goodness-of-fit on F² 1.070

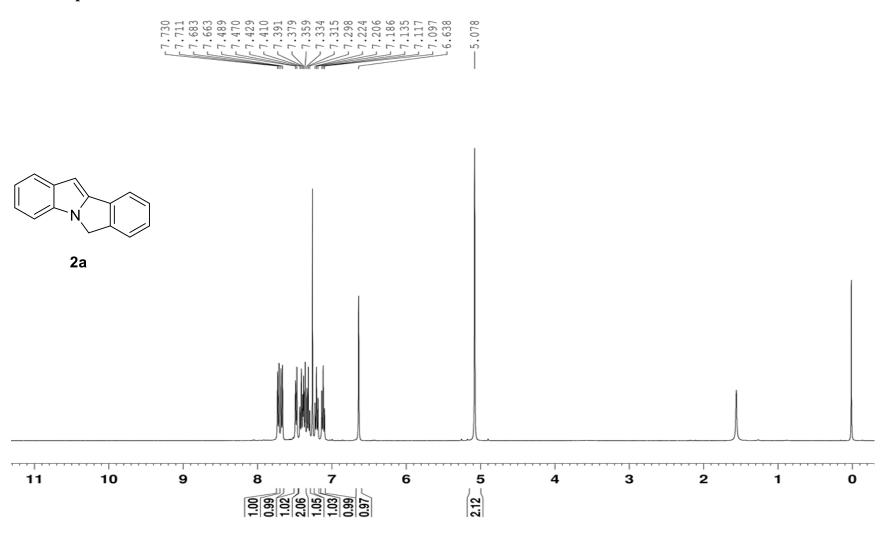
Final R indexes [I>= 2σ (I)] $R_1 = 0.0436, wR_2 = 0.1186$ Final R indexes [all data] $R_1 = 0.0487, wR_2 = 0.1235$

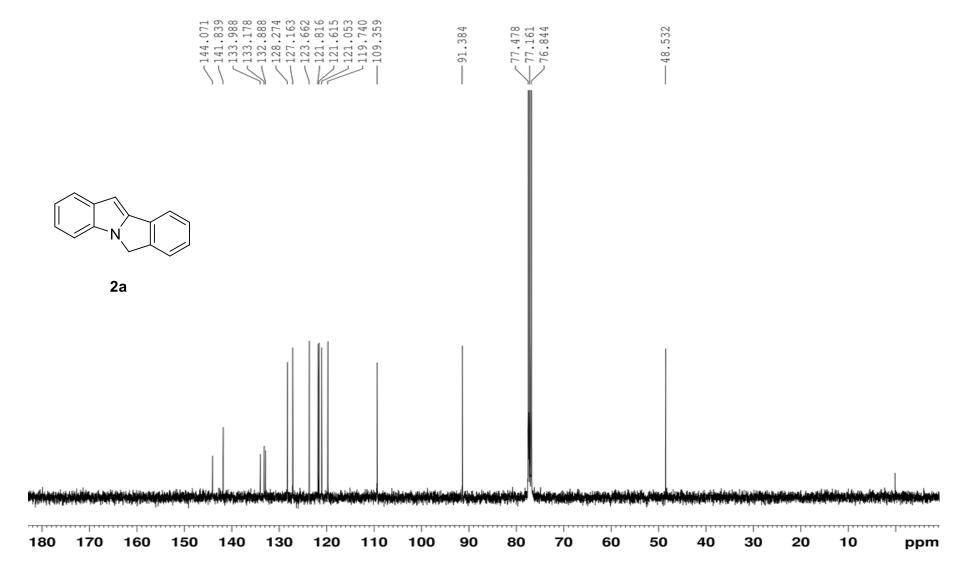
Largest diff. peak/hole / e Å-3 0.25/-0.27

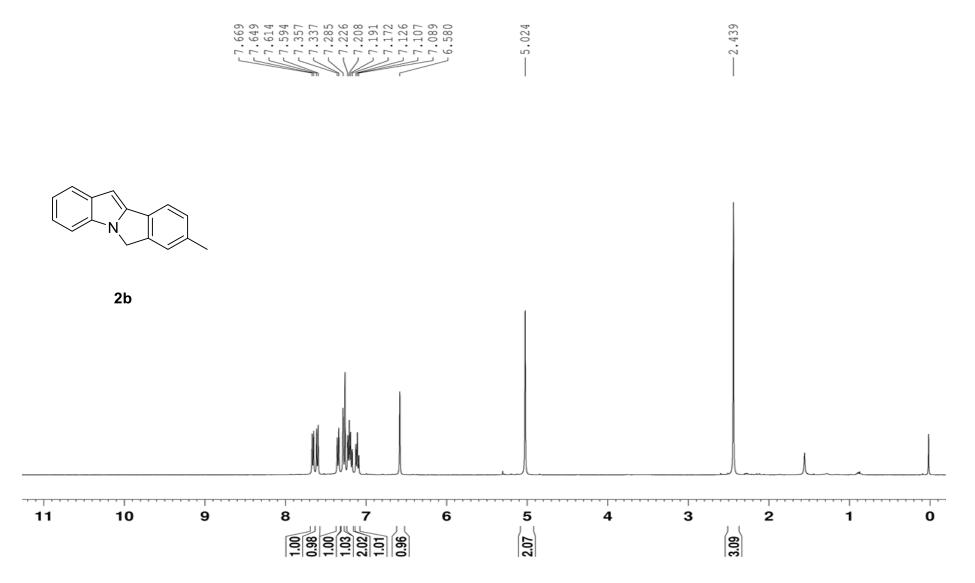
4. Reference

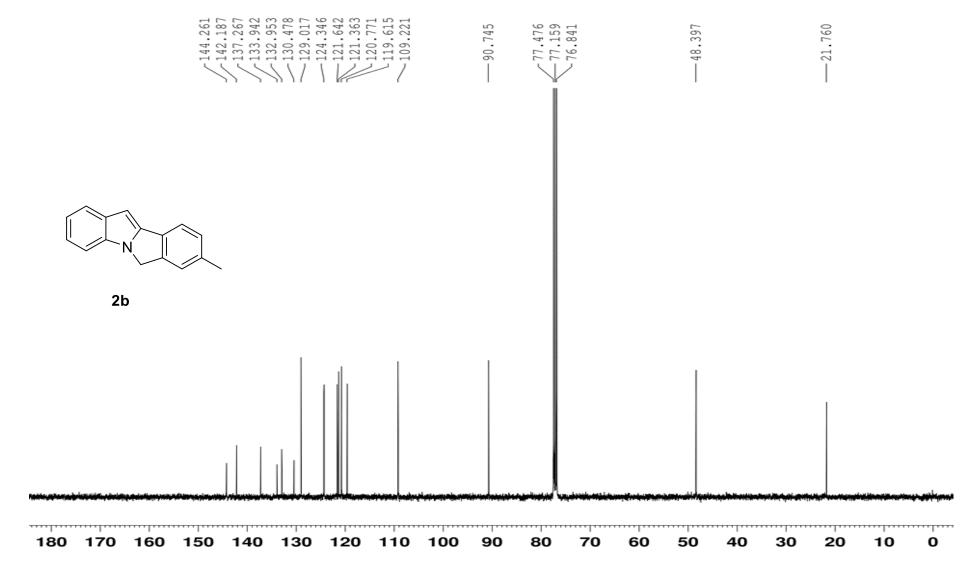
- 1 Zheng, H.-X.; Xiao, Z.-F.; Yao, C.-Z.; Li, Q.-Q.; Ning, X.-S.; Kang, Y.-B.; Tang, Y. Org. Lett. 2015, 17, 6102.
- 2 Ruiz, J.; Ardeo, A.; Ignacio, R.; Sotomayor, N.; Lete, E. Tetrahedron 2005, 61, 3311.
- 3 Piers, E.; Harrison, C. L.; Zetina-Rocha, C. Org. Lett. 2001, 3, 3245.
- 4 Bartoli, G.; Palmieri, G. Tetrahedron Lett. 1989, 30, 2129.
- 5 Barbero, N.; SanMartin, R.; Dominguez, E. Tetrahedron Lett. 2009, 50, 2129.
- 6 Zhang, Q.; Kuwabara, H.; Potscavage, W. J.; Huang, S.; Hatae, Y.; Shibata, T.; Adachi, C. J. Am. Chem. Soc. 2014, 136, 18070.

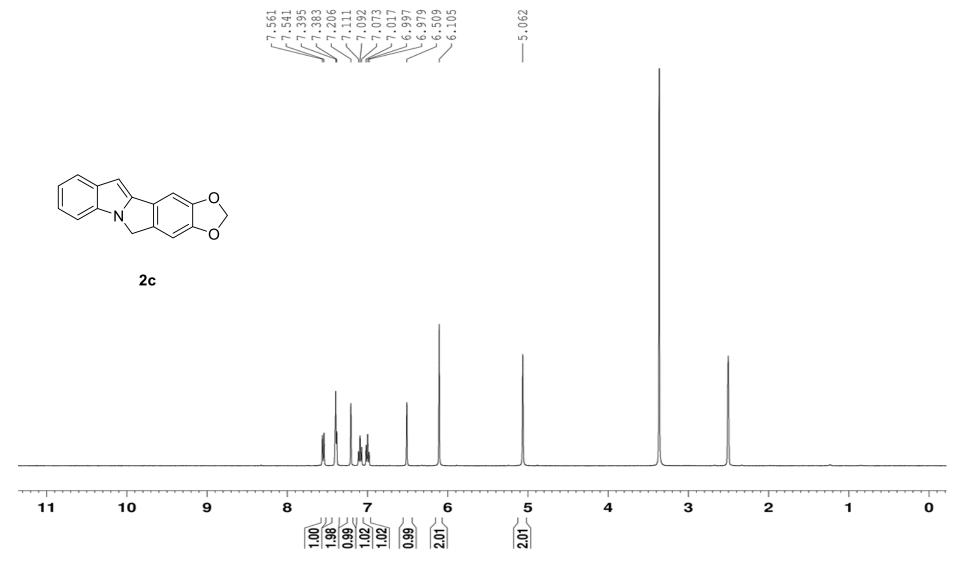
5. NMR spectra

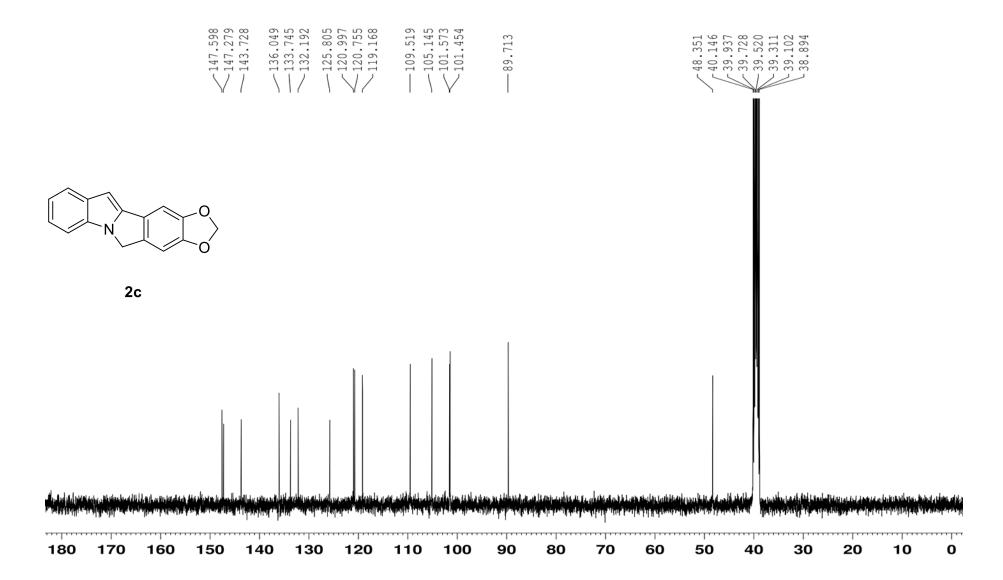


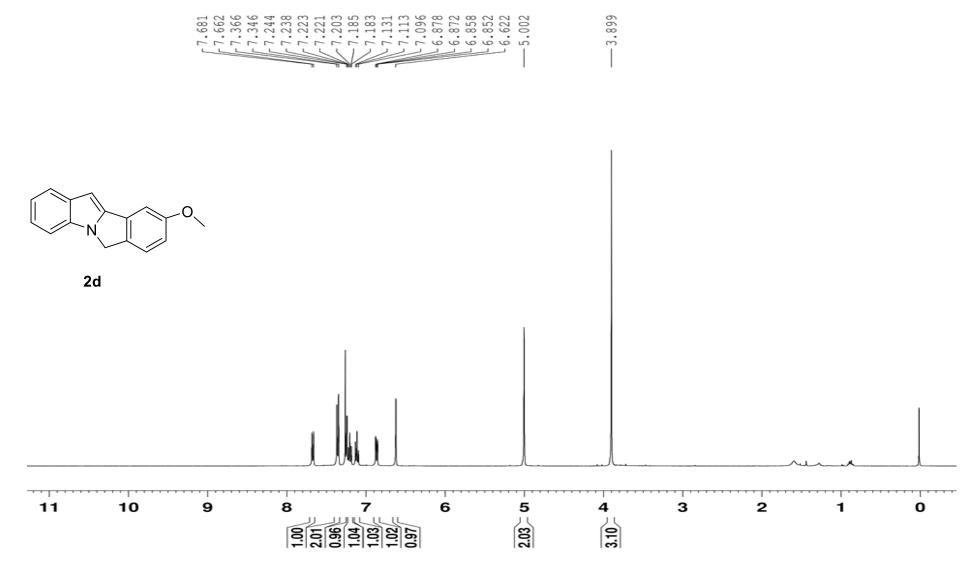


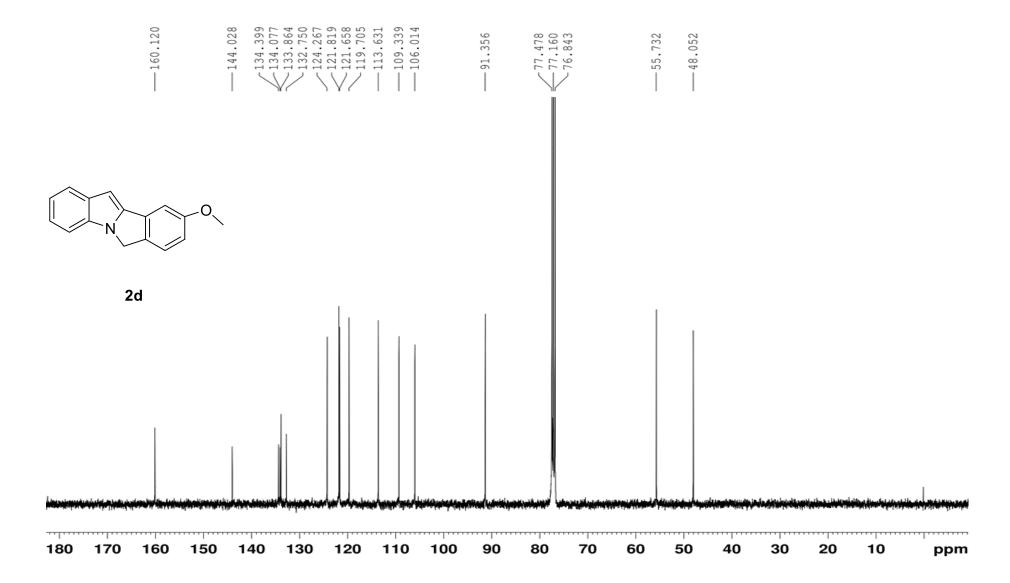




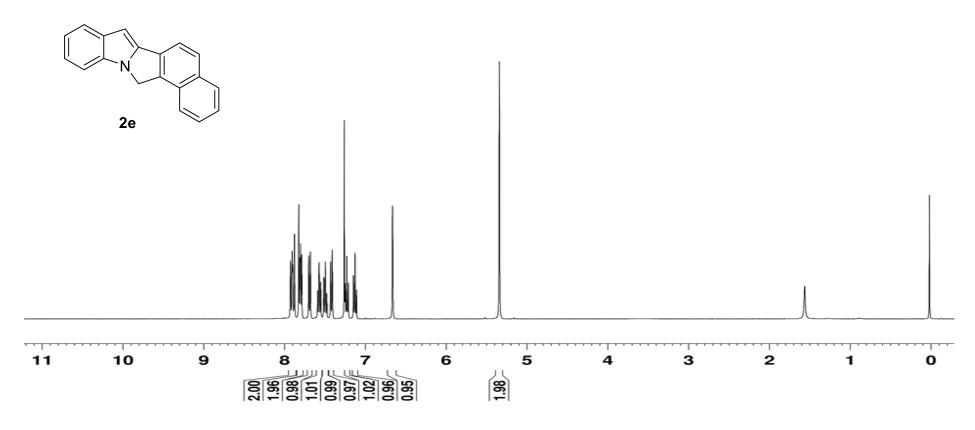


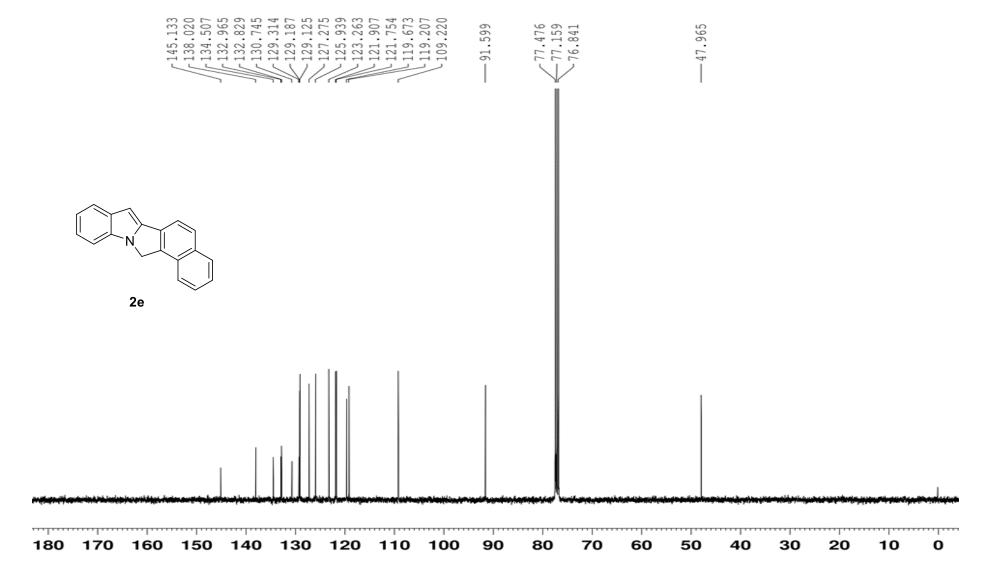


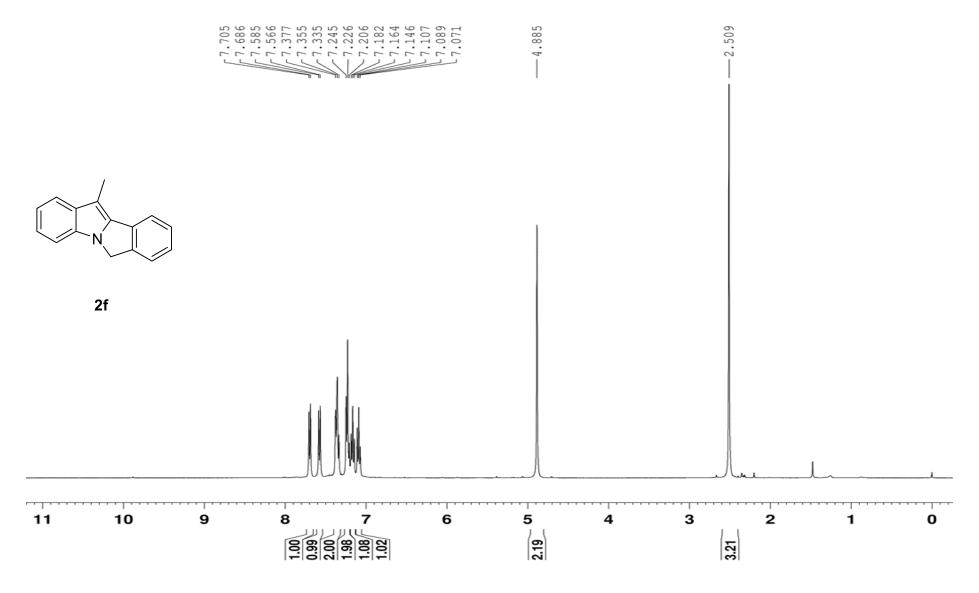


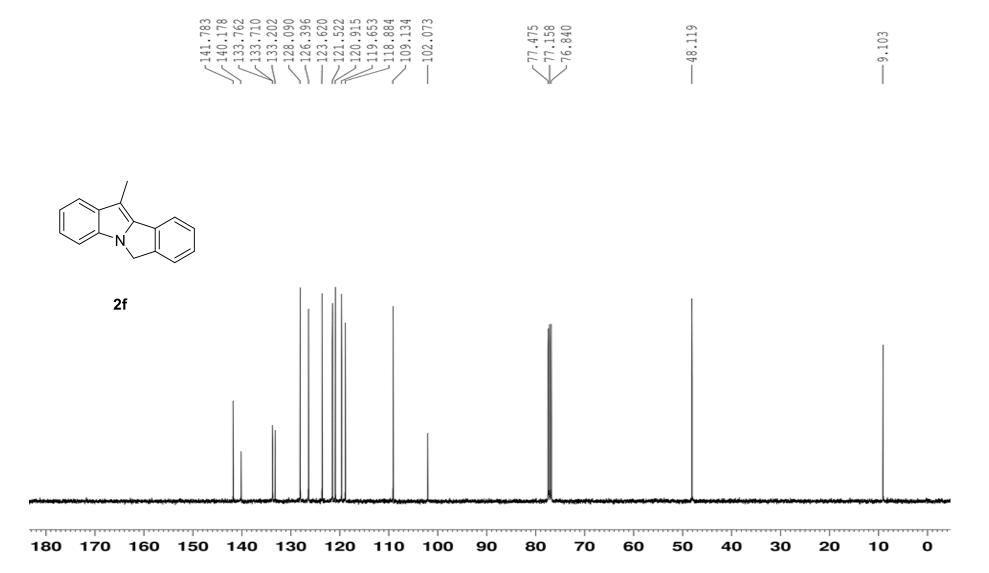


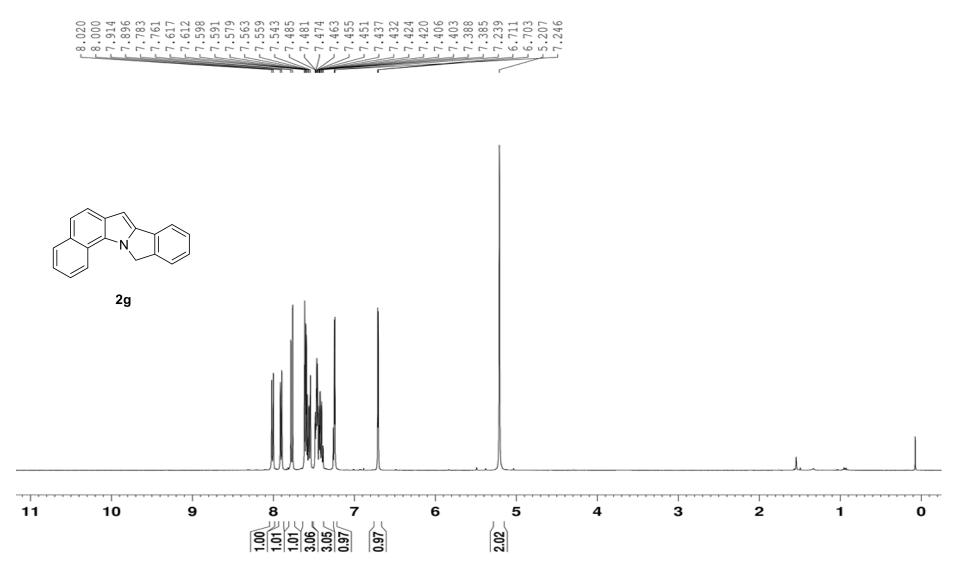


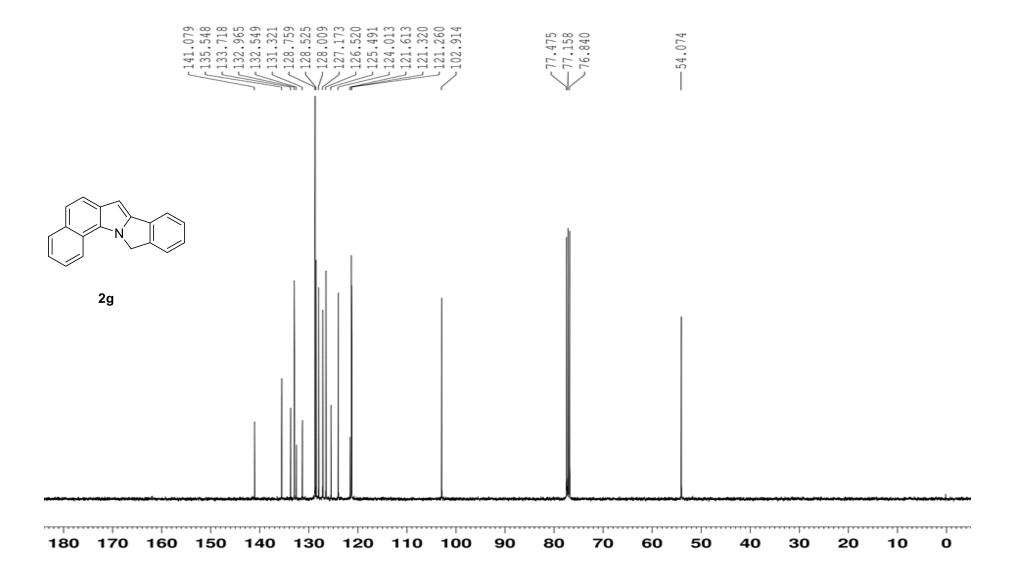


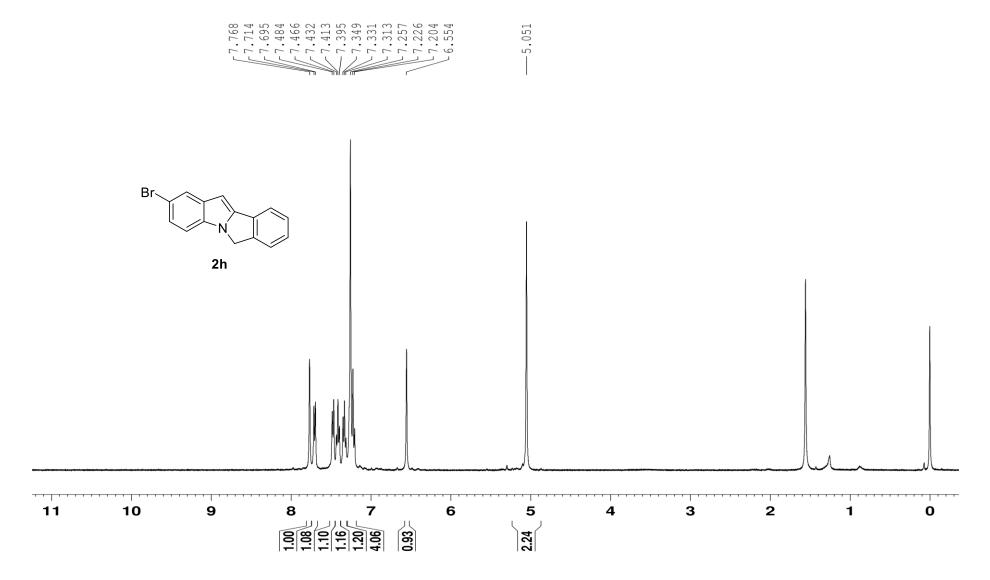


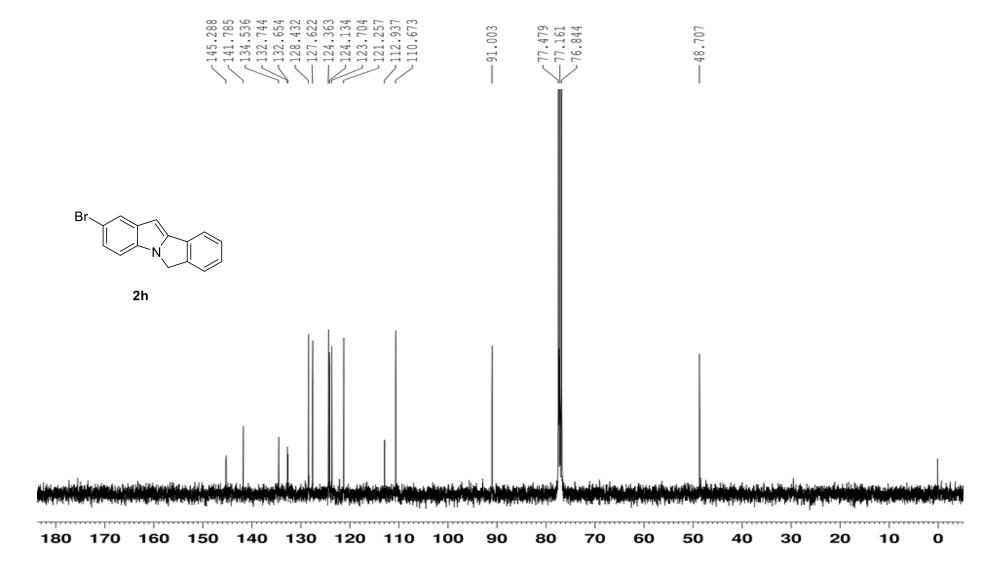


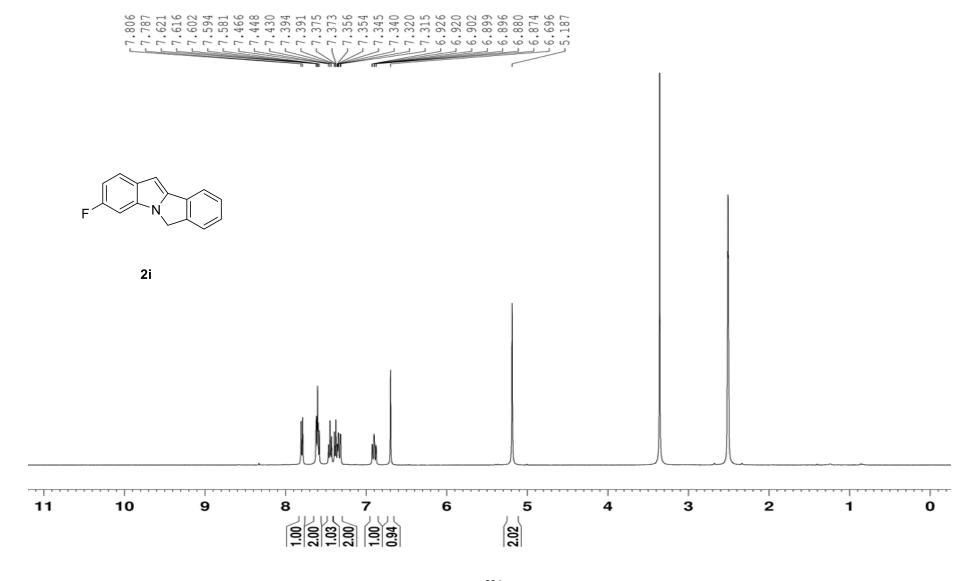


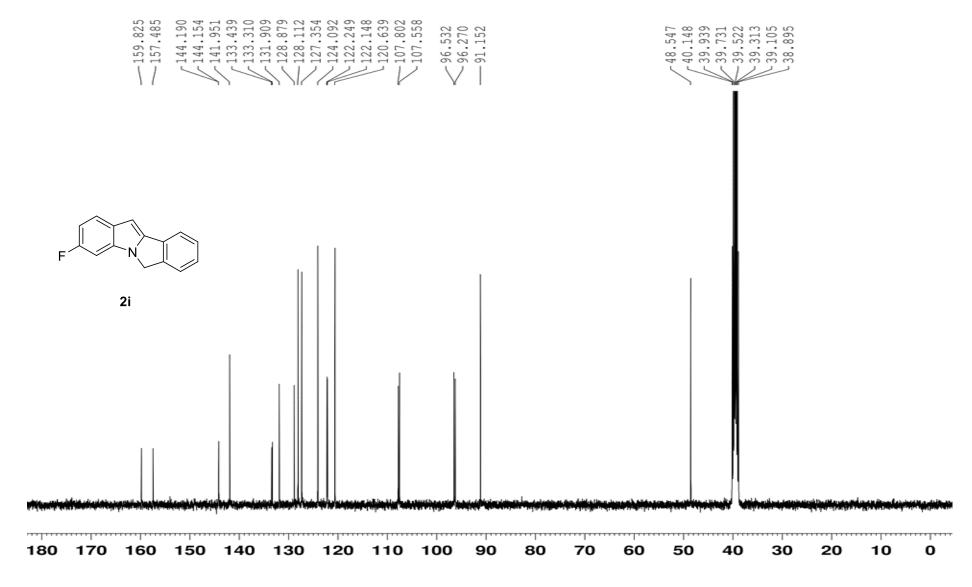




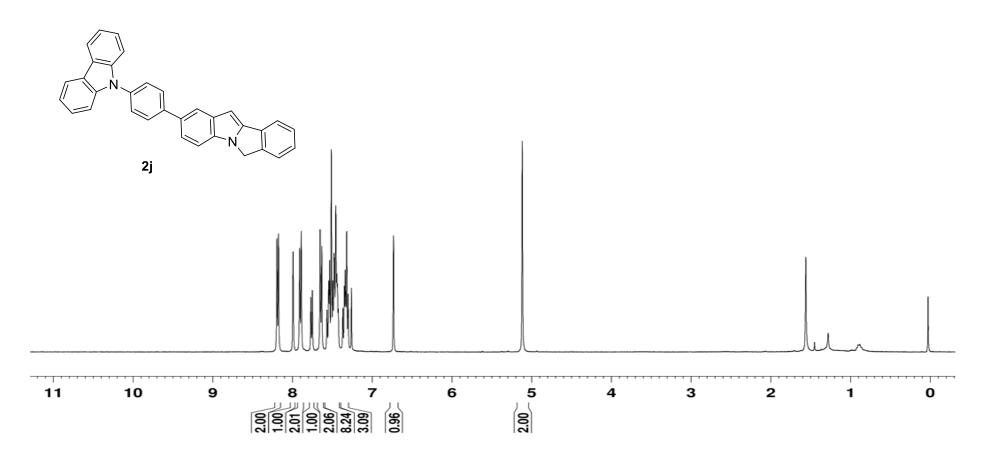


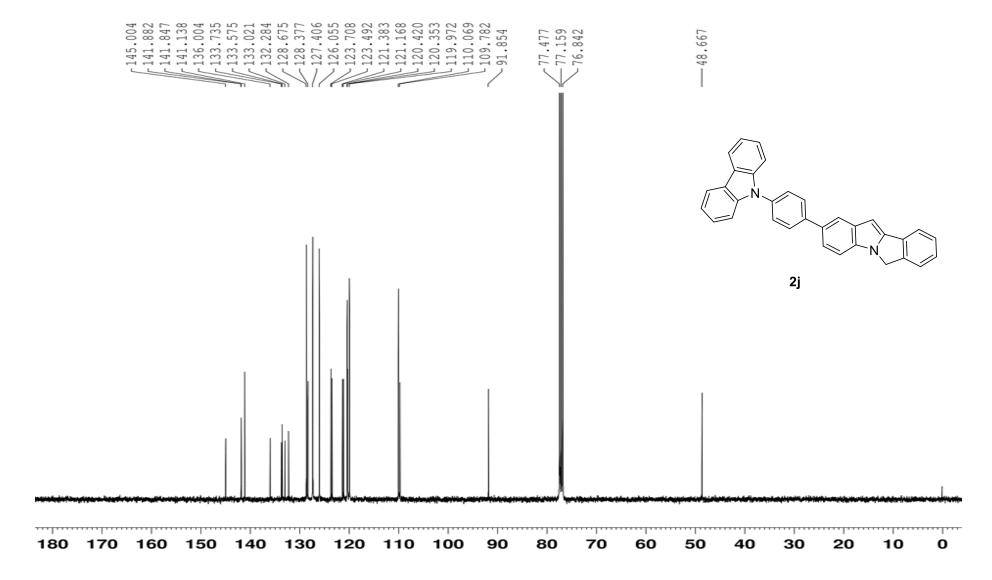


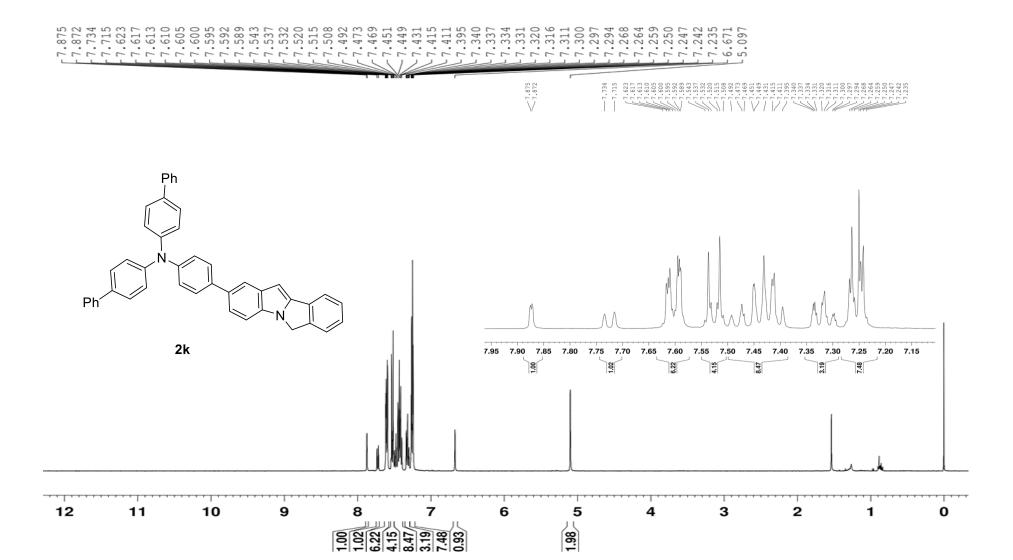


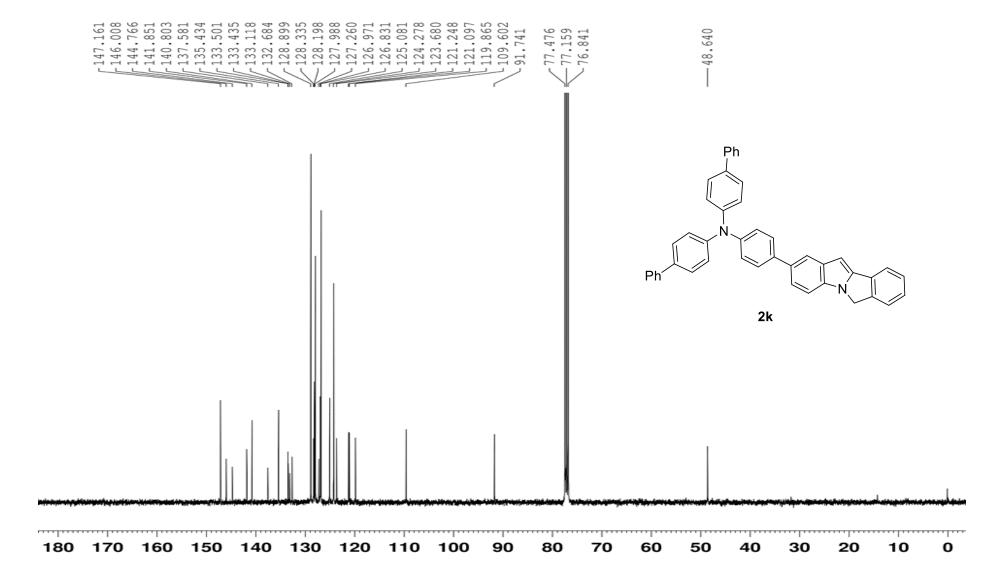


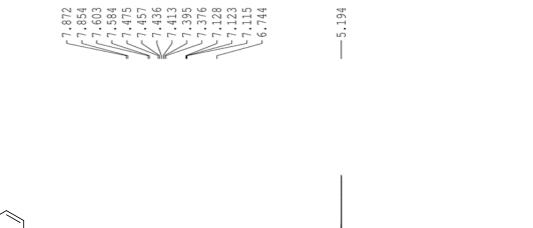


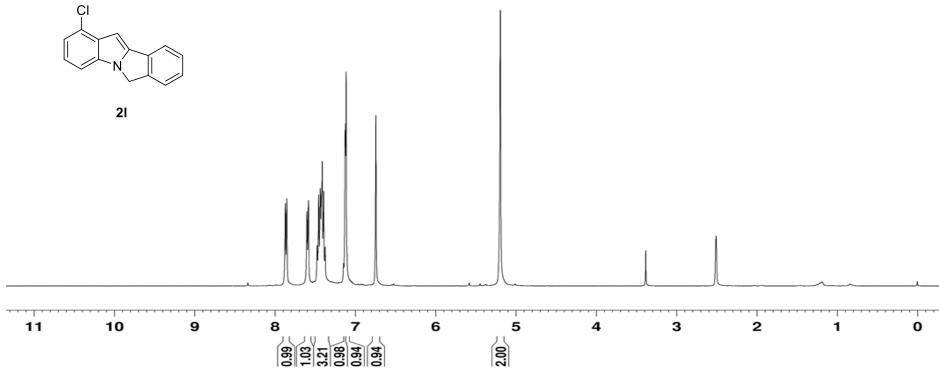


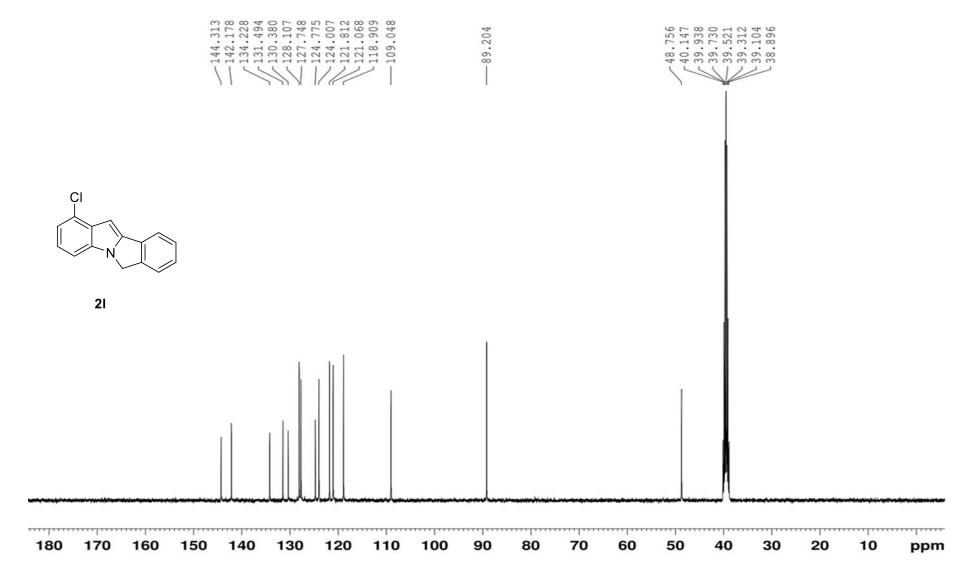


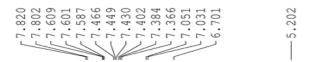


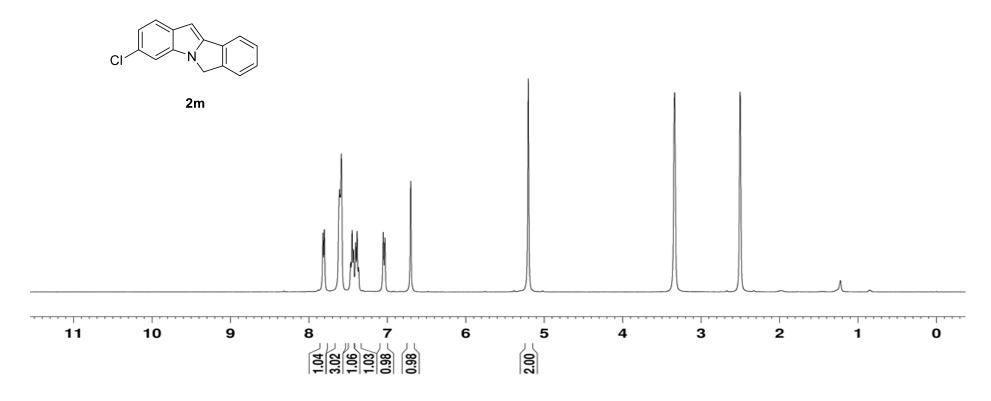


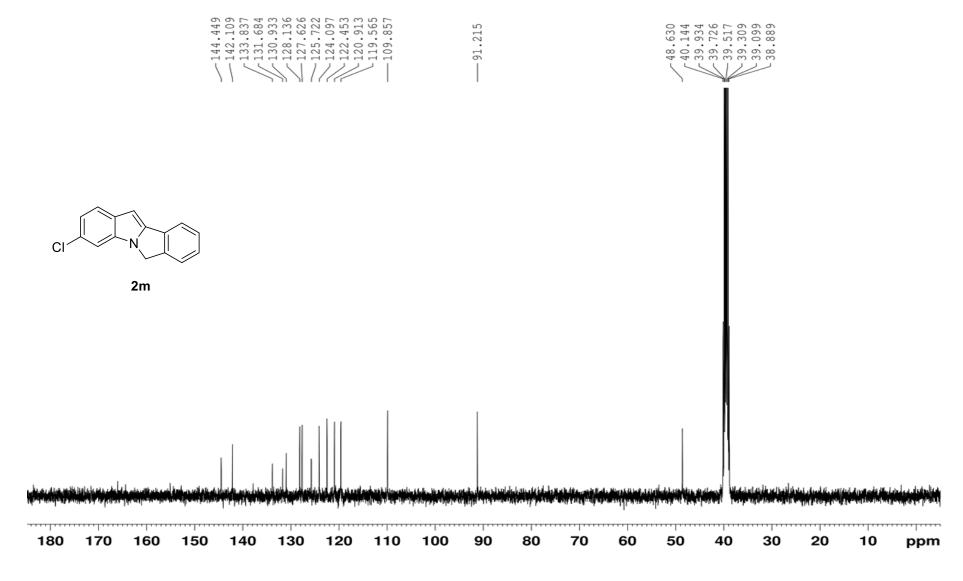




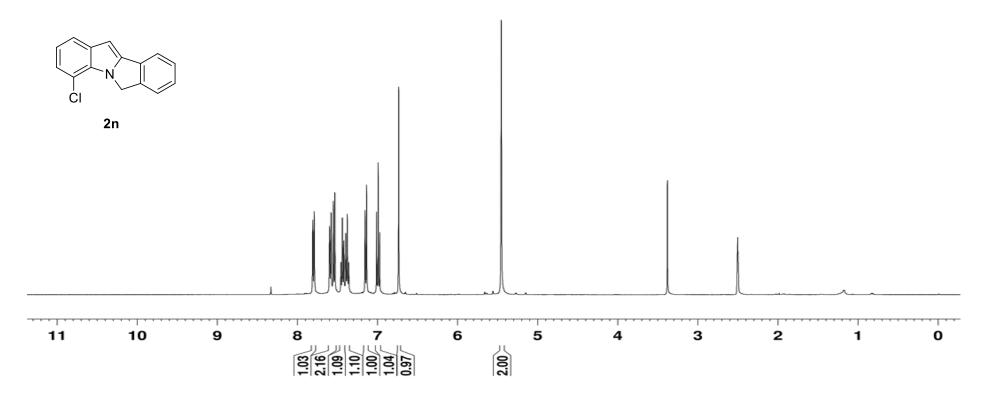


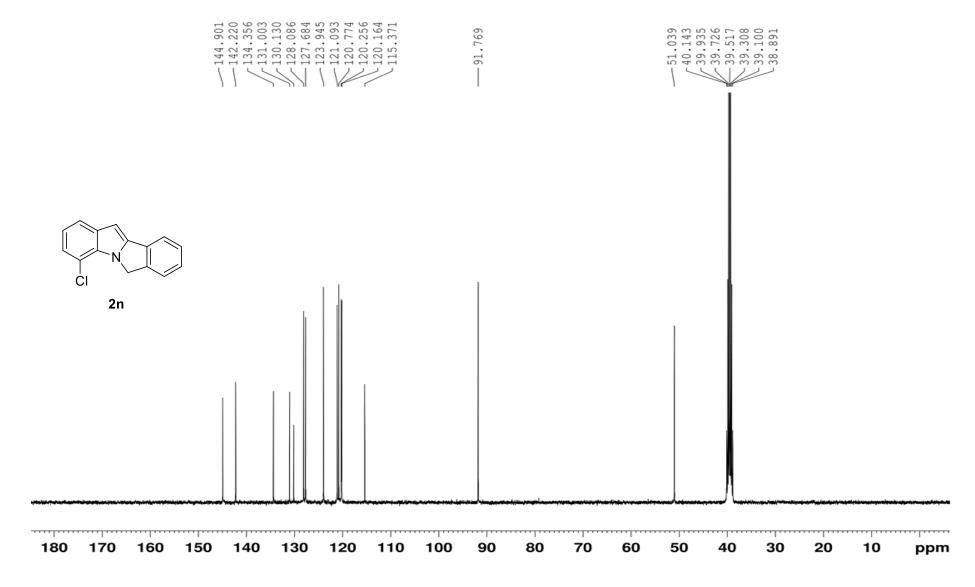




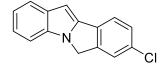


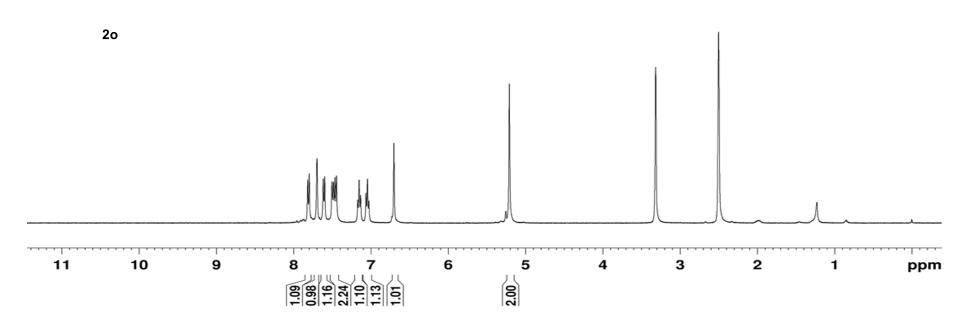


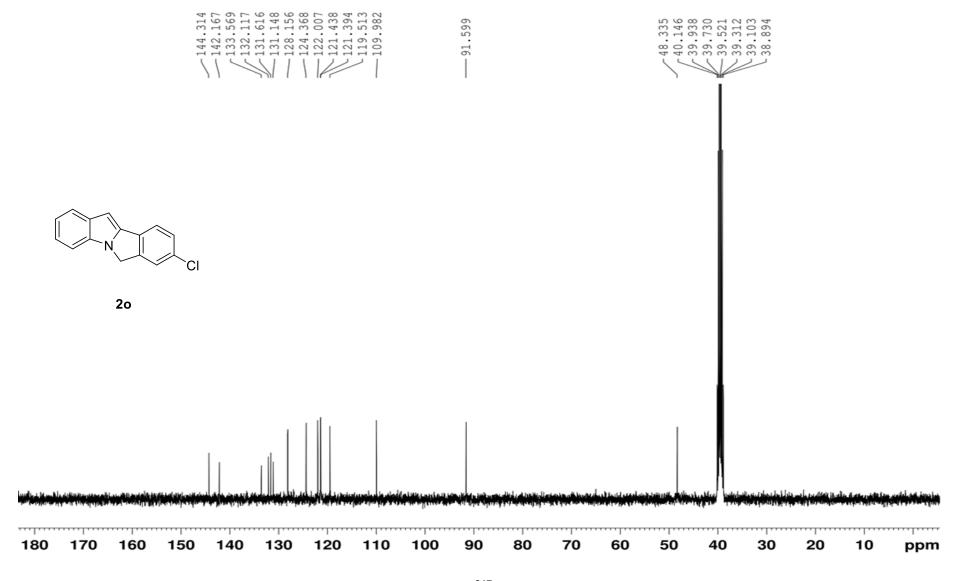


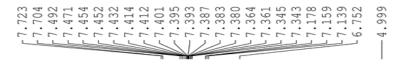


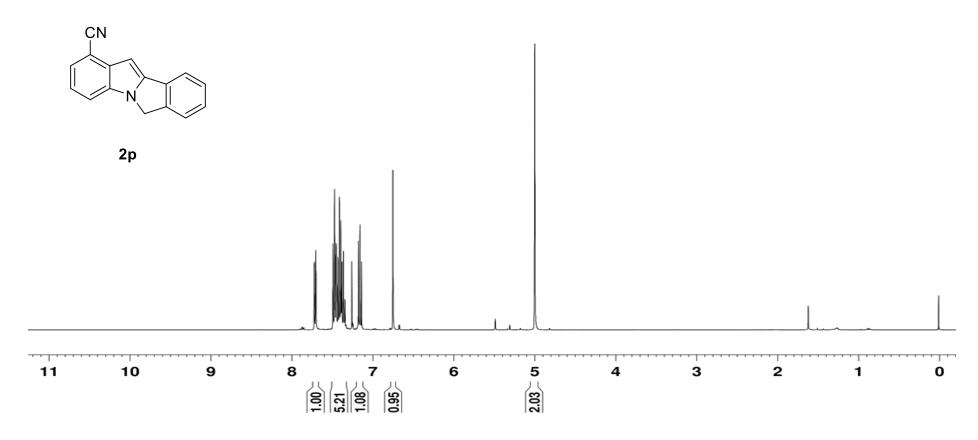


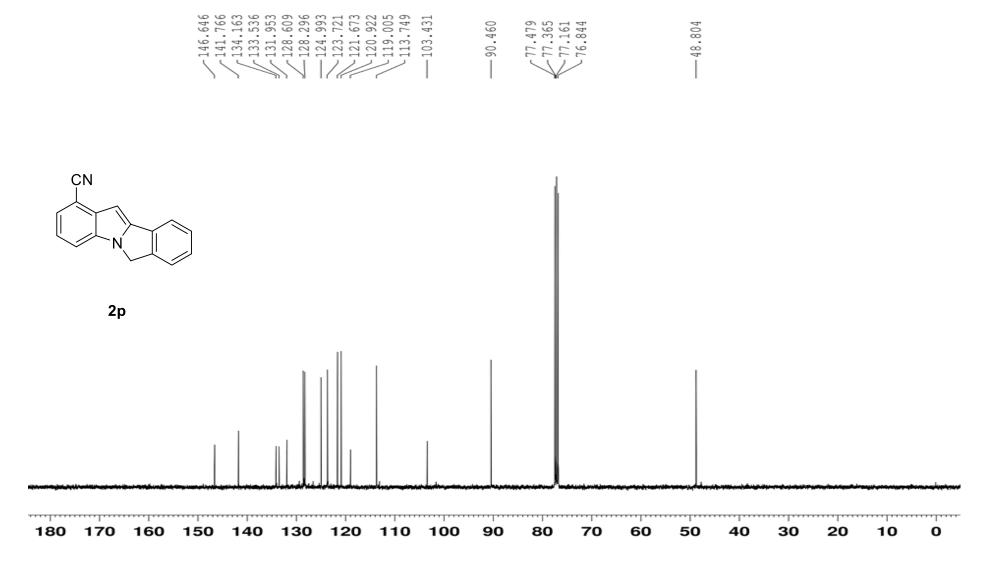




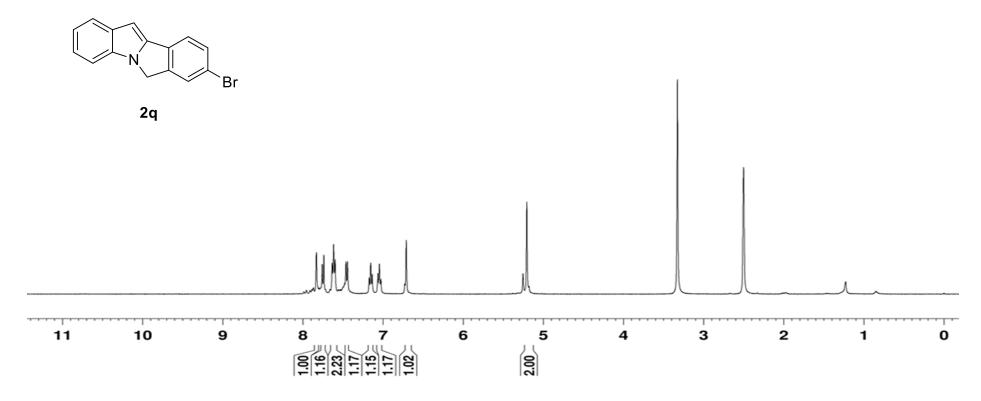


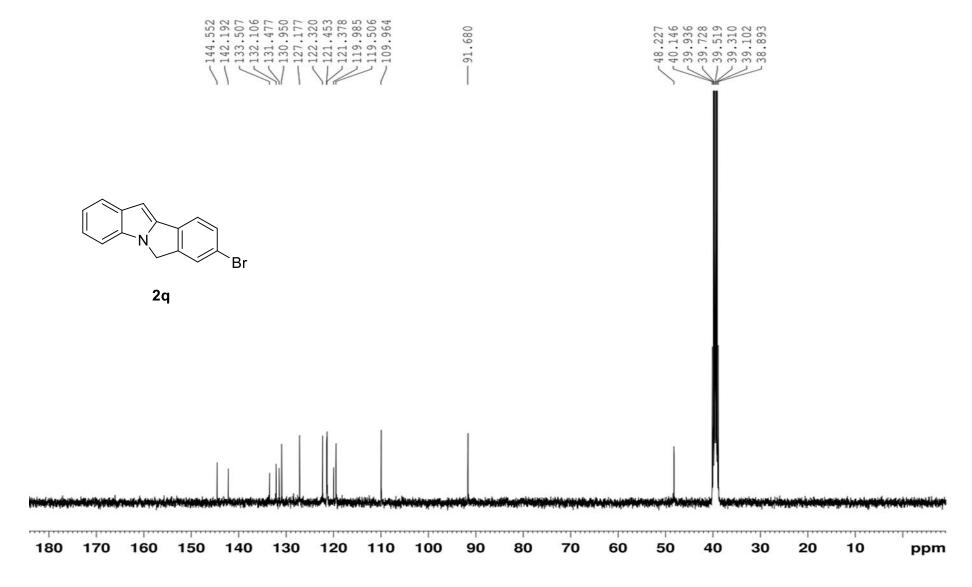


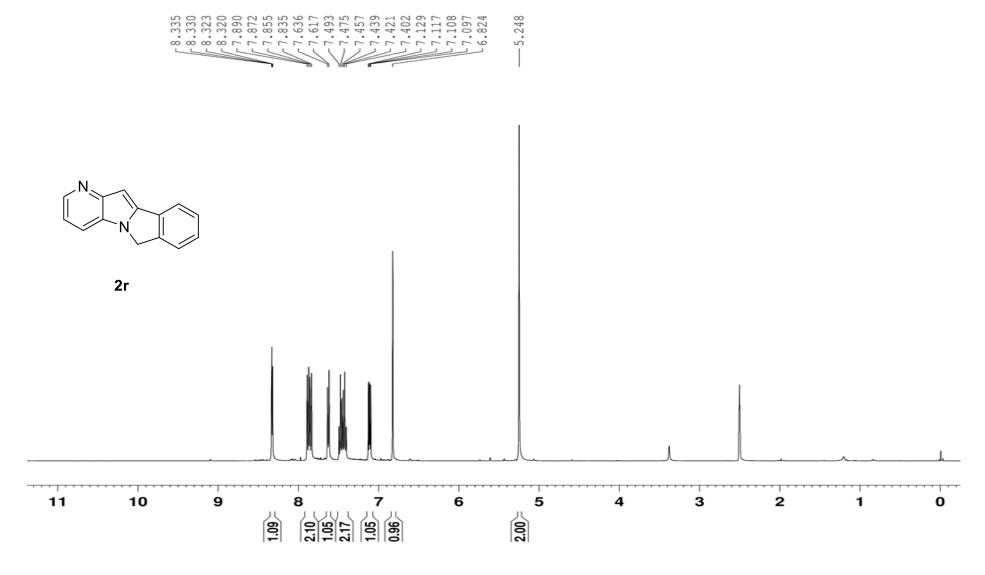


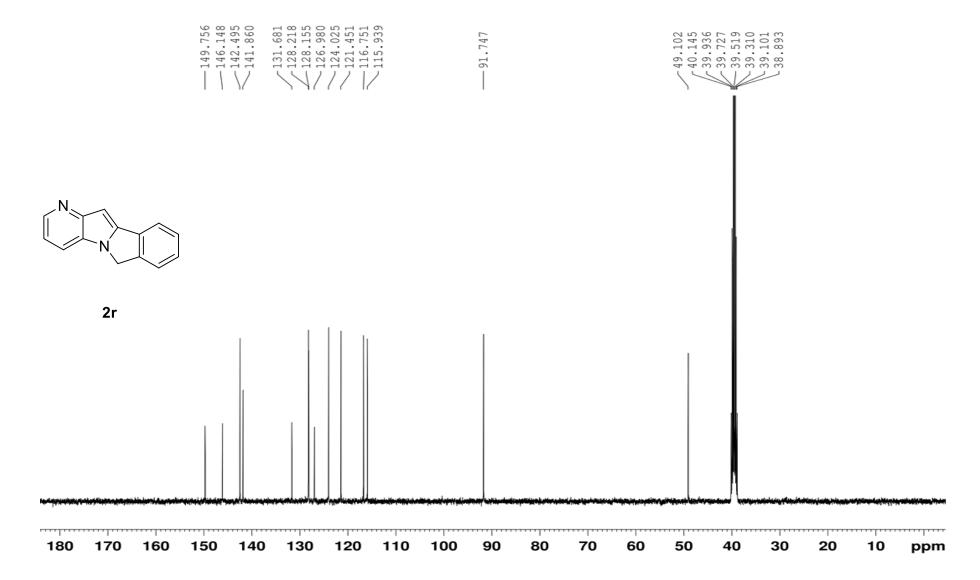


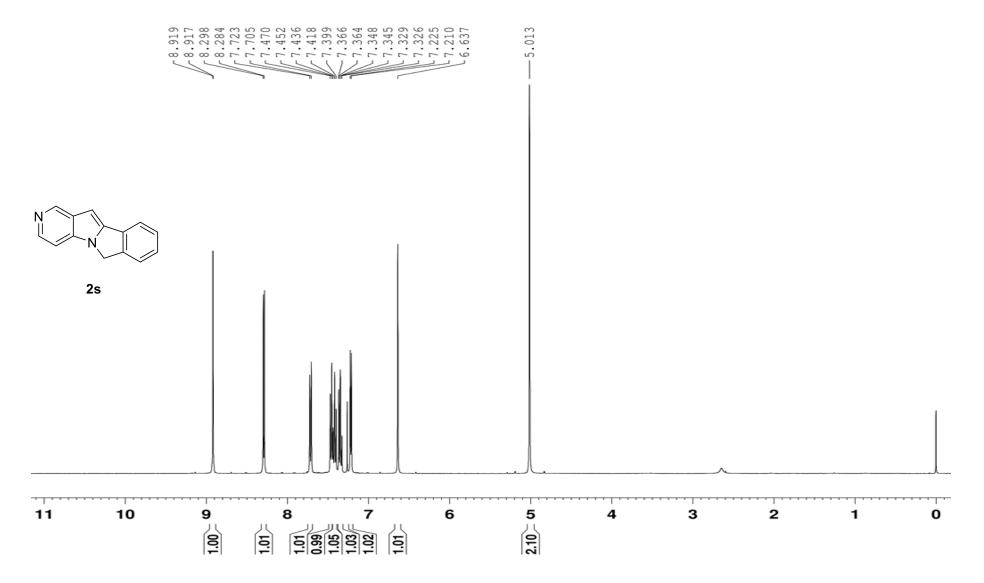


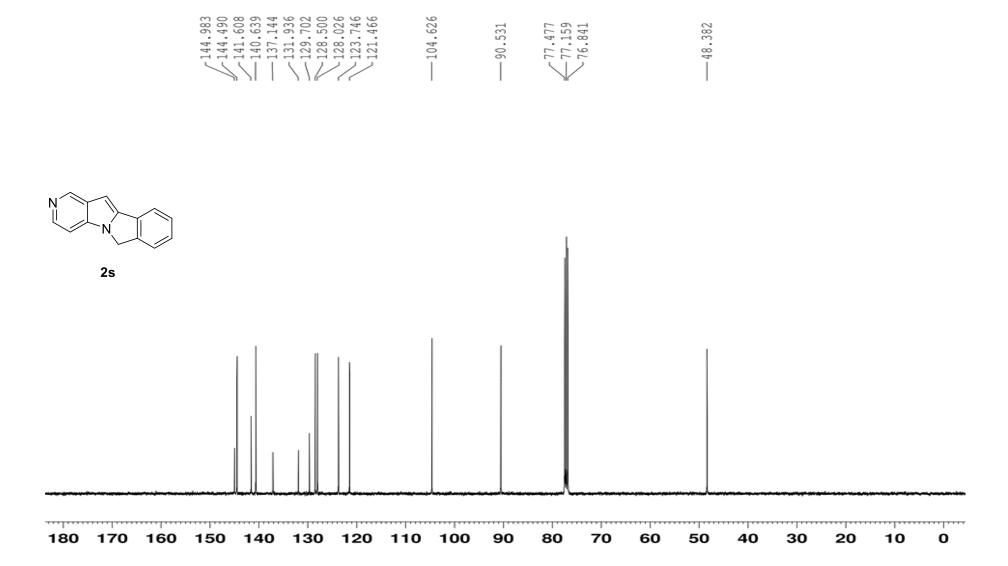


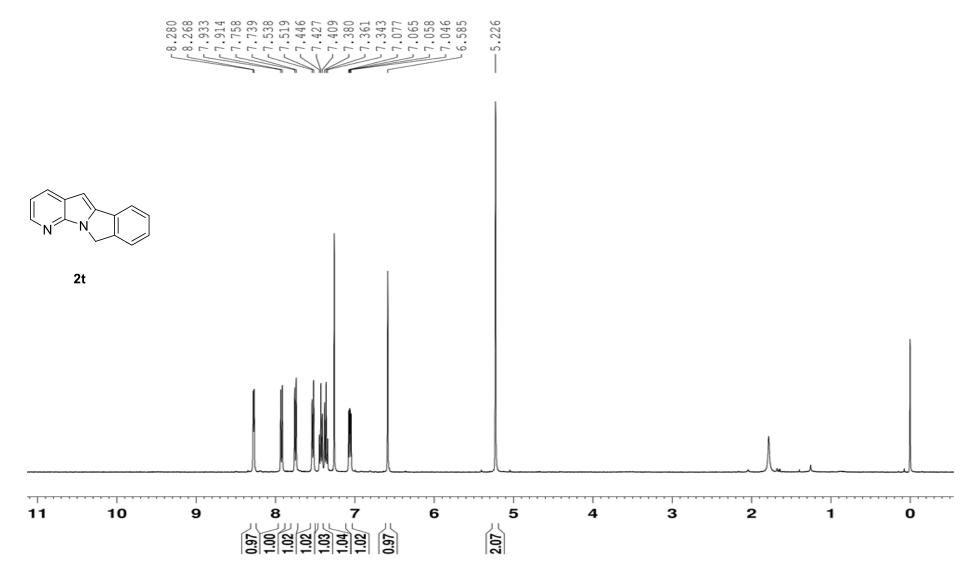


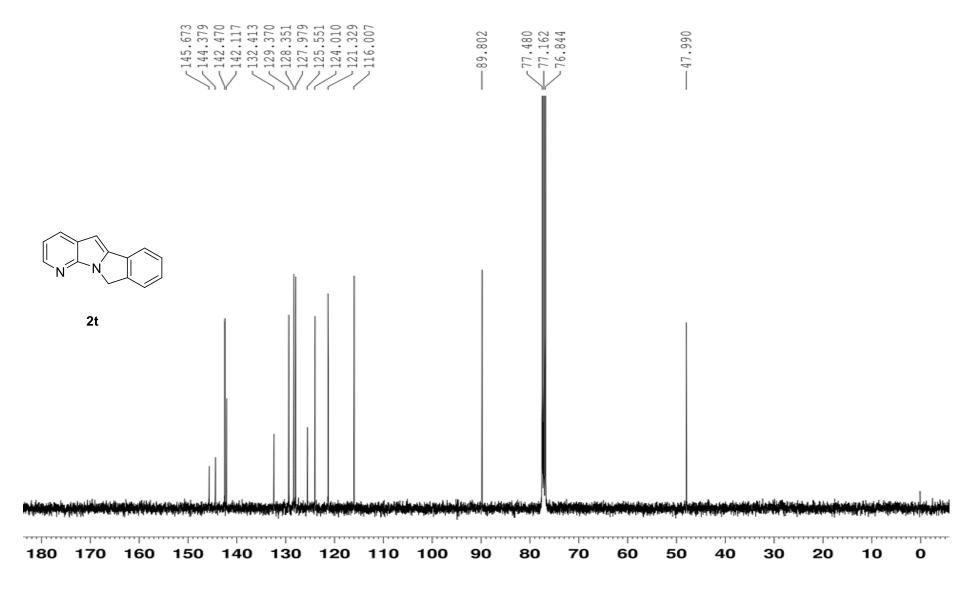


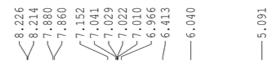


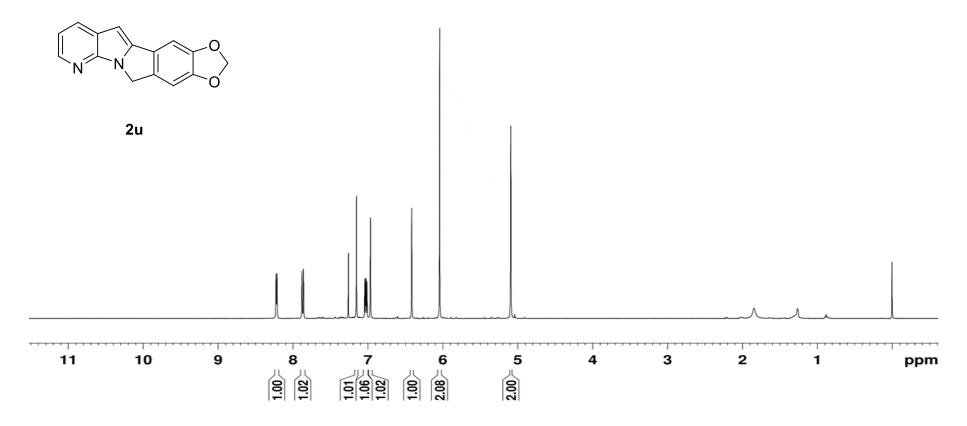


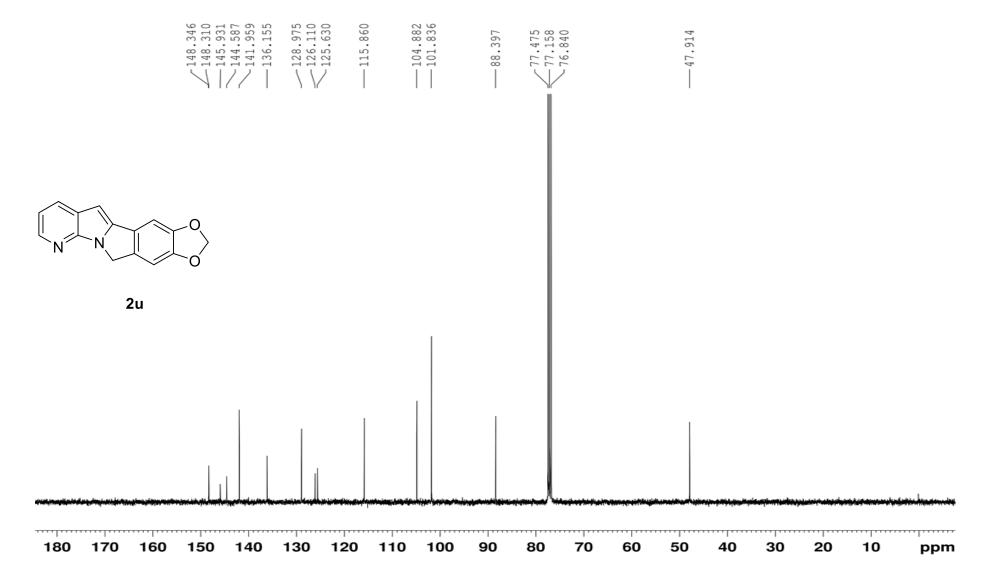




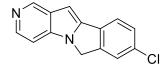


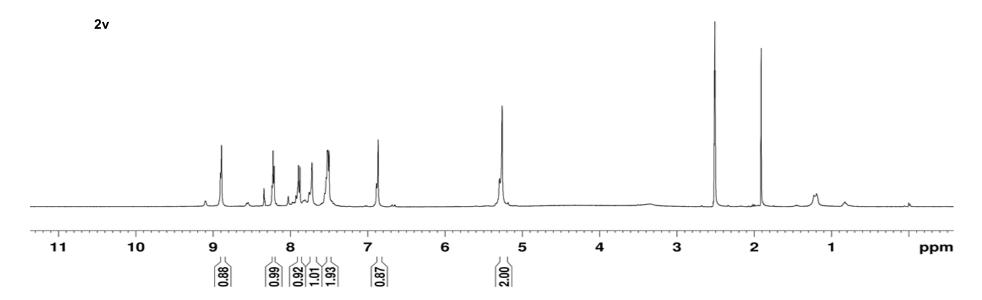


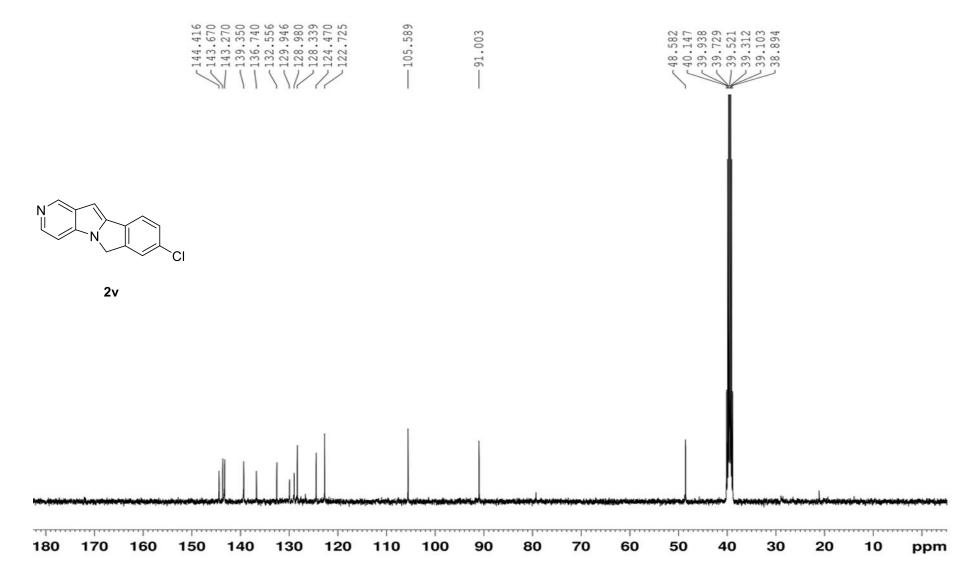




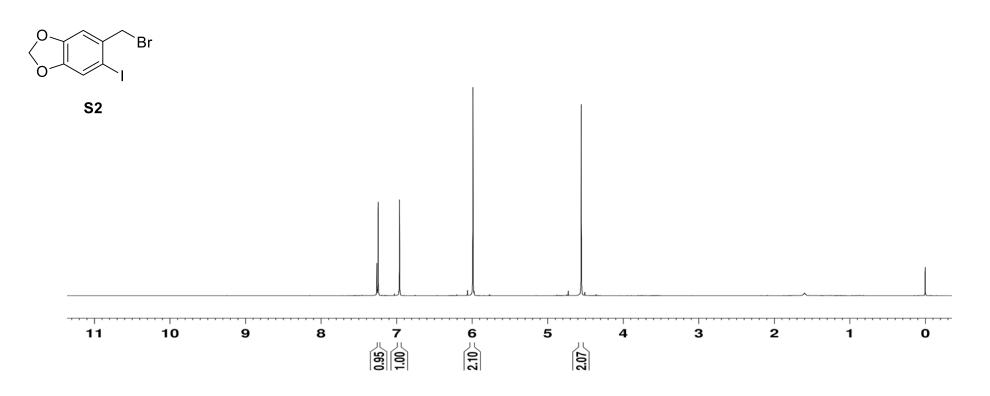




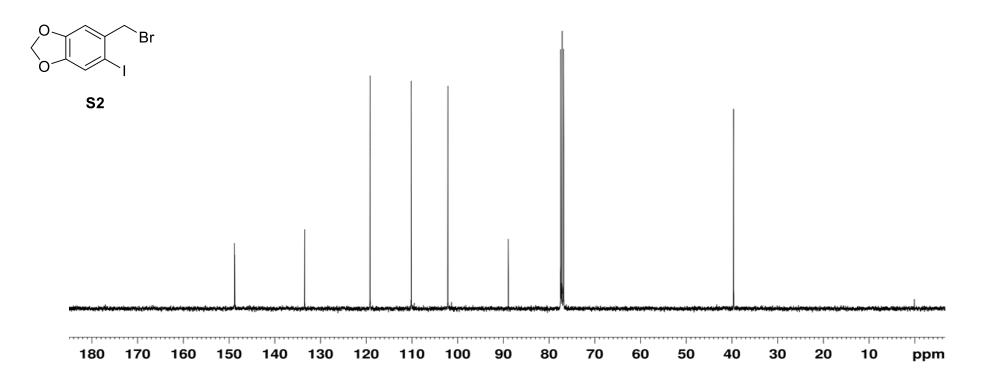


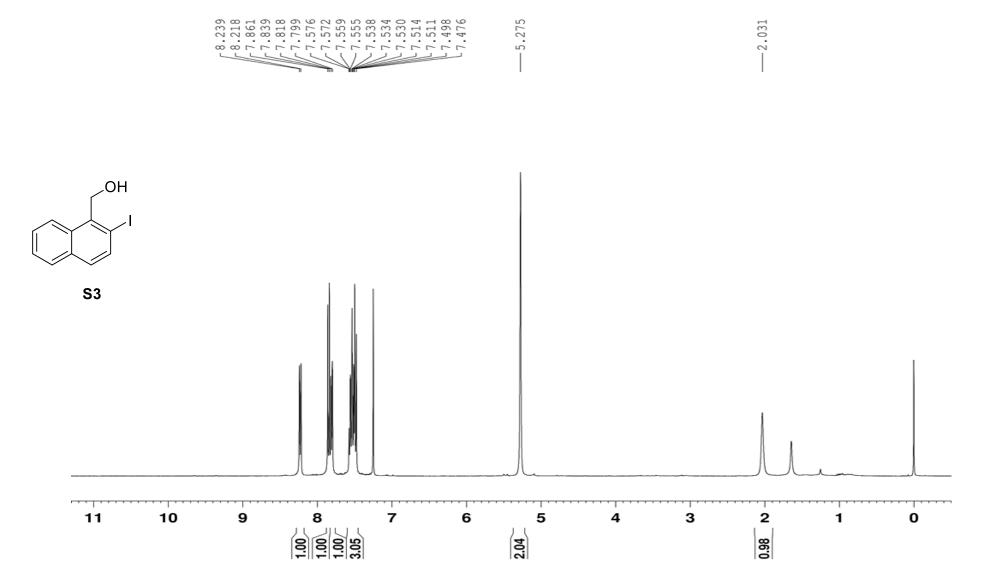


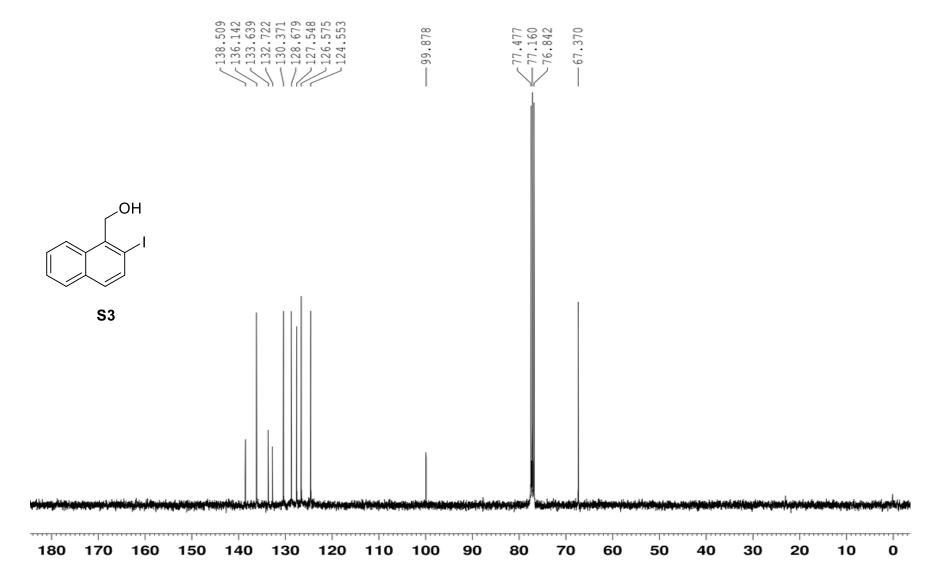




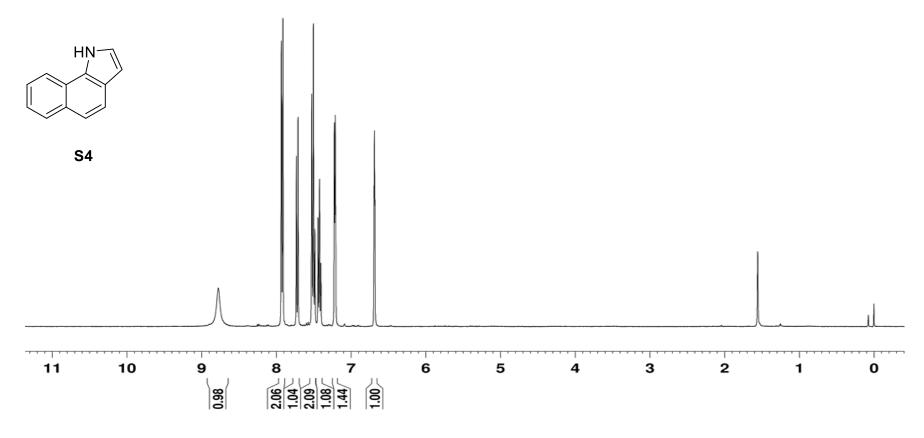


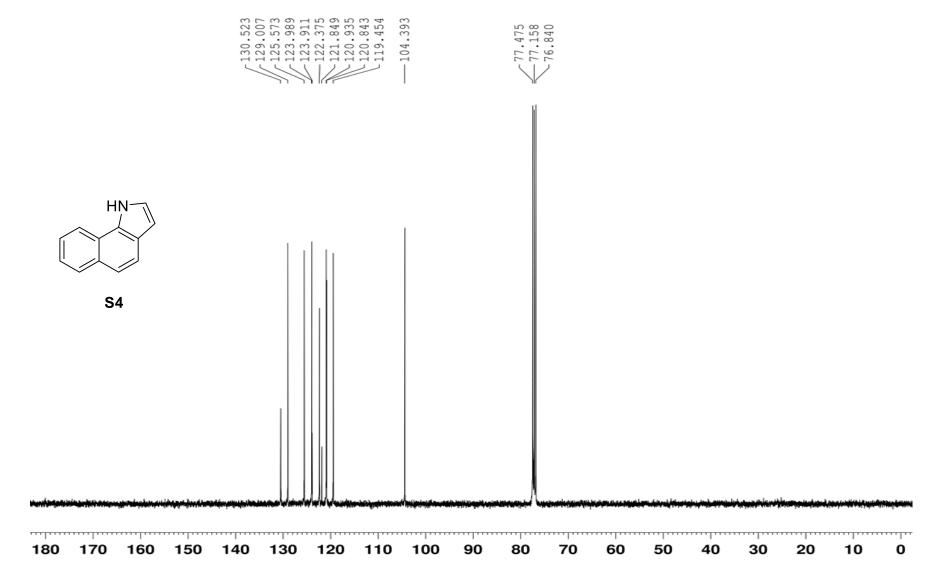


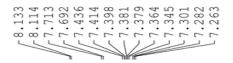


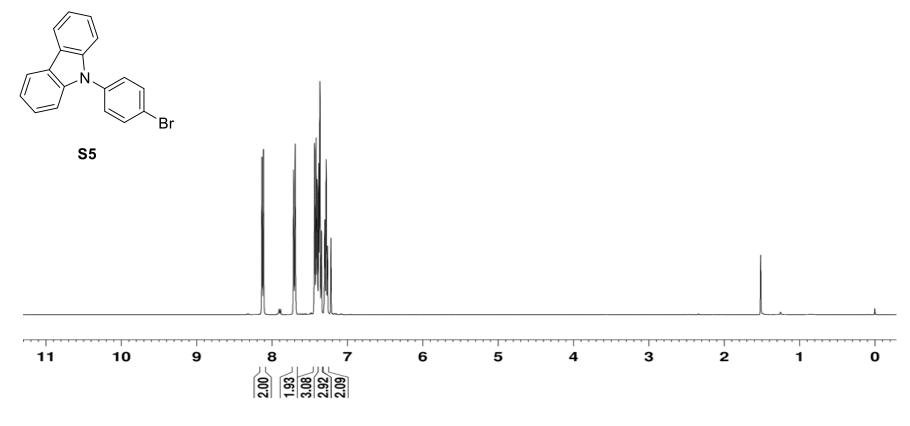


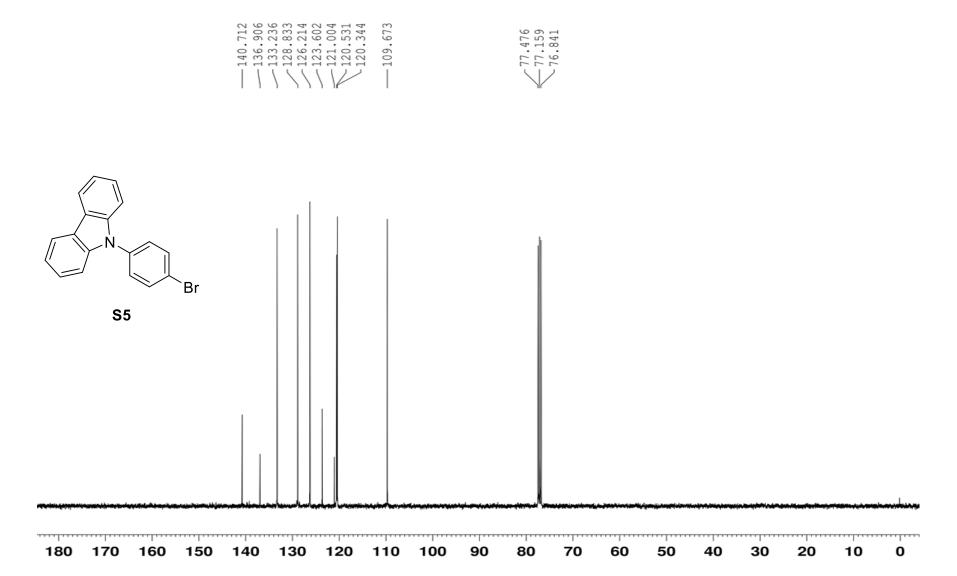


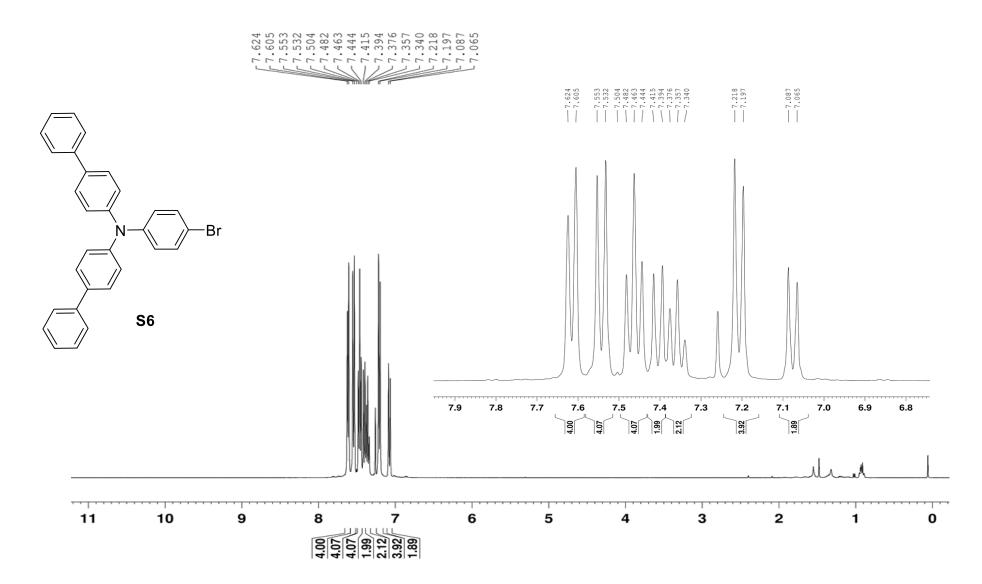


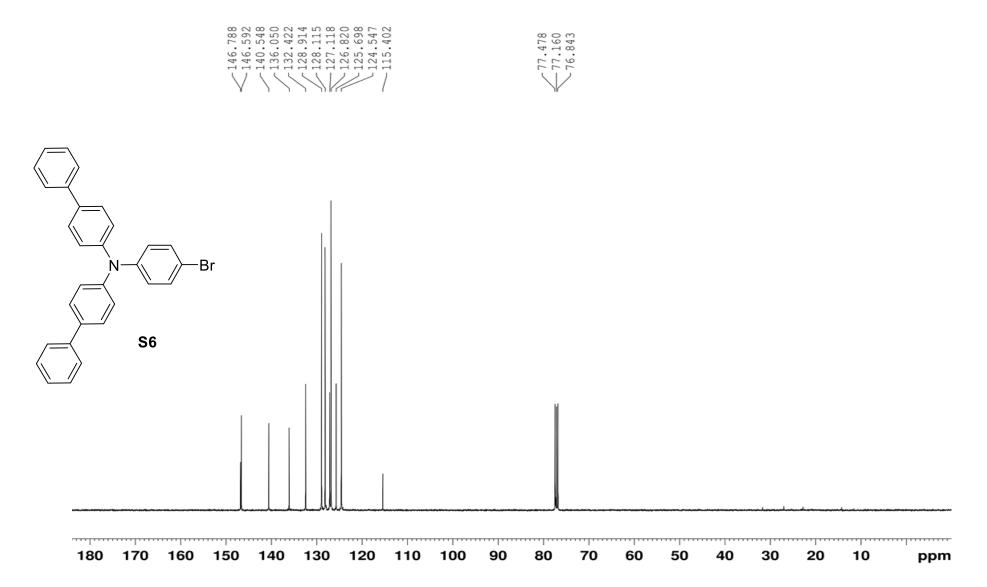


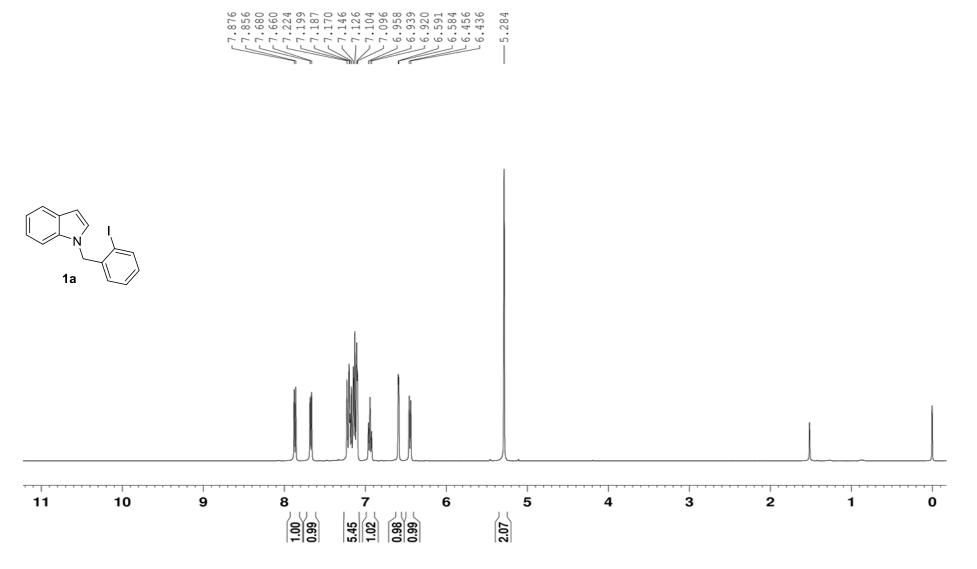


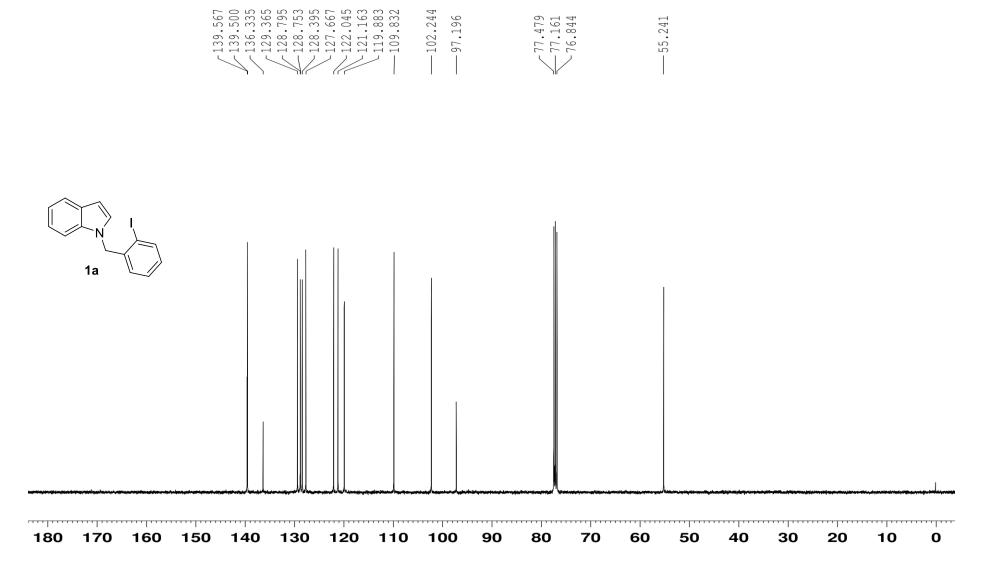


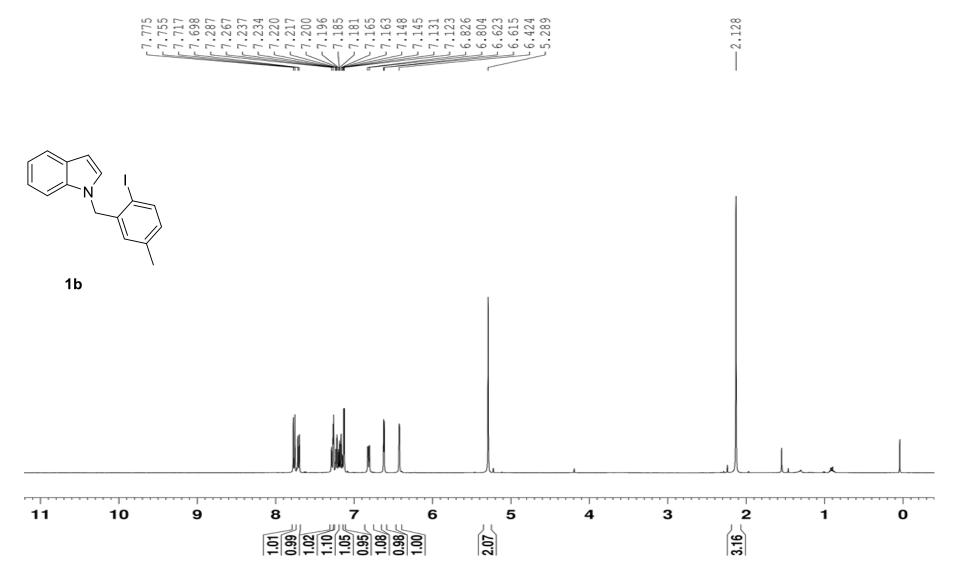


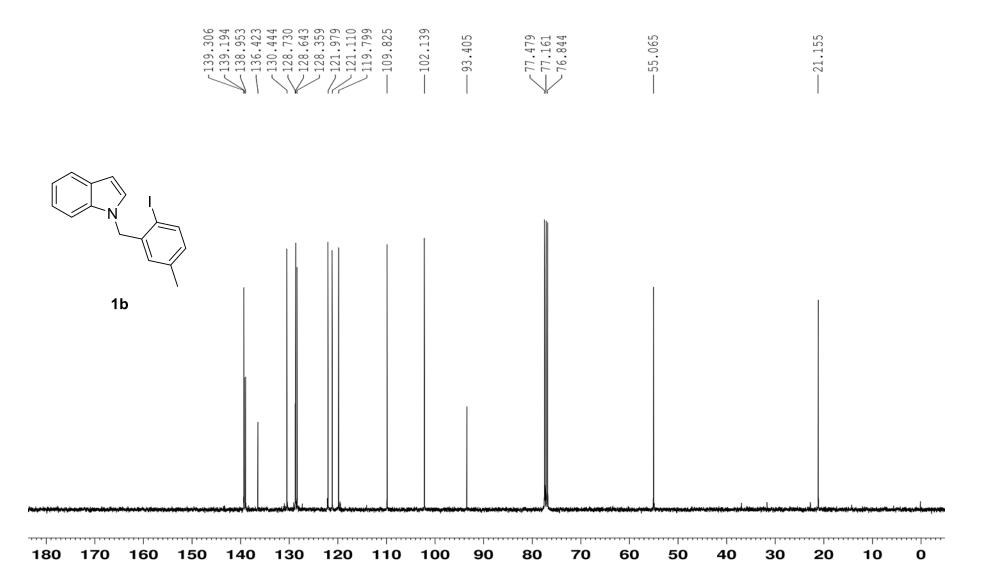


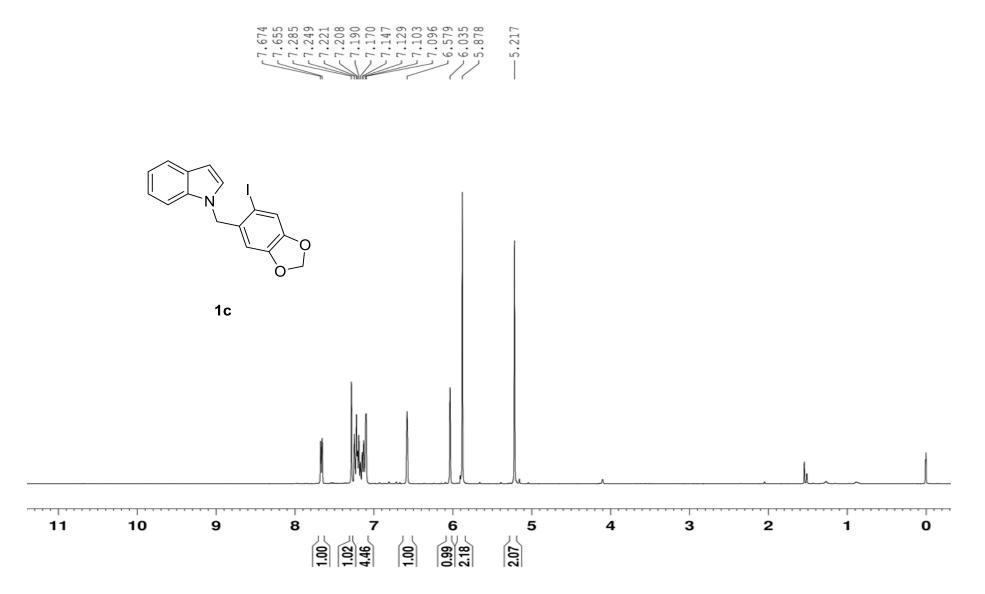


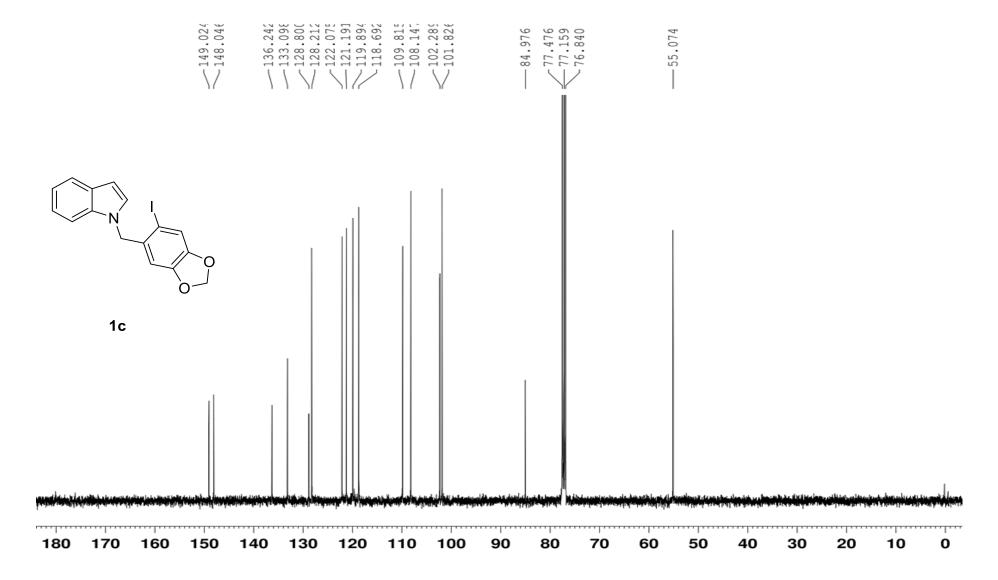


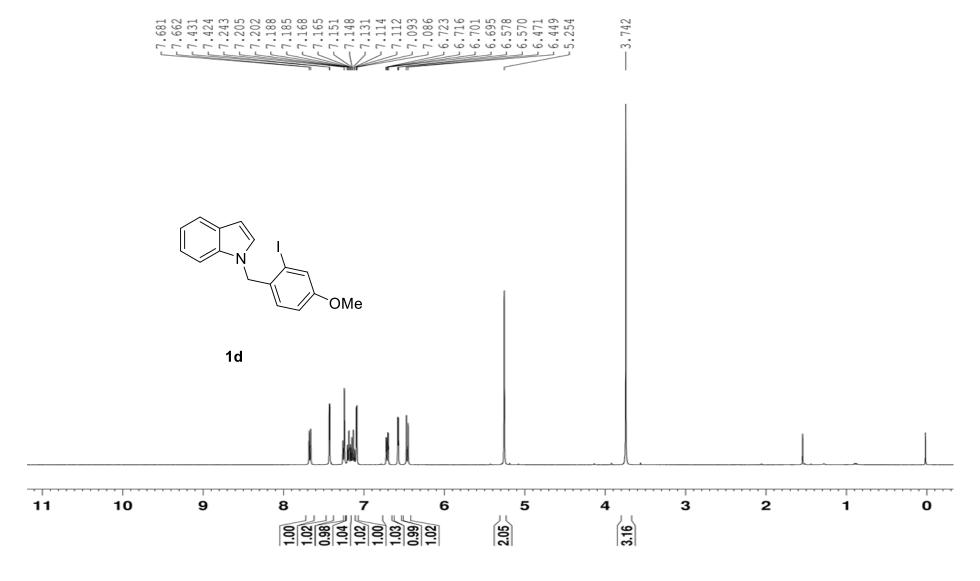


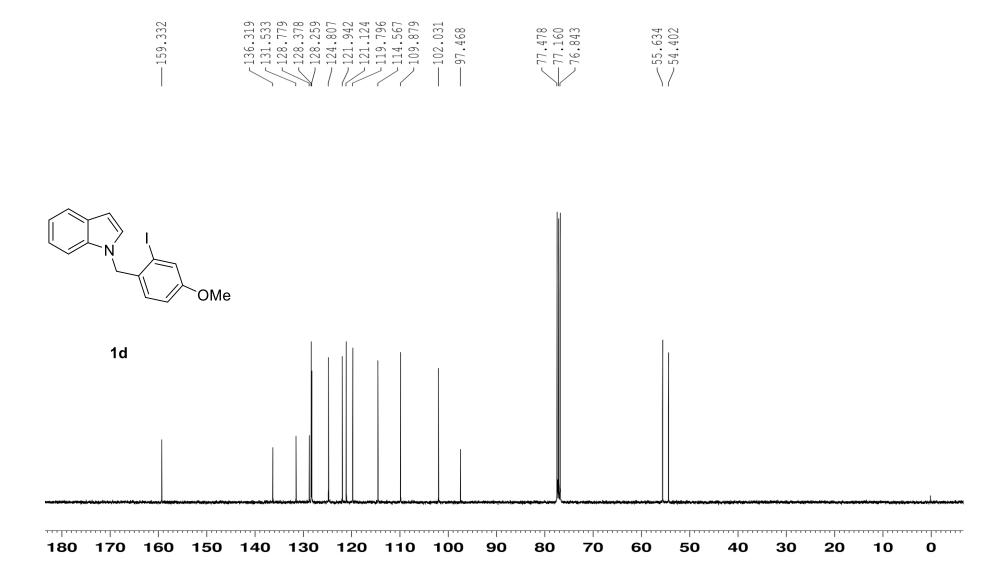


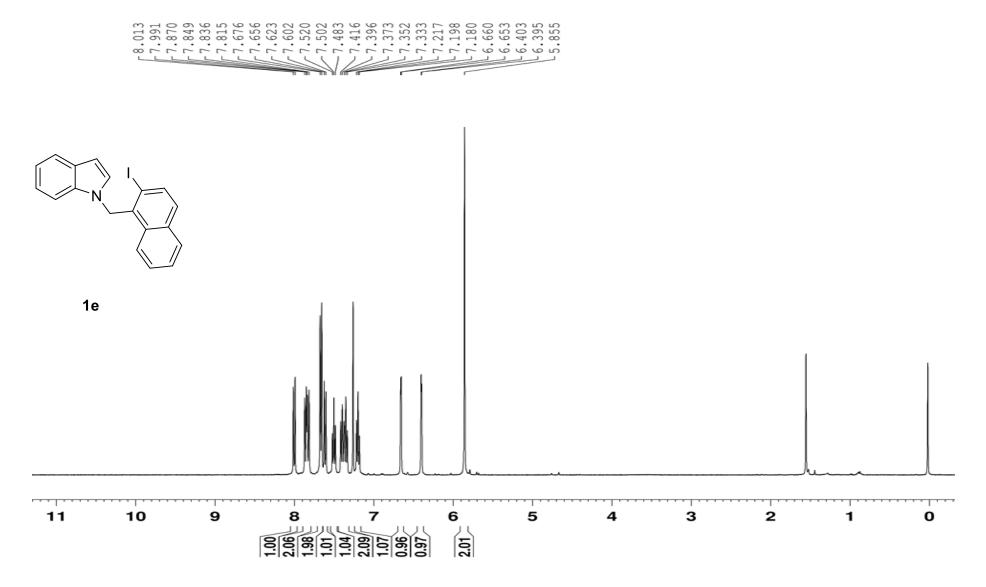


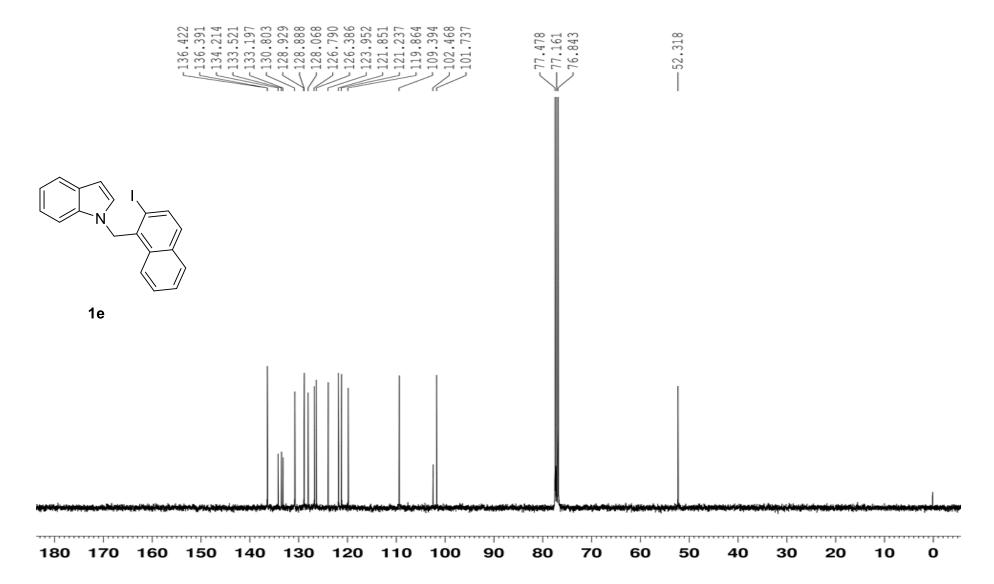


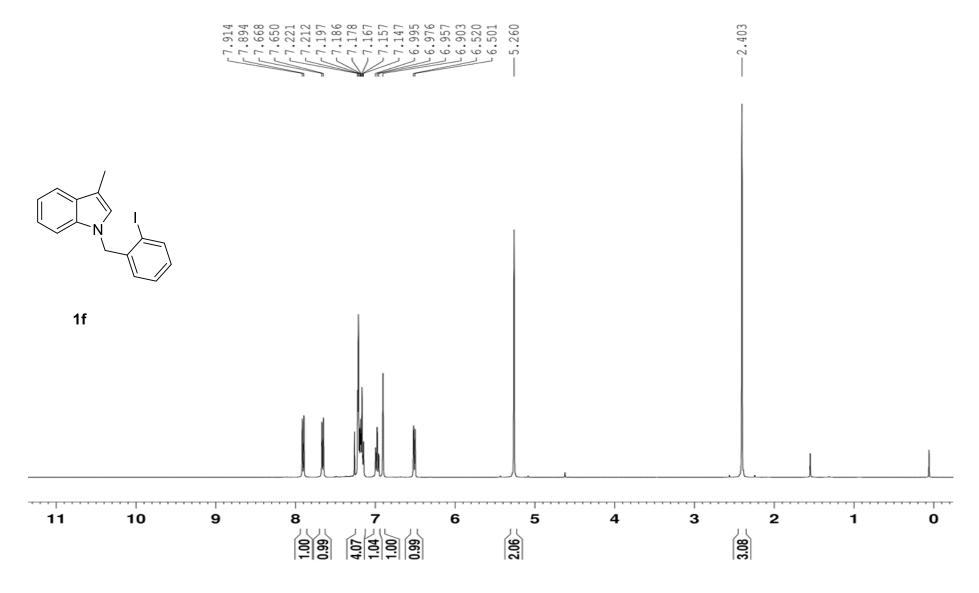


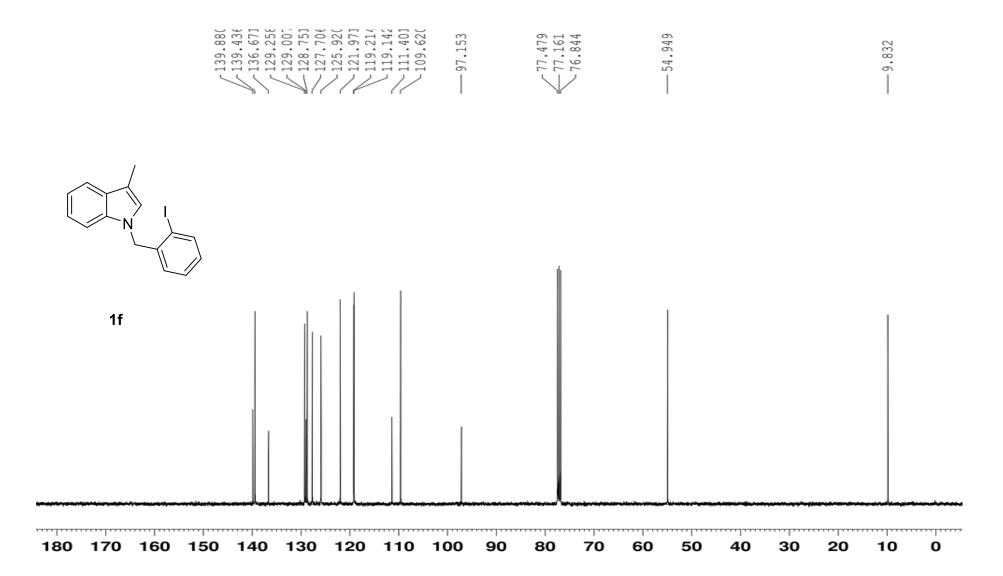


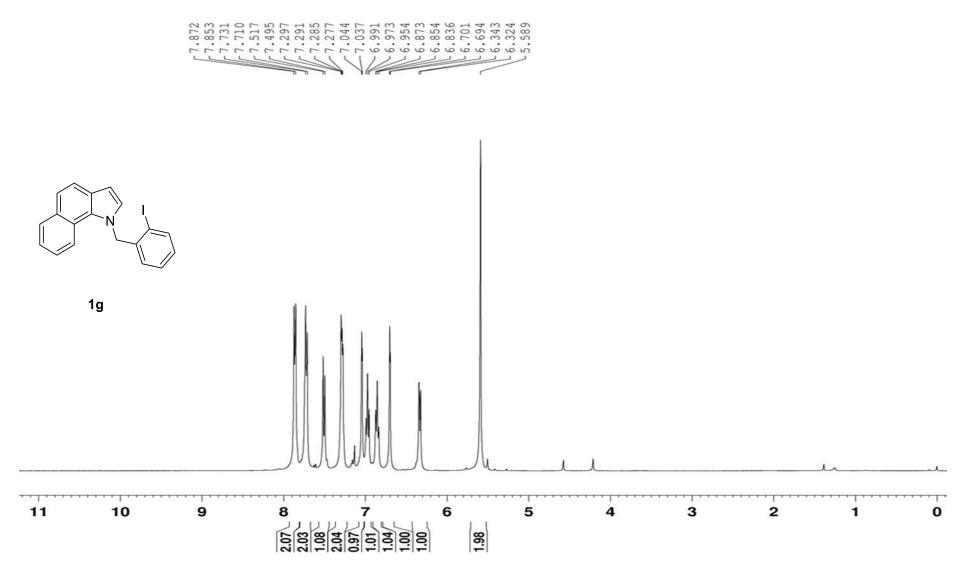




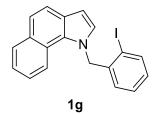


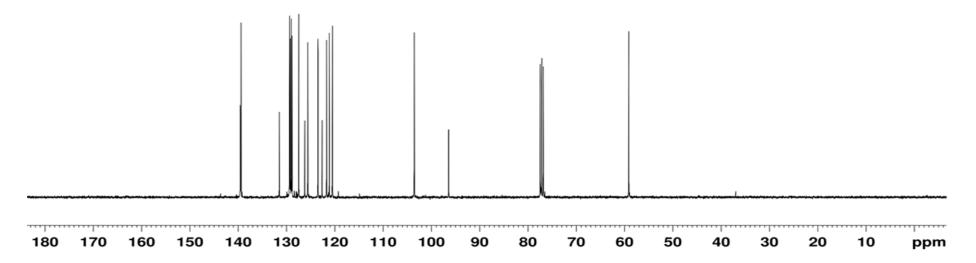


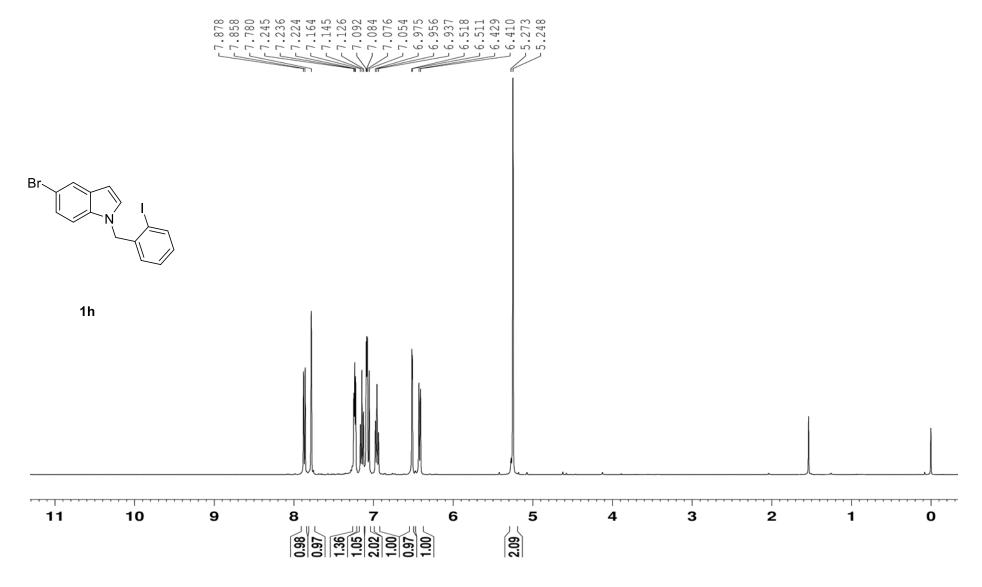




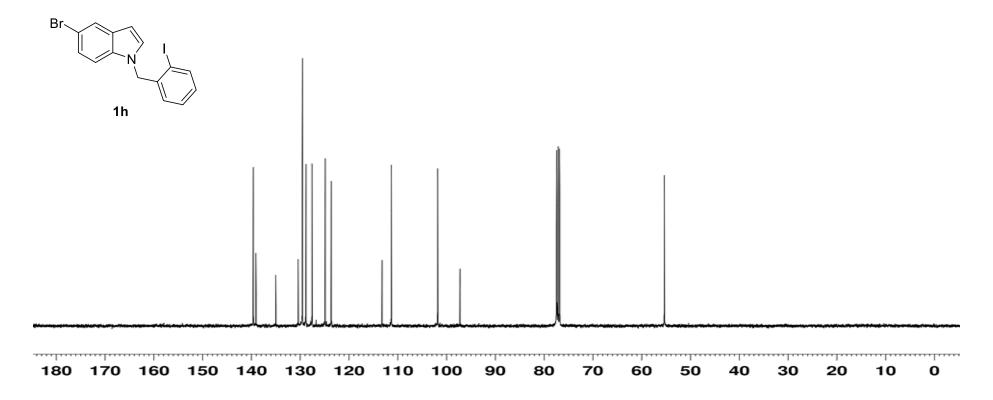


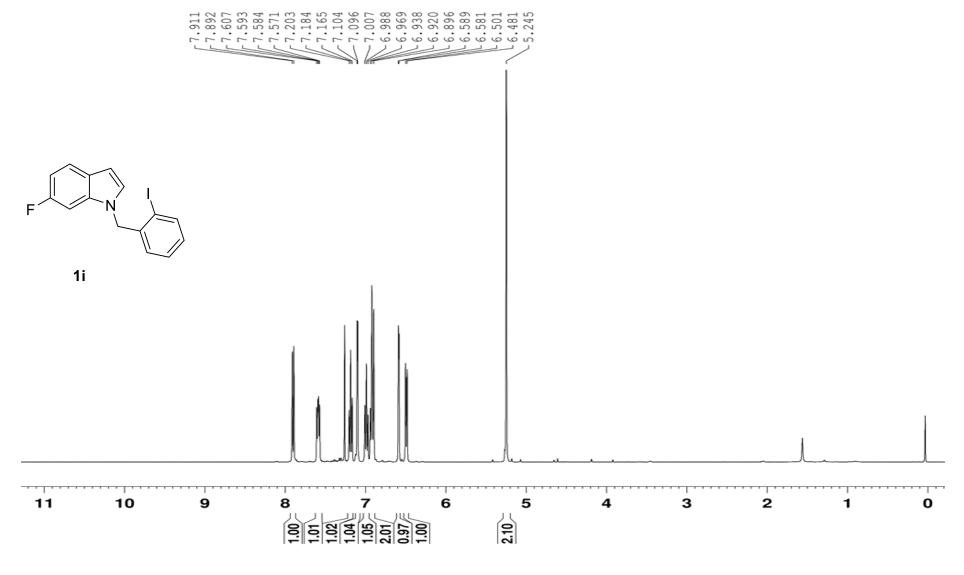


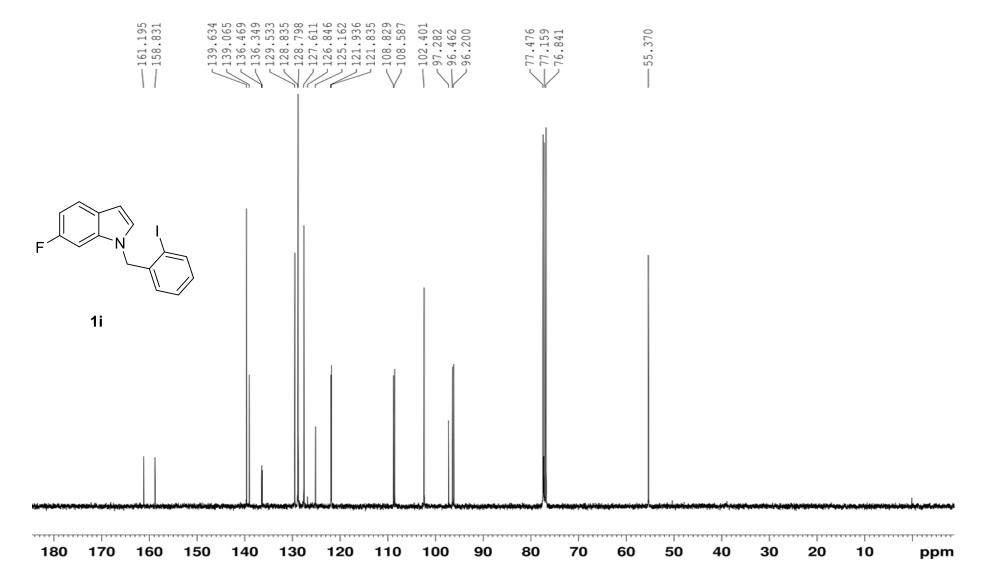


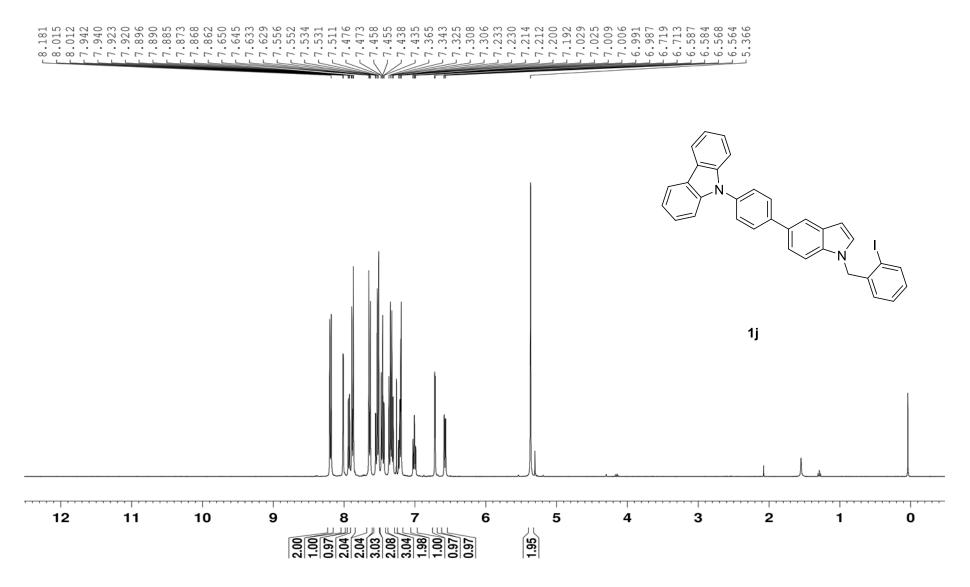


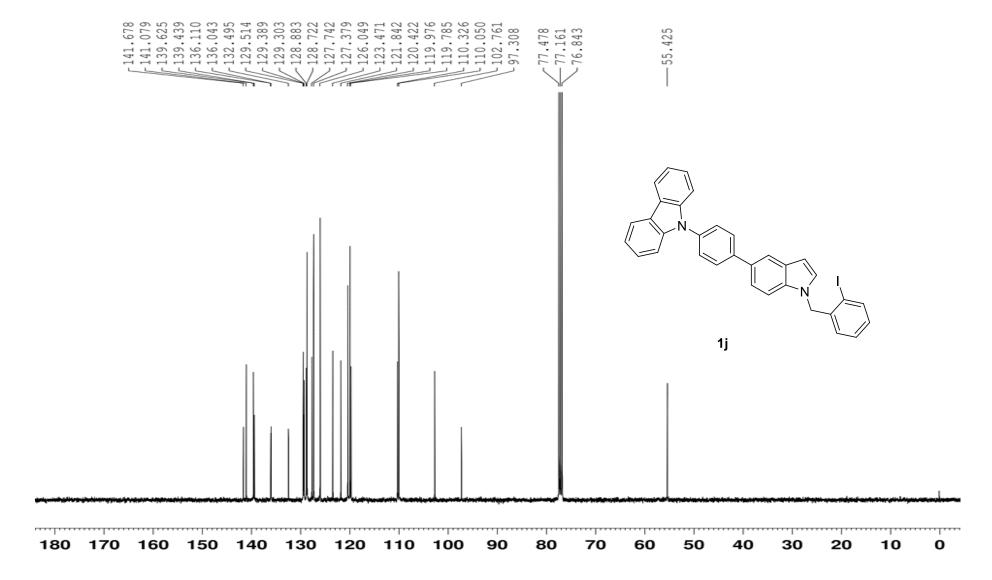


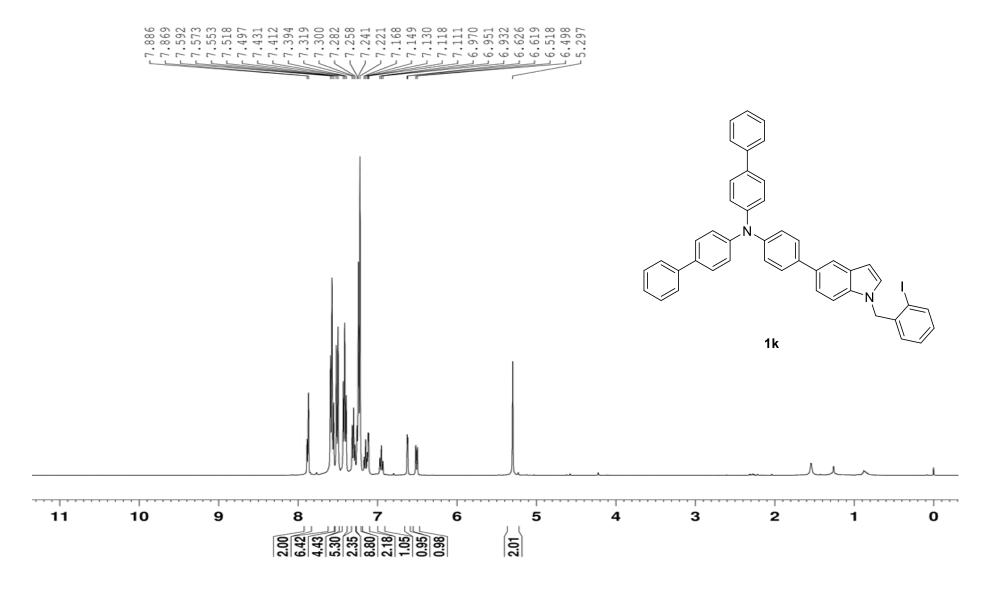


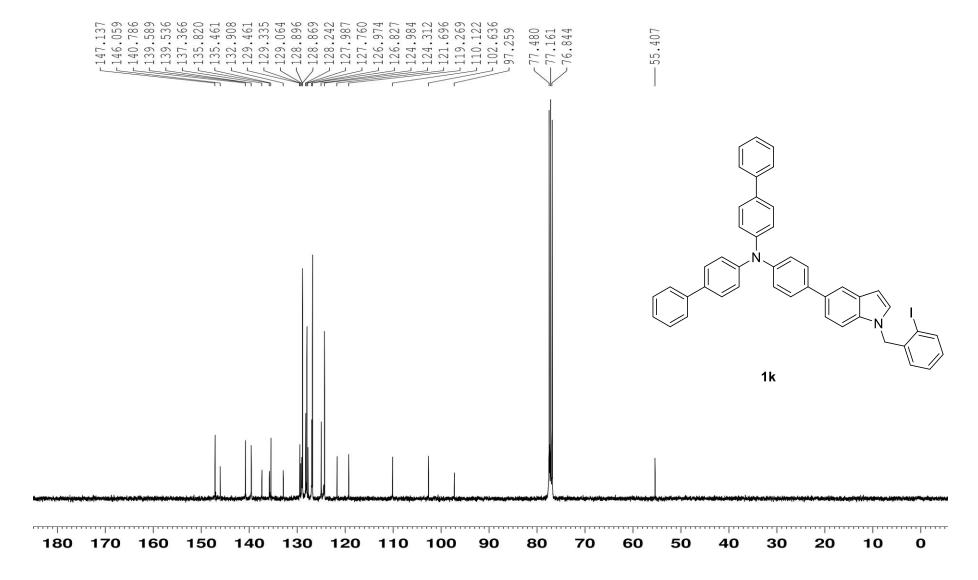




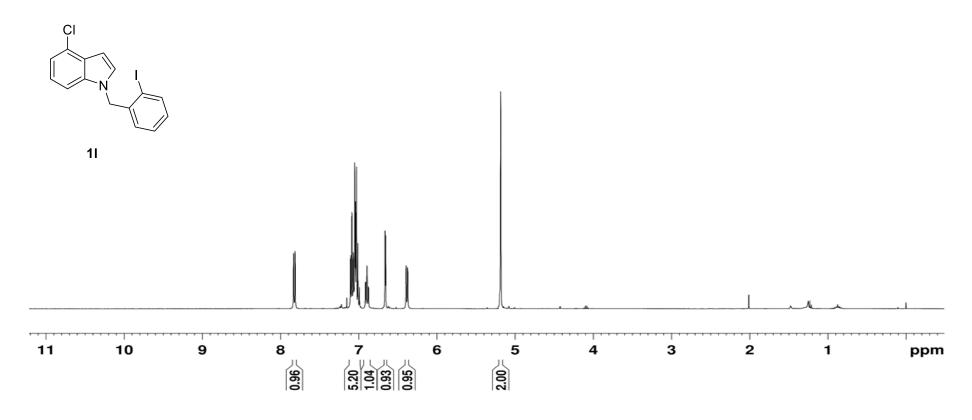


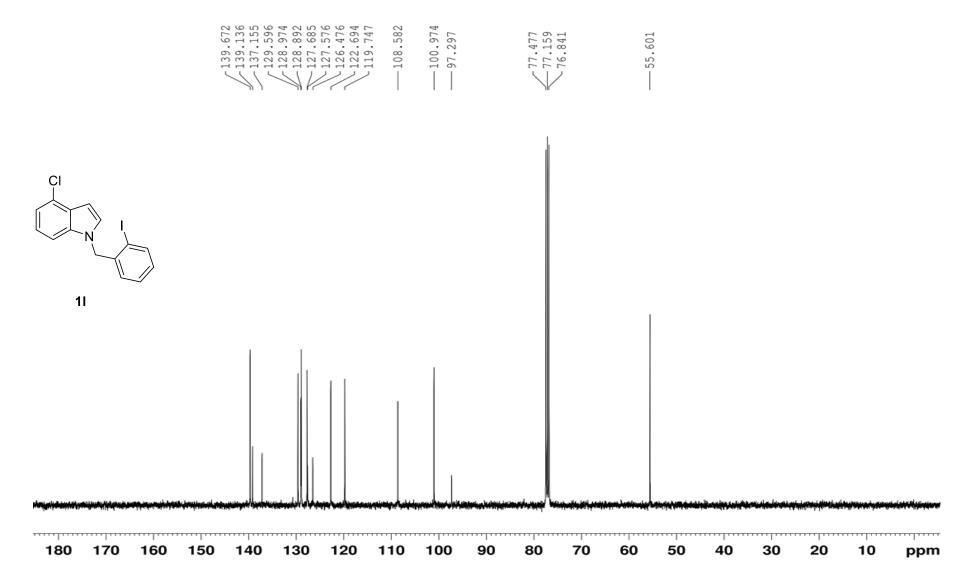


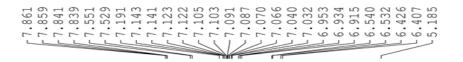


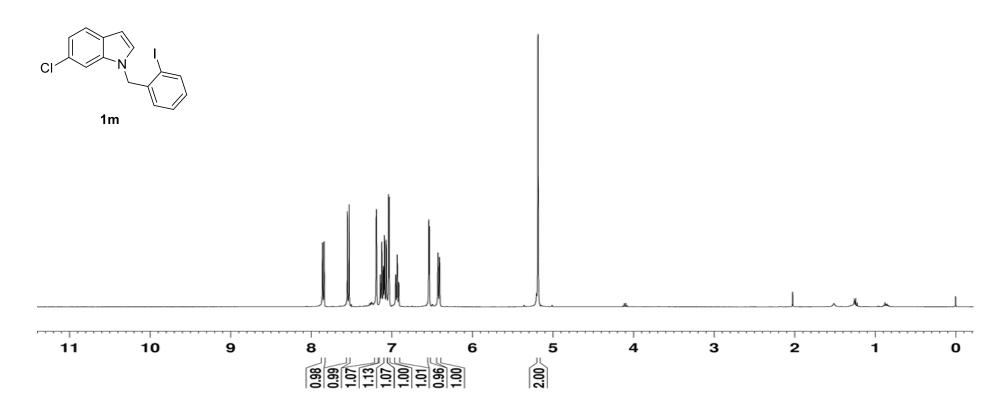


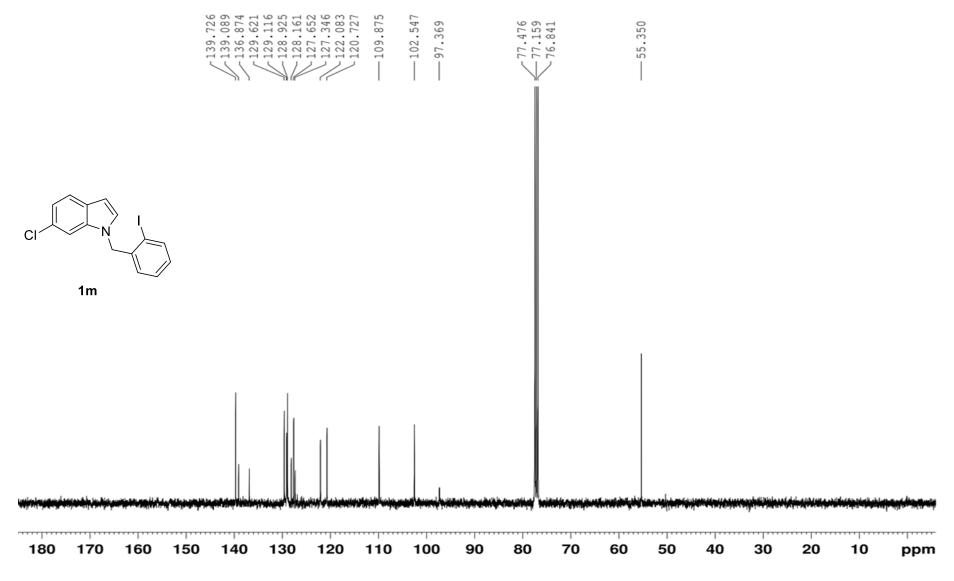




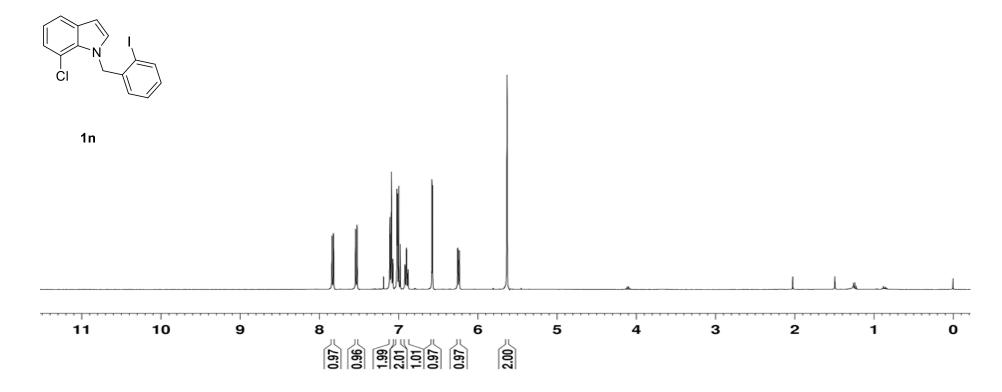


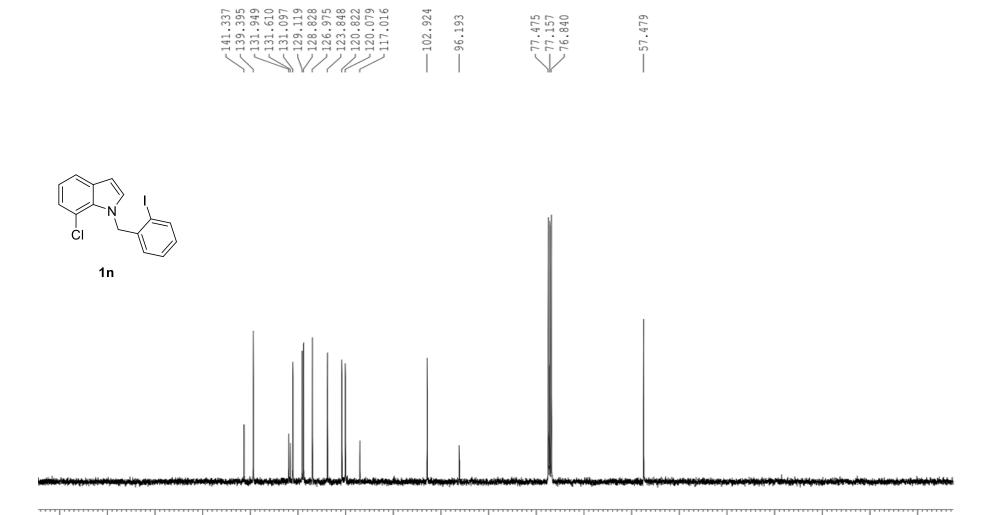






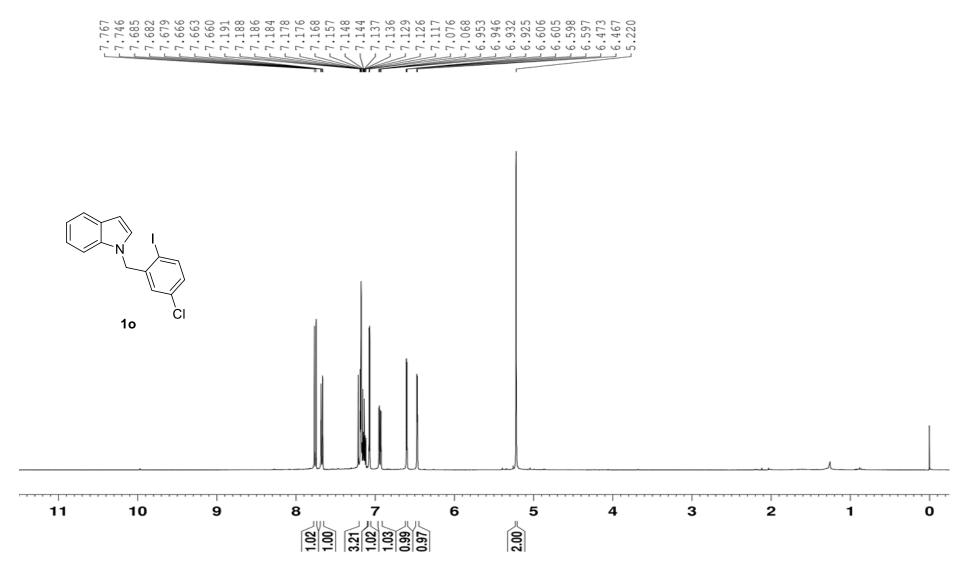


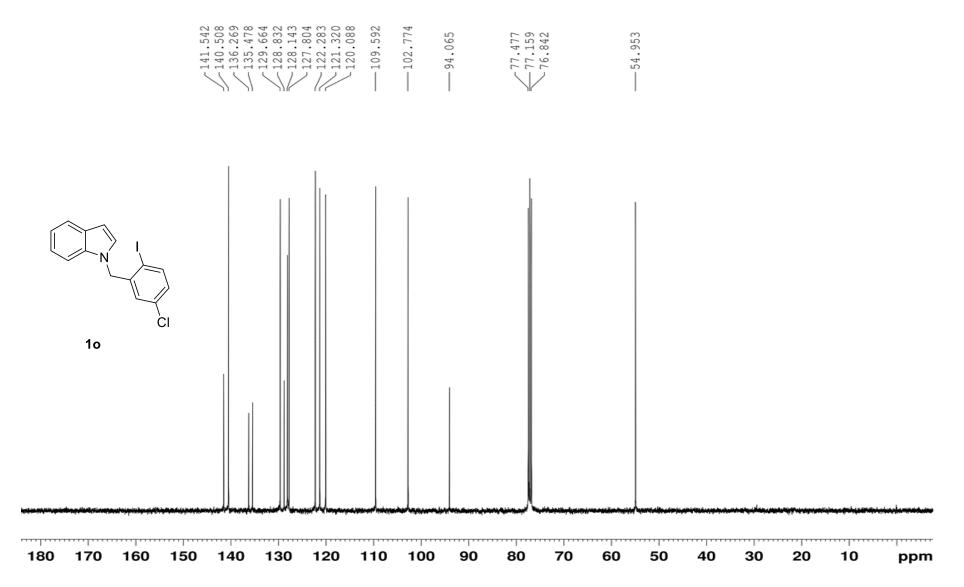


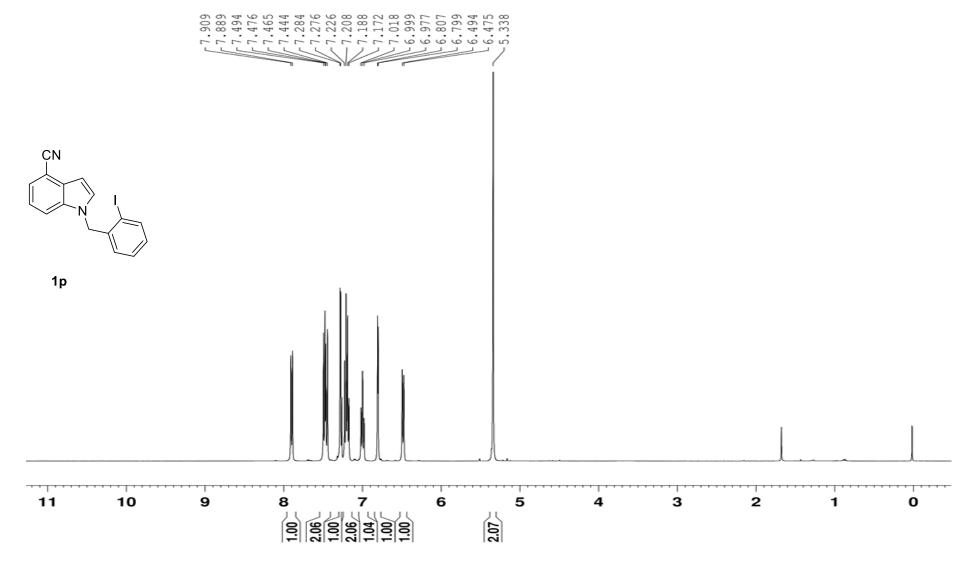


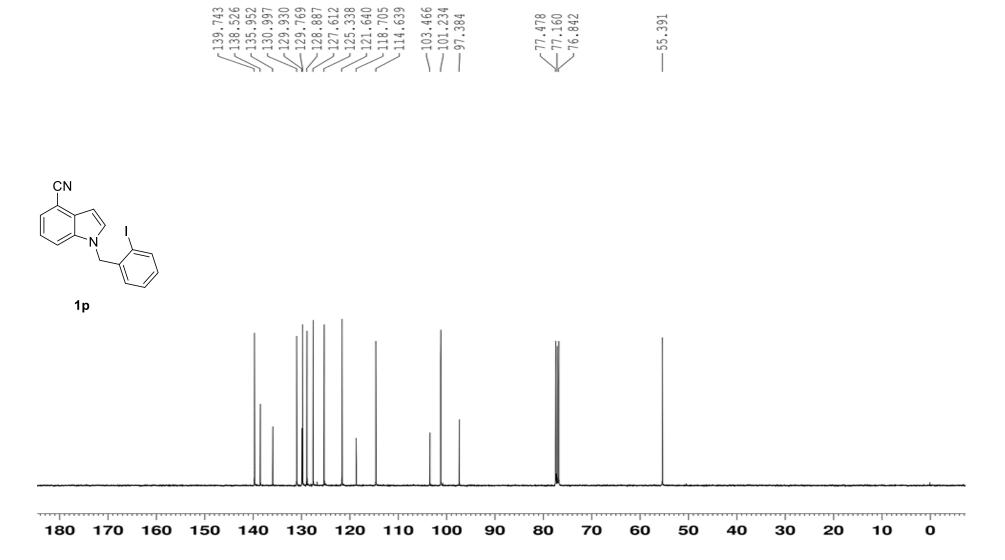
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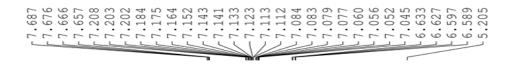
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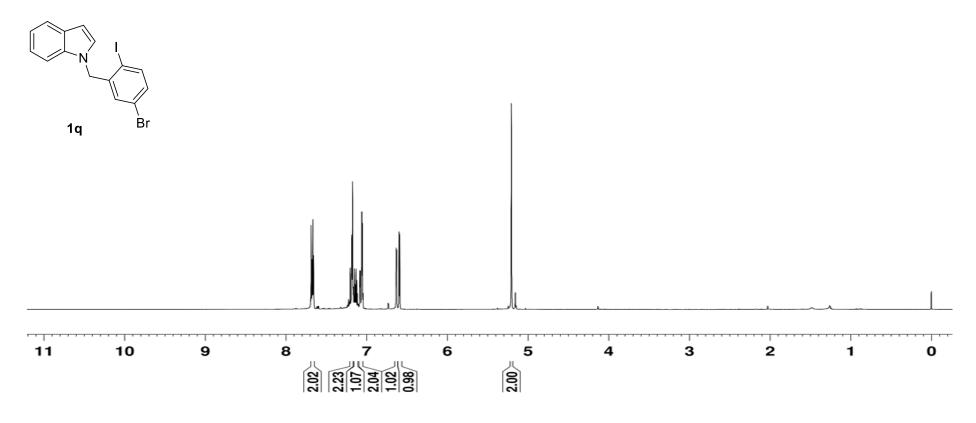




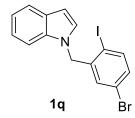


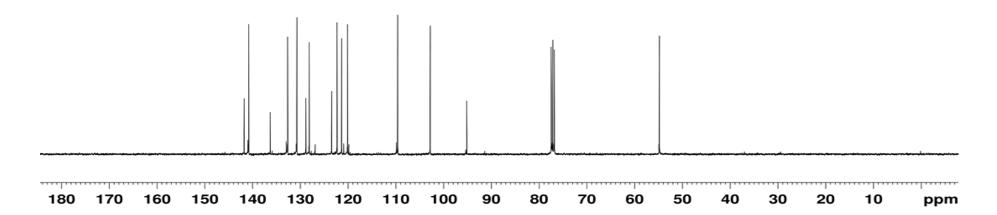




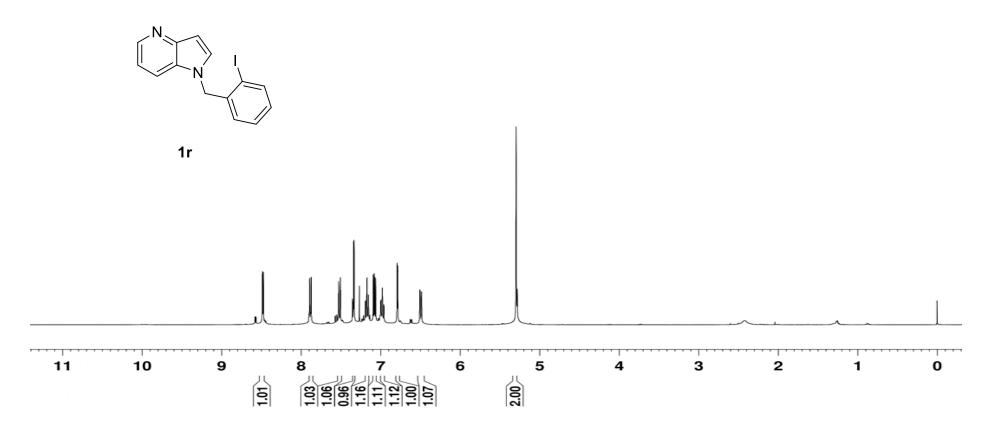


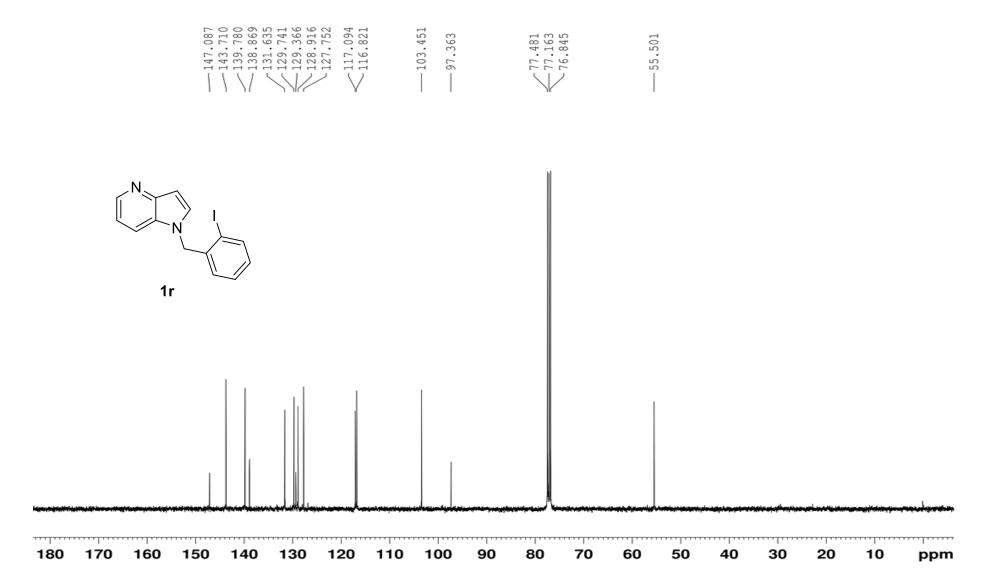


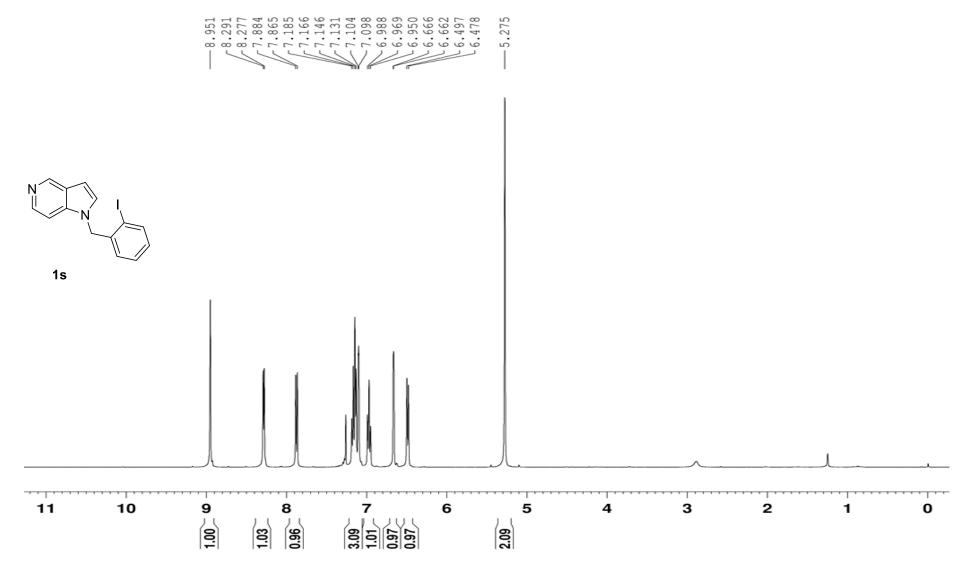




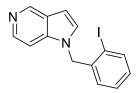












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