Supplementary Information for:

Dearomative 1,6-Enyne Cycloisomerization of Alkyne-Tethered Benzofurans and Indoles via a 6-*endo*-dig Cyclization

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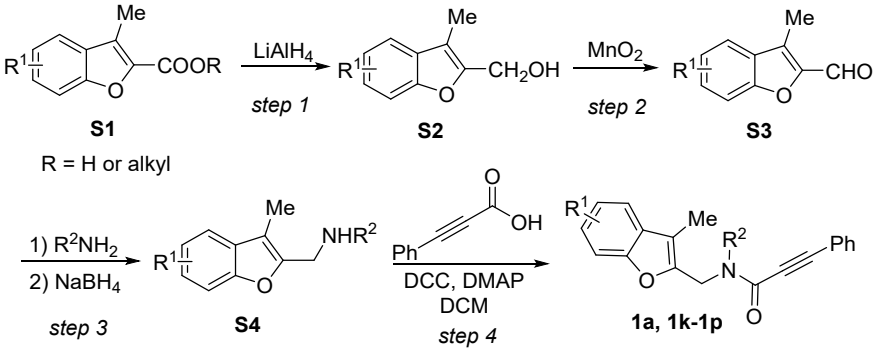
1. General information

Reactions and manipluations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware dried by heating gun for 5 min prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 MHz or 500 MHz using $CDCl_3$ as solvent with TMS as the internal standard. Anhydrous 1,4-dioxane, THF, and toluene were freshly distilled over Na and benzophenone. Anhydrous DCM and DMF were freshly distilled over CaH_2. MeOH was freshly distilled with magnesium and iodine. Melting points were measured on a Büchi Melting Point B-545 apparatus and uncorrected. Commercial reagents were used as received without further purification unless otherwise noticed. HRMS were recorded on Thermo Scientific LTQ Orbitrap XL or Agilent 6210 TOF LC/MS mass spectrometer. Single crystal X-ray diffraction analysis was determined using Bruker D8 Venture. Column chromatography was carried out using silica gel (200-300 mesh).

2. Synthesis of C2-alkyne-tethered benzofurans 1

2.1 For compounds 1a, 1k-1p



Step 1:[1]

To a dried flask was charged with $LiAlH_4$ (60.0 mmol, 2.0 equiv) and THF (50 mL). A solution of **S1** (30.0 mmol, 1.0 equiv) in THF (10 mL) was slowly added into the mixture under N_2 at 0 °C. The resulting mixture was stirred at room temperature overnight. The reaction system was then quenched by 10% NaOH solution (15 mL), extracted with ethyl acetate, and dried over Na_2SO_4. The organic phase was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v) to give compound **S2**.

Step 2:[2]

To a dried flask was charged with **S2** (18.0 mmol, 1.0 equiv), MnO_2 (120 mmol, 10.4 g), and anhydrous CH_2Cl_2 (30 mL) under air atmosphere. The resulting mixture was stirred at room temperature for 48 h. When the reaction was completed, the solid was removed by flash filtration. The filtrate was concentrated under reduced pressure and

purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v) to give compound **S3**.

Step 3:[3]

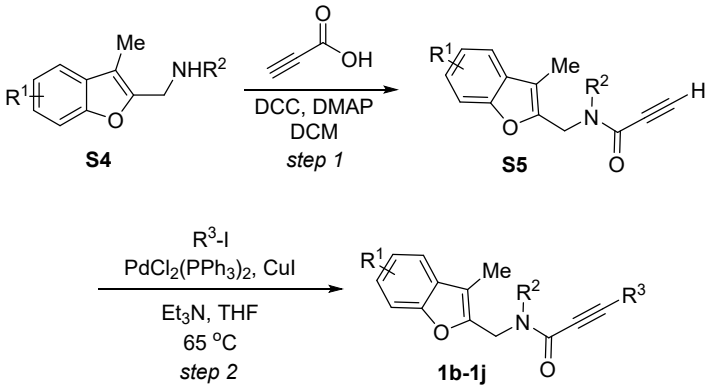
To a dried flask was charged with **S3** (10.0 mmol, 1.0 equiv), anhydrous $MgSO_4$ (50.0 mmol, 6.0 g), and anhydrous CH_2Cl_2 (25 mL) under nitrogen atmosphere. R^2NH_2 (9.0 mmol, 0.98 mL) was then added via a syringe. The resulting mixture was stirred at 50 °C (oil bath) for 12 h. When the reaction was completed, the solution was concentrated under reduced pressure. The crude was then used without further purification.

To the solution of the above crude in anhydrous MeOH (25 mL) was added $NaBH_4$ (15.0 mmol, 0.57 g) at 0 °C in portions. The resulting mixture was then stirred at room temperature for 2 h. The solution was extracted with ethyl acetate and the organic phase was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v) to give compound **S4**.

Step 4:[4]

To a stirred solution of **S4** (6.0 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) was added 4-DMAP (10 mol%) and DCC (6.6 mmol, 1.36 g) at 0 °C. The mixture was stirred at 0 °C for 5 min and a solution of phenylpropiolic acid (6.6 mmol) in CH_2Cl_2 (10 mL) was then added slowly. The resulting mixture was stirred at room temperature for 10 h. When the reaction was completed, the solid was removed by flash filtration. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v) to give compounds **1a**, **1k-1p**.

2.2 For compounds 1b-1j



Step 1:[4]

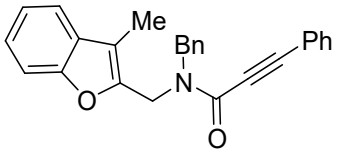
To a stirred solution of **S4** (6.0 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) were added 4-DMAP (10.0 mol%) and DCC (6.6 mmol, 1.36 g) at 0 °C. The mixture was stirred at 0 °C for 5 min and a solution of propiolic acid (6.6 mmol) in CH_2Cl_2 (10 mL) was then

added slowly. The resulting mixture was stirred at room temperature for 10 h. When the reaction was completed, the solid was removed by flash filtration. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v) to give compound **S5**.

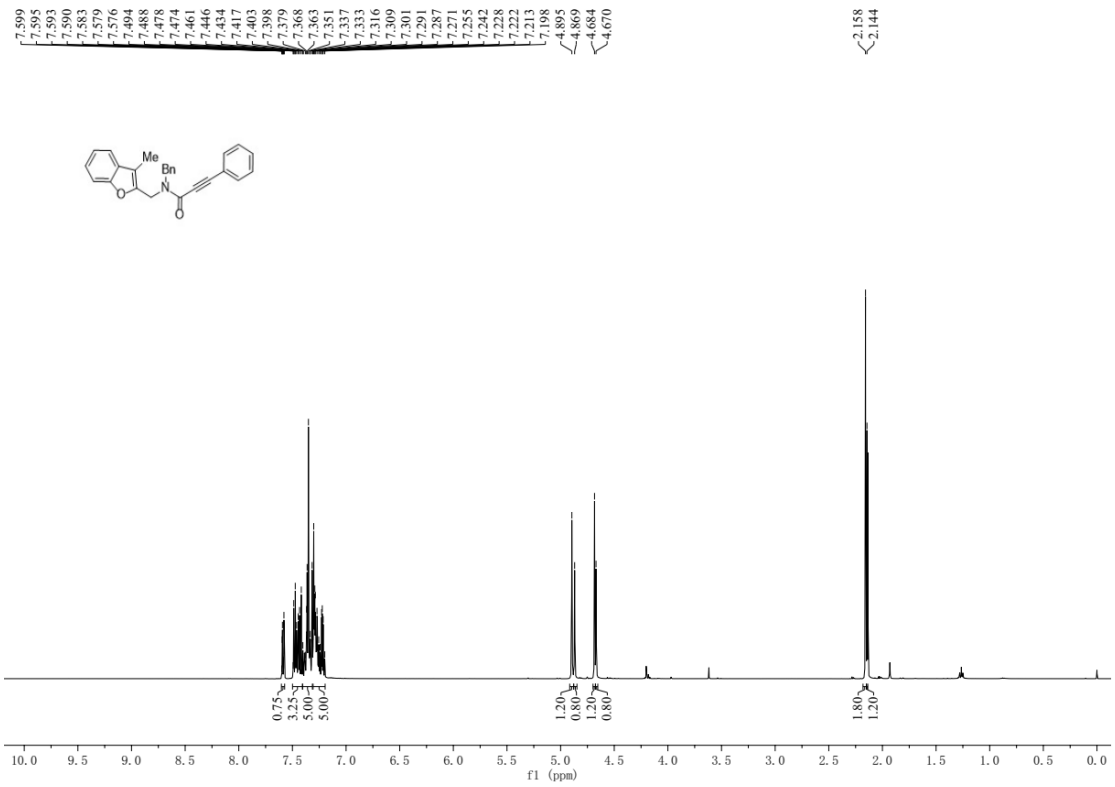
Step 2:[5]

To a dried Schlenk tube was charged with $PdCl_2(PPh_3)_2$ (2.0 mol%, 56.2 mg), CuI (4.0 mol%, 30.5 mg), **S5** (4.0 mmol), Et_3N (3.0 equiv), and the corresponding aryliodines (R^3-I, 6.0 mmol, 1.5 equiv) under N_2. THF (25 mL) was then introduced via a syringe. The resulting mixture was stirred at 65 °C (oil bath) for 12 h. After filtration, the solution was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v) to give compounds **1b-1j**.

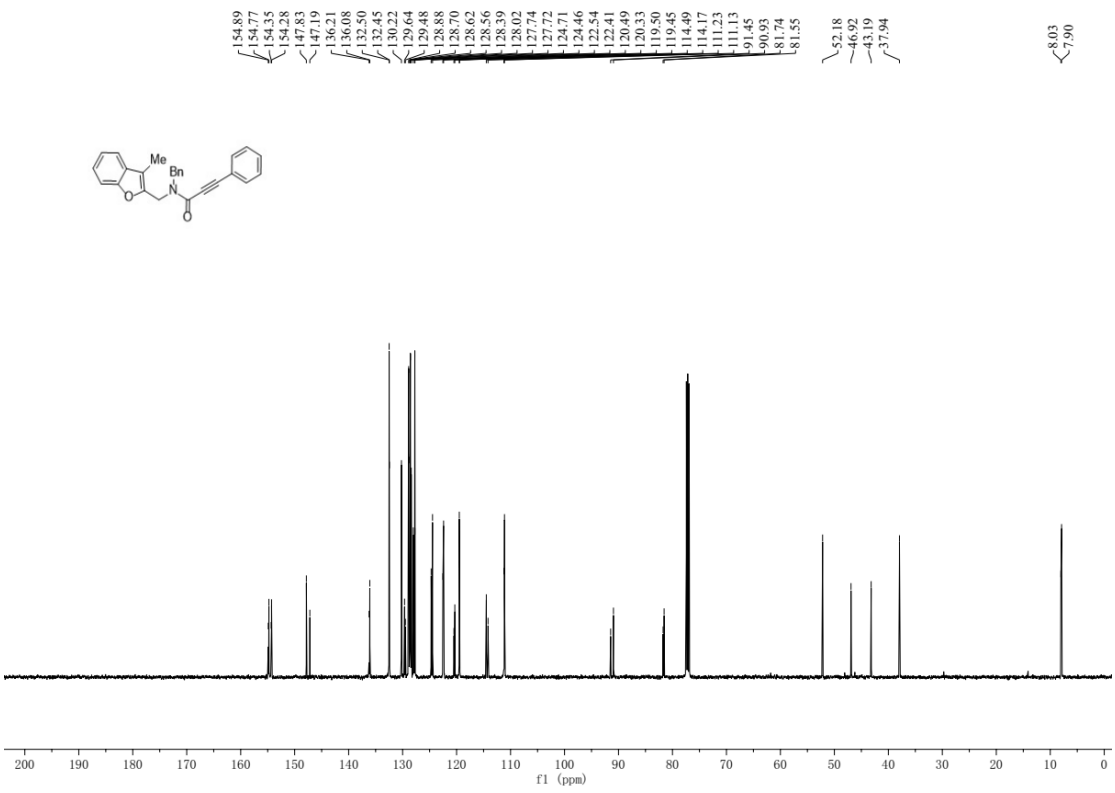
N-Benzyl-N-((3-methylbenzofuran-2-yl)methyl)-3-phenylpropiolamide (1a):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow oil; 85% yield (for the last step); A 3:2 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60-7.58 (m, 0.75H), 7.49-7.42 (m, 3,25H), 7.40-7.32 (m, 5.00H), 7.31-7.20 (m, 5.00H), 4.90 (s, 1.20H), 4.87 (s, 0.80H), 4.68 (s, 1.20H), 4.67 (s, 0.80H), 2.16 (s, 1.80H), 2.14 (s, 1.20H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9, 154.8, 154.4, 154.3, 147.8, 147.2, 136.2, 136.1, 132.50, 132.45, 130.2, 129.6, 129.5, 128.9, 128.7, 128.62, 128.56, 128.4, 128.0, 127.74, 127.72, 124.7, 124.5, 122.5, 122.4, 120.5, 120.3, 119.50, 119.45, 114.5, 114.2, 111.2, 111.1, 91.5, 90.9, 81.7, 81.6, 52.2, 46.9, 43.2, 37.9, 8.0, 7.9. HRMS *m/z* (ESI+): Calculated for $C_{26}H_{22}NO_2^+$ ($[M+H]^+$): 380.1645, found 380.1650.

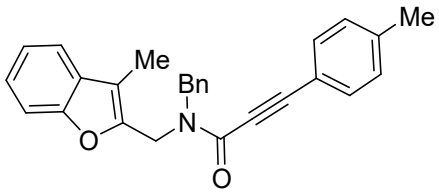


^{1}H NMR of compound **1a** (500 MHz, $CDCl_3$)

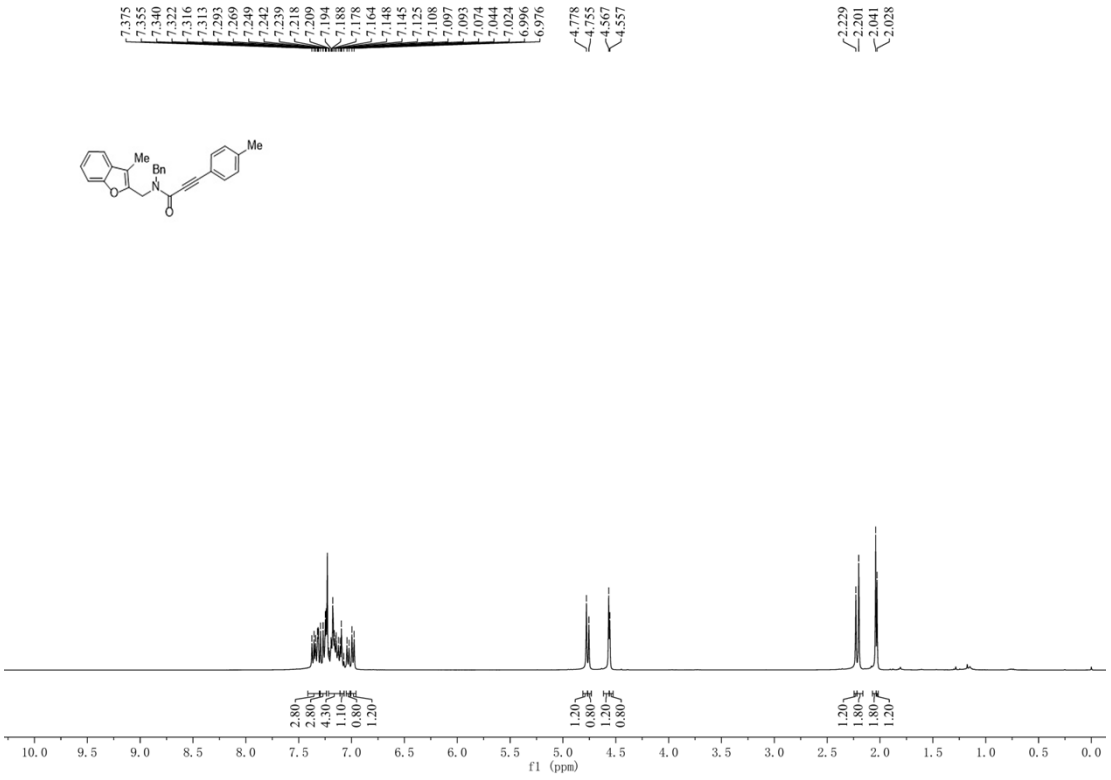


^{13}C NMR of compound **1a** (125 MHz, $CDCl_3$)

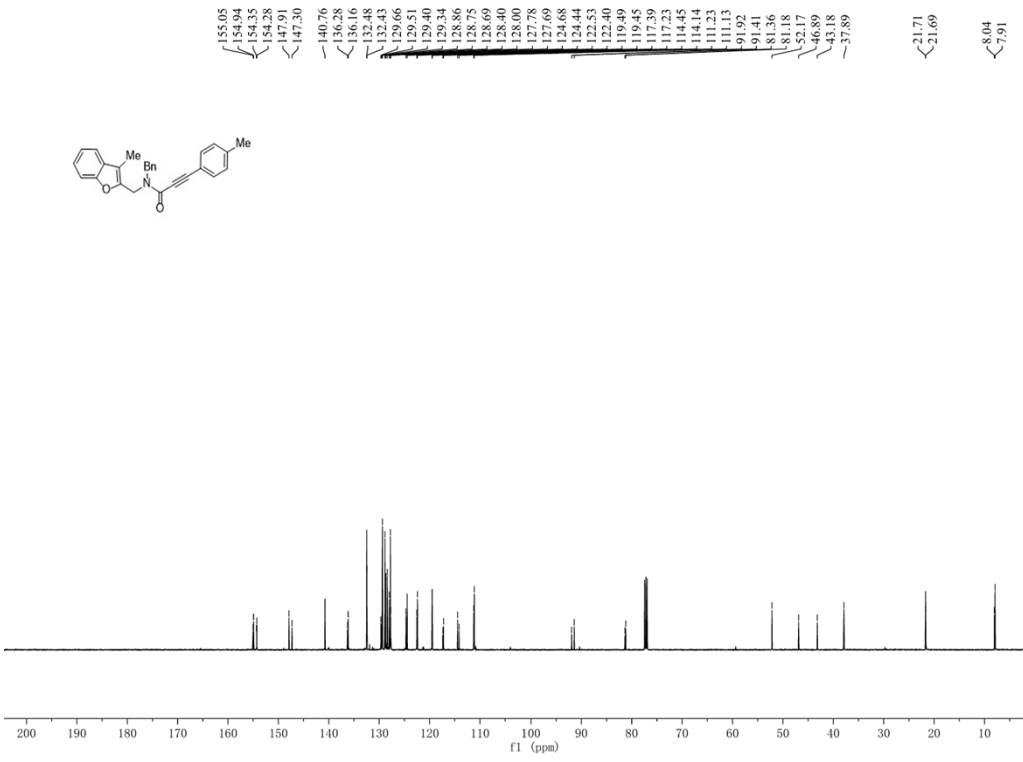
N-Benzyl-N-((3-methylbenzofuran-2-yl)methyl)-3-(p-tolyl)propiolamide (1b):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow oil; 63% yield (for the last step); A 3:2 isomeric mixture; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.31 (m, 2.80H), 7.29-7.24 (m, 2.80H), 7.22-7.13 (m, 4.30H), 7.11-7.07 (m, 1.10H), 7.03 (d, J = 8.0 Hz, 0.80H), 6.99 (d, J = 8.0 Hz, 1.20H), 4.78 (s, 1.20H), 4.75 (s, 0.80H), 4.57 (s, 1.20H), 4.56 (s, 0.80H), 2.23 (s, 1.20H), 2.20 (s, 1.80H), 2.04 (s, 1.80H), 2.03 (s, 1.20H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.1, 154.9, 154.4, 154.3, 147.9, 147.3, 140.8, 136.3, 136.2, 132.5, 132.4, 129.7, 129.5, 129.4, 129.3, 128.9, 128.8, 128.7, 128.4, 128.0, 127.8, 127.7, 124.7, 124.4, 122.5, 122.4, 119.49, 119.45, 117.4, 117.2, 114.5, 114.1, 111.2, 111.1, 91.9, 91.4, 81.4, 81.2, 52.2, 46.9, 43.2, 37.9, 21.71, 21.69, 8.0, 7.9. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_2^+$ ([M+H]$^+$): 394.1802, found 394.1806.

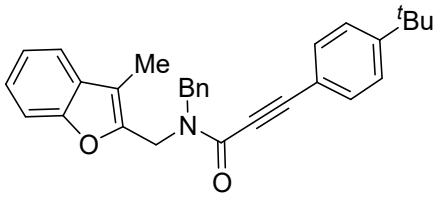


^{1}H NMR of compound **1b** (400 MHz, $CDCl_3$)

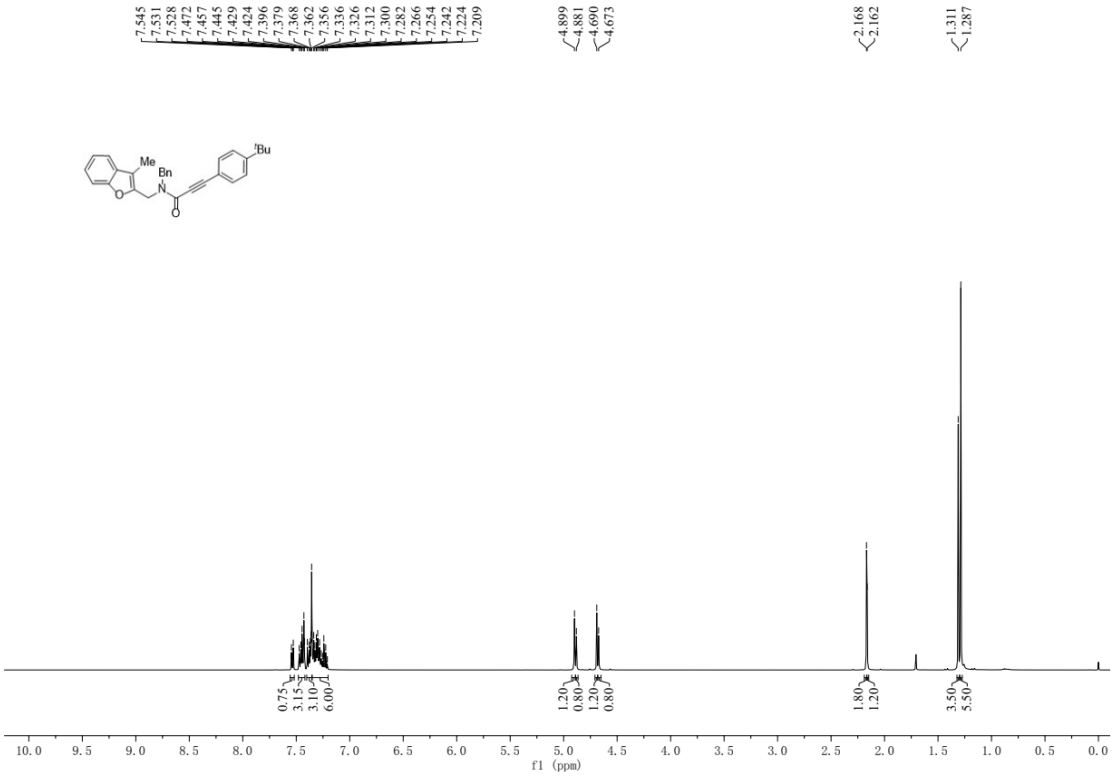


^{13}C NMR of compound **1b** (125 MHz, $CDCl_3$)

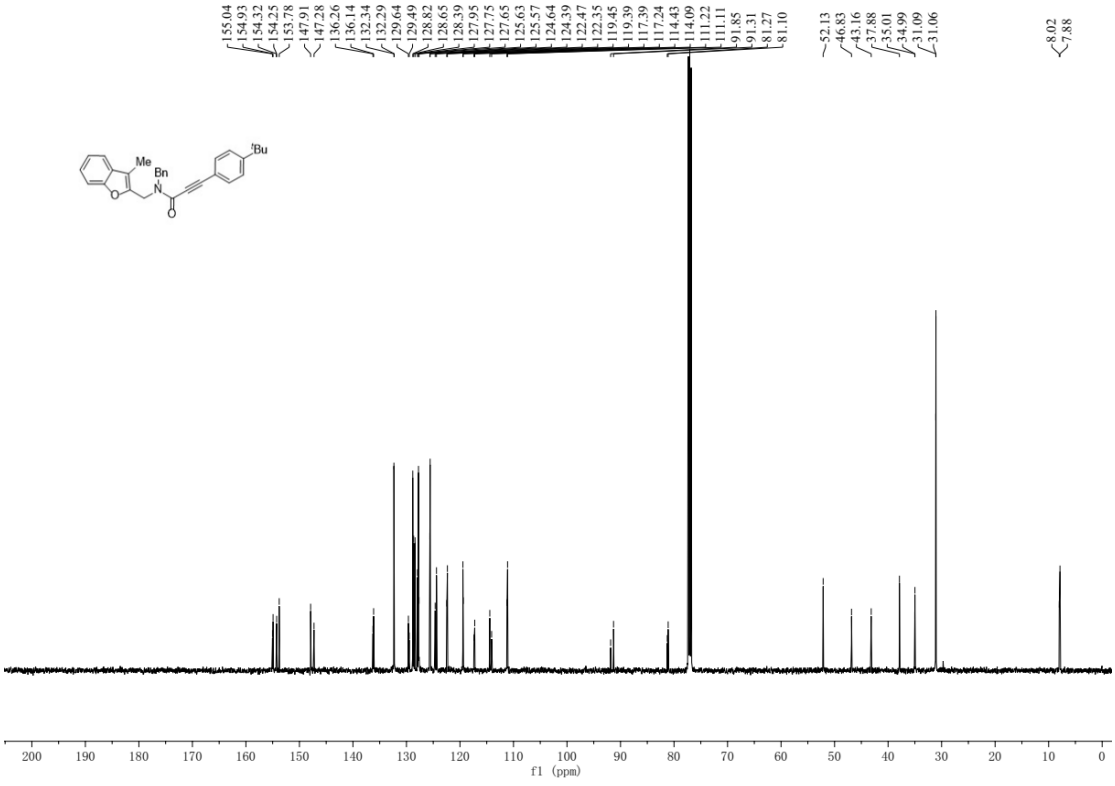
N-Benzyl-3-(4-(tert-butyl)phenyl)-N-((3-methylbenzofuran-2-yl)methyl)-propiolamide (1c):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); light yellow solid, Mp = 135-136 °C; 53% yield (for the last step); A 3:2 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55-7.53 (m, 0.75H), 7.47-7.42 (m, 3.15H), 7.40-7.36 (m, 3.10H), 7.34-7.21 (m, 6.00H), 4.90 (s, 1.20H), 4.88 (s, 0.80H), 4.69 (s, 1.20H), 4.67 (s, 0.80H), 2.17 (s, 1.80H), 2.16 (s, 1.20H), 1.31 (s, 3.50H), 1.29 (s, 5.50H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.0, 154.9, 154.32, 154.25, 153.8, 147.9, 147.3, 136.3, 136.1, 132.34, 132.29, 129.6, 129.5, 128.8, 128.7, 128.4, 128.0, 127.8, 127.7, 125.63, 125.57, 124.6, 124.4, 122.5, 122.4, 119.5, 119.4, 117.4, 117.2, 114.4, 114.1, 111.2, 111.1, 91.9, 91.3, 81.3, 81.1, 52.1, 46.8, 43.2, 37.9, 35.01, 34.99, 31.09, 31.06, 8.0, 7.9. HRMS *m/z* (ESI+): Calculated for $C_{30}H_{30}NO_2^+$ ([M+H]$^+$): 436.2271, found 436.2276.

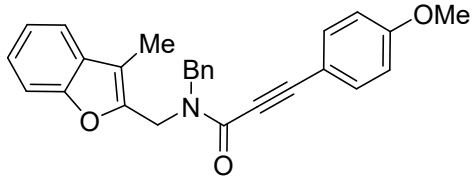


^{1}H NMR of compound **1c** (500 MHz, $CDCl_3$)

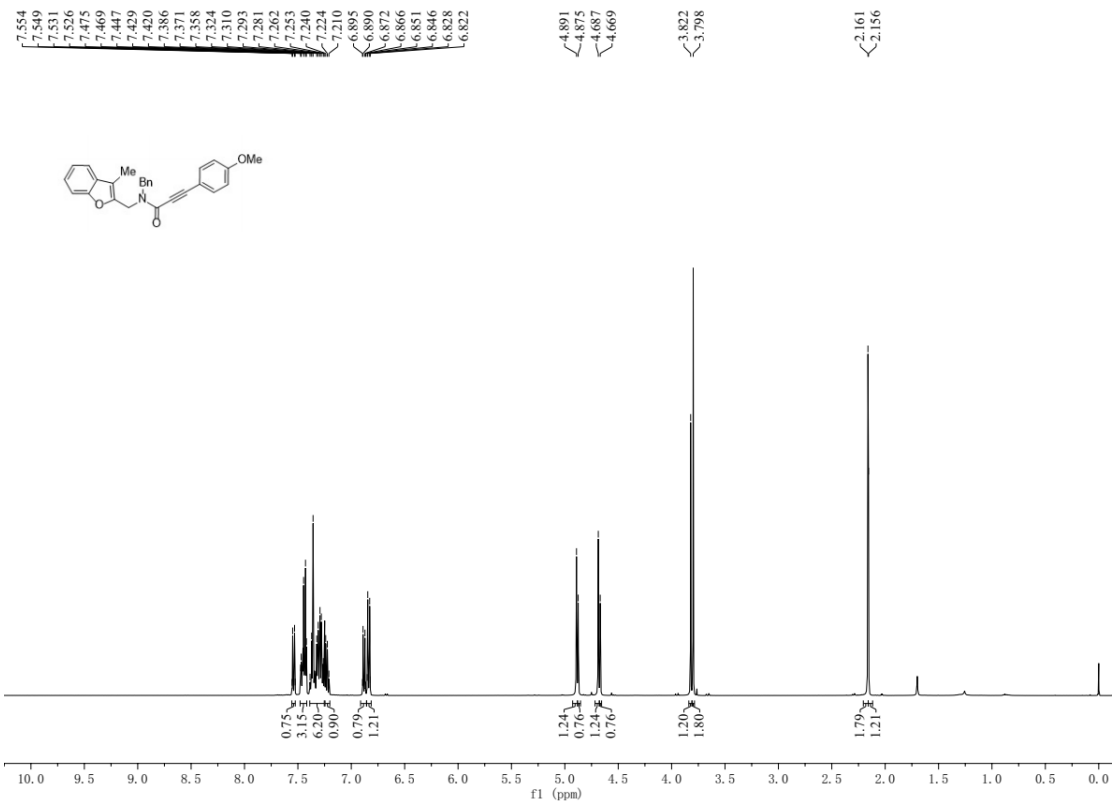


^{13}C NMR of compound **1c** (125 MHz, $CDCl_3$)

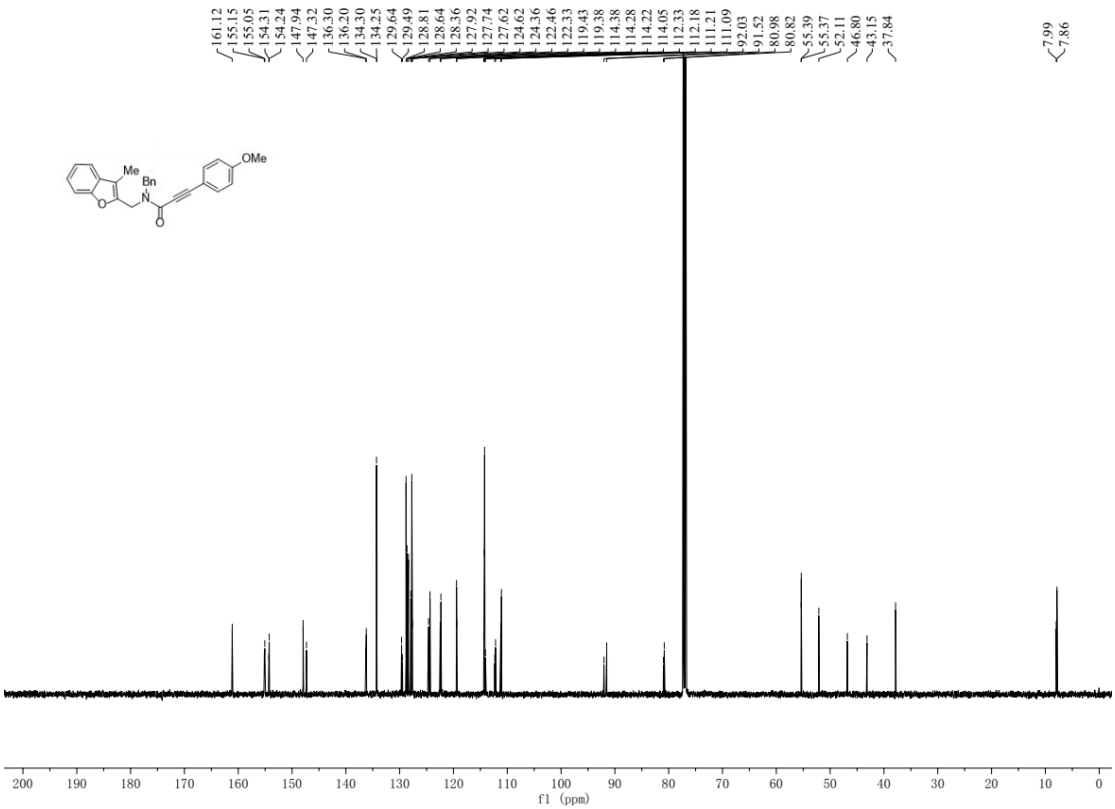
N-Benzyl-3-(4-methoxyphenyl)-N-((3-methylbenzofuran-2-yl)methyl)propiolamide (1d):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); light yellow solid, Mp = 114-115 °C; 50% yield (for the last step); A 3:2 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55-7.53 (m, 0.75H), 7.48-7.42 (m, 3.15H), 7.39-7.25 (m, 6.20H), 7.24-7.21 (m, 0.90H), 6.90-6.87 (m, 0.79H), 6.85-6.82 (m, 1.21H), 4.89 (s, 1.24H), 4.88 (s, 0.76H), 4.69 (s, 1.24H), 4.67 (s, 0.76H), 3.82 (s, 1.20H), 3.80 (s, 1.80H), 2.161 (s, 1.79H), 2.156 (s, 1.21H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.1, 155.2, 155.1, 154.3, 154.2, 147.9, 147.3, 136.3, 136.2, 134.30, 134.25, 129.6, 129.5, 128.8, 128.6, 128.4, 127.9, 127.7, 127.6, 124.6, 124.4, 122.5, 122.3, 119.43, 119.38, 114.4, 114.3, 114.2, 114.1, 112.3, 112.2, 111.2, 111.1, 92.0, 91.5, 81.0, 80.8, 55.39, 55.37, 52.1, 46.8, 43.2, 37.8, 8.0, 7.9. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_3^+$ ([M+H]$^+$): 410.1751, found 410.1752.

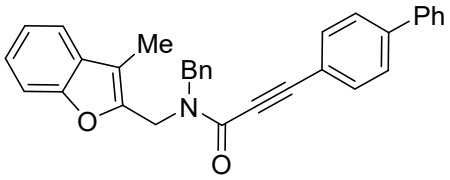


^{1}H NMR of compound **1d** (500 MHz, $CDCl_3$)

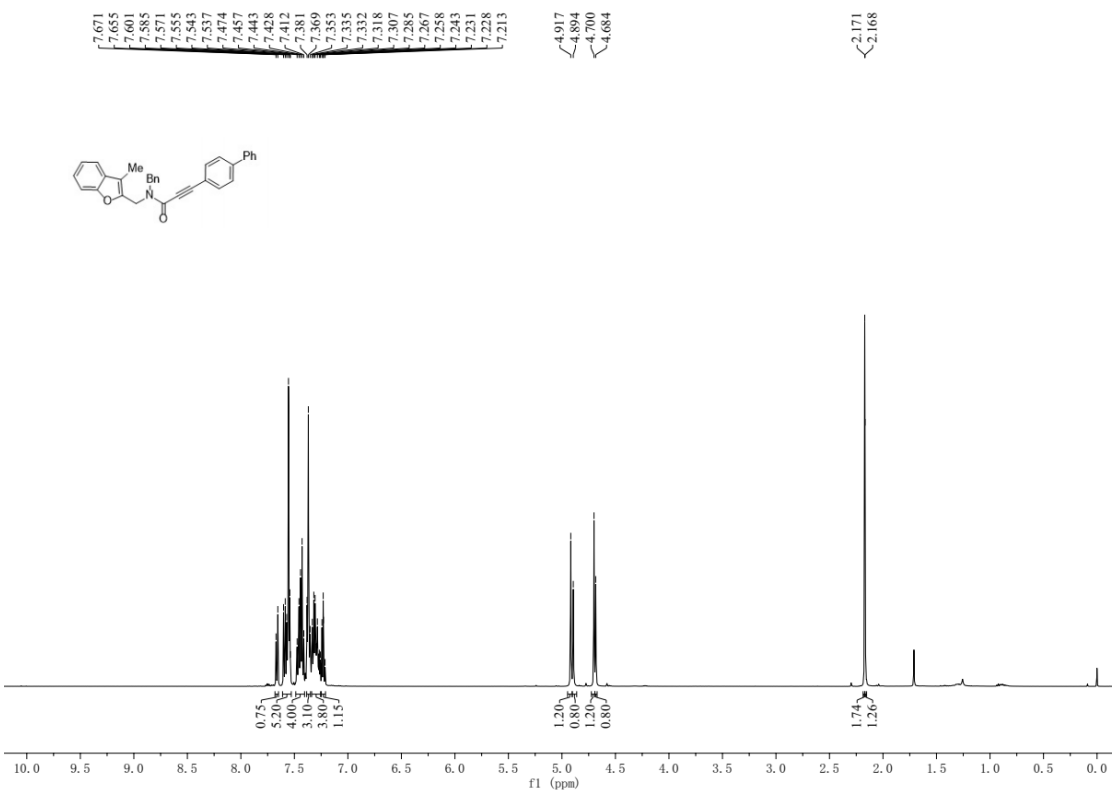


^{13}C NMR of compound **1d** (125 MHz, $CDCl_3$)

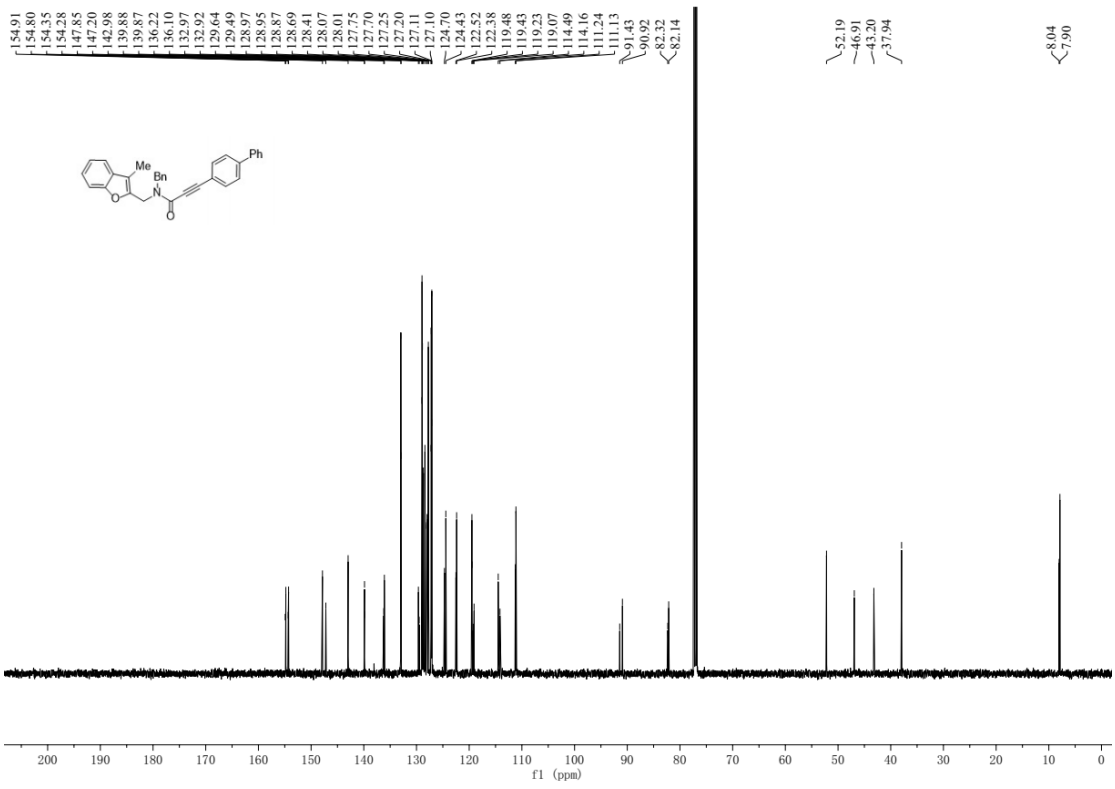
3-([1,1'-Biphenyl]-4-yl)-N-benzyl-N-((3-methylbenzofuran-2-yl)methyl)-propiolamide (1e):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); light yellow solid, Mp = 107-108 °C; 62% yield (for the last step); A 3:2 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67-7.66 (m, 0.75H), 7.60-7.54 (m, 5.20H), 7.47-7.41 (m, 4.00H), 7.38-7.35 (m, 3.10H), 7.34-7.26 (m, 3.80H), 7.24-7.21 (m, 1.15H), 4.92 (s, 1.20H), 4.89 (s, 0.80H), 4.70 (s, 1.20H), 4.68 (s, 0.80H), 2.171 (s, 1.74H), 2.168 (s, 1.26H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9, 154.8, 154.4, 154.3, 147.9, 147.2, 143.0, 139.88, 139.87, 136.2, 136.1, 133.0, 132.9, 129.6, 129.5, 128.97, 128.95, 128.9, 128.7, 128.4, 128.1, 128.0, 127.8, 127.7, 127.3, 127.2, 127.11, 127.10, 124.7, 124.4, 122.5, 122.4, 119.5, 119.4, 119.2, 119.1, 114.5, 114.1, 111.2, 111.1, 91.4, 90.9, 82.3, 82.1, 52.2, 46.9, 43.2, 37.9, 8.0, 7.9. HRMS *m/z* (ESI+): Calculated for $C_{32}H_{26}NO_2^+$ ([M+H]$^+$): 456.1958, found 456.1961.

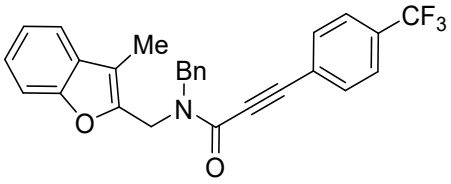


^{1}H NMR of compound **1e** (500 MHz, $CDCl_3$)

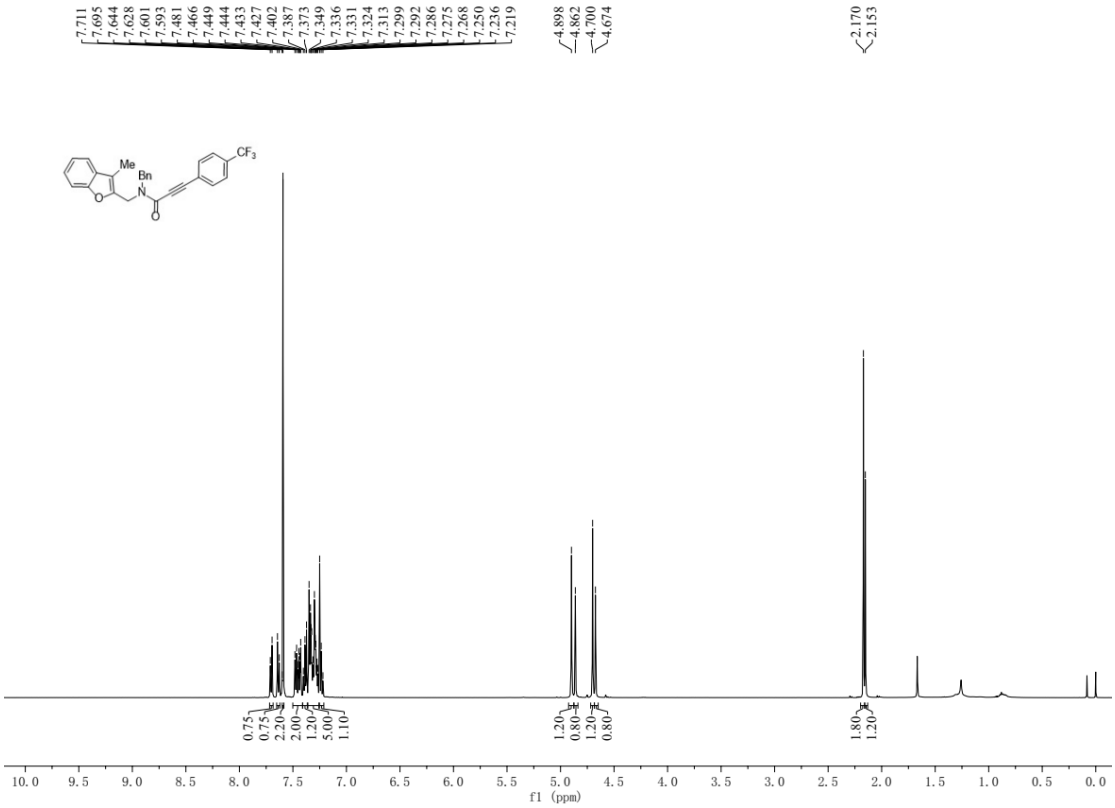


^{13}C NMR of compound **1e** (125 MHz, $CDCl_3$)

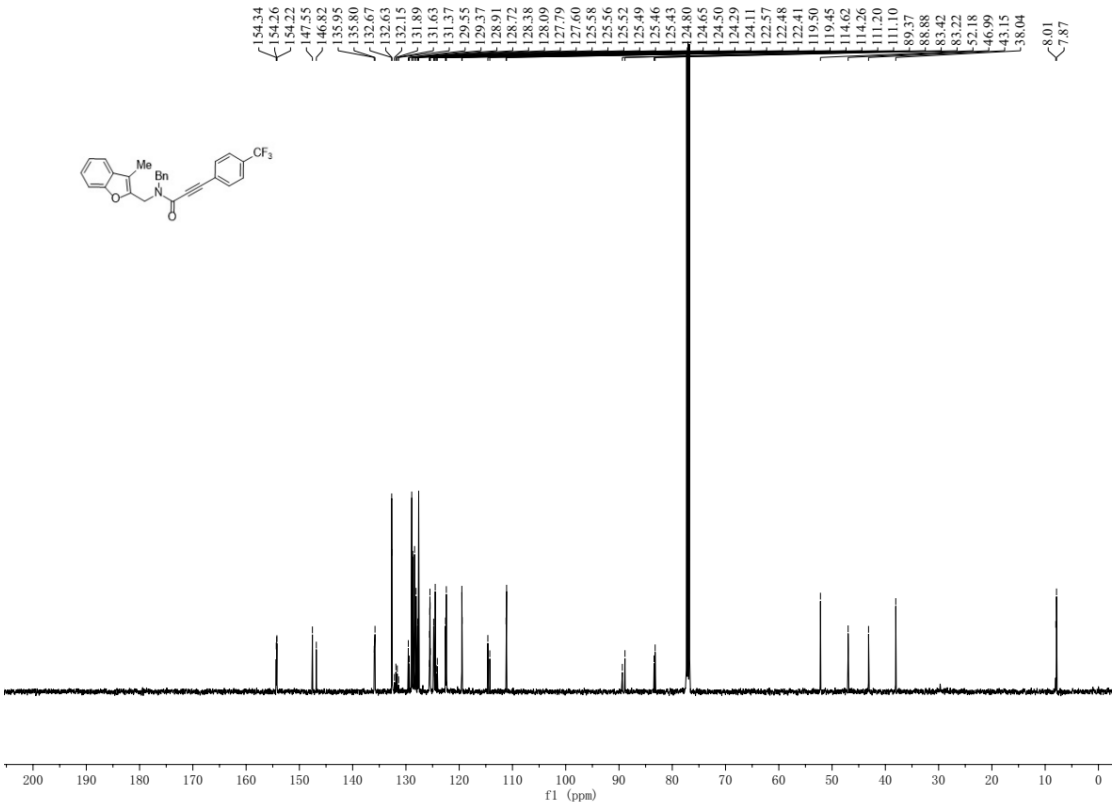
N-Benzyl-N-((3-methylbenzofuran-2-yl)methyl)-3-(4-(trifluoromethyl)phenyl)-propiolamide (1f):



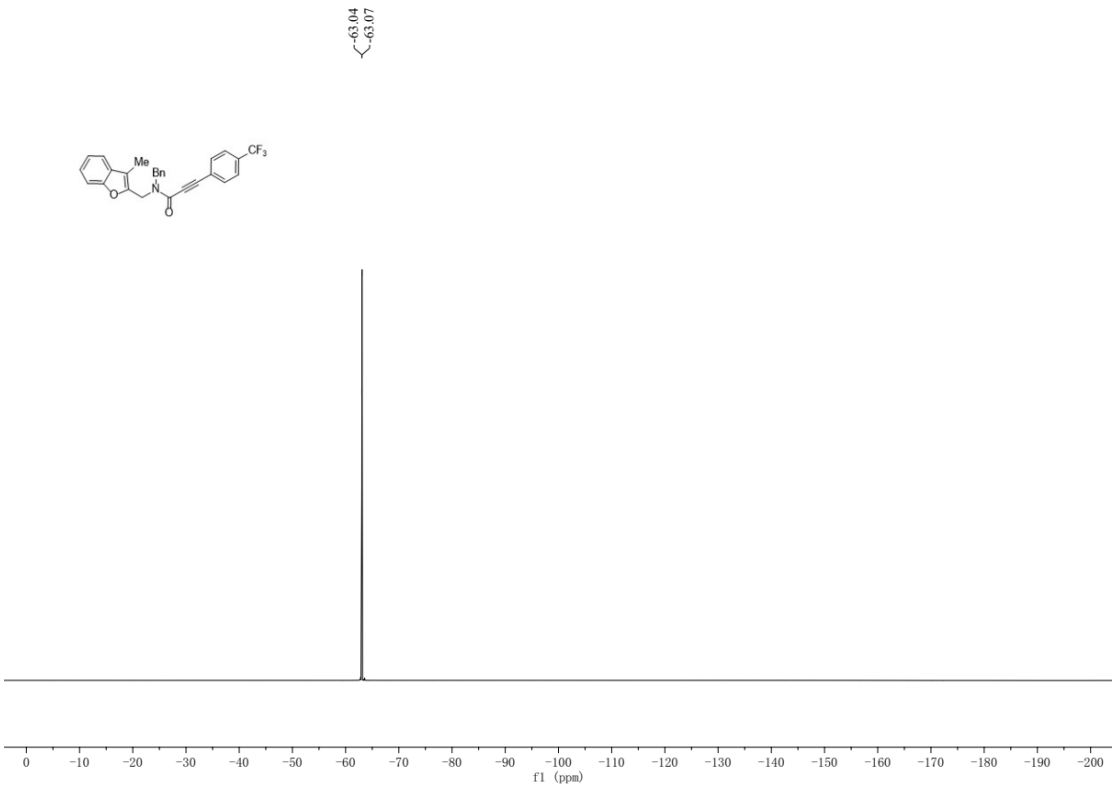
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow solid, Mp = 78-80 °C; 77% yield (for the last step); A 3.4:1 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, J = 8.0 Hz, 0.75H), 7.64 (d, J = 8.0 Hz, 0.75H), 7.60-7.59 (s, 2.20H), 7.48-7.43 (m, 2.00H), 7.40-7.37 (m, 1.20H), 7.35-7.27 (m, 5.00H), 7.25-7.22 (m, 1.10H), 4.90 (s, 1.20H), 4.86 (s, 0.80), 4.70 (s, 1.20H), 4.67 (s, 0.80H), 2.17 (s, 1.80H), 2.15 (s, 1,20H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.34, 154.26, 154.2, 147.6, 146.8, 136.0, 135.8, 132.7, 132.6, 131.8 (q, J = 32.5 Hz), 129.6, 129.4, 128.9, 128.7, 128.4, 128.1, 127.8, 127.6, 125.54 (q, J = 3.8 Hz), 125.48 (q, J = 3.8 Hz), 124.8, 124.7, 124.5, 124.3, 124.1, 122.6, 122.5, 122.4, 119.50, 119.45, 114.6, 114.3, 111.2, 111.1, 89.4, 88.9, 83.4, 83.2, 52.2, 47.0, 43.2, 38.0, 8.0, 7.9. ^{19}F NMR (375 MHz, $CDCl_3$) δ -63.04, -63.07. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{21}F_3NO_2^+$ ([M+H]$^+$): 448.1519, found 448.1521.



^{1}H NMR of compound **1f** (500 MHz, $CDCl_3$)

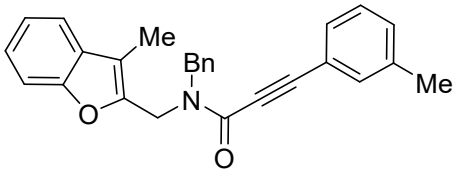


^{13}C NMR of compound **1f** (125 MHz, $CDCl_3$)

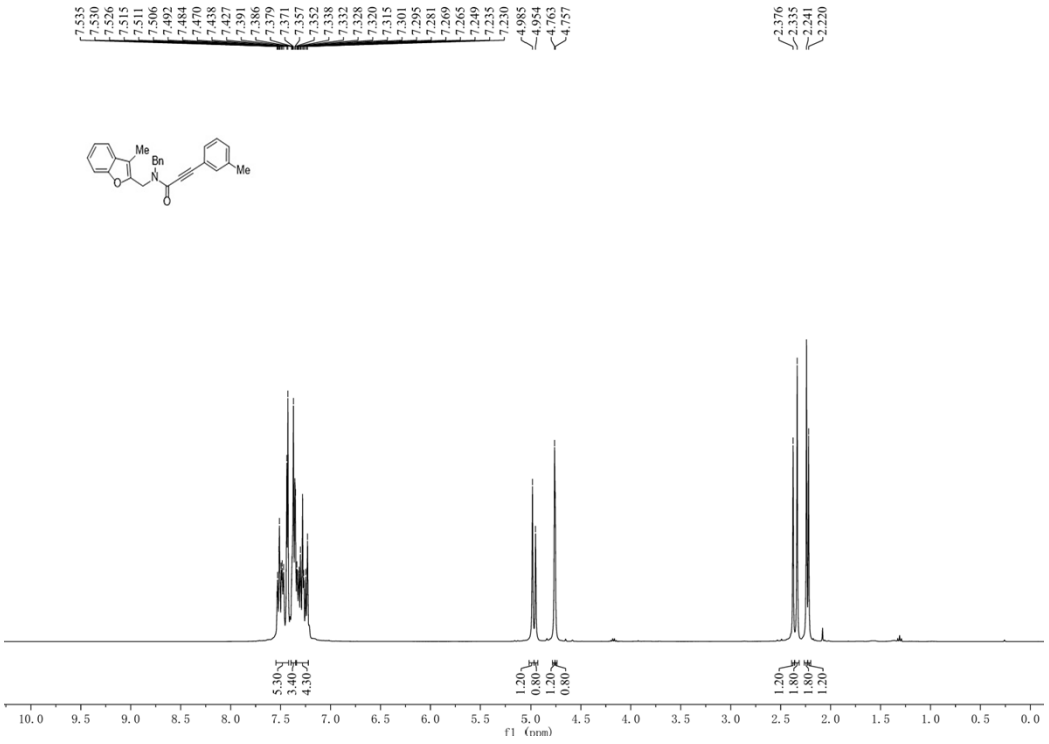


^{19}F NMR of compound **1f** (375 MHz, $CDCl_3$)

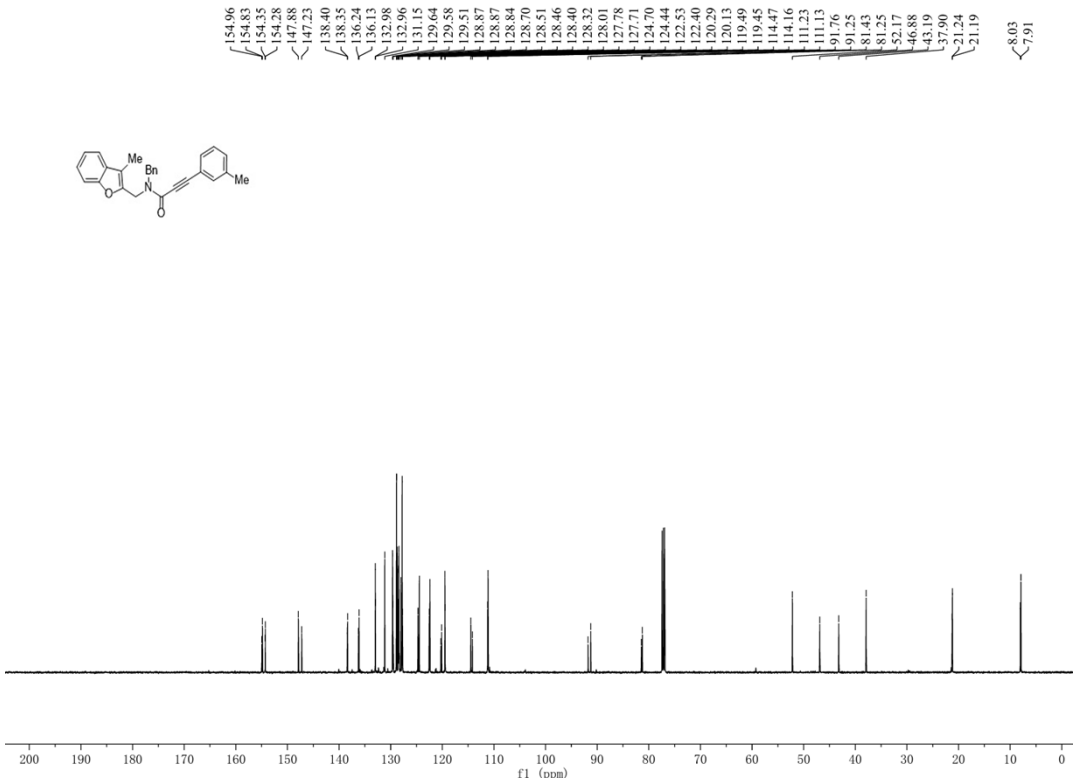
N-Benzyl-N-((3-methylbenzofuran-2-yl)methyl)-3-(m-tolyl)propiolamide (1g):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow oli; 58% yield (for the last step); A 3:2 isomeric mixture; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.43 (m, 5.30H), 7.39-7.35 (m, 3.40H), 7.34-7.23 (m, 4.30H), 4.98 (s, 1.20H), 4.95 (s, 0.80H), 4.76 (s, 1.20H), 4.76 (s, 0.80H), 2.38 (s, 1.20H), 2.33 (s, 1.80H), 2.24 (s, 1.80H), 2.22 (s, 1.20H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.0, 154.8, 154.4, 154.3, 147.9, 147.2, 138.40, 138.35, 136.2, 136.1, 132.98, 132.96, 131.2, 129.64, 129.58, 129.5, 128.9, 128.8, 128.7, 128.51, 128.46, 128.4, 128.3, 128.0, 127.8, 127.7, 124.7, 124.4, 122.5, 122.4, 120.3, 120.1, 119.49, 119.45, 114.5, 114.2, 111.2, 111.1, 91.8, 91.3, 81.4, 81.3, 52.2, 46.9, 43.2, 37.9, 21.24, 21.19, 8.0, 7.9. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_2^+$ ([M+H]$^+$): 394.1802, found 394.1806.

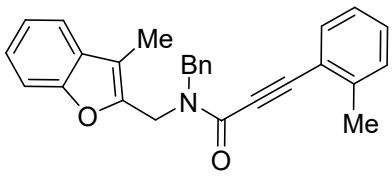


^{1}H NMR of compound **1g** (400 MHz, $CDCl_3$)

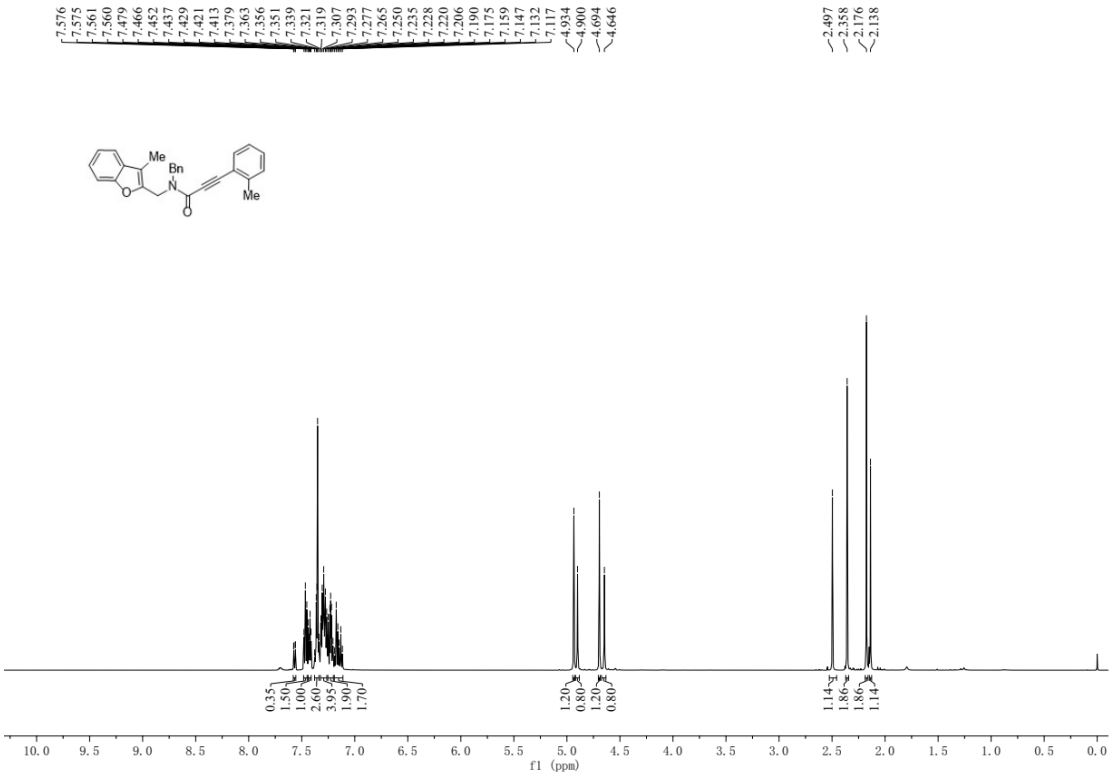


^{13}C NMR of compound **1g** (125 MHz, $CDCl_3$)

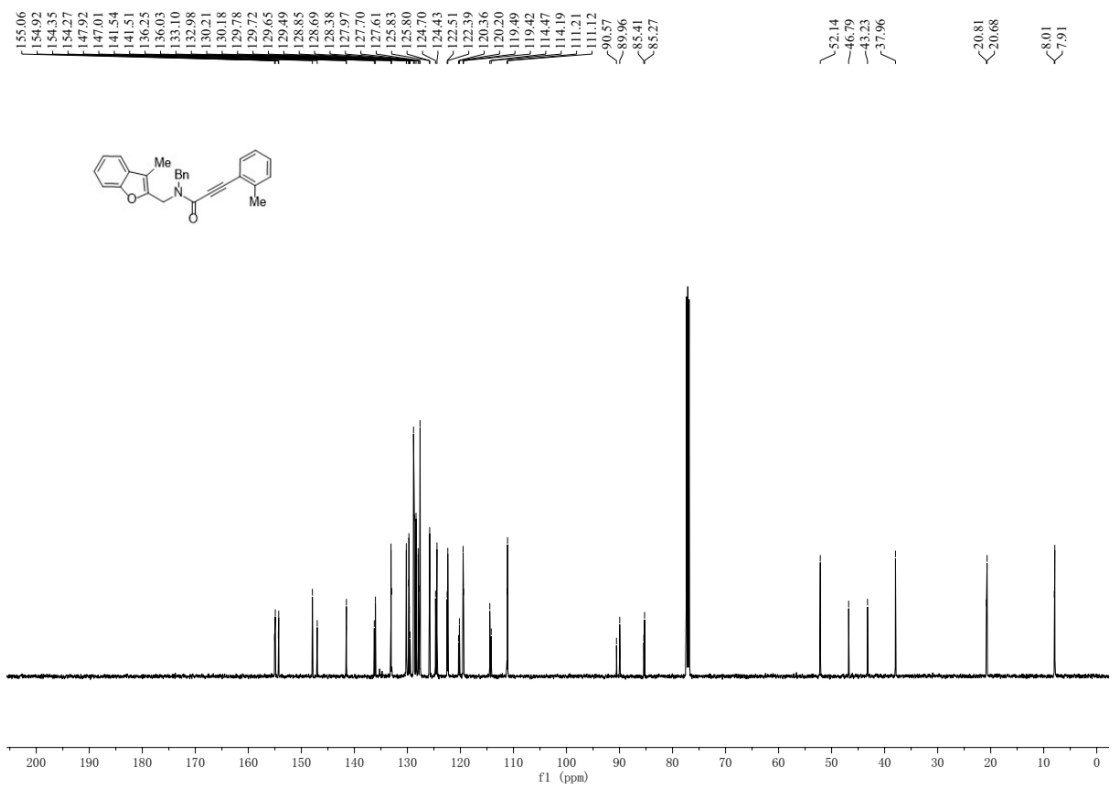
N-Benzyl-N-((3-methylbenzofuran-2-yl)methyl)-3-(o-tolyl)propiolamide (1h):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow oil; 51% yield (for the last step); A 3:2 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58-7.56 (m, 0.35H), 7.48-7.45 (m, 1.50H), 7.44-7.41 (m, 1.00H), 7.38-7.34 (m, 2.60H), 7.32-7.27 (m, 3.95H), 7.25-7.21 (m, 1.90H), 7.19-7.12 (m, 1.70H), 4.93 (s, 1.20H), 4.90 (s, 0.80H), 4.69 (s, 1.20H), 4.65 (s, 0.80H), 2.50 (s, 1.14H), 2.36 (s, 1.86H), 2.18 (s, 1.86H), 2.14 (s, 1.14H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.1, 154.9, 154.4, 154.3, 147.9, 147.0, 141.54, 141.51, 136.3, 136.0, 133.1, 133.0, 130.21, 130.18, 129.8, 129.7, 129.6, 129.5, 128.9, 128.7, 128.4, 128.0, 127.7, 127.6, 125.83, 125.80, 124.7, 124.4, 122.5, 122.4, 120.4, 120.2, 119.5, 119.4, 114.5, 114.2, 111.2, 111.1, 90.6, 90.0, 85.4, 85.3, 52.1, 46.8, 43.2, 38.0, 20.8, 20.7, 8.0, 7.9. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_2^+$ ([M+H]$^+$): 394.1802, found 394.1805.

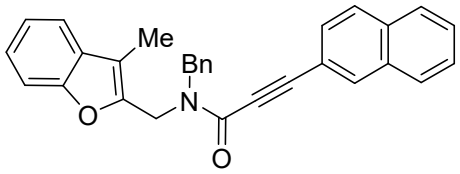


^{1}H NMR of compound **1h** (500 MHz, $CDCl_3$)

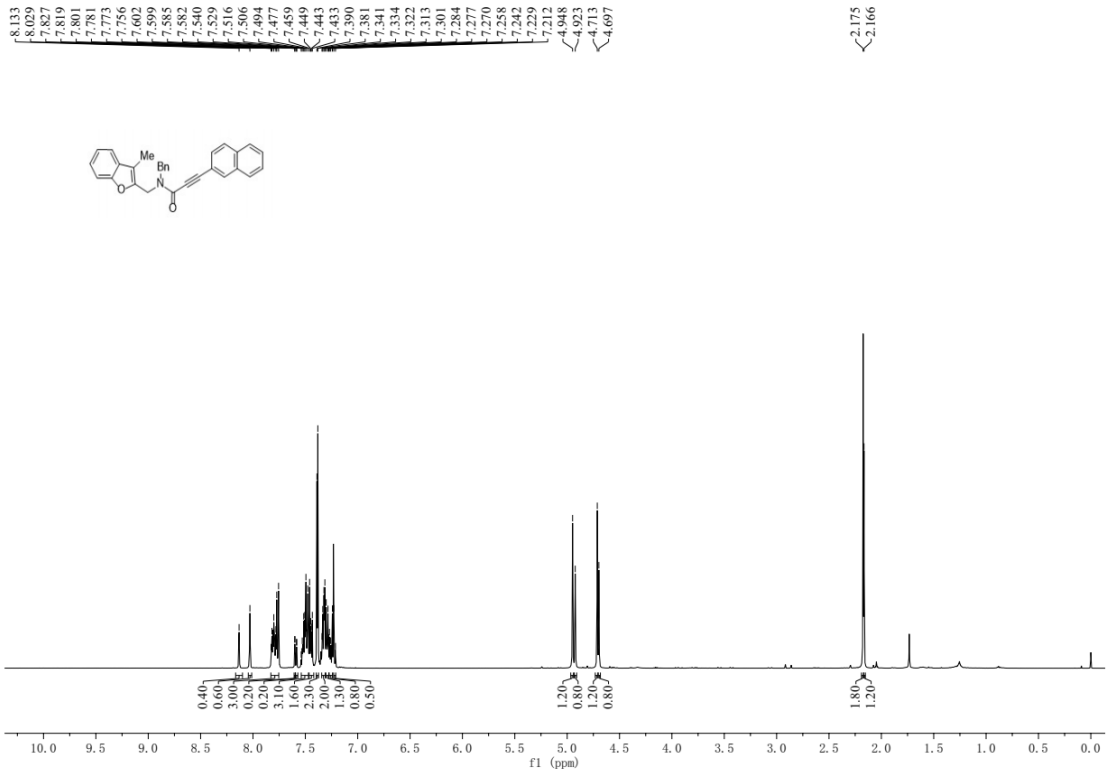


^{13}C NMR of compound **1h** (125 MHz, $CDCl_3$)

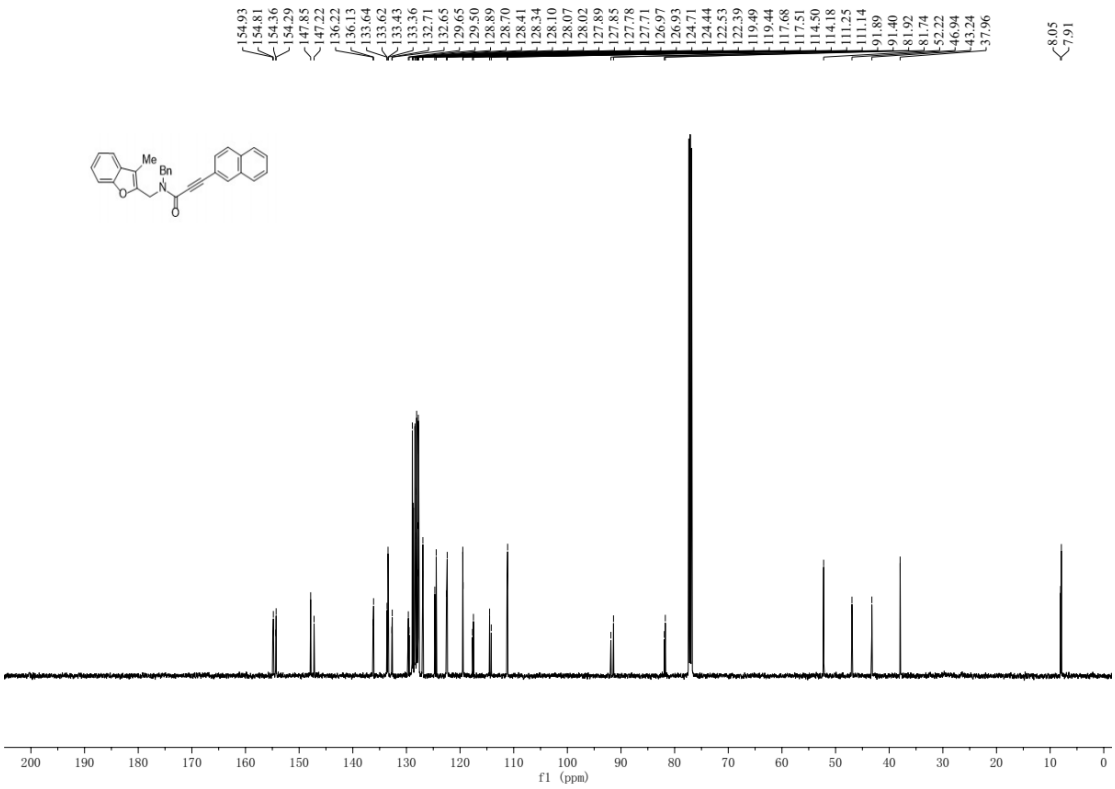
N-Benzyl-N-((3-methylbenzofuran-2-yl)methyl)-3-(naphthalen-2-yl)propiolamide (1i):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow oil; 55% yield (for the last step); A 3:2 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (s, 0.40H), 8.03 (s, 0.60H), 7.83-7.76 (m, 3.00H), 7.60 (d, J = 1.5Hz, 0.20H), 7.58 (d, J = 1.5Hz, 0.20H), 7.54-7.48 (m, 3.10H), 7.46-7.43 (m, 1.60H), 7.39-7.38 (m, 2.30H), 7.34-7.31 (m, 2.00H), 7.30-7.28 (m, 1.30H), 7.27-7.24 (m, 0.80H), 7.23-7.21 (s, 0.50H), 4.95 (s, 1.20H), 4.92 (s, 0.80H), 4.71 (s, 1.20H), 4.70 (s, 0.80H), 2.18 (s, 1.80H), 2.17 (s, 1.20H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9, 154.8, 154.4, 154.3, 147.9, 147.2, 136.2, 136.1, 133.64, 133.62, 133.43, 133.36, 132.71, 132.65, 129.7, 129.5, 128.9, 128.7, 128.4, 128.3, 128.10, 128.07, 128.0, 127.89, 127.85, 127.8, 127.7, 127.0, 126.9, 124.7, 124.4, 122.5, 122.4, 119.5, 119.4, 117.7, 117.5, 114.5, 114.2, 111.3, 111.1, 91.9, 91.4, 81.9, 81.7, 52.2, 46.9, 43.2, 38.0, 8.1, 7.9. HRMS *m/z* (ESI+): Calculated for $C_{30}H_{24}NO_2^+$ ([M+H]$^+$): 430.1802, found 430.1805.

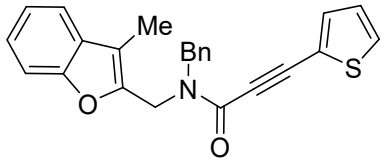


^{1}H NMR of compound **1i** (500 MHz, $CDCl_3$)

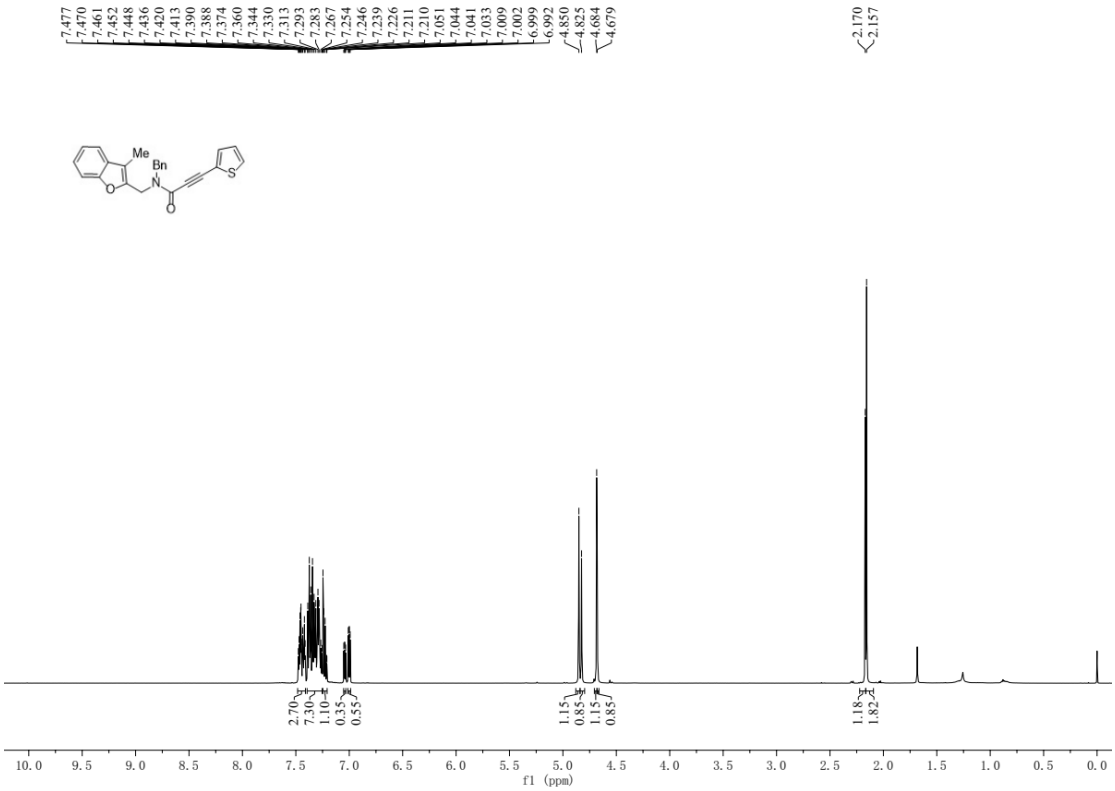


^{13}C NMR of compound **1i** (125 MHz, $CDCl_3$)

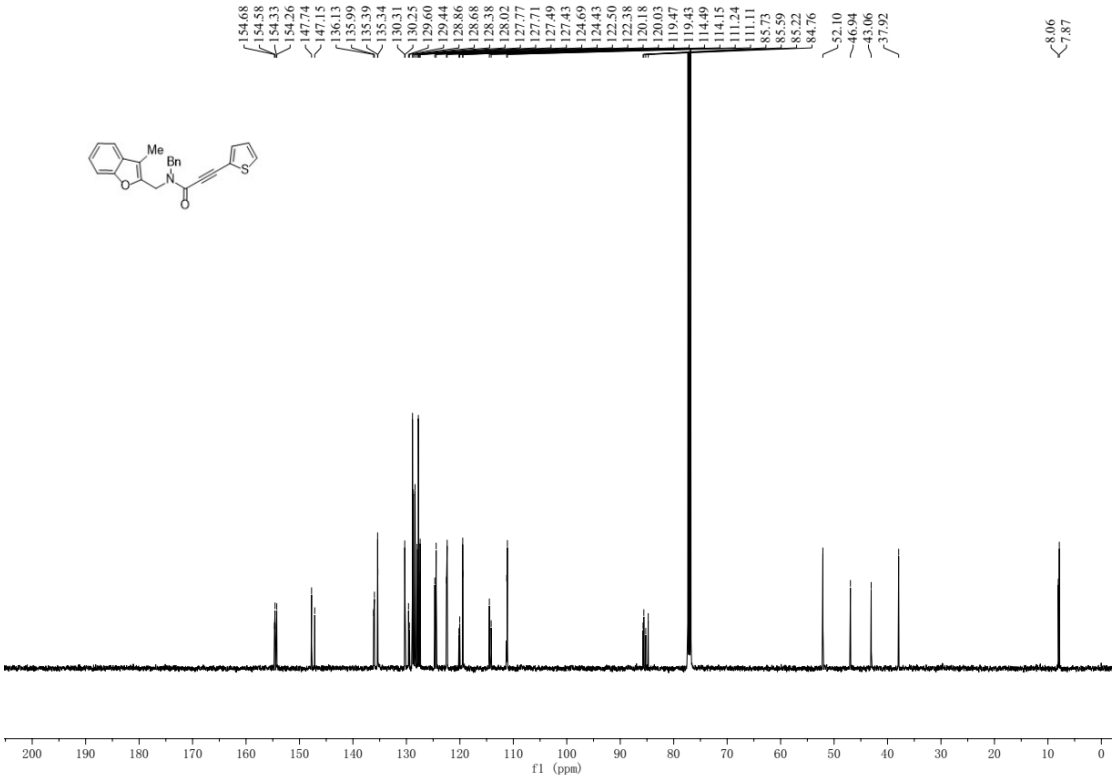
N-Benzyl-N-((3-methylbenzofuran-2-yl)methyl)-3-(thiophen-2-yl)propiolamide (1j):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow solid, Mp = 81-82 °C; 62% yield (for the last step); A 1.4:1 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48-7.41 (m, 2.70H), 7.39-7.25 (m, 7.30H), 7.24-7.21 (m, 1.10H), 7.05-7.03 (m, 0.35H), 7.01-6.99 (m, 0.55H), 4.85 (s, 1.15H), 4.83 (s, 0.85H), 4.684 (s, 1.15H), 4.679 (s, 0.85H), 2.17 (s, 1.18H), 2.16 (s, 1.82H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.7, 154.6, 154.33, 154.26, 147.7, 147.2, 136.1, 136.0, 135.4, 135.3, 130.31, 130.25, 129.6, 129.4, 128.9, 128.7, 128.4, 128.0, 127.8, 127.7, 127.5, 127.4, 124.7, 124.4, 122.5, 122.4, 120.2, 120.0, 119.5, 119.4, 114.5, 114.2, 111.2, 111.1, 85.7, 85.6, 85.2, 84.8, 52.1, 46.9, 43.1, 37.9, 8.1, 7.9. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{20}NO_2S^+$ ($[M+H]^+$): 386.1209, found 386.1208.

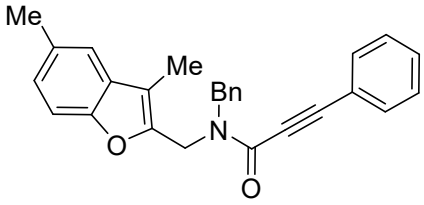


^{1}H NMR of compound **1j** (500 MHz, $CDCl_3$)

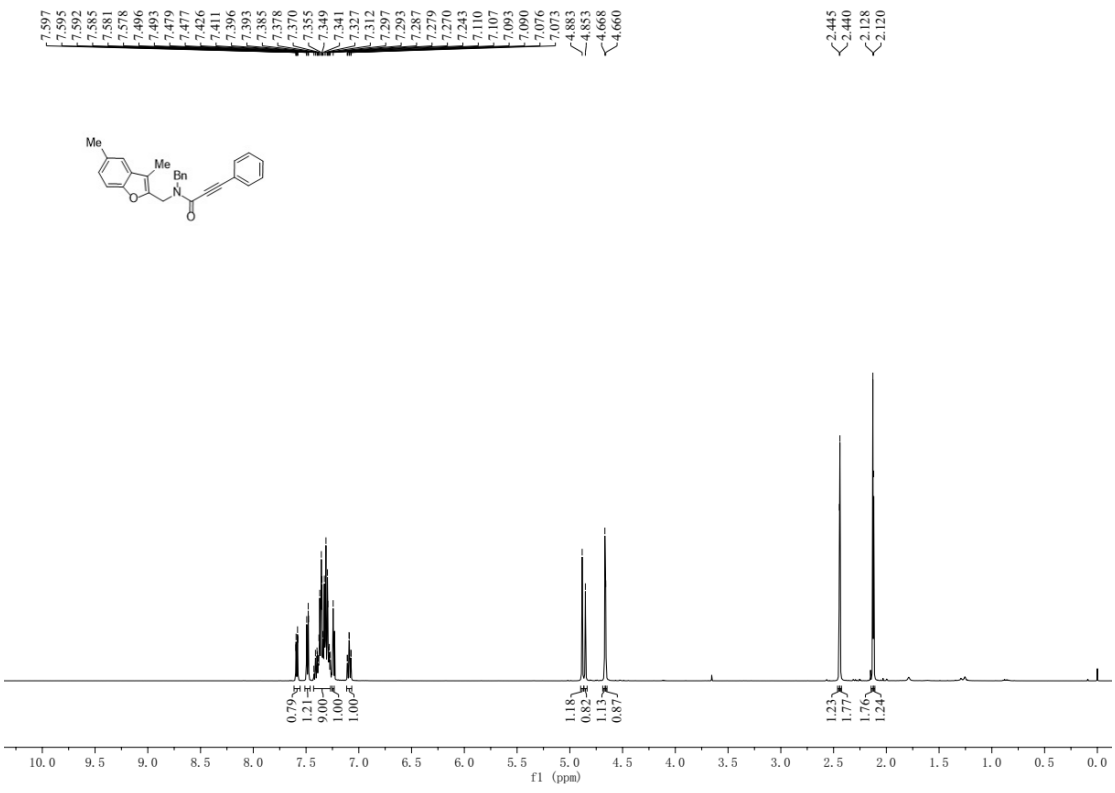


^{13}C NMR of compound **1j** (125 MHz, $CDCl_3$)

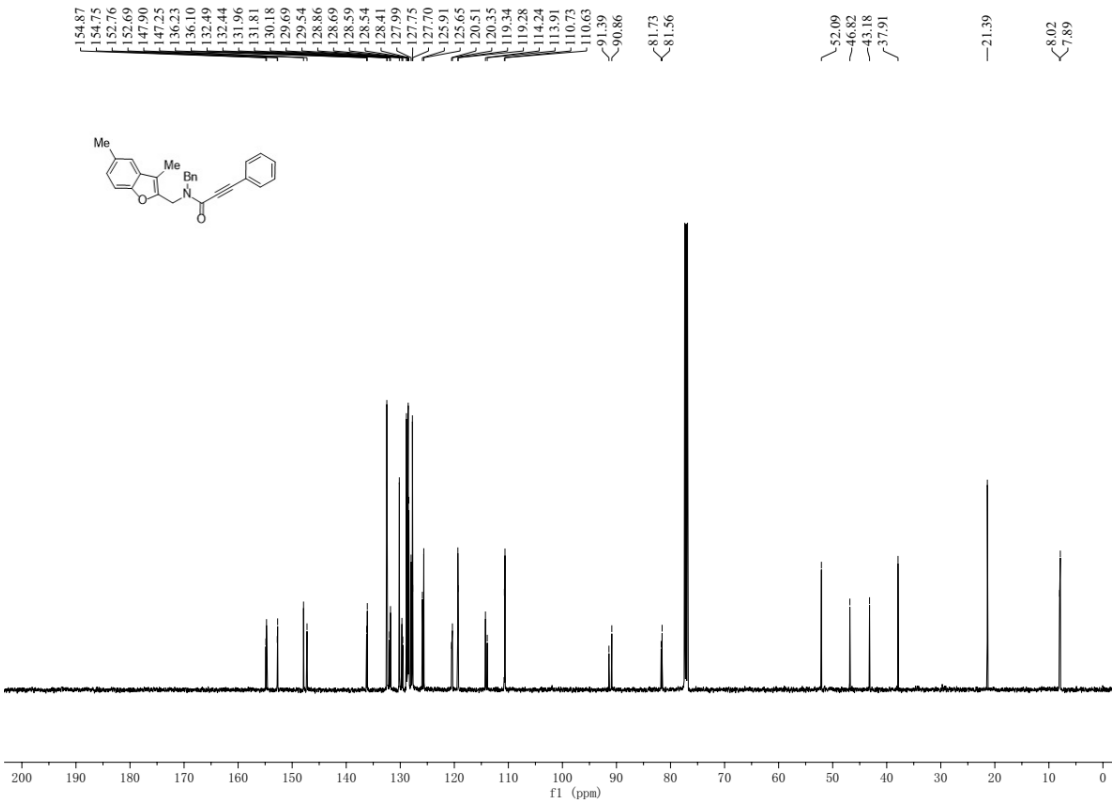
N-Benzyl-N-((3,5-dimethylbenzofuran-2-yl)methyl)-3-phenylpropiolamide (1k):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); light yellow oil; 63% yield (for the last step); A 1.4:1 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60-7.58 (m, 1.00H), 7.50-7.48 (m, 1.21H), 7.43-7.27 (m, 9.00H), 7.24 (s, 1.00H), 7.09 (td, J = 8.5, 1.5 Hz, 1.00H), 4.88 (s, 1.18H), 4.85 (s, 0.82H), 4.67 (s, 1.13H), 4.66 (s, 0.87H), 2.45 (s, 1.23H), 2.44 (s, 1.77H), 2.13 (s, 1.76H), 2.12 (s, 1.24H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9, 154.8, 152.8, 152.7, 147.9, 147.3, 136.2, 136.1, 132.5, 132.4, 132.0, 131.8, 130.2, 129.7, 129.5, 128.9, 128.7, 128.6, 128.5, 128.4, 128.0, 127.8, 127.7, 125.9, 125.7, 120.5, 120.4, 119.34, 119.28, 114.2, 113.9, 110.7, 110.6, 91.4, 90.9, 81.7, 81.6, 52.1, 46.8, 43.2, 37.9, 21.4, 8.0, 7.9. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_2^+$ ([M+H]$^+$): 394.1802, found 394.1805.

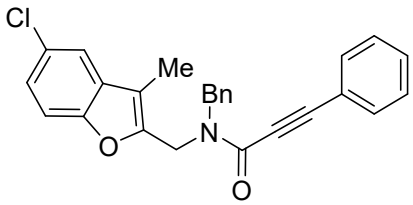


^{1}H NMR of compound **1k** (500 MHz, $CDCl_3$)

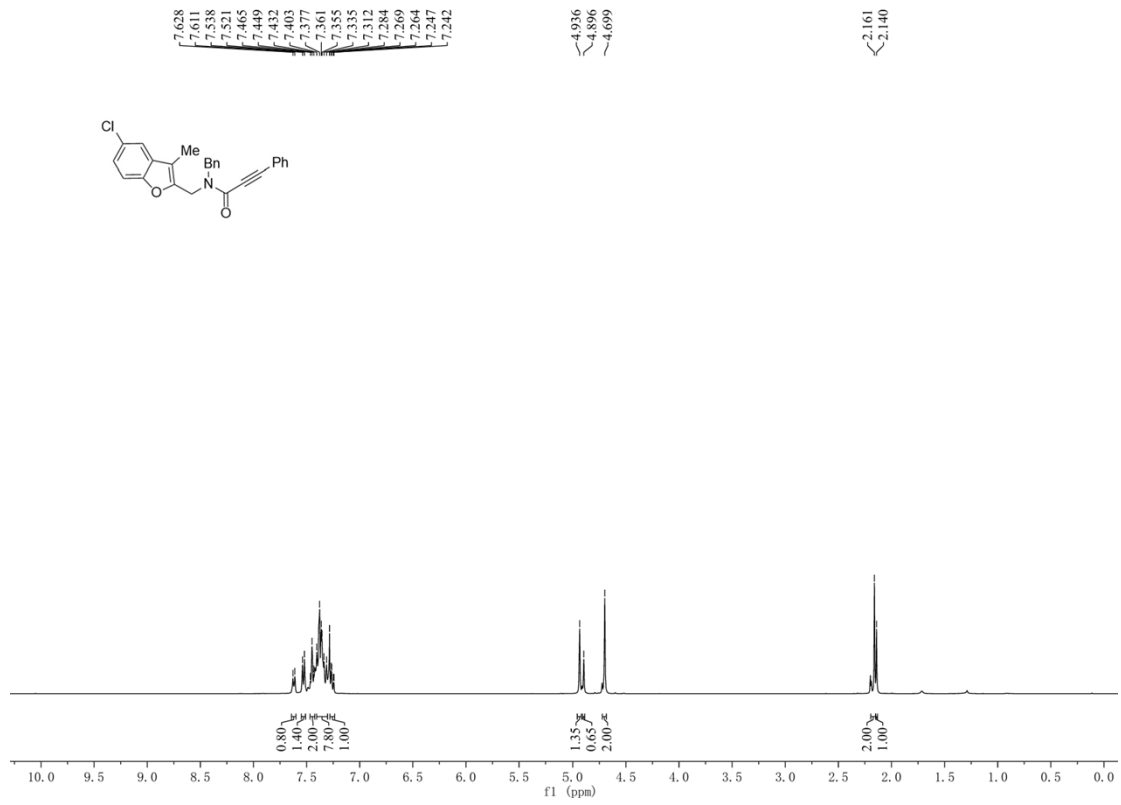


^{13}C NMR of compound **1k** (125 MHz, $CDCl_3$)

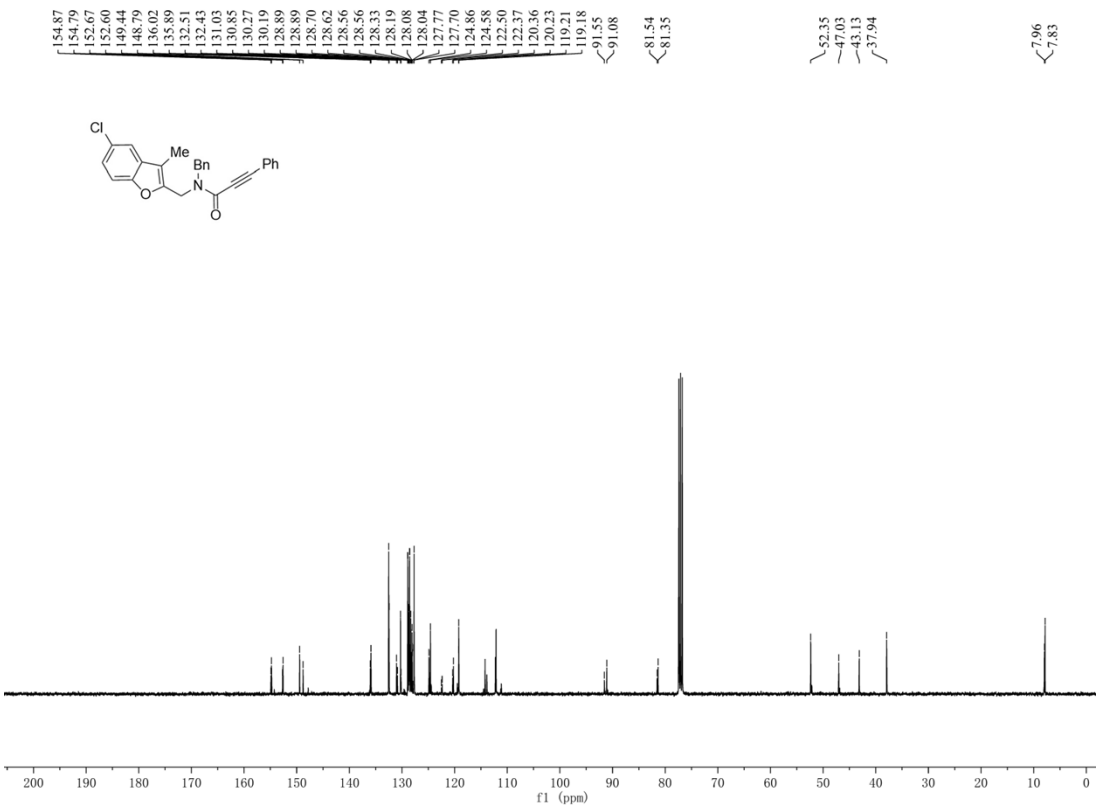
N-benzyl-N-((5-chloro-3-methylbenzofuran-2-yl)methyl)-3-phenyl-propiolamide (1l):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); light yellow oil; 80% yield (for the last step); A 2:1 isomeric mixture; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 7.2 Hz, 0.80H), 7.53 (d, J = 7.2 Hz, 1.40H), 7.47-7.43 (m, 2.00H), 7.40-7.31 (m, 7.80H), 7.28-7.24 (m, 1.00H), 4.94 (s, 1.35H), 4.90 (s, 0.65H), 4.70 (s, 2.00H), 2.16 (s, 2.00H), 2.14 (s, 1.00H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 154.8, 152.7, 152.6, 149.4, 148.8, 136.0, 135.9, 132.5, 132.4, 131.0, 130.9, 130.3, 130.2, 128.9, 128.7, 128.62, 128.60, 128.5, 128.3, 128.1, 128.0, 127.8, 127.7, 124.9, 124.6, 120.4, 120.2, 119.21, 119.18, 114.2, 113.9, 112.3, 112.1, 91.6, 91.0, 81.5, 81.4, 52.4, 47.0, 43.1, 37.9, 8.0, 7.8. HRMS *m/z* (ESI+): Calculated for $C_{26}H_{21}ClNO_2^+$ ($[M+H]^+$): 414.1255, found 414.1262.

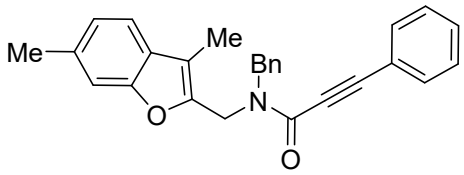


^{1}H NMR of compound **1l** (400 MHz, $CDCl_3$)

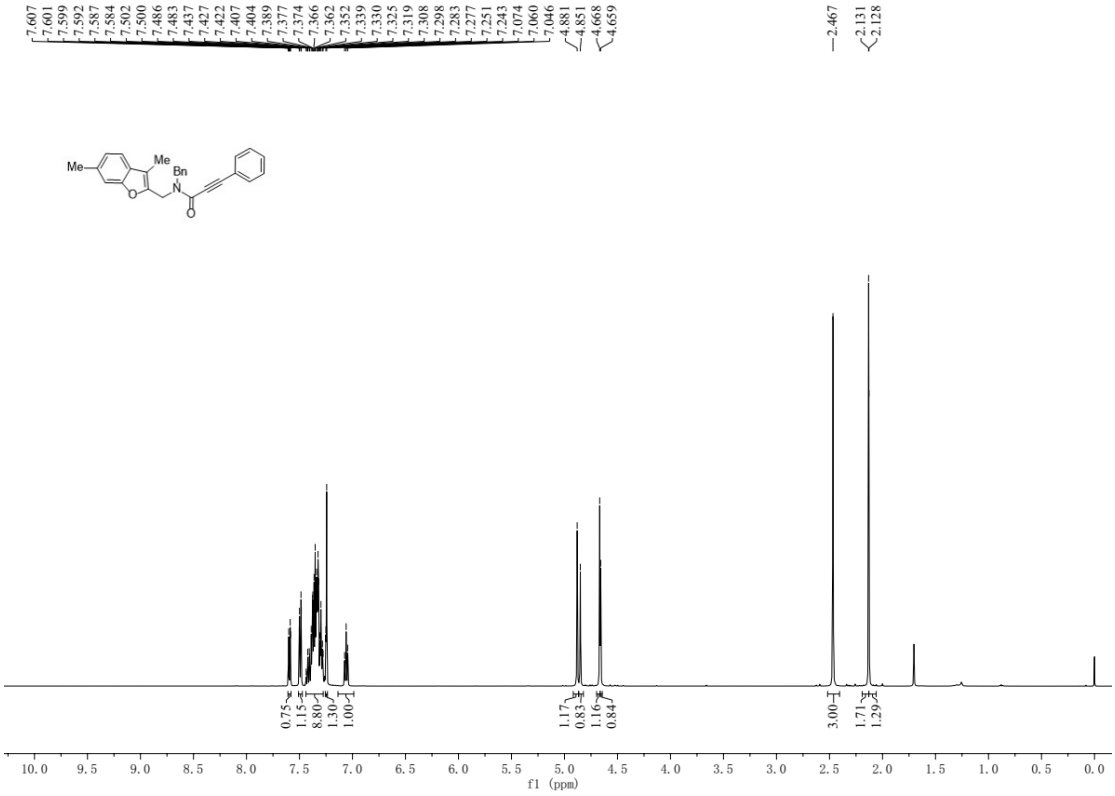


^{13}C NMR of compound **1l** (100 MHz, $CDCl_3$)

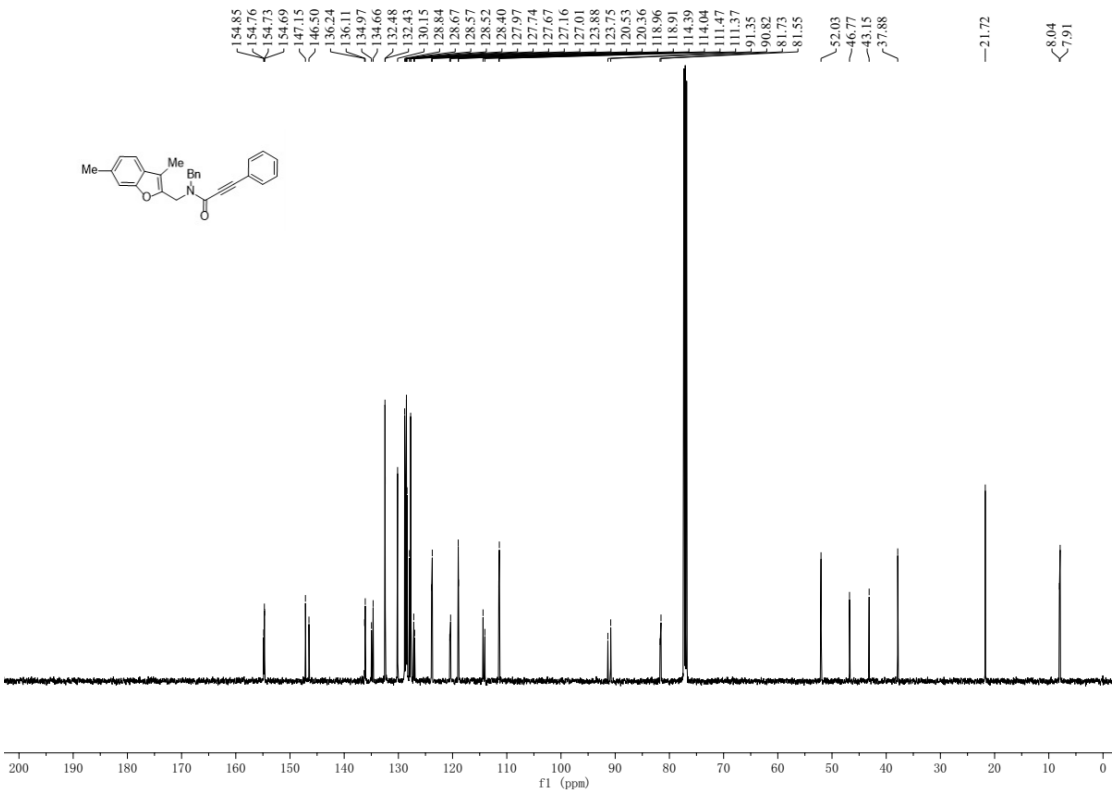
N-Benzyl-N-((3,6-dimethylbenzofuran-2-yl)methyl)-3-phenylpropiolamide (1m):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); light yellow solid, Mp = 86-87 °C; 89% yield (for the last step); A 1.4:1 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61-7.58 (m, 0.75H), 7.50-7.48 (m, 1.15H), 7.44-7.28 (m, 8.80H), 7.25-7.24 (m, 1.30H), 7.06 (t, J = 8.0 Hz, 1.00H), 4.88 (s, 1.17H), 4.85 (s, 0.83H), 4.67 (s, 1.16H), 4.66 (s, 0.84H), 2.47 (s, 3.00H), 2.131 (s, 1.71H), 2.128 (s, 1.29H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9, 154.8, 154.73, 154.69, 147.2, 146.5, 136.2, 136.1, 135.0, 134.7, 132.5, 132.4, 130.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.0, 127.74, 127.67, 127.2, 127.0, 123.9, 123.8, 120.5, 120.4, 119.0, 118.9, 114.4, 114.0, 111.5, 111.4, 91.4, 90.8, 81.7, 81.6, 52.0, 46.8, 43.2, 37.9, 21.7, 8.0, 7.9. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_2^+$ ([M+H]$^+$): 394.1802, found 394.1804.

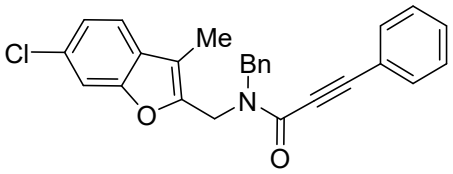


^{1}H NMR of compound **1m** (500 MHz, $CDCl_3$)

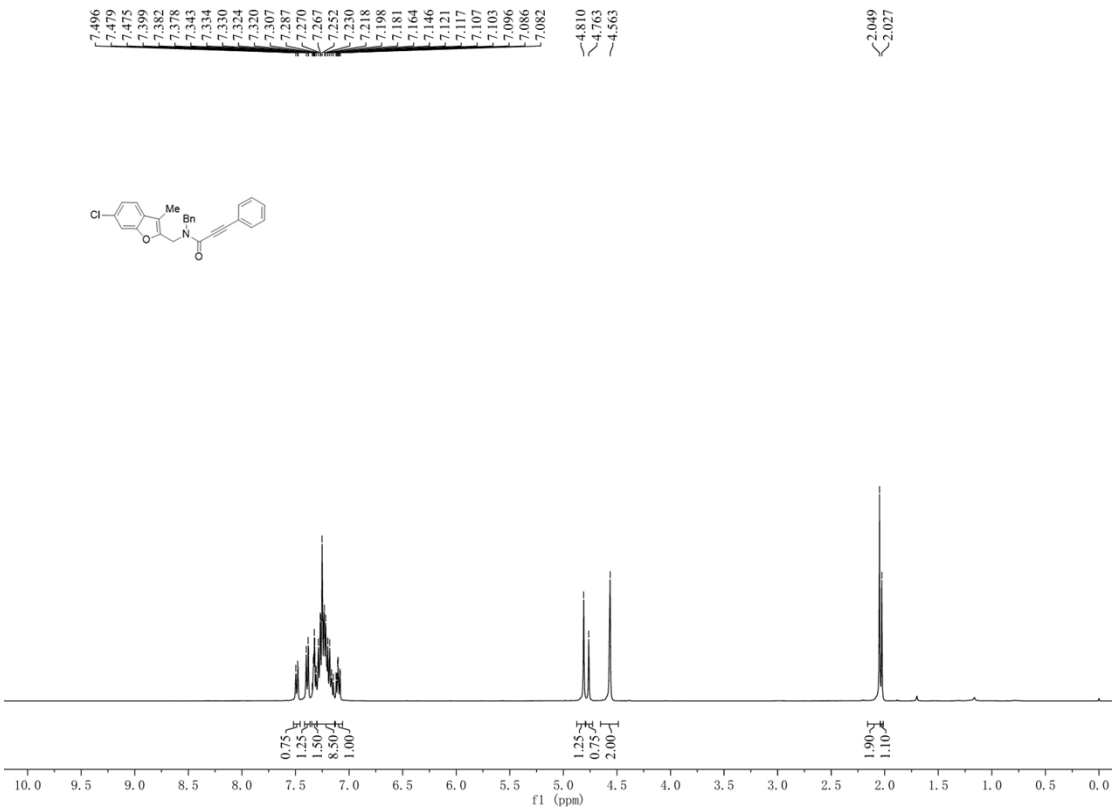


^{13}C NMR of compound **1m** (125 MHz, $CDCl_3$)

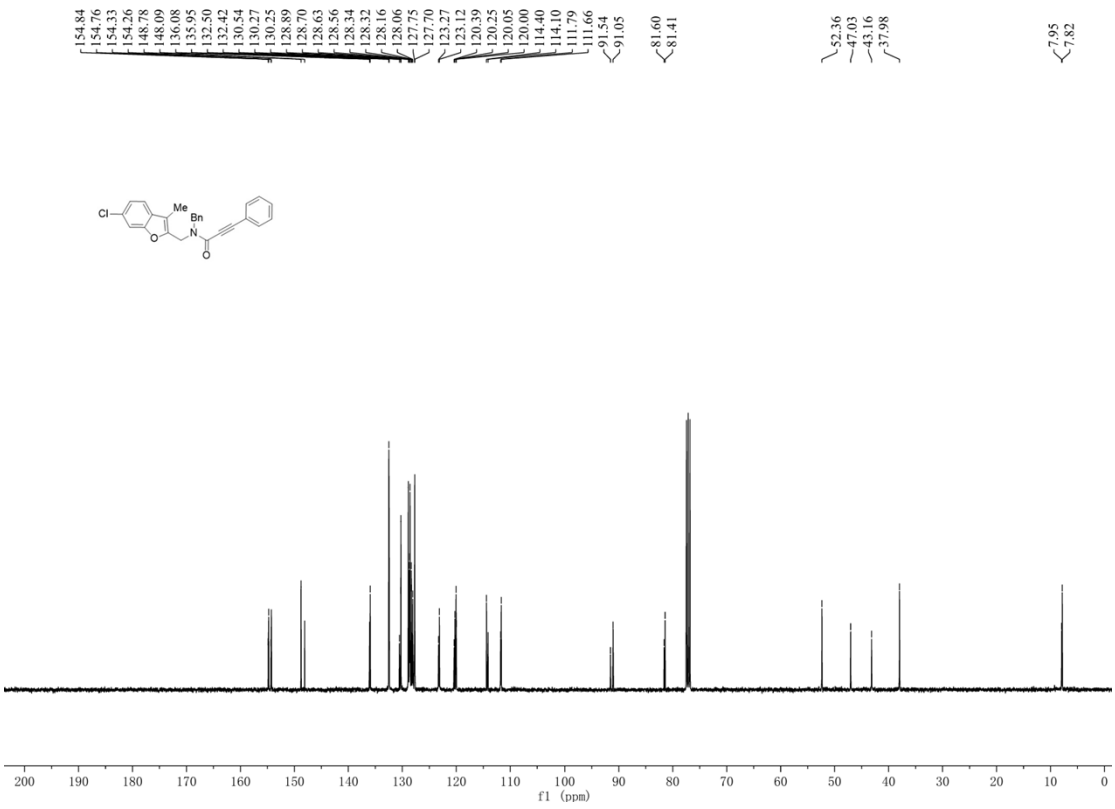
N-benzyl-N-((6-chloro-3-methylbenzofuran-2-yl)methyl)-3-phenyl-propiolamide (1n):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); light yellow oil; 84% yield (for the last step); A 1.7:1 isomeric mixture; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50- 7.48 (m, 0.75H), 7.40-7.38 (m, 1.25H), 7.34-7.31 (m, 1.50H), 7.29-7,15 (m, 8.50H), 7.12-7.08 (m, 1.00H), 4.81 (s, 1.25H), 4.76 (s, 0.75H), 4.56 (s, 2.00H), 2.05 (s, 1.90H), 2.03 (s, 1.10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.84, 154.76, 154.33, 154.26, 148.8, 148.1, 136.1, 136.0, 132.5, 132.4, 130.5, 130.27, 130.25, 128.9, 128.7, 128.63, 128.56, 128.34, 128.32, 128.2, 128.1, 127.8, 127.7, 123.3, 123.1, 120.4, 120.3, 120.1, 120.0, 114.4, 114.1, 111.8, 111.7, 91.5, 91.1, 81.6, 81.4, 52.4, 47.0, 43.2, 38.0, 8.0, 7.8. HRMS *m/z* (ESI+): Calculated for $C_{26}H_{21}ClNO_2^+$ ([M+H]$^+$): 414.1255, found 414.1265.

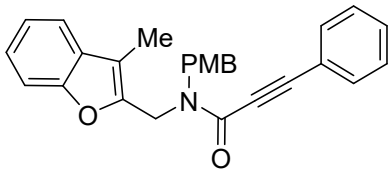


^{1}H NMR of compound **1n** (400 MHz, $CDCl_3$)

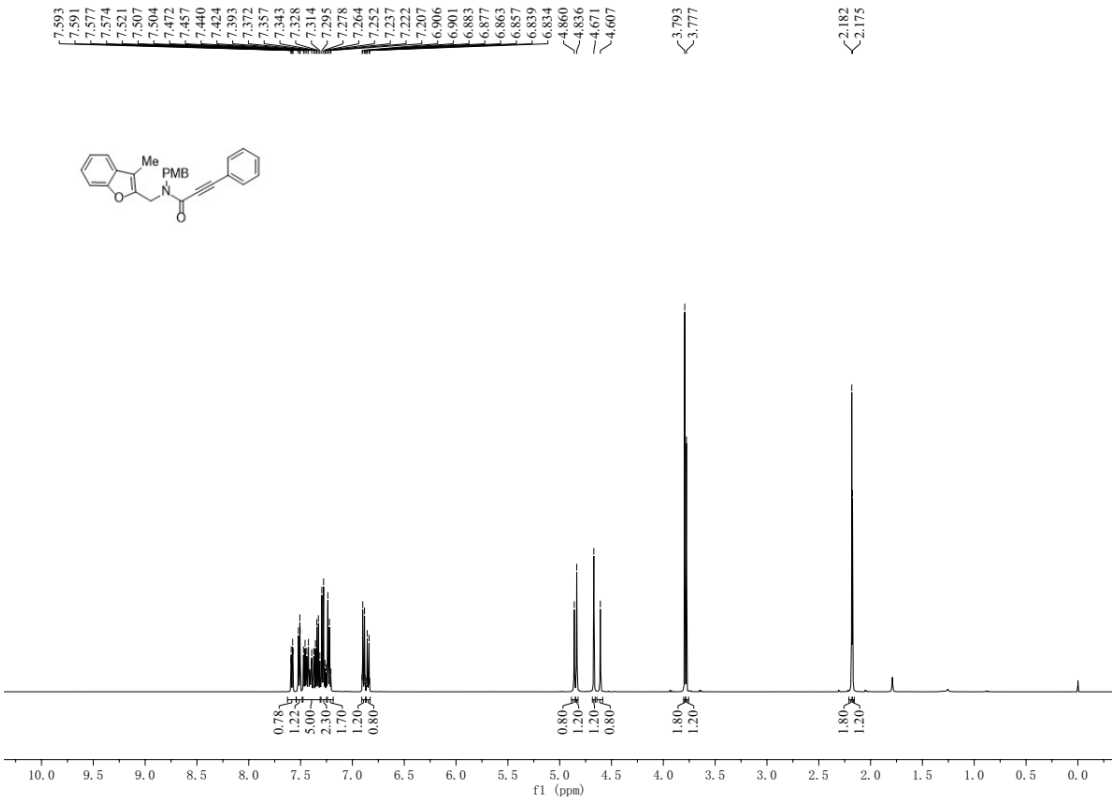


^{31}C NMR of compound **1n** (100 MHz, $CDCl_3$)

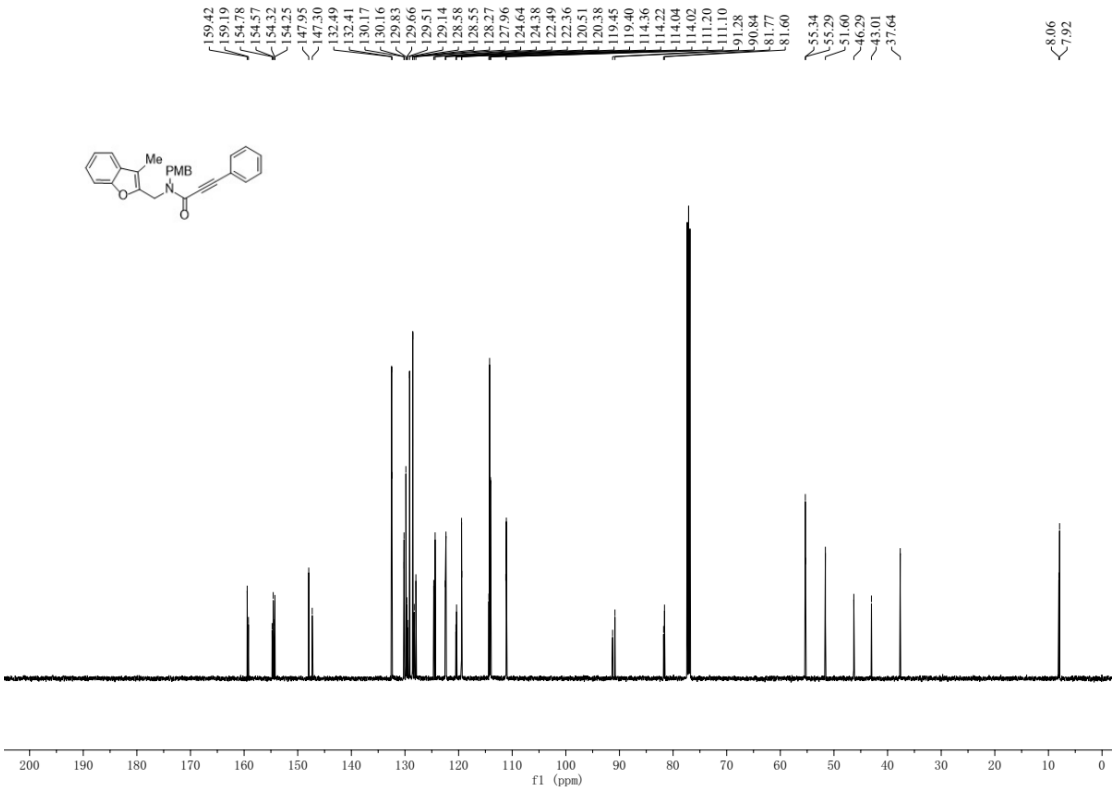
N-(4-Methoxybenzyl)-N-((3-methylbenzofuran-2-yl)methyl)-3-phenylpropiolamide (1o):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow oil; 83% yield (for the last step); A 3:2 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59-7.57 (m, 0.78H), 7.52-7.50 (m, 1.22H), 7.47-7.31 (m, 5.00H), 7.30-7.25 (m, 2.30H), 7.24-7.21 (m, 1.70H), 6.91-6.88 (m, 1.20H), 6.86-6.83 (m, 0.80H), 4.86 (s, 0.80H), 4.84 (s, 1.20H), 4.67 (s, 1.20H), 4.61 (s, 0.80H), 3.79 (s, 1.80H), 3.78 (s, 1.20H), 2.182 (s, 1.80H), 2.175 (s, 1.20H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.4, 159.2, 154.8, 154.6, 154.32, 154.25, 148.0, 147.3, 132.5, 132.4, 130.17, 130.16, 129.8, 129.7, 129.5, 129.1, 128.58, 128.55, 128.3, 128.0, 124.6, 124.4, 122.5, 122.4, 120.5, 120.4, 119.5, 119.4, 114.4, 114.2, 114.04, 114.02, 111.2, 111.1, 91.3, 90.8, 81.8, 81.6, 55.34, 55.29, 51.6, 46.3, 43.0, 37.6, 8.1, 7.9. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_3^+$ ([M+H]$^+$): 410.1751, found 410.1754.

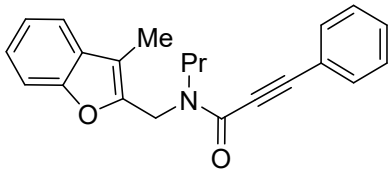


^{1}H NMR of compound **1o** (500 MHz, $CDCl_3$)

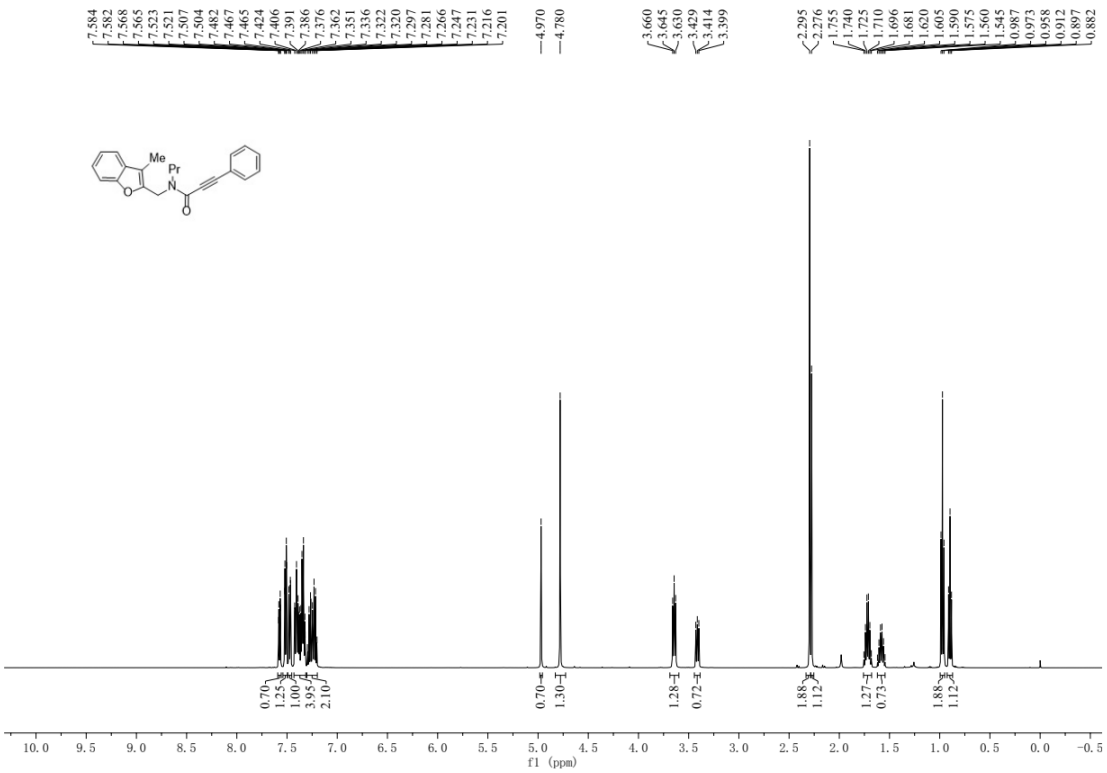


^{13}C NMR of compound **1o** (125 MHz, $CDCl_3$)

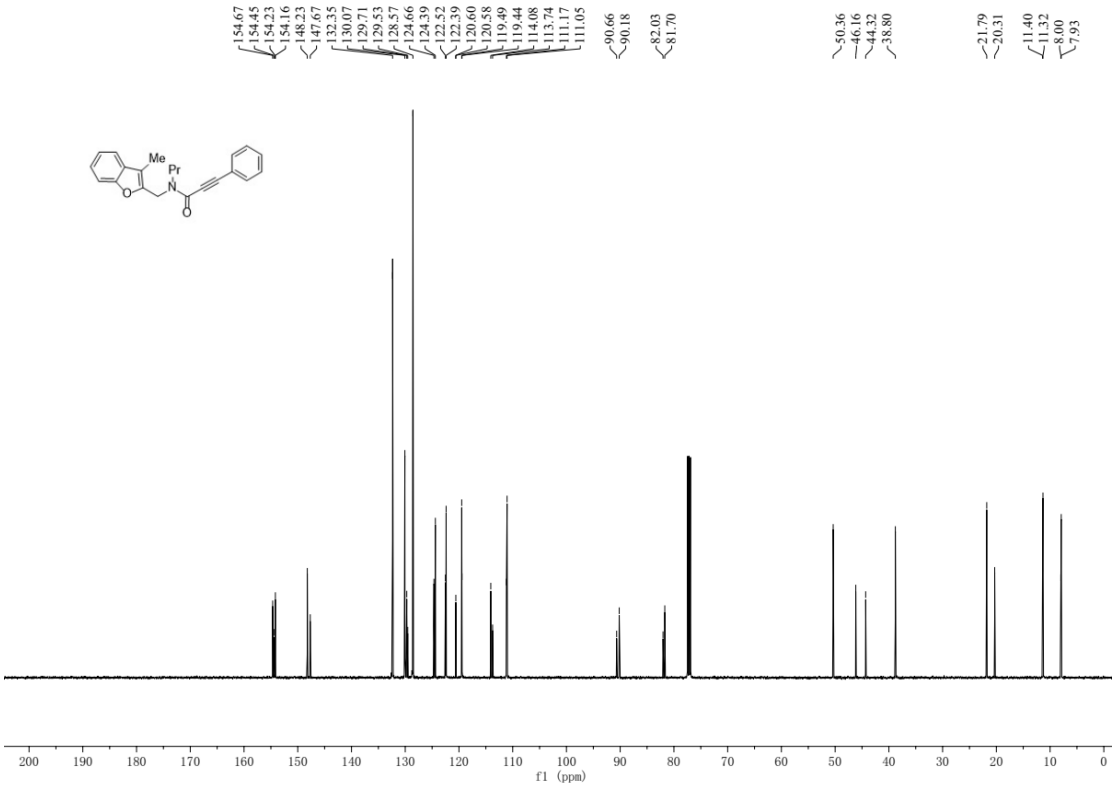
N-((3-methylbenzofuran-2-yl)methyl)-3-phenyl-N-propylpropiolamide (1p):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); light yellow oil; 86% yield (for the last step); A 1.8:1 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58-7.57 (m, 0.70H), 7.52-7.50 (m, 1.25H), 7.48-7.47 (m, 1.00H), 7.42-7.32 (m, 3.95H), 7.30-7.20 (m, 2.10H), 4.97 (s, 0.70H), 4.78 (s, 1.30H), 3.65 (t, J = 7.5 Hz, 1.28H), 3.41 (t, J = 7.5 Hz,, 0.72H), 2.30 (s, 1.88H), 2.28 (s, 1.12H), 1.76-1.68 (m, 1.27H), 1.62-1.55 (m, 0.73H), 0.97 (t, J = 7.3 Hz, 1.88H), 0.90 (t, J = 7.5 Hz, 1.12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.7, 154.5, 154.23, 154.16, 148.2, 147.7, 132.4, 130.1, 129.7, 129.5, 128.6, 124.7, 124.4, 122.5, 122.4, 120.60, 120.58, 119.5, 119.4, 114.1, 113.7, 111.2, 111.1, 90.7, 90.2, 82.0, 81.7, 50.4, 46.2, 44.3, 38.8, 21.8, 20.3, 11.4, 11.3, 8.0, 7.9. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{22}NO_2^+$ ([M+H]$^+$): 332.1645, found 332.1650.

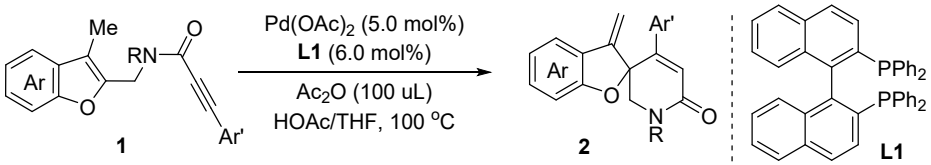


^{1}H NMR of compound **1p** (500 MHz, $CDCl_3$)



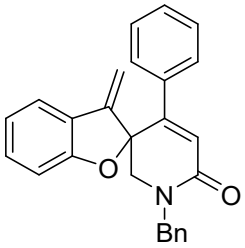
^{13}C NMR of compound **1p** (125 MHz, $CDCl_3$)

3. Procedure for dearomative 1,6-enyne cycloisomerization of 1

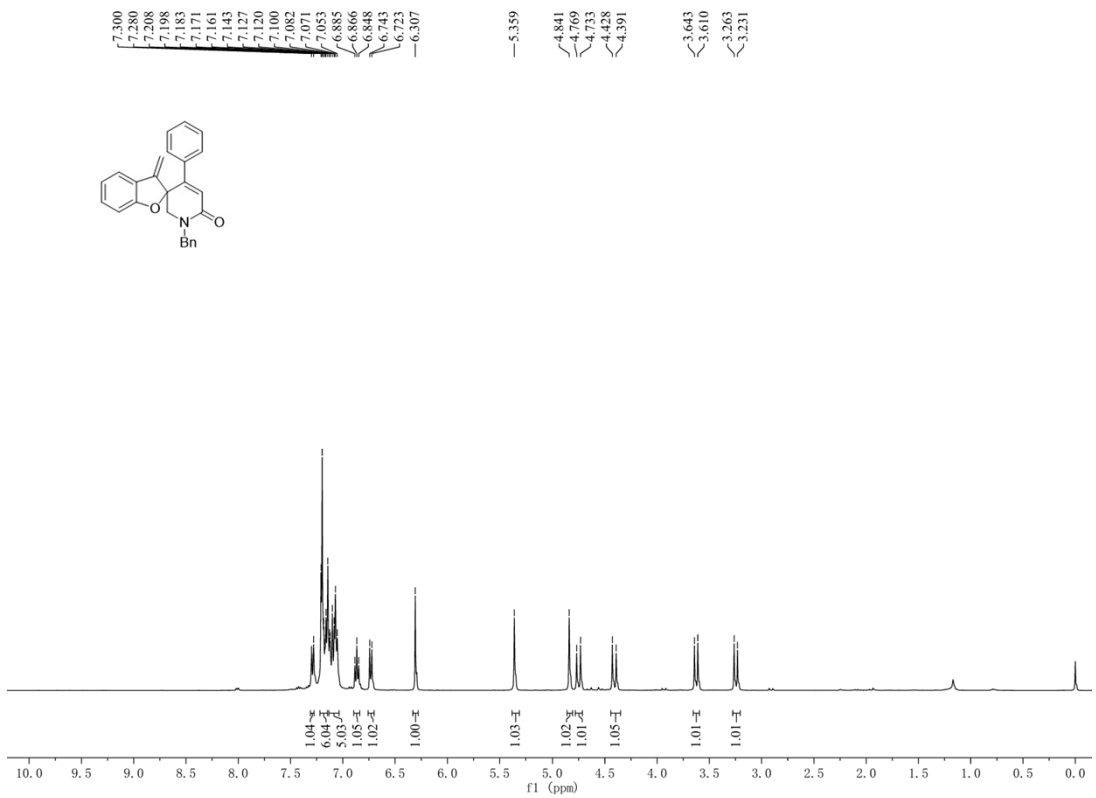


To a dried Schlenk tube were charged with $Pd(OAc)_2$ (5 mol%, 2.3 mg), **L1** (6 mol%, 7.5 mg) and **1** (0.2 mmol) under air atmosphere. Ac_2O (100 μL), HOAc (1.6 mL), and THF (0.4 mL) was then introduced via syringe. The resulting mixture was stirred at 100 ^oC (heating block) until the reaction was completed (monitored by TLC). The mixture was quenched with a solution of saturated sodium bicarbonate at 0 °C and extracted with ethyl acetate. The solvent was then removed under reduced pressure and the residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v) to afford product **2**.

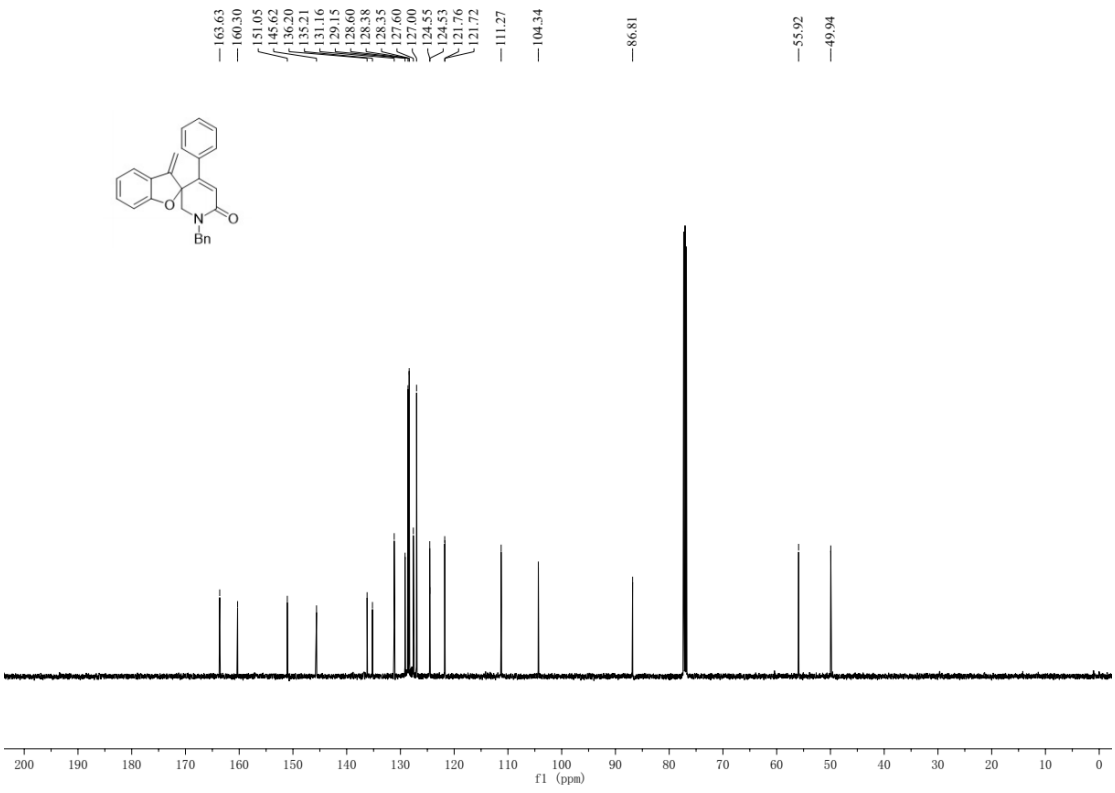
1'-Benzyl-3-methylene-4'-phenyl-1',2'-dihydro-3H,6'H-spiro[benzofuran-2,3'-pyridin]-6'-one (2a):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 57.6 mg, 76% yield; ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 8.0 Hz, 1H), 7.21-7.14 (m, 6H), 7.13-7.05 (m, 5H), 6.87 (t, J = 7.6 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 6.31 (s, 1H), 5.36 (s, 1H), 4.84 (s, 1H), 4.75 (d, J = 14.8 Hz, 1H), 4.41 (d, J = 14.8 Hz, 1H), 3.63 (d, J = 13.2 Hz, 1H), 3.25 (d, J = 13.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.6, 160.3, 151.1, 145.6, 136.2, 135.2, 131.2, 129.2, 128.6, 128.38, 128.35, 127.6, 127.0, 124.6, 124.5, 121.8, 121.7, 111.3, 104.3, 86.8, 55.9, 49.9. HRMS *m/z* (ESI+): Calculated for $C_{26}H_{22}NO_2^+$ ($[M+H]^+$): 380.1645, found 380.1647.

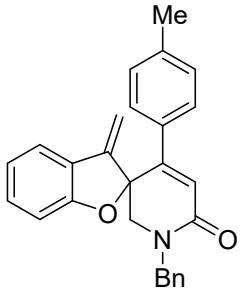


^{1}H NMR of compound **2a** (400 MHz, $CDCl_3$)

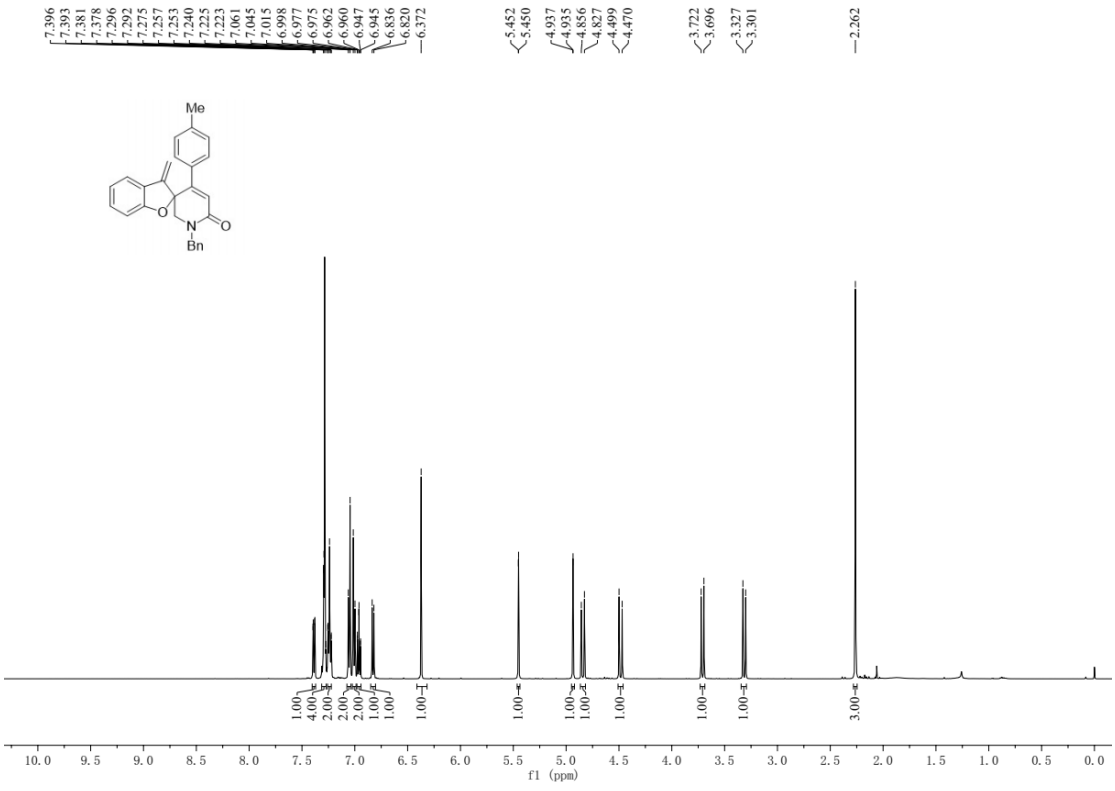


^{13}C NMR of compound **2a** (125 MHz, $CDCl_3$)

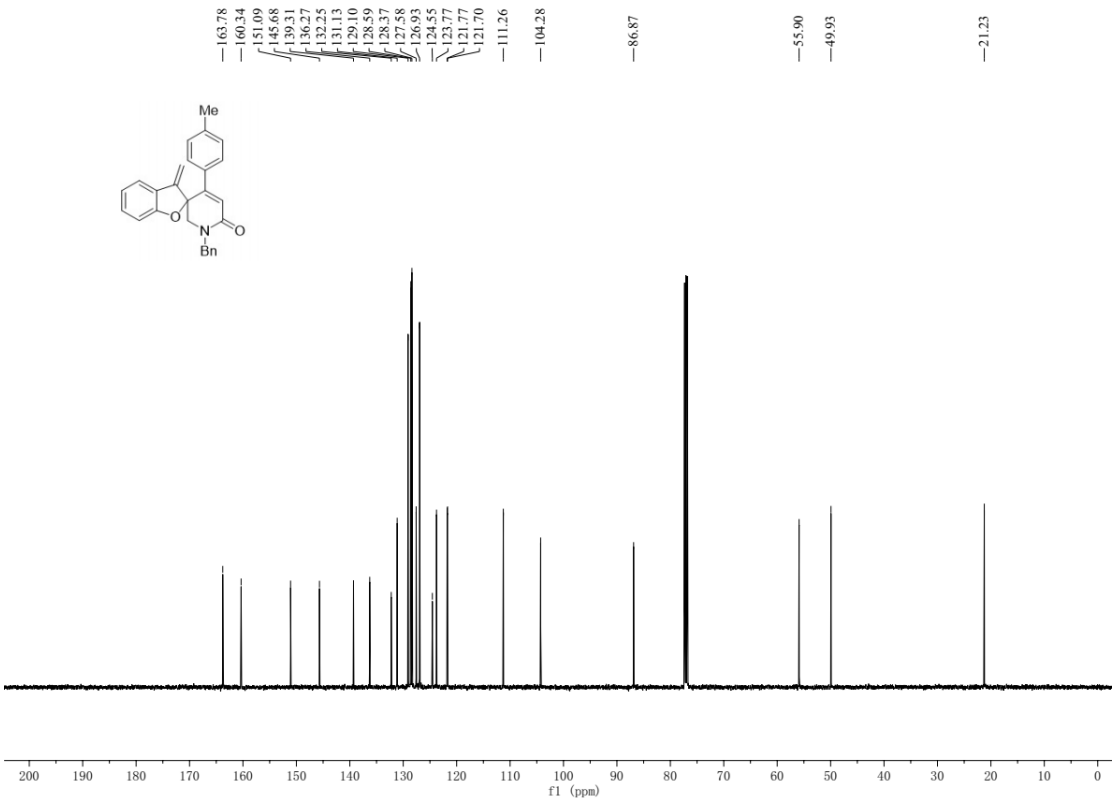
1'-Benzyl-3-methylene-4'-(p-tolyl)-1',2'-dihydro-3H,6'H-spiro[benzofuran-2,3'-pyridin]-6'-one (2b):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 58.9 mg, 75% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.30-7.28 (m, 4H), 7.26-7.22 (m, 2H), 7.05 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.5 Hz, 2H), 7.00-6.95 (m, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.37 (s, 1H), 5.45 (d, J = 1.0 Hz, 1H), 4.94 (d, J = 1.0 Hz, 1H), 4.84 (d, J = 14.5 Hz, 1H), 4.48 (d, J = 14.5 Hz, 1H), 3.71 (d, J = 13.0 Hz, 1H), 3.31 (d, J = 13.0 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8, 160.3, 151.1, 145.7, 139.3, 136.3, 132.3, 131.1, 129.1, 128.6, 128.4, 127.6, 126.9, 124.6, 123.8, 121.8, 121.7, 111.3, 104.3, 86.9, 55.9, 49.9, 21.2. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_2^+$ ([M+H]$^+$): 394.1802, found 394.1809.

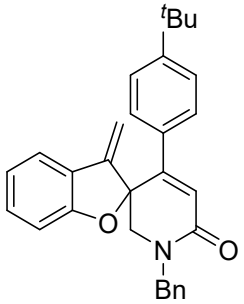


^{1}H NMR of compound **2b** (500 MHz, $CDCl_3$)

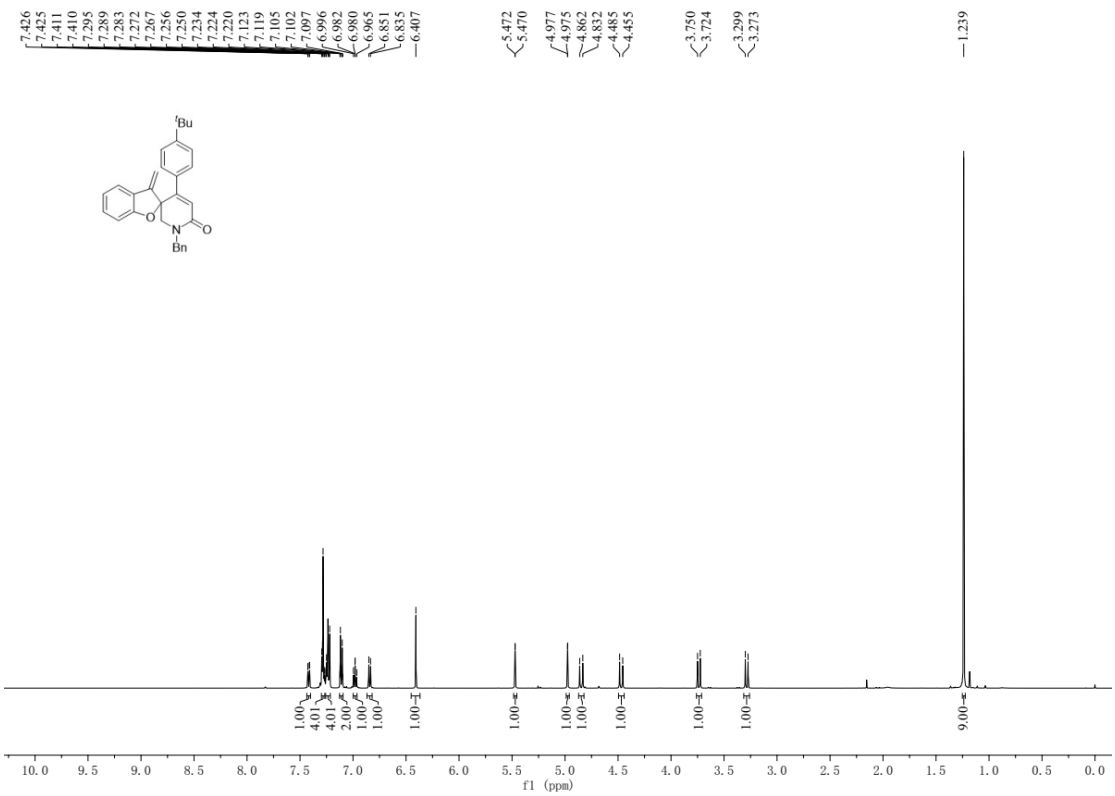


^{13}C NMR of compound **2b** (125 MHz, $CDCl_3$)

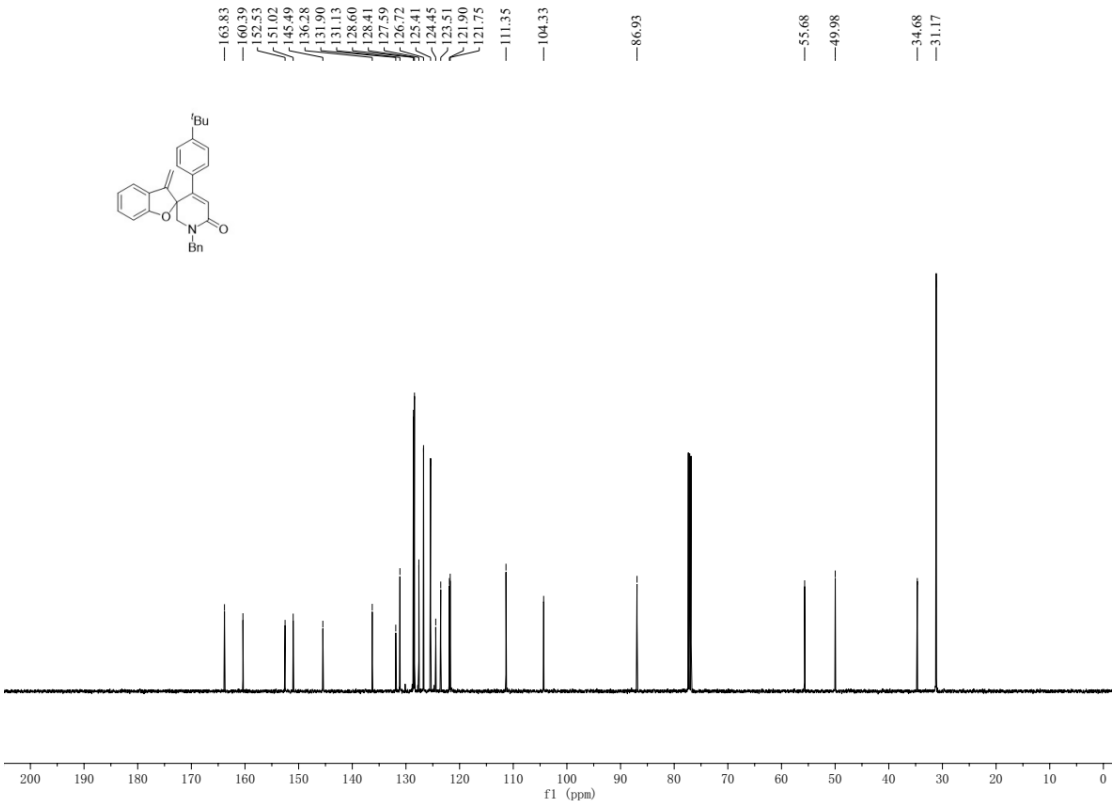
1'-Benzyl-4'-(4-(tert-butyl)phenyl)-3-methylene-1',2'-dihydro-3H,6'H-spiro-[benzofuran-2,3'-pyridin]-6'-one (2c):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 49.6 mg, 57% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.41 (m, 1H), 7.30-7.27 (m, 4H), 7.26-7.22 (m, 4H), 7.12-7.10 (m, 2H), 7.00-6.97 (m, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.41 (s, 1H), 5.47 (d, J = 1.0 Hz, 1H), 4.98 (d, J = 1.0 Hz, 1H), 4.85 (d, J = 15.0 Hz, 1H), 4.47 (d, J = 15.0 Hz, 1H), 3.74 (d, J = 13.0 Hz, 1H), 3.29 (d, J = 13.0 Hz, 1H), 1.24 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8, 160.4, 152.5, 151.0, 145.5, 136.3, 131.9, 131.1, 128.6, 128.4, 127.6, 126.7, 125.4, 124.5, 123.5, 121.9, 121.8, 111.4, 104.3, 86.9, 55.7, 50.0, 34.7, 31.2. HRMS *m/z* (ESI+): Calculated for $C_{30}H_{30}NO_2^+$ ([M+H]$^+$): 436.2271, found 436.2274.

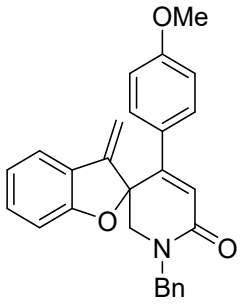


^{1}H NMR of compound **2c** (500 MHz, $CDCl_3$)

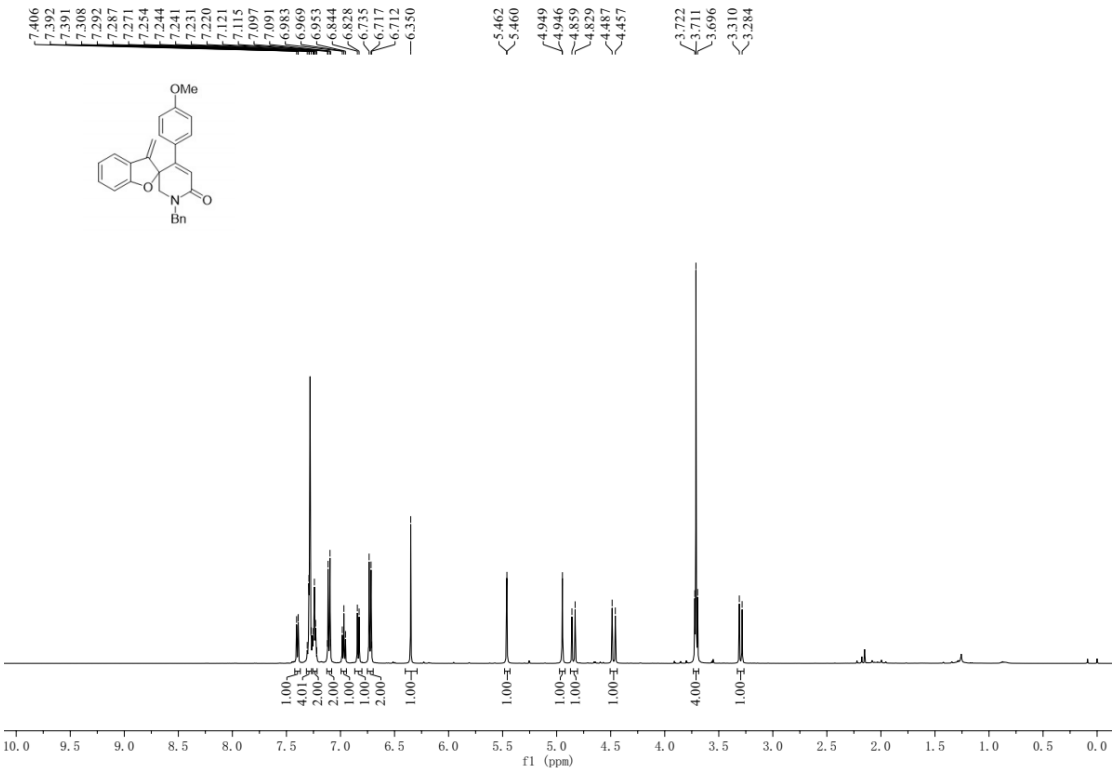


^{13}C NMR of compound **2c** (125 MHz, $CDCl_3$)

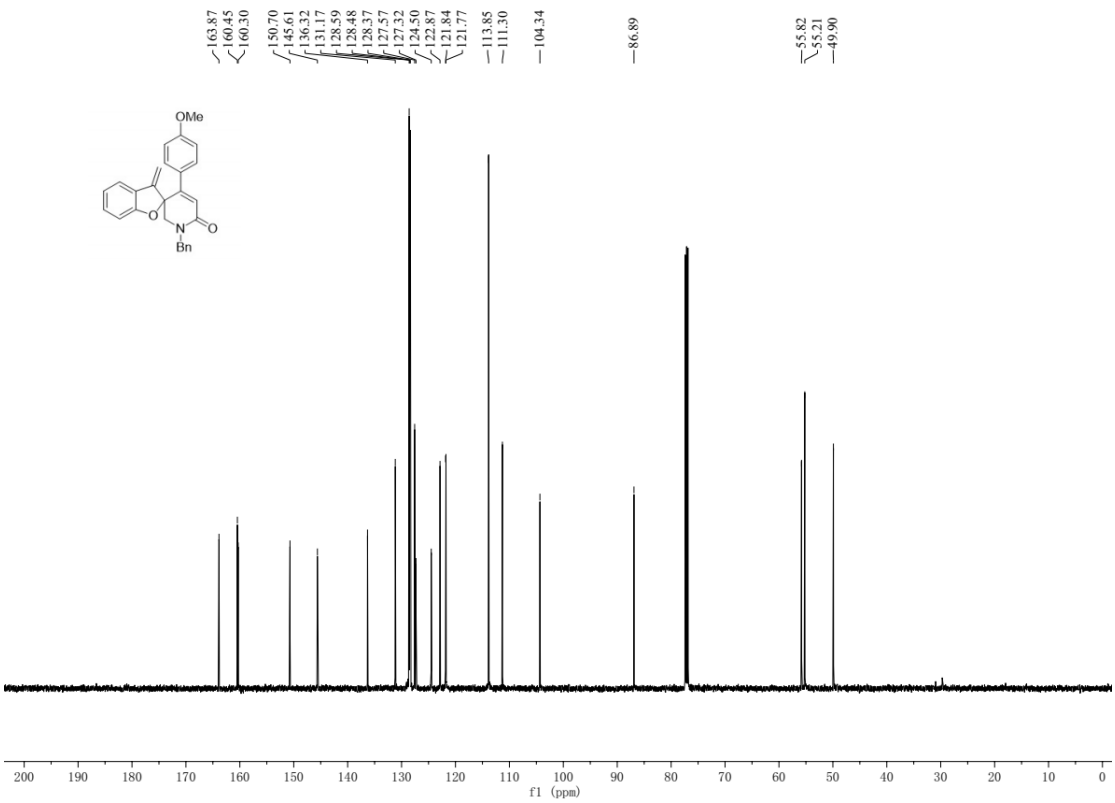
1'-Benzyl-4'-(4-methoxyphenyl)-3-methylene-1',2'-dihydro-3H,6'H-spiro-[benzofuran-2,3'-pyridin]-6'-one (2d):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 69.5 mg, 85% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41-7.39 (m, 1H), 7.31-7.27 (m, 4H), 7.25-7.22 (m, 2H), 7.12-7.09 (m, 2H), 6.97 (t, J = 7.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.74-6.71 (m, 2H), 6.35 (s, 1H), 5.46 (d, J = 1.0 Hz, 1H), 4.95 (d, J = 1.0 Hz, 1H), 4.84 (d, J = 15.0 Hz, 1H), 4.47 (d, J = 15.0 Hz, 1H), 3.72-3.70 (m, 4H), 3.30 (d, J = 13.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.9, 160.5, 160.3, 150.7, 145.6, 136.3, 131.2, 128.6, 128.5, 128.4, 127.6, 127.3, 124.5, 122.9, 121.84, 121.77, 113.9, 111.3, 104.3, 86.9, 55.8, 55.2, 49.9. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_3^+$ ([M+H]$^+$): 410.1751, found 410.1755.

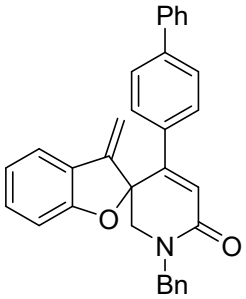


^{1}H NMR of compound **2d** (500 MHz, $CDCl_3$)

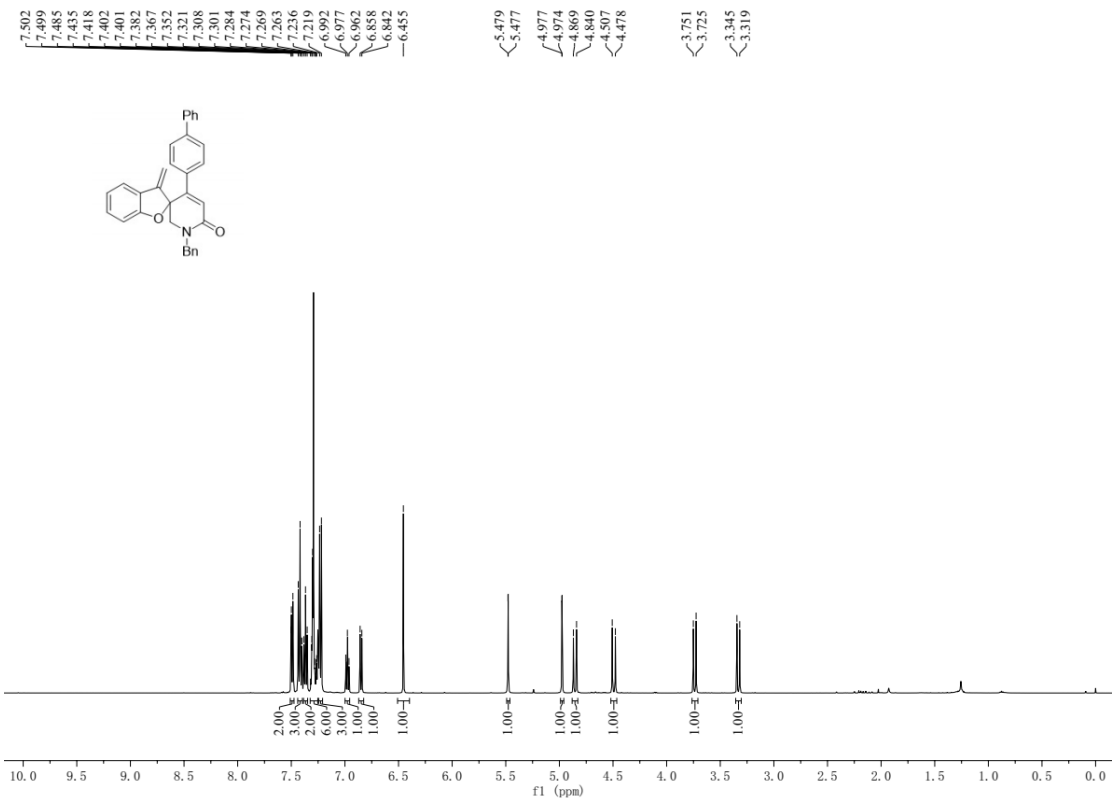


^{13}C NMR of compound **2d** (125 MHz, $CDCl_3$)

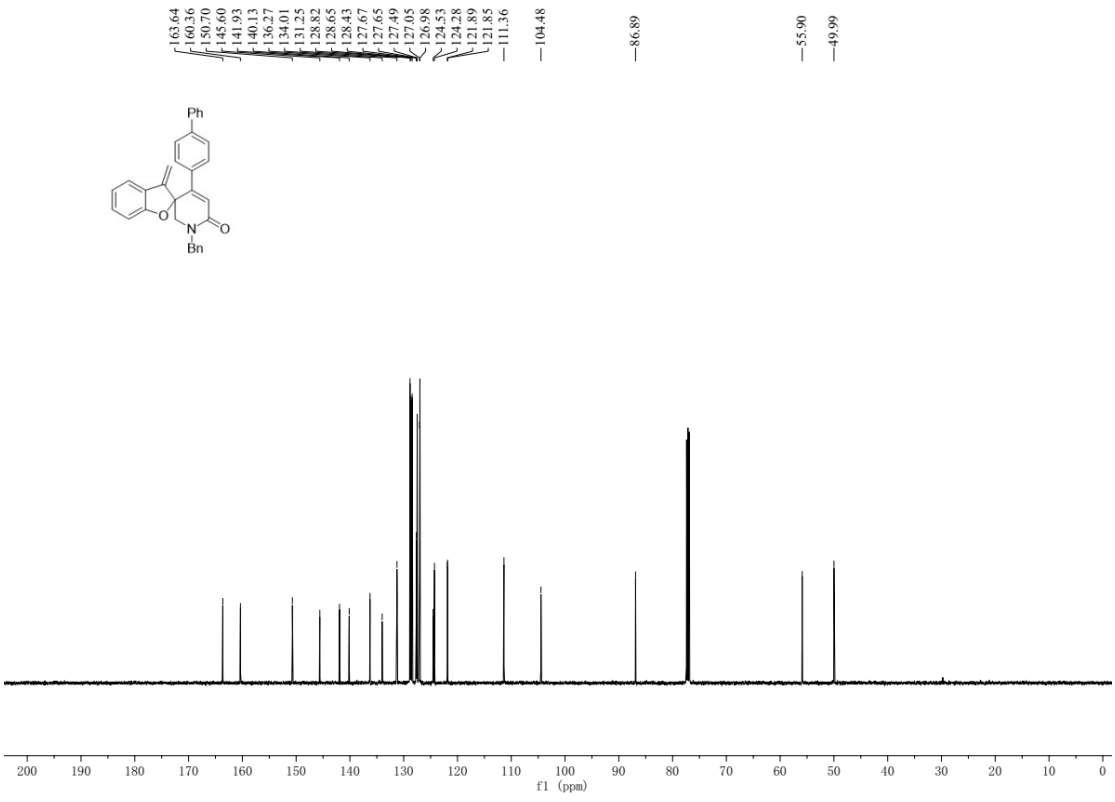
4'-([1,1'-Biphenyl]-4-yl)-1'-benzyl-3-methylene-1',2'-dihydro-3H,6'H-spiro-[benzofuran-2,3'-pyridin]-6'-one (2e):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 79.2 mg, 87% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50-7.49 (m, 2H), 7.44-7.40 (m, 3H), 7.38-7.35 (m, 2H), 7.32-7.26 (m, 6H), 7.24-7.22 (m, 3H), 6.98 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.46 (s, 1H), 5.48 (d, J = 1.0 Hz, 1H), 4.98 (d, J = 1.0 Hz, 1H), 4.85 (d, J = 14.5 Hz, 1H), 4.49 (d, J = 14.5 Hz, 1H), 3.74 (d, J = 13.0 Hz, 1H), 3.33 (d, J = 13.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.6, 160.4, 150.7, 145.6, 141.9, 140.1, 136.3, 134.0, 131.3, 128.8, 128.7, 128.4, 127.67, 127.65, 127.5, 127.1, 127.0, 124.5, 124.3, 121.89, 121.85, 111.4, 104.5, 86.9, 55.9, 50.0. HRMS *m/z* (ESI+): Calculated for $C_{32}H_{26}NO_2^+$ ([M+H]$^+$): 456.1958, found 456.1961.

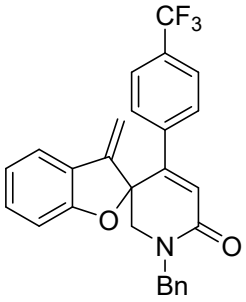


^{1}H NMR of compound **2e** (500 MHz, $CDCl_3$)

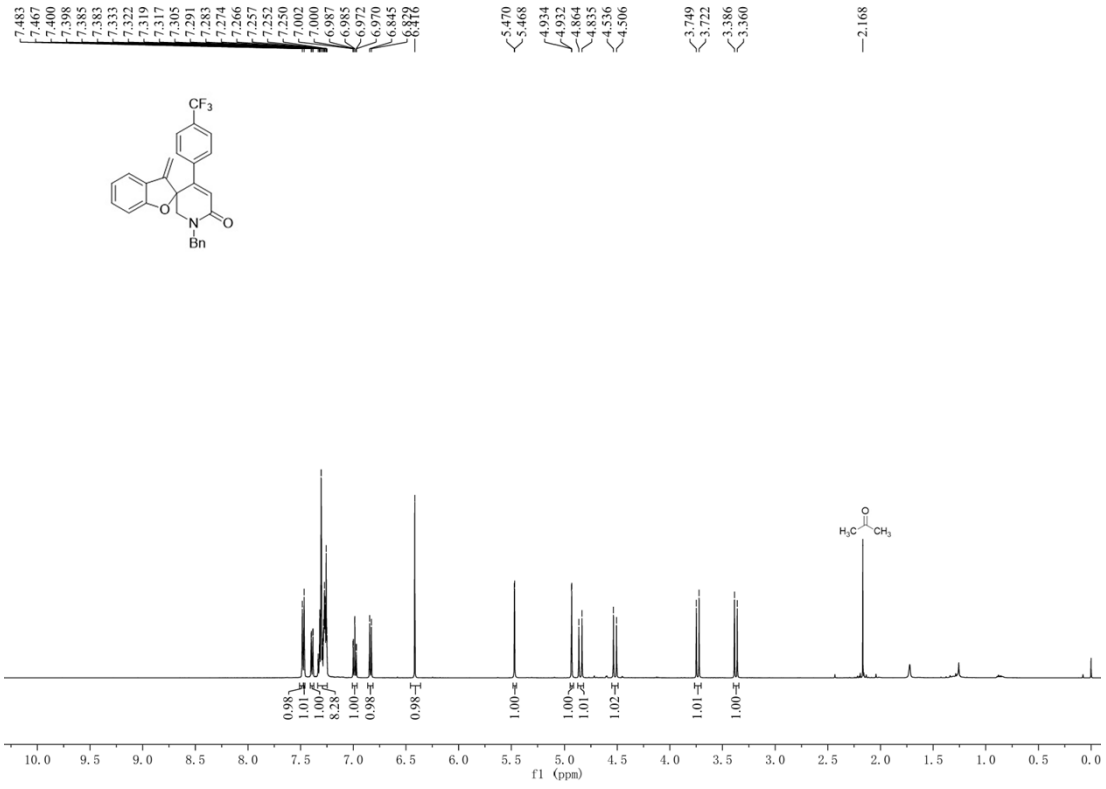


^{13}C NMR of compound **2e** (125 MHz, $CDCl_3$)

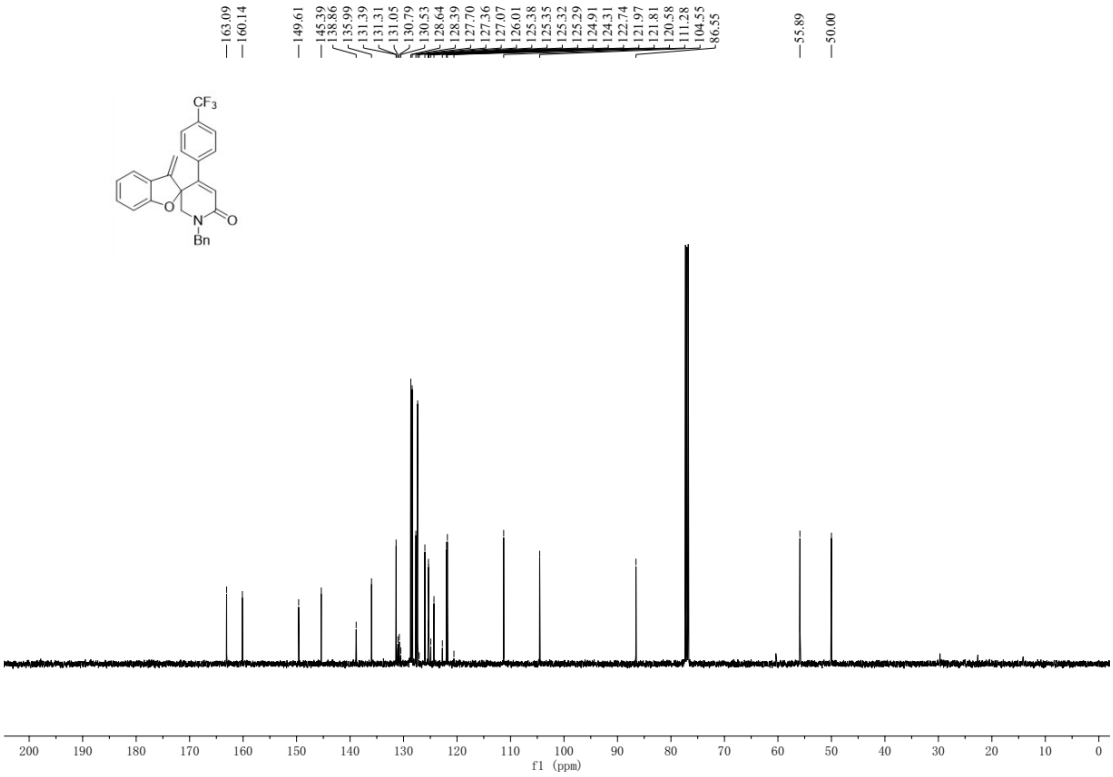
1'-Benzyl-3-methylene-4'-(4-(trifluoromethyl)phenyl)-1',2'-dihydro-3H,6'H-spiro-[benzofuran-2,3'-pyridin]-6'-one (2f):



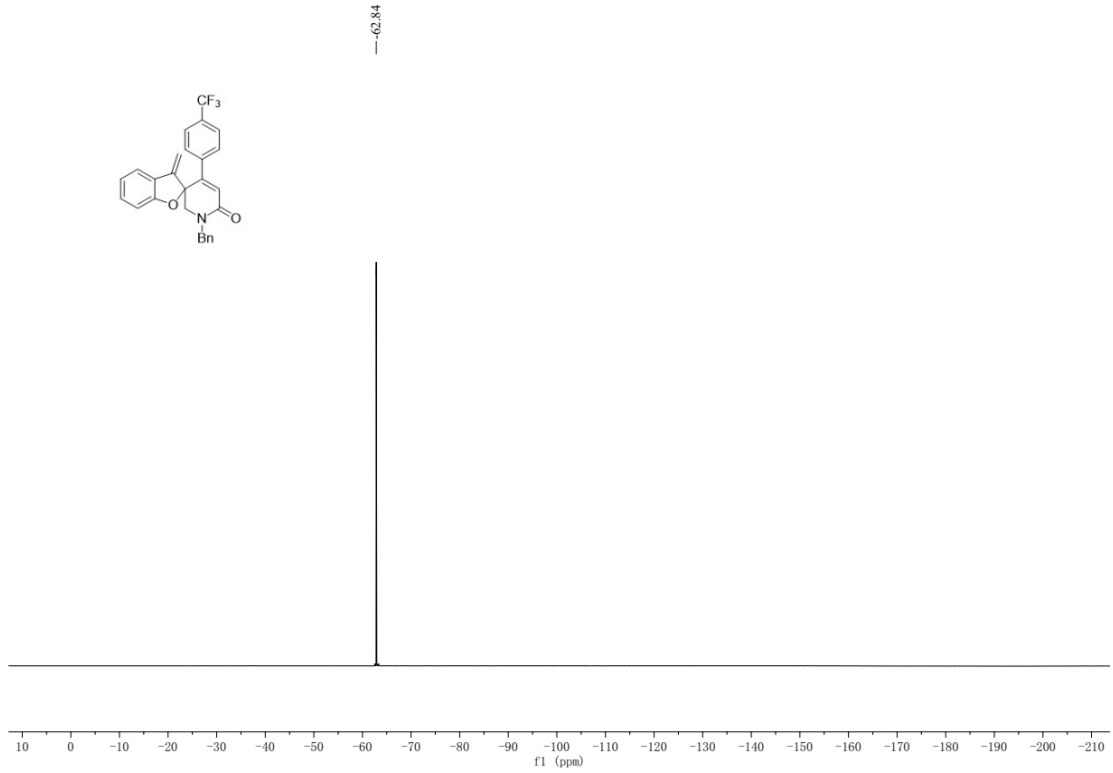
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 34.0 mg, 38% yield; ^{1}H NMR (500 MHz,$CDCl_3$): δ 7.48 (s, 1H), 7.47 (s, 1H), 7.40-7.38 (m, 1H), 7.34-7.25 (m, 8H), 6.99 (td, J = 7.5, 1.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.42 (s, 1H), 5.47 (d, J = 1.0 Hz, 1H), 4.93 (d, J = 1.0 Hz, 1H), 4.85 (d, J = 14.5 Hz, 1H), 4.52 (d, J = 14.5 Hz, 1H), 3.74 (d, J = 13.0 Hz, 1H), 3.37 (d, J = 13.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.1, 160.1, 149.6, 145.4, 138.9, 136.0, 131.4, 130.9 (q, J = 32.5 Hz), 128.6, 128.4, 127.7, 127.4, 126.0, 125.3 (q, J = 3.8 Hz), 124.3, 123.8 (q, J = 271.3 Hz), 122.0, 121.8, 111.3, 104.6, 86.6, 55.9, 50.0. ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.8. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{21}F_3NO_2^+$ ([M+H]$^+$): 448.1519, found 448.1528.



^{1}H NMR of compound **2f** (500 MHz, $CDCl_3$)

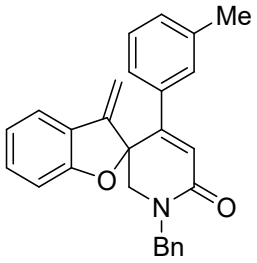


^{13}C NMR of compound **2f** (125 MHz, $CDCl_3$)

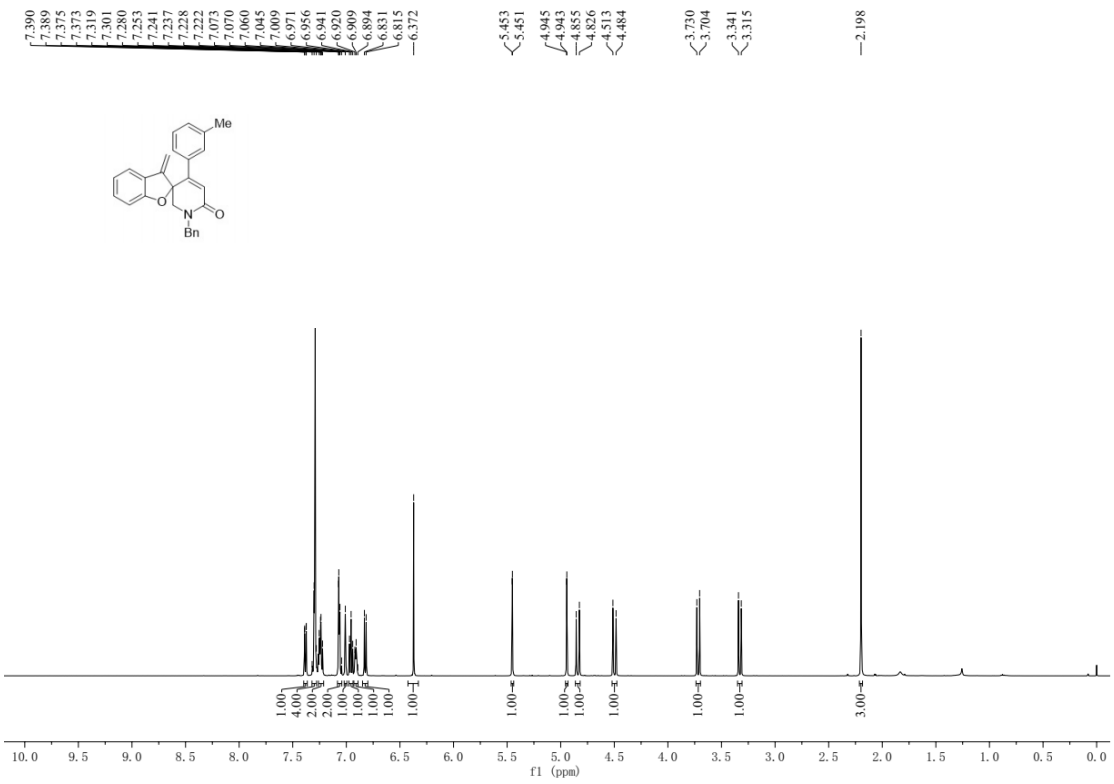


^{19}F NMR of compound **2f** (375 MHz, $CDCl_3$)

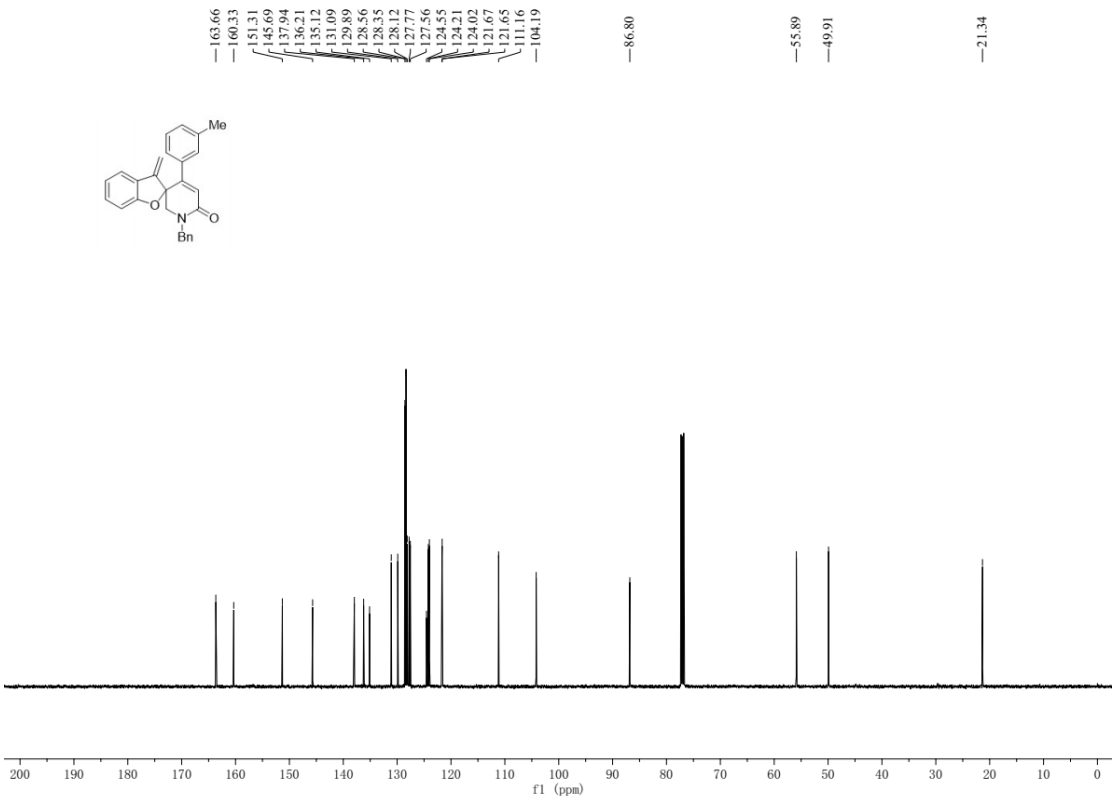
1'-Benzyl-3-methylene-4'-(m-tolyl)-1',2'-dihydro-3H,6'H-spiro[benzofuran-2,3'-pyridin]-6'-one (2g):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 56.6 mg, 72% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.37 (m, 1H), 7.32-7.28 (m, 4H), 7.25-7.22 (m, 2H), 7.07-7.05 (m, 2H), 7.01 (s, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.92-6.89 (m, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.37 (s, 1H), 5.45 (d, J = 1.0 Hz, 1H), 4.94 (d, J = 1.0 Hz, 1H), 4.84 (d, J = 14.5 Hz, 1H), 4.50 (d, J = 14.5 Hz, 1H), 3.72 (d, J = 13.0 Hz, 1H), 3.33 (d, J = 13.0 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7, 160.3, 151.3, 145.7, 137.9, 136.2, 135.1, 131.1, 129.9, 128.6, 128.4, 128.1, 127.8, 127.6, 124.6, 124.2, 124.0, 121.67, 121.65, 111.2, 104.2, 86.8, 55.9, 49.9, 21.3. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_2^+$ ([M+H]$^+$): 394.1802, found 394.1808.

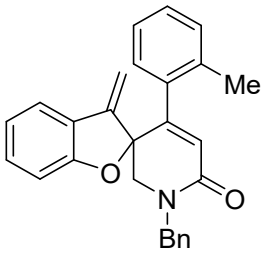


^{1}H NMR of compound **2g** (500 MHz, $CDCl_3$)

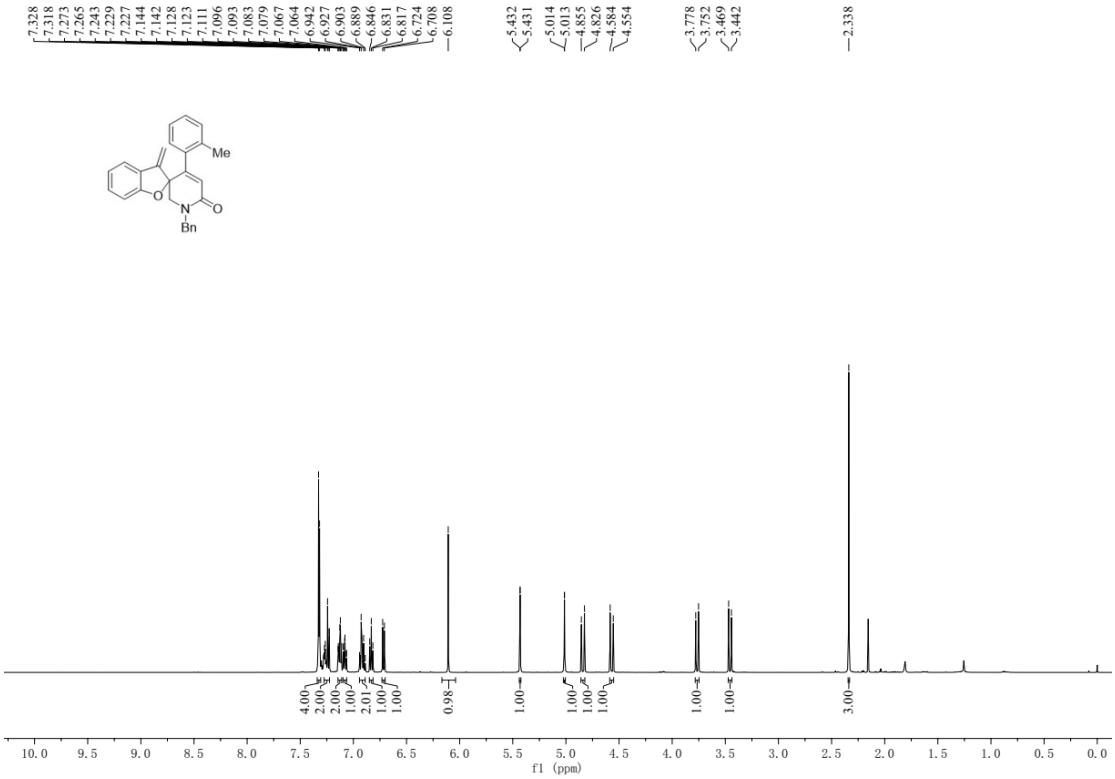


^{13}C NMR of compound **2g** (125 MHz, $CDCl_3$)

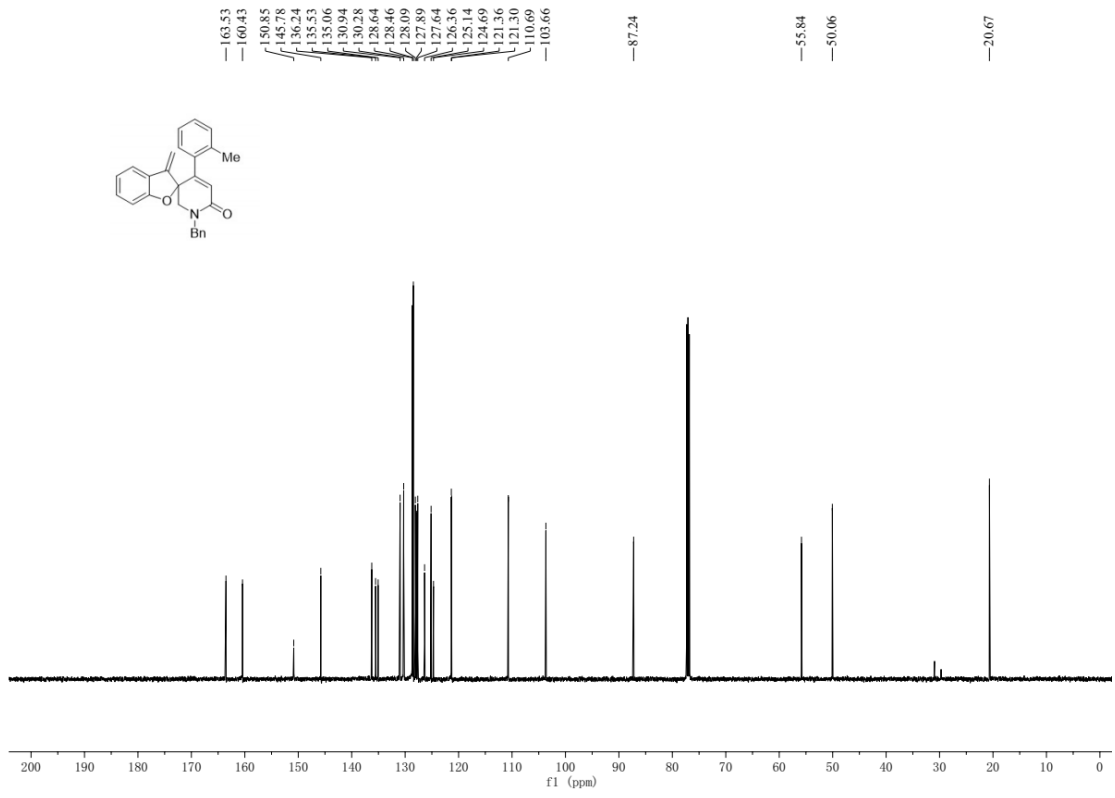
1'-Benzyl-3-methylene-4'-(o-tolyl)-1',2'-dihydro-3H,6'H-spiro[benzofuran-2,3'-pyridin]-6'-one (2h):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 23.6 mg, 30% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.32 (m, 4H), 7.27-7.23 (m, 2H), 7.14-7.11 (m, 2H), 7.10-7.06 (m, 1H), 6.94-6.89 (m, 2H), 6.83 (t, J = 7.5 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 6.11 (s, 1H), 5.43 (d, J = 0.5 Hz, 1H), 5.01 (d, J = 0.5 Hz, 1H), 4.84 (d, J = 14.5 Hz, 1H), 4.57 (d, J = 14.5 Hz, 1H), 3.77 (d, J = 13.0 Hz, 1H), 3.46 (d, J = 13.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.5, 160.4, 150.9, 145.8, 136.2, 135.5, 135.1, 130.9, 130.3, 128.6, 128.5, 128.1, 127.9, 127.6, 126.4, 125.1, 124.7, 121.4, 121.3, 110.7, 103.7, 87.2, 55.8, 50.1, 20.7. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_2^+$ ([M+H]$^+$): 394.1802, found 394.1806.

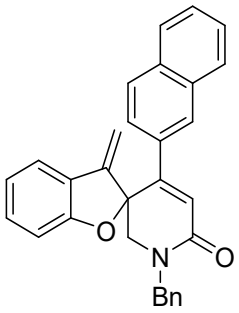


^{1}H NMR of compound **2h** (500 MHz, $CDCl_3$)

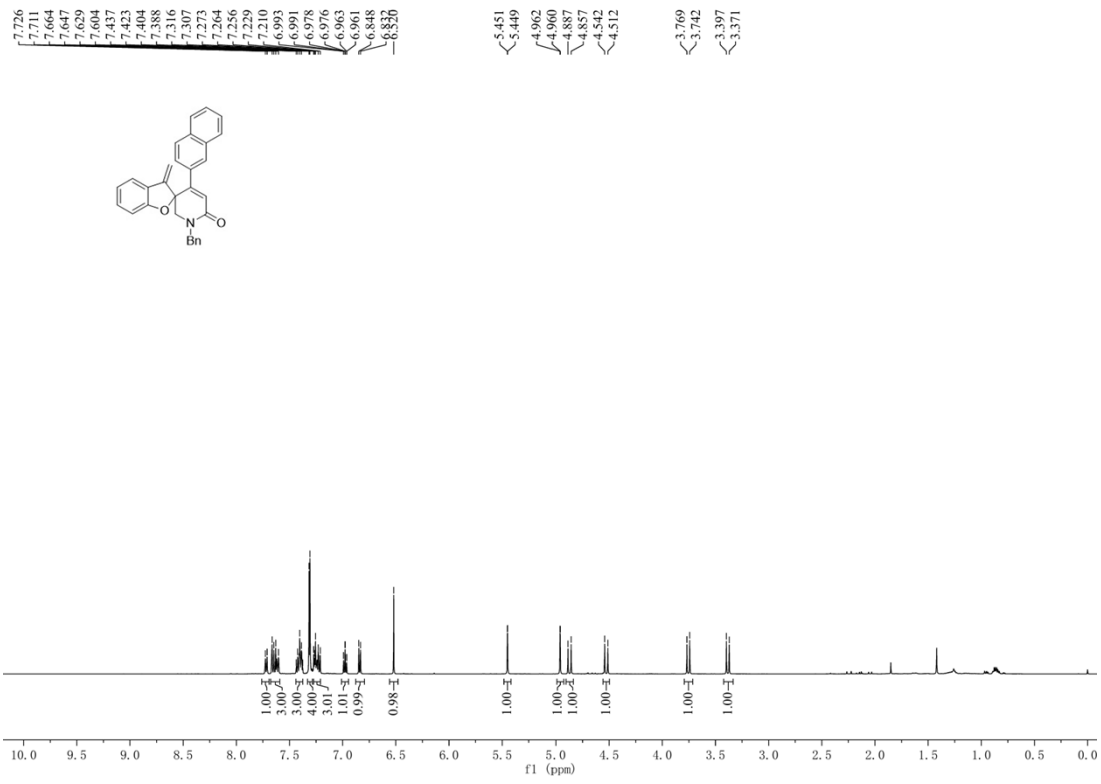


^{13}C NMR of compound **2h** (125 MHz, $CDCl_3$)

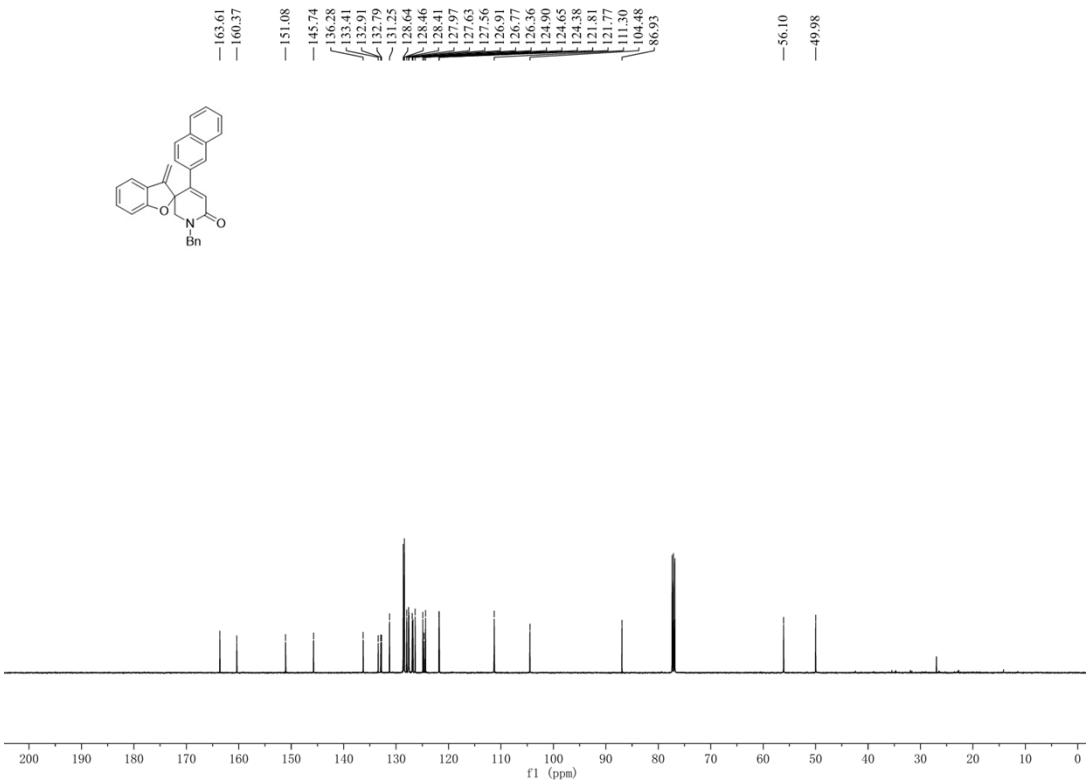
1'-Benzyl-3-methylene-4'-(naphthalen-2-yl)-1',2'-dihydro-3H,6'H-spiro-[benzofuran-2,3'-pyridin]-6'-one (2i):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 54.9 mg, 64% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, J = 7.5 Hz, 1H), 7.66-7.60 (m, 3H), 7.44-7.38 (m, 3H), 7.32-7.31 (m, 4H), 7.27-7.21 (m, 3H), 7.00-6.96 (m, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.52 (s, 1H), 5.45 (d, J = 1.0 Hz, 1H), 4.96 (d, J = 1.0 Hz, 1H), 4.87 (d, J = 15.0 Hz, 1H), 4.53 (d, J = 15.0 Hz, 1H), 3.76 (d, J = 13.5 Hz, 1H), 3.38 (d, J = 13.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.6, 160.4, 151.1, 145.7, 136.3, 133.4, 132.9, 132.8, 131.3, 128.6, 128.5, 128.4, 128.0, 127.63, 127.56, 126.9, 126.8, 126.4, 124.9, 124.7, 124.4, 121.81, 121.77, 111.3, 104.5, 86.9, 56.1, 50.0. HRMS *m/z* (ESI+): Calculated for $C_{30}H_{24}NO_2^+$ ([M+H]$^+$): 430.1802, found 430.1804.

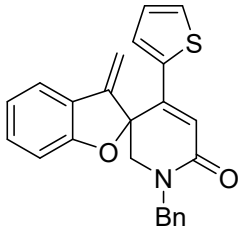


^{1}H NMR of compound **2i** (500 MHz, $CDCl_3$)

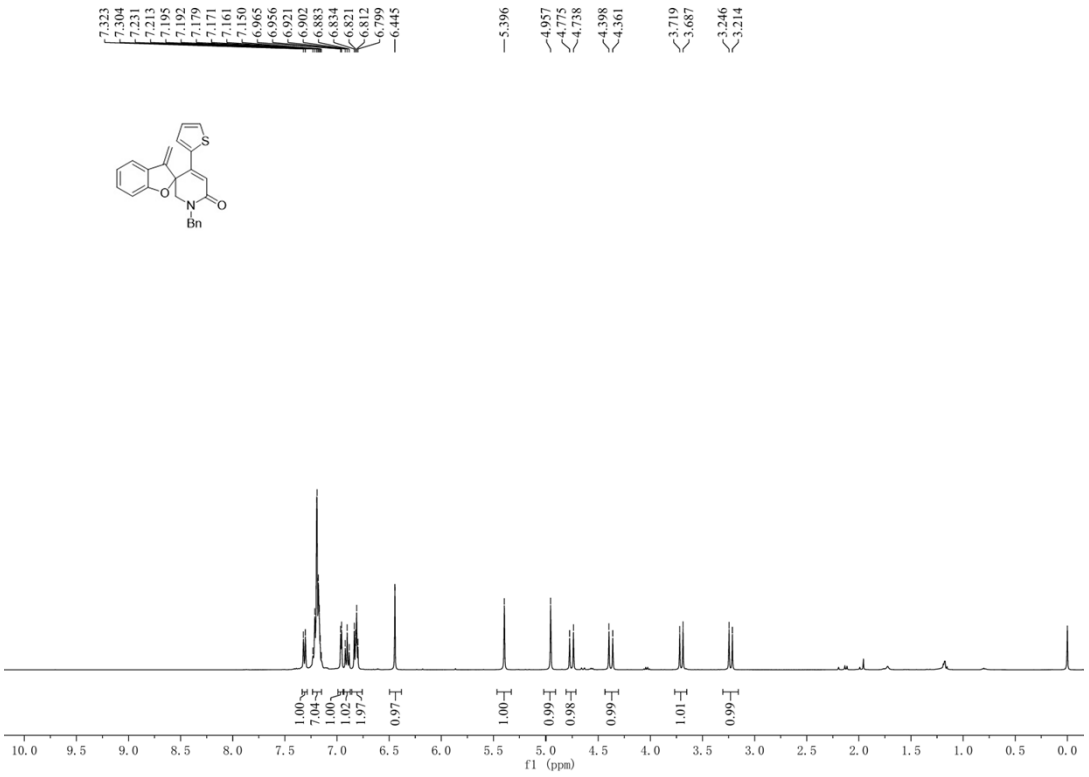


^{13}C NMR of compound **2i** (125 MHz, $CDCl_3$)

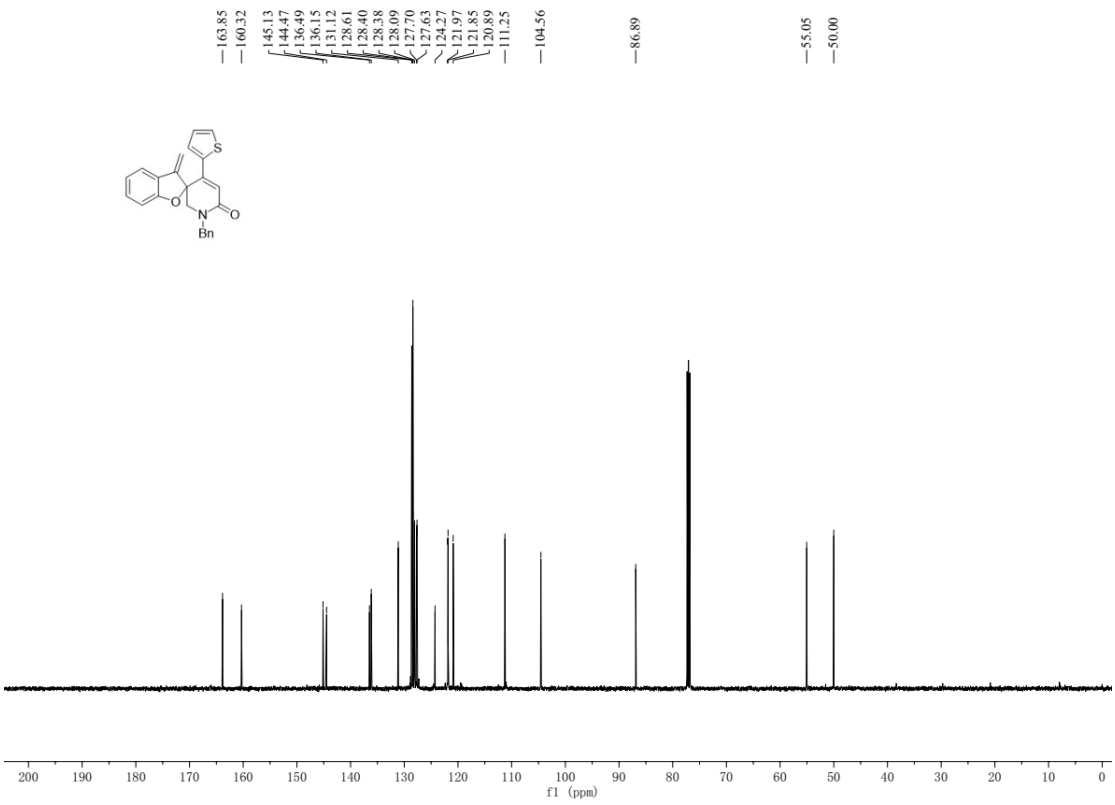
1'-Benzyl-3-methylene-4'-(thiophen-2-yl)-1',2'-dihydro-3H,6'H-spiro[benzofuran-2,3'-pyridin]-6'-one (2j):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 57.0 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 7.6 Hz, 1H), 7.23-7.15 (m, 7H), 6.96 (d, J = 3.6 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.83-6.80 (m, 2H), 6.45 (s, 1H), 5.40 (s, 1H), 4.96 (s, 1H), 4.76 (d, J = 14.8 Hz, 1H), 4.38 (d, J = 14.8 Hz, 1H), 3.70 (d, J = 12.8 Hz, 1H), 3.23 (d, J = 12.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 163.9, 160.3, 145.1, 144.5, 136.5, 136.2, 131.1, 128.6, 128.40, 128.38, 128.1, 127.7, 127.6, 124.3, 122.0, 121.9, 120.9, 111.3, 104.6, 86.9, 55.1, 50.0. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{20}NO_2S^+$ ([M+H]$^+$): 386.1209, found 386.1212.

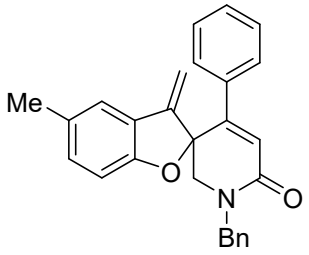


^{1}H NMR of compound **2j** (400 MHz, $CDCl_3$)

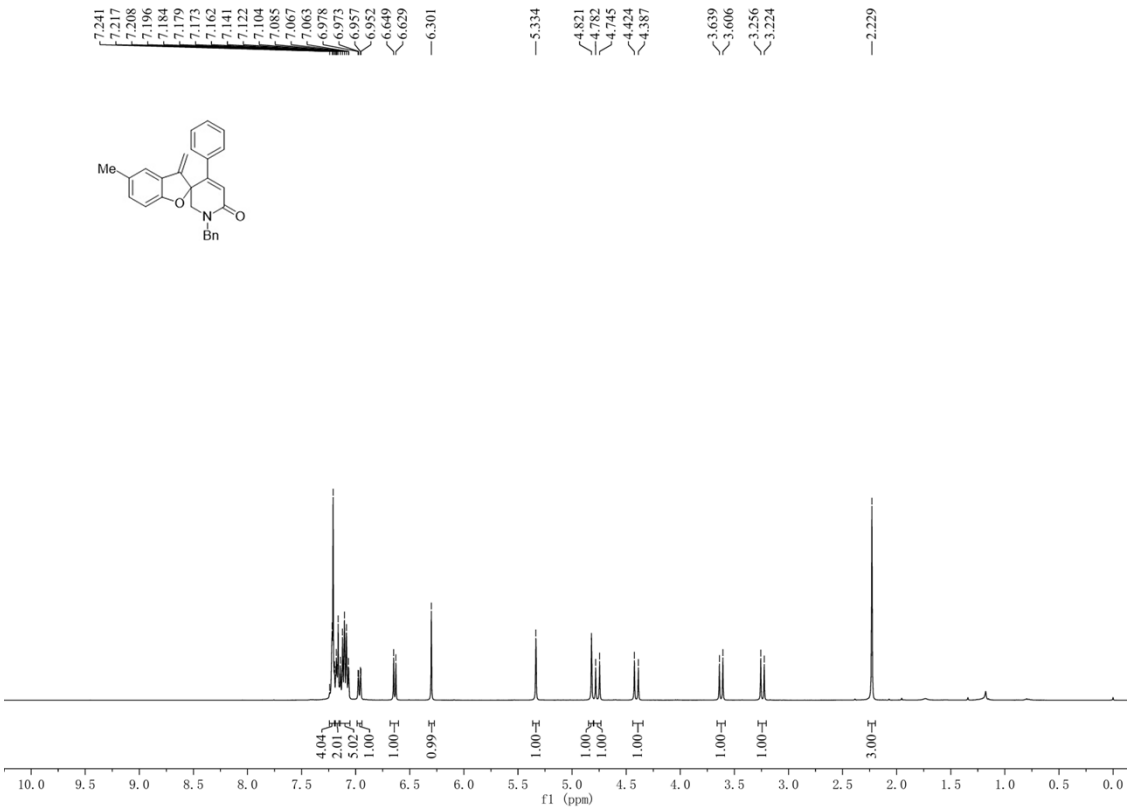


^{13}C NMR of compound **2j** (125 MHz, $CDCl_3$)

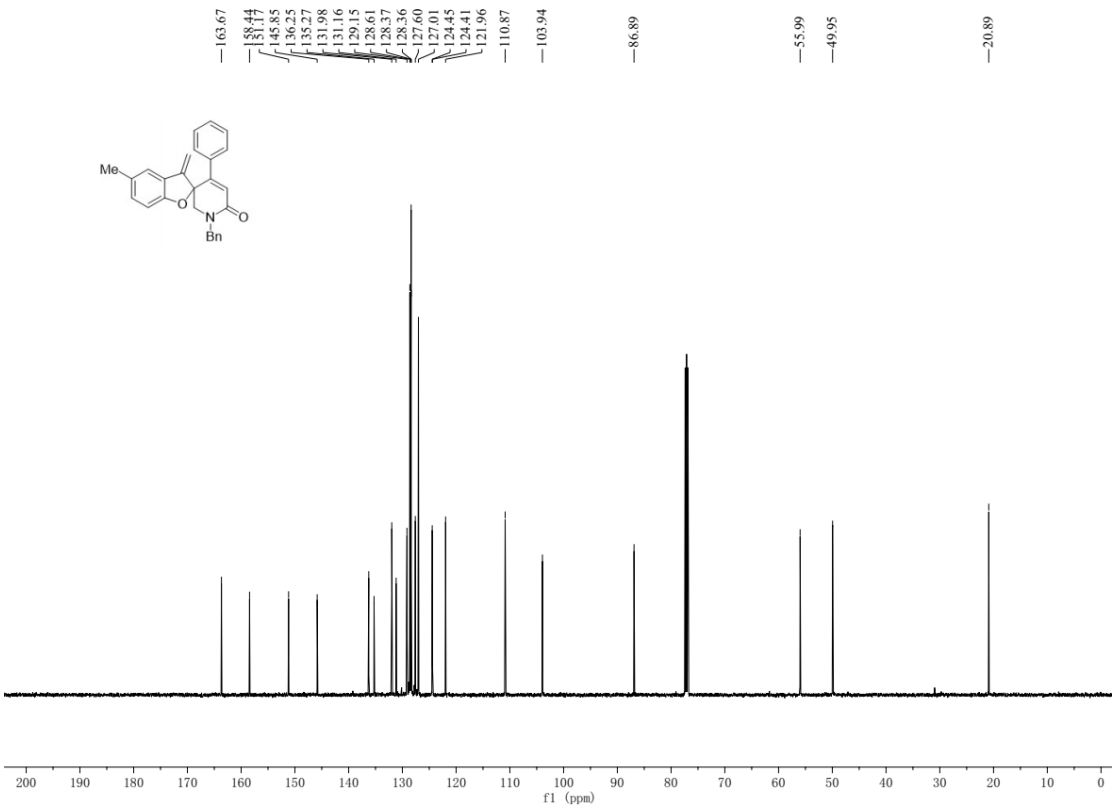
1'-Benzyl-5-methyl-3-methylene-4'-phenyl-1',2'-dihydro-3H,6'H-spiro[benzofuran-2,3'-pyridin]-6'-one (2k):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 58.1 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-2.20 (m, 4H), 7.18-7.16 (m, 2H), 7.14-7.06 (m, 5H), 6.96 (dd, J = 8.4, 2.0 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 6.30 (s, 1H), 5.33 (s, 1H), 4.82 (s, 1H), 4.76 (d, J = 14.8 Hz, 1H), 4.41 (d, J = 14.8 Hz, 1H), 3.62 (d, J = 12.8 Hz, 1H), 3.24 (d, J = 12.8 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7, 158.4, 151.2, 145.9, 136.3, 135.3, 132.0, 131.2, 129.2, 128.6, 128.37, 128.36, 127.6, 127.0, 124.5, 124.4, 122.0, 110.9, 103.9, 86.9, 56.0, 50.0, 20.9. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_2^+$ ([M+H]$^+$): 394.1802, found 394.1806.

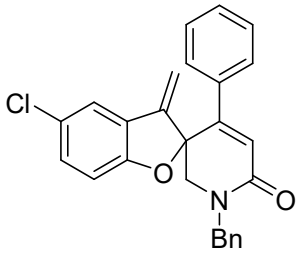


^{1}H NMR of compound **2k** (400 MHz, $CDCl_3$)

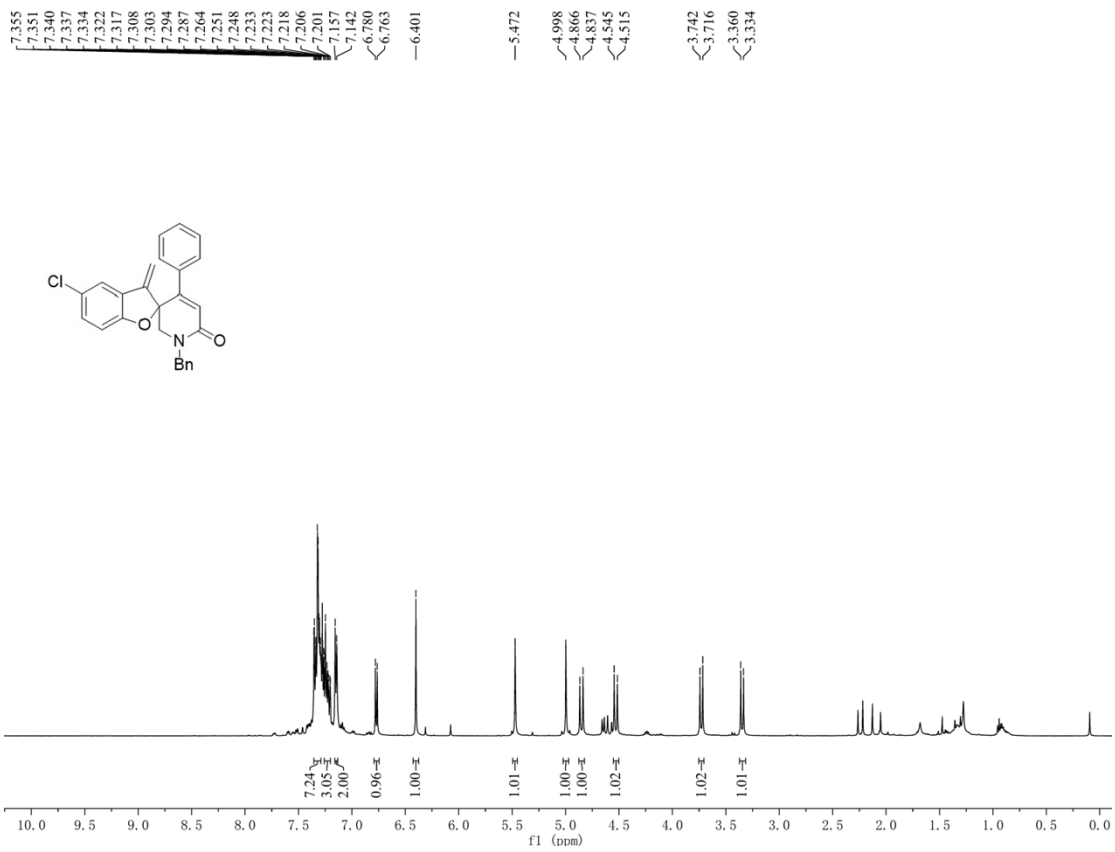


^{13}C NMR of compound **2k** (125 MHz, $CDCl_3$)

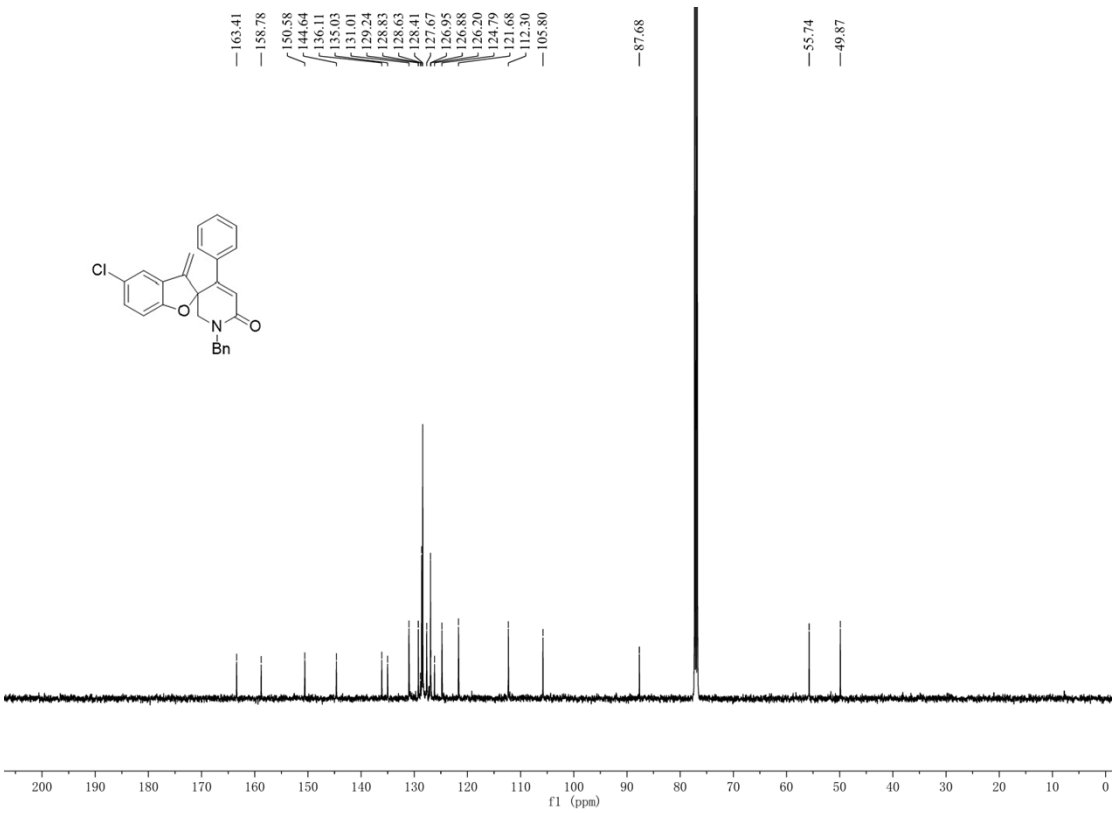
1'-benzyl-5-chloro-3-methylene-4'-phenyl-1',2'-dihydro-3H,6'H-spiro[benzofuran-2,3'-pyridin]-6'-one (2l):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 13.2 mg, 16% yield; The impurities could not be completely removed by chromatography at this stage, the characteristic data for this compound are as follow: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.29 (m, 7H), 7.26-7.20 (m, 3H), 7.15 (d, J = 7.5 Hz, 2H), 6.77 (d, J = 8.5 Hz, 1H), 6.40 (s, 1H), 5.47 (s, 1H), 5.00 (s, 1H), 4.85 (d, J = 14.5 Hz, 1H), 4.53 (d, J = 14.5 Hz, 1H), 3.73 (d, J = 13.0 Hz, 1H), 3.35 (d, J = 13.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.4, 158.8, 150.6, 144.6, 136.1, 135.0, 131.0, 129.2, 128.8, 128.6, 128.4, 127.7, 127.0, 126.7, 126.2, 124.8, 121.7, 112.3, 105.8, 87.7, 55.7, 49.9. HRMS *m/z* (ESI+): Calculated for $C_{26}H_{20}ClNNaO_2^+$ ([M+Na]$^+$): 436.1075, found 436.1080.

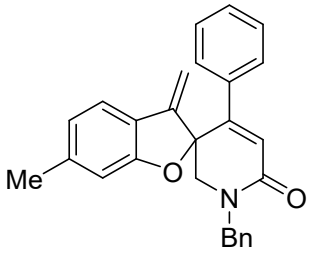


^{1}H NMR of compound **2l** (500 MHz, $CDCl_3$)

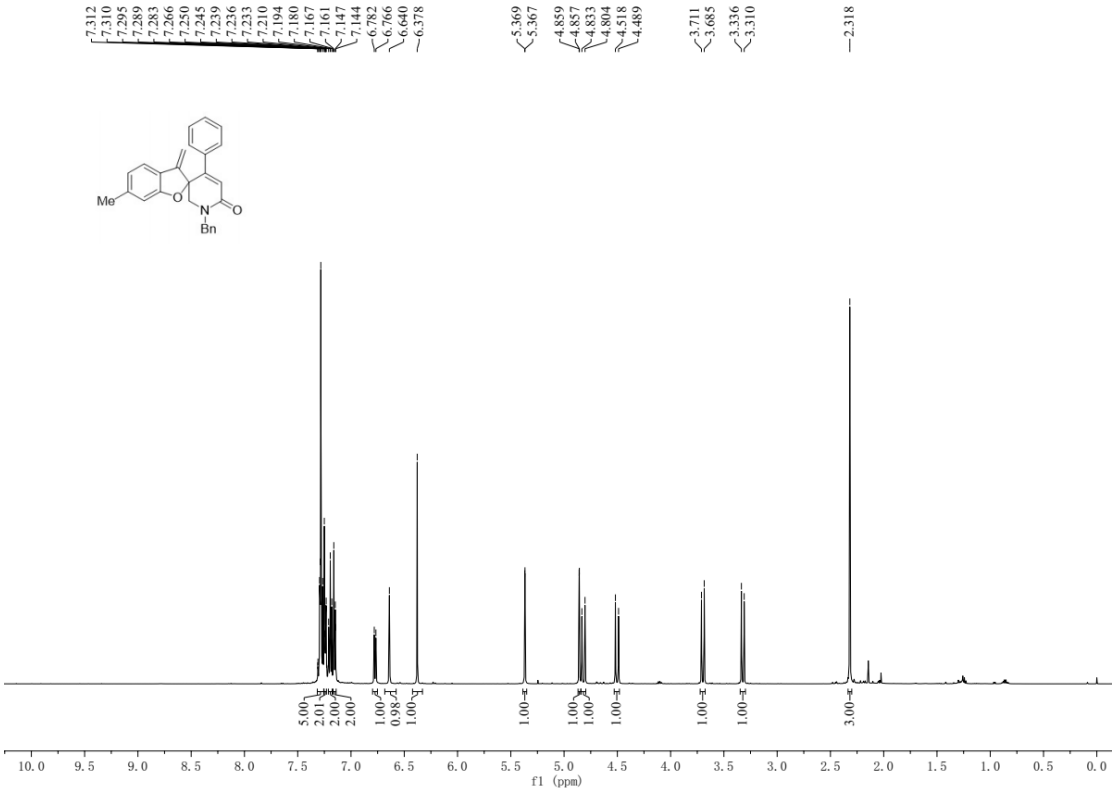


^{13}C NMR of compound **2l** (125 MHz, $CDCl_3$)

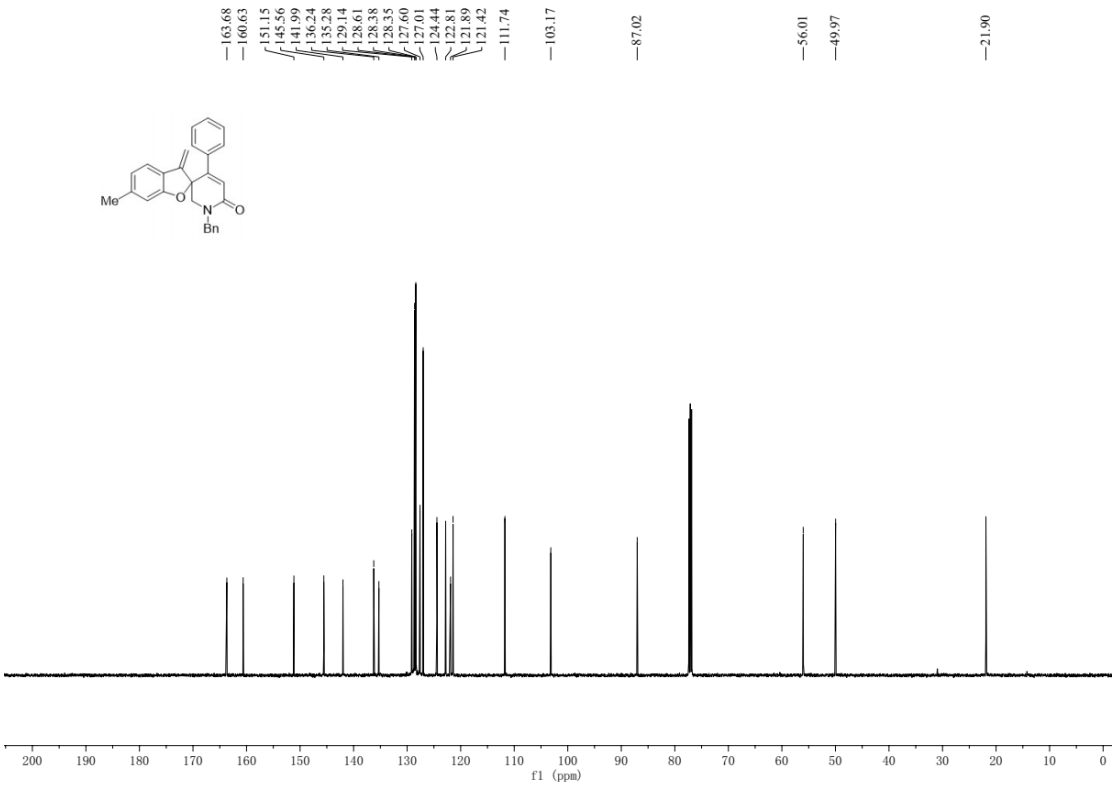
1'-Benzyl-6-methyl-3-methylene-4'-phenyl-1',2'-dihydro-3H,6'H-spiro[benzofuran-2,3'-pyridin]-6'-one (2m):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 59.0 mg, 75% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.27 (m, 5H), 7.25-7.23 (m, 2H), 7.21-7.18 (m, 2H), 7.17-7.14 (m, 2H), 6.77 (d, J = 3.0 Hz, 1H), 6.64 (s, 1H), 6.38 (s, 1H), 5.37 (d, J = 1.0 Hz, 1H), 4.86 (d, J = 1.0 Hz, 1H), 4.82 (d, J = 15.0 Hz, 1H), 4.50 (d, J = 15.0 Hz, 1H), 3.70 (d, J = 13.0 Hz, 1H), 3.32 (d, J = 13.0 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7, 160.6, 151.2, 145.6, 142.0, 136.2, 135.3, 129.1, 128.6, 128.38, 128.35, 127.6, 127.0, 124.4, 122.8, 121.9, 121.4, 111.7, 103.2, 87.0, 56.0, 50.0, 21.9. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_2^+$ ($[M+H]^+$): 394.1802, found 394.1804.

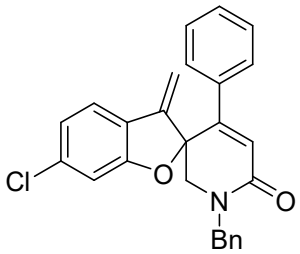


^{1}H NMR of compound **2m** (500 MHz, $CDCl_3$)

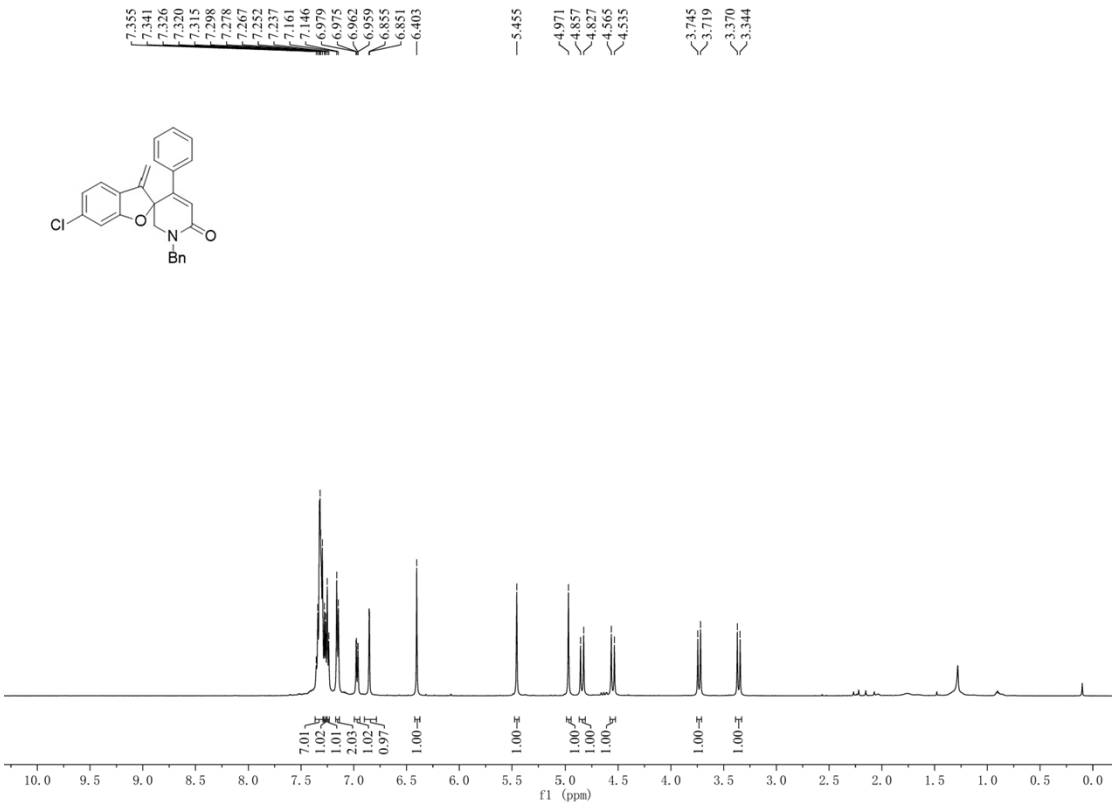


^{13}C NMR of compound **2m** (125 MHz, $CDCl_3$)

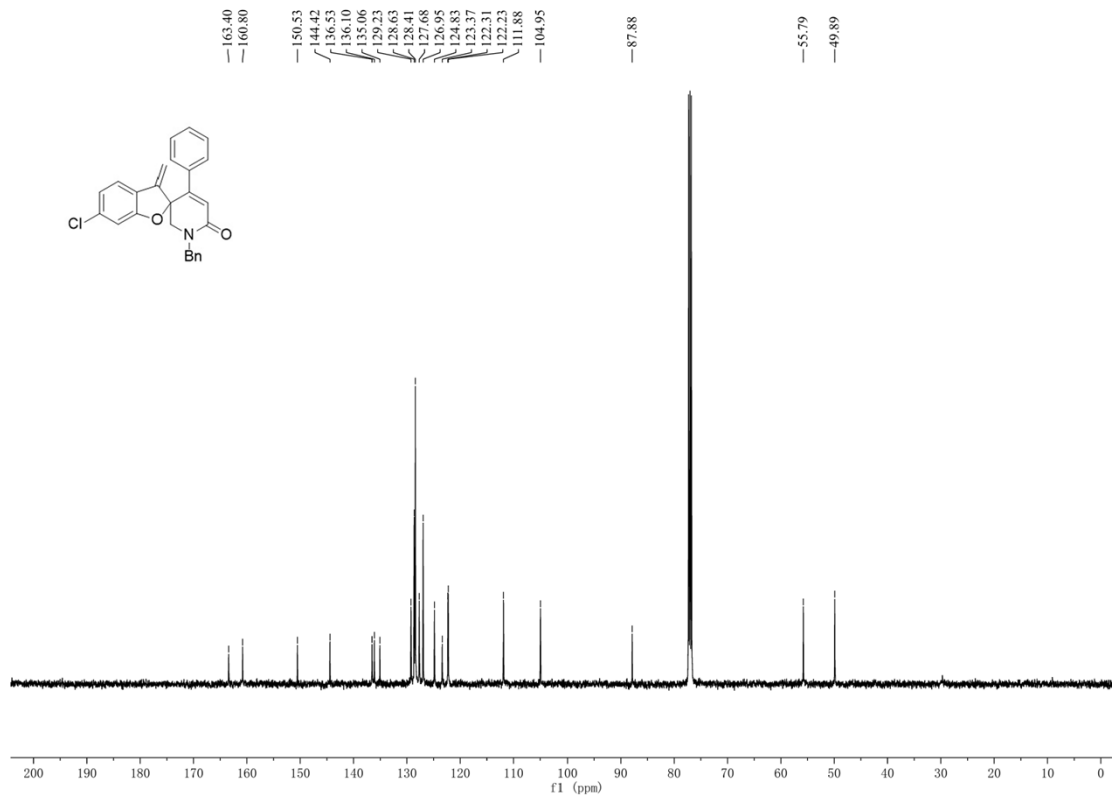
1'-benzyl-6-chloro-3-methylene-4'-phenyl-1',2'-dihydro-3H,6'H-spiro[benzofuran-2,3'-pyridin]-6'-one (2n):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 33.8 mg, 41% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.30 (m, 7H), 7.27 (d, J = 5.5 Hz, 1H), 7.24 (d, J = 7.5 Hz, 1H), 7.15 (d, J = 7.5 Hz, 2H), 6.97 (dd, J = 8.0, 2.0 Hz, 1H), 6.85 (d, J = 2.0 Hz, 1H), 6.40 (s, 1H), 5.46 (s, 1H), 4.97 (s, 1H), 4.84 (d, J = 15.0 Hz, 1H), 4.55 (d, J = 15.0 Hz, 1H), 3.73 (d, J = 13.0 Hz, 1H), 3.36 (d, J = 13.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.4, 160.8, 150.5, 144.4, 136.5, 136.1, 135.1, 129.2, 128.6, 128.4, 127.7, 127.0, 124.8, 123.4, 122.3, 122.2, 111.9, 105.0, 87.9, 55.8, 49.9. HRMS *m/z* (ESI+): Calculated for $C_{26}H_{21}ClNO_2^+$ ([M+H]$^+$): 414.1255, found 414.1264.

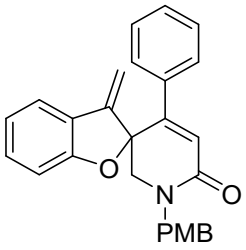


^{1}H NMR of compound **2n** (500 MHz, $CDCl_3$)

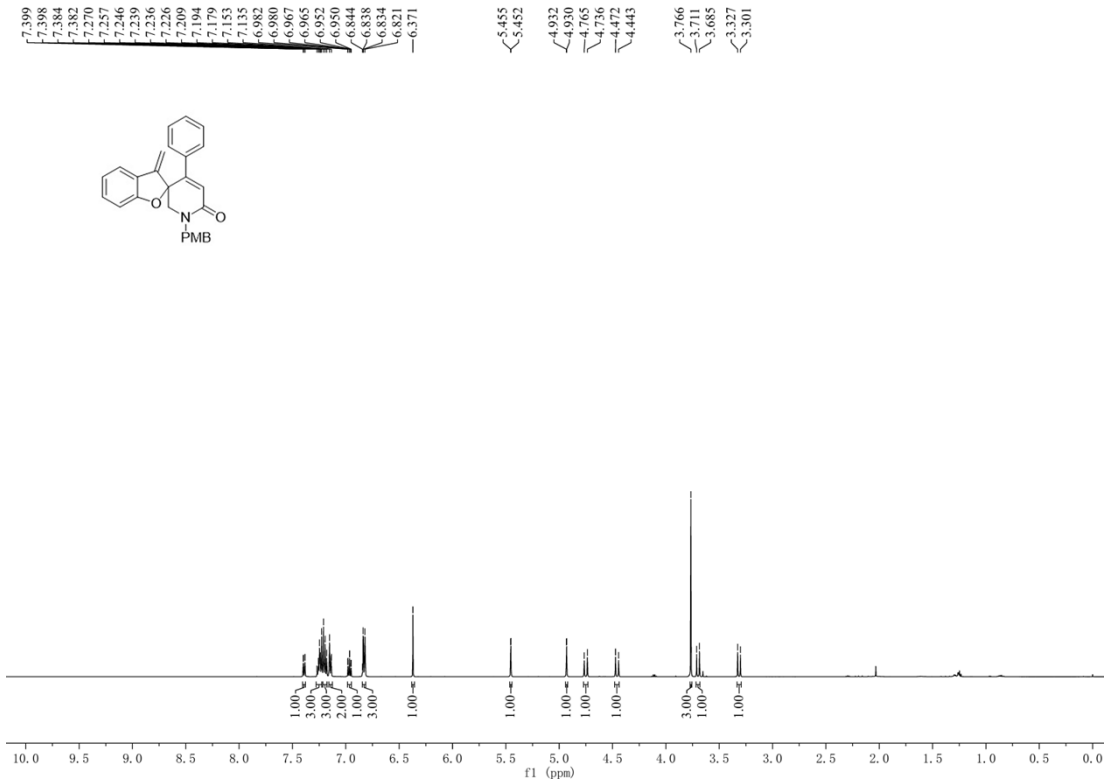


^{13}C NMR of compound **2n** (125 MHz, $CDCl_3$)

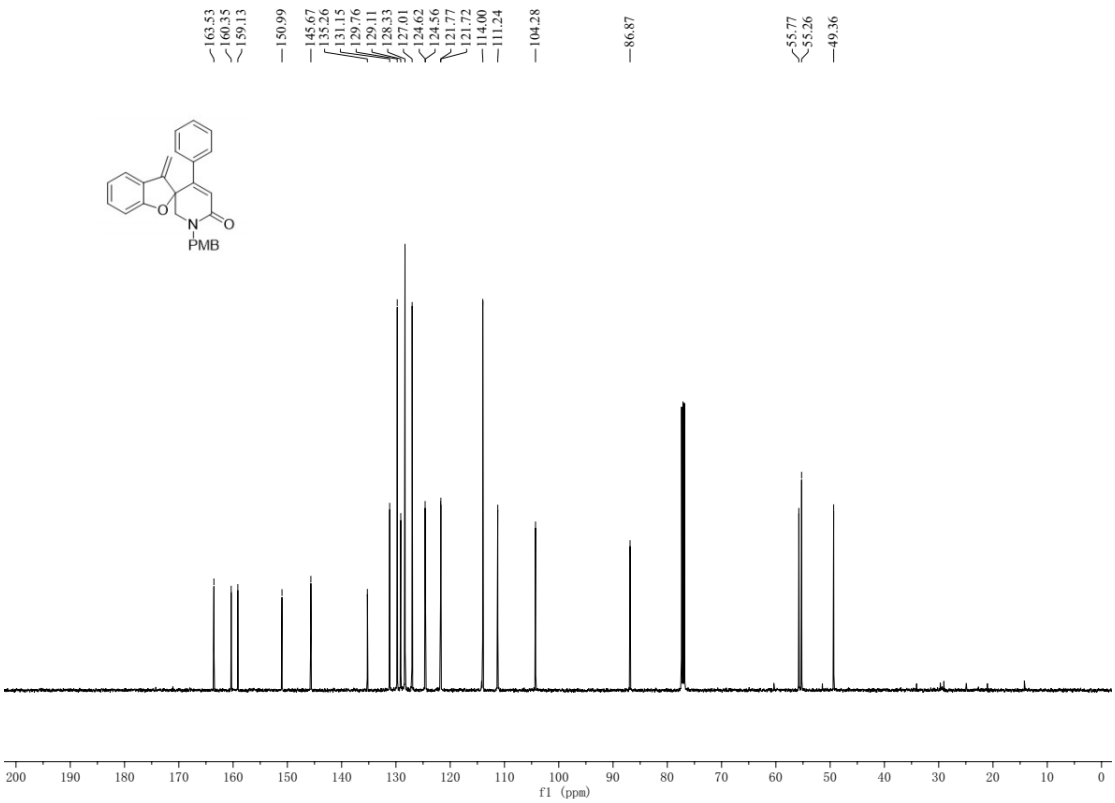
1'-(4-Methoxybenzyl)-3-methylene-4'-phenyl-1',2'-dihydro-3H,6'H-spiro-[benzofuran-2,3'-pyridin]-6'-one (2o):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 57.3 mg, 70% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.38 (m, 1H), 7.27-7.23 (m, 3H), 7.21-7.18 (m, 3H), 7.15-7.14 (m, 2H), 6.97 (td, J = 7.5, 1.0 Hz, 1H), 6.84-6.82 (m, 3H), 6.37 (s, 1H), 5.45 (d, J = 1.5 Hz, 1H), 4.93 (d, J = 1.5 Hz, 1H), 4.75 (d, J = 14.5 Hz, 1H), 4.46 (d, J = 14.5 Hz, 1H), 3.77 (s, 3H), 3.70 (d, J = 13.0 Hz, 1H), 3.31 (d, J = 13.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.5, 160.4, 159.1, 151.0, 145.7, 135.3, 131.2, 129.8, 129.1, 128.3, 127.0, 124.62, 124.56, 121.8, 121.7, 114.0, 111.2, 104.3, 86.9, 55.8, 55.3, 49.4. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_3^+$ ([M+H]$^+$): 410.1751, found 410.1754.

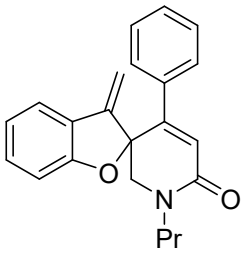


^{1}H NMR of compound **2o** (500 MHz, $CDCl_3$)

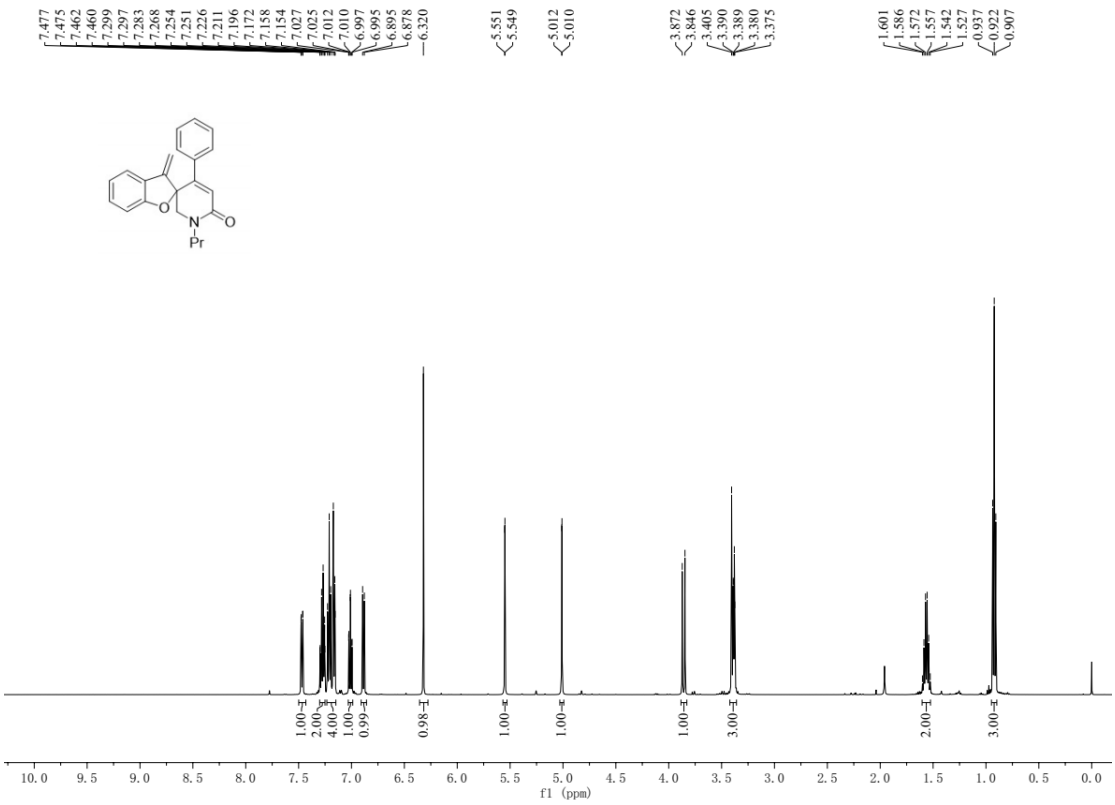


^{13}C NMR of compound **2o** (125 MHz, $CDCl_3$)

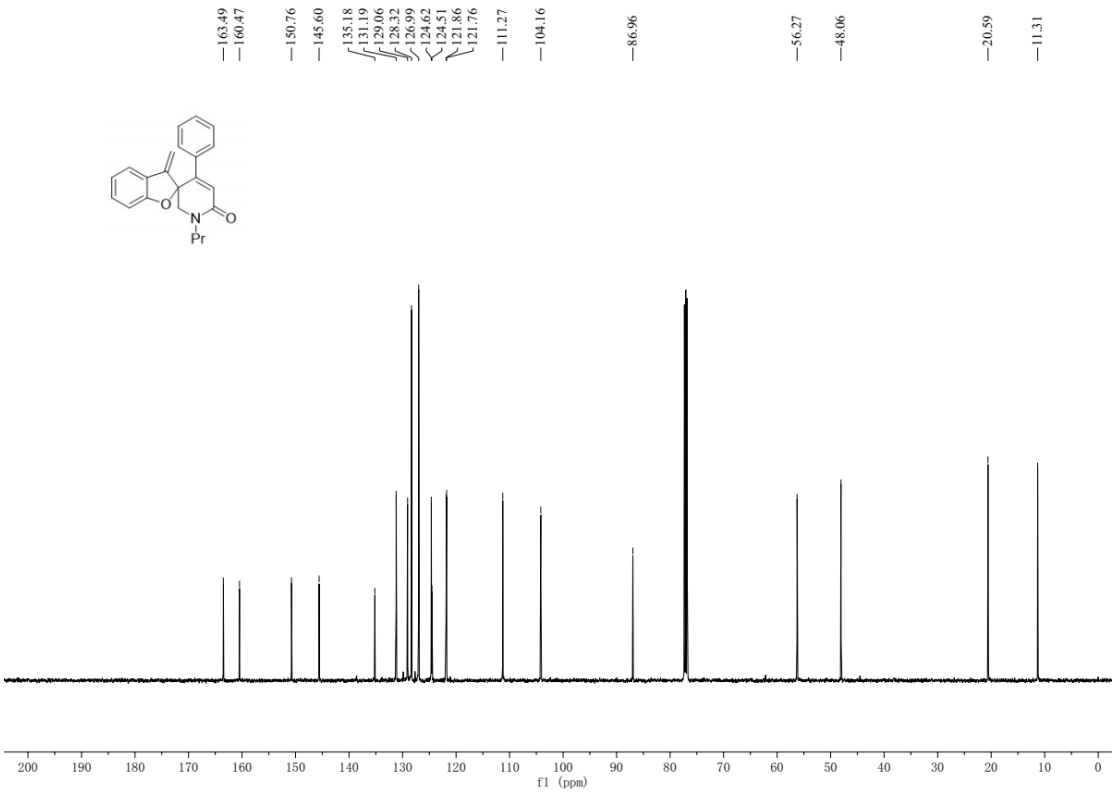
3-Methylene-4'-phenyl-1'-propyl-1',2'-dihydro-3H,6'H-spiro[benzofuran-2,3'-pyridin]-6'-one (2p):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); light yellow solid, Mp = 103-104 °C; 55.6 mg, 84% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48-7.46 (m, 1H), 7.30-7.25 (m, 2H), 7.23-7.15 (m, 4H), 7.01 (td, J = 7.5, 1.0 Hz, 1H), 6.89 (d, J = 8.5 Hz, 1H), 6.32 (s, 1H), 5.55 (d, J = 1.0 Hz, 1H), 5.01 (d, J = 1.0 Hz, 1H), 3.86 (d, J = 13.0 Hz, 1H), 3.42-3.36 (m, 3H), 1.56 (m, 2H), 0.92 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.5, 160.5, 150.8, 145.6, 135.2, 131.2, 129.1, 128.3, 127.0, 124.6, 124.5, 121.9, 121.8, 111.3, 104.2, 87.0, 56.3, 48.1, 20.6, 11.3. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{22}NO_2^+$ ([M+H]$^+$): 332.1645, found 332.1650.

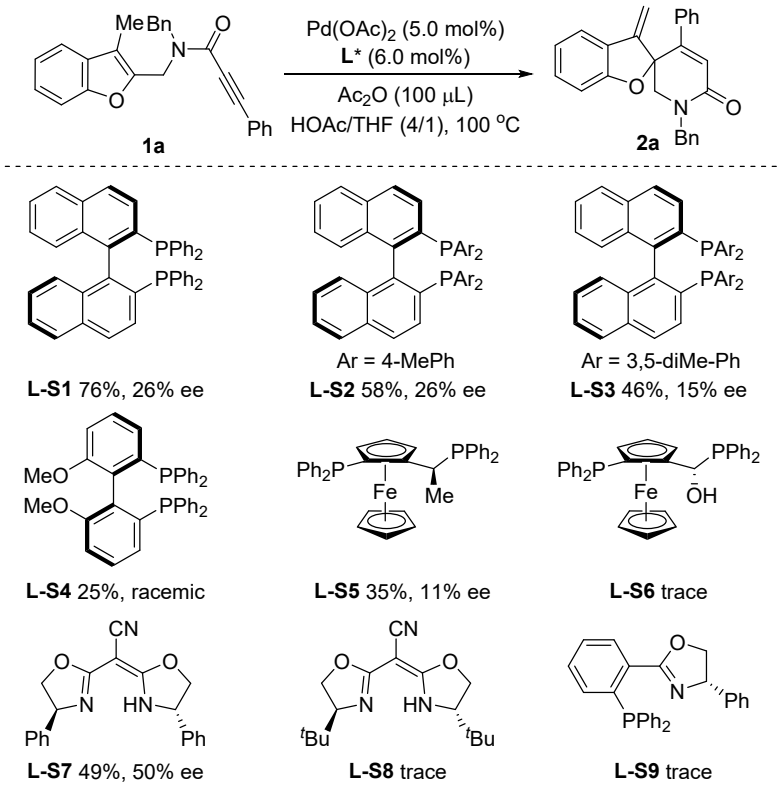


^{1}H NMR of compound **2p** (500 MHz, $CDCl_3$)



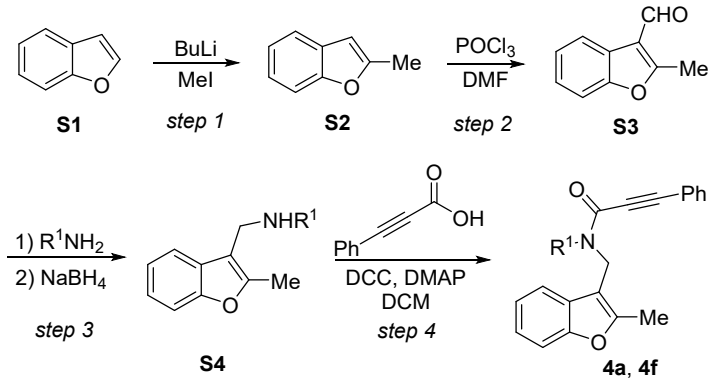
^{13}C NMR of compound **2p** (125 MHz, $CDCl_3$)

4. Table S1. Exploration for the Pd-catalyzed asymmetric dearomative 1,6-enyne cycloisomerization



5. Synthesis of C3-alkyne-tethered benzofurans 4

5.1 For compounds 4a, 4f



Step 1:[7]

To a dried flask was charged with **S1** (2.36 g, 20.0 mmol) and THF (100 mL). *n*-Butyllithium (9.0 mL of 2.5 M hexane solution, 22.5 mmol) was then added via a syringe at -78 °C under nitrogen. The resulting solution was stirred for 30 min at -78 °C, then methyl iodide (5.0 mL, 80.0 mmol) was added dropwise at -78 °C. The reaction was gradually warmed to room temperature and stirred overnight. When the reaction was completed, the solution was poured into saturated aqueous ammonium chloride

(100 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with petroleum ether to give compound **S2**.

Step 2:[8]

To a dried flask was charged with **S2** (1.32g, 10.0 mmol) and anhydrous DMF (15 mL) under air atmosphere. The resulting mixture was stirred at 0 °C for 5 min, then $POCl_3$ (1.4 mL, 15 mmol) was added dropwise. The reaction was allowed to stir at 70 °C (oil bath) for 20 h. When the reaction was completed, the solution was poured into saturated aqueous $NaHCO_3$ and extracted with diethyl ether. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v) to give compound **S3**.

Step 3:[3]

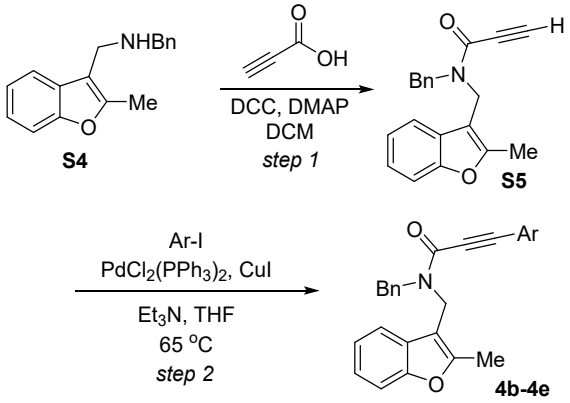
To a dried flask was charged with **S3** (10.0 mmol, 1.0 equiv), anhydrous $MgSO_4$ (50.0 mmol, 6.0 g), and anhydrous CH_2Cl_2 (25 mL) under nitrogen atmosphere. R^1NH_2 (9.0 mmol, 0.98 mL) was then added via a syringe. The resulting mixture was stirred at 50 °C (oil bath) for 12 h. When the reaction was completed, the solution was concentrated under reduced pressure. The residue was then used without further purification.

To the solution of the above crude in anhydrous MeOH (25 mL) was added $NaBH_4$ (15.0 mmol, 0.57 g) at 0 °C in portions. The resulting mixture was then stirred at room temperature for 2 h. The solution was extracted with ethyl acetate and the combined organic phases were concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v) to give compound **S4**.

Step 4:[4]

To a stirred solution of **S4** (6.0 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) was added 4-DMAP (10 mol%) and DCC (6.6 mmol, 1.36 g) at 0 °C. The resulting mixture was stirred at 0 °C for 5 min and a solution of phenylpropiolic acid (6.6 mmol) in CH_2Cl_2 (10 mL) was then added slowly. The reaction system was stirred at room temperature for 10 h. When the reaction was completed, the solid was removed by flash filtration. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v) to give compounds **4a** and **4f**.

5.2 For compounds 4b-4e



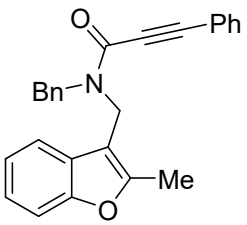
Step 1:[4]

To a stirred solution of **S4** (6.0 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) were added 4-DMAP (10.0 mol%) and DCC (6.6 mmol, 1.36 g) at 0 °C. The mixture was stirred at 0 °C for 5 min and a solution of propiolic acid (6.6 mmol) in CH_2Cl_2 (10 mL) was then added slowly. The resulting mixture was stirred at room temperature for 10 h. When the reaction was completed, the solid was removed by flash filtration. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v) to give compound **S5**.

Step 2:[5]

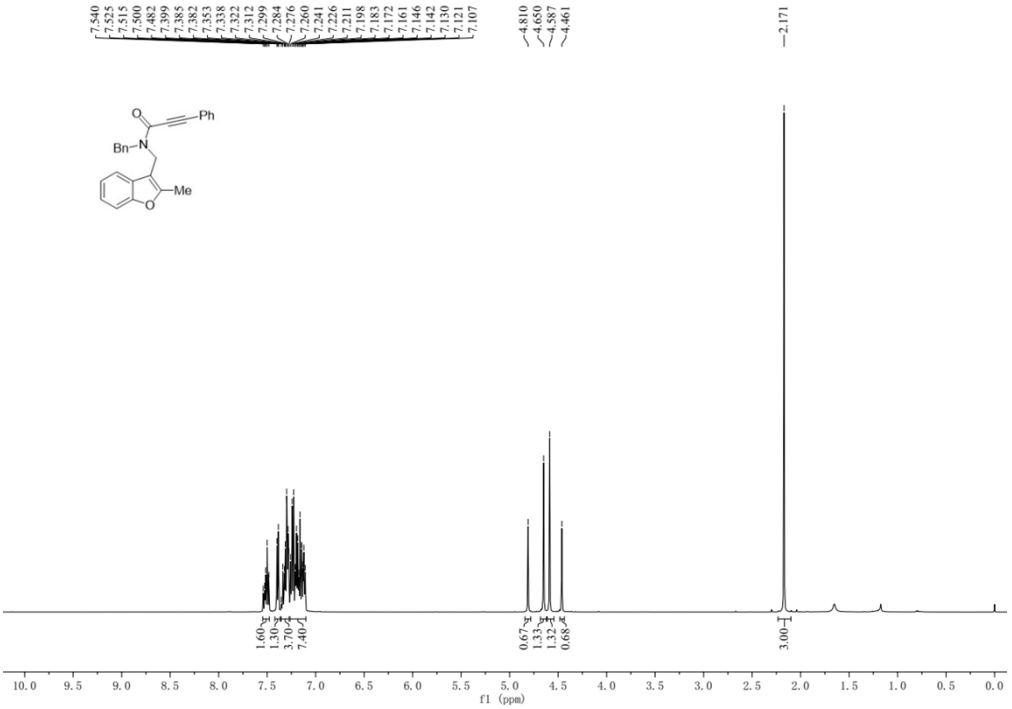
To a dried Schlenk tube was charged with $PdCl_2(PPh_3)_2$ (2.0 mol%, 56.2 mg), CuI (4.0 mol%, 30.5 mg), **S5** (4.0 mmol), Et_3N (3.0 equiv), and the corresponding aryliodines (Ar-I, 6.0 mmol, 1.5 equiv) under N_2. THF (25 mL) was then introduced via a syringe. The resulting mixture was stirred at 65 °C (oil bath) for 12h. After filtration, the solution was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v) to give compound **4b-4e**.

N-Benzyl-N-((2-methylbenzofuran-3-yl)methyl)-3-phenylpropiolamide (4a):

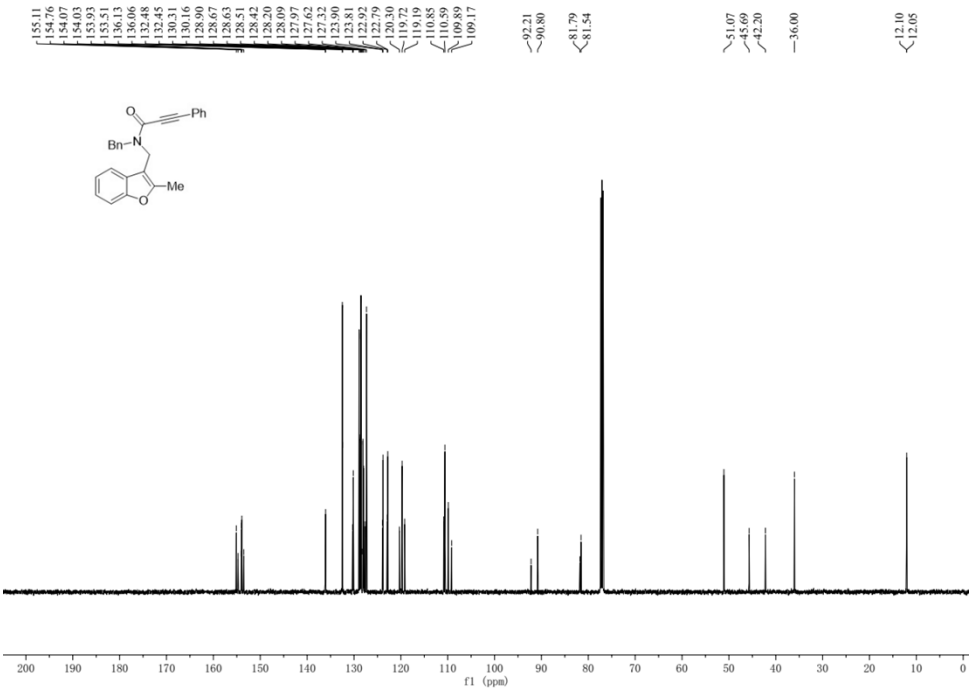


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); light yellow oil; 88% yield (for the last step); A 2:1 isomeric mixture; ^1H NMR (500 MHz, $CDCl_3$): δ 7.54-7.48 (m, 1.60H), 7.40-7.38 (m, 1.30H), 7.35-7.28 (m,

3.70H), 7.26-7.11 (m, 7.40H), 4.81 (s, 0.67H), 4.65 (s, 1.33H), 4.59 (s, 1.32H), 4.46 (s, 0.68H), 2.17 (s, 3.00H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.1, 154.8, 154.1, 154.0, 153.9, 153.5, 136.13, 136.06, 132.48, 132.45, 130.3, 130.2, 128.9, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.6, 127.3, 123.9, 123.8, 122.9, 122.8, 120.3, 119.7, 119.2, 110.9, 110.6, 109.9, 109.2, 92.2, 90.8, 81.8, 81.5, 51.1, 45.7, 42.2, 36.0, 12.10, 12.05. HRMS *m/z* (ESI+): Calculated for $C_{26}H_{22}NO_2^+$ ([M+H]$^+$): 380.1651, found 380.1652.

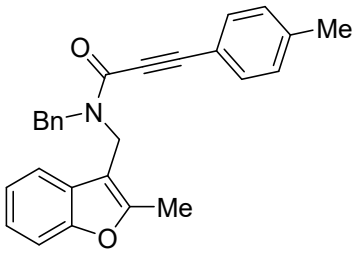


^{1}H NMR of compound **4a** (500 MHz, $CDCl_3$)

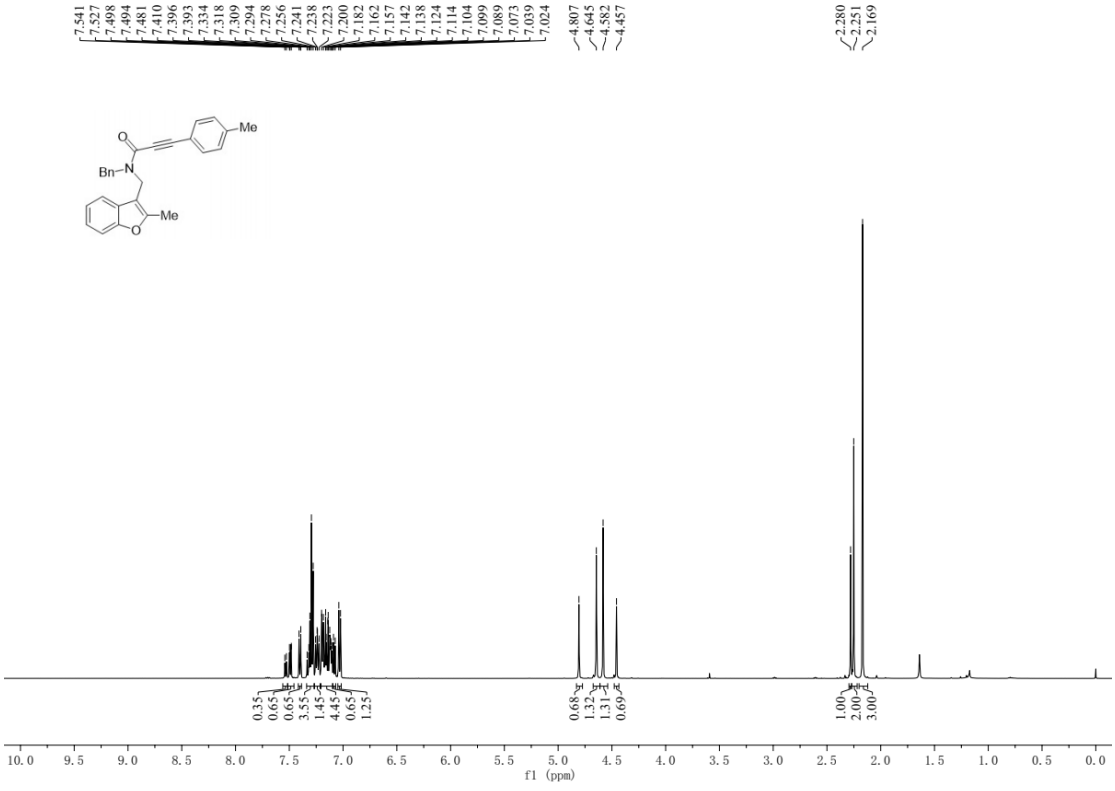


^{13}C NMR of compound **4a** (125 MHz, $CDCl_3$)

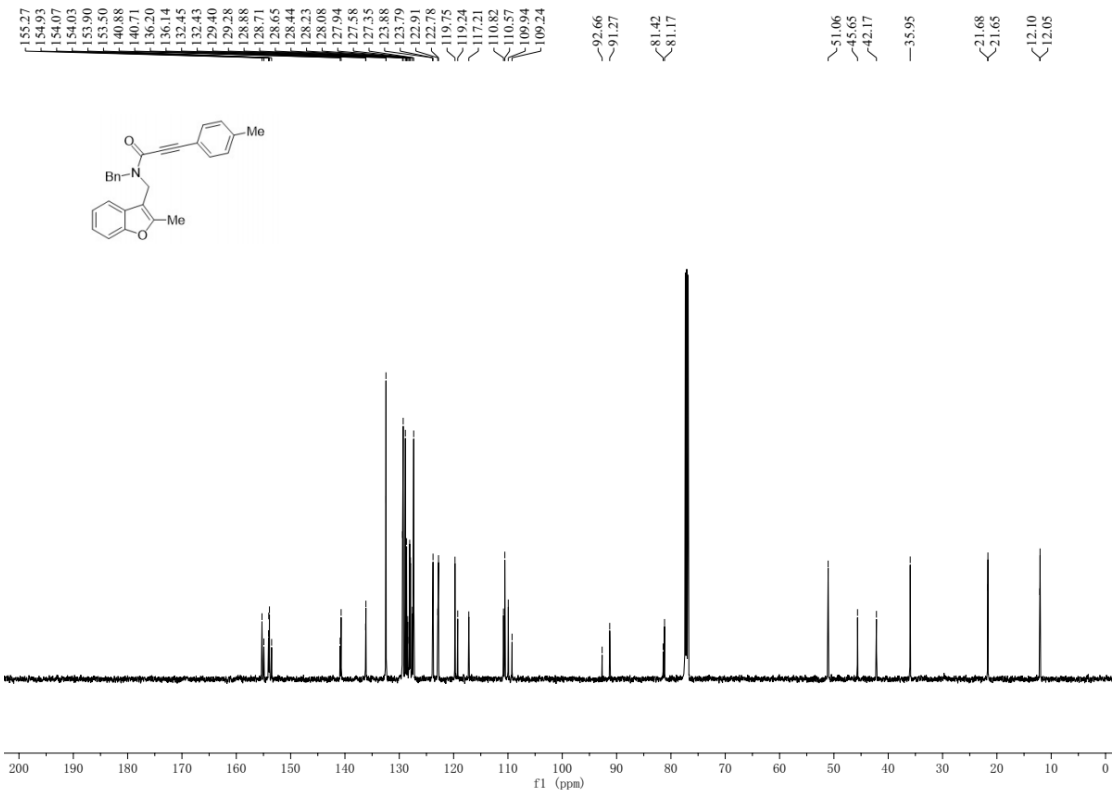
N-Benzyl-N-((2-methylbenzofuran-3-yl)methyl)-3-(p-tolyl)propiolamide (4b):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); light yellow oil; 72% yield (for the last step); A 2:1 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54-7.53 (m, 0.35H), 7.50-7.48 (m, 0.65H), 7.41-7.39 (m, 0.65H), 7.33-7.28 (m, 3.55H), 7.26-7.22 (m, 1.45H), 7.20-7.10 (m, 4.45H), 7.08 (d, J = 8.0 Hz, 0.65H), 7.03 (d, J = 7.5 Hz, 1.25H), 4.81 (s, 0.68H), 4.65 (s, 1.32H), 4.58 (s, 1.31H), 4.46 (s, 0.69H), 2.28 (s, 1.00H), 2.25 (s, 2.00H), 2.17 (s, 3.00H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.3, 154.9, 154.1, 154.0, 153.9, 153.5, 140.9, 140.7, 136.2, 136.1, 132.5, 129.4, 129.3, 128.9, 128.7, 128.4, 128.2, 128.1, 127.9, 127.6, 127.4, 123.9, 123.8, 122.9, 122.8, 119.8, 119.2, 117.2, 110.8, 110.6, 109.9, 109.2, 92.7, 91.3, 81.4, 81.2, 51.1, 45.7, 42.2, 36.0, 21.68, 21.65, 12.10, 12.05. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_2^+$ ([M+H]$^+$): 394.1807, found 394.1803.

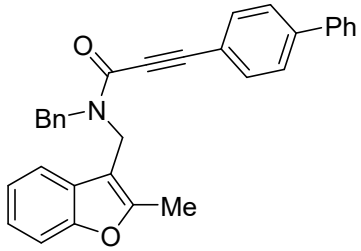


^{1}H NMR of compound **4b** (500 MHz, $CDCl_3$)



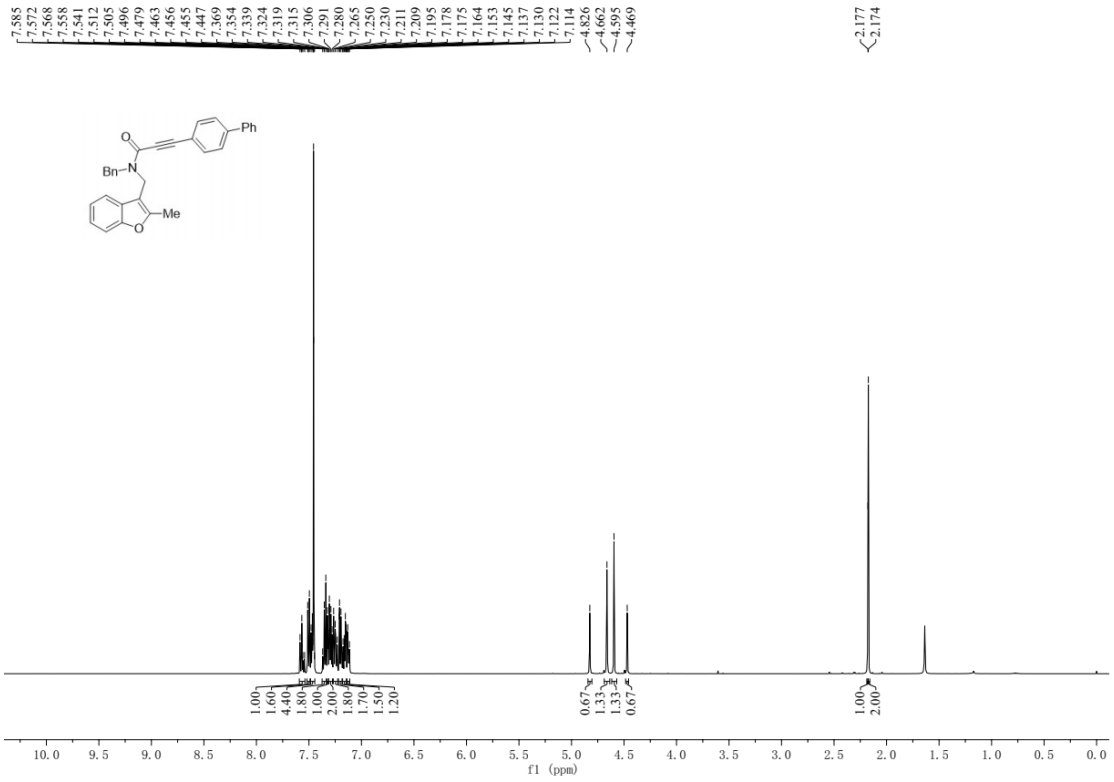
^{13}C NMR of compound **4b** (125 MHz, $CDCl_3$)

3-([1,1'-Biphenyl]-4-yl)-N-benzyl-N-((2-methylbenzofuran-3-yl)methyl)-propiolamide (4c):

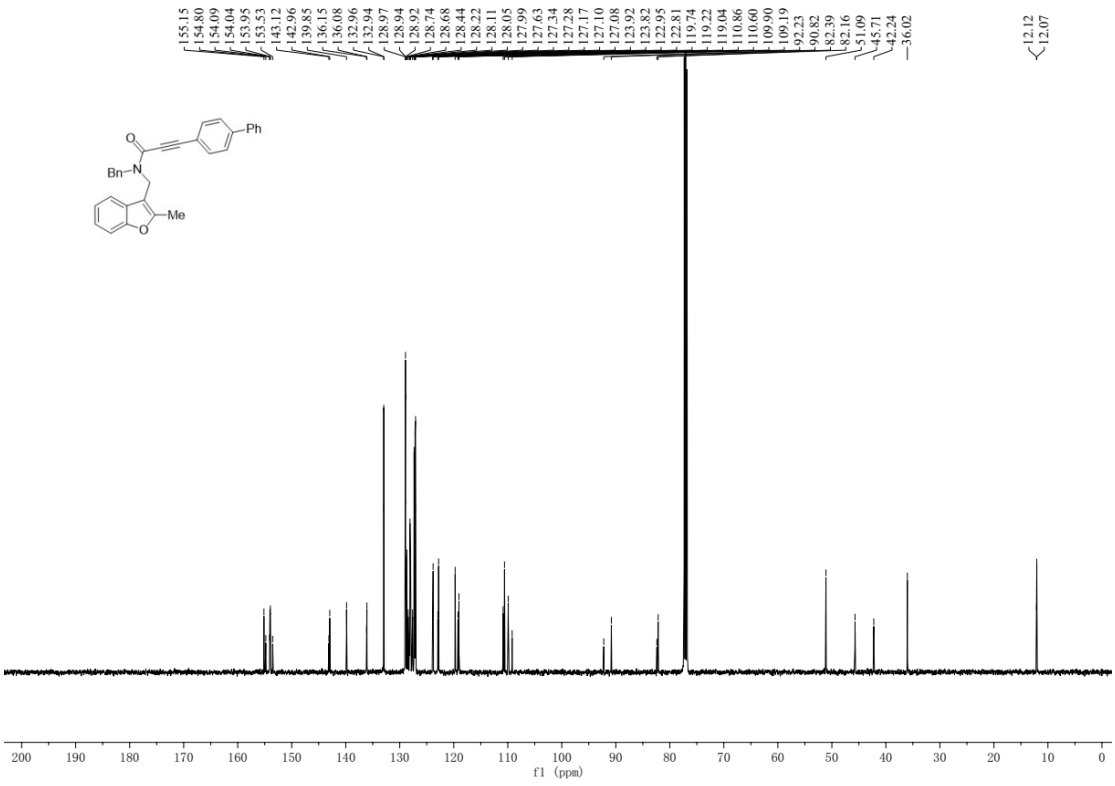


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow solid, Mp = 106-107 °C; 67% yield (for the last step); A 2:1 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59-7.54 (m, 1.00H), 7.51-7.50 (m, 1.60H), 7.48-7.45 (m, 4.40H), 7.37-7.34 (m, 1.80H), 7.33-7.32 (m, 1.00H), 7.31-7.28 (m, 2.00H), 7.27-7.23 (m, 1.80H), 7.21-7.19 (m, 1.70H), 7.18-7.15 (m, 1.50H), 7.14-7.11 (m, 1.20H), 4.83 (s, 0.67H), 4.66 (s, 1.33H), 4.60 (s, 1.33H), 4.47 (s, 0.67H), 2.18 (s, 1.00H), 2.17 (s, 2.00H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2, 154.8, 154.1, 154.04, 153.95, 153.5, 143.1, 143.0, 139.9, 136.2, 136.1, 133.0, 129.0, 128.94, 128.92, 128.74, 128.68, 128.4, 128.2, 128.11, 128.05, 128.0, 127.6, 127.34, 127.28, 127.2, 127.10, 127.08, 123.9, 123.8, 123.0, 122.8, 119.7, 119.2, 119.0, 110.9, 110.6, 109.9, 109.2,

92.2, 90.8, 82.4, 82.2, 51.1, 45.7, 42.2, 36.0, 12.12, 12.07. HRMS *m/z* (ESI+): Calculated for $C_{32}H_{26}NO_2^+$ ([M+H]$^+$): 456.1964, found 456.1959.

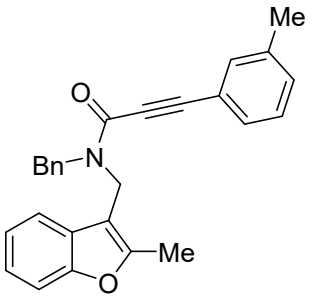


^{1}H NMR of compound **4c** (500 MHz, $CDCl_3$)

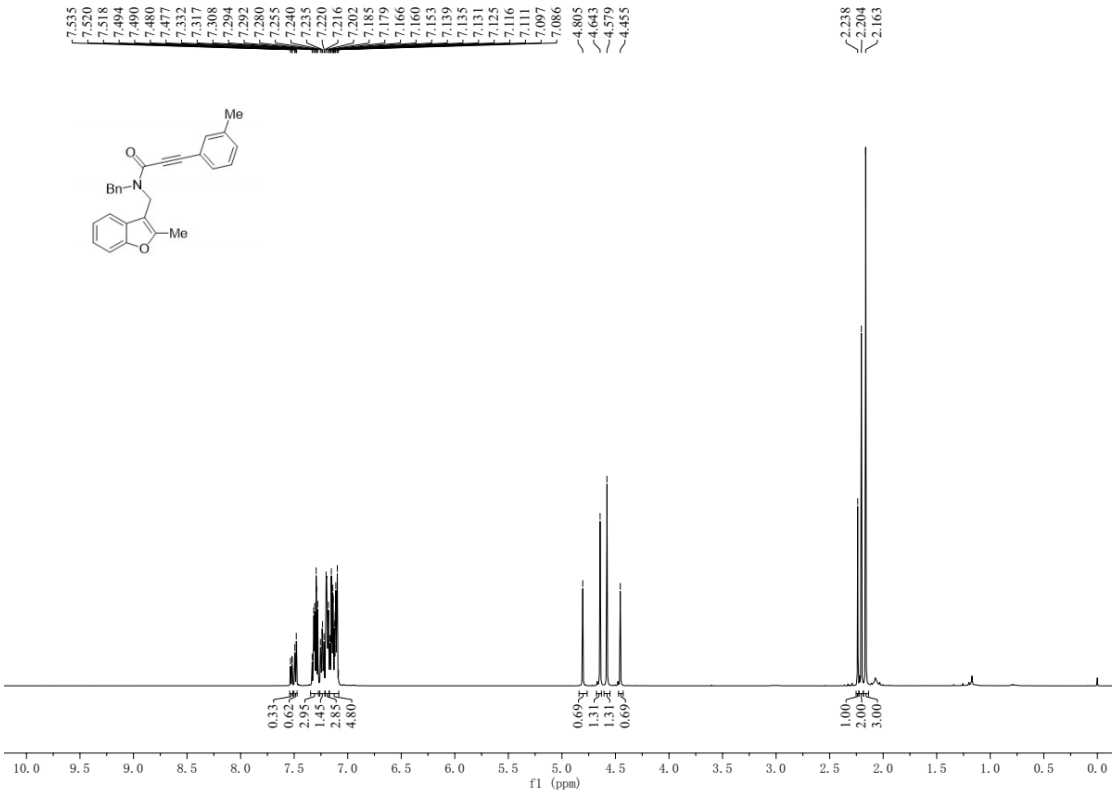


^{13}C NMR of compound **4c** (125 MHz, $CDCl_3$)

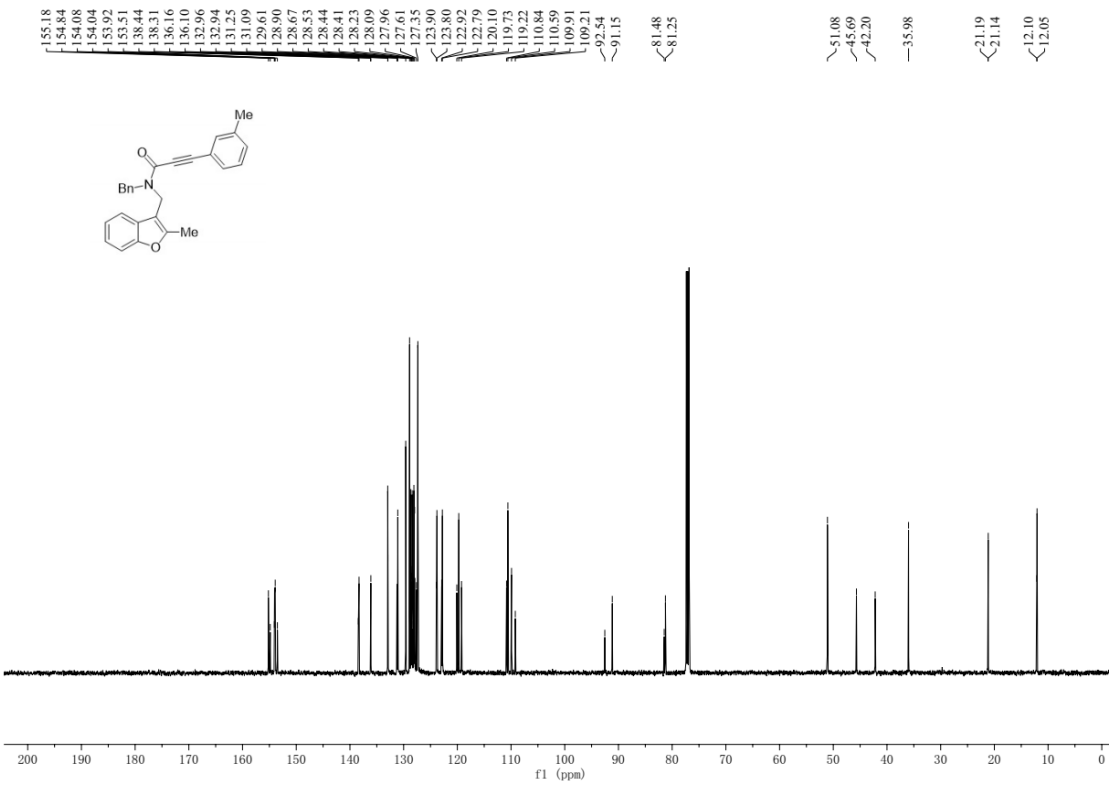
N-Benzyl-N-((2-methylbenzofuran-3-yl)methyl)-3-(m-tolyl)propiolamide (4d):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); light yellow oil; 70% yield (for the last step); A 2:1 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54-7.52 (m, 0.33H), 7.49-7.48 (m, 0.62H), 7.33-7.28 (m, 2.95H), 7.26-7.22 (m, 1.45H), 7.21-7.18 (m, 2.85H), 7.17-7.09 (m, 4.80H), 4.81 (s, 0.69H), 4.64 (s, 1.31H), 4.58 (s, 1.31H), 4.45 (s, 0.69H), 2.24 (s, 1.00H), 2.20 (s, 2.00H), 2.16 (s, 3.00H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2, 154.8, 154.1, 154.0, 153.9, 153.5, 138.4, 138.3, 136.2, 136.1, 133.0, 132.9, 131.3, 131.1, 129.6, 128.9, 128.7, 128.5, 128.44, 128.41, 128.2, 128.1, 128.0, 127.6, 127.4, 123.9, 123.8, 122.9, 122.8, 120.1, 119.7, 119.2, 110.8, 110.6, 109.9, 109.2, 92.5, 91.2, 81.5, 81.3, 51.1, 45.7, 42.2, 36.0, 21.2, 21.1, 12.10, 12.05. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_2^+$ ($[M+H]^+$): 394.1807, found 394.1811.

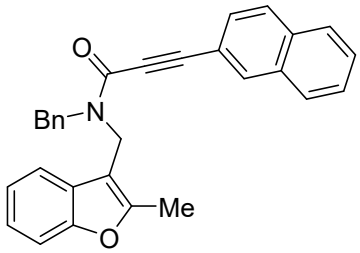


^{1}H NMR of compound **4d** (500 MHz, $CDCl_3$)

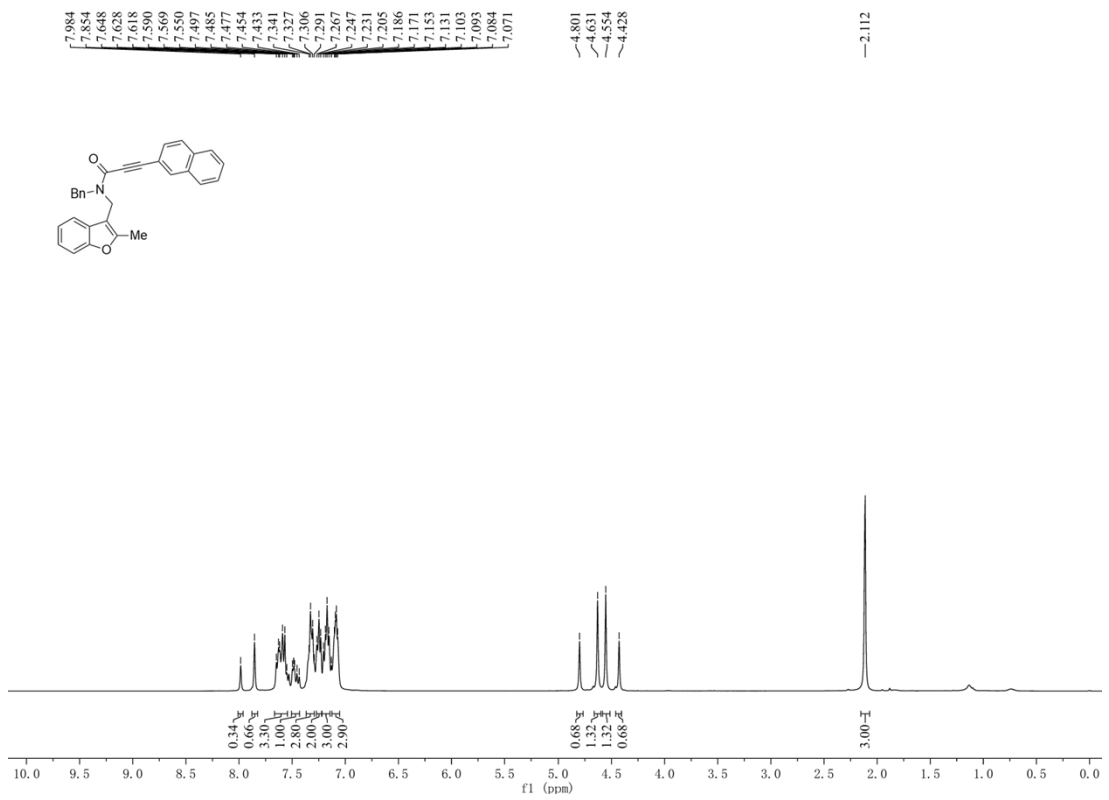


^{13}C NMR of compound **4d** (125 MHz, $CDCl_3$)

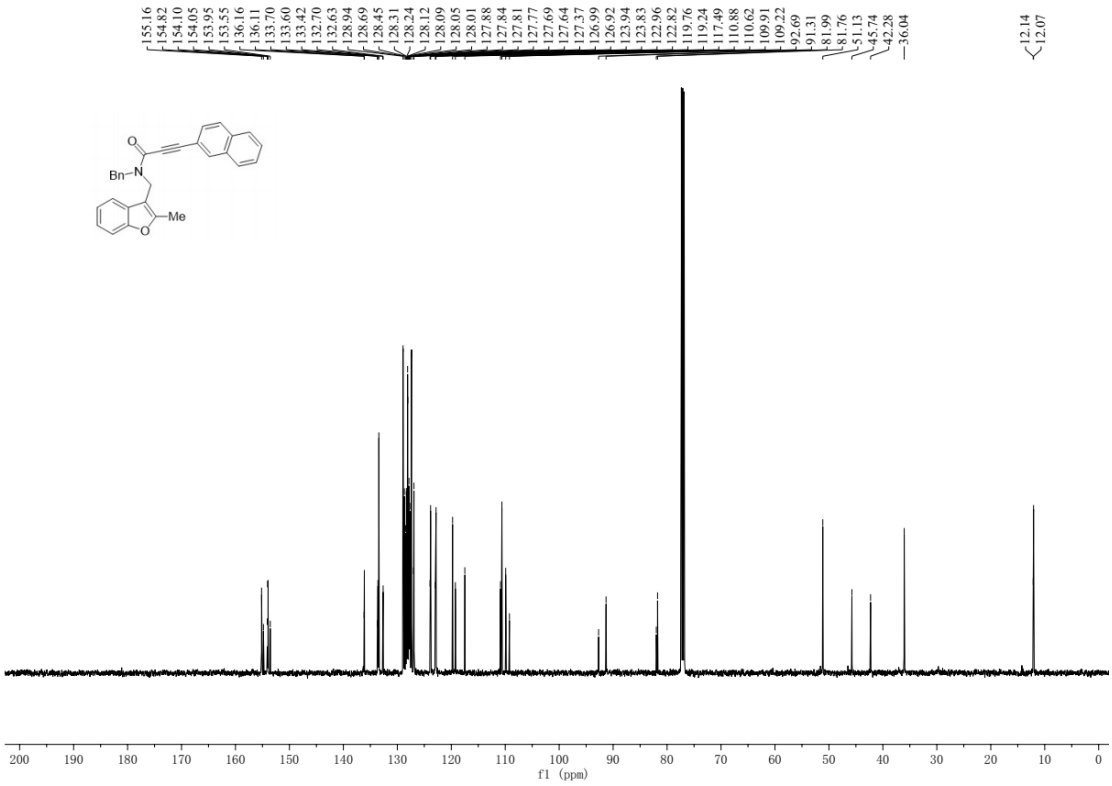
N-Benzyl-N-((2-methylbenzofuran-3-yl)methyl)-3-(naphthalen-2-yl)propiolamide (4e):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow solid, Mp = 105-106 °C; 60% yield (for the last step); A 2:1 isomeric mixture; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 0.34 H), 7.85 (s, 0.66H), 7.65-7.55 (m, 3.30H), 7.50-7.43 (m, 1.00H), 7.34-7.29 (m, 2.80H), 7.27-7.23 (m, 2.00H), 7.21-7.15 (m, 3.00H), 7.10-7.07 (m, 2.90H), 4.80 (s, 0.68H), 4.63 (s, 1.32H), 4.55 (s, 1.32H), 4.43 (s, 0.68H), 2.11 (s, 3.00H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2, 154.8, 154.10, 154.05, 154.0, 153.6, 136.2, 136.1, 133.7, 133.6, 133.4, 132.7, 132.6, 128.9, 128.7, 128.5, 128.3, 128.2, 128.12, 128.09, 128.05, 128.0, 127.9, 127.84, 127.77, 127.7, 127.6, 127.4, 127.0, 126.9, 123.9, 123.8, 123.0, 122.8, 119.8, 119.2, 117.5, 110.9, 110.6, 109.9, 109.2, 92.7, 91.3, 82.0, 81.8, 51.1, 45.7, 42.3, 36.0, 12.14, 12.07. HRMS *m/z* (ESI+): Calculated for $C_{30}H_{24}NO_2^+$ ($[M+H]^+$): 430.1807, found 430.1805.

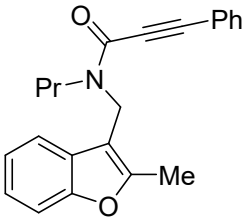


^{1}H NMR of compound **4e** (400 MHz, $CDCl_3$)

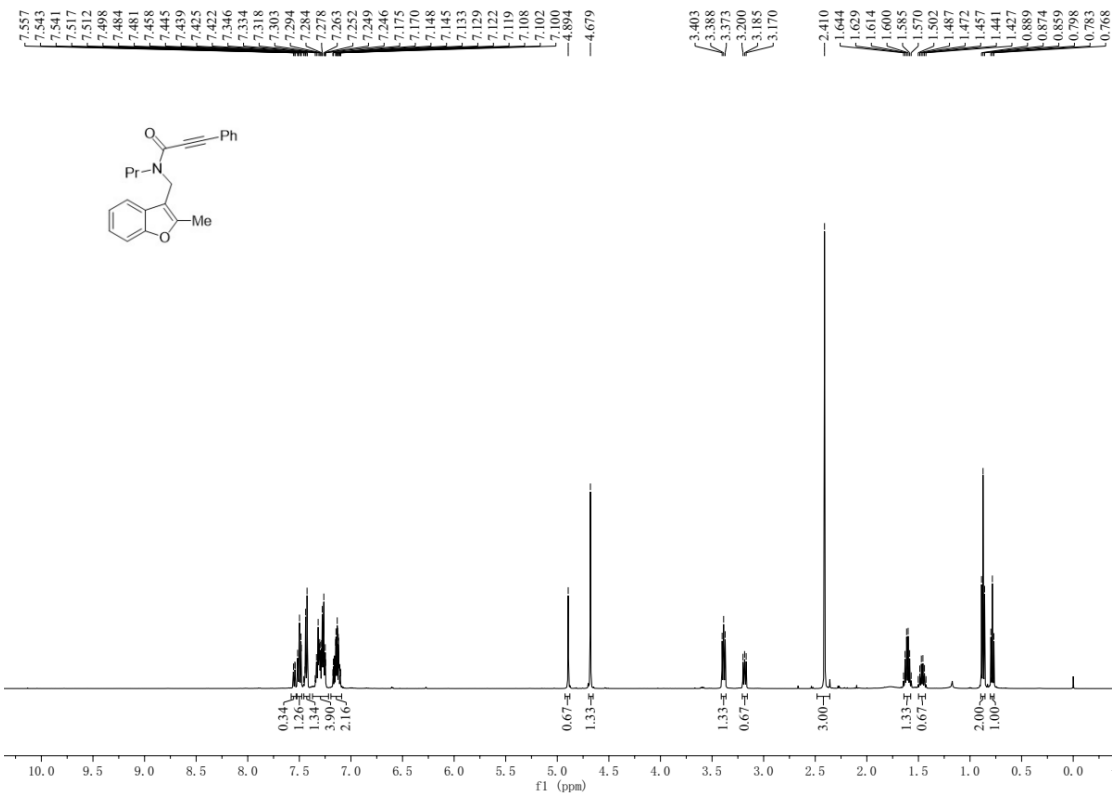


^{13}C NMR of compound **4e** (125 MHz, $CDCl_3$)

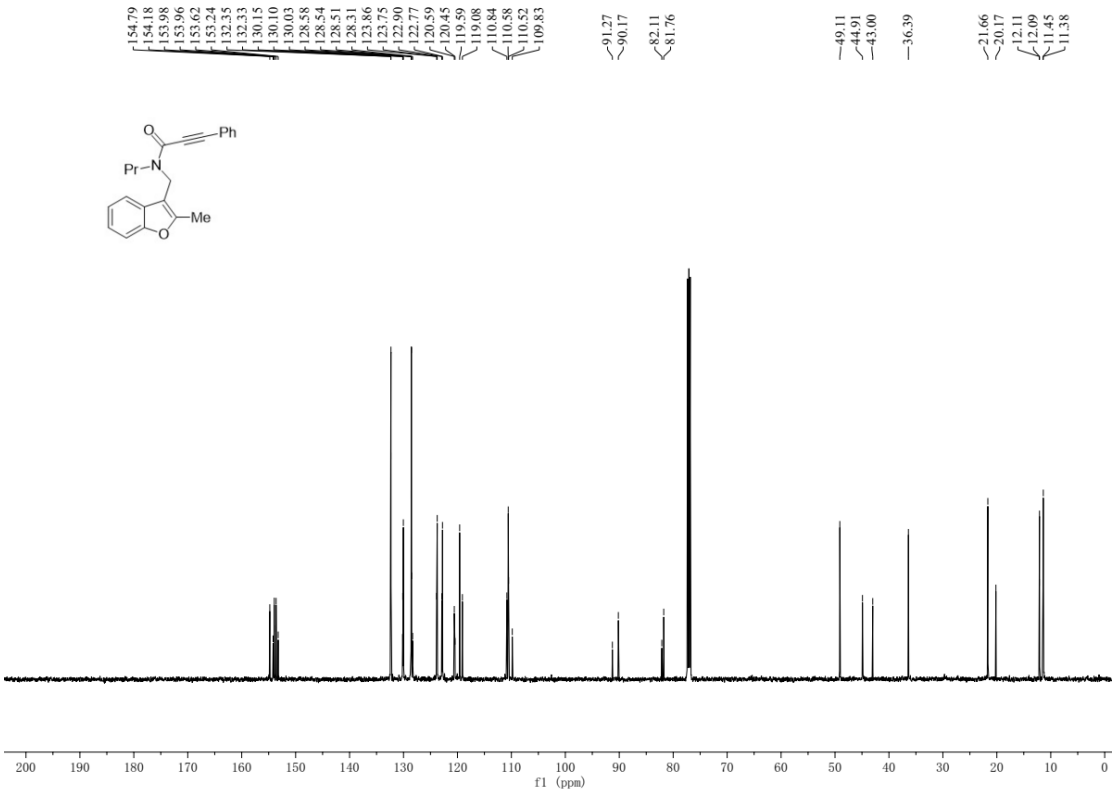
N-((2-Methylbenzofuran-3-yl)methyl)-3-phenyl-N-propylpropiolamide (4f):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); light yellow oil; 85% yield (for the last step); A 2:1 isomeric mixture; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56-7.54 (m, 0.34H), 7.52-7.48 (m, 1.26H), 7.46-7.42 (m, 1.34H), 7.35-7.25 (m, 3.90H), 7.18-7.10 (m, 2.16H), 4.89 (s, 0.67H), 4.68 (s, 1.33H), 3.39 (t, J = 7.5 Hz, 1.33H), 3.19 (t, J = 7.5 Hz, 0.67H), 2.41 (s, 3.00H), 1.64-1.57 (m, 1.33H), 1.50-1.43 (m, 0.67H), 0.87 (t, J = 7.5 Hz, 2.00H), 0.78 (t, J = 7.5 Hz, 1.00H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.8, 154.2, 153.98, 153.96, 153.6, 153.2, 132.4, 132.3, 130.2, 130.0, 128.6, 128.54, 128.51, 128.3, 123.9, 123.8, 122.9, 122.8, 120.6, 120.5, 119.6, 119.1, 110.8, 110.6, 110.5, 109.8, 91.3, 90.2, 82.1, 81.8, 49.1, 44.9, 43.0, 36.4, 21.7, 20.2, 12.11, 12.09, 11.5, 11.4. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{22}NO_2^+$ ([M+H]$^+$): 332.1651, found 332.1649.

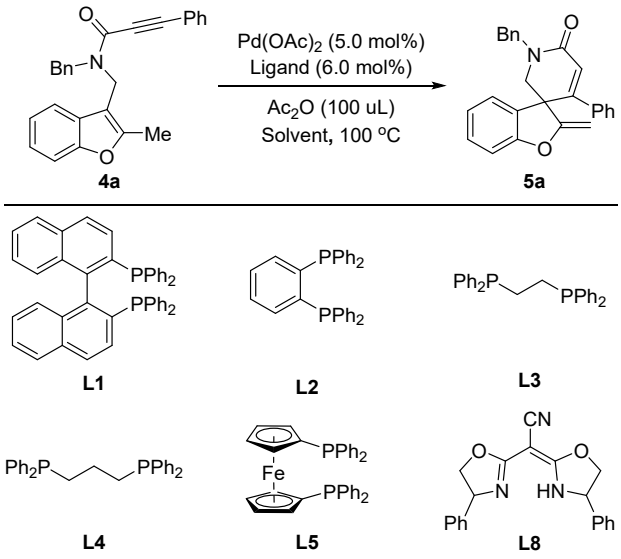


^{1}H NMR of compound **4f** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **4f** (125 MHz, $CDCl_3$)

6. Table S2. Condition re-optimization for reaction of 4a[a]

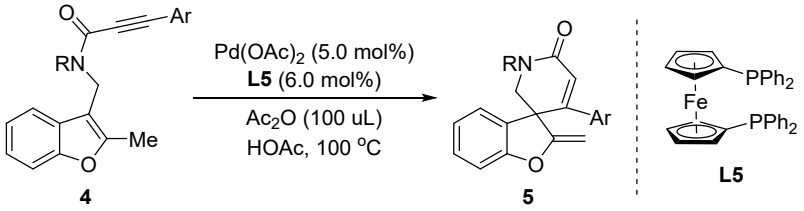


Entry	Ligand	Solvent	Yield (%)
1[b]	**L1**	HOAc/THF (v/v, 4:1)	40
2	**L1**	HOAc	44
3	**L2**	HOAc	8
4	**L3**	HOAc	10

5	**L4**	HOAc	13
6	**L5**	HOAc	62
7	**L8**	HOAc	10

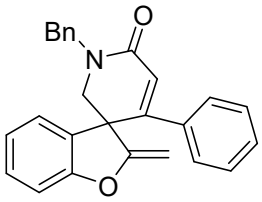
[a]conditions: **4a** (0.2 mmol), $Pd(OAc)_2$ (5.0 mol%), ligand (6.0 mol%), Ac_2O (100 uL) in HOAc (2.0 mL) at 100 °C for 18 h under air atmosphere. [b]HOAc (1.6 mL) and THF (0.4 mL) as solvent.

7. Procedure for dearomative 1,6-enyne cycloisomerization of 4

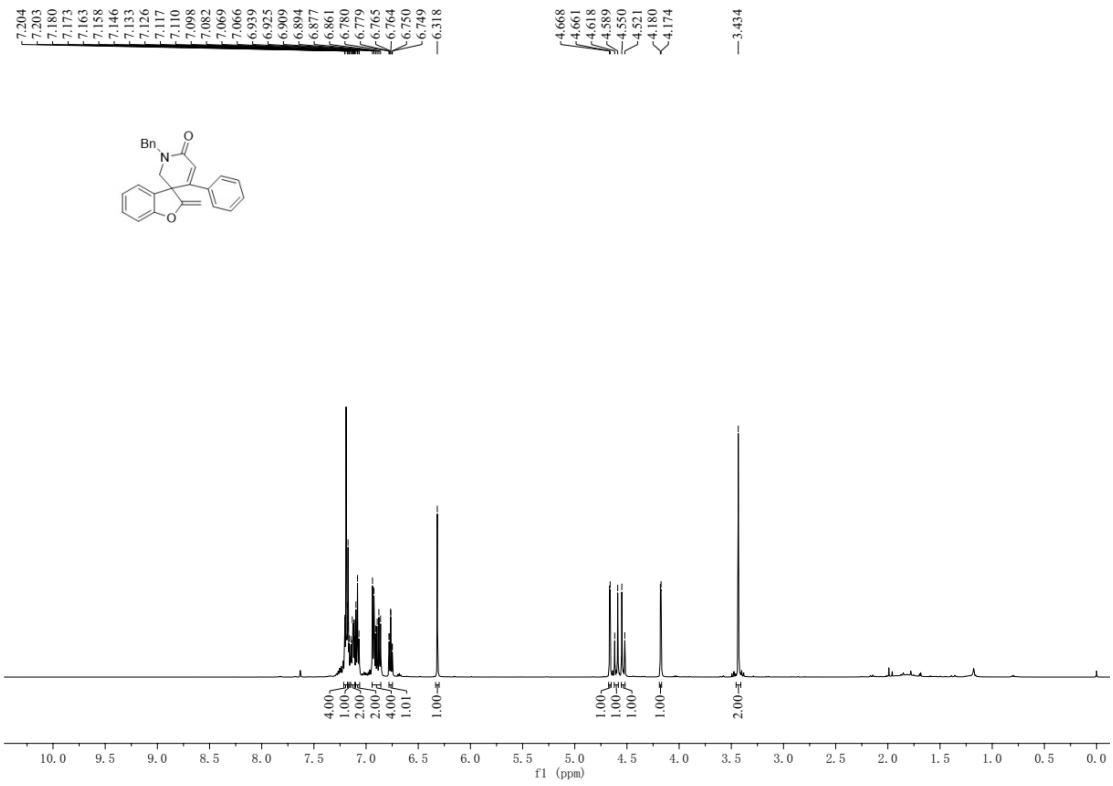


To a dried Schlenk tube were charged with $Pd(OAc)_2$ (5 mol%, 2.3 mg), **L5** (6 mol%, 6.7 mg), and **4** (0.2 mmol) under air atmosphere. Ac_2O (100 μL), HOAc (2.0 mL) was then introduced via syringe. The resulting mixture was stirred at 100 °C (heating block) until the reaction was completed (monitored by TLC). The mixture was quenched with a solution of saturated sodium bicarbonate at 0 ℃ and extracted with ethyl acetate. The solvent was then removed under reduced pressure and the residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:6 (v/v) to afford product **5**.

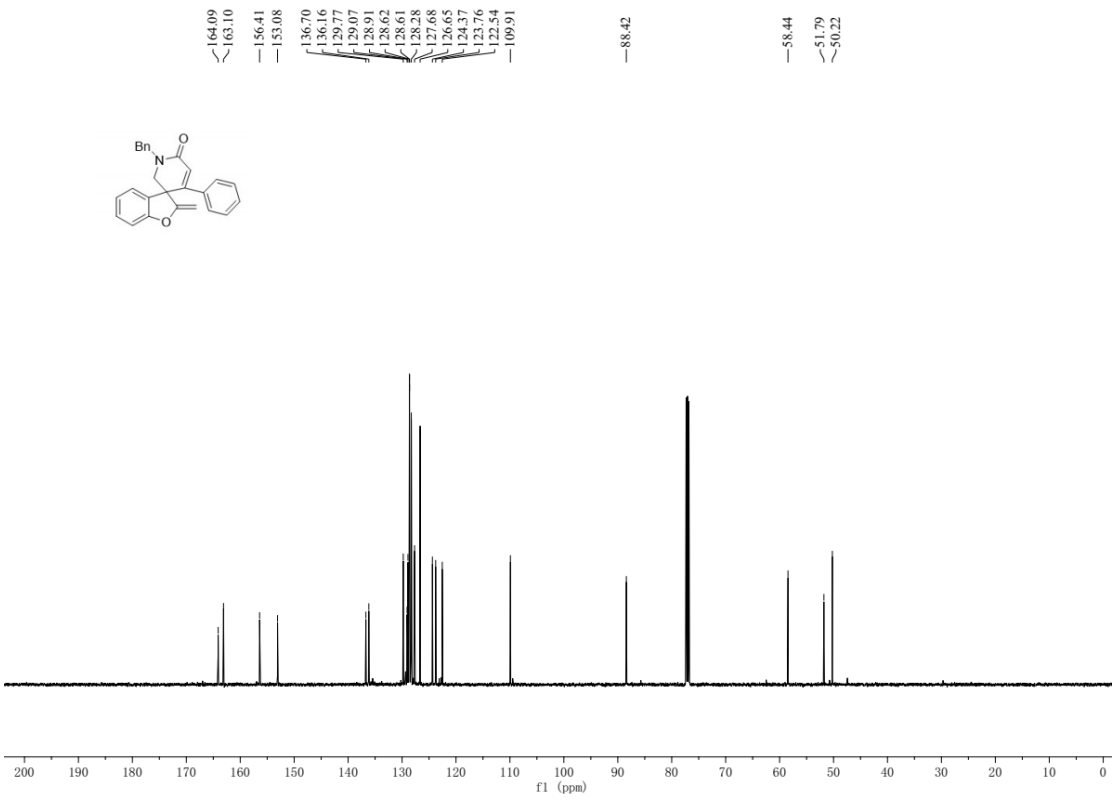
1'-Benzyl-2-methylene-4'-phenyl-1',2'-dihydro-2H,6'H-spiro[benzofuran-3,3'-pyridin]-6'-one (5a):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); light yellow oil; 47.1 mg, 62% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20-7.18 (m, 4H), 7.17-7.16 (m, 1H), 7.15-7.11 (m, 2H), 7.10-7.07 (m, 2H), 6.94-6.86 (m, 4H), 6.78-6.75 (m, 1H), 6.32 (s, 1H), 4.66 (d, J = 3.0 Hz, 1H), 4.60 (d, J = 14.5 Hz, 1H), 4.54 (d, J = 14.5 Hz, 1H), 4.18 (d, J = 3.2 Hz, 1H), 3.43 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.1, 163.1, 156.4, 153.1, 136.7, 136.2, 129.8, 129.1, 128.9, 128.62, 128.61, 128.3, 127.7, 126.7, 124.4, 123.8, 122.5, 109.9, 88.4, 58.4, 51.8, 50.2. HRMS *m/z* (ESI+): Calculated for $C_{26}H_{22}NO_2^+$ ($[M+H]^+$): 380.1651, found 380.1654.

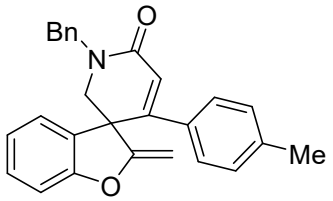


^{1}H NMR of compound **5a** (500 MHz, $CDCl_3$)

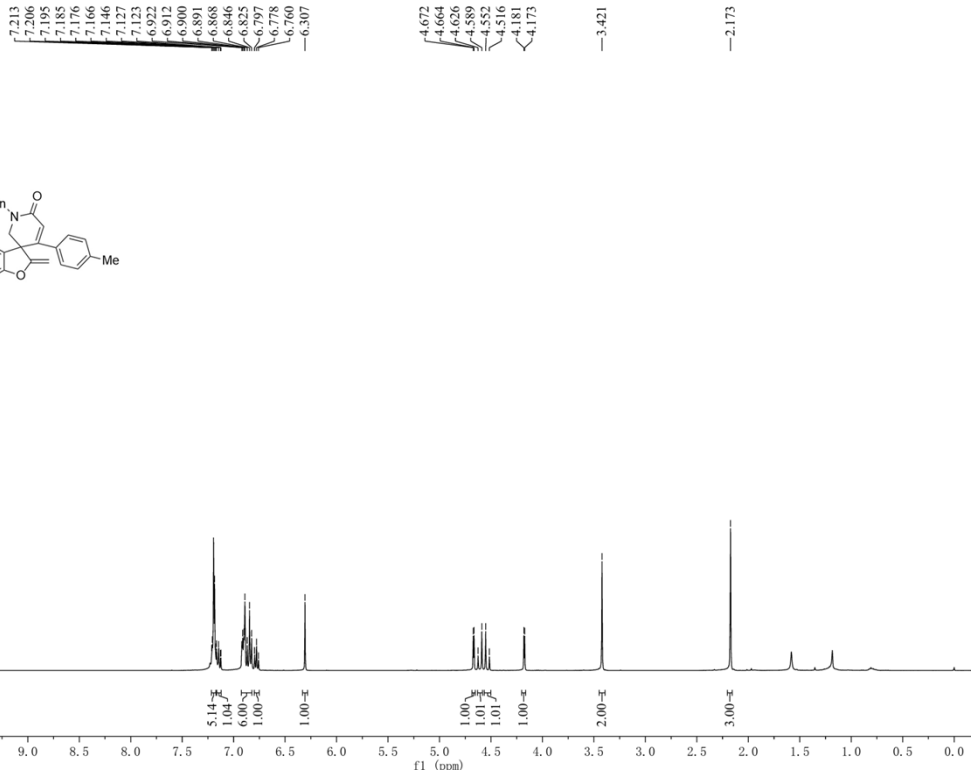


^{13}C NMR of compound **5a** (125 MHz, $CDCl_3$)

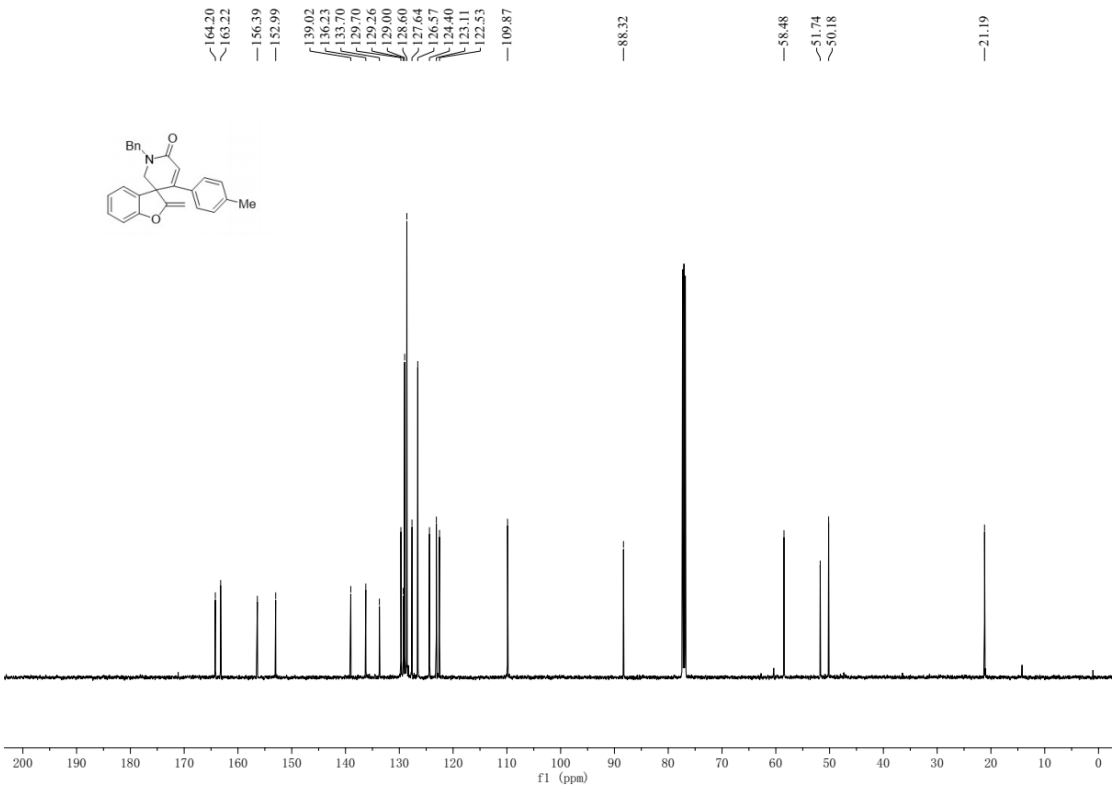
1'-Benzyl-2-methylene-4'-(p-tolyl)-1',2'-dihydro-2H,6'H-spiro[benzofuran-3,3'-pyridin]-6'-one (5b):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:6 (v/v); light yellow oil; 53.5 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.18 (m, 5H), 7.17-7.12 (m, 1H), 6.92-6.82 (m, 6H), 6.78 (t, J = 7.6 Hz, 1H), 6.31 (s, 1H), 4.67 (d, J = 3.2 Hz, 1H), 4.61 (d, J = 14.8 Hz, 1H), 4.53 (d, J = 14.8 Hz, 1H), 4.18 (d, J = 3.2 Hz, 1H), 3.42 (s, 2H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 163.2, 156.4, 153.0, 139.0, 136.2, 133.7, 129.7, 129.3, 129.0, 128.6, 127.6, 126.6, 124.4, 123.1, 122.5, 109.9, 88.3, 58.5, 51.7, 50.2, 21.2. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_2^+$ ([M+H]$^+$): 394.1807, found 394.1806.

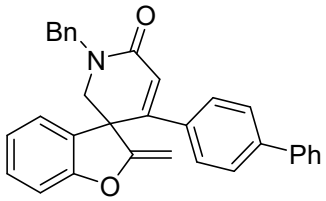


^{1}H NMR of compound **5b** (400 MHz, $CDCl_3$)

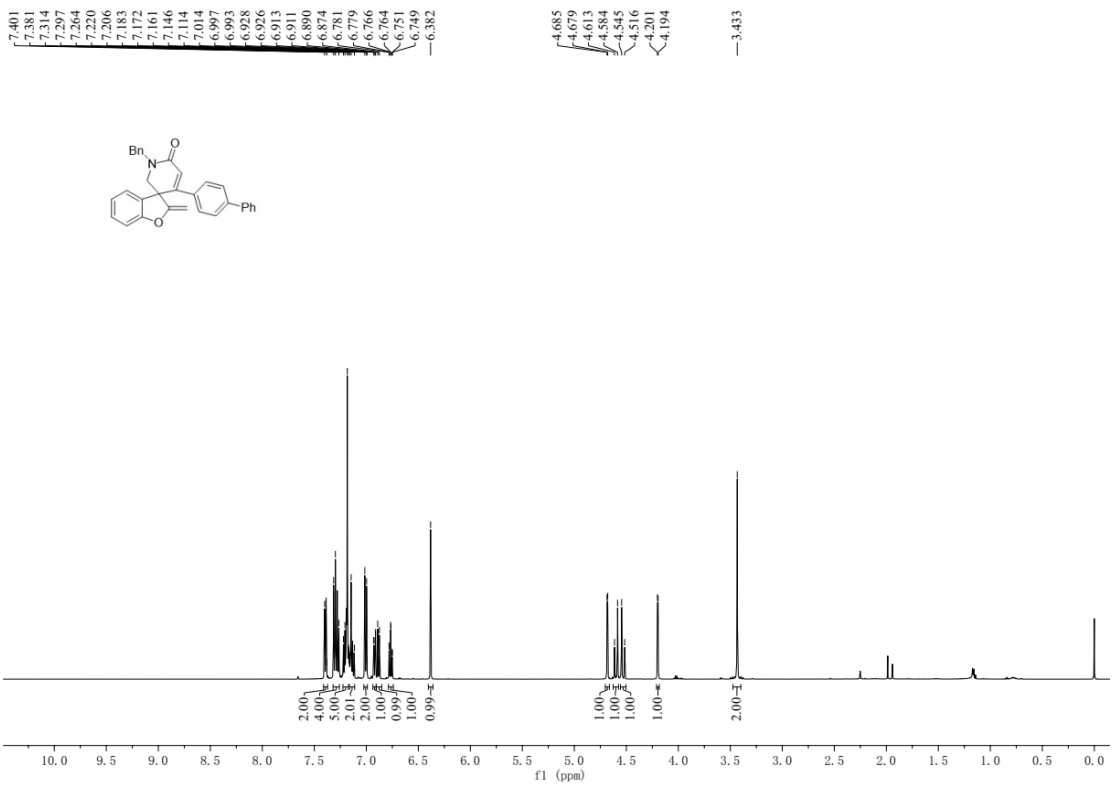


^{13}C NMR of compound **5b** (125 MHz, $CDCl_3$)

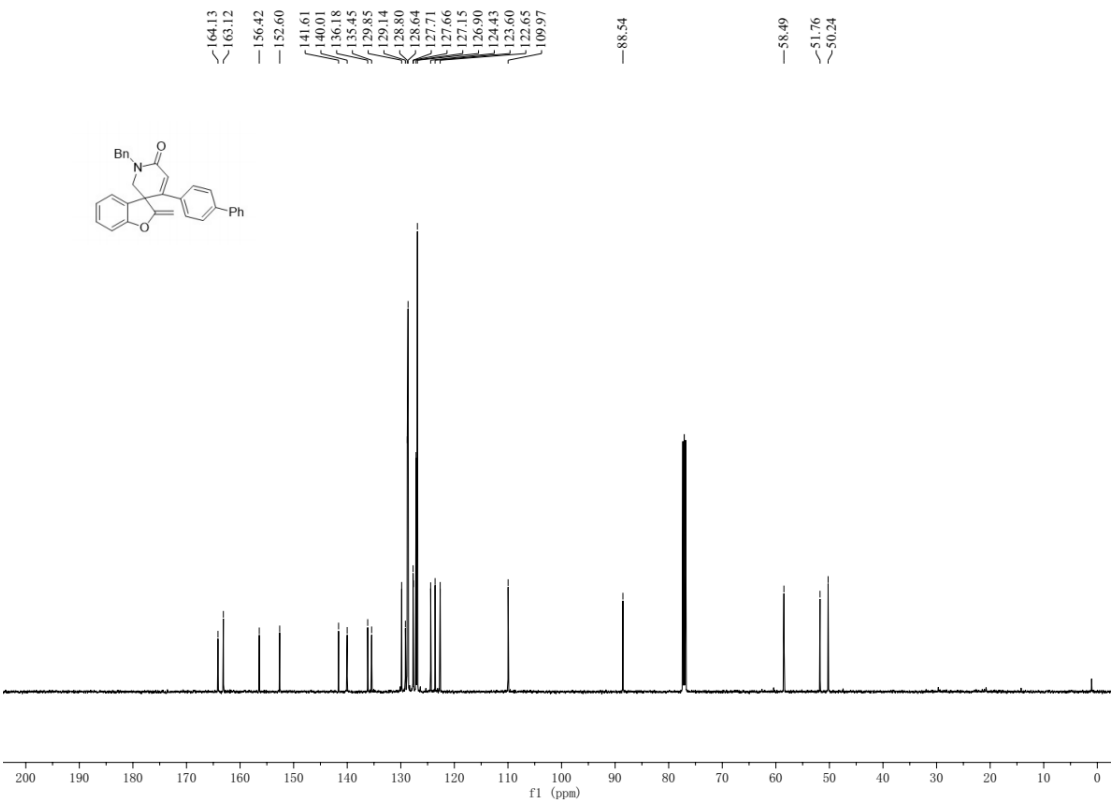
***4'-([1,1'-Biphenyl]-4-yl)-1'-benzyl-2-methylene-1',2'-dihydro-2H,6'H-spiro-[benzofuran-3,3'-pyridin]-6'-one (5c)*:**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:6 (v/v); light yellow oil; 63.7 mg, 70% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.38 (m, 2H), 7.31-7.26 (m, 4H), 7.22-7.17 (m, 5H), 7.16-7.11 (m, 2H), 7.01-6.99 (m, 2H), 6.92 (dd, J = 7.5, 1.0 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.77 (td, J = 7.5, 1.0 Hz, 1H), 6.38 (s, 1H), 4.68 (d, J = 3.0 Hz, 1H), 4.60 (d, J = 14.5 Hz, 1H), 4.53 (d, J = 14.5 Hz, 1H), 4.20 (d, J = 3.0 Hz, 1H), 3.43 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.1, 163.1, 156.4, 152.6, 141.6, 140.0, 136.2, 135.5, 129.9, 129.1, 128.8, 128.6, 127.71, 127.66, 127.2, 126.9, 124.4, 123.6, 122.7, 110.0, 88.5, 58.5, 51.8, 50.2. HRMS *m/z* (ESI+): Calculated for $C_{32}H_{26}NO_2^+$ ($[M+H]^+$): 456.1964, found 456.1968.

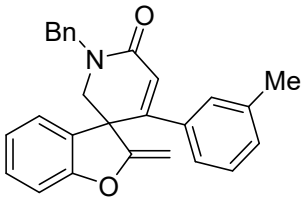


^{1}H NMR of compound **5c** (500 MHz, $CDCl_3$)

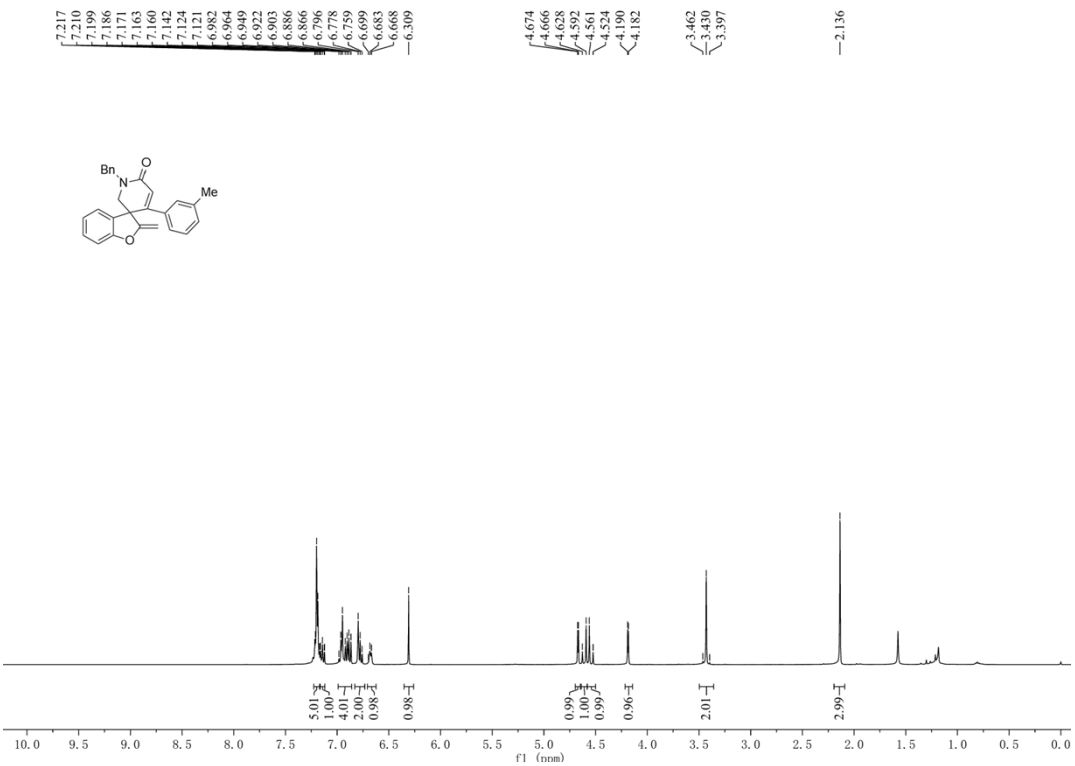


^{13}C NMR of compound **5c** (125 MHz, $CDCl_3$)

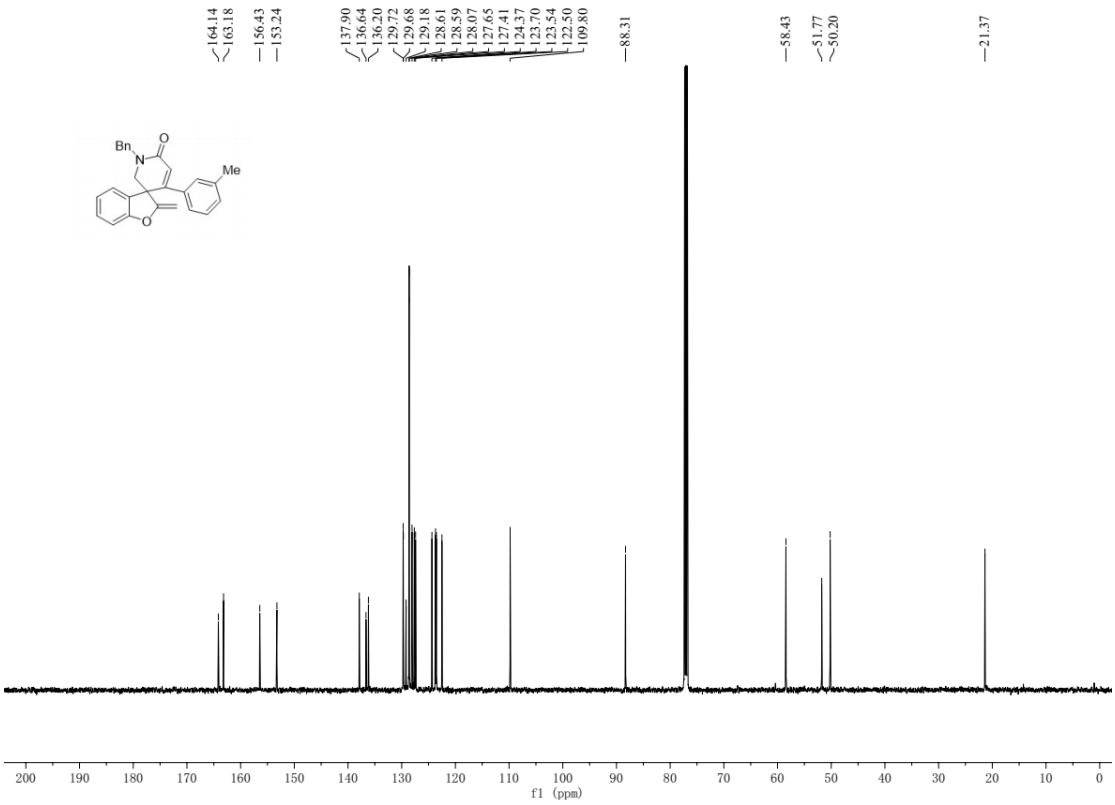
1'-Benzyl-2-methylene-4'-(m-tolyl)-1',2'-dihydro-2H,6'H-spiro[benzofuran-3,3'-pyridin]-6'-one (5d):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:6 (v/v); light yellow oil; 47.3 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.17 (m, 5H), 7.16-7.12 (m, 1H), 6.98-6.87 (m, 4H), 6.80-6.76 (m, 2H), 6.70-6.67 (m, 1H), 6.31 (s, 1H), 4.67 (d, J = 3.2 Hz, 1H), 4.61 (d, J = 14.8 Hz, 1H), 4.54 (d, J = 14.8 Hz, 1H), 4.19 (d, J = 3.2 Hz, 1H), 3.43 (s, 2H), 2.14 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.1, 163.2, 156.4, 153.2, 137.9, 136.6, 136.2, 129.72, 129.68, 129.2, 128.61, 128.59, 128.1, 127.7, 127.4, 124.4, 123.7, 123.5, 122.5, 109.8, 88.3, 58.4, 51.8, 50.2, 21.4. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{24}NO_2^+$ ([M+H]$^+$): 394.1807, found 394.1806.

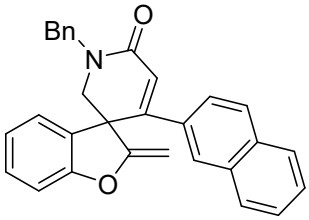


^{1}H NMR of compound **5d** (400 MHz, $CDCl_3$)

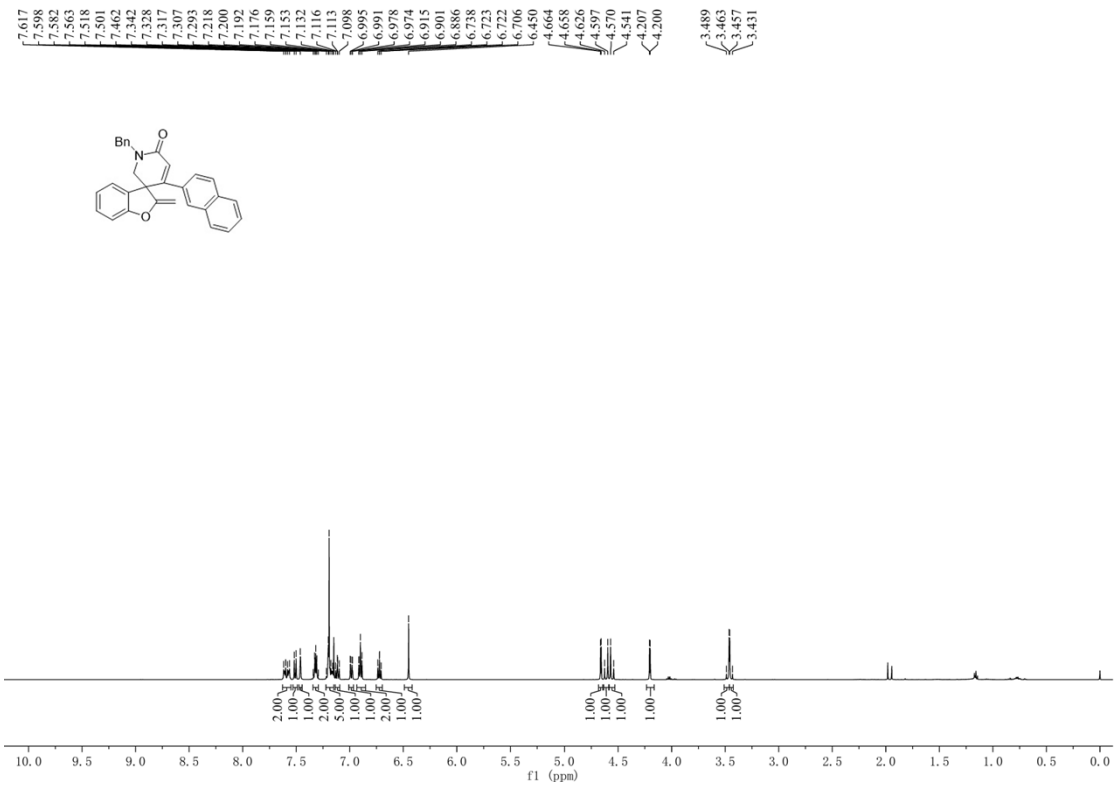


^{13}C NMR of compound **5d** (125 MHz, $CDCl_3$)

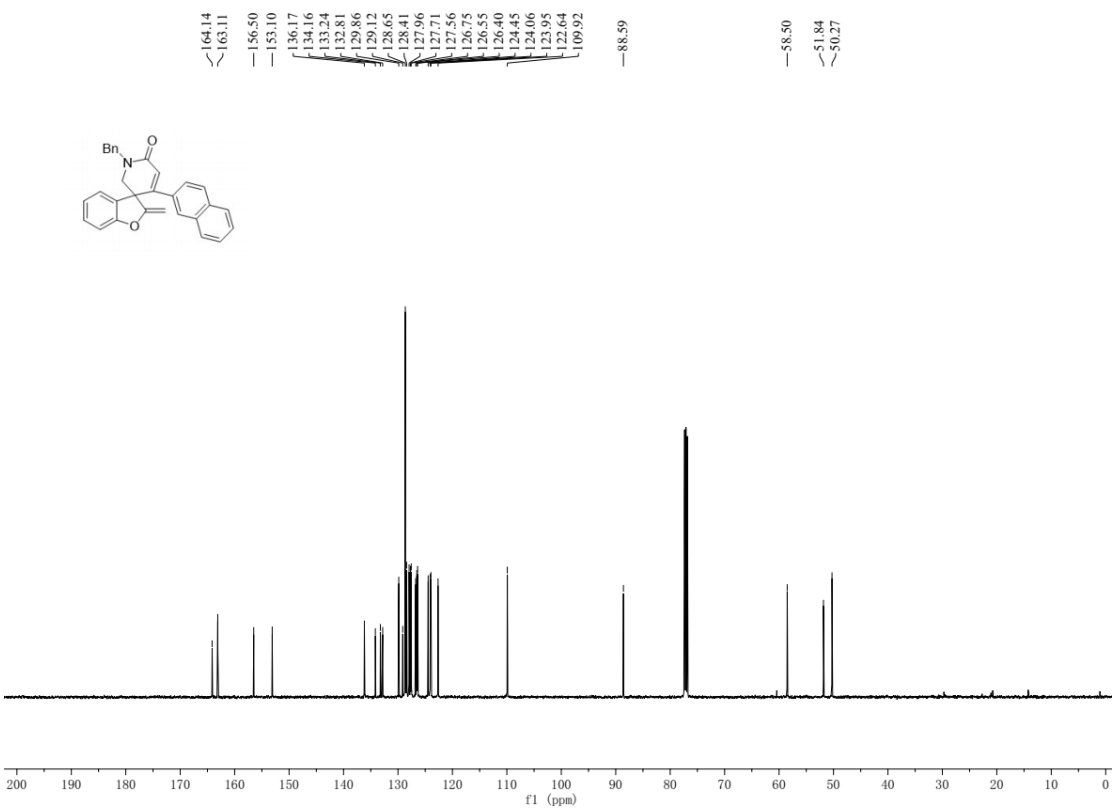
***1'-Benzyl-2-methylene-4'-(naphthalen-2-yl)-1',2'-dihydro-2H,6'H-spiro-[benzofuran-3,3'-pyridin]-6'-one (5e)*:**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:6 (v/v); light yellow oil; 55.0 mg, 64% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62-7.56 (m, 2H), 7.51 (d, J = 8.5 Hz, 1H), 7.46 (s, 1H), 7.34-7.29 (m, 2H), 7.22-7.15 (m, 5H), 7.13-7.10 (m, 1H), 6.98 (dd, J = 8.5, 2.0 Hz, 1H), 6.92-6.89 (m, 2H), 6.74-6.71 (m, 1H), 6.45 (s, 1H), 4.66 (d, J = 3.0 Hz, 1H), 4.61 (d, J = 14.5 Hz, 1H), 4.56 (d, J = 14.5 Hz, 1H), 4.20 (d, J = 3.0 Hz, 1H), 3.48 (d, J = 13.0 Hz, 1H), 3.44 (d, J = 13.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.1, 163.1, 156.5, 153.1, 136.2, 134.2, 133.2, 132.8, 129.9, 129.1, 128.7, 128.4, 128.0, 127.7, 127.6, 126.8, 126.6, 126.4, 124.5, 124.1, 124.0, 122.6, 109.9, 88.6, 58.5, 51.8, 50.3. HRMS *m/z* (ESI+): Calculated for $C_{30}H_{24}NO_2^+$ ($[M+H]^+$): 430.1807, found 430.1810.

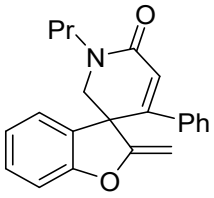


^{1}H NMR of compound **5e** (500 MHz, $CDCl_3$)

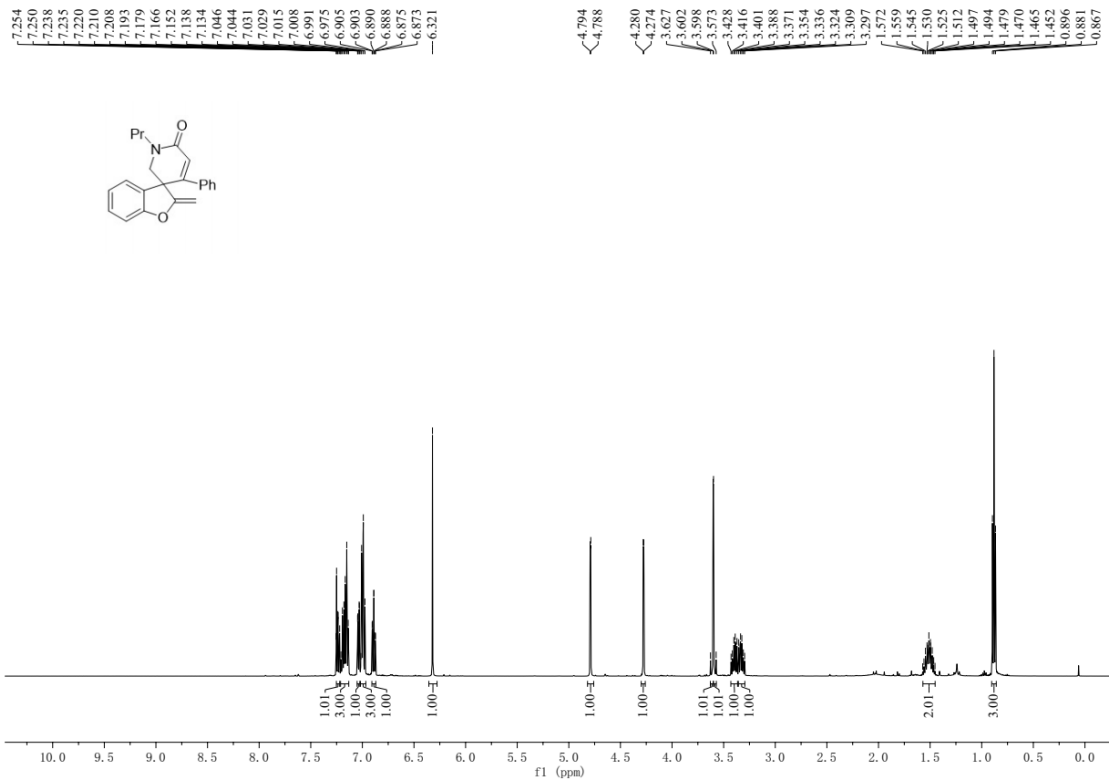


^{13}C NMR of compound **5e** (125 MHz, $CDCl_3$)

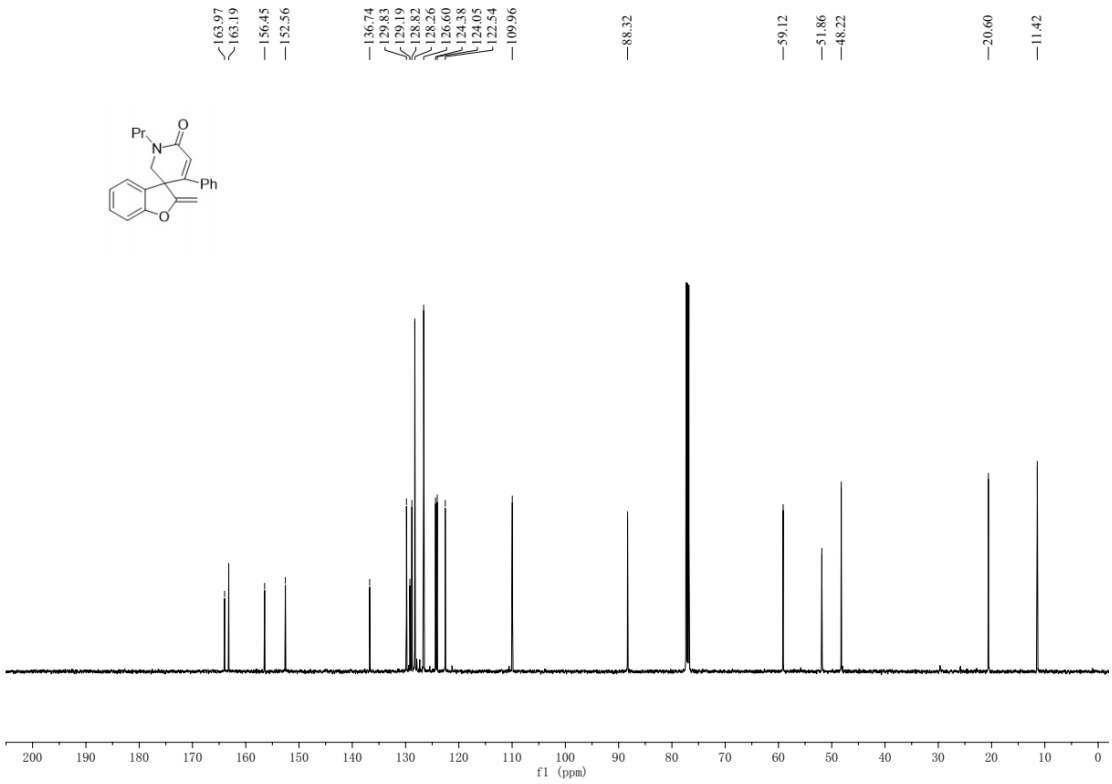
***2-Methylene-4'-phenyl-1'-propyl-1',2'-dihydro-2H,6'H-spiro[benzofuran-3,3'-pyridin]-6'-one (5f)*:**



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:6 (v/v); light yellow oil; 35.8 mg, 54% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25-7.22 (m, 1H), 7.21-7.13 (m, 3H), 7.04 (dd, J = 7.5, 1.0 Hz, 1H), 7.02-6.98 (m, 3H), 6.89 (td, J = 7.5, 1.0 Hz, 1H), 6.32 (s, 1H), 4.79 (d, J = 3.0 Hz, 1H), 4.28 (d, J = 3.0 Hz, 1H), 3.61 (d, J = 12.5 Hz, 1H), 3.59 (d, J = 12.5 Hz, 1H), 3.43-3.37 (m, 1H), 3.35-3.30 (m, 1H), 1.57-1.45 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0, 163.2, 156.5, 152.6, 136.7, 129.8, 129.2, 128.8, 128.3, 126.6, 124.4, 124.1, 122.5, 110.0, 88.3, 59.1, 51.9, 48.2, 20.6, 11.4. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{22}NO_2^+$ ($[M+H]^+$): 332.1651, found 332.1648.



^{1}H NMR of compound **5f** (500 MHz, $CDCl_3$)

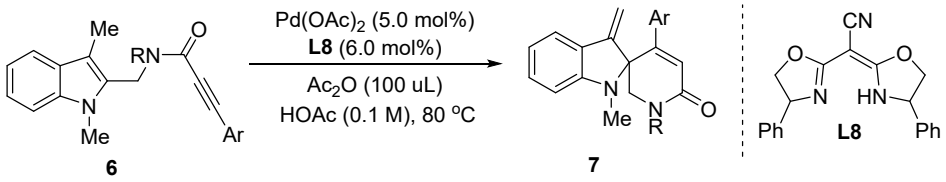


^{13}C NMR of compound **5f** (125 MHz, $CDCl_3$)

8. Synthesis of C2-alkyne-tethered indoles 6

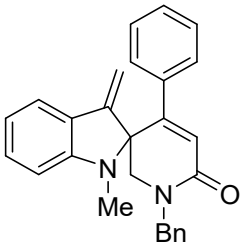
6a-6d are known compounds previously reported by our group.[6]

9. Procedure for dearomative 1,6-enyne cycloisomerization of 6

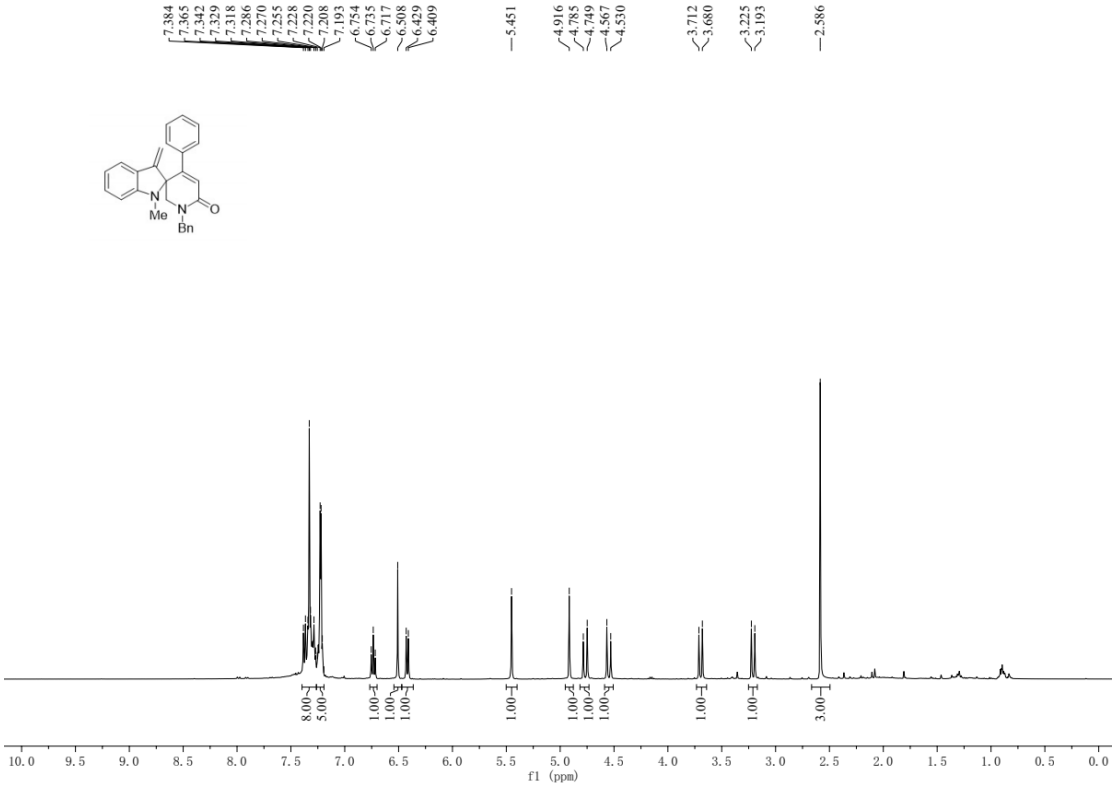


To a dried Schlenk tube were charged with $Pd(OAc)_2$ (5.0 mol%, 2.3 mg), **L8** (6.0 mol%, 7.5 mg) and **6** (0.2 mmol) under air atmosphere. HOAc (2.0 mL) was then introduced via syringe. The resulting mixture was stirred at 80 °C (heating block) until the reaction was completed (monitored by TLC). The reaction was quenched with a solution of saturated sodium bicarbonate at 0 °C and the mixture was extracted with ethyl acetate. The combined organic phases were then concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v) to afford product **7**.

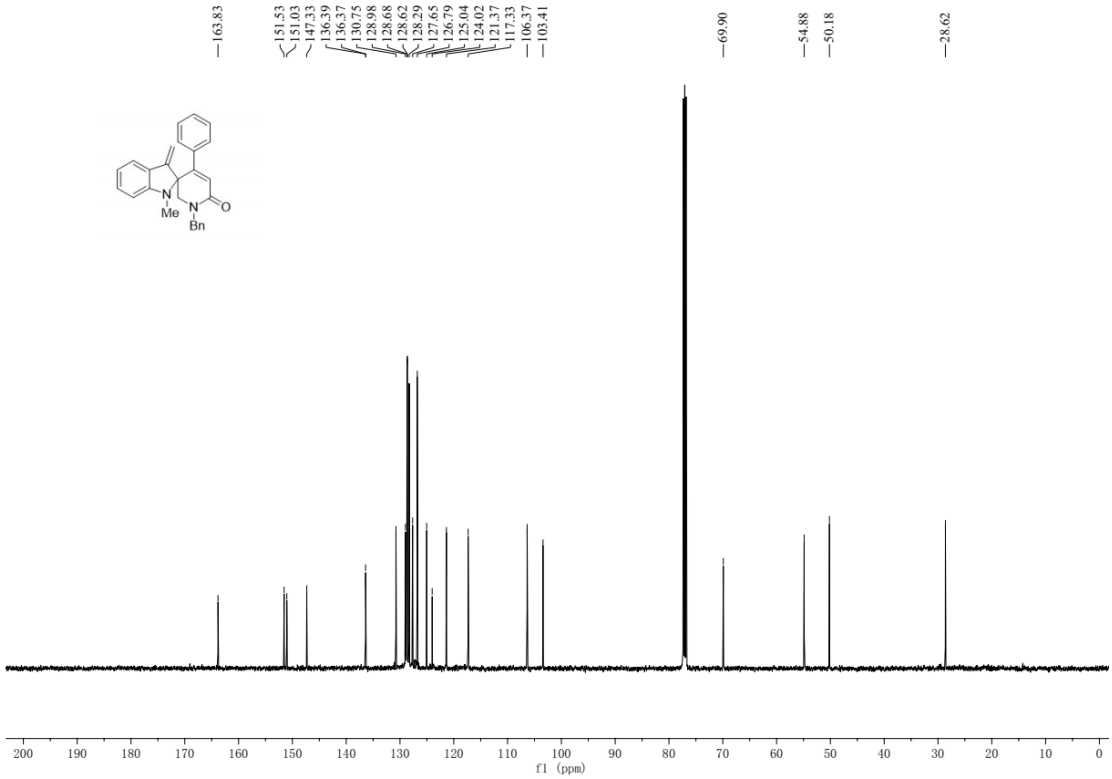
1'-Benzyl-1-methyl-3-methylene-4'-phenyl-1',2'-dihydro-6'H-spiro[indoline-2,3'-pyridin]-6'-one (7a):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); light yellow oil; 41.5 mg, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.27 (m, 8H), 7.26-7.19 (m, 5H), 6.74 (t, J = 7.6 Hz, 1H), 6.51 (s, 1H), 6.42 (d, J = 8.0 Hz, 1H), 5.45 (s, 1H), 4.92 (s, 1H), 4.77 (d, J = 14.4 Hz, 1H), 4.55 (d, J = 14.4 Hz, 1H), 3.70 (d, J = 12.8 Hz, 1H), 3.21 (d, J = 12.8 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8, 151.5, 151.0, 147.3, 136.39, 136.37, 130.8, 129.0, 128.7, 128.6, 128.3, 127.7, 126.8, 125.0, 124.0, 121.4, 117.3, 106.4, 103.4, 69.9, 54.9, 50.2, 28.6. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{25}N_2O^+$ ([M+H]$^+$): 393.1967, found 393.1963.

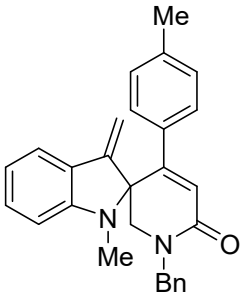


^{1}H NMR of compound **7a** (400 MHz, $CDCl_3$)

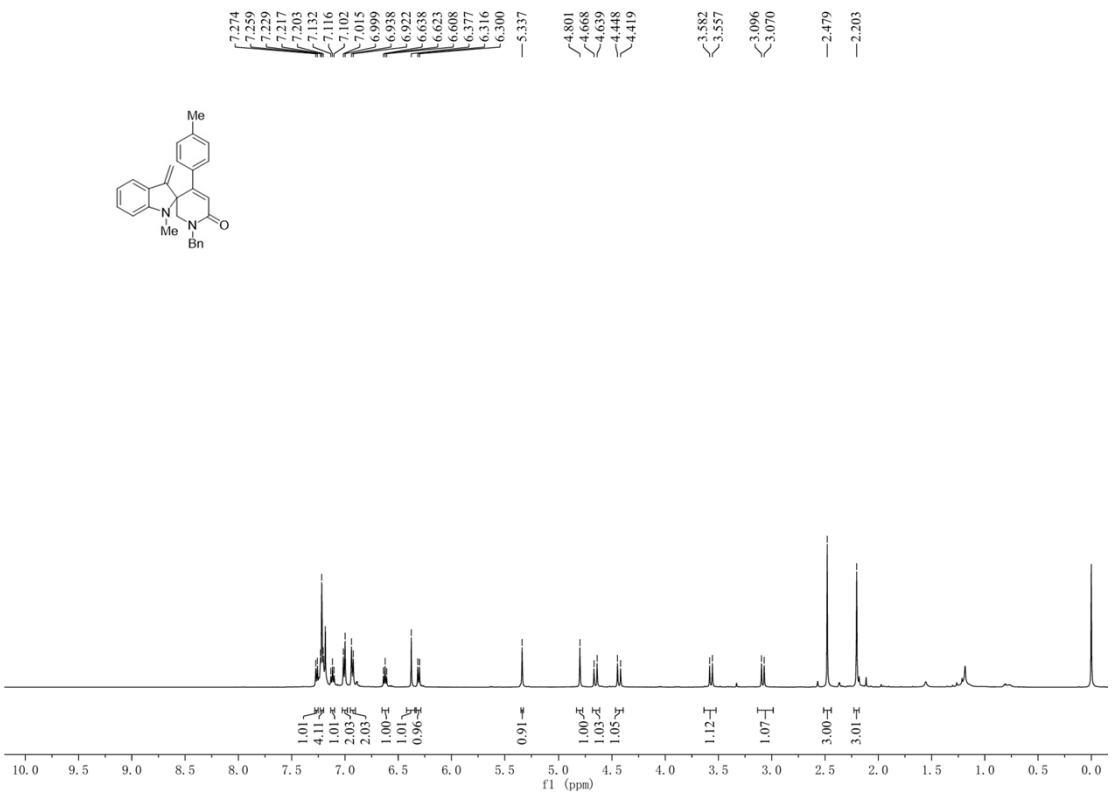


^{13}C NMR of compound **7a** (125 MHz, $CDCl_3$)

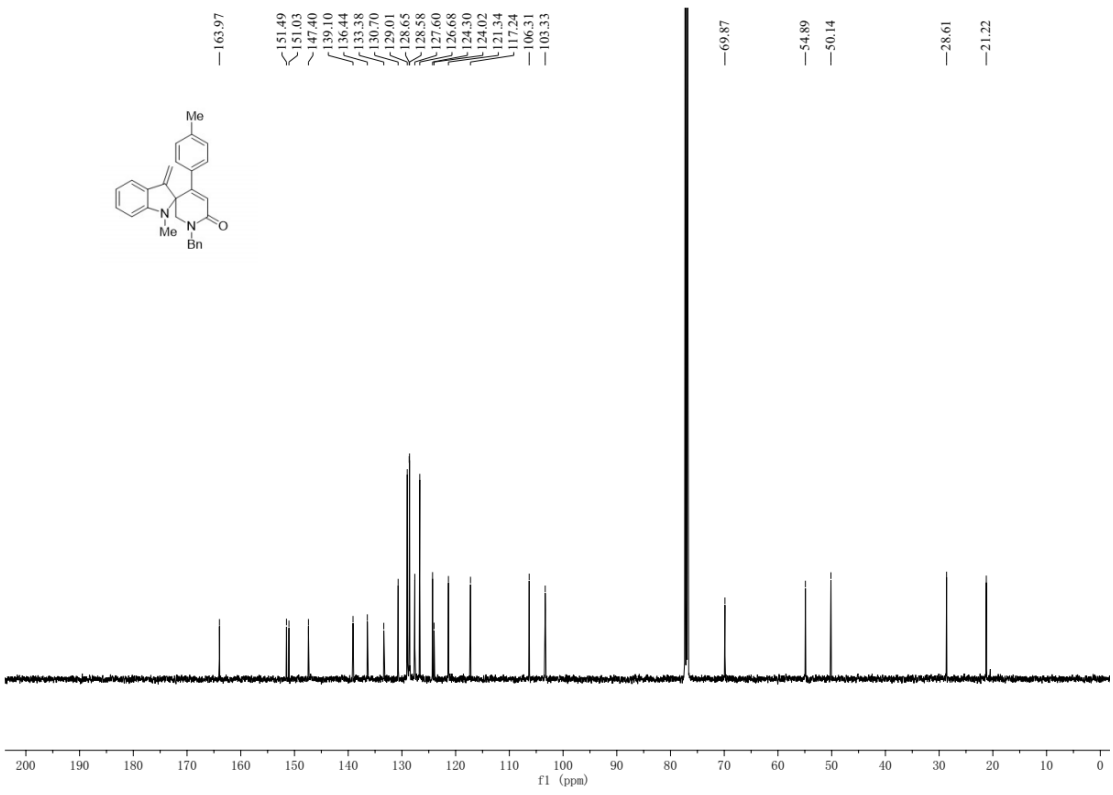
1'-Benzyl-1-methyl-3-methylene-4'-(p-tolyl)-1',2'-dihydro-6'H-spiro[indoline-2,3'-pyridin]-6'-one (7b):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); light yellow oil; 33.3 mg, 41% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (d, J = 7.5 Hz, 1H), 7.23-7.20 (m, 4H), 7.12 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.62 (t, J = 7.5 Hz, 1H), 6.38 (s, 1H), 6.31 (d, J = 8.0 Hz, 1H), 5.34 (s, 1H), 4.80 (s, 1H), 4.65 (d, J = 14.5 Hz, 1H), 4.43 (d, J = 14.5 Hz, 1H), 3.57 (d, J = 13.0 Hz, 1H), 3.08 (d, J = 3.0 Hz, 1H), 2.48 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.0, 151.5, 151.0, 147.4, 139.1, 136.4, 133.4, 130.7, 129.0, 128.7, 128.6, 127.6, 126.7, 124.3, 124.0, 121.3, 117.2, 106.3, 103.3, 69.9, 54.9, 50.1, 28.6, 21.2. HRMS *m/z* (ESI+): Calculated for $C_{28}H_{27}N_2O^+$ ([M+H]$^+$): 407.2123, found 407.2121.

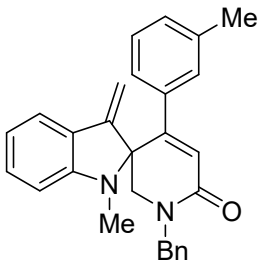


^{1}H NMR of compound **7b** (500 MHz, $CDCl_3$)

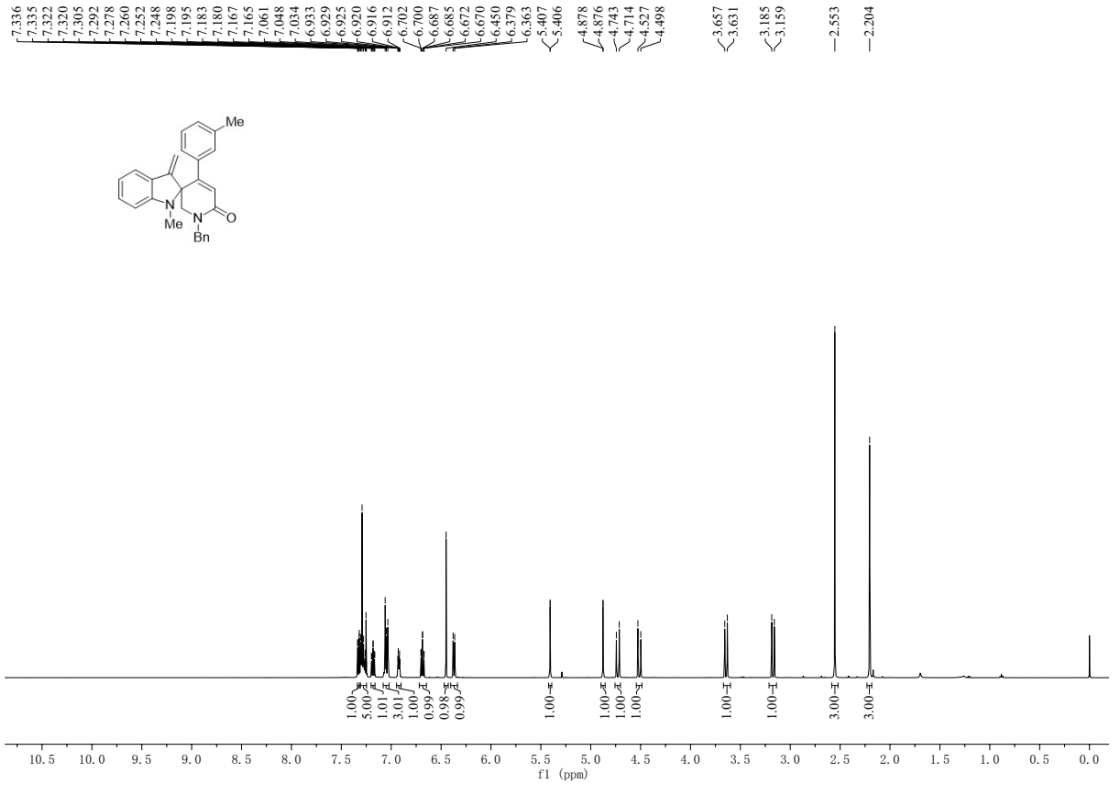


^{13}C NMR of compound **7b** (125 MHz, $CDCl_3$)

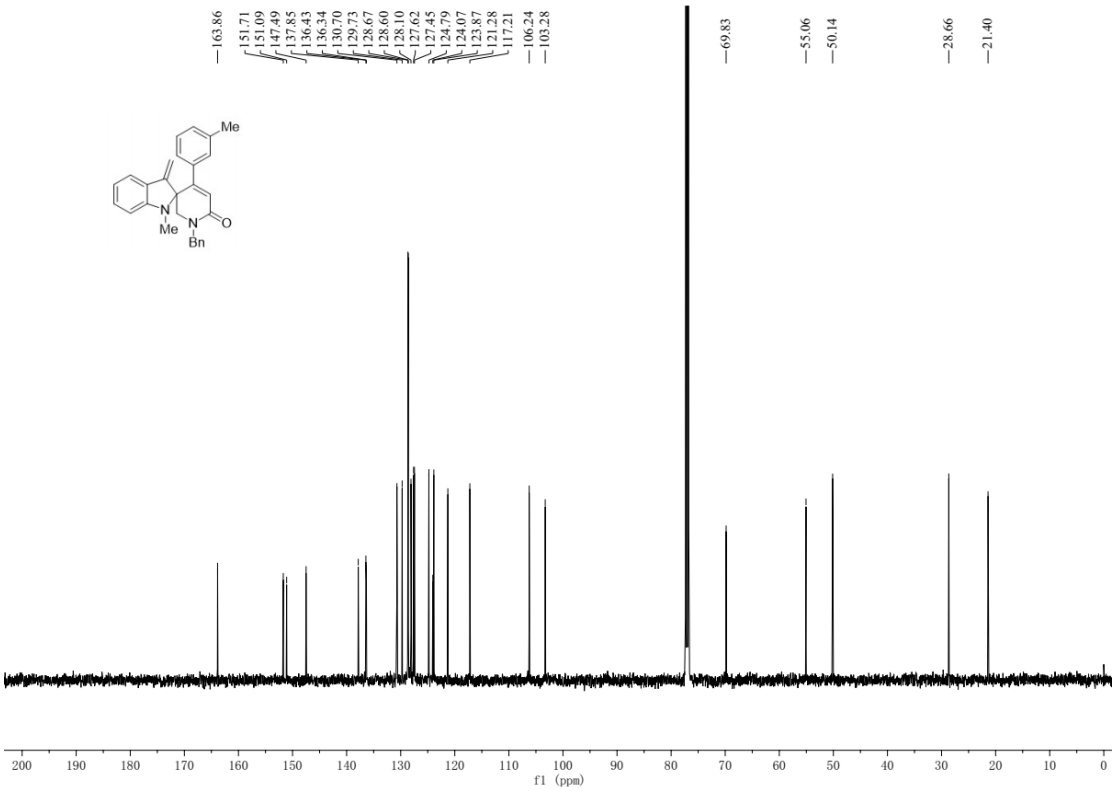
1'-Benzyl-1-methyl-3-methylene-4'-(m-tolyl)-1',2'-dihydro-6'H-spiro[indoline-2,3'-pyridin]-6'-one (7c):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow solid, Mp = 145-146 °C; 44.6 mg, 55% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.32 (m, 1H), 7.31-7.25 (m, 5H), 7.18 (td, J = 7.5, 1.5 Hz, 1H), 7.06-7.03 (m, 3H), 6.93-6.91 (m, 1H), 6.69 (td, J = 7.5, 1.0 Hz, 1H), 6.45 (s, 1H), 6.37 (d, J = 8.0 Hz, 1H), 5.41 (d, J = 1.0 Hz, 1H), 4.88 (d, J = 1.0 Hz, 1H), 4.73 (d, J = 14.5 Hz, 1H), 4.51 (d, J = 14.5 Hz, 1H), 3.64 (d, J = 13.0 Hz, 1H), 3.17 (d, J = 13.0 Hz, 1H), 2.55 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.9, 151.7, 151.1, 147.5, 137.9, 136.4, 136.3, 130.7, 129.7, 128.7, 128.6, 128.1, 127.6, 127.5, 124.8, 124.1, 123.9, 121.3, 117.2, 106.2, 103.3, 69.8, 55.1, 50.1, 28.7, 21.4. HRMS *m/z* (ESI+): Calculated for $C_{28}H_{27}N_2O^+$ ([M+H]$^+$): 407.2123, found 407.2116.

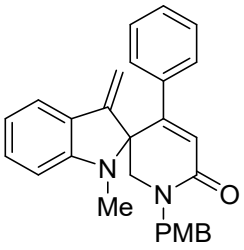


^{1}H NMR of compound **7c** (500 MHz, $CDCl_3$)

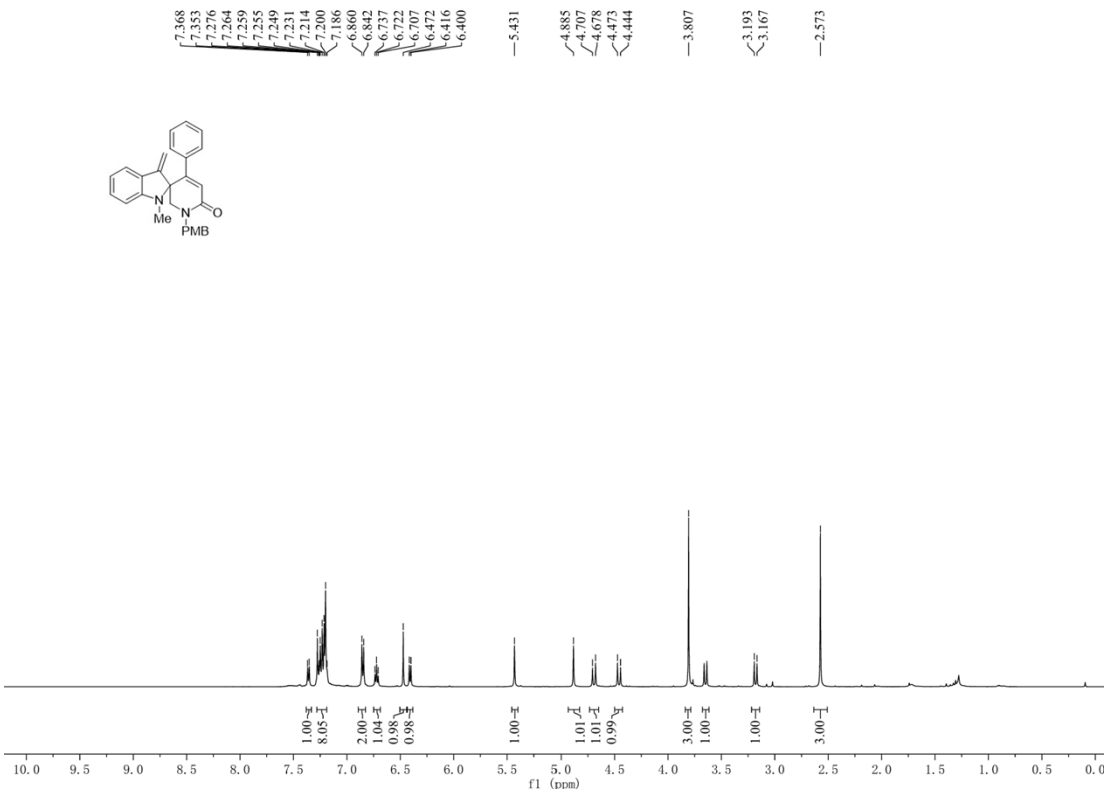


^{13}C NMR of compound **7c** (125 MHz, $CDCl_3$)

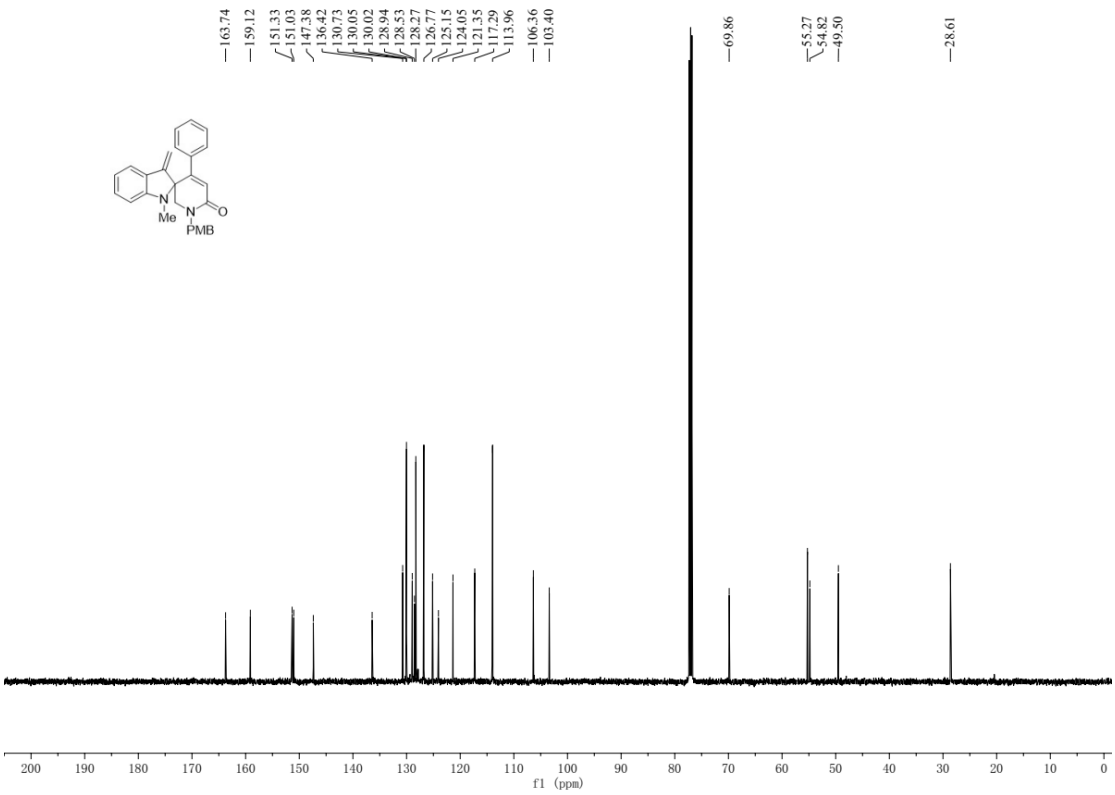
1'-(4-Methoxybenzyl)-1-methyl-3-methylene-4'-phenyl-1',2'-dihydro-6'H-spiro-[indoline-2,3'-pyridin]-6'-one (7d):



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow oil; 30.0 mg, 35% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, J = 7.5 Hz, 1H), 7.28-7.19 (m, 8H), 6.85 (d, J = 8.5 Hz, 2H), 6.72 (t, J = 7.5 Hz, 1H), 6.47 (s, 1H), 6.41 (d, J = 8.0 Hz, 1H), 5.43 (s, 1H), 4.89 (s, 1H), 4.69 (d, J = 14.5 Hz, 1H), 4.46 (d, J = 14.5 Hz, 1H), 3.81 (s, 3H), 3.65 (d, J = 13.0 Hz, 1H), 3.18 (d, J = 3.0 Hz, 1H), 2.57 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7, 159.1, 151.3, 151.0, 147.4, 136.4, 130.7, 130.0, 128.9, 128.5, 128.3, 126.8, 125.2, 124.1, 121.4, 117.3, 114.0, 106.4, 103.4, 69.9, 55.3, 54.8, 49.5, 28.6. HRMS *m/z* (ESI+): Calculated for $C_{28}H_{27}N_2O_2^+$ ([M+H]$^+$): 423.2073, found 423.2074.



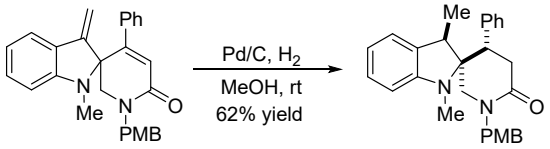
^{1}H NMR of compound **7d** (500 MHz, $CDCl_3$)



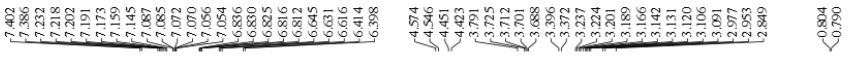
^{13}C NMR of compound **7d** (125 MHz, $CDCl_3$)

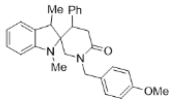
10. Synthetic transformation and mechanistic study

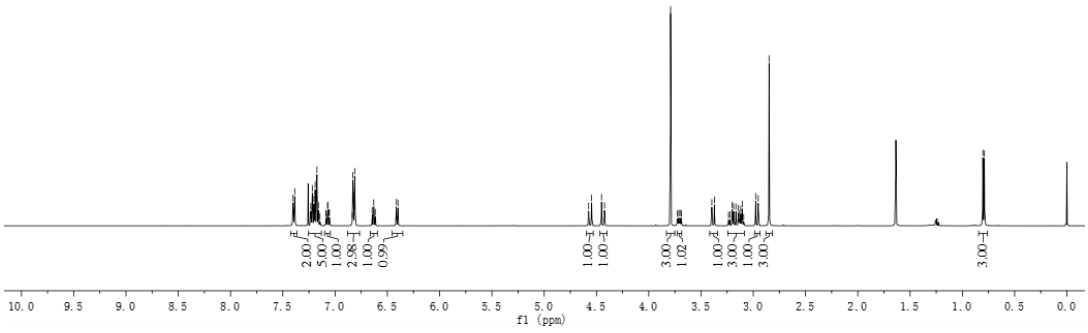
10.1 Hydrogenation of 7d



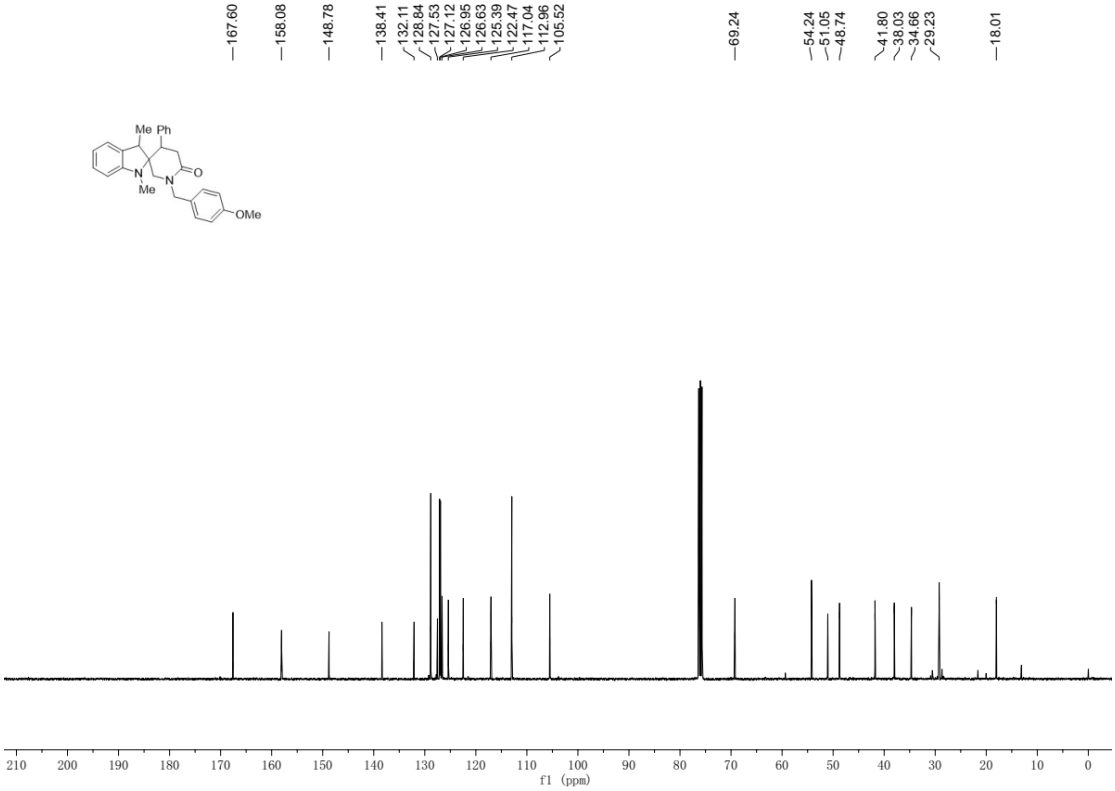
To a suspension of Pd/C (0.01 mmol, 14.0 mg) in MeOH (1.0 mL) under hydrogen atmosphere with a H_2 balloon was added the solution of **7d** (0.1 mmol, 42.2 mg) in MeOH (1.0 mL) via syringe. The mixture was stirred at room temperature for 12 h. After filtration, the filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v) to give compound **8** (26.4 mg, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, J = 8.0 Hz, 2H), 7.23-7.14 (m, 5H), 7.07 (td, J = 7.5, 1.0 Hz, 1H), 6.84-6.81 (m, 3H), 6.63 (t, J = 7.5 Hz, 1H), 6.41 (d, J = 8.0 Hz, 1H), 4.56 (d, J = 14.0 Hz, 1H), 4.44 (d, J = 14.0 Hz, 1H), 3.79 (s, 3H), 3.71 (dd, J = 12.0, 6.5 Hz, 1H), 3.38 (d, J = 12.0 Hz, 1H), 3.24-3.09 (m, 3H), 2.96 (d, J = 12.0 Hz, 1H), 2.85 (s, 3H), 0.80 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 158.1, 148.8, 138.4, 132.1, 128.8, 127.5, 127.1, 127.0, 126.6, 125.4, 122.5, 117.0, 113.0, 105.5, 69.2, 54.2, 51.1, 48.7, 41.8, 38.0, 34.7, 29.2, 18.0. HRMS m/z (ESI+): Calculated for $C_{28}H_{31}N_2O_2^+$ ([M+H]+): 427.2380, found 427.2378.





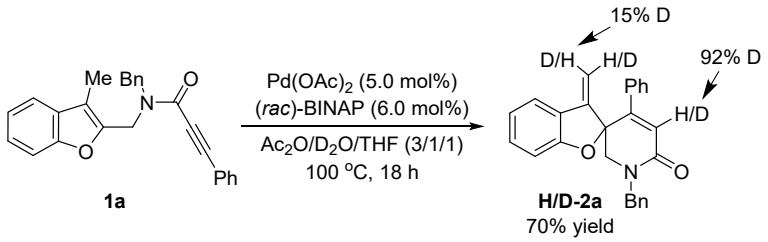


^{1}H NMR of compound **8** (500 MHz, $CDCl_3$)



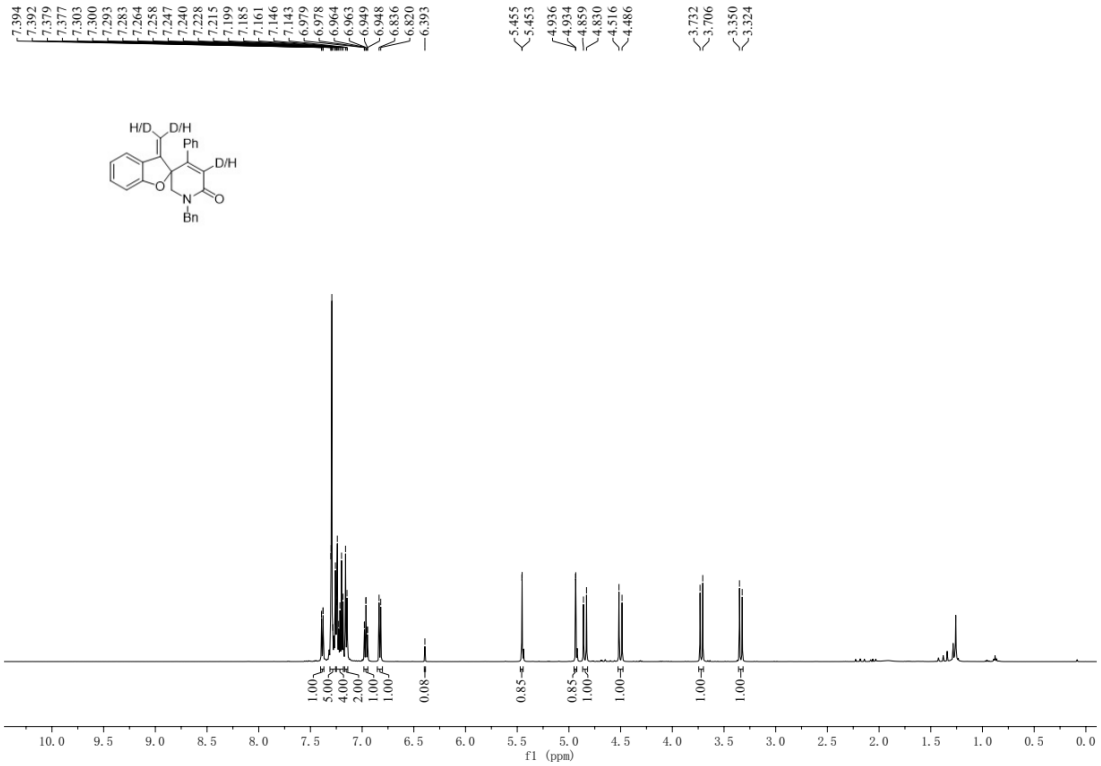
^{13}C NMR of compound **8** (100 MHz, $CDCl_3$)

10.2 Deuterium-labeling Experiment



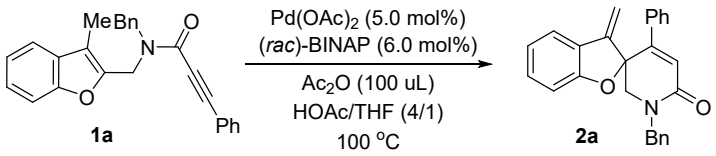
To a dried Schlenk tube were charged with $Pd(OAc)_2$ (5.0 mol%, 2.2 mg), **1a** (0.2 mmol), and (*rac*)-BINAP (6.0 mol%, 7.5 mg) under air atmosphere. Ac_2O (1.2 mL), D_2O (0.4 mL), and THF (0.4 mL) were then introduced via syringe. The resulting mixture was stirred at 100 °C (heating block) for 18 h. When the reaction was completed, the reaction was quenched with a solution of saturated sodium bicarbonate at 0 ℃ and mixture was extracted with ethyl acetate. The combined organic phases were concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:6 (v/v) to afford product **H/D-2a** in 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.38 (m, 1H), 7.30-7.26 (m, 5H), 7.25-7.19 (m, 4H), 7.16-7.14 (m, 2H), 6.98-6.95 (m, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.39 (s, 0.08H), 5.45 (d, J = 1.0 Hz, 0.85H), 4.94 (d, J = 1.0 Hz, 0.85H), 4.84 (d, J = 14.5 Hz, 1H), 4.50 (d, J = 14.5 Hz, 1H), 3.72 (d, J = 13.0 Hz, 1H), 3.34 (d,

J = 13.1 Hz, 1H). HRMS m/z (ESI+): Calculated for $C_{26}H_{21}DNO_2^+$ ([M+H]$^+$): 381.1708, found 381.1714.



^{1}H NMR of compound **H/D-2a** (500 MHz, $CDCl_3$)

10.3 Kinetic studies



To a dried Schlenk tube were charged with $Pd(OAc)_2$ (5.0 mol%, 2.3 mg), (*rac*)-BINAP (6 mol%, 7.5 mg), and **1a** (0.2 mmol) under air atmosphere. Ac_2O (100 μL), HOAc (1.6 mL), and THF (0.4 mL) were then introduced via syringe. The reaction was stopped at the corresponding time point (30 min, 60 min, 90 min, 120 min, 180 min, 210 min). The reaction was quenched with a solution of saturated sodium bicarbonate at 0 ℃ and the mixture was extracted with ethyl acetate. The combined organic phases were concentrated under reduced pressure and the residue was analyzed by ^{1}H NMR. The ratio of c_t/c_0 was calculated through ^{1}H NMR based on the ratio of the product and remaining substrate in the reaction.

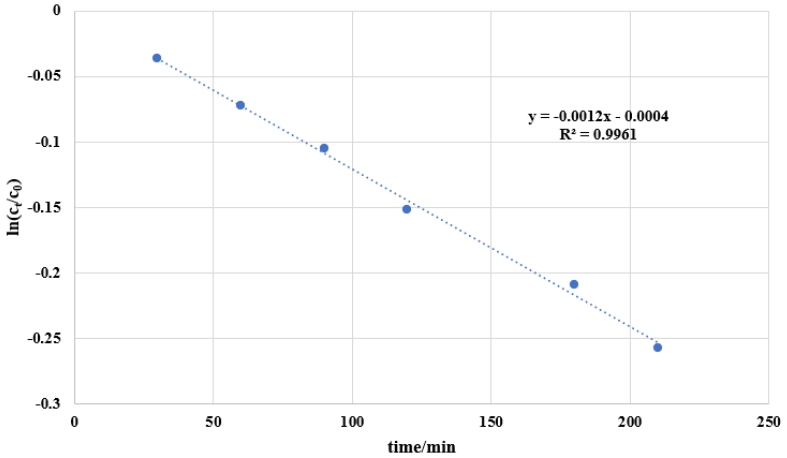
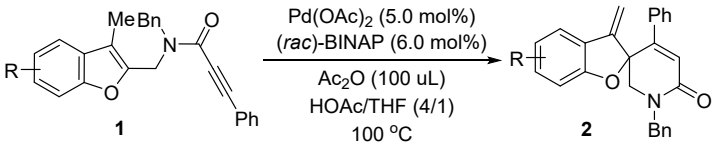


Figure S1. Kinetic order in benzofuran substrate

10.4 Hammett plot



To a dried Schlenk tube were charged with $Pd(OAc)_2$ (5.0 mol%, 2.3 mg), (*rac*)-BINAP (6 mol%, 7.5 mg), and corresponding benzofuran substrates **1** (0.2 mmol) under air atmosphere. Ac_2O (100 μL), HOAc (1.6 mL), and THF (0.4 mL) was then introduced via syringe. Follow the same procedures as **1a**, the ratio of *Kx*/*Kh* was caculated and results were summarized.

Table S3. The collected data for Hammett plot

entry	R	K_x (min^{-1})	Log(K_X/K_H)	σ^9
1	6-Me	0.0051	0.6284	-0.170
2	5-Me	0.0027	0.3522	-0.069
3	H	0.0012	0	0
4	6-Cl	0.0005	-0.3802	0.227
5	5-Cl	0.00009	-1.1249	0.373

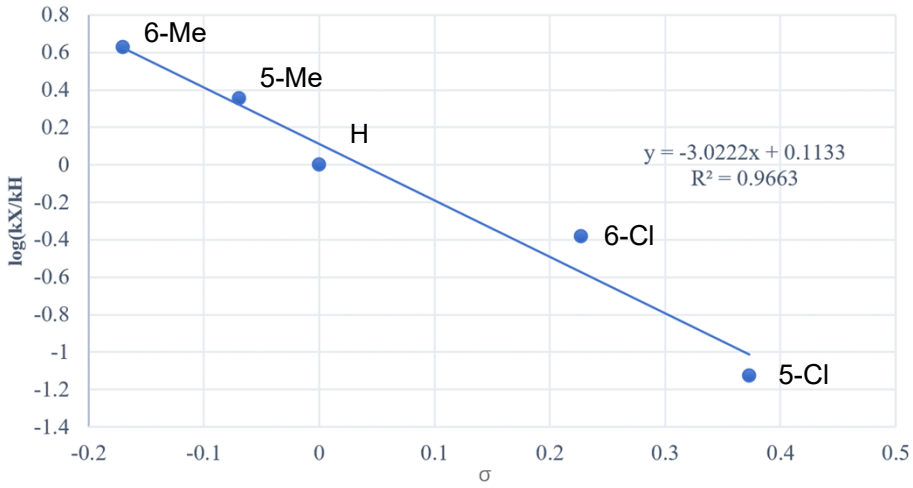


Figure S2. Hammett plot for reactions of benzofurans.

11. Crystal reports of compound 2p and 8

11.1 Crystal report of 2p

The crystal of **2p** was grown from a mixture solvent of dichloromethane and hexane at room temperature. The deposition number for **2p** at the Cambridge Crystallographic Data Centre is 2417895.

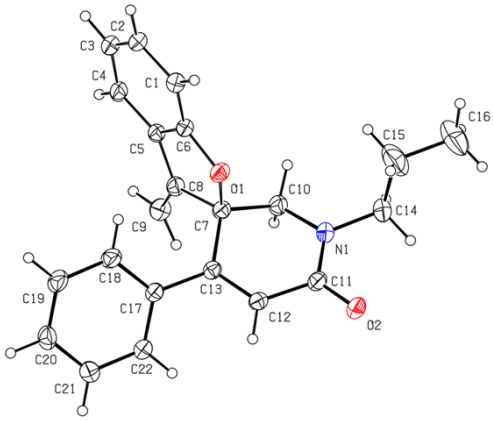


Figure S3. Ortep drawing of compound **2p** with 50% ellipsoids

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 230303_ljb_3_npr_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 230303_ljb_3_npr_0m

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Bond precision:   C-C = 0.0036 A          Wavelength=1.34139

Cell:             a=24.3399(15)     b=12.3406(8)         c=14.444(1)
                  alpha=90          beta=120.693(2)      gamma=90
Temperature:      170 K

                 Calculated                Reported
Volume           3730.8(4)                 3730.8(4)
Space group      C 2/c                     C 1 2/c 1
Hall group       -C 2yc                    -C 2yc
Moiety formula   C22 H21 N O2 [+ solvent]  C22 H21 N O2
Sum formula      C22 H21 N O2 [+ solvent]  C22 H21 N O2
Mr               331.40                    331.40
Dx,g cm-3        1.180                     1.180
Z                8                         8
Mu (mm-1)        0.379                     0.379
F000             1408.0                    1408.0
F000'            1411.03
h,k,lmax         31,16,18                  31,16,18
Nref             4293                      4271
Tmin,Tmax        0.969,0.981               0.667,0.752
Tmin'            0.941

Correction method= # Reported T Limits: Tmin=0.667 Tmax=0.752
AbsCorr = MULTI-SCAN

Data completeness= 0.995           Theta(max)= 60.643

R(reflections)= 0.0669( 3350)                    wR2(reflections)=
                                                 0.1765( 4271)
S = 1.105                 Npar= 297
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

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PLAT222_ALERT_3_C NonSolvent Resd 1  H   Uiso(max)/Uiso(min) Range        4.3 Ratio
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C14 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      4.911 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         14 Report
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Alert level G

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ABSMU01_ALERT_1_G  Calculation of _exptl_absorpt_correction_mu
                 not performed for this radiation type.
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         19 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         19 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records         25 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT188_ALERT_3_G A Non-default SIMU Restraint Value has been used     0.0100 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
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PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
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PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
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PLAT398_ALERT_2_G Deviating  C-O-C   Angle From 120 for O1       .      108.3 Degree
PLAT398_ALERT_2_G Deviating  C-O-C   Angle From 120 for O1A      .      108.1 Degree
PLAT605_ALERT_4_G Largest Solvent Accessible VOID in the Structure         25 A**3
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          2 Note
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #         30 Check
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....          ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        313 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          9 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          5 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          1 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by          2 Check
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
32 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

```
  8 ALERT type 2 Indicator that the structure model may be wrong or deficient
 20 ALERT type 3 Indicator that the structure quality may be low
  6 ALERT type 4 Improvement, methodology, query or suggestion
  2 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 28/11/2022; check.def file version of 28/11/2022

11.2 Crystal report of 8

The crystal of **8** was grown from a mixture solvent of dichloromethane and hexane at room temperature. The deposition number for **8** at the Cambridge Crystallographic Data Centre is 2417896.

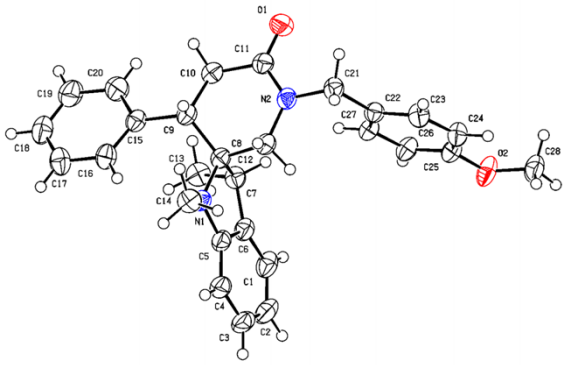

Figure S4. Ortep drawing of compound **8** with 50% ellipsoids

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) cu_220705_ljb_pd_c_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: cu_220705_ljb_pd_c_0m

```
Bond precision:   C-C = 0.0019 A          Wavelength=1.54178

Cell:             a=12.3912(6)     b=11.2049(6)      c=16.6414(9)
                  alpha=90         beta=91.031(2)    gamma=90
Temperature:      169 K

                 Calculated                Reported
Volume           2310.2(2)                 2310.2(2)
Space group      P 21/n                    P 1 21/n 1
Hall group       -P 2yn                    -P 2yn
Moiety formula   C28 H30 N2 O2             C28 H30 N2 O2
Sum formula      C28 H30 N2 O2             C28 H30 N2 O2
Mr               426.54                    426.54
Dx,g cm-3        1.226                     1.226
Z                4                         4
Mu (mm-1)        0.604                     0.604
F000             912.0                     912.0
F000'            914.53
h,k,lmax         14,13,20                  14,13,20
Nref             4238                      4227
Tmin,Tmax        0.828,0.897               0.433,0.753
Tmin'            0.762

Correction method= # Reported T Limits: Tmin=0.433 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 68.381

R(reflections)= 0.0443( 3920)                wR2(reflections)=
                                             0.1145( 4227)
S = 1.073                 Npar= 292
```

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level C

```
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          3 Report
```

Alert level G

```
PLAT793_ALERT_4_G Model has Chirality at C7          (Centro SPGR)          R Verify
PLAT793_ALERT_4_G Model has Chirality at C8          (Centro SPGR)          R Verify
PLAT793_ALERT_4_G Model has Chirality at C9          (Centro SPGR)          S Verify
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          7 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          7 Info
```

```
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```

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PLATON version of 18/05/2022; check.def file version of 17/05/2022

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