Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Rh(III)-Catalyzed Csp^2-Csp^3 Bond Alkoxylation of α-Indolyl Alcohols *via* C-C σ Bond Cleavage

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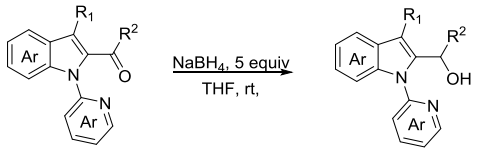
I. General Experimental Information

All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. Reagents were purchased from Accela, Acros, Aladdin, Adamas, Energy Chemical or TCI. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Purifications of reaction products were carried out by flash chromatography using Qingdao Haiyang Chemical Co. Ltd silica gel (400-630 mesh). Infrared spectra (IR) were recorded on a Brucker TENSOR 27 FTIR spectrophotometer and are reported as wavelength numbers (cm^{-1}). Infrared spectra were recorded by preparing a KBr pellet containing the title compounds. ^{1}H NMR and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature on a Bruker Avance III 400 MHz or 500 MHz for ^{1}H NMR and 100 MHz or 126 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), doublet of doublet (dd), quartet (q). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). High resolution mass spectra (HRMS) were recorded on an IF-TOF spectrometer (Micromass). Crystal data were collected on a Bruker D8 Advance employing graphite monochromated Mo - Kα radiation (λ = 0.71073 Å) at 293(2) K and operating in the φ-ω scan mode. Alcohols **1y**[1], **1z**[1], indole **10**[4], and arylalkyl ketone **11**[4] were prepared according to the previous literatures.

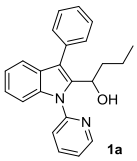
II. Experimental Procedures for the Preparation of Starting Materials

1. Procedure for the synthesis of secondary alcohol substrates 1a~1r, 1v, 8

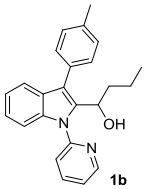


S1 **1 and 8**

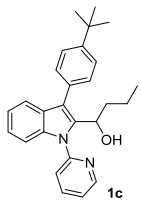
The secondary alcohols **1a~1r, 1w, 8** were prepared from ketones **S1**, which were synthesized according to the previous literature [4]. Ketone **S1** (3.0 mmol) was dissolved in 20 mL THF, then $NaBH_4$ (15.0 mmol) was added in portions, and stirred for 24-48 h at room temperature. The reaction was monitored by TLC to achieve full conversion, then was quenched by saturated NH_4Cl (aq), extracted by EtOAc for three times (3 × 5 mL), dried over Na_2SO_4, and evaporated in vacuum to afford the crude product, which was further purified by flash chromatography on silica gel with petroleum ether/EtOAc (20:1 ~ 5:1) to give excellent yields of the corresponding alcohols **1 and 8**.



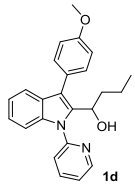
1-(3-Phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1a)[7]: 975 mg, 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 3.6 Hz, 1H), 8.04 (t, *J* = 7.4 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.66 (dd, *J* = 14.7, 7.5 Hz, 3H), 7.53 (t, *J* = 7.6 Hz, 3H), 7.40 (dd, *J* = 13.3, 6.9 Hz, 2H), 7.31 – 7.22 (m, 2H), 6.41 (d, *J* = 10.4 Hz, 1H), 4.97 (dd, *J* = 16.5, 7.4 Hz, 1H), 1.52 – 1.38 (m, 1H), 1.24 – 1.10 (m, 2H), 1.10 – 0.96 (m, 1H), 0.62 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 148.7, 139.4, 138.4, 136.2, 134.2, 130.5, 128.6, 126.9, 123.5, 122.0, 121.6, 120.4, 120.2, 120.1, 119.0, 110.0, 66.7, 37.9, 19.4, 13.7.



1-(1-(Pyridin-2-yl)-3-(*p*-tolyl)-1H-indol-2-yl)butan-1-ol (1b)[9]: white solid; 833 mg, 78% yield; m.p. 80.4-81.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 4.9, 1.2 Hz, 1H), 8.05 – 8.01 (m, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 3H), 7.40 – 7.37 (m, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.23 (dd, *J* = 11.0, 3.9 Hz, 1H), 6.37 (d, *J* = 10.5 Hz, 1H), 4.99 – 4.94 (m, 1H), 2.47 (s, 3H), 1.51 – 1.40 (m, 1H), 1.25 – 1.11 (m, 2H), 1.08 – 0.95 (m, 1H), 0.62 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 148.7, 139.4, 138.3, 136.6, 136.2, 131.2, 130.3, 129.3, 128.7, 123.5, 121.9, 121.5, 120.5, 120.2, 120.1, 110.0, 66.7, 37.9, 21.4, 19.5, 13.7; HR-MS [ESI-MS(+)] calcd for $[M + H]^+$: $C_{24}H_{25}N_2O$: 357.1961, found: 357.1990; IR (KBr): 3290, 3026, 2953, 2863, 1589, 1475, 1435, 1361, 1219, 1014, 825, 741, 647 cm^{-1}.

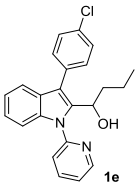


1-(3-(4-(*tert*-Butyl)phenyl)-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1c)[9]: white solid; 1051 mg, 88% yield; m.p. 159.9-162.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 3.5 Hz, 1H), 8.03 (t, *J* = 7.2 Hz, 1H), 7.74 (dd, *J* = 16.7, 7.8 Hz, 2H), 7.55 (t, *J* = 6.4 Hz, 5H), 7.42 – 7.36 (m, 1H), 7.32 – 7.22 (m, 2H), 6.40 (d, *J* = 10.3 Hz, 1H), 4.99 (d, *J* = 9.0 Hz, 1H), 1.44 (s, 10H), 1.21 (dd, *J* = 15.4, 8.7 Hz, 2H), 1.04 (dd, *J* = 16.5, 8.2 Hz, 1H), 0.63 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 149.7, 148.6, 139.4, 138.4, 136.3, 131.2, 130.1, 128.7, 125.5, 123.4, 122.0, 121.5, 120.6, 120.2, 120.1, 110.0, 66.7, 38.0, 34.6, 31.5, 19.5, 13.8; HR-MS [ESI-MS(+)] calcd for $[M + H]^+$: $C_{27}H_{31}N_2O$: 399.2431, found: 399.2503; IR (KBr): 3316, 3057, 2956, 2867, 1588, 1474, 1458, 1424, 1370, 1319, 1045, 1023, 779, 744 cm^{-1}.

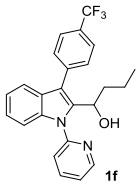


1-(3-(4-Methoxyphenyl)-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1d)[9]: colorless solid; 1071 mg, 96% yield; m.p. 143.1-144.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.9, 1.2 Hz, 1H), 8.04 – 8.00 (m, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.56 (dd, *J* = 13.7, 8.4 Hz, 3H), 7.38 (dd, *J* = 7.0, 5.3 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.39 (d, *J* = 10.4 Hz, 1H), 4.96 (dd, *J* = 17.6, 7.5 Hz, 1H), 3.92 (s, 3H), 1.52 – 1.42 (m, 1H), 1.25 – 1.13 (m, 2H), 1.07 – 1.01 (m, 1H), 0.63 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 152.2, 148.6,

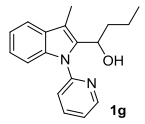
139.4, 138.2, 136.2, 131.5, 128.8, 126.5, 123.5, 121.9, 121.5, 120.4, 120.2, 119.8, 114.1, 109.9, 66.7, 55.3, 37.9, 19.5, 13.7; HR-MS [ESI-MS(+)] calcd for $[M + H]^+$: $C_{24}H_{25}N_2O_2$: 373.1911, found: 373.1968; IR (KBr): 3320, 3049, 2950, 2862, 1588, 1556, 1506, 1473, 1373, 1282, 1245, 1172, 1104, 1019, 998, 837, 791, 740 cm^{-1}.



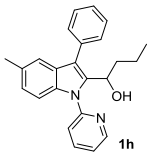
1-(3-(4-Chlorophenyl)-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1e)[9]: light yellow solid; 812 mg, 72% yield; m.p. 171.9-173.0 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 4.9, 1.2 Hz, 1H), 8.06 – 8.03 (m, 1H), 7.76 (dd, *J* = 8.0, 4.5 Hz, 1H), 7.64 (t, *J* = 6.5 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.52 (dd, *J* = 17.2, 8.4 Hz, 3H), 7.42 – 7.39 (m, 1H), 7.31 – 7.27 (m, 1H), 7.24 (dd, *J* = 10.9, 3.9 Hz, 1H), 6.31 (d, *J* = 10.3 Hz, 1H), 4.90 (dd, *J* = 17.6, 7.5 Hz, 1H), 1.50 – 1.40 (m, 1H), 1.22 – 1.12 (m, 2H), 1.08 – 0.96 (m, 1H), 0.62 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 148.8, 139.5, 138.6, 136.2, 132.8, 131.7, 130.4, 128.8, 128.2, 123.7, 122.2, 121.8, 120.2, 120.1, 118.8, 110.1, 66.6, 37.8, 19.4, 13.6; HR-MS [ESI-MS(+)] calcd for $[M + H]^+$: $C_{23}H_{22}N_2OCl$: 377.1415, found: 377.1409; IR (KBr): 3310, 3061, 2954, 2861,1587, 1566, 1472, 1455, 1435, 1365, 1314, 1215, 1088, 1014, 1000, 832, 779, 746, 716 cm^{-1}.



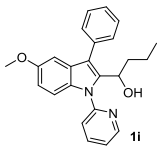
1-(1-(Pyridin-2-yl)-3-(4-(trifluoromethyl)phenyl)-1H-indol-2-yl)butan-1-ol (1f)[9]: colorless solid; 984 mg, 80% yield; m.p. 110.5-111.3 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.9, 1.3 Hz, 1H), 8.08 – 8.04 (m, 1H), 7.85 – 7.74 (m, 5H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.42 (dd, *J* = 7.3, 5.0 Hz, 1H), 7.35 – 7.25 (m, 2H), 6.41 (dd, *J* = 24.1, 10.5 Hz, 1H), 5.03 – 4.89 (m, 1H), 1.53 – 1.44 (m, 1H), 1.25 – 1.15 (m, 2H), 1.09 – 1.00 (m, 1H), 0.65 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 148.8, 139.6, 139.0, 138.3, 136.3, 130.7, 129.0 (q, *J* = 32.3 Hz, $^2J_{CF}$), 128.0, 125.5 (q, *J* = 4.0 Hz, $^3J_{CF}$), 124.5 (d, *J* = 273.7Hz, $^1J_{CF}$), 123.9, 122.4, 122.0, 120.3, 120.0, 118.7, 110.2, 66.7, 37.8, 19.5, 13.6; HR-MS [ESI-MS(-)] calcd for $[M - H]^-$: $C_{24}H_{20}F_3N_2O$: 409.1533, found: 409.1532; IR (KBr): 3456, 3057, 2926, 2860, 1618, 1589, 1474, 1458, 1438, 1371, 1323, 1123, 1068, 1021, 843, 782, 741 cm^{-1}.



1-(3-Methyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1g)[9]: colorless oily liquid; 756 mg, 90% yield; ^1H NMR (500 MHz, $CDCl_3$) δ 8.58 – 8.56 (m, 1H), 8.00 – 7.95 (m, 1H), 7.67 – 7.62 (m, 2H), 7.49 – 7.46 (m, 1H), 7.34 – 7.32 (m, 1H), 7.25 – 7.22 (m, 2H), 6.54 (d, *J* = 10.1 Hz, 1H), 5.05 – 4.99 (m, 1H), 2.44 (s, 3H), 1.64 – 1.56 (m, 1H), 1.34 – 1.24 (m, 3H), 1.17 – 1.11 (m, 1H), 0.77 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3, 148.4, 139.3, 138.0, 136.1, 129.8, 123.1, 121.6, 120.9, 120.0, 119.5, 112.6, 109.9, 66.1, 38.2, 19.6, 13.8, 9.2; HR-MS (ESI) calcd for $[M - H]^-$: $C_{18}H_{19}N_2O$: 279.1503, found: 279.1503; IR (KBr): 3690, 3062, 2956, 2868, 1867, 1747, 1730, 1515, 1361, 1222, 780, 741 cm^{-1}.

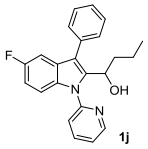


1-(5-Methyl-3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1h)[9]: colorless oily liquid; 940 mg, 88% yield; ^1H NMR (500 MHz, $CDCl_3$) δ 8.63 – 8.60 (m, 1H), 8.04 – 8.00 (m, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.63 (dd, *J* = 8.0, 1.1 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.39 – 7.36 (m, 1H), 7.11 (dd, *J* = 8.5, 1.2 Hz, 1H), 6.43 (d, *J* = 10.5 Hz, 1H), 4.96 – 4.91 (m, 1H), 2.46 (s, 3H), 1.50 – 1.41 (m, 1H), 1.23 – 1.10 (m, 2H), 1.06 – 0.96 (m, 1H), 0.61 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 148.6, 139.4, 138.5, 134.5, 134.4, 131.1, 130.5, 128.8, 128.5, 126.9, 125.0, 121.8, 120.1, 120.0, 119.9, 109.8, 66.7, 37.9, 21.4, 19.4, 13.7; HR-MS [ESI-MS(-)] calcd for $[M - H]^-$: $C_{24}H_{23}N_2O$: 355.1816, found: 355.1816; IR (KBr): 3565, 3064, 2959, 1867, 1747, 1681, 1516, 1506, 1372, 1261, 1100, 799, 744 cm^{-1}.

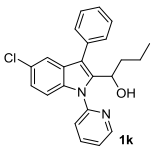


1-(5-Methoxy-3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1i)[9]: colorless oily liquid; 770 mg, 69% yield; ^1H NMR (500 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 5.0, 1.2 Hz, 1H), 8.04 – 8.00 (m, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.38 – 7.36 (m, 1H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.92 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.44 (s, 0.81H), 4.92 (t, *J* = 7.5 Hz, 1H), 3.84 (s, 3H), 1.49 – 1.39 (m, 1H), 1.23 – 1.12 (m, 2H), 1.02 (m, 1H), 0.61 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5, 152.2, 148.6, 139.4, 139.0, 134.4, 131.1, 130.4, 129.1, 128.6,

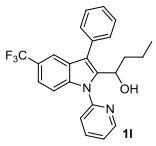
126.9, 121.8, 119.9, 119.9, 113.3, 110.9, 102.0, 66.7, 55.9, 37.9, 19.4, 13.6; HR-MS [ESI-MS(+)] calcd for [M + H]$^+$: $C_{24}H_{25}N_2O_2$: 373.1911, found: 373.1902; IR (KBr): 3260, 3036, 3011, 2988, 2953, 2863, 1473, 1441, 1206, 1150, 1069, 965, 703, 521 cm^{-1}.



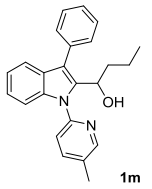
1-(5-Fluoro-3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1j)[9]: colorless solid; 972 mg, 90% yield; m.p. 94.3-95.9 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 4.9, 1.1 Hz, 1H), 8.03 – 8.00 (m, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.37 (m, 3H), 7.28 (dd, *J* = 9.3, 2.5 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.28 (d, *J* = 10.5 Hz, 1H), 4.94 – 4.89 (m, 1H), 1.45 – 1.35 (m, 1H), 1.20 – 1.10 (m, 2H), 1.04 – 0.95 (m, 1H), 0.59 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0 (d, *J* = 238.1 Hz, $^1J_{CF}$), 152.0, 148.8, 140.0, 139.6, 133.8, 132.7, 130.3, 129.2 (d, *J* = 10.1 Hz, $^3J_{CF}$), 128.7, 127.1, 122.3, 120.1, 119.9, 111.6 (d, *J* = 26.5 Hz, $^2J_{CF}$), 110.9 (d, *J* = 8.8 Hz, $^3J_{CF}$), 105.4 (d, *J* = 23.9 Hz, $^2J_{CF}$), 66.6, 37.7, 19.4, 13.6; HR-MS [ESI-MS(+)] calcd for [M + H]$^+$: $C_{23}H_{22}N_2OF$: 361.1711, found: 361.1761; IR (KBr): 3379, 3305, 3082, 2961, 2927, 2866, 1588, 1472, 1444, 1370, 1137, 1024, 811, 774, 700 cm^{-1}.



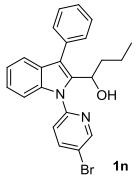
1-(5-Chloro-3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1k)[9]: white solid; 959 mg, 85% yield; m.p. 102.4-104.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.8 Hz, 1H), 8.05 (t, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.58 (m, 3H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.46 – 7.38 (m, 3H), 7.22 (d, *J* = 8.8 Hz, 1H), 6.29 (d, *J* = 10.5 Hz, 1H), 4.94 (dd, *J* = 17.8, 7.6 Hz, 1H), 1.43 (dd, *J* = 17.1, 8.3 Hz, 1H), 1.23 – 1.11 (m, 2H), 1.02 (dd, *J* = 16.8, 7.7 Hz, 1H), 0.62 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 148.8, 139.7, 139.6, 134.6, 133.6, 130.3, 129.7, 128.7, 127.2, 123.7, 122.4, 120.1, 119.8, 119.5, 111.1, 66.6, 37.7, 19.4, 13.7; HR-MS [ESI-MS(+)] calcd for [M - H]$^-$: $C_{23}H_{20}ClN_2O$: 375.1270, found: 375.1269; IR (KBr): 3352, 3053, 2955, 2862, 1866, 1747, 1472, 1442, 1368, 1262, 1042, 1016, 799, 704 cm^{-1}.



1-(3-Phenyl-1-(pyridin-2-yl)-5-(trifluoromethyl)-1H-indol-2-yl)butan-1-ol (1l)[9]: colorless oily liquid; 1033 mg, 84% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 – 8.67 (m, 1H), 8.10 – 8.07 (m, 1H), 7.95 – 7.92 (m, 1H), 7.73 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.64 – 7.60 (m, 2H), 7.58 – 7.54 (m, 3H), 7.51 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.48 – 7.43 (m, 2H), 6.16 (d, *J* = 10.4 Hz, 1H), 4.99 – 4.94 (m, 1H), 1.47 – 1.40 (m, 1H), 1.22 – 1.13 (m, 2H), 1.06 – 0.98 (m, 1H), 0.62 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 149.0, 140.2, 139.7, 137.7, 133.3, 130.4, 128.8, 128.1, 127.4, 125.0 (d, *J* = 272.7 Hz, $^1J_{CF}$), 124.0 (d, *J* =32.3 Hz, $^2J_{CF}$), 122.8, 120.4, 120.3, 120.2 (q, *J* = 4.0 Hz, $^3J_{CF}$), 118.0 (q, *J* = 5.0 Hz, $^3J_{CF}$), 110.4, 66.6, 37.7, 19.4, 13.6; HR-MS [ESI-MS(+)] calcd for [M + H]$^+$: $C_{24}H_{22}F_3N_2O$: 411.1679, found: 411.1673; IR (KBr): 3437, 3056, 2961, 1473, 1442, 1325, 1272, 1162, 1115, 1000, 896, 774, 617 cm^{-1}.

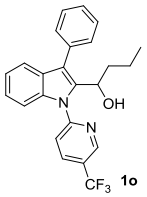


1-(1-(5-Methylpyridin-2-yl)-3-phenyl-1H-indol-2-yl)butan-1-ol (1m)[9]: white solid; 854 mg, 80% yield; m.p. 96.2-97.2 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.2 Hz, 1H), 7.84 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.65 – 7.62 (m, 3H), 7.54 – 7.49 (m, 3H), 7.42 – 7.38 (m, 1H), 7.28 – 7.25 (m, 1H), 7.22 (dd, *J* = 10.9, 4.0 Hz, 1H), 6.37 (d, *J* = 9.0 Hz, 1H), 4.95 (d, *J* = 7.1 Hz, 1H), 2.49 (d, *J* = 6.3 Hz, 3H), 1.50 – 1.41 (m, 1H), 1.21 – 1.12 (m, 2H), 1.06 – 0.97 (m, 1H), 0.62 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 148.7, 140.0, 138.3, 136.3, 134.3, 131.9, 130.4, 128.5, 128.4, 126.8, 123.3, 121.4, 120.3, 119.7, 119.6, 110.0, 66.7, 37.8, 19.4, 18.1, 13.7; HR-MS [ESI-MS(+)] calcd for [M + H]$^+$: $C_{24}H_{25}N_2O$: 357.1961, found: 357.1992; IR (KBr): 3265, 3047, 2954, 2926, 1599, 1484, 1455, 1390, 1219, 1012, 961, 745, 704 cm^{-1}.

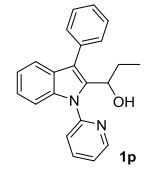


1-(1-(5-Bromopyridin-2-yl)-3-phenyl-1H-indol-2-yl)butan-1-ol (1n)[9]: light yellow solid; 844 mg, 67% yield; m.p. 111.2-112.3 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.71 – 7.61 (m, 4H), 7.53 (dd, *J* = 17.6, 8.4 Hz, 3H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.32 – 7.22 (m, 2H), 5.81 (d, *J* = 10.3 Hz, 1H), 4.96 (dd, *J* = 17.4, 7.7 Hz, 1H), 1.55 – 1.45 (m, 1H), 1.29 –

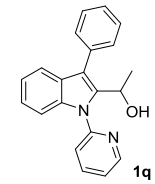
1.13 (m, 2H), 1.10 – 1.00 (m, 1H), 0.65 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 149.8, 142.1, 138.1, 136.2, 134.1, 130.5, 128.7, 128.6, 127.1, 123.9, 122.0, 121.4, 120.7, 120.6, 117.9, 109.9, 66.7, 37.9, 19.5, 13.7; HR-MS [ESI-MS(+)] calcd for $[M + H]^+$: $C_{23}H_{22}BrN_2O$: 421.0910, found: 421.0915; IR (KBr): 3305, 3039, 2953, 2922, 1571, 1454, 1470, 1458, 1034, 1012, 775, 753, 703 cm^{-1}.



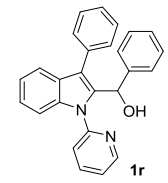
1-(3-Phenyl-1-(5-(trifluoromethyl)pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1o)[9]: coloress solid; 935 mg, 76% yield; m.p. 72.8-73.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, J = 0.8 Hz, 1H), 8.27 (dd, J = 8.5, 2.3 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.54 (dd, J = 15.0, 7.7 Hz, 3H), 7.45 – 7.41 (m, 1H), 7.34 – 7.30 (m, 1H), 7.28 (s, 1H), 5.85 (d, J = 10.3 Hz, 1H), 4.98 – 4.93 (m, 1H), 1.53 – 1.44 (m, 1H), 1.27 – 1.14 (m, 2H), 1.08 – 1.01 (m, 1H), 0.63 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 146.0 (q, J = 4.0 Hz, $^3J_{CF}$), 138.2, 136.7 (q, J = 4.0 Hz, $^3J_{CF}$), 136.1, 133.7, 130.4, 129.0, 128.7, 127.3, 124.2, 124.1 (q, J = 24.2 Hz, $^2J_{CF}$), 123.3 (d, J = 272.7 Hz, $^1J_{CF}$), 122.4, 121.6, 120.8, 119.7, 109.9, 66.7, 38.0, 19.4, 13.6; HR-MS [ESI-MS(-)] calcd for $[M - H]^-$: $C_{24}H_{20}F_3N_2O$: 409.1533, found: 409.1533; IR (KBr): 3364, 3052, 2956, 2867, 1602, 1489, 1456, 14325, 1169, 1133, 1081, 1019, 749, 702 cm^{-1}.



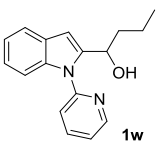
1-(3-Phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)propan-1-ol (1p)[9]: colorless liquid; 925 mg, 94% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 – 8.58 (m, 1H), 8.05 – 8.01 (m, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.67 (dd, J = 15.0, 7.4 Hz, 3H), 7.54 (t, J = 7.8 Hz, 3H), 7.46 – 7.35 (m, 2H), 7.31 – 7.27 (m, 1H), 7.24 (t, J = 7.4 Hz, 1H), 6.38 (d, J = 10.4 Hz, 1H), 4.87 (dd, J = 18.0, 7.9 Hz, 1H), 1.56 – 1.43 (m, 1H), 1.28 – 1.21 (m, 1H), 0.68 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 148.7, 139.4, 138.2, 136.2, 134.3, 130.5, 128.6, 126.9, 123.5, 122.0, 121.6, 120.4, 120.3, 120.2, 110.0, 68.4, 28.8, 10.7; HR-MS [ESI-MS(+)] calcd for $[M + H]^+$: $C_{22}H_{21}N_2O$: 329.1648, found: 329.1669; IR (KBr): 3674, 3026, 2967, 2922, 2869, 1867, 1588, 1471, 1439, 1222, 1091, 1962, 741, 703 cm^{-1}.



1-(3-Phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)ethan-1-ol (1q)[9]: light yellow solid; 829 mg, 88% yield; m.p. 148.5-150.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 – 8.63 (m, 1H), 8.06 – 8.02 (m, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.65 (dd, J = 8.0, 1.1 Hz, 2H), 7.55 (dd, J = 8.0, 3.5 Hz, 3H), 7.44 – 7.38 (m, 2H), 7.30 – 7.27 (m, 1H), 7.25 – 7.22 (m, 1H), 6.52 (s, 1H), 5.20 (s, 1H), 1.15 (d, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 148.7, 139.4, 139.3, 136.2, 134.2, 130.5, 128.6, 128.5, 127.0, 123.6, 122.0, 121.7, 120.5, 120.3, 119.1, 110.0, 62.4, 22.2; HR-MS [ESI-MS(+)] calcd for $[M + H]^+$: $C_{21}H_{19}N_2O$: 315.1492, found: 315.1510; IR (KBr): 3211, 3025, 2959, 1867, 1747, 1730, 1506, 1539, 1361, 1224, 094, 1018, 771, 748 cm^{-1}.

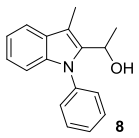


Phenyl(3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)methanol (1r)[9]: white power; 948 mg, 84% yield; m.p. 167.0-168.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (dd, J = 5.0, 1.2 Hz, 1H), 7.87 – 7.78 (m, 3H), 7.66 – 7.62 (m, 1H), 7.57 (t, J = 7.7 Hz, 2H), 7.49 (dd, J = 7.0, 1.5 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.33 – 7.25 (m, 3H), 7.13 – 7.05 (m, 3H), 7.00 (dd, J = 16.2, 9.3 Hz, 3H), 6.94 (t, J = 7.2 Hz, 1H), 6.27 (d, J = 11.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.5, 148.1, 142.8, 138.8, 138.3, 136.2, 134.0, 130.3, 128.8, 128.1, 127.4, 127.2, 126.1, 125.2, 123.8, 121.7, 121.6, 121.2, 120.6, 120.2, 110.2, 67.4; HR-MS [ESI-MS(+)] calcd for $[M + H]^+$: $C_{26}H_{21}N_2O$: 377.1648, found: 377.1675; IR (KBr): 3409, 3026, 2927, 1589, 1488, 1434, 1367, 1149, 1039, 774, 756, 609 cm^{-1}.



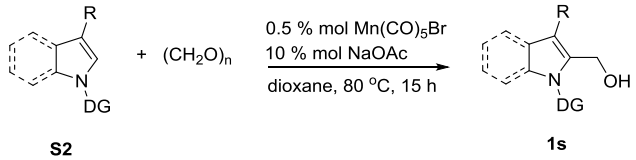
1-(1-(Pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1w)[9]: white solid; 758 mg, 95% yield; m.p. 60.7-63.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 4.8 Hz, 1H), 7.98 (t, J = 7.7 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.51 (d, J = 7.6 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.23 (p, J = 7.2 Hz, 2H), 6.71 (s, 1H), 6.11 (d, J = 2.1 Hz, 1H), 4.63 (s, 1H), 2.10 – 1.98 (m, 1H), 1.95 – 1.84 (m, 1H), 1.65 – 1.56 (m, 1H), 1.54 – 1.39 (m, 1H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 148.7, 143.9, 139.1, 136.6, 128.8, 122.8, 121.7, 121.3, 121.3, 120.1, 110.3, 102.8, 65.7, 36.4, 19.7, 14.1; HR-MS

[ESI-MS(-)] calcd for [M - H]$^-$: $C_{17}H_{17}N_2O$: 265.1346, found: 265.1345; IR (KBr): 3317, 3059, 2955, 2922, 2867, 1591, 1474, 1454, 1345, 1154, 1031, 1021, 803, 746, 523 cm^{-1}.


8

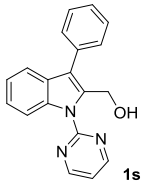
1-(3-Methyl-1-phenyl-1H-indol-2-yl)ethan-1-ol (8)[9]: light yellow power; 685 mg, 91% yield; m.p. 122.3-124.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 1H), 7.58 – 7.48 (m, 3H), 7.41 (d, *J* = 7.0 Hz, 2H), 7.22 – 7.16 (m, 2H), 7.04 (dd, *J* = 6.1, 2.8 Hz, 1H), 5.06 (q, *J* = 6.7 Hz, 1H), 2.56 (s, 3H), 1.56 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.3, 137.8, 129.5, 128.9, 128.8, 128.1, 122.3, 119.8, 118.6, 110.3, 109.0, 63.6, 22.9, 9.1; HR-MS [ESI-MS(+)] calcd for [M + H]$^+$: $C_{17}H_{18}NO$: 252.1383, found: 252.1374; IR (KBr): 3436, 3067, 2966, 1923, 1637, 1498, 1454, 1370, 1110, 1070, 760, 742, 700 cm^{-1}.

2. Procedure for the synthesis of primary alcohol 1s and 1x

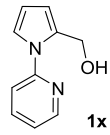


S2 1s

The alcohol **1s** and **1x** was prepared from **S2**, which were synthesized according to the previous literature [4,10]. To a pressure tube (35 mL) equipped with a stirring bar were added [$Mn(CO)_5Br$] (2 mg, 0.005 mmol), $(CH_2O)_n$ (90.0 mg, 3.0 mmol), NaOAc (8.0 mg, 0.10 mmol) and **S2** (1.0 mmol) under air. The reaction vessel was evacuated and backfilled with argon for three times. Dioxane (1.0 mL) was added under an argon atmosphere, the tube was sealed and the reaction was stirred for 15 h at 80 ℃. The mixture was cooled to room temperature and concentrated afterwards. Purification by column chromatography on silica gel (petroleum ether /ethyl acetate=15:1) afforded the pure desired product **1s** and **1x**.

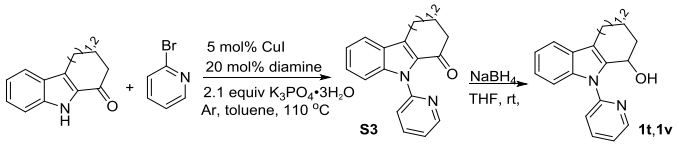

1s

(3-Phenyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)methanol (1s)[9]: light yellow power; 200 mg, 66% yield; m.p. 138.1-138.9 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.9 Hz, 2H), 8.59 (d, *J* = 8.4 Hz, 1H), 7.75 (dd, *J* = 8.1, 1.3 Hz, 3H), 7.58 (dd, *J* = 10.5, 4.7 Hz, 2H), 7.49 – 7.38 (m, 2H), 7.35 – 7.28 (m, 1H), 7.15 (t, *J* = 4.9 Hz, 1H), 5.50 (t, *J* = 7.3 Hz, 1H), 4.74 (d, *J* = 7.3 Hz, 2H);^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 157. 8, 136.1, 135.7, 133.6, 130.2, 128.9, 128.7, 127.3, 124.7, 123.0, 122.8, 120.1, 116.8, 115.1, 55.7; HR-MS [ESI-MS(-)] calcd for [M - H]$^-$: $C_{19}H_{14}N_3O$: 300.1142, found: 300.1142; IR (KBr): 3262, 3042, 2929, 2883, 1565, 1453, 1430, 1268, 1231, 1010, 783, 728 cm^{-1}.


1x

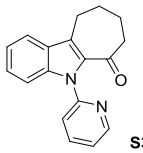
(1-(Pyridin-2-yl)-1H-pyrrol-2-yl)methanol (1x): colorless oil; 100 mg, 57% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 – 8.42 (m, 1H), 7.87 – 7.83 (m, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.09 (dd, *J* = 2.9, 1.7 Hz, 1H), 6.32 (dd, *J* = 3.0, 1.6 Hz, 1H), 6.27 (t, *J* = 3.2 Hz, 1H), 5.86 (t, *J* = 6.9 Hz, 1H), 4.55 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3, 147.8, 139.6, 134.3, 120.8, 120.7, 115.5, 112.5, 110.4, 56.7; HR-MS [ESI-MS(+)] calcd for [M + H]$^+$: $C_{10}H_{11}N_2O$: 175.0866, found: 175.0868; IR (KBr): 3671, 2922, 2860, 1593, 1553, 1480, 1442, 1334, 1285, 1213, 1162, 1111, 1010, 948, 879, 783, 712 cm^{-1}.

3. Procedure for the synthesis of primary alcohols 1t and 1v



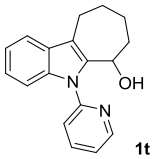
S3 1t,1v

General Procedure for the Synthesis of Arylalkylketone S3: Indoles (3.0 mmol) was coupled with 2-bromopyridine (569 mg, 3.6 mmol) using K_3PO_4 $3H_2O$ (1.68 g, 6.3 mmol), CuI (29 mg, 1.5 mmol, 5 mol %), and N_1, N_2-dimethylcyclohexane-1,2-diamine (85 mg, 6.0 mmol, 20 mol%). Flash chromatography on silica gel (hexane: ethyl acetate 20:1) provided of the desired prouct **S3**. [8]

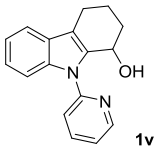


5-(Pyridin-2-yl)-7,8,9,10-tetrahydrocyclohepta[b]indol-6(5H)-one (**S3**)[9]: white solid; 432 mg, 55% yield; m.p. 108.7-110.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 (dd, *J* = 5.0, 1.8 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.30 (m, 4H), 7.26 – 7.21 (m, 1H), 3.19 (dd, *J* = 6.9, 4.9 Hz, 2H), 2.87 (dd, *J* = 7.3, 4.8 Hz, 2H), 2.10 – 1.99 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 152.3, 149.2, 139.4, 138.0, 134.8, 128.3, 127.4, 126.9, 122.2, 121.6, 121.2, 121.0, 111.3, 42.9, 25.8, 24.0, 22.3; HR-MS [ESI-MS(+)] calcd for $[M + H]^+$: $C_{18}H_{17}N_2O$: 277.1335, found: 277.1332; IR (KBr): 3465, 3051, 2926, 2854, 1747, 1704, 1649, 1589, 1468, 1220, 1150, 1135, 1049, 778, 744, 684 cm^{-1}.

General Procedure for the Synthesis of Secondary Alcohol Substrates 1t, 1v: [1] Ketones (1.0 mmol) was dissolved in 20 mL THF, then $NaBH_4$ (5.0 mol) was added in portions, and stirred for 24-48 h at room temperature. The reaction was monitored by TLC to achieve full conversion, then was quenched by saturated NH_4Cl (aq), extracted by EtOAc for three times (3 × 5 mL), dried over Na_2SO_4, and evaporated in vacuum to afford the crude product, which was further purified by flash chromatography on silica gel with petroleum ether/EtOAc (20:1 ~ 5:1) to give the corresponding alcohols**.**

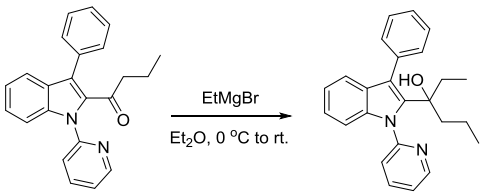


5-(Pyridin-2-yl)-5,6,7,8,9,10-hexahydrocyclohepta[b]indol-6-ol (1t)[9]: white power; 150 mg, 54% yield; m.p. 98.7 – 99.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.6 Hz, 1H), 7.94 – 7.85 (m, 1H), 7.71 – 7.65 (m, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.26 (dd, *J* = 7.9, 4.7 Hz, 3H), 5.61 (s, 1H), 4.97 – 4.85 (m, 1H), 3.16 – 2.93 (m, 2H), 2.43 – 2.18 (m, 3H), 2.05 (t, *J* = 12.9 Hz, 1H), 1.97 – 1.85 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 148.9, 139.4, 138.9, 135.3, 129.3, 123.0, 121.5, 120.9, 120.2, 119.3, 117.9, 110.0, 65.0, 32.1, 27.6, 23.1, 23.1; HR-MS [ESI-MS(+)] calcd for $[M + H]^+$: $C_{18}H_{19}N_2O$: 279.1492, found: 279.1490; IR (KBr): 3451, 2928, 1634, 1591, 1475, 1457, 1367, 1218, 1095, 1002, 775, 739 cm^{-1}.



9-(Pyridin-2-yl)-2,3,4,9-tetrahydro-1H-carbazol-1-ol (1v)[9] : white power; 180 mg, 68% yield; m.p.105.2 – 107.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.96 – 7.92 (m, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.55 (m, 2H), 7.30 – 7.22 (m, 3H), 6.25 (s, 1H), 4.76 (s, 1H), 3.03 – 2.92 (m, 1H), 2.75 – 2.62 (m, 1H), 2.33 – 2.13 (m, 2H), 2.02 – 1.87 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 148.6, 139.0, 137.7, 135.5, 128.7, 123.2, 121.1, 120.7, 119.4, 118.5, 115.2, 110.4, 60.5, 31.0, 21.5, 18.0; HR-MS [ESI-MS(+)] calcd for $[M + H]^+$: $C_{17}H_{17}N_2O$: 265.1335, found: 265.1331; IR (KBr): 3296, 2946, 2920, 2852, 1590, 1474, 1444, 1371, 1308, 1227, 1168, 983, 756, 743 cm^{-1}.

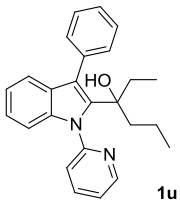
4. Procedure for the synthesis of primary alcohols 1u



10 **1u**

General Procedure for the Synthesis of Tertiary Alcohol Substrates 1u

Ketones **10** (1.0 mmol) was dissolved in anhydrous diethyl ether (10 mL) in an oven dried round bottom flask under Ar environment. The solution was then cooled to 0 ℃ and a solution of vinylmagnesium bromide in THF (2.0 mL, 2.0 mmol, 1.0 M) was added dropwise. The reaction was warmed to RT and stirred overnight. then was quenched by saturated NH_4Cl (aq), extracted by EtOAc for three times (3 × 5 mL), dried over Na_2SO_4, and evaporated in vacuum to afford the crude product, which was further purified by flash chromatography on silica gel with petroleum ether/EtOAc (50:1 ~ 10:1) to give the corresponding alcohols**.**

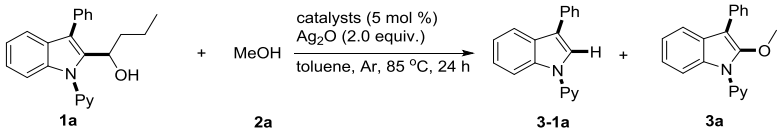


1u

3-(3-Phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)hexan-3-ol (1u) : white soild; 320 mg, 86% yield; m.p.139.0 – 140.4 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 4.6, 1.5 Hz, 1H), 7.96 – 7.93 (m, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.38 (m, 6H), 7.11 (dd, *J* = 11.9, 4.4 Hz, 2H), 7.07 – 7.04 (m, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 3.81 (s, 1H), 1.74 (dd, *J* = 14.2, 7.3 Hz, 1H), 1.50 (dd, *J* = 14.2, 7.2 Hz, 1H), 1.39 – 1.34 (m, 1H), 1.27 (s, 1H), 0.90 – 0.83 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H), 0.69 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 149.2, 140.2, 138.8, 137.5, 136.3, 131.1, 130.3, 128.0, 127.1, 123.2, 123.0, 122.6, 120.7, 119.5, 117.5, 109.8, 77.4, 42.9, 34.2, 17.3, 14.2, 8.3. HR-MS [ESI-MS(+)] calcd for $[M + H]^+$: $C_{25}H_{27}N_2O$: 371.2118, found: 371.2117; IR (KBr): 3621, 3152, 3076, 2960, 2928, 2872, 1730, 1585, 1548, 1466, 1384, 1356, 1306, 1233, 1186, 1095, 1015, 846, 744, 704 cm^{-1}.

III. Optimization of Reaction Conditions

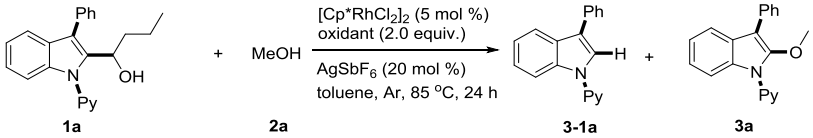
Table S1. Catalyst screening for the cross-coupling reaction of α-indolyl alcohol 1a with methanol 2a[a]



entry	catalysts	yield **3-1a**/**3a**(%)[b]
1	$[Cp^*IrCl_2]_2/AgSbF_6$	0/0
2	$Cp^*Co(CO)I_2/AgSbF_6$	0/0
3	$Mn(CO)_5Br$	26/0
4	$[Rh(cod)Cl]_2$	68/0
5	$[Cp^*RhCl_2]_2/AgSbF_6$	43/15

[a]The mixture of α-indolyl alcohol **1a** (0.10 mmol), **2a** (0.5 mL), $AgSbF_6$ (20 mol %), and Ag_2O (0.2 mmol) with catalysts (5 mol %) in toluene (0.5 mL) was striired at 85 ˚C for 24 h under Ar atmosphere in a sealed tube, followed by flash chromatography on SiO_2. [b]Isolated yield.

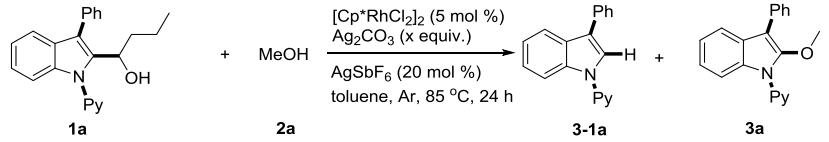
Table S2. Oxidant screening for the cross-coupling reaction of α-indolyl alcohol 1a with Methanol 2a[a]



entry	oxidant	yield **3-1a**/**3a** (%)[b]
1	MnO_2	31/5%
2	$AgOA_C$	37/trace
3	$AgNO_3$	0/0
4	Ag_2O	43/15
5	$AgClO_4$	0/0
6	$AgOCOCF_3$	0/0
7	Ag_2CO_3	38/42
8	$PhI(OAc)_2$	0/0
9	$Cu(OAc)_2$	0/0

[a]The mixture of α-indolyl alcohol **1a** (0.10 mmol), **2a** (0.5 mL), $AgSbF_6$ (20 mol %), and oxidant (0.2 mmol) with $[Cp^*RhCl_2]_2$ (5 mol %) in toluene (0.5 mL) was stirred at 85 ˚C for 24 h under Ar atmosphere in a sealed tube, followed by flash chromatography on SiO_2. [b]Isolated yield.

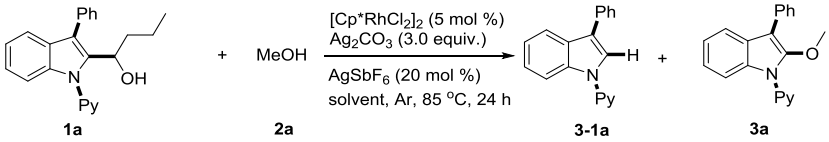
Table S3. The dosage of Ag_2CO_3 screening for the cross-coupling reaction of α-indolyl alcohol 1a with methanol 2a[a]



entry	Ag_2CO_3(x equiv.)	yield **3-1a**/**3a**(%)[b]
1	1	61/trace
2	2	38/42
3	2.5	trace/69
4	3	0/73
5	3.5	0/72

[a]The mixture of α-indolyl alcohol **1a** (0.10 mmol), **2a** (0.5 mL), $AgSbF_6$ (20 mol %), and Ag_2CO_3 (x equiv.) with $[Cp^*RhCl_2]_2$ (5 mol %) in toluene (0.5 mL) was stirred at 85 ˚C for 24 h under Ar atmosphere in a sealed tube, followed by flash chromatography on SiO_2. [b]Isolated yield.

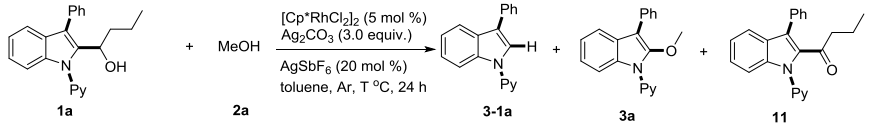
Table S4. Various solvents screening for the cross-coupling reaction of α-indolyl alcohol 1a with methanol 2a[a]



entry	solvent	yield **3-1a** /**3a** (%)[b]
1	THF	0/60
2	CH_3CN	0/0
3	1,4-dioxane	0/0
4	MeOH	trace/40
5	DMF	0/0
6	DCE	0/0
7	Toluene	0/73
8	n-Hexane	10/33
9	Cyclohexane	0/57
10	Benzotrifluoride	0/51

[a]The mixture of α-indolyl alcohol **1a** (0.10 mmol), **2a** (0.5 mL), $AgSbF_6$ (20 mol %), and Ag_2CO_3 (0.3 mmol) with $[Cp^*RhCl_2]_2$ (5 mol %) in solvent (0.5 mL) was stirred at 85 ˚C for 24 h under Ar atmosphere in a sealed tube, followed by flash chromatography on SiO_2. [b]Isolated yield.

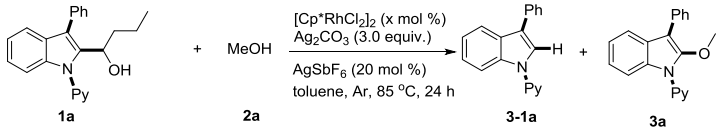
Table S5. The effect of the reaction temperature for the cross-coupling reaction of α-indolyl alcohol 1a with methanol 2a[a]



entry	T(^{o}C)	yield **3-1a** /**3a** /**11** (%)[b]
1	60	31/45/0
2	85	0/73/0
3	100	0/0/65

[a]The mixture of α-indolyl alcohol **1a** (0.10 mmol), **2a** (0.5 mL), $AgSbF_6$ (20 mol %), and Ag_2CO_3 (0.3 mmol) with $[Cp^*RhCl_2]_2$ (5 mol %) in toluene (0.5 mL) was stirred at 60-100 ˚C for 24 h under Ar atmosphere in a sealed tube, followed by flash chromatography on SiO_2. [b]Isolated yield.

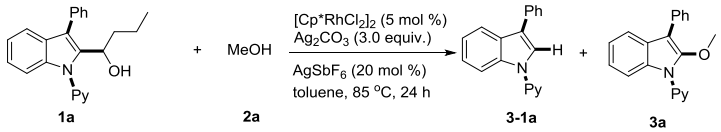
Table S6. The dosage of catalyst screening for the cross-coupling reaction of α-indolyl alcohol 1a with methanol 2a[a]



entry	$[Cp^*RhCl_2]_2$ (x mol%)	yield **3-1a**/**3a**(%)[b]
1	5	0/73
2	2.5	trace/57

[a]The mixture of α-indolyl alcohol **1a** (0.10 mmol), **2a** (0.5 mL), $AgSbF_6$ (20 mol %), and Ag_2CO_3 (0.3 mmol) with $[Cp^*RhCl_2]_2$ (x mol %) in toluene (0.5 mL) was stirred at 85 ˚C for 24 h under Ar atmosphere in a sealed tube, followed by flash chromatography on SiO_2. [b]Isolated yield.

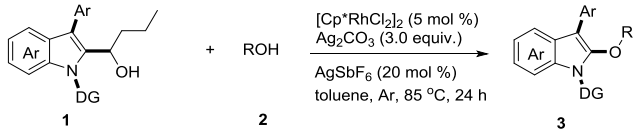
Table S7. The effect of conditions for the cross-coupling reaction of α-indolyl alcohol 1a with methanol 2a[a]



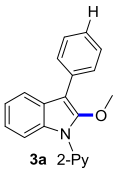
entry	conditions	yield **3-1a**/**3a**(%)[b]
1	Ar	0/73
2	Air	0/69

[a]The mixture of α-indolyl alcohol **1a** (0.10 mmol), **2a** (0.5 mL), $AgSbF_6$ (20 mol %), and Ag_2CO_3 (0.3 mmol) with $[Cp^*RhCl_2]_2$ (x mol %) in toluene (0.5 mL) was stirred at 85 ˚C for 24 h under different gas conditions in a sealed tube, followed by flash chromatography on SiO_2. [b]Isolated yield.

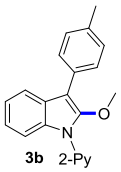
IV. Detail Characterization for the Compounds 3



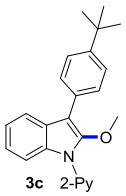
An oven-dried sealed tube charged α-indolyl alcohols **1** (0.10 mmol), alcohols **2** (0.50 mL), $AgSbF_6$ (20 mol %), Ag_2CO_3 (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %) and toluene (0.5 mL) was added under Ar atmosphere. The reaction mixture was then allowed to stir at 85 ℃ for 24 h. After the reaction mixture was cooled down and filtrated, the corresponding filtrate was further concentrated under reduced pressure, followed by flash chromatography on silica gel using ethyl acetate/petroleum ether (1 : 50) as eluent to afford the desired products **3**.



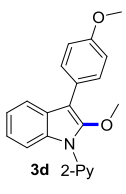
2-Methoxy-3-phenyl-1-(pyridin-2-yl)-1H-indole (3a): The title compound was prepared from α-indolyl alcohol **1a** (34 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow solid; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); m.p. 88.3-92.3 °C; 22 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 4.8, 1.1 Hz, 1H), 7.92-7.88 (m, 1H), 7.75 (dd, *J* = 9.9, 4.5 Hz, 4H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.29 (m, 2H), 7.27 – 7.18 (m, 2H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 149.1, 148.4, 138.2, 133.5, 131.8, 129.1, 128.6, 126.6, 126.2, 122.4, 121.6, 121.5, 120.3, 118.7, 111.5, 101.7, 62.3; HR-MS (ESI) calcd for $[M + H]^+$: $C_{20}H_{17}N_2O$: 301.1335, found: 301,1324; IR (KBr): 3752, 3560, 2919, 2851, 2297, 1458, 1363, 1228, 739, 649 cm^{-1}.



2-Methoxy-1-(pyridin-2-yl)-3-(*p*-tolyl)-1H-indole (3b): The title compound was prepared from α-indolyl alcohol **1b** (36 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 20 mg, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.56 (m, 1H), 7.87 – 7.83 (m, 1H), 7.75 – 7.68 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.23 (m, 3H), 7.22- 7.17 (m, 2H), 3.66 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 149.1, 148.2, 138.1, 135.8, 131.7, 130.4, 129.3, 129.0, 126.8, 122.3, 121.5, 121.4, 120.2, 118.8, 111.5, 101.5, 62.2, 21.3; HR-MS (ESI) calcd for $[M + H]^+$: $C_{21}H_{19}N_2O$: 315.1492, found: 315.1481; IR (KBr): 3713, 3673, 3558, 3027, 2908, 2334, 1750, 1511, 1289, 902, 748 cm^{-1}.

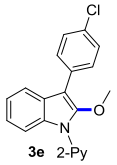


3-(4-(*tert*-Butyl)phenyl)-2-methoxy-1-(pyridin-2-yl)-1H-indole (3c): The title compound was prepared from α-indolyl alcohol **1c** (40 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 19 mg, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 3.9 Hz, 1H), 7.92 – 7.88 (m, 1H), 7.78 (dd, *J* = 6.5, 2.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.31 (dd, *J* = 7.3, 5.0 Hz, 1H), 7.24-7.21 (m, 2H), 3.71 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 149.1, 148.9, 148.3, 138.1, 131.8, 130.4, 128.6, 126.7, 125.4, 122.2, 121.5, 121.4, 120.2, 118.9, 111.4, 101.6, 62.3, 34.6, 31.5; HR-MS (ESI) calcd for $[M + H]^+$: $C_{24}H_{25}N_2O$: 357.1961, found: 357.1951; IR (KBr): 3672, 3566, 3024, 2911, 2379, 1749, 1508, 1288, 905, 834, 745 cm^{-1}.

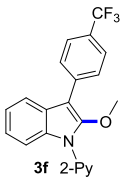


2-Methoxy-3-(4-methoxyphenyl)-1-(pyridin-2-yl)-1H-indole (3d): The title compound was prepared from α-indolyl alcohol **1d** (37 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a brown oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 15 mg, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.78 (d, *J* = 7.4 Hz, 1H), 7.69 (t, *J* = 8.9 Hz, 3H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.26 (m, 1H), 7.27 – 7.17 (m, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 3.91 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 150.4, 149.1, 148.0, 138.1, 131.7, 130.2, 126.9, 125.8, 122.2, 121.5, 121.4, 120.2,

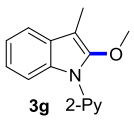
118.6, 114.1, 111.5, 101.2, 62.1, 55.3; HR-MS (ESI) calcd for $[M + H]^+$: $C_{21}H_{19}N_2O_2$: 331.1441, found: 331.1432; IR (KBr): 3714, 3666, 3613, 3567, 2334, 1748, 1515, 1287, 904, 834, 751 cm^{-1}.



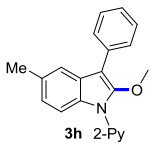
3-(4-Chlorophenyl)-2-methoxy-1-(pyridin-2-yl)-1H-indole (3e): The title compound was prepared from α-indolyl alcohol **1e** (38 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil. R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 20 mg, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.93 – 7.88 (m, 1H), 7.76 (t, *J* = 2.9 Hz, 1H), 7.75 – 7.68 (m, 3H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.33 (dd, *J* = 7.0, 5.3 Hz, 1H), 7.28 – 7.23 (m, 2H), 3.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 149.2, 148.5, 138.2, 132.0, 131.8, 130.2, 129.1, 128.8, 128.6, 126.2, 122.5, 121.8, 121.7, 120.3, 118.5, 111.6, 100.7, 62.3; HR-MS (ESI) calcd for $[M + H]^+$: $C_{20}H_{16}ClN_2O$: 335.0946, found: 335.0936; IR (KBr): 3714, 3666, 3612, 3567, 1747,1563, 1489, 1338, 901, 747 cm^{-1}.



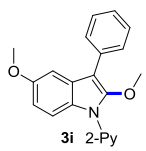
2-Methoxy-1-(pyridin-2-yl)-3-(4-(trifluoromethyl)phenyl)-1H-indole (3f): The title compound was prepared from α-indolyl alcohol **1f** (41 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow solid; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); m.p. 85.4-86.3 ^{o}C ; 20 mg, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.7 Hz, 1H), 7.97 – 7.87 (m, 3H), 7.80 – 7.73 (m, 4H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.36 (dd, *J* = 7.3, 5.0 Hz, 1H), 7.27 (dd, *J* = 6.9, 3.1 Hz, 2H), 3.69 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 149.3, 149.1, 138.3, 137.5, 131.9, 128.8, 128.5 (d, *J* = 222.2 Hz, $^1J_{CF}$), 127.9 (d, *J* = 33.3 Hz, $^2J_{CF}$), 125.8, 125.5 (q, *J* = 4.0 Hz, $^3J_{CF}$), 123.1, 122.7, 121.9 (d, *J* = 8.1 Hz, $^3J_{CF}$), 120.3, 118.5, 111.7, 100.7, 62.5; HR-MS (ESI) calcd for $[M + H]^+$: $C_{21}H_{16}F_3N_2O$: 369.1209, found: 369.1201; IR (KBr): 3699, 2970, 2305, 1457, 1317, 1170, 1110, 741 cm^{-1}.



1-(3-methyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (3g): The title compound was prepared from α-indolyl alcohol **1g** (28 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 16.3 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.53 (m, 1H), 7.90 – 7.72 (m, 2H), 7.54 – 7.51 (m, 2H), 7.30 – 7.20 (m, 3H), 3.85 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 148.9, 148.3, 138.1, 131.8, 128.3, 122.0, 120.9, 119.3, 117.9, 111.5, 96.0, 62.6, 7.4.HR-MS (ESI) calcd for $[M + H]^+$: $C_{15}H_{15}N_2O$: 239.1179, found: 239.1172; IR (KBr): 3652, 3007, 1866, 1747, 1506, 1471, 1434, 1361, 1212, 1065, 741 cm^{-1}.

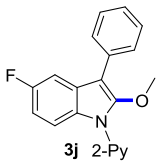


2-Methoxy-5-methyl-3-phenyl-1-(pyridin-2-yl)-1H-indole (3h): The title compound was prepared from α-indolyl alcohol **1h** (36 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 23 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 4.8, 1.0 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.77 (d, *J* = 7.3 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.53 (dd, *J* = 13.3, 5.5 Hz, 3H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.30 (dd, *J* = 7.2, 5.1 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 3.70 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 149.1, 148.5, 138.1, 133.7, 131.0, 130.0, 129.1, 128.5, 126.7, 126.1, 123.7, 121.3, 120.0, 118.6, 111.3, 101.5, 62.3, 21.6; HR-MS (ESI) calcd for $[M + H]^+$: $C_{21}H_{19}N_2O$: 315.1492, found: 315.1481; IR (KBr): 3852, 3698, 3627, 1964, 1570, 1467, 1365, 1238, 975, 745, 503 cm^{-1}.

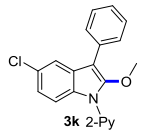


2,5-Dimethoxy-3-phenyl-1-(pyridin-2-yl)-1H-indole (3i): The title compound was prepared from α-indolyl alcohol **1i** (37 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow soild; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); m.p. 95.2-97.3 ^{o}C; 21 mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.1 Hz, 1H), 7.90 – 7.86 (m, 1H), 7.75 (d, *J* = 8.4 Hz, 3H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.52 (t, *J* = 7.6

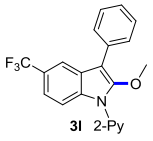
Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.29 (dd, *J* = 7.4, 4.8 Hz, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.87 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 150.5, 149.0, 148.8, 138.1, 133.6, 129.0, 128.6, 127.2, 126.6, 126.2, 121.2, 119.8, 112.7, 111.3, 101.9, 101.6, 62.3, 55.9; HR-MS (ESI) calcd for $[M + H]^+$: $C_{21}H_{19}N_2O_2$：331.1441，found: 331.1439; IR (KBr): 3852, 3730, 3628, 1963, 1563, 1466, 1267, 1200, 968, 907, 968, 743 cm^{-1}.



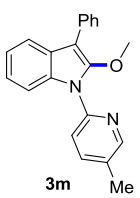
5-Fluoro-2-methoxy-3-phenyl-1-(pyridin-2-yl)-1H-indole (3j): The title compound was prepared from α-indolyl alcohol **1j** (36 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a brown oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 24.8 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.0 Hz, 1H), 7.97 – 7.86 (m, 1H), 7.80 – 7.67 (m, 3H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.41- 7.31 (m, 3H), 6.99 – 6.94 (m, 1H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2 (d, *J* = 237.4 Hz, $^1J_{CF}$), 150.2, 149.3, 149.1, 138.3, 133.0, 128.9, 128.7, 128.0, 127.4 (d, *J* = 10 Hz, $^3J_{CF}$), 126.4, 121.6, 120.0, 112.7 (d, *J* = 9 Hz, $^3J_{CF}$), 110.0 (d, *J* = 25 Hz, $^2J_{CF}$), 104.2 (d, *J* = 24.5 Hz, $^2J_{CF}$), 101.8 (d, *J* = 4.0 Hz, $^4J_{CF}$), 62.2; HR-MS (ESI) calcd for $[M + H]^+$: $C_{20}H_{16}FN_2O$: 319.1241, found: 319.1235; IR (KBr): 3654, 3016, 1573, 1468, 1370, 1264, 976, 740 cm^{-1}.



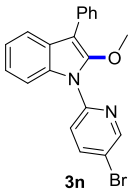
5-Chloro-2-methoxy-3-phenyl-1-(pyridin-2-yl)-1H-indole (3k): The title compound was prepared from α-indolyl alcohol **1k** (38 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 25 mg, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.8 Hz, 1H), 7.91 (t, *J* = 7.8 Hz, 1H), 7.77 – 7.64 (m, 4H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.29 (m, 2H), 7.19 (dd, *J* = 8.7, 1.9 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 149.1, 149.1, 138.3, 132.8, 130.0, 129.1, 128.7, 128.0, 127.2, 126.6, 122.4, 121.8, 120.1, 118.2, 112.9, 101.2, 100.0, 62.3; HR-MS (ESI) calcd for $[M + H]^+$: $C_{20}H_{16}ClN_2O$: 335.0946, found: 335,0936; IR (KBr): 3445, 2923, 2328, 1708, 1640, 1445, 1270, 964, 756 cm^{-1}.



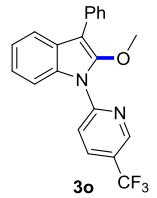
2-Methoxy-3-phenyl-1-(pyridin-2-yl)-5-(trifluoromethyl)-1H-indole (3l): The title compound was prepared from α-indolyl alcohol **1l** (41 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a yellow oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 23 mg, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 4.7, 1.0 Hz, 1H), 7.98 – 7.90 (m, 2H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.49 – 7.45 (m, 1H), 7.42 – 7.35 (m, 2H), 3.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 149.4, 149.2, 138.4, 133.1, 132.6, 129.3, 128.8, 126.8, 126.5, 125.2. (d, *J* = 272.7 Hz, $^1J_{CF}$), 123.8. (d, *J* = 31.3 Hz, $^2J_{CF}$), 122.1, 120.4, 119.0 (q, *J* = 4.0 Hz, $^3J_{CF}$), 116.1 (q, *J* = 4.0 Hz, $^3J_{CF}$), 111.8, 101.7, 62.3; HR-MS (ESI) calcd for $[M + H]^+$: $C_{21}H_{16}F_3N_2O$: 369.1209, found: 369.1197; IR (KBr): 3668, 2454, 1469, 1363, 1318, 1236, 1106, 749 cm^{-1}.



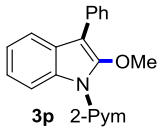
2-Methoxy-1-(5-methylpyridin-2-yl)-3-phenyl-1H-indole (3m): The title compound was prepared from α-indolyl alcohol **1m** (38 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 21 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 1.5 Hz, 1H), 7.77 (d, *J* = 7.4 Hz, 3H), 7.73 – 7.66 (m, 2H), 7.54 – 7.47 (m, 3H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.18 (m, 2H), 3.70 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 148.5, 147.9, 138.8, 133.7, 131.9, 131.4, 129.0, 128.5, 126.5, 126.1, 122.2, 121.4, 119.9, 118.7, 111.2, 101.3, 62.2, 18.1; HR-MS (ESI) calcd for $[M + H]^+$: $C_{21}H_{19}N_2O$: 315.1492, found: 315.1483; IR (KBr): 3714, 3668, 3612, 3566, 2914, 1716, 1514, 1338, 904, 752 cm^{-1}.



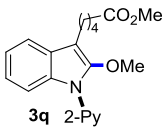
1-(5-Bromopyridin-2-yl)-2-methoxy-3-phenyl-1H-indole (3n): The title compound was prepared from α-indolyl alcohol **1n** (42 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 21 mg, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 2.4 Hz, 1H), 8.00 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.81 (dd, *J* = 6.9, 1.9 Hz, 1H), 7.74 (dd, *J* = 9.1, 4.5 Hz, 3H), 7.52 (dd, *J* = 12.4, 5.2 Hz, 3H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.28 - 7.22 (m, 2H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 149.0, 148.1, 140.7, 133.2, 131.5, 129.1, 128.6, 126.8, 126.4, 122.6, 121.9, 121.1, 118.8, 117.5, 111.7, 102.1, 62.3; HR-MS (ESI) calcd for $[M + H]^+$: $C_{20}H_{16}BrN_2O$: 379.0441, found: 379.0436; IR (KBr): 3738, 2828, 2298, 1716, 1508, 1334, 1266, 837, 743, 630 cm^{-1}.



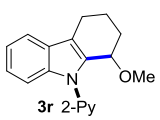
2-Methoxy-3-phenyl-1-(5-(trifluoromethyl)pyridin-2-yl)-1H-indole (3o): The title compound was prepared from α-indolyl alcohol **1o** (41 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 19 mg, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.10 (dd, *J* = 8.6, 2.2 Hz, 1H), 8.05 – 7.97 (m, 1H), 7.83 – 7.68 (m, 4H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.22 (m, 2H), 3.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 148.0, 146,1 (q, *J* = 5.1 Hz, $^3J_{CF}$), 135.3 (q, *J* = 4.4 Hz, $^3J_{CF}$), 132.9, 131.5, 129.2, 128.7, 127.1, 126.6, 123.6 (d, *J* = 272.7 Hz, $^1J_{CF}$), 123.5 (d, *J* = 33.3 Hz, $^2J_{CF}$), 123.0, 122.4, 118.9, 118.8, 112.4, 103.0, 62.4; HR-MS (ESI) calcd for $[M + H]^+$: $C_{21}H_{16}F_3N_2O$: 369.1209, found: 369.1201; IR (KBr): 3712, 3448, 2917, 1716, 1645, 1504, 1326, 957, 750 cm^{-1}.



2-Methoxy-3-phenyl-1-(pyrimidin-2-yl)-1H-indole (3p): The title compound was prepared from α-indolyl alcohol **1s** (30 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.50 (10:1 petroleum ether: ethyl acetate); 20 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 4.8 Hz, 2H), 8.16 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 7.3 Hz, 2H), 7.75 – 7.63 (m, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.23 (m, 3H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 157.0, 149.0, 133.0, 131.7, 129.2, 128.5, 127.1, 126.4, 122.8, 122.3, 118.8, 117.6, 113.0, 104.0, 62.7; HR-MS (ESI) calcd for $[M + H]^+$: $C_{19}H_{16}N_3O$: 302.1288, found: 302.1282; IR (KBr): 3679, 3610, 2950, 2741, 1498, 1461, 1421, 1262, 1068, 908, 804, 743, 703 cm^{-1}.

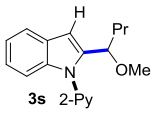


Methyl 5-(2-methoxy-1-(pyridin-2-yl)-1H-indol-3-yl)pentanoate (3q): The title compound was prepared from α-indolyl alcohol **1t** (28 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.40 (10:1 petroleum ether: ethyl acetate); 15 mg, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 3.8 Hz, 1H), 7.88 – 7.83 (m, 1H), 7.78 (dd, *J* = 6.1, 2.9 Hz, 1H), 7.51 (dd, *J* = 9.9, 5.2 Hz, 2H), 7.26 (dd, *J* = 7.3, 4.9 Hz, 1H), 7.22 – 7.14 (m, 2H), 3.77 (s, 3H), 3.68 (s, 3H), 2.79 (t, *J* = 6.6 Hz, 2H), 2.41 (d, *J* = 6.9 Hz, 2H), 1.84 – 1.74 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 150.7, 149.0, 148.3, 138.1, 132.0, 127.4, 122.0, 121.0, 120.9, 119.4, 118.2, 111.5, 100.8, 62.9, 51.5, 34.0, 29.6, 25.0, 22.6; HR-MS (ESI) calcd for $[M + H]^+$: $C_{20}H_{23}N_2O_3$: 339.1703, found: 339.1701; IR (KBr): 3714, 3665, 3613, 3027, 2896, 2336, 1734, 1467, 1265, 909, 742 cm^{-1}.

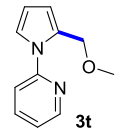


1-Methoxy-9-(pyridin-2-yl)-2,3,4,9-tetrahydro-1H-carbazole (3r): The title compound was prepared from α-indolyl alcohol **1v** (26 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.50 (10:1 petroleum ether: ethyl acetate); 10 mg, 36% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.90 (m, 1H), 7.65 – 7.48 (m, 3H), 7.28 (t, *J* = 6.1 Hz, 1H), 7.26 – 7.13 (m, 2H), 4.84 (t, *J* = 3.6 Hz, 1H), 3.16 (s, 3H), 2.97 – 2.87 (m, 1H), 2.76 – 2.68 (m, 1H), 2.24 – 2.16 (m, 1H), 2.09 – 2.01

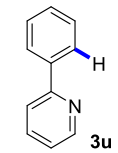
(m, 1H), 1.94 – 1.85 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 149.2, 138.2, 136.9, 134.3, 127.7, 123.1, 121.3, 120.3, 119.9, 119.0, 115.9, 110.8, 70.5, 55.7, 27.3, 21.2, 18.5; HR-MS (ESI) calcd for $[M + H]^+$: $C_{18}H_{19}N_2O$: 279.1492, found: 279.1502; IR (KBr): 3714, 3664, 3613, 2920, 2337, 1792, 1471, 1456, 1438, 1289, 905, 743 cm^{-1}.



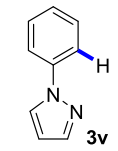
2-(1-Methoxybutyl)-1-(pyridin-2-yl)-1H-indole (3s): The title compound was prepared from α-indolyl alcohol **1w** (27 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.40 (10:1 petroleum ether: ethyl acetate); 10 mg, 33% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 – 8.52 (m, 1H), 7.95 – 7.91 (m, 1H), 7.66 (dd, *J* = 6.4, 2.6 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.22 – 7.15 (m, 2H), 6.71 (s, 1H), 4.79 – 4.68 (m, 1H), 3.26 (s, 3H), 1.84 – 1.75 (m, 2H), 1.46 – 1.39 (m, 2H), 0.86 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 149.6, 141.1, 138.3, 137.7, 128.2, 122.3, 121.5, 120.8, 120.6, 110.4, 102.8, 75.6, 55.7, 37.2, 19.0, 13.9; HR-MS (ESI) calcd for $[M + H]^+$: $C_{18}H_{21}N_2O$: 281.1648，found: 281.1643; IR (KBr): 3827, 3658, 2956, 2319, 1750, 1468, 1215, 1087, 799, 743 cm^{-1}.



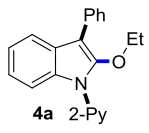
2-(2-(methoxymethyl)-1H-pyrrol-1-yl)pyridine (3t) : The title compound was prepared from (1-(pyridin-2-yl)-1H-pyrrol-2-yl)methanol **1x** (17 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (10:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.50 (10:1 petroleum ether: ethyl acetate); 8 mg, 41% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 – 8.46 (m, 1H), 7.81 – 7.77 (m, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.32 (dd, *J* = 3.0, 1.8 Hz, 1H), 7.22 – 7.16 (m, 1H), 6.39 – 6.35 (m, 1H), 6.27 (t, *J* = 3.2 Hz, 1H), 4.54 (s, 2H), 3.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.9, 138.4, 128.9, 122.3, 121.2, 116.8, 114.1, 109.1, 66.1, 57.0; HR-MS (ESI) calcd for $[M + H]^+$:$C_{11}H_{13}N_2O$, 189.1022, found: 189.1022; IR (KBr): 3677, 2955, 2923, 2854, 1475, 1372, 1331, 1295, 1192, 1081, 1017, 971, 945, 887, 791, 733 cm^{-1}.



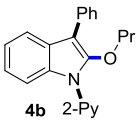
2-Phenylpyridine (3u) [2]: The title compound was prepared from phenyl(2-(pyridin-2-yl)phenyl)methanol **1y** (26 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow liquid; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 11 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.7 Hz, 1H), 8.02 (d, *J* = 7.3 Hz, 2H), 7.78 – 7.71 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.25 – 7.22 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 149.7, 139.4, 136.8, 129.0, 128.8, 126.9, 122.1, 120.6.



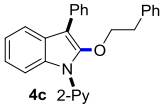
1-Phenyl-1H-pyrazole (3v)[3]: The title compound was prepared from (2-(1H-pyrazol-1-yl)phenyl)(phenyl)methanol **1z** (25 mg, 0.10 mmol) and methanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 11 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.3 Hz, 1H), 7.74 (dd, *J* = 12.4, 4.3 Hz, 3H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 9.2 Hz, 1H), 6.49 (t, *J* = 2.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 140.2, 129.4, 126.8, 126.5, 119.2, 107.6.



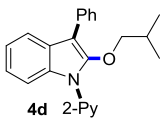
2-Ethoxy-3-phenyl-1-(pyridin-2-yl)-1H-indole (4a): The title compound was prepared from α-indolyl alcohol **1a** (34 mg, 0.10 mmol) and ethanol **2a** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 19 mg, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 3.6 Hz, 1H), 7.90 (s, 1H), 7.80 (d, *J* = 7.1 Hz, 4H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 3.6 Hz, 2H), 3.89 (q, *J* = 6.8 Hz, 2H), 1.10 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 149.1, 147.4, 138.0, 133.7, 131.9, 128.9, 128.6, 126.5, 126.1, 122.3, 121.6, 121.5, 120.4, 118.8, 111.6, 102.4, 71.2, 15.2; HR-MS (ESI) calcd for $[M + H]^+$: $C_{21}H_{19}N_2O$: 315.1492, found: 315.1479; IR (KBr): 3678, 2918, 1747, 1456, 1433, 1338, 1228, 948, 844, 739 cm^{-1}.



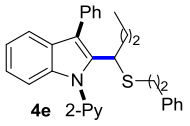
3-Phenyl-2-propoxy-1-(pyridin-2-yl)-1H-indole (4b): The title compound was prepared from α-indolyl alcohol **1a** (34 mg, 0.10 mmol) and n-propanol **2b** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 19 mg, 58% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 3.9 Hz, 1H), 7.85 (t, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 4H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.24 (m, 2H), 7.23 – 7.16 (m, 2H), 3.73 (t, *J* = 6.4 Hz, 2H), 1.45 (dd, *J* = 13.9, 6.9 Hz, 2H), 0.71 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 149.1, 147.6, 138.0, 133.7, 131.8, 129.0, 128.5, 126.5, 126.0, 122.3, 121.6, 121.5, 120.5, 118.7, 111.5, 102.2, 77.0, 22.9, 10.3; HR-MS (ESI) calcd for $[M + H]^+$: $C_{22}H_{21}N_2O$: 329.1648, found: 329.1639; IR (KBr): 3670, 3050, 2922, 1747, 1569, 1460, 1362, 1231, 1181, 1059, 967, 740 cm^{-1}.



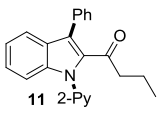
2-Phenethoxy-3-phenyl-1-(pyridin-2-yl)-1H-indole (4c): The title compound was prepared from α-indolyl alcohol **1a** (34 mg, 0.10 mmol) and phenylethyl alcohol **2c** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.50 (10:1 petroleum ether: ethyl acetate); 24 mg, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 4.8, 1.1 Hz, 1H), 7.82 – 7.68 (m, 5H), 7.52 – 7.43 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.19 (m, 6H), 7.02 – 6.97 (m, 2H), 4.05 (t, *J* = 6.9 Hz, 2H), 2.79 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 149.0, 147.2, 137.9, 137.6, 133.5, 131.8, 129.0, 128.9, 128.6, 128.3, 126.5, 126.3, 126.1, 122.3, 121.6, 121.4, 120.4, 118.7, 111.6, 102.2, 75.4, 36.1; HR-MS (ESI) calcd for $[M + H]^+$: $C_{27}H_{23}N_2O$: 391.1805, found : 391.1791; IR (KBr): 3137, 2825, 2334, 1758, 1495, 1265, 907, 742 cm^{-1}.



2-Isobutoxy-3-phenyl-1-(pyridin-2-yl)-1H-indole (4d): The title compound was prepared from α-indolyl alcohol **1a** (34 mg, 0.10 mmol) and isobutyl alcohol **2d** (0.5 mL) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 18 mg, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.67 (m, 1H), 7.93 – 7.87 (m, 1H), 7.79 (d, *J* = 7.6 Hz, 4H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.26 – 7.21 (m, 2H), 3.59 (d, *J* = 6.2 Hz, 2H), 1.80 (dd, *J* = 13.1, 6.6 Hz, 1H), 0.76 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 149.1, 147. 8, 137.9, 133.6, 131.9, 129.1, 128. 5, 127.9, 126.6, 126.0, 122.2, 121.5, 120.7, 118.7, 111.5, 102.1, 81.6, 28.6, 18.9; HR-MS (ESI) calcd for $[M + H]^+$: $C_{23}H_{23}N_2O$: 343.1805, found: 343.1795; IR (KBr): 3749, 3647, 1747, 1455, 1434, 1362, 1230, 1182, 982, 739 cm^{-1}.



2-(1-(phenethylthio)butyl)-3-phenyl-1-(pyridin-2-yl)-1H-indole (4e): The title compound was prepared from α-indolyl alcohol **1a** (34 mg, 0.10 mmol) and 2-phenylethane-1-thiol **2e** (0.5 mL) and was purified by column chromatography (20:1 petroleum ether: ethyl acetate) to give a pale yellow oil; R_f = 0.60 (10:1 petroleum ether: ethyl acetate); 36 mg, 75% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.2 Hz, 1H), 7.86 (t, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.48 (dd, *J* = 16.8, 9.1 Hz, 3H), 7.41 – 7.35 (m, 2H), 7.21 (t, *J* = 7.3 Hz, 2H), 7.19 – 7.11 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 7.3 Hz, 2H), 4.31 (t, *J* = 8.0 Hz, 1H), 2.63 – 2.48 (m, 4H), 1.72 – 1.62 (m, 2H), 1.35 – 1.27 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 149.5, 140.6, 138.2, 137.8, 136.5, 134.9, 130.8, 128.4, 128.4, 128.3, 128.1, 126.9, 126.2, 123.8, 123.2, 122.9, 120.8, 119.4, 118.7, 110.3, 41.3, 36.9, 36.0, 33.6, 21.3, 13.7. HR-MS (ESI) calcd for $[M + H]^+$: $C_{31}H_{31}N_2S$: 463.2202, found: 463.2199; IR (KBr): 3513, 3054, 2937, 2860, 2732, 2068, 1807, 1586, 1455, 1366, 1205, 1006, 921, 745 cm^{-1}.

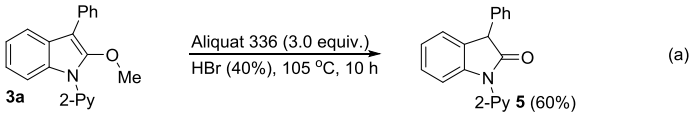


1-(3-Phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-one (11) [4]**:** yellow solid; 22 mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 – 8.58 (m, 1H), 7.97- 7.92 (m, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.52 (m, 5H), 7.50 – 7.46 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.26 – 7.21 (m, 1H), 2.47 (t, *J* = 7.3 Hz, 2H), 1.62 – 1.53 (m, 2H), 0.76 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR

(126 MHz, $CDCl_3$) δ 196.8, 151.8, 149.4, 138.2, 137.8, 134.7, 133.8, 130.4, 128.6, 128.0, 127.8, 126.1, 124.9, 122.3, 121.9, 121.7, 120.9, 110.9, 44.4, 17.8, 13.6.

V. Chemical Transformation of the 3a

a) Removal of the methyl group of 3a [5]

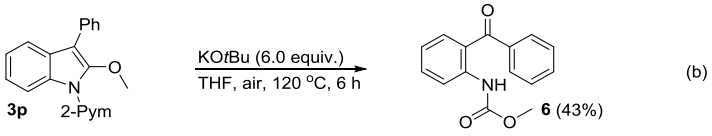


(a)

Aliquat-336 (10 wt. % of **3a**, 6 mg) was added in a single lot to a stirred solution of **3a** (0.2 mmol, 60 mg) and aqueous HBr (40%, 4.5 mmol equiv of **3a**). The resulting reaction mixture was heated at 105 ^oC for 10 h. After completion of the reaction, it was cooled to room temperature and quenched by adding water (5 mL). The resulting reaction mass was extracted with 3 ×5 mL ethyl acetate. The ethyl acetate layer washed twice with 5 mL of water, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether = 1:5 as eluent to afford the desired product **5** (34 mg).

3-Phenyl-1-(pyridin-2-yl)indolin-2-one (5): Pale yellow oil, R_f = 0.40 (5:1 petroleum ether: ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 4.8, 0.9 Hz, 1H), 7.90 – 7.84 (m, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.34 – 7.27 (m, 4H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 4.85 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 149.5, 148.4, 142.6, 138.2, 136.7, 129.0, 128.6, 128.5, 128.3, 127.8, 125.1, 123.7, 122.0, 112.0, 112.7, 52.5; HR-MS (ESI) calcd for $[M + H]^+$: $C_{19}H_{15}N_2O$: 287.1179, found: 287.1173; IR (KBr): 3714, 3665, 3613, 2959, 2334, 1734, 1467, 1334, 1265, 909, 742 cm^{-1}.

b) Removal of the pyrimidine group of 3p[6]



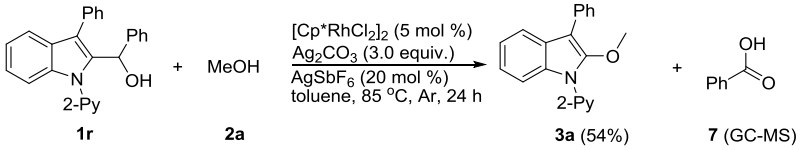
(b)

To an oven-dried sealed tube charged with **3p** (90 mg, 0.3 mmol) and *t*-BuOK (202 mg, 1.8 mmol) followed by addition of anhydrous THF (3 mL) through syringe. After stirring at 120 ^oC for 6 h, saturated NH_4Cl (5 mL) was added and resulting misture was extracted with EtOAc (3 × 5 mL), and the combined organic layers were dried over Na_2SO_4, the solvent was removed in vacuo and the resultant residue was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether = 1:5 as eluent to afford the desired product **6** (33 mg).

2-Methoxy-3-phenyl-1H-indole (6)[11,12]: Pale yellow oil, R_f = 0.60 (10:1 petroleum ether: ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.63 – 7.54 (m, 3H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.08 – 7.03 (m, 1H), 3.81 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.3, 154.3, 140.9, 138.8, 134.2, 133.6, 132.3, 129.8, 128.3, 122.9, 121.1, 119.9, 52.3; HR-MS (ESI) calcd for $[M + H]^+$: $C_{15}H_{14}NO$: 256.0968, found: 256.0969; IR (KBr): 3729, 2923, 1738, 1635, 1584, 1525, 1451, 1319, 1262, 1215, 1065, 924, 753, 699, 642 cm^{-1}.

VI. Control Experiments for the Mechanism Studies

a) Isolation and characterization of benzoic acid 7



To an oven-dried sealed tube charged with **1r** (38 mg, 0.1 mmol), **2a** (0.5 mL), $AgSbF_6$ (20 mol %), Ag_2CO_3 (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %) and toluene (0.5 mL) was added under Ar atmosphere. The reaction mixture was then allowed to stir at 85 ℃ for 24 h. After the reaction, 23 μl (0.1 mmol) of n-dodecane was added as internal standard to determine the yield of the side products **7** (34% yield) by GC-MS. The corresponding reaction mixture was then cooled down and filtrated. The corresponding filtrate was further concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether = 1:50 as eluent to afford the desired product **3a** (16 mg).

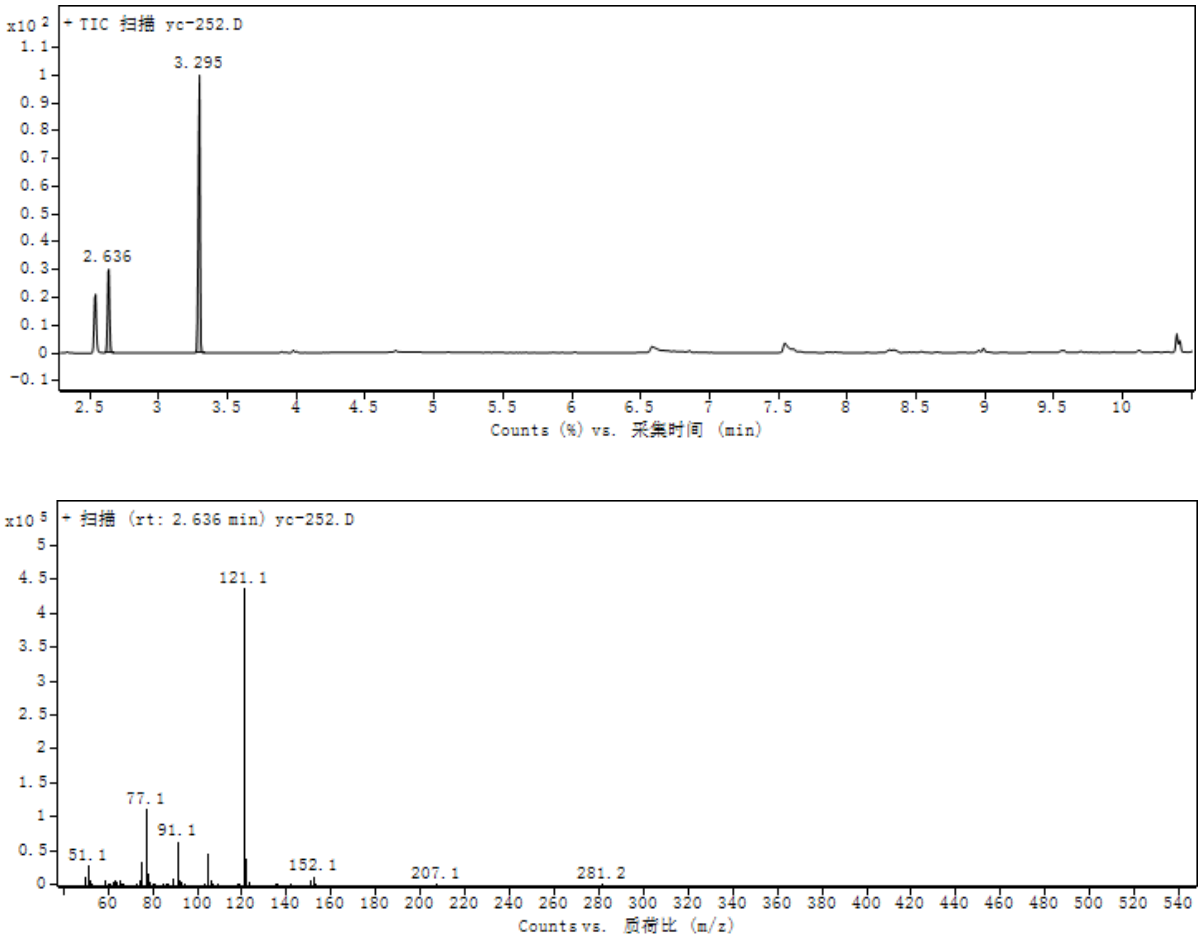
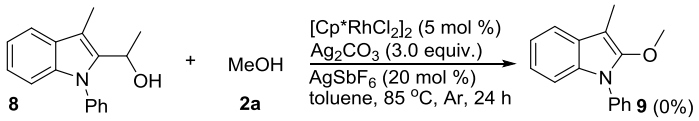


Figure S1. The GC-MS spectra of **7**

Table S8. The GC-MS yield of **7**

RT	Peak	Area	Summation of peak areas %	Peak area percentage	Peak height	Peak width
2.636	1	909217.36	25.55	34.33	862930.76	0.065
3.295	2	2648689.06	74.45	100	2863436.34	0.067

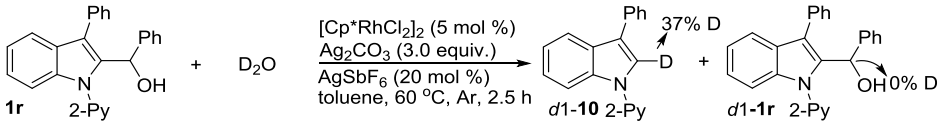
b) The coupling reaction of 1-(3-methyl-1-phenyl-1H-indol-2-yl)ethan-1-ol (8) and Methanol (2a) under standard conditions



To an oven-dried sealed tube charged with **8** (38 mg, 0.1 mmol), **2a** (0.5 mL), $AgSbF_6$ (20 mol %), Ag_2CO_3 (0.3

mmol), $[Cp^*RhCl_2]_2$ (5 mol %) and toluene (0.5 mL) was added under Ar atmosphere. The reaction mixture was then allowed to stir at 85 ℃ for 24 h. The corresponding reaction mixture was then cooled down and filtrated. The corresponding filtrate was further concentrated under reduced pressure. We did not find the formation of the product **9** by TLC and ^{1}H NMR method.

c) The H/D exchange of phenyl (3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)methanol (1r) with D_2O



To an oven-dried sealed tube charged with **1r** (38 mg, 0.1 mmol), $AgSbF_6$ (20 mol %), Ag_2CO_3 (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %) , D_2O (10 mg, 0.5 mmol) and toluene (1 mL) was added under Ar atmosphere. The reaction mixture was then allowed to stir at 60 ℃ for 2.5 h. The corresponding reaction mixture was then cooled down and filtrated. The corresponding filtrate was further concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether = 1:50 as eluent to afford the product *d*1-**10** (37% D) and *d*1-**1r** (0% D).

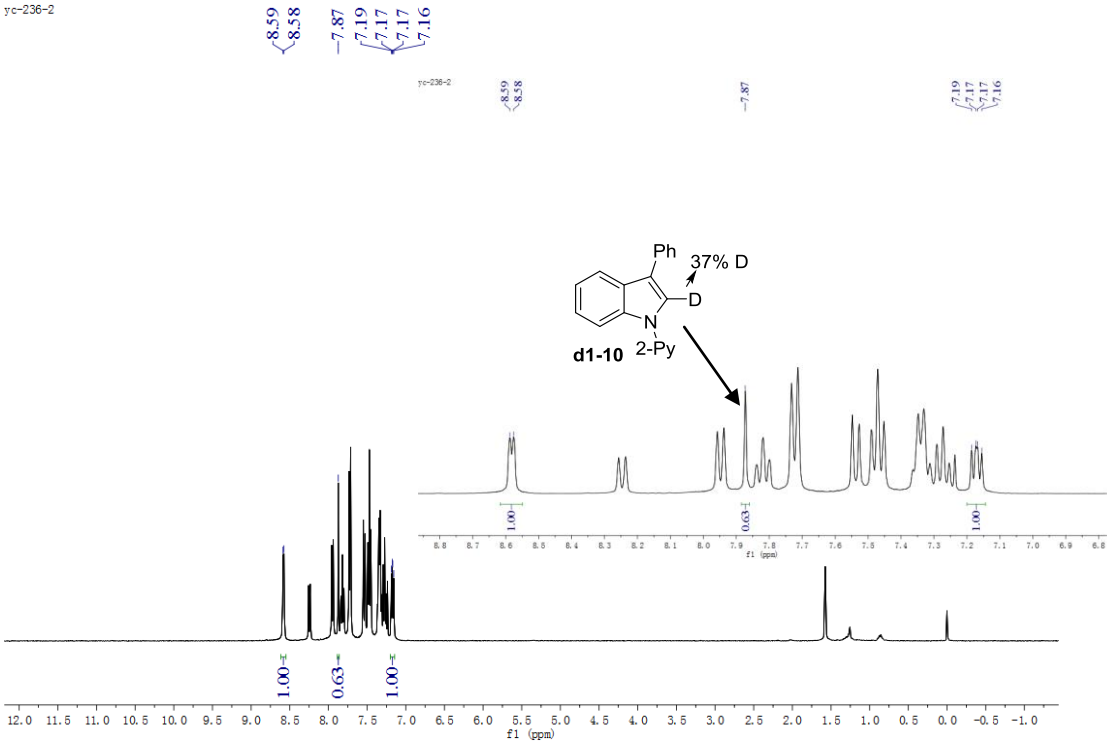


Figure S2. The ^{1}H NMR spectra of *d*1-**10**

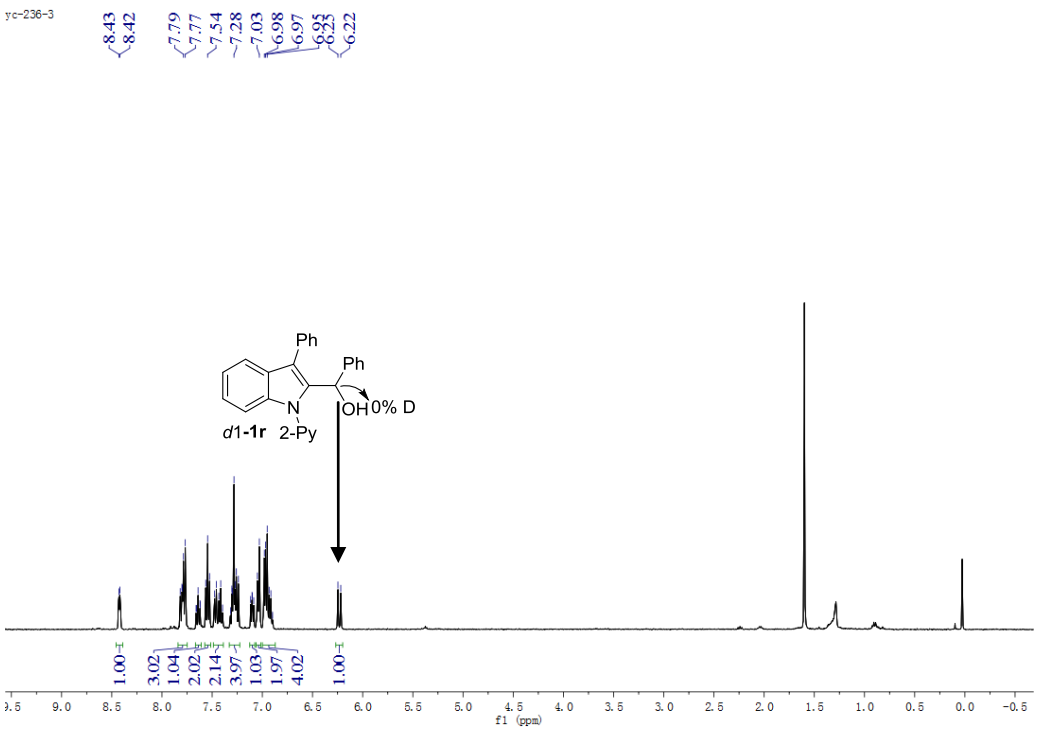
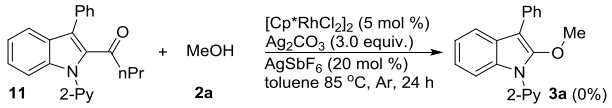


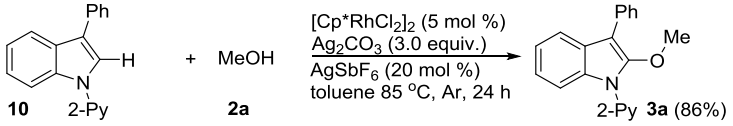
Figure S3. The ^{1}H NMR spectra of *d*1-**1r**

d) The cross-coupling reaction of 1-(3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-one (11) and methanol (2a) under standard conditions



To an oven-dried sealed tube charged with **11** (34 mg, 0.1 mmol), **2a** (0.5 mL), $AgSbF_6$ (20 mol %), Ag_2CO_3 (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %) and toluene (0.5 mL) was added under Ar atmosphere. The reaction mixture was then allowed to stir at 85 ℃ for 24 h. The corresponding reaction mixture was then cooled down and filtrated. The corresponding filtrate was further concentrated under reduced pressure. We did not find the formation of the product **3a** by TLC and ^{1}H NMR method.

e) The cross-coupling reaction of 1-(3-methyl-1-phenyl-1H-indol-2-yl)ethan-1-ol (10) and methanol (2a) under standard conditions



To an oven-dried sealed tube charged with **10** (27 mg, 0.1 mmol), **2a** (0.5mL), $AgSbF_6$ (20 mol %), Ag_2CO_3 (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %) and toluene (0.5 mL) was added under Ar atmosphere. The reaction mixture was then allowed to stir at 85 ℃ for 24 h. The corresponding reaction mixture was then cooled down and filtrated. The corresponding filtrate was further concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether = 1: 50 as eluent to afford the desired product **3a** (26 mg).

VII. Single Crystal Structure and Data

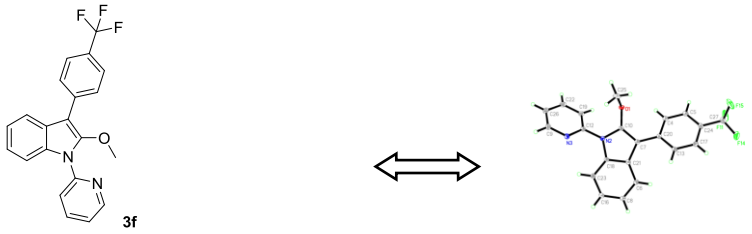


Table S9. Crystal data and structure refinement for 3f.

Identification code	**3f**
Empirical formula	$C_{21}H_{15}F_3N_2O$
Formula weight	368.35
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.1916(8)
b/Å	8.4604(4)
c/Å	15.8473(9)
α/°	90
β/°	104.037(6)
γ/°	90
Volume/$Å^3$	1715.84(17)
Z	4
$\rho_{calc}g/cm^3$	1.426
μ/mm^{-1}	0.111
F(000)	760.0
Crystal size/mm^3	0.24 × 0.22 × 0.19
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/ °	4.608 to 59.016
Index ranges	$-18 \le h \le 15$, $-10 \le k \le 11$, $-21 \le l \le 15$
Reflections collected	8441
Independent reflections	4038 [R_{int} = 0.0243, R_{sigma} = 0.0395]
Data/restraints/parameters	4038/0/245
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0506, wR_2 = 0.1454
Final R indexes [all data]	R_1 = 0.0641, wR_2 = 0.1622
Largest diff. peak/hole / e $Å^{-3}$	0.44/-0.45

Table S10. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3f. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
O1	5423.7(9)	6792.5(13)	589.1(7)	20.2(3)
N2	7080.9(10)	8029.1(15)	890.2(9)	17.7(3)
N3	8532.2(11)	6396.2(17)	993.6(9)	20.2(3)
C4	3823.4(13)	9240.4(19)	800.4(10)	19.1(4)
C5	2850.1(13)	9631(2)	911.3(11)	20.8(4)
C6	6949.1(13)	11895.3(19)	1777.4(10)	18.4(3)
C7	5766.1(12)	9434.3(19)	1236.2(10)	16.5(3)
C8	7945.8(13)	12484(2)	1852.3(11)	20.1(4)
C9	9007.9(14)	5222(2)	667.0(12)	24.5(4)
C10	6029.1(12)	8059.4(19)	890.4(10)	17.1(3)
F11	1050.1(10)	11480(2)	935.1(8)	55.4(4)
C12	7588.4(13)	6815.3(18)	529.7(10)	17.9(3)
C13	4621.3(13)	10809.0(19)	2052.3(11)	19.2(4)
F14	1686.2(10)	12255.8(19)	2221.5(11)	62.1(5)
F15	1220.2(11)	9880.0(16)	1989.6(13)	65.6(5)
C16	8721.9(13)	11570(2)	1629.3(11)	20.7(4)
C17	3643.7(13)	11209(2)	2158.8(11)	21.2(4)
C18	7520.0(12)	9458.1(18)	1241.1(10)	16.5(3)
C19	7096.1(14)	6135(2)	-264.0(11)	23.4(4)
C20	4732.0(12)	9832.9(18)	1365.5(10)	16.5(3)
C21	6715.3(12)	10354.2(19)	1458.9(10)	16.6(3)
C22	7594.8(15)	4911(2)	-570.3(12)	28.3(4)
C23	8526.6(13)	10033.9(19)	1327.1(11)	19.1(3)
C24	2754.2(13)	10623(2)	1587.4(11)	20.4(4)
C25	5567.4(15)	5477(2)	1182.9(12)	29.3(4)
C26	8567.7(15)	4433(2)	-92.8(13)	28.0(4)
C27	1690.1(14)	11052(2)	1679.8(12)	25.0(4)

Table S11. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3f. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	18.3(6)	16.2(6)	23.5(6)	-2.5(5)	0.2(5)	-3.0(4)
N2	14.9(7)	15.5(6)	21.5(7)	-2.0(5)	2.0(5)	-0.2(5)
N3	18.6(7)	19.5(7)	23.4(7)	1.8(6)	6.6(6)	0.9(5)
C4	20.1(8)	19.6(8)	16.7(8)	0.7(6)	2.5(6)	-0.1(6)
C5	17.5(8)	22.6(8)	20.0(8)	3.3(7)	0.2(6)	-1.2(6)
C6	20.5(8)	15.8(8)	18.6(8)	1.4(6)	4.2(6)	0.9(6)
C7	15.5(8)	17.0(7)	15.2(7)	1.3(6)	0.5(6)	-0.3(6)
C8	22.8(8)	16.8(8)	19.5(8)	-0.5(6)	3.0(6)	-3.6(6)

C9	21.9(9)	22.1(9)	32.3(10)	2.8(7)	12.0(7)	2.3(7)
C10	14.2(7)	17.5(8)	17.9(8)	0.3(6)	0.9(6)	-1.8(6)
F11	25.8(7)	100.0(12)	39.9(7)	15.7(7)	7.0(5)	26.4(7)
C12	19.1(8)	16.6(8)	19.0(8)	1.0(6)	6.4(6)	-0.5(6)
C13	16.1(8)	19.8(8)	19.5(8)	1.6(7)	0.1(6)	-1.8(6)
F14	29.6(7)	73.4(10)	85.9(11)	-43.5(9)	18.6(7)	4.0(7)
F15	35.4(8)	47.2(8)	127.7(15)	37.0(9)	46.2(9)	9.7(6)
C16	18.0(8)	22.4(8)	20.8(8)	1.0(7)	2.9(6)	-4.5(6)
C17	22.9(9)	19.4(8)	21.9(8)	-1.0(7)	7.0(7)	-0.6(6)
C18	16.1(8)	15.5(7)	16.3(7)	1.3(6)	0.9(6)	-1.1(6)
C19	23.9(9)	24.0(9)	21.8(8)	-3.3(7)	4.7(7)	-3.7(7)
C20	17.2(8)	14.9(7)	16.9(8)	4.1(6)	3.1(6)	0.1(6)
C21	16.2(8)	17.6(8)	15.1(7)	3.5(6)	1.8(6)	0.5(6)
C22	33.1(10)	28.2(10)	26.1(9)	-8.3(8)	12.0(8)	-8.2(8)
C23	17.0(8)	20.0(8)	19.3(8)	0.8(6)	2.6(6)	0.7(6)
C24	17.8(8)	21.3(8)	22.9(8)	5.0(7)	6.5(7)	2.1(6)
C25	33.4(10)	23.4(9)	27.5(9)	1.6(8)	0.6(8)	-11.9(8)
C26	31.4(10)	21.4(9)	37.4(10)	-5.0(8)	20.5(8)	-1.8(7)
C27	21.1(9)	25.8(9)	29.2(9)	4.8(8)	8.2(7)	2.8(7)

Table S12. Bond Lengths for 3f.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C10	1.3527(19)	C8	C16	1.395(2)
O1	C25	1.440(2)	C9	C26	1.376(3)
N2	C10	1.388(2)	F11	C27	1.324(2)
N2	C12	1.419(2)	C12	C19	1.392(2)
N2	C18	1.396(2)	C13	C17	1.383(2)
N3	C9	1.344(2)	C13	C20	1.402(2)
N3	C12	1.331(2)	F14	C27	1.333(2)
C4	C5	1.378(2)	F15	C27	1.325(2)
C4	C20	1.403(2)	C16	C23	1.387(2)
C5	C24	1.391(2)	C17	C24	1.388(2)
C6	C8	1.384(2)	C18	C21	1.414(2)
C6	C21	1.405(2)	C18	C23	1.390(2)
C7	C10	1.366(2)	C19	C22	1.377(3)
C7	C20	1.467(2)	C22	C26	1.383(3)
C7	C21	1.444(2)	C24	C27	1.491(2)

Table S13. Bond Angles for 3f.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°

C10	O1	C25	114.14(12)	N2	C18	C21	107.33(13)
C10	N2	C12	125.64(13)	C23	C18	N2	129.55(14)
C10	N2	C18	107.59(13)	C23	C18	C21	122.97(14)
C18	N2	C12	126.58(13)	C22	C19	C12	118.12(17)
C12	N3	C9	116.47(15)	C4	C20	C7	120.53(14)
C5	C4	C20	120.74(15)	C13	C20	C4	118.18(15)
C4	C5	C24	120.31(15)	C13	C20	C7	121.29(14)
C8	C6	C21	119.08(15)	C6	C21	C7	133.62(15)
C10	C7	C20	125.95(14)	C6	C21	C18	118.23(14)
C10	C7	C21	105.52(14)	C18	C21	C7	108.02(14)
C21	C7	C20	128.52(14)	C19	C22	C26	119.09(17)
C6	C8	C16	121.26(15)	C16	C23	C18	117.08(15)
N3	C9	C26	123.93(17)	C5	C24	C27	119.09(15)
O1	C10	N2	119.34(14)	C17	C24	C5	119.84(15)
O1	C10	C7	129.10(15)	C17	C24	C27	121.07(15)
C7	C10	N2	111.53(14)	C9	C26	C22	118.41(17)
N3	C12	N2	116.08(14)	F11	C27	F14	105.29(15)
N3	C12	C19	123.89(15)	F11	C27	F15	106.29(16)
C19	C12	N2	120.03(15)	F11	C27	C24	113.01(14)
C17	C13	C20	120.99(15)	F14	C27	C24	113.58(15)
C23	C16	C8	121.37(15)	F15	C27	F14	104.95(16)
C13	C17	C24	119.93(15)	F15	C27	C24	112.98(15)

Table S14. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3f.

Atom	*x*	*y*	*z*	U(eq)
H4	3878.89	8576.87	345.86	23
H5	2254.44	9228.56	532.33	25
H6	6441.11	12511.04	1935.76	22
H8	8101.2	13508.94	2055.01	24
H9	9674.64	4924.95	972.86	29
H13	5214.29	11193.24	2442.23	23
H16	9383.85	11998.92	1684.51	25
H17	3582.08	11869.48	2612.76	25
H19	6448.75	6497.35	-578.33	28
H22	7281.47	4411.72	-1091.22	34
H23	9046.49	9416.58	1188.12	23
H25A	5389.22	4512.91	861.46	44
H25B	5124.82	5606.02	1577.77	44
H25C	6283.97	5434.19	1505.34	44

H26	8916.31	3598.74	-280.73	34

VIII. References

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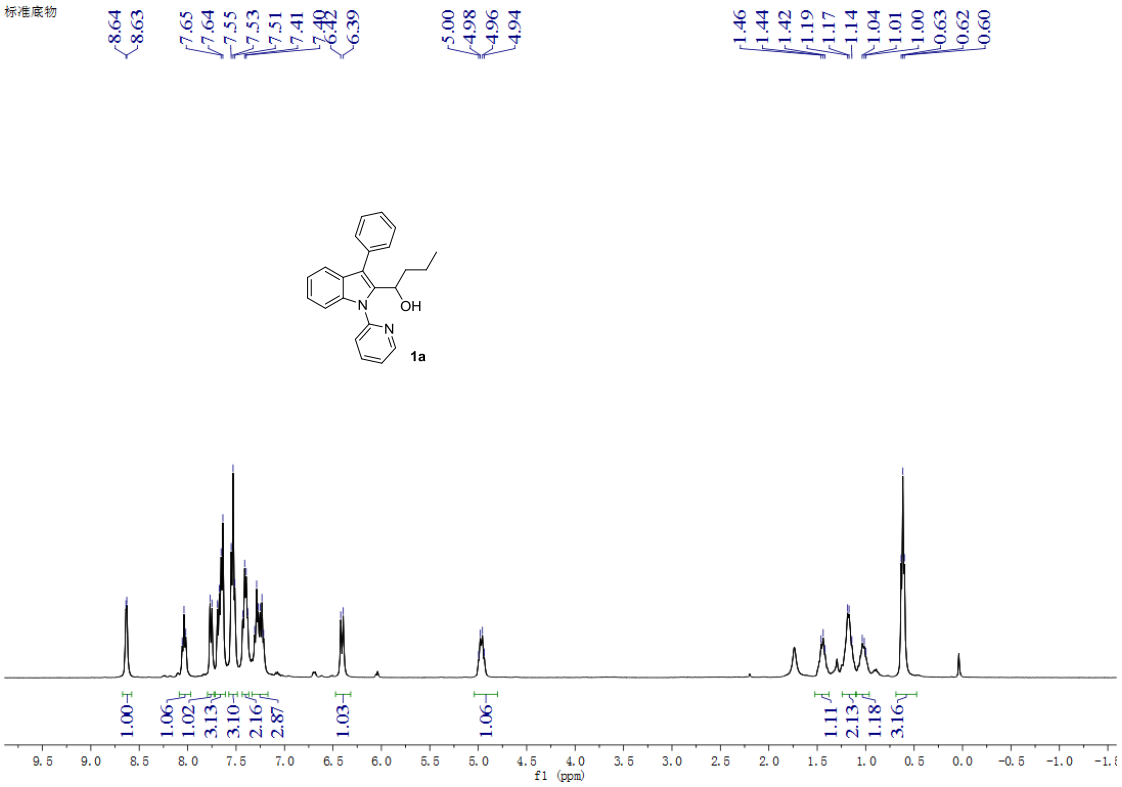
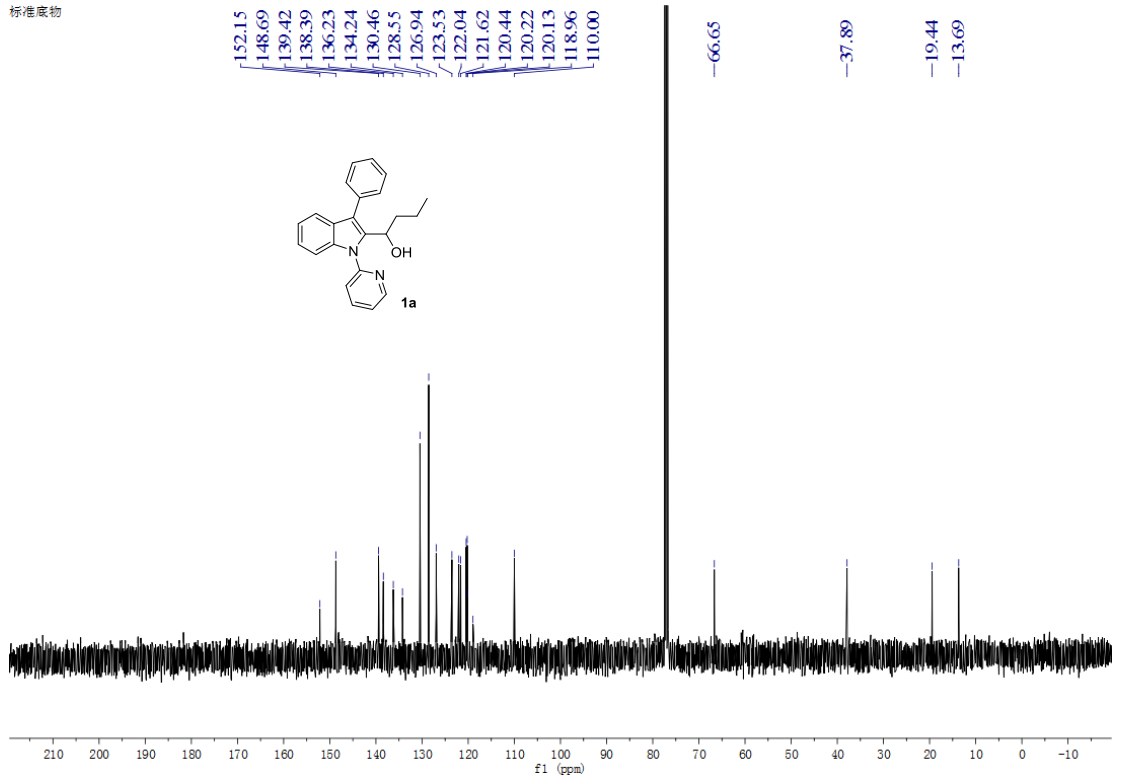
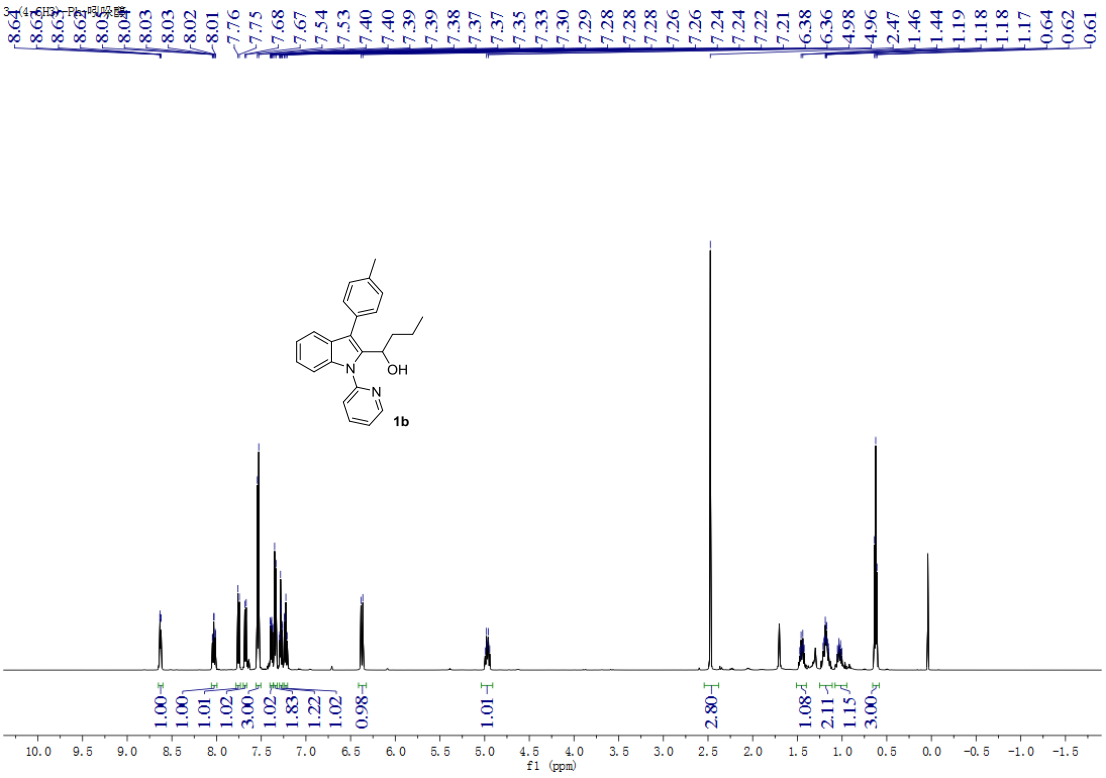
IX. ^{1}H NMR and ^{13}C NMR Spectrum of All Products.

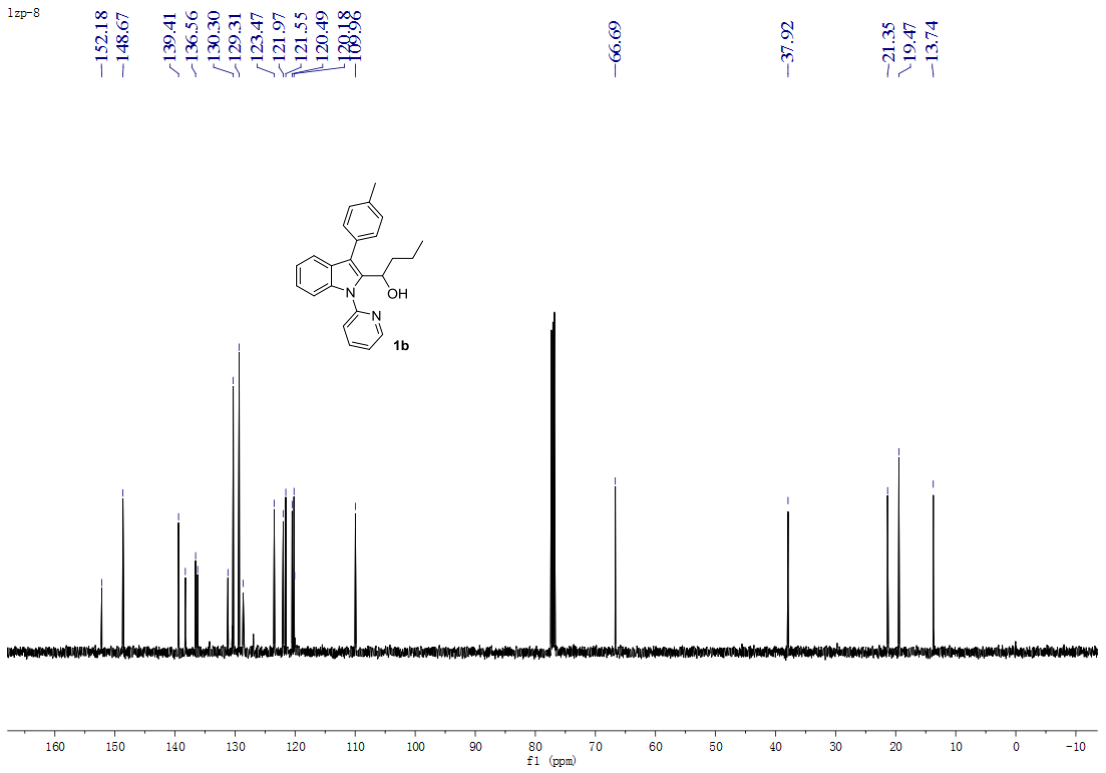
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **1a** (using $CDCl_3$ as solvent)



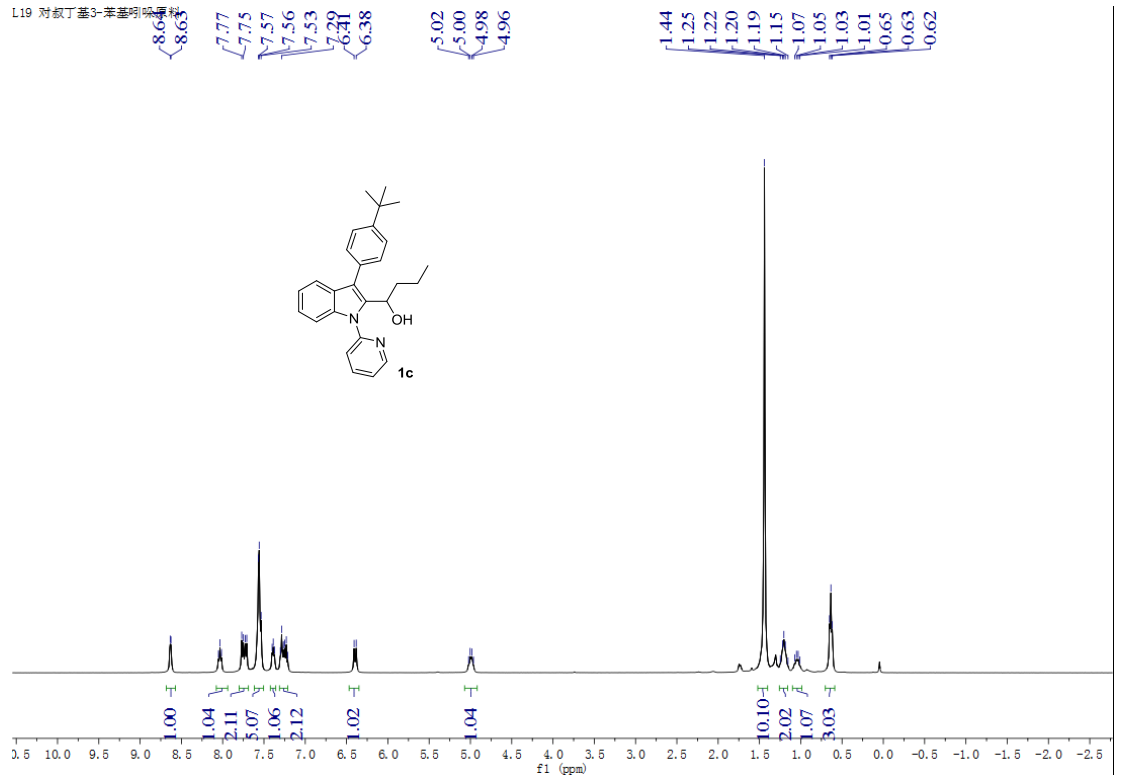


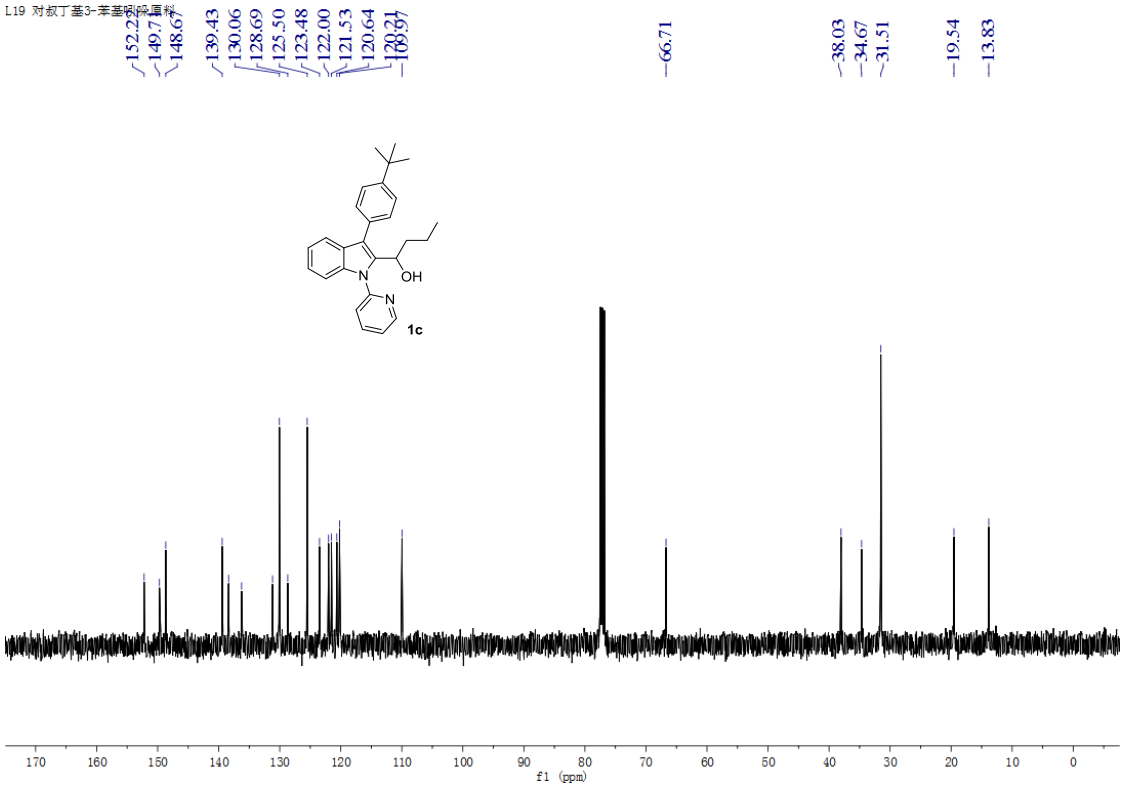
The ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum for **1b** (using $CDCl_3$ as solvent)



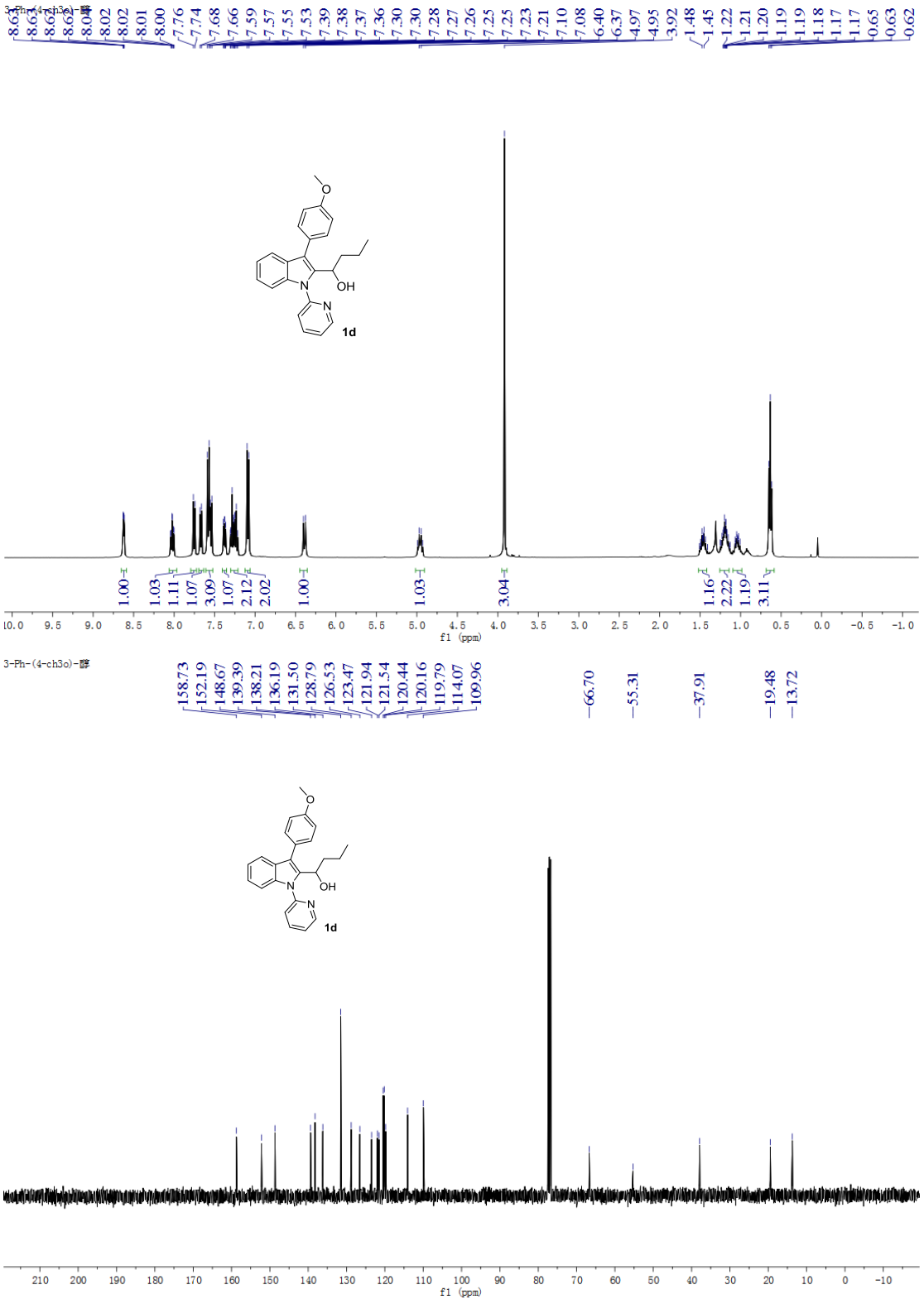


The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **1c** (using $CDCl_3$ as solvent)

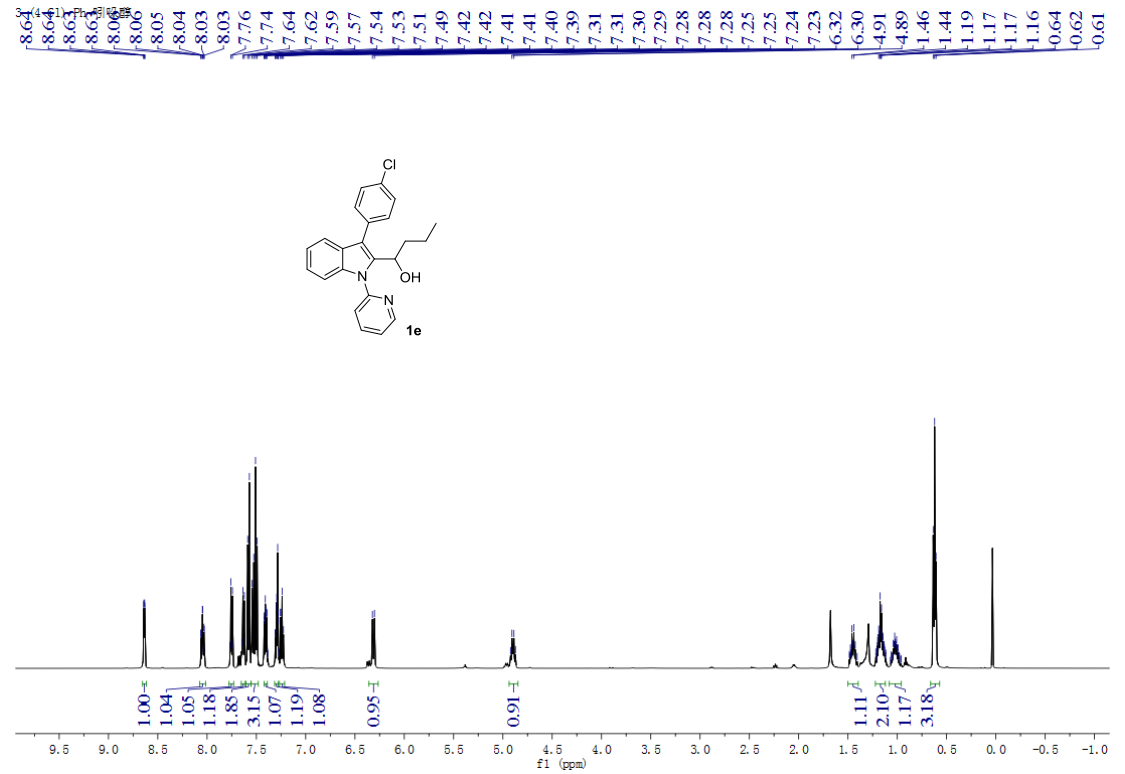


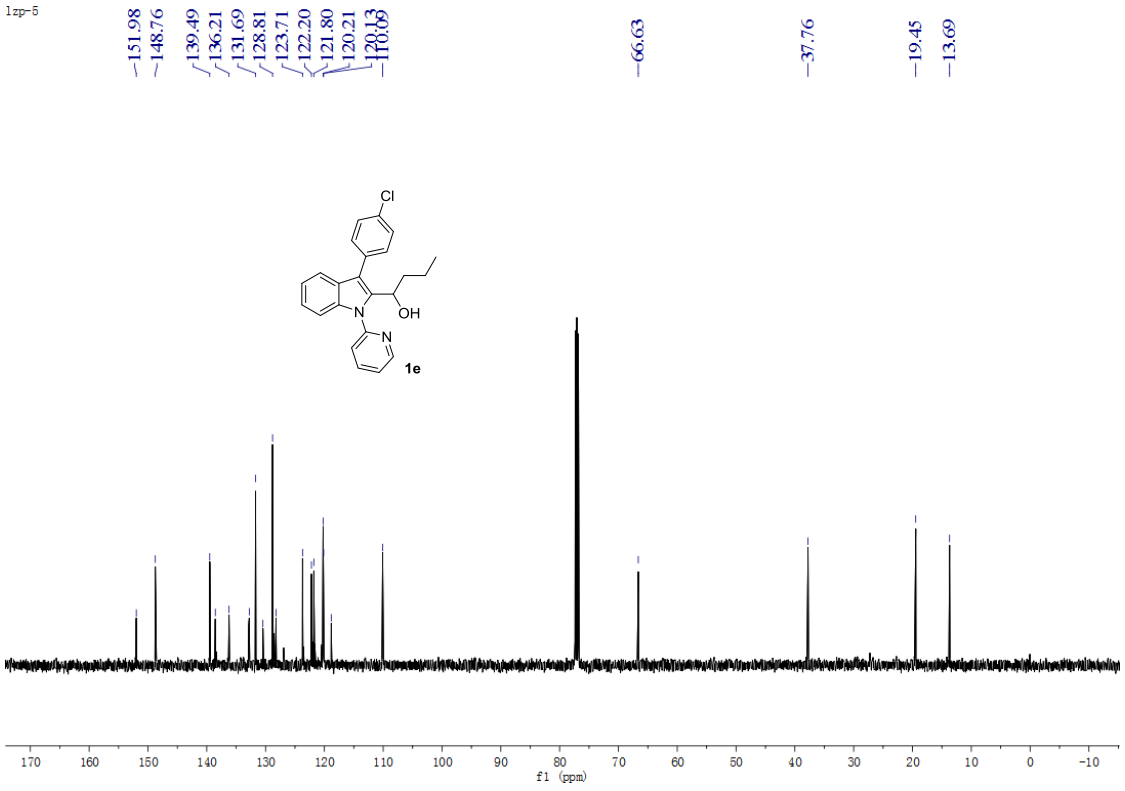


The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **1d** (using $CDCl_3$ as solvent)

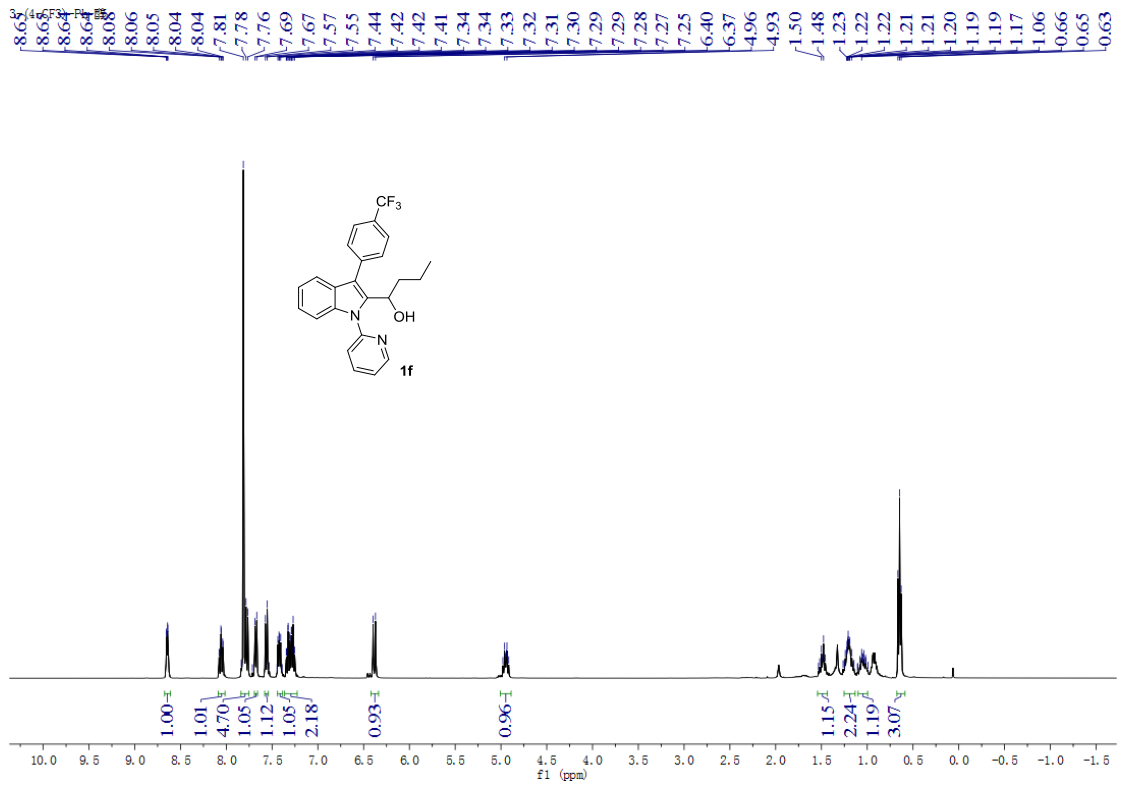


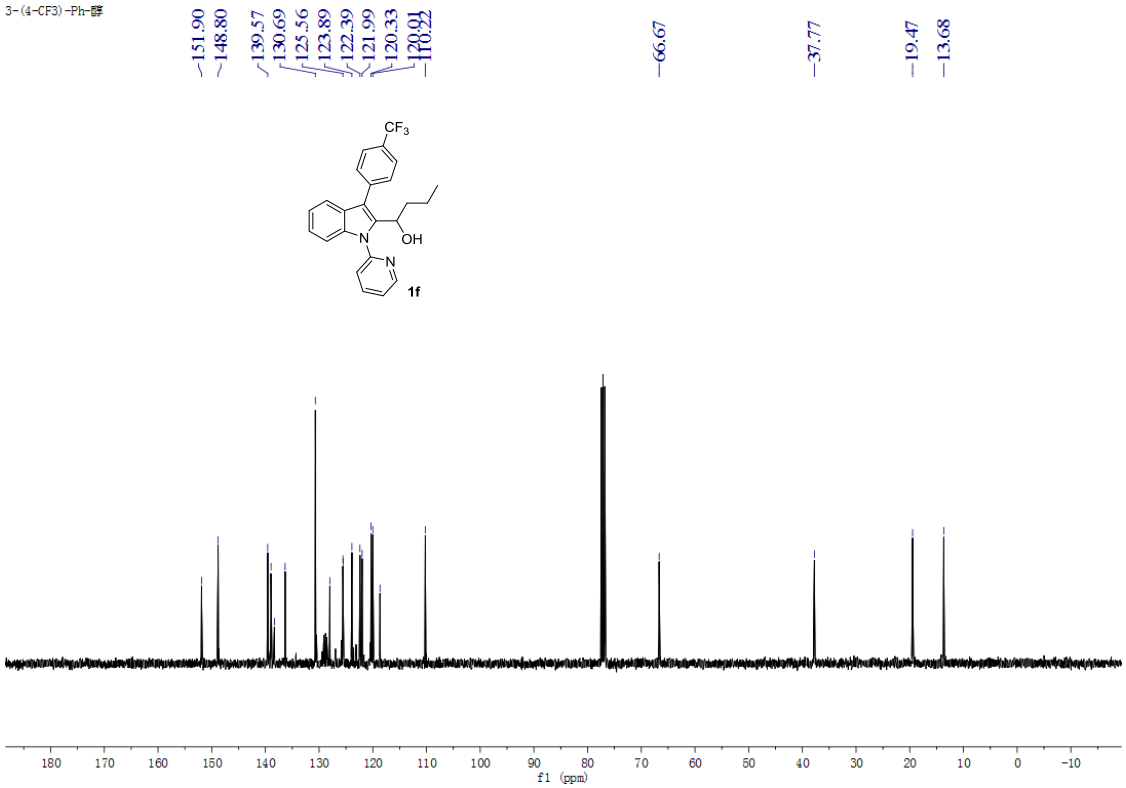
The ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum for **1e** (using $CDCl_3$ as solvent)



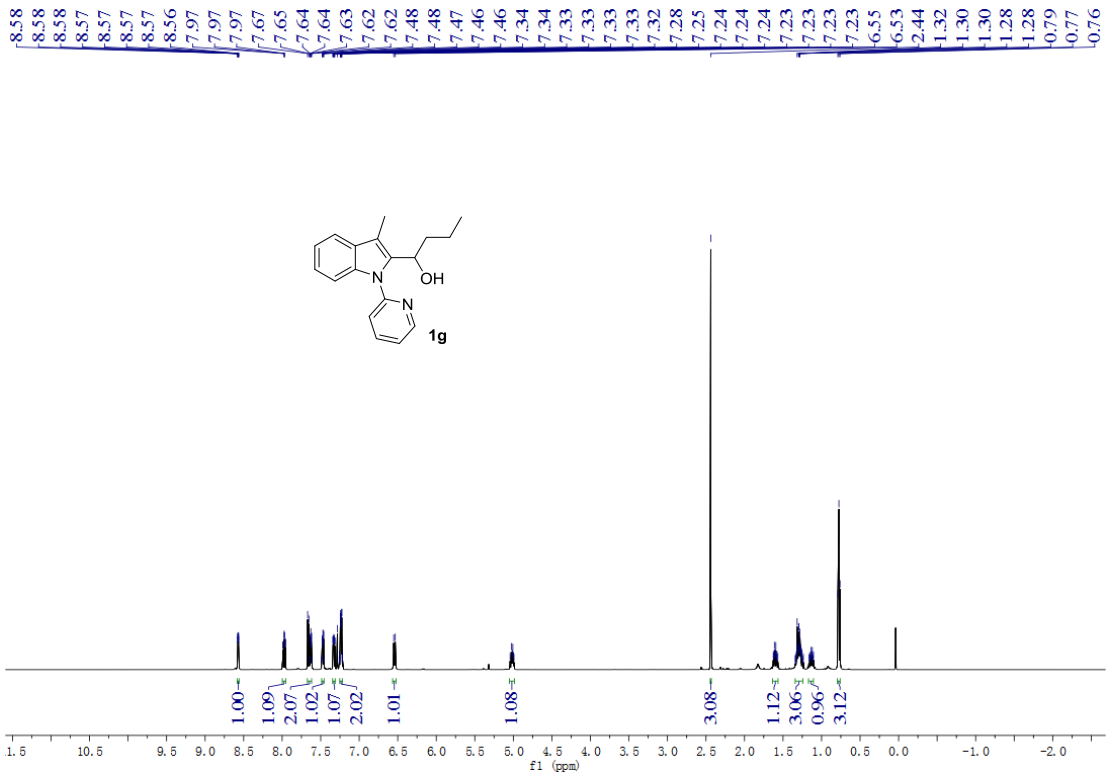


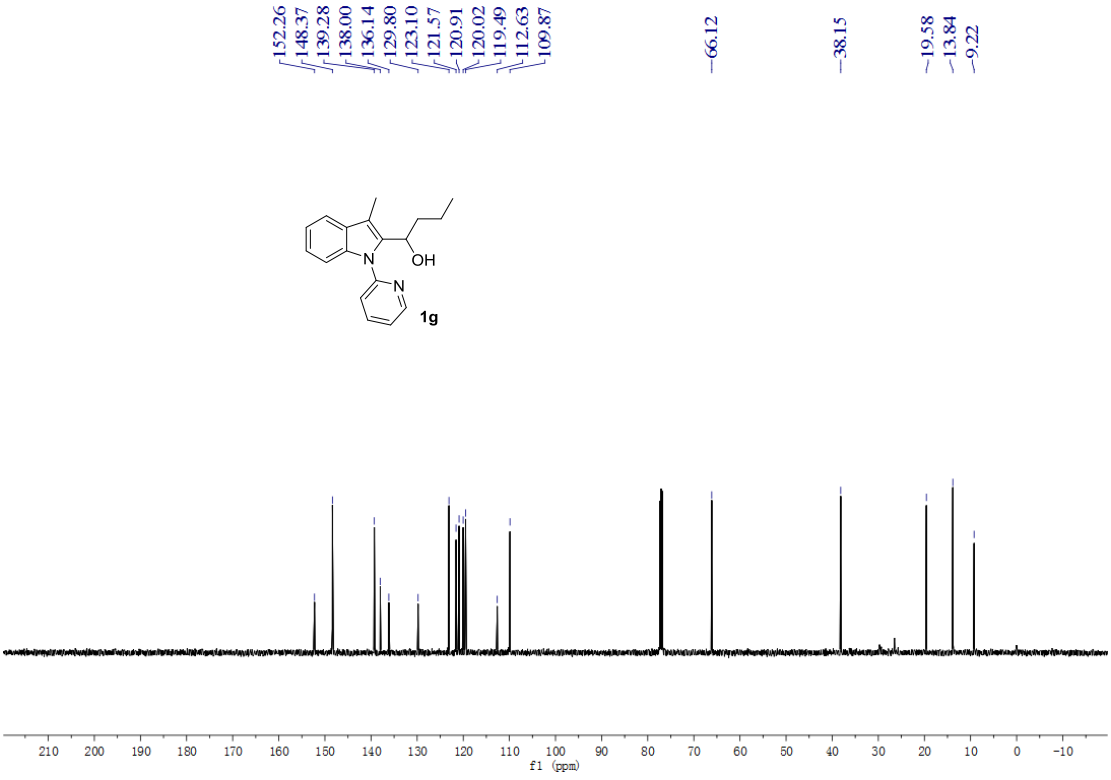
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **1f** (using $CDCl_3$ as solvent)



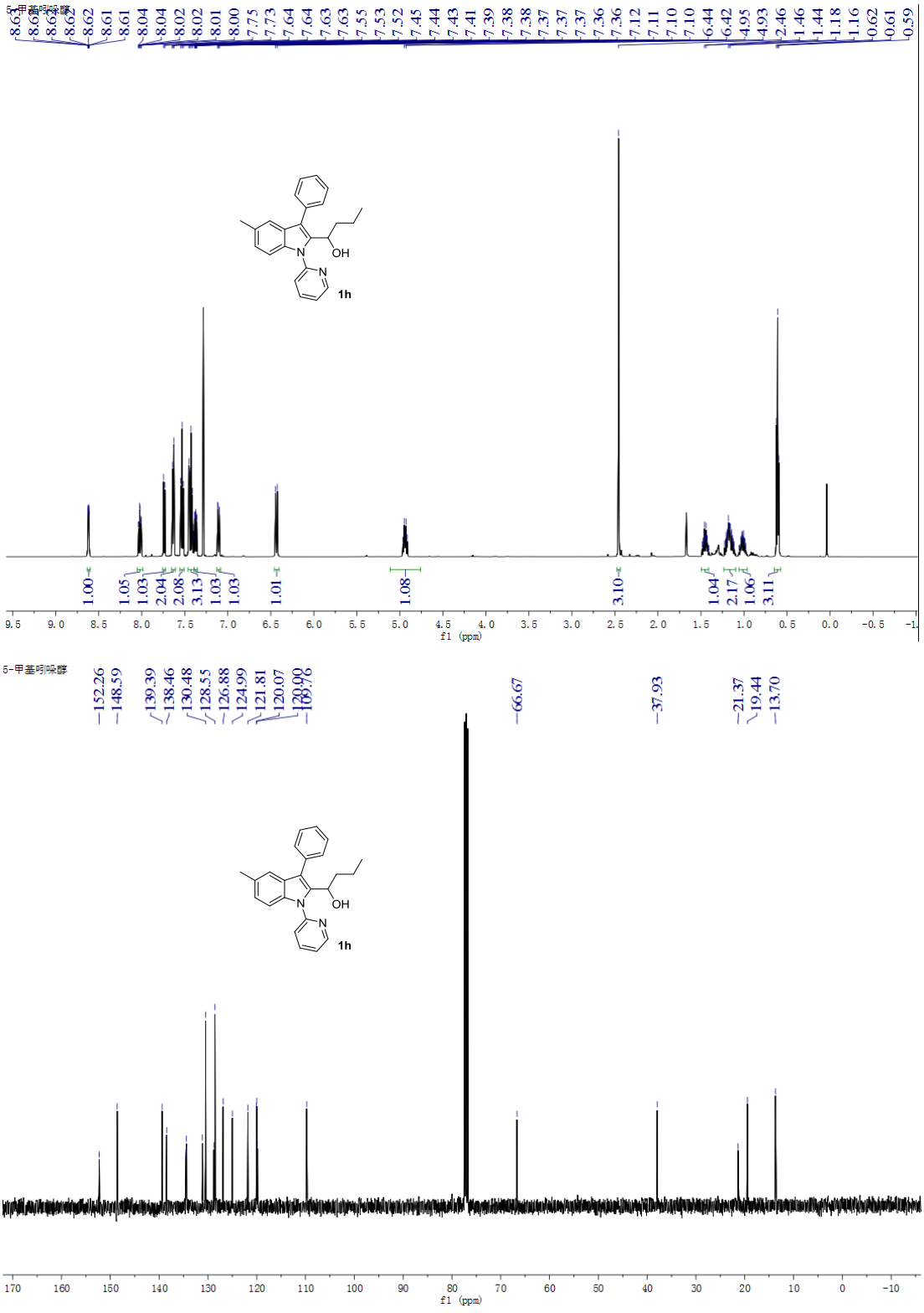


The ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum for **1g** (using $CDCl_3$ as solvent)

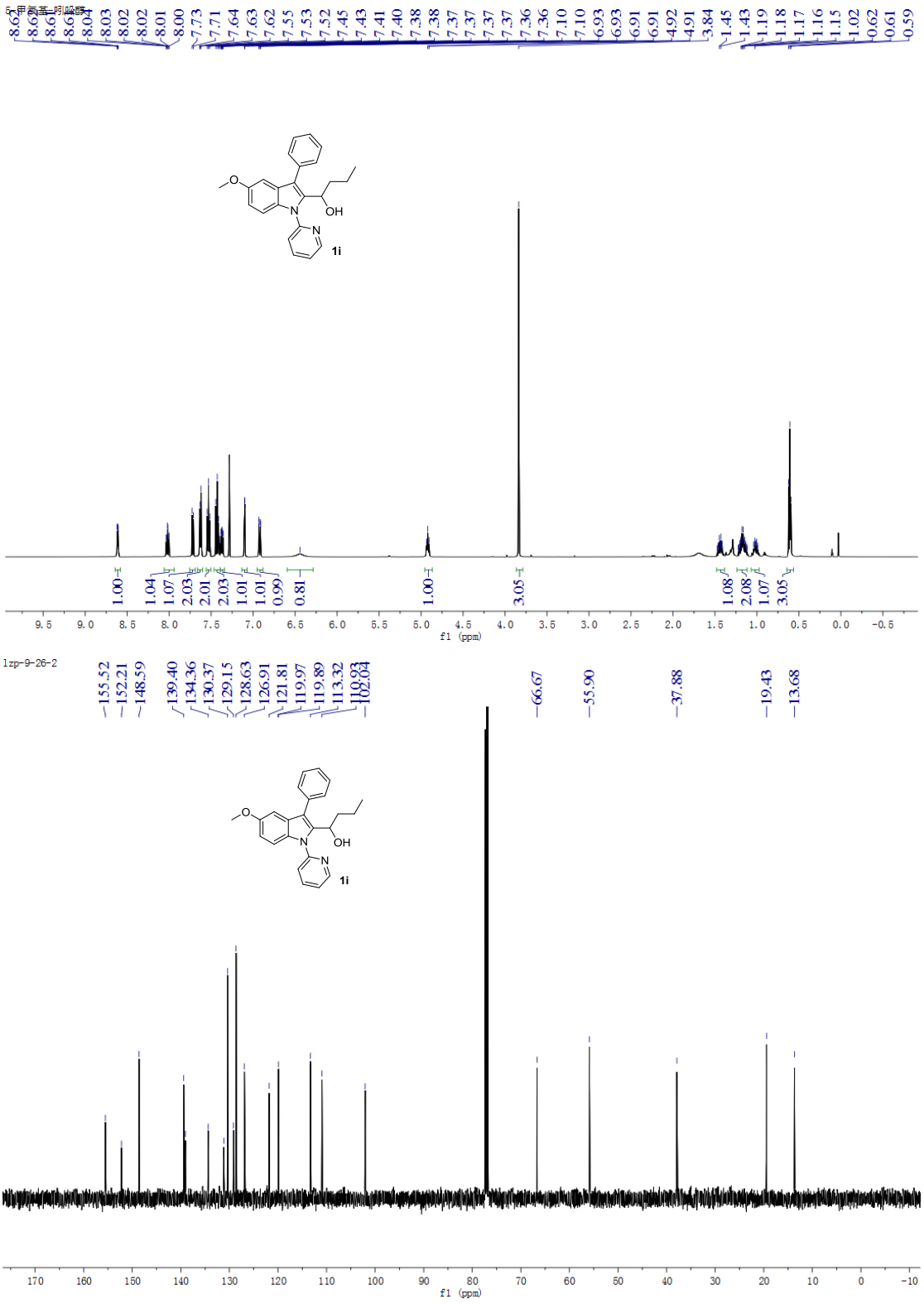




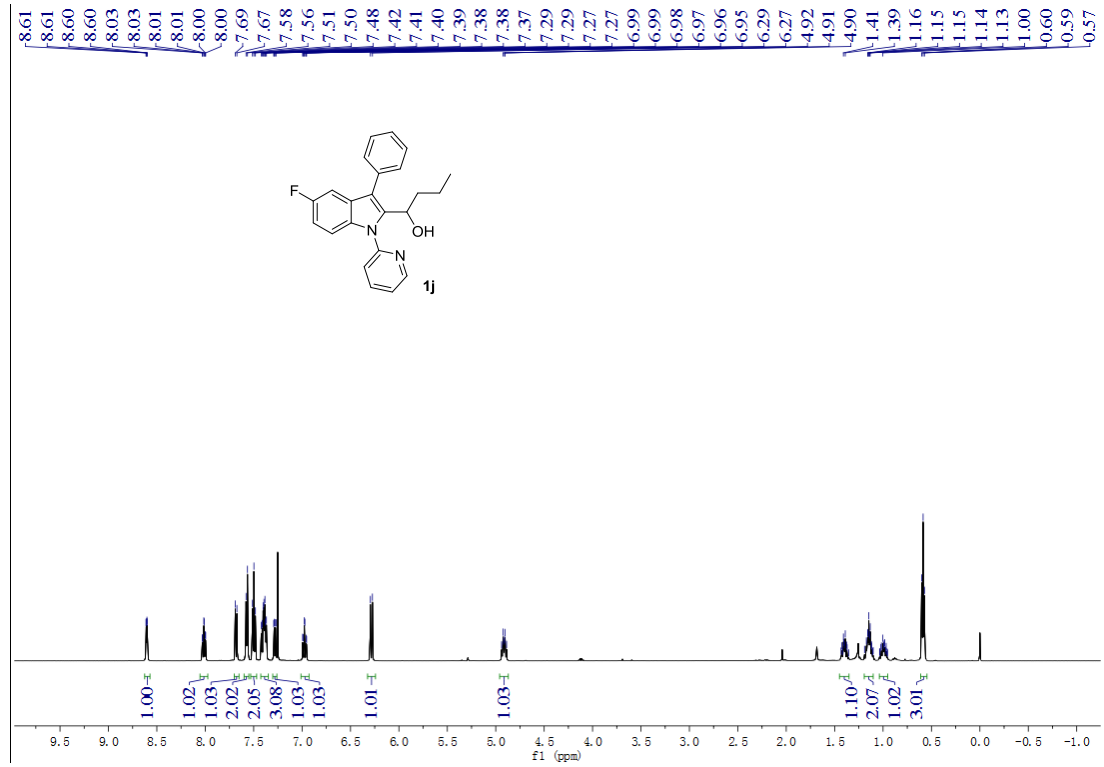
The ^{1}H NMR (500 MHz) and ^{13}C NMR (101 MHz) spectrum for **1h** (using $CDCl_3$ as solvent)

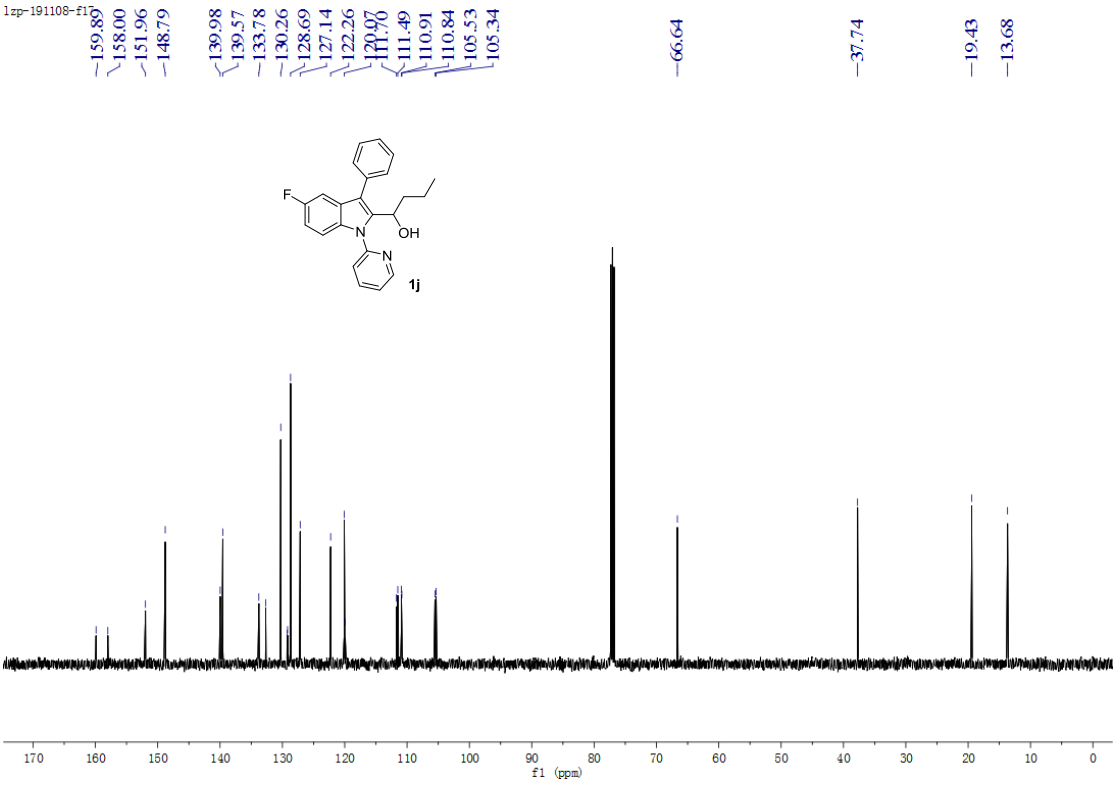


The ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum for **1i** (using $CDCl_3$ as solvent)

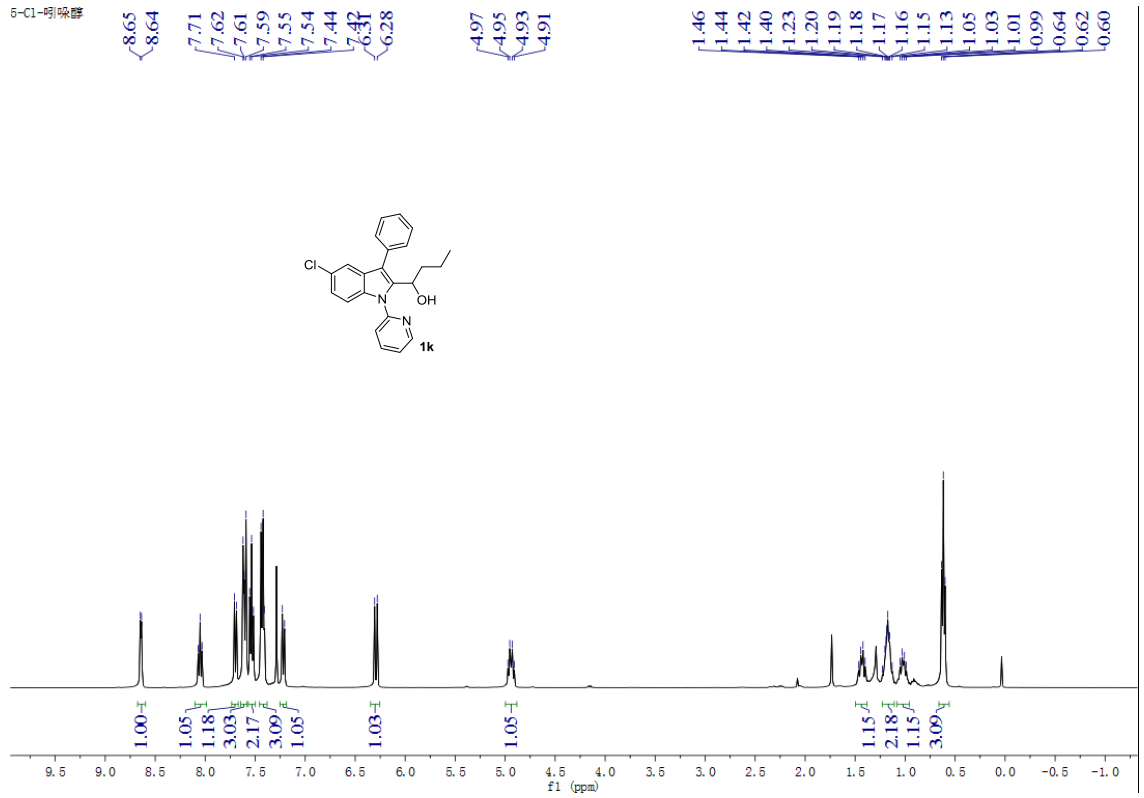


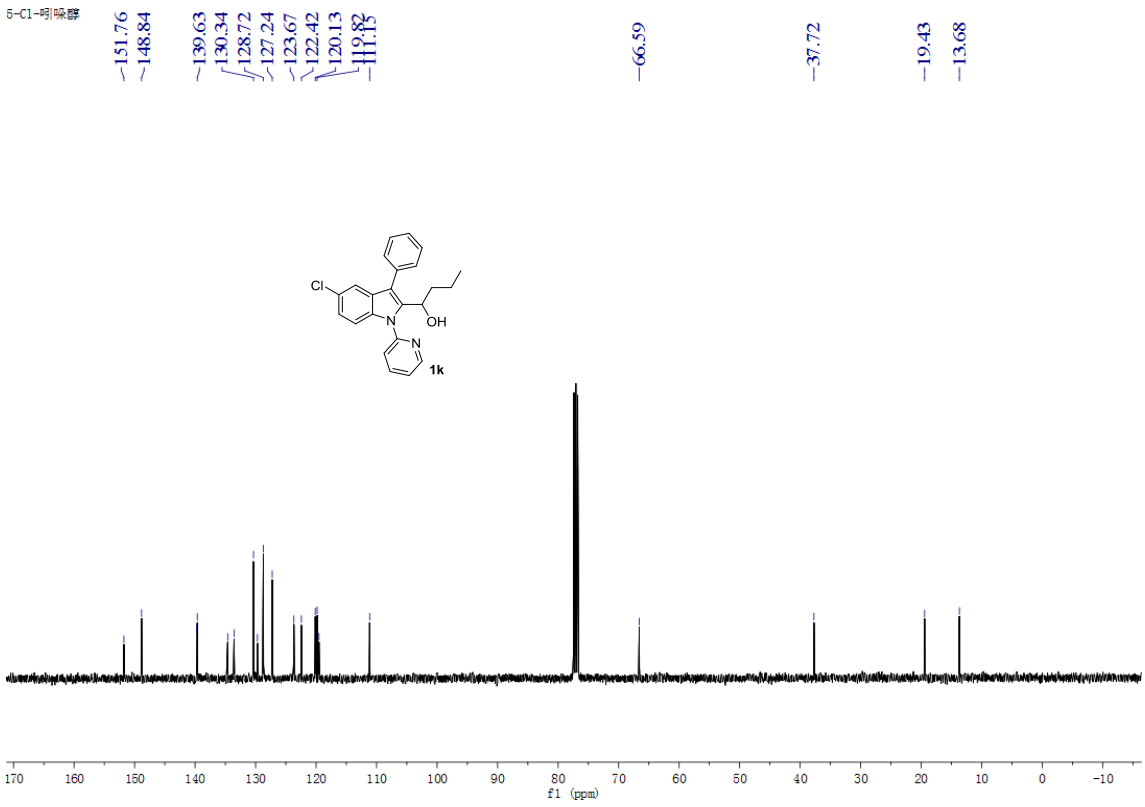
The ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum for **1j** (using $CDCl_3$ as solvent)



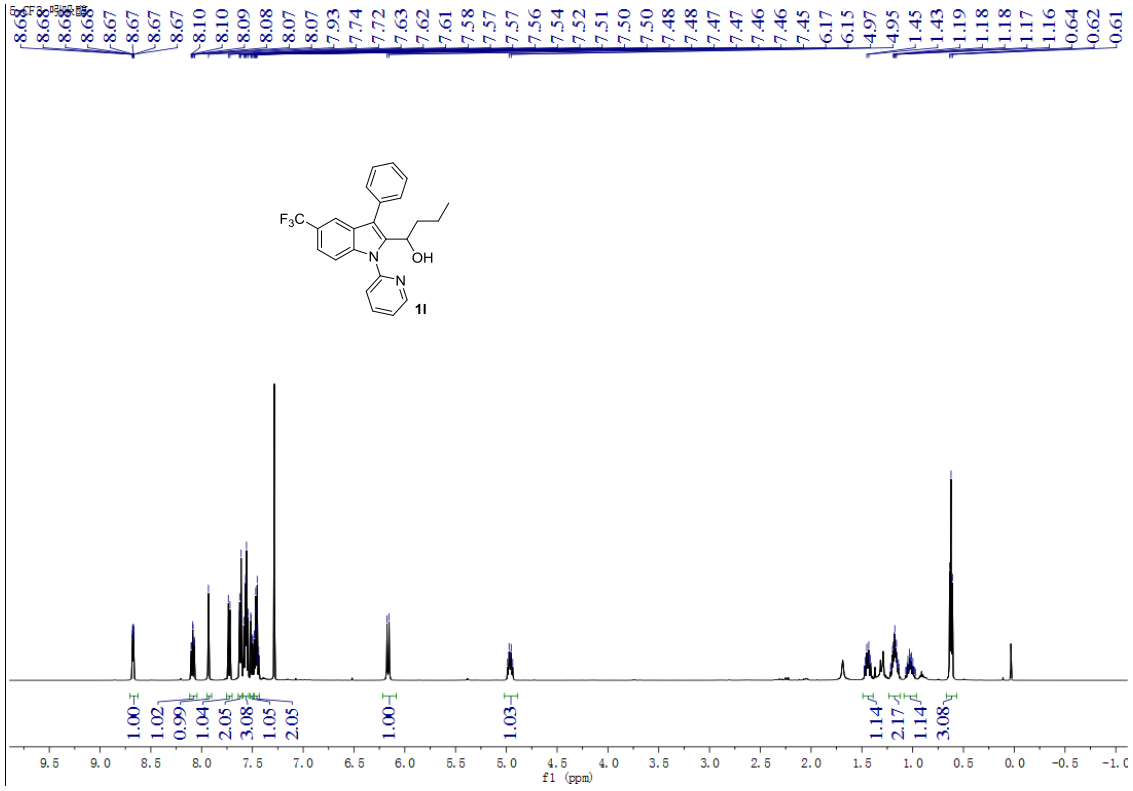


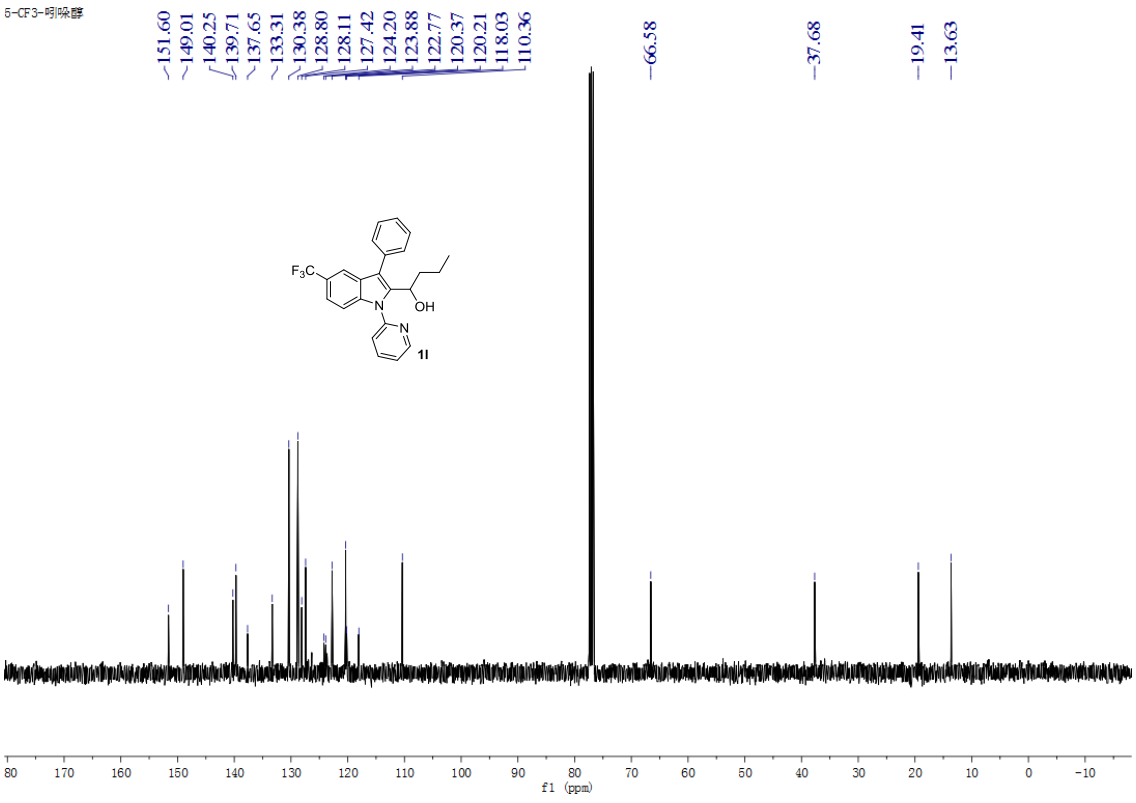
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **1k**(using $CDCl_3$ as solvent)



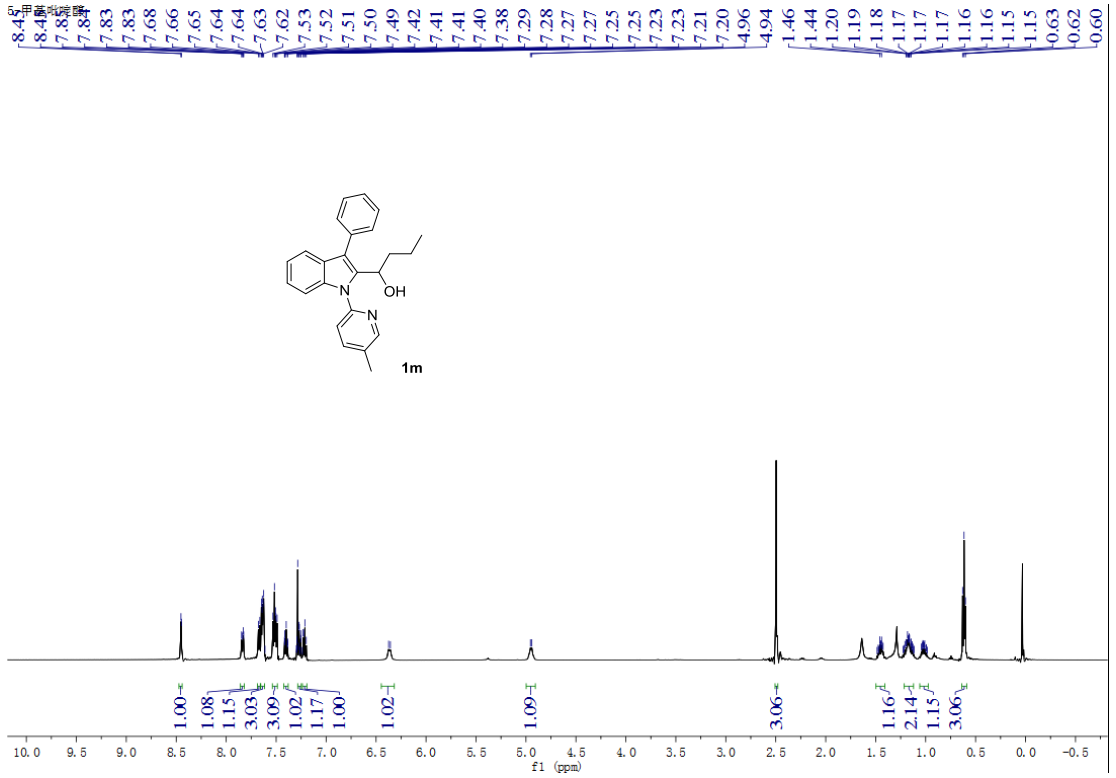


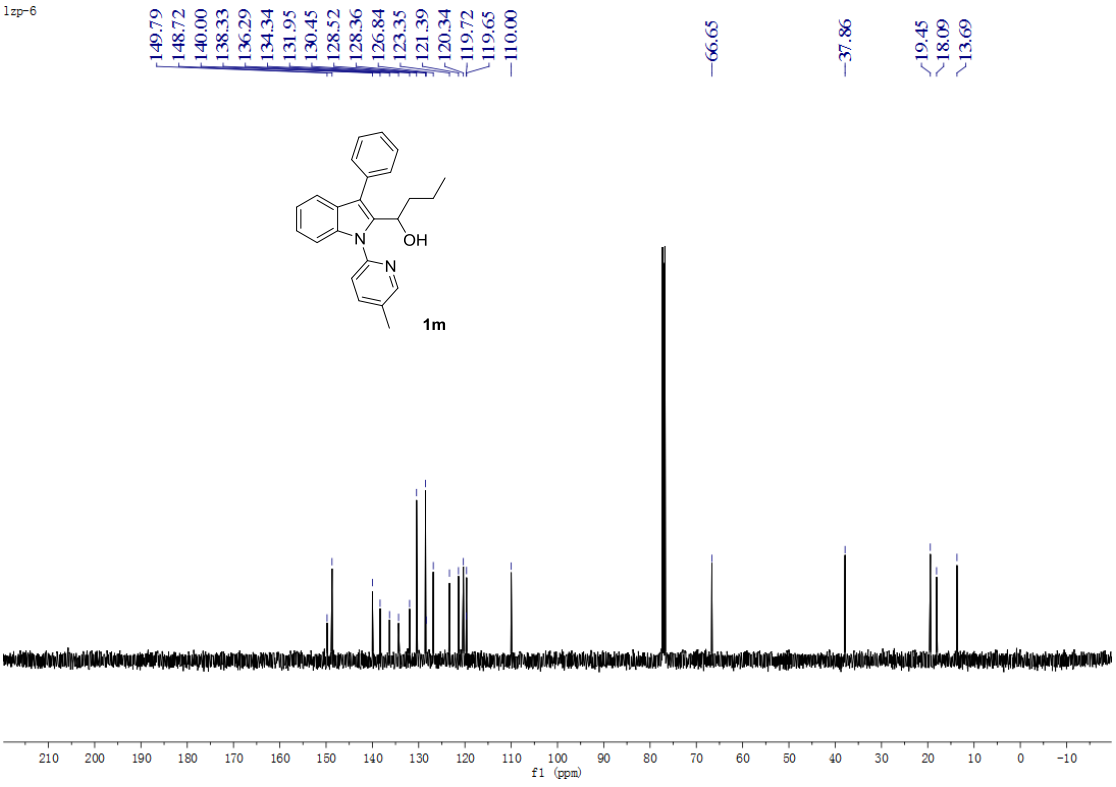
The ^{1}H NMR (500 MHz) and ^{13}C NMR (101 MHz) spectrum for **1l** (using $CDCl_3$ as solvent)



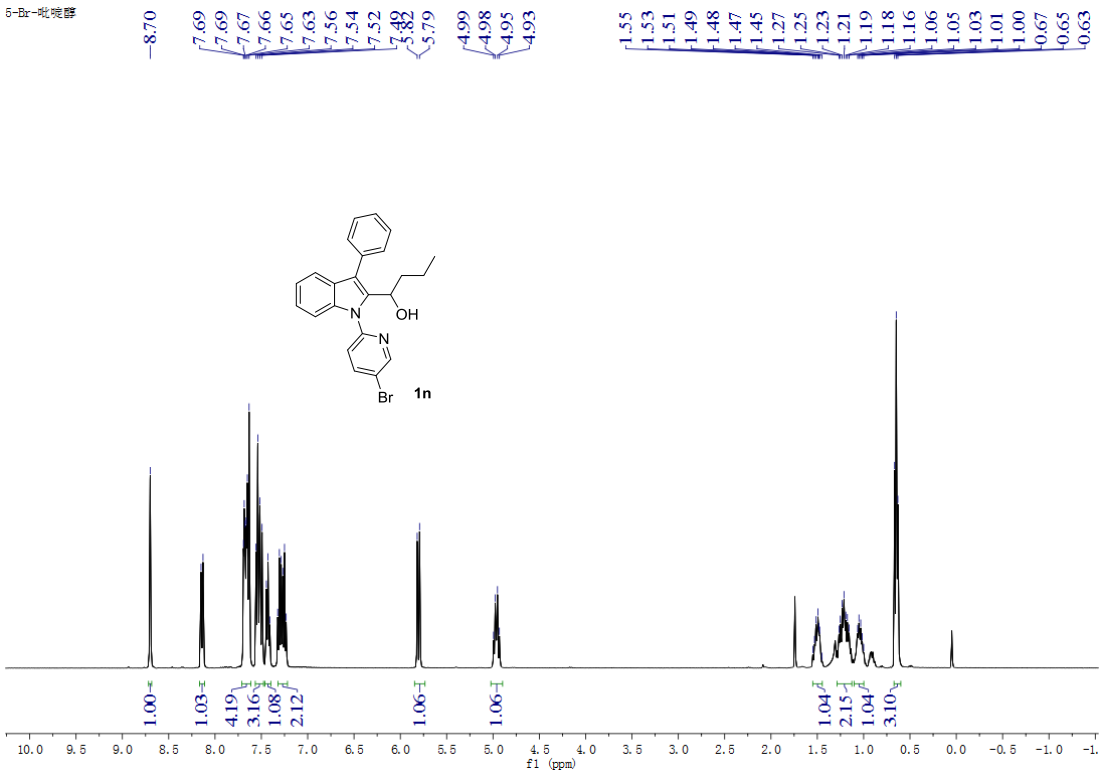


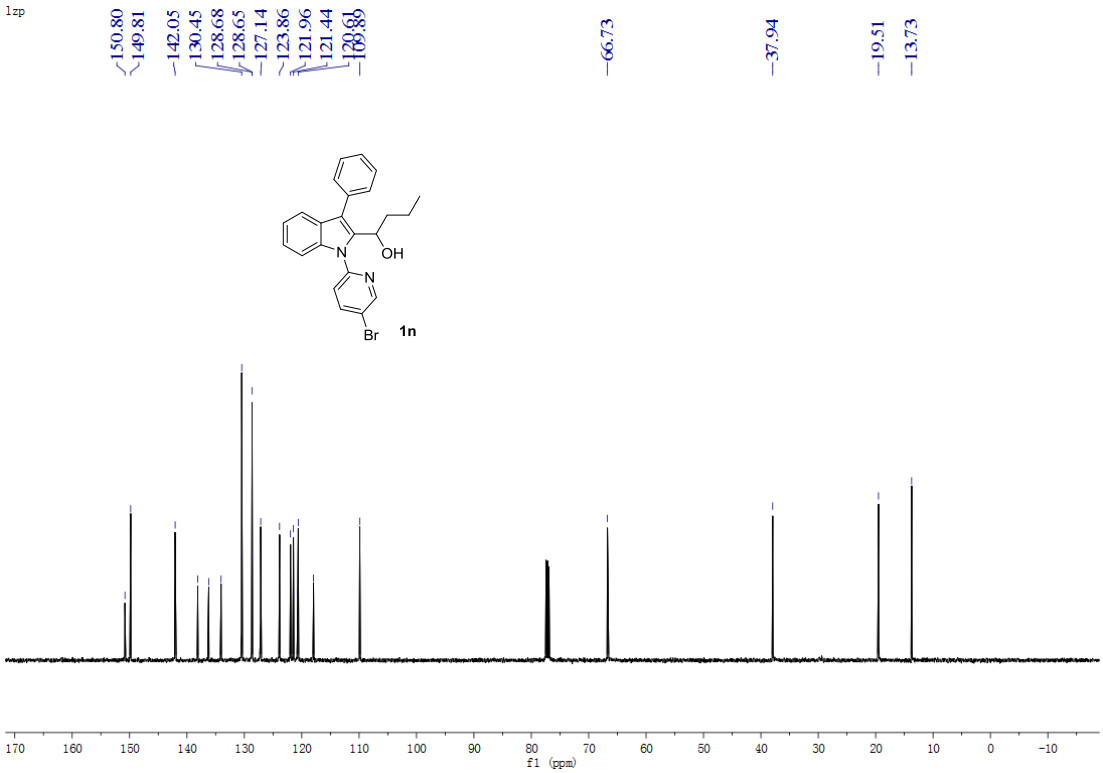
The ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum for **1m** (using $CDCl_3$ as solvent)



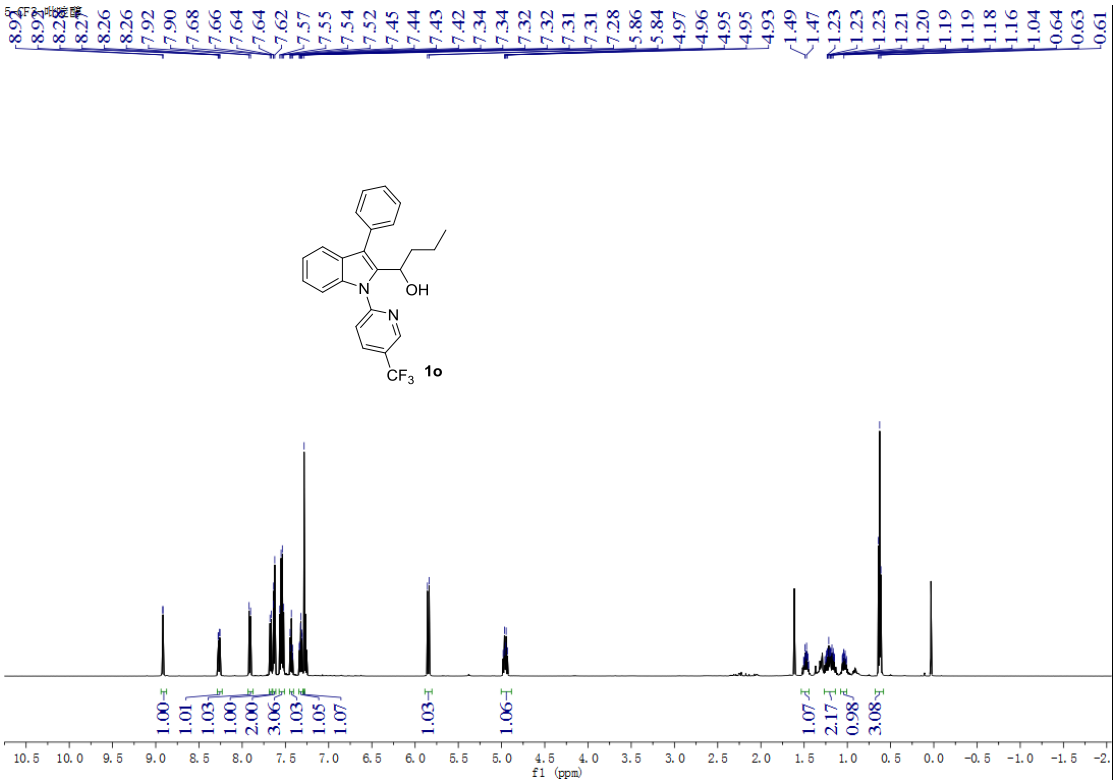


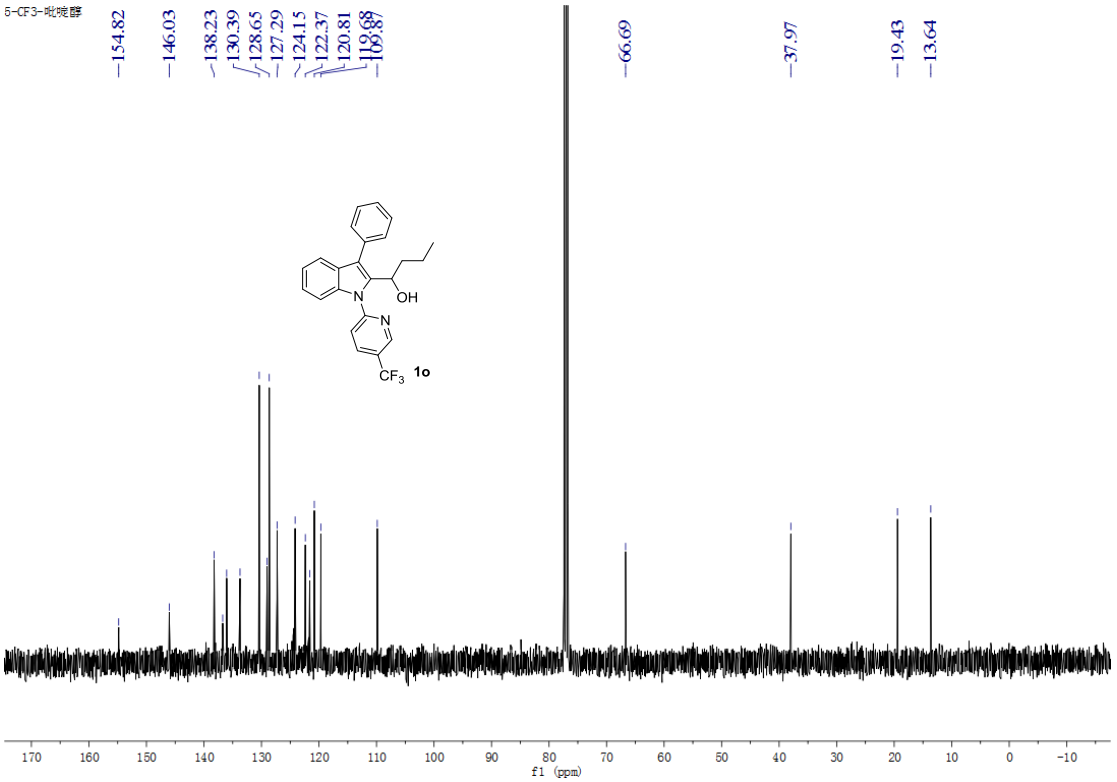
The ^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectrum for **1n** (using $CDCl_3$ as solvent)



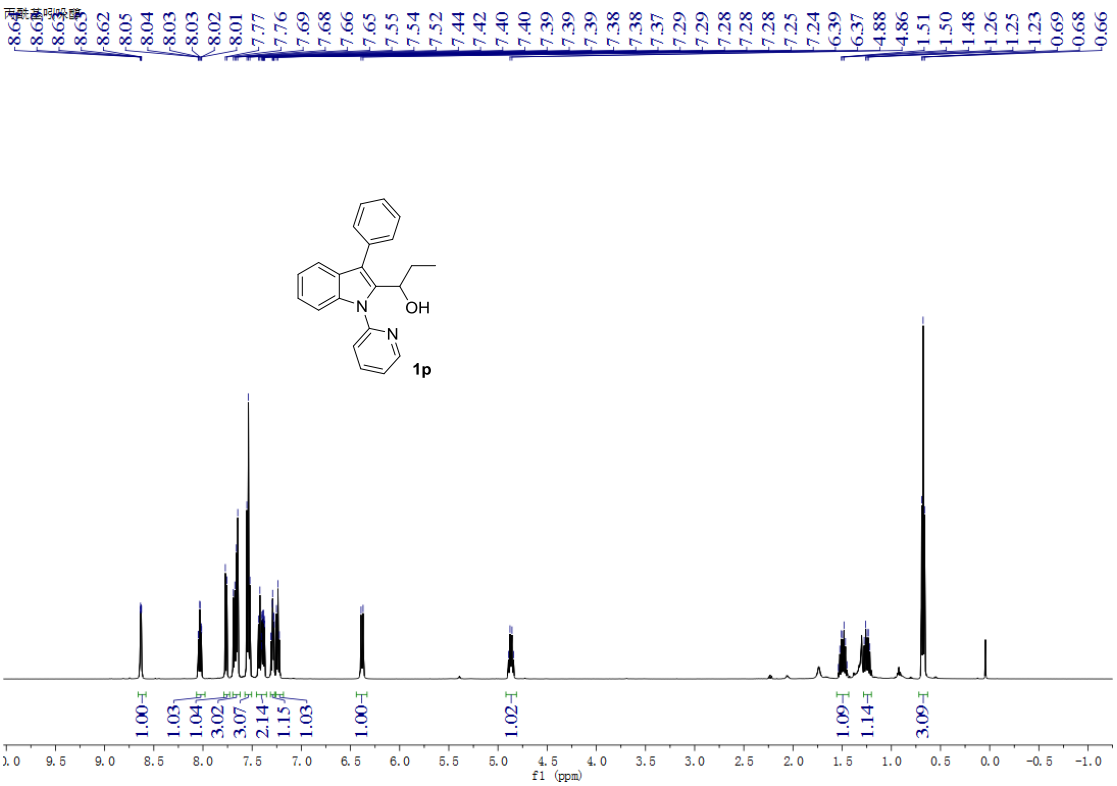


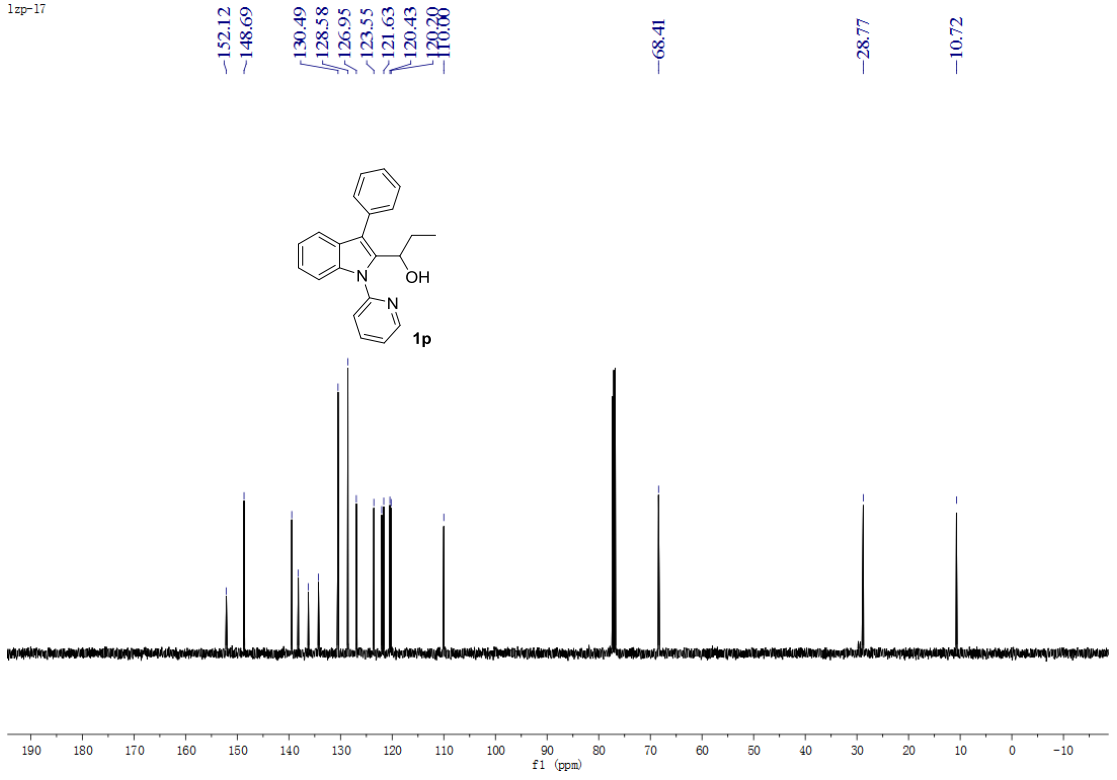
The ^{1}H NMR (500 MHz) and ^{13}C NMR (101 MHz) spectrum for **1o** (using $CDCl_3$ as solvent)



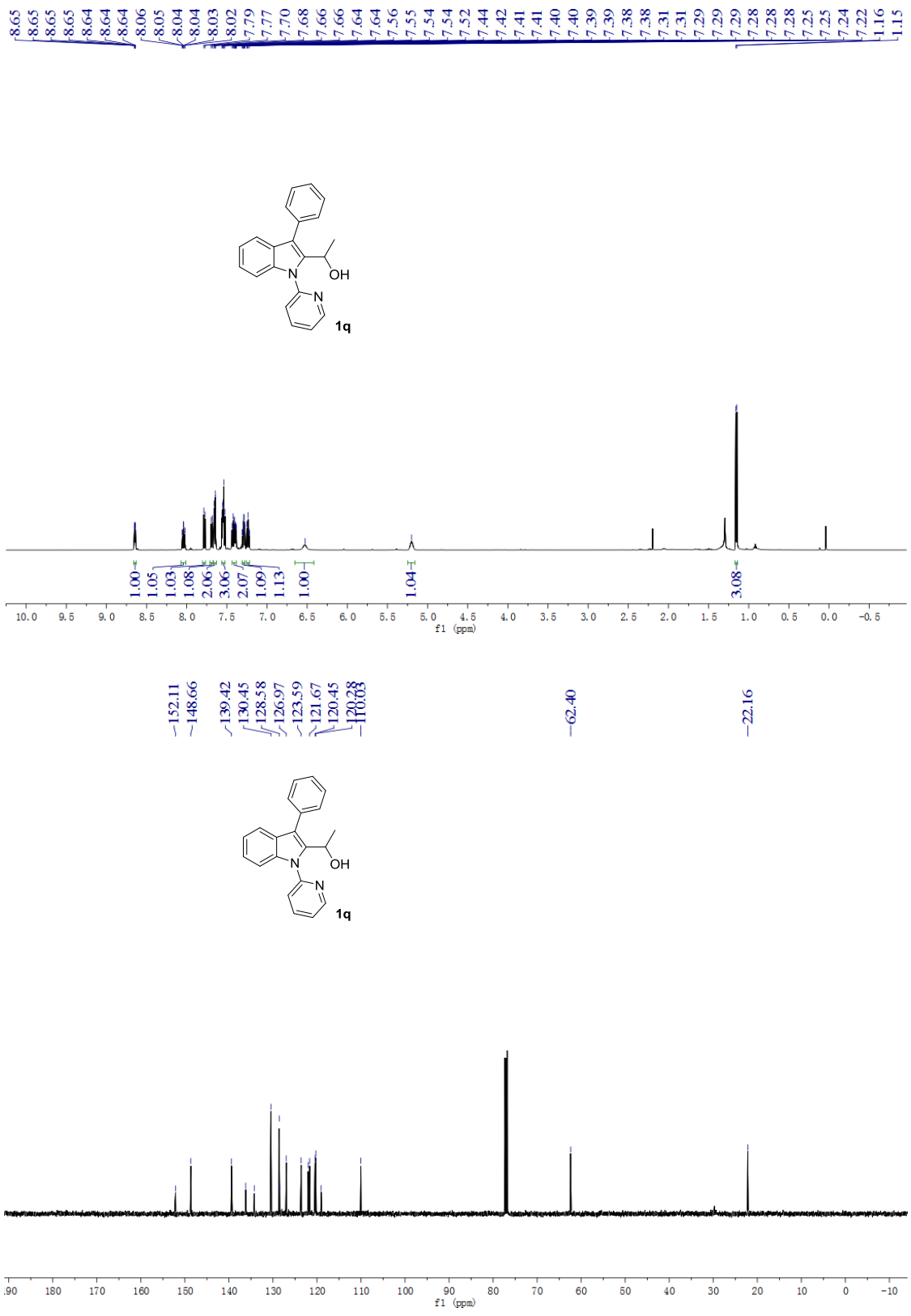


The ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum for **1p** (using $CDCl_3$ as solvent)

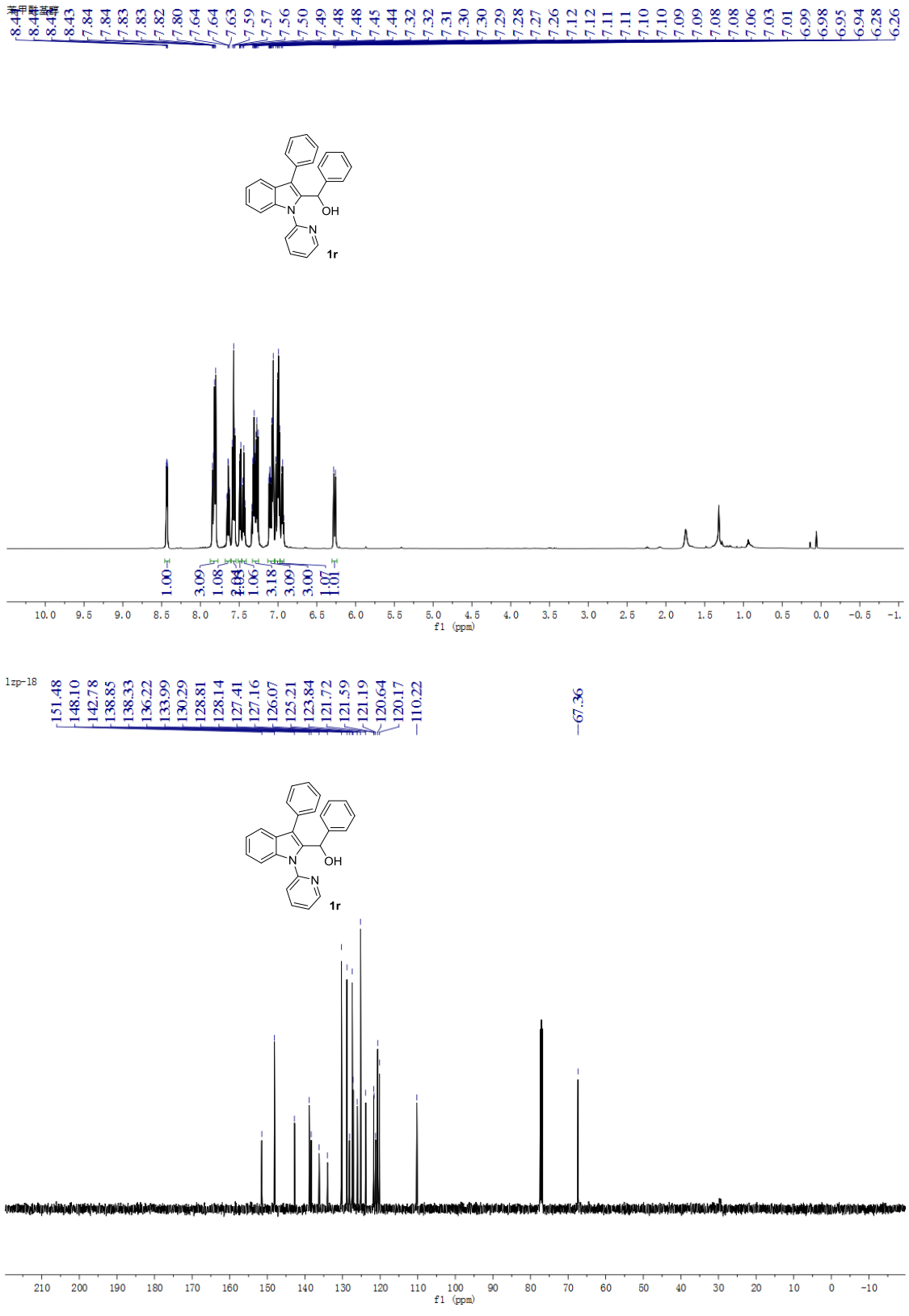




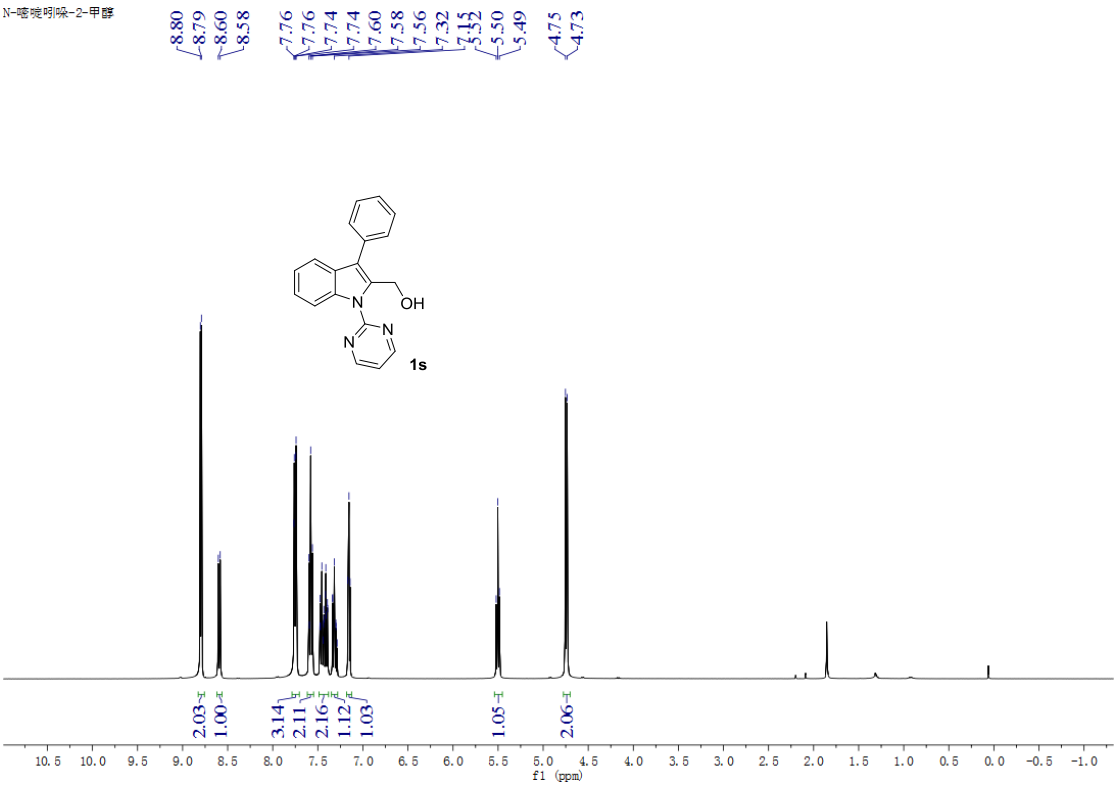
The ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum for **1q** (using $CDCl_3$ as solvent)

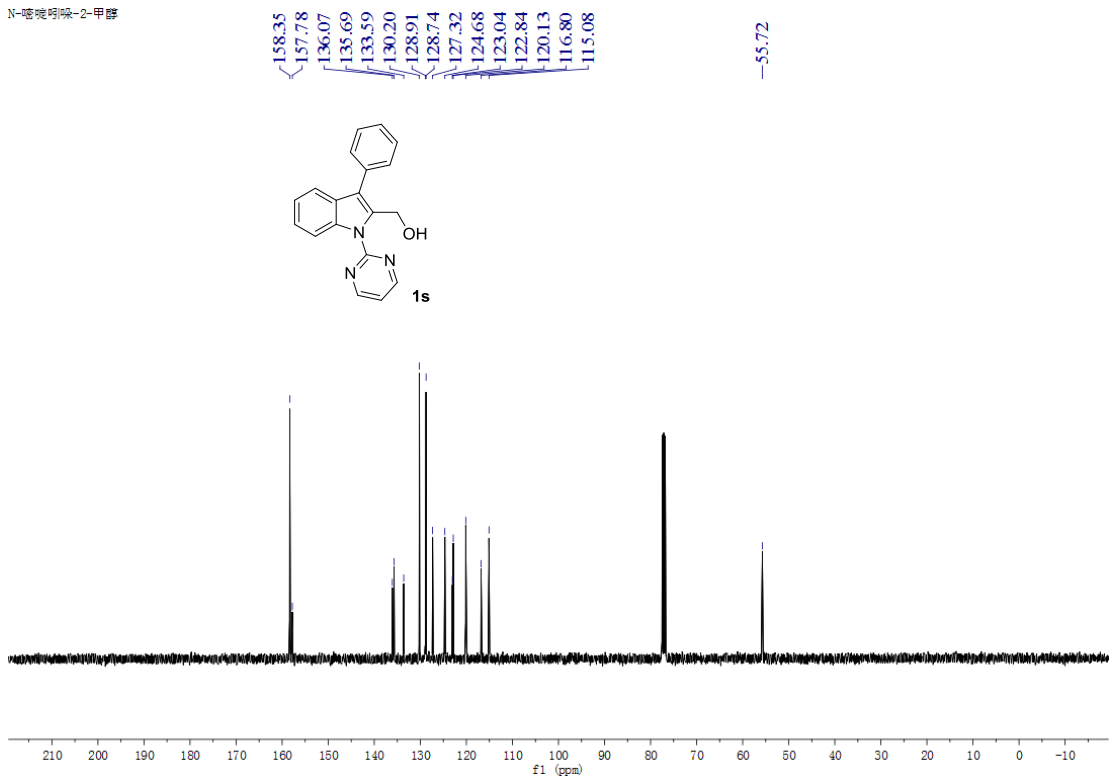


The ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum for **1r** (using $CDCl_3$ as solvent)

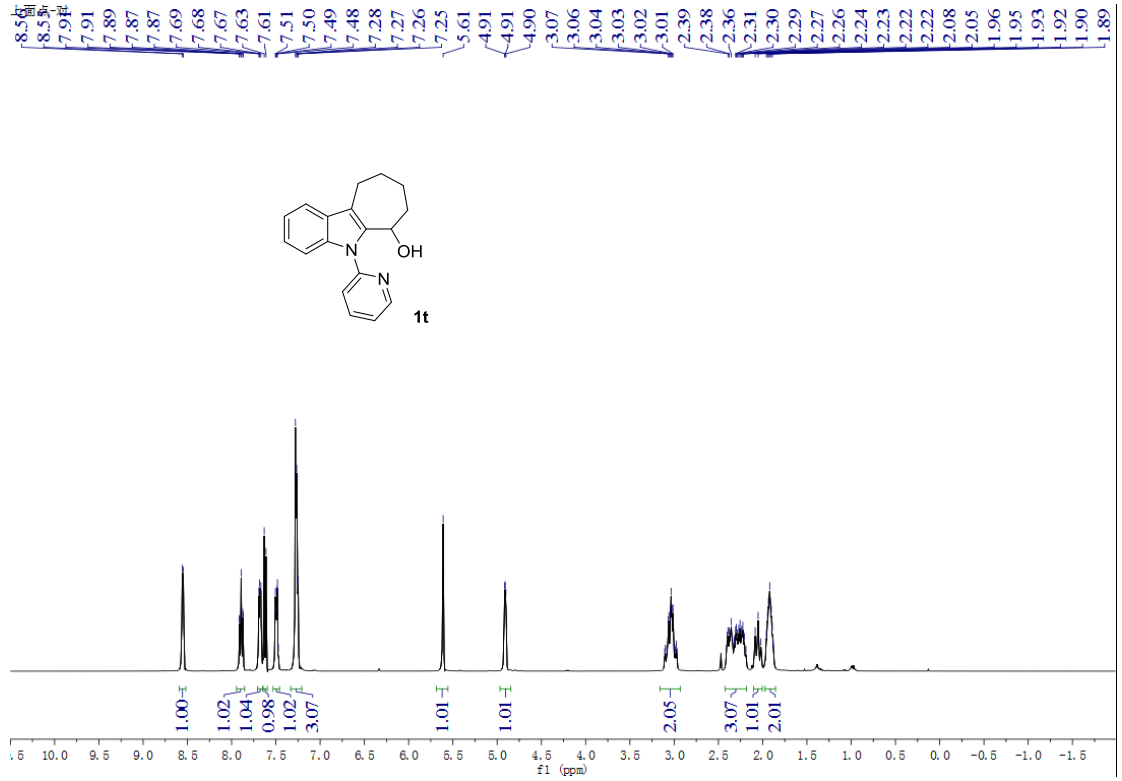


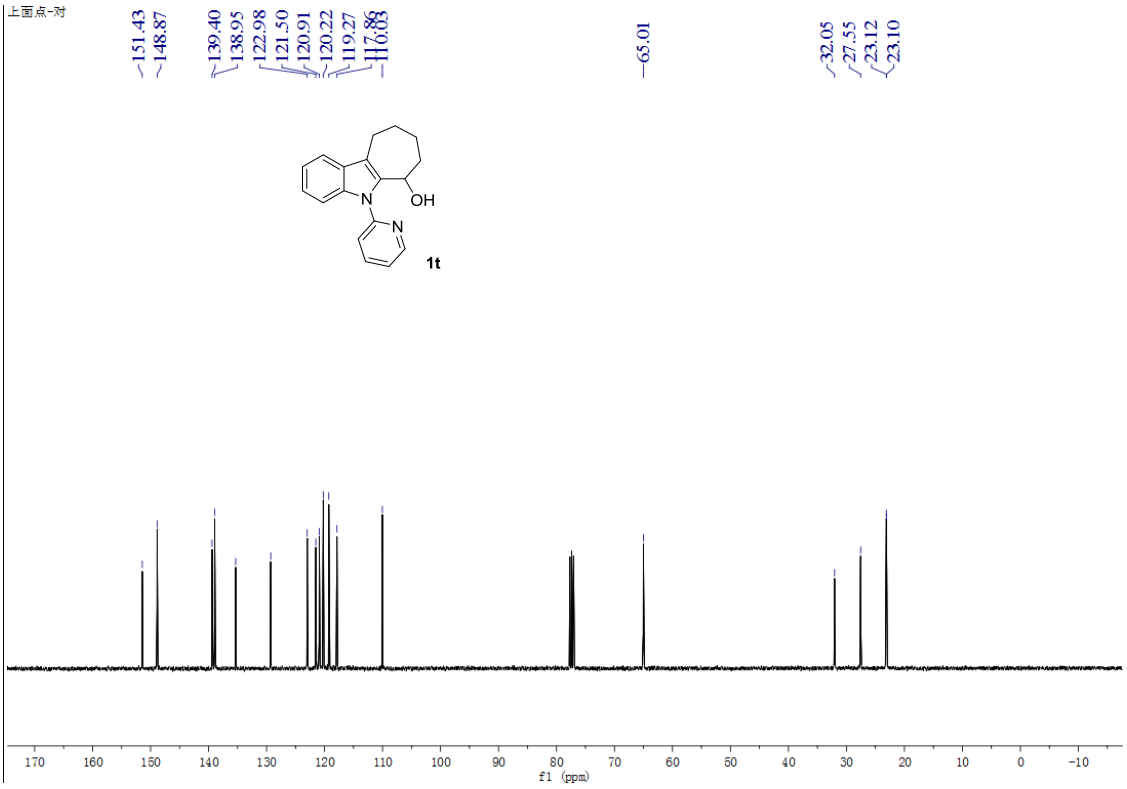
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **1s** (using $CDCl_3$ as solvent)



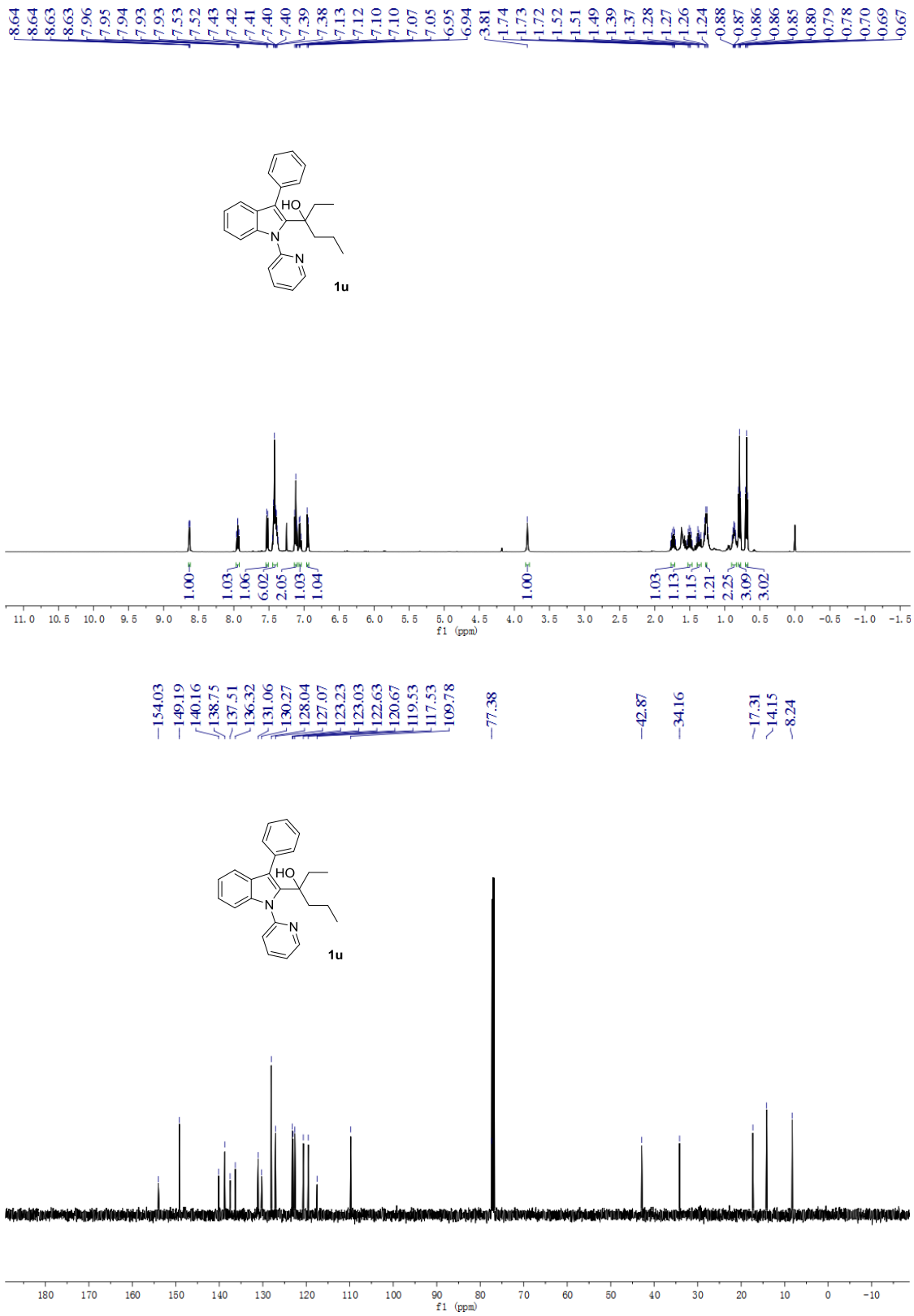


The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **1t** (using $CDCl_3$ as solvent)

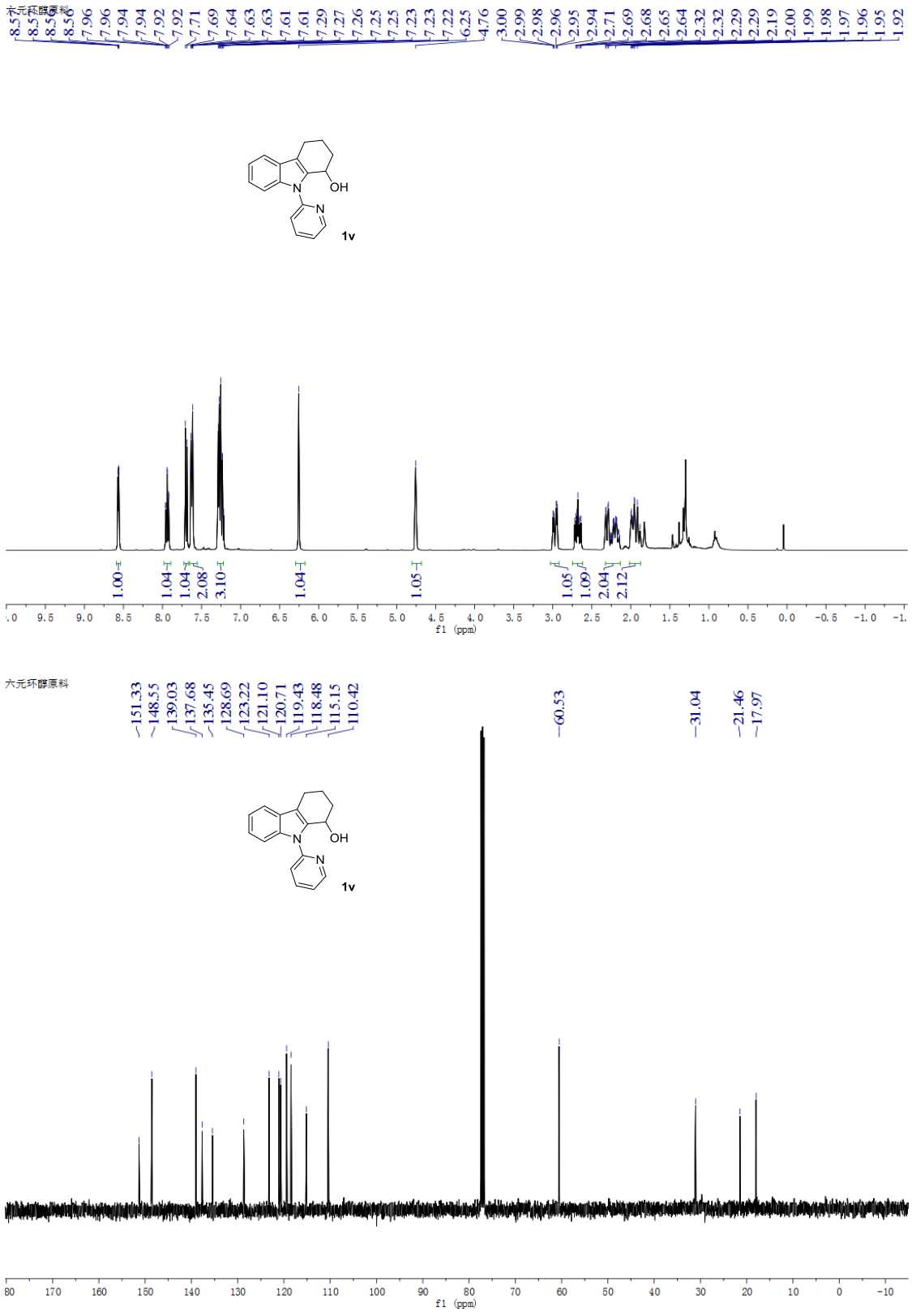




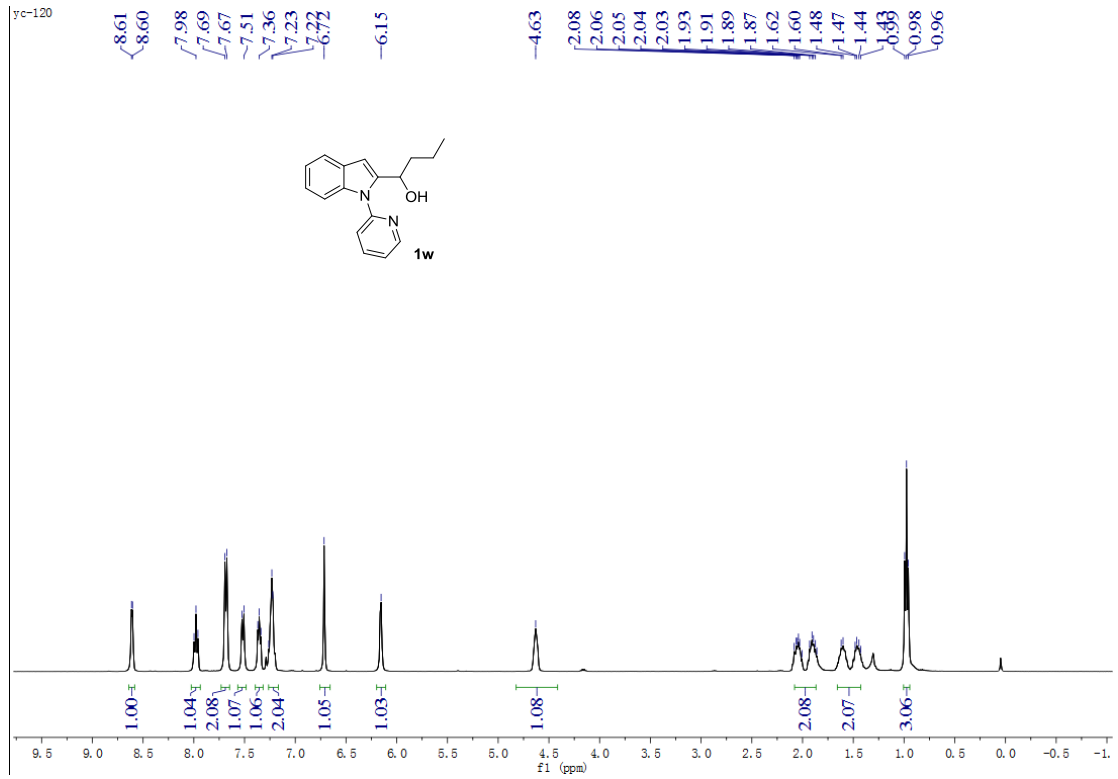
The ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum for **1u** (using $CDCl_3$ as solvent)

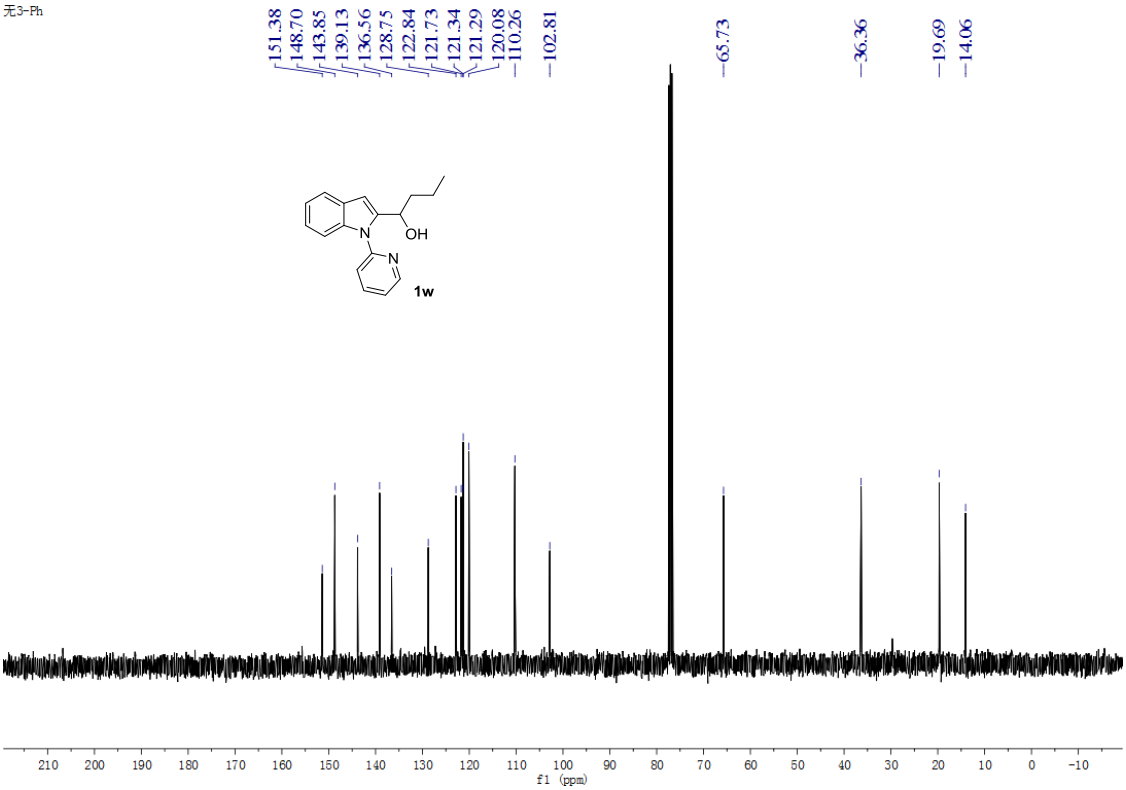


The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **1v** (using $CDCl_3$ as solvent)

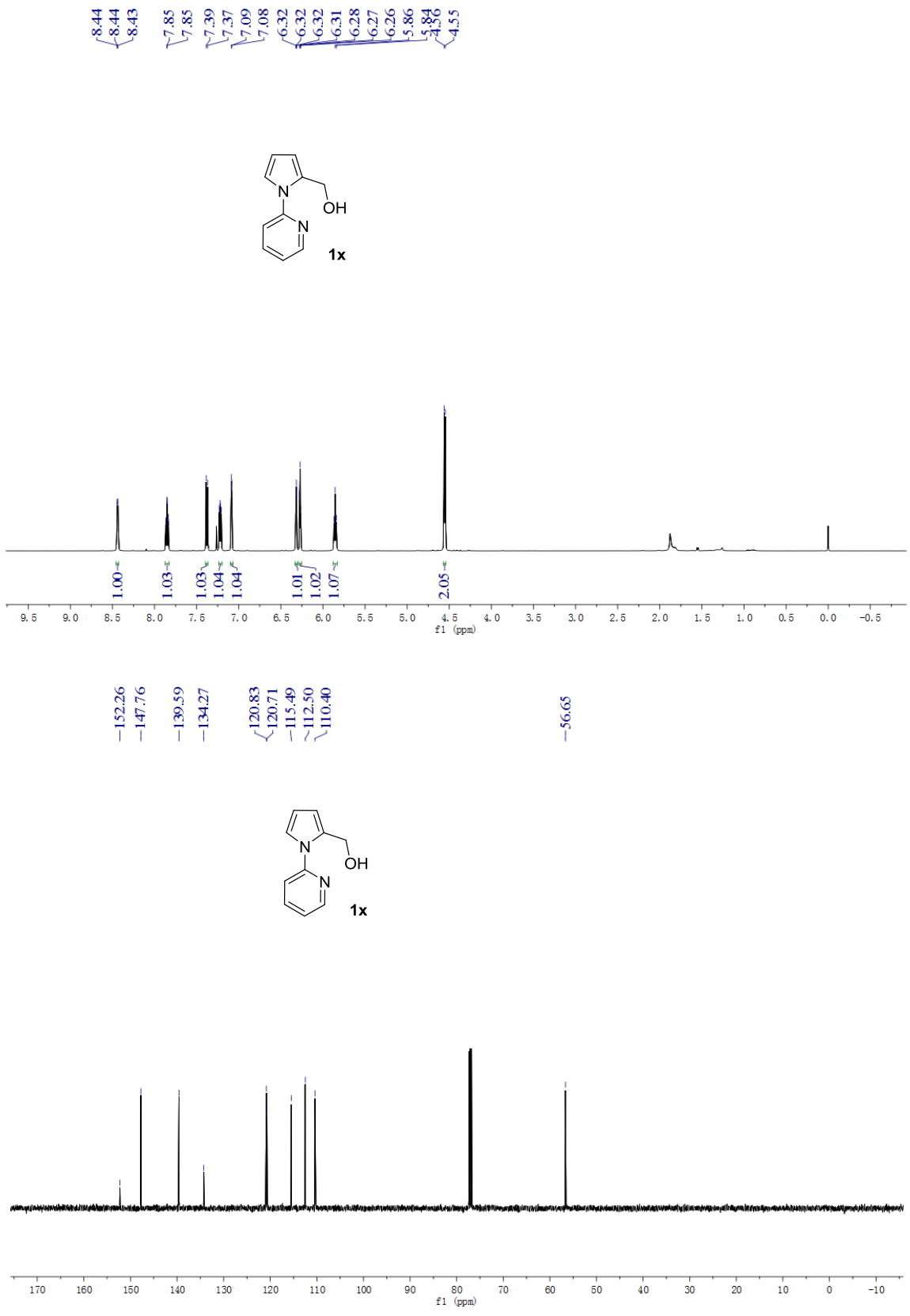


The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **1w** (using $CDCl_3$ as solvent)

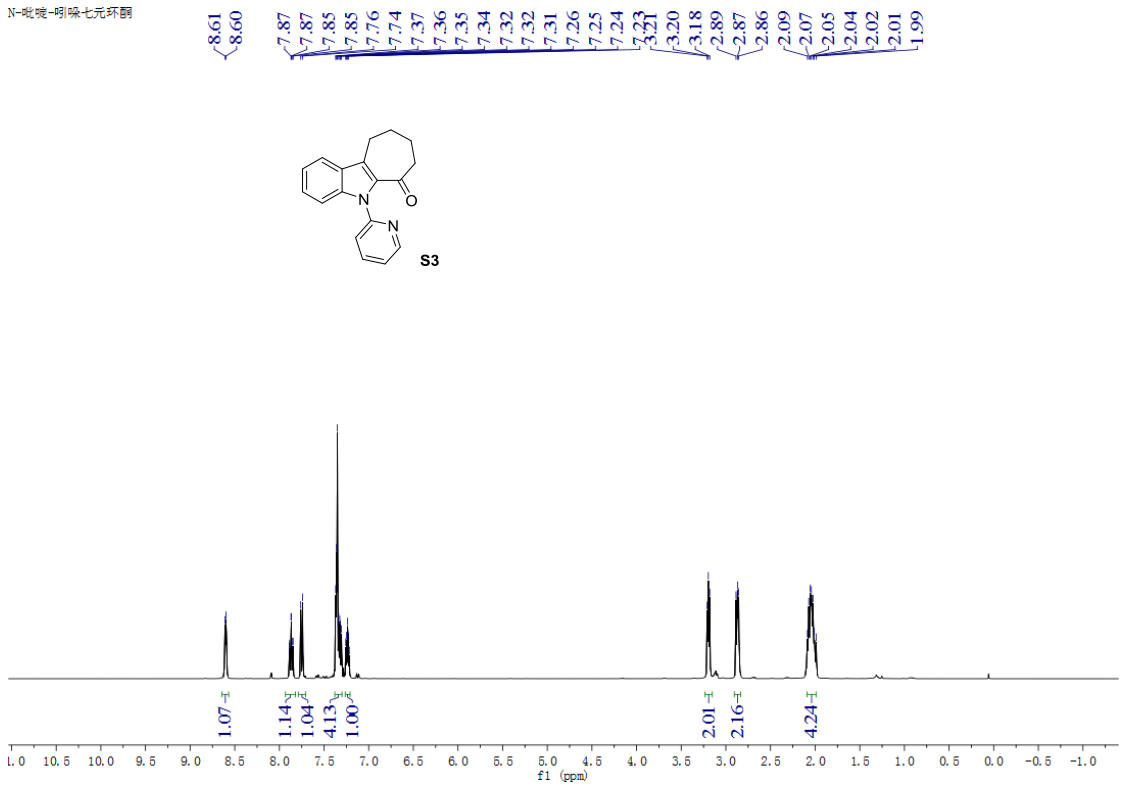


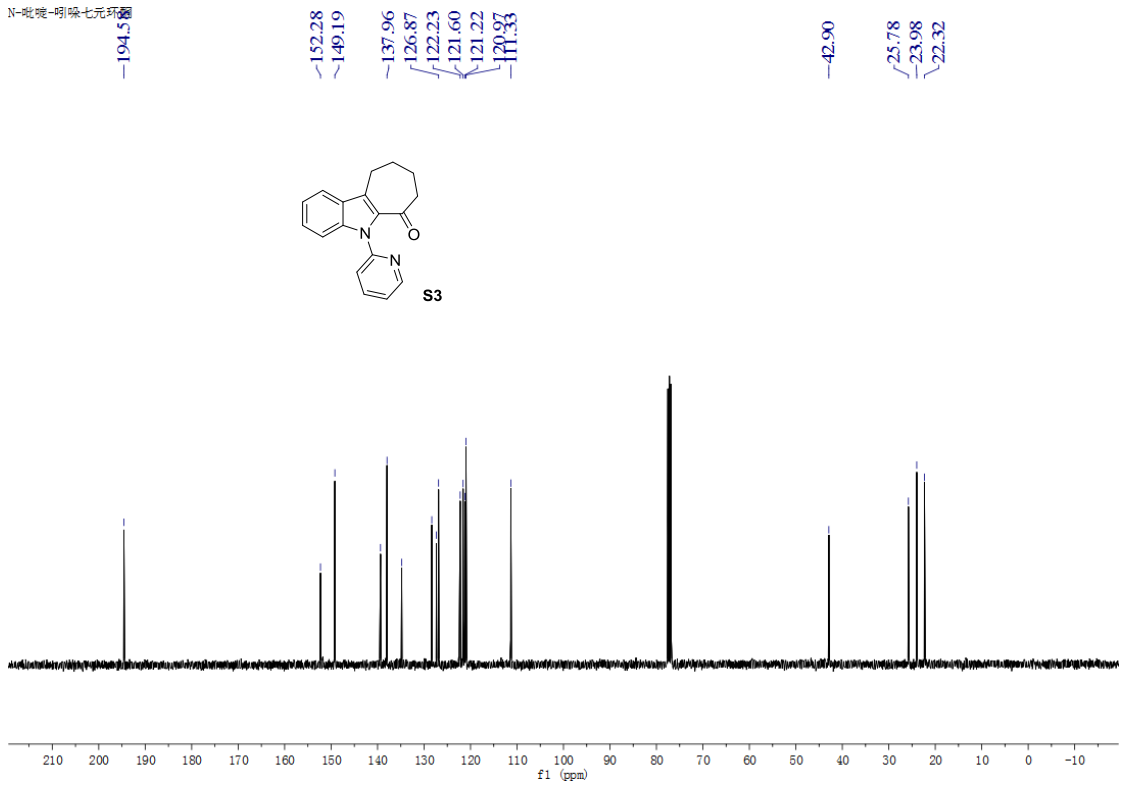


The ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum for **1x** (using $CDCl_3$ as solvent)

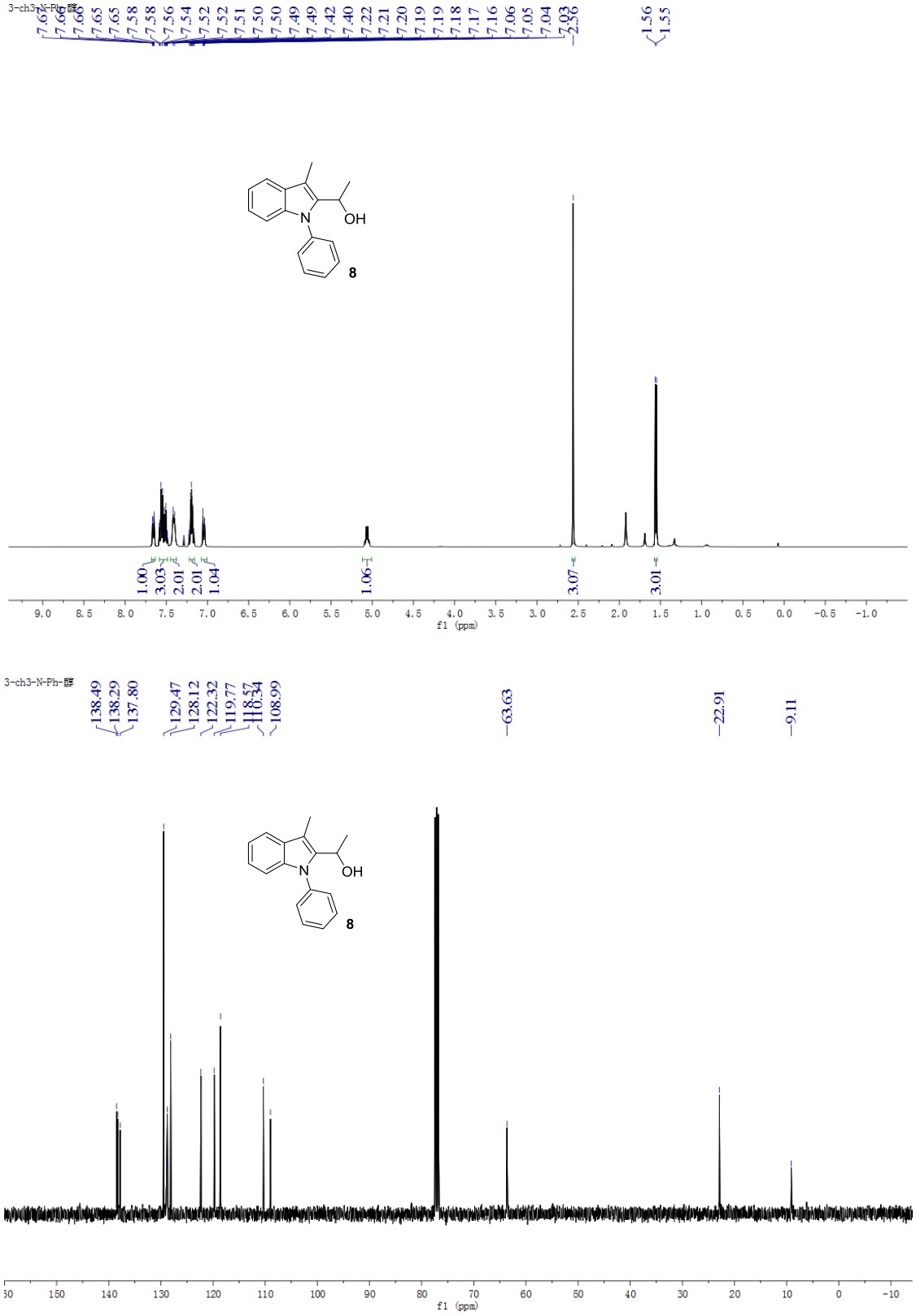


The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **S3** (using $CDCl_3$ as solvent)

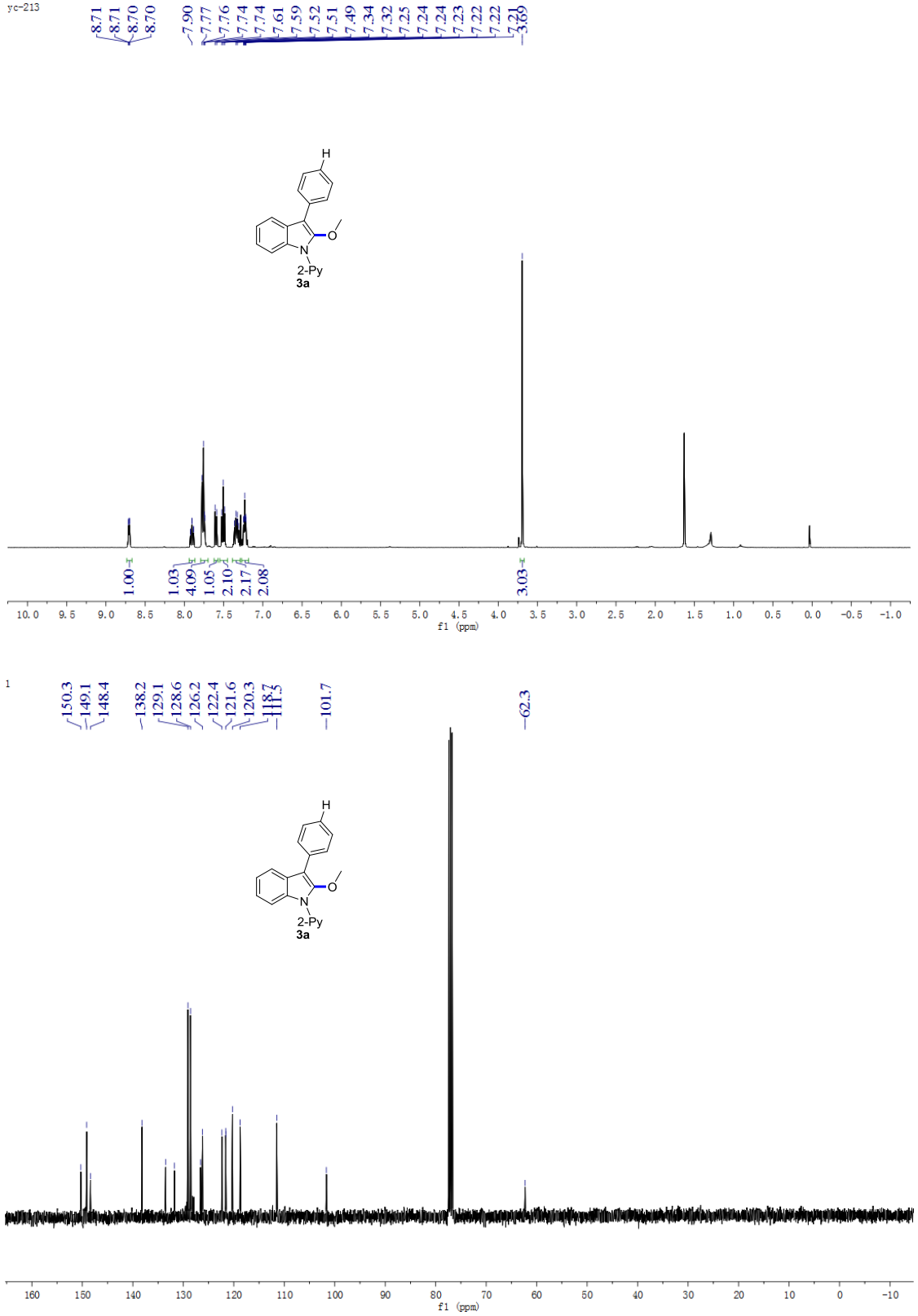




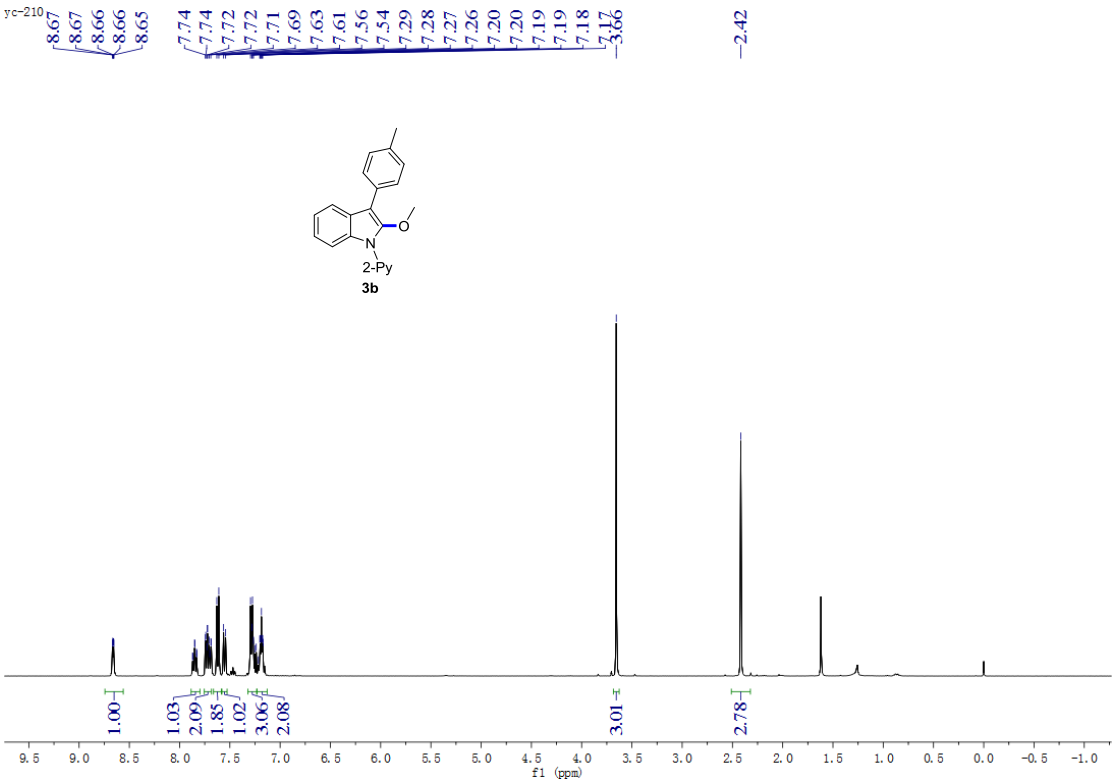
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **8** (using $CDCl_3$ as solvent)

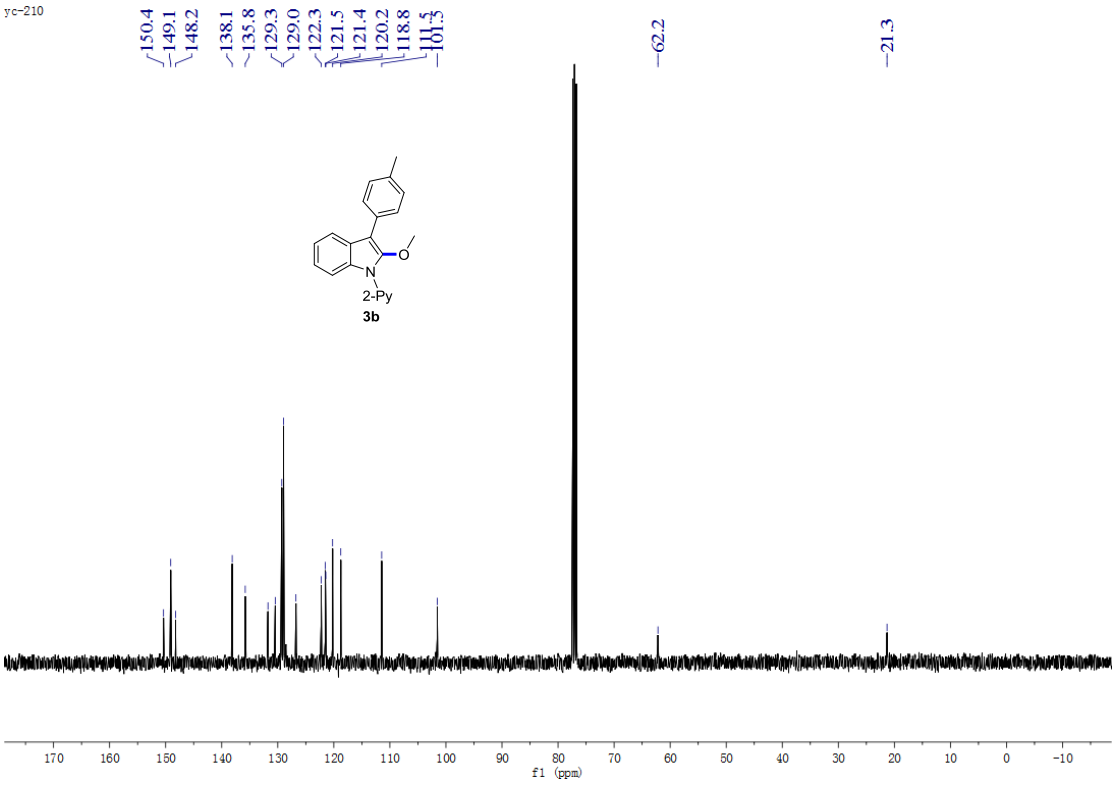


The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3a** (using $CDCl_3$ as solvent)

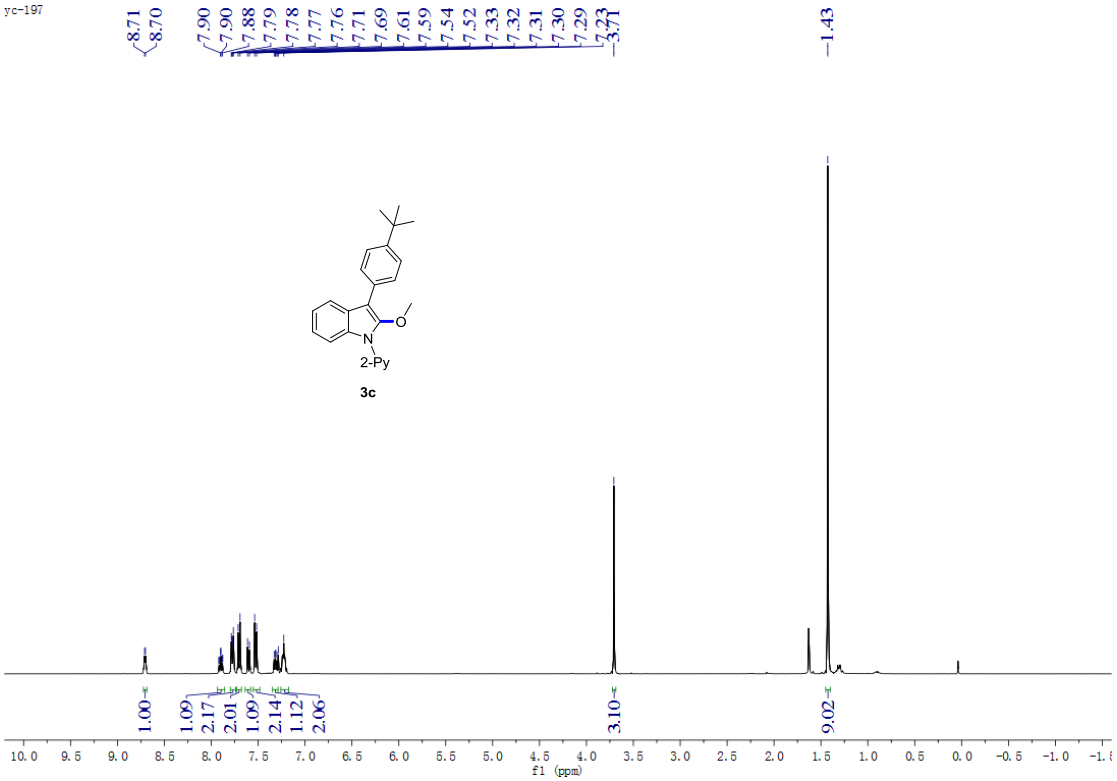


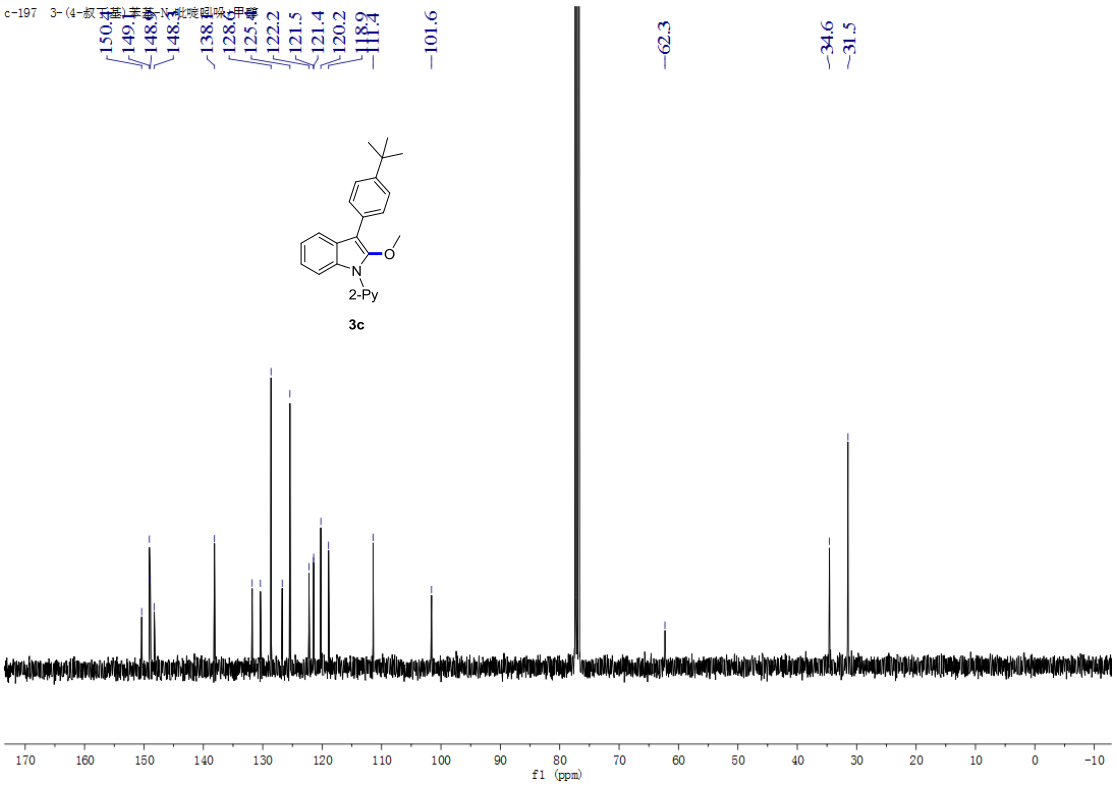
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3b** (using $CDCl_3$ as solvent)



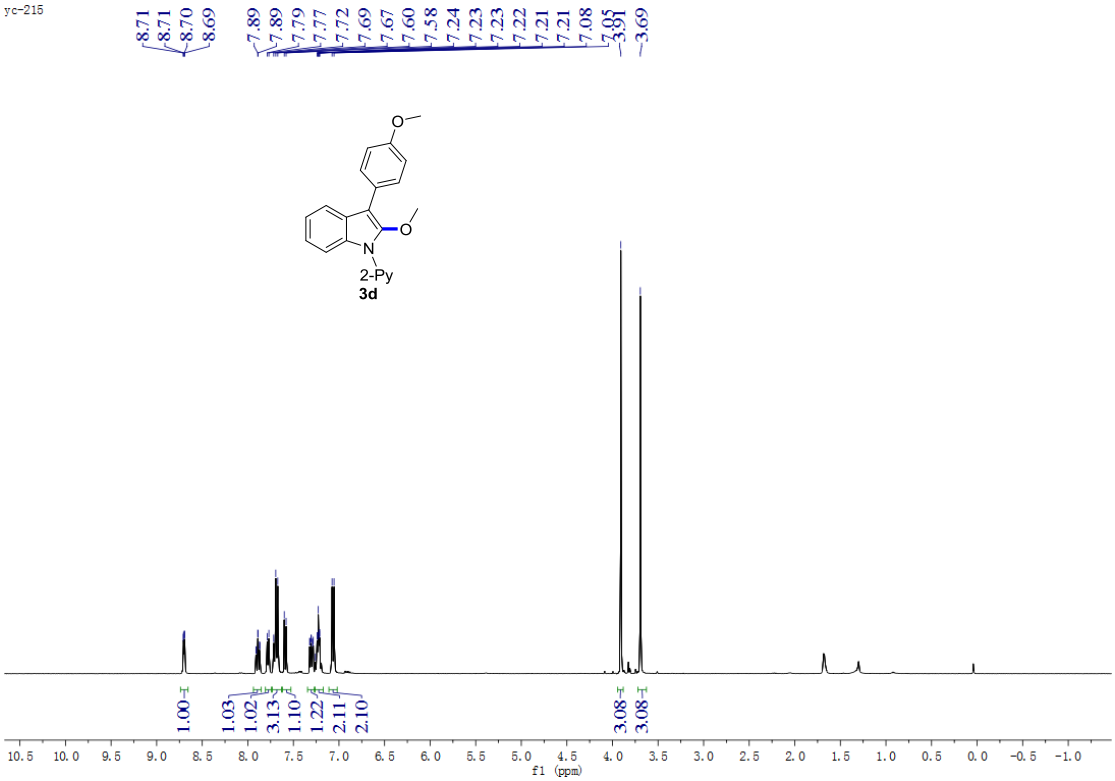


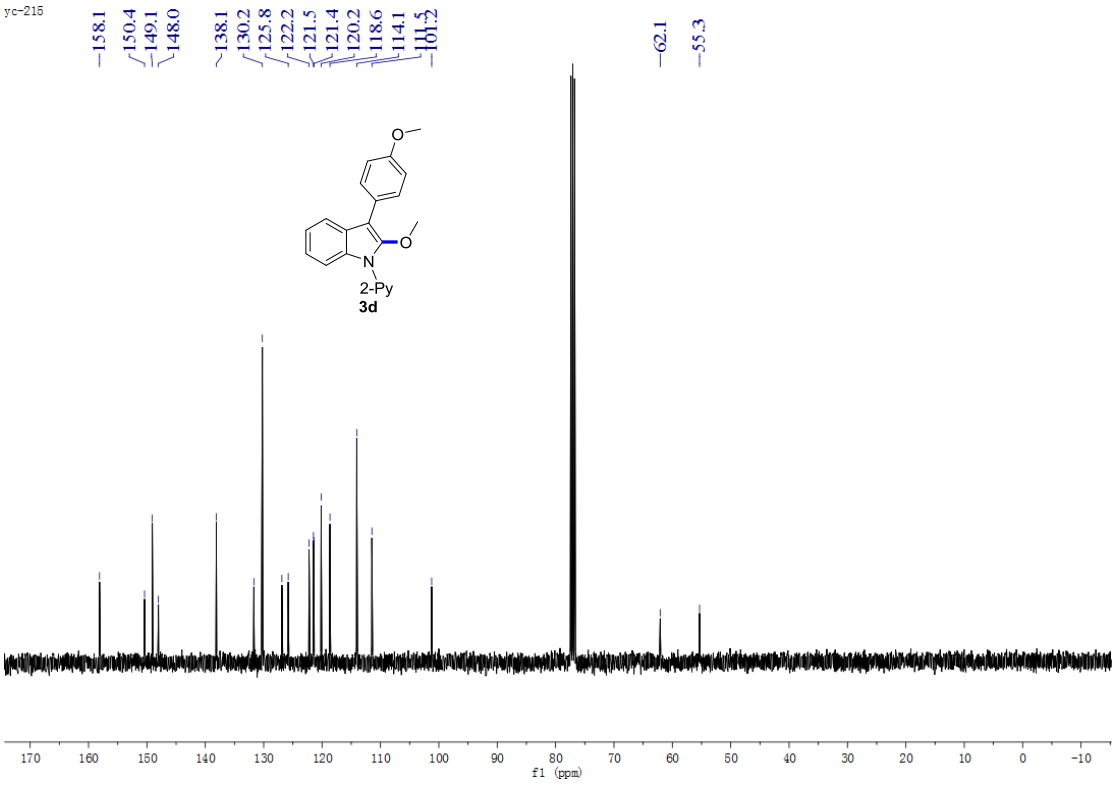
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3c** (using $CDCl_3$ as solvent)



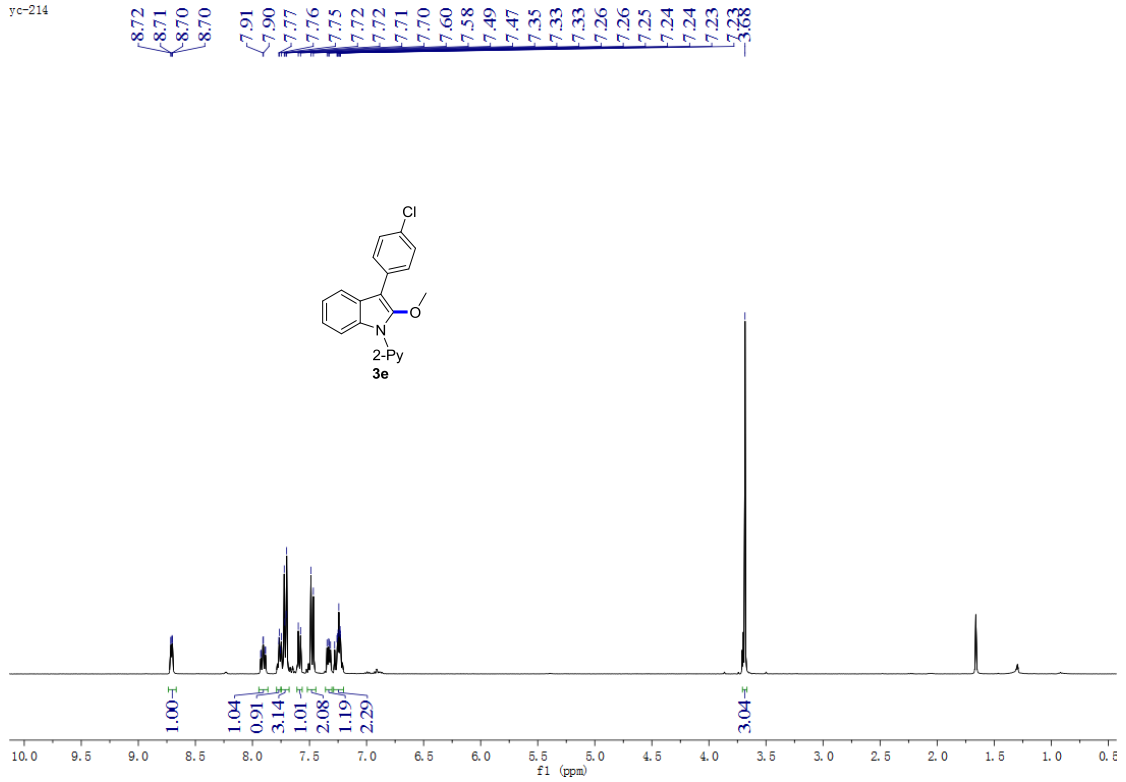


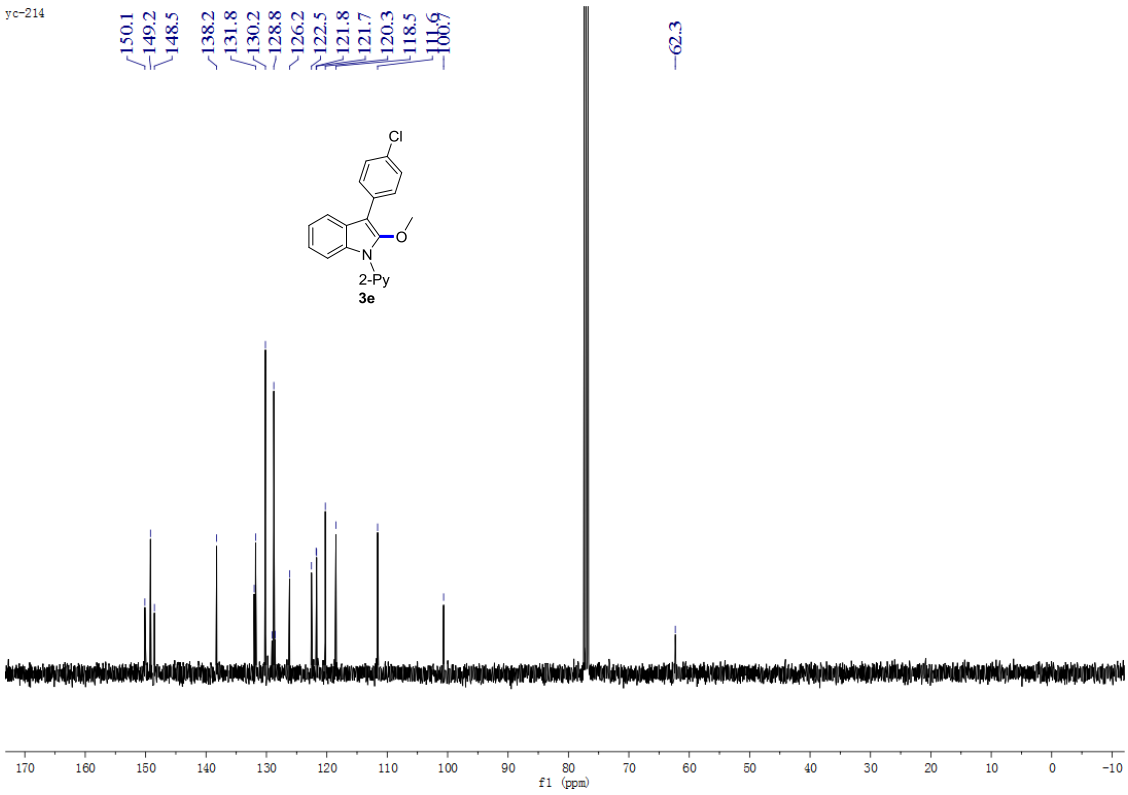
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for 3**d** (using $CDCl_3$ as solvent)



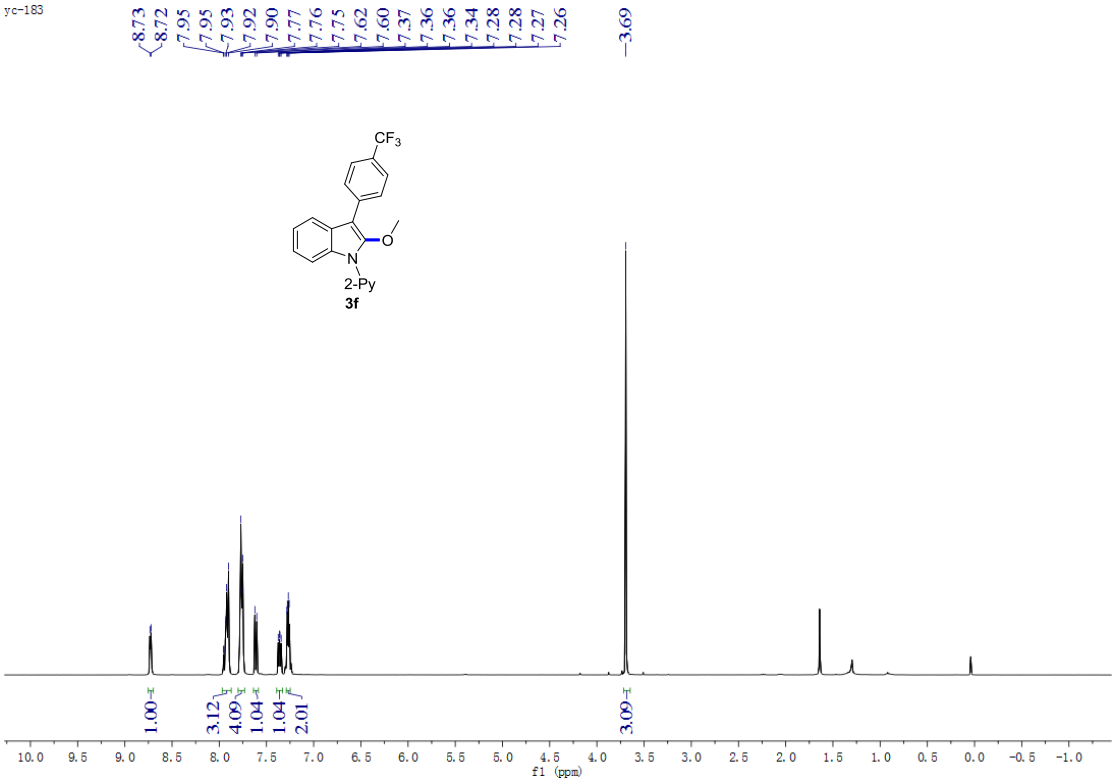


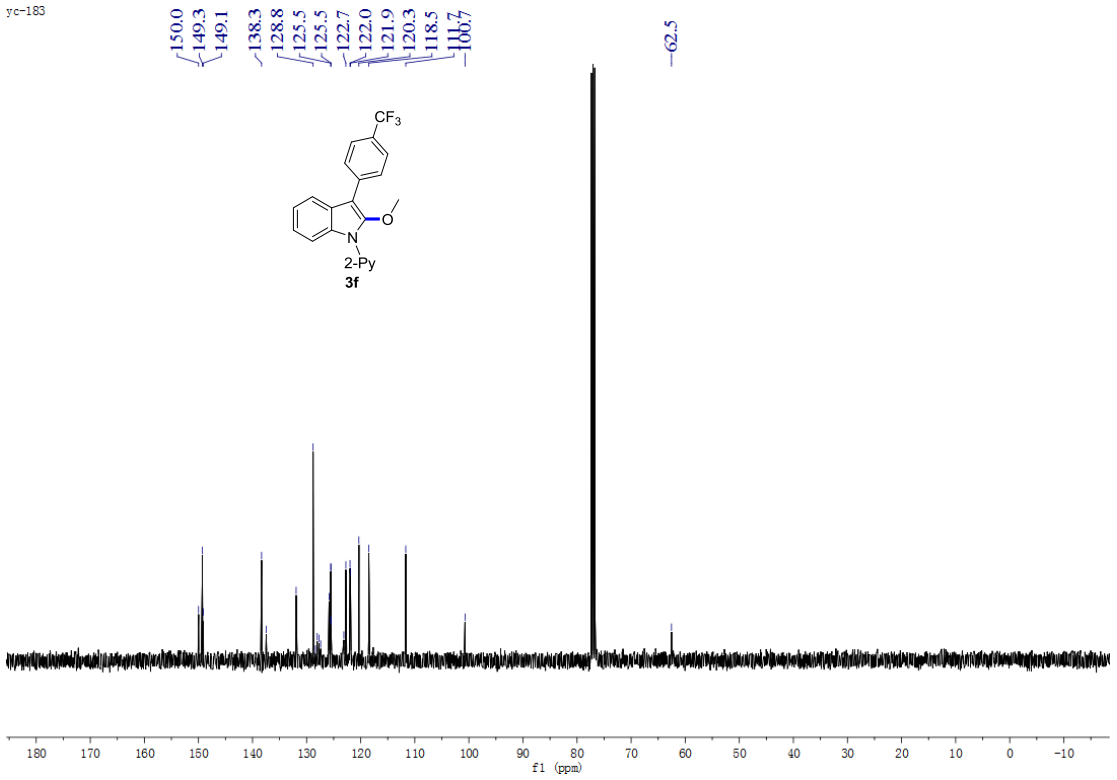
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3e** (using $CDCl_3$ as solvent)



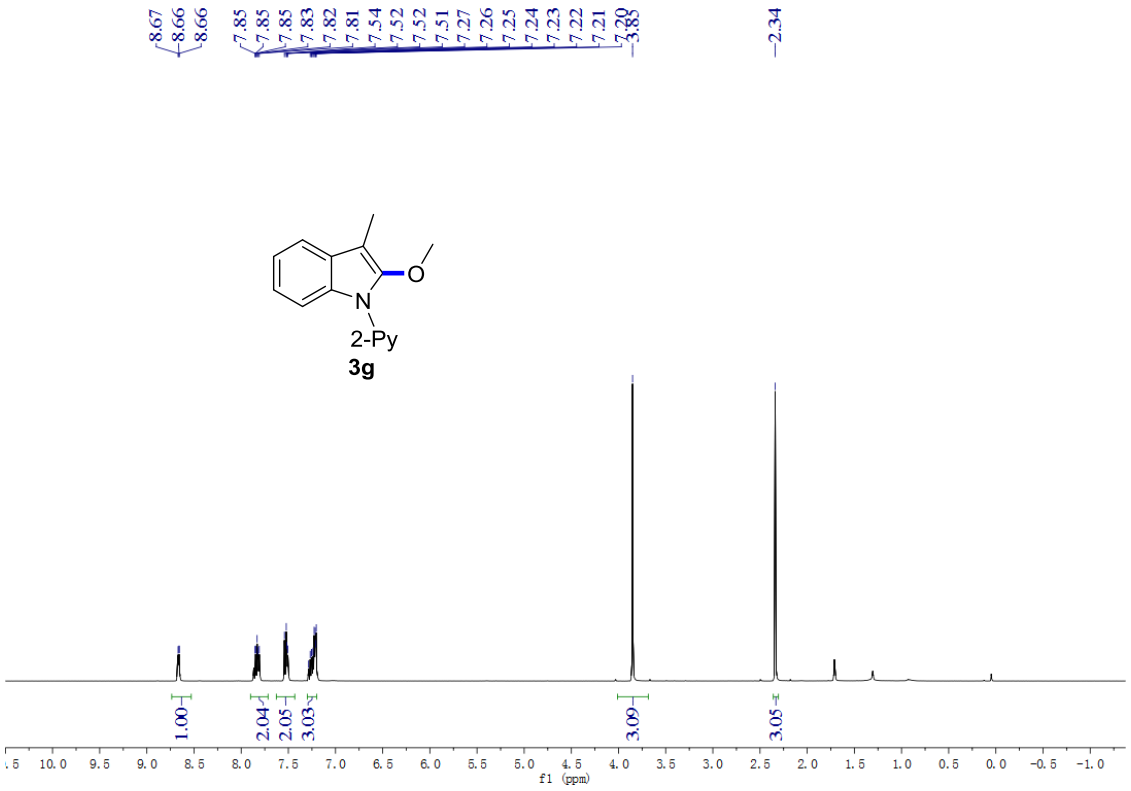


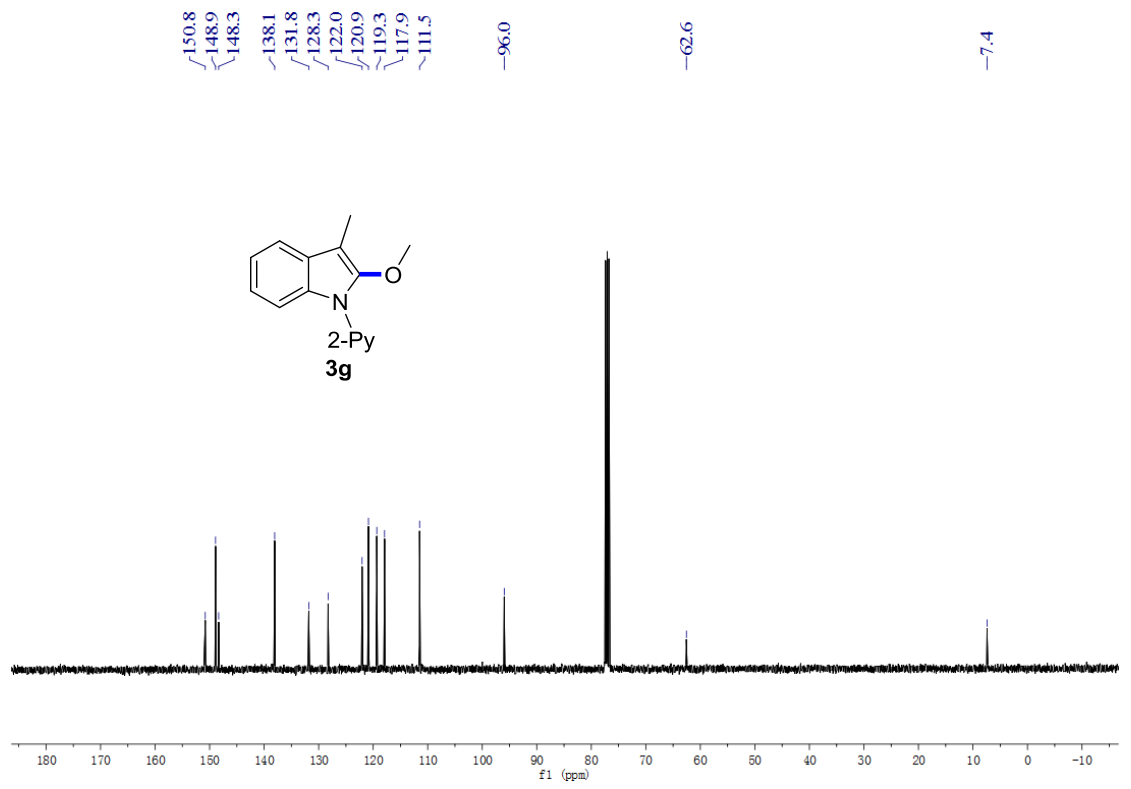
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3f** (using $CDCl_3$ as solvent)



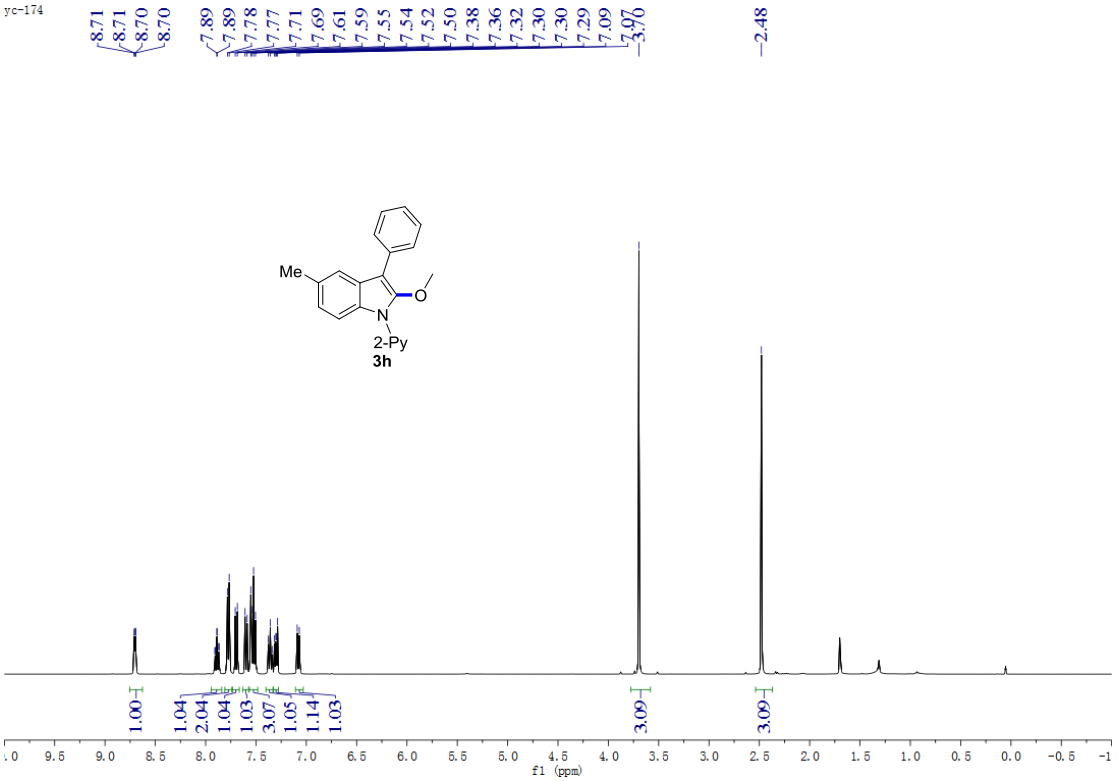


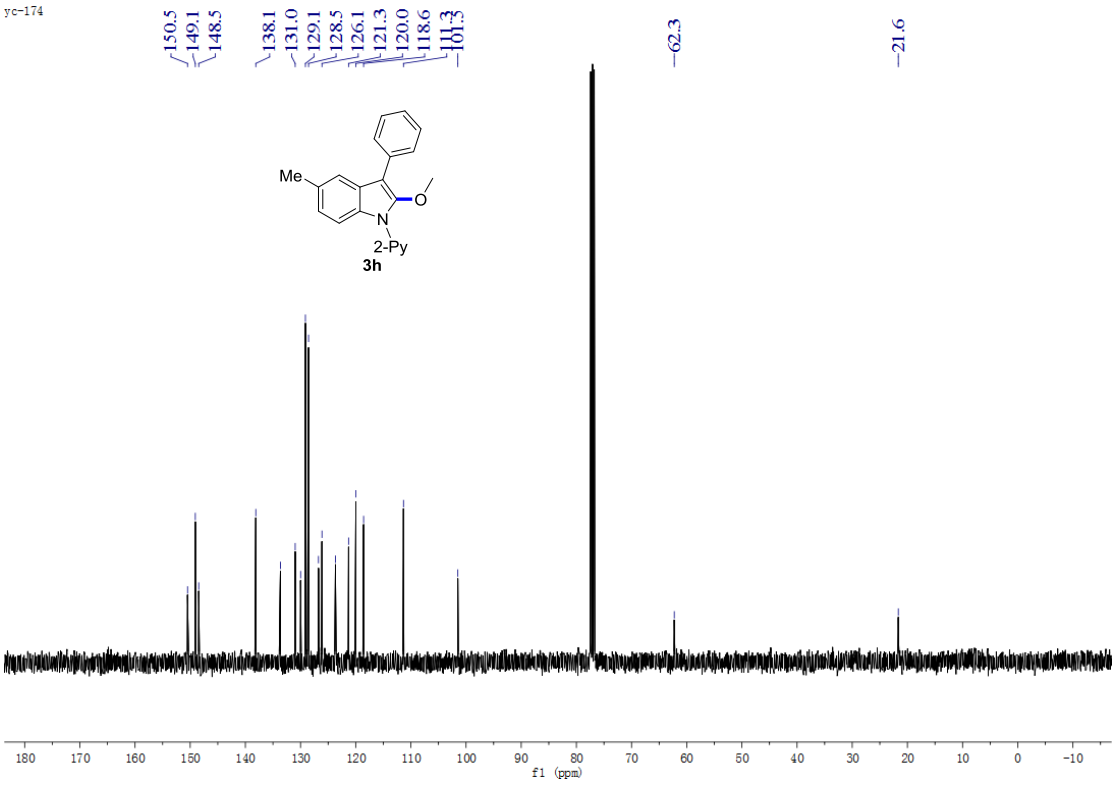
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3g** (using $CDCl_3$ as solvent)



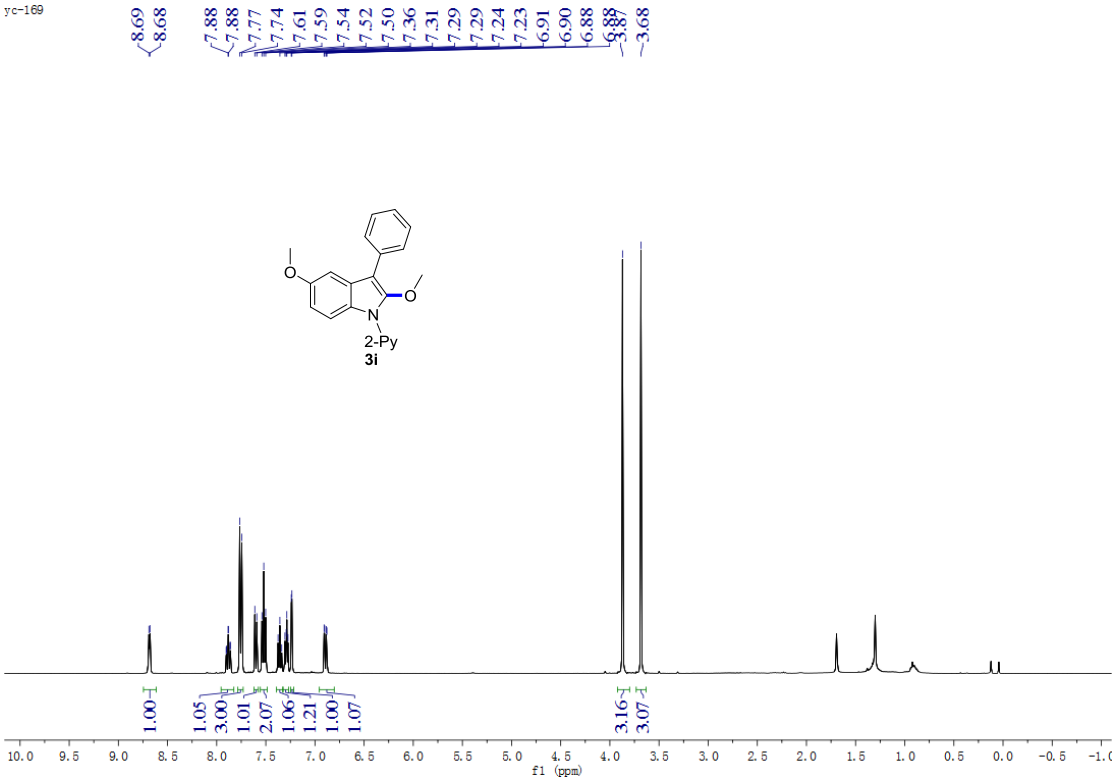


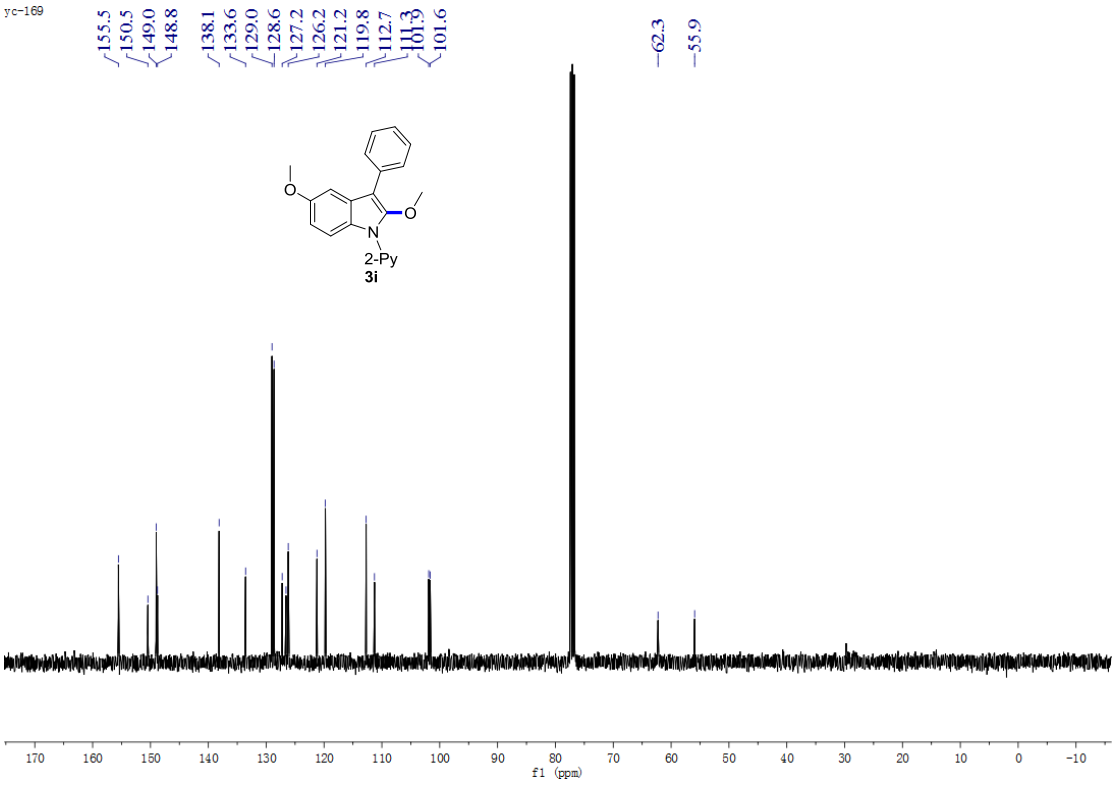
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3h** (using $CDCl_3$ as solvent)



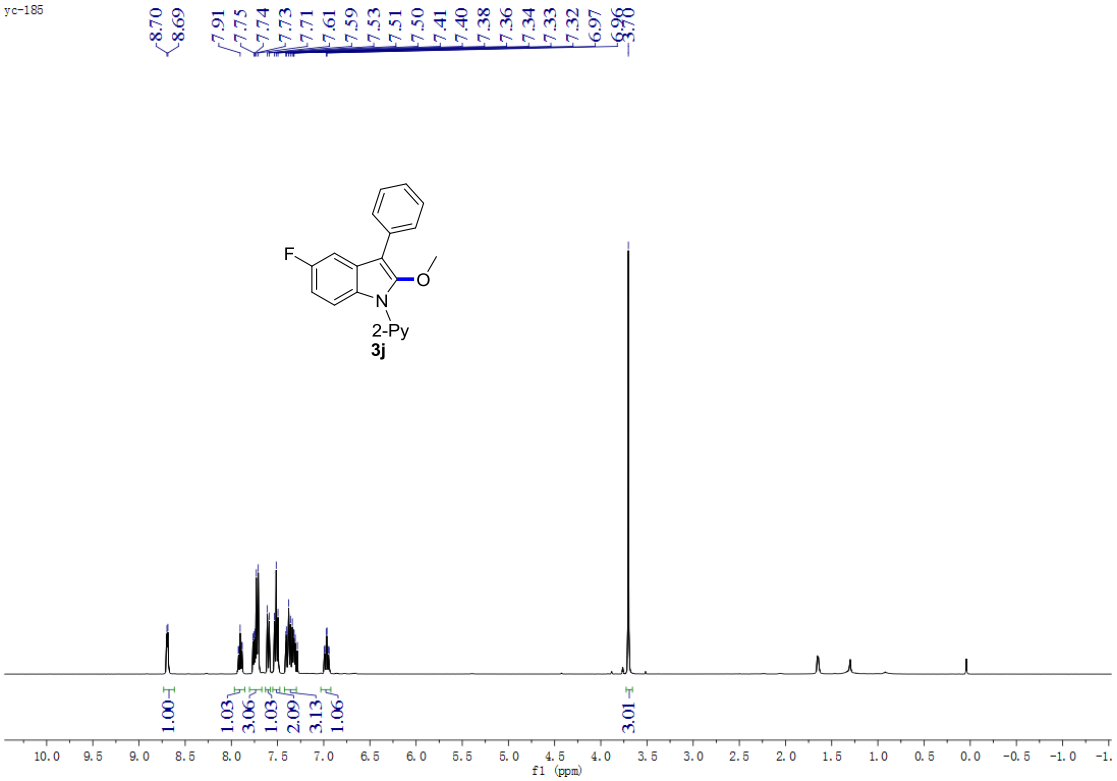


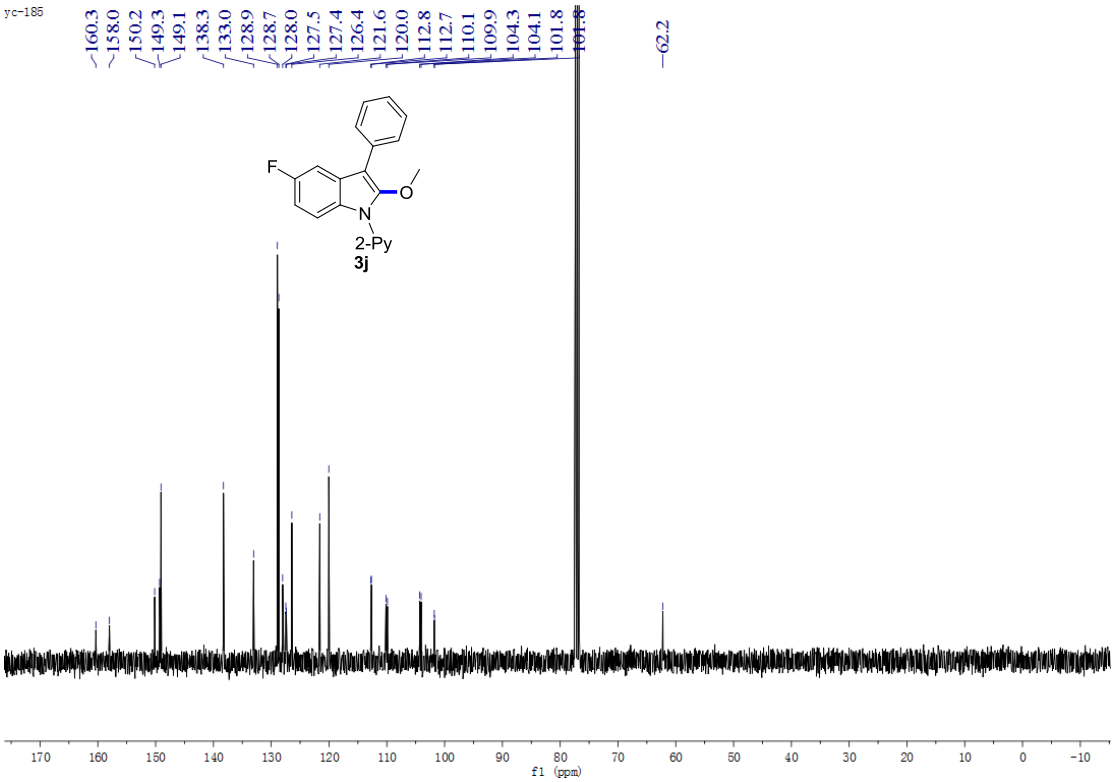
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3i** (using $CDCl_3$ as solvent)



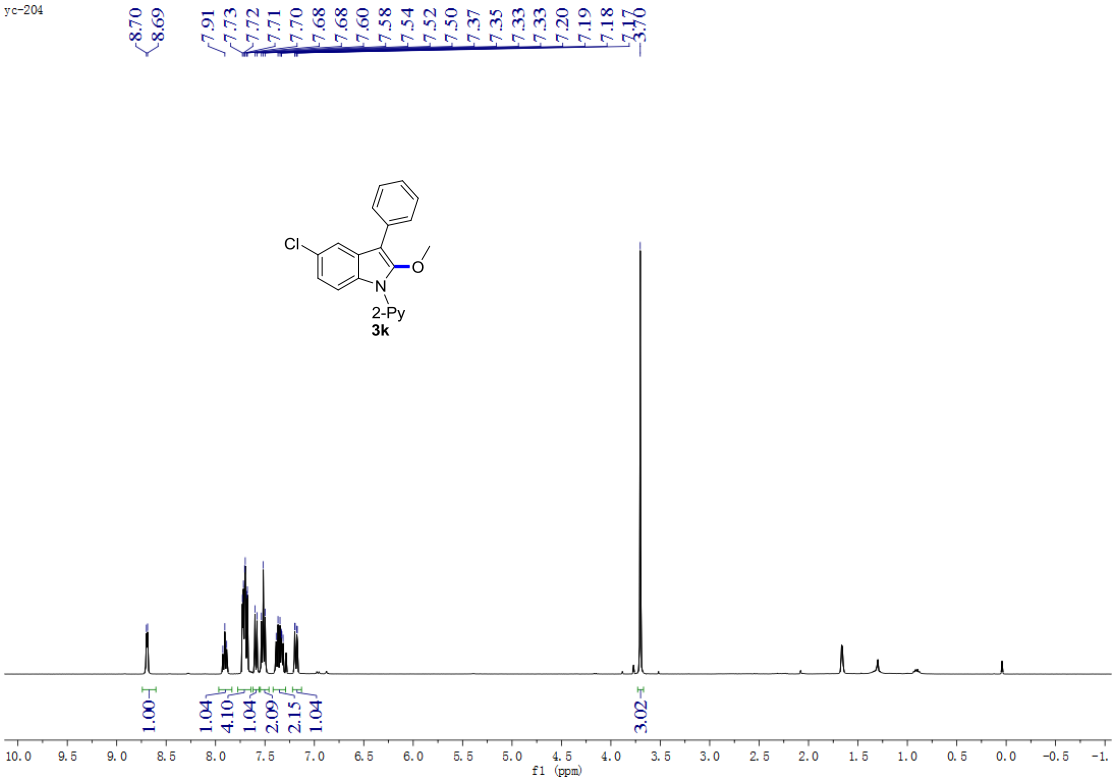


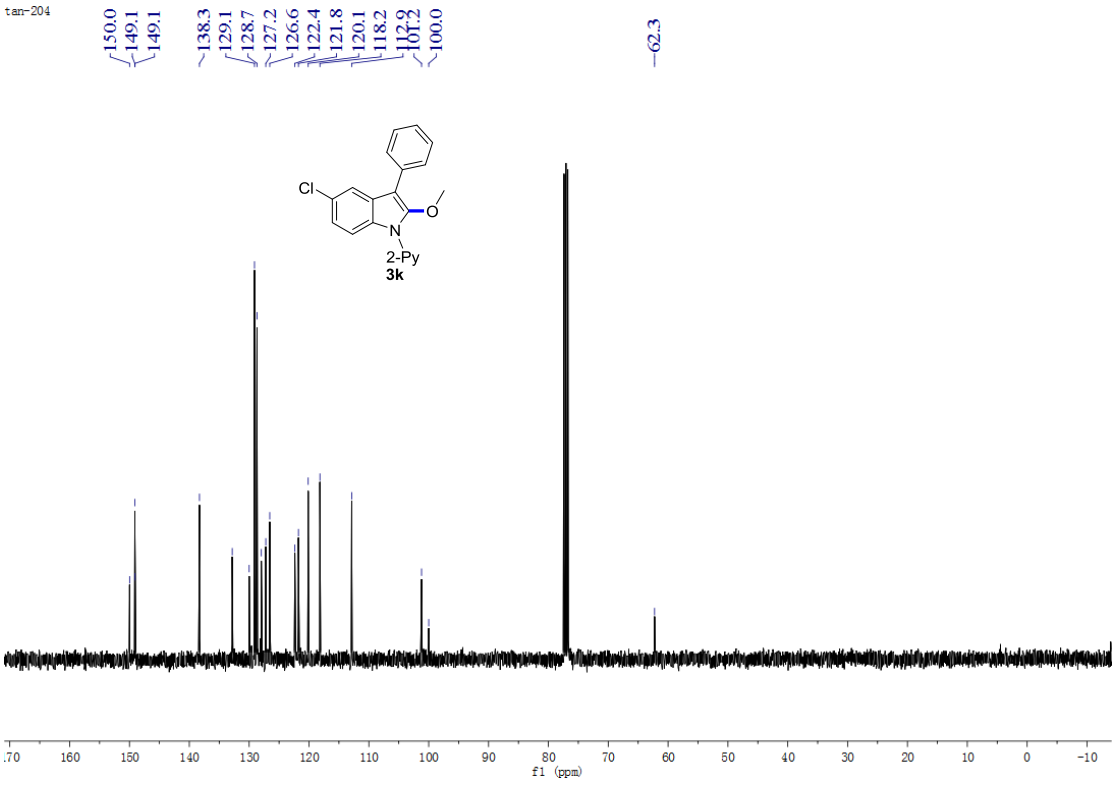
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3j** (using $CDCl_3$ as solvent)



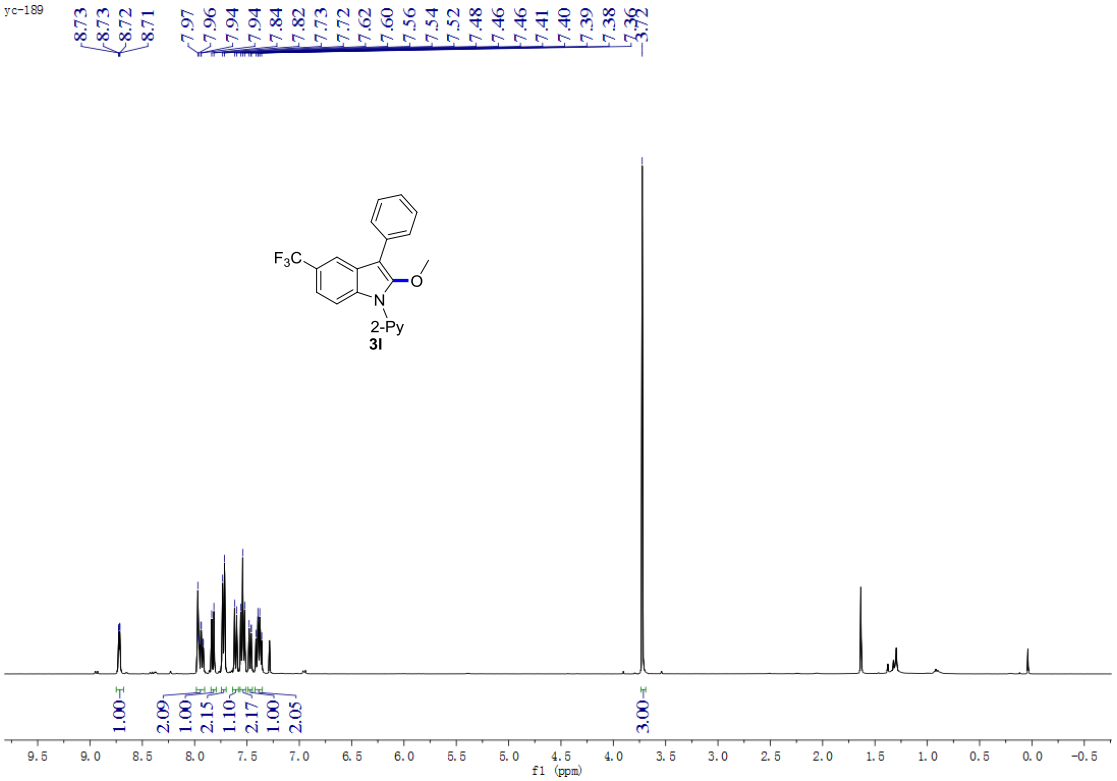


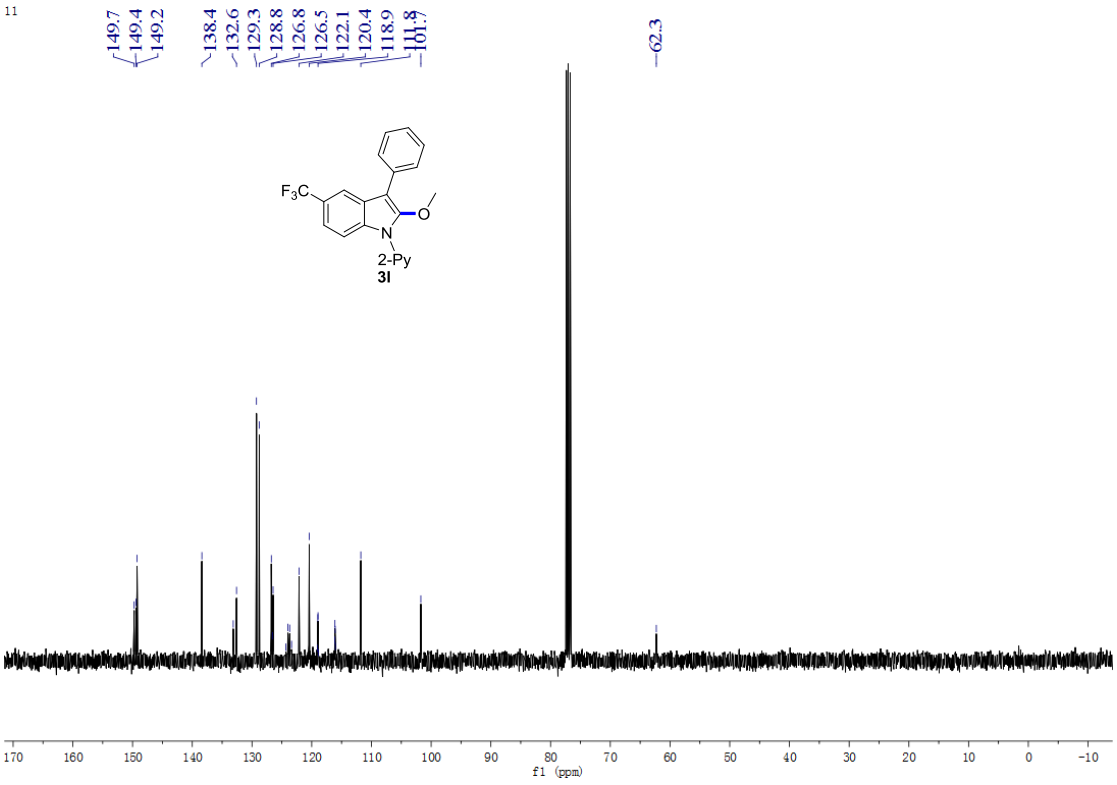
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for 3**k** (using $CDCl_3$ as solvent)



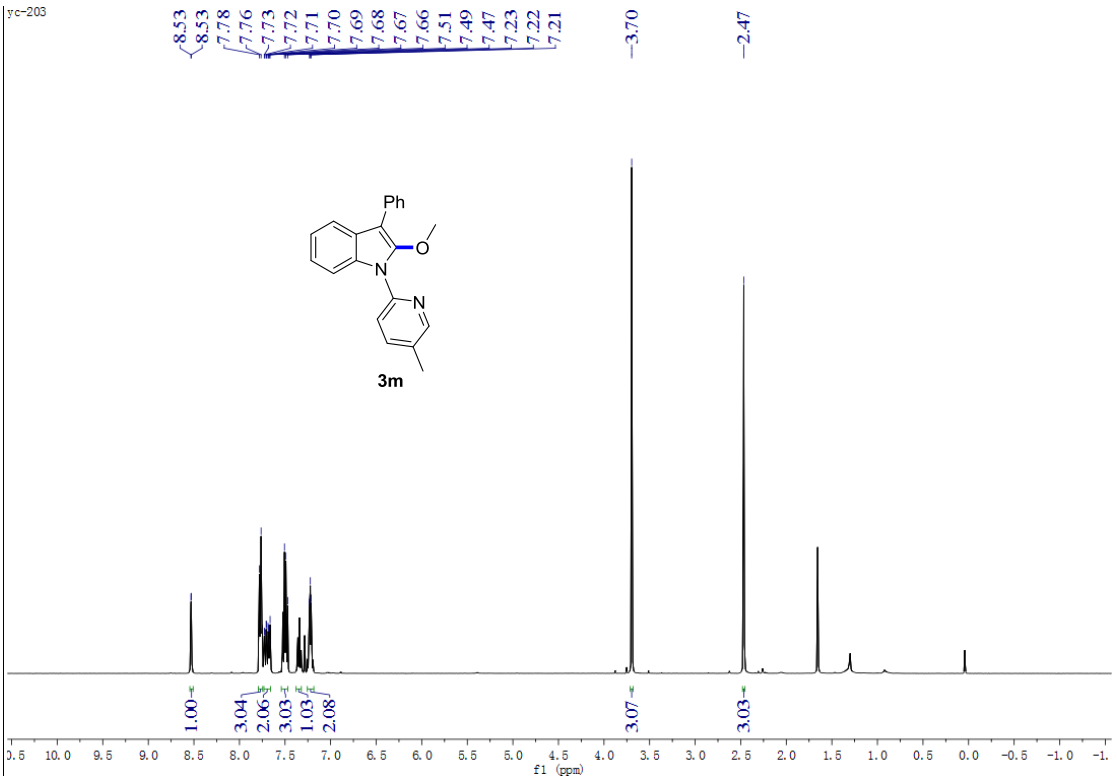


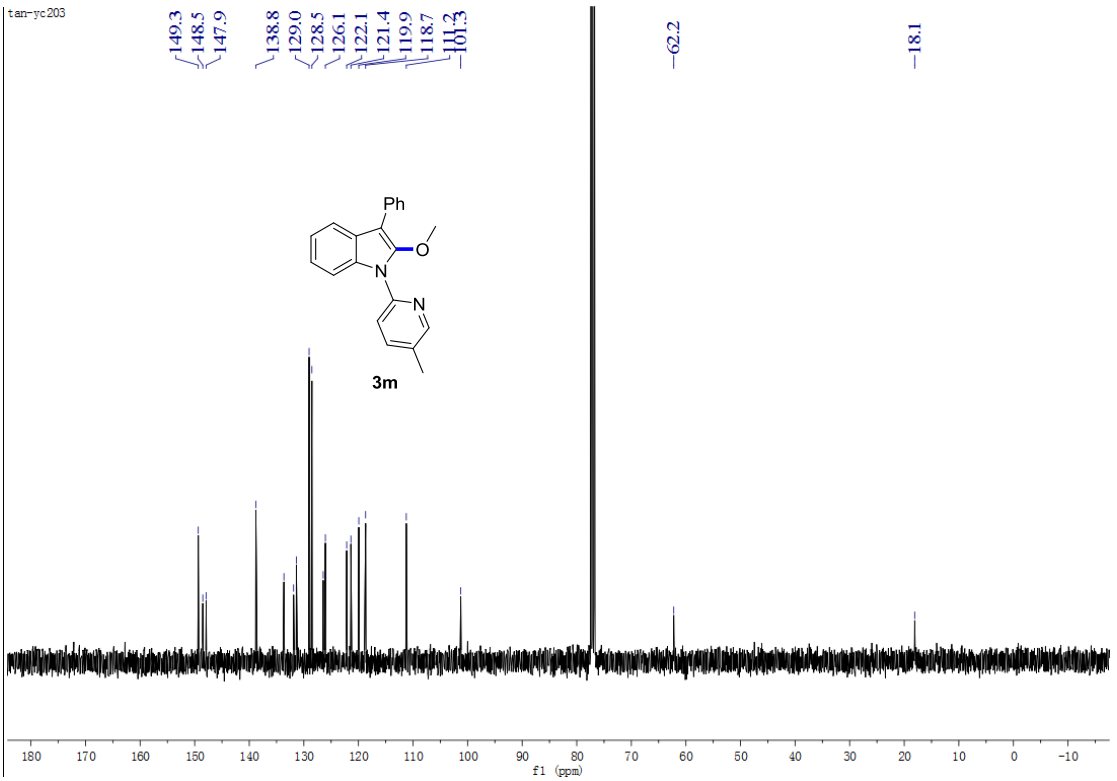
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3l** (using $CDCl_3$ as solvent)



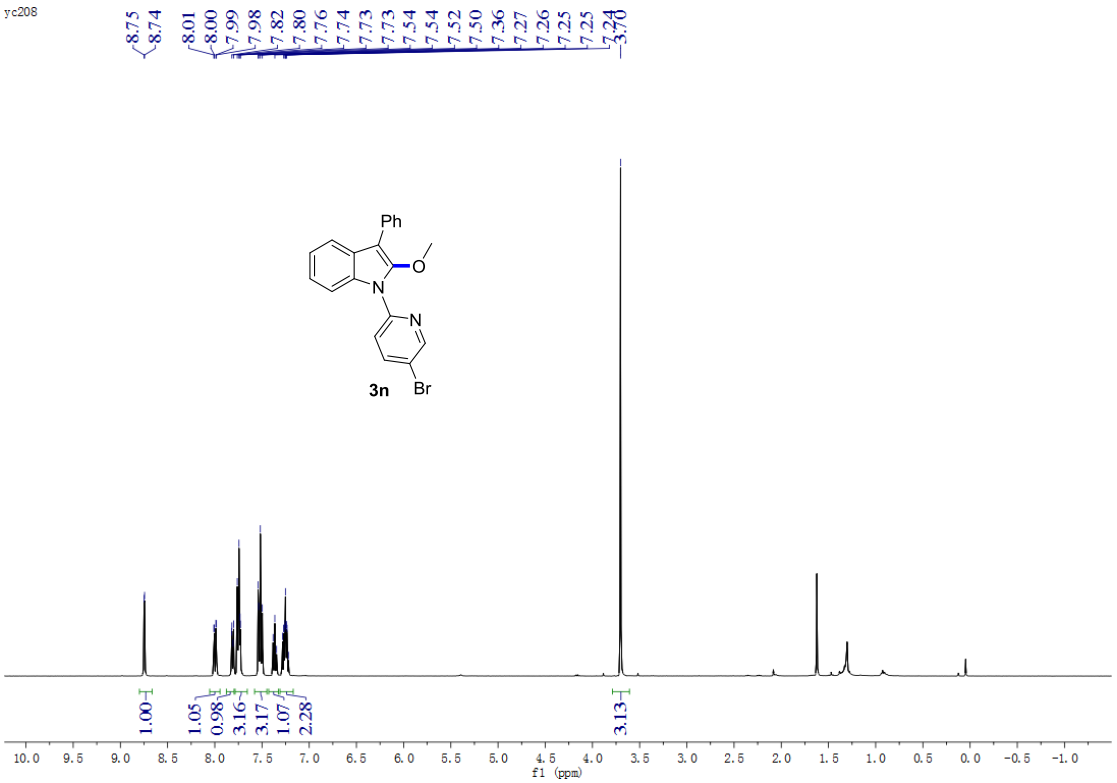


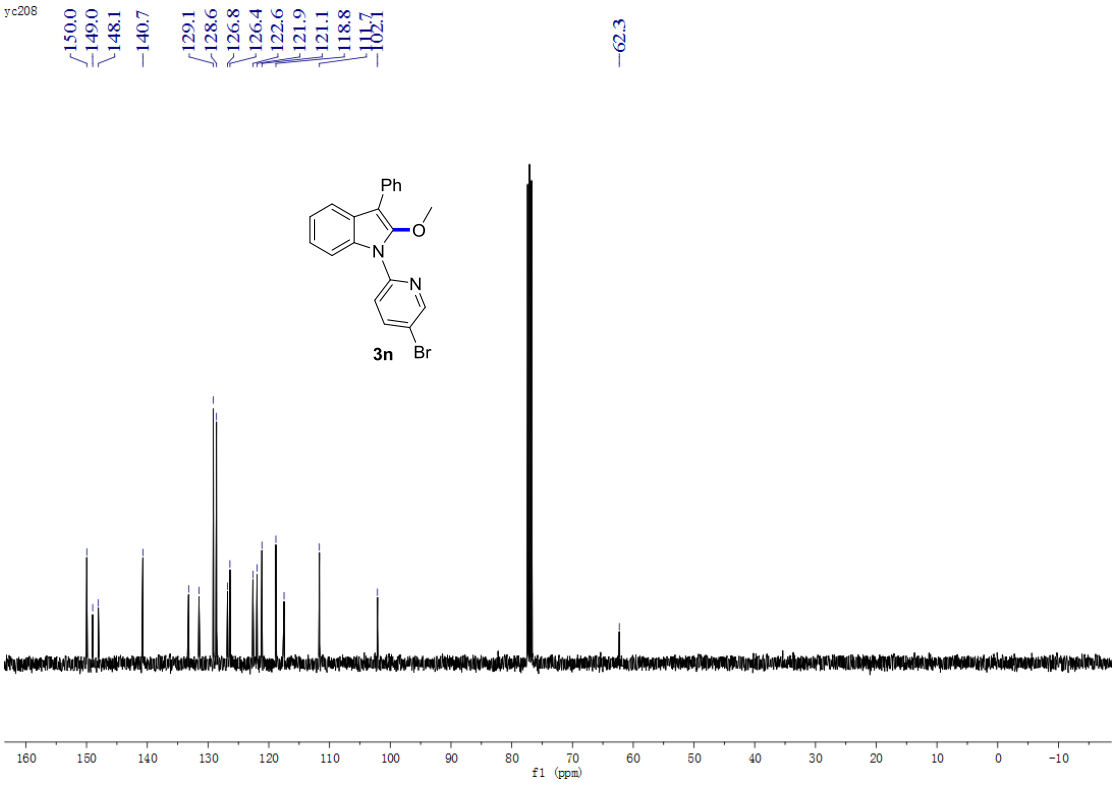
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3m** (using $CDCl_3$ as solvent)



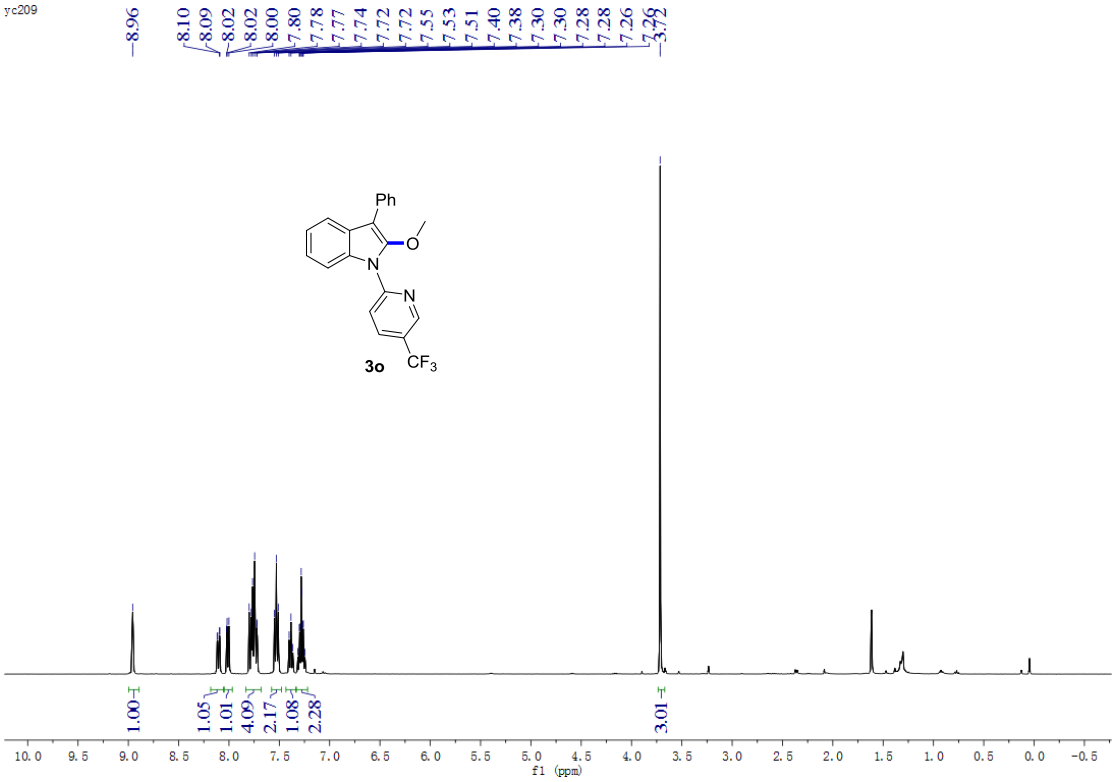


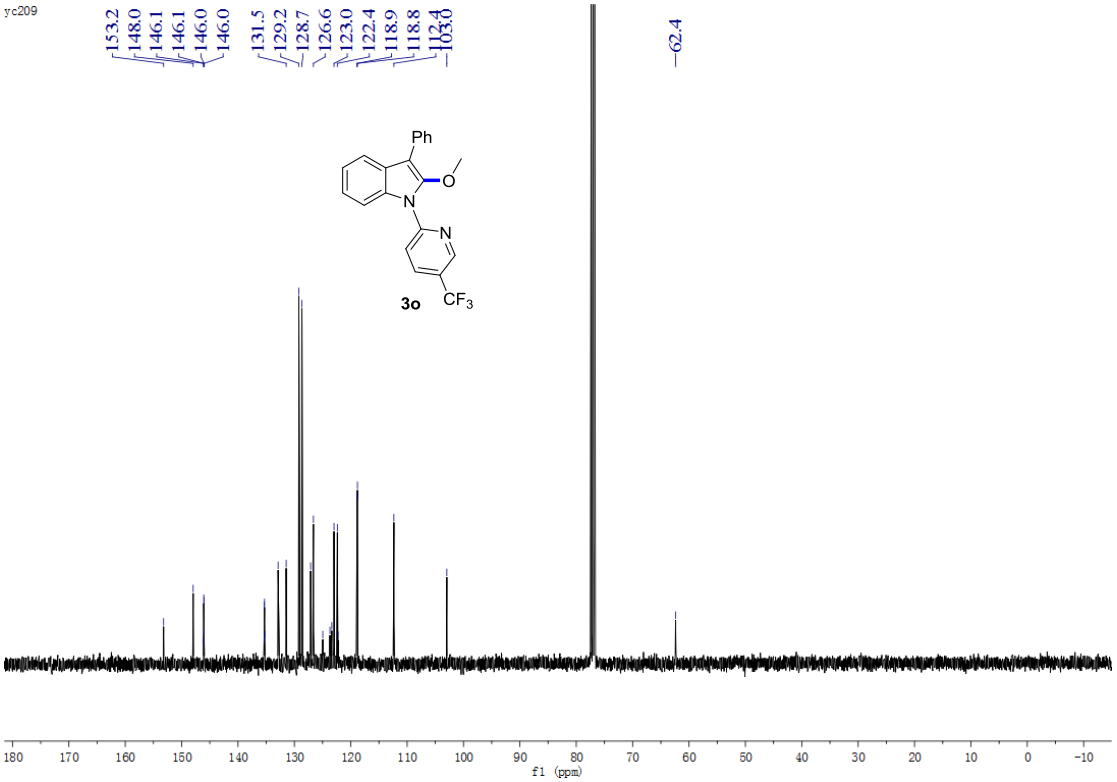
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3n** (using $CDCl_3$ as solvent)



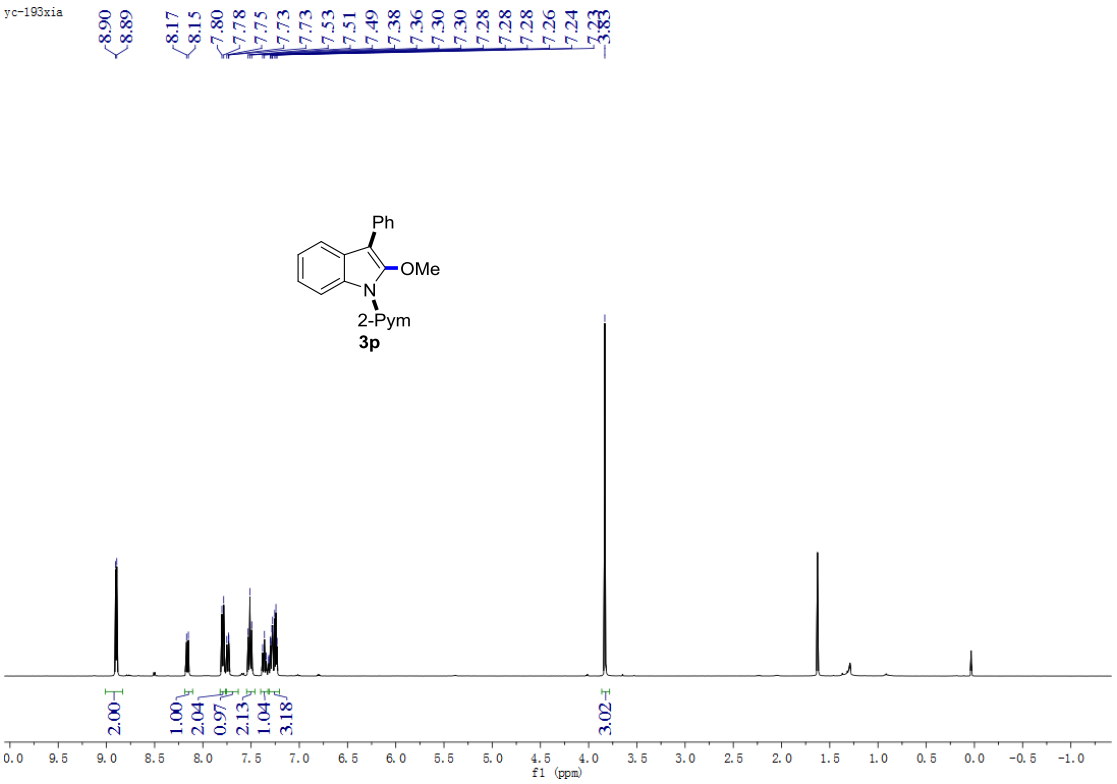


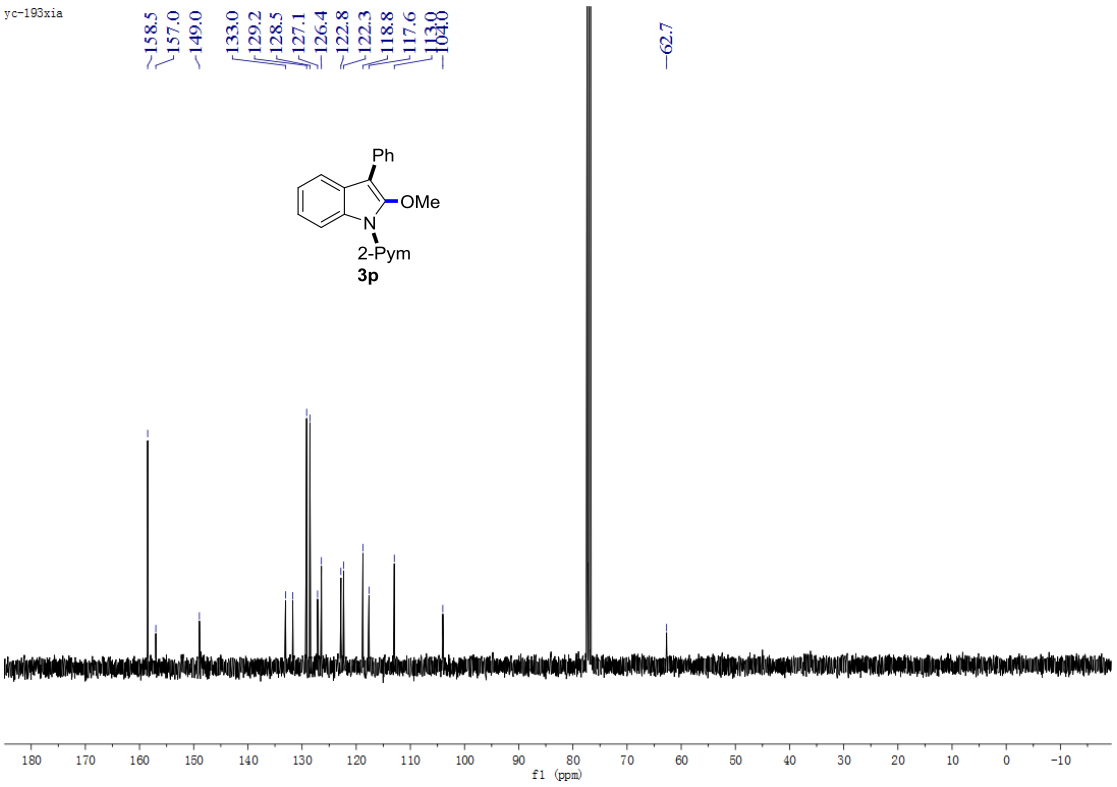
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3o** (using $CDCl_3$ as solvent)



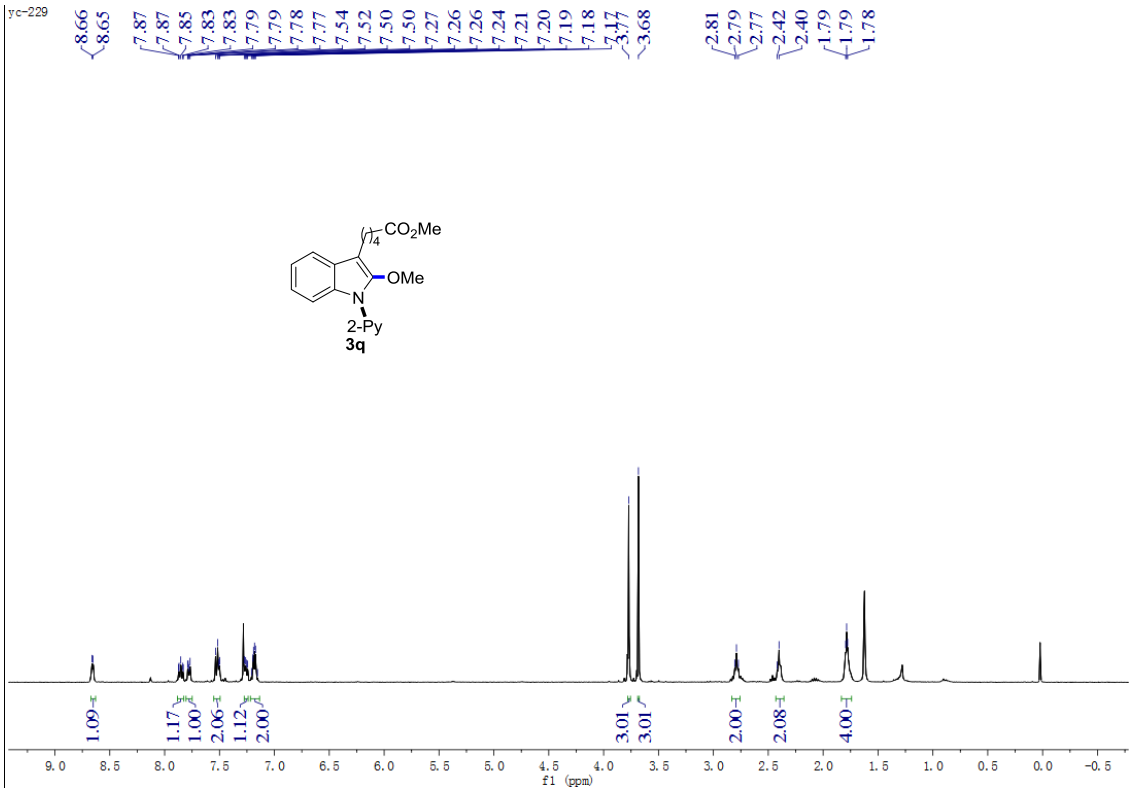


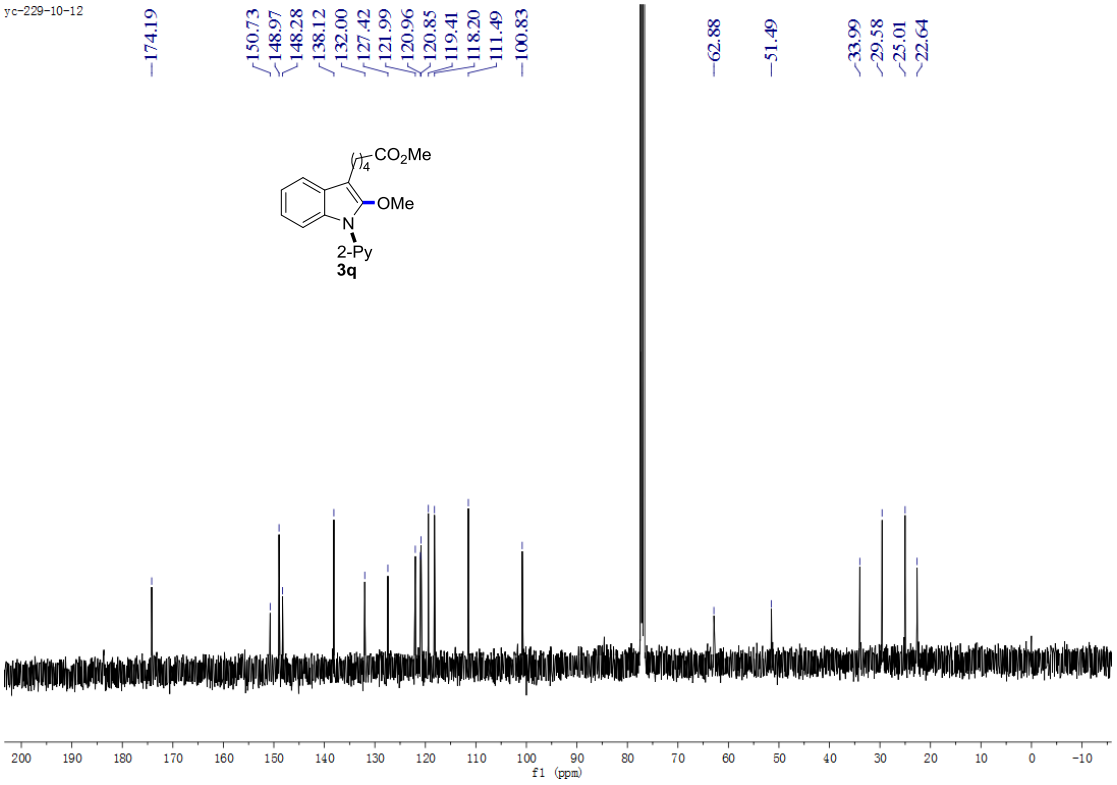
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3p** (using $CDCl_3$ as solvent)



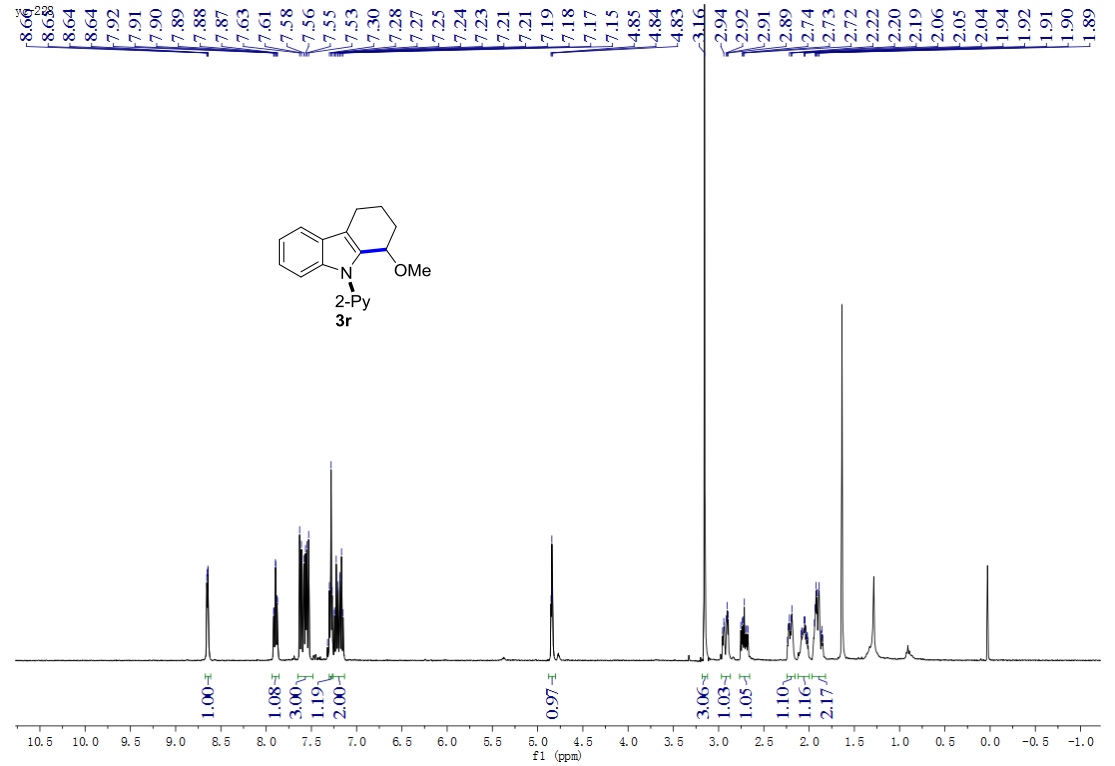


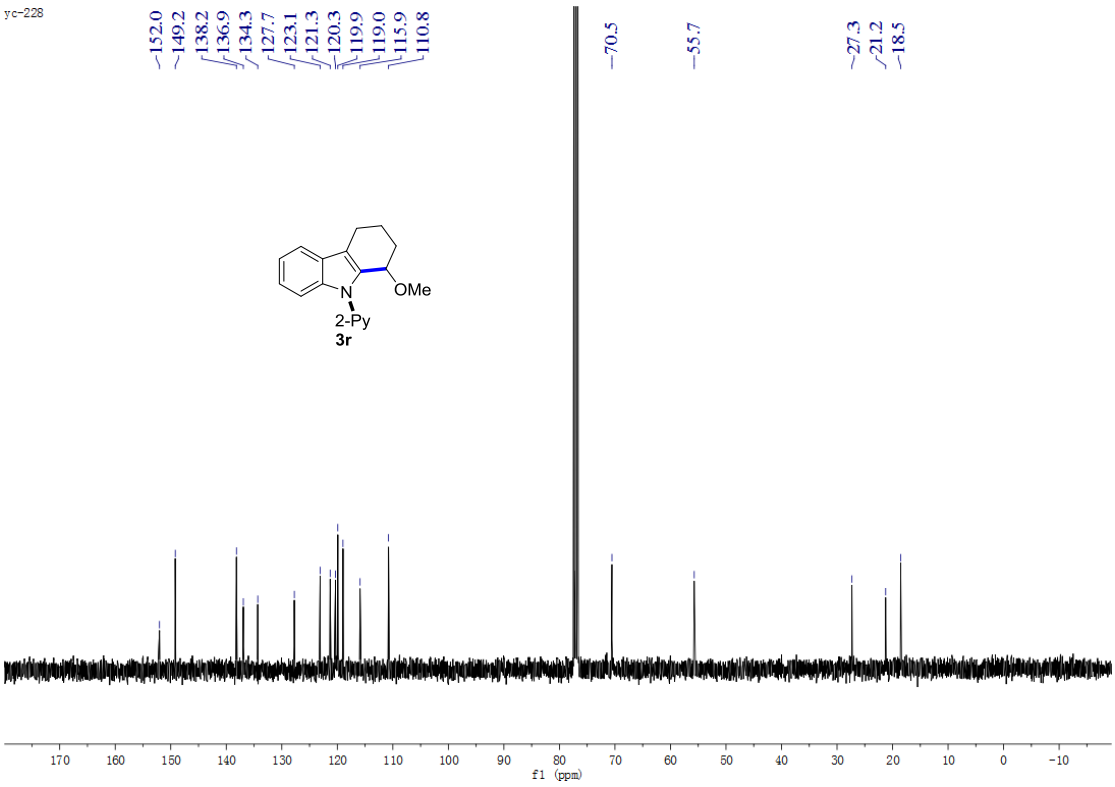
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for 3**q** (using $CDCl_3$ as solvent)



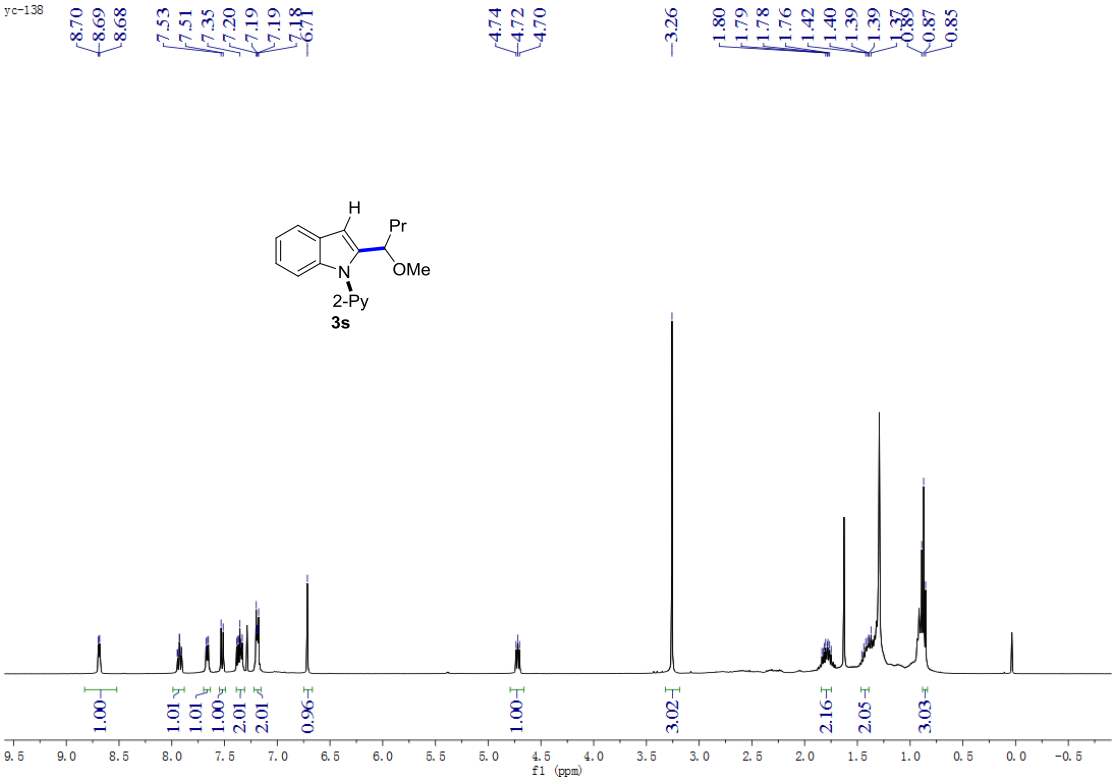


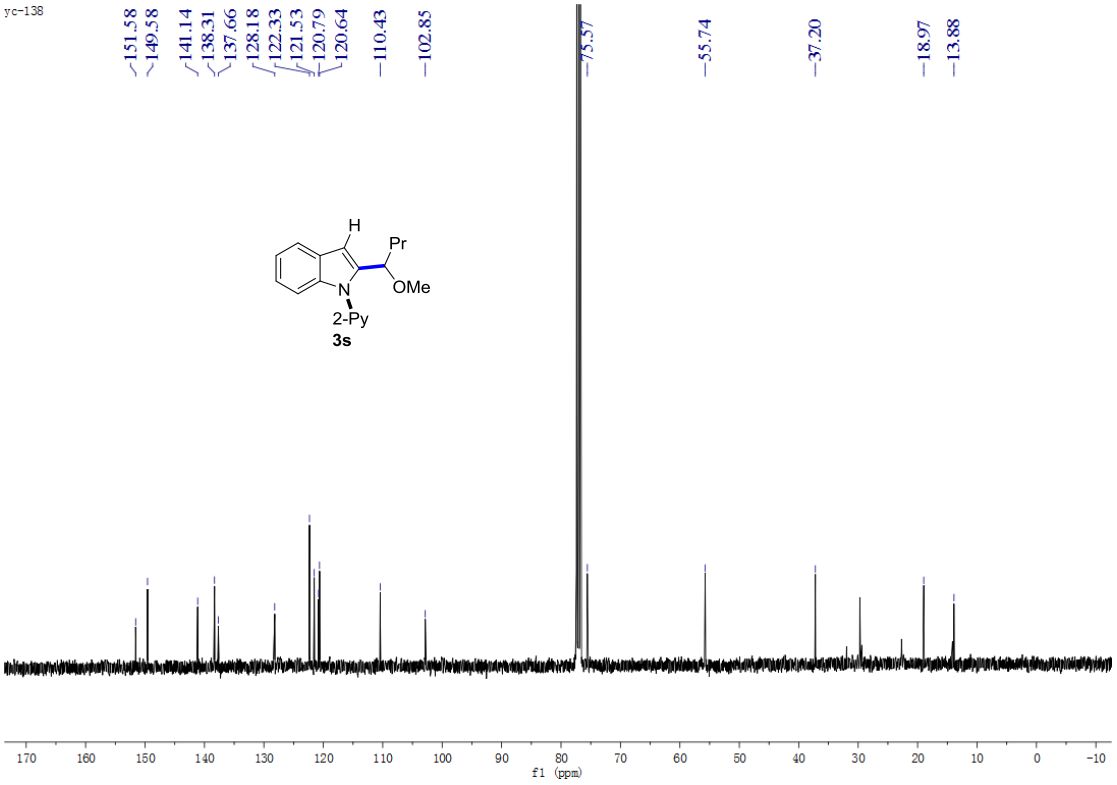
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3r** (using $CDCl_3$ as solvent)



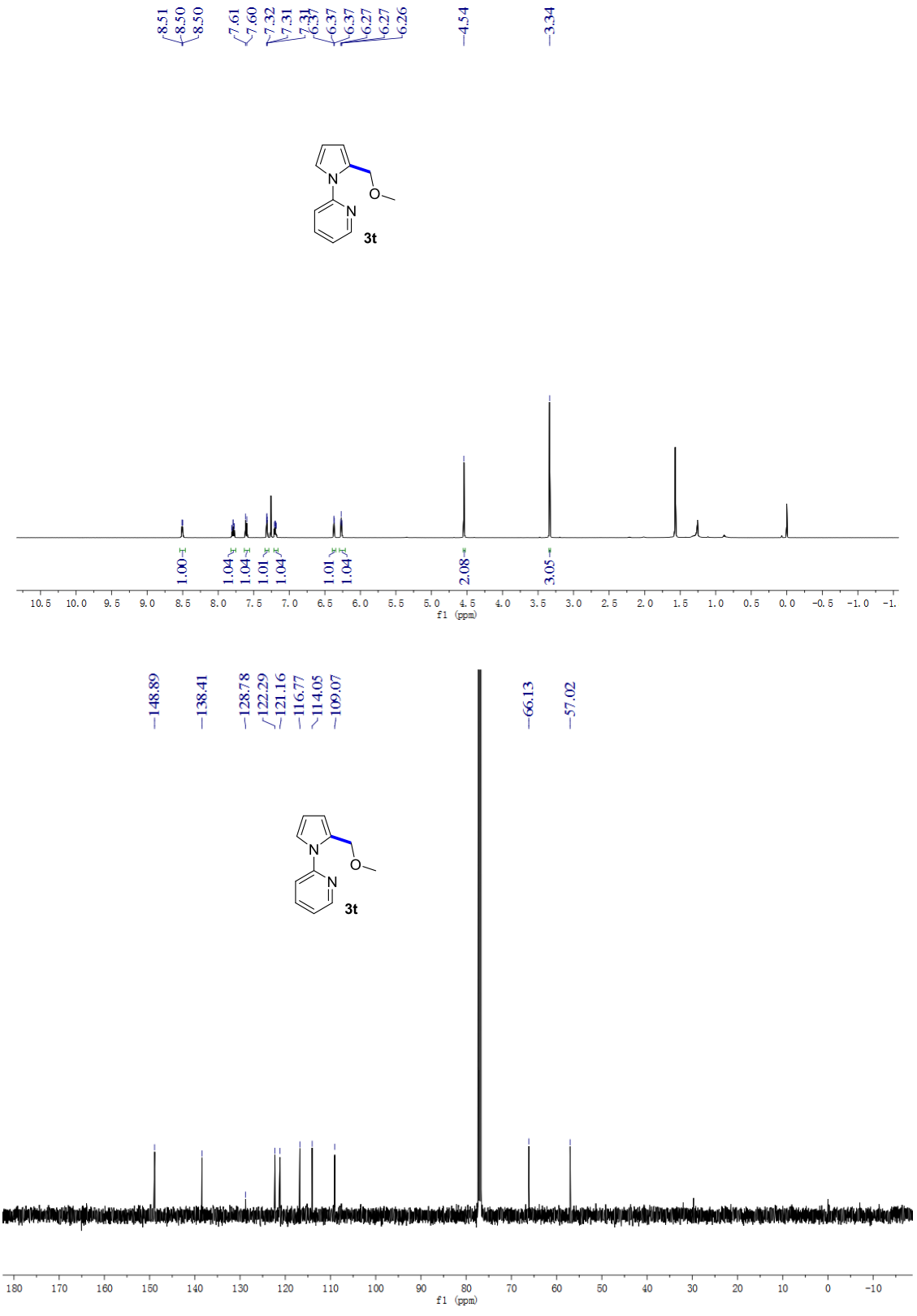


The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3s** (using $CDCl_3$ as solvent)

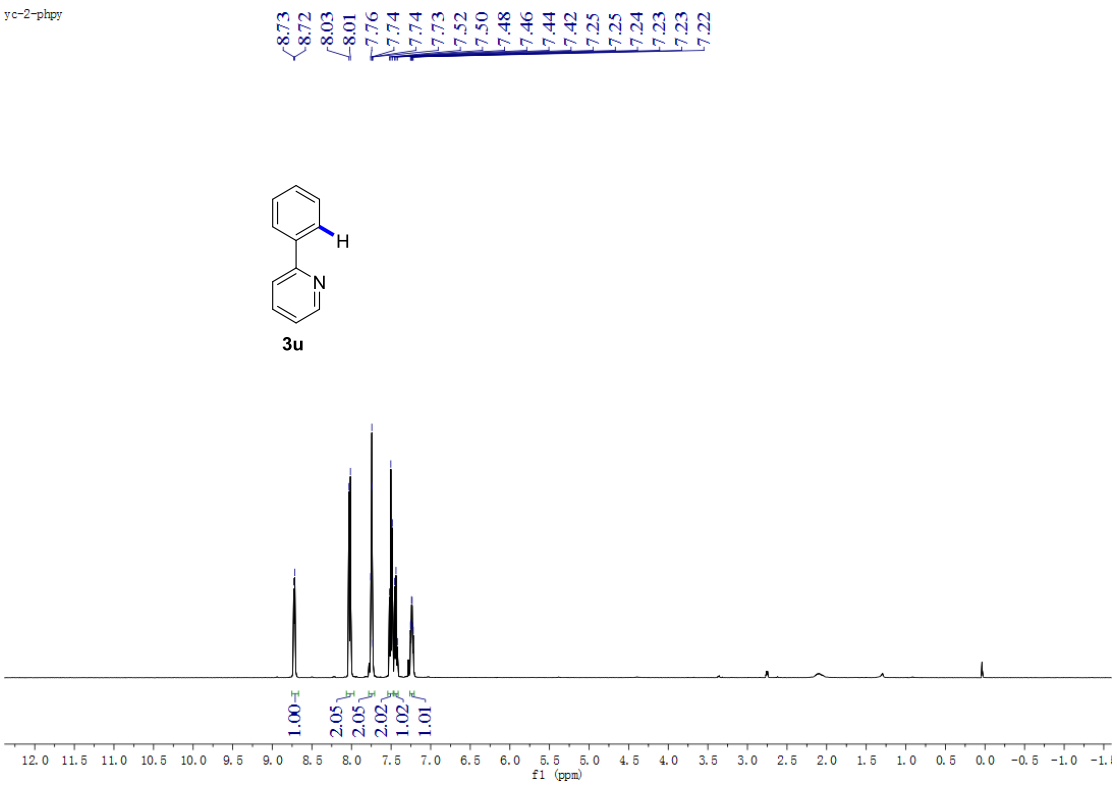


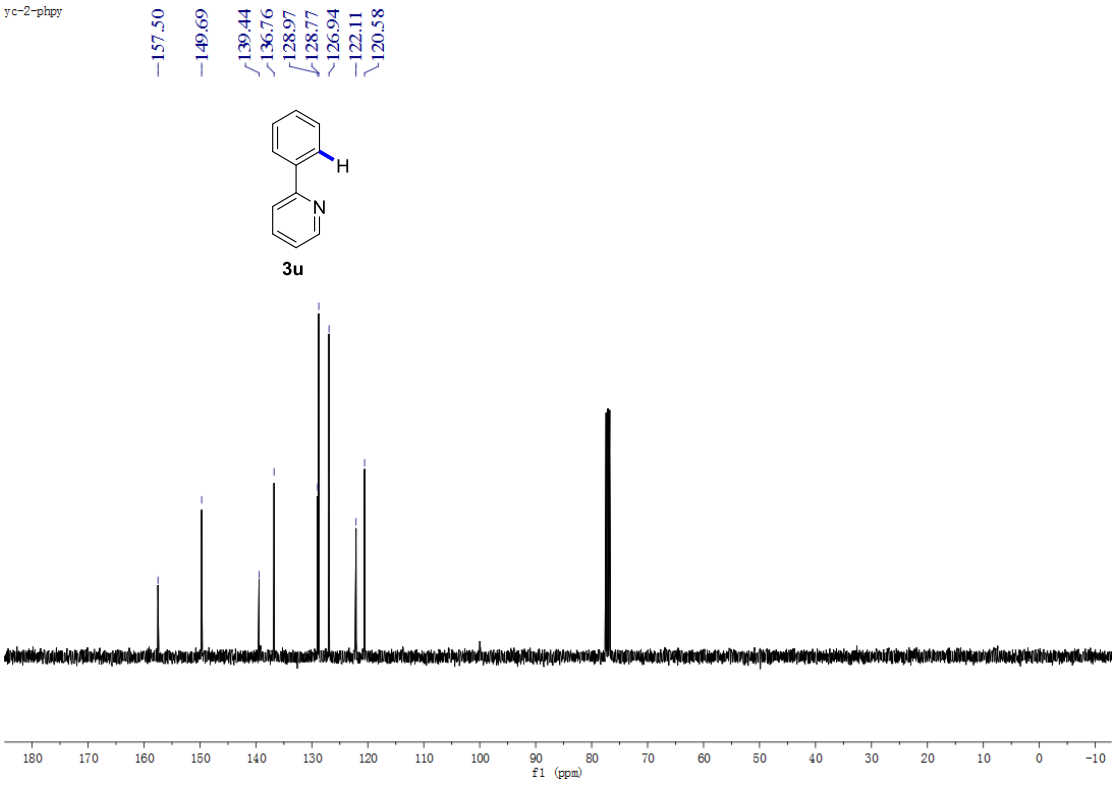


The ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum for **3t** (using $CDCl_3$ as solvent)

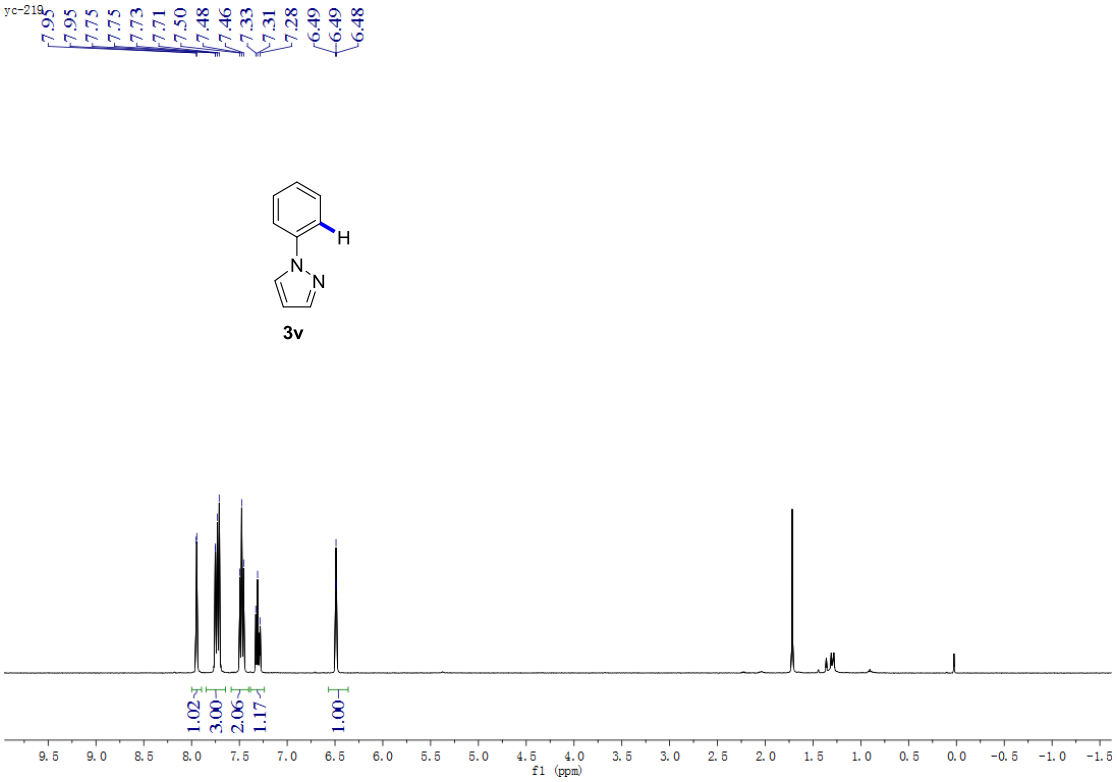


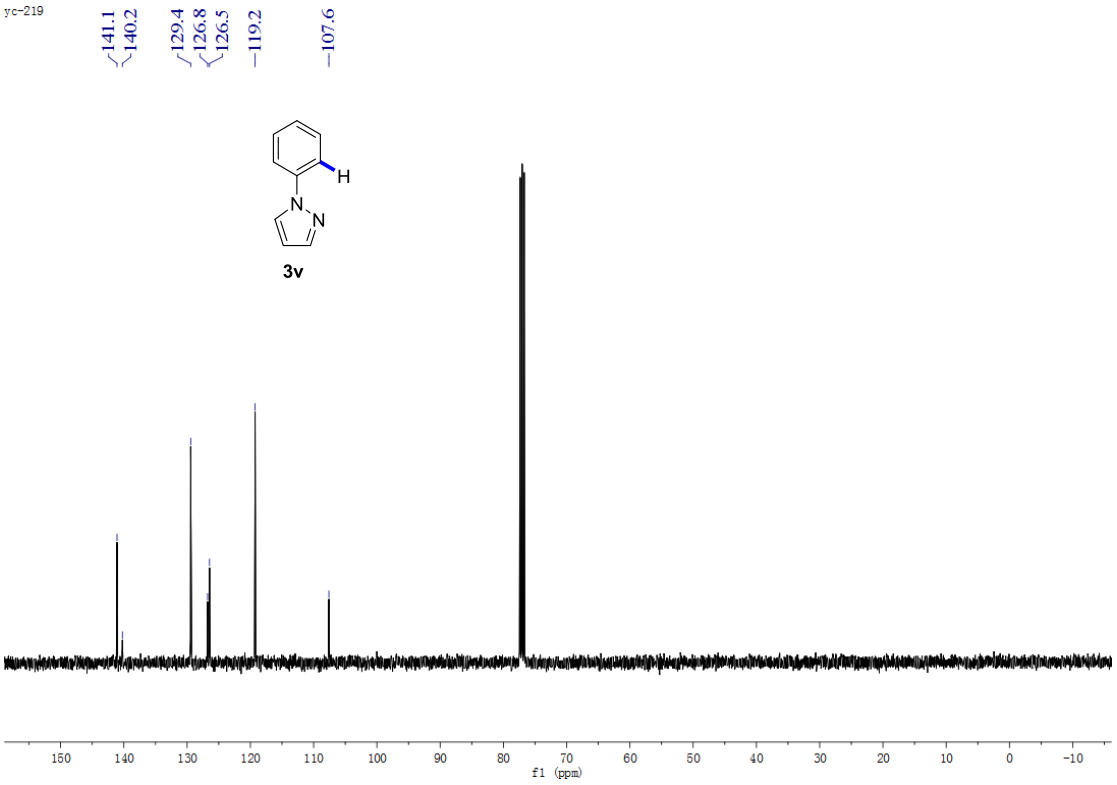
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3u** (using $CDCl_3$ as solvent)



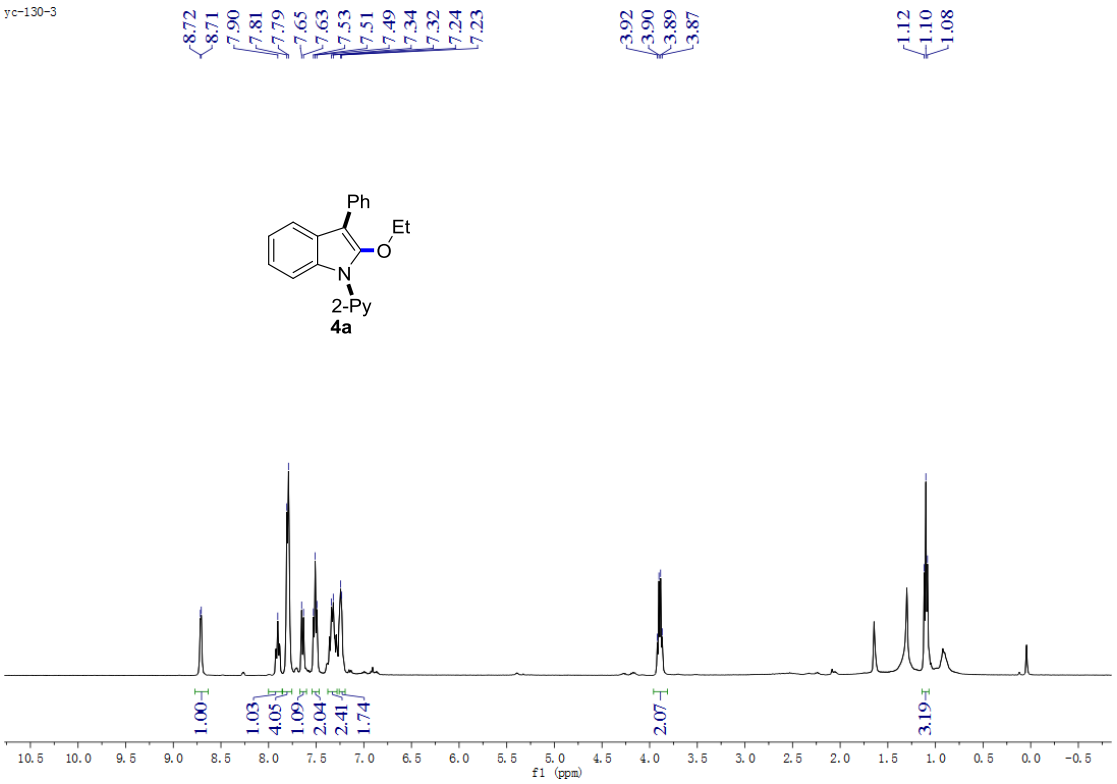


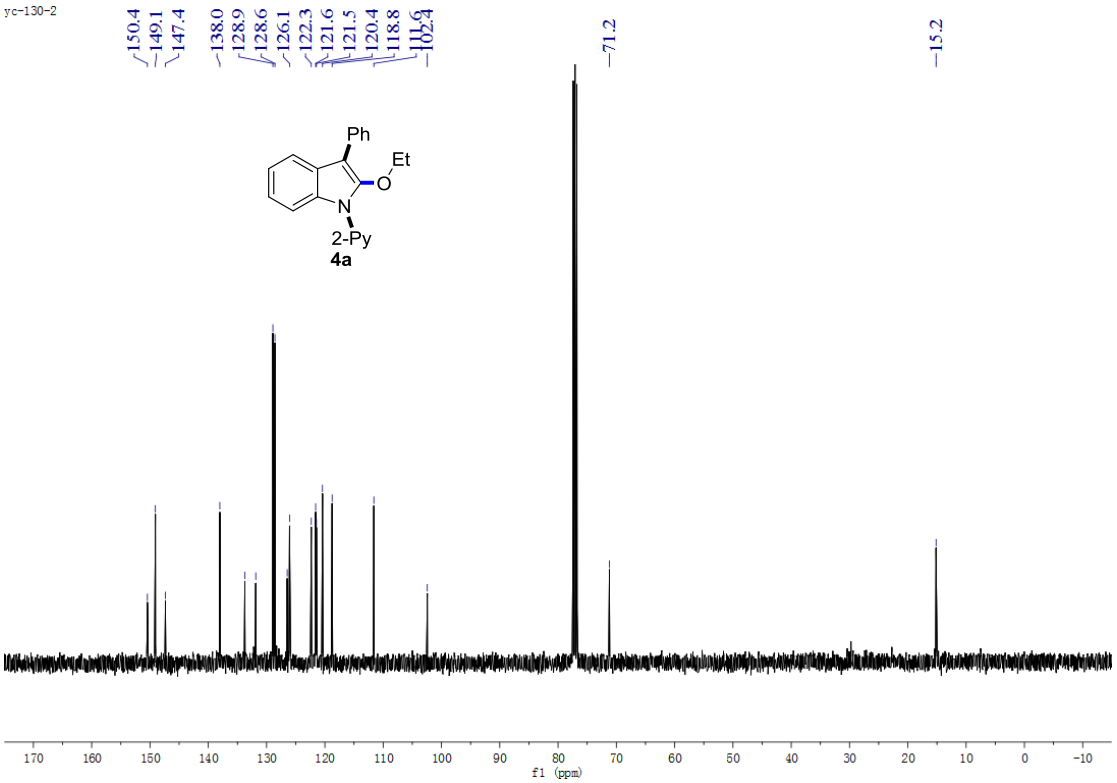
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **3v** (using $CDCl_3$ as solvent)



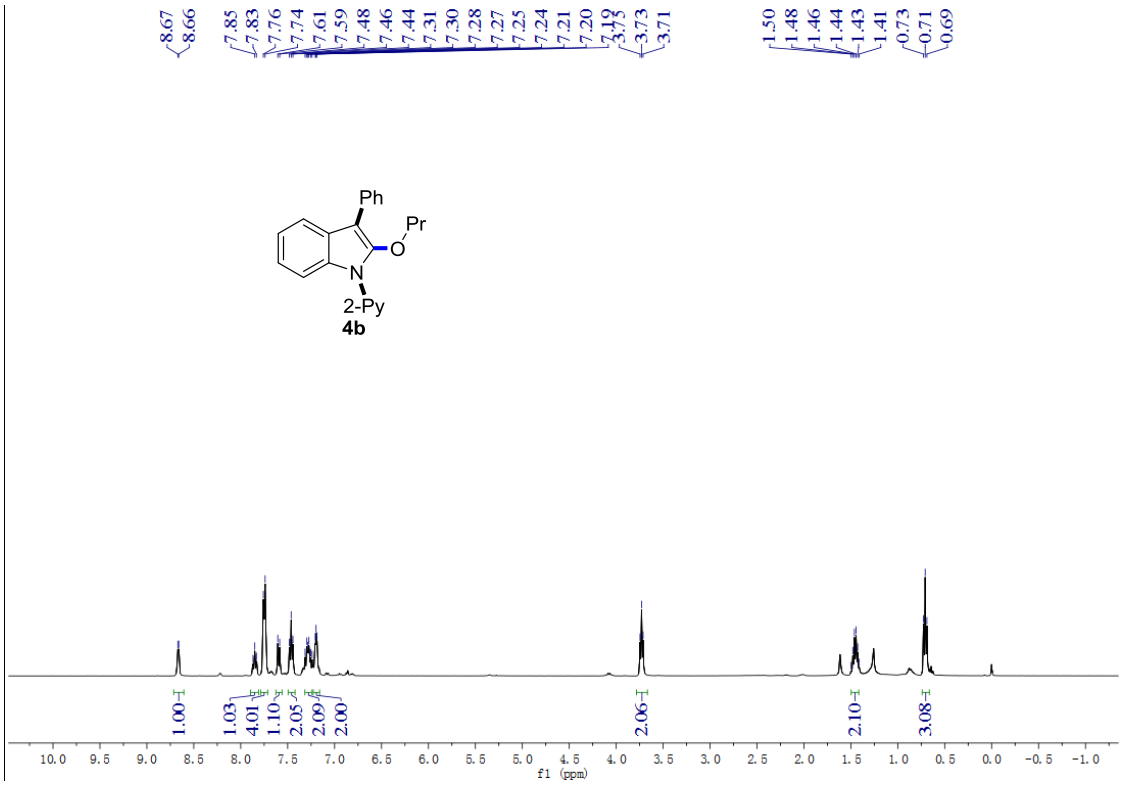


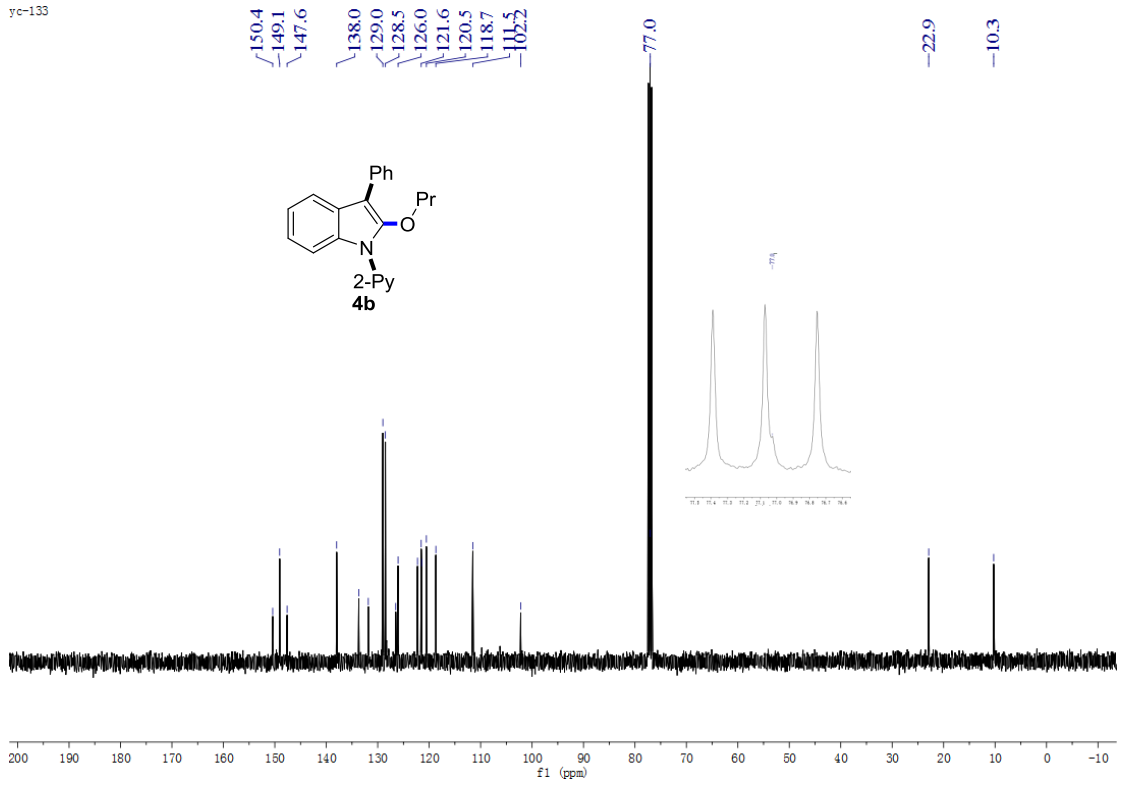
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **4a** (using $CDCl_3$ as solvent)



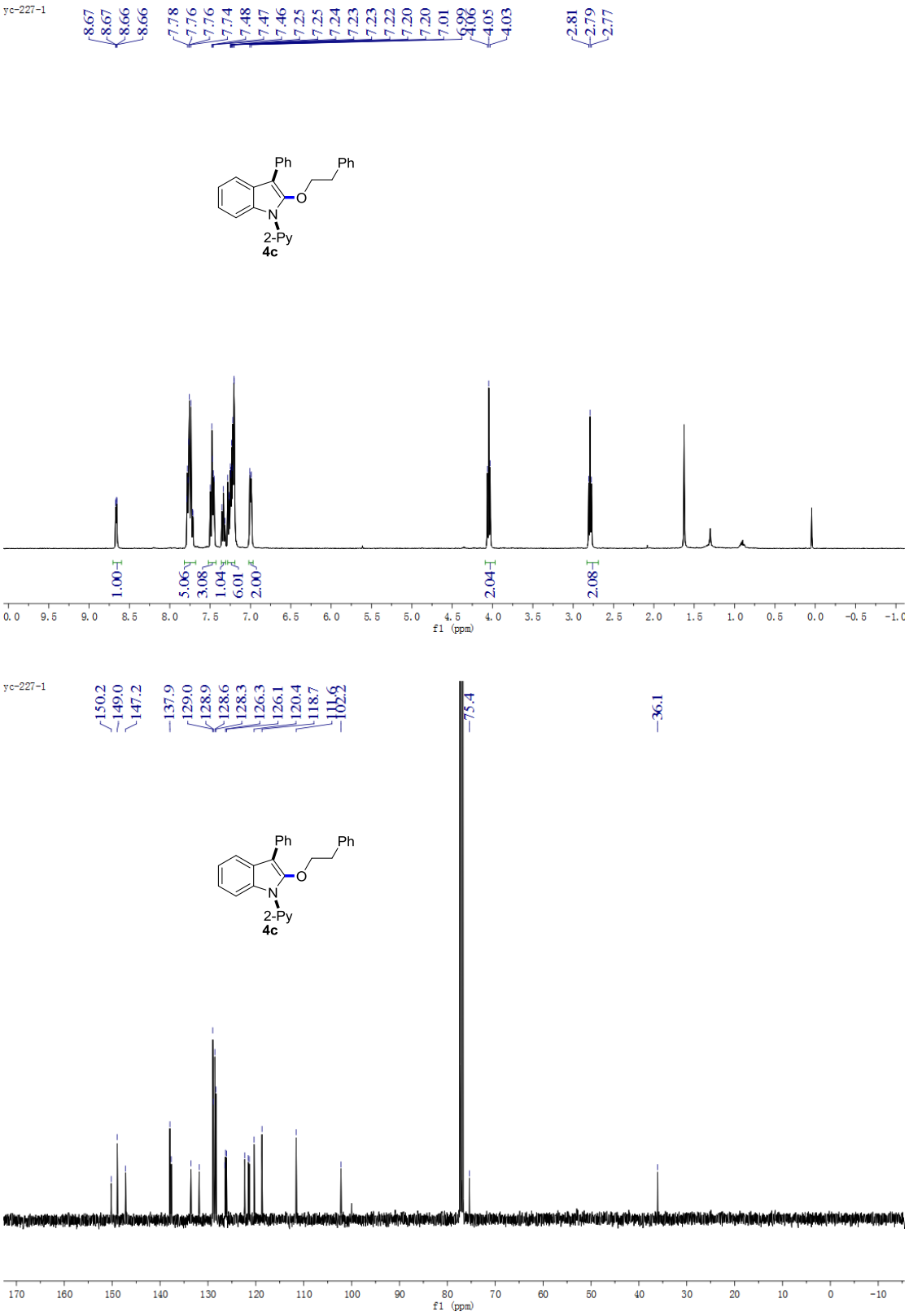


The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **4b** (using $CDCl_3$ as solvent)

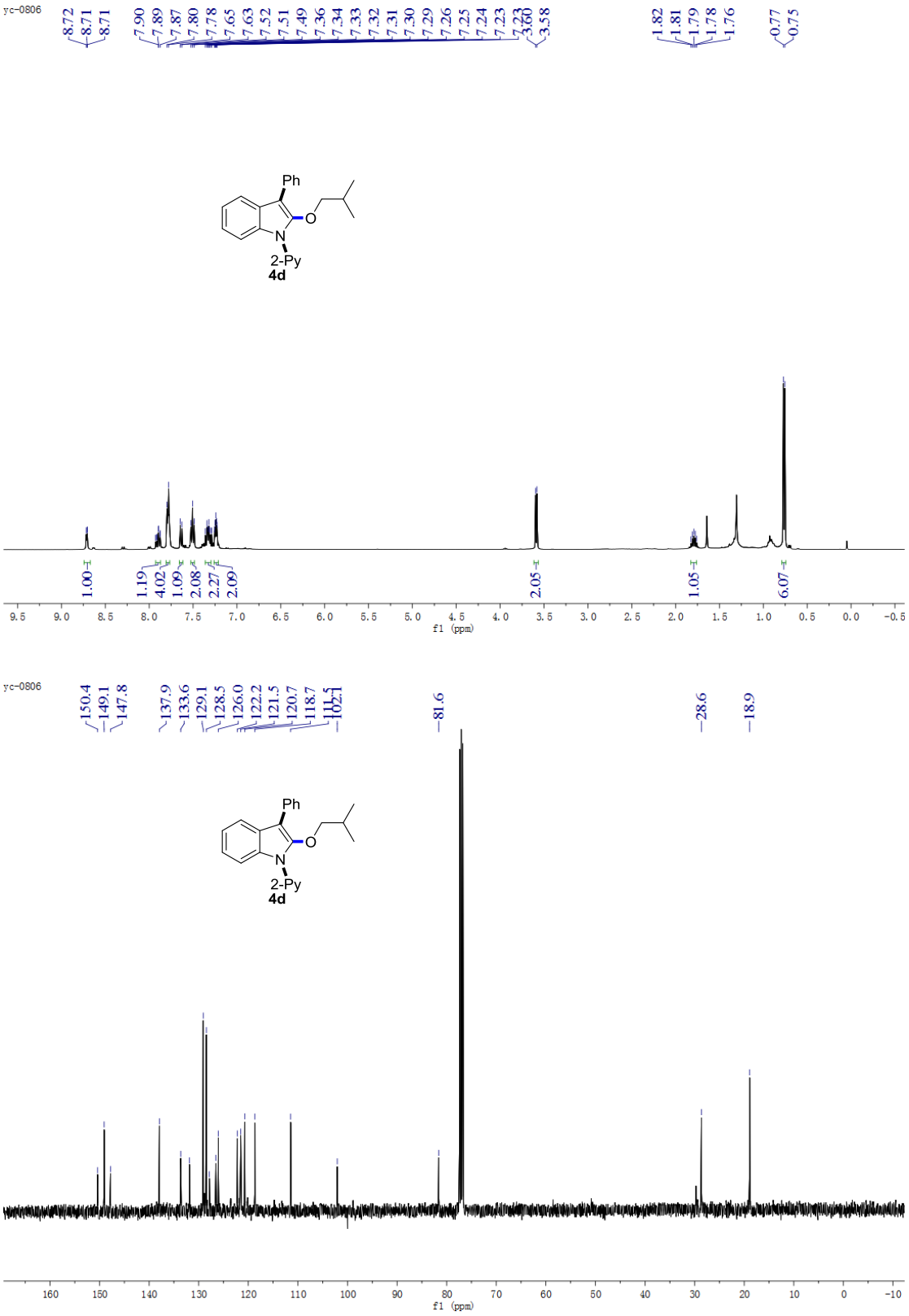




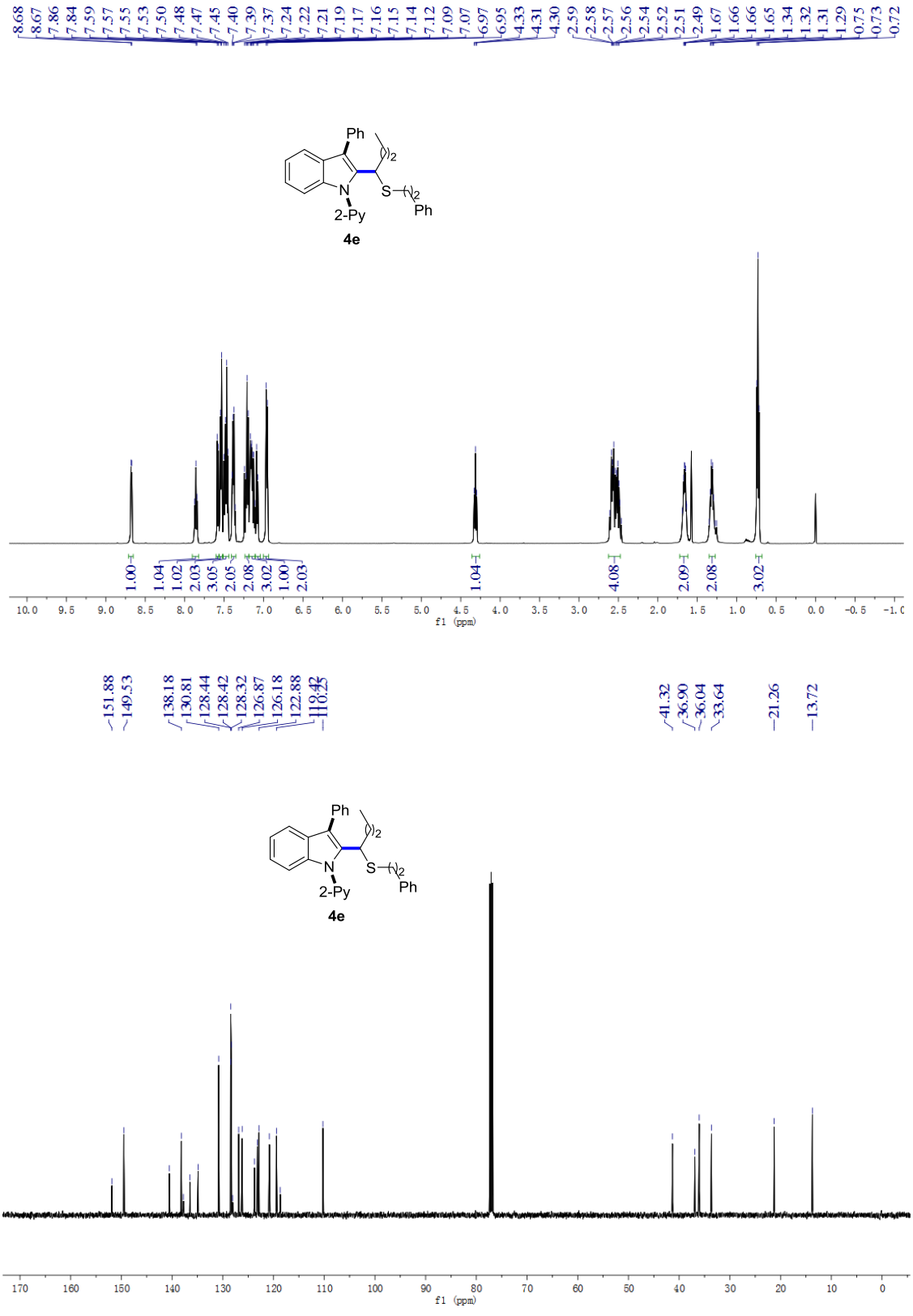
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **4c** (using $CDCl_3$ as solvent)



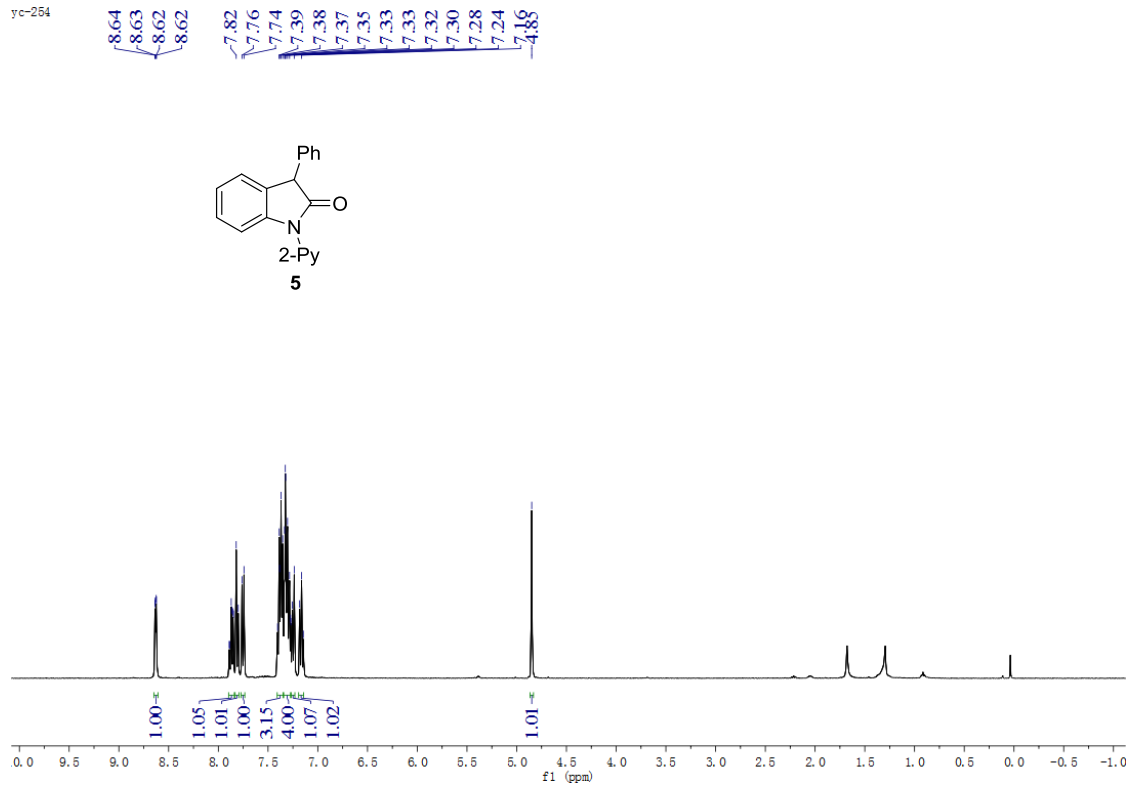
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum for **4d** (using $CDCl_3$ as solvent)

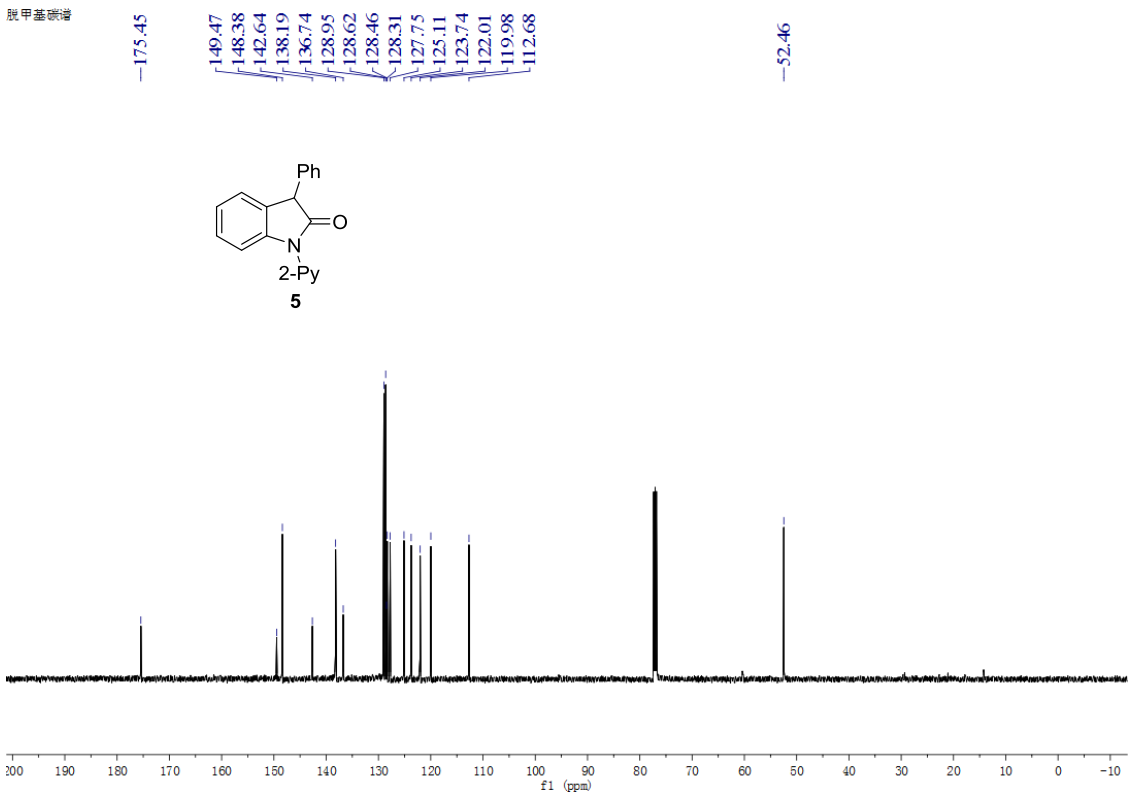


The ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum for **4e** (using $CDCl_3$ as solvent)

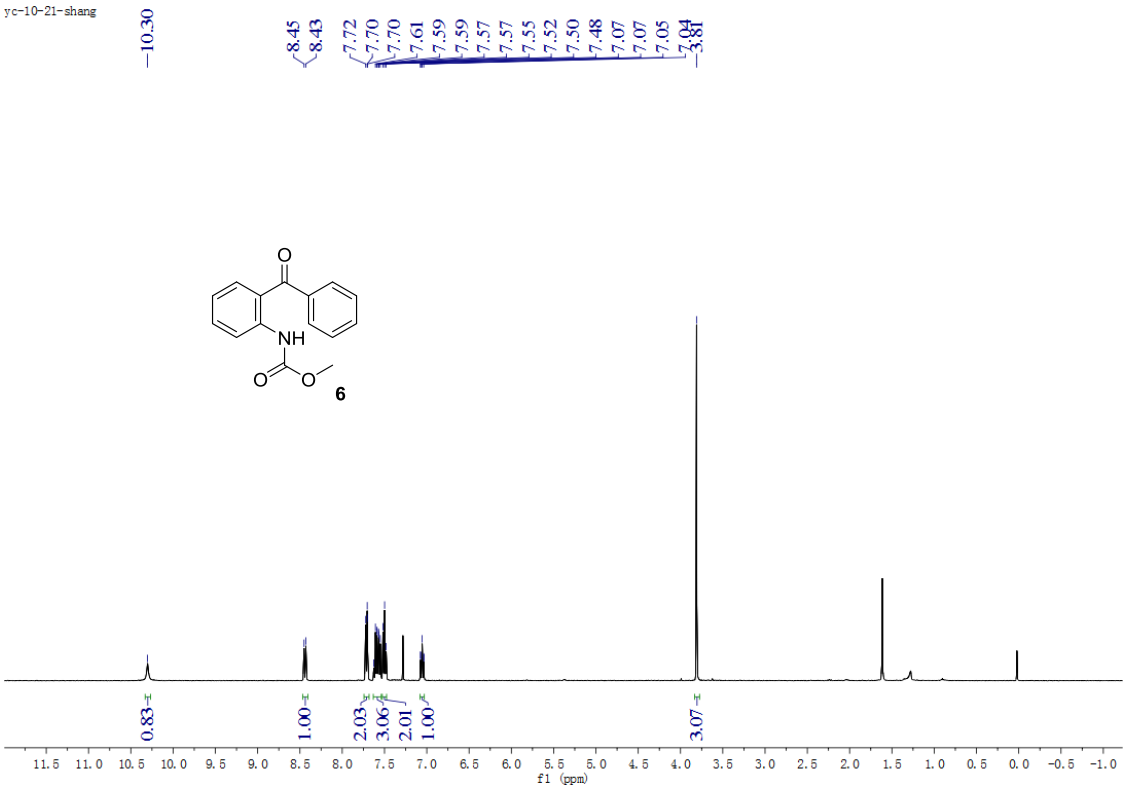


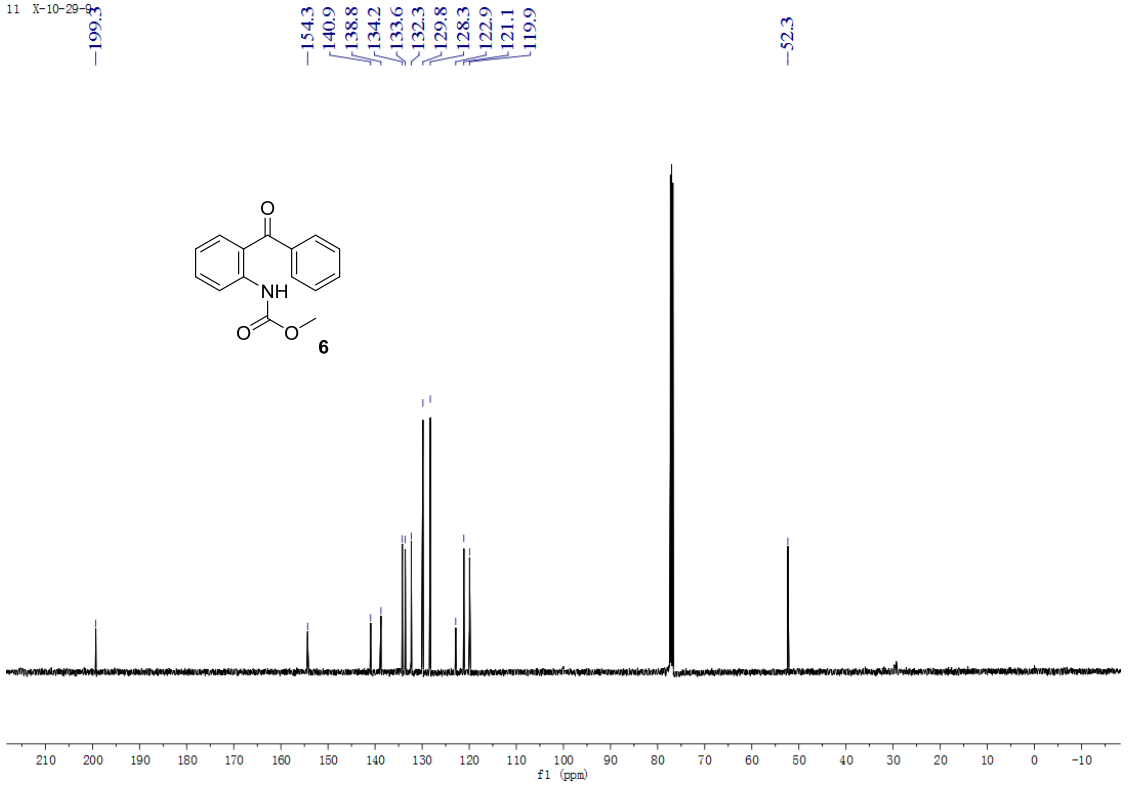
The ^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectrum for **5** (using $CDCl_3$ as solvent)





The ^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectrum for **6** (using $CDCl_3$ as solvent)





The ^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectrum for **11** (using $CDCl_3$ as solvent)