Supporting Information

for

Facile Synthesis of 3-Aryl Oxindoles via Brønsted Acid-Catalyzed Friedel-Crafts Alkylation of Electron-Rich Arenes with 3-Diazooxindoles

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1. General

All isolated compounds were characterized on the basis of ^{1}H NMR and ^{13}C NMR spectroscopic data (Brucker Ascend-400 MHz spectrometer) and HRMS (TOF-Q) data (Bruker micrOTOF-Q 10198 mass spectrometer). IR spectra were recorded on a FT IR spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts are reported in ppm using tetramethylsilane (TMS) as an internal standard. All reactions were run in open flasks under air atmosphere. A.R. grade solvents were directly used and further purification or degas of the solvents was not required.

2. General Experimental Procedure and Supplemental Experiments

2.1 General procedure for the preparation of 3-diazooxindoles

3-Diazooxindoles were prepared with modified methods according to the literatures.[1]

A mixture of isatin (2.0 g, 13.6 mmol) and $TsNHNH_2$ (2.66 g, 14.3 mmol) in THF (20 mL) was stirred at 65 ºC for 1 h, the mixture was filtered. The filter cake was stirred in 0.2 N aqueous NaOH solution (102 mL, 20.4 mmol) at 65 ºC for 1 h. After cooled to ambient temperature, the reaction mixture was neutralized with dry ice. The red solid was filtered off and dried in the air to give 3-diazooxindole (1.8 g, 83% over two steps), which was used in the next step without further purification.

A mixture of 3-diazooxindole (1.0 g, 6.3 mmol), K_2CO_3 (1.0 g, 7.5 mmol) and BnBr (0.82 mL, 6.9 mmol) was stirred in DMF (6 mL) at room temperature for 15 h. Then the mixture was diluted with ether and washed with water (60 mL× 3). The organic phase was dried by Na_2SO_4 and the solvent was removed under reduced pressure. The resulting residue was purified by flash chromatography to give **N**-benzyl-3-diazooxindole **1a** (1.4 g, 89%) as an orange solid. The NMR spectral data was consistent with that reported.[1]

Other 3-diazooxindoles were prepared following similar methods.

2.2 General procedure for the TfOH-catalyzed reaction between diazo compounds and toluene

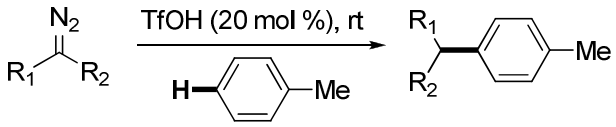
Under an air atmosphere, to the mixture of TfOH (20 mol %) in 0.7 mL of toluene at room temperature, a solution of diazo compound (0.2 mmol) in 1 mL of toluene was added *via* syringe pump over 30 min. After completion of the addition, the mixture was stirred for another 10 min. Then excess solid sodium bicarbonate was added to neutralize the acid. After filtration, the solvent was removed under reduced pressure and subjected to ^{1}H NMR analysis to determine the regioisomeric ratio. The crude product was then purified by flash chromatography on silica gel to afford the corresponding products.

2.3 General procedure for the TfOH-catalyzed reaction of 3-diazooxindole and

arenes

Under an air atmosphere, to the mixture of TfOH (20 mol %) and arene **2** (1.0 mmol) in 0.7 mL of DCE at room temperature, a solution of 1-benzyl-3-diazooxindole (0.2 mmol) in 1.0 mL of DCE was added *via* syringe pump over 30 min. After completion of the addition, the mixture was stirred for another 10 min. Then excess solid sodium bicarbonate was added to neutralize the acid. After filtration, the solvent was removed under reduced pressure and subjected to ^{1}H NMR analysis to determine the regioisomeric ratio. The crude product was then purified by flash chromatography on silica gel to afford the corresponding products.

Table S1. Screening of different diazo compounds



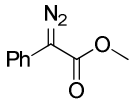
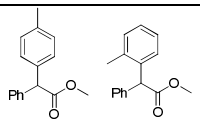
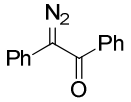
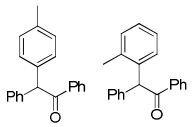
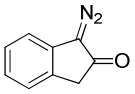
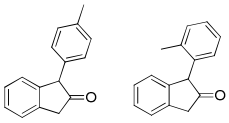
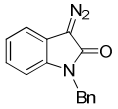
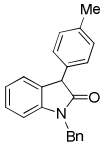
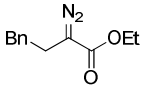
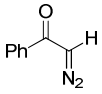
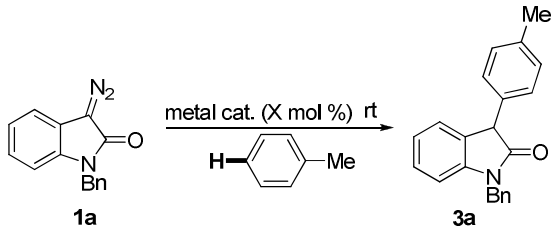
entry	diazo compound	product	yield (%)	regioisomeric ratio (*para*/*ortho*)
1			78	77 : 23
2			86	65 : 35
3			72	68 : 32
4			**96**	**> 95:5**
5		--	< 5	--
6		--	< 5	--
7		--	< 5	--

Table S2. Metal catalyzed reaction of 1-benzyl-3-diazooxindole and toluene



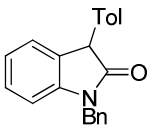
1a 3a

entry	metal cat.	X	conversion (%)	yield (%)
1	$Rh_2(OAc)_4$	2	> 95	< 5
2	$[Rh(COD)Cl]_2$	2	< 20	< 5
3	$Cu(OTf)_2$	10	> 95	< 5
4	$CuPF_6(CH_3CN)_4$	10	< 50	< 5
5	$[Ru(COD)Cl]_2$	2	< 20	< 5
6	$[PdCl(allyl)]_2$	2	> 95	< 5

2.4 Procedure for gram-scale synthesis of 3a

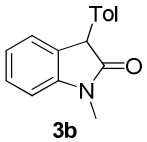
Under an air atmosphere, to the mixture of TfOH (53 μL, 10 mol %) and toluene (10 mL) at 0 °C, was added a solution of N-benzyl-3-diazooxindole (1.50 g, 6.0 mmol) in toluene (12 mL) *via* syringe pump over 60 min. After completion of the addition, the mixture was stirred for another 20 min. Then excess solid sodium bicarbonate was added to neutralize the acid. After filtration, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel to afford **3a** (1.41 g, 75%).

3. Characterization Data of the Products



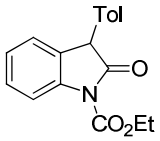
3a

1-Benzyl-3-*p*-tolylindolin-2-one (3a): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 – 7.24 (m, 5H), 7.21 – 7.09 (m, 6H), 7.02 – 6.98 (m, 1H), 6.77 (d, *J* = 7.8 Hz 1H), 4.99 (d, *J* = 15.6 Hz 1H), 4.88 (d, *J* = 15.6 Hz 1H), 4.66 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.3, 143.6, 137.3, 136.0, 133.8, 129.7, 129.2, 128.8, 128.3, 128.2, 127.6, 127.4, 125.1, 122.7, 109.2, 51.8, 44.0, 21.1. FTIR (KBr): 3050, 2922, 1711, 1612, 1487, 1464, 1383, 1347, 1177, 1083, 1030, 1008, 890, 753, 733, 698 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{19}NNaO$ $[M+Na]^+$ = 336.1364, found 336.1348.



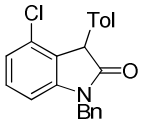
3b

1-Methyl-3-*p*-tolylindolin-2-one (3b): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 – 7.29 (m, 1H), 7.16 – 7.03 (m, 6H), 6.88 (d, *J* = 8.0 Hz 1H), 4.56 (s, 1H), 3.24 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 144.5, 137.3, 133.6, 129.6, 129.1, 128.3, 128.3, 125.0, 122.7, 108.1, 51.7, 26.4, 21.1. FTIR (KBr): 3054, 2922, 1693, 1607, 1495, 1468, 1376, 1344, 1086, 748, 693 cm^{-1}. HRMS (ESI): calcd for $C_{16}H_{15}NNaO$ $[M+Na]^+$ = 260.1051, found 260.1051.



3c

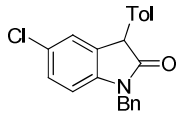
Ethyl 2-oxo-3-*p*-tolylindoline-1-carboxylate (3c): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, *J* = 8.2 Hz 1H), 7.38 – 7.34 (m, 1H), 7.21 – 7.06 (m, 6H), 4.71 (s, 1H), 4.45 (q, *J* = 7.1 Hz 2H), 2.32 (s, 3H), 1.42 (t, *J* = 7.1 Hz 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 151.1, 140.2, 137.7, 133.2, 130.0, 128.7, 128.4, 127.8, 125.1, 124.9, 115.2, 63.4, 52.2, 21.1, 14.2. FTIR (KBr): 2986, 2924, 1776, 1723, 1480, 1465, 1373, 1344, 1287, 1236, 1150, 1089, 1048, 764 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{17}NNaO_3$ $[M+Na]^+$ = 318.1106, found 318.1091.



3d

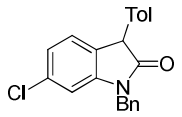
1-Benzyl-4-chloro-3-p-tolylindolin-2-one (3d): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.24 (m, 5H), 7.17 – 7.13 (m, 3H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 4.97 (d, *J* = 15.6 Hz, 1H), 4.82 (d, *J* = 15.6 Hz, 1H), 4.68 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 145.3, 137.4, 135.6, 131.8, 131.6, 129.7, 129.7, 128.9, 128.0, 127.8, 127.3, 126.6,

123.3, 107.5, 51.7, 44.2, 21.2. FTIR (KBr): 3408, 3024, 2919, 1711, 1606, 1460, 1334, 1232, 1161, 1142, 1025, 802, 774, 724, 699, 503 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{18}ClNNaO$ $[M+Na]^+$ = 370.0975, found 370.0974.



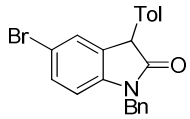
3e

1-Benzyl-5-chloro-3-p-tolylindolin-2-one (3e): ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.23 (m, 5H), 7.17 – 7.12 (m, 4H), 7.08 (d, *J* = 8.0 Hz 2H), 6.67 (d, *J* = 8.3 Hz 1H), 4.97 (d, *J* = 15.6 Hz 1H), 4.86 (d, *J* = 15.6 Hz 1H), 4.64 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.8, 142.1, 137.7, 135.5, 133.0, 130.9, 129.8, 128.9, 128.3, 128.2, 128.2, 127.8, 127.3, 125.5, 110.1, 51.8, 44.1, 21.1. FTIR (KBr): 3031, 2922, 1722, 1711, 1607, 1484, 1427, 1340, 1160, 1113, 804, 744, 700 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{18}ClNNaO$ $[M+Na]^+$ = 370.0975, found 370.0962.



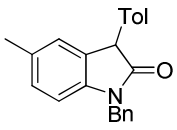
3f

1-Benzyl-6-chloro-3-p-tolylindolin-2-one (3f): ^1H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.24 (m, 5H), 7.15 (d, *J* = 7.9 Hz 2H), 7.08 – 7.04 (m, 3H), 6.98 (d, *J* = 7.9, 1.5 Hz 1H), 6.77 (d, *J* = 1.3 Hz 1H), 4.95 (d, *J* = 15.6 Hz 1H), 4.84 (d, *J* = 15.6 Hz 1H), 4.62 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 144.8, 137.6, 135.4, 134.0, 133.2, 129.8, 128.9, 128.2, 127.9, 127.5, 127.3, 126.0, 122.7, 109.7, 51.3, 44.1, 21.1. FTIR (KBr): 3411, 3030, 2923, 1711, 1609, 1490, 1336, 1183, 1080, 798, 698 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{18}ClNNaO$ $[M+Na]^+$ = 370.0975, found 370.0972.



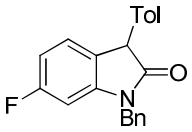
3g

1-Benzyl-5-bromo-3-p-tolylindolin-2-one (3g): ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.24 (m, 7H), 7.16 (d, *J* = 8.0 Hz 2H), 7.07 (d, *J* = 8.0 Hz 2H), 6.63 (d, *J* = 8.3 Hz 1H), 4.97 (d, *J* = 15.6 Hz 1H), 4.86 (d, *J* = 15.6 Hz 1H), 4.65 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 142.6, 137.7, 135.5, 133.0, 131.3, 131.1, 129.8, 128.9, 128.3, 128.2, 127.8, 127.3, 115.5, 110.6, 51.7, 44.0, 21.1. FTIR (KBr): 3428, 2922, 1722, 1712, 1604, 1484, 1423, 1347, 1184, 1159, 1112, 1023, 803, 739, 698 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{18}BrNNaO$ $[M+Na]^+$ = 414.0469, found 414.0465.



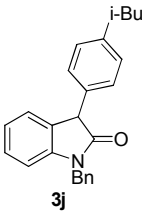
3h

1-Benzyl-5-methyl-3-p-tolylindolin-2-one (3h): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.22 (m, 5H), 7.15 (d, J = 8.0 Hz 2H), 7.10 (d, J = 8.0 Hz 2H), 6.97 (d, J = 8.7 Hz 2H), 6.65 (d, J = 7.7 Hz 1H), 4.97 (d, J = 15.6 Hz 1H), 4.86 (d, J = 15.6 Hz 1H), 4.62 (s, 1H), 2.33 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.3, 141.2, 137.3, 136.1, 134.0, 132.3, 129.7, 129.3, 128.8, 128.5, 128.4, 127.6, 127.4, 125.9, 108.9, 51.9, 44.0, 21.2, 21.0. FTIR (KBr): 3028, 2918, 1709, 1600, 1494, 1346, 1186, 1022, 890, 818, 758, 732, 694, 653 cm^{-1}. HRMS (ESI): calcd for $C_{23}H_{21}NNaO$ $[M+Na]^+$ = 350.1521, found 350.1536.



3i

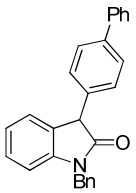
1-Benzyl-6-fluoro-3-p-tolylindolin-2-one (3i): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.24 (m, 5H), 7.15 (d, J = 7.9 Hz 2H), 7.09 – 7.05 (m, 3H), 6.72 – 6.64 (m, 1H), 6.51 (dd, J_1 = 8.9 Hz, J_2 = 2.2 Hz 1H), 4.95 (d, J = 15.6 Hz 1H), 4.84 (d, J = 15.6 Hz 1H), 4.62 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6, 163.0 (d, $J_{C\text{-}F}$ = 245.0 Hz) 145.0 (d, $J_{C\text{-}F}$ = 11.5 Hz), 137.5, 135.5, 133.5, 129.7, 128.9, 128.2, 127.9, 127.4, 126.0 (d, $J_{C\text{-}F}$ = 9.6 Hz), 124.4 (d, $J_{C\text{-}F}$ = 3.0 Hz), 108.9 (d, $J_{C\text{-}F}$ = 22.4 Hz), 98.0 (d, $J_{C\text{-}F}$ = 27.7 Hz), 51.2, 44.1, 21.1. FTIR (KBr): 3400, 3067, 2923, 1710, 1605, 1497, 1453, 1374, 1342, 1167, 1079, 939, 697 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{18}FNNaO$ $[M+Na]^+$ = 354.1270, found 354.1259.



3j

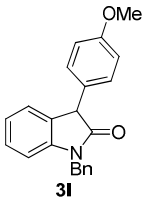
1-Benzyl-3-(4-isobutylphenyl)indolin-2-one (3j): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 – 7.12 (m, 11H), 7.02 – 6.98 (m, 1H), 6.77 (d, J = 7.8 Hz 1H), 4.98 (d, J = 15.6 Hz 1H), 4.90 (d, J = 15.6 Hz 1H), 4.67 (s, 1H), 2.45 (d, J = 7.1 Hz 2H), 1.90 – 1.80 (m, 1H), 0.90 (d, J = 6.6 Hz 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 143.6, 141.1, 136.0, 133.9, 129.7, 129.2, 128.8, 128.2, 128.1, 127.6, 127.4, 125.1, 122.7, 109.2, 51.8, 45.1, 44.0, 30.2, 22.4, 22.4. FTIR (KBr): 3411, 3056, 2948, 2922, 1711, 1609, 1488, 1466, 1357, 1199, 1165, 748, 731, 699 cm^{-1}. HRMS (ESI): calcd for $C_{25}H_{25}NNaO$

$[M+Na]^+$ = 378.1270, found 378.1287.



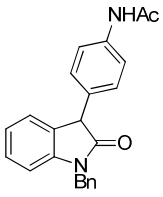
3k

1-Benzyl-3-(biphenyl-4-yl)indolin-2-one (3k): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, *J* = 8.1 Hz 4H), 7.44 – 7.40 (m, 2H), 7.35 – 7.23 (m, 8H), 7.23 – 7.19 (m, 2H), 7.05 – 7.01 (m, 1H), 6.80 (d, *J* = 7.7 Hz 1H), 5.00 (d, *J* = 15.6 Hz 1H), 4.91 (d, *J* = 15.6 Hz 1H), 4.74 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 143.7, 140.8, 140.7, 135.9, 135.8, 128.9, 128.8, 128.8, 128.4, 127.8, 127.7, 127.4, 127.6, 127.1, 125.20, 122.6, 109.3, 51.8, 44.0. FTIR (KBr): 3411, 3031, 2923, 1711, 1608, 1487, 1466, 1354, 1197, 1007, 762, 750, 695 cm^{-1}. HRMS (ESI): calcd for $C_{27}H_{21}NNaO$ $[M+Na]^+$ = 398.1521, found 398.1520.



3l

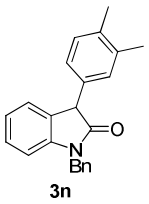
1-Benzyl-3-(4-methoxyphenyl)indolin-2-one (3l): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 – 7.13 (m, 9H), 7.02 – 6.99 (m, 1H), 6.88 (d, *J* = 8.6 Hz 2H), 6.77 (d, *J* = 7.7 Hz 1H), 4.98 (d, *J* = 15.6 Hz 1H), 4.88 (d, *J* = 15.6 Hz 1H), 4.64 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 159.1, 143.6, 136.0, 129.5, 129.2, 128.8, 128.7, 128.3, 127.6, 127.4, 125.1, 122.8, 114.4, 109.2, 55.3, 51.3, 43.9. FTIR (KBr): 3025, 2923, 1710, 1609, 1515, 1486, 1467, 1346, 1255, 1180, 1023, 752, 696 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{19}NNaO_2$ $[M+Na]^+$ = 352.1313, found 352.1300.



3m

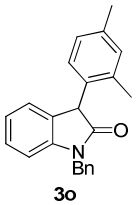
***N*-(4-(1-benzyl-2-oxoindolin-3-yl)phenyl)acetamide (3m):** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (s, 1H), 7.38 (d, *J* = 8.3 Hz 2H), 7.30 – 7.19 (m, 6H), 7.13 (d, *J* = 7.3 Hz 1H), 7.08 (d, *J* = 8.3 Hz 2H), 7.04 – 7.00 (m, 1H), 6.80 (d, *J* = 7.8 Hz 1H), 4.99 (d, *J* = 15.6 Hz 1H), 4.90 (d, *J* = 15.6 Hz 1H), 4.65 (s, 1H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.5, 168.6, 143.4, 137.7, 135.8, 132.0, 128.9,

128.9, 128.4, 127.7, 127.3, 125.2, 123.0, 120.6, 109.3, 51.7, 44.0, 24.4. FTIR (KBr): 3314, 2923, 2852, 1710, 1692, 1609, 1513, 1487, 1465, 1410, 1363, 1316, 1268, 1182, 1010, 751, 697 cm^{-1}. HRMS (ESI): calcd for $C_{23}H_{21}N_2O_2$ $[M+H]^+$ = 357.1603, found 357.1615.



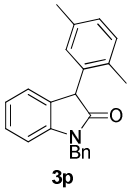
3n

1-Benzyl-3-(3,4-dimethylphenyl)indolin-2-one (3n): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 – 7.13 (m, 7H), 7.09 (d, *J* = 7.7 Hz 1H), 7.01 – 6.98 (m, 2H), 6.92 (d, *J* = 7.7 Hz 1H), 6.77 (d, *J* = 7.8 Hz 1H), 4.98 (d, *J* = 15.6 Hz 1H), 4.88 (d, *J* = 15.6 Hz 1H), 4.62 (s, 1H), 2.23 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 143.6, 137.2, 136.1, 136.0, 134.2, 130.2, 129.7, 129.7, 128.8, 128.2, 127.7, 127.4, 125.8, 125.1, 122.8, 109.1, 51.8, 44.0, 19.9, 19.5. FTIR (KBr): 3032, 2921, 1711, 1611, 1486, 1466, 1346, 1181, 1081, 751, 697 cm^{-1}. HRMS (ESI): calcd for $C_{23}H_{21}NNaO$ $[M+Na]^+$ = 350.1521, found 350.1511.



3o

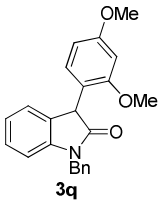
1-Benzyl-3-(2,4-dimethylphenyl)indolin-2-one (3o): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34 – 7.16 (m, 6H), 7.06 – 6.91 (m, 4H), 6.80 – 6.60 (m, 2H), 4.97 – 4.85 (m, 3H), 2.64 – 2.05 (br, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 143.6, 137.4, 137.1, 136.1, 132.5, 131.9, 129.5, 128.8, 128.1, 127.9, 127.7, 127.5, 127.1, 124.7, 122.8, 109.1, 44.0, 21.0, 19.8. FTIR (KBr): 3407, 3033, 2917, 1711, 1610, 1487, 1466, 1357, 1202, 1164, 754, 726, 696 cm^{-1}. HRMS (ESI): calcd for $C_{23}H_{21}NNaO$ $[M+Na]^+$ = 350.1521, found 350.1504.



3p

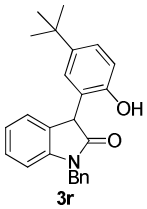
1-Benzyl-3-(2,5-dimethylphenyl)indolin-2-one (3p): ^{1}H NMR (400 MHz, d^6-DMSO, 70 °C): δ 7.39 – 7.18 (m, 6H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.00 – 6.93 (m, 4H), 6.69 (s, 1H), 5.03 (s, 1H), 5.03 – 4.90 (m, 2H), 2.17 (s, 6H). ^{13}C NMR (100 MHz, d^6-DMSO, 70 °C): δ 175.6, 143.2, 136.5, 135.8, 135.0,

133.7, 130.6, 129.4, 128.5, 127.9, 127.9, 127.4, 127.3, 124.1, 122.3, 109.0, 49.6, 43.1, 20.4, 18.6. FTIR (KBr): 3031, 2924, 1702, 1614, 1487, 1466, 1353, 1170, 754, 699 cm^{-1}. HRMS (ESI): calcd for $C_{23}H_{21}NNaO$ $[M+Na]^+$ = 350.1521, found 350.1521.



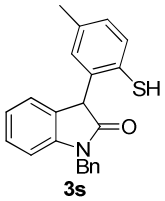
3q

1-Benzyl-3-(2,4-dimethoxyphenyl)indolin-2-one (3q): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 – 7.24 (m, 5H), 7.15 – 7.11 (m, 1H), 7.04 – 7.02 (m, 2H), 6.04 – 6.90 (m, 1H), 6.74 (d, J = 7.8 Hz 1H), 6.47 – 6.45 (m, 2H), 5.10 (d, J = 15.6 Hz 1H), 4.85 (d, J = 15.6 Hz 1H), 4.82 (s, 1H), 3.78 (s, 3H), 3.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 160.6, 158.5, 143.3, 136.3, 130.9, 130.1, 128.7, 127.6, 127.6, 127.5, 124.0, 122.4, 118.2, 108.7, 104.7, 99.5, 55.6, 55.4, 48.0, 43.9. FTIR (KBr): 3410, 3024, 2923, 1711, 1611, 1487, 1466, 1347, 1209, 1160, 1129, 1082, 1047, 1025, 750, 699 cm^{-1}. HRMS (ESI): calcd for $C_{23}H_{21}NNaO_3$ $[M+Na]^+$ = 382.1419, found 382.1434.



3r

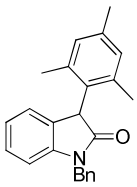
1-Benzyl-3-(5-tert-butyl-2-hydroxyphenyl)indolin-2-one (3r): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.72 (s, 1H), 7.33 – 7.24 (m, 7H), 7.20 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.16 – 7.12 (m, 1H), 6.96 (d, J = 8.2 Hz 2H), 6.86 (d, J = 7.8 Hz 1H), 5.18 (s, 1H), 4.94 (s, 2H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.7, 153.5, 143.7, 143.6, 135.3, 128.9, 128.5, 127.8, 127.3, 126.6, 126.0, 125.9, 124.5, 123.1, 122.5, 118.2, 110.0, 48.2, 44.1, 34.3, 31.5. FTIR (KBr): 3338, 3062, 2960, 2866, 1691, 1679, 1612, 1487, 1467, 1369, 1276, 1186, 821, 697 cm^{-1}. HRMS (ESI): calcd for $C_{25}H_{25}NNaO_2$ $[M+Na]^+$ = 394.1783, found 394.1778.



3s

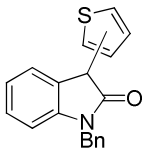
1-Benzyl-3-(2-mercapto-5-methylphenyl)indolin-2-one (3s): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (d, J = 7.3 Hz 1H), 7.25 (s, 1H), 7.20 – 7.15 (m, 3H), 7.12 – 7.08 (m, 1H), 7.06 – 7.02 (m, 1H), 6.96

(d, J = 7.9 Hz 2H), 6.93 – 6.91 (m, 2H), 6.49 (d, J = 7.7 Hz, 1H), 4.93 (d, J = 15.8 Hz 1H), 4.57 (d, J = 15.8 Hz 1H), 4.57 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 143.2, 139.1, 135.3, 135.1, 129.6, 128.9, 128.6, 127.4, 127.1, 126.8, 126.4, 125.3, 122.7, 109.2, 49.6, 44.0, 21.3. FTIR (KBr): 3408, 3060, 2921, 1710, 1610, 1487, 1466, 1453, 1377, 1351, 1177, 803, 746, 733, 723, 699 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{20}NOS$ $[M+H]^+$ = 346.1266, found 346.1268.



3t

1-Benzyl-3-mesitylindolin-2-one (3t): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (d, J = 7.2 Hz 2H), 7.33 – 7.30 (m, 1H), 7.27 – 7.24 (m, 1H), 7.19 – 7.15 (m, 1H), 6.96 – 6.93 (m, 3H), 6.82 (d, J = 7.8 Hz 2H), 6.75 (s, 1H), 5.08 (s, 1H), 5.06 (d, J = 15.4 Hz 1H), 4.91 (d, J = 15.4 Hz 1H), 2.52 (s, 3H), 2.25 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 143.2, 137.9, 137.1, 137.0, 136.1, 130.5, 130.3, 129.1, 128.8, 127.9, 127.80, 127.7, 123.7, 122.7, 108.8, 48.2, 44.3, 21.3, 20.9, 19.3. FTIR (KBr): 3426, 3055, 2922, 1723, 1611, 1485, 1465, 1351, 1199, 1164, 1096, 1011, 922, 885, 859, 748, 727, 697 cm^{-1}. HRMS (ESI): calcd for $C_{24}H_{24}NO$ $[M+H]^+$ = 342.1858, found 342.1861.



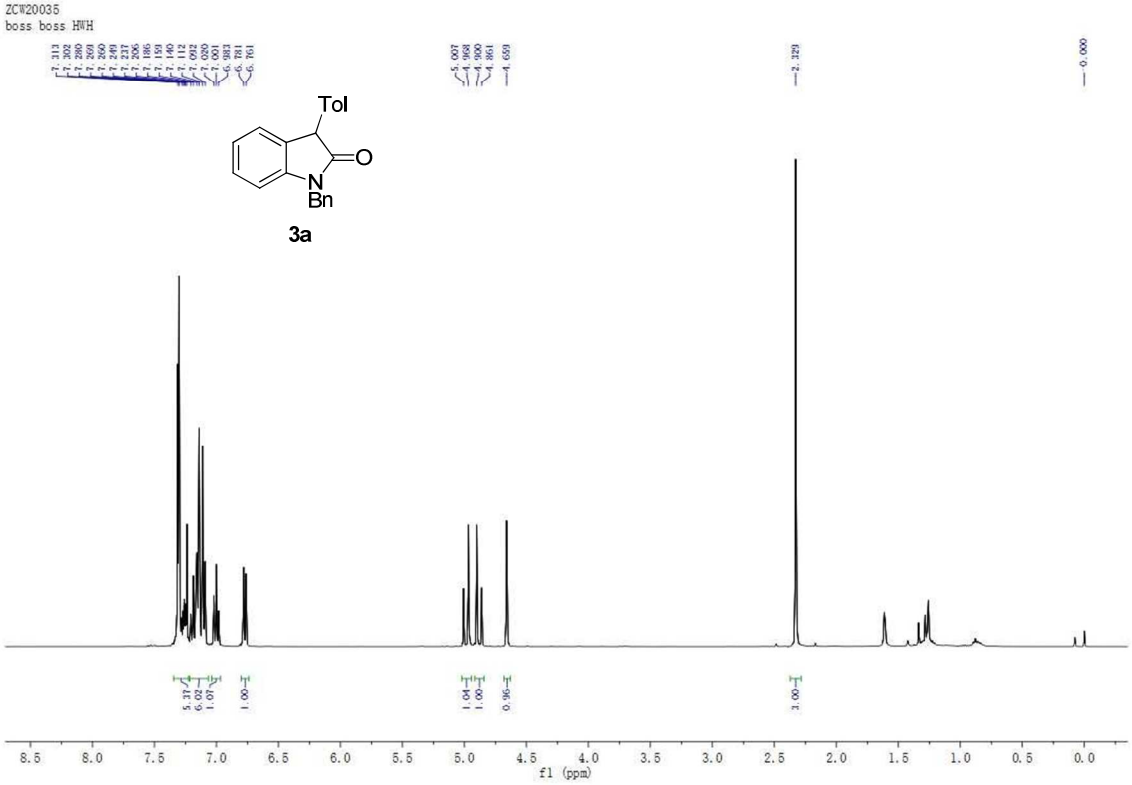
3u

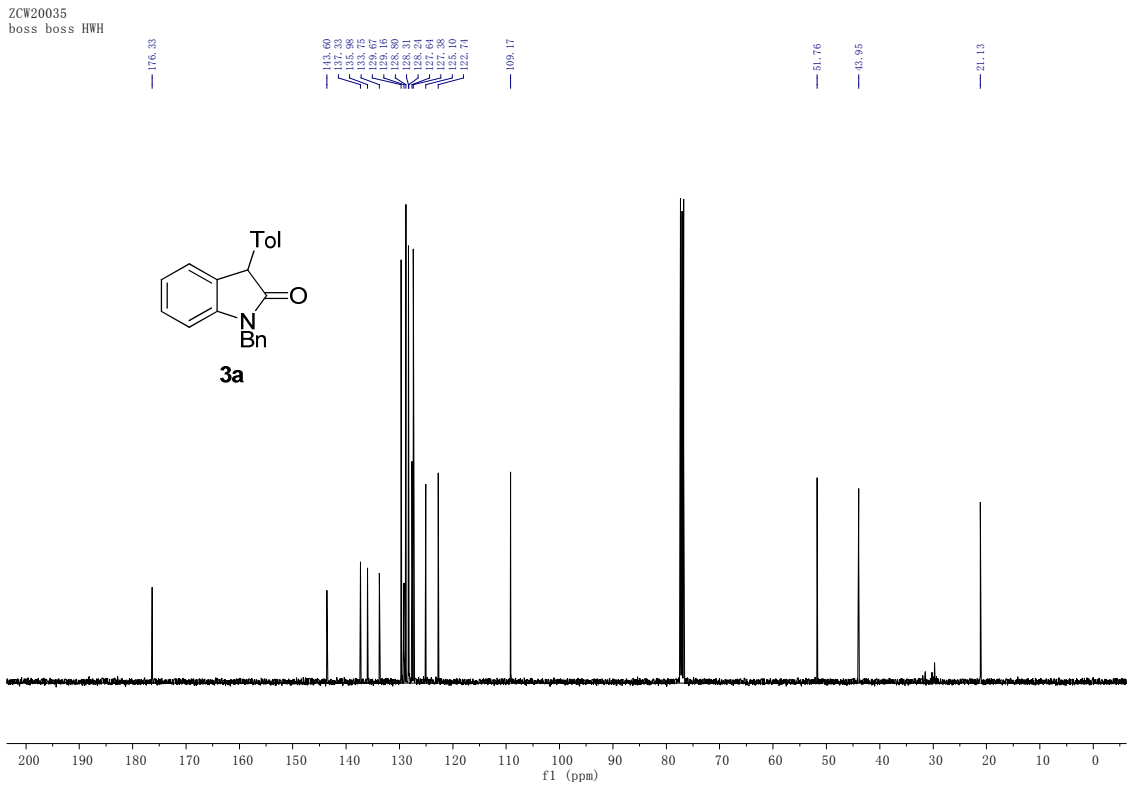
1-Benzyl-3-(thiophen-2-yl)indolin-2-one (3u): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34 – 7.16 (m, 8H), 7.06 – 6.99 (m, 3H), 6.77 (d, J = 7.8 Hz 1H), 4.97 (d, J = 15.7 Hz 1H), 4.95 (s, 1H), 4.88 (d, J = 15.7 Hz 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ174.8, 143.3, 138.2, 135.9, 135.7, 128.8, 128.7, 127.7, 127.3, 127.1, 126.2, 125.3, 125.2, 122.6, 109.4, 47.1, 44.1. HRMS (ESI): calcd for $C_{19}H_{15}NNaOS$ $[M+Na]^+$ = 328.0772, found 328.0769.

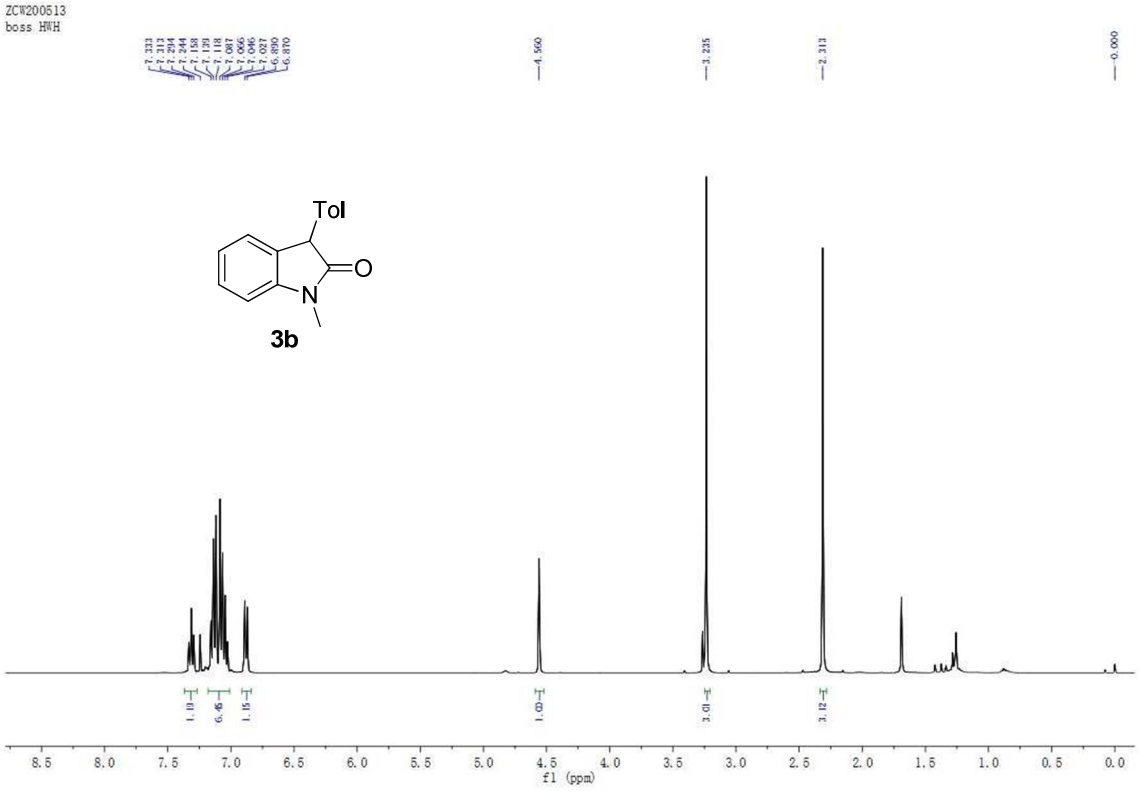
4. Reference

1 (a) Song, H.; Yang, J.; Chen, W.; Qin, Y. *Org. Lett.* **2006***, 8,* 6011. (b) Marti, C.; Carreira, E. M. *J. Am. Chem. Soc.* **2005**, *127*, 11505. (c) Muthusamy S.; Gunanathan C.; Nethaji M. *J. Org. Chem*. **2004**, *69*, 5631−5637.

5. NMR spectra



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7.081
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7.027
6.990
6.970
4.560
3.235
2.313
0.000
Tol
O
N
3b
1.19
6.45
1.15
1.00
3.01
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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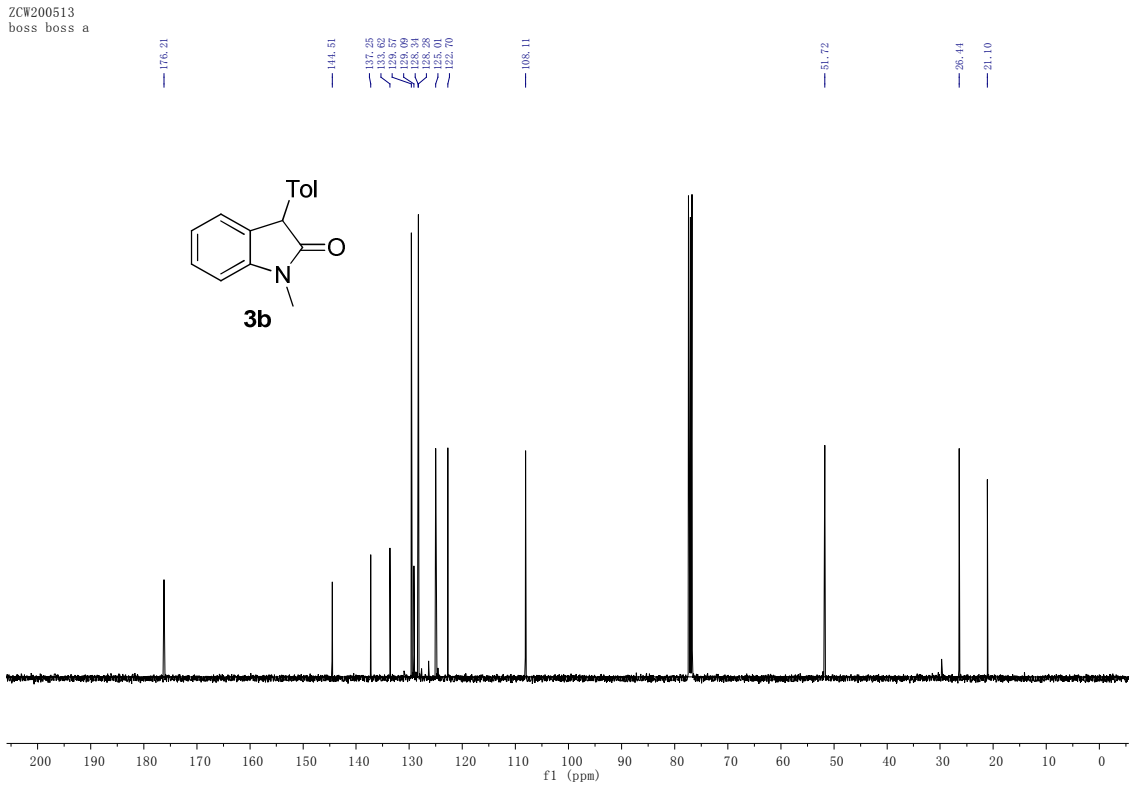
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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boss boss a
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108.11
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N
3b
200
190
180
170
160
150
140
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90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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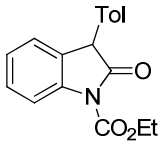
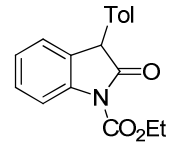
boss HWH

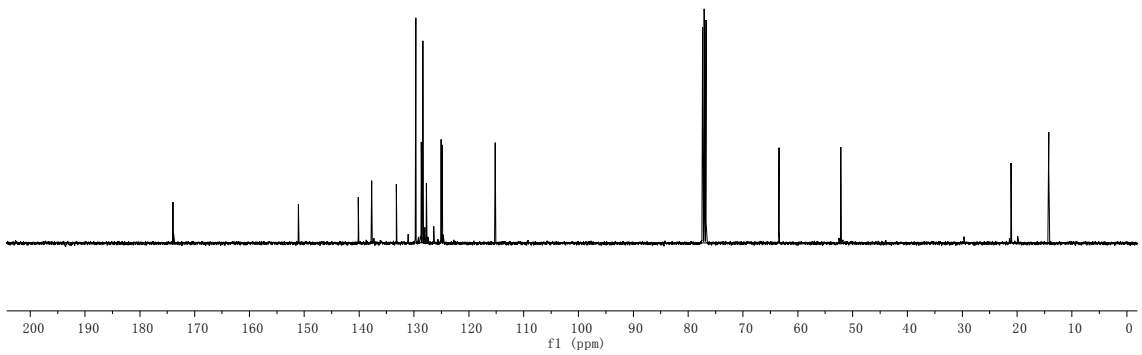


3c

ZCW200512
boss boss a



3c



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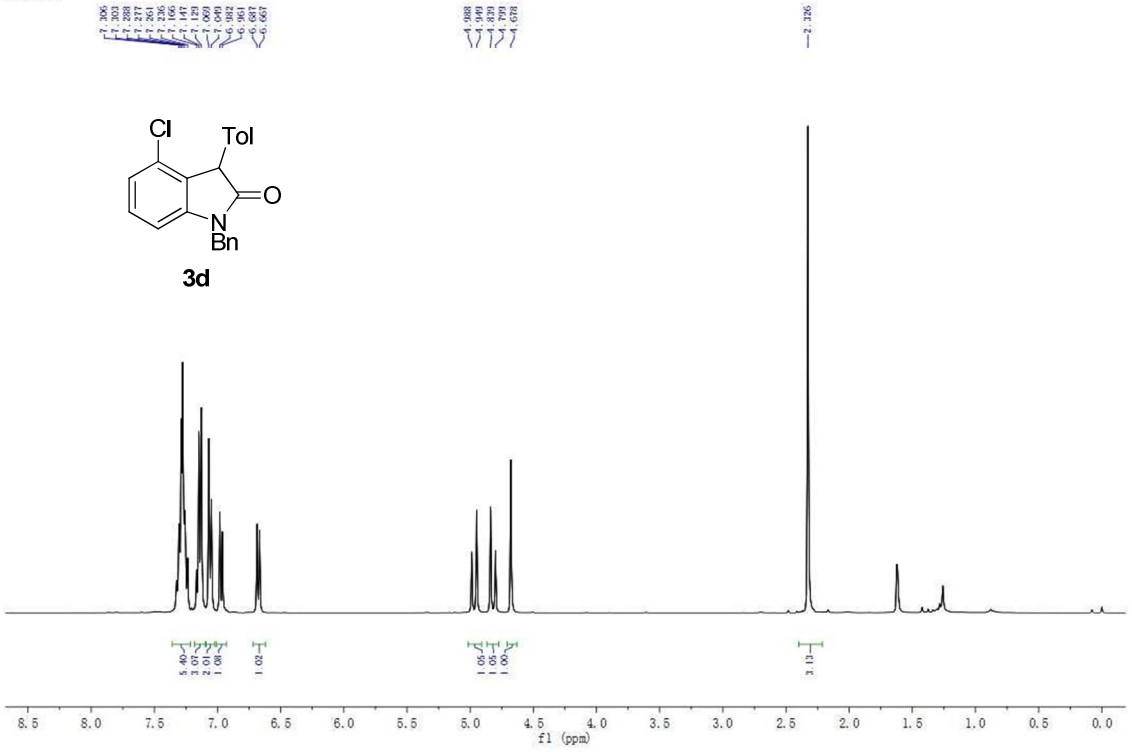

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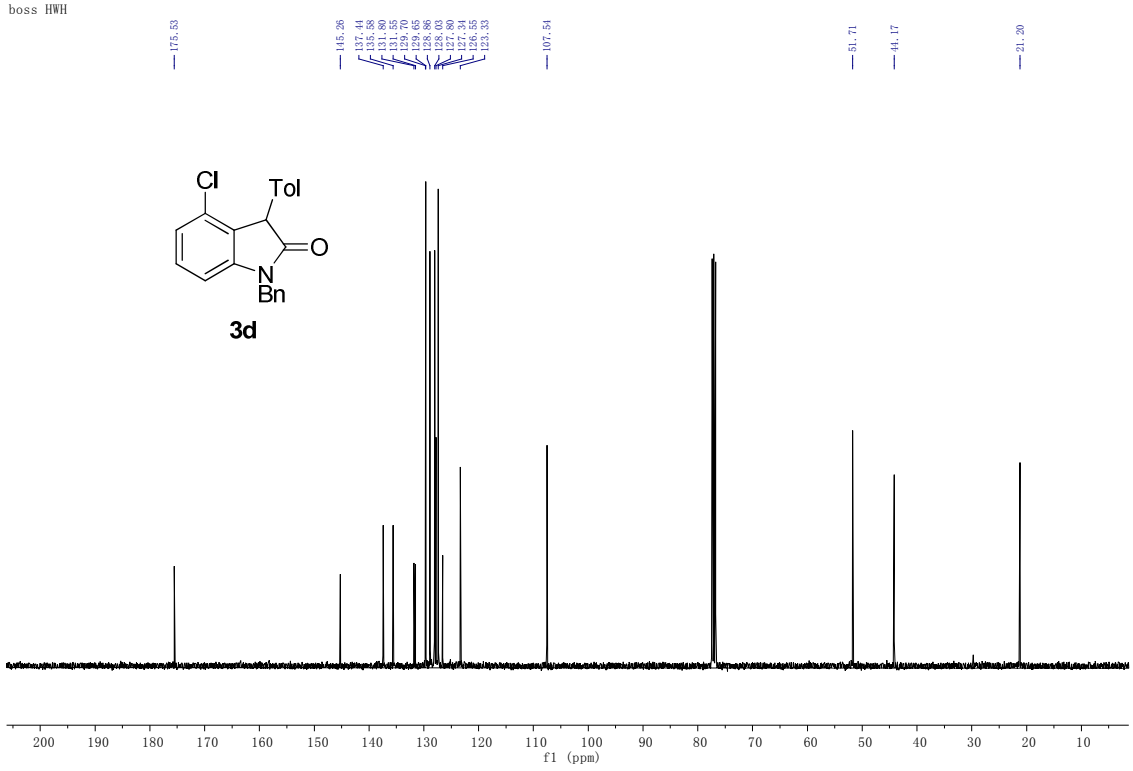

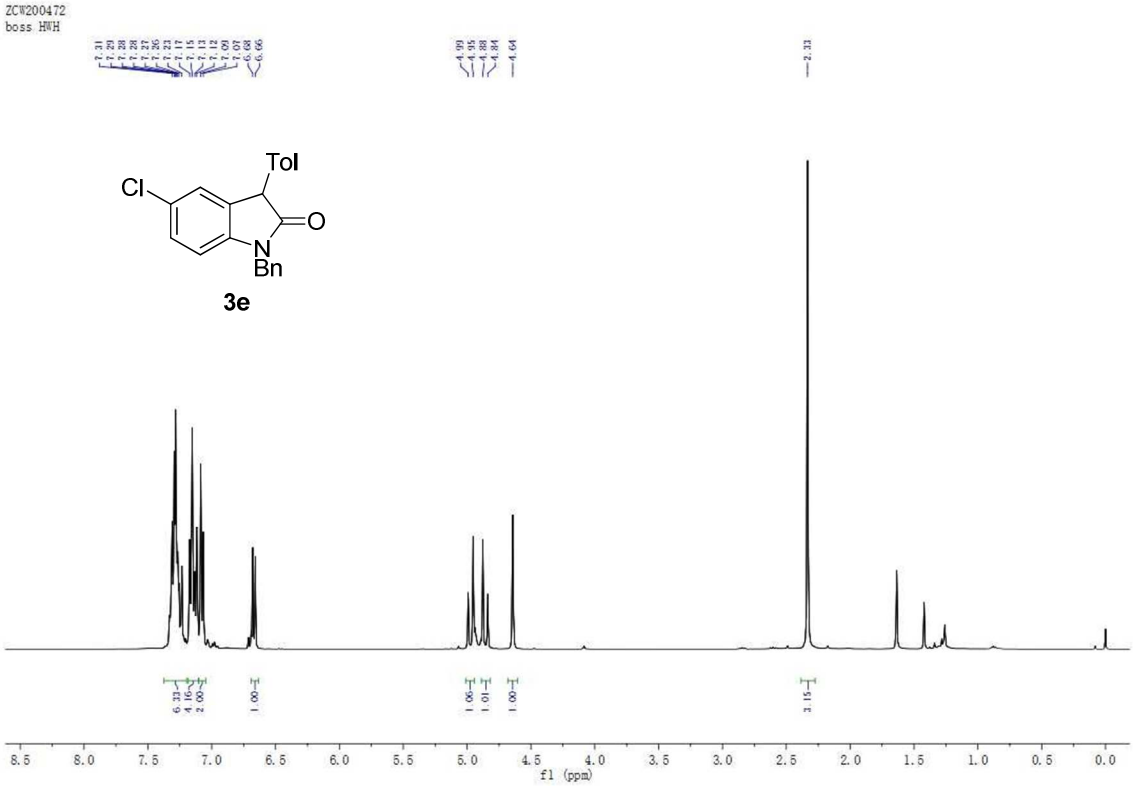
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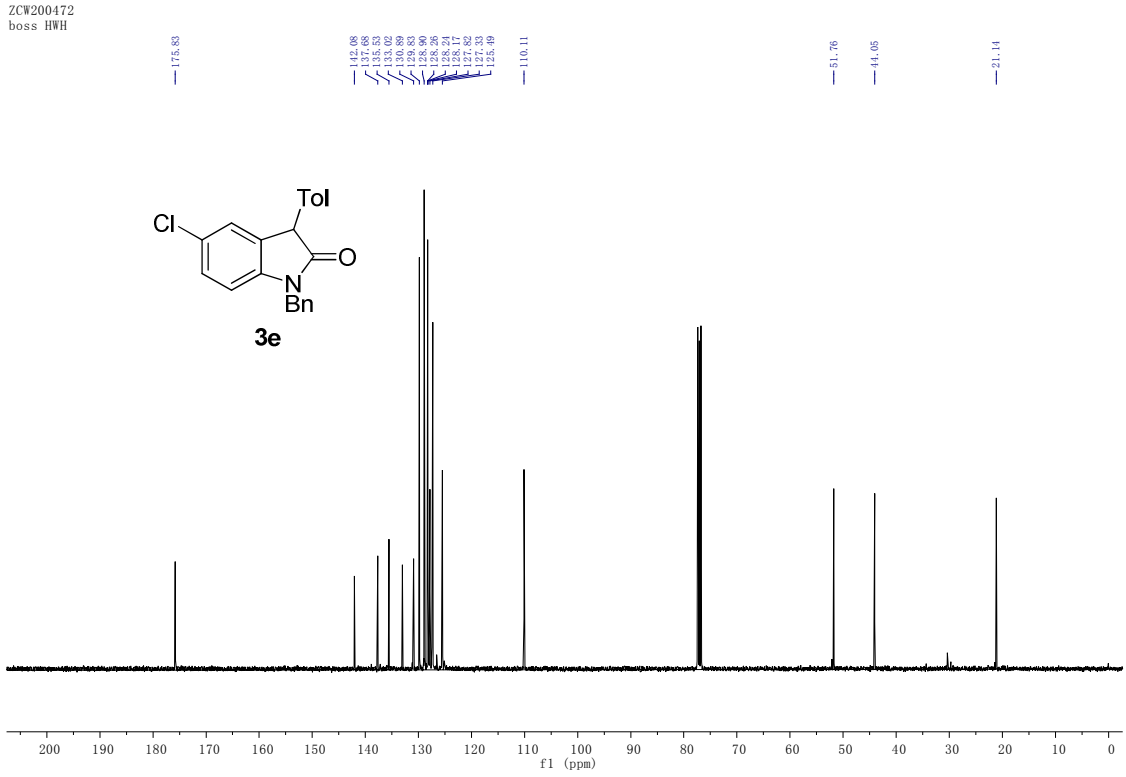
Cl
O
N
Bn
3e
f1 (ppm)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N
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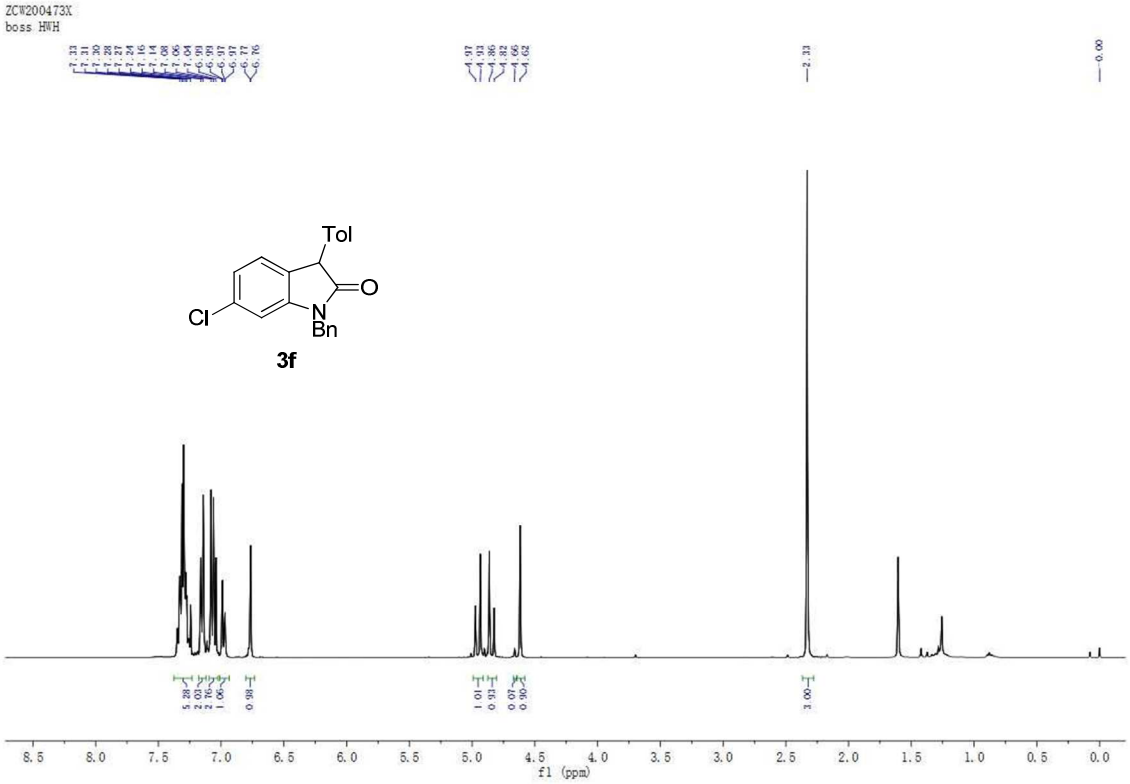
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Cl
O
N
Bn
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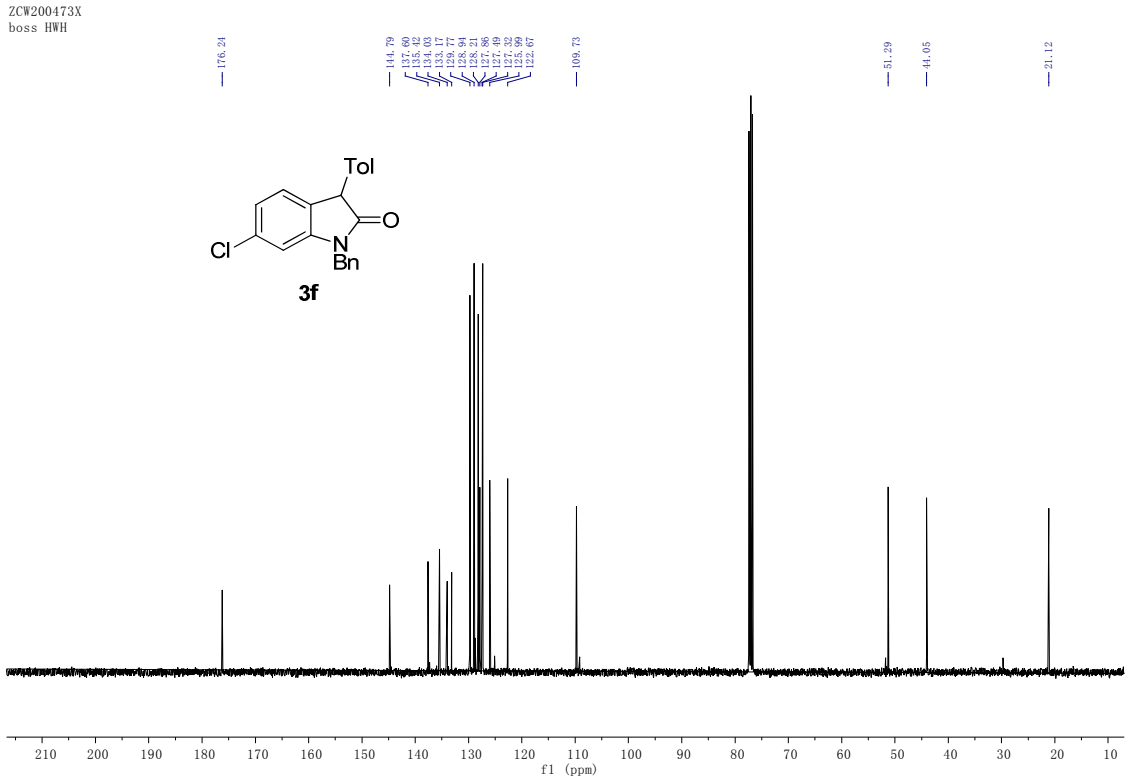
f1 (ppm)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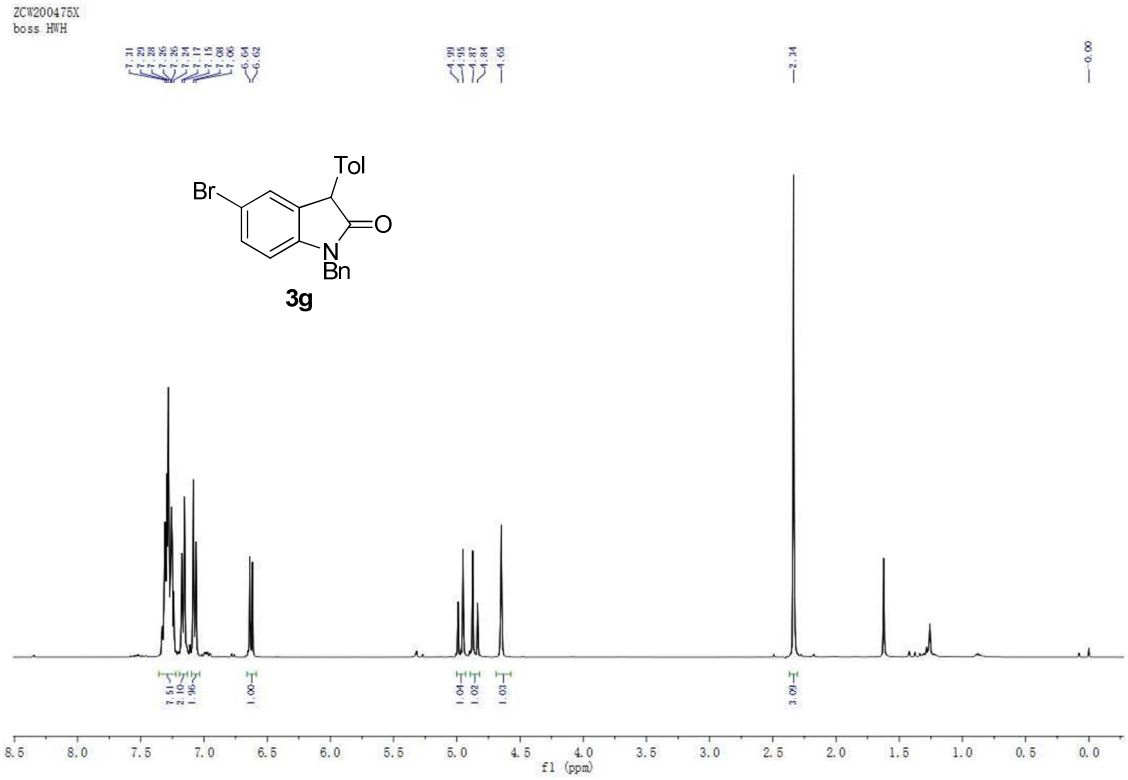
Tol
Cl
O
N
Bn
3f
f1 (ppm)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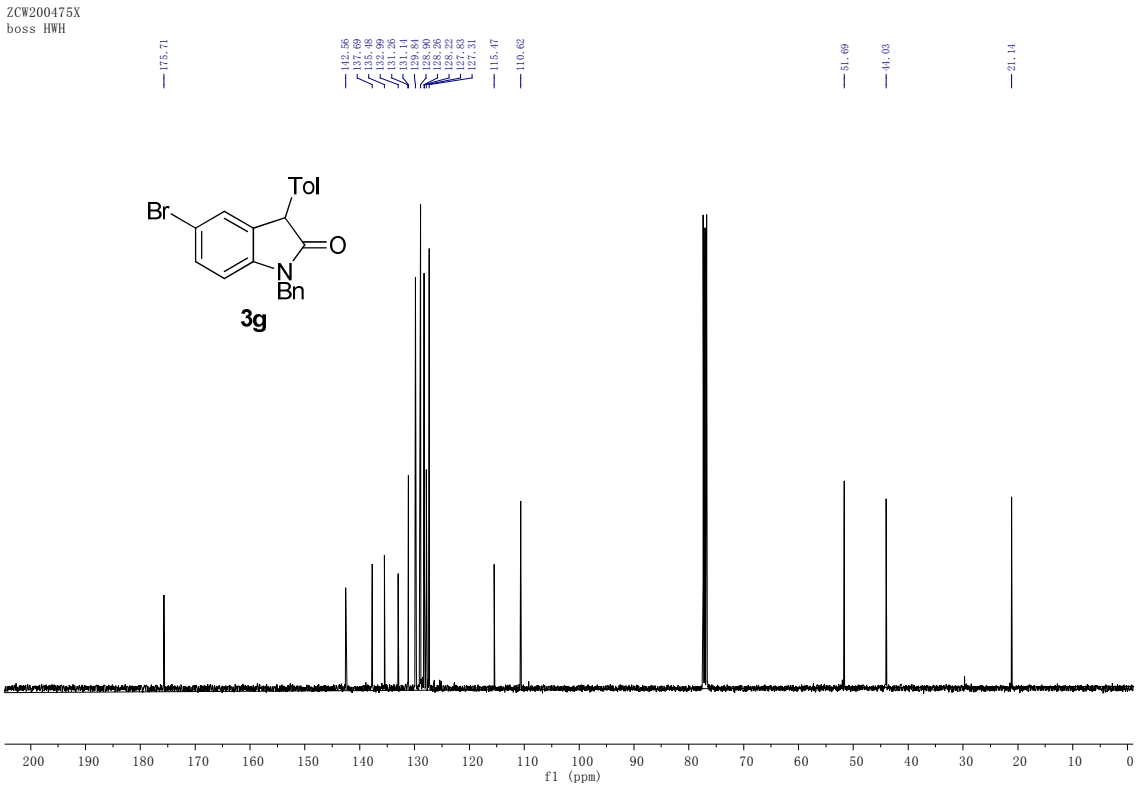
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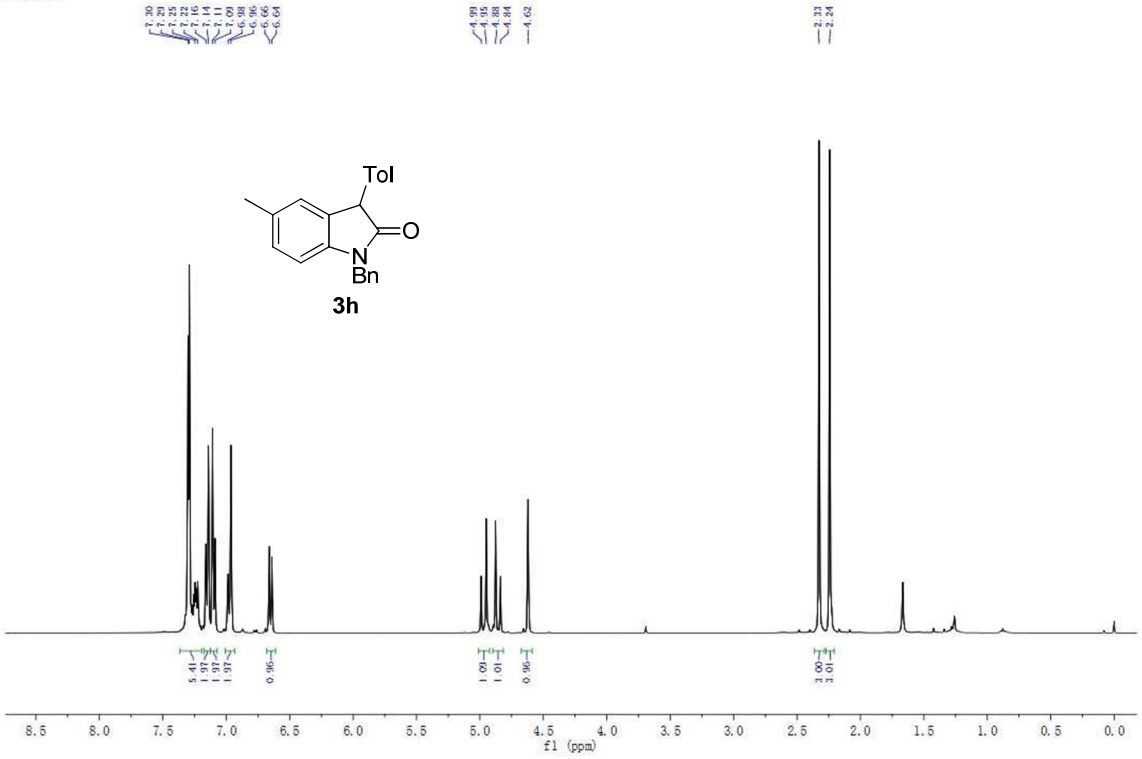
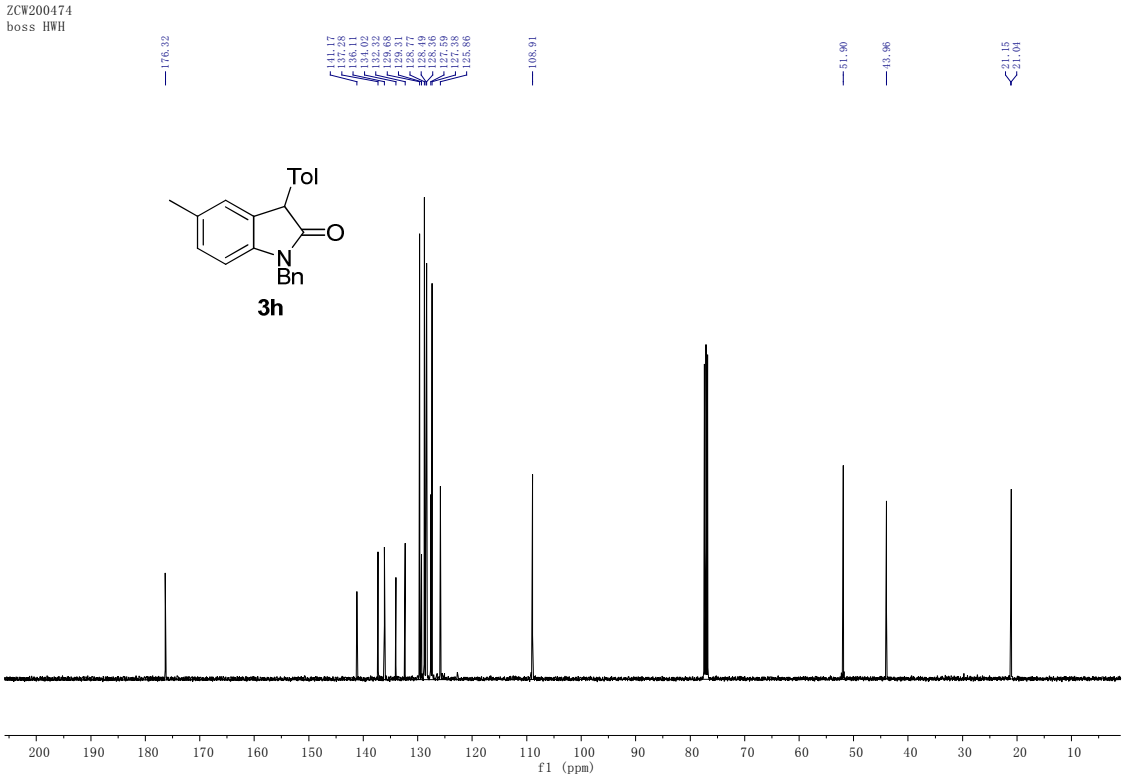
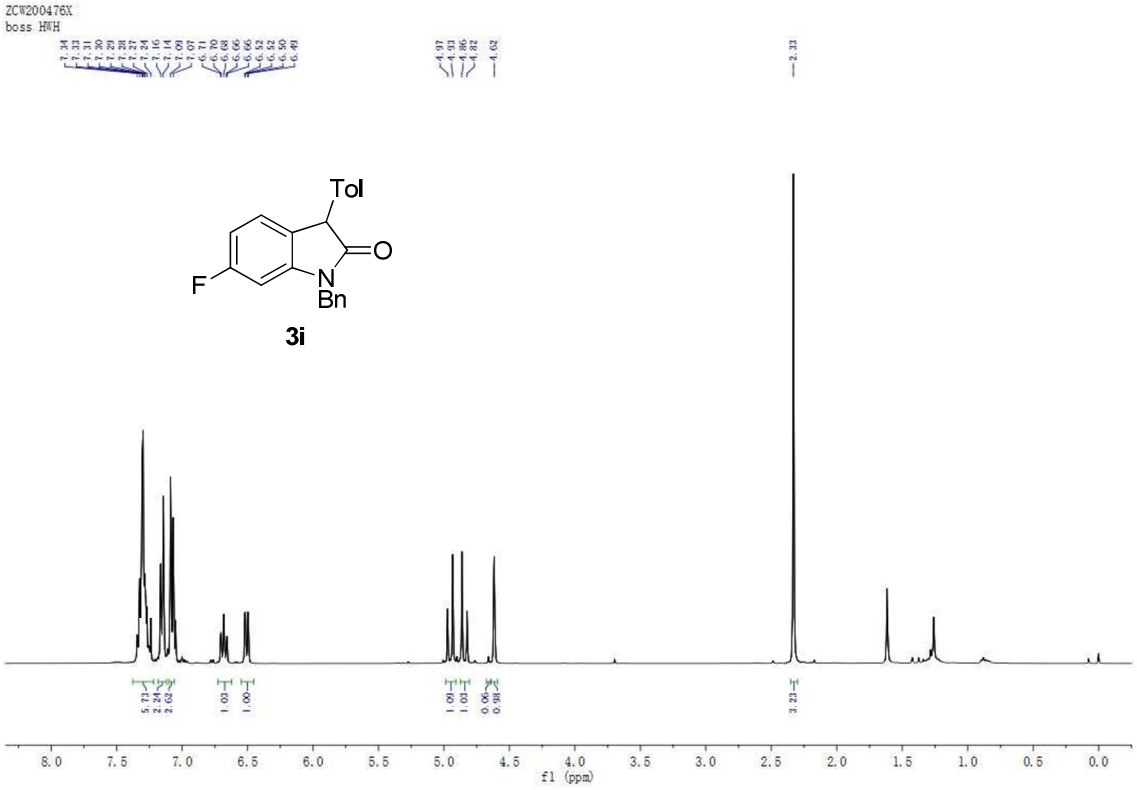
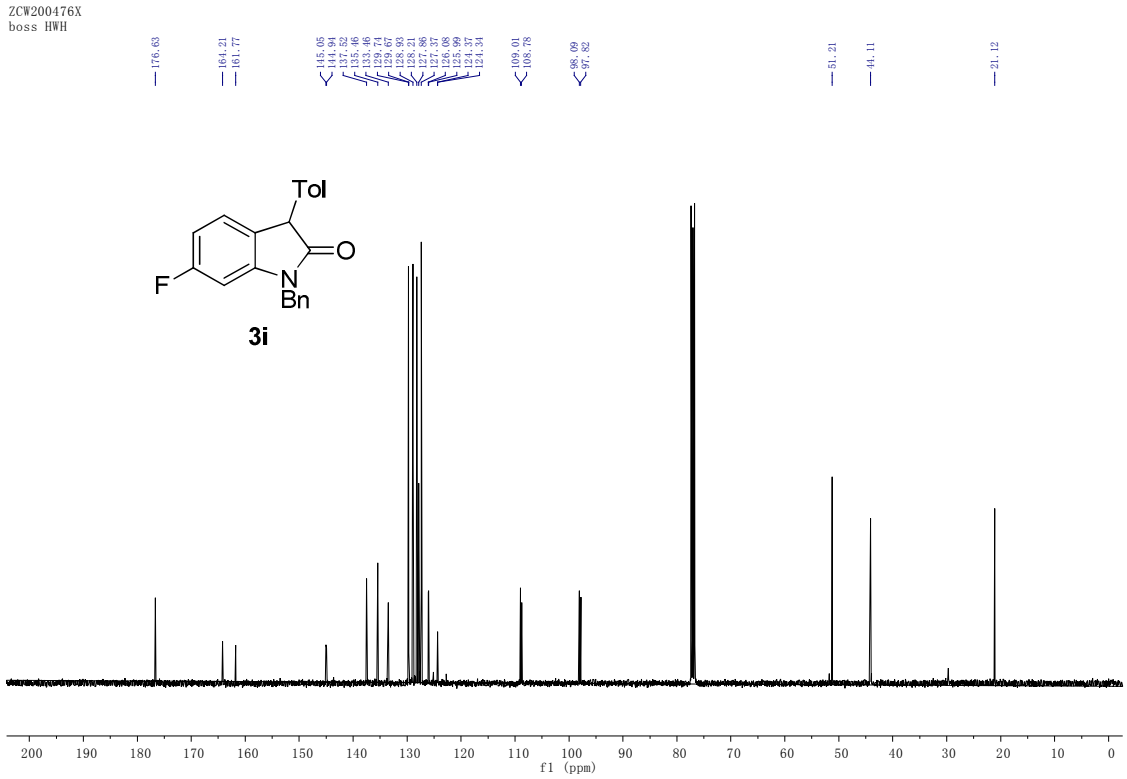
boss HWH

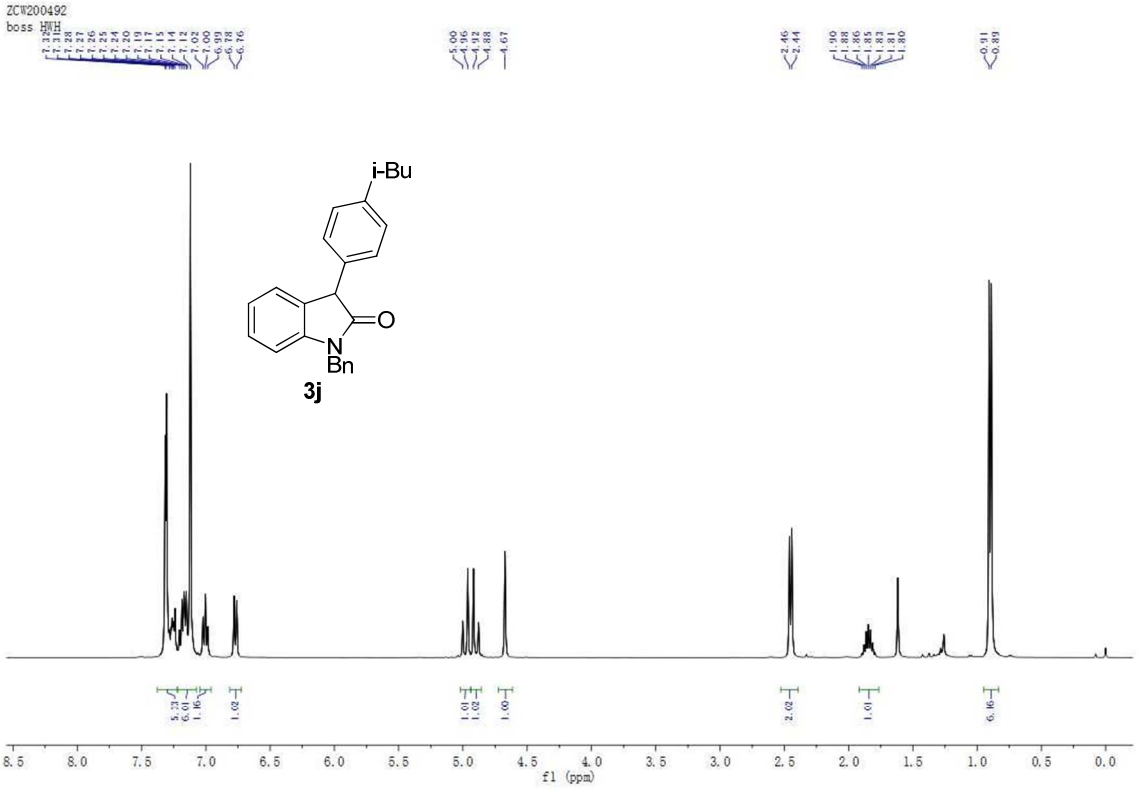


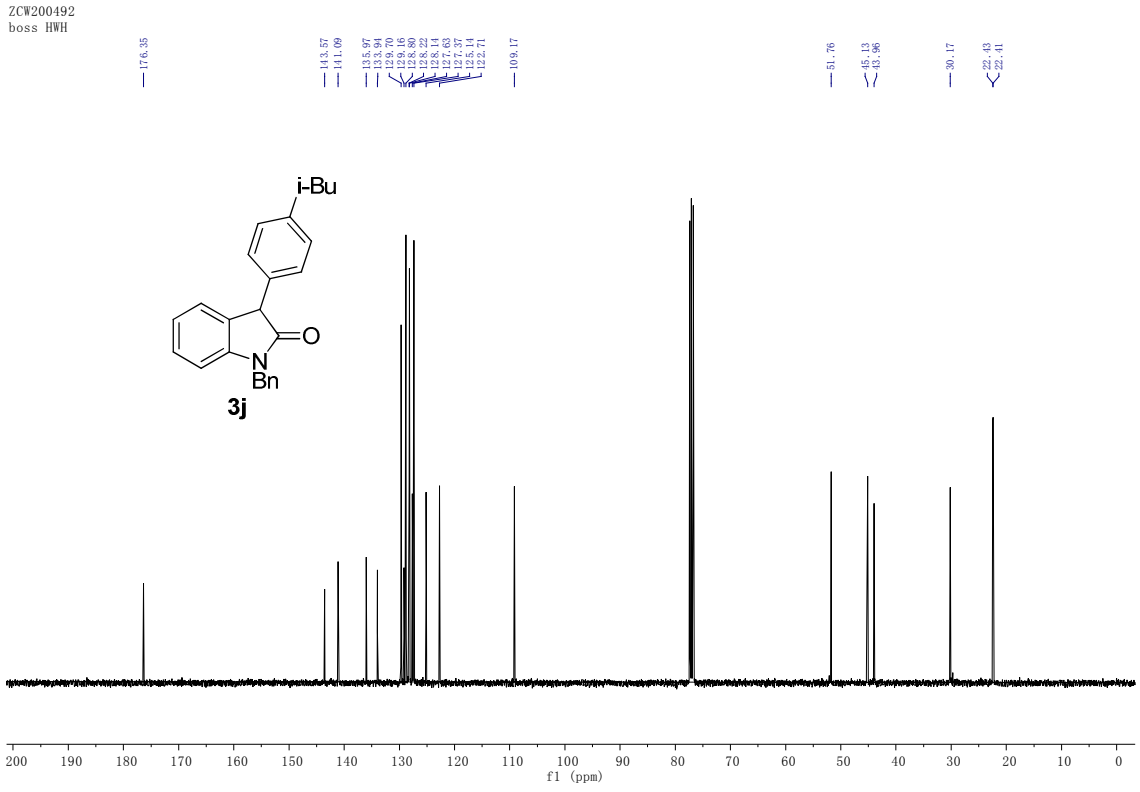
ZCW200474
boss HWH

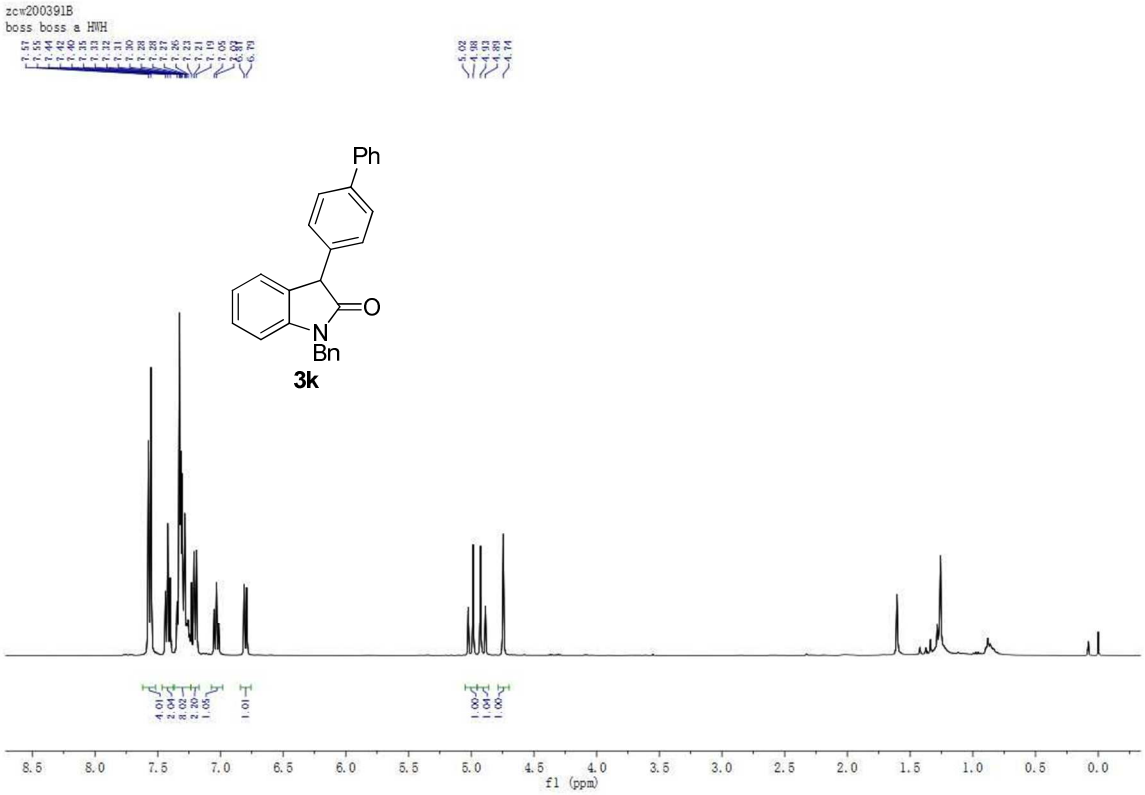


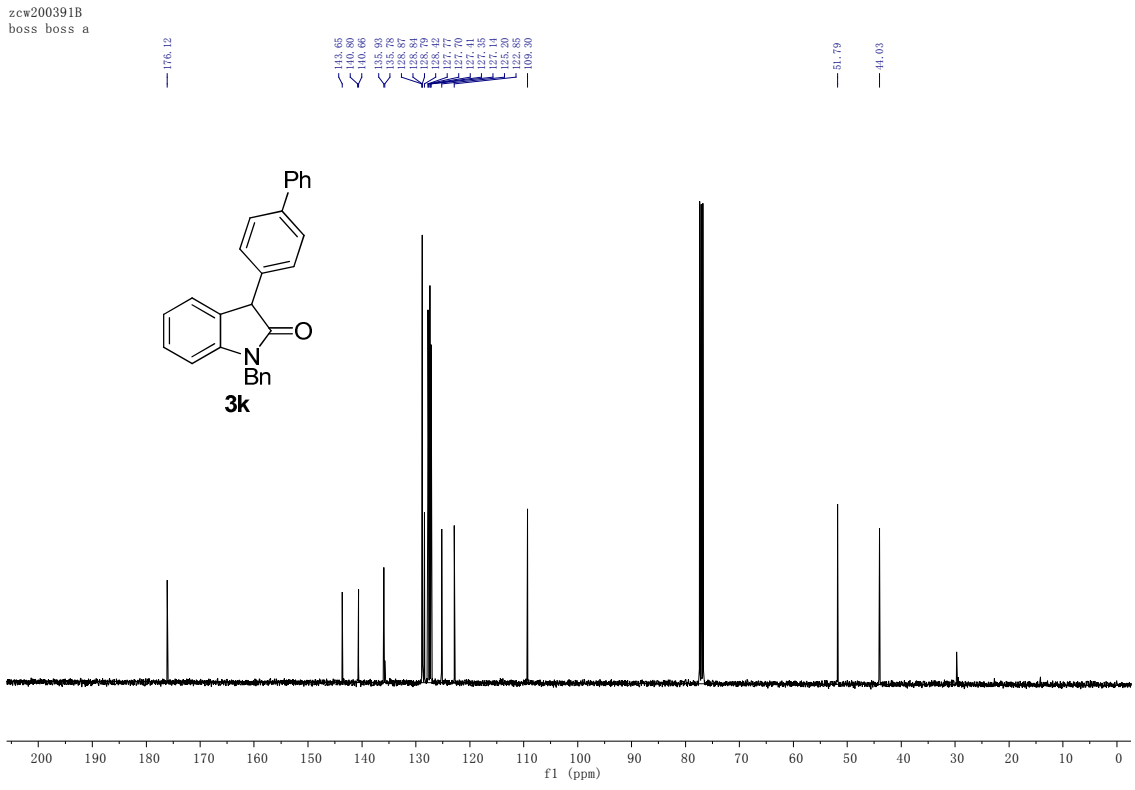

ZCW200476X
boss HWH
Tol
O
F
N
Bn
3i
f1 (ppm)

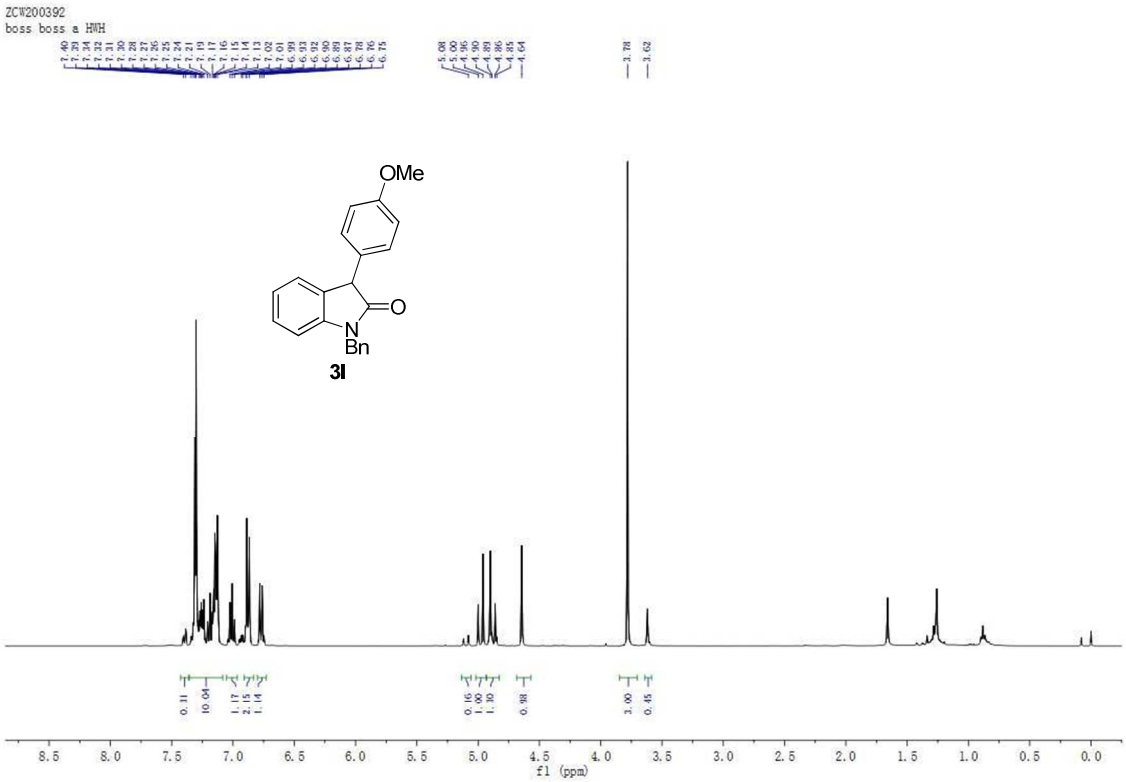

ZCW200476X
boss HWH
Tol
O
F
N
Bn
3i
f1 (ppm)

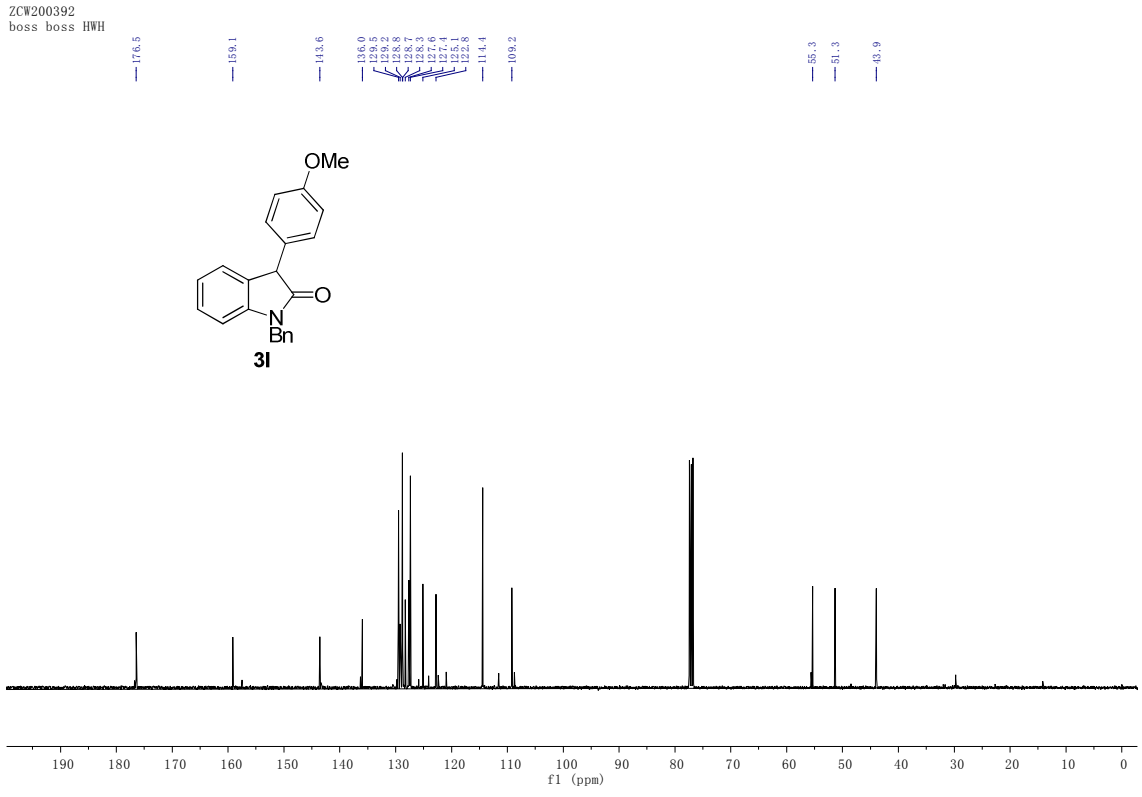

ZCW200492
boss HWH
i-Bu
O
N
Bn
3j
f1 (ppm)


ZCW200492
boss HWH
i-Bu
O
N
Bn
3j
f1 (ppm)

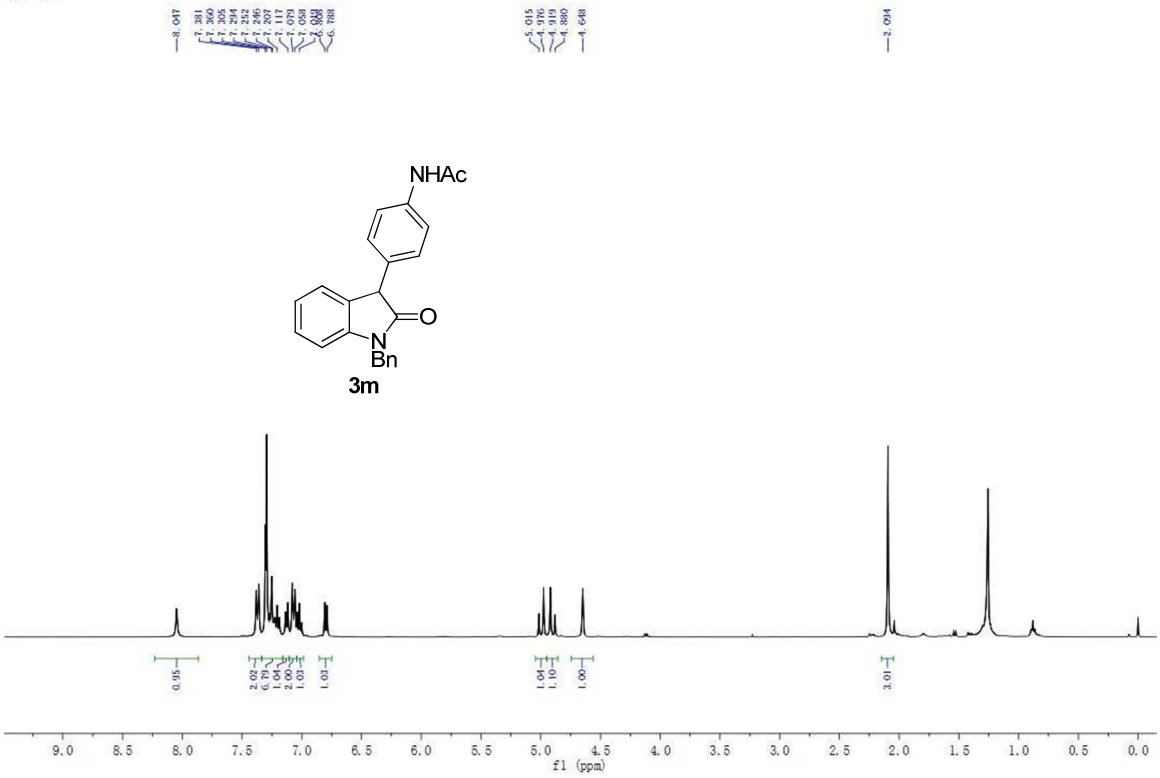

zcw200391B
boss boss a HNH
Ph
O
N
Bn
3k
f1 (ppm)


zcw200391B
boss boss a
Ph
O
N
Bn
3k
f1 (ppm)

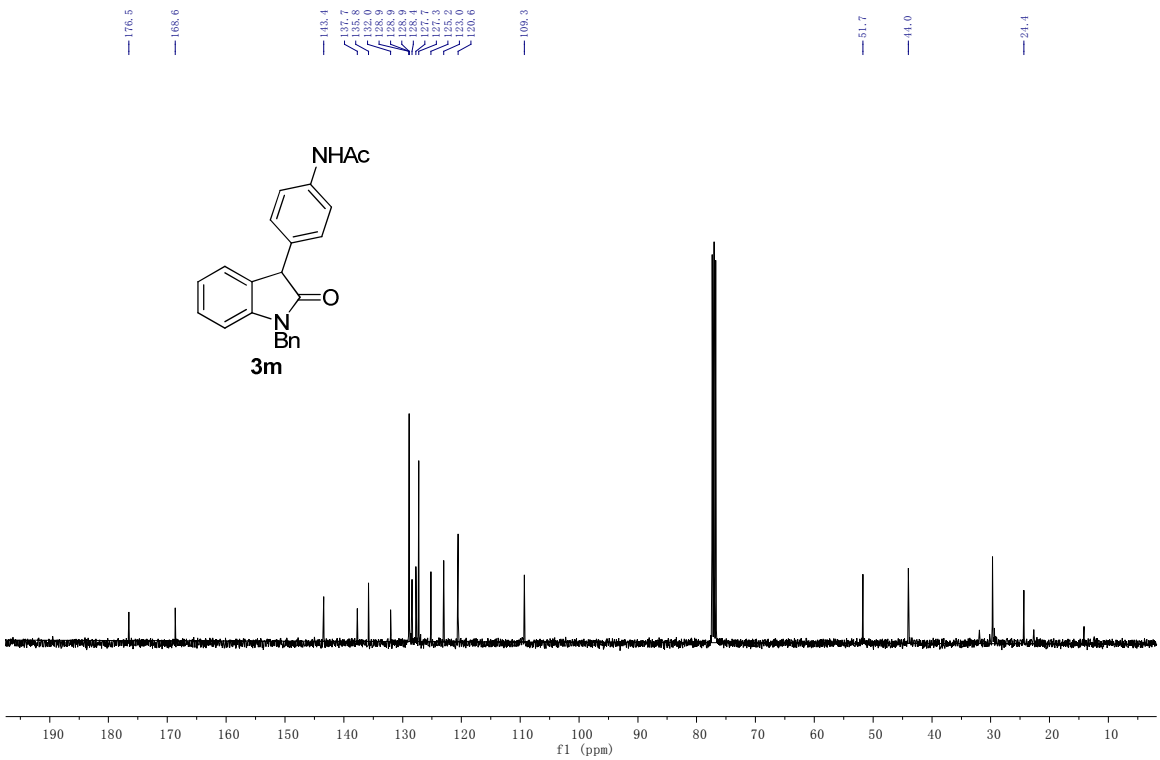

ZCW200392
boss boss a HWH
OMe
O
N
Bn
3l
f1 (ppm)

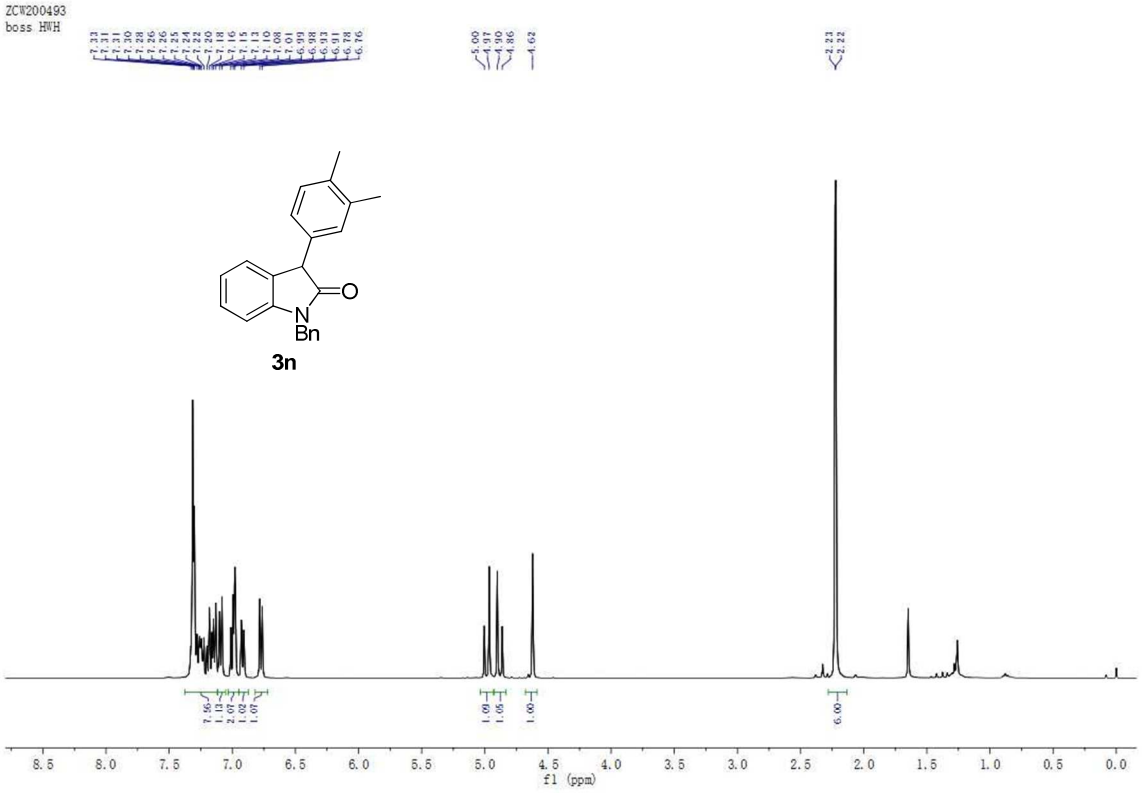

ZCW200392
boss boss HWH
OMe
O
N
Bn
3l
f1 (ppm)

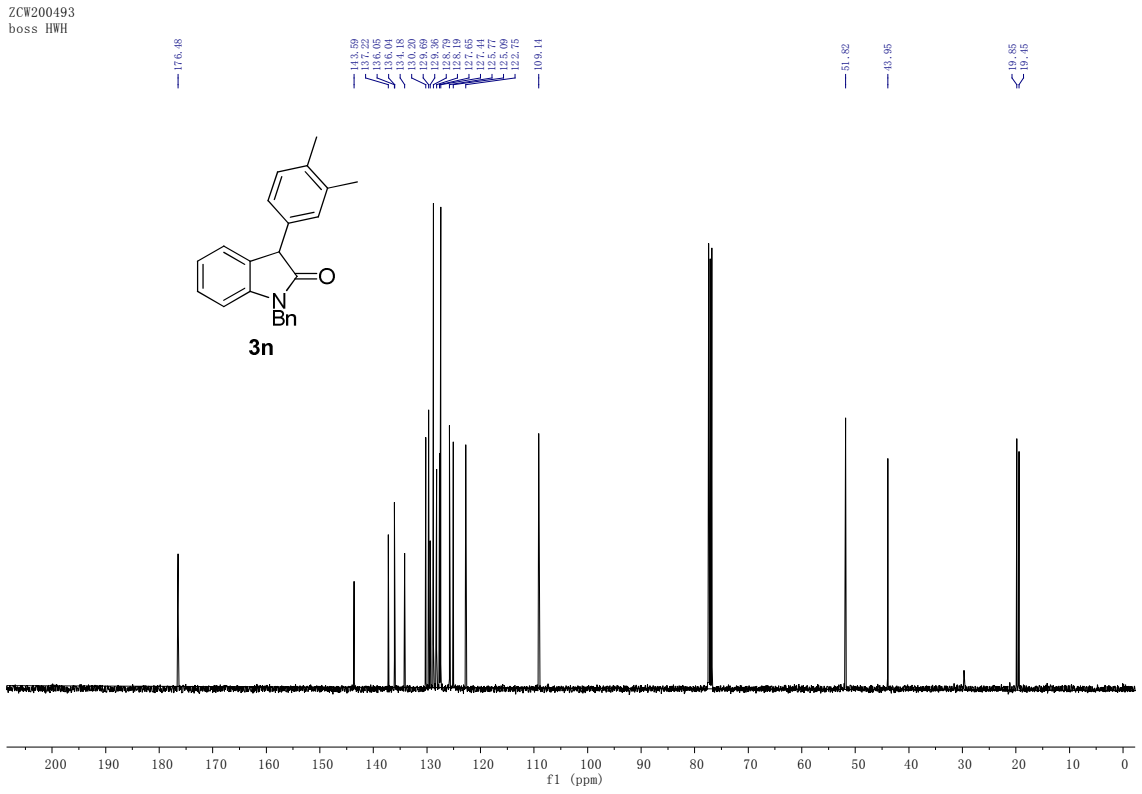
ZCW20-148-1Y
boss HWH

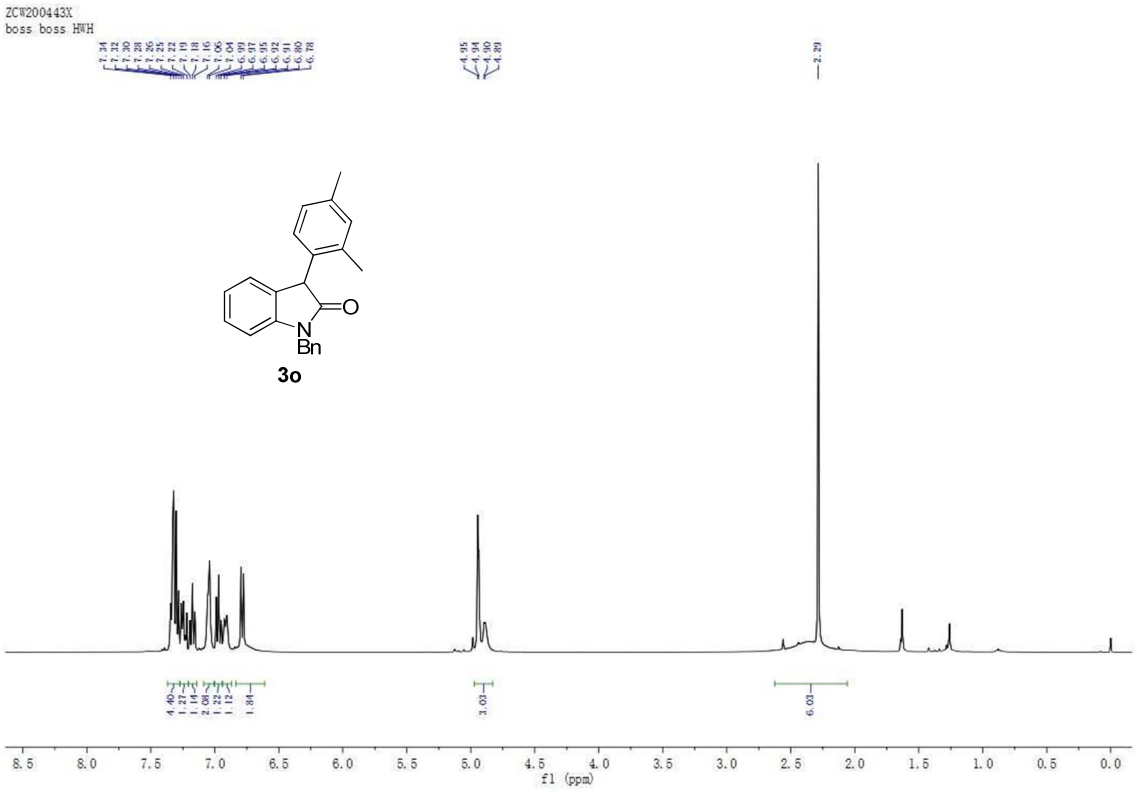


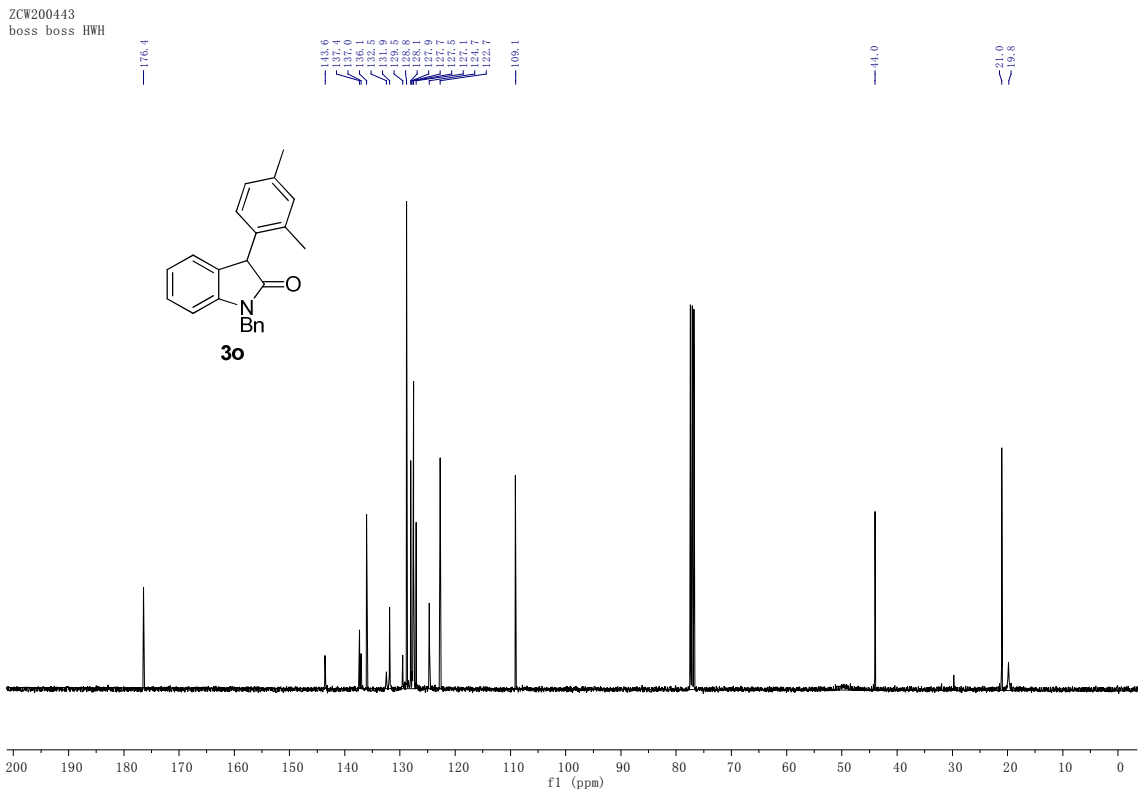
ZCW20-148-1Z
boss HWH

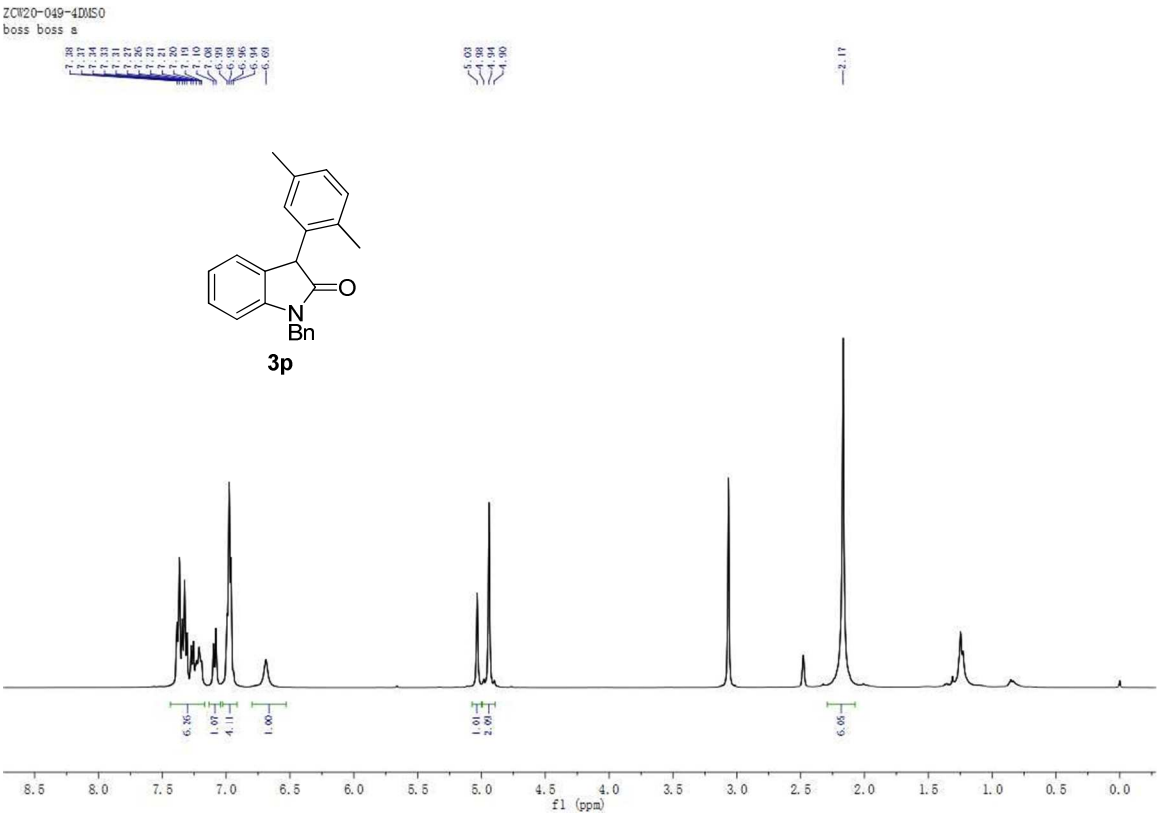


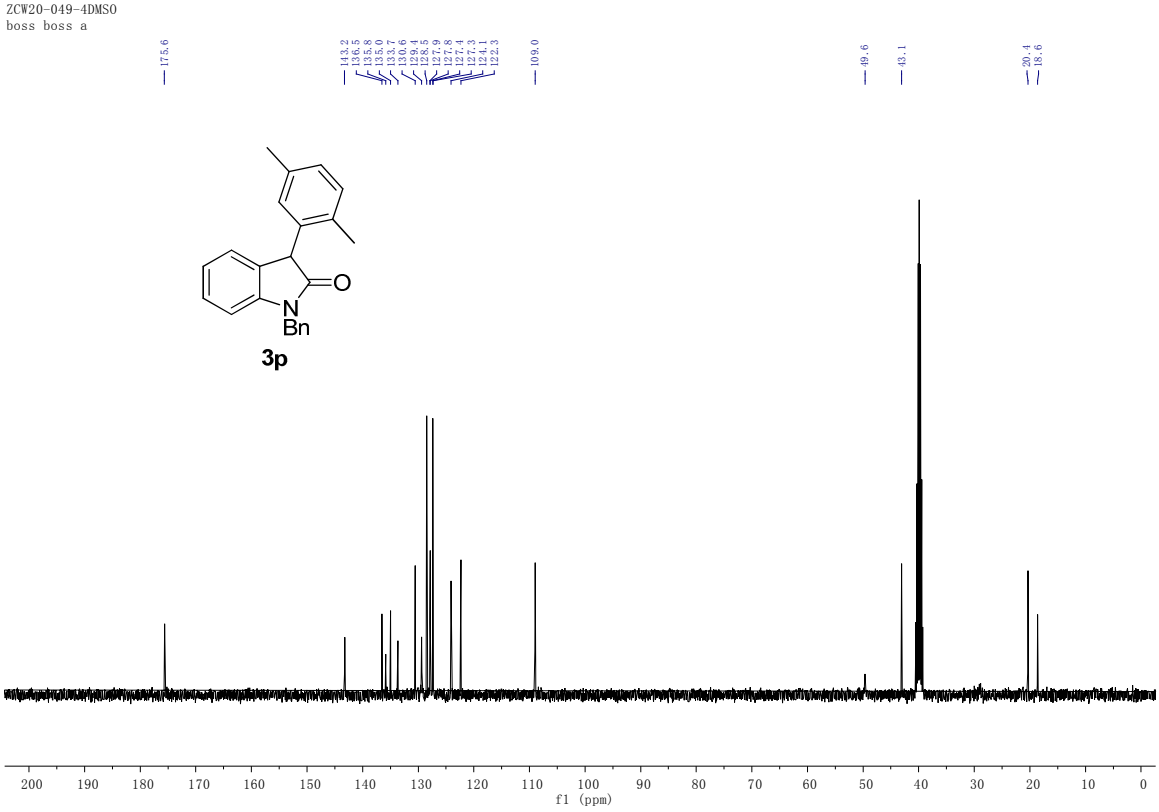

ZCW200493
boss HWH
3n
f1 (ppm)

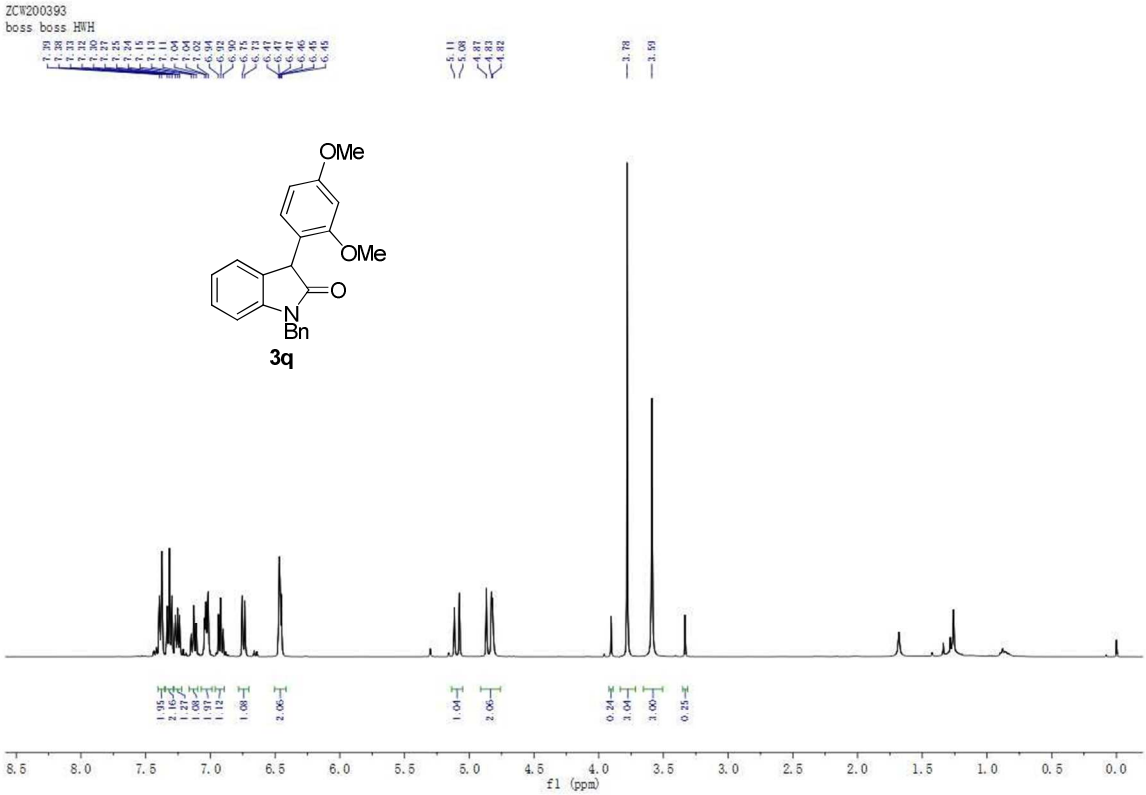

ZCW200493
boss HWH
3n
f1 (ppm)

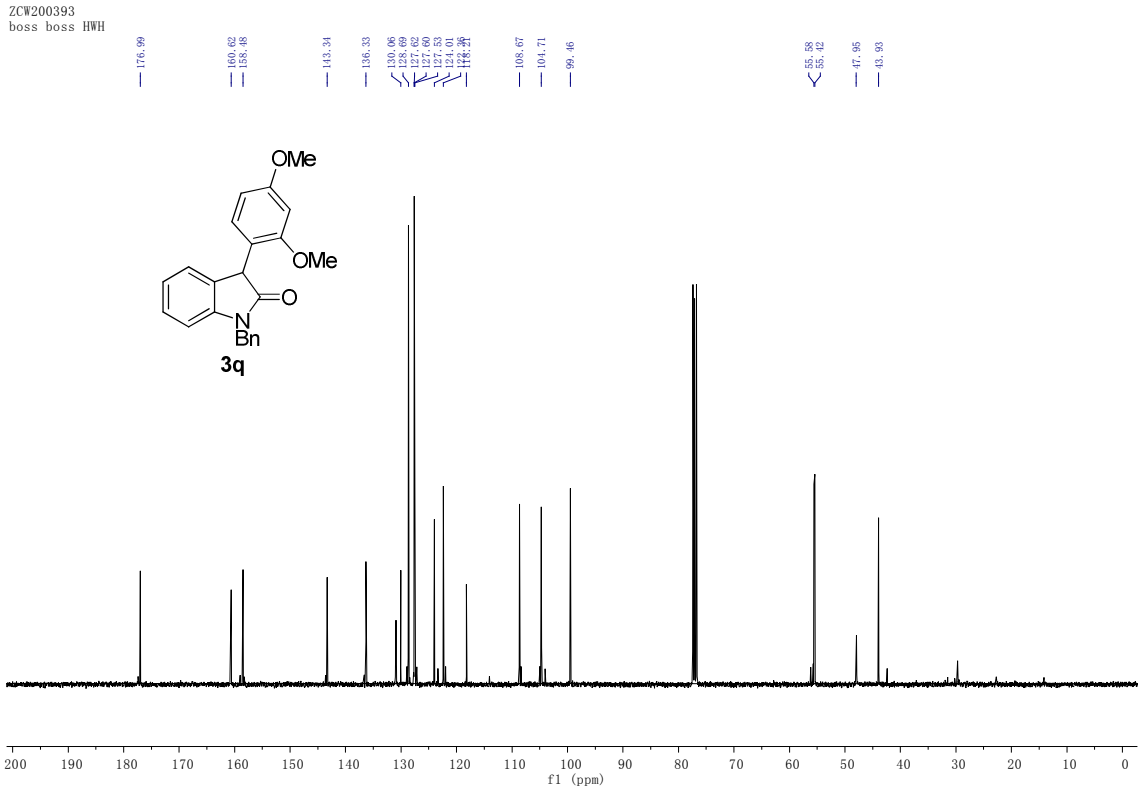

ZCW200443X
boss boss HWH
7.34
7.32
7.30
7.28
7.26
7.25
7.23
7.22
7.19
7.18
7.16
7.06
7.05
6.99
6.97
6.95
6.92
6.91
6.80
6.78
4.95
4.94
4.90
4.89
2.29
O
N
Bn
3o
4.40
1.27
1.14
2.08
2.02
1.12
1.84
3.03
6.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

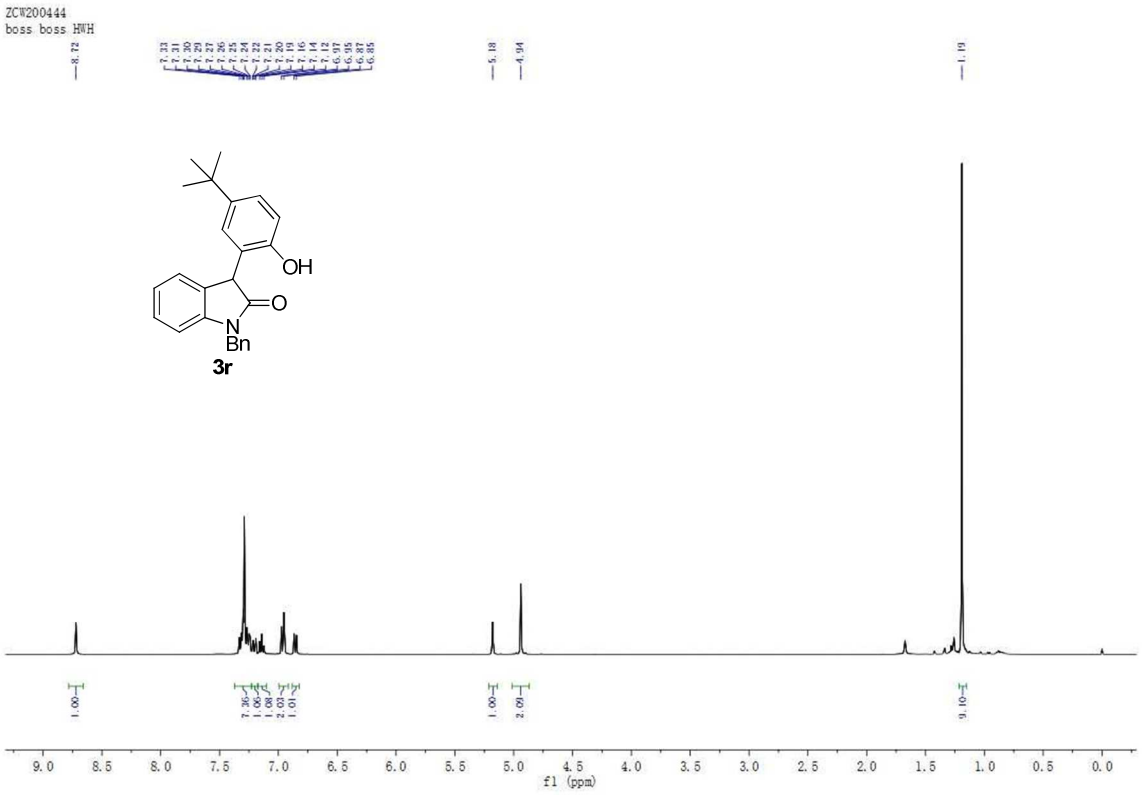

ZCW200443
boss boss HWH
176.4
143.6
137.4
137.0
136.1
132.5
131.9
129.5
128.8
128.1
127.9
127.7
127.5
127.1
124.7
122.7
109.1
44.0
21.0
19.8
O
N
Bn
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

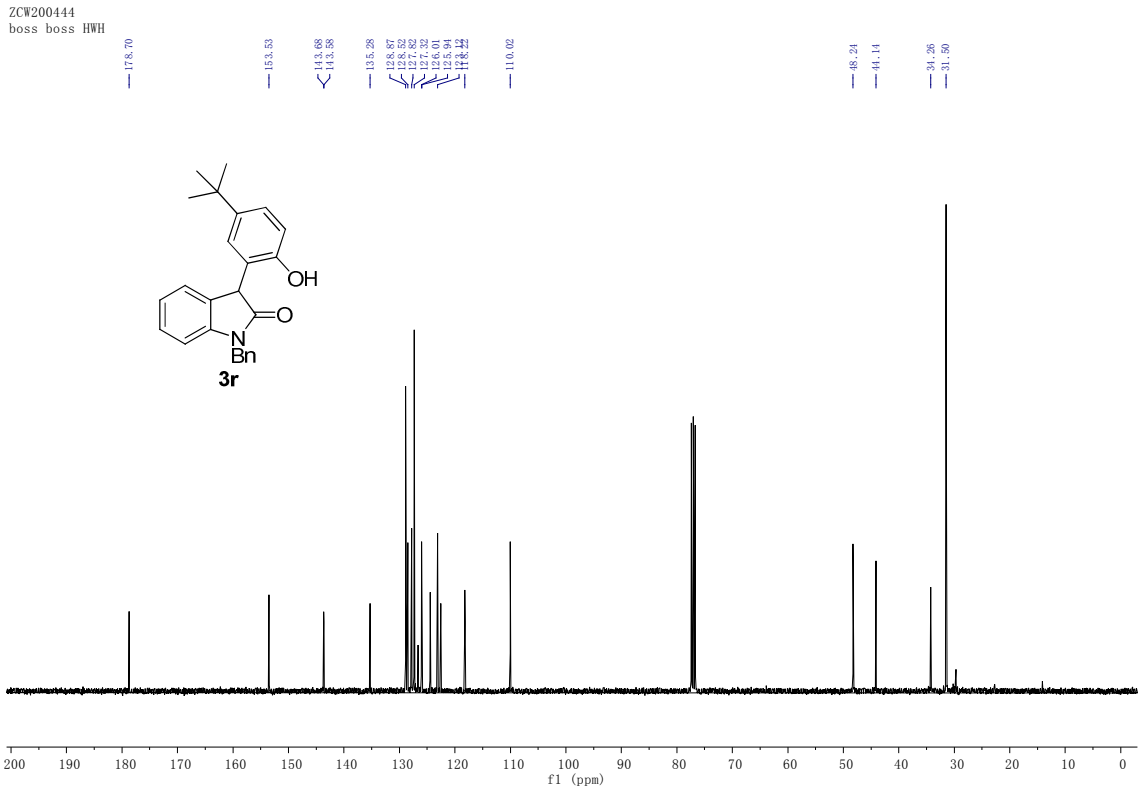

ZCW20-049-4DMSO
boss boss a
3p
f1 (ppm)

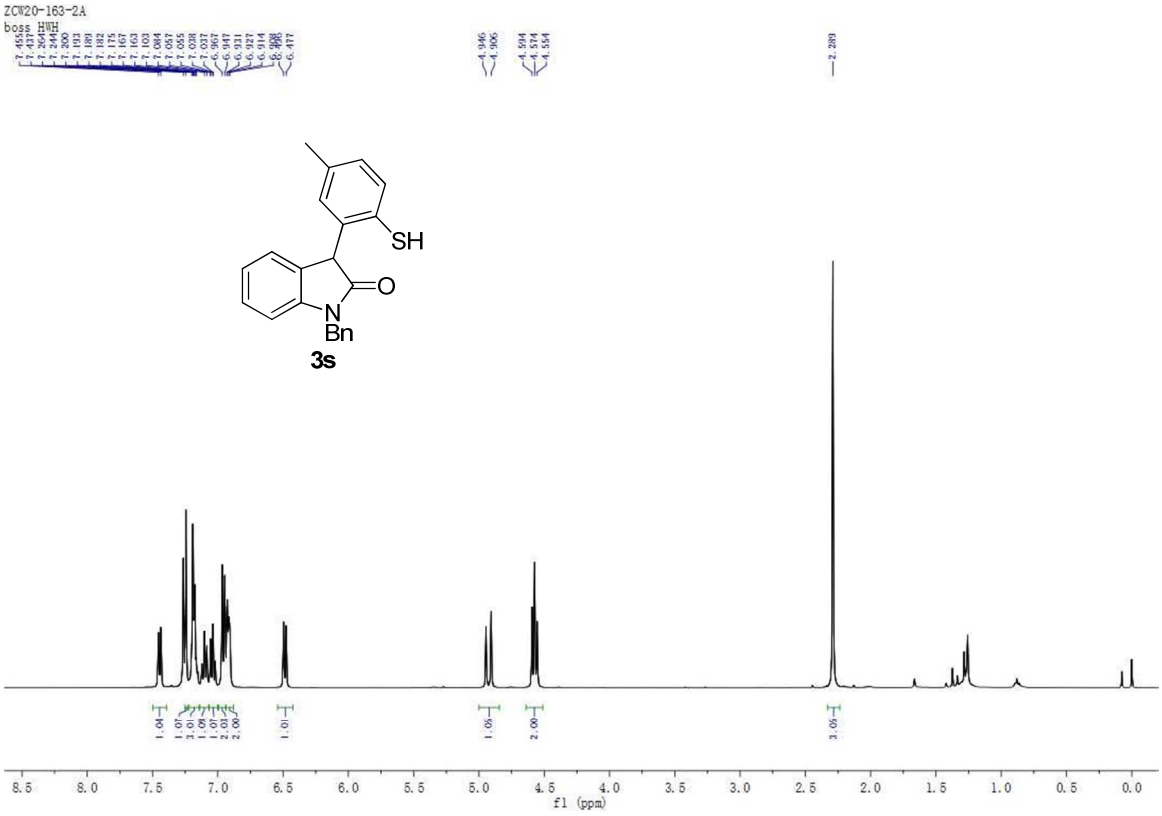

ZCW20-049-4DMSO
boss boss a
3p
f1 (ppm)

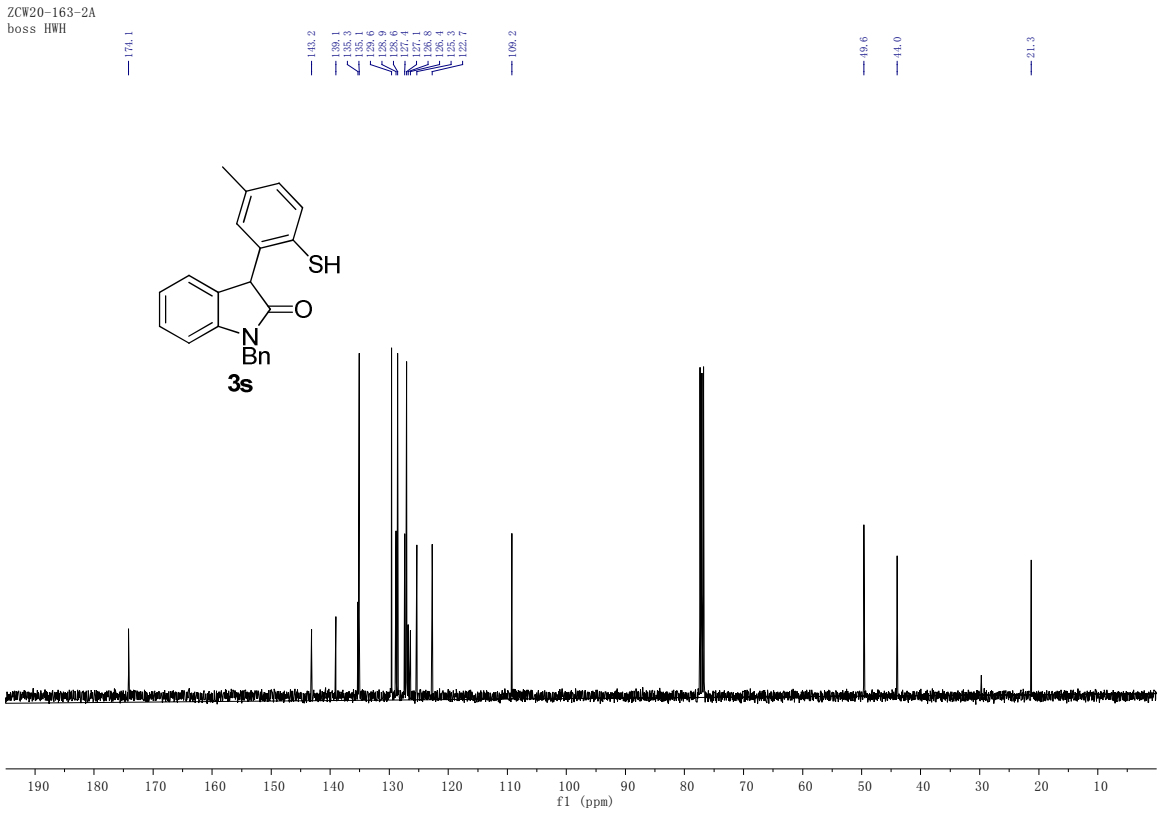

ZCW200393
boss boss HWH
OMe
OMe
O
N
Bn
3q
f1 (ppm)

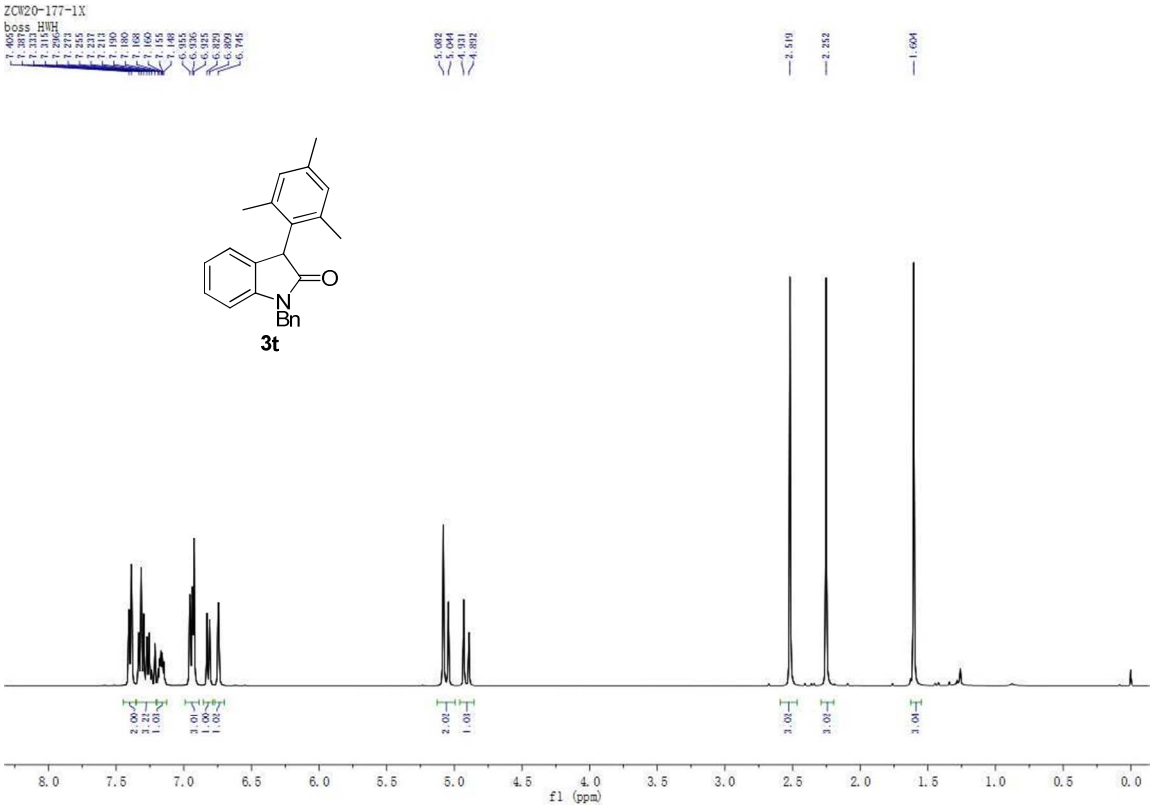

ZCW200393
boss boss HWH
OMe
OMe
O
N
Bn
3q
f1 (ppm)

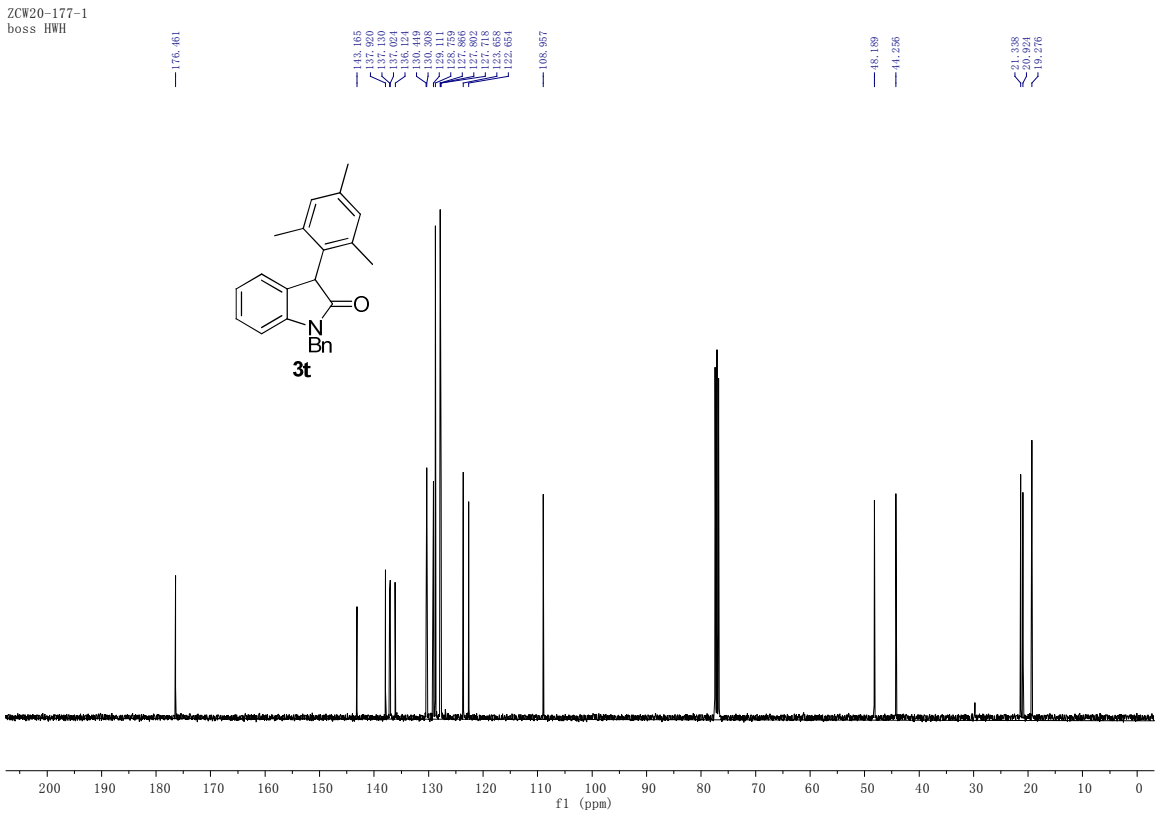

ZCW200444
boss boss HWH
OH
O
N
Bn
3r
f1 (ppm)

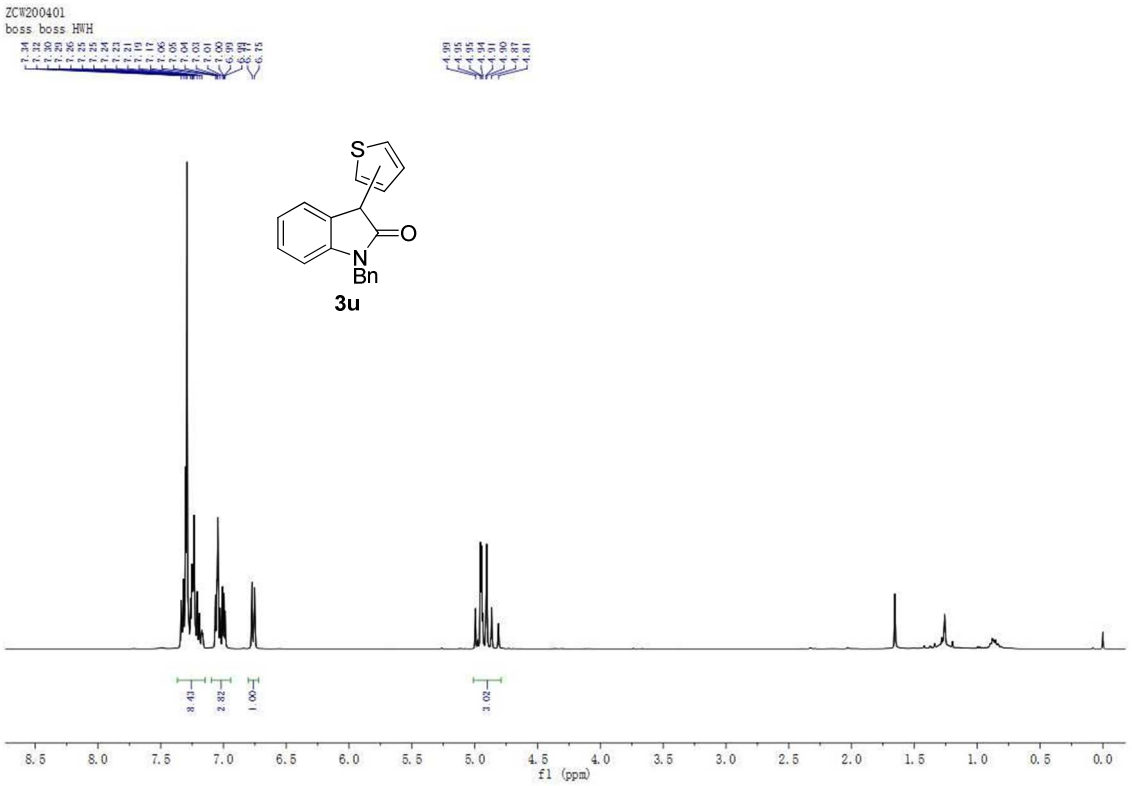

ZCW200444
boss boss HWH
OH
O
N
Bn
3r
f1 (ppm)

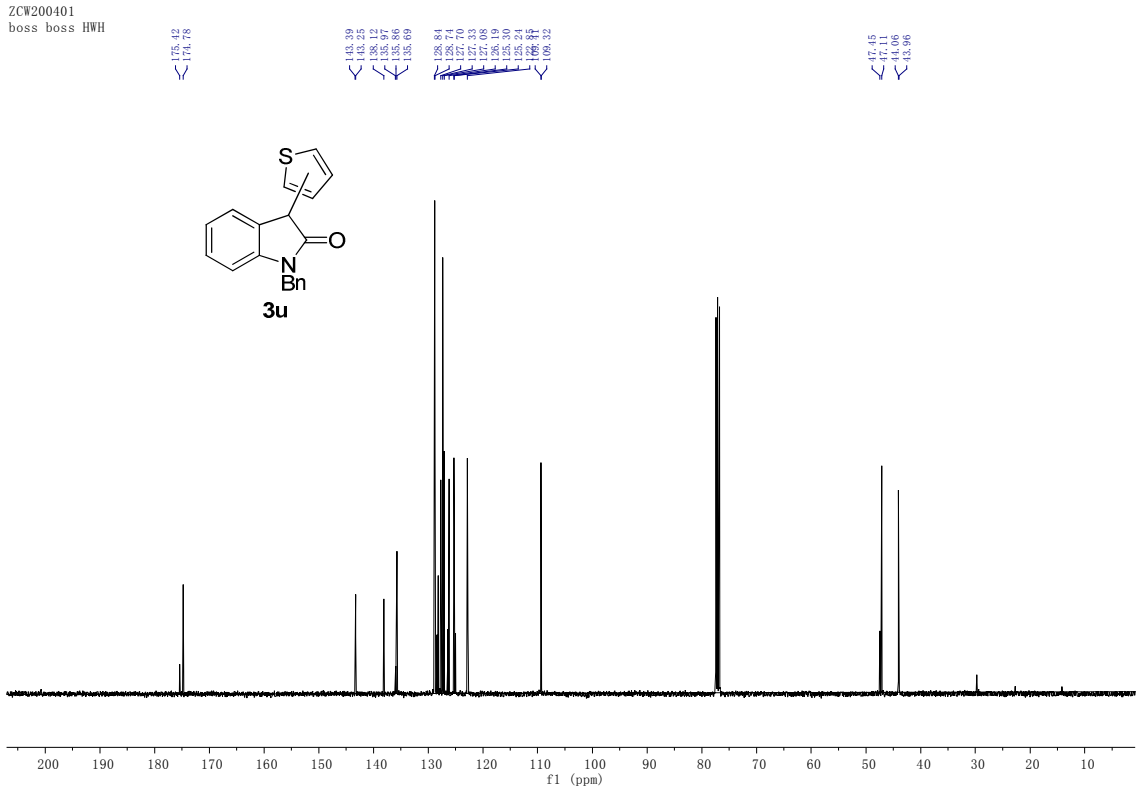

ZCW20-163-2A
boss HWH
SH
O
N
Bn
3s
f1 (ppm)


ZCW20-163-2A
boss HWH
SH
O
N
Bn
3s
f1 (ppm)


ZCW20-177-1X
boss HWH
7.409
7.387
7.331
7.313
7.298
7.273
7.255
7.237
7.213
7.190
7.180
7.168
7.160
7.155
7.146
6.955
6.936
6.925
6.829
6.809
6.746
5.082
5.064
4.931
4.892
2.519
2.252
1.604
N
Bn
3t
f1 (ppm)


ZCW20-177-1
boss HWH
176.461
143.165
137.920
137.130
137.024
136.124
130.449
130.308
129.111
128.759
128.586
127.802
127.718
123.658
122.654
108.957
48.189
44.256
21.338
20.924
19.276
N
Bn
3t
f1 (ppm)


ZCW200401
boss boss HWH
S
O
N
Bn
3u
f1 (ppm)


ZCW200401
boss boss HWH
S
O
N
Bn
3u
f1 (ppm)