

Supporting Information

Highly Regioselective Synthesis of Fused Seven-Membered Ring through Copper-Catalyzed Cross-Coupling

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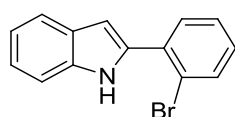
General experimental procedures

Unless otherwise stated, all reactions were carried out under N₂, 2-halophenols and solvents were obtained from commercial sources and used without any further purification. ¹H NMR spectra were recorded at 400 MHz or 500 MHz using TMS as internal standard. ¹³C NMR spectra were recorded at 100 MHz or 125MHz using TMS as internal standard. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), multiplet (m). Coupling constants are reported in Hertz (Hz). Mass spectroscopy data were collected on HRMS-EI and HRMS-ESI instrument.

General procedure for synthesis of substrates

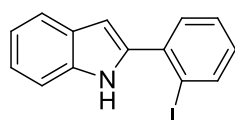
2a-g were prepared according to the method of reference 1, and **2h** was prepared according to the method of reference 2.

Characterization data of compounds 2a-h



2a

2-(2-Bromophenyl)-1H-indole (2a). ¹H NMR (CDCl₃, 500 MHz) δ 8.63 (s, 1H), 7.66-7.79 (m, 2H), 7.61 (dd, 1H, *J* = 7.5 Hz, 1.5Hz), 7.42 (d, 1H, *J* = 8.5 Hz), 7.38 (td, 1H, *J* = 7.5 Hz, 1.0Hz), 7.19-7.23 (m, 2H), 7.14 (t, 1H, *J* = 7.0 Hz), 6.82 (d, 1H, *J* = 1.0 Hz). ¹³C NMR (CDCl₃, 125 MHz) δ 131.0, 131.0, 128.8, 128.2, 126.2, 124.0, 122.9, 122.5, 117.4, 116.1, 115.6, 115.0, 105.8, 98.4.



2b

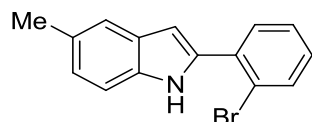
2-(2-Iodophenyl)-1H-indole (2b). ³ ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.38 (s, 1H), 8.04 (t, 1H, *J* = 7.0 Hz), 7.60 (d, 1H, *J* = 8.0 Hz), 7.50-7.55 (m, 2H), 7.42 (d, 1H, *J* = 8.0 Hz), 7.13-7.18 (m, 2H), 7.03-7.06 (m, 1H), 6.70 (d, 1H, *J* = 1.5 Hz). ¹³C NMR

(DMSO-*d*₆, 125 MHz) δ 139.9, 139.0, 137.9, 136.2, 130.9, 129.7, 128.3, 127.7, 121.5, 120.2, 119.2, 111.4, 102.0, 98.5.



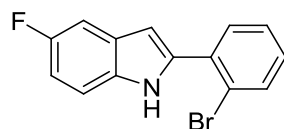
2c

2-(2-Chlorophenyl)-1H-indole (2c). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.45 (s, 1H), 7.74 (dd, 1H, *J* = 7.5 Hz, 1.0 Hz), 7.60 (t, 2H, *J* = 7.0 Hz), 7.43-7.49 (m, 2H), 7.39 (t, 1H, *J* = 7.5 Hz), 7.13-7.16 (m, 1H), 7.03 (t, 1H, *J* = 7.0 Hz), 6.89 (d, 1H, *J* = 1.0 Hz). ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 136.5, 134.2, 131.3, 131.0, 130.6, 130.6, 129.0, 127.9, 127.5, 121.9, 120.3, 119.3, 111.4, 103.0.



2d

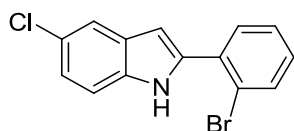
2-(2-Bromophenyl)-5-methyl-1H-indole (2d). ¹H NMR (CDCl₃, 500 MHz) δ 8.55 (s, 1H), 7.67 (d, 1H, *J* = 8.0 Hz), 7.59 (dd, 1H, *J* = 7.5 Hz, 1.0 Hz), 7.44 (s, 1H), 7.35-7.38 (m, 1H), 7.31 (d, 1H, *J* = 8.5 Hz), 7.19 (td, 1H, *J* = 8.0 Hz, 1.5 Hz), 7.05 (d, 1H, *J* = 8.0 Hz), 6.73 (d, 1H, *J* = 1.5 Hz), 2.46 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz) δ 136.3, 134.6, 134.0, 133.6, 131.4, 129.4, 129.1, 128.5, 127.7, 124.3, 121.3, 120.4, 110.7, 103.2, 21.5.



2e

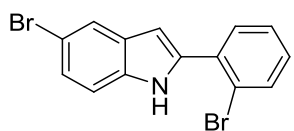
2-(2-Bromophenyl)-5-fluoro-1H-indole (2e). ¹H NMR (CDCl₃, 500 MHz) δ 8.61 (s, 1H), 7.67 (d, 1H, *J* = 8.0 Hz), 7.57 (d, 1H, *J* = 7.5 Hz), 7.37 (t, 1H, *J* = 7.5 Hz), 7.28-7.32 (m, 2H), 7.19-7.22 (m, 1H), 6.96 (td, 1H, *J* = 9.5 Hz, 2.5 Hz), 6.76 (s, 1H). ¹³C

NMR (CDCl₃, 125 MHz) δ 158.1 ($J_{CF} = 233.1$ Hz), 138.0, 134.1, 133.1, 132.8, 131.4, 129.5, 128.5 ($J_{CF} = 9.1$ Hz), 127.8, 121.3, 111.5 ($J_{CF} = 72.8$ Hz), 111.3 ($J_{CF} = 90.4$ Hz), 105.5 ($J_{CF} = 23.6$ Hz), 103.7 ($J_{CF} = 4.4$ Hz). (EI): m/z (%) = 291 ([M⁺+H], 97), 290 ([M]⁺, 17), 209 (33), 183 (100), 149 (31), 104 (38).



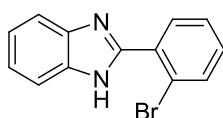
2f

2-(2-Bromophenyl)-5-chloro-1H-indole (2f). ¹H NMR (CDCl₃, 500 MHz) δ 8.61 (s, 1H), 7.66 (d, 1H, $J = 8.0$ Hz), 7.60 (s, 1H), 7.55 (d, 1H, $J = 8.0$ Hz), 7.34-7.37 (m, 1H), 7.29 (d, 1H, $J = 8.5$ Hz), 7.18-7.21 (m, 1H), 7.14-7.16 (m, 1H), 6.72 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 137.7, 134.6, 134.1, 133.0, 131.4, 129.6, 129.2, 127.8, 125.8, 122.9, 121.3, 120.2, 112.1, 103.2. (EI): m/z (%) = 307 ([M]⁺, 40), 305 (31), 165 (100), 65 (21), 51 (23).



2g

5-Bromo-2-(2-bromophenyl)-1H-indole (2g). ¹H NMR (CDCl₃, 500 MHz) δ 8.68 (s, 1H), 7.77 (s, 1H), 7.68 (d, 1H, $J = 8.0$ Hz), 7.58 (dd, 1H, $J = 8.0$ Hz, 1.5 Hz), 7.36-7.39 (m, 1H), 7.29 (s, 2H), 7.22 (td, 1H, $J = 8.0$ Hz, 1.5 Hz), 6.73 (d, 1H, $J = 2.0$ Hz). ¹³C NMR (CDCl₃, 125 MHz) δ 137.5, 134.8, 134.1, 132.9, 131.5, 129.9, 129.6, 127.8, 125.4, 123.3, 121.3, 113.4, 112.5, 103.1. (EI): m/z (%) = 351 ([M]⁺, 1), 250 (100), 206 (23), 172 (16), 71 (23).



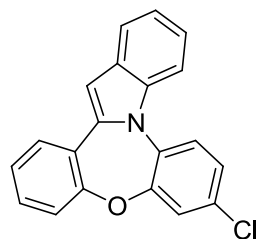
2h

2-(2-Bromophenyl)-1H-benzo[d]imidazole (2h). ^1H NMR (DMSO- d_6 , 400 MHz) δ 12.79 (s, 1H), 7.82 (d, 1H, $J = 7.6$ Hz), 7.76 (d, 1H, $J = 7.2$ Hz), 7.70 (d, 1H, $J = 6.4$ Hz), 7.55 (t, 2H, $J = 6.8$ Hz), 7.46 (t, 1H, $J = 7.2$ Hz), 7.24 (s, 2H). ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 150.8, 143.5, 134.8, 133.8, 132.7, 132.6, 131.8, 128.2, 123.1, 122.0, 121.9, 119.5, 112.0.

General procedure for synthesis of indole-fused dibenzo[*b,f*][1,4]oxazepines

A sealable tube (20 mL) was charged with CuI (3.8 mg, 0.02mmol), dibenzoylmethane (4.5 mg, 0.02 mmol), tripotassium phosphate (127.4 mg, 0.6 mmol), the 2-halophenol (**1**, 0.24 mmol) and the 2-(2-halophenyl)-1H-indole (**2**, 0.20 mmol). DMF (2 mL) was added and the tube sealed. The mixture was allowed to stir under N_2 at 120 °C for 12 h. Saturated aqueous NaCl (25 mL), and EtOAc (25 mL) were added to the cooled reaction mixture successively. The organic phase was separated, and the aqueous phase was further extracted with EtOAc (2×25 mL). The combined organic layers were dried over anhydrous NaSO_4 and concentrated. The residue was purified by column chromatography on silica gel using petroleum ether as eluent to provide the desired products (**3**).

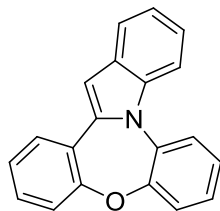
Characterization data of compounds 3a-l



3a

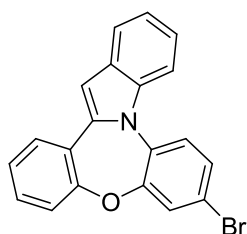
8-Chlorodibenzo[*b,f*]indolo[1,2-*d*][1,4]oxazepine (3a) [New compound]. Eluent: petroleum ether. White solid, mp = 133-135 °C (uncorrected). ^1H NMR (DMSO- d_6 , 400 MHz) δ 7.75-7.79 (m, 3H), 7.69 (t, 2H, $J = 7.2$ Hz), 7.49 (d, 1H, $J = 8.0$ Hz), 7.38-7.44 (m, 2H), 7.19-7.33 (m, 3H), 7.05 (s, 1H). ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 157.3, 153.6, 136.4, 136.3, 131.0, 130.8, 130.4, 129.7, 129.0, 126.8, 126.6, 125.9,

124.3, 123.6, 123.2, 122.0, 121.5, 121.4, 111.7, 104.1. HRMS (EI) Calcd for $C_{20}H_{12}NOCl$ (M)⁺ 317.0607; Found, 317.0604.



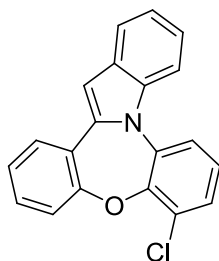
3b

Indolo[1,2-*d*]dibenzo[*b,f*][1,4]oxazepine (3b) [New compound]. Eluent: petroleum ether. White solid, mp = 135-137 °C (uncorrected). ¹H NMR (DMSO-*d*₆, 400 MHz) δ 7.75-7.79 (m, 2H), 7.70 (d, 2H, *J* = 8.8 Hz), 7.54-7.57 (m, 1H), 7.37-7.44 (m, 2H), 7.31-7.35 (m, 2H), 7.18-7.29 (m, 3H), 7.02 (s, 1H). ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 157.7, 153.3, 136.7, 136.4, 131.3, 130.7, 129.7, 129.0, 128.0, 126.6, 126.5, 124.8, 124.5, 123.5, 123.0, 121.9, 121.5, 121.3, 111.7, 103.7. HRMS (EI) Calcd for $C_{20}H_{13}NO$ (M)⁺ 283.0997; Found, 283.0996.



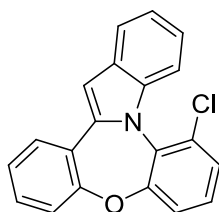
3c

8-Bromodibenzo[*b,f*]indolo[1,2-*d*][1,4]oxazepine (3c) [New compound]. Eluent: petroleum ether. White solid, mp = 133-135 °C (uncorrected). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 7.91 (d, 1H, *J* = 2.0 Hz), 7.82 (dd, 1H, *J* = 8.0 Hz, 1.5 Hz), 7.72-7.77 (m, 3H), 7.56 (dd, 1H, *J* = 8.0 Hz, 2.0 Hz), 7.52 (dd, 1H, *J* = 8.5 Hz, 1.0 Hz), 7.46 (td, 1H, *J* = 7.5 Hz, 1.5 Hz), 7.35 (td, 1H, *J* = 7.5 Hz, 1.0 Hz), 7.30 (td, 1H, *J* = 7.0 Hz, 1.0 Hz), 7.23-7.26 (m, 1H), 7.08 (s, 1H). ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 162.2, 158.6, 141.2, 135.8, 135.7, 134.6, 134.5, 133.9, 131.6, 131.2, 130.9, 129.2, 128.5, 126.9, 126.4, 126.3, 123.7, 116.5, 109.1, 109.0. HRMS (EI) Calcd for $C_{20}H_{12}NOBr$ (M)⁺ 361.0102; Found, 361.0107.



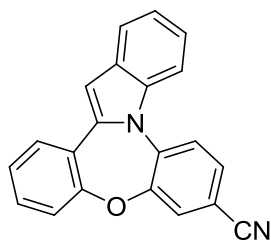
3d

9-Chlorodibenzo[*b,f*]indolo[1,2-*d*][1,4]oxazepine (3d) [New compound]. Eluent: petroleum ether. White solid, mp = 133-135 °C (uncorrected). ^1H NMR (DMSO- d_6 , 500 MHz) δ 7.83 (d, 1H, $J = 7.5$ Hz), 7.71-7.75 (m, 3H), 7.51-7.55 (m, 2H), 7.44-7.47 (m, 1H), 7.35 (t, 2H, $J = 8.5$ Hz), 7.29 (t, 1H, $J = 7.0$ Hz), 7.24 (t, 1H, $J = 7.5$ Hz), 7.08 (s, 1H). ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 156.5, 148.3, 136.2, 135.9, 132.7, 130.3, 129.4, 128.6, 127.5, 126.9, 126.7, 126.6, 124.1, 123.3, 121.8, 121.3, 121.2, 111.5, 104.0. HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{12}\text{ClNO}$ (M^+) 317.0607; Found, 317.0608.



3e

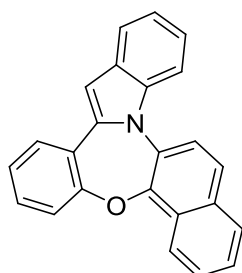
6-Chlorodibenzo[*b,f*]indolo[1,2-*d*][1,4]oxazepine (3e) [New compound]. Eluent: petroleum ether. White solid, mp = 151-153 °C (uncorrected). ^1H NMR (CDCl_3 , 500 MHz) δ 7.69-7.73 (m, 2H), 7.33-7.36 (m, 2H), 7.26-7.32 (m, 4H), 7.21-7.24 (m, 3H), 6.84 (s, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 158.9, 157.8, 136.6, 136.3, 130.0, 129.8, 129.6, 128.8, 128.3, 128.0, 127.7, 126.1, 125.3, 122.2, 121.2, 120.9, 120.8, 120.5, 113.8, 104.4. HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{12}\text{ClNO}$ (M^+) 317.0607; Found, 317.0606.



3f

Dibenzo[*b,f*]indolo[1,2-*d*][1,4]oxazepine-8-carbonitrile (3f) [New compound].

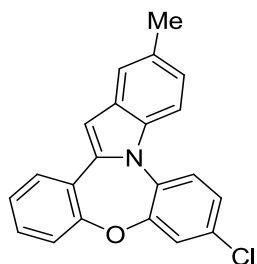
Eluent: petroleum ether. White solid, mp = 173-175 °C (uncorrected). ¹H NMR (CDCl₃, 500 MHz) δ 7.87 (d, 1H, *J* = 8.0 Hz), 7.68-7.73 (m, 4H), 7.57 (dd, 1H, *J* = 8.5 Hz, 2.0 Hz), 7.36-7.39 (m, 1H), 7.32-7.34 (m, 1H), 7.27-7.30 (m, 3H), 6.93 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 157.2, 153.3, 136.7, 136.6, 136.6, 130.3, 129.6, 129.4, 128.7, 126.7, 126.3, 125.2, 124.3, 123.6, 122.4, 121.5, 120.9, 117.7, 111.4, 109.9, 104.8. HRMS (EI) Calcd for C₂₁H₁₂N₂O (M)⁺ 308.0950; Found, 308.0955.



3g

Benzo[*f*]naphtho[1,2-*b*]indolo[1,2-*d*][1,4]oxazepine (3g) [New compound].

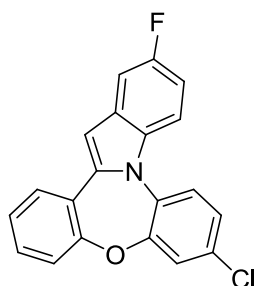
Eluent: petroleum ether. White solid, mp = 166-168 °C (uncorrected). ¹H NMR (CDCl₃, 500 MHz) δ 8.63 (d, 1H, *J* = 8.0 Hz), 7.89 (t, 2H, *J* = 9.0 Hz), 7.79 (d, 1H, *J* = 8.0 Hz), 7.73-7.76 (m, 3H), 7.65 (t, 1H, *J* = 8.0 Hz), 7.53 (t, 2H, *J* = 8.5 Hz), 7.31-7.34 (m, 1H), 7.26-7.28 (m, 2H), 7.21-7.24 (m, 1H), 6.93 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 158.5, 148.3, 137.3, 136.9, 132.7, 129.6, 129.3, 129.1, 128.2, 128.0, 127.7, 127.1, 126.4, 125.7, 125.5, 125.2, 122.8, 122.6, 121.9, 121.5, 121.2, 111.6, 103.3. HRMS (EI) Calcd for C₂₄H₁₅NO (M)⁺ 333.1154; Found, 333.1156.



3h

2-Methyl-8-chlorodibenzo[*b,f*]indolo[1,2-*d*][1,4]oxazepine (3h) [New compound].

Eluent: petroleum ether. White solid, mp = 143-145 °C (uncorrected). ¹H NMR (CDCl₃, 500 MHz) δ 7.71 (dd, 1H, *J* = 8.0 Hz, 1.5Hz), 7.67 (d, 1H, *J* = 8.5 Hz), 7.57 (d, 1H, *J* = 8.5 Hz), 7.49 (s, 1H), 7.45 (d, 1H, *J* = 2.5 Hz), 7.30-7.34 (m, 2H), 7.26 (t, 1H, *J* = 1.0 Hz), 7.23-7.25 (m, 1H), 7.10 (dd, 1H, *J* = 8.0 Hz, 1.0Hz), 6.80 (s, 1H), 2.48 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz) δ 152.3, 148.5, 131.5, 129.8, 126.1, 125.8, 125.7, 124.6, 124.2, 124.0, 120.7, 120.5, 119.7, 119.6, 119.4, 117.9, 115.7, 115.6, 105.8, 98.0, 16.2. HRMS (EI) Calcd for C₂₁H₁₄NOCl (M)⁺ 331.0764; Found, 331.0768.

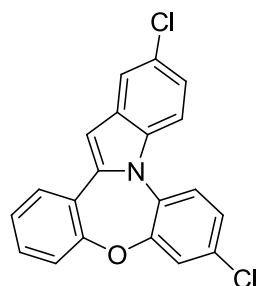


3i

2-Fluoro-8-chlorodibenzo[*b,f*]indolo[1,2-*d*][1,4]oxazepine (3i) [New compound].

Eluent: petroleum ether. White solid, mp = 162-164 °C (uncorrected). ¹H NMR (CDCl₃, 500 MHz) δ 7.70 (d, 1H, *J* = 8.0 Hz), 7.64 (d, 1H, *J* = 8.0 Hz), 7.59-7.61 (m, 1H), 7.46 (d, 1H, *J* = 2.0 Hz), 7.31-7.38 (m, 3H), 7.26-7.28 (m, 2H), 7.00 (td, 1H, *J* = 9.0 Hz, 2.5 Hz), 6.83 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 158.7 (*J*_{CF} = 235 Hz), 155.8 (*J*_{CF} = 463.1 Hz), 138.3, 133.2, 131.8, 130.6, 130.3, 129.8, 129.7, 129.3, 126.1, 125.9, 124.9, 124.4, 123.3, 121.0, 111.8 (*J*_{CF} = 100.1 Hz), 111.7 (*J*_{CF} = 116.4 Hz),

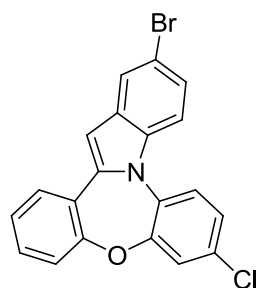
106.0 ($J_{CF} = 23.9$ Hz), 103.3 ($J_{CF} = 5.0$ Hz). HRMS (EI) Calcd for $C_{20}H_{11}NOFCl$ (M)
+ 335.0513; Found, 335.0512.



3j

2-Chloro-8-chlorodibenzo[*b,f*]indolo[1,2-*d*][1,4]oxazepine (3j) [New compound].

Eluent: petroleum ether. White solid, mp = 165-167 °C (uncorrected). 1H NMR (CDCl₃, 500 MHz) δ 7.64 (dd, 1H, $J = 8.0$ Hz, 1.5 Hz), 7.61 (d, 1H, $J = 2.0$ Hz), 7.52-7.54 (m, 2H), 7.42 (d, 1H, $J = 2.5$ Hz), 7.27-7.34 (m, 2H), 7.19-7.23 (m, 2H), 7.16 (dd, 1H, $J = 9.0$ Hz, 2.0 Hz), 6.75 (s, 1H). ^{13}C NMR (CDCl₃, 125 MHz) δ 157.6, 153.9, 138.1, 135.0, 132.0, 130.4, 130.3, 129.4, 127.2, 126.1, 125.9, 124.9, 124.3, 123.3, 123.2, 121.1, 120.6, 112.4, 103.0. HRMS (EI) Calcd for $C_{20}H_{11}NOCl_2$ (M)⁺ 351.0218; Found, 351.0219.

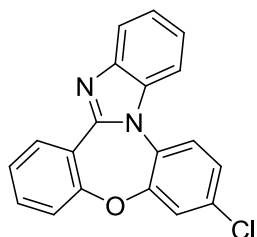


3k

2-Bromo-8-chlorodibenzo[*b,f*]indolo[1,2-*d*][1,4]oxazepine (3k) [New compound].

Eluent: petroleum ether. White solid, mp = 174-176 °C (uncorrected). 1H NMR (CDCl₃, 500 MHz) δ 7.79 (d, 1H, $J = 1.5$ Hz), 7.67 (d, 1H, $J = 8.0$ Hz), 7.57 (d, 1H, $J = 8.5$ Hz), 7.51 (d, 1H, $J = 9.0$ Hz), 7.44 (d, 1H, $J = 2.0$ Hz), 7.29-7.37 (m, 3H), 7.23-

7.26 (m, 2H), 6.78 (s, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 157.7, 154.0, 137.9, 135.3, 132.0, 130.9, 130.4, 130.3, 129.4, 126.1, 125.9, 125.8, 125.0, 124.3, 123.7, 123.3, 121.0, 114.7, 112.7, 102.8. HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{11}\text{NOBrCl}$ (M) $^+$ 394.9713; Found, 394.9712.

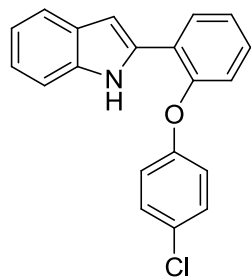


3I

8-Chlorodibenzo[*b,f*]benzimidazo[1,2-*d*][1,4]oxazepine (3I) [New compound].

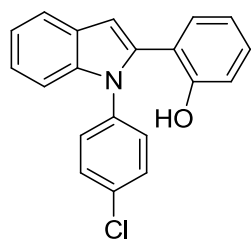
Eluent: petroleum ether / ethyl acetate (20:1). White solid, mp = 199-201 °C (uncorrected). ^1H NMR (CDCl_3 , 500 MHz) δ 8.22 (dd, 1H, $J = 7.5$ Hz, 2.0Hz), 7.94 (dd, 1H, $J = 7.0$ Hz, 1.0Hz), 7.68-7.71 (m, 2H), 7.50-7.53 (m, 2H), 7.31-7.43 (m, 5H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 158.9, 153.4, 149.5, 143.8, 134.1, 133.1, 132.5, 130.7, 128.8, 126.3, 126.2, 124.0, 123.9, 123.8, 123.5, 122.7, 121.0, 120.7, 111.2. HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{11}\text{N}_2\text{OCl}$ (M) $^+$ 318.0560; Found, 318.0561.

Characterization data of intermediates 6a and 7a in control experiments



6a

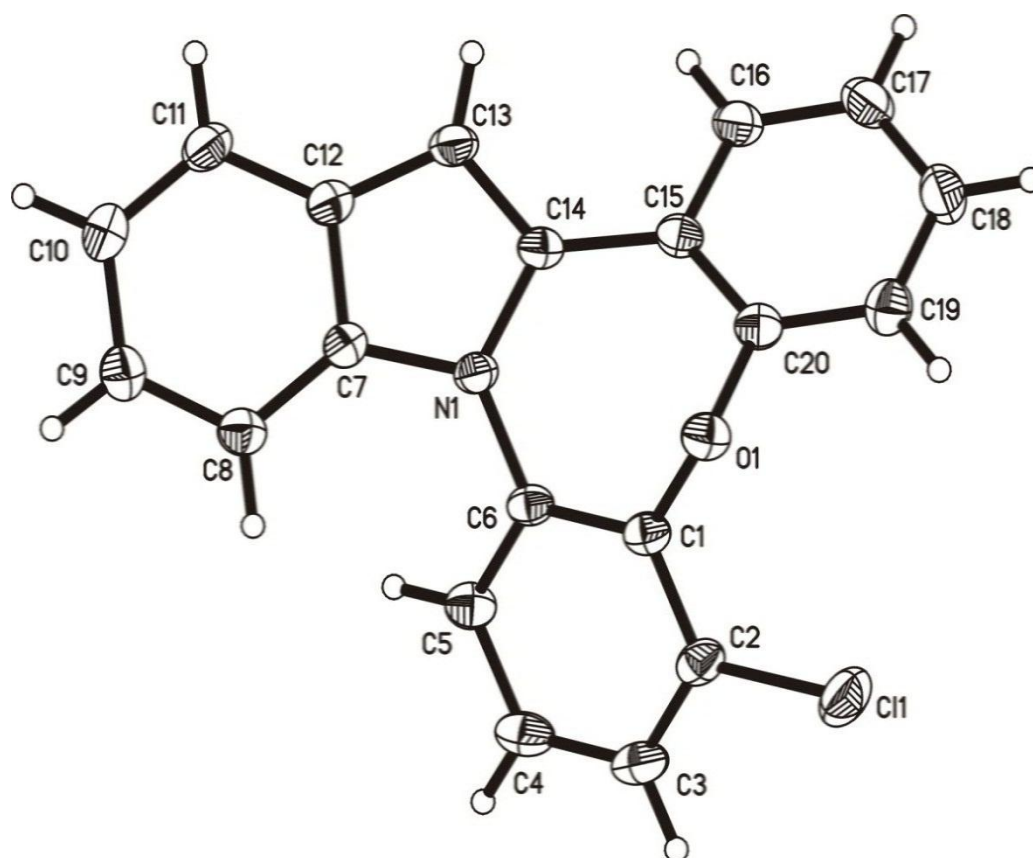
2-(2-(4-chlorophenoxy)phenyl)-1H-indole (6a) [New compound]. ^1H NMR (CDCl_3 , 400 MHz) δ 9.31 (s, 1H), 7.88-7.90 (m, 1H), 7.63 (d, 1H, $J = 8.0$ Hz), 7.36 (d, 1H, $J = 7.6$ Hz), 7.31-7.33 (m, 2H), 7.21-7.24 (m, 2H), 7.17 (t, 1H, $J = 7.6$ Hz), 7.10 (t, 1H, $J = 7.2$ Hz), 7.02 (d, 2H, $J = 9.2$ Hz), 6.95 (d, 1H, $J = 1.2$ Hz), 6.89-6.92 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 155.0, 153.2, 136.3, 134.5, 130.0, 129.1, 128.6, 128.5, 128.0, 124.4, 123.3, 122.2, 120.4, 120.4, 120.0, 119.6, 110.9, 101.1. HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{14}\text{NOCl}$ (M) $^+$ 319.0764; Found, 319.0770.



7a

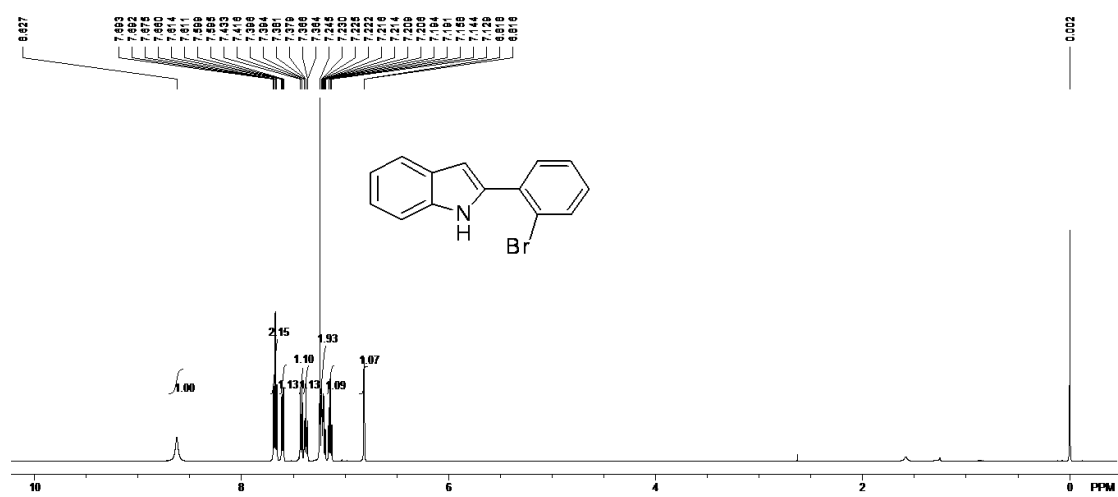
2-(1-(4-chlorophenyl)-1H-indol-2-yl)phenol (7a) [New compound]. ^1H NMR (CDCl_3 , 400 MHz) δ 7.68-7.70 (m, 1H), 7.29-7.32 (m, 3H), 7.21-7.23 (m, 2H), 7.18 (d, 1H, $J = 8.0$ Hz), 7.12 (d, 2H, $J = 8.4$ Hz), 6.93 (d, 1H, $J = 8.0$ Hz), 6.88 (d, 1H, $J = 7.2$ Hz), 6.81 (s, 1H), 6.75 (t, 1H, $J = 7.2$ Hz), 5.84 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.8, 138.4, 136.1, 134.5, 133.0, 131.0, 130.1, 129.4, 128.7, 128.0, 123.1, 121.2, 120.8, 120.1, 118.1, 115.6, 110.6, 104.5. HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{14}\text{NOCl}$ (M) $^+$ 319.0764; Found, 319.0763.

Representation of the X-ray crystal structure of 3d (CCDC 890740)

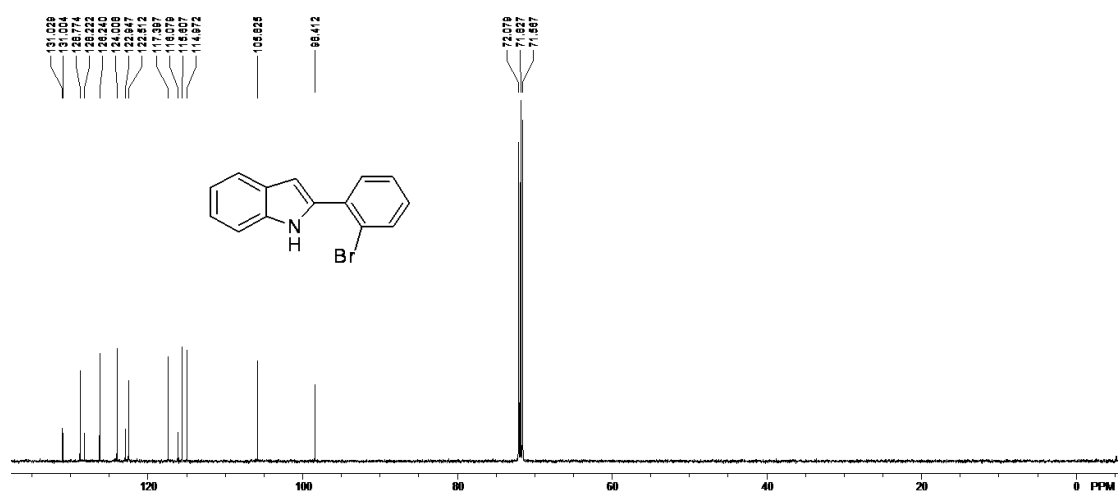


References

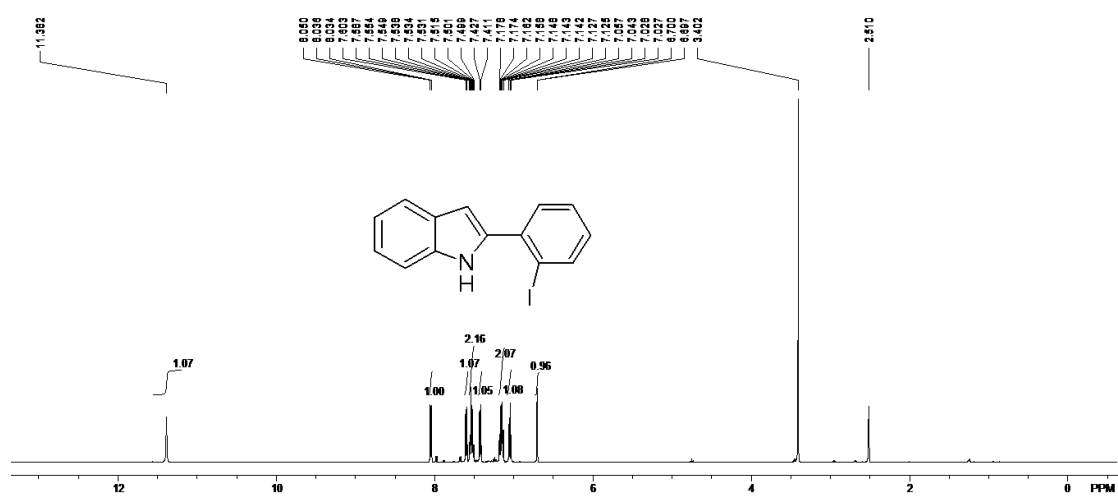
- 1 (a) E. Fischer and F. Jourdan, *Chem. Ber.*, 1883, **16**, 2241; (b) Y. Liu and W. W. McWhorter, *J. Am. Chem. Soc.*, 2003, **125**, 4240.
- 2 S. Xu, J. Lu and H. Fu, *Chem. Commun.*, 2011, **47**, 5596.
- 3 I. Bennacef, C. N. Haile, A. Schmidt, A. O. Koren, J. P. Seibyl, J. K. Staley, F. Bois, R. M. Baldwin and G. Tamagnan, *Bioorg. Med. Chem.*, 2006, **14**, 7582.



¹H NMR of substrate **2a**



¹³C NMR of substrate **2a**



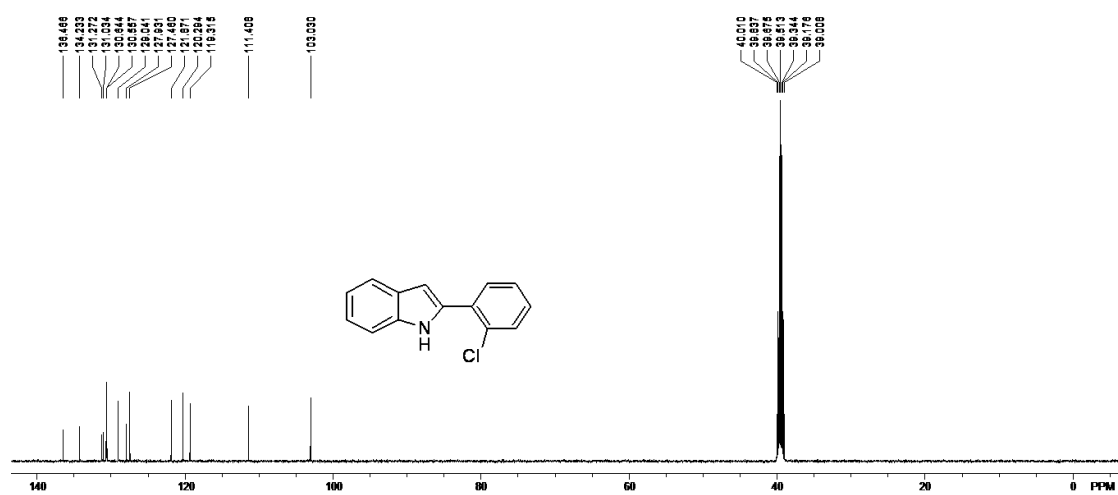
¹H NMR of substrate **2b**



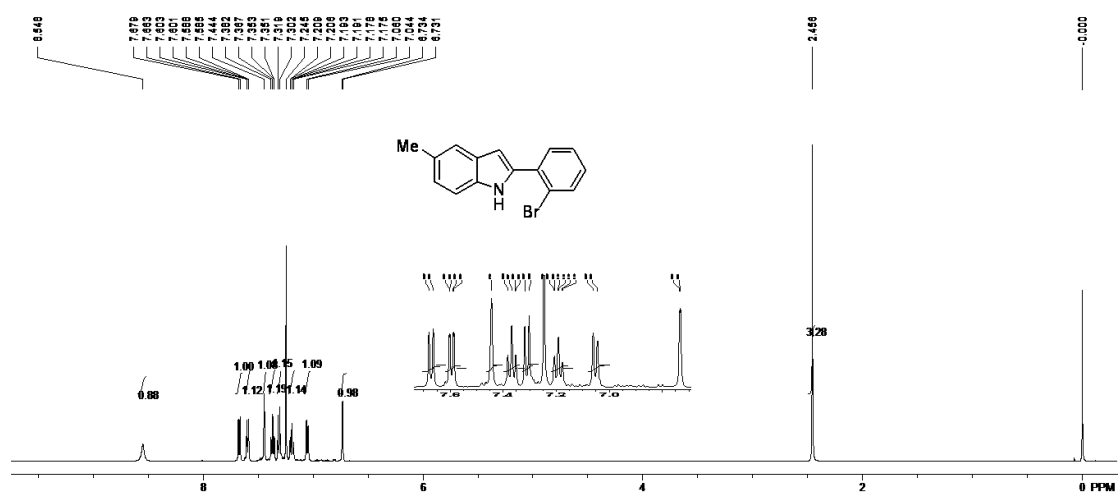
¹³C NMR of substrate **2b**



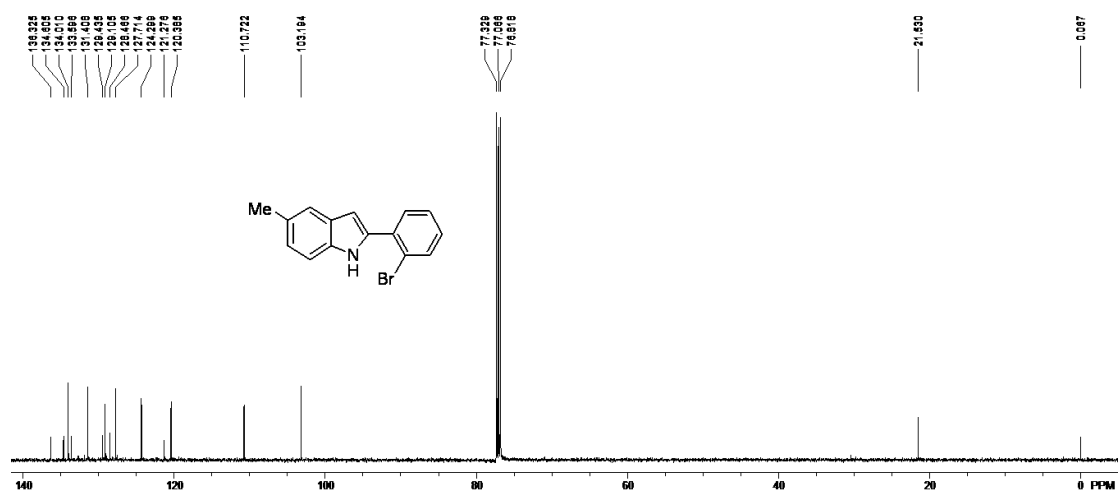
¹H NMR of substrate **2c**



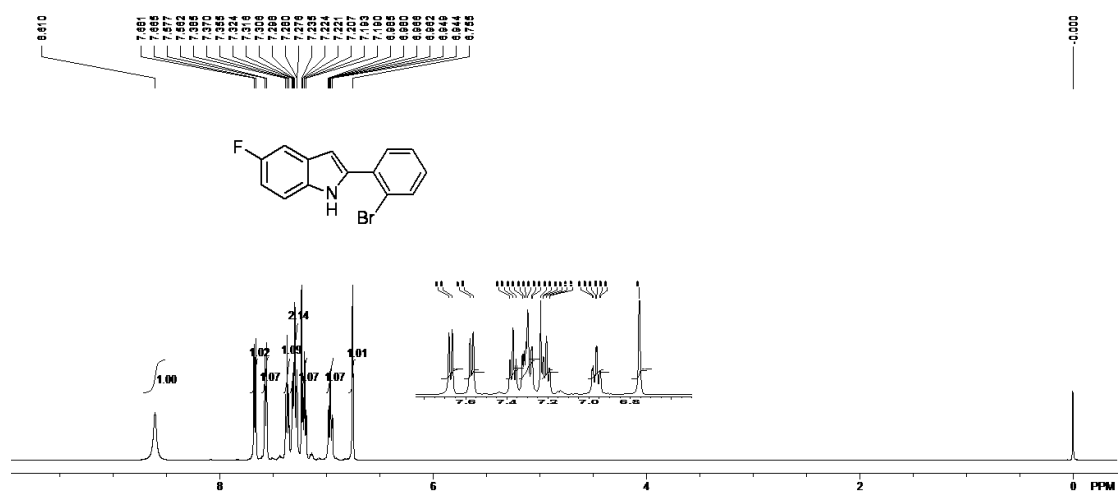
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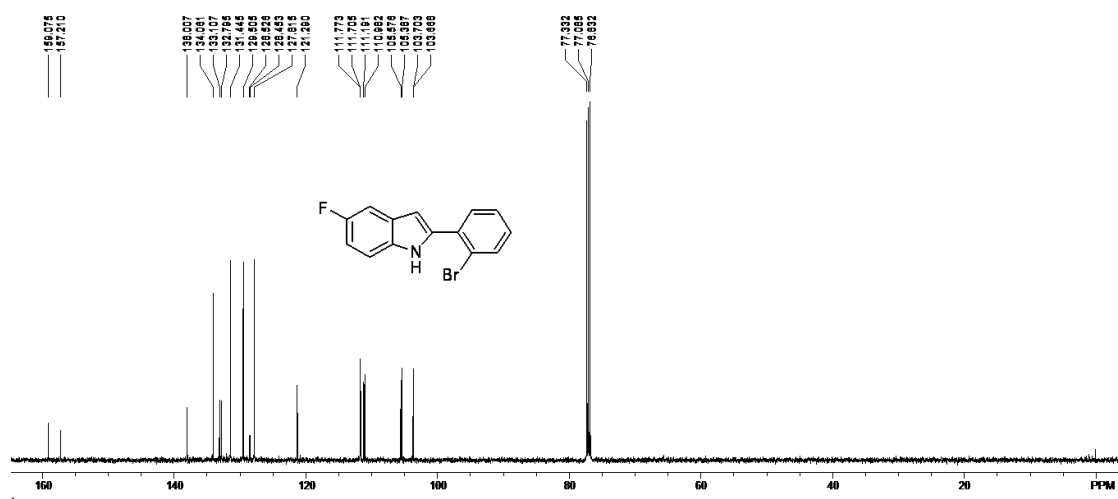
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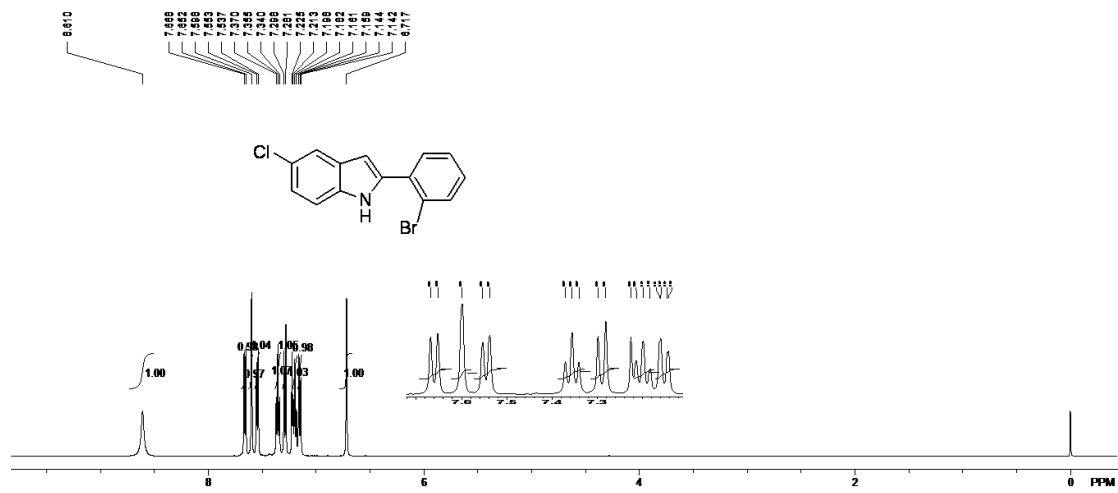
¹³C NMR of substrate **2d**



¹H NMR of substrate **2e**



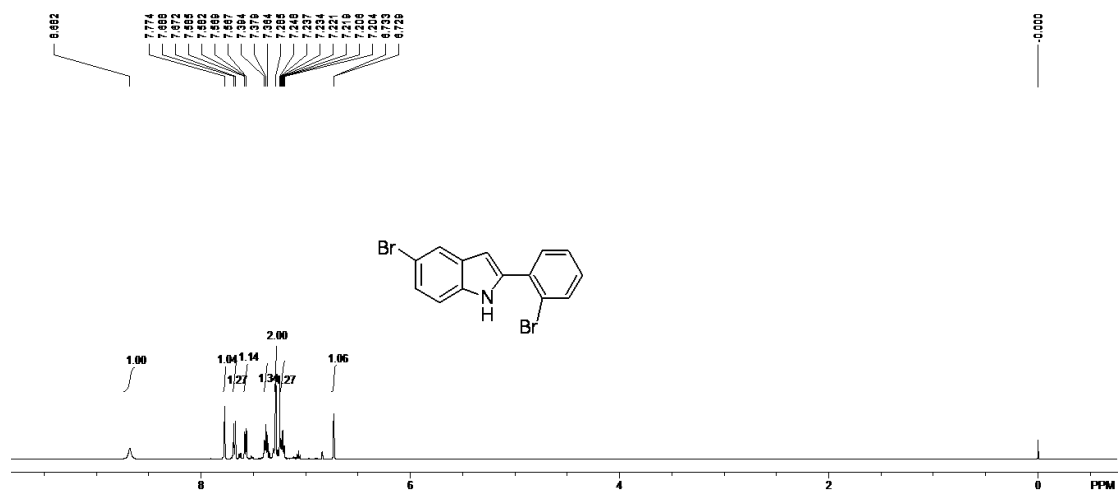
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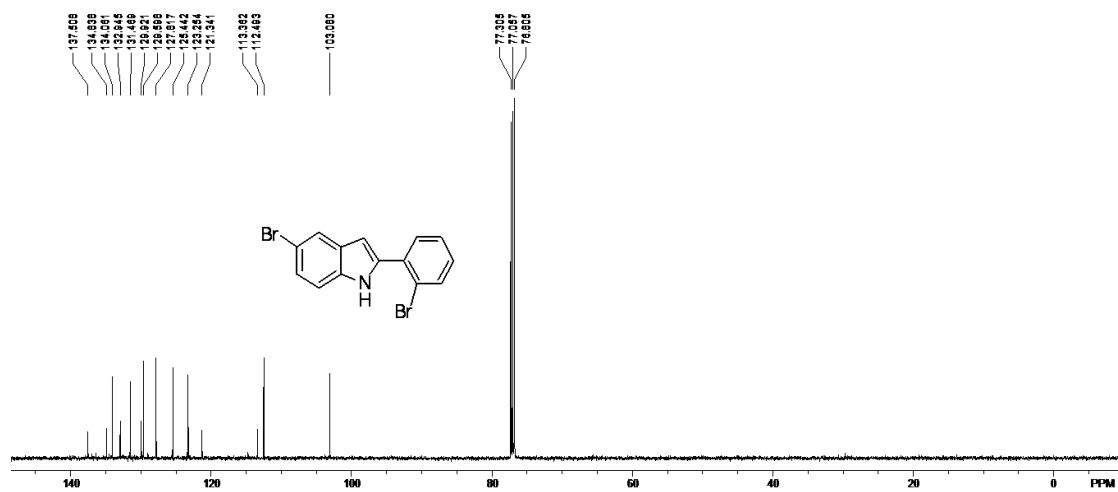
^1H NMR of substrate **2f**



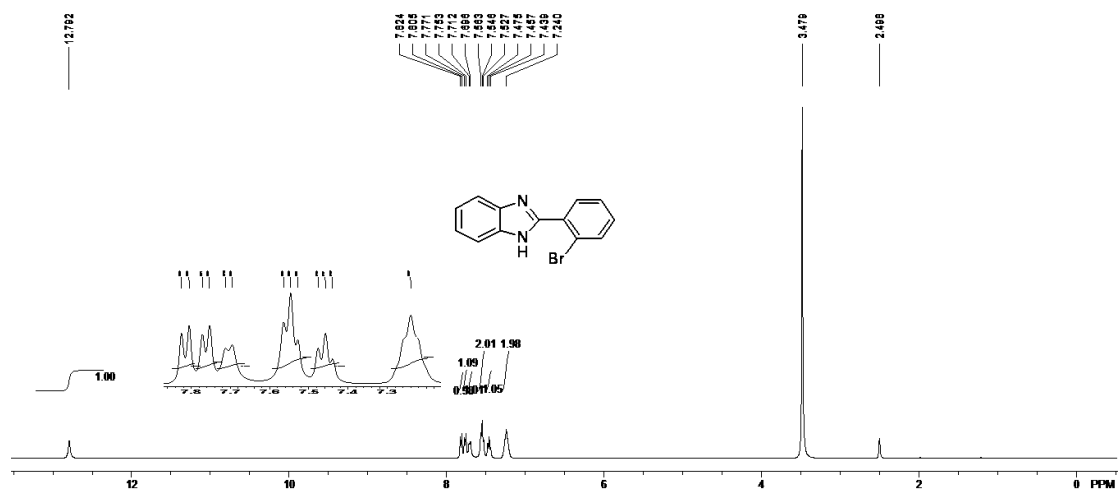
^{13}C NMR of substrate **2f**



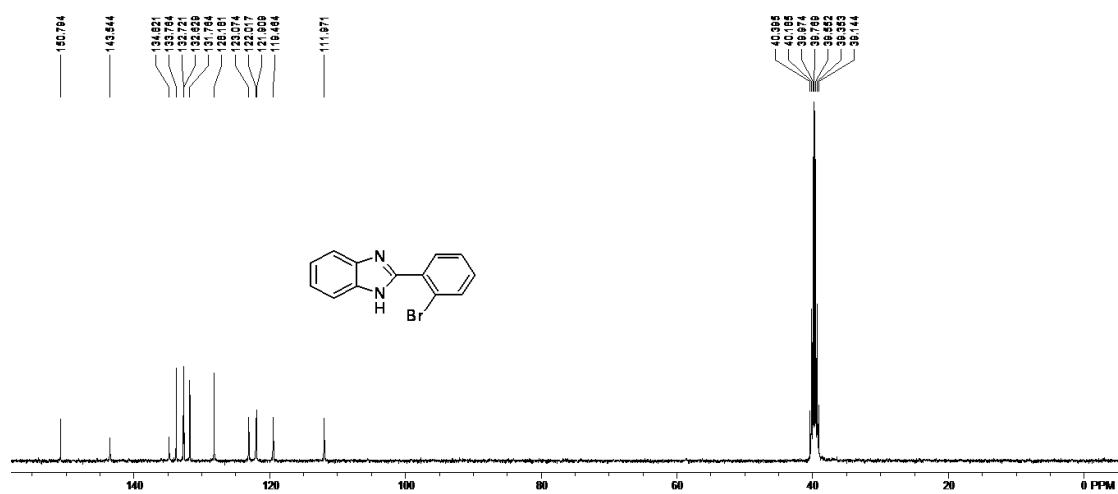
^1H NMR of substrate **2g**



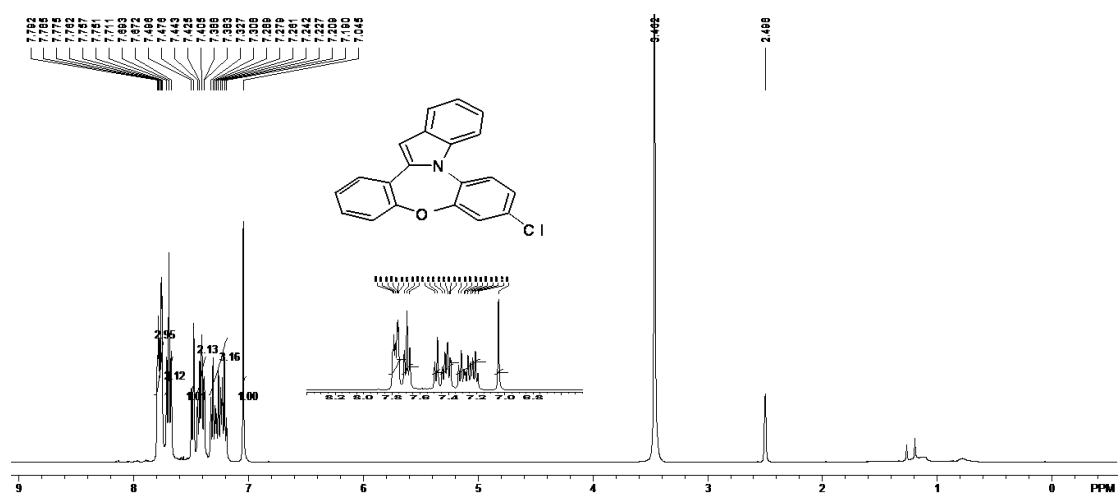
¹³C NMR of substrate **2g**



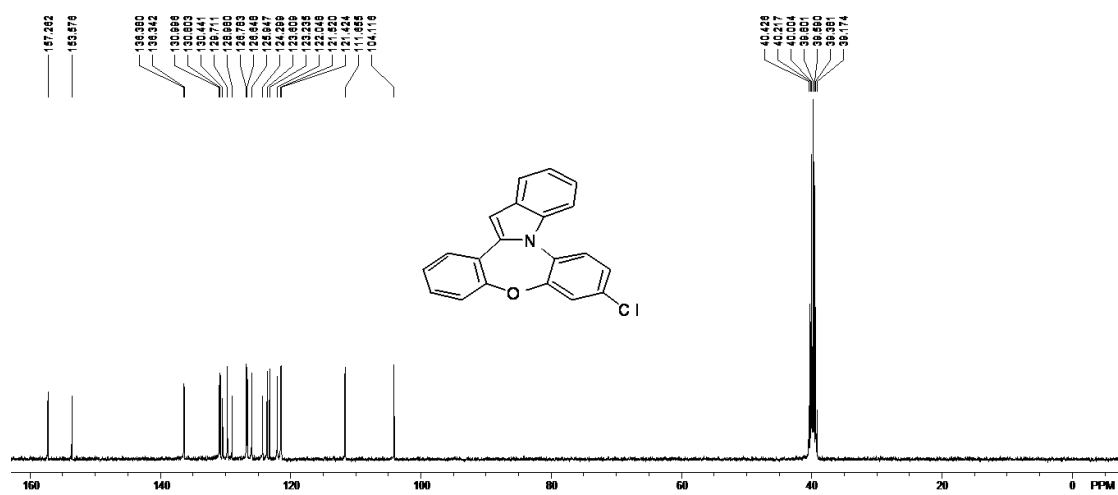
¹H NMR of substrate **2h**



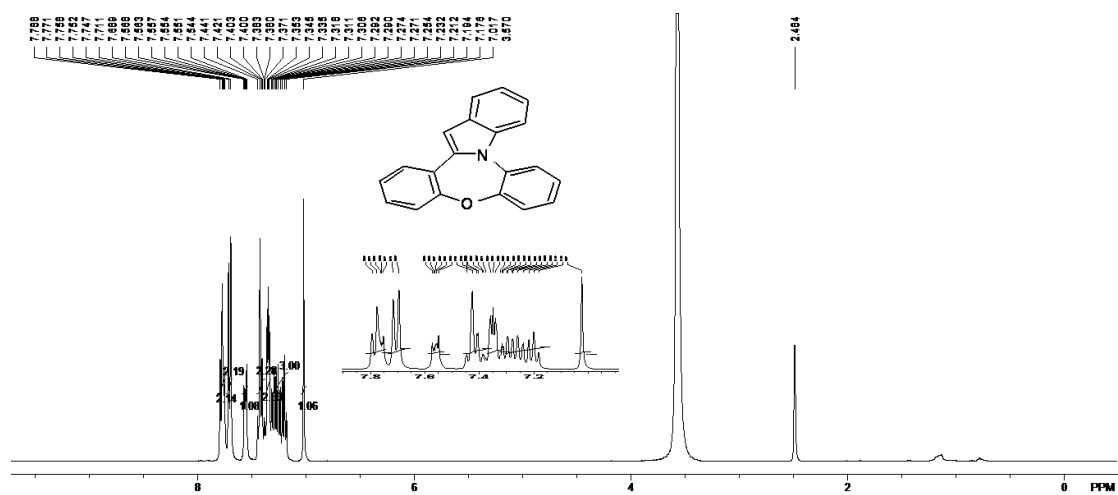
¹³C NMR of substrate **2h**



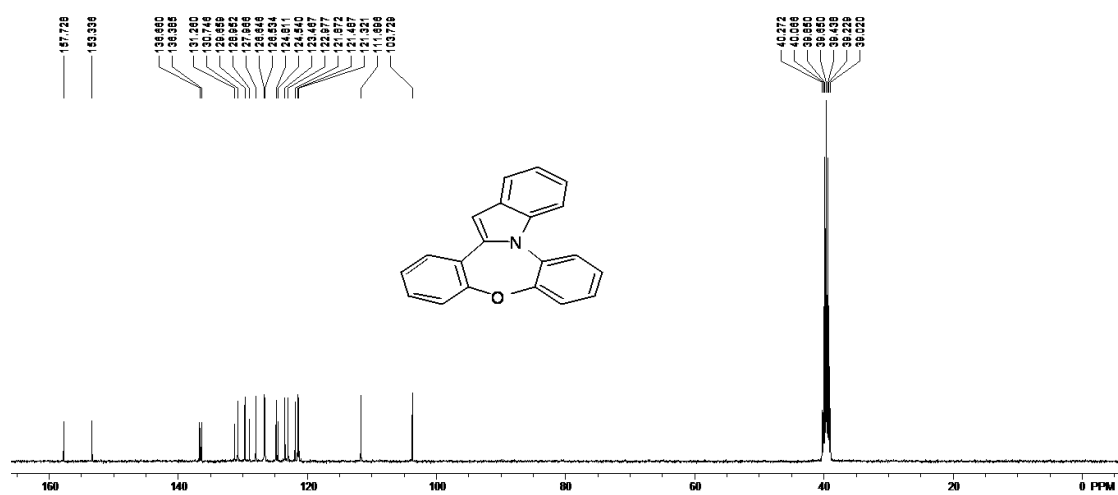
¹H NMR of product **3a**



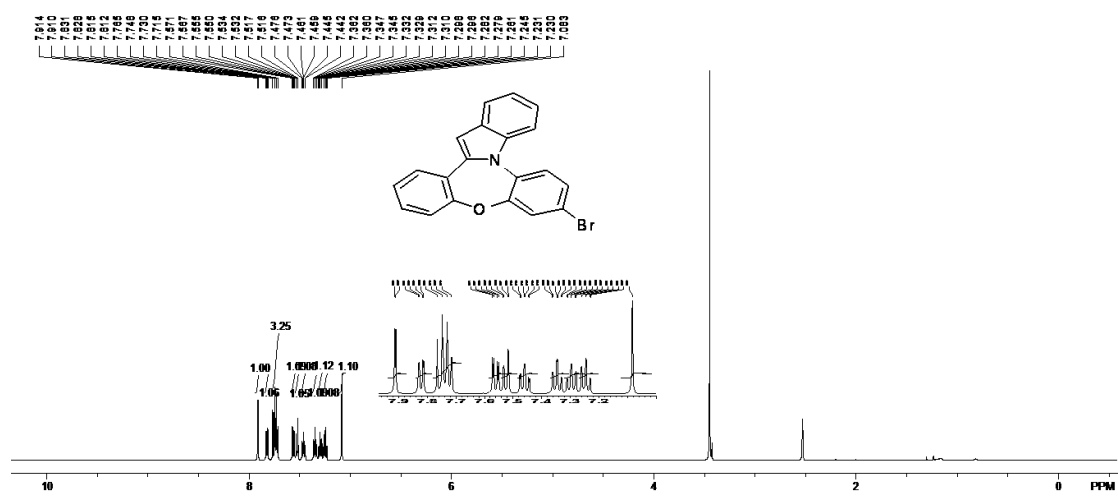
¹³C NMR of product **3a**



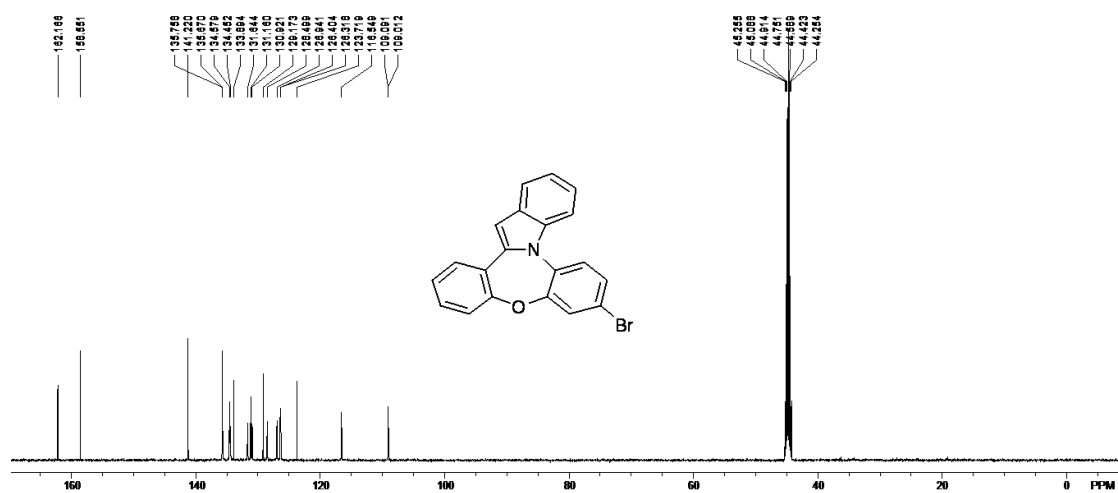
¹H NMR of product **3b**



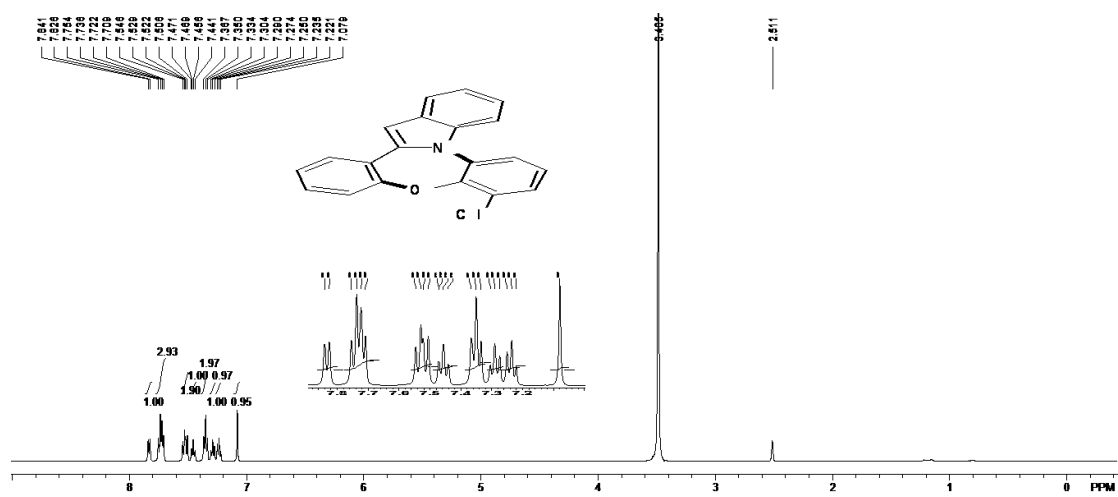
¹³C NMR of product **3b**



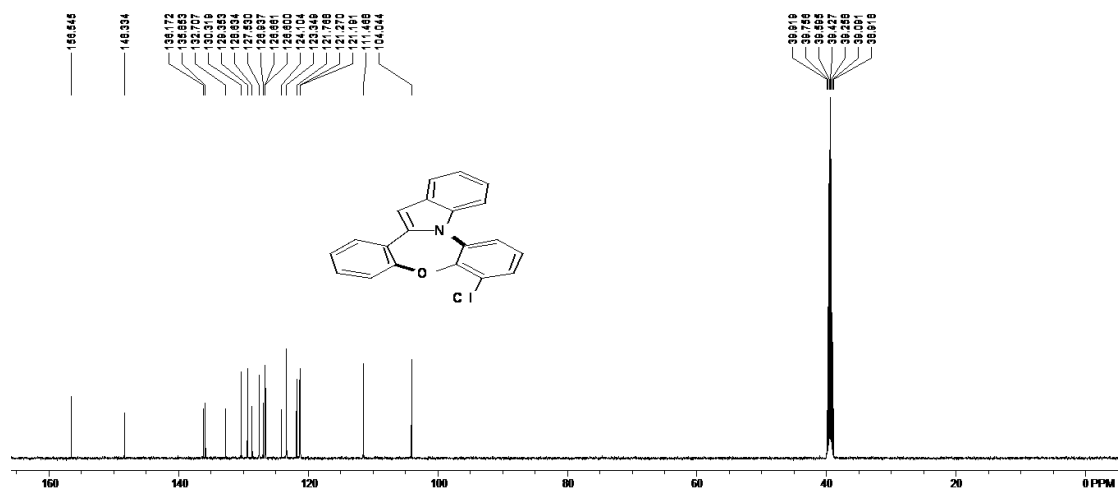
¹H NMR of product **3c**



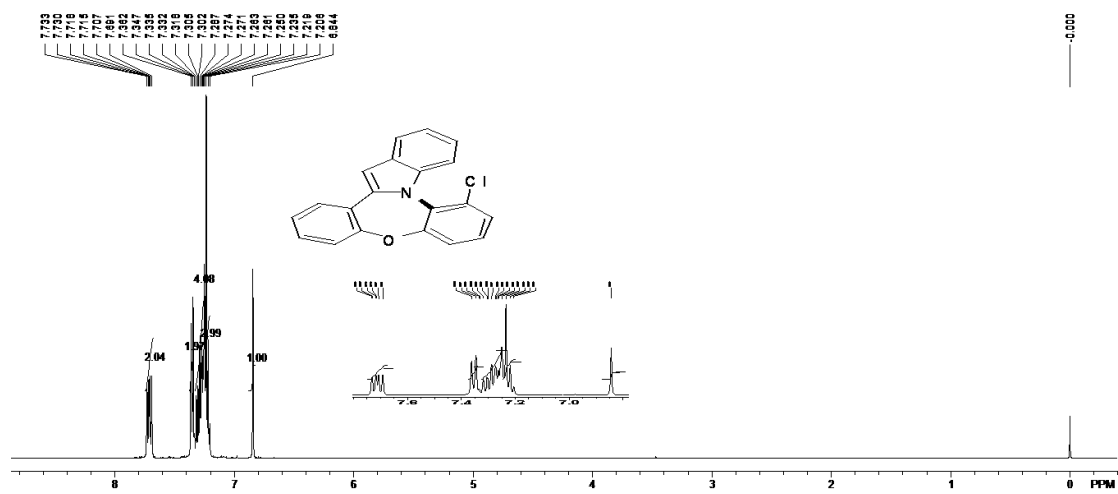
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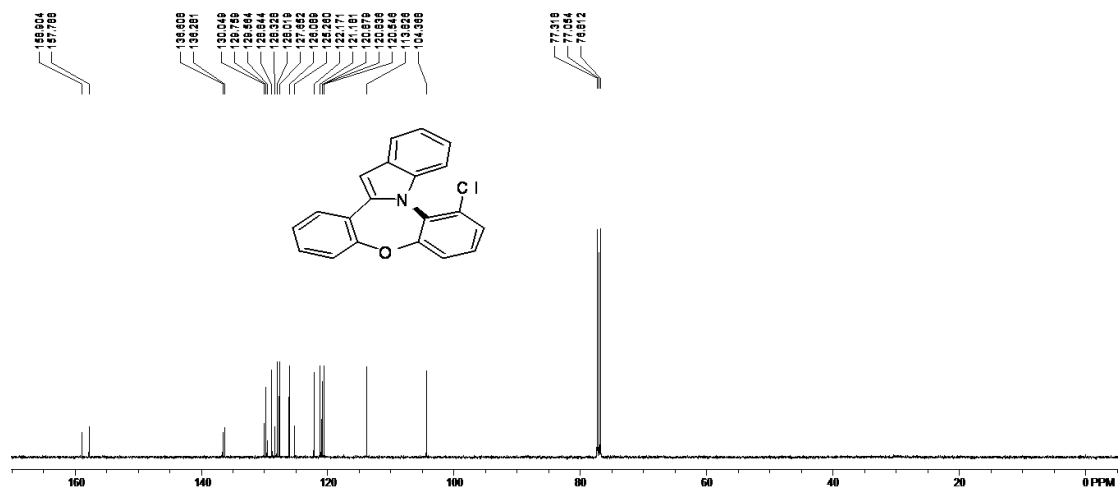
¹H NMR of product **3d**



¹³C NMR of product 3d

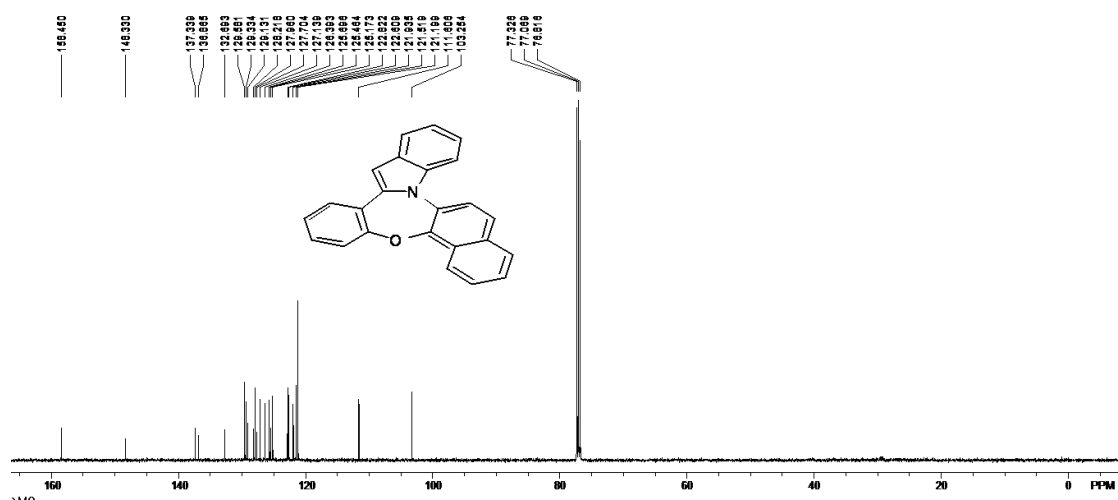


¹H NMR of product 3e

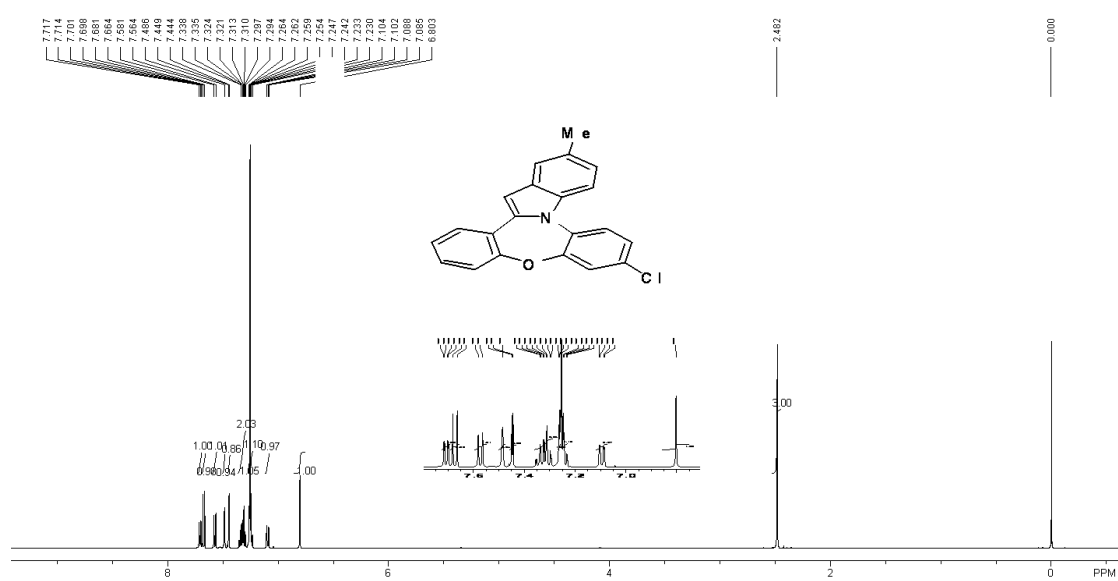


¹³C NMR of product 3e

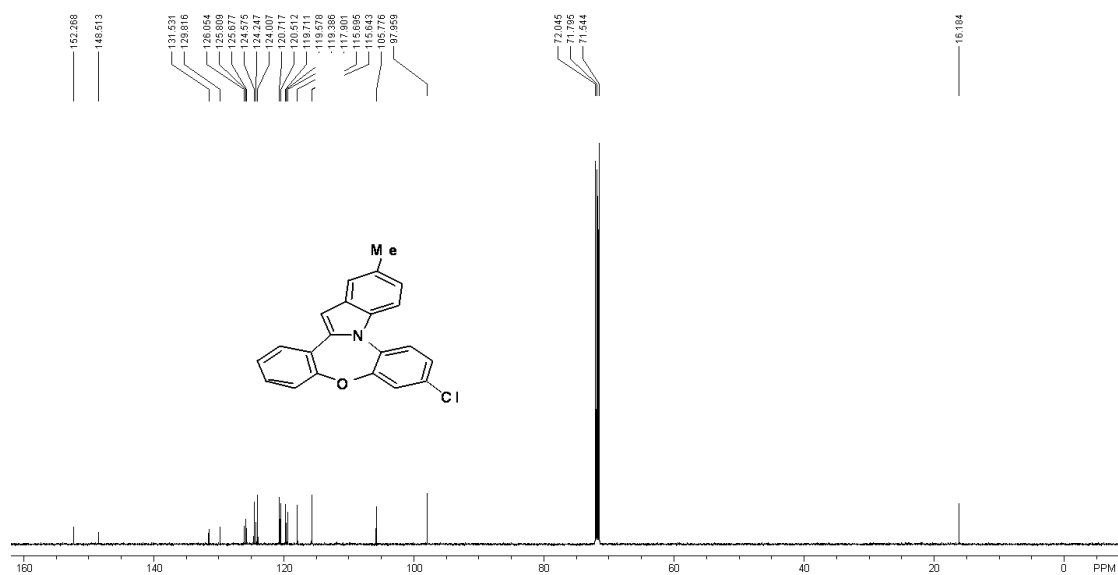
^1H NMR of product **3g**



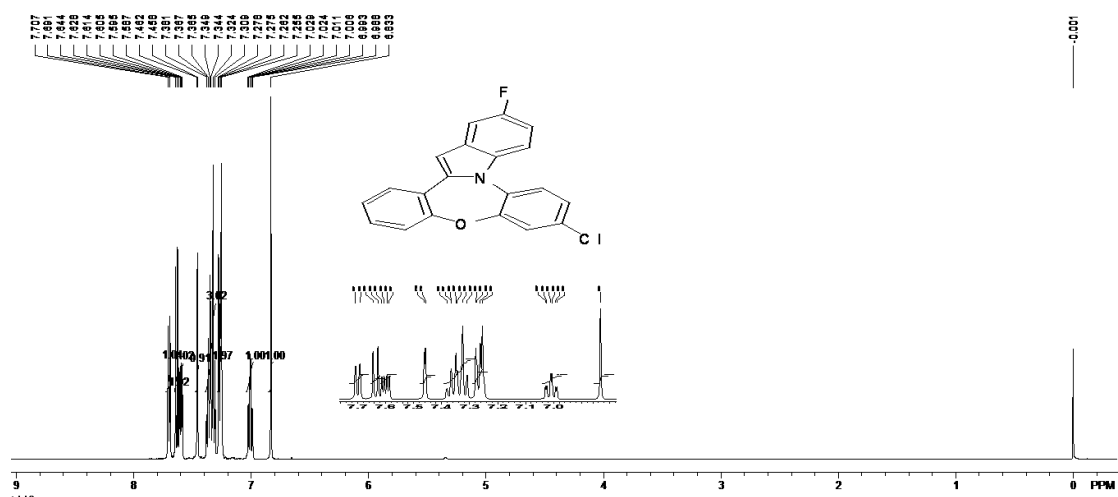
^{13}C NMR of product **3g**



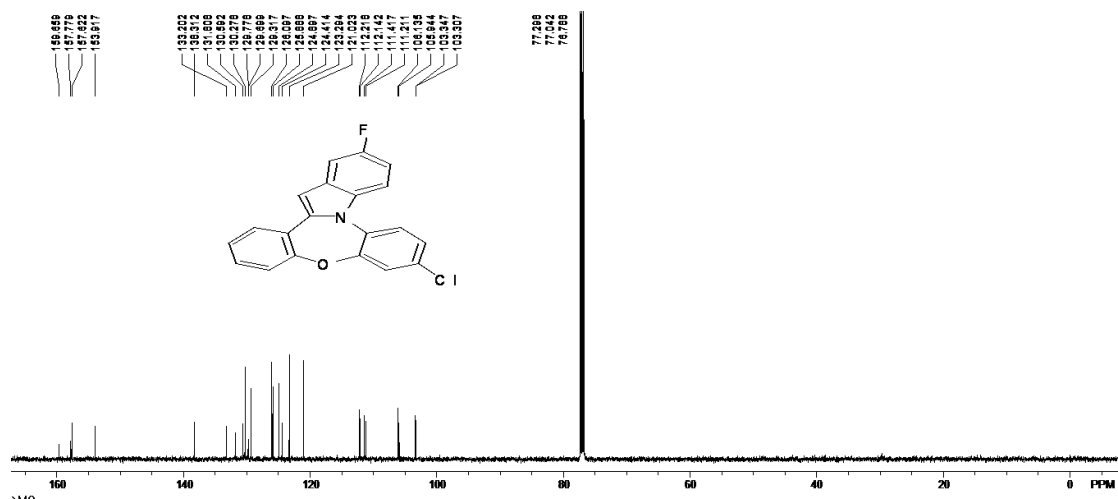
^1H NMR of product **3h**

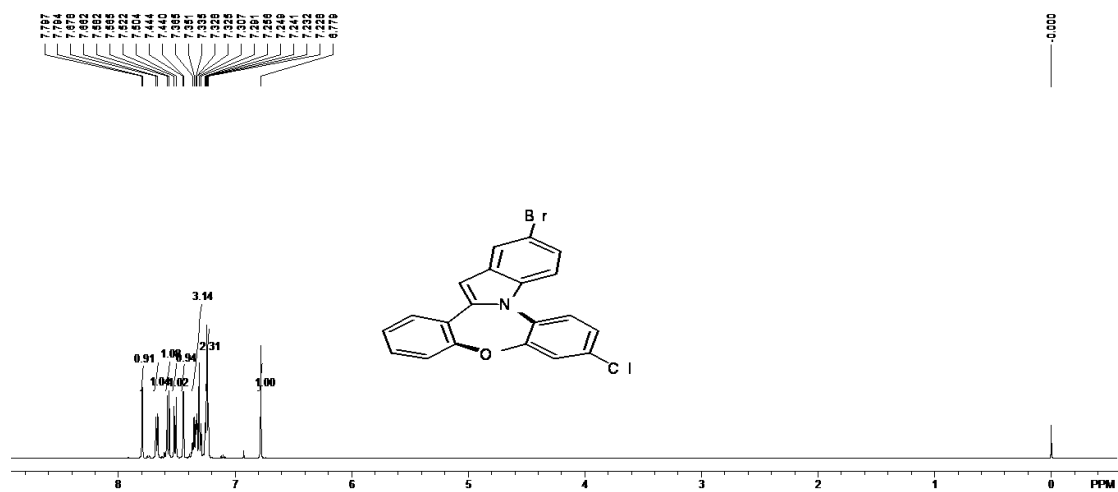


^{13}C NMR of product 3h

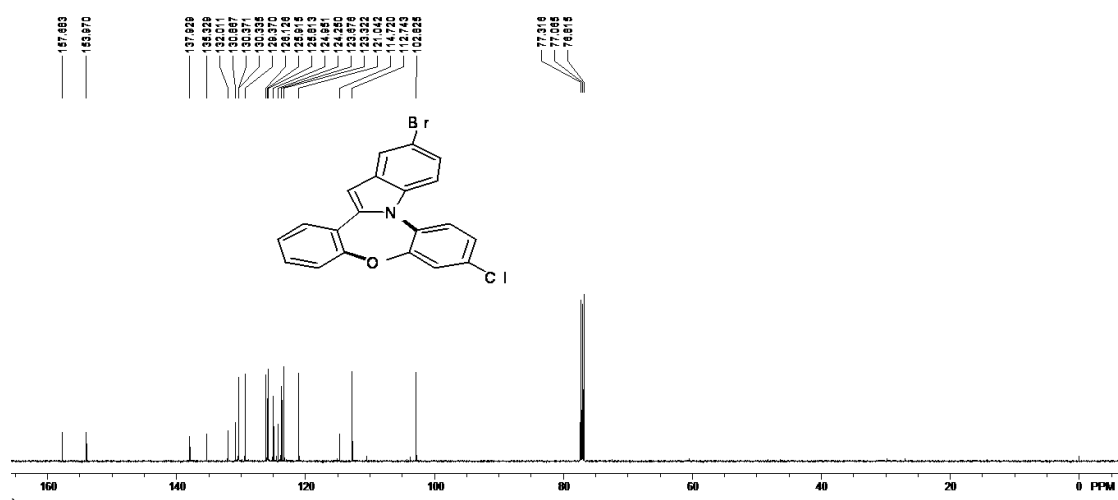


^1H NMR of product 3i

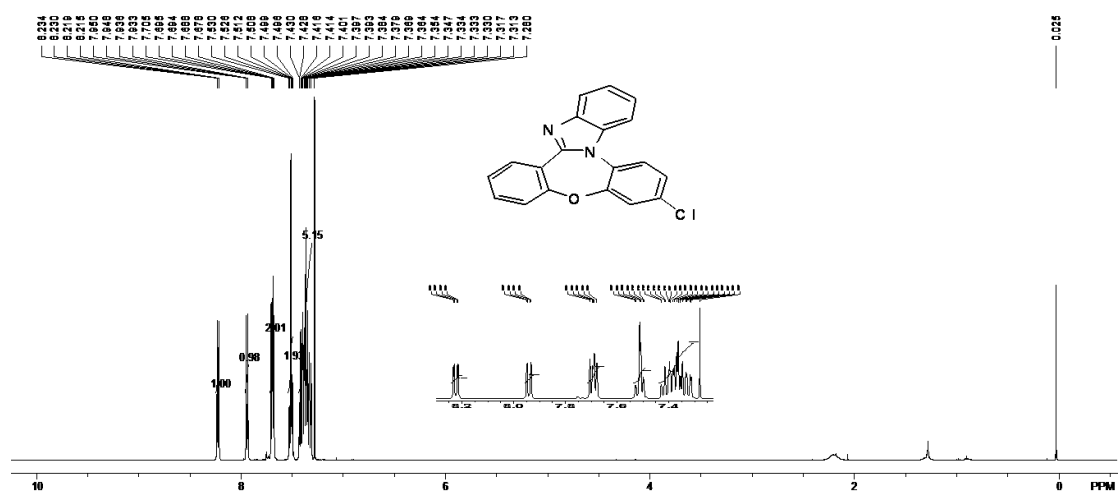




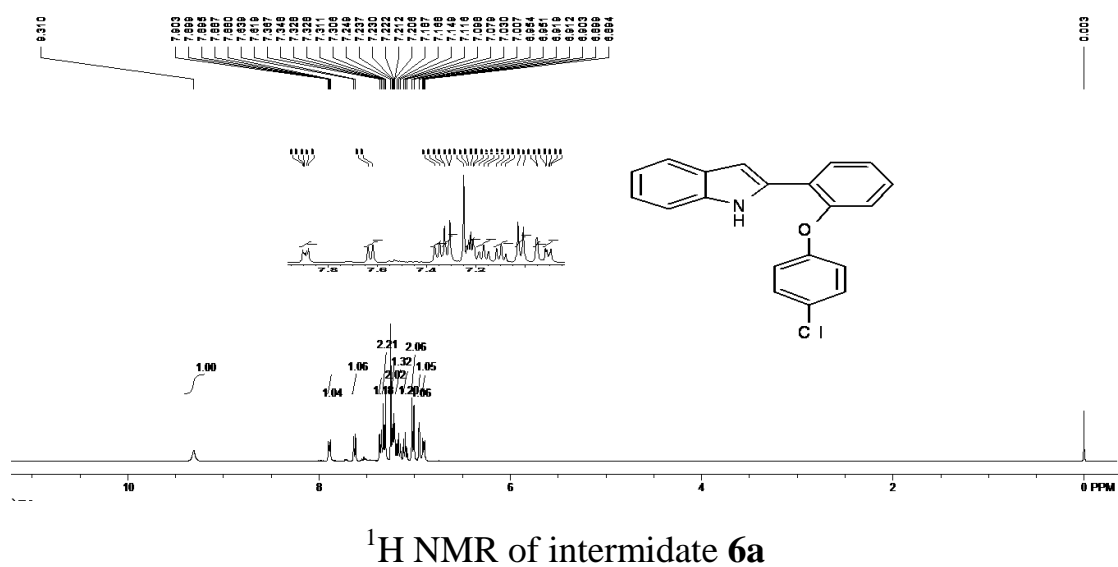
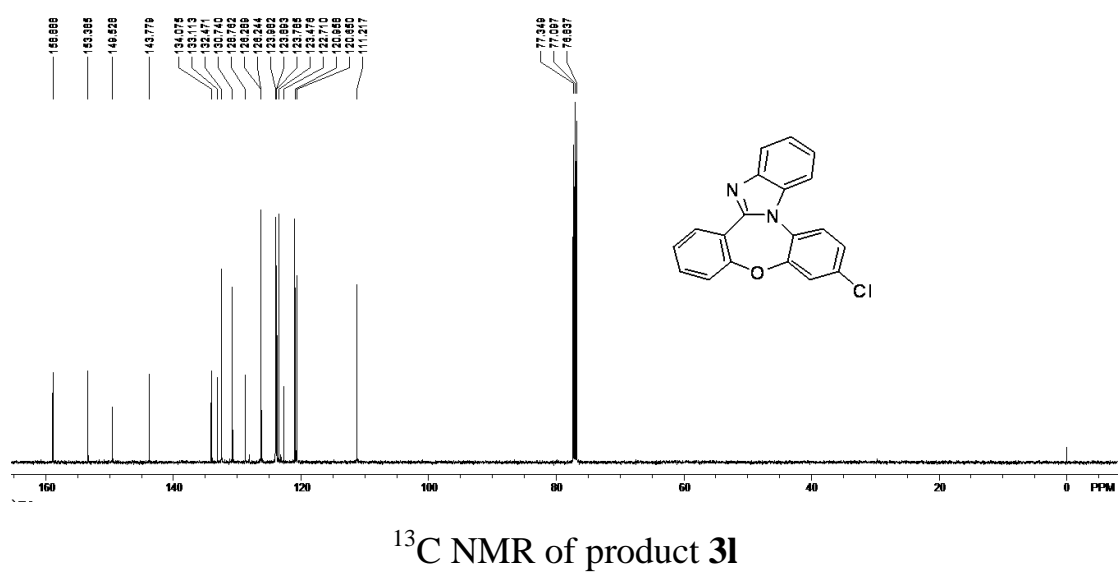
¹H NMR of product 3k



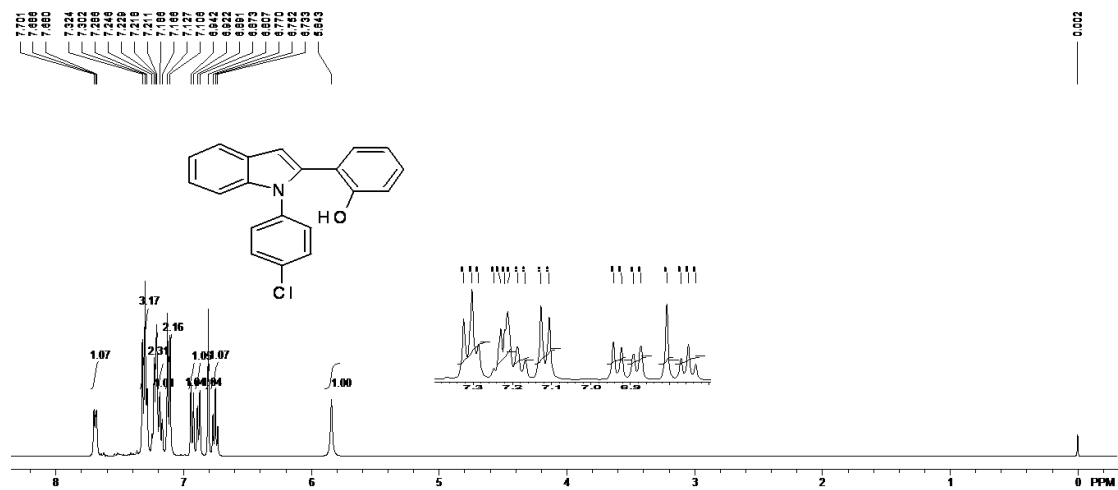
¹³C NMR of product 3k



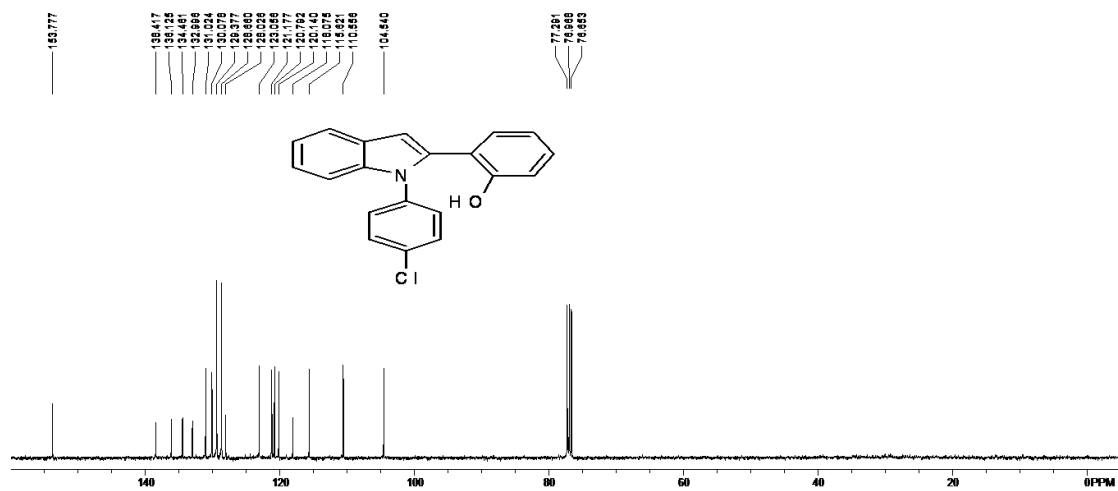
¹H NMR of product 3l



¹³C NMR of intermediate **6a**



¹H NMR of intermediate **7a**



¹³C NMR of intermediate **7a**