$La(OTf)_3$ Facilitated Self-condensation of 2-Indolylmethanol: Construction of Highly Substituted Indeno[1,2-*b*]indoles

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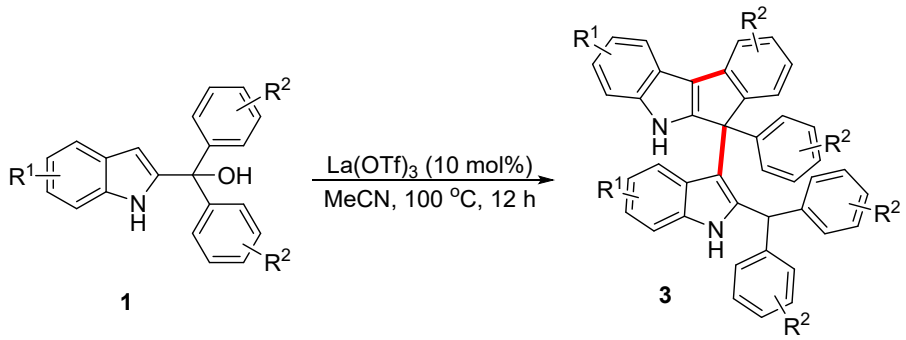
Contents

Experimental Section

All reactions were carried out under air unless otherwise noted. Commercial reagents were used as received without additional purification unless otherwise noted. 2-Indolylmethanols were prepared according to the literature procedure.[1] Reactions were monitored by thin layer chromatography (TLC) using Silicycle glass-backed TLC plates with 250 μm silica and F254 indicator. Visualization was accomplished by UV light.

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a AM-500 Fourier transform NMR spectrometer at 400/600 MHz, 125/150 MHz, 376 MHz respectively. Chemical shifts are reported relative to the solvent resonance peak δ 2.50 (DMSO-d_6) for ^{1}H; δ 39.52 (DMSO-d_6) or 77.16 ($CDCl_3$) for ^{13}C. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, b = broad singlet, m = multiplet), coupling constants, and number of protons. High resolution mass spectra were obtained using a VG autospec with an ionization mode of EI-TOF. Infrared spectra are reported in cm^{-1}. Column chromatography was performed with silica gel (50-63 μm mesh particle size).

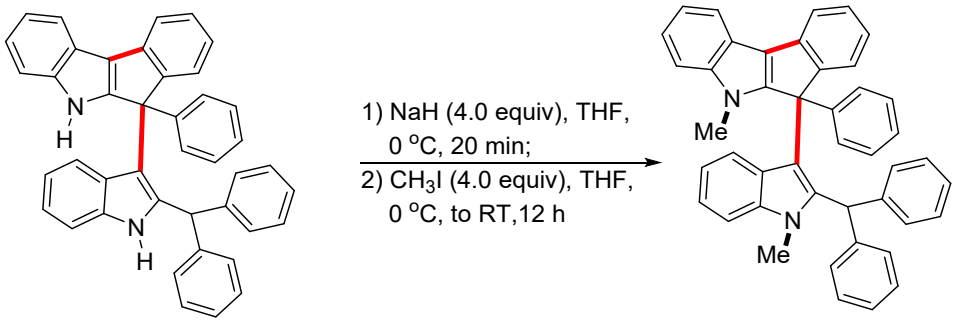
1.1 General Experimental Procedures



General Procedure A – Self-condensation of 2-Indolylmethanols.

2-Indolylmethanols **1** (0.5 mmol, 1 equiv), $La(OTf)_3$ (58.61 mg, 0.1 mmol, 0.2 equiv),

CH_3CN (2 mL) and a stir bar were added to a sealed tube. After being stirred at 100 ℃ for indicated time, the mixture was evaporated under vacuum. The corresponding product **3** was isolated by silica gel column chromatography with a petroleum ether (PE)/dichloromethane mixture as eluent.



3a, 1.0 mmol　　**3r**, 99%

General Procedure B – The methylation of the indeno[1,2-*b*]indole derivatives.

To a solution of Indeno[1,2-*b*]indoles **3a** (1.0 mmol) in dry tetrahydrofuran (THF; 25 mL), NaH (4.0 mmol) was added. After the mixture was stirred 20 min, CH_3I (4.0 mmol) in 5 mL THF was added dropwise under 0 °C. The reaction mixture was stirred at room temperature for 12h. Then the reaction mixture was cooled to room temperature, diluted with 30 mL saturated NH_4Cl solution, and extracted with EtOAc (3×30 mL). The organic layer dried over anhydrous $MgSO_4$ and concentrated in vacuo. The pure product **3r** was obtained by column chromatography on silica gel (Petroleum ether/ Dichloromethane = 100:50) with yield of 99%.

1.2 Control Experiments

Control experiment (Scheme 2a): (1*H*-indol-2-yl)diphenylmethanol **1a** (0.5 mmol, 149.7 mg, 1 equiv), $La(OTf)_3$ (58.61 mg, 0.1 mmol, 0.2 equiv), TEMPO (1.5 mmol, 234.4 mg, 3 equiv) or BHT (1.5 mmol, 330.5 mg, 3 equiv), CH_3CN (2 mL) and a stir bar were added to a sealed tube. After being stirred at 100 ℃ for 8 h, the mixture was evaporated under vacuum. The corresponding product **3a** was isolated by silica gel column chromatography with a petroleum ether/dichloromethane mixture as eluent.

Control experiment (Scheme 2b): (1-methyl-1*H*-indol-2-yl)diphenylmethanol **1r** (0.5 mmol, 1 equiv), $La(OTf)_3$ (58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) and a stir bar were added to a sealed tube. After being stirred at 100 ℃ for 8 h, only trace product was observed.

Control experiment (capture intermediate **4**): (1*H*-indol-2-yl)diphenylmethanol **1a** (0.5 mmol, 149.7 mg, 1 equiv), $La(OTf)_3$ (58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) and a stir bar were added to a sealed tube. After being stirred at 100 ℃ for 1 h. Part of the mixture was analyzed by HRMS, and compound **4** was observed (calcd for $C_{21}H_{16}N$ [M+H]+ m/z =282.1283; found, 282.1292).

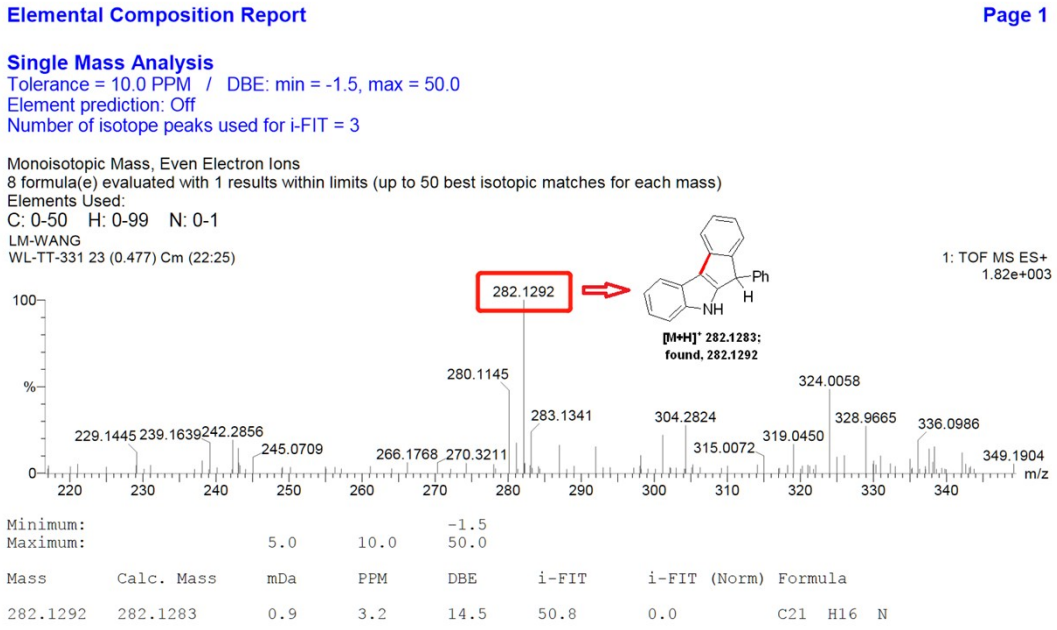
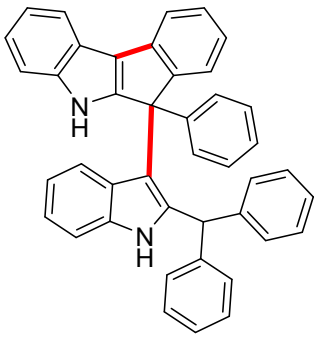


Figure S1. The HRMS spectrum of the reaction mixture

1.3 Characterization Data of Products

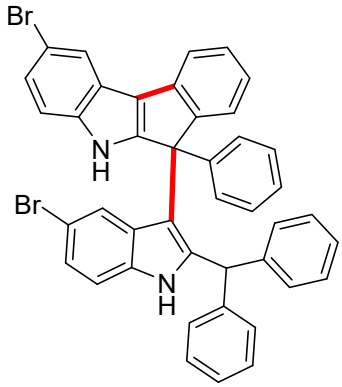
6-(2-benzhydryl-1*H*-indol-3-yl)-6-phenyl-5,6-dihydroindeno[2,1-*b*]indole (3a)



General procedure A was followed using **1a** (149.2 mg, 0.5 mmol), $La(OTf)_3$(58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) at 100 °C for 12 h. Chromatography (30% DCM/PE) afforded **3a** in 94% yield (130.7 mg) as a white solid (mp 272-274 ℃): ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.53 (s, 1H), 10.54 (s, 1H), 7.89 (d, J = 7.3 Hz, 1H), 7.61 (s, 2H), 7.39 – 7.32 (m, 3H), 7.27 (d, J = 4.9 Hz, 4H), 7.20 (t, J = 8.0 Hz, 2H),

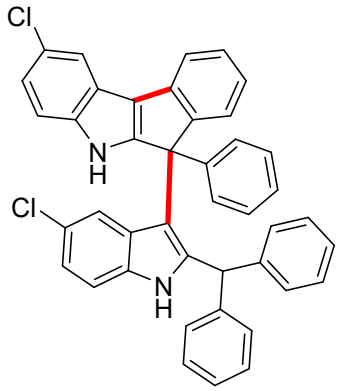
7.17 – 7.10 (m, 4H), 7.02 – 6.91 (m, 5H), 6.87 – 6.72 (m, 4H), 6.44 (s, 2H), 4.64 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 153.5 , 151.4 , 143.7 , 142.2 , 141.1 , 138.2 , 137.0 , 136.5 , 129.0 , 128.5 , 127.9 , 127.4 , 127.2 , 126.1 , 125.2 , 122.7 , 121.3 , 120.7 , 120.2 , 119.2 , 118.7 , 118.5 , 117.4 , 112.8 , 111.5 , 56.1 , 46.9; IR (film) 3393, 3056, 1724, 1599, 1447, 777, 737, 697 cm^{-1}; HRMS (EI-TOF) calcd for $C_{42}H_{30}N_2$ $[M]^+$ m/z = 562.2409; found, 562.2411.

6-(2-benzhydryl-5-bromo-1*H*-indol-3-yl)-2-bromo-6-phenyl-5,6-dihydroindeno[2,1-*b*]indole (3b)



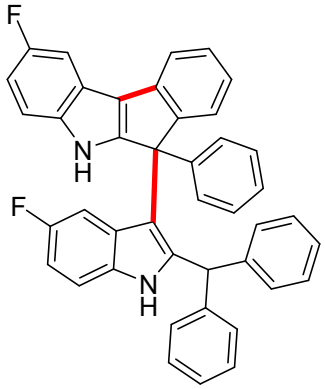
General procedure A was followed using **1b** (189.1 mg, 0.5 mmol), La(OTf)$_3$(58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) at 100 °C for 12 h. Chromatography (30% DCM/PE) afforded **3b** in 88% yield (158.4 mg) as a white solid (mp 264-267 °C)； ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.74 (s, 1H), 10.77 (s, 1H), 8.08 (s, 1H), 7.70 (s, 1H), 7.32 (s, 4H), 7.28 – 7.18 (m, 7H), 7.05 (d, J = 9.0 Hz, 6H), 6.86 (m, 2H), 6.61 (m, 2H), 6.48 – 6.25 (m, 2H), 4.57 (s, 1H).^{13}C NMR (150 MHz, DMSO-d_6) δ 154.3 , 151.1 , 142.8 , 141.6 , 139.8 , 138.8 , 137.3 , 135.1 , 128.6 , 128.4 , 127.9 , 127.6 , 127.4 , 127.0 , 126.2 , 125.2 , 123.8 , 123.1 , 122.7 , 121.5 , 119.1 , 117.2 , 114.6 , 113.3 , 112.7 , 111.3 , 55.7, 46.8; IR (film) 3403, 3057, 2922, 1600, 1490, 1466 , 742, 700 cm^{-1}; HRMS (EI-TOF): calcd for $C_{42}H_{28}Br_2N_2$ $[M]^+$ m/z =718.0619; found, 718.0610.

6-(2-benzhydryl-5-chloro-1*H*-indol-3-yl)-2-chloro-6-phenyl-5,6-dihydroindeno[2,1-*b*]indole (3c)



General procedure A was followed using **1c** (167.0 mg, 0.5 mmol), $La(OTf)_3$(58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) at 100 °C for 12 h. Chromatography (30% DCM/PE) afforded **3c** in 83% yield (130.8 mg) as a white solid (mp 235-237 ℃): ^{1}H NMR (400 MHz, DMSO-d_6) 11.77 (s, 1H), 10.80 (s, 1H), 7.99 (s, 1H), 7.71 (s, 1H), 7.58 (s, 1H), 7.47 (dd, J = 8.8, 5.0 Hz, 1H), 7.44 – 7.28 (m, 6H), 7.22 (t, J = 7.5 Hz, 2H), 7.19 – 7.11 (m, 2H), 7.03 (d, J = 15.9 Hz, 5H), 6.88 (d, J = 11.2 Hz, 2H), 6.67 (s, 2H), 6.46 (s, 1H), 6.26 (s, 1H), 4.63 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 154.5 , 151.1 , 142.8 , 141.6 , 139.5 , 139.1 , 137.4 , 134.9 , 128.8 , 128.6 , 128.0 , 127.7 , 127.5 , 126.8 , 126.3 , 125.3 , 124.8 , 123.2 , 122.1 , 121.3 , 120.7 , 120.0 , 119.2 , 118.5 , 114.2 , 112.9 , 55.8 , 46.9; IR (film) 3487 , 3396 , 3061 , 2920 , 1597 , 1443 , 799, 733, 696 cm^{-1}; HRMS (EI-TOF): calcd for $C_{42}H_{28}Cl_2N_2$ $[M]^+$ m/z =630.1630; found, 630.1603.

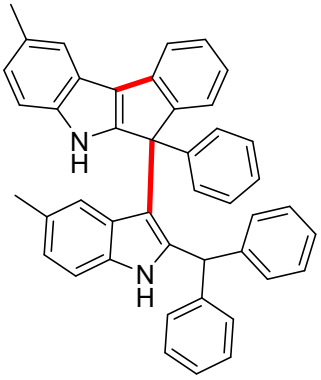
6-(2-benzhydryl-5-fluoro-1*H*-indol-3-yl)-2-fluoro-6-phenyl-5,6-dihydroindeno[2,1-*b*]indole (3d)



General procedure A was followed using **1d** (158.7 mg, 0.5 mmol), $La(OTf)_3$(58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) at 100 °C for 12 h. Chromatography (30% DCM/PE) afforded **3d** in 92% yield (137.6 mg) as a white solid (mp 206-208 ℃): ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.64 (s, 1H), 10.64 (s, 1H), 7.67 (d, J = 10.7 Hz, 4H),

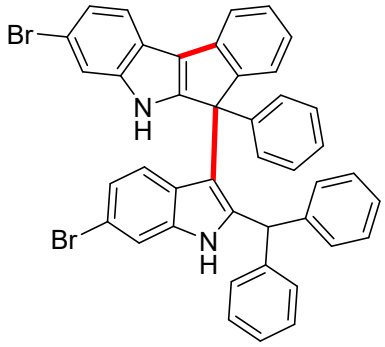
7.36 – 7.26 (m, 7H), 7.20 (t, *J* = 7.5, 1.1 Hz, 3H), 7.06 (s, 4H), 7.00 – 6.91 (m, 2H), 6.80 (d, *J* = 9.0 Hz, 3H), 6.71 – 6.59 (m, 1H), 6.43 (d, *J* = 7.1 Hz, 1H), 4.61 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 158.5 , 157.1 , 157.0 , 155.6 , 143.0 , 141.8 , 137.6 , 133.1 , 128.7 , 128.5 , 128.1 , 127.7 , 127.5 , 126.3 , 125.4 , 123.1 , 121.2 , 119.0 , 117.8 , 113.7 (d, *J* = 9.8 Hz), 112.4 (d, *J* = 9.8 Hz), 109.3 (d, *J* = 26.1 Hz), 108.9 (d, *J* = 25.6 Hz), 104.3 (d, *J* = 24.2 Hz), 55.9 , 47.1; ^{19}F NMR (377 MHz, DMSO-d_6) δ -123.38, -124.51; IR (film) 3435, 3398, 3048, 1481, 1447, 799, 752, 734, 699 cm^{-1}; HRMS (EI-TOF) calcd for $C_{42}H_{28}F_2N_2$ [M]$^+$ m/z = 598.2221; found, 598.2224.

6-(2-benzhydryl-5-methyl-1*H*-indol-3-yl)-2-methyl-6-phenyl-5,6-dihydroindeno[2,1-*b*]iindole (3e)



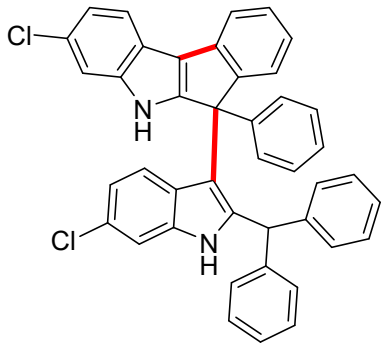
General procedure A was followed using **1e** (156.7 mg, 0.5 mmol), La(OTf)$_3$(58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) at 100 °C for 12 h. Chromatography (30% DCM/PE) afforded **3e** in 81% yield (119.5 mg) as a yellow solid (mp 184-186 ℃): ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.37 (s, 1H), 10.36 (s, 1H), 7.66 (s, 1H), 7.55 (s, 1H), 7.36 – 7.23 (m, 6H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 2H), 7.08 (s, 2H), 6.95 (d, *J* = 8.5 Hz, 4H), 6.78 (s, 4H), 6.40 (s, 2H), 6.18 (s, 1H), 4.60 (s, 1H), 2.43 (s, 3H), 2.12 – 2.04 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 153.7 , 151.6 , 144.0 , 142.3 , 139.6 , 138.3 , 137.2 , 135.1 , 129.1 , 128.8 , 128.7 , 128.6 , 128.5 , 128.2 , 127.9 , 127.5 , 127.1 , 126.6 , 126.3 , 125.3 , 122.9 , 122.2 , 121.6 , 119.0 , 118.6 , 117.0 , 112.6 , 111.2 , 56.1 , 47.0 , 21.8 , 21.5; IR (film) 3405 , 2918 , 1599 , 1490 , 1446 , 740 , 700 cm^{-1}; HRMS (EI-TOF) calcd for $C_{44}H_{34}N_2$ [M]$^+$ m/z = 590.2722; found, 590.2727.

6-(2-benzhydryl-6-bromo-1*H*-indol-3-yl)-3-bromo-6-phenyl-5,6-dihydroindeno[2,1-*b*]indole (3f)



General procedure A was followed using **1f** (189.1 mg, 0.5 mmol), $La(OTf)_3$(58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) at 100 °C for 12 h. Chromatography (30% DCM/PE) afforded **3f** in 76% yield (136.9 mg) as a white solid (mp 272-274 ℃): ^1H NMR (400 MHz, DMSO-d_6) δ 11.67 (s, 1H), 10.65 (s, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 1.9 Hz, 3H), 7.36 – 7.22 (m, 6H), 7.19 (t, J = 7.6 Hz, 2H), 7.06 (s, 5H), 6.87 – 6.73 (m, 3H), 6.68 (d, J = 8.4 Hz, 2H), 6.36 (s, 2H), 4.55 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 141.9 , 137.5 , 128.8 , 128.4 , 128.2 , 127.8 , 127.6 , 126.5 , 123.1 , 121.5 , 121.0 , 119.1 , 115.4 , 114.1 , 113.9 , 113.7 , 56.0 , 47.0; IR (film) 3386 , 3059 , 1600 , 1489 , 1446, 741, 697 cm^{-1}; HRMS (EI-TOF): calcd for $C_{42}H_{28}Br_2N_2$ $[M]^+$ m/z=718.0619; found, 718.0607.

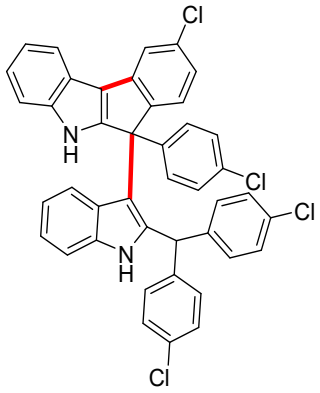
6-(2-benzhydryl-6-chloro-1*H*-indol-3-yl)-3-chloro-6-phenyl-5,6-dihydroindeno[2,1-*b*]indole (3g)



General procedure A was followed using **1g** (167.0 mg, 0.5 mmol), $La(OTf)_3$(58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) at 100 °C for 12 h. Chromatography (30% DCM/PE) afforded **3g** in 88% yield (139.1 mg) as a white solid (mp 300-302 ℃): ^1H NMR (400 MHz, DMSO-d_6) δ 11.66 (s, 1H), 10.67 (s, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.61 (s, 1H), 7.49 (s, 1H), 7.30 (dd, J = 9.5, 2.6 Hz, 7H), 7.20 (t, J = 7.5 Hz, 2H), 7.14 (dd, J = 8.4, 1.9 Hz, 2H), 7.06 (s, 4H), 6.83 (s, 2H), 6.68 (s, 2H), 6.38 (s, 3H), 4.57 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 141.5, 137.4 , 128.7 , 128.4 , 128.0 , 127.6 ,

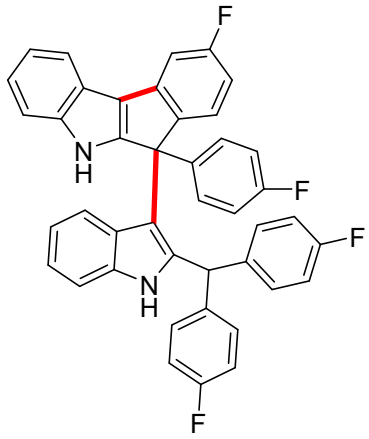
127.4 , 126.4 , 125.8 , 125.6 , 123.2 , 120.5, 120.0 , 119.0, 118.8 , 117.6 , 112.4 , 111.0 , 55.9 , 46.9; IR (film) 3419 , 3387 , 3050 , 1600 , 1490 , 1445 , 796 , 742 , 598 cm^{-1}; HRMS (EI-TOF) calcd for $C_{42}H_{28}Cl_2N_2$ $[M]^+$ m/z =630.1630; found, 630.1619.

6-(2-(bis(4-chlorophenyl)methyl)-1*H*-indol-3-yl)-9-chloro-6-(4-chlorophenyl)-5,6-dihydroindeno[2,1-*b*]indole (3h)



General procedure A was followed using **1h** (184.13 mg, 0.5 mmol), $La(OTf)_3$(58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) at 100 °C for 12 h. Chromatography (30% DCM/PE) afforded **3h** in 86% yield (150.5 mg) as a yellow solid (mp 262-264 °C): ^1H NMR (400 MHz, DMSO-d_6) δ 11.76 (s, 1H), 10.66 (s, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 7.3 Hz, 1H), 7.53 – 7.39 (m, 3H), 7.40 – 7.20 (m, 7H), 7.13 (m, 5H), 6.76 (m, 4H), 6.33 (m, 2H), 4.65 (m, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 142.0 , 137.8 , 129.7 , 128.7 , 128.4 , 128.0 , 123.3 , 121.7 , 121.3 , 120.5 , 119.4 , 115.7 , 114.4 , 114.1 , 113.7 , 56.2 , 47.2; IR (film) 3432 , 2923, 1592 , 1485 , 1089 , 1011 , 811 , 741 cm^{-1}; HRMS (EI-TOF): calcd for $C_{42}H_{26}Cl_4N_2$ $[M]^+$ m/z=698.0850; found, 698.0803.

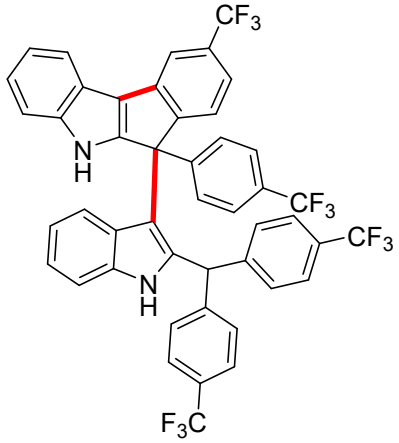
6-(2-(bis(4-fluorophenyl)methyl)-1*H*-indol-3-yl)-9-fluoro-6-(4-fluorophenyl)-5,6-dihydroindeno[2,1-*b*]indole (3i)



General procedure A was followed using **1i** (167.7 mg, 0.5 mmol), $La(OTf)_3$(58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) at 100 °C for 12 h. Chromatography (30%

DCM/PE) afforded **3i** in 74% yield (117.4 mg) as a yellow solid (mp 202-204 °C): ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.84 (s, 1H), 10.45 (s, 1H), 7.90 (s, 1H), 7.76 (s, 1H), 7.44 – 7.39 (m, 2H), 7.35 (d, J = 8.1 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.20 (dd, J = 6.2, 3.1 Hz, 1H), 7.18 – 7.11 (m, 3H), 7.09 (t, J = 8.9 Hz, 2H), 7.02 – 6.93 (m, 3H), 6.87 – 6.74 (m, 5H), 6.65 – 6.58 (m, 1H), 6.45 (s, 1H), 6.24 (s, 1H), 4.47 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 163.2 , 162.2 , 161.7 , 161.6 , 160.6 , 160.1 , 159.9 , 146.5 , 141.0 , 134.0 , 139.4 , 137.9 , 137.5 , 136.4 , 130.5 , 130.2 (d, J = 8.3 Hz), 129.9 , 127.3 , 125.7 , 121.7 , 121.1 , 120.8 , 120.5 , 119.4 , 118.8 , 116.7 , 115.2 , 114.9 , 114.5 , 112.8 , 111.7 , 108.5 (d, J = 22.9 Hz), 105.9 (d, J = 6.8 Hz), 105.8 , 54.7 , 45.4; ^{19}F NMR (376 MHz, DMSO-d_6) δ -115.6 , -116.6 , -117.1; IR (film) 3447, 3058 ,1890 , 1600 , 1501 , 1222 , 1155 , 832 , 815 , 738 cm^{-1}; HRMS (EI-TOF): calcd for $C_{42}H_{26}F_4N_2$ $[M]^+$ m/z=634.2032; found, 634.2035.

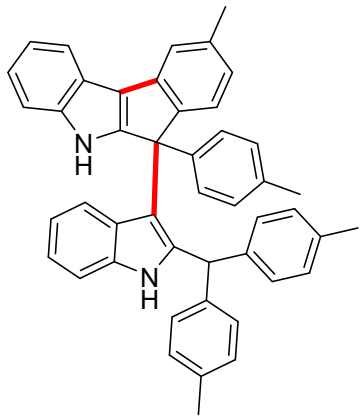
6-(2-(bis(4-(trifluoromethyl)phenyl)methyl)-1*H*-indol-3-yl)-9-(trifluoromethyl)-6-(4-(trifluoromethyl)phenyl)-5,6-dihydroindeno[2,1-*b*]indole (3j)



General procedure A was followed using **1j** (217.7 mg, 0.5 mmol), La(OTf)$_3$(58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) at 100 °C for 12 h. Chromatography (30% DCM/PE) afforded **3j** in 79% yield (164.8 mg) as an orange solid (mp 163-165 °C): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.32 (s, 1H), 10.81 (s, 1H), 7.89 (s, 1H), 7.83 (d, J = 7.4 Hz, 1H), 7.70 (d, J = 7.9 Hz, 2H), 7.60 – 7.33 (m, 9H), 7.26 – 7.15 (m, 3H), 7.09 – 6.99 (m, 3H), 6.94 (s, 1H), 6.77 (s, 1H), 6.53 – 6.21 (m, 2H), 4.60 (s, 1H); ^{13}C NMR (150 MHz, Chloroform-d) δ 153.9 , 147.1 , 145.6 , 144.6 , 141.3 , 136.7 , 129.7 , 129.2 , 128.9 , 128.7 , 128.4 , 128.2 , 127.8 , 127.6 , 125.8 , 125.5 , 125.3 , 125.1 , 124.6 , 123.7 , 123.5 , 123.3 , 122.4 , 121.4 , 121.6 (d, J = 5.6 Hz), 121.5 (d, J = 5.6 Hz), 121.0

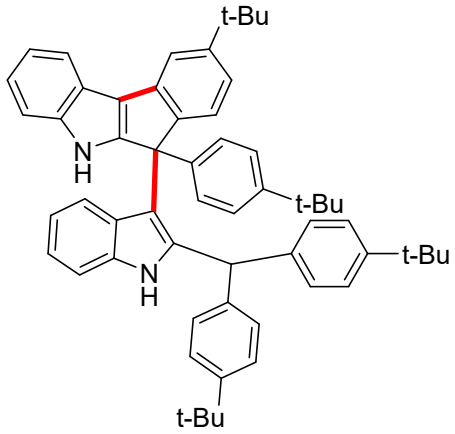
, 120.1 , 119.7 , 119.3 (d, J = 6.9 Hz) , 117.1 , 114.6 , 113.0 , 112.5 (d, J = 11.3 Hz) , 106.6 , 31.2 , 30.0; ^{19}F NMR (377 MHz, DMSO-d_6) δ -58.93 , -60.18 , -61.11 , -61.25; IR (film) 3457 , 3061 , 2926, 1612 , 1450 , 1323 , 1113 , 1071 , 763 , 700 cm^{-1}; HRMS (EI-TOF): calcd for $C_{46}H_{26}F_{12}N_2$ $[M]^+$ m/z=834.1904; found, 834.1902.

6-(2-(di-*p*-tolylmethyl)-1*H*-indol-3-yl)-9-methyl-6-(*p*-tolyl)-5,6-dihydroindeno[2,1-*b*]indole (3k)



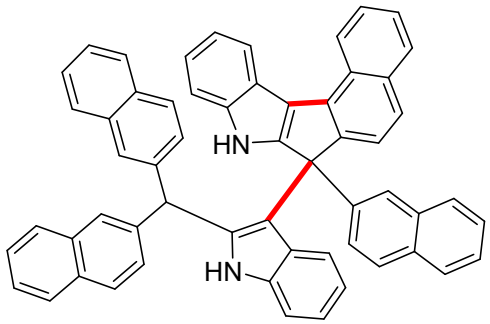
General procedure A was followed using **1k** (163.7 mg, 0.5 mmol), La(OTf)$_3$(58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) at 100 °C for 12 h. Chromatography (30% DCM/PE) afforded **3k** in 76% yield (111.7 mg) as a yellow solid (mp 238-240 ℃): ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.47 (s, 1H), 10.35 (s, 1H), 7.82 (d, J = 6.5 Hz, 1H), 7.35 (dd, J = 6.2, 2.8 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.15 – 7.08 (m, 4H), 7.08 – 7.03 (m, 3H), 6.96 – 6.84 (m, 4H), 6.77 – 6.44 (m, 6H), 6.25 (d, J = 18.2 Hz, 1H), 4.51 (s, 1H), 2.29 (s, 3H), 2.24 (s, 9H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 141.1 , 139.5 , 138.3 , 136.5 , 135.6 , 135.4 , 129.4 , 128.6 , 123.2 , 121.5 , 121.2 , 120.6 , 120.2 , 119.5 , 119.3 , 118.5 , 112.9 , 111.5 , 73.4 , 56.0, 55.6, 21.4, 21.0, 20.8; IR (film) 3403, 2919, 1689 , 1507, 1449, 805, 737 cm^{-1}; HRMS (EI-TOF): calcd for $C_{46}H_{38}N_2$ $[M]^+$ m/z=618.3035; found, 618.3040.

6-(2-(bis(4-(*tert*-butyl)phenyl)methyl)-1*H*-indol-3-yl)-9-(*tert*-butyl)-6-(4-(*tert*-butyl)phenyl)-5,6-dihydroindeno[2,1-*b*]indole (3l)



General procedure A was followed using **1l** (205.8 mg, 0.5 mmol), La(OTf)$_3$(58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) at 100 °C for 12 h. Chromatography (30% DCM/PE) afforded **3l** in 71% yield (139.7 mg) as a yellow solid (mp 230-232 ℃): ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.52 (s, 1H), 10.57 (s, 1H), 8.07 – 7.81 (m, 1H), 7.81 – 7.57 (m, 1H), 7.48 – 7.21 (m, 7H), 7.21 (s, 6H), 6.88 (t, J = 6.9 Hz, 2H), 6.77 (dq, J = 17.3, 8.1 Hz, 2H), 6.69 – 6.18 (m, 4H), 4.91 – 4.29 (m, 1H), 1.42 – 1.08 (m, 36H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 150.2 , 149.7 , 139.8 , 128.9 , 126.5 , 121.5 , 120.8 , 120.3 , 119.8 , 116.0 , 113.1 , 111.6 , 73.5 , 55.7 , 34.9 , 34.5 , 31.9 , 31.6 ; IR (film) 3046, 2956 , 2865, 1611 , 1453 , 820 , 739 cm^{-1}; HRMS (EI-TOF): calcd for $C_{58}H_{62}N_2$ $[M]^+$ m/z=786.4913; found, 786.4911.

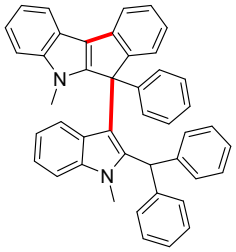
7-(2-(di(naphthalen-2-yl)methyl)-1*H*-indol-3-yl)-7-(naphthalen-2-yl)-7,8-dihydrobenzo[6,7]indeno[2,1-*b*]indole (3m)



General procedure A was followed using **1m** (199.7 mg, 0.5 mmol), La(OTf)$_3$(58.61 mg, 0.1 mmol, 0.2 equiv), CH_3CN (2 mL) at 100 °C for 12 h. Chromatography (30% DCM/PE) afforded **3m** in 65% yield (123.9 mg) as a yellow solid (mp 302-304 ℃): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.10 (s, 1H), 10.79 (s, 1H), 8.85 – 8.59 (m, 1H), 8.29 (d, J = 8.1 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 8.00 – 7.95 (m, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.74 (t, J = 8.6 Hz, 3H), 7.65 (t, J = 8.2 Hz, 2H), 7.59 (t, J

= 7.6 Hz, 3H), 7.50 – 7.39 (m, 6H), 7.35 (dd, 4H), 7.30 – 7.10 (m, 6H), 7.07 (d, *J* = 6.7 Hz, 1H),6.96 (t, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 7.1 Hz, 1H), 6.65 (s, 1H), 6.47 (s, 1H), 4.88 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 146.7 , 141.3 , 141.1 , 139.2 , 138.8 , 137.0 , 136.6 , 133.2 , 132.8 , 132.2 , 131.8 , 129.7 , 128.3 , 128.2 , 127.8 , 127.5 , 127.5 , 127.4 , 127.3 , 127.2 , 127.0 , 126.7 , 126.7 , 126.5 , 126.3 , 126.0 , 125.7 , 125.5 , 125.3 , 125.2 , 121.2 , 120.5 , 118.6 , 117.2 , 113.2 , 111.6 , 55.7 , 48.6; IR (film) 3399 , 3049 , 2922, 1450 , 800 , 735 cm^{-1}; HRMS (EI-TOF) calcd for $C_{58}H_{38}N_2$ $[M]^+$ m/z = 762.3035; found, 762.3026.

(*S*)-6-(2-benzhydryl-1-methyl-1*H*-indol-3-yl)-5-methyl-6-phenyl-5,6-dihydroindeno[2,1-*b*]indole (3r)



General procedure B was followed using **3a** (562.2 mg, 1.0 mmol), NaH(160.0 mg, 4.0 mmol, 4.0 equiv), CH_3I (567.8 mg, 4.0 mmol, 4.0 equiv), THF (30 mL) at 0 °C for 12 h. Chromatography (50% DCM/PE) afforded **3r** in 99% yield (292.4 mg) as a white solid (m283-285 ℃): ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.16 – 7.89 (m, 2H), 7.76 – 7.70 (m, 1H), 7.51 (dd, *J* = 7.8, 4.2 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.27 – 7.18 (m, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.10 – 7.04 (m, 3H), 7.02 – 6.94 (m, 3H), 6.92 (d, *J* = 7.1 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 2H), 6.78 (t, *J* = 7.7 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 8.2 Hz, 1H), 6.39 (d, *J* = 7.4 Hz, 2H), 6.31 (d, *J* = 7.5 Hz, 2H), 5.20 (s, 1H), 3.08 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6/$CDCl_3$=1:1) δ 153.6 , 153.2 , 141.8 , 141.1 , 140.9 , 139.0 , 138.1 , 137.4 , 128.5 , 128.2 , 127.9 , 127.7 , 127.6 , 127.3 , 126.9 , 125.8 , 125.7 , 124.2 , 123.0 , 121.7 , 121.0 , 120.8 , 120.0 , 119.1 , 118.6 , 118.0 , 116.9 , 110.1 , 109.2 , 56.5 , 45.1 , 32.1 , 30.7; IR (film) 354 , 2922 , 1596 , 1523, 1490 , 1466, 757 , 735 , 693 cm^{-1}; HRMS (EI-TOF) calcd for $C_{44}H_{34}N_2$ $[M]^+$ m/z = 590.2722; found, 590.2766.

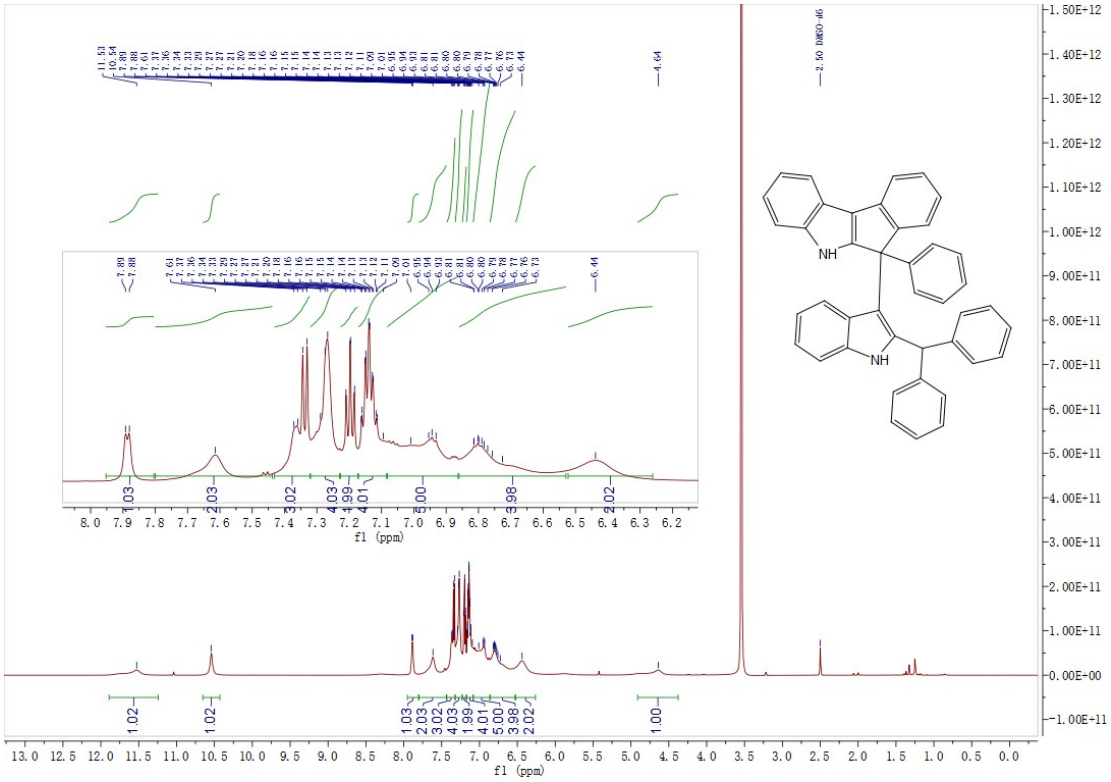
References

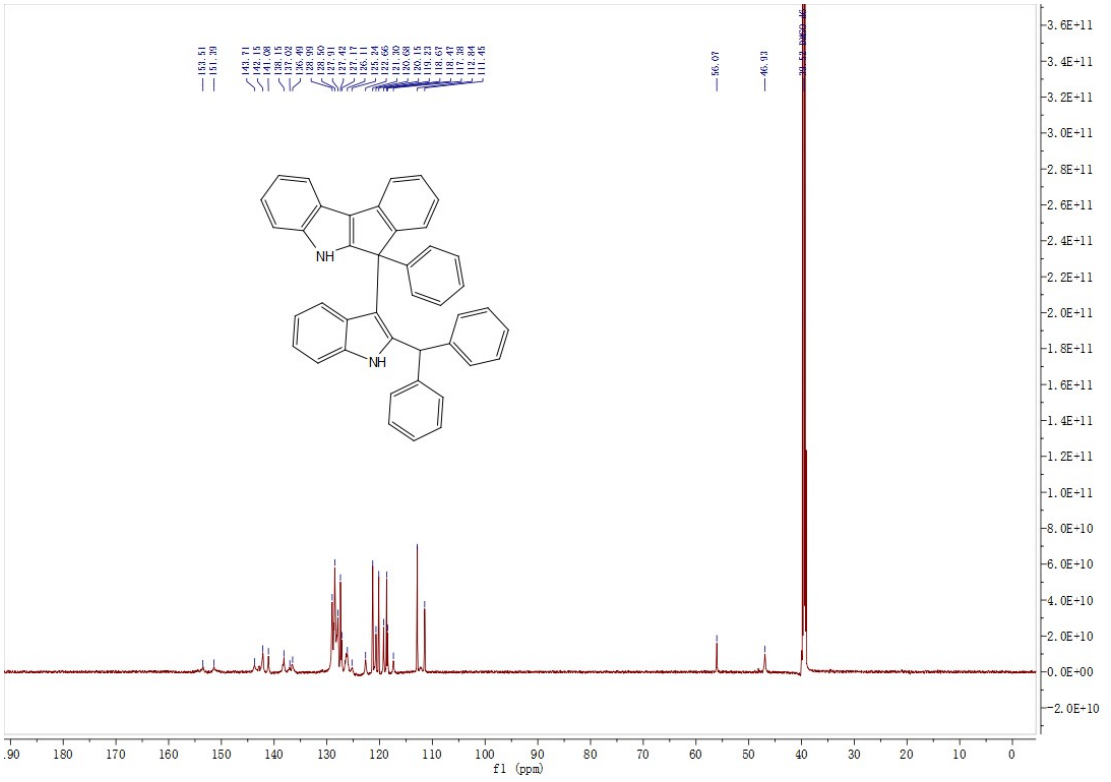
(a) H. H. Zhang, C. S. Wang, C. Li, G. J. Mei, Y. Li and F. Shi, *Angew. Chem., Int. Ed.* 2017, **56**, 116; (b) Z. Q. Zhu, Y. Shen, X. X. Sun, J. Y. Tao, J. X. Liu and F. Shi, *Adv.*

Synth. Catal. 2016, **358**, 3797.

Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR

3a





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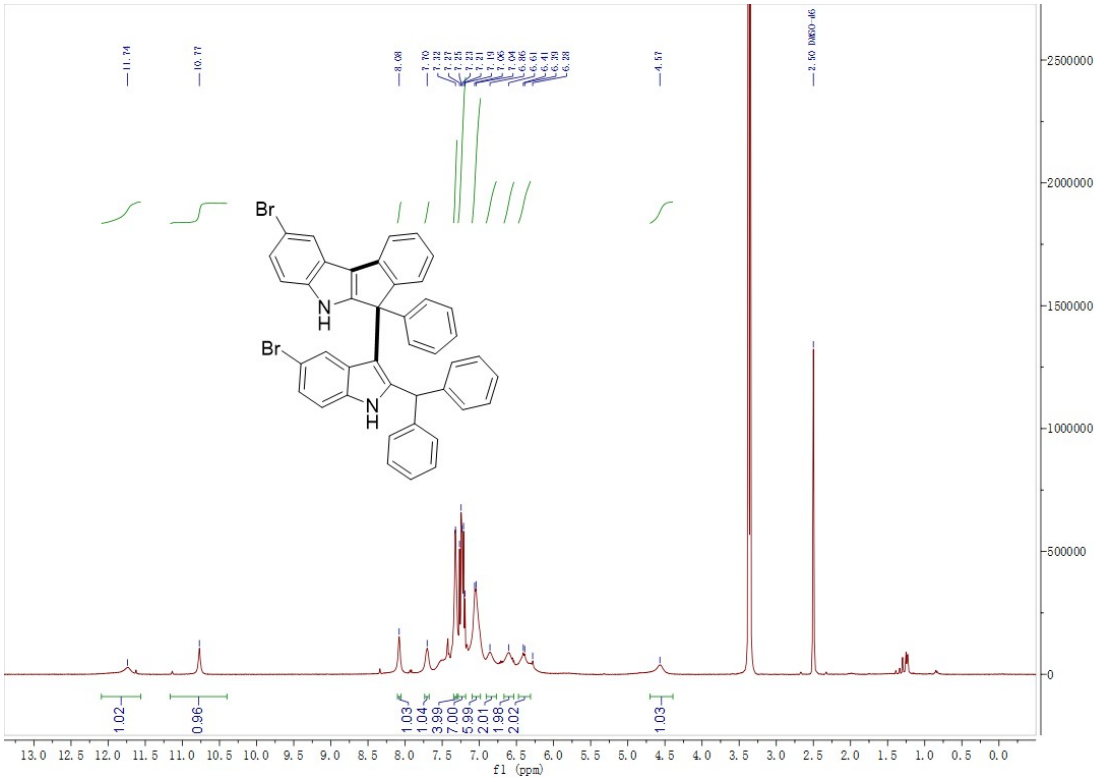
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6.41
6.39
6.28
4.57
2.50
Br
Br
N
H
N
H
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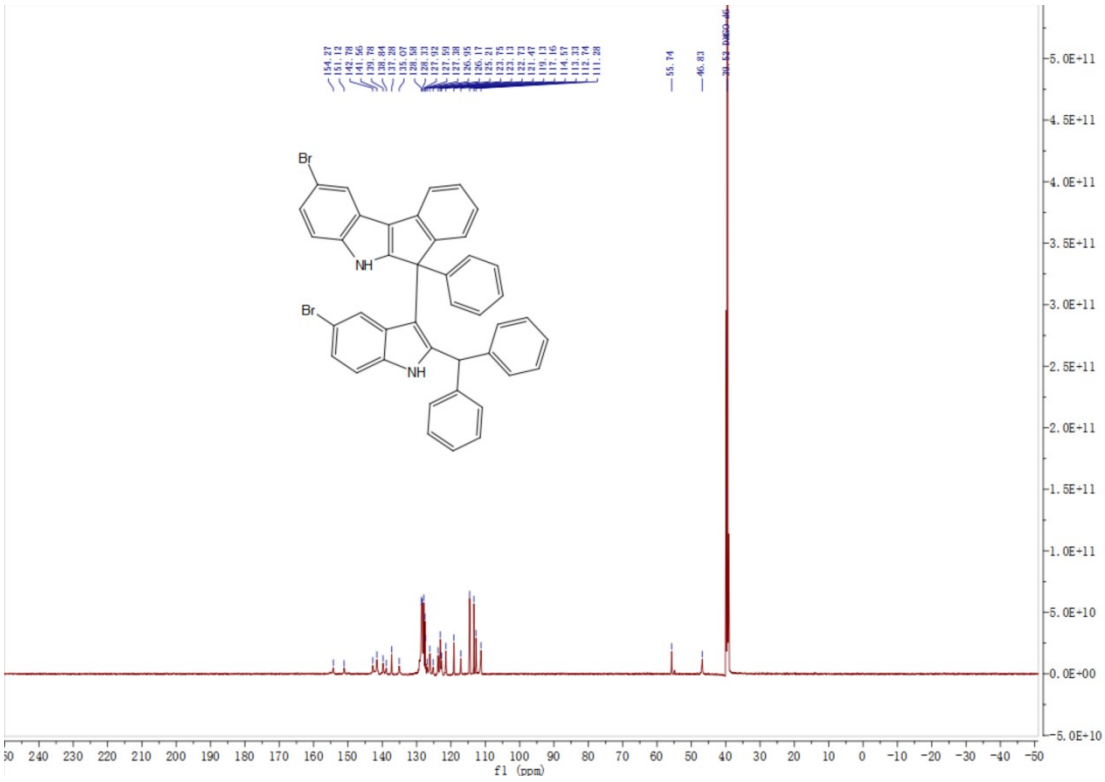
1.03
f1 (ppm)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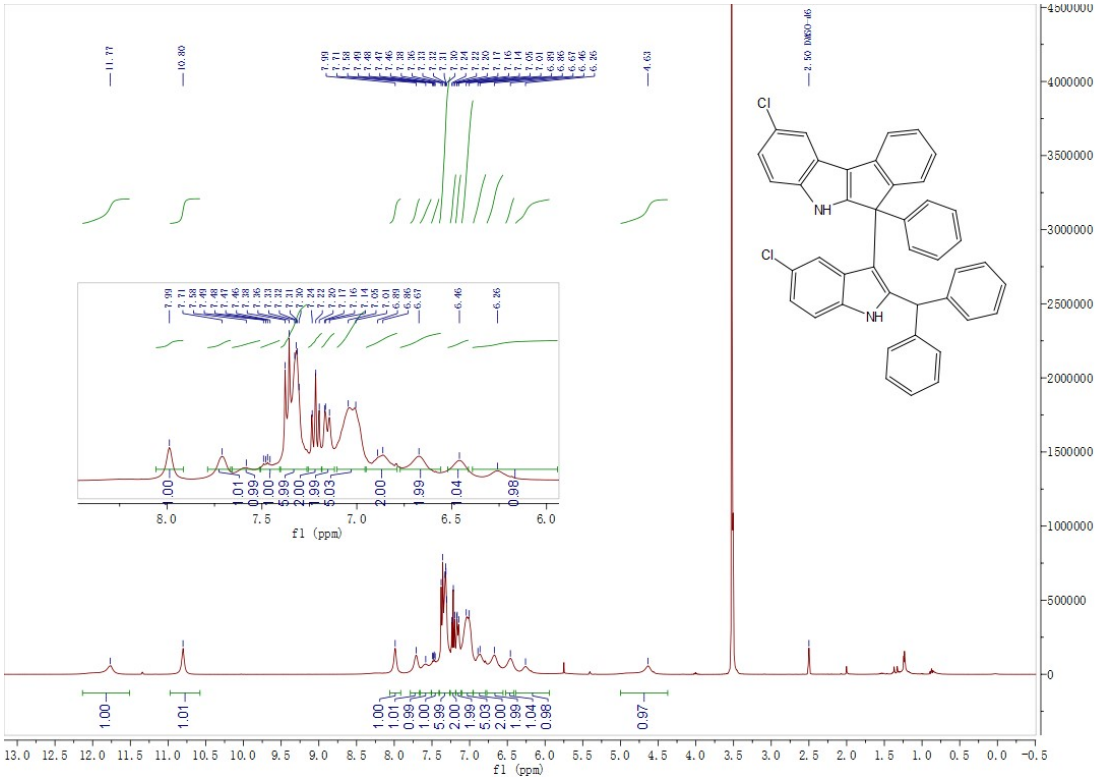

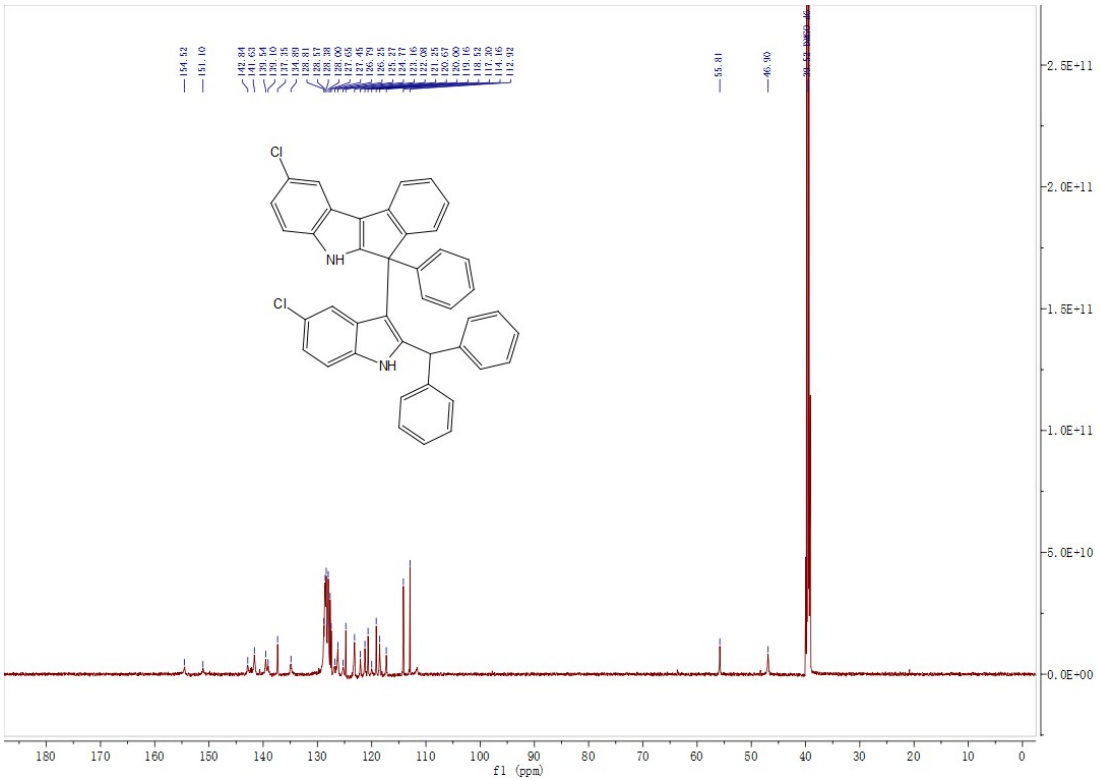

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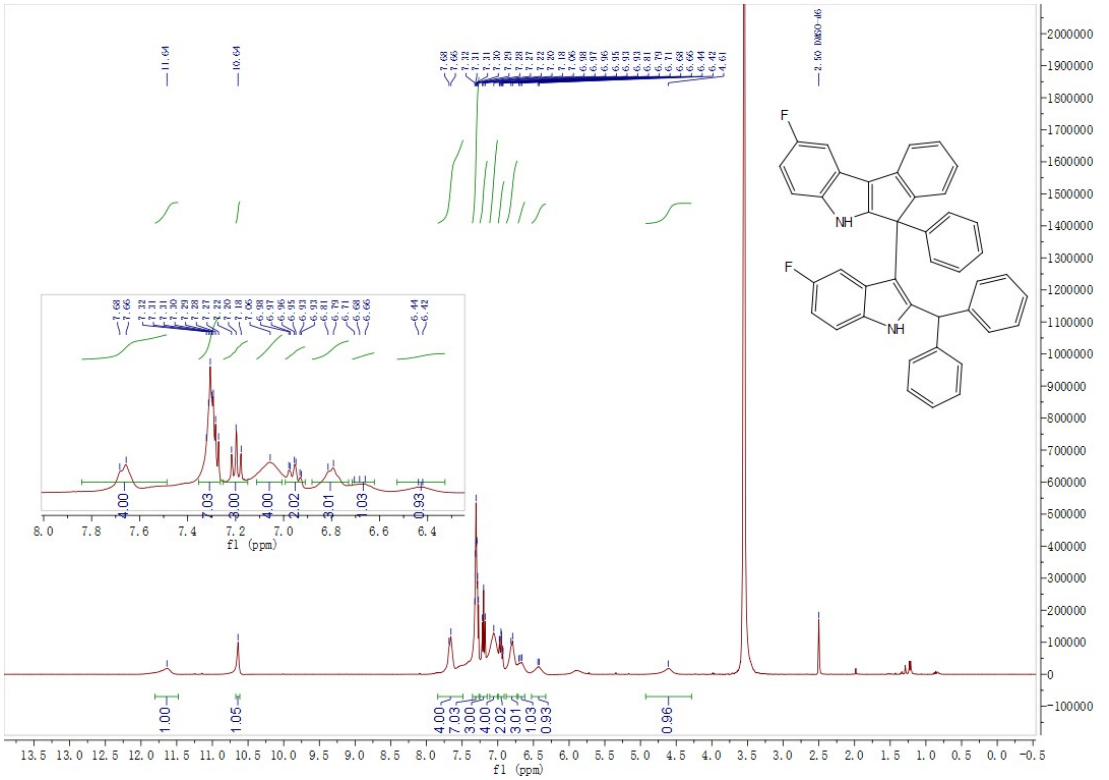

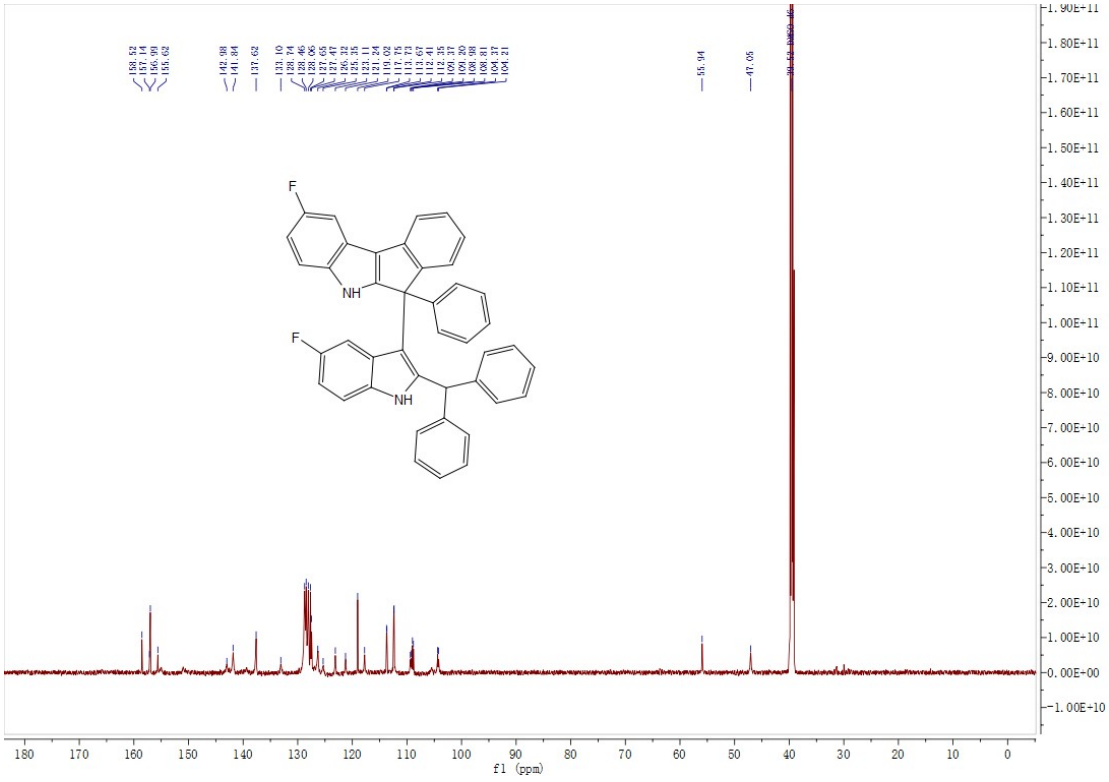

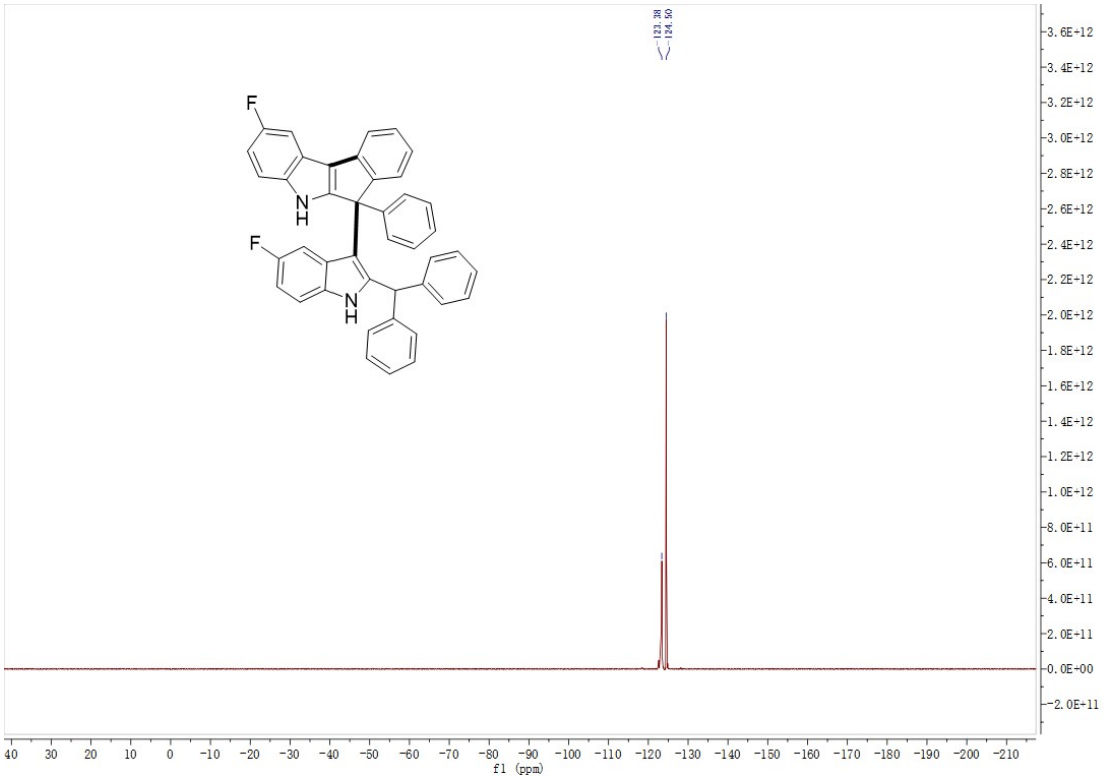

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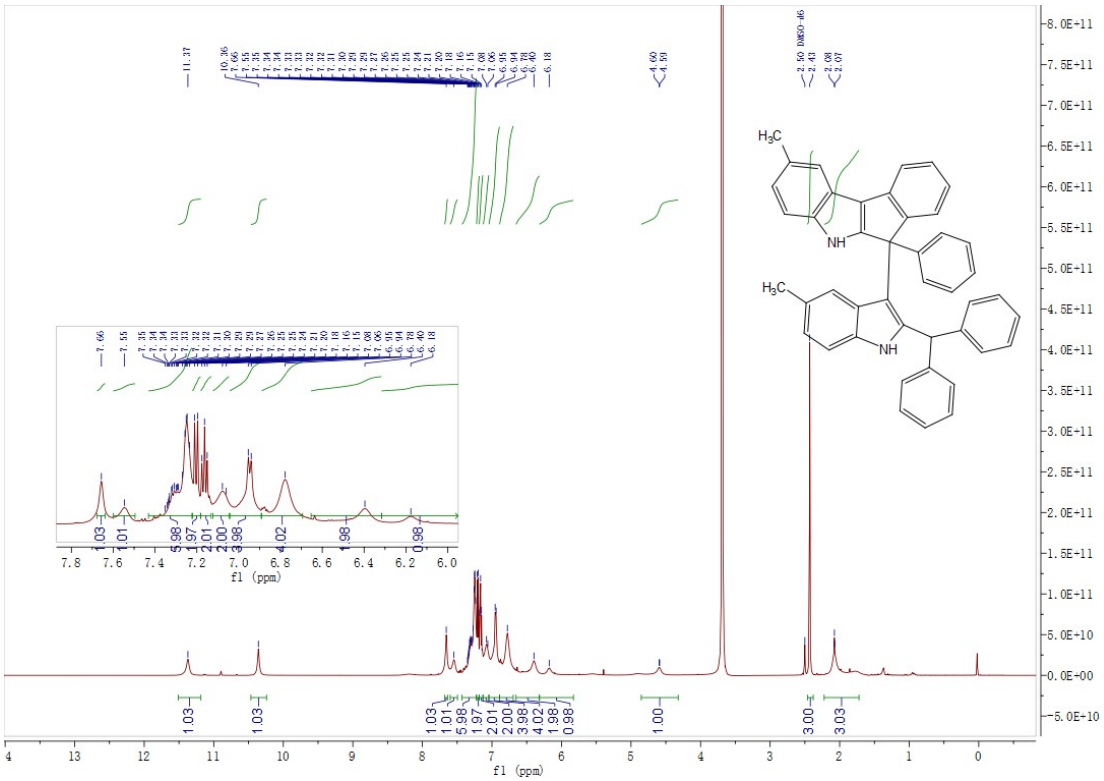

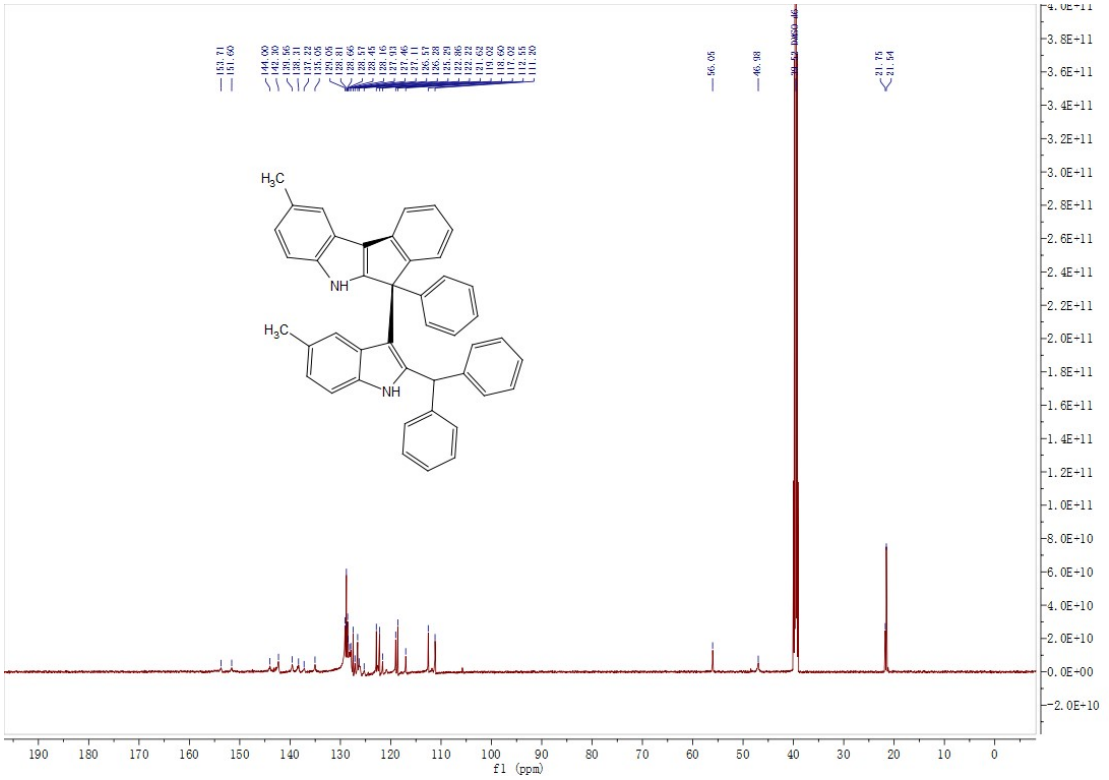

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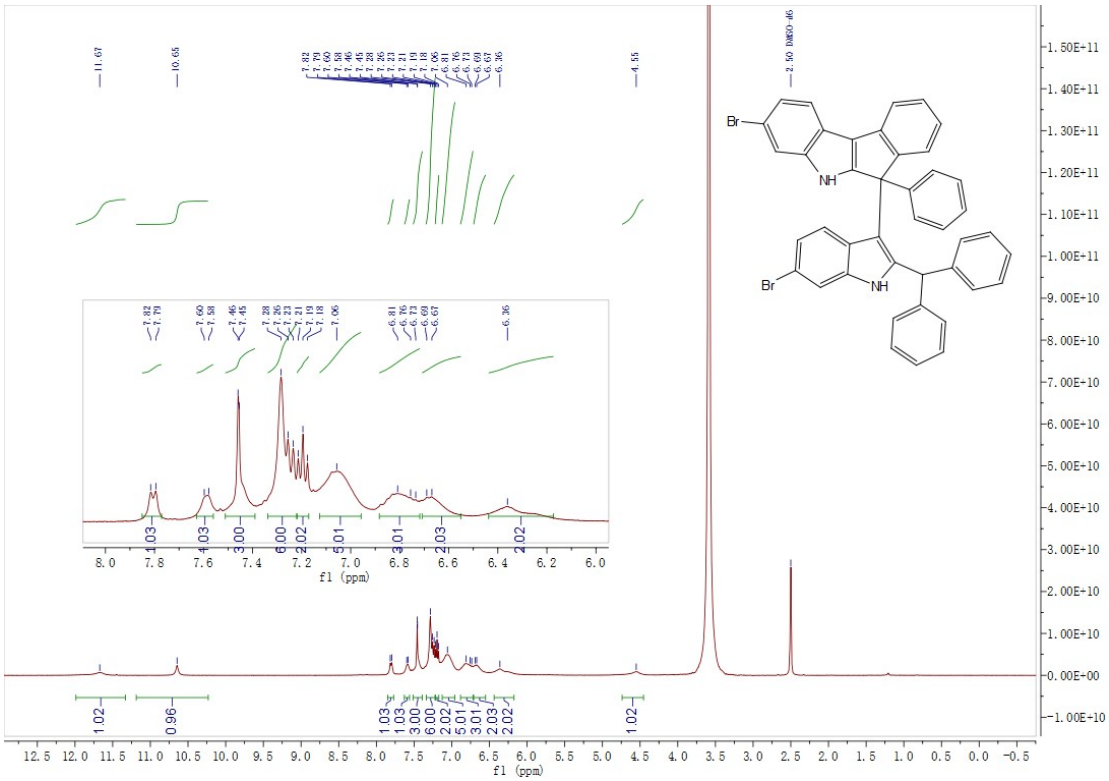

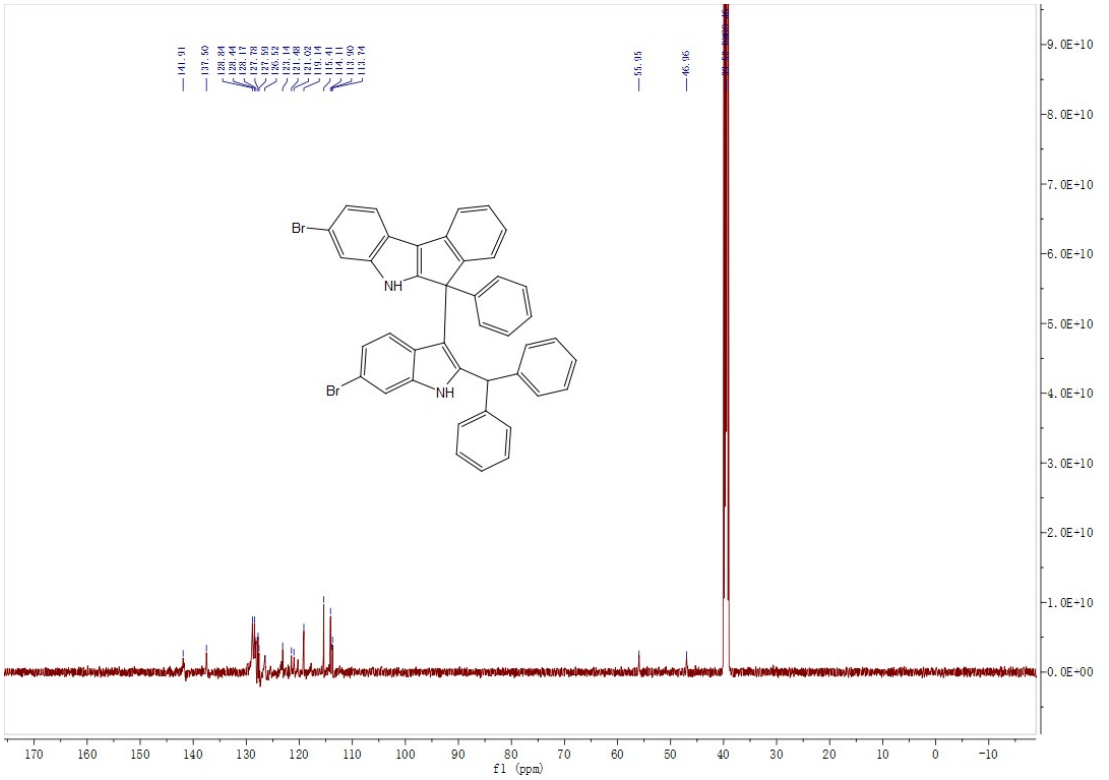

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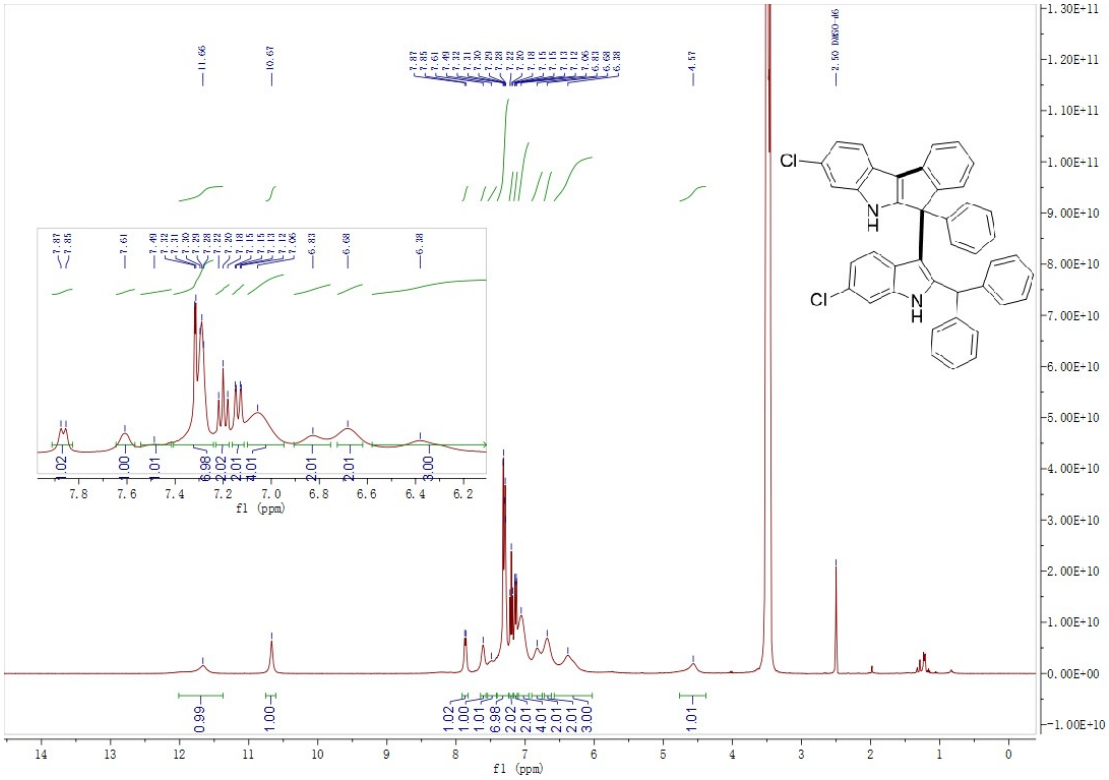

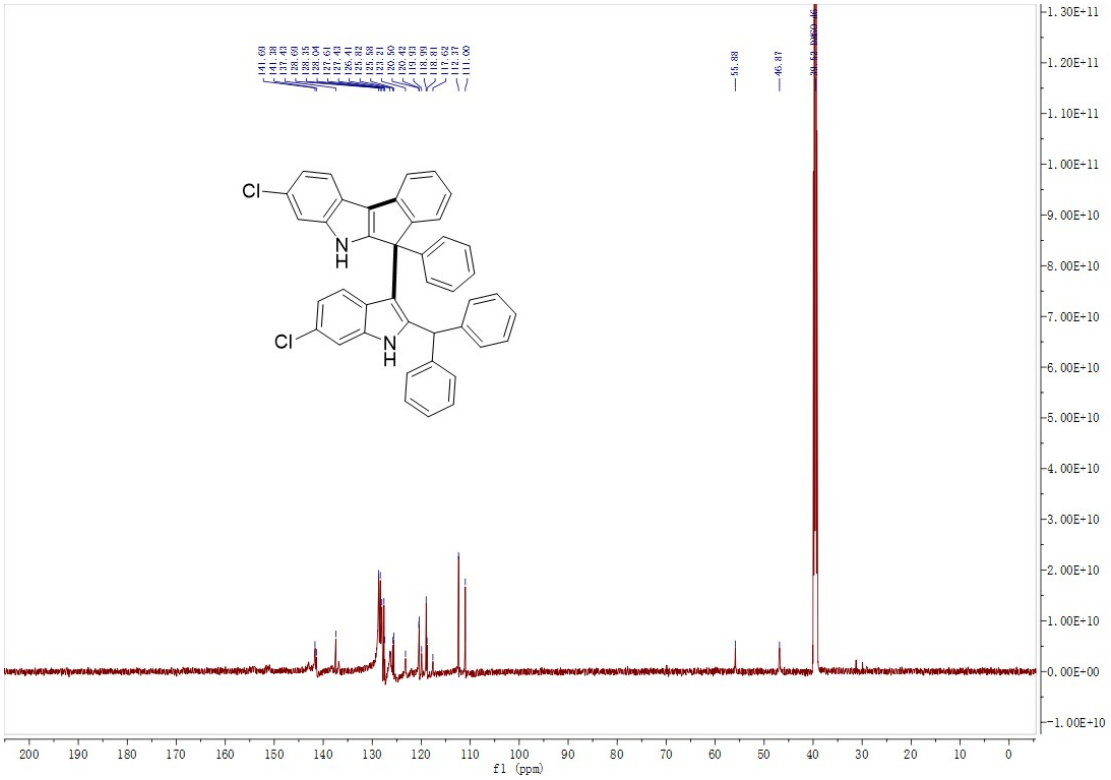
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H
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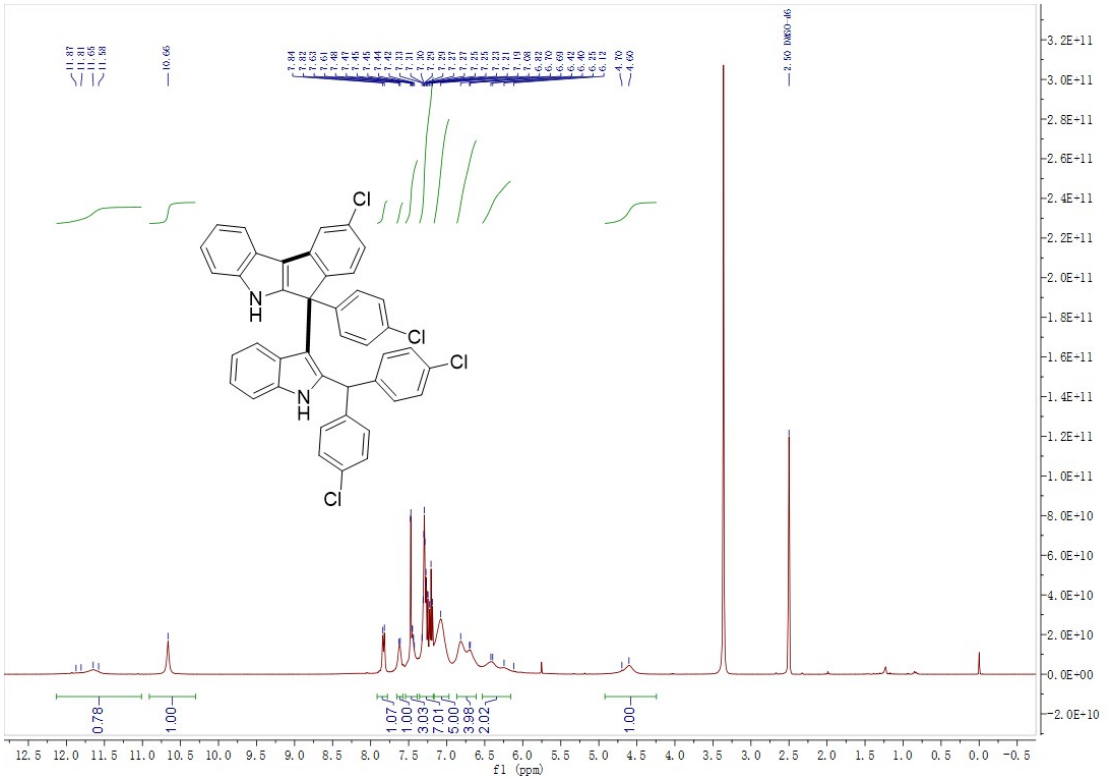
3h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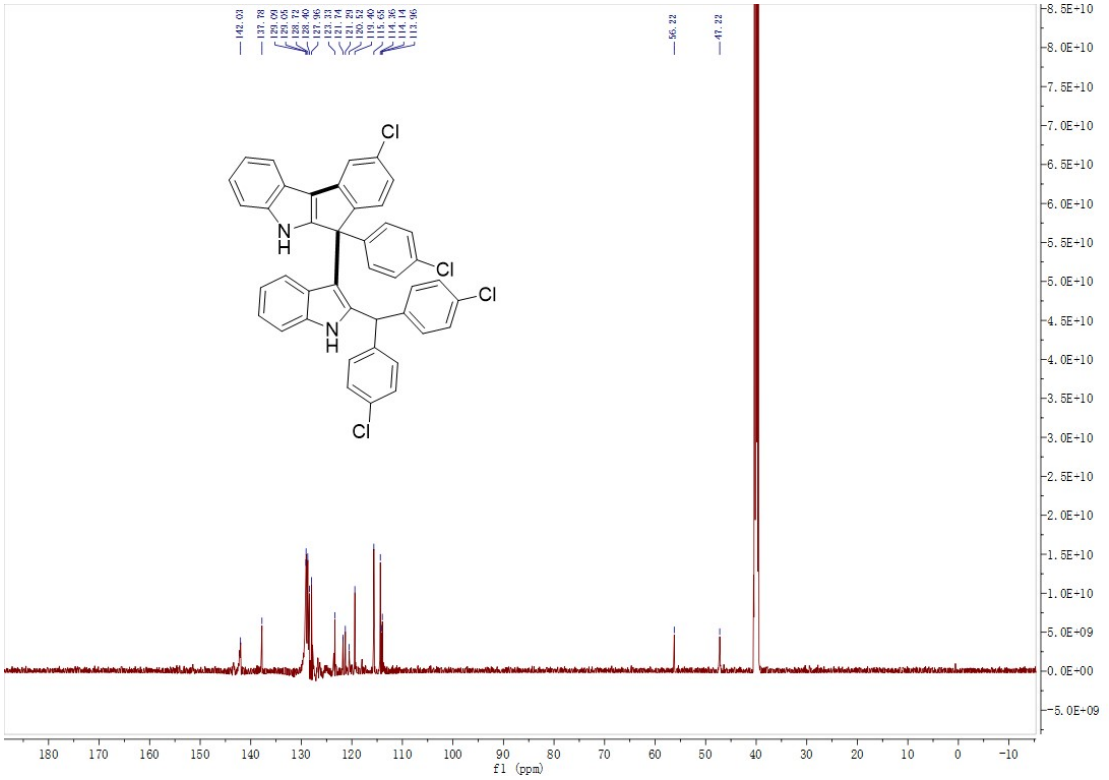
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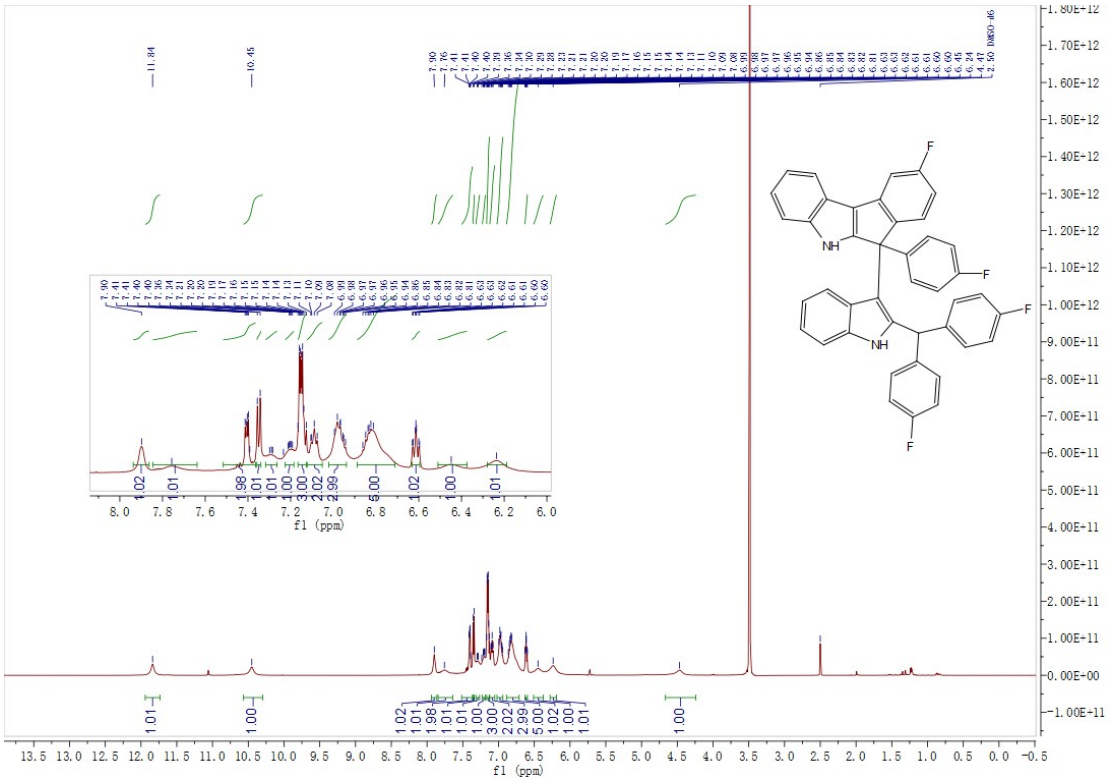
f1 (ppm)

3i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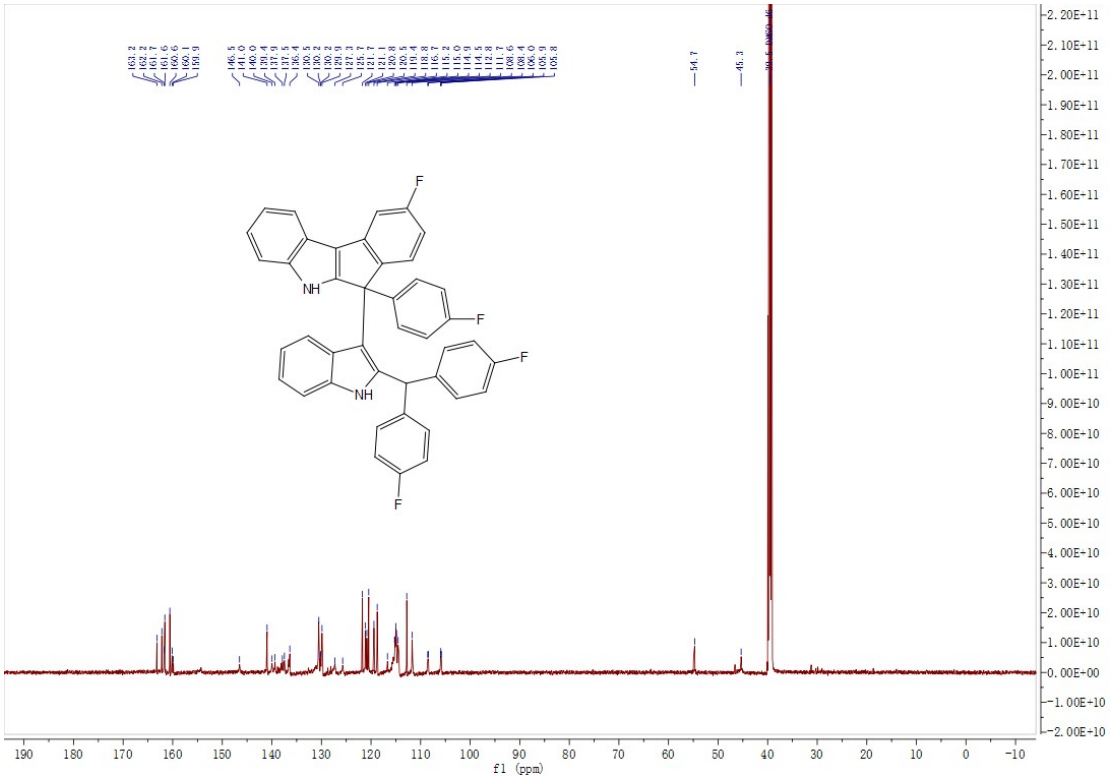
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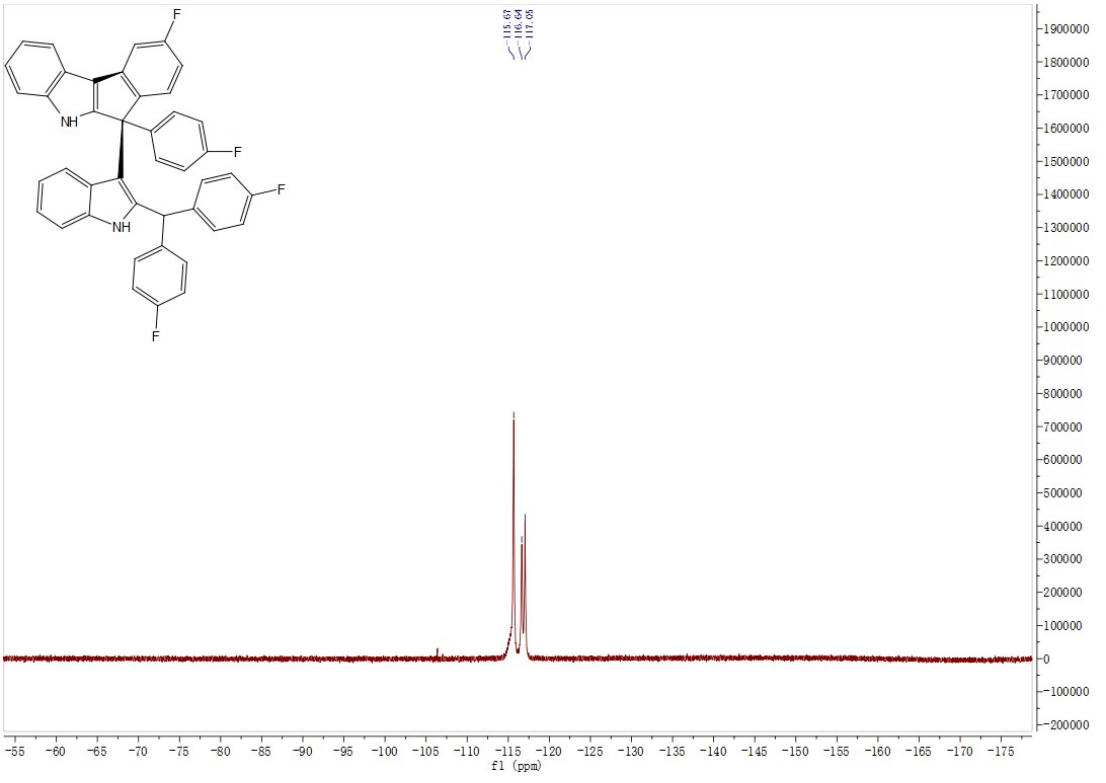
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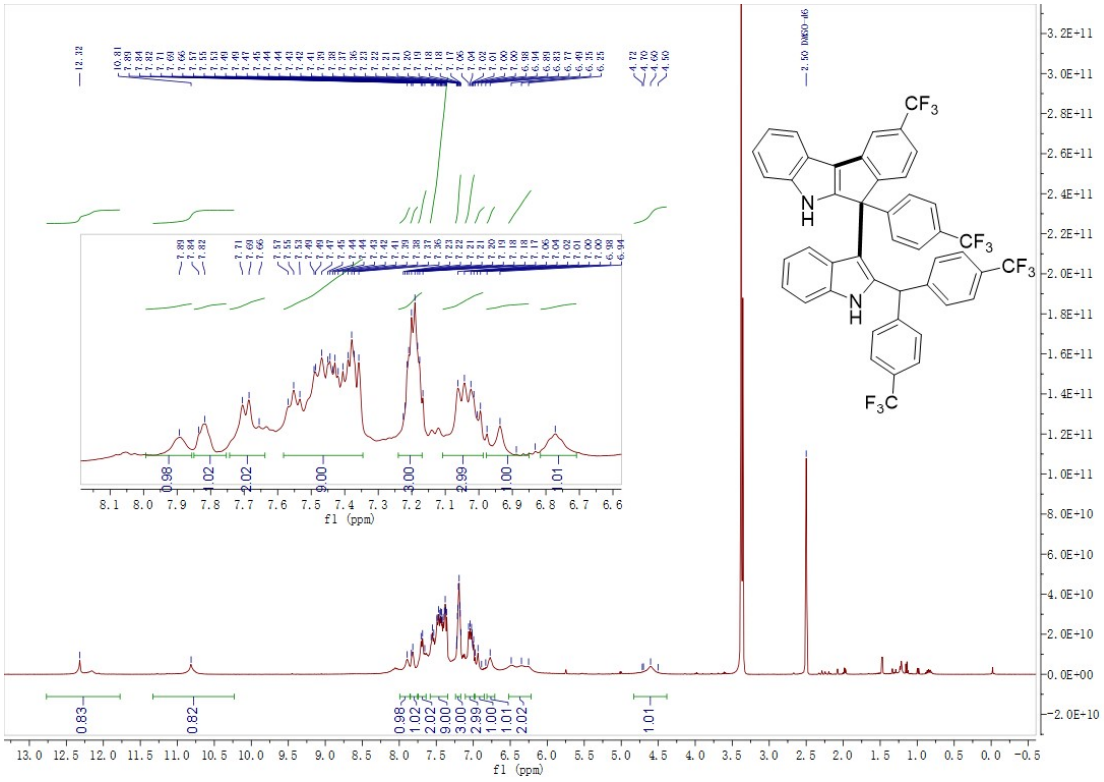
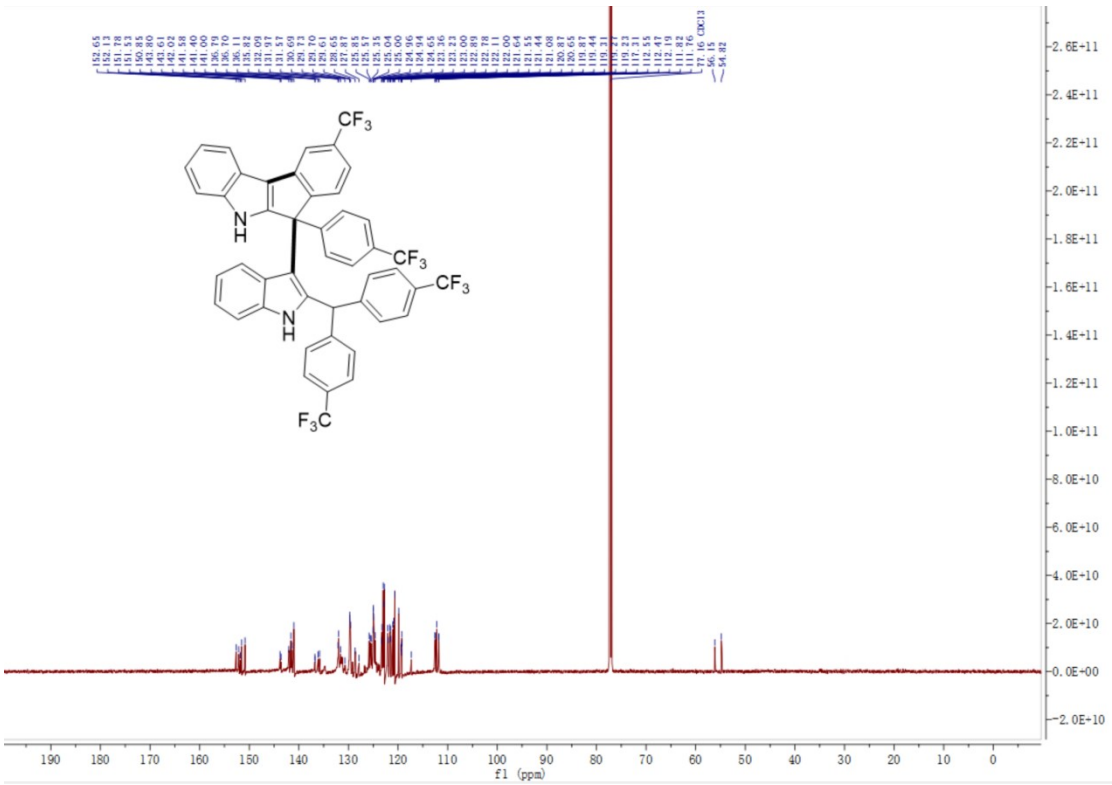
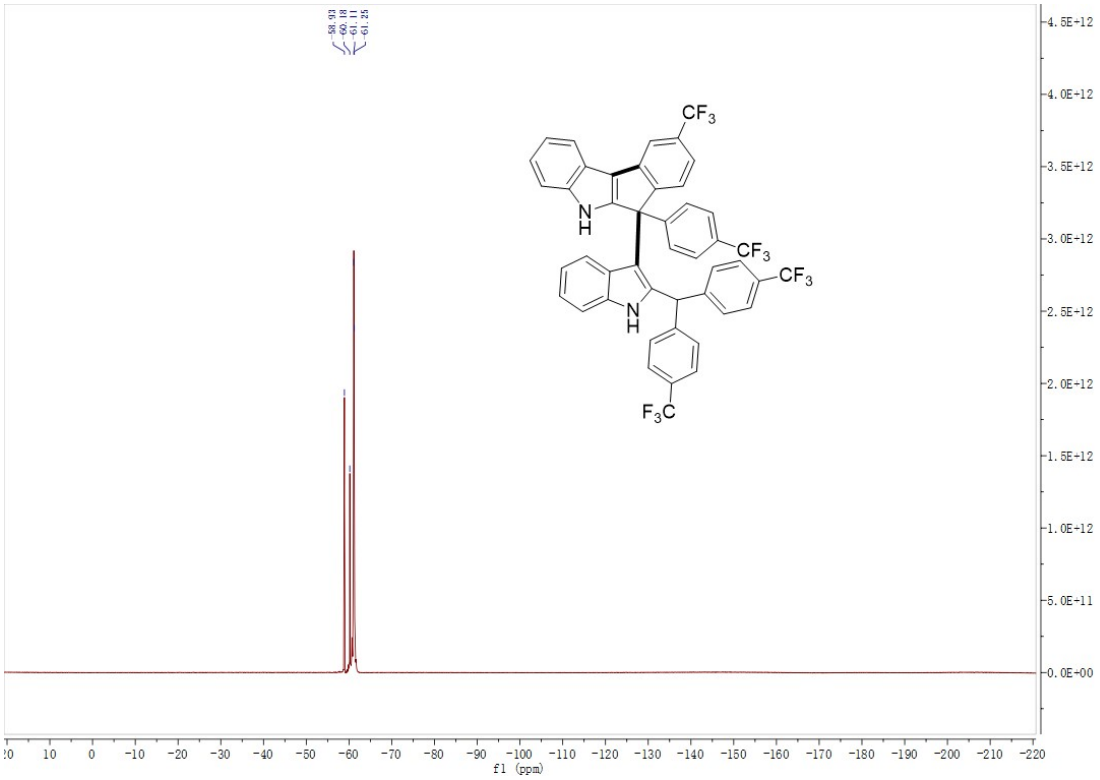
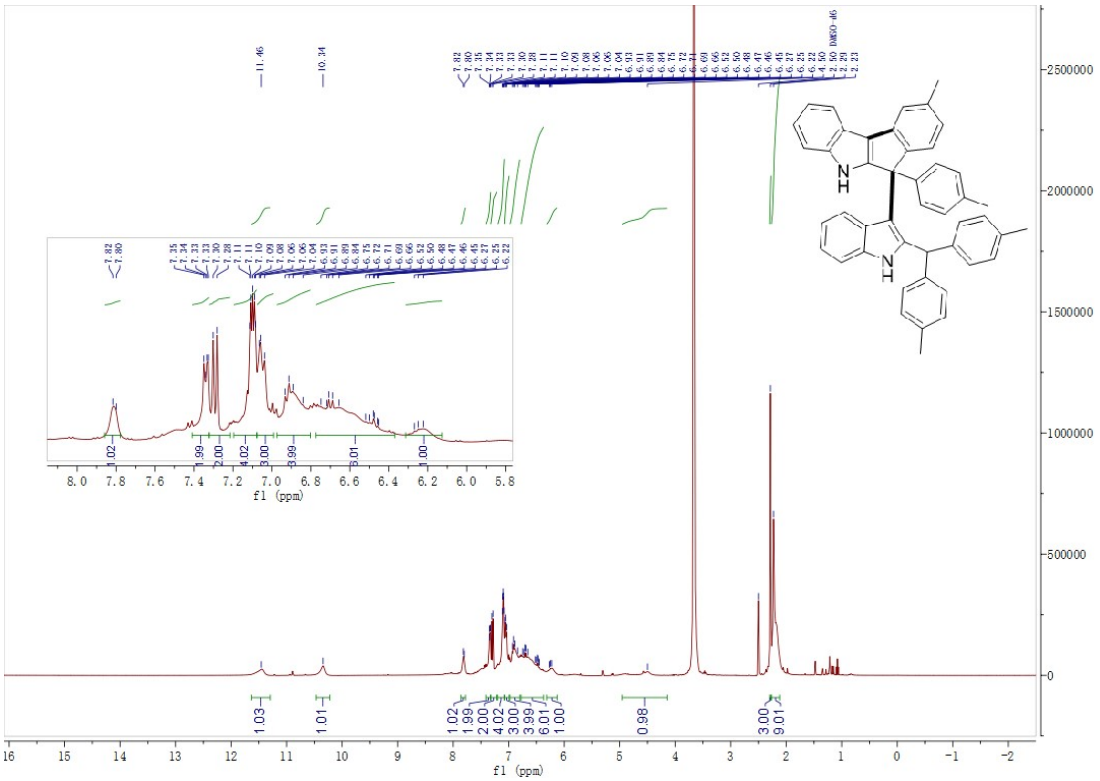
3j

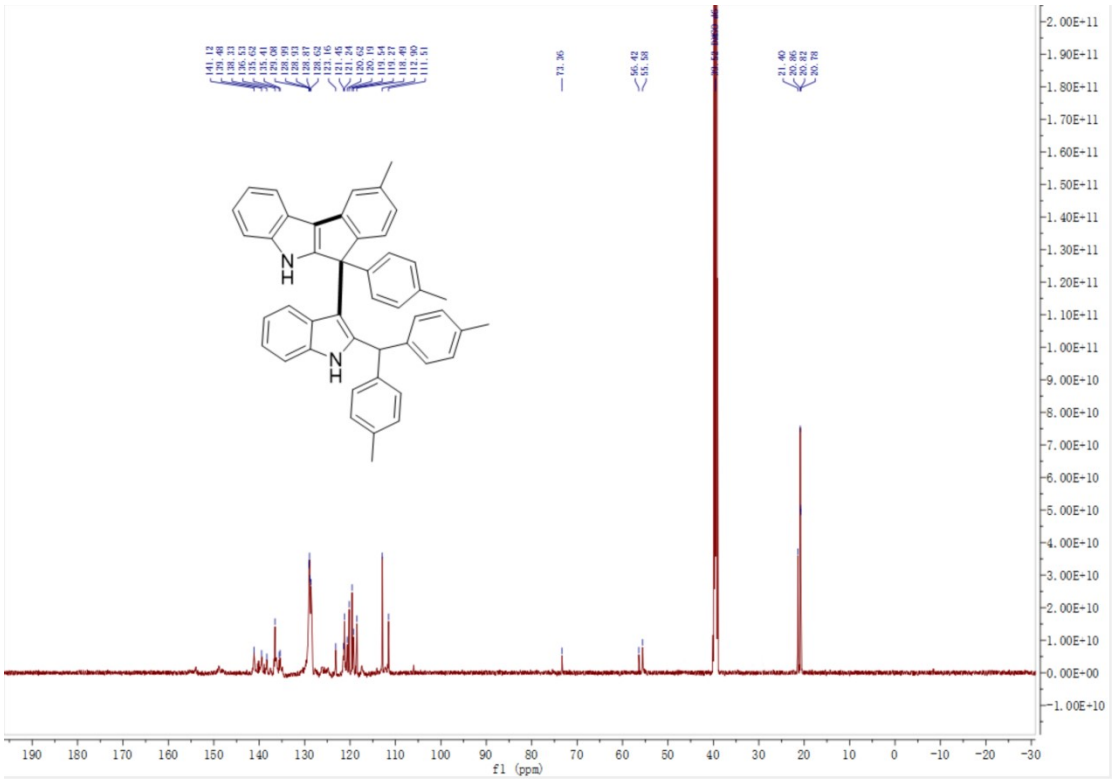




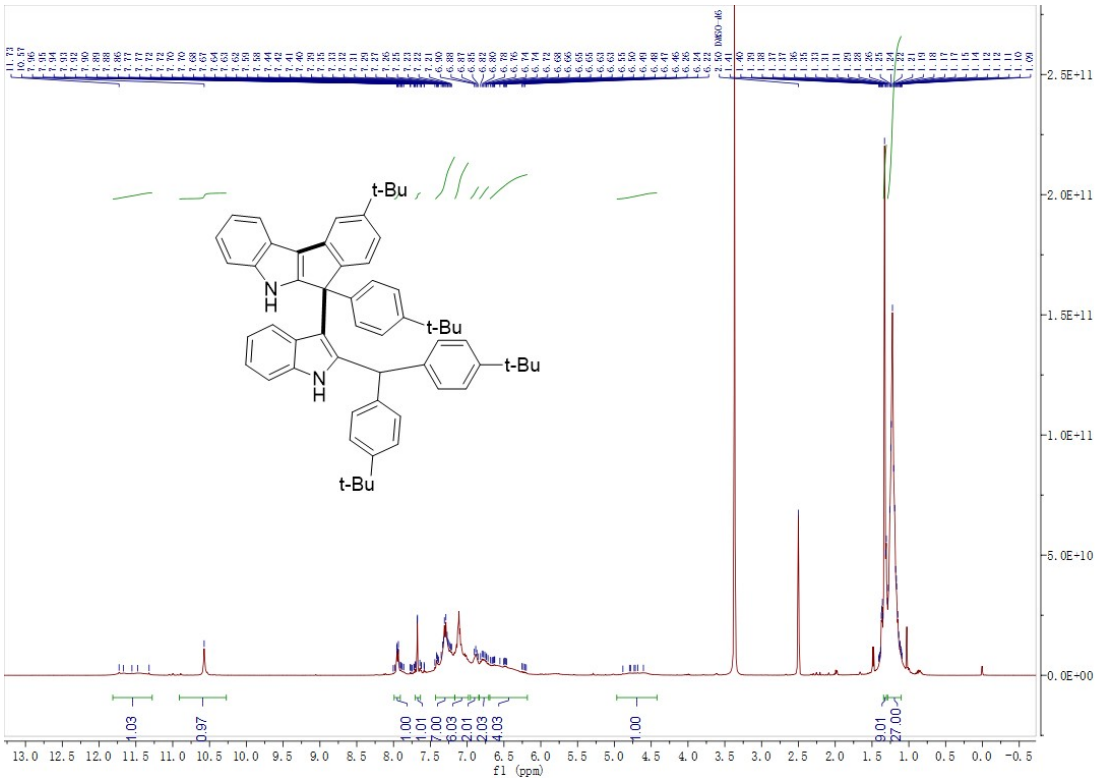


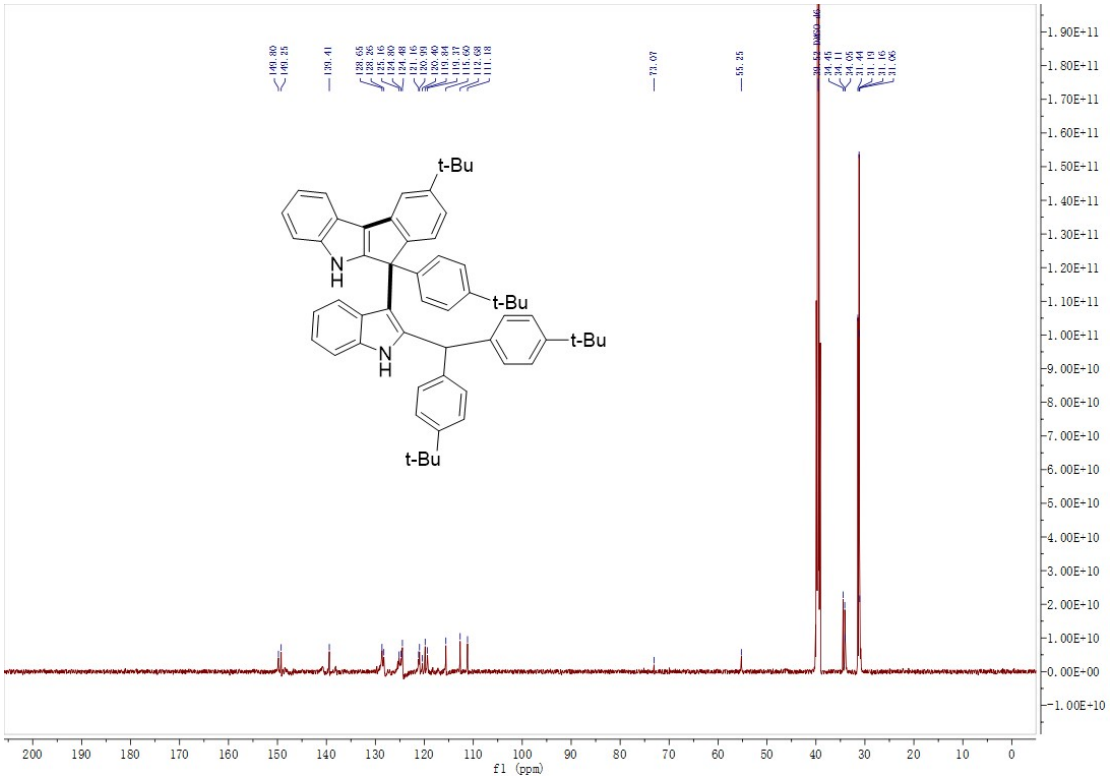
3k



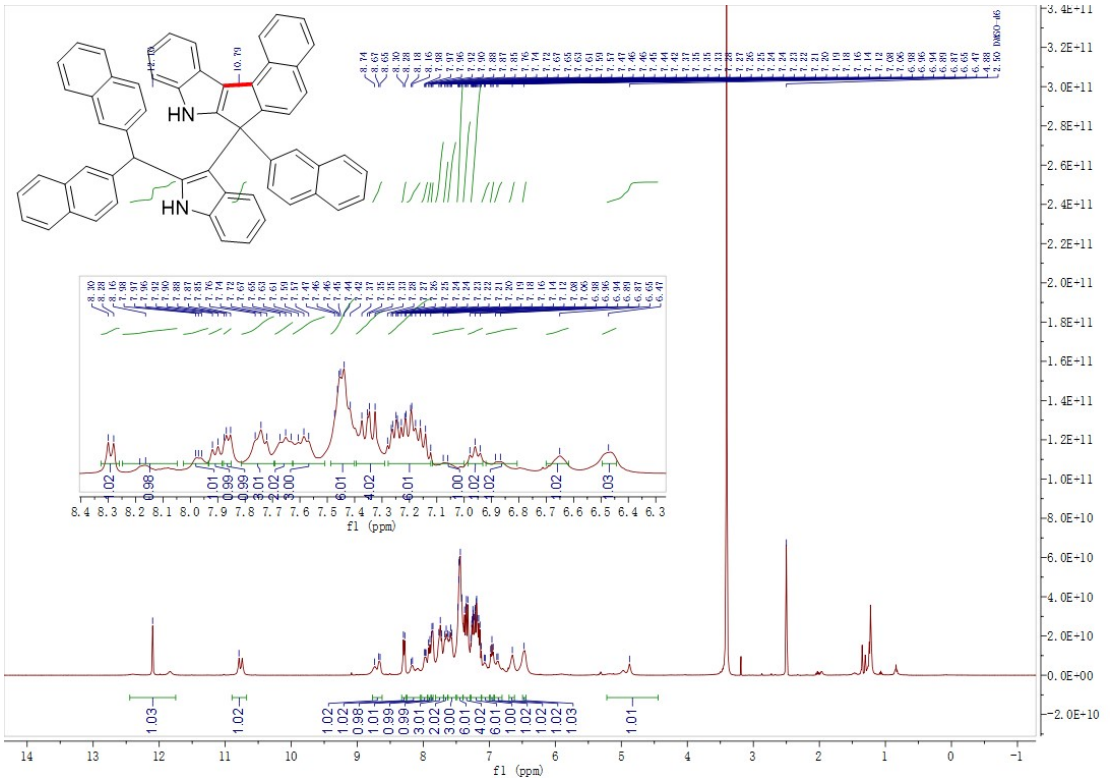


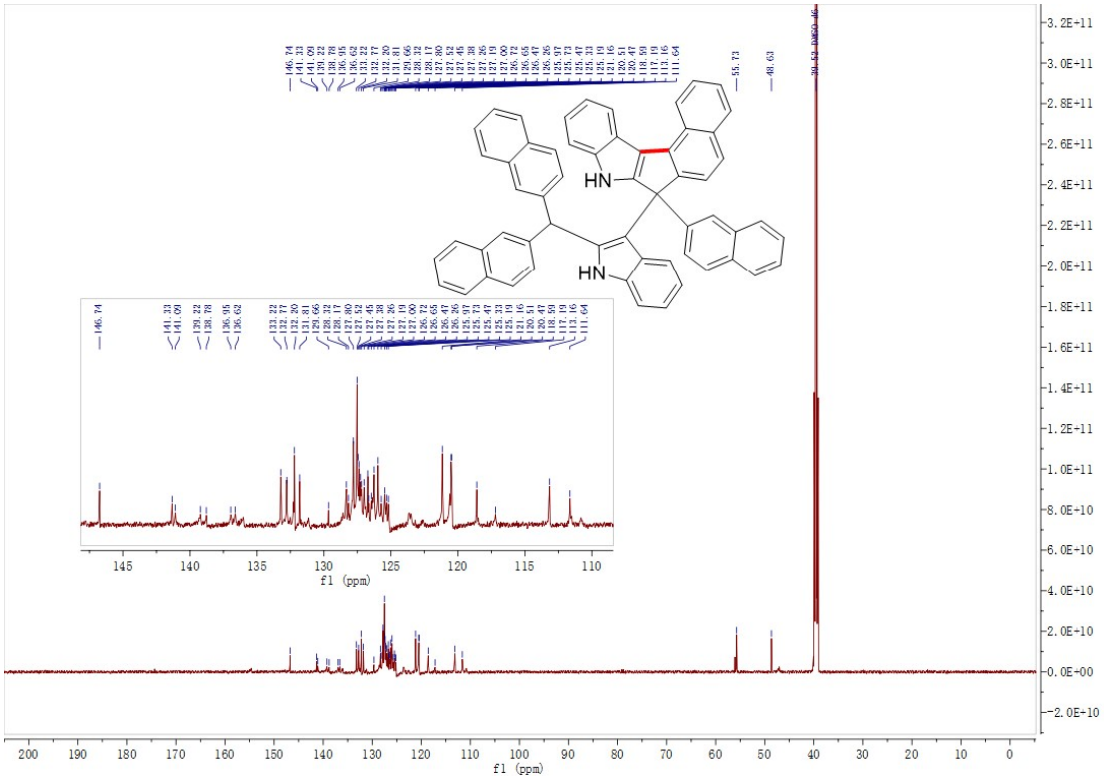
3l



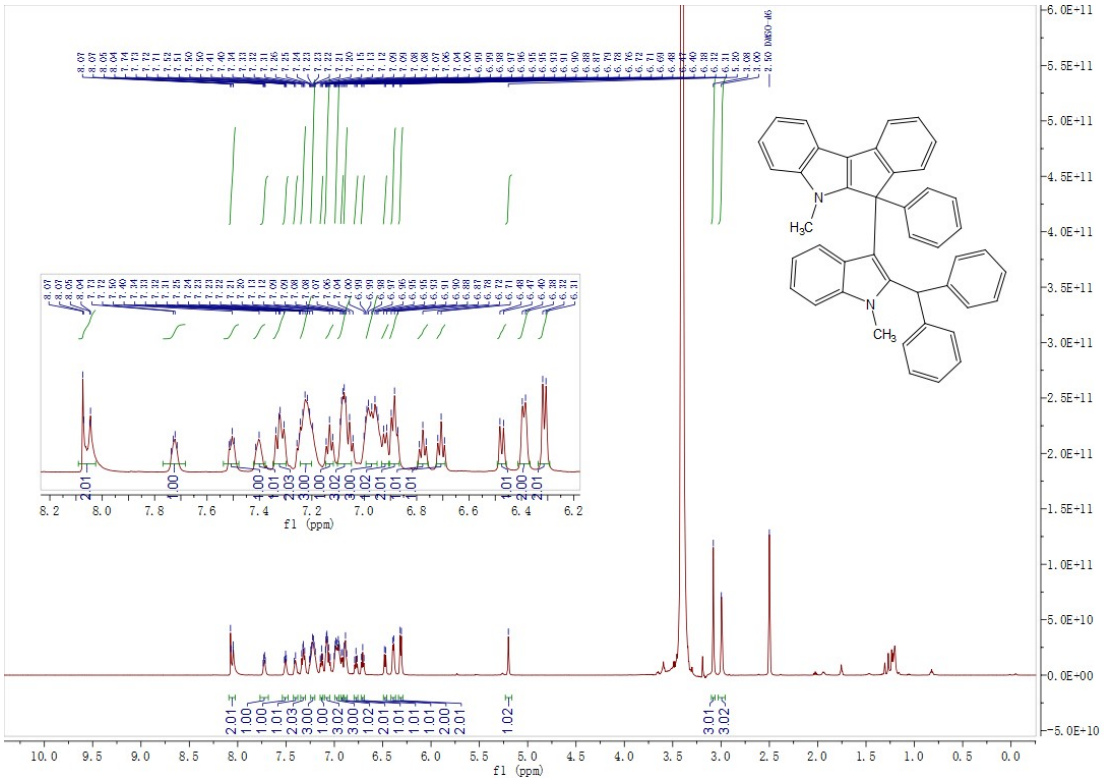


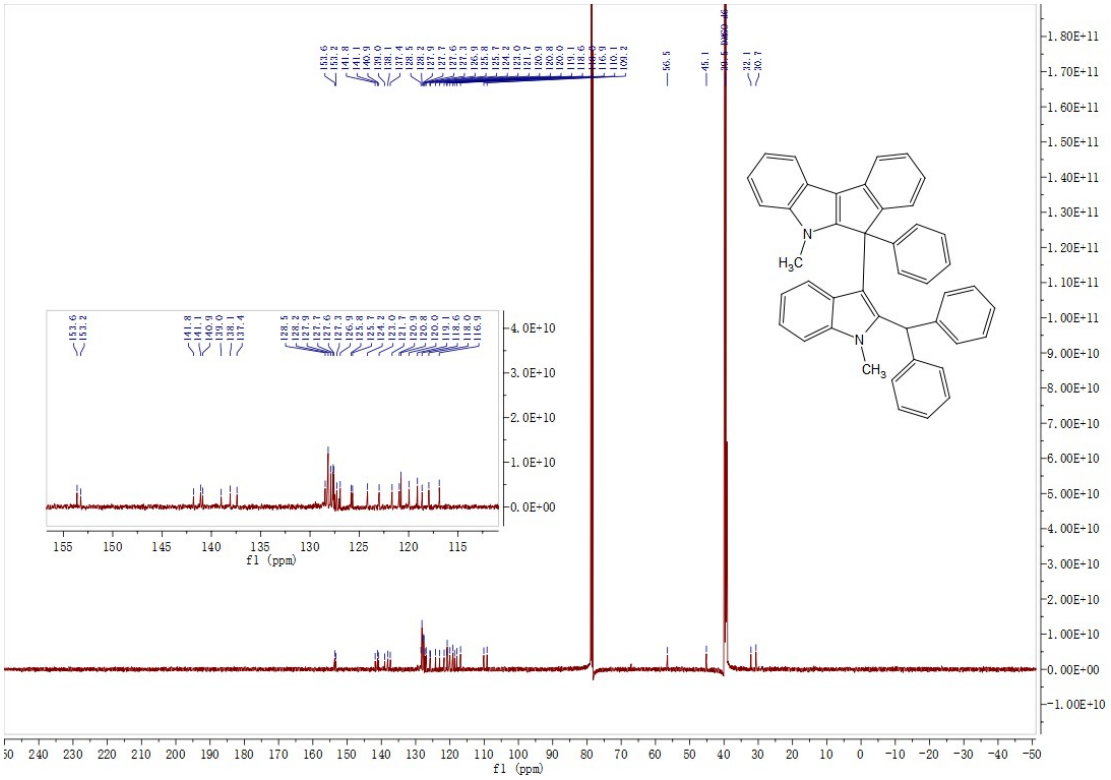
3m



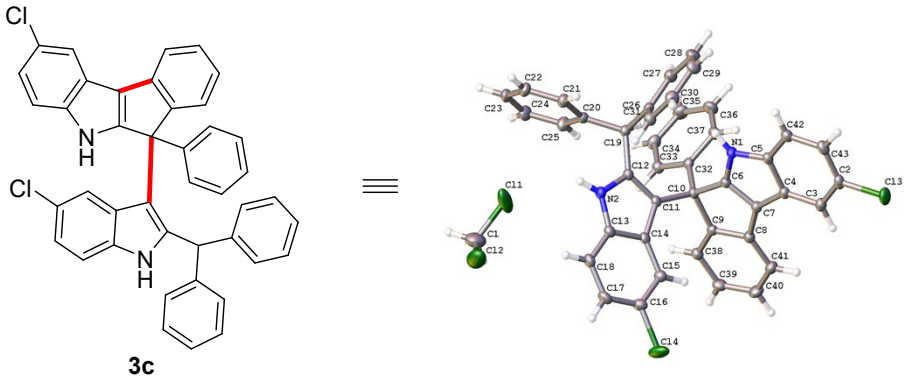


3r





Crystallographic Data for Compounds 3c & 3j



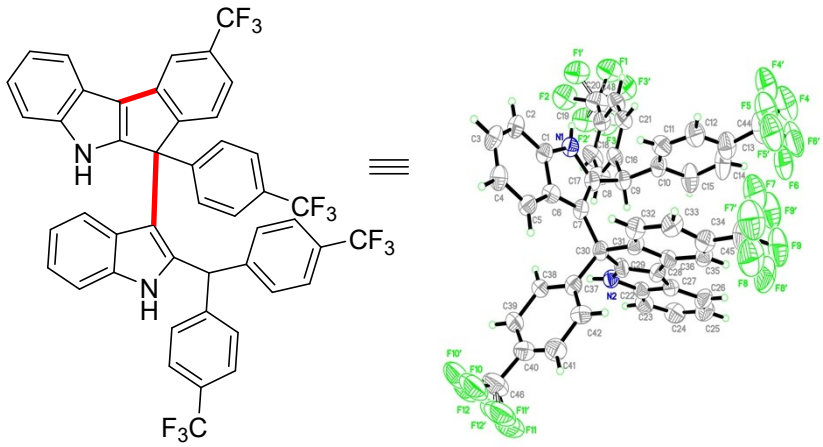
The ellipsoid was drawn at the 50% probability level.

The crystal structure of 3**c** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 2095611.

Table S2 Crystal data and structure refinement for **3c**.

Identification code	mj21120_0m
Empirical formula	C43 H30 Cl4 N2
Formula weight	716.49
Temperature	193 K
Wavelength	1.34139 Å
Crystal system	Monoclinic

Space group	P 1 21/n 1	
Unit cell dimensions	a = 13.9191(4) Å	a= 90°
	b = 12.8360(4) Å	b= 106.3160(10)°
	c = 20.3504(6) Å	γ= 90°
Volume	3489.49(18) $Å^3$	
Z	4	
Density (calculated)	1.364 Mg/m^3	
Absorption coefficient	2.186 mm^{-1}	
F(000)	1480	
Crystal size	0.07 x 0.06 x 0.05 mm^3	
Theta range for data collection	2.996 to 54.966Å	
Index ranges	-16<=h<=16, -15<=k<=14, -24<=l<=24	
Reflections collected	30275	
Independent reflections	6596 [R(int) = 0.0572]	
Completeness to theta = 53.594?	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.5394	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6596 / 0 / 442	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1263	
R indices (all data)	R1 = 0.0574, wR2 = 0.1325	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.722 and -0.726 $e.Å^{-3}$	



3j

The ellipsoid was drawn at the 50% probability level.

The crystal structure of **3j** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 2100661.

Table S3 Crystal data and structure refinement for **3j**.

Identification code	exp_12297_sq
Empirical formula	C46 H26 F12 N2
Formula weight	178.21
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 12.1173(8) A alpha = 78.960(4) deg.
	b = 13.9790(9) A beta = 80.192(5) deg.
	c = 17.7969(7) A gamma = 68.596(6) deg.
Volume	2738.0(3) A^3
Z, Calculated density	1, 0.108 Mg/m^3
Absorption coefficient	0.064 mm^-1
F(000)	94
Crystal size	0.130 x 0.120 x 0.100 mm
Theta range for data collection	3.430 to 67.248 deg.
Limiting indices	-14<=h<=13, -16<=k<=14, -21<=l<=15
Reflections collected / unique	17778 / 9769 [R(int) = 0.0279]
Completeness to theta = 67.248	99.5 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9769 / 700 / 653
Goodness-of-fit on F^2	1.289
Final R indices [I>2sigma(I)]	R1 = 0.0993, wR2 = 0.3321
R indices (all data)	R1 = 0.1291, wR2 = 0.3679
Extinction coefficient	n/a
Largest diff. peak and hole	0.348 and -0.378 e.A^-3