Supporting Information

Copper-catalyzed enantioselective Mannich reaction between *N*-acylpyrazoles and isatin-derived ketimines

Jian Lu, Ying Fan, Feng Sha, Qiong Li, Xin-Yan Wu*

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China

E-mail: xinyanwu@ecust.edu.cn

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1. General Information

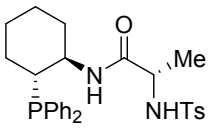
Melting points were taken on WRS-1B digital melting-point apparatus without correction. Optical rotations were measured on a WZZ-2A digital polarimeter at the wavelength of the sodium D-line (589 nm). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 spectrometer, and the chemical shifts were referenced to tetramethylsilane (δ = 0.00 ppm) for ^{1}H NMR and central $CDCl_3$ resonance (δ = 77.0 ppm) for ^{13}C NMR. IR spectra were recorded on Nicolet Magna-1 550 spectrometer. High Resolution Mass spectra (HRMS) were recorded on Micromass GCT with Electron Spray Ionization (ESI) resource. HPLC analysis was performed on Waters equipment using Daicel Chiralcel OD-H column or Chiralpak AD-H column.

Anhydrous solvents were distilled from CaH_2 (Dichloromethane, ethyl acetate, acetonitrile) or sodium-benzophenone (toluene, ether, THF) under N_2. Anhydrous DMF was dried over CaH_2 and distilled under reduced pressure. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 10-40 μm. Silica gel column chromatography was performed using silica gel (300-400 mesh).

Chiral cyclohexane-based *N*,*P*-ligands **L1-L12** were prepared according to literature procedures.[1] *N*-Boc ketimines[2] and *N*-acylpyrazoles[3,4] were synthesized according to literature.

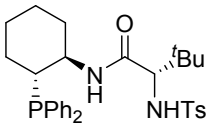
2. Characterization Data of the New Chiral Ligands L7, L10 and L11

(*S*)-N-((1*R*,2*R*)-2-(diphenylphosphanyl)cyclohexyl)-2-((4-methylphenyl)sulfonamido) propanamide (L7)



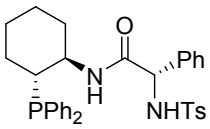
White solid, 94% yield, mp 75.6-77.3 °C, $[\alpha]_D^{20}$ -38.9 (*c* 1.27, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.61 (td, *J* = 7.6, 1.6 Hz, 2H), 7.44-7.39 (m, 5H), 7.32-7.28 (m, 5H), 6.18 (d, *J* = 9.2 Hz, 1H), 4.09 (d, *J* = 7.6 Hz, 1H), 3.87-3.77 (m, 1H), 3.60-3.52 (m, 1H), 2.39 (s, 3H), 2.36-2.29 (m, 1H), 1.97-1.94 (m, 1H), 1.69-1.56 (m, 4H), 1.21-1.16 (m, 2H), 1.09-1.03 (m, 1H), 0.96 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.5, 143.7, 138.0 (d, *J* = 14.1 Hz), 136.4, 135.7 (d, *J* = 15.5 Hz), 134.1 (d, *J* = 20.7 Hz), 133.0 (d, *J* = 19.2 Hz), 129.8, 128.8, 128.7 (d, *J* = 6.6 Hz), 128.3, 128.1 (d, *J* = 7.5 Hz), 126.9, 52.5, 51.5 (d, *J* = 16.8 Hz), 39.7 (d, *J* = 15.4 Hz), 33.6 (d, *J* = 7.2 Hz), 27.8 (d, *J* = 6.0 Hz), 25.5 (d, *J* = 6.1 Hz), 24.6, 21.4, 18.5; ^{31}P NMR ($CDCl_3$, 162 MHz): δ -7.60; IR (KBr, cm^{-1}) ν 3396, 2930, 1651, 1539, 1328, 1165, 1094, 698, 667, 566; HRMS (ESI) calcd for $C_{28}H_{33}N_2NaO_3PS^+$ ($[M+Na]^+$): 531.1842, found: 531.1846.

(*S*)-N-((1*R*,2*R*)-2-(diphenylphosphanyl)cyclohexyl)-3,3-dimethyl-2-((4-methylphenyl) sulfonamido)butanamide (L10)



White solid, 63% yield, mp 132.7-134.4 °C, $[\alpha]_D^{20}$ -1.8 (*c* 2.28, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.49-7.45 (m, 2H), 7.42-7.36 (m, 3H), 7.35-7.29 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.65 (d, *J* = 8.0 Hz, 1H), 5.50 (d, *J* = 8.4 Hz, 1H), 3.68-3.60 (m, 1H), 3.17 (d, *J* = 8.4 Hz, 1H), 2.20 (s, 3H), 2.15 (td, *J* = 8.4, 3.2 Hz, 2H), 1.73-1.69 (m, 1H), 1.60-1.49 (m, 2H), 1.38-1.32 (m, 1H), 1.24-1.13 (m, 2H), 0.98-0.85 (m, 1H), 0.90 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.1, 143.4, 137.1, 136.5 (d, *J* = 13.6 Hz), 135.6 (d, *J* = 17.0 Hz), 134.2 (d, *J* = 20.4 Hz), 132.8 (d, *J* = 18.5 Hz), 129.8, 129.0, 128.8 (d, *J* = 6.1 Hz), 128.6, 128.2 (d, *J* = 7.6 Hz), 127.1, 64.9, 50.9 (d, *J* = 13.6 Hz), 39.0 (d, *J* = 16.4 Hz), 34.7, 32.1, 26.8, 26.4, 24.7, 23.7, 21.4; ^{31}P NMR ($CDCl_3$, 162 MHz): δ -10.31; IR (KBr, cm^{-1}) *v* 3378, 2926, 2121, 1661, 1527, 1336, 1158, 1089, 696, 573; HRMS (ESI) calcd for $C_{31}H_{39}N_2NaO_3PS^+$ ($[M+Na]^+$): 573.2311, found: 573.2316.

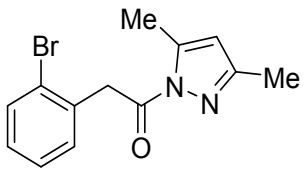
(*S*)-N-((1*R*,2*R*)-2-(diphenylphosphanyl)cyclohexyl)-2-((4-methylphenyl)sulfonamido)-2-phenylacetamide (L11)



White solid, 72% yield, mp 79.8-82.3 °C; $[\alpha]_D^{20}$ +32.5 (*c* 0.80, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.52-7.48 (m, 2H), 7.39-7.34 (m, 5H), 7.30-7.27 (m, 3H), 7.21-7.16 (m, 5H), 6.90-6.88 (m, 3H), 5.71 (d, *J* = 4.8 Hz, 1H), 5.50 (d, *J* = 8.8 Hz, 1H), 4.30 (d, *J* = 4.8 Hz, 1H), 3.82-3.73 (m, 1H), 2.34 (s, 3H), 2.20 (t, *J* = 10.4 Hz, 1H), 1.90-1.86 (m, 1H), 1.65-1.57 (m, 3H), 1.30-1.24 (m, 1H), 1.18-1.12 (m, 1H), 1.04-0.95 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.5, 143.3, 137.3 (d, *J* = 13.6 Hz), 136.7 (d, *J* = 16.3 Hz), 135.4 (d, *J* = 15.5 Hz), 134.1 (d, *J* = 20.6 Hz), 132.9 (d, *J* = 19.1 Hz), 129.4, 128.9, 128.8, 128.7, 128.6, 128.3, 128.2, 128.1, 127.6, 127.1, 60.1, 52.2 (d, *J* = 16.6 Hz), 39.7 (d, *J* = 15.5 Hz), 33.3 (d, *J* = 7.2 Hz), 27.8 (d, *J* = 5.6 Hz), 25.4 (d, *J* = 5.5 Hz), 24.4, 21.4; ^{31}P NMR ($CDCl_3$, 162 MHz): δ -7.82; IR (KBr, cm^{-1}) *v* 3373, 2930, 1661, 1527, 1327, 1162, 1089, 747, 700, 664; HRMS (ESI) calcd for $C_{33}H_{35}N_2NaO_3PS^+$ ($[M+Na]^+$): 593.1998, found: 593.2005.

3. Characterization Data of the *N*-Acylpyrazoles 1h-1j and 1p

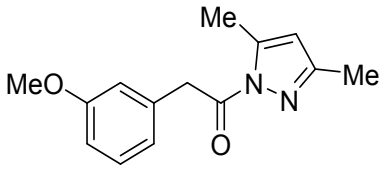
2-(2-bromophenyl)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one (1h)



White solid, 83% yield, mp 64.1-66.1 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 4.0 Hz, 2H), 7.19-7.15 (m, 1H), 6.00 (s, 1H), 4.62 (s, 2H), 2.53 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz): δ 170.5, 152.3, 144.4, 134.4, 132.8,

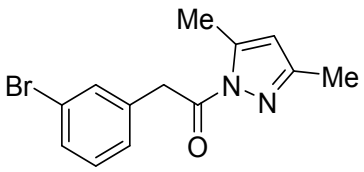
131.9, 128.9, 127.5, 125.4, 111.3, 42.7, 14.4, 13.9; IR (KBr, cm^{-1}) ν 3448, 1729, 1583, 1378, 1355, 1243, 1032, 989, 963, 739; HRMS (ESI) calcd for $C_{13}H_{14}{}^{79}BrN_2O^+$ ($[M+H]^+$): 293.0284, found: 293.0284.

1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(3-methoxyphenyl)ethan-1-one (1i)



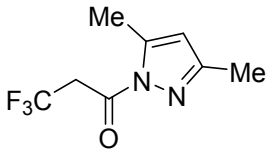
White solid, 81% yield, mp 53.5-53.8 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27-7.23 (m, 1H), 6.95-6.91 (m, 2H), 6.82 (dd, J = 8.0, 2.0 Hz, 1H), 5.97 (s, 1H), 4.40 (s, 2H), 3.80 (s, 3H), 2.51 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.7, 159.6, 152.1, 144.4, 135.5, 129.4, 122.3, 115.5, 112.6, 111.4, 55.1, 41.7, 14.5, 13.8; IR (KBr, cm^{-1}) ν 3428, 1724, 1580, 1490, 1375, 1347, 1263, 1154, 1046, 965, 770, 750, 729, 691; HRMS (ESI) calcd for $C_{14}H_{17}N_2O_2^+$ ($[M+H]^+$): 245.1285, found: 245.1281.

2-(3-bromophenyl)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one (1j)



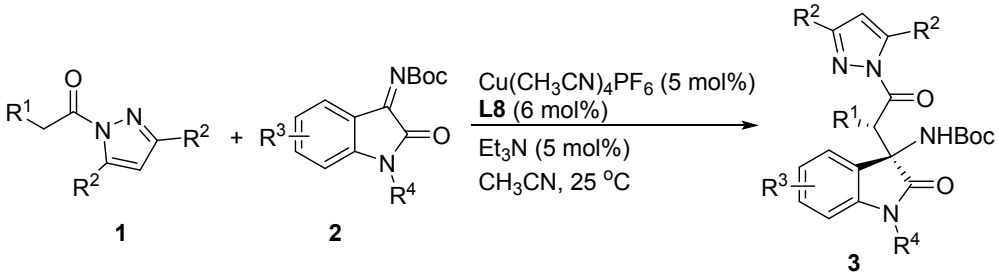
White solid, 81% yield, mp 48.5-49.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (t, J = 1.6 Hz, 1H), 7.41 (dt, J = 7.6, 1.6 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 5.99 (s, 1H), 4.40 (s, 2H), 2.52 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.1, 152.3, 144.4, 136.2, 132.9, 130.2, 130.0, 128.6, 122.4, 111.6, 41.3, 14.5, 13.8; IR (KBr, cm^{-1}) ν 3436, 1727, 1586, 1476, 1380, 1355, 1248, 986, 965, 747, 686, 668; HRMS (ESI) calcd for $C_{13}H_{14}{}^{79}BrN_2O^+$ ($[M+H]^+$): 293.0284, found: 293.0279.

1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-3,3,3-trifluoropropan-1-one (1p)



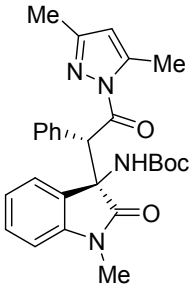
White solid, 93% yield, mp 87.3-88.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.01 (s, 1H), 4.04 (q, J = 10.0 Hz, 2H), 2.56 (s, 3H), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.0, 153.1, 144.5, 125.1 (q, J = 274.5 Hz), 112.1, 39.5 (q, J = 29.7 Hz), 14.3, 13.7; IR (KBr, cm^{-1}) ν 3430, 1725, 1586, 1473, 1339, 1192, 610, 524, 440; HRMS (ESI) calcd for $C_8H_{10}F_3N_2O^+$ ($[M+H]^+$): 207.0740, found: 207.0742.

4. General Procedure for the Asymmetric Mannich Reaction



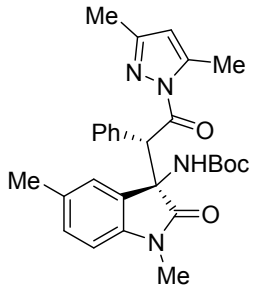
$Cu(CH_3CN)_4PF_6$ (0.01 mmol, 3.7 mg) were added to a flame-dried Schlenk tube equipped a stir bar under N_2 atmosphere. Ligand **L8** (0.012 mmol, 7.0 mg) in 1 mL CH_3CN was added to the tube via a syringe and the mixture was stirred for an hour at 25 °C. Then *N*-acylpyrazole **1** (0.24 mmol), *N*-Boc ketimine **2** (0.2 mmol) and Et_3N (0.01 mmol, 1.5 μL) in 1.0 mL CH_3CN were added, and the mixture was stirred at this temperature until the reaction was completed (monitored by TLC). The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (20:1 CH_2Cl_2/EtOAc) to afford the desire product **3**.

***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxo-1-phenylethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3aa)**



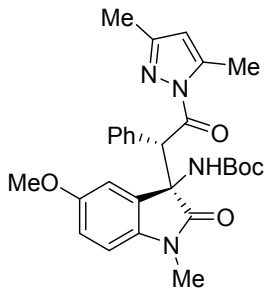
White solid, 99% yield, 99:1 dr, 98% ee; $[\alpha]_D^{20}$ +62.6 (*c* 3.53, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (m, 2H), 7.23-7.20 (m, 3H), 7.17 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.80 (br, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.90 (s, 1H), 5.60 (s, 1H), 3.16 (s, 3H), 2.49 (s, 3H), 2.17 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 169.2, 153.6, 152.4, 144.8, 143.9, 131.9, 130.5, 129.5, 128.8, 128.2, 127.9, 123.2, 121.9, 111.9, 107.6, 80.0, 63.4, 53.7, 29.6, 27.9, 26.3, 14.6, 13.7; IR (KBr, cm^{-1}): *v* 3423, 2966, 1717, 1614, 1471, 1383, 1219, 1162, 1080, 772; HRMS (ESI) calcd for $C_{27}H_{31}N_4O_4^+$ ($[M+H]^+$): 475.2340, found: 475.2338; HPLC analysis (Daicel Chiralcel OD-H column, λ = 254 nm, eluent: 100:1 hexane/ethanol, flow rate: 0.9 mL/min): t_R = 20.54 min (major), 26.15 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxo-1-phenylethyl)-1,5-dimethyl-2-oxoindolin-3-yl)carbamate (3ab)**



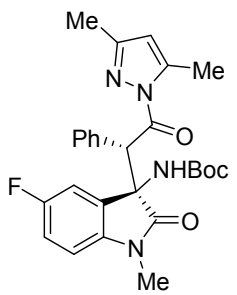
White solid, 99% yield, 99:1 dr, 98% ee; $[\alpha]_D^{20}$ +54.4 (*c* 1.83, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (m, 2H), 7.24-7.19 (m, 3H), 6.97 (d, J = 7.6 Hz, 1H), 6.87 (s, 1H), 6.71 (br, 1H), 6.54 (d, J = 8.0 Hz, 1H), 5.90 (s, 1H), 5.59 (s, 1H), 3.13 (s, 3H), 2.49 (s, 3H), 2.24 (s, 3H), 2.17 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 169.3, 153.7, 152.3, 144.7, 141.5, 131.9, 131.2, 129.4, 129.0, 128.1, 127.8, 124.1, 111.8, 107.2, 80.0, 63.4, 53.7, 29.6, 27.9, 26.3, 21.0, 14.6, 13.7; IR (KBr, cm^{-1}): ν 3419, 2982, 1723, 1620, 1497, 1363, 1255, 1176, 972, 731; HRMS (ESI) calcd for $C_{28}H_{33}N_4O_4^+$ ($[M+H]^+$): 489.2496, found: 489.2499; HPLC analysis (Daicel Chiralcel OD-H column, λ = 254 nm, eluent: 150:1 hexane/ethanol, flow rate: 0.9 mL/min): t_R = 25.35 min (major), 34.98 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxo-1-phenylethyl)-5-methoxy-1-methyl-2-oxoindolin-3-yl)carbamate (3ac)**



White solid, 99% yield, 99:1 dr, 98% ee; $[\alpha]_D^{20}$ +67.8 (*c* 1.90, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.35 (m, 2H), 7.24-7.23 (m, 3H), 6.74-6.67 (m, 3H), 6.57 (d, J = 8.4 Hz, 1H), 5.90 (s, 1H), 5.59 (s, 1H), 3.70 (s, 3H), 3.14 (s, 3H), 2.48 (s, 3H), 2.16 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.8, 169.2, 155.4, 153.6, 152.3, 144.7, 137.5, 131.8, 130.6, 130.5, 128.2, 127.9, 113.5, 111.8, 110.7, 107.9, 80.1, 63.6, 55.7, 53.8, 29.6, 27.9, 26.4, 14.5, 13.7; IR (KBr, cm^{-1}): ν 3470, 2962, 1717, 1496, 1363, 1290, 1168, 1035, 962, 746; HRMS (ESI) calcd for $C_{28}H_{33}N_4O_5^+$ ($[M+H]^+$): 505.2445, found: 505.2444; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 20.79 min (major), 91.43 min (minor).

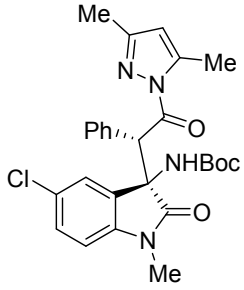
***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxo-1-phenylethyl)-5-fluoro-1-methyl-2-oxoindolin-3-yl)carbamate (3ad)**



White solid, 99% yield, 99:1 dr, 97% ee; $[\alpha]_D^{20}$ +83.3 (*c* 1.85, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.33 (m, 2H), 7.25-7.24 (m, 3H), 6.91-6.82 (m, 3H), 6.58 (dd, J = 8.4, 4.0 Hz, 1H), 5.91 (s, 1H), 5.58 (s, 1H), 3.16 (s, 3H), 2.49 (s, 3H), 2.18 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 169.0, 153.8 (d, J = 238.9 Hz), 153.5, 152.6, 144.8, 140.0, 131.6, 131.1, 130.4, 128.4, 128.1, 114.9 (d, J = 23.3 Hz), 112.0, 111.5 (d, J = 25.0 Hz), 108.1 (d, J = 7.1 Hz), 80.3, 63.4, 53.7, 29.6, 27.9, 26.5, 14.6,

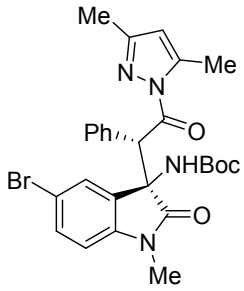
13.7; IR (KBr, cm^{-1}): ν 3428, 2977, 1723, 1501, 1373, 1275, 1162, 962, 814, 735; HRMS (ESI) calcd for $C_{27}H_{30}FN_4O_4^+$ ([M+H]$^+$): 493.2246, found: 493.2247; HPLC analysis (Daicel Chiralcel OD-H column, λ = 254 nm, eluent: 150:1 hexane/ethanol, flow rate: 0.9 mL/min): t_R = 27.44 min (major), 35.03 min (minor).

***tert*-butyl ((*R*)-5-chloro-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxo-1-phenylethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3ae)**



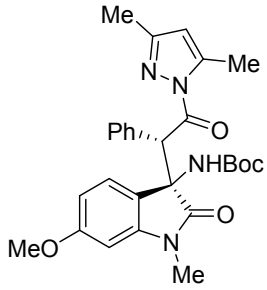
White solid, 99% yield, 99:1 dr, 97% ee; $[\alpha]_D^{20}$ +78.0 (*c* 1.91, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.33 (m, 2H), 7.26-7.24 (m, 3H), 7.16 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.02 (d, *J* = 1.6 Hz, 1H), 6.74 (br, 1H), 6.58 (d, *J* = 8.4 Hz, 1H), 5.91 (s, 1H), 5.58 (s, 1H), 3.15 (s, 3H), 2.48 (s, 3H), 2.17 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 168.9, 153.4, 152.6, 144.8, 142.6, 131.5, 131.1, 130.5, 128.7, 18.4, 128.1, 127.2, 123.8, 112.0, 108.5, 80.3, 63.2, 53.7, 29.6, 27.9, 26.4, 14.5, 13.7; IR (KBr, cm^{-1}): ν 3418, 2972, 1723, 1609, 1492, 1368, 1250, 1157, 962, 735; HRMS (ESI) calcd for $C_{27}H_{29}{}^{35}ClN_4NaO_4^+$ ([M+Na]$^+$): 531.1770, found: 531.1775; HPLC analysis (Daicel Chiralcel OD-H column, λ = 254 nm, eluent: 100:1 hexane/ethanol, flow rate: 0.9 mL/min): t_R = 17.96 min (major), 22.90 min (minor).

***tert*-butyl ((*R*)-5-bromo-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxo-1-phenylethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3af)**



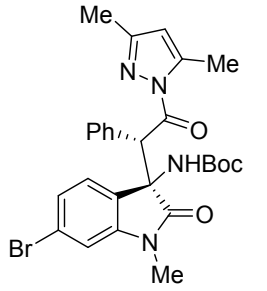
White solid, 99% yield, 99:1 dr, 97% ee; $[\alpha]_D^{20}$ +57.1 (*c* 2.11, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.33 (m, 2H), 7.30 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.26-7.25 (m, 3H), 7.14 (d, *J* = 1.6 Hz, 1H), 6.72 (br, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 5.91 (s, 1H), 5.58 (s, 1H), 3.15 (s, 3H), 2.48 (s, 3H), 2.17 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 168.9, 153.4, 152.6, 144.8, 143.1, 131.6, 131.5, 131.4, 130.5, 128.4, 128.1, 126.5, 114.4, 112.0, 109.1, 80.4, 63.1, 53.7, 29.6, 28.0, 26.4, 14.5, 13.7; IR (KBr, cm^{-1}): ν 3428, 2977, 1728, 1610, 1492, 1363, 1250, 1162, 962, 741; HRMS (ESI) calcd for $C_{27}H_{30}{}^{79}BrN_4NaO_4^+$ ([M+Na]$^+$): 575.1264, found: 575.1265; HPLC analysis (Daicel Chiralcel OD-H column, λ = 254 nm, eluent: 100:1 hexane/ethanol, flow rate: 0.9 mL/min): t_R = 19.06 min (major), 24.80 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxo-1-phenylethyl)-6-methoxy-1-methyl-2-oxoindolin-3-yl)carbamate (3ag)**



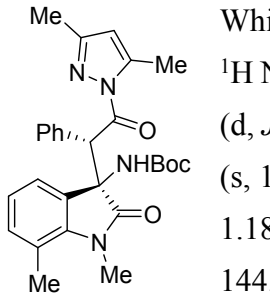
White solid, 98% yield, 98:2 dr, 97% ee; $[\alpha]_D^{20}$ +74.2 (*c* 1.88, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (m, 2H), 7.25-7.23 (m, 3H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.62 (br, 1H), 6.41 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.27 (d, *J* = 2.4 Hz, 1H), 5.89 (s, 1H), 5.58 (s, 1H), 3.76 (s, 3H), 2.15 (s, 3H), 2.48 (s, 3H), 2.16 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.6, 169.4, 160.6, 153.7, 152.3, 145.3, 144.6, 132.0, 130.5, 128.2, 127.9, 124.1, 121.4, 111.8, 105.6, 95.6, 79.9, 63.0, 55.3, 53.9, 29.6, 27.9, 26.3, 14.6, 13.7; IR (KBr, cm^{-1}): *v* 3419, 2977, 1723, 1625, 1471, 1379, 1250, 1162, 1090, 736; HRMS (ESI) calcd for $C_{28}H_{32}N_4NaO_5^+$ ([M+Na]$^+$): 527.2265, found: 527.2268; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 15.21 min (major), 48.44 min (minor).

***tert*-butyl ((*R*)-6-bromo-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxo-1-phenylethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3ah)**



White solid, 99% yield, 99:1 dr, 97% ee; $[\alpha]_D^{20}$ +59.5 (*c* 2.10, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.32 (m, 2H), 7.27-7.25 (m, 3H), 7.05 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 1.6 Hz, 1H), 6.63 (br, 1H), 5.90 (s, 1H), 5.58 (s, 1H), 3.16 (s, 3H), 2.47 (s, 3H), 2.16 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 169.1, 153.5, 152.5, 145.4, 144.7, 131.6, 130.5, 128.5, 128.2, 124.6, 122.5, 112.0, 111.2, 80.3, 62.9, 53.7, 29.6, 28.0, 26.5, 14.6, 13.7; IR (KBr, cm^{-1}): *v* 3434, 2971, 1723, 1609, 1496, 1363, 1250, 1168, 1023, 731; HRMS (ESI) calcd for $C_{27}H_{30}{}^{79}BrN_4NaO_4^+$ ([M+Na]$^+$): 575.1264, found: 575.1266; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 9.14 min (major), 20.60 min (minor).

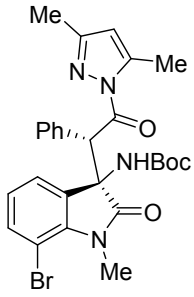
***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxo-1-phenylethyl)-1,7-dimethyl-2-oxoindolin-3-yl)carbamate (3ai)**



White solid, 98% yield, 99:1 dr, 97% ee; $[\alpha]_D^{20}$ +105.3 (*c* 1.82, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.31 (m, 2H), 7.21-7.20 (m, 3H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.79 (t, *J* = 7.2 Hz, 1H), 5.91 (s, 1H), 5.53 (s, 1H), 3.43 (s, 3H), 2.50 (s, 3H), 2.42 (s, 3H), 2.19 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.6, 169.3, 153.7, 152.4, 144.9, 141.5, 132.5, 132.0, 130.6, 130.3, 128.1, 127.7, 121.8, 121.0, 119.0, 111.9, 79.9, 63.1, 53.9, 29.7, 29.6, 27.9, 18.9, 14.6, 13.7; IR (KBr, cm^{-1}): *v* 3424, 2936,

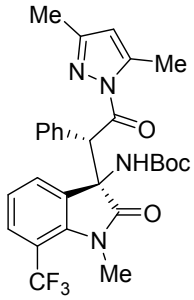
1723, 1605, 1461, 1363, 1250, 1162, 962, 742; HRMS (ESI) calcd for $C_{28}H_{32}N_4NaO_4^+$ ([M+Na]$^+$): 511.2316, found: 511.2317; HPLC analysis (Daicel Chiralcel OD-H column, λ = 254 nm, eluent: 150:1 hexane/ethanol, flow rate: 0.9 mL/min): t_R = 37.43 min (major), 52.86 min (minor).

***tert*-butyl ((*R*)-7-bromo-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxo-1-phenylethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3aj)**



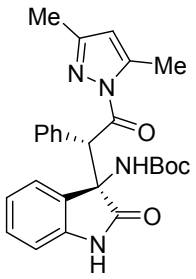
White solid, 99% yield, 99:1 dr, 97% ee; $[\alpha]_D^{20}$ +74.4 (*c* 2.09, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.30 (m, 2H), 7.27-7.22 (m, 4H), 6.99 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.89 (br, 1H), 6.75 (t, *J* = 8.0 Hz, 1H), 5.92 (s, 1H), 5.53 (s, 1H), 3.55 (s, 3H), 2.50 (s, 3H), 2.19 (s, 3H), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.5, 168.9, 153.5, 152.6, 144.9, 141.2, 134.4, 132.9, 131.5, 130.5, 128.4, 127.9, 123.0, 122.1, 112.0, 102.1, 80.4, 63.1, 29.9, 29.6, 27.9, 14.6, 13.7; IR (KBr, cm^{-1}): ν 3429, 2977, 1728, 1599, 1461, 1368, 1245, 1162, 968, 736; HRMS (ESI) calcd for $C_{27}H_{30}{}^{79}BrN_4NaO_4^+$ ([M+Na]$^+$): 575.1264, found: 575.1270; HPLC analysis (Daicel Chiralcel OD-H column, λ = 254 nm, eluent: 100:1 hexane/ethanol, flow rate: 0.9 mL/min): t_R = 13.25 min (major), 18.47 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxo-1-phenylethyl)-1-methyl-2-oxo-7-(trifluoromethyl)indolin-3-yl)carbamate (3ak)**



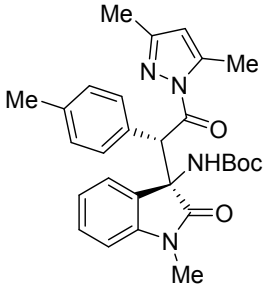
White solid, 99% yield, 99:1 dr, 95% ee; $[\alpha]_D^{20}$ +102.7 (*c* 2.04, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.30-7.26 (m, 3H), 7.21-7.16 (m, 3H), 6.99 (t, *J* = 8.0 Hz, 1H), 5.95 (s, 1H), 5.57 (s, 1H), 3.36 (d, *J* = 2.4 Hz, 3H), 2.51 (s, 3H), 2.22 (s, 3H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.9, 168.5, 153.4, 152.8, 145.2, 141.7, 132.4, 131.3, 130.5, 128.4, 127.9, 126.6 (q, *J* = 5.9 Hz), 126.3, 123.4 (q, *J* = 270.0 Hz), 121.2, 112.1, 111.7, 80.5, 62.2, 53.8, 29.6, 28.9, 27.8, 14.6, 13.7; IR (KBr, cm^{-1}): ν 3434, 2982, 1728, 1599, 1471, 1342, 1178, 1122, 962, 746; HRMS (ESI) calcd for $C_{28}H_{29}F_3N_4NaO_4^+$ ([M+Na]$^+$): 565.2033, found: 565.2040; HPLC analysis (Daicel Chiralcel OD-H column, λ = 254 nm, eluent: 100:1 hexane/ethanol, flow rate: 0.9 mL/min): t_R = 9.49 min (major), 13.35 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxo-1-phenylethyl)-2-oxoindolin-3-yl)carbamate (3al)**



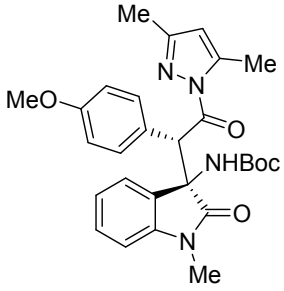
White solid, 92% yield, 97:3 dr, 97% ee; $[\alpha]_D^{20}$ +66.9 (*c* 1.69, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 8.43 (br, 1H), 7.48-7.46 (m, 2H), 7.28-7.26 (m, 3H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.84 (br, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 5.88 (s, 1H), 5.60 (s, 1H), 2.52 (s, 3H), 2.11 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 154.0, 152.4, 144.5, 140.9, 131.8, 130.6, 130.2, 128.8, 128.3, 128.2, 123.4, 122.0, 112.0, 110.0, 80.6, 63.7, 53.4, 29.6, 27.9, 14.7, 13.7; IR (KBr, cm^{-1}): *v* 3280, 2977, 1728, 1620, 1471, 1384, 1250, 1168, 1050, 757; HRMS (ESI) calcd for $C_{26}H_{28}N_4NaO_4^+$ ($[M+Na]^+$): 483.2003, found: 483.2008; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 20.43 min (major), 58.30 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxo-1-(p-tolyl)ethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3ba)**



White solid, 99% yield, 99:1 dr, 98% ee; $[\alpha]_D^{20}$ +88.5 (*c* 1.83, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.21 (td, *J* = 8.0, 1.2 Hz, 1H), 7.07-7.05 (m, 3H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.66 (br, 1H), 5.88 (s, 1H), 5.55 (s, 1H), 3.18 (s, 3H), 2.47 (s, 3H), 2.27 (s, 3H), 2.14 (s, 3H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 169.6, 153.7, 152.3, 144.6, 144.0, 138.0, 130.4, 129.6, 128.8, 128.7, 123.3, 121.9, 111.8, 107.6, 80.0, 63.2, 53.3, 29.6, 27.9, 26.4, 21.1, 14.6, 13.7; IR (KBr, cm^{-1}): *v* 3429, 2977, 1717, 1610, 1470, 1378, 1250, 1162, 1029, 757; HRMS (ESI) calcd for $C_{28}H_{32}N_4NaO_4^+$ ($[M+Na]^+$): 511.2316, found: 511.2318; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 13.84 min (maor), 57.51 min (minor).

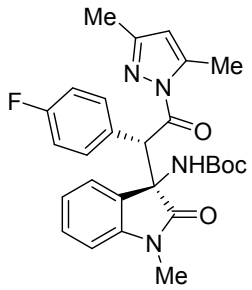
***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(4-methoxyphenyl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3ca)**



White solid, 98% yield, 99:1 dr, 98% ee; $[\alpha]_D^{20}$ +112.5 (*c* 1.88, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 9.6 Hz, 2H), 7.20 (td, *J* = 7.6, 1.2 Hz, 1H), 7.08 (d, *J* = 6.8 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.69-6.68 (m, 2H), 5.89 (s, 1H), 5.54 (s, 1H), 3.74 (s, 3H), 3.17 (s, 3H), 2.48 (s, 3H), 2.16 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 169.6, 159.4, 153.7, 152.3, 144.7, 143.9, 131.7, 129.6, 128.8, 123.7, 123.2, 121.9, 113.4, 111.8,

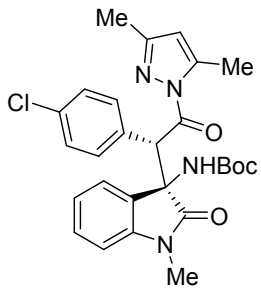
107.6, 80.0, 63.3, 55.1, 52.9, 29.6, 27.9, 26.3, 14.6, 13.7 ; IR (KBr, cm^{-1}): *v* 3413, 2971, 1723, 1610 1378, 1255, 1162, 1029, 957, 757; HRMS (ESI) calcd for $C_{28}H_{32}N_4NaO_5^+$ ($[M+Na]^+$): 527.2265, found: 527.2265; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 16.25 min (major), 127.73 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(4-fluorophenyl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3da)**



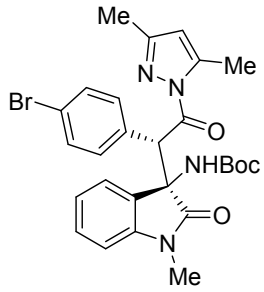
White solid, 99% yield, 99:1 dr, 98% ee; $[\alpha]_D^{20}$ +118.2 (*c* 1.85, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (m, 2H), 7.18 (td, *J* = 7.6, 1.2 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 1H), 6.98 (br, 1H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.91-6.86 (m, 2H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.94 (s, 1H), 5.54 (s, 1H), 3.16 (s, 3H), 2.52 (s, 3H), 2.19 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, CDl_3): δ 173.7, 169.3, 162.5 (d, *J* = 246.0 Hz), 153.7, 152.7, 145.0, 143.6, 132.2 (d, *J* = 8.1 Hz), 129.5, 129.0, 127.7 (d, *J* = 3.2 Hz), 122.9, 122.1, 114.7 (d, *J* = 21.3 Hz), 112.1, 107.7, 80.1, 63.5, 52.7, 29.6, 27.9, 26.3, 14.6, 13.7 ; IR (KBr, cm^{-1}): *v* 3404, 2977, 1717, 1609, 1512, 1379, 1250, 1162, 962, 757; HRMS (ESI) calcd for $C_{27}H_{29}FN_4NaO_4^+$ ($[M+Na]^+$): 515.2065, found: 515.2070; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 13.21 min (major), 76.61 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-1-(4-chlorophenyl)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3ea)**



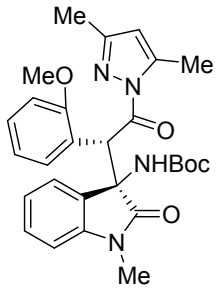
White solid, 99% yield, 99:1 dr, 99% ee; $[\alpha]_D^{20}$ +116.3 (*c* 1.92, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.21-7.17 (m, 3H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.95-6.92 (m, 2H), 6.67 (d, *J* = 7.6 Hz, 1H), 5.93 (s, 1H), 5.52 (s, 1H), 3.17 (s, 3H), 2.51 (s, 3H), 2.17 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 169.2, 153.7, 152.7, 144.9, 143.6, 134.2, 131.8, 130.5, 129.5, 129.0, 128.0, 122.9, 122.1, 112.1, 107.8, 80.2, 63.4, 52.8, 29.6, 27.9, 26.3, 14.6, 13.7; IR (KBr, cm^{-1}): *v* 3413, 2971, 1723, 1614, 1497, 1368, 1250, 1162, 1013, 757; HRMS (ESI) calcd for $C_{27}H_{29}{}^{35}ClN_4NaO_4^+$ ($[M+Na]^+$): 531.1770, found: 531.1773; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 13.28 min (major), 75.46 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-1-(4-bromophenyl)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3fa)**



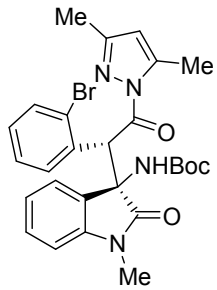
White solid, 99% yield, 99:1 dr, 98% ee; $[\alpha]_D^{20}$ +106.4 (*c* 2.10, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 7.20 (td, J = 7.6, 1.2 Hz, 1H), 7.13 (d, J = 7.2 Hz, 1H), 6.95-6.91 (m, 2H), 6.68 (d, J = 7.6 Hz, 1H), 5.93 (s, 1H), 5.50 (s, 1H), 3.17 (s, 3H), 2.51 (s, 3H), 2.17 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 169.1, 153.7, 152.7, 144.9, 143.6, 132.1, 130.9, 129.4, 129.0, 122.9, 122.5, 122.1, 112.1, 107.8, 80.1, 63.3, 52.9, 29.6, 27.9, 26.3, 14.6, 13.7; IR (KBr, cm^{-1}): ν 3413, 2977, 1717, 1610, 1492, 1384, 1255, 1162, 1019, 751; HRMS (ESI) calcd for $C_{27}H_{29}{}^{79}BrN_4NaO_4^+$ ([M+Na]$^+$): 575.1264, found: 575.1266; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 13.10 min (major), 77.89 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(2-methoxyphenyl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3ga)**



White solid, 99% yield, 99:1 dr, 98% ee; $[\alpha]_D^{20}$ -41.6 (*c* 1.90, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.23 (m, 2H), 7.03 (d, J = 7.2 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.84 (t, J = 7.6 Hz, 2H), 6.78 (d, J = 7.6 Hz, 1H), 6.58 (d, J = 6.8 Hz, 1H), 6.39 (s, 1H), 5.80 (s, 1H), 3.99 (s, 3H), 3.23 (s, 3H), 2.38 (s, 3H), 2.08 (s, 3H), 1.26 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.4, 169.4, 157.0, 153.6, 151.7, 144.9, 144.1, 130.7, 129.5, 128.6, 124.2, 121.4, 121.2, 120.4, 111.8, 111.4, 107.4, 79.6, 63.8, 56.2, 46.6, 29.6, 27.8, 26.3, 14.4, 13.7; IR (KBr, cm^{-1}): ν 3382, 2982, 1728, 1615, 1492, 1379, 1245, 1168, 1023, 757; HRMS (ESI) calcd for $C_{28}H_{32}N_4NaO_5^+$ ([M+Na]$^+$): 527.2265, found: 527.2258; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 8.18 min (major), 27.72 min (minor).

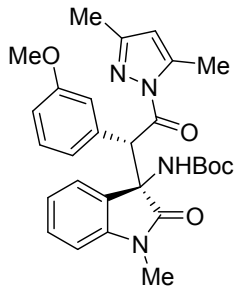
***tert*-butyl ((*R*)-3-((*S*)-1-(2-bromophenyl)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3ha)**



White solid, 99% yield, 99:1 dr, 97% ee; $[\alpha]_D^{20}$ +113.0 (*c* 2.08, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 7.6 Hz, 1H), 7.44 (dd, J = 8.0, 1.2 Hz, 1H), 7.24 (d, J = 7.2 Hz, 1H), 7.17 (t, J =7.6 Hz, 2H), 7.03 (td, J = 8.0, 1.6 Hz, 1H), 6.89 (t, J = 7.6 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 6.20 (s, 1H), 5.92 (s, 1H), 3.21 (s, 3H), 2.52 (s, 3H), 2.17 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 169.5, 153.7, 152.7,

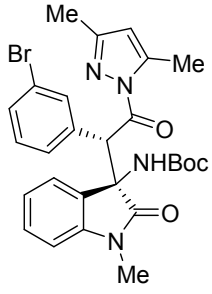
144.8, 143.6, 132.6, 131.8, 130.6, 129.4, 128.9, 126.9, 126.6, 123.0, 121.9, 112.0, 107.6, 79.8, 63.7, 51.4, 29.5, 27.9, 26.3, 14.5, 13.6; IR (KBr, cm^{-1}): ν 3413, 2977, 1717, 1610, 1470, 1377, 1255, 1157, 1028, 751; HRMS (ESI) calcd for $C_{27}H_{29}{}^{79}BrN_4NaO_4^+$ ([M+Na]$^+$): 575.1264, found: 575.1266; HPLC analysis (Daicel Chiralcel OD-H column, λ = 254 nm, eluent: 100:1 hexane/ethanol, flow rate: 0.9 mL/min): t_R = 22.38 min (major), 47.83 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(3-methoxyphenyl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3ia)**



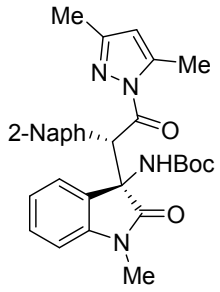
White solid, 99% yield, 99:1 dr, 97% ee; $[\alpha]_D^{20}$ +68.3 (*c* 1.90, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.94 (d = 7.6 Hz, 1H), 6.91-6.89 (m, 1H), 6.78 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.62 (br, 1H), 5.89 (s, 1H), 5.61 (s, 1H), 3.72 (s, 3H), 3.17 (s, 3H), 2.46 (s, 3H), 2.16 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 169.0, 158.9, 153.5, 152.3, 144.5, 144.0, 133.1, 129.3, 128.8, 123.4, 122.9, 121.7, 116.0, 113.9, 111.8, 107.6, 80.0, 63.1, 55.1, 29.5, 27.8, 26.3, 14.5, 13.7; IR (KBr, cm^{-1}): ν 3424, 2977, 1723, 1610, 1486, 1379, 1250, 1162, 1050, 757; HRMS (ESI) calcd for $C_{28}H_{32}N_4NaO_5^+$ ([M+Na]$^+$): 527.2265, found: 527.2268; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 95:5 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 41.70 min (major), 242.01 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-1-(3-bromophenyl)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3ja)**



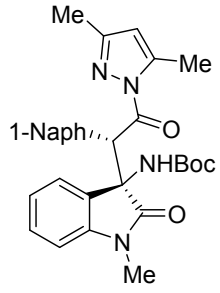
White solid, 99% yield, 99:1 dr, 97% ee; $[\alpha]_D^{20}$ +102.3 (*c* 2.11, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (t, *J* = 2.0 Hz, 1H), 7.32-7.30 (m, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.19-7.13 (m, 2H), 7.09 (br, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 5.96 (s, 1H), 5.52 (s, 1H), 3.18 (s, 3H), 2.53 (s, 3H), 2.21 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 168.6, 153.6, 152.8, 145.1, 143.5, 134.1, 133.2, 131.1, 129.4, 129.2, 129.1, 129.0, 122.9, 122.1, 121.6, 112.1, 107.7, 80.1, 63.6, 53.0, 29.6, 27.9, 26.3, 14.6, 13.7; IR (KBr, cm^{-1}): ν 3413, 2977, 1723, 1610, 1471, 1373, 1250, 1168, 1080, 757; HRMS (ESI) calcd for $C_{27}H_{29}{}^{79}BrN_4NaO_4^+$ ([M+Na]$^+$): 575.1264, found: 575.1269; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 95:5 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 23.56 min (major), 118.39 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(naphthalen-2-yl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3ka)**



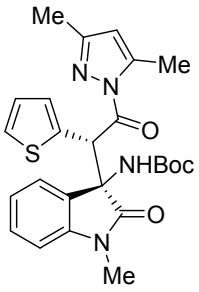
White solid, 99% yield, 99:1 dr, 98% ee; $[\alpha]_D^{20}$ +121.7 (*c* 1.97, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.80-7.73 (m, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.47-7.41 (m, 3H), 7.16 (td, *J* = 7.6, 0.8 Hz, 1H),7.09 (d, *J* = 7.2 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.77 (br, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 5.88 (s, 1H), 5.78 (s, 1H), 3.18 (s, 3H), 2.48 (s, 3H), 2.16 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 169.3, 153.6, 152.4, 144.7, 144.0, 132.8, 129.9, 129.5, 128.9, 128.2, 128.1, 127.4, 127.4, 126.3, 126.0, 123.3, 121.9, 111.9, 107.7, 80.1, 63.4, 53.9, 29.6, 27.9, 26.4, 14.6, 13.7 ; IR (KBr, cm^{-1}): *v* 3419, 2977, 1723, 1615, 1471, 1373, 1255, 1168, 957, 757; HRMS (ESI) calcd for $C_{31}H_{32}N_4NaO_4^+$ ([M+Na]$^+$): 547.2316, found: 547.2314; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 17.26 min (major), 75.04 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(naphthalen-1-yl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3la)**



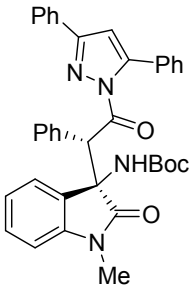
White solid, 98% yield, 99:1 dr, 98% ee; $[\alpha]_D^{20}$ -79.8 (*c* 1.96, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.63-7.59 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.73 (s, 1H), 6.40 (br, 1H), 5.78 (s, 1H), 3.20 (s, 3H), 2.43 (s, 3H), 1.98 (s, 3H), 1.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.5, 169.7, 153.6, 152.0, 144.2, 133.8, 132.5, 129.2, 128.9, 128.8, 127.9, 126.6, 125.6, 124.5, 123.8, 123.1, 121.6, 111.7, 107.6, 80.0, 63.8, 47.4, 29.6, 27.8, 26.4, 14.4, 13.6; IR (KBr, cm^{-1}): *v* 3429, 2925, 1728, 1610, 1471, 1379, 1250, 1162, 968, 751; HRMS (ESI) calcd for $C_{31}H_{32}N_4NaO_4^+$ ([M+Na]$^+$): 547.2316, found: 547.2318; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 9.34 min (major), 35.61 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-oxo-1-(thiophen-2-yl)ethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3ma)**



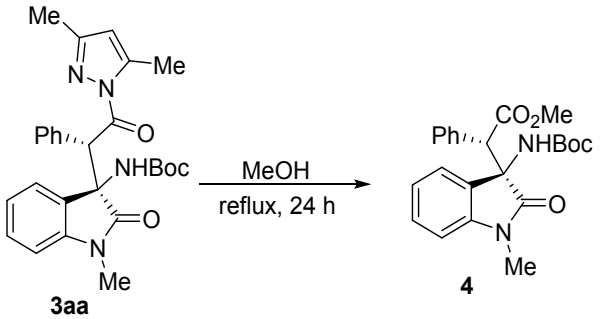
White solid, 99% yield, 98:2 dr, 94% ee; $[\alpha]_D^{20}$ +133.6 (*c* 1.81, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.17 (m, 3H), 7.12 (br, 1H), 6.96-6.92 (m, 2H), 6.82 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.97 (s, 1H), 5.92 (s, 1H), 3.14 (s, 3H), 2.54 (s, 3H), 2.22 (s ,3H), 1.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 168.5, 153.6, 152.9, 145.2, 143.7, 132.7, 129.4, 129.2, 129.0, 126.6, 125.8, 122.8, 112.2, 107.6, 80.0, 63.7, 49.0, 29.6, 27.9, 26.3, 14.6, 13.7; IR (KBr, cm^{-1}): *v* 3413, 2977, 1723, 1615, 1471, 1379, 1255, 1162, 1091, 751; HRMS (ESI) calcd for $C_{25}H_{29}N_4O_4S^+$ ([M+H]$^+$): 481.1904, found: 481.1905; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 11.96 min (major), 57.97 min (minor).

***tert*-butyl ((*R*)-3-((*S*)-2-(3,5-diphenyl-1*H*-pyrazol-1-yl)-2-oxo-1-phenylethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3na)**



White solid, 98% yield, 99:1 dr, 98% ee; $[\alpha]_D^{20}$ +48.0 (*c* 2.35, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.43-7.35 (m, 10H), 7.33-7.28 (m, 3H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.60 (s, 1H), 6.48 (br, 1H), 5.70 (s, 1H), 3.20 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 168.8, 153.7, 147.5, 144.0, 131.7, 131.2, 130.6, 130.5, 129.3, 129.0, 128.8, 128.7, 128.6, 128.4, 128.2, 127.9, 126.3, 123.6, 121.9, 110.5, 107.9, 80.2, 63.1, 54.7, 27.9, 26.5; IR (KBr, cm^{-1}): *v* 3429, 2977, 1717, 1615, 1471, 1368, 1250, 1168, 941, 736; HRMS (ESI) calcd for $C_{37}H_{34}N_4NaO_4^+$ ([M+Na]$^+$): 621.2472, found: 621.2475; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 13.77 min (major), 57.84 min (minor).

5. Esterification of Compound 3aa



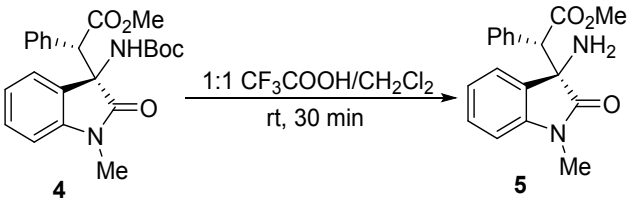
3aa **4**

Compound **3aa** (0.15 mmol) and 2 mL CH_3OH was added to a vial equipped with a

magnetic stirring bar and the solution was heated to reflux for 24 hours. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (20:1 CH_2Cl_2/EtOAc) to afford compound **4**.[3]

White solid, 92% yield, 99:1 dr, 98% ee; $[\alpha]_D^{20}$ +57.7 (*c* 1.02, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.22 (m, 6H), 7.10 (d, J = 7.2 Hz, 1H), 6.98 (td, J = 7.6, 0.8 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 5.91 (br, 1H), 4.11 (s, 1H), 3.63 (s, 3H), 3.15 (s, 3H) 1.20 (s, 9H); HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 80:20, flow rate: 0.9 mL/min): t_R = 28.99 min (major), 33.11 min (minor).

6. De-*tert*-butyloxy Carbonyl of Compound 4



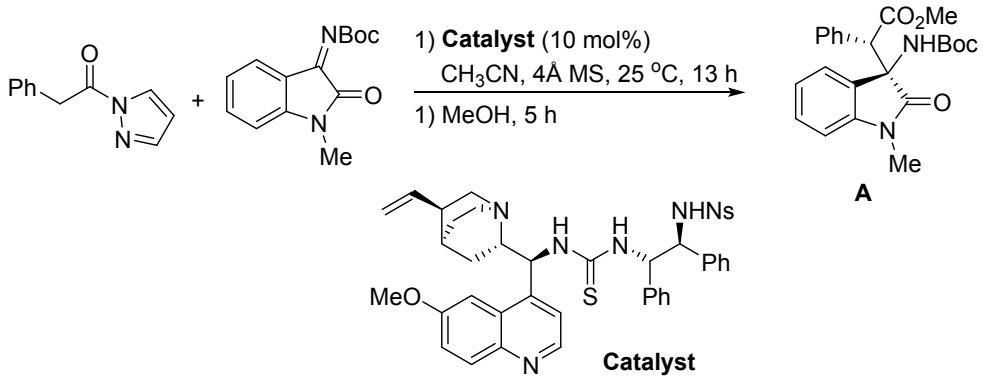
Compound **4** (0.1 mmol) and 1 mL dichloromethane was added to a round flask, and then 1 mL trifluoroacetic acid was added. The mixture was stirred at room temperature for 30 minutes. After the reaction was completed (monitored by TLC), the resulting mixture was quenched with saturated $NaHCO_3$ and extracted with dichloromethane (5 mL × 2), the organic layers were combined and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (5:1 CH_2Cl_2/EtOAc) to give the de-*tert*-butyloxy carbonylated compound **5**.

Colorless oil, 92% yield; $[\alpha]_D^{20}$ -34.3 (*c* 1.07, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.30 (m, 3H), 7.27 (td, J = 8.0, 1.2 Hz, 1H), 7.24-7.20 (m, 2H), 6.93 (t, J = 7.6 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.72 (d, J = 7.2 Hz, 1H), 4.19 (s, 1H), 3.58 (s, 3H), 3.17 (s, 3H), 2.00 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.4, 171.2, 143.8, 133.2, 130.3, 129.7, 129.1, 127.9, 127.9, 124.7, 122.1, 108.1, 61.7, 58.1, 52.0, 26.2; IR (KBr, cm^{-1}): ν 3373, 3059, 1717, 1615, 1497, 1373, 1162, 1019, 757, 700; HRMS (ESI) calcd for $C_{18}H_{19}N_2O_3^+$ ([M+H]$^+$): 311.1390, found: 311.1392.

7. Determination of Absolute Configuration of the Product 3aa

In order to determine the absolute configuration of the Mannich reaction products **3**, we

synthesized the β-amino ester **A** according to the literature (Scheme S1).[3] Comparison of their CD spectra (Fig. S1) and HPLC chromatograms showed that the absolute configuration of product **4** is consistence with compound **A**. In the transformation from product **3aa** to compound **4**, there is no variation in chirality, so the absolute configuration of product **3aa** is assigned as 3*R*,1'*S* according to the literature,[3] and the absolute configuration of other Mannich adducts were tentatively assigned by referring to that of compound **3aa**.



Scheme S1. Synthesis of compound **A** using literature's method

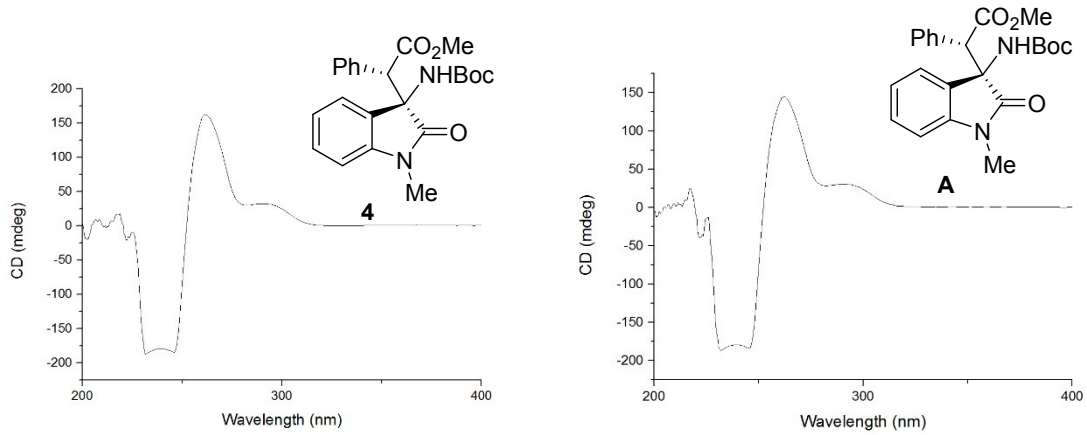
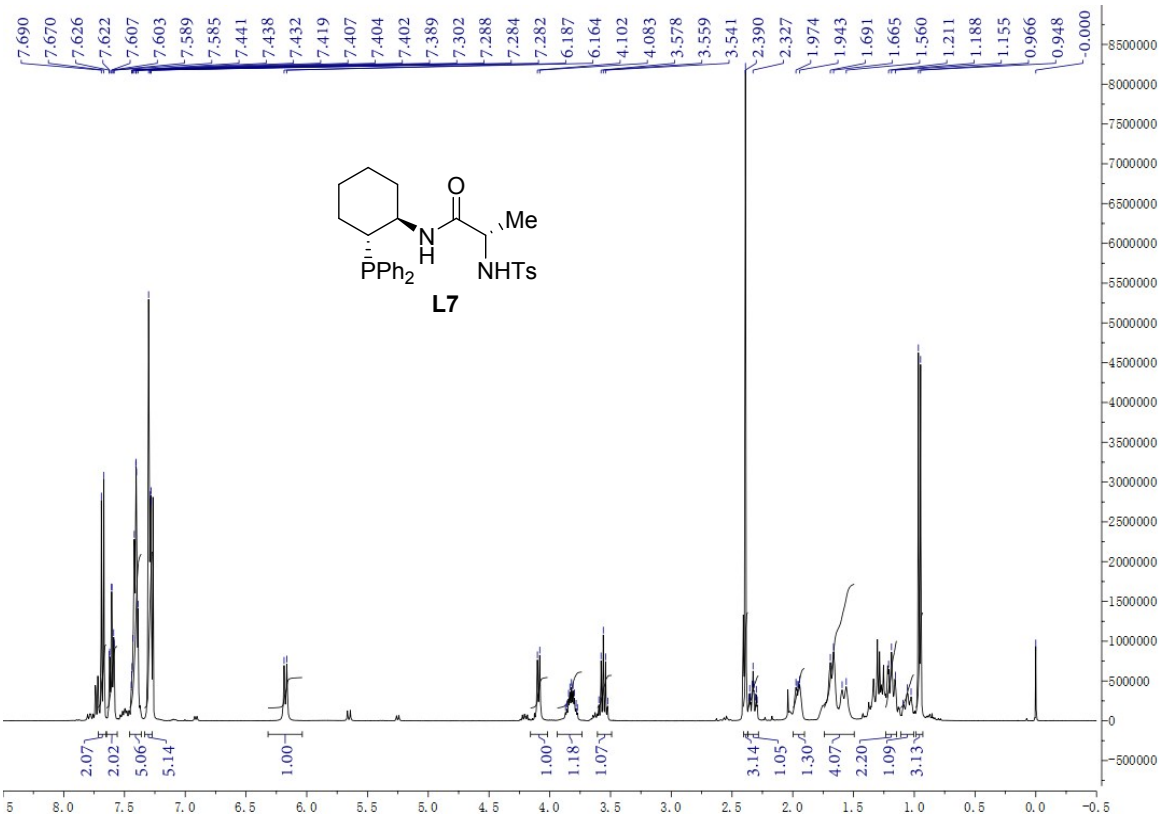


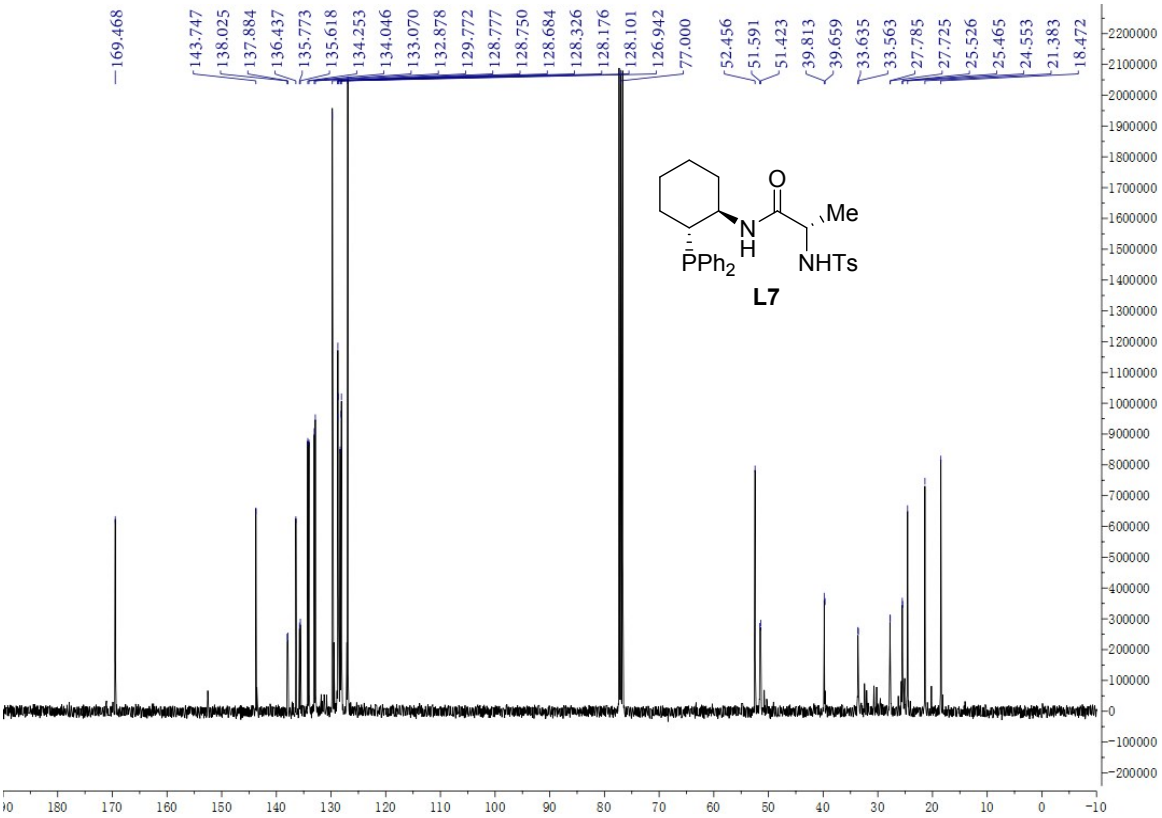
Fig. S1. CD spectra of product **4** and compound **A**

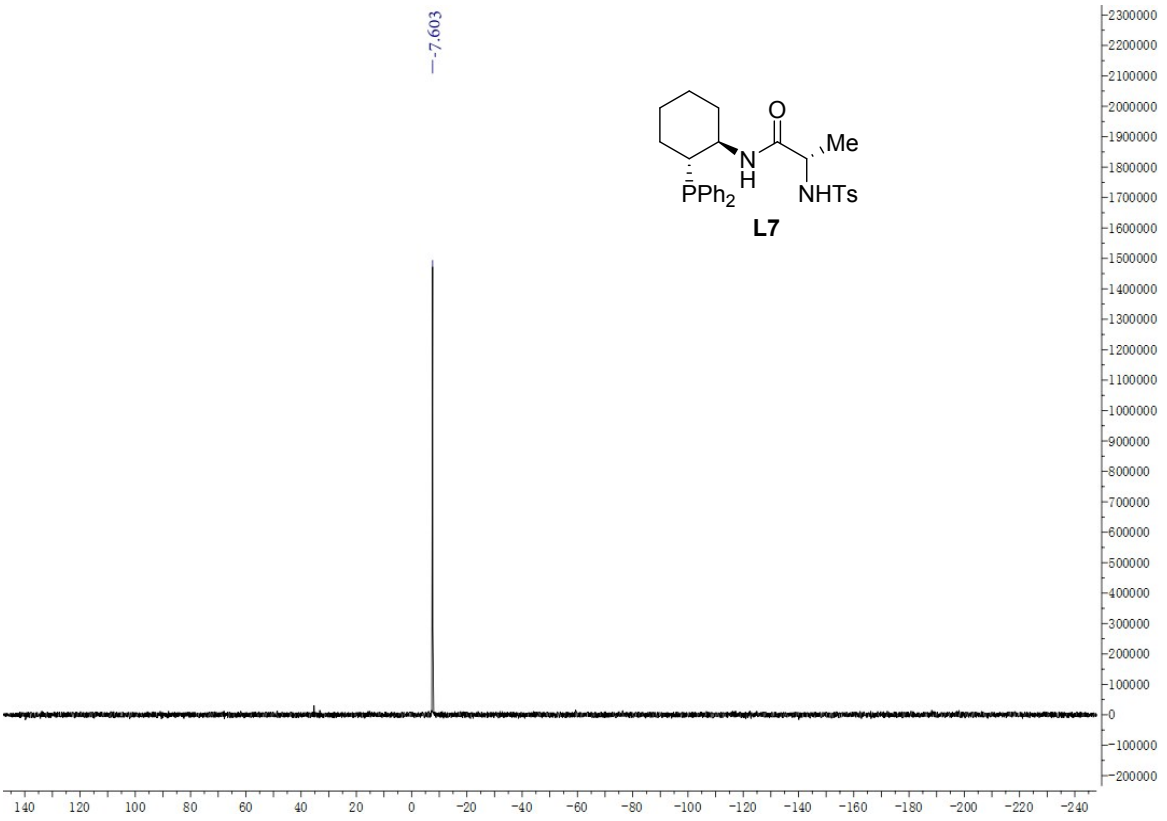
8. References

1. (a) Song, H.-L.; Yuan, K.; Wu, X.-Y. *Chem. Commun.* **2011**, *47*, 1012-1014; (b) Rexiti, R.; Lu, J.; Wang, G.; Sha, F.; Wu, X.-Y. *Tetrahedron: Asymmetry* **2016**, *27*, 923-929; (c) Kang, T.-C.; Wu, L.-P.; Sha, F.; Wu, X.-Y. *Tetrahedron* **2018**, *74*, 1017-1023; (d) Rexiti, R.; Zhang, Z.-G.; Lu, J.; Sha, F.; Wu, X.-Y. *J. Org. Chem.* **2019**, *84*, 1330-1338.
2. Yan, W.; Wang, D.; Feng, J.; Li, P.; Zhao, D.; Wang, R. *Org. Lett.* **2012**, *14*, 2512-2515.
3. Li, T.-Z.; Wang, X.-B.; Sha, F.; Wu, X.-Y. *J. Org. Chem.* **2014**, *79*, 4332-4339.
4. Zhang, H.-J.; Shi, C.-Y.; Zhong, F.; Yin, L. *J. Am. Chem. Soc.* **2017**, *139*, 2196-2199.

9. Copies of NMR Spectra for the New Chiral Ligands L7, L10 and L11



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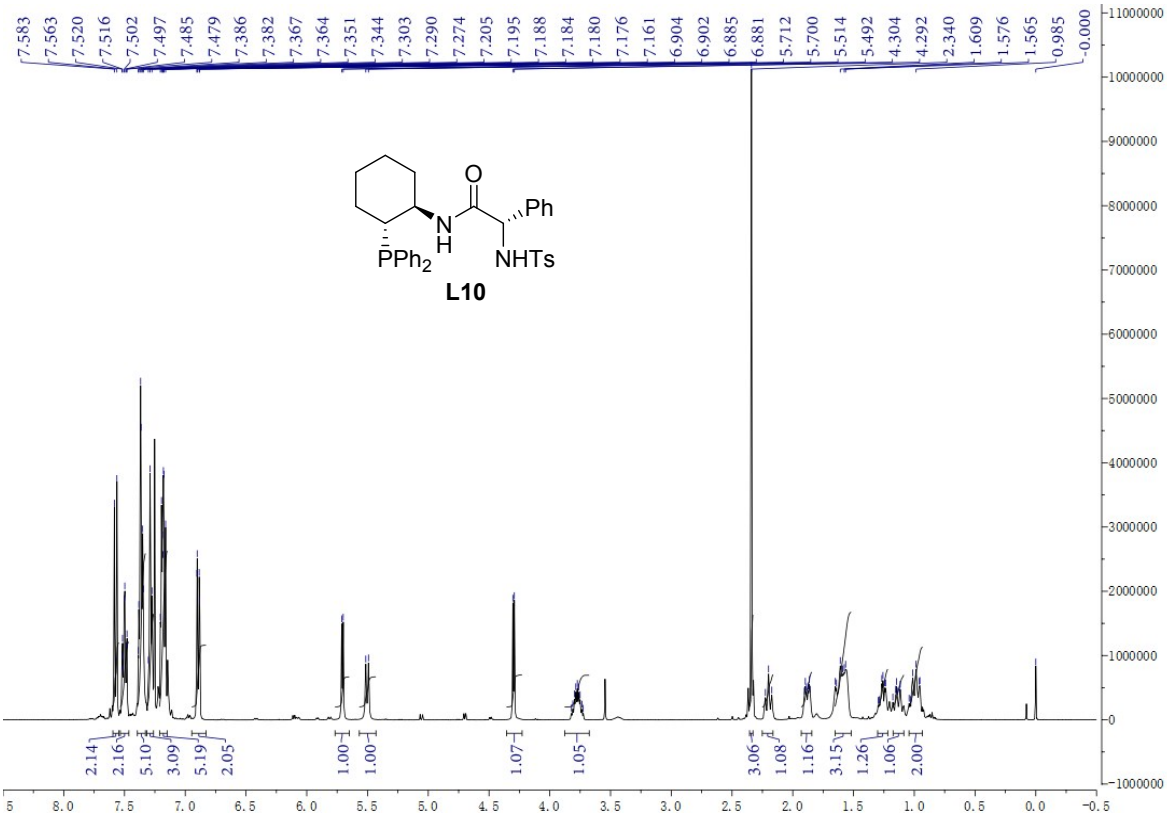
O
Me
N
H
PPh2
NHTs
L7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7.520
7.516
7.502
7.497
7.485
7.479
7.386
7.382
7.367
7.364
7.351
7.344
7.303
7.290
7.274
7.205
7.195
7.188
7.184
7.180
7.176
7.161
6.904
6.902
6.885
6.881
5.712
5.700
5.514
5.492
4.304
4.292
2.340
1.609
1.576
1.565
0.985
-0.000
O
Ph
N
H
PPh2
NHTs
L10
2.14
2.16
5.10
3.09
5.19
2.05
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1.07
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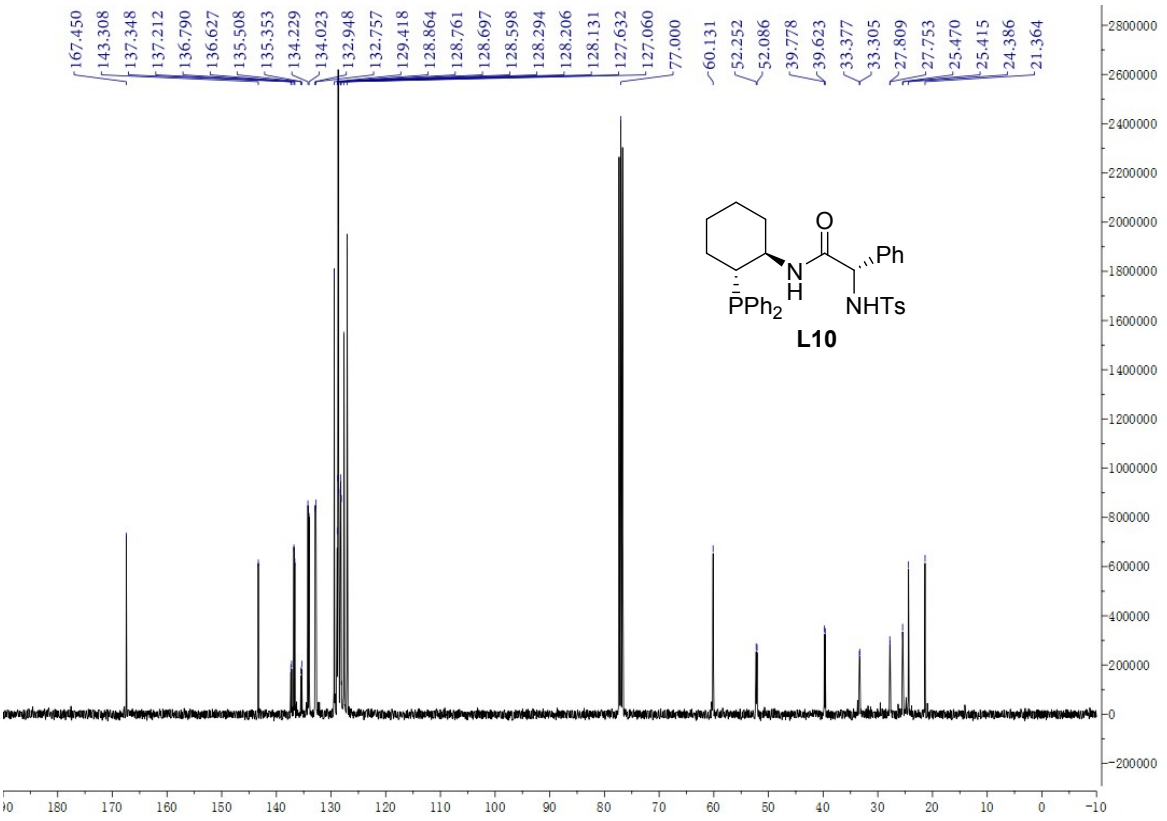
1.08
1.16
3.15
1.26
1.06
2.00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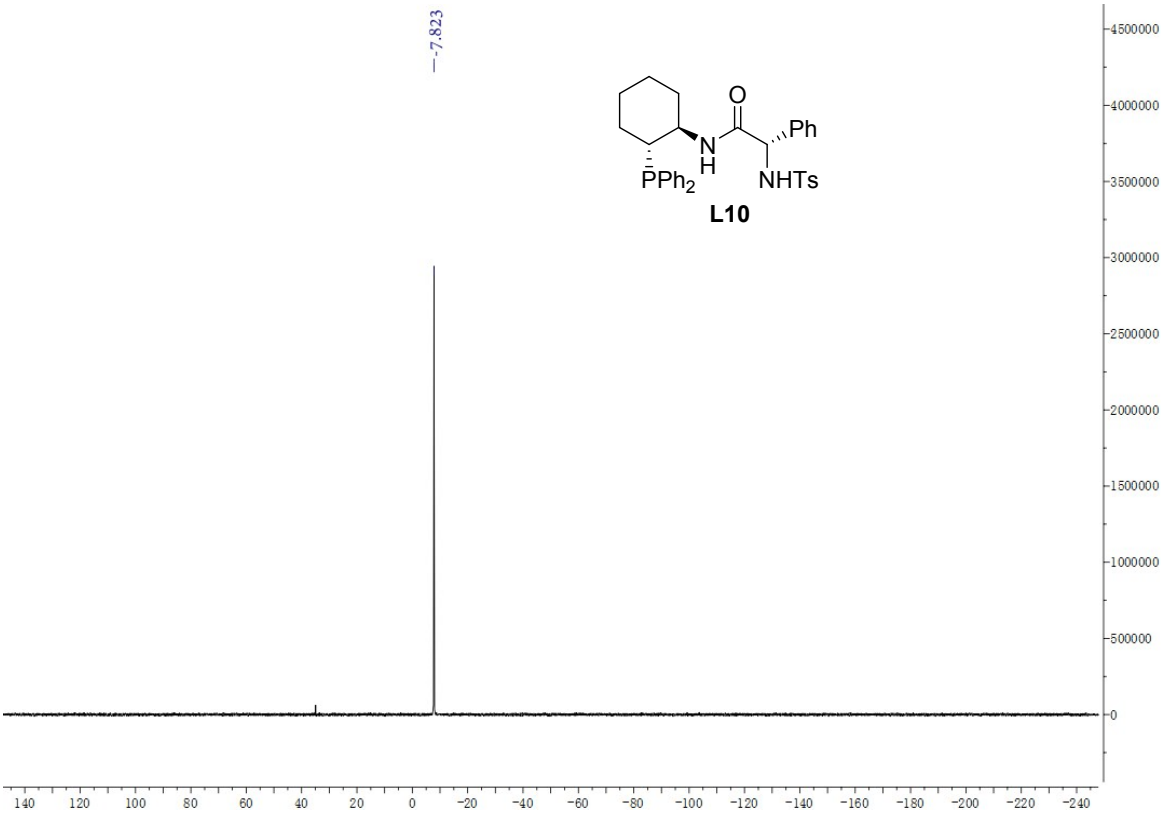
137.212
136.790
136.627
135.508
135.353
134.229
134.023
132.948
132.757
129.418
128.864
128.761
128.697
128.598
128.294
128.206
128.131
127.632
127.060
77.000
60.131
52.252
52.086
39.778
39.623
33.377
33.305
27.809
27.753
25.470
25.415
24.386
21.364
O
Ph
N
H
PPh2
NHTs
L10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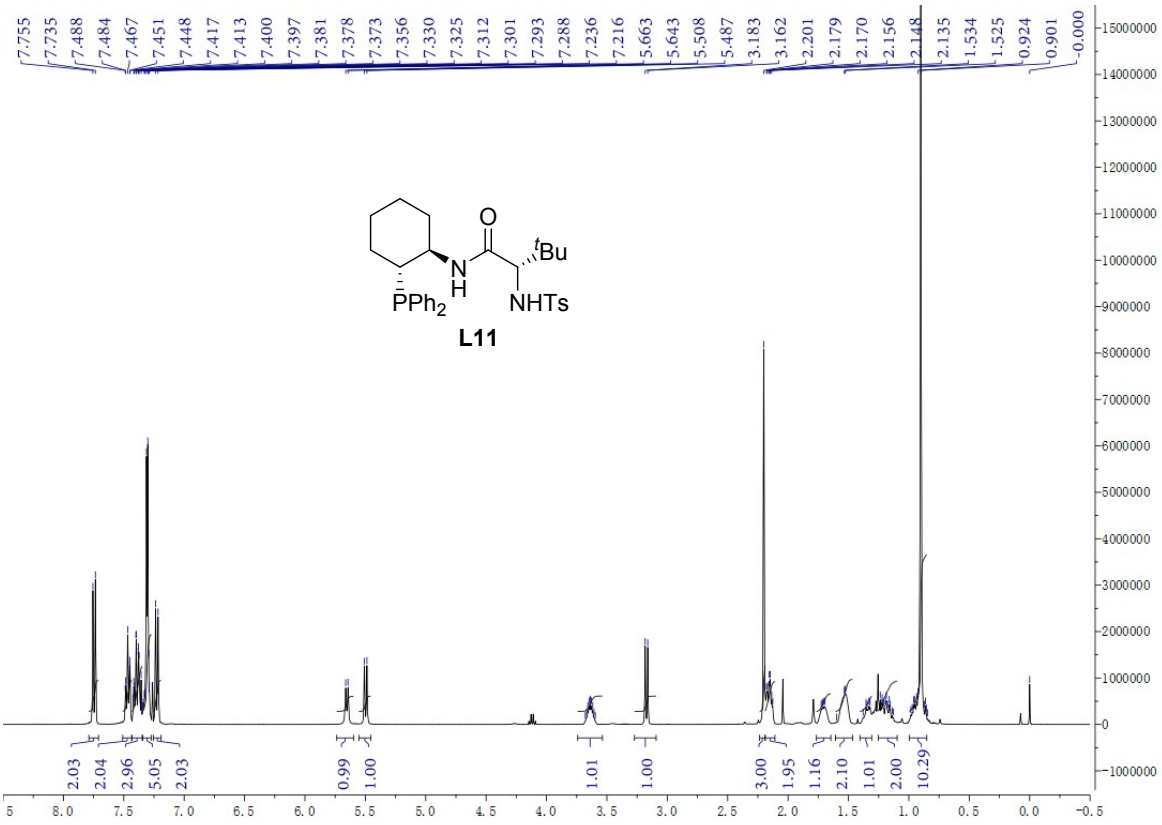
NHTs
L10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7.484
7.467
7.451
7.448
7.417
7.413
7.400
7.397
7.381
7.378
7.373
7.356
7.330
7.325
7.312
7.301
7.293
7.288
7.236
7.216
5.663
5.643
5.508
5.487
3.183
3.162
2.201
2.179
2.170
2.156
2.148
2.135
1.534
1.525
0.924
0.901
0.000
O
tBu
N
H
PPh2
NHTs
L11
2.03
2.04
2.96
5.05
2.03
0.99
1.00
1.01
1.00
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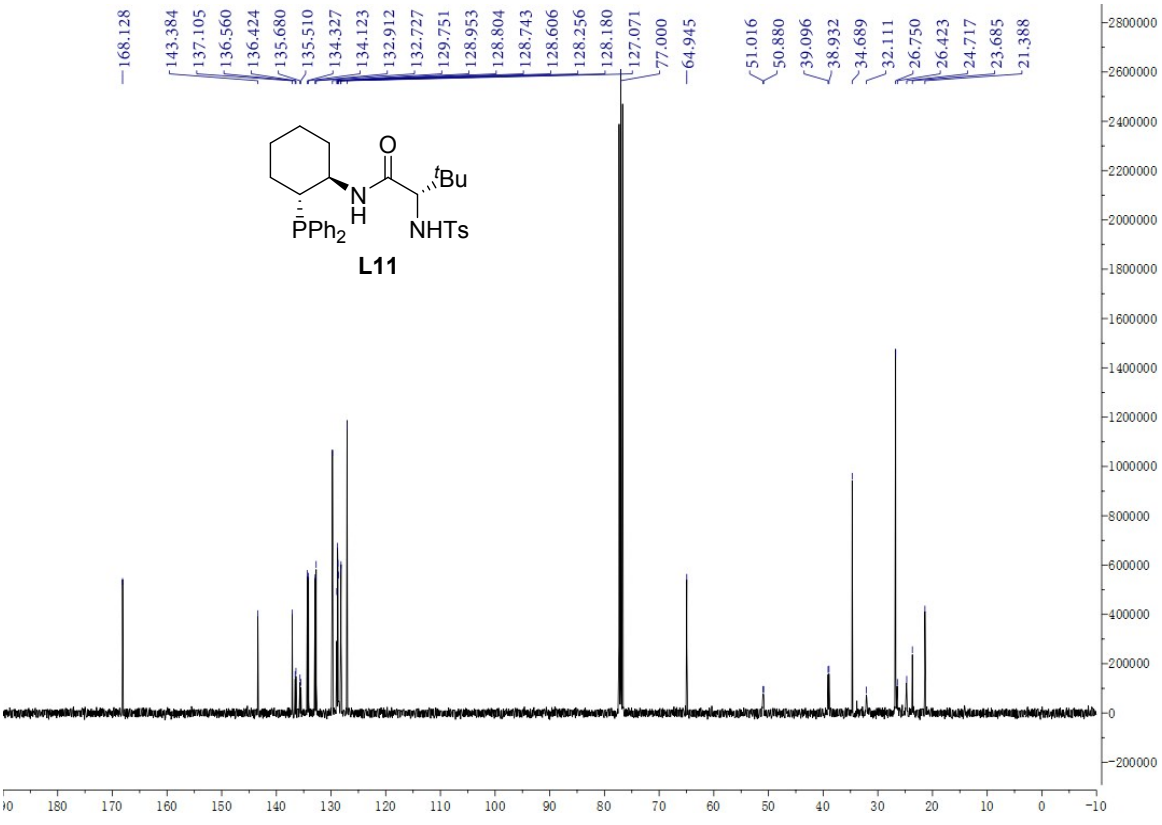
1.95
1.16
2.10
1.01
2.00
10.29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134.327
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132.912
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128.953
128.804
128.743
128.606
128.256
128.180
127.071
77.000
64.945
51.016
50.880
39.096
38.932
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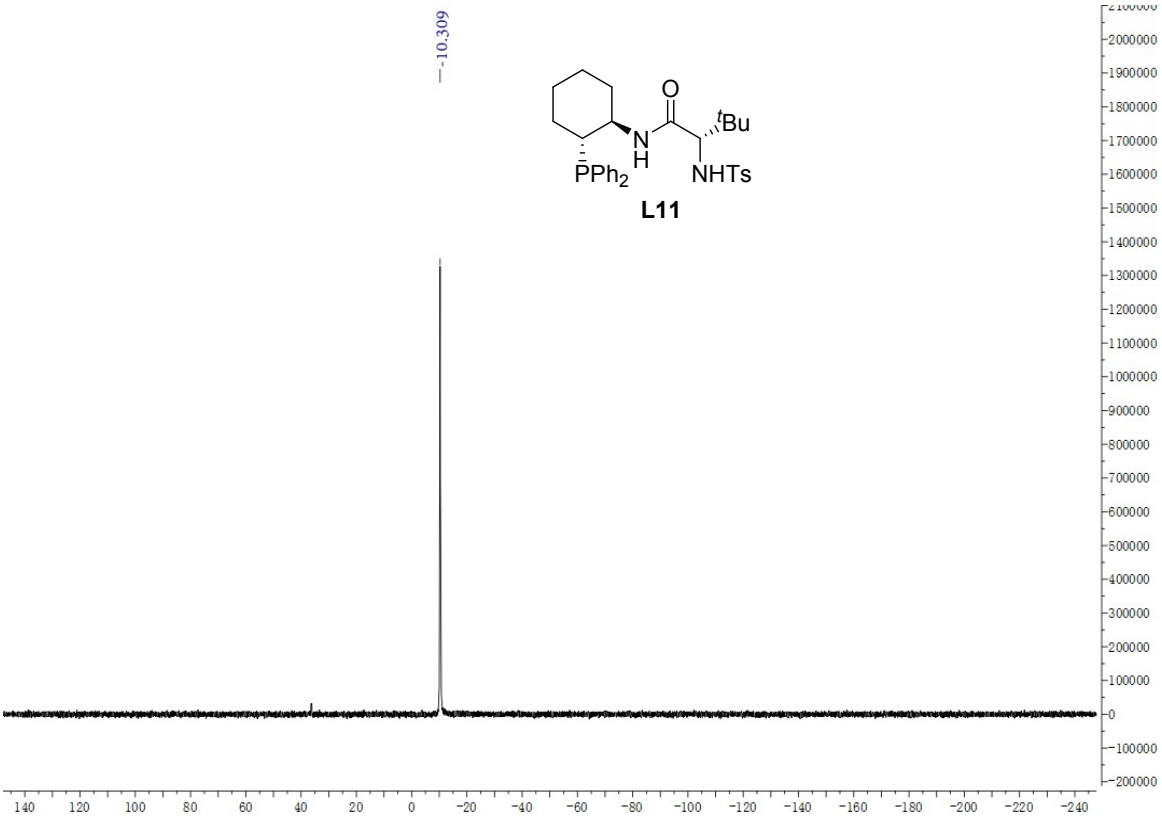
23.685
21.388
O
tBu
N
H
PPh2
NHTs
L11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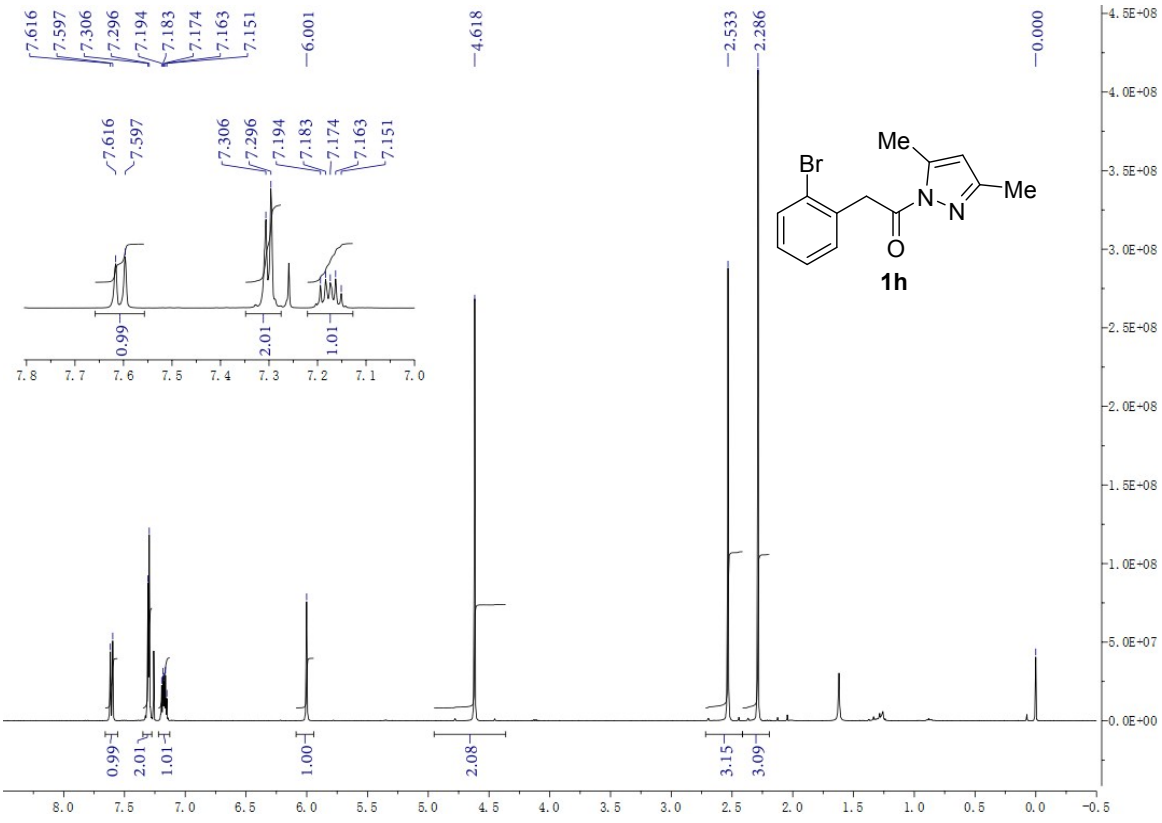
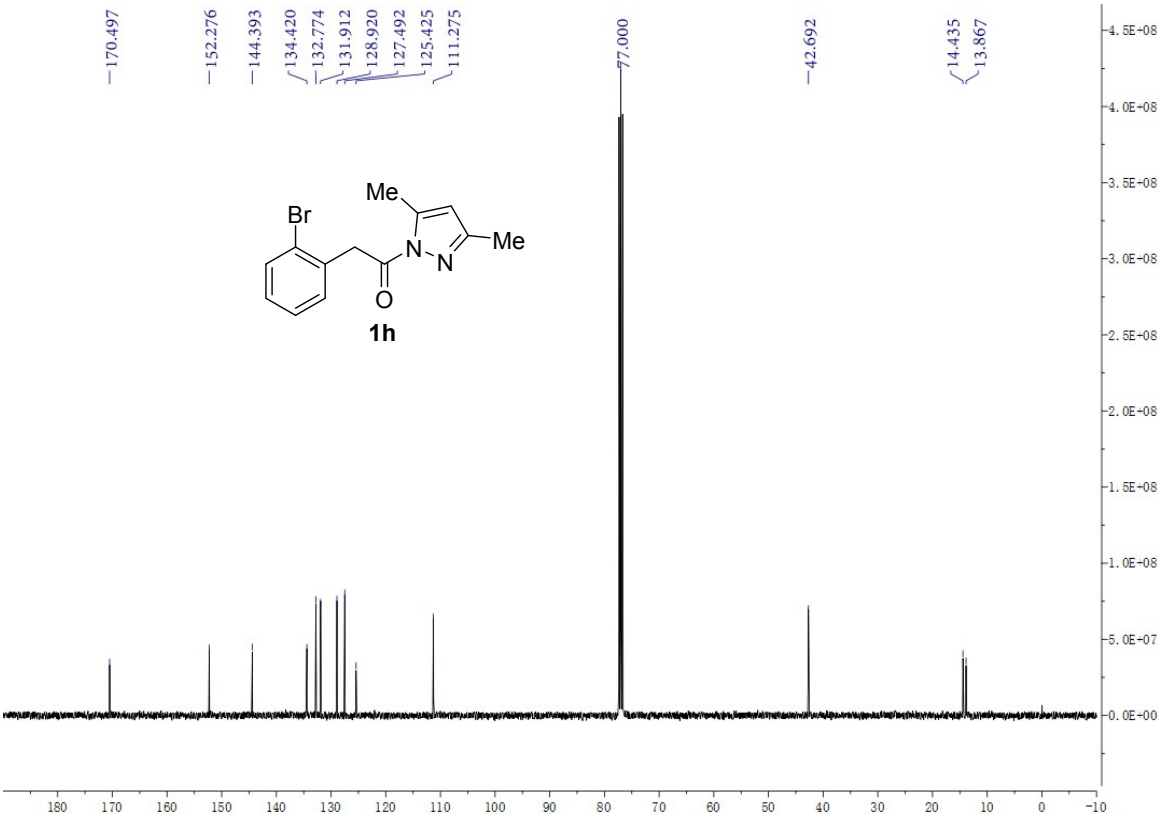
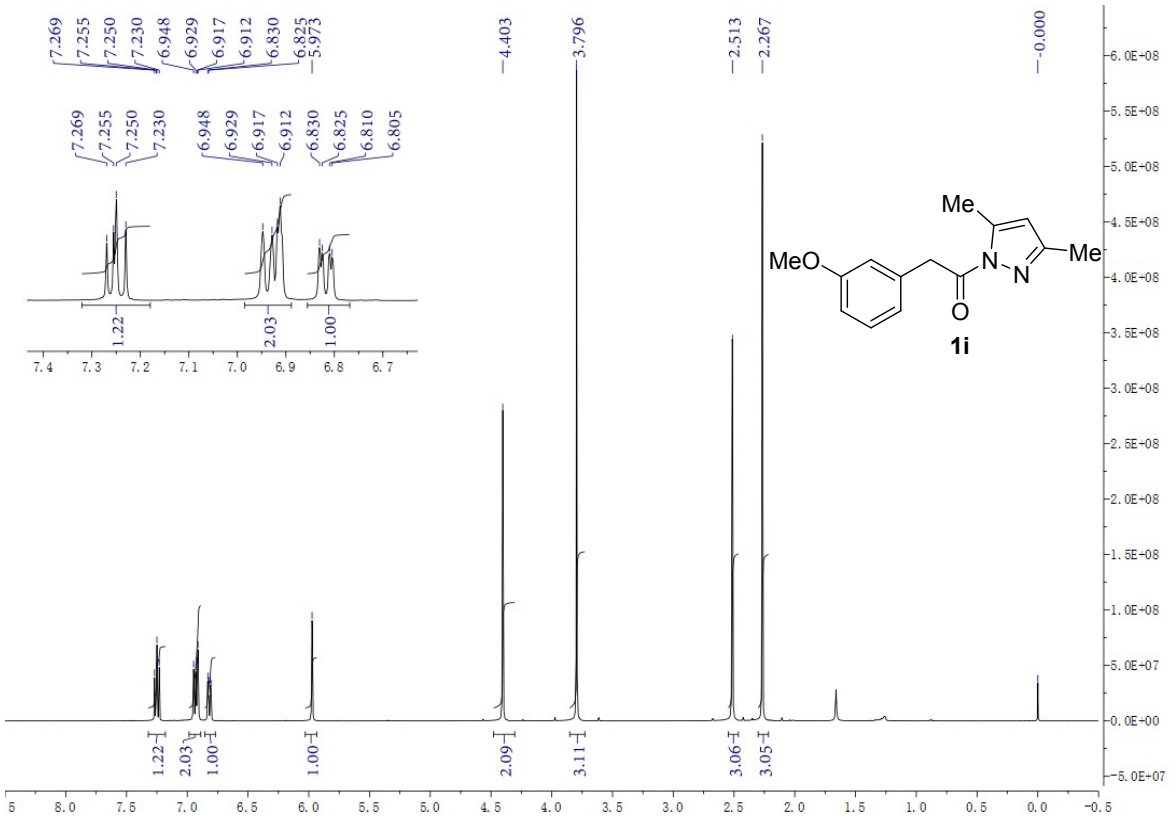
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240

10. Copies of NMR Spectra for the *N*-Acylpyrazoles 1h-1j and 1p



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7.230
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6.929
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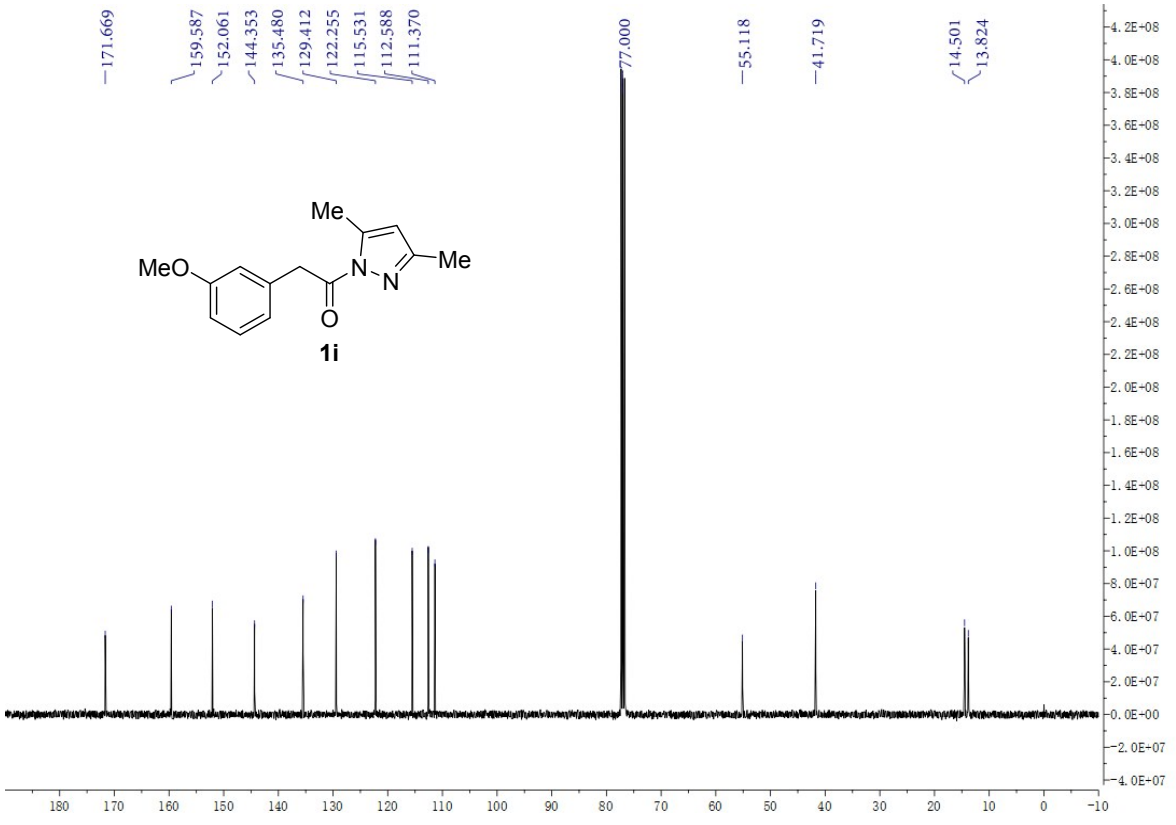
6.830
6.825
5.973
4.403
3.796
2.513
2.267
-0.000
6.810
6.805
1.22
2.03
1.00
2.09
3.11
3.06
3.05
Me
MeO
N
O
1i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135.480
129.412
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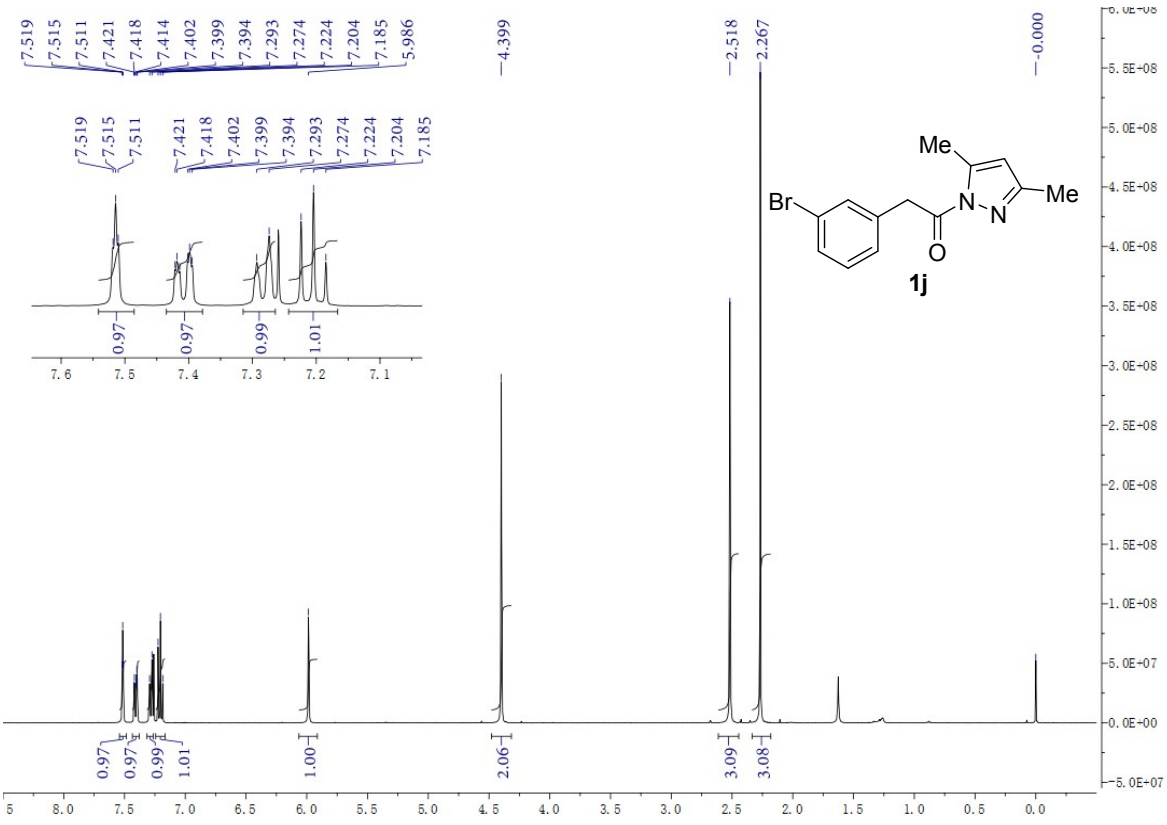
111.370
77.000
55.118
41.719
14.501
13.824
Me
MeO
N
O
1i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7.293
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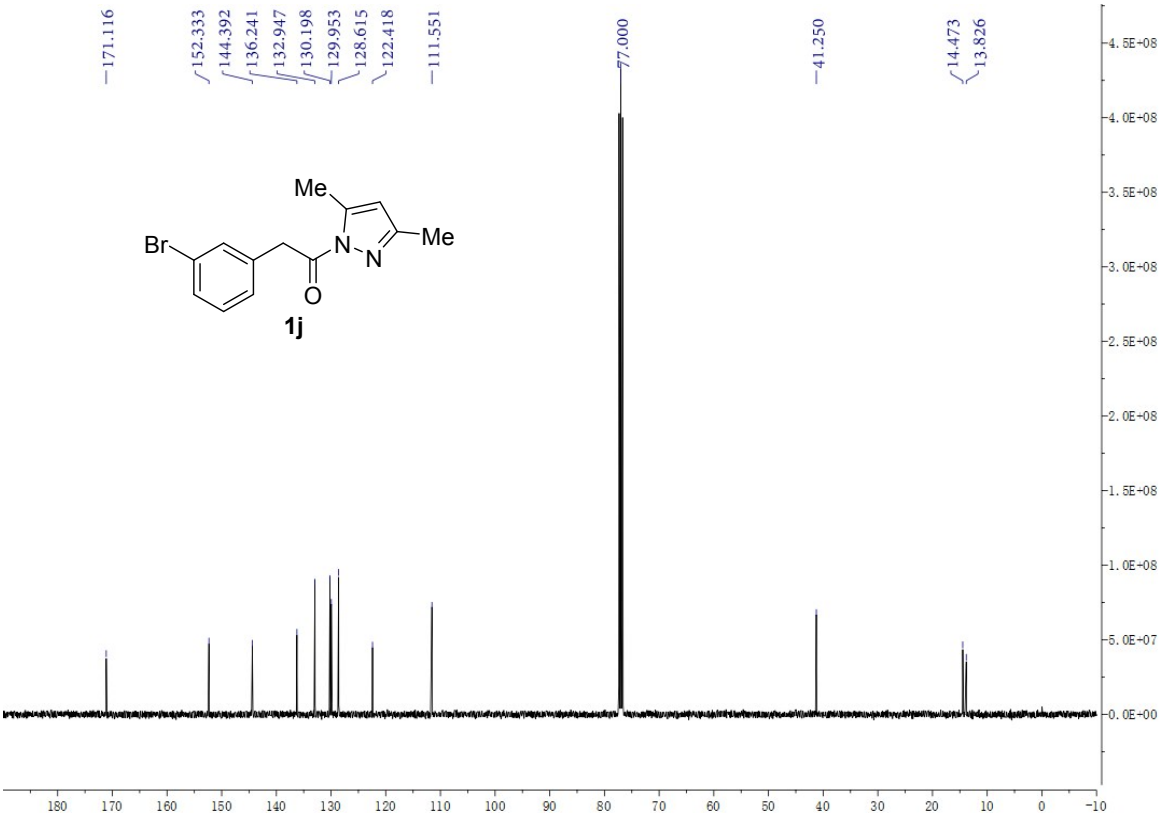
7.204
7.185
5.986
4.399
2.518
2.267
-0.000
0.97
0.97
0.99
1.01
1.00
2.06
3.09
3.08
Me
Br
N
N
Me
O
1j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144.392
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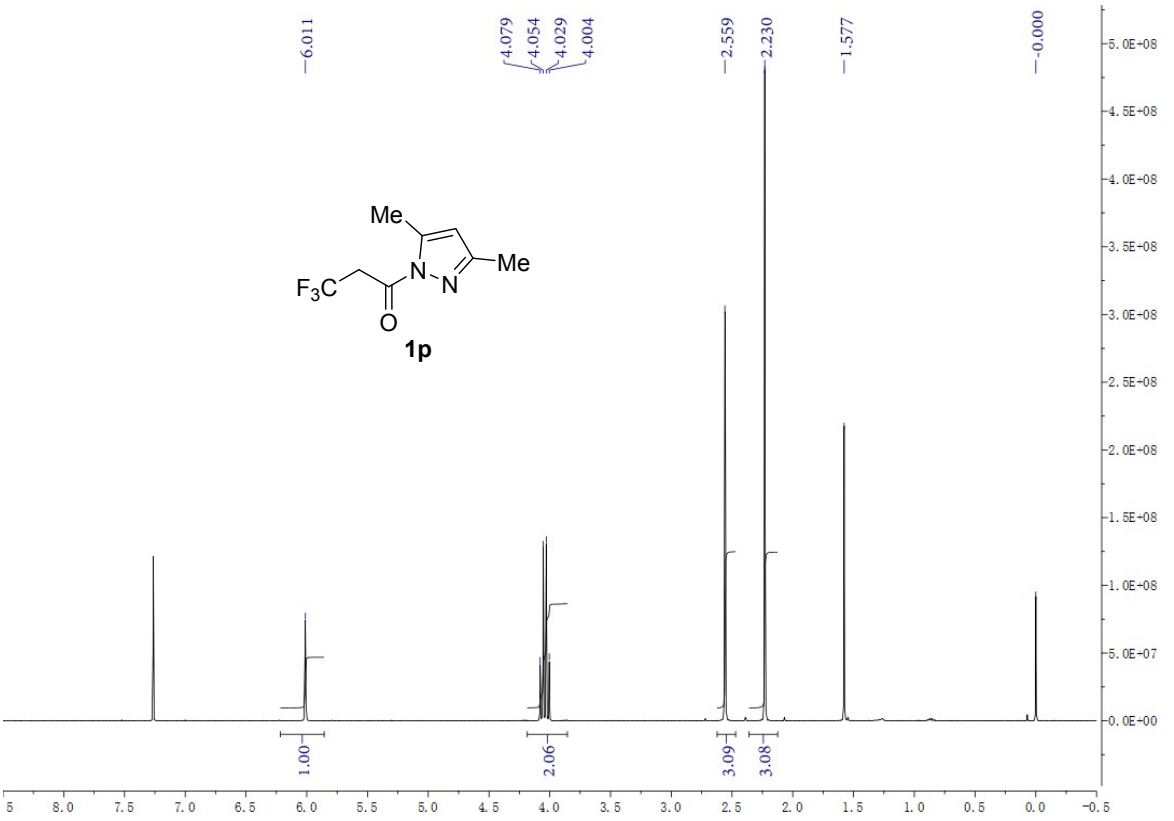
132.947
130.198
129.953
128.615
122.418
111.551
77.000
41.250
14.473
13.826
Me
Br
N
N
Me
O
1j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4.079
4.054
4.029
4.004
2.559
2.230
1.577
-0.000
Me
Me
F3C
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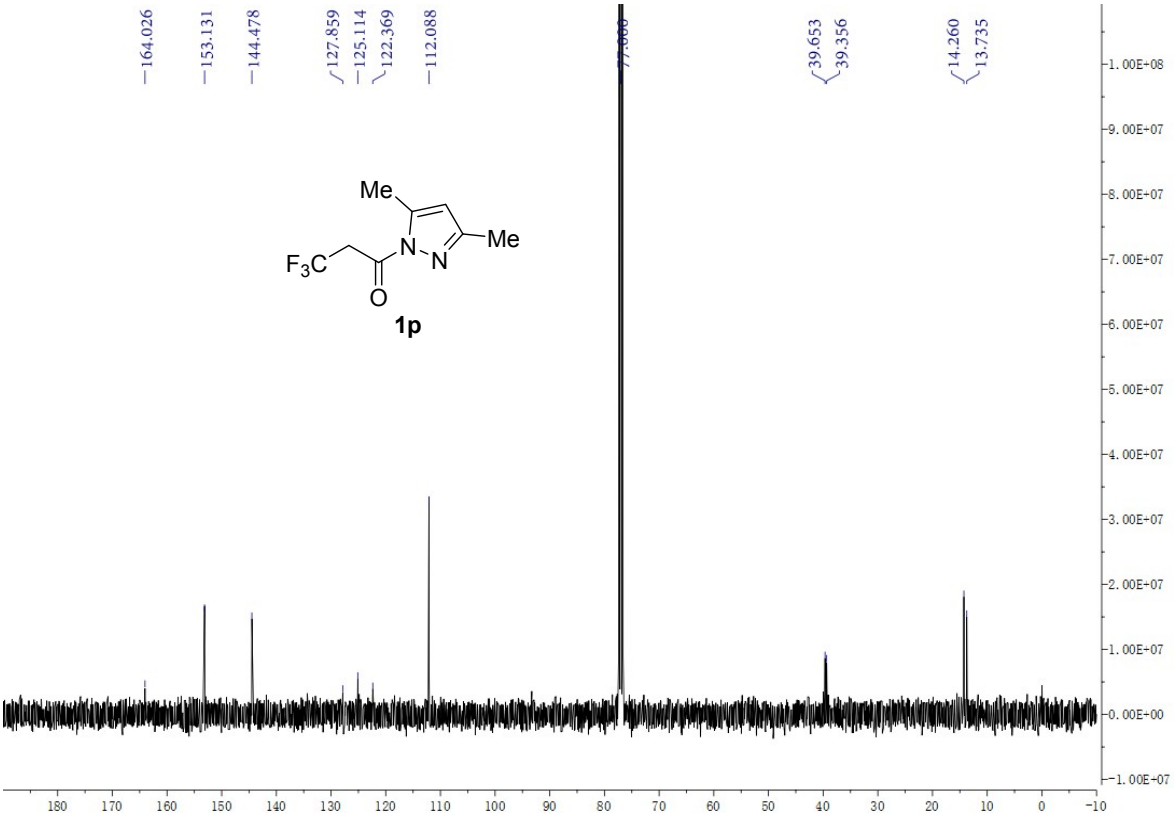
N
O
1p
1.00
2.06
3.09
3.08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77.000
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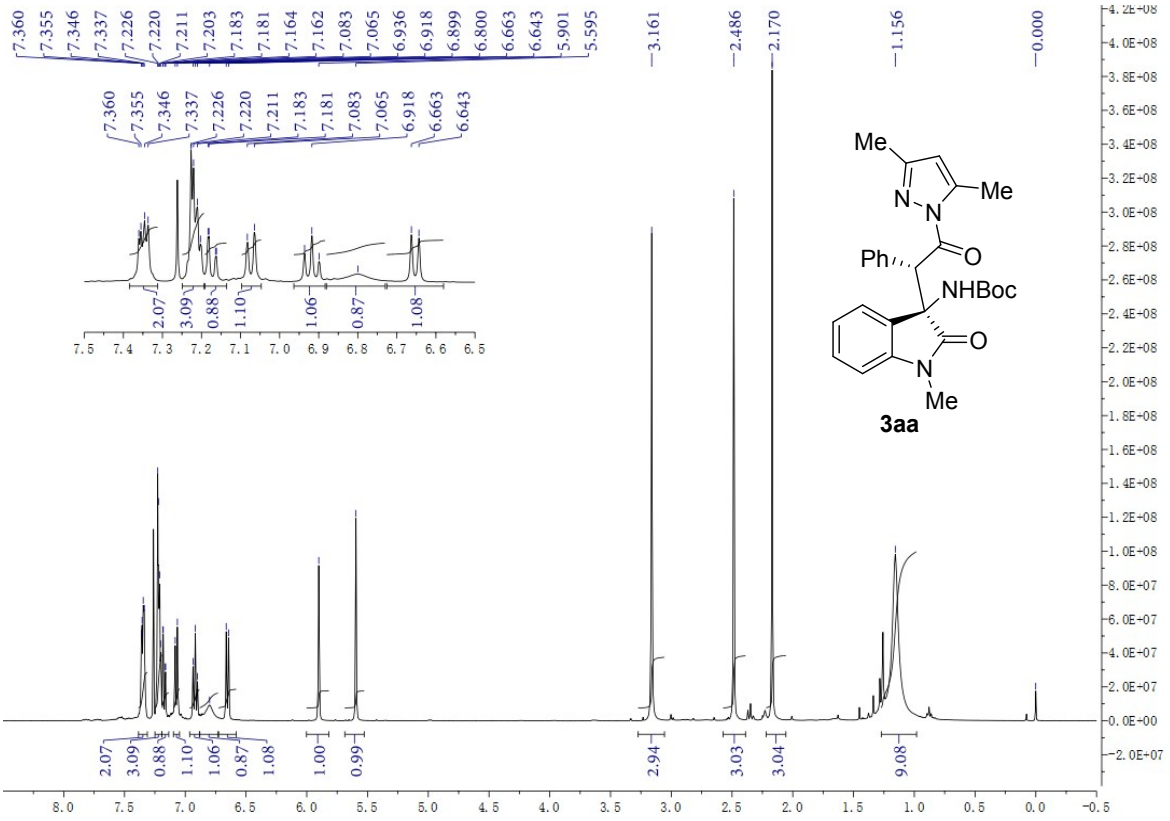
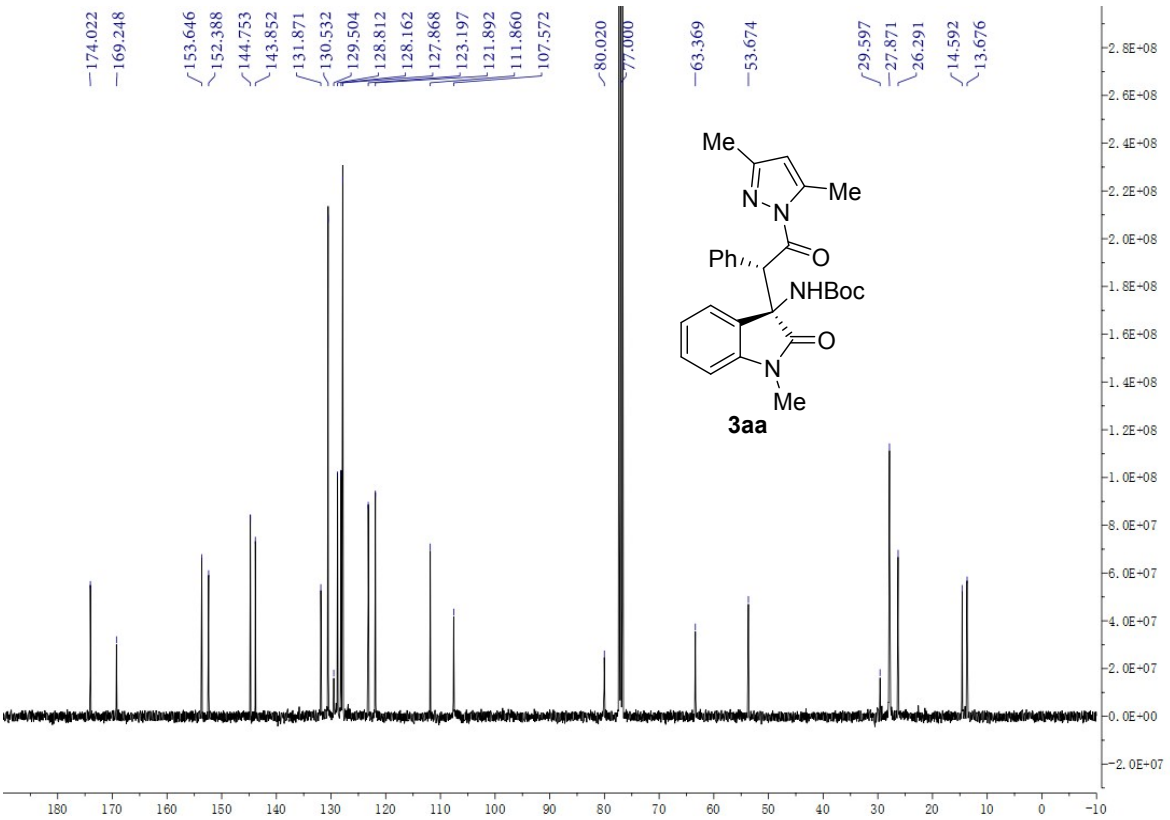
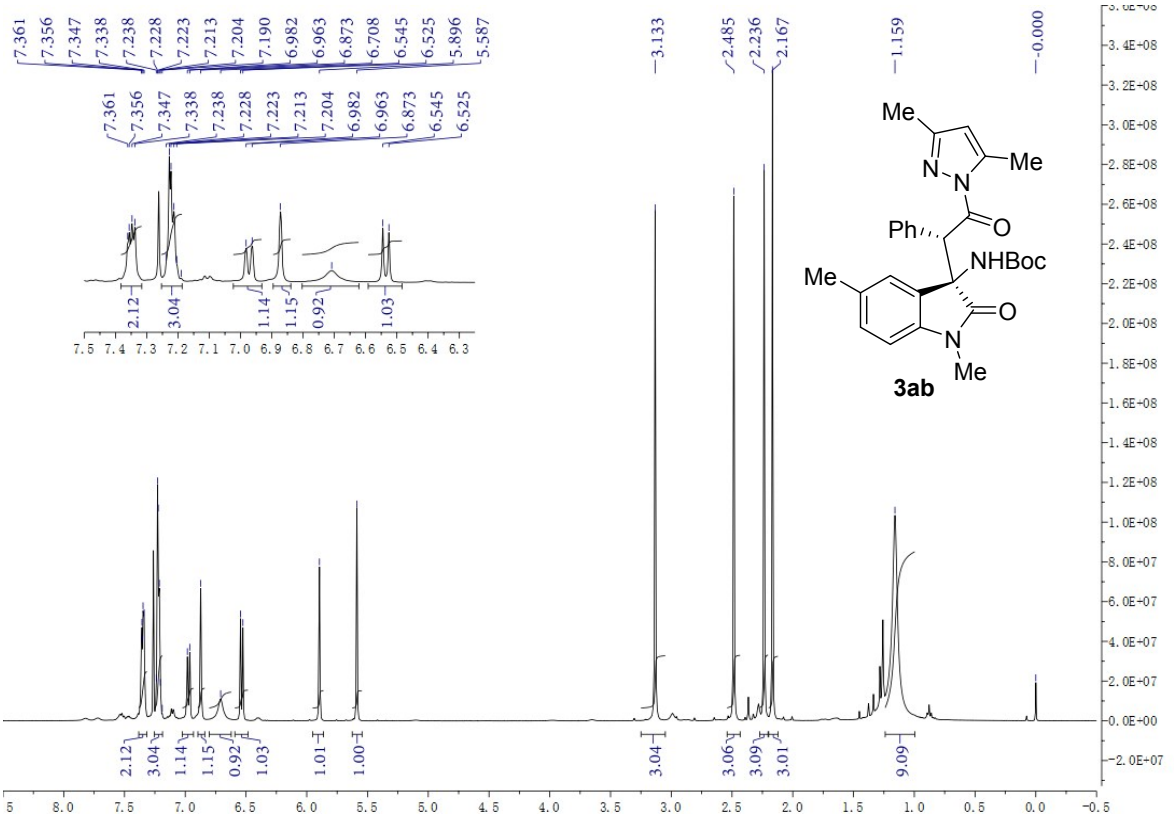
13.735
Me
Me
F3C
N
N
O
1p

11. Copies of NMR Spectra for Products 3-5



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7.190
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6.873
6.708
6.545
6.525
5.896
5.587
3.133
2.485
2.236
2.167
1.159
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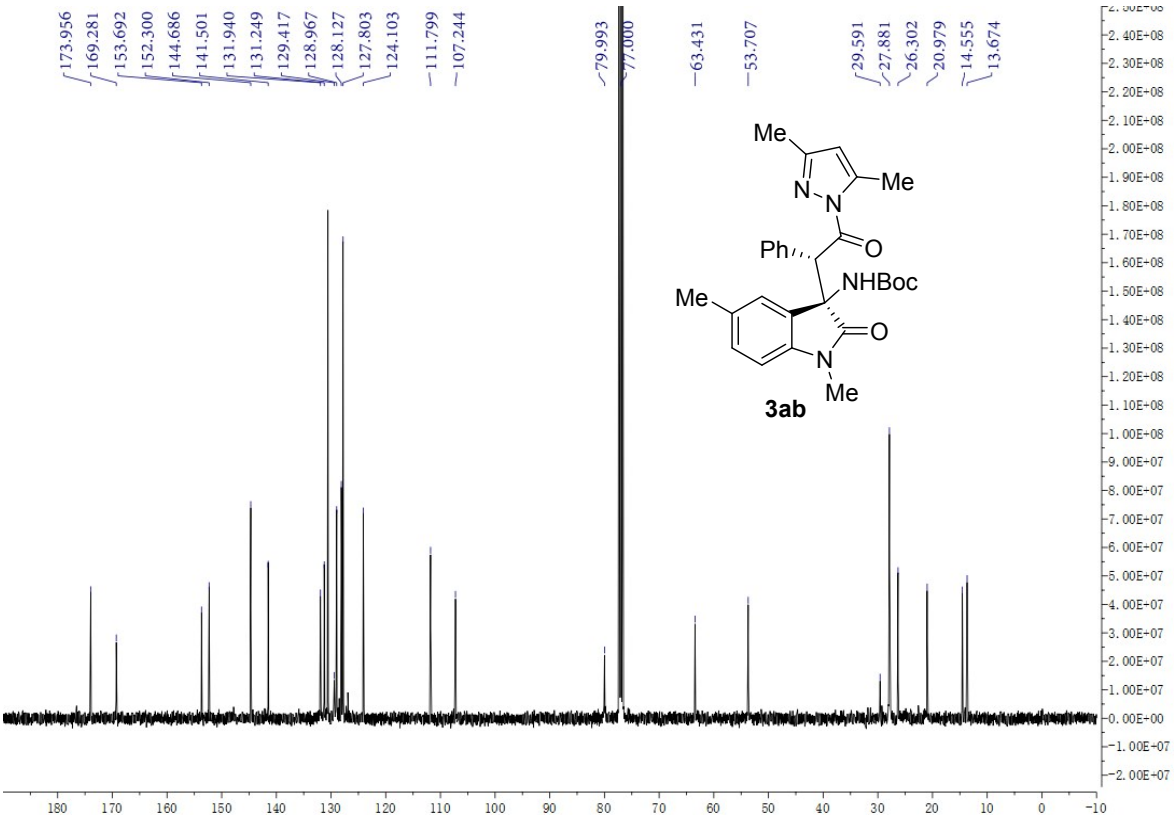
2.12
3.04
1.14
1.15
0.92
1.03
1.01
1.00
3.04
3.06
3.09
3.01
9.09
Me
N
N
Me
Ph
O
NHBoc
Me
O
N
Me
3ab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141.501
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128.967
128.127
127.803
124.103
111.799
107.244
79.993
77.000
63.431
53.707
29.591
27.881
26.302
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14.555
13.674
Me
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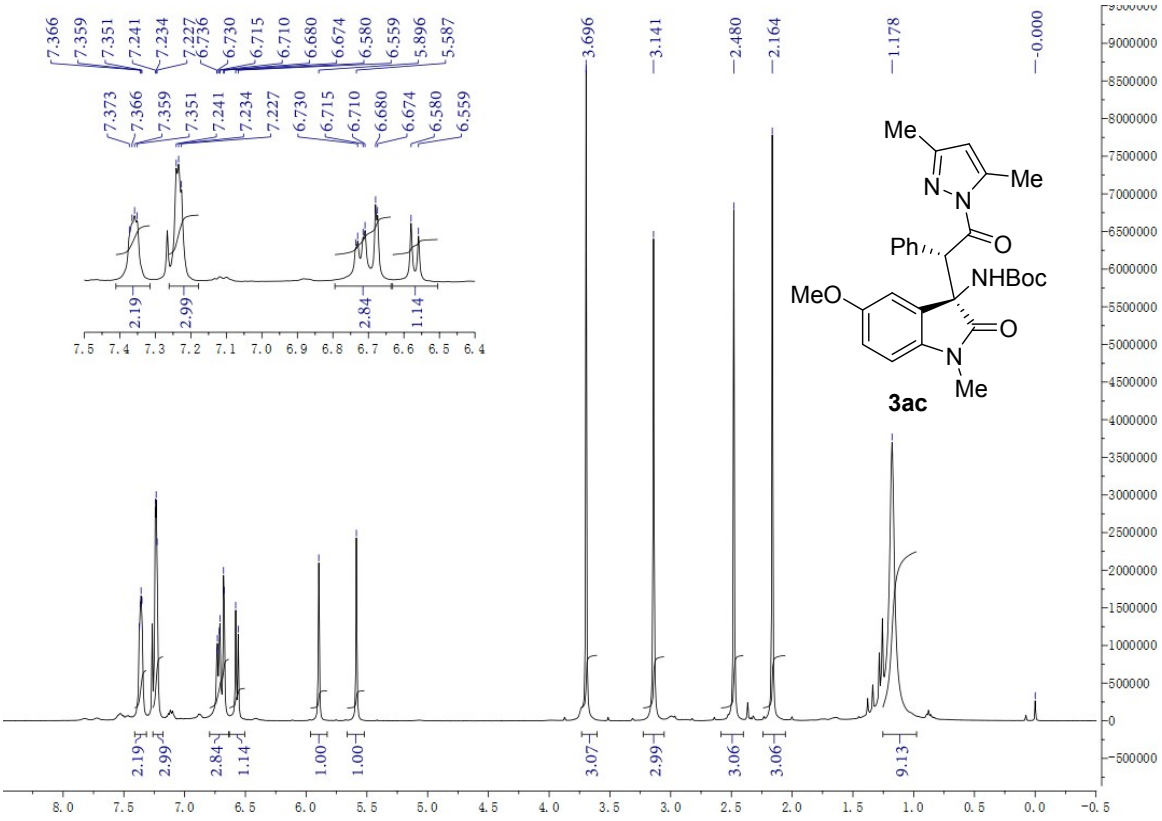
N
Me
Ph
O
NHBoc
Me
O
N
Me
3ab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6.710
6.680
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6.580
6.559
5.896
5.587
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3.141
2.480
2.164
1.178
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2.99
2.84
1.14
1.00
1.00
3.07
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9.13
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N
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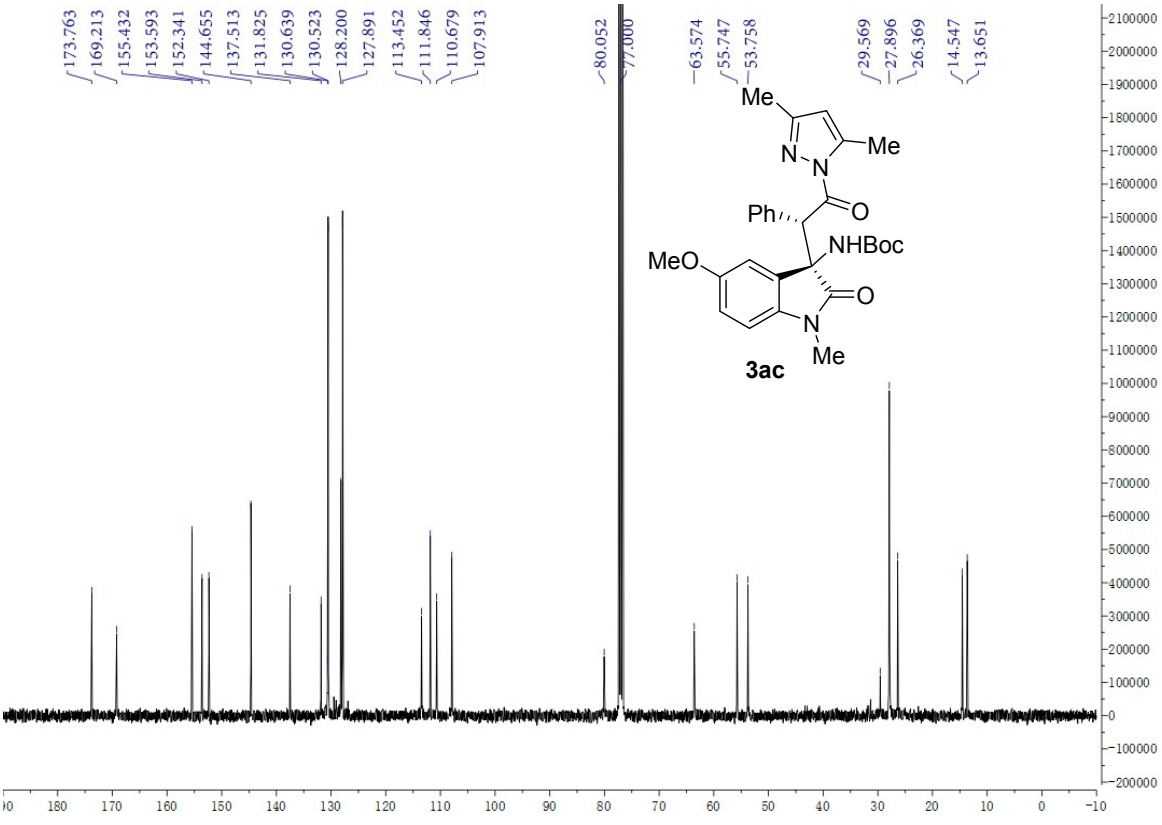
Ph
O
NHBoc
MeO
O
N
Me
3ac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127.891
113.452
111.846
110.679
107.913
80.052
77.000
63.574
55.747
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Ph
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O
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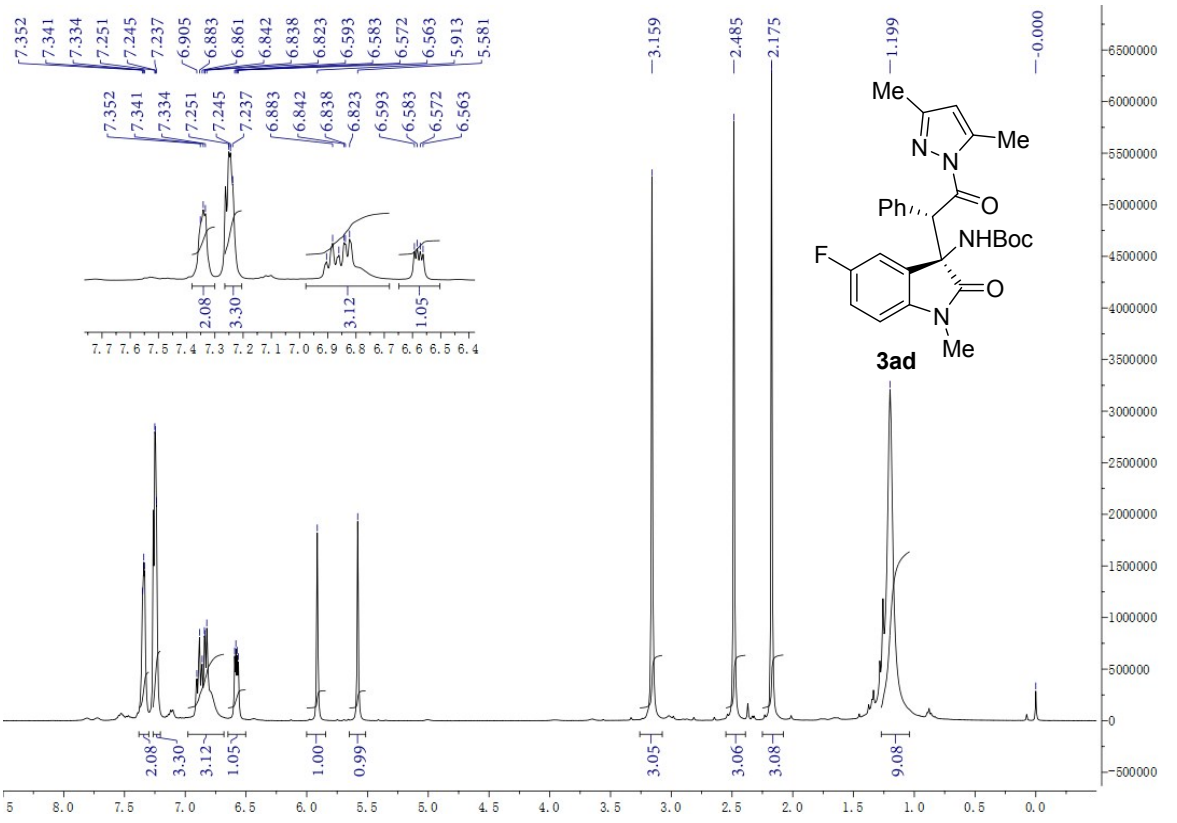
Me
3ac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7.245
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6.883
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6.823
6.593
6.583
6.572
6.563
5.913
5.581
3.159
2.485
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1.199
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N
Me
Ph
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NHBoc
F
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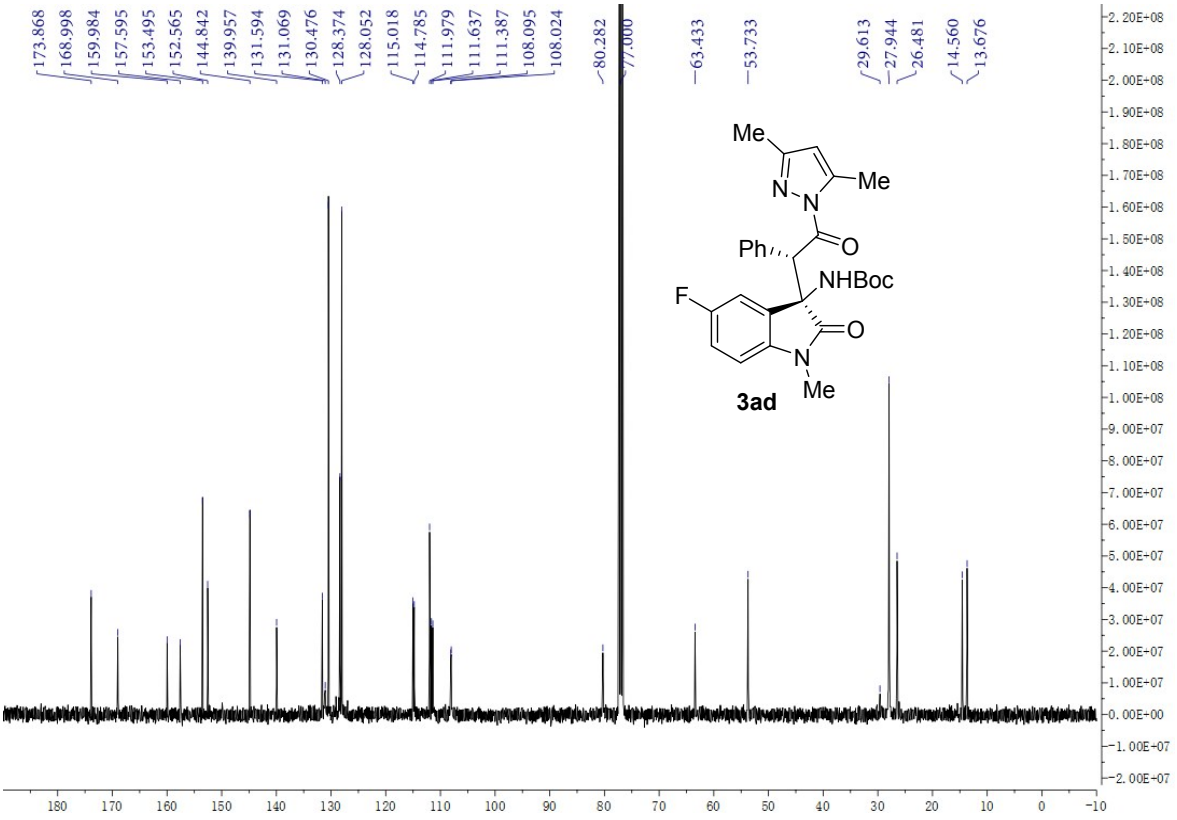
3.08
9.08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153.495
152.565
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128.052
115.018
114.785
111.979
111.637
111.387
108.095
108.024
80.282
77.000
63.433
53.733
29.613
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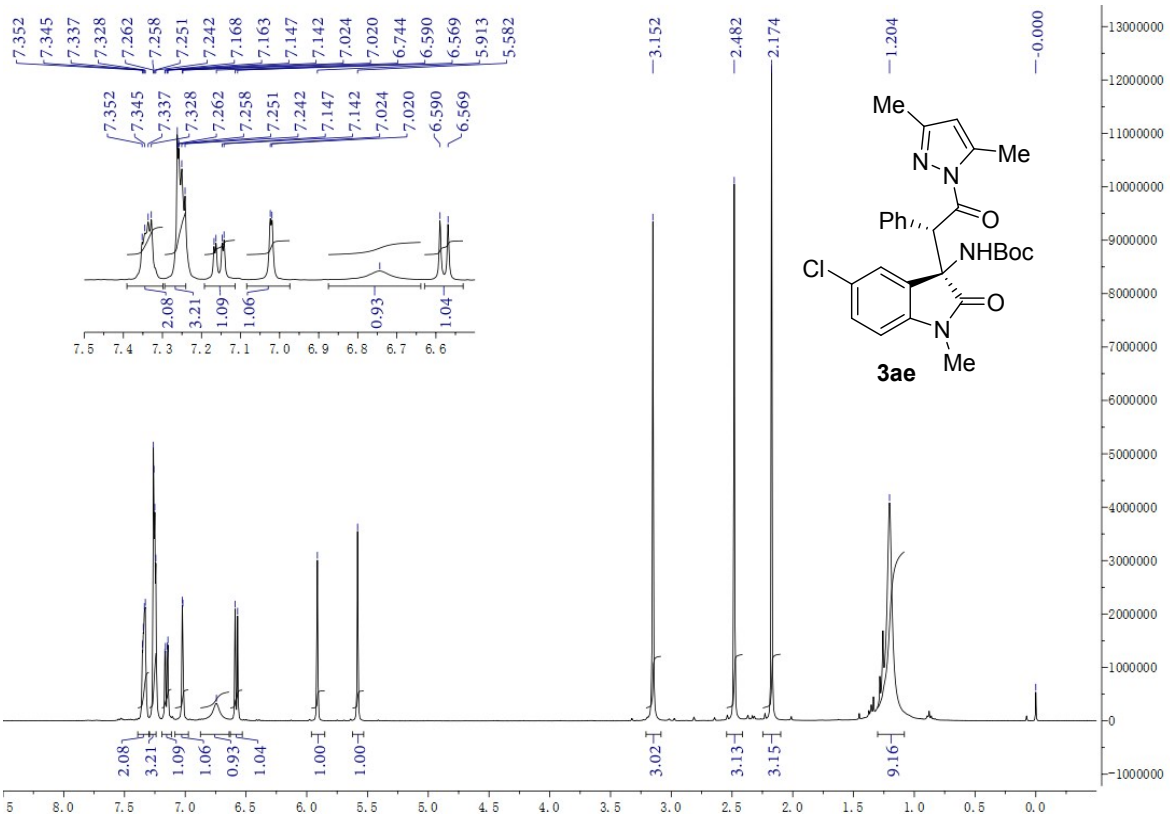
Me
3ad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7.262
7.258
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7.163
7.147
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6.569
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2.08
3.21
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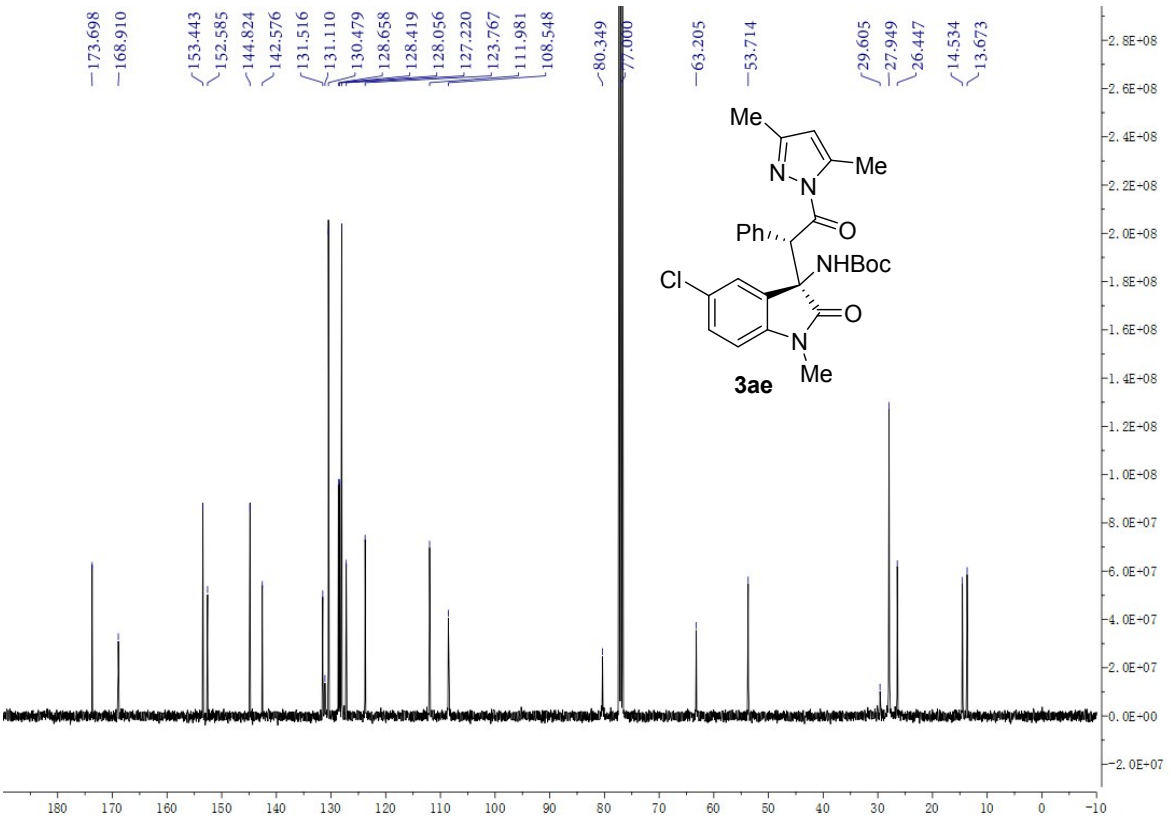
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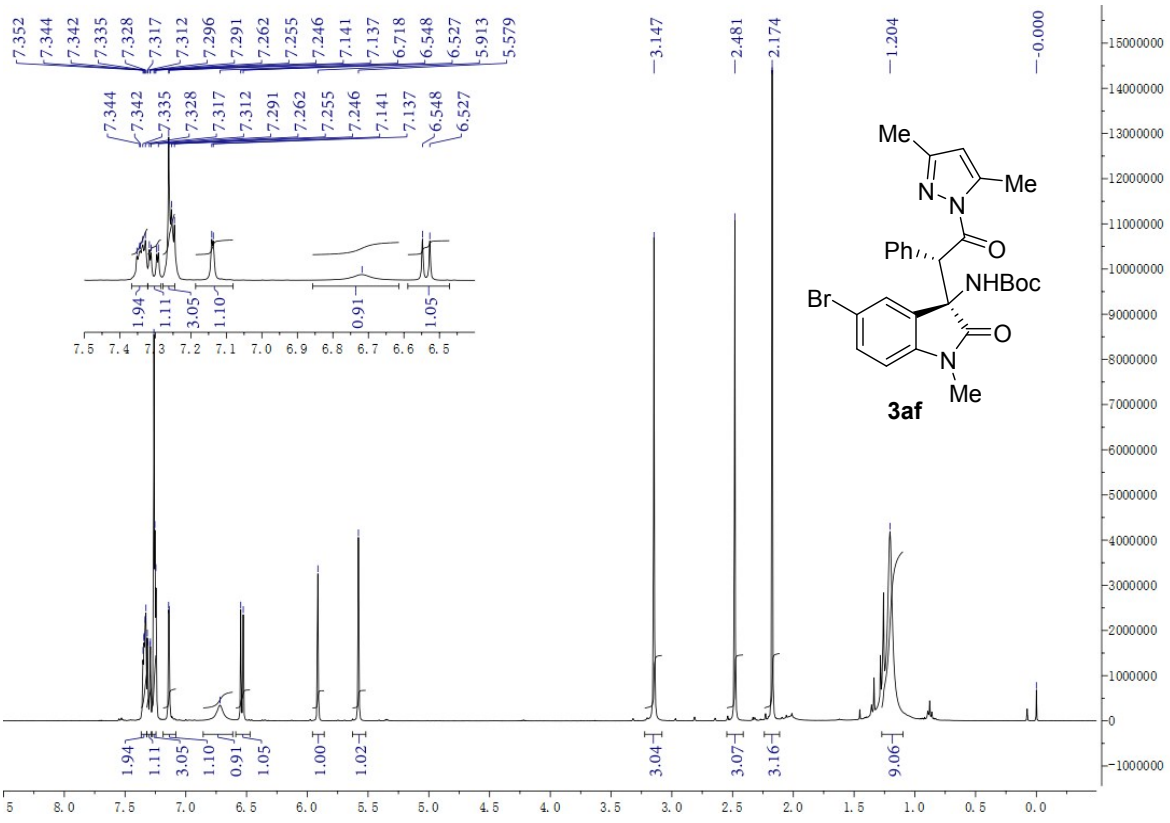
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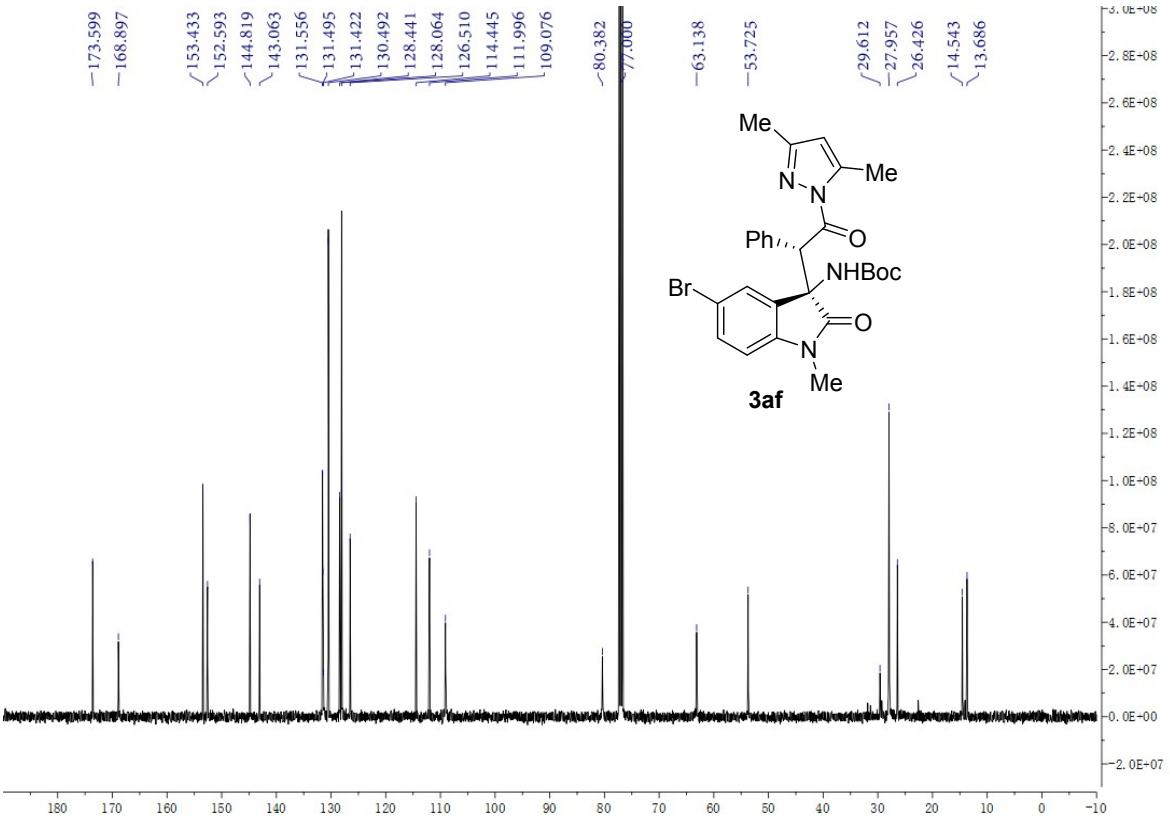
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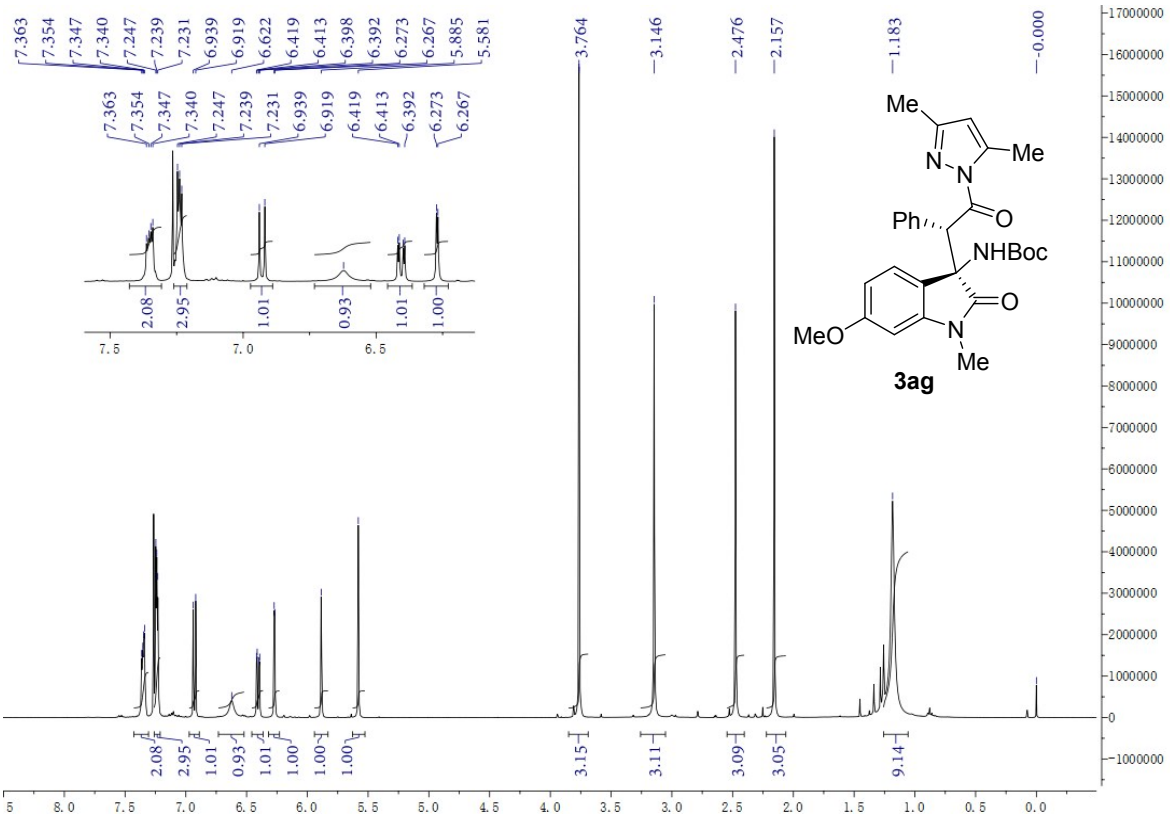
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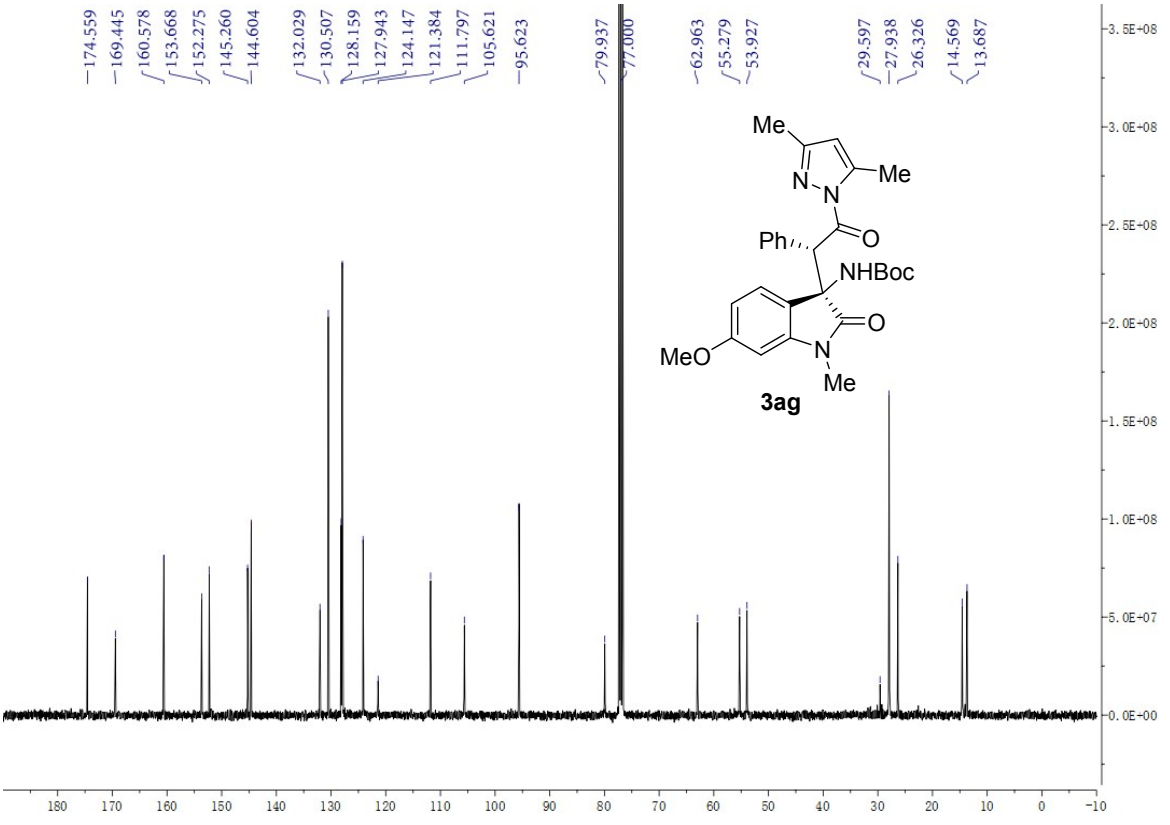
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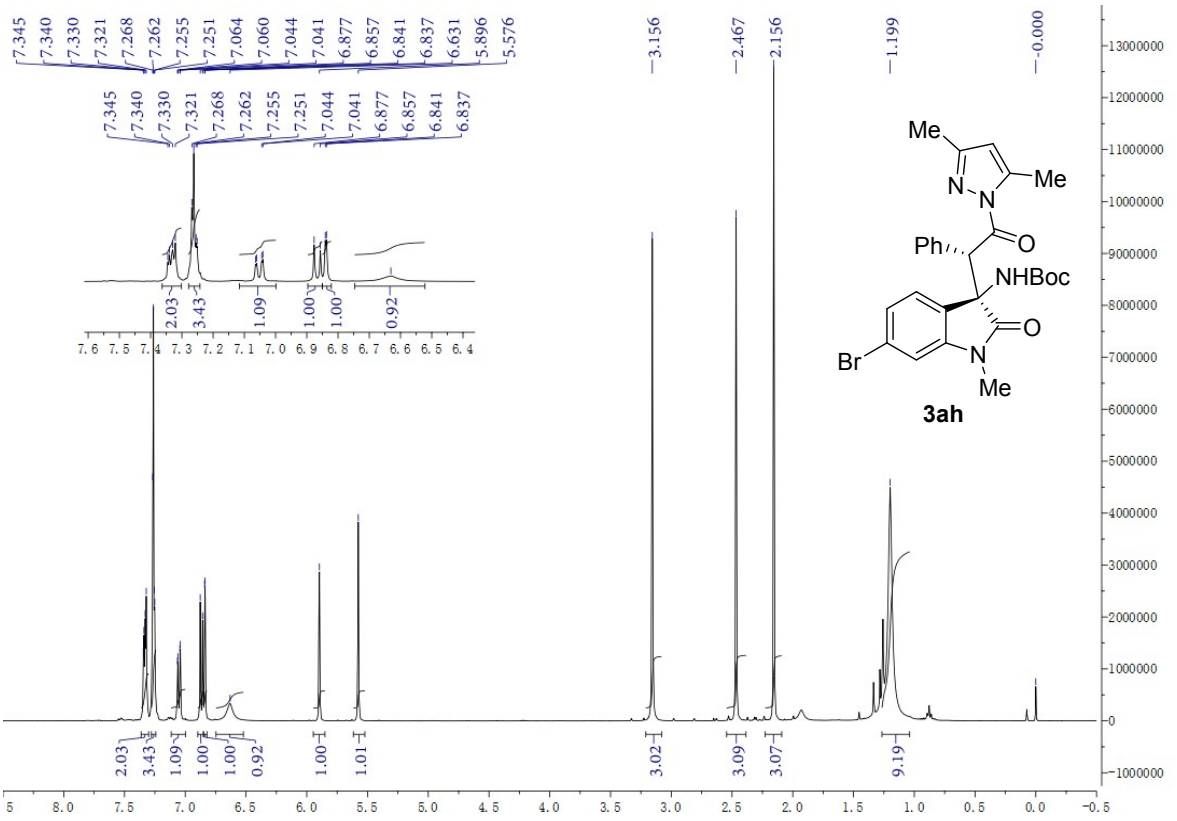
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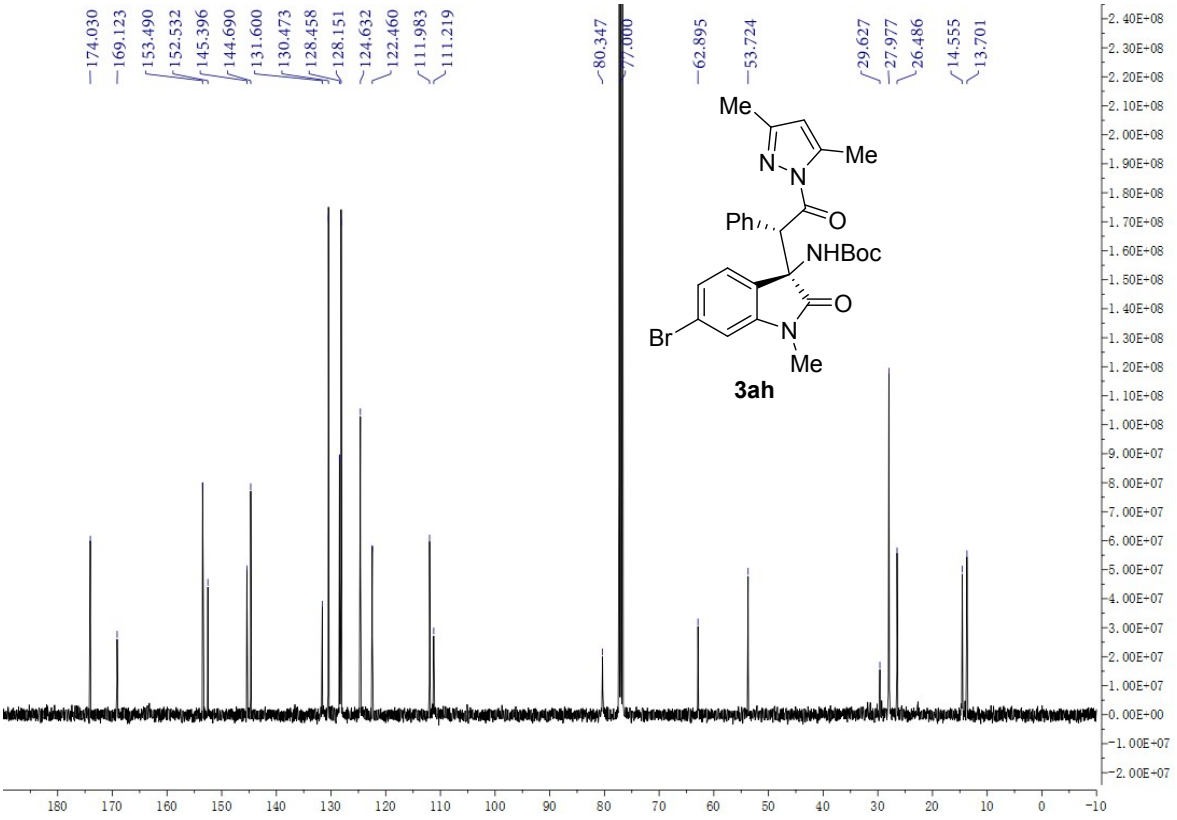
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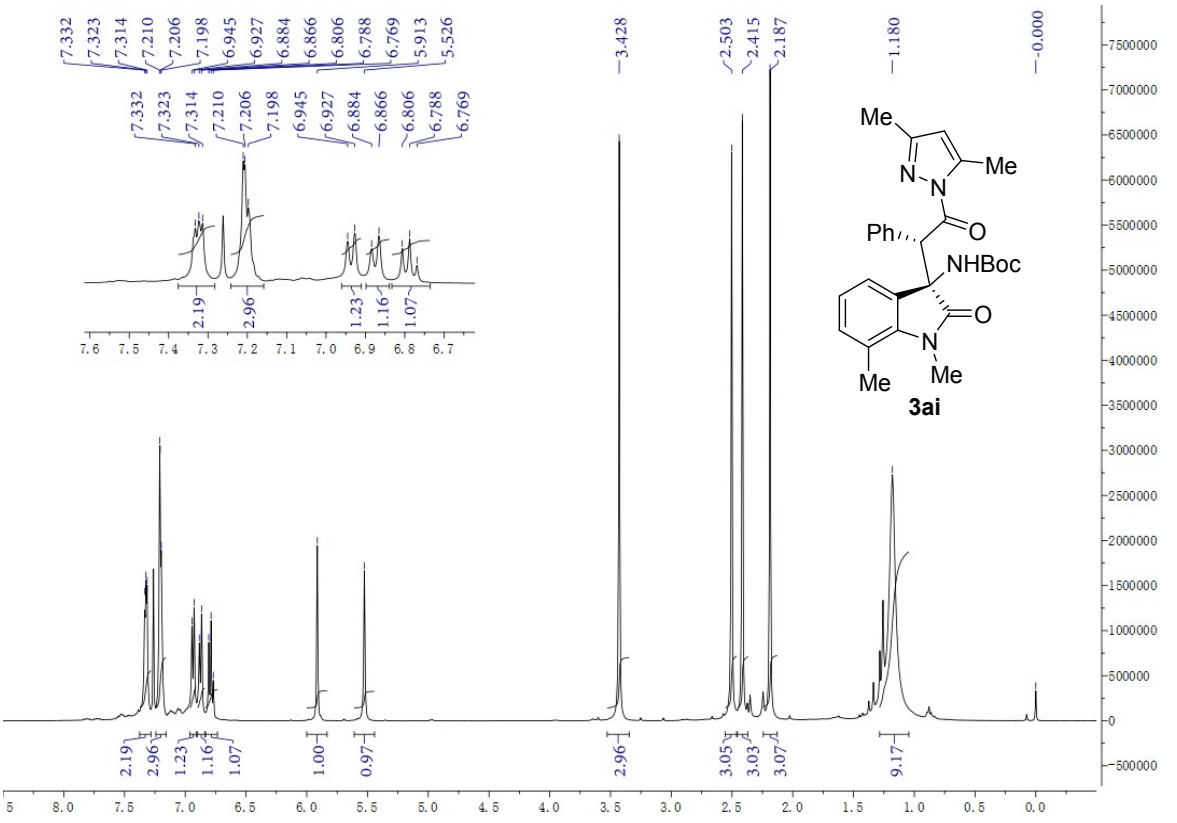
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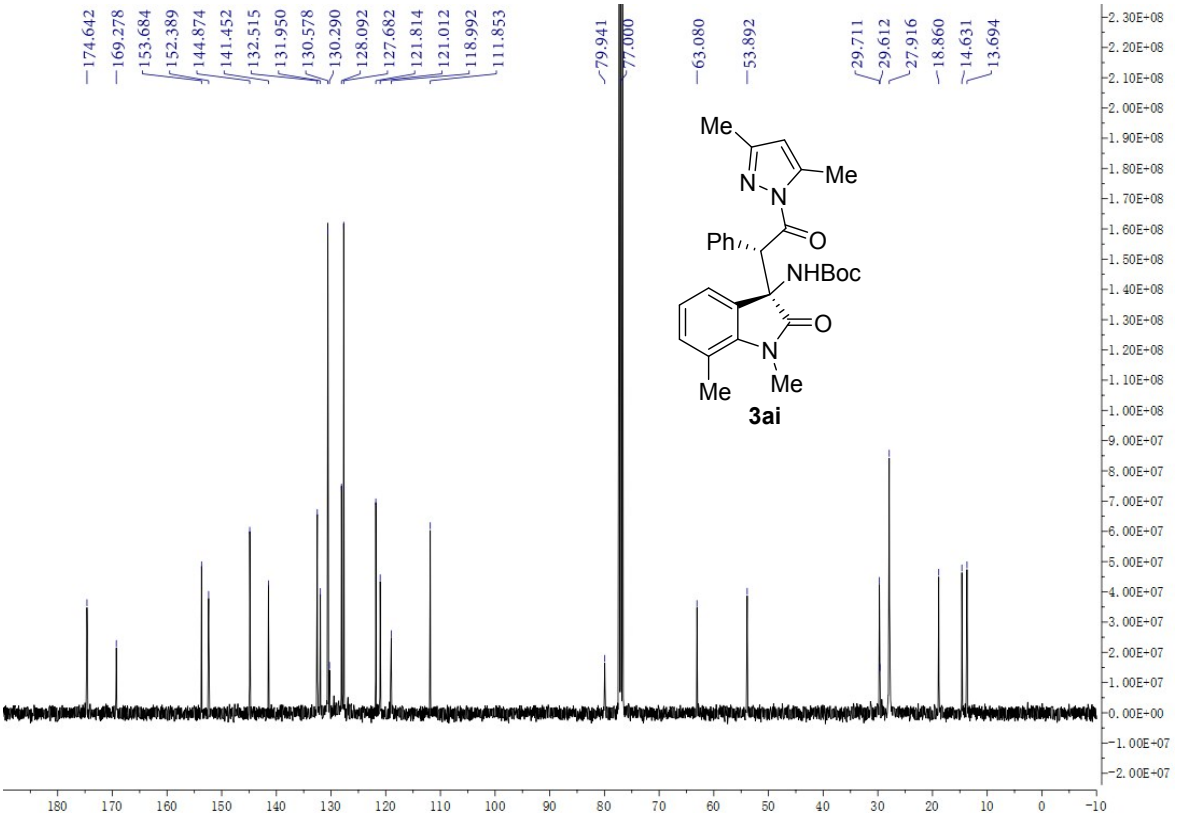
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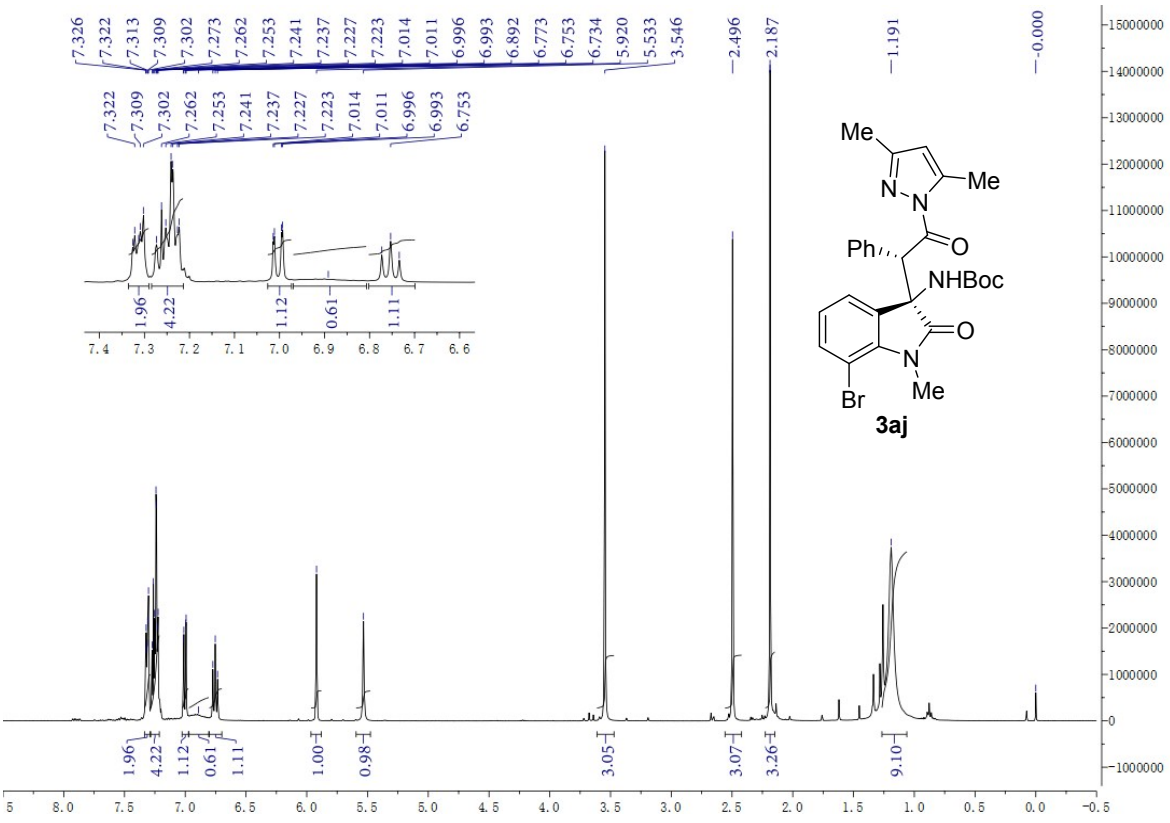
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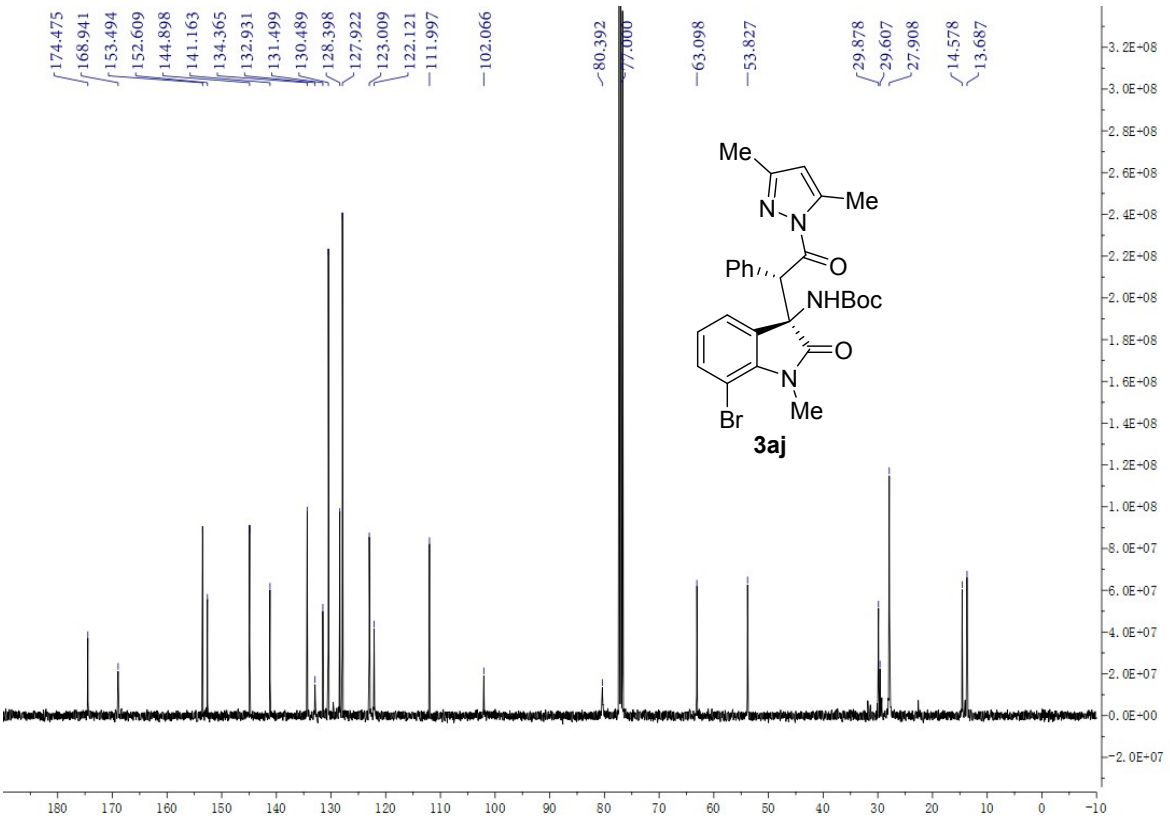
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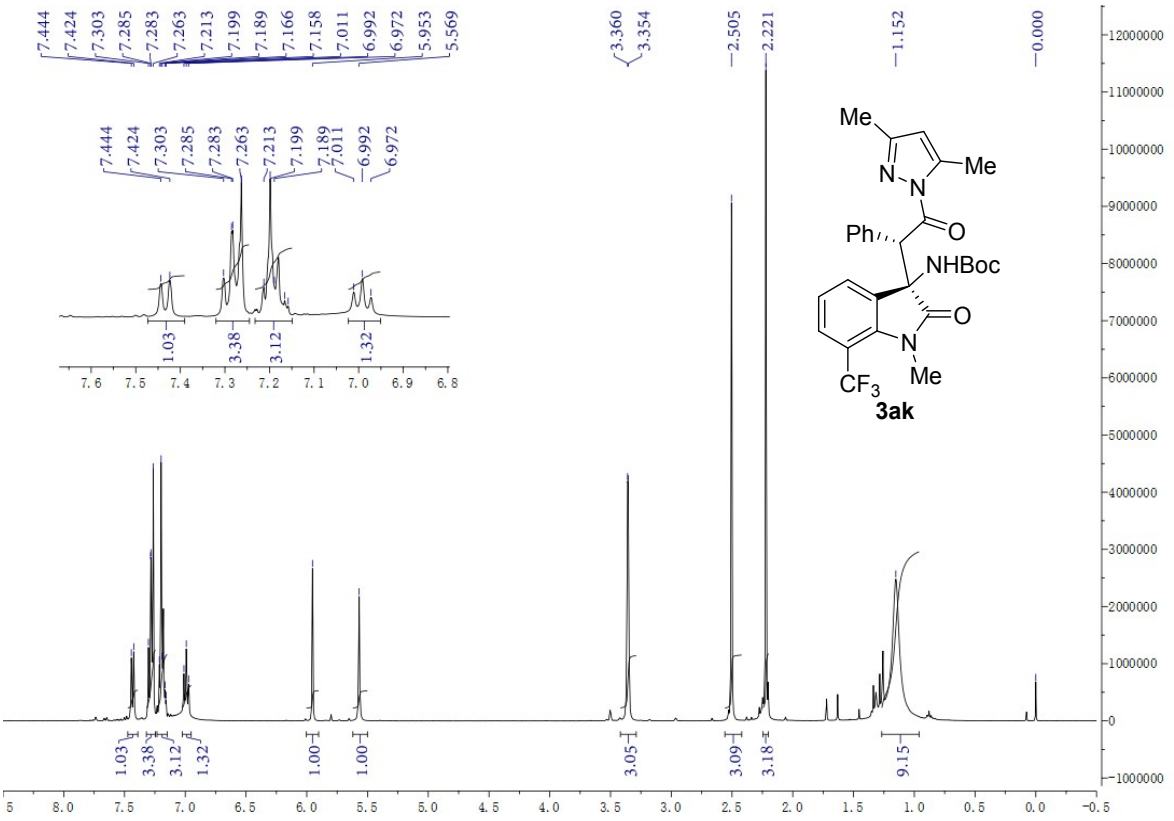
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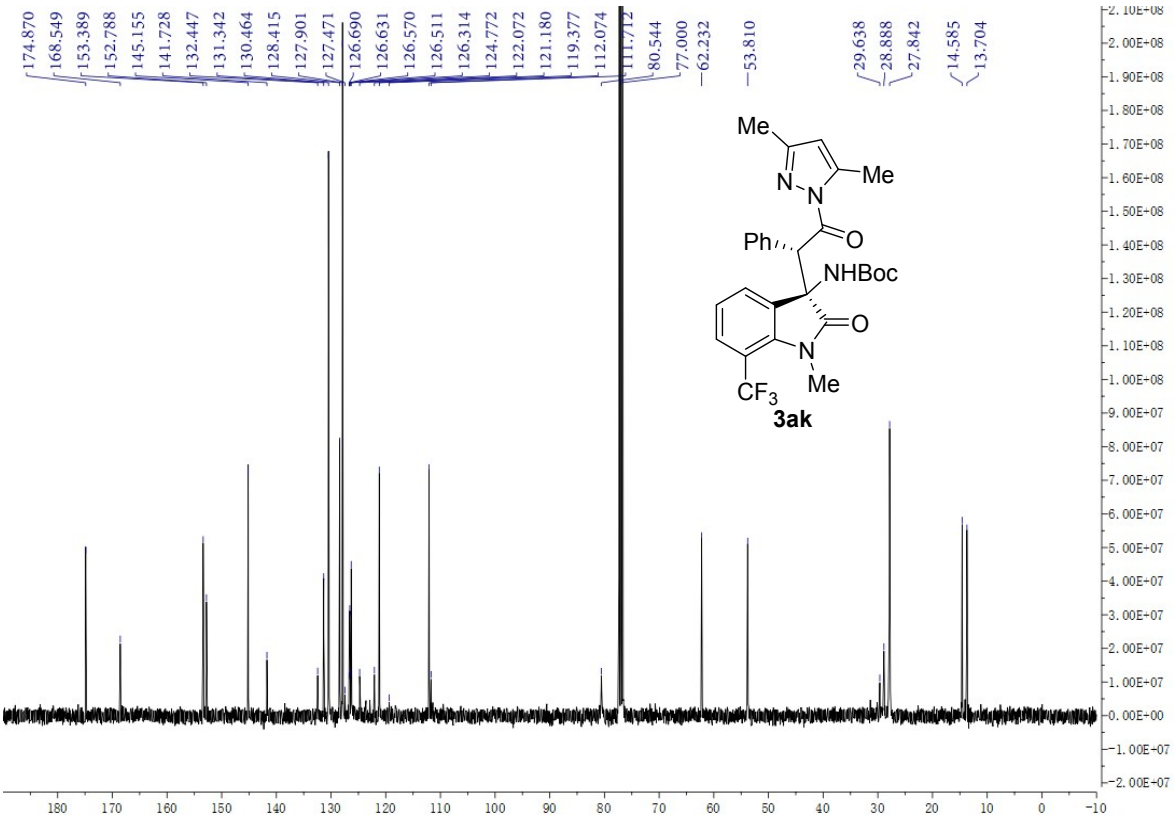
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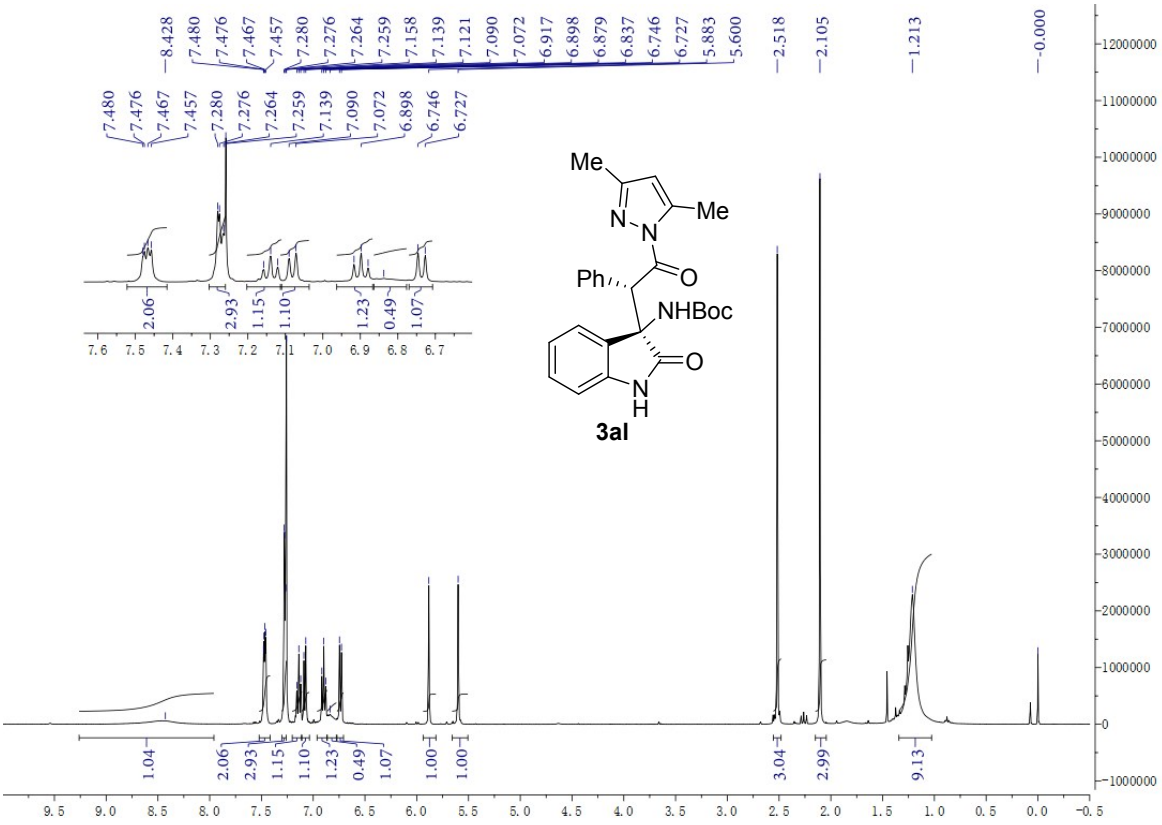
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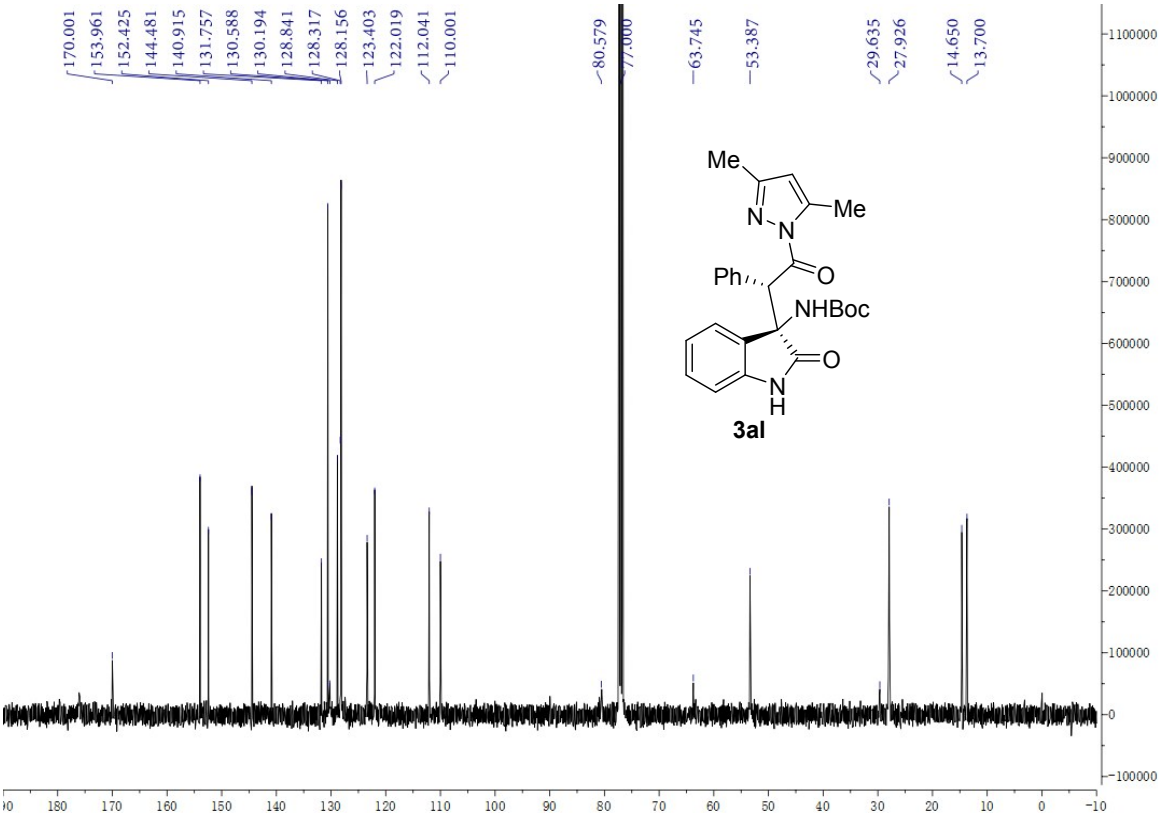
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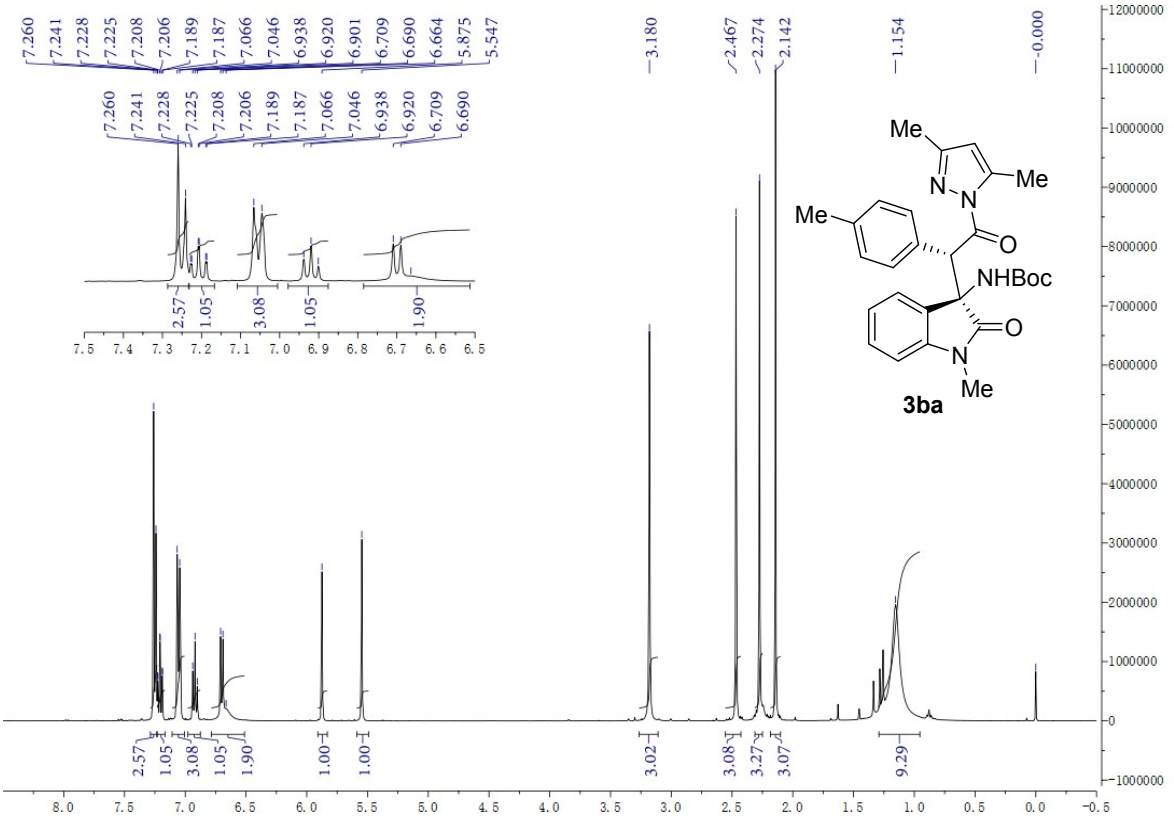
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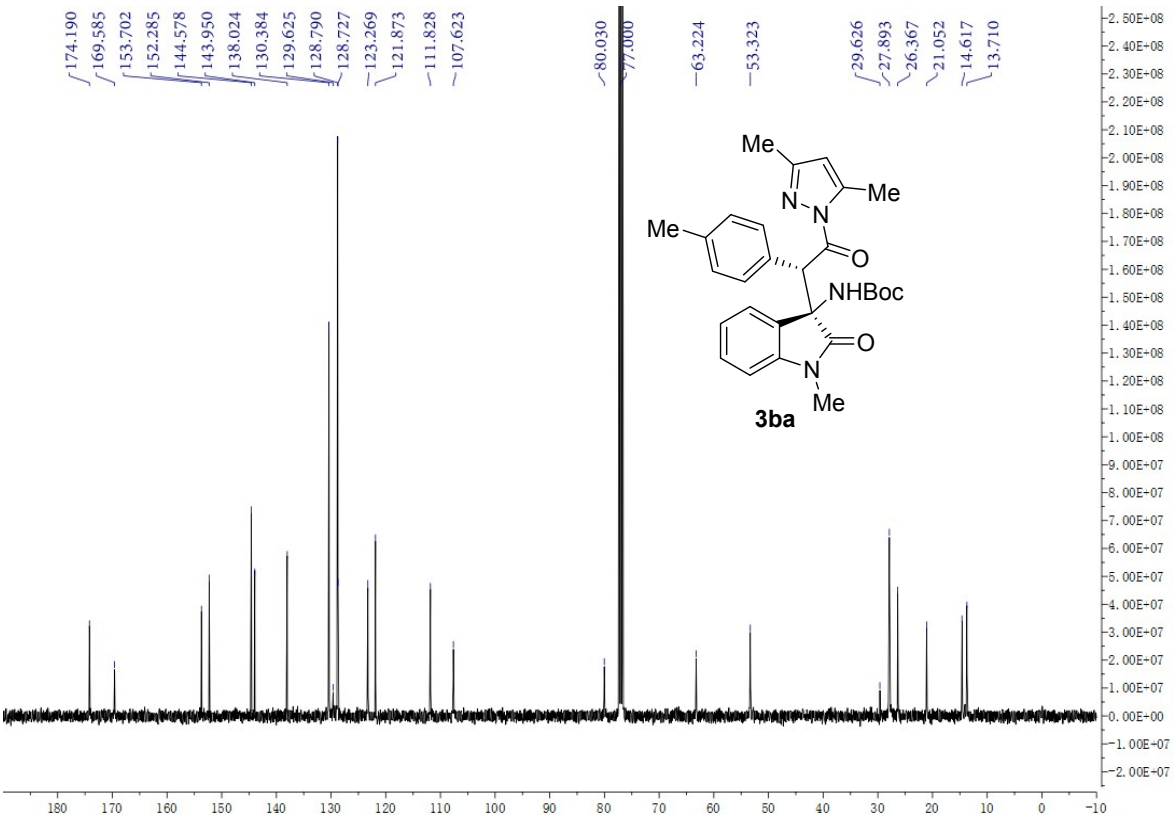
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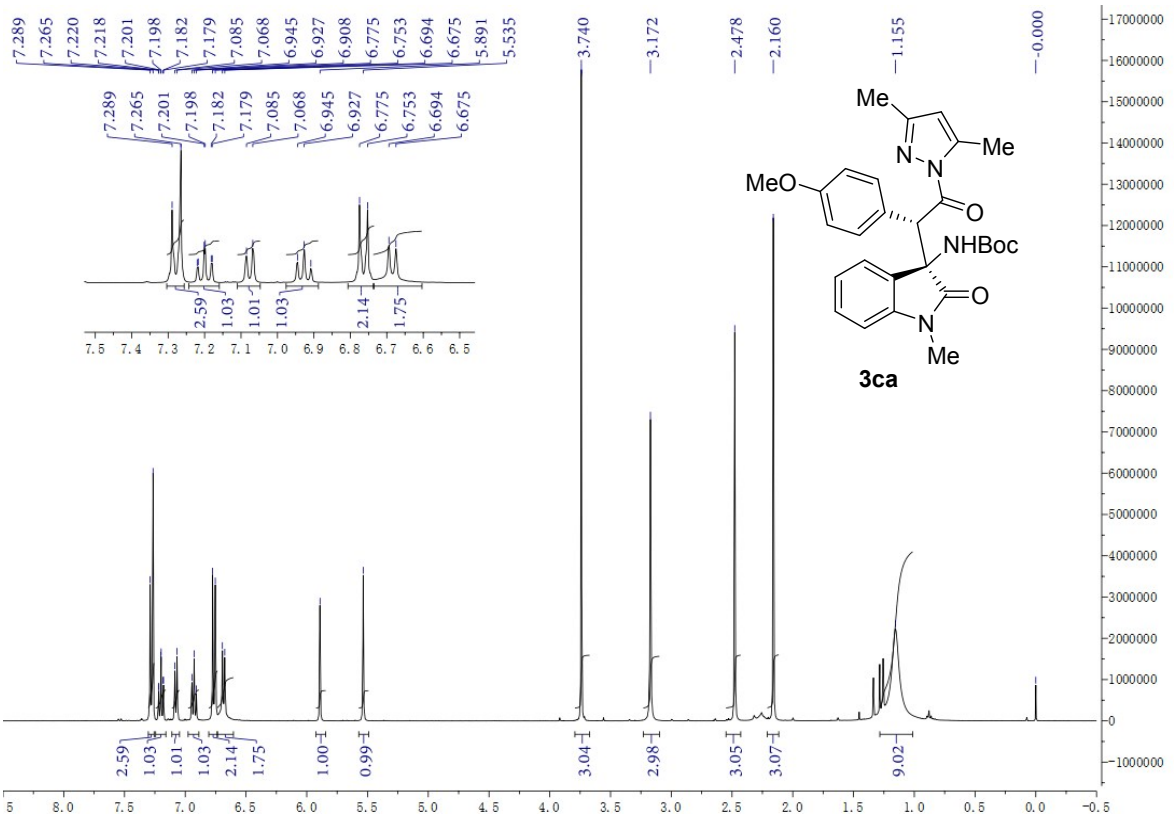
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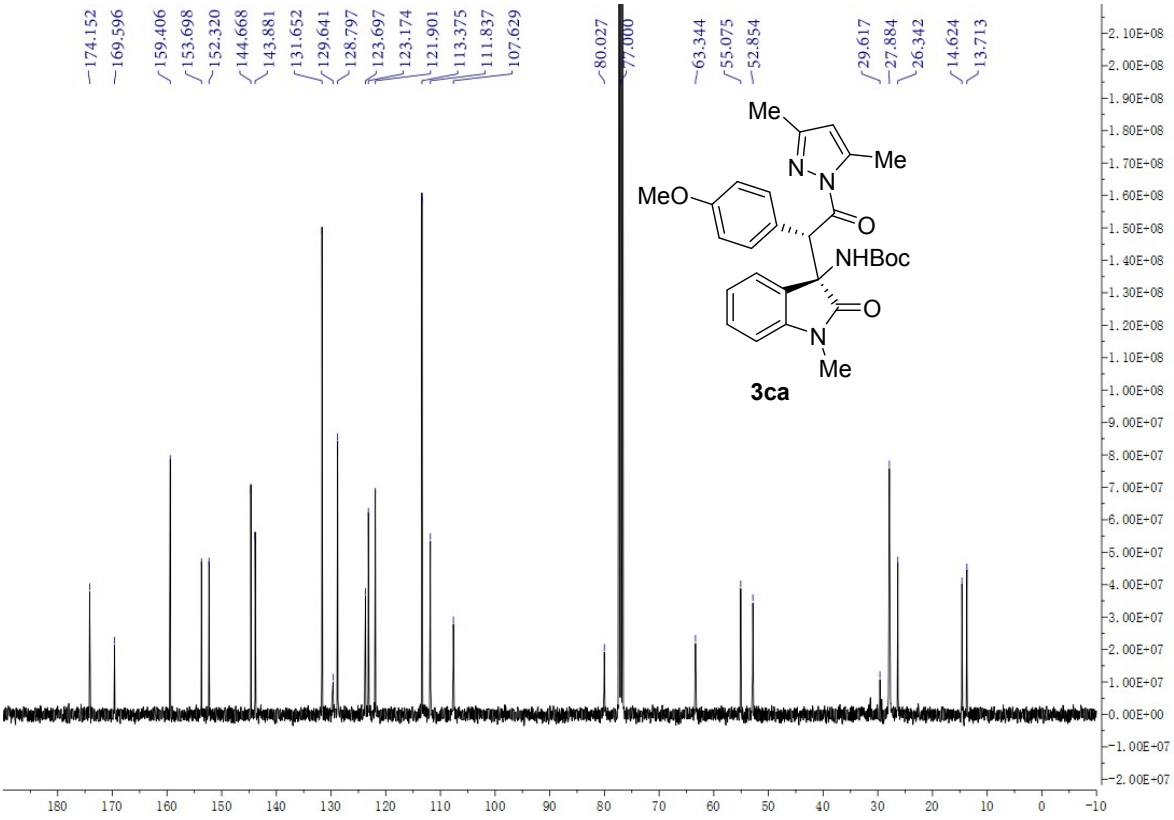
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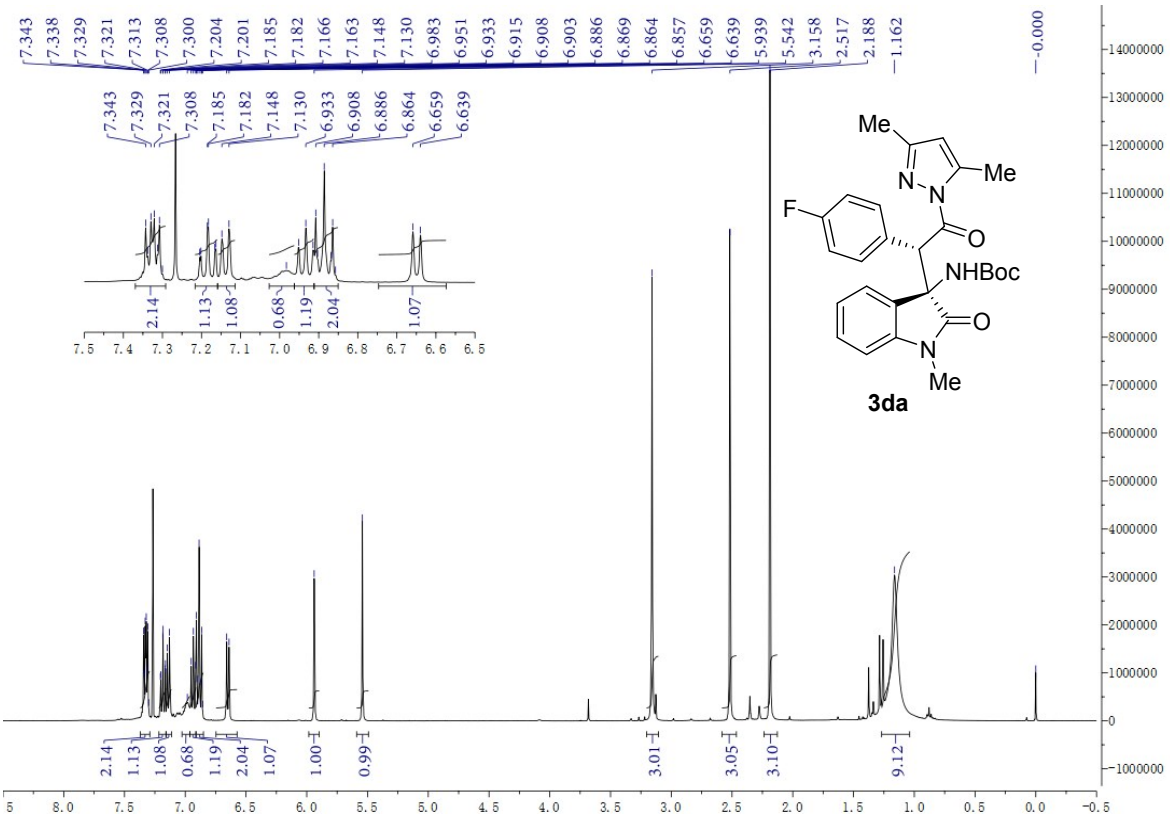
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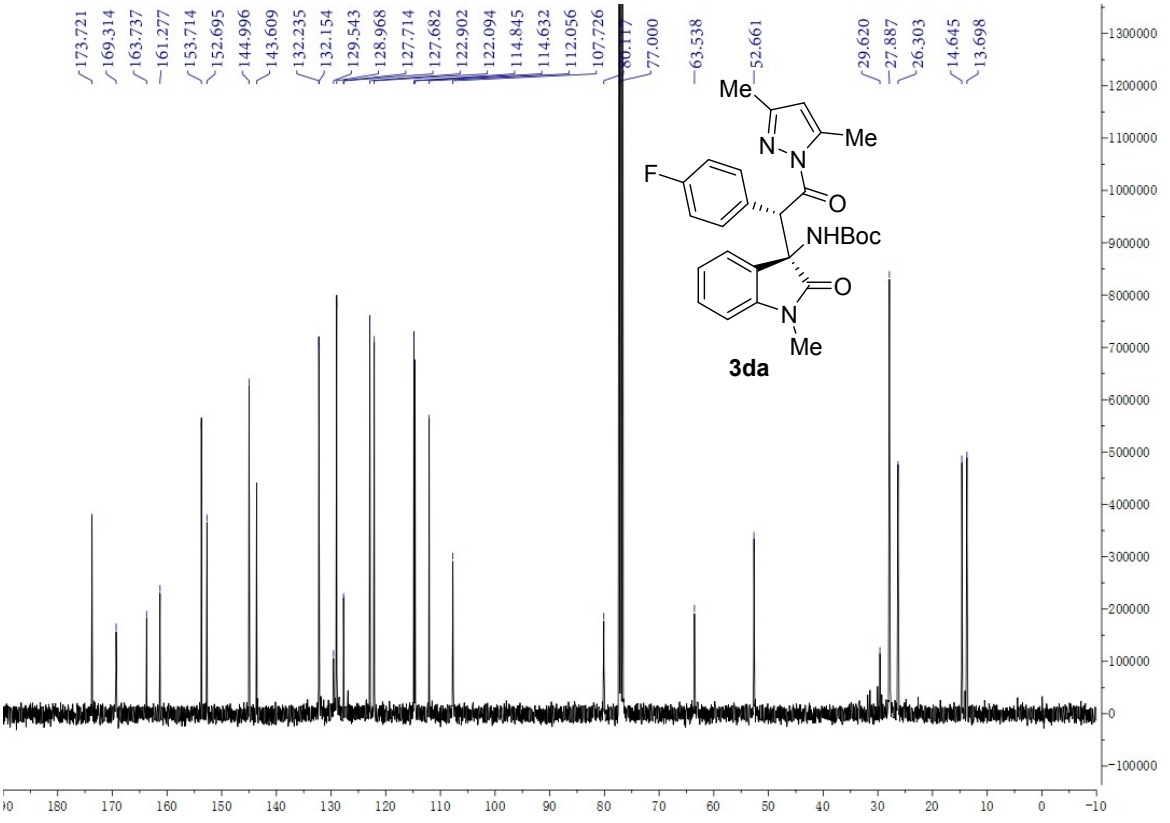
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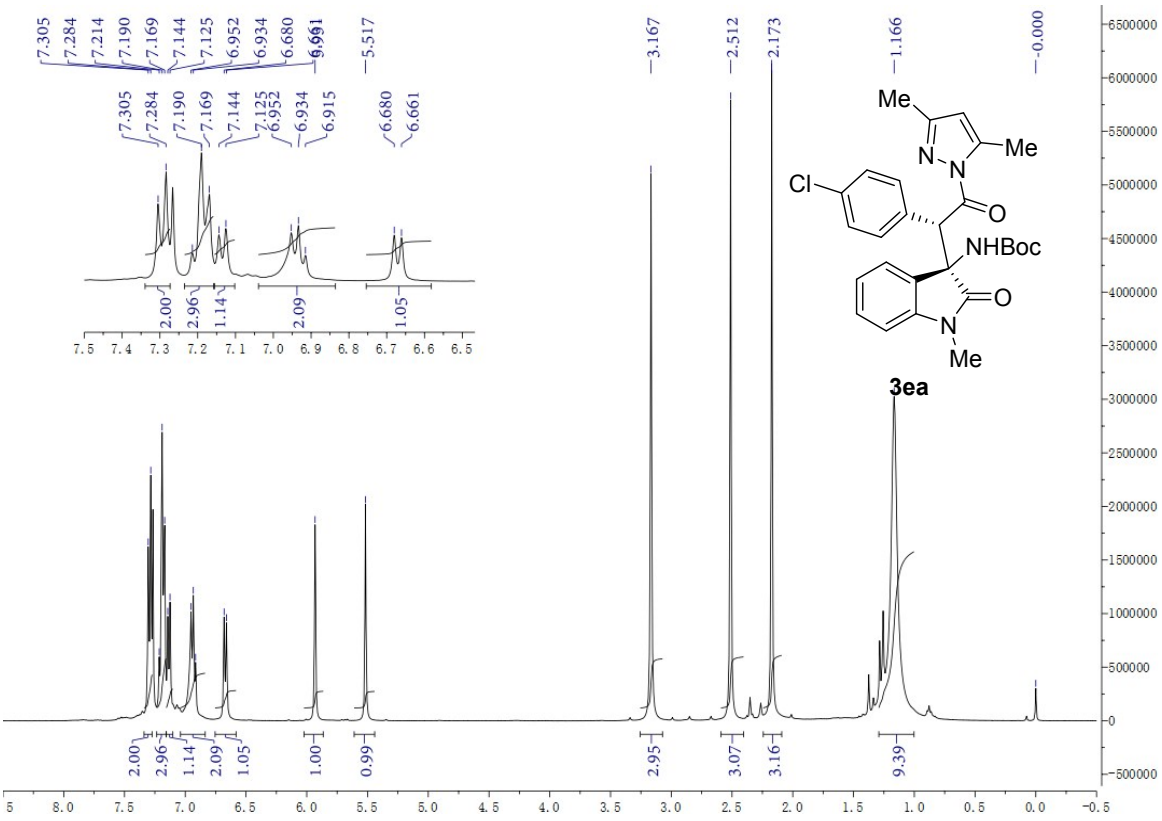
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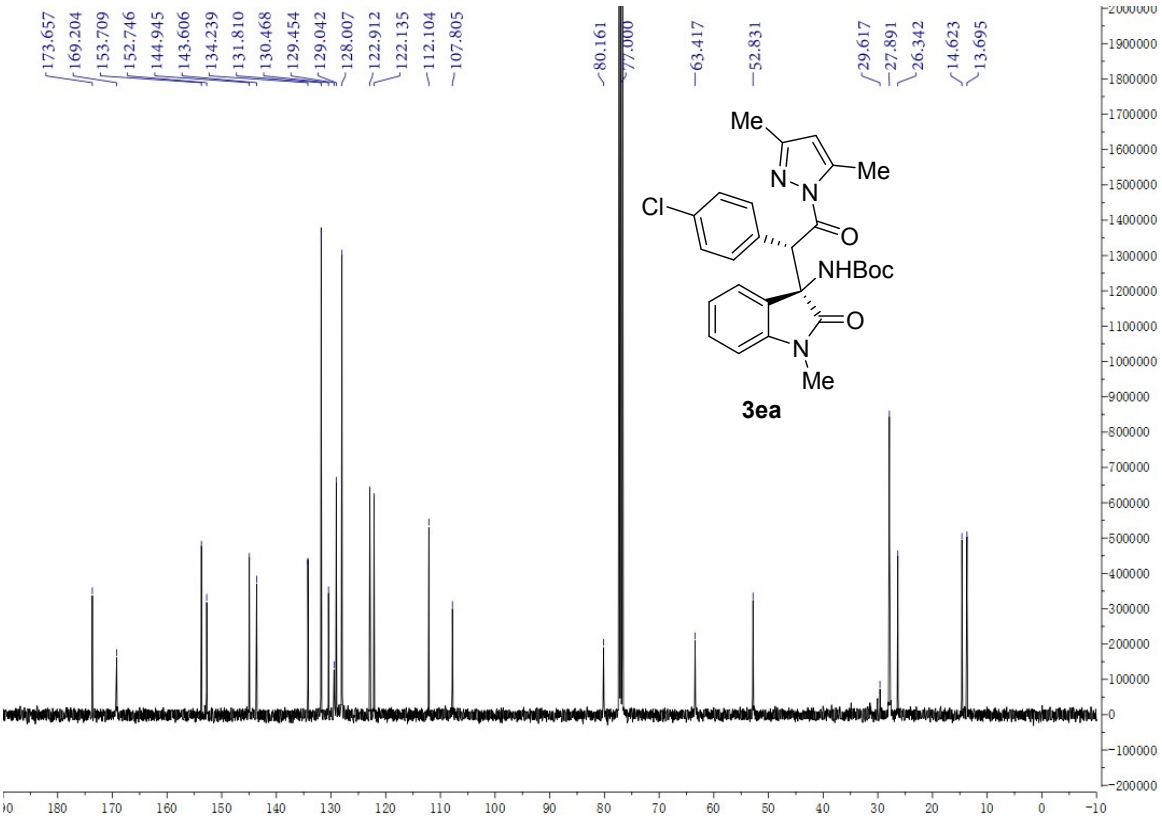
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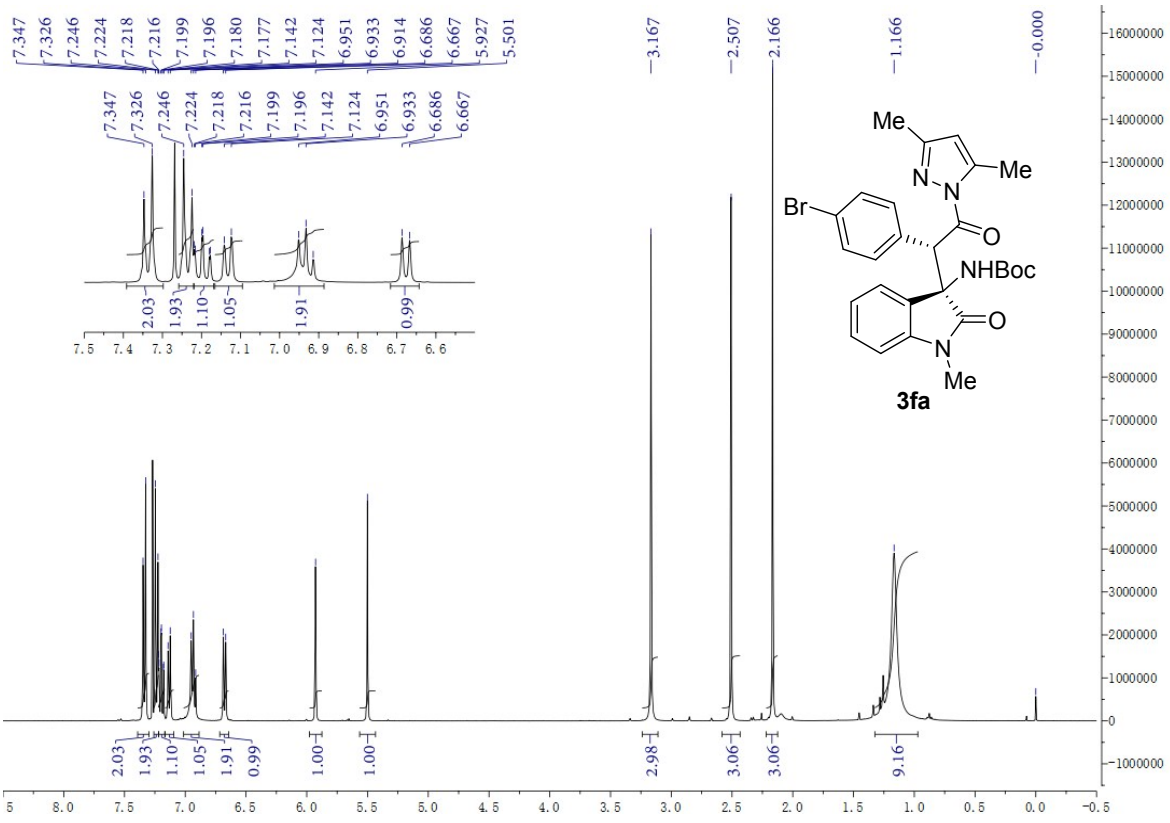
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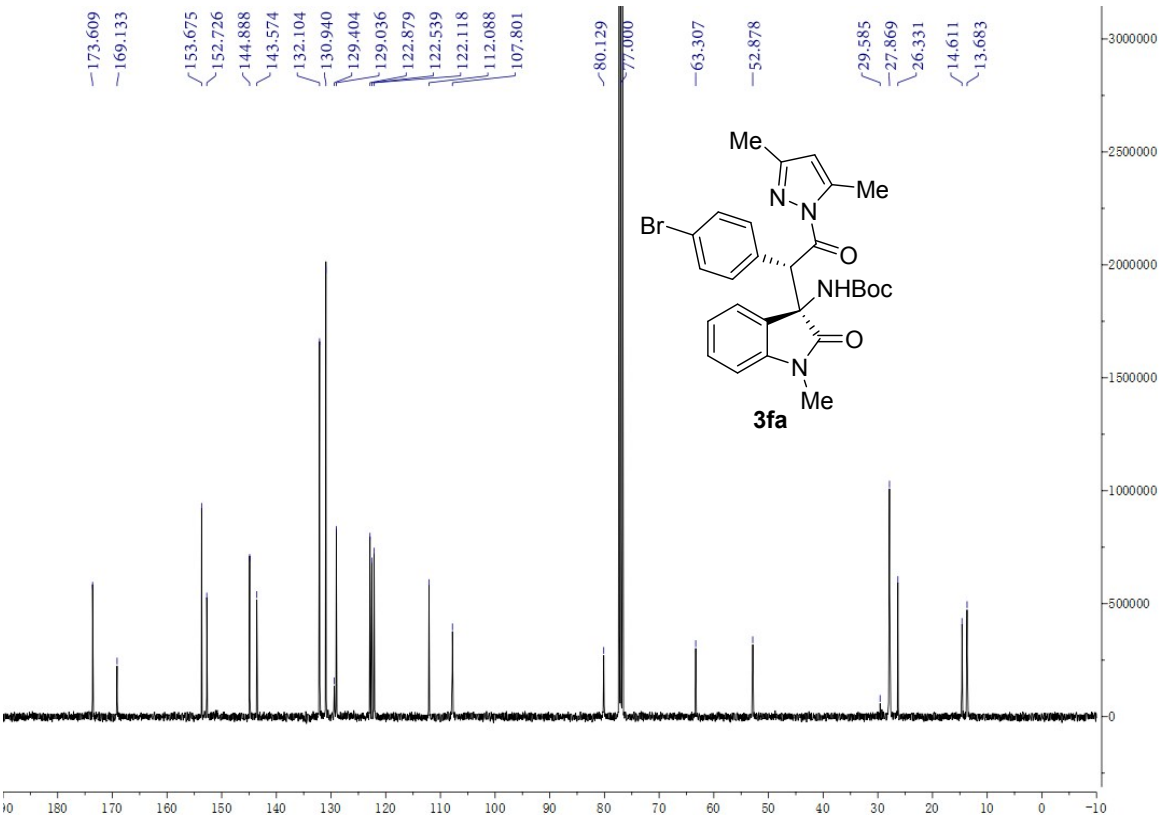
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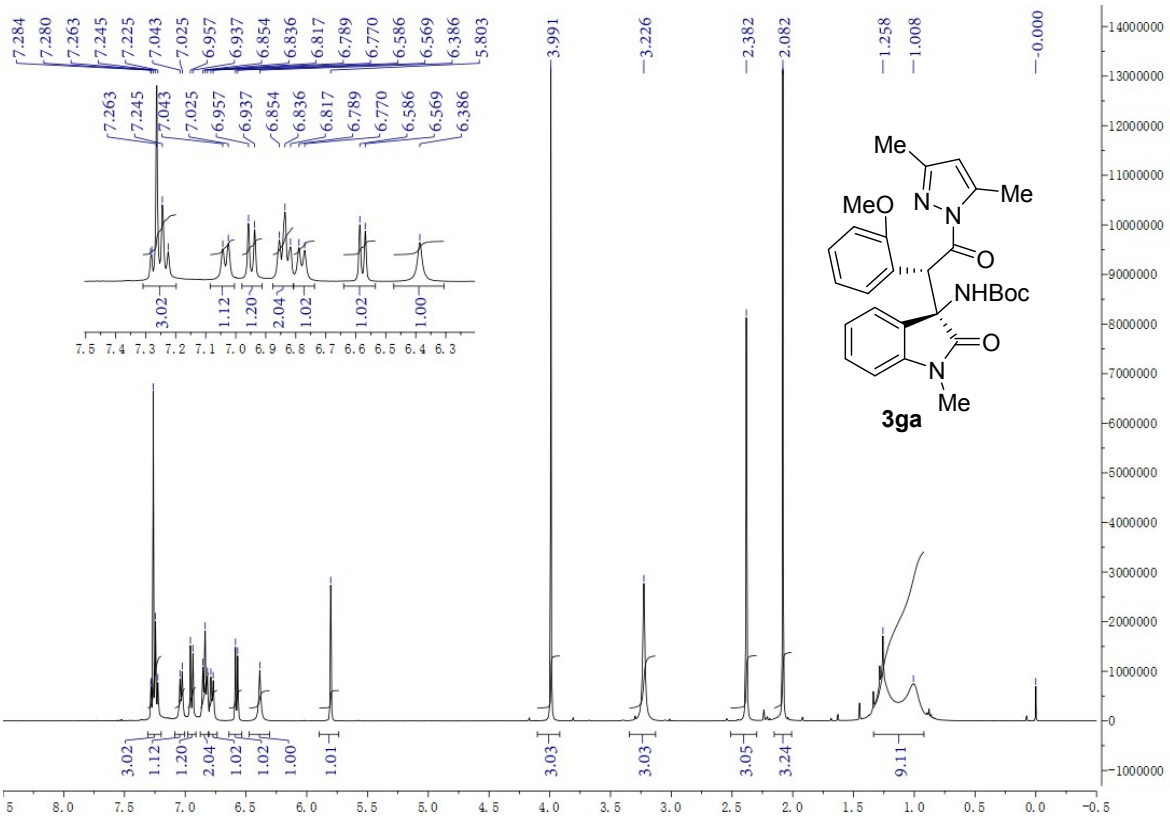
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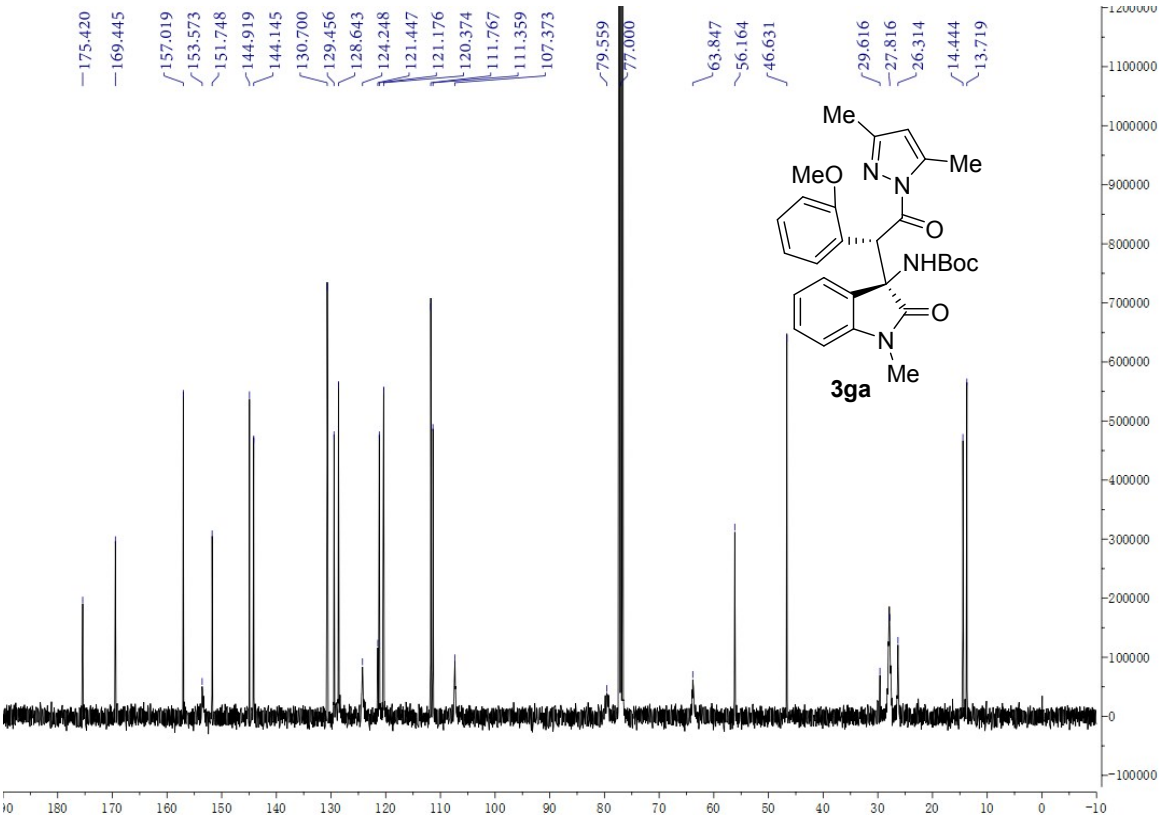
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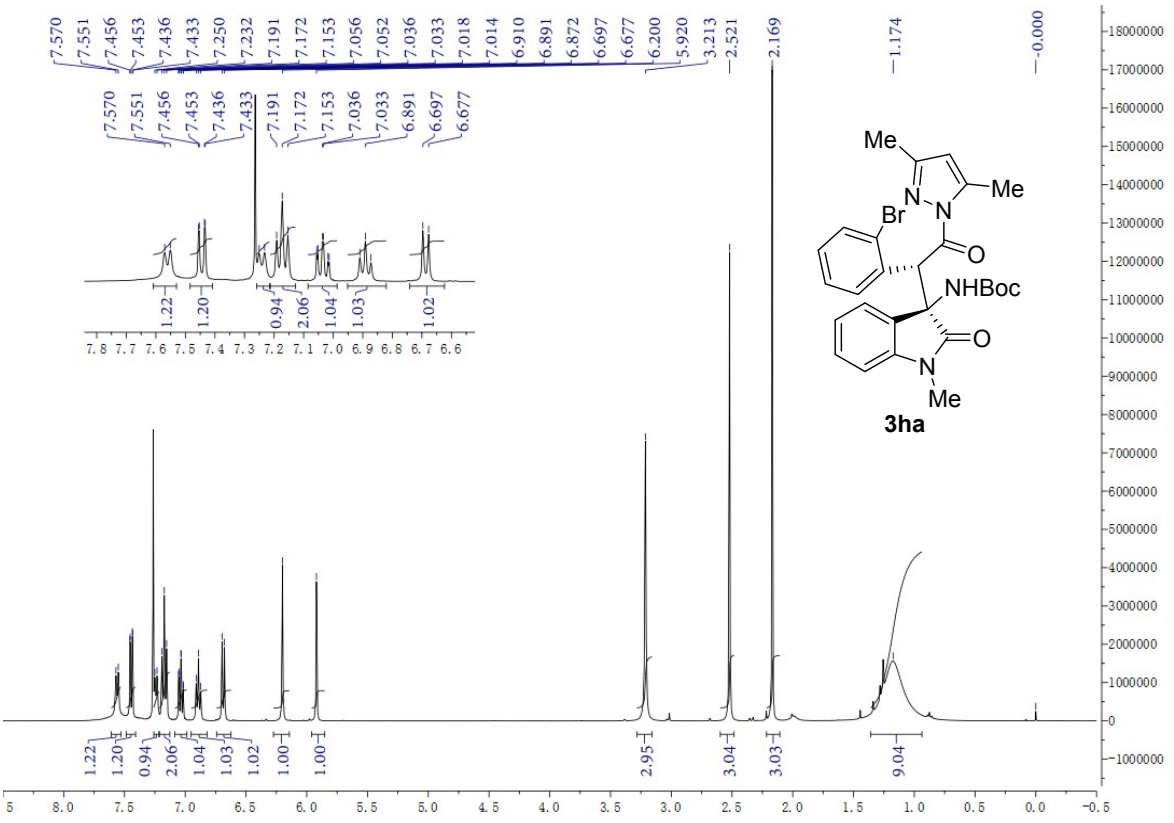
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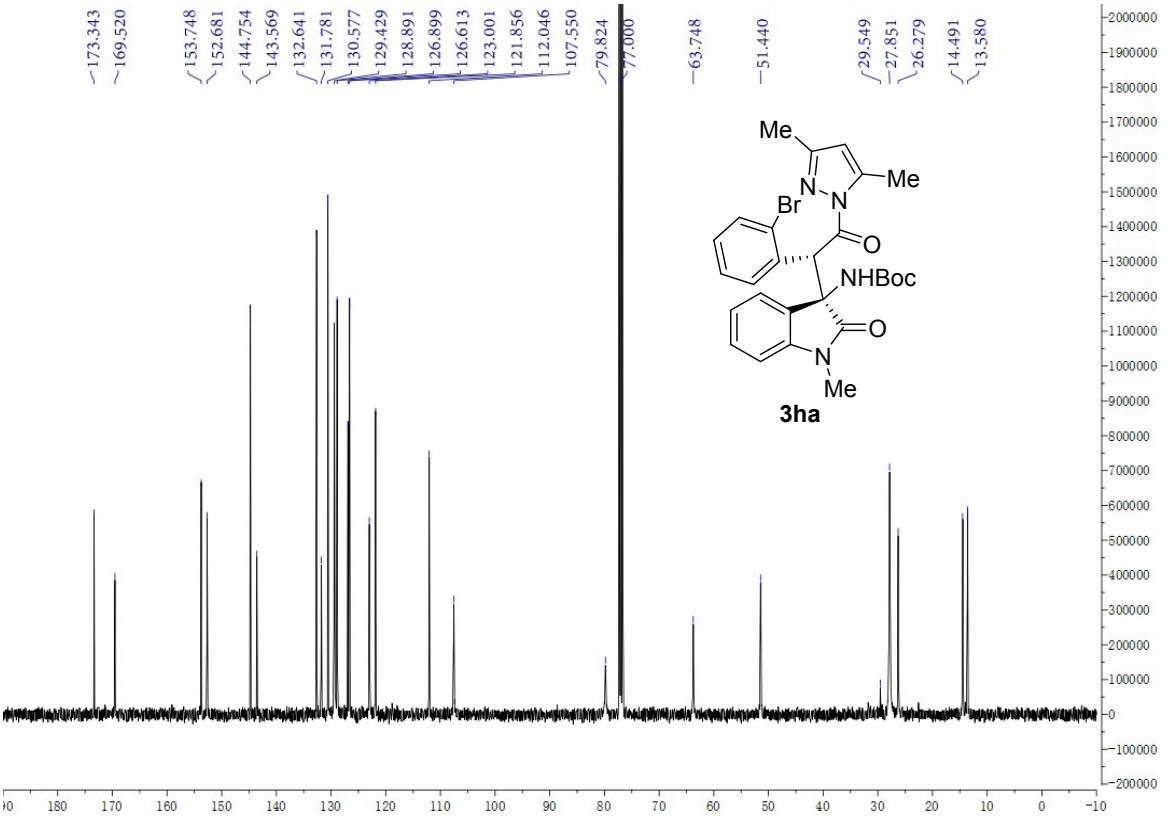
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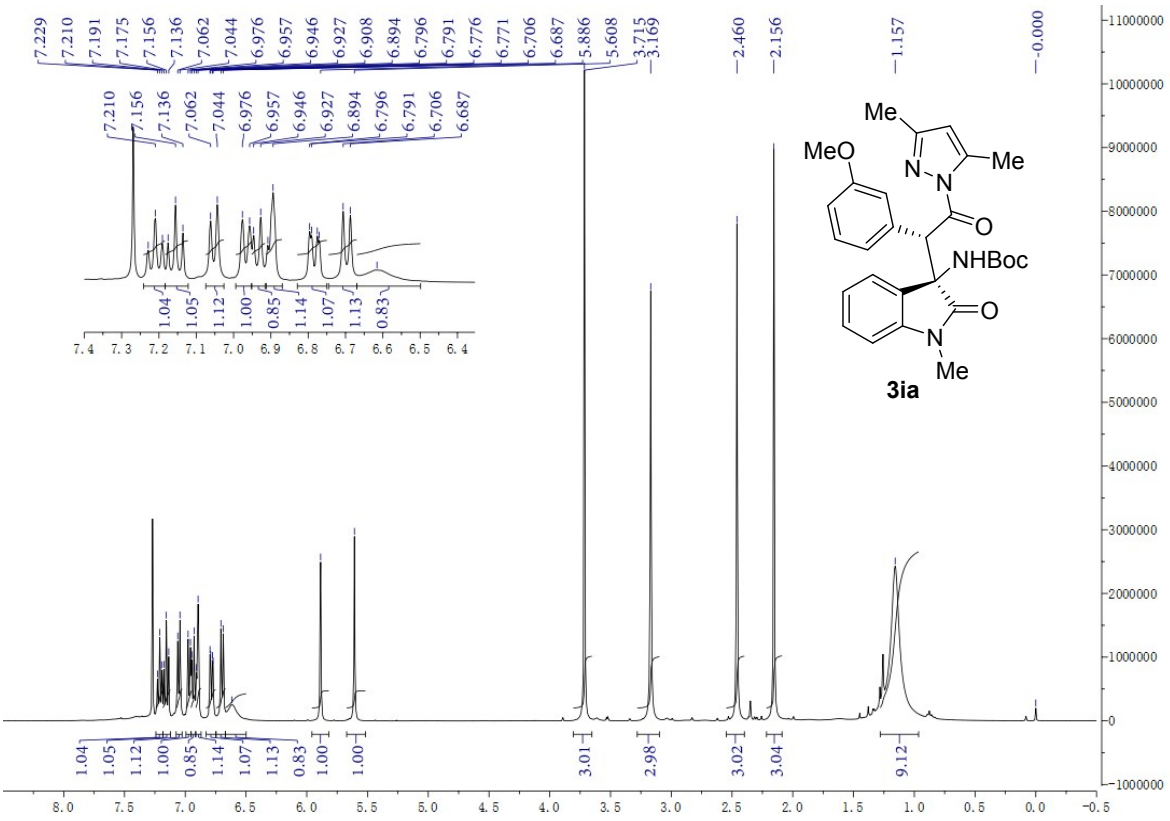
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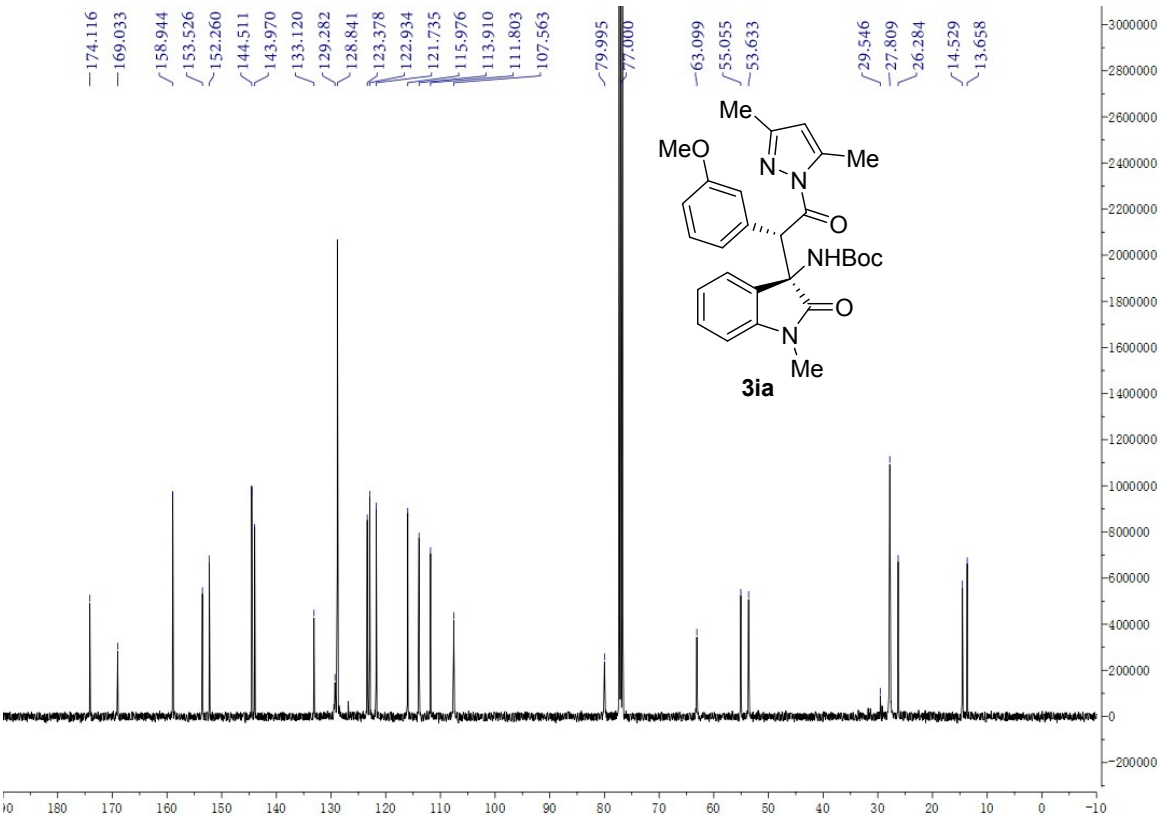
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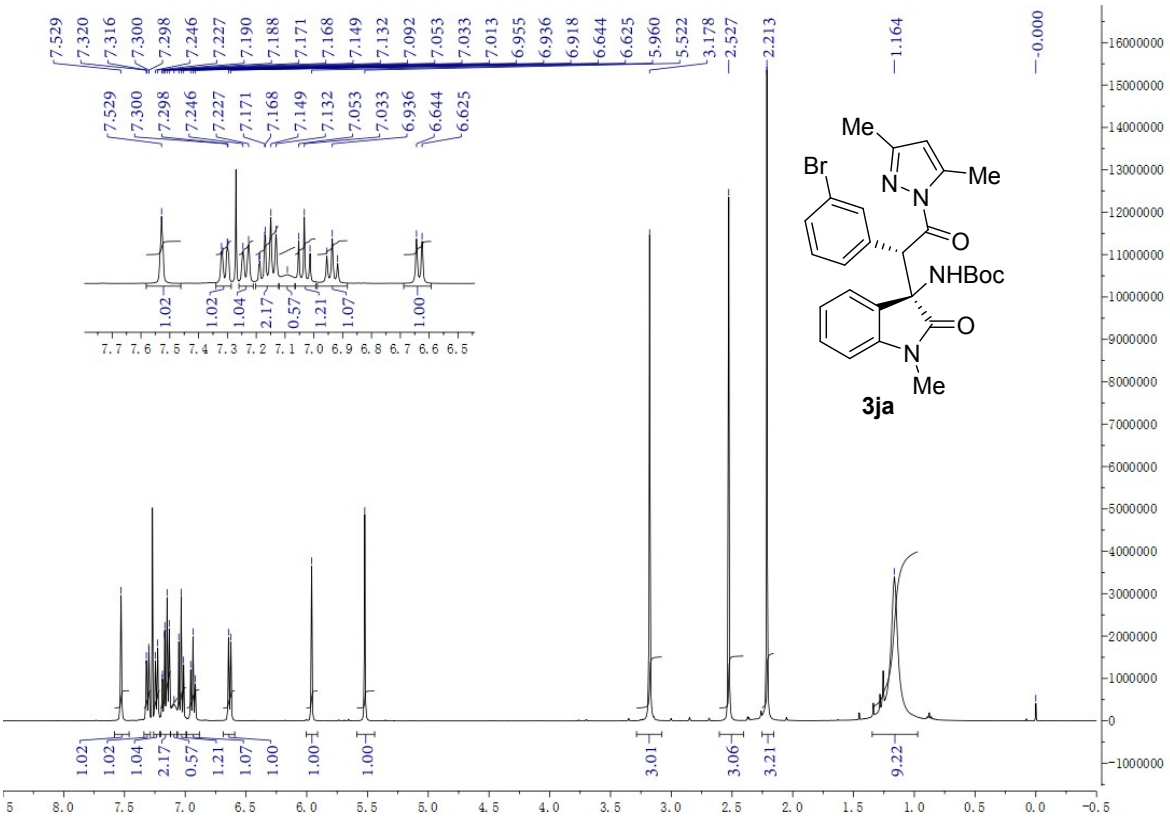
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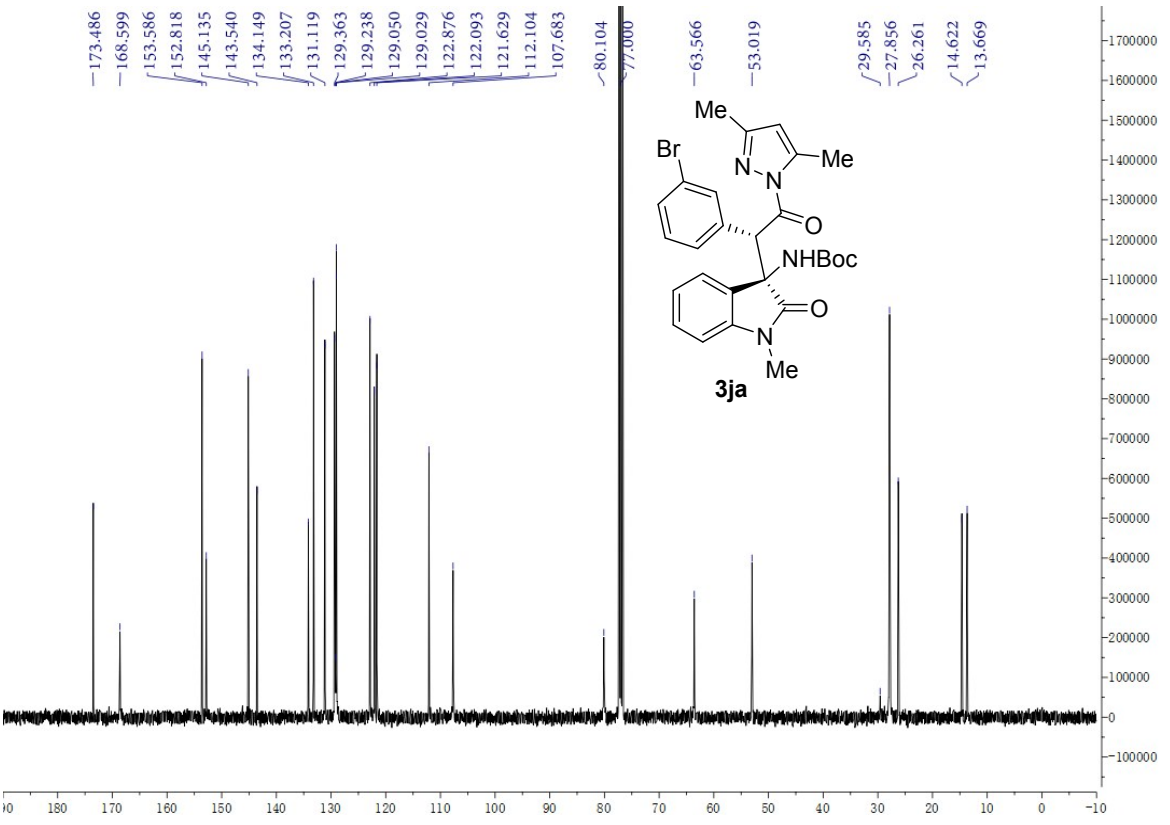
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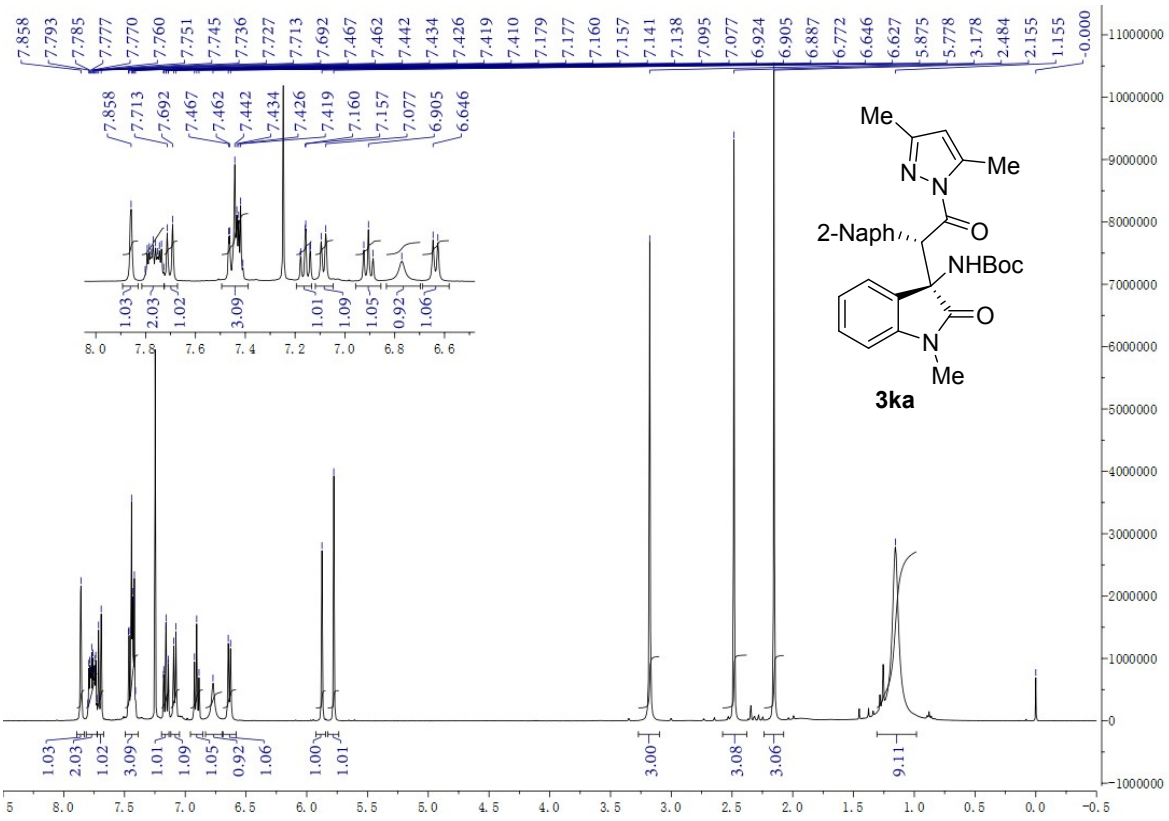
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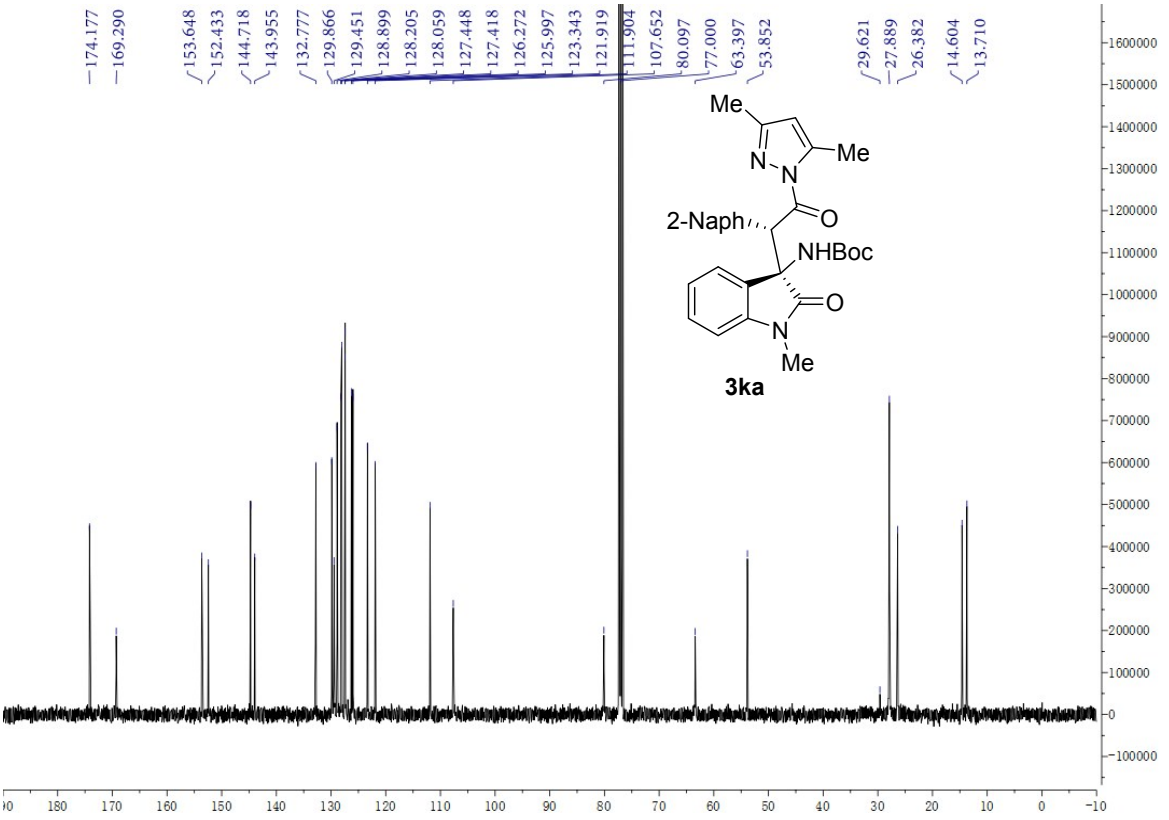
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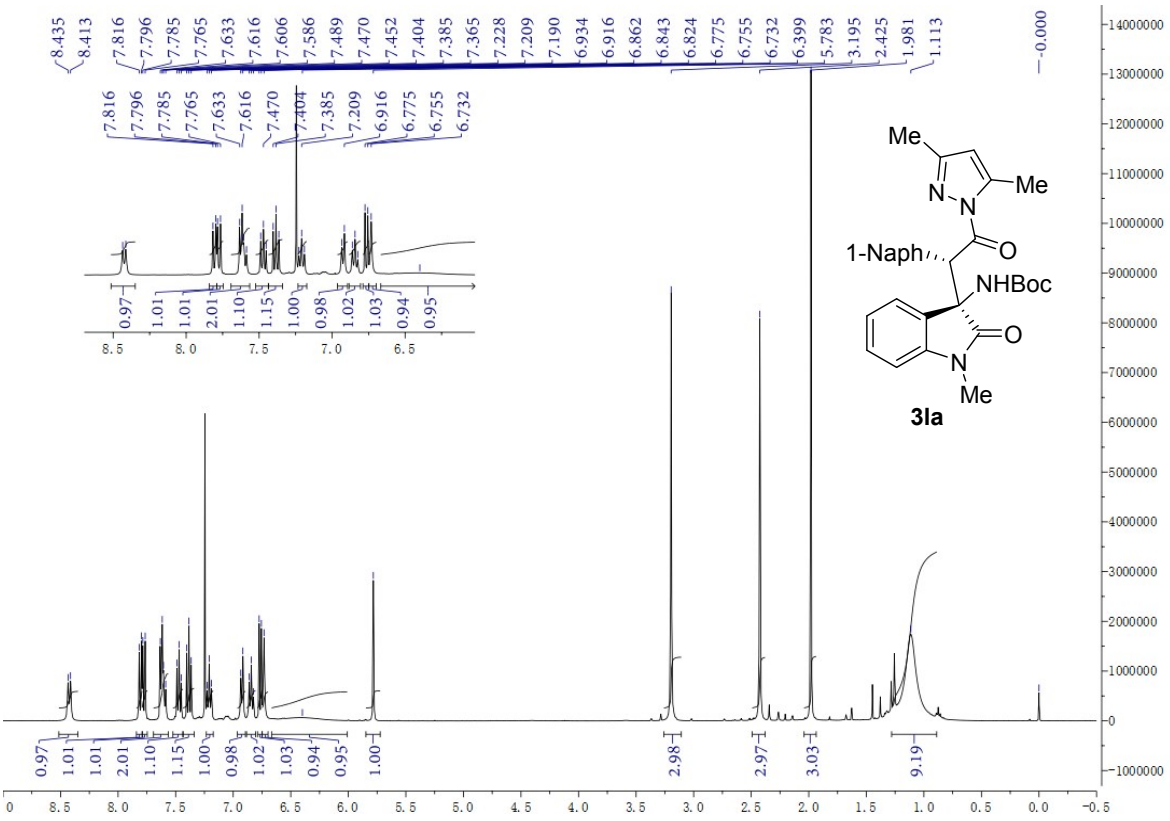
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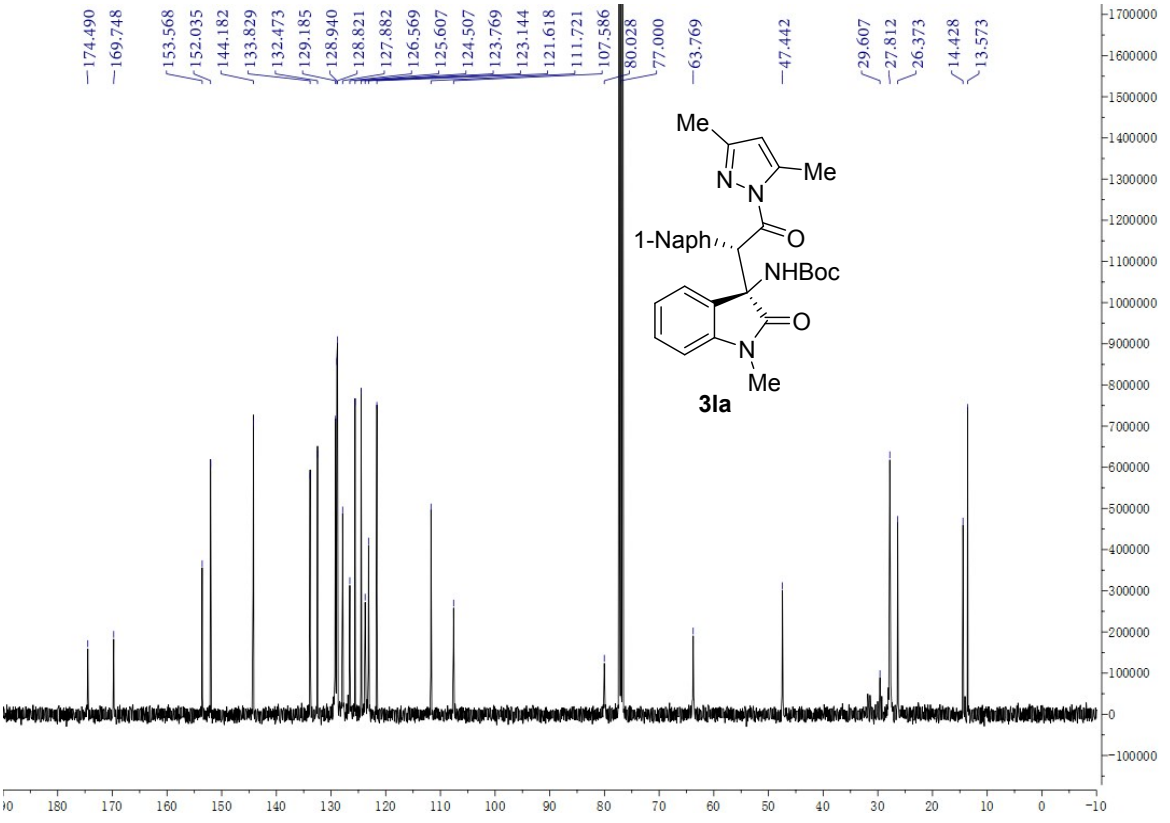
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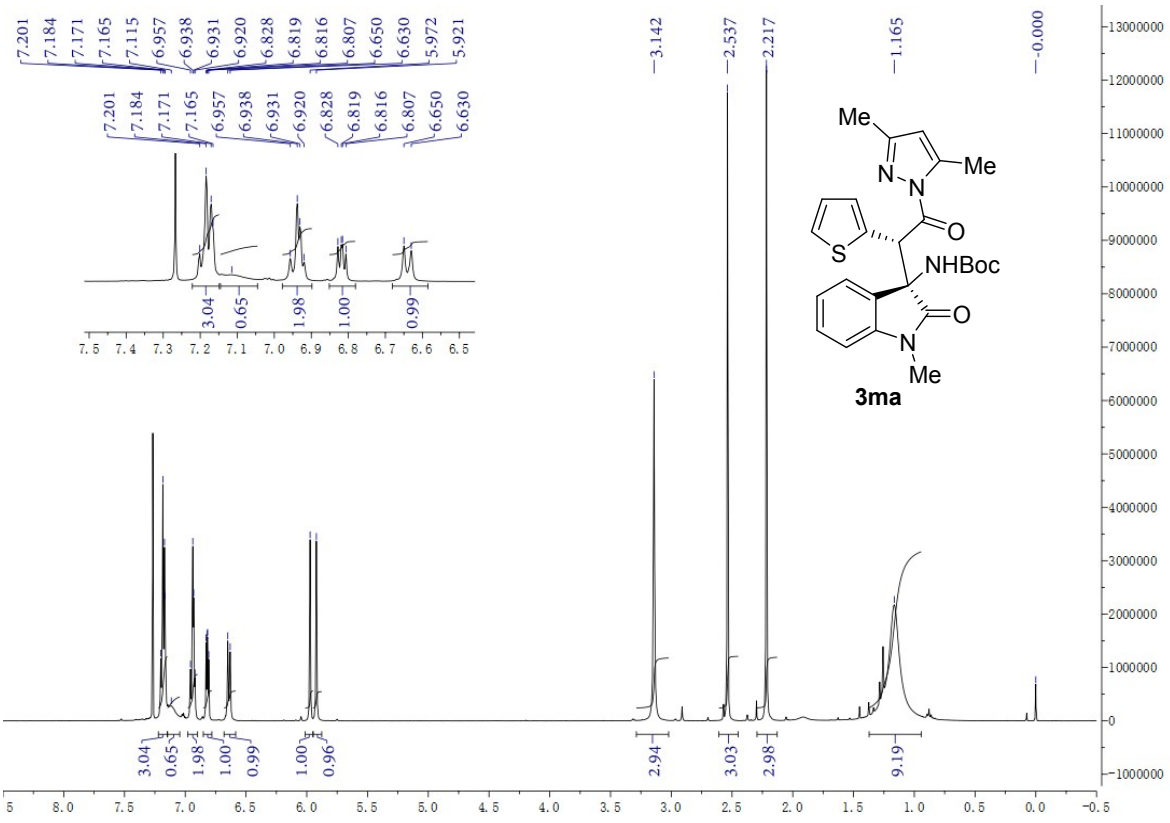
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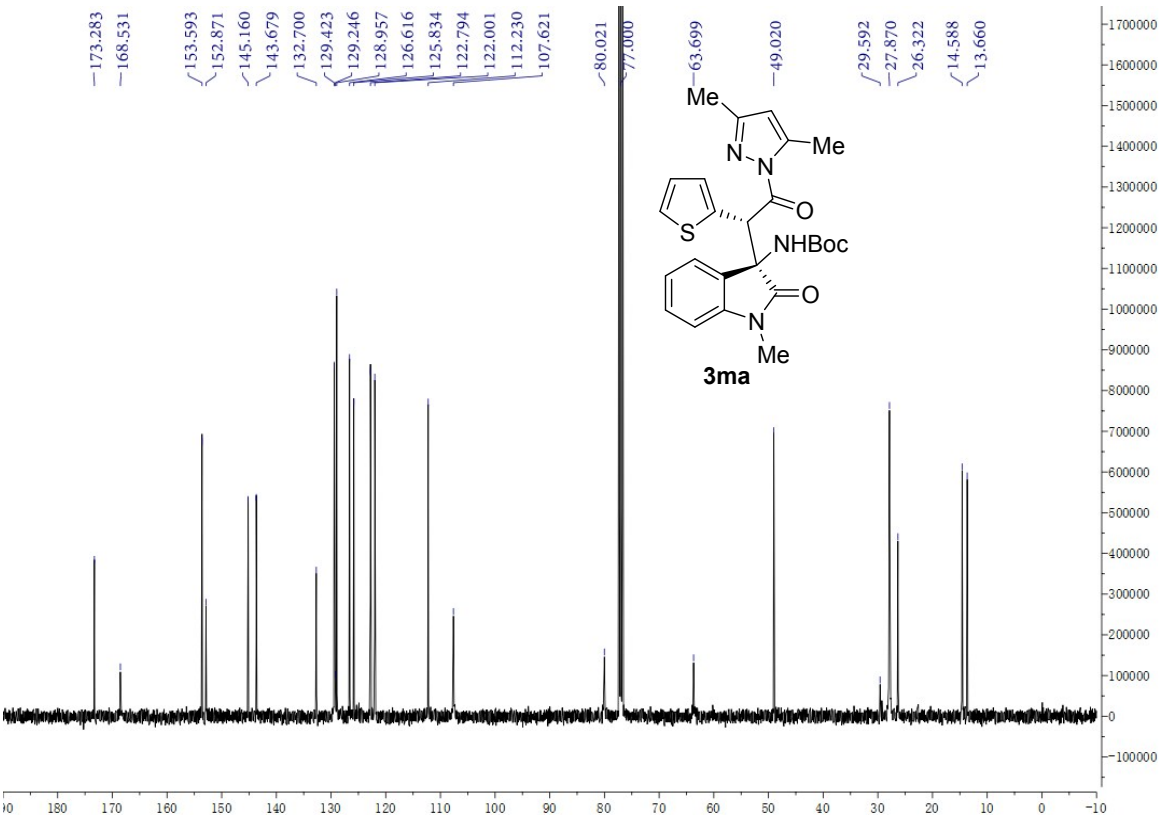
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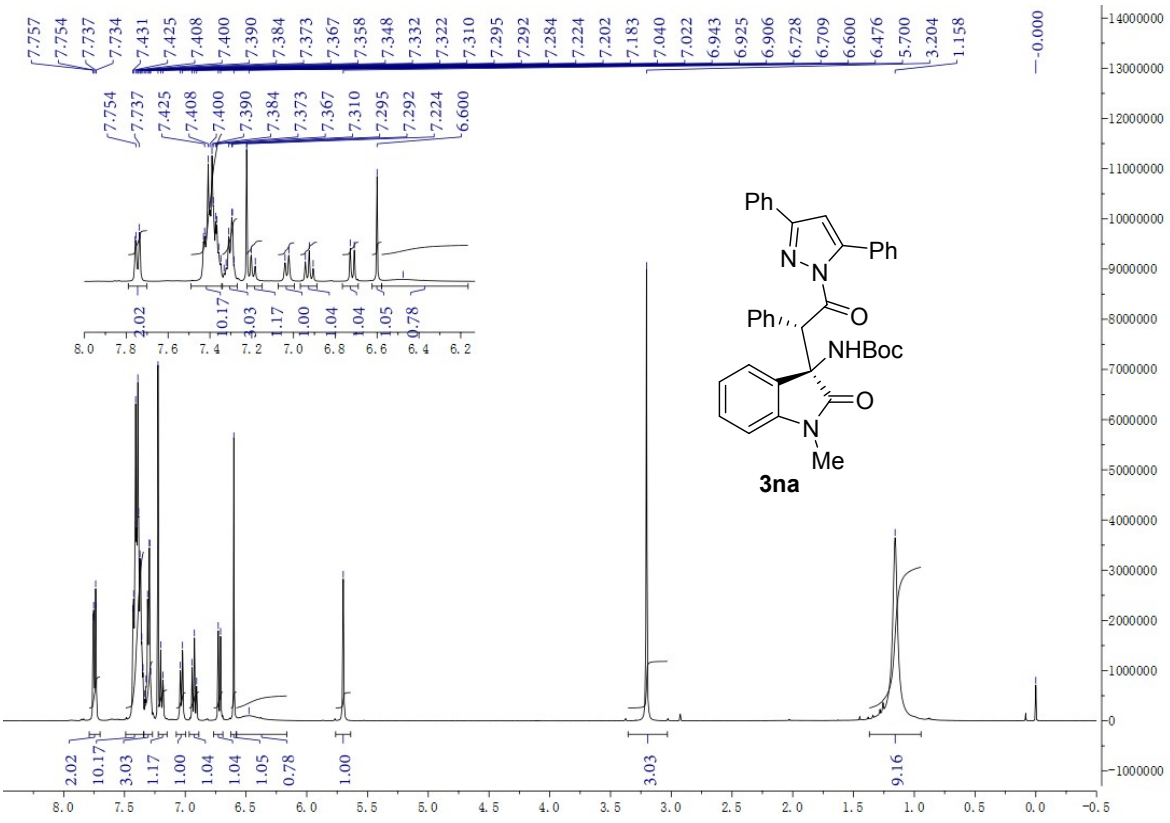
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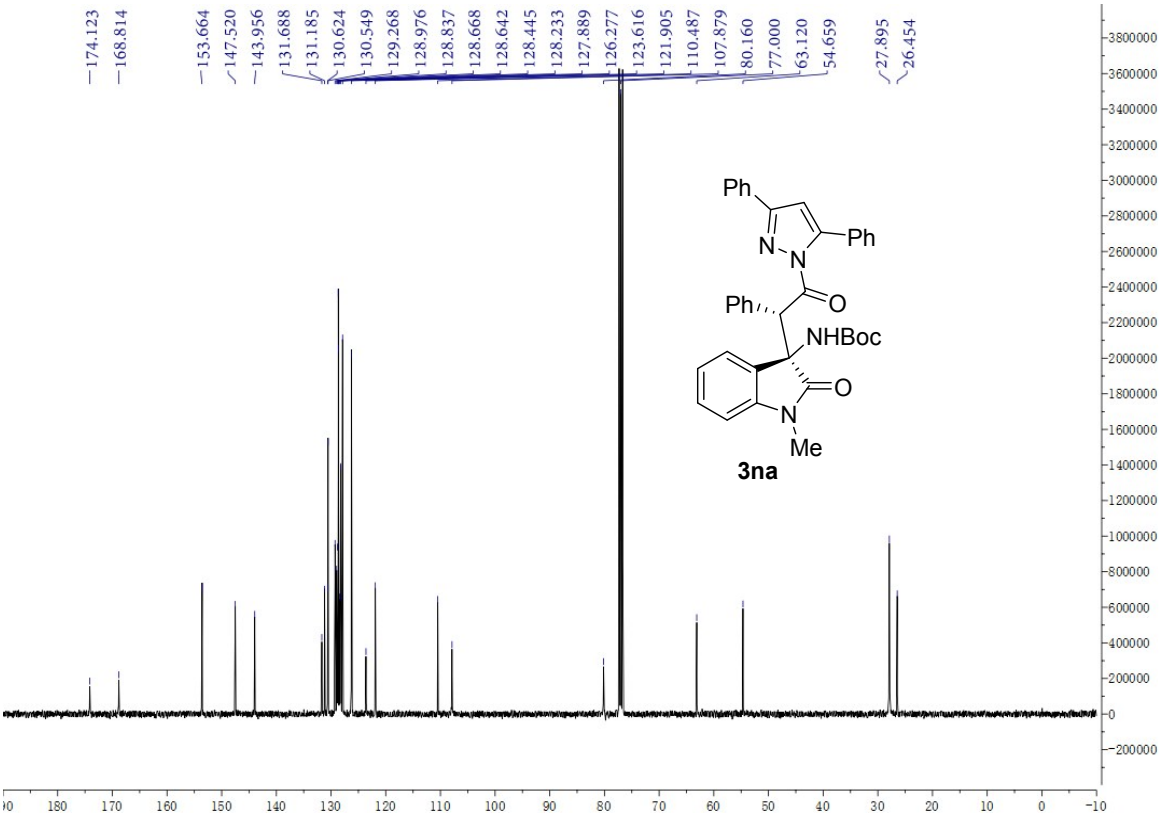
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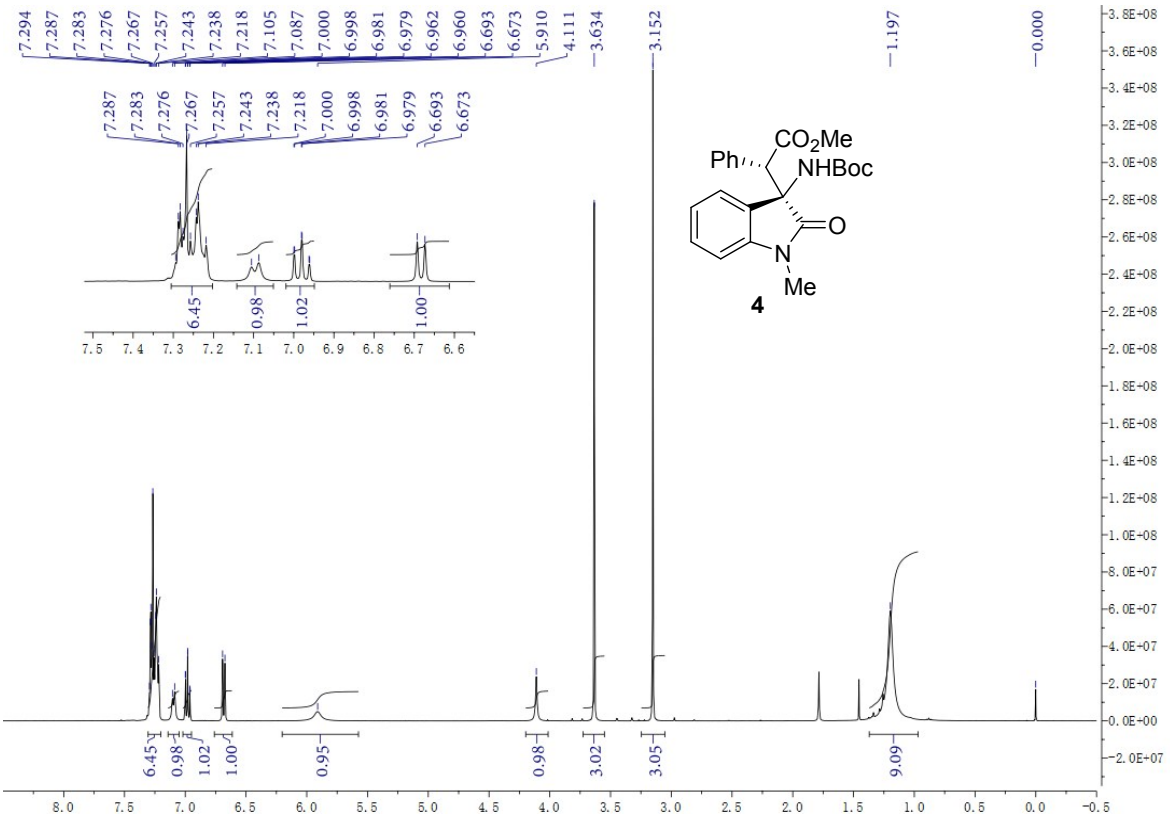
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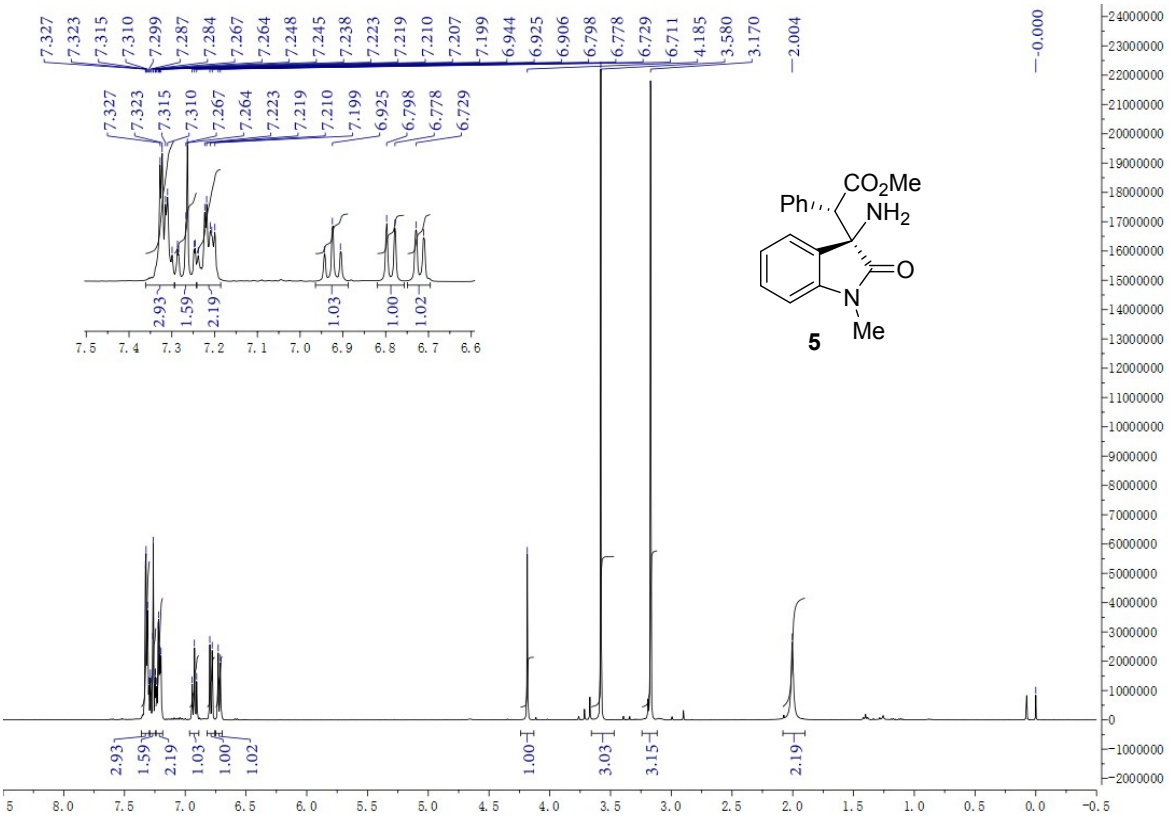
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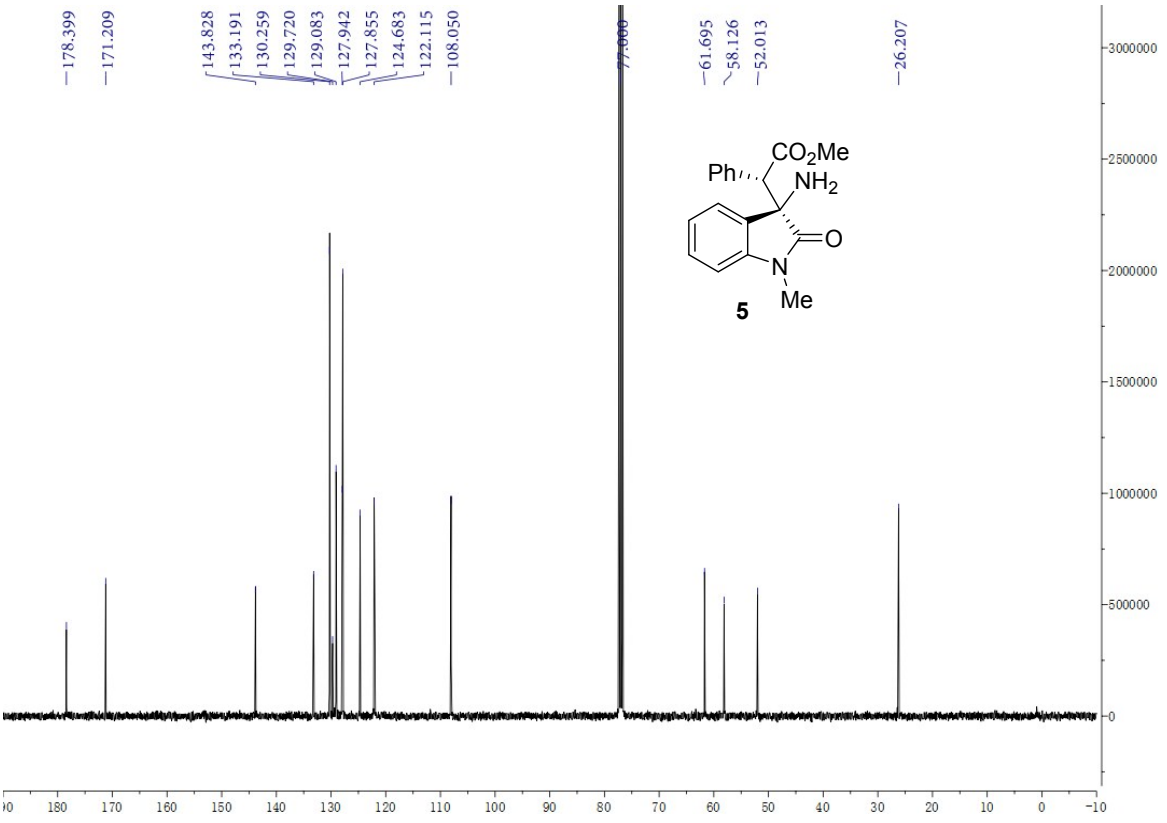
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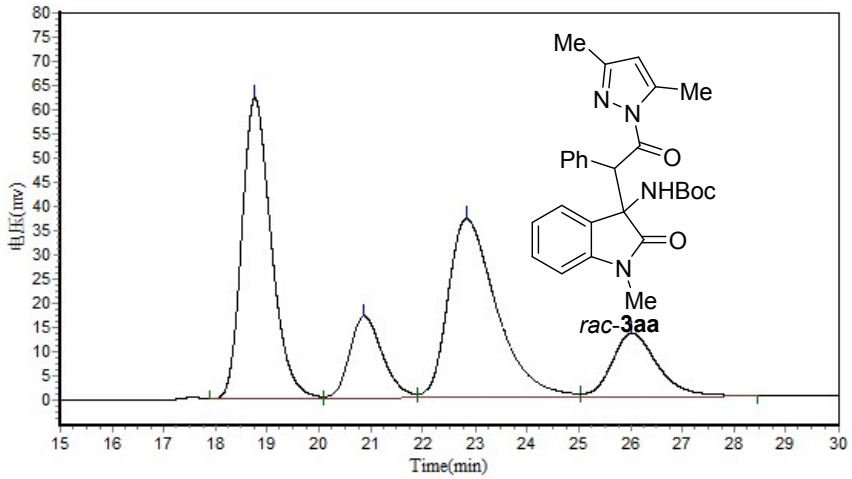
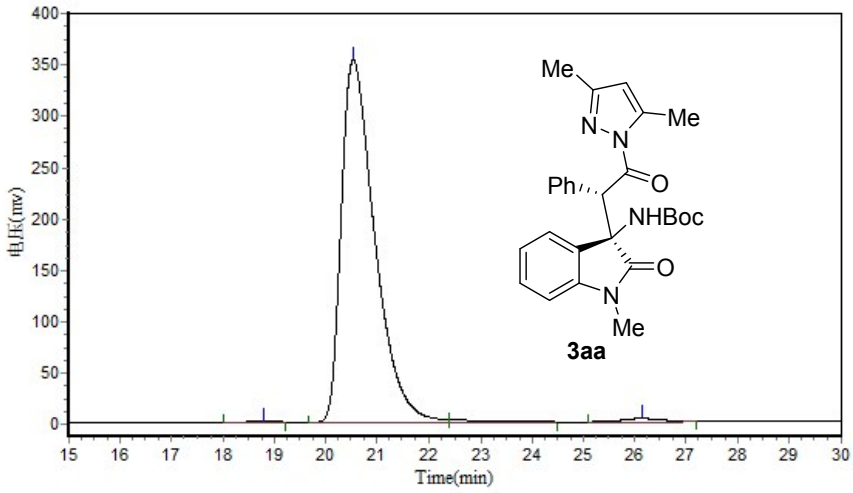
12. Copies of HPLC Chromatograms for Products 3 and 4



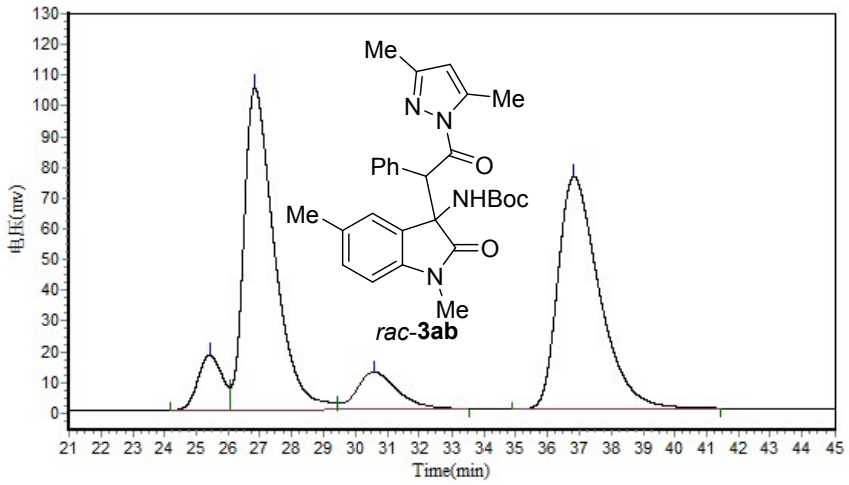
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.758	62269.930	2449097.500	38.2209
2		20.875	17039.428	756527.250	11.8065
3		22.828	37002.387	2411660.500	37.6367
4		26.020	13104.442	790451.063	12.3359
Total			129416.187	6407736.313	100.0000



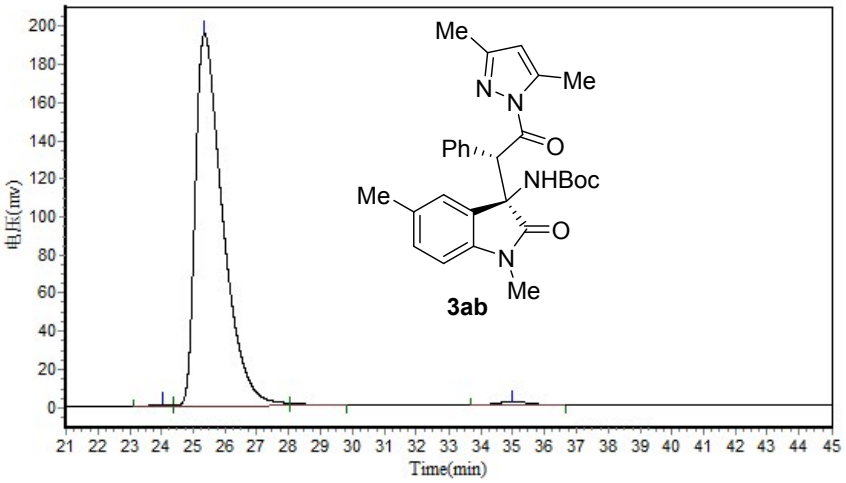
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.782	895.508	28669.992	0.1763
2		20.542	352451.781	15952109.000	98.1205
3		20.542	2196.623	111013.289	0.6828
4		26.152	3076.449	165882.672	1.0203
Total			358620.361	16257674.953	100.0000



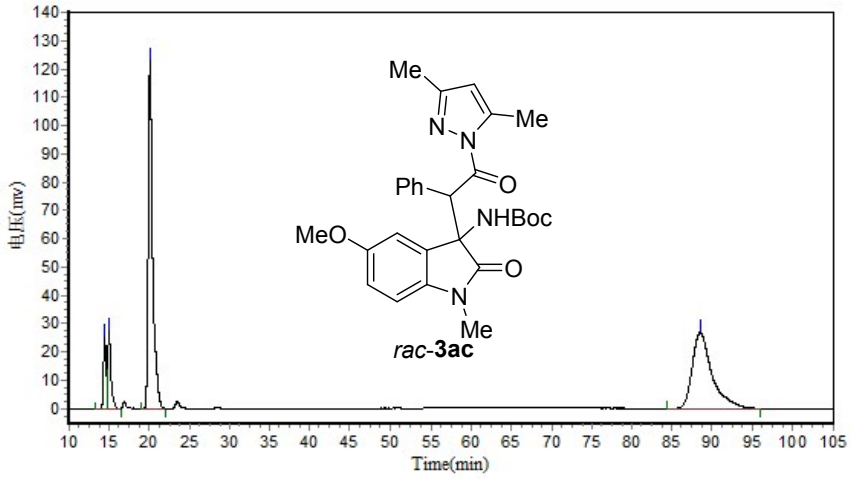
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.418	17809.563	942484.938	5.9747
2		26.842	104760.188	6957989.000	44.1087
3		30.575	12206.070	1075915.750	6.8205
4		36.822	75538.672	6798238.500	43.0960
Total			210314.492	15774628.188	100.0000



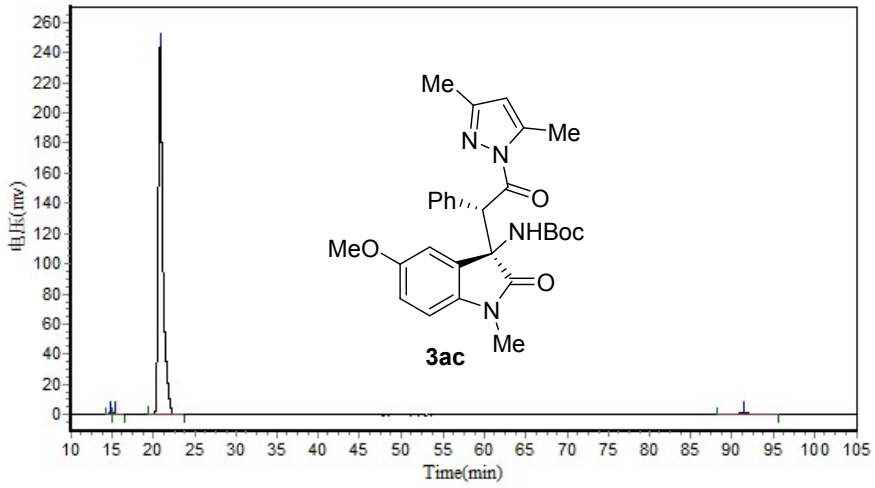
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.043	690.656	28711.311	0.2409
2		25.353	195638.641	11703912.000	98.2083
3		25.353	1453.506	45436.176	0.3813
4		34.980	1832.937	139383.594	1.1696
Total			199615.740	11917443.080	100.0000



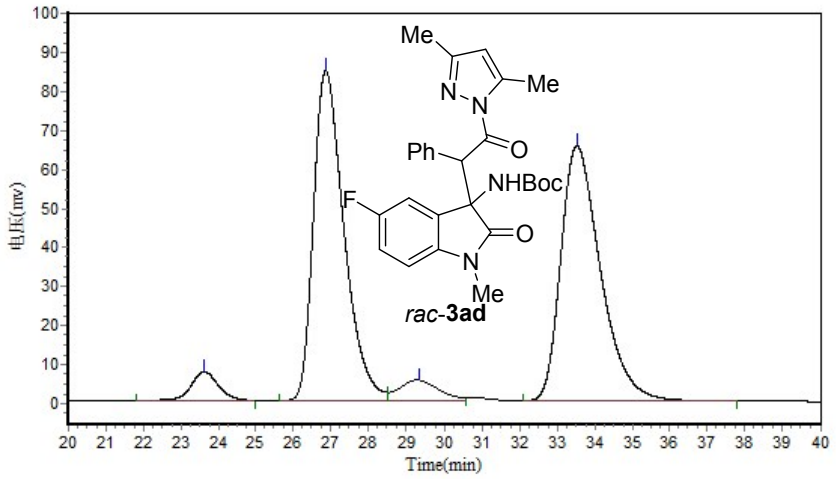
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.417	25227.033	550461.813	5.1922
2		14.967	27359.076	785768.063	7.4118
3		20.077	122899.023	4653198.500	43.8914
4		88.537	26876.082	4612183.500	43.5046
Total			202361.215	10601611.875	100.0000



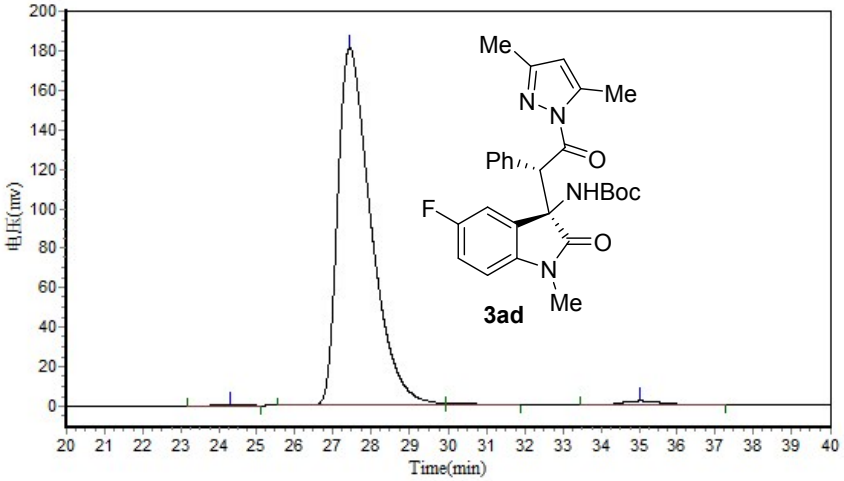
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.738	1221.898	27948.656	0.2861
2		15.302	1337.025	40867.844	0.4184
3		20.788	244049.016	9579275.000	98.0746
4		91.432	747.593	119246.453	1.2209
Total			247355.531	9767337.953	100.0000



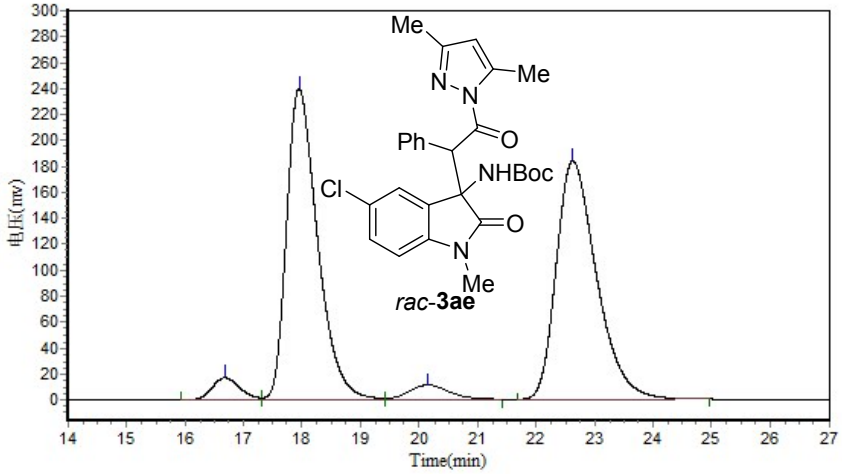
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.613	7469.854	380808.750	3.6874
2		26.860	84448.867	4766974.000	46.1589
3		29.298	5251.602	378564.656	3.6657
4		33.520	65406.773	4800971.500	46.4881
Total			162577.096	10327318.906	100.0000



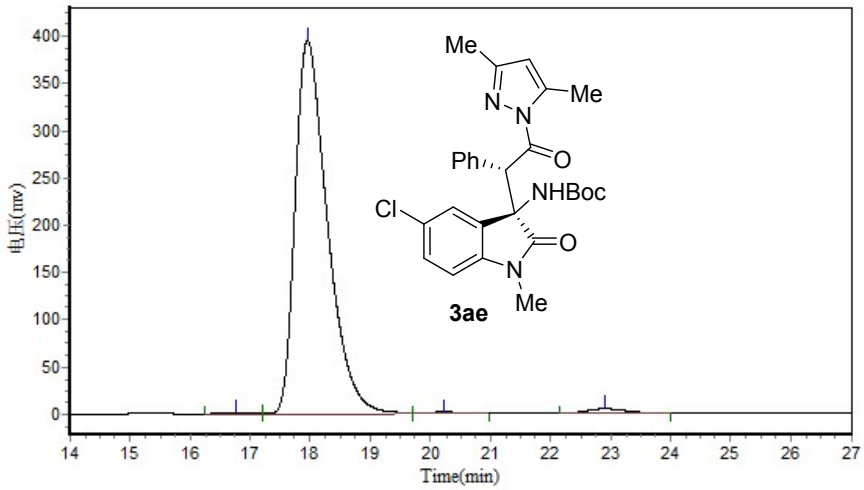
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.288	522.868	23451.246	0.2088
2		27.437	180796.641	10986677.000	97.8039
3		27.437	1065.586	59118.023	0.5263
4		35.028	2128.174	164127.297	1.4611
Total			184513.269	11233373.566	100.0000



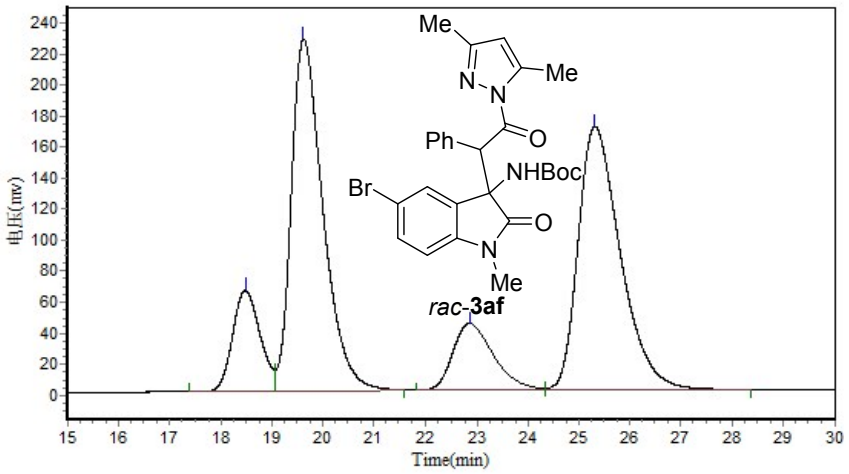
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.687	17041.174	560305.125	2.9851
2		17.957	239735.219	8853888.000	47.1704
3		20.137	11344.331	545864.313	2.9082
4		22.623	183722.063	8809954.000	46.9363
Total			451842.786	18770011.438	100.0000



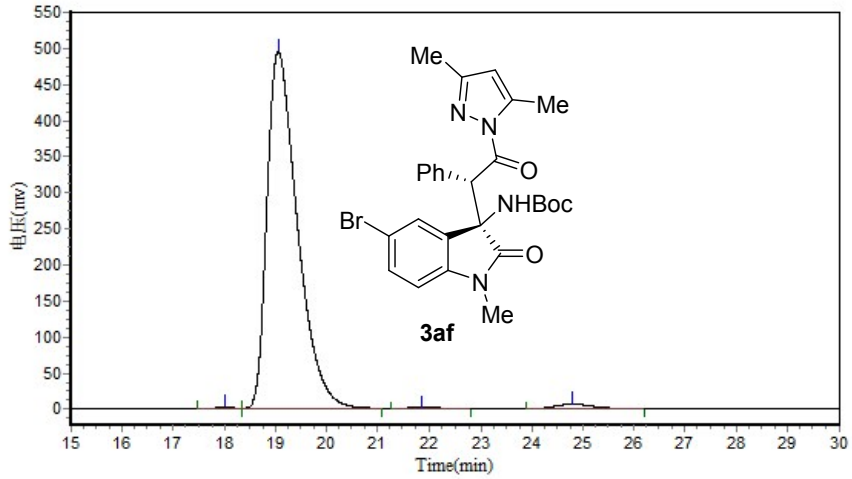
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.775	1611.260	49362.676	0.3270
2		17.958	394699.938	14752517.000	97.7146
3		20.217	1460.050	67850.383	0.4494
4		22.900	4940.058	227833.891	1.5091
Total			402711.306	15097563.949	100.0000



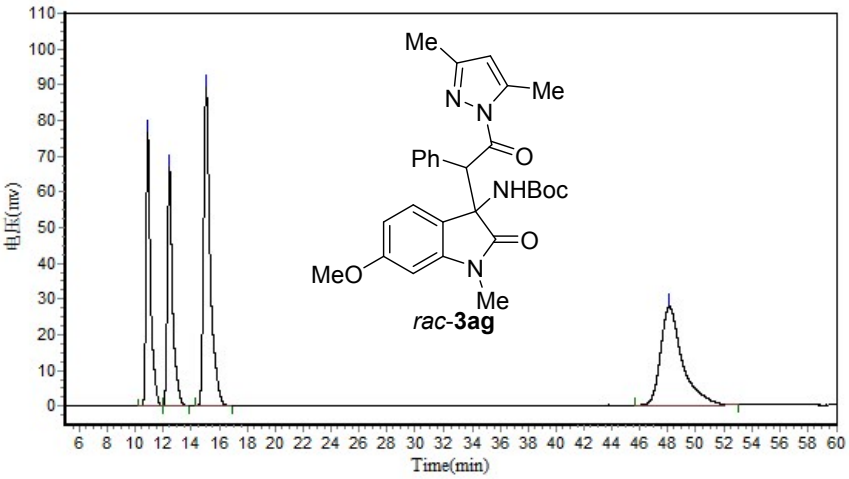
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.480	65214.156	2436010.000	9.9591
2		19.623	226972.047	9806128.000	40.0902
3		22.853	43328.320	2414784.750	9.8723
4		25.315	170003.078	9803251.000	40.0784
Total			505517.602	24460173.750	100.0000



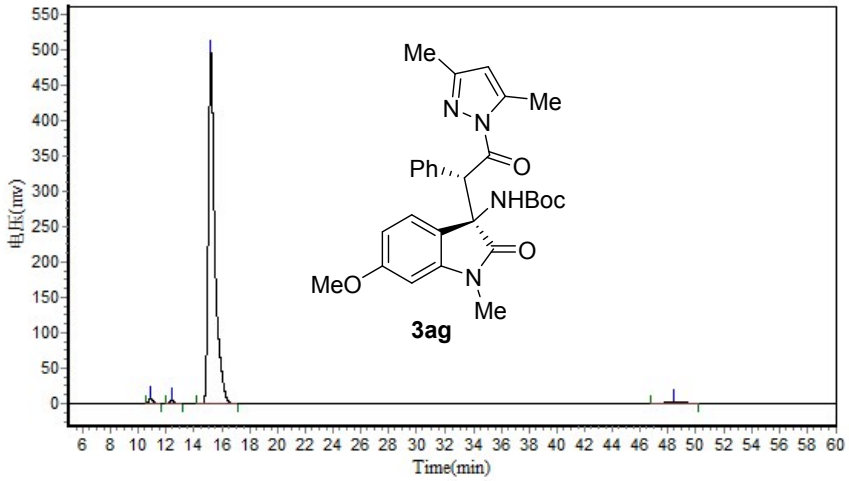
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.000	1847.944	56503.262	0.2698
2		19.055	495236.375	20475394.000	97.7637
3		21.877	1681.197	74093.500	0.3538
4		24.802	6442.942	337774.719	1.6128
Total			505208.458	20943765.480	100.0000



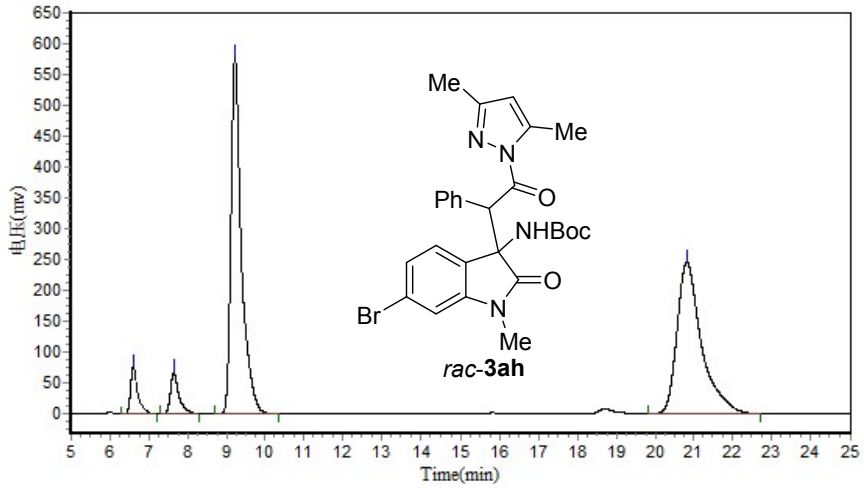
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.882	76521.375	1736629.250	18.5024
2		12.427	66852.164	1739050.750	18.5282
3		15.060	89404.773	2951636.250	31.4473
4		48.108	27644.227	2958662.750	31.5222
Total			260422.539	9385979.000	100.0000



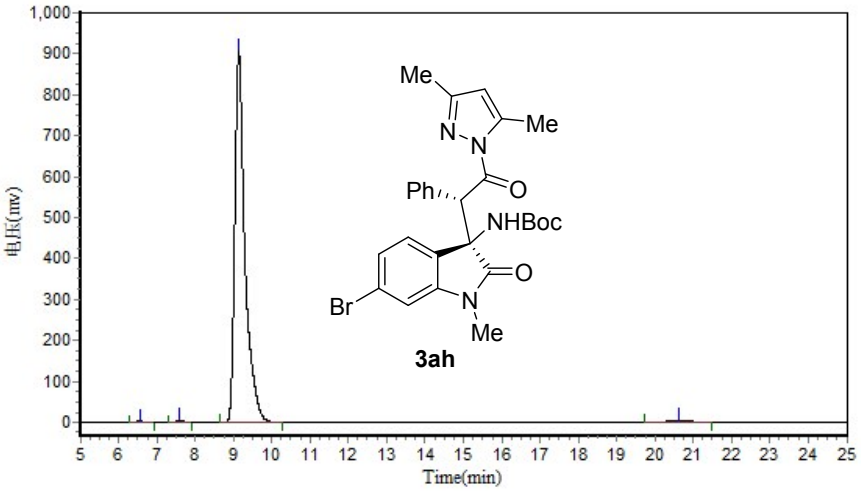
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.880	8193.564	178089.203	1.0506
2		12.405	4881.351	121550.805	0.7171
3		15.205	496130.281	16407819.000	96.7954
4		48.435	2822.278	243564.016	1.4369
Total			512027.474	16951023.023	100.0000



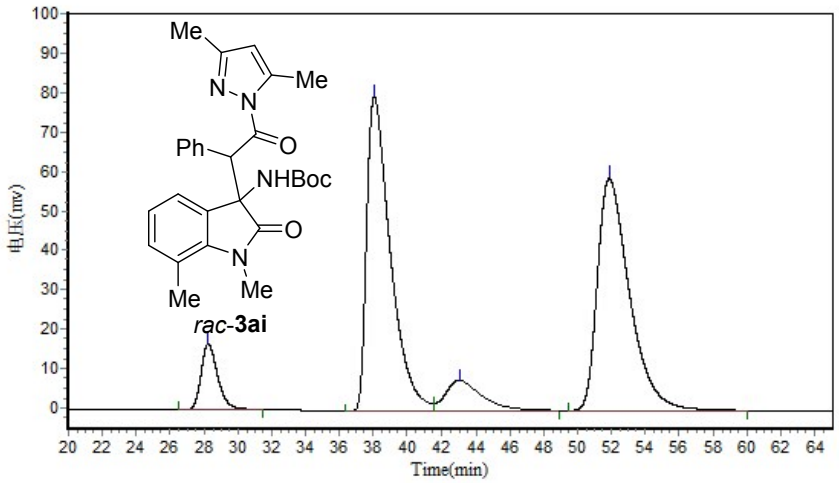
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.600	75810.398	971211.000	4.1300
2		7.638	66289.297	987387.250	4.1988
3		9.217	578624.500	10786933.000	45.8703
4		20.817	246360.063	10770626.000	45.8010
Total			967084.258	23516157.250	100.0000



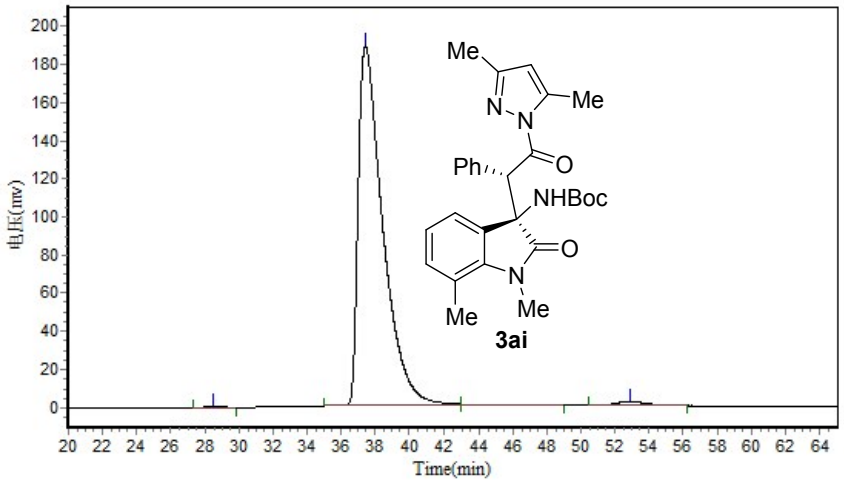
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.547	3471.674	41591.902	0.2444
2		7.578	3555.863	45383.199	0.2666
3		9.137	905371.125	16704907.000	98.1425
4		20.603	5412.270	229186.906	1.3465
Total			917810.932	17021069.008	100.0000



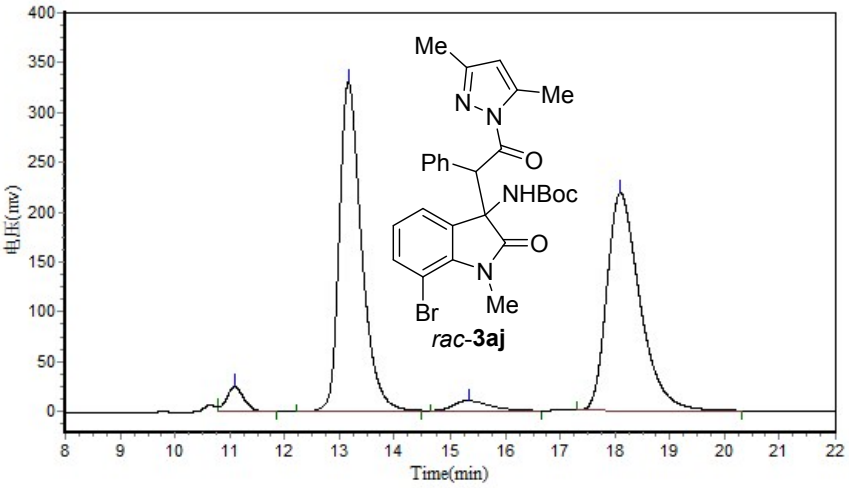
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.258	16803.412	1132625.000	6.3581
2		38.072	79552.023	7738516.000	43.4406
3		43.025	7688.851	1169138.375	6.5630
4		51.870	58907.320	7773720.500	43.6383
Total			162951.607	17813999.875	100.0000



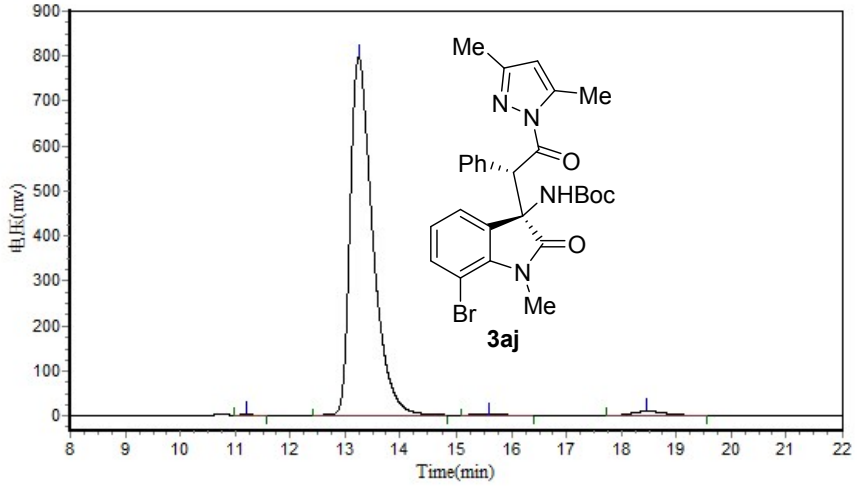
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.532	701.975	43619.301	0.2253
2		37.432	188713.578	18955978.000	97.9137
3		37.432	835.569	88474.766	0.4570
4		52.863	2104.958	271818.094	1.4040
Total			192356.080	19359890.160	100.0000



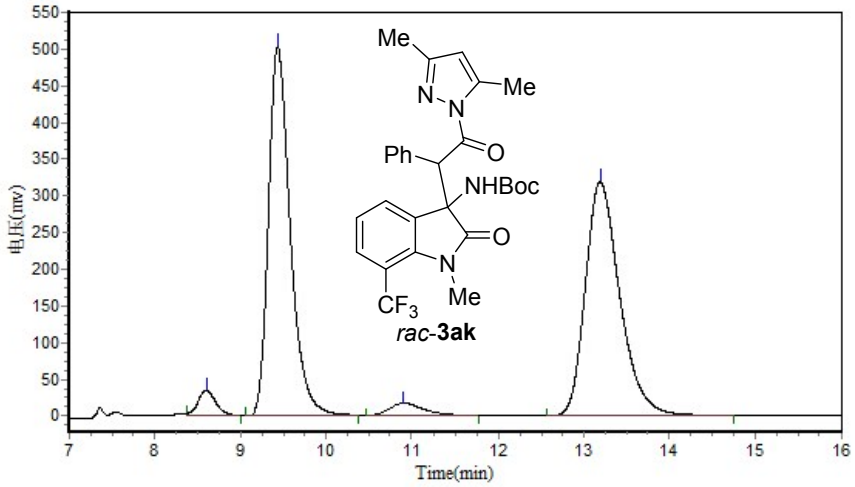
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.090	25522.012	566404.500	2.9104
2		13.163	330570.531	9313288.000	47.8560
3		15.330	10016.852	459457.438	2.3609
4		18.098	218385.922	9121919.000	46.8727
Total			584495.316	19461068.938	100.0000



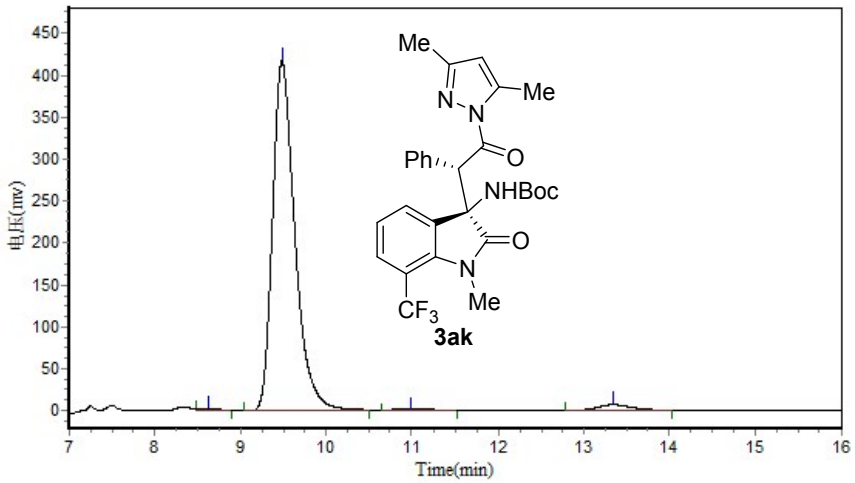
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.212	2492.820	49555.918	0.2138
2		13.247	796073.438	22660288.000	97.7760
3		15.580	1828.537	63916.398	0.2758
4		18.472	9632.538	401944.094	1.7343
Total			810027.333	23175704.410	100.0000



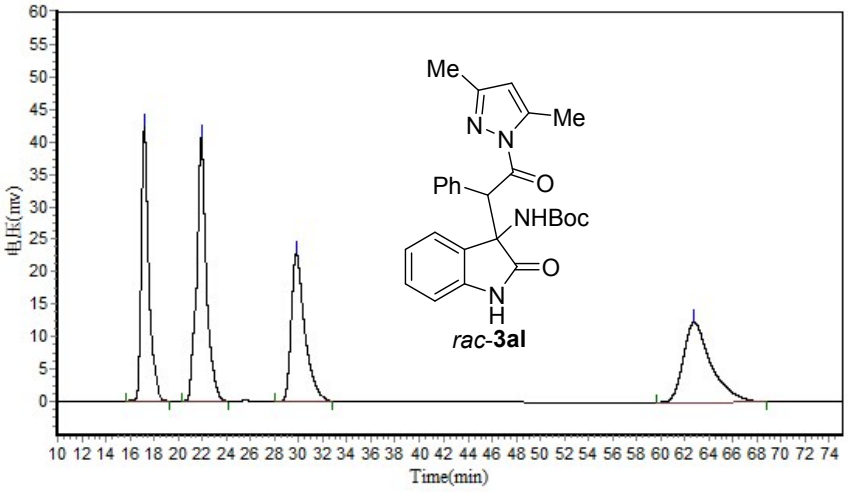
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.602	34392.969	501120.344	2.6744
2		9.435	502119.031	8862745.000	47.2997
3		10.907	16524.551	453641.000	2.4210
4		13.190	318314.156	8919932.000	47.6049
Total			871350.707	18737438.344	100.0000



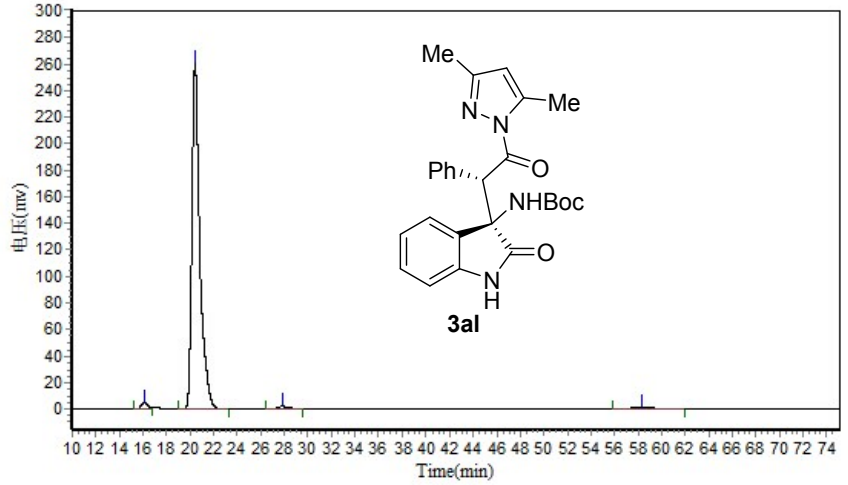
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.623	2767.095	39335.711	0.5057
2		9.487	416526.688	7520314.000	96.6874
3		10.990	1570.750	37541.055	0.4827
4		13.345	6592.800	180772.297	2.3242
Total			427457.332	7777963.063	100.0000



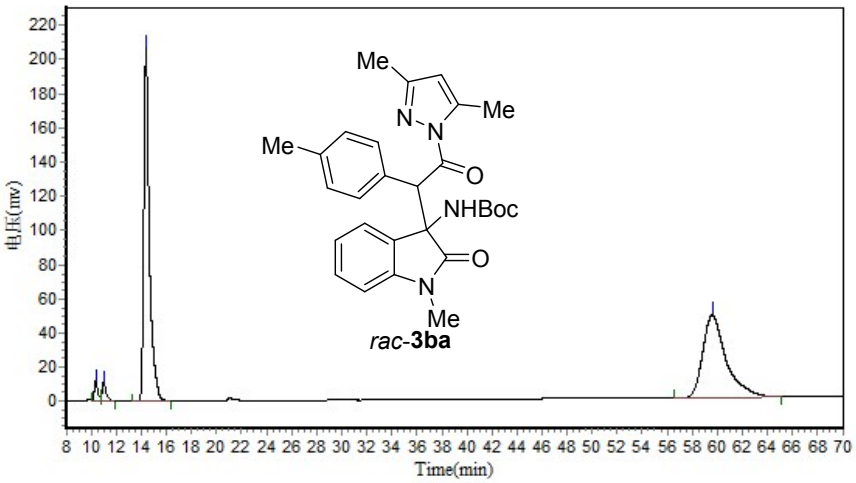
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.200	42309.535	1761759.000	23.3769
2		21.933	40520.660	2019382.750	26.7954
3		29.848	22825.205	1781777.375	23.6426
4		62.790	12335.225	1973389.750	26.1851
Total			117990.625	7536308.875	100.0000



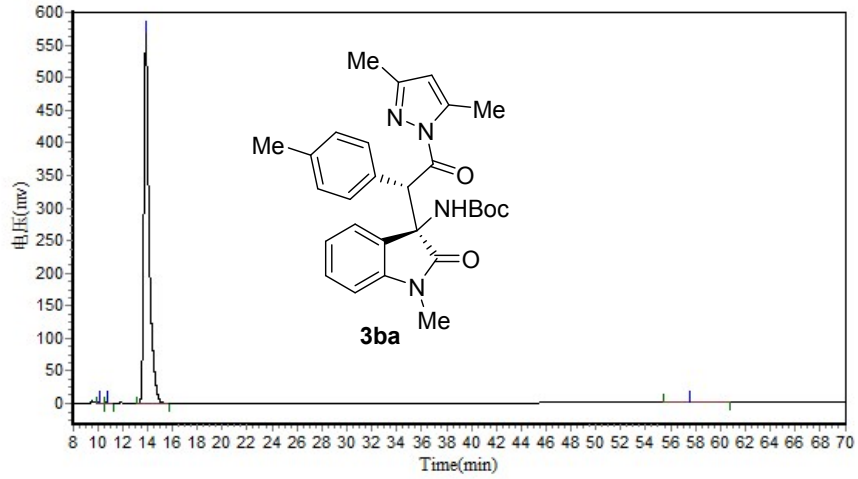
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.085	4870.856	185327.000	1.4580
2		20.430	261160.938	12186217.000	95.8699
3		27.862	1992.877	138237.797	1.0875
4		58.303	1444.556	201415.063	1.5845
Total			269469.227	12711196.859	100.0000



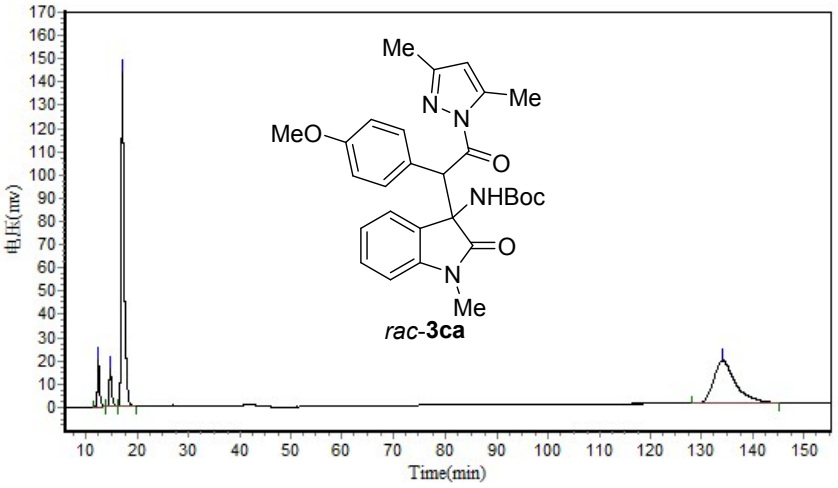
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.312	11690.533	238589.813	1.8095
2		10.968	11034.979	262823.531	1.9933
3		14.340	206089.703	6428485.500	48.7545
4		59.612	48098.762	6255522.000	47.4427
Total			276913.977	13185420.844	100.0000



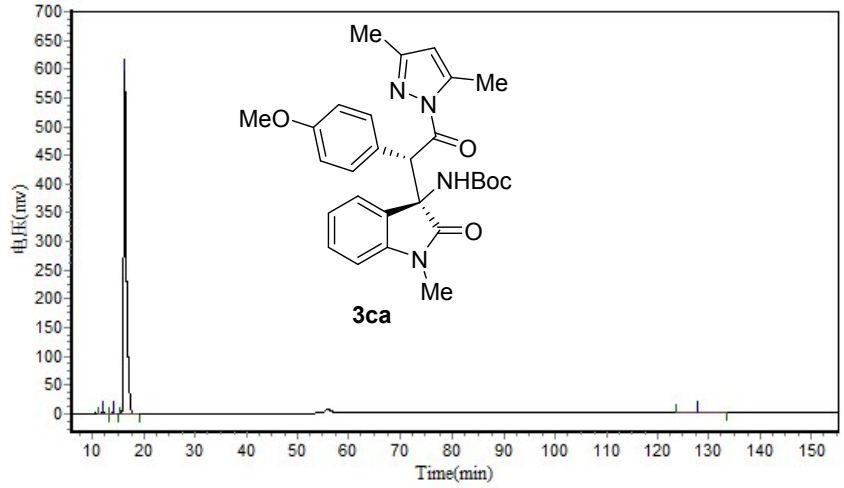
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.095	2306.610	46127.586	0.2710
2		10.725	1679.559	35375.406	0.2078
3		13.840	567706.563	16765200.000	98.4793
4		57.507	1545.984	177383.688	1.0420
Total			573238.715	17024086.680	100.0000



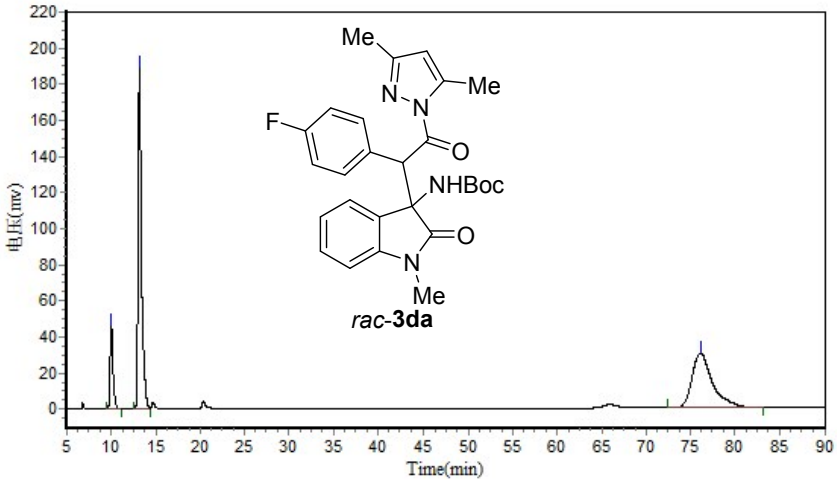
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.353	20652.881	567454.563	4.6048
2		14.690	16926.246	564652.438	4.5820
3		17.057	143602.609	5628040.500	45.6704
4		134.130	18410.813	5563009.500	45.1427
Total			199592.549	12323157.000	100.0000



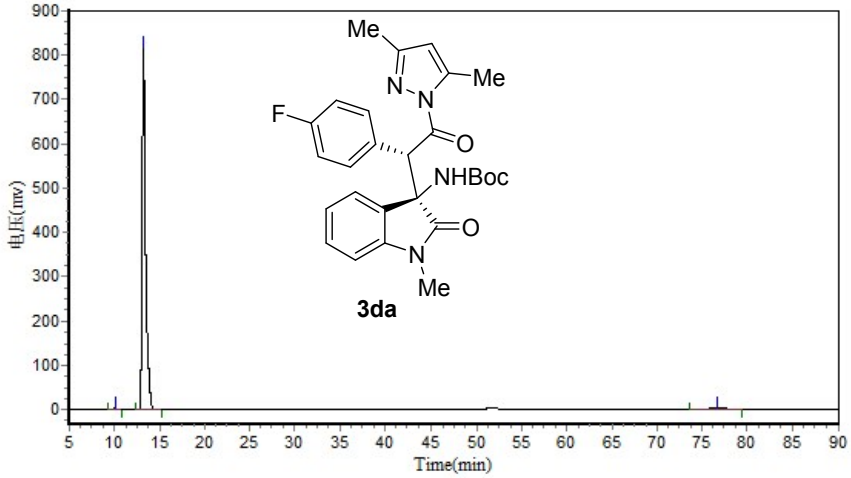
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.935	3017.862	105044.305	0.4744
2		14.055	1442.995	53852.996	0.2432
3		16.247	596293.500	21786082.000	98.3955
4		127.730	748.692	196358.500	0.8868
Total			601503.049	22141337.801	100.0000



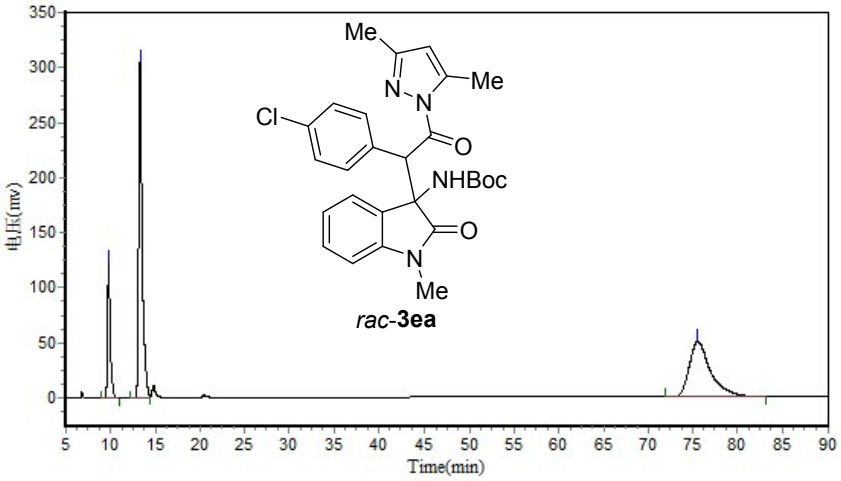
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.000	45800.766	1095521.000	9.9363
2		13.160	188508.859	4964616.500	45.0286
3		76.103	30629.090	4965343.000	45.0352
Total			264938.715	11025480.500	100.0000



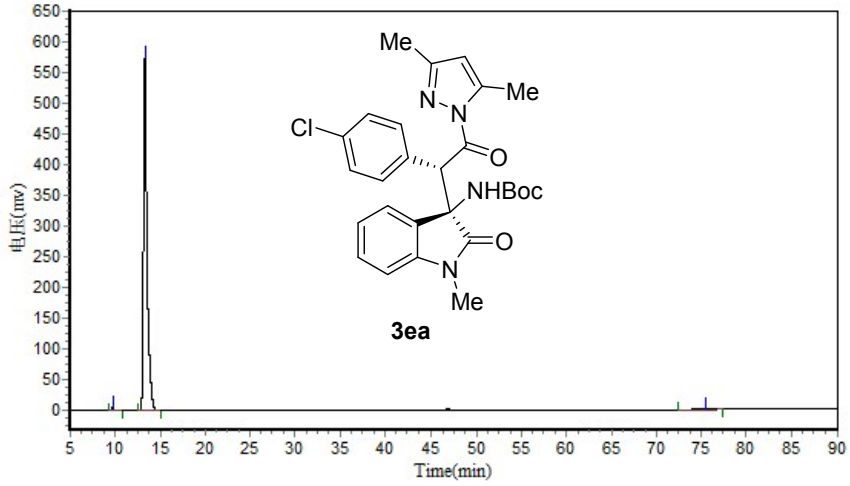
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.037	3402.115	87037.898	0.3973
2		13.213	815811.563	21639880.000	98.7908
3		76.605	1285.254	177830.844	0.8118
Total			820498.932	21904748.742	100.0000



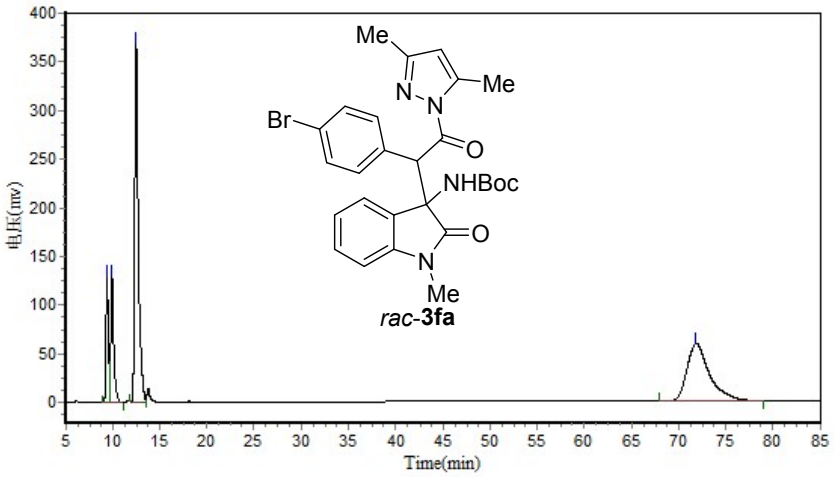
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.763	122731.805	2592606.500	13.3721
2		13.287	304784.563	8370971.000	43.1757
3		75.558	50202.773	8424595.000	43.4522
Total			477719.141	19388172.500	100.0000



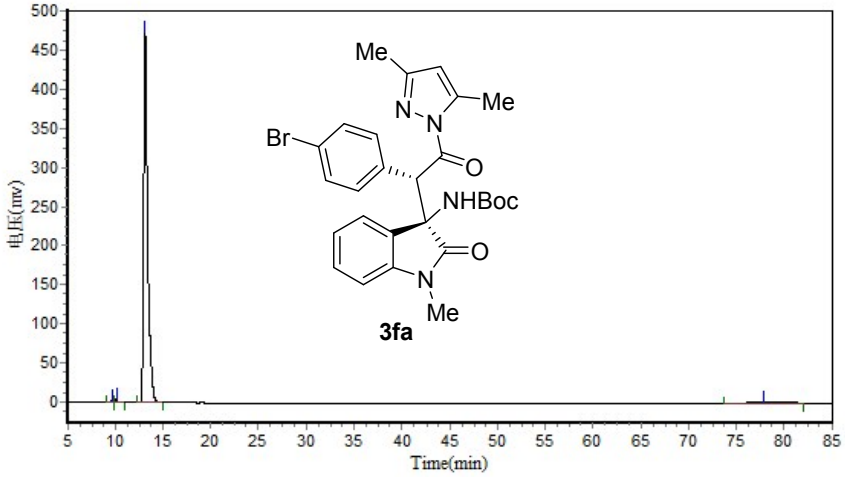
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.750	4894.943	109159.297	0.6852
2		13.280	572755.500	15707858.000	98.6028
3		75.457	992.597	113419.695	0.7120
Total			578643.041	15930436.992	100.0000



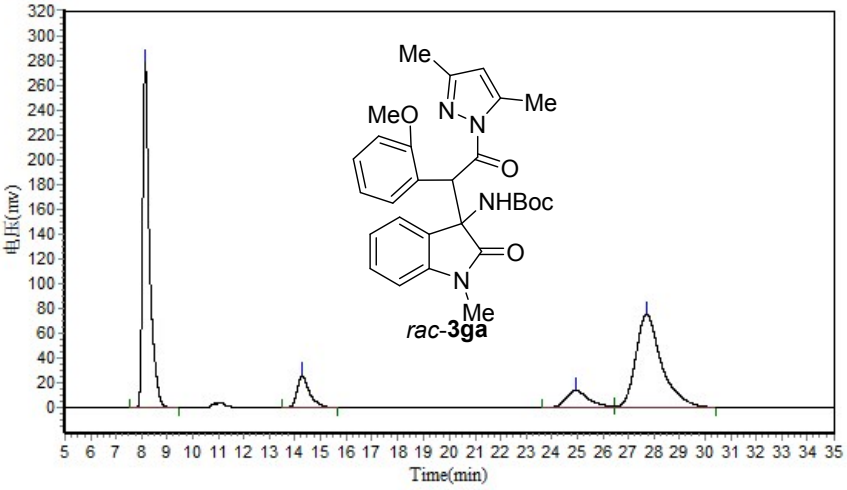
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.345	128125.320	2254367.750	9.0872
2		9.887	127259.781	2819332.250	11.3645
3		12.445	367050.031	9832157.000	39.6328
4		71.898	59012.660	9902287.000	39.9155
Total			681447.793	24808144.000	100.0000



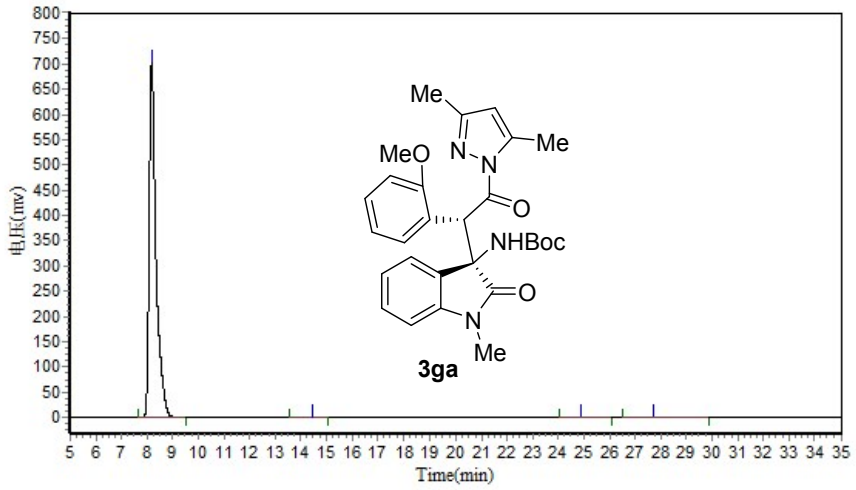
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.597	2740.663	48449.484	0.3463
2		10.083	3818.932	85119.883	0.6084
3		13.097	470458.281	13702345.000	97.9458
4		77.892	931.866	153803.516	1.0994
Total			477949.742	13989717.883	100.0000



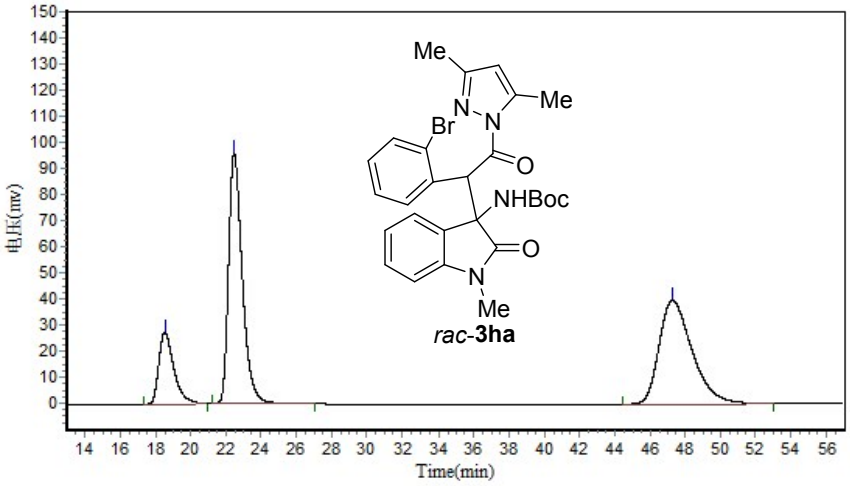
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.138	278284.813	5233469.000	43.0168
2		14.285	25636.393	866018.438	7.1183
3		24.945	13481.890	838096.938	6.8888
4		27.702	75021.008	5228511.500	42.9761
Total			392424.103	12166095.875	100.0000



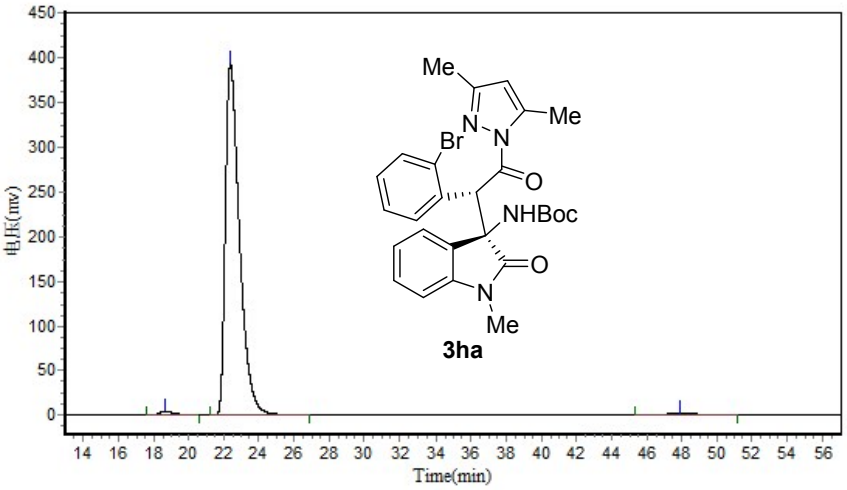
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.177	703145.625	13043430.000	98.7483
2		14.435	1097.554	31132.852	0.2357
3		24.863	310.173	16584.900	0.1256
4		27.717	1792.631	117619.008	0.8905
Total			706345.983	13208766.760	100.0000



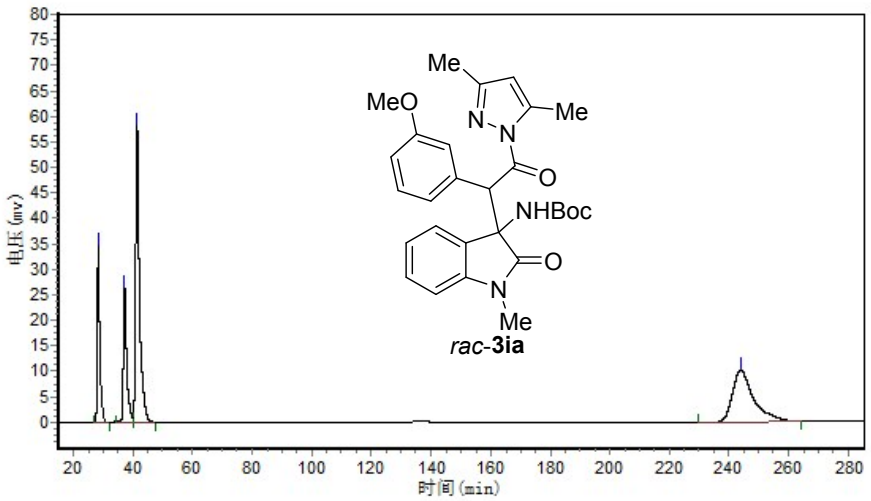
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.525	27641.688	1623292.750	13.5499
2		22.465	96132.484	5200742.000	43.4115
3		47.283	39726.750	5156072.000	43.0386
Total			163500.922	11980106.750	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.647	4170.822	258113.547	1.1428
2		22.380	393376.531	22018826.000	97.4864
3		47.873	2466.389	309625.781	1.3708
Total			400013.742	22586565.328	100.0000



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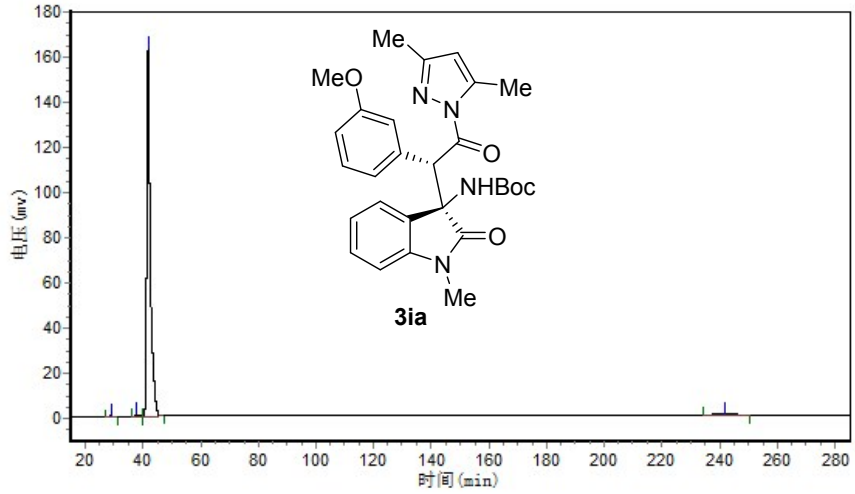
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		28.217	34576.355	1997217.250	14.1225
2		37.097	25943.801	1990920.000	14.0780
3		41.268	57626.418	5114439.000	36.1646
4		243.890	10148.404	5039538.500	35.6350
总计			128294.979	14142114.750	100.0000



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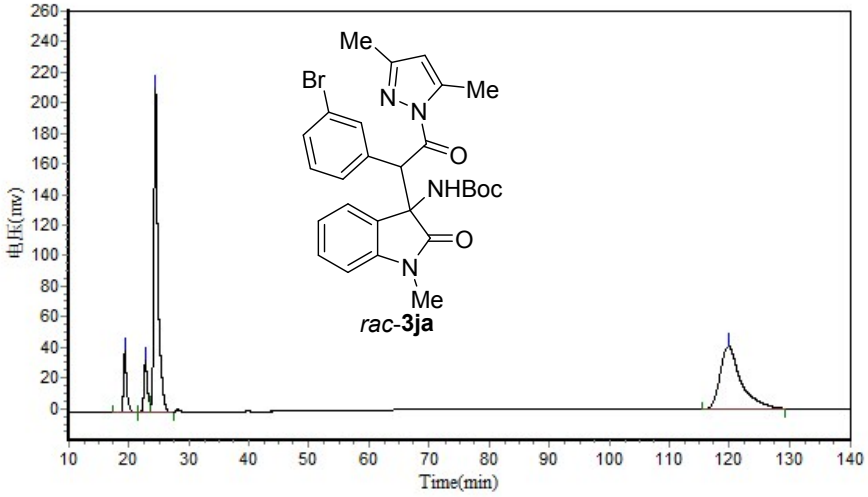
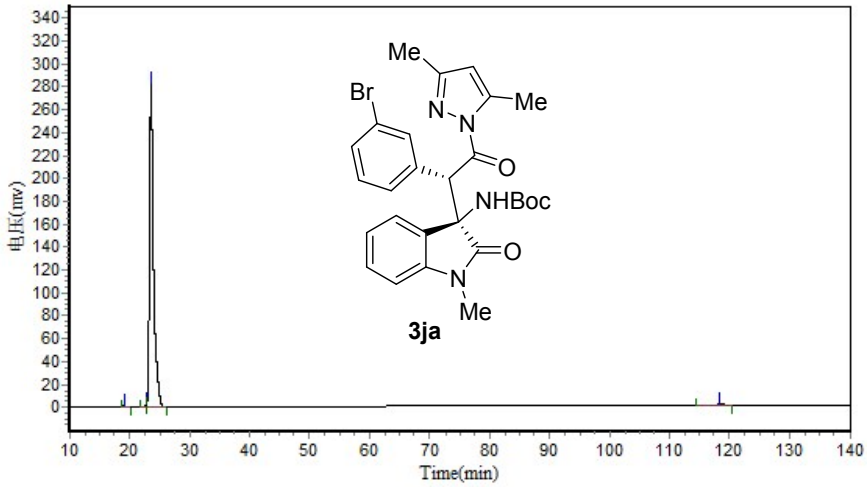
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		28.980	719.438	38943.895	0.2724
2		37.812	669.705	46856.621	0.3278
3		41.703	162462.672	14027411.000	98.1326
4		242.010	480.781	181137.219	1.2672
总计			164332.596	14294348.734	100.0000



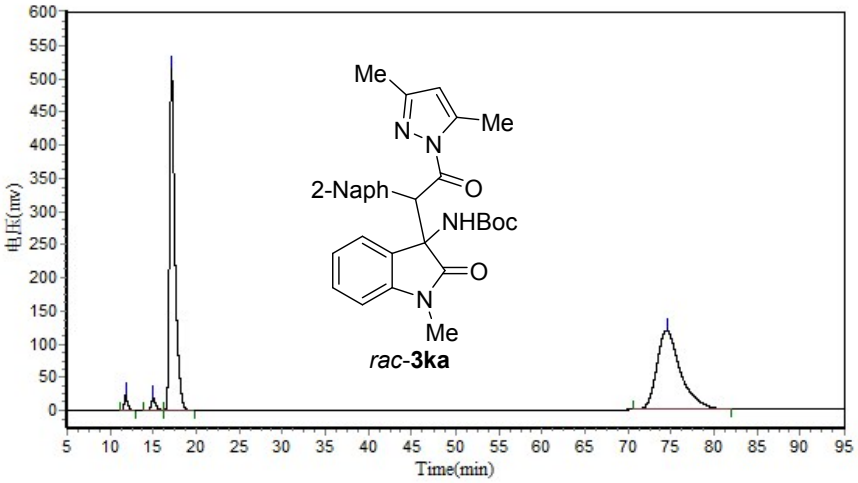
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.320	40044.414	1491252.625	6.4891
2		22.753	33471.363	1396536.875	6.0770
3		24.437	212022.125	10158411.000	44.2039
4		119.813	41334.793	9934580.000	43.2299
Total			326872.695	22980780.500	100.0000



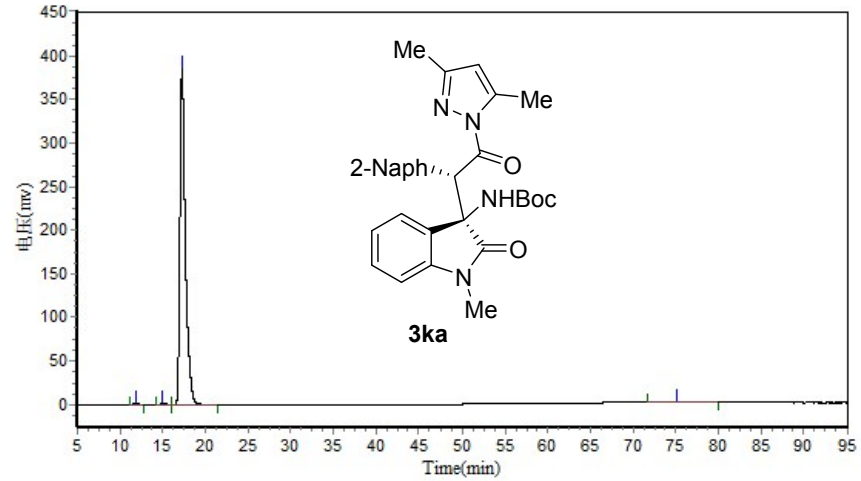
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.112	1603.086	53469.898	0.4004
2		22.732	1292.025	24595.793	0.1842
3		23.555	282089.719	13169890.000	98.6137
4		118.387	717.799	107079.070	0.8018
Total			285702.629	13355034.762	100.0000



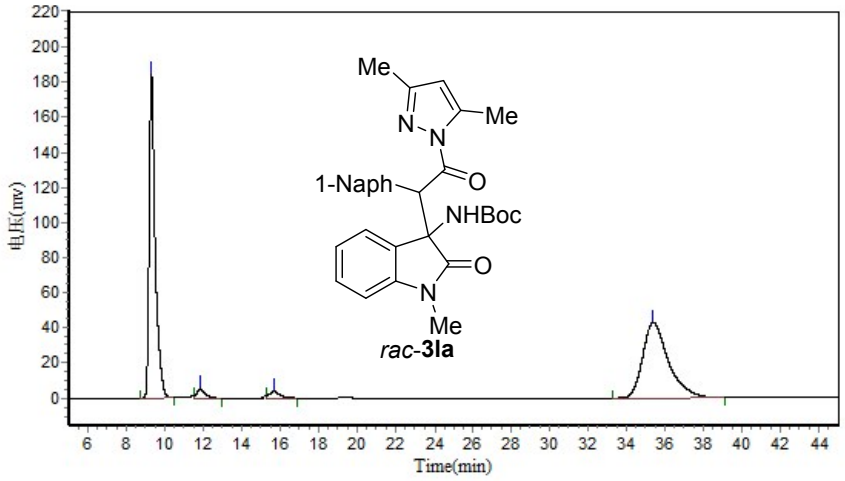
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.778	23845.746	652526.625	1.3947
2		14.995	18039.502	650952.250	1.3913
3		17.127	515725.563	22697726.000	48.5130
4		74.490	119282.211	22785650.000	48.7010
Total			676893.021	46786854.875	100.0000



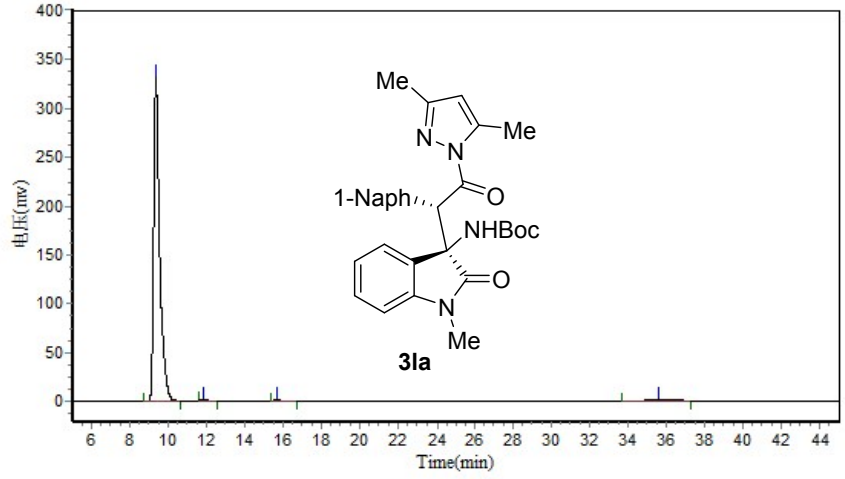
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.780	1543.413	42047.297	0.2414
2		14.993	1214.023	44188.488	0.2537
3		17.260	385761.063	17163280.000	98.5237
4		75.037	959.965	170944.766	0.9813
Total			389478.463	17420460.551	100.0000



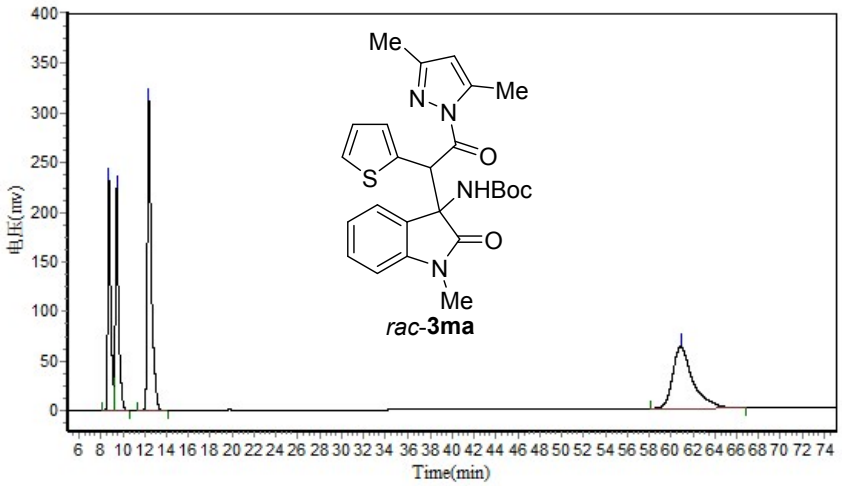
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.278	184796.234	4021890.500	48.1758
2		11.817	5257.965	152272.813	1.8240
3		15.680	3851.591	150260.391	1.7999
4		35.400	43123.090	4023939.250	48.2003
Total			237028.880	8348362.953	100.0000



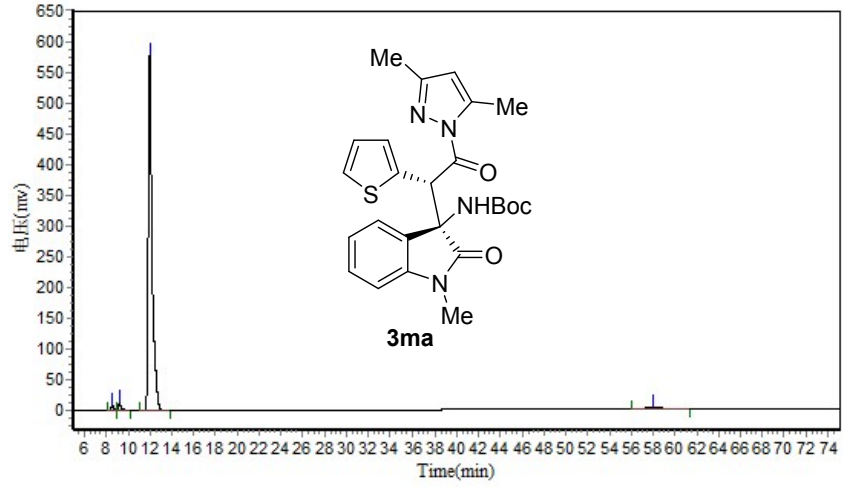
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.337	331996.313	7205224.000	98.1140
2		11.840	894.544	24721.322	0.3366
3		15.660	747.680	26778.400	0.3646
4		35.612	1067.003	87001.242	1.1847
Total			334705.540	7343724.965	100.0000



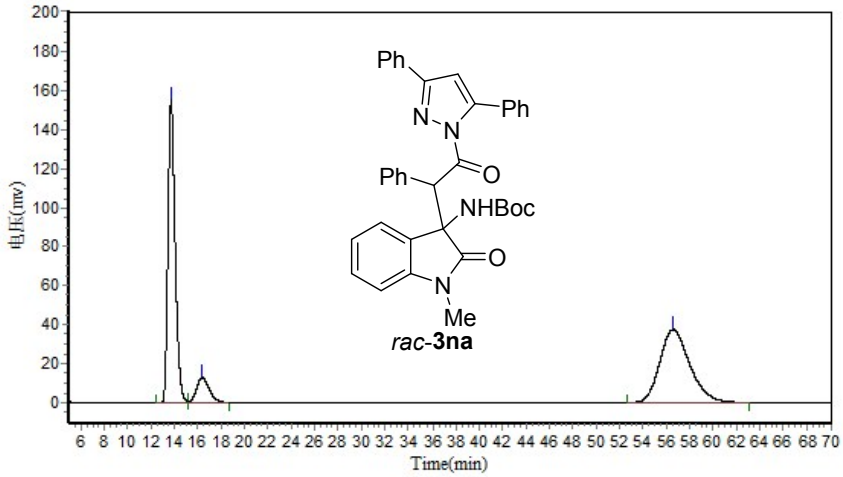
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.723	231409.906	4303823.500	17.4015
2		9.428	223922.203	4523752.000	18.2907
3		12.377	312432.688	8000210.000	32.3469
4		60.885	62526.020	7904722.500	31.9609
Total			830290.816	24732508.000	100.0000



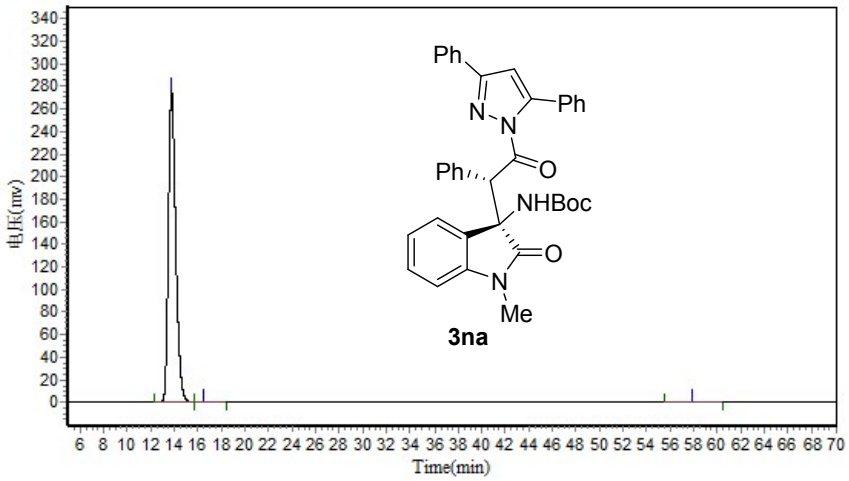
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.532	7610.633	129964.320	0.8744
2		9.177	11366.471	216687.047	1.4578
3		11.960	577234.188	14087520.000	94.7779
4		57.972	3690.537	429543.875	2.8899
Total			599901.828	14863715.242	100.0000



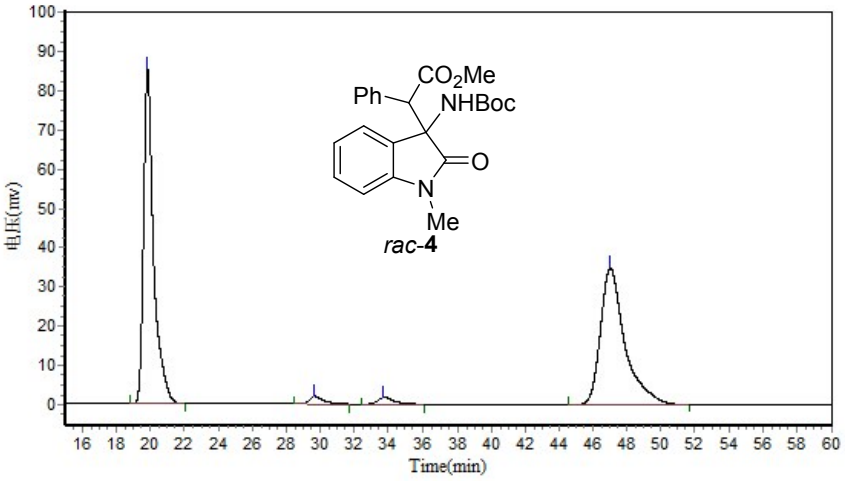
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.725	154889.813	6591247.500	46.4468
2		16.392	12789.339	988970.438	6.9690
3		56.572	37283.703	6610751.000	46.5842
Total			204962.854	14190968.938	100.0000



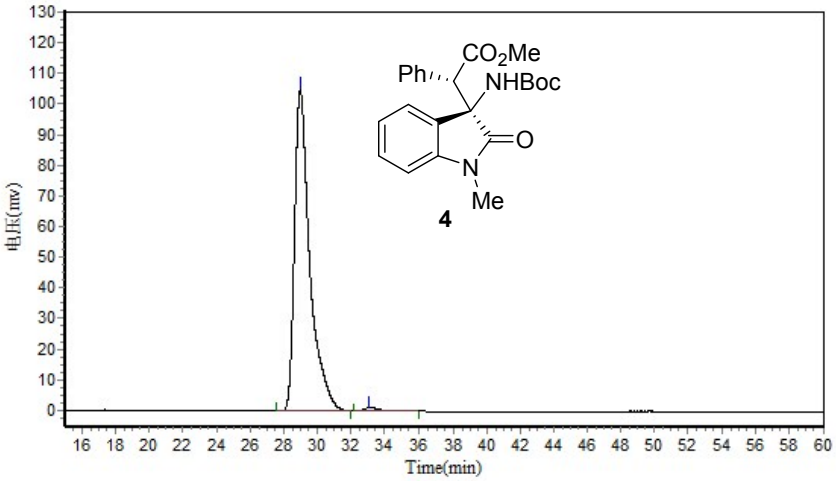
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.772	276970.094	11991001.000	98.5790
2		16.507	969.219	82097.531	0.6749
3		57.835	602.608	90745.102	0.7460
Total			278541.920	12163843.633	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.828	84940.875	3499221.500	48.4669
2		29.653	1982.337	117974.102	1.6340
3		33.745	1777.405	119397.859	1.6538
4		47.022	34823.000	3483221.500	48.2453
Total			123523.617	7219814.961	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.987	104736.523	6632230.500	98.8547
2		33.108	1157.547	76842.055	1.1453
Total			105894.071	6709072.555	100.0000