Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of 1-Aminoindole Derivatives trough Rh(III)-Catalyzed Annulation Reaction of Hydrazines with Sulfoxonium Ylides

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Contents

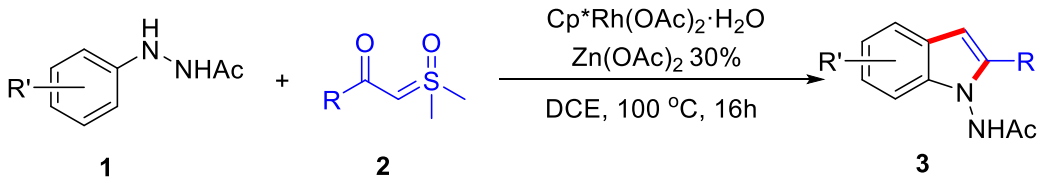
Experimental Section

General Information: All the reactions were carried out under N_2 atmosphere using standard Schlenk technique. ^{1}H NMR (400 MHz), ^{19}F (376 M Hz), and ^{13}C NMR (100 MHz) were recorded on a NMR spectrometer with DMSO-d_6 as solvent. Chemical shifts of ^{1}H, ^{19}F and ^{13}C NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (DMSO-d_6: δ H = 2.50 ppm, δ C = 39.43 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200−300 mesh or alumina 200−300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). High-resolution mass spectrometry (HRMS) was done on an Agilentn6210 ESI/TOF mass spectrometer. $[Cp^*RhCl_2]_2$ was prepared from $RhCl_3 \cdot xH_2O$ following a literature procedure.[1] $[Cp^*Rh(OAc)_2]$ was prepared from $[Cp^*RhCl_2]_2$ following a literature procedure.[2] Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available without any further purification.

General Procedure: Preparation of the Substrates

The substrates **1a-1s**,[3] **2a-2p**,[4] were prepared according to the literature reports.

General Procedure for Synthesis of 3 via Rh(III)-Catalyzed C-H Activation and Annulation with Sulfoxonium Ylides



1 **2** **3**

A mixture of **1** (0.2 mmol), **2** (0.24 mmol, 1.2 equiv), Cp*Rh(OAc)$_2$·H$_2$O (7.5 mg, 0.02mmol, 10.0 mol%), and Zn(OAc)$_2$ (11.0 mg, 0.3 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry DCE (2.0 mL) was added and the mixture was stirred at 100 °C for 16 h under N_2 atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EA:PE = 1:3).

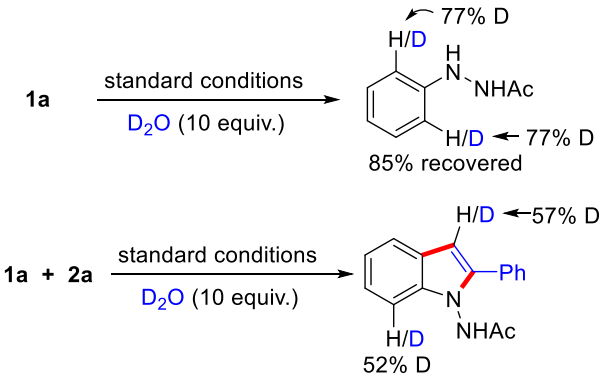
Gram-scale synthesis of 3aa:

A mixture of **1a** (4 mmol), **2a** (4.8 mmol, 1.2 equiv), Cp*Rh(OAc)$_2$·H$_2$O (149.7 mg, 0.4 mmol, 10.0 mol%), and Zn(OAc)$_2$ (220.2 mg, 0.3 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry DCE (2.0 mL) was added and the mixture was stirred at 100 °C for 16 h under N_2 atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel and good yield of **3aa** 81% (0.8137 g) was still attained (eluent: EA:PE = 1:3).

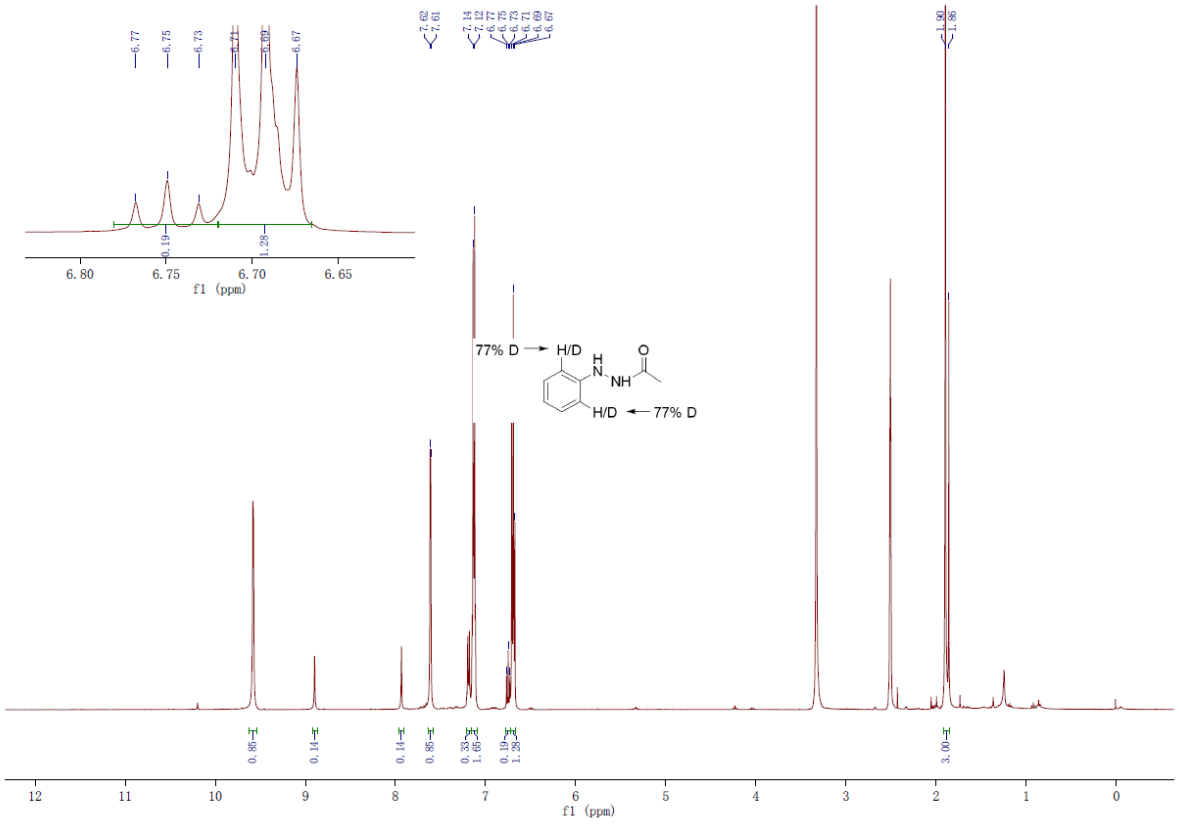
Derivatization of 3aa:

A 50 mL Schlenk tube was charged with **3aa** (50.1 mg, 0.20 mmol) and 4 M HCl (2.0 mL) dissolved in THF (2.0 mL) was added, subsequently, the solution was sealed with a Teflon-lined cap and heated to reflux (in an 80 °C oil bath) for 6 h. After cooling to room temperature, the reaction was quenched by saturated aqueous solution of sodium bicarbonate (10 mL). The aqueous layer was extracted with CH_2Cl_2. The combined organic extract was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (eluent EA:PE = 8:1) to give the product **4** in 74% yield (30.2 mg) as a white solid.

H/D Exchange Experiments:

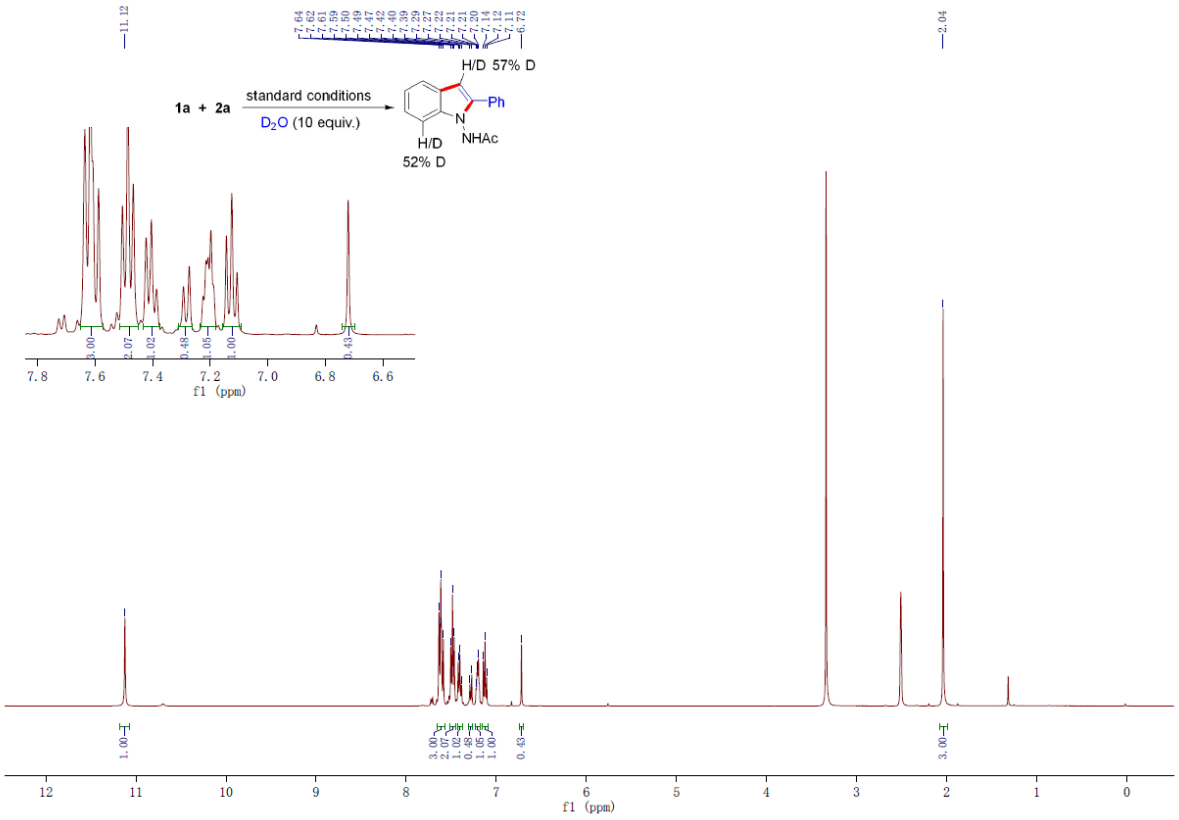


Procedure for the reaction without 2a: A mixture of 2-acetyl-1-phenylhydrazine **1a** (0.2 mmol), Cp*Rh(OAc)$_2$·H$_2$O (7.5 mg, 0.02mmol, 10.0 mol%), and Zn(OAc)$_2$ (11.0 mg, 0.3 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry DCE (2.0 mL) and D$_2$O (2.0 mmol, 10.0 equiv) was added and the mixture was stirred at 100 ºC for 16 h under N$_2$ atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The residue was purified by flash column chromatography on silica gel (eluent: EA/DCM = 1:2) to recover **1a** in 85% yield.



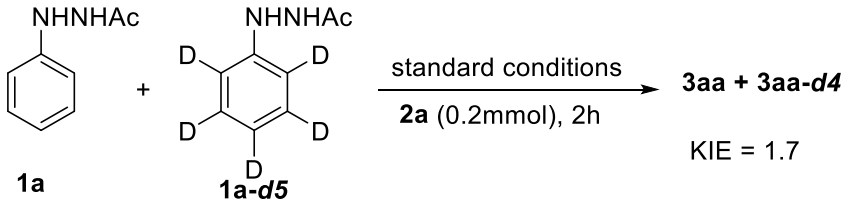
^{1}H NMR of the recovered **1a** of the reaction without **2a**

Procedure for the reaction in the presence of 2a: A mixture of 2-acetyl-1-phenylhydrazine **1a** (0.2 mmol), α-benzoyl sulfur ylide **2a** (0.24 mmol, 1.2 equiv), Cp*Rh(OAc)$_2$·H$_2$O (7.5 mg, 0.02mmol, 10.0 mol%), and Zn(OAc)$_2$ (11.0 mg, 0.3 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry DCE (2.0 mL) and D$_2$O (2.0 mmol, 10.0 equiv) was added and the mixture was stirred at 100 °C for 16 h under N$_2$ atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The residue was purified by flash column chromatography on silica gel (eluent: EA/PE = 1:3) to give the product **3aa** (25.3 mg).

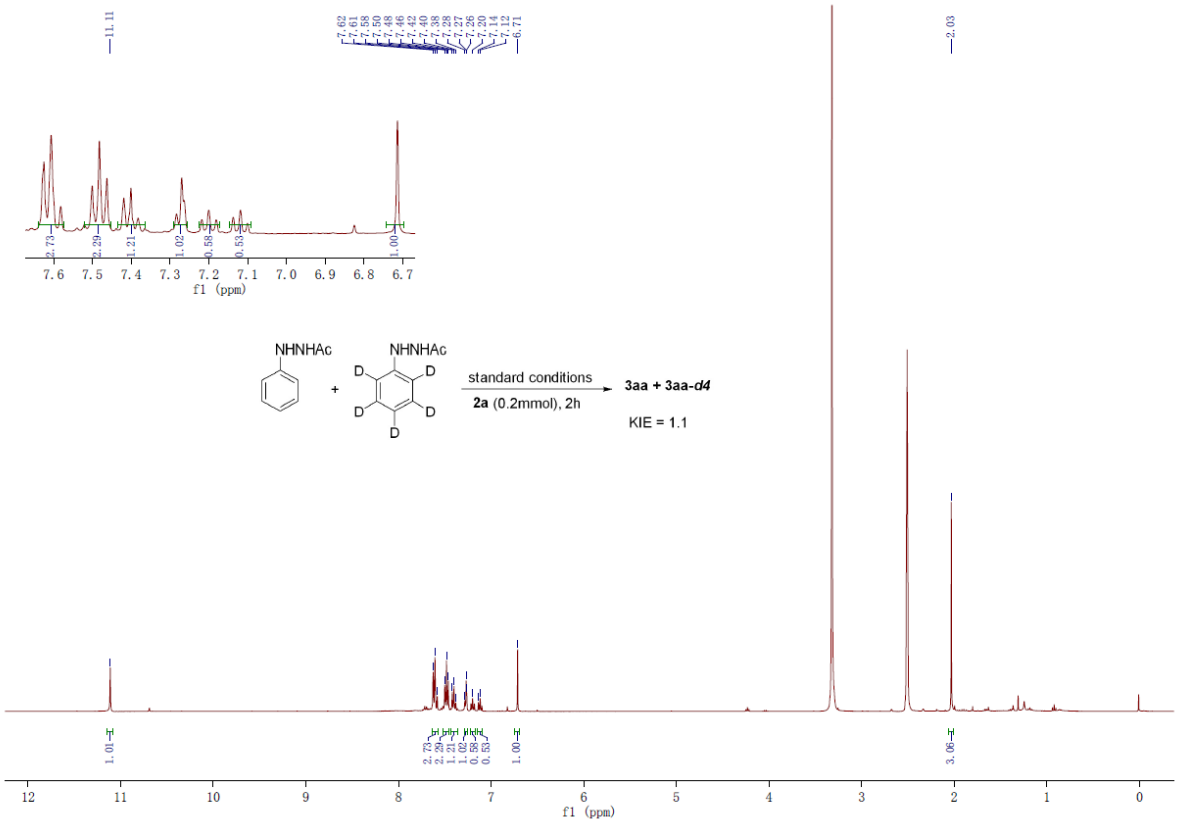


^{1}H NMR of the product **3aa** for the H/D exchange reaction in presence of **2a**

Competition KIE Experiment:

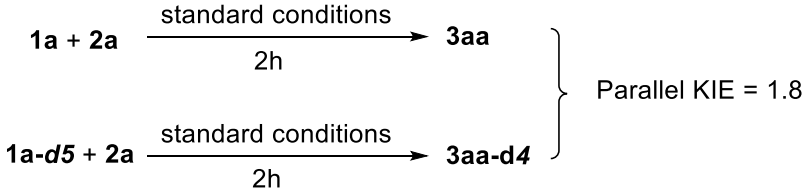


A mixture of 2-acetyl-1-phenylhydrazine **1a** (0.2 mmol, 1.0 equiv), **1a-*d*$_5$** (0.2mmol, 1.0 equiv), *α*-benzoyl sulfur ylide **2a** (0.24 mmol, 1.2 equiv), Cp*Rh(OAc)$_2$·H$_2$O (7.5 mg, 0.02mmol, 10.0 mol%), and Zn(OAc)$_2$ (11.0 mg, 0.3 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry DCE (2.0 mL) was added and the mixture was stirred at 100 ºC for 2h under N_2 atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The residue was purified by flash column chromatography on silica gel (eluent: EA/PE = 1:3) to give the product **3aa** and *d4*-**3aa** (2.7 mg). The KIE value was determined to be k_H/k_D = 1.1 on the basis of ^{1}H NMR analysis.

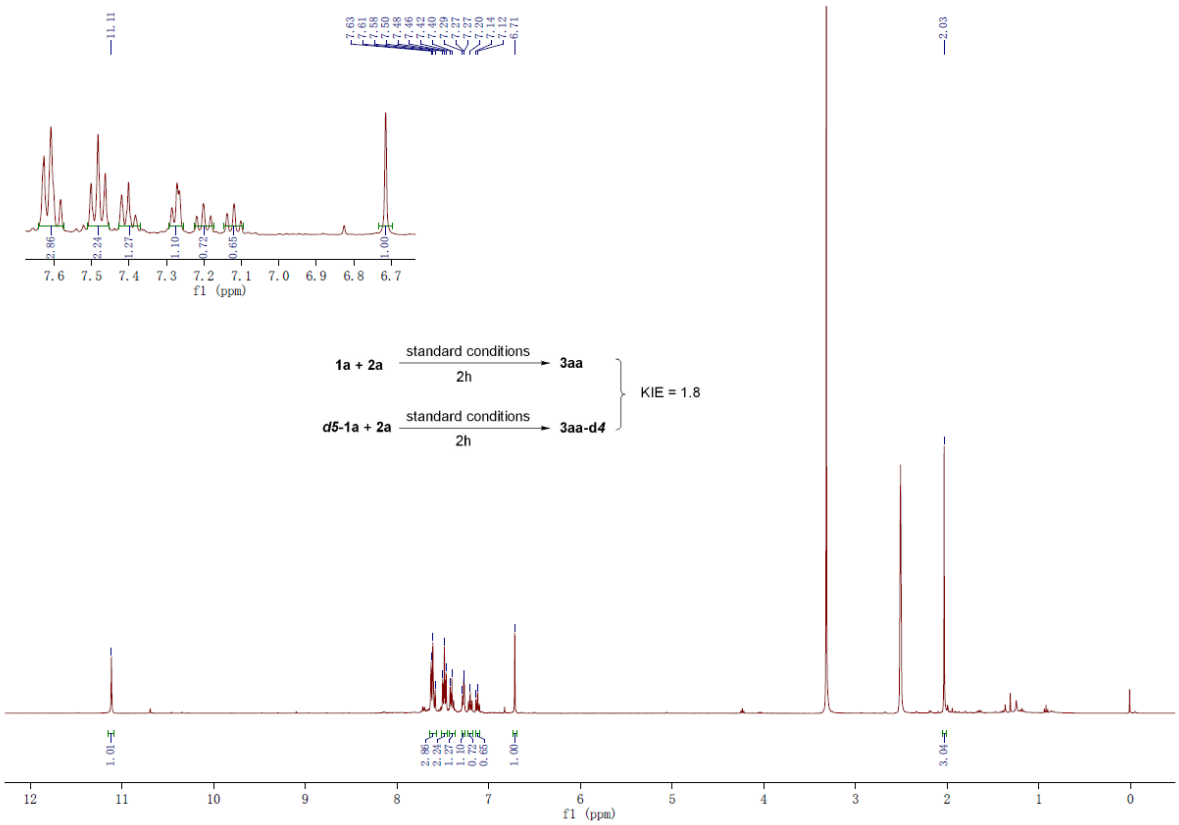


^{1}H NMR of product **3aa** obtained from the competition KIE experiment

Parallel KIE Experiment:

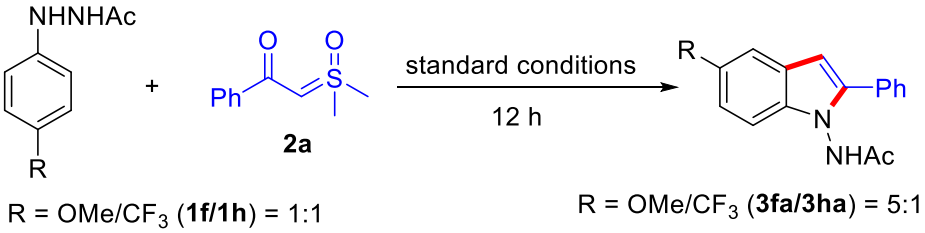


A mixture of 2-acetyl-1-phenylhydrazine **1a** (0.2 mmol), *α*-benzoyl sulfur ylide **2a** (0.24 mmol), Cp*Rh(OAc)$_2$·H$_2$O (7.5 mg, 0.02mmol), Zn(OAc)$_2$ (11.0 mg) and DCE (2.0 mL) were charged into Schlenk tube. To another tube **1a-*d*$_5$** (0.2mmol,), *α*-benzoyl sulfur ylide **2a** (0.24 mmol), Cp*Rh(OAc)$_2$·H$_2$O (7.5 mg, 0.02mmol), Zn(OAc)$_2$ (11.0 mg) and DCE (2.0 mL) were added. These two reaction mixtures were stirred side-by-side in the same oil bath at 100 °C for 2h under N_2 atmosphere. The reactions tubes were quenched at 0 °C and these two mixtures were rapidly combined. The combined mixture was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The residue was purified by flash column chromatography on silica gel (eluent: EA/PE = 1:3) to give the product **3aa** and *d4*-**3aa** (7.5 mg). The KIE value was determined to be k_H/k_D = 1.8 on the basis of ^{1}H NMR analysis.

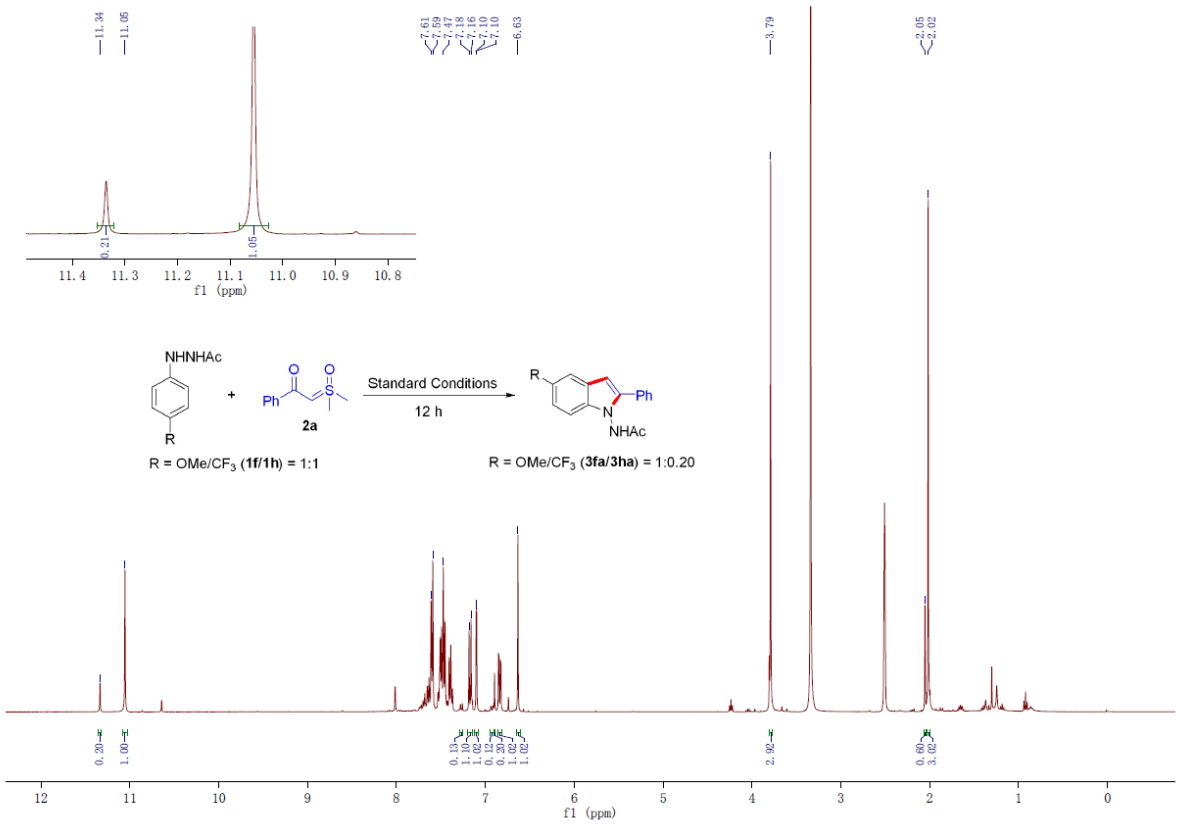


^{1}H NMR of product **3aa** obtained from the parallel KIE experiment

Competition Experiment:

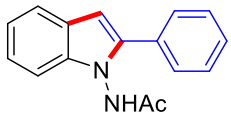


A mixture of *N'*-(4-methoxyphenyl)acetohydrazide **1f** (0.2 mmol, 1.0 equiv), *N'*-(4-(trifluoromethyl)phenyl)acetohydrazide **1h** (0.2mmol, 1.0 equiv), *α*-benzoyl sulfur ylide **2a** (0.24 mmol, 1.2 equiv), Cp*Rh(OAc)$_2$·H$_2$O (7.5 mg, 0.02mmol, 10.0 mol%), and Zn(OAc)$_2$ (11.0 mg, 0.3 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry DCE (2.0 mL) was added and the mixture was stirred at 100 °C for 16h under N$_2$ atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give a mixture of products **3fa** and **3ha** at a ratio of 1:0.20.

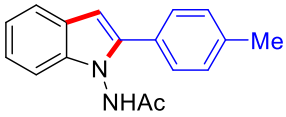


^{1}H NMR of products **3fa** and **3ha** obtained from the competition experiment

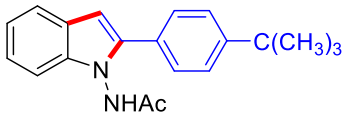
Characterization of Products:



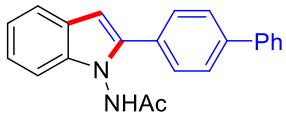
N-(2-phenyl-1H-indol-1-yl)acetamide (3aa): pale yellow solid (46.2 mg, 92%); M.p.: 224-227 °C. IR (cm^{-1}): *v* 3026, 2361, 1690, 1678, 1528, 1456, 1335, 1269, 800,7 66, 745, 704. ^{1}H NMR (400 MHz, DMSO): δ 11.26 (s, 1H), 7.76 – 7.71 (m, 2H), 7.68 (d, J = 7.7 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H), 7.48 – 7.37 (m, 2H), 7.32 – 7.27 (m, 1H), 7.24 – 7.18 (m, 1H), 6.80 (s, 1H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.73, 140.59, 138.15, 131.50, 129.11, 128.50, 128.31, 126.12, 122.88, 121.15, 120.93, 109.96, 100.83, 20.99. HRMS (ESI): Calcd for $C_{16}H_{15}N_2O$ $[M+H]^+$ 251.1179, Found 251.1182.



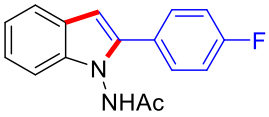
N-(2-(p-tolyl)-1H-indol-1-yl)acetamide (3ab): pale yellow solid (47.5 mg, 90%); M.p.:213-215 °C. IR (cm^{-1}): *v* 3264, 3024, 2359, 2342, 1680, 1531, 1265, 1099, 781, 745. ^{1}H NMR (400 MHz, DMSO): δ 11.11 (s, 1H), 7.55 (dd, J = 24.3, 7.9 Hz, 3H), 7.32 – 7.25 (m, 3H), 7.22 – 7.16 (m, 1H), 7.15 – 7.09 (m, 1H), 6.67 (s, 1H), 2.37 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.59, 140.57, 137.93, 129.67, 128.56, 128.13, 126.03, 122.61, 121.00, 120.69, 109.82, 100.21, 21.29, 20.94. HRMS (ESI): Calcd for $C_{17}H_{17}N_2O$ $[M+H]^+$ 265.1335, Found 265.1333.



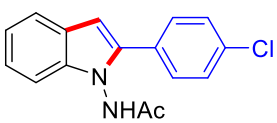
N-(2-(4-(tert-butyl)phenyl)-1H-indol-1-yl)acetamide (3ac): pale yellow solid (45.9 mg, 75%); M.p.: 209 - 211 °C. IR (cm^{-1}): *v* 3256, 3032, 2963, 2359, 2344, 1684, 1539, 1458, 1369, 1267, 785, 740. ^{1}H NMR (400 MHz, DMSO): δ 11.12 (s, 1H), 7.60 – 7.47 (m, 5H), 7.27 (d, J = 7.9 Hz, 1H), 7.23 – 7.16 (m, 1H), 7.15 – 7.08 (m, 1H), 6.68 (s, 1H), 2.07 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, DMSO): δ 169.66, 150.99, 140.34, 137.91, 128.56, 127.90, 126.02, 125.88, 122.61, 120.99, 120.69, 109.83, 100.30, 34.86, 31.53, 21.01. HRMS (ESI): Calcd for $C_{20}H_{23}N_2O$ $[M+H]^+$ 307.1805, Found 307.1802.



N-(2-([1,1'-biphenyl]-4-yl)-1H-indol-1-yl)acetamide ***(3ad):*** pale yellow solid (47.5 mg, 73%); M.p.: 239-242 °C. IR (cm^{-1}): *v* 3279, 2359, 2332, 1672, 1601, 1487, 1447, 1408, 1368, 1258, 1007, 845, 764. ^{1}H NMR (400 MHz, DMSO): δ 11.19 (s, 1H), 7.83 – 7.71 (m, 6H), 7.61 (d, J = 7.7 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 7.3 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.16 – 7.11 (m, 1H), 6.79 (s, 1H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.69, 140.02, 140.00, 139.92, 138.15, 130.42, 129.47, 128.64, 128.13, 127.31, 127.08, 126.02, 122.89, 121.12, 120.85, 109.90, 100.85, 21.00. HRMS (ESI): Calcd for $C_{22}H_{19}N_2O$ $[M+H]^+$ 327.1492, Found 327.1488.

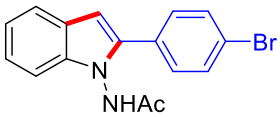


N-(2-(4-fluorophenyl)-1H-indol-1-yl)acetamide ***(3ae):*** pale yellow solid (44.3 mg, 82%); M.p.: 251-254 °C. IR (cm^{-1}): *v* 3248, 3030, 2925, 2359, 1678, 1537, 1498, 1223, 843, 783, 745. ^{1}H NMR (400 MHz, DMSO): δ 11.14 (s, 1H), 7.70 – 7.63 (m, 2H), 7.60 (d, J = 7.7 Hz, 1H), 7.37 – 7.27 (m, 3H), 7.25 – 7.19 (m, 1H), 7.16 – 7.10 (m, 1H), 6.71 (s, 1H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.73, 162.45 (d, J = 245.6 Hz), 139.47, 137.91, 130.35 (d, J = 8.3 Hz), 130.35 (d, J = 8.3 Hz), 127.90 (d, J = 3.2 Hz), 125.92, 122.86, 121.13, 120.98 (d, J = 29.4 Hz), 120.83, 116.20, 116.09 (d, J = 21.6 Hz), 115.98, 109.89, 100.74, 20.92. ^{19}F NMR (376 MHz, DMSO): δ -113.71. HRMS (ESI): Calcd for $C_{16}H_{14}FN_2O$ $[M+H]^+$ 269.1085, Found 269.1081.

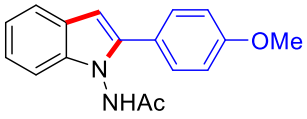


N-(2-(4-chlorophenyl)-1H-indol-1-yl)acetamide ***(3af):*** pale yellow solid (31.5 mg, 55%); M.p.: 254-257 °C. IR (cm^{-1}): *v* 3252, 3030, 2924, 2361, 2344, 1680, 1508, 1456, 1273, 1092, 1012, 783. ^{1}H NMR (400 MHz, DMSO): δ 11.15 (s, 1H), 7.69 – 7.52 (m, 5H), 7.29 (d, J = 8.1 Hz, 1H), 7.23 (d, J = 7.2 Hz, 1H), 7.14 (d,

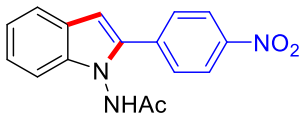
J = 7.3 Hz, 1H), 6.76 (s, 1H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.72, 139.16, 138.10, 133.25, 131.61, 130.23, 129.83, 129.17, 123.09, 121.21, 120.95, 109.95, 101.19, 20.93. HRMS (ESI): Calcd for $C_{16}H_{14}ClN_2O$ $[M+H]^+$ 285.0789, Found 285.0790.



N-(2-(4-bromophenyl)-1H-indol-1-yl)acetamide (3ag): pale yellow solid (47.4 mg, 72%); M.p.: 265-267 °C. IR (cm^{-1}): *v* 3246, 3028, 2359, 2344, 1682, 1533, 1456, 1273, 1103, 1008, 781, 745. ^{1}H NMR (400 MHz, DMSO): δ 11.15 (s, 1H), 7.69 (d, J = 8.5 Hz, 2H), 7.59 (dd, J = 13.0, 8.1 Hz, 3H), 7.29 (d, J = 8.1 Hz, 1H), 7.23 (d, J = 7.1 Hz, 1H), 7.16 – 7.10 (m, 1H), 6.77 (s, 1H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.72, 139.20, 138.12, 132.09, 130.59, 130.10, 125.89, 123.11, 121.88, 121.23, 120.97, 109.96, 101.19, 20.94; HRMS (ESI): Calcd for $C_{16}H_{14}BrN_2O$ $[M+H]^+$ 329.0284, Found 329.0283.

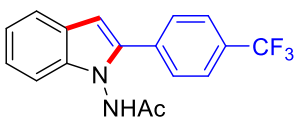


N-(2-(4-methoxyphenyl)-1H-indol-1-yl)acetamide (3ah): pale yellow solid (29.8 mg, 53%); M.p.: 185-187 °C. IR (cm^{-1}): *v* 3254, 2359, 1678, 1501, 1456，1248, 1028, 787, 745. ^{1}H NMR (400 MHz, DMSO): δ 11.09 (s, 1H), 7.58 – 7.52 (m, 3H), 7.25 (d, J = 7.9 Hz, 1H), 7.17 (dd, J = 7.5, 6.5 Hz, 1H), 7.12 – 7.03 (m, 3H), 6.62 (s, 1H), 3.81 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.63, 159.66, 140.43, 137.78, 129.58, 126.08, 123.79, 122.39, 120.95, 120.54, 114.59, 109.73, 99.68, 55.68, 20.95. HRMS (ESI): Calcd for $C_{17}H_{17}N_2O_2$ $[M+H]^+$ 281.1285, Found 281.1282.

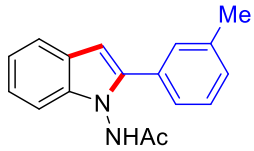


N-(2-(4-nitrophenyl)-1H-indol-1-yl)acetamide (3ai): pale yellow solid (13.2 mg, 22%); M.p.: 295-298 °C. IR (cm^{-1}): *v* 3198, 2924, 2359, 1601, 1489, 1341, 1280, 746, 692. ^{1}H NMR (400 MHz, DMSO): δ 11.28 (s, 1H), 8.36 – 8.30 (m, 2H), 7.94 – 7.88 (m, 2H), 7.66 (d, J = 7.9 Hz, 1H), 7.33 (s, 1H), 7.28 (d, J = 1.0 Hz,

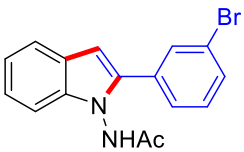
1H), 7.17 (s, 1H), 7.01 (s, 1H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.79, 146.97, 138.78, 138.02, 137.75, 128.73, 125.76, 124.40, 124.06, 121.58, 121.46, 110.21, 103.57, 20.96. HRMS (ESI): Calcd for $C_{16}H_{14}N_3O_3$ $[M+H]^+$ 296.1030, Found 296.1028.



N-(2-(4-(trifluoromethyl)phenyl)-1H-indol-1-yl)acetamide (3aj): pale yellow solid (44.8 mg, 73%); M.p.: 278-280 °C. IR (cm^{-1}): *v* 3250, 3024, 2357, 1680, 1618, 1325, 1159, 1125, 745. ^{1}H NMR (400 MHz, DMSO): δ 11.23 (s, 1H), 7.87 – 7.80 (m, 4H), 7.64 (d, J = 7.8 Hz, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.19 – 7.13 (m, 1H), 6.89 (s, 1H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.76, 138.70, 138.37, 135.35, 128.63, 126.01 (dd, J = 7.7, 3.9 Hz), 125.79, 123.53, 121.36, 121.21, 110.08, 102.31, 20.93. HRMS (ESI): Calcd for $C_{17}H_{14}F_3N_2O$ $[M+H]^+$ 319.1053, Found: 319.1051.

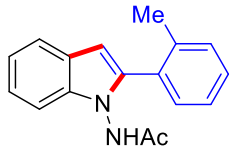


N-(2-(m-tolyl)-1H-indol-1-yl)acetamide (3ak): pale yellow solid (33.4 mg, 63%); M.p.: 178-179 °C. IR (cm^{-1}): *v* 3240, 3026, 2359, 1601, 1489, 1341, 1280, 746, 692. ^{1}H NMR (400 MHz, DMSO): δ 11.12 (s, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.37 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 8.2 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.15 – 7.09 (m, 1H), 6.70 (s, 1H), 2.38 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.58, 140.57, 138.22, 138.00, 131.30, 129.10, 128.91, 128.90, 125.97, 125.27, 122.72, 121.02, 120.77, 109.85, 100.56, 21.54, 20.92. HRMS (ESI): Calcd for $C_{17}H_{17}N_2O$ $[M+H]^+$ 265.1335, Found 265.1333.

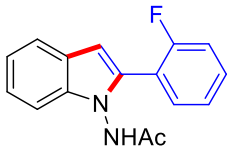


N-(2-(3-bromophenyl)-1H-indol-1-yl)acetamide (3al): pale yellow solid (43.4 mg, 66%); M.p.: 197-200 °C. IR (cm^{-1}): *v* 3265, 3024, 2359, 1680, 1450, 1265, 781, 717, 669. ^{1}H NMR (400 MHz, DMSO): δ 11.19 (s, 1H), 7.82 (t, J = 1.7 Hz,

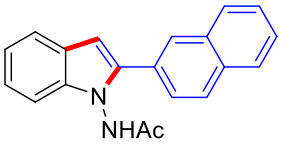
1H), 7.66 – 7.57 (m, 3H), 7.45 (t, J = 7.9 Hz, 1H), 7.31 (d, J = 7.9 Hz, 1H), 7.26 – 7.19 (m, 1H), 7.18 – 7.11 (m, 1H), 6.82 (s, 1H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.72, 138.67, 138.19, 133.62, 131.24, 131.13, 130.49, 127.14, 125.81, 123.30, 122.33, 121.28, 121.09, 109.99, 101.70, 20.90. HRMS (ESI): Calcd for $C_{16}H_{14}BrN_2O$ $[M+H]^+$ 329.0284, Found 329.0285.



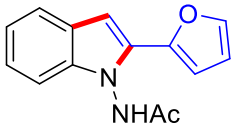
N-(2-(o-tolyl)-1H-indol-1-yl)acetamide (3am): pale yellow solid (39.0 mg, 74%); M.p.: 197-200 ºC. IR (cm^{-1}): *v* 3244, 3030, 2359, 1676, 1531, 1456, 1329, 1269, 804, 769, 741, 615. ^{1}H NMR (400 MHz, DMSO): δ 10.90 (s, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.36 – 7.24 (m, 5H), 7.23 – 7.18 (m, 1H), 7.15 – 7.10 (m, 1H), 6.53 (d, J = 0.6 Hz, 1H), 2.31 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.46, 139.52, 137.76, 136.76, 130.91, 130.68, 130.62, 128.86, 125.92, 125.69, 122.39, 120.76, 120.66, 109.72, 101.59, 20.78, 20.60. HRMS (ESI): Calcd for $C_{17}H_{17}N_2O$ $[M+H]^+$ 265.1335, Found 265.1336.



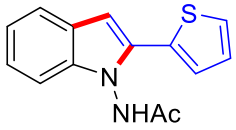
N-(2-(2-fluorophenyl)-1H-indol-1-yl)acetamide (3an): pale yellow solid (37.9 mg, 70%); M.p.: 237-239 ºC. IR (cm^{-1}): *v* 3229, 3022, 2361, 1678, 1489, 1267, 1105, 772, 745. ^{1}H NMR (400 MHz, DMSO): δ 11.09 (s, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.58 – 7.44 (m, 2H), 7.40 – 7.28 (m, 3H), 7.27 – 7.21 (m, 1H), 7.18 – 7.12 (m, 1H), 6.73 (d, J = 0.9 Hz, 1H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.53, 159.85 (d, J = 247.7 Hz), 137.44, 133.95, 131.37 (d, J = 2.3 Hz), 130.85 (d, J = 8.3 Hz), 125.84, 124.87 (d, J = 3.5 Hz), 123.07, 121.02 (d, J = 7.2 Hz), 119.11 (d, J = 13.8 Hz), 116.48 (d, J = 22.0 Hz), 109.89, 102.90 (d, J = 3.6 Hz), 20.82. ^{19}F NMR (376 MHz, DMSO): δ -114.06. HRMS (ESI): Calcd for $C_{16}H_{14}FN_2O$ $[M+H]^+$ 269.1085, Found 269.1089.



N-(2-(naphthalen-2-yl)-1H-indol-1-yl)acetamide (3ao)*:* pale yellow solid (52.4 mg, 87%); M.p.: 168-172 °C. IR (cm^{-1}): *v* 3267, 3032, 2926, 1676, 1512, 1381, 1253, 800, 472. ^{1}H NMR (400 MHz, DMSO): δ 11.24 (s, 1H), 8.19 (s, 1H), 8.03 – 7.94 (m, 3H), 7.80 (d, J = 1.7 Hz, 1H), 7.65 – 7.54 (m, 3H), 7.32 (s, 1H), 7.24 (s, 1H), 7.15 (s, 1H), 6.87 (s, 1H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.68, 140.34, 138.26, 133.41, 132.81, 128.86, 128.57, 128.48, 128.06, 127.10, 126.97, 126.91, 126.21, 126.07, 122.97, 121.16, 120.90, 109.94, 101.33, 20.95. HRMS (ESI): Calcd for $C_{20}H_{17}N_2O$ $[M+H]^+$ 301.1335, Found: 301.1339.

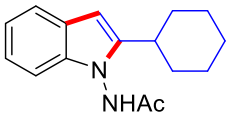


N-(2-(furan-2-yl)-1H-indol-1-yl)acetamide (3ap)*:* pale yellow solid (42.4 mg, 88%); M.p.: 225-227 °C. IR (cm^{-1}): *v* 3231, 1678, 1520, 1437, 1371, 1333, 1269, 1011, 800, 741. ^{1}H NMR (400 MHz, DMSO): δ 11.25 (s, 1H), 7.81 (d, J = 1.4 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.27 (s, 1H), 7.21 (d, J = 1.0 Hz, 1H), 7.13 (s, 1H), 6.82 (s, 1H), 6.77 (d, J = 3.4 Hz, 1H), 6.65 (dd, J = 3.4, 1.8 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.69, 145.74, 143.51, 137.68, 130.98, 125.74, 123.14, 121.21, 120.99, 112.35, 109.59, 107.75, 98.70, 21.08. HRMS (ESI): Calcd for $C_{14}H_{12}N_2NaO$ $[M+Na]^+$ 263.0791, Found: 263.0795.

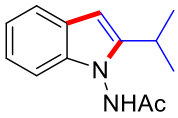


N-(2-(thiophen-2-yl)-1H-indol-1-yl)acetamide (3ap)*:* pale yellow solid (33.8 mg, 66%); M.p.: 110-113 °C. IR (cm^{-1}): *v* 3435, 1655, 1524, 1441, 1385, 1107, 691. ^{1}H NMR (400 MHz, DMSO): δ 11.27 (s, 1H), 7.62 (d, J = 5.0 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 3.5 Hz, 1H), 7.25 (s, 1H), 7.18 (dd, J = 7.9, 2.5 Hz, 2H), 7.12 (s, 1H), 6.86 (s, 1H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.90, 137.57, 134.09,

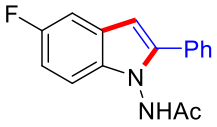
132.27, 128.17, 127.00, 126.20, 125.83, 122.93, 121.23, 120.70, 109.63, 99.49, 21.18. HRMS (ESI): Calcd for $C_{14}H_{12}N_2NaOS$ $[M+Na]^+$ 279.0563, Found: 279.0569.



N-(2-cyclohexyl-1H-indol-1-yl)acetamide (3ar): pale yellow solid (15.5 mg, 30%); M.p.: 203-205 °C. IR (cm^{-1}): *v* 2924, 1458, 1442, 779, 744, 732, 723, 526. ^1H NMR (400 MHz, DMSO): δ 10.88 (s, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.14 (d, J = 8.1 Hz, 1H), 7.10 – 7.05 (m, 1H), 7.04 – 6.99 (m, 1H), 6.19 (s, 1H), 2.13 (s, 3H), 2.01 (d, J = 8.3 Hz, 1H), 1.89 (d, J = 12.8 Hz, 1H), 1.80 (d, J = 12.0 Hz, 2H), 1.72 (d, J = 11.8 Hz, 2H), 1.43 – 1.23 (m, 6H). ^{13}C NMR (101 MHz, DMSO): δ 169.65, 146.73, 136.31, 125.98, 121.38, 120.19, 120.12, 109.02, 95.70, 34.85, 33.50, 32.32, 26.49, 26.44, 26.15, 20.96. HRMS (ESI): Calcd for $C_{16}H_{20}N_2NaO$ $[M+Na]^+$ 279.1468, Found: 279.1464.

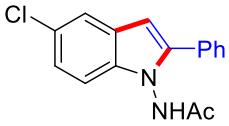


N-(2-isopropyl-1H-indol-1-yl)acetamide (3as): pale yellow solid (17.1 mg, 39%); M.p.: 115-117 °C. IR (cm^{-1}): *v* 3234, 2933, 1680, 1525, 1384, 1116. ^1H NMR (400 MHz, DMSO): δ 10.92 (s, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.14 (s, 1H), 7.08 (s, 2H), 7.02 (s, 1H), 2.88 (dt, J = 13.7, 6.8 Hz, 1H), 2.13 (s, 3H), 1.25 (dd, J = 11.7, 6.9 Hz, 6H). ^{13}C NMR (101 MHz, DMSO): δ 169.62, 147.72, 136.49, 129.46, 125.90, 121.43, 120.21, 120.14, 119.15, 109.00, 95.38, 25.17, 23.17, 22.16, 20.96. HRMS (ESI): Calcd for $C_{13}H_{16}N_2NaO$ $[M+Na]^+$ 239.1155, Found: 239.1151.

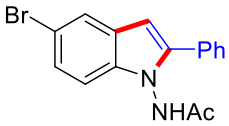


N-(5-fluoro-2-phenyl-1H-indol-1-yl)acetamide (3ba): pale yellow solid (45.2 mg, 84%); M.p.: 273-275 °C. IR (cm^{-1}): *v* 3254, 2363, 1676, 1520, 1470, 1263, 750. ^1H NMR (400 MHz, DMSO): δ 11.17 (s, 1H), 7.65 – 7.59 (m, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.44 – 7.35 (m, 2H), 7.30 (dd, J = 8.8, 4.5 Hz, 1H), 7.06 (dd, J = 9.3, 2.4 Hz, 1H), 6.72 (s, 1H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.68, 158.29 (d, J = 233.1

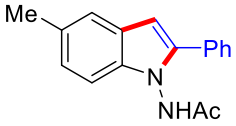
Hz), 142.18, 134.64, 131.06, 129.13, 128.75, 128.25, 126.26 (d, J = 10.4 Hz), 111.10, 110.98 (d, J = 4.2 Hz), 110.70, 105.64 (d, J = 23.8 Hz), 100.69 (d, J = 4.4 Hz), 20.93. ^{19}F NMR (376 MHz, DMSO): δ -123.41. HRMS (ESI): Calcd for $C_{16}H_{14}FN_2O$ $[M+H]^+$ 269.1085, Found 269.1087



N-(5-chloro-2-phenyl-1H-indol-1-yl)acetamide (3ca): pale yellow solid (42.3 mg, 74%); M.p.: 243-244 °C. IR (cm^{-1}): *v* 3244, 3026, 2361, 1678, 1458, 1271, 754. ^{1}H NMR (400 MHz, DMSO): 1H NMR (400 MHz, DMSO) δ 11.22 (s, 1H), 7.67 – 7.60 (m, 3H), 7.50 (t, J = 7.5 Hz, 2H), 7.45 – 7.40 (m, 1H), 7.33 (d, J = 8.6 Hz, 1H), 7.22 (dd, J = 8.6, 2.0 Hz, 1H), 6.72 (s, 1H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.67, 141.98, 136.51, 130.87, 129.16, 128.85, 128.30, 127.08, 125.58, 122.75, 120.03, 111.54, 100.32, 20.92. HRMS (ESI): Calcd for $C_{16}H_{14}ClN_2O$ $[M+H]^+$ 285.0789, Found: 285.0787.

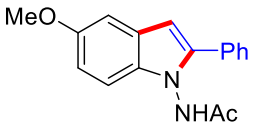


N-(5-bromo-2-phenyl-1H-indol-1-yl)acetamide (3da): pale yellow solid (58.6 mg, 89%); M.p.: 236-238 °C. IR (cm^{-1}): *v* 3244, 3024, 2357, 1678, 1524, 1458, 1368, 1269, 754, 694. ^{1}H NMR (400 MHz, DMSO): δ 11.23 (s, 1H), 7.81 (d, J = 1.6 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.53 – 7.40 (m, 3H), 7.36 – 7.27 (m, 2H), 6.73 (s, 1H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.65, 141.82, 136.78, 130.83, 129.16, 128.86, 128.32, 127.76, 125.30, 123.05, 113.47, 111.98, 100.22, 20.93. HRMS (ESI): Calcd for $C_{16}H_{14}BrN_2O$ $[M+H]^+$ 329.0284, Found 329.0281.

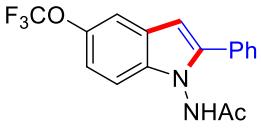


N-(5-methyl-2-phenyl-1H-indol-1-yl)acetamide (3ea): pale yellow solid (40.1 mg, 76%); M.p.: 213-214 °C. IR (cm^{-1}): *v* 3221, 2360, 1678, 1514, 1265, 795, 694. ^{1}H NMR (400 MHz, DMSO): δ 11.08 (s, 1H), 7.65 – 7.59 (m, 2H), 7.51 –

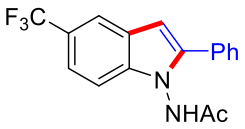
7.37 (m, 4H), 7.20 – 7.15 (m, 1H), 7.06 – 7.01 (m, 1H), 6.63 (s, 1H), 2.41 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.59, 140.45, 136.53, 131.50, 129.71, 129.04, 128.33, 128.10, 126.22, 124.30, 120.43, 109.63, 100.29, 21.56, 20.93. HRMS (ESI): Calcd for $C_{17}H_{17}N_2O$ $[M+H]^+$ 265.1335, Found 265.1336.



N-(5-methoxy-2-phenyl-1H-indol-1-yl)acetamide (3fa): pale yellow solid (24.1mg, 43%); M.p.: 188-190 °C; IR (cm^{-1}): *ν* 3250, 2360, 1678, 1471, 1263, 1099, 1034, 804. ^{1}H NMR (400 MHz, DMSO): δ 11.06 (s, 1H), 7.63 – 7.58 (m, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 7.17 (d, J = 8.8 Hz, 1H), 7.10 (d, J = 2.3 Hz, 1H), 6.84 (dd, J = 8.8, 2.4 Hz, 1H), 6.63 (s, 1H), 3.79 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, DMSO): δ 169.64, 155.00, 140.90, 133.21, 131.47, 129.06, 128.37, 128.08, 126.43, 112.71, 110.67, 102.71, 100.49, 55.92, 20.94; HRMS (ESI): Calcd for $C_{17}H_{17}N_2O_2$ $[M+H]^+$ 281.1285, Found 281.1283.

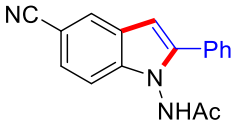


N-(2-phenyl-5-(trifluoromethoxy)-1H-indol-1-yl)acetamide (3ga): pale yellow solid (56.7mg, 78%); M.p.: 212-214 °C. IR (cm^{-1}): *ν* 3250, 3028, 2361, 1684, 1526, 1254, 1165, 756. ^{1}H NMR (400 MHz, DMSO): δ 11.28 (s, 1H), 7.66 – 7.59 (m, 3H), 7.54 – 7.39 (m, 4H), 7.19 (dd, J = 8.8, 1.3 Hz, 1H), 6.81 (s, 1H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.71, 143.37 (d, J = 1.8 Hz), 142.53, 136.39, 130.84, 129.16, 128.91, 128.35, 126.14, 116.39, 113.20, 111.12, 100.98, 20.89. ^{19}F NMR (376 MHz, DMSO): δ -57.01. HRMS (ESI): Calcd for $C_{17}H_{14}F_3N_2O_2$ $[M+H]^+$ 335.1002, Found 335.0999.

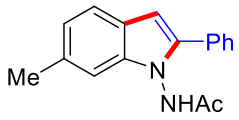


N-(2-phenyl-5-(trifluoromethyl)-1H-indol-1-yl)acetamide (3ha): pale yellow solid (52.7 mg, 86%); M.p.: 216-218 °C. IR (cm^{-1}): *ν* 3246, 3028, 2361, 1684, 1528, 1344, 1163, 1101, 746. ^{1}H NMR (400 MHz, DMSO): δ 11.36 (s, 1H), 8.02

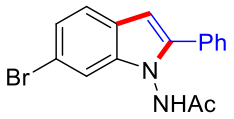
(s, 1H), 7.68 – 7.63 (m, 2H), 7.55 – 7.41 (m, 5H), 6.90 (s, 1H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.67 (s), 139.44 (s), 130.65 (s), 129.19 (s), 129.03 (s), 128.42 (s), 122.08 (q, J = 31.2 Hz), 119.22 (d, J = 3.5 Hz), 118.52 (d, J = 4.2 Hz), 110.75 (s), 101.49 (s), 20.90 (s). ^{19}F NMR (376 MHz, DMSO): δ -58.76. HRMS (ESI): Calcd for $C_{17}H_{14}F_3N_2O$ $[M+H]^+$ 19.1053, Found 319.1050.



N-(5-cyano-2-phenyl-1H-indol-1-yl)acetamide (3ia): yellow solid (47.7 mg, 86%); M.p.: 226-228 °C. IR (cm^{-1}): *ν* 3240, 2361, 2224, 1676, 1522, 1265, 759, 741. ^{1}H NMR (400 MHz, DMSO):δ 11.38 (s, 1H), 8.15 (d, J = 0.8 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.61 – 7.56 (m, 1H), 7.55 – 7.42 (m, 4H), 6.88 (s, 1H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.67, 142.82, 139.58, 130.36, 129.21, 129.18, 128.46, 126.32, 125.75, 125.72, 120.72, 111.27, 103.39, 101.25, 20.92. HRMS (ESI): Calcd for $C_{17}H_{14}N_3O$ $[M+H]^+$ 276.1131, Found 276.1130.

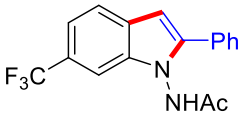


N-(6-methyl-2-phenyl-1H-indol-1-yl)acetamide (3ja): *pale* yellow solid (26.8 mg, 51%); M.p.: 207-209 °C. IR (cm^{-1}): *ν* 3256, 2361, 1676, 1522, 1265, 812, 746. ^{1}H NMR (400 MHz, DMSO): δ 11.06 (s, 1H), 7.60 (d, J = 7.2 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.38 (t, J = 7.3 Hz, 1H), 7.07 (s, 1H), 6.96 (d, J = 8.0 Hz, 1H), 6.65 (s, 1H), 2.43 (s, 3H), 2.04 (s, 3H).^{13}C NMR (101 MHz, DMSO): δ 169.61, 139.82, 138.45, 132.20, 131.55, 129.73, 129.04, 128.25, 128.07, 123.88, 122.75, 120.56, 109.67, 100.58, 21.92, 20.96. HRMS (ESI): Calcd for $C_{17}H_{17}N_2O$ $[M+H]^+$ 276.1135, Found 265.1337.

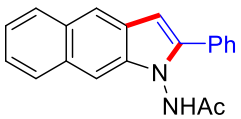


N-(6-bromo-2-phenyl-1H-indol-1-yl)acetamide (3ka): pale yellow solid (38.6 mg, 53%); M.p.: 255-259°C. IR (cm^{-1}): ν 3250, 2361, 1676, 1522, 1456, 1260, 814, 756, 689. ^{1}H NMR (400 MHz, DMSO): δ 11.19 (s, 1H), 7.62 (d, J = 7.3 Hz,

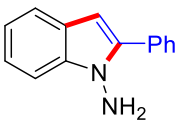
2H), 7.57 – 7.38 (m, 5H), 7.26 (dd, J = 8.3, 1.7 Hz, 1H), 6.75 (s, 1H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.76, 141.33, 138.82, 130.87, 129.73, 129.14, 129.03, 128.77, 128.27, 125.01, 124.06, 122.64, 115.61, 112.63, 100.83, 20.99. HRMS (ESI): Calcd for $C_{16}H_{14}BrN_2O$ $[M+H]^+$ 329.0284, Found 329.0286.



N-(2-phenyl-6-(trifluoromethyl)-1H-indol-1-yl)acetamide (3la): pale yellow solid (48.8 mg, 79%); M.p.: 227-229 °C. IR (cm^{-1}): *v* 3254, 3017, 2357, 1682, 1522, 1456, 1341, 1285, 1155, 1109, 824, 756. ^{1}H NMR (400 MHz, DMSO): δ 11.32 (s, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.67 (d, J = 7.2 Hz, 3H), 7.55 – 7.40 (m, 4H), 6.88 (s, 1H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.84, 143.56, 136.94, 130.59, 129.18, 129.14, 128.64, 128.47, 127.01, 124.31, 123.40, 123.09, 121.75, 117.44, 117.41, 107.29, 107.25, 100.95, 40.40, 39.98, 20.98. ^{19}F NMR (376 MHz, DMSO): δ -58.90. HRMS (ESI): Calcd for $C_{17}H_{14}F_3N_2O$ $[M+H]^+$ 319.1053, Found 319.1049.



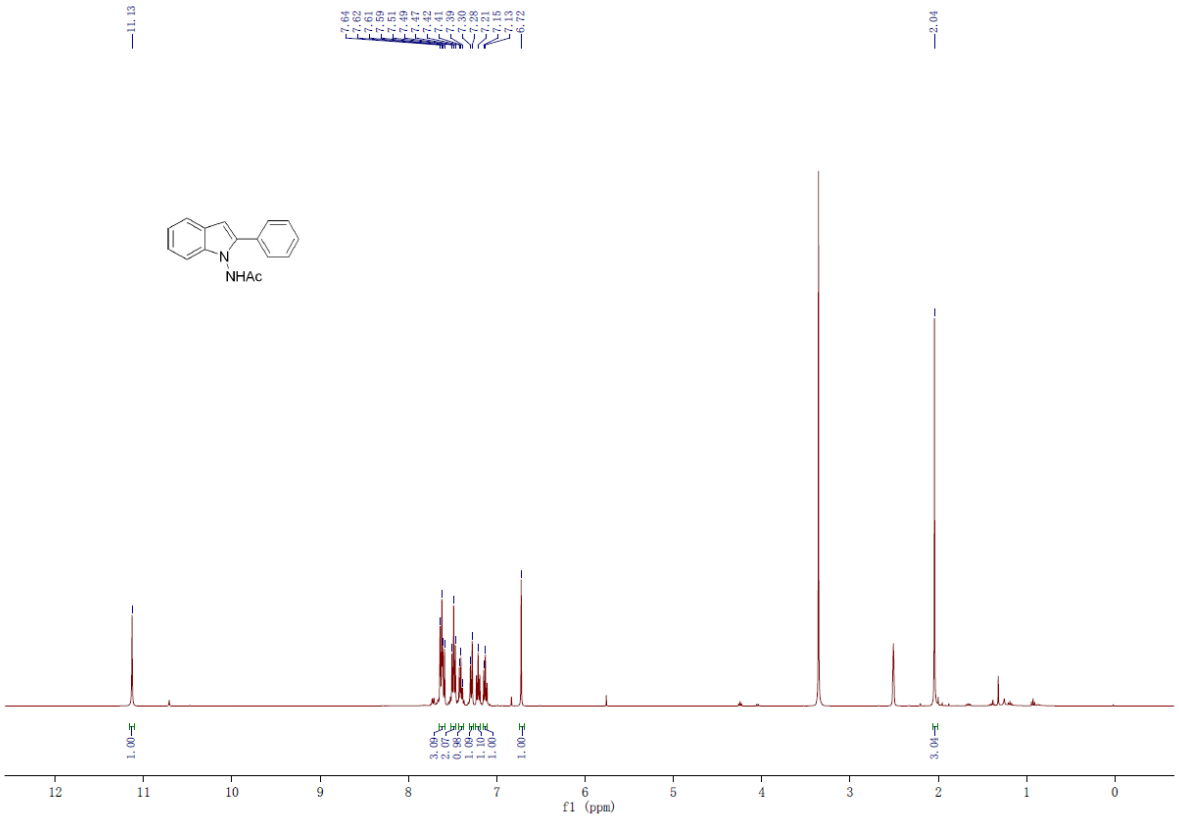
N-(2-phenyl-1H-benzo[f]indol-1-yl)acetamide (3pa): pale yellow solid (40.6 mg, 67%); M.p.: 264-268 °C. **I**R (cm^{-1}): *v* 3258, 2357, 1676, 1518, 1489, 1449, 1368, 1265, 856, 762, 741, 690. ^{1}H NMR (400 MHz, DMSO): δ 11.21 (s, 1H), 8.15 (s, 1H), 7.99 (d, J = 9.5 Hz, 2H), 7.79 (s, 1H), 7.76 – 7.71 (m, 2H), 7.53 (t, J = 7.4 Hz, 2H), 7.47 – 7.34 (m, 3H), 6.90 (s, 1H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 169.75, 144.85, 138.99, 131.08, 130.59, 129.60, 129.15, 128.99, 128.39, 128.36, 127.76, 127.66, 124.46, 123.34, 118.25, 105.15, 100.35, 21.05. HRMS (ESI): Calcd for $C_{20}H_{17}N_2O$ $[M+H]^+$ 301.1335, Found 301.1338.



2-phenyl-1H-indol-1-amine (4): pale yellow solid (30.2 mg, 74%); M.p.: 140-146 °C. **I**R (cm^{-1}): *v* 3394, 2933, 2295, 1591, 1471, 1379, 1120, 823, 746,

686, 559. ^{1}H NMR (400 MHz, DMSO): δ 9.97 (s, 1H), 7.82 – 7.73 (m, 2H), 7.44 – 7.30 (m, 3H), 7.13 (d, J = 7.3 Hz, 2H), 6.92 – 6.76 (m, 2H), 3.76 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ 139.72, 138.90, 137.50, 128.77, 128.56, 128.48, 127.50, 125.38, 122.00, 116.08, 111.96. HRMS (ESI): Calcd for $C_{14}H_{13}N_2$ $[M+H]^+$ 209.1073, Found 200.1069.

Spectral Copies of ^{1}H, ^{13}C, and ^{19}F NMR of Compounds Obtained in This Study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7.28
7.21
7.15
7.13
6.72
2.04
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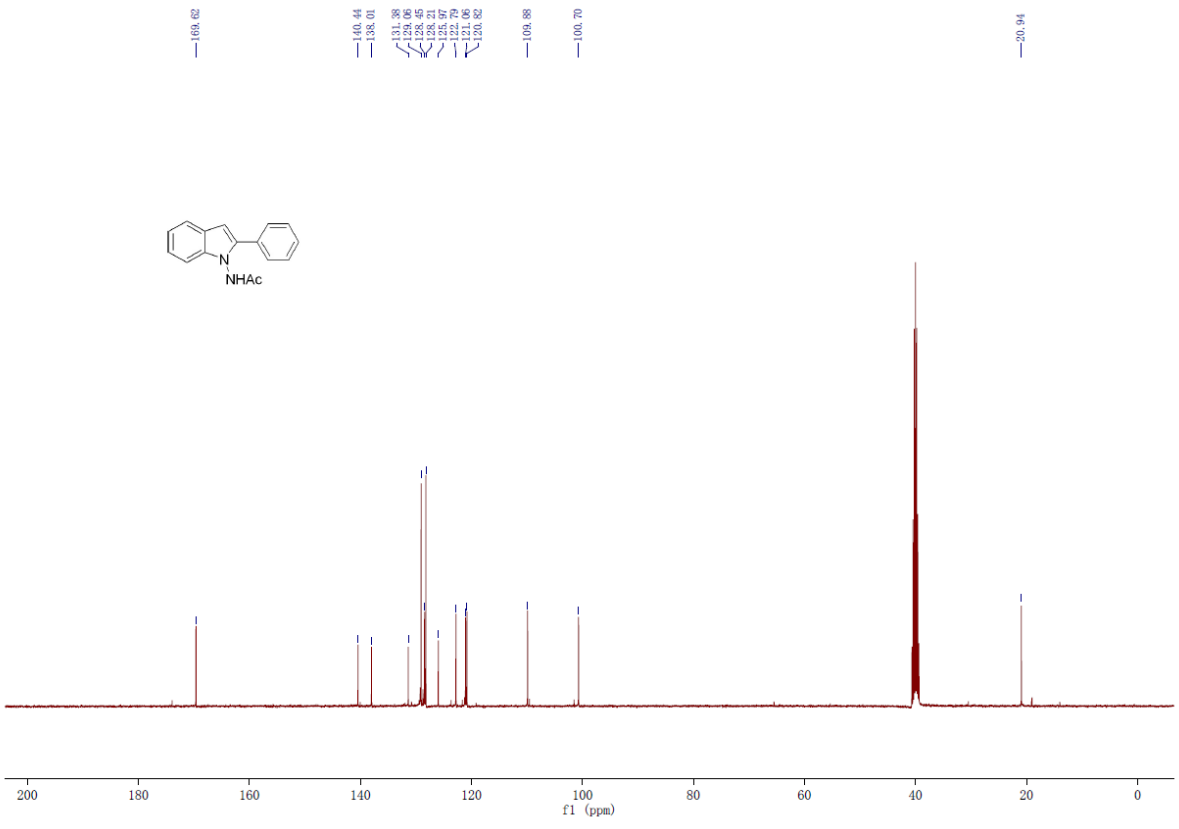
3.09
2.07
0.98
1.09
1.10
1.00
1.00
3.04
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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100
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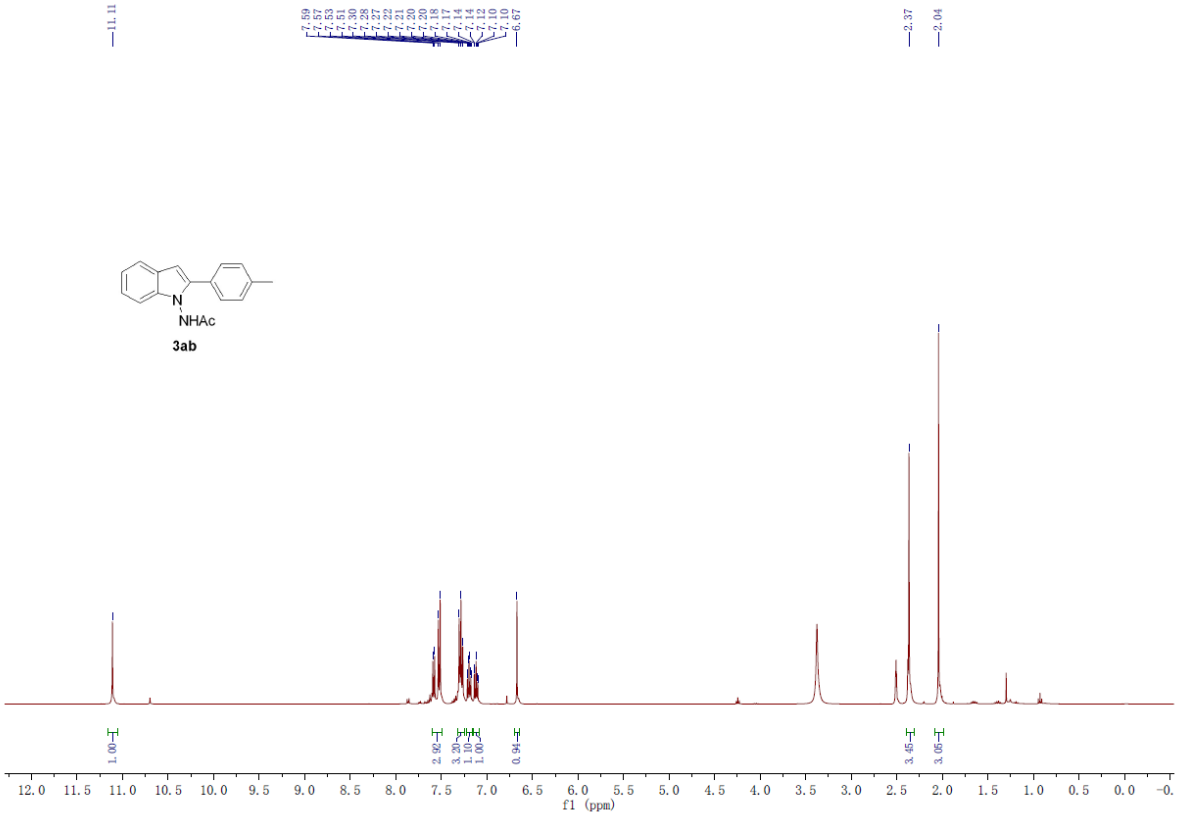
f1 (ppm)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7.14
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3.20
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1.00
0.94
3.45
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
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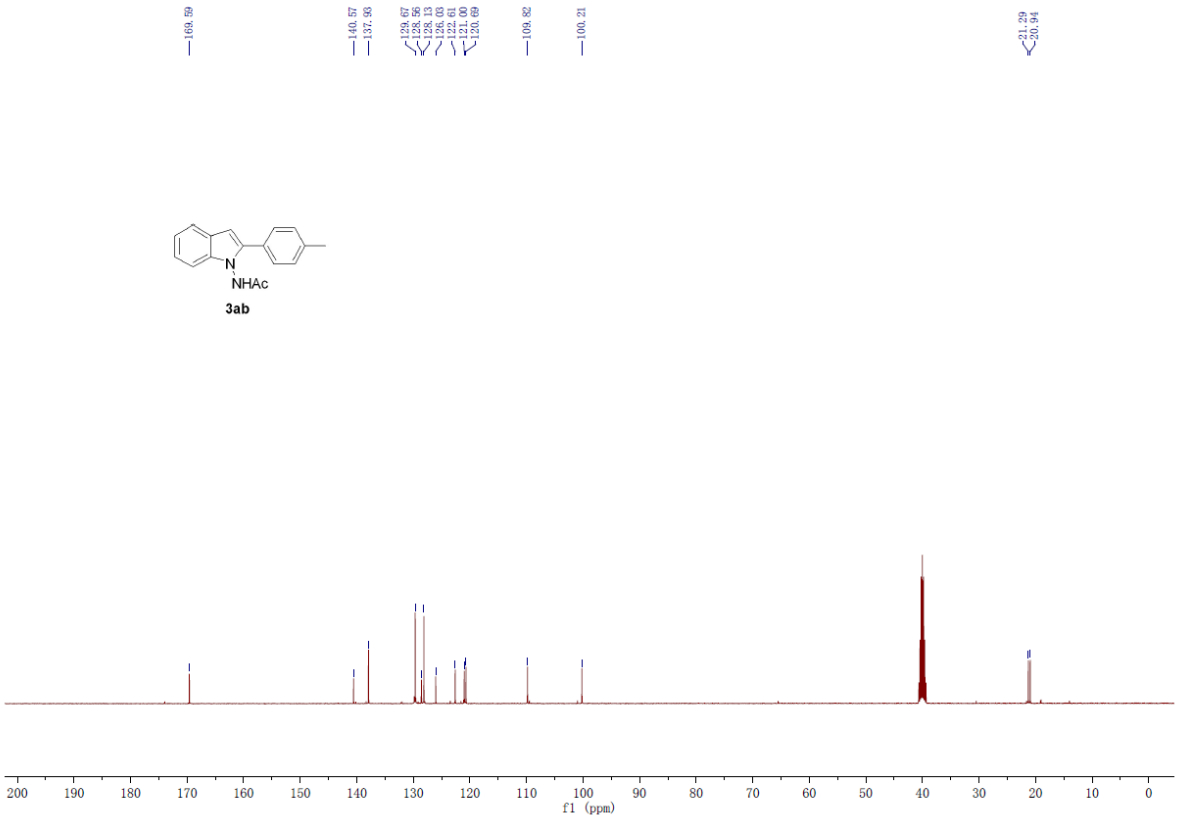
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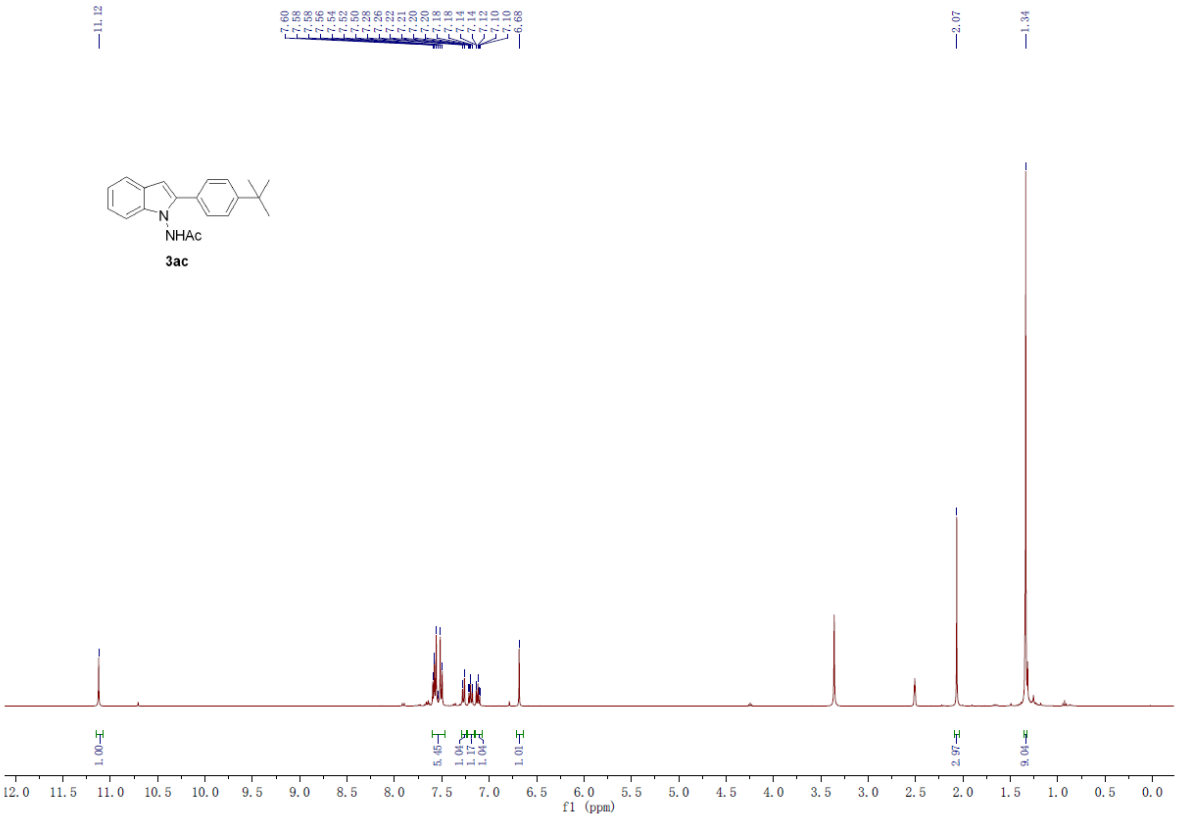
f1 (ppm)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7.18
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7.14
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7.10
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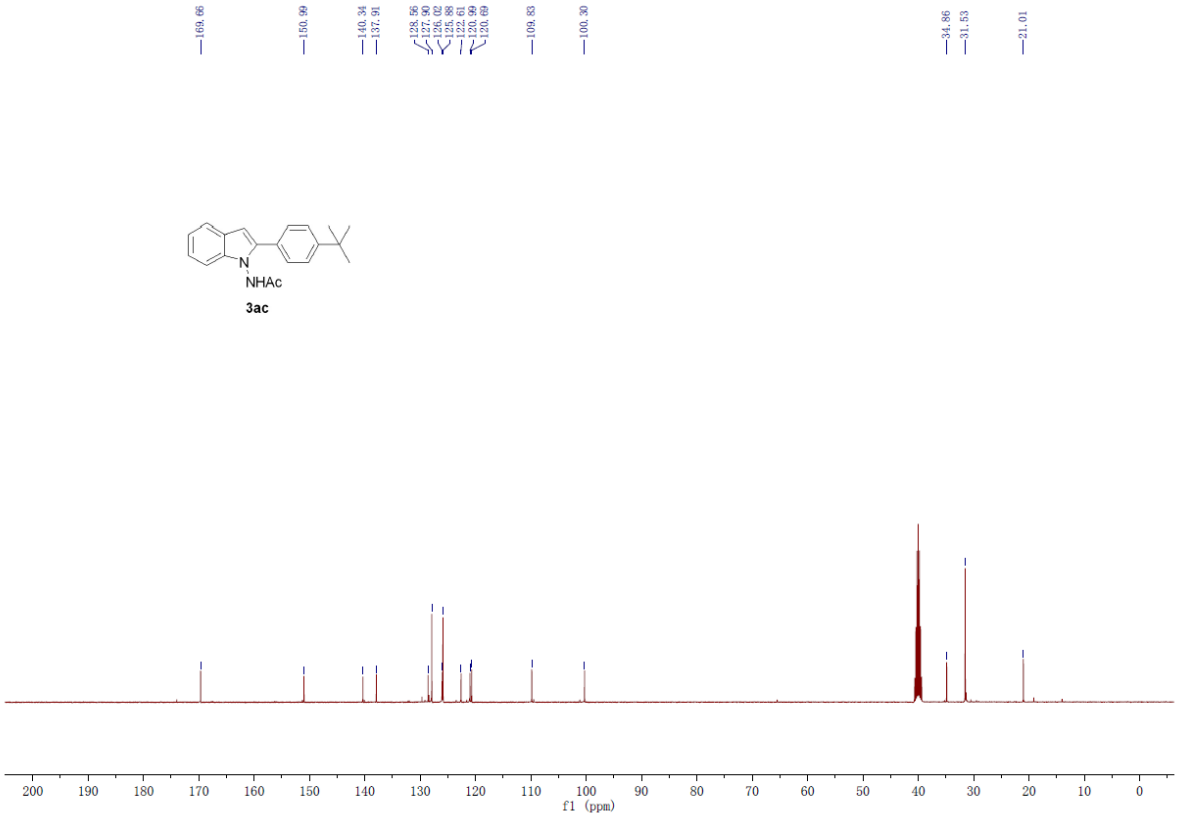
f1 (ppm)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31.53
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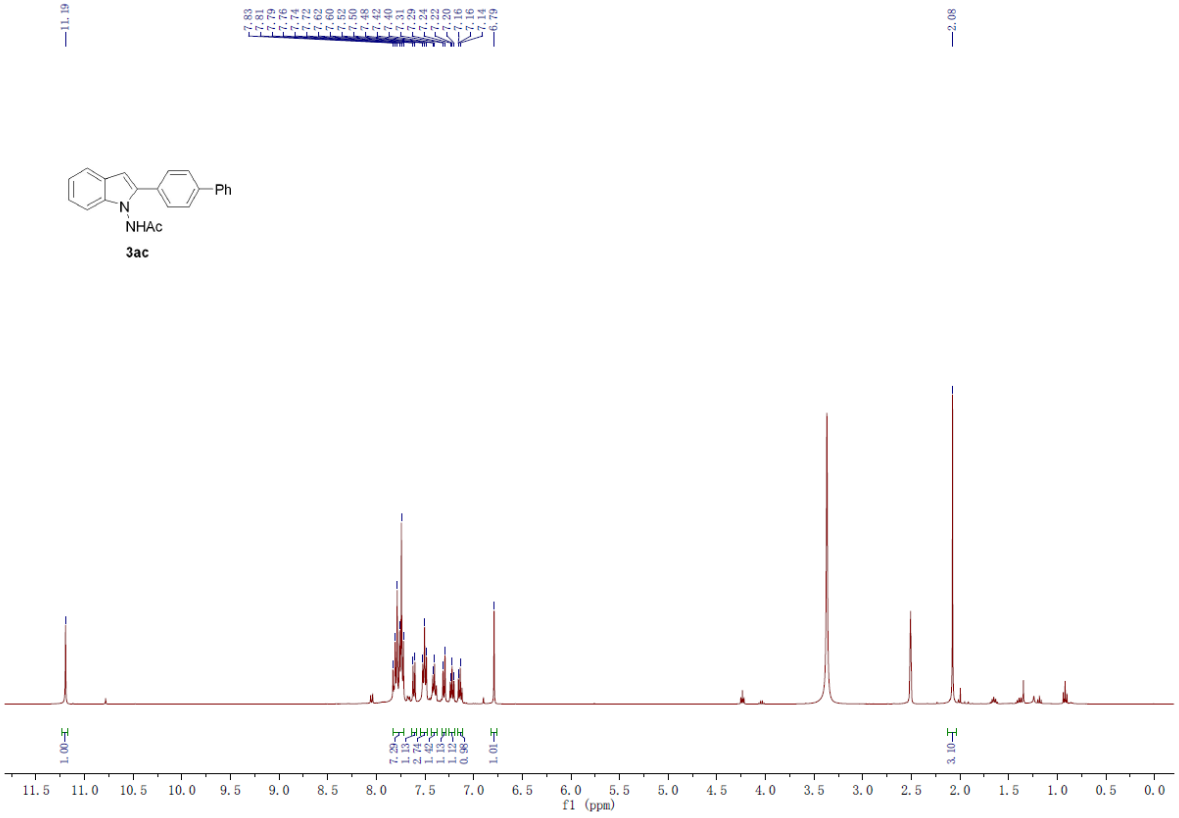
NHAc
3ac
f1 (ppm)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7.14
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2.08
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1.13
2.74
1.62
1.13
1.13
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1.01
3.10
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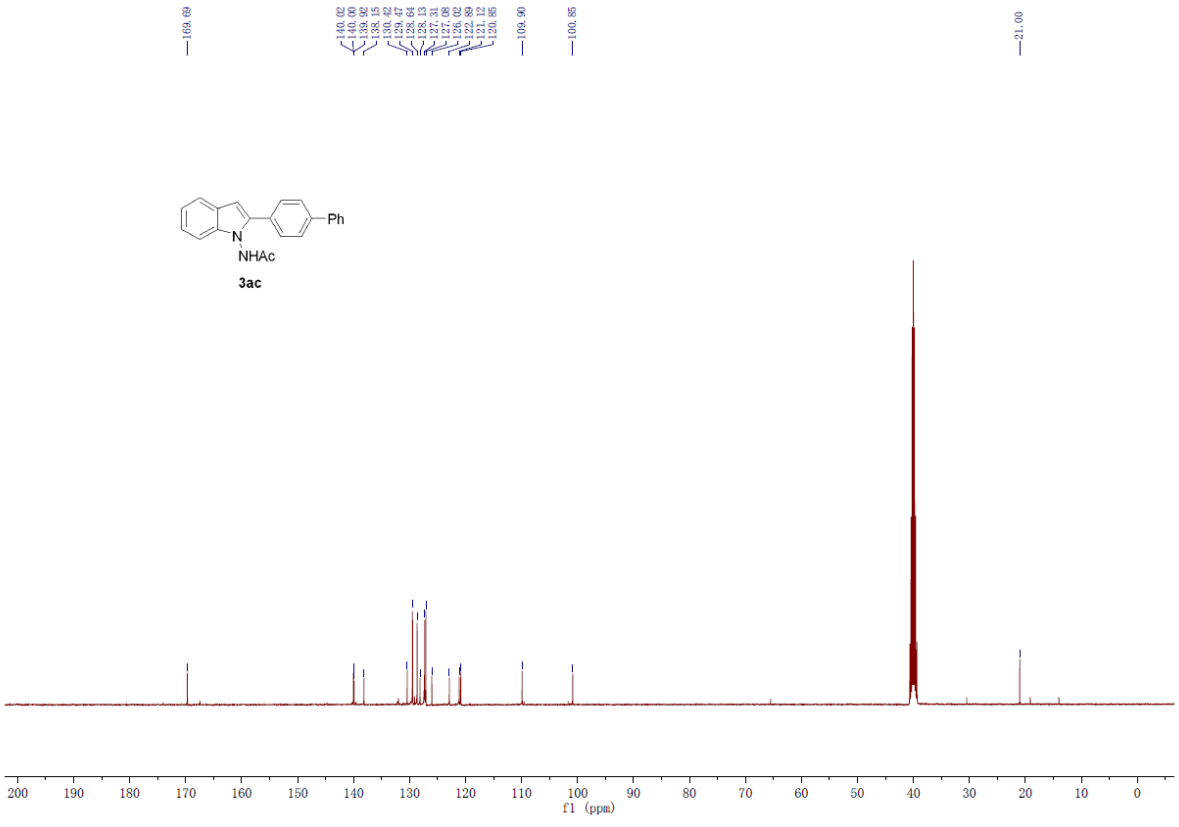
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21.00
Ph
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3ac
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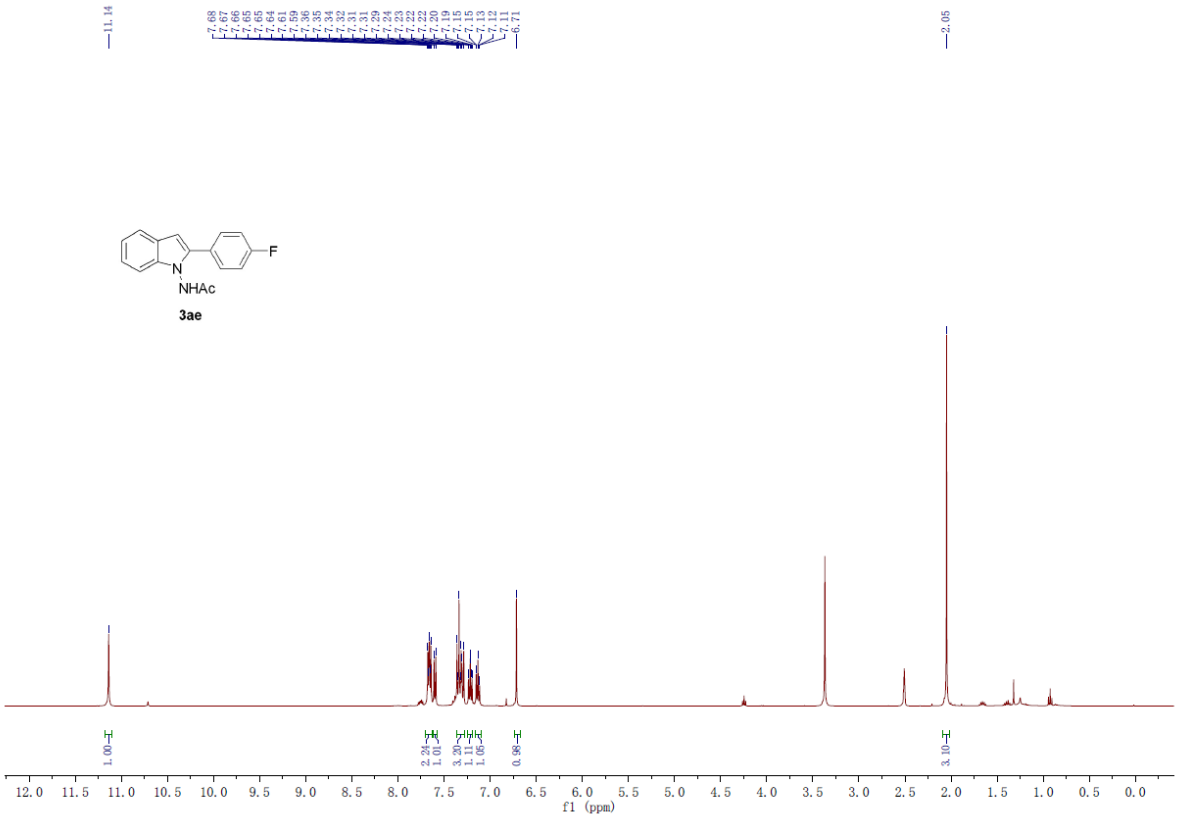
f1 (ppm)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3.10
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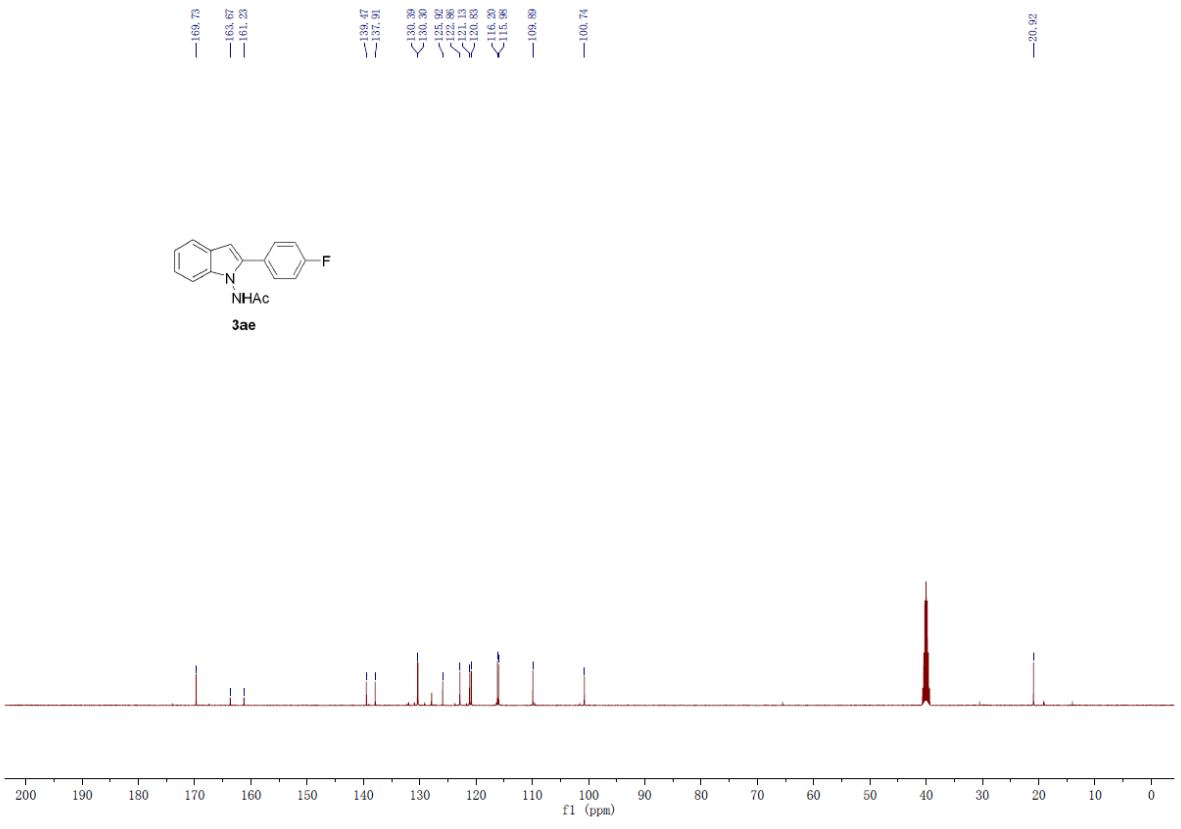
f1 (ppm)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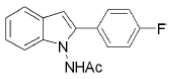
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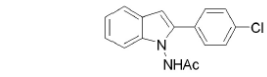
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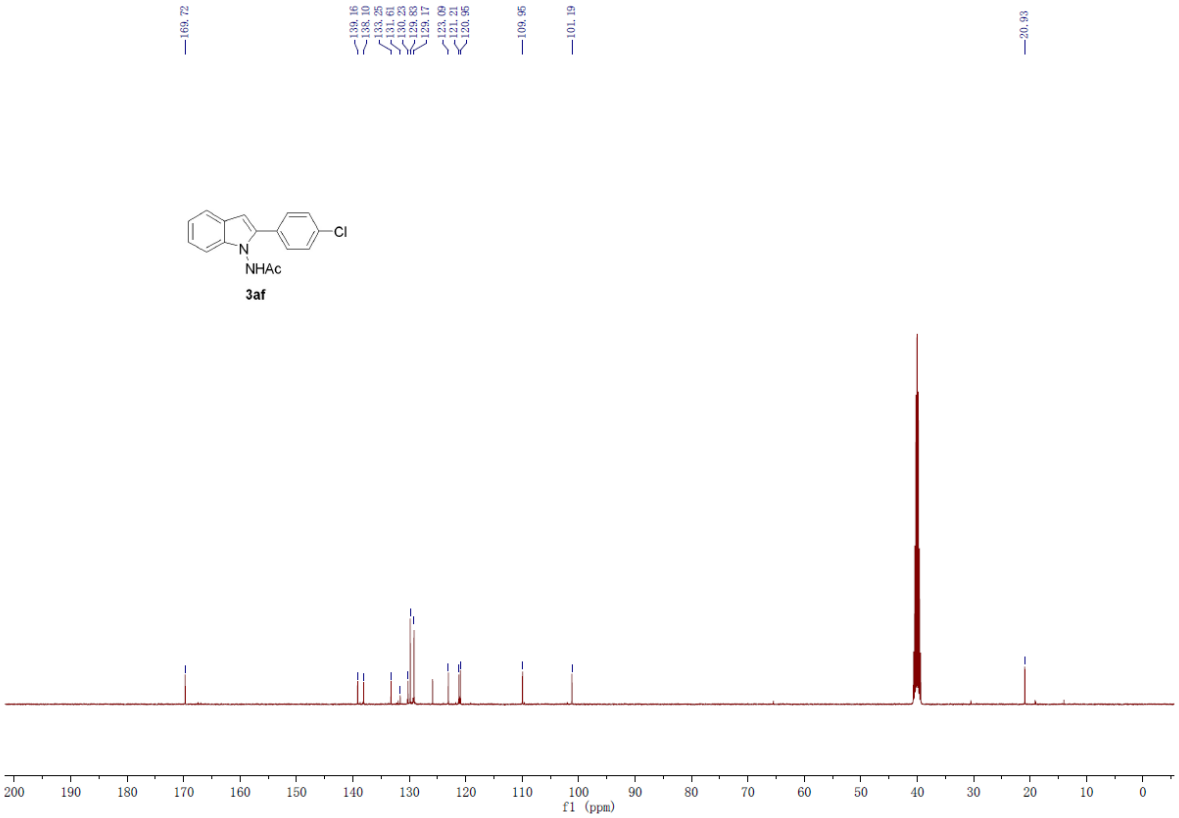
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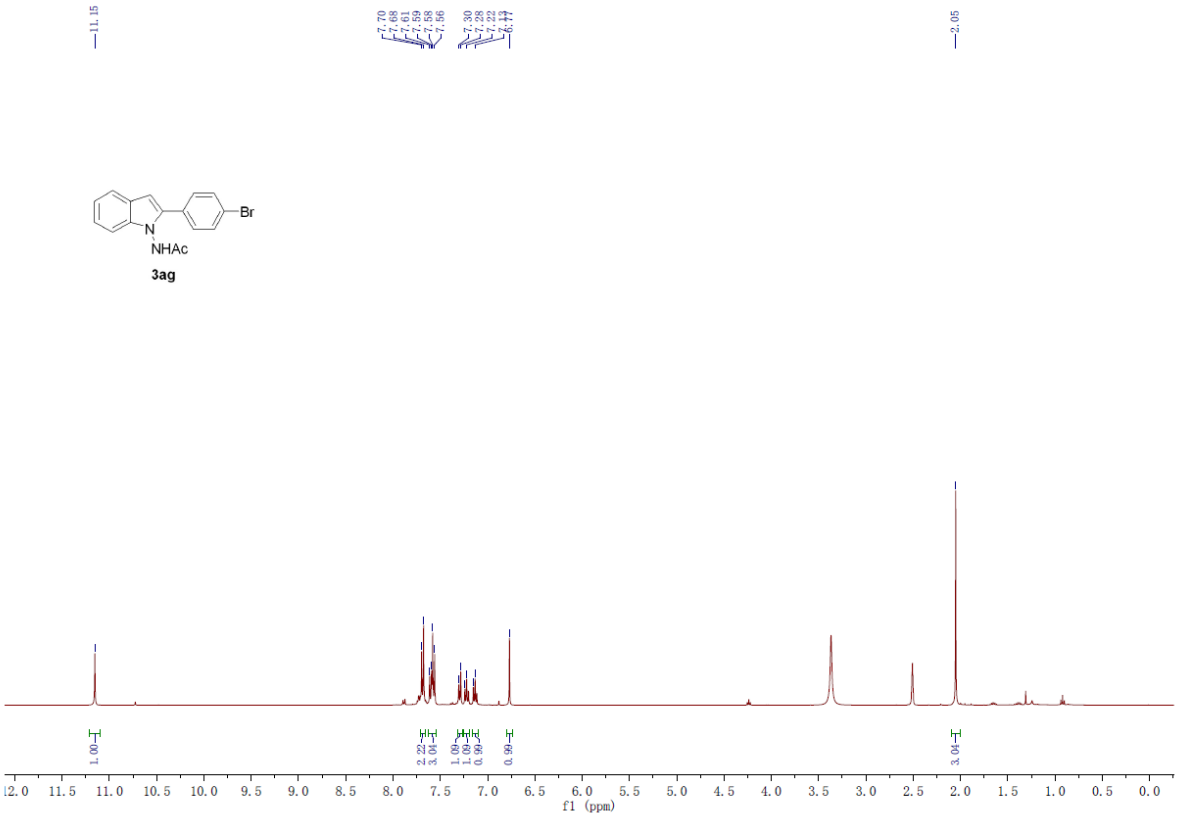
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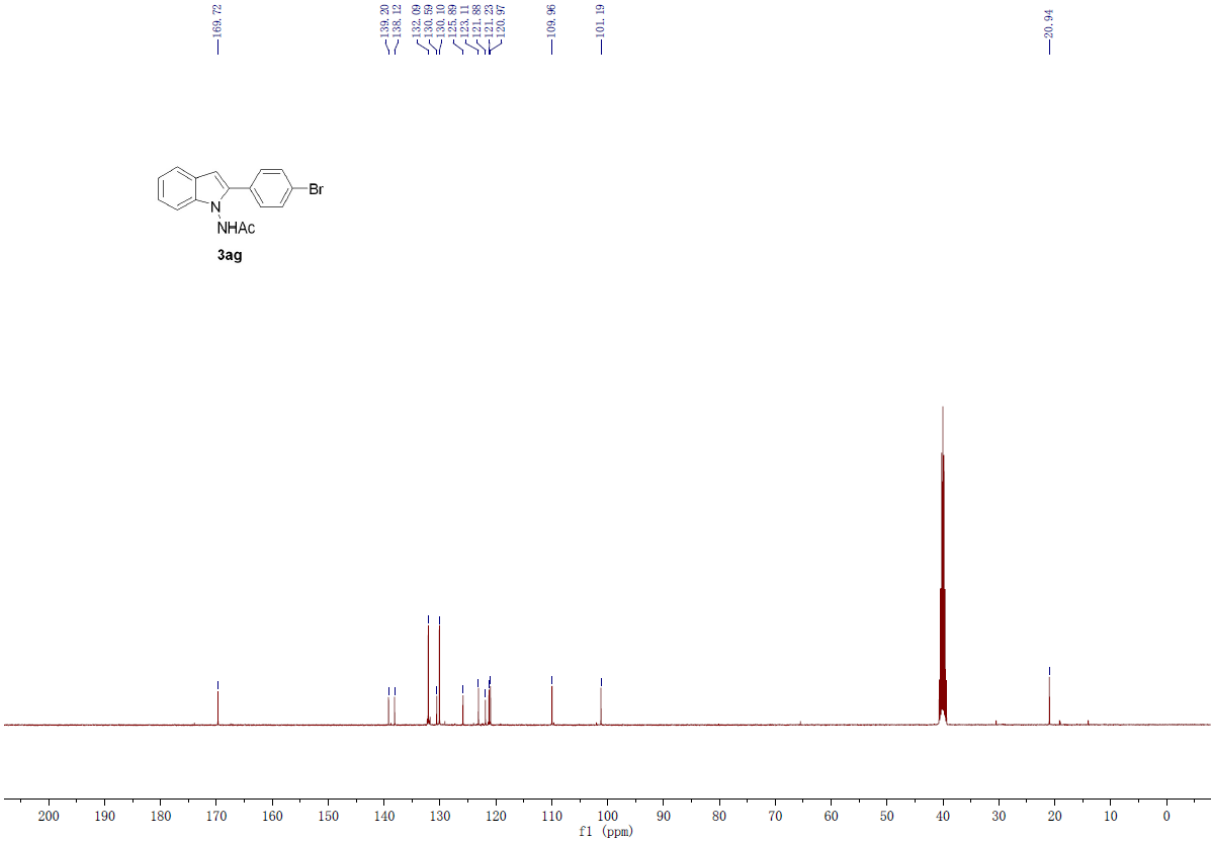
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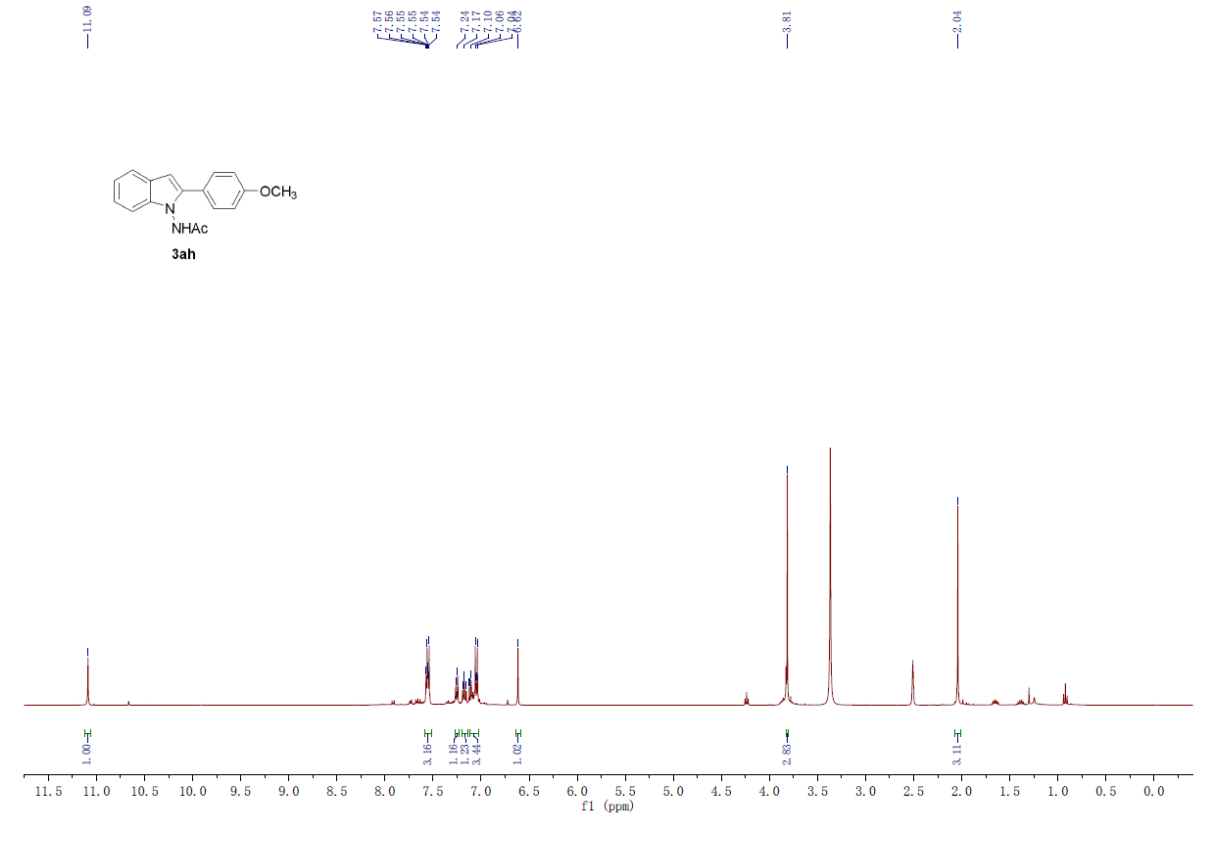
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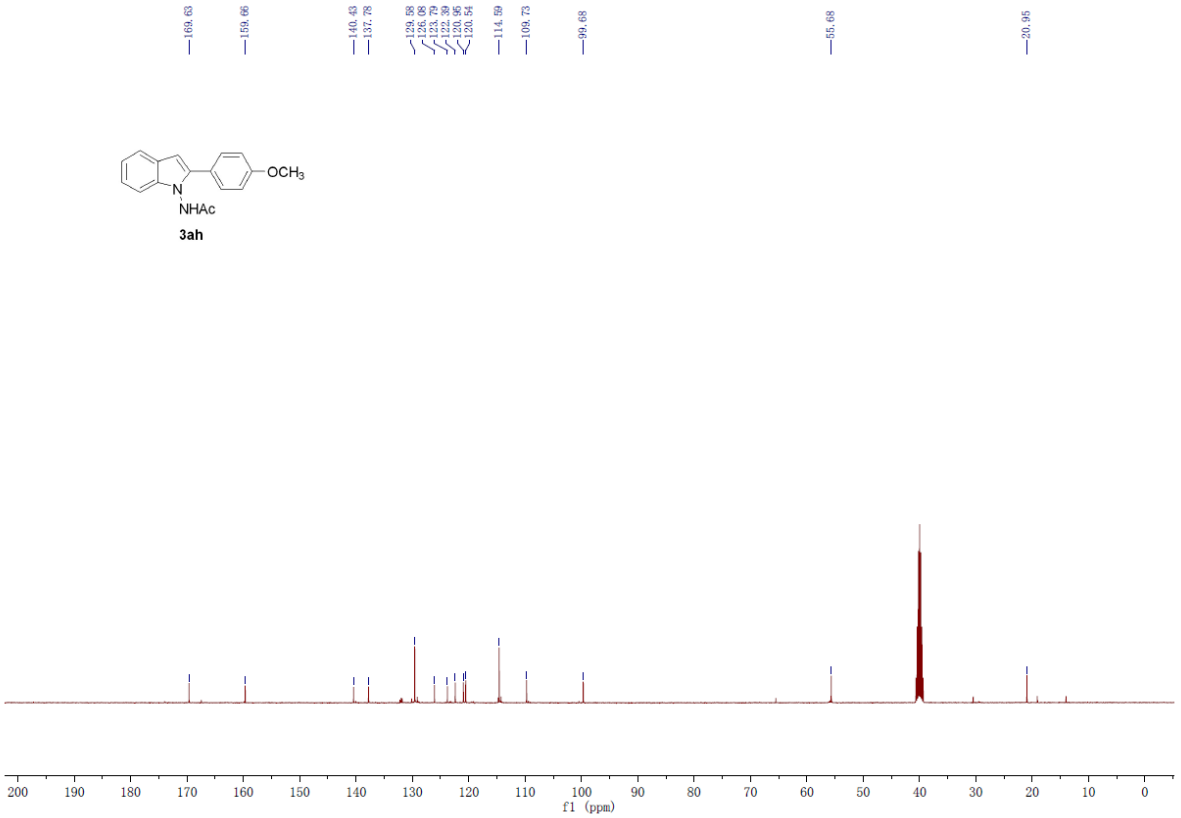
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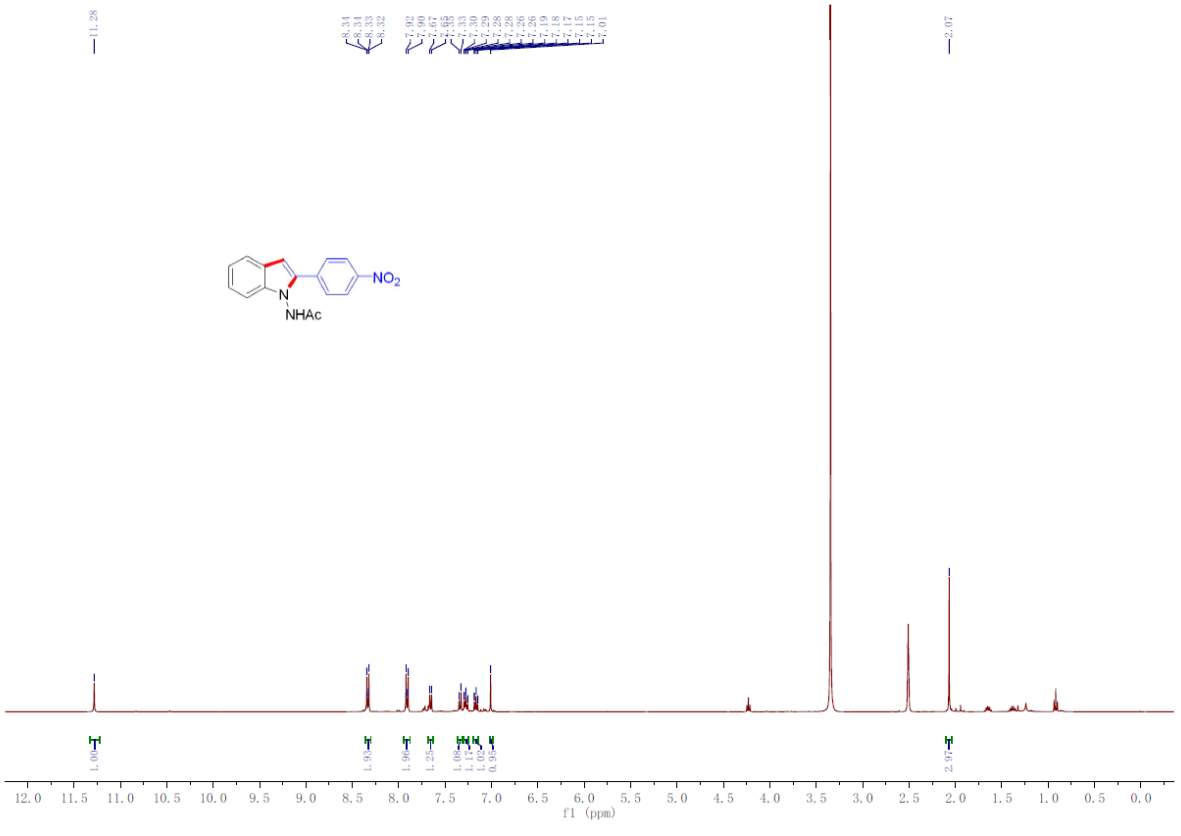
OCH3
N
NHAc
f1 (ppm)

3ah


11.28
8.34
8.33
8.32
7.92
7.90
7.67
7.33
7.30
7.29
7.28
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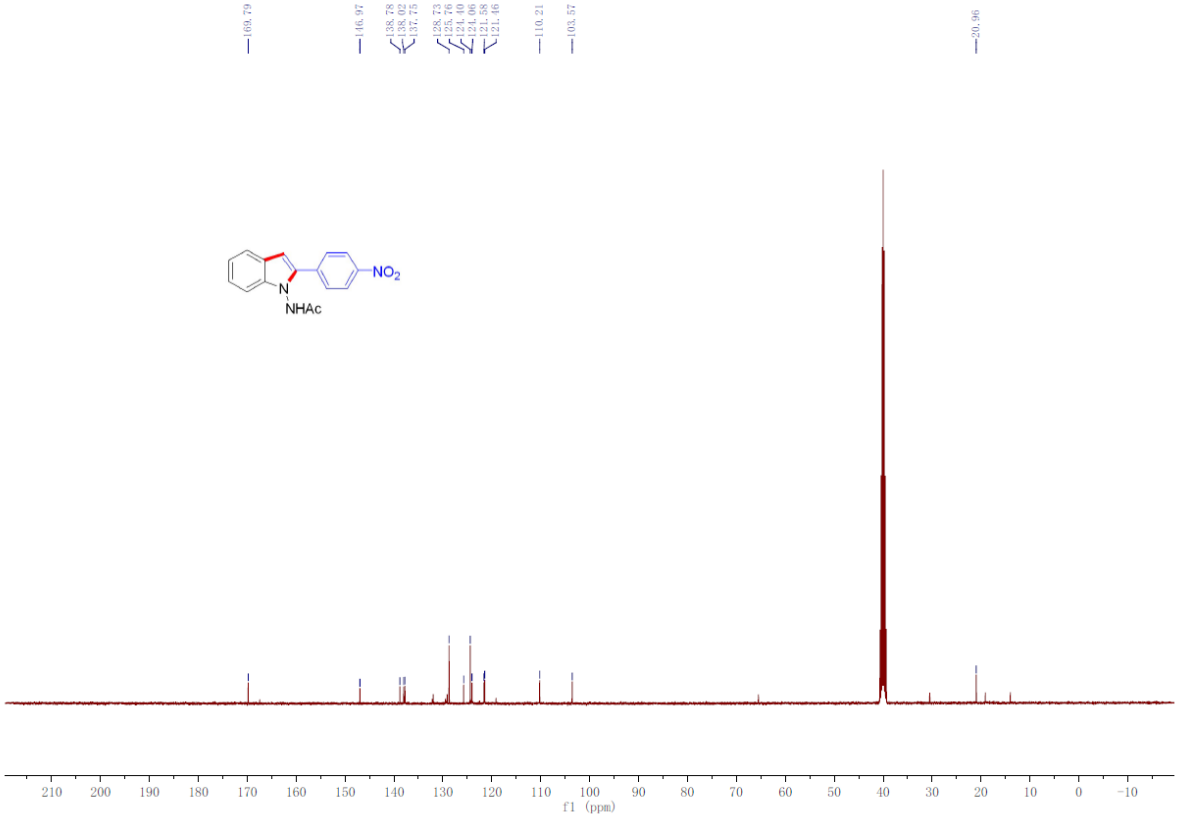
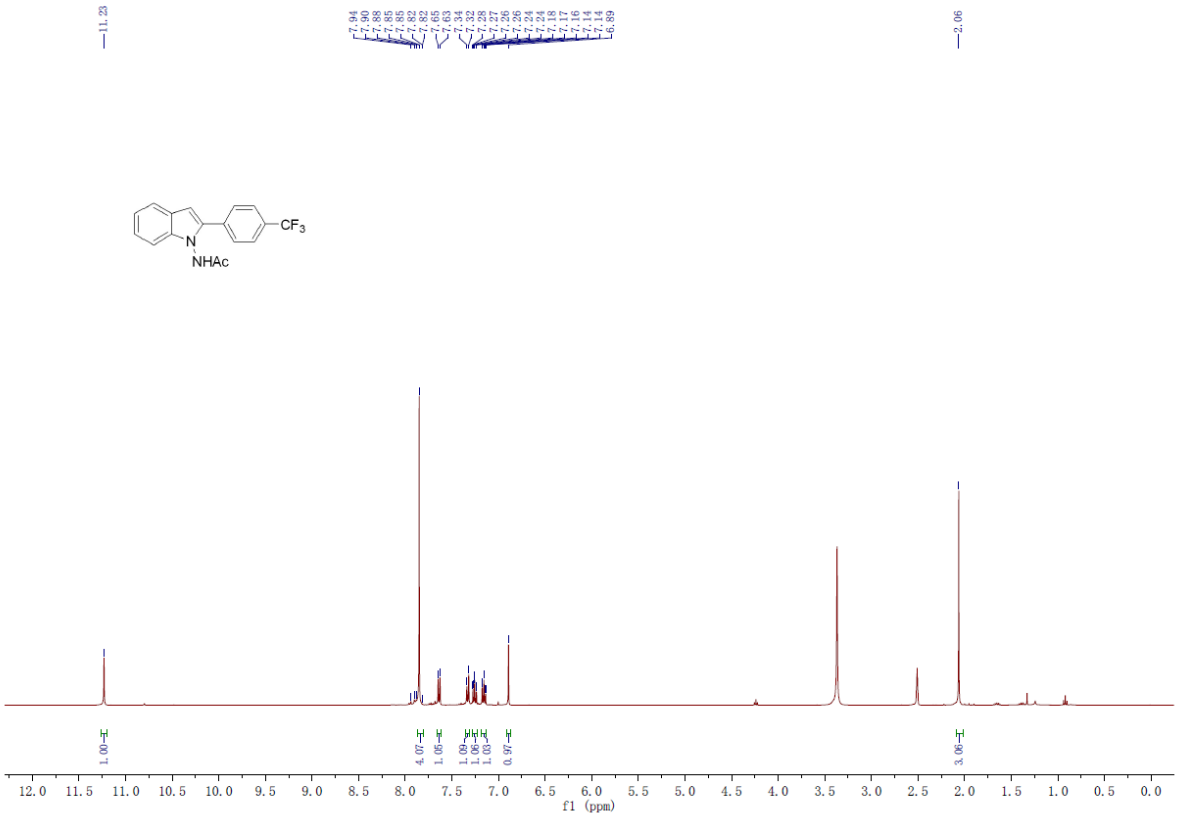
7.19
7.18
7.17
7.15
7.01
2.07
NO2
N
NHAc
f1 (ppm)


169.79
146.97
138.78
138.02
137.75
128.73
125.76
124.40
124.06
121.38
121.46
110.21
103.57
20.96
NO2
N
NHAc
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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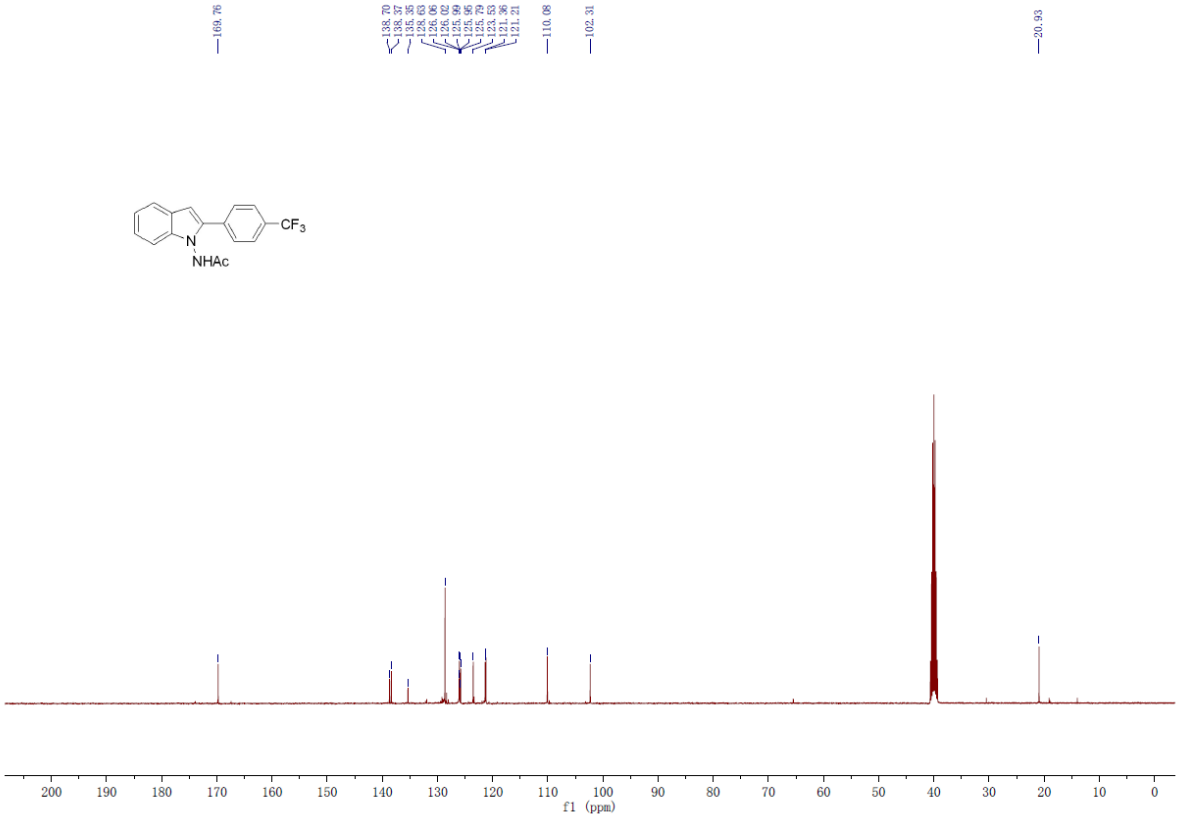
7.94
7.90
7.88
7.85
7.85
7.82
7.82
7.65
7.63
7.34
7.32
7.28
7.27
7.26
7.26
7.24
7.24
7.18
7.17
7.16
7.14
7.14
6.89
2.06
CF3
N
NHAc
1.00
4.07
1.05
1.09
1.08
1.03
0.97
3.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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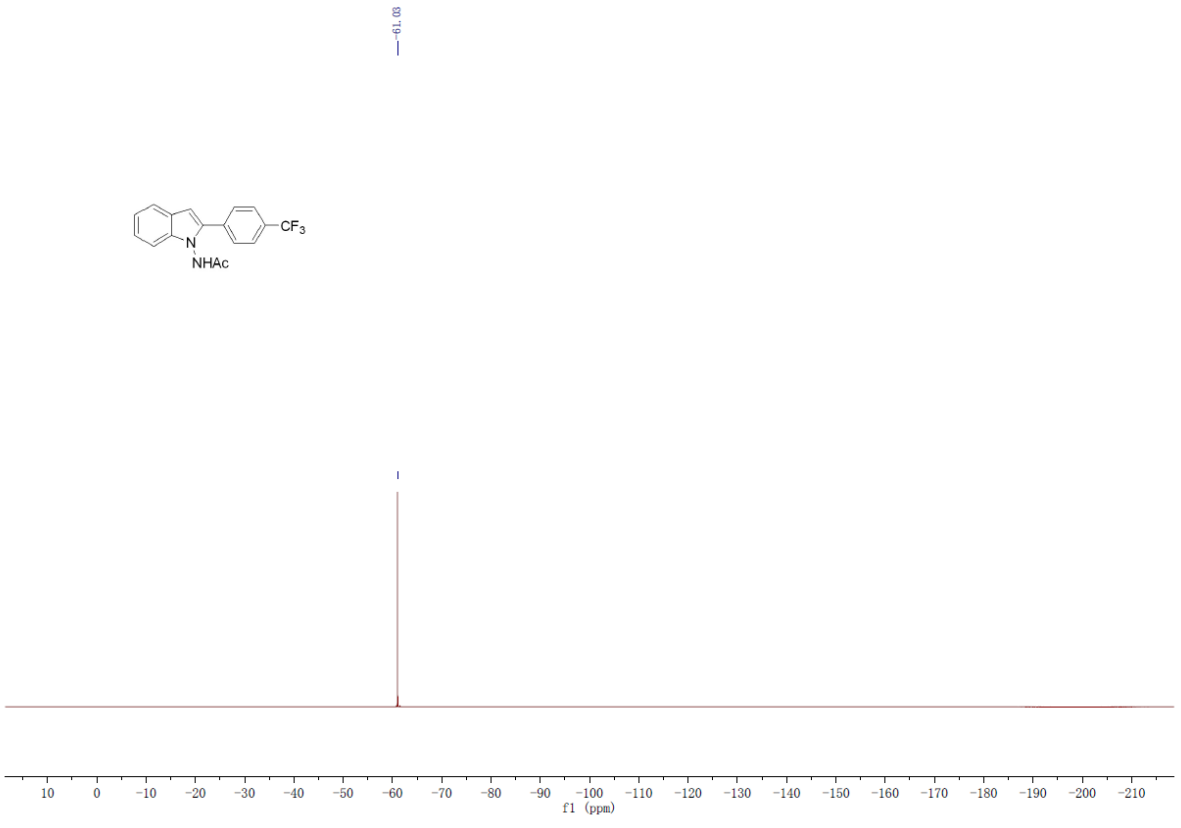
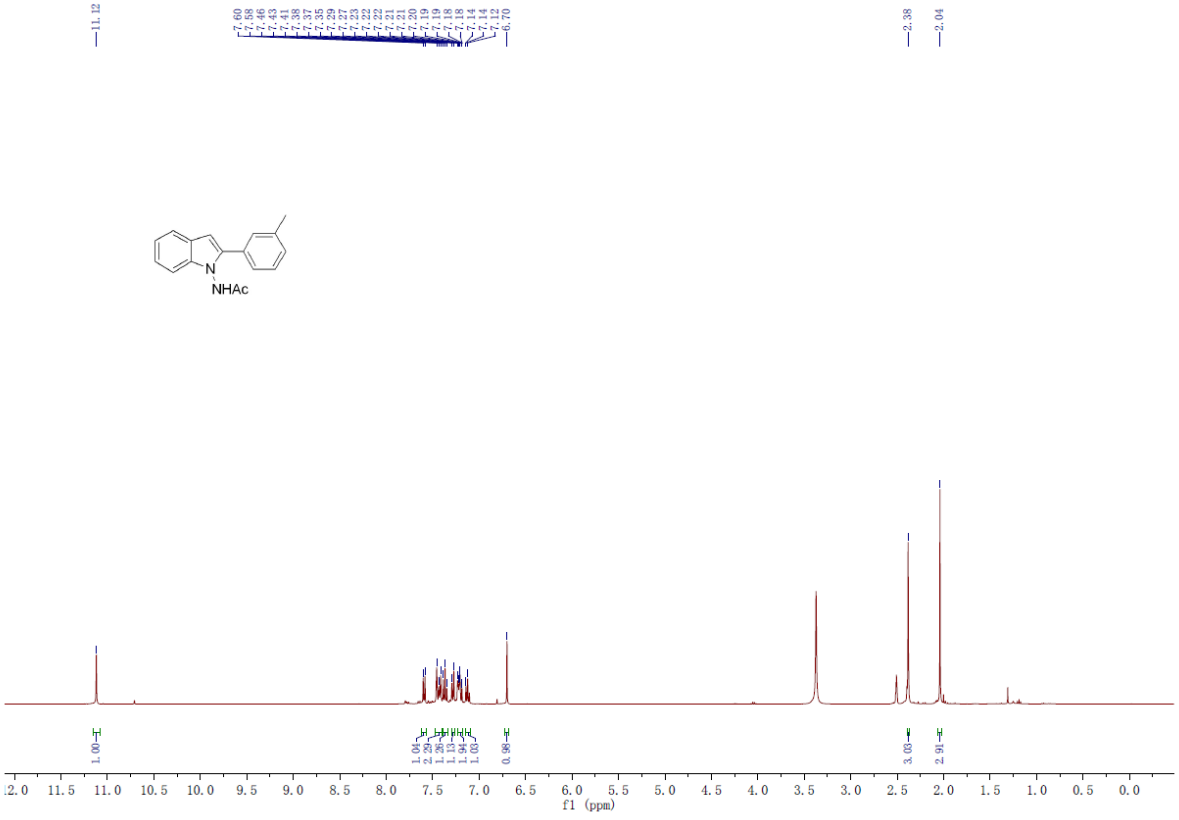
138.70
138.37
135.35
128.63
126.06
126.02
125.99
125.95
125.79
123.53
121.36
121.21
110.08
102.31
20.93
CF3
N
NHAc
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


61.03
CF3
N
NHAc
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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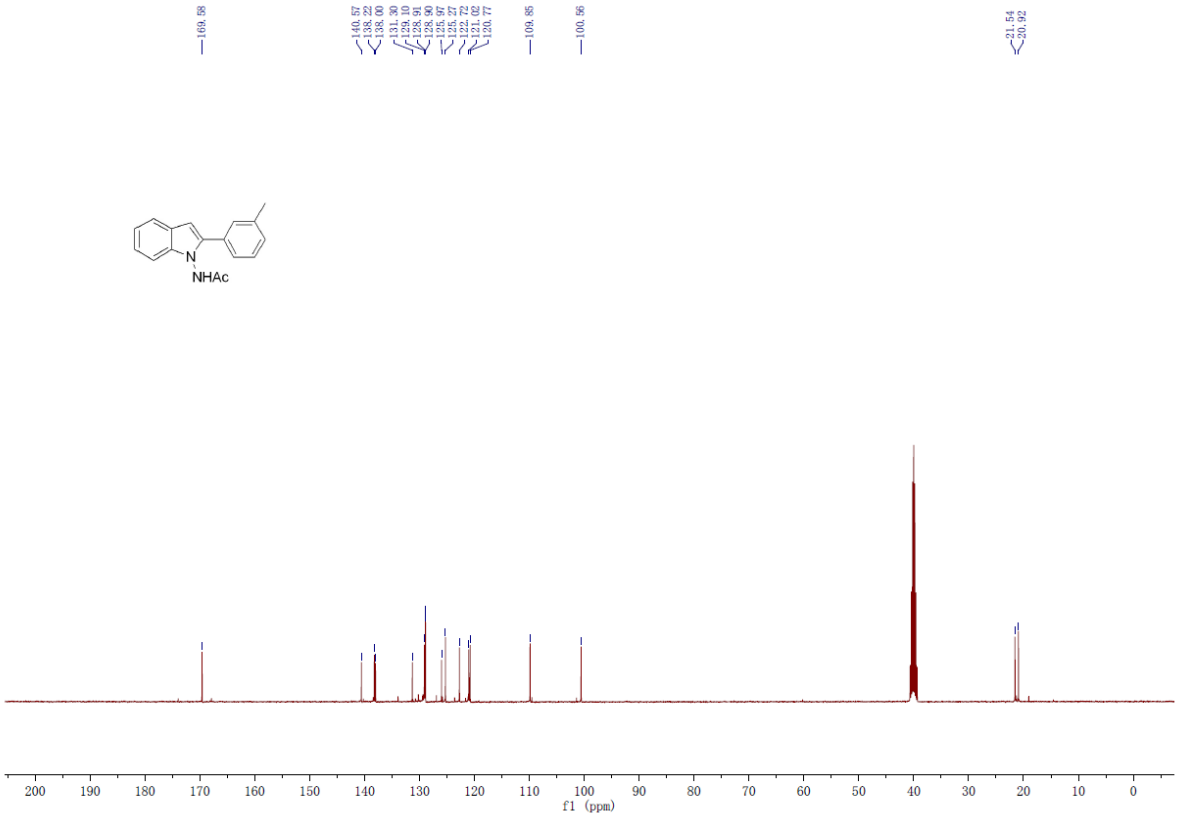
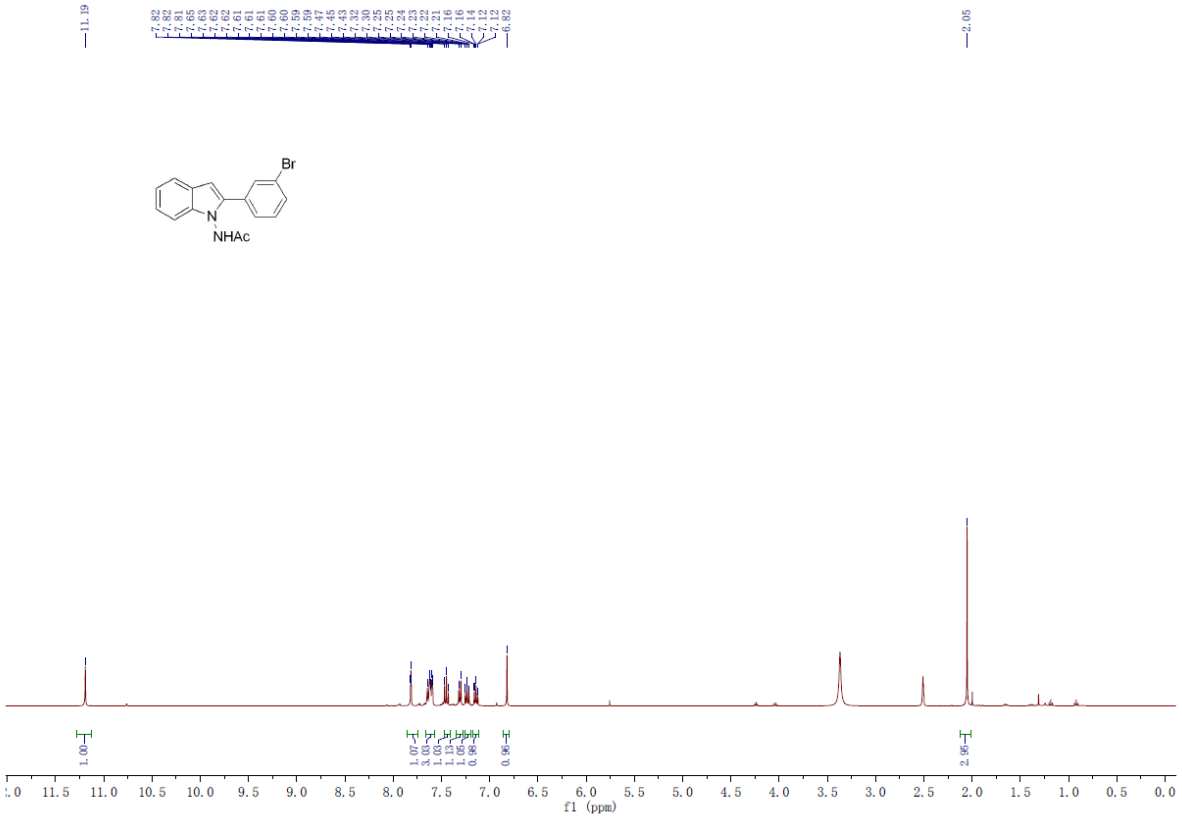
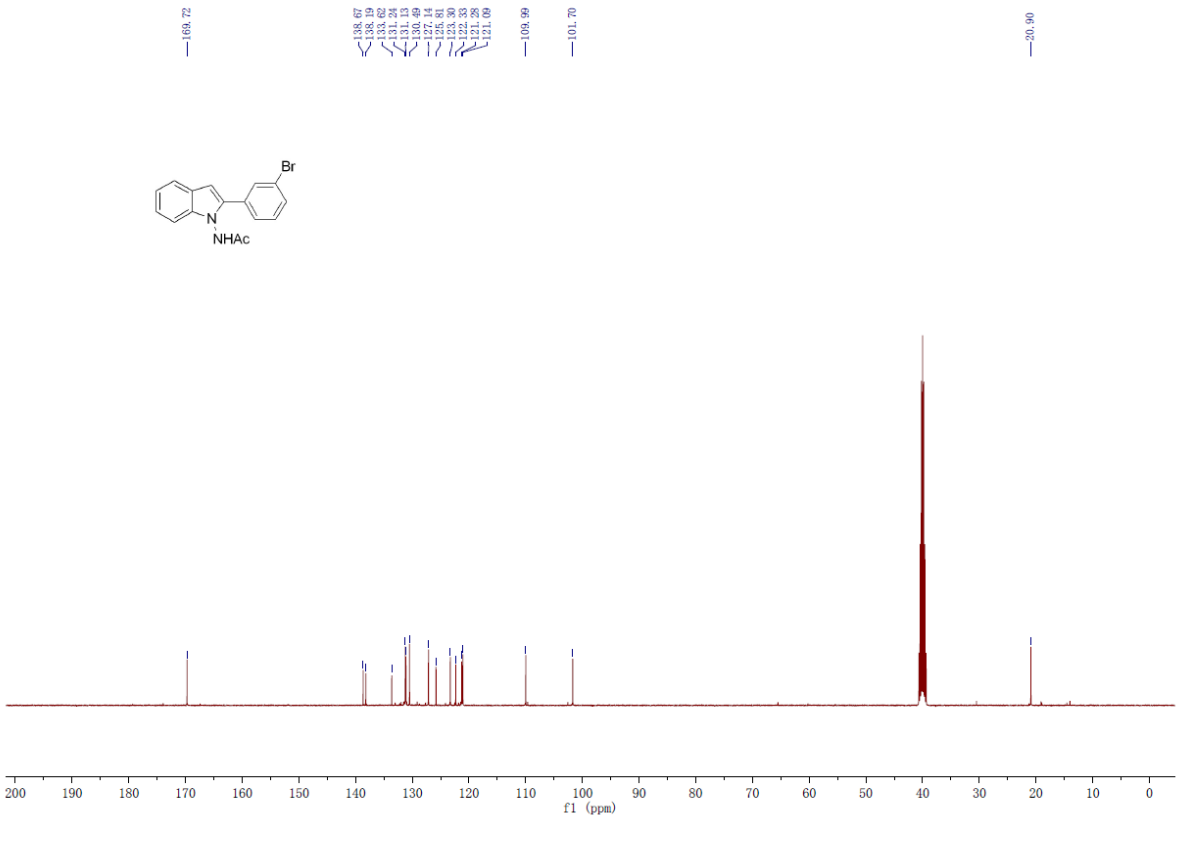
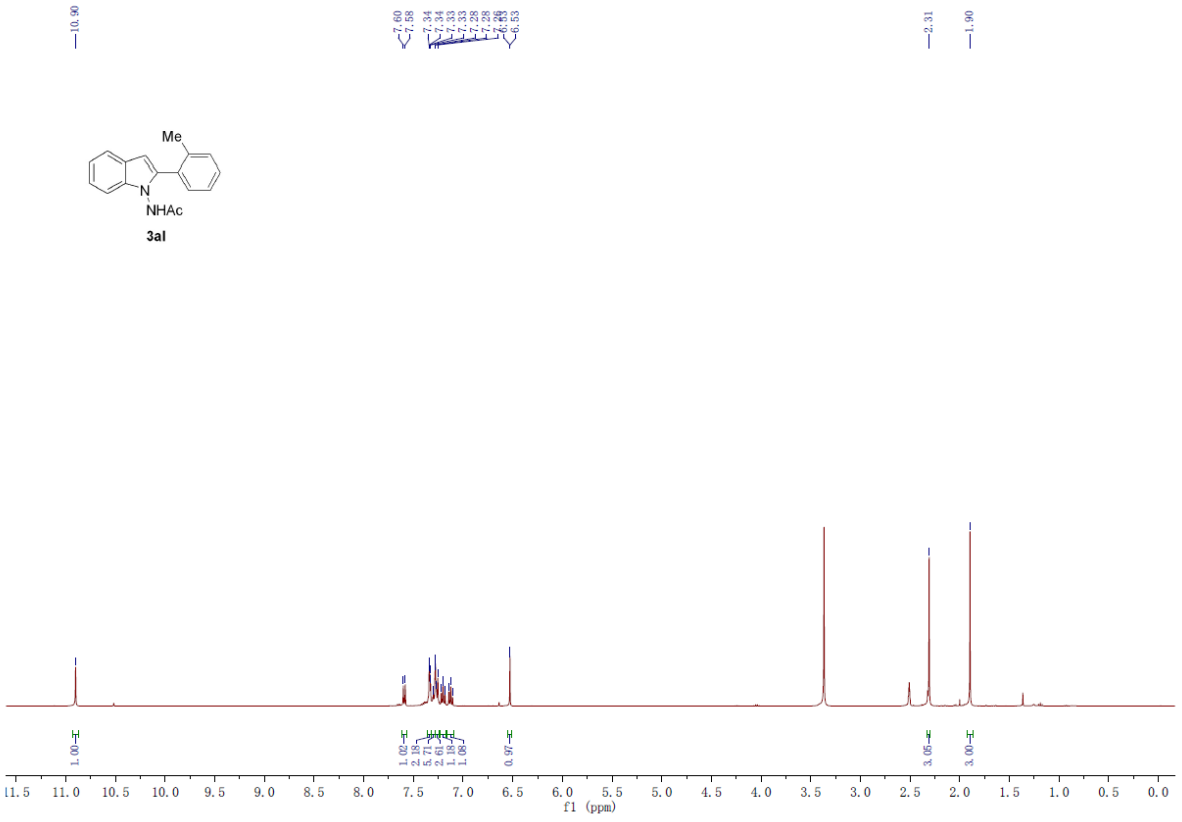
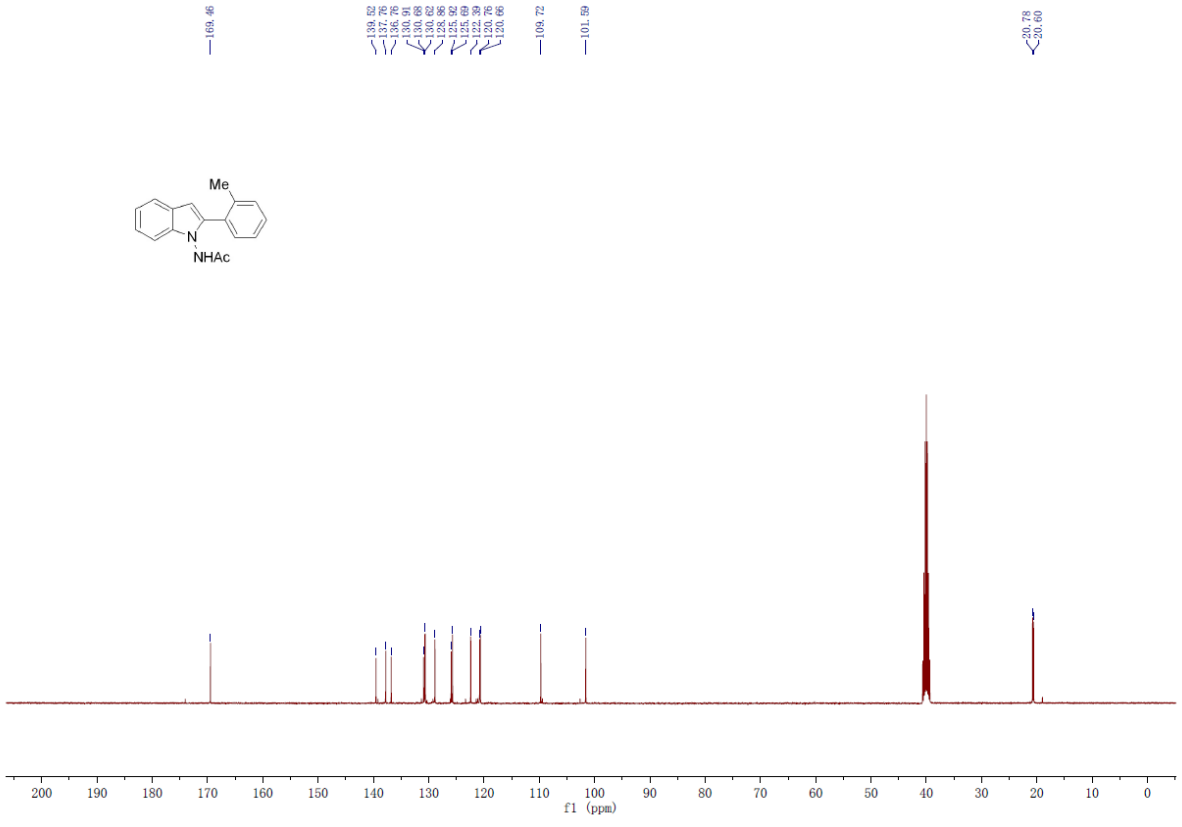
7.60
7.58
7.46
7.43
7.41
7.38
7.37
7.35
7.29
7.27
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.18
7.18
7.14
7.14
7.12
6.70
2.38
2.04
NHAc
1.00
1.04
2.29
1.13
1.13
1.94
1.03
0.98
3.03
2.91
f1 (ppm)


169.58
140.57
138.22
138.00
131.30
129.10
128.91
128.90
125.97
125.27
122.72
121.02
120.77
109.85
100.96
21.54
20.92
NHAc
f1 (ppm)


11.19
7.82
7.82
7.81
7.65
7.63
7.62
7.62
7.61
7.61
7.61
7.60
7.60
7.59
7.59
7.47
7.45
7.43
7.32
7.30
7.25
7.25
7.24
7.23
7.22
7.21
7.16
7.16
7.14
7.12
7.12
6.82
2.05
Br
N
NHAc
1.00
1.07
3.05
1.03
1.13
1.05
0.98
0.96
2.95
f1 (ppm)


169.72
138.67
138.19
133.62
131.24
131.13
130.49
127.14
125.81
123.30
122.33
121.28
121.09
109.99
101.70
20.90
Br
N
NHAc
f1 (ppm)


10.90
7.60
7.58
7.34
7.34
7.33
7.33
7.28
7.28
6.53
6.53
2.31
1.90
Me
N
NHAc
3al
1.00
1.02
2.18
5.67
1.19
1.08
0.97
3.05
3.00
f1 (ppm)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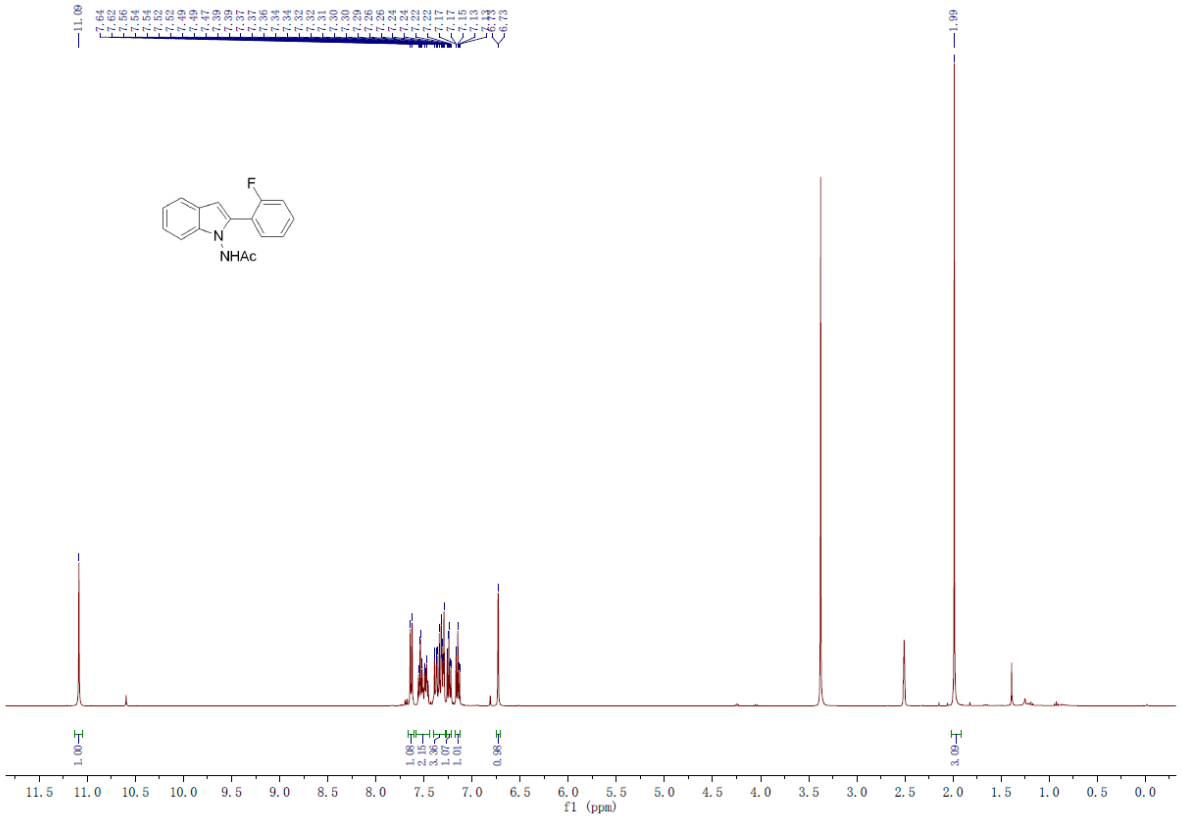
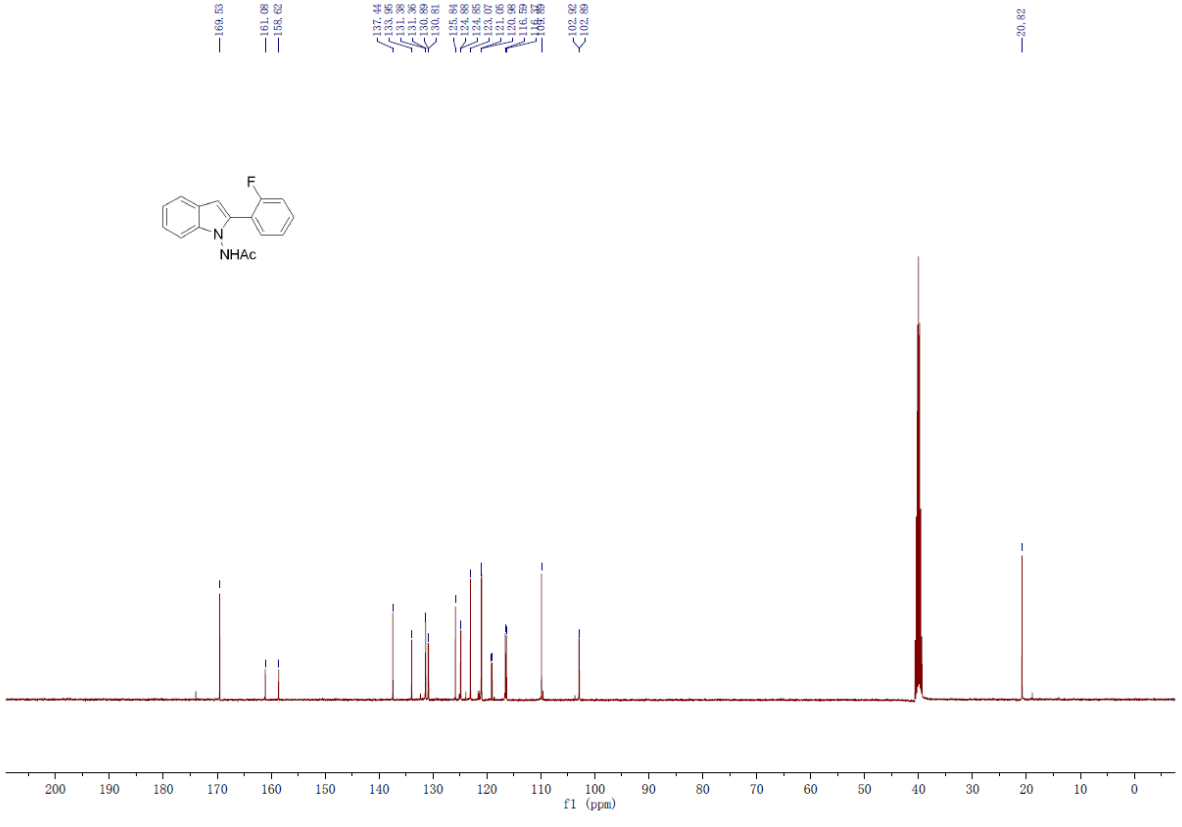
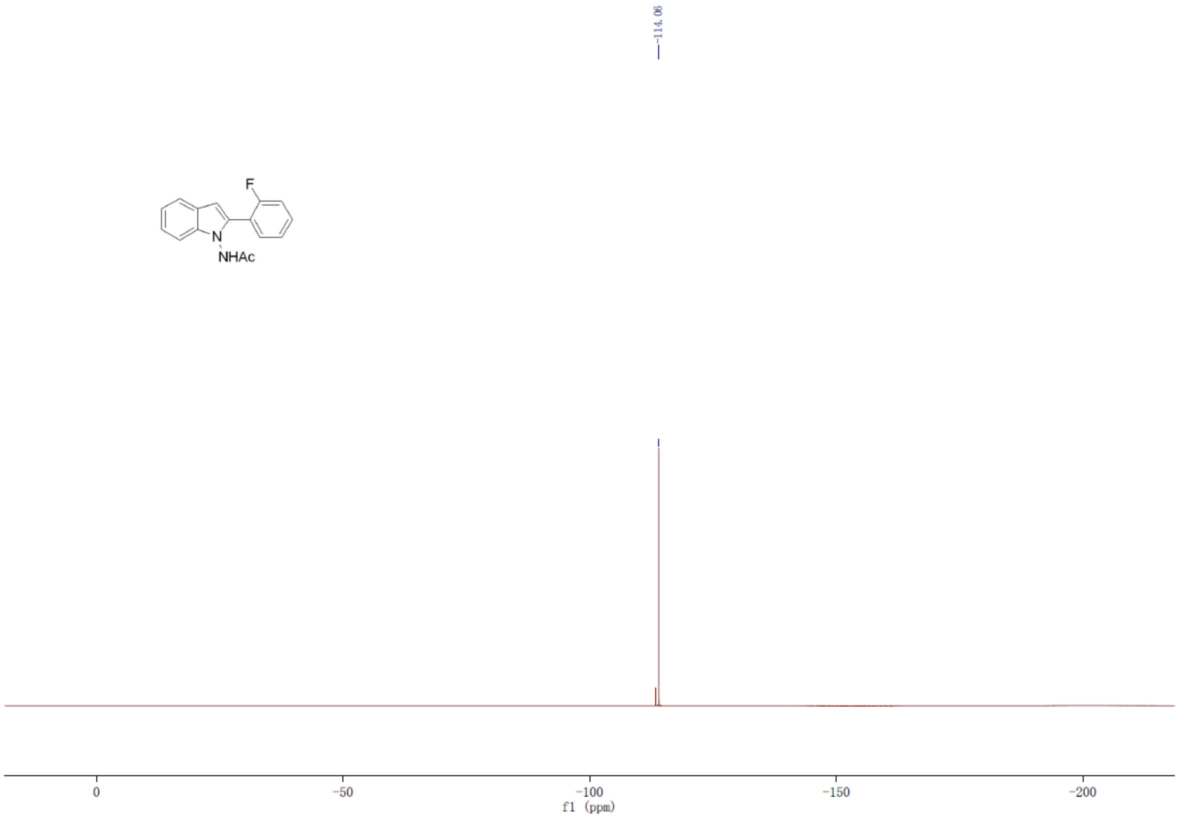
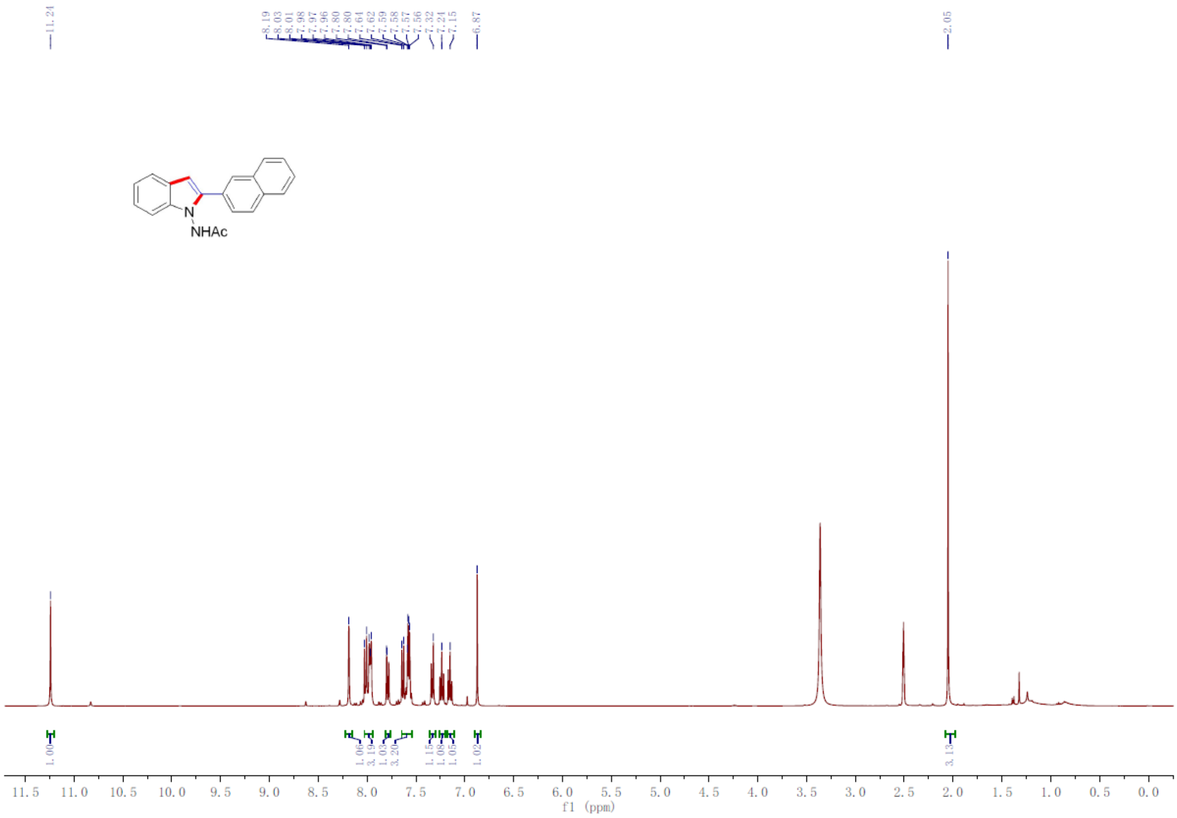
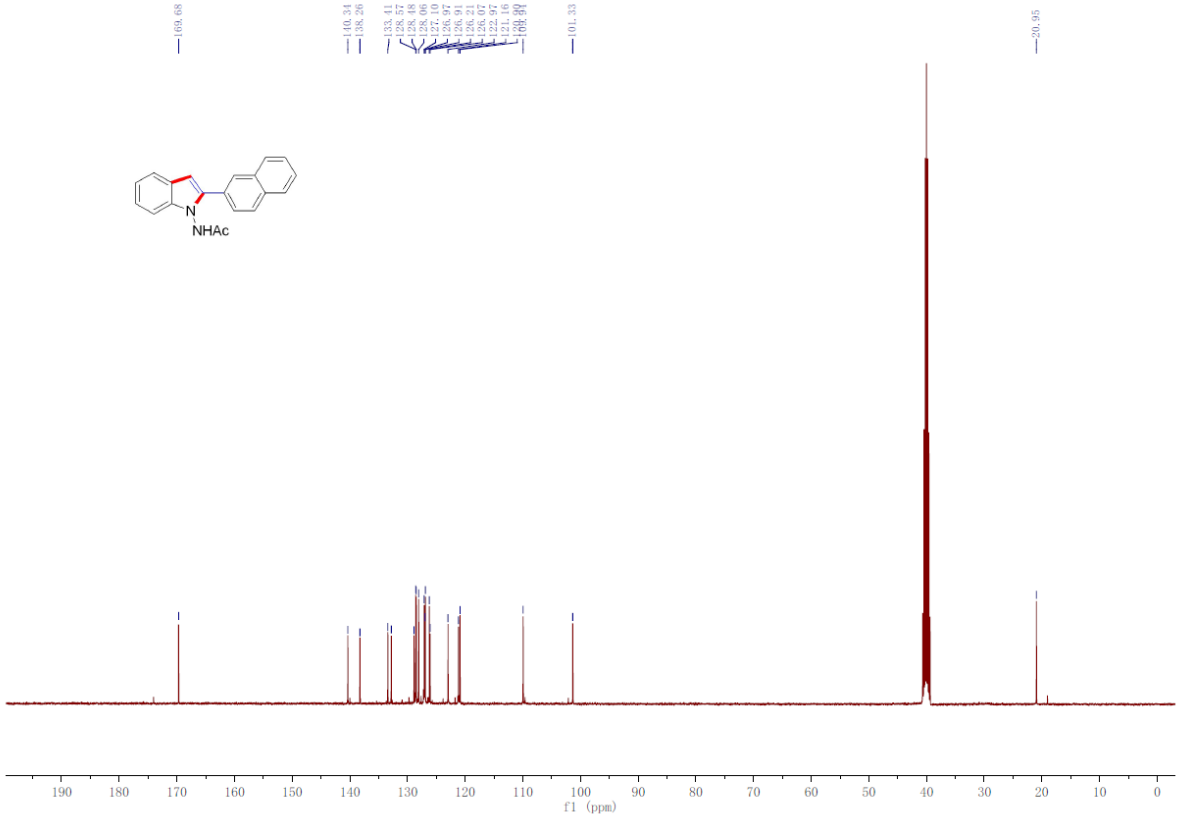
139.52
137.76
136.76
130.91
130.69
130.62
128.96
128.52
125.69
122.39
120.76
120.66
109.72
101.59
20.78
20.60
Me
N
NHAc
f1 (ppm)


11.09
7.64
7.62
7.56
7.54
7.54
7.52
7.52
7.49
7.49
7.47
7.39
7.39
7.37
7.37
7.36
7.34
7.34
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.26
7.24
7.24
7.22
7.22
7.17
7.15
7.13
6.73
1.99
F
N
NHAc
1.00
1.08
2.15
3.36
1.07
1.01
0.98
3.09
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.53
161.08
158.62
137.44
133.96
131.38
131.36
130.89
130.81
125.84
124.88
124.85
123.07
121.05
120.98
120.89
116.37
116.29
102.92
102.89
20.82
F
N
NHAc
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-114.06
F
N
NHAc
0
-50
-100
-150
-200
f1 (ppm)


11.24
8.19
8.03
8.01
7.98
7.97
7.96
7.80
7.80
7.64
7.62
7.59
7.58
7.57
7.56
7.32
7.24
7.15
6.87
2.05
N
NHAc
1.00
1.06
3.19
1.03
3.20
1.15
1.08
1.05
1.02
3.13
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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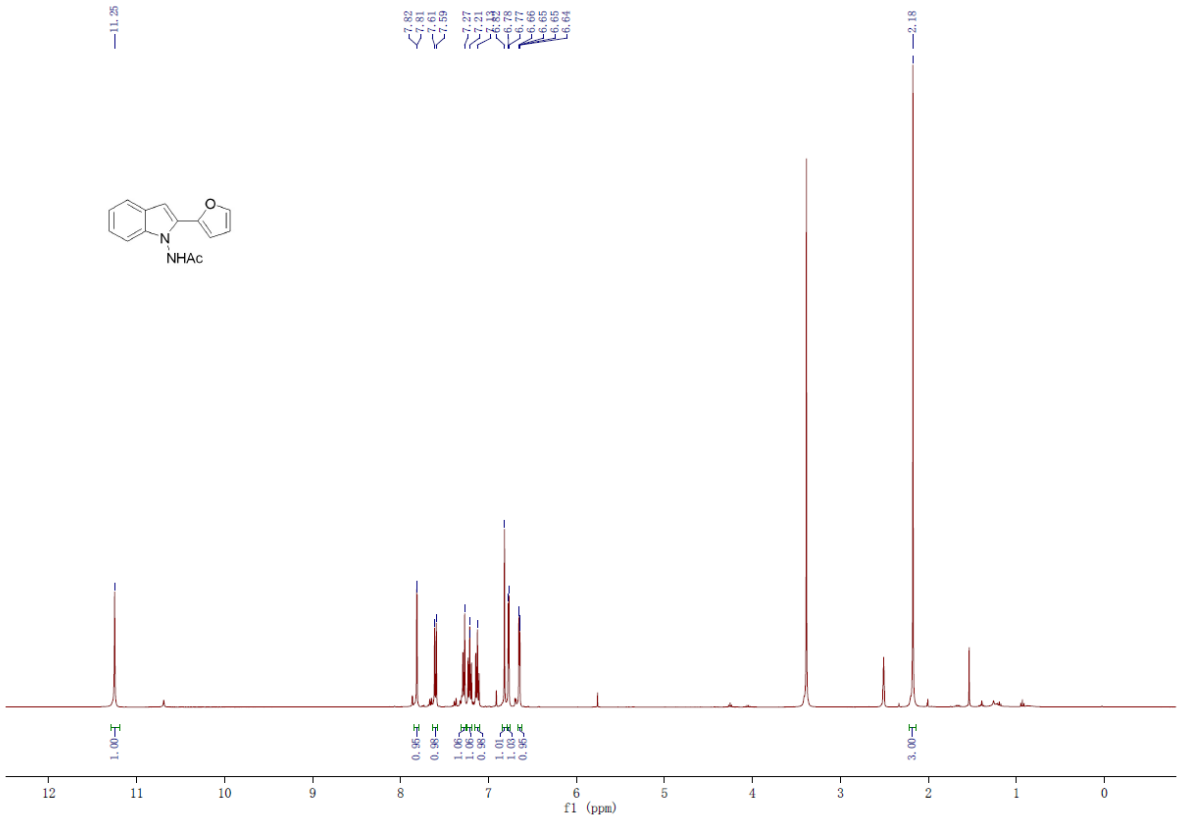
140.34
138.26
133.41
128.57
128.48
128.06
127.10
126.97
126.91
126.21
125.67
122.97
121.16
101.33
20.95
N
NHAc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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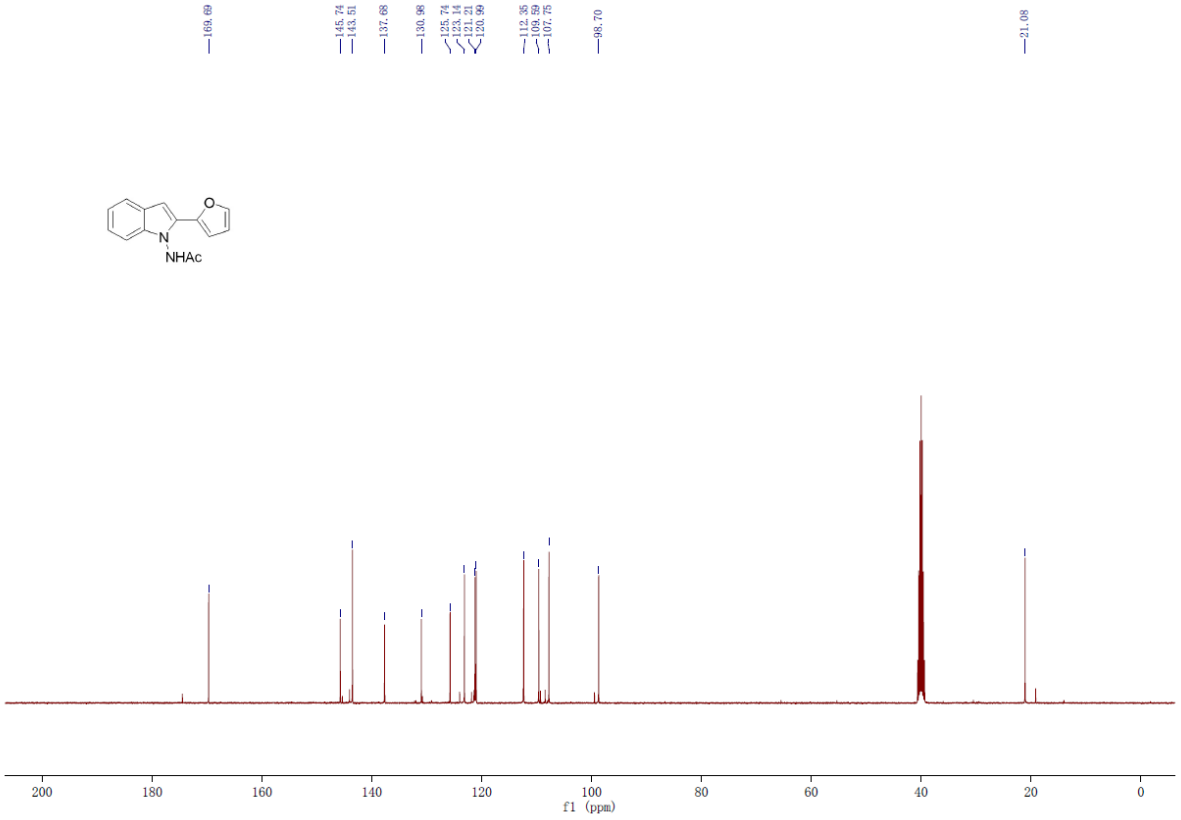
7.82
7.81
7.61
7.59
7.27
7.21
7.43
6.78
6.77
6.66
6.65
6.64
2.18
O
N
NHAc
1.00
0.96
0.98
1.06
1.06
0.98
1.01
1.03
0.98
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


169.69
145.74
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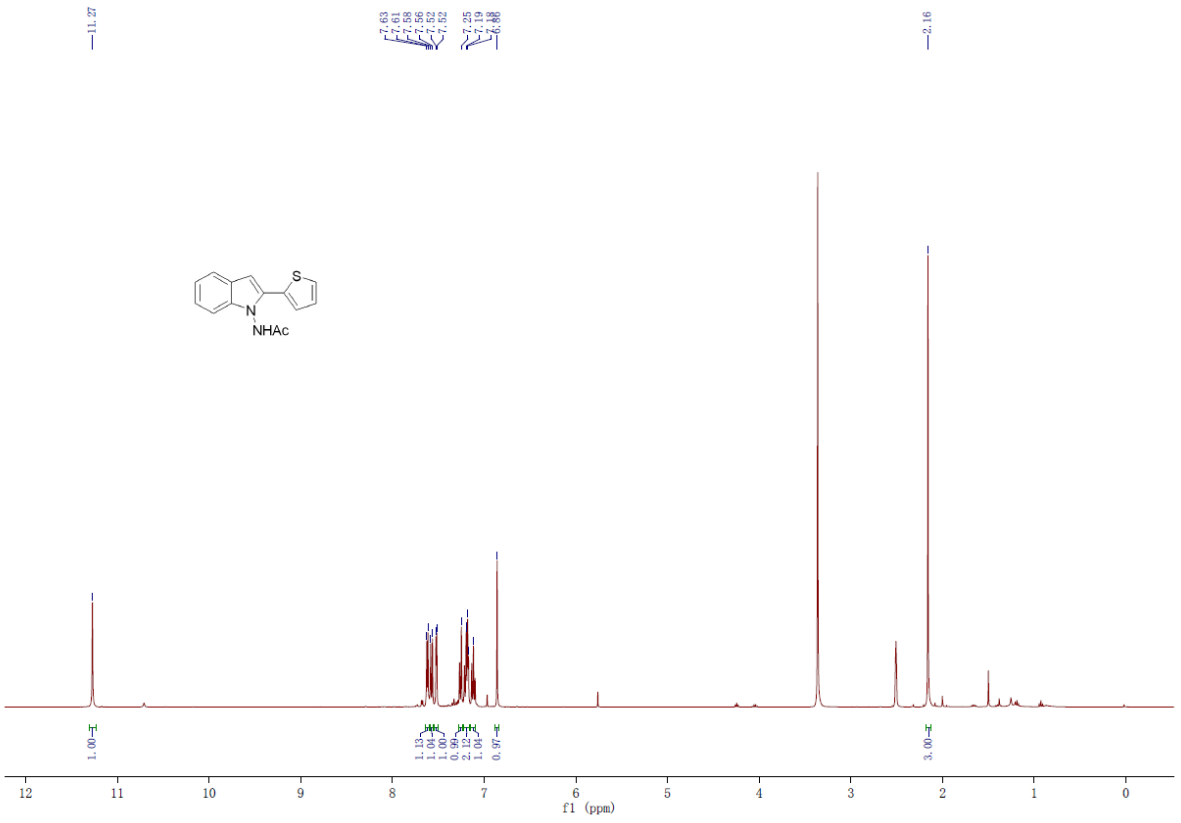
130.98
125.74
123.14
121.21
120.99
112.35
109.89
107.75
98.70
21.08
O
N
NHAc
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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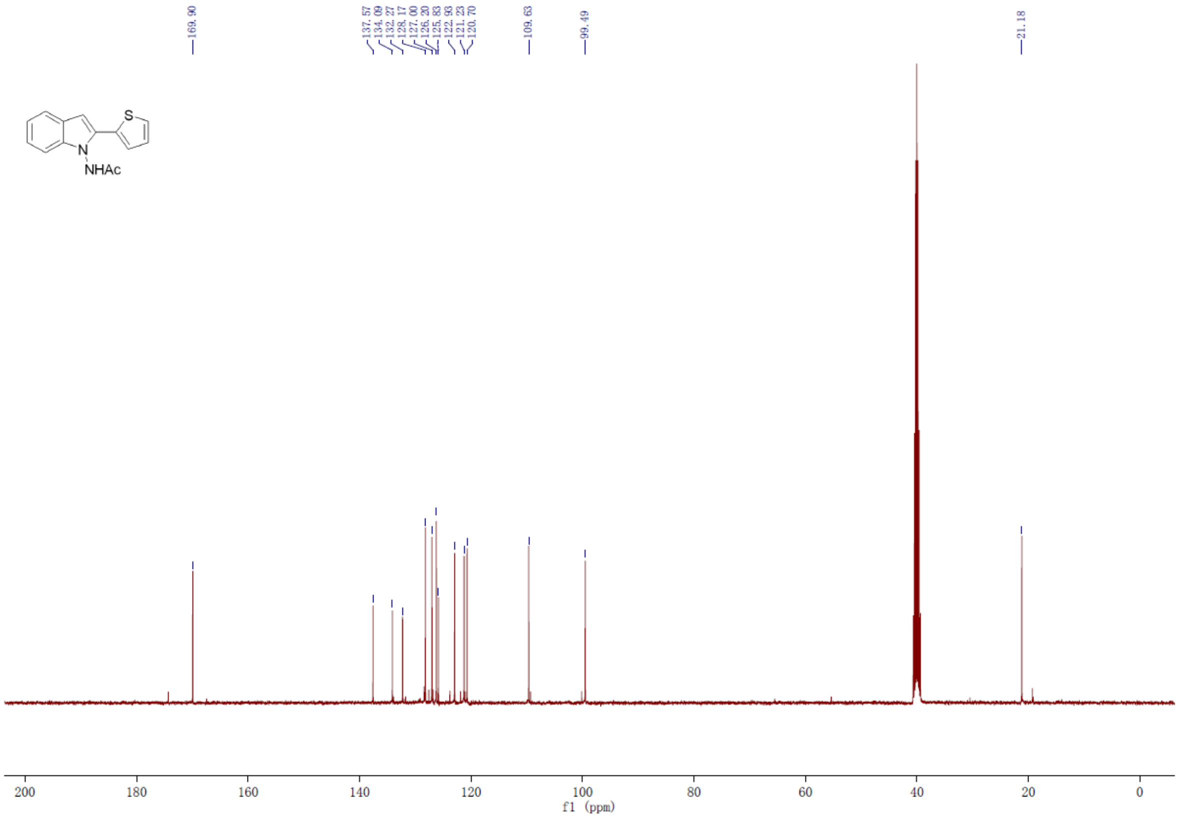
7.63
7.61
7.58
7.56
7.52
7.52
7.25
7.19
6.86
2.16
S
N
NHAc
1.00
1.13
1.04
1.00
0.97
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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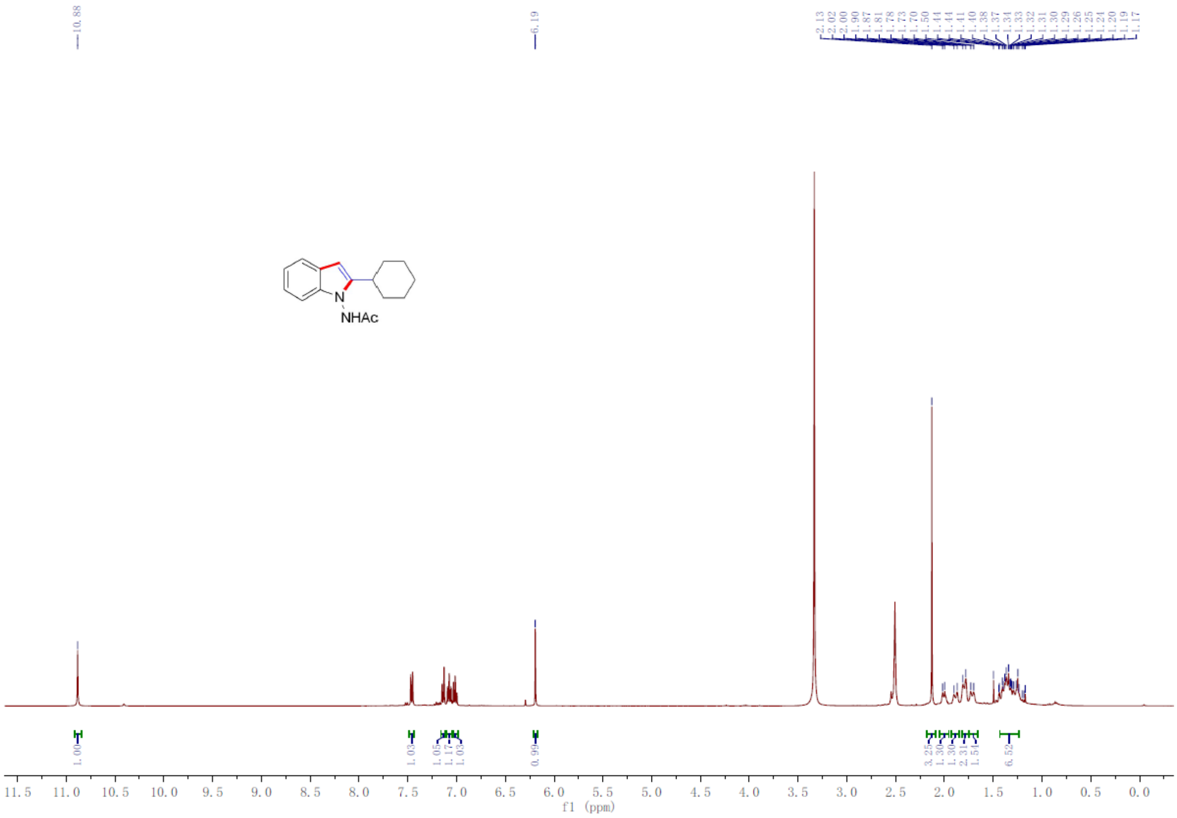
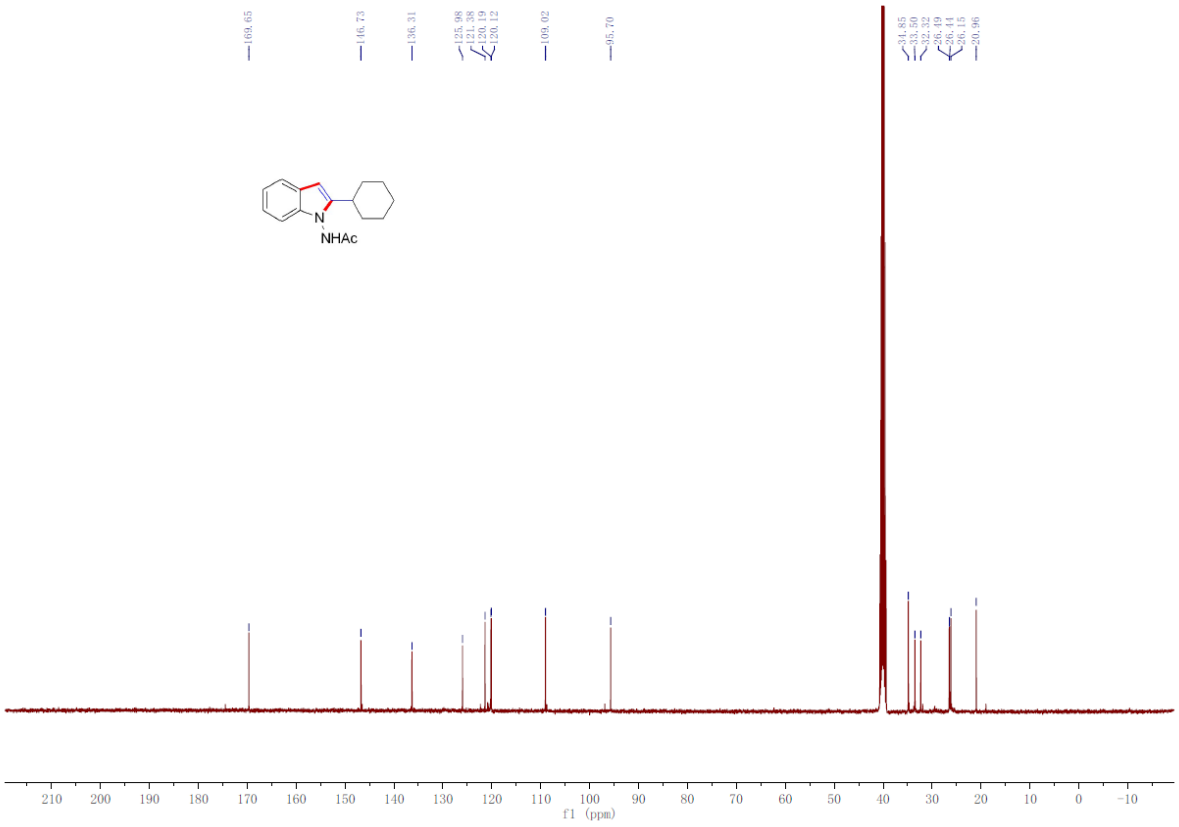
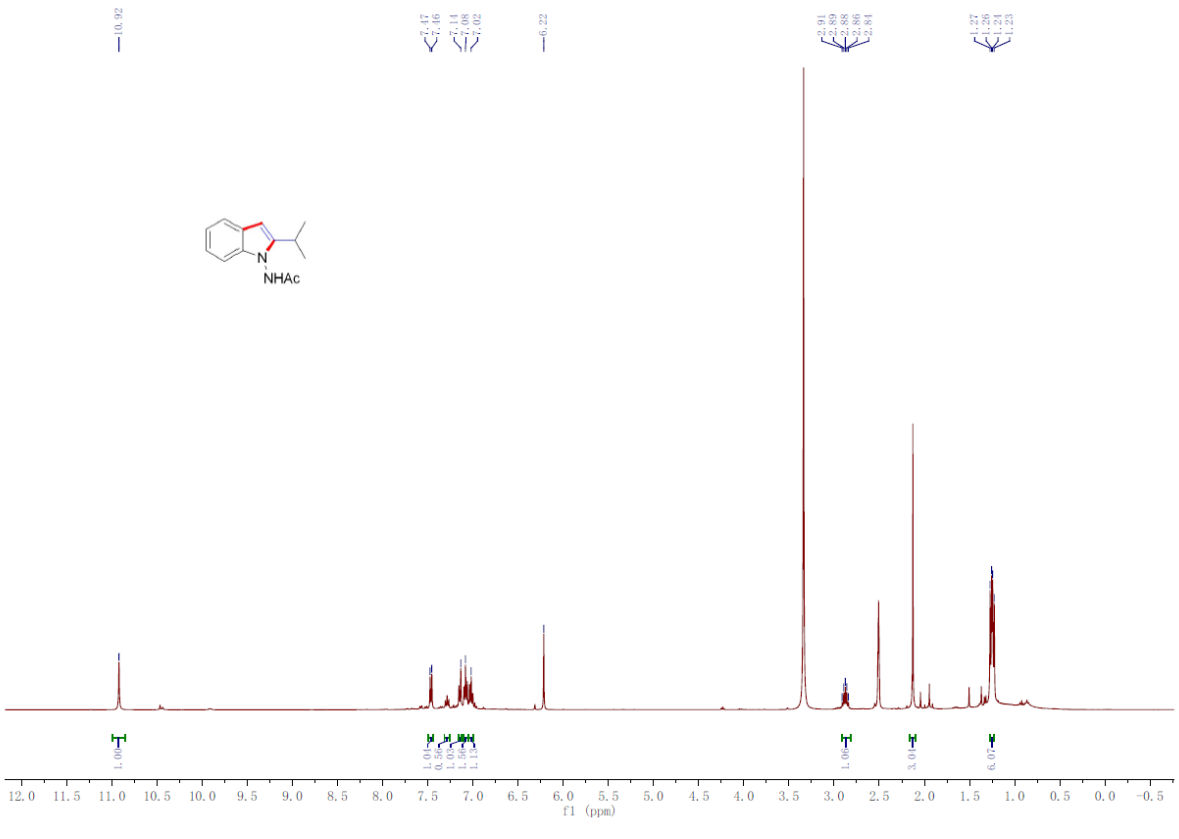
132.27
128.17
127.00
126.20
125.83
122.93
121.23
120.70
109.63
99.49
21.18
S
N
NHAc
f1 (ppm)


10.88
6.19
N
NHAc
f1 (ppm)


169.65
146.73
136.31
125.98
121.38
120.19
120.12
109.02
95.70
34.85
33.50
32.32
26.49
26.14
26.15
20.96
NHAc
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


10.92
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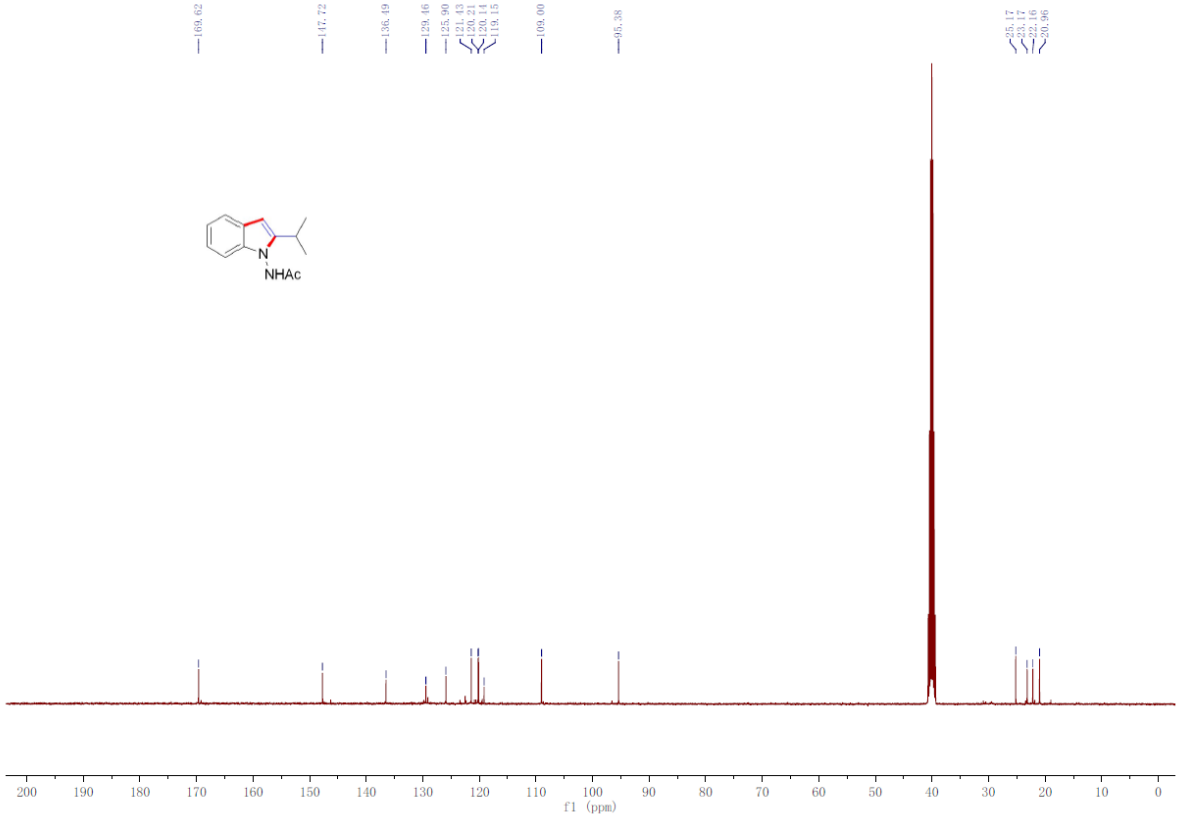
7.08
7.02
6.22
2.91
2.89
2.88
2.86
2.84
1.27
1.26
1.24
1.23
NHAc
1.00
1.04
0.98
1.05
1.06
1.13
1.06
3.01
6.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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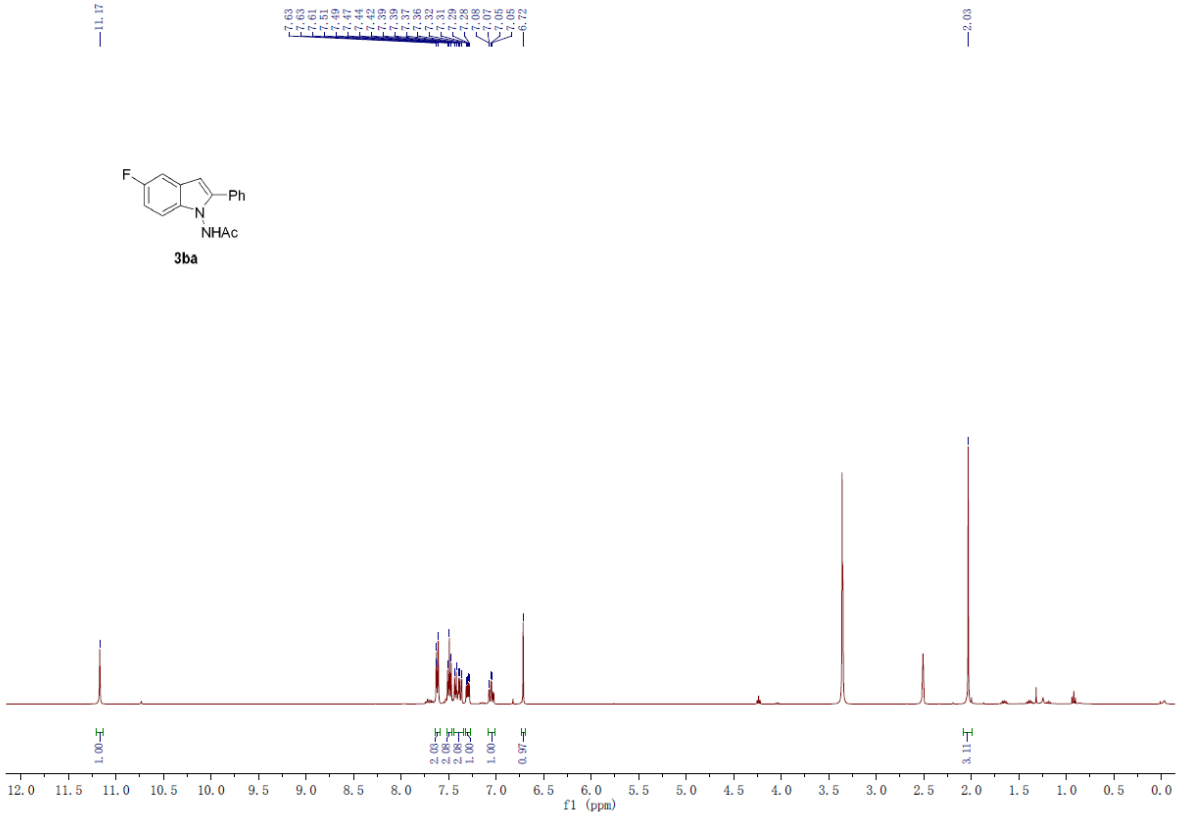
147.72
136.49
129.46
125.90
121.43
120.21
120.14
119.15
109.00
95.38
25.17
23.17
22.16
20.96
NHAc
f1 (ppm)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7.63
7.61
7.51
7.49
7.47
7.44
7.42
7.39
7.39
7.37
7.36
7.32
7.31
7.29
7.28
7.08
7.07
7.06
7.05
6.72
2.03
F
Ph
N
NHAc
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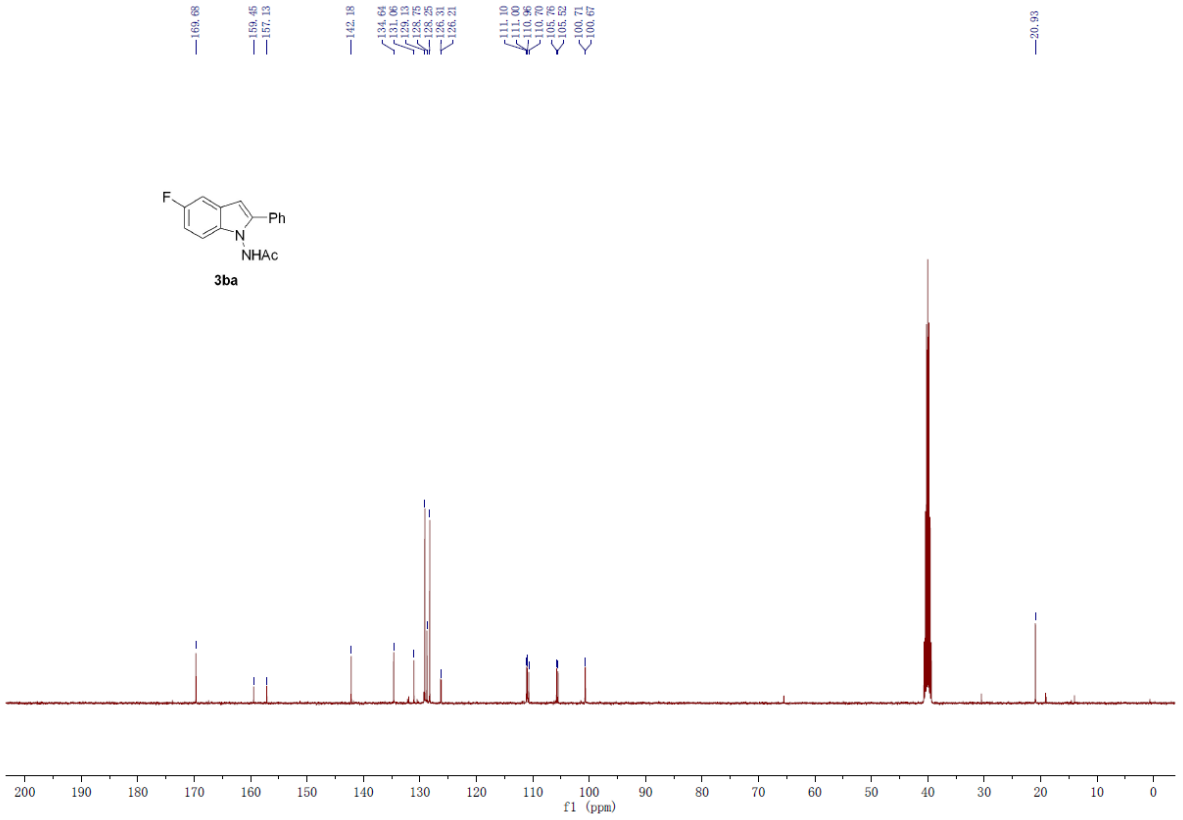
2.03
2.08
2.08
1.00
1.00
0.97
3.11
f1 (ppm)

3ba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159.45
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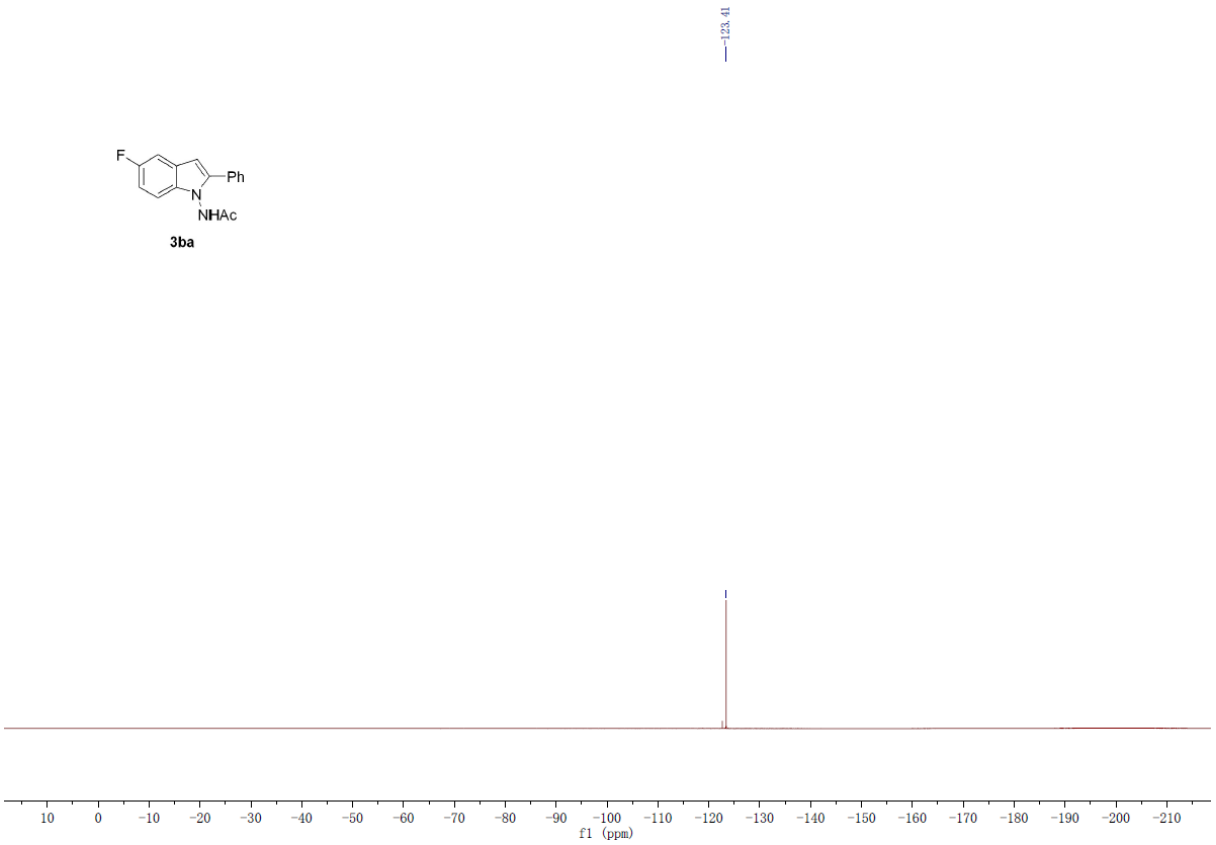
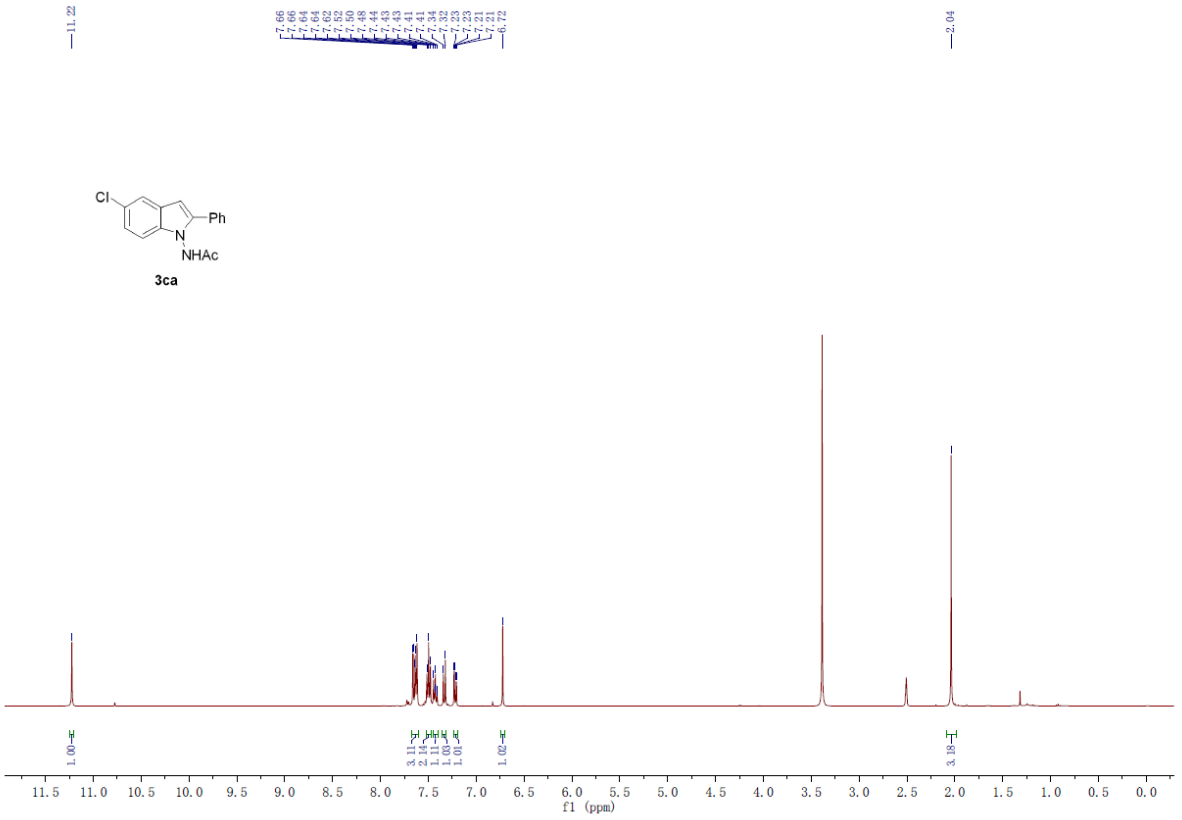
142.18
134.64
131.06
129.13
128.75
128.25
126.31
126.21
111.10
111.00
110.96
110.79
105.76
105.52
100.71
100.67
20.93
F
Ph
N
NHAc
3ba
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


123.41
F
Ph
N
NHAc
3ba
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.64
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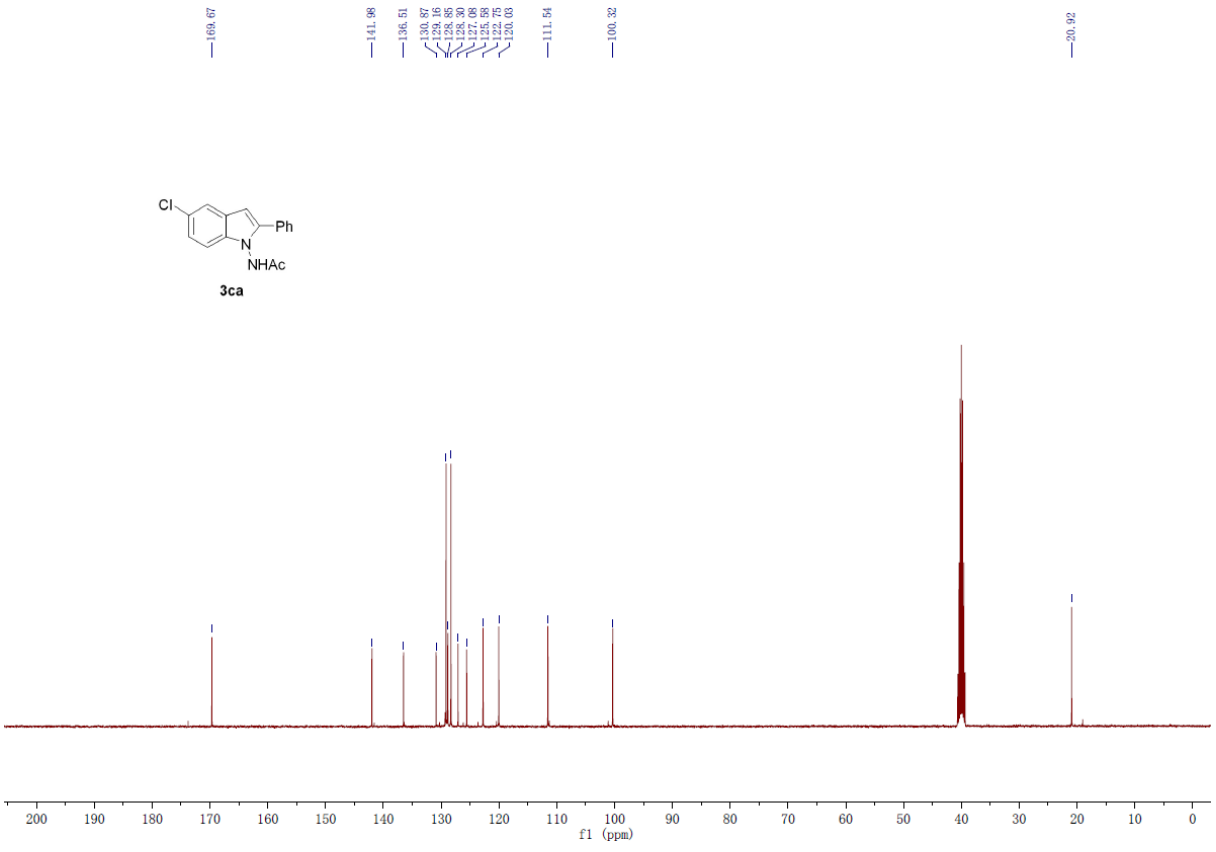
7.62
7.62
7.52
7.50
7.48
7.44
7.43
7.43
7.41
7.41
7.34
7.32
7.23
7.23
7.21
7.21
6.72
2.04
Cl
Ph
N
NHAc
3ca
1.00
3.11
2.14
1.11
1.03
1.01
1.02
3.18
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.67
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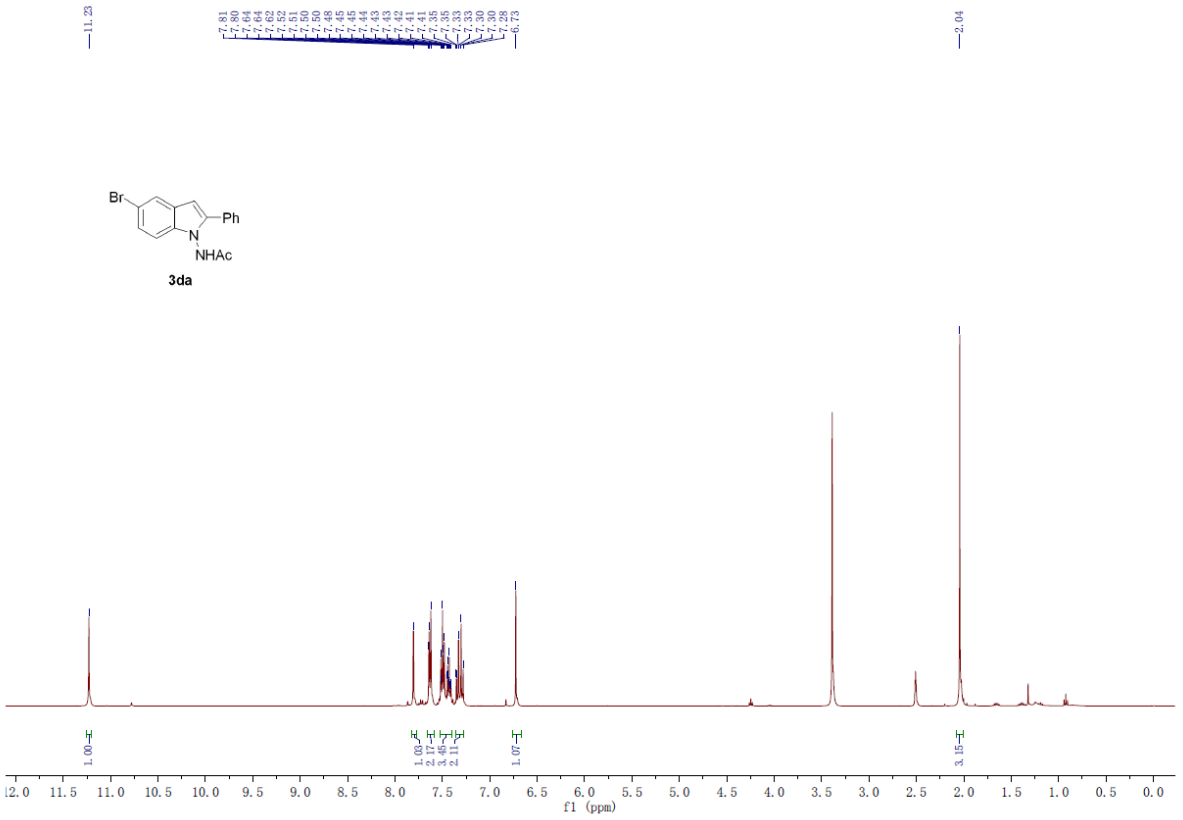
136.51
130.87
129.16
128.85
128.30
127.98
125.68
122.75
120.03
111.54
100.32
20.92
Cl
Ph
N
NHAc
3ca
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


11.23
7.81
7.80
7.64
7.64
7.62
7.52
7.51
7.50
7.50
7.48
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.35
7.33
7.33
7.30
7.30
7.28
6.73
2.04
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Ph
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1.00
1.03
2.17
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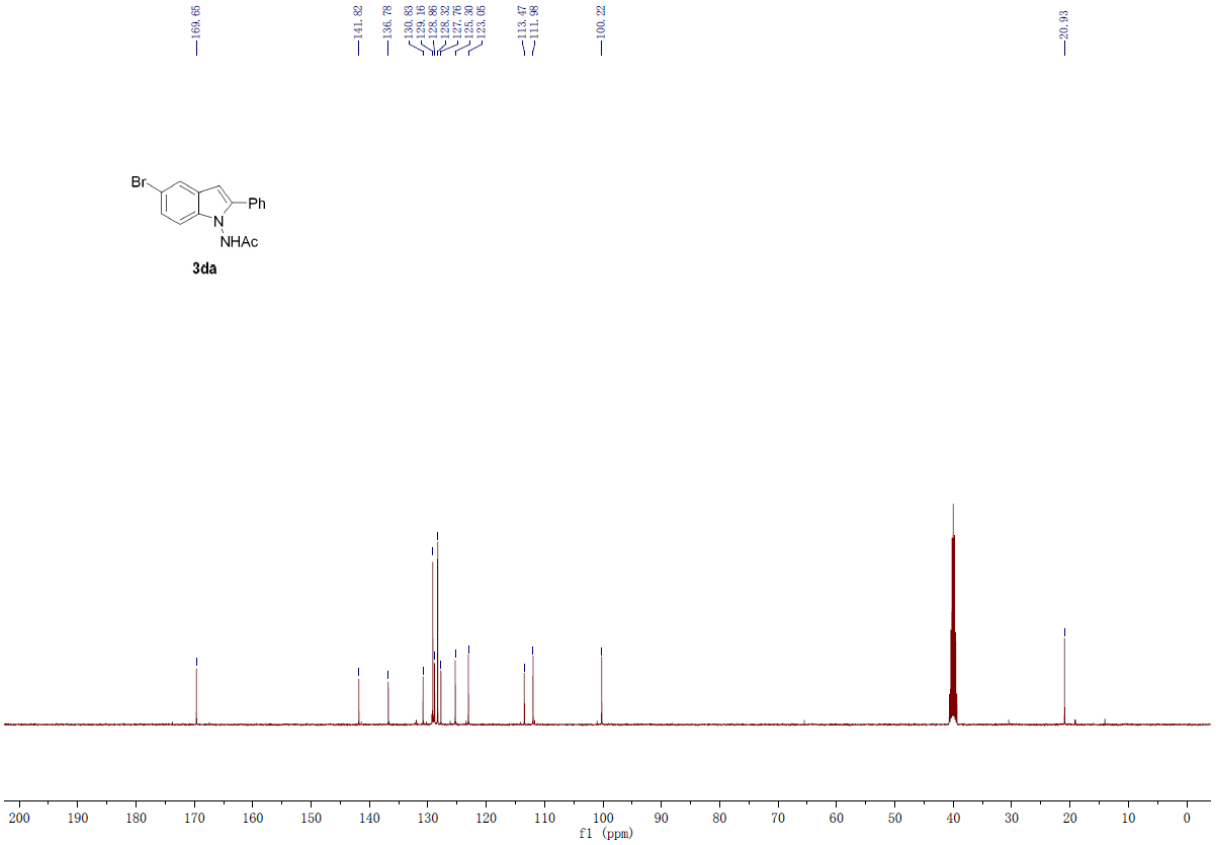
2.11
1.07
3.15
f1 (ppm)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129.16
128.86
128.32
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123.05
113.47
111.98
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20.93
Br
Ph
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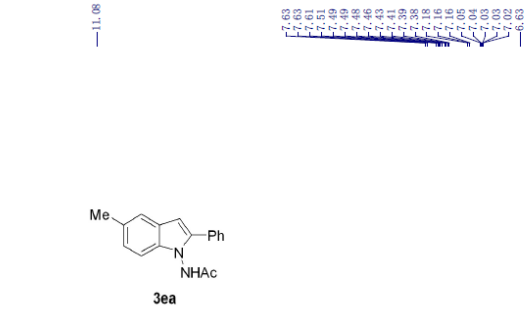
NHAc
3da
f1 (ppm)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7.63
7.63
7.61
7.51
7.49
7.49
7.48
7.46
7.43
7.41
7.39
7.38
7.18
7.16
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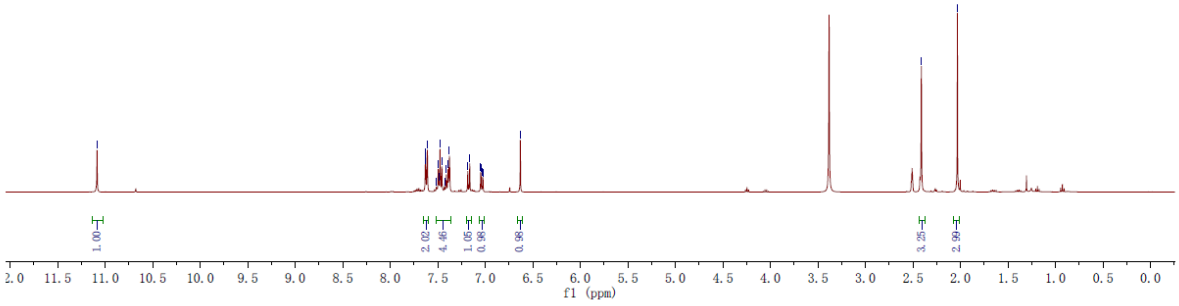
7.04
7.03
7.03
7.02
6.63
2.41
2.03
Me
Ph
N
NHAc

3ea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2.02
4.46
1.05
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0.98
3.25
2.99
f1 (ppm)


169.69
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136.63
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129.04
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124.30
120.43
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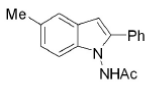
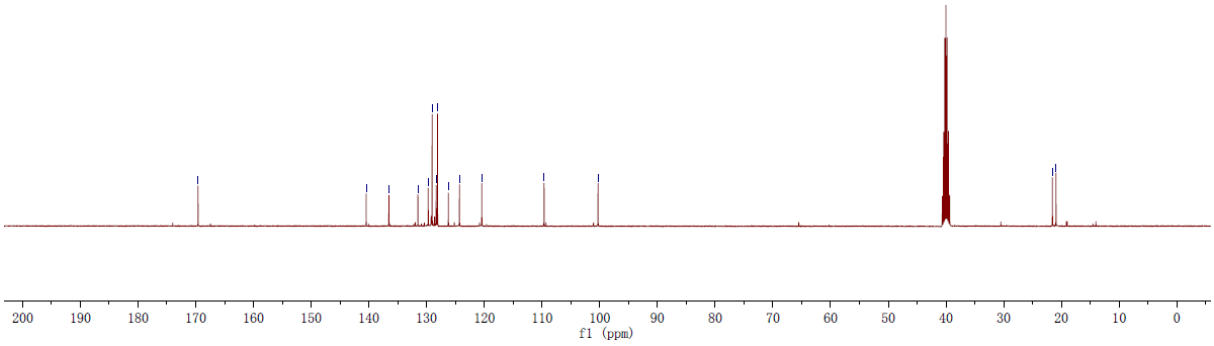
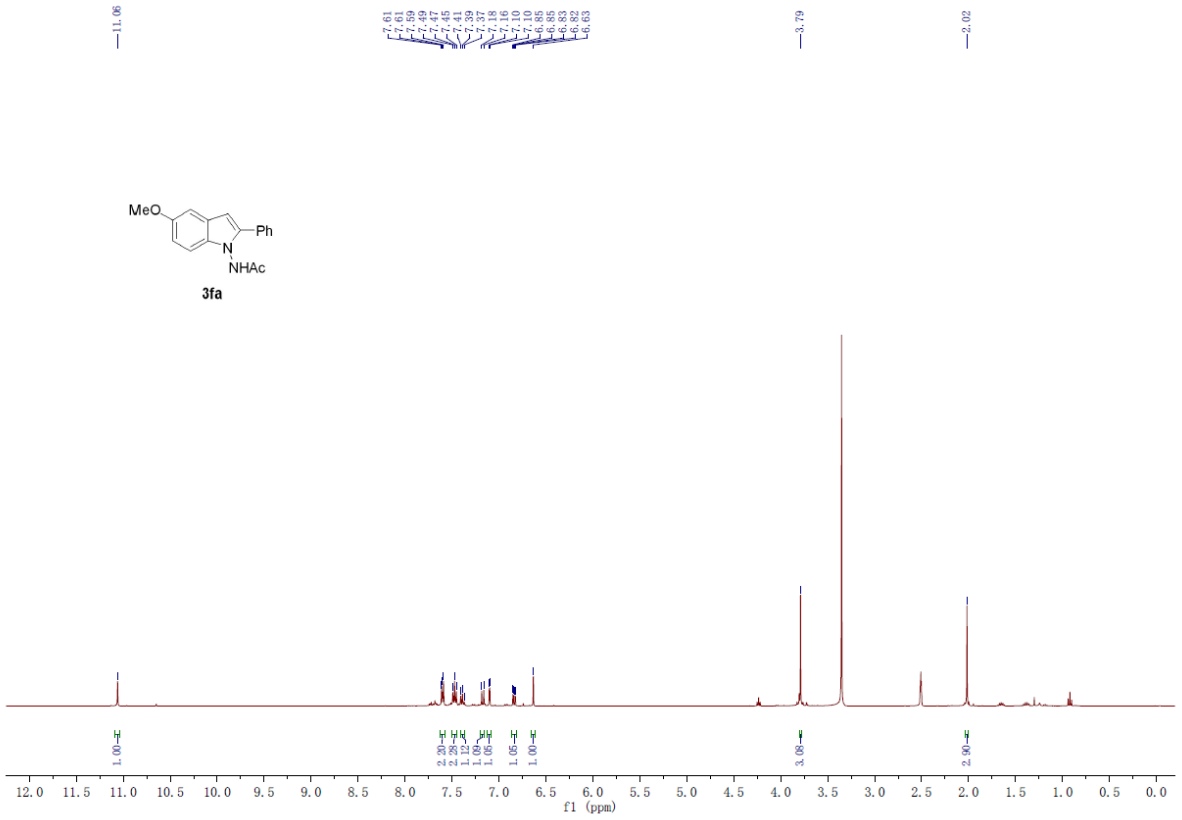
21.56
20.93


Me
Ph
N
NHAc

3ea


f1 (ppm)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7.61
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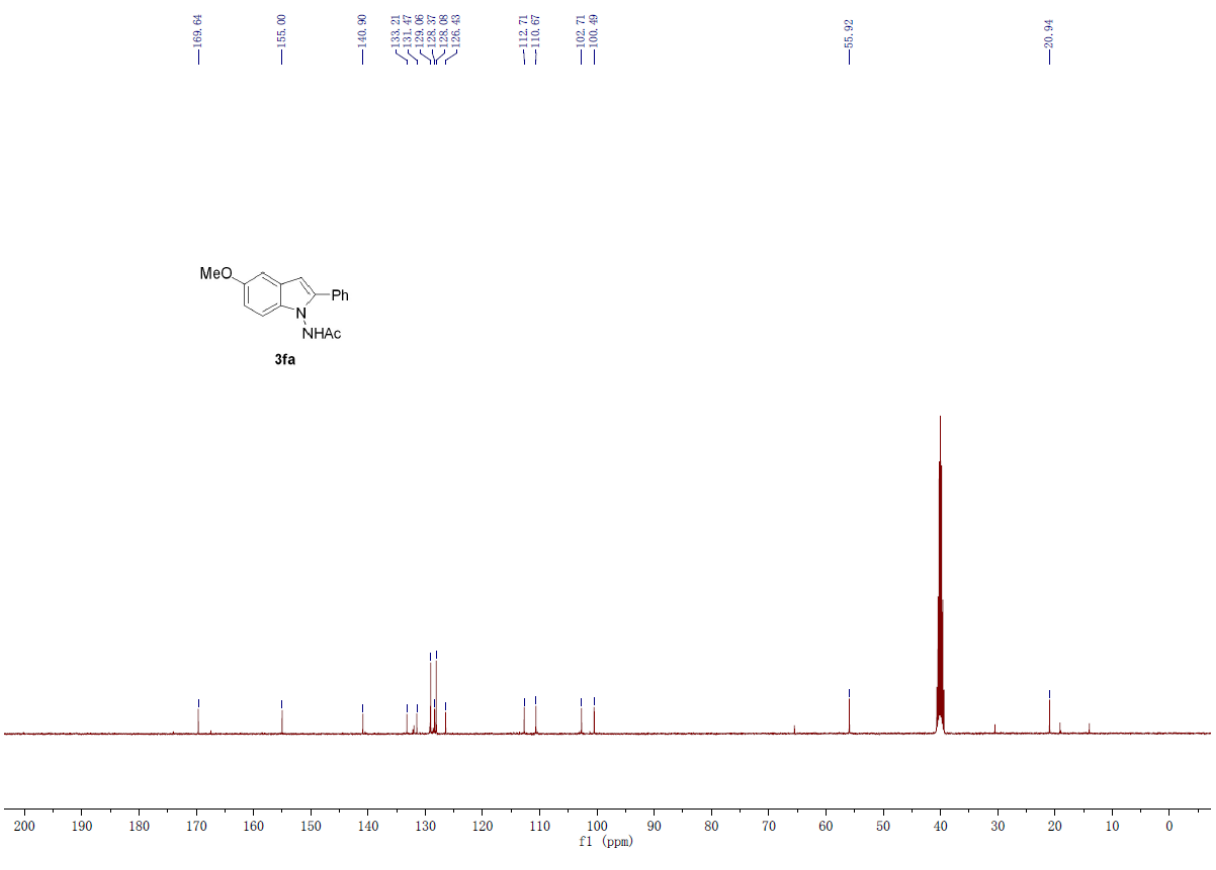
7.47
7.45
7.41
7.39
7.37
7.18
7.16
7.10
7.10
6.85
6.83
6.82
6.63
3.79
2.02
MeO
Ph
N
NHAc
3fa
1.00
2.20
2.39
1.12
1.09
1.05
1.05
1.00
3.08
2.90
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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155.00
140.90
133.21
131.47
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128.57
128.08
126.43
112.71
110.67
102.71
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20.94
MeO
Ph
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NHAc
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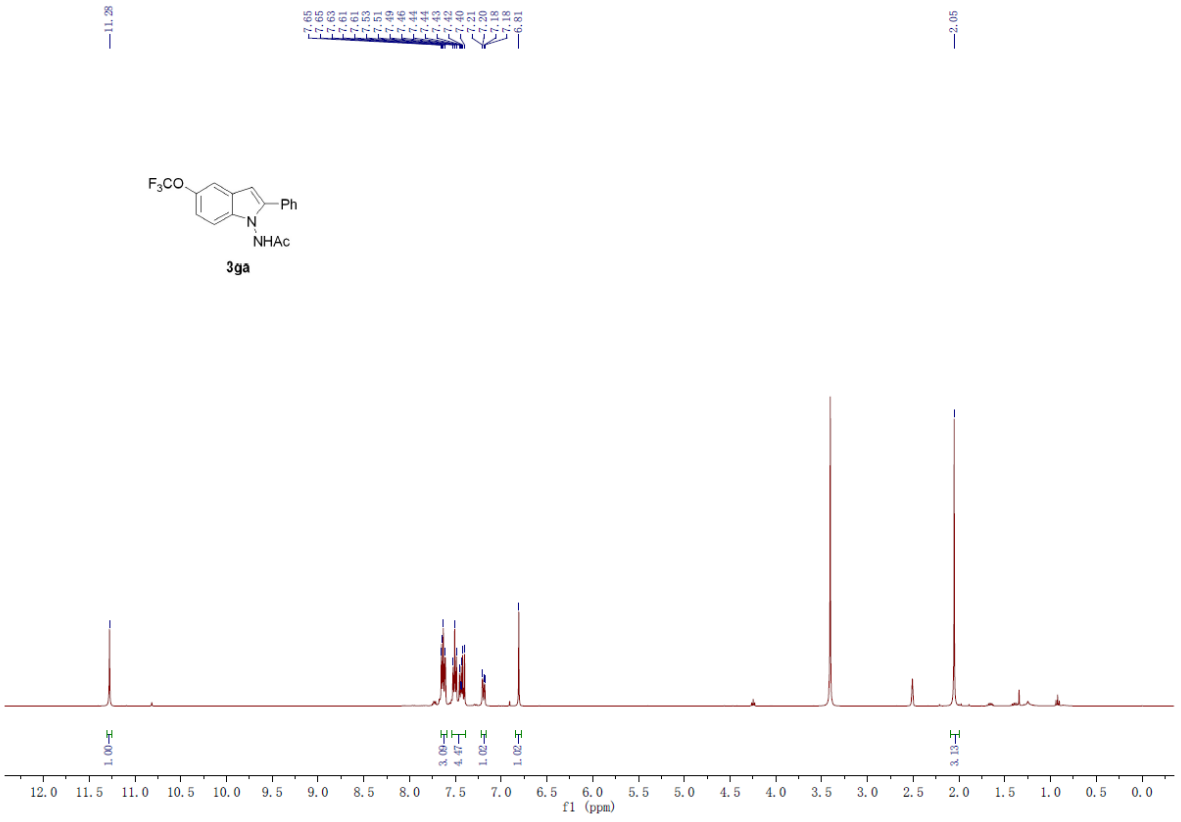
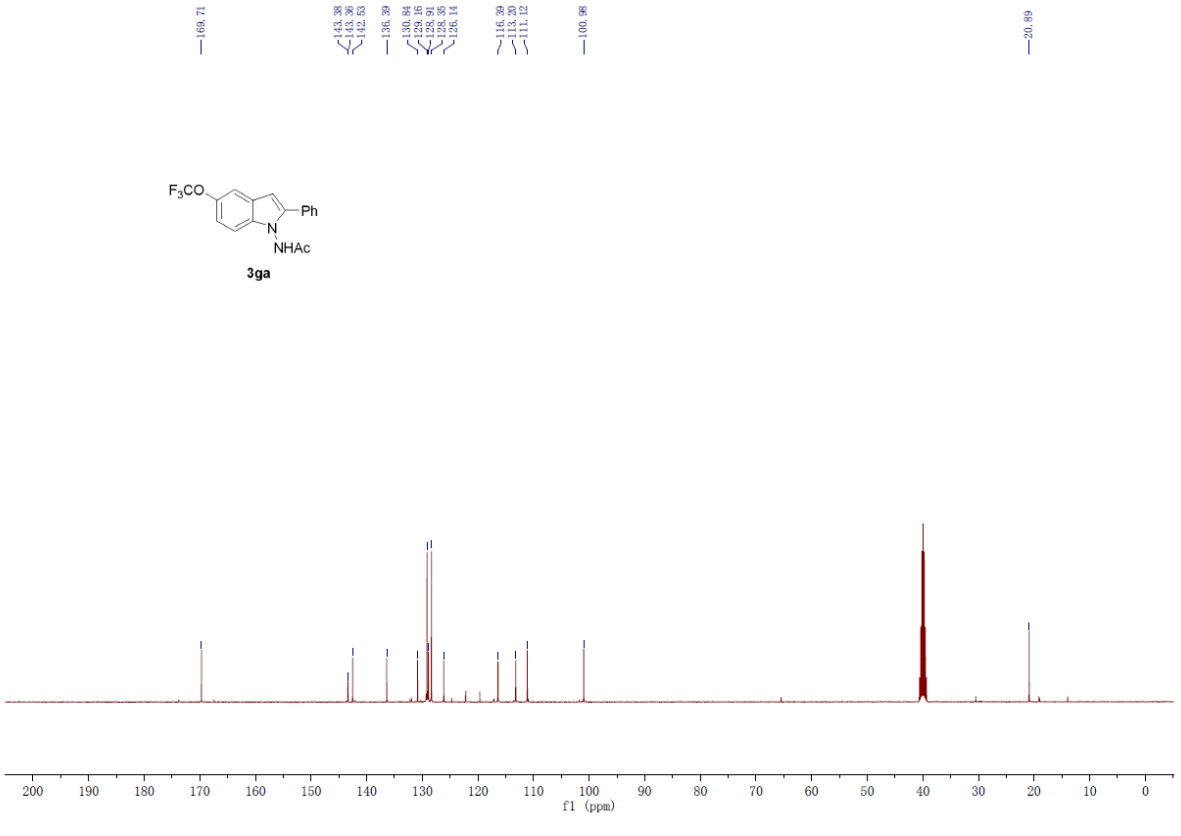
f1 (ppm)


11.28
7.65
7.65
7.63
7.61
7.61
7.53
7.51
7.49
7.46
7.44
7.44
7.43
7.42
7.40
7.21
7.20
7.18
6.81
2.05
F3CO
Ph
N
NHAc
3ga
1.00
3.09
4.47
1.02
1.02
3.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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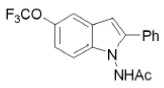
143.36
142.53
136.39
130.84
129.16
128.91
128.35
126.14
116.39
113.20
111.12
100.98
20.89
F3CO
Ph
N
NHAc
3ga
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

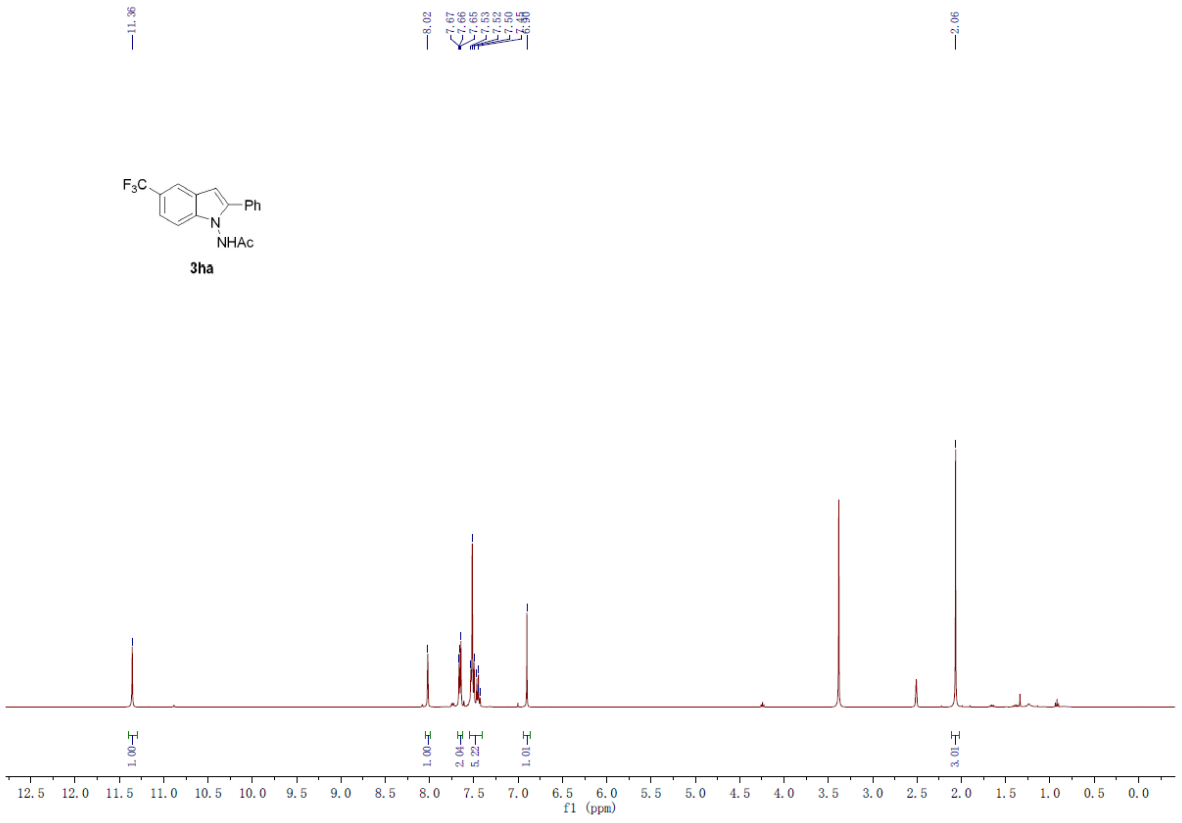

F3CO
Ph
N
NHAc

3ga

-57.01
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

F3C
Ph
N
NHAc

3ha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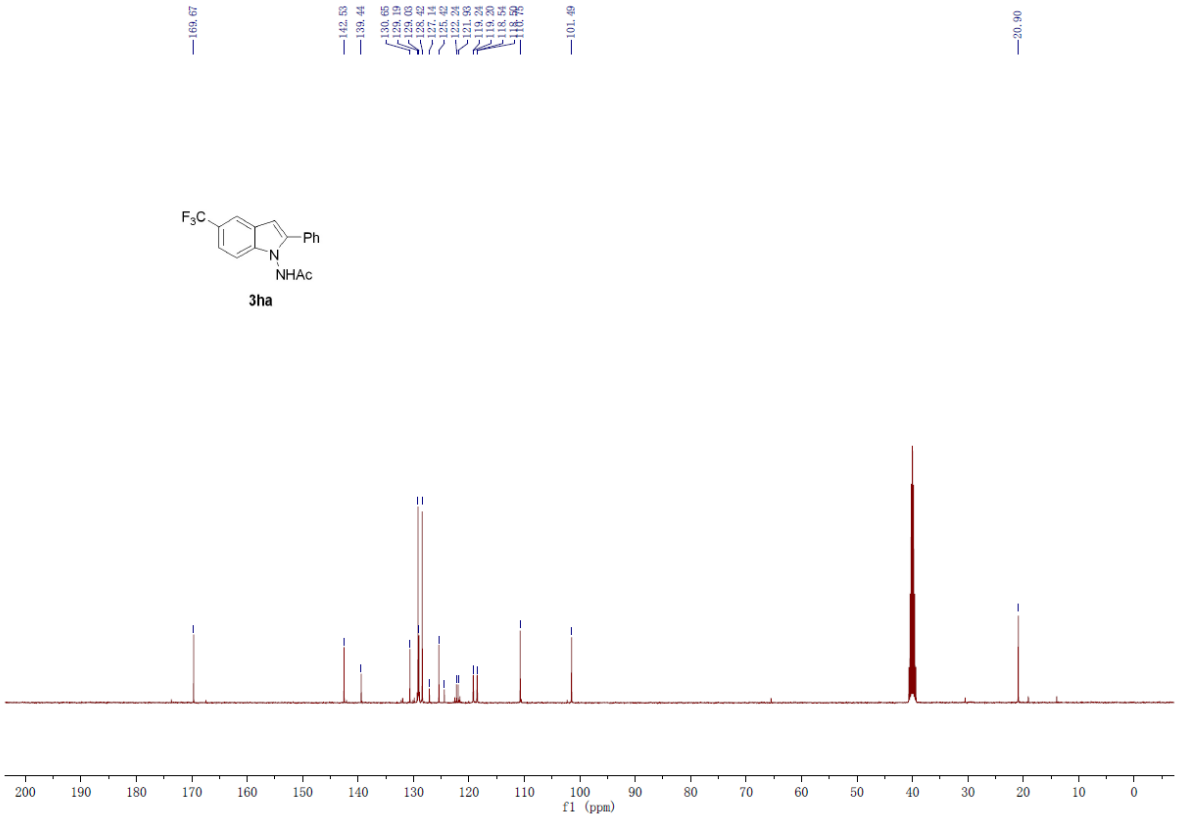
8.02
7.67
7.66
7.65
7.53
7.52
7.50
7.45
7.44
2.06
1.00
1.00
2.04
5.22
1.01
3.01
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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142.53
139.44
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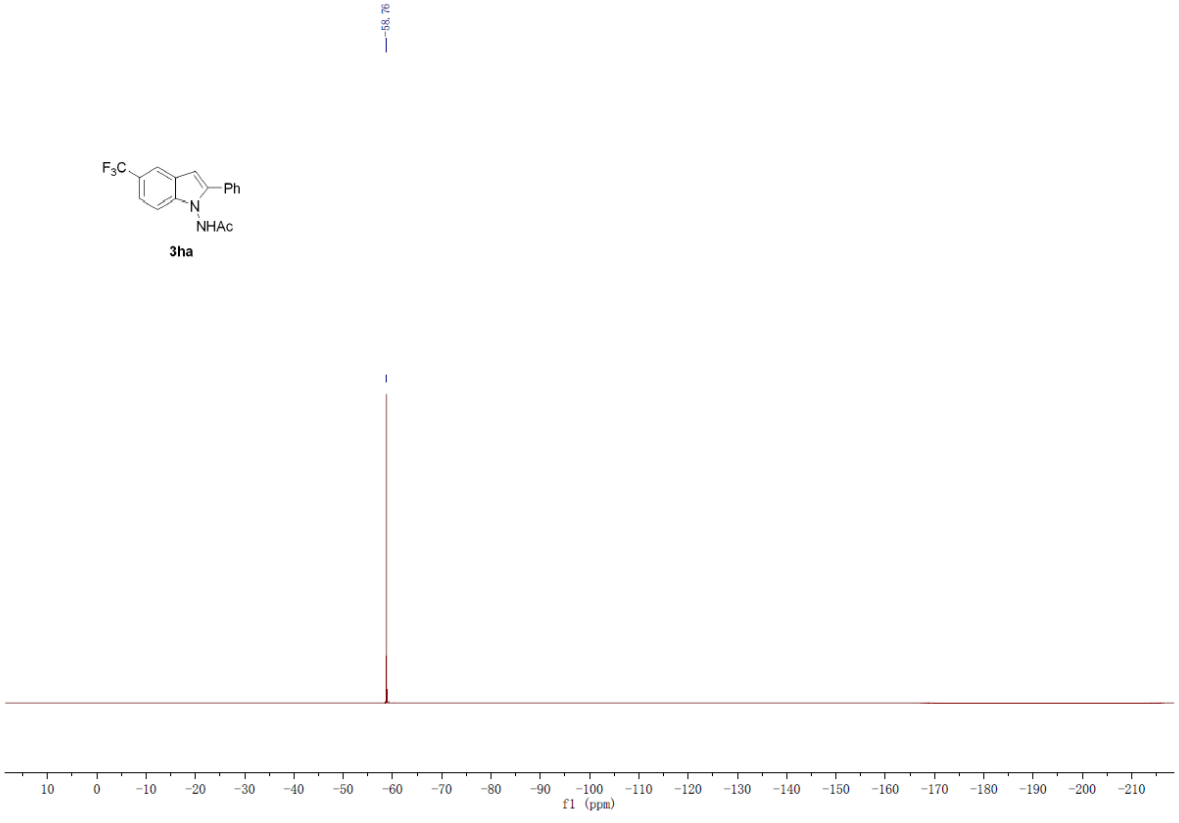
129.19
129.03
128.42
127.14
125.42
122.24
121.95
119.24
119.20
118.54
118.49
101.49
20.90
F3C
Ph
N
NHAc
3ha
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


58.76
F3C
Ph
N
NHAc
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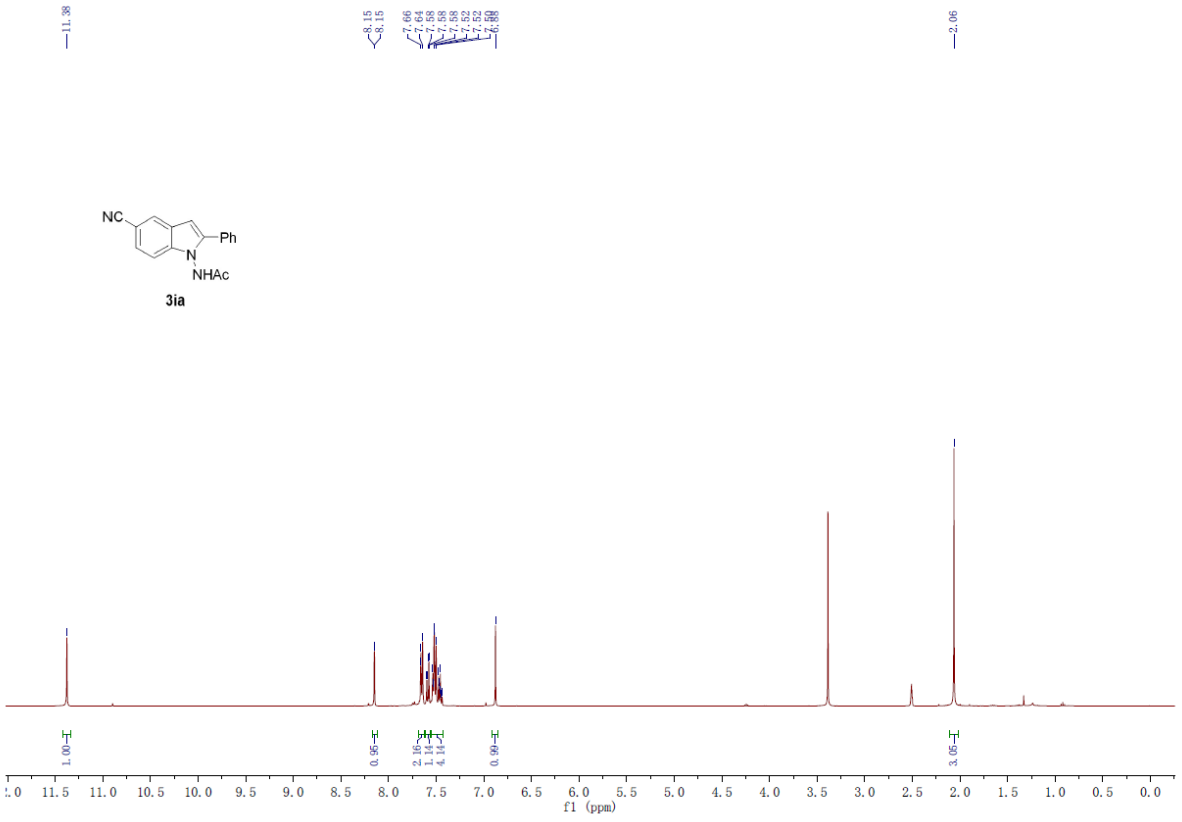
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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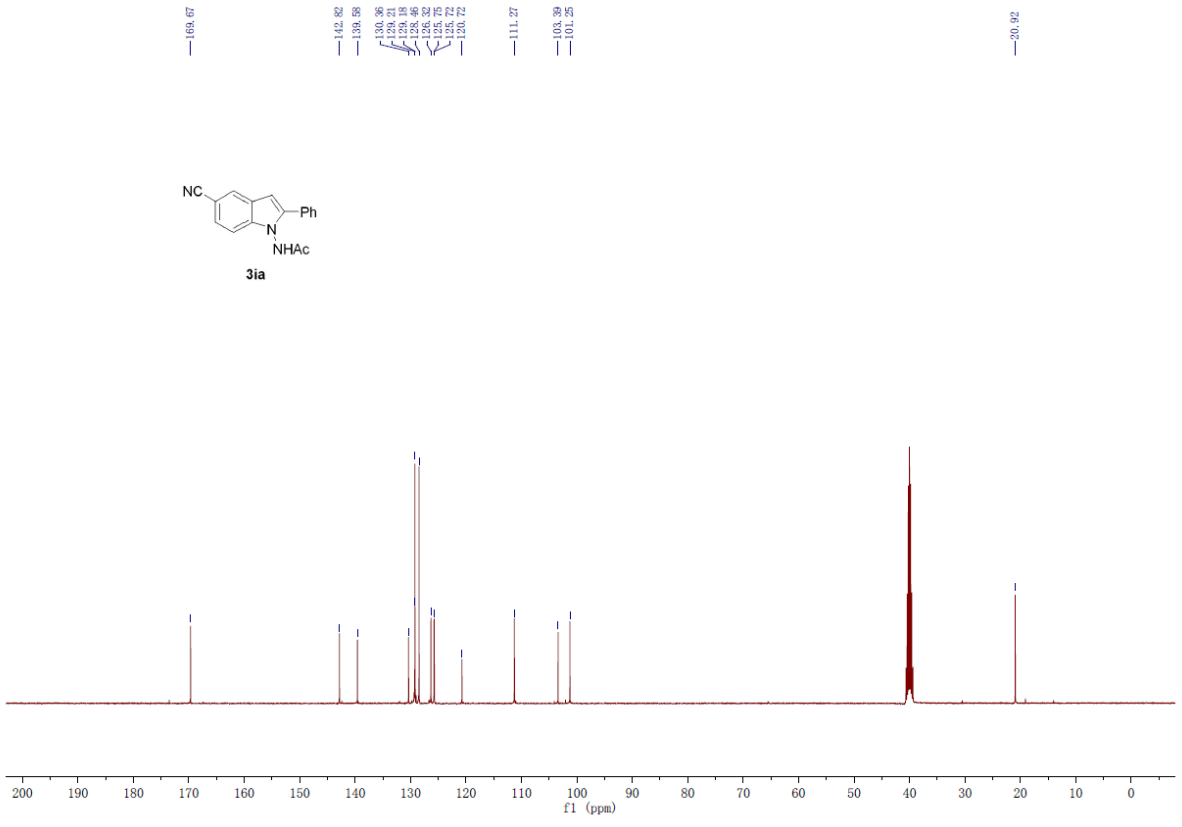
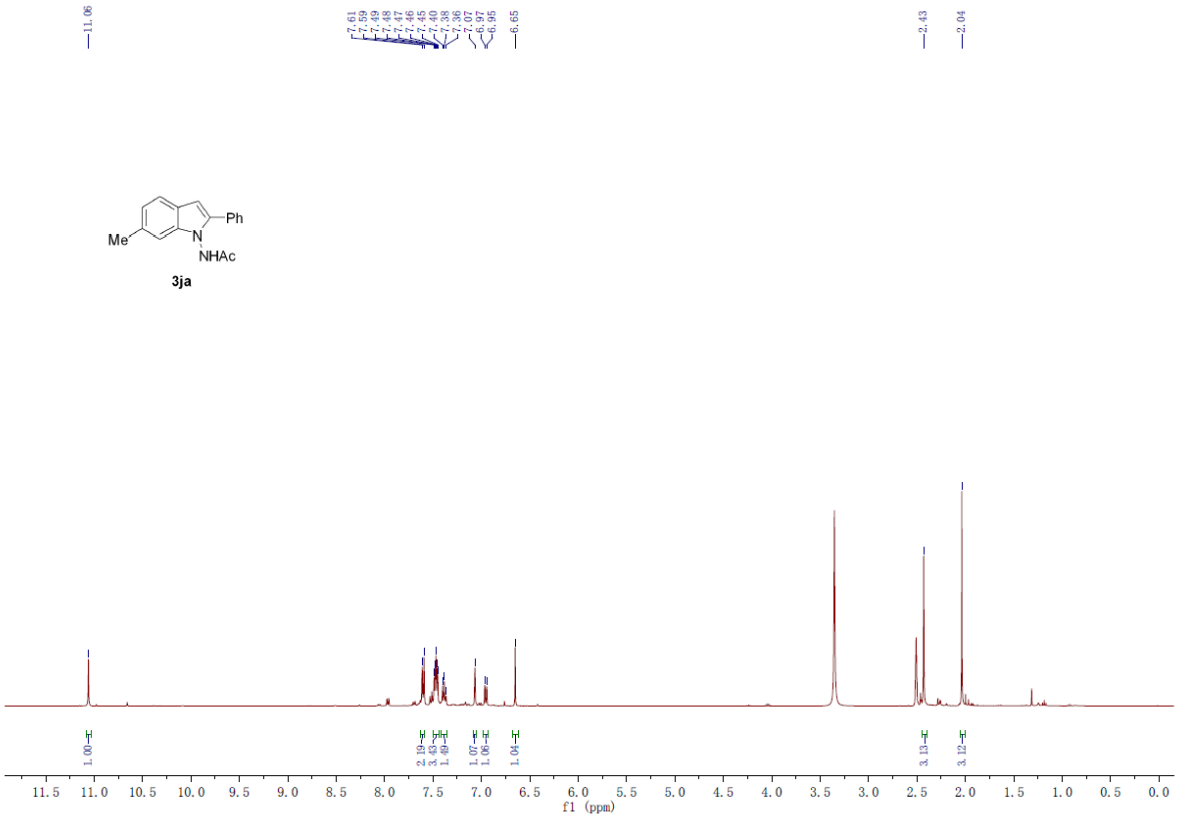
8.15
8.15
7.66
7.64
7.58
7.58
7.58
7.52
7.52
2.06
NC
Ph
N
NHAc
3ia
1.00
0.95
2.16
1.14
4.14
0.99
3.05
f1 (ppm)


169.67
142.82
139.58
130.36
129.21
129.18
128.46
126.32
125.75
125.72
120.72
111.27
103.39
101.25
20.92
NC
Ph
N
NHAc
3ia
f1 (ppm)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7.61
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7.49
7.48
7.47
7.46
7.45
7.40
7.38
7.36
7.07
6.97
6.95
6.65
2.43
2.04
Ph
Me
N
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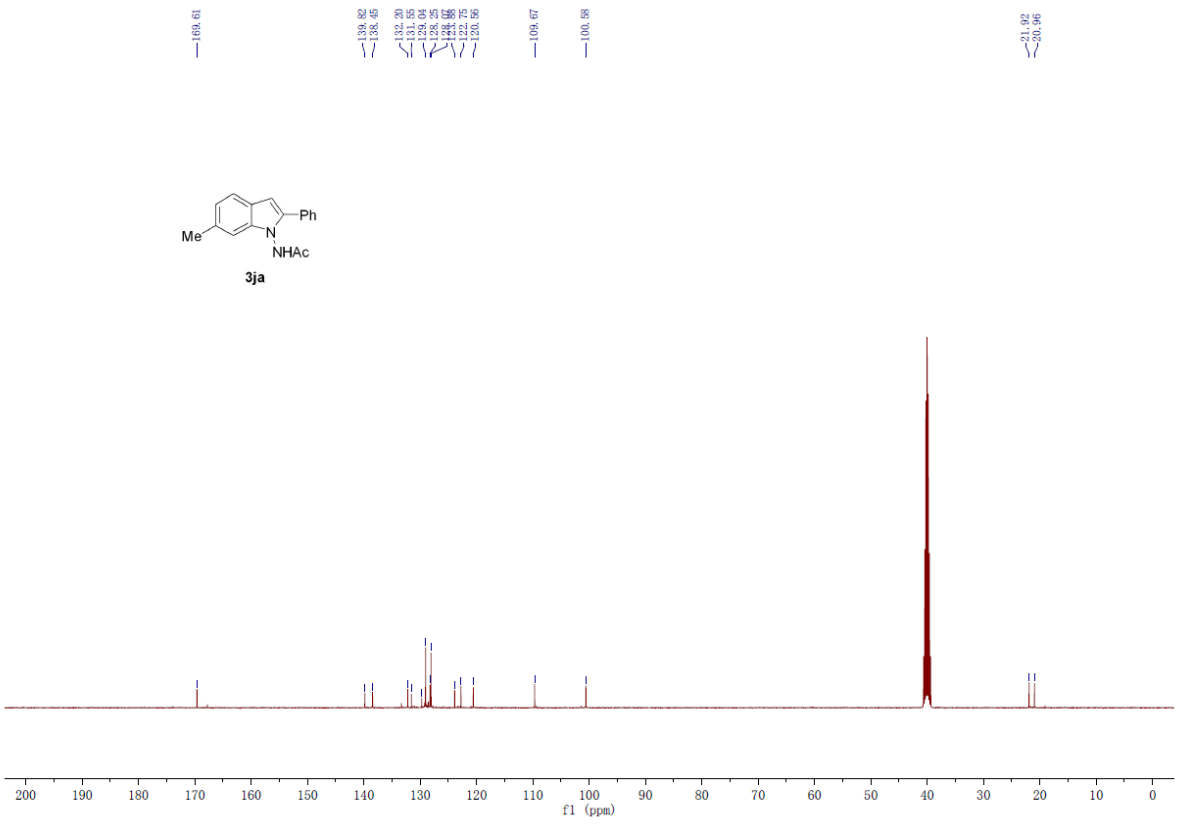
2.19
3.43
1.49
1.07
1.06
1.04
3.13
3.12
f1 (ppm)


169.61
139.82
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129.04
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109.67
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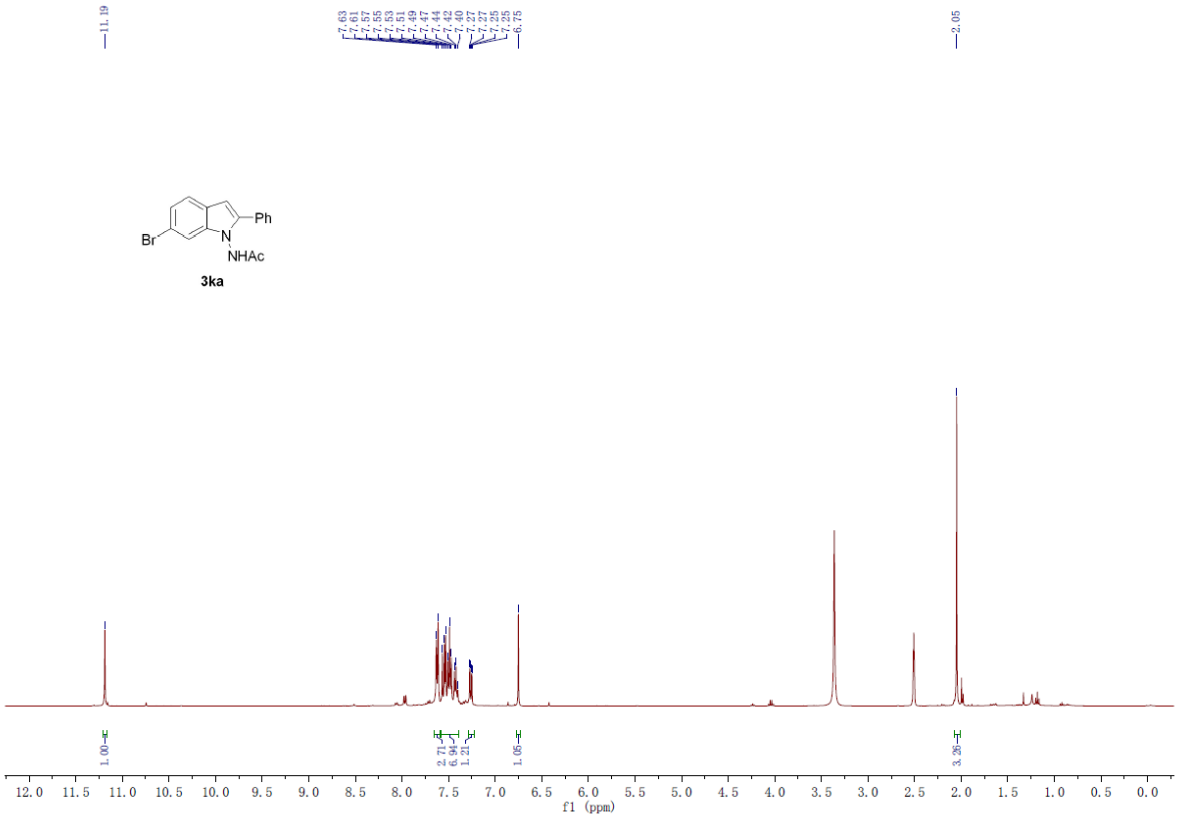
21.92
20.96
Ph
Me
N
NHAc
3ja
f1 (ppm)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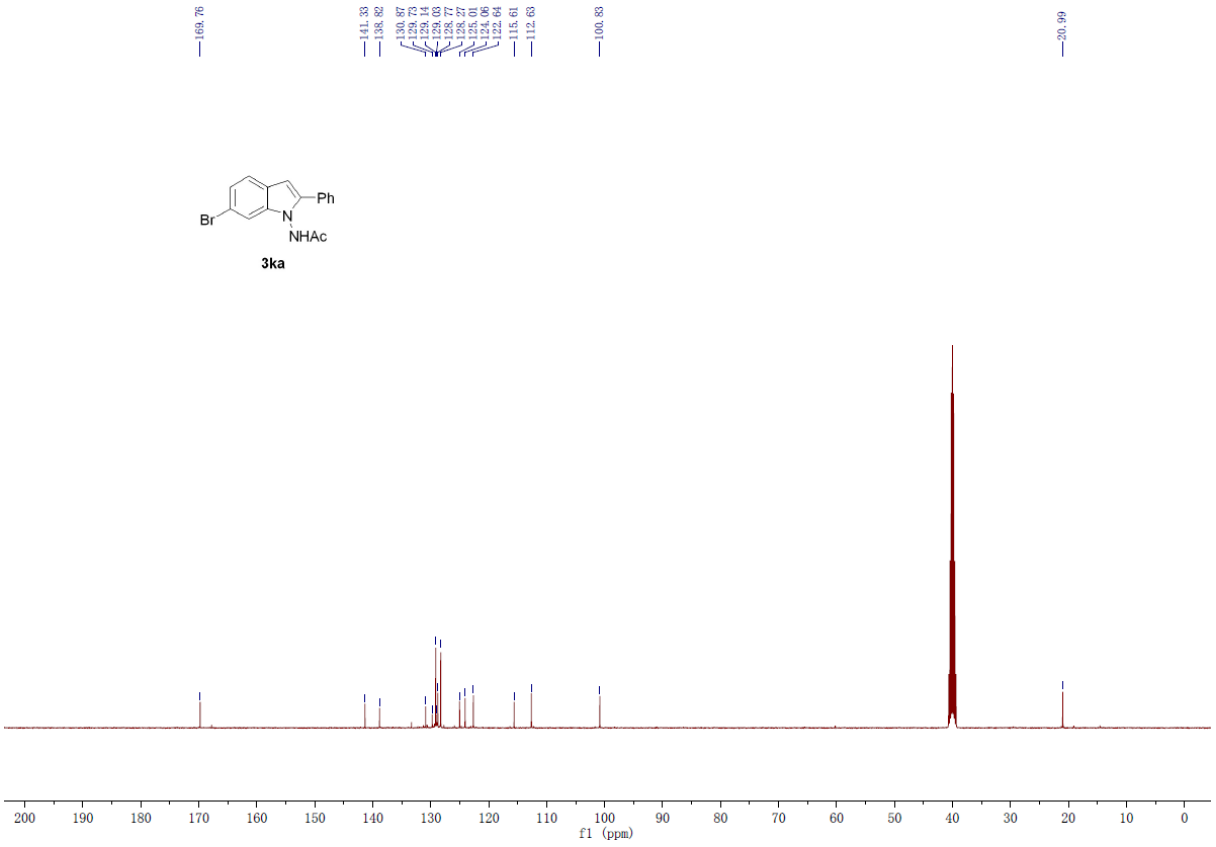
7.47
7.44
7.42
7.40
7.27
7.27
7.25
6.75
2.05
Br
Ph
N
NHAc
3ka
1.00
2.71
2.04
1.94
1.21
1.06
3.26
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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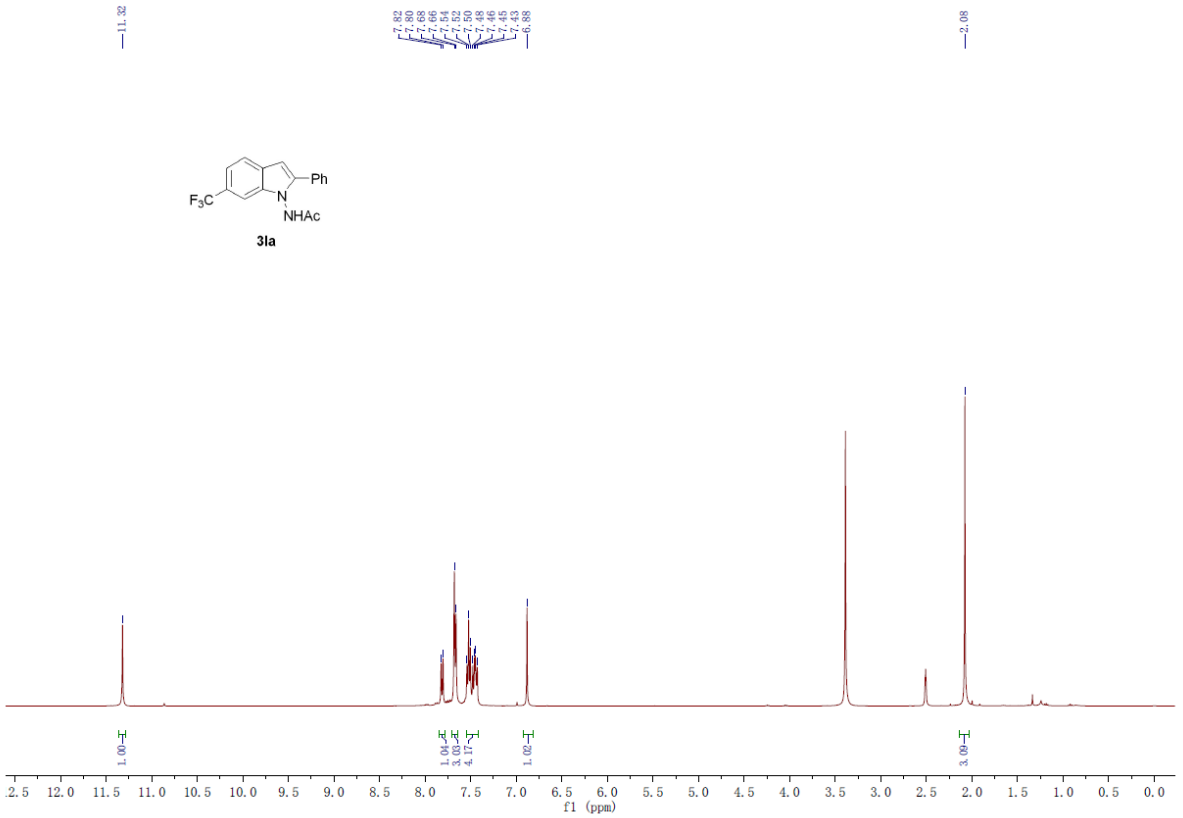
138.82
130.87
129.73
129.14
129.03
128.77
128.27
125.01
124.06
122.64
115.61
112.63
100.83
20.99
Br
Ph
N
NHAc
3ka
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.52
7.50
7.48
7.46
7.45
7.43
6.88
2.08
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N
NHAc
3la
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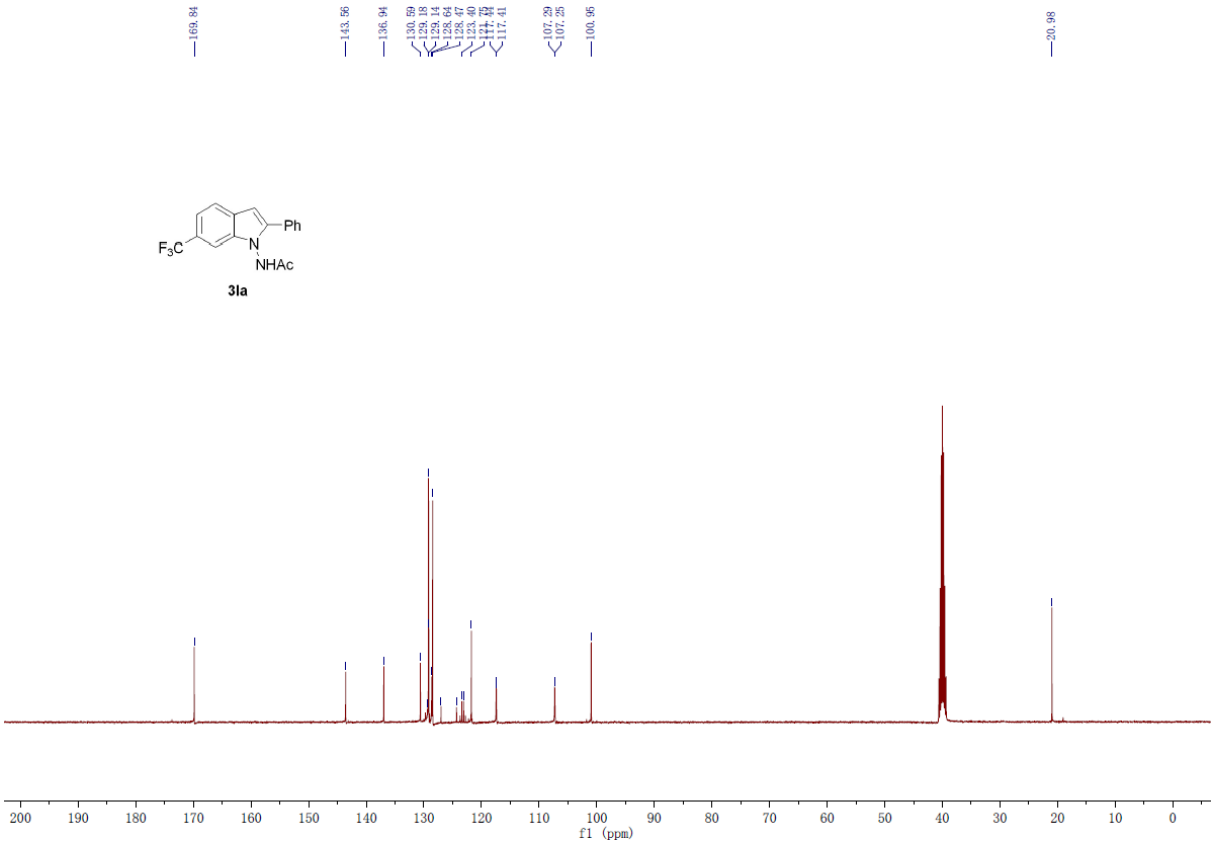
1.04
3.03
4.17
1.02
3.09
f1 (ppm)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129.18
129.14
128.64
128.47
123.40
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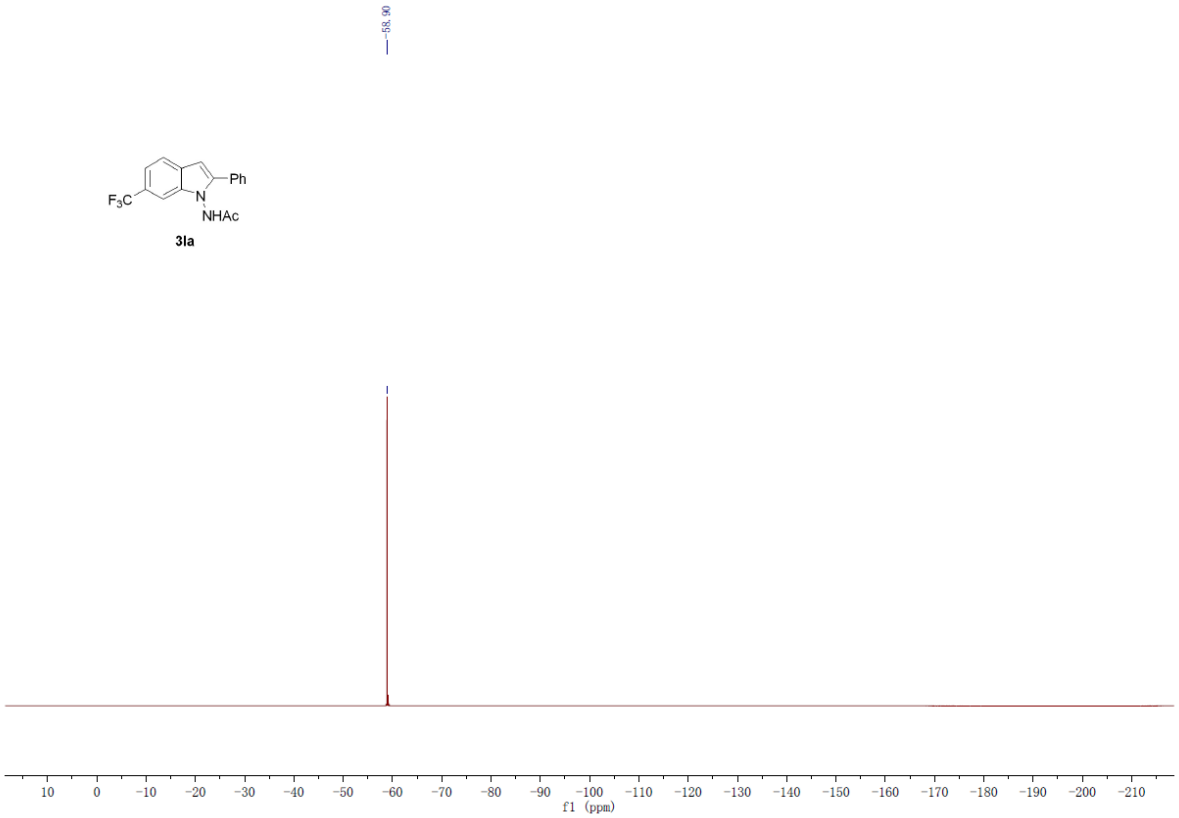
121.44
117.41
107.29
107.25
100.96
20.98
Ph
F3C
N
NHAc
3la
f1 (ppm)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Ph
F3C
N
NHAc
3la
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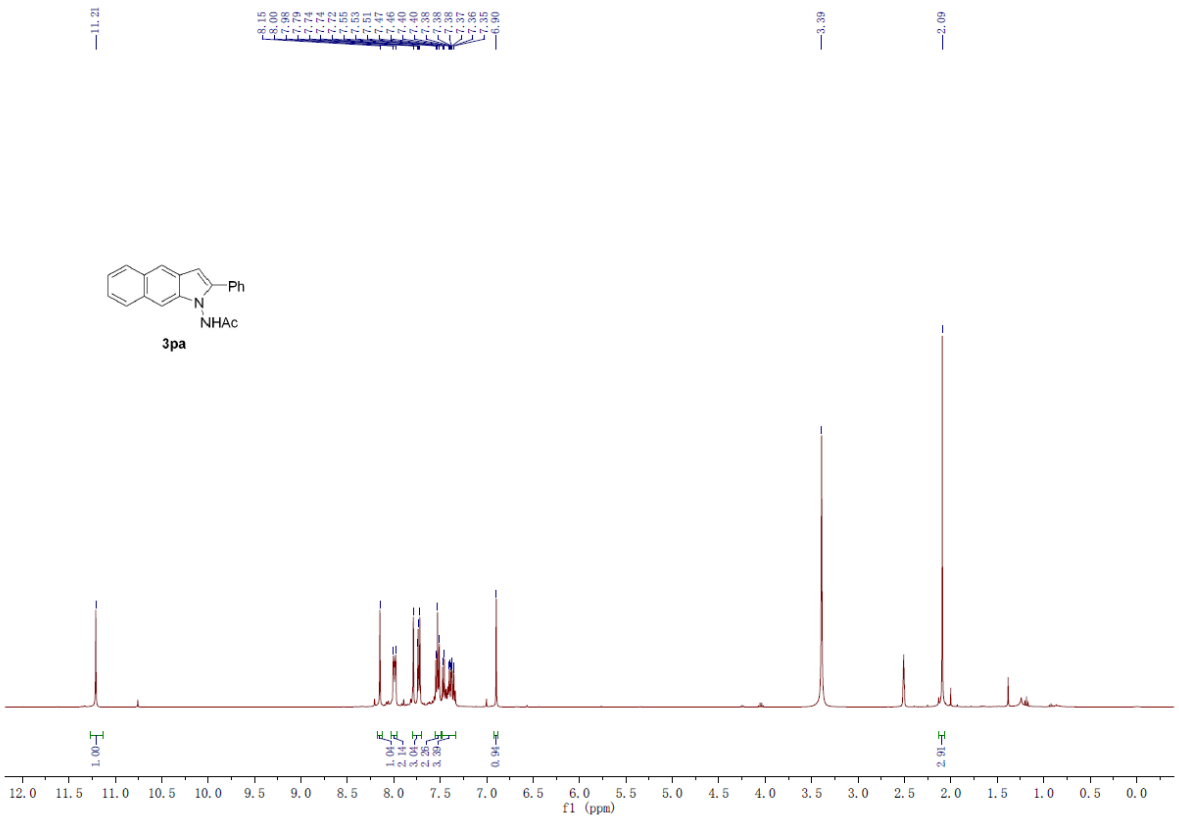
f1 (ppm)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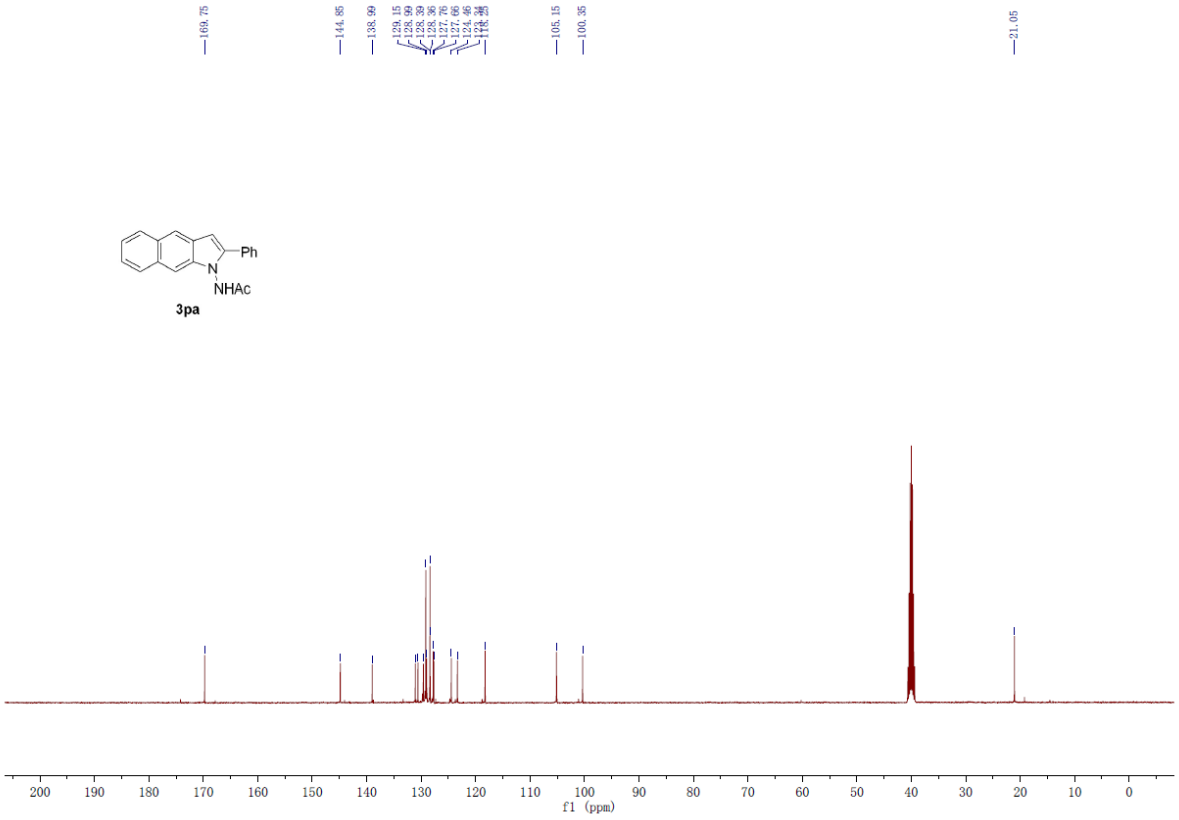
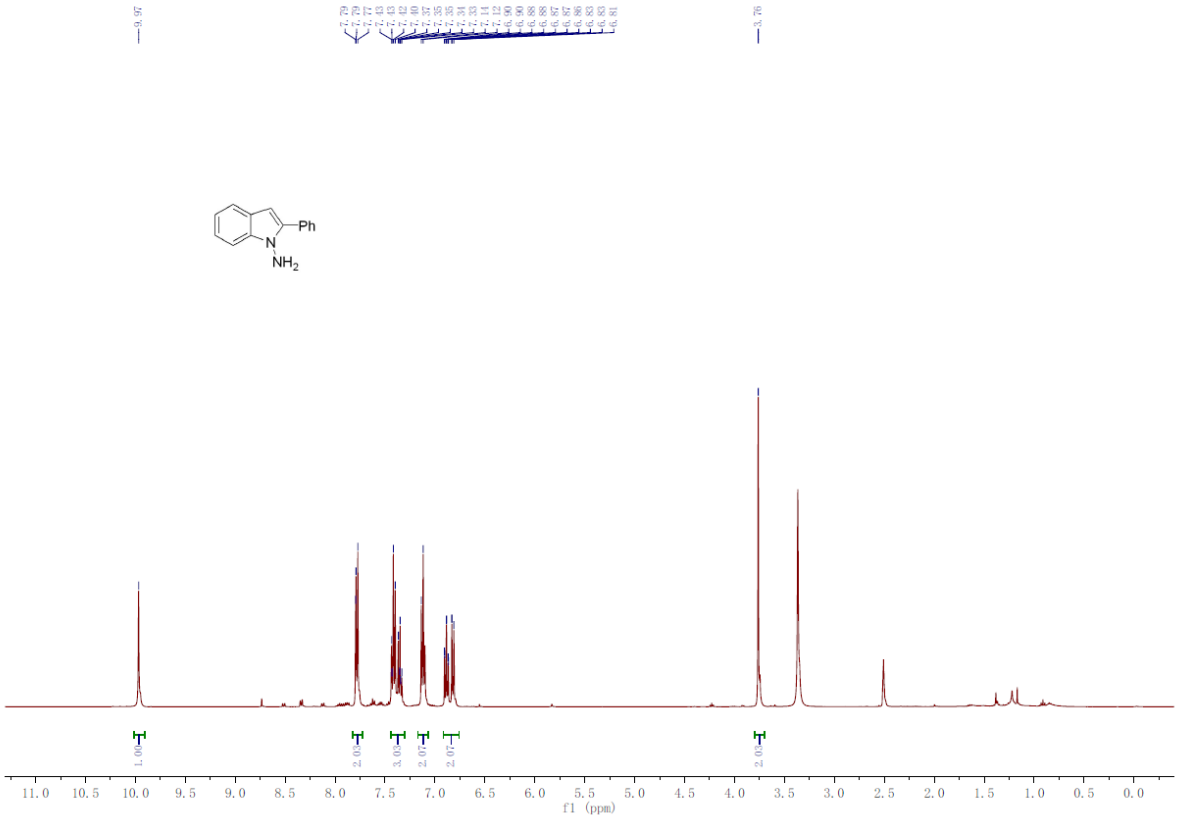
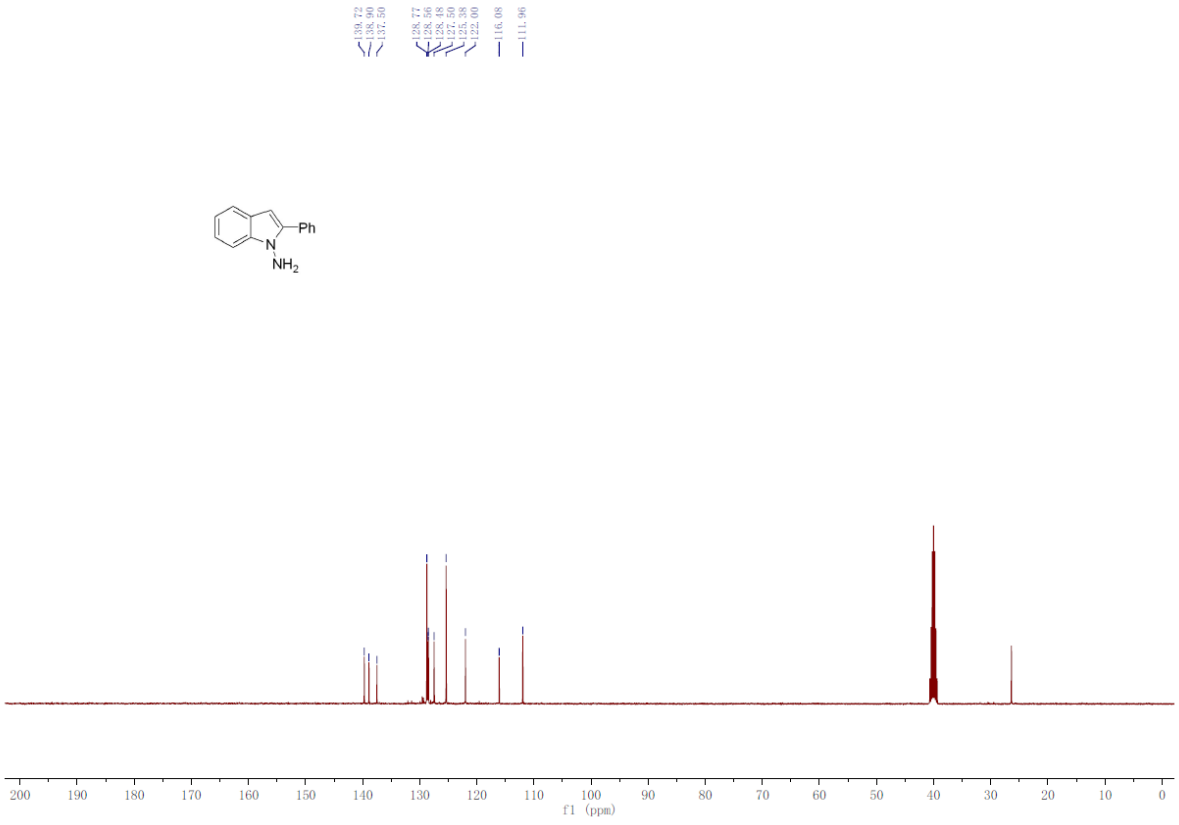
7.72
7.55
7.53
7.51
7.47
7.46
7.40
7.40
7.38
7.38
7.37
7.36
7.35
6.90
3.39
2.09
Ph
N
NHAc
3pa
1.00
1.04
2.14
3.04
3.05
3.39
0.94
2.91
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.75
144.85
138.99
129.15
128.99
128.39
128.36
127.76
127.66
124.46
123.34
123.25
105.15
100.35
21.05
Ph
N
NHAc
3pa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.97
7.79
7.79
7.77
7.43
7.42
7.40
7.37
7.35
7.35
7.34
7.33
7.14
7.12
6.99
6.90
6.88
6.87
6.87
6.86
6.83
6.81
3.76
Ph
N
NH2
1.00
2.02
3.03
2.07
2.07
2.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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138.60
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128.56
128.34
127.59
125.38
122.00
116.08
111.96
Ph
N
NH2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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1) C. White, A. Yates, P. M. Maitlis, *Inorg. Synth.* **1992**, *29*, 228.
2) P. M. Boyer, C. P. Roy, J. M. Bielski, J. S. Merpla, *Inorg. Chim. Acta* **1996**, *245*, 7.
3) Y. Liang, K. Yu, B. Li, S. Xu, H. Song and B. Wang, Chem. Commun. **2014**, 50, 6130.
4) (a) J. Vaitla, A. Bayer and K. H. Hopmann, Angew. Chem., Int. Ed. **2017**, 56, 4277. (b) Y. Xu, X. Yang, X. Zhou, L. Kong and X. Li, Org. Lett. **2017**, 19, 4307. (c)M. Zenzola, R. Doran, L. Degennaro, R. Luisi and J. A. Bull, Angew. Chem., Int. Ed. **2016**, 55,7203.