

Supporting Information

Chemoselective metal-free indole arylation with cyclohexanones

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General information

All reactions were carried out under an atmosphere of air unless otherwise noted. Column chromatography was performed using silica gel 48-75 μm . ^1H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded at the Institute of Chemistry, Chinese Academy of Sciences. The structures of known compounds were further corroborated by comparing their ^1H NMR, ^{13}C NMR data and MS data with those of literature. Most reagents were obtained from commercial suppliers and used without further purification.

General procedure for indole arylation

Sulfur powder (25.6 mg, 0.8 mmol), 1-methyl-1*H*-indole (**1a**, 26.0 μL , 0.2 mmol), cyclohexanone (**2a**, 52 μL , 0.5 mmol), boron trifluoride diethyl etherate (25.0 μL , 0.2 mmol), 1,1-diphenylethylene (0.4 mmol, 69 μL), DMF (0.6 mL) were added to a 10 mL reaction vessel. The sealed reaction vessel under air atmosphere was stirred at 150 $^\circ\text{C}$ for 16 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (5 mL) and washed with saturated salt water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over sodium sulfate, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **3aa** as light yellow liquid (34.8 mg, 84% yield).

7 mmol scale: Sulfur powder (896 mg, 28 mmol), 1-methyl-1*H*-indole (**1a**, 910 μL , 7 mmol), 4-(*tert*-butyl)cyclohexan-1-one (**2g**, 2750 mg, 17.5 mmol), boron trifluoride diethyl etherate (875 μL , 7 mmol), 1,1-diphenylethylene (14 mmol, 2415 μL), DMF (7 mL) were added to a 50 mL reaction vessel. The reaction vessel under air atmosphere was stirred at 150 $^\circ\text{C}$ for 16 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (5 mL) and washed with saturated salt water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over sodium sulfate, the volatiles were removed under reduced pressure. The residue was purified by column

chromatography on silica gel (petroleum ether/EtOAc = 400:1) to yield the desired product **3ag** as pale yellow liquid (1325 mg, 72% yield).

General procedure for benzothienoindole synthesis

Sulfur powder (25.6 mg, 0.8 mmol), 1-methyl-1*H*-indole (**1a**, 38.0 μ L, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol), iodine (50.8 mg, 0.2 mmol), NMP (0.6 mL) were added to a 10 mL reaction vessel. The sealed reaction vessel under air atmosphere was stirred at 150 °C for 16 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (5 mL) and washed with saturated salt water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over sodium sulfate, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1, R_f = 0.3) to yield the desired product **4aa** as pale yellow solid (30.7 mg, 65% yield).

General procedure for 2,3-diphenylindole synthesis

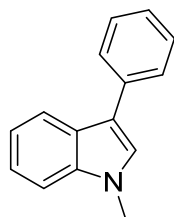
0.2 mmol scale: Iodine bromide (105 mg, 0.5 mmol), 1-methyl-2-phenyl-1*H*-indole (**5a**, 62 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol), 1,1-diphenylethylene (0.4 mmol, 69 μ L), DMAc (0.6 mL) were added to a 10 mL reaction vessel. The sealed reaction vessel under air atmosphere was stirred at 150 °C for 16 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (5 mL) and washed with saturated salt water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over sodium sulfate, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.35) to yield the desired product **6aa** as white solid (52.6 mg, 93% yield).

6 mmol scale: Iodine bromide (3150 mg, 15 mmol), 1-methyl-2-phenyl-1*H*-indole (**5a**, 1920 mg, 9 mmol), cyclohexanone (**2a**, 630 μ L, 6 mmol), 1,1-diphenylethylene (12 mmol, 2070 μ L), DMAc (9 mL) were added to a 50 mL reaction vessel. The reaction vessel under air atmosphere was stirred at 150 °C for 16 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (5 mL) and washed with saturated salt water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer

was dried over sodium sulfate, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1) to yield the desired product **6aa** as white solid (1188 mg, 70% yield).

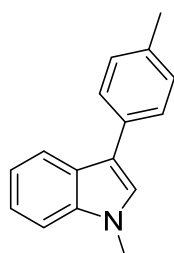
Characterization data of products

1-Methyl-3-phenyl-1*H*-indole (**3aa**, CAS: 30020-98-5)^[1]



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 26.0 μ L, 0.2 mmol), cyclohexanone (**2a**, 52 μ L, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **3aa** as pale yellow liquid (34.8 mg, 84% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, J = 8.0 Hz, 1H), 7.68-7.63 (m, 2H), 7.43 (t, J = 7.56 Hz, 2H), 7.36 (d, J = 8.2 Hz, 1H), 7.30-7.22 (m, 3H), 7.21-7.16 (m, 1H), 3.83 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 137.4, 135.6, 128.7, 127.3, 126.5, 126.1, 125.7, 121.9, 119.9, 119.9, 116.7, 109.5, 32.9.

1-Methyl-3-(*p*-tolyl)-1*H*-indole (**3ab**, CAS: 154796-08-4)^[2]

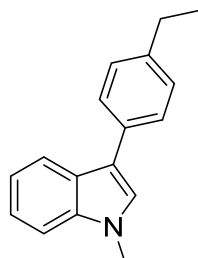


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 26.0 μ L, 0.2 mmol), 4-methylcyclohexanone (**2b**, 61 μ L, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **3ab** as pale yellow liquid (38.9 mg, 88% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.2 Hz, 1H), 7.29-7.23 (m, 3H), 7.20-7.15 (m, 2H), 3.82 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100

MHz, Chloroform-*d*) δ 137.4, 135.3, 132.7, 129.4, 127.2, 126.2, 126.2, 121.9, 119.9, 119.7, 116.6, 109.4, 32.8, 21.1.

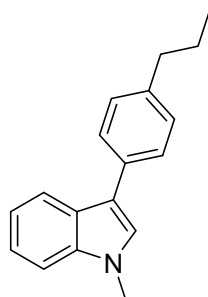
3-(4-Ethylphenyl)-1-methyl-1*H*-indole (3ac)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 26.0 μ L, 0.2 mmol), 4-ethylcyclohexanone (**2c**, 70 μ L, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **3ac** as pale yellow liquid (39.5 mg, 84% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.2 Hz, 1H), 7.29-7.23 (m, 3H), 7.20-7.15 (m, 2H), 3.81 (s, 3H), 2.69 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.7, 137.4, 132.9, 128.2, 127.3, 126.3, 126.2, 121.8, 120.0, 119.7, 116.7, 109.4, 32.8, 28.6, 15.6; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 236.1434, found 236.1434.

1-Methyl-3-(4-propylphenyl)-1*H*-indole (3ad)

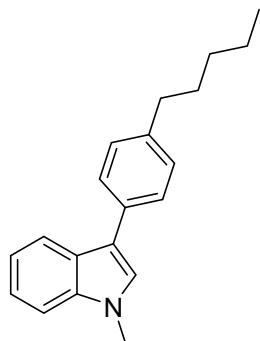


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 26.0 μ L, 0.2 mmol), 4-*n*-propylcyclohexanone (**2d**, 77 μ L, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **3ad** as pale yellow liquid (42.3 mg, 85% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 7.7 Hz, 2H), 7.34 (d, J

= 8.2 Hz, 1H), 7.29-7.22 (m, 3H), 7.20-7.14 (m, 2H), 3.80 (s, 3H), 2.62 (t, $J = 7.7$ Hz, 2H), 1.75-1.63 (m, 2H), 0.98 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.1, 137.4, 132.9, 128.9, 127.2, 126.3, 126.2, 121.8, 120.0, 119.7, 116.7, 109.4, 37.8, 32.8, 24.6, 13.9; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{20}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 250.1590, found 250.1591.

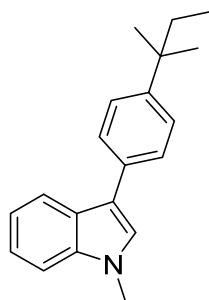
1-Methyl-3-(4-pentylphenyl)-1H-indole (3ae)



The reaction was conducted with 1-methyl-1H-indole (**1a**, 26.0 μL , 0.2 mmol), 4-*n*-pentylcyclohexanone (**2e**, 94 μL , 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, $R_f = 0.4$) to yield the desired product **3ae** as pale yellow liquid (49.3 mg, 89% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.2$ Hz, 1H), 7.29-7.23 (m, 3H), 7.20-7.15 (m, 2H), 3.82 (s, 3H), 2.64 (t, $J = 7.6$ Hz, 2H), 1.71-1.61 (m, 2H), 1.40-1.33 (m, 4H), 0.91 (t, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.4, 137.4, 132.9, 128.7, 127.2, 126.3, 126.2, 121.8, 120.0, 119.7, 116.7, 109.4, 35.6, 32.8, 31.6, 31.3, 22.6, 14.0; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{24}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 278.1903, found 278.1908.

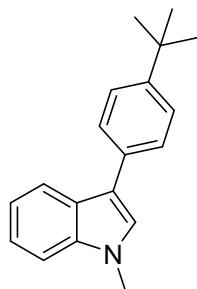
1-Methyl-3-(4-(*tert*-pentyl)phenyl)-1H-indole (3af)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 26.0 μ L, 0.2 mmol), 4-*tert*-pentylcyclohexanone (**2f**, 94 μ L, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **3af** as pale yellow liquid (45.4 mg, 82% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, J = 8.0 Hz, 1H), 7.61-7.56 (m, 2H), 7.41-7.37 (m, 2H), 7.30 (d, J = 8.2 Hz, 1H), 7.29-7.22 (m, 1H), 7.20-7.15 (m, 2H), 3.80 (s, 3H), 1.68 (q, J = 7.4 Hz, 2H), 1.33 (s, 6H), 0.74 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.9, 137.4, 132.6, 126.8, 126.3, 126.3, 126.2, 121.8, 120.1, 119.7, 116.6, 109.4, 37.7, 36.9, 32.8, 28.5, 9.2; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{24}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 278.1903, found 278.1902.

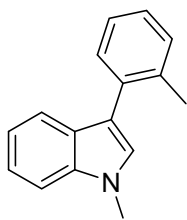
3-(4-(*tert*-Butyl)phenyl)-1-methyl-1*H*-indole (**3ag**)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 26.0 μ L, 0.2 mmol), 4-*tert*-butylcyclohexanone (**2g**, 77 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **3ag** as pale yellow liquid (46.8 mg, 89% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, J = 8.0 Hz, 1H), 7.62-7.56 (m, 2H), 7.48-7.43 (m, 2H), 7.28 (d, J = 8.2 Hz, 1H), 7.29-7.23 (m, 1H), 7.20-7.15 (m, 2H), 3.81 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.5, 137.4, 132.7, 127.0, 126.3, 126.2, 125.6, 121.8, 120.0, 119.7, 116.6, 109.4, 34.5, 32.8, 31.4; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{22}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 264.1747, found 264.1744.

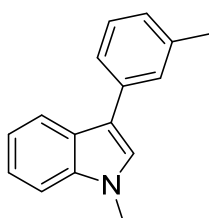
1-Methyl-3-(*o*-tolyl)-1*H*-indole (**3ai**, CAS: 883141-51-3)^[2]



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 26.0 μ L, 0.2 mmol), 2-methylcyclohexanone (**2i**, 63 μ L, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.35) to yield the desired product **3ai** as pale yellow liquid (26.5 mg, 60% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, J = 7.9 Hz, 1H), 7.44-7.35 (m, 2H), 7.33-7.29 (m, 1H), 7.28-7.22 (m, 3H), 7.13 (t, J = 7.5 Hz, 1H), 7.04 (s, 1H), 3.84 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 136.7, 134.5, 130.9, 130.3, 127.6, 127.5, 127.5, 126.5, 125.6, 121.7, 120.2, 119.4, 115.9, 109.3, 32.8, 20.8.

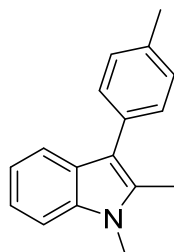
1-Methyl-3-(*m*-tolyl)-1*H*-indole (**3aj**)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 26.0 μ L, 0.2 mmol), 3-methylcyclohexanone (**2j**, 62 μ L, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.35) to yield the desired product **3aj** as pale yellow liquid (34.5 mg, 78% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 7.7 Hz, 2H), 7.33 (q, J = 7.9 Hz, 2H), 7.29-7.23 (m, 1H), 7.21-7.15 (m, 2H), 7.08 (d, J = 7.6 Hz, 1H), 3.81 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.2, 137.4, 135.5, 128.6, 128.1, 126.5, 126.5, 126.2, 124.4, 121.9, 120.0, 119.8, 116.8, 109.5, 32.8, 21.6; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{16}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 222.1277, found 222.1274.

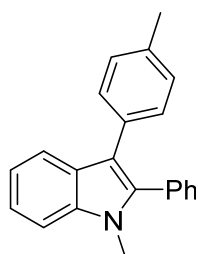
1,2-Dimethyl-3-(*p*-tolyl)-1*H*-indole (**3bb**)



The reaction was conducted with 1,2-dimethyl-1*H*-indole (**1b**, 29 mg, 0.2 mmol), 4-methylcyclohexanone (**2b**, 61 μ L, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **3bb** as pale yellow solid (29.1 mg, 62% yield), mp 127-129 $^{\circ}$ C.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, J = 7.9 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.33-7.25 (m, 3H), 7.23-7.17 (m, 1H), 7.12-7.06 (m, 1H), 3.72 (s, 3H), 2.47 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 136.5, 135.2, 133.1, 132.7, 129.5, 129.2, 127.0, 121.0, 119.5, 118.7, 113.9, 108.6, 29.6, 21.2, 11.0; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 236.1434, found 236.1430.

1-Methyl-2-phenyl-3-(*p*-tolyl)-1*H*-indole (**3cb** or **6ab**)^[4]



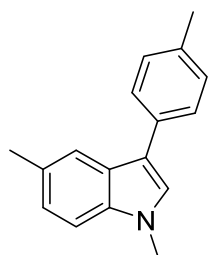
Condition A: The reaction was conducted with 1-methyl-2-phenyl-1*H*-indole (**1c**, 42 mg, 0.2 mmol), 4-methylcyclohexanone (**2b**, 61 μ L, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **3cb** as white solid (20.7 mg, 35% yield).

Condition C: The reaction was conducted with 1-methyl-2-phenyl-1*H*-indole (**5a**, 62 mg, 0.3 mmol), 4-methylcyclohexanone (**2b**, 26 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1) to yield the desired product **6ab** as white solid (55.2 mg, 93% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, J = 8.0 Hz, 1H), 7.42-7.26 (m, 7H), 7.22-7.14 (m,

3H), 7.07 (d, $J = 7.8$ Hz, 2H), 3.64 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 137.5, 137.3, 134.9, 132.1, 132.0, 131.1, 129.7, 128.9, 128.3, 127.9, 127.0, 122.1, 120.0, 119.6, 114.9, 109.5, 30.9, 21.1.

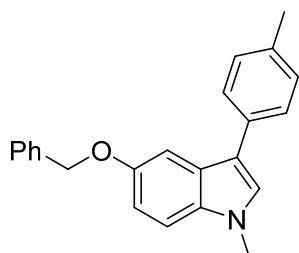
1,5-Dimethyl-3-(*p*-tolyl)-1*H*-indole (3eb)



The reaction was conducted with 1,5-dimethyl-1*H*-indole (**1e**, 29 mg, 0.2 mmol), 4-methylcyclohexanone (**2b**, 61 μL , 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, $R_f = 0.4$) to yield the desired product **3eb** as pale yellow solid (37.6 mg, 80% yield), mp 48-51 $^\circ\text{C}$.

^1H NMR (400 MHz, Chloroform- d) δ 7.64 (d, $J = 0.72$ Hz, 1H), 7.48 (dd, $J = 8.1, 1.8$ Hz, 2H), 7.27-7.22 (m, 3H), 7.15 (s, 1H), 7.09 (d, $J = 8.3$ Hz, 1H), 3.79 (s, 3H), 2.47 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform- d) δ 135.8, 135.1, 132.8, 129.4, 129.0, 127.2, 126.4, 126.3, 123.4, 119.5, 116.1, 109.1, 32.8, 21.6, 21.1; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 236.1434, found 236.1431.

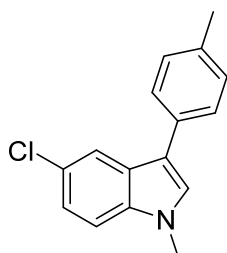
5-(Benzyloxy)-1-methyl-3-(*p*-tolyl)-1*H*-indole (3fb)



The reaction was conducted with 5-(benzyloxy)-1-methyl-1*H*-indole (**1f**, 47.4 mg, 0.2 mmol), 4-methylcyclohexanone (**2b**, 61 μL , 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1, $R_f = 0.3$) to yield the desired product **3fb** as pale yellow solid (48.4 mg, 74% yield), mp 126-129 $^\circ\text{C}$.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.51-7.43 (m, 5H), 7.37 (t, $J = 7.6$ Hz, 2H), 7.30 (t, $J = 7.3$ Hz, 1H), 7.25-7.19 (m, 3H), 7.13 (s, 1H), 6.99 (d, $J = 9.9$ Hz, 1H), 5.09 (s, 2H), 3.74 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.5, 137.6, 135.1, 132.9, 132.7, 129.4, 128.5, 127.7, 127.6, 127.0, 126.9, 126.4, 116.1, 112.8, 110.2, 103.5, 71.0, 32.9, 21.1; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{22}\text{NO}^+$ ($\text{M}+\text{H}$) $^+$ 328.1696, found 328.1694.

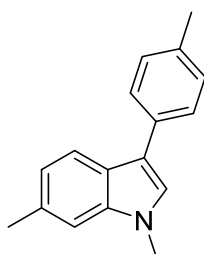
5-Chloro-1-methyl-3-(*p*-tolyl)-1*H*-indole (**3gb**)



The reaction was conducted with 5-chloro-1-methyl-1*H*-indole (**1g**, 33 mg, 0.2 mmol), 4-methylcyclohexanone (**2b**, 61 μL , 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, $R_f = 0.35$) to yield the desired product **3gb** as pale yellow liquid (30.6 mg, 60% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.47 (d, $J = 7.9$ Hz, 2H), 7.27-7.19 (m, 4H), 7.18 (s, 1H), 3.77 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.8, 135.6, 131.9, 129.5, 127.4, 127.1, 127.1, 125.6, 122.1, 119.3, 116.4, 110.5, 33.0, 21.1; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{15}\text{ClN}^+$ ($\text{M}+\text{H}$) $^+$ 256.0888, found 256.0885.

1,6-Dimethyl-3-(*p*-tolyl)-1*H*-indole (**3hb**, CAS: 32030324)^[1]

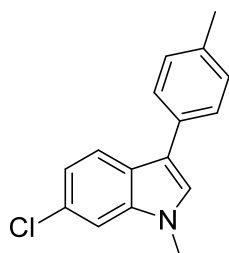


The reaction was conducted with 1,6-dimethyl-1*H*-indole (**1h**, 29 mg, 0.2 mmol), 4-methylcyclohexanone (**2b**, 61 μL , 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, $R_f = 0.4$) to yield the desired

product **3hb** as pale yellow liquid (38.5 mg, 82% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, $J = 8.3, 1.3$ Hz, 1H), 7.57-7.50 (m, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.2$ Hz, 2H), 7.00 (d, $J = 8.2$ Hz, 1H), 3.76 (s, 3H), 2.51 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.8, 135.1, 132.8, 131.7, 129.4, 127.1, 125.6, 124.0, 121.5, 119.6, 116.4, 109.4, 32.7, 21.8, 21.1.

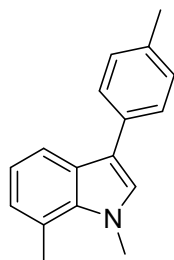
6-Chloro-1-methyl-3-(*p*-tolyl)-1*H*-indole (**3ib**)



The reaction was conducted with 6-chloro-1-methyl-1*H*-indole (**1i**, 33 mg, 0.2 mmol), 4-methylcyclohexanone (**2b**, 61 μL , 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, $R_f = 0.35$) to yield the desired product **3ib** as pale yellow solid (30.6 mg, 60% yield), mp 67-69 $^\circ\text{C}$.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, $J = 8.5$ Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 1.5$ Hz, 1H), 7.25 (d, $J = 6.4$ Hz, 2H), 7.17 (s, 1H), 7.13 (dd, $J = 8.5, 1.7$ Hz, 1H), 3.79 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.7, 135.6, 132.0, 129.5, 127.8, 127.1, 126.7, 124.7, 120.8, 120.3, 116.8, 109.4, 32.8, 21.1; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{15}\text{ClN}^+$ ($\text{M}+\text{H}$) $^+$ 256.0886, found 256.0884.

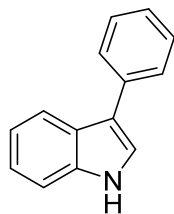
1,7-Dimethyl-3-(*p*-tolyl)-1*H*-indole (**3jb**)



^1H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, $J = 7.9$ Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.24 (d, J

= 7.4 Hz, 2H), 7.08-7.00 (m, 2H), 6.95 (d, $J = 7.0$ Hz, 1H), 4.09 (s, 3H), 2.79 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 136.1, 135.3, 132.6, 129.4, 128.1, 127.5, 127.4, 124.5, 121.4, 120.0, 118.0, 116.5, 36.9, 21.1, 19.8; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 236.1434, found 236.1431.

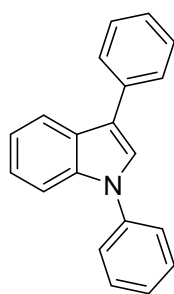
3-Phenyl-1H-indole (3ka, CAS: 1504-16-1)^[8]



The reaction was conducted with 1H-indole (**1k**, 23 mg, 0.2 mmol), cyclohexanone (**2a**, 52 μL , 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1, $R_f = 0.3$) to yield the desired product **3ka** as light yellow solid (13.5 mg, 35% yield).

^1H NMR (400 MHz, Chloroform- d) δ 8.13 (s, 1H), 7.94 (d, $J = 7.8$ Hz, 1H), 7.70-7.63 (m, 2H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.37 (d, $J = 7.9$ Hz, 1H), 7.31-7.15 (m, 4H); ^{13}C NMR (100 MHz, Chloroform- d) δ 136.6, 135.5, 128.7, 127.4, 125.9, 125.7, 122.4, 121.8, 120.3, 119.8, 118.2, 111.4.

1,3-diphenyl-1H-indole (3la, CAS: 20538-11-8)^[9]

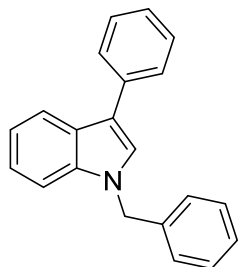


The reaction was conducted with 1-phenyl-1H-indole (**1l**, 39 mg, 0.2 mmol), cyclohexanone (**2a**, 52 μL , 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, $R_f = 0.35$) to yield the desired product **3la** as colourless liquid (17.8 mg, 33% yield).

^1H NMR (400 MHz, Chloroform- d) δ 8.02-7.96 (m, 1H), 7.74-7.69 (m, 2H), 7.59 (dd, $J = 7.1, 1.6$

Hz, 1H), 7.57-7.51 (m, 4H), 7.50-7.44 (m, 3H), 7.39-7.34 (m, 1H), 7.33-7.21 (m, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.5, 136.6, 135.1, 129.7, 128.8, 127.6, 127.1, 126.6, 126.2, 125.5, 124.5, 122.8, 120.9, 120.1, 119.1, 110.8.

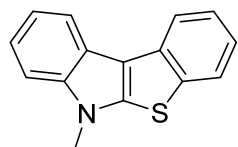
1-Benzyl-3-phenyl-1*H*-indole (3ma, CAS: 23073-17-8)^[10]



The reaction was conducted with 1-benzyl-1*H*-indole (**1m**, 41 mg, 0.2 mmol), cyclohexanone (**2a**, 52 μL , 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **3ma** as pale yellow liquid (27.2 mg, 48% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, J = 7.8 Hz, 1H), 7.69-7.64 (m, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.34-7.29 (m, 2H), 7.27-7.14 (m, 7H), 5.30 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.2, 137.1, 135.5, 128.8, 128.7, 127.7, 127.3, 126.9, 126.4, 125.9, 125.8, 122.1, 120., 120.0, 117.3, 109.9, 50.1.

6-Methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (4aa, CAS: 1269621-22-8)^[5]

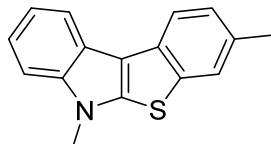


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 38.0 μL , 0.3 mmol), cyclohexanone (**2a**, 21 μL , 0.2 mmol), sulfur powder (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1, R_f = 0.3) to yield the desired product **4aa** as pale yellow solid (30.7 mg, 65% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, J = 7.8 Hz, 1H), 7.97 (dd, J = 6.4, 2.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.48-7.43 (m, 1H), 7.39-7.35 (m, 1H), 7.33-7.26 (m, 2H), 7.25-7.21 (m, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.4, 141.7, 138.0, 133.3, 125.1, 123.7,

122.6, 121.8, 121.4, 120.5, 120.0, 118.8, 116.6, 109.2, 32.3.

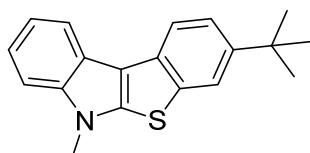
3,6-Dimethyl-6H-benzo[4,5]thieno[2,3-b]indole (**4ab**)^[5]



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 38.0 μ L, 0.3 mmol), 4-methylcyclohexanone (**2b**, 26 μ L, 0.2 mmol), sulfur powder (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1, R_f = 0.3) to yield the desired product **4ab** as pale yellow solid (41.7 mg, 83% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.98-7.94 (m, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.56 (s, 1H), 7.34-7.31 (m, 1H), 7.27-7.22 (m, 3H), 3.76 (s, 3H), 2.46 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 142.7, 141.6, 138.2, 131.5, 130.8, 126.4, 123.7, 122.5, 121.2, 120.1, 119.8, 118.7, 116.4, 109.1, 32.2, 21.5.

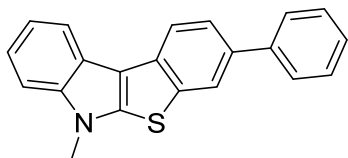
3-(*tert*-butyl)-6-methyl-6H-benzo[4,5]thieno[2,3-*b*]indole (**4ac**)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 38.0 μ L, 0.3 mmol), 4-*tert*-butylcyclohexanone (**2c**, 31 mg, 0.2 mmol), sulfur powder (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1, R_f = 0.3) to yield the desired product **4ac** as pale yellow liquid (46.9 mg, 80% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.00-7.95 (m, 2H), 7.81 (s, 1H), 7.54-7.49 (m, 1H), 7.37-7.33 (m, 1H), 7.30-7.23 (m, 2H), 3.82 (s, 3H), 1.41 (s, 9H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 145.2, 143.1, 141.6, 138.2, 130.8, 122.9, 122.6, 121.2, 120.1, 120.0, 119.8, 118.7, 116.4, 109.1, 34.8, 32.3, 31.7; HRMS (ESI) m/z calcd for C₁₉H₂₀NS⁺ (M+H)⁺ 294.1311, found 294.1317.

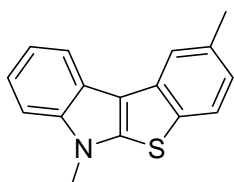
6-Methyl-3-phenyl-6H-benzo[4,5]thieno[2,3-*b*]indole (**4ad**)^[5]



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 38.0 μL , 0.3 mmol), 4-phenylcyclohexanone (**2d**, 35 mg, 0.2 mmol), sulfur powder (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1, R_f = 0.3) to yield the desired product **4ad** as pale yellow solid (26.3 mg, 42% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, J = 8.2 Hz, 1H), 7.99 (dd, J = 6.4, 1.4 Hz, 2H), 7.74-7.67 (m, 3H), 7.50-7.42 (m, 3H), 7.37-7.30 (m, 3H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.7, 141.7, 141.2, 138.8, 135.2, 132.4, 128.8, 127.1, 126.9, 124.6, 122.6, 122.2, 121.6, 120.6, 120.1, 118.9, 116.4, 109.3, 32.4.

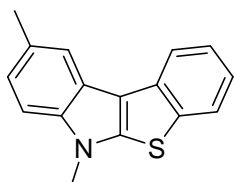
2,6-Dimethyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (**4af**)^[5]



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 38.0 μL , 0.3 mmol), 3-methylcyclohexanone (**2f**, 26 μL , 0.2 mmol), sulfur powder (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1, R_f = 0.3) to yield the desired product **4af** as pale yellow solid (35.1 mg, 70% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.99 (dd, J = 6.5, 2.0 Hz, 1H), 7.87 (s, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.39-7.36 (m, 1H), 7.32-7.26 (m, 2H), 7.06 (d, J = 8.1 Hz, 1H), 3.84 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.8, 141.7, 135.0, 134.9, 133.4, 123.3, 122.6, 121.3, 121.0, 119.9, 118.8, 116.4, 109.2, 32.3, 21.7.

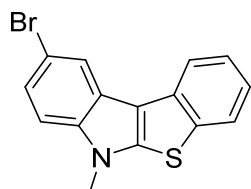
6,9-Dimethyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (**4ba**)^[5]



The reaction was conducted with 1,5-dimethyl-1*H*-indole (**1b**, 43.5 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol), sulfur powder (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1, R_f = 0.3) to yield the desired product **4ba** as pale yellow solid (30.1 mg, 60% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, J = 7.8 Hz, 1H), 7.83-7.78 (m, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.30-7.20 (m, 2H), 7.13 (d, J = 8.3 Hz, 1H), 3.85 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.5, 140.2, 137.9, 133.4, 129.3, 125.1, 123.6, 122.8, 122.8, 121.7, 120.5, 118.8, 116.3, 108.9, 32.4, 21.5.

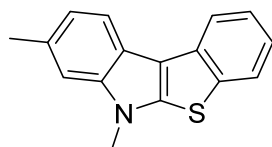
9-Bromo-6-methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (**4ca**)^[5]



The reaction was conducted with 5-bromo-1-methyl-1*H*-indole (**1c**, 63 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol), sulfur powder (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1, R_f = 0.25) to yield the desired product **4ca** as pale yellow solid (29.0 mg, 46% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.08-8.05 (m, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.36 (dd, J = 8.7, 1.8 Hz, 1H), 7.28-7.24 (m, 1H), 7.21 (d, J = 8.6 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.5, 140.3, 137.9, 132.7, 125.3, 124.1, 123.9, 123.7, 122.3, 121.3, 120.6, 115.9, 113.2, 110.5, 32.4.

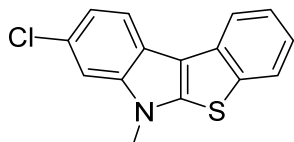
6,8-Dimethyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (**4da**)^[5]



The reaction was conducted with 1,6-dimethyl-1*H*-indole (**1d**, 43.5 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol), sulfur powder (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1, R_f = 0.3) to yield the desired product **4da** as pale yellow solid (32.1 mg, 64% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.48-7.42 (m, 1H), 7.25-7.17 (m, 2H), 7.10 (d, J = 8.0 Hz, 1H), 3.83 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.8, 142.2, 137.9, 133.3, 131.4, 125.0, 123.7, 123.7, 121.6, 121.4, 120.4, 118.4, 116.5, 109.5, 32.2, 21.9.

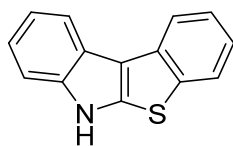
8-Chloro-6-methyl-6H-benzo[4,5]thieno[2,3-*b*]indole (4ea)^[5]



The reaction was conducted with 6-chloro-1-methyl-1*H*-indole (**1e**, 50 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μL , 0.2 mmol), sulfur powder (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1, R_f = 0.25) to yield the desired product **4ea** as white solid (29.3 mg, 54% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, J = 7.8 Hz, 1H), 7.79 (t, J = 8.7 Hz, 2H), 7.45 (t, J = 7.6 Hz, 1H), 7.32 (d, J = 1.5 Hz, 1H), 7.27 – 7.18 (m, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.9, 142.0, 138.0, 132.8, 127.4, 125.2, 123.7, 122.2, 121.0, 120.5, 120.4, 119.3, 116.5, 109.4, 32.3.

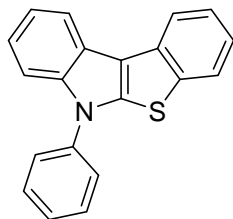
6H-Benzo[4,5]thieno[2,3-*b*]indole (4fa, CAS: 111550-86-8)^[11]



The reaction was conducted with 1*H*-indole (**1f**, 36 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μL , 0.2 mmol), sulfur powder (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1, R_f = 0.3) to yield the desired product **4fa** as pale yellow solid (20.1 mg, 45% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 8.10 (d, J = 7.8 Hz, 1H), 8.05-8.00 (m, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.51-7.45 (m, 2H), 7.31-7.25 (m, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.3, 139.9, 138.5, 132.7, 125.1, 123.6, 122.8, 122.4, 122.1, 120.7, 120.6, 119.1, 118.7, 111.4.

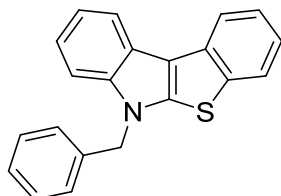
6-Phenyl-6H-benzo[4,5]thieno[2,3-b]indole (4ga, CAS: 1269621-16-0)^[12]



The reaction was conducted with 1-phenyl-1*H*-indole (**1g**, 58 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol), sulfur powder (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **4ga** as pale yellow solid (16.7 mg, 28% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, J = 7.9 Hz, 1H), 8.08-8.04 (m, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.72-7.67 (m, 2H), 7.58 (q, J = 8.2, 7.6 Hz, 3H), 7.51-7.46 (m, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.35-7.25 (m, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 142.6, 141.1, 138.5, 137.7, 132.9, 130.0, 127.3, 125.2, 124.0, 123.6, 123.4, 122.5, 122.2, 121.0, 120.7, 119.0, 118.7, 110.7.

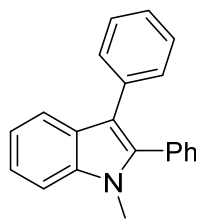
6-Benzyl-6H-benzo[4,5]thieno[2,3-b]indole (4ha, CAS: 1269621-18-2)^[13]



The reaction was conducted with 1-benzyl-1*H*-indole (**1h**, 62 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol), sulfur powder (25.6 mg, 0.8 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **4ha** as pale yellow solid (34.4 mg, 55% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, J = 7.8 Hz, 1H), 8.04-8.00 (m, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.47-7.38 (m, 2H), 7.29-7.25 (m, 5H), 7.23-7.18 (m, 3H), 5.36 (s, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 142.8, 141.5, 138.3, 135.6, 133.0, 128.9, 128.1, 127.4, 125.1, 123.5, 122.8, 122.0, 121.7, 120.5, 120.2, 118.9, 117.4, 109.7, 49.8.

1-Methyl-2,3-diphenyl-1*H*-indole (6aa, CAS: 6121-45-5)^[3]

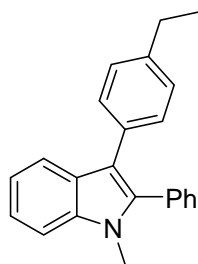


The reaction was conducted with 1-methyl-2-phenyl-1*H*-indole (**5a**, 62 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **6aa** as white solid (52.6 mg, 93% yield).

From 2-chlorocyclohexanone: The reaction was conducted with 1-methyl-2-phenyl-1*H*-indole (**5a**, 62 mg, 0.3 mmol), 2-chlorocyclohexanone (**2a'**, 27 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **6aa** as white solid (34.0 mg, 60% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, J = 8.0 Hz, 1H), 7.42-7.34 (m, 4H), 7.33-7.23 (m, 7H), 7.21-7.13 (m, 2H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.7, 137.3, 135.2, 131.9, 131.1, 129.8, 128.4, 128.1, 128.0, 126.9, 125.5, 122.1, 120.2, 119.6, 115.0, 109.6, 30.9.

3-(4-Ethylphenyl)-1-methyl-2-phenyl-1*H*-indole (**6ac**)

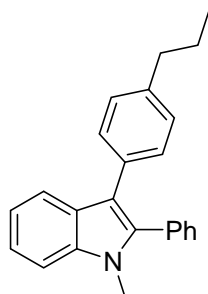


The reaction was conducted with 1-methyl-2-phenyl-1*H*-indole (**5a**, 62 mg, 0.3 mmol), 4-ethylcyclohexanone (**2c**, 29 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **6ac** as colorless oil liquid (56.6 mg, 91% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, J = 7.9 Hz, 1H), 7.41-7.25 (m, 7H), 7.24-7.14 (m, 3H), 7.09 (d, J = 8.2 Hz, 2H), 3.64 (s, 3H), 2.62 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.2, 137.5, 137.3, 132.3, 132.0, 131.1, 129.7, 128.3, 127.9, 127.6, 127.0, 122.1, 120.0, 119.7, 115.0, 109.5, 30.9, 28.5, 15.3; HRMS (ESI) m/z calcd for

$C_{23}H_{22}N^+$ (M+H)⁺ 312.1747, found 312.1746.

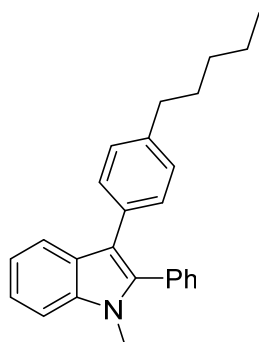
1-Methyl-2-phenyl-3-(4-propylphenyl)-1H-indole (6ad)



The reaction was conducted with 1-methyl-2-phenyl-1H-indole (**5a**, 62 mg, 0.3 mmol), 4-propylcyclohexanone (**2d**, 32 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **6ad** as colorless oil liquid (59.8 mg, 92% yield).

1H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, J = 7.9 Hz, 1H), 7.41-7.25 (m, 7H), 7.22-7.14 (m, 3H), 7.07 (d, J = 8.0 Hz, 2H), 3.65 (s, 3H), 2.54 (t, J = 7.6 Hz, 3H), 1.69-1.57 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.8, 137.5, 137.3, 132.3, 132.0, 131.2, 129.6, 128.3, 128.2, 127.9, 127.0, 122.0, 120.0, 119.7, 115.0, 109.5, 37.8, 30.9, 24.4, 14.0; HRMS (ESI) m/z calcd for $C_{24}H_{24}N^+$ (M+H)⁺ 326.1903, found 326.1904.

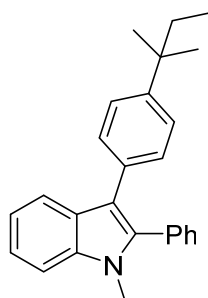
1-Methyl-3-(4-pentylphenyl)-2-phenyl-1H-indole (6ae)



The reaction was conducted with 1-methyl-2-phenyl-1H-indole (**5a**, 62 mg, 0.3 mmol), 4-*n*-pentylcyclohexanone (**2e**, 39 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.4) to yield the desired product **6ae** as colorless oil liquid (63.5 mg, 90% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.82-7.77 (m, 1H), 7.41-7.25 (m, 7H), 7.23-7.14 (m, 3H), 7.10-7.04 (m, 2H), 3.64 (s, 3H), 2.56 (t, $J = 7.8$ Hz, 2H), 1.66-1.56 (m, 2H), 1.38-1.27 (m, 4H), 0.89 (t, $J = 6.0$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.1, 137.6, 137.4, 132.4, 132.1, 131.3, 129.7, 128.4, 128.3, 128.00, 127.1, 122.1, 120.1, 119.8, 115.1, 109.6, 35.7, 31.8, 31.6, 31.0, 22.7, 14.2; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{28}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 354.2216, found 354.2212.

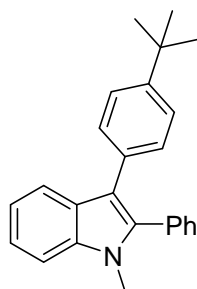
1-Methyl-3-(4-(*tert*-pentyl)phenyl)-2-phenyl-1H-indole (6af)



The reaction was conducted with 1-methyl-2-phenyl-1H-indole (**5a**, 62 mg, 0.3 mmol), 4-*tert*-pentylcyclohexanone (**2f**, 38 μL , 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, $R_f = 0.35$) to yield the desired product **6af** as colorless oil liquid (65.7 mg, 93% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, $J = 7.9$ Hz, 1H), 7.42-7.25 (m, 7H), 7.24-7.13 (m, 5H), 3.65 (s, 3H), 1.61 (q, $J = 8.5$ Hz, 2H), 1.26 (s, 6H), 0.68 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.5, 137.5, 137.3, 132.1, 131.9, 131.2, 129.3, 128.3, 127.9, 127.1, 125.7, 122.0, 120.0, 119.8, 115.0, 109.5, 37.6, 36.9, 30.9, 28.3, 9.2; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{28}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 354.2216, found 354.2213.

3-(4-(*tert*-Butyl)phenyl)-1-methyl-2-phenyl-1H-indole (6ag)

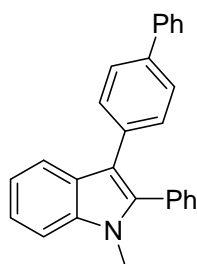


The reaction was conducted with 1-methyl-2-phenyl-1H-indole (**5a**, 62 mg, 0.3 mmol), 4-*tert*-butylcyclohexanone (**2g**, 31 mg, 0.2 mmol). The residue was purified by column

chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.35) to yield the desired product **6ag** as colorless oil liquid (64.4 mg, 95% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, J = 7.9 Hz, 1H), 7.41-7.32 (m, 6H), 7.31-7.21 (m, 5H), 7.20-7.14 (m, 1H), 3.64 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.0, 137.5, 137.3, 132.1, 132.1, 131.2, 129.3, 128.3, 127.9, 127.0, 125.0, 122.0, 120.0, 119.8, 114.9, 109.5, 34.4, 31.4, 30.9; HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{26}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 340.2060, found 340.2057.

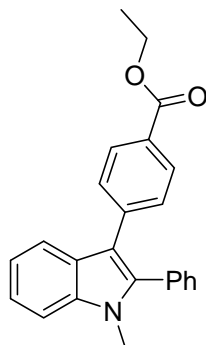
3-([1,1'-Biphenyl]-4-yl)-1-methyl-2-phenyl-1*H*-indole (**6ah**, CAS: 1160172-08-6)^[6]



The reaction was conducted with 1-methyl-2-phenyl-1*H*-indole (**5a**, 62 mg, 0.3 mmol), 4-phenylcyclohexanone (**2h**, 35 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.35) to yield the desired product **6ah** as white solid (61.0 mg, 85% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, J = 7.9 Hz, 1H), 7.61-7.56 (m, 2H), 7.50 (d, J = 8.3 Hz, 2H), 7.43-7.34 (m, 10H), 7.33-7.26 (m, 2H), 7.23-7.18 (m, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.9, 138.0, 137.8, 137.3, 134.3, 131.9, 131.2, 130.1, 128.7, 128.4, 128.1, 126.9, 126.9, 126.8, 126.8, 122.2, 120.2, 119.6, 114.6, 109.6, 31.02.

Ethyl 4-(1-methyl-2-phenyl-1*H*-indol-3-yl)benzoate (**5ai**, CAS: 1160172-07-5)^[6]

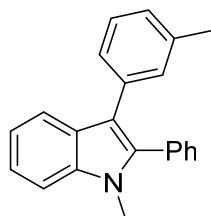


The reaction was conducted with 1-methyl-2-phenyl-1*H*-indole (**5a**, 62 mg, 0.3 mmol), ethyl

4-cyclohexanonecarboxylate (**2i**, 32 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1, R_f = 0.3) to yield the desired product **6ai** as colorless oil liquid (45.4 mg, 64% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 7.9 Hz, 1H), 7.44-7.28 (m, 9H), 7.19-7.15 (m, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.67 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 140.3, 138.5, 137.4, 131.5, 131.0, 129.5, 129.4, 128.6, 128.4, 127.2, 126.5, 122.4, 120.6, 119.3, 114.1, 109.8, 60.7, 30.9, 14.3.

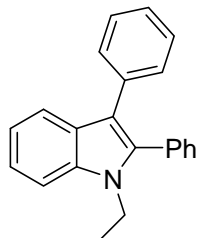
1-Methyl-2-phenyl-3-(*m*-tolyl)-1*H*-indole (**6aj**)^[4]



The reaction was conducted with 1-methyl-2-phenyl-1*H*-indole (**5a**, 62 mg, 0.3 mmol), 3-methylcyclohexanone (**2j**, 26 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.3) to yield the desired product **6aj** as white solid (55.2 mg, 93% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, J = 8.0 Hz, 1H), 7.42-7.26 (m, 7H), 7.22-7.10 (m, 3H), 7.04 (d, J = 7.4 Hz, 1H), 6.98 (d, J = 7.4 Hz, 1H), 3.65 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.7, 137.5, 137.3, 135.0, 131.9, 131.1, 130.5, 128.3, 128.3, 128.0, 127.9, 126.9, 126.2, 122.1, 120.1, 119.7, 115.1, 109.5, 30.9, 21.5.

1-Ethyl-2,3-diphenyl-1*H*-indole (**6ba**, CAS: 55653-99-1)^[3]

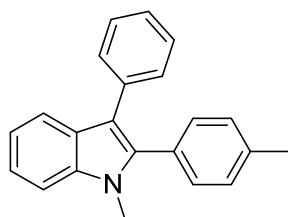


The reaction was conducted with 1-ethyl-2,3-diphenyl-1*H*-indole (**5b**, 66 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.35) to yield the desired product **6ba** as white

solid (52.9 mg, 89% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 8.2 Hz, 1H), 7.40-7.32 (m, 5H), 7.31-7.21 (m, 5H), 7.20-7.11 (m, 2H), 4.12 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.2, 136.0, 135.2, 132.2, 131.0, 129.8, 128.4, 128.1, 128.1, 127.2, 125.4, 122.0, 120.1, 119.7, 115.3, 109.8, 38.6, 15.4.

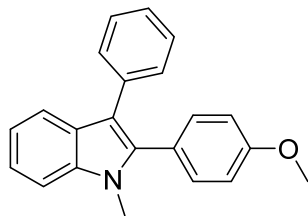
1-methyl-3-phenyl-2-(*p*-tolyl)-1H-indole (**6ca**)^[4]



The reaction was conducted with 1-methyl-2-(*p*-tolyl)-1H-indole (**5c**, 66 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μL , 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.3) to yield the desired product **6ca** as white solid (50.5 mg, 85% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, J = 7.9 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.34-7.24 (m, 5H), 7.22-7.14 (m, 6H), 3.65 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.8, 137.2, 135.3, 131.0, 129.8, 129.1, 128.8, 128.1, 127.0, 125.4, 122.0, 120.1, 119.5, 114.9, 109.5, 30.9, 21.3.

2-(4-Methoxyphenyl)-1-methyl-3-phenyl-1H-indole (**6da**)

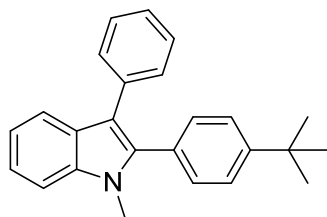


The reaction was conducted with 2-(4-methoxyphenyl)-1-methyl-1H-indole (**5d**, 71 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μL , 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1, R_f = 0.3) to yield the desired product **6da** as white solid (55.1 mg, 88% yield), mp 169-171 $^\circ\text{C}$.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, J = 7.9 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.34-7.22

(m, 7H), 7.21-7.13 (m, 2H), 6.94-6.88 (m, 2H), 3.83 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.4, 137.6, 137.2, 135.4, 132.3, 129.8, 128.1, 126.9, 125.3, 124.0, 122.0, 120.1, 119.4, 114.7, 113.9, 109.5, 55.2, 30.8; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{20}\text{NO}^+$ ($\text{M}+\text{H}$) $^+$ 314.15394, found 314.15375.

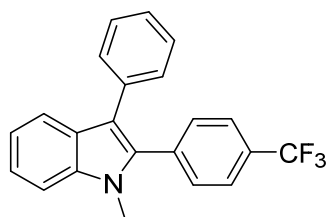
2-(4-(*tert*-Butyl)phenyl)-1-methyl-3-phenyl-1*H*-indole (6ea)



The reaction was conducted with 2-(4-(*tert*-butyl)phenyl)-1-methyl-1*H*-indole (**5e**, 79 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μL , 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.35) to yield the desired product **6ea** as colorless oil liquid (61.7 mg, 91% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, J = 7.9 Hz, 1H), 7.42-7.35 (m, 3H), 7.34-7.21 (m, 8H), 7.20-7.14 (m, 2H), 3.67 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.9, 137.9, 137.2, 135.4, 130.7, 129.9, 128.7, 128.1, 127.0, 125.3, 125.2, 122.0, 120.1, 119.5, 114.8, 109.5, 34.7, 31.3, 31.0; HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{26}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 340.206, found 340.2059.

1-Methyl-3-phenyl-2-(4-(trifluoromethyl)phenyl)-1*H*-indole (6fa, CAS: 1160172-09-7)^[6]

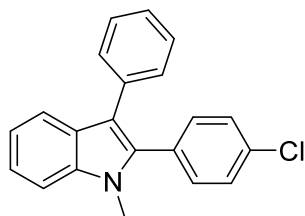


The reaction was conducted with 1-methyl-2-(4-(trifluoromethyl)phenyl)-1*H*-indole (**5f**, 83 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μL , 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.3) to yield the desired product **6fa** as white solid (56.9 mg, 81% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.1 Hz, 2H), 7.46-7.40 (m, 3H), 7.36-7.25 (m, 5H), 7.23-7.17 (m, 2H) 3.68 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*)

δ 137.6, 135.9, 135.7, 134.6, 131.4, 129.9, 129.9 (q, $J = 32$ Hz), 128.4, 126.9, 125.9, 125.3 (q, $J = 3.8$ Hz), 124.1, (q, $J = 271$ Hz), 122.8, 120.5, 119.8, 116.2, 109.7, 31.1.

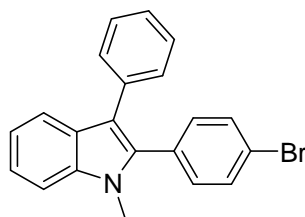
2-(4-Chlorophenyl)-1-methyl-3-phenyl-1H-indole (6ga)



The reaction was conducted with 2-(4-chlorophenyl)-1-methyl-1H-indole (**5g**, 72 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, $R_f = 0.3$) to yield the desired product **6ga** as white solid (53.9 mg, 85% yield), mp 162-164 $^{\circ}$ C.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, $J = 7.9$ Hz, 1H), 7.40 (d, $J = 8.2$ Hz, 1H), 7.38-7.31 (m, 3H), 7.30-7.25 (m, 5H), 7.24-7.16 (m, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.4, 136.3, 134.8, 134.1, 132.4, 130.3, 129.8, 128.7, 128.3, 126.9, 125.7, 122.4, 120.3, 119.7, 115.5, 109.6, 30.9; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{17}\text{ClN}^+$ ($\text{M}+\text{H}$) $^+$ 318.1044, found 318.1048.

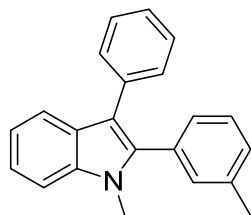
2-(4-Bromophenyl)-1-methyl-3-phenyl-1H-indole (6ha)



The reaction was conducted with 2-(4-bromophenyl)-1-methyl-1H-indole (**5h**, 86 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, $R_f = 0.3$) to yield the desired product **6ha** as white solid (60.6 mg, 84% yield), mp 185-188 $^{\circ}$ C.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, $J = 7.9$ Hz, 1H), 7.48-7.43 (m, 2H), 7.36 (d, $J = 8.2$ Hz, 1H), 7.29-7.22 (m, 5H), 7.20-7.12 (m, 4H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.4, 136.3, 134.8, 132.7, 131.7, 130.8, 129.8, 128.3, 126.9, 125.7, 122.5, 122.4, 120.3, 119.7, 115.5, 109.6, 31.0; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{17}\text{BrN}^+$ ($\text{M}+\text{H}$) $^+$ 362.0539, found 362.0543.

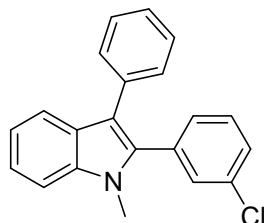
1-Methyl-3-phenyl-2-(*m*-tolyl)-1*H*-indole (**6ia**)



The reaction was conducted with 1-methyl-2-(*m*-tolyl)-1*H*-indole (**5i**, 67 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.3) to yield the desired product **6ia** as colorless oil liquid (53.5 mg, 90% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, J = 7.9 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.34-7.22 (m, 6H), 7.21-7.08 (m, 5H), 3.65 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.9, 137.9, 137.3, 135.3, 131.8, 131.6, 129.8, 128.8, 128.3, 128.2, 128.1, 126.9, 125.4, 122.0, 120.1, 119.6, 114.9, 109.5, 30.9, 21.4; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{20}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 298.1590, found 298.1589.

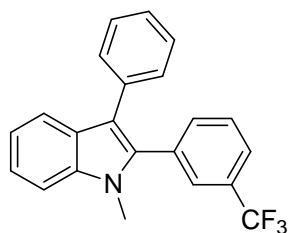
2-(3-Chlorophenyl)-1-methyl-3-phenyl-1*H*-indole (**6ja**)



The reaction was conducted with 2-(3-chlorophenyl)-1-methyl-1*H*-indole (**5j**, 73 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.3) to yield the desired product **6ja** as colorless oil liquid (42.5 mg, 67% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.36-7.25 (m, 8H), 7.24-7.16 (m, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.4, 135.9, 134.7, 134.2, 133.8, 130.8, 129.8, 129.7, 129.5, 128.3, 128.2, 126.8, 125.8, 122.5, 120.3, 119.8, 115.8, 109.6, 31.0; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{17}\text{ClN}^+$ ($\text{M}+\text{H}$) $^+$ 318.10440, found 318.10416.

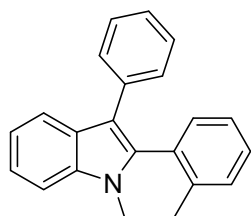
1-Methyl-3-phenyl-2-(3-(trifluoromethyl)phenyl)-1*H*-indole (**6ka**)



The reaction was conducted with 1-methyl-2-(3-(trifluoromethyl)phenyl)-1*H*-indole (**5k**, 83 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.3) to yield the desired product **6ka** as colorless oil liquid (54.1 mg, 77% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, J = 8.0 Hz, 1H), 7.58 (s, 2H), 7.49-7.39 (m, 3H), 7.36-7.24 (m, 5H), 7.22-7.16 (m, 2H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.5, 135.8, 134.5, 134.5, 132.7, 130.80 (q, J = 32.4 Hz), 129.9, 128.9, 128.3, 127.7 (q, J = 3.8 Hz), 126.9, 125.9, 124.67 (q, J = 3.8 Hz), 123.9 (q, J = 270.8 Hz), 122.7, 120.4, 119.8, 116.1, 109.7, 31.04; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{17}\text{F}_3\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 352.1308, found 352.1304.

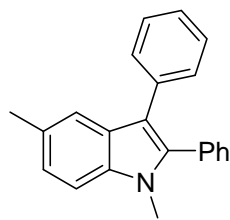
1-Methyl-3-phenyl-2-(*o*-tolyl)-1*H*-indole (**6la**)^[4]



The reaction was conducted with 1-methyl-2-(*o*-tolyl)-1*H*-indole (**5l**, 67 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.3) to yield the desired product **6la** as colorless oil liquid (41.0 mg, 69% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, J = 7.9 Hz, 1H), 7.41 (d, J = 8.2 Hz, 1H), 7.36-7.18 (m, 10H), 7.16-7.10 (m, 1H), 3.52 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.6, 137.1, 137.0, 135.4, 131.7, 131.6, 130.1, 128.9, 128.7, 128.1, 126.7, 125.7, 125.3, 121.8, 120.0, 119.6, 114.9, 109.4, 30.3, 19.8.

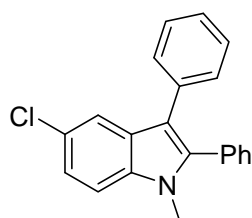
1,5-Dimethyl-2,3-diphenyl-1*H*-indole (**6ma**, CAS: 36362-82-0)^[3]



The reaction was conducted with 1,5-dimethyl-2-phenyl-1*H*-indole (**5m**, 67 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.3) to yield the desired product **6ma** as colourless liquid (50.1 mg, 85% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.57 (s, 1H), 7.39-7.33 (m, 3H), 7.32-7.19 (m, 7H), 7.18-7.10 (m, 2H), 3.63 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.8, 135.8, 135.4, 132.0, 131.1, 129.9, 129.5, 128.3, 128.1, 127.9, 127.1, 125.4, 123.7, 119.1, 114.6, 109.2, 30.9, 21.5.

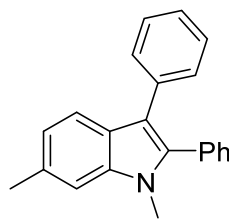
5-Chloro-1-methyl-2,3-diphenyl-1*H*-indole (**6na**)^[3]



The reaction was conducted with 5-chloro-1-methyl-2-phenyl-1*H*-indole (**5n**, 73 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.3) to yield the desired product **6na** as white solid (46.9 mg, 74% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 7.40-7.35 (m, 3H), 7.33-7.29 (m, 3H), 7.28-7.21 (m, 5H), 7.20-7.15 (m, 1H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.9, 135.7, 134.5, 131.3, 131.0, 129.7, 128.4, 128.3, 128.3, 128.0, 125.9, 125.8, 122.3, 118.9, 114.8, 110.6, 31.11.

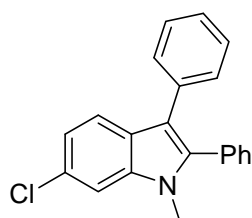
1,6-Dimethyl-2,3-diphenyl-1*H*-indole (**6oa**, CAS: 1610871-11-8)^[3]



The reaction was conducted with 1,6-dimethyl-2-phenyl-1*H*-indole (**5o**, 67 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.3) to yield the desired product **6oa** as white solid (39.2 mg, 66% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, J = 8.1 Hz, 1H), 7.40-7.34 (m, 3H), 7.33-7.22 (m, 6H), 7.20 (s, 1H), 7.18-7.13 (m, 1H), 7.05-7.00 (m, 1H), 3.64 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.7, 137.1, 135.4, 132.1, 132.0, 131.1, 129.8, 128.3, 128.1, 127.9, 125.4, 124.8, 121.9, 119.3, 114.9, 109.5, 30.8, 21.9.

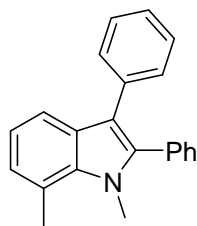
6-Chloro-1-methyl-2,3-diphenyl-1*H*-indole (**6pa**)^[7]



The reaction was conducted with 6-chloro-1-methyl-2-phenyl-1*H*-indole (**5p**, 73 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.3) to yield the desired product **6pa** as white solid (50.1 mg, 79% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, J = 8.5 Hz, 1H), 7.42-7.35 (m, 4H), 7.33-7.29 (m, 2H), 7.28-7.23 (m, 4H), 7.21-7.16 (m, 1H), 7.14 (d, J = 8.5 Hz, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.2, 137.7, 134.6, 131.4, 131.0, 129.7, 128.4, 128.31, 128.2, 127.9, 125.8, 125.5, 120.7, 120.5, 115.2, 109.6, 31.0.

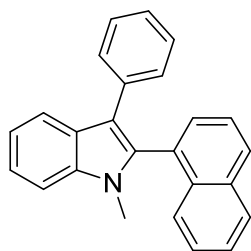
1,7-Dimethyl-2,3-diphenyl-1*H*-indole (**6qa**, CAS: 1610871-13-0)^[3]



The reaction was conducted with 1,7-dimethyl-2-phenyl-1*H*-indole (**5q**, 67 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.35) to yield the desired product **6qa** as white solid (39.2 mg, 66% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, J = 7.4 Hz, 1H), 7.40-7.28 (m, 5H), 7.25 (d, J = 4.3 Hz, 4H), 7.20-7.13 (m, 1H), 7.07-6.98 (m, 2H), 3.89 (s, 3H), 2.85 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.9, 136.5, 135.3, 132.1, 131.3, 130.0, 128.3, 128.1, 128.0, 127.9, 125.5, 125.2, 121.4, 120.3, 117.7, 115.6, 34.3, 20.4.

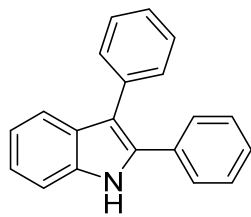
1-Methyl-2-(naphthalen-1-yl)-3-phenyl-1*H*-indole (**6ra**)



The reaction was conducted with 1-methyl-2-(naphthalen-1-yl)-1*H*-indole (**5r**, 86 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 400:1, R_f = 0.3) to yield the desired product **6ra** as white solid (40.0 mg, 60% yield), mp 213-215 $^{\circ}\text{C}$.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, J = 8.0 Hz, 3H), 7.60 (d, J = 8.4 Hz, 1H), 7.52-7.45 (m, 2H), 7.44-7.32 (m, 4H), 7.27-7.22 (m, 3H), 7.09 (t, J = 7.4 Hz, 2H), 7.09-7.03 (m, 1H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.2, 136.0, 135.2, 133.4, 133.4, 130.0, 129.7, 129.1, 129.0, 128.4, 128.1, 127.3, 126.9, 126.8, 126.1, 125.9, 125.4, 122.1, 120.1, 119.8, 116.3, 109.5, 30.6; HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{20}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 334.1590, found 334.1589.

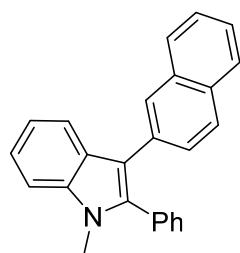
2,3-diphenyl-1*H*-indole (**6sa**, CAS: 3469-20-3)^[14]



The reaction was conducted with 2-phenyl-1*H*-indole (**5s**, 60 mg, 0.3 mmol), cyclohexanone (**2a**, 21 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15:1, R_f = 0.25) to yield the desired product **6sa** as yellow solid (35.0 mg, 65% yield)

^1H NMR (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.67 (d, J = 7.7 Hz, 1H), 7.45-7.34 (m, 7H), 7.31-7.21 (m, 5H), 7.14 (dt, J = 7.9, 4.1 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.9, 135.0, 134.1, 132.7, 130.1, 128.7, 128.5, 128.2, 128.1, 127.7, 126.2, 122.7, 120.4, 119.7, 115.0, 110.9.

1-Methyl-3-(naphthalen-1-yl)-2-phenyl-1*H*-indole (**6ak**)



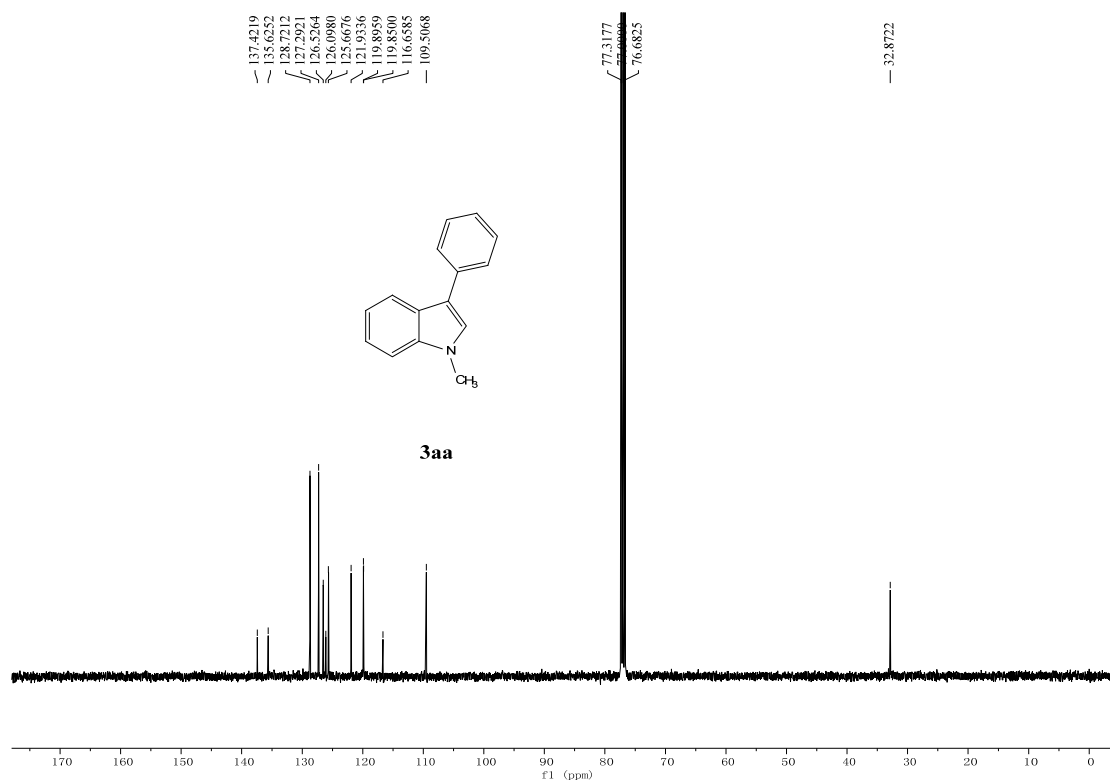
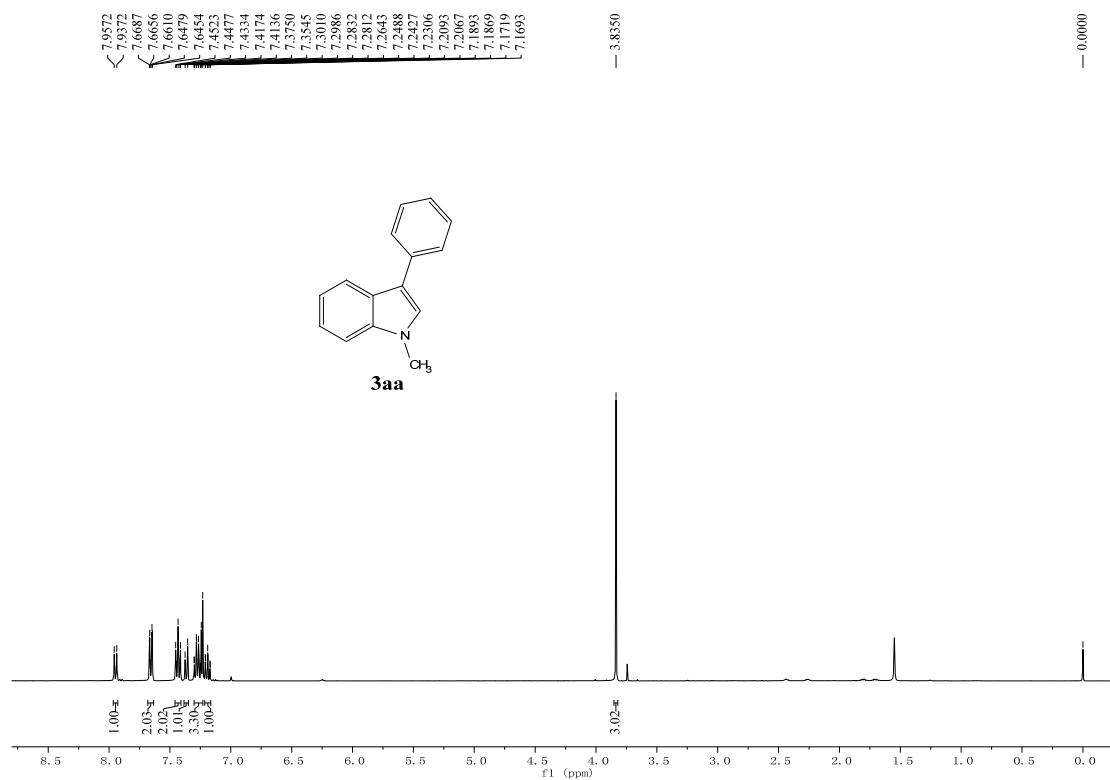
The reaction was conducted with 1-methyl-2-phenyl-1*H*-indole (**5a**, 62 mg, 0.3 mmol), 2-tetralone (**2k**, 27 μ L, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1, R_f = 0.3) to yield the desired product **6ak** as pale green solid (55.3 mg, 83% yield), mp 157-159 $^{\circ}\text{C}$.

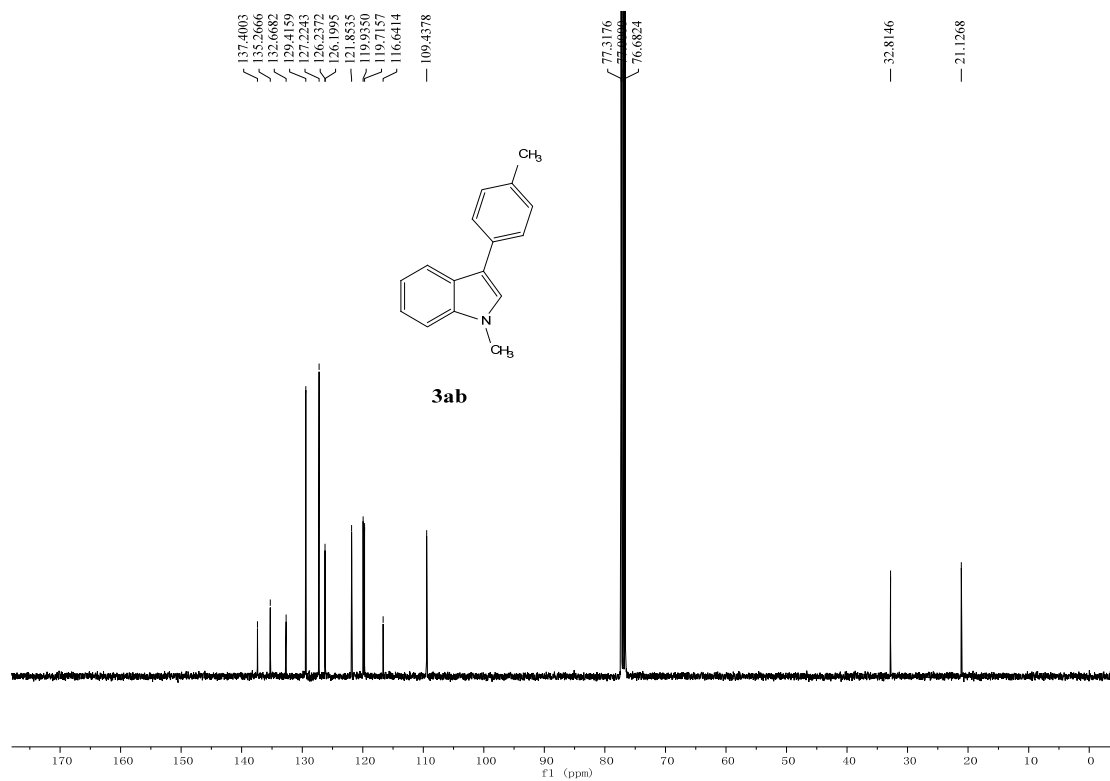
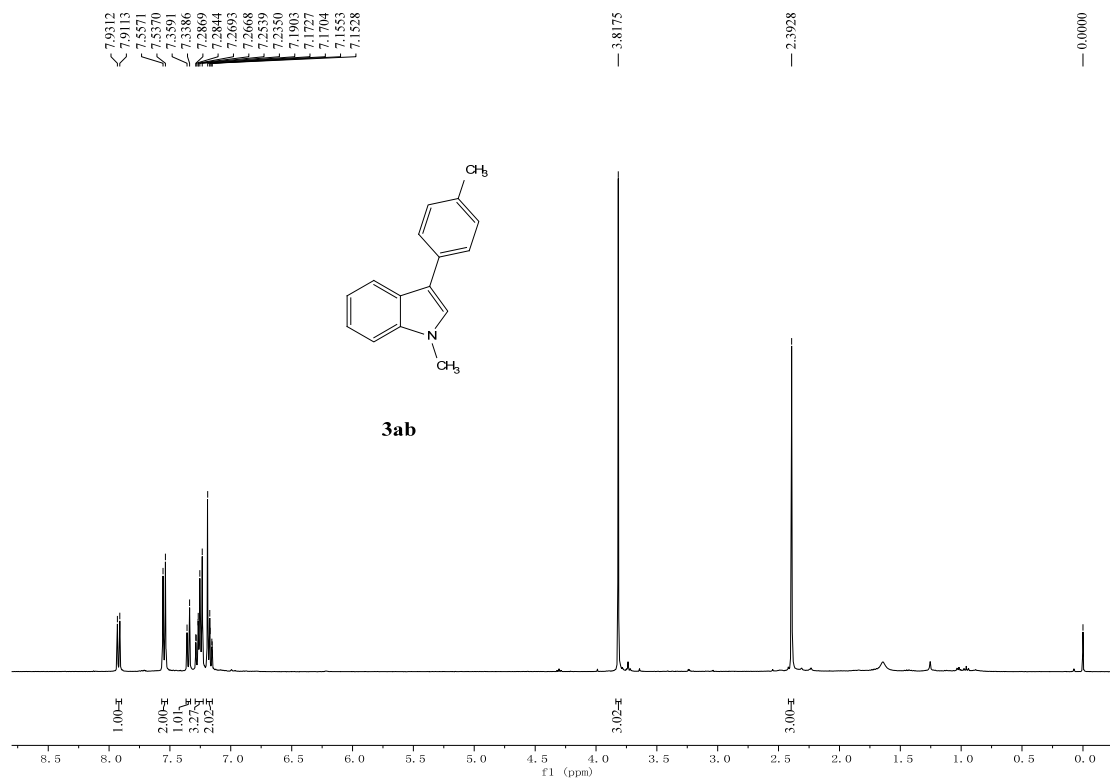
^1H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, J = 8.4 Hz, 2H), 7.77-7.69 (m, 2H), 7.65 (d, J = 8.5 Hz, 1H), 7.44-7.28 (m, 10H), 7.21 (t, J = 7.4 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.0, 137.4, 133.7, 132.9, 131.8, 131.6, 131.1, 128.6, 128.4, 128.1, 128.0, 127.7, 127.5, 127.5, 127.1, 125.7, 125.2, 122.3, 120.3, 119.6, 114.9, 109.6, 30.9; HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{20}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 334.1590, found 334.1589.

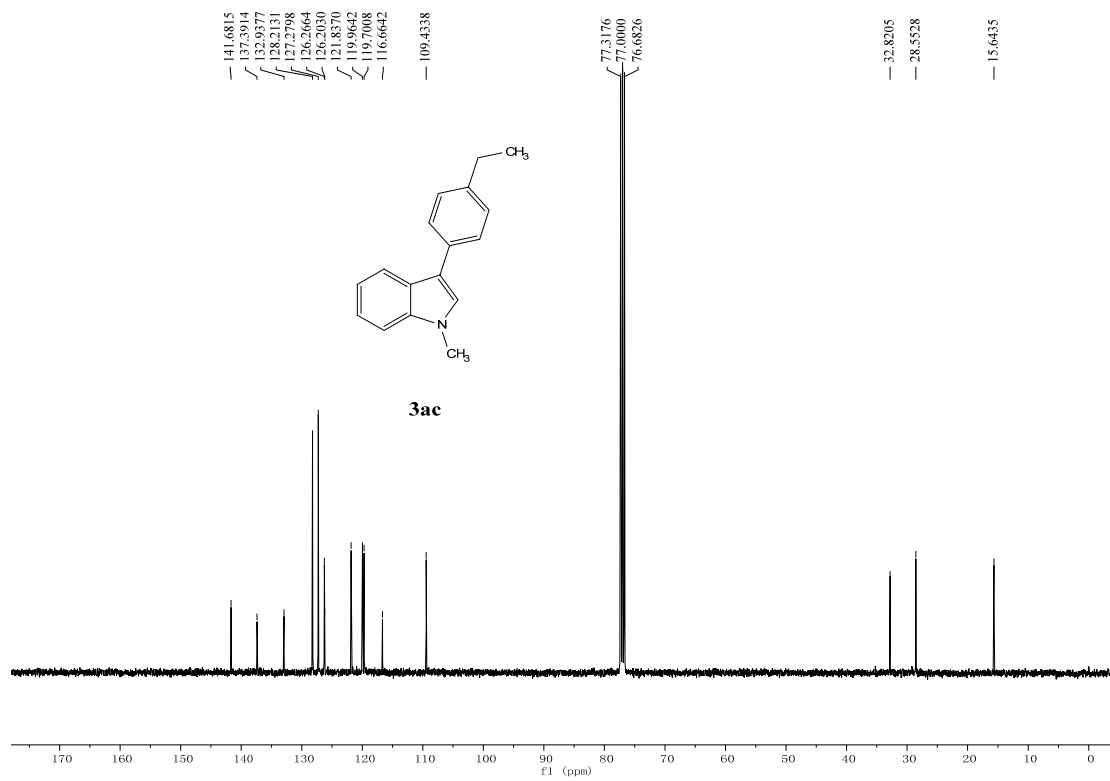
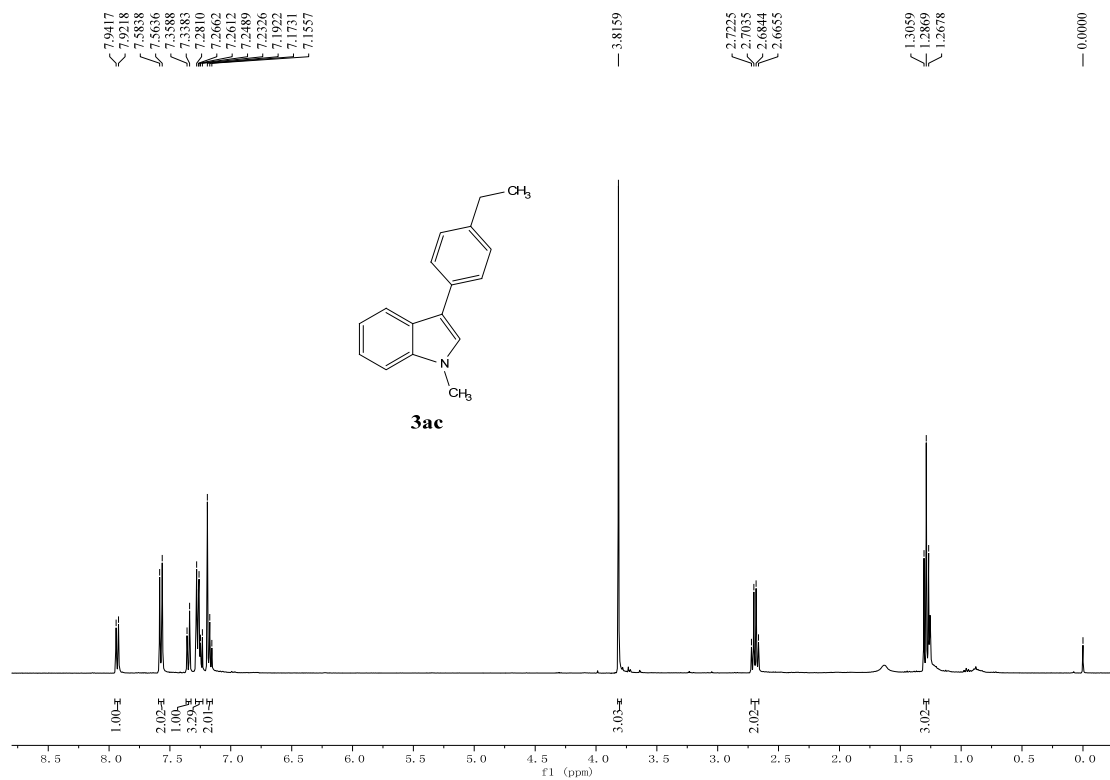
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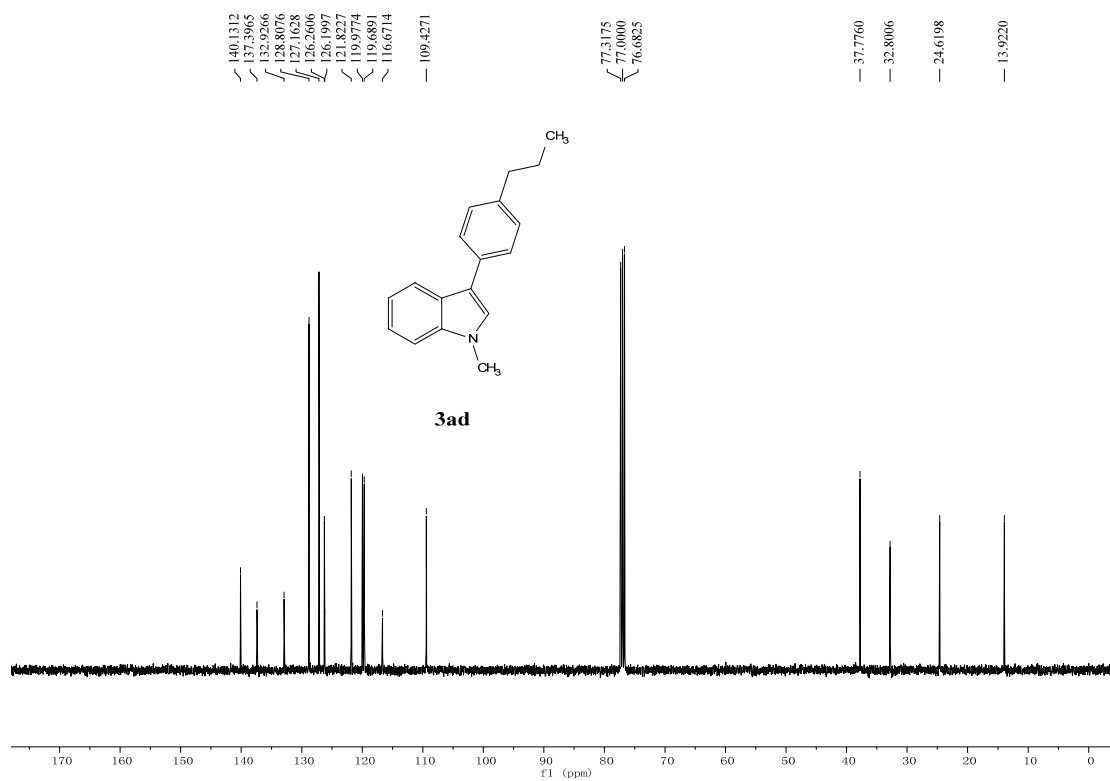
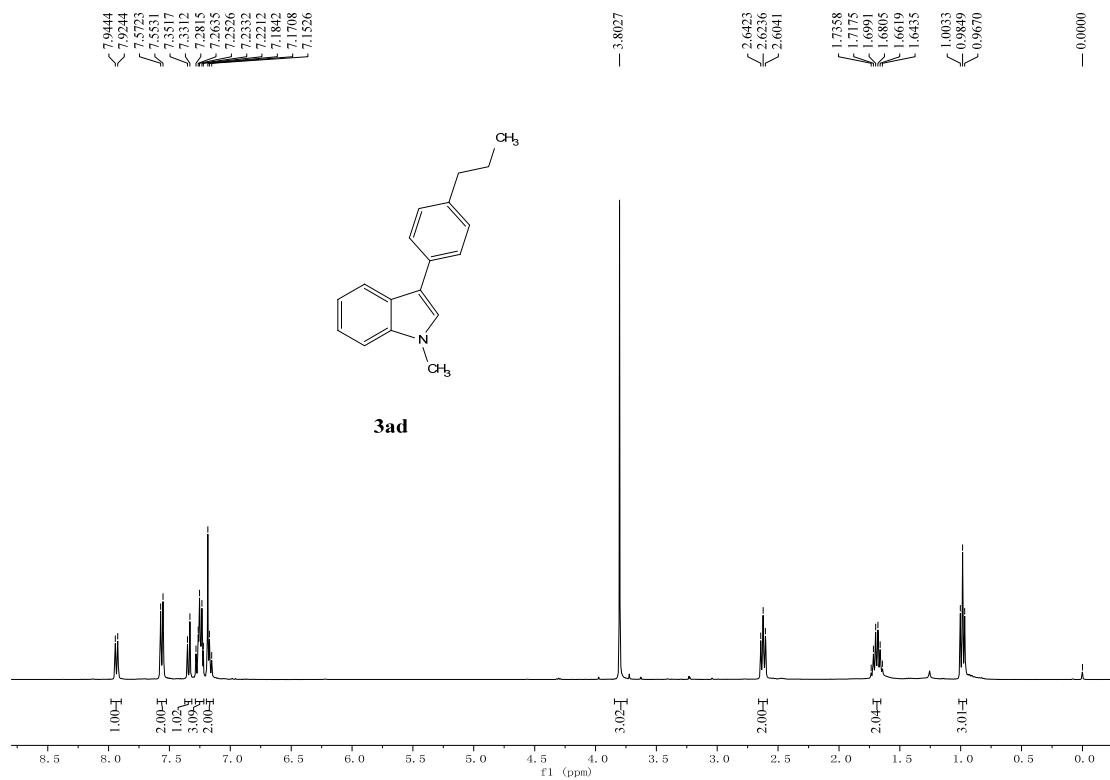
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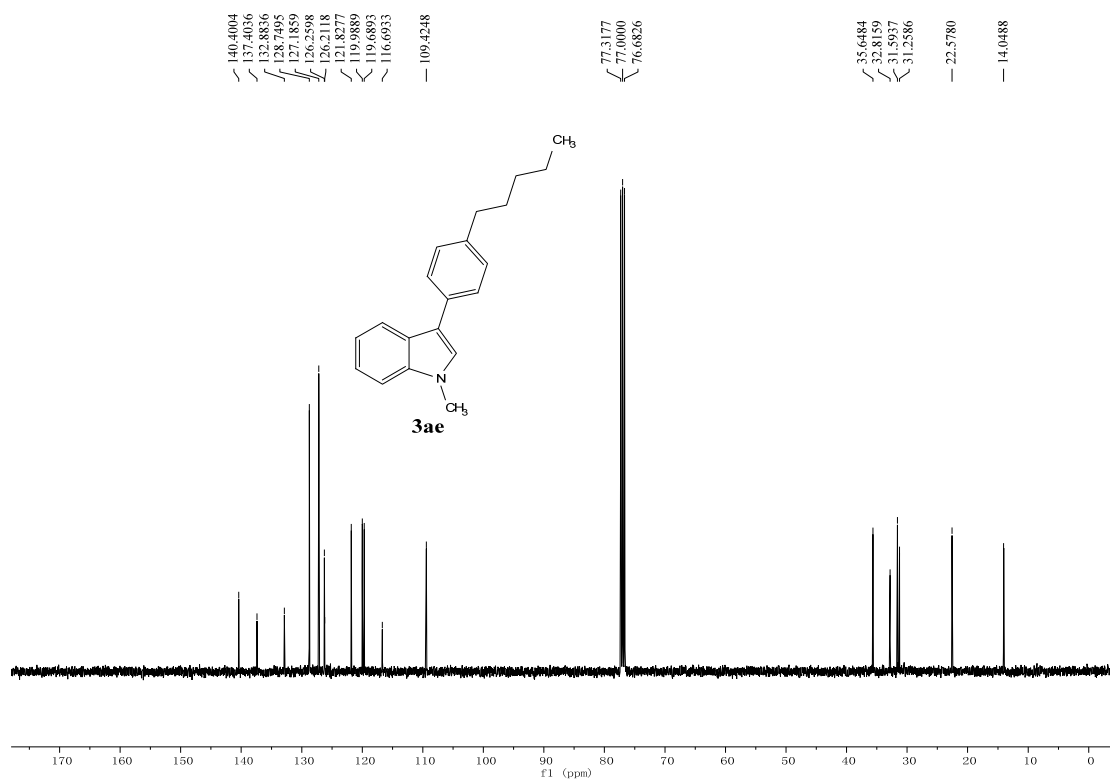
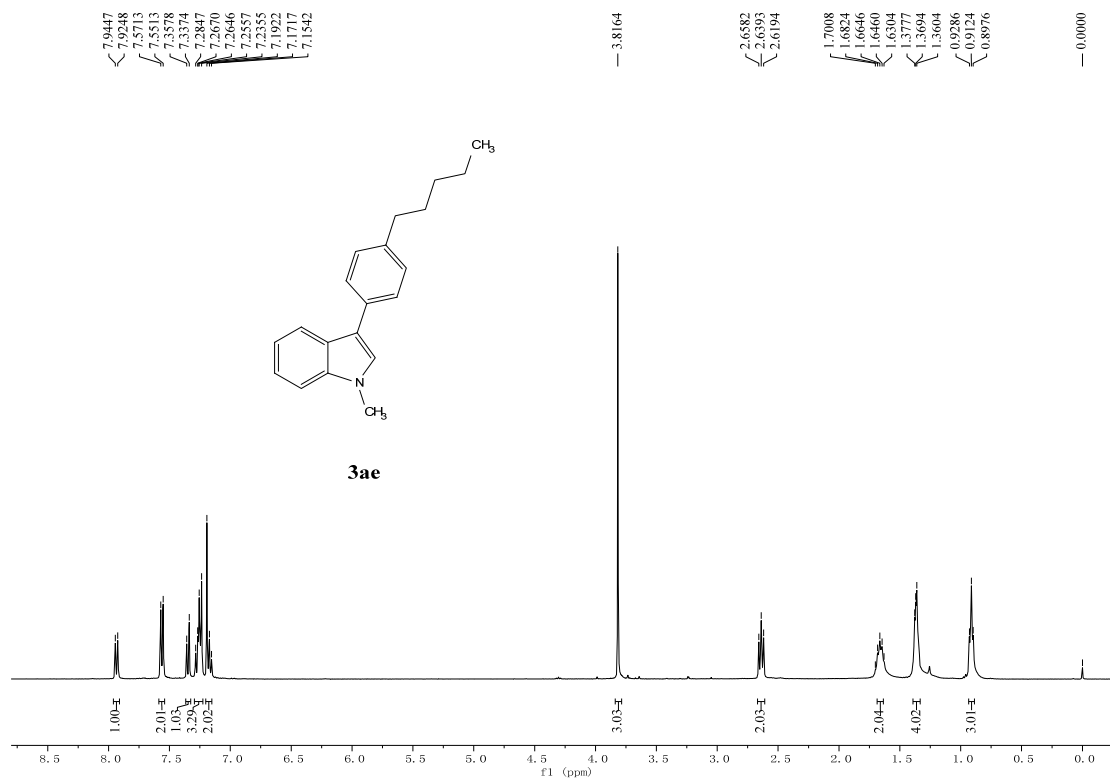
¹H NMR and ¹³C NMR spectra of products

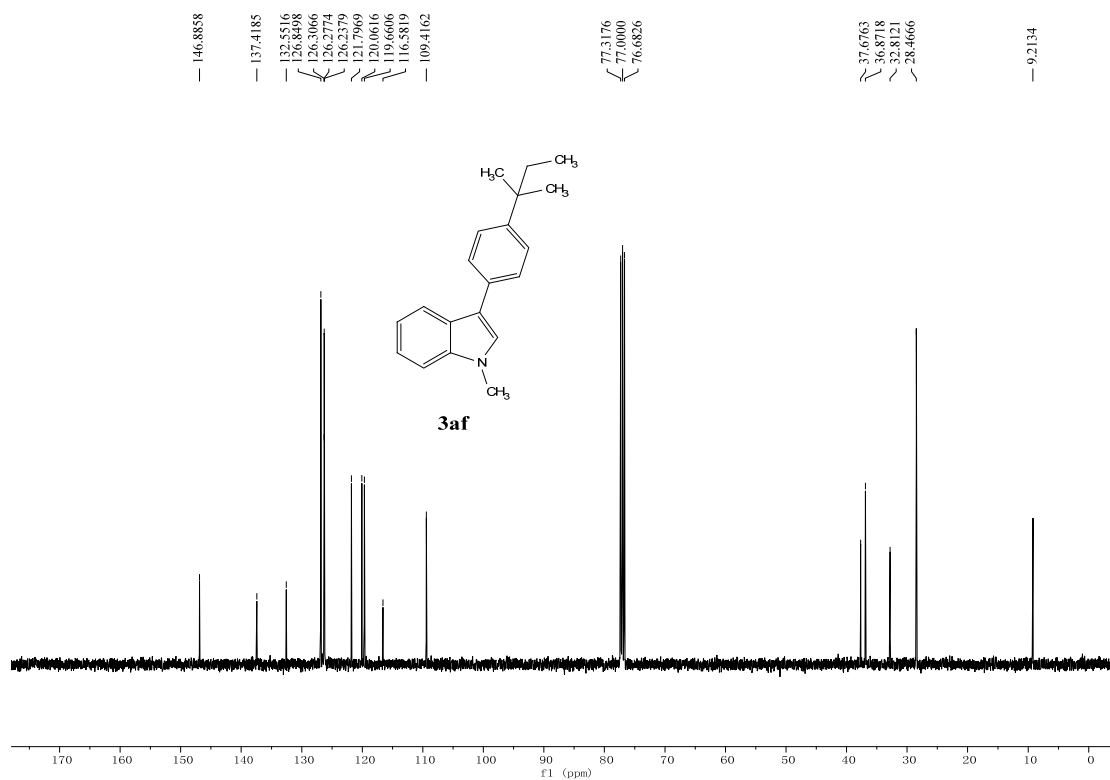
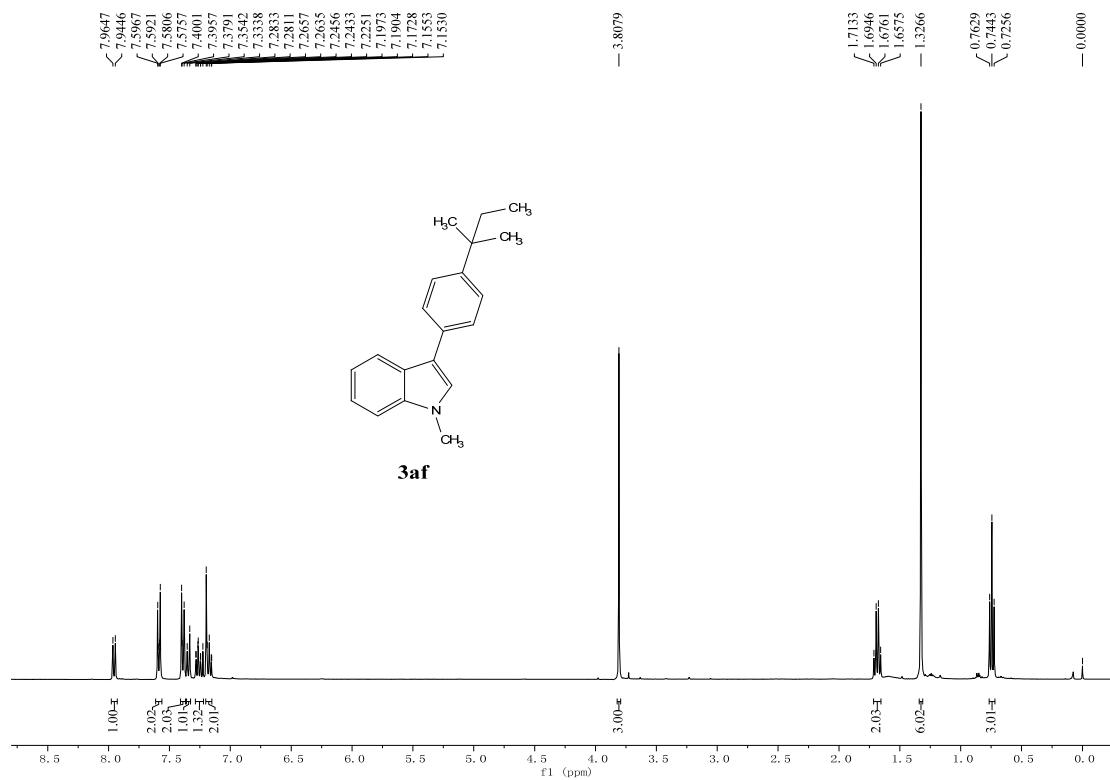


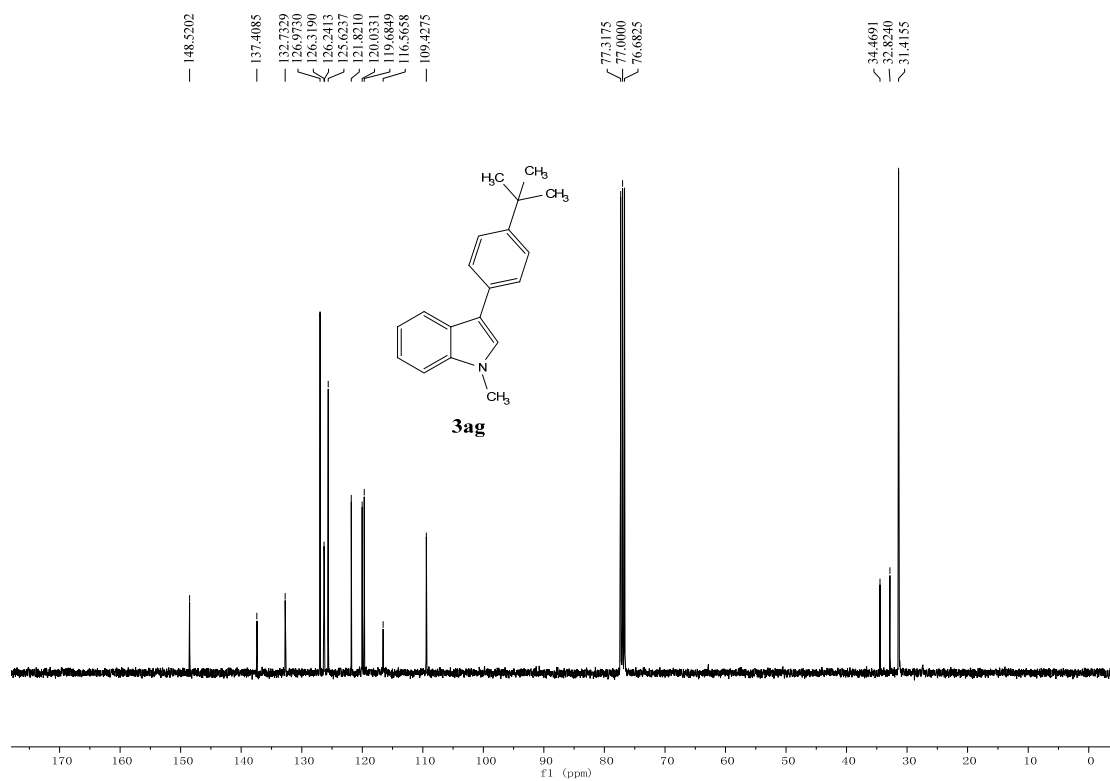
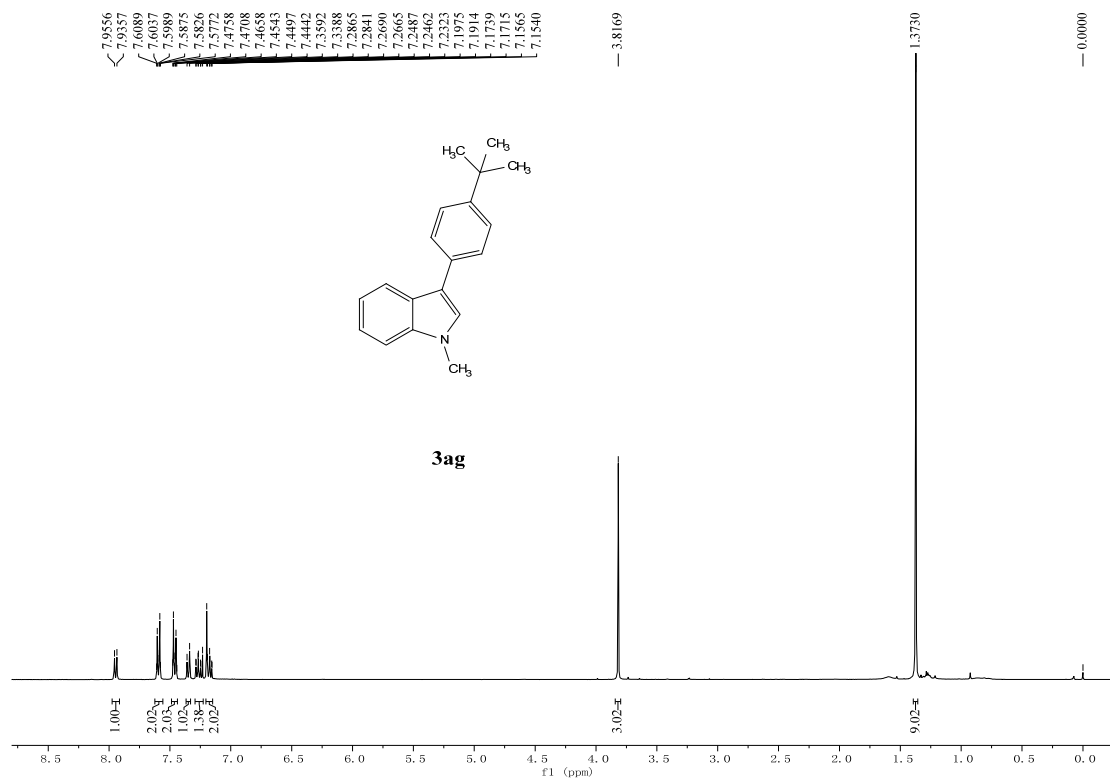


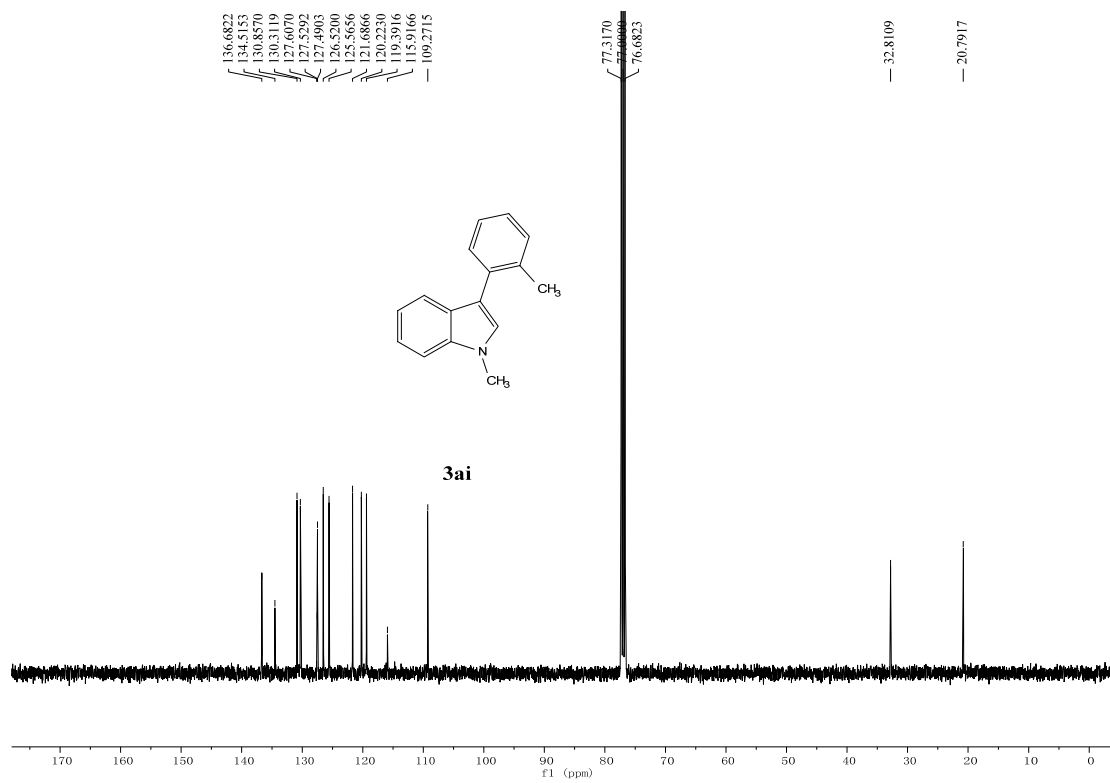
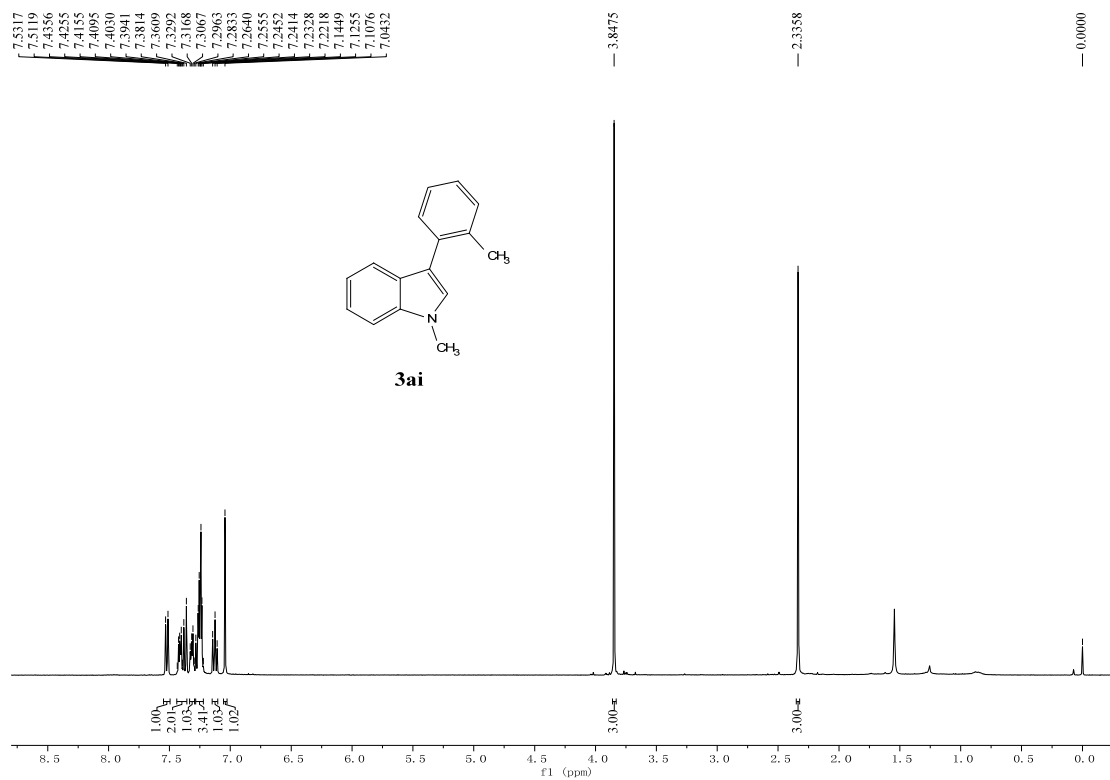


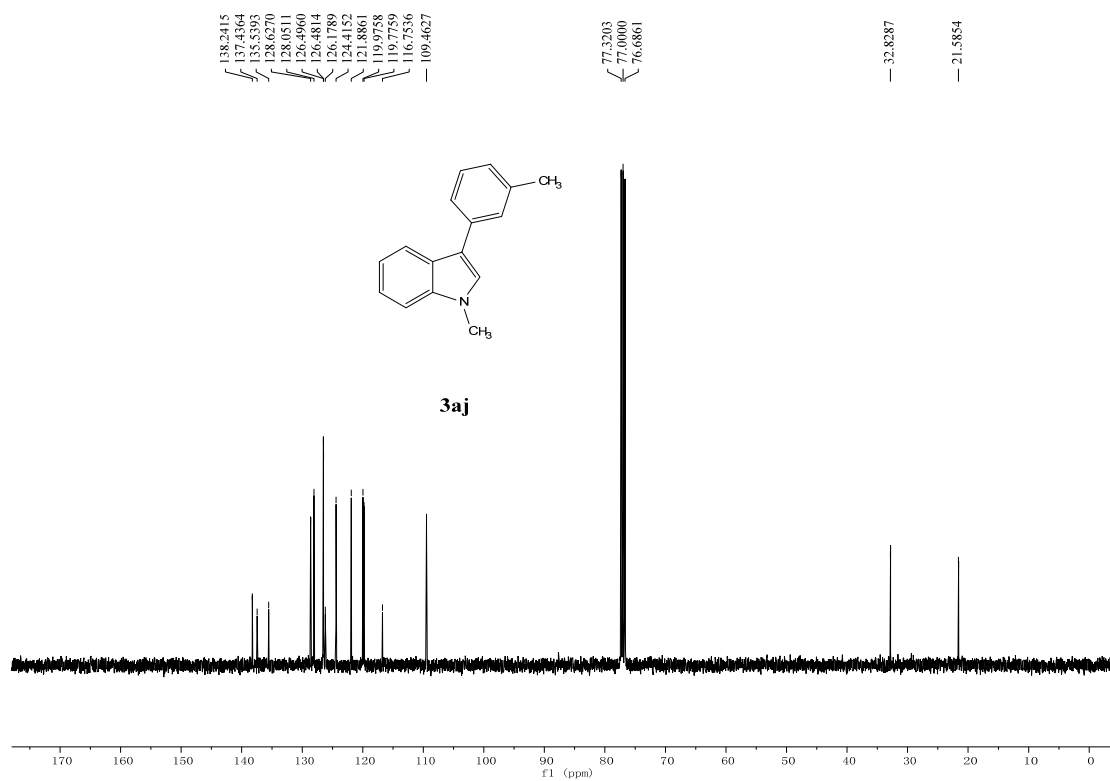
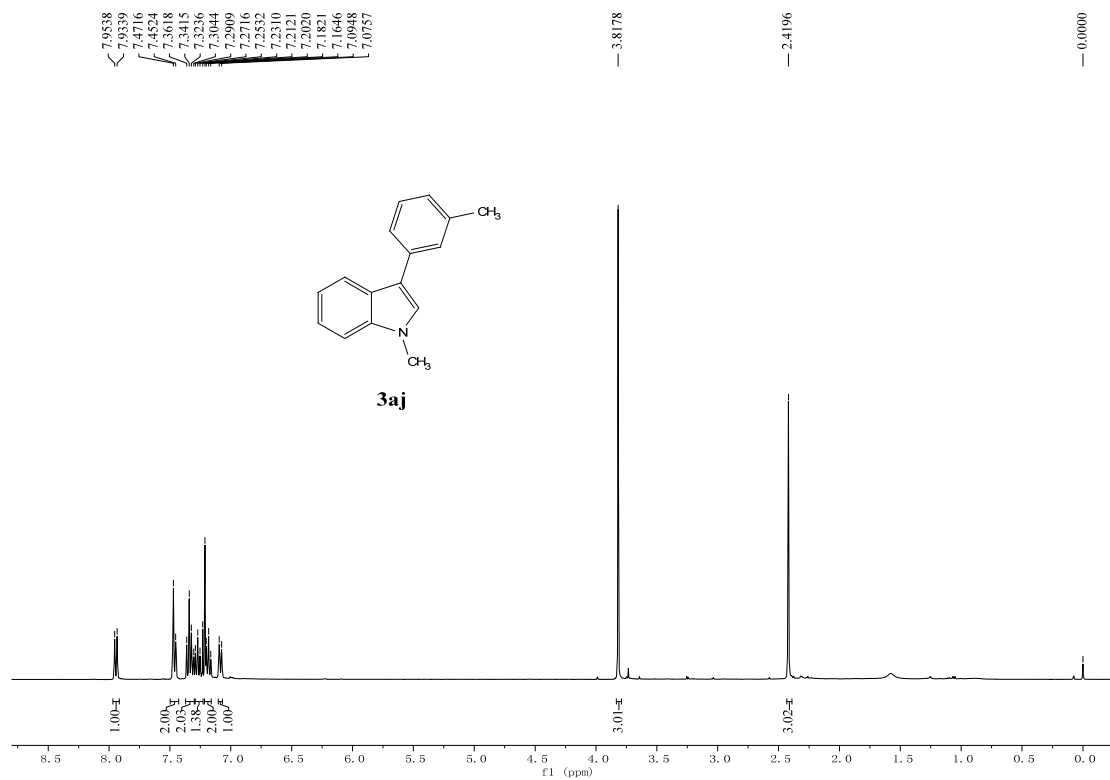


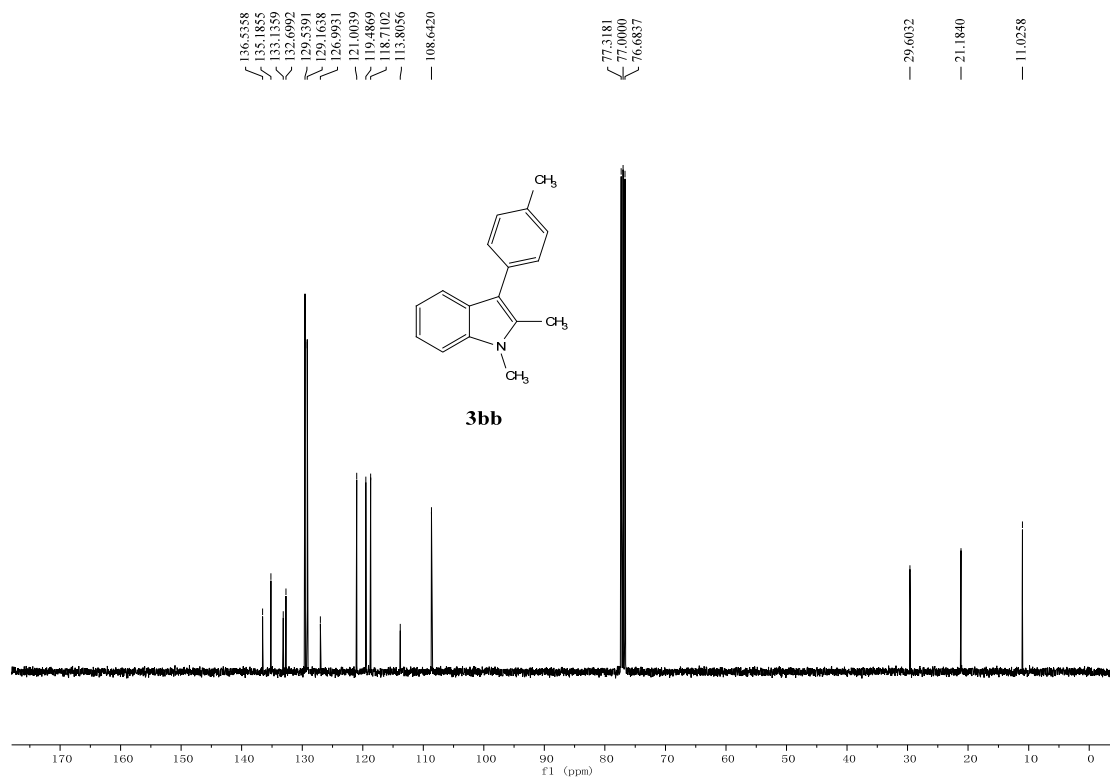
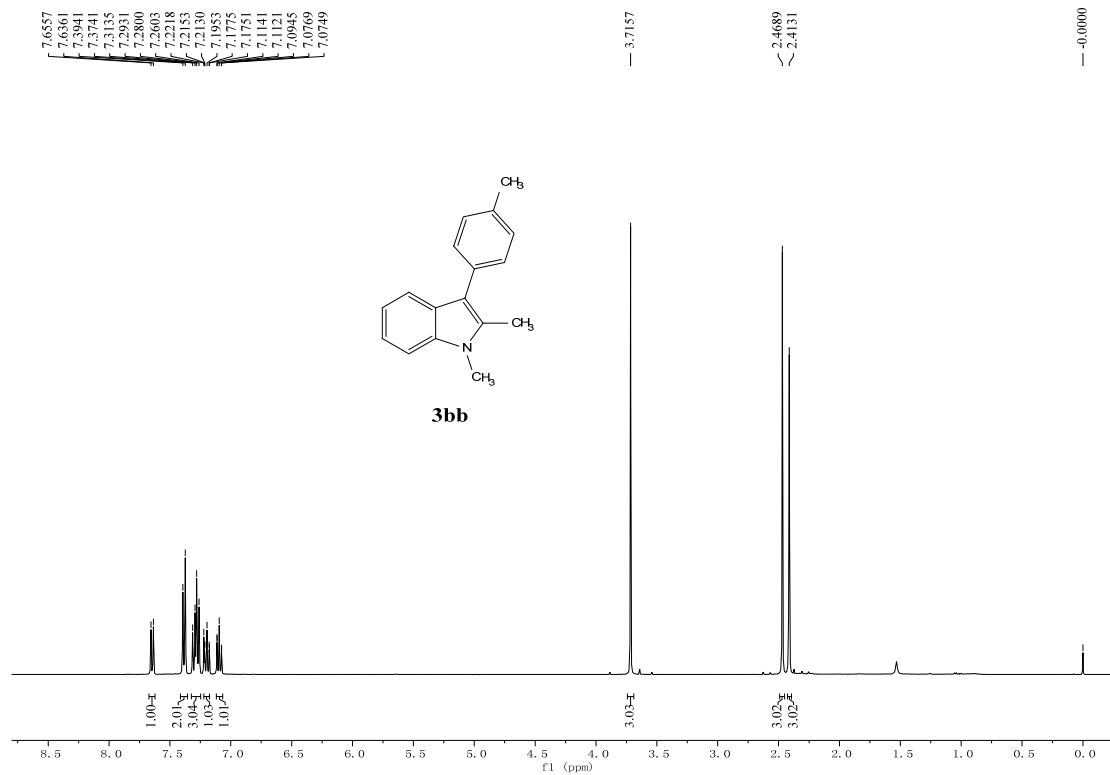


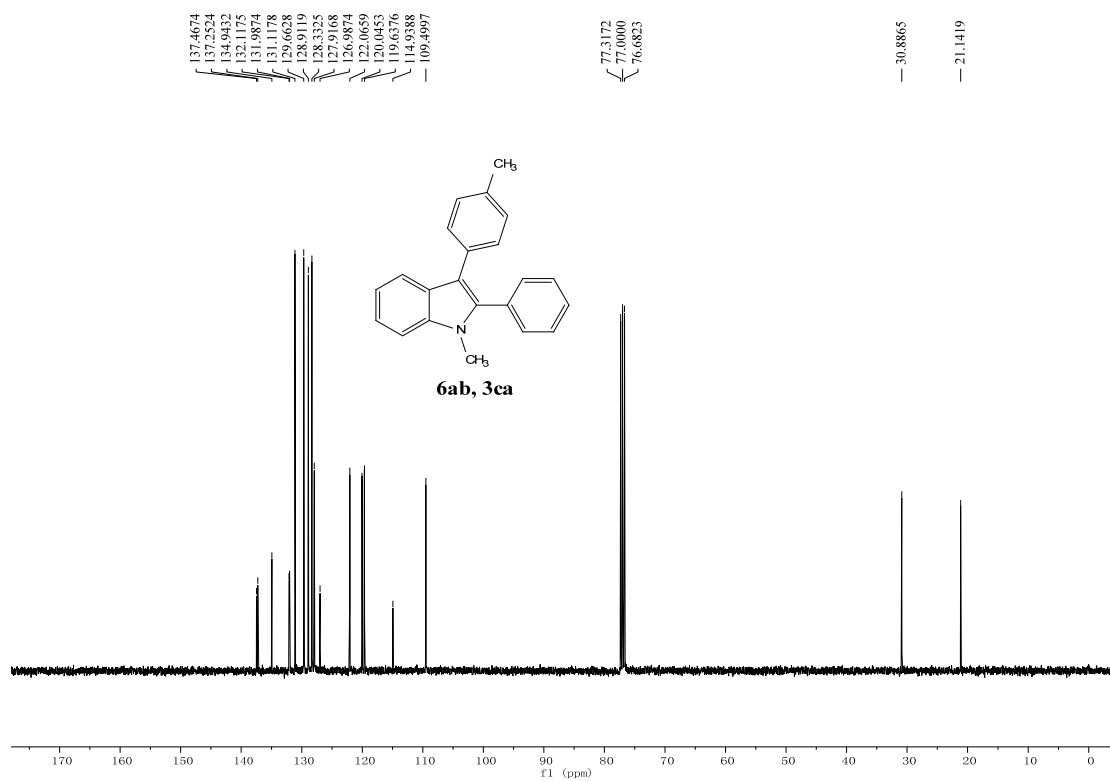
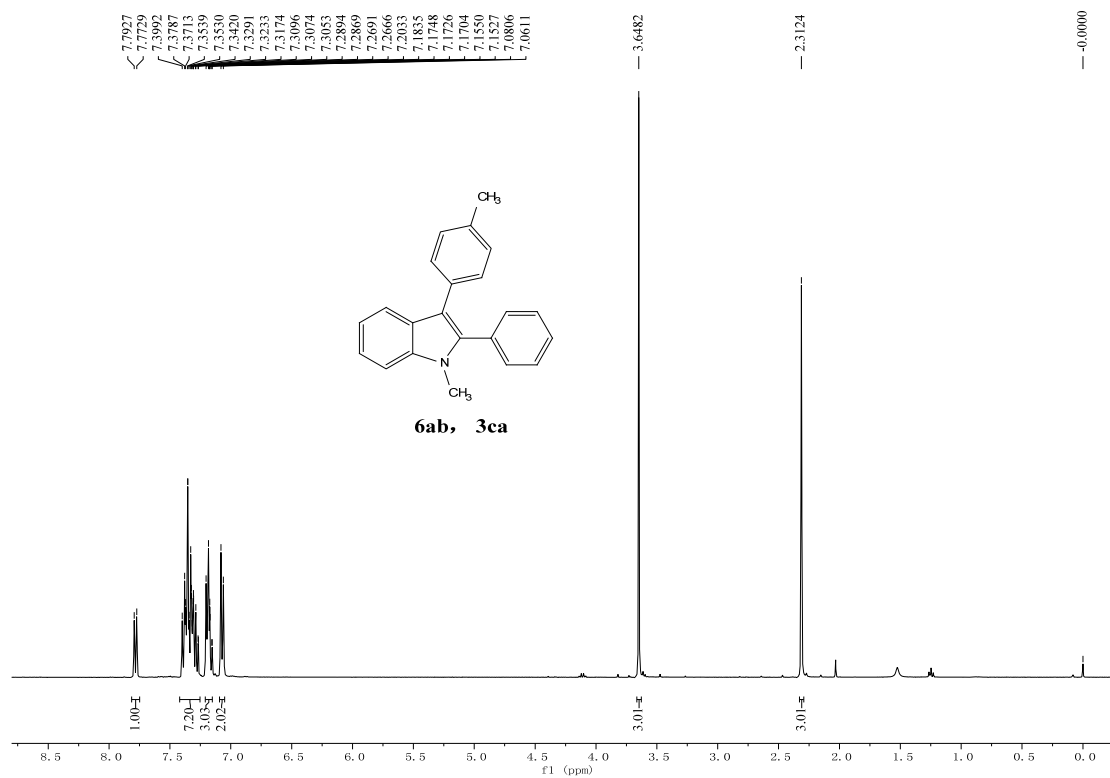


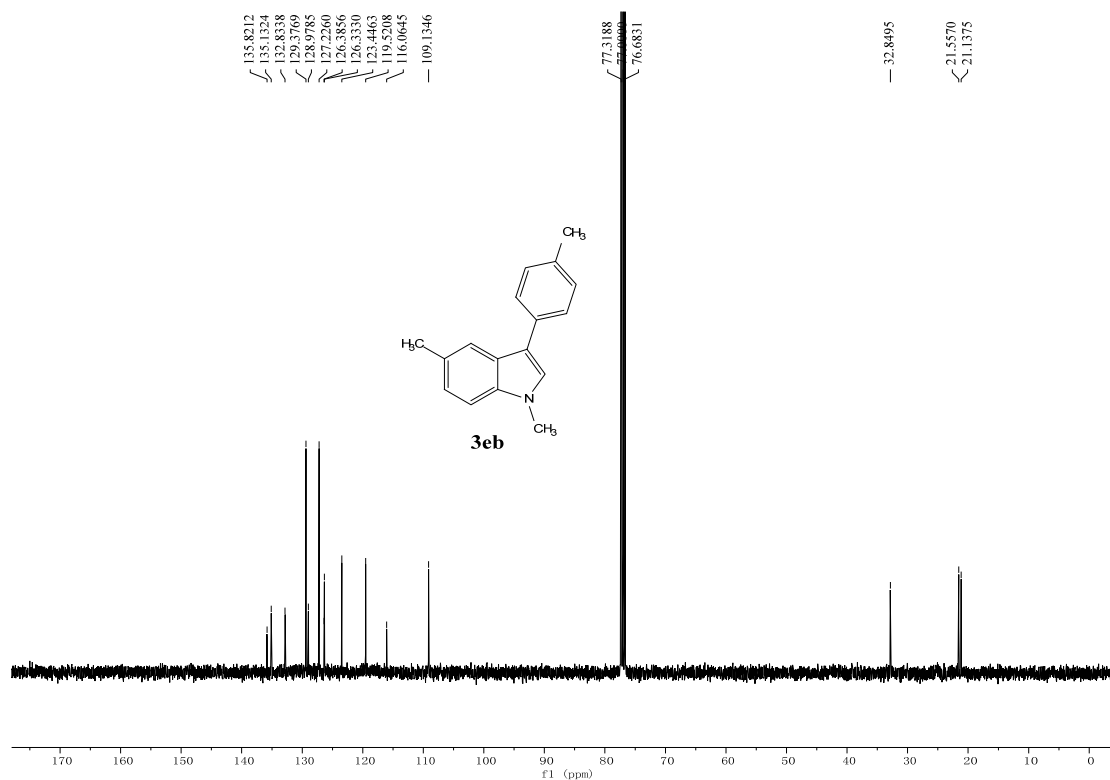
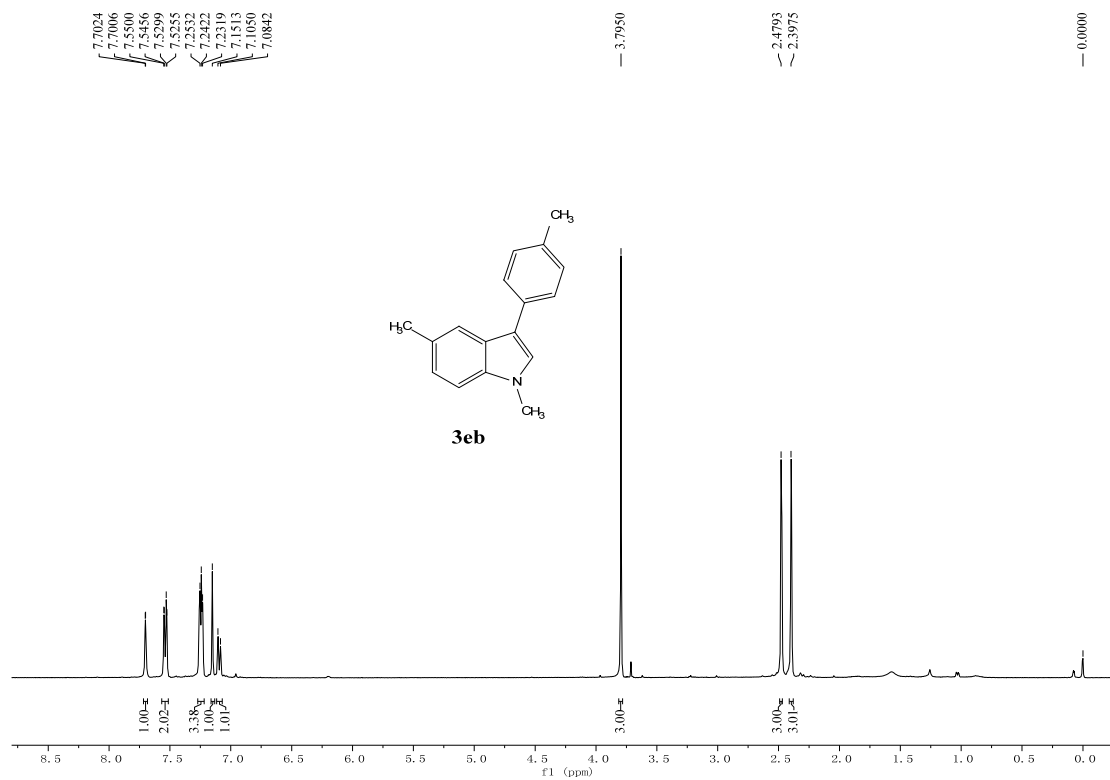


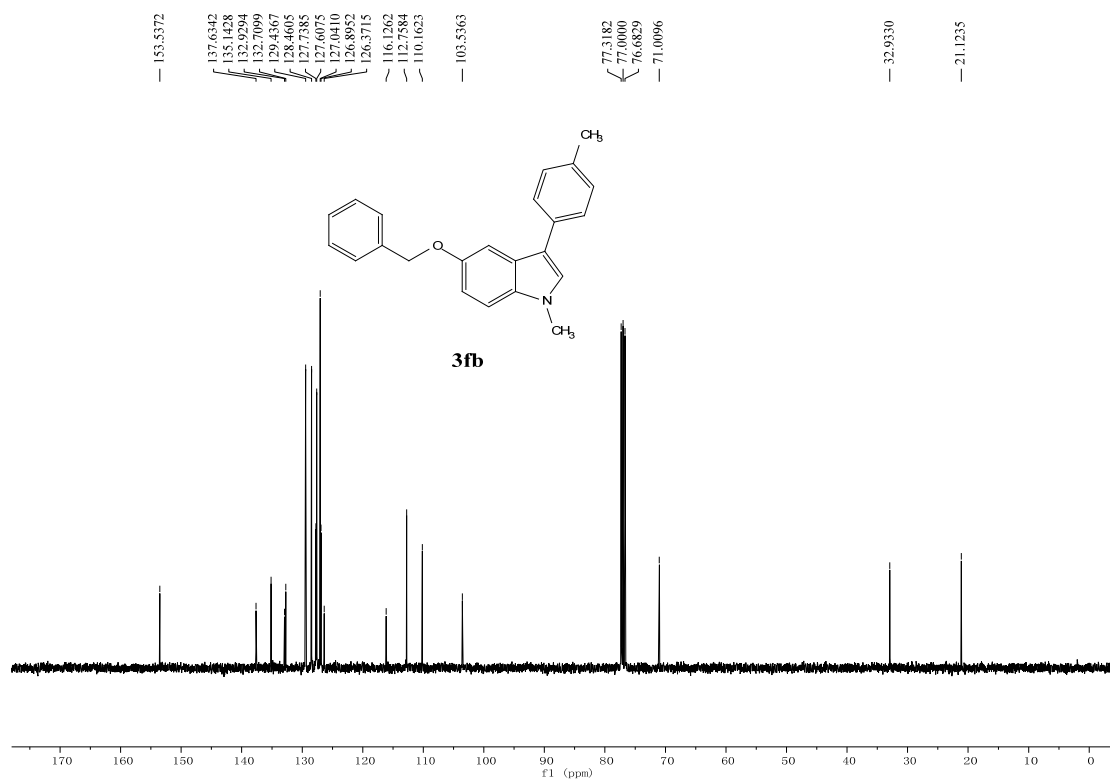
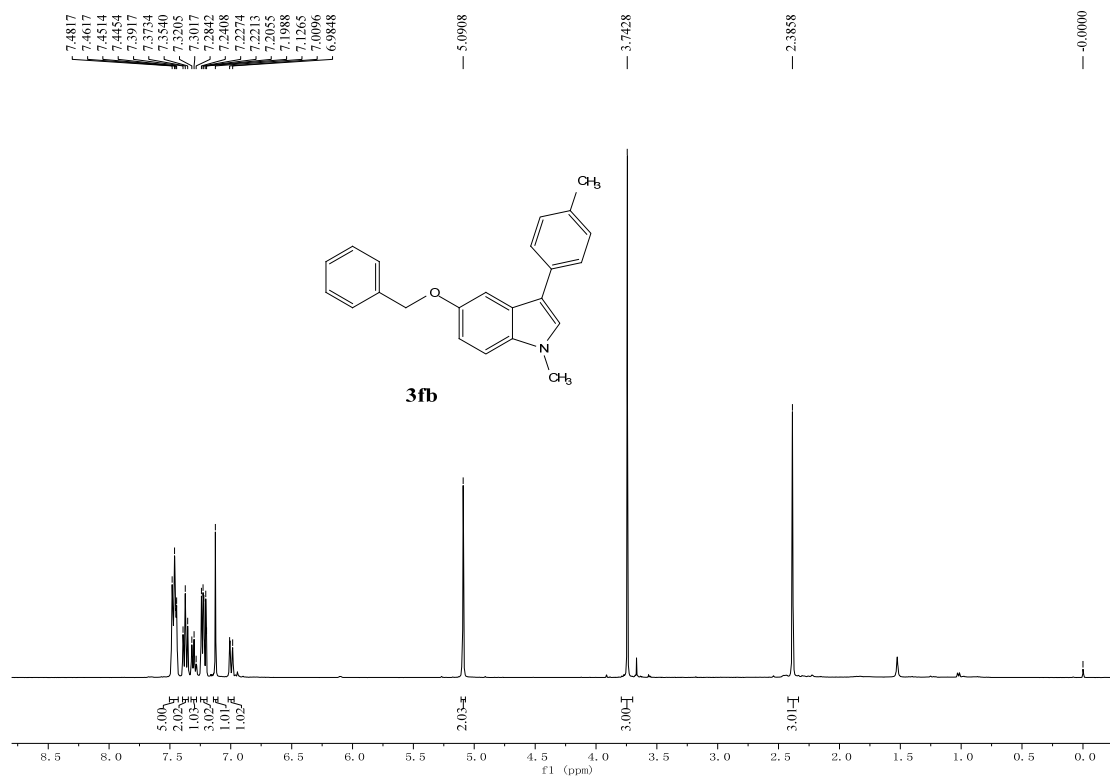


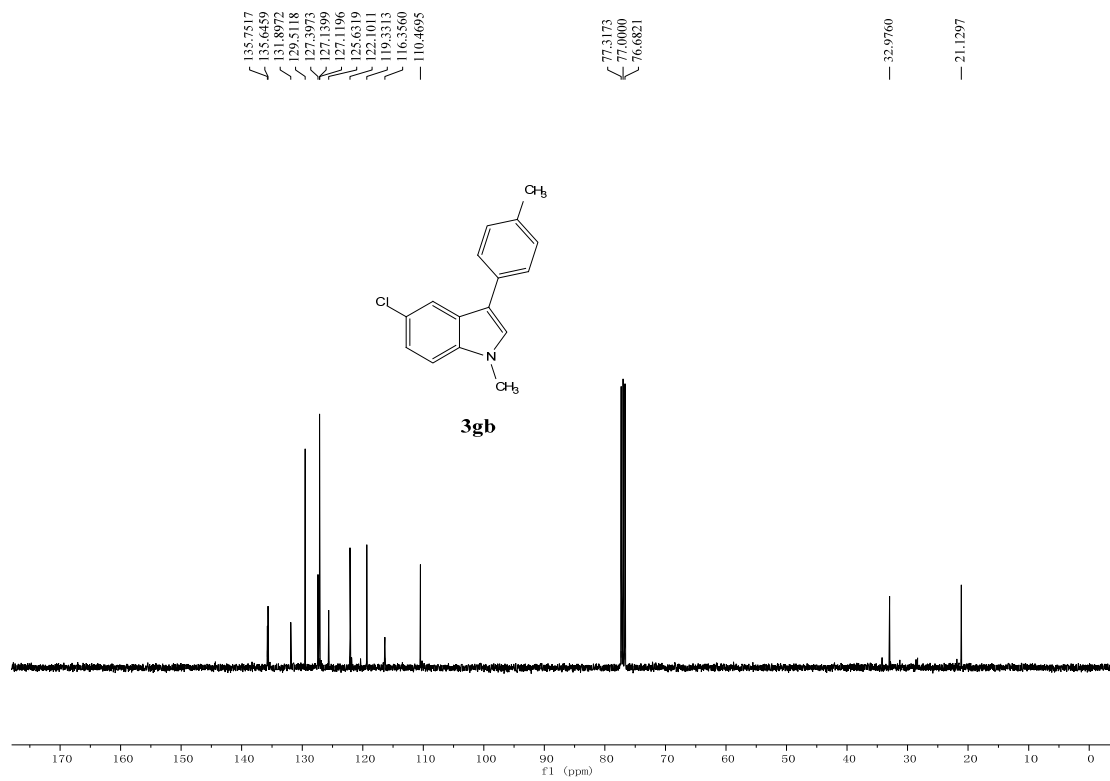
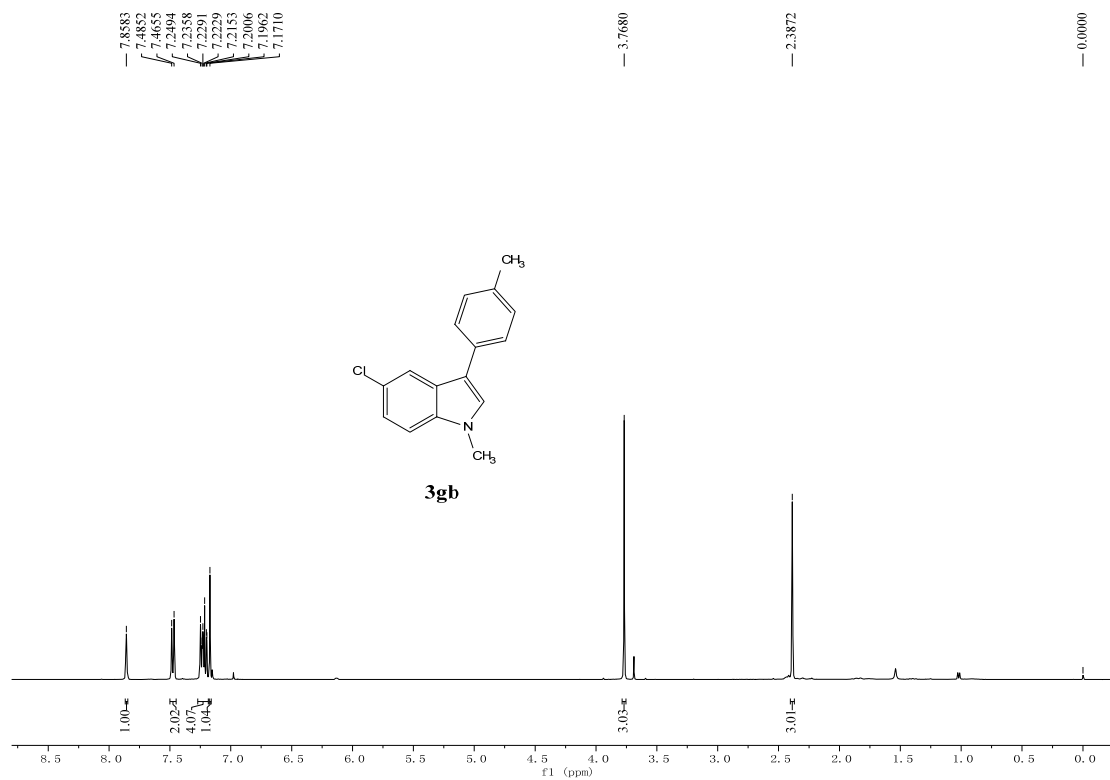


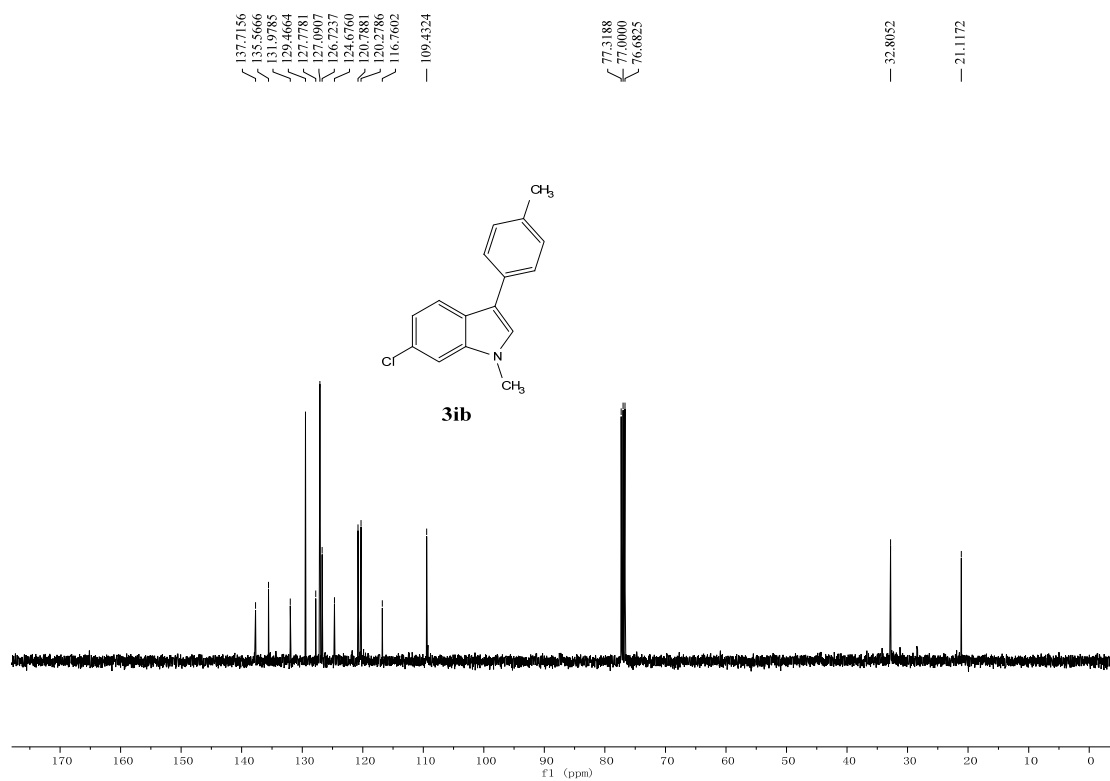
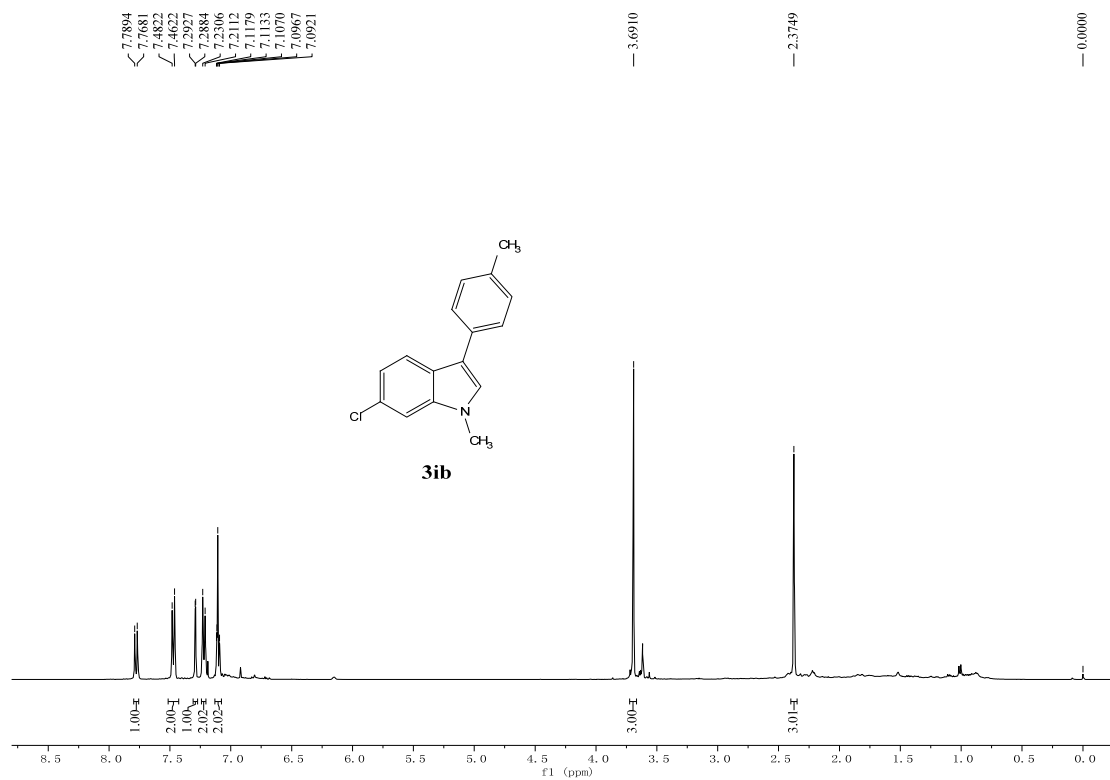


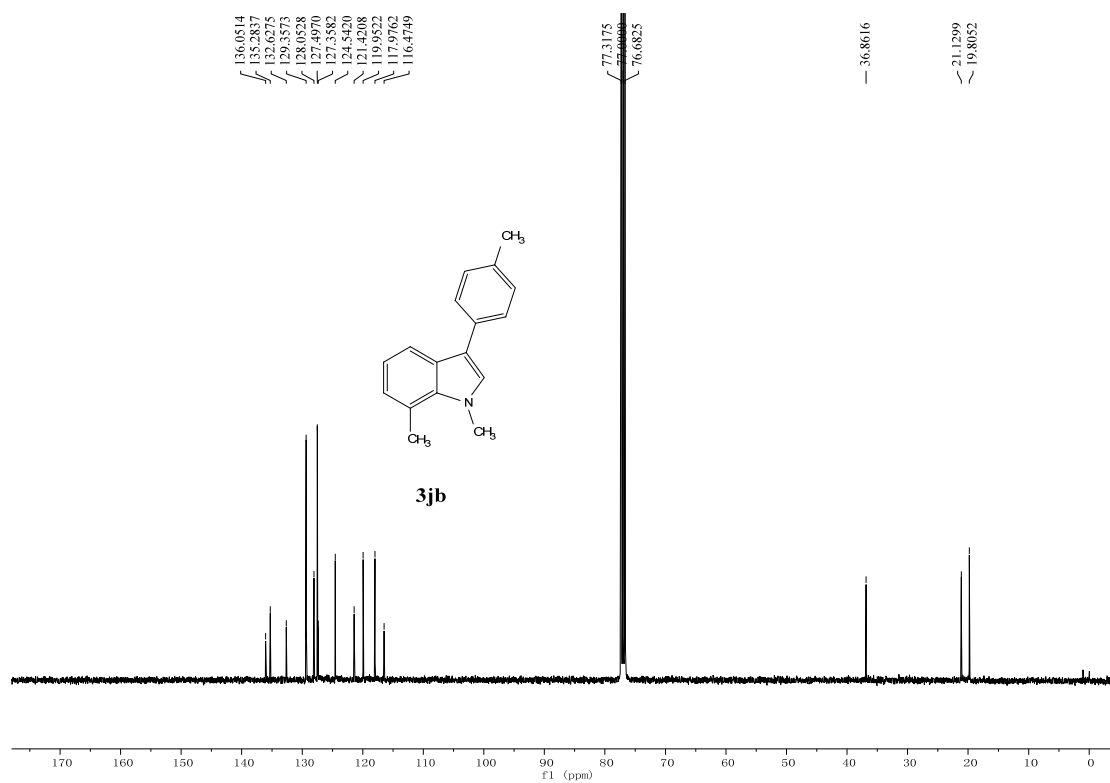
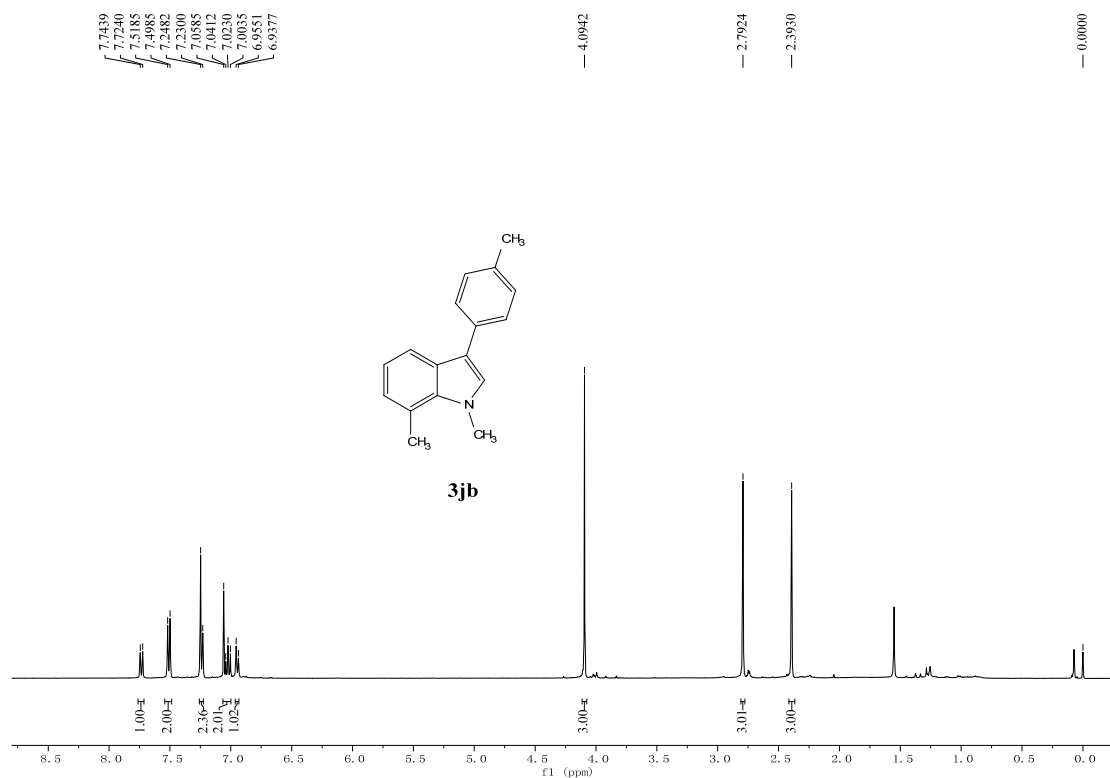


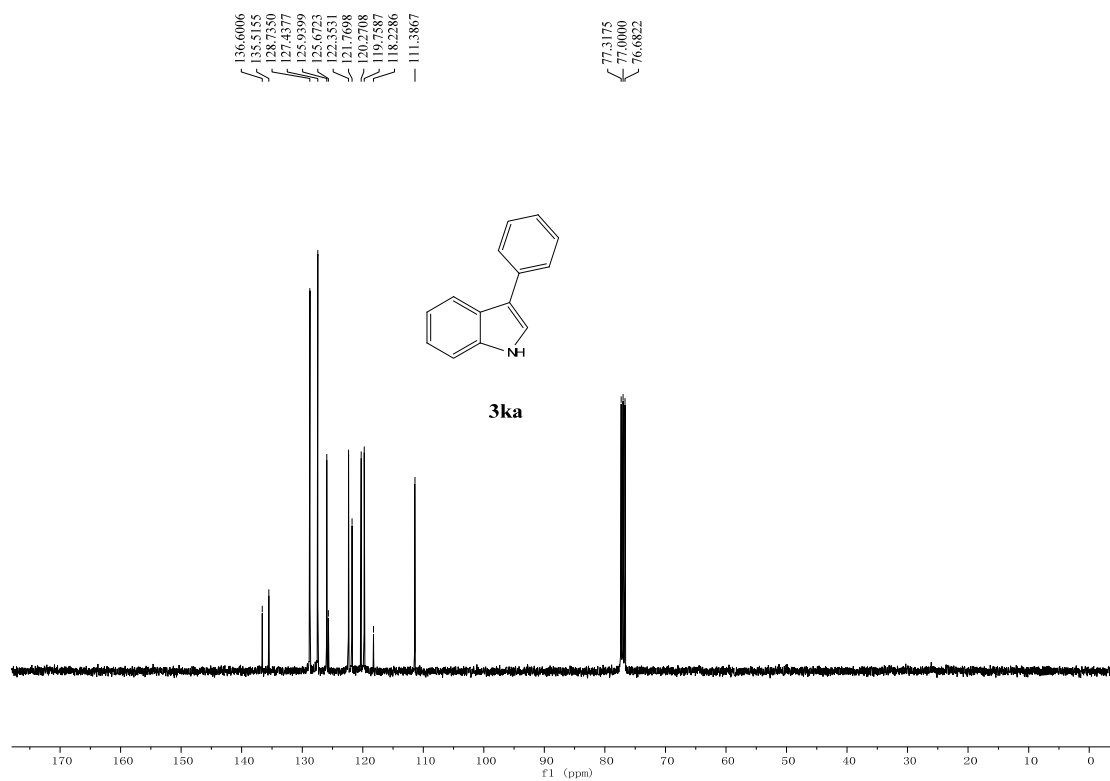
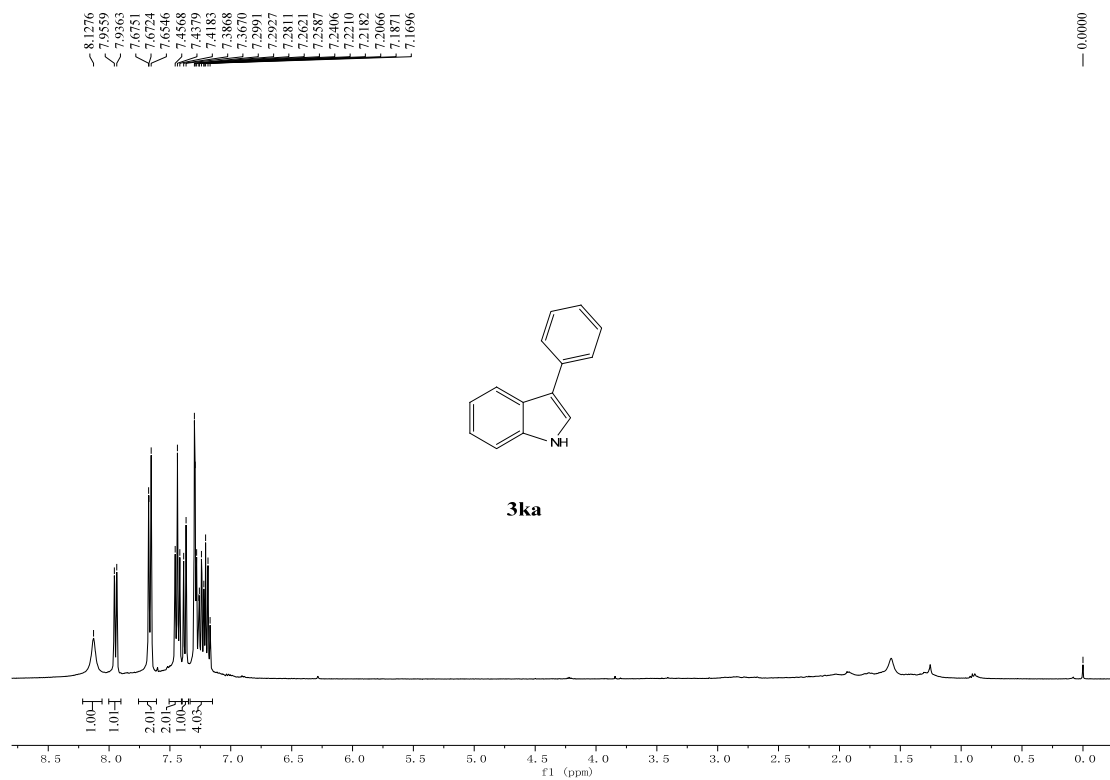


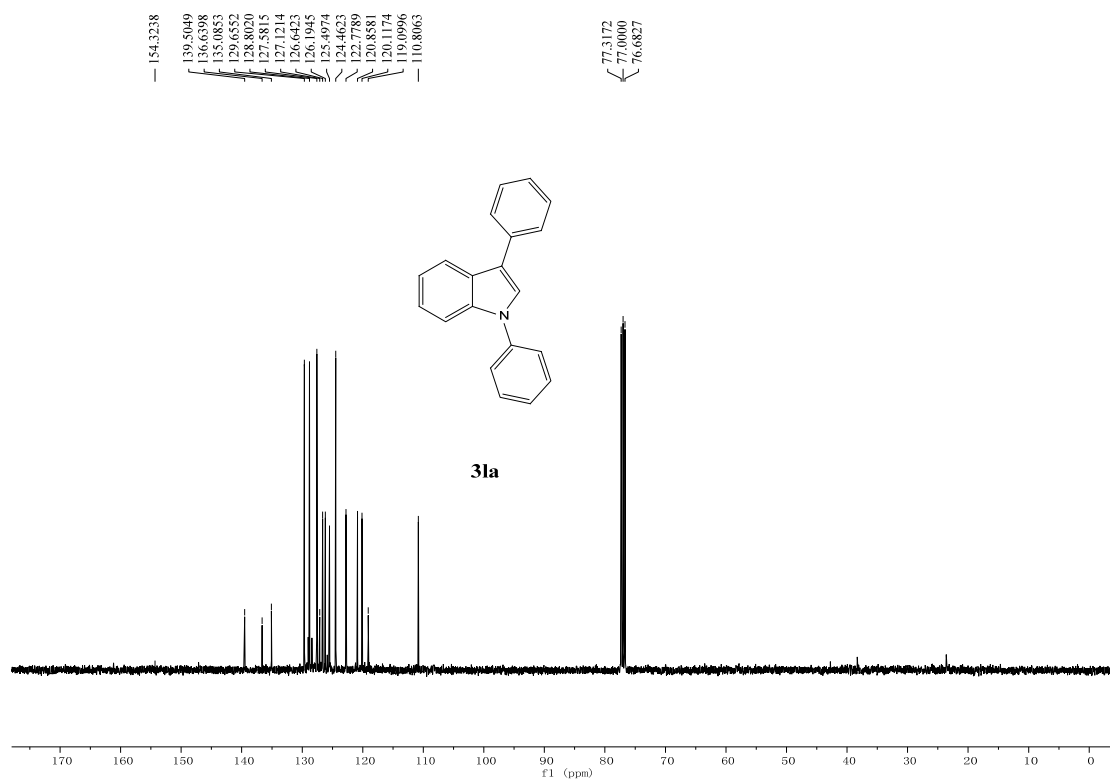
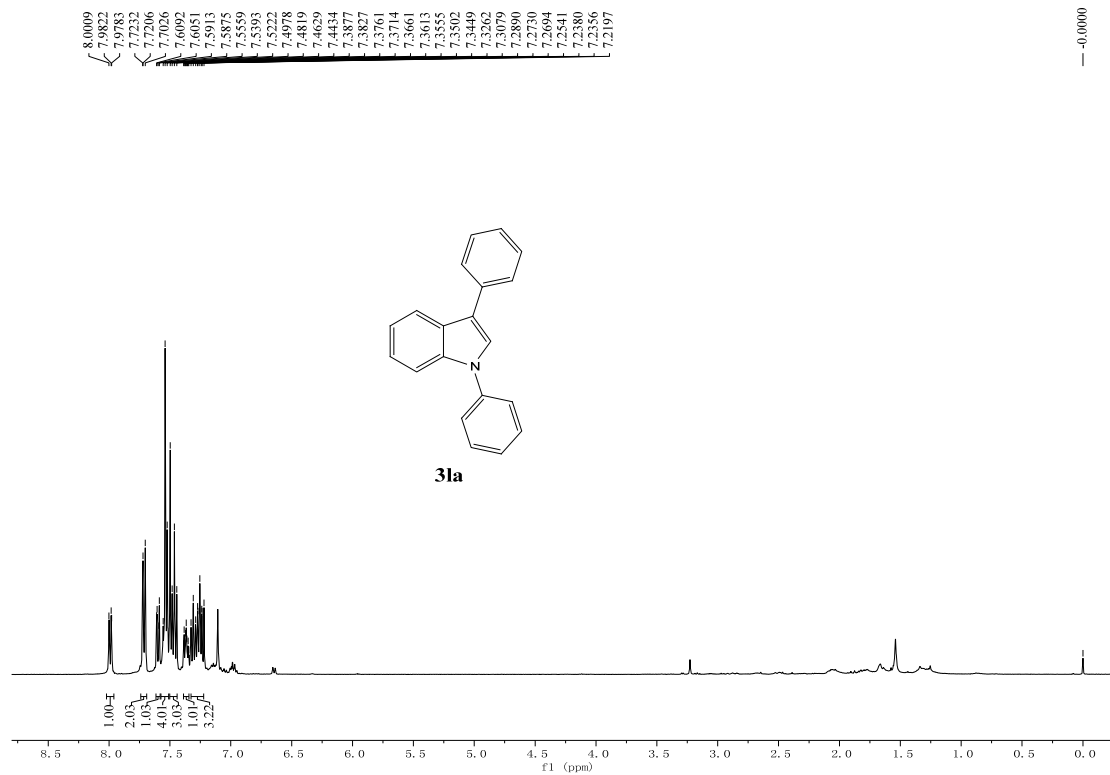


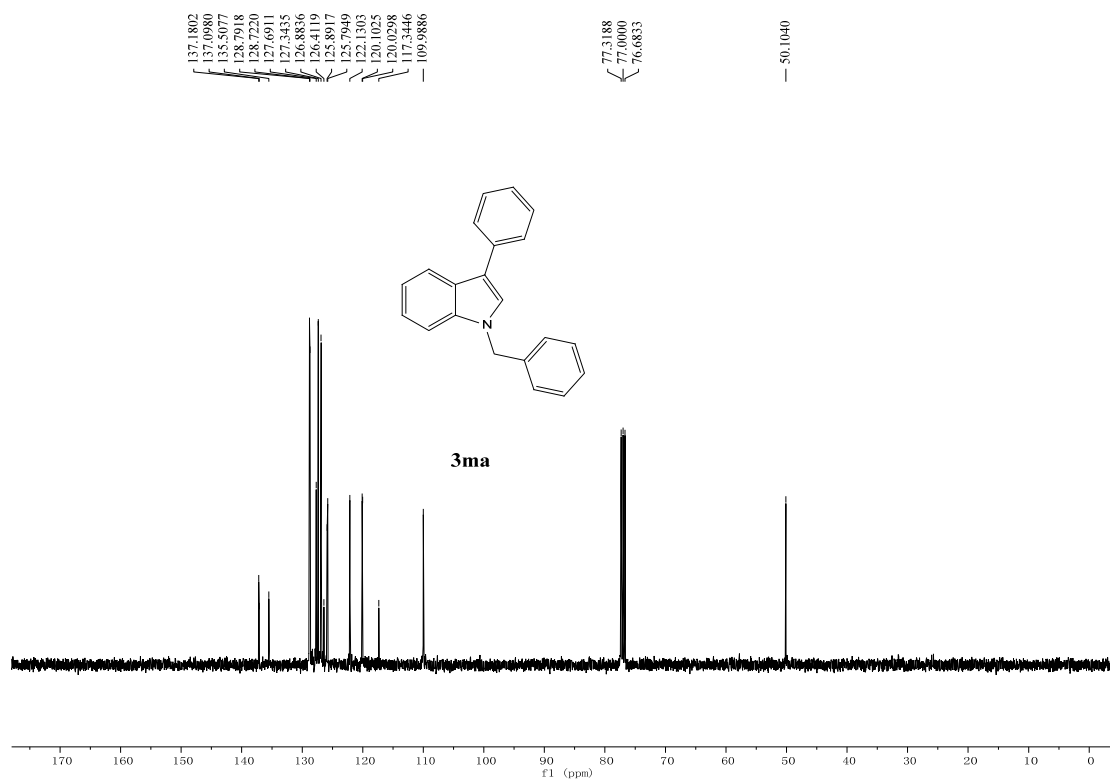
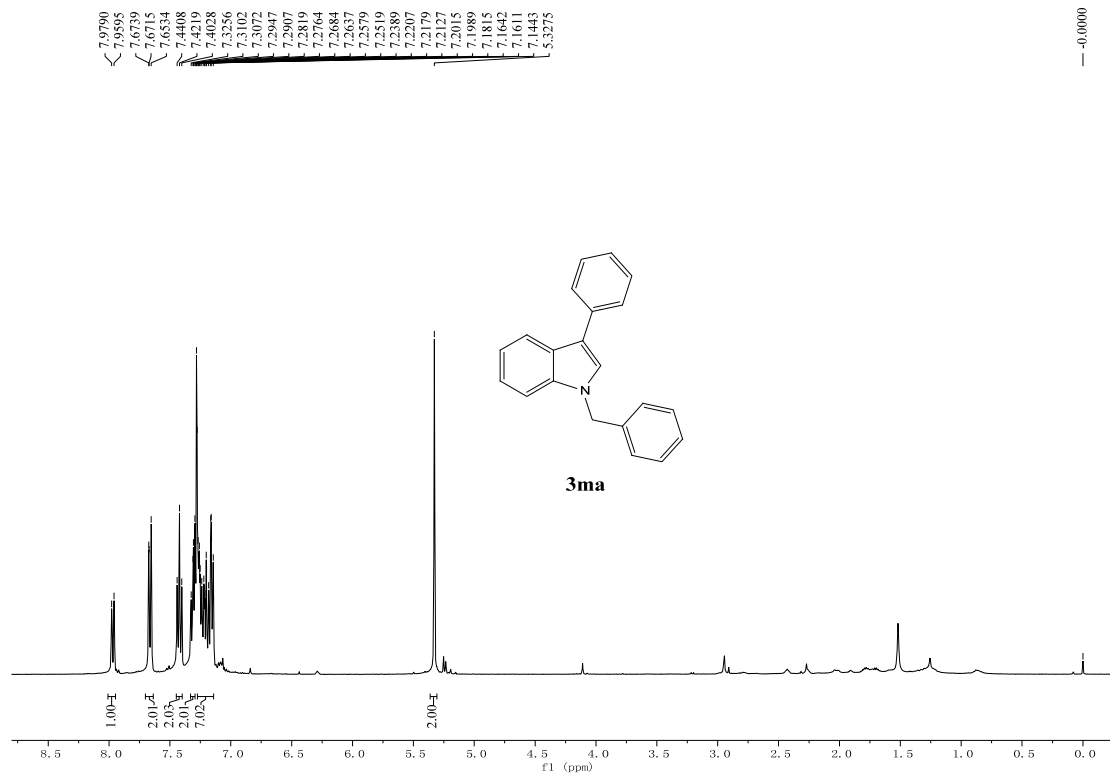


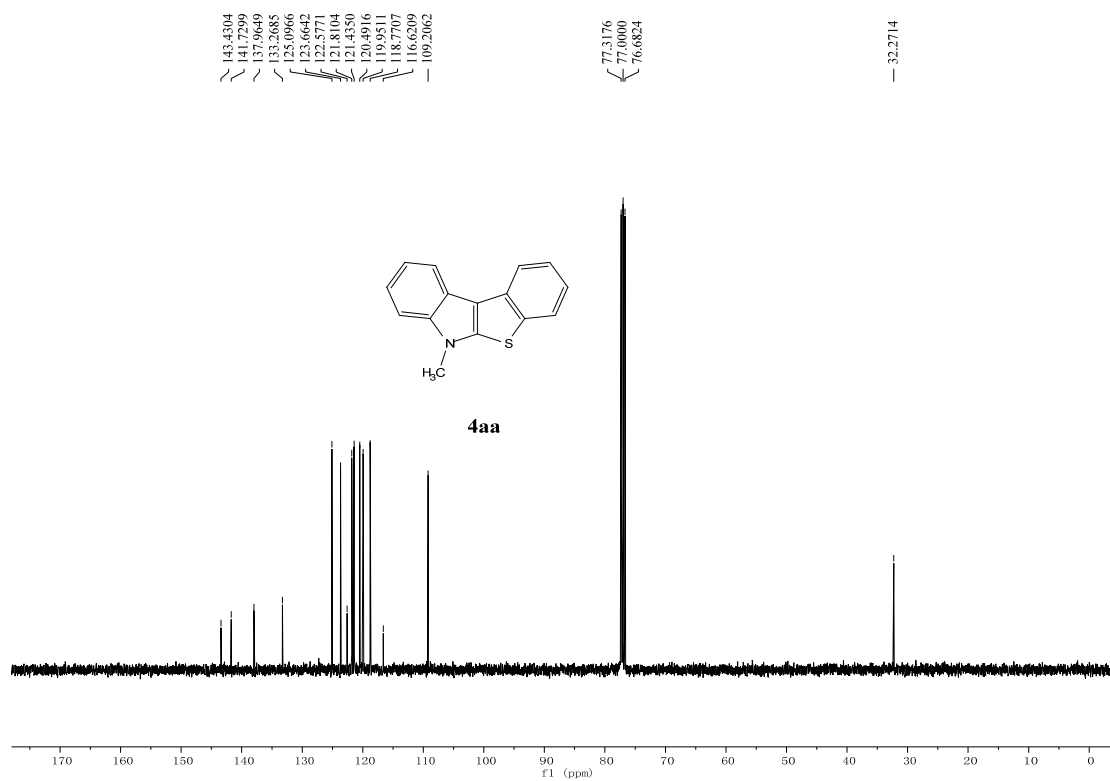
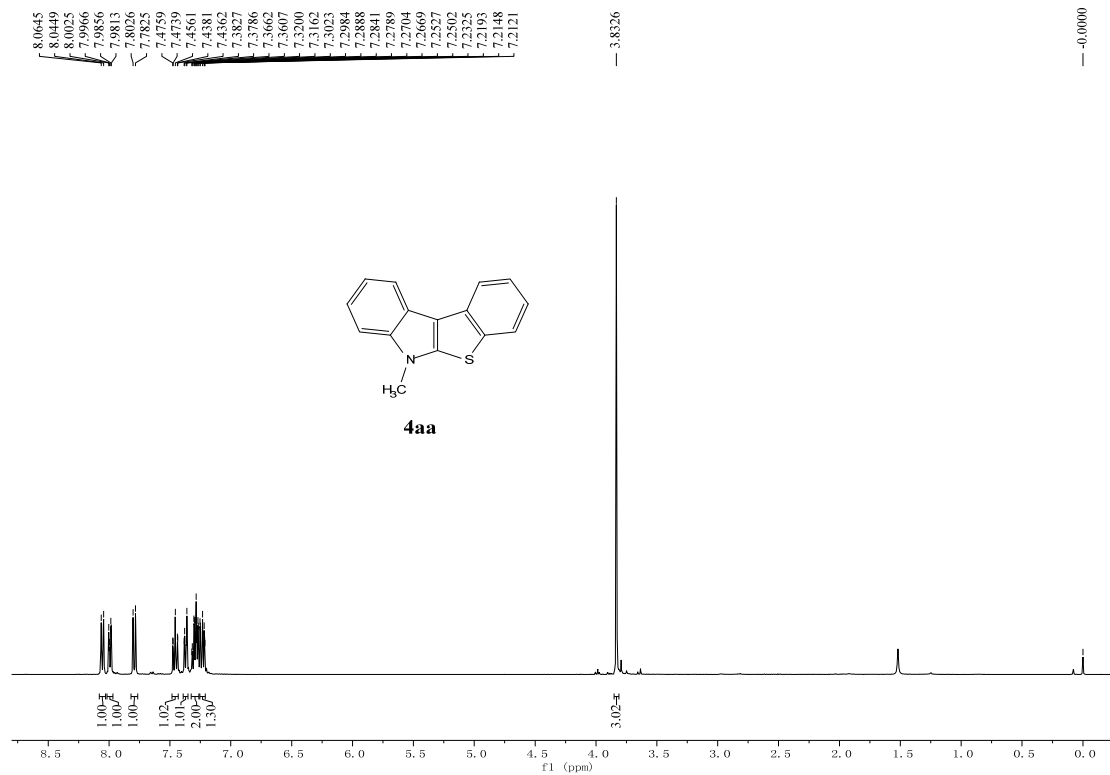


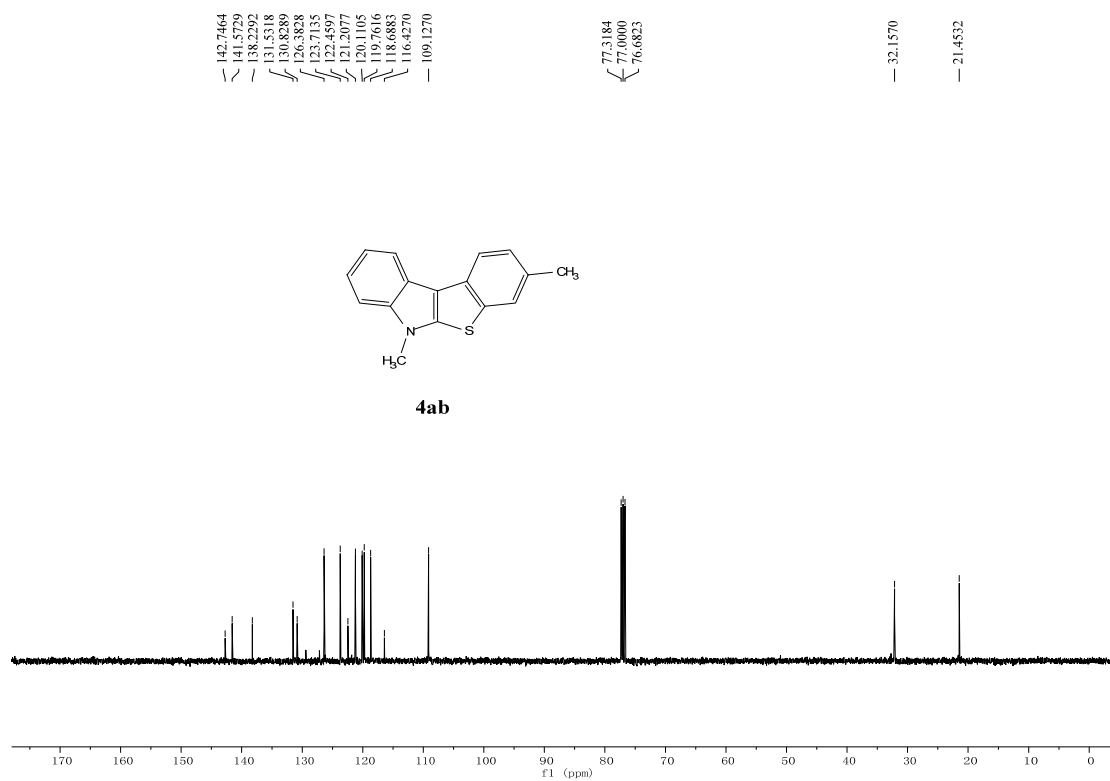
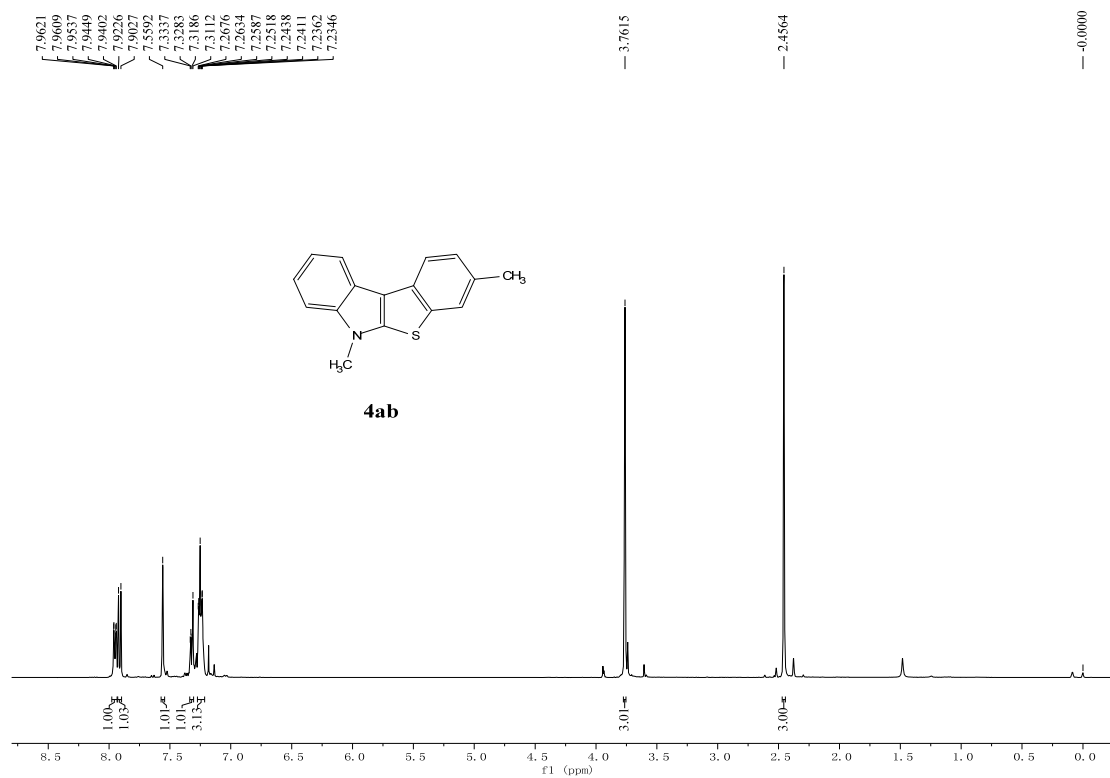


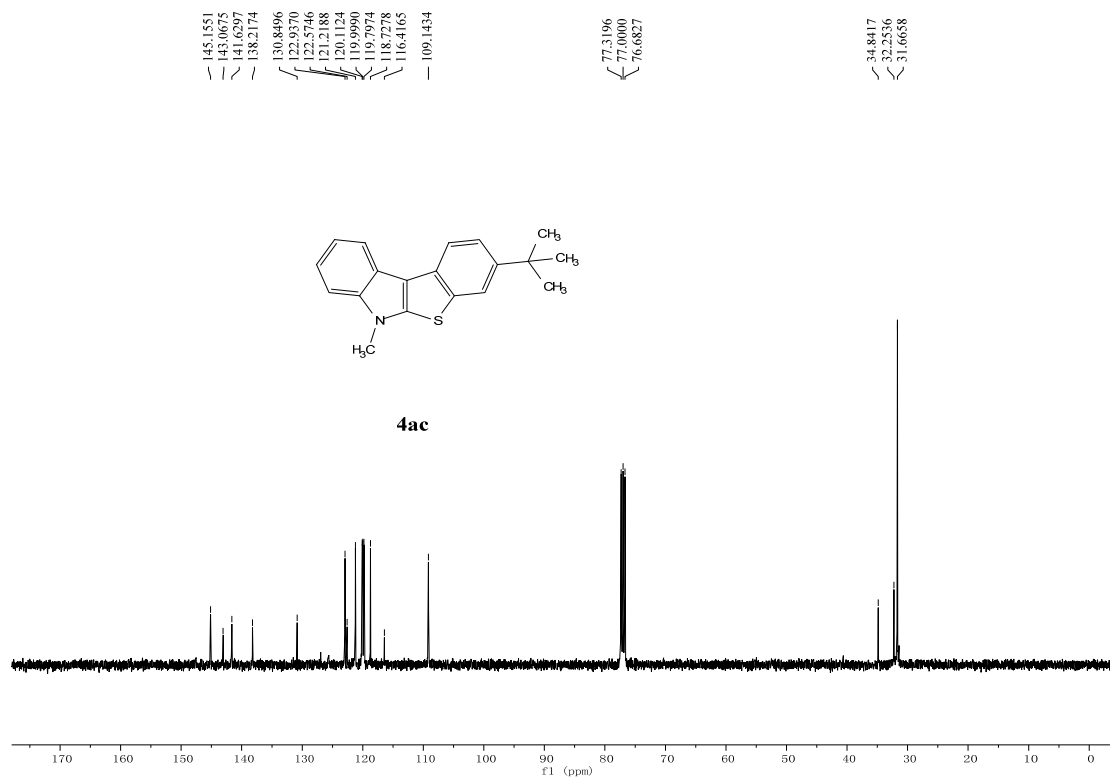
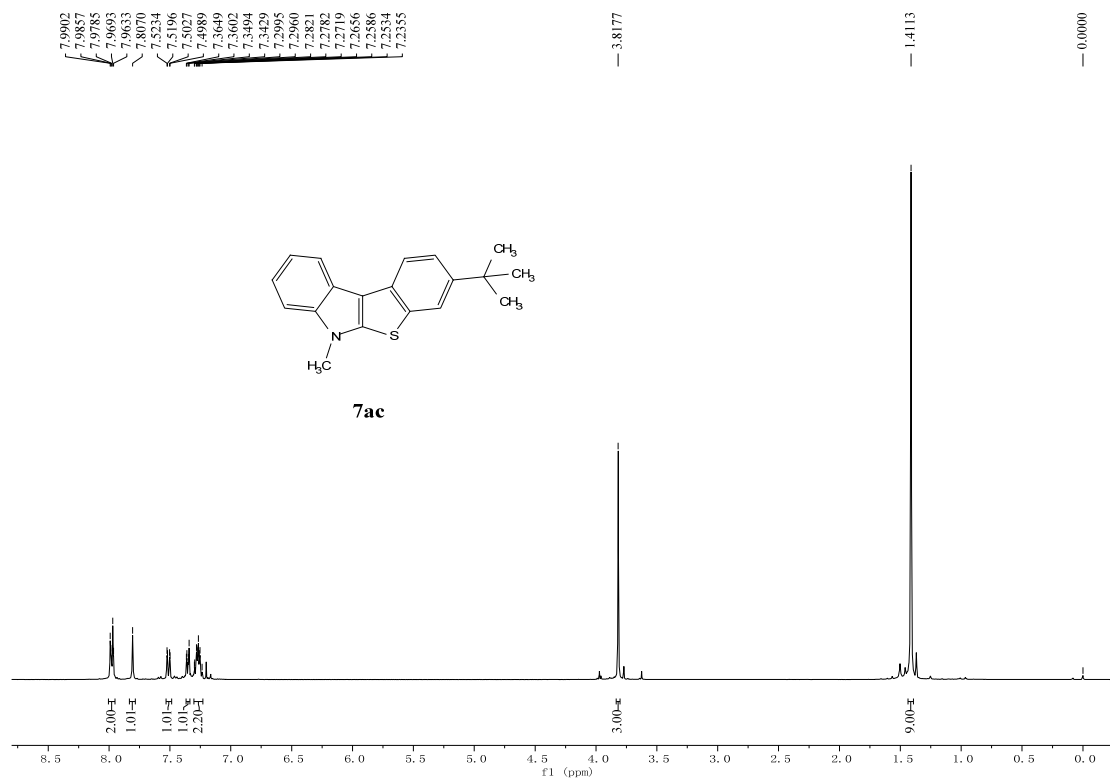


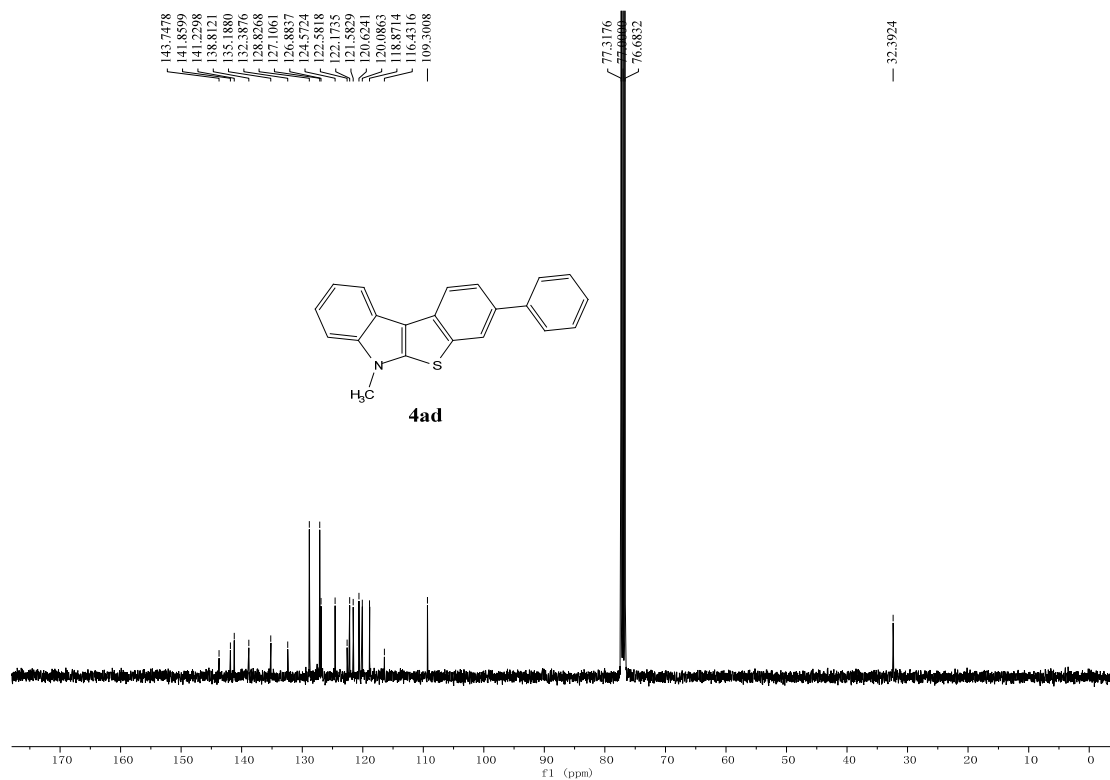
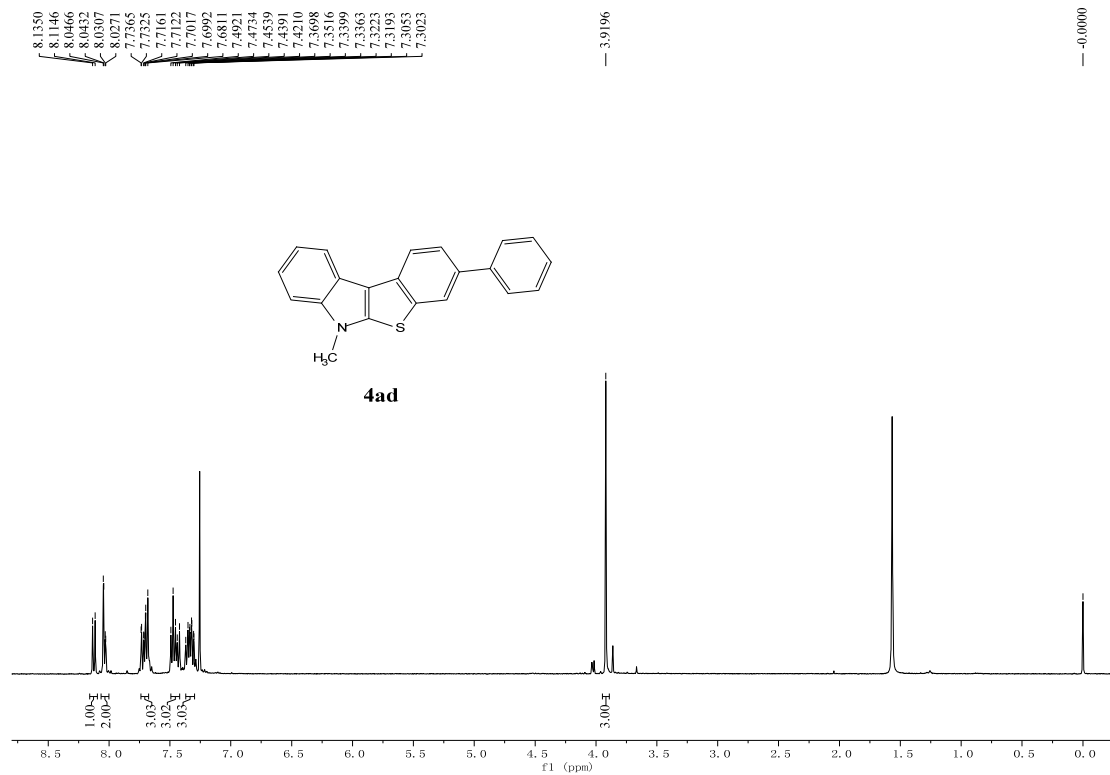


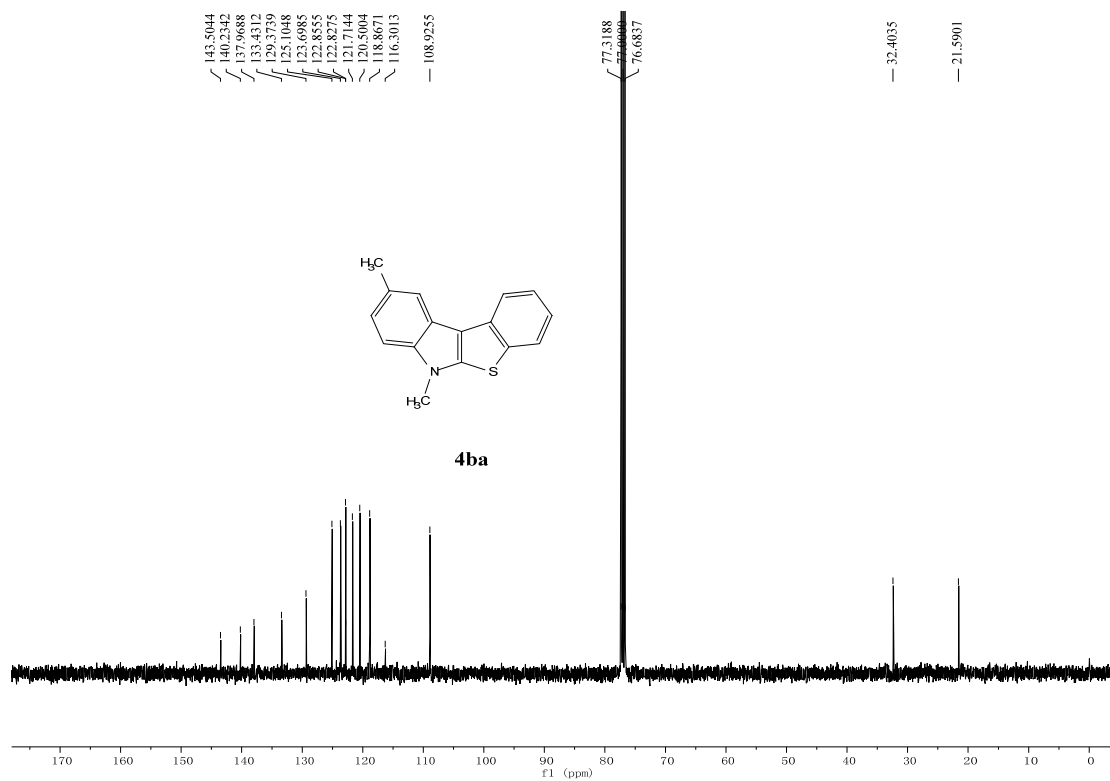
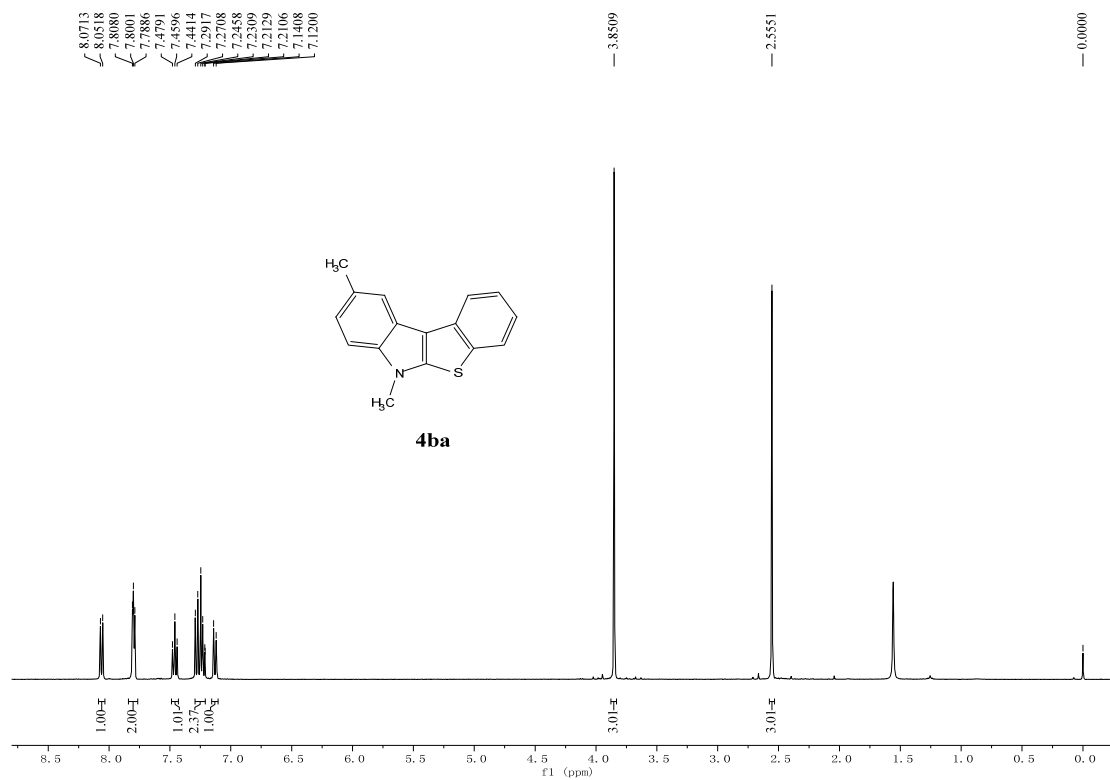


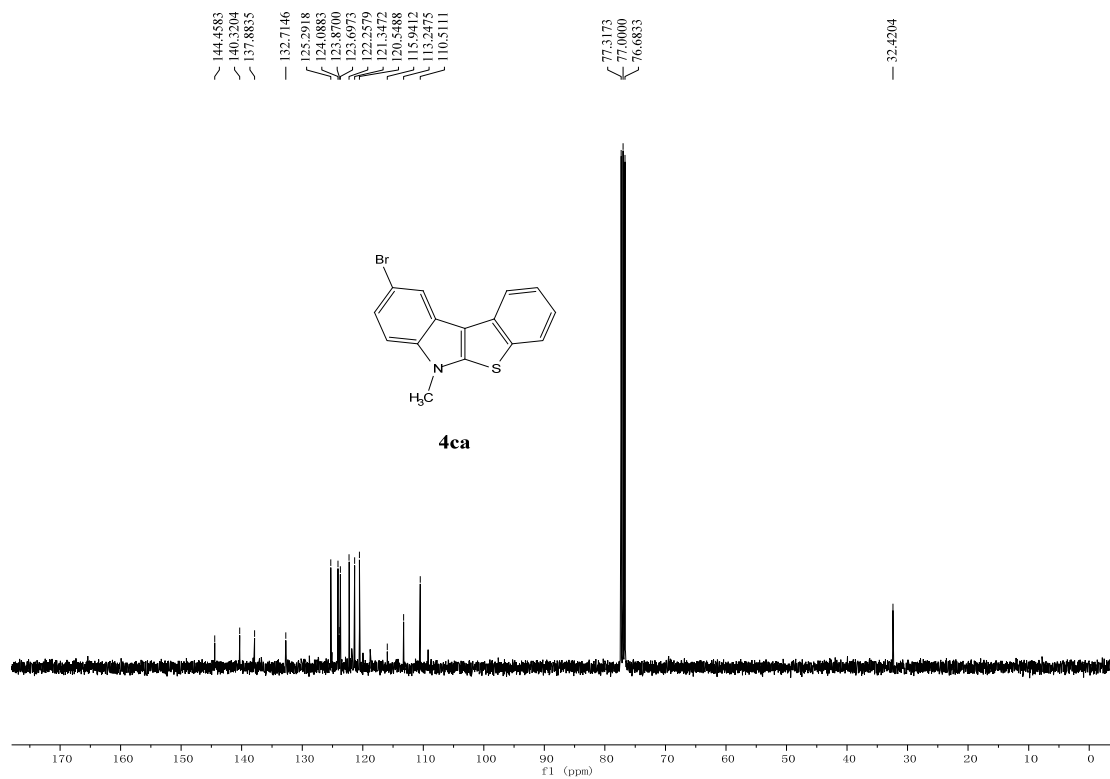
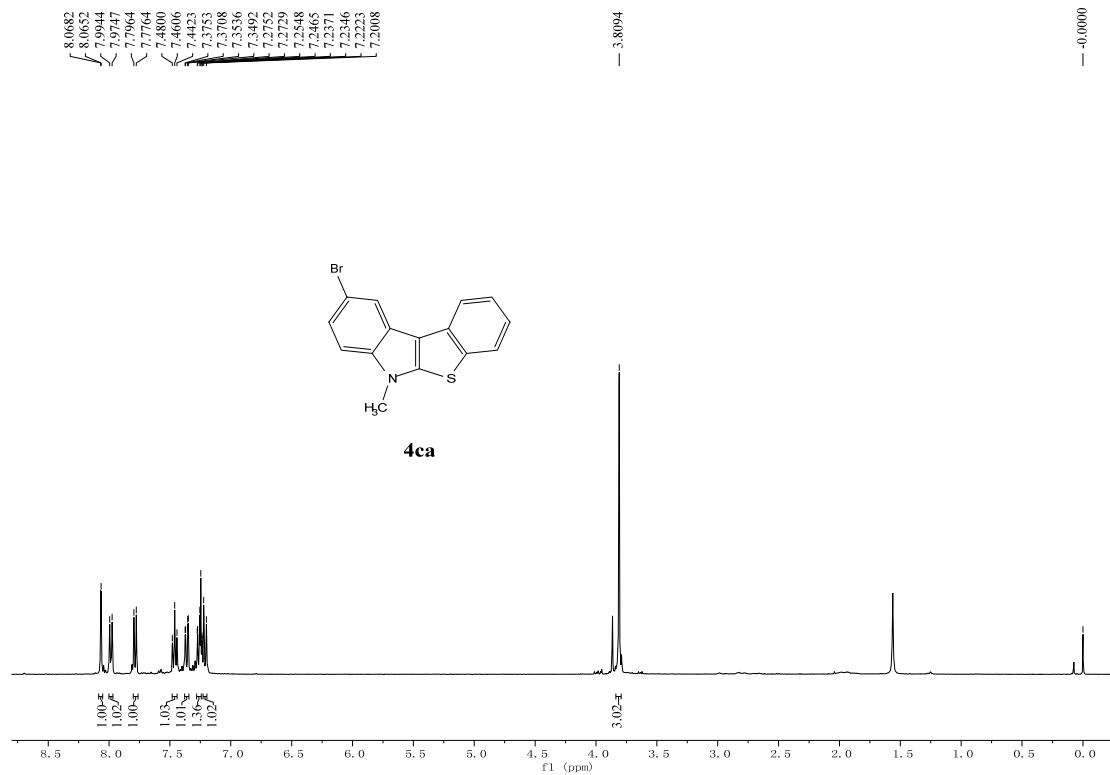


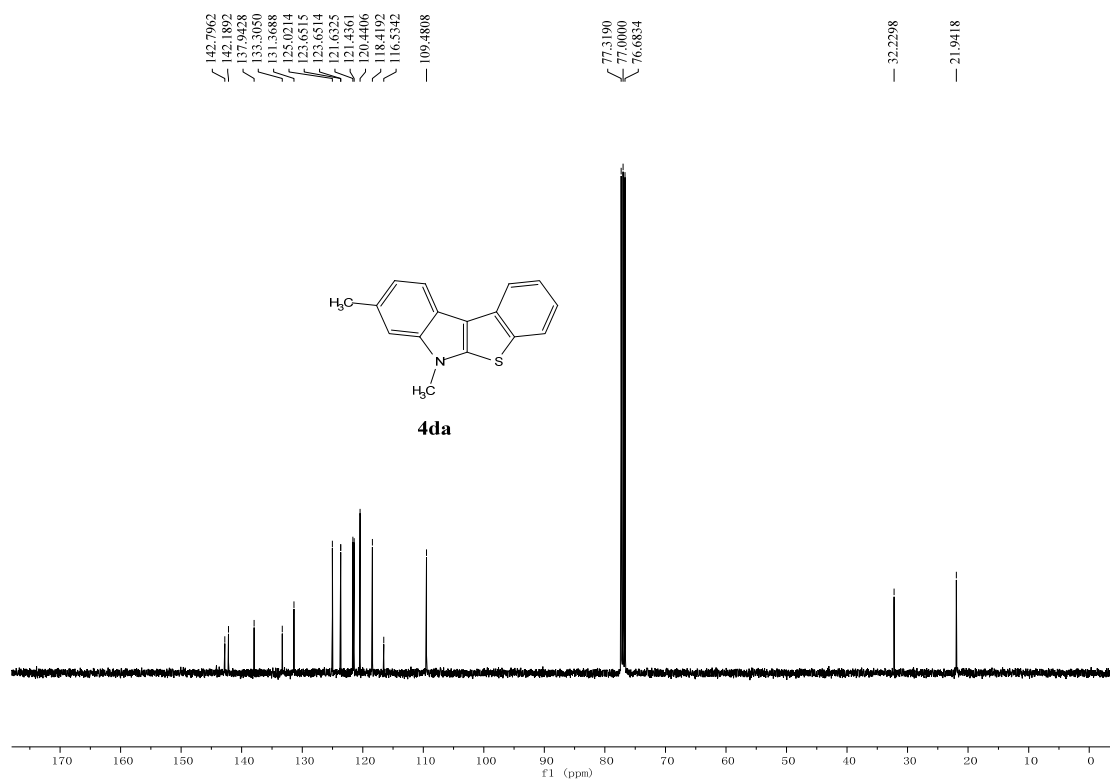
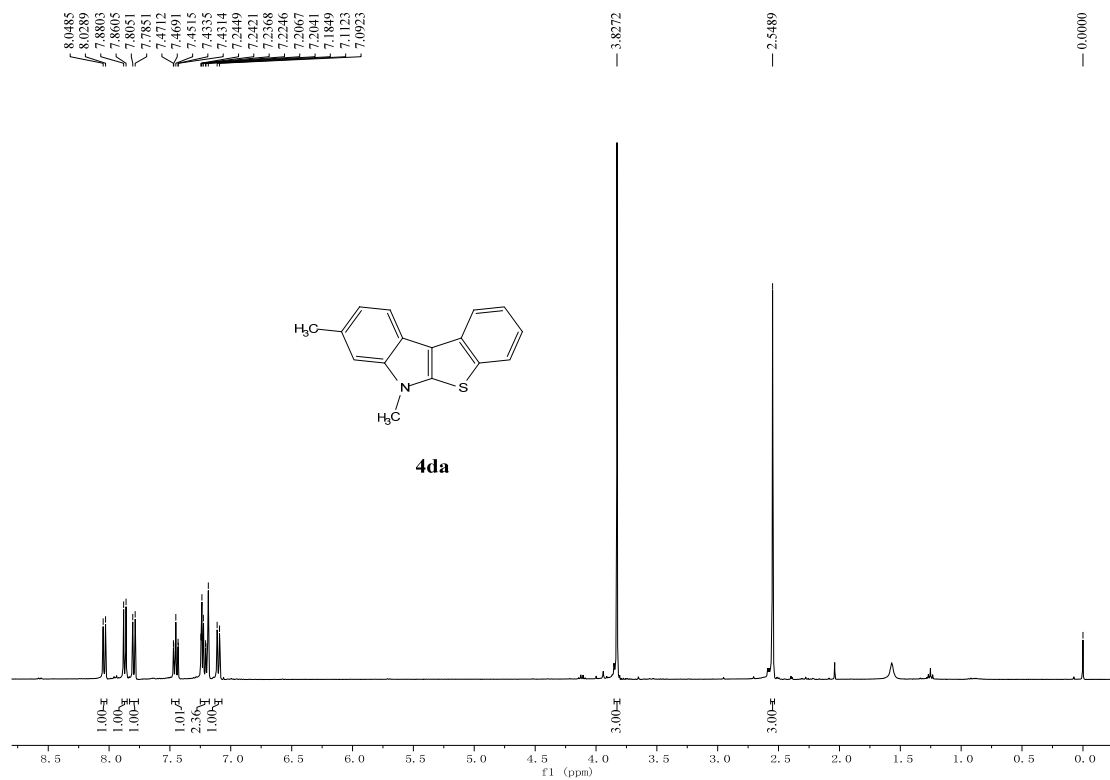


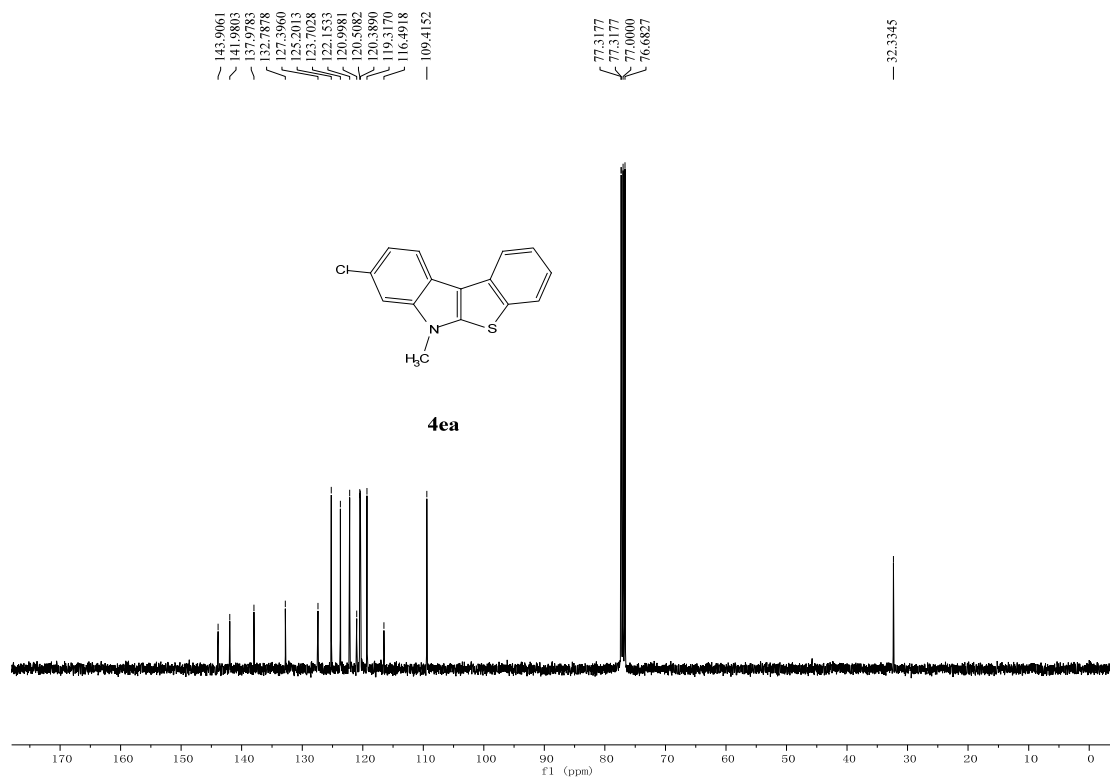
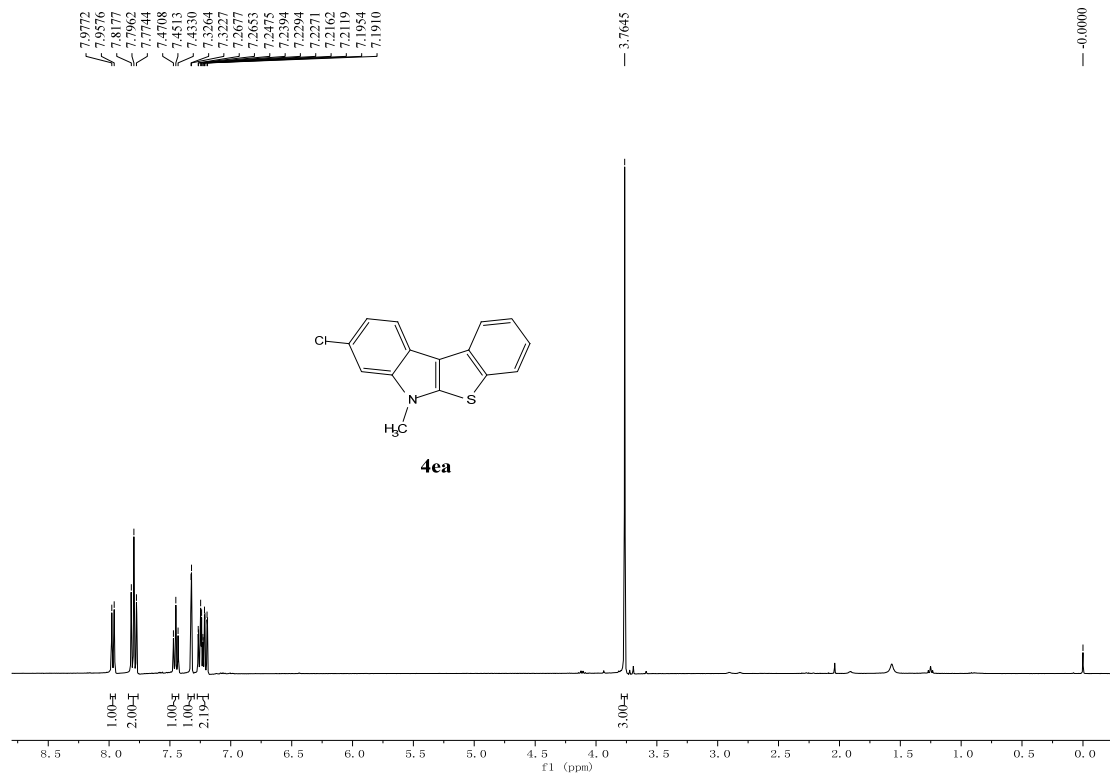


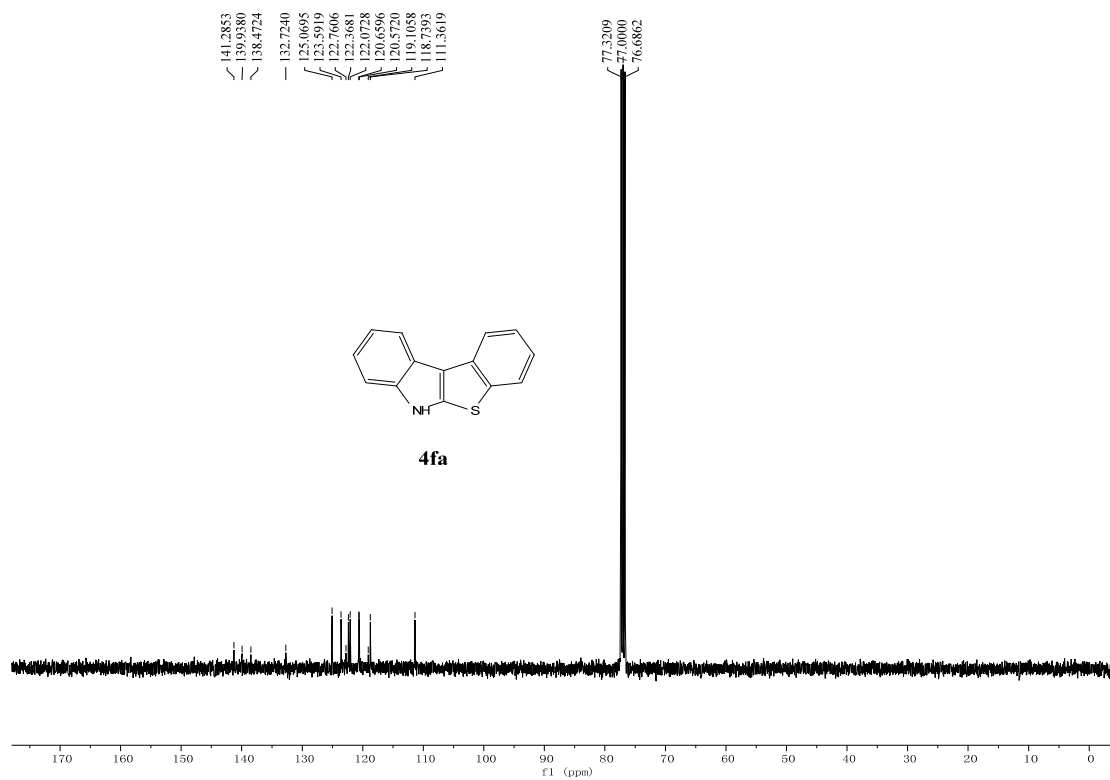
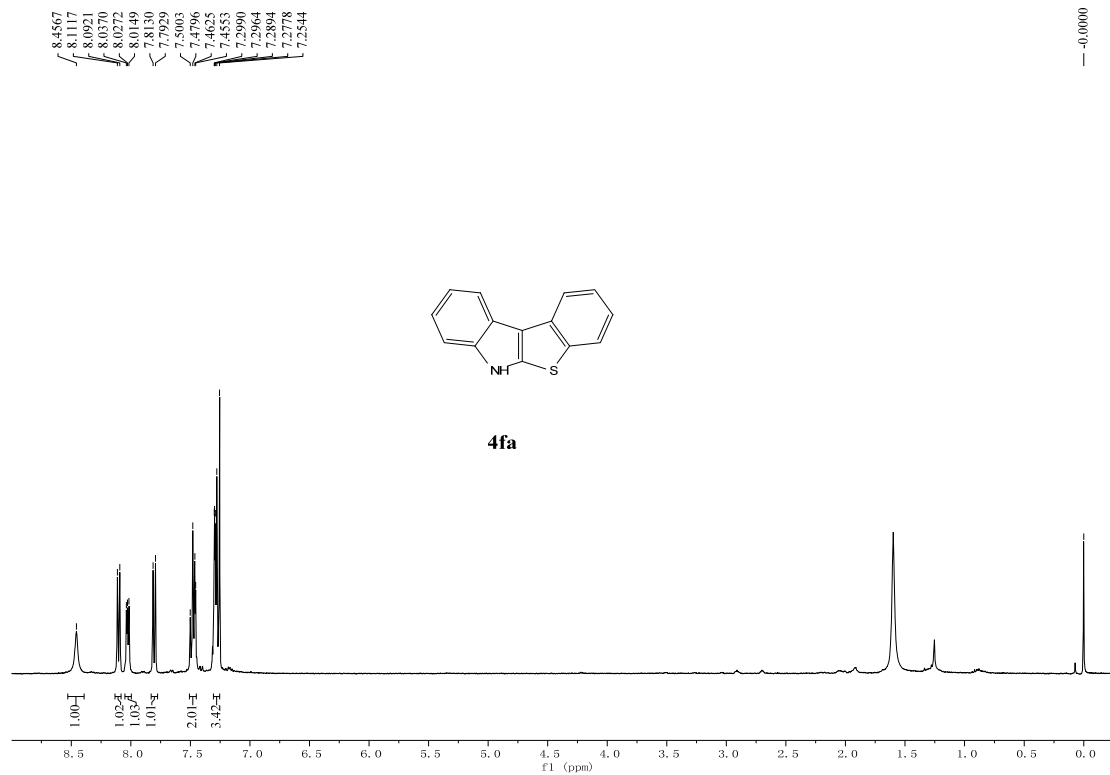


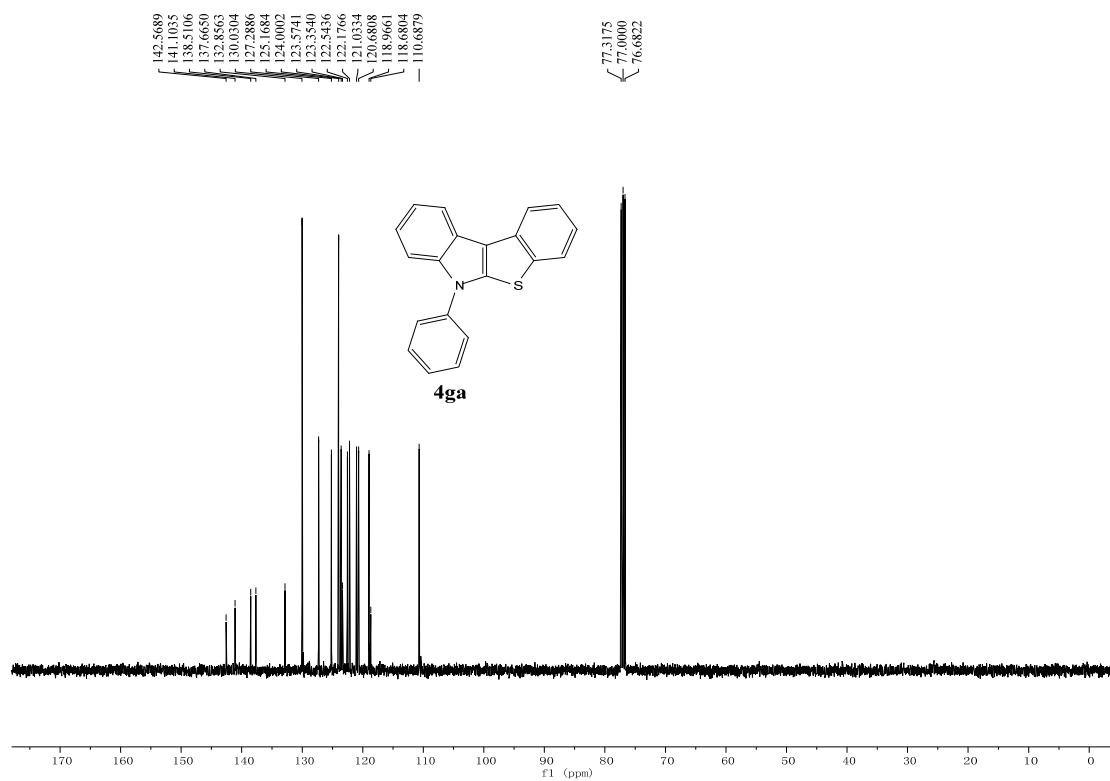
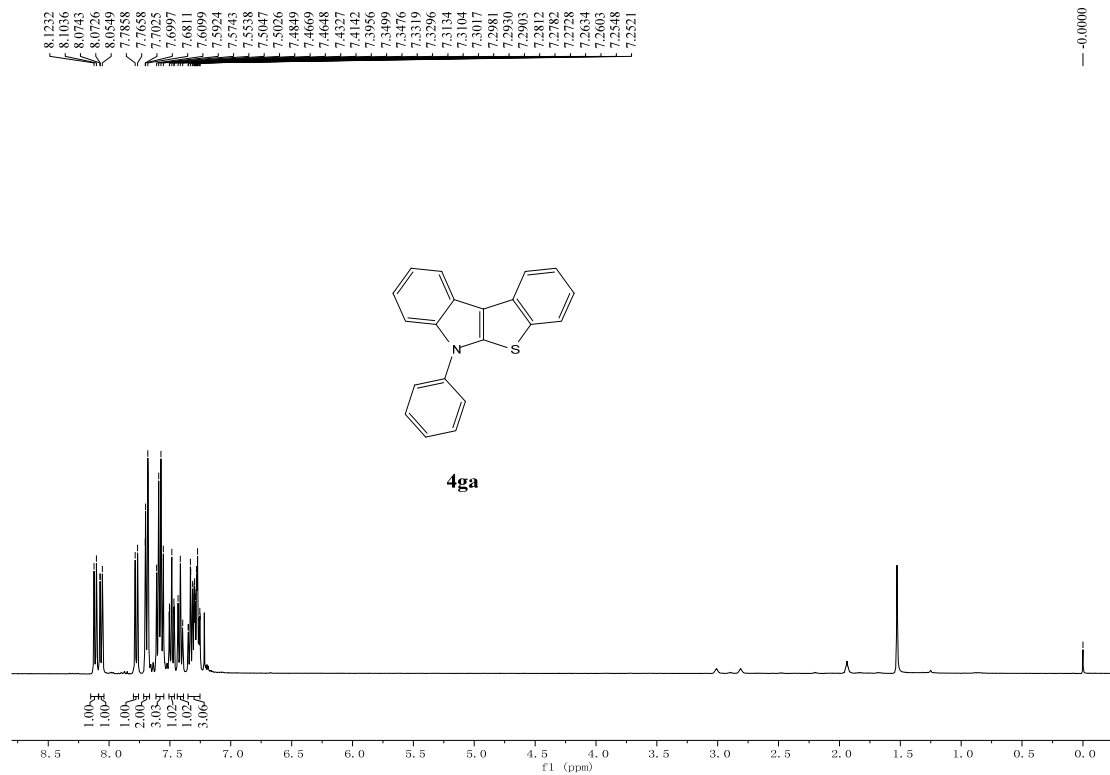


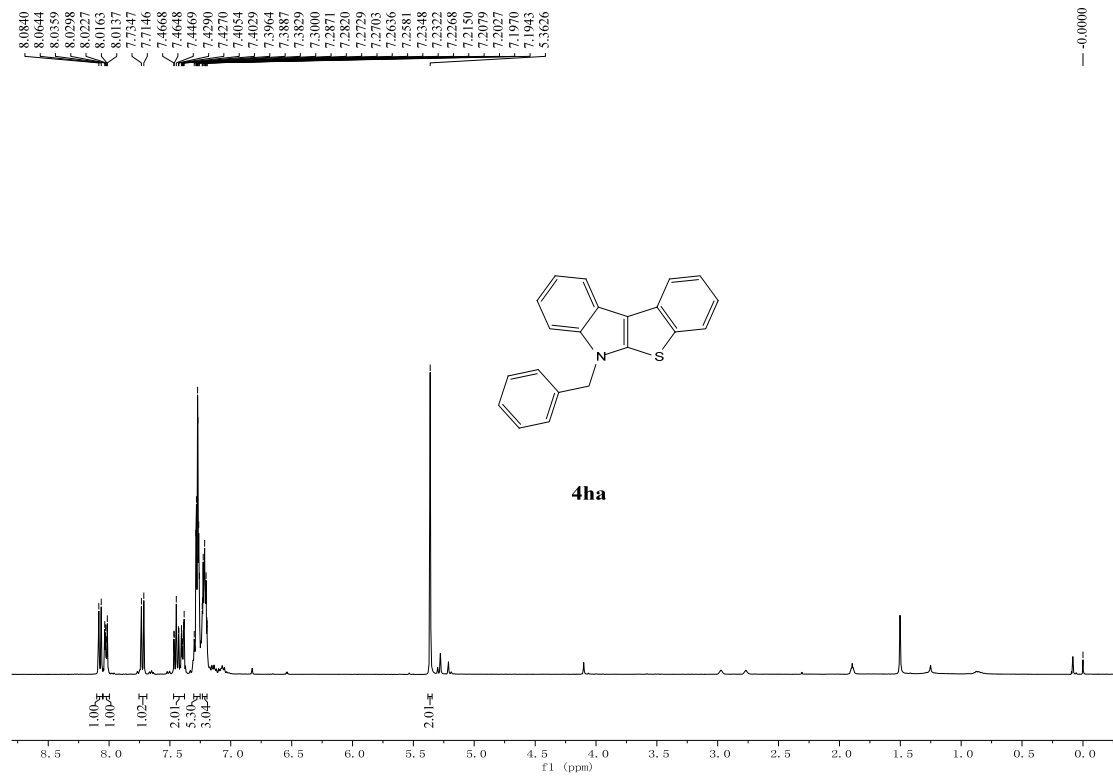












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