Supporting Information

Asymmetric [3+2] Cycloaddition of Donor–Acceptor Cyclopropanes with Azadienes Enabled by Brønsted Base Catalysis

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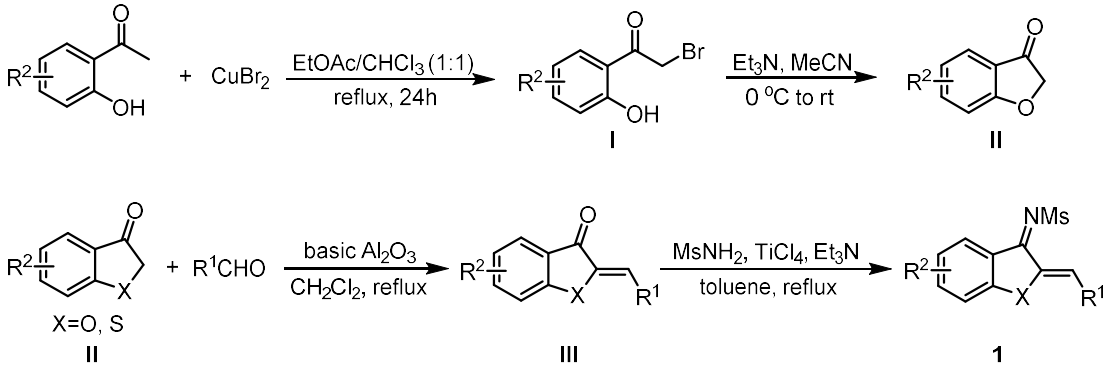
1. General information

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. All the reagents were obtained from commercial supplier and used as received, without further purification unless otherwise noted. Solvents used in the reactions were distilled from appropriate drying agents prior to use. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded respectively at 400 MHz, 100 MHz, 377 MHz on Bruker Avance 400M. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz) and signal area integration in natural numbers. Optical rotations were measured in the indicated solvents on Perkin Elmer polarimeter (Polartronic MH8) with a 10 cm cell (c given in g/100 mL). Flash column chromatography was performed using 200-300 mesh silica gel. Enantiomeric excess (*ee*) were determined by HPLC analysis on a Shimadzu LC-20A, using Daicel Chiralpak IA columns, IC columns, IE columns, and OD-H columns. High resolution mass spectra were obtained on Waters Vion® IMS Q-TOf andThermo Fisher Scientific orbtrip120 in ESI mode. The X-ray single-crystal determination was performed on Bruker D8 VENTURE X-ray single crystal diffractometer. The catalysts were commercially available.

2. Preparation of azadienes 1

Route 1 :



The azadienes **1** were prepared according to the literature procedures.[1] To a solution of *o*-Acetyl phenol (30.0 mmol, 1.0 equiv.) in $CHCl_3$ was added $CuBr_2$ (51.0 mmol, 1.7 equiv.) dissolved in ethyl acetate, the reaction was kept at reflux until the starting material was consumed. The reaction mixture was concentrated under vacuum and the

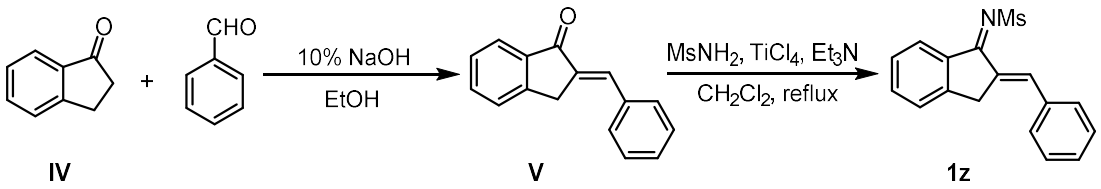
residue was purified by flash chromatography on silica gel to give the desired compound **I**.

The compound **I** (20.0 mmol, 1.0 equiv.) was dissolved in MeCN, then cooled to 0 °C, Et_3N (40.0 mmol, 2.0 equiv.) was slowly added. The solution was quenched with water (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel to afford the product **II**.

Under nitrogen, aluminium oxide (50.0 mmol, 10 equiv., activated, basic) was added to a solution of ketones **II** (10.0 mmol, 1.0 equiv.) and aldehydes (20.0 mmol, 2.0 equiv.) in CH_2Cl_2 (40 mL). The mixture was thoroughly stirred at 40 °C under nitrogen. The progress of the reaction was monitored by TLC analysis. The suspension was filtered off, the residue washed with CH_2Cl_2, and the washes were combined with the filtrate. The solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel and recrystallized from ethyl acetate/hexane to give pure enones **III**.

Methanesulfonamide (3.0 mmol, 1.0 equiv.) and compound **III** (3.0 mmol, 1.0 equiv.) were added in a round bottom flask under nitrogen, then toluene (30 mL) was added and cooled to 0 °C. Et_3N (6.0 mmol, 2.0 equiv.) and $TiCl_4$ (3.0 mmol, 1.0 equiv.) were slowly added and the mixture was kept at reflux under nitrogen overnight. The solution was then cooled to room temperature, quenched with water (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel to afford azadienes **1**.

Route 2 :

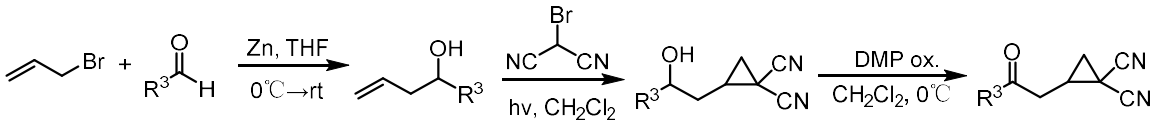


The azadienes **1z** was prepared according to the reported literature procedures.[2] 1-Indanone **IV** was added in ethanol followed by the addition of equivalent amount of aryl aldehydes. The 10% aqueous solution of NaOH was added drop wise to the mixture

at room temperature which resulted in precipitation. The mixture was then cooled for 30 minutes, filtered, washed with cold methanol, and dried to solid compounds **V**.

To a solution of methanesulfonamide (5.0 mmol) and solid compounds **V** (5.0 mmol) in DCM (15 mL) were successively added Et_3N (10 mmol) and $TiCl_4$ (5.0 mmol) at 0 ^oC with stirring. The resulting mixture was heated at reflux overnight. After being cooled to room temperature and quenched with water (100 mL), the organic layer was separated and the aqueous layer was extracted with DCM (3 × 50 mL). The combined organic phase was washed with water (3 × 20 mL) and dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel to afford azadienes **1z**.

3. Preparation of cyclopropanes 2



VI VII VIII **2**

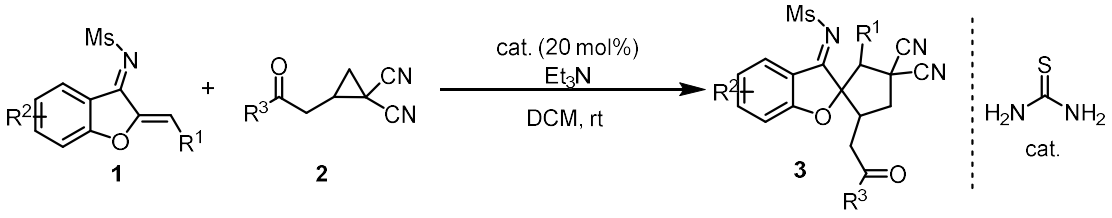
Cyclopropanes was synthesized according to literature procedure.[3] To the corresponding aldehyde **VI** (50 mmol, 1.0 equiv.) in THF (50 mL) were added allyl bromide (5.19 mL, 60 mmol, 1.2 equiv.) followed by Zn dust (4.25 g, 65 mmol, 1.3 equiv.) in one portion. The reaction was cooled to 0 ^oC in an ice-bath. With vigorous stirring, a saturated aqueous solution of NH_4Cl (50 mL) was added dropwise from an addition funnel over 1 h. The ice bath was removed following the addition of NH_4Cl and the reaction warmed to rt. After 2 h at rt, an aqueous solution of citric acid (100 mL) was added and the mixture vigorously stirred for 15 min. Diethyl ether (120 mL) was added and the organic layer separated. The organic layer was then washed sequentially with aq. HCl (1 M, 50 mL), sat. aq. $NaHCO_3$ and sat. aq. brine, and the combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude products were then purified by vacuum distillation or column chromatography to afford the desired products **VII**.

In a 100 mL Schlenk flask was added dry CH_2Cl_2 (70 mL, 0.15 M). The flask was purged with argon, fitted with an argon balloon and then sonicated for 20 min to de-gas the solvent. Bromomalononitrile (2.17 g, 15 mmol, 1.5 equiv.) and the corresponding homoallyl alcohol **VII** (10 mmol, 1 equiv.) were then added and the reaction mixture

subjected to photo-irradiation (365-370 nm, 15 V, 1 A, 45 W). Reaction progress was monitored by crude NMR. After full consumption of the homoallyl alcohol, photoirradiation was halted and the reaction mixture was cooled to 0 °C. Triethylamine (2.09 mL, 15 mmol, 1.5 eq.) was added and the reaction stirred for 2 h. The crude mixture was poured into a round-bottomed flask and concentrated under reduced pressure, then directly column chromatographed (silica gel) to afford the desired cyclopropanes **VIII** as mixtures of diastereomers.

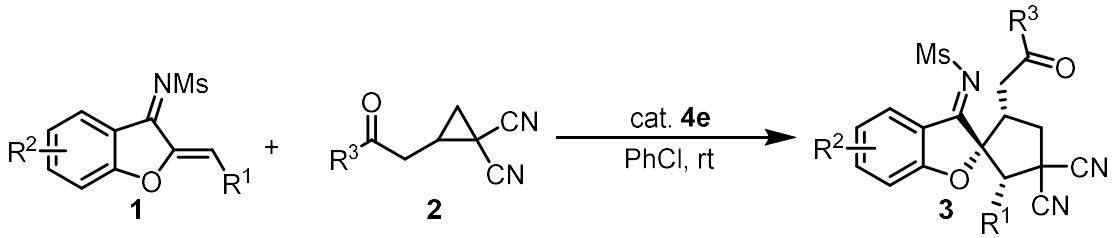
The corresponding cyclopropyl alcohol **VIII** (5 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (120 mL) and cooled to 0 °C. Dess-Martin periodinane (6 mmol, 1.2 equiv.) was added in two portions with a 10 min interval. The mixture was stirred for 2 h while slowly warming. The crude mixture was then concentrated to one-third volume and column chromatographed (silica gel) to afford the desired product **2**.

4. General procedure for the racemic [3 + 2] cycloaddition



A flame-dried vial equipped with a magnetic stirring bar was charged with benzofuranone **1** (0.1 mmol, 1.0 equiv.), catalyst (0.002 mmol, 0.02 equiv.), Et_3N (0.002 mmol, 0.02 equiv.) and CH_2Cl_2 (1.0 mL) were added to the vial which was then sealed with a septum. The vial was connected to an argon-vacuum line, evacuated, backfilled with argon and then filled with a solution of ketone **2** (0.15 mmol, 1.5 equiv.) in CH_2Cl_2 (1.0 mL). The mixture was then reacted at room temperature for 2 hours. After confirming full conversion by TLC, the reaction mixture was filtered through a short pad of Celite®. The solvent was then evaporated in vacuo and the crude reaction mixture was purified by column chromatography on silica gel to give the corresponding racemic product **3**.

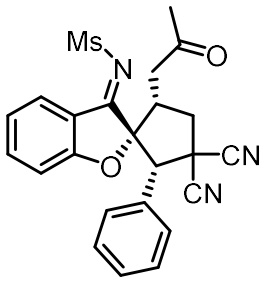
5. General procedure for the enantioselective [3+2] cycloaddition



A flame-dried vial equipped with a magnetic stirring bar was charged with benzofuranone **1** (0.1 mmol, 1.0 equiv.), Catalyst **4e** (0.002 mmol, 0.02 equiv.) and PhCl (1.0 mL) were added to the vial which was then sealed with a septum. The vial was connected to an argon-vacuum line, evacuated, backfilled with argon and then filled with a solution of ketone **2** (0.15 mmol, 1.5 equiv.) in PhCl (1.0 mL). The mixture was allowed to react for 24-48 h at rt. After confirming full conversion by TLC, the reaction mixture was filtered through a short pad of Celite®. The solvent was then evaporated in vacuo and the crude reaction mixture was purified by column chromatography on silica gel to give the corresponding product **3**.

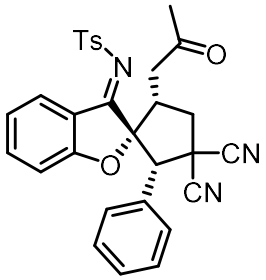
6. Characterization of the Products of 3

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(2-oxopropyl)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3a)



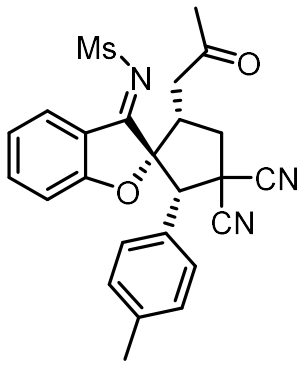
White solid, 43.4 mg. 97% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 7:1 dr. Mp = 86.9-87.3 ℃, $[\alpha]_D^{25}$ = +66.15 (*c* = 0.214, $CHCl_3$). 91% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.27 (d, *J* = 8.2 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.22 (dt, *J* = 13.3, 5.8 Hz, 4H), 7.06 (t, *J* = 7.7 Hz, 1H), 3.92 (s, 1H), 3.44 (dd, *J* = 14.3, 9.6 Hz, 1H), 3.30 (s, 3H), 3.28 – 3.18 (m, 1H), 2.77 – 2.58 (m, 2H), 2.49 (dd, *J* = 18.5, 4.2 Hz, 1H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.1, 177.5, 169.5, 140.0, 131.1, 130.1, 129.9, 129.2, 128.5, 123.4, 117.9, 115.9, 115.5, 112.5, 98.8, 64.0, 44.4, 43.2, 43.0, 42.2, 39.0, 30.0. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 22.945 min (major), 28.097 min (minor). **HRMS (ESI)**: calcd for $C_{24}H_{22}N_3O_4S$ $[M+H]^+$ 448.1326, found 448.1323.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(2-oxopropyl)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)-4-methylbenzenesulfonamide(3a')



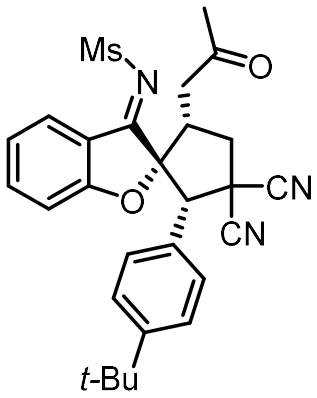
White solid, 35.6 mg. 68% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 6:1 dr. Mp = 85.4-86.7 ℃, $[\alpha]_D^{25}$ = +70.38 (*c* = 0.152, $CHCl_3$). 90% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.46 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.67 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.2 – 7.24 (m, 1H), 7.21 (t, *J* = 7.4 Hz, 3H), 7.11 (t, *J* = 7.7 Hz, 1H), 3.79 (s, 1H), 3.36 (dd, *J* = 14.4, 9.8 Hz, 1H), 3.15 (d, *J* = 9.3 Hz, 1H), 2.71 – 2.56 (m, 2H), 2.51 (m, 4H), 2.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.1, 176.7, 169.7, 144.4, 139.9, 137.8, 131.3, 130.1, 129.9, 129.1, 128.6, 127.3, 123.5, 118.0, 115.8, 115.6, 112.5, 99.0, 63.6, 44.4, 43.1, 42.3, 38.9, 30.1, 21.8. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 40.287 min (major), 92.622 min (minor). **HRMS (ESI)**: calcd for $C_{30}H_{25}N_3O_4S$ $[M+H]^+$ 524.1566, found 524.1568.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(2-oxopropyl)-2'-(p-tolyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3b)



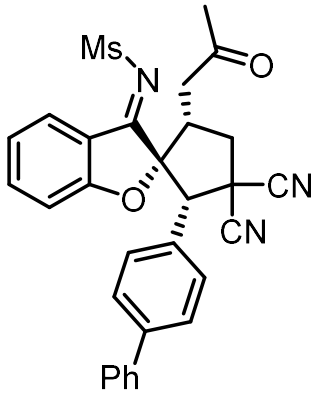
White solid, 43.8 mg. 95% yield. R_f = 0.3 (petroleum ether/ ethyl acetate= 2:1), 6:1 dr. Mp = 94.3–96.1 ℃, $[\alpha]_D^{25}$ = +48.33 (*c* = 0.418, $CHCl_3$). 90% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.28 (d, *J* = 8.2 Hz, 1H), 7.65 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.07 (ddd, *J* = 8.2, 7.2, 0.9 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 2H), 3.89 (s, 1H), 3.42 (dd, *J* = 14.3, 9.7 Hz, 1H), 3.30 (s, 3H), 3.22 (dt, *J* = 10.6, 5.3 Hz, 1H), 2.72 – 2.54 (m, 2H), 2.47 (dd, *J* = 18.5, 4.1 Hz, 1H), 2.21 (s, 3H), 2.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.2, 177.6, 169.6, 140.1, 140.0, 131.1, 129.9, 129.7, 125.4, 123.4, 118.0, 116.0, 115.6, 112.5, 98.9, 63.8, 44.5, 43.1, 43.0, 42.2, 39.2, 30.0, 21.2. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 21.537 min (major), 27.078 min (minor). **HRMS (ESI)**: calcd for $C_{25}H_{24}N_3O_4S$ $[M+H]^+$ 462.1482, found 462.1488.

N-((2*R*,2'*S*,5'*S*,*E*)-2'-(4-(tert-butyl)phenyl)-3',3'-dicyano-5'-(2-oxopropyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3c)



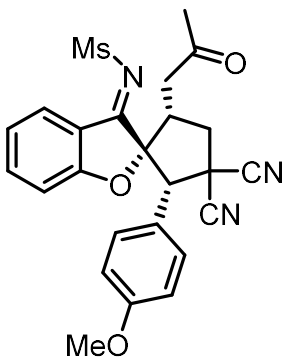
White solid, 46.6 mg. 95% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 6:1 dr. Mp = 65.8–68.4 ℃, $[\alpha]_D^{25}$ = +23.97 (*c* = 0.406, $CHCl_3$). 90% ee. **^{1}H NMR** (400 MHz, CDCl3, ppm) δ 8.29 (d, *J* = 8.2 Hz, 1H), 7.67 (ddd, *J* = 8.5, 7.1, 1.4 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.24 – 7.18 (m, 3H), 7.08 (t, *J* = 7.7 Hz, 1H), 3.92 (s, 1H), 3.42 (dd, *J* = 14.3, 9.6 Hz, 1H), 3.30 (s, 3H), 3.22 (dt, *J* = 9.8, 4.9 Hz, 1H), 2.71 – 2.55 (m, 2H), 2.46 (dd, *J* = 18.5, 4.1 Hz, 1H), 2.06 (s, 3H), 1.20 (s, 9H).**^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.2, 177.7, 169.6, 153.0, 140.0, 131.1, 129.5, 126.1, 125.5, 123.4, 118.0, 116.0, 115.6, 112.6, 99.0, 63.5, 44.8, 43.1, 43.0, 42.1, 39.3, 34.7, 31.2, 30.1. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 16.082 min (major), 20.892 min (minor). **HRMS (ESI)**: calcd for $C_{28}H_{30}N_3O_4S$ $[M+H]^+$ 504.1952, found 504.1954.

N-((2*R*,2'*S*,5'*S*,*E*)-2'-([1,1'-biphenyl]-4-yl)-3',3'-dicyano-5'-(2-oxopropyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3d)



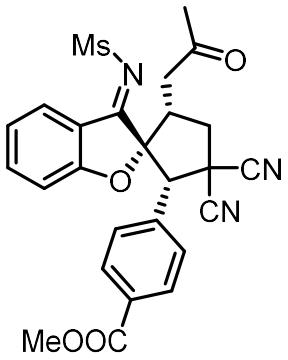
White solid, 49.5 mg. 94% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 5:1 dr. Mp = 115.1–118.4 ℃, $[\alpha]_D^{25}$ = +80.74 (*c* = 0.244, $CHCl_3$). 90% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.65 (ddd, *J* = 8.6, 7.2, 1.4 Hz, 1H), 7.54 – 7.41 (m, 6H), 7.41 – 7.34 (m, 2H), 7.35 – 7.28 (m, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.07 (ddd, *J* = 8.2, 7.2, 0.9 Hz, 1H), 3.98 (s, 1H), 3.45 (dd, *J* = 14.3, 9.7 Hz, 1H), 3.32 (s, 3H), 3.27 (dd, *J* = 9.5, 3.9 Hz, 1H), 2.73 – 2.59 (m, 2H), 2.51 (dd, *J* = 18.5, 4.2 Hz, 1H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.1, 177.6, 169.5, 142.8, 140.1, 139.9, 131.1, 130.3, 128.9, 127.8, 127.7, 127.4, 127.2, 123.5, 118.0, 115.9, 115.6, 112.5, 98.9, 63.7, 44.6, 43.1, 43.0, 42.1, 39.2, 30.0. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 22.223 min (major), 33.294 min (minor). **HRMS (ESI)**: calcd for $C_{30}H_{26}N_3O_4S$ $[M+H]^+$ 524.1639, found 524.1648.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-2'-(4-methoxyphenyl)-5'-(2-oxopropyl)-3H-spiro [benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3e)



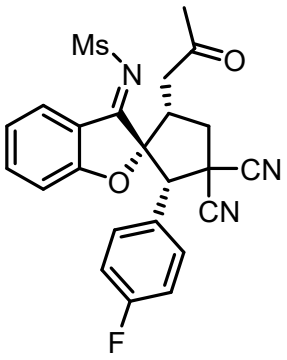
White solid, 44.9 mg. 94% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 5:1 dr. Mp = 61.8–62.9 ℃, $[\alpha]_D^{25}$ = +71.26 (*c* = 0.218, $CHCl_3$). 90% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.28 (d, *J* = 8.0 Hz, 1H), 7.65 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.12 – 7.03 (m, 1H), 6.78 – 6.68 (m, 2H), 3.89 (s, 1H), 3.70 (s, 3H), 3.41 (dd, *J* = 14.3, 9.7 Hz, 1H), 3.30 (s, 3H), 3.27 – 3.17 (m, 1H), 2.62 (m, 2H), 2.48 (dd, *J* = 18.5, 4.0 Hz, 1H), 2.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.1, 177.7, 169.5, 160.8, 140.0, 131.1, 131.1, 123.4, 120.3, 118.0, 116.0, 115.7, 114.6, 112.5, 99.0, 63.6, 55.2, 44.3, 43.0, 42.9, 42.2, 39.2, 30.0. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 25.947 min (major), 35.451 min (minor). **HRMS (ESI)**: calcd for $C_{25}H_{24}N_3O_5S$ $[M+H]^+$ 478.1431, found 478.1429.

methyl 4-((2*R*,2'*S*,5'*S*,*E*)-4',4'-dicyano-3-((methylsulfonyl)imino)-2'-(2-oxopropyl) -3H-spiro[benzofuran-2,1'-cyclopentan]-5'-yl)benzoate (3f)



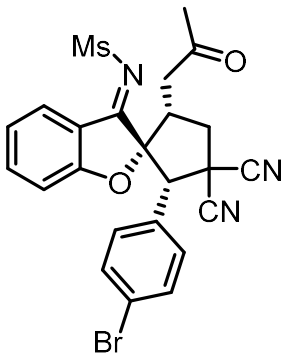
White solid, 48.0mg. 95% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 5:1 dr. Mp = 106.9–107.8℃, $[\alpha]_D^{25}$ = +58.33(*c* = 0.228, $CHCl_3$). 92% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.27 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.65 (ddd, *J* = 8.6, 7.2, 1.4 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 3.97 (s, 1H), 3.84 (s, 3H), 3.45 (dd, *J* = 14.3, 9.6 Hz, 1H), 3.30 (s, 3H), 3.26 (dd, *J* = 9.5, 4.2 Hz, 1H), 2.75 – 2.58 (m, 2H), 2.50 (dd, *J* = 18.5, 4.2 Hz, 1H), 2.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 204.9, 177.0, 169.2, 166.1, 140.2, 133.2, 131.7, 131.1, 130.2, 129.9, 123.6, 117.7, 115.5, 115.1, 112.3, 98.5, 63.5, 52.3, 44.4, 43.1, 42.9, 42.0, 38.6, 29.9. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 30.627 min (major), 47.157 min (minor). **HRMS (ESI)**: calcd for $C_{26}H_{24}N_3O_6S$ $[M+H]^+$ 506.1381, found 506.1377.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-2'-(4-fluorophenyl)-5'-(2-oxopropyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3g)



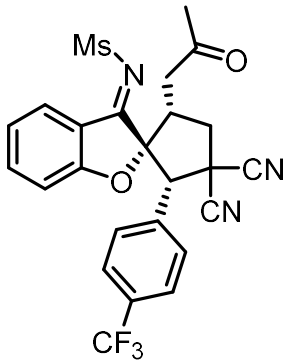
White solid, 44.2 mg. 95% yield. R_f = 0.3 (petroleum ether/ ethyl acetate= 2:1), 5:1 dr. Mp = 93.8–95.9 ℃, $[\alpha]_D^{25}$ = +52.43 (*c* = 0.206, $CHCl_3$). 90% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.29 (d, *J* = 8.2 Hz, 1H), 7.66 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.42 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.92 (t, *J* = 8.6 Hz, 2H), 3.91 (s, 1H), 3.42 (dd, *J* = 14.3, 9.7 Hz, 1H), 3.30 (s, 3H), 3.24 (dd, *J* = 9.5, 4.1 Hz, 1H), 2.73 – 2.57 (m, 2H), 2.49 (dd, *J* = 18.5, 4.2 Hz, 1H), 2.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.1, 177.4, 169.4, 163.7 (d, *J* = 250.4 Hz), 140.2, 131.9(d, *J*=8.5 Hz), 131.2, 124.4(d, *J*=3.4 Hz), 123.6, 117.9, 116.4(d, *J*=21.7 Hz), 115.7, 115.4, 112.4, 98.7, 63.3, 44.3, 43.0, 42.2, 39.0, 30.0. **^{19}F NMR** (377 MHz, $CDCl_3$, ppm) δ –110.5(s). **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 20.360 min (major), 27.069 min (minor). **HRMS (ESI)**: calcd for $C_{24}H_{21}FN_3O_4S$ $[M+H]^+$ 466.1232, found 466.1232.

N-((2*R*,2'*S*,5'*S*,*E*)-2'-(4-bromophenyl)-3',3'-dicyano-5'-(2-oxopropyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3h)



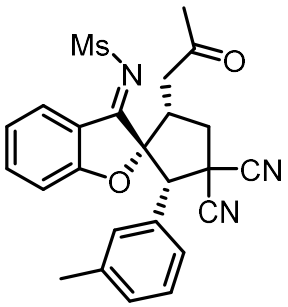
White solid, 50.0 mg. 95% yield. R_f = 0.3 (petroleum ether/ ethyl acetate= 2:1), 5:1 dr. Mp = 99.6–101.4 ℃, $[\alpha]_D^{25}$ = +44.91 (*c* = 0.190, $CHCl_3$). 89% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.67 (ddd, *J* = 8.6, 7.3, 1.4 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.10 (ddd, *J* = 8.2, 7.2, 0.9 Hz, 1H), 3.89 (s, 1H), 3.42 (dd, *J* = 14.3, 9.6 Hz, 1H), 3.30 (s, 3H), 3.27 – 3.15 (m, 1H), 2.71 – 2.56 (m, 2H), 2.48 (dd, *J* = 18.5, 4.2 Hz, 1H), 2.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 204.9, 1z77.1, 169.2, 140.2, 132.4, 131.3, 131.1, 127.4, 124.7, 123.6, 117.7, 115.5, 115.2, 112.3, 98.5,63.1, 44.4, 42.9, 42.9, 42.0, 38.8, 29.9. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 24.323 min (major), 29.952 min (minor). **HRMS (ESI)**: calcd for $C_{24}H_{21}BrN_3O_4S$ $[M+H]^+$ 526.0431, found 526.0429.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(2-oxopropyl)-2'-(4-(trifluoromethyl)phenyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3i)



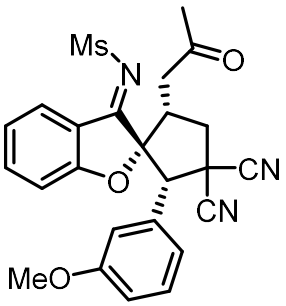
White solid, 49.0 mg. 96% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 4:1 dr. Mp = 94.5–97.0 ℃, $[\alpha]_D^{25}$ = +41.67 (*c* = 0.172, $CHCl_3$). 87% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.30 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 3.99 (s, 1H), 3.44 (dd, *J* = 14.3, 9.7 Hz, 1H), 3.31 (s, 3H), 3.29 – 3.21 (m, 1H), 2.78 – 2.58 (m, 2H), 2.50 (dd, *J* = 18.5, 3.9 Hz, 1H), 2.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 204.8, 176.9, 169.1, 140.2, 132.5,132.2(q, *J* = 33.0 Hz), 131.2, 130.2, 126.14 (q, *J* = 3.7 Hz), 123.8, 123.6(q, *J* =272.6 Hz), 117.8, 115.5, 115.2, 112.4, 98.5, 83.2, 44.7, 43.1, 43.0, 42.0, 38.9, 30.0. **^{19}F NMR** (377 MHz, $CDCl_3$, ppm) δ –63.1(s). **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 17.774 min (major), 23.898 min (minor). **HRMS (ESI)**: calcd for $C_{25}H_{21}F_3N_3O_4S$ $[M+H]^+$ 516.1200, found 516.1191.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(2-oxopropyl)-2'-(m-tolyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3j)



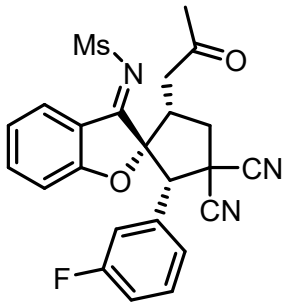
White solid, 42.8 mg. 94% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 6:1 dr. Mp = 83.2–84.8℃, $[\alpha]_D^{25}$ = +57.50 (*c* = 0.240, $CHCl_3$). 90% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.27 (d, *J* = 8.2 Hz, 1H), 7.64 (ddd, *J* = 8.6, 7.2, 1.4 Hz, 1H), 7.25 – 7.15 (m, 3H), 7.07 (dt, *J* = 12.7, 7.6 Hz, 3H), 3.87 (s, 1H), 3.42 (dd, *J* = 14.3, 9.6 Hz, 1H), 3.30 (s, 3H), 3.23 (m, 1H), 2.70 – 2.56 (m, 2H), 2.49 (dd, *J* = 18.5, 4.1 Hz, 1H), 2.21 (s, 3H), 2.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.1, 177.6, 169.5, 140.0, 138.8, 131.1, 130.8, 130.7, 128.9, 128.4, 126.7, 123.4, 118.0, 115.9, 115.6, 112.4, 98.9, 63.9, 44.3, 43.2, 43.0, 42.2, 39.0, 30.0, 21.4. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 16.636 min (major), 20.497 min (minor). **HRMS (ESI)**: calcd for $C_{25}H_{24}N_3O_4S$ $[M+H]^+$ 462.1482, found 462.1488.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-2'-(3-methoxyphenyl)-5'-(2-oxopropyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3k)



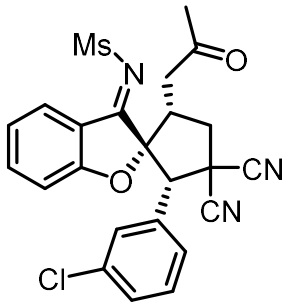
White solid, 44.9 mg. 94% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 6:1 dr. Mp = 135.6–136.9°C, $[\alpha]_D^{25}$ = +57.79 (*c* = 0.184, $CHCl_3$). 90% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.65 (ddd, *J* = 8.6, 7.2, 1.4 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.17 – 7.04 (m, 2H), 7.01 – 6.93 (m, 2H), 6.79 (ddd, *J* = 8.3, 2.4, 1.1 Hz, 1H), 3.89 (s, 1H), 3.67 (s, 3H), 3.42 (dd, *J* = 14.3, 9.8 Hz, 1H), 3.30 (s, 3H), 3.23 (dt, *J* = 9.3, 4.7 Hz, 1H), 2.64 (ddd, *J* = 16.7, 9.6, 2.4 Hz, 2H), 2.49 (dd, *J* = 18.5, 4.3 Hz, 1H), 2.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.1, 177.5, 169.5, 159.8, 140.0, 131.2, 130.1, 129.8, 123.5, 122.1, 118.0, 116.0, 115.8, 115.6, 115.0, 112.4, 98.8, 63.8, 55.3, 44.4, 43.2, 43.0, 42.2, 39.0, 30.0. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 23.936 min (major), 29.150 min (minor). **HRMS (ESI)**: calcd for $C_{25}H_{24}N_3O_5S$ $[M+H]^+$ 478.1431, found 478.1431.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-2'-(3-fluorophenyl)-5'-(2-oxopropyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3l)



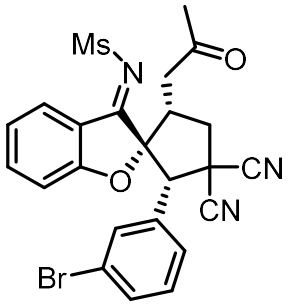
White solid, 43.8 mg. 95% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 5:1 dr. Mp = 83.6–85.5°C, $[\alpha]_D^{25}$ = +13.54 (*c* = 0.288, $CHCl_3$). 90% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.68 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.25 – 7.14 (m, 4H), 7.10 (t, *J* = 7.7 Hz, 1H), 7.03 – 6.93 (m, 1H), 3.91 (s, 1H), 3.44 (dd, *J* = 14.4, 9.7 Hz, 1H), 3.31 (s, 3H), 3.24 (dd, *J* = 9.5, 4.0 Hz, 1H), 2.74 – 2.56 (m, 2H), 2.49 (dd, *J* = 18.5, 4.2 Hz, 1H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.1, 177.2, 169.3, 162.7 (d, *J* = 247.8 Hz), 140.3, 131.2, 130.8(d, *J* = 8.4 Hz), 130.7, 125.9 (d, *J* = 3.2 Hz), 123.7, 117.8, 117.4 (d, *J* = 21.0 Hz), 116.8 (d, *J* = 23.2 Hz), 115.4, 115.6, 115.2,112.5, 98.6, 63.2, 44.5, 43.1, 43.0, 42.1, 38.9, 30.0. **^{19}F NMR** (377 MHz, $CDCl_3$, ppm) δ –110.8(s). **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 23.828 min (major), 30.781 min (minor). **HRMS (ESI)**: calcd for $C_{24}H_{21}FN_3O_4S$ $[M+H]^+$ 466.1232, found 466.1222.

N-((2*R*,2'*S*,5'*S*,*E*)-2'-(3-chlorophenyl)-3',3'-dicyano-5'-(2-oxopropyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3m)



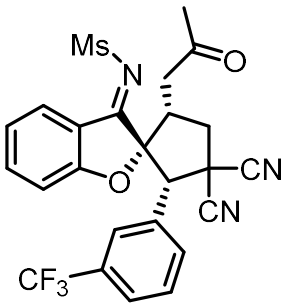
White solid, 42.9 mg. 94% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 5:1 dr. Mp = 75.3–77.9℃, $[\alpha]_D^{25}$ = +42.54(*c* = 0.286, $CHCl_3$). 91% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.29 (d, *J* = 8.2 Hz, 1H), 7.67 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.45 (t, *J* = 2.0 Hz, 1H), 7.29 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.25 – 7.13 (m, 3H), 7.09 (ddd, *J* = 8.2, 7.2, 0.9 Hz, 1H), 3.88 (s, 1H), 3.43 (dd, *J* = 14.4, 9.7 Hz, 1H), 3.30 (s, 3H), 3.23 (dt, *J* = 13.6, 6.8 Hz, 1H), 2.72 – 2.56 (m, 2H), 2.50 (dd, *J* = 18.5, 4.3 Hz, 1H), 2.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.0, 177.1, 169.3, 140.2, 135.0, 131.2, 130.5, 130.4, 129.9, 128.1, 123.7, 117.8, 115.6, 115.2, 112.4, 98.6, 63.2, 44.4, 43.1, 43.0, 42.1, 38.8, 30.0. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 20.238 min (major), 25.830 min (minor).**HRMS (ESI)**: calcd for $C_{24}H_{21}ClN_3O_4S$ $[M+H]^+$ 482.0936, found 482.0936.

N-((2*R*,2'*S*,5'*S*,*E*)-2'-(3-bromophenyl)-3',3'-dicyano-5'-(2-oxopropyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3n)



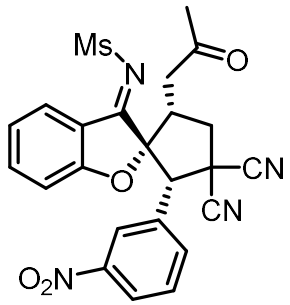
White solid, 49.9 mg. 96% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 5:1 dr. Mp = 73.7–75.9℃, $[\alpha]_D^{25}$ = +44.33 (*c* = 0.200, $CHCl_3$). 90% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.2 Hz, 1H), 7.67 (ddd, *J* = 8.6, 7.2, 1.4 Hz, 1H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.40 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.34 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.16 – 7.01 (m, 2H), 3.86 (s, 1H), 3.43 (dd, *J* = 14.3, 9.7 Hz, 1H), 3.30 (s, 3H), 3.27 – 3.18 (m, 1H), 2.74 – 2.56 (m, 2H), 2.50 (dd, *J* = 18.5, 4.3 Hz, 1H), 2.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.1, 177.5, 169.5, 159.8, zz140.0, 131.2, 130.0, 129.8, 123.5, 122.1, 118.0, 116.0, 115.8, 115.6, 115.0, 112.4, 98.8, 63.8, 55.3, 44.4, 43.2, 43.0, 42.2, 39.0, 30.0. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 21.632 min (major), 27.283 min (minor). **HRMS (ESI)**: calcd for $C_{24}H_{21}BrN_3O_4S$ $[M+H]^+$ 526.0431, found 526.0430.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(2-oxopropyl)-2'-(3-(trifluoromethyl)phenyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3o)



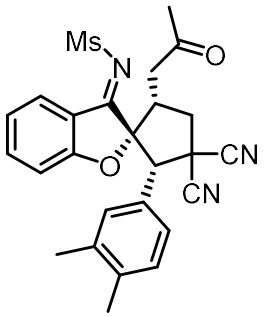
White solid, 46.9 mg. 91% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 5:1 dr. Mp = 81.2–83.4°C, $[\alpha]_D^{25}$ = +20.83 (*c* = 0.296, $CHCl_3$). 91% ee.**^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.27 (d, *J* = 8.2 Hz, 1H), 7.78 (s, 1H), 7.66 (ddd, *J* = 8.6, 7.2, 1.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 3.97 (s, 1H), 3.46 (dd, *J* = 14.3, 9.6 Hz, 1H), 3.31 (s, 3H), 3.27 (dd, *J* = 9.5, 4.1 Hz, 1H), 2.76 – 2.59 (m, 2H), 2.52 (dd, *J* = 18.5, 4.3 Hz, 1H), 2.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.0, 177.0, 169.2, 140.3, 133.5, 131.5(q, *J* = 32.9 Hz), 131.1, 129.8, 129.6, 127.0(q, *J*=3.3 Hz), 126. 6(q, *J*=3.8 Hz), 123.7, 123.5(q, *J*=272.4 Hz), 117.8, 115.5, 115.1, 112.4, 98.6, 63.5, 44.2, 43.1, 43.0, 42.1, 38.7, 30.0. **^{19}F NMR** (377 MHz, $CDCl_3$, ppm) δ –63.1(s). **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 18.094 min (major), 25.218 min (minor). **HRMS (ESI)**: calcd for $C_{25}H_{21}F_3N_3O_4S$ $[M+H]^+$ 516.1200, found 516.1195.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-2'-(3-nitrophenyl)-5'-(2-oxopropyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3p)



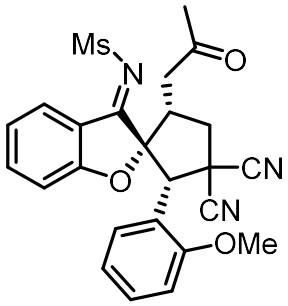
White solid, 46.3 mg. 95% yield. R_f = 0.3 (petroleum ether/ ethyl acetate= 2:1), 6:1 dr. Mp = 98.1–99.2 °C, $[\alpha]_D^{25}$ = +4.88 (*c* = 0.328, $CHCl_3$). 94% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.42 (t, *J* = 2.1 Hz, 1H), 8.28 (d, *J* = 8.2 Hz, 1H), 8.16 (ddd, *J* = 8.3, 2.3, 1.0 Hz, 1H), 7.79 – 7.60 (m, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 9.6 Hz, 1H), 7.15 – 7.04 (m, 1H), 4.04 (s, 1H), 3.48 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.33 (s, 3H), 3.27 (dt, *J* = 9.4, 4.7 Hz, 1H), 2.76 – 2.61 (m, 2H), 2.52 (dd, *J* = 18.5, 4.3 Hz, 1H), 2.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 204.8, 176.6, 169.0, 148.3, 140.4, 135.9, 131.1, 130.5, 130.2, 125.0, 124.8, 123.8, 117.6, 115.2, 114.8, 112.5, 98.4, 62.8, 44.3, 42.9, 41.9, 38.7, 29.9. **HPLC:** Chiralpak IA (250 mm); detected at 265 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 36.138 min (major), 50.420 min (minor). **HRMS (ESI)**: calcd for $C_{26}H_{26}N_3O_4S$ $[M+H]^+$ 493.1177, found 493.1176.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-2'-(3,4-dimethylphenyl)-5'-(2-oxopropyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3q)



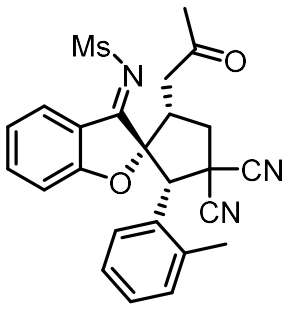
White solid, 43.8 mg. 92% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 4:1 dr. Mp = 111.7–114.2℃, $[\alpha]_D^{25}$ = +63.09 (*c* = 0.140, $CHCl_3$). 94% ee.**^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.28 (d, *J* = 8.2 Hz, 1H), 7.65 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.18 – 7.10 (m, 2H), 7.06 (ddd, *J* = 8.2, 7.2, 0.9 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 3.86 (s, 1H), 3.41 (dd, *J* = 14.3, 9.7 Hz, 1H), 3.29 (s, 3H), 3.27 – 3.15 (m, 1H), 2.62 (ddd, *J* = 16.6, 9.7, 2.3 Hz, 2H), 2.47 (dd, *J* = 18.5, 4.1 Hz, 1H), 2.11 (s, 6H), 2.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.1, 177.7, 169.6, 139.9, 138.7, 137.3, 131.1, 131.1, 130.4, 127.0, 125.8, 123.4, 118.1, 116.0, 115.7, 112.4, 99.0, 63.7, 44.5, 43.1, 43.0, 42.2, 39.2, 30.0, 19.8, 19.5. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 18.421 min (major), 23.572 min (minor). **HRMS (ESI)**: calcd for $C_{26}H_{26}N_3O_4S$ $[M+H]^+$ 476.1639, found 476.1632.

N-((2*R*,2'*R*,5'*S*,*E*)-3',3'-dicyano-2'-(2-methoxyphenyl)-5'-(2-oxopropyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3r)



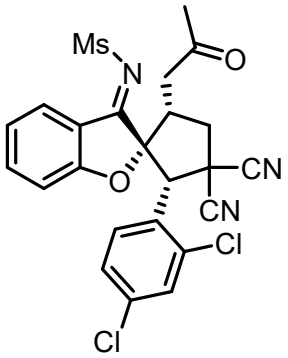
White solid, 44.8 mg. 95% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 12:1 dr. Mp = 60.4–62.7℃, $[\alpha]_D^{25}$ = +23.83 (*c* = 0.214, $CHCl_3$). 82% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.26 (d, *J* = 8.2 Hz, 1H), 7.62 (ddd, *J* = 14.5, 8.2, 1.5 Hz, 2H), 7.23 – 7.14 (m, 2H), 7.05 (t, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.78 – 6.71 (m, 1H), 4.99 (s, 1H), 3.83 (s, 3H), 3.44 (dd, *J* = 14.1, 9.4 Hz, 1H), 3.27 (s, 4H), 2.73 – 2.54 (m, 2H), 2.48 (dd, *J* = 18.5, 4.2 Hz, 1H), 2.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.2, 177.4, 169.4, 157.6, 139.8, 130.9, 130.9, 129.9, 123.3, 120.9, 117.9, 117.4, 116.0, 115.8, 112.5, 111.3, 99.5, 56.1, 53.2, 44.4, 43.4, 43.0, 42.1, 38.5, 30.0. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 21.191 min (major), 30.190 min (minor). **HRMS (ESI)**: calcd for $C_{25}H_{24}N_3O_5S$ $[M+H]^+$ 478.1431, found 478.1436.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(2-oxopropyl)-2'-(o-tolyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3s)



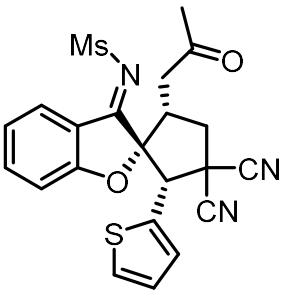
White solid, 43.8 mg. 95% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 7:1 dr. Mp = 88.1–90.0°C, $[\alpha]_D^{25}$ = +38.36 (*c* = 0.232, $CHCl_3$). 71% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.77 – 7.69 (m, 1H), 7.64 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.16 – 7.08 (m, 2H), 7.08 – 6.99 (m, 2H), 4.54 (s, 1H), 3.48 (dd, *J* = 14.3, 9.4 Hz, 1H), 3.32 (dt, *J* = 9.6, 4.8 Hz, 1H), 3.28 (s, 3H), 2.72 – 2.57 (m, 2H), 2.47 (m, 4H), 2.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.1, 177.7, 169.6, 140.1, 137.7, 131.3, 131.1, 129.7, 129.4, 127.1, 126.5, 123.4, 117.8, 116.1, 115.6, 112.5, 99.7, 57.1, 44.6, 43.5, 43.0, 42.1, 38.7, 30.0, 20.3. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 17.869 min (major), 21.950 min (minor). **HRMS (ESI)**: calcd for $C_{25}H_{24}N_3O_4S$ $[M+H]^+$ 462.1482, found 462.1482.

N-((2R,2'R,5'S,E)-3',3'-dicyano-2'-(2,4-dichlorophenyl)-5'-(2-oxopropyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3t)



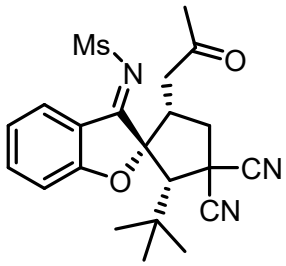
White solid, 41.3 mg. 80% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 10:1 dr. Mp = 96.6–98.2°C, $[\alpha]_D^{25}$ = -21.01 (*c* = 0.164, $CHCl_3$). 70% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.31 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.42 (d, *J* = 2.3 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.16 – 7.07 (m, 2H), 4.99 (s, 1H), 3.52 (dd, *J* = 14.4, 9.5 Hz, 1H), 3.30 (s, 4H), 2.77 – 2.54 (m, 2H), 2.45 (dd, *J* = 18.5, 3.9 Hz, 1H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 204.9, 176.0, 169.0, 140.3, 136.8, 136.4, 131.5, 131.3, 130.4, 128.0, 125.3, 123.9, 117.7, 115.2, 115.1, 112.4, 99.3, 55.9, 44.7, 43.3, 43.0, 41.9, 38.1, 30.1. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 25.258 min (major), 37.529 min (minor). **HRMS (ESI)**: calcd for $C_{24}H_{20}Cl_2N_3O_4S$ $[M+H]^+$ 516.0546, found 516.0546.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(2-oxopropyl)-2'-(thiophen-2-yl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3u)



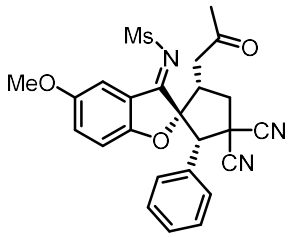
White solid, 43.1 mg. 95% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 3:1 dr. Mp = 90.1–92.9℃, $[\alpha]_D^{25}$ = +13.74 (*c* = 0.182, $CHCl_3$). 90% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.32 (d, *J* = 8.2 Hz, 1H), 7.69 (ddd, *J* = 8.6, 7.2, 1.4 Hz, 1H), 7.26 – 7.16 (m, 3H), 7.12 (ddd, *J* = 8.2, 7.2, 0.9 Hz, 1H), 6.89 (dd, *J* = 5.2, 3.7 Hz, 1H), 4.32 (s, 1H), 3.41 (dd, *J* = 14.4, 9.8 Hz, 1H), 3.30 (s, 3H), 3.22 (m, 1H), 2.72 – 2.56 (m, 2H), 2.48 (dd, *J* = 18.5, 4.1 Hz, 1H), 2.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.0, 177.2, 169.8, 140.1, 131.1, 129.8, 128.4, 128.2, 127.3, 123.6, 117.9, 115.6, 115.3, 112.9, 98.3, 59.7, 44.3, 43.0, 42.6, 42.2, 40.1, 30.0. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 25.703 min (major), 31.571 min (minor). **HRMS (ESI)**: calcd for $C_{22}H_{20}N_3O_4S_2$ $[M+H]^+$ 454.0890, found 454.0885.

N-((2*R*,2'*S*,5'*S*,*E*)-2'-(tert-butyl)-3',3'-dicyano-5'-(2-oxopropyl)-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3v)



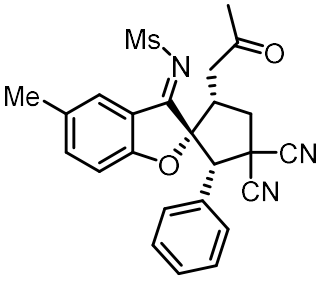
White solid, 38.4 mg. 90% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 9:1 dr. Mp = 151.5–154.3℃, $[\alpha]_D^{25}$ = -44.24 (*c* = 0.220, $CHCl_3$). 91% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.58 – 8.43 (m, 1H), 7.75 (ddd, *J* = 8.5, 7.1, 1.4 Hz, 1H), 7.32 – 7.11 (m, 3H), 3.37 (dt, *J* = 13.4, 6.7 Hz, 1H), 3.30 (s, 3H), 3.04 – 2.84 (m, 2H), 2.51 (dd, *J* = 14.0, 12.3 Hz, 1H), 2.32 (dd, *J* = 18.3, 10.0 Hz, 1H), 2.20 (dd, *J* = 18.3, 3.4 Hz, 1H), 2.02 (s, 3H), 1.10 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 204.9, 178.1, 169.3, 140.2, 131.4, 123.6, 118.2, 118.1, 116.5, 113.0, 99.3, 67.2, 46.5, 44.0, 43.2, 40.3, 35.1, 33.8, 30.3, 30.0. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 19.552 min (major), 32.208 min (minor). **HRMS (ESI)**: calcd for $C_{22}H_{26}N_3O_4S$ $[M+H]^+$ 428.1639, found 428.1640.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5-methoxy-5'-(2-oxopropyl)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3w)



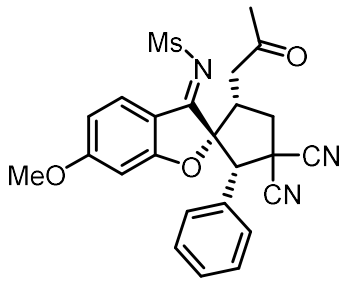
Yellow solid, 44.9 mg. 95% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), 4:1 dr. Mp = 91.6–93.7℃, $[\alpha]_D^{25}$ = +33.14 (*c* = 0.174, $CHCl_3$). 84% ee.**^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.67 (d, *J* = 2.8 Hz, 1H), 7.47 – 7.36 (m, 2H), 7.31 – 7.19 (m, 5H), 7.12 (d, *J* = 9.1 Hz, 1H), 3.91 (s, 1H), 3.74 (s, 3H), 3.43 (dd, *J* = 14.3, 9.6 Hz, 1H), 3.30 (d, *J* = 1.0 Hz, 3H), 3.23 (dd, *J* = 9.6, 4.0 Hz, 1H), 2.70 – 2.57 (m, 2H), 2.48 (dd, *J* = 18.5, 4.1 Hz, 1H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.2, 177.7, 165.1, 155.3, 130.8, 130.1, 129.9, 129.2, 128.7, 118.0, 115.9, 115.5, 113.3, 110.1, 99.4, 63.9, 56.0, 44.6, 43.1, 43.0, 42.1, 39.1, 30.1. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 16.817 min (minor), 21.647 min (major). **HRMS (ESI)**: calcd for $C_{26}H_{24}N_3O_5S$ $[M+H]^+$ 478.1431, found 478.1435.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5-methyl-5'-(2-oxopropyl)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3x)



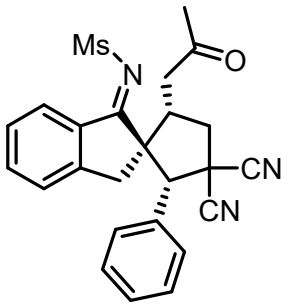
White solid, 42.9 mg. 93% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), 3:1 dr. Mp = 85.6–87.2℃, $[\alpha]_D^{25}$ = +10.17 (*c* = 0.436, $CHCl_3$). 88% ee.**^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.03 (s, 1H), 7.53 – 7.36 (m, 3H), 7.31 – 7.18 (m, 4H), 7.10 (d, *J* = 8.6 Hz, 1H), 3.91 (s, 1H), 3.43 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.29 (s, 3H), 3.22 (dd, *J* = 9.5, 3.8 Hz, 1H), 2.73 – 2.56 (m, 2H), 2.47 (dd, *J* = 18.5, 4.0 Hz, 1H), 2.29 (s, 3H), 2.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.2, 177.5, 168.1, 141.7, 133.3, 130.2, 130.1, 129.9, 129.2, 128.7, 117.9, 115.9, 115.6, 112.1, 99.0, 63.8, 44.6, 43.1, 43.0, 42.1, 39.1, 30.0, 21.0. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 16.833 min (major), 20.950 min (minor). **HRMS (ESI)**: calcd for $C_{25}H_{24}N_3O_4S$ $[M+H]^+$ 462.1482, found 462.1479.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-6-methoxy-5'-(2-oxopropyl)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3y)



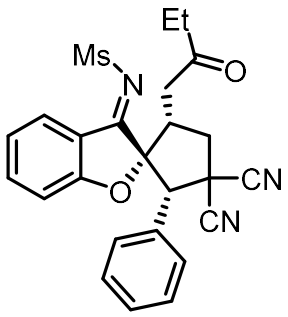
White solid, 45.9 mg. 96% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 5:1 dr. Mp = 81.1–83.2℃, $[\alpha]_D^{25}$ = -49.55 (*c* = 0.224, $CHCl_3$). 95% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.17 (d, *J* = 9.7 Hz, 1H), 7.46 – 7.35 (m, 2H), 7.33 – 7.17 (m, 4H), 6.67 – 6.53 (m, 2H), 3.92 (d, *J* = 4.4 Hz, 4H), 3.44 (dd, *J* = 14.4, 9.7 Hz, 1H), 3.24 (s, 4H), 2.70 – 2.55 (m, 2H), 2.47 (dd, *J* = 18.5, 3.8 Hz, 1H), 2.09 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.2, 174.9, 172.4, 170.0, 132.3, 130.1, 129.8, 129.2, 128.7, 115.9, 115.7, 113.3, 111.3, 100.2, 95.3, 63.4, 56.4, 44.2, 43.2, 42.8, 42.1, 39.0, 30.1. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 28.643 min (major), 35.055 min (minor). **HRMS (ESI)**: calcd for $C_{26}H_{24}N_3O_5S$ $[M+H]^+$ 478.1431, found 478.1436.

N-((1*S*,2*R*,5*S*,*Z*)-3,3-dicyano-5-(2-oxopropyl)-2-phenylspiro[cyclopentane-1,2'-inden]-1'(3'H)-ylidene)methanesulfonamide (3z)



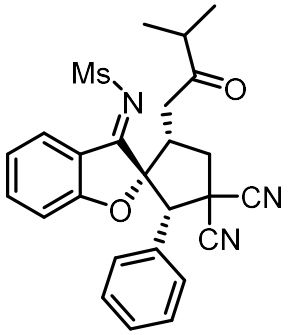
White solid, 46.4 mg. 95% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 2:1), 6:1 dr. Mp = 90.8–93.7℃, $[\alpha]_D^{25}$ = -11.82 (*c* = 0.206, $CHCl_3$). 82% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.67 (d, *J* = 8.1 Hz, 1H), 7.65 (td, *J* = 7.5, 1.1 Hz, 1H), 7.51 – 7.40 (m, 2H), 7.27 (s, 5H), 4.34 (s, 1H), 3.55 – 3.36 (m, 2H), 3.29 (s, 3H), 3.18 – 2.99 (m, 2H), 2.44 (dd, *J* = 14.5, 10.5 Hz, 1H), 2.32 (dd, *J* = 18.0, 10.2 Hz, 1H), 2.20 (dd, *J* = 17.9, 3.8 Hz, 1H), 1.98 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 204.9, 184.8, 152.2, 136.5, 132.3, 132.0, 131.2, 129.3, 128.8, 128.6, 127.9, 126.0, 116.6, 116.6, 62.4, 61.3, 45.5, 43.7, 43.4, 42.5, 36.5, 31.6, 30.0. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 93/7, flow = 1.0 mL/min; Retention time: 41.584 min (major), 46.316 min (minor). **HRMS (ESI)**: calcd for $C_{25}H_{24}N_3O_3S$ $[M+H]^+$ 446.1533, found 446.1536.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(2-oxobutyl)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3aa)



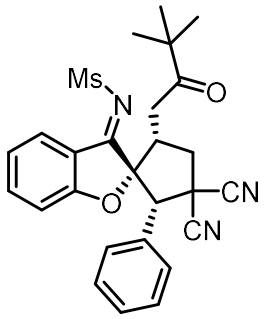
White solid, 44.3 mg. 96% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 4:1), 9:1 dr. Mp = 80.8–82.5°C, $[\alpha]_D^{25}$ = +43.58 (*c* = 0.218, $CHCl_3$). 90% ee.**^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.26 (d, J = 8.2 Hz, 1H), 7.65 (ddd, J = 8.6, 7.2, 1.4 Hz, 1H), 7.47 – 7.36 (m, 2H), 7.22 (dt, J = 13.3, 5.6 Hz, 4H), 7.06 (t, J = 7.7 Hz, 1H), 3.93 (s, 1H), 3.43 (dd, J = 14.3, 9.6 Hz, 1H), 3.30 (s, 5H), 2.71 – 2.53 (m, 2H), 2.45 (dd, J = 18.2, 4.2 Hz, 1H), 2.31 (qd, J = 7.3, 2.0 Hz, 2H), 0.96 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 208.0, 177.5, 169.5, 140.0, 131.1, 130.1, 129.9, 129.2, 128.5, 123.4, 117.9, 115.9, 115.5, 112.5, 98.9, 64.0, 44.5, 43.2, 43.0, 40.8, 39.0, 36.1, 7.7. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 17.692 min (major), 26.627 min (minor). **HRMS (ESI)**: calcd for $C_{25}H_{24}N_3O_4S$ $[M+H]^+$ 462.1482, found 462.1480.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(3-methyl-2-oxobutyl)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3ab)



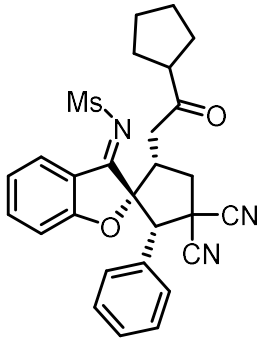
White solid, 44.3 mg. 94% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 4:1), 17:1 dr. Mp = 74.6-77.9°C, $[\alpha]_D^{25}$ = +46.86 (*c* = 0.318, $CHCl_3$). 85% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.26 (d, *J* = 8.2 Hz, 1H), 7.62 (ddd, *J* = 8.5, 7.1, 1.4 Hz, 1H), 7.52 – 7.35 (m, 2H), 7.21 (ddd, *J* = 17.0, 11.1, 8.9 Hz, 4H), 7.04 (t, *J* = 7.6 Hz, 1H), 3.94 (s, 1H), 3.38 (dd, *J* = 13.6, 9.7 Hz, 1H), 3.30 (s, 4H), 2.79 – 2.57 (m, 2H), 2.57 – 2.38 (m, 2H), 1.01 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 211.2, 177.6, 169.4, 139.8, 131.0, 130.0, 129.8, 129.0, 128.5, 123.3, 117.8, 115.7, 115.5, 112.4, 98.6, 64.0, 44.2, 43.1, 42.9, 40.8, 39.0, 38.9, 18.3, 17.9. **HPLC:** Chiralpak IA(250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 17.782 min (major), 22.946 min (minor). **HRMS (ESI)**: calcd for $C_{26}H_{26}N_3O_4S$ $[M+H]^+$ 476.1639, found 476.1645.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(3,3-dimethyl-2-oxobutyl)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3ac)



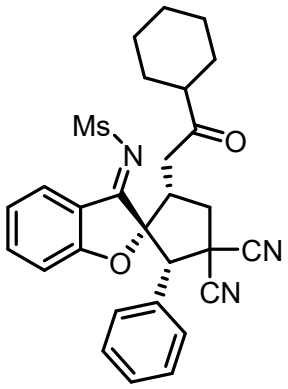
White solid, 41.1 mg. 84% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 4:1), 20:1 dr. Mp = 75.8-76.9°C, $[\alpha]_D^{25}$ = +50.00 (*c* = 0.240, $CHCl_3$). 81% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.25 (d, *J* = 8.2 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.48 – 7.35 (m, 2H), 7.25 – 7.12 (m, 4H), 7.02 (t, *J* = 7.7 Hz, 1H), 3.94 (s, 1H), 3.32 (d, *J* = 16.2 Hz, 5H), 2.81 – 2.52 (m, 3H), 1.00 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 212.7, 177.8, 169.4, 139.8, 131.0, 130.1, 129.8, 129.1, 128.5, 123.3, 117.9, 115.8, 115.6, 112.4, 98.7, 64.3, 44.3, 44.2, 43.3, 42.9, 38.9, 35.7, 26.3. **HPLC:** Chiralpak IA(250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 42.570 min (major), 60.110 min (minor). **HRMS (ESI)**: calcd for $C_{27}H_{28}N_3O_4S$ $[M+H]^+$ 490.1795, found 490.1791.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(2-cyclopentyl-2-oxoethyl)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3ad)



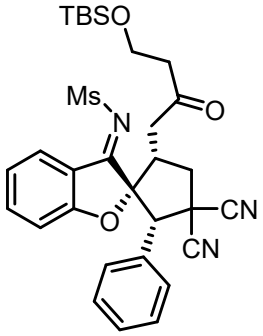
White solid, 42.7 mg. 90% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 4:1), 11:1 dr. Mp = 80.2–82.4°C, $[\alpha]_D^{25}$ = +22.40 (*c* = 0.250, $CHCl_3$). 93% ee. **H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.27 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.46 – 7.38 (m, 2H), 7.26 – 7.15 (m, 4H), 7.05 (t, *J* = 7.7 Hz, 1H), 3.94 (s, 1H), 3.40 (dd, *J* = 13.8, 9.7 Hz, 1H), 3.31 (s, 3H), 2.77 – 2.59 (m, 3H), 2.52 (dd, *J* = 18.2, 4.6 Hz, 1H), 1.80 – 1.48 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 209.9, 177.7, 169.5, 139.9, 131.1, 130.1, 129.9, 129.1, 128.6, 123.4, 118.0, 115.8, 115.6, 112.5, 98.8, 64.1, 51.3, 44.4, 43.3, 43.0, 40.5, 39.0, 29.4, 28.7, 26.0, 25.9. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 80/20, flow = 1.0 mL/min; Retention time: 18.902 min (major), 38.139 min (minor). **HRMS (ESI)**: calcd for $C_{28}H_{28}N_3O_4S$ $[M+H]^+$ 502.1795, found 502.1791.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(2-cyclohexyl-2-oxoethyl)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3ae)



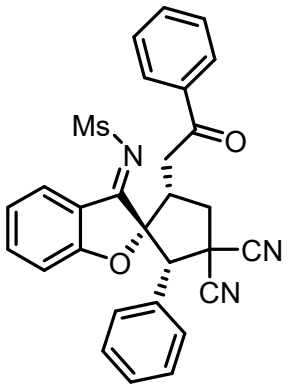
White solid, 48.5 mg. 95% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 4:1), 15:1 dr. Mp = 69.7–71.6℃, $[\alpha]_D^{25}$ = +18.08 (*c* = 0.284, $CHCl_3$). 81% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.26 (d, *J* = 8.2 Hz, 1H), 7.63 (td, *J* = 7.7, 1.4 Hz, 1H), 7.49 – 7.37 (m, 2H), 7.25 – 7.14 (m, 4H), 7.05 (t, *J* = 7.7 Hz, 1H), 3.93 (s, 1H), 3.46 – 3.33 (m, 1H), 3.30 (s, 3H), 2.70 – 2.55 (m, 2H), 2.50 (dd, *J* = 18.3, 4.6 Hz, 1H), 2.19 (td, *J* = 9.7, 4.3 Hz, 1H), 1.80 – 1.61 (m, 5H), 1.19 (dd, *J* = 19.6, 9.7 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 210.6, 177.6, 169.4, 139.8, 131.0, 130.0, 129.7, 129.0, 128.5, 123.3, 117.9, 115.7, 115.5, 112.4, 98.7, 64.1, 50.6, 44.2, 43.2, 42.9, 39.2, 38.9, 28.5, 28.1, 25.6, 25.5, 25.3. **HPLC:** Chiralpak IE(250 mm); detected at 210 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 49.318 min (major), 57.447 min (minor). **HRMS (ESI)**: calcd for $C_{29}H_{30}N_3O_4S$ $[M+H]^+$ 516.1952, found 516.1958.

N-((2*R*,2'*S*,5'*S*,*E*)-5'-(4-((tert-butyldimethylsilyl)oxy)-2-oxobutyl)-3',3'-dicyano-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3af)



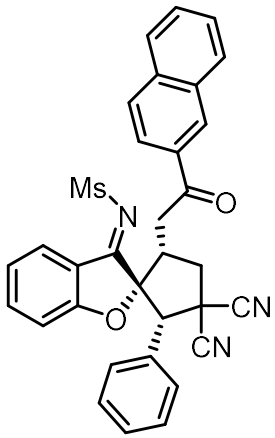
Yellow oil, 55.1 mg. 94% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 4:1), 6:1 dr. Mp = 65.1-67.3℃, $[\alpha]_D^{25}$ = +15.63 (*c* = 0.610, $CHCl_3$). 87% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.26 (d, *J* = 8.2 Hz, 1H), 7.65 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.50 – 7.38 (m, 2H), 7.26 – 7.16 (m, 4H), 7.06 (t, *J* = 7.6 Hz, 1H), 3.92 (s, 1H), 3.88 – 3.71 (m, 2H), 3.44 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.29 (s, 4H), 2.85 – 2.35 (m, 5H), 0.86 (s, 9H), 0.02 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 207.0, 177.5, 169.5, 140.0, 131.1, 130.1, 129.9, 129.2, 128.6, 123.4, 118.0, 116.0, 115.5, 112.5, 99.0, 64.0, 59.1, 45.8, 44.4, 43.2, 43.0, 42.4, 39.0, 26.0, 18.3, -5.4. **HPLC:** Chiralpak IA(250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 11.138 min (major), 15.956 min (minor). **HRMS (ESI)**: calcd for $C_{31}H_{38}N_3O_5SSi$ $[M+H]^+$ 592.2296, found 592.2299.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(2-oxo-2-phenylethyl)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3ag)



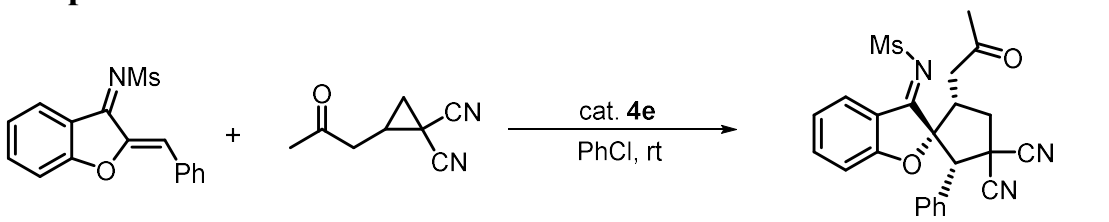
White solid, 48.4 mg. 95% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 4:1), 3:1 dr. Mp = 99.6–100.7℃, $[\alpha]_D^{25}$ = +23.30 (*c* = 0.236, $CHCl_3$). 86% ee.**^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.28 (d, J = 8.2 Hz, 1H), 7.85 – 7.72 (m, 2H), 7.68 – 7.59 (m, 1H), 7.59 – 7.51 (m, 1H), 7.51 – 7.33 (m, 5H), 7.30 – 7.15 (m, 5H), 7.05 (t, J = 7.7 Hz, 1H), 3.99 (s, 1H), 3.59 – 3.43 (m, 2H), 3.31 (s, 3H), 3.25 – 3.11 (m, 1H), 3.10 – 3.00 (m, 1H), 2.82 – 2.70 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 196.7, 177.8, 169.6, 140.0, 136.0, 133.9, 131.1, 130.1, 129.9, 129.2, 128.9, 128.5, 128.2, 123.4, 118.0, 115.9, 115.6, 112.5, 99.0, 64.2, 44.9, 43.3, 43.0, 39.1, 37.5. **HPLC:** Chiralpak IA (250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 80/20, flow = 1.0 mL/min; Retention time: 42.071 min (major), 62.719 min (minor). **HRMS (ESI)**: calcd for $C_{29}H_{24}N_3O_4S$ $[M+H]^+$ 510.1482, found 510.1490.

N-((2*R*,2'*S*,5'*S*,*E*)-3',3'-dicyano-5'-(2-(naphthalen-1-yl)-2-oxoethyl)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentan]-3-ylidene)methanesulfonamide (3ah)



White solid, 52.1 mg. 94% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 4:1), 6:1 dr. Mp = 101.5-103.1℃, $[\alpha]_D^{25}$ = +12.34 (*c* = 0.154, $CHCl_3$). 82% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.34 – 8.24 (m, 2H), 7.99 – 7.89 (m, 1H), 7.89 – 7.81 (m, 3H), 7.66 – 7.57 (m, 2H), 7.55 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.32 – 7.26 (m, 1H), 7.26 – 7.17 (m, 3H), 7.05 (h, *J* = 8.7 Hz, 1H), 4.00 (d, *J* = 4.5 Hz, 1H), 3.63 – 3.47 (m, 2H), 3.32 (s, 3H), 3.29 – 3.15 (m, 2H), 2.83 (q, *J* = 6.9 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 196.7, 177.9, 169.6, 140.0, 135.9, 133.3, 132.5, 131.1, 130.2, 130.1, 129.9, 129.8, 129.2, 129.0, 128.8, 128.5, 127.9, 127.2, 123.6, 123.4, 118.0, 115.9, 115.6, 112.6, 99.0, 64.3, 45.0, 43.3, 43.0, 39.1, 37.6. **HPLC:** Chiralpak IA(250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 27.013 min (major), 36.661 min (minor). **HRMS (ESI)**: calcd for $C_{33}H_{26}N_3O_4S$ $[M+H]^+$ 560.1639, found 560.1648.

7. Experimental Procedure for the Gram-Scale Reaction

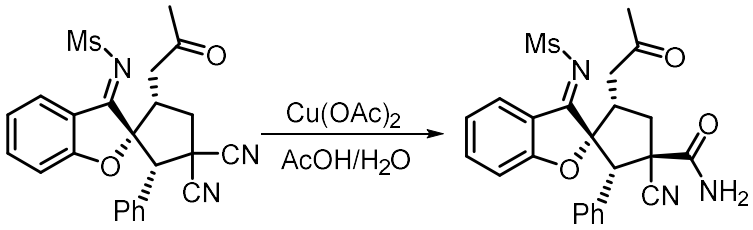


1a (2.5 mmol) **2a** (3.7 mmol) **3a** (95% yield, 7:1 dr, 89% ee)

An oven-dried round bottom flask equipped with a magnetic stirring bar was charged with benzofuranone **1a** (2.5 mmol, 1 equiv.), catalyst **4e** (0.5 mmol, 0.2 equiv.), PhCl (30 mL) and then sealed with a septum. The vial was connected to an argon-vacuum line, evacuated and backfilled with argon. After that, a solution of ketone **2** (3.7 mmol, 1.5 equiv.) in PhCl (20 mL) was added. The mixture was allowed to react at room temperature for 24 hours. After confirming full conversion by TLC, the reaction mixture was filtered through a short pad of Celite®. The solvent was then evaporated under vacuum, and the crude reaction mixture was purified using column chromatography on silica gel to obtain the corresponding product **3a** (1.063g).

8. Transformations of the Product 3a

(2*R*,2'*S*,5'*S*,*E*)-3'-cyano-3-((methylsulfonyl)imino)-5'-(2-oxopropyl)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentane]-3'-carboxamide (5)

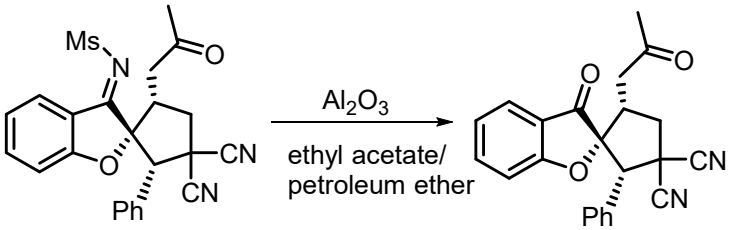


3a (89% ee) **5** (81% yield, 89% ee)

The preparation of **5** was conducted in accordance with previously reported literature procedures.[3a] A glass screw-top vial, equipped with a stirring magnet, was charged with **3a** (0.14 mmol, 1.0 equiv.), $Cu(AcO)_2$ (0.028 mmol, 0.2 equiv.), H_2O (0.1 mL.) and AcOH (glacial, 2.0 mL). The mixture was allowed to react at 80 ºC for 16 h, after which full consumption of **3a** was achieved. The crude mixture was diluted with brine (2 mL) and then extracted with EtOAc (3 × 3 mL). The combined organic phases was sequentially washed with water (2 × 2 mL), brine (1×2 mL), then dried over Na_2SO_4 and finally concentrated under N_2 flow. The crude reaction mixture was

purified using column chromatography on silica gel to obtain the corresponding product **5** (81% yield, 37.7 mg) as a white solid. Mp = 85.3-87.1℃, $[\alpha]_D^{25}$ = +10.71 (*c* = 0.296, $CHCl_3$). 89% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.63 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.46 – 7.33 (m, 2H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.19 – 7.12 (m, 3H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.08 (s, 1H), 5.49 (s, 1H), 4.15 (s, 1H), 3.29 (s, 5H), 2.62 (dd, *J* = 18.1, 9.3 Hz, 1H), 2.47 (dd, *J* = 18.0, 4.1 Hz, 1H), 2.37 (dd, *J* = 13.2, 8.3 Hz, 1H), 2.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.6, 178.4, 169.6, 168.4, 139.6, 131.0, 130.7, 130.0, 129.3, 128.8, 123.0, 121.5, 118.3, 112.5, 100.8, 62.0, 52.3, 44.8, 43.1, 42.6, 41.7, 30.1. **HPLC:** Chiralpak IA(250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 23.359 min (major), 28.467 min (minor). **HRMS (ESI)**: calcd for $C_{24}H_{24}N_3O_5S$ $[M+H]^+$ 466.1431, found 466.1434.

(2*R*,2'*S*,5'*S*)-3-oxo-5'-(2-oxopropyl)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarbonitrile (6)



3a (89% ee) **6** (75% yield, 89% ee)

The preparation of **6** was conducted in accordance with previously reported literature protocols.[4] A solution of **3a** (44.75 mg, 0.1 mmol) in ethyl acetate (12 mL) and petroleum ether (12 mL) was added Al_2O_3 (550 mg.) The solution was stirred at r.t about 5 hours. After the reaction was completed as monitored by TLC, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel. White solid, 27.8 mg. 75% yield. R_f = 0.3 (petroleum ether/ ethyl acetate = 3:1). Mp = 75.8-77.1℃, $[\alpha]_D^{25}$ = -14.42 (*c* = 0.104, $CHCl_3$). 89% ee. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.63 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.49 (ddd, *J* = 16.0, 8.0, 1.7 Hz, 3H), 7.26 – 7.17 (m, 4H), 7.04 (t, *J* = 7.5 Hz, 1H), 3.93 (s, 1H), 3.41 – 3.27 (m, 2H), 2.70 – 2.56 (m, 3H), 2.02 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 205.0, 198.0, 171.3, 139.2, 130.0, 129.9, 129.0, 128.9, 124.8, 123.1, 121.1, 115.7, 115.5, 113.1, 96.3, 61.9, 43.3, 42.8, 41.7, 39.6, 29.9. **HPLC:** Chiralpak IA(250 mm); detected at 280 nm; *n*-hexane/*i*-propanol = 90/10, flow = 1.0 mL/min; Retention time: 22.700 min

(major), 28.561 min (minor). **HRMS (ESI)**: calcd for $C_{23}H_{19}N_2O_3$ $[M+H]^+$ 371.1390, found 371.1389.

9. References

[1] a) Z. Gu; J. Zhou; G.-F. Jiang; Y.-G. Zhou, *Org. Chem. Front.* 2018, **5**, 1148; b) J. Qi; H. Tang; C. Chen; S. Cui; G. Xu, *Org. Chem. Front*. 2019, **6**, 2760.

[2] a) S.Park; T. M. Kadayat; K.-Y. Jun; T.B. Magar; G. Bist; A. Shrestha; E.-S. Lee; Y. Kwon, *Eur. J. Med. Chem*. 2017, **125**, 14; b) A. Stukalov; V. V. Suslonov; M. A. Kuznetsov, *Eur. J. Org. Chem*. 2018, **14**, 1634; c) J. Tian; R. Zhou; H. Sun; H. Song; Z. He, *J. Org. Chem*. 2011, **76**, 2374.

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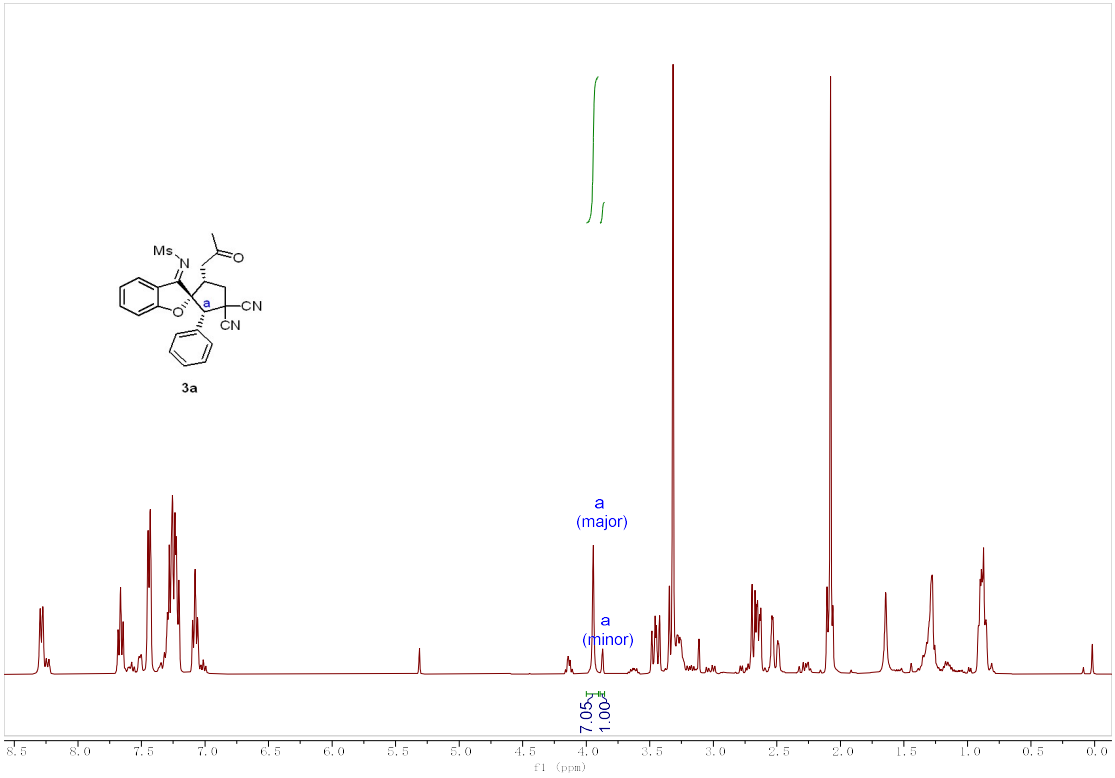
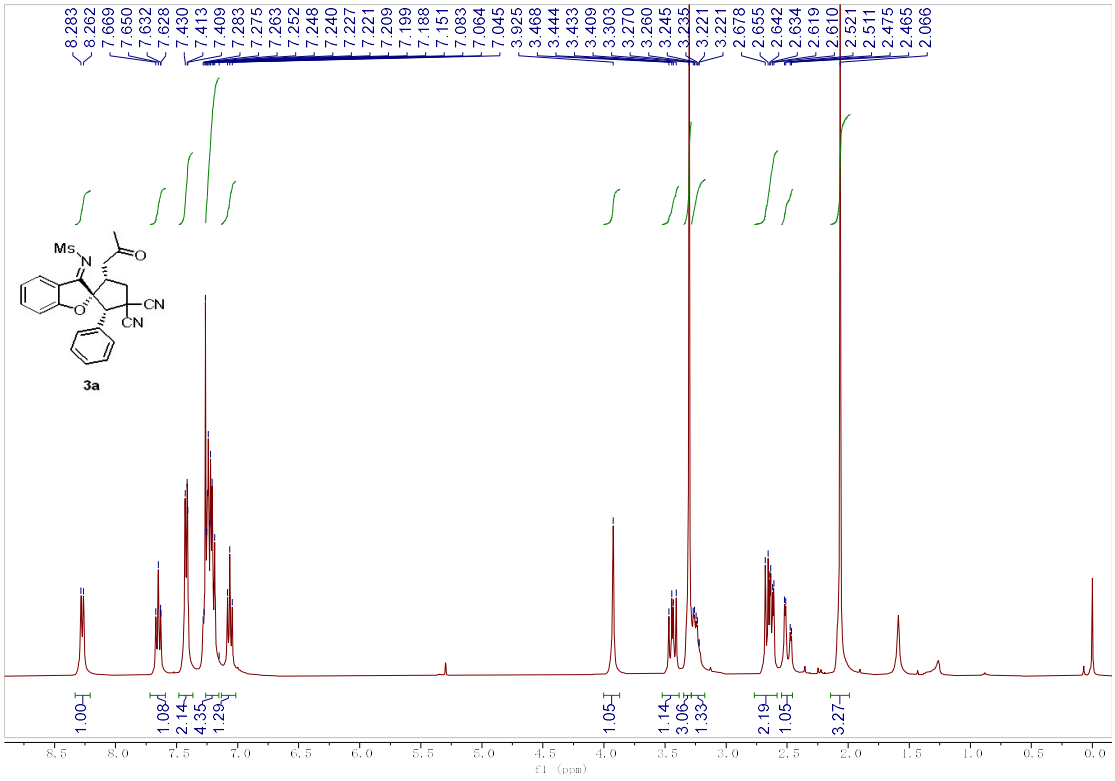
10. NMR spectra of the products

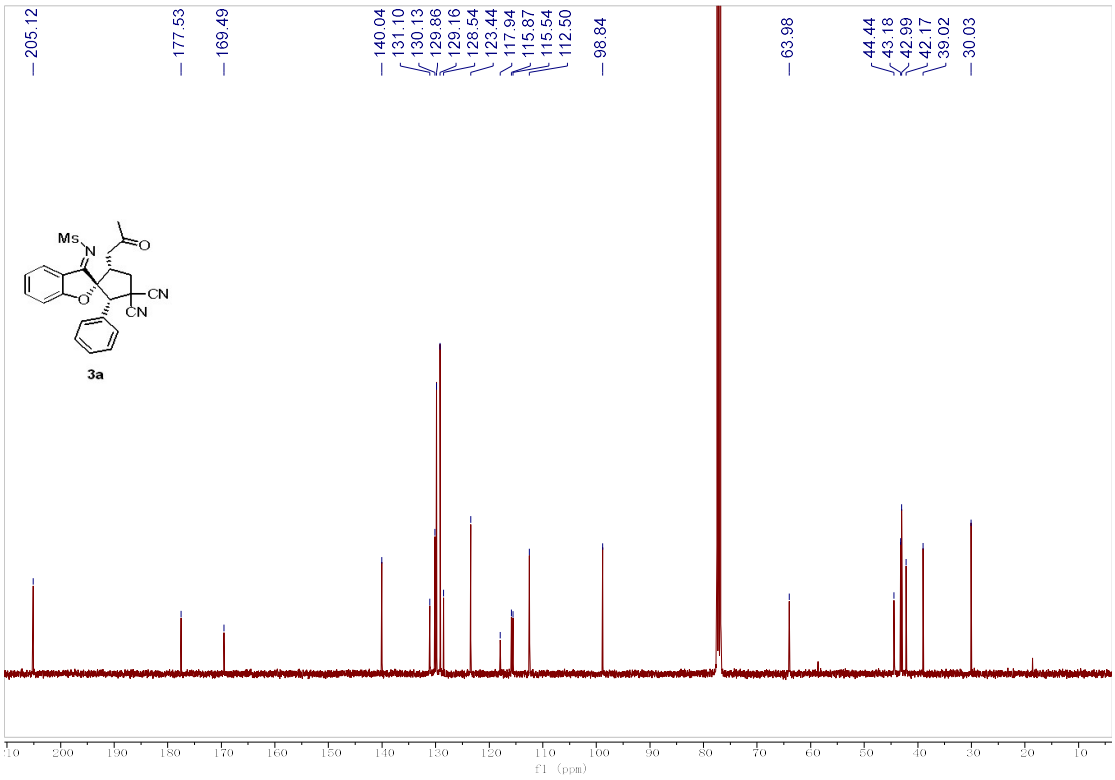
^{1}H NMR spectra of a crude mixture



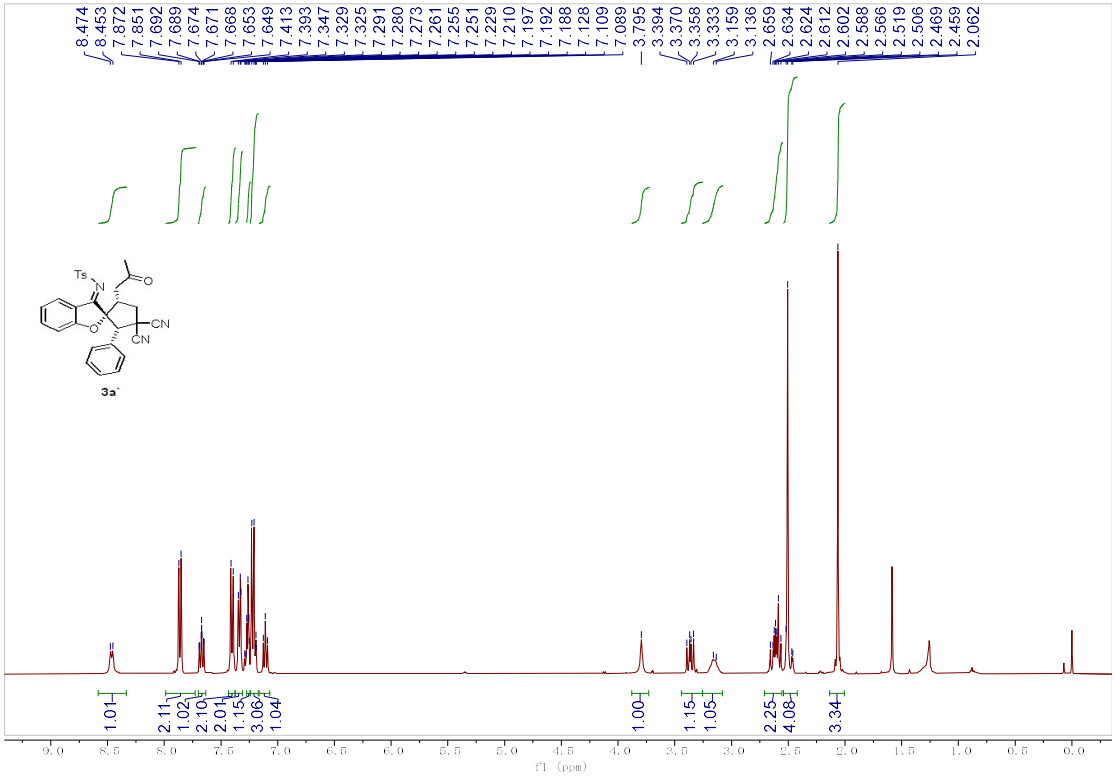
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



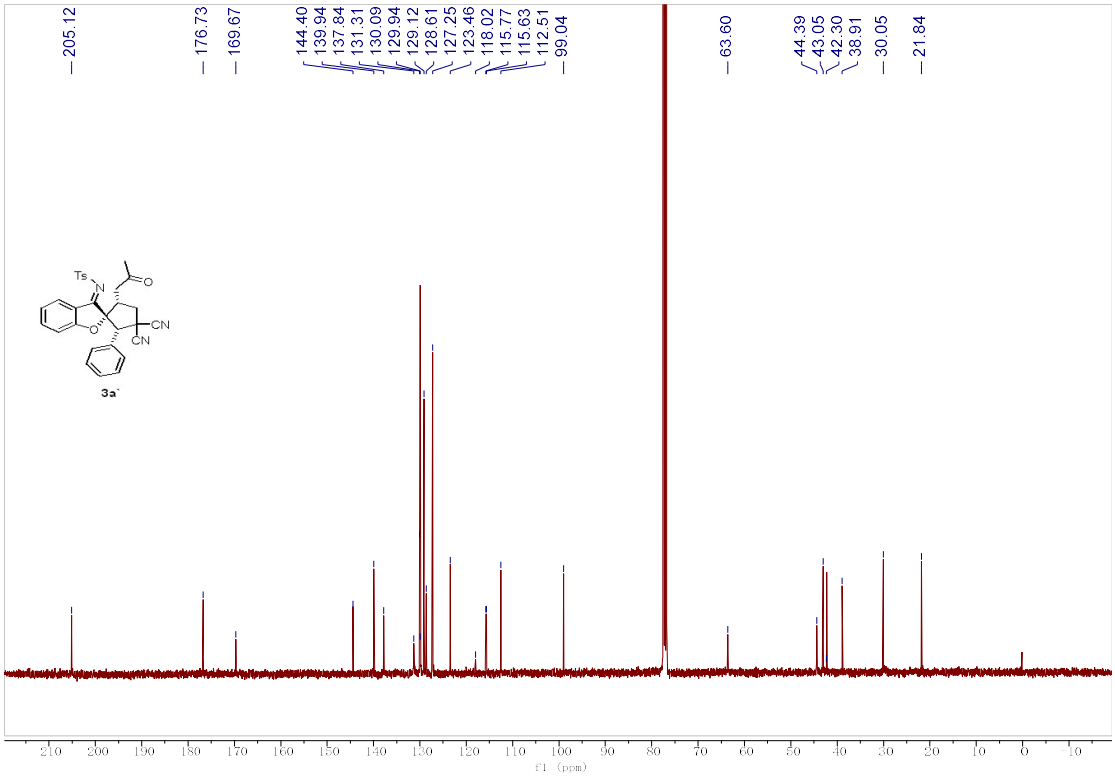
^{13}C NMR (100 MHz, $CDCl_3$) of **3a**



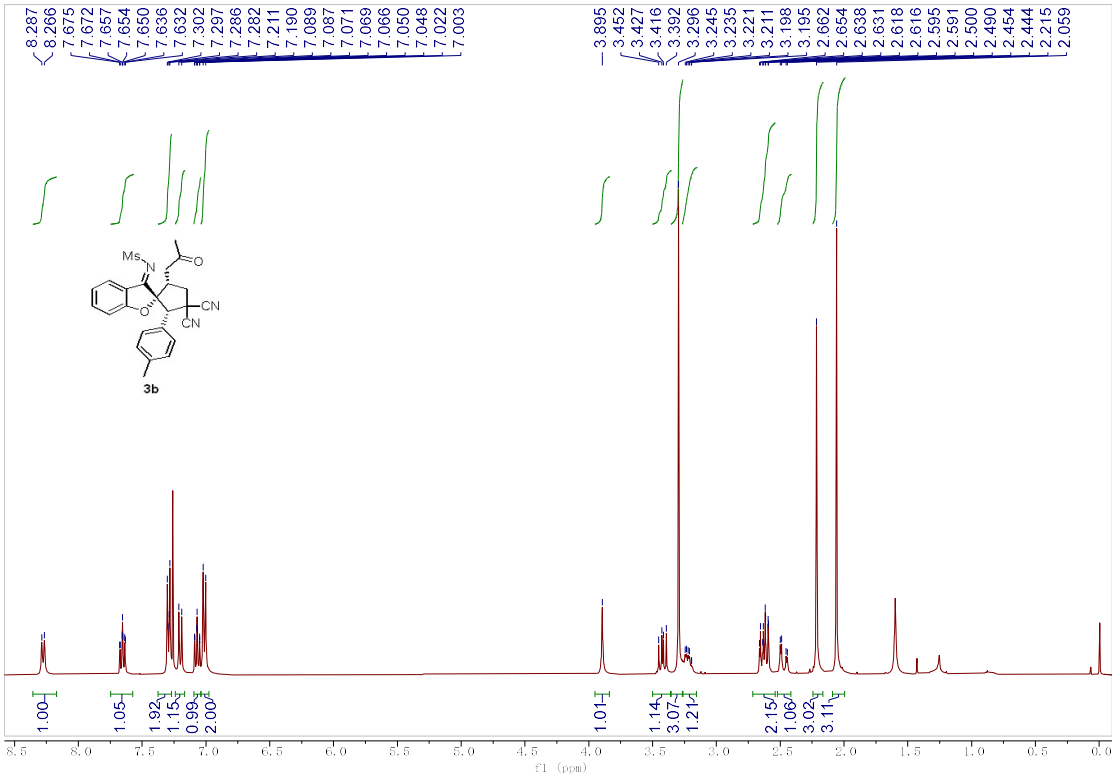
^{1}H NMR (400 MHz, $CDCl_3$) of **3a'**



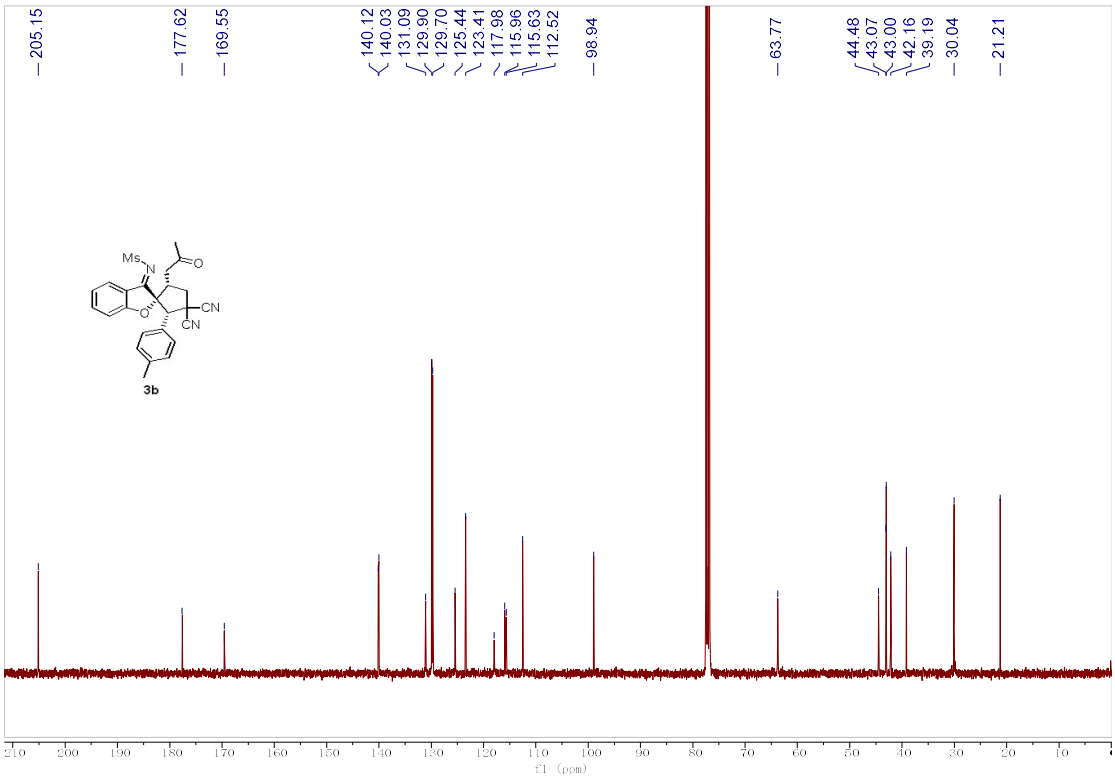
^{13}C NMR (100 MHz, $CDCl_3$) of **3a'**



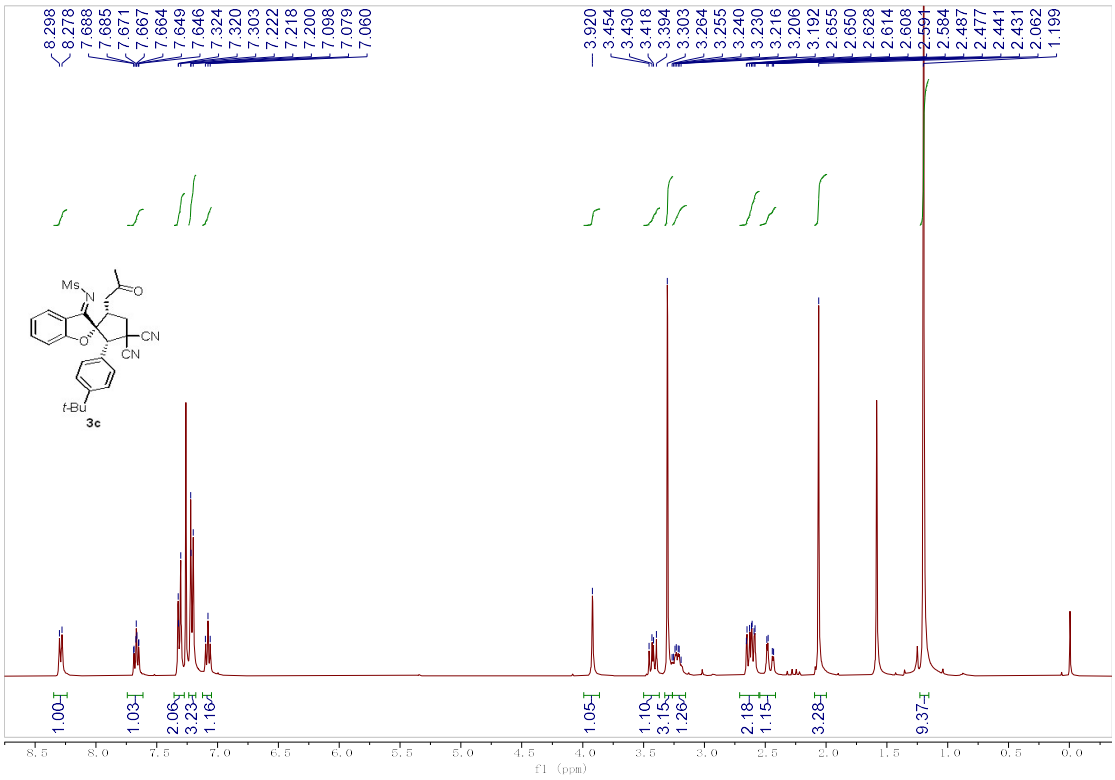
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



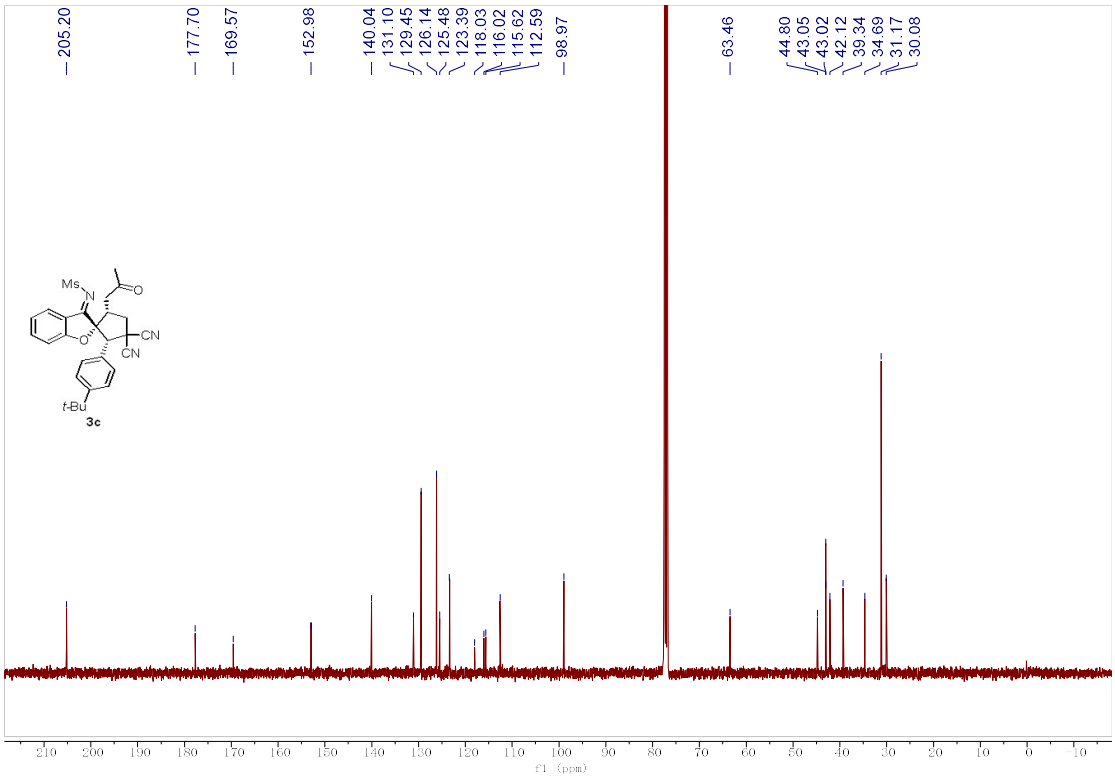
^{13}C NMR (100 MHz, $CDCl_3$) of **3b**



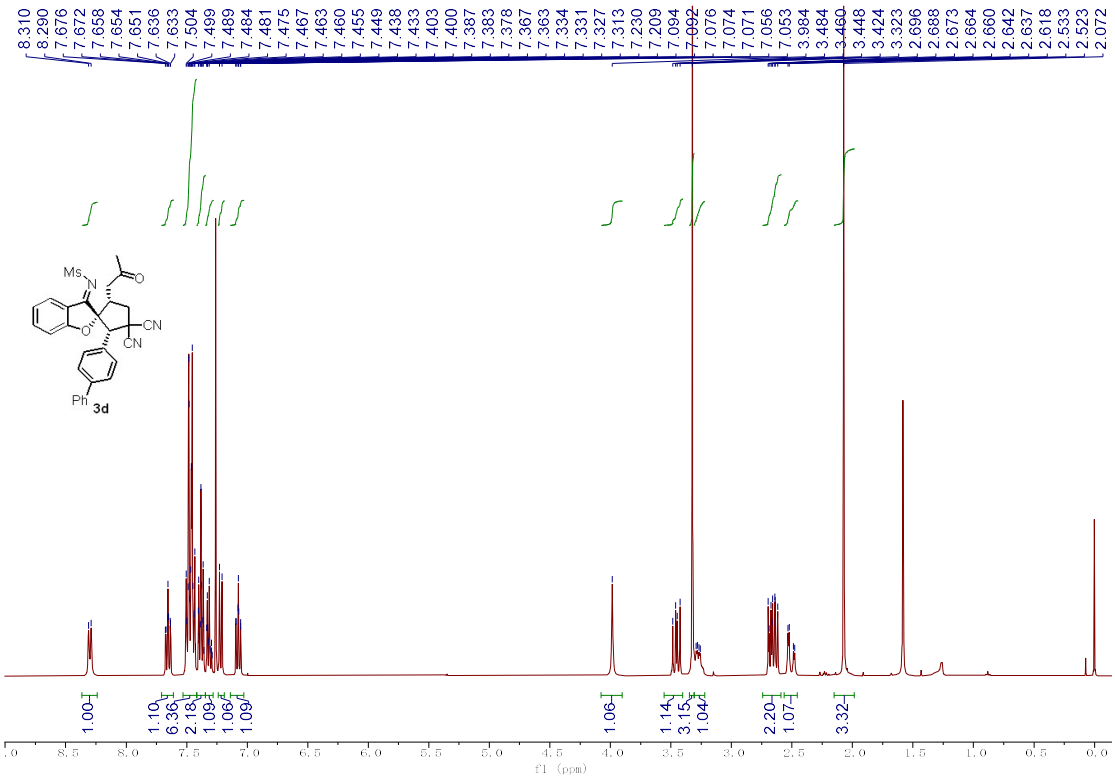
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



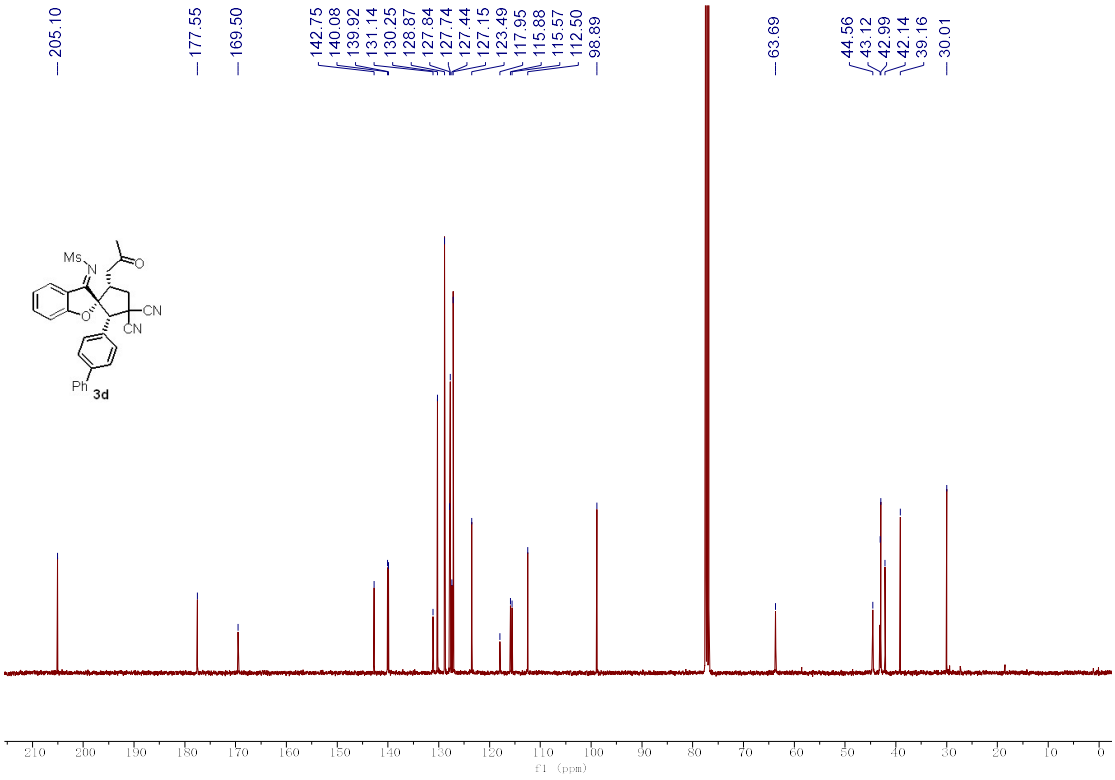
^{13}C NMR (100 MHz, $CDCl_3$) of **3c**



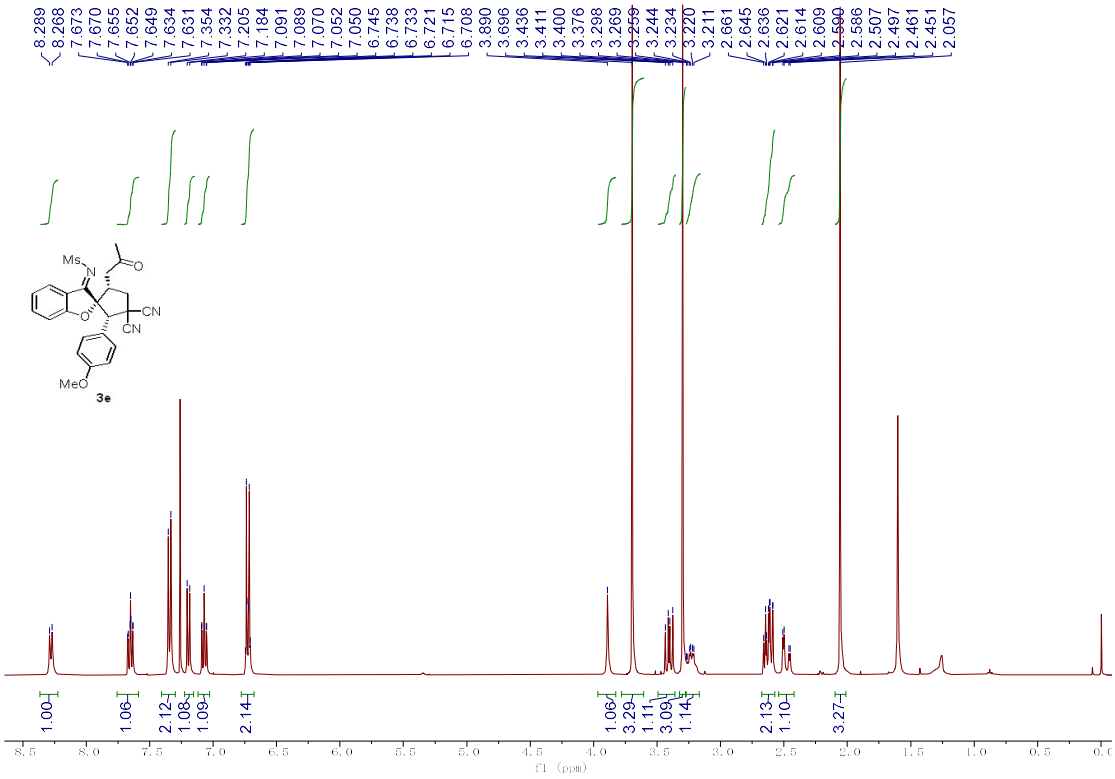
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



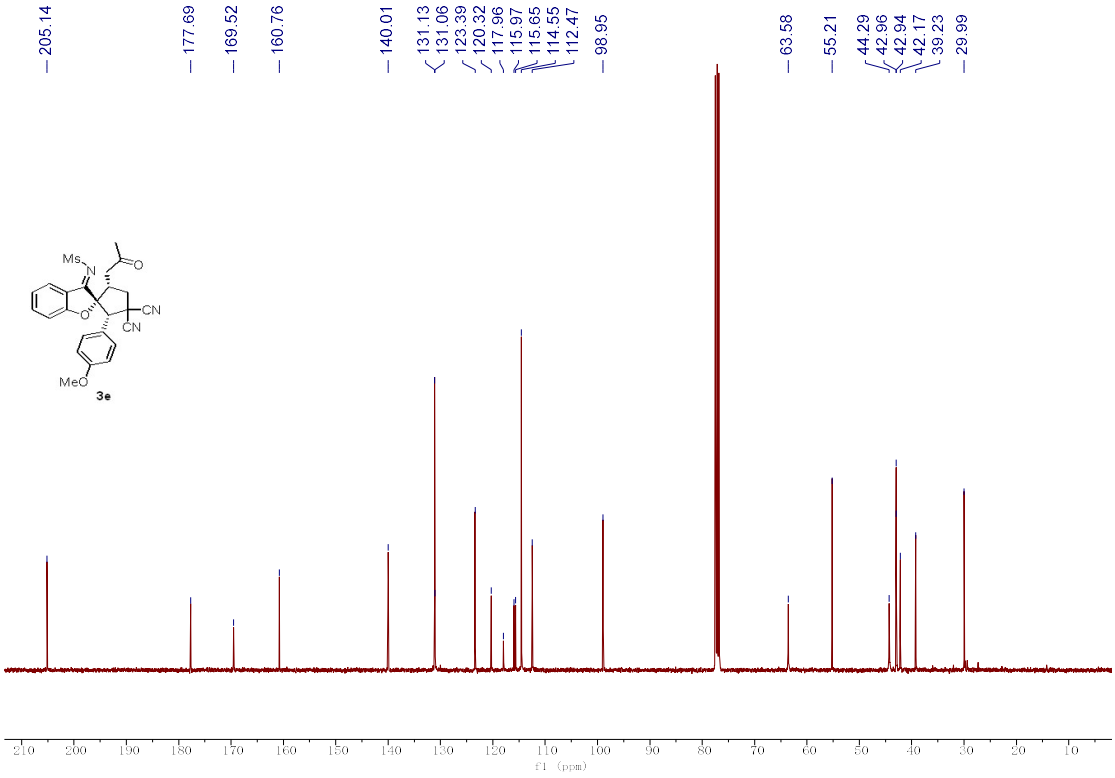
^{13}C NMR (100 MHz, $CDCl_3$) of **3d**



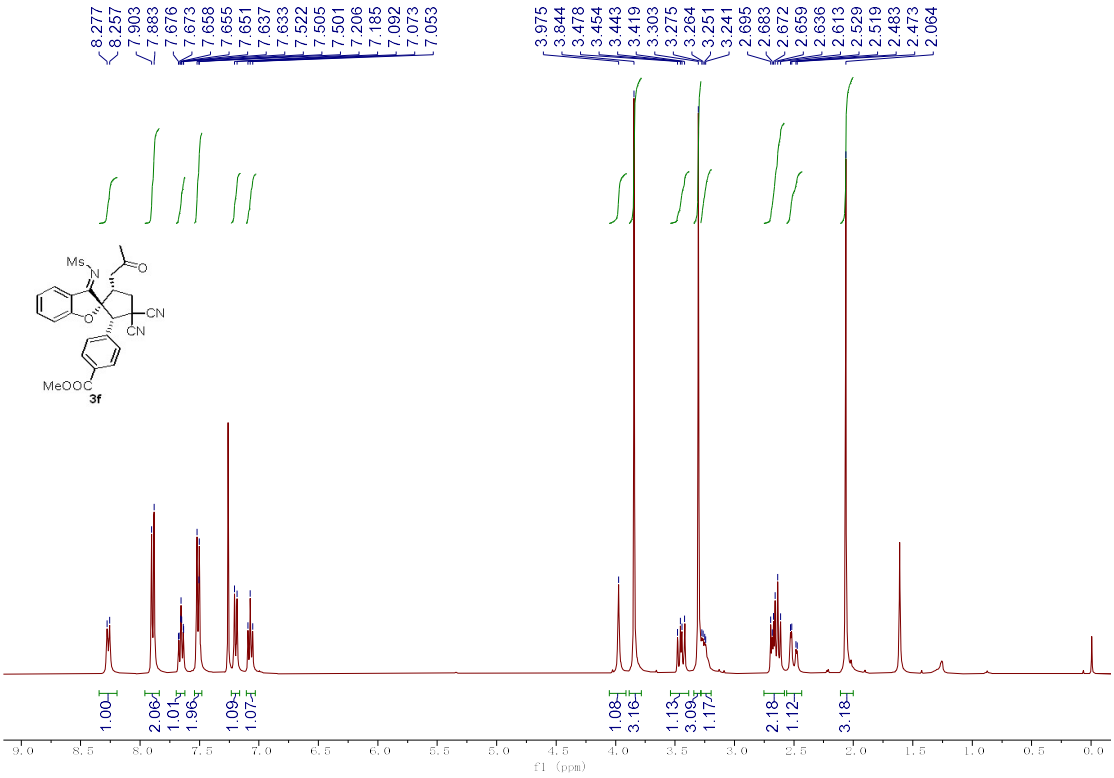
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



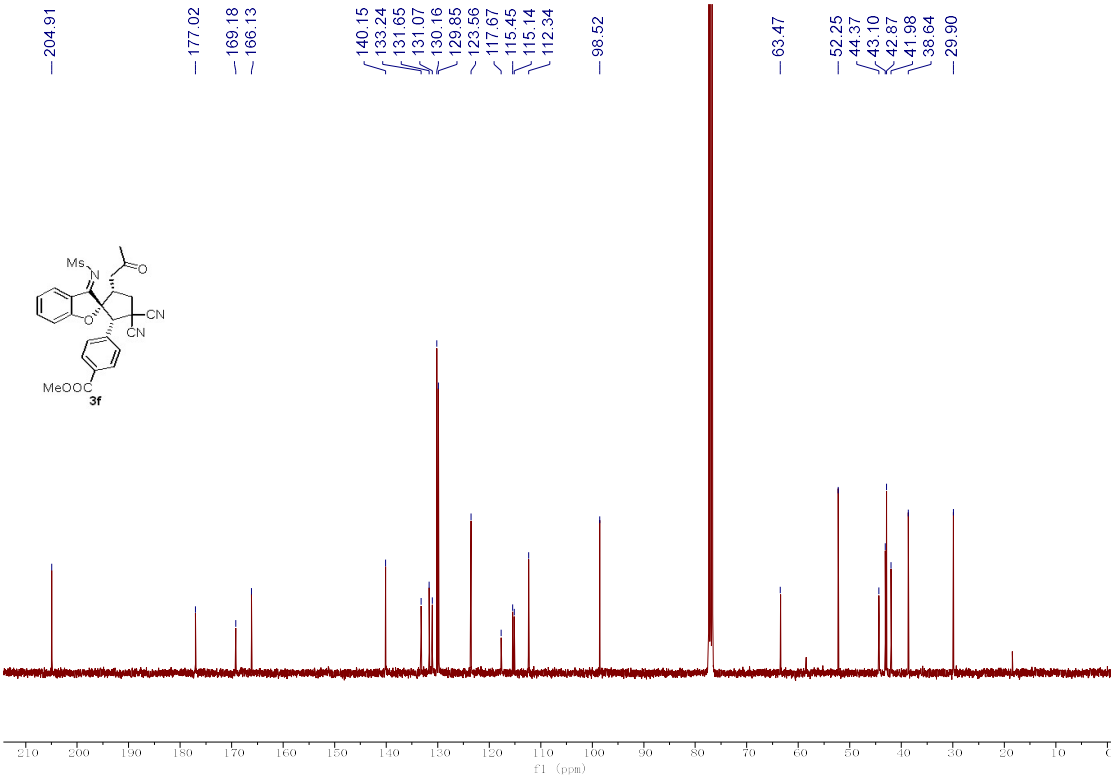
^{13}C NMR (100 MHz, $CDCl_3$) of **3e**



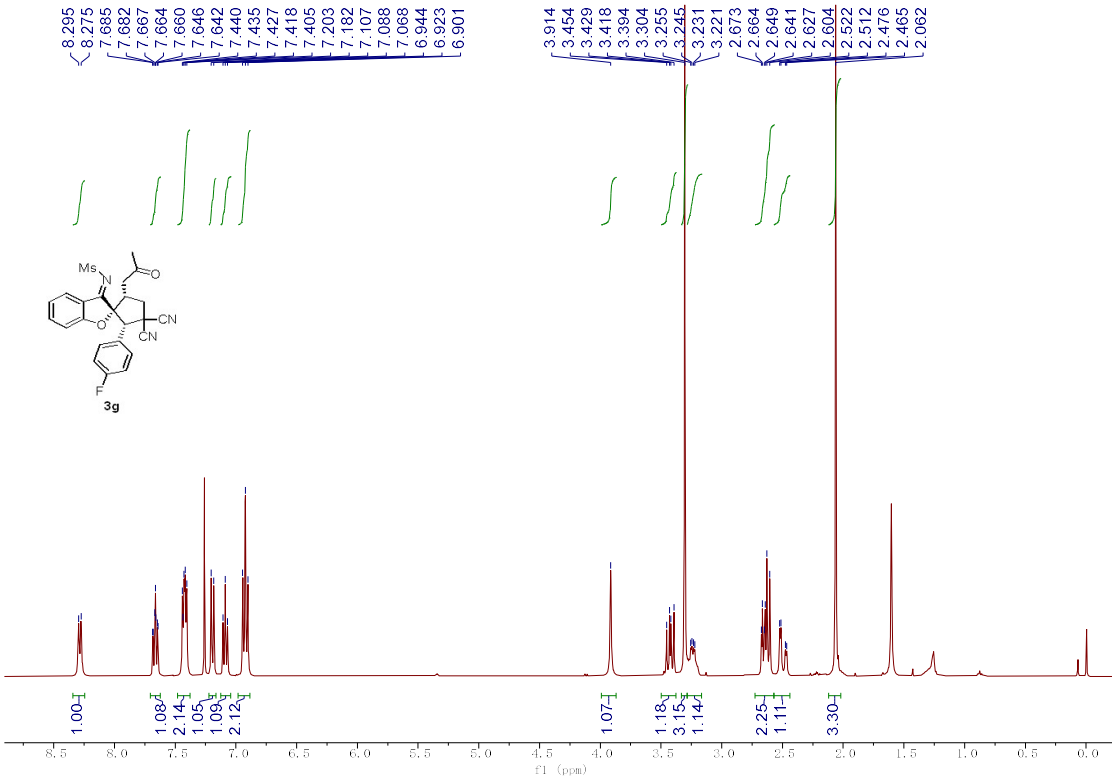
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



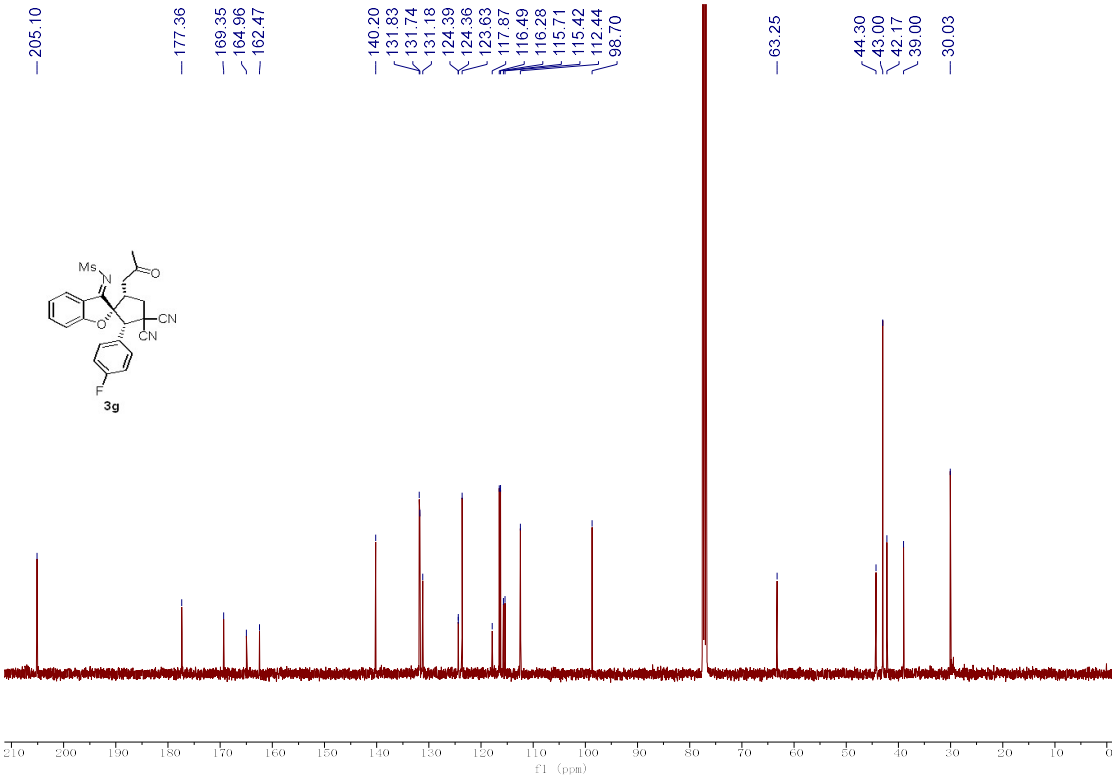
^{13}C NMR (100 MHz, $CDCl_3$) of **3f**



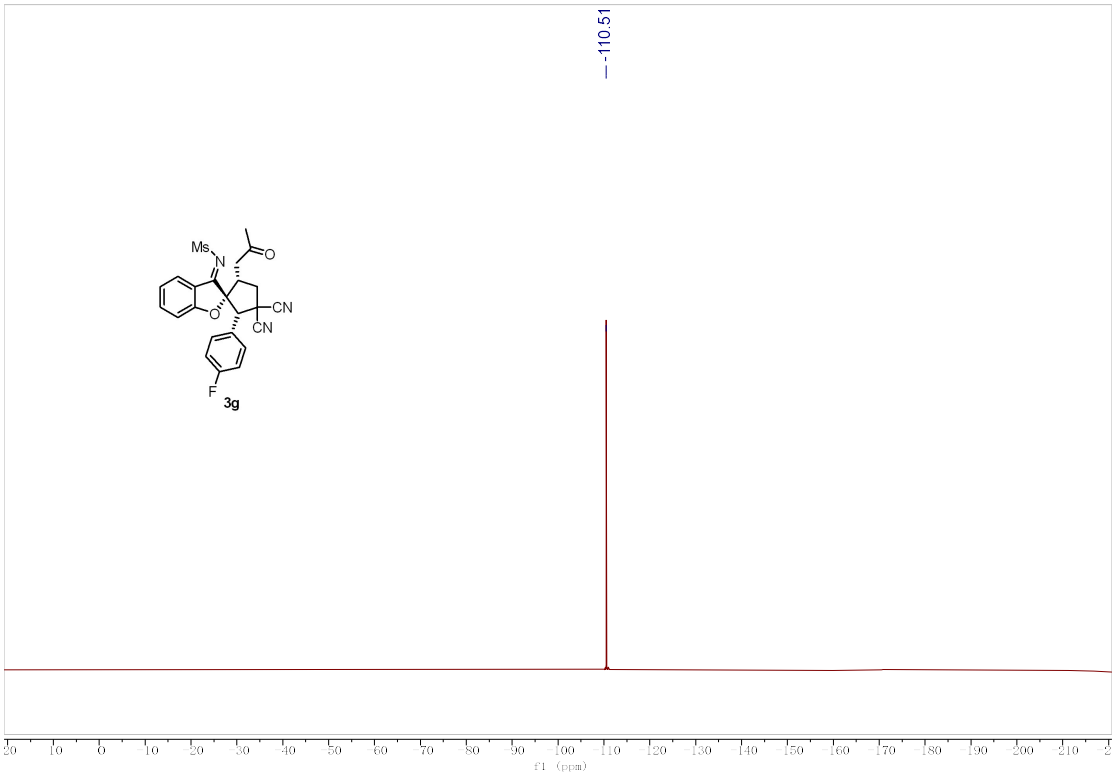
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



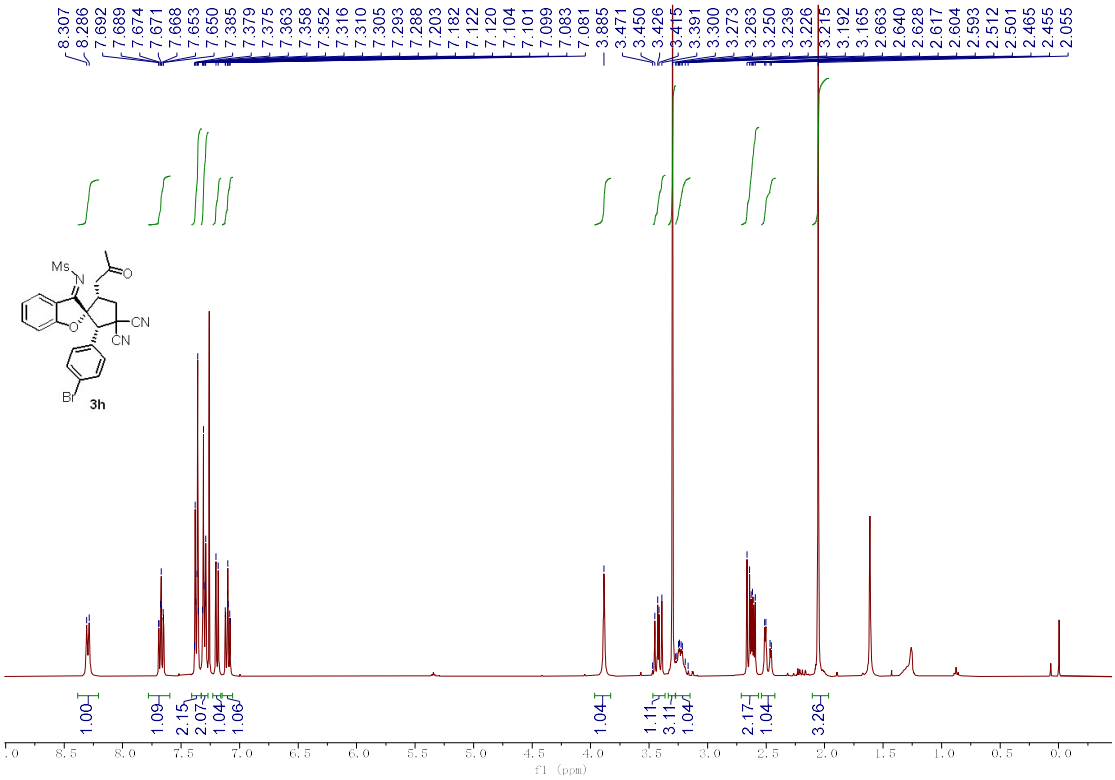
^{13}C NMR (100 MHz, $CDCl_3$) of **3g**



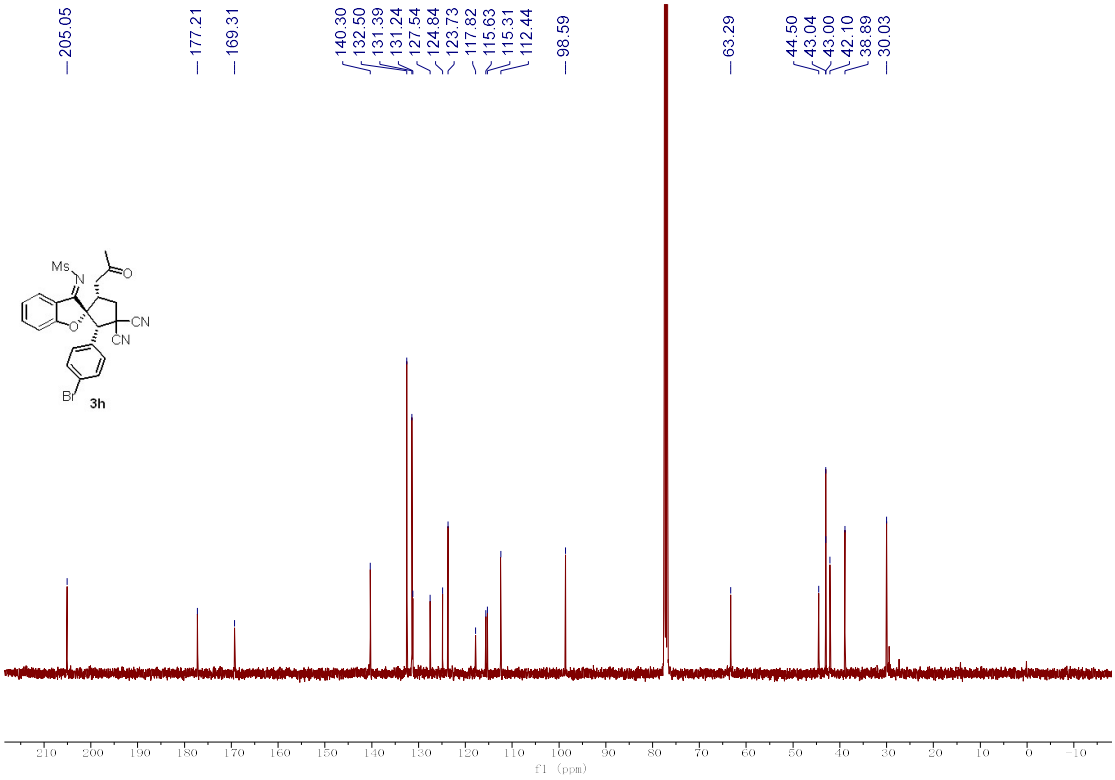
^{19}F NMR (377 MHz, $CDCl_3$) of **3g**



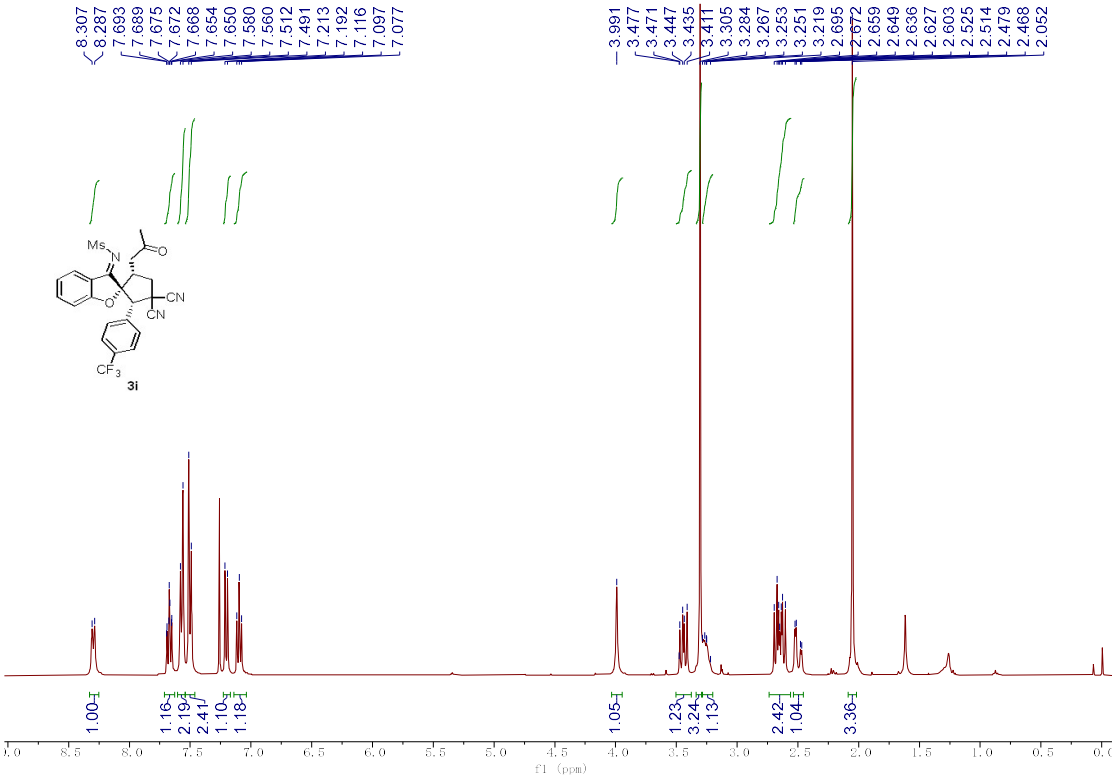
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



^{13}C NMR (100 MHz, $CDCl_3$) of **3h**



^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



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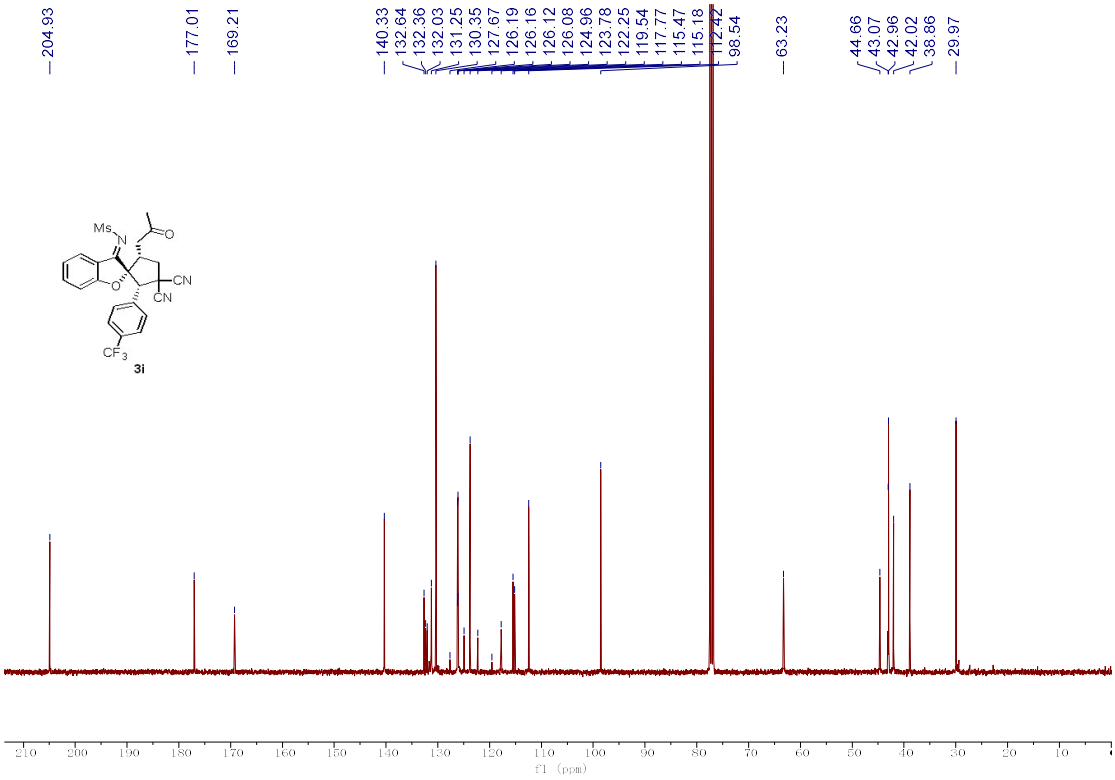
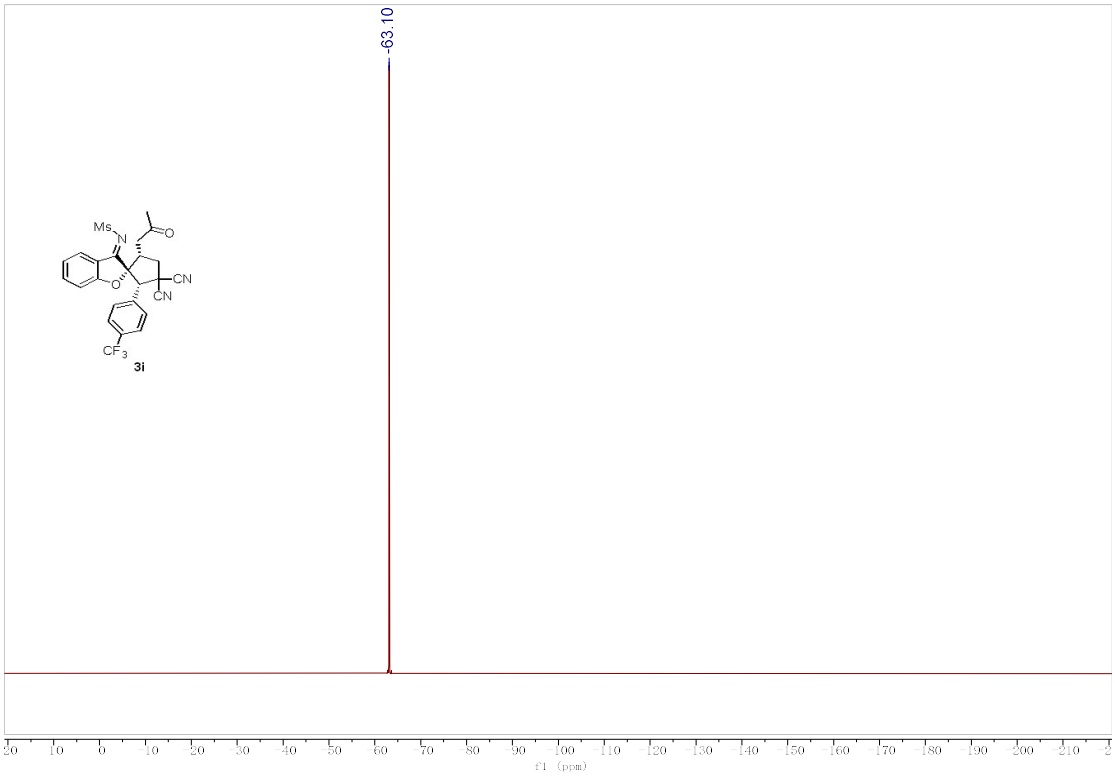


^{19}F NMR (377 MHz, $CDCl_3$) of **3i**



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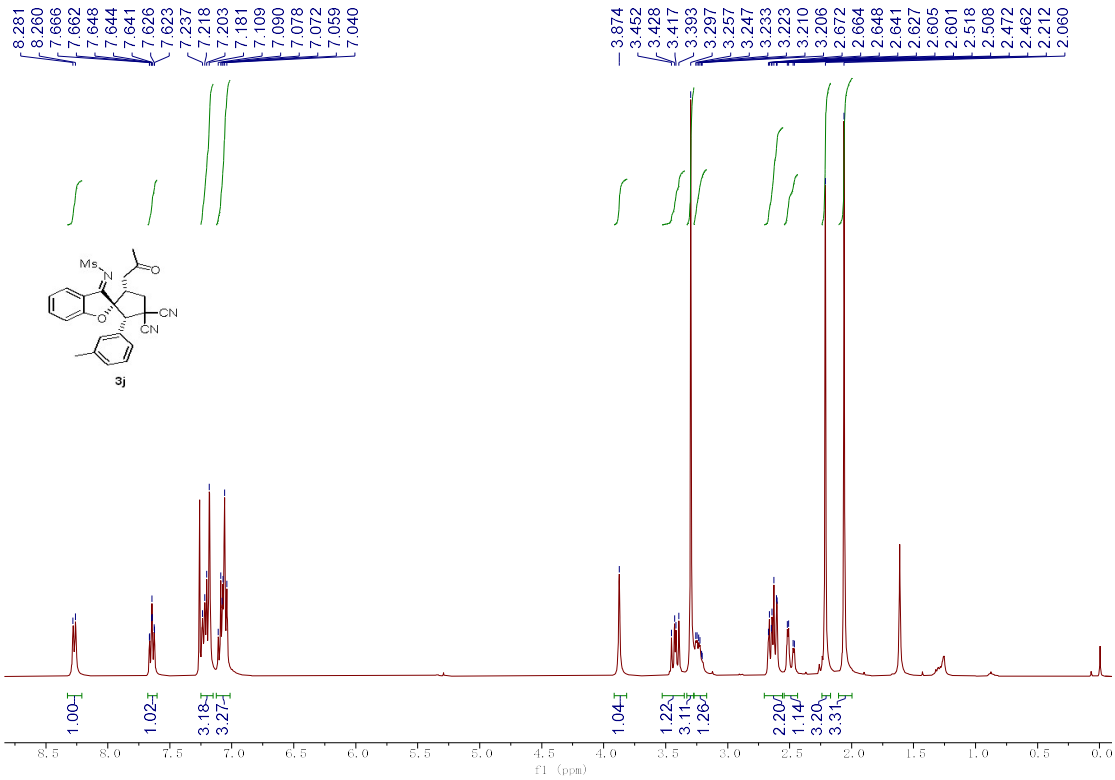
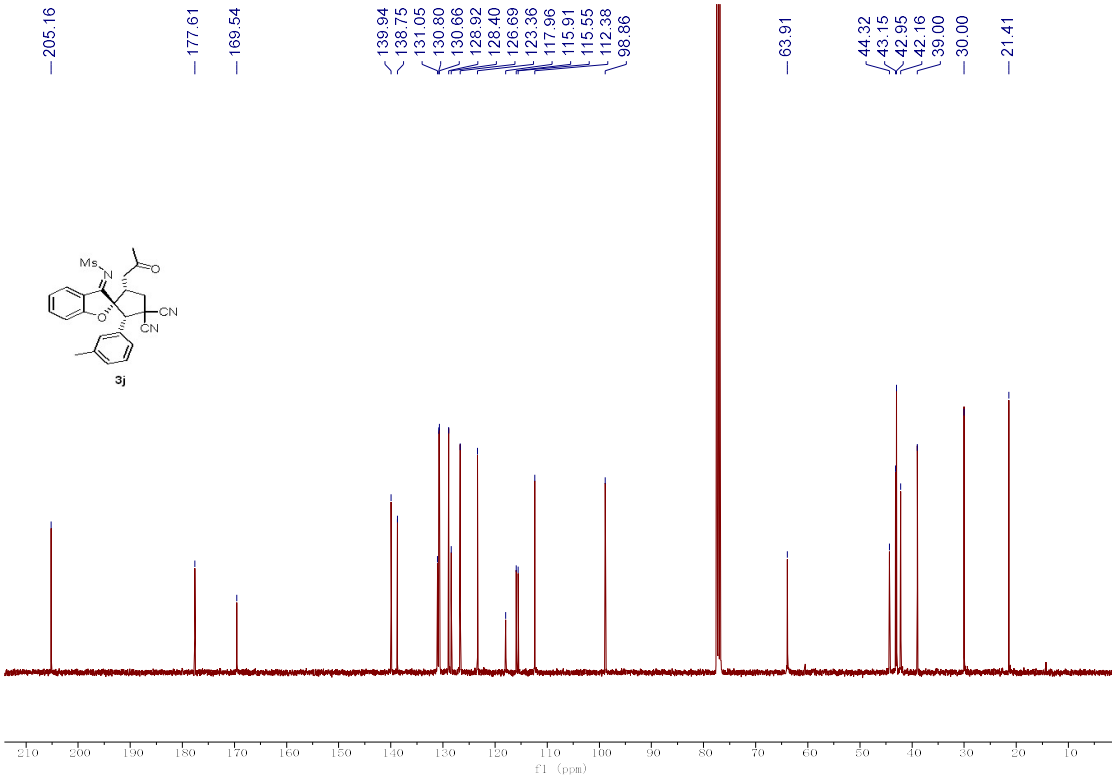
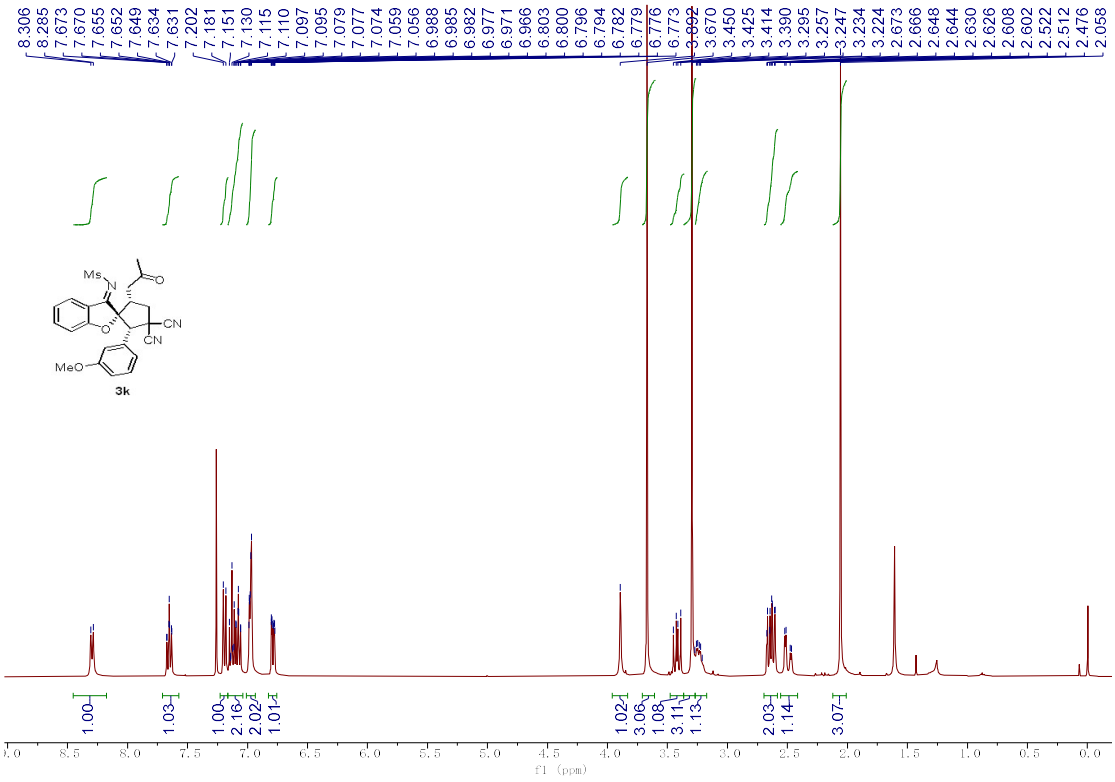


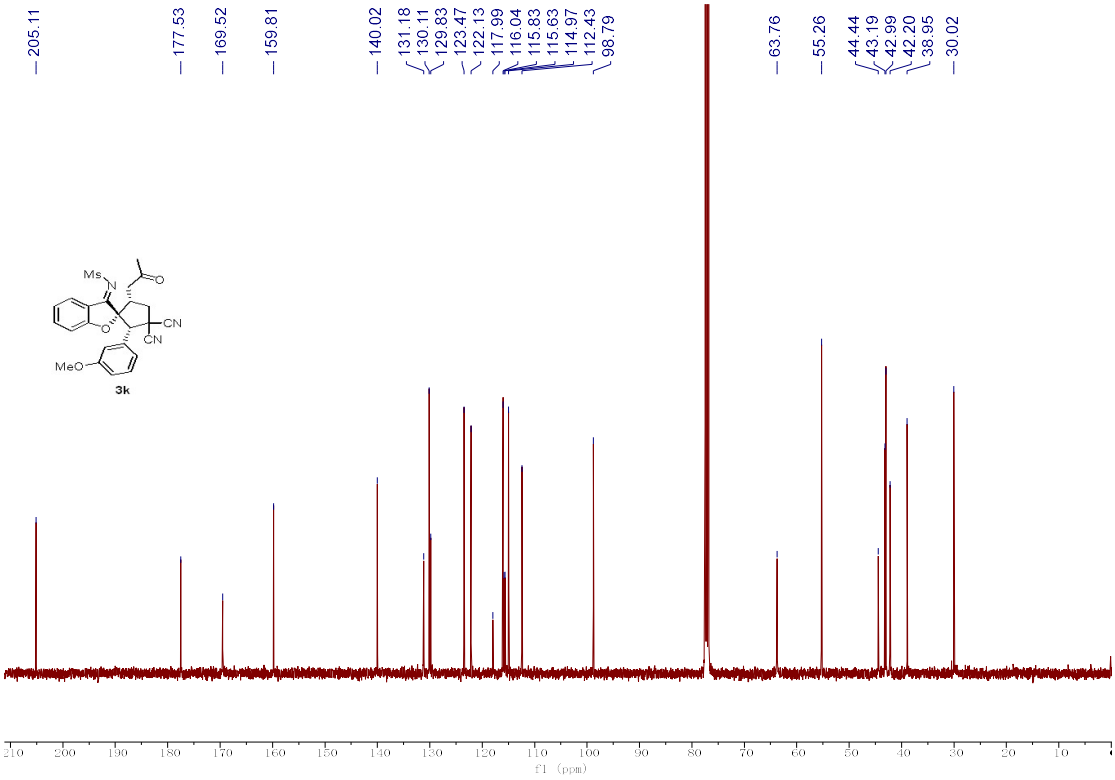
^{13}C NMR (100 MHz, $CDCl_3$) of **3j**



^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



^{13}C NMR (100 MHz, $CDCl_3$) of **3k**



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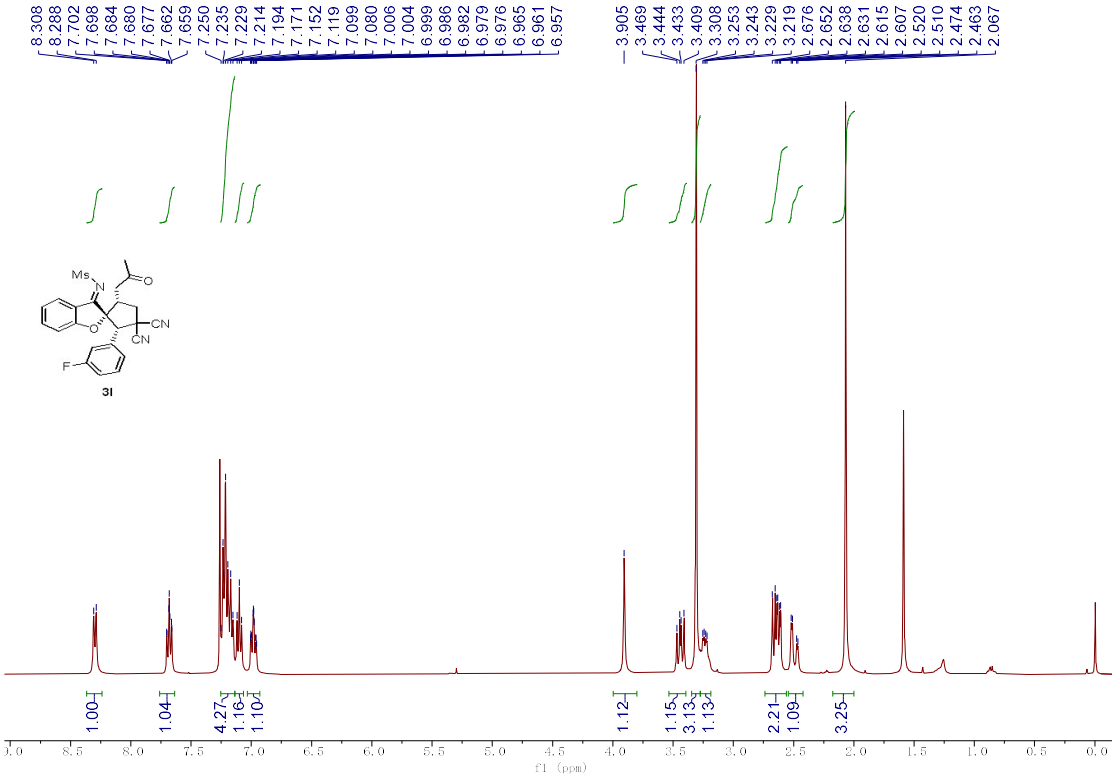

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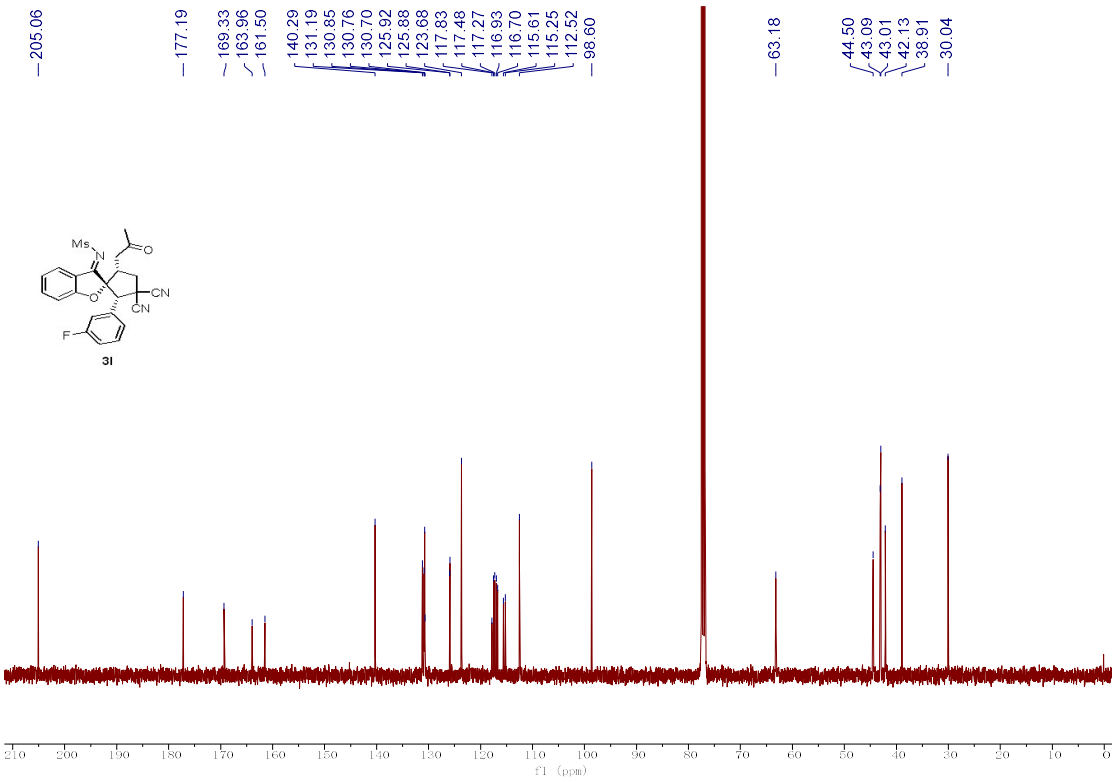
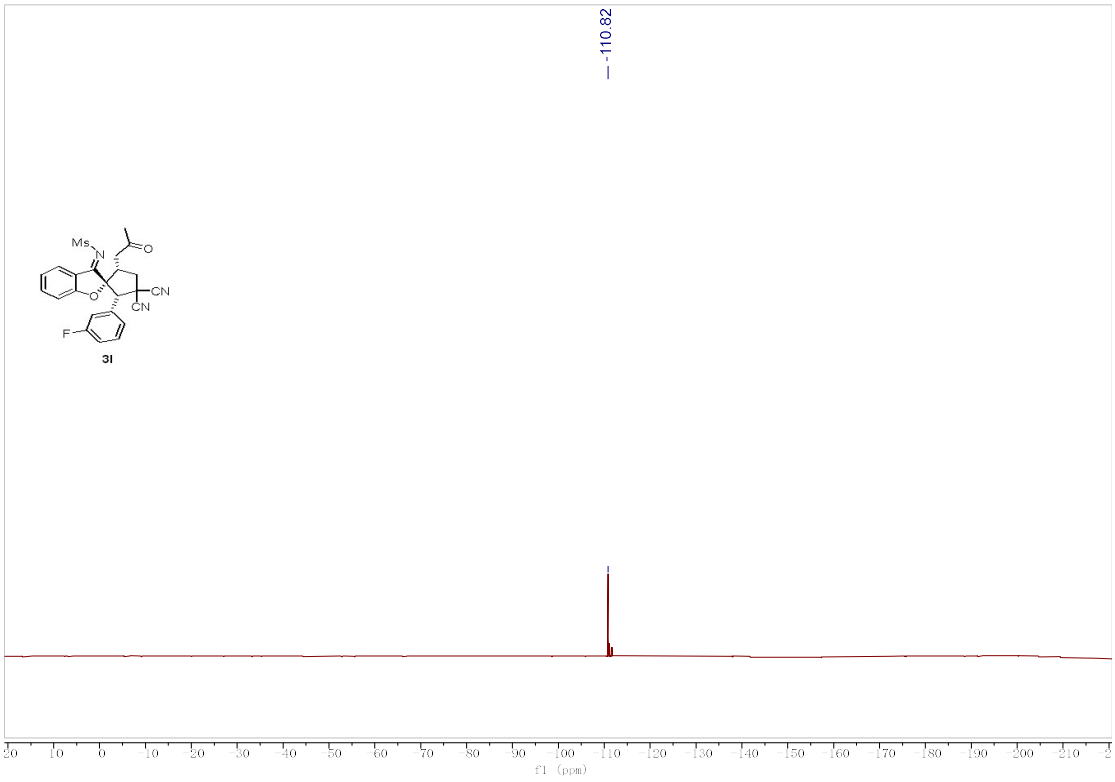
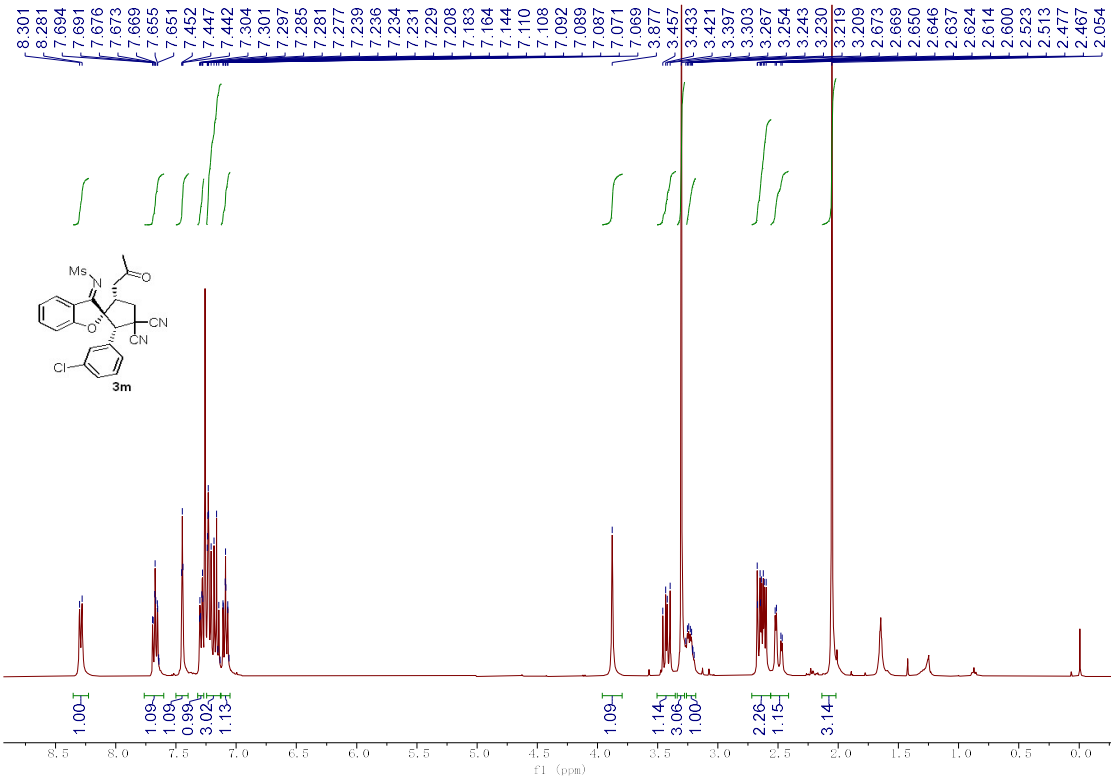


^{19}F NMR (377 MHz, $CDCl_3$) of **3l**



^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



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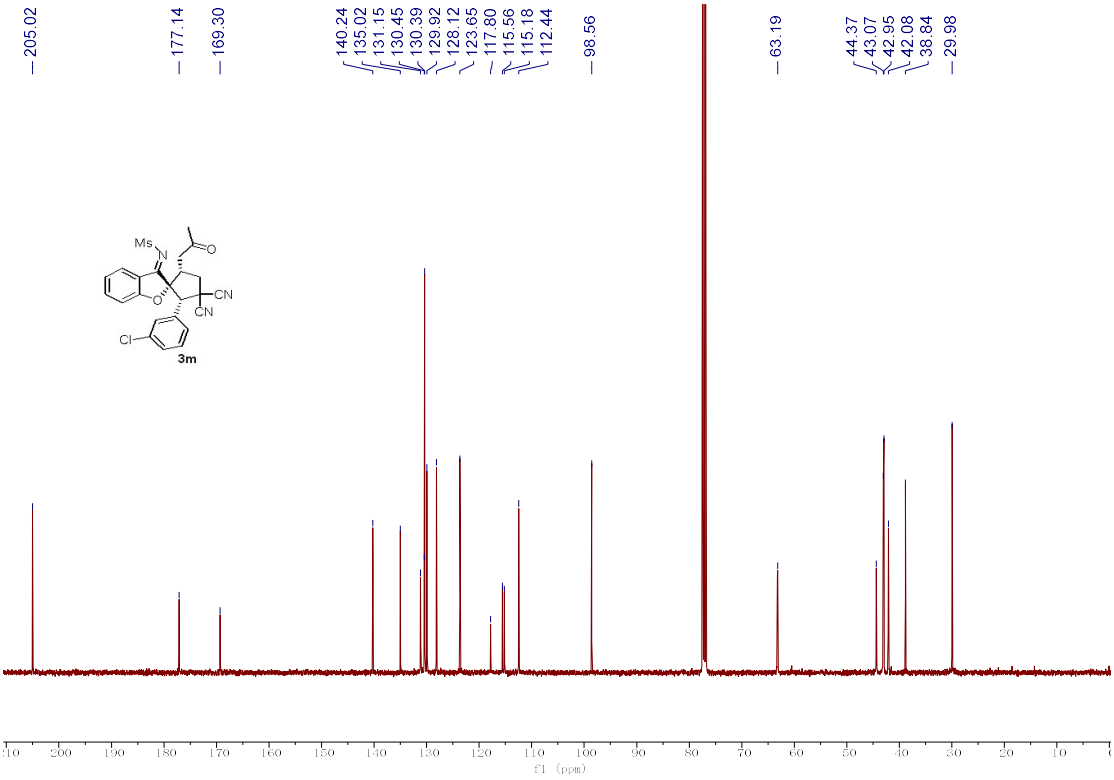

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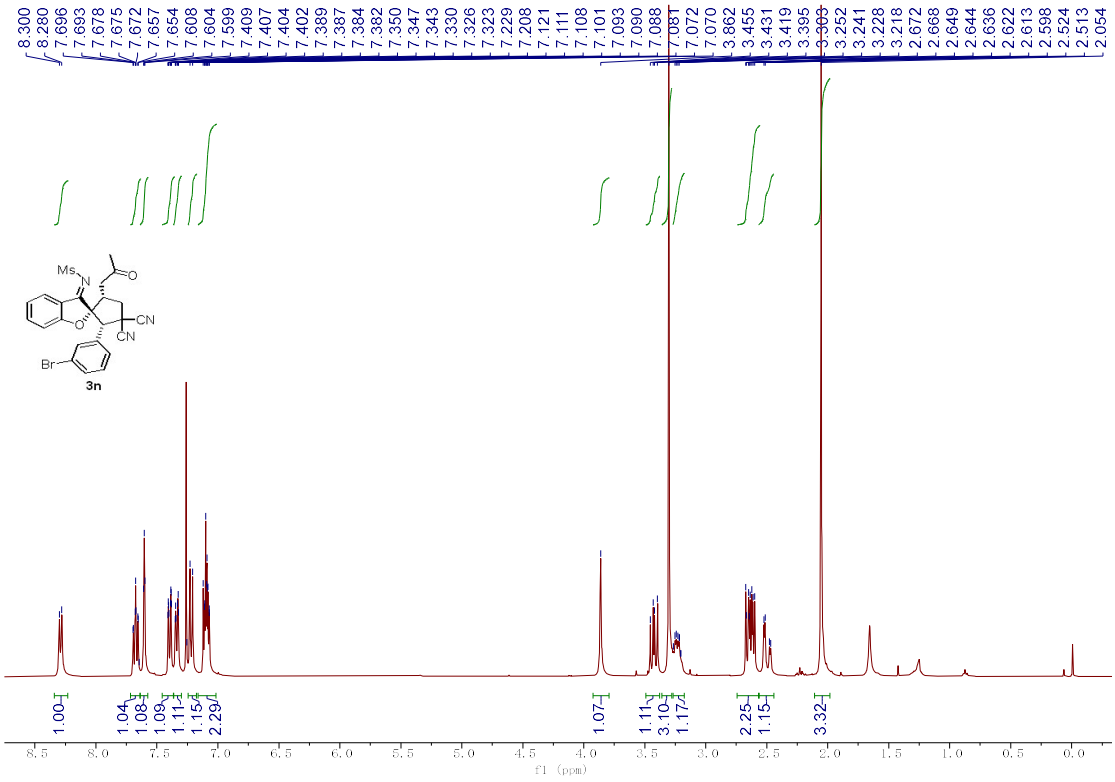

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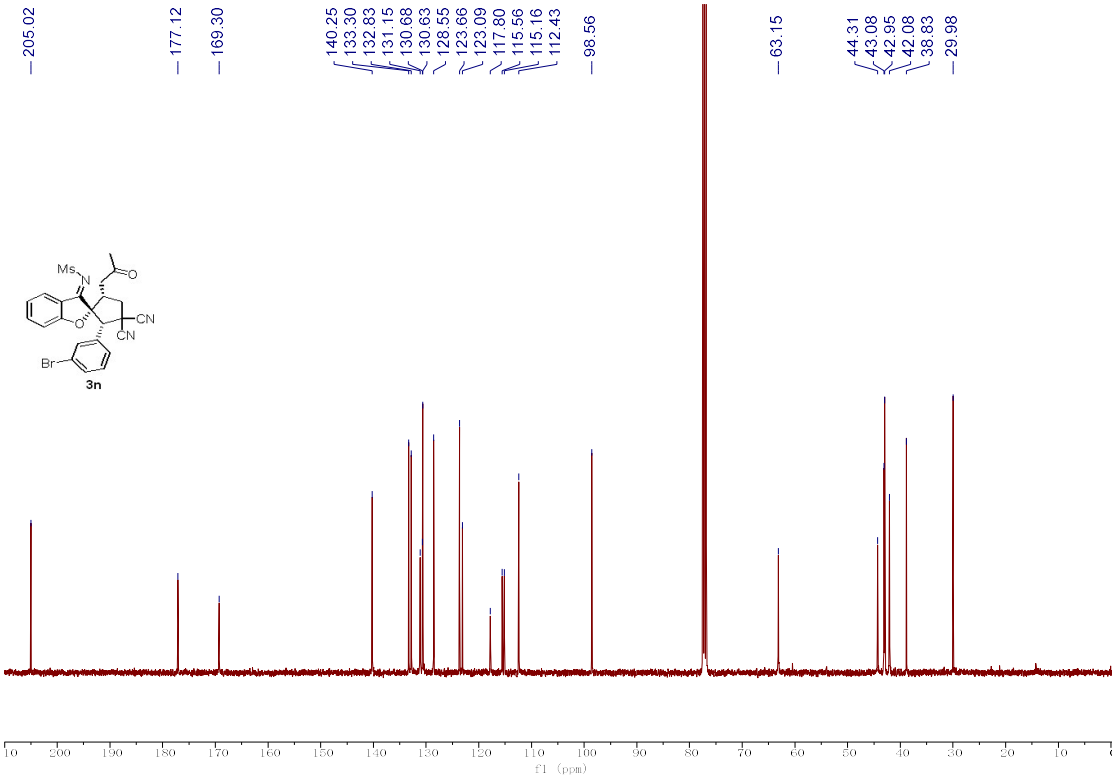

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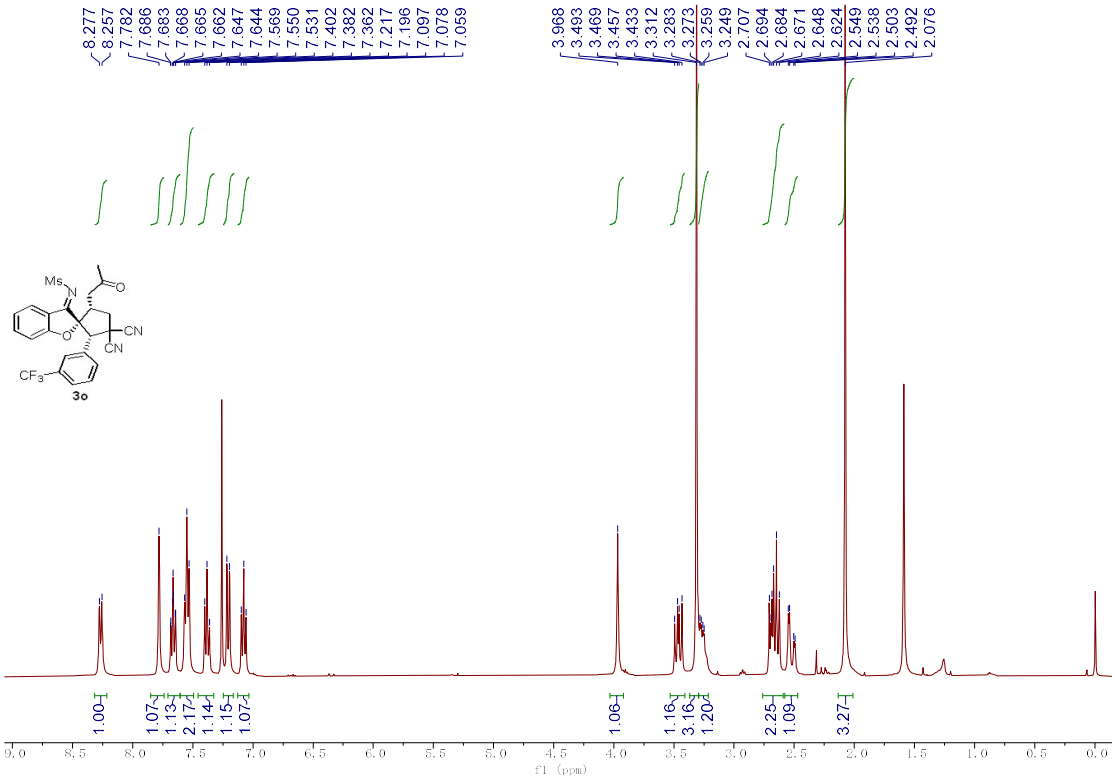

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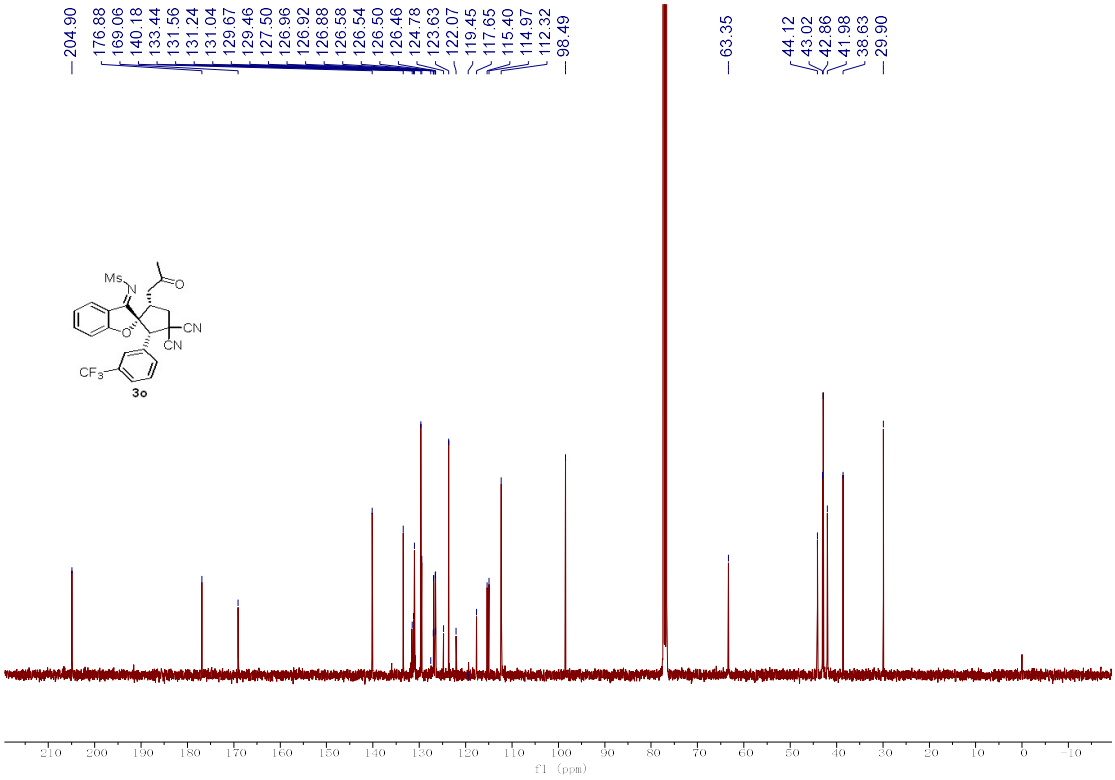
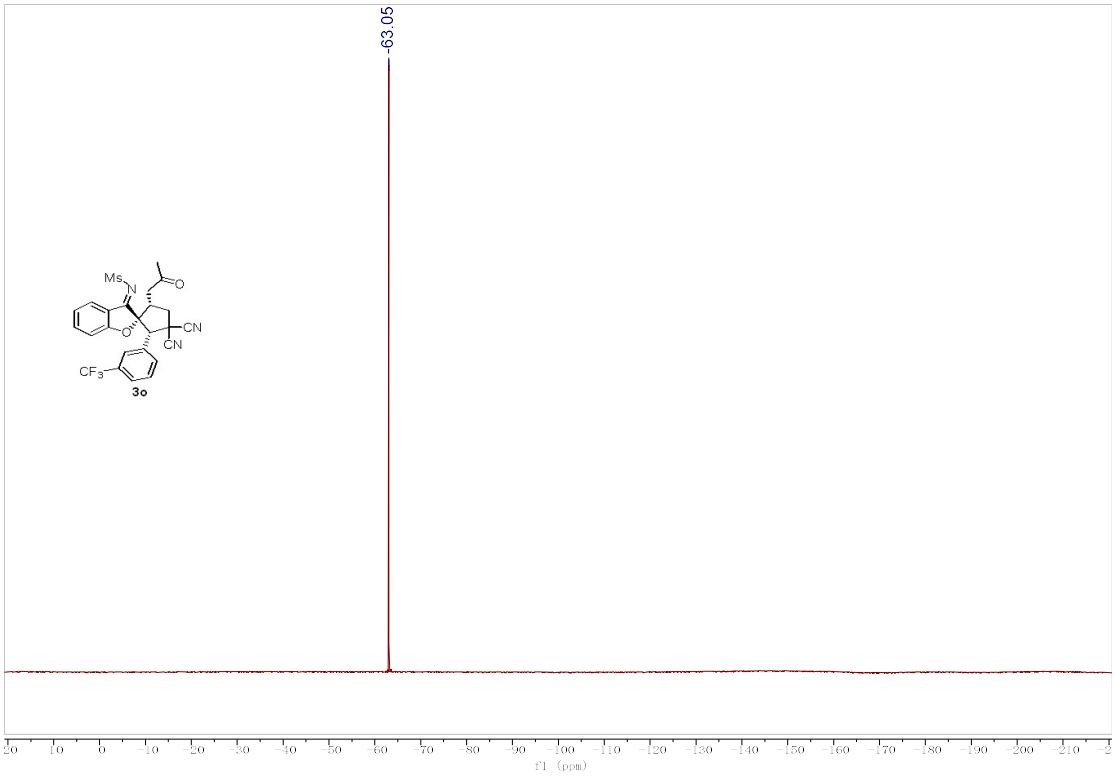


^{19}F NMR (377 MHz, $CDCl_3$) of **3o**



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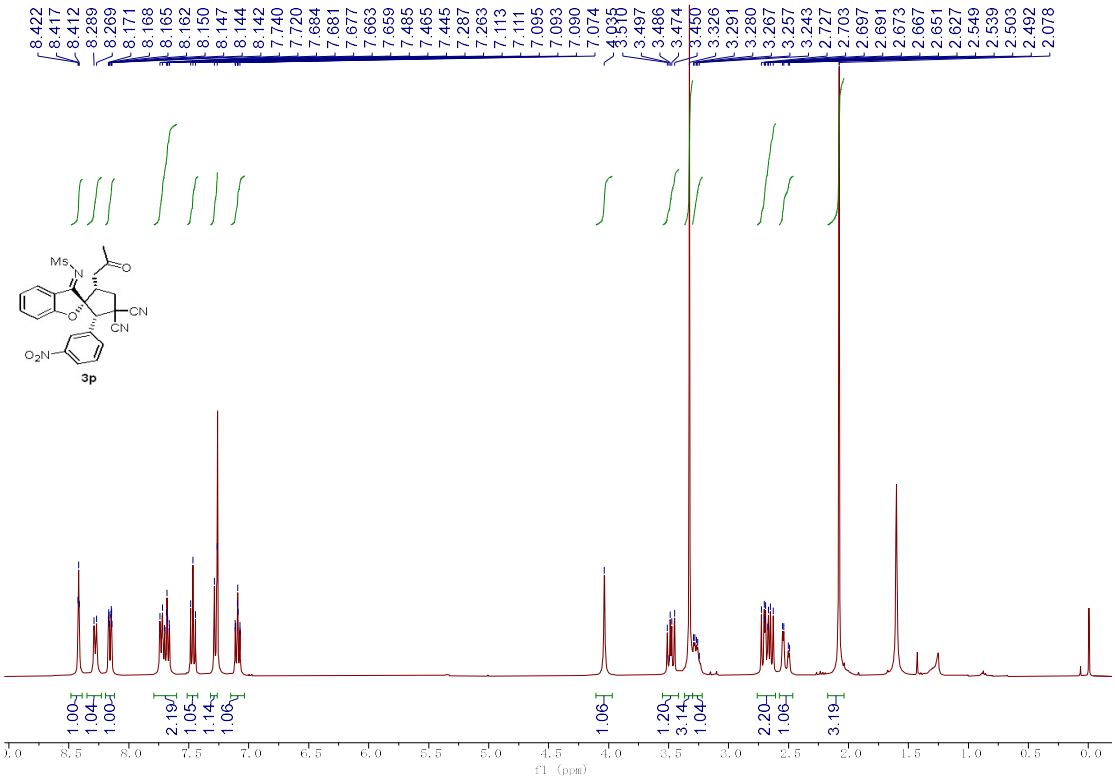
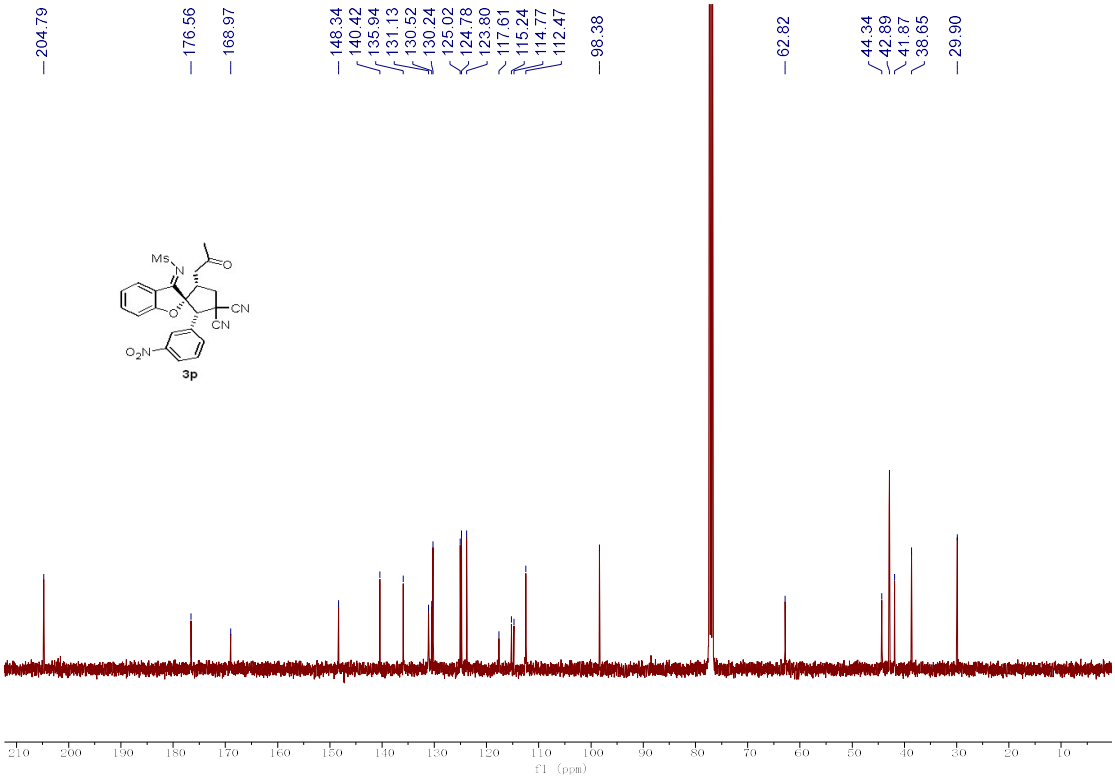


^{13}C NMR (100 MHz, $CDCl_3$) of **3p**



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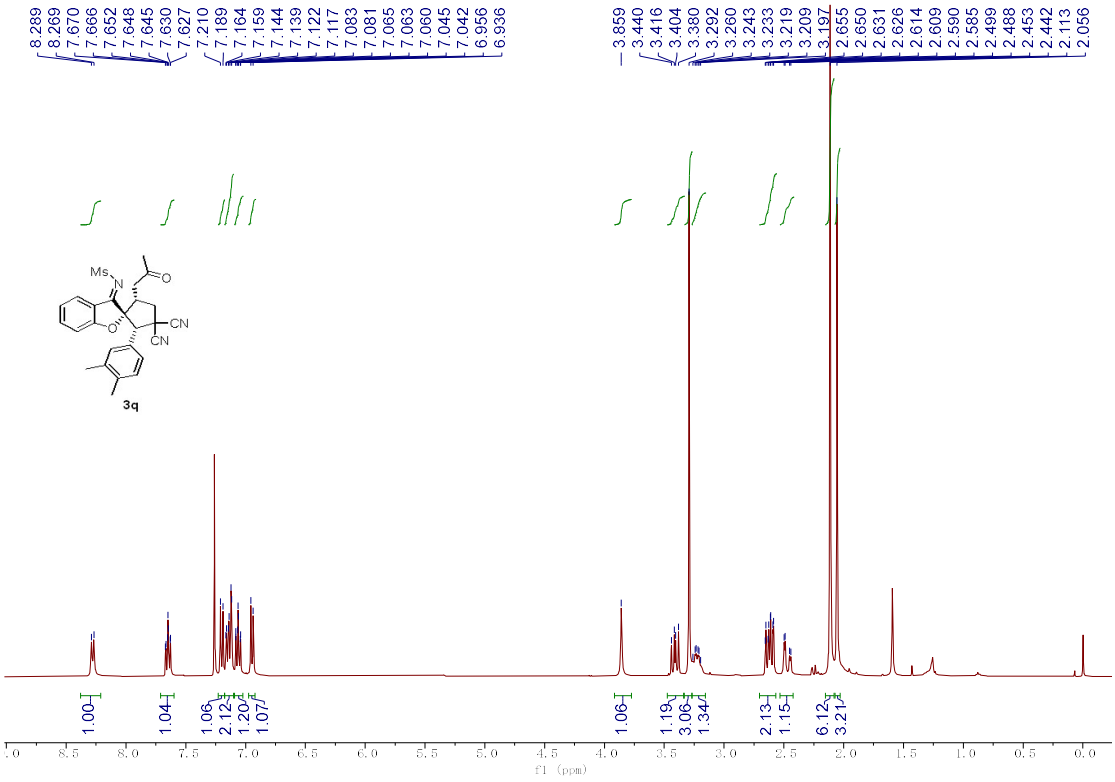

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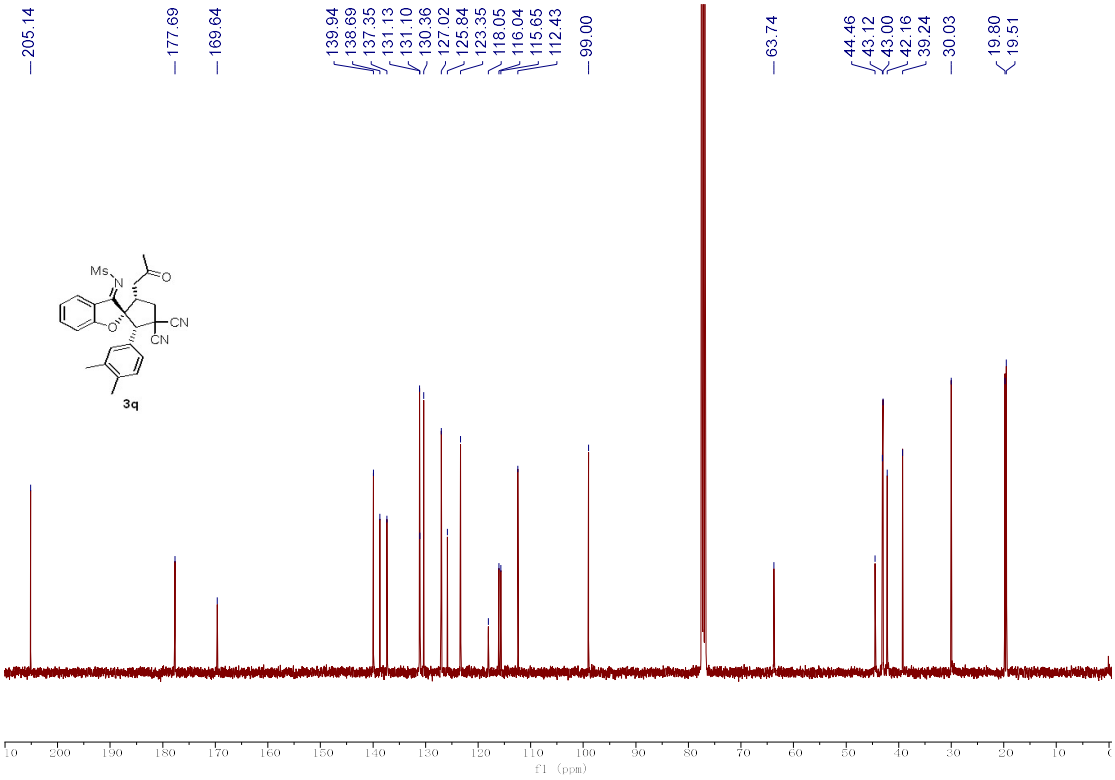

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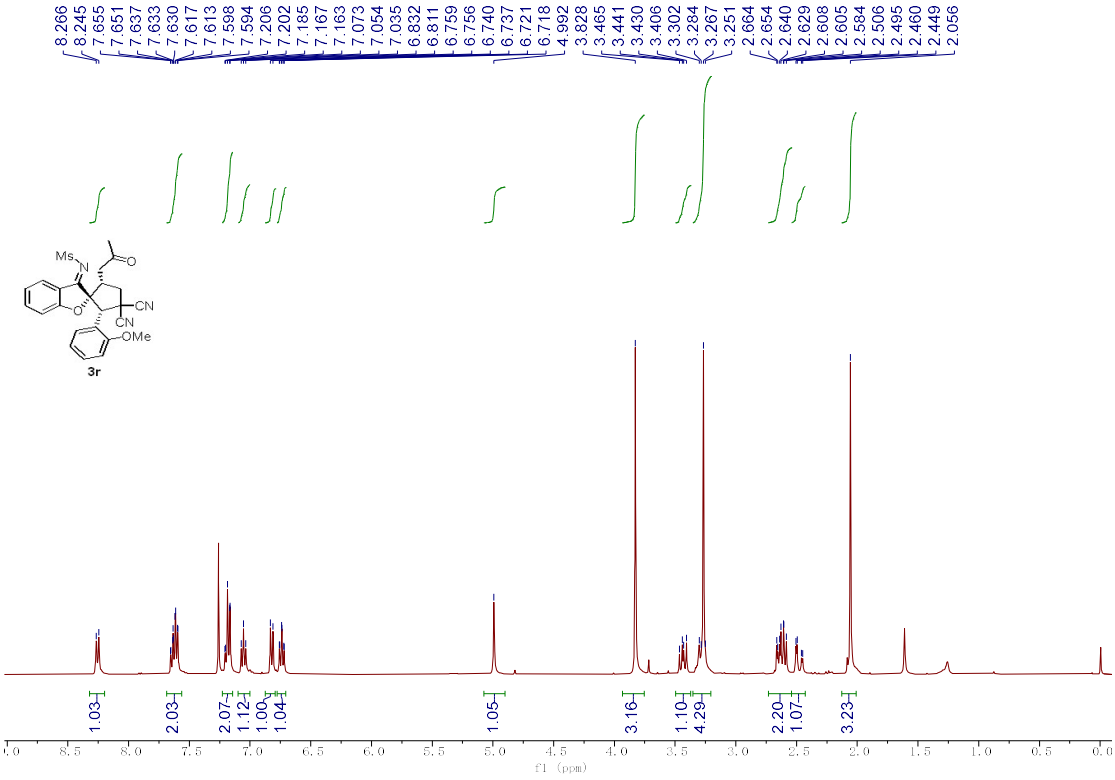

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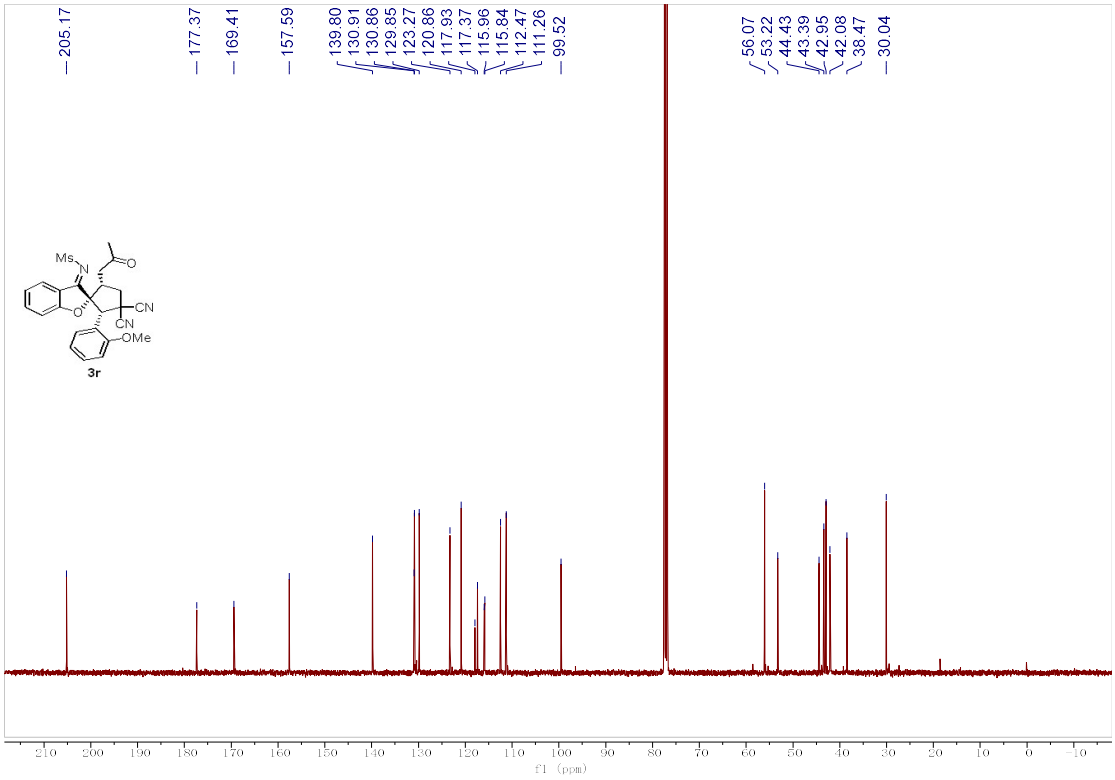

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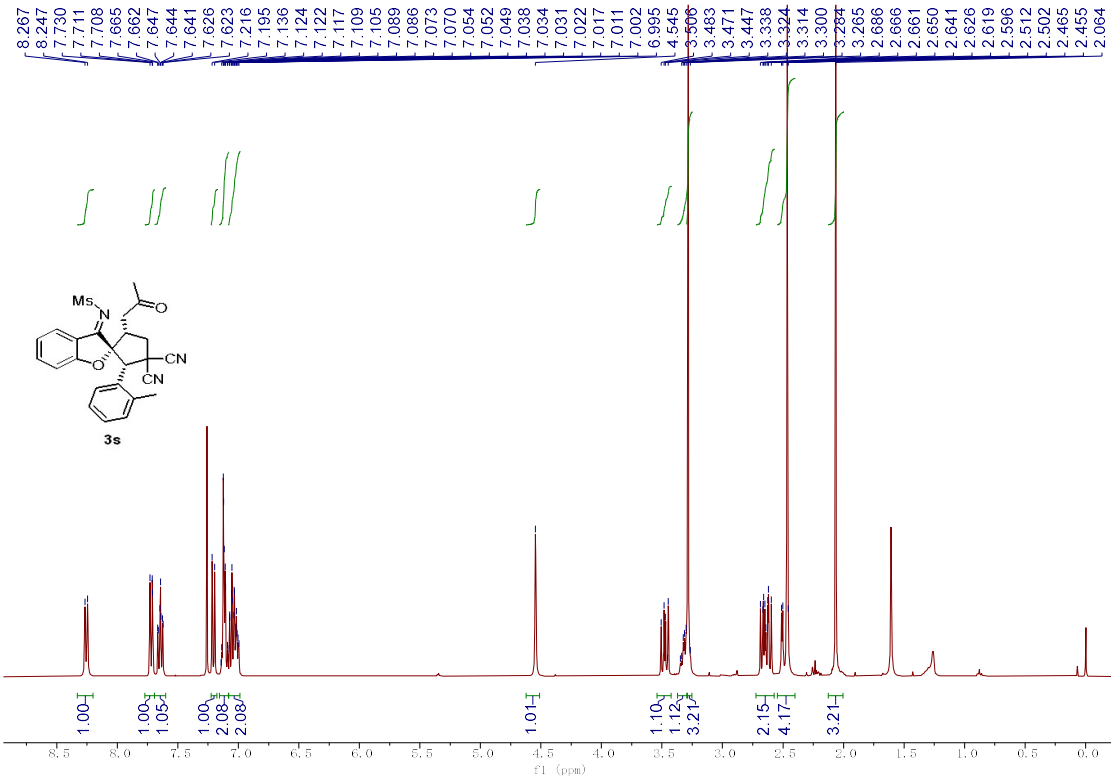

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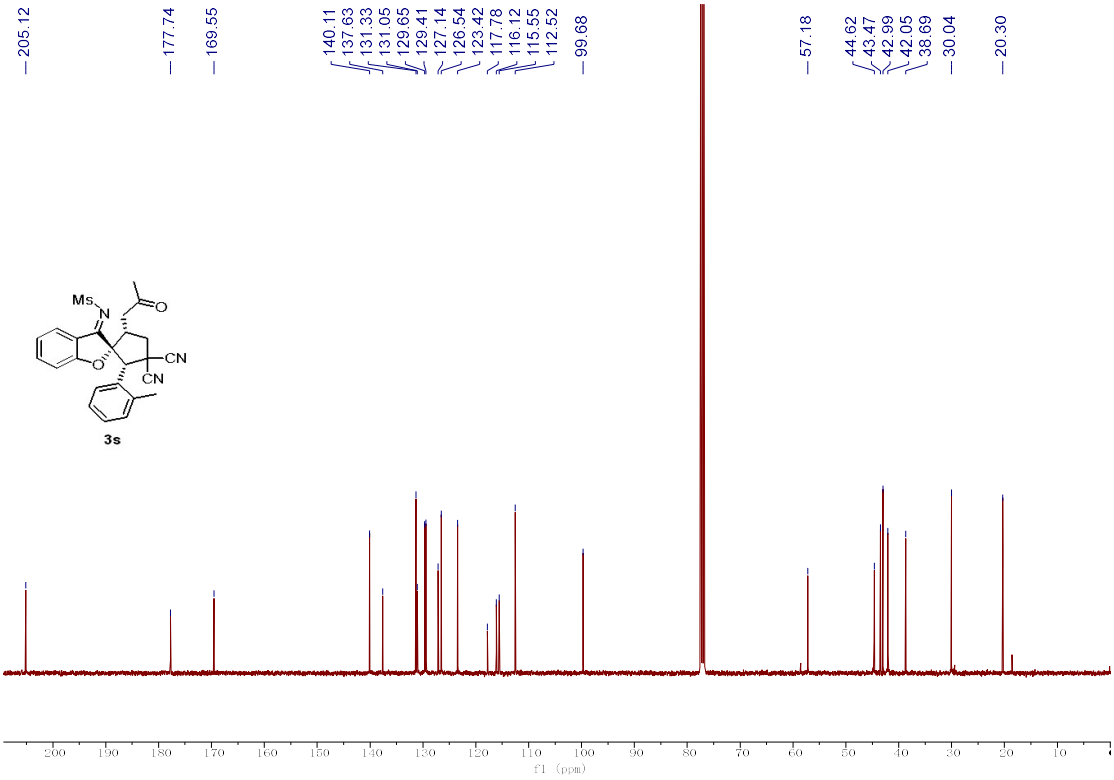

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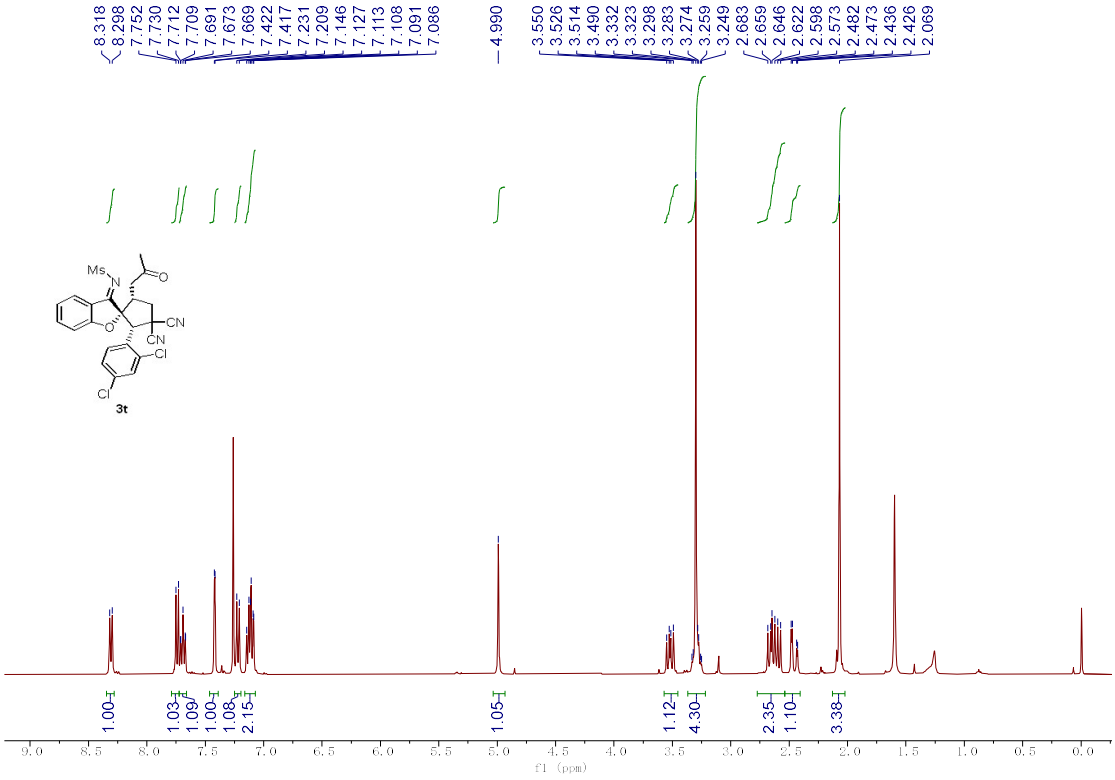

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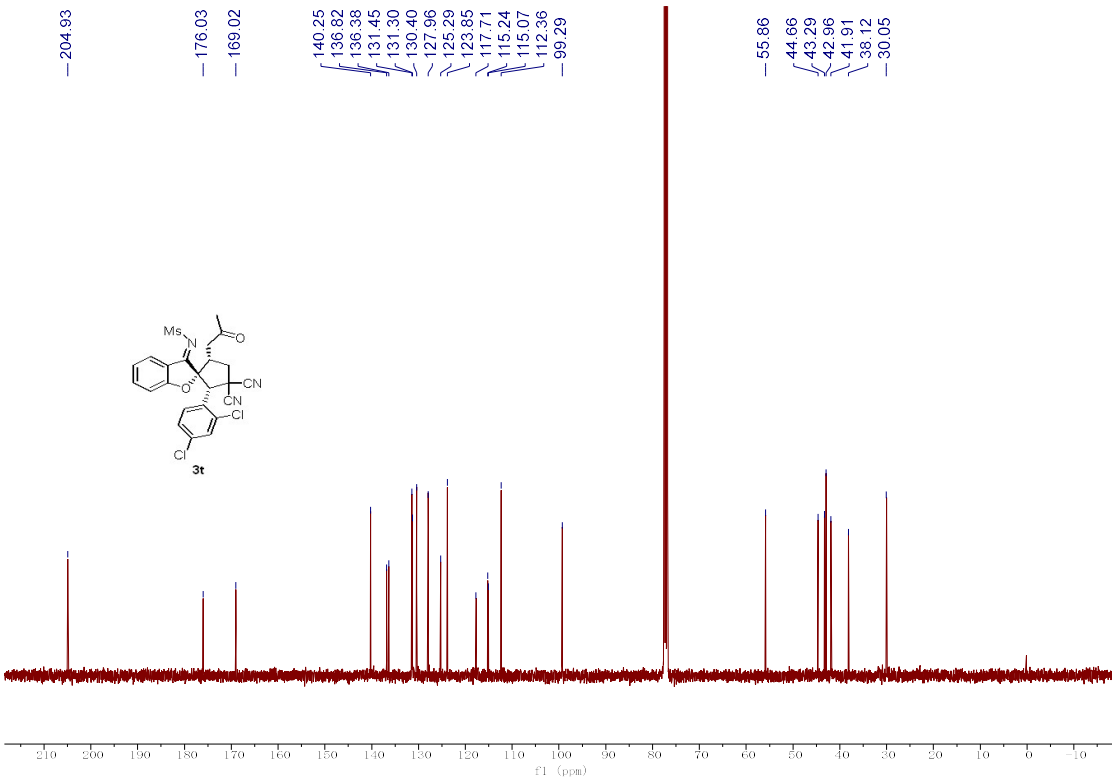

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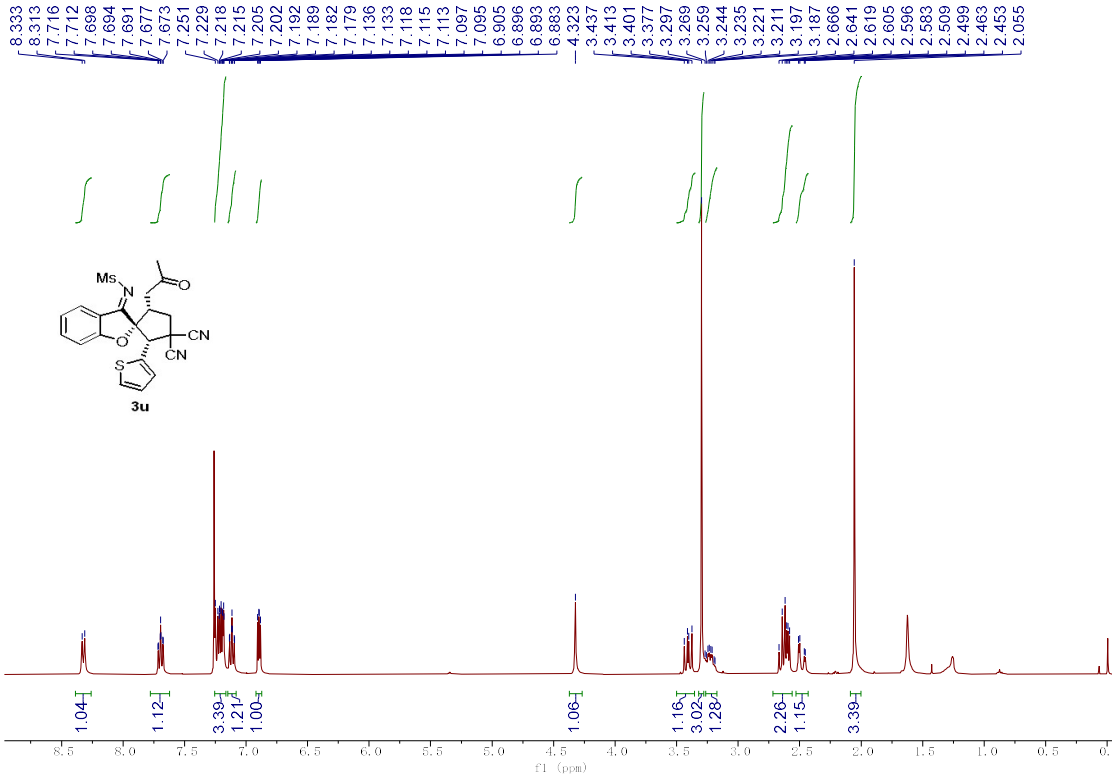

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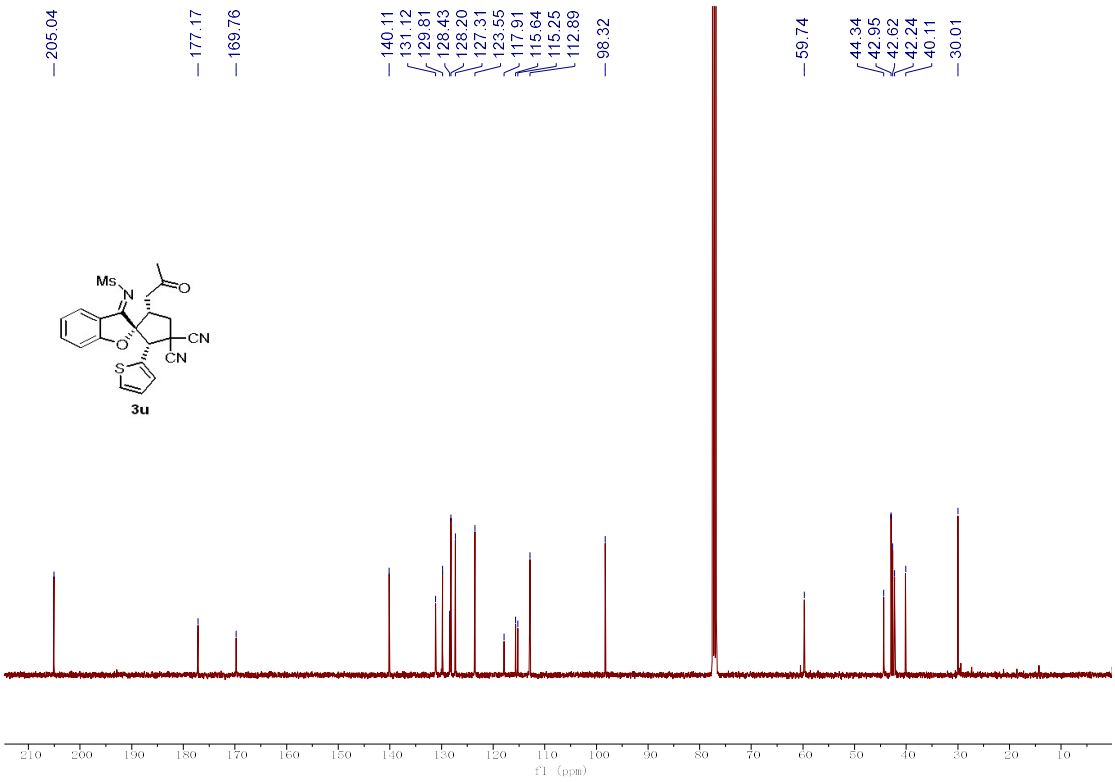

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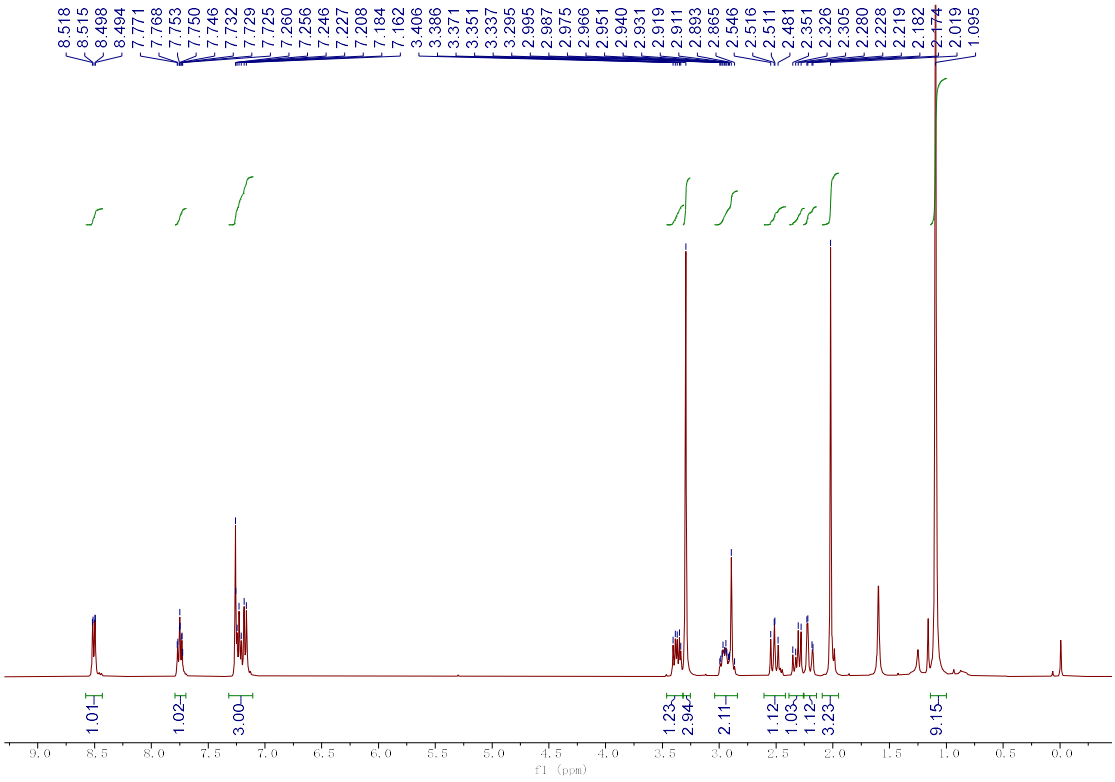
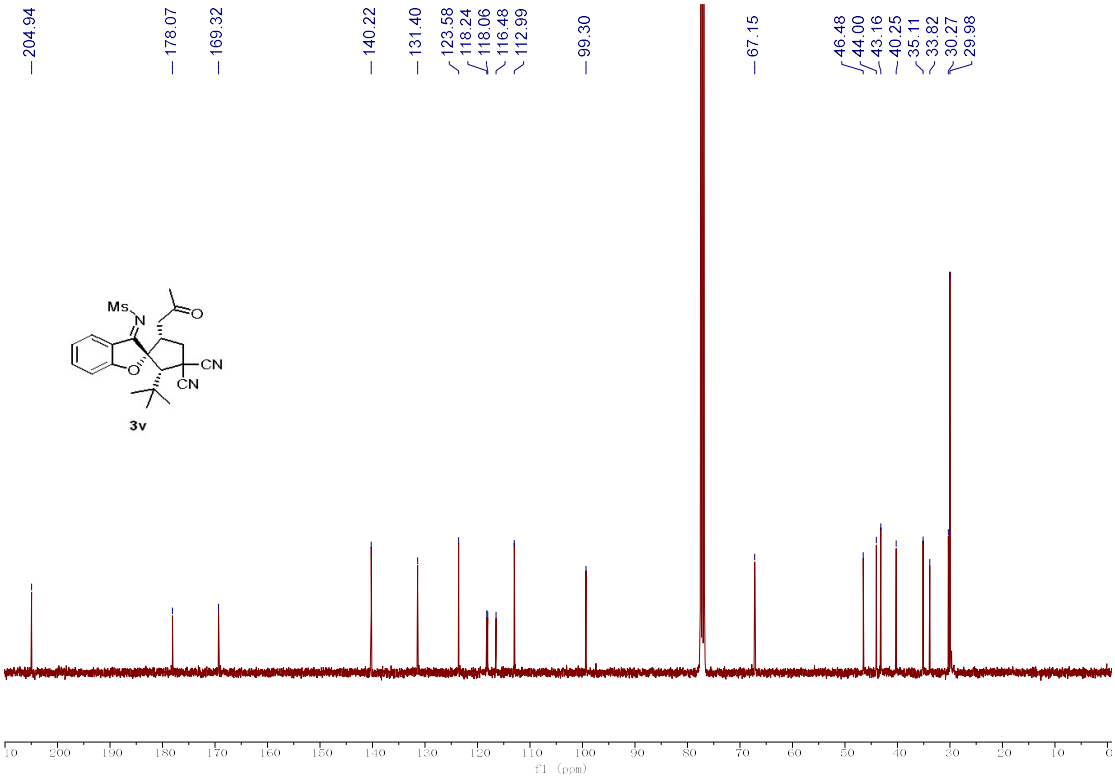
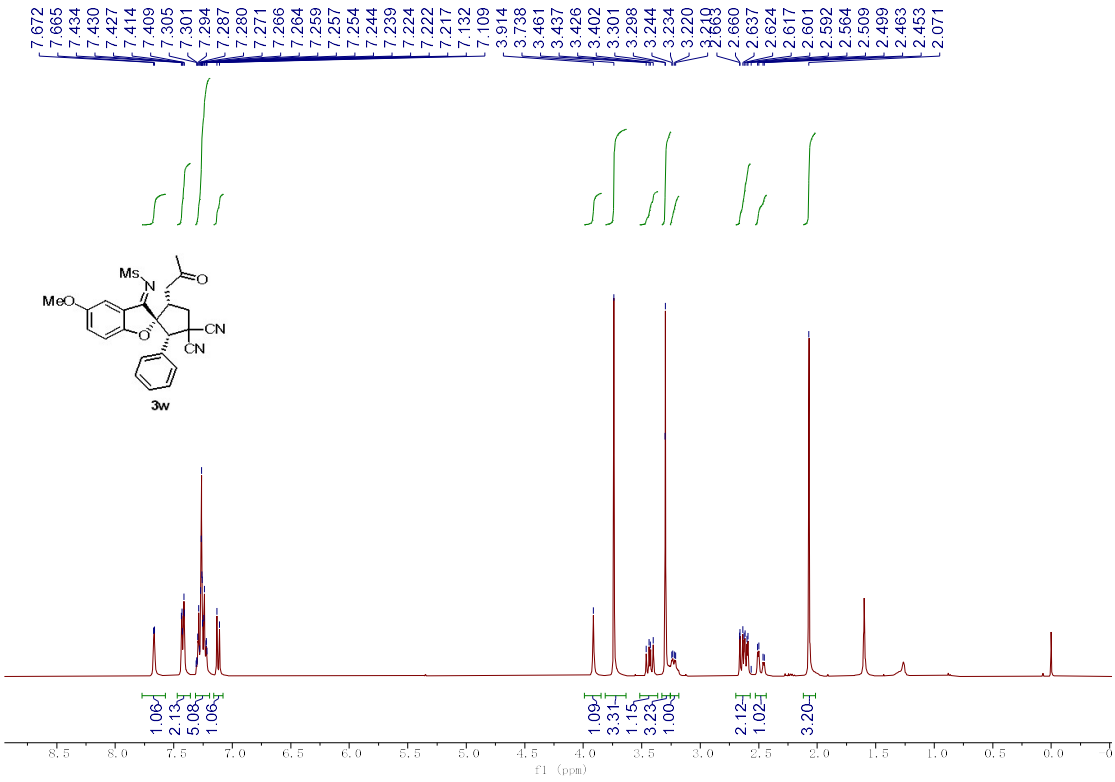


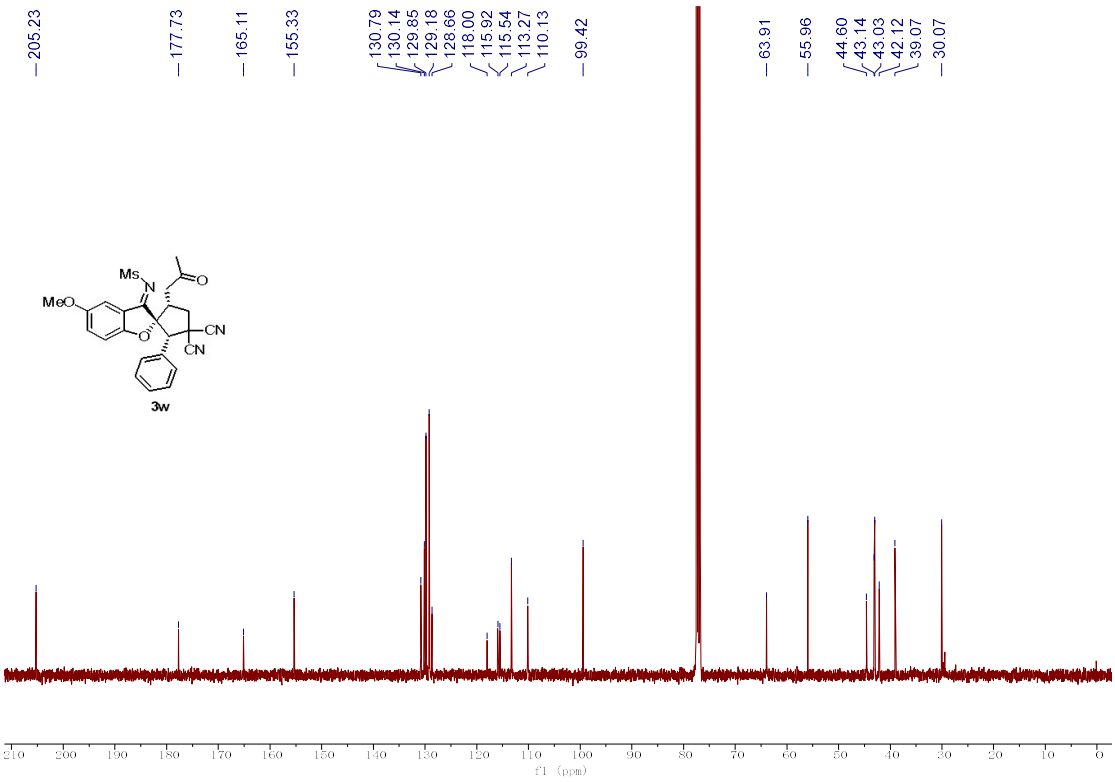
^{13}C NMR (100 MHz, $CDCl_3$) of **3v**



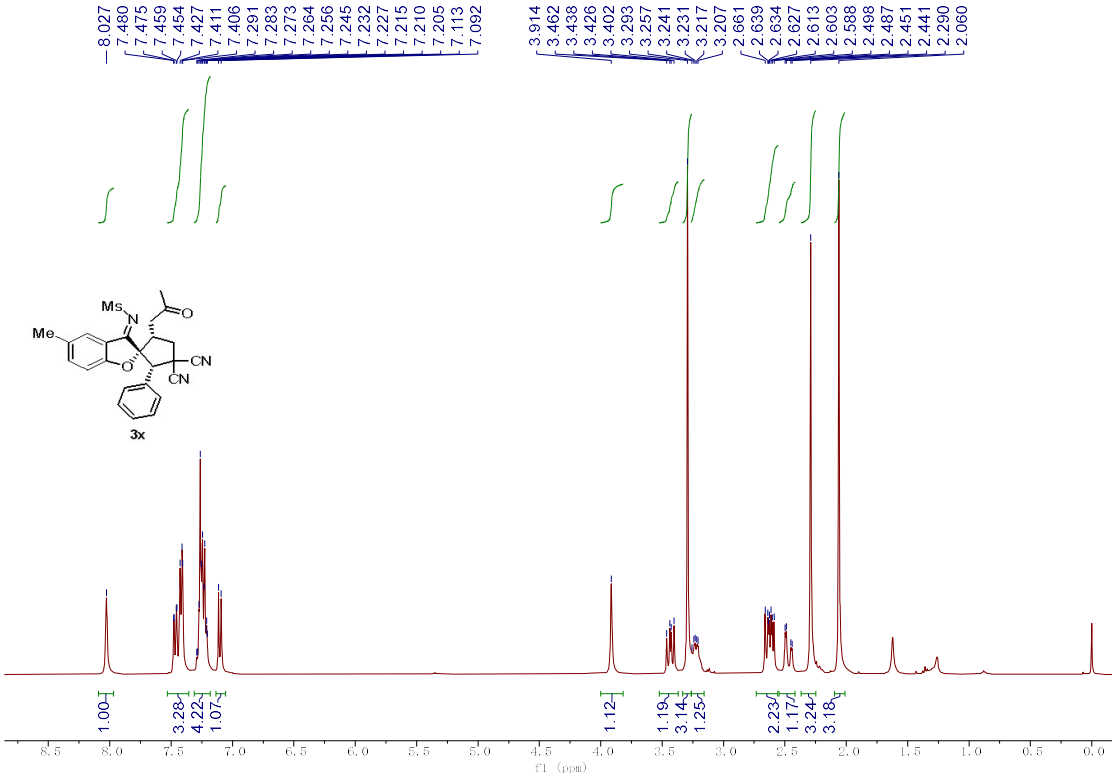
^{1}H NMR (400 MHz, $CDCl_3$) of **3w**



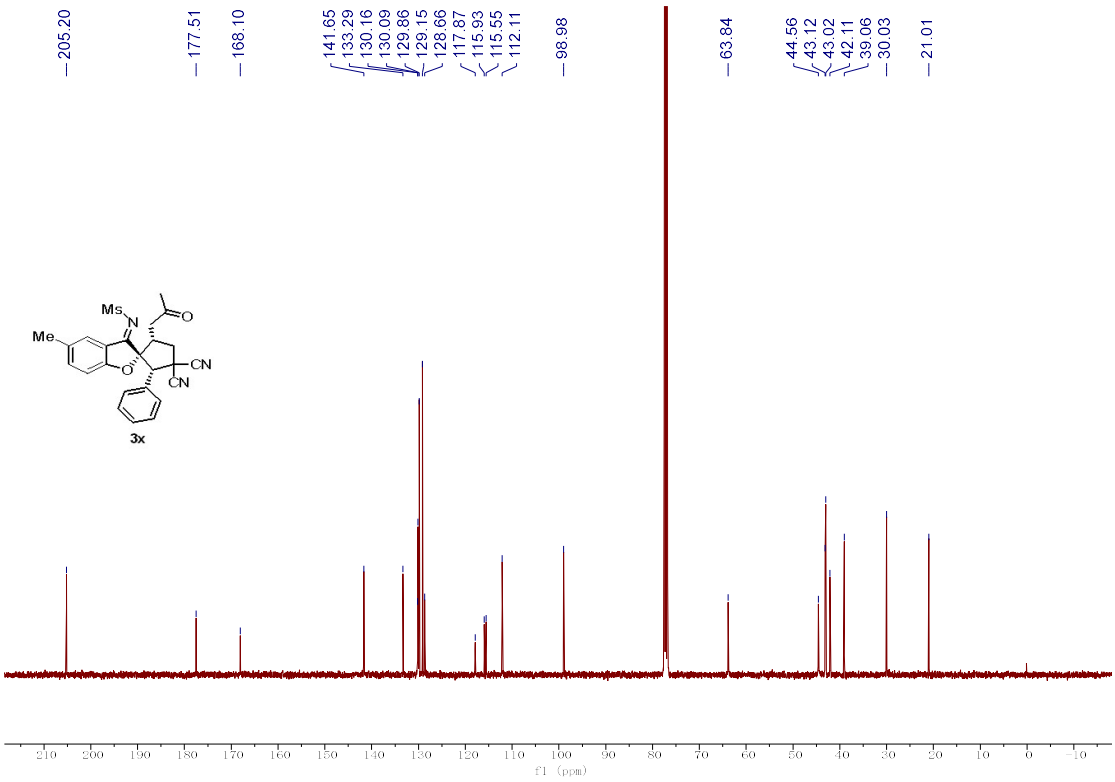
^{13}C NMR (100 MHz, $CDCl_3$) of **3w**



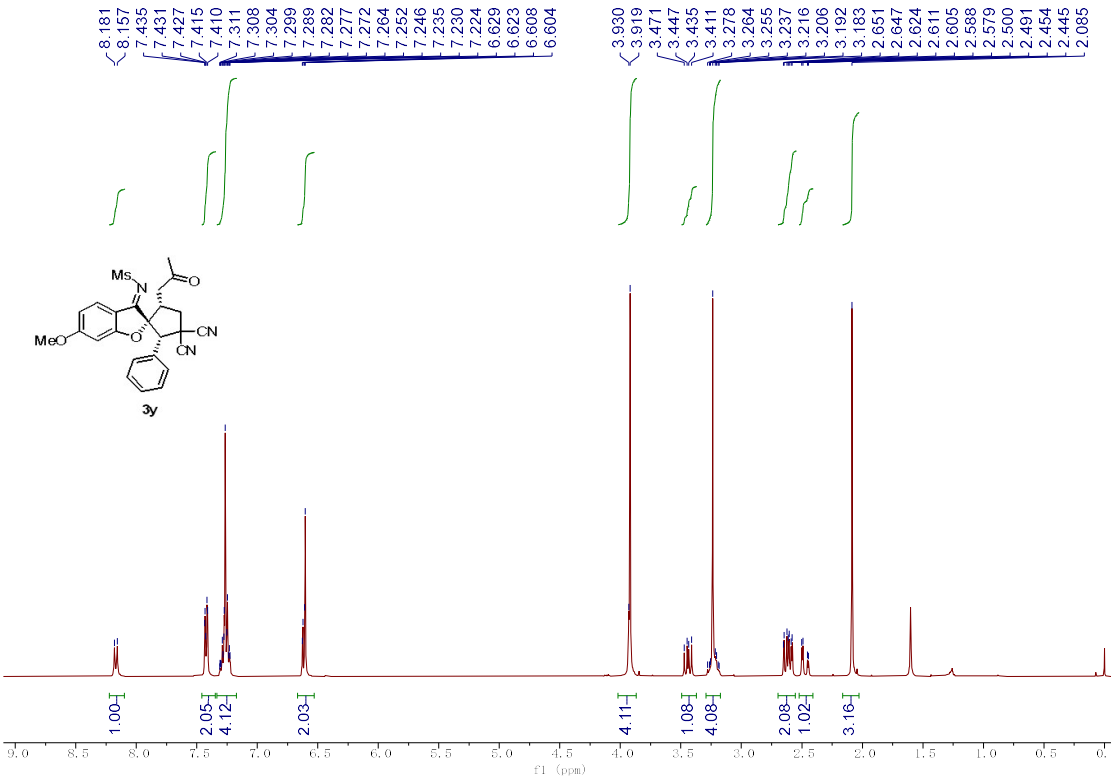
^{1}H NMR (400 MHz, $CDCl_3$) of **3x**



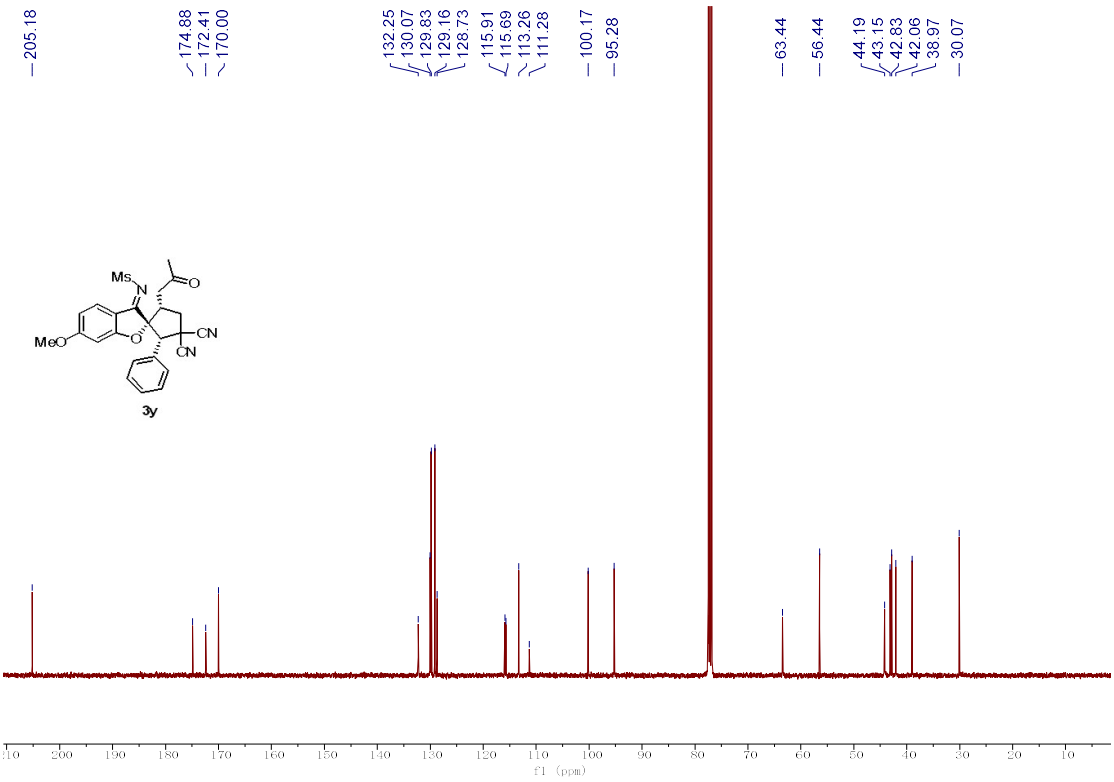
^{13}C NMR (100 MHz, $CDCl_3$) of **3x**



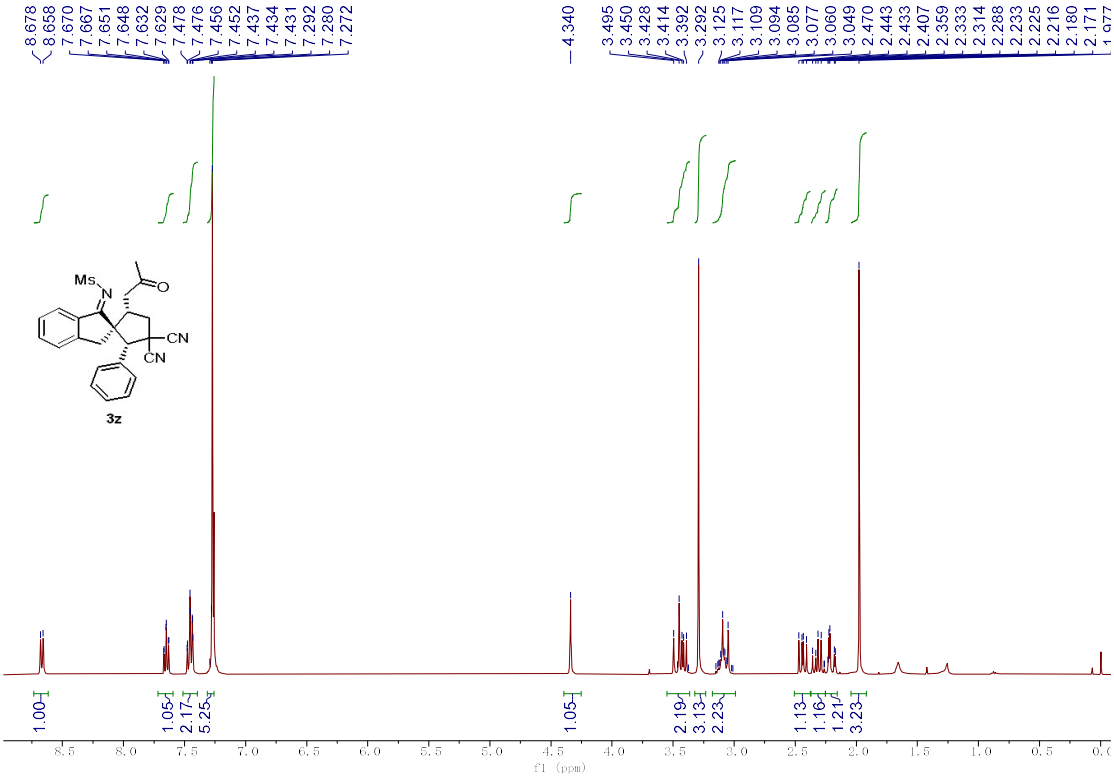
^{1}H NMR (400 MHz, $CDCl_3$) of **3y**



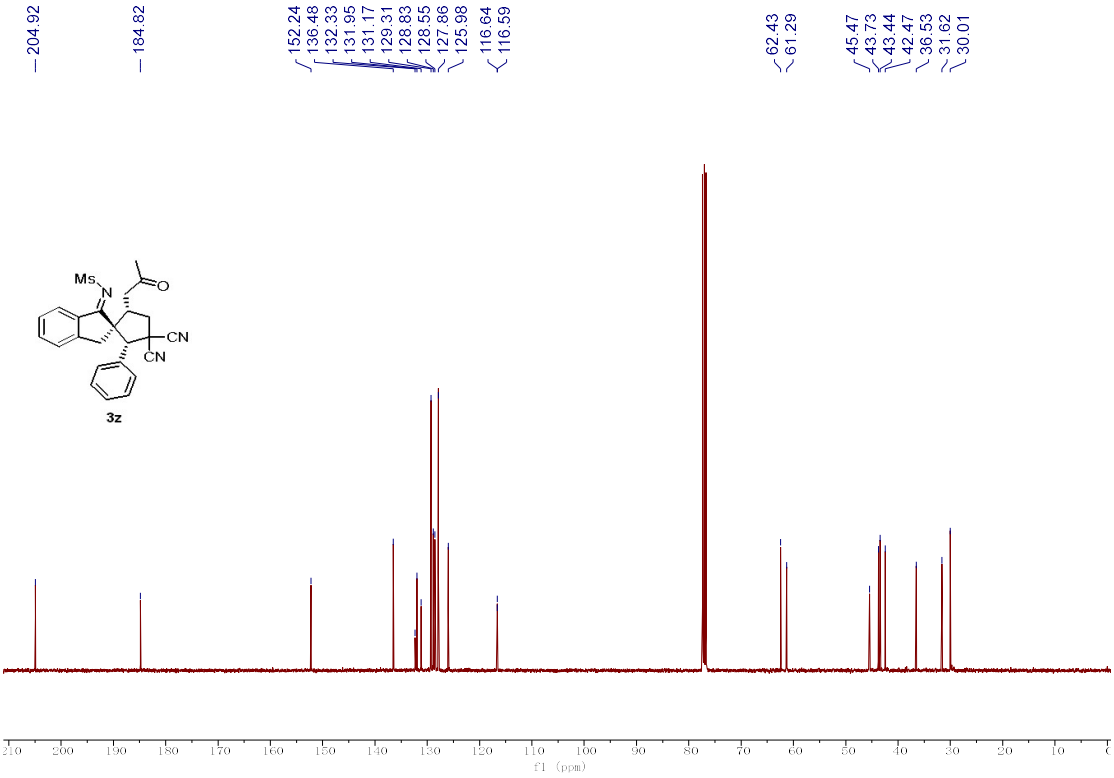
^{13}C NMR (100 MHz, $CDCl_3$) of **3y**



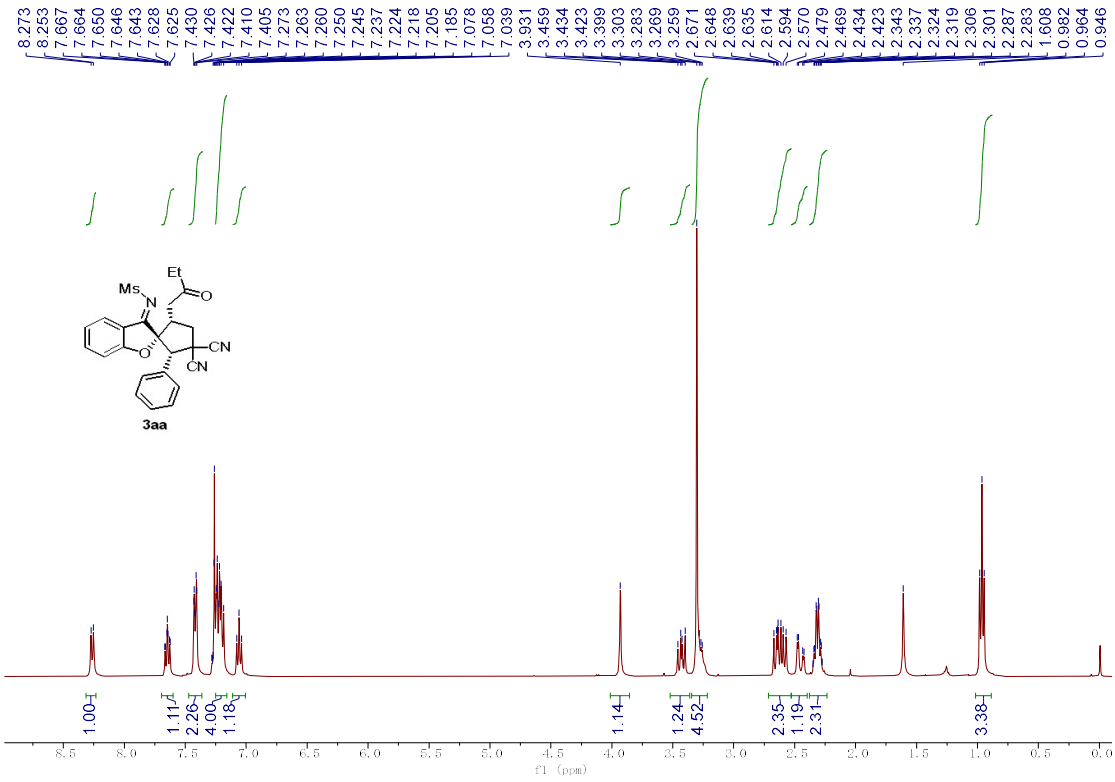
^{1}H NMR (400 MHz, $CDCl_3$) of **3z**



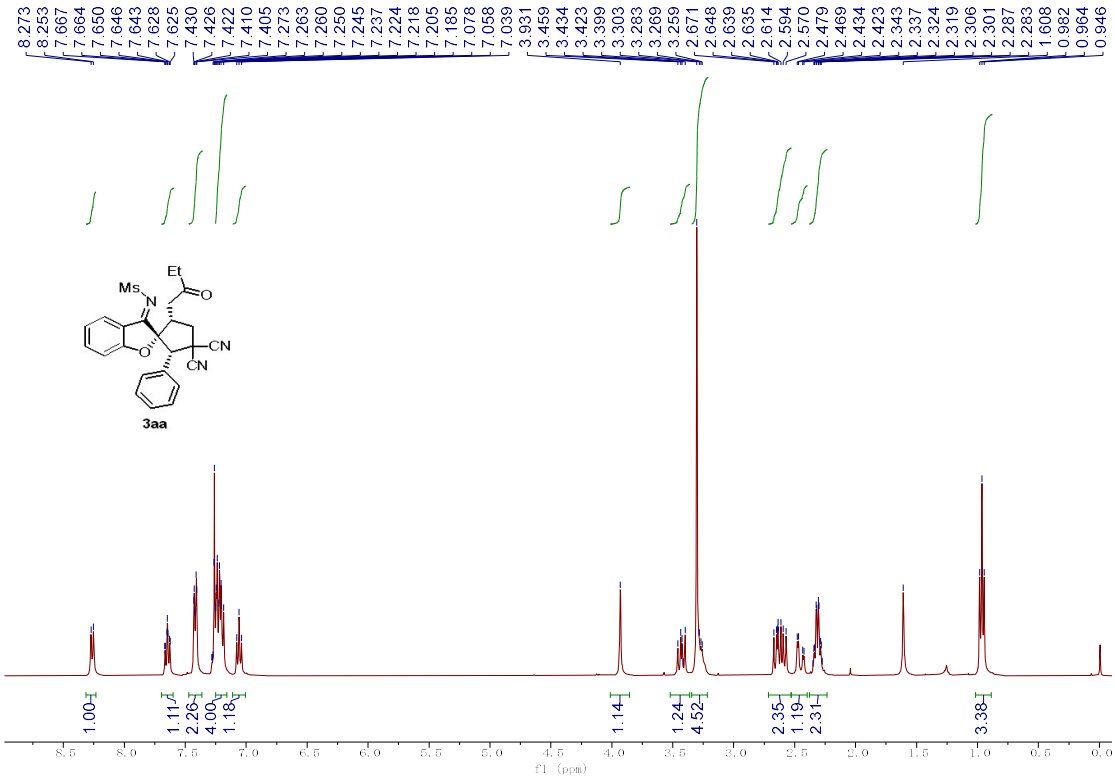
^{13}C NMR (100 MHz, $CDCl_3$) of **3z**



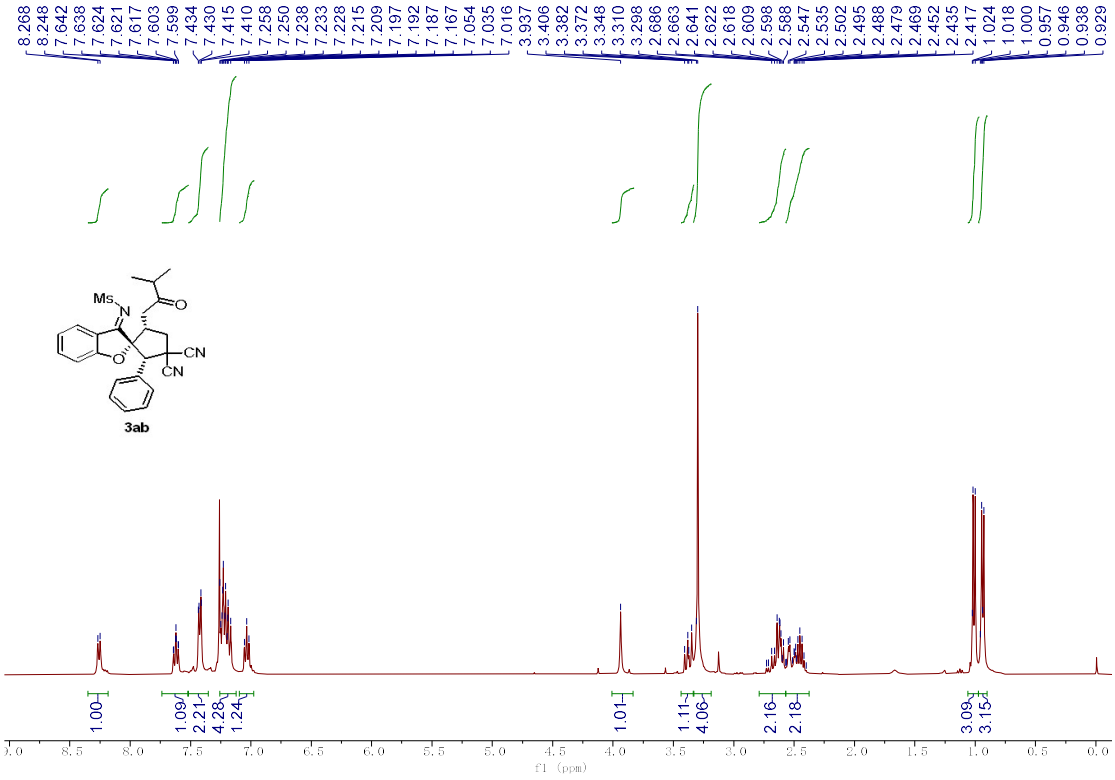
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



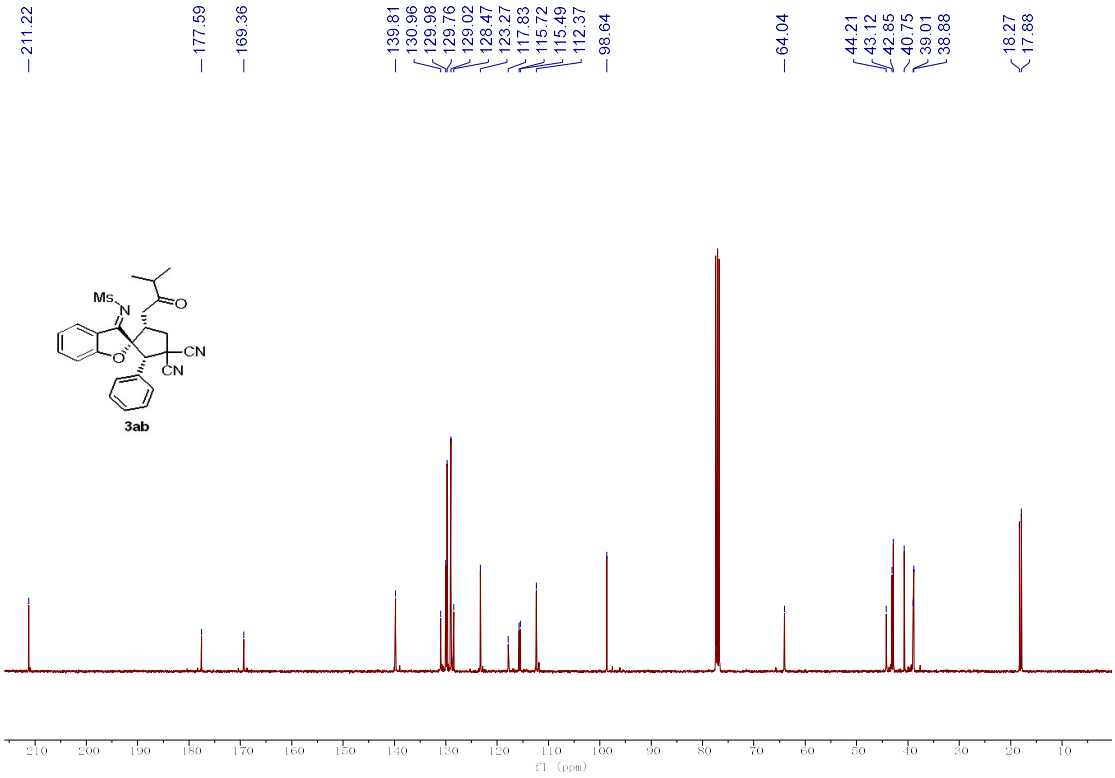
^{13}C NMR (100 MHz, $CDCl_3$) of **3aa**



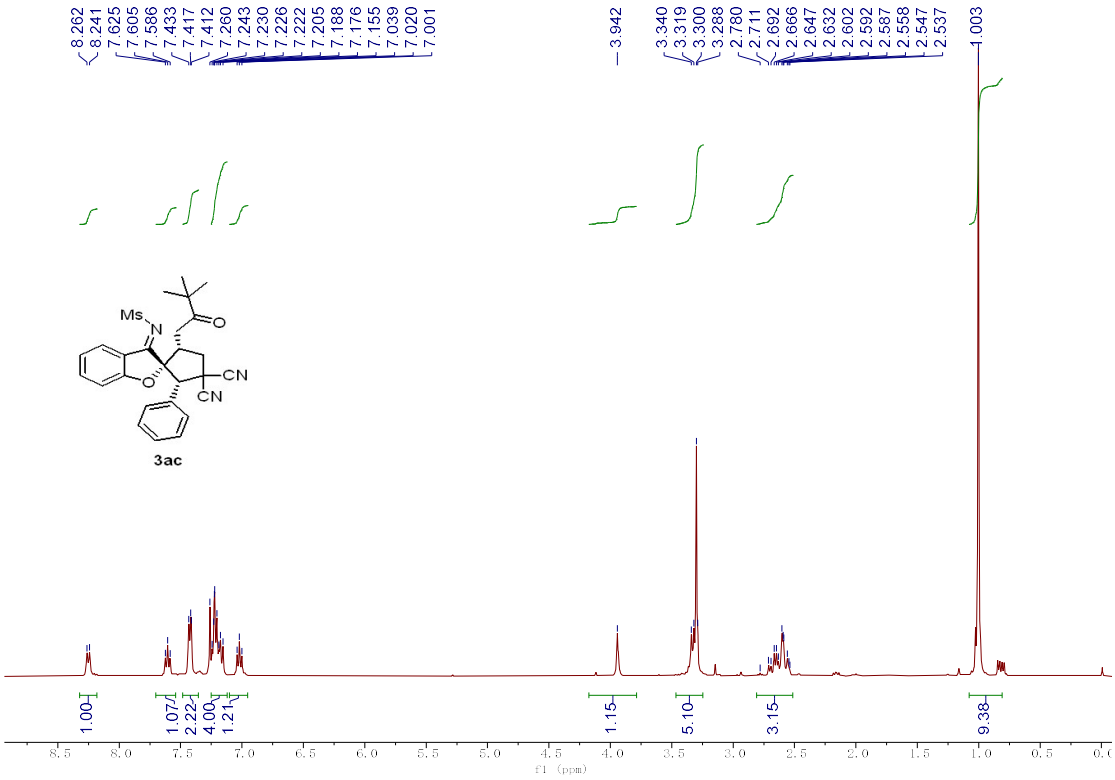
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**



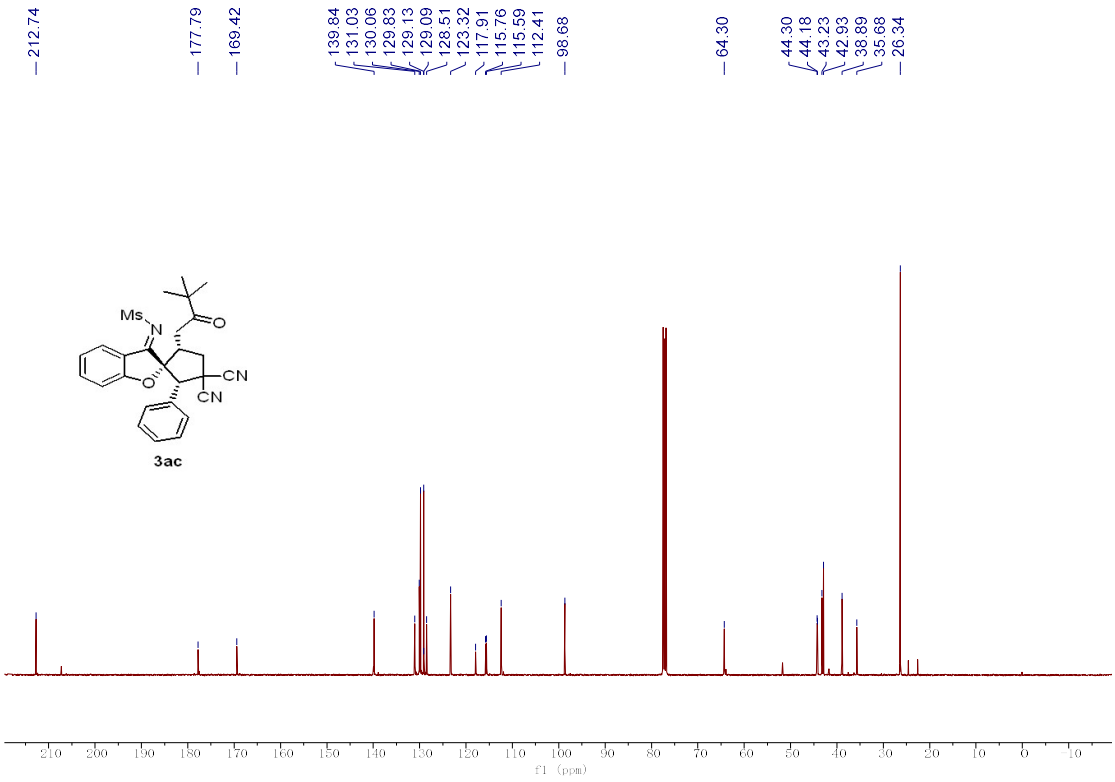
^{13}C NMR (100 MHz, $CDCl_3$) of **3ab**



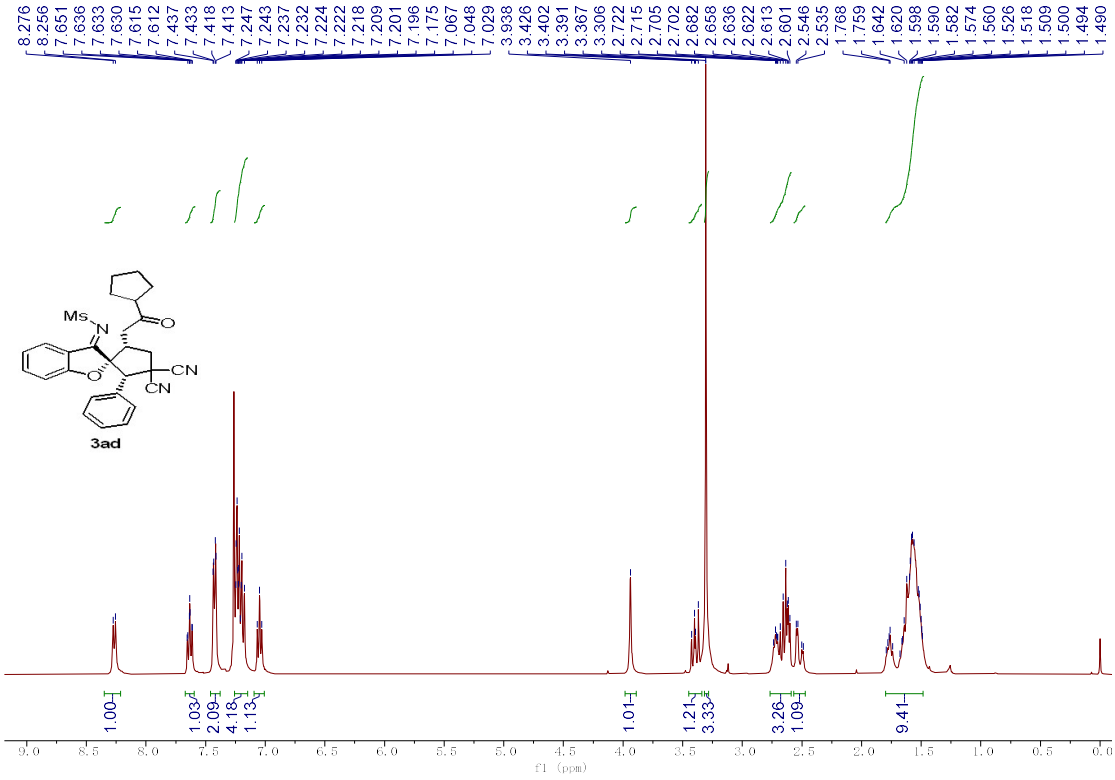
^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**



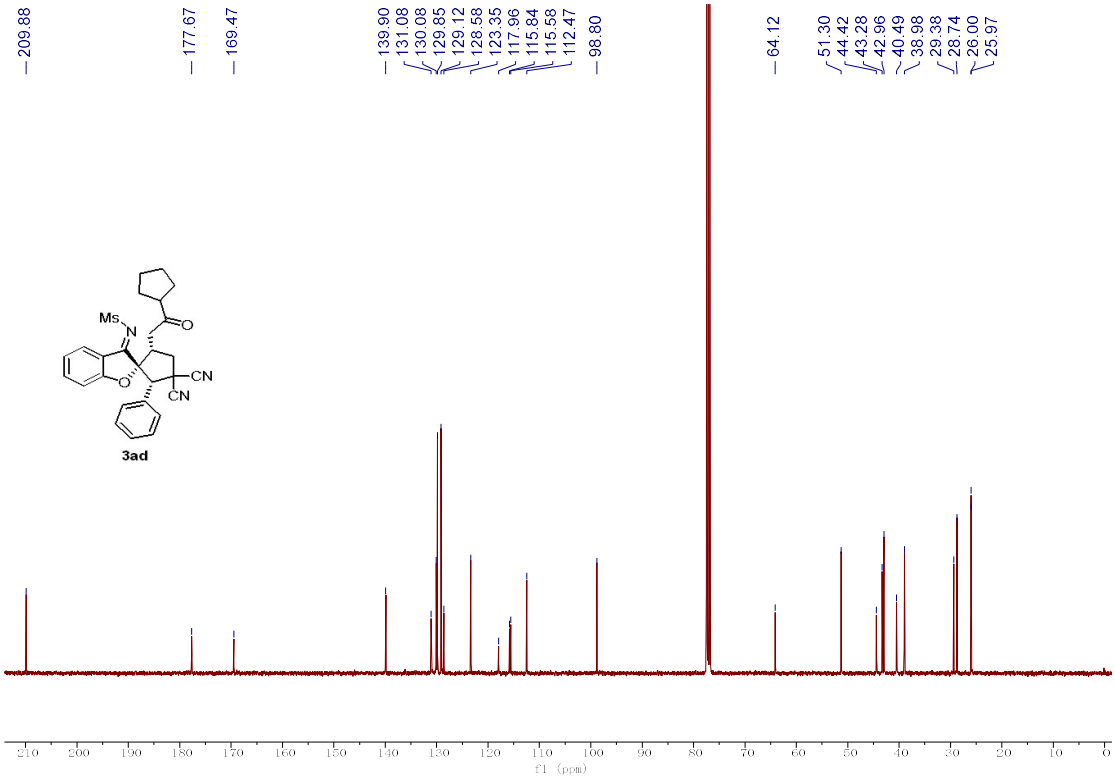
^{13}C NMR (100 MHz, $CDCl_3$) of **3ac**



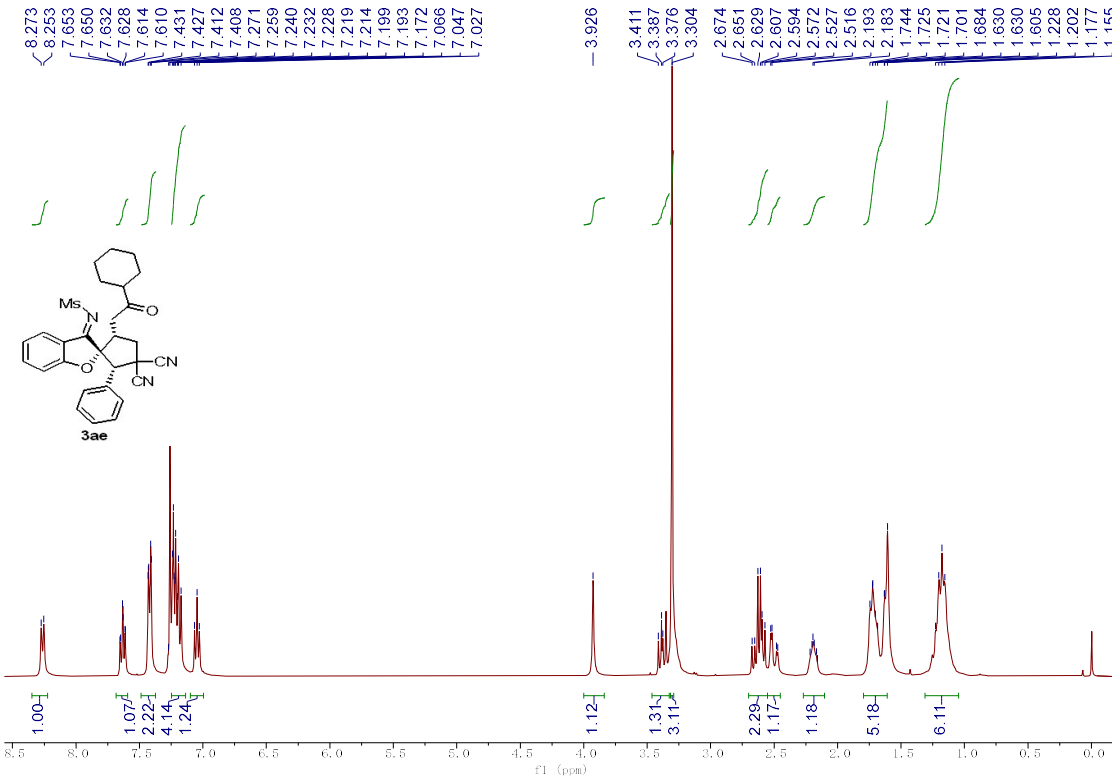
^{1}H NMR (400 MHz, $CDCl_3$) of **3ad**



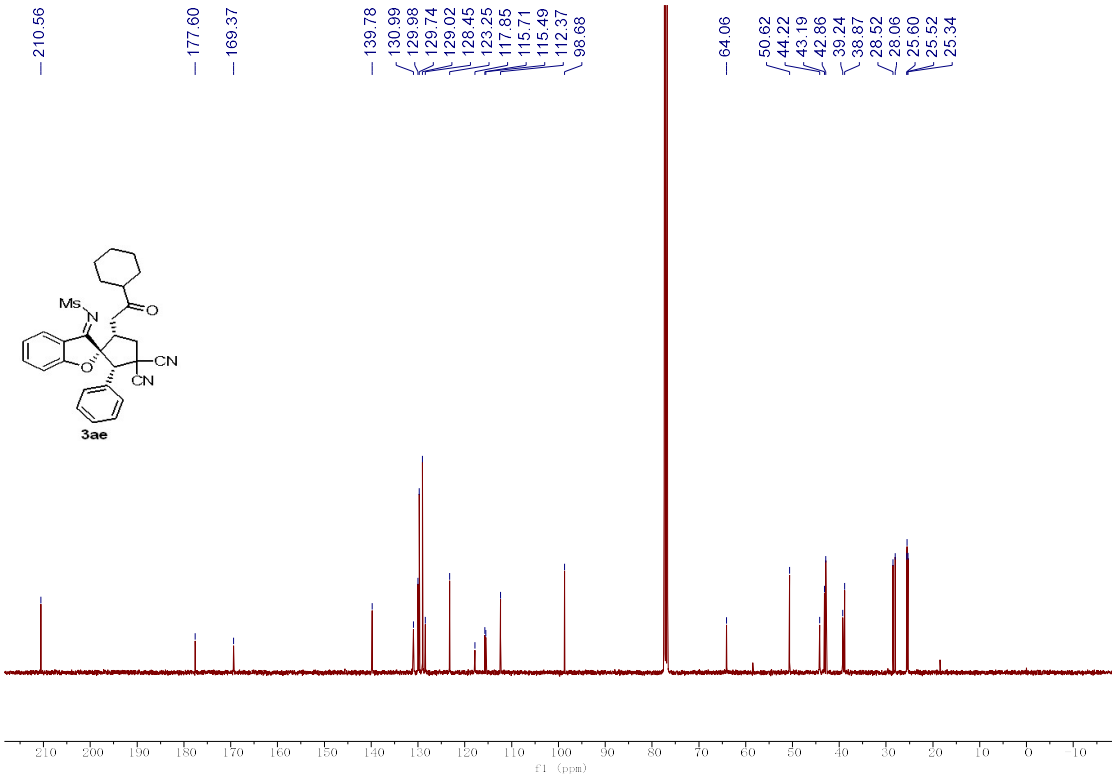
^{13}C NMR (100 MHz, $CDCl_3$) of **3ad**



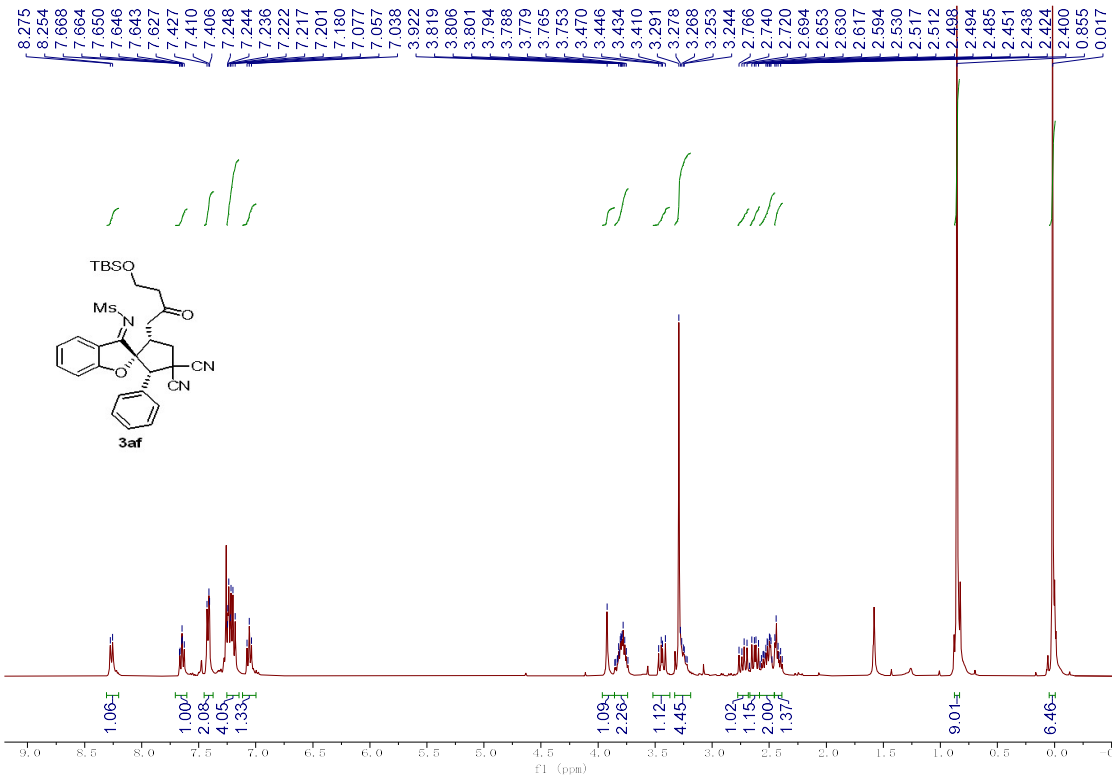
^{1}H NMR (400 MHz, $CDCl_3$) of **3ae**



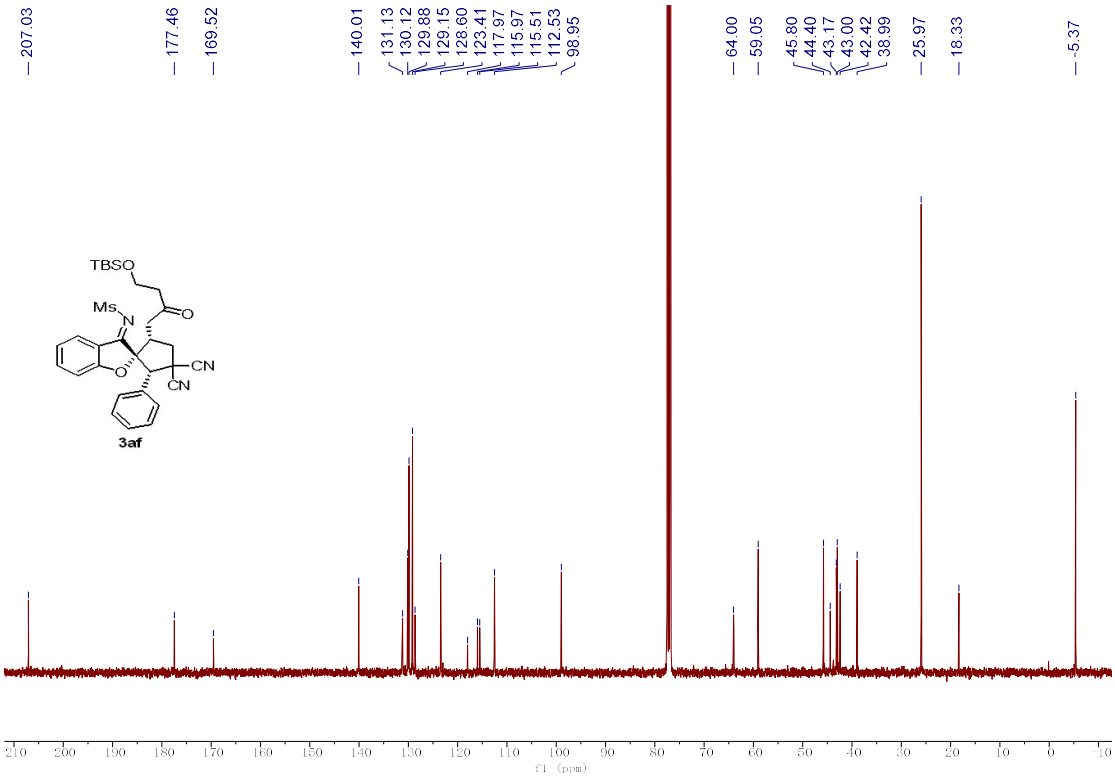
^{13}C NMR (100 MHz, $CDCl_3$) of **3ae**



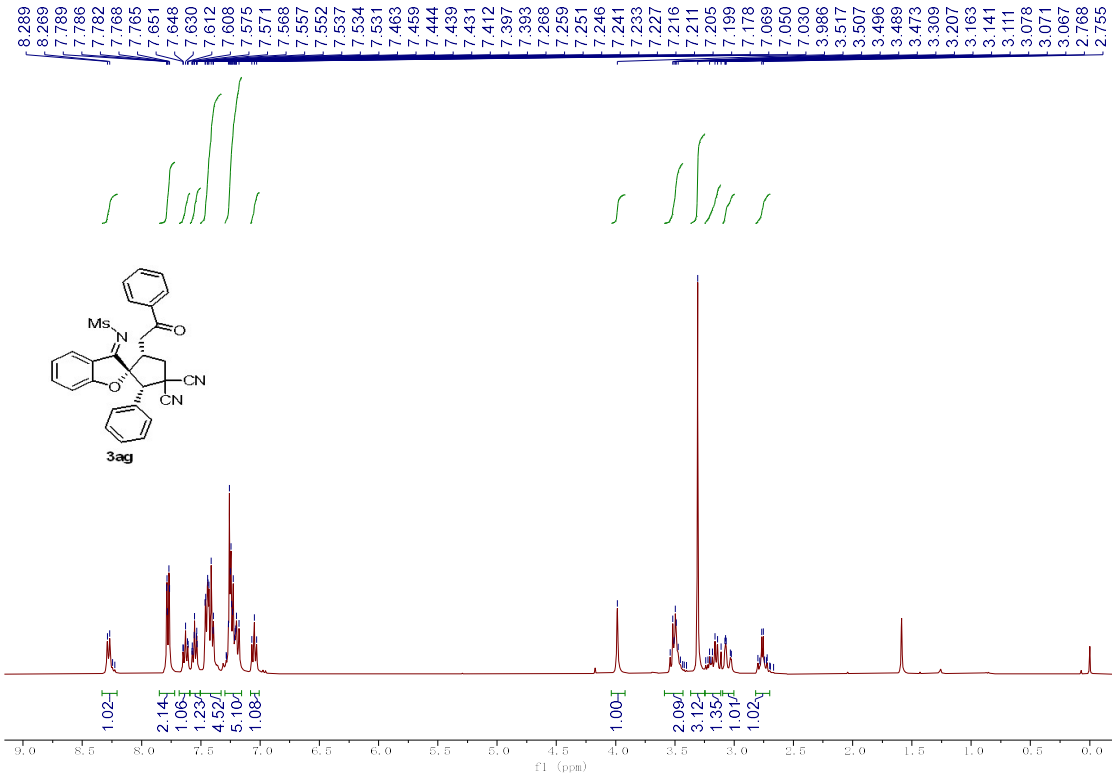
^{1}H NMR (400 MHz, $CDCl_3$) of **3af**



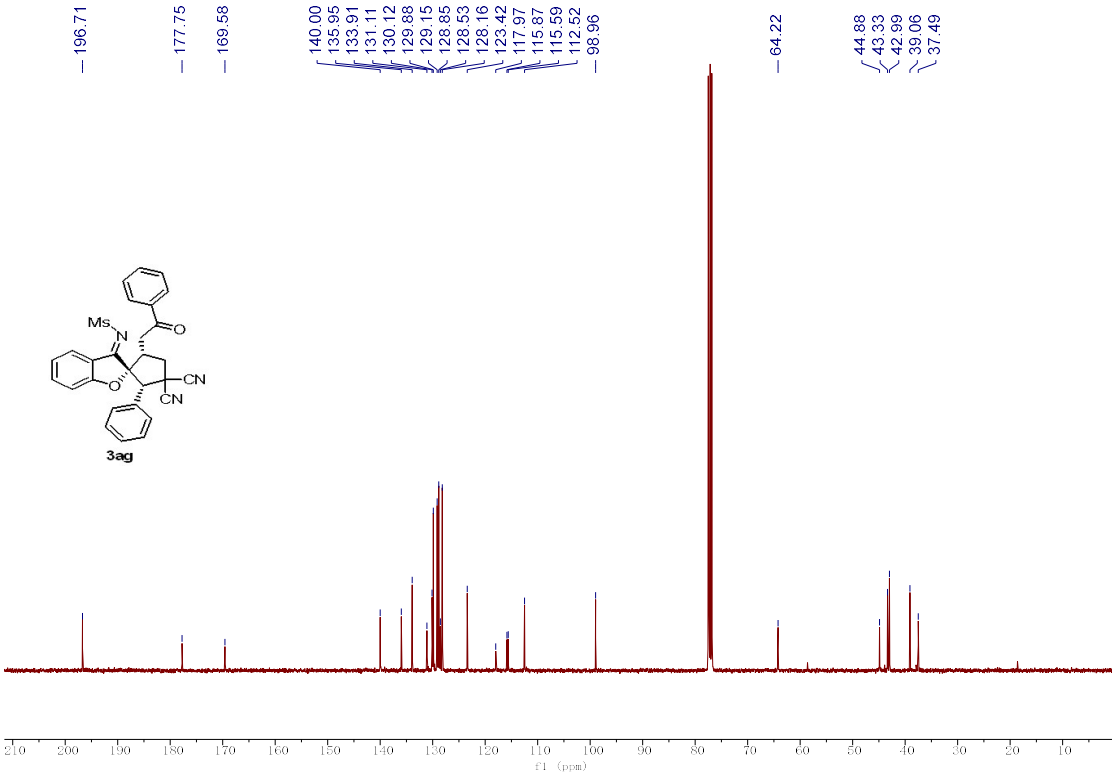
^{13}C NMR (100 MHz, $CDCl_3$) of **3af**



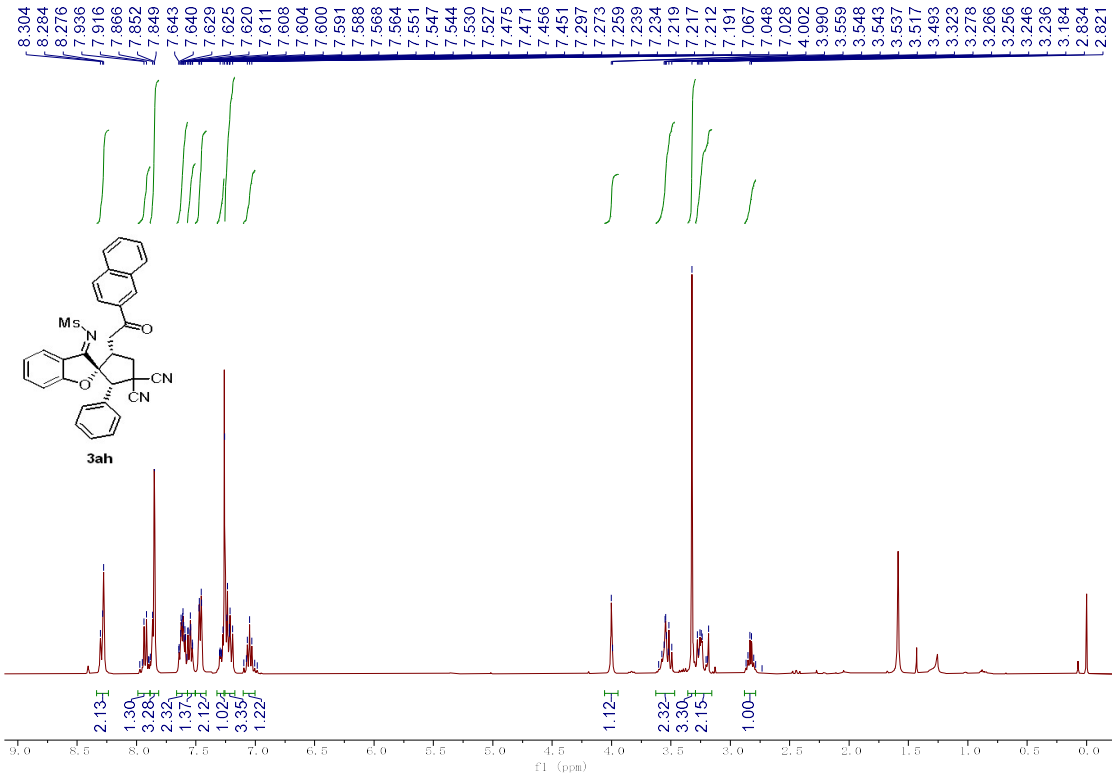
^{1}H NMR (400 MHz, $CDCl_3$) of **3ag**



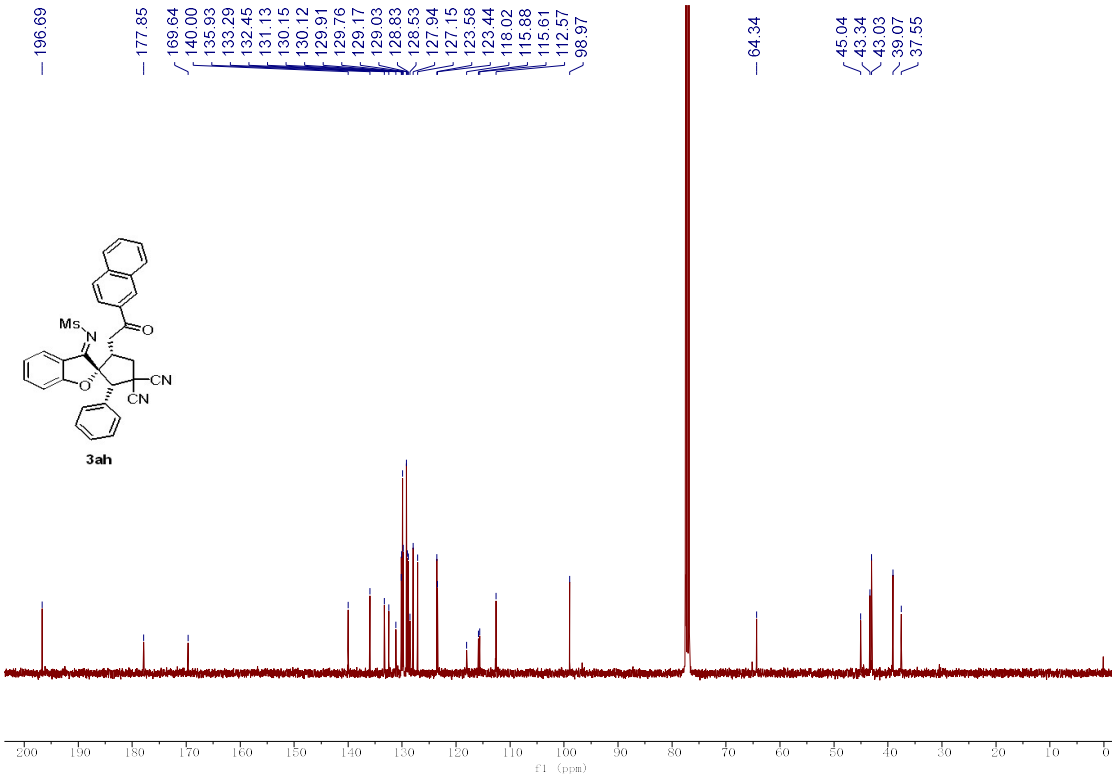
^{13}C NMR (100 MHz, $CDCl_3$) of **3ag**



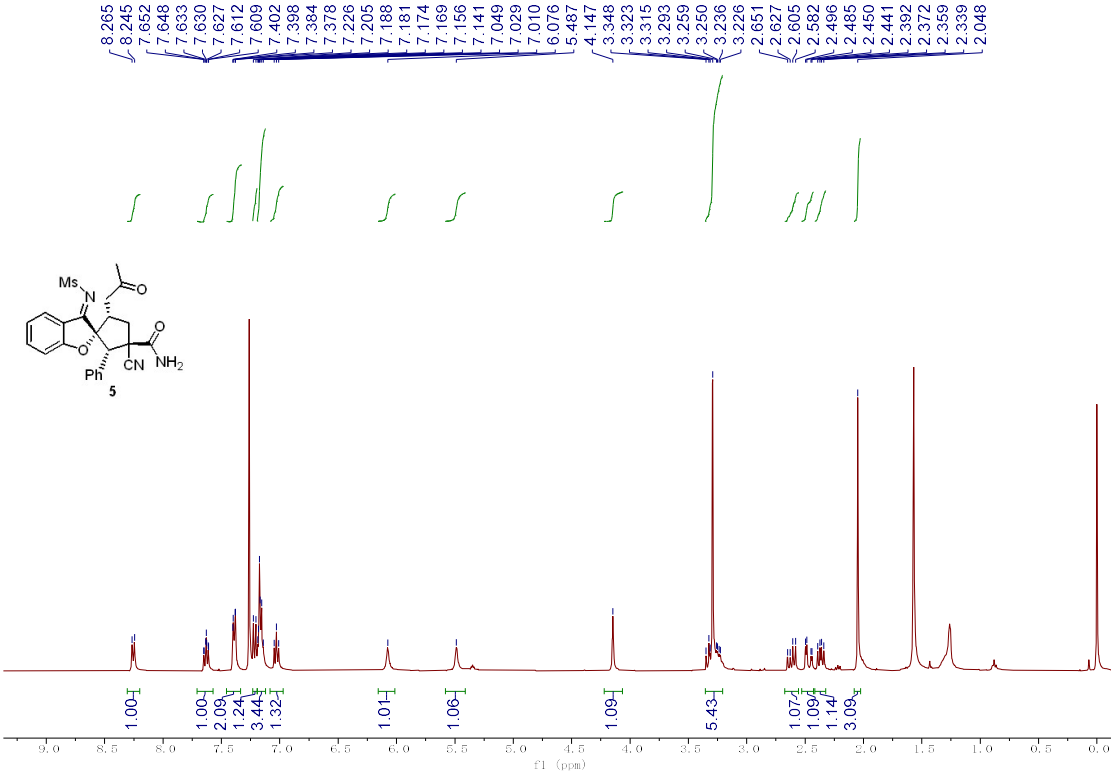
^{1}H NMR (400 MHz, $CDCl_3$) of **3ah**



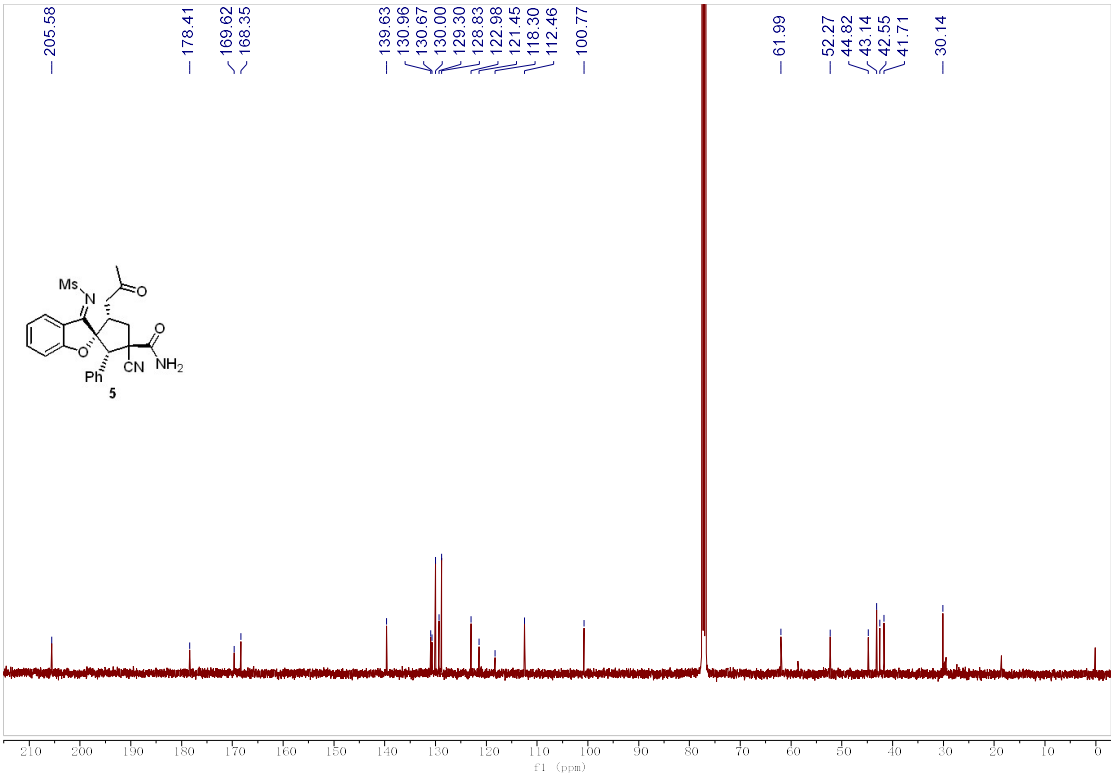
^{13}C NMR (100 MHz, $CDCl_3$) of **3ah**



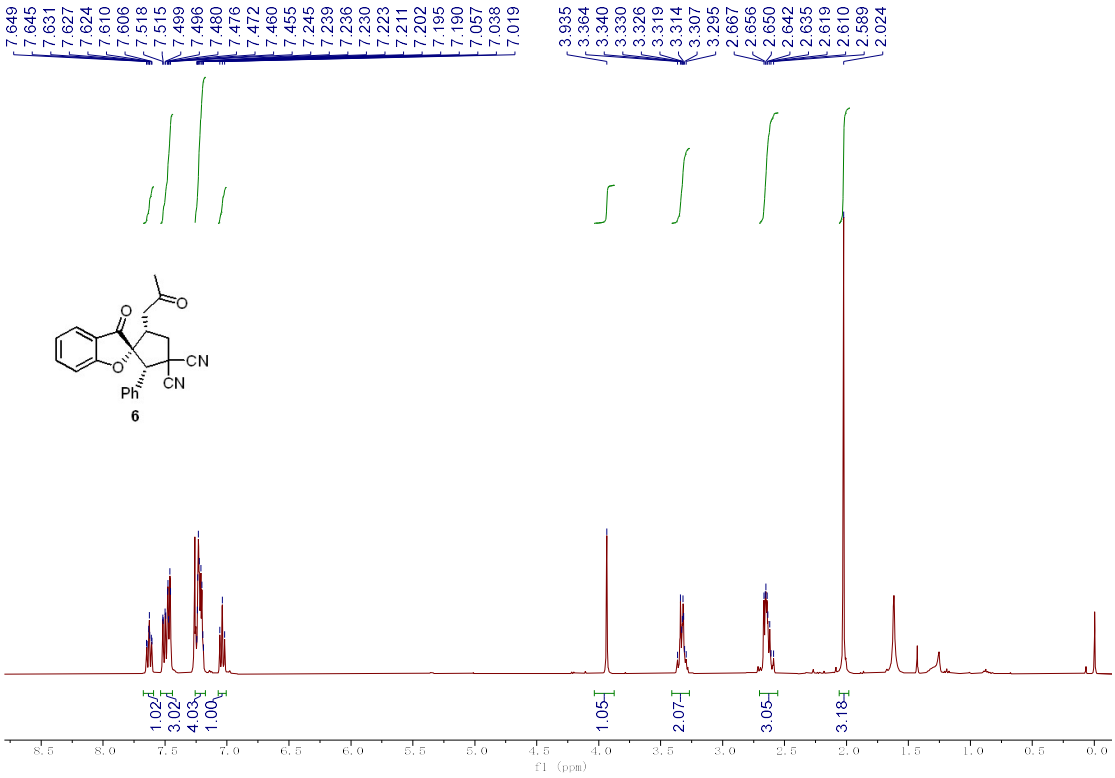
^{1}H NMR (400 MHz, $CDCl_3$) of **5**



^{13}C NMR (100 MHz, $CDCl_3$) of **5**

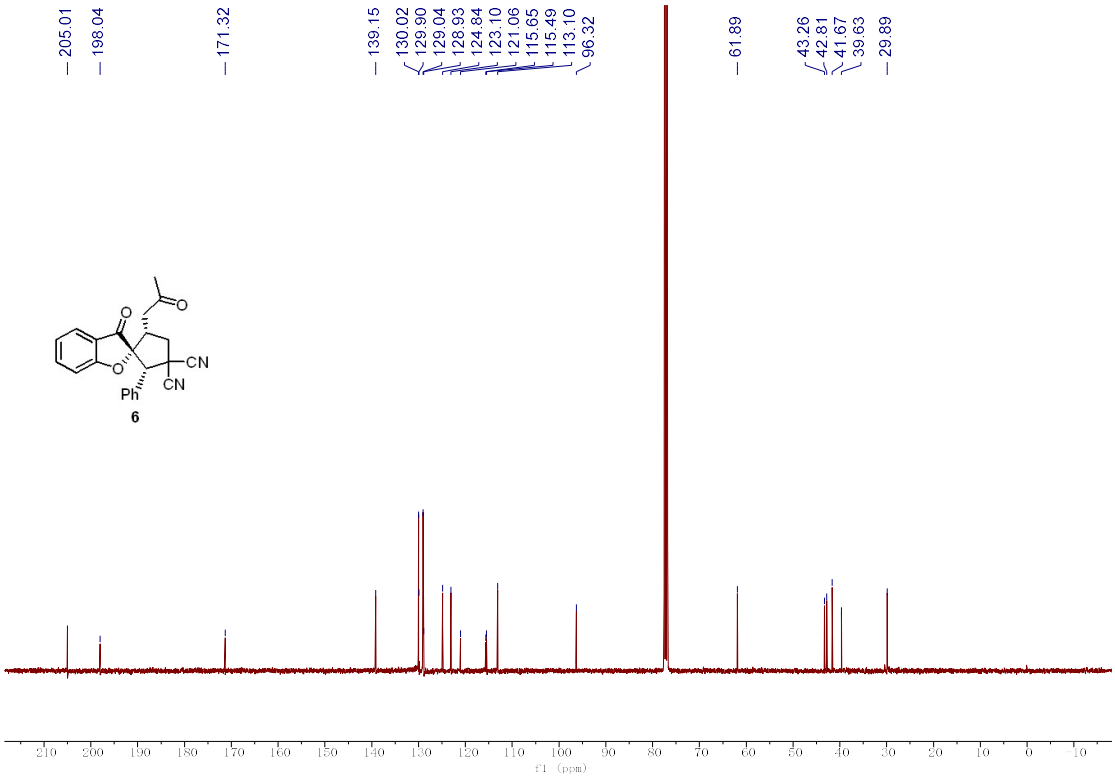


^{1}H NMR (400 MHz, $CDCl_3$) of **6**



6

^{13}C NMR (100 MHz, $CDCl_3$) of **6**

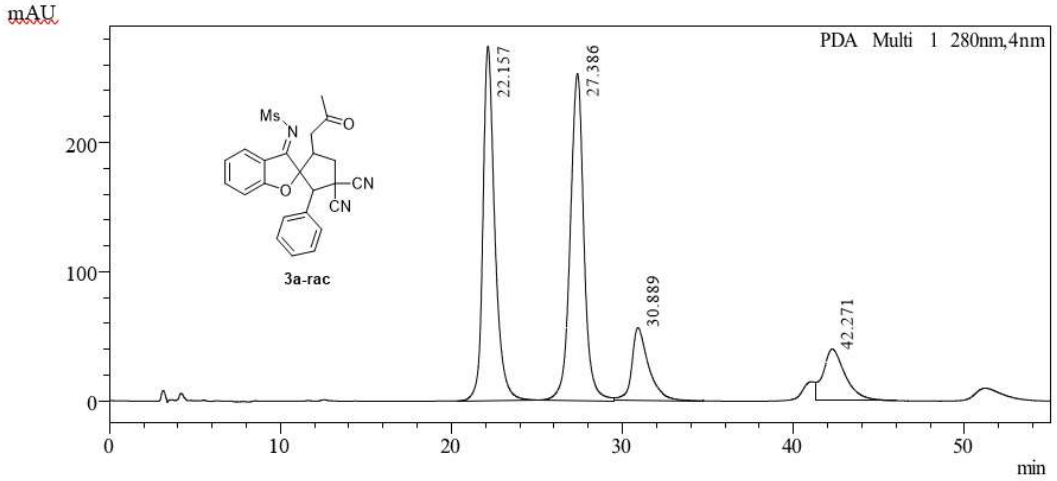


6

11. HPLC spectra of the products

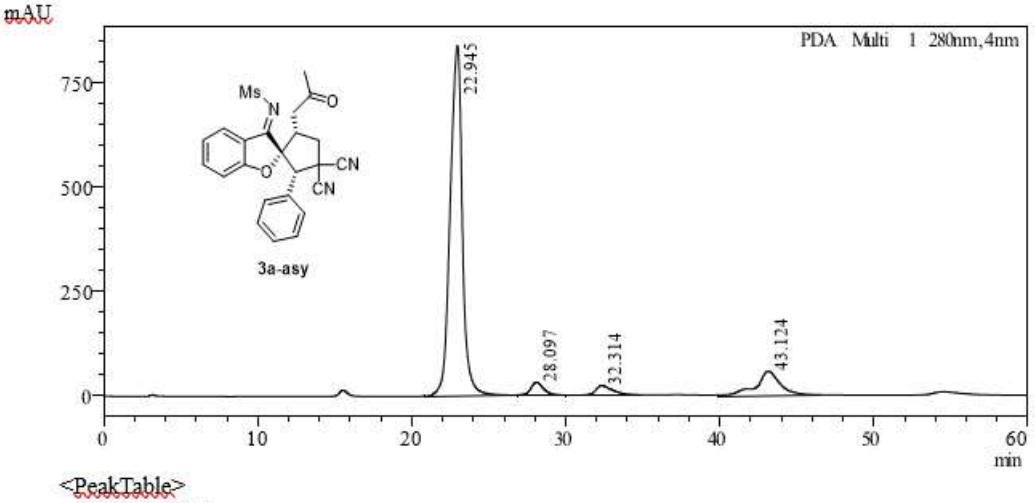
HPLC spectra of **3a**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	22.157	13268224	274331	38.531
2	27.386	13809538	252745	40.103
3	30.889	3802167	56536	11.042
4	42.271	3554972	39693	10.324
Total		34434903	623305	100.000

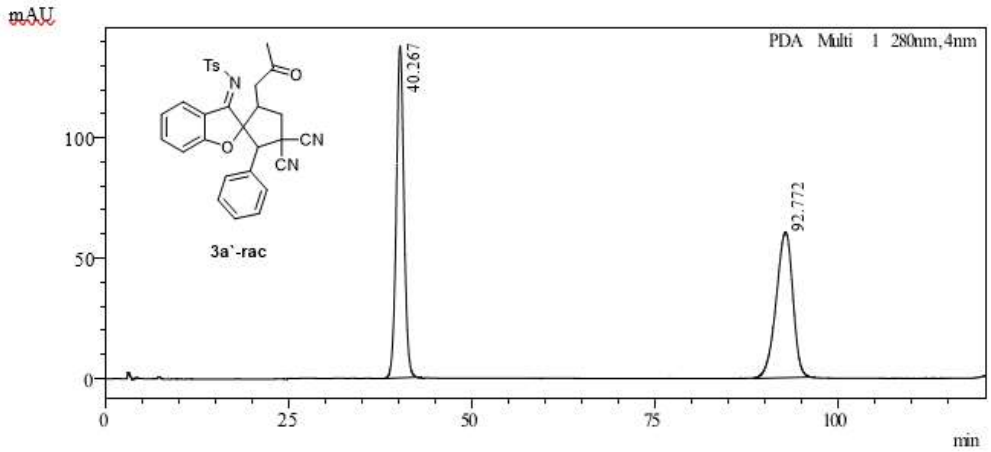


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	22.945	45050094	839037	81.586
2	28.097	2071284	34057	3.751
3	32.314	1822234	25026	3.300
4	43.124	6274588	58772	11.363
Total		55218200	956892	100.000

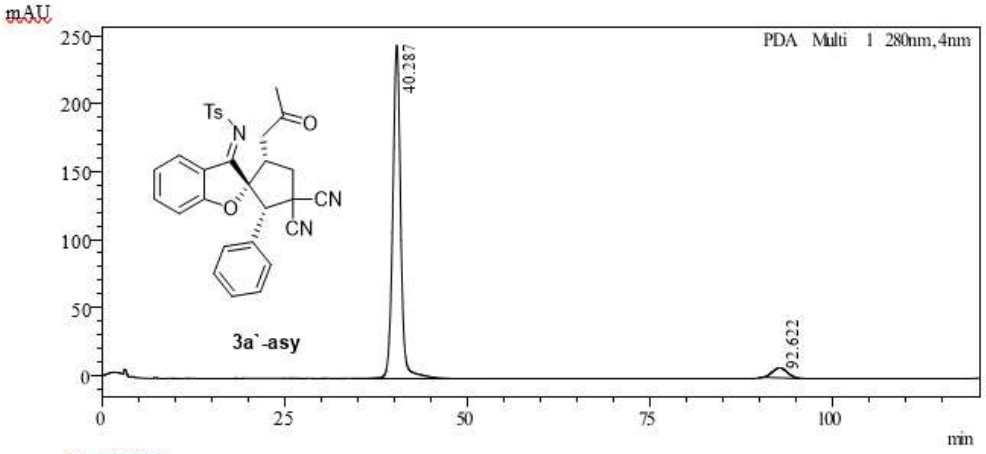
HPLC spectra of **3a`**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	40.267	9776111	137802	49.977
2	92.772	9785060	60503	50.023
Total		19561171	198305	100.000

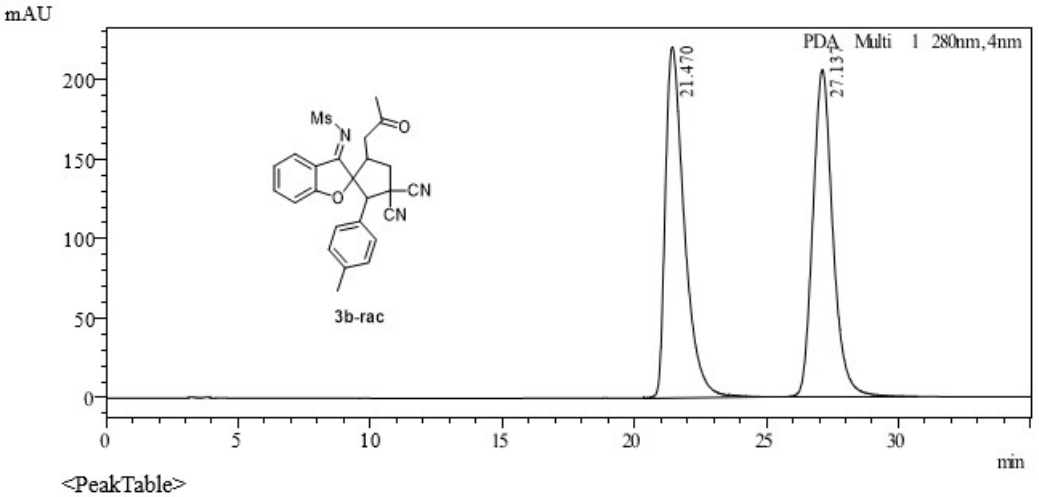


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	40.287	18443531	244411	94.757
2	92.622	1020566	6942	5.243
Total		19464097	251353	100.000

HPLC spectra of **3b**

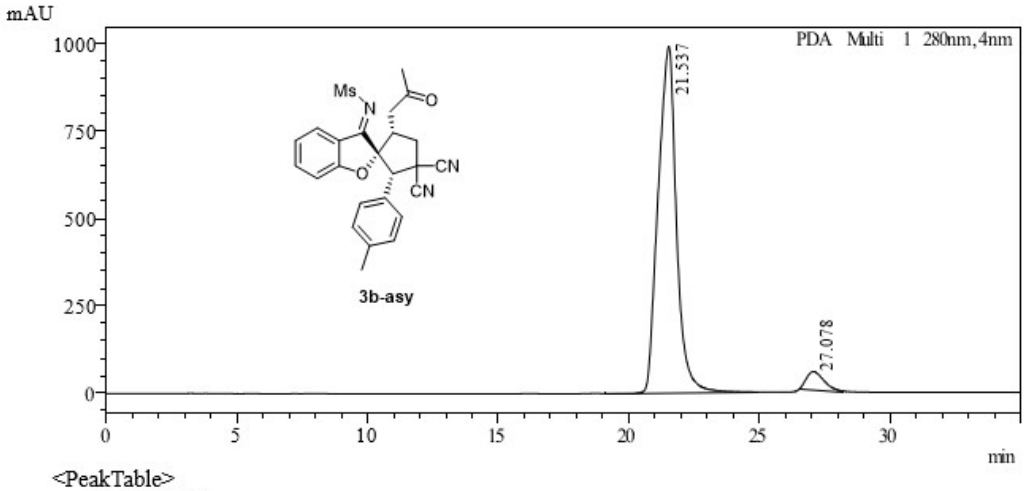
Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	21.470	10918753	219964	50.153
2	27.137	10852081	205488	49.847
Total		21770833	425452	100.000



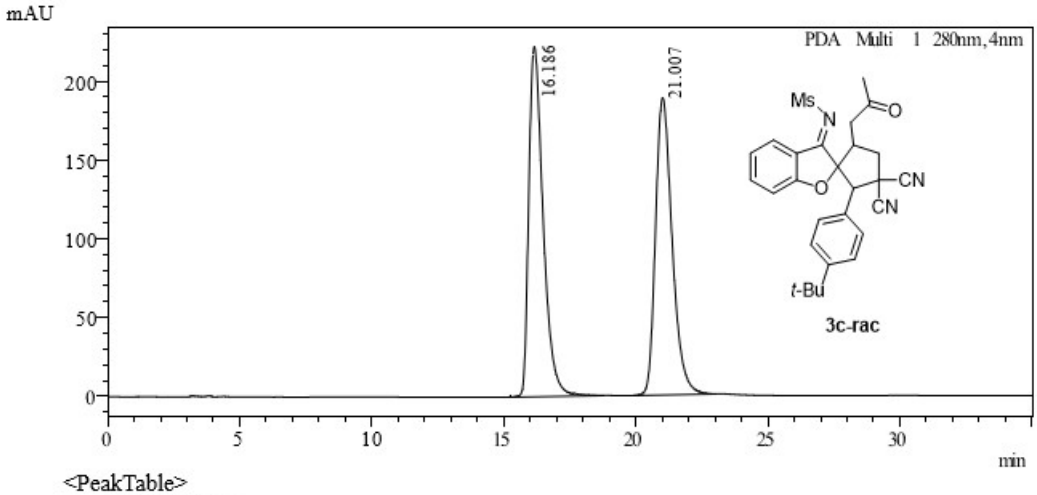
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	21.537	48235934	990894	95.123
2	27.078	2472878	54198	4.877
Total		50708812	1045092	100.000

HPLC spectra of **3c**

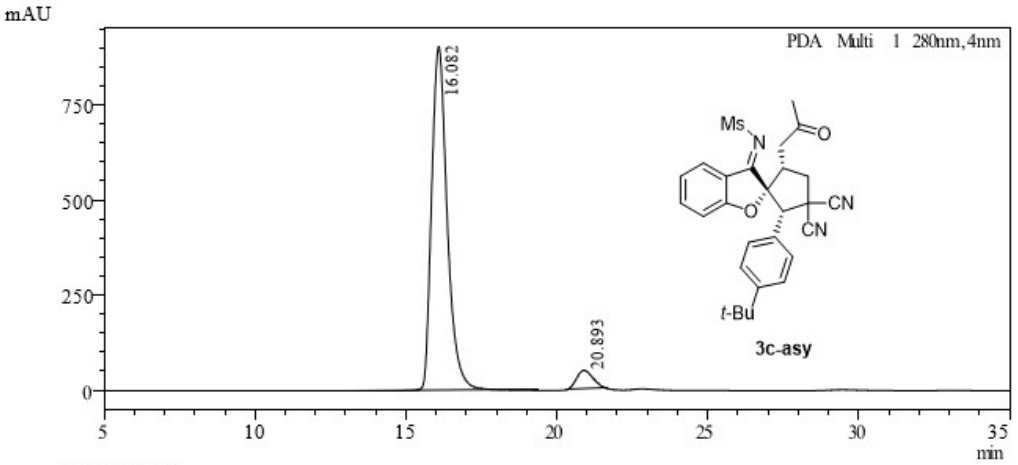
Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Area%
1	16.186	8354249	221836	50.359
2	21.007	8235139	188780	49.641
Total		16589388	410616	100.000



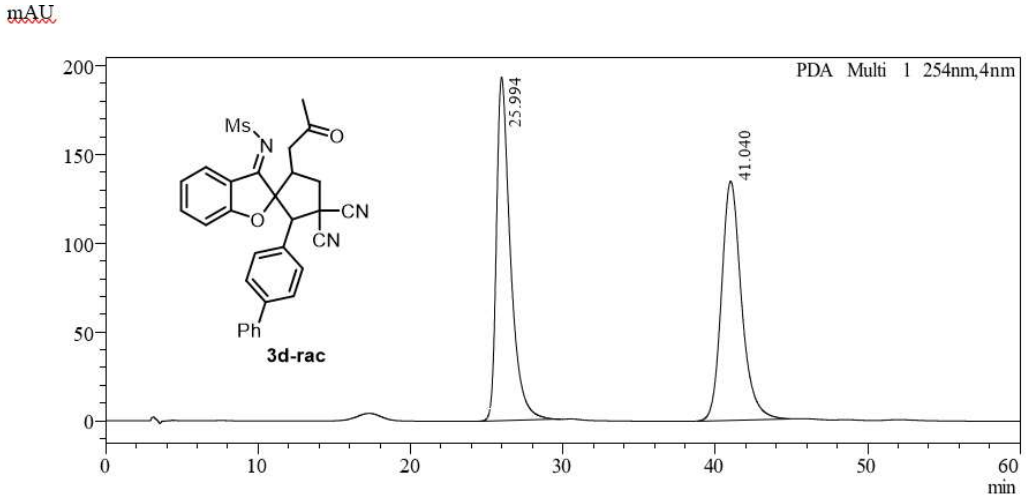
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	16.082	32520993	902371	94.805
2	20.893	1782043	46595	5.195
Total		34303035	948966	100.000

HPLC spectra of **3d**

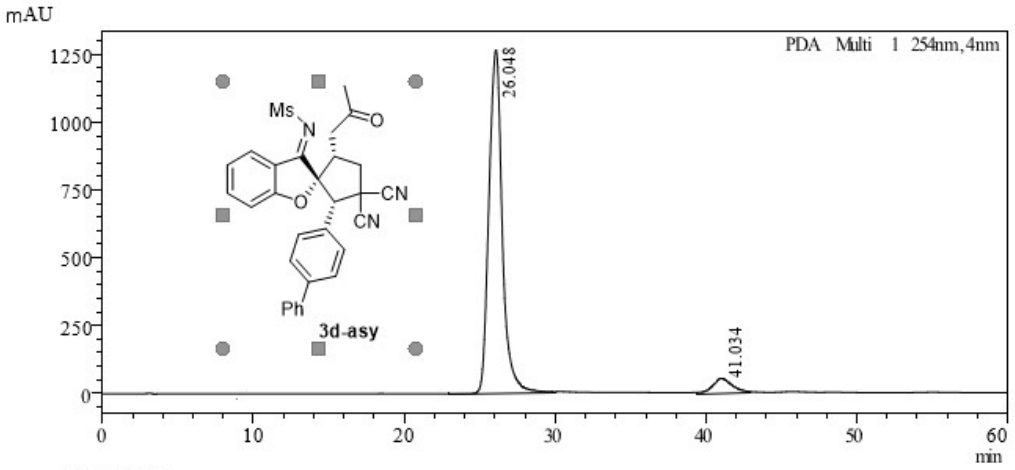
Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 254 nm, temp. = 25 ℃.



<Peak Table>

PDA Ch1 254nm

Peak#	Ret.Time	Area	Height	Area%
1	25.994	12278659	193426	50.263
2	41.040	12150081	134872	49.737
Total		24428741	328298	100.000



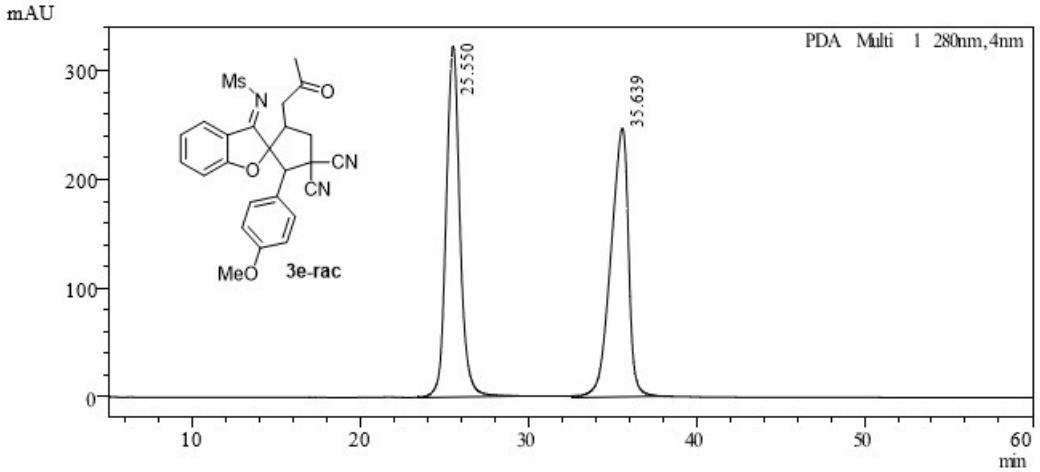
<PeakTable>

PDA Ch1 254nm

Peak#	Ret.Time	Area	Height	Area%
1	26.048	77260825	1263136	94.899
2	41.034	4152533	49434	5.101
Total		81413358	1312571	100.000

HPLC spectra of **3e**

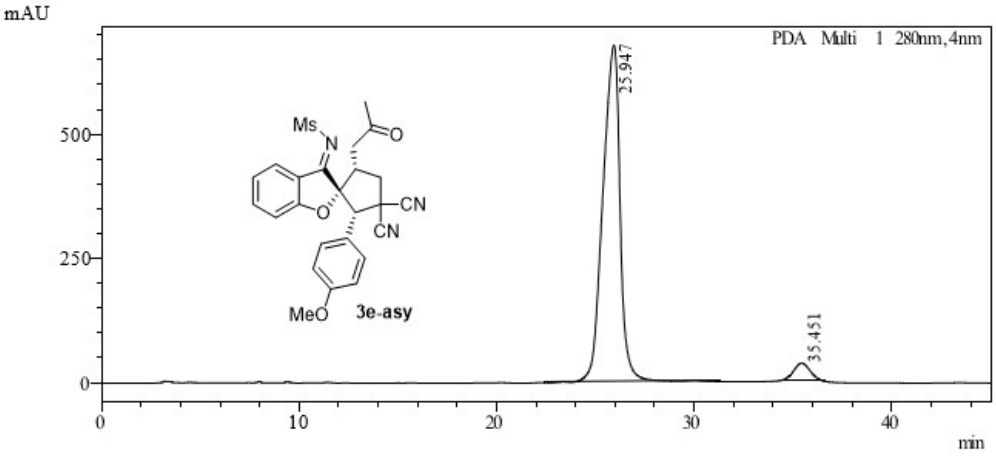
Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	25.550	18241751	322165	50.270
2	35.639	18045735	246093	49.730
Total		36287486	568258	100.000



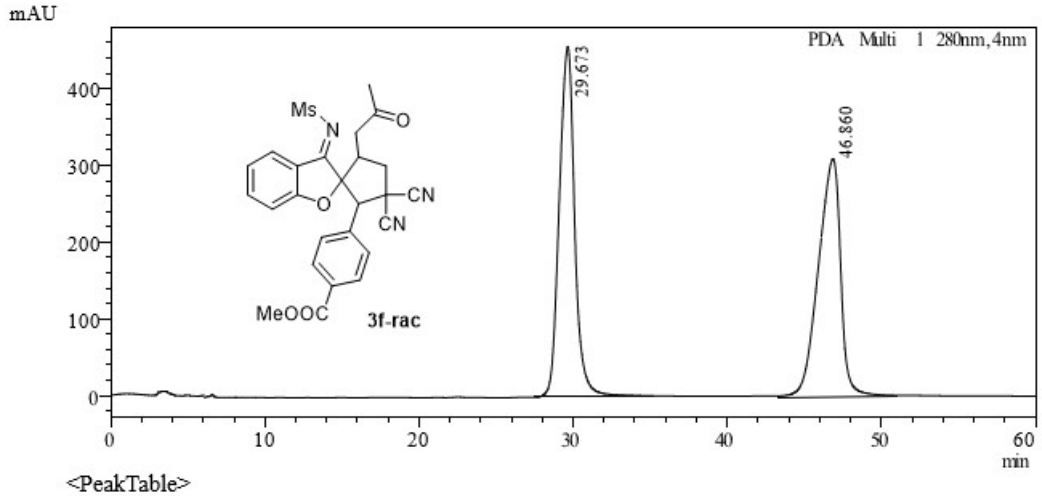
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	25.947	40547119	676116	95.089
2	35.451	2094194	35613	4.911
Total		42641314	711729	100.000

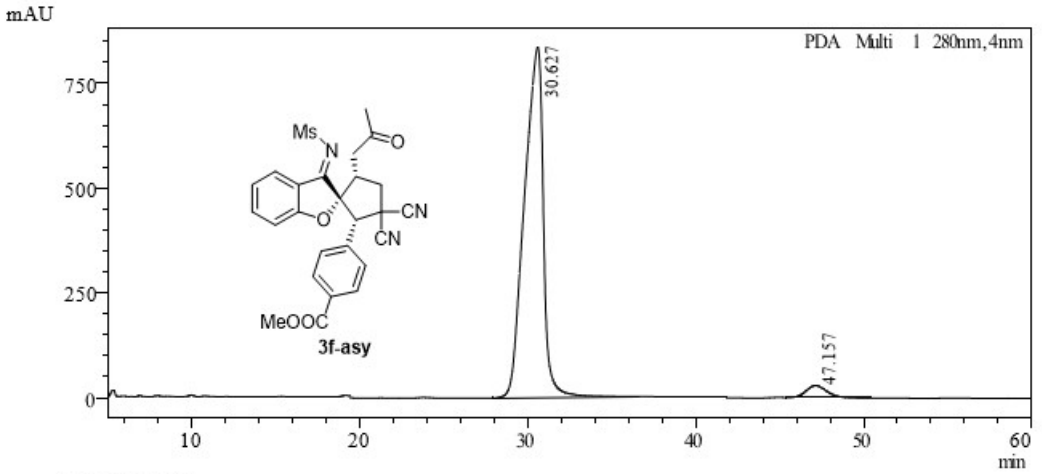
HPLC spectra of **3f**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	29.673	31843801	455503	50.187
2	46.860	31605894	309558	49.813
Total		63449695	765061	100.000

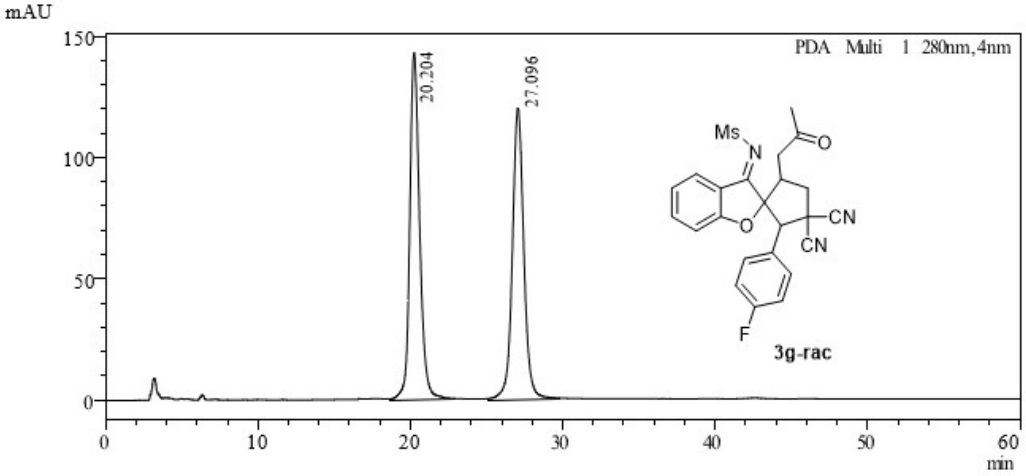


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	30.627	65162857	834343	96.133
2	47.157	2621507	28654	3.867
Total		67784363	862997	100.000

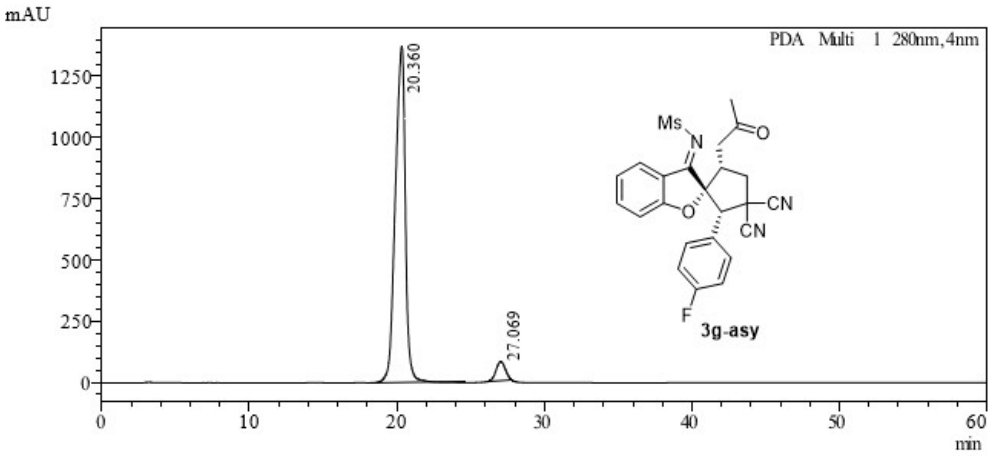
HPLC spectra of **3g**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	20.204	6355428	142498	50.473
2	27.096	6236395	119840	49.527
Total		12591823	262338	100.000

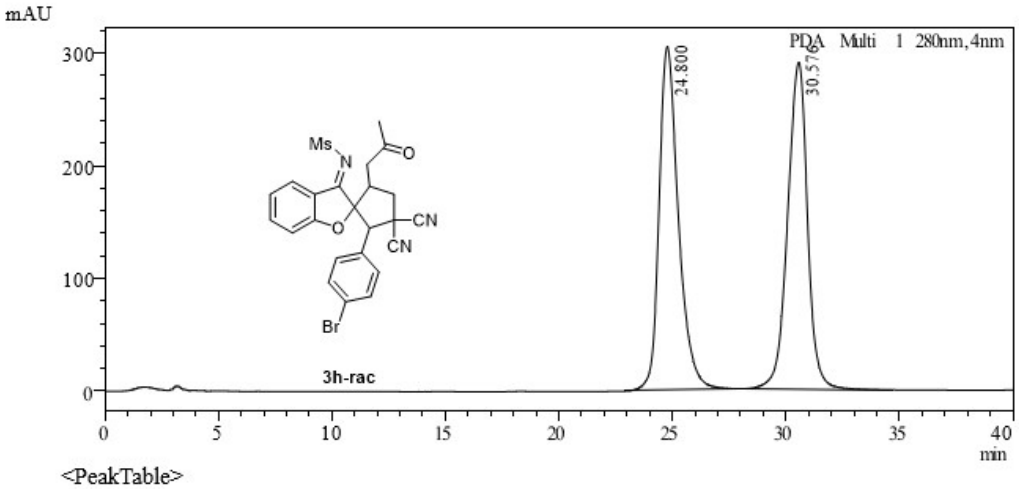


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	20.360	64916580	1370211	95.136
2	27.069	3319204	76475	4.864
Total		68235784	1446686	100.000

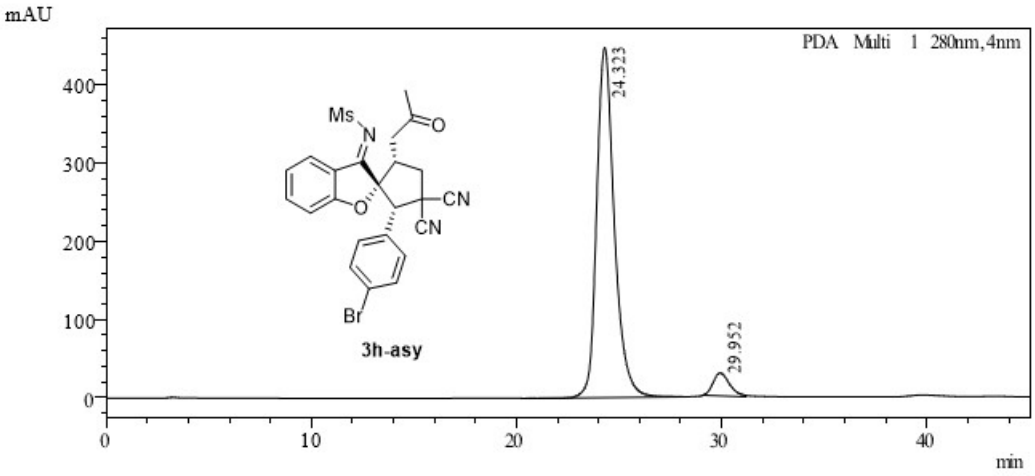
HPLC spectra of **3h**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	24.800	17958550	304816	50.398
2	30.576	17675234	290718	49.602
Total		35633784	595534	100.000

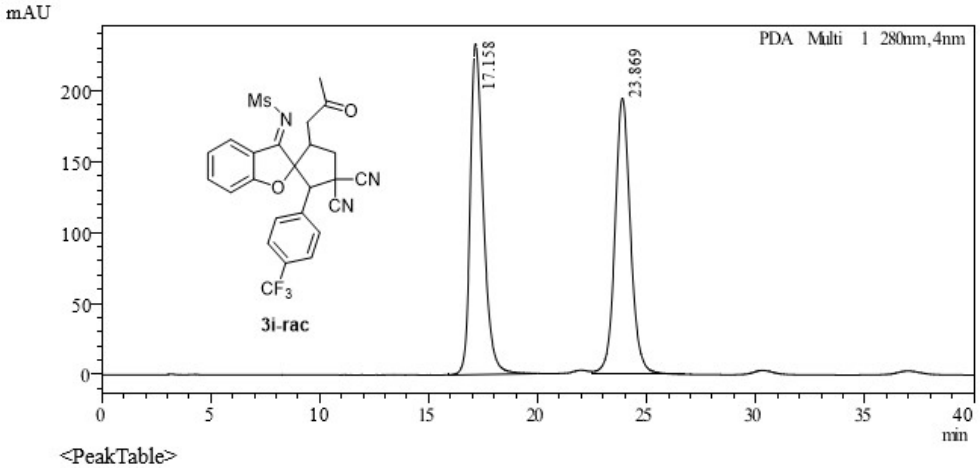


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	24.323	26206854	447282	94.558
2	29.952	1508125	28403	5.442
Total		27714979	475685	100.000

HPLC spectra of **3i**

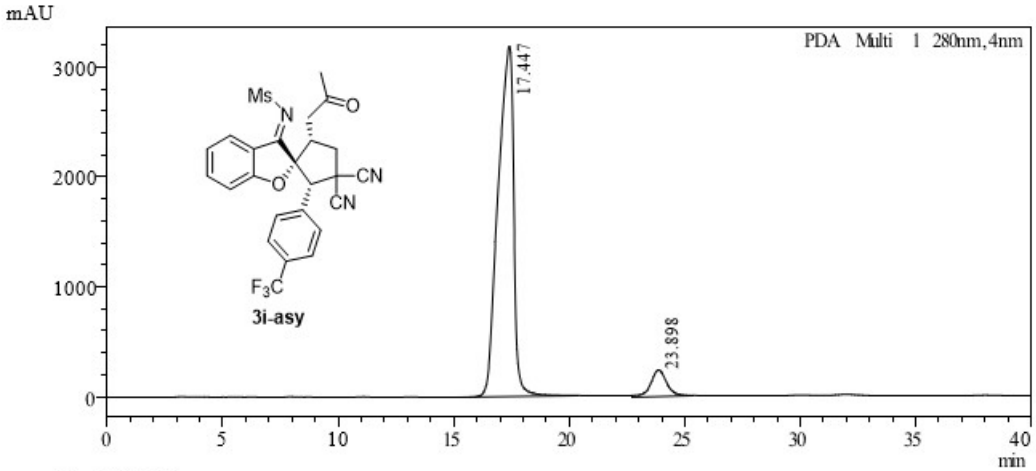
Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	17.158	9668952	232664	50.473
2	23.869	9487885	194537	49.527
Total		19156838	427201	100.000



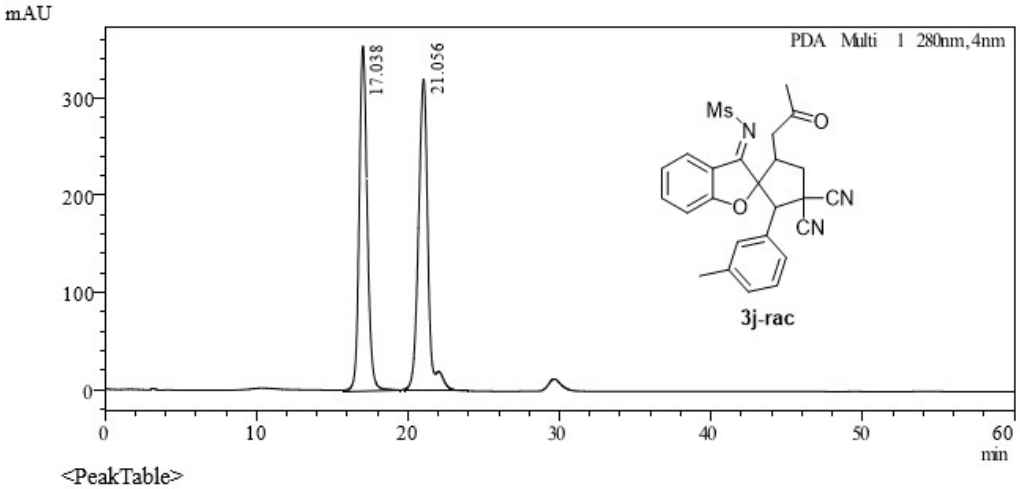
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	17.447	149834666	3181953	93.356
2	23.898	10663267	237349	6.644
Total		160497934	3419302	100.000

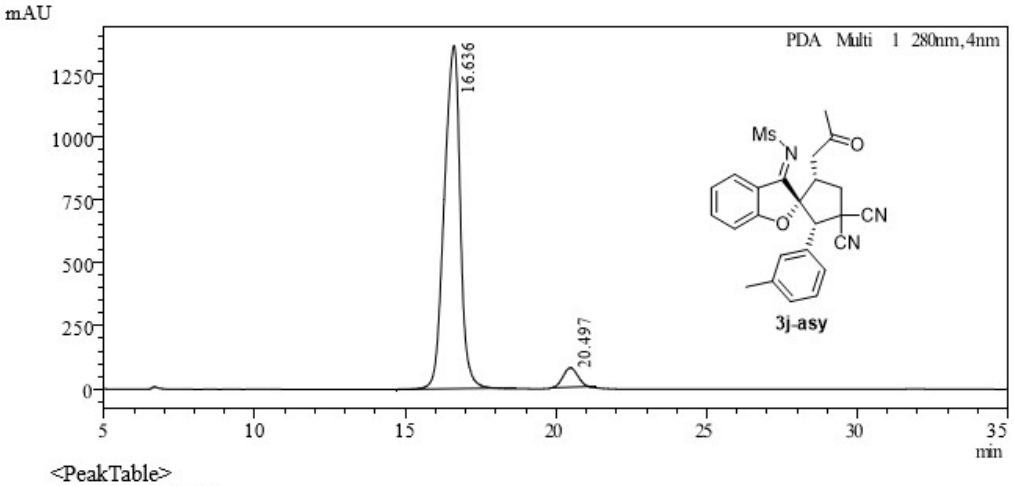
HPLC spectra of **3j**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	17.038	13100579	354234	48.580
2	21.056	13866598	321589	51.420
Total		26967177	675824	100.000

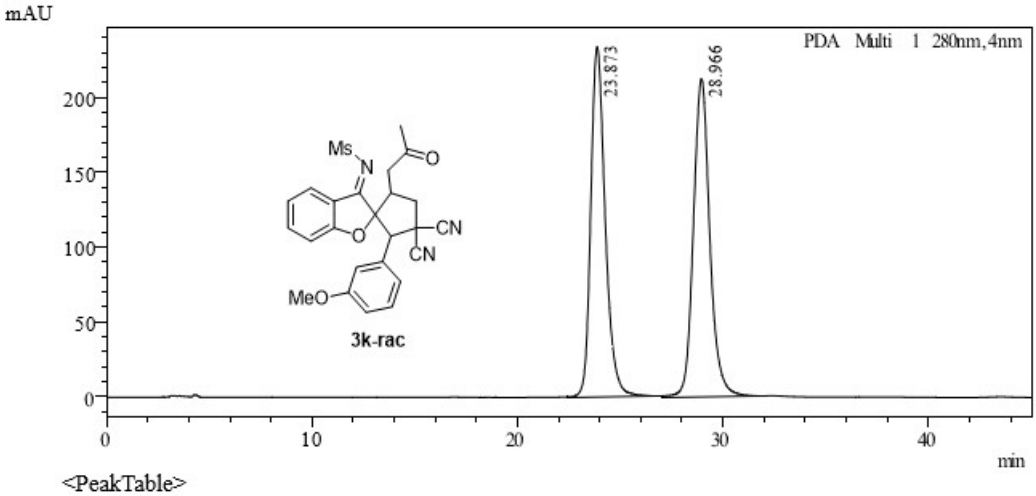


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	16.636	50211155	1361473	94.987
2	20.497	2650079	75608	5.013
Total		52861234	1437082	100.000

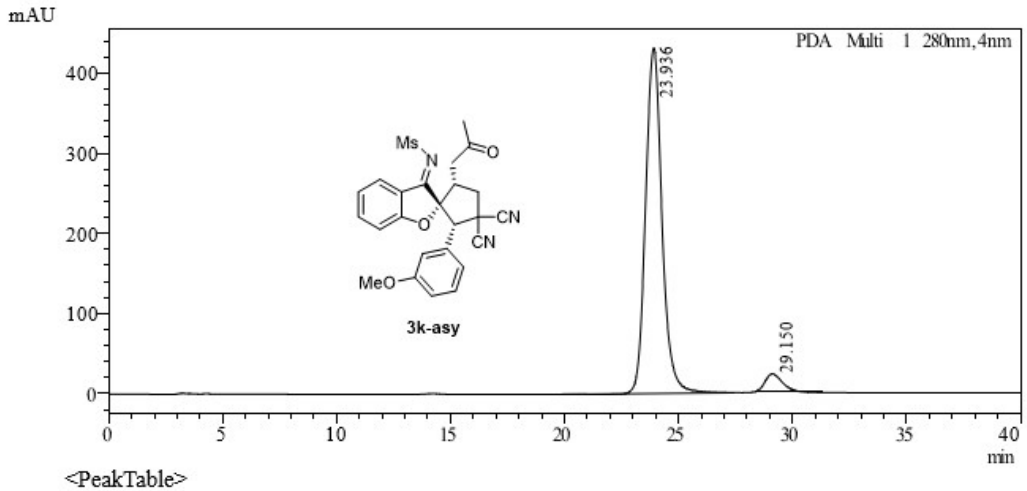
HPLC spectra of **3k**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	23.873	11704583	233445	50.153
2	28.966	11633198	212159	49.847
Total		23337781	445604	100.000

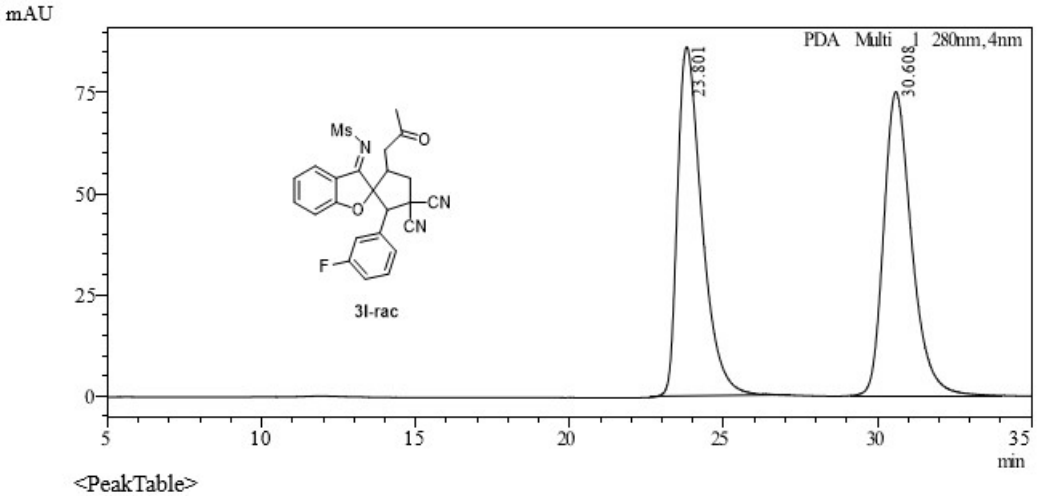


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	23.936	21567543	430315	95.245
2	29.150	1076629	22862	4.755
Total		22644172	453177	100.000

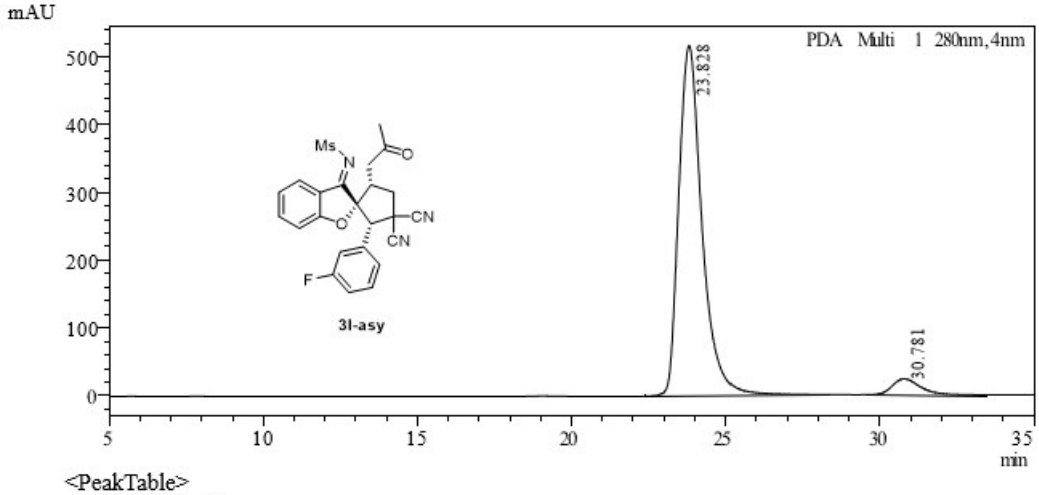
HPLC spectra of **3l**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	23.801	4817682	86280	50.416
2	30.608	4738088	75155	49.584
Total		9555771	161435	100.000

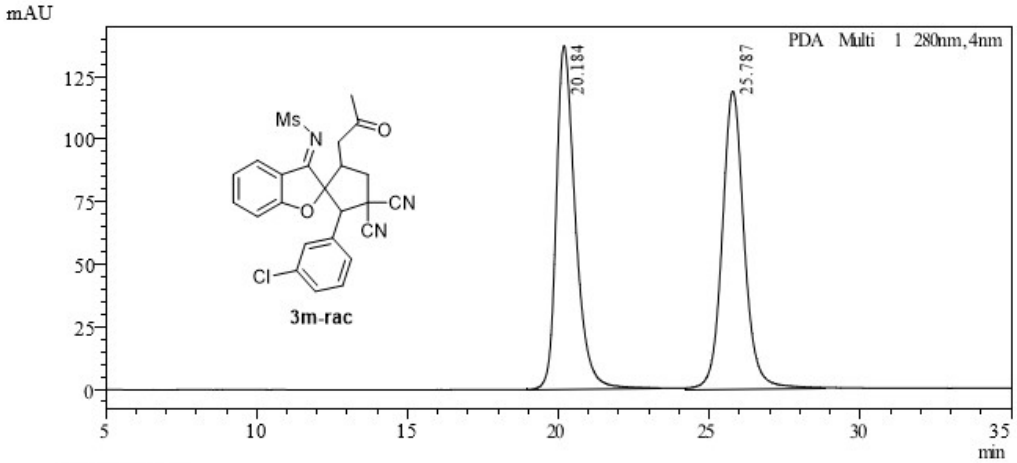


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	23.828	27148405	516260	94.825
2	30.781	1481610	23716	5.175
Total		28630015	539976	100.000

HPLC spectra of **3m**

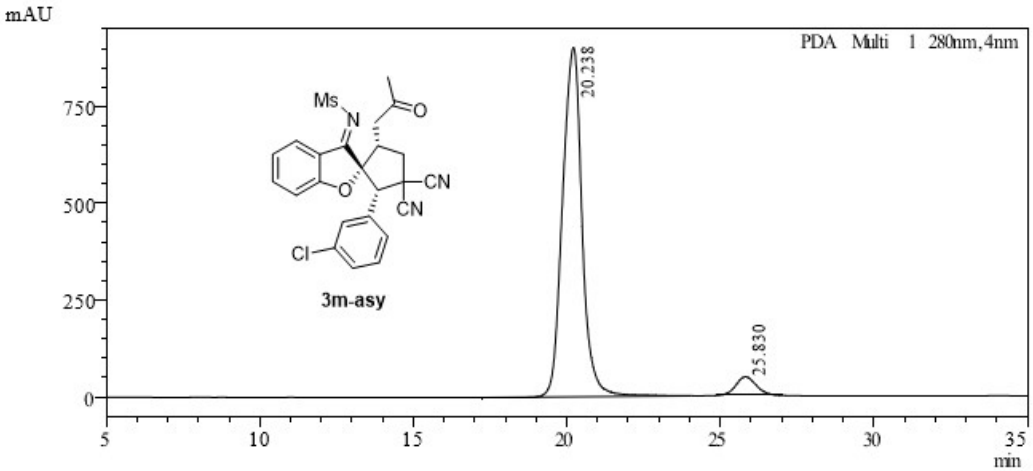
Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	20.184	5988825	136983	50.159
2	25.787	5950767	118596	49.841
Total		11939592	255579	100.000



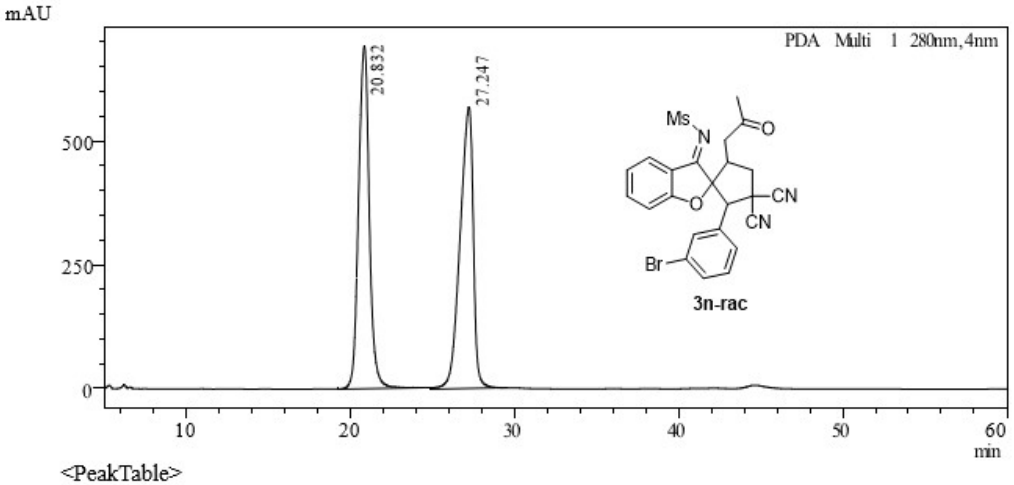
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	20.238	40074045	901188	95.669
2	25.830	1814210	46594	4.331
Total		41888255	947783	100.000

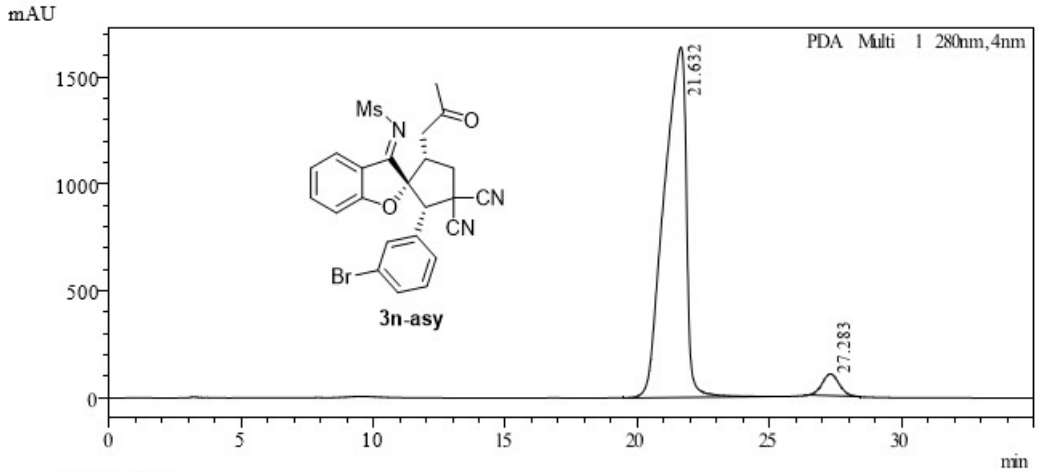
HPLC spectra of **3n**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	20.832	31918151	690906	50.189
2	27.247	31677345	567710	49.811
Total		63595496	1258616	100.000

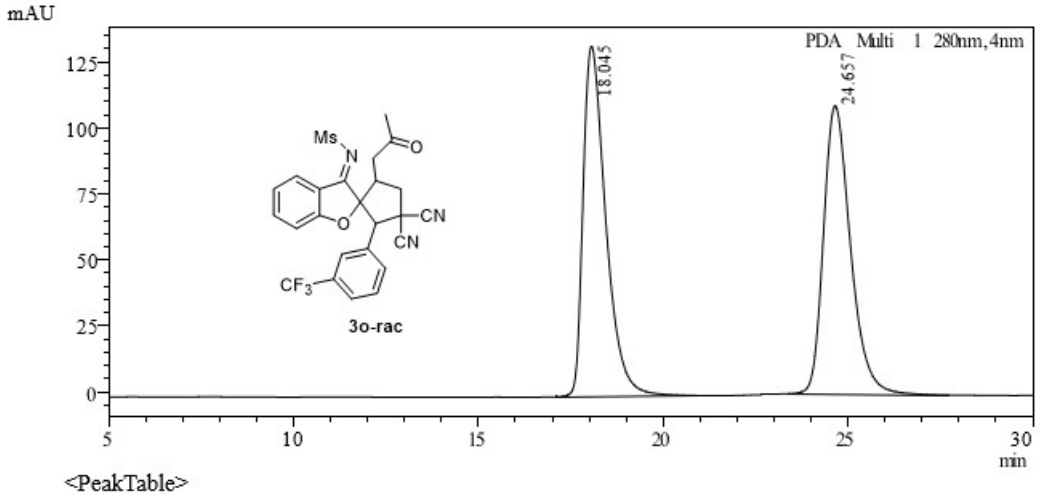


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	21.632	95264281	1637115	95.276
2	27.283	4723057	100945	4.724
Total		99987338	1738060	100.000

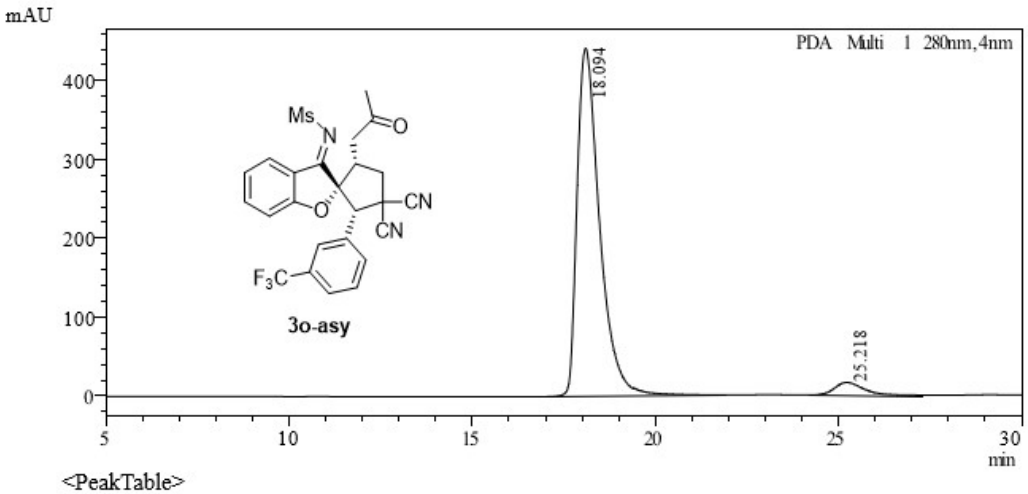
HPLC spectra of **3o**

Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	18.045	5647342	132475	50.265
2	24.657	5587727	109607	49.735
Total		11235069	242082	100.000

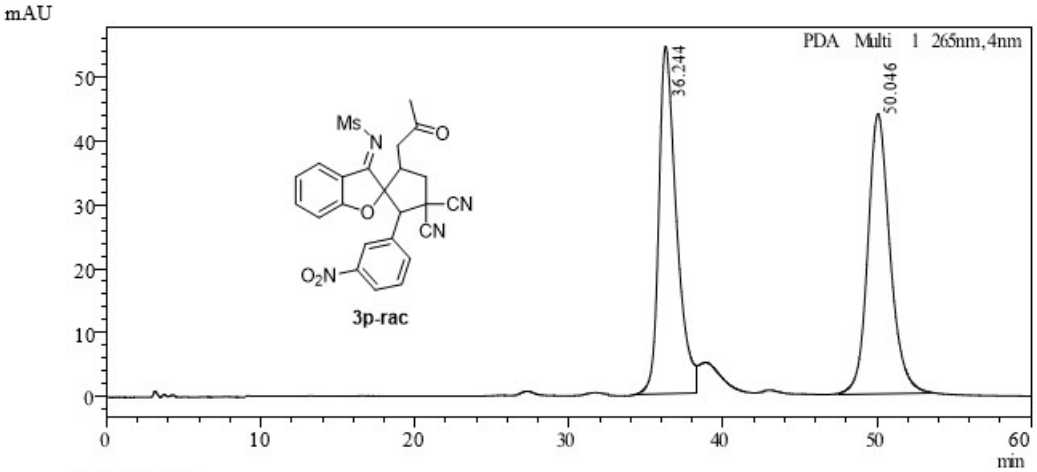


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	18.094	18854944	440638	95.693
2	25.218	848677	15925	4.307
Total		19703621	456563	100.000

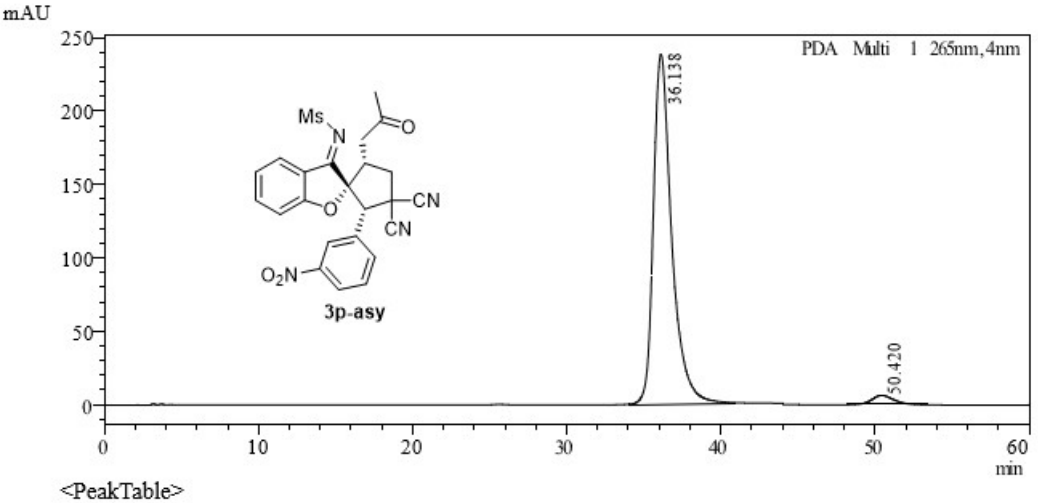
HPLC spectra of **3p**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 265 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 265nm

Peak#	Ret.Time	Area	Height	Area%
1	36.244	4336103	54201	50.062
2	50.046	4325285	43686	49.938
Total		8661388	97887	100.000

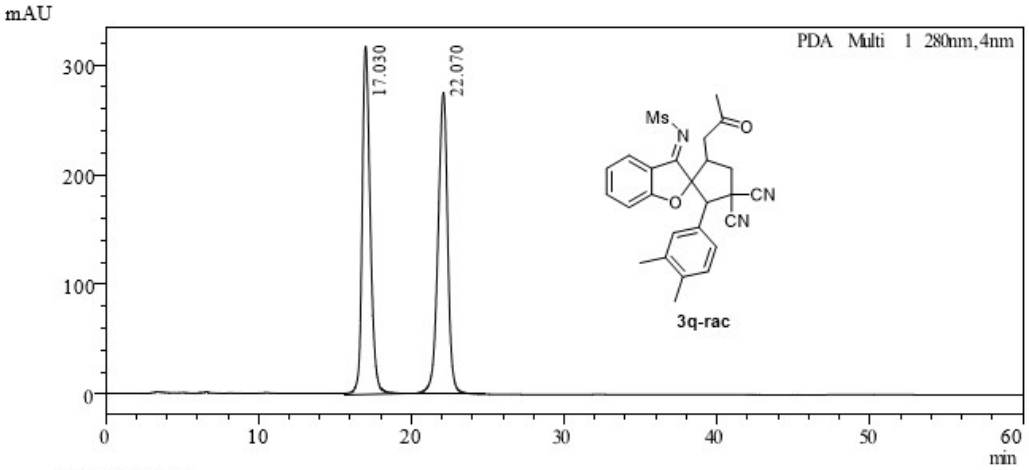


<PeakTable>
PDA Ch1 265nm

Peak#	Ret.Time	Area	Height	Area%
1	36.138	18761315	237623	96.947
2	50.420	590841	5808	3.053
Total		19352156	243432	100.000

HPLC spectra of **3q**

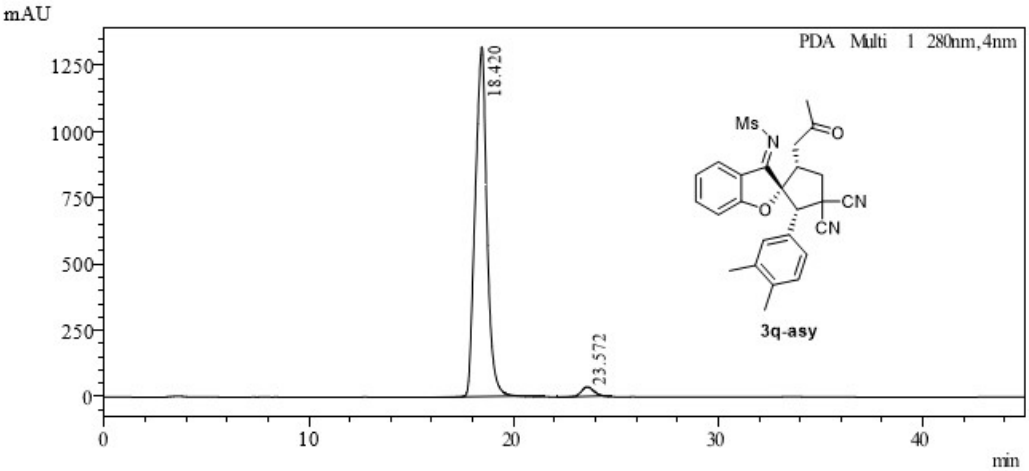
Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	17.030	11957334	316316	50.040
2	22.070	11938228	274378	49.960
Total		23895562	590695	100.000



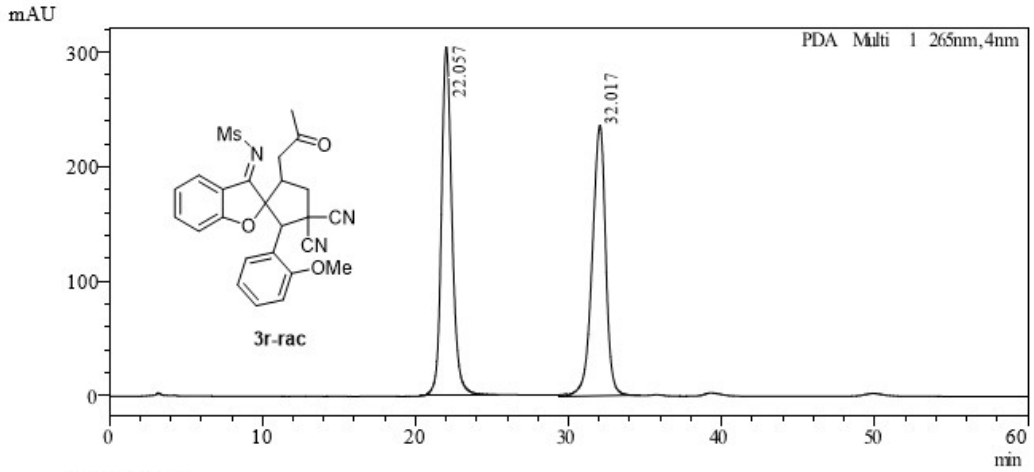
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	18.420	52485322	1316413	96.914
2	23.572	1671178	36850	3.086
Total		54156500	1353263	100.000

HPLC spectra of **3r**

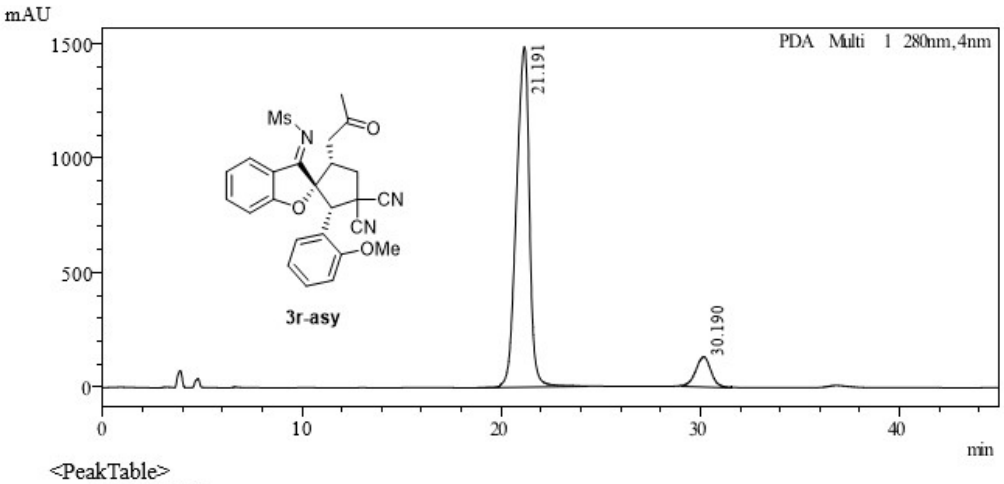
Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 265nm

Peak#	Ret.Time	Area	Height	Area%
1	22.057	14472231	303844	50.240
2	32.017	14334075	236466	49.760
Total		28806306	540311	100.000



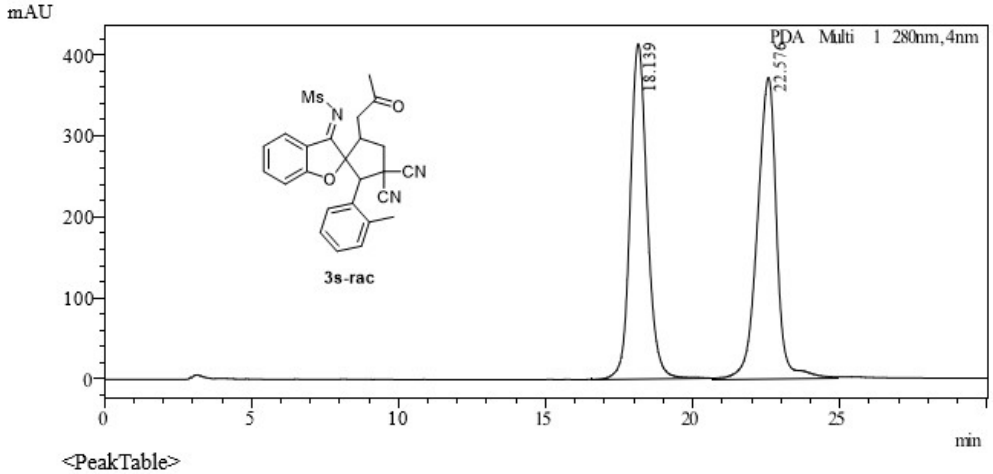
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	21.191	68278358	1483193	90.929
2	30.190	6811241	131981	9.071
Total		75089600	1615174	100.000

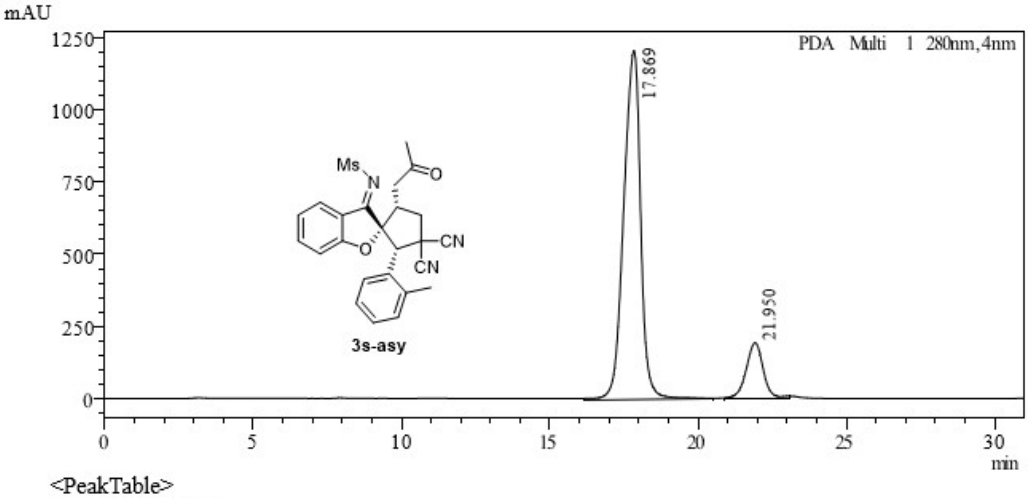
HPLC spectra of **3s**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	18.139	16726631	412523	50.149
2	22.576	16627458	371138	49.851
Total		33354089	783661	100.000

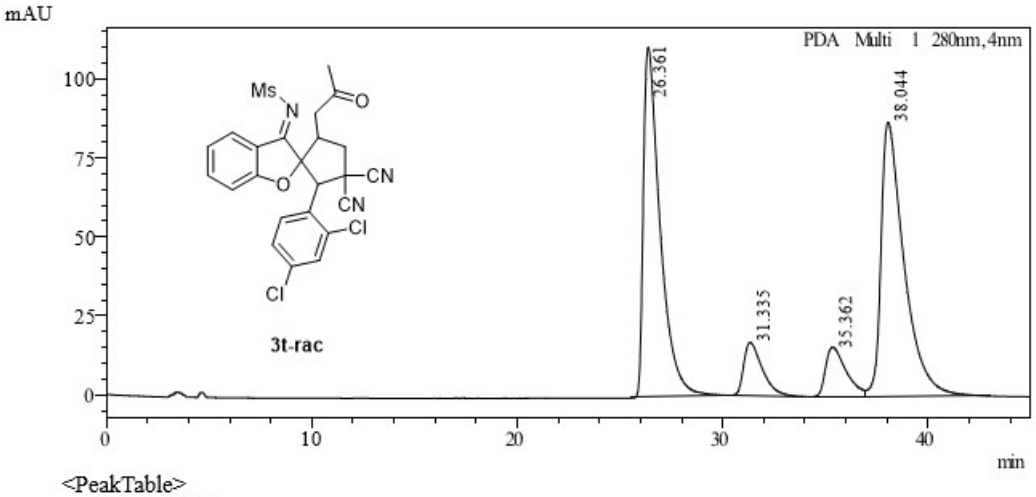


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	17.869	47386513	1204581	85.598
2	21.950	7973087	195593	14.402
Total		55359600	1400174	100.000

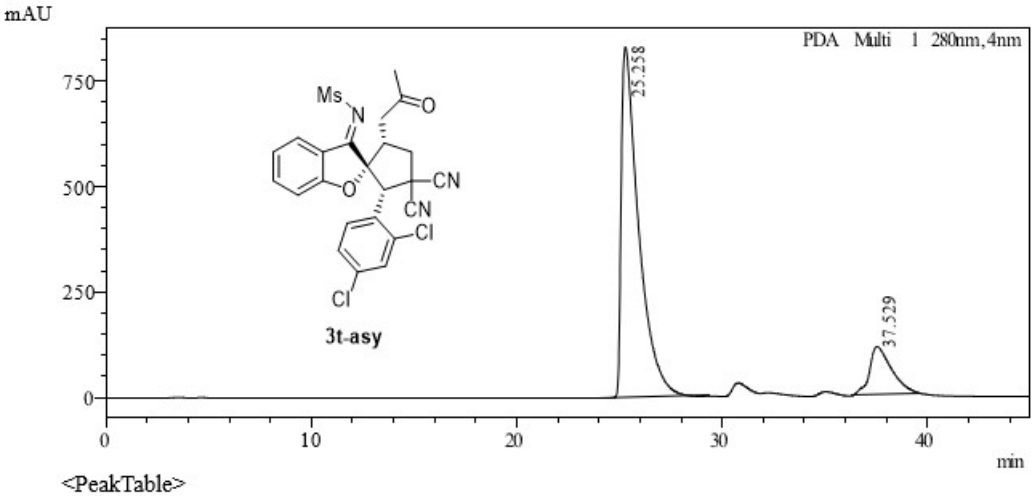
HPLC spectra of **3t**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	26.361	6305907	110632	41.005
2	31.335	1076385	17118	6.999
3	35.362	1049270	15511	6.823
4	38.044	6946782	86644	45.172
Total		15378344	229905	100.000

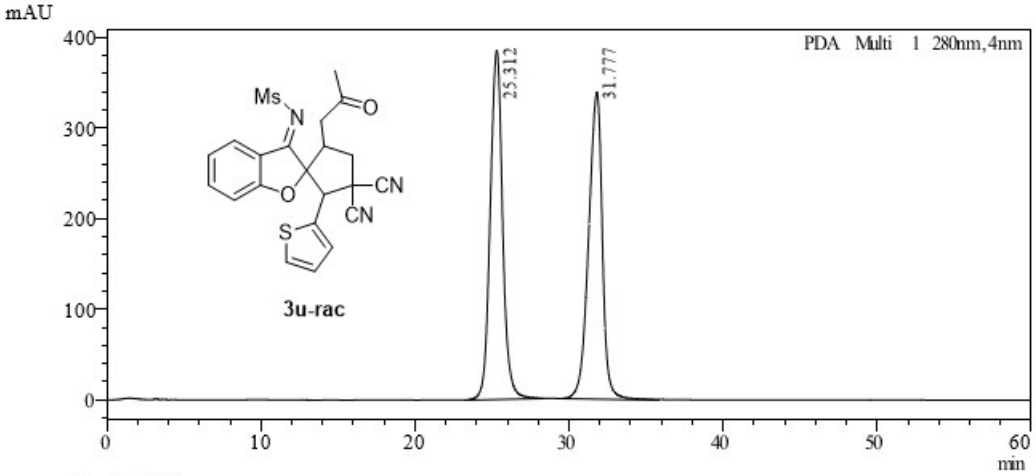


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	25.258	48752544	827913	85.207
2	37.529	8463966	112272	14.793
Total		57216510	940186	100.000

HPLC spectra of **3u**

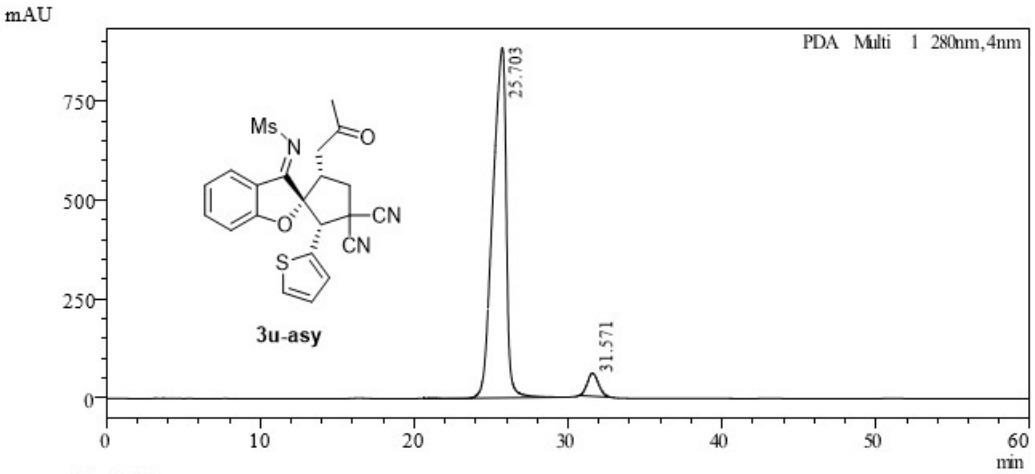
Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	25.312	21042113	385310	50.052
2	31.777	20998090	339144	49.948
Total		42040203	724455	100.000



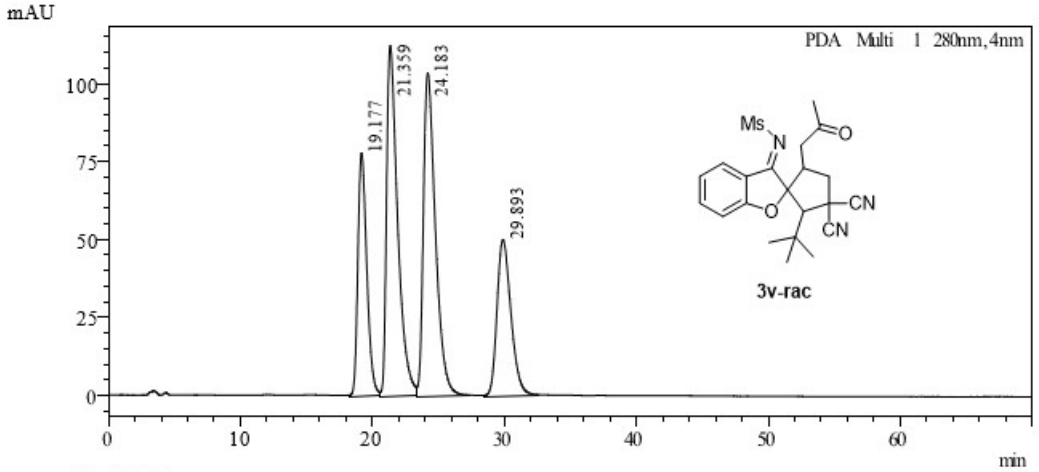
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	25.703	54138211	882708	94.877
2	31.571	2923183	56986	5.123
Total		57061395	939694	100.000

HPLC spectra of **3v**

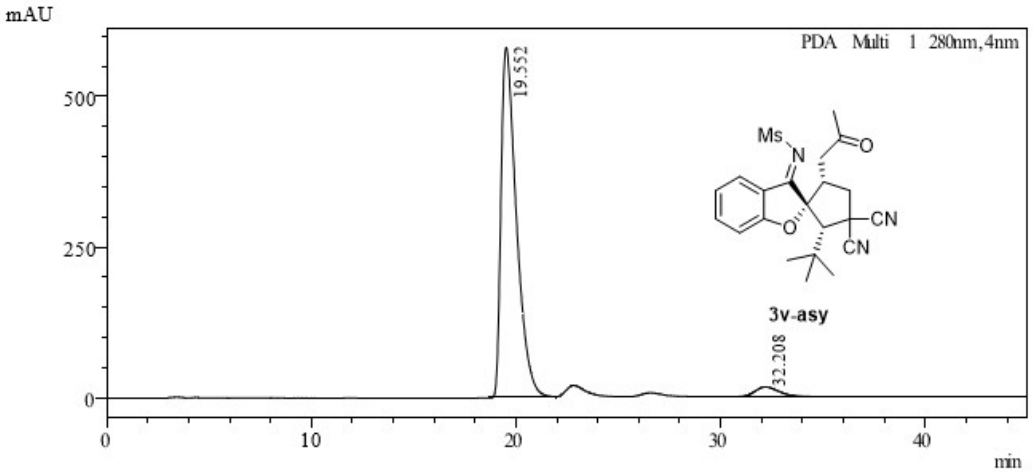
Conditions: Chiralpak OD-H, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	19.177	3640847	77873	17.880
2	21.359	6546578	111942	32.150
3	24.183	6550030	103369	32.167
4	29.893	3624917	49494	17.802
Total		20362372	342678	100.000



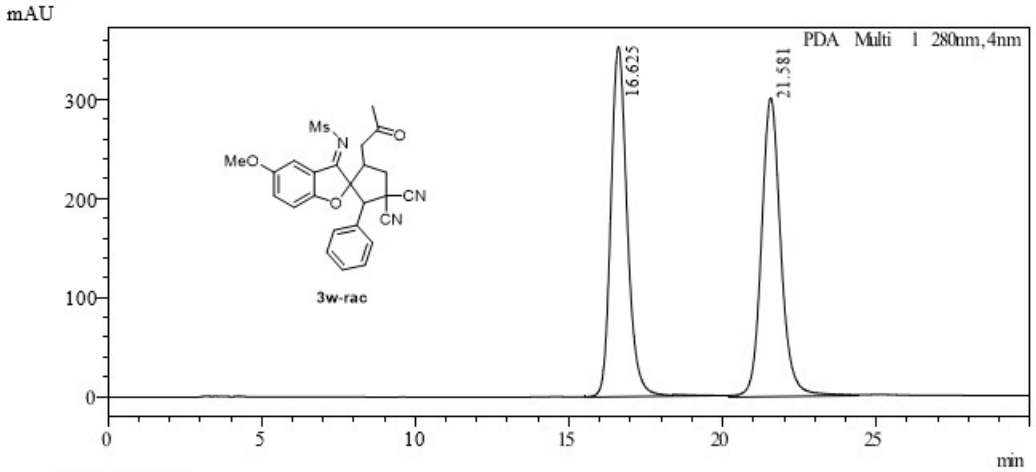
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	19.552	30412585	579840	95.551
2	32.208	1416183	17568	4.449
Total		31828768	597408	100.000

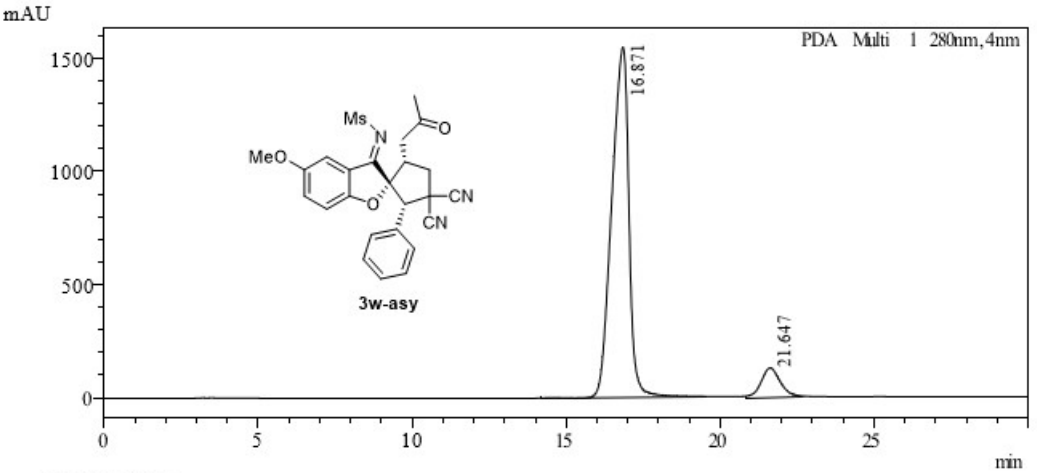
HPLC spectra of **3w**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	16.625	13028257	352376	50.085
2	21.581	12984176	300177	49.915
Total		26012433	652553	100.000

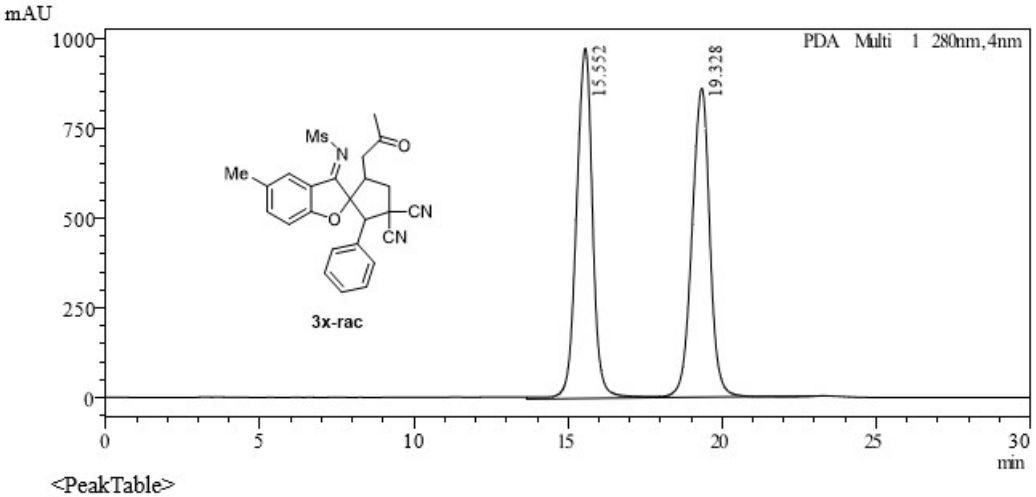


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	16.871	59879416	1546185	91.890
2	21.647	5284895	129170	8.110
Total		65164312	1675356	100.000

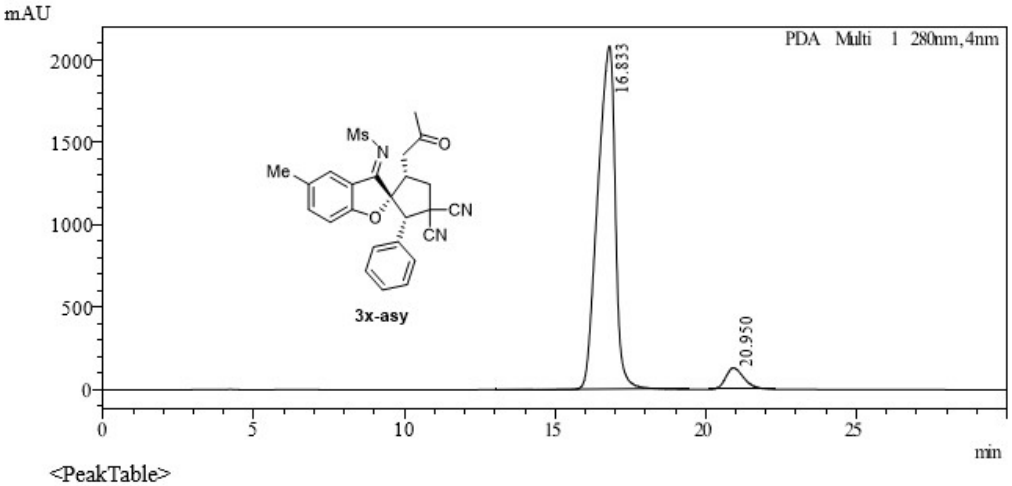
HPLC spectra of **3x**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	15.552	34519702	970816	50.213
2	19.328	34226486	857202	49.787
Total		68746188	1828017	100.000

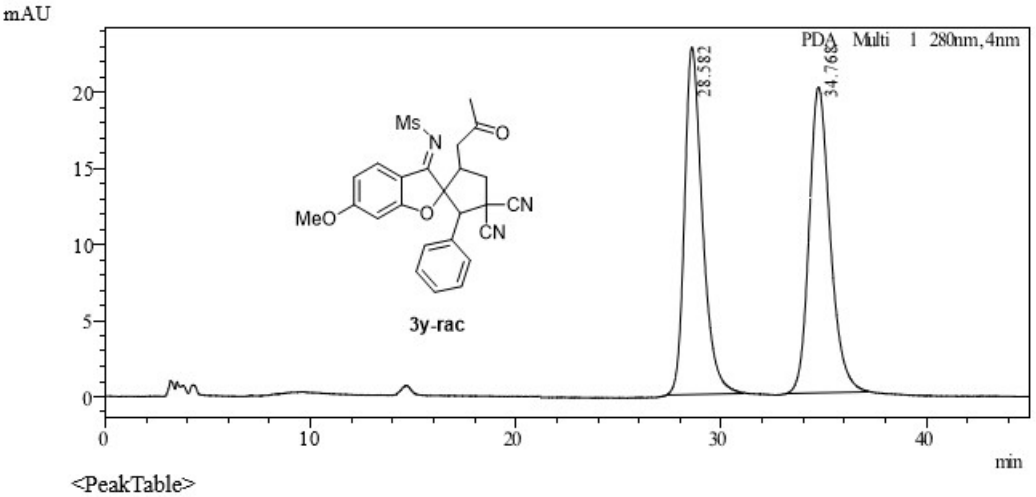


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	16.833	84499410	2081740	93.853
2	20.950	5534457	129788	6.147
Total		90033867	2211527	100.000

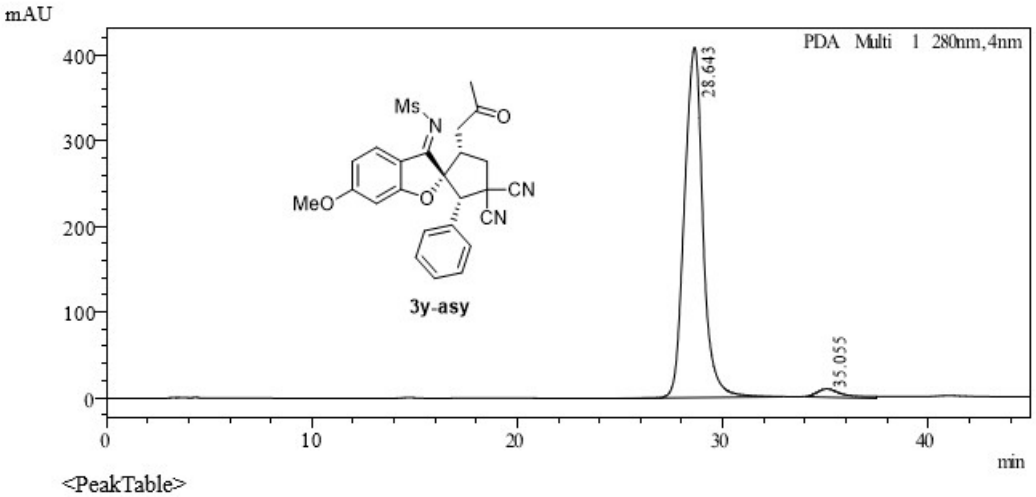
HPLC spectra of **3y**

Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	28.582	1395937	22787	49.798
2	34.768	1407257	20076	50.202
Total		2803194	42863	100.000

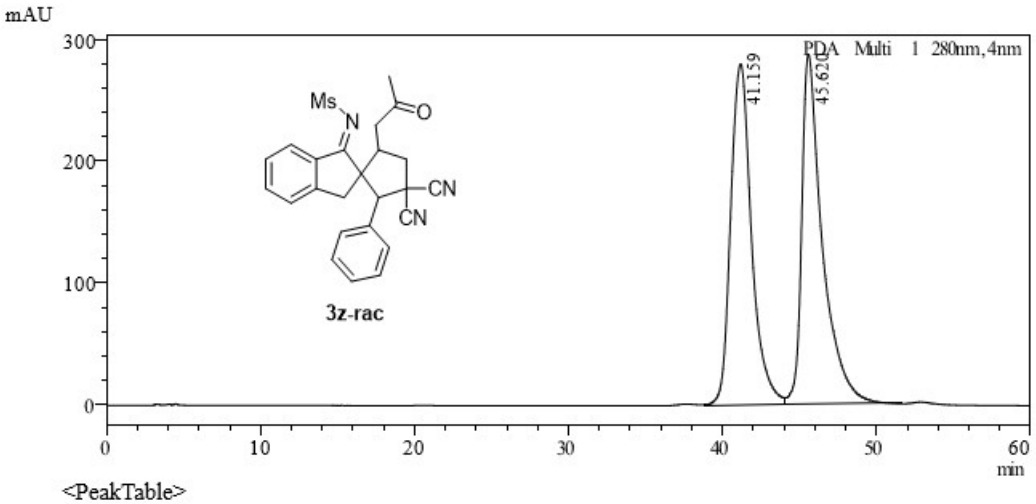


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	28.643	25166682	407997	97.581
2	35.055	623795	9349	2.419
Total		25790477	417346	100.000

HPLC spectra of **3z**

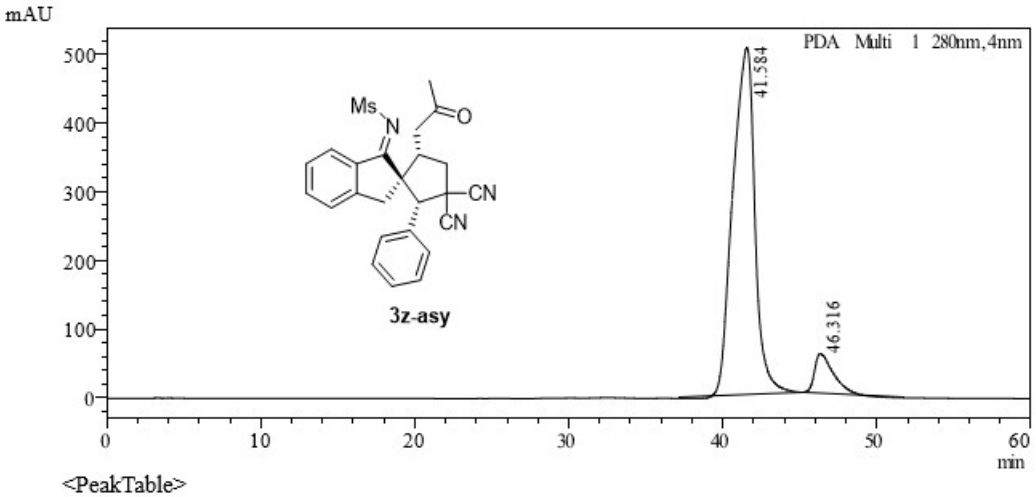
Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 93/7, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	41.159	26249435	279581	49.819
2	45.620	26440011	286157	50.181
Total		52689446	565739	100.000



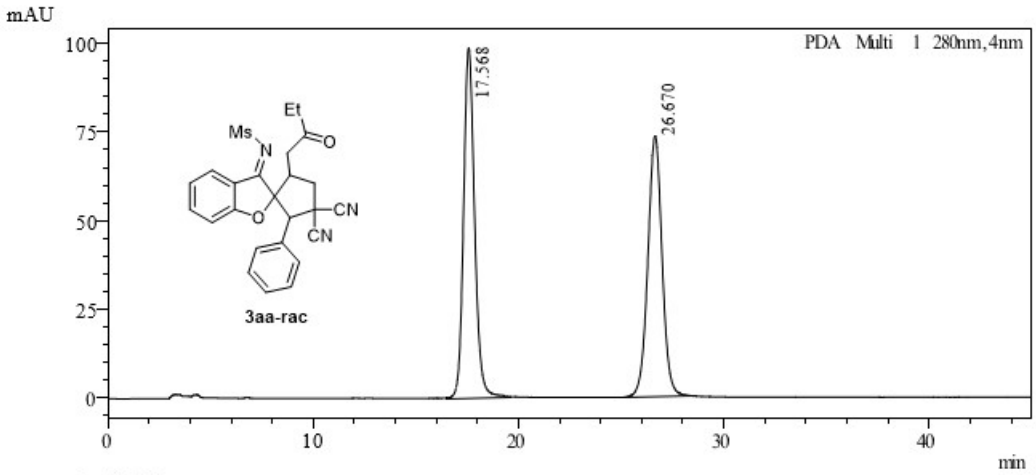
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	41.584	50454514	504619	91.235
2	46.316	4847109	57565	8.765
Total		55301623	562184	100.000

HPLC spectra of **3aa**

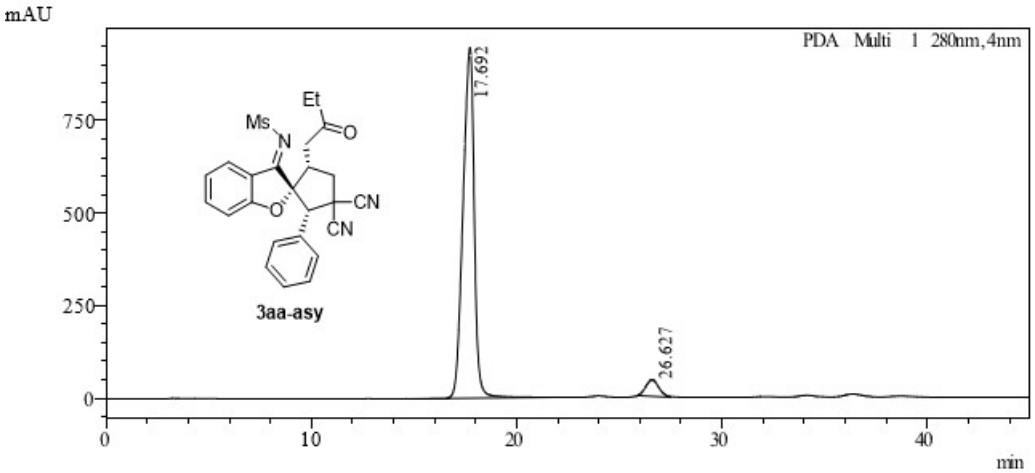
Conditions: Chiralpak IA, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	17.568	3600678	98289	50.292
2	26.670	3558860	73346	49.708
Total		7159538	171635	100.000



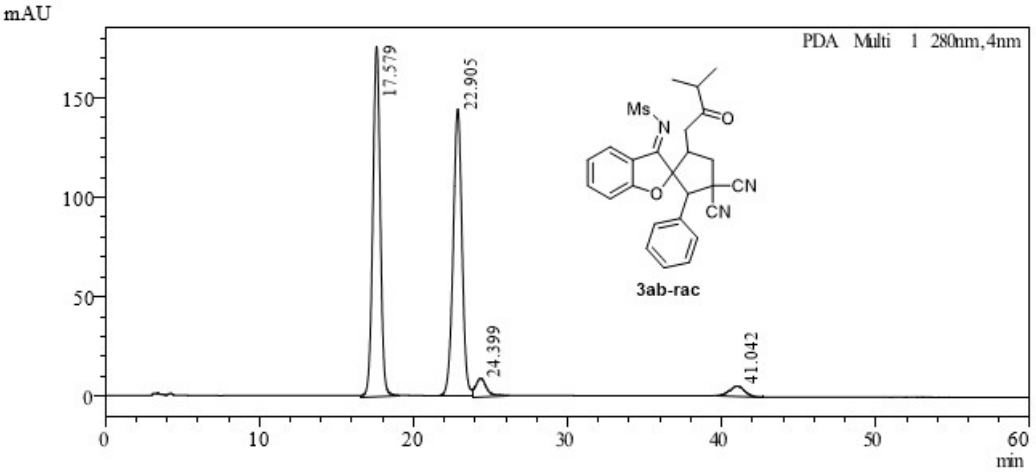
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	17.692	35877676	945729	94.976
2	26.627	1897862	44624	5.024
Total		37775537	990354	100.000

HPLC spectra of **3ab**

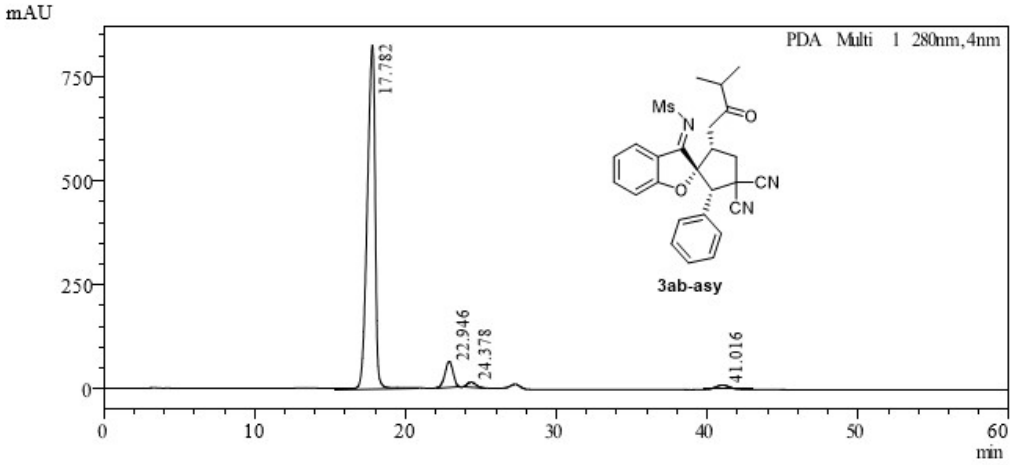
Conditions: Chiralpak IA *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	17.579	5823921	175351	46.877
2	22.905	5820873	144055	46.853
3	24.399	413318	8829	3.327
4	41.042	365629	5481	2.943
Total		12423742	333717	100.000



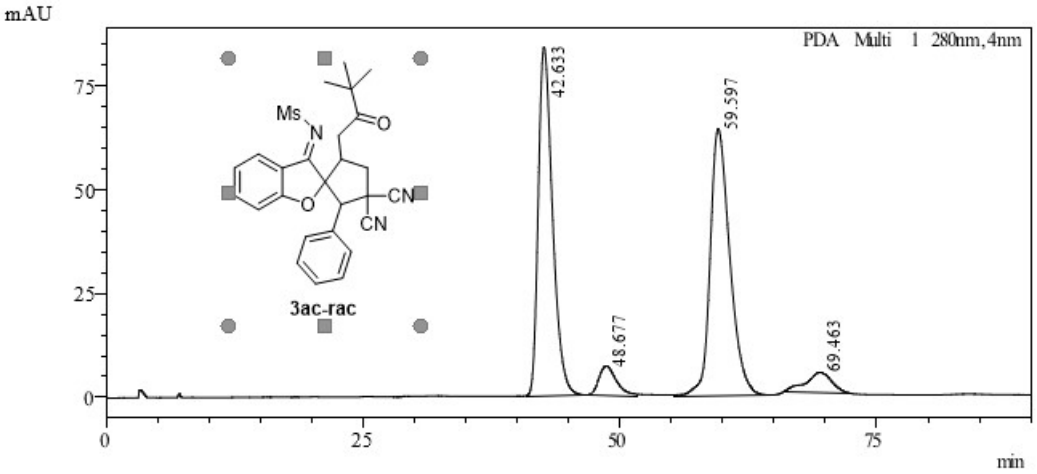
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	17.782	29432353	824166	88.726
2	22.946	2406055	63814	7.253
3	24.378	595309	15525	1.795
4	41.016	738547	11161	2.226
Total		33172263	914665	100.000

HPLC spectra of **3ac**

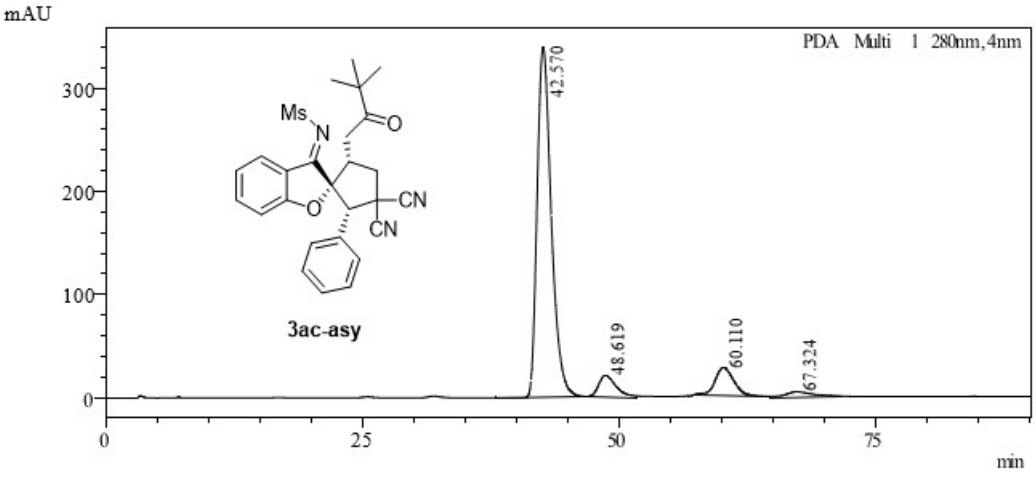
Conditions: Chiralpak IC *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	42.633	8111785	83587	44.631
2	48.677	752229	6752	4.139
3	59.597	8442625	63849	46.452
4	69.463	868475	4998	4.778
Total		18175114	159187	100.000



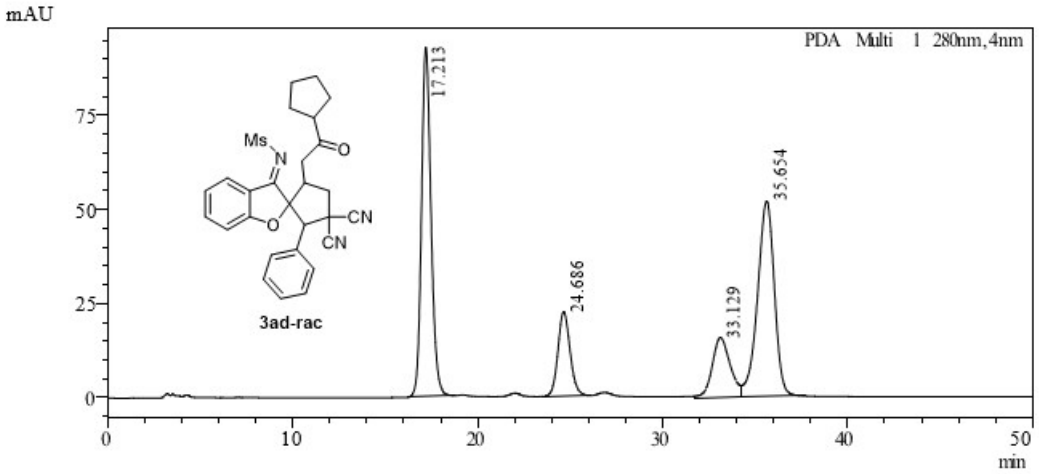
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	42.570	32317121	339014	83.381
2	48.619	2214578	20043	5.714
3	60.110	3475624	26889	8.967
4	67.324	751059	4601	1.938
Total		38758382	390546	100.000

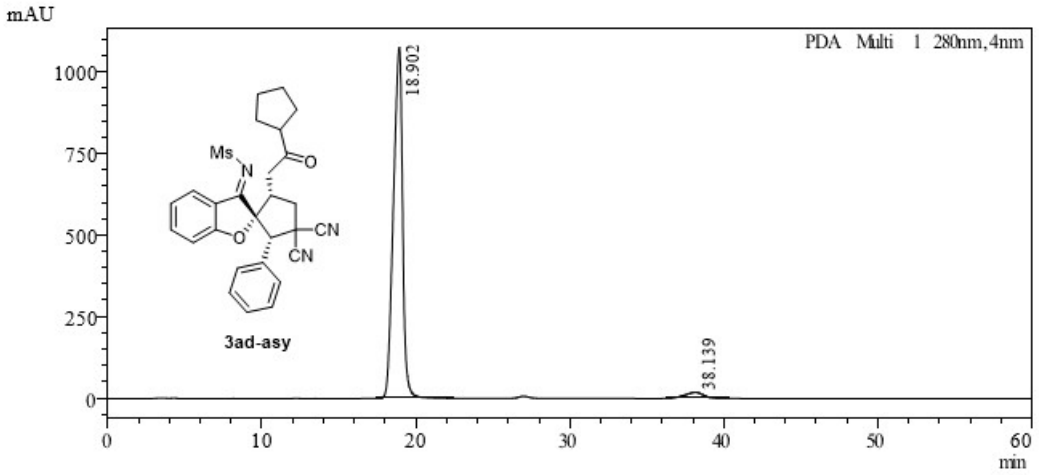
HPLC spectra of **3ad**

Conditions: Chiralpak IA *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	17.213	3286237	92717	37.981
2	24.686	1034717	22393	11.959
3	33.129	1032372	15620	11.932
4	35.654	3298987	51903	38.128
Total		8652312	182633	100.000

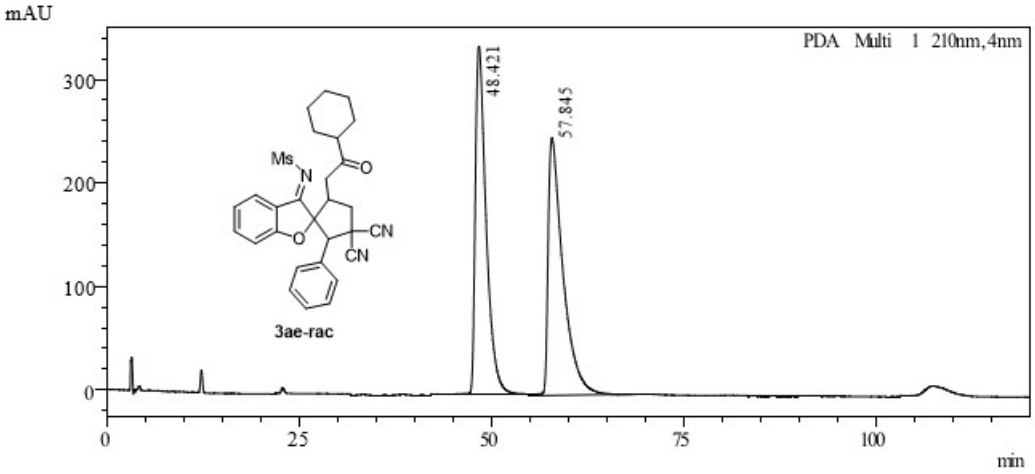


<PeakTable>
PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	18.902	44472031	1072801	96.604
2	38.139	1563215	18395	3.396
Total		46035247	1091196	100.000

HPLC spectra of **3ae**

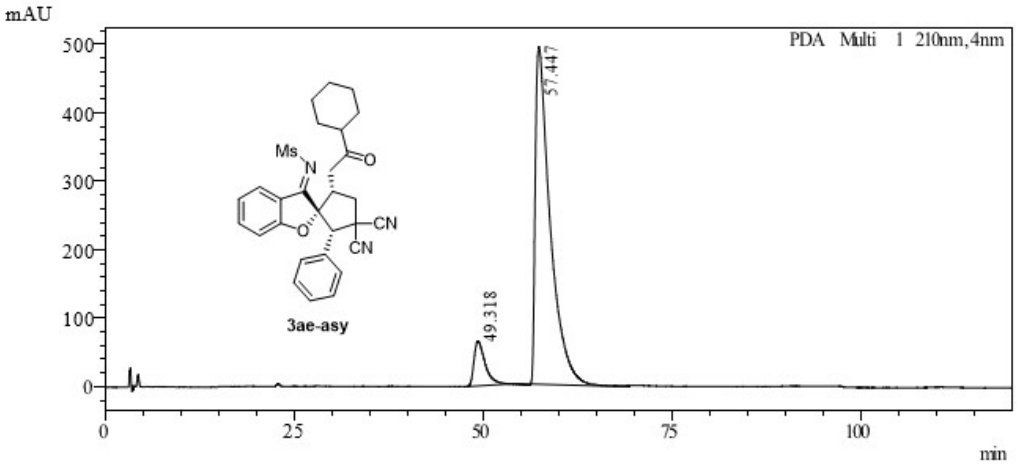
Conditions: Chiralpak IE *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 210 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 210nm

Peak#	Ret.Time	Area	Height	Area%
1	48.421	33034728	336598	50.002
2	57.845	33032494	247855	49.998
Total		66067222	584453	100.000



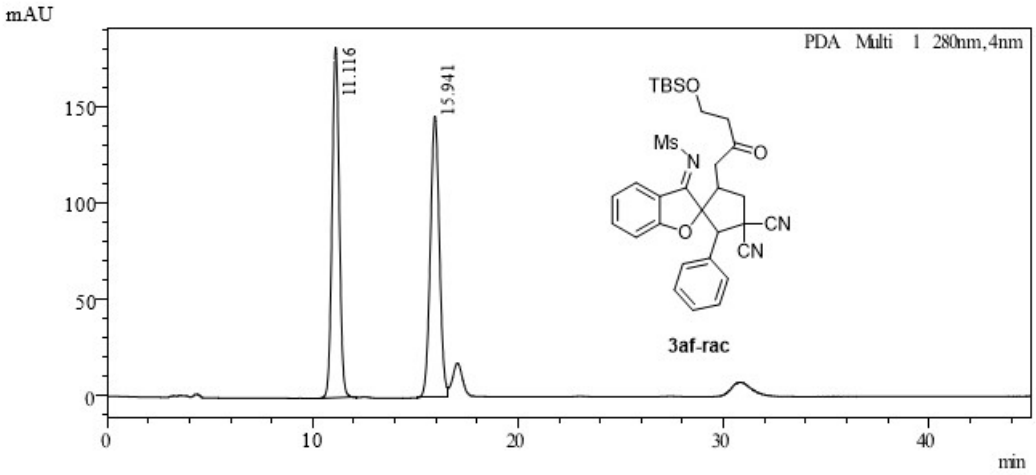
<PeakTable>

PDA Ch1 210nm

Peak#	Ret.Time	Area	Height	Area%
1	49.318	6897665	64451	9.511
2	57.447	65628483	492735	90.489
Total		72526148	557186	100.000

HPLC spectra of **3af**

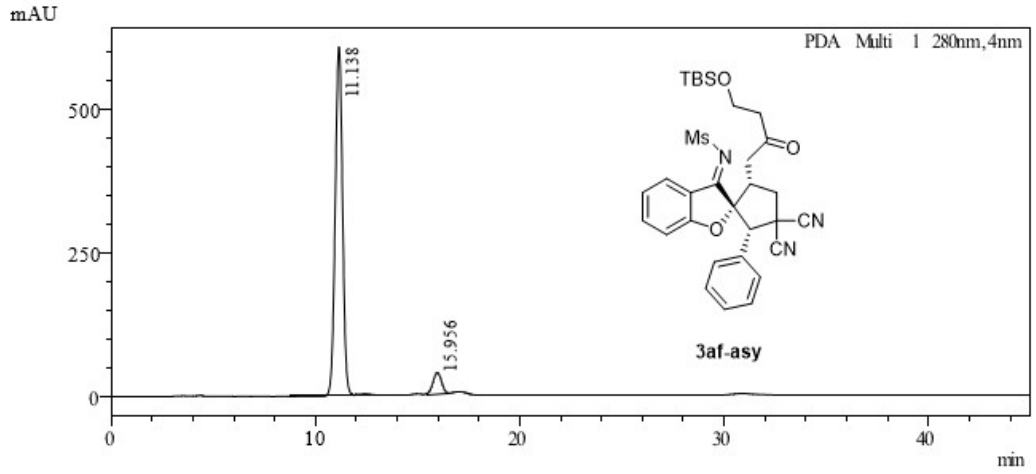
Conditions: Chiralpak IA *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	11.116	4441619	181686	49.597
2	15.941	4513784	146274	50.403
Total		8955403	327960	100.000



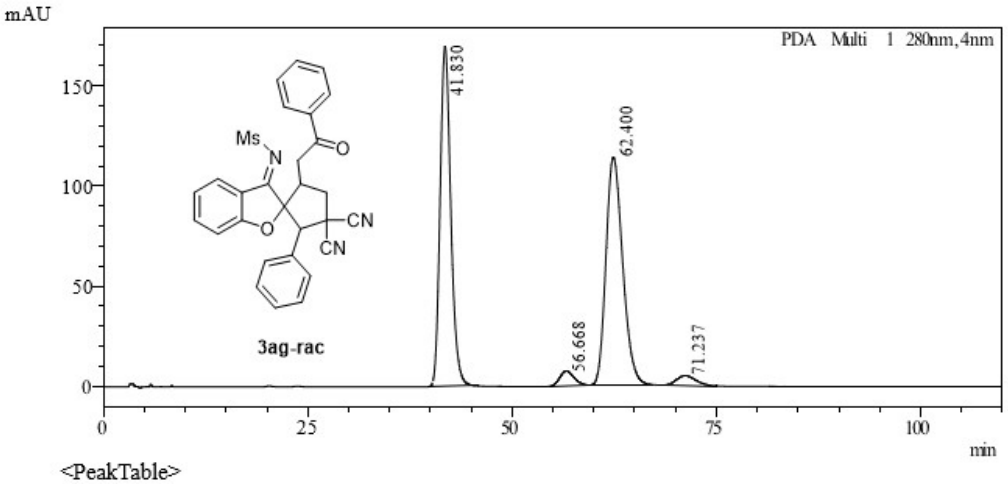
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	11.138	15250091	606867	93.364
2	15.956	1083950	37846	6.636
Total		16334041	644713	100.000

HPLC spectra of **3ag**

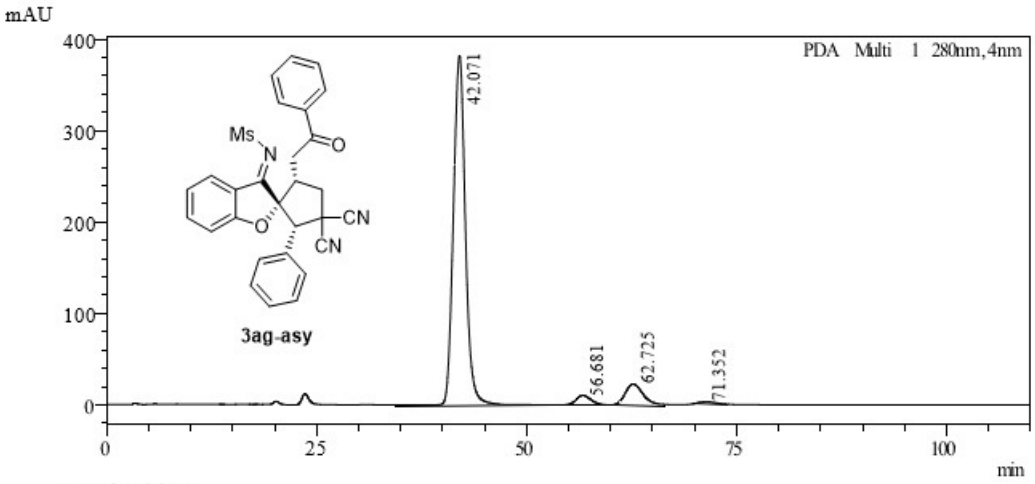
Conditions: Chiralpak IC, *n*-hexane/*i*-propanol = 80/20, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	41.830	16032943	169168	47.629
2	56.668	869880	7113	2.584
3	62.400	15916765	114001	47.284
4	71.237	842224	5210	2.502
Total		33661812	295492	100.000



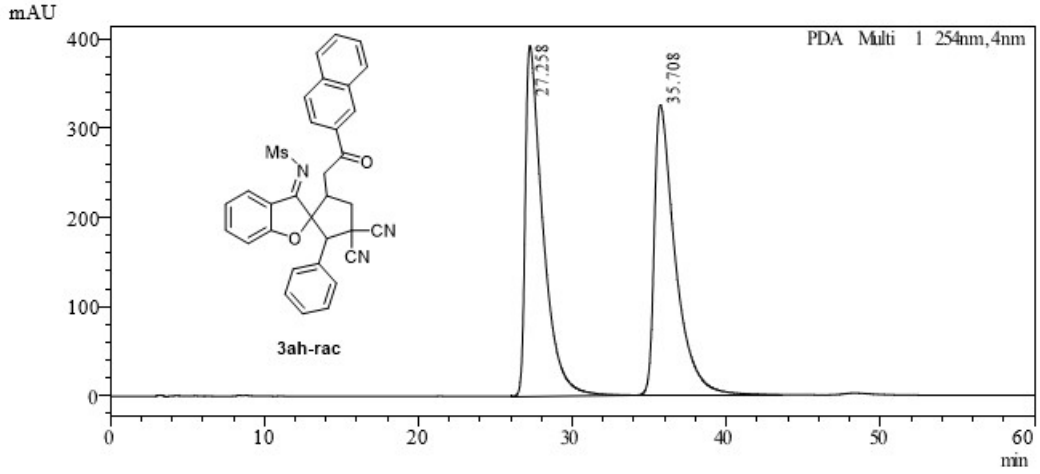
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	42.071	37438006	381716	89.120
2	56.681	1157488	9589	2.755
3	62.725	3054739	21913	7.272
4	71.352	358470	2671	0.853
Total		42008703	415888	100.000

HPLC spectra of **3ah**

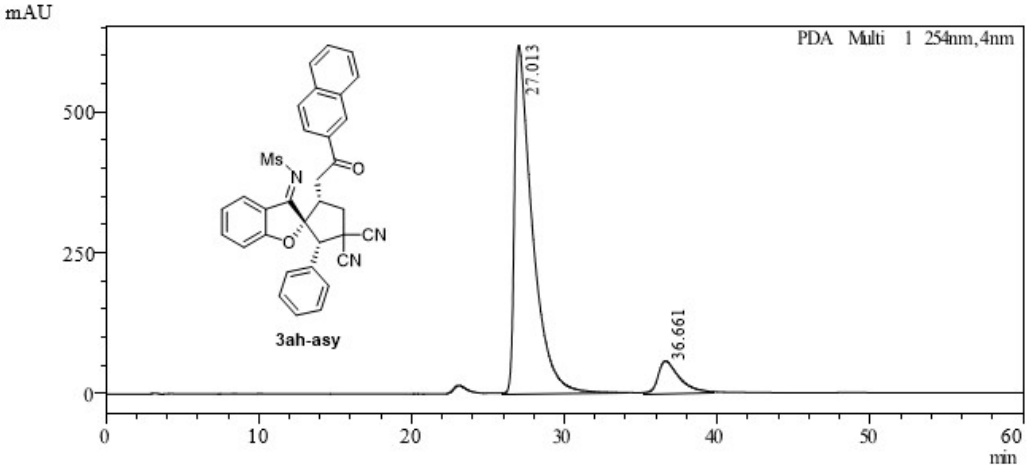
Conditions: Chiralpak IB *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 254 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 254nm

Peak#	Ret.Time	Area	Height	Area%
1	27.258	30678452	391509	49.653
2	35.708	31106674	324864	50.347
Total		61785125	716374	100.000



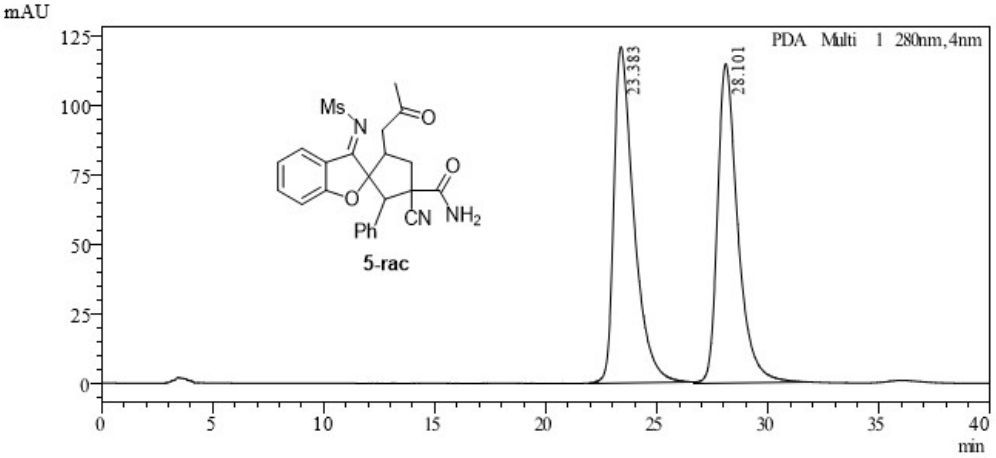
<PeakTable>

PDA Ch1 254nm

Peak#	Ret.Time	Area	Height	Area%
1	27.013	49736425	616455	90.840
2	36.661	5015274	54846	9.160
Total		54751699	671301	100.000

HPLC spectra of **5**

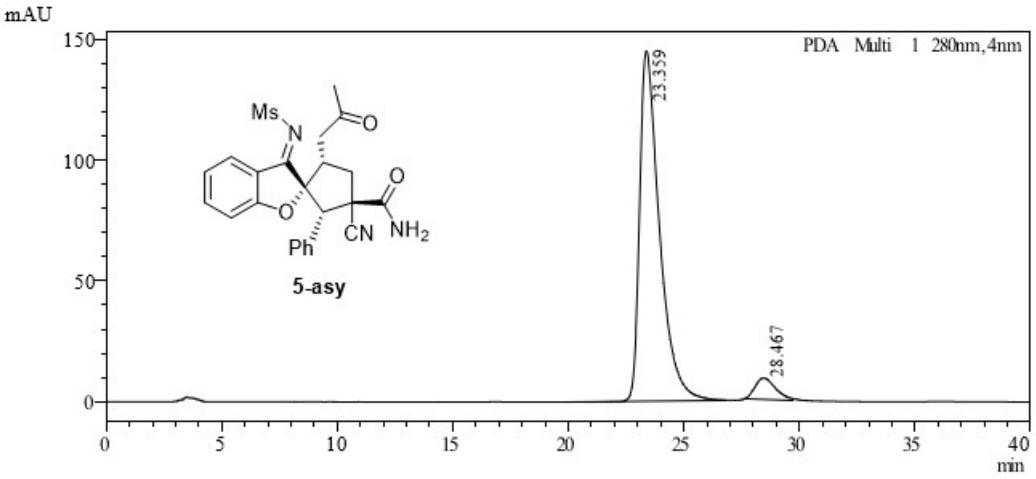
Conditions: Chiralpak IA *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 280 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	23.383	7471152	121032	50.383
2	28.101	7357488	114571	49.617
Total		14828640	235603	100.000



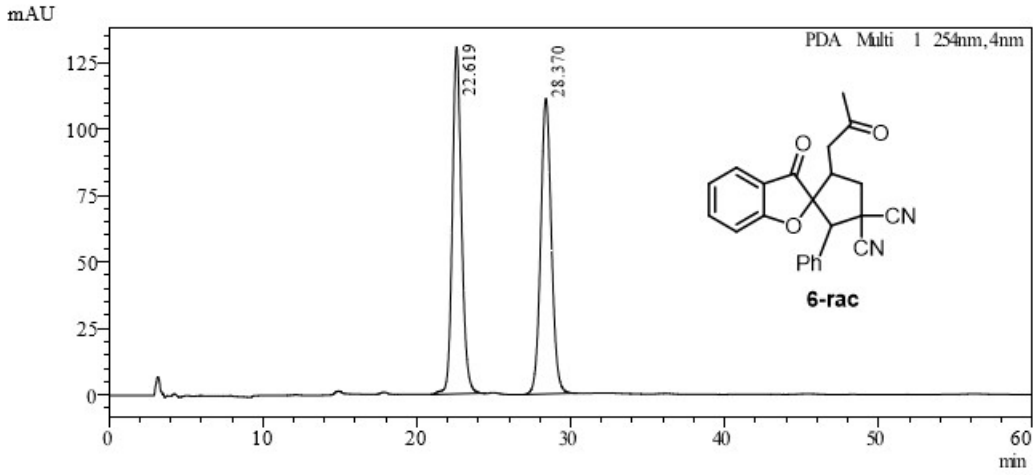
<PeakTable>

PDA Ch1 280nm

Peak#	Ret.Time	Area	Height	Area%
1	23.359	8701913	144503	94.662
2	28.467	490694	8446	5.338
Total		9192608	152949	100.000

HPLC spectra of **6**

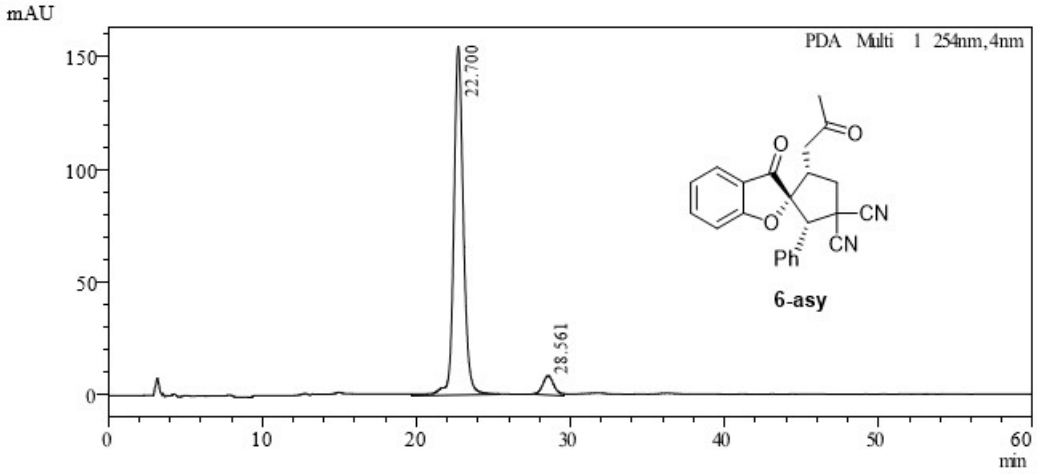
Conditions: Chiralpak IA *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, I = 254 nm, temp. = 25 ℃.



<PeakTable>

PDA Ch1 254nm

Peak#	Ret.Time	Area	Height	Area%
1	22.619	5391866	130312	50.160
2	28.370	5357382	111111	49.840
Total		10749248	241424	100.000



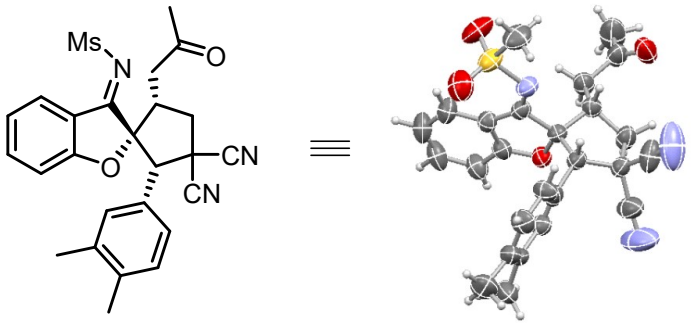
<PeakTable>

PDA Ch1 254nm

Peak#	Ret.Time	Area	Height	Area%
1	22.700	6475751	153998	94.522
2	28.561	375308	8128	5.478
Total		6851059	162126	100.000

12. X-ray crystallographic data of 3q

The single crystal of **3q**, which was used for the determination of its configuration via X-ray crystallography (see below), was recrystallized from a mixed solution of **3q** in CH_2Cl_2 and hexane.



3q x ray of **3q**

ORTEP drawing (50% probability ellipsoids) of **3q** (CCDC 2322514)

Crystal data and structure refinement for **3q**

Identification code	**3q**
CCDC Deposit number	2322514
Empirical formula	$3(C_{26}H_{25}N_3O_4S)$
Formula weight	475.55
Temperature (K)	298.34
Wavelength (Å)	1.5418
Crystal system	orthorhombic
space group	$P2_12_12_1$
a/Å	10.46620(10)
b/Å	13.1332(2)
c/Å	18.2388(2)
α/°	90
β/°	90
γ/°	90
Volume/ $Å^3$	2507.01(5)
Z	4
$\rho_{calc}g/cm^3$	1.260
μ /mm^{-1}	1.445
F (000)	1000

Crystal size/mm^3	0.2 × 0.18 × 0.16
Radiation	CuKα(λ = 1.54184)
2Θ range for data collection/°	8.296 to 153.618
Index ranges	$-13 \leq h \leq 12$, $-16 \leq k \leq 9$, $-20 \leq l \leq 22$
Reflections collected	14876
Goodness-of-fit on F^2	1.066
Independent reflections	5022 [R_{int} = 0.0239, R_{sigma} = 0.0237]
Data/restraints/parameters	5022/54/378
Final R indexes [I>=2σ (I)]	R_1 = 0.0431, wR_2 = 0.1252
Final R indexes [all data]	R_1 = 0.0453, wR_2 = 0.1276
Largest diff. peak/hole / e $Å^{-3}$	0.39/-0.25
Flack parameter	-0.006(7)