Protecting group-directed annulations of tetra-substituted oxindole olefins and sulfur ylides: regio- and chemoselective synthesis of cyclopropane- and dihydrofuran-fused spirooxindoles

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Supporting Information

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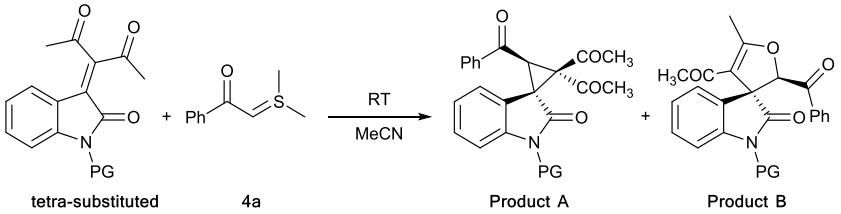
1. General method

NMR spectroscopic data were obtained for ^{1}H at 400 MHz or ^{13}C at 100 MHz, or for ^{1}H at 600 MHz or ^{13}C at 150 MHz. Chemical shifts were reported in parts per million (ppm) from tetramethylsilane utilizing solvent resonance in $CDCl_3$ solution as the internal standard. ESI was performed on a Waters SYNAPT G2 as the ionization method. ESI-HRMS spectra were measured according to a Q-TOF instrument. Column chromatography was performed on silica gel (200–300 mesh) using an eluent of ethyl acetate and petroleum ether. Melting points were mensurated by a Mel-Temp apparatus, and were not accuracy in one hundred percent. All reactions were monitored by thin layer chromatography (TLC) with silica gelcoated paltes; and products were visualized using UV light.

2. Investigation of the influence of protecting groups (Table S1) [a]

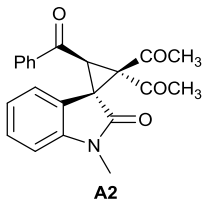


Entry	PG	Yield (%)[b] product **A**/**B**	d.r.[c] product **A**/**B**
1	H	45/48	8:1/10:1
2	Me	10/44	1:1/8:1
3	Allyl	12/45	1:1/5:1
4	Bn	19/48	7:1/9:1
5	Ac	36/11	20:1/10:1
6	Boc	48/21	15:1/12:1

[a] Unless otherwise noted, all reactions were performed with tetra-sustituted oxoindole olefin (0.15 mmol), **4a** (0.165 mmol) in 2 mL MeCN at room temperature for 2 h; [b] Isolated yields of the product **A** and **B**; [c] The diastereoselective ratio of the product **A** and **B** were calculated based on ^{1}H-NMR analysis of the crude reaction mixture.

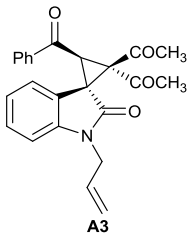
We screened a broad type of protecting groups including methyl (-Me), allyl, acetyl (-Ac), benzyl (-Bn) and tert-butyloxycarboryl (-Boc) groups to investigate the influence on chemo- and regioselectivity. Generally, *N*-Bn and *N*-Boc substrates showed the best tendency on the synthesis of dihydrofuran- and cyclopropane-fused spirooxindole respectively (**B4**/**A6**) in 48% yields with high diastereoselectivities of 9:1 and up to 12:1 dr values (Table S1, entry 4 and 6). The tetra-

substituted oxoindole olefins with *N*-Me and *N*-Allyl protecting groups both produced cyclopropane-fused spirooxindoles **A2**/**A3** in low yields with very poor diastereoselective value of 1:1, while demonstrating good reaction performance for the synthesis of products **B2**/**B3** with 8:1 and 5:1 dr values (entry 2 and 3). Besides, in spite of high diastereoselectivity, *N*-Ac protected tetra-substituted oxoindole olefin did not react well at this condition resulting products **A5**/**B5** in a low yield (entry 5). Hence, we chose *N*-Bn- and *N*-Boc-protected oxoindole olefins as model substrates for the construction of desirable dihydrofuran- and cyclopropane-fused spirooxindoles respectively.



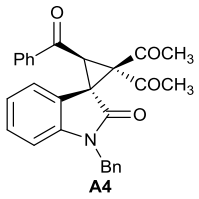
A2

A2 was obtained according to the similar procedure. White solid, 10% yield (5.4 mg). The diastereomeric ratio was determined to be 1:1 by crude ^{1}H-NMR analysis. m.p. 158–159 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.78 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.51 (tt, *J* = 7.8, 1.2 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.29 (td, *J* = 7.8, 1.2 Hz, 1H), 6.99 (td, *J* = 7.8, 0.6 Hz, 1H), 6.89 (dd, *J* = 15.0, 7.8 Hz, 2H), 4.25 (s, 1H), 3.16 (s, 3H), 2.58 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 198.1, 192.2, 169.5, 144.3, 136.5, 133.7, 129.3, 128.9, 128.6, 128.3, 126.5, 122.6, 120.6, 108.7, 63.5, 43.5, 40.9, 32.3, 29.9, 28.9, 27.0; ESI HRMS: calcd. For $C_{22}H_{19}NO_4Na^+$ 384.1212, found 384.1214.



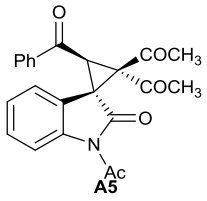
A3

A3 was obtained according to the similar procedure. White solid, 12% yield (7.0 mg). The diastereomeric ratio was determined to be 1:1 by crude ^{1}H-NMR analysis. m.p. 159–160 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.76 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.44 – 7.40 (m, 2H), 7.24 (td, *J* = 7.8, 1.2 Hz, 1H), 6.97 (td, *J* = 7.2, 0.6 Hz, 1H), 6.86 (d, *J* = 3.0 Hz, 1H), 5.67 – 5.61 (m, 1H), 5.30 (s, 1H), 5.08 (dt, *J* = 10.8, 1.2 Hz, 2H), 4.40 – 4.36 (m, 1H), 4.25 – 4.23 (m, 2H), 2.61 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 198.2, 197.9, 192.1, 171.6, 143.5, 131.0, 129.2, 128.9, 128.7, 128.3, 126.5, 122.5, 120.7, 117.9, 109.6, 63.6, 43.6, 42.7, 29.9, 28.4; ESI HRMS: calcd. For $C_{24}H_{21}NO_4Na^+$ 410.1368, found 410.1366.



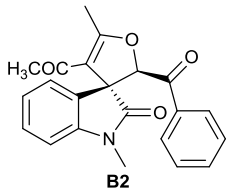
A4

A4 was obtained according to the similar procedure. White solid, 19% yield (12.5 mg). The diastereomeric ratio was determined to be 7:1 by crude ^{1}H-NMR analysis. m.p. 147–148 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.86 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.30 (m, 2H), 7.29 (d, *J* = 6.6 Hz, 3H), 7.17 (td, *J* = 7.8, 1.2 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.95 (td, *J* = 7.8, 1.2 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 5.02 (d, *J* = 15.6 Hz, 1H), 4.95 (d, *J* = 15.6 Hz, 1H), 4.31 (s, 1H), 2.38 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 198.0, 196.3, 192.0, 171.9, 143.3, 136.5, 135.4, 134.1, 128.9, 128.8, 128.6, 128.5, 127.9, 127.3, 126.3, 122.5, 120.6, 109.3, 99.9, 62.5, 44.3, 43.8, 29.9, 28.4; HRMS (ESI) m/z calcd for $C_{28}H_{23}NO_4Na^+$ 460.1525, found 460.1526.



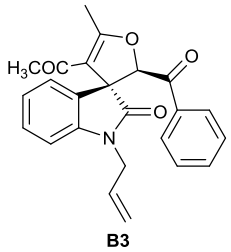
A5

A5 was obtained according to the similar procedure. White solid, 36% yield (21.0 mg). The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis. m.p. 169–170 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.27 (d, *J* = 7.8 Hz, 1H), 7.89 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.47 – 7.42 (m, 2H), 7.33 – 7.29 (m, 1H), 7.11 (td, *J* = 7.8, 0.6 Hz, 1H), 7.05 (dd, *J* = 7.8, 1.2 Hz, 1H), 4.29 (s, 1H), 2.69 (s, 3H), 2.36 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 197.7, 195.7, 191.5, 173.5, 170.3, 140.9, 136.5, 134.4, 129.2, 129.0, 128.5, 125.9, 124.9, 120.0, 116.2, 63.2, 44.5, 43.2, 29.9, 28.5, 27.1; ESI HRMS: calcd. For $C_{23}H_{19}NO_5Na^+$ 412.1162, found 412.1164.



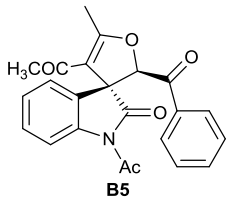
B2

B2 was obtained according to the similar procedure. White solid, 44% yield (23.9 mg). The diastereomeric ratio was determined to be 8:1 by crude ^{1}H-NMR analysis. m.p. 163–164 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.40 (tt, *J* = 7.2, 1.8 Hz, 1H), 7.22 – 7.17 (m, 4H), 7.04 (ddd, *J* = 7.2, 6.6, 2.4 Hz, 1H), 6.92 – 6.89 (m, 2H), 6.31 (d, *J* = 7.8 Hz, 1H), 6.25 (s, 1H), 2.97 (s, 3H), 2.54 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 192.9, 191.3, 117.0, 170.1, 142.7, 135.0, 133.4, 129.1, 128.2, 127.4, 127.0, 124.5, 122.9, 118.1, 107.6, 89.3, 61.9, 28.9, 26.5, 15.9; ESI HRMS: calcd. For $C_{22}H_{19}NO_4Na^+$ 384.1212, found 384.1210.



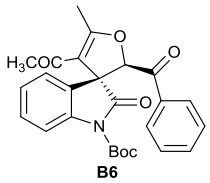
B3

B3 was obtained according to the similar procedure, white solid, 45% yield (26.2 mg). The diastereomeric ratio was determined to be 5:1 by crude ^{1}H-NMR analysis. m.p. 159–160 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.42 (t, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.01 (td, *J* = 7.2, 0.6 Hz, 1H), 6.93 (d, *J* = 6.6 Hz, 1H), 6.91 – 6.87 (m, 1H), 6.35 (d, *J* = 7.8 Hz, 1H), 6.27 (s, 1H), 5.68 – 5.62 (m, 1H), 5.28 (dd, *J* = 17.4, 0.6 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1H), 4.39 (dd, *J* = 16.2, 4.8 Hz, 1H), 3.76 (dd, *J* = 16.2, 5.4 Hz, 1H), 2.55 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 193.0, 191.1, 176.8, 170.0, 142.2, 133.4, 130.8, 129.0, 128.4, 127.5, 124.7, 122.8, 118.0, 108.7, 89.1, 61.9, 42.9, 29.0, 15.9; ESI HRMS: calcd. For $C_{24}H_{21}NO_4Na^+$ 410.1368, found 410.1370.



B5

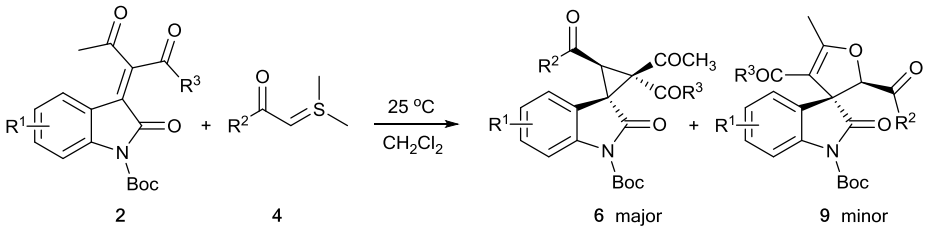
B5 was obtained according to the similar procedure. White solid, 11% yield (6.4 mg). The diastereomeric ratio was determined to be 10:1 by crude ^{1}H-NMR analysis. m.p. 159–160 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.72 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 4.2 Hz, 1H), 7.19 (d, *J* = 4.8 Hz, 4H), 7.10 (td, *J* = 7.8, 1.2 Hz, 1H), 7.04 (td, *J* = 7.8, 1.2 Hz, 1H), 6.93 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.27 (s, 1H), 2.64 (s, 3H), 2.57 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 192.7, 178.6, 170.1, 169.4, 139.3, 134.9, 134.0, 129.5, 128.5, 127.1, 125.1, 124.0, 120.4, 116.0, 89.8, 62.7, 29.8, 28.8, 26.6, 15.7; ESI HRMS: calcd. For $C_{23}H_{19}NO_5Na^+$ 412.1162, found 412.1160.



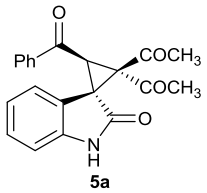
B6

B6 was obtained according to the similar procedure White solid, 21% yield (14.1 mg). The diastereomeric ratio was determined to be 12:1 by crude ^{1}H-NMR analysis. m.p. 161–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.30 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.09 – 7.02 (m, 2H), 4.28 (s, 1H), 2.36 (s, 3H), 2.27 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 197.6, 195.8, 191.6, 170.9, 148.4, 140.4, 136.3, 134.2, 128.8, 128.5, 125.9, 124.0, 119.7, 114.5, 85.2, 62.9, 44.4, 43.0, 29.8, 28.3, 28.0; ESI HRMS: calcd. For $C_{24}H_{25}NO_6Na^+$ 470.1580, found 470.1581.

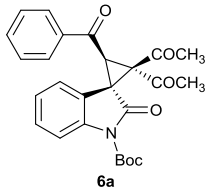
3. General procedure for the synthesis of spirooxindole compounds 6



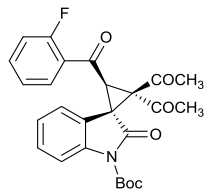
To a solution of Boc-protected tetra-substituted oxindole olefines **2** (0.15 mmol) in CH_2Cl_2 (2.0 mL) was added sulfur ylides **4** (0.165 mmol) at 25 °C. The reaction mixture was stirred until the reaction completed (monitored by TLC). Then the reaction mixture was concentrated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 8:1) to give the compounds **6** which were dried under vacuum and further analyzed by ^{1}H-NMR, ^{13}C-HMR, HRMS, *etc*.



5a was obtained according to the similar procedure. white solid, 45% yield (23.4 mg). The diastereomeric ratio was determined to be 18:1 by crude ^{1}H-NMR analysis. m.p. 165–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.37 (s, 1H), 7.89 (dd, *J* = 8.0, 0.8 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.48 – 7.39 (m, 2H), 7.22 (td, *J* = 7.6, 1.2 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.96 (td, *J* = 7.6, 1.2 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 4.26 (s, 1H), 2.36 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.0, 196.1, 192.0, 173.5, 141.2, 136.5, 134.1, 128.9, 128.7, 128.5, 126.7, 122.5, 121.1, 110.1, 62.5, 43.6, 42.9, 29.8, 28.4; ESI HRMS: calcd. For $C_{21}H_{17}NO_4Na^+$ 370.1055, found 370.1056.

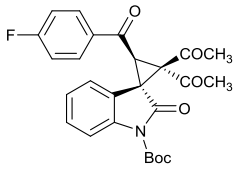


6a was obtained as white solid in 82% yield (55.0 mg). The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis. m.p. 170–171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 (dd, *J* = 8.0, 0.8 Hz , 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.09 – 7.02 (m, 2H), 4.28 (s, 1H), 2.35 (s, 3H), 2.26 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.7, 195.9, 191.7, 170.9, 148.5, 140.5, 136.4, 134.2, 128.9, 128.6, 126.0, 124.1, 119.8, 114.6, 85.3, 63.0, 44.5, 43.1, 29.8, 28.4, 28.1; ESI HRMS: calcd. For $C_{26}H_{25}NO_6Na^+$ 470.1580, found 470.1581.



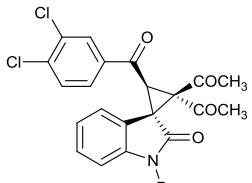
6b

6b was obtained as white solid, 74% yield (51.7 mg). The diastereomeric ratio was determined to be 18:1 by crude ^{1}H-NMR analysis. m.p. 143–144 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.75 (td, *J* = 7.2, 1.8 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.32 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.08 – 7.03 (m, 2H), 6.93 (dd, *J* = 7.8, 1.2 Hz, 1H), 4.17 (d, *J* = 3.0 Hz, 1H), 2.37 (s, 3H), 2.29 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 198.0, 195.9, 190.1 (d, J_{CF} = 3.0 Hz), 170.9, 161.9 (d, J_{CF} = 255.0 Hz), 148.7, 140.7, 135.8 (d, J_{CF} = 9.0 Hz), 130.7 (d, J_{CF} = 1.5 Hz), 128.9, 125.6, 124.8 (d, J_{CF} = 4.5 Hz), 124.0, 119.9, 117.0, 116.9, 114.7, 85.2, 63.2, 48.6 (d, J_{CF} = 7.5 Hz), 43.3 (d, J_{CF} = 3.0 Hz), 29.9, 28.6, 28.2; ESI HRMS: calcd. For $C_{26}H_{24}FNO_6Na^+$ 488.1485, found 488.1487.



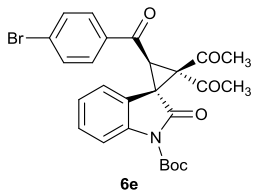
6c

6c was obtained as white solid, 70% yield (48.9mg). The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis. m.p. 145–146 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.96 – 7.93 (m, 2H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.31 (dt, *J* = 9.0, 1.8 Hz, 1H), 7.12 – 7.09 (m, 2H), 7.07 (td, *J* = 7.8, 1.2 Hz, 1H), 7.01 (dd, *J* = 7.8, 1.2 Hz, 1H), 4.22 (s, 1H), 2.35 (s, 3H), 2.26 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 197.7, 195.9, 190.1, 171.0, 166.4 (d, J_{CF} = 255.0 Hz), 148.6, 140.5, 132.9 (d, J_{CF} = 4.5 Hz), 131.4 (d, J_{CF} = 10.5 Hz), 129.1, 126.0, 124.2, 119.7, 116.2 (d, J_{CF} = 22.5 Hz), 114.7, 85.4, 63.1, 44.3, 43.1, 29.9, 28.5, 28.1; ESI HRMS: calcd. For $C_{26}H_{24}FNO_6Na^+$ 488.1485, found 488.1487.



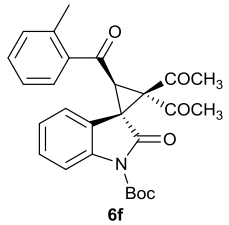
6d

6d was obtained as yellow solid, 63% yield (48.8mg). The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis. m.p. 144–145 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01 (d, *J* = 2.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.75 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.33 (td, *J* = 8.8, 1.6 Hz, 1H), 7.08 (td, *J* = 8.0, 1.2 Hz, 1H), 6.98 (dd. *J* = 8.0, 1.2 Hz, 1H), 4.13 (s, 1H), 2.32 (s, 3H), 2.28 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.5, 195.6, 189.7, 170.7, 148.4, 140.5, 139.0, 135.9, 133.8, 131.0, 130.3, 129.2, 127.5, 125.8, 124.2, 119.4, 114.8, 85.4, 63.3, 43.8, 43.3, 29.8, 28.5, 28.1; ESI HRMS: calcd. For $C_{26}H_{23}Cl_2NO_6Na^+$ 538.0800, found 538.0802.



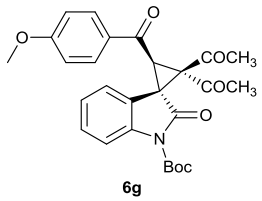
6e

6e was obtained as yellow solid, 75% yield (59.2mg). The diastereomeric ratio was determined to be 18:1 by crude ^{1}H-NMR analysis. m.p. 147–148 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.86 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.29 (m, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 4.20 (s, 1H), 2.35 (s, 3H), 2.27 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 197.7, 195.8, 190.8, 170.9, 148.5, 140.5, 135.2, 132.3, 130.0, 129.1, 125.9, 124.2, 119.6, 114.8, 85.5, 63.1, 44.2, 43.1, 29.9, 28.5, 28.2; ESI HRMS: calcd. For $C_{26}H_{24}BrNO_6Na^+$ 548.0685, found 548.0686.



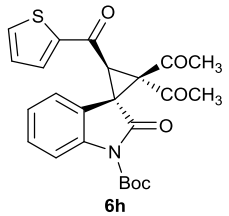
6f

6f was obtained as white solid, 80% yield (55.4mg). The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis. m.p. 142–143 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.88 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.38 (td, *J* = 7.8, 1.2 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.22 (dd, *J* = 15.6, 9.0 Hz, 2H), 7.09 (dd, *J* = 6.0, 2.4 Hz, 2H), 4.12 (s, 1H), 2.42 (s, 3H), 2.36 (s, 3H), 2.25 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 195.9, 194.7, 170.9, 148.5, 140.5, 132.6, 132.1, 129.5, 128.9, 126.2, 126.1, 124.0, 119.8, 114.6, 85.3, 63.2, 47.3, 43.5, 29.8, 28.4, 28.1, 21.2; ESI HRMS: calcd. For $C_{27}H_{27}NO_6Na^+$ 484.1736, found 484.1734.



6g

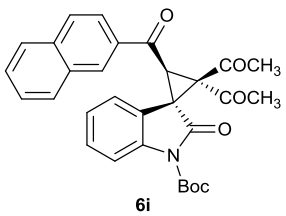
6g was obtained as white solid, 81% yield (58.0mg). The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis. m.p. 145–146 ^{o}C; ^{1}H NMR(400 MHz, $CDCl_3$) δ (ppm) 7.88 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.06 – 7.04 (m, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.25 (s, 1H), 3.83 (s, 3H), 2.36 (s, 3H), 2.25 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.9, 196.0, 189.7, 171.1, 164.5, 148.6, 140.4, 131.1, 129.5, 128.7, 126.1, 124.0, 120.0, 114.5, 114.1, 85.2, 62.8, 55.6, 44.6, 42.8, 29.9, 28.3, 28.1; ESI HRMS: calcd. For $C_{27}H_{27}NO_7H^+$ 500.1685, found 500.1688.



6h

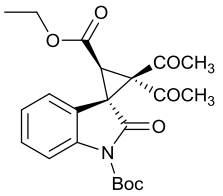
6h was obtained as white solid, 68% yield (46.3mg). The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis. m.p. 137–138 ^{o}C; ^{1}H NMR(600 MHz, $CDCl_3$) δ (ppm) 7.86 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 3.0 Hz, 1H), 7.69 (d, *J* = 4.8 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.14 – 7.10 (m, 3H), 4.15 (s, 1H), 2.35 (s, 3H), 2.25 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 197.5, 195.6, 183.9,

170.9, 148.6, 143.7, 140.6, 135.9, 134.1, 129.0, 128.9, 126.5, 124.2, 119.8, 114.7, 85.4, 62.9, 60.5, 45.0, 43.2, 29.8, 28.1; ESI HRMS: calcd. For $C_{24}H_{23}NO_6SNa^+$ 476.1144, found 476.1145.



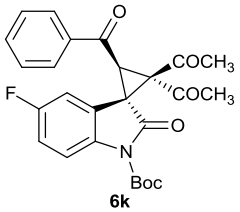
6i

6i was obtained as white solid, 65% yield (48.5 mg). The diastereomeric ratio was determined to be 10:1 by crude ^{1}H-NMR analysis. m.p. 153–154 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.47 (s, 1H), 7.97 – 7.92 (m, 2H), 7.85 – 7.82 (m, 3H), 7.60 – 7.55 (m, 2H), 7.30 – 7.26 (m, 1H), 7.13 – 7.05 (m, 2H), 4.46 (s, 1H), 2.38 (s, 3H), 2.30 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.8, 195.9, 191.4, 171.1, 148.5, 140.5, 135.9, 133.8, 132.3, 130.9, 129.9, 129.3, 128.9, 128.8, 127.8, 127.2, 126.2, 124.1, 123.5, 119.8, 114.6, 85.3, 63.1, 44.6, 43.3, 29.9, 28.4, 28.1; ESI HRMS: calcd. For $C_{30}H_{27}NO_6Na^+$ 520.1736, found 520.1738.



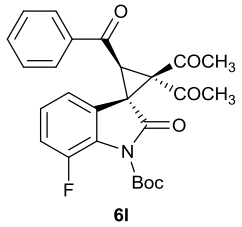
6j

6j was obtained as white solid, 79% yield (49.2mg). The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis. m.p. 149–150 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.91 (d, J = 8.4 Hz, 1H), 7.36 (dt, J = 8.4, 2.4 Hz, 1H), 7.14 – 7.12 (m, 2H), 4.21 – 4.18 (m, 1H), 4.14 – 4.11 (m, 1H), 3.33 (s, 1H), 2.30 (s, 3H), 2.27 (s, 3H), 1.63 (s, 9H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 197.4, 195.5, 170.6, 166.0, 148.6, 140.8, 129.1, 125.9, 124.0, 119.9, 114.8, 85.3, 62.2, 62.1, 41.6, 40.5, 29.6, 28.6, 28.1, 14.13; ESI HRMS: calcd. For $C_{22}H_{25}NO_7Na^+$ 438.1529, found 438.1531.



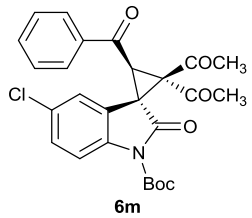
6k

6k was obtained as white solid, 68% yield (47.5mg). The diastereomeric ratio was determined to be 13:1 by crude ^{1}H-NMR analysis. m.p. 172–173 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.92 (dd, J = 8.4, 1.2 Hz, 2H), 7.84 (dd, J = 9.0, 4.8 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.46 (dd, J = 7.8, 1.8 Hz, 2H), 7.00 (td, J = 9.0, 3.0 Hz, 1H), 6.82 (dd, J = 9.6, 3.0 Hz, 1H), 4.30 (s, 1H), 2.35 (s, 3H), 2.26 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 197.4, 195.8, 191.5, 170.7, 159.3 (d, J_{CF} = 240 Hz), 148.5, 136.4 (d, J_{CF} = 36 Hz), 134.5, 129.1, 128.7, 121.7 (d, J_{CF} = 10.5 Hz), 115.7 (d, J_{CF} = 9.0 Hz), 115.6, 114.1, 113.9, 85.6, 63.2, 44.7, 43.0, 29.8, 28.4, 28.1; ESI HRMS: calcd. For $C_{26}H_{24}FNO_6Na^+$ 488.1485, found 488.1483.



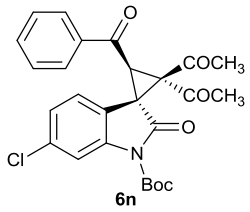
6l

6l was obtained as white solid, 70% yield (48.9mg). The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis. m.p. 157–158 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ(ppm) 7.90 (d, *J* = 7.2 Hz, 2H), 7.60 – 7.58 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.07 – 7.01 (m, 2H), 6.84 (dd, *J* = 7.8, 1.2 Hz, 1H), 4.30 (s, 1H), 2.35 (s, 3H), 2.27 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ(ppm) 197.2, 195.8, 191.5, 170.4, 148.4 (d, J_{CF} = 247.5 Hz), 147.0, 136.3, 134.5, 129.1, 128.7, 127.6 (d, J_{CF} = 10.5 Hz), 124.9 (d, J_{CF} = 7.5 Hz), 122.9 (d, J_{CF} = 3.0 Hz), 122.1 (d, J_{CF} = 3.0 Hz), 117.1 (d, J_{CF} = 21.0 Hz), 86.0, 63.2, 44.5, 43.0, 29.9, 28.4, 27.7; ESI HRMS: calcd. For $C_{26}H_{24}FNO_6Na^+$ 488.1485, found 488.1483.



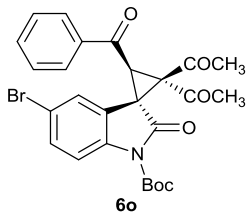
6m

6m was obtained as yellow solid, 72% yield (41.9mg). The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis. m.p. 136–137 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 1.2 Hz, 1H), 7.05 (s, 1H), 4.29 (s, 1H), 2.34 (s, 3H), 2.26 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 197.2, 195.2, 191.3, 170.3, 148.3, 138.9, 136.2, 134.4, 129.7, 128.9, 128.8, 128.6, 126.2, 121.5, 115.6, 85.6, 63.1, 44.6, 42.7, 29.6, 28.3, 28.0; ESI HRMS: calcd. For $C_{26}H_{24}ClNO_6Na^+$ 504.1190, found 504.1189.



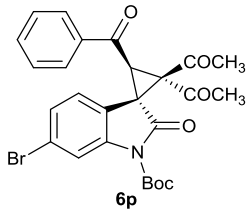
6n

6n was obtained as yellow solid, 79% yield (57.1mg). The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis. m.p. 145–146 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (d, *J* = 2.0 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.05 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 4.28 (s, 1H), 2.34 (s, 3H), 2.25 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.3, 195.8, 191.6, 170.5, 148.3, 141.3, 136.3, 135.0, 134.4, 129.0, 128.6, 127.0, 124.2, 118.2, 115.4, 85.8, 62.9, 44.6, 42.8, 29.8, 28.3, 28.0; ESI HRMS: calcd. For $C_{26}H_{24}ClNO_6Na^+$ 504.1190, found 504.1191.



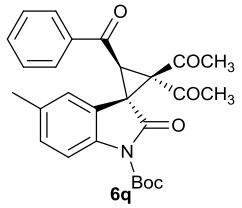
6o

6o was obtained as yellow solid, 80% yield (63.2mg). The diastereomeric ratio was determined to be 15:1 by crude ^{1}H-NMR analysis. m.p. 142–143 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.93 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.446 (t, *J* = 7.8 Hz, 2H), 7.43 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.19 (d, *J* = 1.8 Hz, 1H), 4.28 (s, 1H), 2.34 (s, 3H), 2.26 (s, 3H), 1.63 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 197.2, 195.5, 191.3, 170.1, 148.2, 139.4, 136.2, 134.4, 131.8, 129.0, 128.9, 128.6, 121.8, 117.3, 115.9, 85.6, 63.2, 44.6, 42.6, 29.6, 28.3, 27.9; ESI HRMS: calcd. For $C_{26}H_{24}BrNO_6Na^+$ 548.0685, found 548.0687.



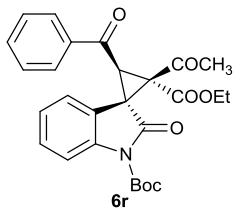
6p

6p was obtained as yellow solid, 81% yield (63.9mg). The diastereomeric ratio was determined to be 9:1 by crude ^{1}H-NMR analysis. m.p. 149–150 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 (d, *J* = 0.8 Hz, 1H), 7.90 (d, *J* = 4.8 Hz, 2H), 7.61 – 7.58 (m, 1H), 7.45 (t, *J* = 5.2 Hz, 2H), 7.20 (dd, *J* = 5.6, 0.8 Hz, 1H), 6.90 (d, *J* = 5.6 Hz, 1H), 4.29 (s, 1H), 2.34 (s, 3H), 2.25 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.3, 195.9, 191.6, 170.5, 148.3, 141.4, 136.3, 134.5, 129.1, 128.7, 127.3, 127.2, 123.1, 118.8, 118.3, 85.9, 63.0, 44.6, 29.9, 28.4, 28.1, 28.0; ESI HRMS: calcd. For $C_{26}H_{24}BrNO_6Na^+$ 548.0685, found 548.0683.



6q

6q was obtained as white solid, 85% yield (58.8mg). The diastereomeric ratio was determined to be 15:1 by crude ^{1}H-NMR analysis. m.p. 168–169 ^{o}C; ^{1}H NMR(400 MHz, $CDCl_3$) δ (ppm) 7.90 (d, *J* = 7.2 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.10 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.84 (s, 1H), 4.25 (s, 1H), 2.35 (s, 3H), 2.29 (s, 3H), 2.26 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.8, 195.9, 191.7, 171.1, 148.6, 138.2, 136.5, 134.2, 133.7, 129.5, 128.9, 128.6, 126.5, 119.7, 114.4, 85.1, 63.0, 44.5, 43.2, 29.8, 28.4, 28.1, 21.0; ESI HRMS: calcd. For $C_{27}H_{27}NO_6Na^+$ 484.1736, found 484.1740.

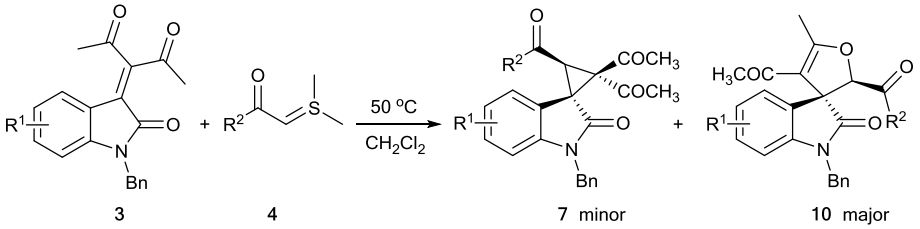


6r

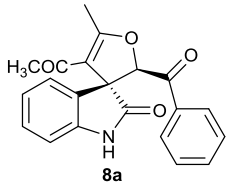
6r was obtained as white solid, 90% yield (64.5mg). The diastereomeric ratio was determined to be 18:1 by crude ^{1}H-NMR analysis. m.p. 147–148 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ(ppm) 8.10 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.47 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.34 – 7.31 (m, 1H), 7.08 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.01 (dd, *J* = 7.8, 1.2 Hz, 1H), 4.43 – 4.39 (m, 1H),

4.32 – 4.29 (m, 1H), 4.10 (s, 1H), 2.29 (s, 3H), 1.65 (s, 9H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 195.3, 191.0, 170.8, 165.5, 148.7, 140.7, 136.6, 133.9, 129.1, 128.9, 128.5, 125.7, 124.1, 119.7, 114.8, 85.0, 63.2, 56.7, 42.1, 42.0, 29.7, 28.2, 14.1; ESI HRMS: calcd. For $C_{27}H_{27}NO_7Na^+$ 500.1685, found 500.1687.

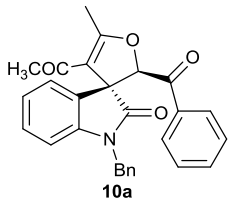
4. General procedure for the synthesis of spirooxindole compounds 10



To a solution of Bn-protected tetra-substituted oxindole olefines **3** (0.15 mmol) in CH_2Cl_2 (2.0 mL) was added sulfur ylides **4** (0.165 mmol) at 50 °C. The reaction mixture was stirred until the reaction completed (monitored by TLC). Then the reaction mixture was concentrated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to give the compounds **10** which were dried under vacuum and further analyzed by ^{1}H-NMR, ^{13}C-HMR, HRMS, *etc*.

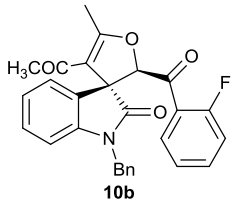


8a was obtained according to the similar procedure. white solid, 48% yield (25.0 mg). The diastereomeric ratio was determined to be 10:1 by crude ^{1}H-NMR analysis. m.p. 164–165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84 (s, 1H), 7.43 – 7.38 (m, 1H), 7.35 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.22 (td, *J* = 7.6, 1.6 Hz, 2H), 6.99 – 6.95 (m, 1H), 6.91 – 6.86 (m, 2H), 6.40 (d, *J* = 7.6 Hz, 1H), 6.27 (s, 1H), 2.55 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.8, 191.3, 178.8, 170.2, 139.9, 134.8, 133.6, 129.0, 128.4, 127.5, 127.4, 124.9, 122.8, 118.3, 109.3, 88.8, 62.2, 28.9, 15.8; ESI HRMS: calcd. For $C_{21}H_{17}NO_4Na^+$ 370.1055, found 370.1054.



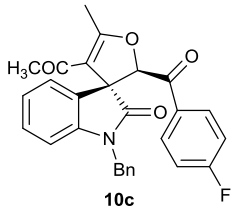
10a was obtained as white solid in 74% yield (48.6 mg). The diastereomeric ratio was determined to be 10:1 by crude ^{1}H-NMR analysis. m.p. 168–169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 4.4 Hz, 4H), 7.25 (d, *J* = 4.8 Hz, 3H), 7.16 (t, *J* = 7.6 Hz, 2H), 6.93 – 6.89 (m, 2H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.30 (s, 1H), 6.17 (d, *J* = 7.6 Hz, 1H), 5.08 (d, *J* = 15.6 Hz, 1H),

4.20 (d, J = 16.0 Hz, 1H), 2.56 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.9, 191.0, 177.3, 169.9, 142.2, 135.3, 135.0, 133.4, 128.9, 128.7, 128.3, 127.5, 127.3, 126.9, 124.7, 122.8, 118.4, 108.8, 89.0, 62.0, 44.6, 29.0, 15.9; ESI HRMS: calcd. For $C_{28}H_{23}NO_4Na^+$ 460.1525, found 460.1526.



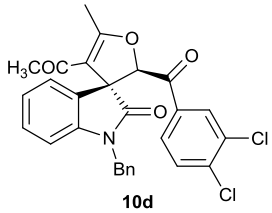
10b

10b was obtained as white solid, 66% yield (45.1 mg). The diastereomeric ratio was determined to be 16:1 by crude ^{1}H-NMR analysis. m.p. 154–155 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.35 – 7.31 (m, 4H), 7.31 – 7.24 (m, 3H), 6.95 (tt, J = 7.2, 1.8 Hz, 2H), 6.90 (t, J = 6.6 Hz, 2H), 6.86 (t, J = 7.8 Hz, 1H), 6.83 – 6.79 (m, 1H), 6.26 (s, 1H), 5.02 (d, J = 15.6 Hz, 1H), 4.33 (d, J = 15.6 Hz, 1H), 2.55 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 191.3 (d, J_{CF} = 4.5 Hz), 191.0, 177.1, 169.9, 160.4 (d, J_{CF} = 253.5 Hz), 142.8, 135.5, 134.7 (d, J_{CF} = 9.0 Hz), 130.3 (d, J_{CF} = 3.0 Hz), 129.0, 128.8, 127.6, 127.5, 127.1, 124.6, 124.3 (d, J_{CF} = 3.0 Hz), 122.8, 115.9, 115.8, 108.9, 90.9 (d, J_{CF} = 4.5 Hz), 61.6, 44.6, 29.1, 15.9; ESI HRMS: calcd. For $C_{28}H_{22}FNO_4Na^+$ 478.1431, found 478.1430.



10c

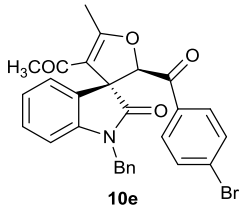
10c was obtained as white solid, 68% yield (46.5mg). The diastereomeric ratio was determined to be 16:1 by crude ^{1}H-NMR analysis. m.p. 151–152 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.33 - 7.32 (m, 4H), 7.31 – 7.28 (m, 3H), 6.94 (td, J = 7.8, 1.2 Hz, 1H), 6.91 (dd, J = 7.2, 1.2 Hz, 1H), 6.86 (td, J = 7.2, 0.6 Hz, 1H), 6.81 – 6.76 (m, 2H), 6.28 (d, J = 7.8 Hz, 1H), 6.25 (s, 1H), 5.04 (d, J = 15.6 Hz, 1H), 4.38 (d, J = 15.6 Hz, 1H), 2.56 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 191.4, 191.0, 177.3, 169.9, 165.8 (d, J_{CF} = 255.0 Hz), 142.3, 135.3, 131.4 (d, J_{CF} = 3.0 Hz), 130.2 (d, J_{CF} = 9.0 Hz), 129.1, 128.9, 127.7, 127.5, 126.9, 124.8, 122.9, 118.6, 115.6 (d, J_{CF} = 22.5 Hz), 108.9, 88.7, 62.1, 44.7, 29.1, 15.9; ESI HRMS: calcd. For $C_{28}H_{22}FNO_4Na^+$ 478.1431, found 478.1429.



10d

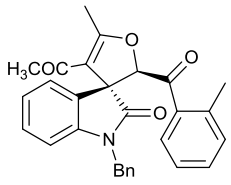
10d was obtained as yellow solid, 71% yield (53.9 mg). The diastereomeric ratio was determined to be 8:1 by crude ^{1}H-NMR analysis. m.p. 196–197 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.37 – 7.34 (m , 3H), 7.33 (d, J = 1.8 Hz, 2H), 7.28 (dt, J = 6.0, 1.2 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 7.08 (dd, J = 8.4, 1.8 Hz, 1H), 6.98 (dt, J = 9.0, 4.8 Hz, 1H), 6.88 (d, J = 4.2 Hz, 2H),

6.31 (d, *J* = 7.8 Hz, 1H), 6.18 (s, 1H), 5.12 (d, *J* = 15.6 Hz, 1H), 4.36 (d, *J* = 15.6 Hz, 1H), 2.55 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 191.0, 190.9, 177.1, 169.7, 142.3, 138.2, 135.2, 134.4, 133.3, 130.4, 129.5, 129.3, 128.9, 127.8, 127.5, 126.7, 126.3, 124.7, 123.0, 118.5, 109.0, 88.8, 62.0, 44.8, 29.1, 15.9; ESI HRMS: calcd. For $C_{28}H_{21}Cl_2NO_4Na^+$ 528.0745, found 528.0748.



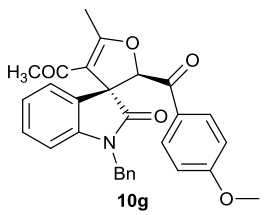
10e

10e was obtained as white solid, 75% yield (58.1mg). The diastereomeric ratio was determined to be 10:1 by crude ^{1}H-NMR analysis. m.p. 152–153 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35 – 7.31 (m, 4H), 7.25 (t, *J* = 4.0 Hz, 3H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.96 (td, *J* = 7.6, 2.0Hz, 1H), 6.90 (dd, *J* = 7.2, 1.6 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.30 (d, *J* = 8.0 Hz, 1H), 6.23 (s, 1H), 5.00 (d, *J* = 15.6 Hz, 1H), 4.41 (d, *J* = 15.6 Hz, 1H), 2.55 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 191.9, 190.9, 177.2, 169.7, 142.3, 135.2, 133.6, 131.6, 129.1, 128.9, 128.8, 128.7, 127.7, 127.5, 127.4, 126.8, 124.7, 122.8, 118.5, 108.9, 88.7, 61.9, 44.8, 29.0, 15.8; ESI HRMS: calcd. For $C_{28}H_{22}BrNO_4Na^+$ 538.0630, found 538.0632.



10f

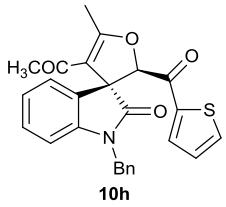
10f was obtained as white solid, 78% yield (52.8mg). The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis. m.p. 178–179 ^{o}C; ^{1}H NMR (600 MHz,) δ(ppm) 7.31 (td, *J* = 7.8, 1.2 Hz, 1H), 7.28 – 7.26 (m, 3H), 7.22 (t, *J* = 6.0 Hz, 3H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.01 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.97 (td, *J* = 7.2, 2.4 Hz, 2H), 6.89 (td, *J* = 7.8, 0.6 Hz, 1H), 6.30 (s, 1H), 6.20 (d, *J* = 7.8 Hz, 1H), 4.97 (d, *J* = 16.2 Hz, 1H), 4.02 (d, *J* = 16.2 Hz, 1H), 2.56 (s, 3H), 2.13 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 194.3, 190.9, 176.9, 169.6, 142.3, 140.1, 140.0, 135.2, 133.9, 132.3, 131.7, 129.1, 128.7, 128.5, 127.4, 127.0, 125.1, 124.5, 122.8, 118.9, 109.1, 89.4, 61.8, 44.5, 28.9, 20.0, 15.8; ESI HRMS: calcd. For $C_{29}H_{25}NO_4Na^+$ 474.1681, found 474.1683.



10g

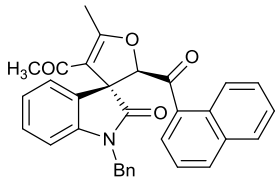
10g was obtained as white solid, 81% yield (56.8mg). The diastereomeric ratio was determined to be 18:1 by crude ^{1}H-NMR analysis. m.p. 188–189 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.33 (t, *J* = 3.0 Hz, 1H), 7.31 (t, *J* = 1.8 Hz, 1H), 7.29 – 7.28 (m, 4H), 7.26 – 7.24 (m, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.92 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.85 (td, *J* = 7.2, 0.6 Hz, 1H), 6.63 (dt, *J* = 9.6, 3.0 Hz, 2H), 6.26 (d, *J* = 7.2 Hz, 2H), 5.03 (d, *J* = 15.6 Hz, 1H), 4.46 (d, *J* = 16.2 Hz, 1H), 3.78 (s, 3H),

2.55 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 191.1, 191.0, 177.5, 170.1, 163.9, 142.3, 135.5, 130.0, 128.9, 128.8, 128.0, 127.5, 127.4, 127.0, 124.9, 122.8, 118.6, 113.7, 108.8, 88.5, 62.2, 55.6, 44.7, 29.1, 16.0; ESI HRMS: calcd. For $C_{29}H_{25}NO_5Na^+$ 490.1630, found 490.1631.



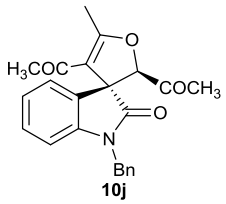
10h

10h was obtained as white solid, 60% yield (39.9 mg). The diastereomeric ratio was determined to be 5:1 by crude ^{1}H-NMR analysis. m.p. 172–173 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.51 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.36 (dd, *J* = 4.2, 1.2 Hz, 3H), 7.34 – 7.31 (m, 2H), 7.28 (dd, *J* = 6.6, 1.2 Hz, 1H), 6.98 (td, *J* = 7.8, 1.2 Hz, 1H), 6.95 (dd, *J* = 7.2, 0.6 Hz, 1H), 6.88 (dd, *J* = 7.2, 0.6 Hz, 1H), 6.83 – 6.82 (m, 1H), 6.40 (d, *J* = 7.8 Hz, 1H), 6.08 (s, 1H), 5.06 (d, *J* = 15.6 Hz, 1H), 4.64 (d, *J* = 15.6 Hz, 1H), 2.56 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 191.2, 184.9, 177.5, 169.9, 142.4, 140.9, 135.5, 135.4, 132.2, 129.1, 128.9, 128.8, 127.9, 127.7, 127.5, 124.8, 123.0, 118.6, 108.9, 89.2, 62.6, 44.7, 29.1, 15.9; ESI HRMS: calcd. For $C_{26}H_{21}NO_4SNa^+$ 466.1089, found 466.1090.



10i

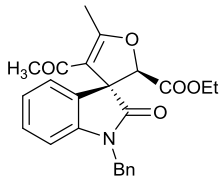
10i was obtained as white solid, 62% yield (45.3 mg). The diastereomeric ratio was determined to be 5:1 by crude ^{1}H-NMR analysis. m.p. 170–171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.90 – 7.86 (m, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.53 (m, 3H), 7.27 (d, *J* = 7.2 Hz, 2H), 7.09 – 7.08 (m, 4H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.87 – 6.83 (m, 2H), 6.48 (s, 1H), 5.95 (d, *J* = 7.2 Hz, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 3.76 (d, *J* = 16.0 Hz, 1H), 2.59 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 192.7, 190.9, 177.3, 169.9, 142.0, 135.4, 134.9, 132.3, 131.8, 129.5, 129.1, 128.9, 128.8, 128.5, 128.3, 127.7, 127.3, 127.0, 126.9, 124.7, 123.0, 122.7, 118.4, 108.8, 89.0, 62.1, 44.4, 29.7, 29.0, 15.9; ESI HRMS: calcd. For $C_{32}H_{25}NO_4Na^+$ 510.1681, found 510.1682.



10j

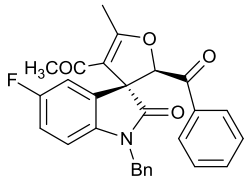
10j was obtained as white solid, 74% yield (41.7 mg). The diastereomeric ratio was determined to be 6:1 by crude ^{1}H-NMR analysis. m.p. 145–146 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.48 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 3H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.15 (dt, *J* = 3.0, 1.2 Hz, 1H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 5.38 (s, 1H), 5.10 (d, *J* = 16.2 Hz, 1H), 4.99 (d, *J* = 15.6 Hz, 1H), 2.50 (s, 3H), 2.12 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 201.4, 191.1, 176.9, 169.3, 142.6, 135.5, 129.4, 128.8, 127.7, 127.4, 123.5, 122.9, 109.6, 91.7, 61.2, 44.7, 28.9,

27.3, 15.7; ESI HRMS: calcd. For $C_{23}H_{21}NO_4Na^+$ 398.1368, found 398.1368.



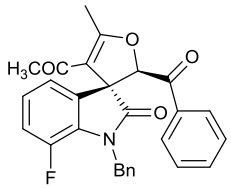
10k

10k was obtained as white solid, 76% yield (46.2 mg). The diastereomeric ratio was determined to be 5:1 by crude ^{1}H-NMR analysis. m.p. 168–169 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.44 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.14 (td, *J* = 7.8, 1.2 Hz, 1H), 7.02 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.93 (td, *J* = 7.8, 0.6 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 5.43 (s, 1H), 5.17 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 4.20 (m, 1H), 3.72 (m, 1H), 2.50 (s, 3H), 2.13 (s, 3H), 0.50 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 191.2, 176.9, 169.5, 166.1, 143.0, 135.8, 128.3, 128.8, 128.0, 127.7, 123.7, 122.7, 109.2, 85.7, 61.5, 44.6, 34.4, 31.8, 29.0, 15.8, 13.3; ESI HRMS: calcd. For $C_{24}H_{23}NO_5Na^+$ 428.1474, found 428.1476.



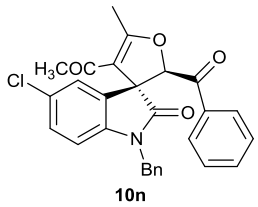
10l

10l was obtained as white solid, 70% yield (47.8mg). The diastereomeric ratio was determined to be 10:1 by crude ^{1}H-NMR analysis. m.p. 158–159 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.46 (tt, *J* = 7.8, 1.2 Hz, 1H), 7.33 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.31 – 7.28 (m, 4H), 7.20 (td, *J* = 7.8, 1.8 Hz, 2H), 6.69 (dd, *J* = 7.8, 2.4 Hz, 1H), 6.60 (td, *J* = 8.4, 2.4 Hz, 1H), 6.31 (s, 1H), 6.07 (dd, *J* = 8.4, 4.2 Hz, 1H), 5.30 (s, 1H), 5.10 (d, *J* = 16.2 Hz, 1H), 4.18 (d, *J* = 16.2 Hz, 1H), 2.57 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 192.6, 190.9, 177.2, 159.2(d, J_{CF} = 241.5 Hz), 138.3, 135.0, 134.9, 128.9, 128.5, 127.7, 127.6, 127.2, 118.6, 115.3 (d, J_{CF} = 24.0 Hz), 112.7 (d, J_{CF} = 24.0 Hz), 109.4 (d, J_{CF} = 9.0 Hz), 88.8, 62.4, 44.8, 29.1, 15.9; ESI HRMS: calcd. For $C_{28}H_{22}FNO_4Na^+$ 478.1431, found 478.1429.



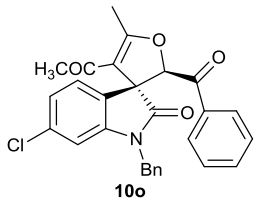
10m

10m was obtained as white solid, 56% yield (38.2mg). The diastereomeric ratio was determined to be 16:1 by crude ^{1}H-NMR analysis. m.p. 160–161 ^{o}C; ^{1}H NMR (600 MHz,$CDCl_3$) δ (ppm) 7.43 (tt, *J* = 7.8, 1.2 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.32 (td, *J* = 7.2, 1.8 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.23 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 2H), 6.82 – 6.79 (m, 1H), 6.72 – 6.68 (m, 2H), 6.27 (s, 1H), 5.09 (d, *J* = 15.6 Hz, 1H), 4.48 (d, *J* = 15.0 Hz, 1H), 2.56 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 192.7, 191.0, 177.1, 170.1, 146.9 (d, J_{CF} = 244.9 Hz), 136.6, 134.8, 133.8, 128.6, 128.4, 127.6 (d, J_{CF} = 2.0 Hz), 127.4, 123.5, 123.4, 120.7, 120.6, 118.6, 117.2, 117.0, 89.0, 62.2, 46.1, 29.1, 15.9; ESI HRMS: calcd. For $C_{28}H_{22}FNO_4Na^+$ 478.1431, found 478.1432.



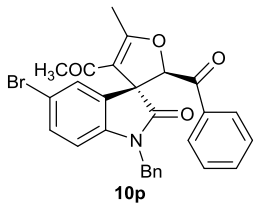
10n

10n was obtained as white solid, 66% yield (46.7mg). The diastereomeric ratio was determined to be 5:1 by crude ^{1}H-NMR analysis. m.p. 159–160 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.46 (t, *J* = 7.8 Hz, 1H), 7.31 (dd, *J* = 7.8, 1.2 Hz, 3H), 7.28 (d, *J* = 5.4 Hz, 3H), 7.24 (dd, J = 6.6, 5.4 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 1.8 Hz, 1H), 6.87 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.29 (s, 1H), 6.06 (d, *J* = 8.4 Hz, 1H), 5.08 (d, *J* = 16.2 Hz, 1H), 4.18 (d, *J* = 16.2 Hz, 1H), 2.57 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 192.7, 191.0, 177.1, 170.1, 147.7, 146.1, 136.6, 134.8, 133.8, 128.6, 128.4, 127.7, 127.6, 127.5, 127.4, 123.5, 123.4, 120.6, 118.6, 117.2, 117.0, 89.0, 62.2, 46.1, 29.0, 15.9; ESI HRMS: calcd. For $C_{28}H_{22}ClNO_4Na^+$ 494.1135, found 494.1133.



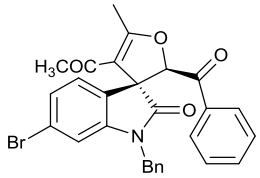
10o

10o was obtained as yellow solid, 67% yield (47.4 mg). The diastereomeric ratio was determined to be 15:1 by crude ^{1}H-NMR analysis. m.p. 164–165 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.47 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.33 – 7.31 (m, 2H), 7.31 – 7.28 (m, 5H), 7.21 (td, *J* = 8.4, 1.8 Hz, 2H), 6.84 (d, *J* = 1.8 Hz, 2H), 6.28 (s, 1H), 6.16 (s, 1H), 5.05 (d, *J* = 15.6 Hz, 1H), 4.18 (d, *J* = 16.2 Hz, 1H), 2.56 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.7, 190.9, 177.4, 170.0, 143.5, 134.9, 134.7, 133.8, 129.0, 128.5, 128.9, 127.8, 127.5, 125.6, 125.5, 122.7, 118.6, 109.4, 88.8, 61.8, 44.7, 29.1, 15.9; ESI HRMS: calcd. For $C_{28}H_{22}ClNO_4Na^+$ 494.1135, found 494.1136.



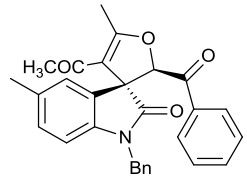
10p

10p was obtained as white solid, 70% yield (54.2 mg). The diastereomeric ratio was determined to be 13:1 by crude ^{1}H-NMR analysis. m.p. 200–201 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.46 (td, *J* = 7.2, 0.6 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 3H), 7.29 – 7.27 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 2H), 7.04 (d, *J* = 1.8 Hz, 1H), 7.02 (dt, *J* = 8.4, 2.4 Hz, 1H), 6.29 (s, 1H), 6.02 (dd, *J* = 7.8, 0.6 Hz, 1H), 5.08 (d, *J* = 15.6 Hz, 1H), 4.18 (d, *J* = 16.2 Hz, 1H), 2.57 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 192.6, 190.9, 176.9, 170.1, 141.4, 135.0, 134.8, 133.7, 131.8, 128.2, 128.9, 128.5, 127.7, 127.7, 127.6, 127.2, 118.6, 115.4, 110.3, 88.8, 62.0, 44.7, 29.1, 16.0; ESI HRMS: calcd. For $C_{28}H_{22}BrNO_4Na^+$ 538.0630, found 538.0632.



10q

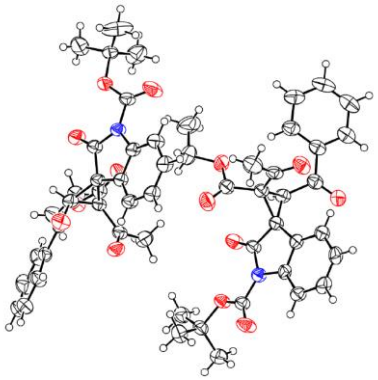
10q was obtained as yellow solid, 69% yield (54.5 mg). The diastereomeric ratio was determined to be 10:1 by crude ^{1}H-NMR analysis. m.p. 184–185 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.47 (tt, *J* = 7.8, 1.2 Hz, 1H), 7.32 – 7.31 (m, 2H), 7.30 – 7.26 (m, 5H), 7.21 (td, *J* = 7.2, 1.2 Hz, 2H), 7.00 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.31 (d, *J* = 1.8 Hz, 1H), 6.28 (s, 1H), 5.05 (d, *J* = 15.6 Hz, 1H), 4.18 (d, *J* = 16.2 Hz, 1H), 2.55 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 192.7, 190.9, 177.3, 170.0, 143.6, 134.8, 134.7, 133.8, 128.9, 128.5, 127.8, 127.5, 127.2, 126.1, 125.9, 125.7, 122.6, 118.5, 112.1, 88.7, 61.8, 44.7, 29.1, 15.9; ESI HRMS: calcd. For $C_{28}H_{22}BrNO_4Na^+$ 538.0630, found 538.0633.



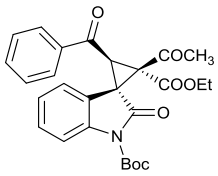
10r

10r was obtained as white solid, 80% yield (54.1 mg). The diastereomeric ratio was determined to be 18:1 by crude ^{1}H-NMR analysis. m.p. 162–163 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 4.4 Hz, 4H), 7.25 (d, *J* = 7.2 Hz, 3H), 7.16 (t, *J* = 7.6 Hz, 2H), 6.74 (s, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.29 (s, 1H), 6.05 (d, *J* = 8.0 Hz, 1H), 5.06 (d, *J* = 16.0 Hz, 1H), 4.16 (d, *J* = 16.0 Hz, 1H), 2.56 (s, 3H), 2.18 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.0, 191.1, 177.1, 169.9, 139.8, 135.4, 135.1, 133.3, 132.3, 129.2, 128.7, 128.5, 128.4, 128.3, 127.5, 127.4, 127.3, 126.9, 125.4, 118.4, 108.5, 89.1, 62.0, 44.6, 29.0, 20.9, 15.9; ESI HRMS: calcd. For $C_{29}H_{25}NO_4Na^+$ 474.1681, found 474.1683.

5. Crystal data of 6r and 10a

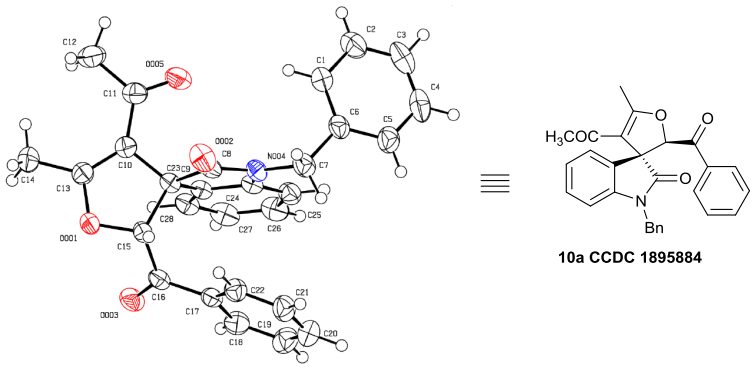


≡



6r CCDC 1895883

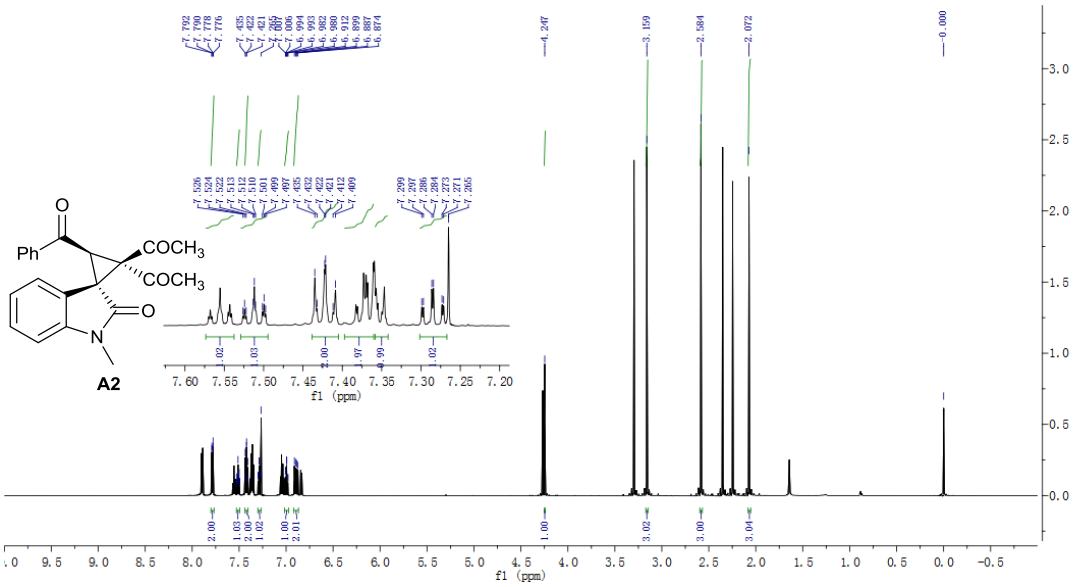
Identification code	ljl-kjw-2-230k
Empirical formula	$C_{27}H_{27}NO_7$
Formula weight	477.49
Temperature/K	230
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	21.1261(6)
b/Å	24.8124(6)
c/Å	9.1976(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4821.3(2)
Z	8
ρ_{calc}g/cm^3	1.316
μ/mm^{-1}	0.788
F(000)	2016.0
Crystal size/mm^3	0.65 × 0.5 × 0.25
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.258 to 145.272
Index ranges	-25 ≤ h ≤ 19, -30 ≤ k ≤ 26, -5 ≤ l ≤ 11
Reflections collected	14596
Independent reflections	6174 [R_{int} = 0.0336, R_{sigma} = 0.0337]
Data/restraints/parameters	6174/1/641
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0568, wR_2 = 0.1589
Final R indexes [all data]	R_1 = 0.0612, wR_2 = 0.1641
Largest diff. peak/hole / e Å^{-3}	0.26/-0.32
Flack parameter	0.29(17)



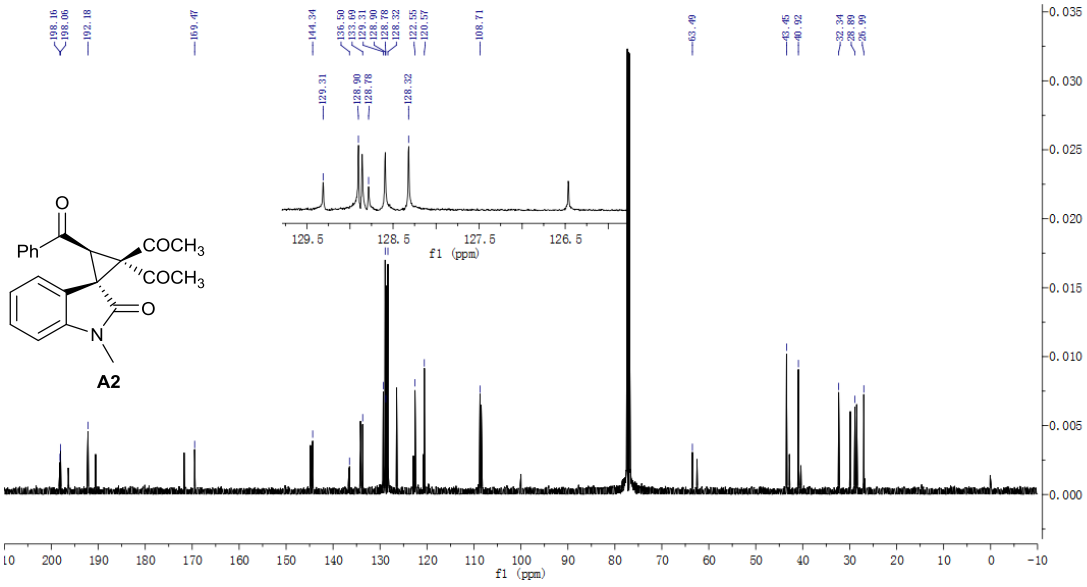
10a CCDC 1895884

Identification code	ljl-kjw-1-230k
Empirical formula	$C_{28}H_{23}NO_4$
Formula weight	437.47
Temperature/K	230
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.0593(3)
b/Å	14.8180(5)
c/Å	14.6664(6)
α/°	90
β/°	97.286(3)
γ/°	90
Volume/Å^3	2168.50(14)
Z	4
ρ_{calc}g/cm^3	1.340
μ/mm^{-1}	0.723
F(000)	920.0
Crystal size/mm^3	0.6 × 0.5 × 0.4
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.094 to 144.7
Index ranges	$-10 \le h \le 12$, $-17 \le k \le 17$, $-18 \le l \le 16$
Reflections collected	11047
Independent reflections	4203 [R_{int} = 0.0224, R_{sigma} = 0.0215]
Data/restraints/parameters	4203/0/300
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0544, wR_2 = 0.1494
Final R indexes [all data]	R_1 = 0.0585, wR_2 = 0.1536
Largest diff. peak/hole / e Å^{-3}	0.23/-0.37

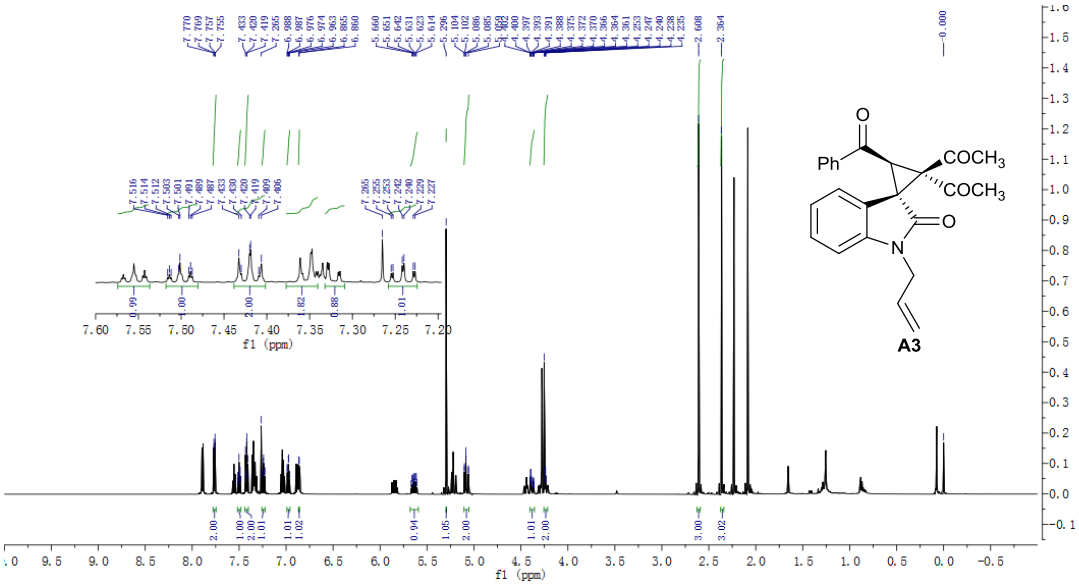
6. NMR spectra and HPLC chromatograms



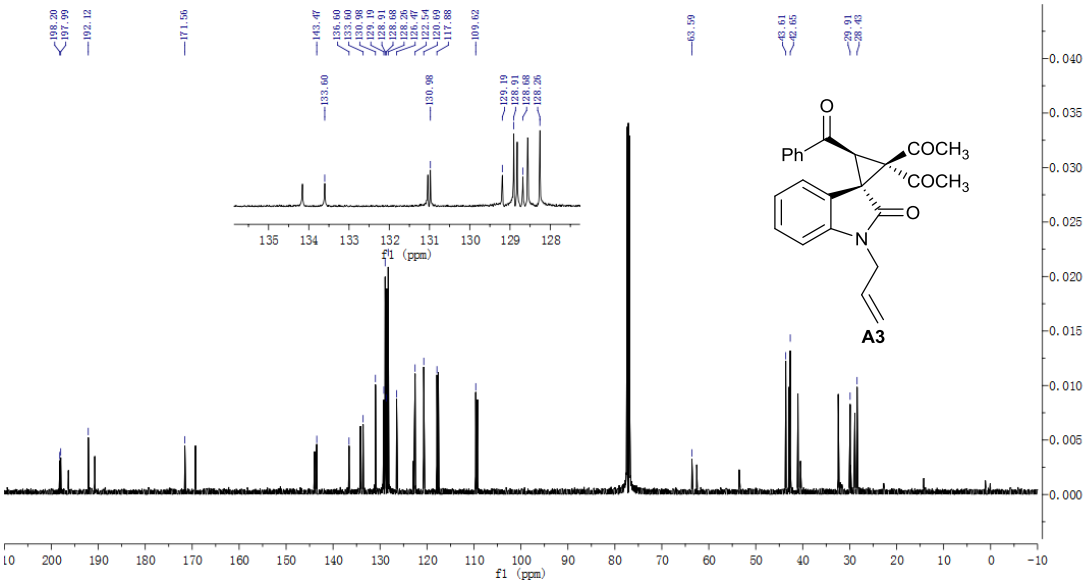
^{1}H spectrum of **A2** in $CDCl_3$ (d.r. = 1:1)



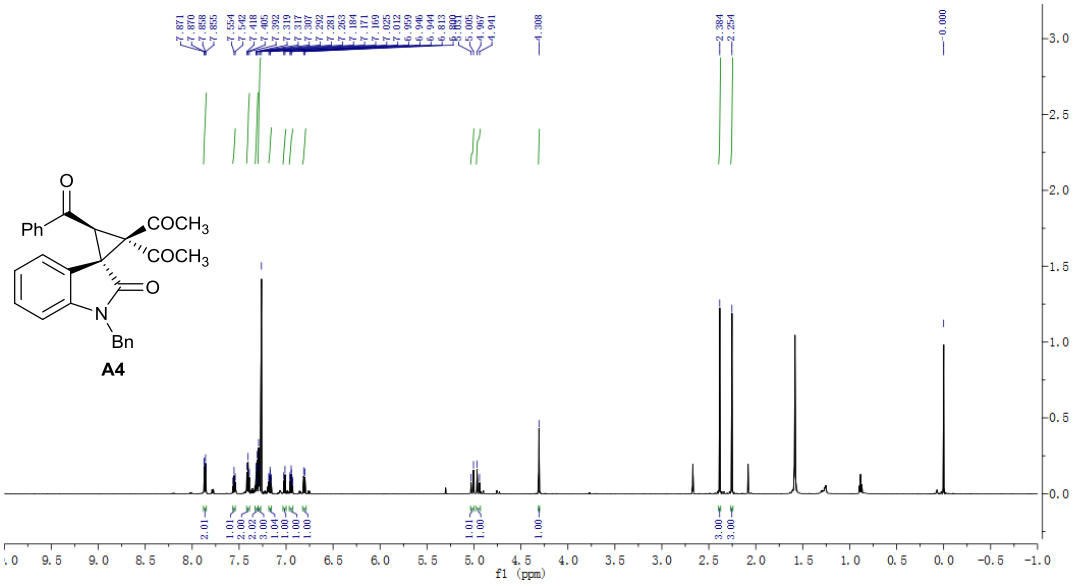
^{13}C spectrum of **A2** in $CDCl_3$



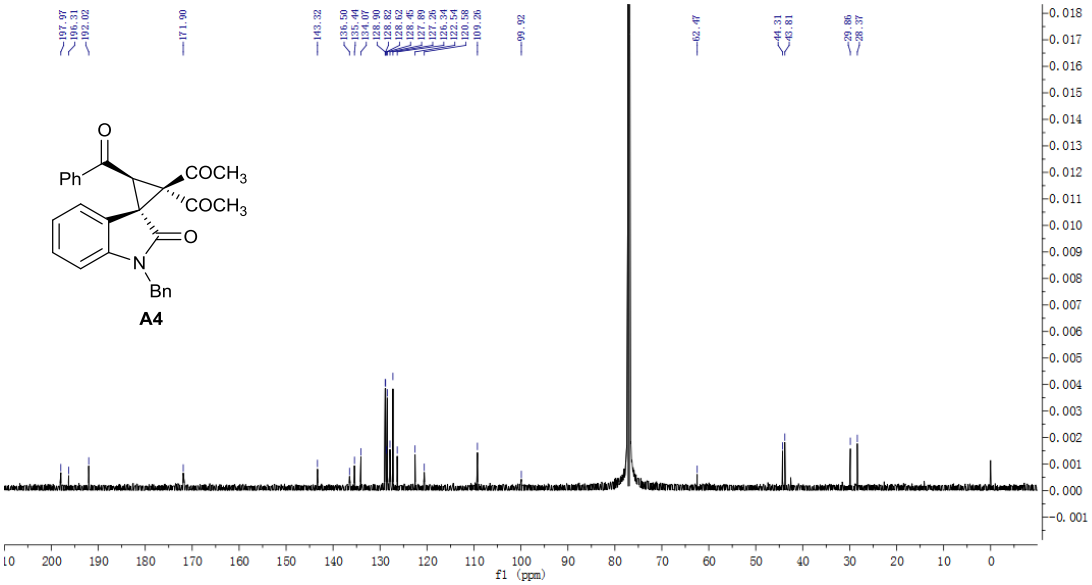
^{1}H spectrum of **A3** in $CDCl_3$ (d.r. =1:1)



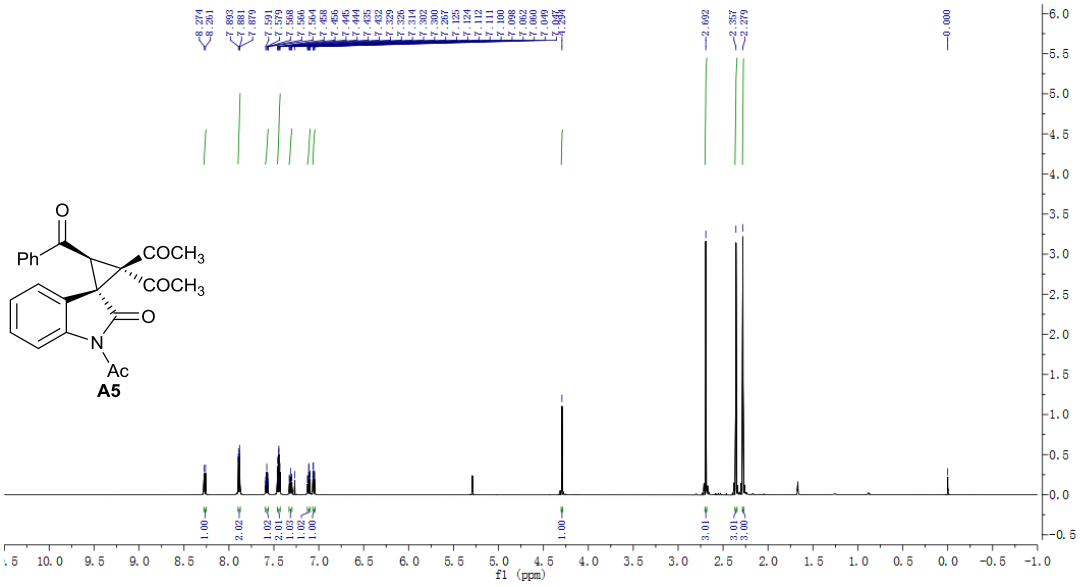
^{13}C spectrum of **A3** in $CDCl_3$



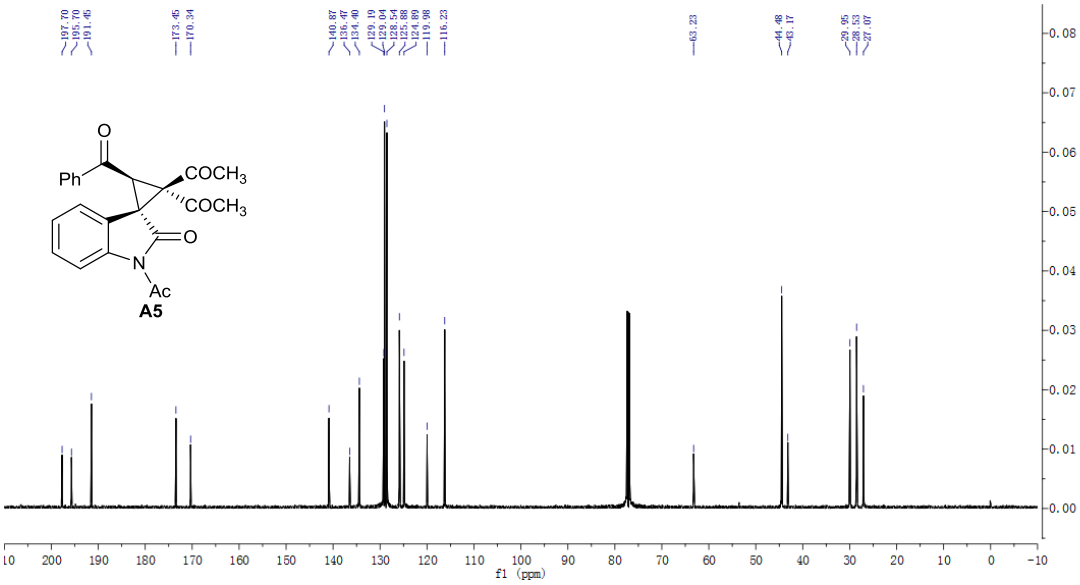
^{1}H spectrum of **A4** in $CDCl_3$ (d.r. =7:1)



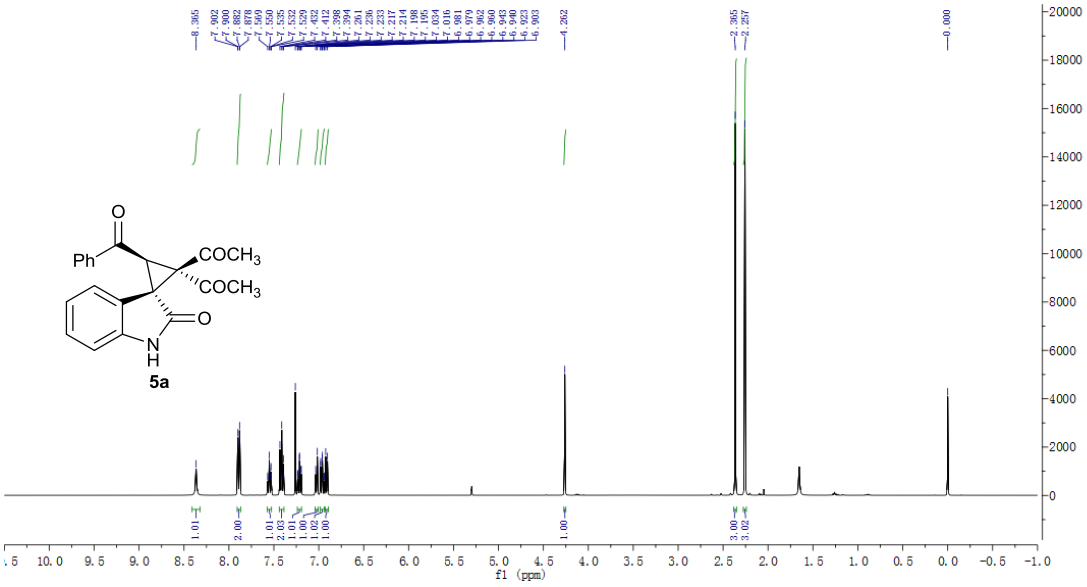
^{13}C spectrum of **A4** in $CDCl_3$



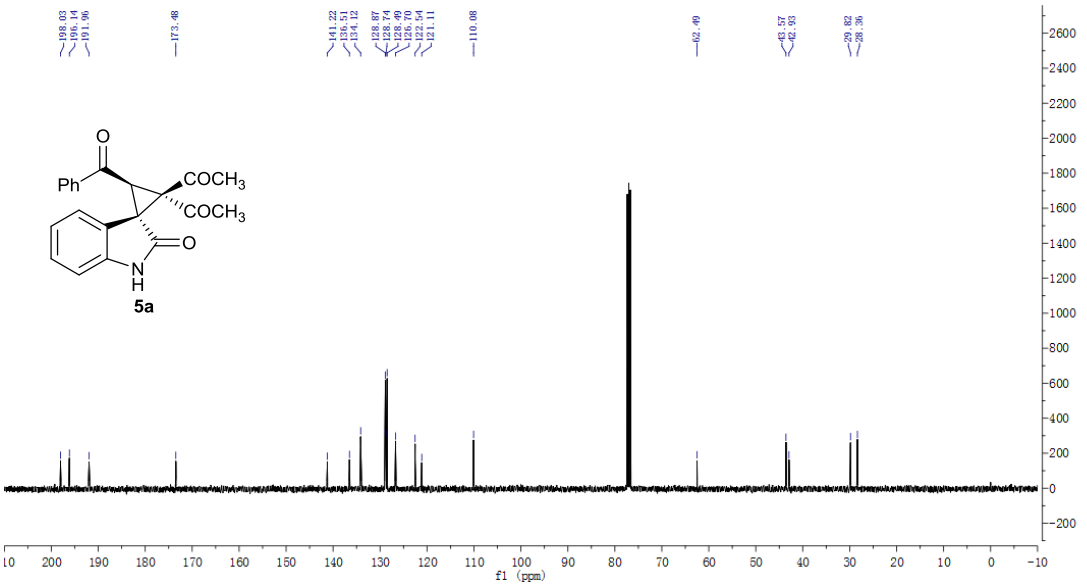
^{1}H spectrum of **A5** in $CDCl_3$ (d.r. =20:1)



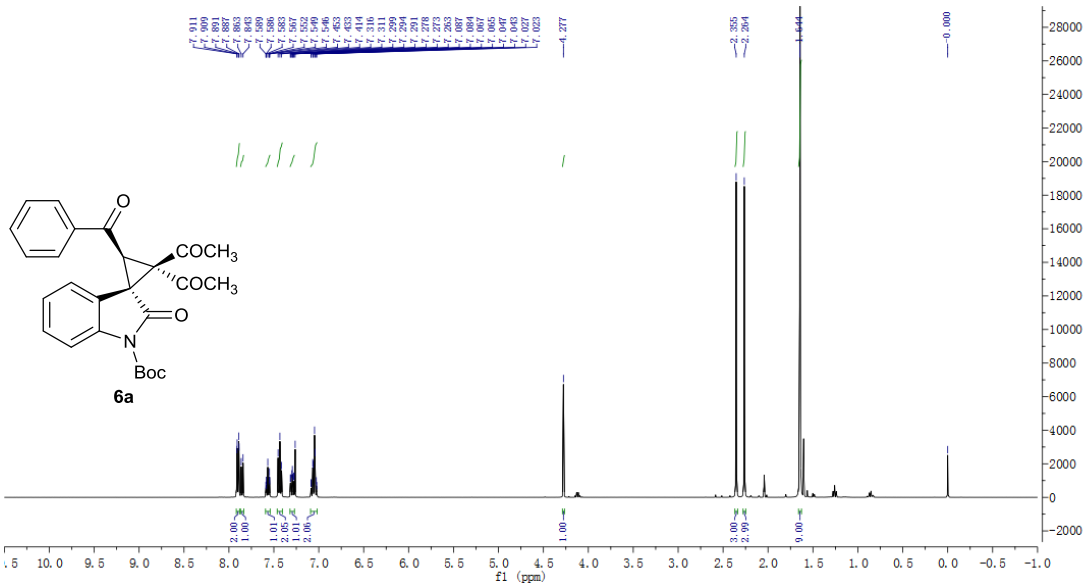
^{13}C spectrum of **A5** in $CDCl_3$



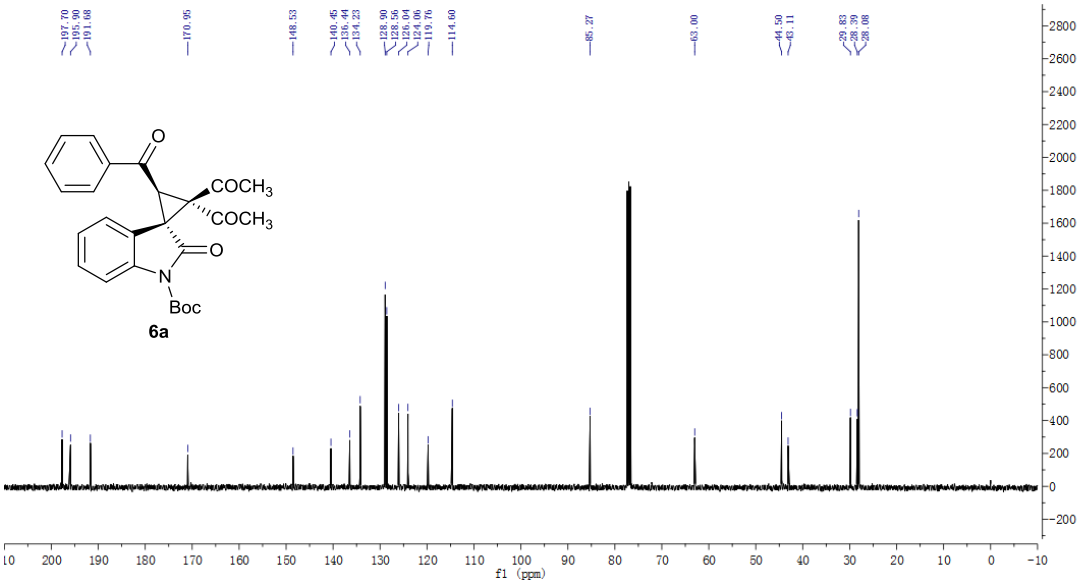
^{1}H NMR spectrum of **5a** in $CDCl_3$ (d.r. = 18:1)



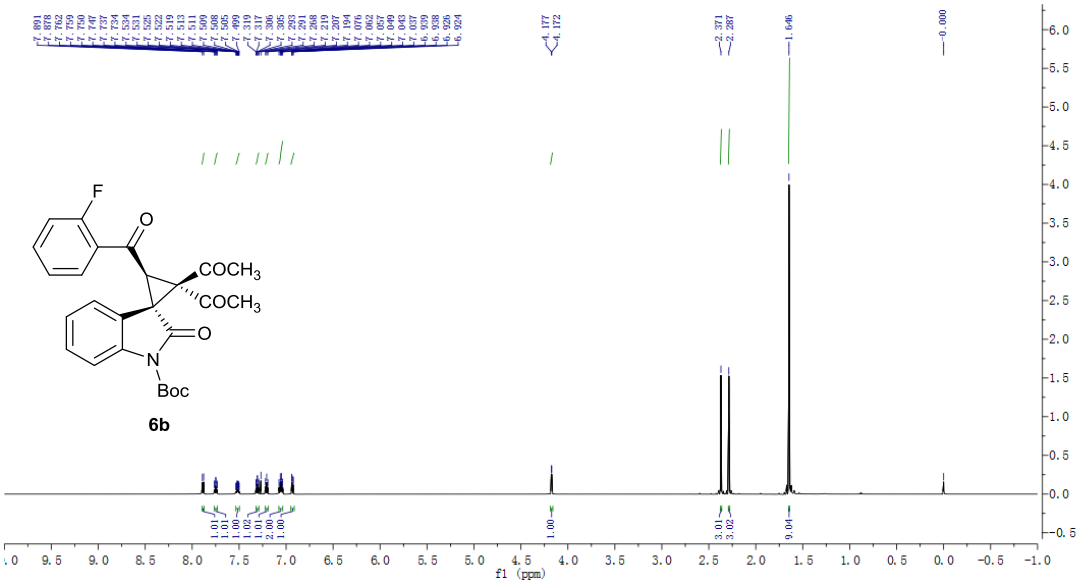
^{13}C NMR spectrum of **5a** in $CDCl_3$



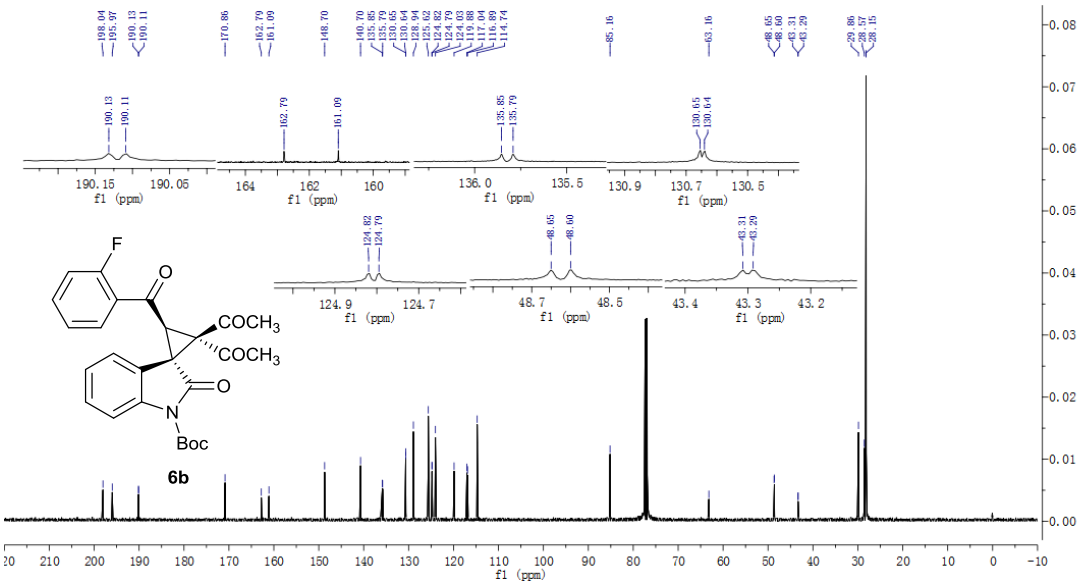
^{1}H NMR spectrum of **6a** in $CDCl_3$ (d.r. = 20:1)



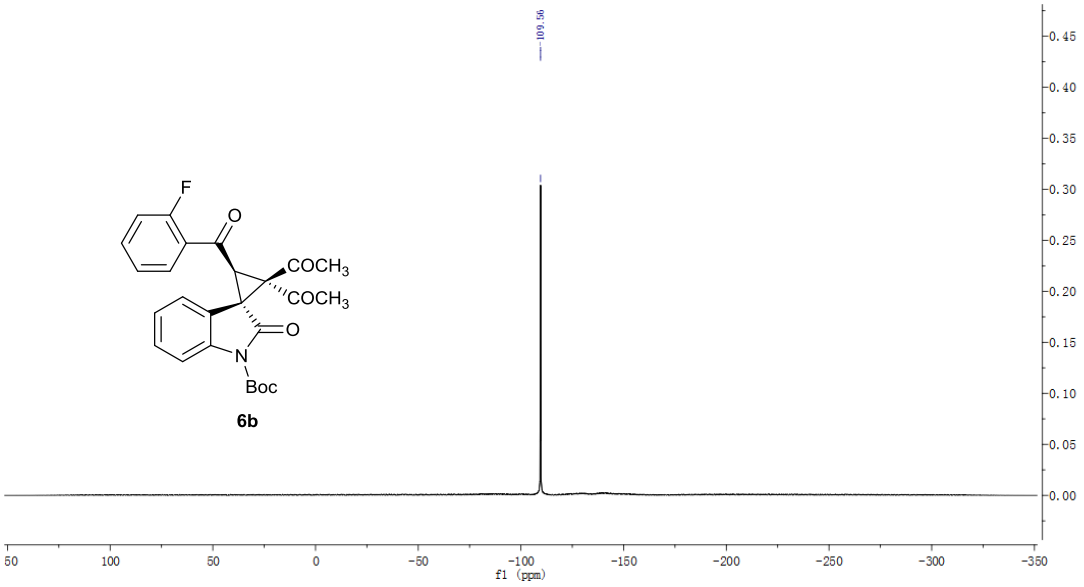
^{13}C NMR spectrum of **6a** in $CDCl_3$



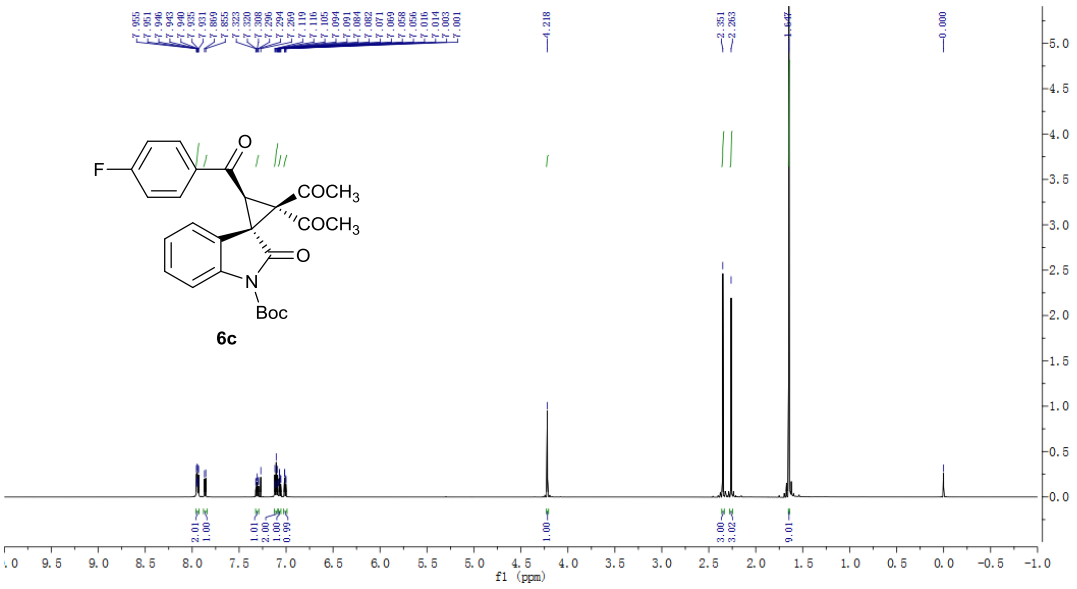
^{1}H NMR spectrum of **6b** in $CDCl_3$ (d.r. = 18:1)



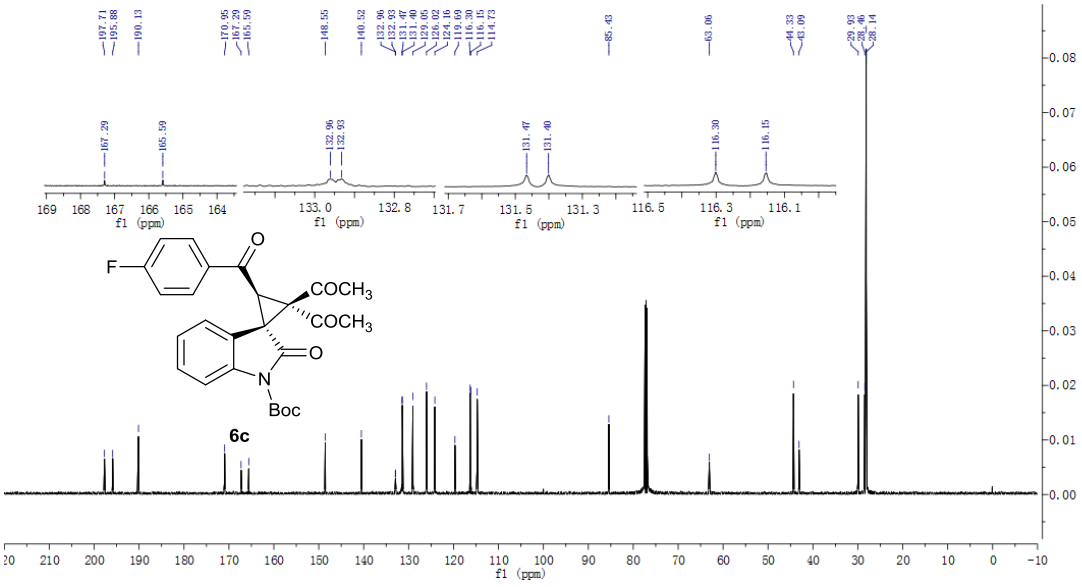
^{13}C NMR spectrum of **6b** in $CDCl_3$



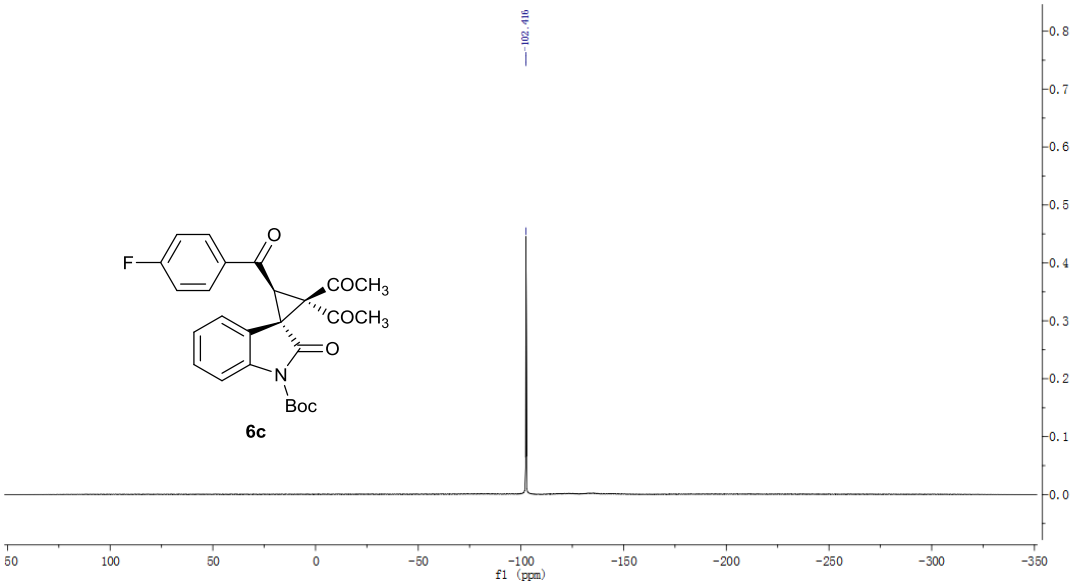
^{19}F NMR spectrum of **6b** in $CDCl_3$



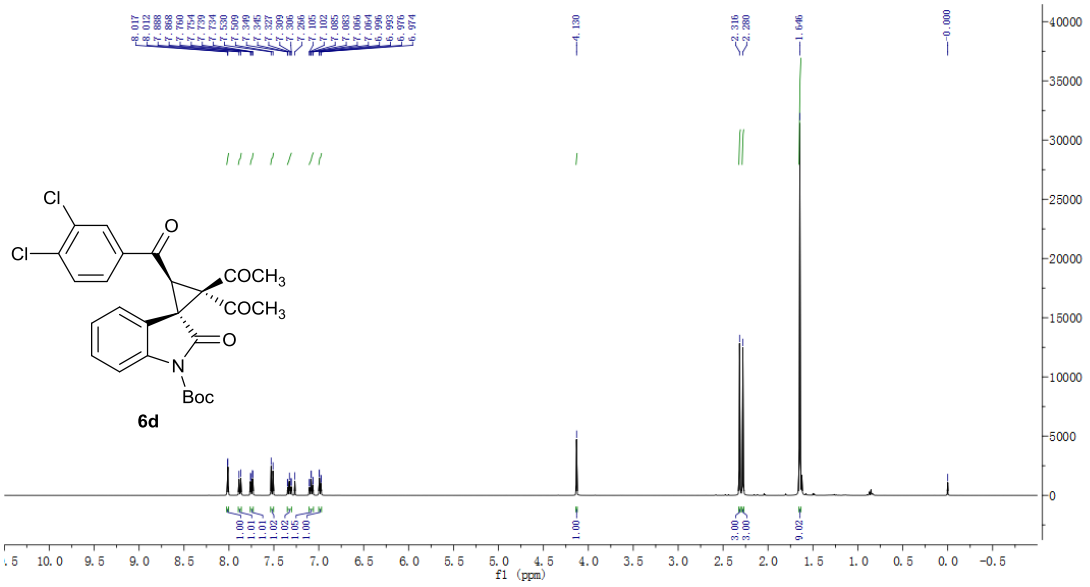
^{1}H NMR spectrum of **6c** in $CDCl_3$ (d.r. = 20:1)



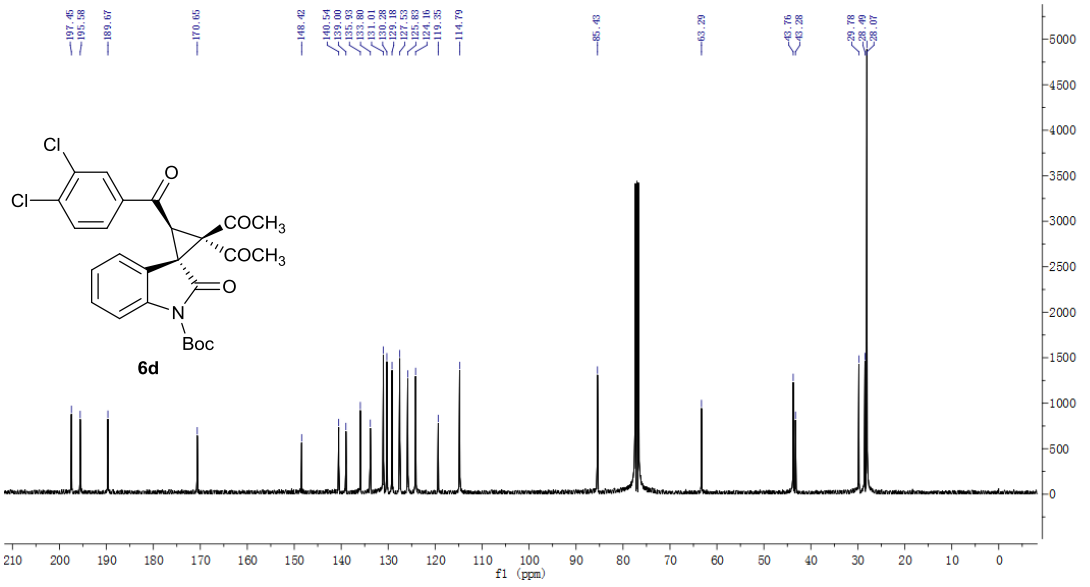
^{13}C NMR spectrum of **6c** in $CDCl_3$



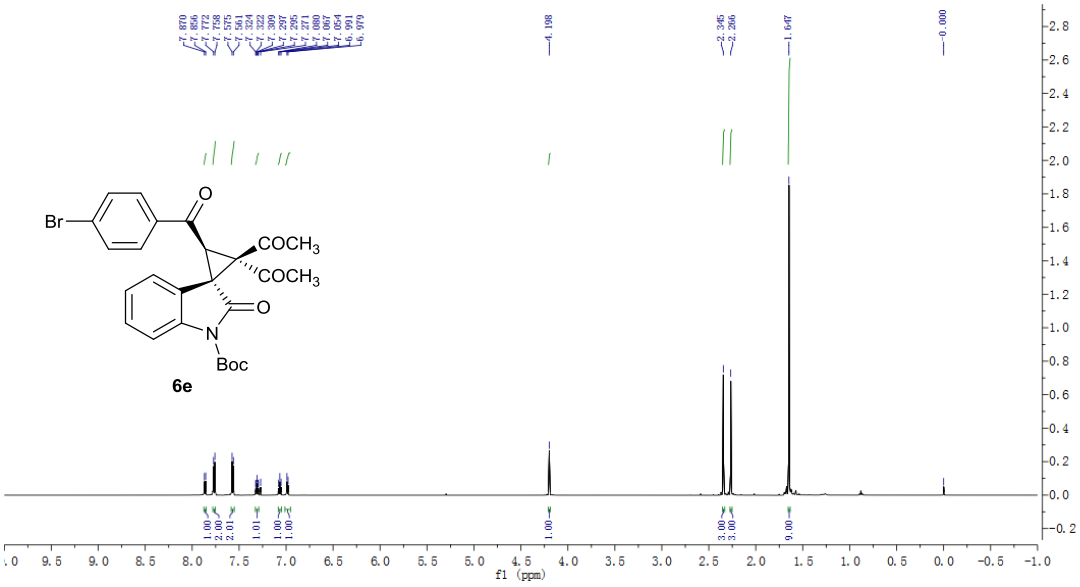
^{19}F NMR spectrum of **6c** in $CDCl_3$



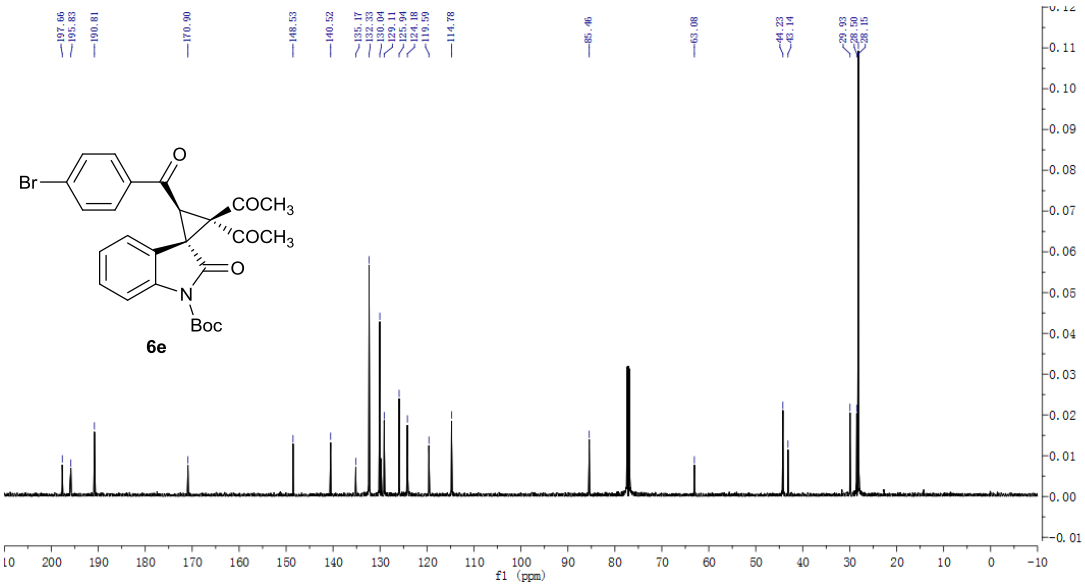
^{1}H NMR spectrum of **6d** in $CDCl_3$ (d.r. = 20:1)



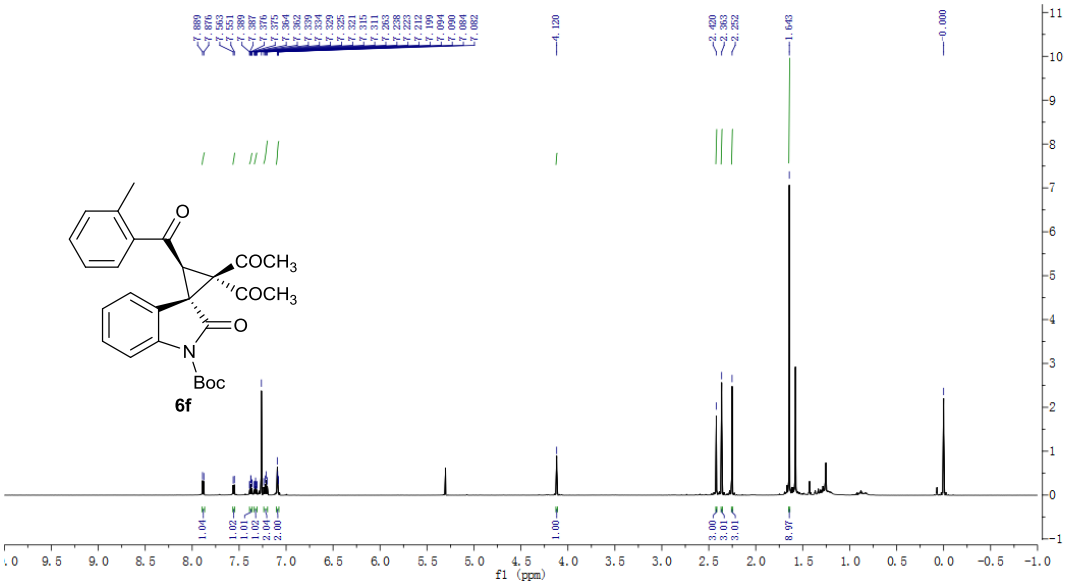
^{13}C NMR spectrum of **6d** in $CDCl_3$



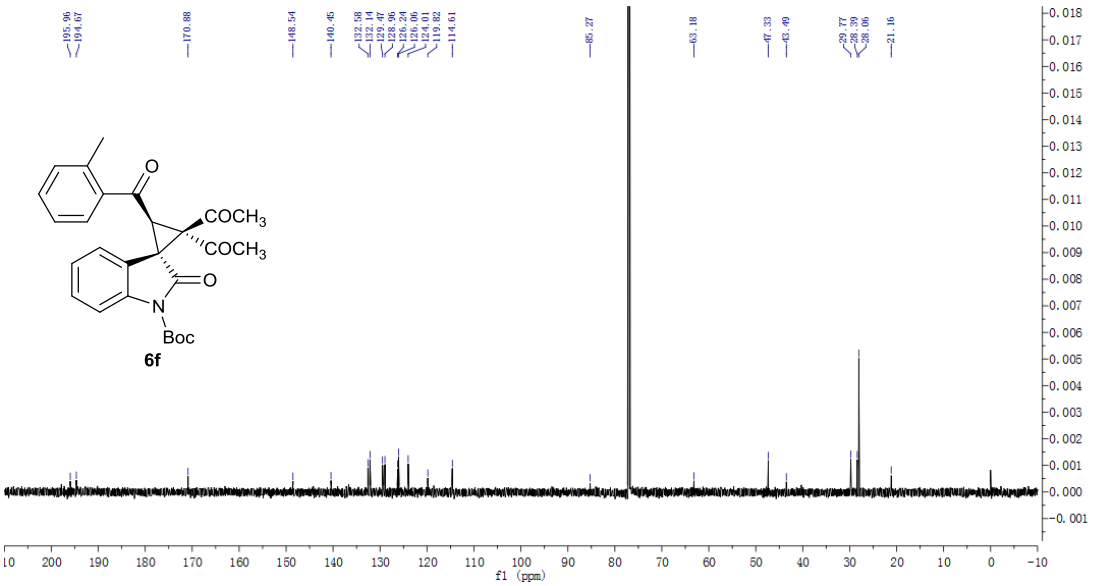
^{1}H NMR spectrum of **6e** in $CDCl_3$ (d.r. = 18:1)



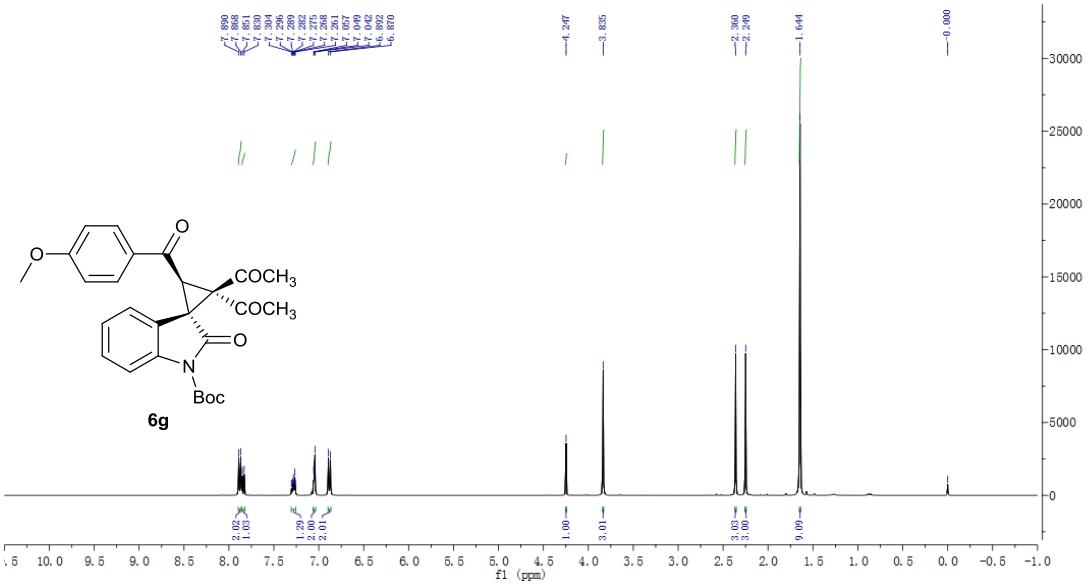
^{13}C NMR spectrum of **6e** in $CDCl_3$



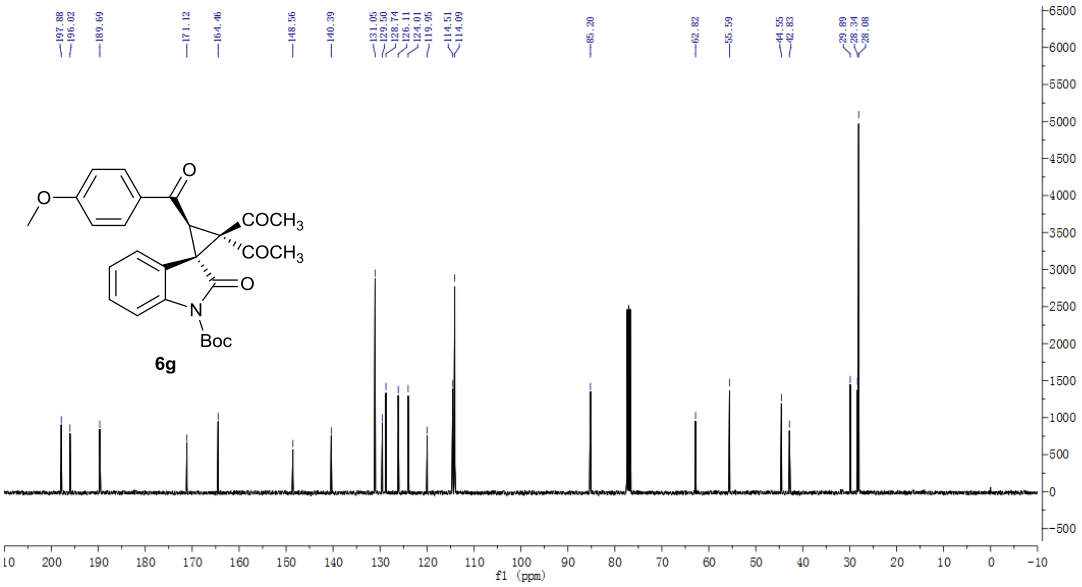
^{1}H NMR spectrum of **6f** in $CDCl_3$ (d.r. = 20:1)



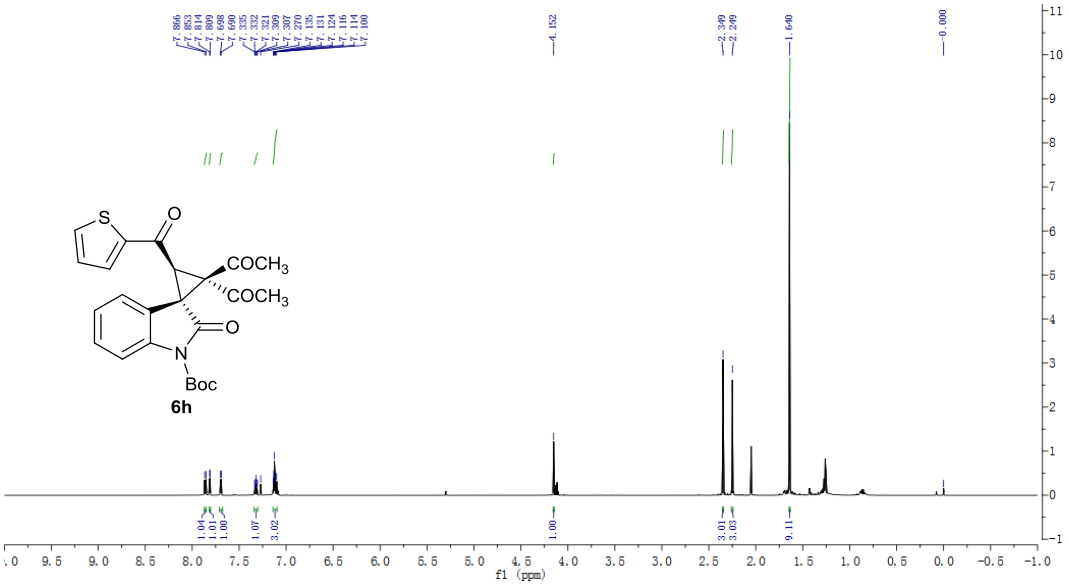
^{13}C NMR spectrum of **6f** in $CDCl_3$



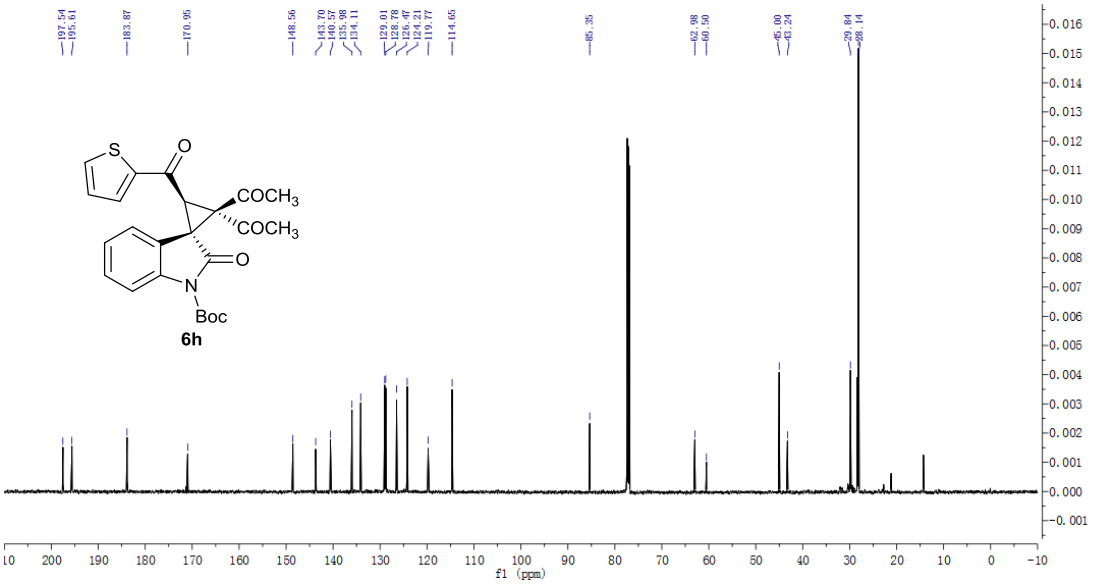
^{1}H NMR spectrum of **6g** in $CDCl_3$ (d.r. = 20:1)



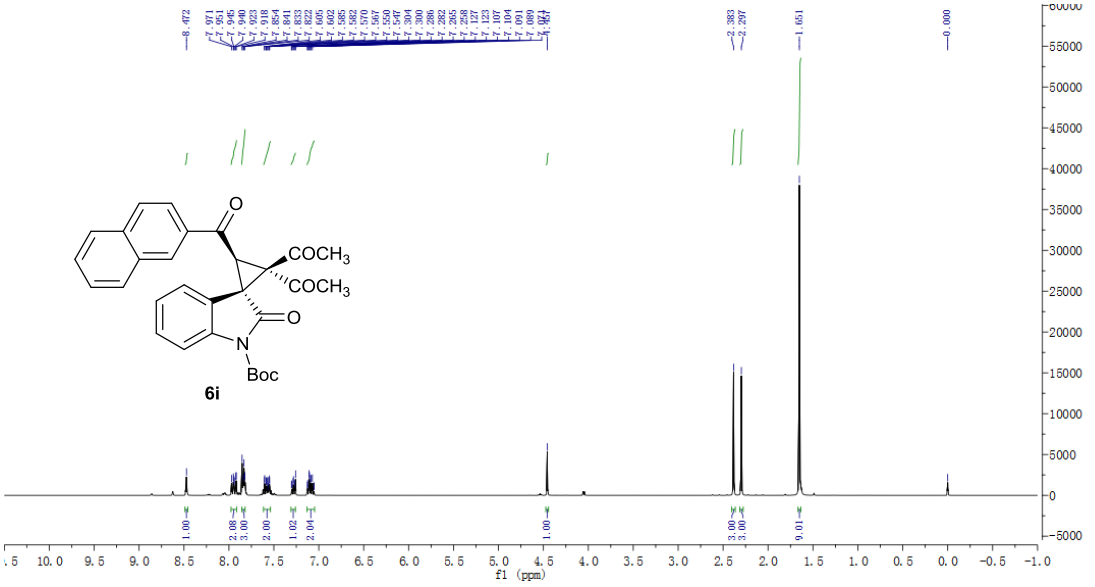
^{13}C NMR spectrum of **6g** in $CDCl_3$



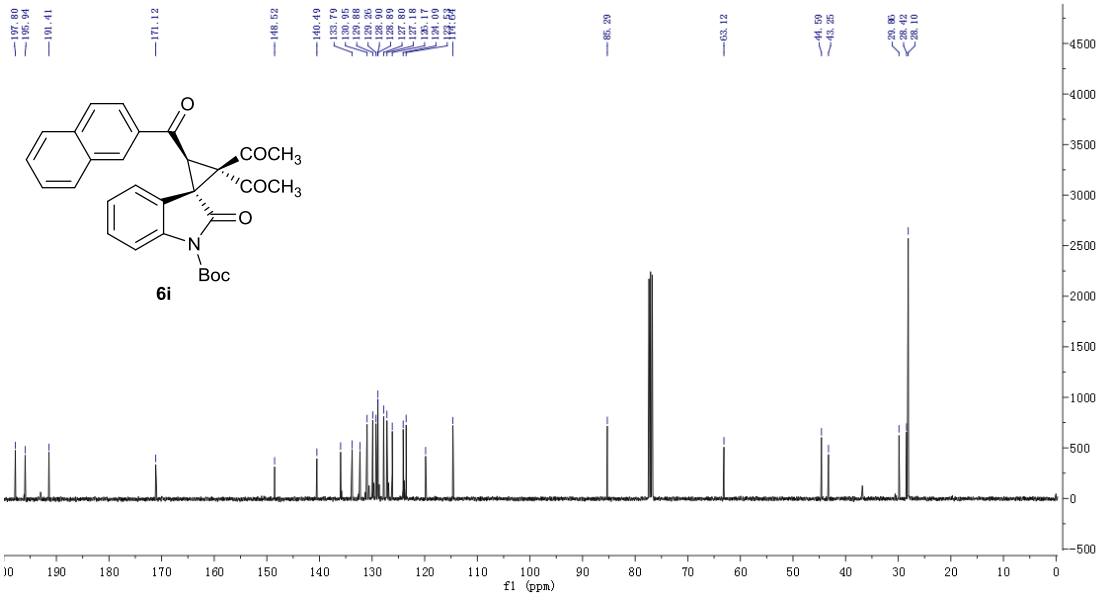
^{1}H NMR spectrum of **6h** in $CDCl_3$ (d.r. = 20:1)



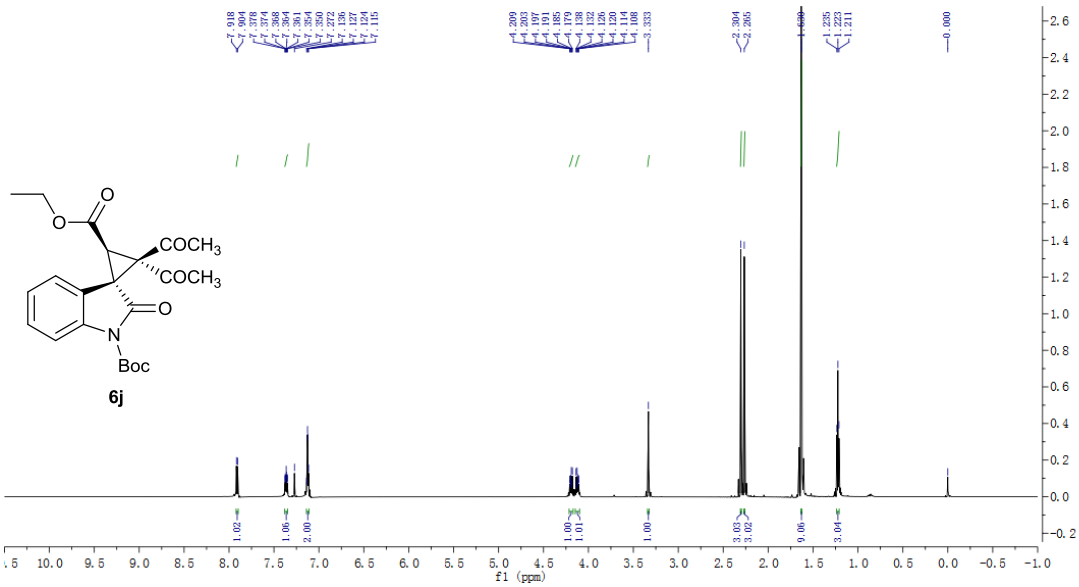
^{13}C NMR spectrum of **6h** in $CDCl_3$



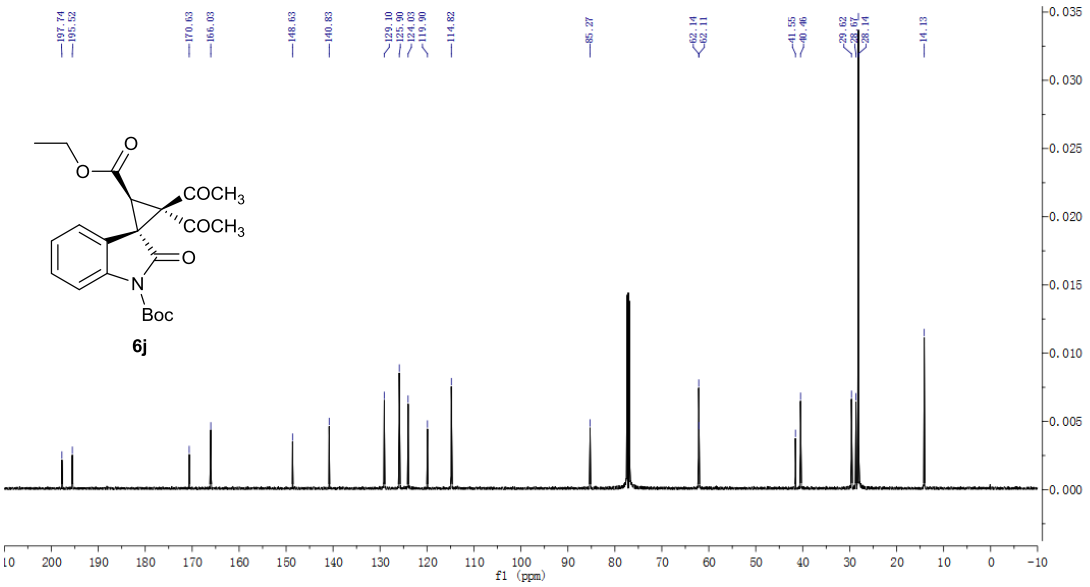
^{1}H NMR spectrum of **6i** in $CDCl_3$ (d.r. = 10:1)



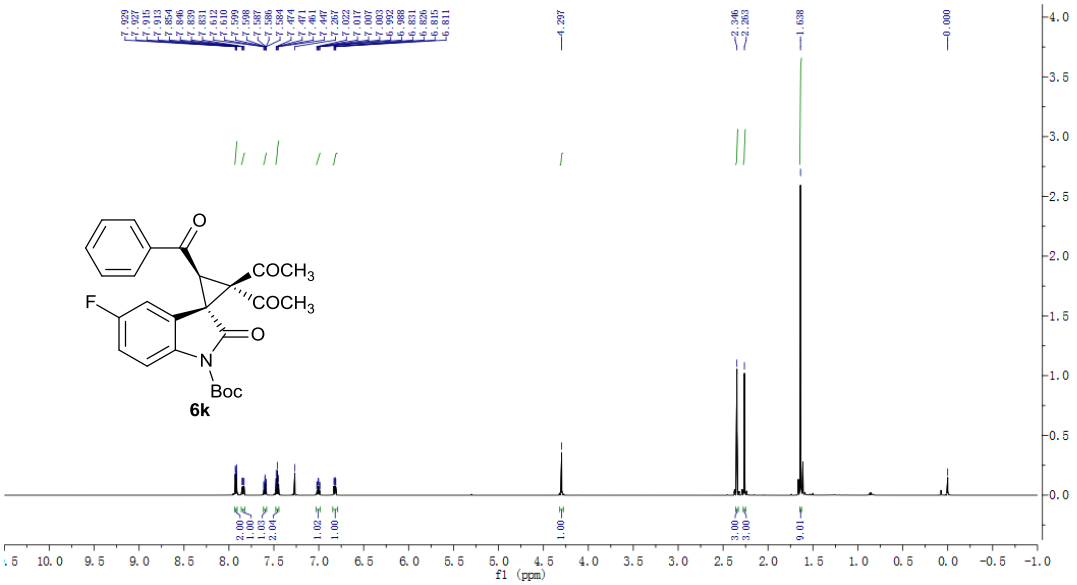
^{13}C NMR spectrum of **6i** in $CDCl_3$



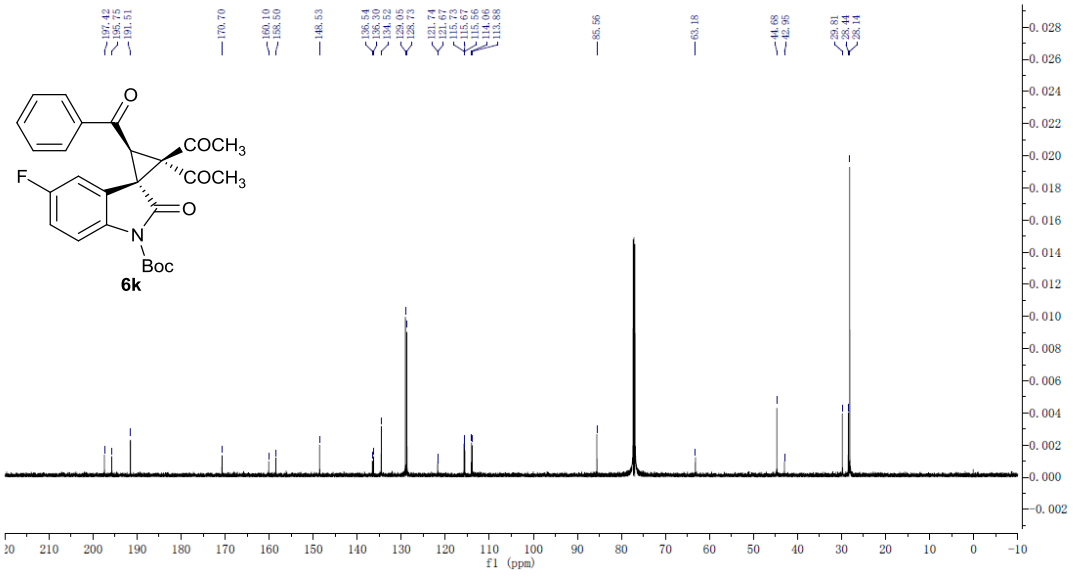
^{1}H NMR spectrum of **6j** in $CDCl_3$ (d.r. = 20:1)



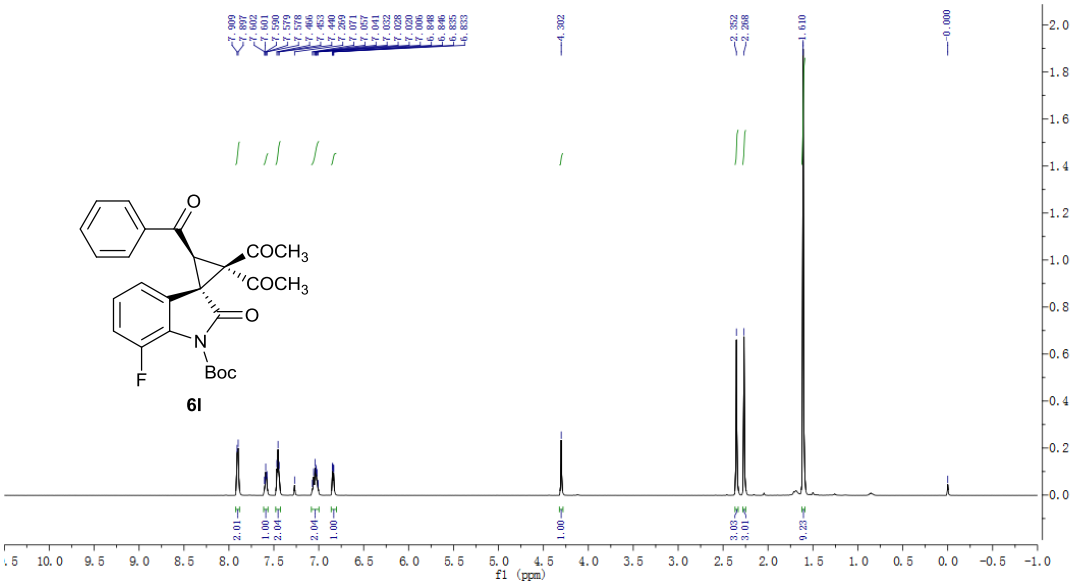
^{13}C NMR spectrum of **6j** in $CDCl_3$



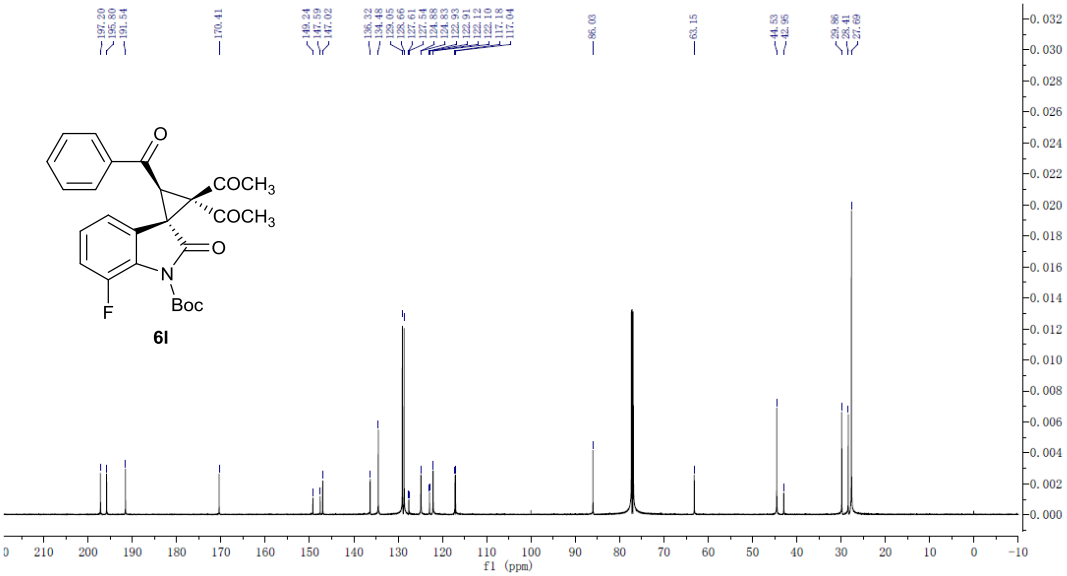
^{1}H NMR spectrum of **6k** in $CDCl_3$ (d.r. = 13:1)



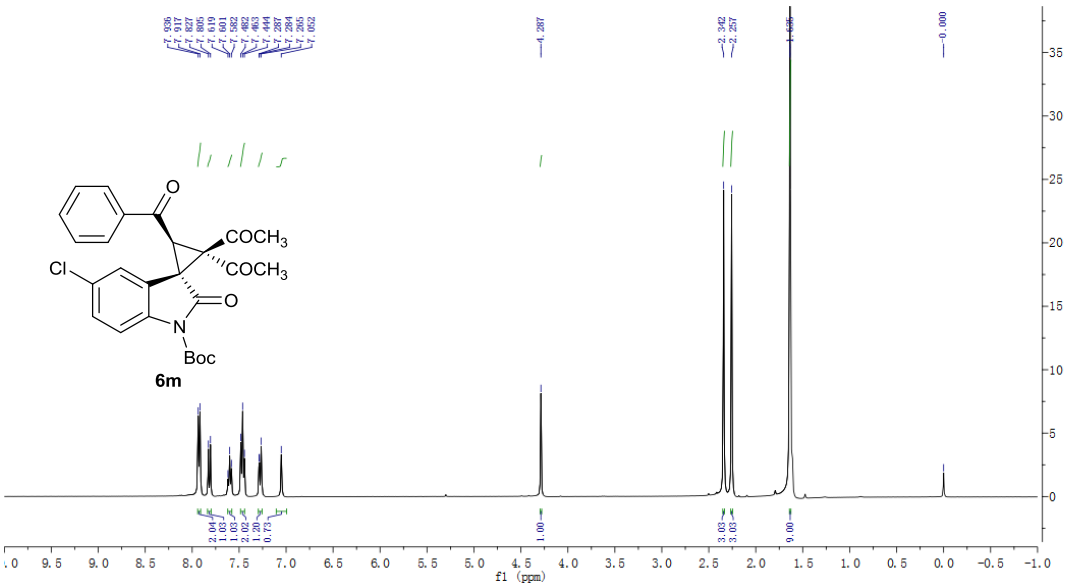
^{13}C NMR spectrum of **6k** in $CDCl_3$



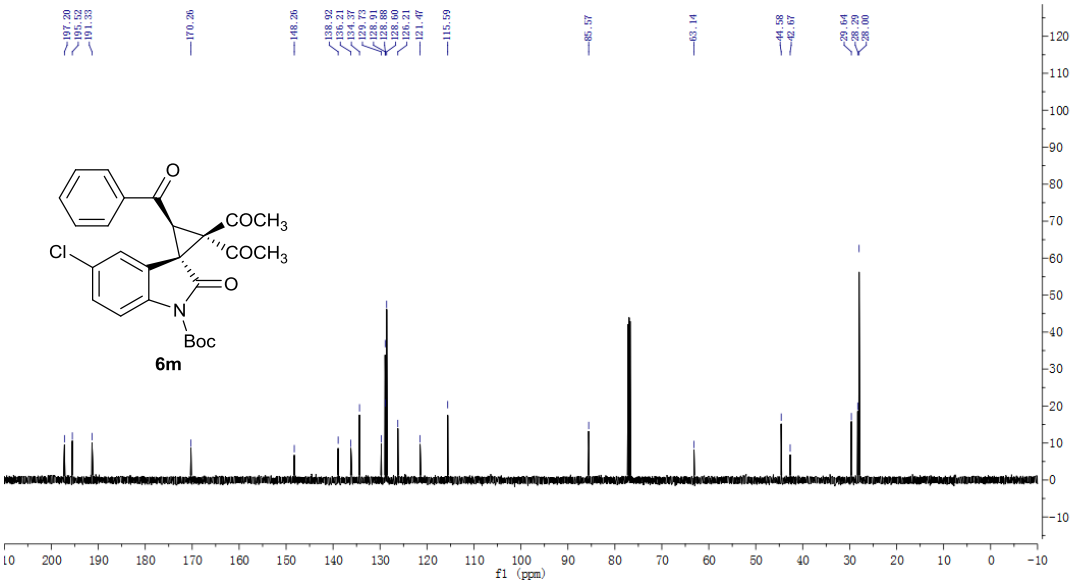
^{1}H NMR spectrum of **6l** in $CDCl_3$ (d.r. = 20:1)



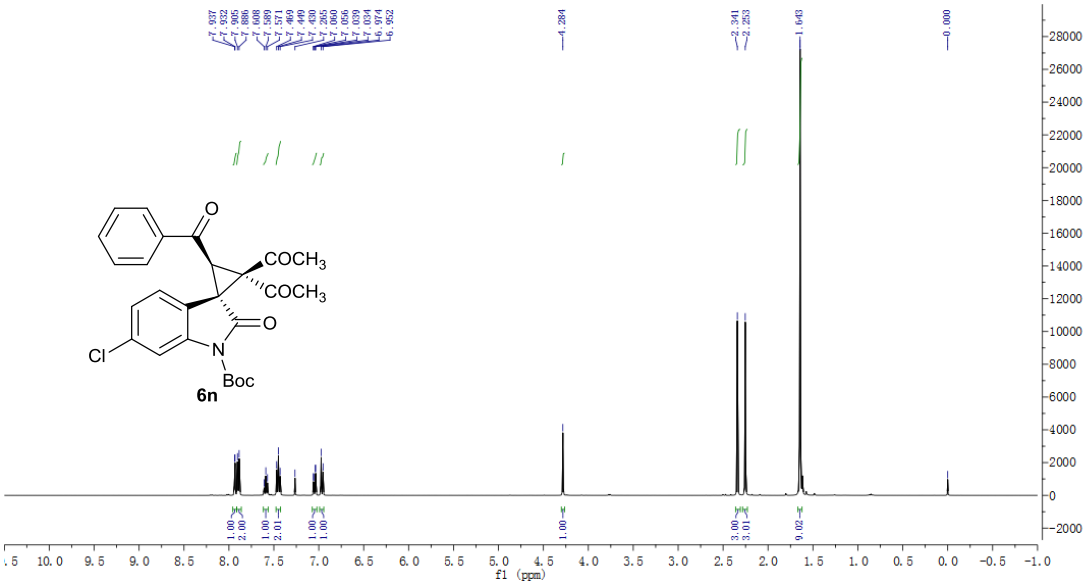
^{13}C NMR spectrum of **6l** in $CDCl_3$



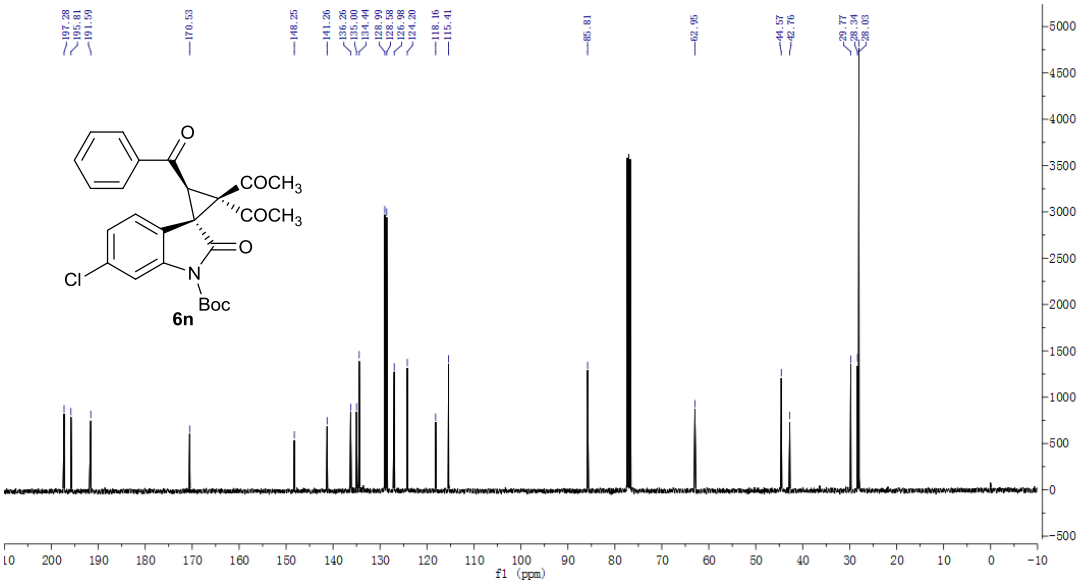
^{1}H NMR spectrum of **6m** in $CDCl_3$ (d.r. = 20:1)



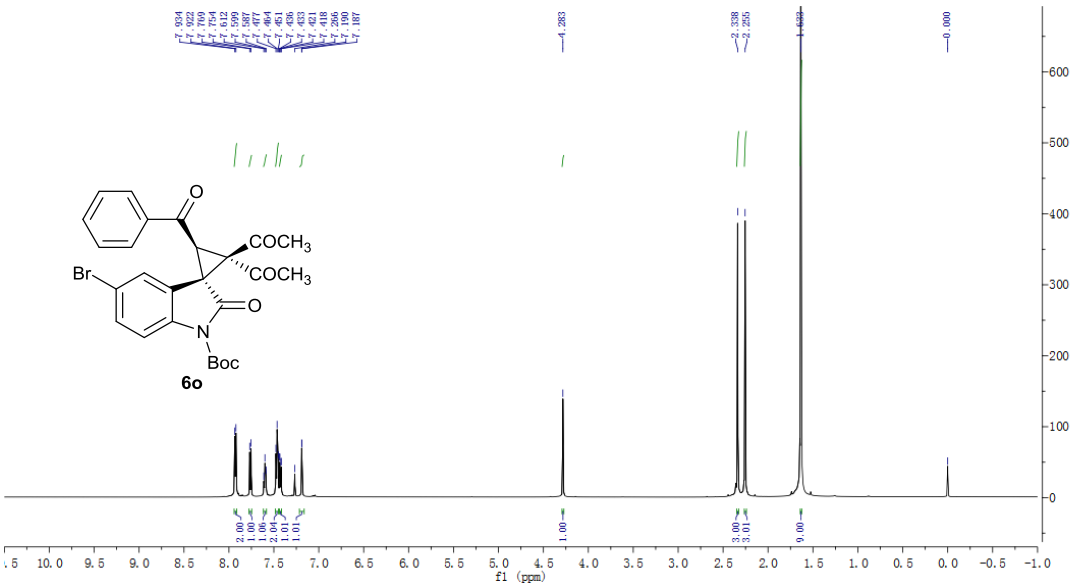
^{13}C NMR spectrum of **6m** in $CDCl_3$



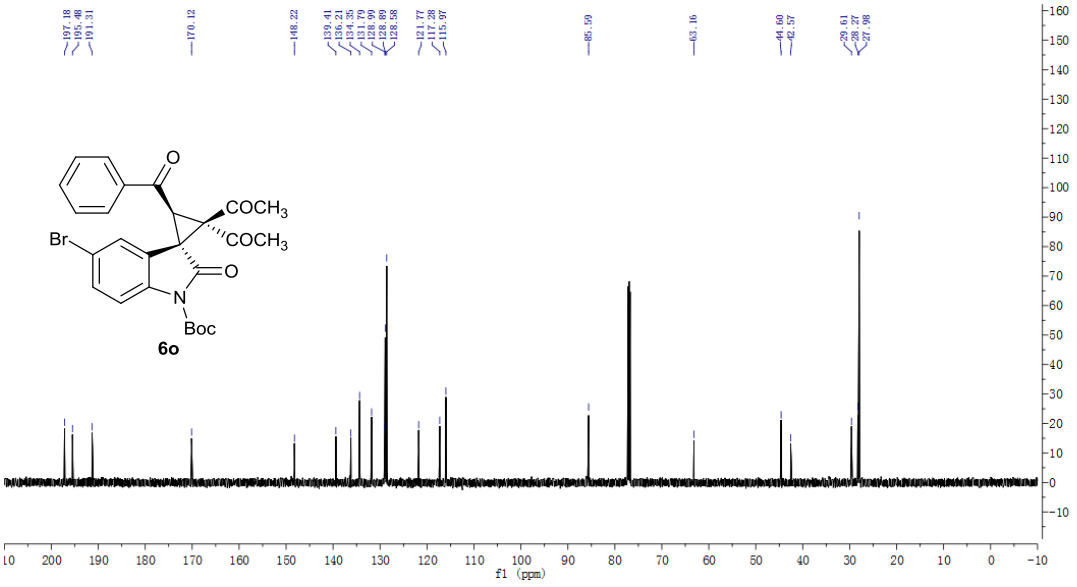
^{1}H NMR spectrum of **6n** in $CDCl_3$ (d.r. = 20:1)



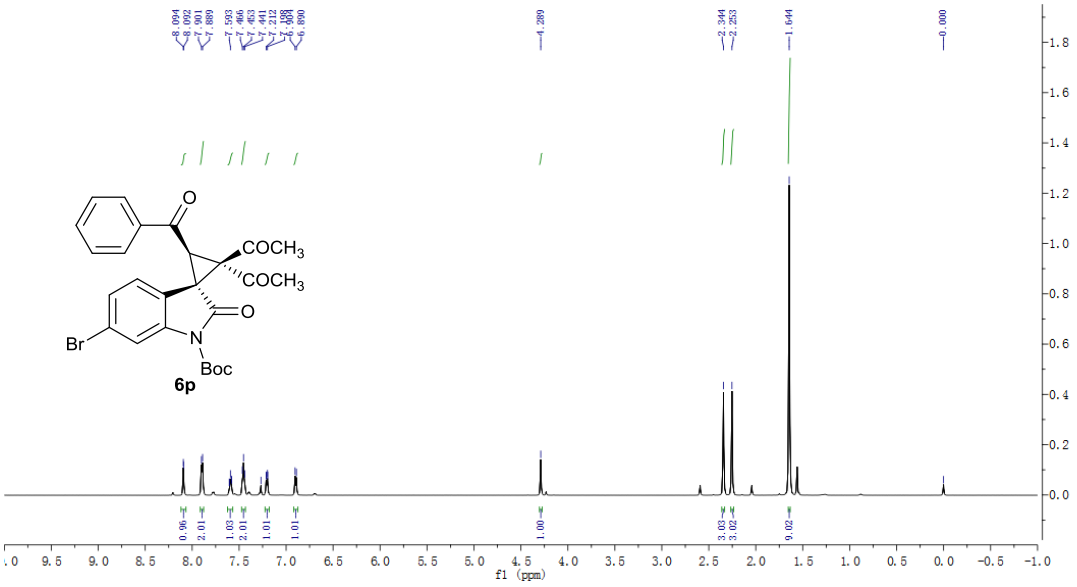
^{13}C NMR spectrum of **6n** in $CDCl_3$



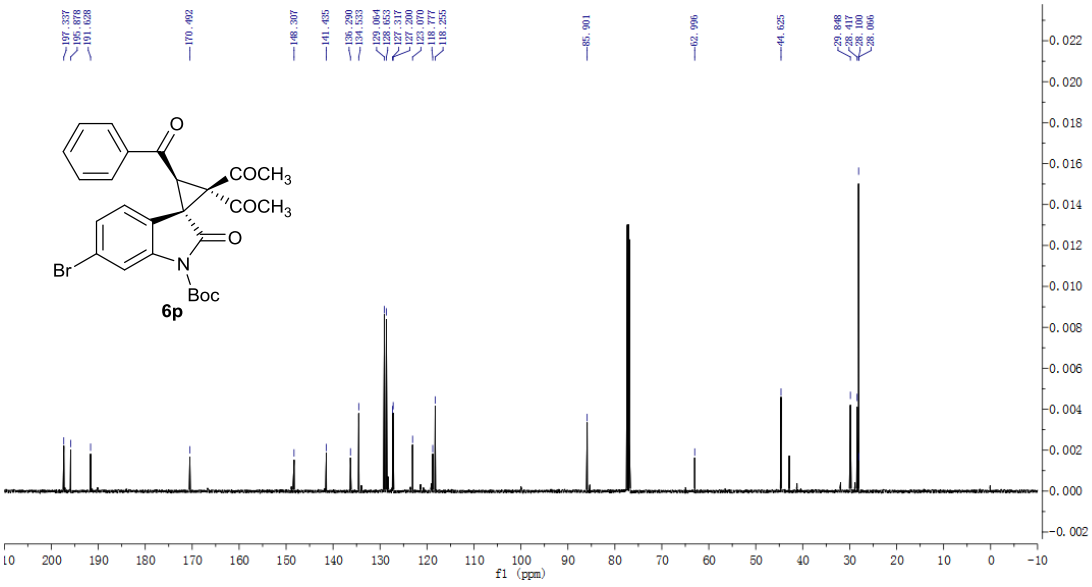
^{1}H NMR spectrum of **6o** in $CDCl_3$ (d.r. = 15:1)



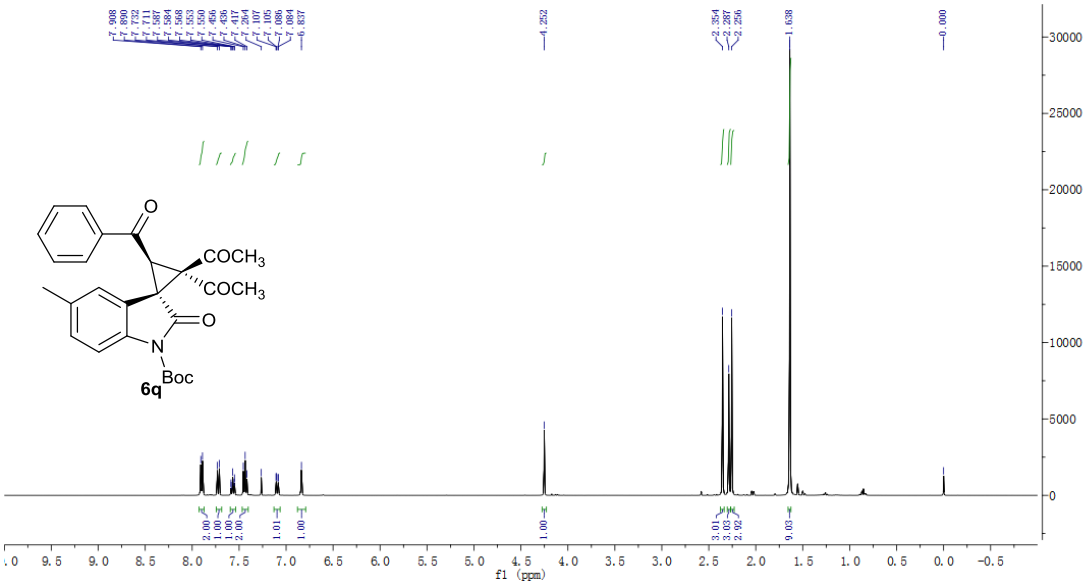
^{13}C NMR spectrum of **6o** in $CDCl_3$



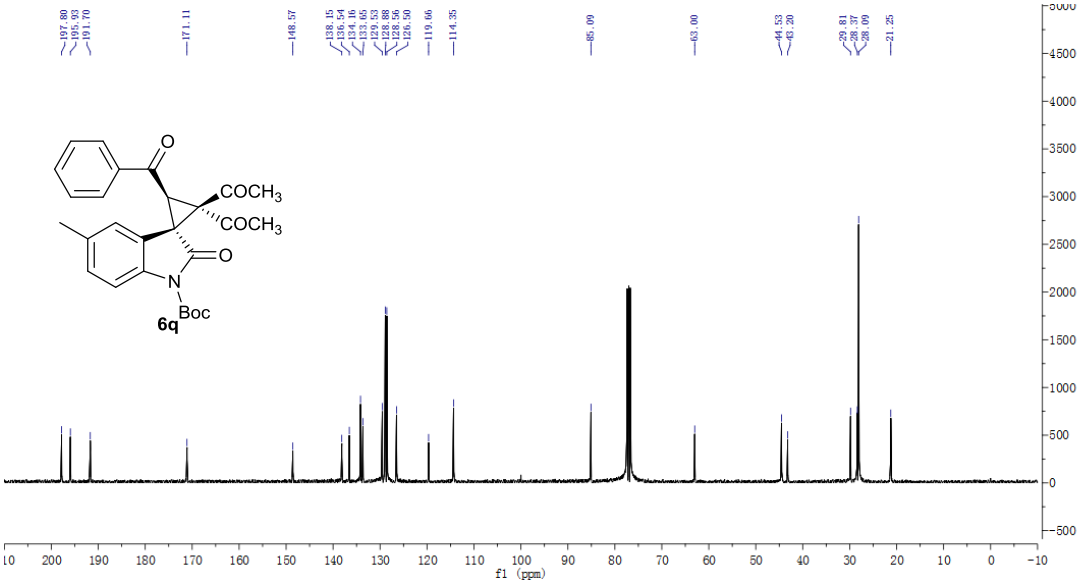
^{1}H NMR spectrum of **6p** in $CDCl_3$ (d.r. = 9:1)



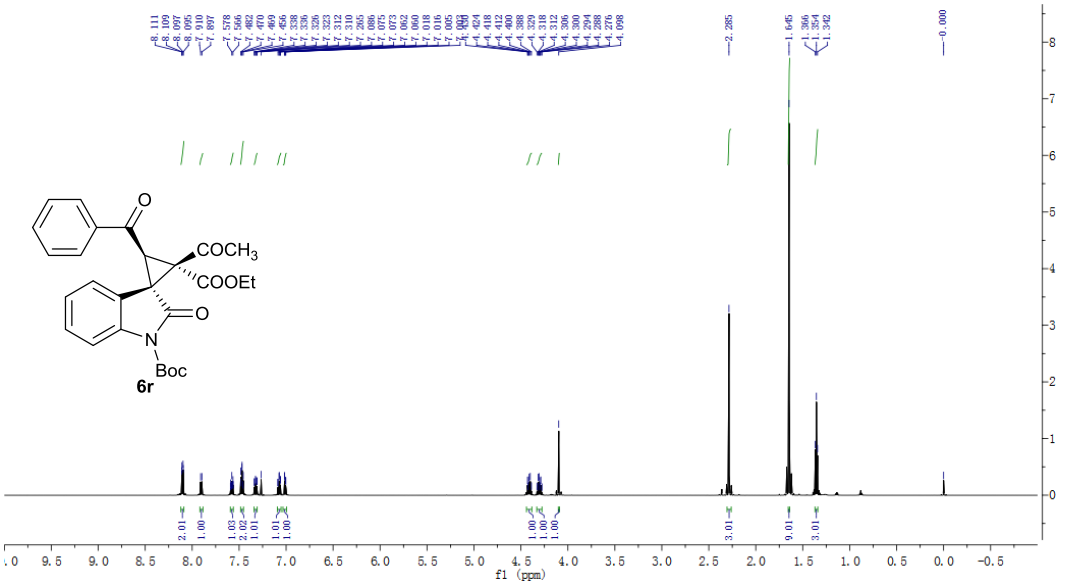
^{13}C NMR spectrum of **6p** in $CDCl_3$



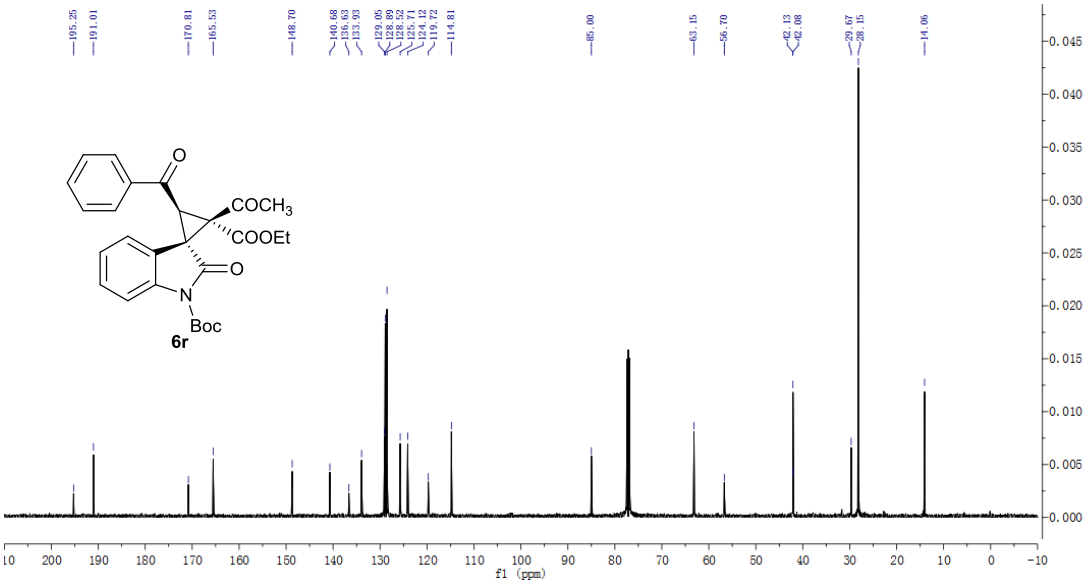
^{1}H NMR spectrum of **6q** in $CDCl_3$ (d.r. = 15:1)



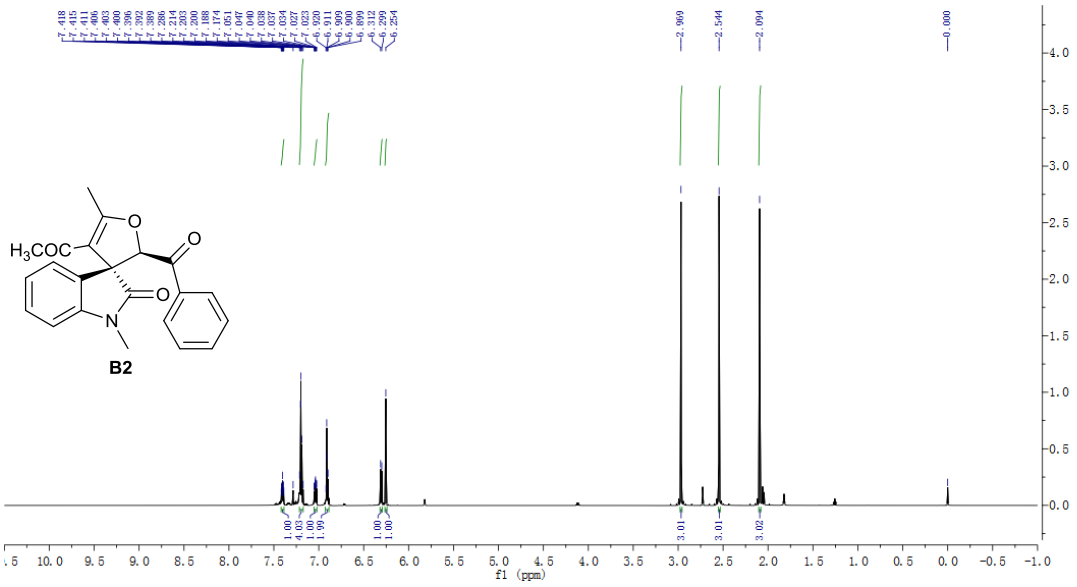
^{13}C NMR spectrum of **6q** in $CDCl_3$



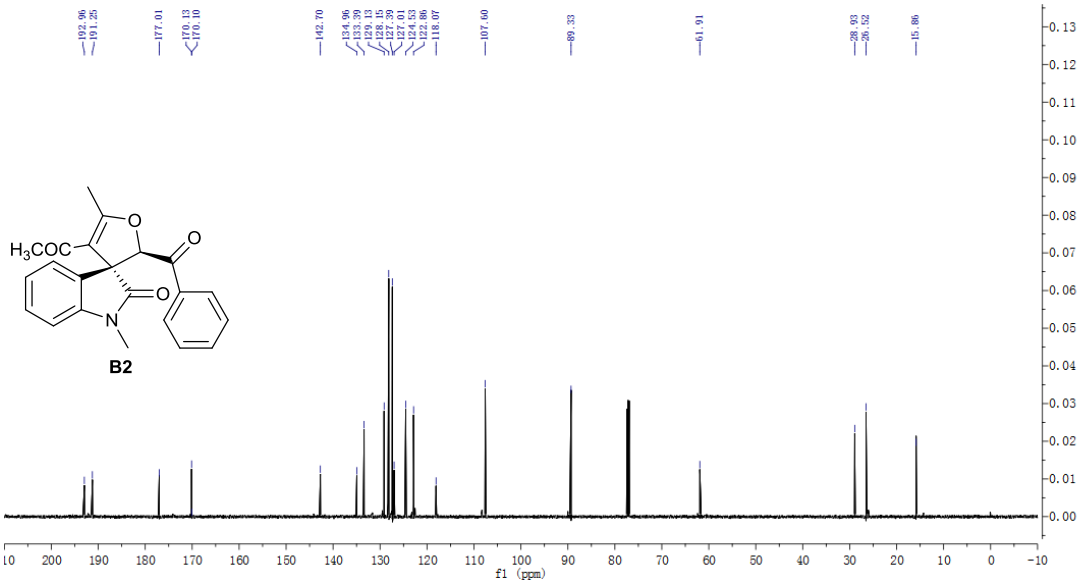
^{1}H NMR spectrum of **6r** in $CDCl_3$ (d.r. = 18:1)



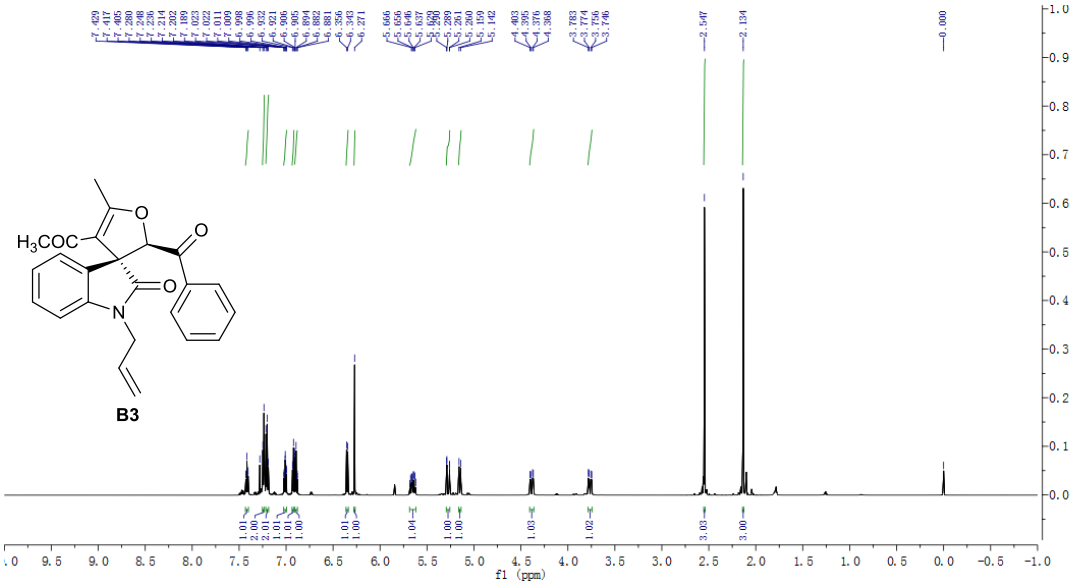
^{13}C NMR spectrum of **6r** in $CDCl_3$



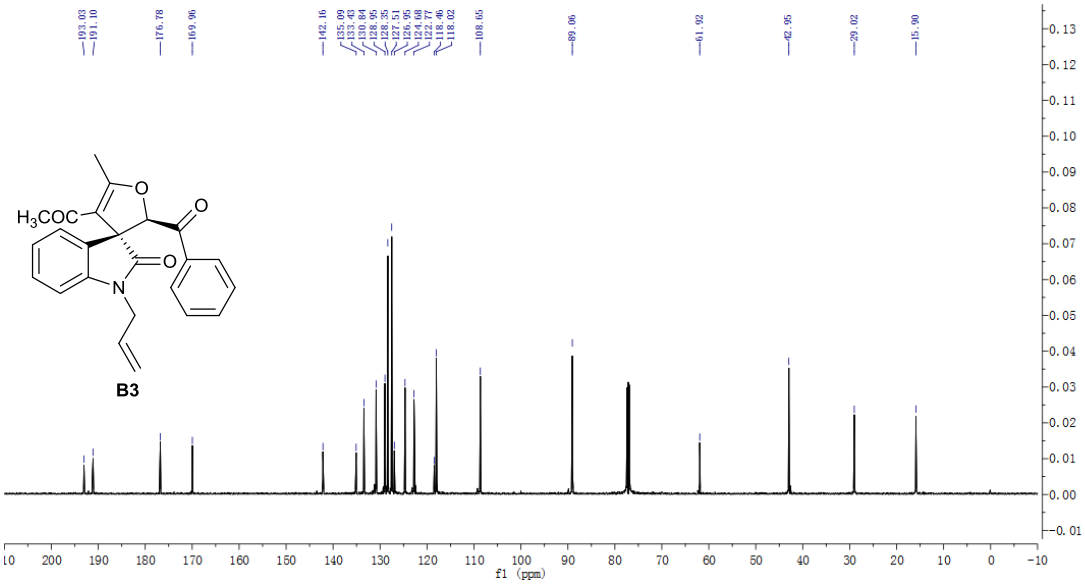
^{1}H spectrum of **B2** in $CDCl_3$ (d.r. = 8:1)



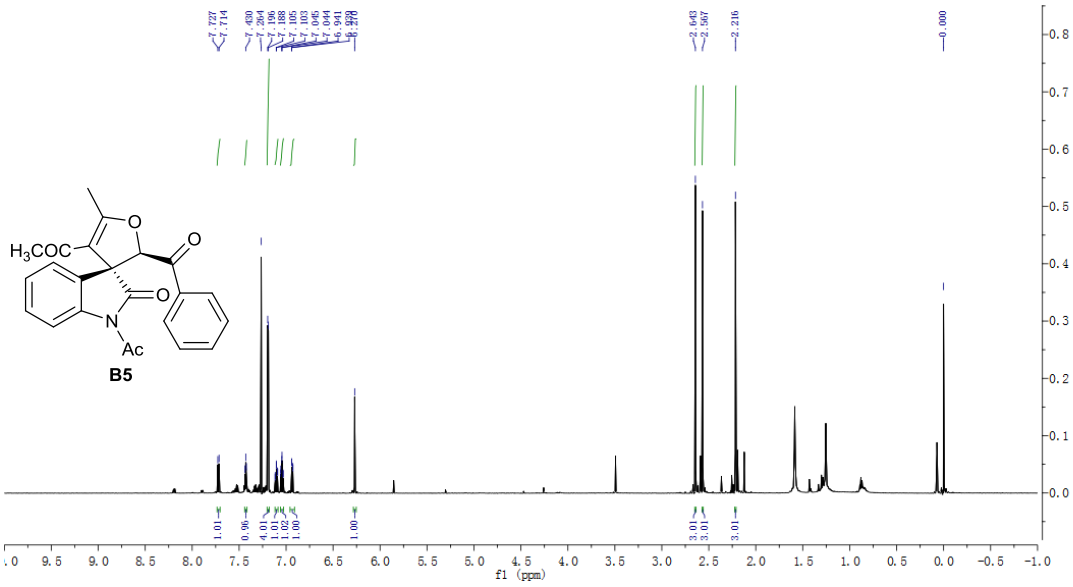
^{13}C spectrum of **B2** in $CDCl_3$



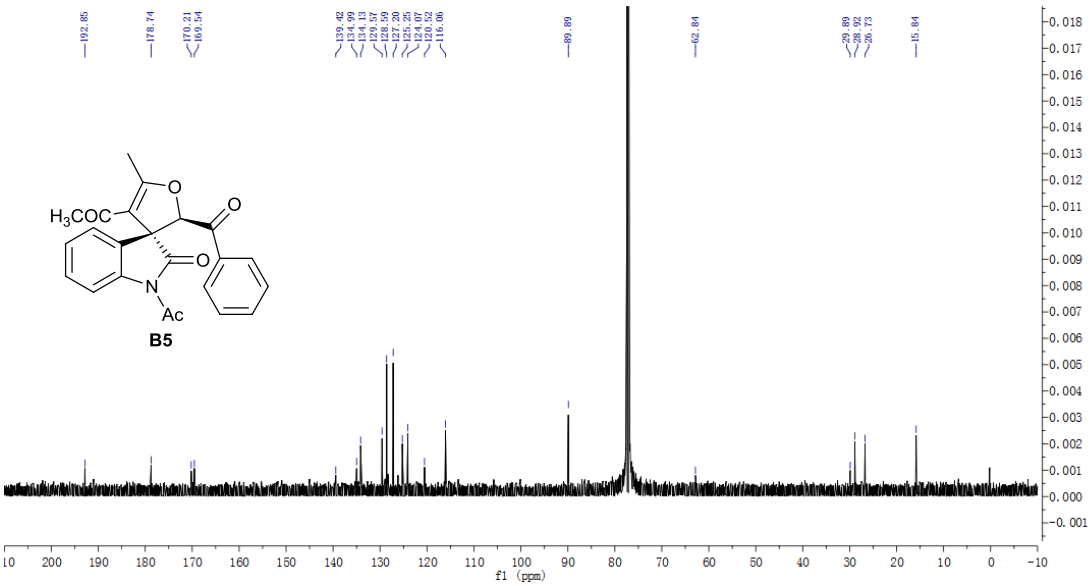
^{1}H spectrum of **B3** in $CDCl_3$ (d.r. =5:1)



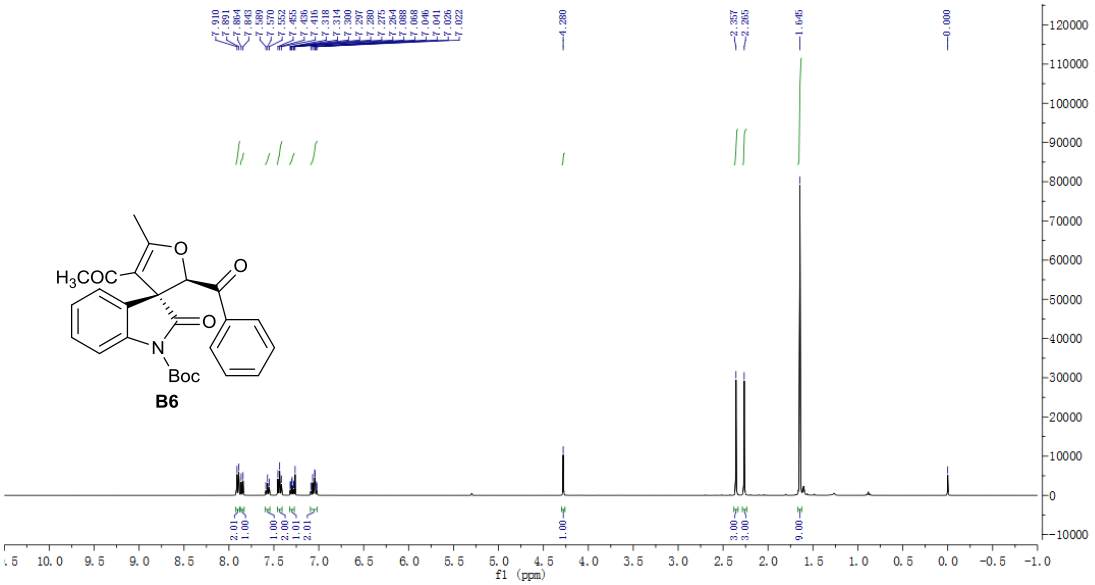
^{13}C spectrum of **B3** in $CDCl_3$



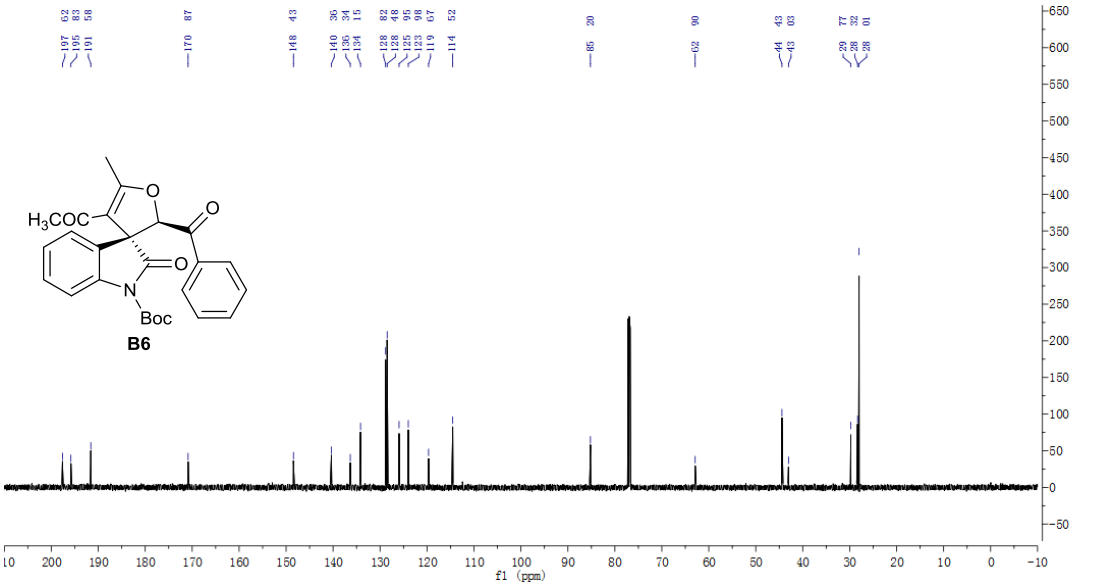
^{1}H spectrum of **B5** in $CDCl_3$ (d.r. =10:1)



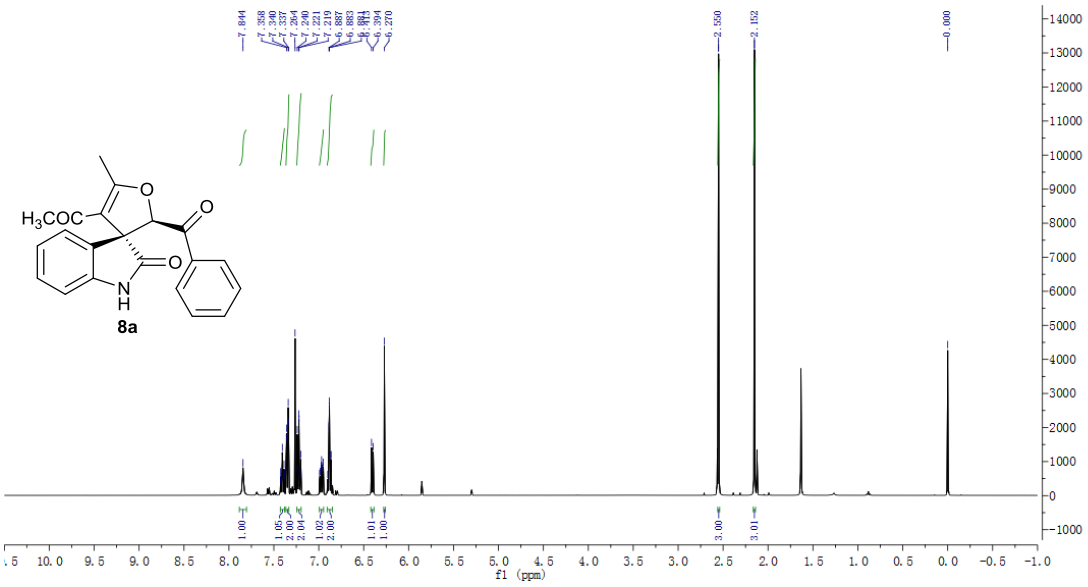
^{13}C spectrum of **B5** in $CDCl_3$



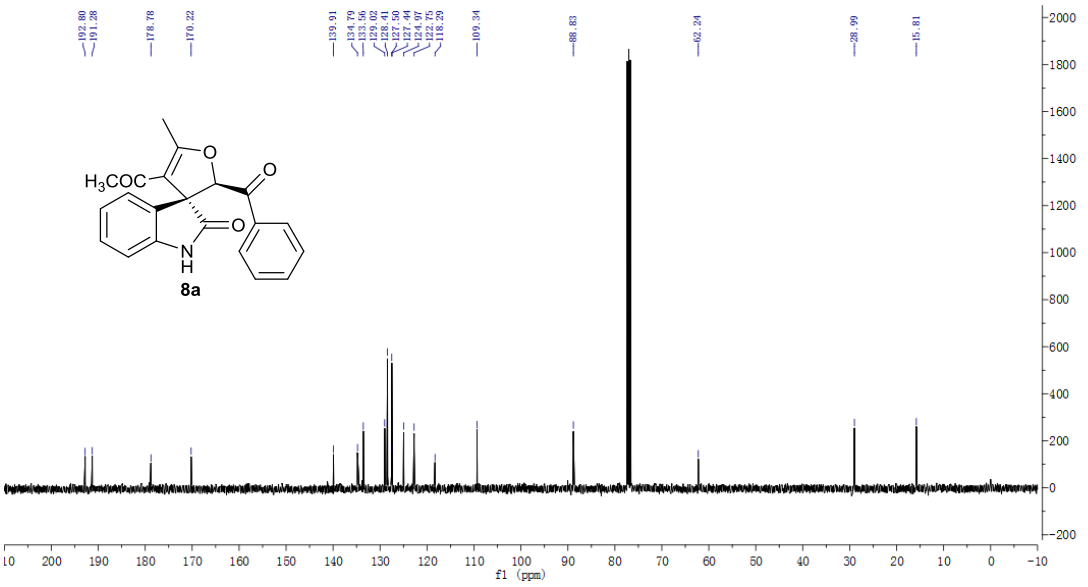
^{1}H spectrum of **B6** in $CDCl_3$ (d.r. =12:1)



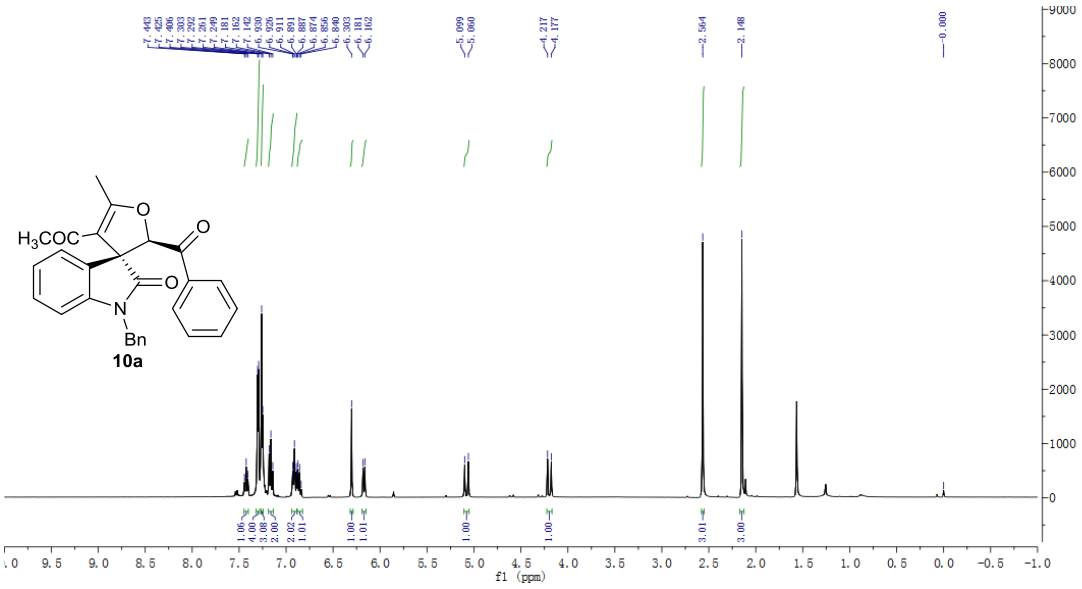
^{13}C spectrum of **B6** in $CDCl_3$



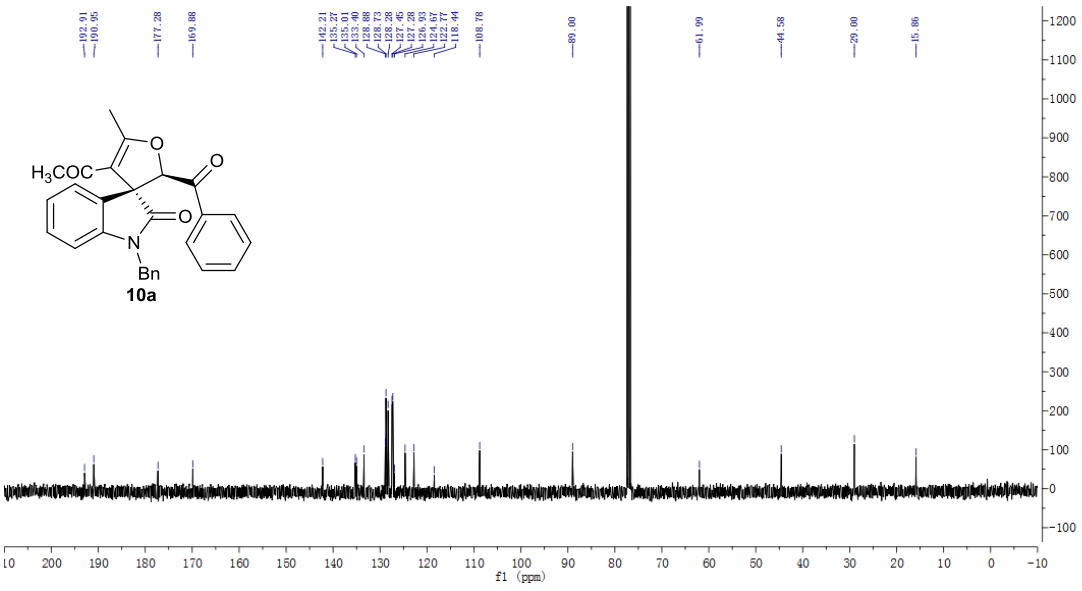
^{1}H NMR spectrum of **8a** in $CDCl_3$ (d.r. =10:1)



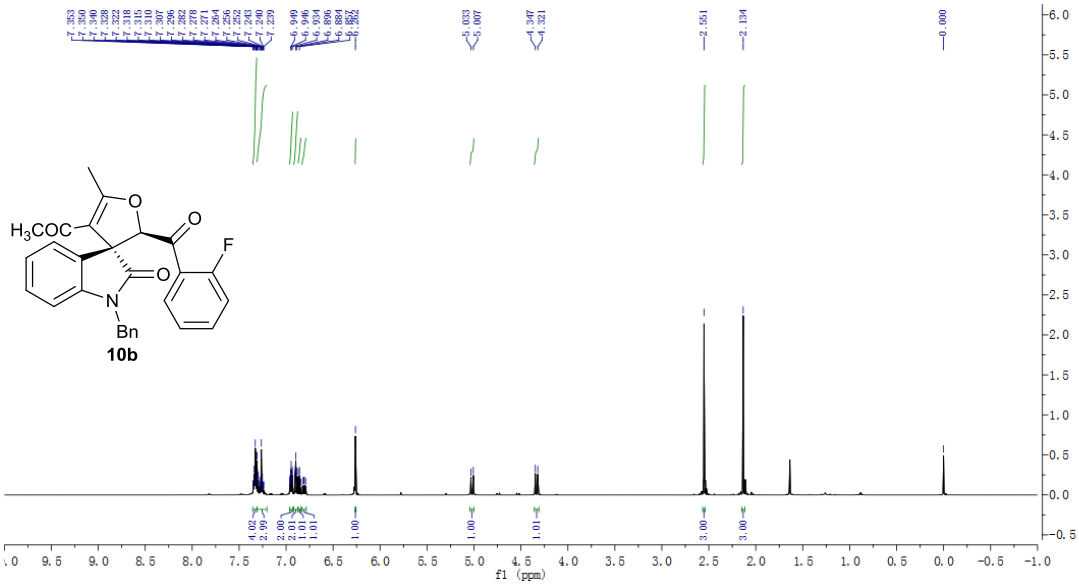
^{13}C NMR spectrum of **8a** in $CDCl_3$



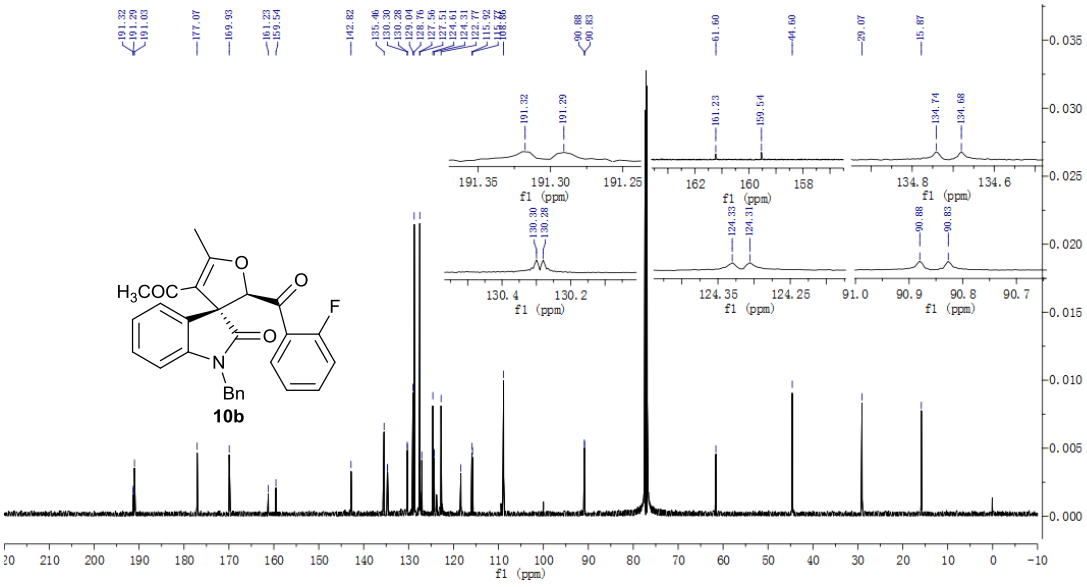
^{1}H NMR spectrum of **10a** in $CDCl_3$ (d.r. = 10:1)



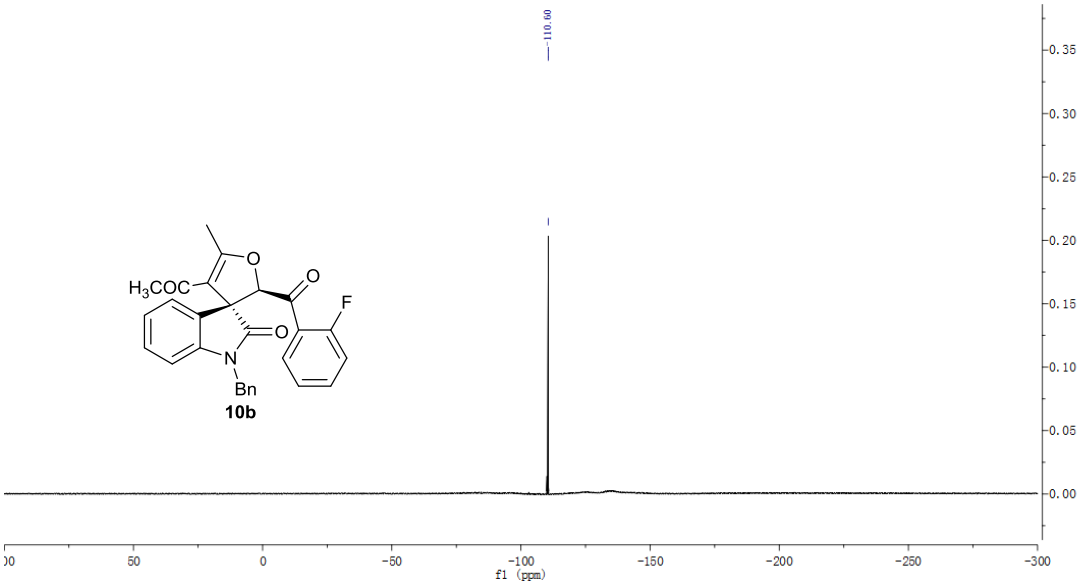
^{13}C NMR spectrum of **10a** in $CDCl_3$



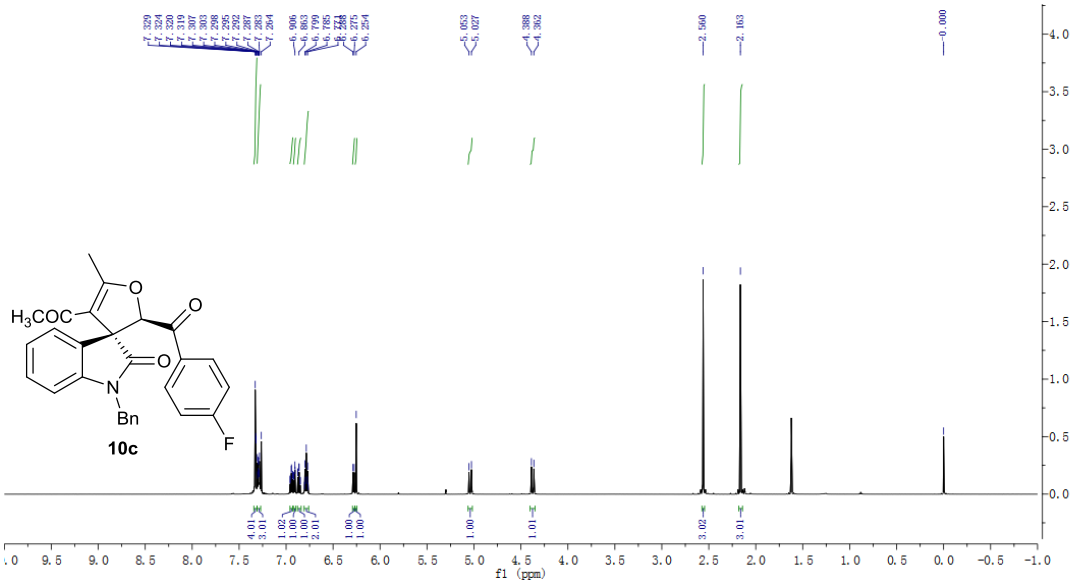
^{1}H NMR spectrum of **10b** in $CDCl_3$ (d.r. = 16:1)



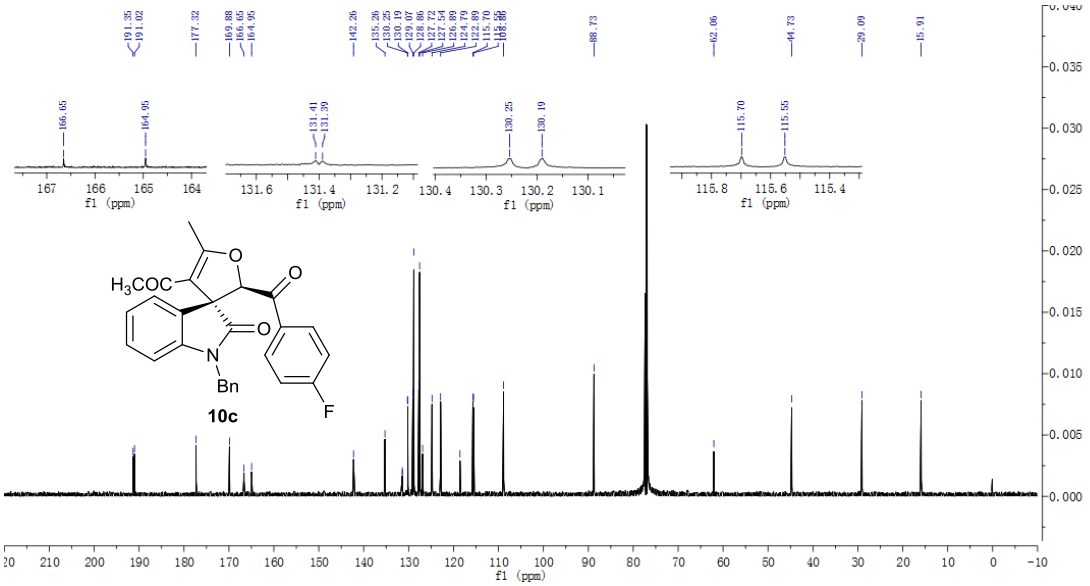
^{13}C NMR spectrum of **10b** in $CDCl_3$



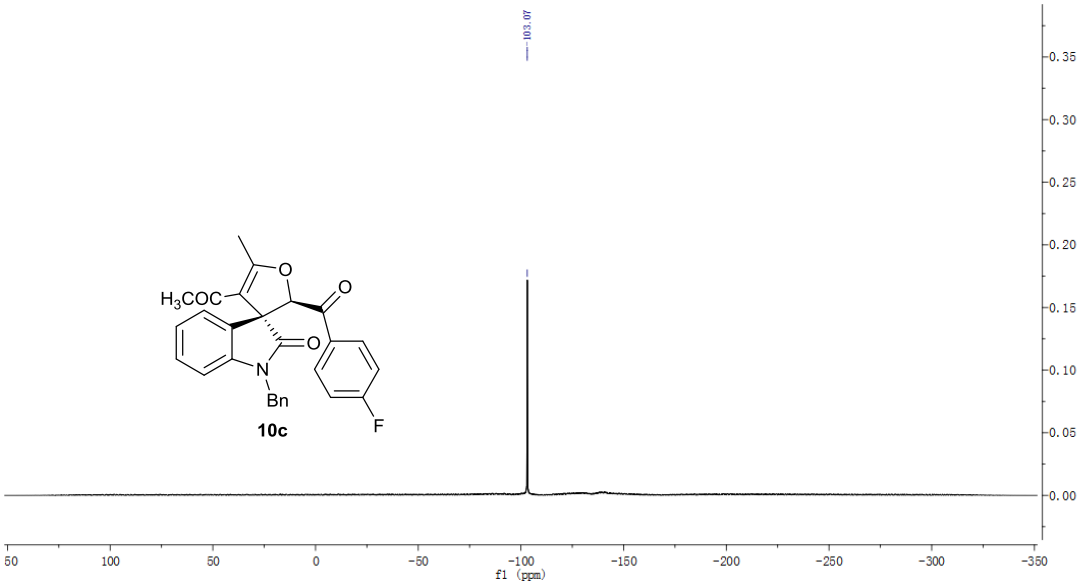
^{19}F NMR spectrum of **10b** in $CDCl_3$



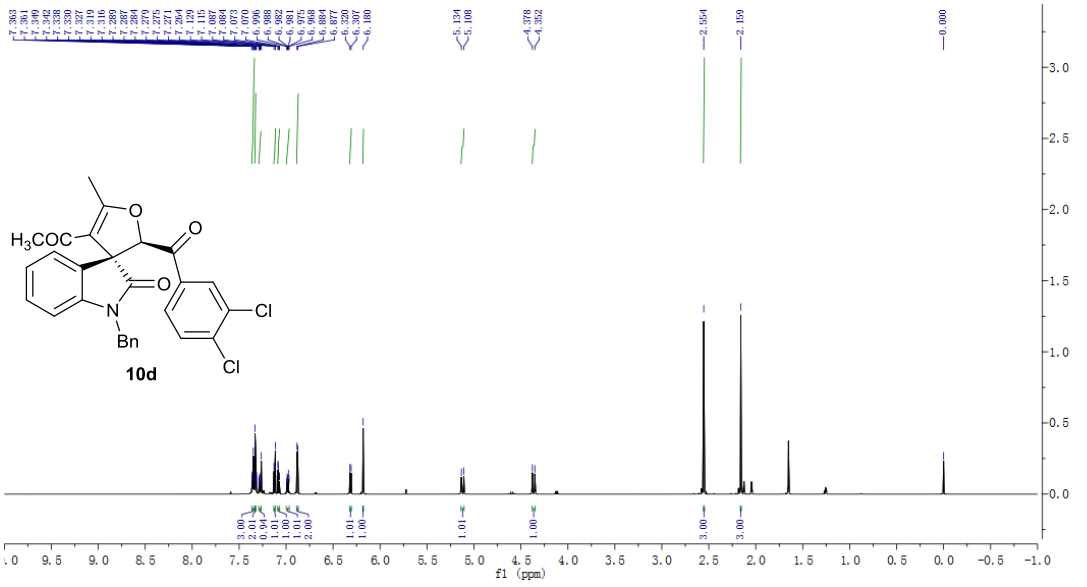
^{1}H NMR spectrum of **10c** in $CDCl_3$ (d.r. = 16:1)



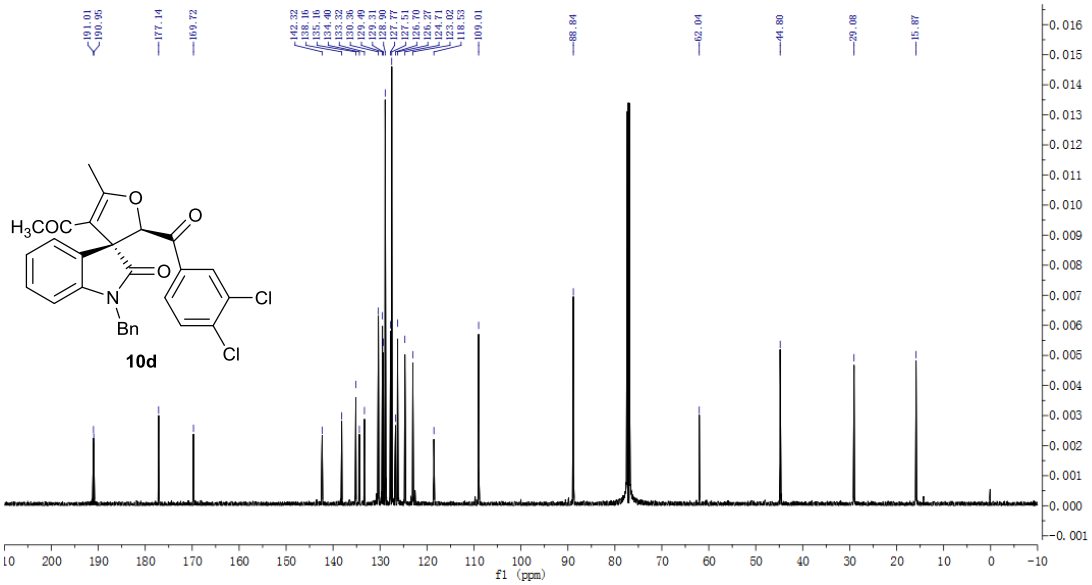
^{13}C NMR spectrum of **10c** in $CDCl_3$



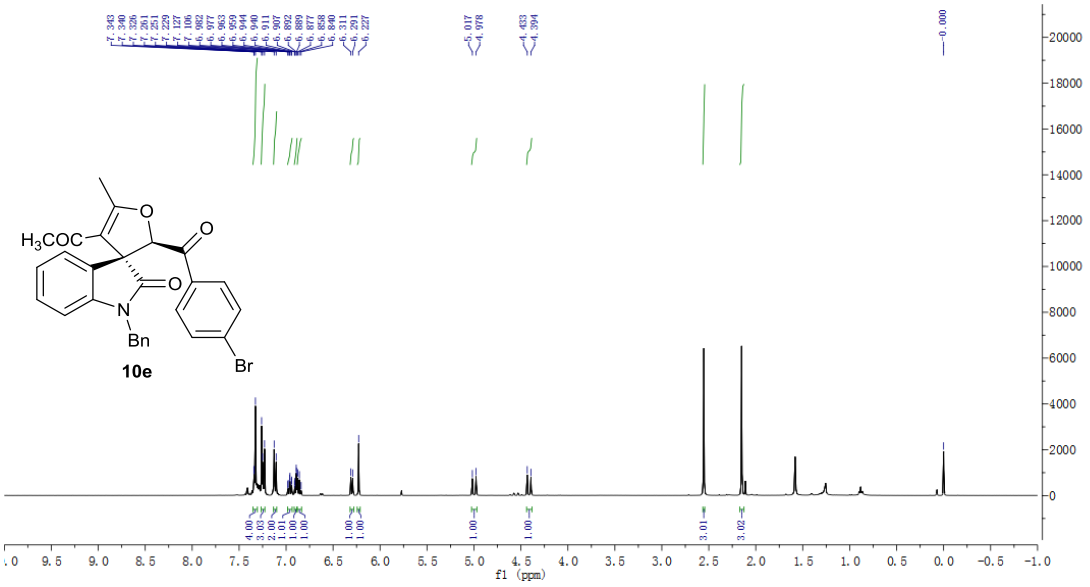
^{19}F NMR spectrum of **10c** in $CDCl_3$



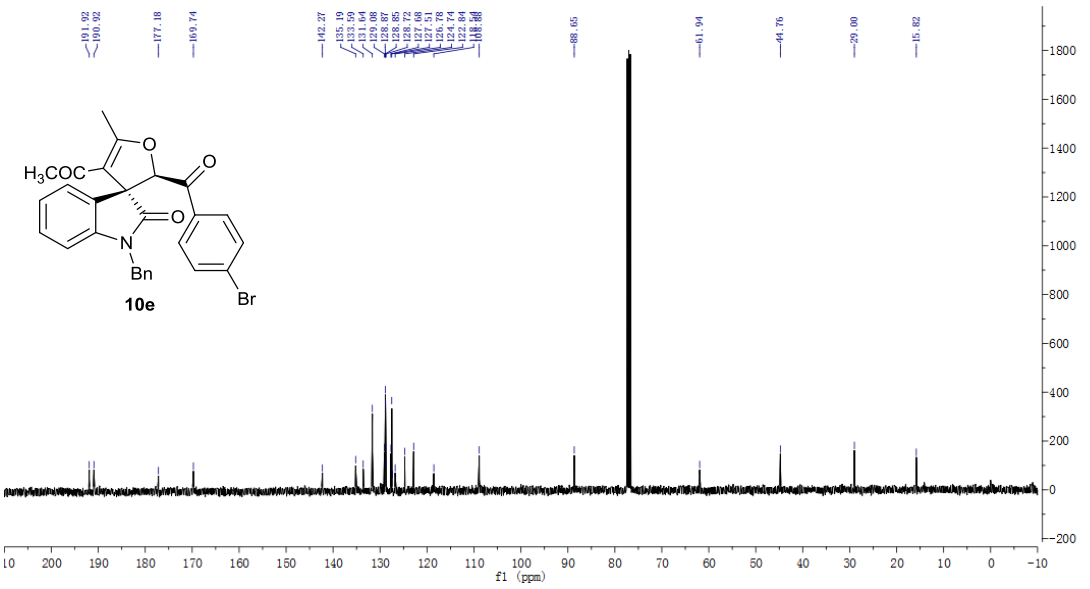
^{1}H NMR spectrum of **10d** in $CDCl_3$ (d.r. = 8:1)



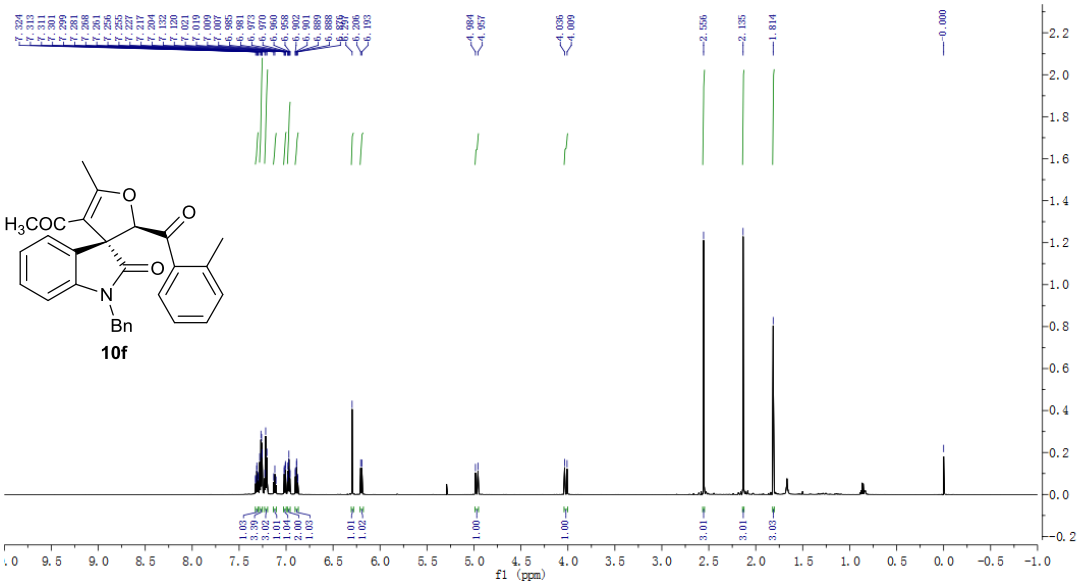
^{13}C NMR spectrum of **10d** in $CDCl_3$



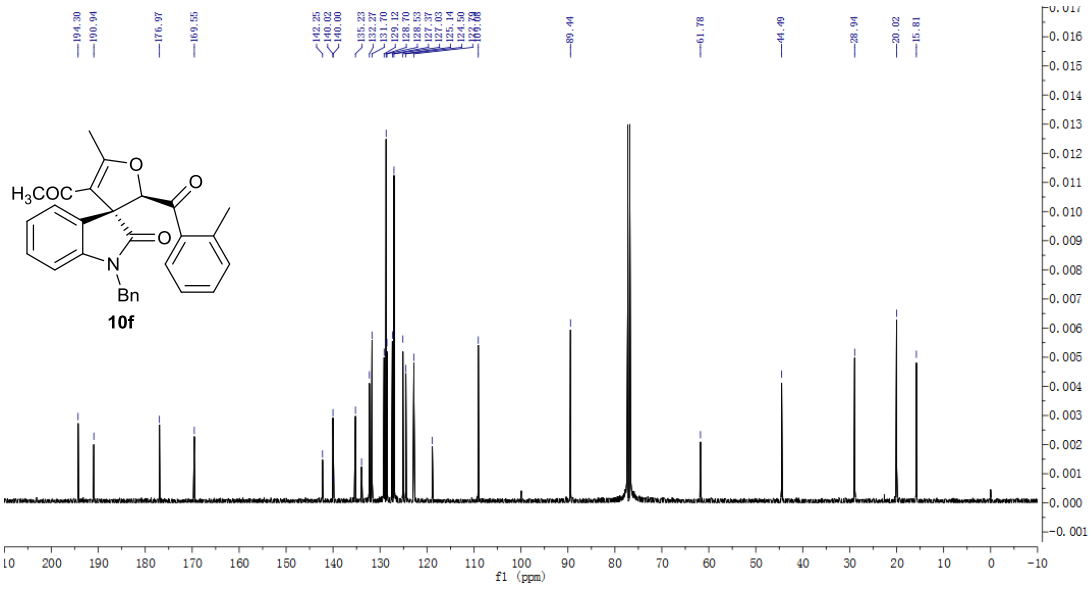
^{1}H NMR spectrum of **10e** in $CDCl_3$ (d.r. = 10:1)



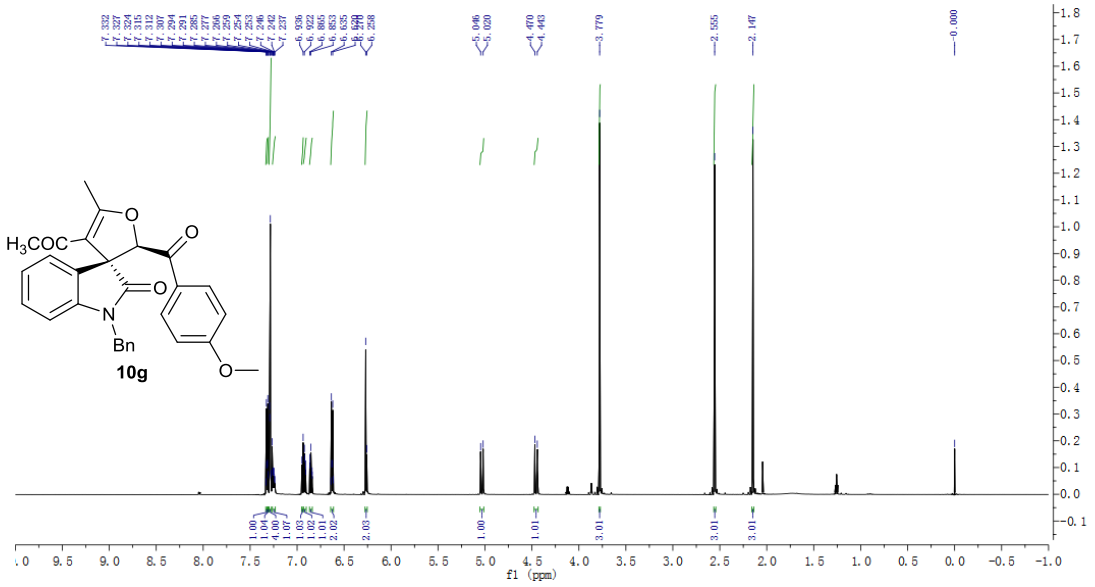
^{13}C NMR spectrum of **10e** in $CDCl_3$



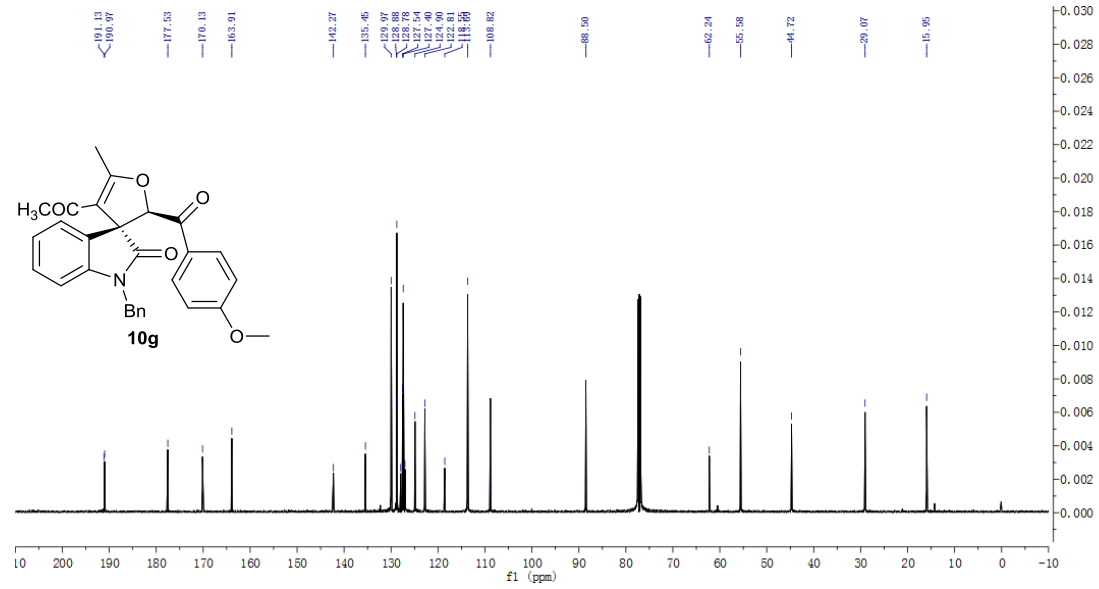
^{1}H NMR spectrum of **10f** in $CDCl_3$ (d.r. = 20:1)



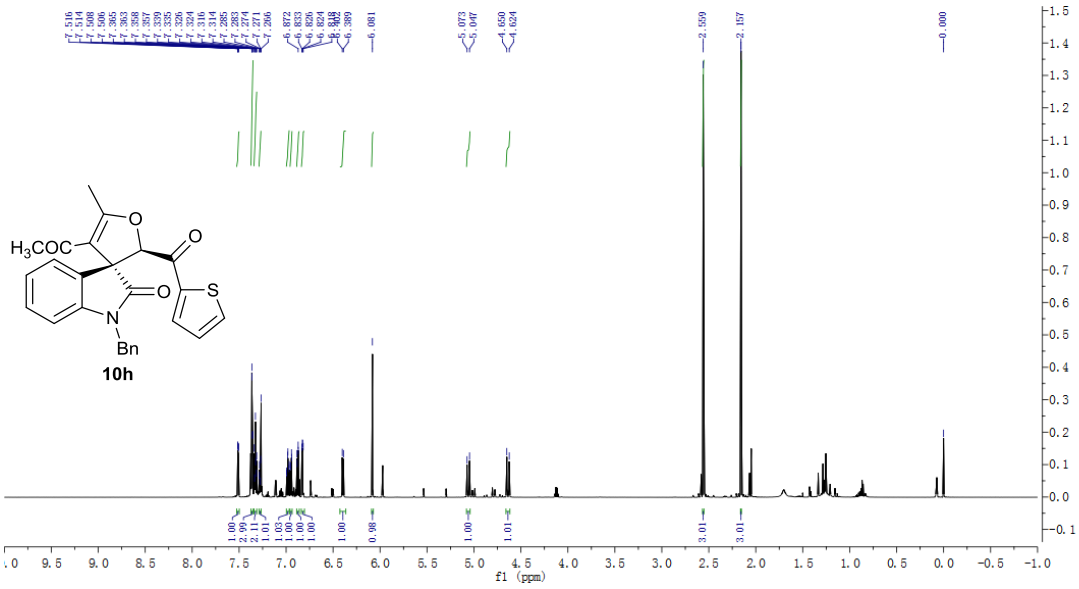
^{13}C NMR spectrum of **10f** in $CDCl_3$



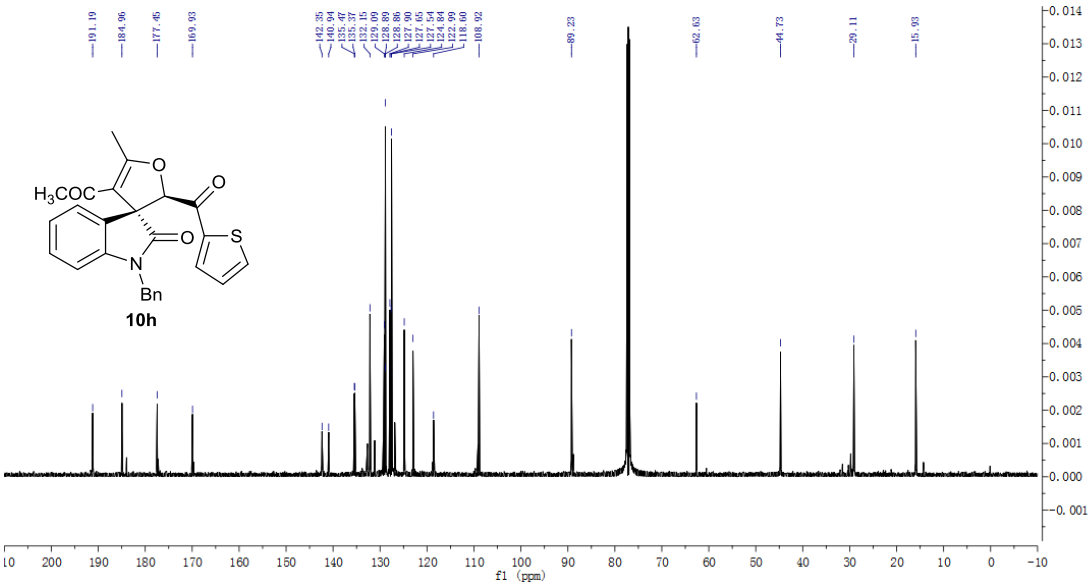
^{1}H NMR spectrum of **10g** in $CDCl_3$ (d.r. = 18:1)



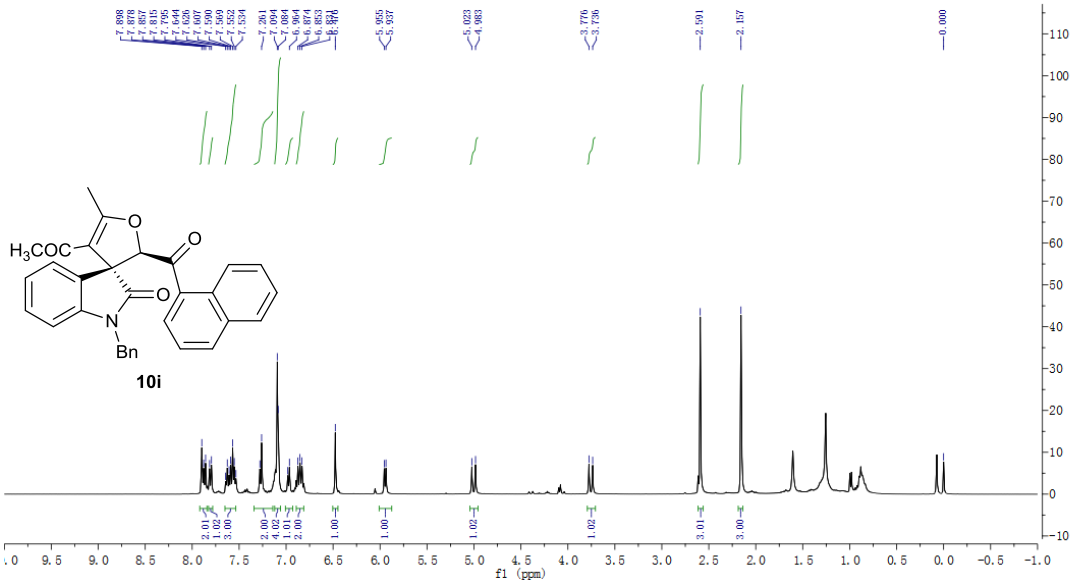
^{13}C NMR spectrum of **10g** in $CDCl_3$



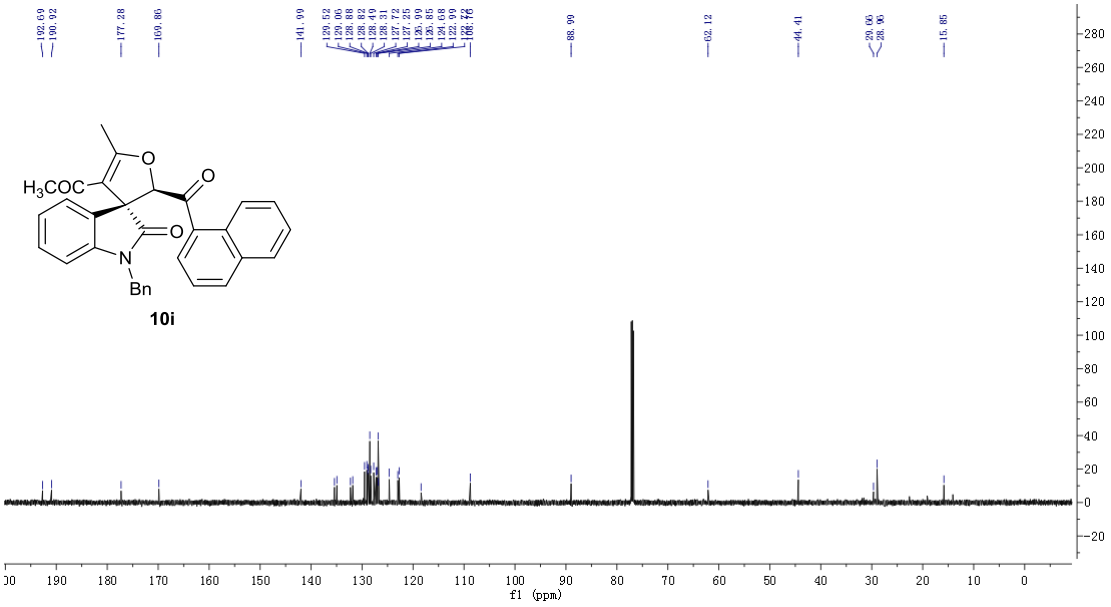
^{1}H NMR spectrum of **10h** in $CDCl_3$ (d.r. = 5:1)



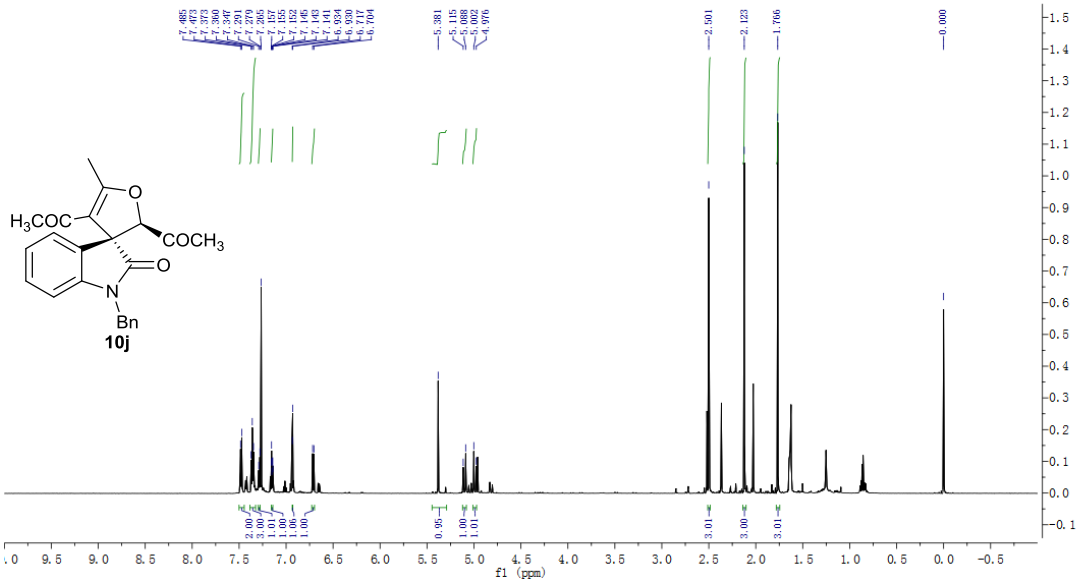
^{13}C NMR spectrum of **10h** in $CDCl_3$



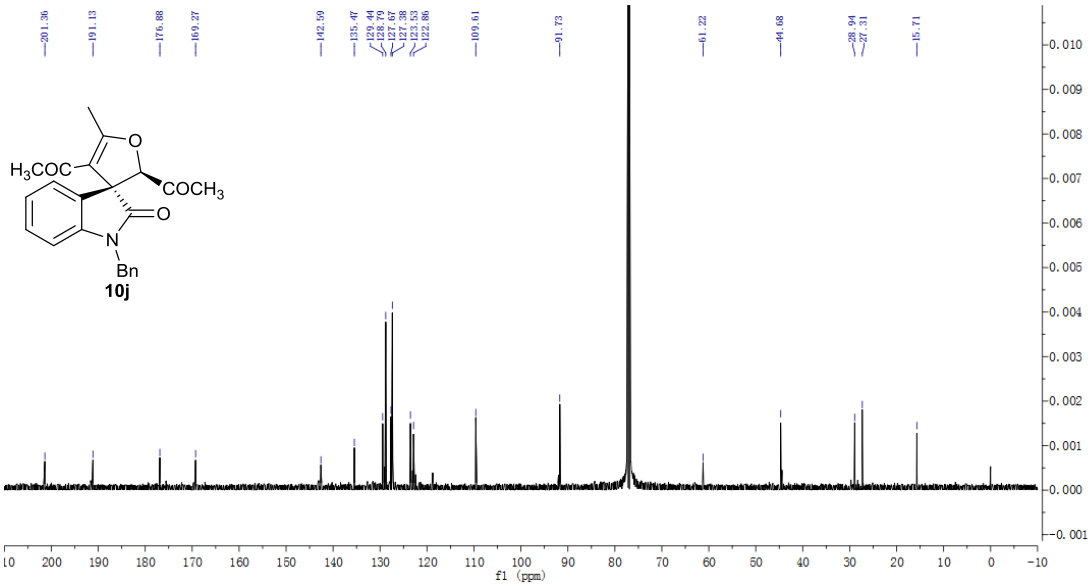
^{1}H NMR spectrum of **10i** in $CDCl_3$ (d.r. = 5:1)



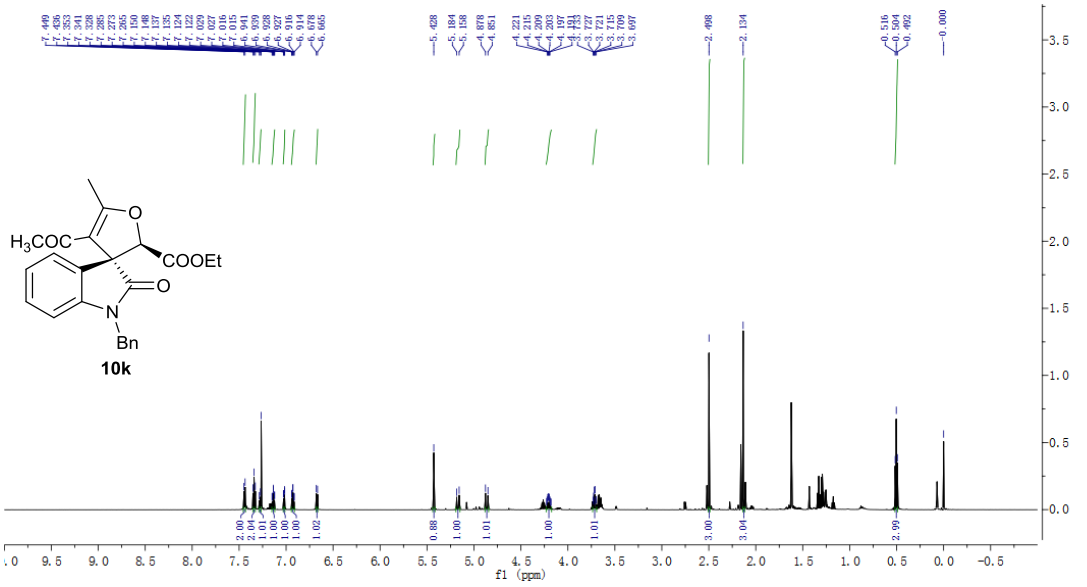
^{13}C NMR spectrum of **10i** in $CDCl_3$



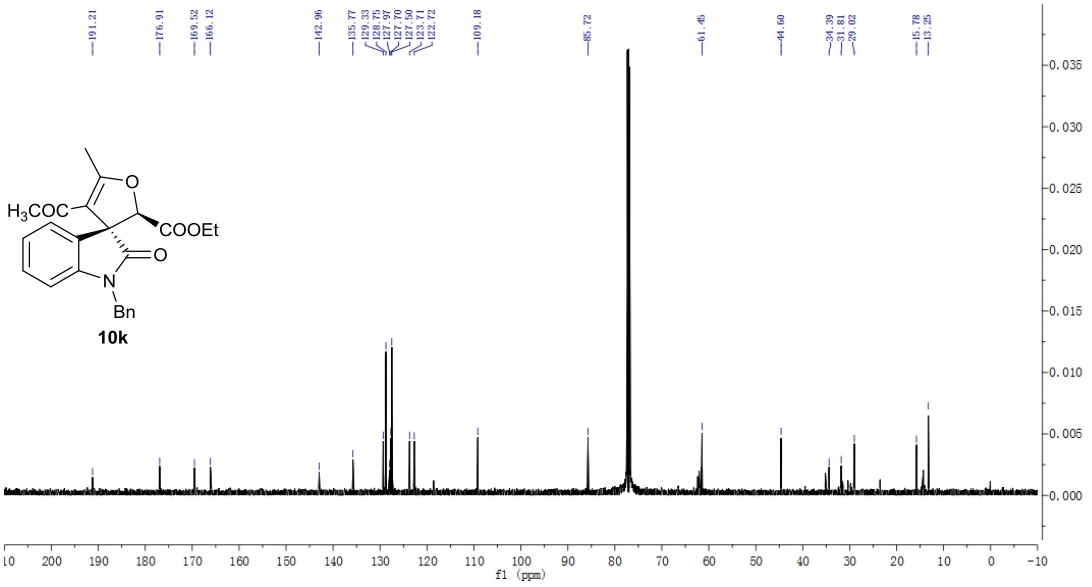
^{1}H NMR spectrum of **10j** in $CDCl_3$ (d.r. = 6:1)



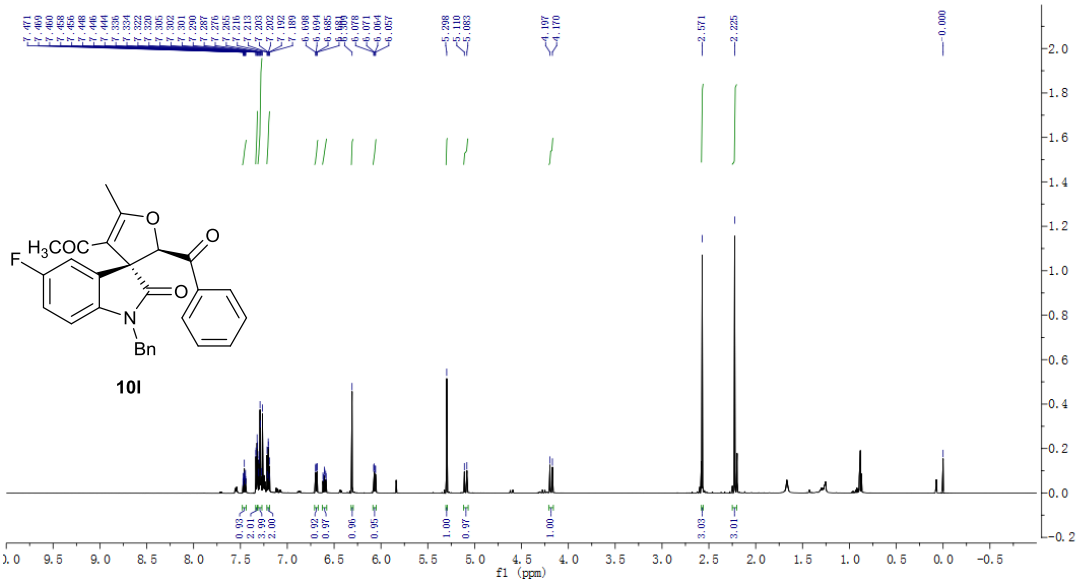
^{13}C NMR spectrum of **10j** in $CDCl_3$



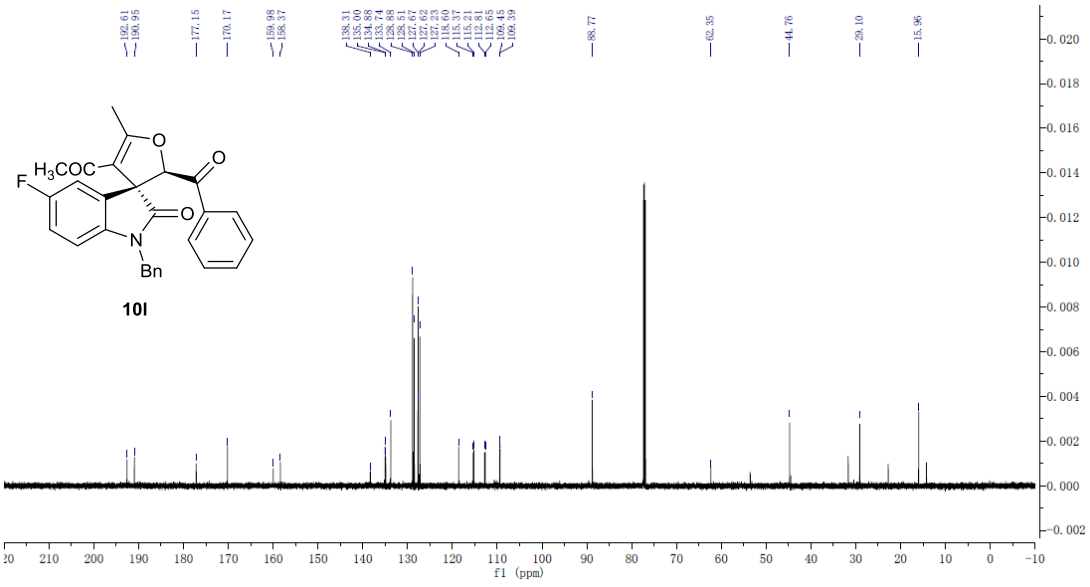
^{1}H NMR spectrum of **10k** in $CDCl_3$ (d.r. = 5:1)



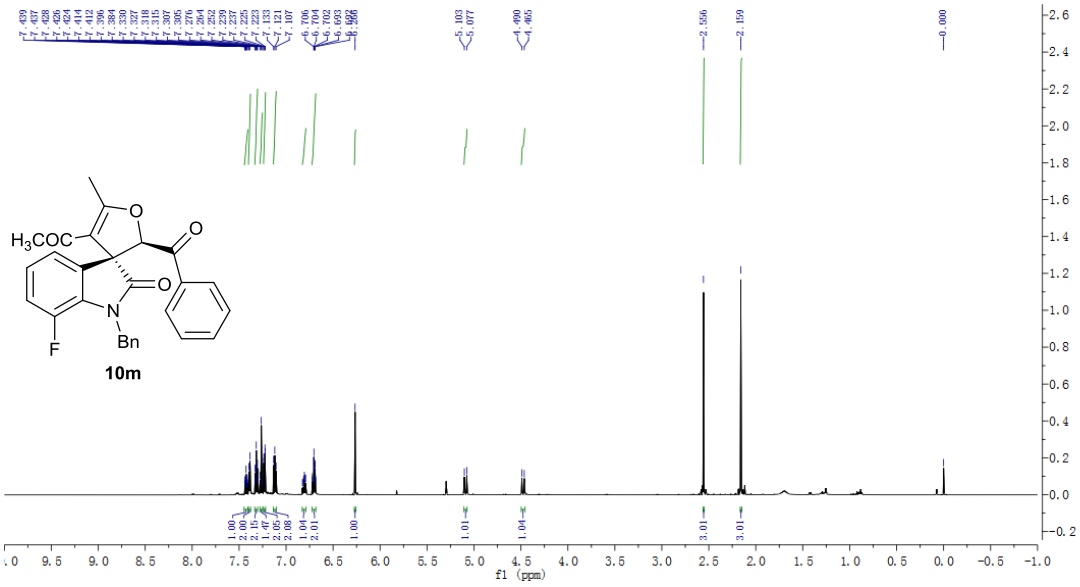
^{13}C NMR spectrum of **10k** in $CDCl_3$



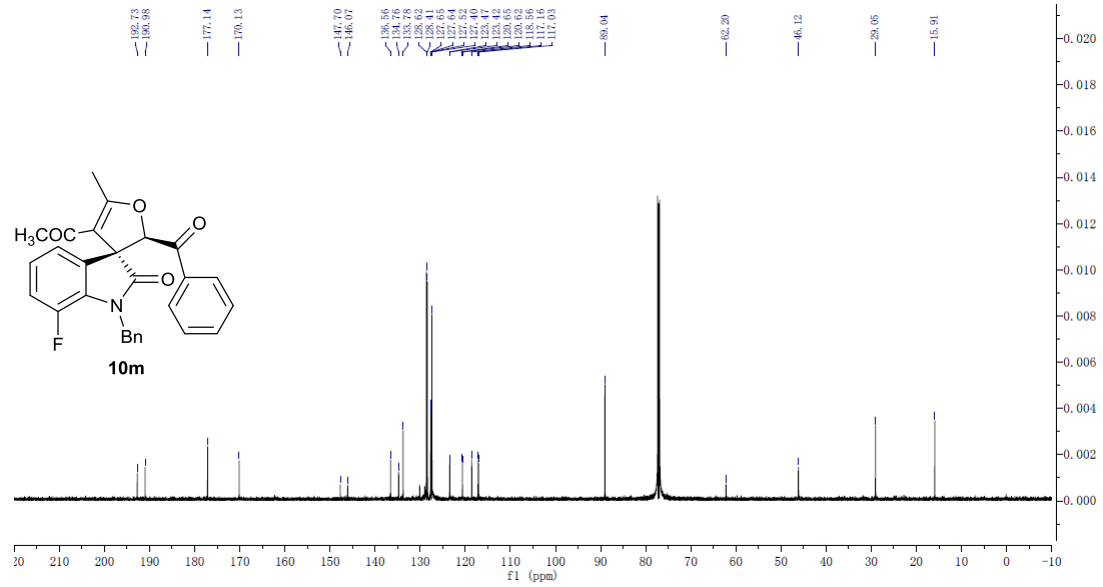
^{1}H NMR spectrum of **10l** in $CDCl_3$ (d.r. = 10:1)



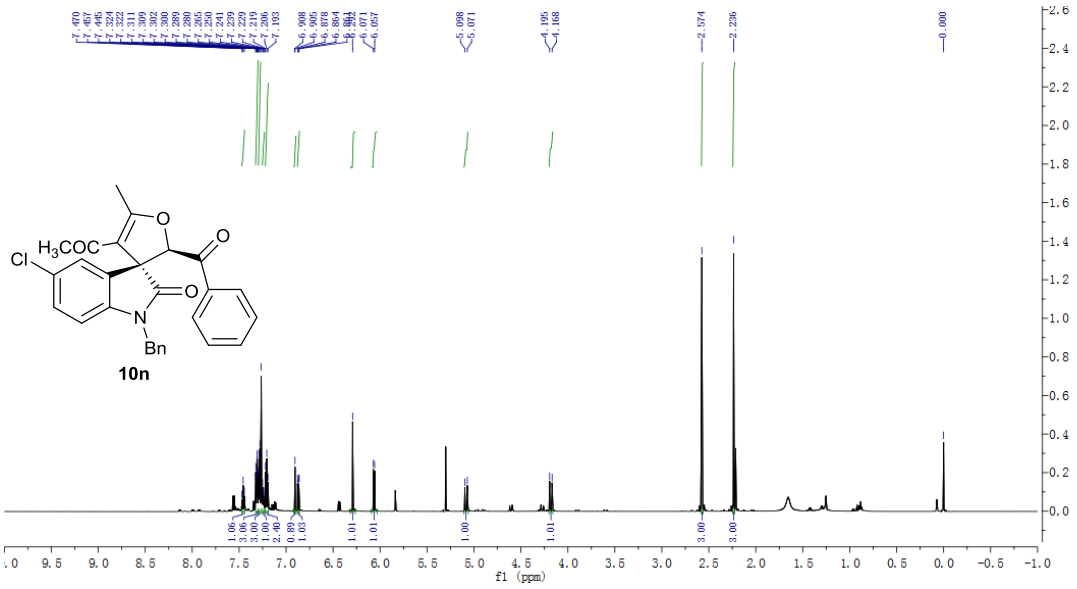
^{13}C NMR spectrum of **10l** in $CDCl_3$



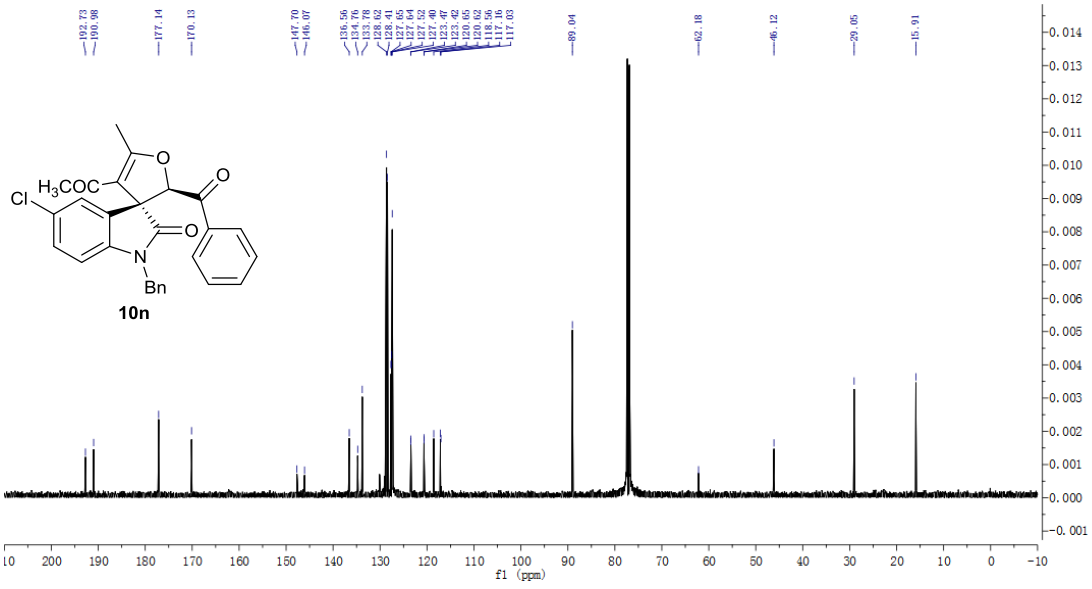
^{1}H NMR spectrum of **10m** in $CDCl_3$ (d.r. = 16:1)



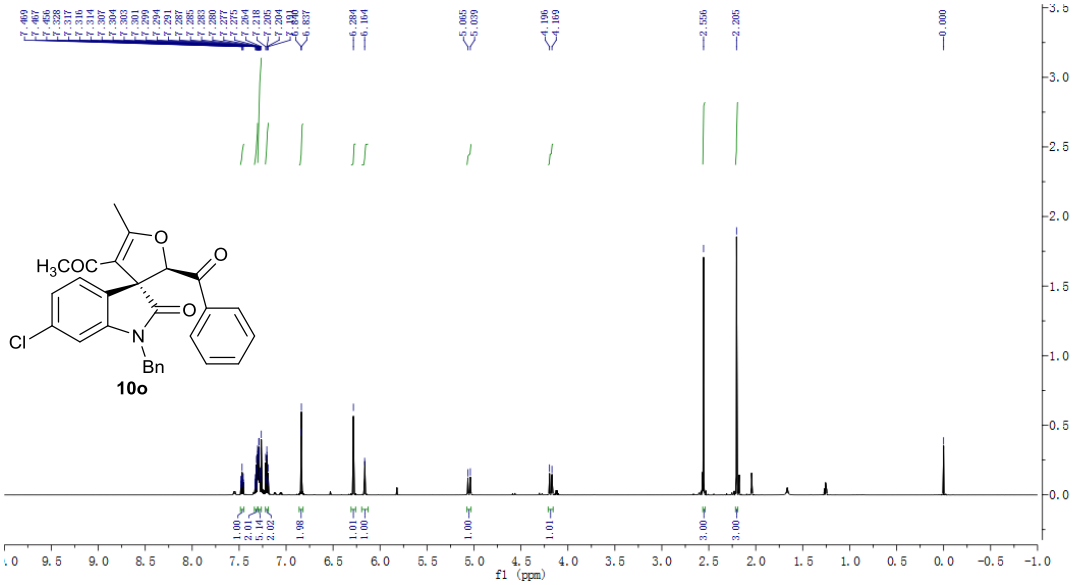
^{13}C NMR spectrum of **10m** in $CDCl_3$



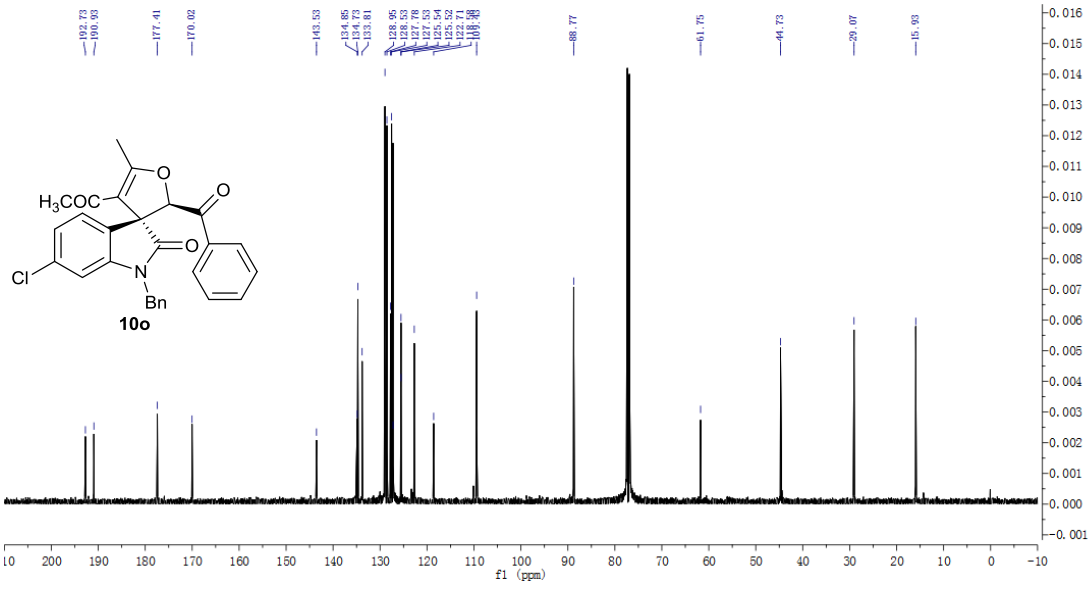
^{1}H NMR spectrum of **10n** in $CDCl_3$ (d.r. = 5:1)



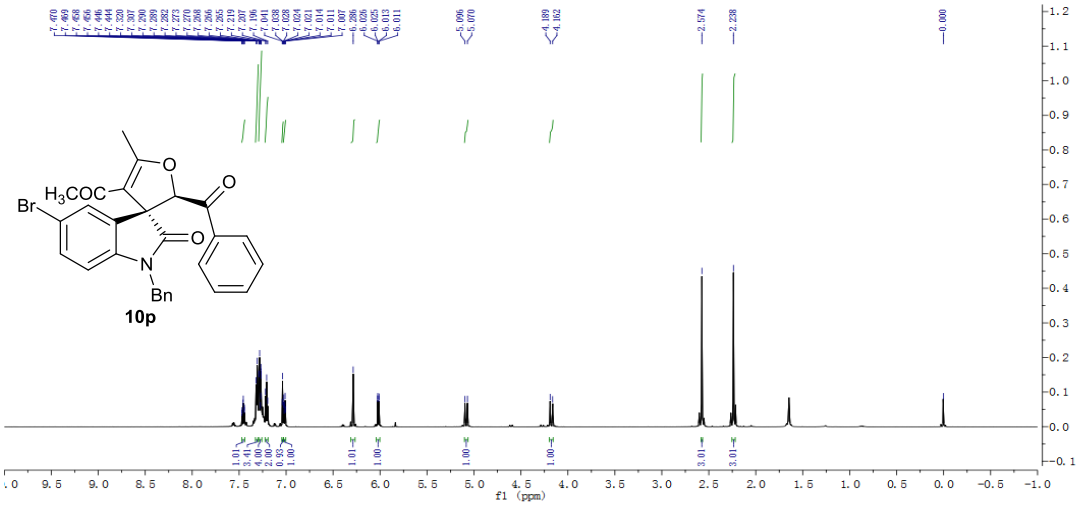
^{13}C NMR spectrum of **10n** in $CDCl_3$



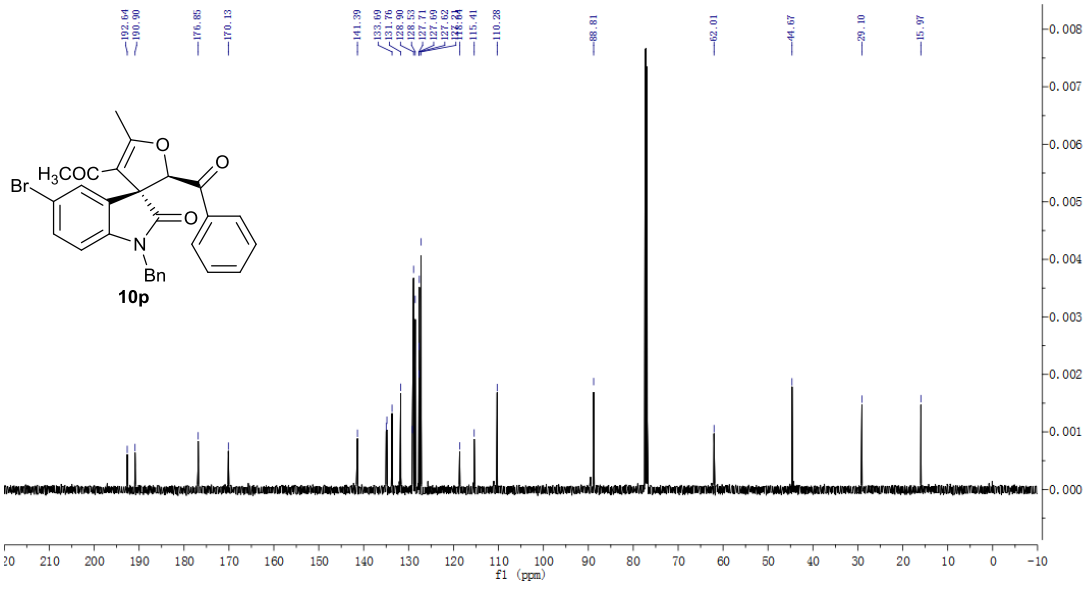
^{1}H NMR spectrum of **10o** in $CDCl_3$ (d.r. = 15:1)



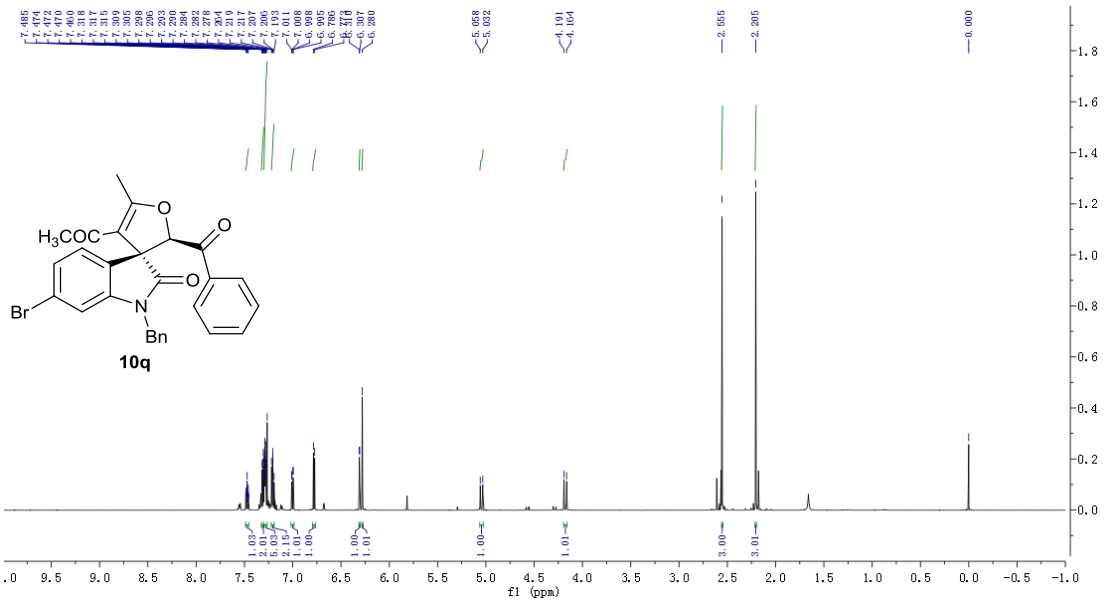
^{13}C NMR spectrum of **10o** in $CDCl_3$



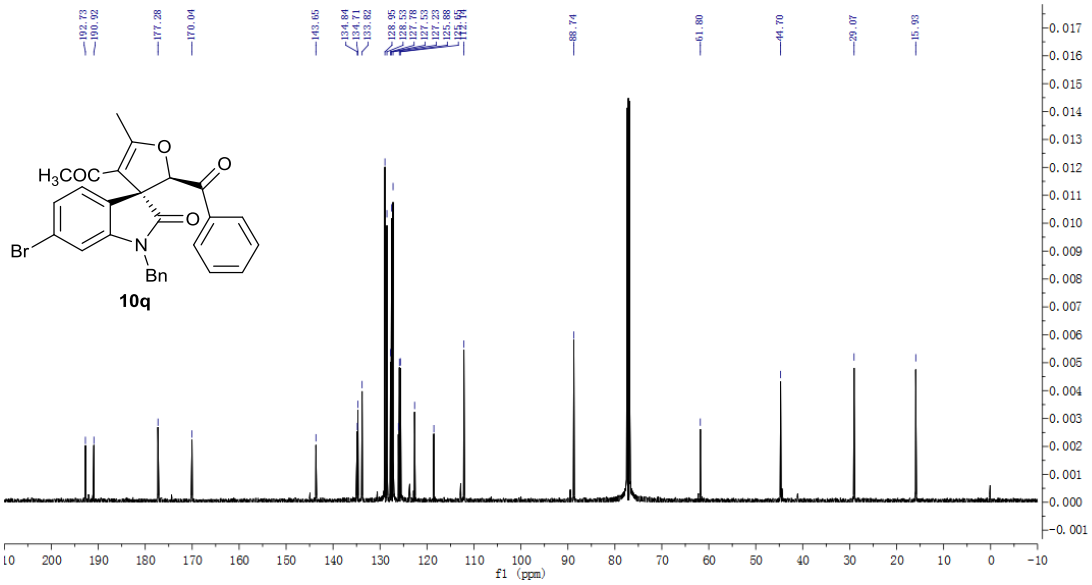
^{1}H NMR spectrum of **10p** in $CDCl_3$ (d.r. = 13:1)



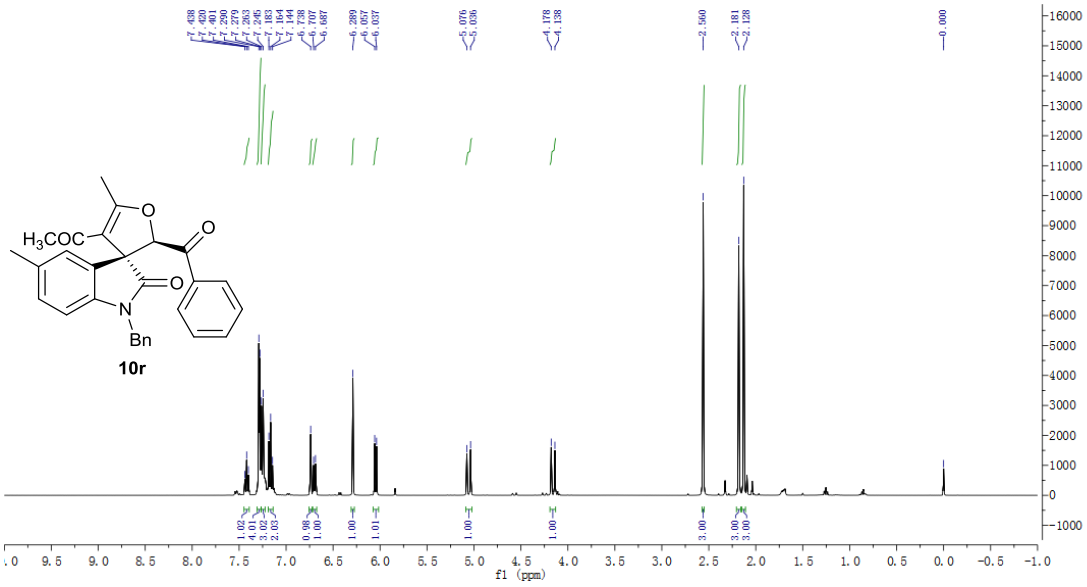
^{13}C NMR spectrum of **10p** in $CDCl_3$



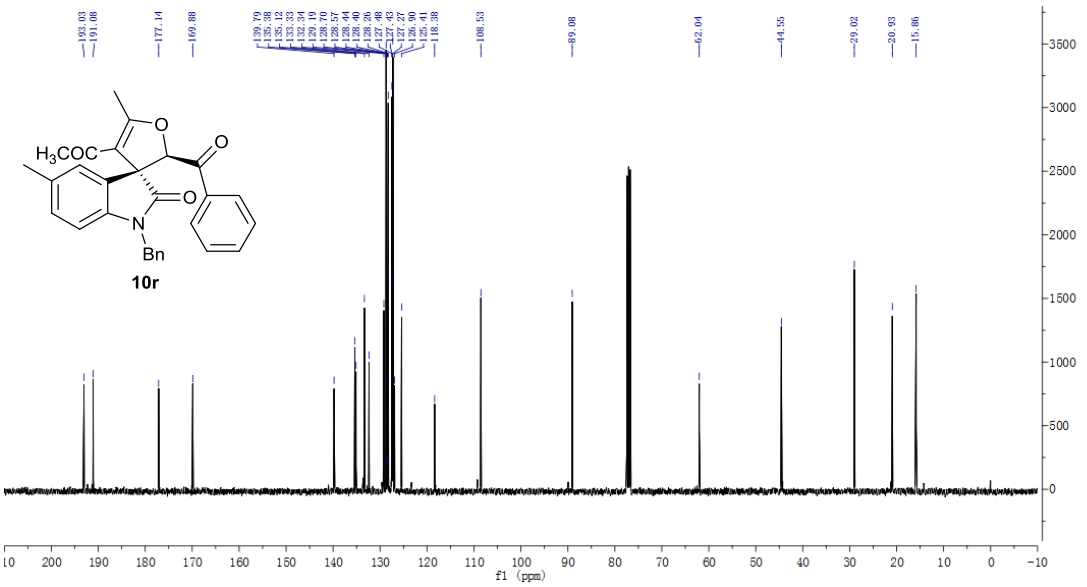
^{1}H NMR spectrum of **10q** in $CDCl_3$ (d.r. = 10:1)



^{13}C NMR spectrum of **10q** in $CDCl_3$



^{1}H NMR spectrum of **10r** in $CDCl_3$ (d.r. = 18:1)



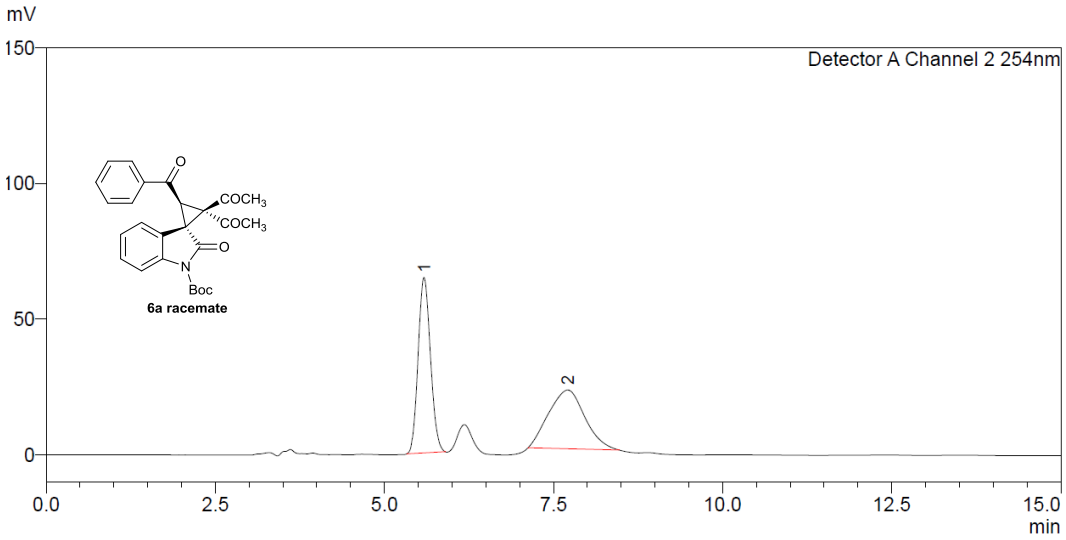
^{13}C NMR spectrum of **10r** in $CDCl_3$

HPLC Spectrum

Peak Analysis Report

Detector A Channel 2 254nm

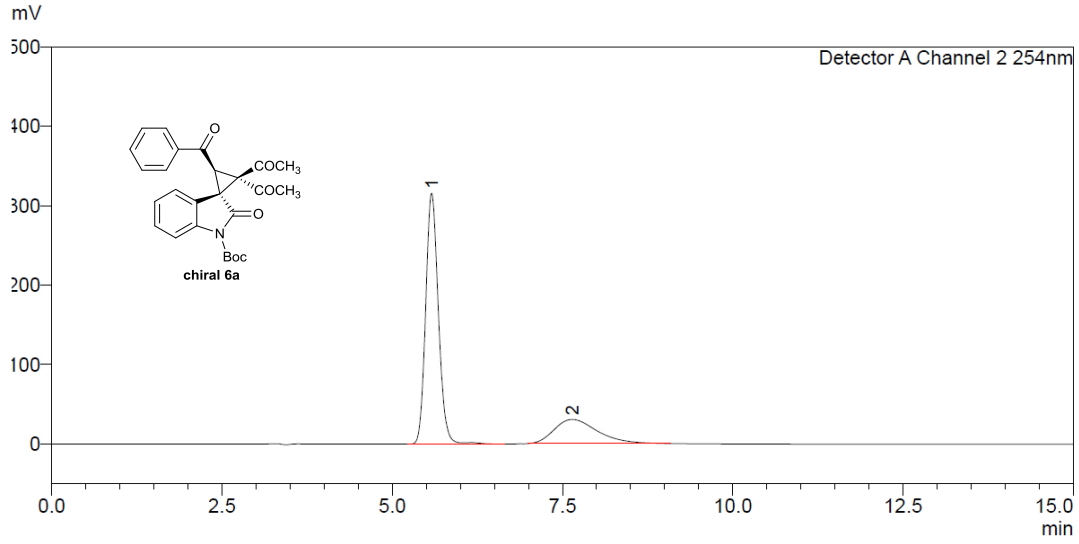
No.	Ret. Time	Height (mAu)	Area (mAu*min)	Rel. Area (%)
1	5.585	64711	821155	50.472
2	7.710	21661	805795	49.528
Total		86372	1626950	100.000



Peak Analysis Report

Detector A Channel 2 254nm

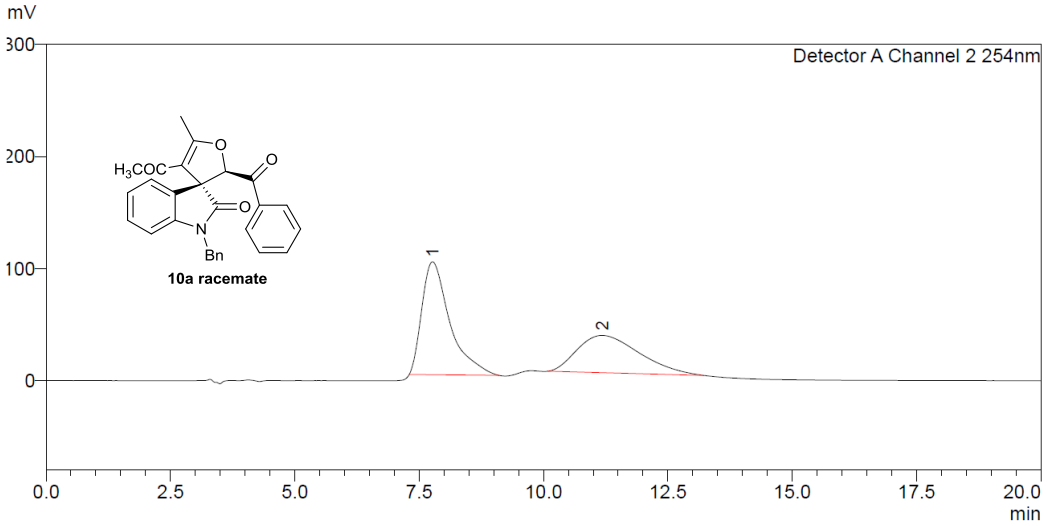
No.	Ret. Time	Height (mAu)	Area (mAu*min)	Rel. Area (%)
1	5.577	315843	4097696	69.888
2	7.577	58781	1765578	30.112
Total		374624	5863274	100.000



Peak Analysis Report

Detector A Channel 2 254nm

No.	Ret. Time	Height (mAu)	Area (mAu*min)	Rel. Area (%)
1	7.768	100795	3948609	57.677
2	11.179	33268	2897464	42.323
Total		134063	6846072	100.000



Peak Analysis Report

Detector A Channel 2 254nm

No.	Ret. Time	Height (mAu)	Area (mAu*min)	Rel. Area (%)
1	7.876	102751	4190718	65.916
2	11.435	27532	2166958	34.084
Total		130283	6357676	100.000