Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

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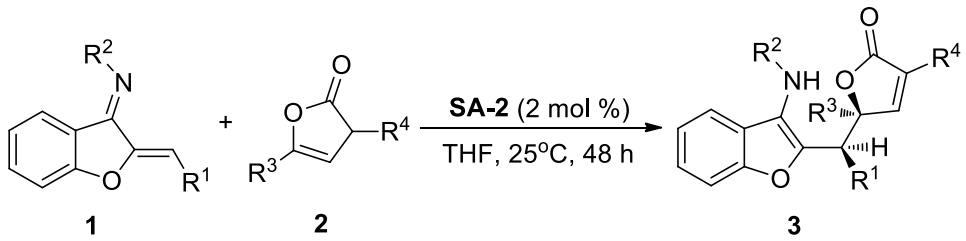
A: General Information and Starting Materials

General Information. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker ACF300 spectrometer (500 MHz and 125 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26; $(CD_3)_2SO$: δ 2.50). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0; $(CD_3)_2SO$: δ 39.50). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

Starting Materials. All solvents, inorganic reagents were from commercial sources and used without purification unless otherwise noted. Azadienes and Butenolides were prepared following the literature procedures.[1,2]

B: General Procedure

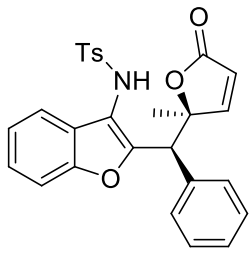


1 2 3

To a solution of THF (0.3 mL) were added azadienes **1** (0.05 mmol), butenolides **2** (0.06 mmol) and catalyst **SA-2** (0.001 mmol). The reaction mixture was stirred at 25 ^{o}C for 48 h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **3**.

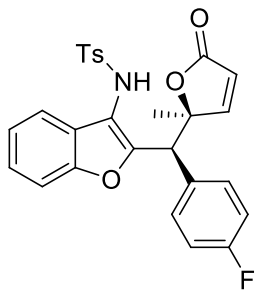
C: Characterization Data

4-Methyl-*N*-(2-((*R*)-((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3aa)



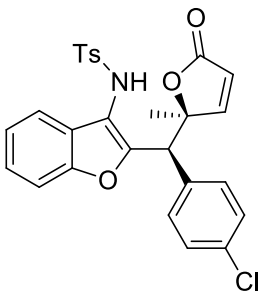
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1. White solid, 22.9 mg, 97% yield. mp 88.3-89.0 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.56 (d, *J* = 10.0 Hz, 2H), 7.48-7.44 (m, 2H), 7.42-7.40 (m, 2H), 7.29-7.25 (m, 2H), 7.22-7.19 (m, 1H), 7.09 (d, *J* = 10.0 Hz, 2H), 7.03-7.00 (m, 1H), 6.92-6.90 (m, 2H), 5.80 (d, *J* = 5.0 Hz, 1H), 4.75 (s, 1H), 2.34 (s, 3H), 1.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 172.1, 159.2, 153.3, 152.5, 144.0, 136.5, 134.9, 129.8, 129.7, 128.5, 127.9, 127.4, 125.1, 124.8, 123.2, 121.2, 118.9, 115.4, 111.7, 89.9, 49.7, 23.0, 21.5. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{24}NO_5S$) requires m/z 474.1375, found m/z 474.1370. The enantiomeric excess was determined to be 92% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 22.6 min (minor), 19.8 min (major). $[\alpha]^{22}_{D}$ = 34.00 (c = 1.00, CH_2Cl_2).

N-(2-((*R*)-(4-fluorophenyl)((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ba)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5:1. White solid, 24.0 mg, 98% yield. mp 87.9-89.6 ^{o}C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.87 (s, 1H), 7.82 (d, *J* = 5.0 Hz, 1H), 7.60 (d, *J* = 10.0 Hz, 1H), 7.40 (d, *J* = 10.0 Hz, 2H), 7.31-7.28 (m, 2H), 7.26-7.22 (m, 1H), 7.13 (d. *J* = 10.0 Hz, 2H), 7.06-6.99 (m, 4H), 5.94 (d, *J* = 5.0 Hz, 1H), 4.87 (s, 1H), 2.24 (s, 3H), 1.26 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.5, 161.8, 161.7 (d, *J* = 970.0 Hz), 153.3, 151.5, 143.7, 137.1, 132.0, 131.9 (d, *J* = 30.0 Hz), 130.0, 127.2, 125.2 (d, *J* = 35.0 Hz), 123.3, 121.0, 120.1, 116.7, 115.2 (d, *J* = 35.0 Hz), 112.0, 110.0, 89.3, 47.1, 22.8, 21.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{23}FNO_5S$) requires m/z 492.1281, found m/z 492.1277. The enantiomeric excess was determined to be 90% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 13.6 min (minor), 12.0 min (major). $[\alpha]^{22}_{D}$ = 30.00 (c = 1.00, CH_2Cl_2).

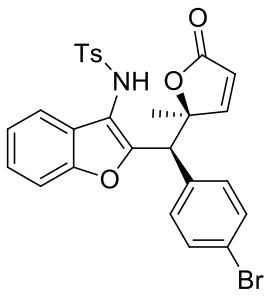
N-(2-((*R*)-(4-chlorophenyl)((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ca)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5:1. White solid, 25.7 mg, >99% yield. mp 94.9-96.5 ^{o}C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.87 (s, 1H), 7.80 (d, *J* = 10.0 Hz, 1H), 7.60 (d, *J* = 10.0 Hz, 1H), 7.38 (d, *J* = 10.0 Hz, 2H), 7.29-7.24 (m, 5H), 7.11-7.09 (m, 2H), 7.07-7.04 (m,

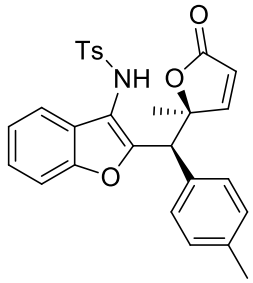
2H), 5.95 (d, *J* = 5.0 Hz, 1H), 4.85 (s, 1H), 2.24 (s, 3H), 1.26 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.4, 161.7, 153.4, 151.1, 143.7, 137.0, 134.7, 132.4, 131.7, 129.9, 128.3, 127.1, 125.3, 125.1, 123.4, 121.1, 120.2, 116.9, 112.0, 89.2, 47.2, 22.8, 21.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{23}ClNO_5S$) requires m/z 508.0985, found m/z 508.0981. The enantiomeric excess was determined to be 84% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 14.4 min (minor), 11.8 min (major). $[\alpha]^{22}_D$ = 39.00 (c = 1.00, CH_2Cl_2).

_N_-(2-((_R_)-(4-bromophenyl)((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3da)



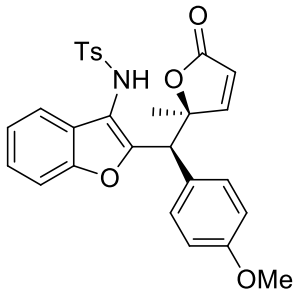
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1. White solid, 26.0 mg, 94% yield. mp 97.0-98.2 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.53 (d, *J* = 5.0 Hz, 2H), 7.46-7.40 (m, 4H), 7.32 (d, *J* = 10.0 Hz, 2H), 7.24-7.20 (m, 1H), 7.09 (d, *J* = 5.0 Hz, 2H), 7.02-6.99 (m, 1H), 6.84-6.79 (m, 2H), 5.84 (d, *J* = 5.0 Hz, 1H), 4.78 (s, 1H), 2.35 (s, 3H), 1.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 172.1, 159.2, 153.3, 151.9, 144.2, 136.2, 134.0, 131.6, 131.5, 129.7, 127.4, 125.0, 124.8, 123.3, 122.1, 121.5, 118.9, 115.7, 111.8, 89.6, 48.9, 22.8, 21.6. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{23}BrNO_5S$) requires m/z 552.0480, found m/z 552.0477. The enantiomeric excess was determined to be 84% by HPLC. [IDA column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 14.7 min (minor), 12.4 min (major). $[\alpha]^{22}_D$ = 36.00 (c =1.00, CH_2Cl_2).

4-Methyl-_N_-(2-((_R_)-((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(_p_-tolyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ea)



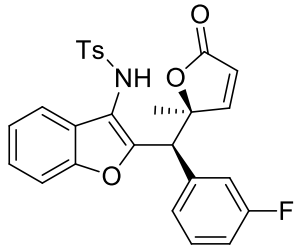
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1. White solid, 17.3 mg, 71% yield. mp 86.8-87.4 ^{o}C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.83 (s, 1H), 7.80 (d, *J* = 5.0 Hz, 1H), 7.58 (d, *J* = 10.0 Hz, 1H), 7.43 (d, *J* = 10.0 Hz, 2H), 7.24-7.20 (m, 1H), 7.17-7.13 (m, 4H), 7.05-7.00 (m, 3H), 6.95-6.94 (m, 1H), 5.92 (d, *J* = 5.0 Hz, 1H), 4.80 (s, 1H), 2.25 (s, 3H), 2.22 (s, 3H), 1.28 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.6, 161.8, 153.2, 152.2, 143.7, 137.3, 136.7, 132.8, 129.9, 129.8, 128.9, 127.2, 125.2, 125.1, 123.2, 120.9, 119.9, 116.4, 111.9, 89.5, 47.8, 23.0, 21.4, 21.1. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{28}H_{26}NO_5S$) requires m/z 488.1532, found m/z 488.1526. The enantiomeric excess was determined to be 91% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 16.0 min (minor), 12.6 min (major). $[\alpha]^{22}_D$ = 17.00 (c = 1.00, CH_2Cl_2).

_N_-(2-((_R_)-(4-methoxyphenyl)((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3fa)



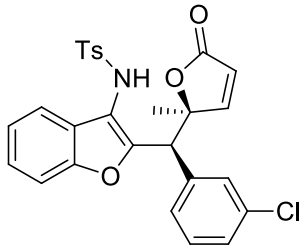
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1. White solid, 23.6 mg, 94% yield. mp 84.1-85.8 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.57 (d, *J* = 5.0 Hz, 2H), 7.46-7.43 (m, 2H), 7.32 (d, *J* = 10.0 Hz, 2H), 7.22-7.18 (m, 1H), 7.12 (d, *J* = 5.0 Hz, 2H), 7.02-6.99 (m, 1H), 6.86 (d, *J* = 10.0 Hz, 1H), 6.81 (d, *J* = 10.0 Hz, 2H), 6.64 (s, 1H), 5.81 (d, *J* = 5.0 Hz, 1H), 4.66 (s, 1H), 3.77 (s, 3H), 2.36 (s, 3H), 1.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 172.2, 159.4, 159.1, 153.3, 152.8, 144.0, 136.5, 130.9, 129.7, 127.4, 127.0, 125.1, 124.7, 123.2, 121.2, 118.9, 115.2, 113.8, 111.7, 90.1, 55.2, 48.9, 22.9, 21.5. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{28}H_{26}NO_6S$) requires m/z 504.1481, found m/z 504.1473. The enantiomeric excess was determined to be 90% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 19.9 min (minor), 15.8 min (major). $[\alpha]^{22}_{D}$ = 14.00 (c = 1.00, CH_2Cl_2).

_N_-(2-((_R_)-(3-fluorophenyl)((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ga)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5:1. White solid, 23.8 mg, 97% yield. mp 96.0-97.7 ^{o}C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.90 (s, 1H), 7.85 (d, *J* = 5.0 Hz, 1H), 7.63 (d, *J* = 5.0 Hz, 1H), 7.40 (d, *J* = 10.0 Hz, 2H), 7.27-7.24 (m, 2H), 7.13-7.12 (m, 3H), 7.07-7.02 (m, 4H), 5.94 (d, *J* = 5.0 Hz, 1H), 4.87 (s, 1H), 2.24 (s, 3H), 1.27 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.5, 165.3, 161.8 (d, *J* = 970.0 Hz), 161.7, 153.4, 151.0, 143.7, 138.3 (d, *J* = 30.0 Hz), 137.1, 130.2 (d, *J* = 35.0 Hz), 130.0, 127.2, 126.1, 125.2 (d, *J* = 100.0 Hz), 123.4, 121.0, 120.1, 117.0, 116.8 (d, *J* = 85.0 Hz), 114.6 (d, *J* = 85.0 Hz), 112.0, 89.2, 47.5, 22.9, 21.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{23}FNO_5S$) requires m/z 492.1281, found m/z 492.1274. The enantiomeric excess was determined to be 87% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 12.6 min (minor), 11.0 min (major). $[\alpha]^{22}_{D}$ = 30.00 (c = 1.00, CH_2Cl_2).

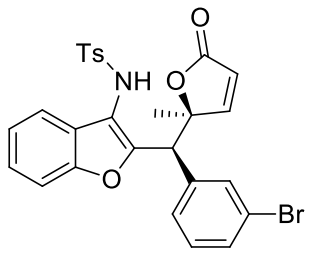
_N_-(2-((_R_)-(3-chlorophenyl)((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ha)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5:1. White solid, 27.4 mg, 88% yield. mp 181.9-183.6 ^{o}C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.91 (s, 1H), 7.85 (d, *J* = 5.0 Hz, 1H), 7.64 (d, *J* = 5.0 Hz, 1H), 7.40 (d, *J* = 10.0 Hz, 2H), 7.28-7.24 (m, 5H), 7.13 (d, *J* = 5.0 Hz, 2H), 7.09-7.06 (m, 1H), 7.03-7.02 (m, 1H), 5.96 (d, *J* = 5.0 Hz, 1H), 4.87 (s, 1H), 2.24 (s, 3H), 1.25 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.5, 161.7, 153.4, 150.9, 143.7, 138.0, 137.0, 132.7, 130.1, 129.9, 129.7, 128.6, 127.7, 127.2, 125.4, 125.1, 123.4, 121.1,

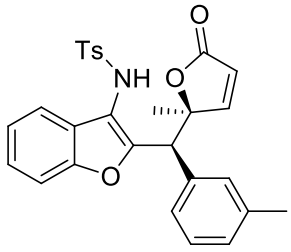
120.2, 117.0, 112.1, 89.2, 47.5, 22.8, 21.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{23}ClNO_5S$) requires m/z 508.0985, found m/z 508.0981. The enantiomeric excess was determined to be 90% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 13.4 min (minor), 11.1 min (major). $[\alpha]^{22}_D$ = 28.00 (c = 1.00, CH_2Cl_2).

_N_-(2-((_R_)-(3-bromophenyl)((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ia)



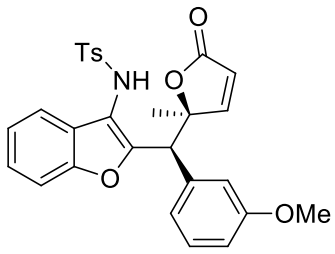
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1.White solid, 20.1 mg, 73% yield. mp 63.3-65.1 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.91 (s, 1H), 7.85 (d, *J* = 5.0 Hz, 1H), 7.64 (d, *J* = 5.0 Hz, 1H), 7.43-7.39 (m, 4H), 7.30-7.24 (m, 2H), 7.20-7.17 (m, 1H), 7.13 (d, *J* = 10.0 Hz, 2H), 7.09-7.06 (m, 1H), 7.02-7.01 (m, 1H), 5.96 (d, *J* = 5.0 Hz, 1H), 4.87 (s, 1H), 2.24 (s, 3H), 1.25 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 177.2, 166.5, 158.1, 155.6, 148.4, 143.0, 141.9, 137.3, 135.4, 135.2, 134.7, 133.7, 131.9, 130.1, 129.8, 128.1, 126.2, 125.9, 124.9, 116.8, 110.0, 93.9, 52.2, 27.6, 26.2. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{23}BrNO_5S$) requires m/z 552.0480, found m/z 552.0477. The enantiomeric excess was determined to be 90% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 14.6 min (minor), 11.8 min (major). $[\alpha]^{22}_D$ = 33.00 (c = 1.00, CH_2Cl_2).

4-Methyl-_N_-(2-((_R_)-((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(_m_-tolyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ja)



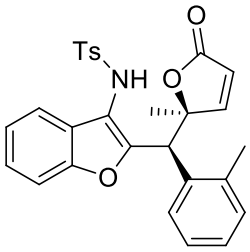
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1. White solid, 20.9 mg, 86% yield. mp 188.2-189.0 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.83 (s, 1H), 7.80 (d, *J* = 5.0 Hz, 1H), 7.60 (d, *J* = 10.0 Hz, 1H), 7.45 (d, *J* = 5.0 Hz, 2H), 7.24-7.21 (m, 1H), 7.16 (d, *J* = 5.0 Hz, 2H), 7.09-7.08 (m, 3H), 7.05-7.01 (m, 2H), 6.93 (d, *J* = 10.0 Hz, 1H), 5.92 (d, *J* = 5.0 Hz, 1H), 4.81 (s, 1H), 2.25 (s, 3H), 2.22 (s, 3H), 1.28 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.6, 161.8, 153.2, 152.1, 143.6, 137.4, 137.2, 135.8, 130.6, 129.9, 128.3, 128.2, 127.2, 127.0, 125.2, 125.1, 123.2, 120.9, 119.9, 116.4, 112.0, 89.4, 48.1, 23.1, 21.6, 21.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{28}H_{26}NO_5S$) requires m/z 488.1532, found m/z 488.1524. The enantiomeric excess was determined to be 91% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 16.3 min (minor), 12.8 min (major). $[\alpha]^{22}_D$ = 17.00 (c = 1.00, CH_2Cl_2).

_N_-(2-((_R_)-(3-methoxyphenyl)((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ka)



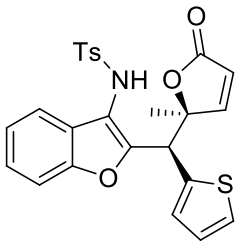
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5:1. White solid, 20.6 mg, 82% yield. mp 175.8-176.9 ^{o}C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.85 (s, 1H), 7.83 (d, *J* = 5.0 Hz, 1H), 7.60 (d, *J* = 10.0 Hz, 1H), 7.44 (d, *J* = 10.0 Hz, 2H), 7.24-7.21 (m, 1H), 7.16-7.11 (m, 3H), 7.04-7.01 (m, 1H), 6.92 (d, *J* = 5.0 Hz, 1H), 6.87-6.85 (m, 2H), 6.78-6.76 (m, 1H), 5.93 (d, *J* = 5.0 Hz, 1H), 4.83 (s, 1H), 3.69 (s, 3H), 2.25 (s, 3H), 1.29 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.7, 161.9, 159.0, 153.2, 151.9, 143.7, 137.3, 137.2, 130.0, 129.3, 127.2, 125.2, 125.1, 123.2, 122.2, 120.8, 119.9, 116.6, 116.2, 112.6, 112.0, 89.4, 55.3, 48.0, 23.1, 21.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{28}H_{26}NO_6S$) requires m/z 504.1481, found m/z 504.1474. The enantiomeric excess was determined to be 90% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 60:40, 1.0 mL/min]: 11.2 min (minor), 7.1 min (major). $[\alpha]^{22}_{D}$ = 16.00 (c = 1.00, CH_2Cl_2).

4-Methyl-*N*-(2-((*R*)-((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(o-tolyl)methyl)benzofuran-3-yl)benzenesulfonamide (3la)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1. White solid, 13.7 mg, 56% yield. mp 67.3-68.7 ^{o}C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.86 (s, 1H), 7.93 (d, *J* = 5.0 Hz, 1H), 7.65-7.63 (m, 1H), 7.58-7.56 (m, 1H), 7.48 (d, *J* = 10.0 Hz, 2H), 7.25-7.19 (m, 3H), 7.10-7.04 (m, 3H), 7.01-6.97 (m, 1H), 6.70 (d, *J* = 5.0 Hz, 1H), 5.96 (d, *J* = 5.0 Hz, 1H), 5.23 (s, 1H), 2.41 (s, 3H), 2.30 (s, 3H), 1.41 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.6, 160.7, 153.3, 153.2, 143.8, 137.6, 136.4, 134.3, 130.8, 130.0, 129.7, 127.6, 127.1, 125.9, 125.1, 125.0, 123.2, 121.4, 119.6, 116.1, 112.0, 89.7, 43.0, 23.0, 21.4, 20.7. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{25}NO_5SNa$) requires m/z 510.1346, found m/z 510.1344. The enantiomeric excess was determined to be 98% by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 8.3 min (minor), 9.7 min (major). $[\alpha]^{22}_{D}$ = 10.00 (c = 0.50, CH_2Cl_2).

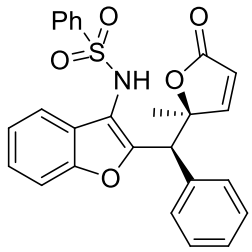
4-Methyl-*N*-(2-((*R*)-((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(thiophen-2-yl)methyl)benzofuran-3-yl)benzenesulfonamide (3ma)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1. White solid, 23.9 mg, >99% yield. mp 81.7-83.5 ^{o}C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.91 (s, 1H), 7.82 (d, *J* = 5.0 Hz, 1H), 7.56 (d, *J* = 10.0 Hz, 1H), 7.47 (d, *J* = 10.0 Hz, 2H), 7.37-7.36 (m, 1H), 7.24-7.20 (m, 1H), 7.18 (d, *J* = 10.0 Hz, 2H), 7.04-7.01 (m, 1H), 6.91-6.87 (m, 3H), 6.01 (d, *J* = 5.0 Hz, 1H), 5.25 (s, 1H), 2.27 (s, 3H), 1.32 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.6, 161.4, 153.1, 150.8, 143.8, 137.3, 136.6, 130.0, 128.4,

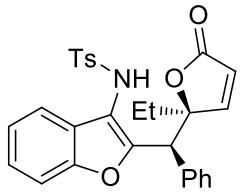
127.2, 126.6, 126.4, 125.3, 125.1, 123.3, 121.2, 119.9, 116.4, 112.0, 89.2, 43.6 22.8, 21.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{25}H_{22}NO_5S_2$) requires m/z 480.0939, found m/z 480.0932. The enantiomeric excess was determined to be 90% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 20.4 min (minor), 16.5 min (major). $[\alpha]^{22}_D$ = 7.00 (c = 1.00, CH_2Cl_2).

_N_-(2-((_R_)-((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3na)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1. White solid, 201.5 mg, 94% yield. mp 97.4-98.5 ^oC. ^1H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.95 (s, 1H) 7.87 (d, *J* = 5.0 Hz, 1H), 7.59 (d, *J* = 10.0 Hz, 3H), 7.53-7.50 (m, 1H), 7.40-7.34 (m, 4H), 7.24-7.19 (m, 4H), 6.99-6.96 (m, 1H), 6.78 (d, *J* = 5.0 Hz, 1H), 5.91 (d, *J* = 5.0 Hz, 1H), 4.91 (s, 1H), 1.31 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.6, 161.9, 153.2, 152.4, 140.4, 135.9, 133.4, 130.0, 129.6, 128.4, 127.7, 127.2, 125.1, 123.3, 120.9, 119.6, 116.4, 112.0, 89.4, 48.2, 23.1. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{26}H_{22}NO_5S$) requires m/z 460.1219, found m/z 460.1209. The enantiomeric excess was determined to be 86% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 15.0 min (minor), 12.2 min (major). $[\alpha]^{22}_D$ = 39.00 (c = 1.00, CH_2Cl_2).

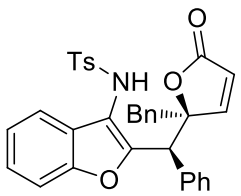
_N_-(2-((_R_)-((_S_)-2-ethyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ab)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1. White solid, 23.9 mg, 98% yield. mp 73.6-75.4 ^oC. ^1H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.87 (s, 1H), 7.73 (d, *J* = 5.0 Hz, 1H), 7.58 (d, *J* = 10.0 Hz, 1H), 7.44 (d, *J* = 10.0 Hz, 2H), 7.32-7.30 (m, 2H), 7.23-7.20 (m, 4H), 7.16 (d, *J* = 10.0 Hz, 2H), 7.04-7.01 (m, 1H), 6.93 (d, *J* = 5.0 Hz, 1H), 5.96 (d, *J* = 5.0 Hz, 1H), 4.88 (s, 1H), 2.26 (s, 3H), 1.78-1.74 (m, 1H), 1.50-1.46 (m, 1H), 0.59 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.8, 160.1, 153.2, 151.9, 143.7, 137.4, 135.7, 130.1, 130.0, 128.3, 127.6, 127.2, 125.2, 125.1, 123.2, 122.3, 119.9, 116.6, 112.0, 92.2, 47.9, 27.9, 21.4, 7.8. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{28}H_{26}NO_5S$) requires m/z 488.1532, found m/z 488.1524. The enantiomeric excess was determined to be 90% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 12.8 min (minor), 11.0 min (major). $[\alpha]^{22}_D$ = 18.00 (c = 1.00, CH_2Cl_2).

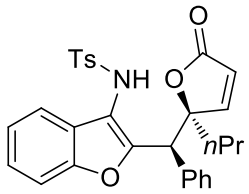
_N_-(2-((_R_)-((_S_)-2-benzyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ac)

Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1. White solid, 26.1 mg, 95% yield. mp 99.4-101.1 ^oC. ^1H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm)



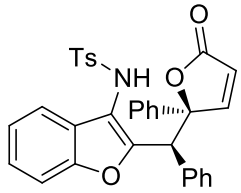
9.95 (s, 1H), 7.76 (d, *J* = 5.0 Hz, 1H), 7.67 (d, *J* = 5.0 Hz, 1H), 7.47 (d, *J* = 10.0 Hz, 2H), 7.36-7.35 (m, 2H), 7.27-7.20 (m, 4H), 7.17-7.11 (m, 5H), 7.06-7.03 (m, 1H), 6.96-6.94 (m, 3H), 5.59 (d, *J* = 5.0 Hz, 1H), 5.04 (s, 1H), 3.16 (d, *J* = 15.0 Hz, 1H), 2.72 (d, *J* = 15.0 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.4, 159.9, 153.4, 151.8, 143.8, 137.4, 135.7, 134.8, 130.7, 130.1, 130.0, 128.4, 128.2, 127.7, 127.3, 127.1, 125.2, 125.1, 123.3, 122.3, 120.0, 116.9, 112.1, 91.3, 48.2, 41.0, 21.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{33}H_{28}NO_5S$) requires m/z 550.1688, found m/z 550.1681. The enantiomeric excess was determined to be 74% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 12.1 min (minor), 13.8 min (major). $[\alpha]^{22}_D$ = 36.00 (c = 1.00, CH_2Cl_2).

4-Methyl-*N*-(2-((*R*)-((*S*)-5-oxo-2-propyl-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ad)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1. White solid, 17.5 mg, 70% yield. mp 76.7-78.2 ^{o}C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.89 (s, 1H), 7.76 (d, *J* = 5.0 Hz, 1H), 7.58 (d, *J* = 10.0 Hz, 1H), 7.45 (d, *J* = 5.0 Hz, 2H), 7.32-7.31 (m, 2H), 7.23-7.19 (m, 4H), 7.17 (d, *J* = 5.0 Hz, 2H), 7.04-7.01 (m, 1H), 6.93 (d, *J* = 10.0 Hz, 1H), 5.94 (d, *J* = 5.0 Hz, 1H), 4.88 (s, 1H), 2.26 (s, 3H), 1.77-1.72 (m, 1H), 1.44-1.38 (m, 1H), 1.03-0.95 (m, 2H), 0.71 (t, *J* = 5.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.8, 160.4, 153.2, 151.9, 143.7, 137.4, 135.6, 130.2, 130.0, 128.3, 127.6, 127.2, 125.2, 125.1, 123.2, 121.9, 119.9, 116.6, 112.0, 91.9, 48.1, 36.9, 21.4, 16.7, 14.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{29}H_{28}NO_5S$) requires m/z 502.1688, found m/z 502.1680. The enantiomeric excess was determined to be 92% by HPLC. [ID column, 254 nm, *n*-hexane:IPA = 80:20, 1.0 mL/min]: 29.0 min (minor), 23.3 min (major). $[\alpha]^{22}_D$ = 26.00 (c = 1.00, CH_2Cl_2).

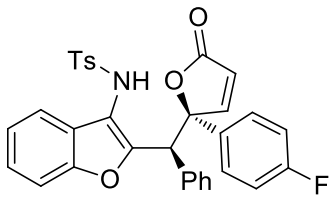
4-Methyl-*N*-(2-((*R*)-((*S*)-5-oxo-2-phenyl-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ae)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 6:1. White solid, 23.6 mg, 88% yield. mp 107.5-109.1 ^{o}C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.42 (s, 1H), 8.42 (d, *J* = 5.0 Hz, 1H), 7.52 (d, *J* = 10.0 Hz, 1H), 7.49 (d, *J* = 5.0 Hz, 2H), 7.45-7.43 (m, 2H), 7.24-7.20 (m, 7H), 7.18-7.16 (m, 1H), 7.13-7.10 (m, 1H), 7.02 (d, *J* = 10.0 Hz, 2H), 6.88-6.85 (m, 1H), 6.68 (d, *J* = 10.0 Hz, 1H), 5.95 (d, *J* = 5.0 Hz, 1H), 5.46 (s, 1H), 2.18 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.4, 161.2, 152.9, 151.6, 143.4, 138.4, 137.1, 135.5, 130.5, 129.7, 128.6, 128.3, 128.2, 127.7, 127.1, 125.7, 124.8, 124.7, 122.8, 120.1, 119.5, 116.3, 111.6, 92.4, 49.8, 21.3. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{26}NO_5S$) requires m/z 536.1532, found m/z 536.1525. The enantiomeric excess was determined

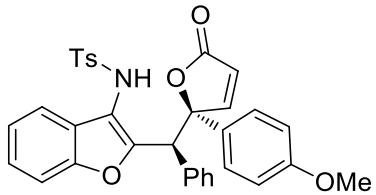
to be 91% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 15.3 min (minor), 10.9 min (major). $[\alpha]^{22}_{D}$ = 106.00 (c = 1.00, CH_2Cl_2).

_N_-(2-((_R_)-((_S_)-2-(4-fluorophenyl)-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3af)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5:1. Yellow solid, 22.9 mg, 83% yield. mp 94.6-96.3 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.41 (s, 1H), 8.45 (d, *J* = 5.0 Hz, 1H), 7.54-7.50 (m, 3H), 7.47 (d, *J* = 5.0 Hz, 2H), 7.27-7.22 (m, 5H), 7.15-7.11 (s, 1H), 7.07-7.03 (m, 4H), 6.89-6.86 (m, 1H), 6.65 (d, *J* = 5.0 Hz, 1H), 5.97 (d, *J* = 5.0 Hz, 1H), 5.42 (s, 1H), 2.19 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.2, 162.9, 160.9, 152.3 (d, *J* = 720.0 Hz), 143.5, 137.1, 135.3, 134.7, 130.5, 129.7, 128.2, 127.9 (d, *J* = 30.0 Hz), 127.7, 127.1, 124.7 (d, *J* = 125.0 Hz), 122.9, 120.3, 119.5, 116.4, 115.5 (d, *J* = 85.0 Hz), 111.7, 92.1, 50.0, 21.3. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{25}FNO_5S$) requires m/z 554.1437, found m/z 554.1433. The enantiomeric excess was determined to be 91% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 14.1 min (minor), 10.5 min (major). $[\alpha]^{22}_{D}$ = 87.00 (c = 1.00, CH_2Cl_2).

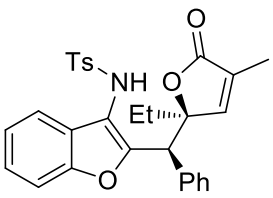
_N_-(2-((_R_)-((_S_)-2-(4-methoxyphenyl)-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ag)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5:1. White solid, 26.3 mg, 93% yield. mp 87.3-88.8 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.44 (s, 1H), 8.39 (d, *J* = 5.0 Hz, 1H), 7.52 (d, *J* = 10.0 Hz, 1H), 7.43 (d, *J* = 5.0 Hz, 2H), 7.38 (d, *J* = 5.0 Hz, 2H), 7.25-7.21 (m, 5H), 7.14-7.11 (m, 1H), 7.04 (d, *J* = 5.0 Hz, 2H), 6.90-6.87 (m, 1H), 6.77 (d, *J* = 10.0 Hz, 2H), 6.70 (d, *J* = 5.0 Hz, 1H), 5.92 (d, *J* = 5.0 Hz, 1H), 5.41 (s, 1H), 3.64 (s, 3H), 2.19 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.5, 161.4, 159.1, 152.9, 151.8, 143.4, 137.1, 135.7, 130.5, 130.3, 129.7, 128.2, 127.6, 127.2, 127.1, 127.0, 124.8, 122.8, 119.8, 119.5, 116.3, 113.9, 111.7, 92.3, 55.5, 49.9, 21.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{33}H_{28}NO_6S$) requires m/z 566.1632, found m/z 566.1631. The enantiomeric excess was determined to be 91% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 24.7 min (minor), 13.3 min (major). $[\alpha]^{22}_{D}$ = 67.00 (c = 1.00, CH_2Cl_2).

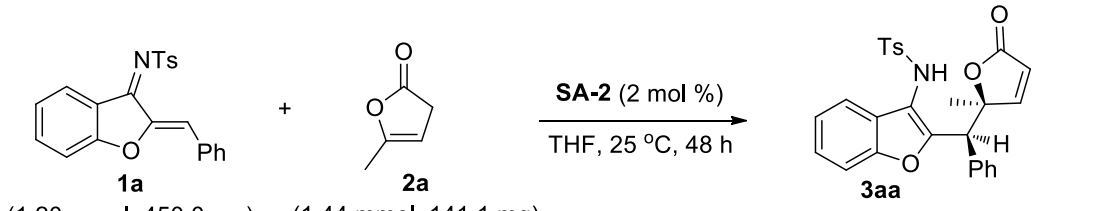
_N_-(2-((_R_)-((_S_)-2-ethyl-4-methyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ah)

Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 24.9 mg, 99% yield. mp 81.2-82.2 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.85 (s, 1H), 7.58 (d, *J* = 5.0 Hz, 1H), 7.43 (d, *J* = 5.0 Hz, 2H), 7.27-7.19 (m, 7H),



7.14 (d, *J* = 5.0 Hz, 2H), 7.06-7.03 (m, 1H), 7.00-6.98 (m, 1H), 4.80 (s, 1H), 2.24 (s, 3H), 1.73-1.68 (m, 1H), 1.51 (s, 3H), 1.47-1.43 (m, 1H), 0.57 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 173.6, 153.2, 152.0, 151.9, 143.6, 137.3, 135.9, 130.2, 130.1, 129.9, 128.2, 127.5, 127.2, 125.3, 125.0, 123.2, 120.0, 116.5, 111.9, 89.8, 48.2, 27.9, 21.4, 10.4, 7.8. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{29}H_{28}NO_5S$) requires m/z 502.1688, found m/z 502.1681. The enantiomeric excess was determined to be 17% by HPLC. [ID column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]:13.8 min (minor), 11.0 min (major). $[\alpha]^{22}_D$ = 4.00 (c = 1.00, CH_2Cl_2).

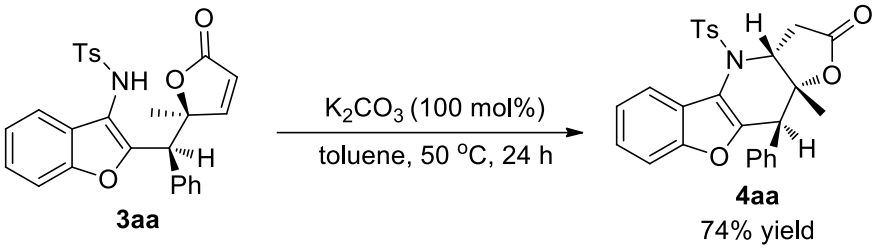
D: Gram Scale Reaction



1a (1.20 mmol, 450.0 mg) + **2a** (1.44 mmol, 141.1 mg) → **3aa** 510.0 mg, 90% yield, 92% ee, >20:1 dr

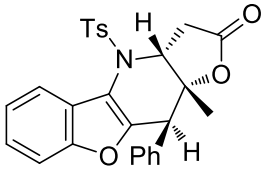
To a solution of THF (7.2 mL) were added azadiene **1a** (450.0 mg, 1.2 mmol), butenolide **2a** (141.1 mg, 1.44 mmol) and catalyst **SA-2** (15.12 mg, 0.024 mmol). The reaction mixture was stirred at 25 ^{o}C for 48 h. The solvent was evaporated to give the crude product, which was purified by silica gel chromatography (PE/EA = 6:1) to provide the desired product **3aa** as a white solid (510.0 mg, 90% yield, 92% ee, >20:1 dr).

E: Synthetic Transformations



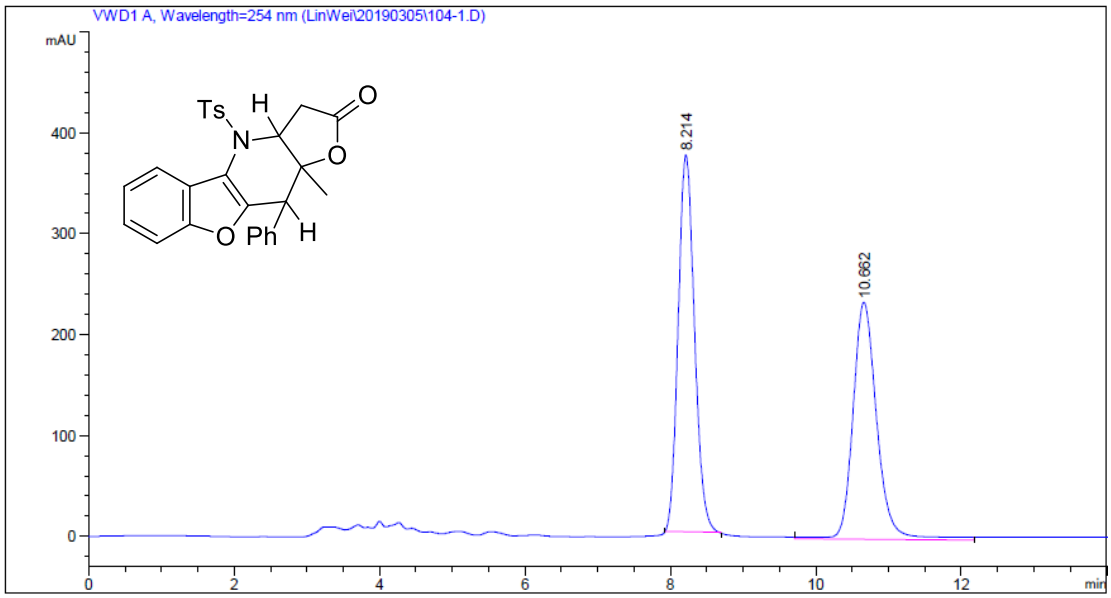
To a solution of **3aa** (23.7 mg, 0.05 mmol) in toluene (0.3 mL) was added K_2CO_3 (6.9 mg, 0.05 mmol). The reaction mixture was stirred at 50 ^oC for 24 h. The solvent was evaporated to give the crude product, which was purified by silica gel chromatography to provide the desired product **4aa** as a white solid (17.4 mg, 74% yield, 92% ee, >20:1 dr).

(3a*R*,10*R*,10a*R*)-10a-methyl-10-phenyl-4-tosyl-3a,4,10,10a-tetrahydrobenzofuro[3,2-b]furo[2,3-e]pyridin-2(3*H*)-one (4aa)

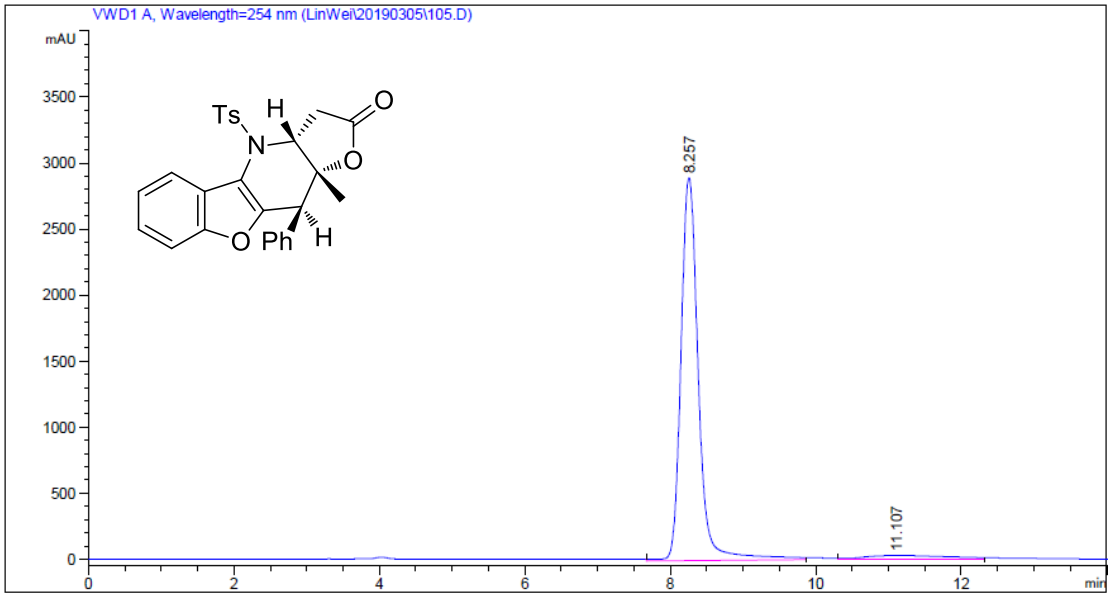


Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12:1. White solid, 17.4 mg, 74% yield. mp 160.5-161.9 ^oC. ^1H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 8.12-8.10 (m, 1H), 7.66 (d, *J* = 5.0 Hz, 2H), 7.52-7.50 (m, 1H), 7.44 (d, *J* = 5.0 Hz, 2H), 7.36-7.34 (m, 2H), 7.27-7.24 (m, 1H), 7.17-7.14 (m, 2H), 6.72 (d, *J* = 10.0 Hz, 2H), 4.93-4.90 (m, 1H), 4.68 (s, 1H), 3.17-3.12 (m, 1H), 2.95-2.90 (m, 1H), 2.39 (s, 3H), 0.72 (s, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 172.7, 154.2, 146.3, 145.5, 135.9, 134.3, 130.7, 129.4, 128.9, 128.2, 128.1, 125.6, 123.7, 123.2, 122.6, 116.5, 112.1, 85.3, 61.6, 48.1, 36.9, 24.2, 21.5. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{24}NO_5S$) requires m/z 474.1370, found m/z 474.1373. The enantiomeric excess was determined to be 92% by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 60:40, 1.0 mL/min]: 11.1 min (minor), 8.3 min (major). $[\alpha]^{22}_D$ = 116.00 (c = 1.00, CH_2Cl_2).

(3a*R*,10*R*,10a*R*)-10a-methyl-10-phenyl-4-tosyl-3a,4,10,10a-tetrahydrobenzofuro[3,2-b]furo[2,3-e]pyridin-2(3*H*)-one (4aa)

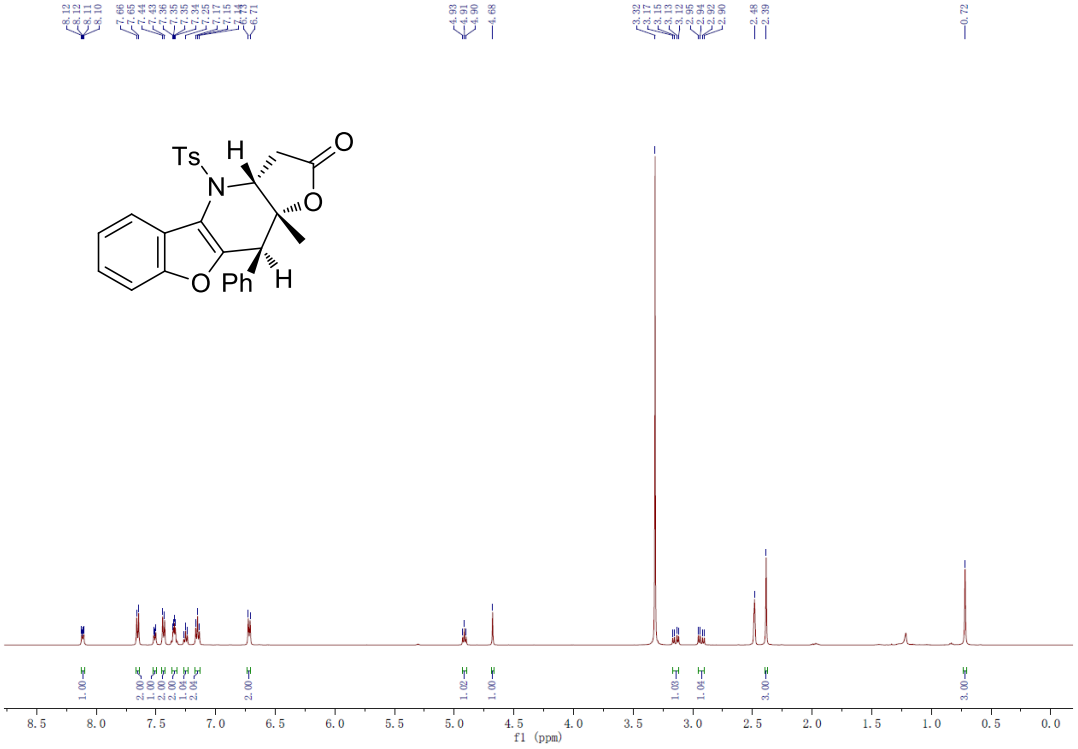


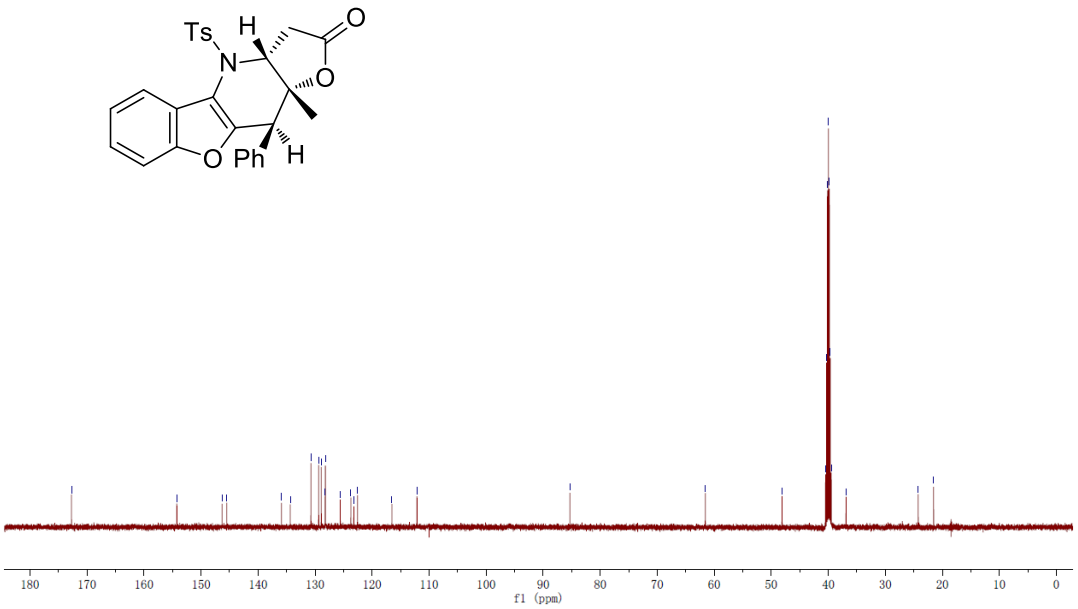
#	Time	Area	Height	Width	Symmetry	Area %
1	8.214	5807.9	373.8	0.2589	0.863	51.814
2	10.662	5401.2	234.9	0.3832	0.801	48.186



#	Time	Area	Height	Width	Symmetry	Area %
1	8.257	48535.3	2900.5	0.2789	0.805	95.971
2	11.107	2037.7	26.1	1.3029	0.559	4.029

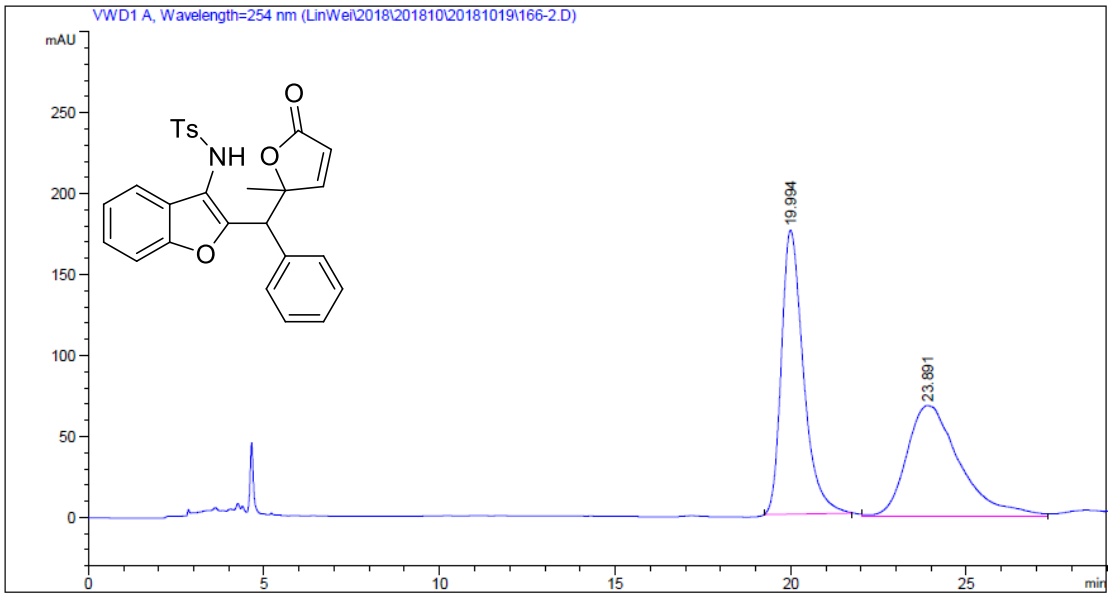
(3a*R*,10*R*,10a*R*)-10a-methyl-10-phenyl-4-tosyl-3a,4,10,10a-tetrahydrobenzofuro[3,2-b]furo[2,3-e]pyridin-2(3*H*)-one (4aa)



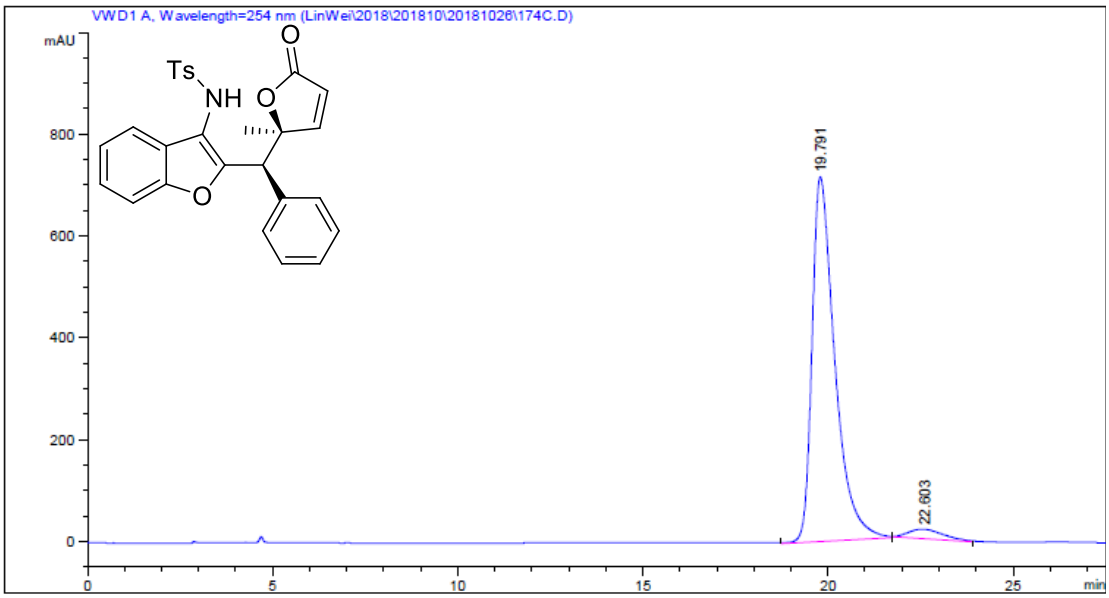


F: HPLC Analysis

4-Methyl-*N*-(2-((*R*)-((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3aa)

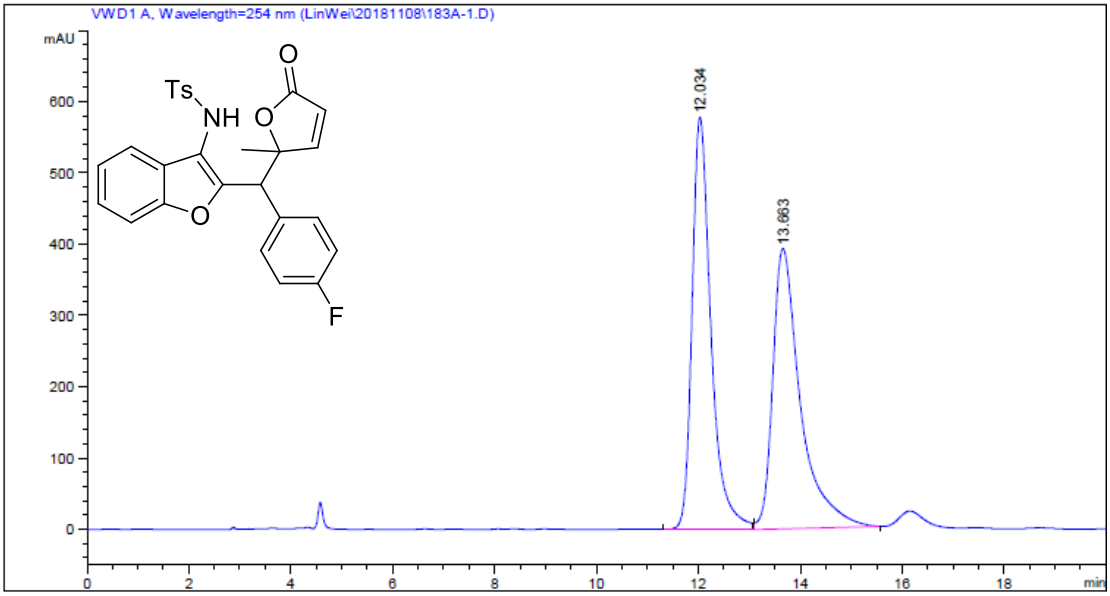


#	Time	Area	Height	Width	Symmetry	Area %
1	19.994	7621.1	175.4	0.7243	0.677	51.447
2	23.891	7192.6	68.4	1.7524	0.625	48.553

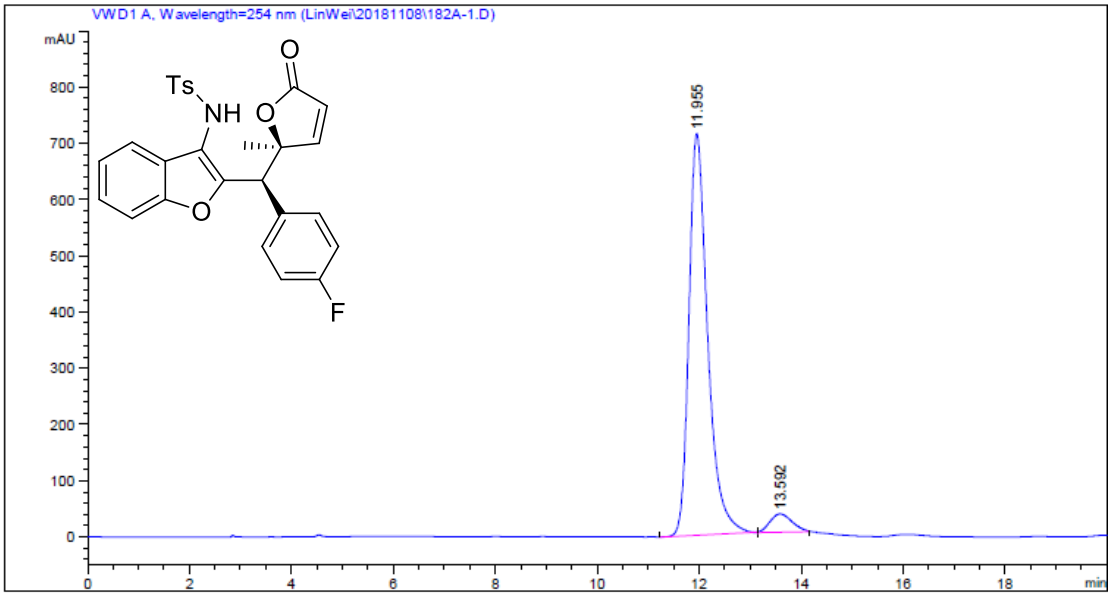


#	Time	Area	Height	Width	Symmetry	Area %
1	19.791	30636.9	716.5	0.7127	0.549	96.052
2	22.603	1259.3	18.9	1.1126	0.595	3.948

_N_-(2-((_R_)-(4-fluorophenyl)((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ba)

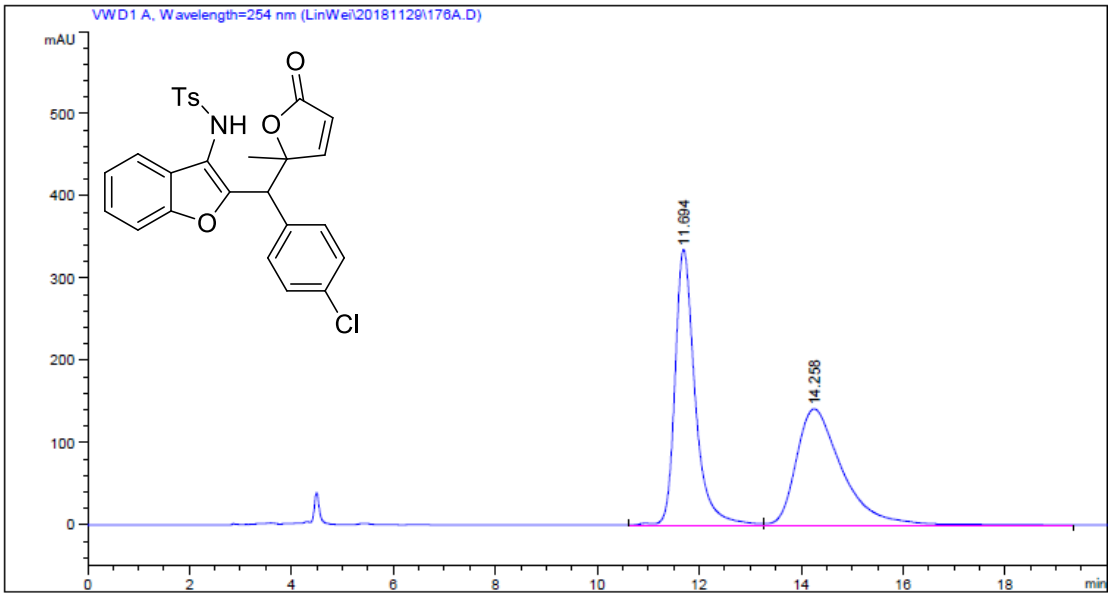


#	Time	Area	Height	Width	Symmetry	Area %
1	12.034	14852	578.2	0.3877	0.661	50.022
2	13.663	14838.8	393.1	0.6291	0.556	49.978

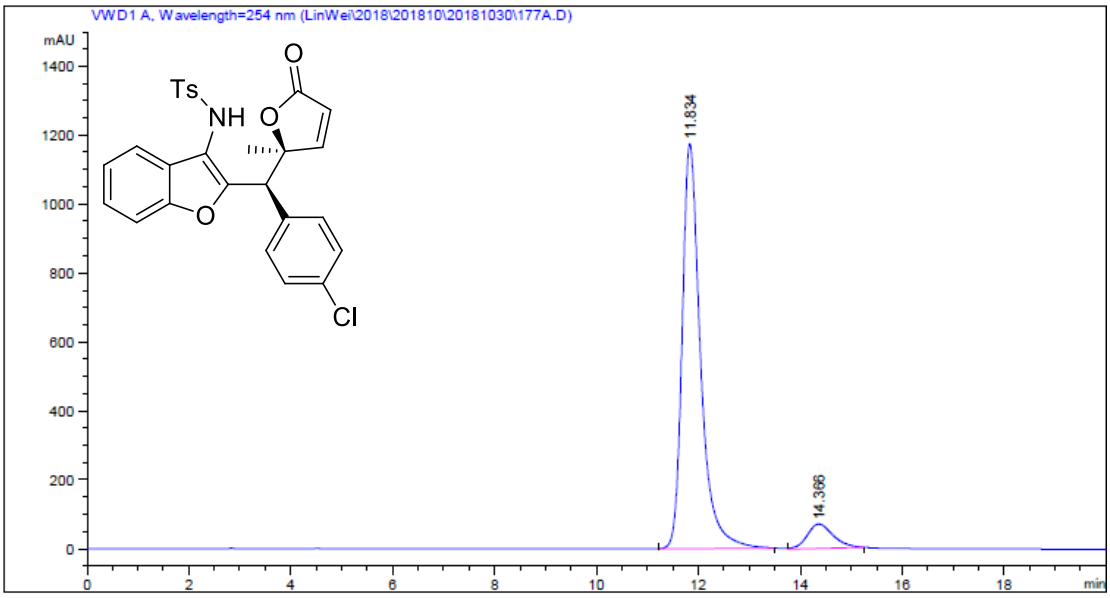


#	Time	Area	Height	Width	Symmetry	Area %
1	11.955	18206.4	714	0.425	0.688	94.822
2	13.592	994.2	32.7	0.5064	0.826	5.178

***N*-(2-((*R*)-(4-chlorophenyl)((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ca)**

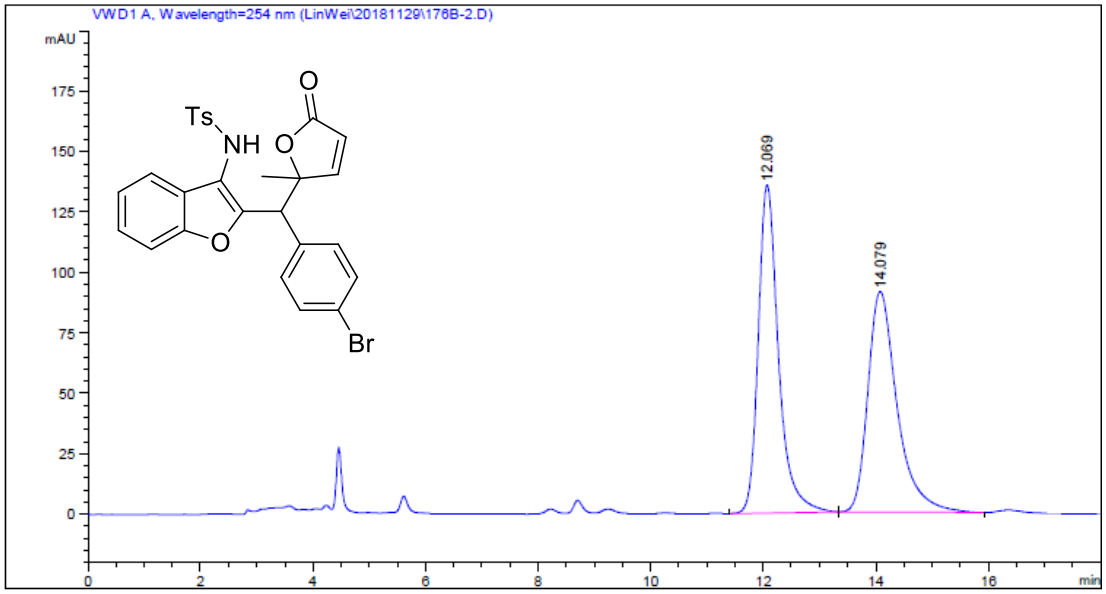


#	Time	Area	Height	Width	Symmetry	Area %
1	11.694	9150.4	335.1	0.4104	0.688	51.012
2	14.258	8787.4	141.1	0.9178	0.599	48.988

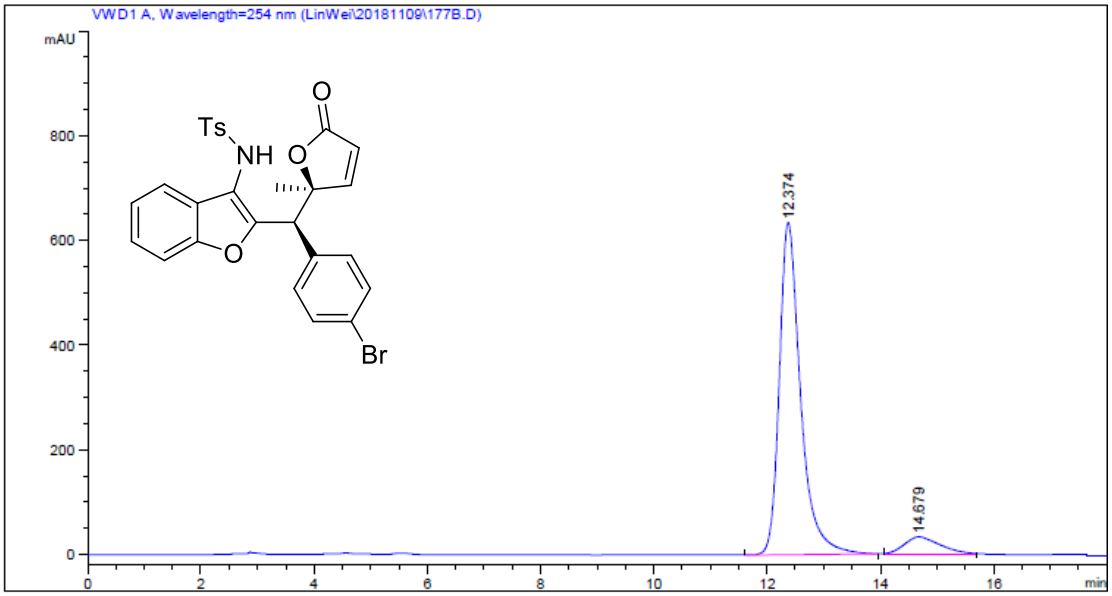


#	Time	Area	Height	Width	Symmetry	Area %
1	11.834	29334	1174.8	0.4162	0.681	91.998
2	14.366	2551.6	71.2	0.5972	0.79	8.002

***N*-(2-((*R*)-(4-bromophenyl)((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3da)**

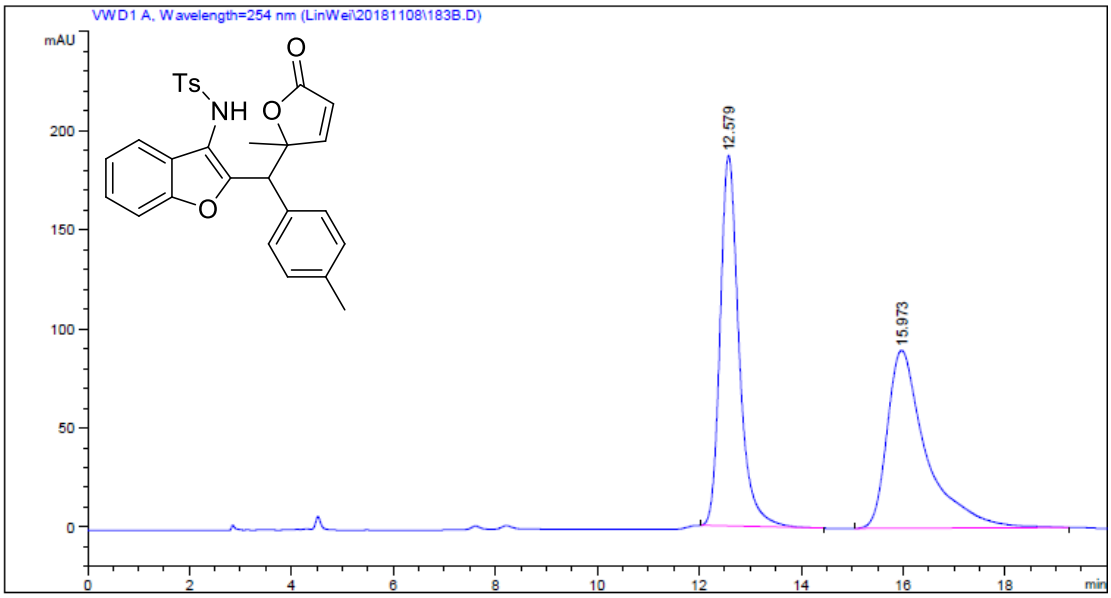


#	Time	Area	Height	Width	Symmetry	Area %
1	12.069	3381.8	135.6	0.3759	0.723	50.731
2	14.079	3284.4	91.1	0.5428	0.672	49.269

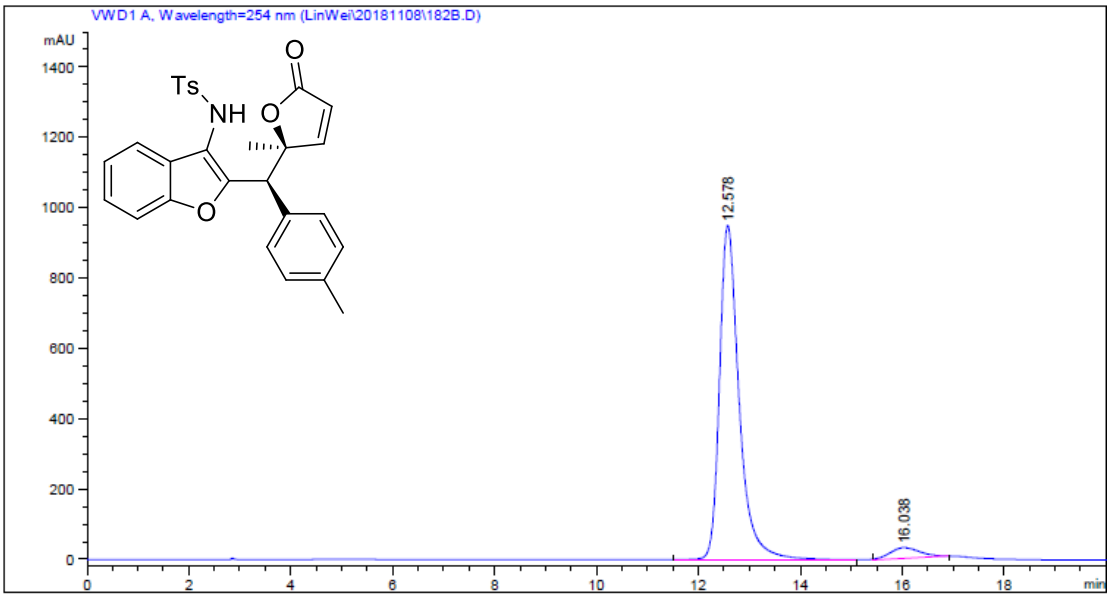


#	Time	Area	Height	Width	Symmetry	Area %
1	12.374	16555.3	633.9	0.4353	0.682	92.185
2	14.679	1403.6	32.5	0.7201	0.672	7.815

4-Methyl-*N*-(2-((*R*)-((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(p-tolyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ea)

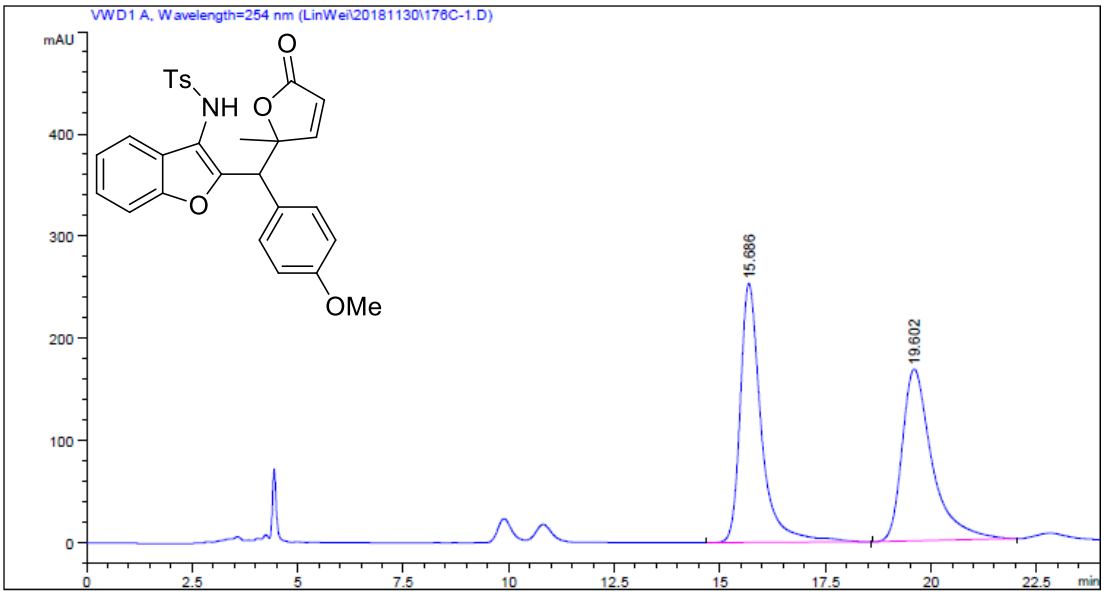


#	Time	Area	Height	Width	Symmetry	Area %
1	12.579	4808.1	187.2	0.4282	0.766	50.189
2	15.973	4771.8	89.8	0.7721	0.531	49.811

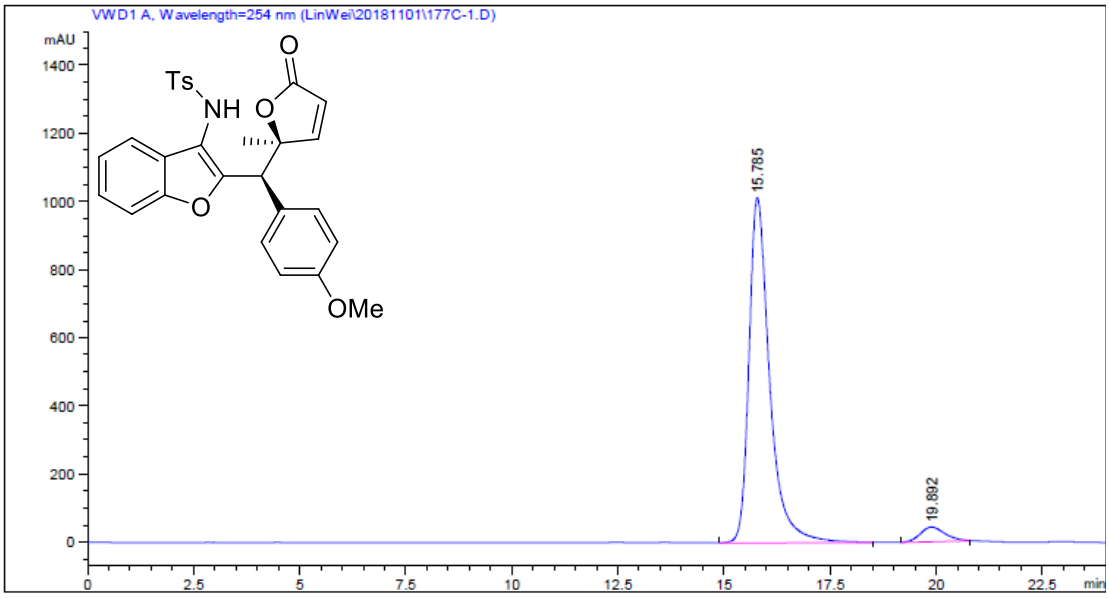


#	Time	Area	Height	Width	Symmetry	Area %
1	12.578	25450.6	951	0.4042	0.661	95.321
2	16.038	1249.3	30.4	0.6842	0.889	4.679

***N*-(2-((*R*)-(4-methoxyphenyl)((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3fa)**

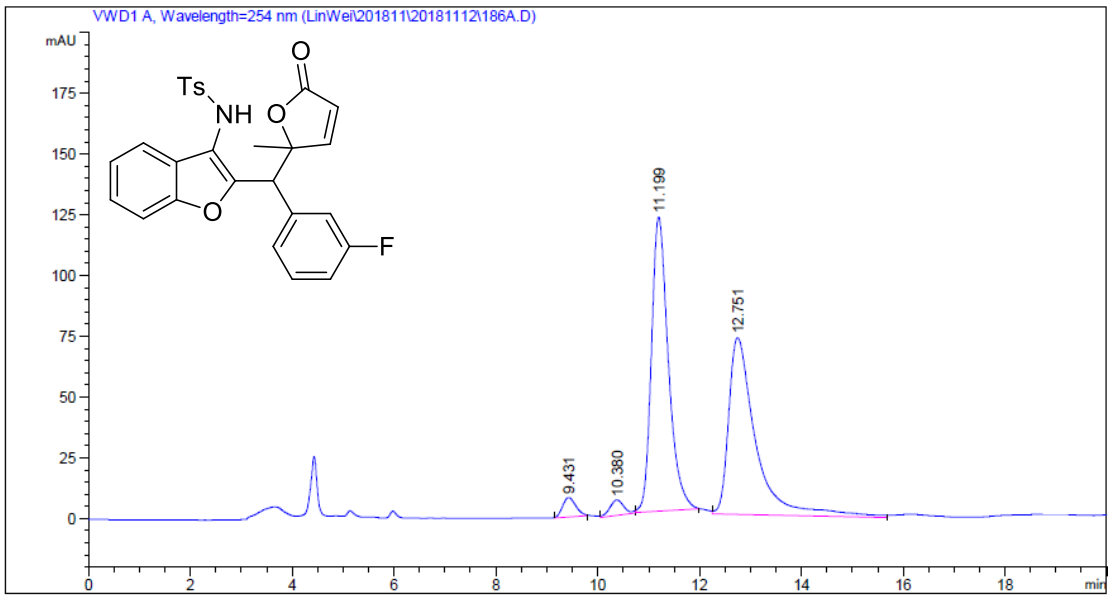


#	Time	Area	Height	Width	Symmetry	Area %
1	15.686	8755.6	253.2	0.5144	0.623	51.270
2	19.602	8321.7	168.1	0.7417	0.609	48.730

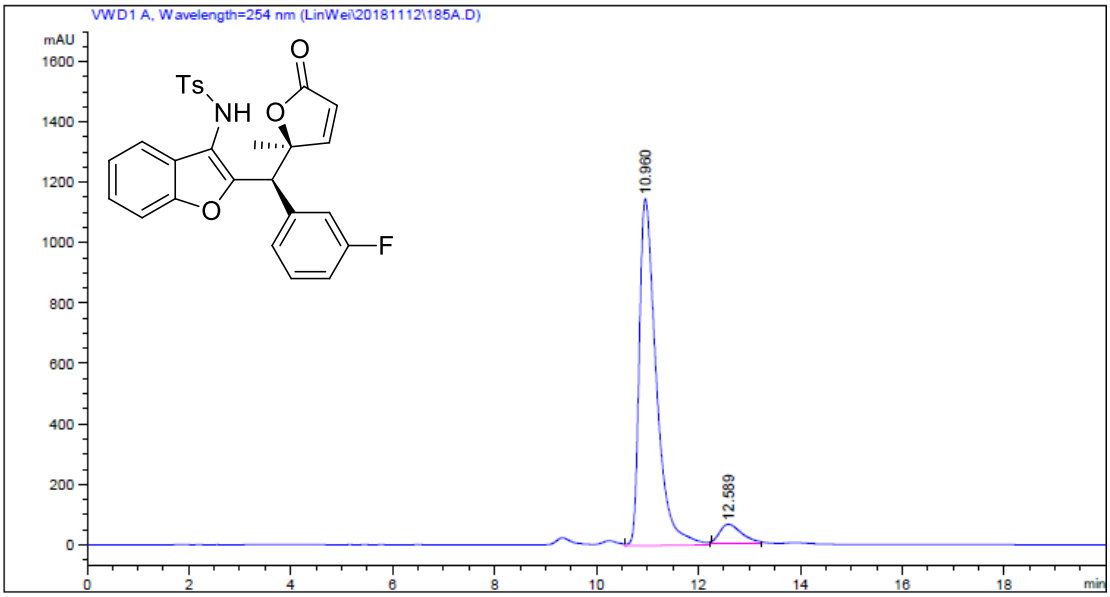


#	Time	Area	Height	Width	Symmetry	Area %
1	15.785	34464.7	1014	0.5665	0	95.184
2	19.892	1743.8	42.8	0.6797	0.827	4.816

_N_-(2-((_R_)-(3-fluorophenyl)((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ga)

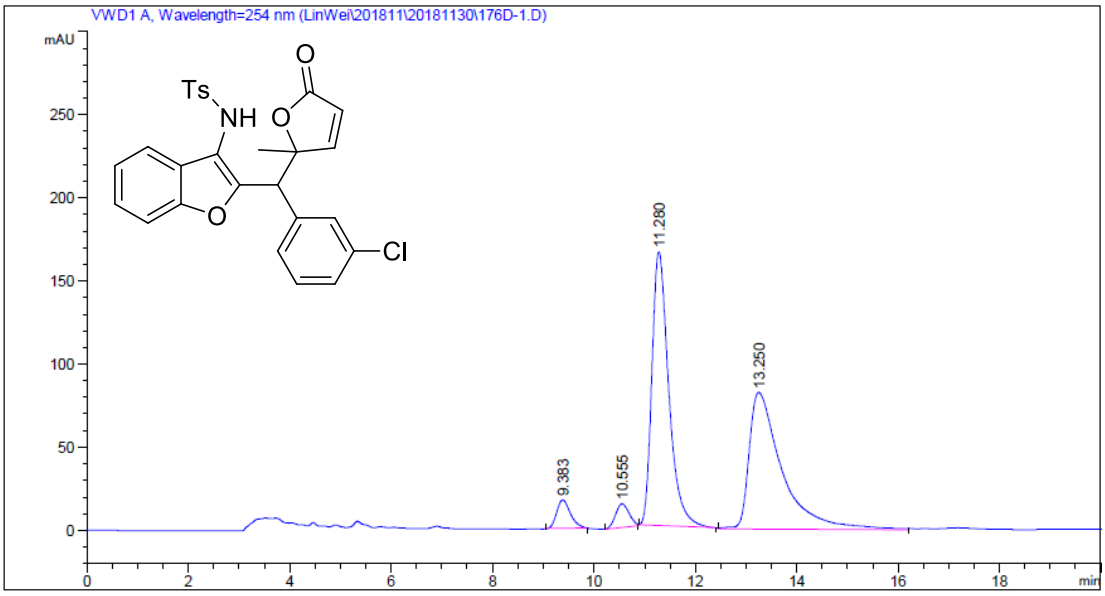


#	Time	Area	Height	Width	Symmetry	Area %
1	9.431	147.5	8.1	0.3053	0.825	2.561
2	10.38	125.2	6.4	0.3254	1.036	2.173
3	11.199	2796.9	121.1	0.3849	0.722	48.555
4	12.751	2690.6	72.6	0.6173	0.475	46.710

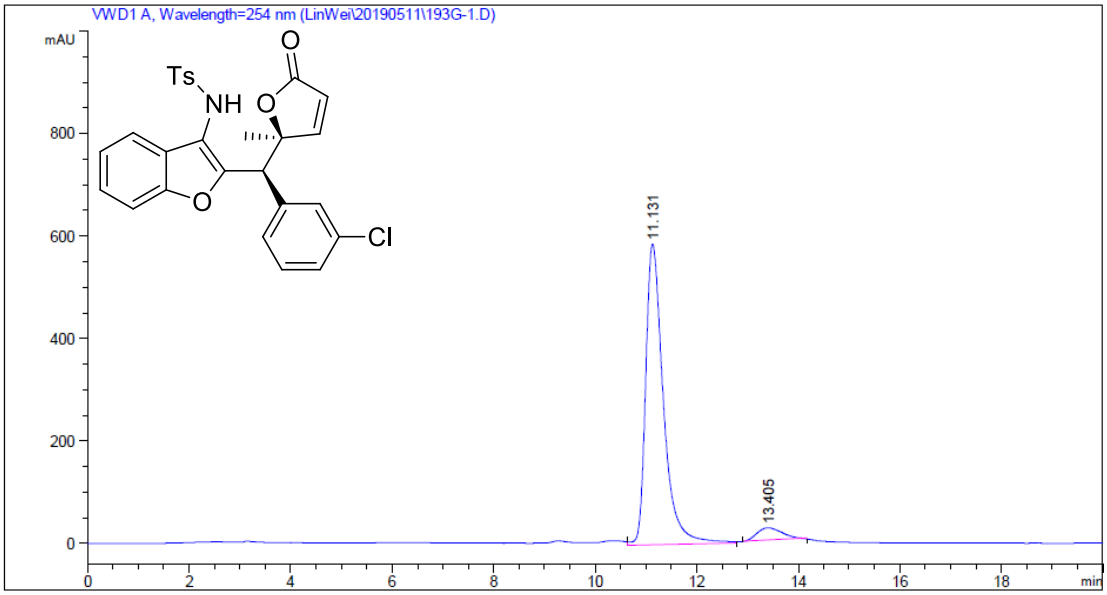


#	Time	Area	Height	Width	Symmetry	Area %
1	10.96	26618.3	1148.2	0.3864	0.529	93.625
2	12.589	1812.5	61.9	0.4881	0.632	6.375

_N_-(2-((_R_)-(3-chlorophenyl)((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ha)

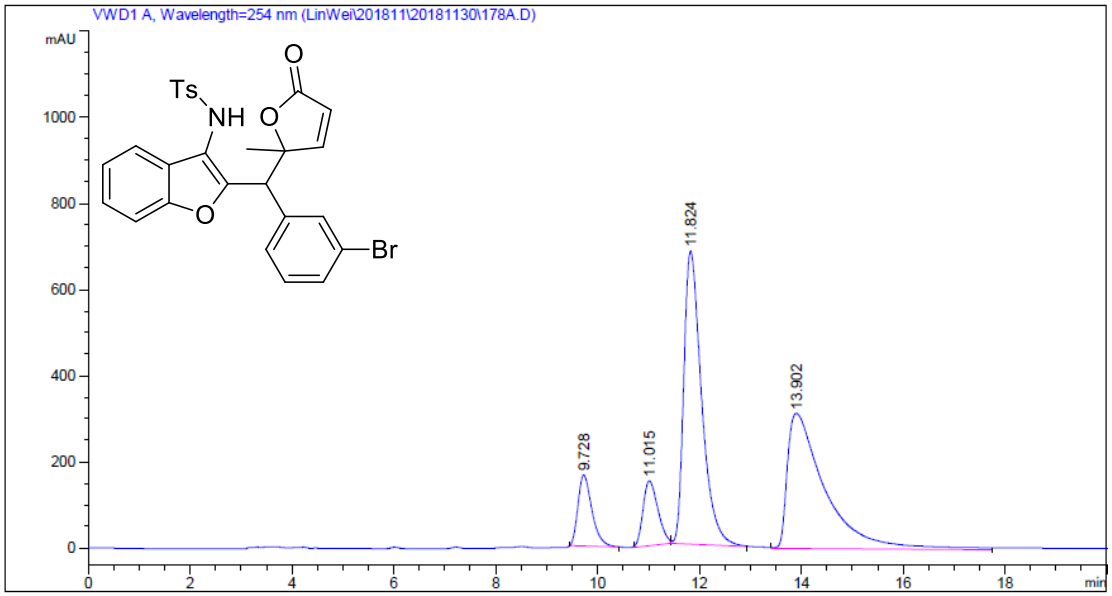


#	Time	Area	Height	Width	Symmetry	Area %
1	9.383	319.7	17.1	0.3115	0.755	3.947
2	10.555	261.5	14.1	0.3089	0.915	3.228
3	11.28	3791.8	164.7	0.3836	0.675	46.804
4	13.25	3728.4	82.3	0.755	0.4	46.021

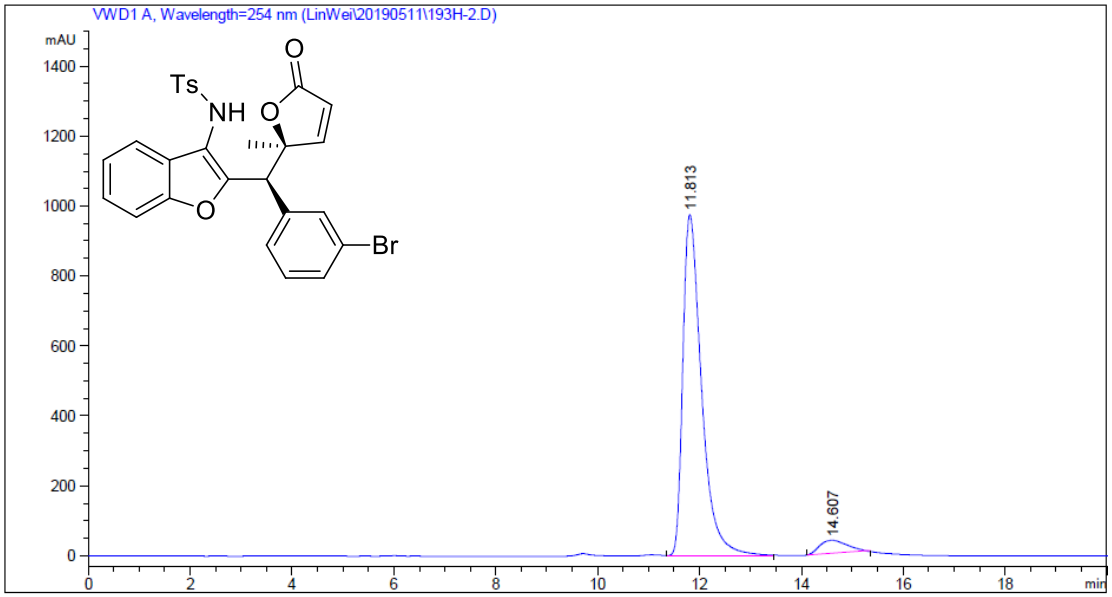


#	Time	Area	Height	Width	Symmetry	Area %
1	11.131	14212.1	587	0.4035	0.609	94.830
2	13.405	774.8	23.4	0.5522	0.797	5.170

_N_-(2-((_R_)-(3-bromophenyl)((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ia)

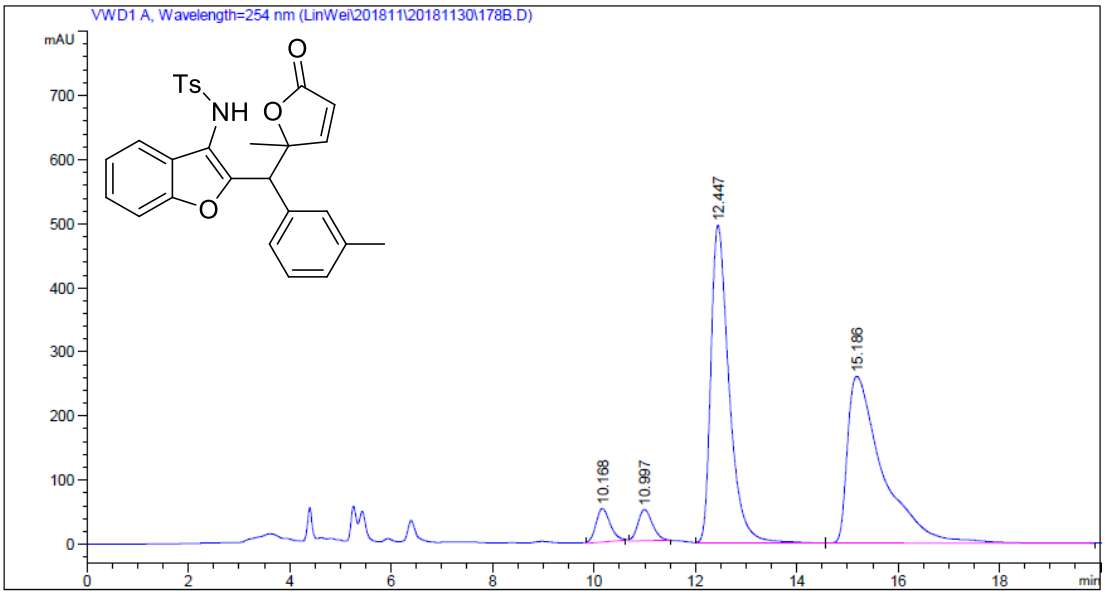


#	Time	Area	Height	Width	Symmetry	Area %
1	9.728	3152.8	165.1	0.3182	0.685	8.120
2	11.015	3049.8	150.9	0.3369	0.723	7.854
3	11.824	16474.8	680.8	0.4033	0.589	42.428
4	13.902	16152.5	313.7	0.8582	0.298	41.598

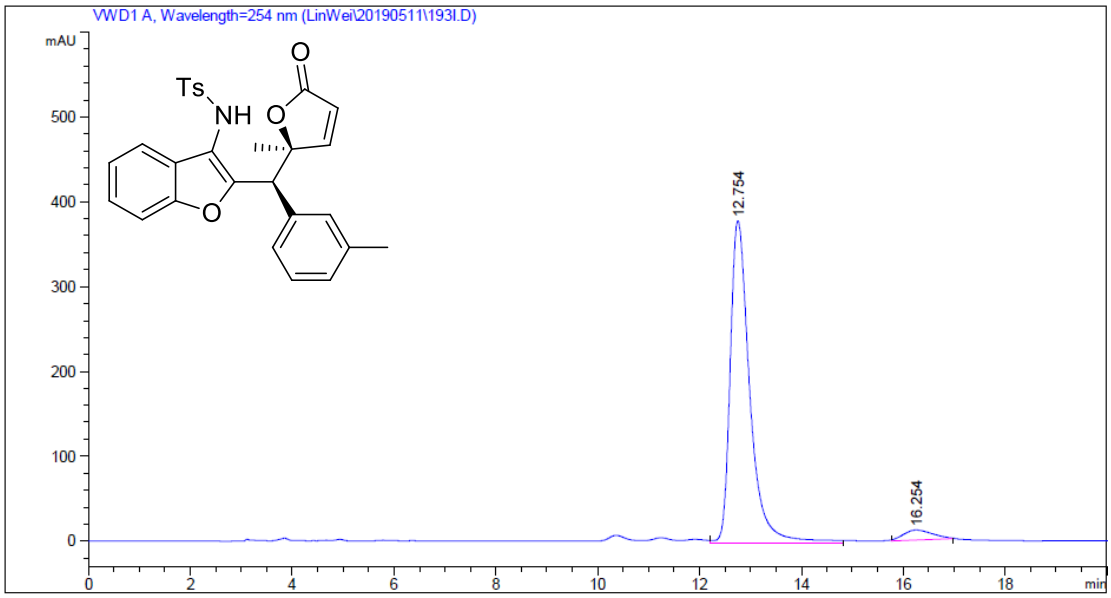


#	Time	Area	Height	Width	Symmetry	Area %
1	11.813	24939.7	975.9	0.4259	0.566	94.927
2	14.607	1332.8	36.6	0.6068	0.873	5.073

4-Methyl-*N*-(2-((*R*)-((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(m-tolyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ja)

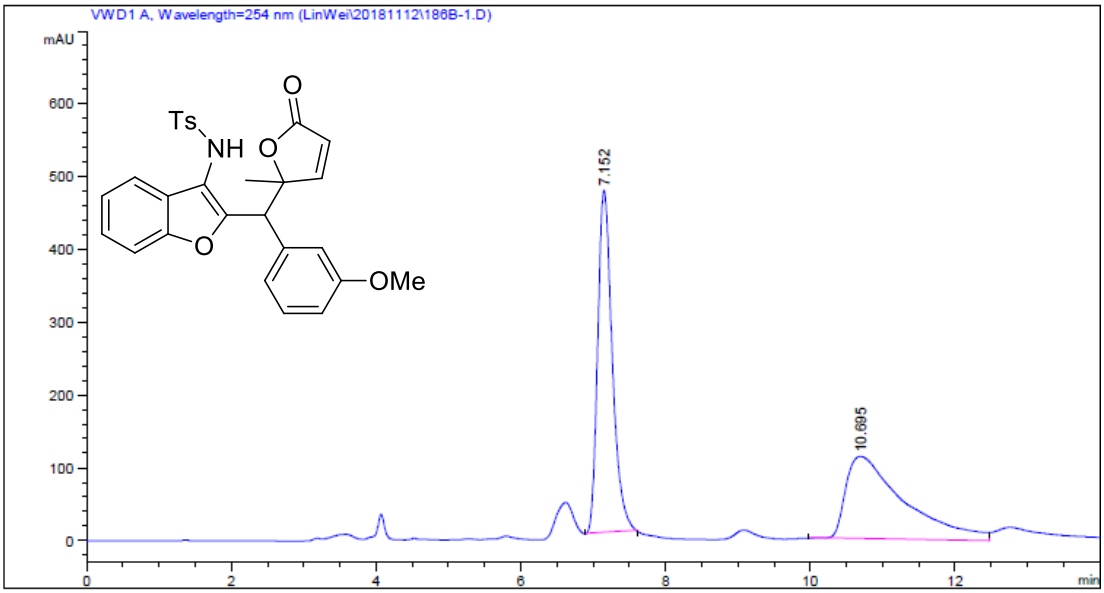


#	Time	Area	Height	Width	Symmetry	Area %
1	10.168	1018.2	52.3	0.3242	0.819	3.764
2	10.997	971.9	48.8	0.3319	0.81	3.592
3	12.447	12412.2	495.9	0.377	0.582	45.881
4	15.186	12651.1	260.3	0.7191	0.314	46.764

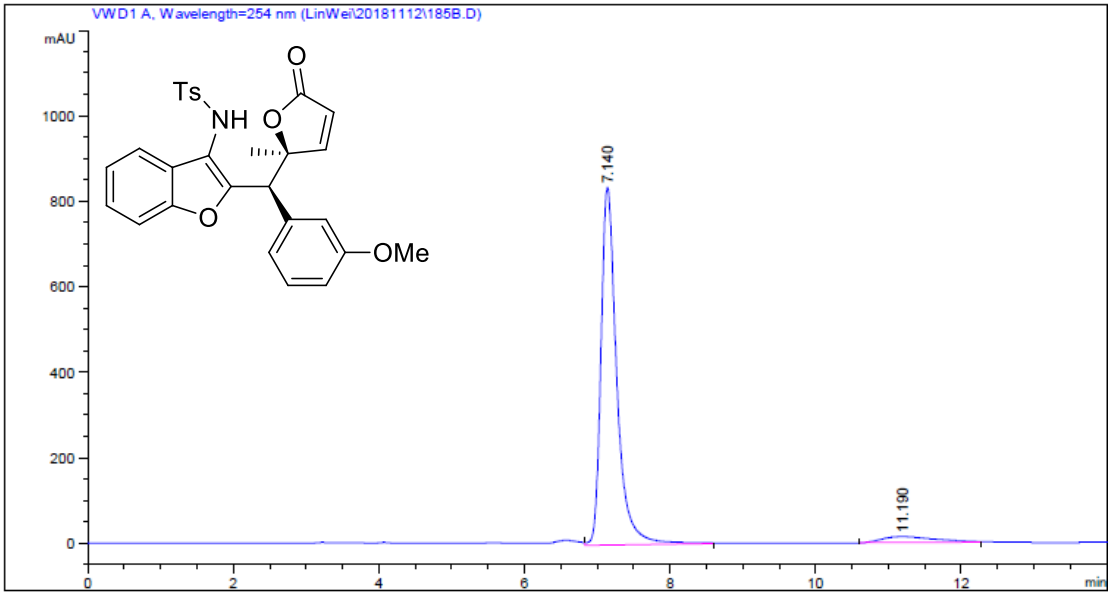


#	Time	Area	Height	Width	Symmetry	Area %
1	12.754	10168.6	380	0.446	0.606	95.619
2	16.254	465.9	11.7	0.6615	0.767	4.381

_N_-(2-((_R_)-(3-methoxyphenyl)((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ka)

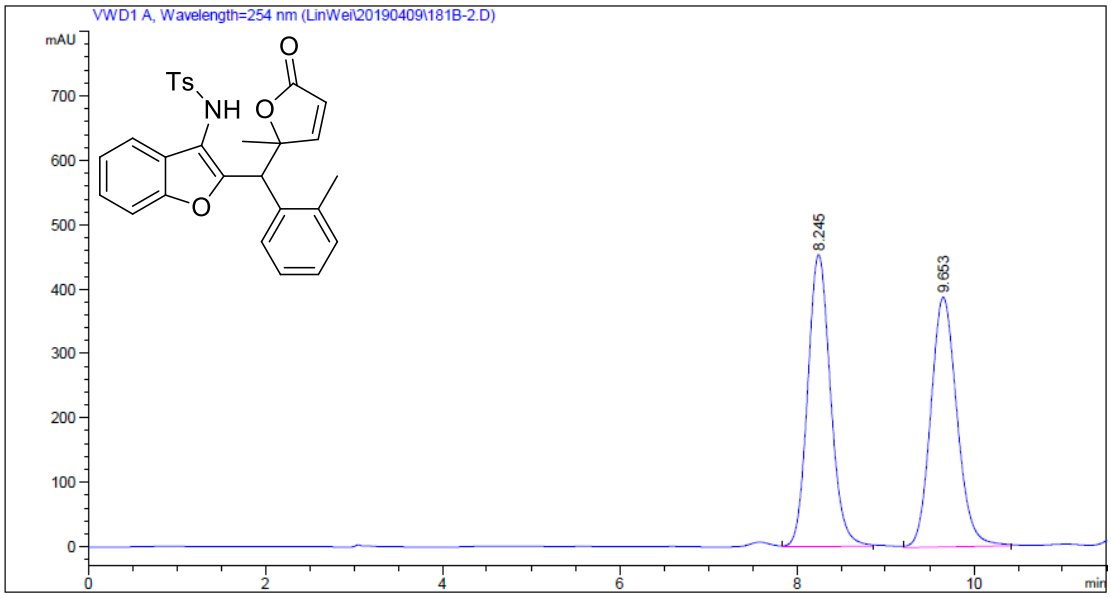


#	Time	Area	Height	Width	Symmetry	Area %
1	7.152	6522.4	469.9	0.2313	0.733	50.881
2	10.695	6296.5	112.8	0.9304	0.322	49.119

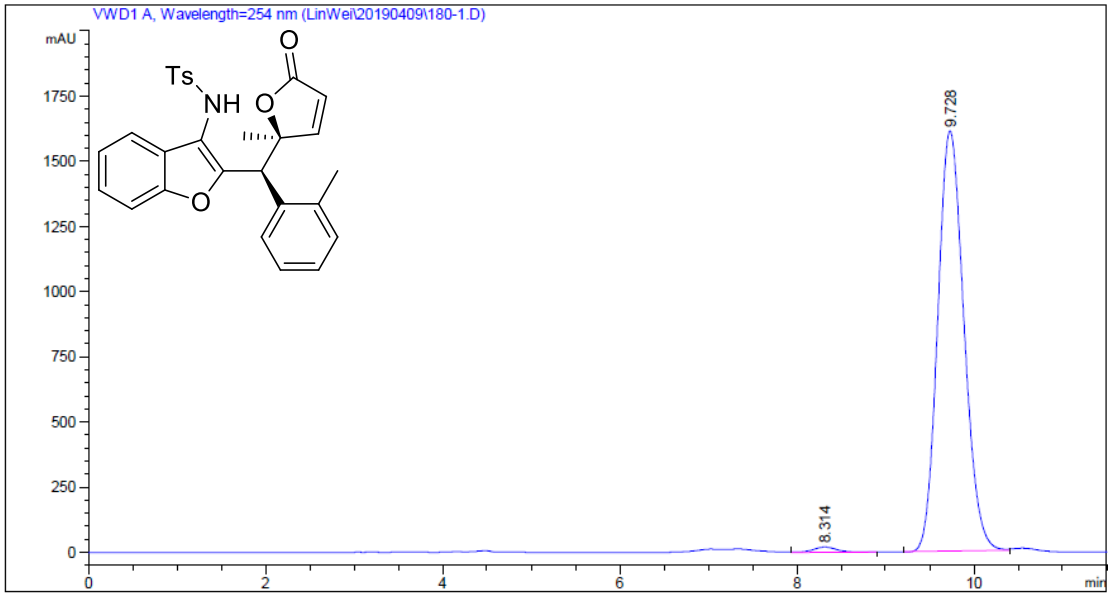


#	Time	Area	Height	Width	Symmetry	Area %
1	7.14	12655.7	837.1	0.252	0.657	94.945
2	11.19	673.9	13.2	0.8526	0.557	5.055

4-Methyl-*N*-(2-((*R*)-((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(o-tolyl)methyl)benzofuran-3-yl)benzenesulfonamide (3la)

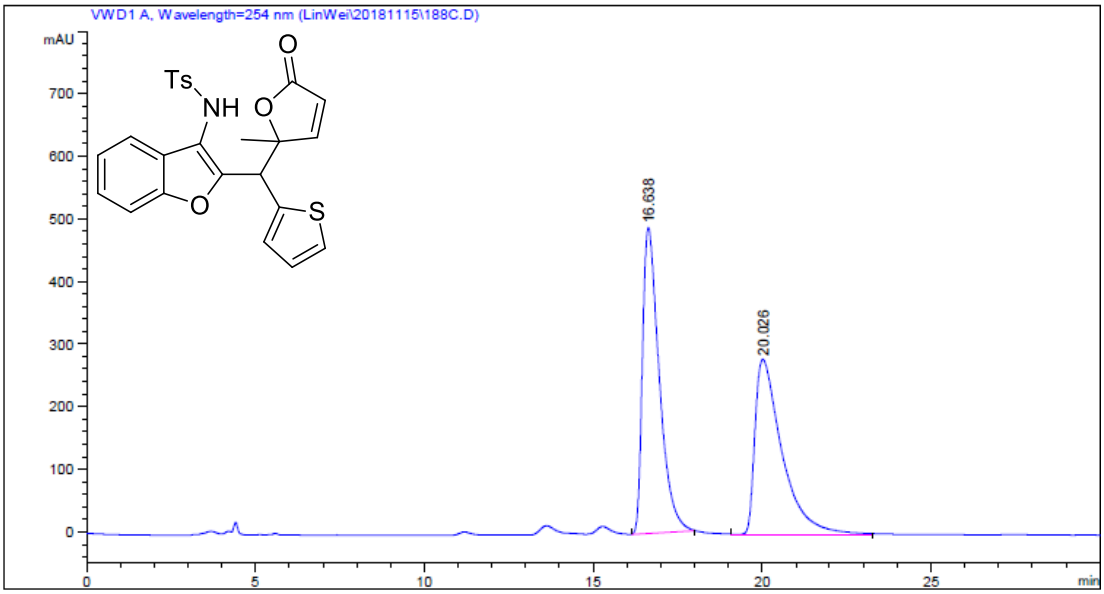


#	Time	Area	Height	Width	Symmetry	Area %
1	8.245	8102.8	453.9	0.2975	0.873	50.381
2	9.653	7980.4	387.9	0.3429	0.869	49.619

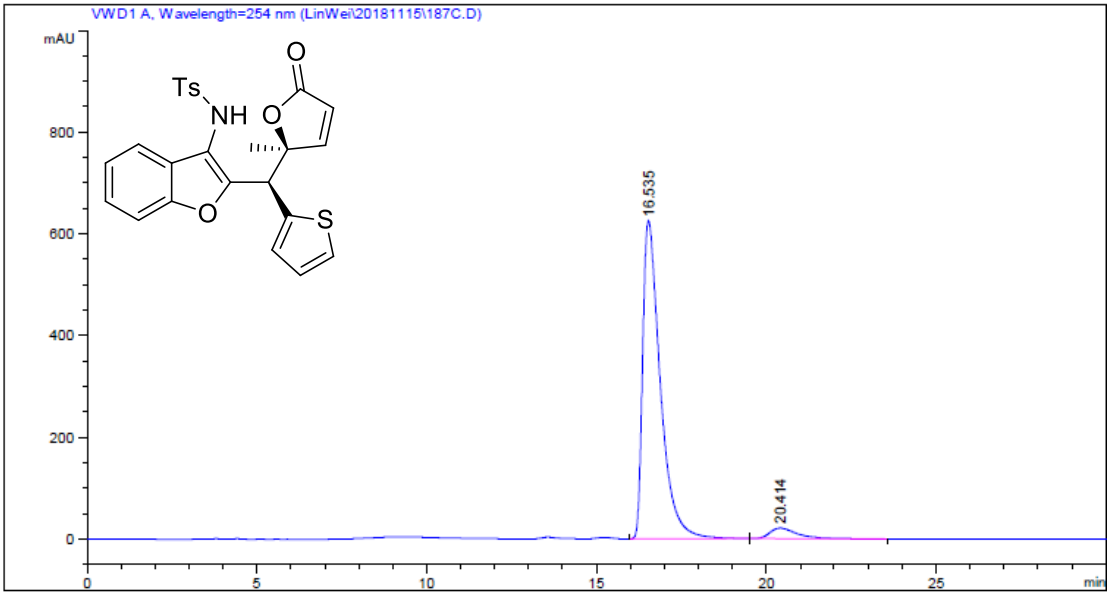


#	Time	Area	Height	Width	Symmetry	Area %
1	8.314	367.7	20	0.2836	0.904	1.099
2	9.728	33098.9	1612	0.3422	0.841	98.901

4-Methyl-*N*-(2-((*R*)-((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(thiophen-2-yl)methyl)benzofuran-3-yl)benzenesulfonamide (3ma)

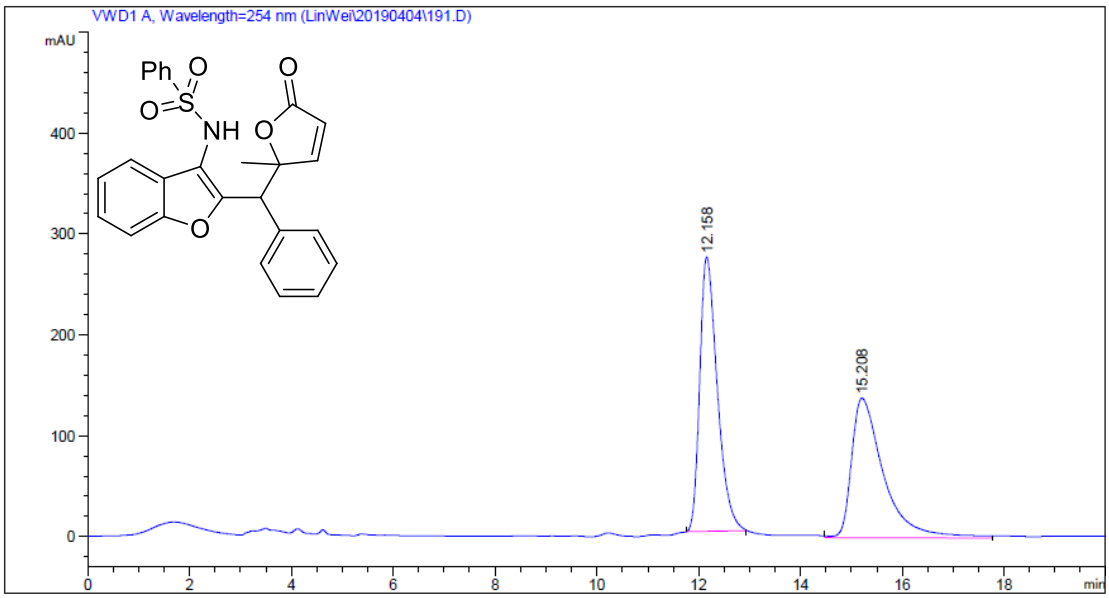


#	Time	Area	Height	Width	Symmetry	Area %
1	16.638	16872.6	488.7	0.5755	0.524	51.542
2	20.026	15862.9	280.9	0.9414	0.394	48.458

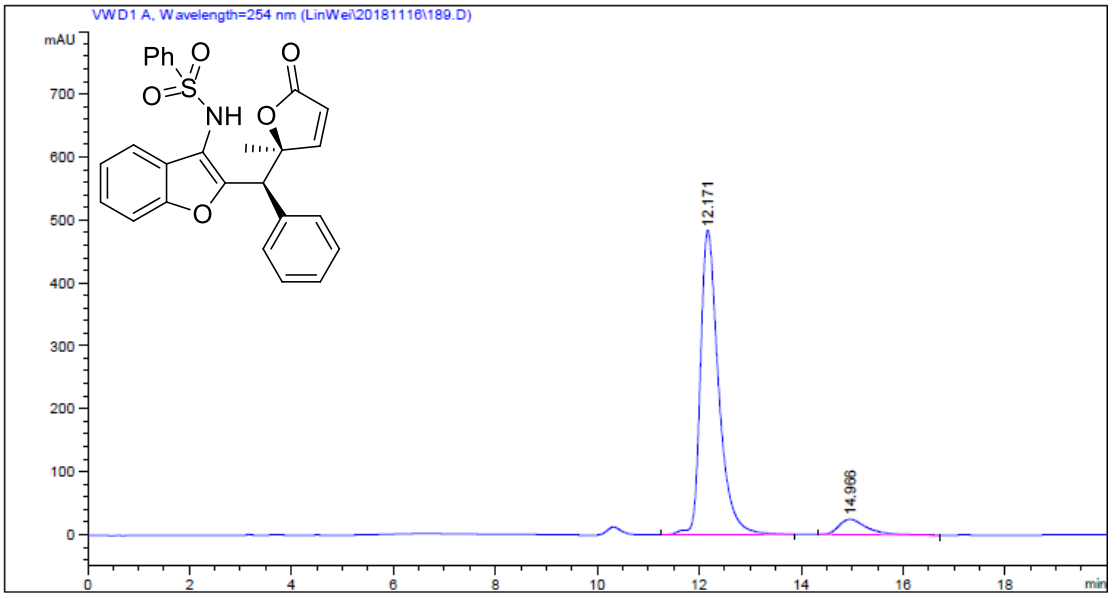


#	Time	Area	Height	Width	Symmetry	Area %
1	16.535	22540.7	625.1	0.5447	0.45	95.133
2	20.414	1153.2	20.8	0.793	0.568	4.867

_N_-(2-((_R_)-((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3na)

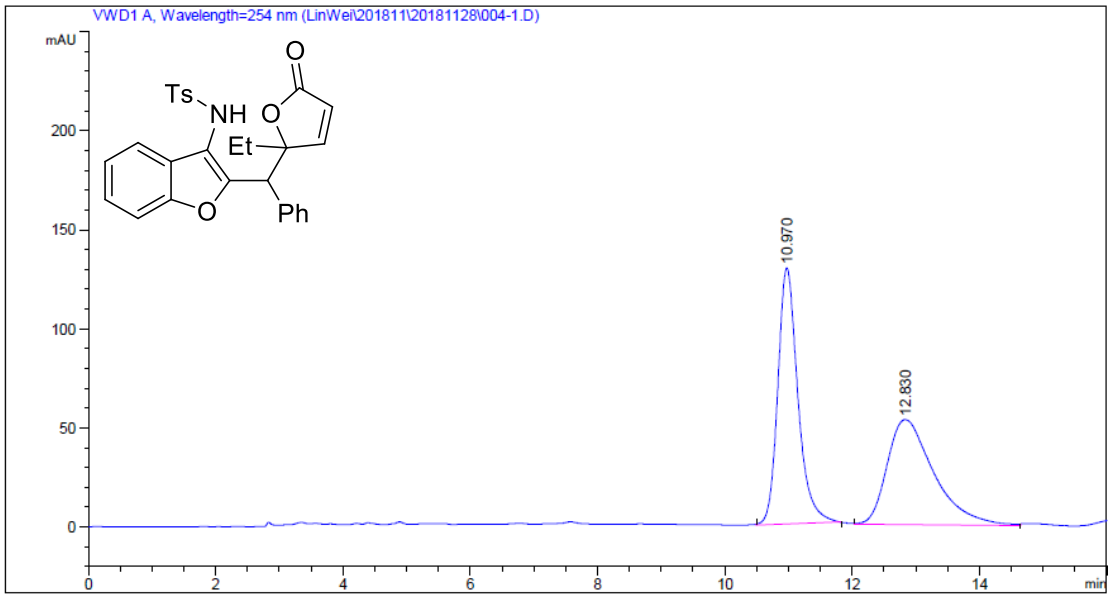


#	Time	Area	Height	Width	Symmetry	Area %
1	12.158	6518.7	272.1	0.3993	0.637	51.649
2	15.208	6102.5	138.7	0.7334	0.465	48.351

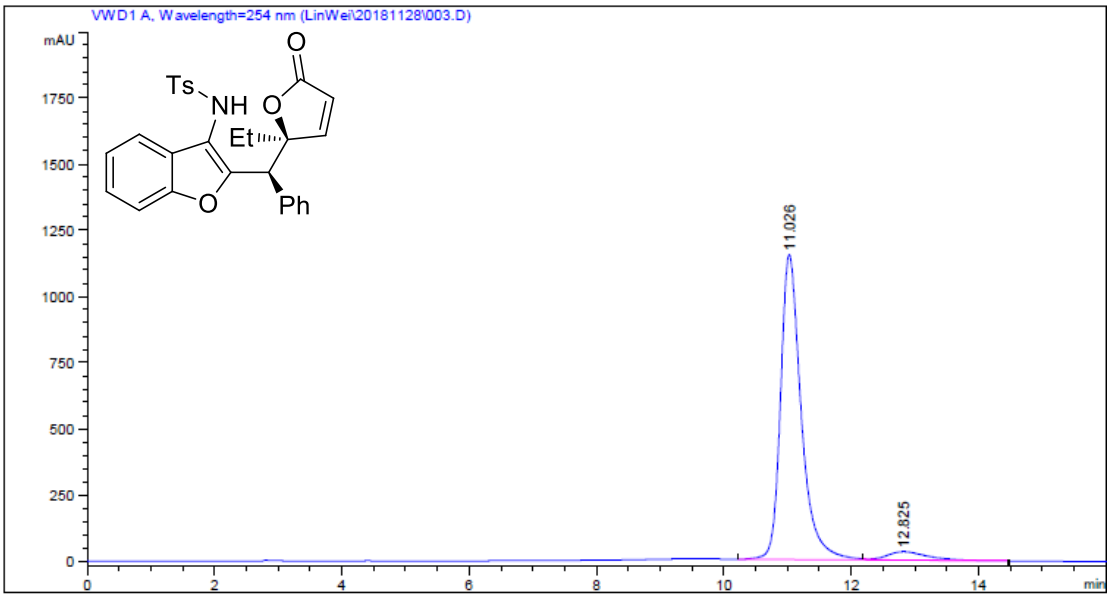


#	Time	Area	Height	Width	Symmetry	Area %
1	12.171	11998.4	483.8	0.3743	0.635	92.795
2	14.966	931.6	24.4	0.5677	0.624	7.205

_N_-(2-((_R_)-((_S_)-2-ethyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ab)

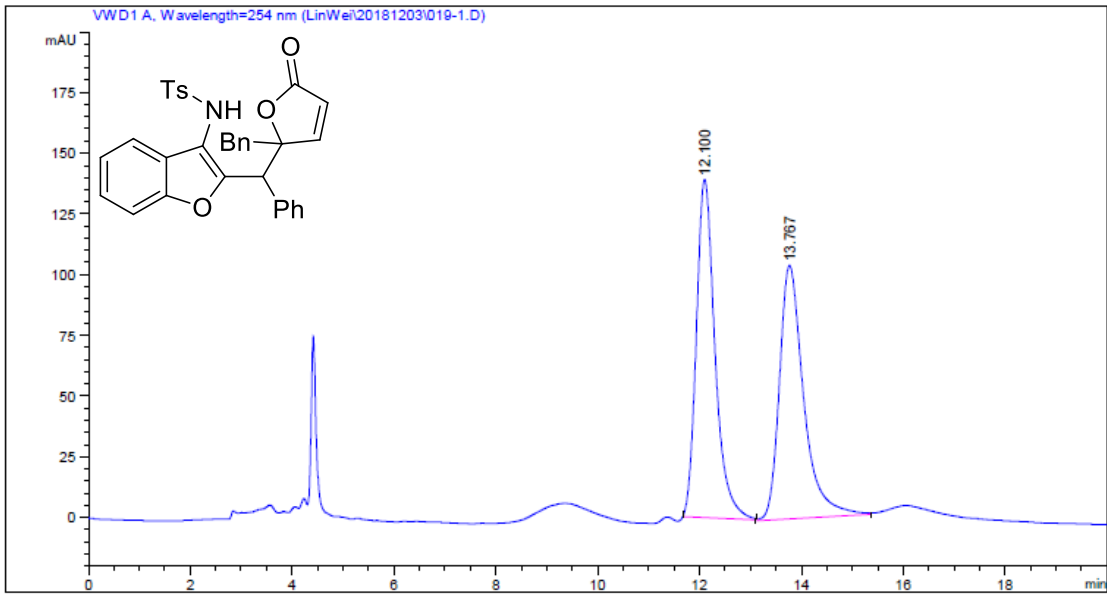


#	Time	Area	Height	Width	Symmetry	Area %
1	10.97	2825.6	129.4	0.364	0.777	51.037
2	12.83	2710.8	53.1	0.8516	0.611	48.963

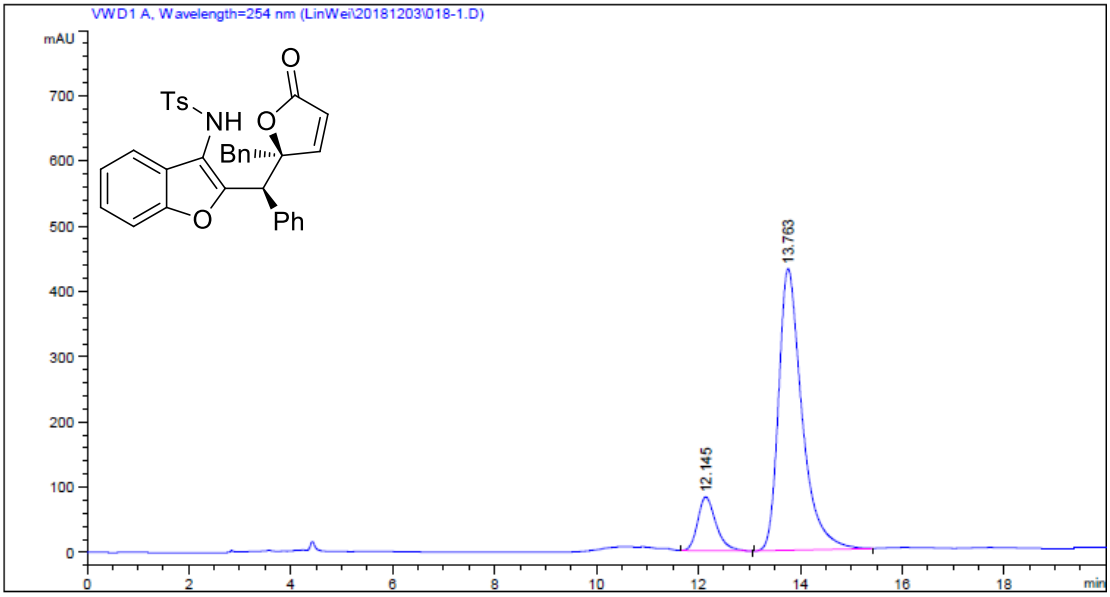


#	Time	Area	Height	Width	Symmetry	Area %
1	11.026	26048.8	1151.7	0.3399	0.676	94.941
2	12.825	1387.9	32.3	0.6499	0.61	5.059

_N_-(2-((_R_)-((_S_)-2-benzyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ac)

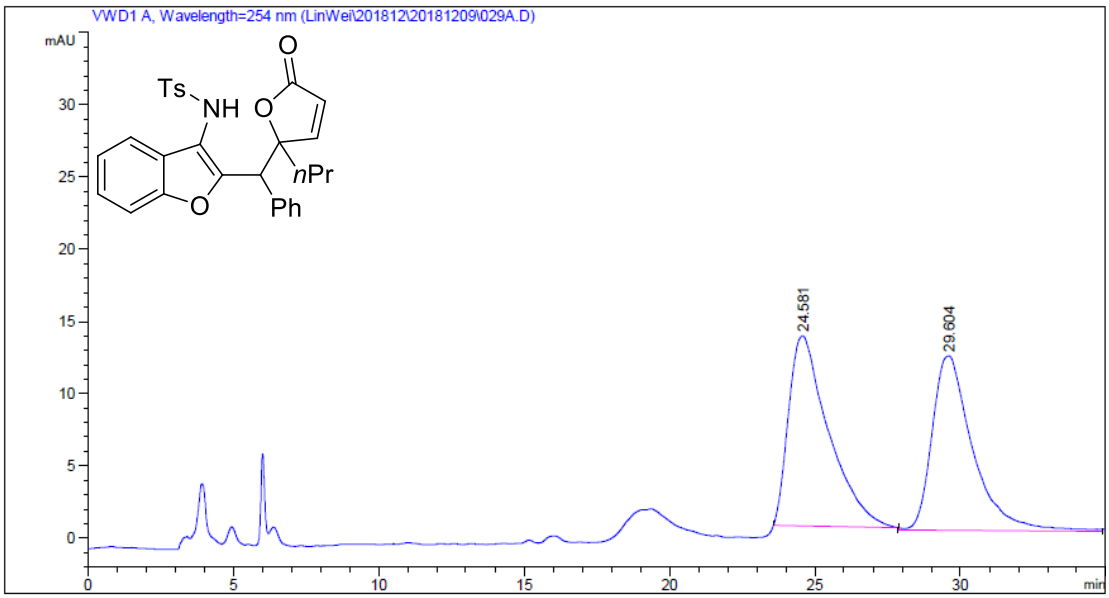


#	Time	Area	Height	Width	Symmetry	Area %
1	12.1	3537.6	139.2	0.4236	0.76	50.603
2	13.767	3453.2	104.3	0.552	0.68	49.397

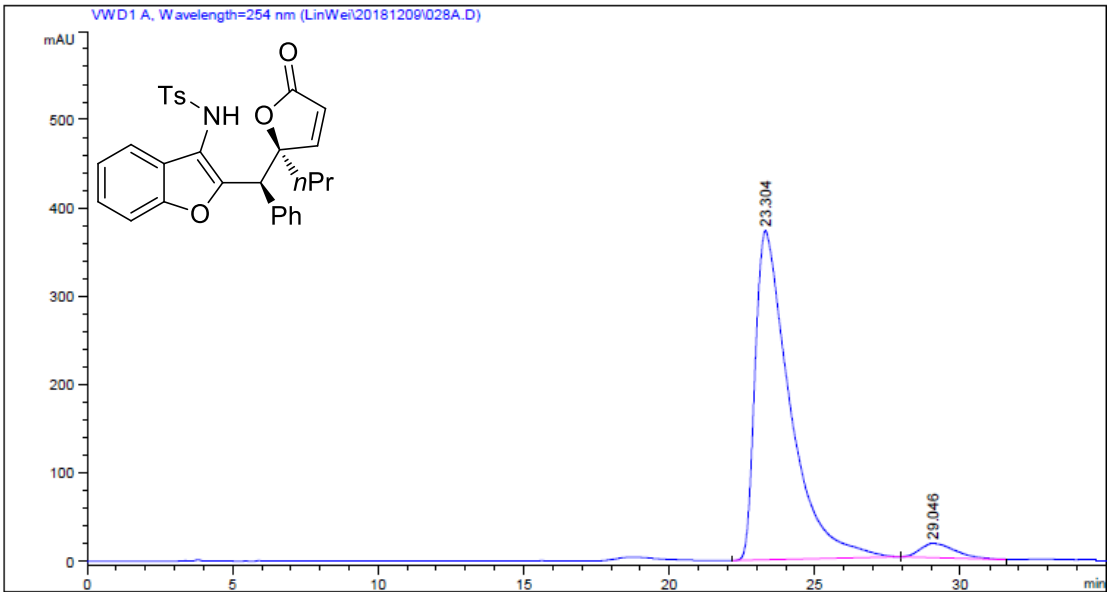


#	Time	Area	Height	Width	Symmetry	Area %
1	12.145	2062	82.4	0.3798	0.731	13.025
2	13.763	13769	431.7	0.4781	0.638	86.975

4-Methyl-*N*-(2-((*R*)-((*S*)-5-oxo-2-propyl-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ad)

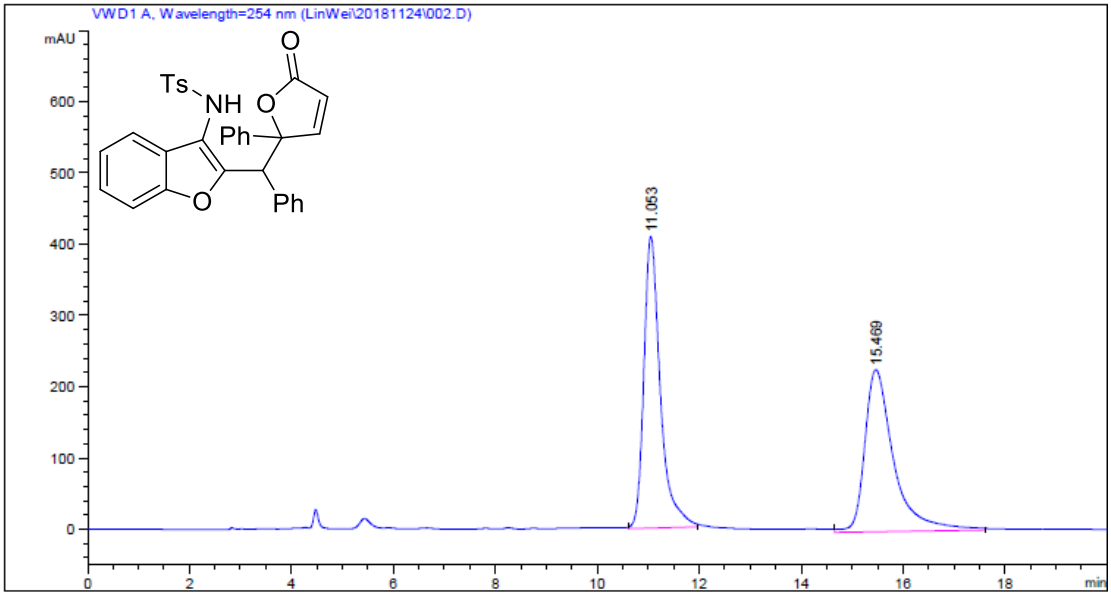


#	Time	Area	Height	Width	Symmetry	Area %
1	24.581	1253.1	13.2	1.5879	0.528	51.526
2	29.604	1178.8	12.1	1.6269	0.659	48.474

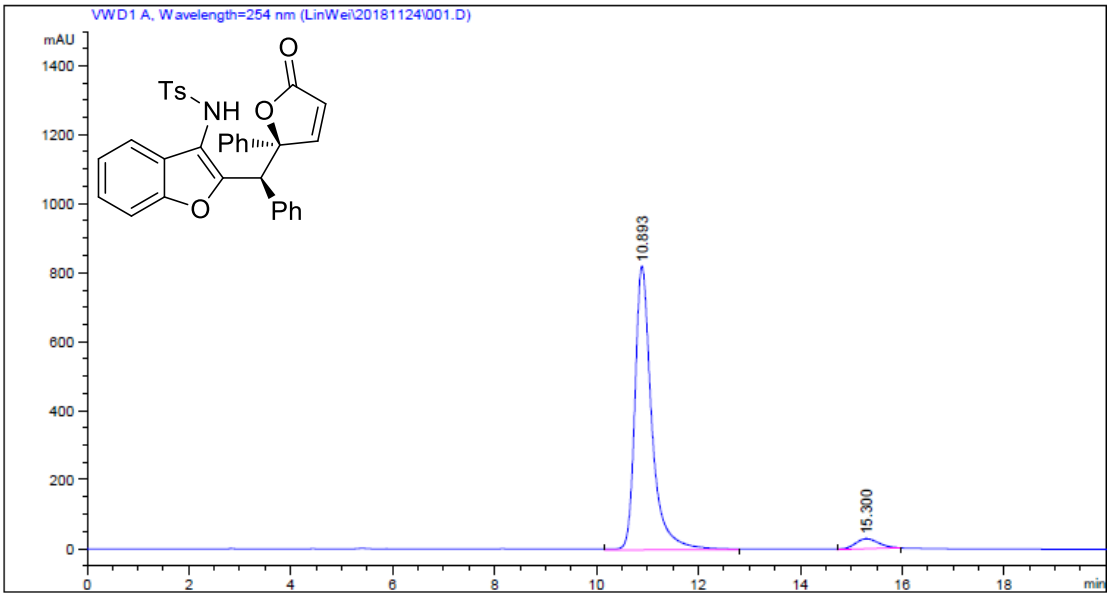


#	Time	Area	Height	Width	Symmetry	Area %
1	23.304	30860.7	372.6	1.1964	0.383	95.859
2	29.046	1333.3	16.1	1.1031	0.547	4.141

4-Methyl-*N*-(2-((*R*)-((*S*)-5-oxo-2-phenyl-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ae)

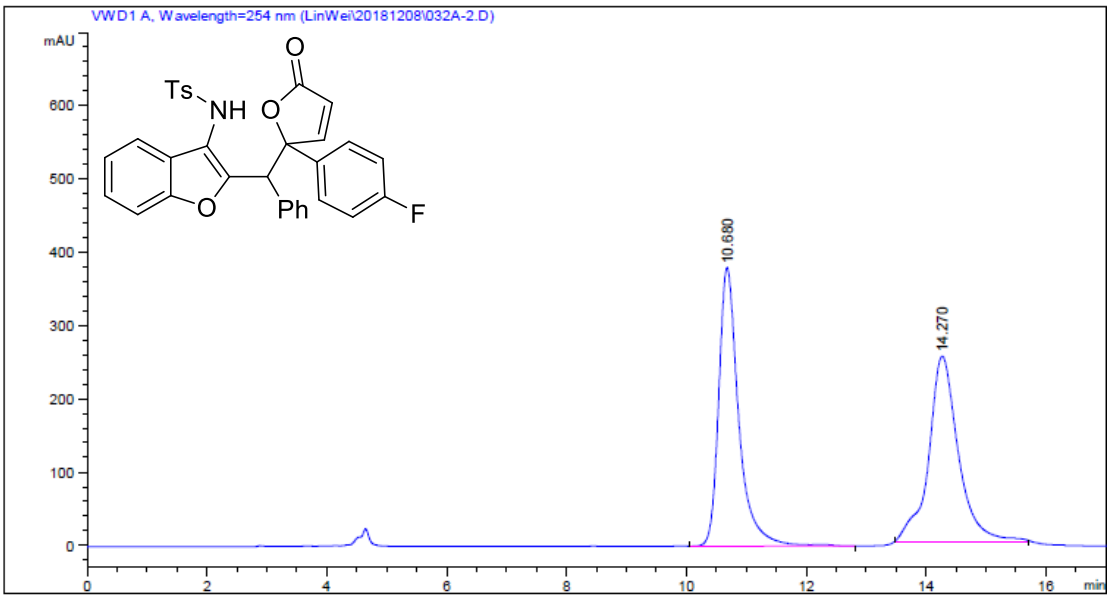


#	Time	Area	Height	Width	Symmetry	Area %
1	11.053	9173.3	409.4	0.3735	0.706	50.552
2	15.469	8972.9	227.3	0.6579	0.601	49.448

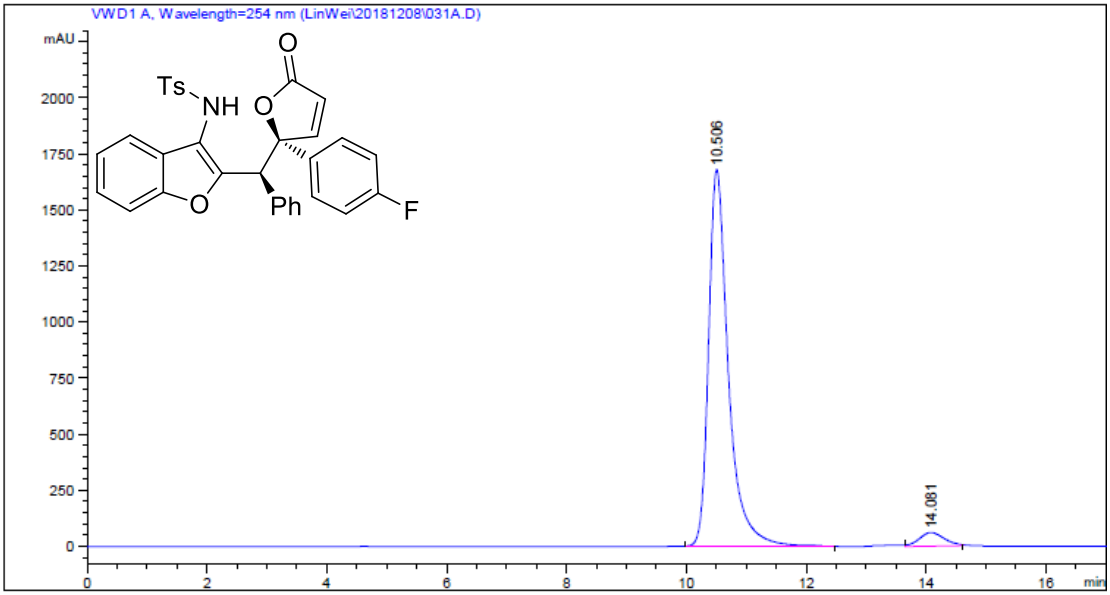


#	Time	Area	Height	Width	Symmetry	Area %
1	10.893	18846.8	822.4	0.382	0.676	95.308
2	15.3	927.9	29	0.5324	0.888	4.692

***N*-(2-((*R*)-((*S*)-2-(4-fluorophenyl)-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3af)**

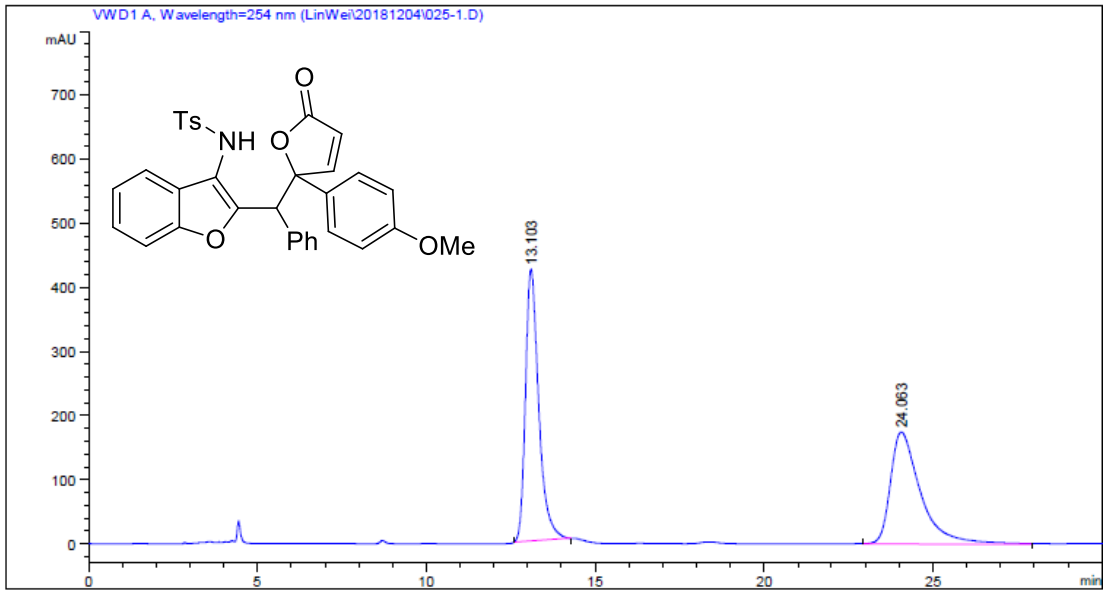


#	Time	Area	Height	Width	Symmetry	Area %
1	10.68	8831.8	379.5	0.3475	0.65	50.008
2	14.27	8828.9	253.8	0.5798	0.815	49.992

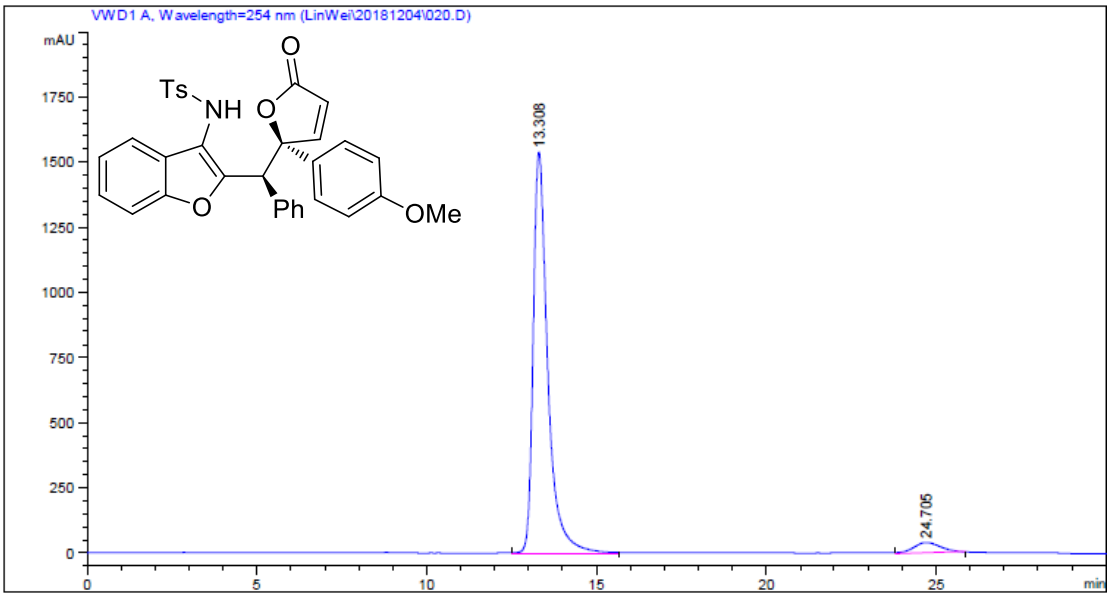


#	Time	Area	Height	Width	Symmetry	Area %
1	10.506	38842.9	1681.3	0.3851	0.655	95.699
2	14.081	1745.6	60.3	0.4823	0.876	4.301

***N*-(2-((*R*)-((*S*)-2-(4-methoxyphenyl)-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl) benzofuran-3-yl)-4-methylbenzenesulfonamide (3ag)**

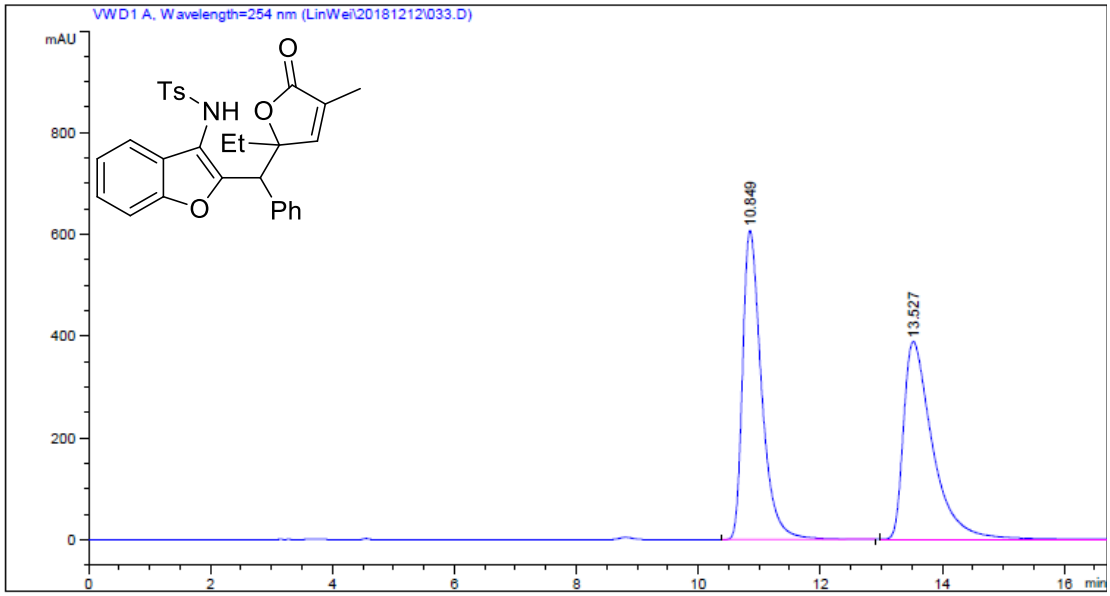


#	Time	Area	Height	Width	Symmetry	Area %
1	13.103	11493.4	423.9	0.4519	0.695	51.154
2	24.063	10974.8	175.1	1.0449	0.532	48.846

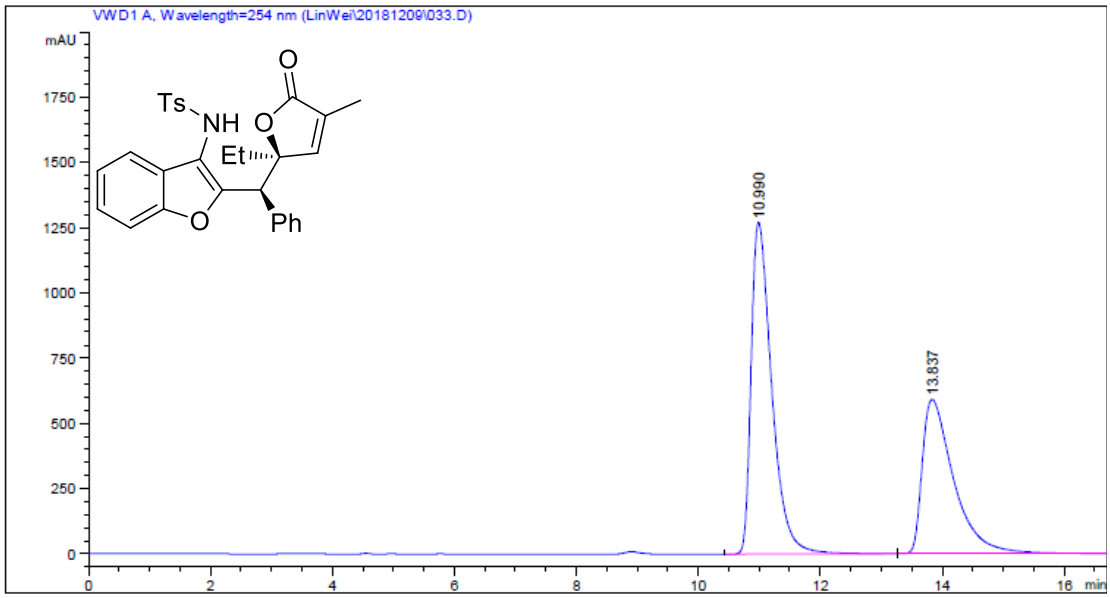


#	Time	Area	Height	Width	Symmetry	Area %
1	13.308	45740.9	1539.3	0.4953	0.61	95.472
2	24.705	2169.3	39.4	0.9166	0.916	4.528

_N_-(2-((_R_)-((_S_)-2-ethyl-4-methyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ah)



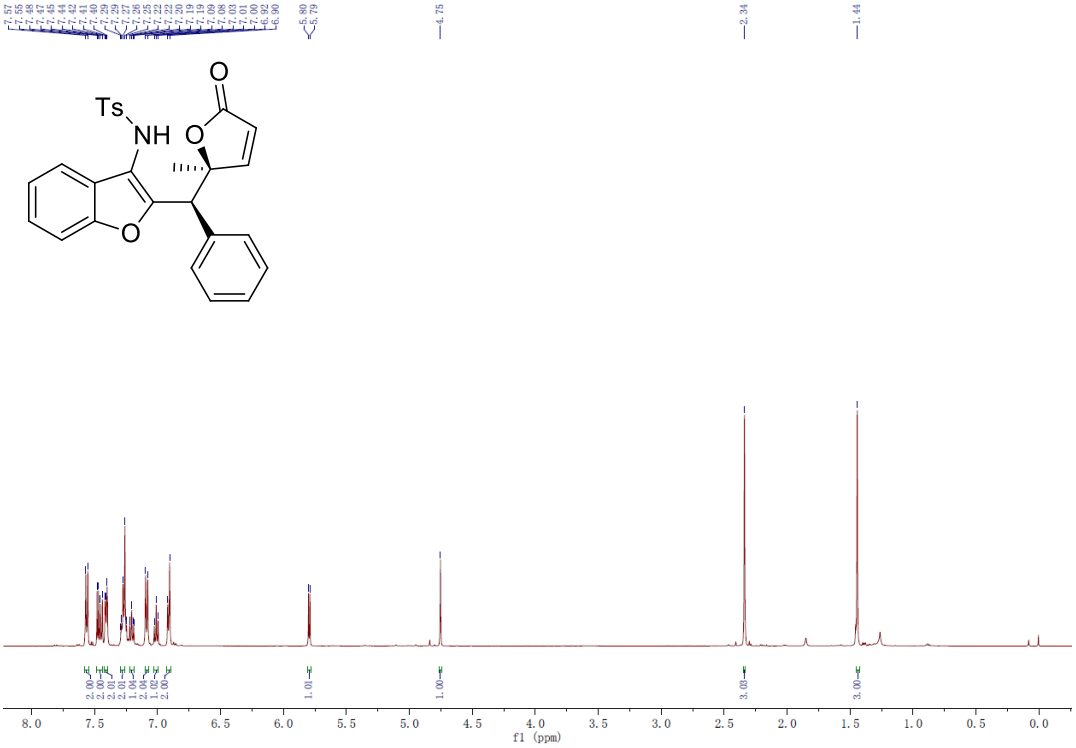
#	Time	Area	Height	Width	Symmetry	Area %
1	10.849	13107.3	607.4	0.3288	0.589	50.471
2	13.527	12862.5	388.3	0.4934	0.461	49.529

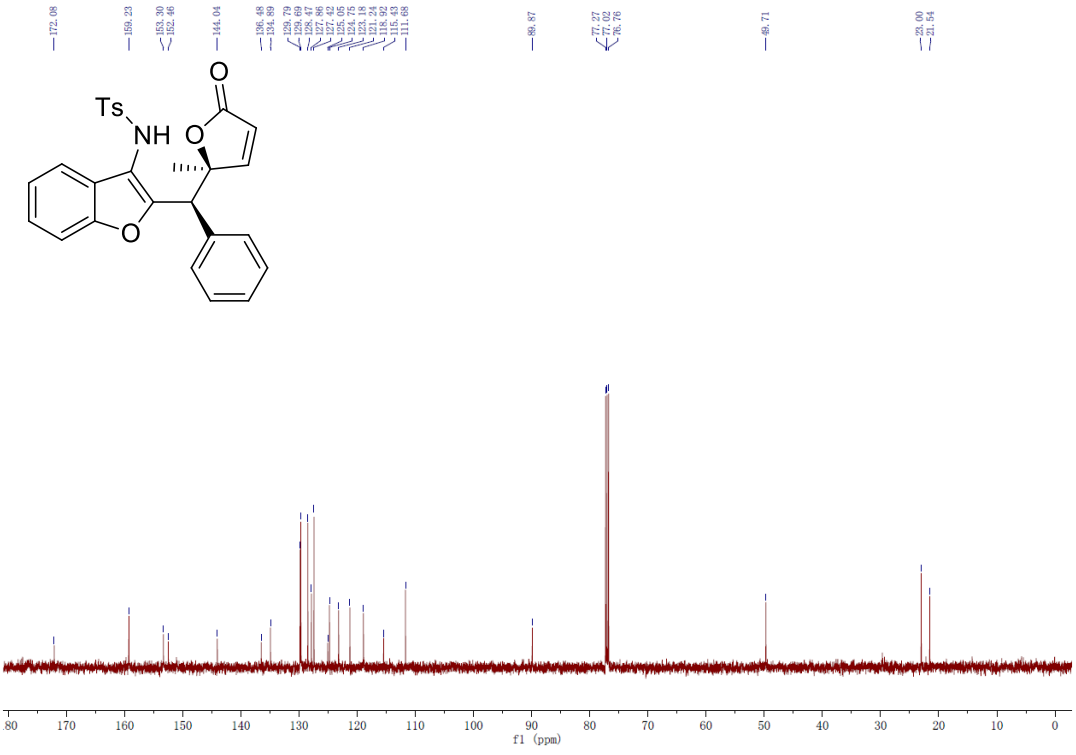


#	Time	Area	Height	Width	Symmetry	Area %
1	10.99	29831	1271.1	0.3598	0.512	58.303
2	13.837	21334.5	591.8	0.5416	0.416	41.697

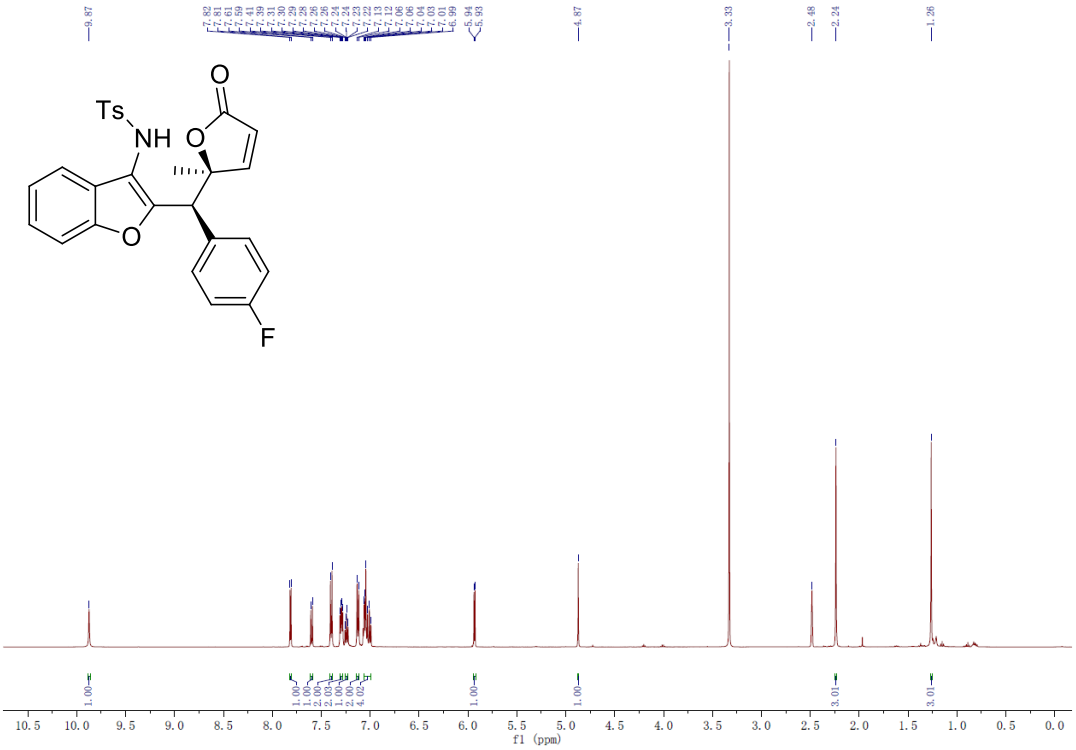
G: NMR Analysis

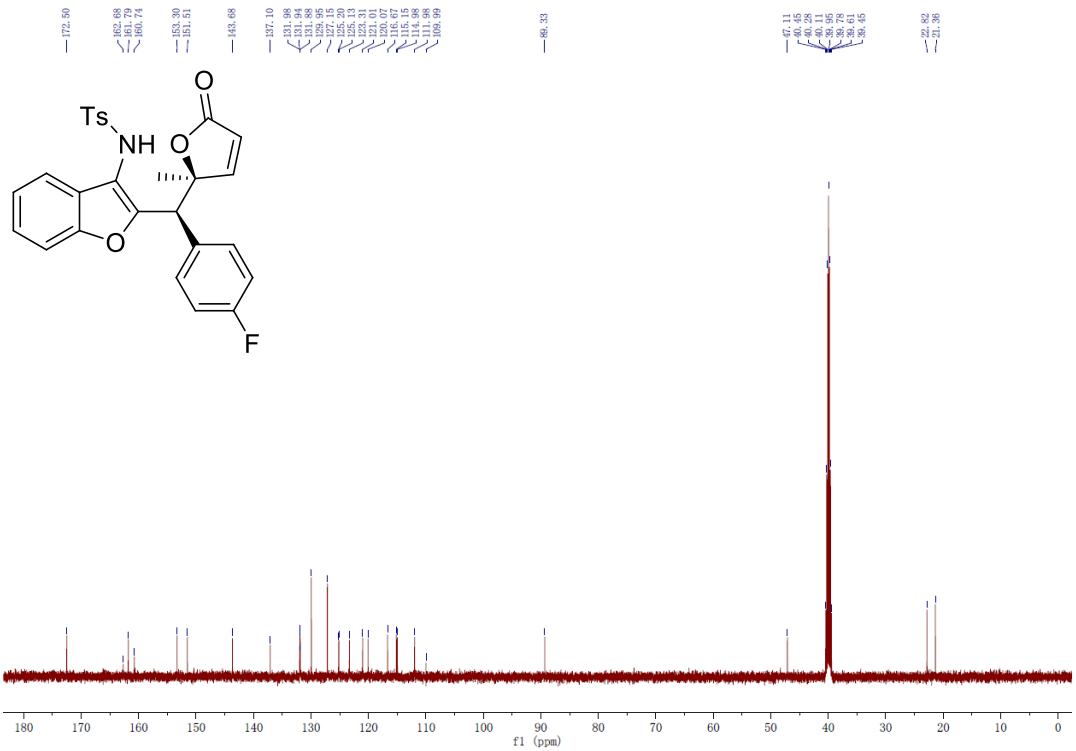
4-Methyl-*N*-(2-((*R*)-((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3aa)



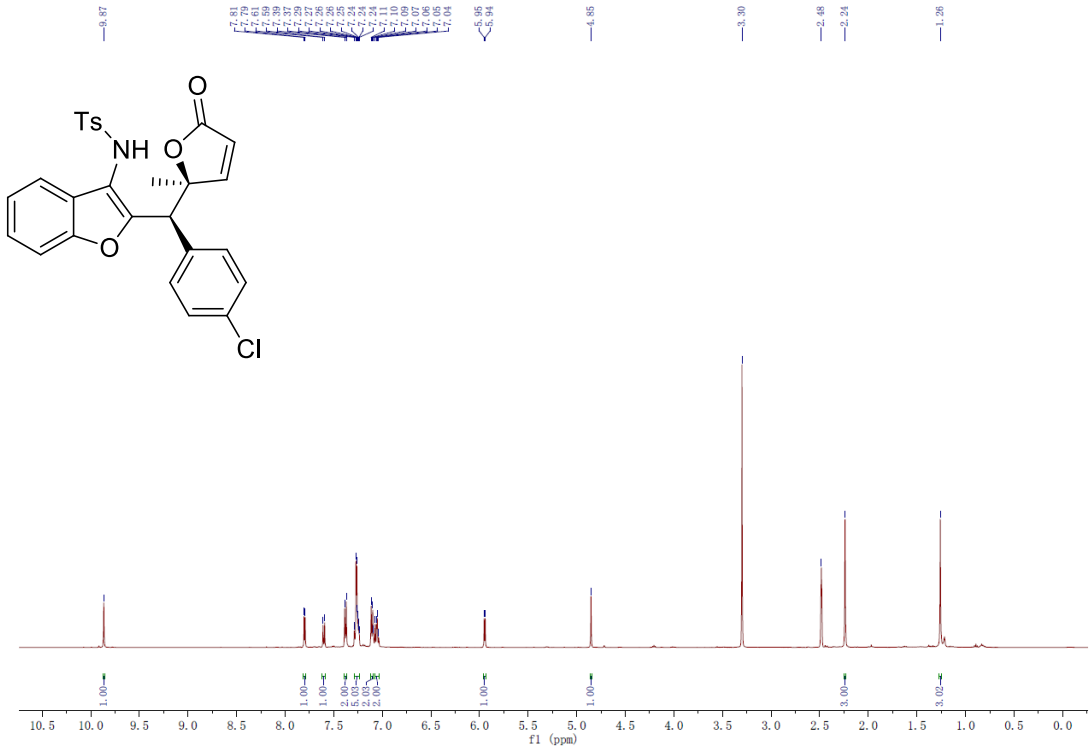


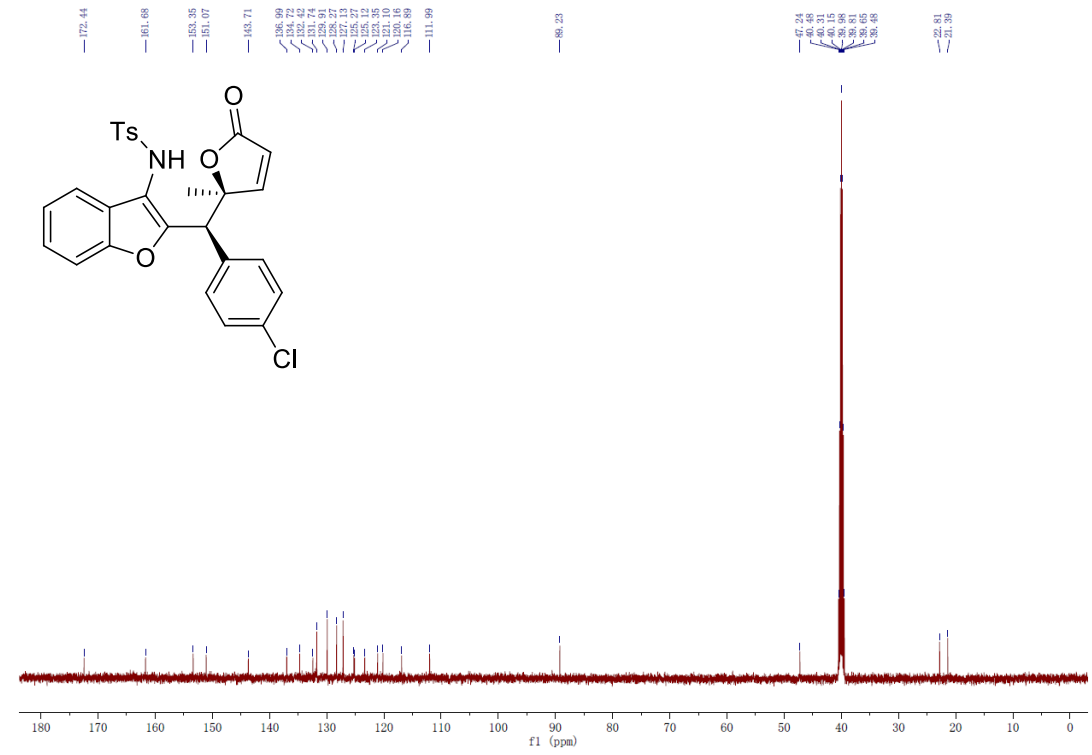
***N*-(2-((*R*)-(4-fluorophenyl)((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ba)**



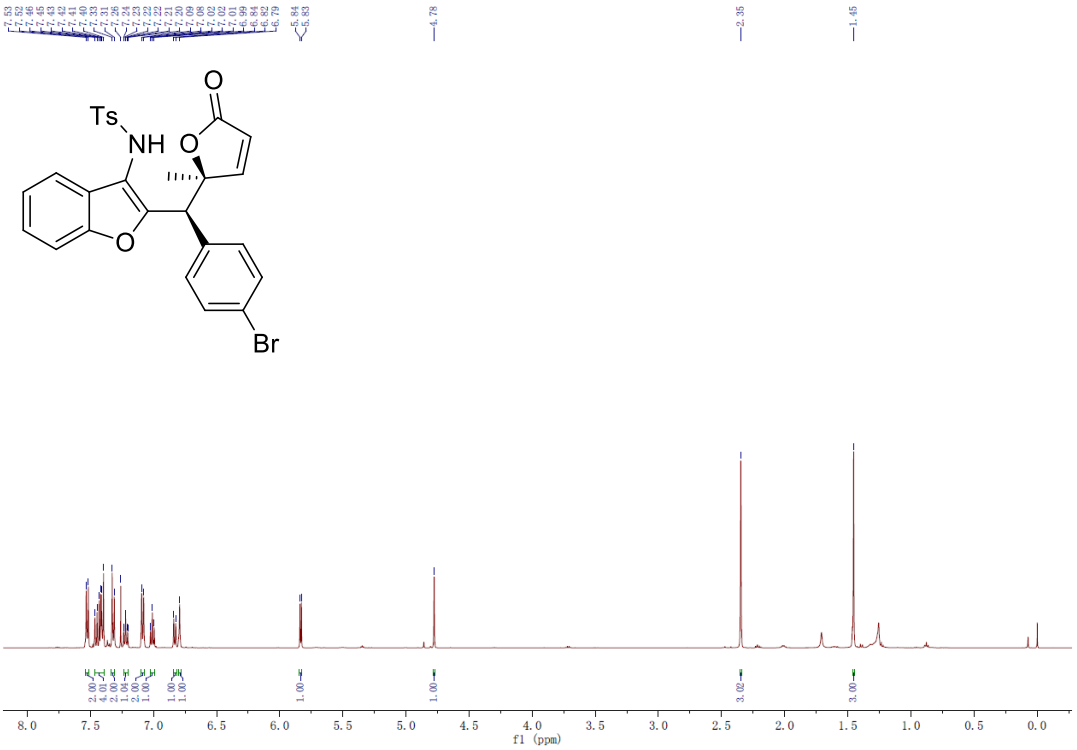


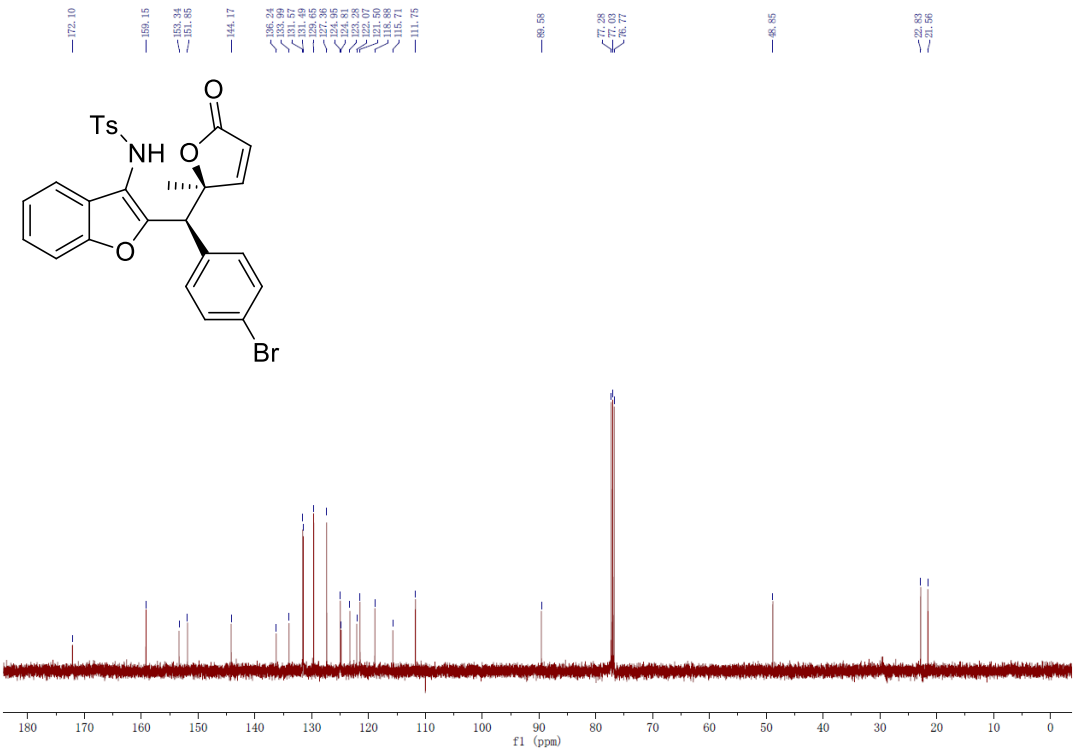
_N_-(2-((_R_)-(4-chlorophenyl)((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide(3ca)



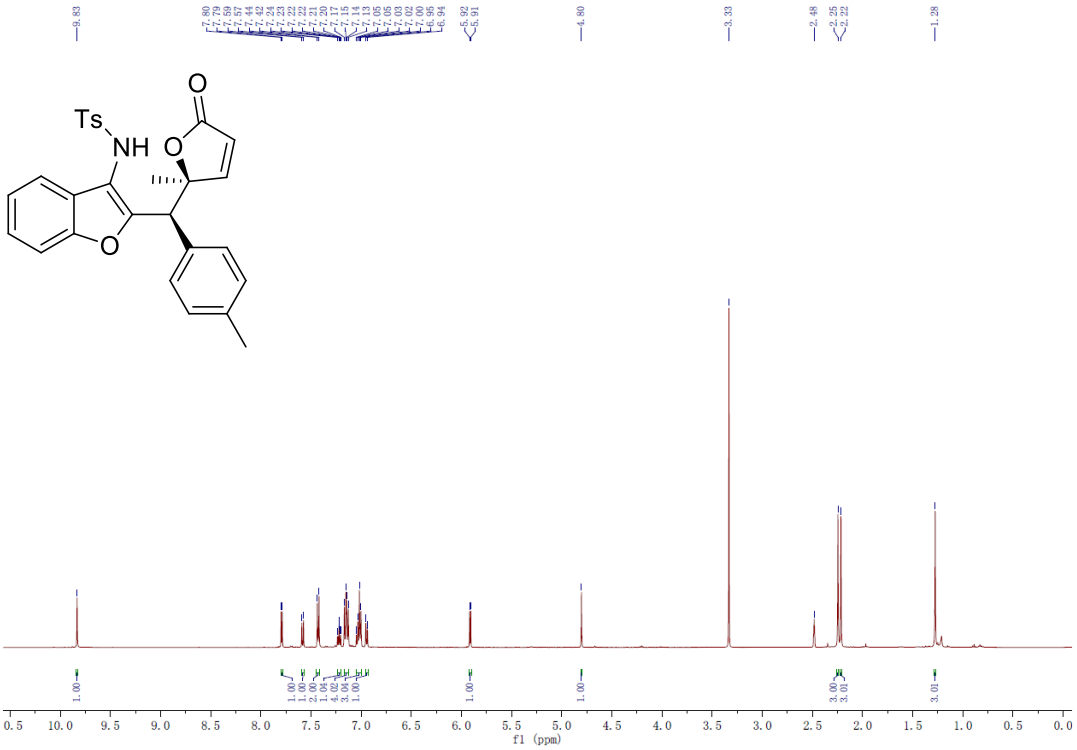


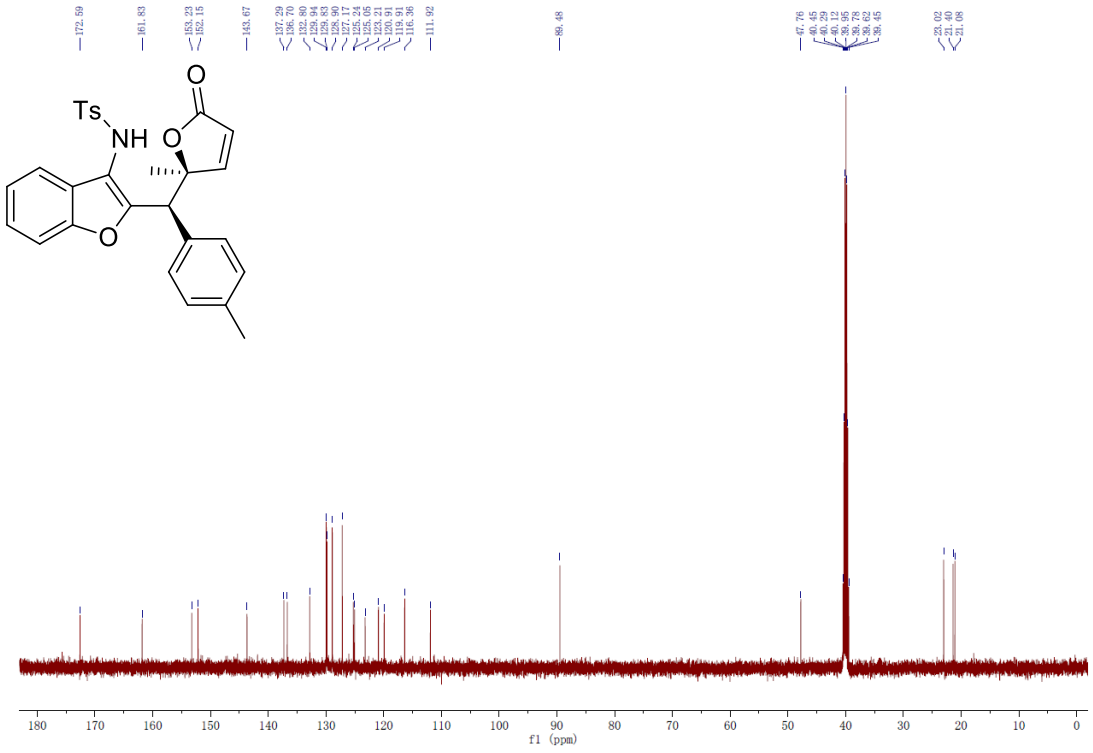
***N*-(2-((*R*)-(4-bromophenyl)((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3da)**



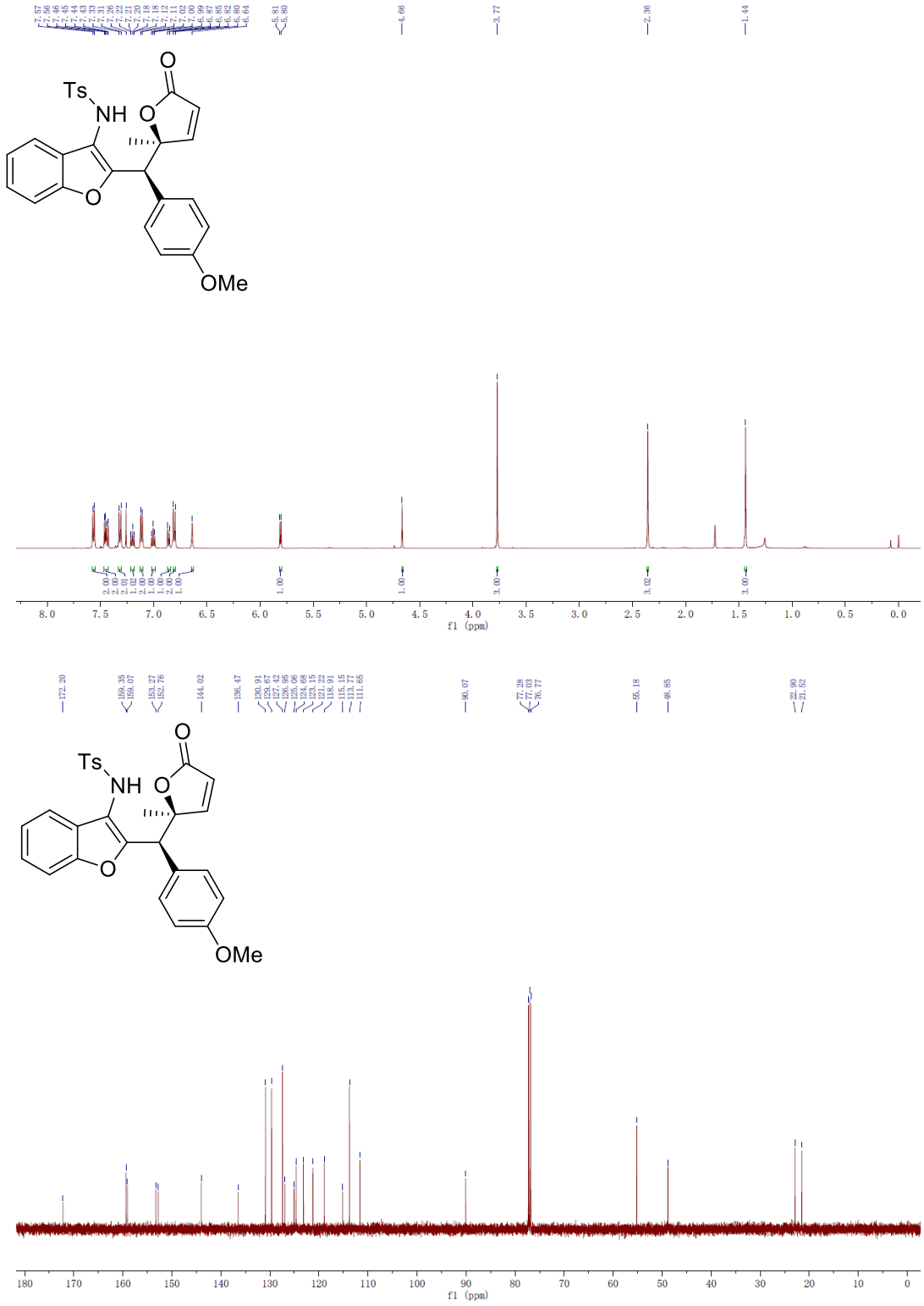


4-Methyl-*N*-(2-((*R*)-((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(p-tolyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ea)

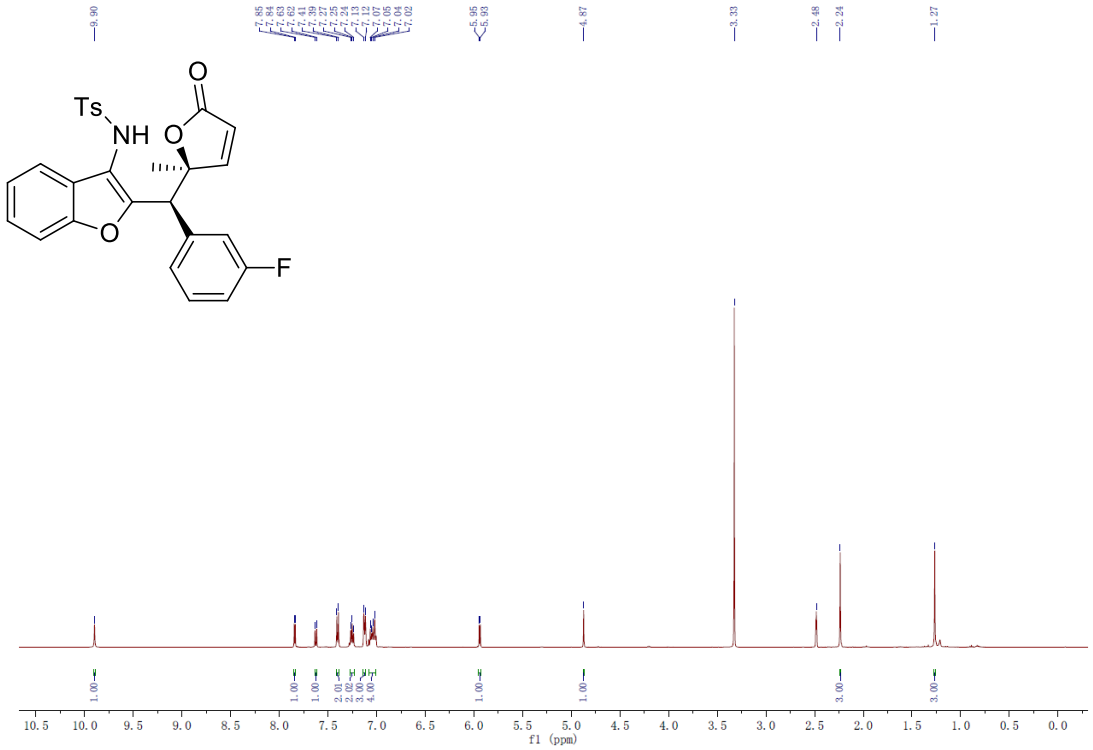


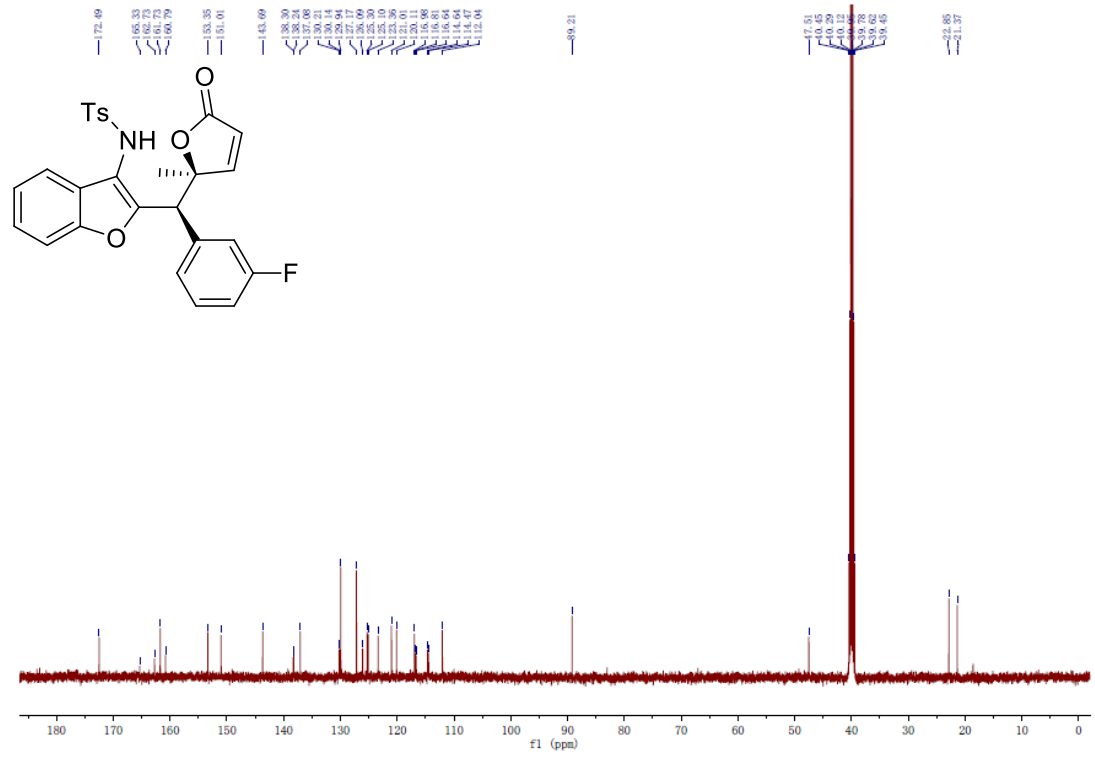


_N_-(2-((_R_)-(4-methoxyphenyl)((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3fa)

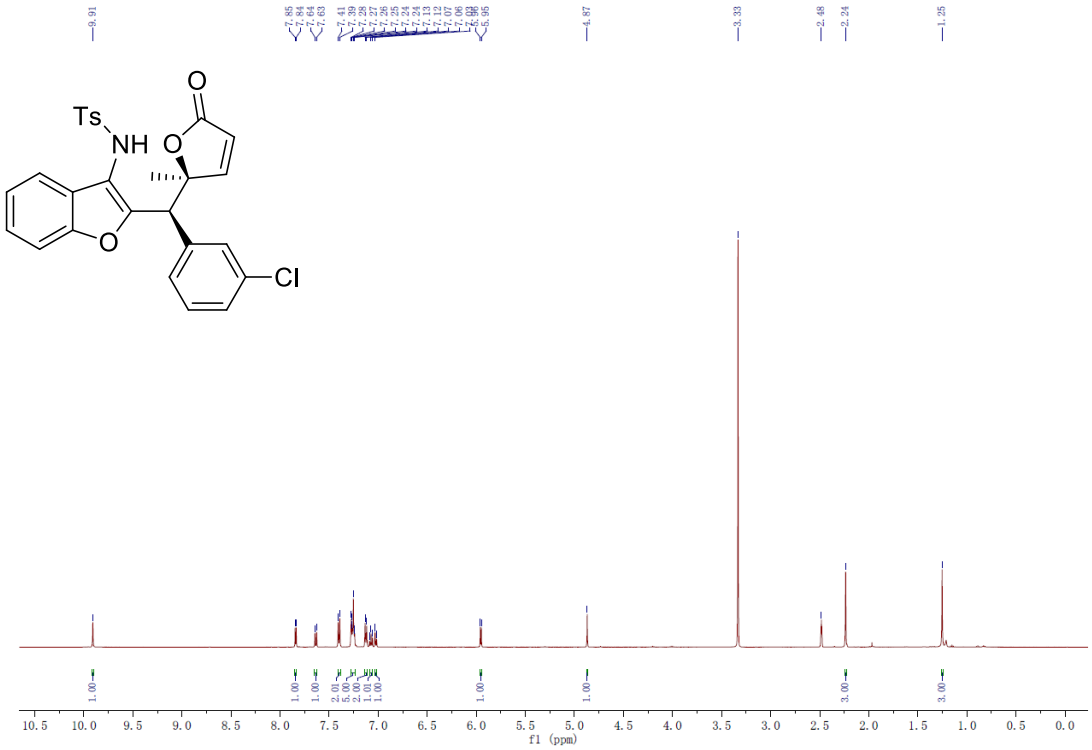


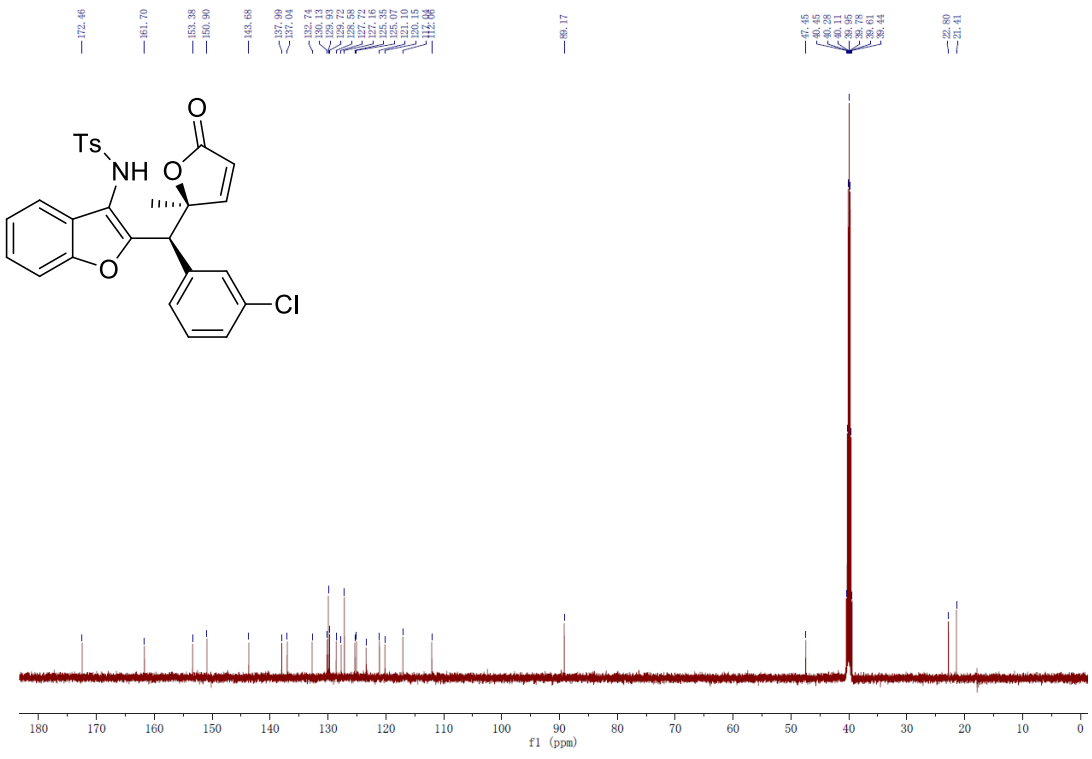
***N*-(2-((*R*)-(3-fluorophenyl)((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ga)**



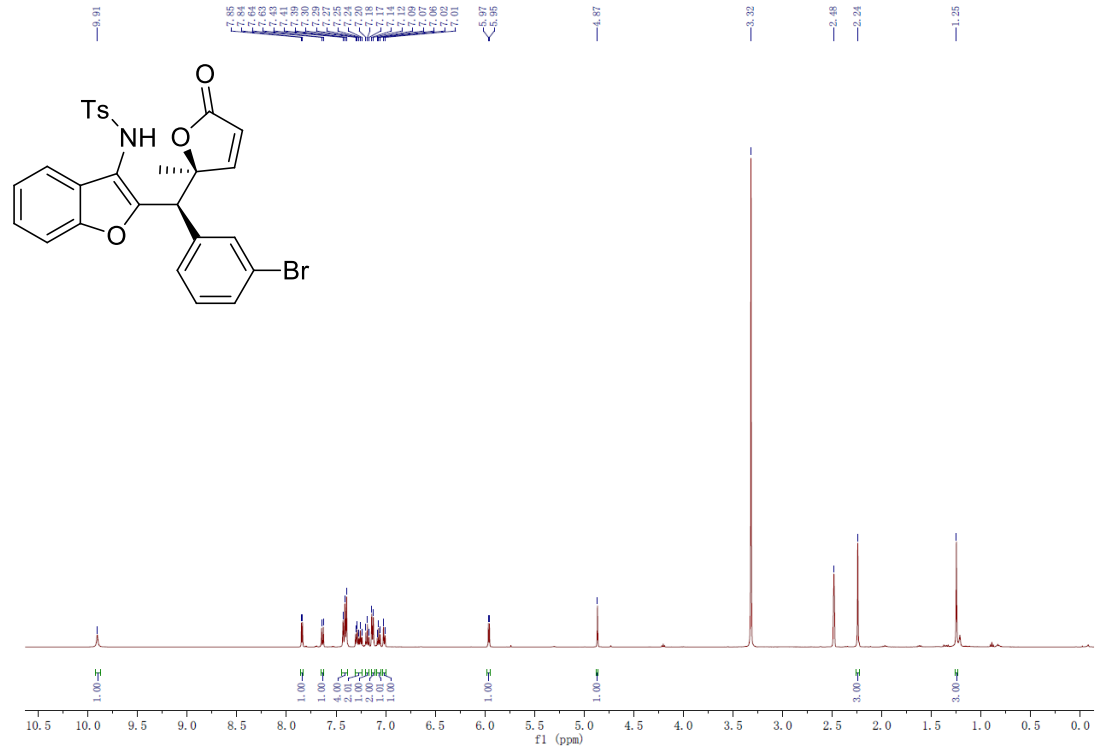


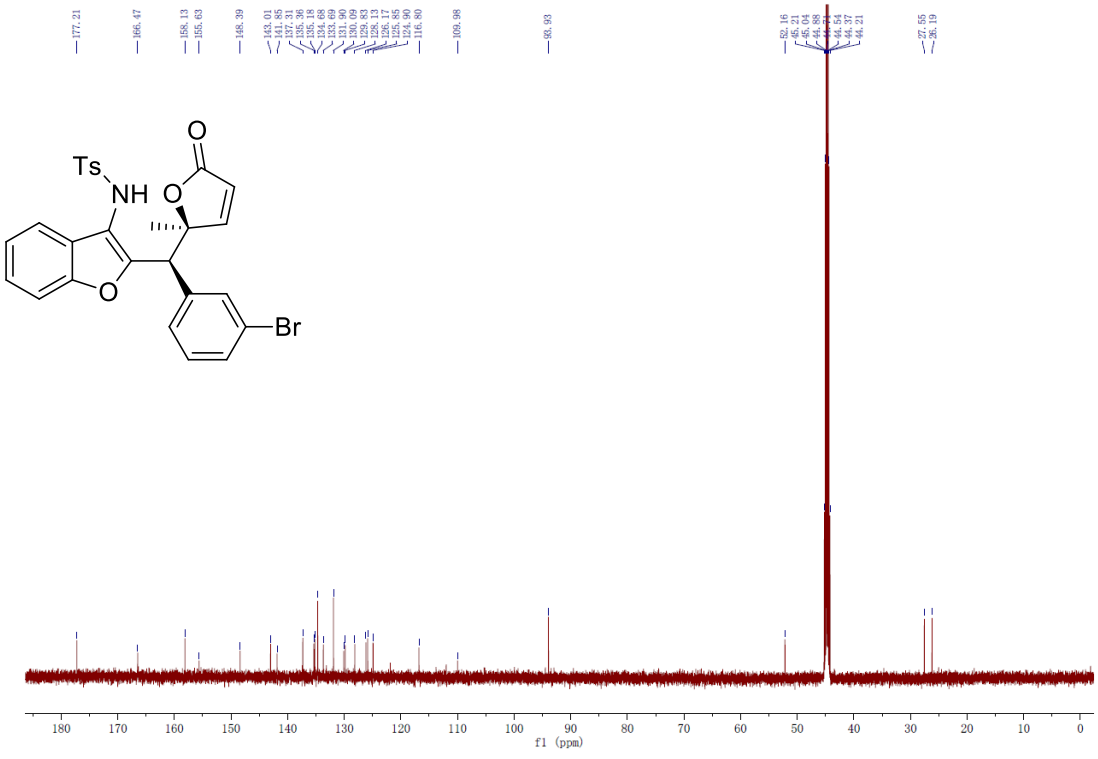
***N*-(2-((*R*)-(3-chlorophenyl)((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ha)**



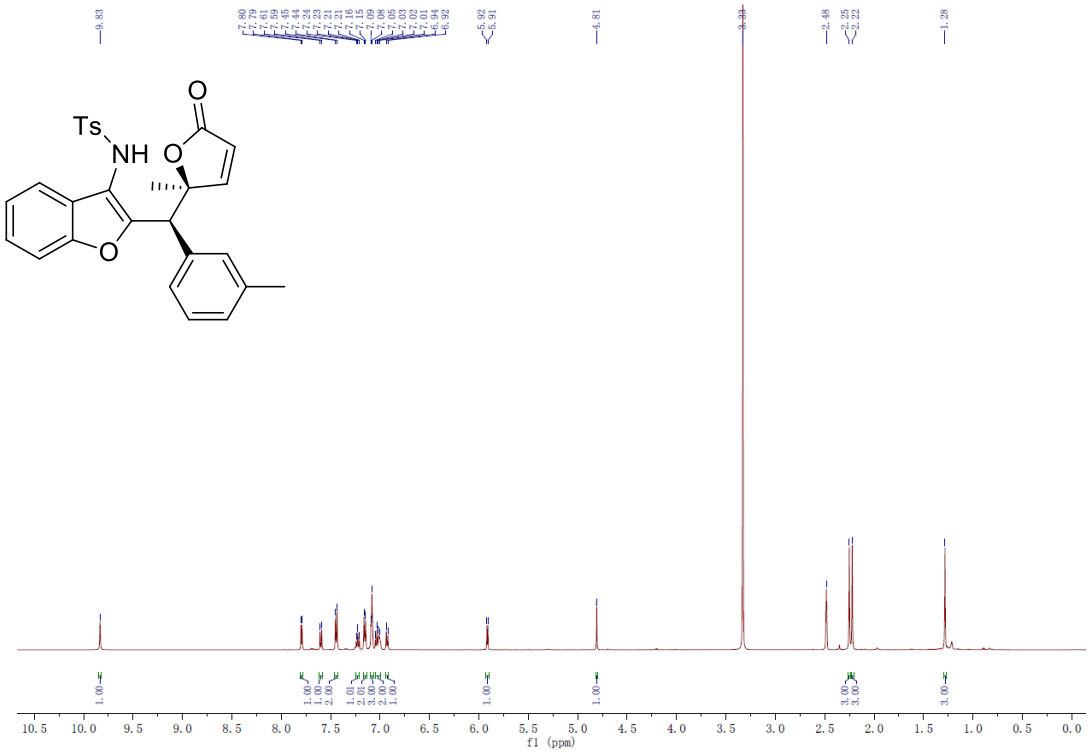


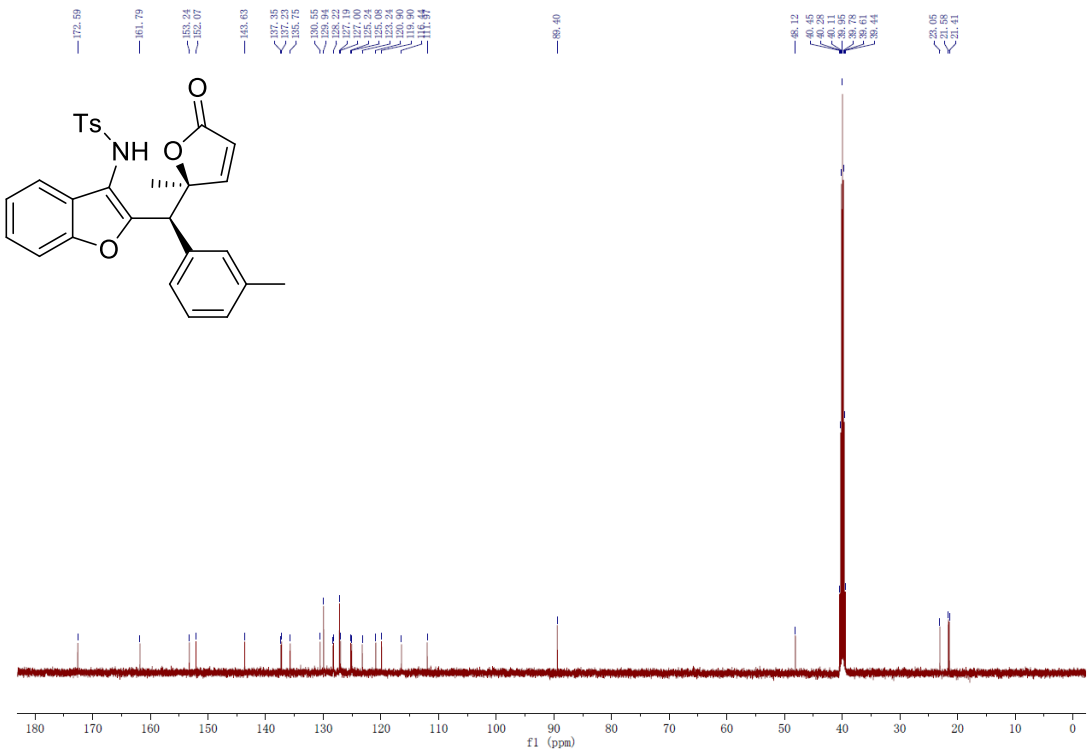
***N*-(2-((*R*)-(3-bromophenyl)((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ia)**



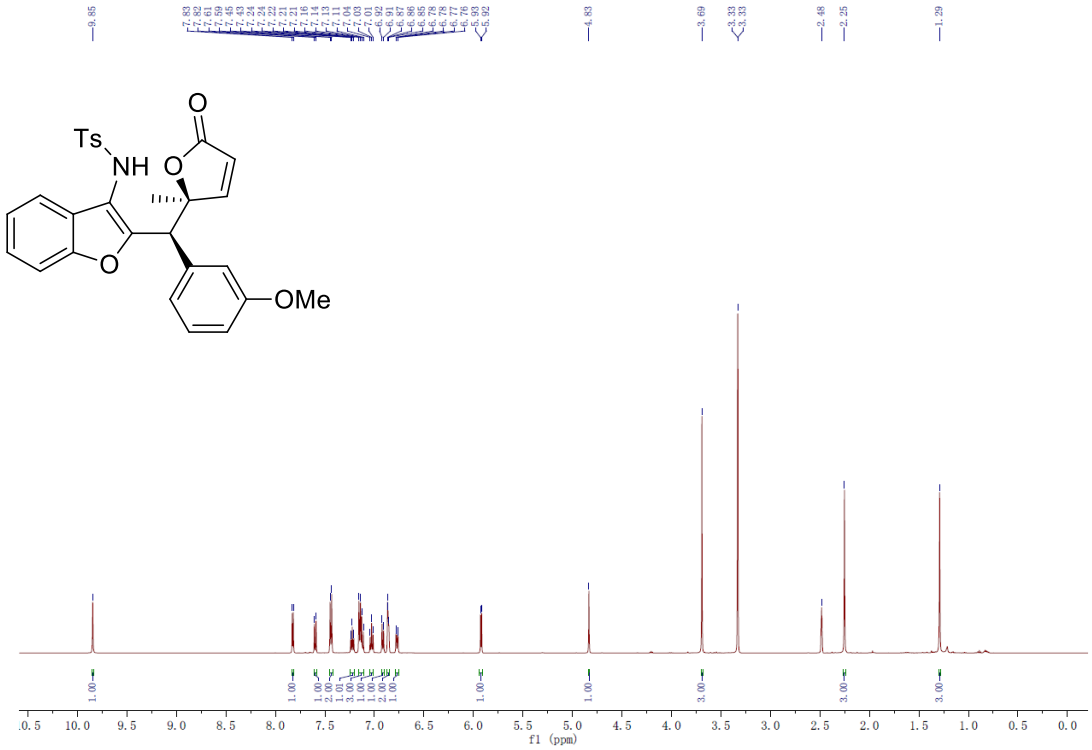


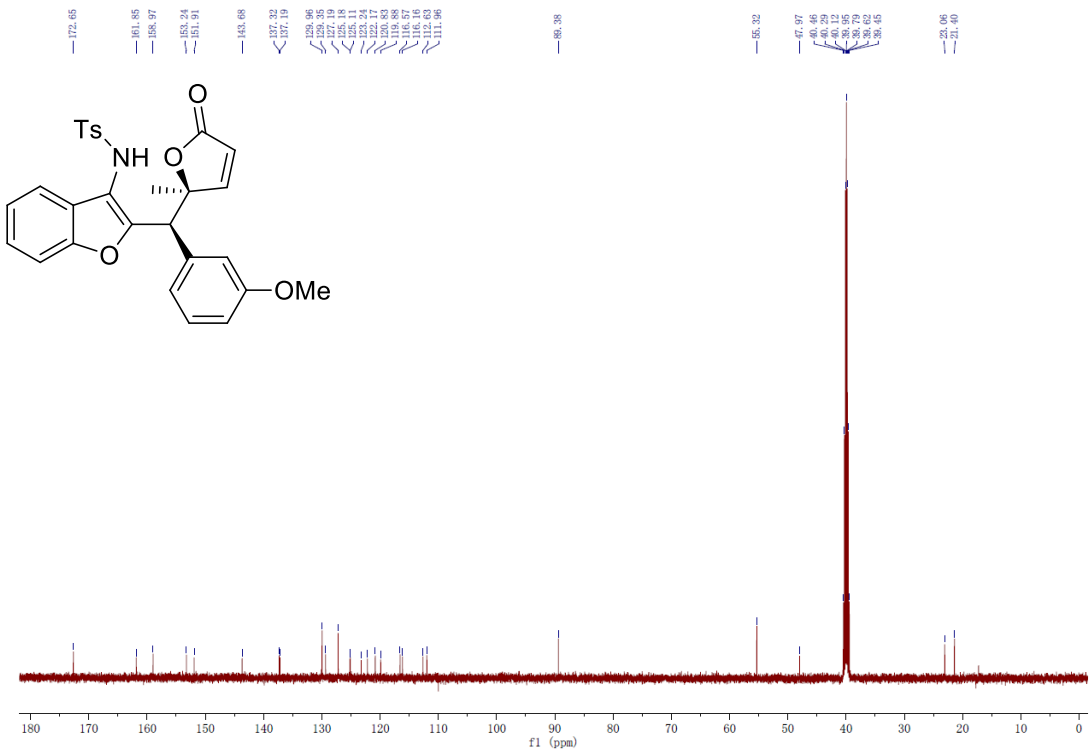
4-Methyl-*N*-(2-((*R*)-((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(m-tolyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ja)



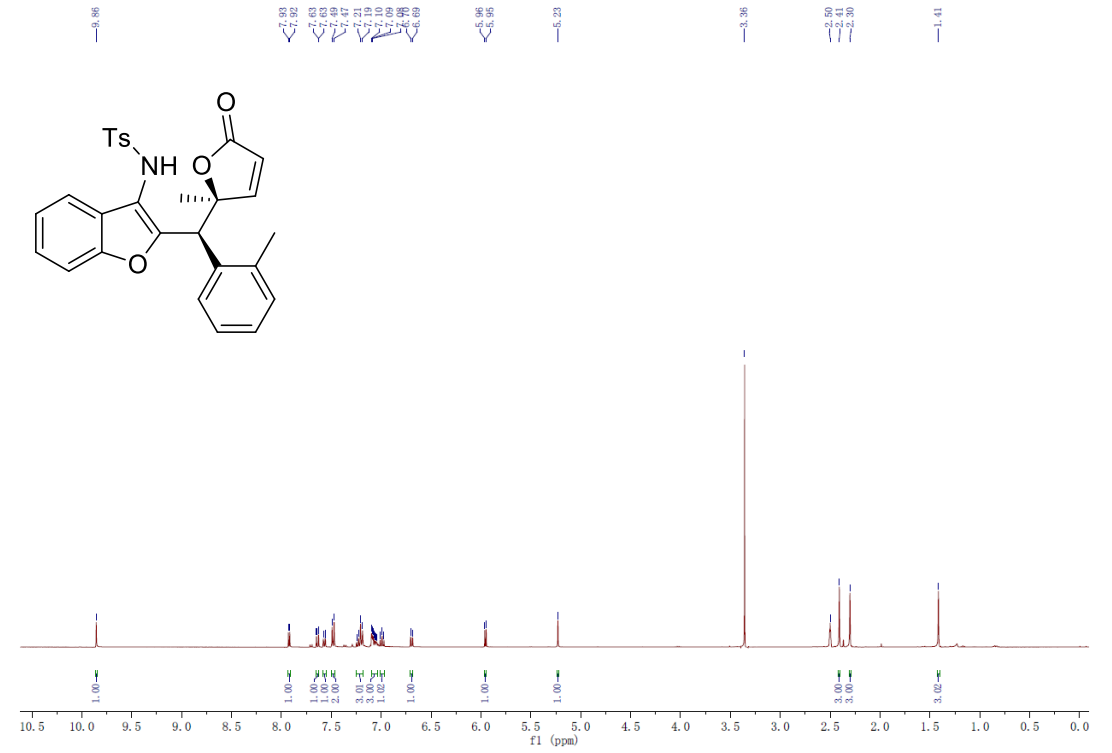


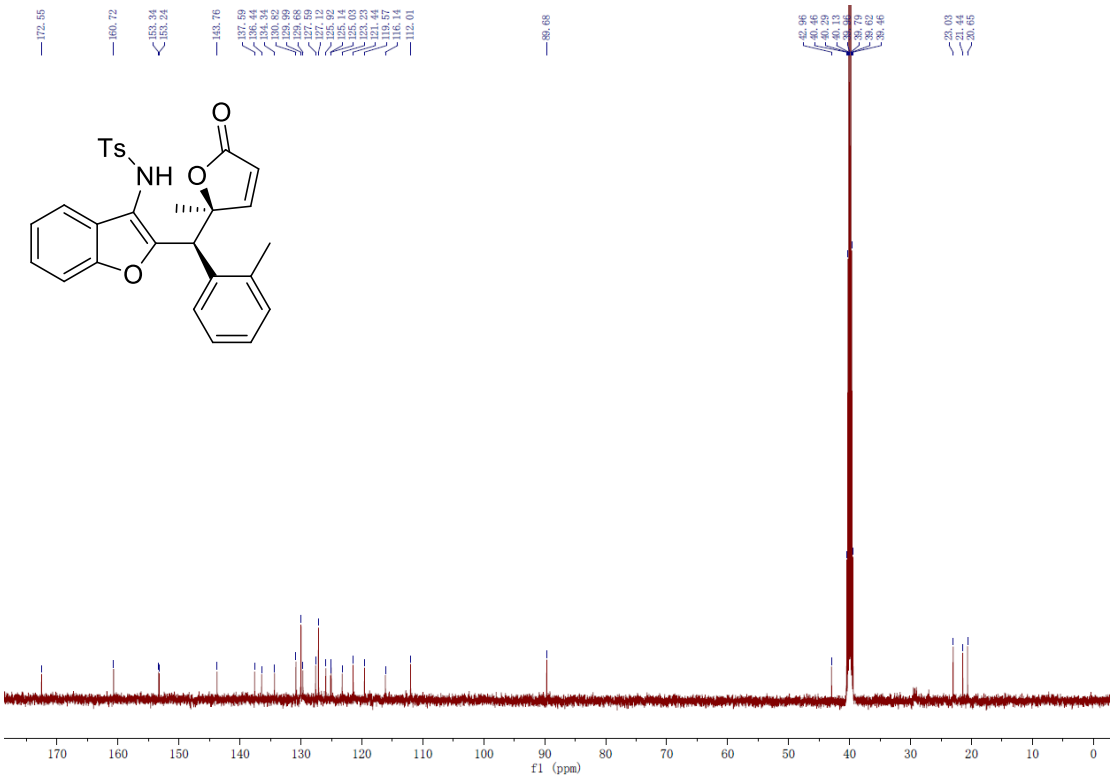
***N*-(2-((*R*)-(3-methoxyphenyl)((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ka)**



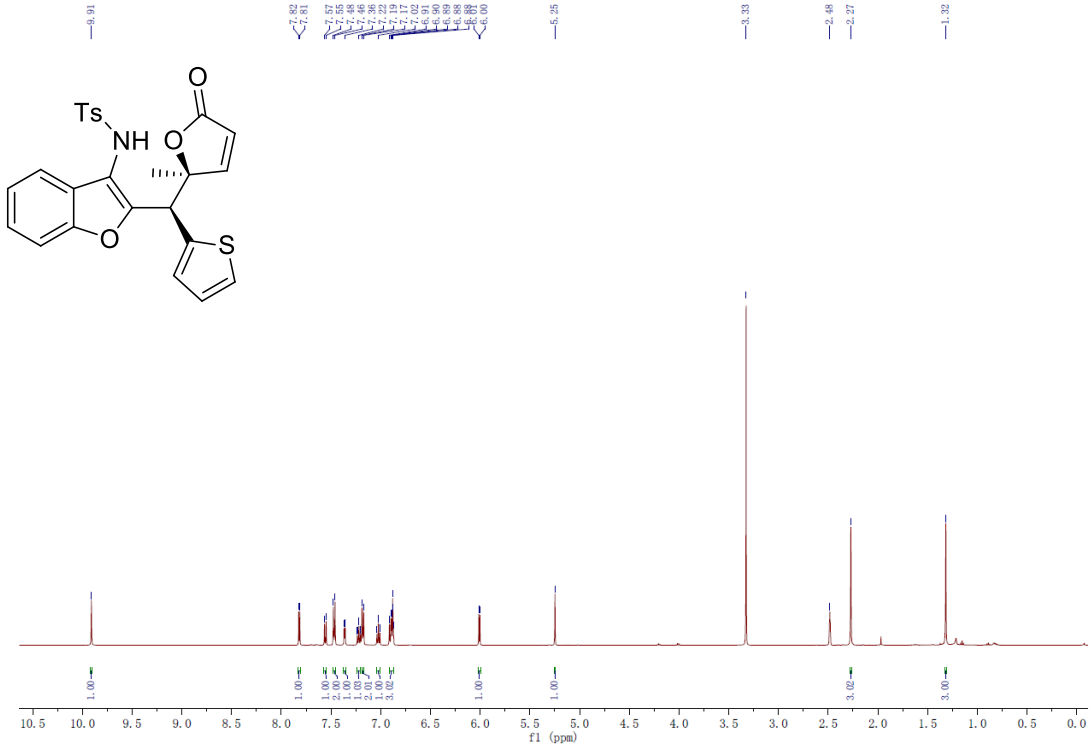


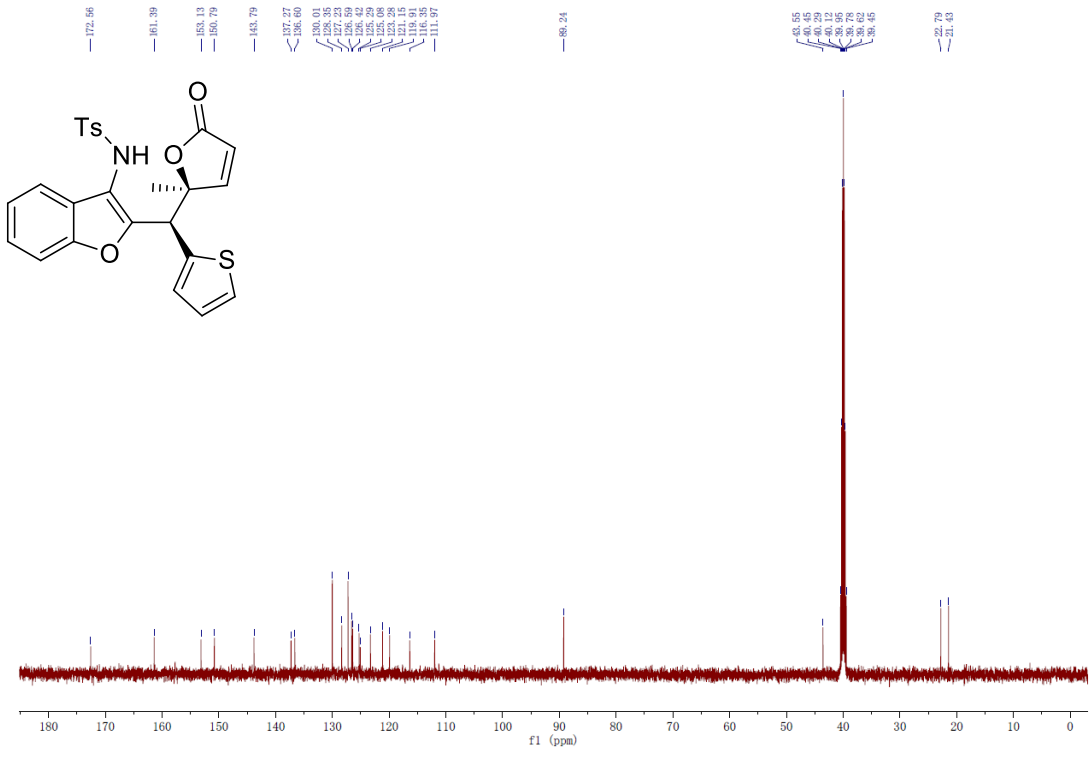
4-Methyl-*N*-(2-((*R*)-((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(o-tolyl)methyl)benzofuran-3-yl)benzenesulfonamide (3la)



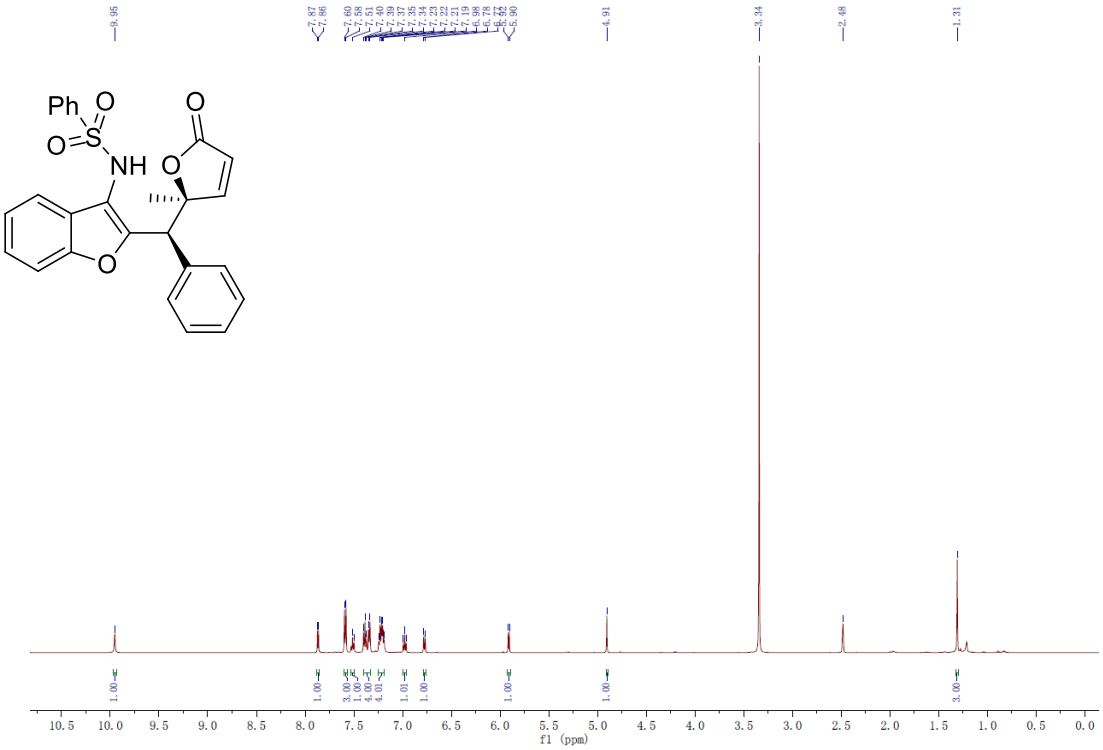


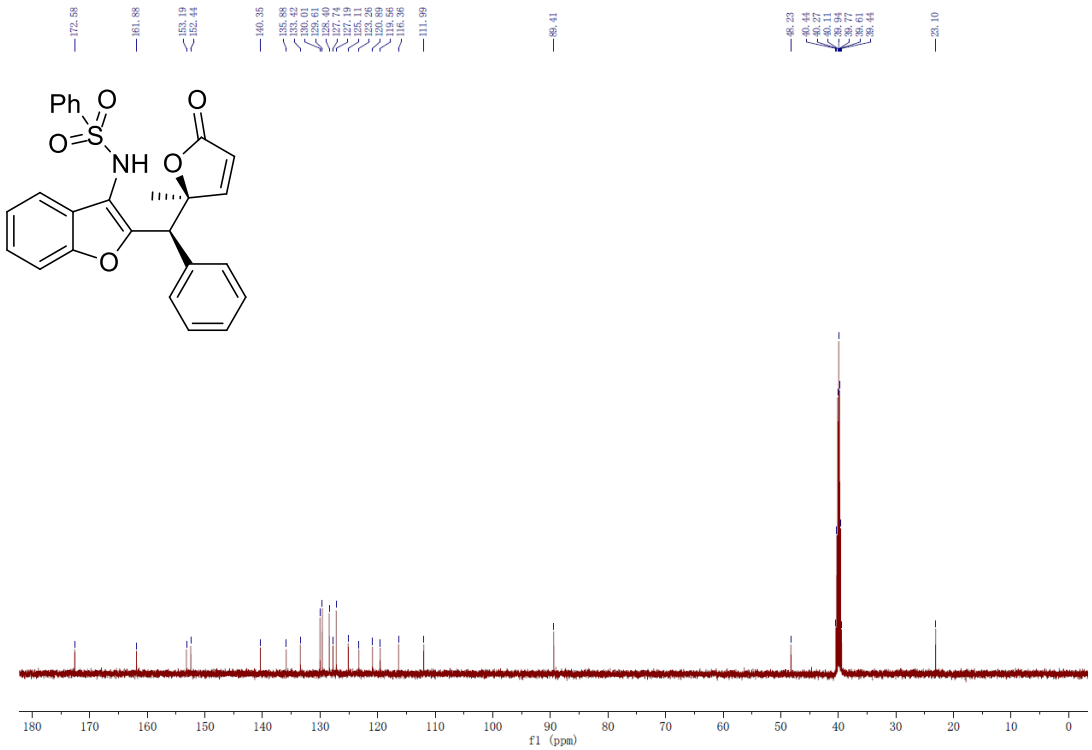
4-Methyl-*N*-(2-((*R*)-((*S*)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(thiophen-2-yl)methyl)benzofuran-3-yl)benzenesulfonamide (3ma)



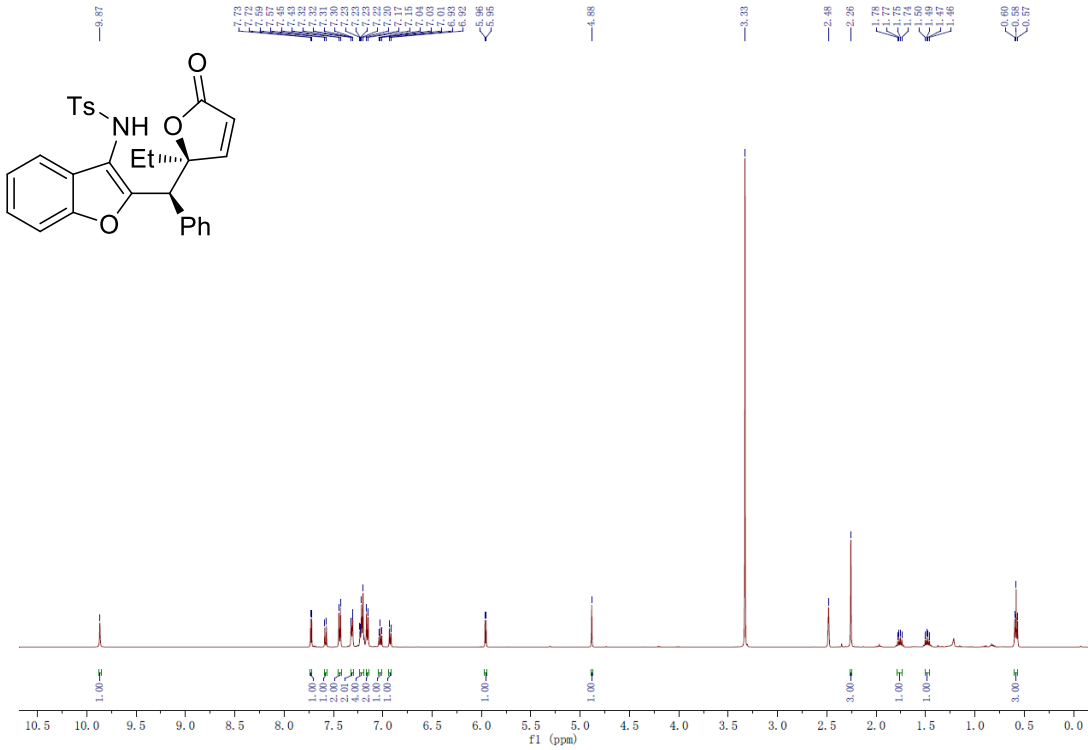


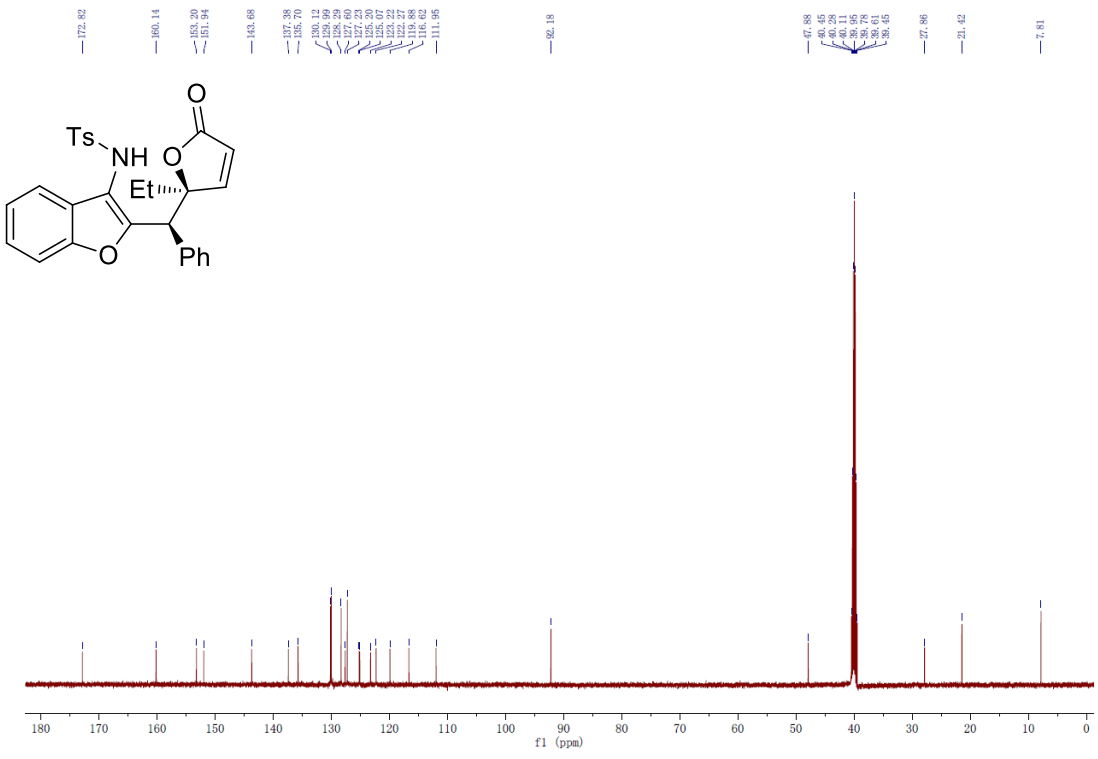
_N_-(2-((_R_)-((_S_)-2-methyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3na)



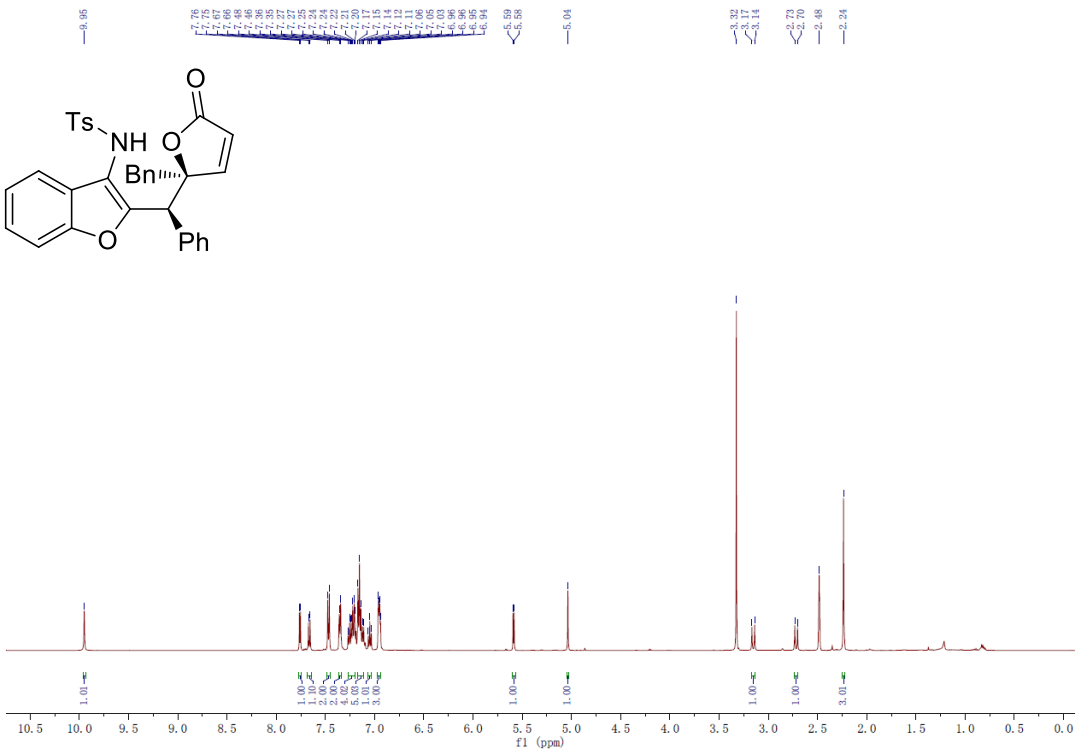


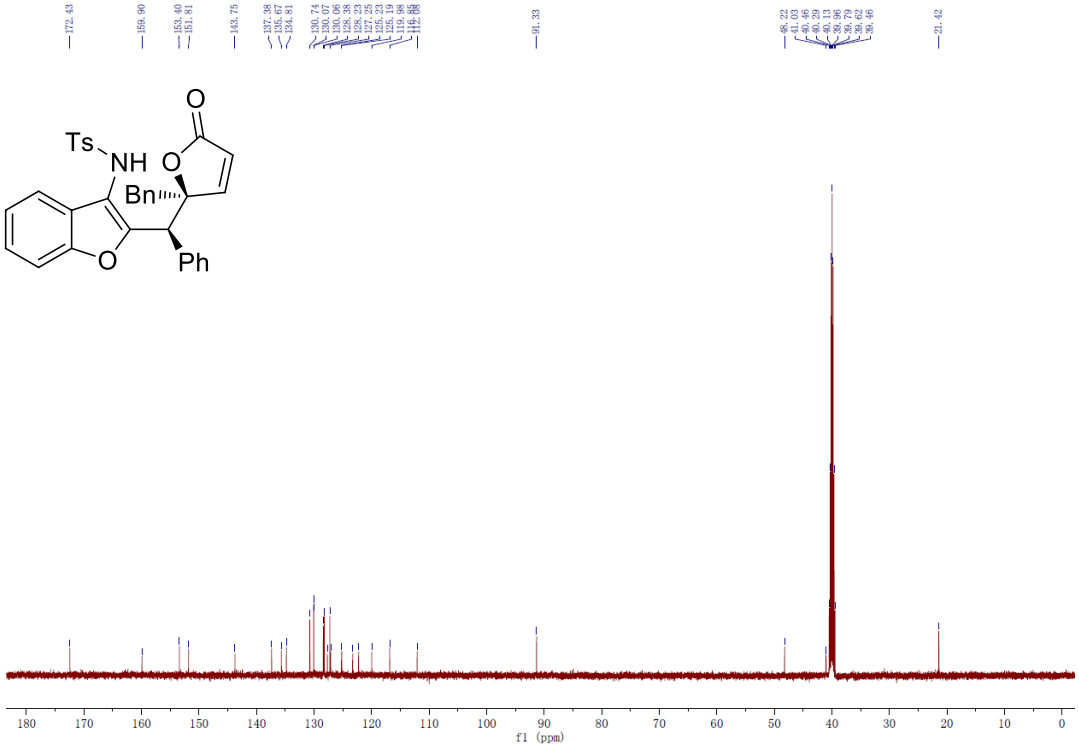
_N_-(2-((_R_)-((_S_)-2-ethyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ab)



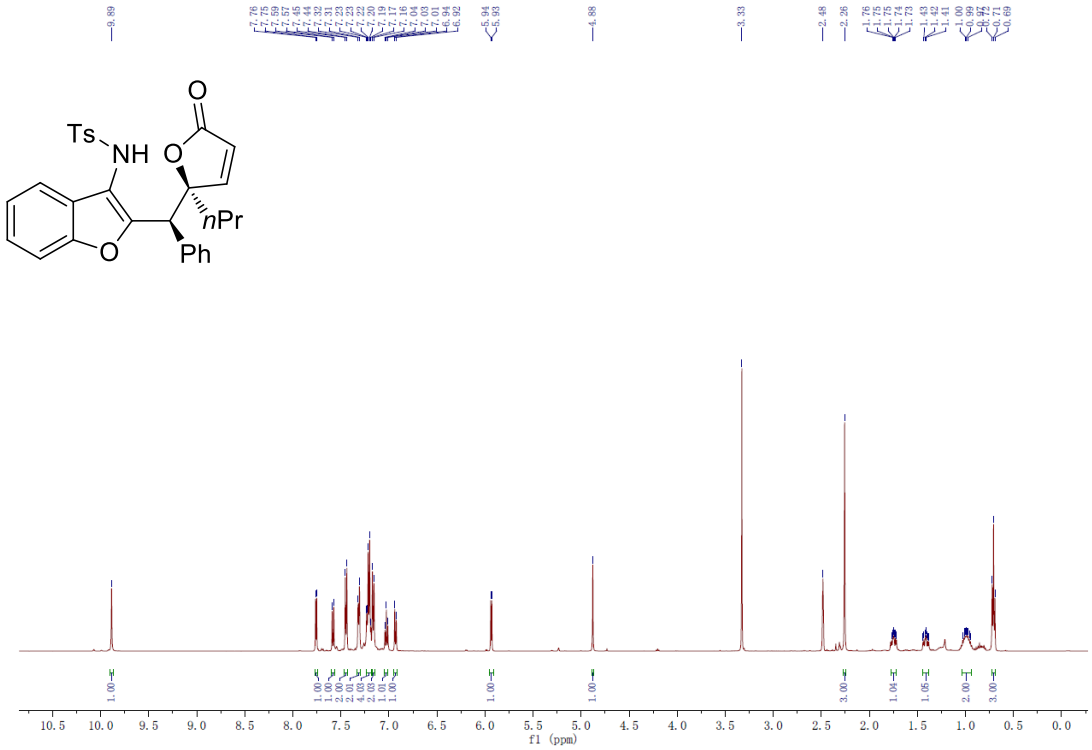


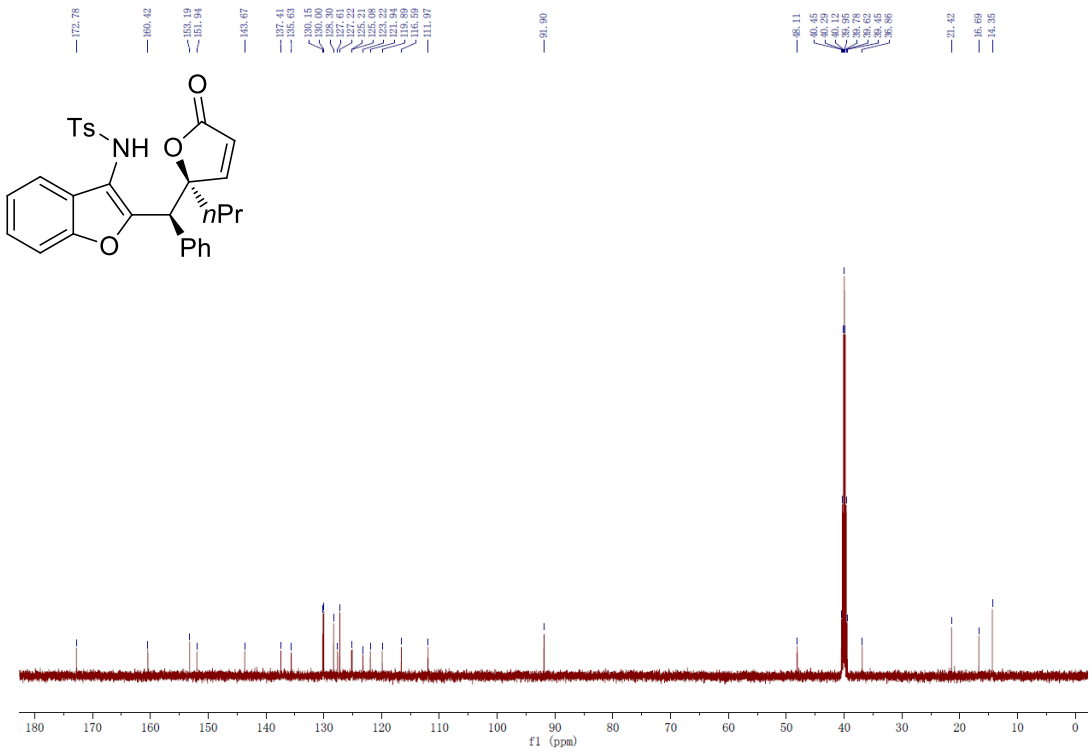
***N*-(2-((*R*)-((*S*)-2-benzyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ac)**



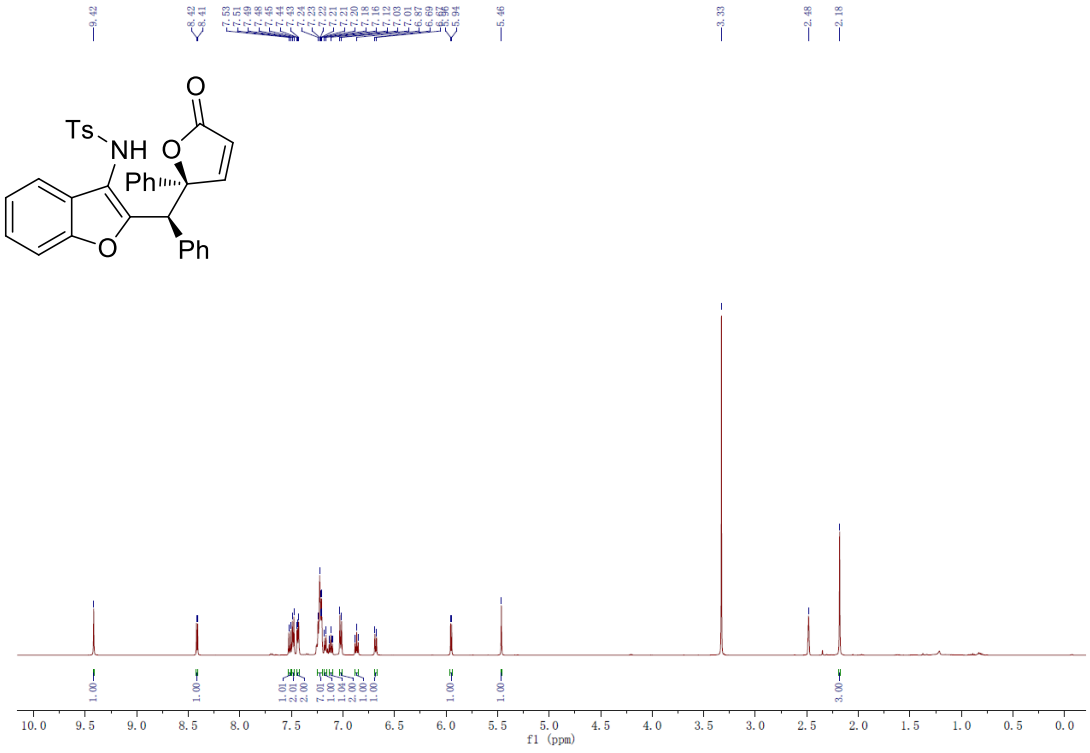


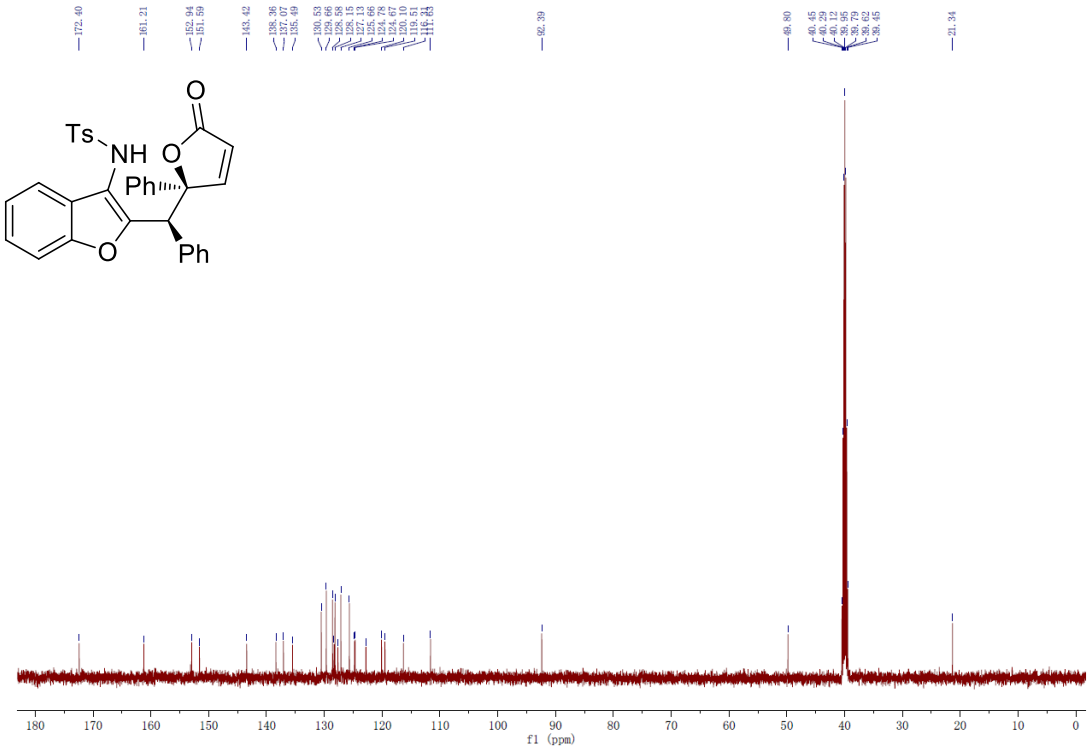
4-Methyl-*N*-(2-((*R*)-((*S*)-5-oxo-2-propyl-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ad)



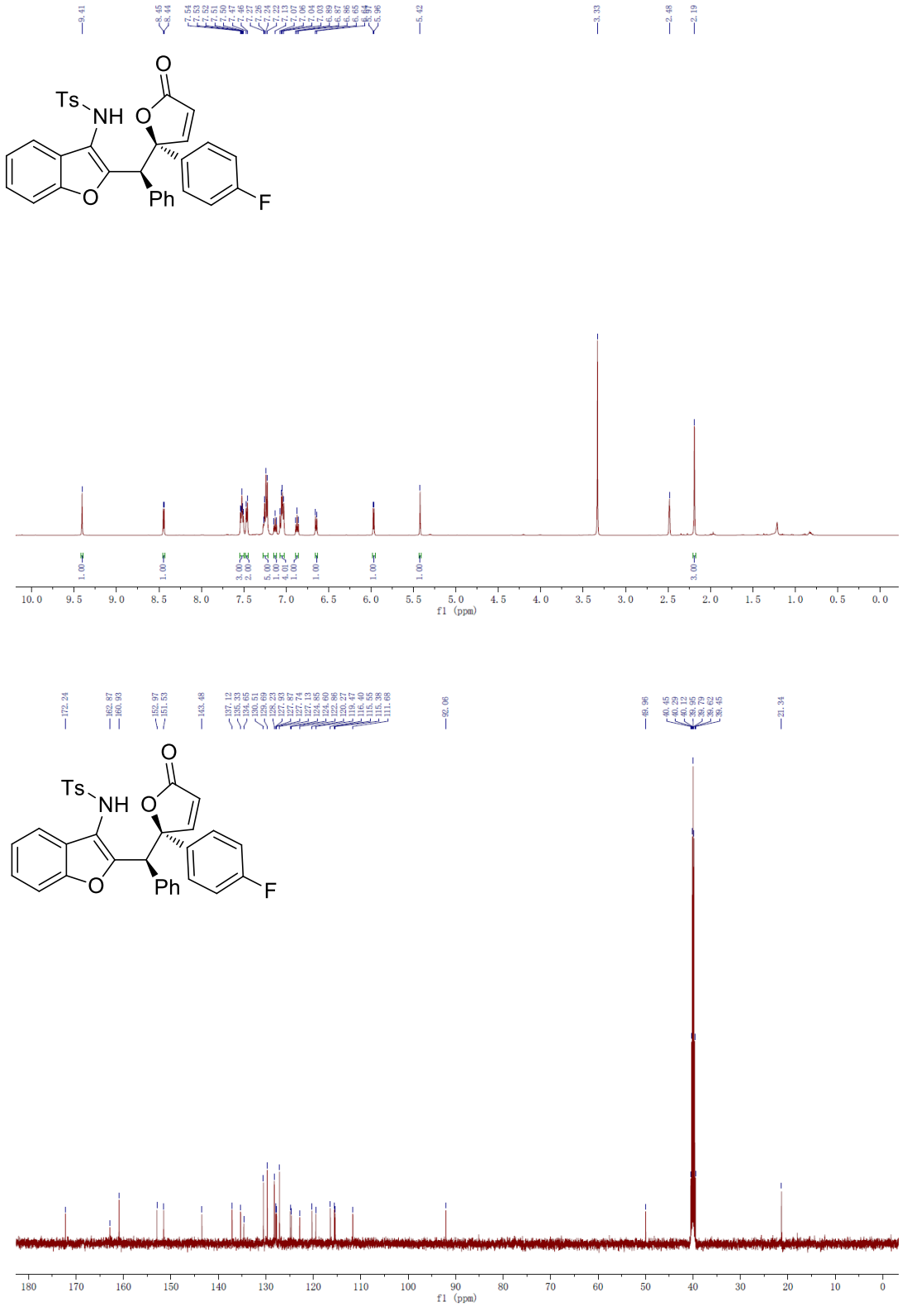


4-Methyl-*N*-(2-((*R*)-((*S*)-5-oxo-2-phenyl-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide (3ae)

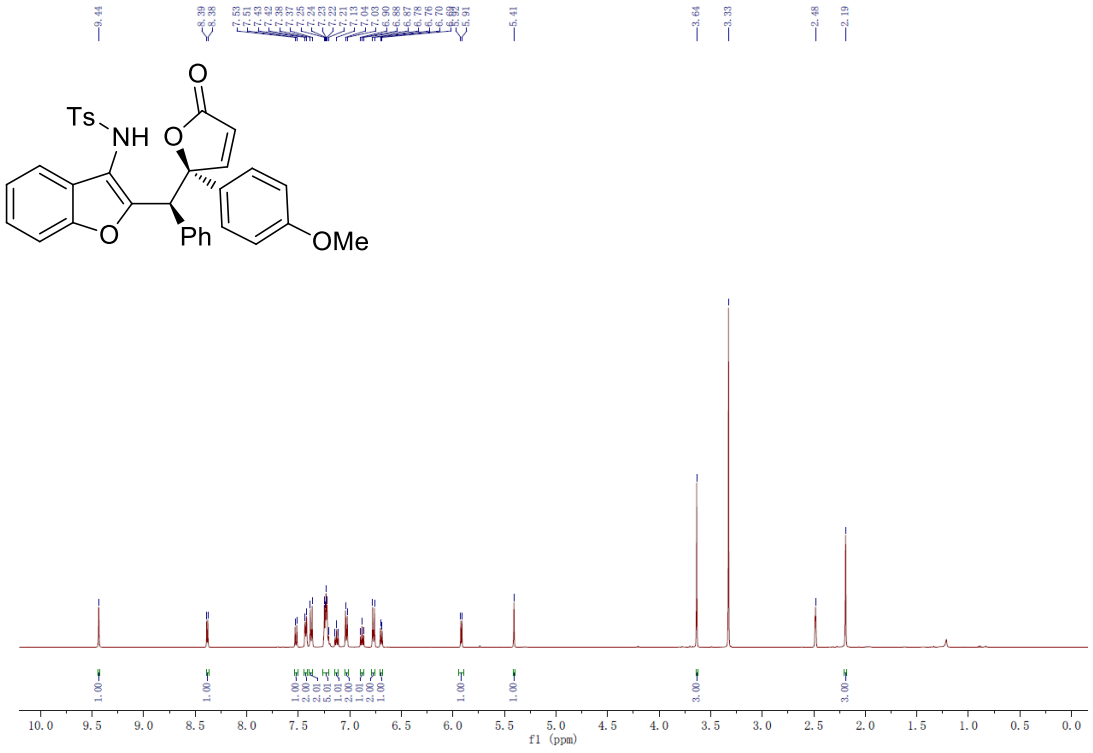


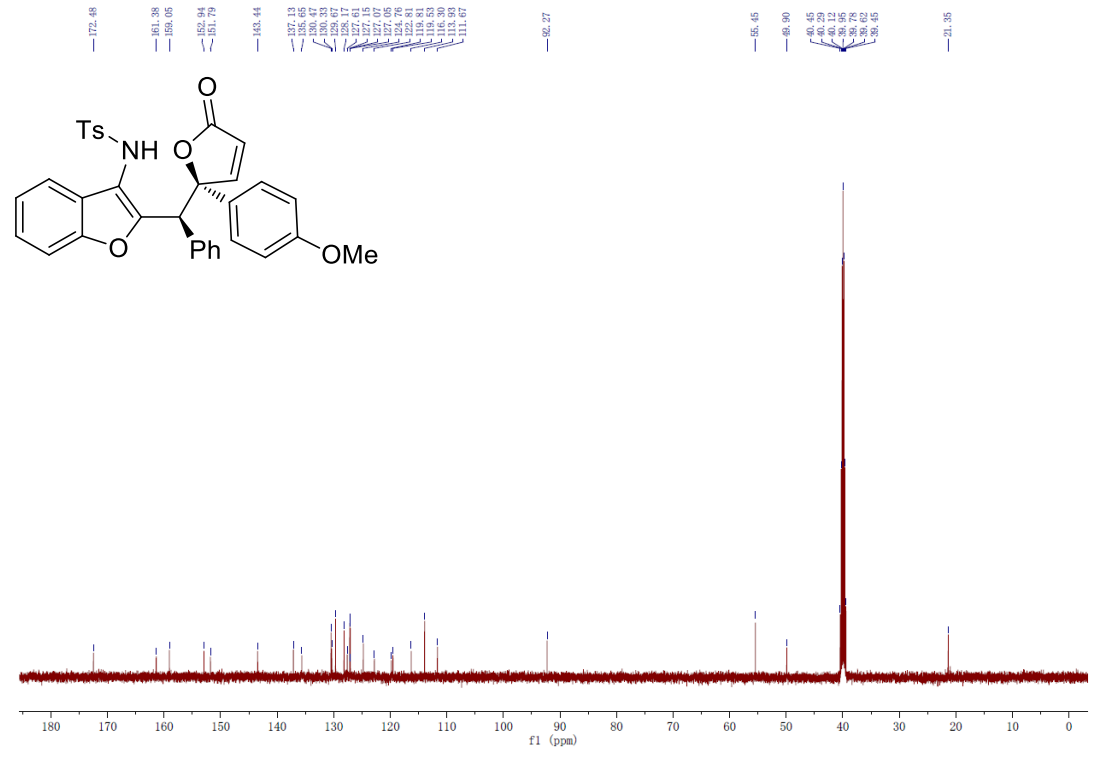


***N*-(2-((*R*)-((*S*)-2-(4-fluorophenyl)-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3af)**

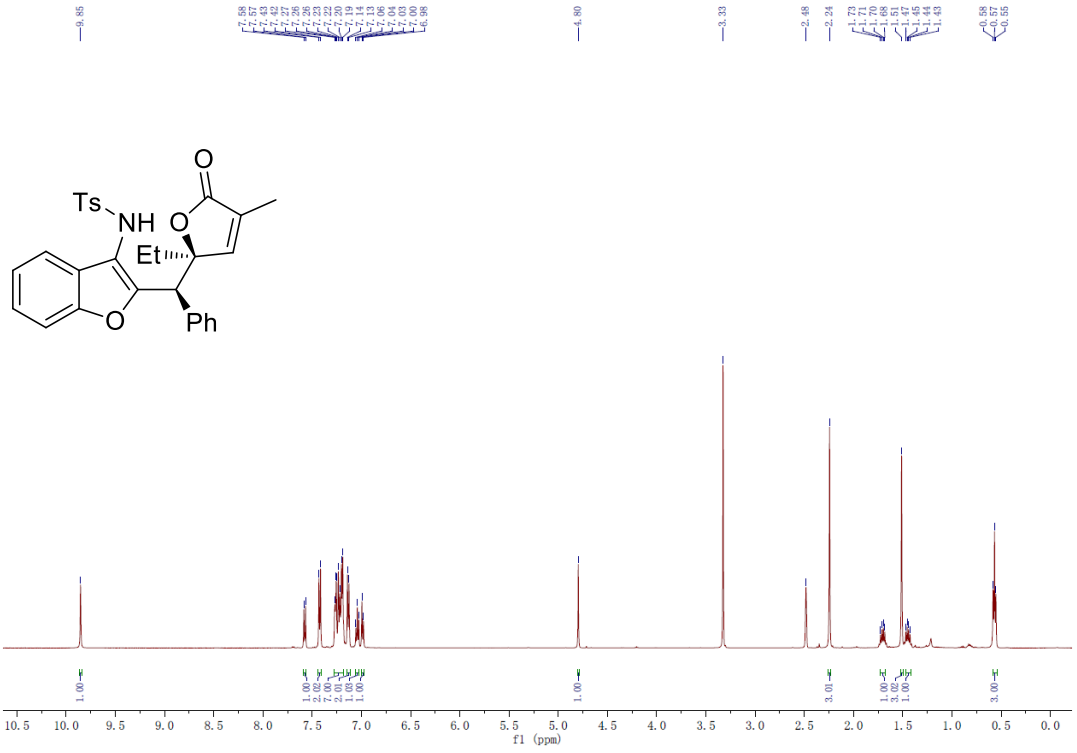


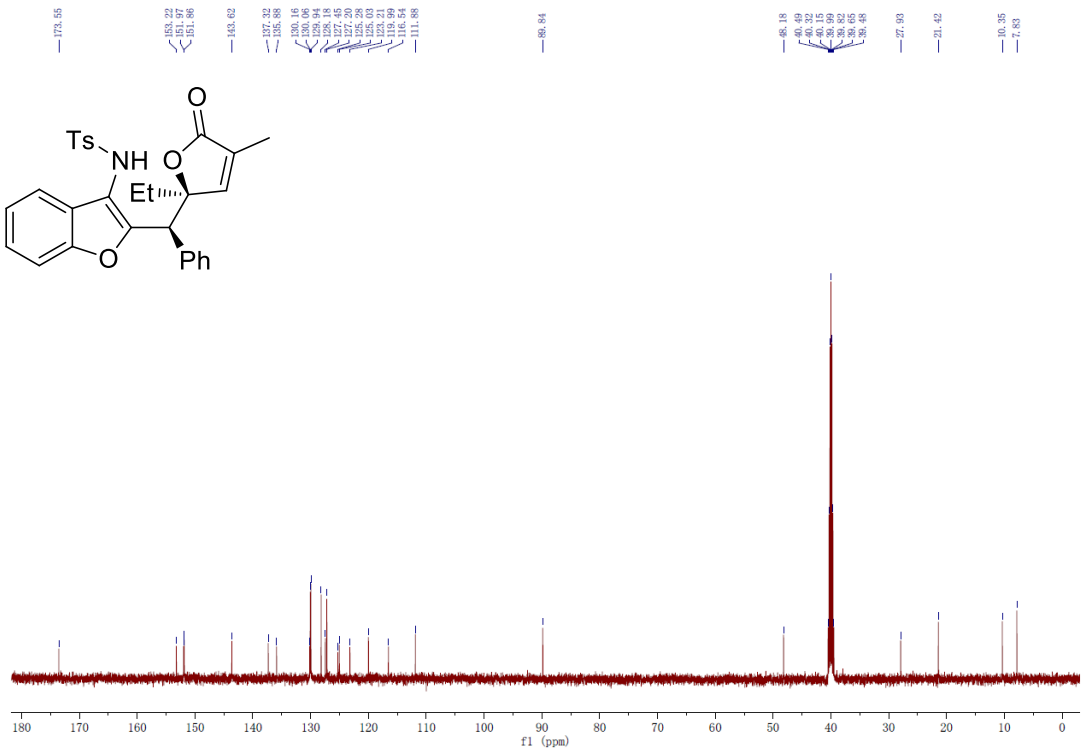
***N*-(2-((*R*)-((*S*)-2-(4-methoxyphenyl)-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl) benzofuran-3-yl)-4-methylbenzenesulfonamide (3ag)**



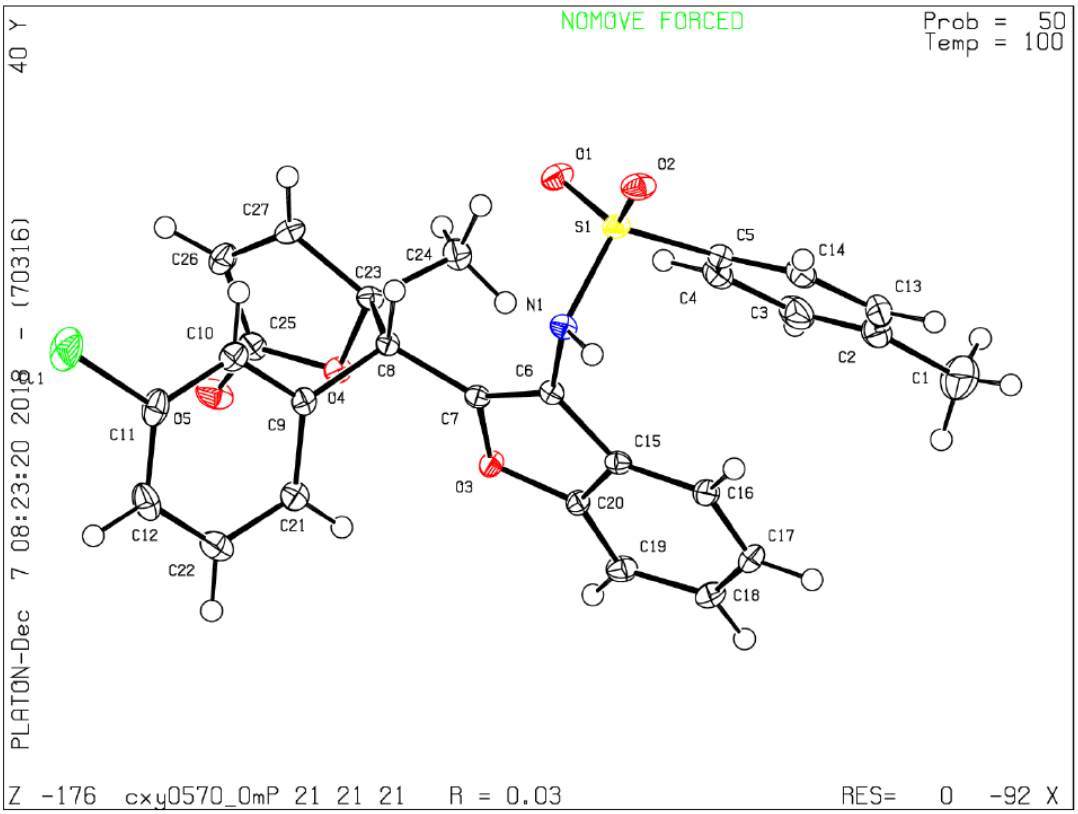


***N*-(2-((*R*)-((*S*)-2-ethyl-4-methyl-5-oxo-2,5-dihydrofuran-2-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide (3ah)**





H: X-ray Analysis



CCDC: 1905200 (**3ha**)

Table 1 Crystal data and structure refinement for 3ha.

Identification code	3ha		
Bond precision:	C-C = 0.0031 A		Wavelength = 0.71073
Cell:	a = 10.1603(5)	b = 10.1730(4)	c = 23.5179(10)
	alpha = 90	beta = 90	gamma = 90
Temperature:	100 K		

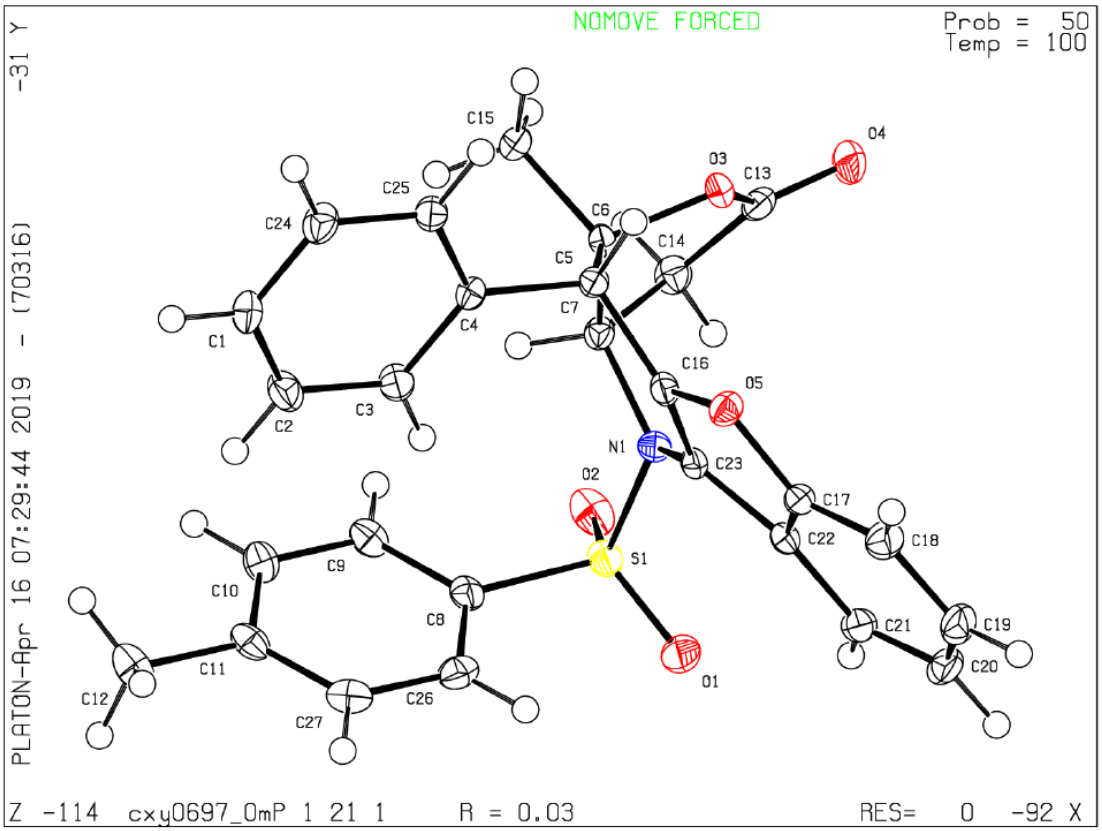
	Calculated	Reported
Volume	2430.83(18)	2430.83(18)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	$C_{27}H_{22}ClNO_5S$	$C_{27}H_{22}ClNO_5S$
Sum formula	$C_{27}H_{22}ClNO_5S$	$C_{27}H_{22}ClNO_5S$
Mr	507.97	507.96
Dx,g cm-3	1.388	1.388
Z	4	4
Mu (mm-1)	0.282	0.282
F000	1056.0	1056.0
F000'	1057.56	
h,k,lmax	13,13,30	13,13,30
Nref	5614[3181]	5612
Tmin,Tmax	0.898,0.921	0.692,0.746
Tmin'	0.898	

Correction method = # Reported T Limits: Tmin = 0.692 Tmax = 0.746
AbsCorr = MULTI-SCAN

Data completeness = 1.76/1.00 Theta(max) = 27.556

R(reflections) = 0.0274(5340) wR2(reflections) = 0.0674(5612)

S = 1.041 Npar = 319



CCDC: 1910685 (**4aa**)

Table 2 Crystal data and structure refinement for 4aa.

Identification code	**4aa**
Empirical formula	$C_{27}H_{23}NO_5S$
Formula weight	473.52
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.0757(11)
b/Å	10.4448(9)
c/Å	10.8094(12)
α/°	90
β/°	92.786(3)
γ/°	90
Volume/Å^3	1136.2(2)
Z	2
ρ_{calc}g/cm^3	1.384
μ/mm^{-1}	0.183
F(000)	496.0
Crystal size/mm^3	0.42 × 0.36 × 0.29
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.398 to 55.084
Index ranges	$-13 \leq h \leq 12$, $-13 \leq k \leq 13$, $-14 \leq l \leq 13$
Reflections collected	16350
Independent reflections	5233 [R_{int} = 0.0217, R_{sigma} = 0.0225]
Data/restraints/parameters	5233/1/310
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0280, wR_2 = 0.0705
Final R indexes [all data]	R_1 = 0.0293, wR_2 = 0.0714
Largest diff. peak/hole / e Å^{-3}	0.26/-0.23
Flack parameter	0.01(2)

I: Reference

1. Z. Q. Rong, L. C. Yang, S. Liu, Z. Yu, Y. N. Wang, Z. Y. Tan, R. Z. Huang, Y. Lan, and Y. Zhao, *J. Am. Chem. Soc.* **2017**, *139*, 15304.
2. B. Wu, Z. Yu, X. Gao, Y. Lan and Y. Zhou, *Angew. Chem. Int. Ed.* **2017**, *56*, 4006.