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SUPPORTING INFORMATION

Highly diastereoselective synthesis of vicinal diamines *via* Rh-catalyzed three-component reaction of diazo compounds with diarylmethanimines and ketimines

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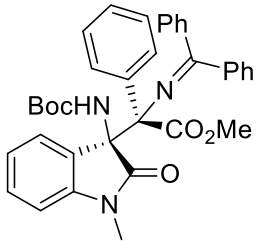
General Information

General. All reactions were carried out in oven-dried glassware. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 400 or 500 MHz spectrometer; chemical shifts were reported in ppm with the solvent signal as reference, and coupling constants (*J*) were given in Hertz. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI or CI Source).

Materials. Anhydrous solvent was distilled from Na by following the standard purification procedure. All catalysts, including $Rh_2(OAc)_4$ and $Rh_2(esp)_2$ were purchased from chemical vendor, and used directly without additional treatment. Diazo compounds **1** were prepared according to the literature[1]. Diarylmethanimines **2** were prepared according to the literature[2] or purchased from chemical vendor. Isatin-derived ketimines **3** were prepared according to the literature[3].

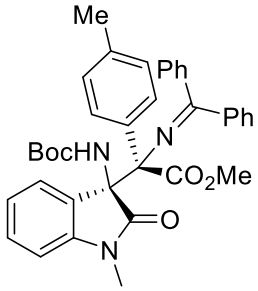
General Procedure for the Synthesis of 4 and 5

To a 10-mL oven-dried vial containing stirring bar, $Rh_2(OAc)_4$ (0.5 mg, 0.5 mol%) or $Rh_2(esp)_2$ (1.5 mg, 1.0 mol%), 50 mg 4Å MS, benzophenone imine **2** (0.24 mmol), and isatin-derived ketimine **3** (0.20 mmol) in 1,4-dioxane (3.0 mL), diazo compounds **1** (0.30 mmol) in 1,4-dioxane (1.0 mL) was added slowly *via* a syringe pump over 2 h under argon atmosphere at room temperature, and the reaction mixture was stirred for additional 36 h or 10 h. After the completion of the reaction (monitored by TLC), the solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (Hexanes : EtOAc = 10:1 to 5:1) to give the pure products **4** or **5** in good to high yields.



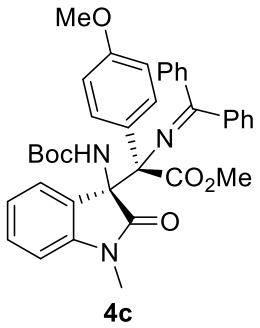
4a

Methyl (*R)-2-((*S**)-3-((*tert*-butoxycarbonyl)amino)-1-methyl-2-oxoindolin-3-yl)-2-((diphenylmethylene)amino)-2-phenylacetate (4a).** 109.8 mg, 93%. Yellow solid; mp = 184.1-185.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 1H), 7.82 – 7.71 (m, 2H), 7.59 – 7.50 (m, 1H), 7.50 – 7.42 (m, 2H), 7.33 – 7.08 (comp, 4H), 7.06 – 6.81 (comp, 6H), 6.80 – 6.51 (comp, 3H), 6.29 – 6.13 (m, 1H), 3.28 (s, 3H), 2.92 (s, 3H), 1.47 – 0.94 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 172.5, 169.2, 154.4, 143.3, 141.3, 136.8, 136.0, 131.0, 129.5, 129.1, 129.0, 128.6, 128.4, 127.4, 127.3, 125.7, 125.1, 122.1, 106.9, 79.9, 75.7, 70.0, 52.2, 28.2, 25.8; HRMS (TOF MS ESI+) calculated for $C_{36}H_{36}N_3O_5$ $[M+H]^+$: 590.2649, found 590.2643.



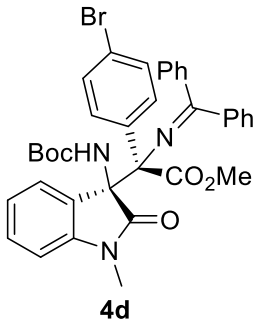
4b

Methyl (*R)-2-((*S**)-3-((*tert*-butoxycarbonyl)amino)-1-methyl-2-oxoindolin-3-yl)-2-((diphenylmethylene)amino)-2-(*p*-tolyl)acetate (4b).** 108.6 mg, 90%. Yellow solid; mp = 161.1-162.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 1H), 7.80 – 7.70 (m, 2H), 7.59 – 7.50 (m, 1H), 7.49 – 7.39 (m, 2H), 7.28 – 7.20 (m, 1H), 7.19 – 6.97 (comp, 4H), 6.95 – 6.82 (m, 2H), 6.81 – 6.48 (comp, 5H), 6.30 – 6.12 (m, 1H), 3.25 (s, 3H), 2.92 (s, 3H), 2.15 (s, 3H), 1.45 – 0.94 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 172.2, 169.3, 154.5, 143.4, 141.4, 136.9, 136.1, 133.7, 130.9, 129.5, 129.0, 128.6, 128.4, 127.4, 126.4, 125.1, 122.0, 106.9, 79.8, 75.6, 70.0, 52.1, 28.2, 25.8, 21.0; HRMS (TOF MS ESI$^+$) calculated for $C_{37}H_{38}N_3O_5$ $[M+H]^+$: 604.2806, found 604.2807.



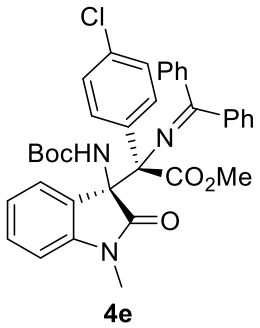
4c

Methyl (*R)-2-((*S**)-3-((*tert*-butoxycarbonyl)amino)-1-methyl-2-oxoindolin-3-yl)-2-((diphenylmethylene)amino)-2-(4-methoxyphenyl)acetate (4c).** 105.7 mg, 85%. Yellow solid; mp = 174.2-175.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 1H), 7.80 – 7.68 (m, 2H), 7.58 – 7.49 (m, 1H), 7.49 – 7.40 (m, 2H), 7.31 – 7.22 (m, 1H), 7.20 – 6.95 (comp, 4H), 6.93 – 6.71 (comp, 4H), 6.69 – 6.29 (comp, 3H), 6.29 – 6.14 (m, 1H), 3.67 (s, 3H), 3.27 (s, 3H), 2.92 (s, 3H), 1.48 – 0.92 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 172.3, 169.2, 158.5, 154.4, 143.3, 141.3, 136.0, 130.9, 129.4, 129.0, 128.9, 128.6, 128.4, 127.4, 125.0, 122.0, 111.0, 107.0, 79.8, 75.3, 70.0, 55.2, 52.1, 28.2, 25.8; HRMS (TOF MS ESI$^+$) calculated for $C_{37}H_{38}N_3O_6$ $[M+H]^+$: 620.2755, found 620.2757.



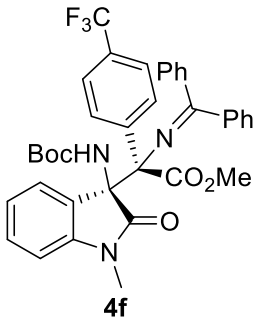
4d

Methyl (*R)-2-(4-bromophenyl)-2-((*S**)-3-((*tert*-butoxycarbonyl)amino)-1-methyl-2-oxoindolin-3-yl)-2-((diphenylmethylene)amino)acetate (4d).** 107.2 mg, 80%. Yellow solid; mp = 169.1-170.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 1H), 7.80 – 7.71 (m, 2H), 7.58 – 7.52 (m, 1H), 7.50 – 7.45 (m, 2H), 7.28 – 7.25 (m, 1H), 7.22 – 6.94 (comp, 6H), 6.93 – 6.88 (m, 1H), 6.86 – 6.43 (comp, 4H), 6.32 – 6.23 (m, 1H), 3.28 (s, 3H), 2.93 (s, 3H), 1.40 – 0.99 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 173.0, 168.7, 154.4, 143.2, 141.1, 136.0, 135.9, 131.2, 129.5, 129.3, 129.0, 128.9, 128.5, 127.5, 125.1, 122.3, 121.9, 107.2, 80.1, 75.3, 69.8, 52.3, 28.2, 25.9; HRMS (TOF MS ESI$^+$) calculated for $C_{36}H_{35}BrN_3O_5$ $[M+H]^+$: 668.1755, found 668.1748.



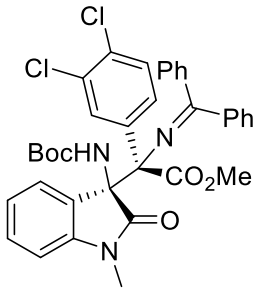
4e

Methyl (*R)-2-((*S**)-3-((*tert*-butoxycarbonyl)amino)-1-methyl-2-oxoindolin-3-yl)-2-(4-chlorophenyl)-2-((diphenylmethylene)amino)acetate (4e).** 107.6 mg, 86%. Yellow solid; mp = 167.1-168.5 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 1H), 7.80 – 7.73 (m, 2H), 7.59 – 7.52 (m, 1H), 7.51 – 7.44 (m, 2H), 7.29 – 7.25 (m, 1H), 7.23 – 7.01 (comp, 4H), 7.00 – 6.39 (comp, 7H), 6.32 – 6.23 (m, 1H), 3.29 (s, 3H), 2.93 (s, 3H), 1.45 – 0.90 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 173.0, 168.7, 154.4, 143.2, 141.1, 135.9, 135.5, 133.4, 131.2, 129.5, 129.2, 129.0, 128.8, 128.5, 127.5, 125.8, 125.1, 122.2, 107.2, 80.0, 75.2, 69.8, 52.3, 28.2, 25.9; HRMS (TOF MS ESI$^+$) calculated for $C_{36}H_{35}ClN_3O_5$ $[M+H]^+$: 624.2260, found 624.2259.



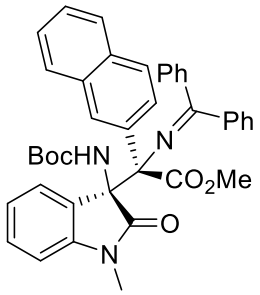
4f

Methyl (*R)-2-((*S**)-3-((*tert*-butoxycarbonyl)amino)-1-methyl-2-oxoindolin-3-yl)-2-((diphenylmethylene)amino)-2-(4-(trifluoromethyl)phenyl)acetate (4f).** 108.1 mg, 82%. Yellow solid; mp = 197.2-198.7 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 1H), 7.81 – 7.74 (m, 2H), 7.59 – 7.53 (m, 1H), 7.52 – 7.46 (m, 2H), 7.32 – 7.27 (m, 1H), 7.23 – 7.08 (comp, 4H), 7.07 – 6.83 (comp, 3H), 6.81 – 6.50 (comp, 3H), 6.26 – 6.13 (m, 1H), 3.31 (s, 3H), 2.91 (s, 3H), 1.34 – 1.03 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 173.3, 168.5, 154.4, 143.0, 141.0, 140.8, 135.8, 131.3, 129.5, 129.34, 129.30, 129.1, 128.8, 128.5, 127.6, 125.1, 124.0 (q, J = 271.3 Hz), 122.4, 122.3, 107.1, 80.1, 75.5, 69.9, 52.4, 28.2, 25.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.8; HRMS (TOF MS ESI$^+$) calculated for $C_{37}H_{35}F_3N_3O_5$ $[M+H]^+$: 658.2523, found 658.2518.



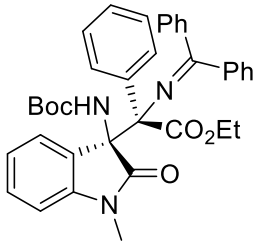
4g

Methyl (*R)-2-((*S**)-3-((*tert*-butoxycarbonyl)amino)-1-methyl-2-oxoindolin-3-yl)-2-(3,4-dichlorophenyl)-2-((diphenylmethylene)amino)acetate (4g).** 112.0 mg, 85%. Yellow solid; mp = 141.1-142.9 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 1H), 7.79 – 7.71 (m, 2H), 7.60 – 7.53 (m, 1H), 7.52 – 7.45 (m, 2H), 7.33 – 7.27 (m, 1H), 7.26 – 6.99 (comp, 4H), 6.99 – 6.38 (comp, 6H), 6.37 – 6.29 (m, 1H), 3.30 (s, 3H), 2.99 (s, 3H), 1.44 – 0.96 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 173.6, 168.4, 154.3, 143.1, 140.9, 137.0, 135.7, 131.6, 131.4, 130.2, 129.6, 129.4, 129.2, 128.8, 128.5, 127.6, 127.4, 125.1, 122.4, 107.3, 80.2, 74.9, 69.8, 52.5, 28.2, 26.0; HRMS (TOF MS ESI$^+$) calculated for $C_{36}H_{34}Cl_2N_3O_5$ $[M+H]^+$: 658.1870, found 658.1871.



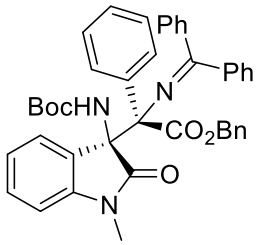
4h

Methyl (*R)-2-((*S**)-3-((*tert*-butoxycarbonyl)amino)-1-methyl-2-oxoindolin-3-yl)-2-((diphenylmethylene)amino)-2-(naphthalen-2-yl)acetate (4h).** 102.3 mg, 80%. Yellow solid; mp = 137.2-138.9 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 1H), 7.86 – 7.80 (m, 2H), 7.73 – 7.54 (comp, 3H), 7.53 – 7.31 (comp, 5H), 7.23 – 7.18 (m, 1H), 7.16 – 6.91 (comp, 3H), 6.89 – 6.50 (comp, 5H), 6.01 – 5.91 (m, 1H), 3.32 (s, 3H), 2.84 (s, 3H), 1.34 – 1.05 (comp, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 172.8, 169.1, 154.4, 143.2, 141.3, 136.0, 132.1, 131.7, 131.1, 129.6, 129.1, 128.9, 128.7, 128.6, 128.5, 128.4, 127.4, 127.1, 126.3, 125.6, 125.1, 124.7, 122.0, 106.9, 79.9, 75.8, 70.1, 52.3, 28.2, 25.9; HRMS (TOF MS ESI$^+$) calculated for $C_{40}H_{38}N_3O_5$ $[M+H]^+$: 640.2806, found 640.2801.



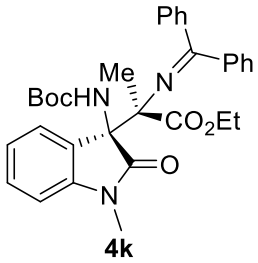
4i

Ethyl (*R)-2-((*S**)-3-((*tert*-butoxycarbonyl)amino)-1-methyl-2-oxoindolin-3-yl)-2-((diphenylmethylene)amino)-2-phenylacetate (4i).** 101.8 mg, 84%. Yellow solid; mp = 172.1-173.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 1H), 7.83 – 7.74 (m, 2H), 7.57 – 7.52 (m, 1H), 7.51 – 7.45 (m, 2H), 7.25 – 7.21 (m, 1H), 7.14 – 7.09 (m, 2H), 7.08 – 6.95 (comp, 3H), 6.95 – 6.83 (comp, 3H), 6.81 – 6.64 (comp, 3H), 6.25 – 6.13 (m, 1H), 3.79 – 3.55 (m, 2H), 2.91 (s, 3H), 1.46 – 0.97 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 172.3, 168.5, 154.4, 143.3, 141.3, 136.9, 136.1, 131.0, 129.5, 129.4, 129.0, 128.6, 128.4, 127.4, 127.3, 125.7, 125.2, 122.0, 106.9, 79.8, 75.6, 70.0, 61.6, 28.3, 25.8, 13.7; HRMS (TOF MS ESI$^+$) calculated for $C_{37}H_{38}N_3O_5$ $[M+H]^+$: 604.2806, found 604.2803.



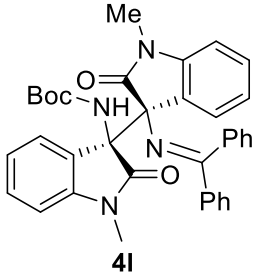
4j

Benzyl (*R)-2-((*S**)-3-((*tert*-butoxycarbonyl)amino)-1-methyl-2-oxoindolin-3-yl)-2-((diphenylmethylene)amino)-2-phenylacetate (4j).** 115.3 mg, 87%. Yellow solid; mp = 175.2-176.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.73 (m, 2H), 7.45 – 7.32 (comp, 5H), 7.29 – 7.25 (m, 2H), 7.23 – 7.14 (m, 2H), 7.11 – 6.87 (comp, 6H), 6.83 – 6.58 (comp, 3H), 6.46 – 6.20 (m, 1H), 6.18 – 5.59 (m, 2H), 5.33 – 4.82 (m, 1H), 4.69 – 4.35 (m, 1H), 2.51 (s, 3H), 1.61 – 0.93 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 173.7, 172.6, 155.0, 143.4, 143.0, 139.9, 135.9, 131.0, 129.3, 129.2, 129.0, 128.7, 128.3, 127.9, 127.7, 127.4, 127.0, 124.9, 123.2, 122.1, 121.6, 108.1, 107.4, 80.0, 71.3, 65.6, 44.2, 28.3, 25.3; HRMS (TOF MS ESI$^+$) calculated for $C_{42}H_{40}N_3O_5$ $[M+H]^+$: 666.2962, found 666.2965.



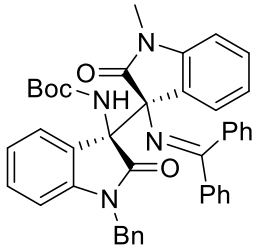
4k

Ethyl (*R)-2-((*S**)-3-((*tert*-butoxycarbonyl)amino)-1-methyl-2-oxoindolin-3-yl)-2-((diphenylmethylene)amino)propanoate (4k).** 98.4 mg, 91%. Yellow solid; mp = 163.1-164.7 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.46 (m, 2H), 7.44 – 7.30 (comp, 6H), 7.28 – 7.19 (m, 2H), 7.12 – 7.01 (m, 2H), 7.00 – 6.89 (m, 1H), 6.84 – 6.70 (m, 1H), 6.68 – 6.27 (m, 1H), 4.01 – 3.57 (m, 2H), 3.21 (s, 3H), 1.42 – 0.91 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.8, 170.8, 169.1, 154.8, 144.9, 140.8, 137.5, 130.6, 129.1, 128.9, 128.6, 128.5, 128.1, 127.9, 124.1, 122.0, 107.4, 80.1, 70.7, 67.2, 61.4, 28.2, 26.4, 19.4, 13.7; HRMS (TOF MS ESI$^+$) calculated for $C_{32}H_{36}N_3O_5$ $[M+H]^+$: 542.2649, found 542.2643.



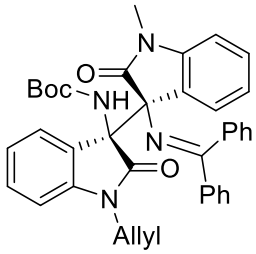
4l

***tert*-Butyl-((3*S**,3'*S**)-3-((diphenylmethylene)amino)-1,1'-dimethyl-2,2'-dioxo-[3,3'-biindolin]-3'-yl)carbamate (4l).** 117.1 mg, 99%. Yellow solid; mp = 203.1-204.5 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.71 (m, 2H), 7.47 – 7.31 (comp, 3H), 7.24 – 6.48 (comp, 11H), 6.41 – 6.27 (m, 1H), 6.21 – 5.62 (m, 2H), 3.06 (s, 3H), 2.54 (s, 3H), 1.59 – 0.95 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 173.6, 172.7, 154.8, 143.8, 143.0, 139.9, 136.1, 131.0, 129.3, 129.2, 129.0, 128.2, 127.7, 127.0, 124.3, 122.8, 121.8, 121.4, 107.4, 107.0, 79.9, 71.2, 65.8, 28.3, 25.8, 25.2; HRMS (TOF MS ESI$^+$) calculated for $C_{36}H_{35}N_4O_4$ $[M+H]^+$: 587.2653, found 587.2655.



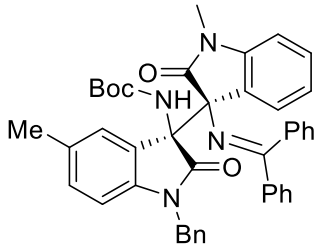
5a

***tert*-Butyl-((3*S**,3'*S**)-1'-benzyl-3-((diphenylmethylene)amino)-1-methyl-2,2'-dioxo-[3,3'-biindolin]-3'-yl)carbamate (5a).** 116.4 mg, 88%. Yellow solid; mp = 201.1-202.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.73 (m, 2H), 7.45 – 7.39 (m, 1H), 7.39 – 7.31 (comp, 4H), 7.30 – 7.10 (comp, 5H), 7.10 – 6.84 (comp, 6H), 6.83 – 6.56 (comp, 3H), 6.46 – 6.19 (m, 1H), 6.20 – 5.66 (m, 2H), 5.07 (s, 1H), 4.56 (s, 1H), 2.51 (s, 3H), 1.59 – 0.94 (M, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 173.7, 172.6, 155.0, 143.4, 143.0, 139.9, 135.9, 131.0, 129.3, 129.2, 129.0, 128.7, 128.3, 127.9, 127.7, 127.4, 127.0, 124.9, 123.2, 122.1, 121.6, 108.1, 107.4, 80.0, 71.3, 65.6, 44.2, 28.3, 25.3; HRMS (TOF MS ESI$^+$) calculated for $C_{42}H_{39}N_4O_4$ $[M+H]^+$: 663.2966, found 663.2960.



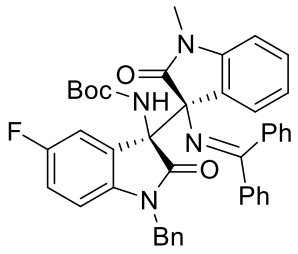
5b

***tert*-Butyl-((3*S**,3'*S**)-1'-allyl-3-((diphenylmethylene)amino)-1-methyl-2,2'-dioxo-[3,3'-biindolin]-3'-yl)carbamate (5b).** 120.1 mg, 98%. Yellow solid; mp = 201.3-202.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.72 (m, 2H), 7.46 – 7.39 (m, 1H), 7.38 – 7.31 (m, 2H), 7.24 – 7.07 (comp, 3H), 7.06 – 6.83 (comp, 5H), 6.83 – 6.53 (comp, 3H), 6.50 – 6.34 (m, 1H), 6.20 – 5.81 (m, 2H), 5.78 – 5.66 (m, 1H), 5.27 (d, *J* = 10.3 Hz, 1H), 5.15 (d, *J* = 10.3 Hz, 1H), 4.61 – 3.89 (m, 2H), 2.54 (s, 3H), 1.48 – 1.08 (M, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 173.3, 172.6, 154.8, 143.4, 143.0, 139.9, 136.0, 131.7, 131.0, 129.4, 129.2, 128.9, 128.2, 127.7, 127.0, 125.1, 123.2, 122.1, 121.4, 118.0, 108.0, 107.4, 79.9, 71.2, 65.6, 42.8, 28.3, 25.3; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}N_4O_4$ $[M+H]^+$: 613.2809, found 613.2795.



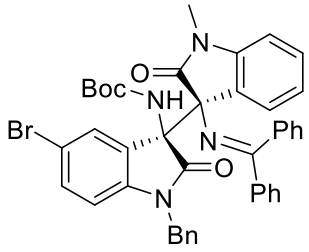
5c

***tert*-Butyl-((3*S**,3'*S**)-1'-benzyl-3-((diphenylmethylene)amino)-1,5'-dimethyl-2,2'-dioxo-[3,3'-biindolin]-3'-yl)carbamate (5c).** 132.1 mg, 97%. Yellow solid; mp = 193.2-194.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.74 (m, 2H), 7.49 – 7.18 (comp, 9H), 7.14 – 6.87 (comp, 6H), 6.83 – 6.53 (comp, 3H), 6.40 – 6.13 (m, 1H), 6.13 – 5.65 (m, 2H), 5.12 (s, 1H), 4.47 (s, 1H), 2.54 (s, 3H), 2.14 (s, 3H), 1.68 – 0.91 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 173.7, 172.6, 155.0, 143.0, 140.9, 140.0, 136.03, 135.99, 131.0, 130.9, 129.2, 128.6, 128.2, 127.9, 127.7, 127.3, 127.0, 124.8, 124.1, 122.0, 107.8, 107.4, 79.9, 71.3, 65.6, 44.1, 28.4, 25.2, 21.1; HRMS (TOF MS ESI$^+$) calculated for $C_{43}H_{41}N_4O_4$ $[M+H]^+$: 677.3122, found 677.3119.



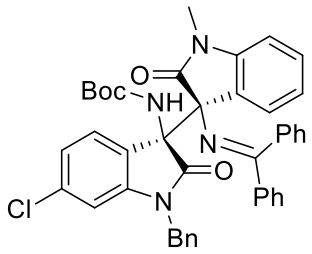
5d

***tert*-Butyl-((3*S**,3'*S**)-1'-benzyl-3-((diphenylmethylene)amino)-5'-fluoro-1-methyl-2,2'-dioxo-[3,3'-biindolin]-3'-yl)carbamate (5d).** 131.2 mg, 96%. Yellow solid; mp = 171.1-172.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.70 (m, 2H), 7.47 – 7.41 (m, 1H), 7.40 – 7.34 (m, 2H), 7.33 – 7.18 (comp, 6H), 7.17 – 7.02 (comp, 3H), 7.00 – 6.85 (comp, 3H), 6.82 – 6.50 (comp, 3H), 6.37 – 6.15 (m, 1H), 6.11 – 5.75 (m, 2H), 5.12 (s, 1H), 4.50 (s, 1H), 2.55 (s, 3H), 1.50 – 1.01 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 173.5, 172.90, 158.8 (d, *J* = 238.8 Hz), 154.9, 142.9, 139.8, 139.4, 135.8, 135.6, 131.1, 129.5, 129.2, 128.7, 128.3, 127.8, 127.7, 127.5, 127.1, 124.9, 122.2, 115.1 (d, *J* = 22.5 Hz), 111.4 (d, *J* = 21.3 Hz), 108.6, 107.6, 80.3, 71.2, 65.8, 44.3, 28.4, 25.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ -121.9; HRMS (TOF MS ESI$^+$) calculated for $C_{42}H_{38}FN_4O_4$ $[M+H]^+$: 681.2872, found 681.2864.



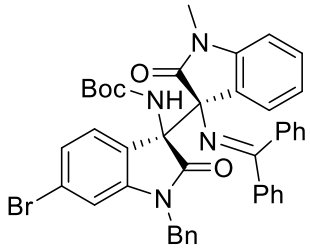
5e

***tert*-Butyl-((3*S**,3'*S**)-1'-benzyl-5'-bromo-3-((diphenylmethylene)amino)-1-methyl-2,2'-dioxo-[3,3'-biindolin]-3'-yl)carbamate (5e).** 142.0 mg, 96%. Yellow solid; mp = 197.1-198.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.72 (m, 2H), 7.46 – 7.41 (m, 1H), 7.40 – 7.12 (comp, 9H), 7.11 – 6.86 (comp, 6H), 6.82 – 6.54 (m, 2H), 6.27 – 6.11 (m, 1H), 6.09 – 5.71 (m, 2H), 5.14 (s, 1H), 4.42 (s, 1H), 2.60 (s, 3H), 1.59 – 1.03 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 173.4, 173.1, 154.9, 142.9, 142.4, 139.8, 135.9, 135.4, 131.6, 131.1, 129.5, 129.2, 128.7, 128.3, 127.9, 127.6, 127.3, 127.0, 126.4, 124.7, 122.1, 114.3, 109.6, 107.7, 80.3, 71.2, 65.6, 44.2, 28.4, 25.3; HRMS (TOF MS ESI$^+$) calculated for $C_{42}H_{38}BrN_4O_4$ $[M+H]^+$: 741.2071, found 741.2062.



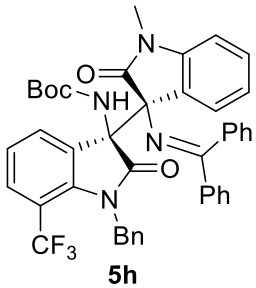
5f

***tert*-Butyl-((3*S**,3'*S**)-1'-benzyl-6'-chloro-3-((diphenylmethylene)amino)-1-methyl-2,2'-dioxo-[3,3'-biindolin]-3'-yl)carbamate (5f).** 138.0 mg, 99%. Yellow solid; mp = 181.1-182.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.70 (m, 2H), 7.50 – 7.40 (m, 1H), 7.39 – 7.17 (comp, 8H), 7.13 – 6.88 (comp, 6H), 6.84 – 6.56 (comp, 3H), 6.43 – 6.20 (m, 1H), 6.15 – 5.74 (m, 2H), 5.05 (s, 1H), 4.52 (s, 1H), 2.52 (s, 3H), 1.57 – 1.02 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 173.6, 172.9, 154.9, 144.7, 142.9, 139.8, 135.9, 135.3, 134.6, 131.1, 129.6, 129.2, 128.8, 128.3, 127.8, 127.6, 127.5, 127.1, 124.8, 124.2, 122.3, 121.6, 108.8, 107.7, 80.3, 71.1, 65.3, 44.3, 28.4, 25.4; HRMS (TOF MS ESI$^+$) calculated for $C_{42}H_{38}ClN_4O_4$ $[M+H]^+$: 697.2576, found 697.2558.



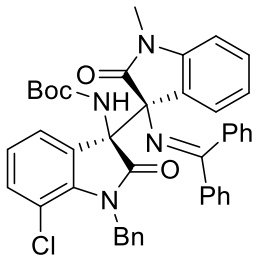
5g

***tert*-Butyl-((3*S**,3'*S**)-1'-benzyl-6'-bromo-3-((diphenylmethylene)amino)-1-methyl-2,2'-dioxo-[3,3'-biindolin]-3'-yl)carbamate (5g).** 146.0 mg, 98%. Yellow solid; mp = 192.1-192.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.67 (m, 2H), 7.49 – 7.18 (comp, 9H), 7.15 – 6.85 (comp, 7H), 6.82 – 6.60 (m, 2H), 6.57 – 6.35 (m, 1H), 6.29 – 5.73 (m, 2H), 5.05 (s, 1H), 4.52 (s, 1H), 2.52 (s, 3H), 1.55 – 1.07 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 173.5, 172.8, 154.9, 144.9, 142.9, 139.8, 135.8, 135.3, 131.1, 129.6, 129.2, 128.8, 128.3, 127.8, 127.6, 127.5, 127.1, 124.8, 124.5, 122.6, 122.3, 111.6, 107.7, 80.3, 71.0, 65.3, 44.3, 28.4, 25.4; HRMS (TOF MS ESI$^+$) calculated for $C_{42}H_{38}BrN_4O_4$ $[M+H]^+$: 741.2071, found 741.2060.



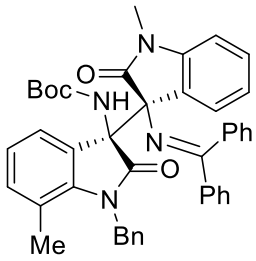
5h

***tert*-Butyl-((3*S**,3'*S**)-1'-benzyl-3-((diphenylmethylene)amino)-1-methyl-2,2'-dioxo-7'-(trifluoromethyl)-[3,3'-biindolin]-3'-yl)carbamate (5h).** 121.8 mg, 83%. Yellow solid; mp = 211.0-212.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.69 (m, 2H), 7.56 – 7.31 (comp, 6H), 7.29 – 7.14 (comp, 5H), 7.13 – 6.94 (comp, 5H), 6.92 – 6.60 (comp, 3H), 6.30 – 5.72 (m, 2H), 5.41 (s, 1H), 4.76 (s, 1H), 2.51 (s, 3H), 1.51 – 1.06 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0, 173.4, 173.1, 155.0, 142.6, 141.3, 139.7, 136.2, 135.9, 131.2, 129.7, 129.2, 128.3, 128.2, 127.9, 127.1, 126.6, 126.3, 124.5, 124.4, 122.2, 120.7, 111.7 (q, *J* = 32.5 Hz), 107.6, 80.4, 71.7, 64.5, 45.9, 28.4, 25.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -54.7; HRMS (TOF MS ESI$^+$) calculated for $C_{43}H_{38}F_3N_4O_4$ $[M+H]^+$: 731.2840, found 731.2839.



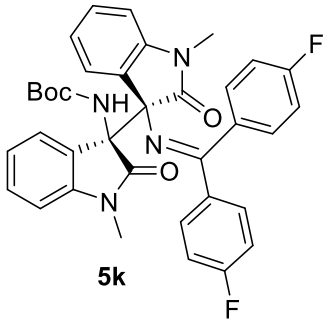
5i

***tert*-Butyl-((3*S**,3'*S**)-1'-benzyl-7'-chloro-3-((diphenylmethylene)amino)-1-methyl-2,2'-dioxo-[3,3'-biindolin]-3'-yl)carbamate (5i).** 123.6 mg, 88%. Yellow solid; mp = 194.2-195.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.70 (m, 2H), 7.57 – 7.24 (comp, 8H), 7.22 – 6.89 (comp, 8H), 6.87 – 6.60 (comp, 3H), 6.36 – 5.72 (m, 2H), 5.45 (s, 1H), 5.00 (d, *J* = 15.9 Hz, 1H), 2.48 (s, 3H), 1.52 – 1.08 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 172.8, 154.9, 142.8, 139.7, 139.4, 137.6, 135.8, 131.6, 131.1, 129.6, 129.1, 128.4, 128.3, 127.9, 127.2, 127.1, 126.9, 124.9, 122.3, 121.8, 114.4, 107.6, 80.3, 71.5, 65.4, 45.3, 28.4, 25.4; HRMS (TOF MS ESI$^+$) calculated for $C_{42}H_{38}ClN_4O_4$ $[M+H]^+$: 697.2576, found 697.2556.



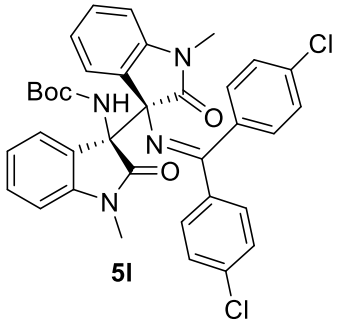
5j

***tert*-Butyl-((3*S**,3'*S**)-1'-benzyl-3-((diphenylmethylene)amino)-1,7'-dimethyl-2,2'-dioxo-[3,3'-biindolin]-3'-yl)carbamate (5j).** 102.7 mg, 75%. Yellow solid; mp = 211.1-212.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.74 (m, 2H), 7.53 – 7.23 (comp, 8H), 7.21 – 7.09 (comp, 3H), 7.07 – 6.92 (comp, 4H), 6.90 – 6.49 (comp, 4H), 6.29 – 5.74 (m, 2H), 5.45 (s, 1H), 4.69 (s, 1H), 2.51 (s, 3H), 1.95 (s, 3H), 1.57 – 0.94 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 173.6, 172.5, 155.1, 143.1, 141.3, 140.0, 137.9, 136.0, 133.0, 131.0, 129.4, 129.2, 128.7, 128.3, 127.8, 127.0, 126.9, 126.4, 124.8, 121.8, 121.6, 121.2, 118.5, 107.5, 80.0, 71.7, 65.3, 45.4, 28.4, 25.4, 18.6; HRMS (TOF MS CI$^+$) calculated for $C_{43}H_{41}N_4O_4$ $[M+H]^+$: 677.3122, found 677.3114.



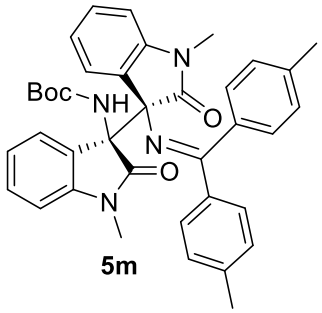
5k

***tert*-Butyl-((3*S**,3'*S**)-3-((bis(4-fluorophenyl)methylene)amino)-1,1'-dimethyl-2,2'-dioxo-[3,3'-biindolin]-3'-yl)carbamate (5k).** 108.0 mg, 87%. Yellow solid; mp = 204.2-205.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.72 (m, 2H), 7.18 – 6.86 (comp, 8H), 6.83 – 6.63 (comp, 3H), 6.54 – 6.28 (m, 2H), 6.14 – 5.75 (m, 2H), 3.07 (s, 3H), 2.62 (s, 3H), 1.44 – 1.06 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 173.5, 170.6, 164.9 (d, *J* = 250.0 Hz), 162.0 (d, *J* = 247.5 Hz), 154.7, 143.7, 142.8, 136.1, 131.9 (d, *J* = 3.8 Hz), 131.4 (d, *J* = 10.0 Hz), 129.9, 129.6, 129.2, 127.5, 124.2, 122.7, 121.9, 121.4, 115.3 (d, *J* = 21.3 Hz), 114.2 (d, *J* = 21.3 Hz), 107.5, 107.2, 80.0, 71.1, 65.8, 28.3, 25.8, 25.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ -109.4, -112.5; HRMS (TOF MS ESI$^+$) calculated for $C_{36}H_{33}F_2N_4O_4$ $[M+H]^+$: 623.2464, found 623.2446.



5l

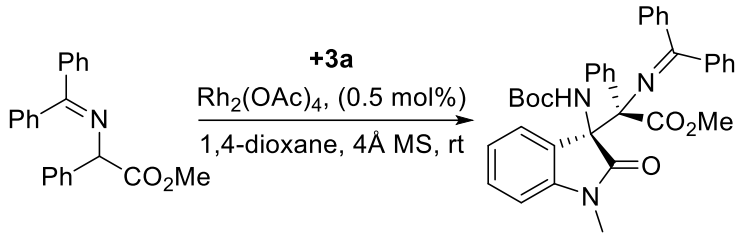
***tert*-Butyl-((3*S**,3'*S**)-3-((bis(4-chlorophenyl)methylene)amino)-1,1'-dimethyl-2,2'-dioxo-[3,3'-biindolin]-3'-yl)carbamate (5l).** 120.9 mg, 92%. Yellow solid; mp = 195.2-196.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.64 (m, 2H), 7.39 – 7.30 (m, 2H), 7.25 – 6.88 (comp, 6H), 6.86 – 6.49 (comp, 4H), 6.41 – 6.28 (m, 1H), 6.07 – 6.00 (m, 1H), 5.99 – 5.69 (m, 1H), 3.07 (s, 3H), 2.60 (s, 3H), 1.45 – 1.01 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 173.4, 170.4, 154.7, 143.7, 142.9, 138.0, 137.6, 134.2, 134.1, 130.5, 129.7, 129.2, 128.6, 127.4, 127.3, 124.3, 122.7, 122.0, 121.5, 107.5, 107.2, 80.1, 71.1, 65.7, 28.3, 25.9, 25.2; HRMS (TOF MS ESI$^+$) calculated for $C_{36}H_{33}Cl_2N_4O_4$ $[M+H]^+$: 655.1873, found 655.1858.



5m

***tert*-Butyl-((3*S**,3'*S**)-3-((di-*p*-tolylmethylene)amino)-1,1'-dimethyl-2,2'-dioxo-[3, 3'-biindolin]-3'-yl)carbamate (5m).** 104.5 mg, 85%. Yellow solid; mp = 184.2-185.6 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.58 (m, 2H), 7.22 – 7.04 (comp, 4H), 7.03 – 6.83 (comp, 4H), 6.82 – 6.13 (comp, 5H), 6.11 – 5.66 (m, 2H), 3.06 (s, 3H), 2.53 (s, 3H), 2.36 (s, 3H), 2.18 (s, 3H), 1.42 – 0.99 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 173.6, 172.8, 154.9, 143.8, 143.0, 141.2, 137.6, 137.3, 133.5, 129.3, 129.2, 129.0, 128.9, 128.0, 127.4, 124.4, 122.9, 121.7, 121.3, 107.2, 107.0, 79.8, 71.2, 65.8, 28.3, 25.8, 25.1, 21.6, 21.2; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{39}N_4O_4$ $[M+H]^+$: 615.2966, found 615.2950.

Control Experiment



6a **4a**, Not observed

To a 10-mL oven-dried vial containing a magnetic stirring bar, **3a** (26.0 mg, 0.10 mmol), 4Å MS (25.0 mg) and $Rh_2(OAc)_4$ (0.2 mg, 0.5 mol%) in 1.4-dioxane (2.0 mL), was added compound **6a** (39.5 mg, 0.12 mmol) in 1,4-dioxane (1.0 mL) at room temperature under argon atmosphere. The resulting reaction mixture was stirred at room temperature for 36 h. Then the reaction mixture was subjected to proton NMR analysis in $CDCl_3$ after the solvent was evaporated, and **4a** was not observed (see Figure S1, the second spectrum).

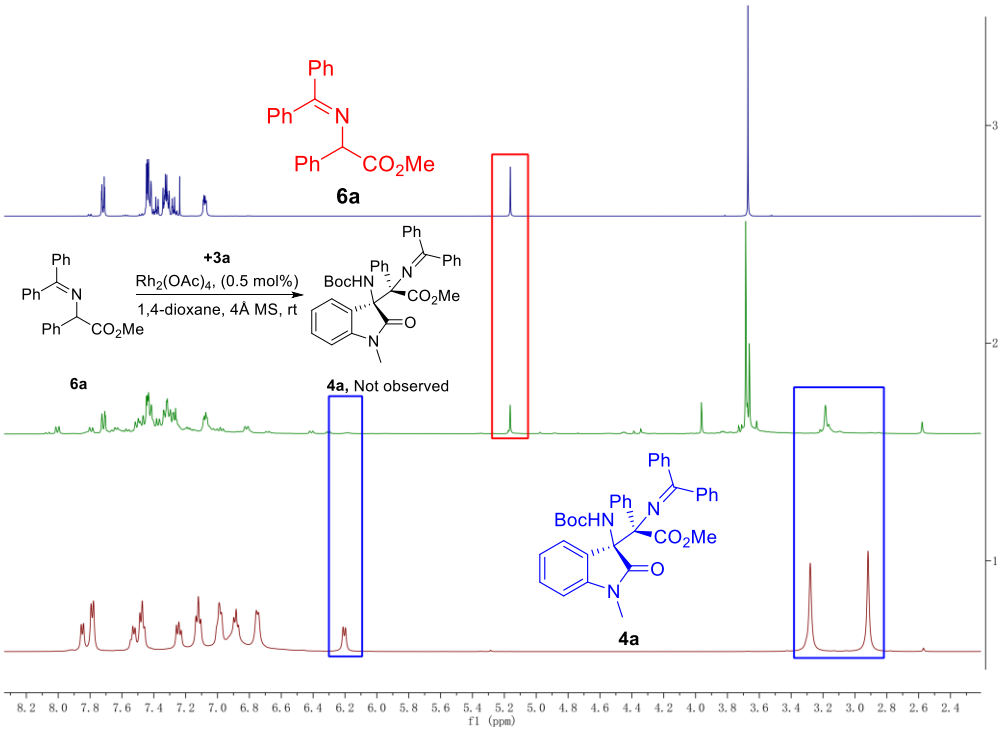
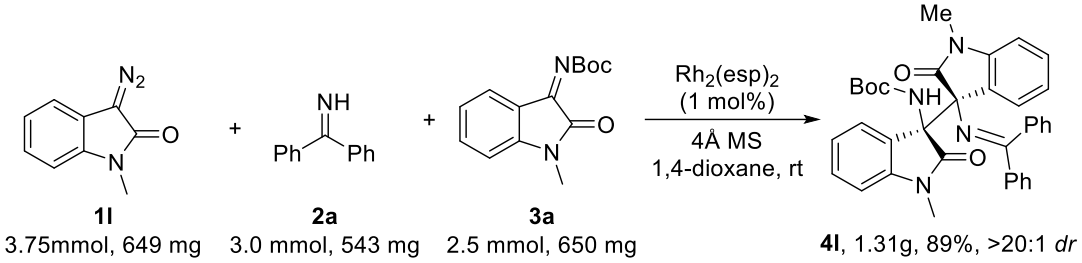


Figure S1. Proton NMR spectrum of crude reaction mixture of **6a** with **3a** under standard conditions

General Procedure for Scale Up



1l
3.75mmol, 649 mg

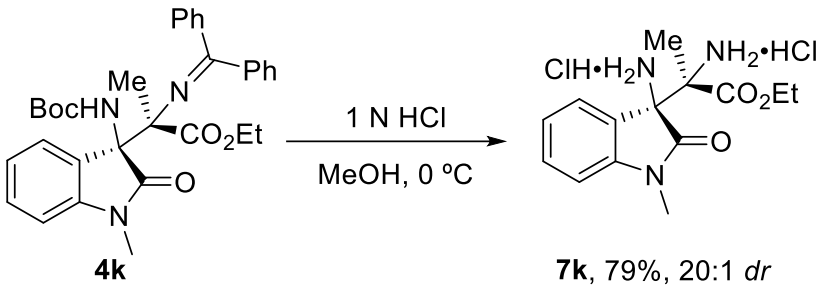
2a
3.0 mmol, 543 mg

3a
2.5 mmol, 650 mg

4l, 1.31g, 89%, >20:1 *dr*

To a 50-mL oven-dried round-bottom flask with a magnetic stirring bar, $Rh_2(esp)_2$ (19.1 mg, 1.0 mol%), 4Å MS (250.0 mg), benzophenone imines **2a** (543.3 mg, 3.0 mmol) and isatin-derived ketimines **3a** (650.3 mg, 2.5 mmol) in 1.4-dioxane (15.0 mL), was added diazo compound **1l** (648.9 mg, 3.75 mmol) in 1.4-dioxane (10.0 mL) *via* a syringe pump for 2 h at room temperature under argon atmosphere. The resulting reaction mixture was stirred at room temperature for 48 h. When the reaction was completed (monitored by TLC), the solvent was evaporated in *vacuo* and the residue was purified by flash column chromatography on silica gel with additional treatment (Hexanes: EtOAc = 5:1 to 3:1) to afford 1.31 g pure product **4l** in 89% yield with >20:1 *dr*.

Derivatization



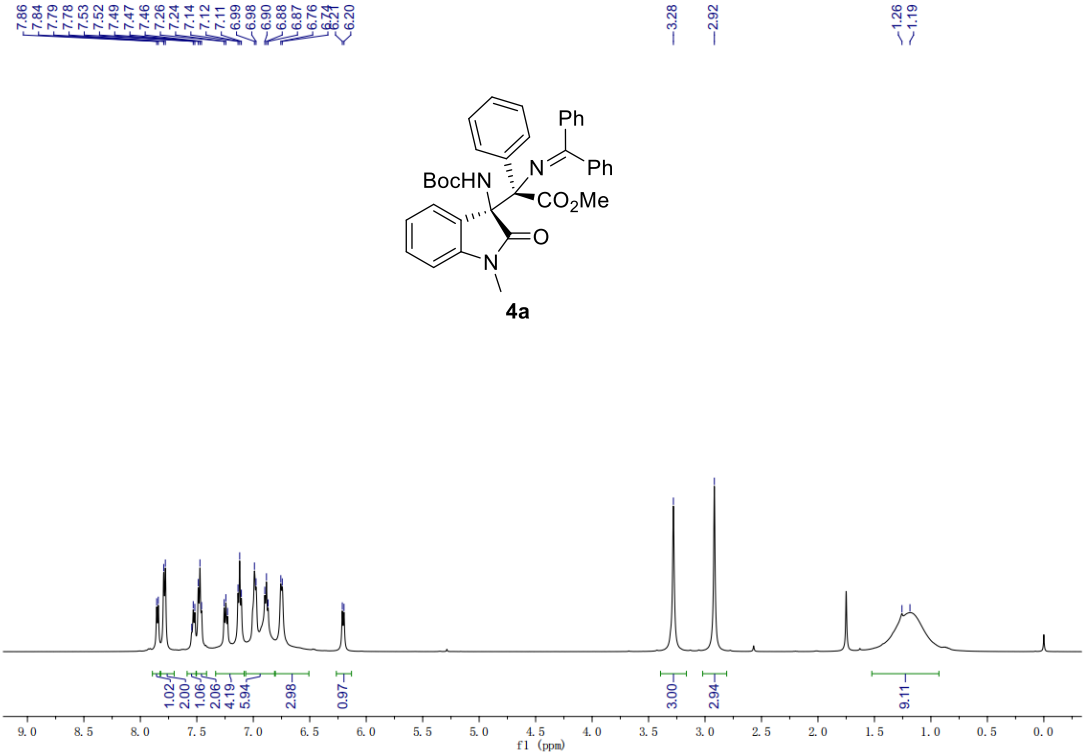
Synthesis of 7k: To a 10-mL oven-dried vial with a magnetic stirring bar, **4k** (74.0 mg, 0.14 mmol) in MeOH (3.0 mL), was added 1 N HCl (0.5 mL) slowly at 0 ℃. Then the reaction solution was stirred for 3 minutes at 0 ºC. After the completion of the reaction (monitored by TLC), the reaction solution was evaporated in vacuo and the residue was filtered off and washed twice with methanol to give 38.0 mg of pure product **7k** as white solid, 79% yield; ^{1}H NMR (500 MHz, DMSO) δ 7.71 – 7.66 (m, 1H), 7.54 – 7.49 (m, 1H), 7.23 – 7.15 (m, 2H), 4.21 – 4.11 (m, 2H), 3.16 (s, 3H), 1.62 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, DMSO) δ 170.5, 167.1, 144.0, 131.8, 128.7, 126.8, 123.1, 109.8, 63.5, 62.5, 61.8, 26.9, 17.8, 13.6; HRMS (TOF MS ESI^{+}) calculated for $C_{14}H_{20}N_3O_3$ $[M+H]^{+}$: 278.1499, found 278.1507.

References:

1 J. Yang, P. Ruan, W. Yang, X. Feng and X. Liu, Enantioselective carbene insertion into the N-H bond of benzophenone imine. *Chem. Sci.*, 2019, **10**, 10305-10309.

2 R. He, Z. Huang, Q. Zheng and C. Wang, Manganese-catalyzed dehydrogenative [4+2] annulation of N-H imines and alkynes by C-H/N-H activation. *Angew. Chem. Int. Ed.*, 2014, **53**, 4950-4953.

3 W. Yan, D. Wang, J. Feng, P. Li, D. Zhao and R. Wang, Synthesis of *N*-alkoxycarbonyl ketimines derived from isatins and their application in enantioselective synthesis of 3-aminooxindoles. *Org. Lett.*, 2012, **14**, 2512-2515.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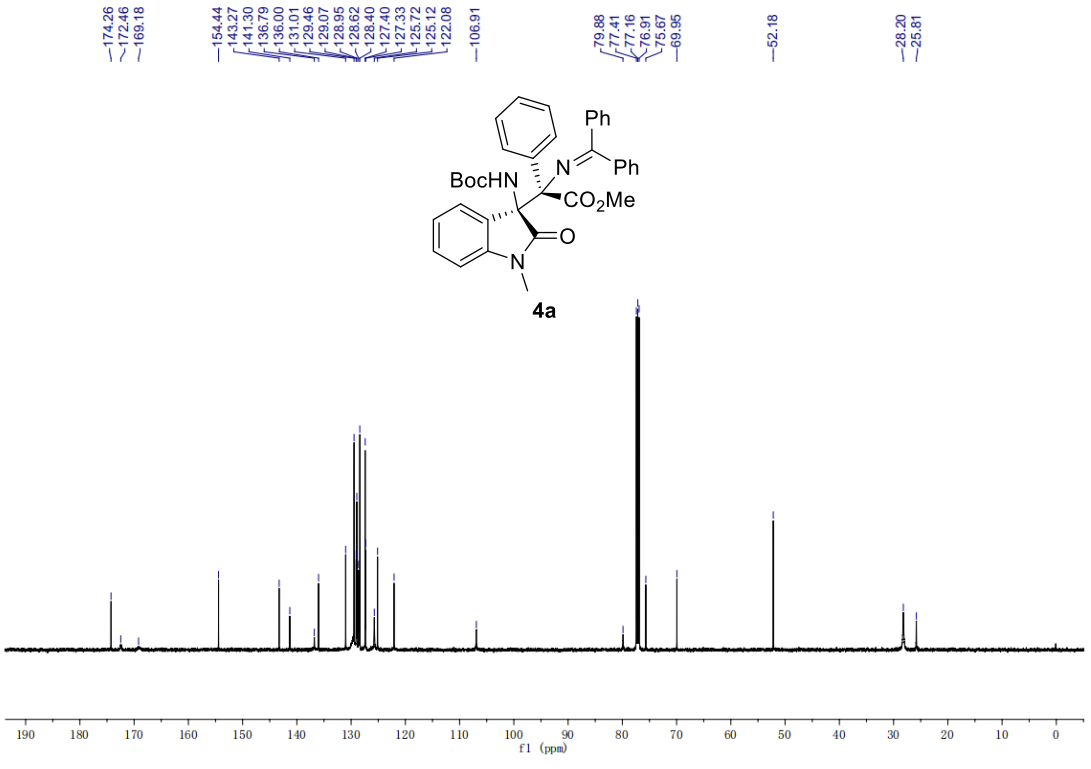
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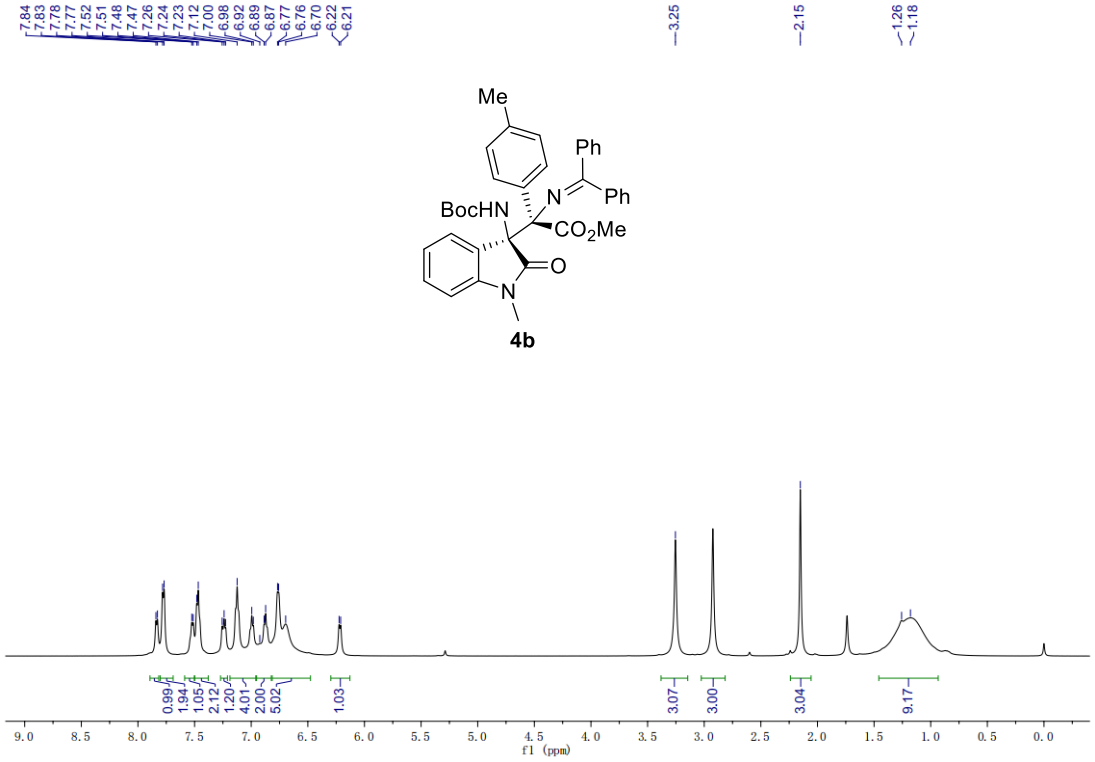
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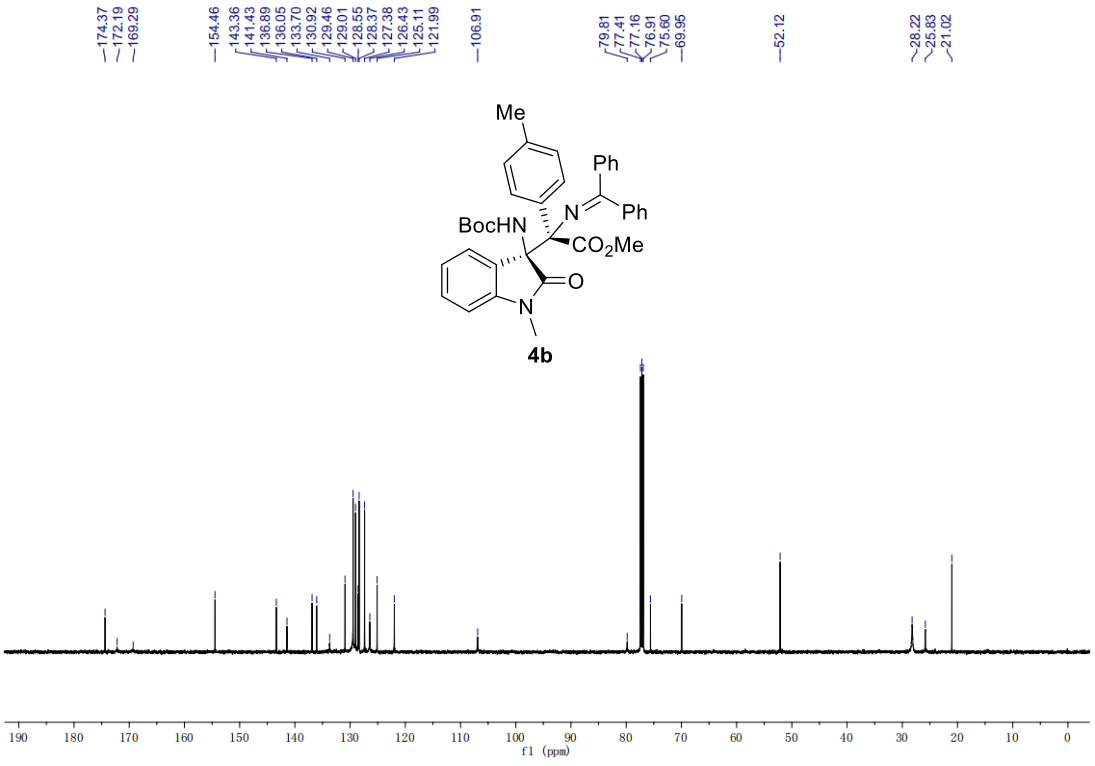
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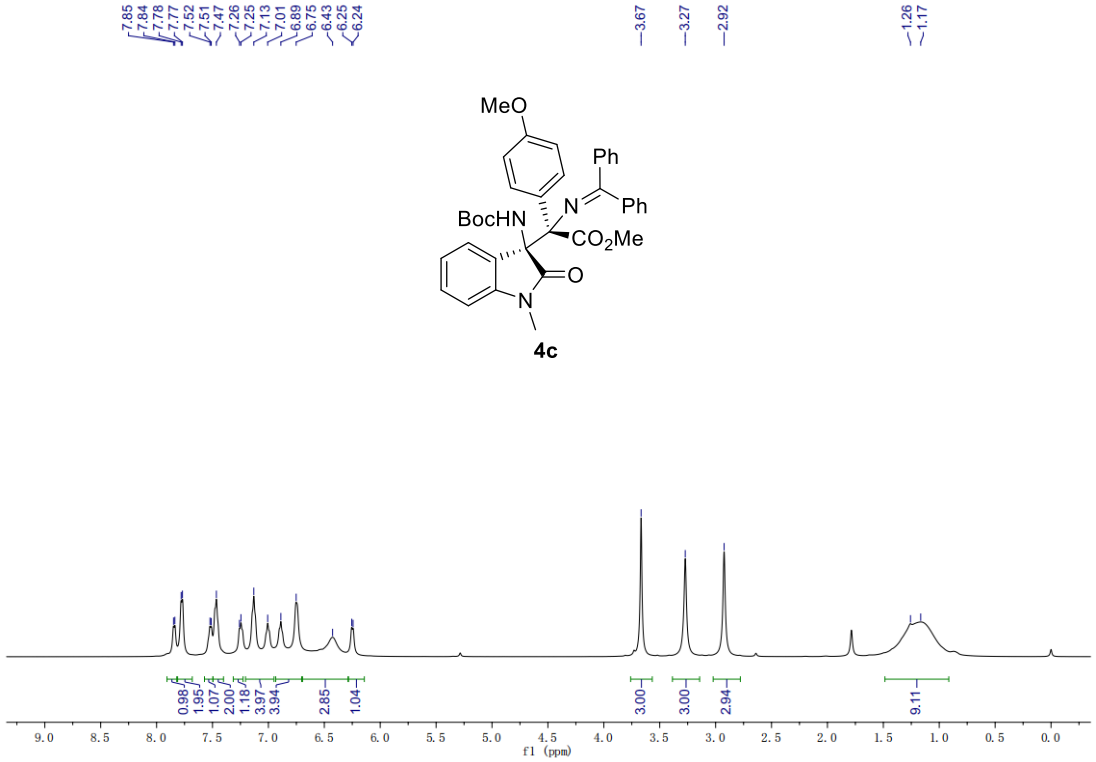
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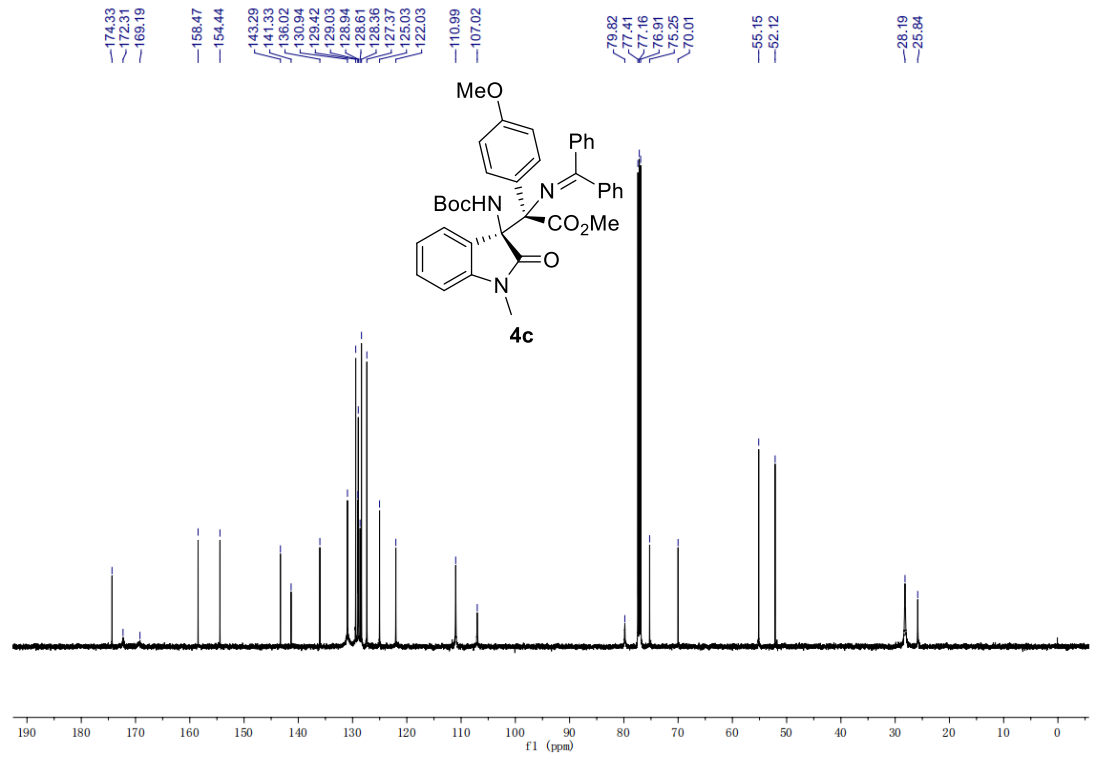
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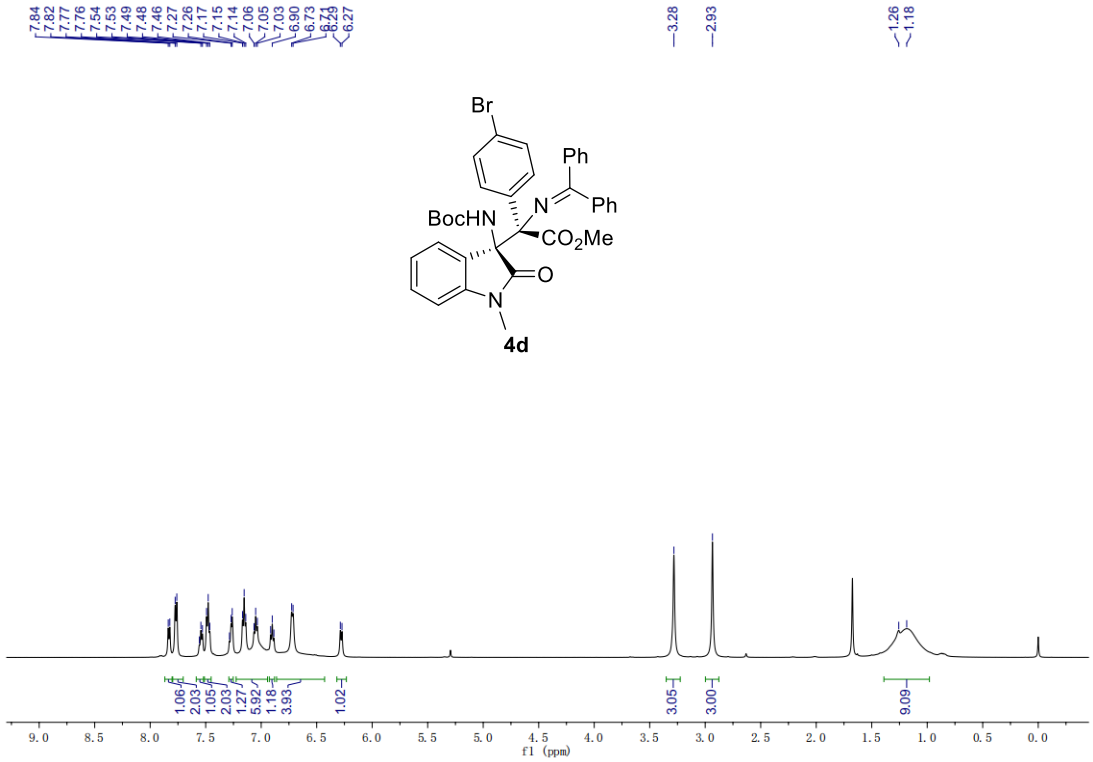
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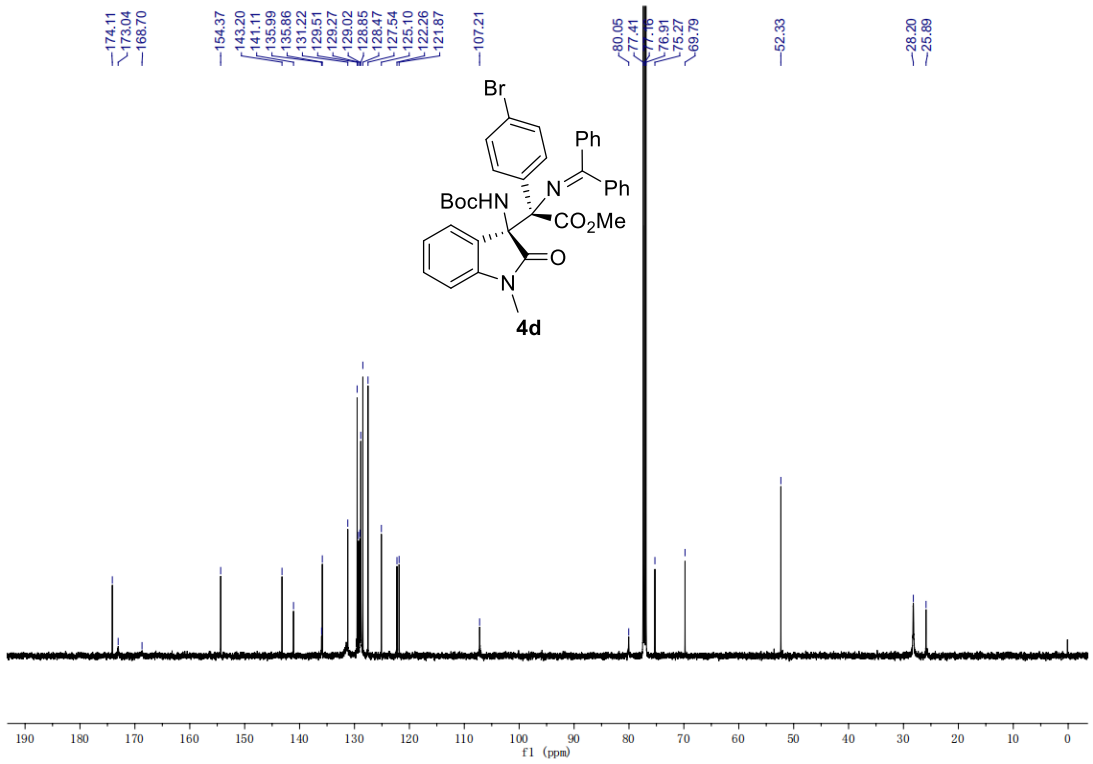
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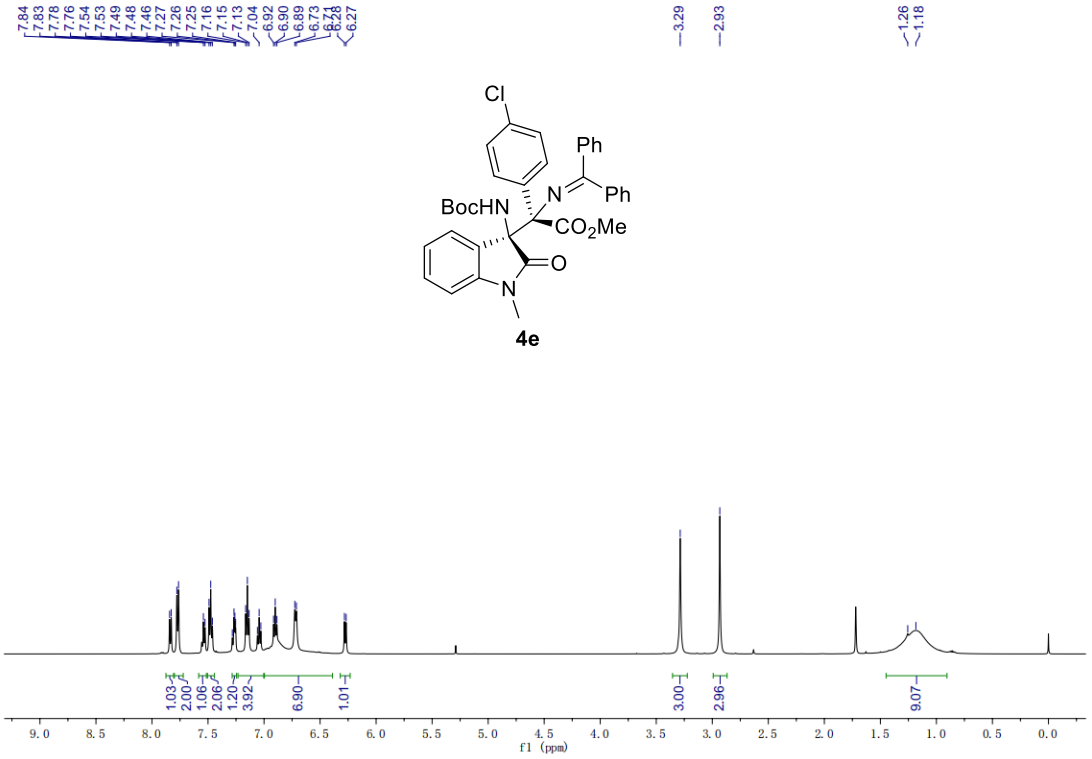
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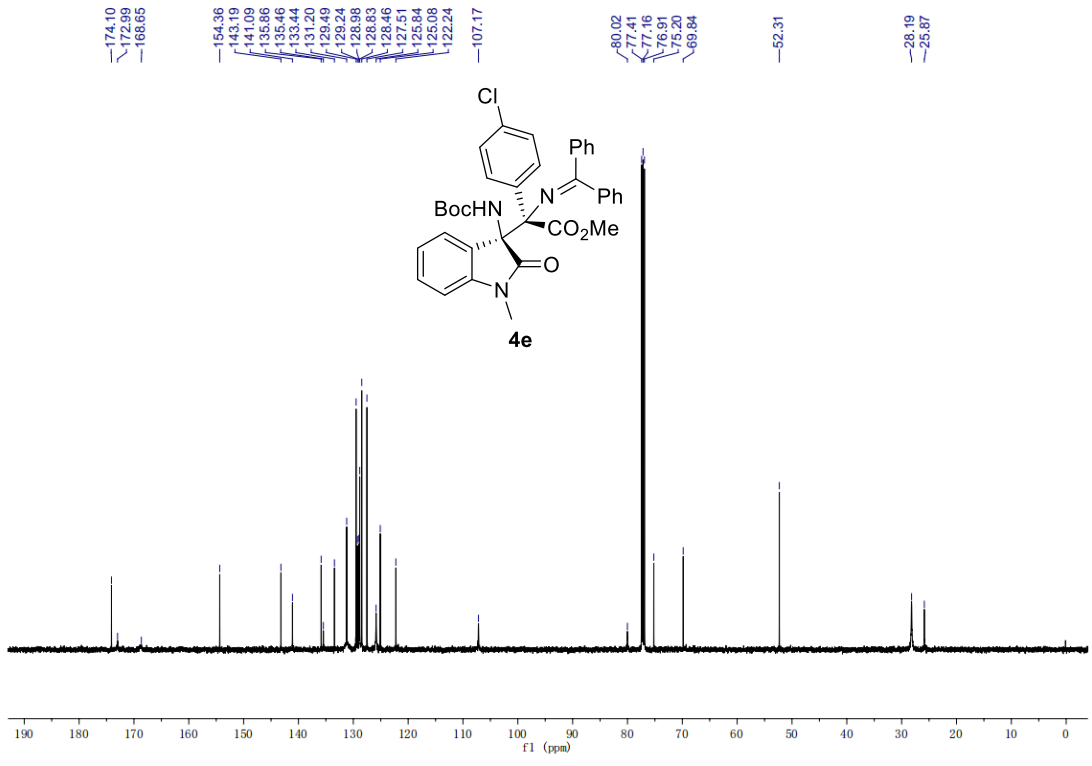
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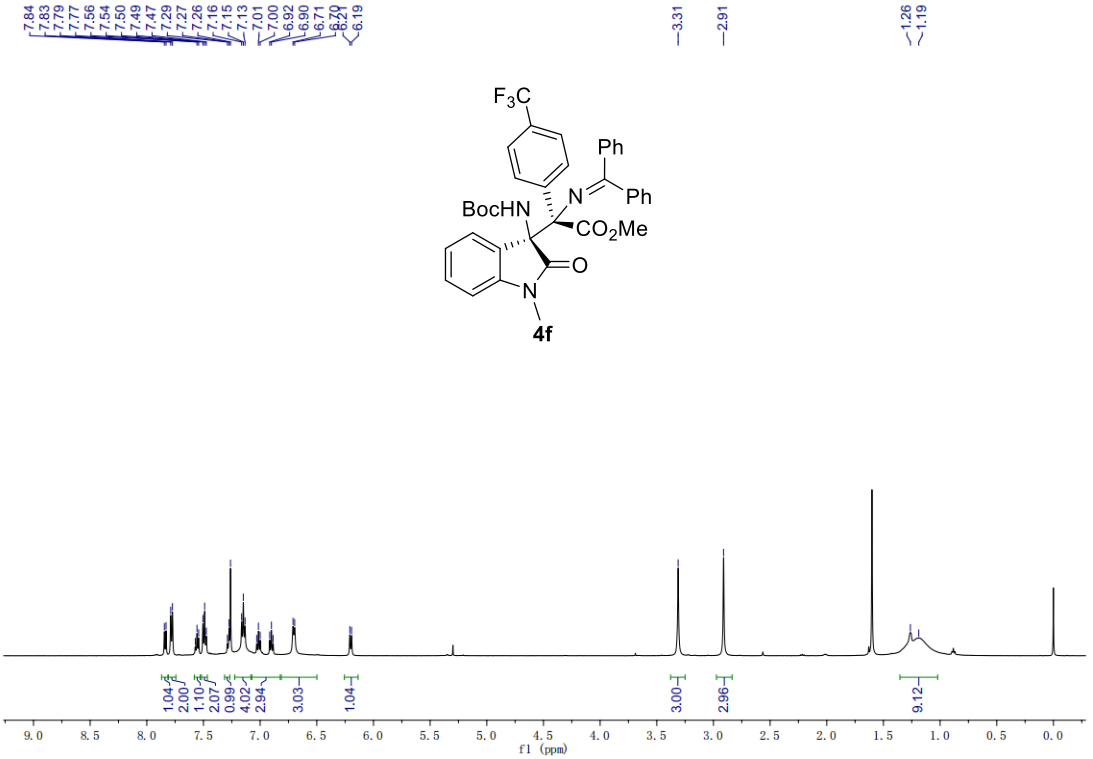
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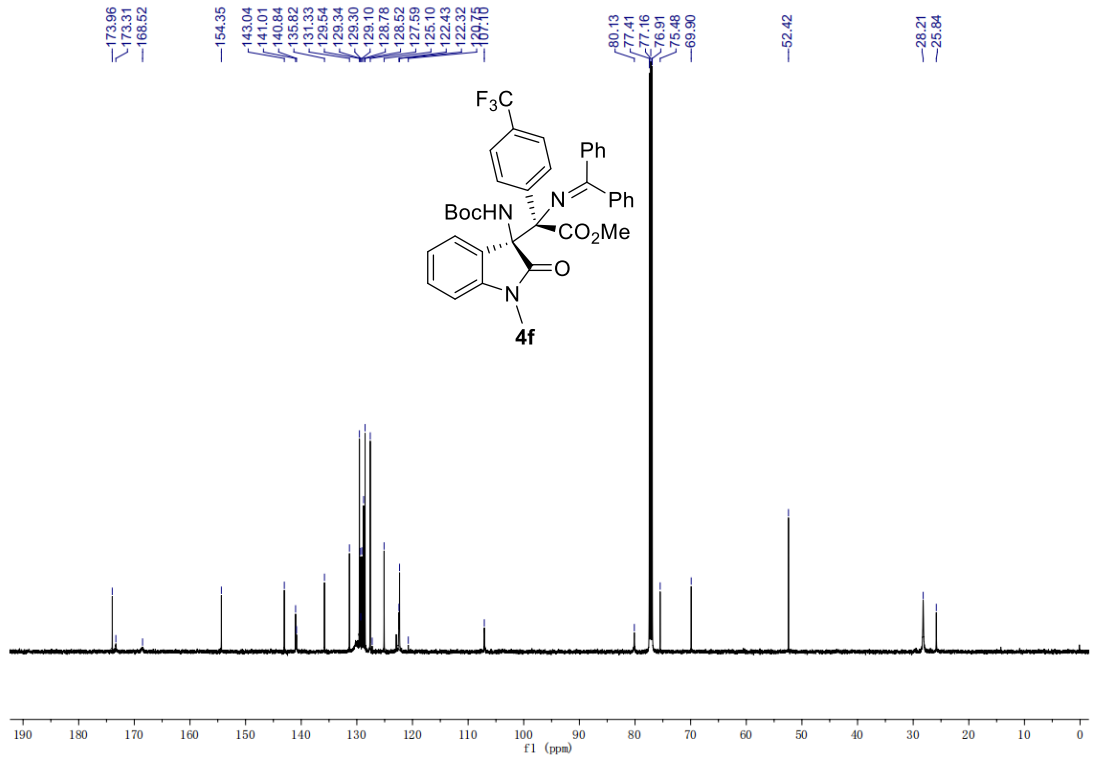
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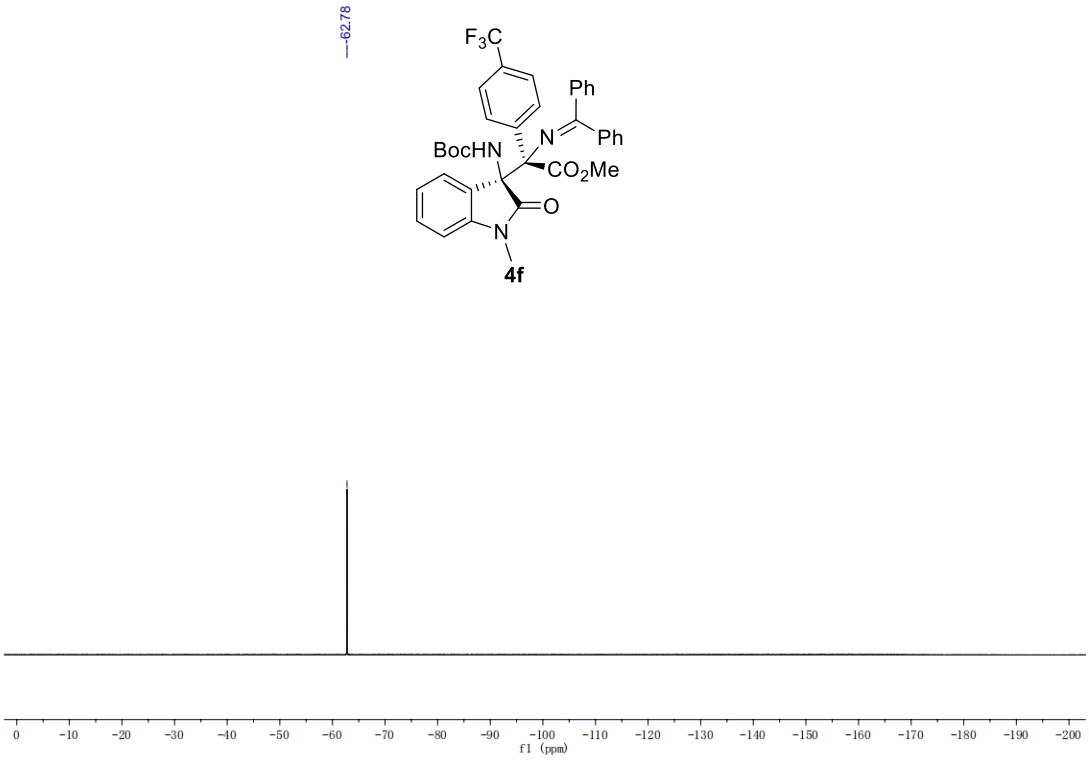
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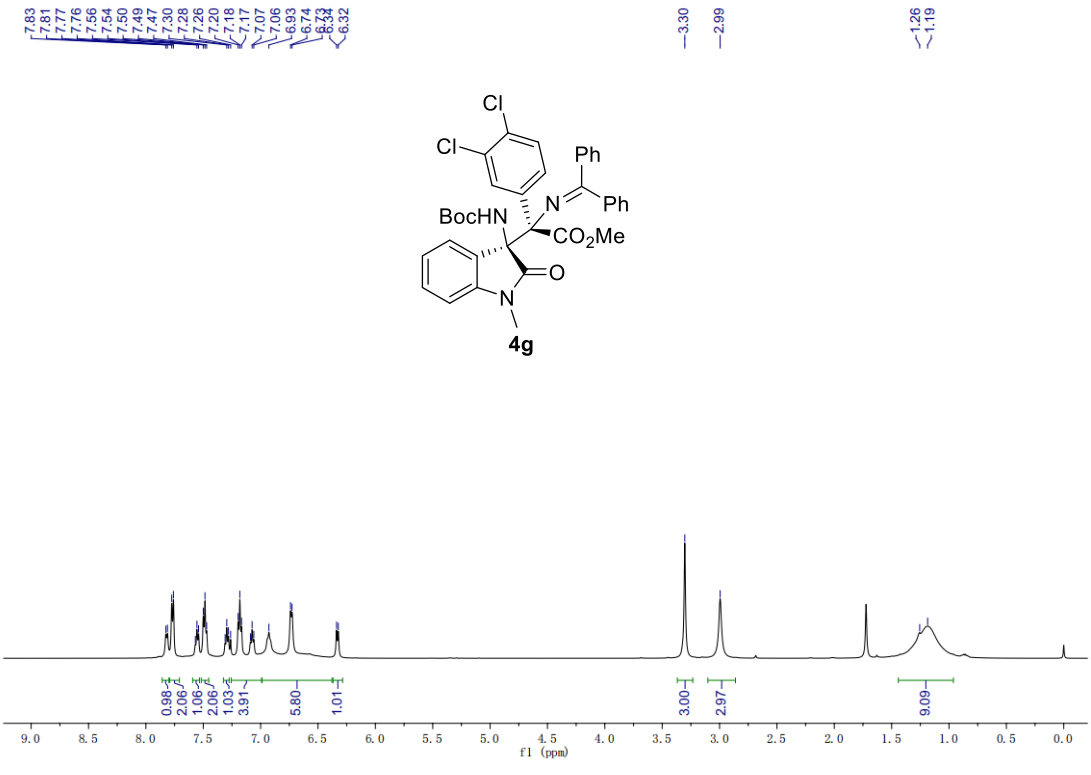
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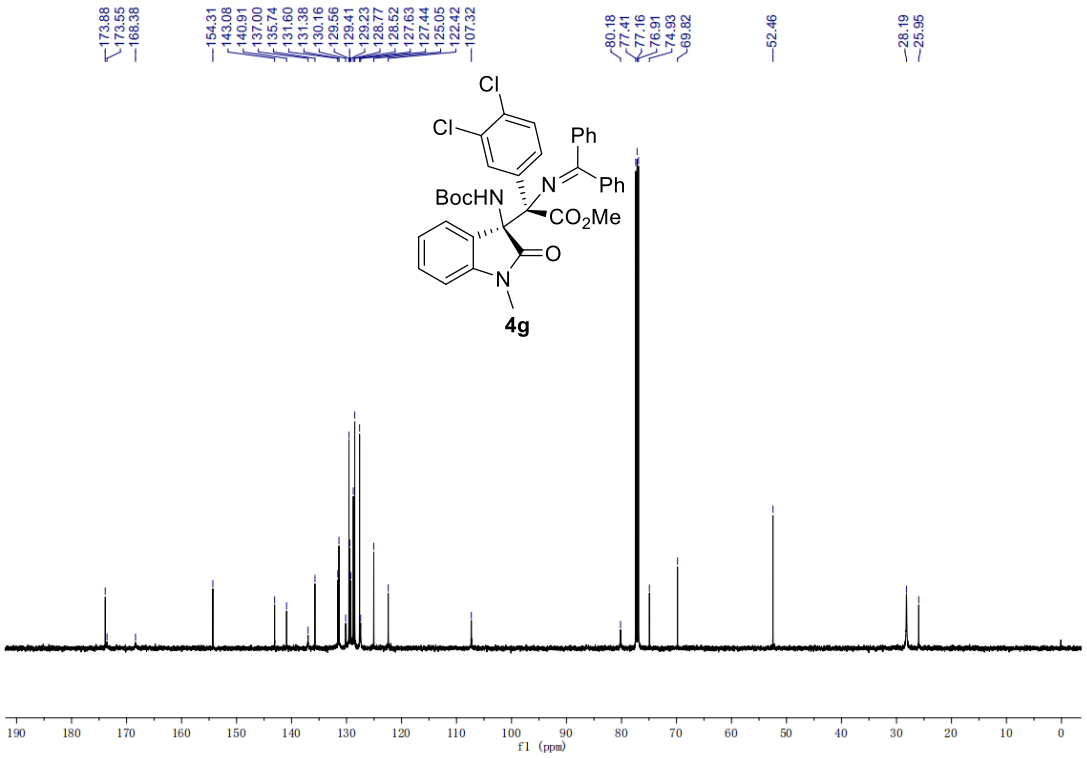
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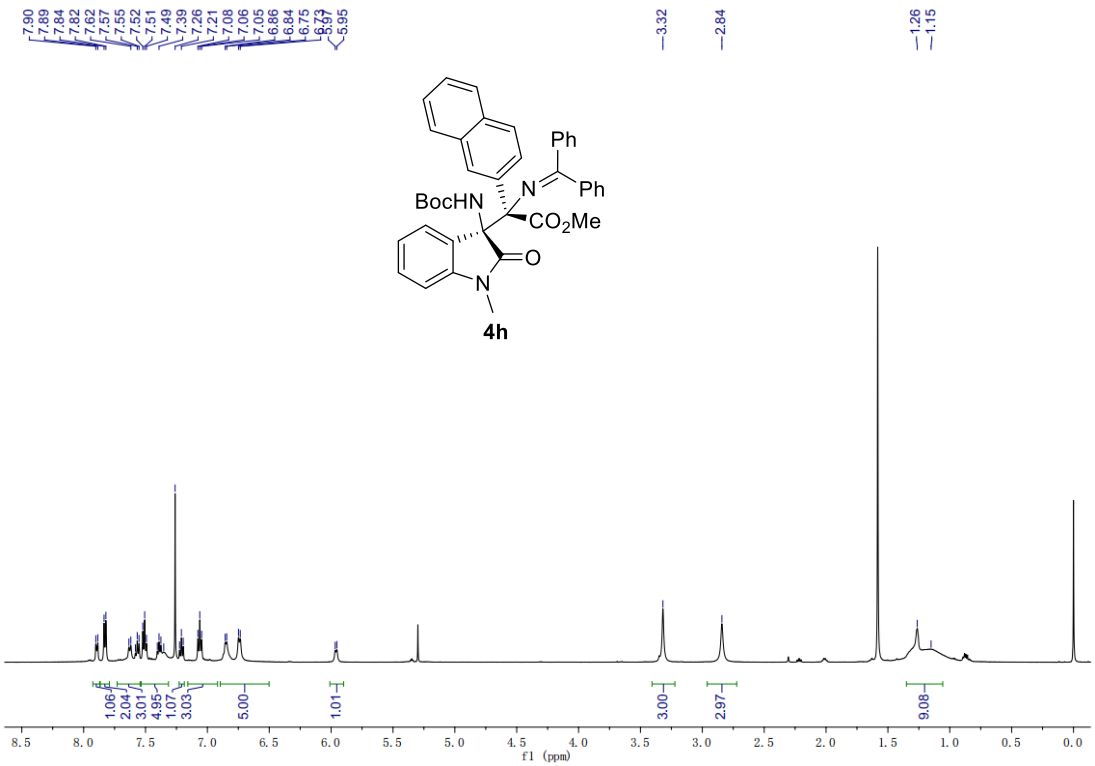
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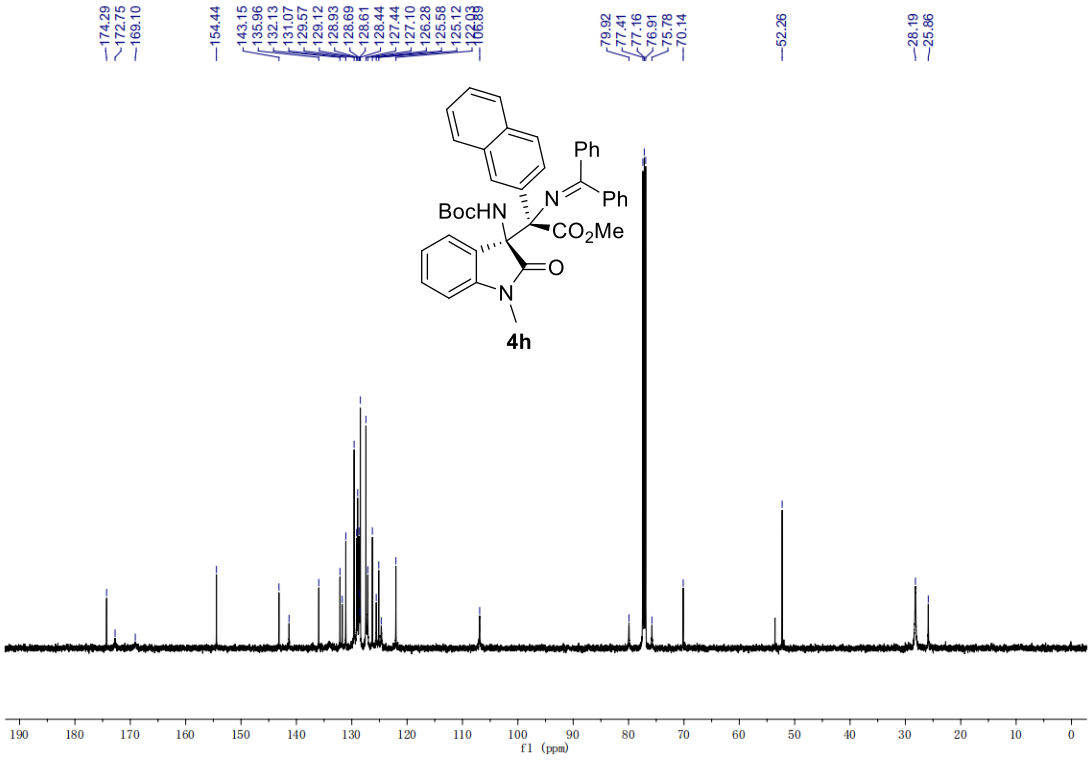
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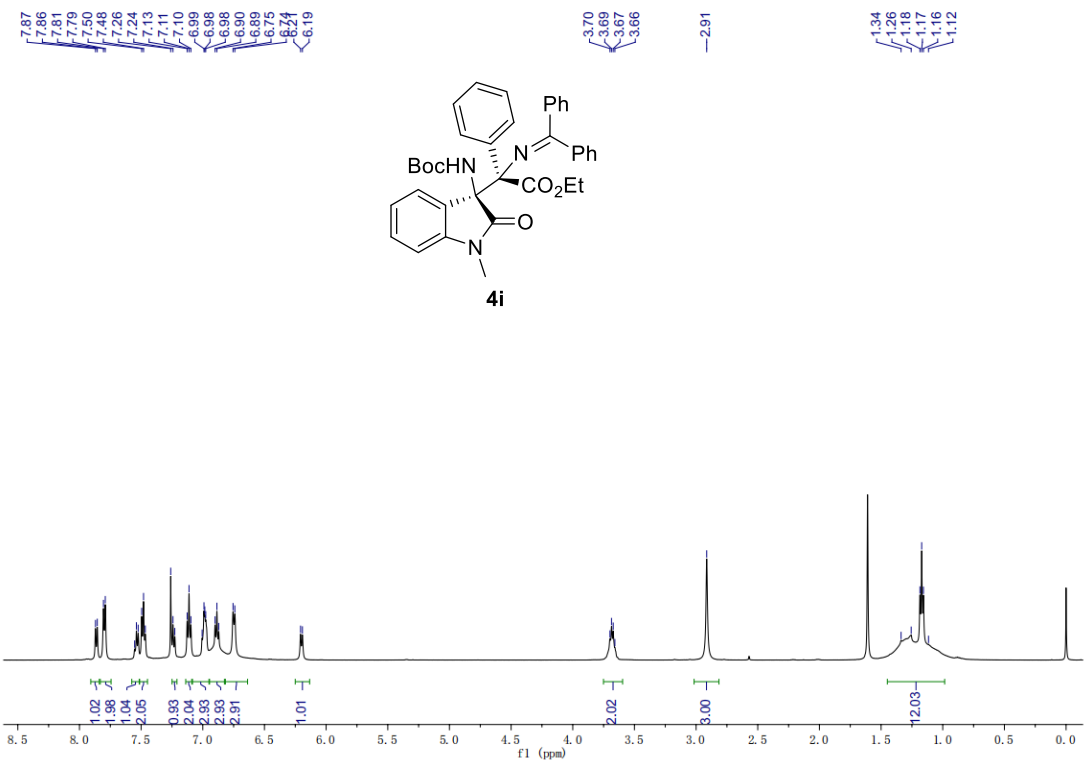
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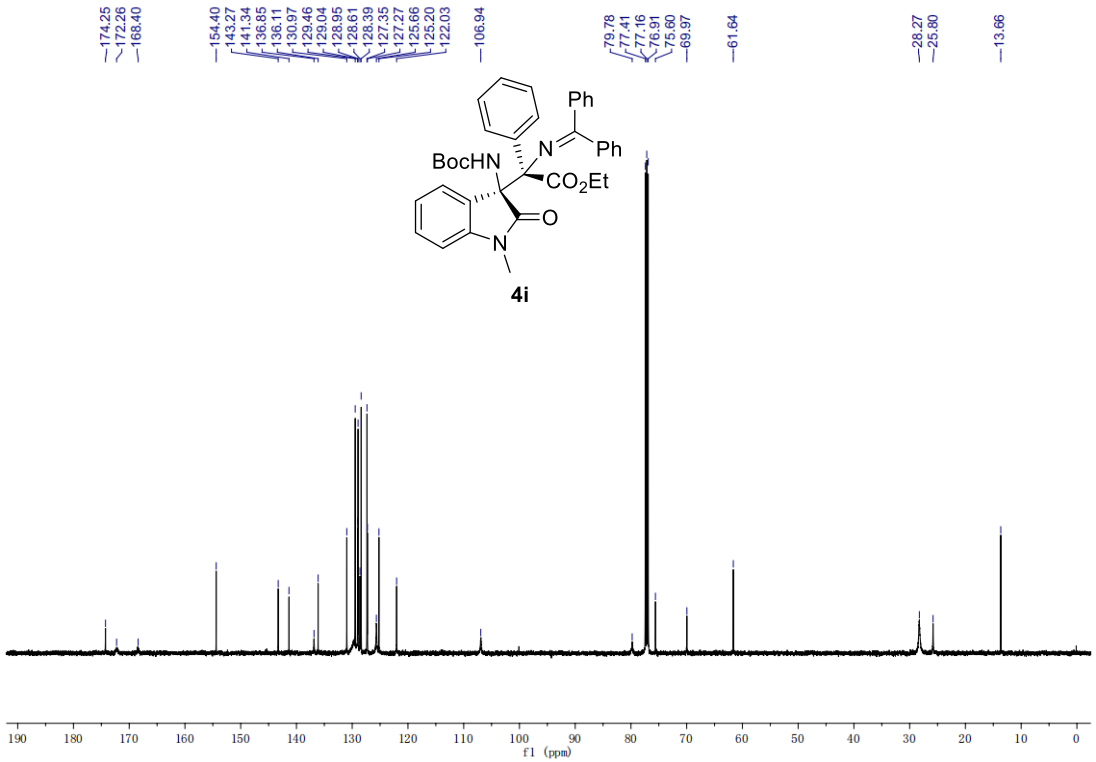
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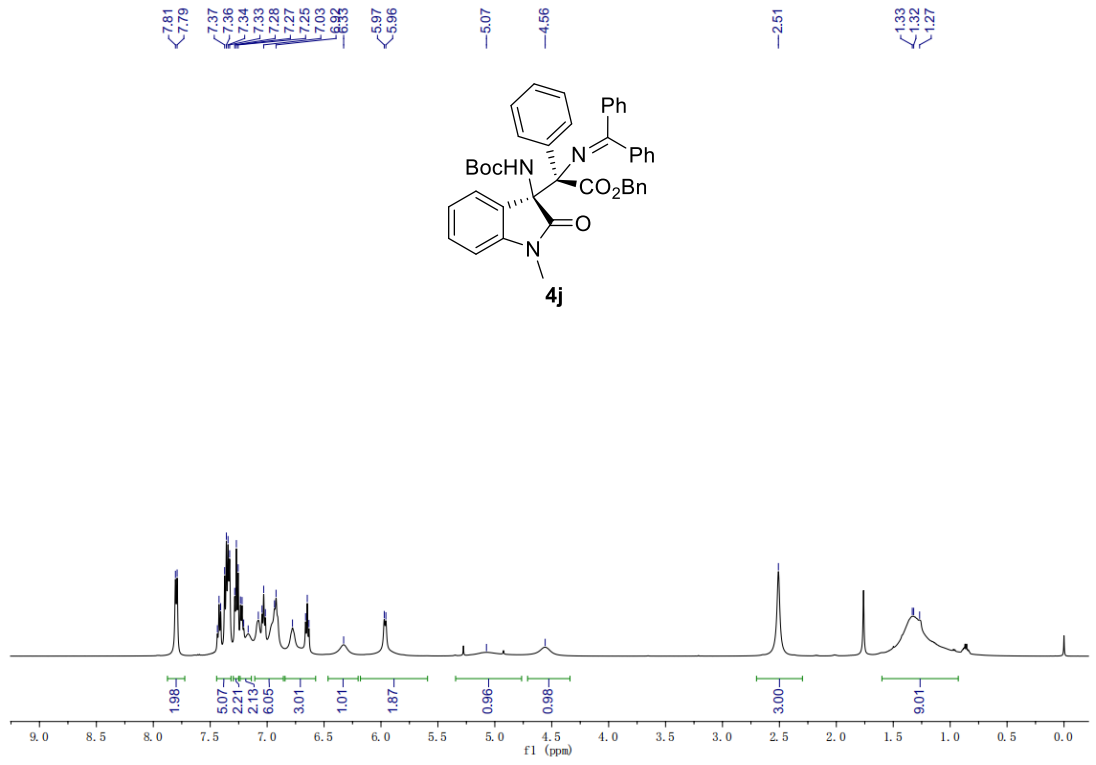
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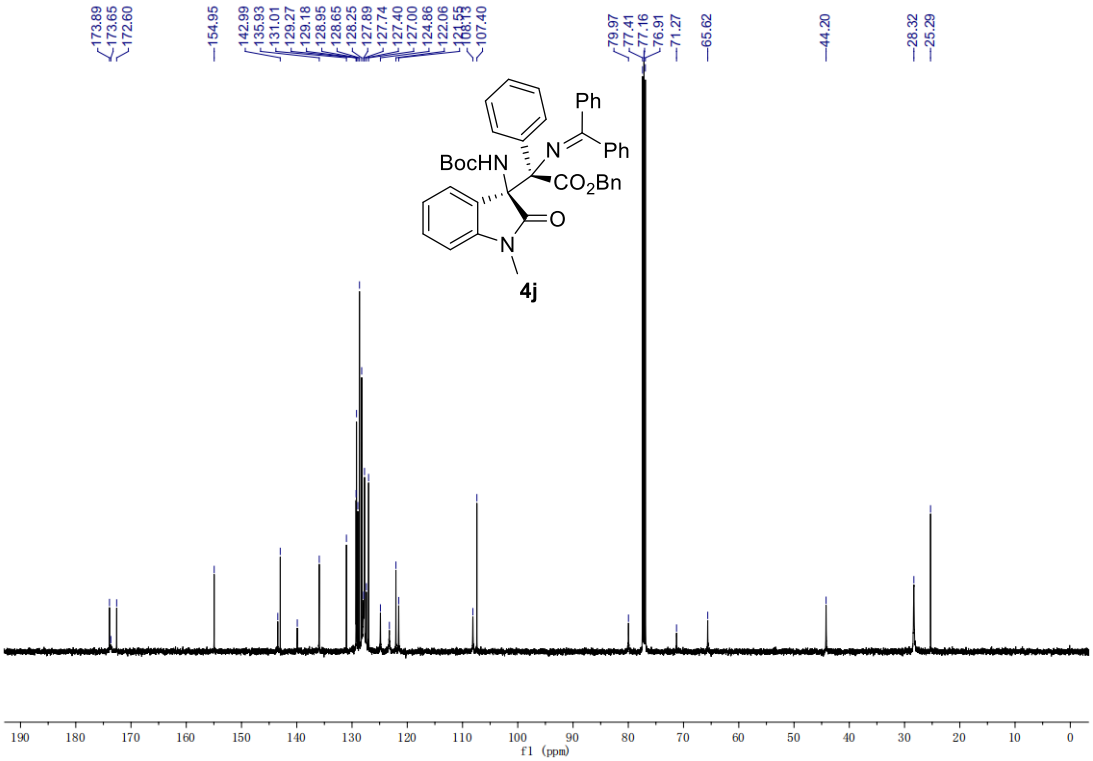
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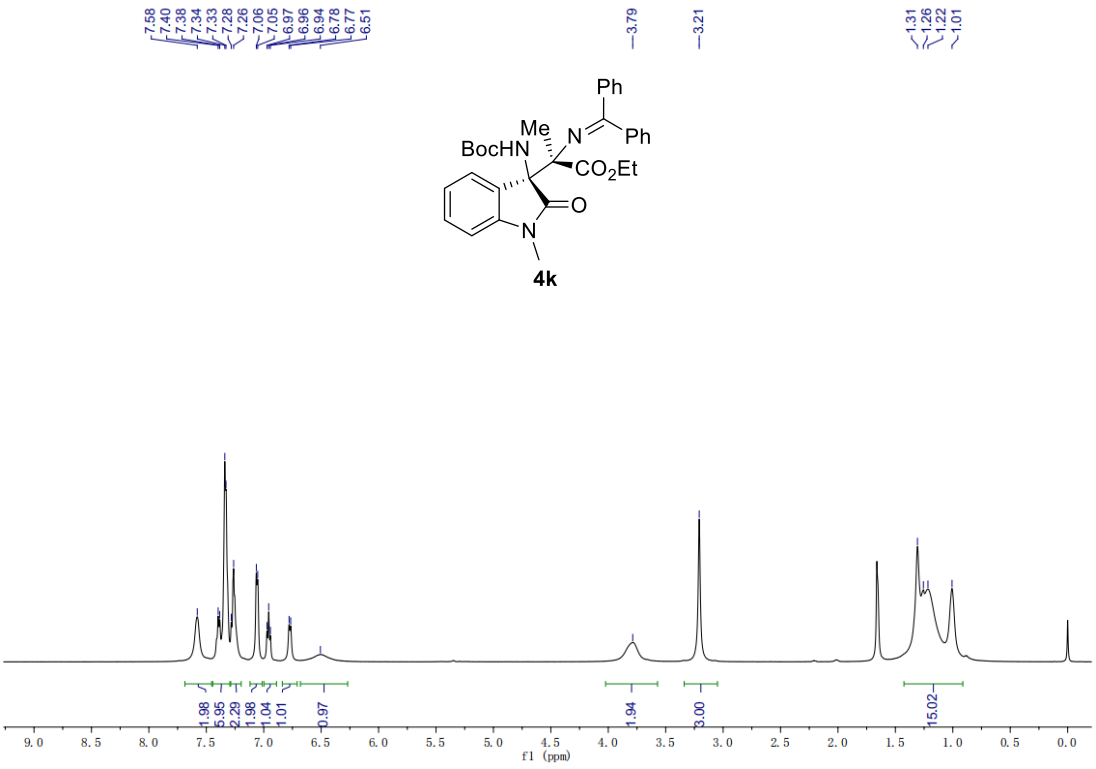
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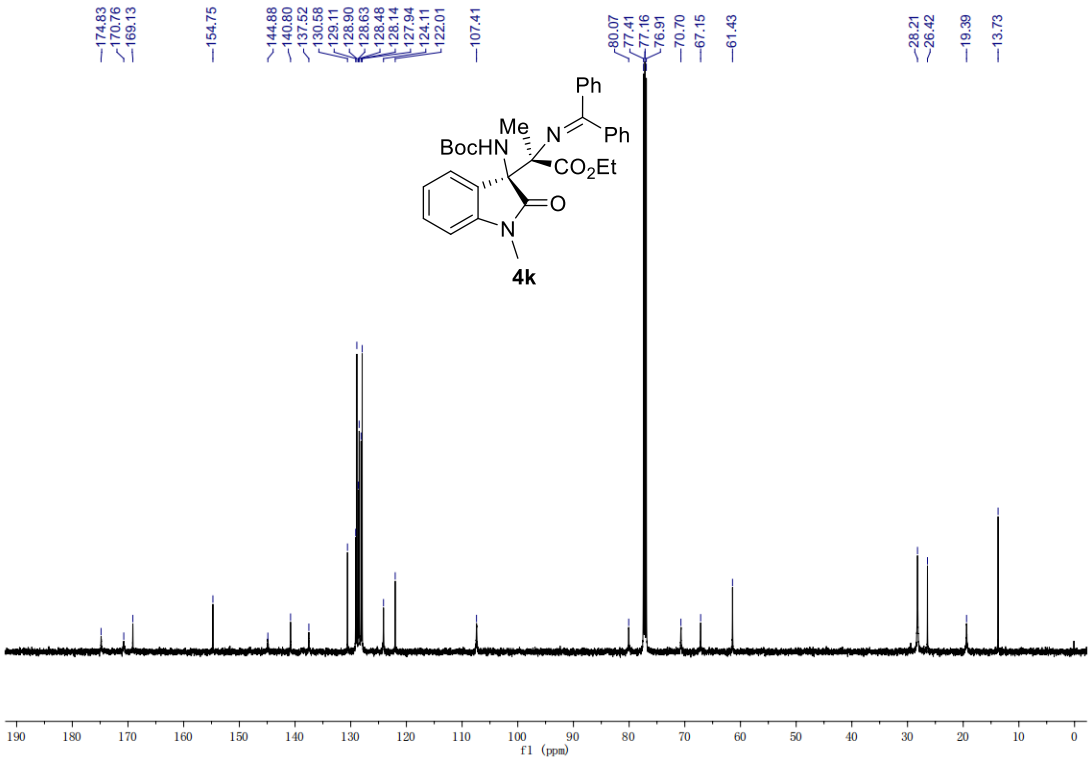
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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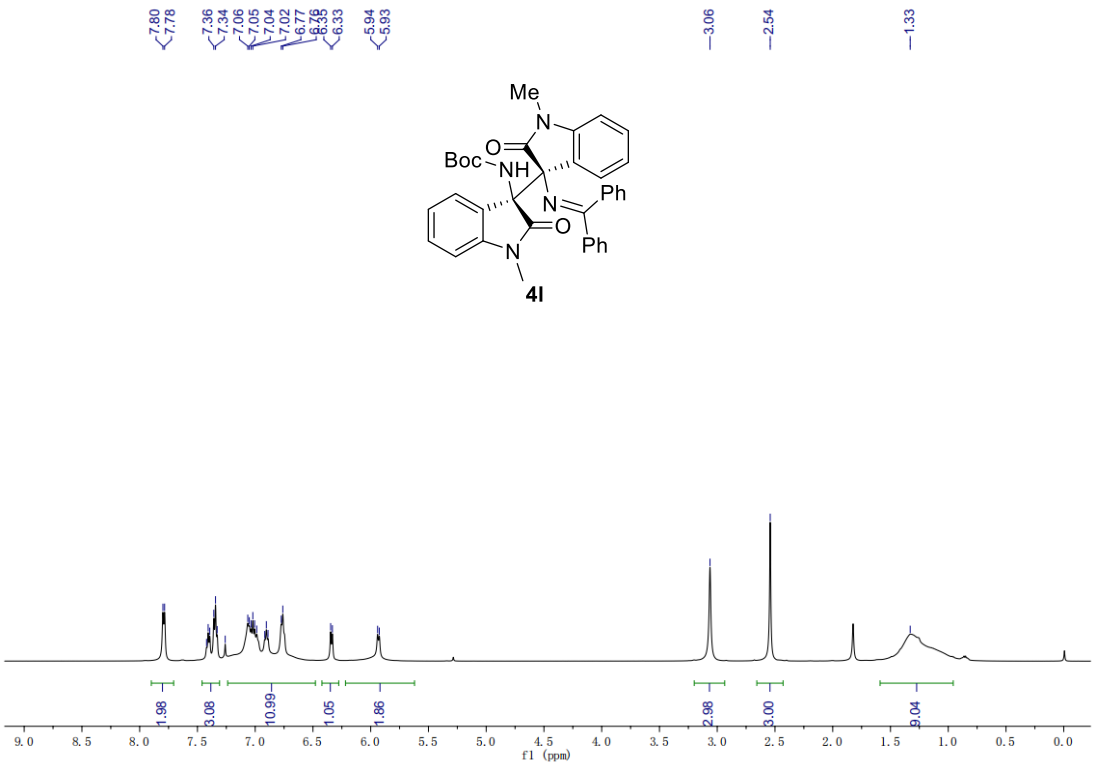
128.63
128.48
128.14
127.94
124.11
122.01
107.41
80.07
77.41
77.16
76.91
70.70
67.15
61.43
28.21
26.42
19.39
13.73
Ph
Me
N
Ph
BocHN
CO2Et
O
N
4k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.05
7.04
7.02
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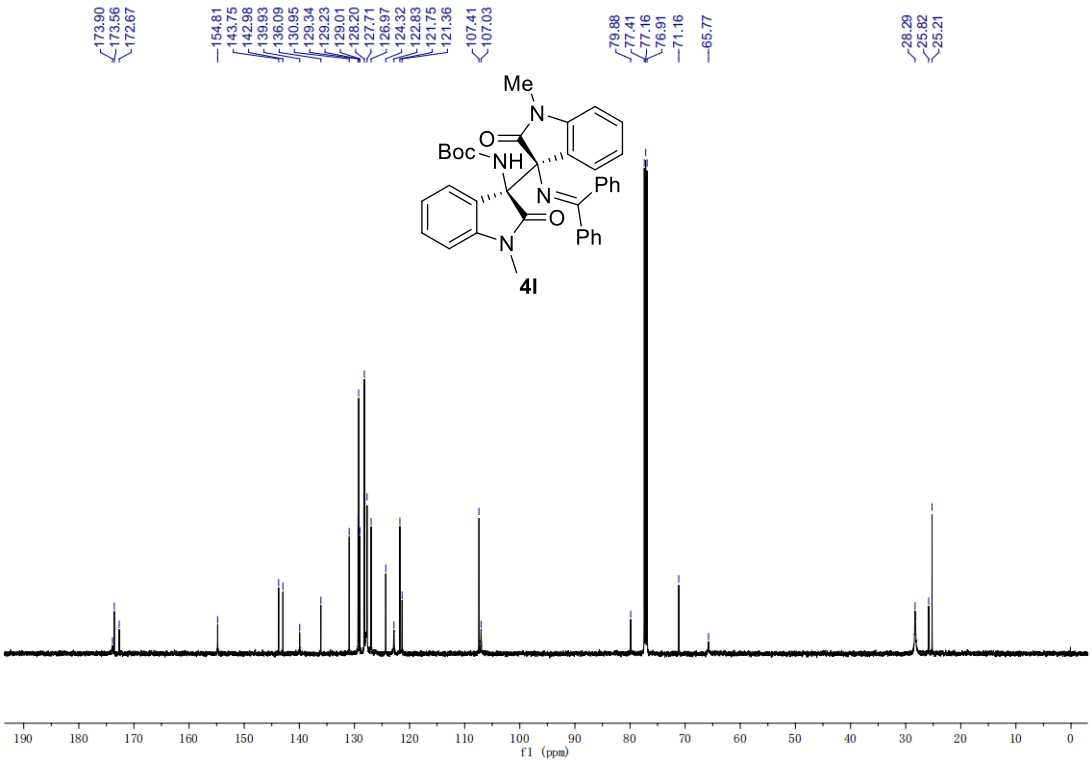
6.76
6.38
6.33
5.94
5.93
3.06
2.54
1.33
Me
N
O
Boc
NH
N
Ph
O
Ph
N
4l
1.98
3.08
10.99
1.05
1.86
2.98
3.00
9.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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126.97
124.32
122.83
121.75
121.36
107.41
107.03
79.88
77.41
77.16
76.91
71.16
65.77
28.29
25.82
25.21
Me
N
O
Boc
NH
N
Ph
O
Ph
N
4l
190
180
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120
110
100
90
80
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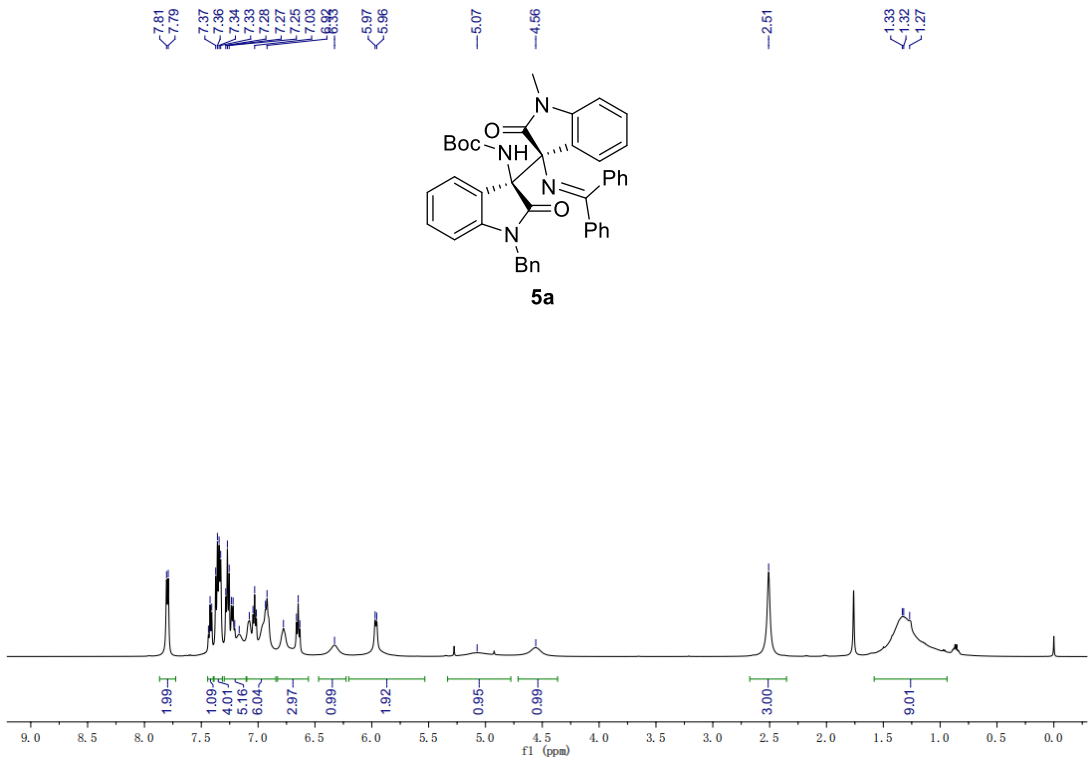
50
40
30
20
10
0
f1 (ppm)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7.03
6.82
6.33
5.97
5.96
5.07
4.56
2.51
1.33
1.32
1.27
N
O
Boc
NH
N
Ph
O
Ph
N
Bn
5a
1.99
1.09
4.01
5.16
6.04
2.97
0.99
1.92
0.95
0.99
3.00
9.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
1.5
1.0
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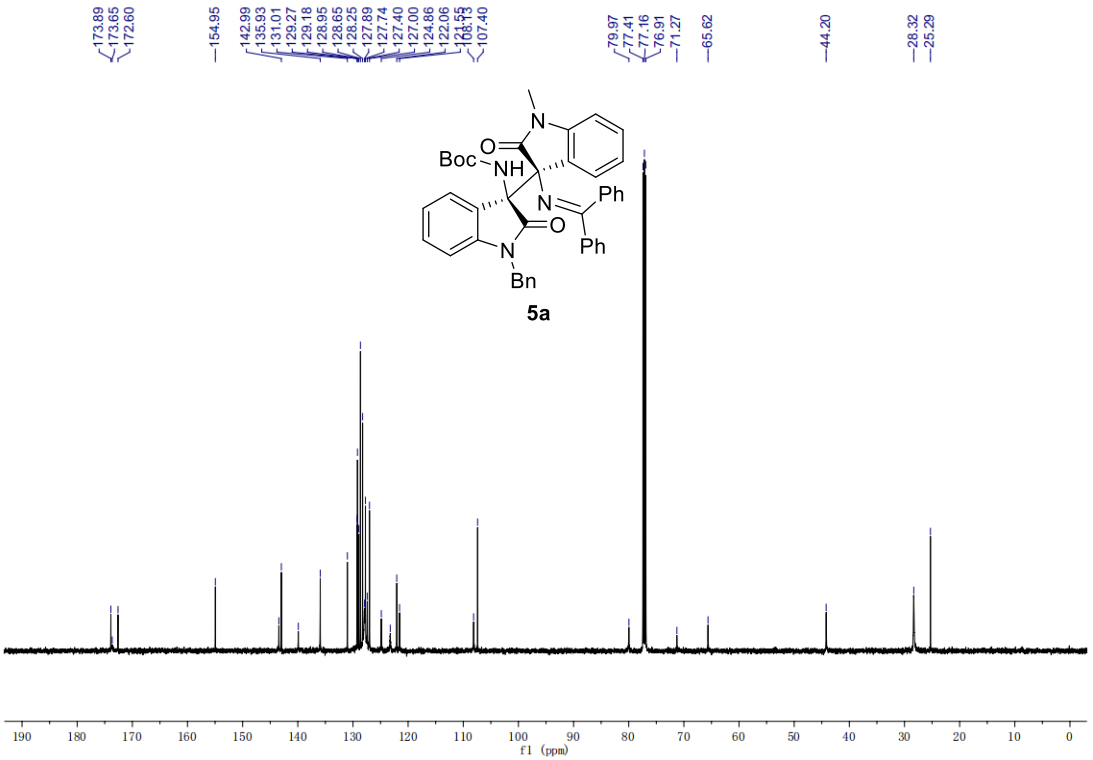
0.0
f1 (ppm)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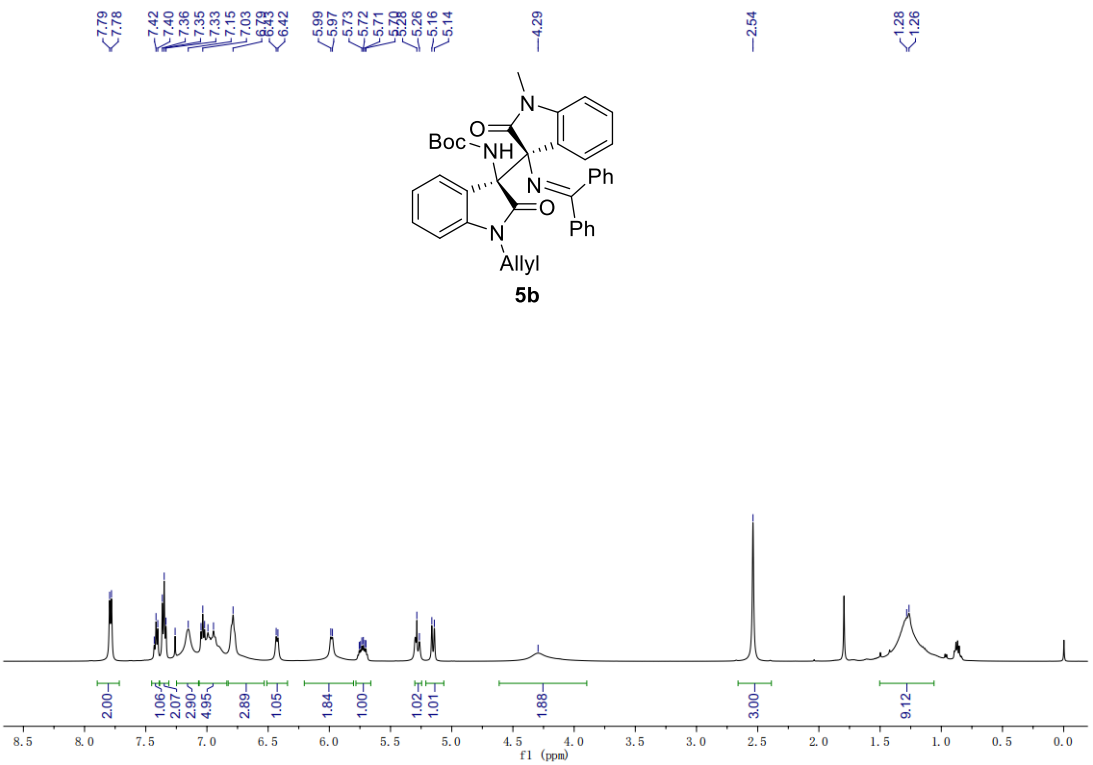
127.74
127.40
127.00
124.86
122.06
107.40
79.97
77.41
77.16
76.91
71.27
65.62
44.20
28.32
25.29
Boc
NH
O
N
Ph
Ph
Bn
5a
f1 (ppm)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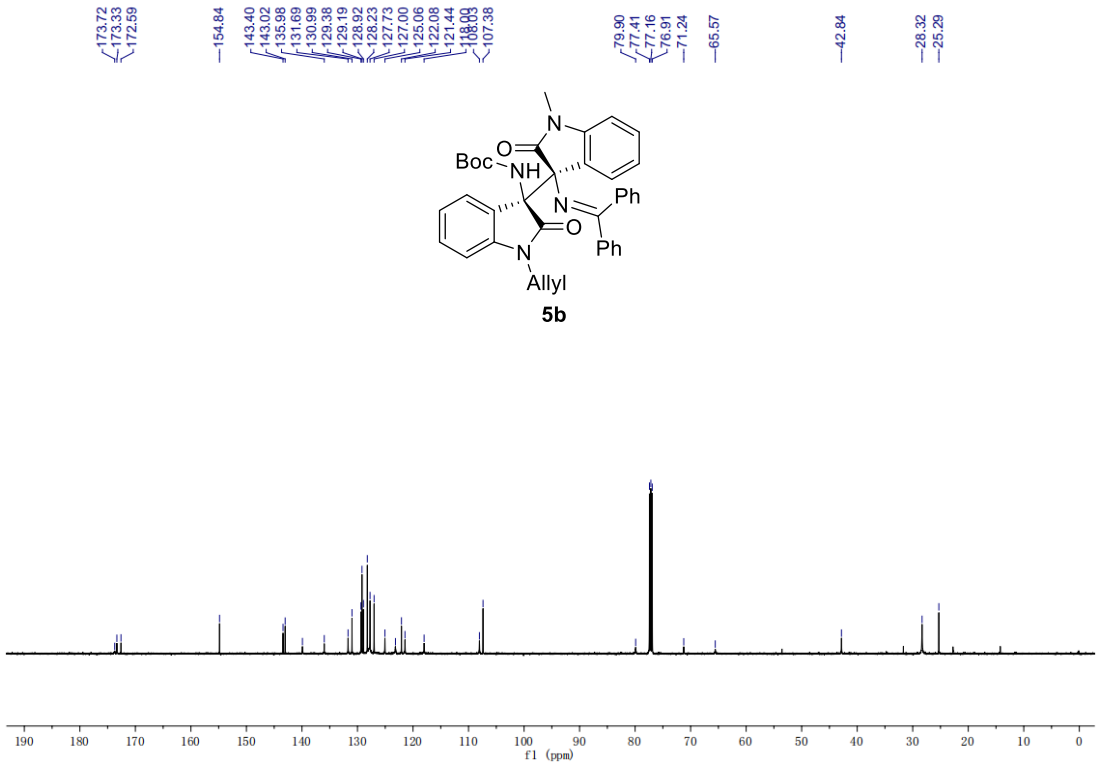
7.33
7.15
7.03
6.43
6.42
5.99
5.97
5.73
5.72
5.71
5.28
5.26
5.16
5.14
4.29
2.54
1.28
1.26
Boc
NH
O
N
Ph
Ph
Allyl
5b
2.00
1.06
2.07
2.90
4.95
2.89
1.05
1.84
1.00
1.02
1.01
1.88
3.00
9.12
f1 (ppm)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154.84
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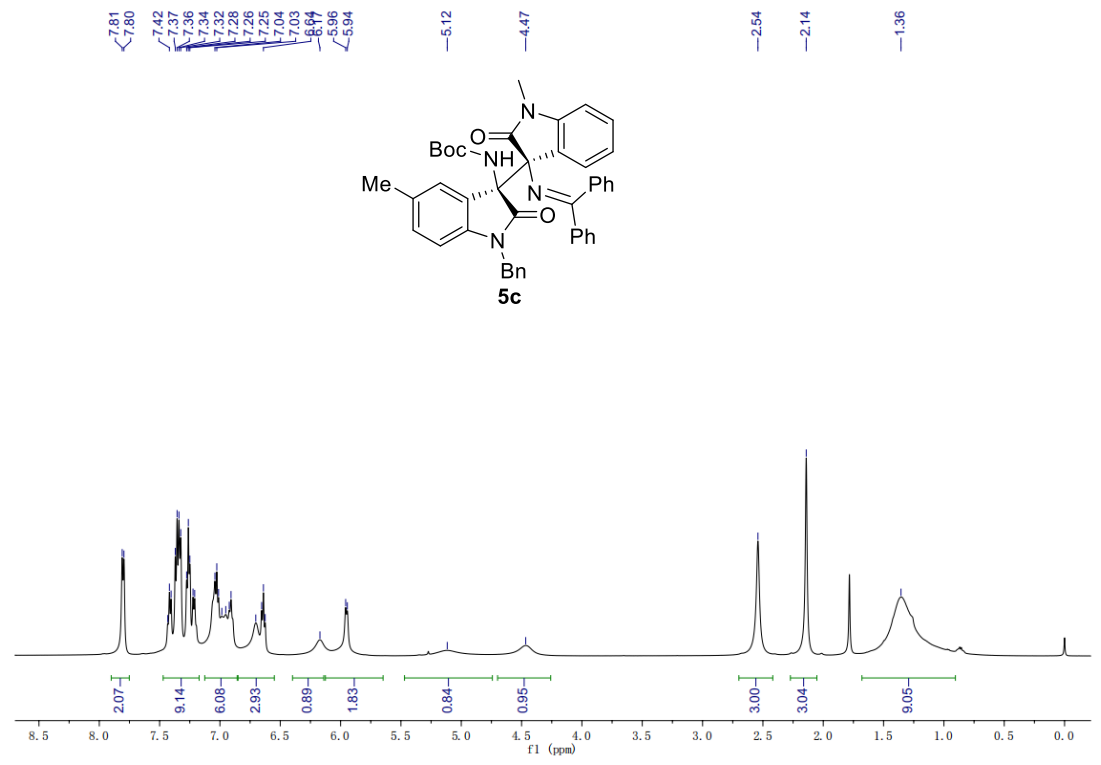
143.02
135.98
131.69
130.99
129.38
129.19
128.92
128.23
127.73
127.00
125.06
122.08
121.44
118.00
108.03
107.38
79.90
77.41
77.16
76.91
71.24
65.57
42.84
28.32
25.29
N
O
Boc
NH
N
Ph
O
Ph
N
Allyl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5b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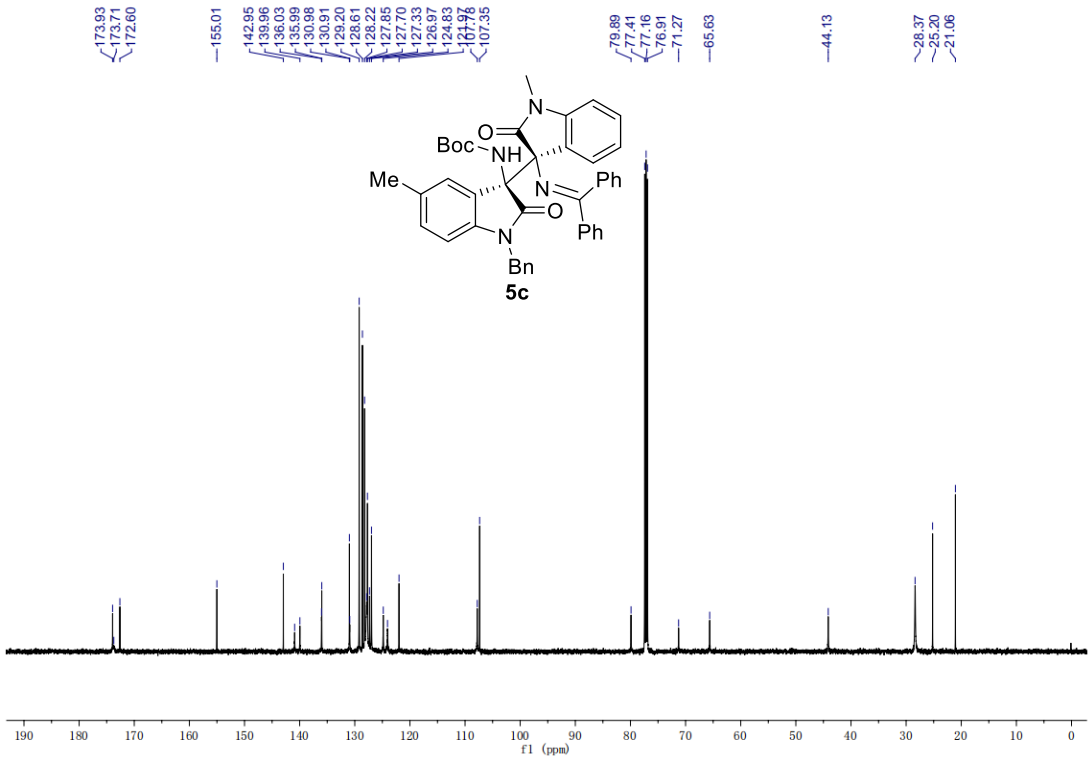
7.80
7.42
7.37
7.36
7.34
7.32
7.28
7.26
7.25
7.04
7.03
6.64
6.61
5.96
5.94
5.12
4.47
2.54
2.14
1.36
N
O
Boc
NH
Me
N
Ph
O
Ph
N
Bn
2.07
9.14
6.08
2.93
0.89
1.83
0.84
0.95
3.00
3.04
9.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

5c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173.71
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139.96
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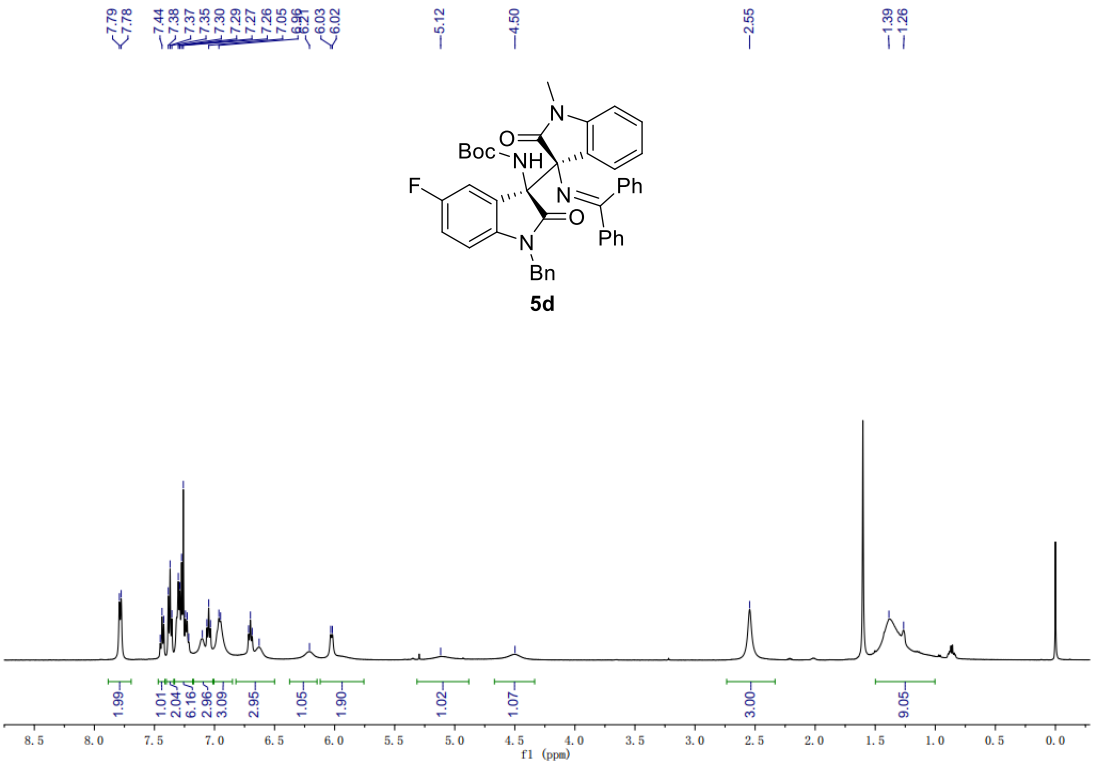
135.99
130.98
130.91
129.20
128.61
128.22
127.85
127.70
127.33
126.97
124.83
121.97
121.78
107.35
79.89
77.41
77.16
76.91
71.27
65.63
44.13
28.37
25.20
21.06
Boc
NH
O
N
Me
Ph
Ph
Bn
5c
f1 (ppm)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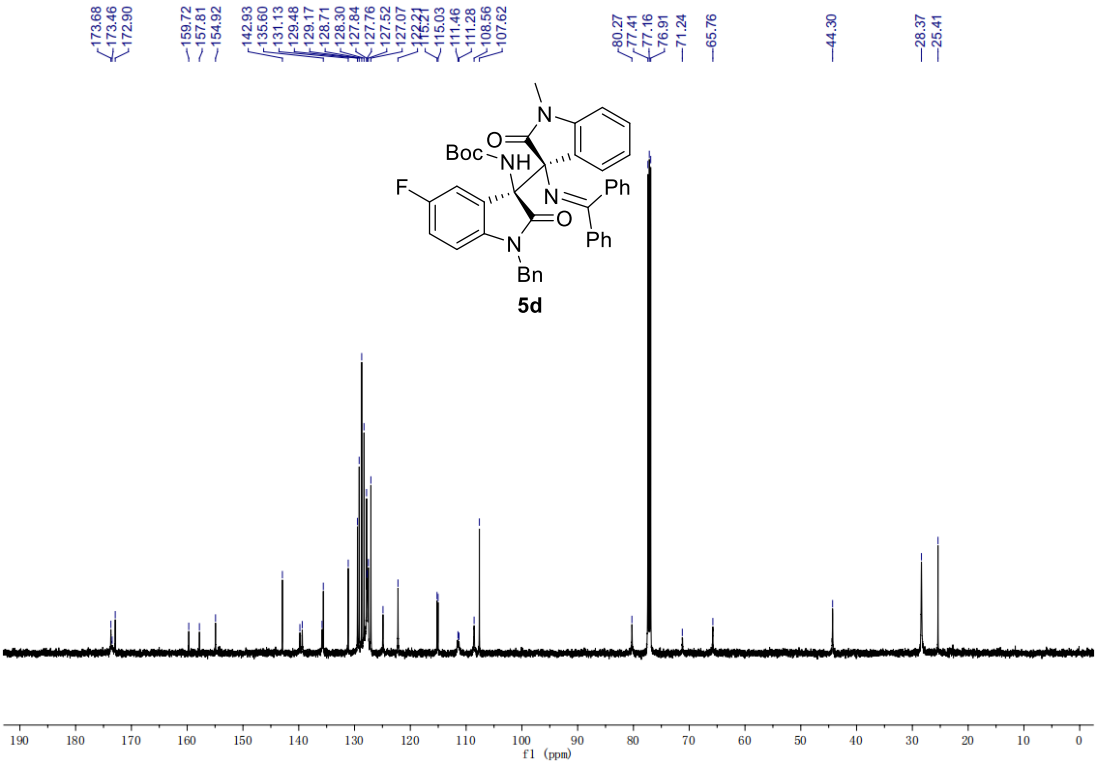
7.78
7.44
7.38
7.37
7.35
7.30
7.29
7.27
7.26
7.05
6.03
6.02
5.12
4.50
2.55
1.39
1.26
Boc
NH
O
N
F
Ph
Ph
Bn
5d
1.99
1.01
2.04
6.16
2.96
3.09
2.95
1.05
1.90
1.02
1.07
3.00
9.05
f1 (ppm)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135.60
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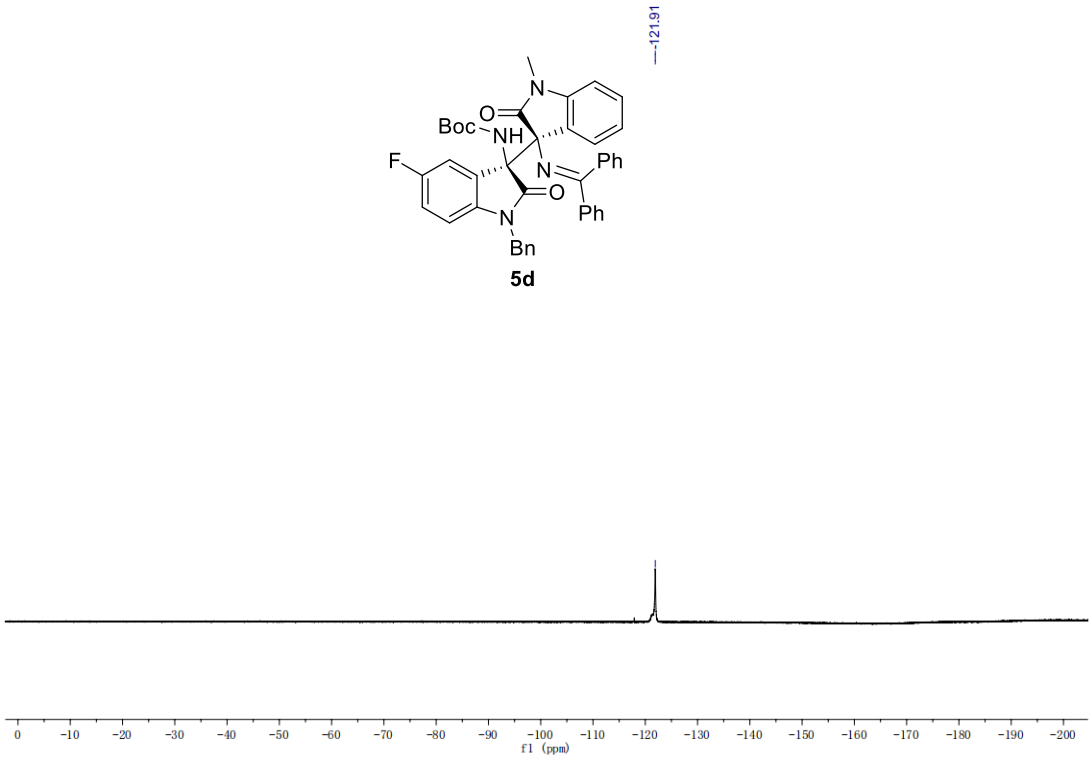
129.48
129.17
128.71
128.30
127.84
127.76
127.52
127.07
115.03
111.46
111.28
108.56
107.62
80.27
77.41
77.16
76.91
71.24
65.76
44.30
28.37
25.41
Boc
NH
N
O
F
Ph
Ph
Bn
5d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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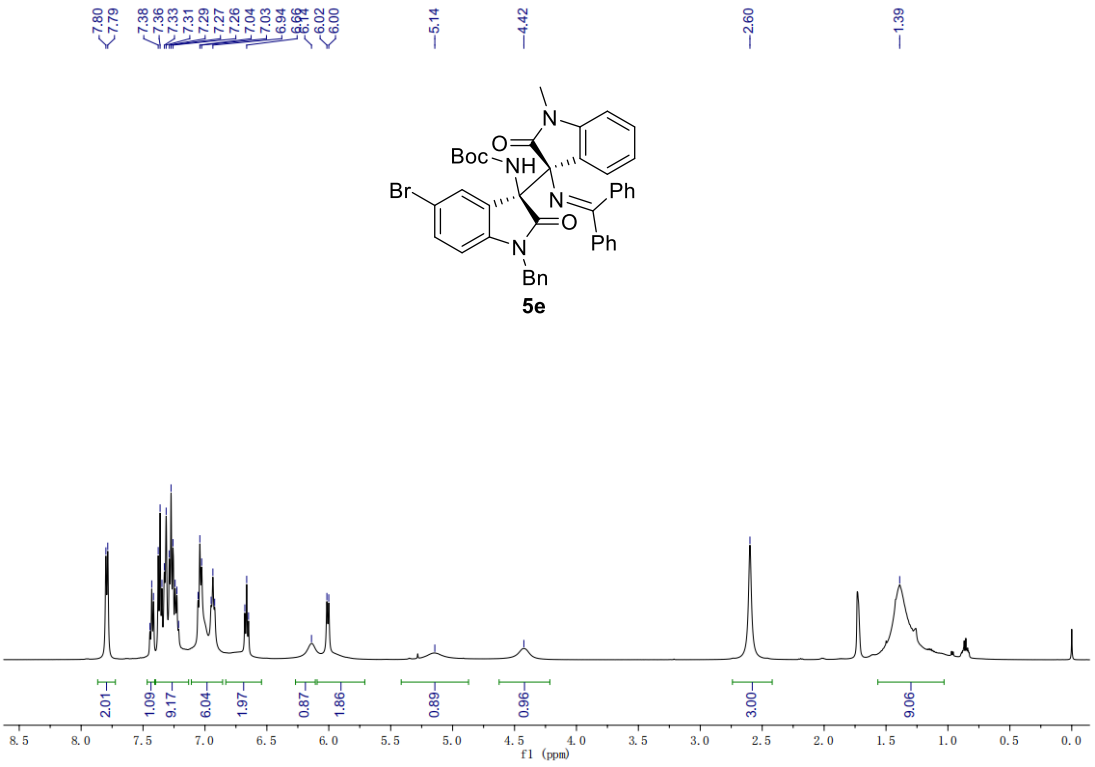
Boc
NH
N
O
F
Ph
Ph
Bn
5d
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)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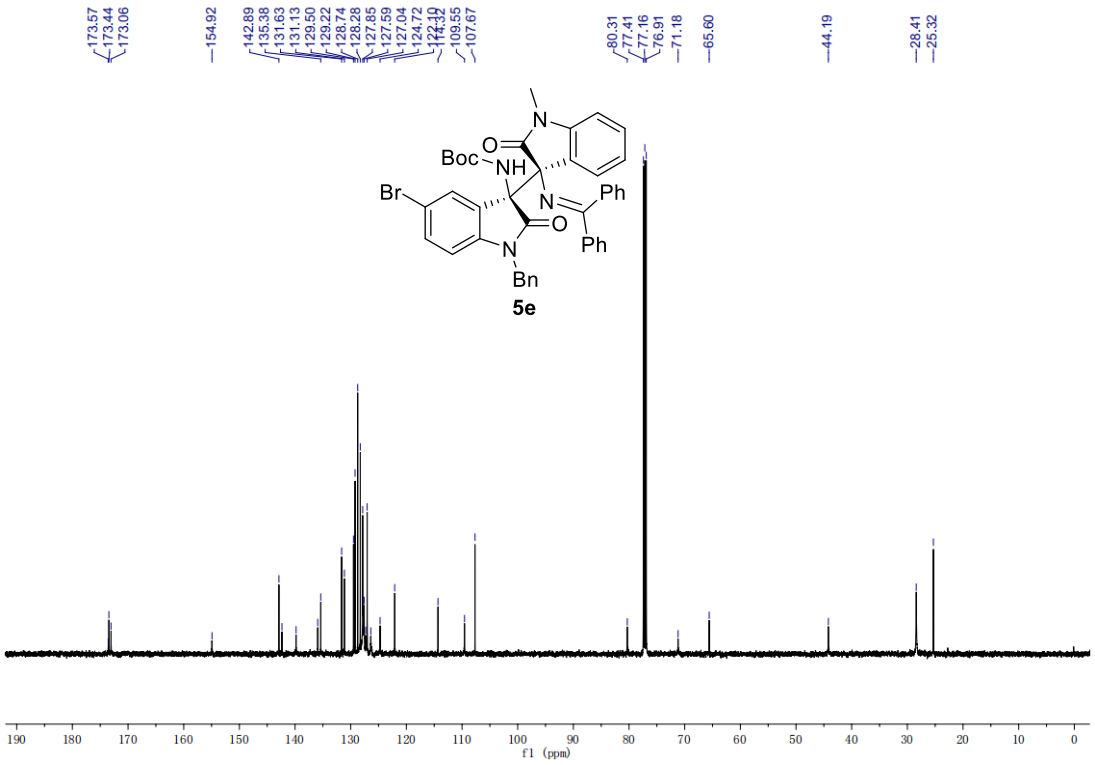
7.79
7.38
7.36
7.33
7.31
7.29
7.27
7.26
7.04
7.03
6.94
6.02
6.00
5.14
4.42
2.60
1.39
Boc
NH
O
N
Br
Ph
Ph
Bn
5e
2.01
1.09
9.17
6.04
1.97
0.87
1.86
0.89
0.96
3.00
9.06
f1 (ppm)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131.13
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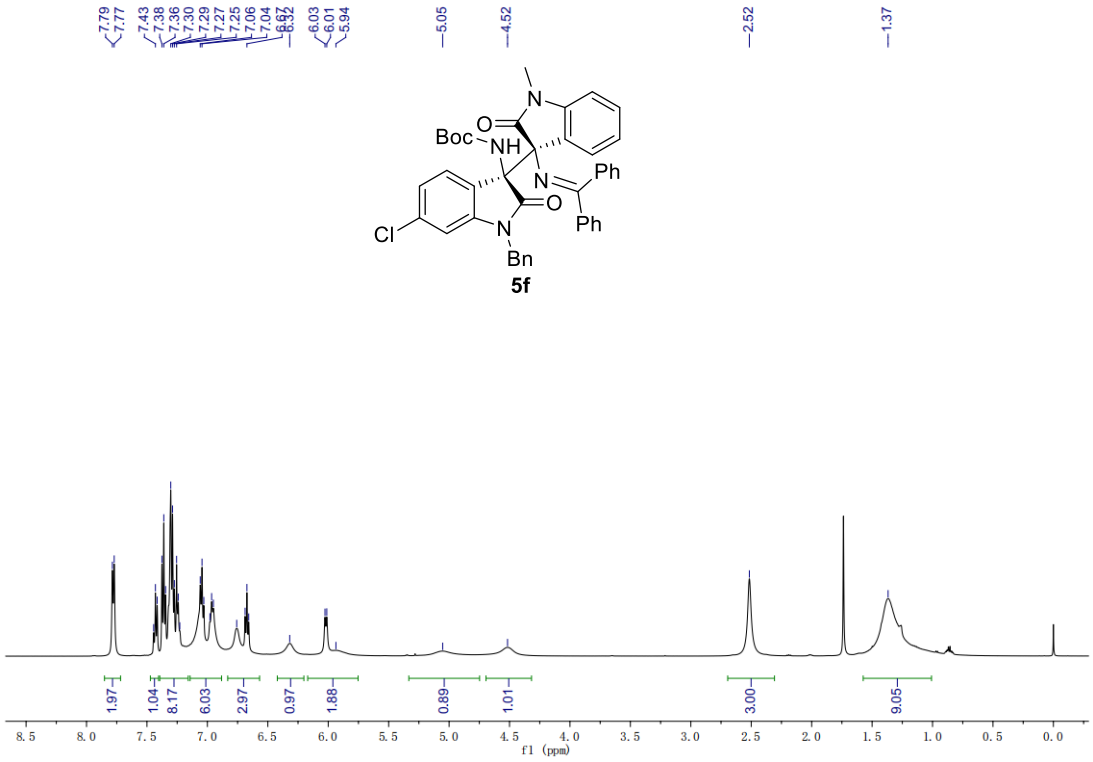
128.28
127.85
127.59
127.04
124.72
109.55
107.67
80.31
77.41
77.16
76.91
71.18
65.60
44.19
28.41
25.32
Boc
NH
O
N
Br
Ph
Ph
Bn
5e
f1 (ppm)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7.29
7.27
7.25
7.06
7.04
6.67
6.32
6.03
6.01
5.94
5.05
4.52
2.52
1.37
Boc
NH
O
N
Ph
Ph
Cl
Bn
5f
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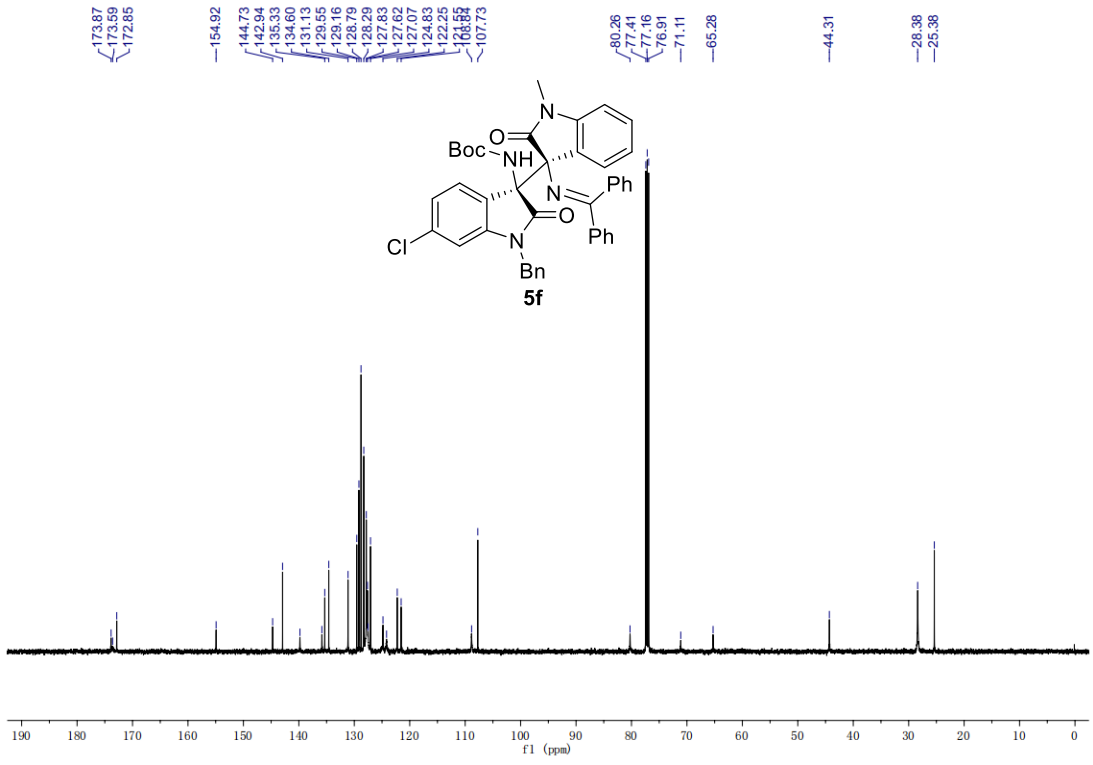
6.03
2.97
0.97
1.88
0.89
1.01
3.00
9.05
f1 (ppm)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127.62
127.07
124.83
122.25
107.73
80.26
77.41
77.16
76.91
71.11
65.28
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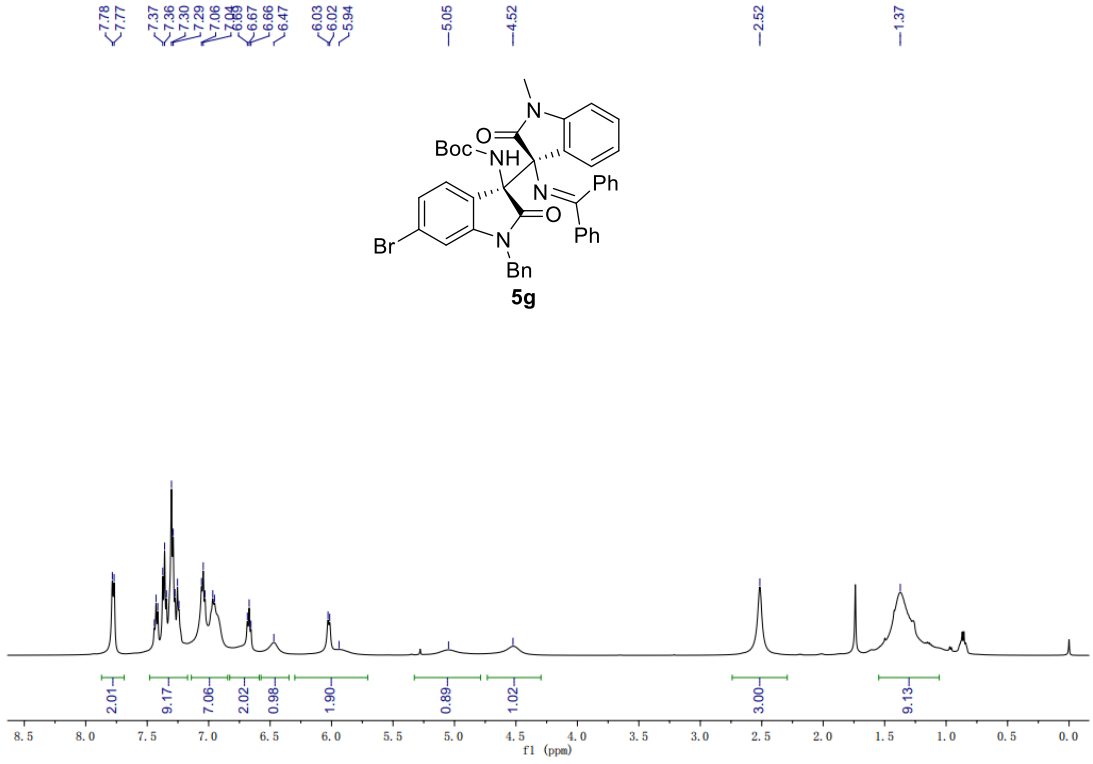
28.38
25.38
Boc
NH
O
N
Ph
Ph
Cl
Bn
5f
f1 (ppm)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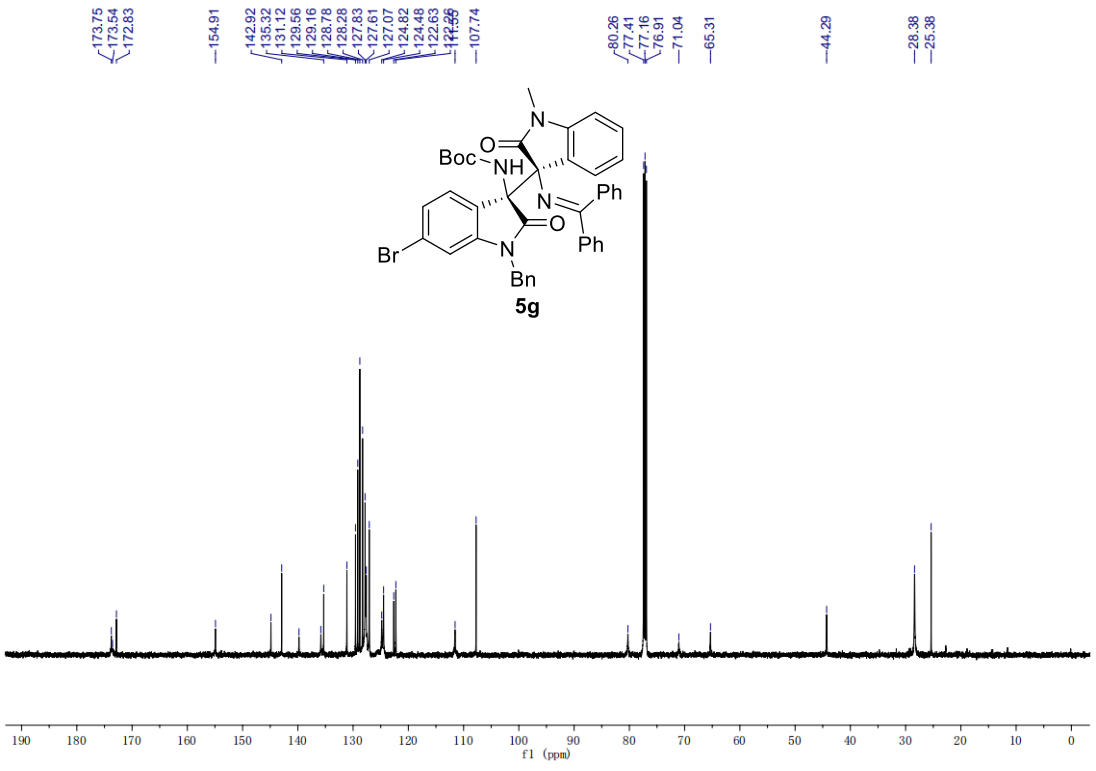
7.29
7.06
6.67
6.66
6.47
6.03
6.02
5.94
5.05
4.52
2.52
1.37
Boc
NH
N
O
Ph
Ph
Br
Bn
5g
2.01
9.17
7.06
2.02
0.98
1.90
0.89
1.02
3.00
9.13
f1 (ppm)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128.28
127.83
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127.07
124.82
124.48
122.63
107.74
80.26
77.41
77.16
76.91
71.04
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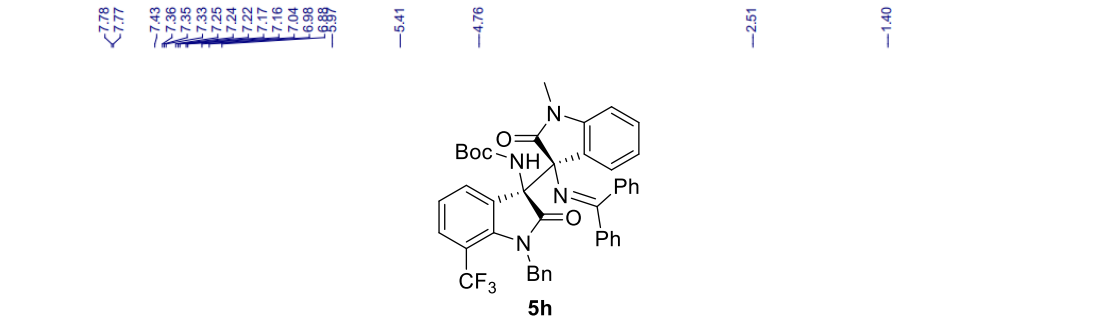
44.29
28.38
25.38
Boc
NH
N
O
Ph
Ph
Br
Bn
5g
f1 (ppm)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7.33
7.25
7.24
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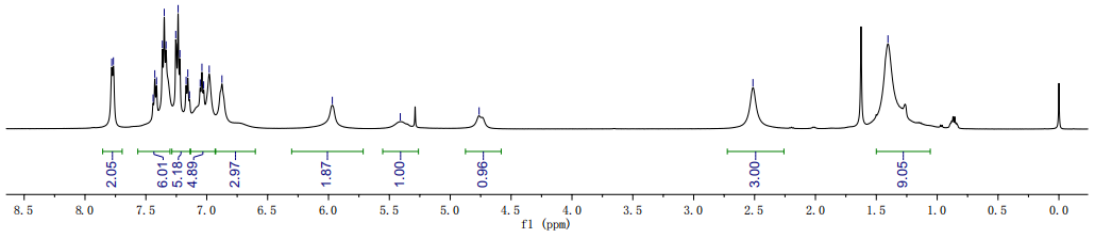
7.17
7.16
7.04
6.98
6.88
5.97
5.41
4.76
2.51
1.40
Boc
NH
N
O
Ph
Ph
Bn
CF3

5h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1.87
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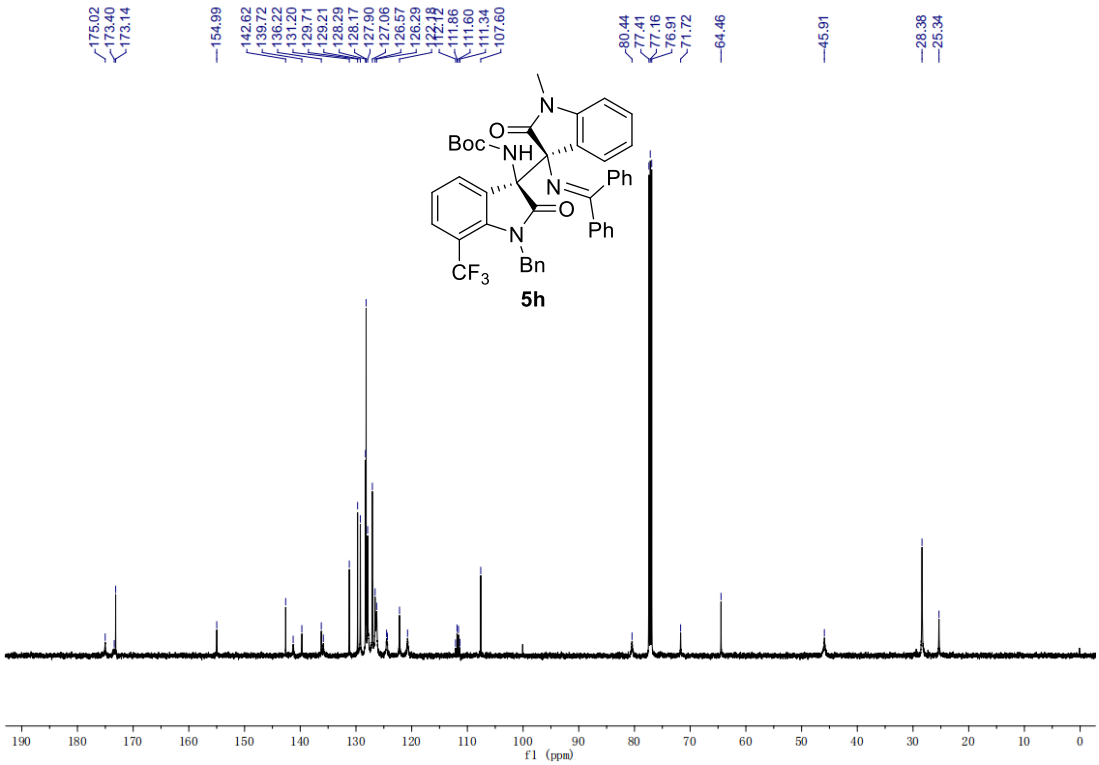
0.96
3.00
9.05
f1 (ppm)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139.72
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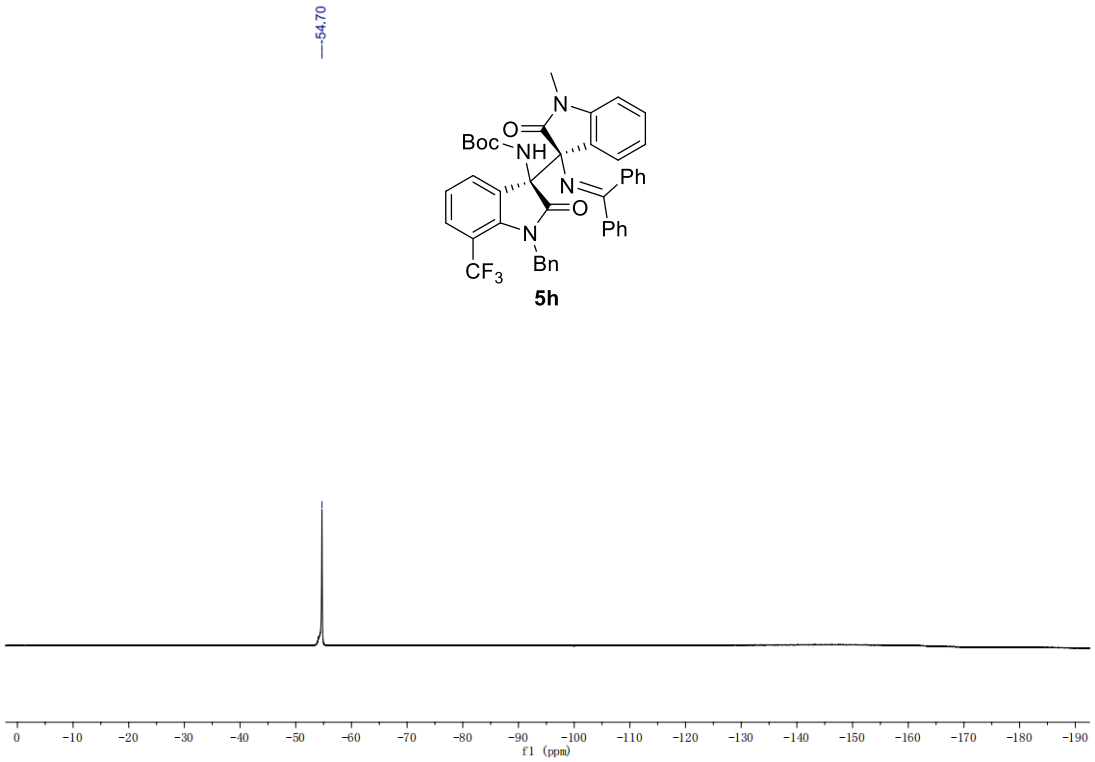
128.17
127.90
127.06
126.57
126.29
111.86
111.60
111.34
107.60
80.44
77.41
77.16
76.91
71.72
64.46
45.91
28.38
25.34
Boc
NH
N
O
Ph
Ph
Bn
CF3
f1 (ppm)

5h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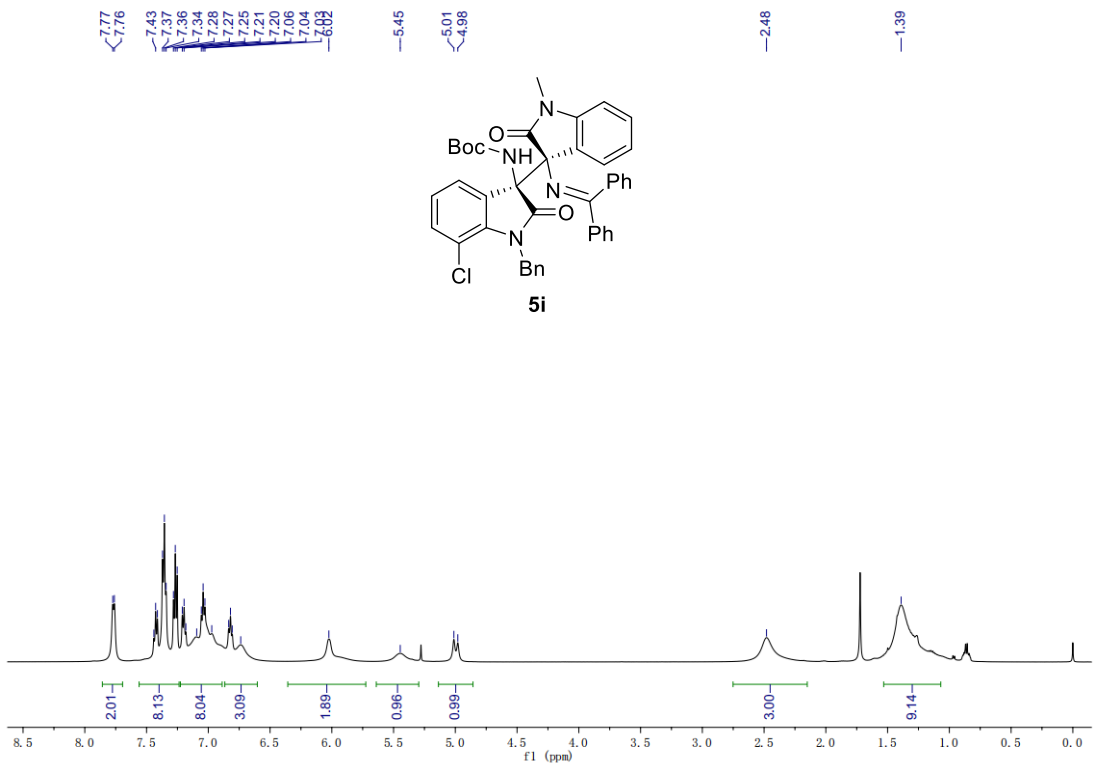
O
N
Ph
Ph
Bn
CF3
f1 (ppm)

5h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7.76
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7.37
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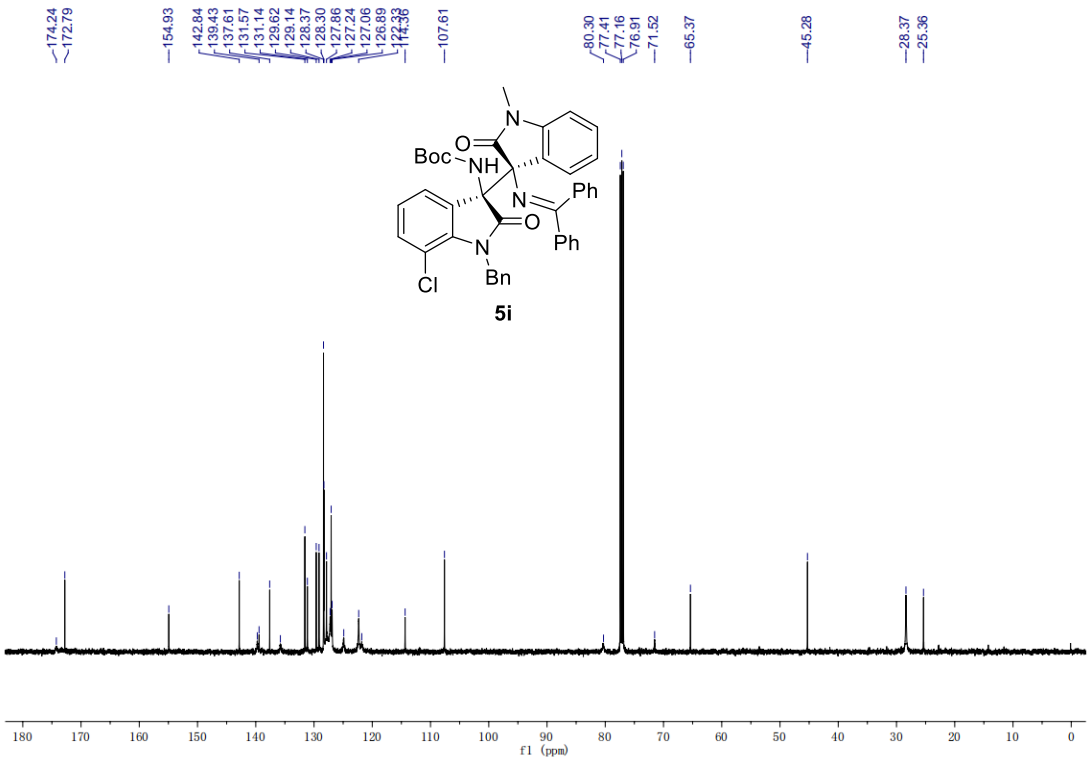
7.28
7.27
7.25
7.21
7.20
7.06
7.04
7.03
7.02
5.45
5.01
4.98
2.48
1.39
Boc
NH
O
N
Ph
Ph
Bn
Cl
2.01
8.13
8.04
3.09
1.89
0.96
0.99
3.00
9.14
f1 (ppm)

5i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137.61
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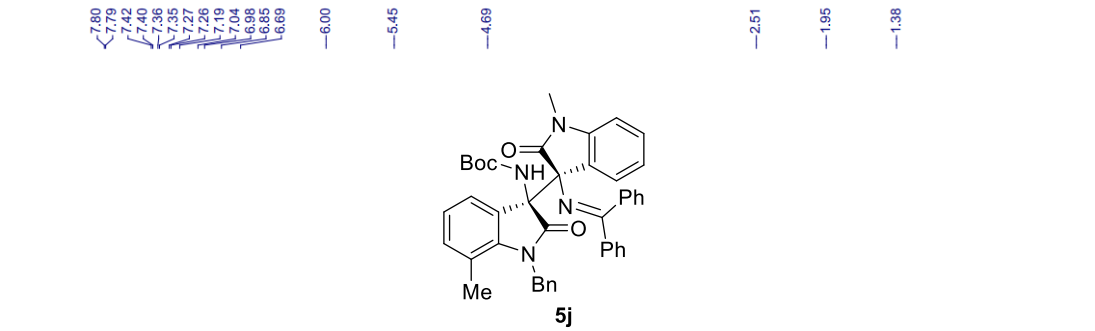
131.14
129.62
129.14
128.37
128.30
127.86
127.24
127.06
126.89
122.33
114.38
107.61
80.30
77.41
77.16
76.91
71.52
65.37
45.28
28.37
25.36
Boc
NH
O
N
Ph
Ph
Cl
Bn
5i
f1 (ppm)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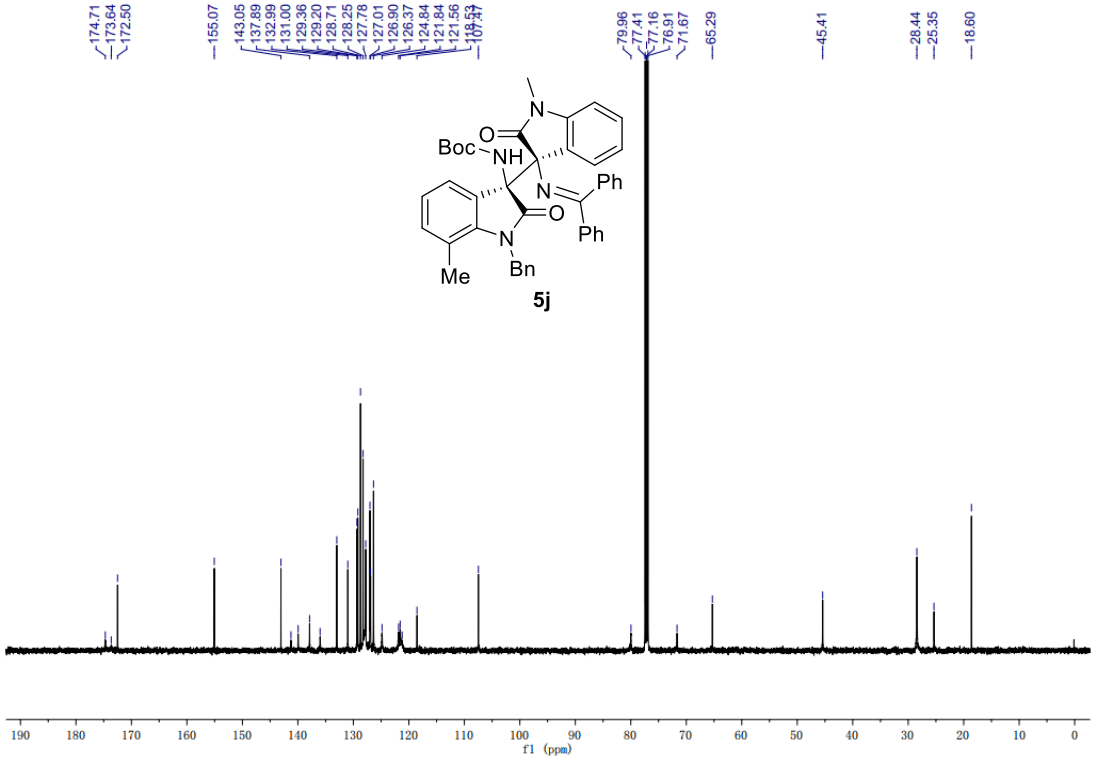
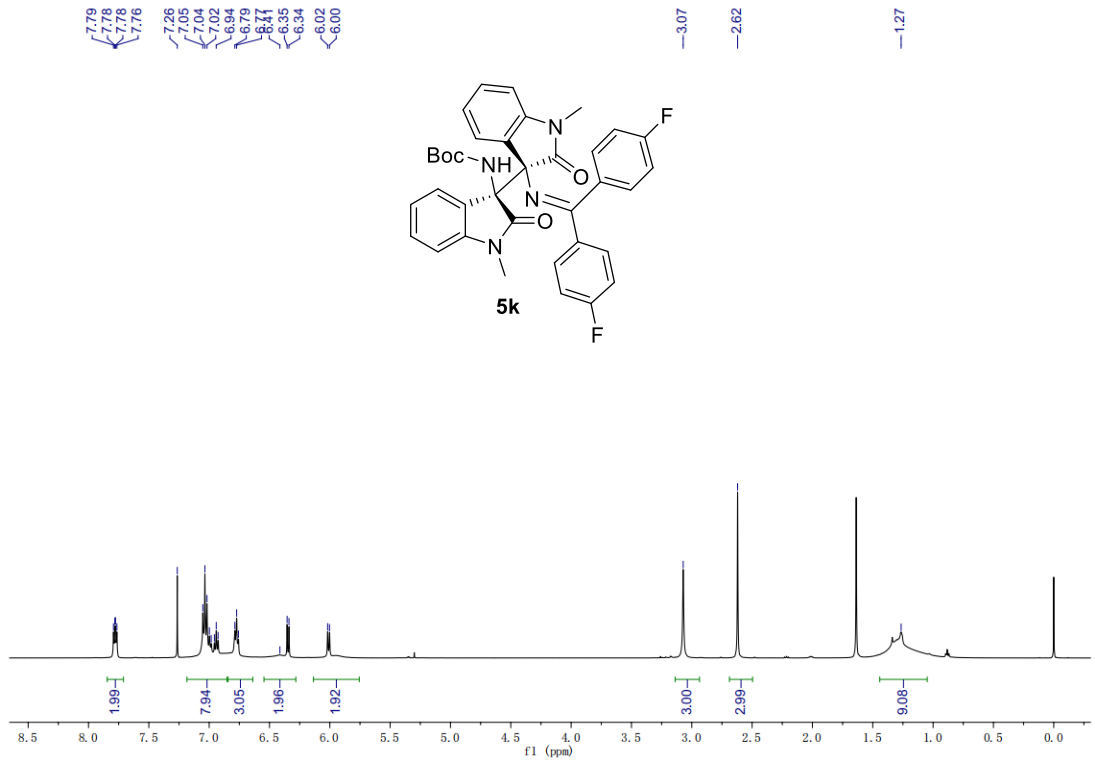
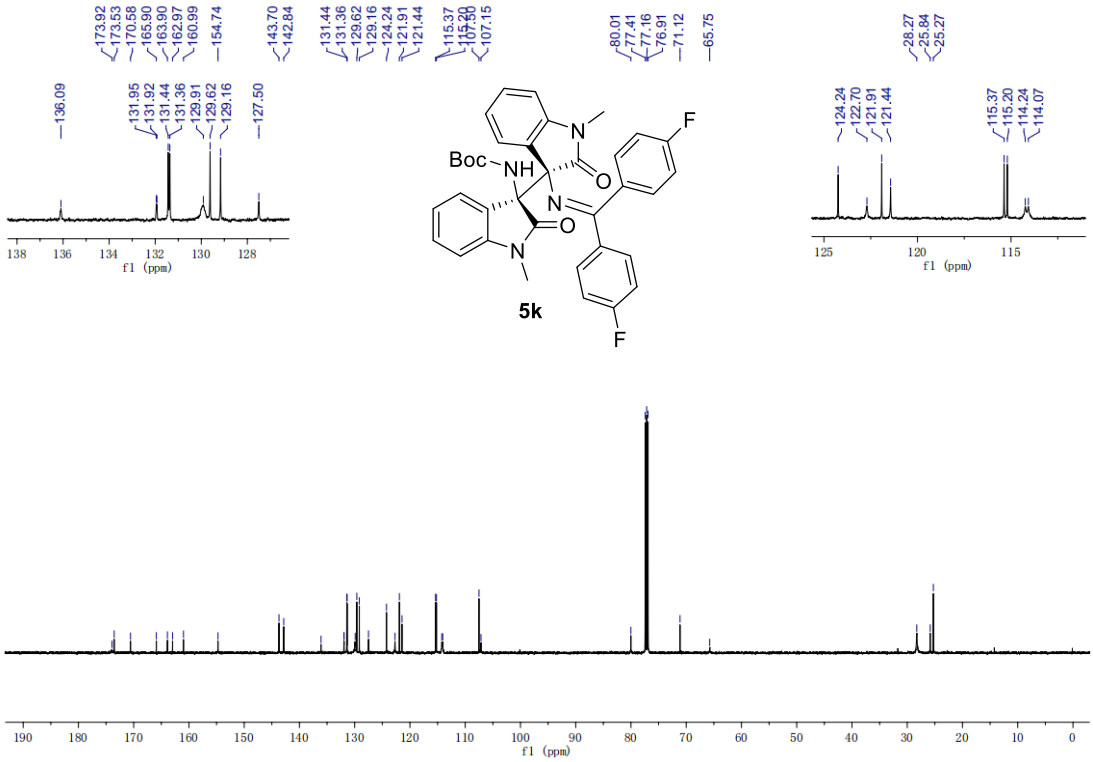
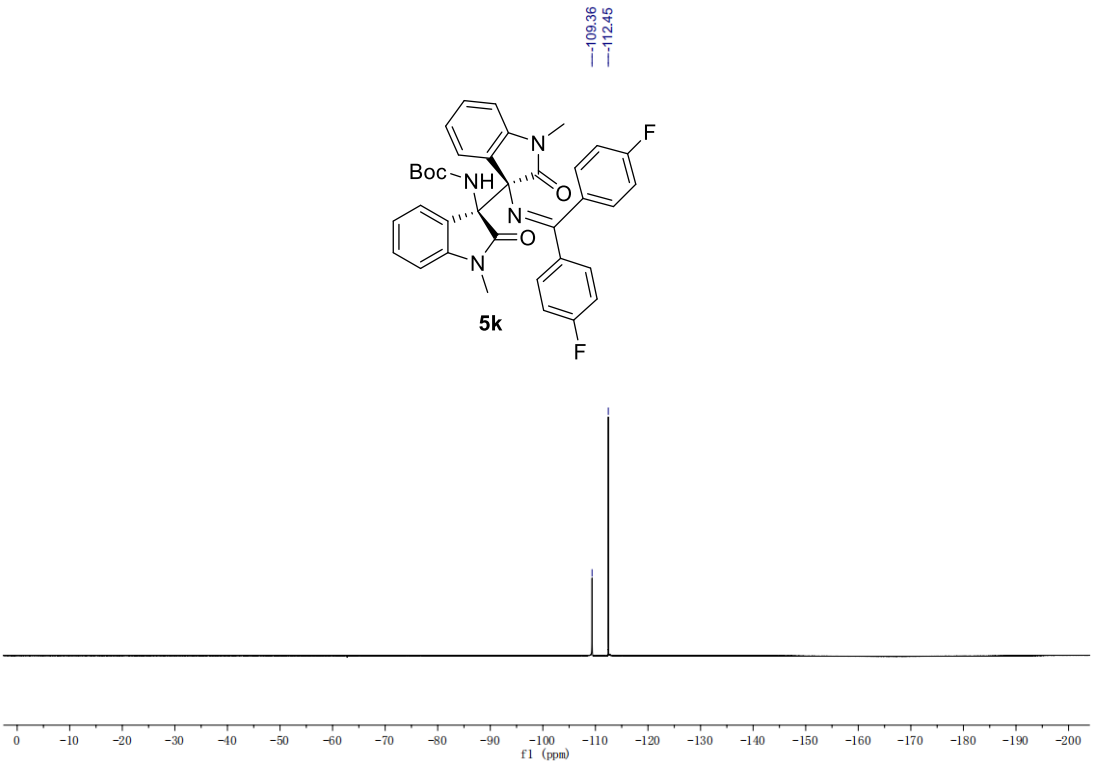
7.27
7.26
7.19
7.04
6.98
6.85
6.69
6.00
5.45
4.69
2.51
1.95
1.38
Boc
NH
O
N
Ph
Ph
Me
Bn
5j
2.05
8.11
3.00
4.03
4.00
1.81
0.86
0.95
3.00
2.95
9.01
f1 (ppm)

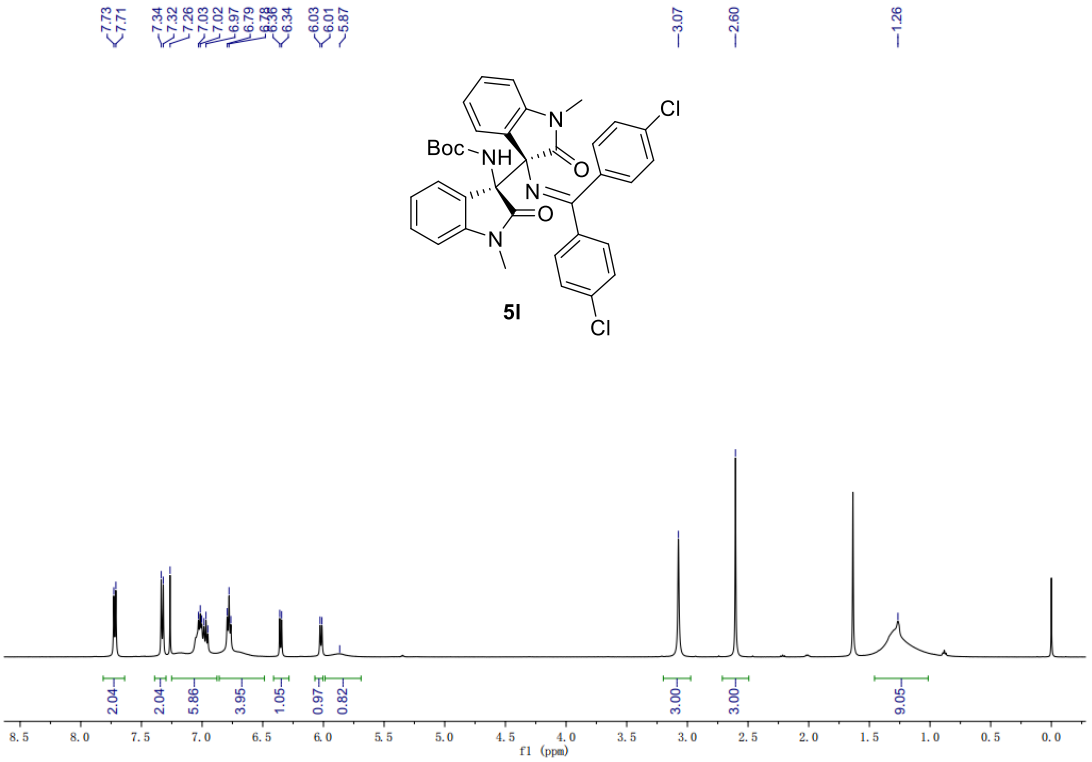

174.71
173.64
172.50
155.07
143.05
137.89
132.99
131.00
129.36
129.20
128.71
128.25
127.78
127.01
126.90
126.37
124.84
121.84
121.56
118.53
107.47
79.96
77.41
77.16
76.91
71.67
65.29
45.41
28.44
25.35
18.60
Boc
NH
N
O
Ph
Ph
Me
Bn
5j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

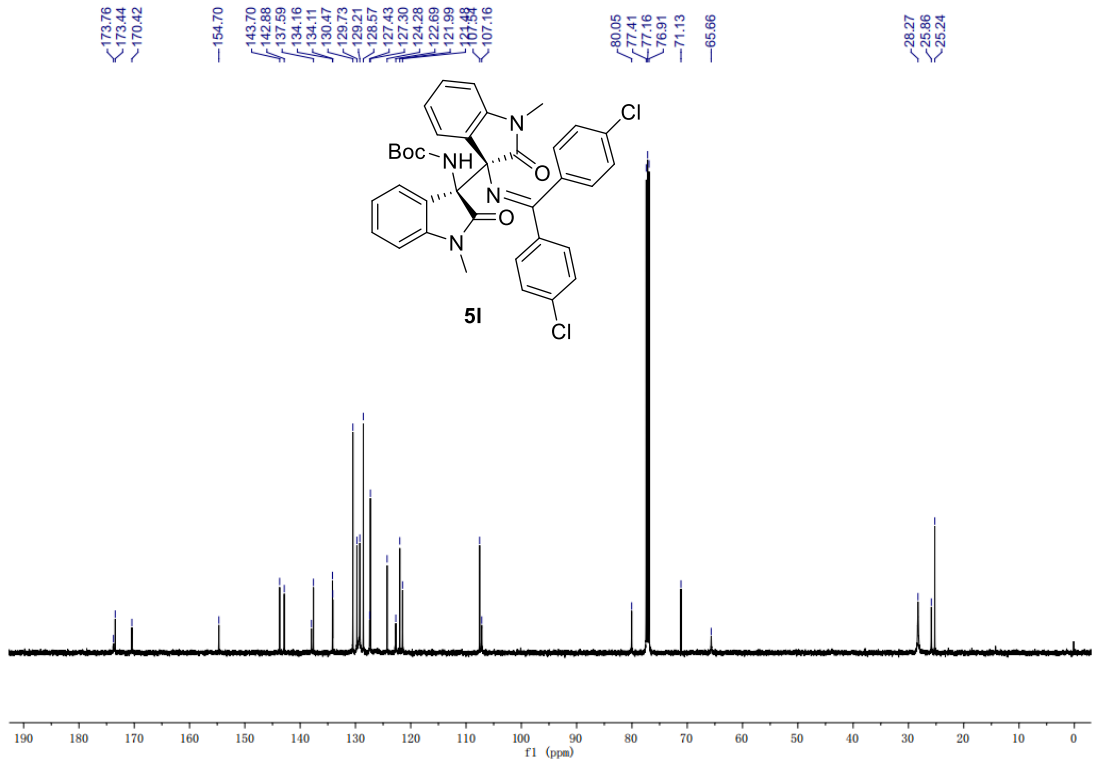

7.79
7.78
7.78
7.76
7.26
7.05
7.04
7.02
6.94
6.79
6.77
6.41
6.35
6.34
6.02
6.00
3.07
2.62
1.27
Boc
NH
N
O
F
F
5k
1.99
7.94
3.05
1.96
1.92
3.00
2.99
9.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

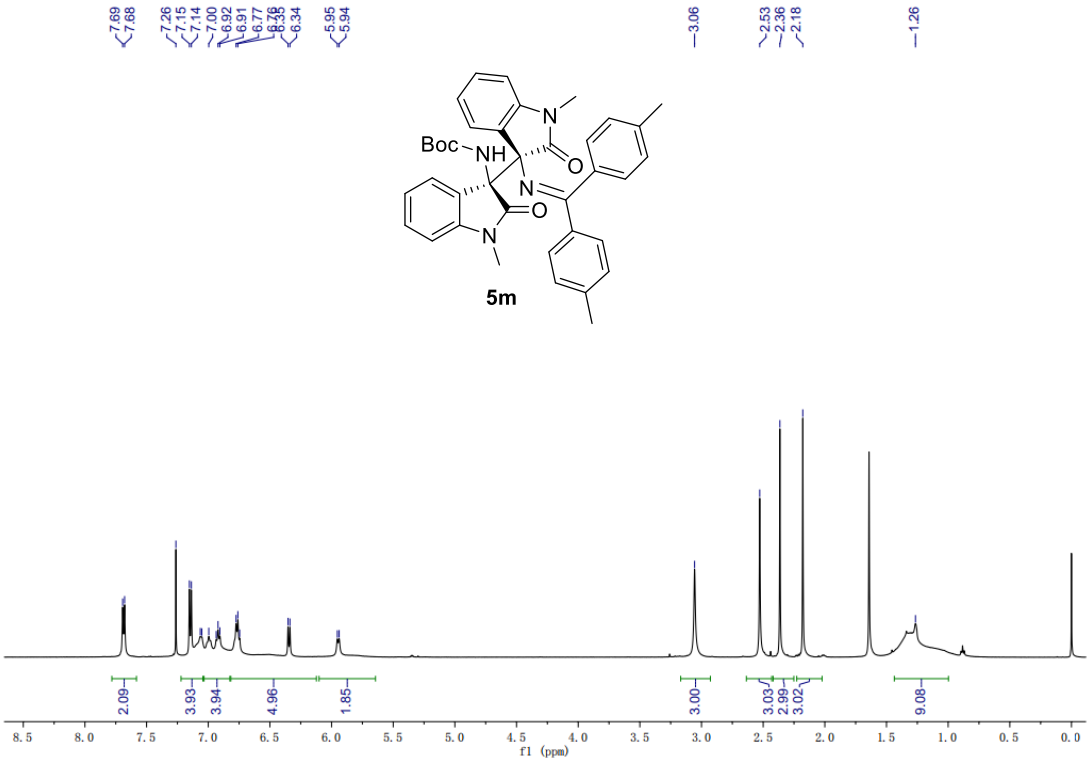

173.92
173.53
170.58
165.90
163.90
162.97
160.99
154.74
143.70
142.84
131.44
131.36
129.62
129.16
124.24
121.91
121.44
115.37
115.20
107.50
107.15
80.01
77.41
77.16
76.91
71.12
65.75
28.27
25.84
25.27
136.09
131.95
131.92
131.44
131.36
129.91
129.62
129.16
127.50
124.24
122.70
121.91
121.44
115.37
115.20
114.24
114.07
Boc
NH
N
O
F
5k
f1 (ppm)

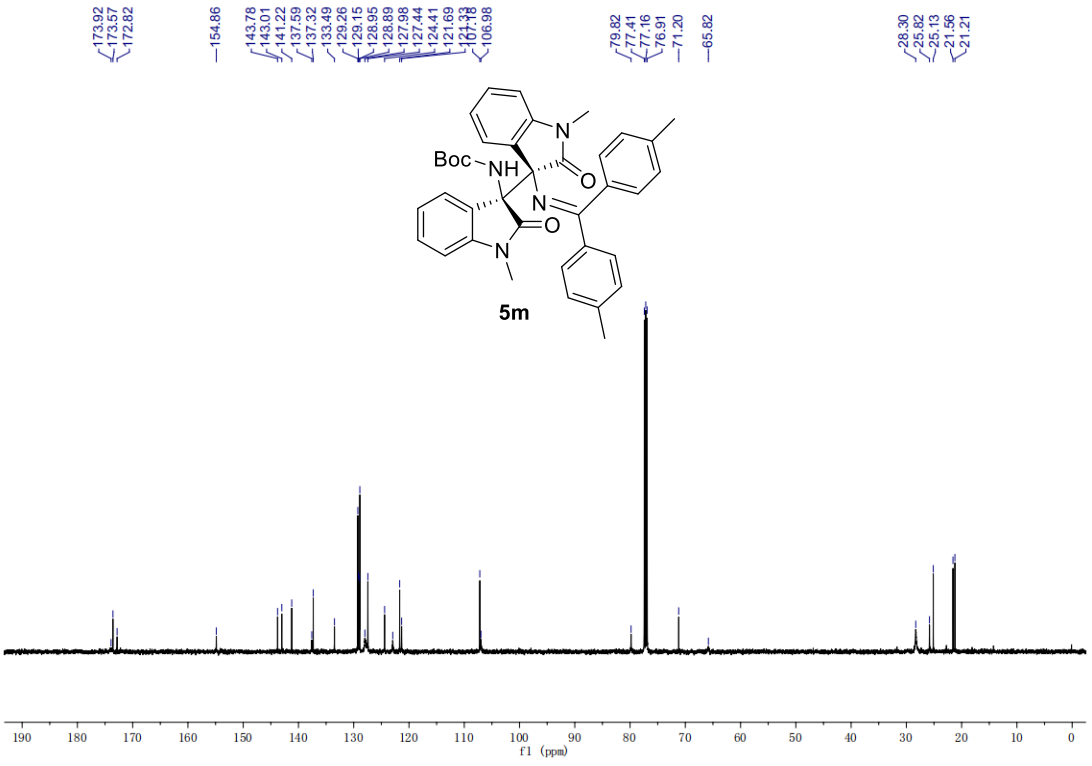
f1 (ppm)

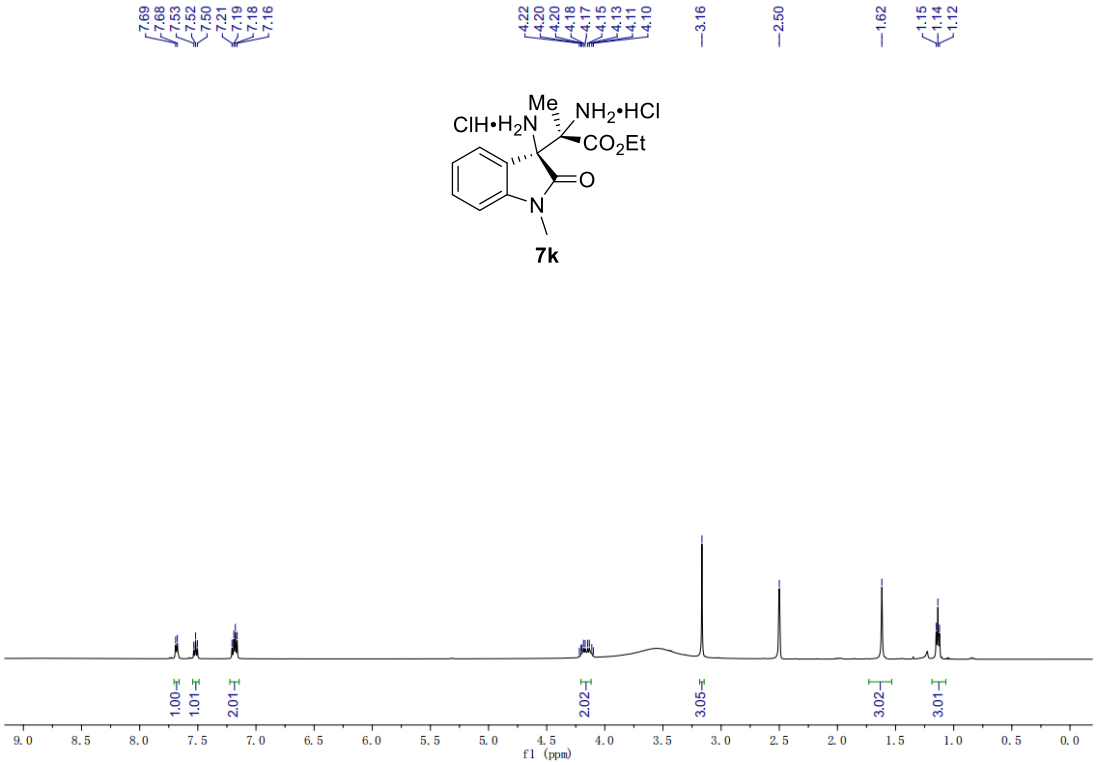

109.36
112.45
Boc
NH
N
O
F
5k
f1 (ppm)


7.73
7.71
7.34
7.32
7.26
7.03
7.02
6.97
6.79
6.38
6.36
6.34
6.03
6.01
5.87
3.07
2.60
1.26
Boc
NH
N
O
Cl
5l
2.04
2.04
5.86
3.95
1.05
0.97
0.82
3.00
3.00
9.05
f1 (ppm)

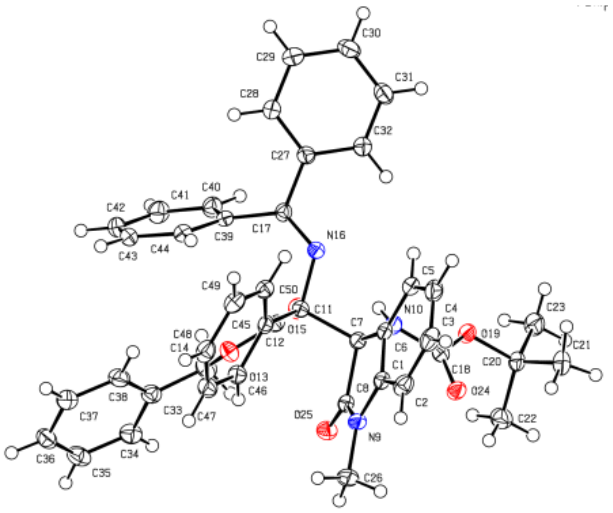

173.76
173.44
170.42
154.70
143.70
142.88
137.59
134.16
134.11
130.47
129.73
129.21
128.57
127.43
127.30
124.28
122.69
121.99
107.16
80.05
77.41
77.16
76.91
71.13
65.66
28.27
25.86
25.24
Boc
NH
N
O
Cl
5l
f1 (ppm)

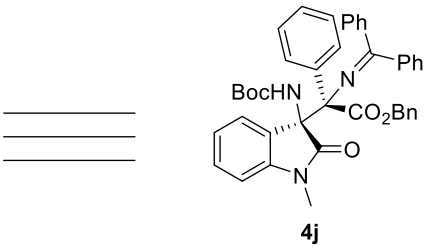

7.69
7.68
7.26
7.15
7.14
7.00
6.92
6.91
6.77
6.38
6.36
6.34
5.95
5.94
3.06
2.53
2.36
2.18
1.26
Boc
NH
N
O
N
O
N
O
5m
2.09
3.93
3.94
4.96
1.85
3.00
3.03
2.99
3.02
9.08
f1 (ppm)


173.92
173.57
172.82
154.86
143.78
143.01
141.22
137.59
137.32
133.49
129.26
129.15
128.95
128.89
127.98
127.44
124.41
121.69
121.33
107.18
106.98
79.82
77.41
77.16
76.91
71.20
65.82
28.30
25.82
25.13
21.56
21.21
Boc
NH
N
O
N
O
N
O
5m
f1 (ppm)


7.69
7.68
7.53
7.52
7.50
7.21
7.19
7.18
7.16
4.22
4.20
4.20
4.18
4.17
4.15
4.13
4.11
4.10
3.16
2.50
1.62
1.15
1.14
1.12
Me
NH2•HCl
ClH•H2N
CO2Et
O
N
7k
1.00
1.01
2.01
2.02
3.05
3.02
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
170.48
167.07
144.03
131.83
128.71
126.78
123.14
109.80
63.49
62.45
61.75
40.10
39.93
39.77
39.60
39.43
39.27
39.10
26.91
17.83
13.58
Me
NH2•HCl
ClH•H2N
CO2Et
O
N
7k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Crystallographic Data for Compound 4j (CCDC: 2031206)





4j

Bond precision: C-C = 0.0018 A Wavelength=1.54184

Cell: a=11.5527(2) b=12.5920(2) c=12.7428(2)
alpha=93.774(1) beta=106.734(1) gamma=92.270(1)
Temperature: 100 K

	Calculated	Reported
Volume	1768.04(5)	1768.03(5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C42 H39 N3 O5	C42 H39 N3 O5
Sum formula	C42 H39 N3 O5	C42 H39 N3 O5
Mr	665.76	665.76
Dx,g cm-3	1.251	1.251
Z	2	2
Mu (mm-1)	0.661	0.661
F000	704.0	704.0
F000'	706.09	
h,k,lmax	14,15,16	14,15,16
Nref	7438	7101
Tmin,Tmax	0.820,0.876	0.871,1.000
Tmin'	0.820	

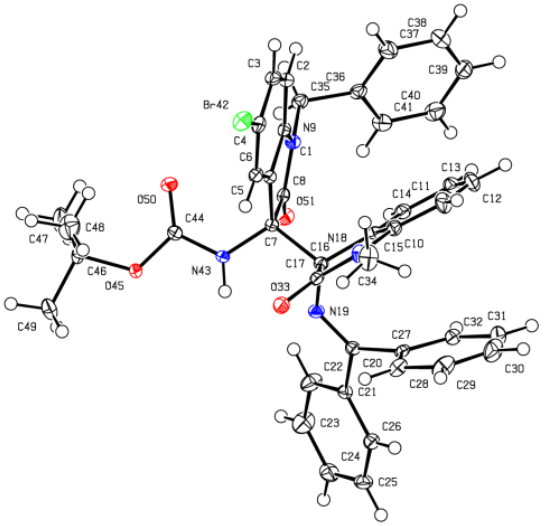
Correction method= # Reported T Limits: Tmin=0.871 Tmax=1.000
AbsCorr = MULTI-SCAN

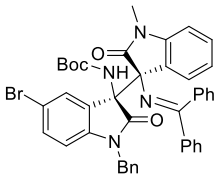
Data completeness= 0.955 Theta(max)= 76.553

R(reflections)= 0.0339(6346) wR2(reflections)= 0.0884(7101)

S = 1.070 Npar= 460

Crystallographic Data for Compound 5e (CCDC: 2027504)





5e

Bond precision: C-C = 0.0025 A Wavelength=1.54184

Cell: a=9.4441(1) b=11.6792(1) c=17.5110(1)
alpha=96.600(1) beta=104.395(1) gamma=100.362(1)
Temperature: 100 K

	Calculated	Reported
Volume	1814.29(3)	1814.29(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C42 H37 Br N4 O4	C42 H37 Br N4 O4
Sum formula	C42 H37 Br N4 O4	C42 H37 Br N4 O4
Mr	741.66	741.66
Dx,g cm-3	1.358	1.358
Z	2	2
Mu (mm-1)	1.930	1.930
F000	768.0	768.0
F000'	768.69	
h,k,lmax	11,14,22	11,14,21
Nref	7566	7215
Tmin,Tmax	0.588,0.680	0.836,1.000
Tmin'	0.534	

Correction method= # Reported T Limits: Tmin=0.836 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.954 Theta(max)= 75.988

R(reflections)= 0.0322(7002) wR2(reflections)= 0.0868(7215)

S = 1.098 Npar= 468
