Formal nucleophilic pyrrolylmethylation via palladium-based auto-tandem catalysis: switchable regiodivergent synthesis and remote chirality transfer

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Supplementary Information

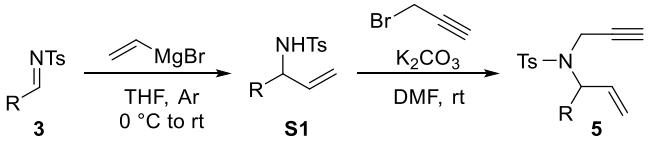
1. General methods

Unless otherwise noted, all reactions were carried out at ambient temperature; when the reactions required heating, the heat source was oil bath. ^{1}H NMR (400 or 600 MHz), ^{13}C NMR (100 or 150 MHz) and ^{19}F NMR (375 MHz) spectra were recorded on Varian INOVA-400/54, Agilent DD2-600/54 or Bruker Ascend^{TM} 400 instruments (Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution, unless otherwise noted). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, dd = double doublet, dt = double triplet; m = multiplet, brs = broad singlet and coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G2, Agilent G1969-85000 or Shimadzu LCMS-IT-TOF using a time-of-flight mass spectrometer equipped with electrospray ionization (ESI) source. X-ray diffraction experiments were carried out on an Agilent Xcalibur or Bruker APEX-II CCD diffractometer, and the data obtained were deposited at the Cambridge Crystallographic Data Centre (CCDC 2184605 and 2184606). In each case, enantiomeric excess was determined by HPLC (Agilent Technologies: 1220 Infinity II, 1200 Series, 1260 Infinity) analysis on a chiral column in comparison with authentic racemate, using a using a Daicel chiralpak IB Column (250 × 4.6 mm), Daicel chiralpak AS-H Column (250 × 4.6 mm), Daicel Chiralpak AD-H Column (250 × 4.6 mm) or Daicel Chiralpak IC Column (250 × 4.6 mm). UV detection was monitored at 254 nm. The specific optical rotation was obtained from Rudolph Research Analytical Autopol I automatic polarimeter in $CHCl_3$ solution at 25 °C. The melting point was obtained from WRX-4 Mel-Temp apparatus. Column chromatography was performed on silica gel (200–300 mesh) eluting with ethyl acetate (EtOAc)/petroleum ether. TLC was performed on glass-backed silica plates. UV light, I_2, and solution of potassium permanganate were used to visualize products or starting materials. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether and EtOAc were distilled. Experiments involving moisture and/or air sensitive components were performed under a positive pressure of argon in oven-dried glassware equipped with a rubber septum inlet. Toluene was freshly distilled from CaH_2 under an atmosphere of dry argon. Dry solvents and liquid reagents were transferred by oven-dried syringe.

2. Preparation and characterization of starting materials

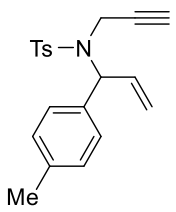
The propargylamines **1**,[1a,1b] allylic carbonate **2**,[1c] aldehyde imines **3**,[2] 1,6-enynes **5**,[3a,3b] and **9**[3c,3d] were prepared according to the literature procedure. Compounds **1a**–**c**,[1a,1b] **2**,[1c] **3a**–**m**,[2] **5a**,[3a] **5b**–**c**,[3b] **9**[3c] and **17**[3d] are know compounds and the spectroscopic data were consistent with the literature report.

2.1 Preparation of 1,6-enyne 5



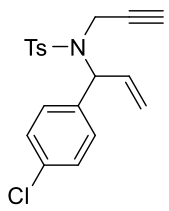
To a solution of aldimine **3** (4.0 mmol) in distilled THF (10.0 mL) was added vinylmagnesium bromide (5.0 mL, 1.25 equiv, 5.0 mmol, 1 M in THF) dropwise under argon atmosphere at 0 °C. The mixture was stirred for 2 h at room temperature. After completion (monitored by TLC), the reaction mixture was quenched with saturated NH_4Cl aqueous solution and extracted with EtOAc (20.0 mL × 3). The combined organic layers were washed with brine (10.0 mL × 2), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give **S1**. The allylic amine **S1** (2.0 mmol) was dissolved in DMF (5.0 mL) and potassium carbonate (0.30 g, 1.1 equiv, 2.2 mmol) was added. The mixture was stired at room temperature for 10 min before propargyl bromide (0.20 mL, 1.1 equiv, 2.2 mmol) was added. The mixture was stirred at room temperature overnight. After completion (monitored by TLC), the reaction was quenched with water and extracted with EtOAc (20.0 mL × 3). The combined organic layers were washed with brine (10.0 mL × 2), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give 1,6-enyne substrate **5**.

Characterization for selected 1,6-enynes 5

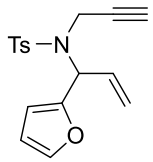


4-Methyl-*N*-(prop-2-yn-1-yl)-*N*-(1-(*p*-tolyl)allyl)benzenesulfonamide (5d): white solid, 400 mg, 72% yield for two steps; mp 74–76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.0 Hz, 3H), 7.18 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.32–6.03 (m, 1H), 5.57 (d, J = 7.6 Hz, 1H), 5.23 (d, J = 10.2 Hz, 1H), 5.15 (d, J = 17.0 Hz, 1H), 4.14 (dd, J = 18.6, 2.4 Hz, 1H), 3.76 (dd, J = 18.6, 2.4 Hz, 1H), 2.42 (s, 3H), 2.33 (s, 3H), 2.03 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.3, 137.8, 137.7, 134.8, 134.2, 129.24, 129.20, 128.1, 127.9, 119.0, 79.5, 72.6, 63.6, 33.8, 21.6, 21.1;

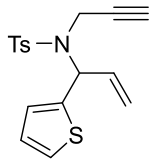
HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{21}NO_2SNa^+$ 362.1185; Found 362.1192.



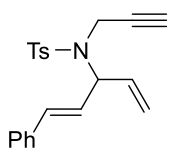
***N*-(1-(4-Chlorophenyl)allyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (5e)**: white solid, 430 mg, 79% yield for two steps; mp 103–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77 (d, J = 8.2 Hz, 2H), 7.33–7.17 (m, 6H), 6.23–6.07 (m, 1H), 5.56 (d, J = 7.6 Hz, 1H), 5.27 (d, J = 10.4 Hz, 1H), 5.15 (d, J = 17.0 Hz, 1H), 4.13 (dd, J = 18.6, 2.6 Hz, 1H), 3.81 (dd, J = 18.6, 2.6 Hz, 1H), 2.43 (s, 3H), 2.05 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.5, 137.4, 136.4, 133.9, 133.5, 129.6, 129.3, 128.7, 127.8, 119.8, 79.1, 73.0, 63.1, 34.0, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{18}{}^{35}ClNO_2SNa^+$ 382.0639; Found 382.0634; Calcd for $C_{19}H_{18}{}^{37}ClNO_2SNa^+$ 384.0609; Found 384.0608.



***N*-(1-(Furan-2-yl)allyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (5f)**: white solid, 482 mg, 76% yield for two steps; mp 59–61 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.26–7.24 (m, 1H), 7.02–6.80 (m, 2H), 6.32–6.12 (m, 1H), 5.81 (d, J = 7.0 Hz, 1H), 5.38–5.21 (m, 2H), 4.17 (dd, J = 18.6, 2.4 Hz, 1H), 3.88 (dd, J = 18.6, 2.4 Hz, 1H), 2.43 (s, 3H), 2.05 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.5, 141.6, 137.4, 133.7, 129.3, 127.8, 127.1, 126.9, 126.2, 119.4, 79.3, 72.6, 59.6, 33.4, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{17}NO_3SNa^+$ 338.0821; Found 338.0829.

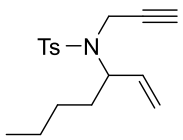


4-Methyl-*N*-(prop-2-yn-1-yl)-*N*-(1-(thiophen-2-yl)allyl)benzenesulfonamide (5g): white solid, 476 mg, 73% yield for two steps; mp 62–64 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79 (d, J = 8.4 Hz, 2H), 7.30–7.27 (m, 2H), 7.26 (d, J = 4.0 Hz, 1H), 6.32–6.26 (m, 1H), 6.24–6.19 (m, 1H), 6.18–6.03 (m, 1H), 5.70 (d, J = 6.0 Hz, 1H), 5.34 (d, J = 1.6 Hz, 1H), 5.33–5.25 (m, 1H), 4.03 (dd, J = 18.4, 2.4 Hz, 1H), 3.94 (dd, J = 18.4, 2.4 Hz, 1H), 2.42 (s, 3H), 1.97 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.7, 143.3, 142.6, 137.3, 132.5, 129.2, 127.8, 119.4, 110.3, 109.9, 78.9, 71.9, 57.3, 33.7, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{17}NO_2S_2Na^+$ 354.0593; Found 354.0601.

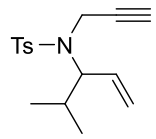


(*E*)-4-Methyl-*N*-(1-phenylpenta-1,4-dien-3-yl)-*N*-(prop-2-yn-1yl)benzenesulfonamide (5h): white solid, 325 mg, 52% yield for two steps; mp 53–55 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80 (d, J = 8.3 Hz, 2H), 7.36–7.19 (m, 7H), 6.38 (d, J = 1.2 Hz, 1H), 6.21 (dd, J = 16.0, 6.8 Hz, 1H), 6.07–5.85 (m, 1H), 5.31–5.21 (m, 2H), 5.17–5.07 (m,

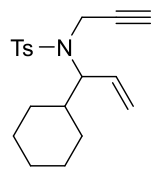
1H), 4.18 (dd, *J* = 18.4, 2.4 Hz, 1H), 4.08 (dd, *J* = 18.4, 2.4 Hz, 1H), 2.37 (s, 3H), 2.16 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 143.4, 137.5, 136.2, 134.8, 133.8, 129.3, 128.5, 128.0, 127.8, 126.5, 125.5, 119.0, 79.9, 72.8, 61.8, 33.7, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{21}NO_2SNa^+$ 374.1185; Found 374.1186.



***N*-(Hept-1-en-3-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (5i)**: colorless oil, 388 mg, 65% yield for two steps; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.78 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.81–5.59 (m, 1H), 5.23–4.83 (m, 2H), 4.40–4.28 (m, 1H), 4.10 (dd, *J* = 18.6, 2.4 Hz, 1H), 3.90 (dd, *J* = 18.6, 2.4 Hz, 1H), 2.42 (s, 3H), 2.14 (t, *J* = 2.4 Hz, 1H), 1.71–1.58 (m, 2H), 1.36–1.16 (m, 4H), 0.83 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.2, 137.8, 136.0, 129.3, 127.6, 117.7, 79.9, 72.1, 60.0, 32.4, 31.4, 28.4, 22.3, 21.5, 13.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{23}NO_2SNa^+$ 328.1342; Found 328.1344.

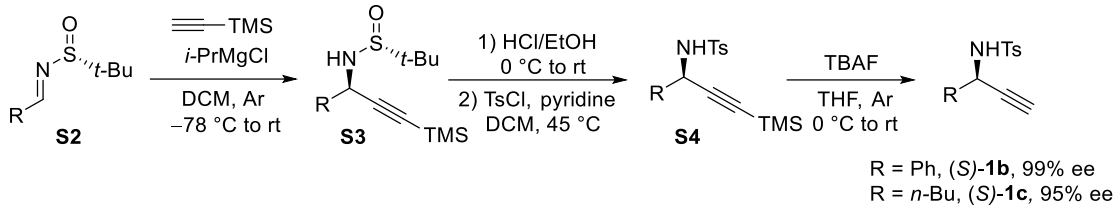


4-Methyl-*N*-(4-methylpent-1-en-3-yl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (5j): white solid, 412 mg, 68% yield for two steps; mp 35–37 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 9.2 Hz, 2H), 5.83–5.65 (m, 1H), 5.07 (d, *J* = 10.4 Hz, 1H), 4.98 (d, *J* = 17.2 Hz, 1H), 4.05 (dd, *J* = 18.6, 2.6 Hz, 1H), 3.99 (dd, *J* = 18.6, 2.6 Hz, 1H), 3.94–3.86 (m, 1H), 2.40 (s, 3H), 2.13 (t, *J* = 2.6 Hz, 1H), 2.03–1.87 (m, 1H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.1, 137.7, 134.3, 129.2, 127.7, 119.2, 79.6, 72.5, 67.6, 33.1, 29.7, 21.5, 20.22, 20.17; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{21}NO_2SNa^+$ 314.1185; Found 314.1194.



***N*-(1-Cyclohexylallyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (5k)**: white solid, 476 mg, 78% yield for two steps; mp 69–72 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.90–5.59 (m, 1H), 5.05 (d, *J* = 10.2 Hz, 1H), 4.95 (d, *J* = 17.2 Hz, 1H), 4.05 (dd, *J* = 18.4, 2.6 Hz, 1H), 4.02–3.93 (m, 2H), 2.40 (s, 3H), 2.13 (t, *J* = 2.6 Hz, 1H), 2.01–1.86 (m, 1H), 1.81–1.59 (m, 4H), 1.27–1.10 (m, 4H), 1.02–0.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.1, 137.7, 134.0, 129.2, 127.7, 119.2, 79.6, 72.3, 66.5, 38.7, 33.0, 30.6, 30.3, 26.2, 26.1, 25.8, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{25}NO_2SNa^+$ 354.1498; Found 354.1507.

2.2 Preparation of chiral propargyl amine (*S*)-1



To a stirred solution of isopropylmagnesium chloride (10.0 mL, 2.0 equiv, 20.0 mmol, 2 M in THF) was added ethynyltrimethylsilane (3.4 mL, 2.4 equiv, 24 mmol) at 0 °C under argon atmosphere. The mixture was stirred for 30 min before warmed to room temperature, and stirred for another 10 min. The freshly prepared trimethylsilylethynylmagnesium chloride solution was added to a stirred solution of (R_S)-*N*-benzylidene-2-methylpropane-2-sulfinamide **S2a** (2.09 g, 10.0 mmol) in dry DCM (50.0 mL) dropwise at –78 °C under argon atmosphere. The mixture was stirred at –78 °C for 2 h before warmed gradually to room temperature and stirred for another 5 h. After completion (monitored by TLC), the reaction was quenched with saturated NH_4Cl solution and extracted with EtOAc (20.0 mL × 3). The combined organic layers were washed with brine (10.0 mL × 2), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give **S3a**: 2.50 g (8.14 mmol), as a white solid, 81% yield.

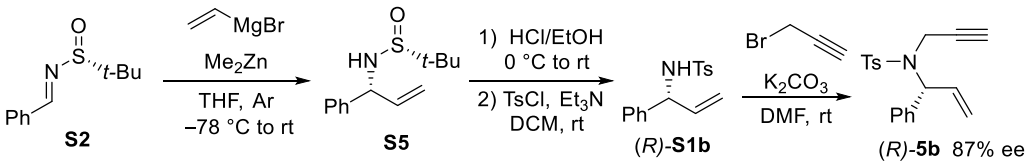
Hydrogen chloride ethanol solution (4.0 mL, 2.0 equiv, 16 mmol, 4 M) was added to a stirred solution of **S3a** (2.46 g, 8.00 mmol) in ethanol (20.0 mL) at 0 °C. The mixture was stirred at room temperature for 2 h. After completion (monitored by TLC), ethanol was removed in vacuo. The residue was diluted with EtOAc (50.0 mL) and basified with 10% sodium hydroxide solution to pH 11. The organic layer was separated, washed with brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was dissolved in DCM (70.0 mL), tosyl chloride (2.30 g, 1.5 equiv, 12.0 mmol) and pyridine (1.9 mL, 3.0 equiv, 24 mmol) was added. The reaction mixture was stirred at 45 °C overnight. After completion, the reaction was quenched with water and extracted with DCM (20.0 mL × 3). The combined organic layers were washed with brine (10.0 mL × 2), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10 to 1/5) to give **S4a**: 1.70 g (4.76 mmol), as a white solid, 59% yield.

To a stirred solution of **S4a** (1.80 g, 5.03 mmol) in THF (20.0 mL) was added tetrabutylammonium fluoride solution (6.0 mL, 1.2 equiv, 6.0 mmol, 1 M in THF) under argon atmosphere at 0 °C. The mixture was stirred at 0 °C for 10 min. After completion (monitored by

TLC), the reaction mixture was quenched with saturated NH_4Cl solution and extracted with EtOAc (20.0 mL × 3). The combined organic layers were washed with brine (10.0 mL × 2), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10 to 1/5) to give crude product (*S*)-**1b** as a white solid. The solid was dissolved in hot EtOAc (10.0 mL) and petroleum ether (5.0 mL), and the resultant solution was gradually cooled to room temperature and left for 1 h. The solid (*S*)-**1b** was collected by filtration: 1.10 g (3.85 mmol), as a whilte solid, 77% yield; $[\alpha]_D^{25}$ = 27.0 (*c* = 0.46 in $CHCl_3$); 99% ee, determined by HPLC analysis (Daicel chiralpak IB, *n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, l = 220 nm) t_R = 21.08 min (major), t_R = 23.23 min (minor). The NMR spectra were consistent with the literature report.[1b]

The chiral propargyl amine (*S*)-**1c** was obtained as a whilte solid via the same procedure described above: 73% yield; $[\alpha]_D^{25}$ = 44.3 (*c* = 0.56 in $CHCl_3$); 95% ee, determined by HPLC analysis (Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, l = 220 nm) t_R = 14.54 min (major), t_R = 17.34 min (minor). The NMR spectra were consistent with the literature report.[1b]

2.3 Procedure for preparation of enantioenriched 1,6-enyne (*R*)-5b



To a stirred solution of dimethylzinc (12.8 mL, 1.7 equiv, 12.8 mmol, 1 M in toluene) was added vinylmagnesium bromide (11.3 mL, 1.5 equiv, 11.3 mmol) at 0 °C under argon. The mixture was stirred at 0 °C for 30 min. The freshly prepared divinylzinc solution was added to a stirred solution of (R_S)-*N*-benzylidene-2-methylpropane-2-sulfinamide **S2** (1.57 g, 7.50 mmol) in distilled THF (35.0 mL) dropwise at –78 °C under argon atmosphere. The mixture was stirred at –78 °C for 2 h before warmed gradually to room temperature and stirred for another 5 h. After completion, the reaction was quenched with 0.5 M hydrochloric acid solution and extracted with EtOAc (20.0 mL × 3). The combined organic layers were washed with brine (10.0 mL × 2), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give **S5**: 1.30 g (5.48 mmol), as a colorless oil, 73% yield.

Hydrogen chloride ethanol solution (2.5 mL, 2.0 equiv, 10 mmol, 4M) was added to a stirred

solution of **S5** (1.19 g, 5.02 mmol) in ethanol (15.0 mL) at 0 °C. The mixture was stirred at room temperature for 2 h. After completion (monitored by TLC), ethanol was removed in vacuo. The residue was diluted with EtOAc (50.0 mL) and basified with 10% sodium hydroxide solution to pH 11. The organic layer was separated, washed with brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was dissolved in DCM (60.0 mL), tosyl chloride (1.14 g, 1.2 equiv, 6.00 mmol) and triethylamine (1.4 mL, 2.0 equiv, 10 mmol) were added. The mixture was stirred at room temperature overnight. After completion (monitored by TLC), the reaction was quenched with water and extracted with DCM (20.0 mL × 3). The combined organic layers were washed with brine (10.0 mL × 2), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10 to 1/5) to give (*R*)-**S1b**: 1.03 g (3.58 mmol), as a yellow solid, 72% yield.

(*R*)-**S1b** (0.86 g, 3.0 mmol) and potassium carbonate (0.46 g, 1.1 equiv, 3.3 mmol) were added to DMF (10.0 mL). The mixture was stired at room temperature for 10 min, and propargyl bromide (0.28 mL, 1.1 equiv, 3.3 mmol) was added. The mixture was stirred at room temperature overnight. After completion (monitored by TLC), the reaction was quenched with water and extracted with EtOAc (10.0 mL × 3). The combined organic layers were washed with brine (10.0 mL × 2), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give (*R*)**-5b**: 0.80 g (2.4 mmol), as a whilte solid, 82% yield; $[\alpha]_D^{25}$ = 16.9 (*c* = 0.49 in $CHCl_3$); 87% ee, determined by HPLC analysis (Daicel chiralpak AS-H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm) t_R = 16.56 min (major), t_R = 23.75 min (minor). The NMR spectra were consistent with the literature report.[3b]

1 (*a*) K. T. Sylvester and P. J. Chirik, *J. Am. Chem. Soc.*, 2009, **131**, 8772; (*b*) N. Li, P. Jia and Y. Huang, *Chem. Commun.*, 2019, **55**, 10976; (*c*) O. Lahtigui, F. Emmetiere, W. Zhang, L. Jirmo, S. Toledo-Roy, J. C. Hershberger, J. M. Macho and A. J. Grenning, *Angew. Chem., Int. Ed.*, 2016, **55**, 15792.

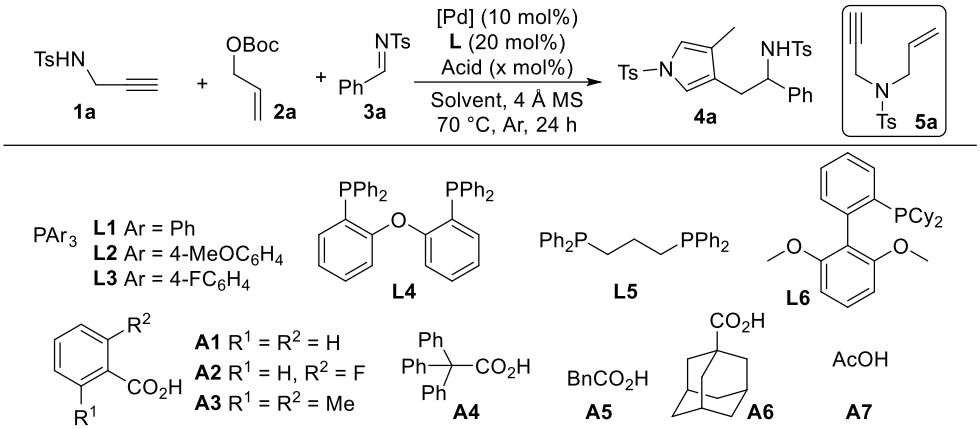
2 (*a*) H. Cai, Y. Zhou, D. Zhang, J. Xu and H. Liu, *Chem. Commun.*, 2014, **50**, 14771; (*b*) S. Morales, F. G. Guijarro, J. L. García Ruano and M. B. Cid, *J. Am. Chem. Soc.*, 2014, **136**, 1082.

3 (*a*) N. Cabrera-Lobera, M. T. Quirós, W. W. Brennessel, M. L. Neidig, E. Buñuel and D. J. Cárdenas, *Org. Lett.*, 2019, **21**, 6552; (*b*) D. Susanti, L.-J. Liu, W. Rao, S. Lin, D.-L. Ma, C.-H. Leung and P.

W. H. Chan, *Chem. Eur. J.*, 2015, **21**, 9111; (*c*) J.-P. Zhao, S.-C. Chan and C.-Y. Ho, *Tetrahedron*, 2015, **71**, 4426; (*d*) F. Malmedy and T. Wirth, *Eur. J. Org. Chem.*, 2017, 786.

3. Detailed screening conditions

Table S3.1. Detailed screening conditions for synthesis of **4a**[a]

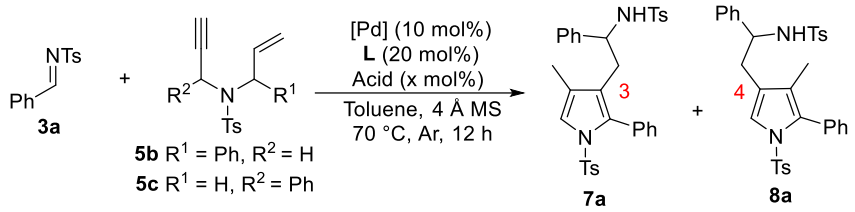


Entry	[Pd]	L	Acid	x	Solvent	Yield (%)[b]
1	Pd_2dba_3	**L1**	**A1**	20	toluene	54
2	Pd_2dba_3	**L2**	**A1**	20	toluene	53
3	Pd_2dba_3	**L3**	**A1**	20	toluene	NR
4	Pd_2dba_3	**L4**	**A1**	20	toluene	NR
5	Pd_2dba_3	**L5**	**A1**	20	toluene	NR
6	Pd_2dba_3	**L6**	**A1**	20	toluene	trace
7	$Pd(PPh_3)_4$	/	**A1**	0	toluene	**5a**, 95
8	$Pd(PPh_3)_4$	/	**A1**	10	toluene	50
9	$Pd(PPh_3)_4$	/	**A1**	20	toluene	58
10	$Pd(PPh_3)_4$	/	**A1**	40	toluene	68
11	$Pd(PPh_3)_4$	/	**A1**	80	toluene	68
12	$Pd(PPh_3)_4$	/	**A1**	100	toluene	64
13	**$Pd(PPh_3)_4$**	/	**A2**	**40**	**toluene**	**86**
14	$Pd(PPh_3)_4$	/	**A3**	40	toluene	54
15	$Pd(PPh_3)_4$	/	**A4**	40	toluene	65
16	$Pd(PPh_3)_4$	/	**A5**	40	toluene	66

17	$Pd(PPh_3)_4$	/	**A6**	40	toluene	47
18	$Pd(PPh_3)_4$	/	**A7**	40	toluene	50
19	$Pd(PPh_3)_4$	/	**A2**	40	THF	trace
20	$Pd(PPh_3)_4$	/	**A2**	40	xylene	41
21[c]	$Pd(PPh_3)_4$	/	**A2**	40	toluene	70
22[d]	$Pd(PPh_3)_4$	/	**A2**	40	toluene	80
22[e]	$Pd(PPh_3)_4$	/	**A2**	40	toluene	80

[a] Unless noted otherwise, reactions were performed with **1a** (0.1 mmol), **2a** (0.1 mmol), **3a** (0.05 mmol), [Pd] source (10 mol%), **L** (20 mol%), acid (x mol%) and 4 Å MS (20 mg) in degassed dry solvent (0.5 mL) at 70 °C for 24 h under Ar. [b] Yield of isolated product **4a**. [c] At 60 °C. [d] At 80 °C. [e] Without 4 Å MS. NR = no reaction.

Table S3.2. Detailed screening conditions for the regiodivergent tandem reaction[a]



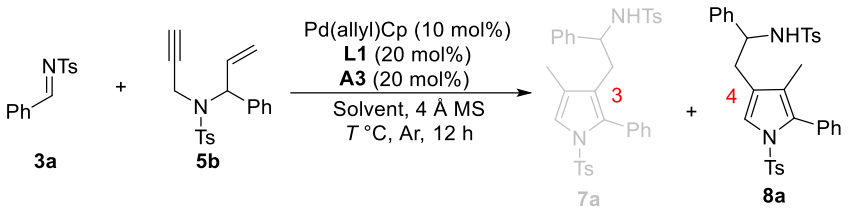
Entry	[Pd]	**L**	Acid	x	Yield (%)[b]	rr[c]
1	$Pd(PPh_3)_4$	/	**A1**	20	75	52:48
2	$Pd(PPh_3)_4$	/	**A2**	20	65	63:37
3	$Pd(PPh_3)_4$	/	**A3**	20	60	54:46
4	$Pd(PPh_3)_4$	/	**A4**	20	52	69:31
5	$Pd(PPh_3)_4$	/	**A1**	50	90	75:25
6	**$Pd(PPh_3)_4$**	/	**A1**	**100**	**91**	**94:6**
7	$Pd(OAc)_2$	/	**A1**	20	48	60:40
8	$[Pd(allyl)Cl]_2$	PPh_3	**A1**	20	36	67:33
9	Pd(allyl)Cp	PPh_3	**A1**	20	71	13:87
10	$Pd(PPh_3)_2Cl_2$	PPh_3	**A1**	20	NR	/
11	$Pd(MeCN)_2Cl_2$	PPh_3	**A1**	20	NR	/
12	$Pd(MeCN)_2(BF_4)_2$	PPh_3	**A1**	20	NR	/

13	Pd(allyl)Cp	PPh_3	**A2**	20	80	40:60
14	**Pd(allyl)Cp**	PPh_3	**A3**	**20**	**82**	**8:92**
15	Pd(allyl)Cp	PPh_3	**A4**	20	47	24:76
16	Pd(allyl)Cp	PPh_3	**A5**	20	trace	/
17	Pd(allyl)Cp	PPh_3	**A6**	20	trace	/
18	Pd(allyl)Cp	PPh_3	**A3**	10	46	10:90
19	Pd(allyl)Cp	PPh_3	**A3**	40	56	22:78
20	Pd(allyl)Cp	PPh_3	**A3**	60	68	33:67
21	Pd(allyl)Cp	PPh_3	**A3**	100	62	44:56
22[d]	$Pd(PPh_3)_4$	/	**A1**	100	87	96:4
23[d]	Pd(allyl)Cp	PPh_3	**A3**	20	73	30:70
24[e]	$Pd(PPh_3)_4$	/	**A2**	40	80	95:5

[a] Unless noted otherwise, reactions were performed with 1,6-enyne **5b** (0.1 mmol), imine **3a** (0.05 mmol), [Pd] source (10 mol%), **L** (20 mol%), acid (x mol%) and 4 Å MS (20 mg) in degassed dry toluene (0.5 mL) at 70 °C for 12 h under Ar. [b] Isolated yield. [c] rr = **7a**:**8a**, determined by ^{1}H-NMR analysis. [d] With **5c** (0.1 mmol) instead of **5b**. [e] With **1b** (0.1 mmol) and **2a** (0.1 mmol) instead of **5b** at 80 °C for 96 h.

After identifying the optimal palladium source [Pd(allyl)Cp], acid additive (**A3**) for the synthesis of **8a**, other reaction parameters, such as solvent, temperature and concentration were further screened. The results were summarized in Table S3.3.

Table S3.3. Detailed screening conditions for the synthesis of **8a**[a]

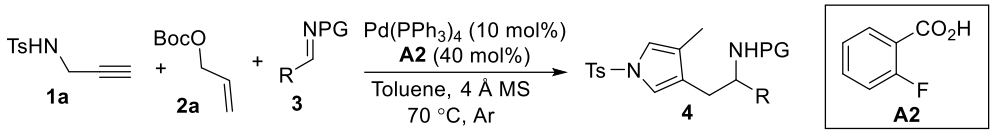


Entry	Solvent	*T* (°C)	Conc.	Yield (%)[b]	rr[c]
1	toluene	60	0.1 M	bad conv.	/
2	toluene	60	0.2 M	38	16:84
3	toluene	70	0.05 M	bad conv.	/
4	toluene	70	0.2 M	66	7:97

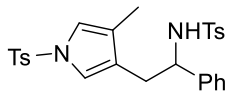
5	toluene	80	0.1 M	55	27:73
6	toluene	80	0.2 M	48	16:84
7	THF	70	0.1 M	trace	/
8	xylene	70	0.1 M	60	8:92
9	$PhCF_3$	70	0.1 M	43	19:81

[a] Unless noted otherwise, reactions were performed with 1,6-enyne **5b** (0.1 mmol), imine **3a** (0.05 mmol), Pd(allyl)Cp (10 mol%), PPh_3 (20 mol%), **A3** (20 mol%) and 4 Å MS (20 mg) in degassed dry solvent for 12 h under Ar. [b] Isolated yield of **8a**. [c] rr = **7a**:**8a**, determined by ^1H NMR analysis.

4. General procedure for synthesis of products 4

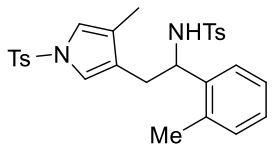


General procedure A: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **1a** (42.0 mg, 0.201 mmol), allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200 mmol), aldimine **3** (0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h to 96 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5 to 1/4) to give product **4**.

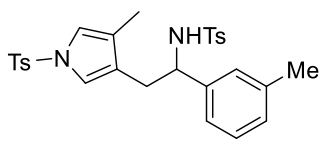


Synthesis of 4a: General procedure A: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl)benzene-sulfonamide **1a** (42.0 mg, 0.201 mmol), allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200 mmol), *N*-benzylidene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4a**: 43.7 mg (0.0859 mmol), as a white solid, 86%

yield; mp 76–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.63 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 9.8 Hz, 2H), 7.20–7.07 (m, 5H), 7.02–6.89 (m, 2H), 6.74–6.70 (m, 1H), 6.67–6.60 (m, 1H), 4.72 (d, J = 6.0 Hz, 1H), 4.31 (dt, J = 6.8, 6.6 Hz, 1H), 2.72 (d, J = 7.0 Hz, 2H), 2.40 (s, 3H), 2.38 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.8, 143.3, 140.3, 136.9, 136.1, 129.9, 129.4, 128.4, 127.6, 127.0, 126.7, 126.5, 124.2, 123.6, 119.3, 118.4, 57.5, 33.7, 21.6, 21.5, 9.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{28}N_2O_4S_2Na^+$ 531.1383; Found 531.1383.

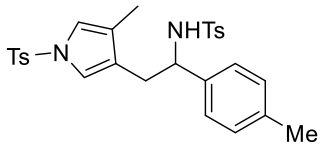


Synthesis of 4b: General procedure A: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl) benzenesulfonamide **1a** (42.0 mg, 0.201 mmol), allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200 mmol), 4-methyl-*N*-(2-methylbenzylidene)benzenesulfonamide **3b** (27.3 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4b**: 48.5 mg (0.0928 mmol), as a white solid, 93% yield; mp 49–50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 6.99–6.94 (m, 1H), 6.94–6.90 (m, 2H), 6.82 (d, J = 7.2 Hz, 1H), 6.68–6.63 (m, 1H), 6.54 (d, J = 2.4 Hz, 1H), 4.84 (d, J = 6.0 Hz, 1H), 4.48 (dt, J = 6.8, 6.4 Hz, 1H), 2.86–2.59 (m, 2H), 2.33 (s, 3H), 2.28 (s, 3H), 1.83 (s, 3H), 1.57 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.9, 143.1, 138.6, 136.9, 136.1, 134.8, 130.1, 129.9, 129.3, 127.2, 126.9, 126.7, 126.3, 125.8, 124.3, 123.6, 119.4, 118.2, 53.1, 33.0, 21.6, 21.4, 18.8, 9.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{30}N_2O_4S_2Na^+$ 545.1539; Found 545.1537.

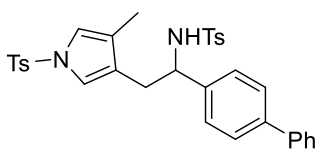


Synthesis of 4c: General procedure A: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl) benzenesulfonamide **1a** (42.0 mg, 0.201 mmol), allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200 mmol), 4-methyl-*N*-(3-methylbenzylidene)benzenesulfonamide **3c** (27.3 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and

monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4c**: 36.8 mg (0.0704 mmol), as a white solid, 70% yield; mp 58–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.23–7.18 (m, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.99–6.93 (m, 1H), 6.89 (d, J = 7.6 Hz, 1H), 6.69 (d, J = 7.6 Hz, 1H), 6.65–6.59 (m, 3H), 4.75–4.63 (m, 1H), 4.20 (d, J = 6.8 Hz, 1H), 2.63 (d, J = 7.0 Hz, 2H), 2.32 (s, 3H), 2.30 (s, 3H), 2.11 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.9, 143.4, 138.9, 137.2, 136.3, 135.0, 130.3, 130.1, 129.5, 127.4, 127.1, 126.9, 126.5, 126.0, 124.5, 123.8, 119.6, 118.4, 53.4, 33.3, 21.8, 21.6, 19.1, 10.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{31}N_2O_4S_2^+$ 523.1720; Found 523.1717.

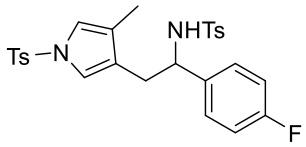


Synthesis of 4d: General procedure A: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl) benzenesulfonamide **1a** (42.0 mg, 0.201 mmol), allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200 mmol), 4-methyl-*N*-(4-methylbenzylidene)benzenesulfonamide **3d** (27.3 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4d**: 41.7 mg (0.0797 mmol), as a yellow solid, 80% yield; mp 52–54 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 7.4 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 7.6 Hz, 2H), 6.77 (d, J = 7.8 Hz, 2H), 6.68–6.62 (m, 1H), 6.60–6.55 (m, 1H), 4.70–4.56 (m, 1H), 4.24–4.07 (m, 1H), 2.64 (d, J = 7.2 Hz, 2H), 2.33 (s, 3H), 2.31 (s, 3H), 2.21 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.7, 143.2, 137.4, 137.2, 137.0, 136.2, 129.9, 129.4, 129.0, 127.0, 126.7, 126.4, 124.3, 123.9, 119.4, 118.3, 57.3, 33.7, 21.6, 21.5, 21.1, 9.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{31}N_2O_4S_2^+$ 523.1720; Found 523.1720.

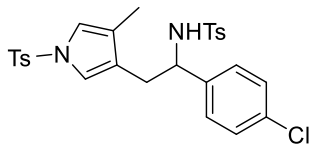


Synthesis of 4e: General procedure A: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl) benzenesulfonamide **1a** (42.0 mg, 0.201 mmol), allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200 mmol), *N*-[(1,1'-biphenyl)-4-ylmethylene]-4-methylbenzene sulfonamide **3e** (33.5 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40

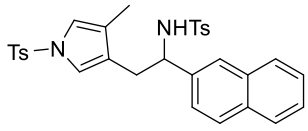
mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4e**: 46.4 mg (0.0794 mmol), as a white solid, 79% yield; mp 55–57 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.54 (d, J = 8.0 Hz, 2H), 7.48–7.42 (m, 2H), 7.41–7.33 (m, 4H), 7.32–7.22 (m, 3H), 7.14 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 7.8 Hz, 2H), 6.66 (s, 1H), 6.63 (s, 1H), 4.85–4.72 (m, 1H), 4.29 (dt, J = 6.8, 6.4 Hz, 1H), 2.68 (d, J = 7.0 Hz, 2H), 2.29–2.22 (m, 6H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.7, 143.2, 140.5, 140.4, 139.3, 136.9, 136.1, 129.9, 129.4, 128.8, 127.4, 127.01, 127.00, 126.97, 126.94, 126.6, 124.1, 123.6, 119.3, 118.4, 57.2, 33.6, 21.5, 21.4, 9.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{32}N_2O_4S_2Na^+$ 607.1696; Found 607.1692.



Synthesis of 4f: General procedure A: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl) benzenesulfonamide **1a** (42.0 mg, 0.201 mmol), allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200 mmol), *N*-(4-fluorobenzylidene)-4-methylbenzenesulfonamide **3f** (27.7 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4f**: 35.6 mg (0.0676 mmol), as a white solid, 68% yield; mp 44–46 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 9.8 Hz, 3H), 7.06 (d, J = 8.0 Hz, 2H), 6.89–6.80 (m, 2H), 6.76–6.67 (m, 2H), 6.69–6.64 (m, 1H), 6.58 (d, J = 2.4 Hz, 1H), 4.79 (d, J = 5.8 Hz, 1H), 4.22 (dt, J = 6.8, 6.4 Hz, 1H), 2.72–2.53 (m, 2H), 2.33 (s, 3H), 2.31 (s, 3H), 1.59 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.0 (d, $^1J_{FC}$ = 246.2 Hz), 144.9, 143.4, 136.8, 136.2 (d, $^4J_{FC}$ = 3.3 Hz), 136.0, 130.0, 129.4, 128.2 (d, $^3J_{FC}$ = 8.2 Hz), 127.0, 126.7, 124.0, 123.4, 119.3, 118.5, 115.2 (d, $^2J_{FC}$ = 21.4 Hz), 56.8, 33.8, 21.6, 21.5, 9.9; ^{19}F NMR (375 MHz, $CDCl_3$): δ (ppm) –114.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{27}FN_2O_4S_2Na^+$ 549.1288; Found 549.1287.

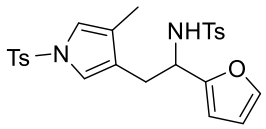


Synthesis of 4g: General procedure A: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl) benzenesulfonamide **1a** (42.0 mg, 0.201 mmol), allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200 mmol), *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide **3g** (29.3 mg, 0.0997 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4g**: 40.2 mg (0.0742 mmol), as a white solid, 74% yield; mp 53–54 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 7.6 Hz, 2H), 6.80 (d, J = 8.4 Hz, 2H), 6.71–6.61 (m, 1H), 6.58 (d, J = 2.4 Hz, 1H), 4.87 (d, J = 5.8 Hz, 1H), 4.20 (dt, J = 6.8, 6.6 Hz, 1H), 3.81–3.63 (m, 1H), 2.68–2.52 (m, 2H), 2.34 (s, 3H), 2.32 (s, 3H), 1.59 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.9, 143.5, 138.9, 136.7, 136.0, 133.3, 130.0, 129.5, 128.4, 128.0, 127.0, 126.7, 123.9, 123.2, 119.3, 118.5, 56.9, 33.6, 21.6, 21.5, 9.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{27}{}^{35}ClN_2O_4S_2Na^+$ 565.0993; Found 565.0993; Calcd for $C_{27}H_{27}{}^{37}ClN_2O_4S_2Na^+$ 567.0969; Found 567.0978.

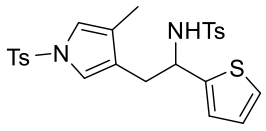


Synthesis of 4h: General procedure A: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **1a** (42.0 mg, 0.201 mmol), allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200 mmol), 4-methyl-*N*-(naphthalen-2-ylmethylene) benzenesulfonamide **3h** (30.9 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4h**: 37.0 mg (0.0662 mmol), as a yellow solid, 66% yield; mp 150–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.82–7.71 (m, 1H), 7.64–7.56 (m, 2H), 7.52 (d, J = 8.2 Hz, 2H), 7.47–7.37 (m, 4H), 7.32 (s, 1H), 7.16–7.07 (m, 3H), 6.97 (d, J = 8.0 Hz, 2H), 6.79–6.66 (m, 2H), 5.07–4.83 (m, 1H), 4.50 (dt, J = 6.8, 6.6 Hz, 1H), 2.83 (d, J = 7.2 Hz, 2H), 2.35 (s, 3H), 2.23 (s, 3H), 1.69 (s, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ (ppm) 144.7, 143.2, 137.4, 137.0, 136.1, 133.0, 132.8, 129.9, 129.3, 128.4, 127.9, 127.6, 127.0, 126.6, 126.2, 126.04, 125.96, 124.19 124.16, 123.7, 119.5, 118.4, 57.7, 33.5, 21.6, 21.3, 10.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{30}N_2O_4S_2Na^+$ 581.1539; Found 581.1545.

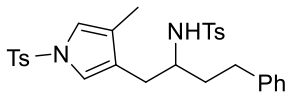


Synthesis of 4i: General procedure A: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl) benzenesulfonamide **1a** (42.0 mg, 0.201 mmol), allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200 mmol), *N*-(furan-2-ylmethylene)-4-methylbenzenesulfonamide **3i** (24.9 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4i**: 39.7 mg (0.0796 mmol), as a brown solid, 80% yield; mp 74–76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.62 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.29–7.21 (m, 2H), 7.22–7.16 (m, 3H), 6.73 (s, 1H), 6.64 (s, 1H), 6.20–6.05 (m, 1H), 5.79 (d, J = 3.2 Hz, 1H), 4.84–4.72 (m, 1H), 4.48 (dt, J = 7.6, 7.4 Hz, 1H), 2.82 (d, J = 6.8 Hz, 2H), 2.40–2.37 (m, 6H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.3, 144.7, 143.3, 141.9, 137.3, 136.2, 129.9, 129.5, 126.9, 126.7, 124.3, 123.3, 119.4, 118.1, 110.2, 107.4, 51.6, 30.8, 21.6, 21.5, 9.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{26}N_2O_5S_2Na^+$ 521.1175; Found 521.1185.

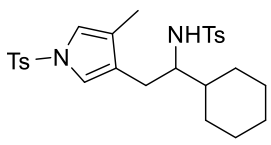


Synthesis of 4j: General procedure A: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added, 4-methyl-*N*-(prop-2-yn-1-yl) benzenesulfonamide **1a** (42.0 mg, 0.201 mmol), allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), 4-methyl-*N*-(thiophen-2-ylmethylene)benzenesulfonamide **3j** (26.5 mg, 0.0999 mmol), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4j**: 36.9 mg (0.0717 mmol), as a white solid, 72% yield; mp 54–56 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)

7.54 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.21–7.17 (m, 2H), 7.11 (d, J = 8.0 Hz, 2H), 7.03 (dd, J = 5.0, 1.2 Hz, 1H), 6.71 (dd, J = 5.0, 3.6 Hz, 1H), 6.67–6.64 (m, 1H), 6.63–6.60 (m, 1H), 6.55 (d, J = 3.4 Hz, 1H), 4.69 (d, J = 6.8 Hz, 1H), 4.64–4.53 (m, 1H), 2.76 (dd, J = 6.8, 2.6 Hz, 2H), 2.33 (s, 3H), 2.32 (s, 3H), 1.69 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.7, 144.2, 143.4, 137.1, 136.1, 129.9, 129.5, 127.0, 126.7, 126.6, 125.0, 124.8, 124.2, 123.3, 119.5, 118.2, 53.4, 34.2, 21.6, 21.5, 10.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{26}N_2O_4S_3Na^+$ 537.0947; Found 537.0956.

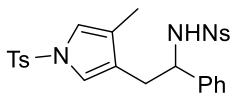


Synthesis of 4k: General procedure A: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **1a** (42.0 mg, 0.201 mmol), allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200 mmol), 4-methyl-*N*-(3-phenylpropylidene)benzenesulfonamide **3k** (28.7 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 96 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4k**: 33.2 mg (0.0618 mmol), as a colorless oil, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.18–7.07 (m, 7H), 6.90 (d, J = 7.0 Hz, 2H), 6.69 (s, 1H), 6.65 (s, 1H), 4.25 (d, J = 7.6 Hz, 1H), 3.18 (dt, J = 6.8, 6.6 Hz, 1H), 2.43–2.36 (m, 4H), 2.35 (s, 3H), 2.30 (s, 3H), 1.72–1.58 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 144.8, 143.4, 141.0, 137.5, 136.2, 130.0, 129.7, 128.4, 128.3, 127.0, 126.7, 126.0, 124.15, 124.10, 119.1, 118.5, 52.9, 36.1, 31.5, 31.0, 21.6, 21.5, 10.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{32}N_2O_4S_2Na^+$ 559.1696; Found 559.1686.



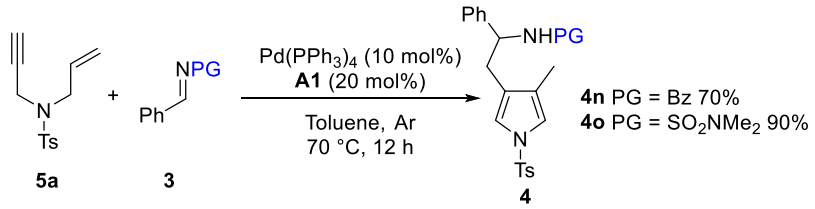
Synthesis of 4l: General procedure A: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl) benzenesulfonamide **1a** (42.0 mg, 0.201 mmol), allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200 mmol), *N*-(cyclohexylmethylene)-4-methylbenzenesulfonamide **3l** (26.5 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 96 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash

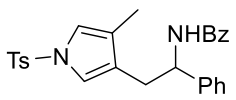
chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4l**: 11.8 mg (0.0229 mmol), as a colorless oil, 23% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.29–7.24 (m, 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 2.2 Hz, 1H), 6.68 (s, 1H), 4.42–4.13 (m, 1H), 3.24–2.99 (m, 1H), 2.48–2.42 (m, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 2.33–2.19 (m, 1H), 1.74 (s, 3H), 1.72–1.60 (m, 3H), 1.54–1.35 (m, 2H), 1.17–0.81 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 144.7, 143.2, 137.6, 136.3, 129.9, 129.5, 126.9, 126.7, 124.8, 123.9, 118.9, 118.4, 58.1, 40.6, 28.8, 27.8, 27.6, 26.4, 26.2, 26.1, 21.6, 21.5, 10.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{34}N_2O_4S_2Na^+$ 537.1852; Found 537.1846



Synthesis of 4m: General procedure A: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200 mmol), *(E)*-*N*-benzylidene-4-nitrobenzenesulfonamide **3m** (26.5 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 96 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4m**: 28.0 mg (0.0519 mmol), as a colorless thick oil, 52% yield: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.07 (d, J = 8.8 Hz, 2H), 7.68–7.60 (m, 4H), 7.28 (d, J = 8.2 Hz, 3H), 7.19–7.06 (m, 3H), 6.97–6.91 (m, 2H), 6.80–6.71 (m, 2H), 5.09 (d, J = 6.8 Hz, 1H), 4.49 (dt, J = 7.0, 6.8 Hz, 1H), 2.76 (d, J = 7.0 Hz, 2H), 2.40 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 149.6, 146.0, 144.9, 139.5, 136.0, 130.0, 128.5, 128.1, 128.0, 126.8, 126.5, 123.9, 123.8, 123.1, 119.3, 118.5, 57.9, 33.6, 21.6, 10.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{25}N_3O_6S_2Na^+$ 562.1077; Found 562.1080.

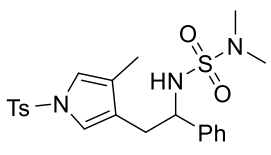
Reaction with aldimine bearing other protecting groups:



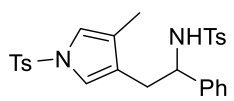


Synthesis of 4n: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-benzylidenebenzamide **3n** (20.9 mg, 0.0999 mmol), *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5a** (49.8 mg, 0.200 mmol), $Pd(PPh_3)_4$ (11.6 mg,

0.0100 mmol, 10 mol%) and **A1** (2.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **4n**: 32.1 mg (0.0700 mmol), as a colorless thick oil, 70% yield: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70 (d, J = 7.2 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.52–7.48 (m, 1H), 7.45–7.41 (m, 2H), 7.35–7.26 (m, 3H), 7.22–7.17 (m, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.81 (s, 1H), 6.76 (s, 1H), 6.38 (d, J = 7.8 Hz, 1H), 5.30 (d, J = 7.0 Hz, 1H), 3.04–2.86 (m, 2H), 2.35 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.7, 144.5, 141.4, 136.2, 134.4, 131.6, 129.8, 128.73, 128,67, 127.6, 126.9, 126.62, 126.56, 124.71, 124.66, 119.1, 118.3, 53.5, 32.2, 21.6, 10.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{26}N_2O_3SNa^+$ 481.1556 Found 481.1556



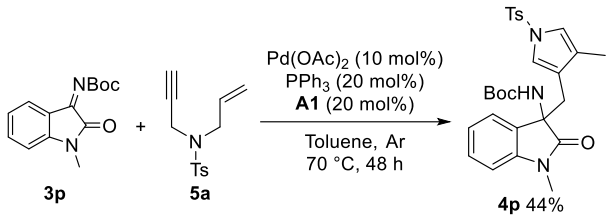
Synthesis of 4o: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added imine **3o** (21.2 mg, 0.0999 mmol), *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5a** (49.8 mg, 0.200 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%) and **A1** (2.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **4o**: 41.4 mg (0.0897 mmol), as a colorless thick oil, 90% yield: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.64 (d, J = 8.2 Hz, 2H), 7.31–7.25 (m, 5H), 7.20–7.09 (m, 2H), 6.85–6.74 (m, 2H), 4.59–4.50 (m, 1H), 4.45 (dt, J = 6.8, 6.6 Hz, 1H), 2.89–2.71 (m, 2H), 2.47 (s, 6H), 2.40 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.7, 141.4, 136.1, 129.9, 128.6, 127.8, 126.7, 126.6, 124.4, 123.8, 119.6, 118.4, 57.8, 37.4, 33.8, 21.6, 10.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{27}N_3O_4S_2Na^+$ 484.1335; Found 484.1335.



Synthesis of 4a on a 1.0 mmol scale: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl) benzenesulfonamide **1a** (420.0 mg, 2.007 mmol), allyl *tert*-butyl carbonate **2a** (316.4 mg, 2.000 mmol), *N*-benzylidene-4-methylbenzenesulfonamide **3a** (259.3 mg, 0.9999 mmol), $Pd(PPh_3)_4$ (115.6 mg, 0.1000 mmol, 10 mol%), **A2** (56.0 mg, 0.400 mmol, 40 mol%) and 4 Å MS

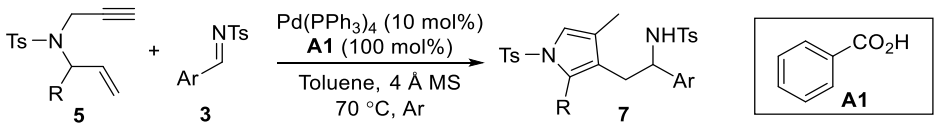
(400 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (10.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5 to 1/4) to give product **4a**: 418.2 mg (0.8229 mmol), as a white solid, 82% yield.

Reaction with a ketimine derived from isatin



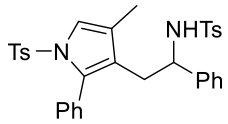
To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added *tert*-butyl (*E*)-(1-methyl-2-oxoindolin-3-ylidene)carbamate **3p** (26.0 mg, 0.0999 mmol), *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5a** (49.8 mg, 0.200 mmol), $Pd(OAc)_2$ (2.2 mg, 0.0098 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%) and **A1** (2.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 48 h, and monitored by TLC (EtOAc/petroleum ether = 1/4). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5 to 1/4) to give product **4p**: 22.4 mg (0.0439 mmol), as a yellow solid, 44% yield; mp 89–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.61 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 7.26–7.19 (m, 1H), 7.13–7.05 (m, 1H), 7.05–6.97 (m, 1H), 6.71 (s, 1H), 6.52 (d, J = 7.8 Hz, 1H), 6.37 (s, 1H), 5.17 (d, J = 6.0 Hz, 1H), 2.96–2.86 (m, 4H), 2.86–2.79 (m, 1H), 2.42 (s, 3H), 1.67 (s, 3H), 1.22 (brs, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 176.2, 153.7, 144.7, 143.4, 136.1, 129.8, 128.9, 128.0, 126.9, 124.6, 122.8, 122.4, 120.2, 119.6, 117.4, 107.8, 80.5, 62.2, 32.9, 28.0, 25.9, 21.6, 10.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{31}N_3O_5SNa^+$ 532.1877; Found 532.1877.

5. General procedure for synthesis of 3-pyrrolylmethylation products 7

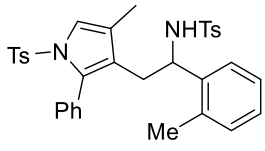


General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were

added 1,6-enyne **5** (0.200 mmol), aldimine **3** (0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h to 60 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give 3-pyrrolylmethylation product **7**.

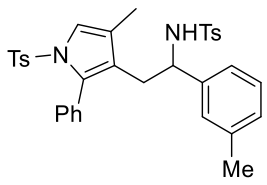


Synthesis of 7a: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), *N*-benzylidene-4-methyl benzenesulfonamide **3a** (25.9 mg, 0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7a**: 52.4 mg (0.0896 mmol), as a light yellow solid, 90% yield; 95:5 rr; mp 77–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 7.4 Hz, 1H), 7.32–7.26 (m, 1H), 7.25–7.18 (m, 1H), 7.18–7.11 (m, 5H), 7.11–7.04 (m, 5H), 7.02 (d, J = 1.2 Hz, 1H), 6.85–6.74 (m, 2H), 6.46 (brs, 1H), 4.58 (s, 1H), 4.09 (dt, J = 7.8, 6.8 Hz, 1H), 2.59–2.44 (m, 2H), 2.41 (s, 3H), 2.35 (s, 3H), 1.82 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.2, 140.8, 136.8, 135.8, 132.6, 131.9, 129.9, 129.39, 129.37, 128.5, 128.3, 127.7, 127.3, 127.1, 126.9, 126.2, 123.2, 121.5, 119.9, 57.7, 33.2, 21.6, 21.5, 10.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{32}N_2O_4S_2Na^+$ 607.1696; Found 607.1696.



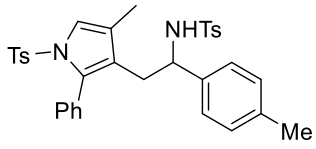
Synthesis of 7b: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), 4-methyl-*N*-(2-methylbenzylidene)benzenesulfonamide **3b** (27.3 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100

mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7b**: 45.5 mg (0.0759 mmol), as a light yellow solid, 76% yield; >95:5 rr; mp 85–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37 (d, J = 8.2 Hz, 2H), 7.35–7.28 (m, 2H), 7.19–7.08 (m, 6H), 7.08–6.94 (m, 4H), 6.93–6.80 (m, 3H), 6.40 (brs, 1H), 4.57 (d, J = 5.4 Hz, 1H), 4.33 (dt, J = 7.2, 6.0 Hz, 1H), 2.63–2.52 (m, 1H), 2.50–2.42 (m, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 1.86 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.2, 139.2, 136.9, 135.9, 134.7, 132.7, 131.9, 130.2, 129.9, 129.4, 128.5, 127.6, 127.12, 127.09, 126.9, 126.4, 126.0, 123.1, 121.8, 119.9, 53.7, 32.4, 21.6, 21.5, 18.6, 10.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858; Found 621.1863.

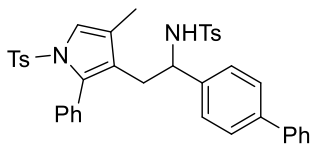


Synthesis of 7c: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), 4-methyl-*N*-(3-methylbenzylidene)benzenesulfonamide **3c** (27.3 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7c**: 52.6 mg (0.0878 mmol), as a white solid, 88% yield; >95:5 rr; mp 135–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44–7.36 (m, 2H), 7.36–7.28 (m, 2H), 7.20–7.11 (m, 5H), 7.11–7.00 (m, 4H), 6.98–6.88 (m, 2H), 6.65–6.53 (m, 2H), 6.48 (brs, 1H), 4.51 (d, J = 5.8 Hz, 1H), 4.06 (dt, J = 7.0, 6.8 Hz, 1H), 2.60–2.44 (m, 2H), 2.41 (s, 3H), 2.35 (s, 3H), 2.13 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.1, 140.6, 137.9, 136.9, 135.8, 132.5, 131.9, 129.9, 129.4, 129.3, 128.5, 128.14, 128.09, 127.6, 127.1, 126.9,

126.8, 123.5, 123.2, 121.5, 119.9, 57.7, 33.2, 21.6, 21.5, 21.2, 10.4; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858; Found 621.1864.

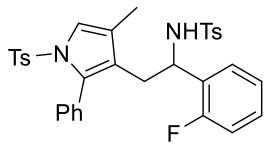


Synthesis of 7d: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), 4-methyl-*N*-(4-methylbenzylidene)benzenesulfonamide **3d** (27.3 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7d**: 42.5 mg (0.0709 mmol), as a light yellow solid, 71% yield; >95:5 rr; mp 175–176 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 7.2 Hz, 1H), 7.28 (d, J = 8.2 Hz, 1H), 7.24–7.05 (m, 8H), 7.02 (s, 1H), 6.88 (d, J = 7.8 Hz, 2H), 6.69 (d, J = 7.8 Hz, 2H), 6.45 (brs, 1H), 4.45 (d, J = 5.8 Hz, 1H), 4.04 (dt, J = 7.0, 6.8 Hz, 1H), 2.60–2.44 (m, 2H), 2.42 (s, 3H), 2.36 (s, 3H), 2.25 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.2, 137.8, 137.0, 136.8, 135.9, 132.5, 131.9, 129.9, 129.38, 129.35, 129.0, 128.5, 127.6, 127.1, 126.9, 126.1, 123.3, 121.5, 119.9, 57.5, 33.2, 21.6, 21.5, 21.0, 10.4; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858; Found 621.1860.

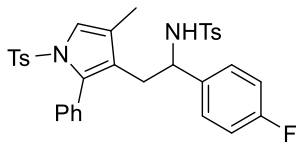


Synthesis of 7e: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), *N*-[(1,1'-biphenyl)-4-ylmethylene]-4-methylbenzenesulfonamide **3e** (33.5 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on

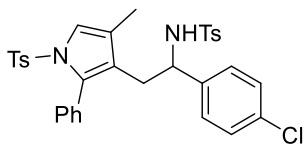
silica gel (EtOAc/petroleum ether = 1/5) to give product **7e**: 42.5 mg (0.0643 mmol), as a light yellow solid, 64% yield; 91:9 rr; mp 91–93 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55–7.46 (m, 2H), 7.46–7.39 (m, 4H), 7.37–7.31 (m, 3H), 7.29–7.22 (m, 2H), 7.18–7.10 (m, 5H), 7.09–7.01 (m, 4H), 6.84 (d, J = 8.0 Hz, 2H), 6.39 (brs, 1H), 4.58 (d, J = 6.0 Hz, 1H), 4.15 (dt, J = 7.0, 6.8 Hz, 1H), 2.64–2.55 (m, 1H), 2.56–2.48 (m, 1H), 2.39 (s, 3H), 2.30 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.3, 140.7, 140.3, 140.0, 136.9, 135.8, 132.6, 131.8, 129.8, 129.4, 129.3, 128.8, 128.5, 127.6, 127.3, 127.1, 126.99, 126.97, 126.92, 126.7, 123.0, 121.4, 120.0, 57.5, 33.2, 21.54, 21.49, 10.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{39}H_{36}N_2O_4S_2Na^+$ 683.2014; Found 683.2011.



Synthesis of 7f: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), *N*-(2-fluoro-benzylidene)-4-methylbenzenesulfonamide **3m** (27.7 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7f**: 34.0 mg (0.0564 mmol), as a light yellow solid, 56% yield; 81:19 rr; mp 85–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 7.0 Hz, 1H), 7.20–7.03 (m, 10H), 7.00 (s, 1H), 6.92–6.79 (m, 2H), 6.81–6.69 (m, 1H), 6.47 (brs, 1H), 4.60 (d, J = 7.4 Hz, 1H), 4.34 (dt, J = 7.6, 7.4 Hz, 1H), 2.62–2.46 (m, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.0 (d, $^{1}J_{FC}$ = 245.2 Hz), 144.5, 143.2, 136.5, 135.8, 132.6, 131.8, 129.8, 129.4 (d, $^{3}J_{FC}$ = 3.3 Hz), 128.9, 128.9, 128.6, 128.5 (d, $^{3}J_{FC}$ = 4.4 Hz), 127.9, 127.7, 127.1, 126.8, 124.1 (d, $^{4}J_{FC}$ = 3.3 Hz), 122.9, 121.5, 119.9, 115.4 (d, $^{2}J_{FC}$ = 21.7 Hz), 53.3, 31.5, 21.6, 21.5, 10.1; ^{19}F NMR (375 MHz, $CDCl_3$): δ (ppm) –119.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{31}FN_2O_4S_2Na^+$ 625.1607; Found 625.1604.

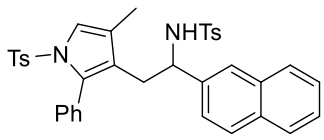


Synthesis of 7g: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), *N*-(4-fluorobenzylidene)-4-methylbenzenesulfonamide **3f** (27.7 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7g**: 45.3 mg (0.0752 mmol), as a light yellow solid, 75% yield; 93:7 rr; mp 151–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44–7.35 (m, 3H), 7.24–7.11 (m, 6H), 7.12–6.97 (m, 4H), 6.80–6.70 (m, 4H), 6.45 (brs, 1H), 4.57–4.44 (m, 1H), 4.08 (dt, J = 7.0, 6.8 Hz, 1H), 2.56–2.44 (m, 2H), 2.42 (s, 3H), 2.36 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.0 (d, $^1J_{FC}$ = 246.0 Hz), 144.6, 143.4, 136.8, 136.5 (d, $^4J_{FC}$ =3.2 Hz), 135.8, 132.6, 131.8, 129.8, 129.4 (d, $^3J_{FC}$ = 5.1 Hz), 128.6, 128.0, 127.9, 127.7, 127.1, 126.9, 122.8, 121.3, 120.0, 115.1 (d, $^2J_{FC}$ =21.5 Hz), 57.1, 33.2, 21.6, 21.5 10.4; ^{19}F NMR (375 MHz, $CDCl_3$): δ (ppm) –115.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{31}FN_2O_4S_2Na^+$ 625.1607; Found 625.1610.

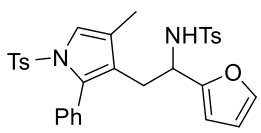


Synthesis of 7h: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide **3g** (29.3 mg, 0.0997 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7h**: 50.9 mg (0.0822 mmol), as a white solid, 82% yield; 95:5 rr; mp 109–110 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42–7.31 (m, 3H), 7.30–

7.20 (m, 2H), 7.20–7.03 (m, 8H), 7.00 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 8.2 Hz, 2H), 6.37 (brs, 1H), 4.56–4.48 (m, 1H), 4.06 (dt, J = 7.0, 6.6 Hz, 1H), 2.57–2.44 (m, 2H), 2.42 (s, 3H), 2.36 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.7, 144.6, 143.5, 139.2, 136.7, 135.8, 133.1, 132.6, 131.8, 129.7, 129.5, 129.4, 128.6, 128.4, 127.7, 127.1, 126.9, 122.6, 121.2, 120.0, 57.1, 33.1, 21.6, 21.5, 10.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{31}{}^{35}ClN_2O_4S_2Na^+$ 641.1311; Found 641.1307; Calcd for $C_{33}H_{31}{}^{37}ClN_2O_4S_2Na^+$ 643.1282; Found 643.1289.

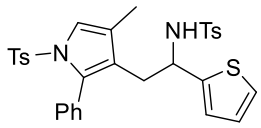


Synthesis of 7i: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), 4-methyl-*N*-(naphthalen-2-ylmethylene)benzenesulfonamide **3h** (30.9 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7i**: 50.9 mg (0.0822 mmol), as a yellow solid, 82% yield; 90:10 rr; mp 142–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67–7.56 (m, 1H), 7.46–7.26 (m, 5H), 7.26–7.19 (m, 3H), 7.18–7.09 (m, 4H), 7.12–7.00 (m, 5H), 6.95 (s, 1H), 6.48 (brs, 1H), 5.07–4.55 (m, 2H), 2.86–2.70 (m, 1H), 2.69–2.54 (m, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.3, 136.4, 135.8, 135.0, 133.6, 132.5, 132.1, 131.8, 130.1, 129.9, 129.4, 129.3, 128.8, 128.6, 127.9, 127.8, 127.1, 126.9, 126.0, 125.3, 125.2, 123.2, 121.9, 121.4, 119.85, 32.23, 32.20, 21.6, 21.5, 10.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{34}N_2O_4S_2Na^+$ 657.1852; Found 657.1845.

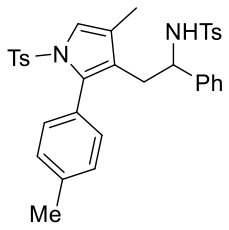


Synthesis of 7j: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), *N*-(furan-2-ylmethylene)-4-methylbenzenesulfonamide **3i** (24.9 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added

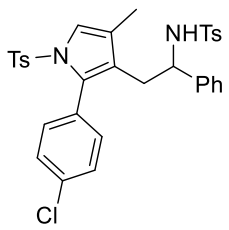
via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7j**: 42.7 mg (0.0742 mmol), as a yellow solid, 74% yield; >95:5 rr; mp 67–68 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (d, J = 8.0 Hz, 2H), 7.39–7.32 (m, 1H), 7.31–7.25 (m, 2H), 7.22–7.12 (m, 5H), 7.12–7.04 (m, 3H), 7.03 (s, 1H), 6.72 (brs, 1H), 6.08 (dd, J = 3.2, 1.8 Hz, 1H), 5.74 (d, J = 3.2 Hz, 1H), 4.50 (d, J = 7.8 Hz, 1H), 4.26 (dt, J = 7.8, 7.6 Hz, 1H), 2.71–2.52 (m, 2H), 2.41 (s, 3H), 2.36 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.4, 144.4, 143.2, 141.8, 137.1, 135.9, 132.7, 131.9, 130.0, 129.4, 129.3, 128.5, 127.6, 127.1, 126.7, 122.8, 121.6, 119.8, 110.1, 107.0, 51.4, 30.2, 21.6, 21.5, 10.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{31}H_{30}N_2O_5S_2Na^+$ 597.1494; Found 597.1490.



Synthesis of 7k: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), 4-methyl-*N*-(thiophen-2-yl methylene)benzenesulfonamide **3j** (26.5 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7k**: 30.0 mg (0.0508 mmol), as a yellow solid, 51% yield; >95:5 rr; mp 75–77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44 (d, J = 8.0 Hz, 2H), 7.39–7.25 (m, 3H), 7.25–7.17 (m, 3H), 7.14 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 7.05–6.99 (m, 2H), 6.77–6.71 (m, 1H), 6.63 (brs, 1H), 6.54 (d, J = 3.6 Hz, 1H), 4.51–4.36 (m, 2H), 2.63 (d, J = 6.8 Hz, 2H), 2.44 (s, 3H), 2.36 (s, 3H), 1.88 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.8, 144.5, 143.4, 137.0, 135.9, 132.7, 131.9, 129.9, 129.5, 129.4, 128.6, 127.7, 127.1, 126.8, 126.6, 124.5, 124.4, 122.9, 121.4, 119.9, 53.4, 33.5, 21.6, 21.5, 10.4; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{31}H_{30}N_2O_4S_3Na^+$ 613.1265; Found 613.1266.

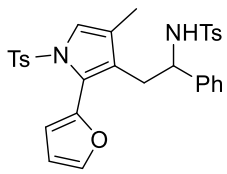


Synthesis of 7l: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(1-(*p*-tolyl)allyl)benzenesulfonamide **5d** (67.8 mg, 0.200 mmol), *N*-benzylidene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7l**: 48.0 mg (0.0805 mmol), as a light yellow solid, 81% yield; 93:7 rr; mp 137–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38 (d, J = 8.0 Hz, 2H), 7.23–7.13 (m, 5H), 7.13–7.05 (m, 6H), 7.02–6.96 (m, 2H), 6.86 (d, J = 6.6 Hz, 2H), 6.38 (brs, 1H), 4.47 (d, J = 5.6 Hz, 1H), 4.10 (dt, J = 8.0, 6.4 Hz, 1H), 2.56–2.44 (m, 2H), 2.42 (s, 3H), 2.41 (s, 3H), 2.36 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.2, 141.0, 138.5, 136.8, 135.9, 132.7, 131.7, 129.42, 129.37, 129.35, 128.5, 128.3, 127.3, 127.1, 126.8, 126.2, 123.0, 121.5, 119.8, 57.7, 33.2, 21.6, 21.5, 21.4, 10.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858; Found 621.1857.

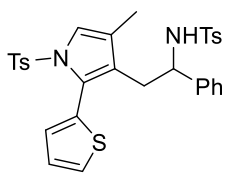


Synthesis of 7m: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-(1-(4-chlorophenyl)allyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5e** (71.8 mg, 0.200 mmol), *N*-benzylidene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7m**: 47.1 mg (0.0762 mmol), as a light yellow solid, 76% yield; 92:8 rr; mp 131–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, J =

8.0 Hz, 2H), 7.23–7.08 (m, 10H), 7.06–7.01 (m, 3H), 6.73 (d, J = 7.2 Hz, 2H), 6.28 (brs, 1H), 4.64 (d, J = 6.2 Hz, 1H), 4.09 (dt, J = 7.2, 7.0 Hz, 1H), 2.68–2.40 (m, 2H), 2.40 (s, 3H), 2.37 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.7, 143.3, 140.2, 136.9, 135.7, 134.6, 133.1, 132.9, 131.3, 129.5, 129.4, 128.4, 128.3, 127.8, 127.4, 127.0, 126.9, 126.3, 123.6, 121.9, 120.3, 57.7, 33.2, 21.6, 21.5, 10.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{31}{}^{35}ClN_2O_4S_2Na^+$ 641.1311; Found 641.1303; Calcd for $C_{33}H_{31}{}^{37}ClN_2O_4S_2Na^+$ 643.1282; Found 643.1288.

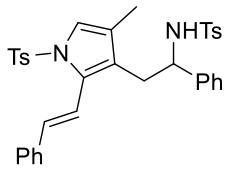


Synthesis of 7n: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-(1-(furan-2-yl)allyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5f** (63.0 mg, 0.200 mmol), *N*-benzylidene-4-methyl benzenesulfonamide **3a** (25.9 mg, 0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7n**: 51.5 mg (0.0896 mmol), as a yellow solid, 90% yield; >95:5 rr; mp 79–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.53–7.50 (m, 1H), 7.43–7.38 (m, 4H), 7.21 (d, J = 8.2 Hz, 2H), 7.17–7.13 (m, 4H), 7.12 (s, 1H), 7.04–6.97 (m, 2H), 6.96 (d, J = 1.2 Hz, 1H), 6.48 (dd, J = 3.2, 2.0 Hz, 1H), 6.23 (d, J = 3.2 Hz, 1H), 4.96–4.89 (m, 1H), 4.20–4.06 (m, 1H), 2.61–2.44 (m, 2H), 2.41 (s, 3H), 2.39 (s, 3H), 1.67 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.7, 143.2, 141.2, 136.7, 135.7, 132.1, 129.52, 129.46, 129.4, 128.5, 128.4, 127.4, 127.2, 126.9, 126.8, 126.2, 126.0, 123.6, 120.9, 57.6, 33.4, 21.6, 21.5, 10.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{30}N_2O_5S_2Na^+$ 597.1488; Found 597.1485.



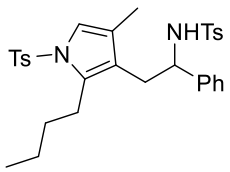
Synthesis of 7o: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(1-(thiophen-2-yl)allyl)benzenesulfonamide **5g** (66.2 mg, 0.200 mmol), *N*-benzylidene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0

mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7o**: 47.2 mg (0.0798 mmol), as a yellow solid, 80% yield; >95:5 rr; mp 76–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.43 (d, J = 8.2, 1H), 7.39 (dd, J = 5.2, 1.2 Hz, 1H), 7.26–7.22 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.16–7.09 (m, 5H), 7.06–7.00 (m, 2H), 6.99–6.92 (m, 2H), 6.67 (d, J = 3.6 Hz, 1H), 4.67–4.56 (m, 1H), 4.16 (dt, J = 7.4, 6.8 Hz, 1H), 2.60–2.52 (m, 2H), 2.43 (s, 3H), 2.37 (s, 3H), 1.79 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.9, 143.5, 143.1, 142.3, 141.2, 136.7, 135.9, 129.6, 129.3, 128.3, 127.4, 127.13, 127.08, 126.9, 126.2, 121.9, 121.5, 121.3, 114.2, 111.1, 57.3, 33.5, 21.6, 21.5, 10.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{30}N_2O_4S_3Na^+$ 613.1260; Found 613.1263.

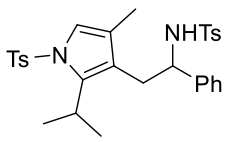


Synthesis of 7p: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*E*)-4-methyl-*N*-(1-phenylpenta-1,4-dien-3-yl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5h** (70.2 mg, 0.200 mmol), *N*-benzylidene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 48 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7p**: 22.0 mg (0.0360 mmol), as a yellow solid, 36% yield; >95:5 rr; mp 93–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.59–7.52 (m, 2H), 7.46–7.35 (m, 6H), 7.36–7.27 (m, 2H), 7.23–7.11 (m, 4H), 7.15–7.05 (m, 3H), 7.03 (d, J = 16.6 Hz, 1H), 6.96–6.86 (m, 2H), 6.35 (d, J = 16.6 Hz, 1H), 4.67 (d, J = 5.8 Hz, 1H), 4.29 (dt, J = 7.4, 6.0 Hz, 1H), 3.03–2.87 (m, 1H), 2.83–2.71 (m, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 1.71 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.8, 143.3, 140.6, 136.9, 136.6, 135.9, 132.7, 130.7, 129.7, 129.5, 128.8, 128.4, 128.1, 127.5, 127.0, 126.9, 126.5, 126.3, 123.2, 122.8, 120.1, 117.4, 57.5, 33.9, 21.6, 21.5, 10.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{34}N_2O_4S_2Na^+$ 631.1852; Found

631.1844.

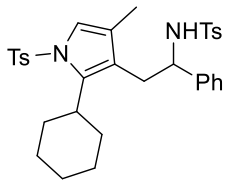


Synthesis of 7q: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-(hept-1-en-3-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5i** (61.0 mg, 0.200 mmol), *N*-benzylidene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 48 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7q**: 49.0 mg (0.0867 mmol), as a yellow solid, 87% yield; >95:5 rr; mp 71–73 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.54 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 7.16–7.08 (m, 3H), 7.07–6.99 (m, 2H), 6.87 (d, J = 1.4 Hz, 1H), 6.85–6.80 (m, 2H), 4.81 (d, J = 5.8 Hz, 1H), 4.18 (dt, J = 7.2, 6.8 Hz, 1H), 2.70 (dd, J = 14.2, 6.8 Hz, 1H), 2.57 (dd, J = 14.1, 8.0 Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H), 2.31–2.24 (m, 2H), 1.59 (d, J = 1.2 Hz, 3H), 1.32–1.10 (m, 4H), 0.81 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.3, 140.3, 136.9, 136.8, 133.9, 129.9, 129.4, 128.2, 127.0, 126.44, 126.36, 122.4, 121.1, 119.5, 58.0, 33.7, 32.9, 25.1, 22.6, 21.6, 21.5, 13.7, 10.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{36}N_2O_4S_2Na^+$ 587.2009; Found 587.2001.



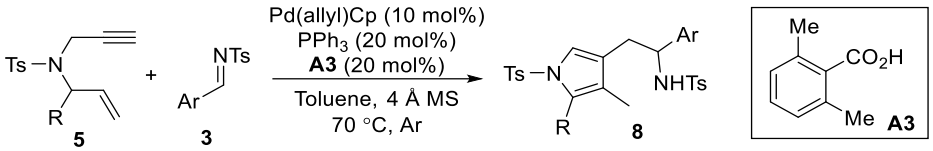
Synthesis of 7r: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(4-methylpent-1-en-3-yl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5j** (58.2 mg, 0.200 mmol), *N*-benzylidene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 48 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether =

1/5) to give product **7r**: 25.8 mg (0.0469 mmol), as a light yellow solid, 47% yield; >95:5 rr; mp 82–84 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.54 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.21–7.08 (m, 5H), 7.07–7.00 (m, 2H), 6.96 (s, 1H), 4.81 (d, J = 5.2 Hz, 1H), 4.32 (dt, J = 7.0, 6.6 Hz, 1H), 2.82 (dd, J = 14.6, 8.6 Hz, 1H), 2.65 (dd, J = 14.6, 7.0 Hz, 1H), 2.41 (s, 3H), 2.38 (s, 3H), 1.63 (d, J = 1.2 Hz, 3H), 1.07 (d, J = 7.2 Hz, 3H), 0.85 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.6, 143.2, 140.8, 137.9, 137.1, 136.8, 129.9, 129.3, 128.3, 127.5, 127.1, 126.5, 126.4, 121.8, 120.5, 119.8, 57.8, 34.3, 22.4, 22.0, 21.6, 21.4, 10.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{34}N_2O_4S_2Na^+$ 573.1858; Found 573.1855.

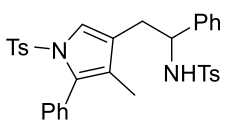


Synthesis of 7s: General procedure B: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-(1-cyclohexylallyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5k** (58.2 mg, 0.200 mmol), *N*-benzylid-ene-4-methylbenzene sulfonamide **3a** (25.9 mg, 0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 48 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was diluted with EtOAc (15.0 mL), washed with saturated sodium bicarbonate solution (5.0 mL × 3) and brine (5.0 mL), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7s**: 46.9 mg (0.0794 mmol), as a yellow solid, 79% yield; >95:5 rr; mp 81–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.22–7.16 (m, 3H), 7.13 (d, J = 8.0 Hz, 2H), 7.10–7.04 (m, 2H), 6.94 (s, 1H), 4.85 (d, J = 5.0 Hz, 1H), 4.30 (dt, J = 7.2, 6.4 Hz, 2H), 3.17–2.93 (m, 1H), 2.82 (dd, J = 14.6, 9.0 Hz, 1H), 2.64 (dd, J = 14.6, 6.8 Hz, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 1.82–1.66 (m, 2H), 1.61 (s, 3H), 1.54–1.36 (m, 2H), 1.22–0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.7, 143.2, 141.1, 137.2, 137.0, 136.8, 129.9, 129.3, 128.4, 127.5, 127.1, 126.6, 126.5, 121.7, 120.4, 119.4, 57.9, 36.5, 34.5, 33.0, 32.4, 27.3, 27.1, 25.8, 21.6, 21.5, 10.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{38}N_2O_4S_2Na^+$ 613.2171; Found 613.2166.

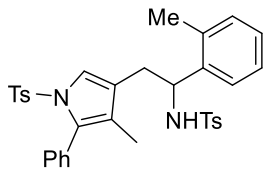
6. General procedure for synthesis of 4-pyrrolylmethylation products 8



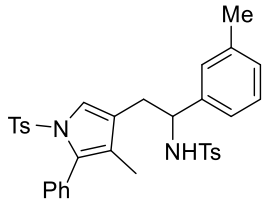
General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 1,6-enyne **5** (0.200 mmol), aldimine **3** (0.100 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h to 96 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give 4-pyrrolylmethylation product **8**.



Synthesis of 8a: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), *N*-benzylidene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **8a**: 43.6 mg (0.0746 mmol), as a white solid, 75% yield; 7:93 rr; mp 90–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.50 (d, J = 8.2 Hz, 2H), 7.39–7.27 (m, 3H), 7.22–7.17 (m, 3H), 7.17–7.10 (m, 6H), 7.04–6.94 (m, 5H), 4.77 (d, J = 5.8 Hz, 1H), 4.40 (dt, J = 6.8, 6.2 Hz, 1H), 2.80 (d, J = 7.0 Hz, 2H), 2.39–2.35 (m, 6H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.3, 140.3, 137.1, 135.7, 132.02, 131.98, 131.7, 130.5, 129.5, 128.4, 128.2, 127.7, 127.3, 127.12, 127.09, 126.6, 123.7, 122.1, 121.2, 57.4, 34.0, 21.6, 21.5, 9.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{32}N_2O_4S_2Na^+$ 607.1696; Found 607.1691.

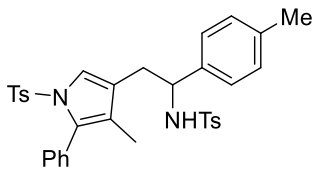


Synthesis of 8b: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), 4-methyl-*N*-(2-methylbenzylidene)benzenesulfonamide **3b** (27.3 mg, 0.0999 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **8b**: 44.5 mg (0.0743 mmol), as a yellow solid, 74% yield; 7:93 rr; mp 81–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.48 (d, J = 8.3 Hz, 2H), 7.37–7.28 (m, 3H), 7.17–7.10 (m, 6H), 7.09–7.04 (m, 1H), 7.04–6.98 (m, 4H), 6.97–6.91 (m, 2H), 4.81 (d, J = 5.6 Hz, 1H), 4.66 (dt, J = 6.8, 6.2 Hz, 1H), 2.88–2.68 (m, 2H), 2.37 (s, 3H), 2.35 (s, 3H), 2.04 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.2, 138.6, 137.1, 135.7, 134.9, 131.9, 131.7, 130.5, 130.2, 129.44, 129.38, 128.2, 127.3, 127.2, 127.1, 127.0, 126.3, 125.9, 123.7, 122.0, 121.2, 53.0, 33.2, 21.6, 21.5, 19.0, 9.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1852; Found 621.1861.

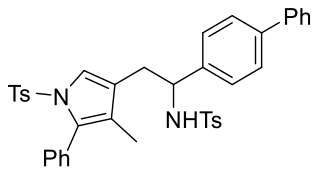


Synthesis of 8c: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), 4-methyl-*N*-(3-methylbenzylidene)benzenesulfonamide **3c** (27.3 mg, 0.0999 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **8c**: 39.3 mg (0.0656 mmol), as a white thick oil, 66% yield; 10:90 rr; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49 (d, J = 8.2 Hz, 2H), 7.35–7.28 (m, 3H), 7.17–7.11 (m, 6H), 7.07–7.03 (m, 2H), 7.02–6.96 (m, 3H), 6.79 (d, J = 7.6 Hz, 1H), 6.73 (s, 1H), 4.89 (brs, 1H), 4.37 (t, J = 7.0 Hz, 1H), 2.78 (d, J = 7.0 Hz, 2H), 2.37 (s, 3H), 2.36 (s, 3H), 2.20 (s, 3H), 1.43 (s, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.2, 140.2, 138.0, 137.2, 135.7, 131.9, 131.7, 130.6, 129.5, 129.3, 128.4, 128.3, 128.1, 127.32, 127.28, 127.14, 127.07, 123.74, 123.73, 122.2, 121.2, 57.4, 33.9, 21.6, 21.5, 21.3, 9.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858; Found 621.1850.

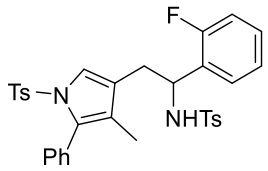


Synthesis of 8d: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), 4-methyl-*N*-(4-methylbenzylidene)benzenesulfonamide **3d** (27.3 mg, 0.0999 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 96 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **8d**: 40.1 mg (0.0670 mmol), as a yellow solid, 67% yield; 18:82 rr; mp 76–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.50 (d, J = 8.0 Hz, 2H), 7.42–7.29 (m, 3H), 7.13 (d, J = 6.0 Hz, 6H), 7.06–6.94 (m, 5H), 6.89 (d, J = 7.8 Hz, 2H), 4.75 (d, J = 5.6 Hz, 1H), 4.33 (dt, J = 6.6, 6.4 Hz, 1H), 2.79 (d, J = 7.0 Hz, 2H), 2.38 (s, 3H), 2.37 (s, 3H), 2.31 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.2, 137.4, 137.1, 135.7, 131.9, 131.7, 130.5, 129.8, 129.4, 129.1, 128.6, 128.1, 127.3, 127.2, 127.1, 126.5, 123.7, 122.3, 121.2, 57.2, 33.9, 21.6, 21.5, 21.1, 9.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858; Found 621.1861.

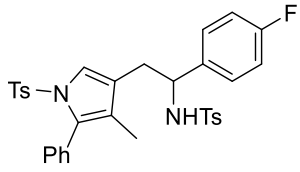


Synthesis of 8e: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), *N*-[(1,1'-biphenyl)-4-ylmethylene]-4-methylbenzenesulfonamide **3e** (33.5 mg, 0.0999 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel

(EtOAc/petroleum ether = 1/6 to 1/5) to give product **8e**: 47.3 mg (0.0716 mmol), as a brown thick oil, 72% yield; <5:95 rr; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58–7.47 (m, 4H), 7.48–7.41 (m, 2H), 7.40–7.27 (m, 3H), 7.35–7.27 (m, 4H), 7.19–7.11 (m, 4H), 7.11–7.04 (m, 4H), 7.04–6.99 (m, 2H), 4.93–4.82 (m, 1H), 4.45 (dt, J = 6.6, 6.4 Hz, 1H), 2.83 (d, J = 7.0 Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.3, 140.6, 139.3, 137.1, 135.7, 132.0, 131.7, 130.5, 129.44, 129.42, 128.8, 128.5, 128.2, 127.4, 127.3, 127.2, 127.1, 127.12, 127.08, 127.06, 127.00, 123.6, 122.1, 121.2, 57.1, 33.9, 21.6, 21.5, 9.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{39}H_{36}N_2O_4S_2Na^+$ 683.2014; Found 683.2017.

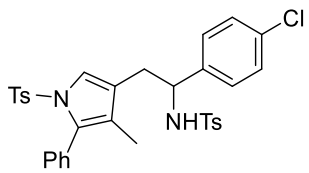


Synthesis of 8f: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), *N*-(2-fluoro-benzylidene)-4-methylbenzenesulfonamide **3m** (27.7 mg, 0.0999 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **8f**: 32.3 mg (0.0536 mmol), as a yellow thick oil, 54% yield; <5:95 rr; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49 (d, J = 8.2 Hz, 2H), 7.37–7.26 (m, 3H), 7.20–7.10 (m, 6H), 7.11–7.03 (m, 2H), 7.02–6.92 (m, 4H), 6.92–6.82 (m, 1H), 5.11–4.93 (m, 1H), 4.75–4.57 (m, 1H), 2.81 (d, J = 7.2 Hz, 2H), 2.37 (s, 3H), 2.34 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.6, 143.3, 136.8, 135.7, 131.7, 130.5, 129.5, 129.4, 129.2, 128.2, 127.3, 127.1, 127.0, 124.1, 123.5, 121.8, 121.2, 115.4 (d, $^2J_{FC}$ = 21.7 Hz), 52.7, 32.7, 21.6, 21.5, 9.4; ^{19}F NMR (375 MHz, $CDCl_3$): δ (ppm) –119.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{31}FN_2O_4S_2Na^+$ 625.1607; Found 625.1602.

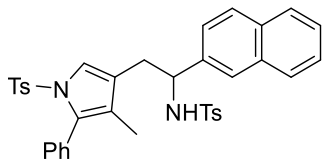


Synthesis of 8g: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), *N*-(4-fluorobenzylidene)-4-methylbenzenesulfonamide **3f** (27.7 mg, 0.0999 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0

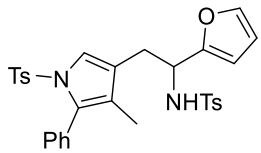
mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **8g**: 43.6 mg (0.0724 mmol), as a yellow solid, 72% yield; <5:95 rr; mp 90–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.48 (d, J = 8.2 Hz, 2H), 7.38–7.28 (m, 3H), 7.21–7.10 (m, 6H), 7.05–7.01 (m, 2H), 7.01–6.93 (m, 3H), 6.89–6.79 (m, 2H), 5.02–4.74 (brs, 1H), 4.38 (t, J = 7.2 Hz, 1H), 2.83–2.70 (m, 2H), 2.38 (s, 3H), 2.37 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.1 (d, $^{1}J_{FC}$ = 246.3 Hz), 144.6, 143.4, 137.0, 136.2 (d, $^{4}J_{FC}$ = 3.2 Hz), 135.6, 132.1, 131.7, 130.4, 129.5, 128.4, 128.3 (d, $^{3}J_{FC}$ = 4.2 Hz), 127.4, 127.1, 127.1, 123.4, 121.8, 121.1, 115.2 (d, $^{2}J_{FC}$ = 21.3 Hz), 56.8, 34.0, 21.6, 21.5, 9.5; ^{19}F NMR (375 MHz, $CDCl_3$): δ (ppm) –114.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{31}FN_2O_4S_2Na^+$ 625.1607; Found 625.1612.



Synthesis of 8h: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide **3g** (29.3 mg, 0.0997 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **8h**: 45.4 mg (0.0733 mmol), as a yellow solid, 73% yield; <5:95 rr; mp 96–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46 (d, J = 8.2 Hz, 2H), 7.40–7.28 (m, 4H), 7.25–7.22 (m, 1H), 7.18–7.10 (m, 7H), 7.04–6.99 (m, 2H), 6.94 (d, J = 8.4 Hz, 2H), 4.94 (brs, 1H), 4.36 (t, J = 7.0 Hz, 1H), 2.78–2.72 (m, 1H), 2.48–2.41 (m, 1H), 2.39 (s, 3H), 2.37 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.6, 143.5, 139.0, 136.9, 135.6, 133.4, 132.1, 131.7, 130.4, 129.5, 128.5, 128.2, 128.1, 127.4, 127.3, 127.12, 127.08, 123.3, 121.6, 121.1, 56.8, 33.9, 21.6, 21.5, 9.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{31}{}^{35}ClN_2O_4S_2Na^+$ 641.1311; Found 641.1309; Calcd for $C_{33}H_{31}{}^{37}ClN_2O_4S_2Na^+$ 643.1282; Found 643.1290.

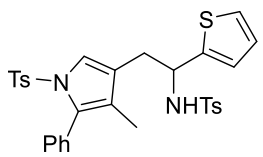


Synthesis of 8i: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), 4-methyl-*N*-(naphthalen-2-ylmethylene)benzenesulfonamide **3h** (30.9 mg, 0.0999 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **8i**: 43.7 mg (0.0689 mmol), as a yellow solid, 69% yield; 14:86 rr; mp 98–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (d, J = 8.0 Hz, 1H), 7.84–7.79 (m, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.51–7.39 (m, 4H), 7.36–7.26 (m, 4H), 7.16–7.05 (m, 6H), 7.04–6.94 (m, 4H), 5.29 (dt, J = 6.8, 6.4 Hz, 1H), 4.99 (d, J = 6.2 Hz, 1H), 3.07–2.99 (m, 1H), 2.98–2.88 (m, 1H), 2.36 (s, 3H), 2.29 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.2, 136.8, 135.9, 135.5, 133.7, 132.0, 131.6, 130.5, 130.4, 129.4, 129.3, 129.0, 128.2, 128.1, 127.3, 127.1, 127.0, 126.3, 125.6, 125.0, 124.2, 123.8, 122.2, 122.1, 121.3, 53.1, 33.0, 21.6, 21.4, 9.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{34}N_2O_4S_2Na^+$ 657.1852; Found 657.1859.

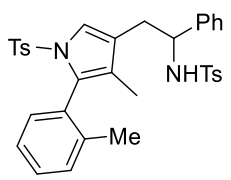


Synthesis of 8j: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), *N*-(furan-2-ylmethylene)-4-methylbenzenesulfonamide **3i** (24.9 mg, 0.0999 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give products **7j** and **8j** as inseparable regioselective isomers: 40.4 mg (0.0703 mmol), as a white solid, 70% yield; 20:80 rr; mp 63–65 °C; For **8j** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 (d, J = 8.0 Hz, 2H), 7.35–7.28 (m, 3H), 7.25–7.17 (m, 4H), 7.12 (t, J = 6.3 Hz, 5H), 7.04–6.98 (m, 2H), 6.96 (s, 1H), 6.18 (t, J = 3.2, 1.8 Hz, 1H), 5.87 (d, J = 3.2 Hz, 1H), 4.82 (d, J = 8.2 Hz, 1H), 4.57 (dt, J = 7.4, 7.2 Hz, 1H),

2.90 (d, J = 7.0 Hz, 2H), 2.40 (s, 3H), 2.36 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.3, 144.4, 143.3, 142.0, 137.4, 135.7, 131.7, 130.6, 129.5, 129.4, 129.3, 128.1, 127.3, 127.1, 127.0, 123.6, 121.7, 121.2, 110.2, 107.5, 51.5, 31.1, 21.6, 21.5, 9.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{30}N_2O_5S_2Na^+$ 597.1494; Found 597.1497.

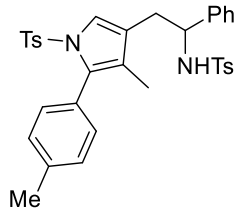


Synthesis of 8k: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (65.0 mg, 0.200 mmol), 4-methyl-*N*-(thiophen-2-ylmethylene)benzenesulfonamide **3j** (26.5 mg, 0.0999 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **8k**: 35.4 mg (0.0599 mmol), as a yellow solid, 60% yield; 26:74 rr; mp 68–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60 (d, J = 8.0 Hz, 2H), 7.36–7.27 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 5.2 Hz, 1H), 7.12–7.07 (m, 4H), 7.05–6.99 (m, 3H), 6.83 (t, J = 5.0, 3.4 Hz, 1H), 6.68 (d, J = 3.4 Hz, 1H), 4.87–4.80 (m, 1H), 4.79–4.70 (m, 1H), 3.05–2.83 (m, 2H), 2.40 (s, 3H), 2.36 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.4, 144.1, 143.4, 137.2, 135.7, 131.8, 131.7, 130.5, 129.5, 129.4, 128.5, 128.1, 127.3, 127.1, 127.0, 126.6, 125.2, 124.9, 123.6, 121.8, 121.3, 53.3, 34.6, 21.6, 21.5, 9.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{30}N_2O_4S_3Na^+$ 613.1266; Found 613.1262.

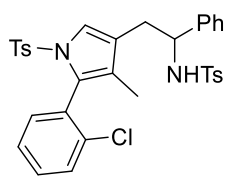


Synthesis of 8l: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(1-(*o*-tolyl)allyl)benzenesulfonamide **5l** (67.8 mg, 0.200 mmol), *N*-benzylidene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give the

product **8l**: 43.6 mg (0.0728 mmol), as a yellow solid, 73% yield; <5:95 rr; 1:1 dr for atropisomer; mp 74–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.24–7.10 (m, 20H), 7.09–7.03 (m, 4H), 7.01–6.89 (m, 6H), 6.74 (d, J = 1.6 Hz, 1H), 6.73 (d, J = 1.6 Hz, 1H), 4.99–4.86 (m, 2H), 4.53–4.31 (m, 2H), 3.02–2.68 (m, 4H), 2.40–2.38 (m, 6H), 2.38–2.35 (m, 6H), 1.73 (s, 3H), 1.71 (s, 3H), 1.37–1.27 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.6, 144.5, 143.3, 140.3, 140.2, 139.9, 139.8, 137.3, 137.2, 135.9, 135.8, 132.3, 132.2, 130.4, 130.3, 130.1, 130.0, 129.44, 129.42, 129.35, 128.84, 128.78, 128.39, 128.36, 127.59, 127.57, 127.4, 127.1, 126.7, 126.6, 124.63, 124.60, 123.3, 123.1, 121.5, 121.1, 120.4, 58.1, 57.5, 34.1, 34.0, 21.6, 21.5, 19.50, 19.47, 9.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858; Found 621.1859.



Synthesis of 8m: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(1-(*p*-tolyl)allyl)benzenesulfonamide **5d** (67.8 mg, 0.200 mmol), *N*-benzyli-dene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **8m**: 37.3 mg (0.0623 mmol), as a yellow solid, 62% yield; 18:82 rr; mp 101−103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49 (d, J = 8.2 Hz, 2H), 7.21–7.14 (m, 7H), 7.14–7.09 (m, 3H), 7.01–6.95 (m, 3H), 6.90 (d, J = 8.0 Hz, 2H), 4.84 (brs, 1H), 4.38 (t, J = 7.0 Hz, 1H), 2.77 (d, J = 7.0 Hz, 2H), 2.39 (s, 3H), 2.38–2.34 (m, 6H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 143.3, 140.4, 138.0, 137.0, 135.7, 132.1, 131.5, 129.4, 129.3, 128.4, 128.1, 127.6, 127.5, 127.12, 127.09, 126.6, 123.6, 122.2, 121.1, 57.4, 34.0, 21.6, 21.5, 21.4, 9.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858; Found 621.1860.

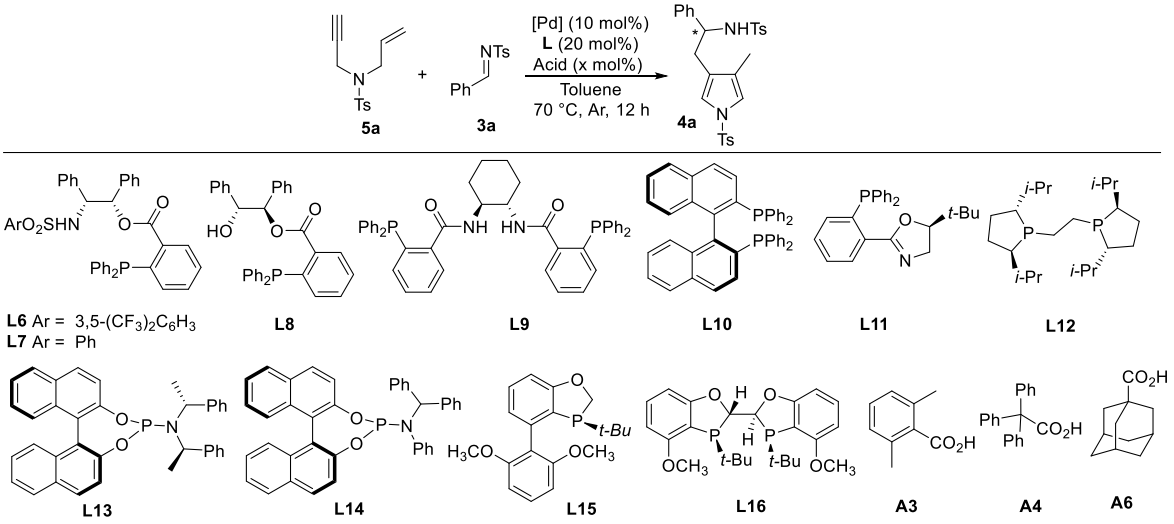


Synthesis of 8n: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-(1-(2-chlorophenyl)allyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5m** (71.8 mg, 0.200 mmol), *N*-benzyli-dene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), Pd(allyl)Cp (2.1

mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **8n**: 41.9 mg (0.0677 mmol), as a light yellow solid, 67% yield; <5:95 rr; 1:1 dr for atropisomer; mp 71–72 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.59–7.51 (m, 4H), 7.33–7.27 (m, 1H), 7.26–7.21 (m, 4H), 7.20–7.12 (m, 16H), 7.11–7.04 (m, 2H), 7.03–6.95 (m, 4H), 6.94–6.90 (m, 2H), 4.98–4.72 (m, 2H), 4.54–4.24 (m, 2H), 3.02–2.63 (m, 4H), 2.40–2.38 (m, 6H), 2.38 (s, 3H), 2.36 (s, 3H), 1.44–1.28 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.6, 143.3, 143.3, 140.11, 140.08, 137.2, 137.1, 136.3, 136.20, 135.7, 135.6, 134.4, 134.2, 130.1, 129.72, 129.67, 129.56, 129.54, 129.49, 129.4, 128.9, 128.40, 128.38, 127.84, 127.79, 127.6, 127.5, 127.3, 127.2, 127.14, 127.12, 126.7, 126.6, 125.7, 124.9, 124.8, 121.5, 121.3, 121.0, 120.9, 58.0, 57.4, 34.0, 33.8, 21.6, 21.50, 21.48, 9.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{31}{}^{35}ClN_2O_4S_2Na^+$ 641.1311; Found 641.1304; Calcd for $C_{33}H_{31}{}^{37}ClN_2O_4S_2Na^+$ 643.1282; Found 643.1288.

7. Asymmetric auto-tandem catalytic reaction exploration

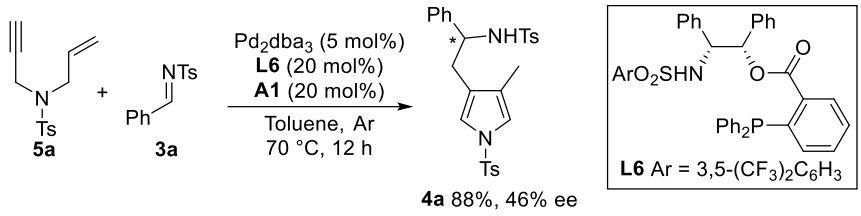
Table S7.1. Detailed screening conditions for asymmetric auto-tandem catalysis[a]



Entry	[Pd]	L	Acid	x	Yield (%)[b]	ee[c]
1	**Pd_2dba_3**	**L6**	**A1**	**20**	**88**	**46**
2	Pd_2dba_3	**L7**	**A1**	20	50	41

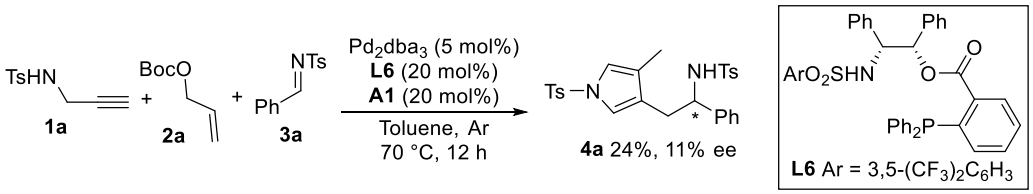
3	Pd_2dba_3	**L8**	**A1**	20	36	–8
4	Pd_2dba_3	**L9**	**A1**	20	trace	/
5	Pd_2dba_3	**L10**	**A1**	20	trace	/
6	Pd_2dba_3	**L11**	**A1**	20	NR	/
7	Pd_2dba_3	**L12**	**A1**	20	NR	/
8	Pd_2dba_3	**L13**	**A1**	20	42	–3
9	Pd_2dba_3	**L14**	**A1**	20	36	1
10	Pd_2dba_3	**L15**	**A1**	20	38	4
11	Pd_2dba_3	**L16**	**A1**	20	84	2
12	$Pd(OAc)_2$	**L6**	**A1**	20	26	45
13	Pd(allyl)Cp	**L6**	**A1**	20	49	46
14	$[Pd(allyl)Cl]_2$	**L6**	**A1**	20	messy	/
15	$Pd_2dba_3 \cdot CHCl_3$	**L6**	**A1**	20	63	40
16	$Pddba_2$	**L6**	**A1**	20	62	42
17	Pd_2dba_3	**L6**	**A3**	20	88	37
18	Pd_2dba_3	**L6**	**A4**	20	78	31
19	Pd_2dba_3	**L6**	**A6**	20	29	33
20	Pd_2dba_3	**L6**	**A1**	10	48	43
21	Pd_2dba_3	**L6**	**A1**	60	81	24
22	Pd_2dba_3	**L6**	**A1**	100	98	8
23[d]	Pd_2dba_3	**L6**	**A1**	20	60	26
24[e]	Pd_2dba_3	**L6**	**A1**	20	messy	/

[a] Unless noted otherwise, reactions were performed with 1,6-enyne **5a** (0.1 mmol), imine **3a** (0.05 mmol), [Pd] source (10 mol%), **L** (20 mol%), acid (x mol%) and 4 Å MS (20 mg) in degassed dry toluene (0.5 mL) at 70 °C for 12 h under Ar. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase. [d] With *t*-BuOH (0.1 mmol). [e] At 60 °C.



Asymetric synthesis of 4a via asymmetric catalysis: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added Pd_2dba_3 (4.6 mg, 0.0050 mmol, 5 mol%), **L6** (15.6 mg, 0.0200 mmol, 20 mol%) and **A1** (2.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (0.5 mL) was added via syringe. The mixture was stirred for 30 min at room temperature. Then *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5a** (49.8 mg, 0.200 mmol) and *N*-benzylidene-4-methylbenzene sulfonamide **3a** (25.9 mg, 0.100 mmol) in degassed dry toluene (0.5 mL) were added to the mixture via syringe under argon atmosphere (0.1 M total concentration), and the tube was evacuated and back-filled with argon for five times again. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4a**: 44.9 mg (0.0883 mmol), as whilte solid, 88% yield; $[\alpha]_D^{25}$ = 13.6 (*c* = 1.50 in $CHCl_3$); 46% ee, determined by HPLC analysis (Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm) t_R = 9.99 min (minor), t_R = 11.83 min (major).

The above reaction was performed with *t*-BuOH (14.8 mg, 19.1 μL, 0.200 mmol) as additive to give product **4a**: 30.5 mg (0.0600 mmol), 60% yield, 26% ee.

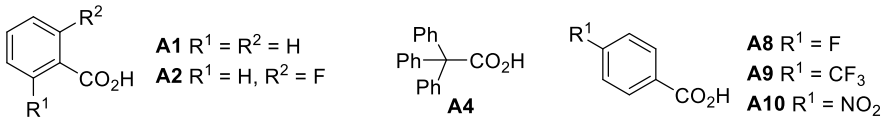


Asymetric synthesis of 4a via three component auto-tamdem catalysis: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added Pd_2dba_3 (4.6 mg, 0.0050 mmol, 5 mol%), **L6** (15.6 mg, 0.0200 mmol, 20 mol%) and **A1** (2.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (0.5 mL) was added via syringe. The mixture was stirred for 30 min at room temperature. Then 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **1a** (42.0 mg, 0.201 mmol), allyl *tert*-butyl carbonate **2a** (31.6 mg, 0.200

mmol) and *N*-benzylidene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol) in degassed dry toluene (0.5 mL) were added to the mixture via syringe sequentially under argon atmosphere (0.1 M total concentration), and the tube was evacuated and back-filled with argon for five times again. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4a**: 12.2 mg (0.0240 mmol), as a whilte solid, 24% yield; 11% ee, determined by HPLC analysis (Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm) t_R = 10.00 min (minor), t_R = 11.87 min (major).

8. Asymmetric synthesis through remote chirality transfer

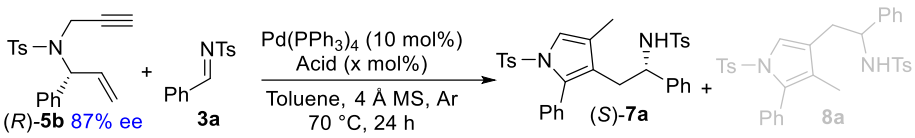
Table S8.1. Detailed screening conditions for asymmetric synthesis of (*R*)-**7a** from (*S*)-**1b**[a]

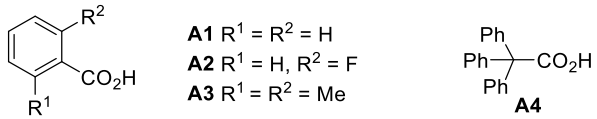


Entry	Acid	x	*T* (°C)	Yield (%)[b]	rr[c]	ee[d]
1	**A1**	40	80	82	84:16	97/80
2	**A2**	**40**	**80**	**81**	**97:3**	**97/ND**
3	**A4**	40	80	trace	/	/
4	**A8**	40	80	56	96:4	96/ND
5	**A9**	40	80	trace	/	/
6	**A10**	40	80	trace	/	/
7	**A2**	60	80	79	92:8	96/ND
8	**A2**	100	80	57	99:1	94/ND
9	**A2**	40	60	messy	/	/
10	**A2**	40	100	53	80:20	94/60

[a] Unless noted otherwise, reactions were performed with (*S*)-**1b** (0.1 mmol), **2a** (0.15 mmol), **3a** (0.05 mmol), $Pd(PPh_3)_4$ (10 mol%), acid (x mol%) and 4 Å MS (20 mg) in degassed dry toluene (0.5 mL) for 96 h under Ar. [b] Isolated yield of (*R*)-**7a**. [c] rr = **7a**:**8a**, determined by ^{1}H NMR analysis. [d] Determined by HPLC analysis on a chiral stationary phase.

Table S8.2. Detailed screening conditions for asymmetric synthesis of (*S*)-**7a** from (*R*)-**5b**[a]

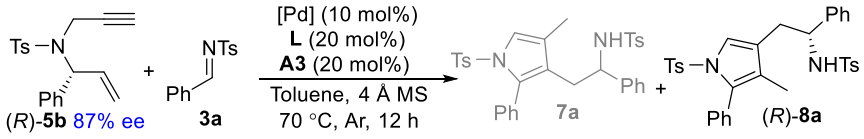


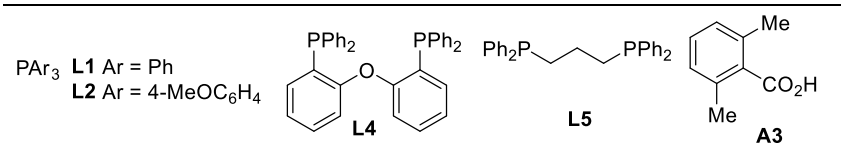


Entry	Acid	x	Yield (%)[b]	rr[c]	ee[d]
1	**A1**	20	75	50:50	83/59
2	**A1**	50	90	75:25	78/70
3	**A1**	100	91	94:6	70/ND
4	**A2**	20	65	63:37	70/65
5	**A3**	20	60	54:46	70/64
6	**A4**	20	52	75:25	87/75
7	**A4**	**100**	**48**	**97:3**	**86/ND**

[a] Unless noted otherwise, reactions were performed with (*R*)-**5b** (0.1 mmol), **3a** (0.05 mmol), $Pd(PPh_3)_4$ (10 mol%), acid (x mol%) and 4 Å MS (20 mg) in degassed dry toluene (0.5 mL) at 70 °C for 24 h under Ar. [b] Isolated yield of (*S*)-**7a**. [c] rr = **7a**:**8a**, determined by ^{1}H-NMR analysis. [d] Determined by HPLC analysis on a chiral stationary phase.

Table S8.3. Detailed screening conditions for asymmetric synthesis of (*R*)-**8a** from (*R*)-**5b**[a]



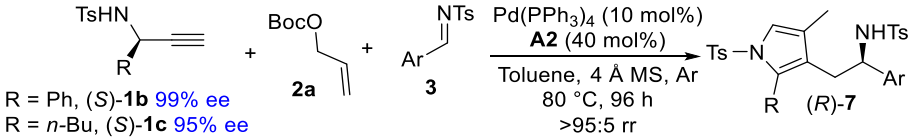


Entry	[Pd]	**L**	Yield (%)[b]	rr[c]	ee[d]
1	**Pd(allyl)Cp**	**L1**	**75**	**5:95**	**ND/68**
2	Pd(allyl)Cp	**L2**	48	17:83	85/66
3	Pd(allyl)Cp	**L4**	trace	/	/
4	Pd(allyl)Cp	**L5**	NR	/	/

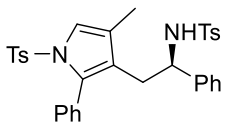
5	Pd(cinnamyl)Cp	**L1**	88	75:25	85/65

[a] Unless noted otherwise, reactions were performed with (*R*)-**5b** (0.1 mmol), **3a** (0.05 mmol), [Pd] source (10 mol%), **L** (20 mol%), **A3** (20 mol%) and 4 Å MS (20 mg) in degassed dry toluene (0.5 mL) at 70 °C for 24 h under Ar. [b] Isolated yield of (*R*)-**8a**. [c] rr = **7a**:**8a**, determined by ^{1}H-NMR analysis. [d] Determined by HPLC analysis on a chiral stationary phase.

8.1 Asymmetric synthesis of chiral product (*R*)-7 from (*S*)-1

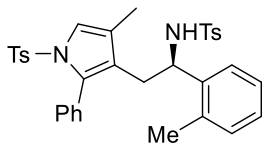


General procedure D: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*S*)-4-methyl-*N*-(1-phenylprop-2-yn-1-yl)benzenesulfonamide (*S*)-**1b** (57.0 ng, 0.200 mmol) or (*S*)-N-(hept-1-yn-3-yl)-4-methylbenzenesulfonamide (*S*)-**1c** (63.0 mg, 0.0200 mmol), allyl *tert*-butyl carbonate **2a** (47.4 mg, 0.299 mmol), aldimine **3** (0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 80 °C for 96 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give chiral product (*R*)-**7**.

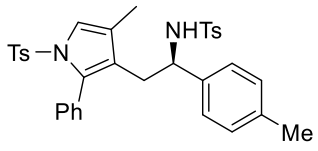


Synthesis of chiral (*R*)-7a: General procedure D: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*S*)-4-methyl-*N*-(1-phenylprop-2-yn-1-yl)benzenesulfonamide (*S*)-**1b** (57.0 ng, 0.200 mmol), allyl *tert*-butyl carbonate **2a** (47.4 mg, 0.299 mmol), *N*-benzylidene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 80 °C for 96 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give chiral product (*R*)-**7a**：46.7 mg (0.0798 mmol), as a whilte solid, 80% yield; >95:5 rr; $[\alpha]_D^{25}$ = 28.9 (*c* = 0.27 in $CHCl_3$); 97% ee, determined by HPLC analysis (Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH =

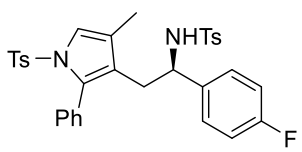
80/20, flow rate = 1.0 mL/min, l = 254 nm) t_R = 18.33 min (minor), t_R = 20.76 min (major).



Synthesis of chiral (*R*)-7b: General procedure D: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*S*)-4-methyl-*N*-(1-phenylprop-2-yn-1-yl)benzenesulfonamide (*S)*-**1b** (57.0 ng, 0.200 mmol), allyl *tert*-butyl carbonate **2a** (47.4 mg, 0.299 mmol), 4-methyl-*N*-(2-methylbenzylidene) benzene-sulfonamide **3b** (27.3 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 80 °C for 96 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give chiral product (*R*)-**7b**： 42.7 mg (0.0713 mmol), as a light yellow solid, 71% yield; >95:5 rr; $[\alpha]_D^{25}$ = –18.9 (*c* = 1.92 in $CHCl_3$); 95% ee, determined by HPLC analysis (Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm) t_R = 16.89 min (major), t_R = 20.87 min (minor).

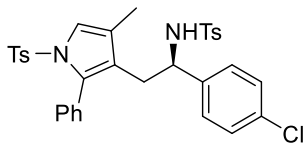


Synthesis of chiral (*R*)-7d: General procedure D: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*S*)-4-methyl-*N*-(1-phenylprop-2-yn-1-yl)benzenesulfonamide (*S)*-**1b** (57.0 ng, 0.200 mmol), allyl *tert*-butyl carbonate **2a** (47.4 mg, 0.299 mmol), 4-methyl-*N*-(4-methylbenzylidene) benzenesulfonamide **3d** (27.3 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 80 °C for 96 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give chiral product (*R*)-**7d**: 35.2 mg (0.0588 mmol), as a whilte solid, 59% yield; >95:5 rr; $[\alpha]_D^{25}$ = –16.9 (*c* = 1.56 in $CHCl_3$); 95% ee, determined by HPLC analysis (Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm) t_R = 18.09 min (major), t_R = 20.46 min (minor).

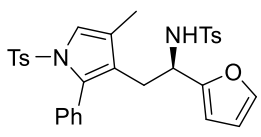


Synthesis of chiral (*R*)-7g: General procedure D: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*S*)-4-methyl-*N*-(1-phenylprop-2-yn-1-yl)benzenesulfonamide (*S)*-**1b** (57.0 ng, 0.200

mmol), allyl *tert*-butyl carbonate **2a** (47.4 mg, 0.299 mmol), *N*-(4-fluorobenzylidene)-4-methyl benzenesulfonamide **3f** (27.7 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 80 °C for 96 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give chiral product (*R*)-**7g**: 38.5 mg (0.0638 mmol), as a whilte solid, 64% yield; >95:5 rr; $[\alpha]_D^{25}$ = 3.3 (*c* = 1.56 in $CHCl_3$); 97% ee, determined by HPLC analysis (Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm) t_R = 17.27 min (minor), t_R = 18.98 min (major).

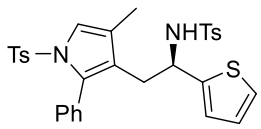


Synthesis of chiral (*R*)-7h: General procedure D: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*S*)-4-methyl-*N*-(1-phenylprop-2-yn-1-yl)benzenesulfonamide (*S)*-**1b** (57.0 ng, 0.200 mmol), allyl *tert*-butyl carbonate **2a** (47.4 mg, 0.299 mmol), *N*-(4-chlorobenzylidene)-4-methyl benzenesulfonamide **3g** (29.3 mg, 0.0997 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 80 °C for 96 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give chiral product (*R*)-**7h**：42.6 mg (0.0688 mmol), as a whilte solid, 69% yield; >95:5 rr; $[\alpha]_D^{25}$ = 4.4 (*c* = 2.08 in $CHCl_3$); 96% ee, determined by HPLC analysis (Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm) t_R = 16.87 min (major), t_R = 19.05 min (minor).

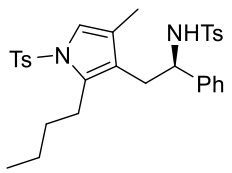


Synthesis of chiral (*R*)-7j: General procedure D: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*S*)-4-methyl-*N*-(1-phenylprop-2-yn-1-yl)benzenesulfonamide (*S)*-**1b** (57.0 ng, 0.200 mmol), allyl *tert*-butyl carbonate **2a** (47.4 mg, 0.299 mmol), 4-methyl-*N*-(thiophen-2-ylmethylene)benzene-sulfonamide **3j** (26.5 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was

stirred at 80 °C for 96 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give chiral product (*R*)-**7j**: 44.2 mg (0.0770 mmol), as a whilte solid, 77% yield; >95:5 rr; $[\alpha]_D^{25}$ = 1.0 (*c* = 1.92 in $CHCl_3$); 96% ee, determined by HPLC analysis (Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm) t_R = 16.15 min (major), t_R = 19.42 min (minor).



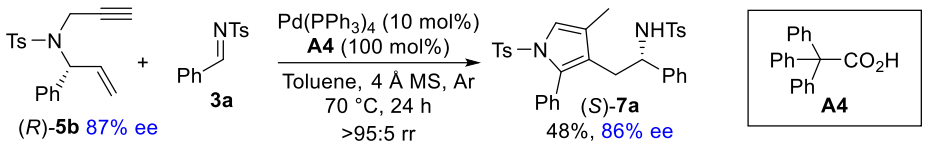
Synthesis of chiral (*R*)-7k: General procedure D: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*S*)-4-methyl-*N*-(1-phenylprop-2-yn-1-yl)benzenesulfonamide (*S)*-**1b** (57.0 ng, 0.200 mmol), allyl *tert*-butyl carbonate **2a** (47.4 mg, 0.299 mmol), *N*-(furan-2-ylmethylene)-4-methylbenzene sulfonamide **3i** (24.9 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 80 °C for 96 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give chiral product (*R*)-**7k**: 35.6 mg (0.0602 mmol), as whilte solid, 60% yield; >95:5 rr; $[\alpha]_D^{25}$ = –6.4 (*c* = 1.57 in $CHCl_3$); 95% ee, determined by HPLC analysis (Daicel chiralpak IA, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm) t_R = 14.82 min (major), t_R = 16.76 min (minor).



Synthesis of chiral (*R*)-7q: General procedure D: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*S*)-*N*-(hept-1-yn-3-yl)-4-methylbenzenesulfonamide (*S)*-**1c** (63.0 mg, 0.0200 mmol), allyl *tert*-butyl carbonate **2a** (47.4 mg, 0.299 mmol), *N*-benzylidene-4-methylbenzene-sulfonamide **3a** (25.9 mg, 0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A2** (5.6 mg, 0.040 mmol, 40 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 80 °C for 48 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give chiral product (*R*)-**7q**: 40.6 mg (0.0719 mmol), as yellow solid, 72% yield; >95:5 rr; $[\alpha]_D^{25}$ = –5.6 (*c* = 0.61 in $CHCl_3$); 90% ee, determined by HPLC analysis (Daicel chiralpak IA, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm) t_R = 9.89 min (minor), t_R = 11.15 min

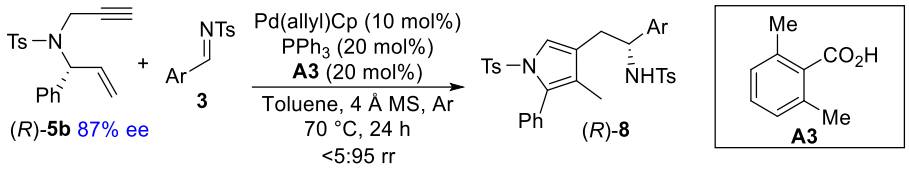
(major).

8.2 Asymmetric synthesis of (*S*)-7a from *(R)*-5b

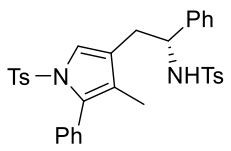


To a 10mL Schlenk tube equipped with a stirring bar were added (*R*)-4-methyl-*N*-(1-phenyl allyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (*R*)-**5b** (65.0 mg, 0.200 mmol), *N*-benzylidene-4-methyl benzenesulfonamide **3a** (25.9 mg, 0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A4** (28.8 mg, 0.0999 mmol, 100 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give chiral product (*S*)-**7a**: 28.2 mg (0.0482 mmol), as whilte solid, 48% yield; >95:5 rr; $[\alpha]_D^{25}$ = –19.3 (*c* = 0.43 in $CHCl_3$); 86% ee, determined by HPLC analysis (Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm) t_R = 18.25 min (major), t_R = 20.65 min (minor).

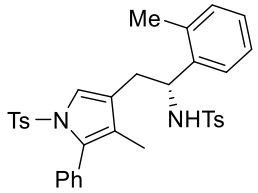
8.3 Asymmetric synthesis of chiral 8 from *(R)*-5b



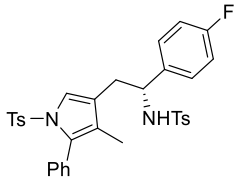
General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*R*)-4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (*R*)-**5b** (65.0 mg, 0.200 mmol), aldimine **3** (0.100 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h to 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give chiral product **8**.



Synthesis of chiral (*R*)-8a: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*R*)-4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (*R*)-**5b** (65.0 mg, 0.200 mmol), *N*-benzylidene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give chiral product (*R*)-**8a**: 43.2 mg (0.0739 mmol), as a white solid, 74*%* yield; 5:95 rr; $[\alpha]_D^{25}$ = 13.0 (*c* = 0.68 in $CHCl_3$); 68% ee, determined by HPLC analysis (Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm) t_R = 14.21 min (minor), t_R = 16.46 min (major).

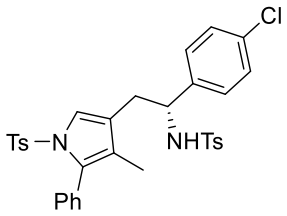


Synthesis of chiral (*R*)-8b: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*R*)-4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (*R*)-**5b** (65.0 mg, 0.200 mmol), 4-methyl-*N*-(2-methylbenzylidene)benzenesulfonamide **3b** (27.3 mg, 0.0999 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give chiral product (*R*)-**8b**: 46.6 mg (0.0779mmol), as a yellow solid, 78% yield; 5:95 rr; $[\alpha]_D^{25}$ = 10.8 (*c* = 2.15 in $CHCl_3$); 80% ee, determined by HPLC analysis (Daicel chiralpak IE, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm) t_R = 19.45 min (major), t_R = 21.79 min (minor).



Synthesis of chiral (*R*)-8g: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*R*)-4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (*R*)-**5b** (65.0 mg, 0.200 mmol), *N*-(4-fluorobenzylidene)-4-methylbenzenesulfonamide **3f** (27.7 mg, 0.0999 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%),

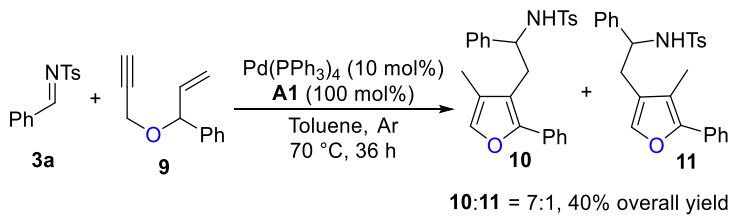
A3 (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give chiral product (*R*)-**8g**: 44.8 mg (0.0743mmol), as a yellow solid, 74% yield; <5:95 rr; $[\alpha]_D^{25}$ = 22.6 (*c* = 2.85 in $CHCl_3$); 74% ee, determined by HPLC analysis (Daicel chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm) t_R = 51.97 min (major), t_R = 59.34 min (minor).



Synthesis of chiral (*R*)-8h: General procedure C: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added (*R*)-4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (*R*)-**5b** (65.0 mg, 0.200 mmol), *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide **3g** (29.3 mg, 0.0997 mmol), Pd(allyl)Cp (2.1 mg, 0.0099 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A3** (3.0 mg, 0.020 mmol, 20 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 24 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give chiral product (*R*)-**8h**: 46.6 mg (0.0753mmol), as a yellow solid, 75% yield; <5:95 rr; $[\alpha]_D^{25}$ = 20.4 (*c* = 2.30 in $CHCl_3$); 78% ee, determined by HPLC analysis (Daicel chiralpak IE, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm) t_R = 16.23 min (major), t_R = 18.54 min (minor).

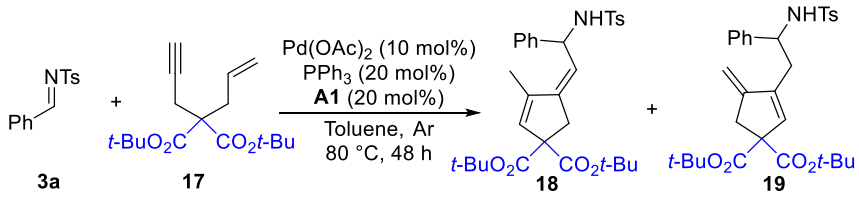
9. Exploration of other substrates

9.1 Exploration of more 1,6-enynes



Synthesis of 10 and 11: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-benzylidene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), 3-(prop-2-yn-1-

yloxy)prop-1-ene **9** (34.4 mg, 0.200 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%), **A1** (12.2 mg, 0.100 mmol, 100 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 36 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give products **10** and **11** as inseparable regioselective isomers: 17.2 mg (0.0399 mmol), as a colorless oil, 40% yield; **10**:**11** = 7:1; for **10**: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46–7.39 (m, 4H), 7.39–7.34 (m, 2H), 7.31–7.27 (m, 1H), 7.17–7.12 (m, 3H), 7.10–7.05 (m, 3H), 7.04–6.99 (m, 2H), 4.95–4.79 (m, 1H), 4.37 (dt, *J* = 7.4, 6.0 Hz, 1H), 3.13 (dd, *J* = 14.4, 7.6 Hz, 1H), 2.93 (dd, *J* = 14.4, 7.4 Hz, 1H), 2.35 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.4, 143.1, 140.6, 138.3, 136.8, 131.2, 129.3, 128.7, 128.4, 127.6, 127.4, 127.0, 126.5, 125.8, 122.0, 116.3, 57.8, 32.9, 21.5, 8.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{25}NO_3SNa^+$ 454.1447; Found 454.1449.

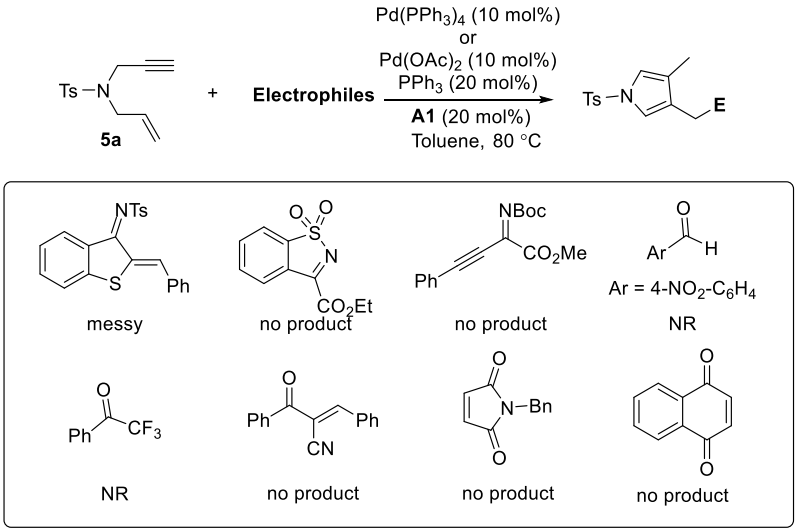


18:**19** = 1:1, 60% overall yield

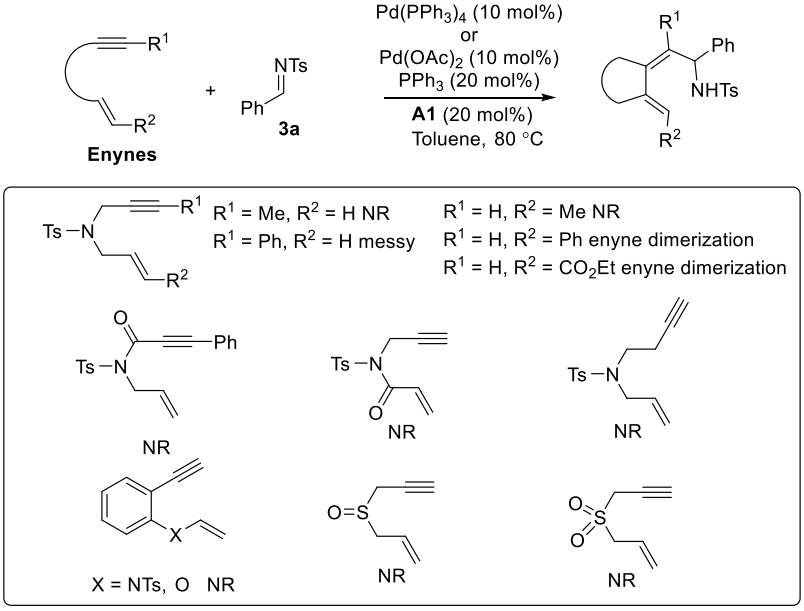
Synthesis of 18 and 19: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-benzylidene-4-methylbenzenesulfonamide **3a** (25.9 mg, 0.100 mmol), di-*tert*-butyl 2-allyl-2-(prop-2-yn-1-yl)malonate **17** (58.8 mg, 0.200 mmol), $Pd(OAc)_2$ (2.2 mg, 0.0098 mmol, 10 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), **A1** (2.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 80 °C for 48 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8 to 1/5) to give products **18** and **19** as inseparable isomers: 34.2 mg (0.0617 mmol), as a colorless oil, 62% total yield; **18**:**19** = 1:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 4.2 Hz, 4H), 7.22–7.11 (m, 8H), 7.08–6.99 (m, 2H), 5.81 (s, 1H), 5.75 (s, 1H), 5.13 (dd, *J* = 9.4, 6.0 Hz, 1H), 5.06–4.96 (m, 2H), 4.90 (d, *J* = 6.5 Hz, 1H), 4.80–4.71 (m, 2H), 4.44 (dt, *J* = 7.2, 5.8 Hz, 1H), 3.15–2.99 (m, 2H), 2.98–2.84 (m, 2H), 2.68 (dd, *J* = 14.6, 7.2 Hz, 1H), 2.59 (dd, *J* = 14.8, 7.0 Hz, 1H), 2.37 (s, 3H), 2.36 (s, 3H), 1.54–1.49 (m, 12H), 1.43 (s, 9H), 1.41 (s, 9H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.69,

169.66, 169.62, 169.2, 149.9, 146.5, 143.09, 143.07, 142.5, 140.4, 137.9, 137.1, 134.9, 132.4, 129.4, 129.3, 128.7, 128.4, 127.8, 127.5, 127.4, 127.3, 126.8, 126.6, 118.4, 103.9, 81.84, 81.76, 81.72, 81.70, 65.2, 65.0, 57.3, 56.2, 37.4, 35.4, 34.7, 27.9, 27.83, 27.82, 27.81, 21.4, 12.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{39}NO_6SNa^+$ 576.2390; Found 576.2387.

9.2 Unsuccessful substrates attempts

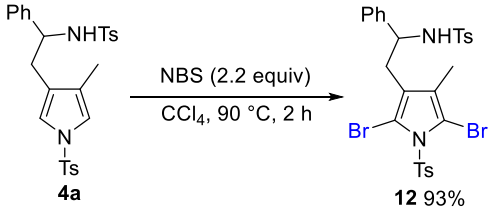


More types of activated ketimine, aldehyde, ketone and Michael acceptors were employed to react with **5a** under the optimal condition. Unfortunately, complex reaction profiles or no obvious conversions were generally observed as outlined above.

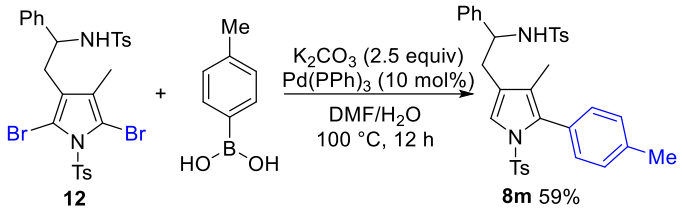


On the other hand, the above outlined enynes (bearing different substituents or linkers) were generally inert to the reation with **3a**.

10. Synthetic transformations

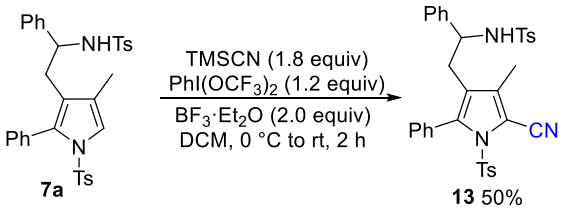


Synthesis of 12: To a 10 mL tube equipped with a stirring bar were added **4a** (30.6 mg, 0.0602 mmol), N-Bromosuccinimide (23.5 mg, 0.132 mmol) and CCl_4 (0.5 mL). The mixture was stirred at 90 °C for 2 h, and monitored by TLC (EtOAc/petroleum ether = 1/10). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **12**: 37.2 mg (0.0558 mmol), as a white solid, 93% yield; mp 69–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.76 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.17–7.11 (m, 3H), 7.08 (d, J = 8.0 Hz, 2H), 7.06–7.00 (m, 2H), 4.95–4.82 (m, 1H), 4.30–4.17 (m, 1H), 2.69 (dd, J = 14.4, 9.2 Hz, 1H), 2.53 (dd, J = 14.4, 5.8 Hz, 1H), 2.35 (s, 3H), 2.35 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 145.7, 143.6, 140.8, 136.6, 135.4, 130.0, 129.5, 128.6, 127.7, 127.6, 126.7, 126.2, 125.9, 125.8, 102.2, 101.9, 57.4, 34.7, 21.73, 21.67, 11.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{26}{}^{79}Br_2N_2O_4S_2Na^+$ 686.9593; Found 686.9686; Calcd for $C_{27}H_{26}{}^{79}Br^{81}Br\ N_2O_4S_2Na^+$ 688.9573; Found 688.9568; Calcd for $C_{27}H_{26}{}^{81}Br_2\ N_2O_4S_2Na^+$ 690.9552; Found 690.9548.

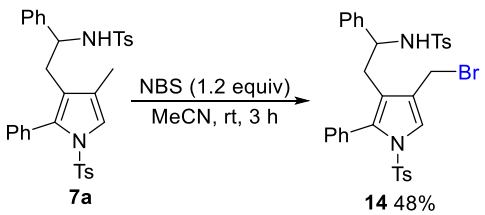


Synthesis of 8m: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-(2-(2,5-dibromo-4-methyl-1-tosyl-1*H*-pyrrol-3-yl)-1-phenylethyl)-4-methylbenzenesulfonamide **12** (39.8 mg, 0.600 mmol), 4-tolylboronic acid (17.9 mg, 0. 132 mmol), potassium carbonate (20.7 mg, 0.150 mmol) and $Pd(PPh_3)_4$ (6.9 mg, 0.0060 mmol, 10 mol%).The tube was capped, evacuated and back-filled with argon for five times. Then degassed DMF (0.3 mL) and H_2O (0.2 mL) were added via syringe. The mixture was stirred at 100 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the reaction was cooled down to room temperature, and diluted with H_2O (3.0 mL) and extracted with EtOAc (3.0 mL × 3). The combined organic layers

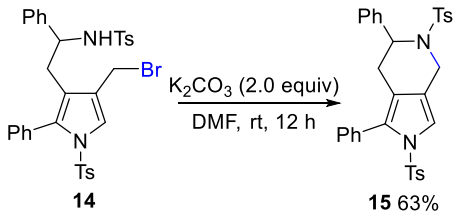
were washed with brine (3.0 mL × 2), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/6 to 1/5) to give product **8m**, which was determined by H-NMR and ^{13}C-NMR, 21.1 mg (0.0352 mmol), as a white solid, 59% yield.



Synthesis of 13: To a stirred solution of phenyliodine bis(trifluoroacetate) (31.0 mg, 0.0721 mmol) in DCM (0.5 mL) was added boron trifluoride diethyl etherate (20.3 mg, 0.144 mmol) and trimethylsilyl cyanide (10.7 mg, 0.108 mmol) via syringe sequentially at 0 °C under argon atmosphere. The mixture was stirred for 30 min at 0 °C before **7a** (35.0 mg, 0.0599 mmol) in DCM (0.5 mL) was added. Then the mixture was gradually warmed to room temperature, and stirred for another 2 h. After completion (monitored by TLC), the mixture was quenched with saturated sodium bicarbonate solution (2.0 mL) and saturated sodium thiosulfate solution (2.0 mL), then extracted with EtOAc (3.0 mL × 3). The combined organic layers were washed with brine (3.0 mL × 2), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **13**: 18.3 mg (0.0300 mmol), as a white solid, 50% yield; mp 79–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49–7.46 (m, 1H), 7.45–7.41 (m, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.24–7.18 (m, 5H), 7.18–7.08 (m, 5H), 6.78 (d, J = 7.0 Hz, 2H), 6.67 (d, J = 7.6 Hz, 1H), 4.51 (d, J = 7.0 Hz, 1H), 4.14–3.98 (m, 1H), 2.61–2.52 (m, 1H), 2.48 (s, 3H), 2.46–2.41 (m, 1H), 2.40 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 145.9, 144.0, 140.3, 138.3, 137.0, 136.7, 134.8, 131.5, 131.2, 129.9, 129.6, 128.9, 128.7, 128.1, 127.8, 127.7, 126.7, 126.0, 123.2, 112.4, 103.8, 57.6, 32.8, 21.7, 21.6, 10.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{31}N_3O_4S_2Na^+$ 632.1648; Found 632.1649.



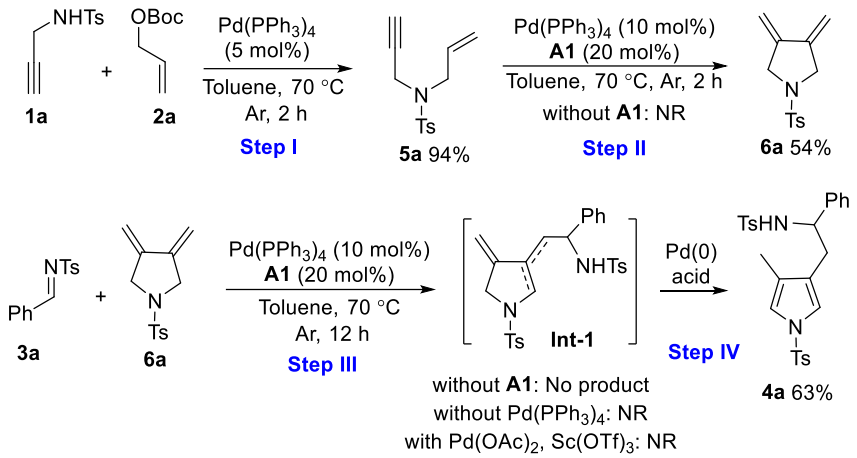
Synthesis of 14: To a stirred solution of **7a** (35.0 mg, 0.0599 mmol) in MeCN (0.6 mL) was added N-Bromosuccinimide (12.8 mg, 0.719 mmol). The mixture was stirred at room temperature for 3 h. After completion (monitored by TLC), the solvent was concentrated in vacuo.The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **14**: 18.9 mg (0.0285 mmol), as a white solid, 48% yield; mp 75–76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.48–7.33 (m, 4H), 7.34–7.28 (m, 1H), 7.27–7.19 (m, 2H), 7.23–7.11 (m, 4H), 7.14–7.03 (m, 5H), 6.82 (d, J = 6.8 Hz, 2H), 6.45 (brs, 1H), 4.74 (d, J = 6.2 Hz, 1H), 4.32–4.04 (m, 3H), 2.76–2.59 (m, 2H), 2.41 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 145.0, 143.3, 140.7, 137.1, 135.2, 133.4, 129.7, 129.5, 129.4, 129.1, 128.9, 128.4, 127.8, 127.4, 127.3, 127.0, 126.2, 122.07, 122.05, 121.8, 57.6, 33.1, 24.7, 21.6, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{31}{}^{79}BrN_2O_4S_2Na^+$ 685.0801; Found 685.0798; Calcd for $C_{33}H_{31}{}^{81}BrN_2O_4S_2Na^+$ 687.0780; Found 687.0780.



Synthesis of 15: To a stirred solution of **14** (39.8 mg, 0.0600 mmol) in DMF (1.2 mL) was added potassium carbonate (16.6 mg, 0.120 mmol), the mixture was stirred at room temperature for 12 h. After completion (monitored by TLC), the mixture was quenched with water and extracted with EtOAc (3.0 mL × 3). The combined organic layers were washed with brine (3.0 mL × 2), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **15**: 22.0 mg (0.0378 mmol), as a white solid, 63% yield; mp 74–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65–7.54 (m, 2H), 7.37–7.27 (m, 4H), 7.23–7.10 (m, 8H), 7.10–7.01 (m, 4H), 6.95 (s, 1H), 6.93 (s, 1H), 5.33 (d, J = 6.2 Hz, 1H), 4.79 (d, J = 16.6 Hz, 1H), 3.84 (d, J = 16.6 Hz, 1H), 2.57 (d, J = 1.6 Hz, 1H), 2.49 (dd, J = 16.8, 6.4 Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.7, 143.1, 138.3, 137.7, 135.8, 131., 130.3, 129.9, 129.4, 128.4, 127.6, 127.5, 127.24, 127.18, 120.8, 118.9, 116.7, 53.8, 38.7, 23.6, 21.7, 21.4.; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{30}N_2O_4S_2Na^+$ 605.1539; Found 605.1549.

11. Mechanism and regiodivergence studies

11.1 Elucidation of the process of tandem reaction



Step I: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **1a** (21.0 mg, 0.100 mmol), allyl *tert*-butyl carbonate **2a** (15.8 mg, 0.0999 mmol) and $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (0.5 mL) was added via syringe. The mixture was stirred at 70 °C for 2 h, and monitored by TLC (EtOAc/petroleum ether = 1/10). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfon amide **5a**: 23.4 mg (0.0938 mmol), as a white solid, 94% yield.

Step II: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5a** (24.9 mg, 0.0999 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol%) and **A1** (2.4 mg, 0.0197 mmol 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (0.5 mL) was added via syringe. The mixture was stirred at 70 °C for 2 h, and monitored by TLC (EtOAc/petroleum ether = 1/10). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give 3,4-dimethylene-1-tosylpyrrolidine **6a**: 13.5 mg (0.0542 mmol), as a white solid, 54% yield. The NMR spectra were consistent with the literature report (*Nat. Prod. Rep.* **2010**, *27*, 1801).

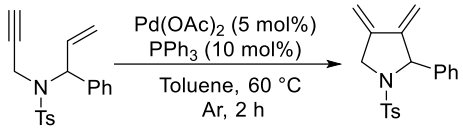
*Notably, no reaction was observed in the absence of **A1**, which indicated that acid was crucial for the cycloisomerization of enyne.*

Step III and Step IV: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-benzylidene-4-methylbenzenesulfonamide **3a** (13.0 mg, 0.0501 mmol) 3,4-dimethylene-1-tosylpyrrolidine **6a** (14.9, 0.0598 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.0050 mmol, 5 mol%) and **A1** (2.4 mg, 0.0197 mmol 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (0.5 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h, and monitored by TLC (EtOAc/petroleum ether = 1/5). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **4a**: 16.1 mg (0.0317 mmol), as a white solid, 63% yield.

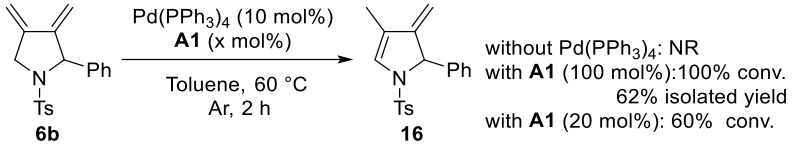
Both **3a** and **6a** were consumed completely, but no product **4a** was detected without **A1**. No obvious conversion was observed without $Pd(PPh_3)_4$. *These results demonstrated that both palladium and acid are crucial in the vinylogous addition and aromatization steps.*

Othe Lewis acid, such as $Pd(OAc)_2$, $Sc(OTf)_3$ could not promote the transformation, which indicated the mechanism would not involve an Alder-ene type process.

11.2 Rationale for regioselective 3-pyrrolylmethylation

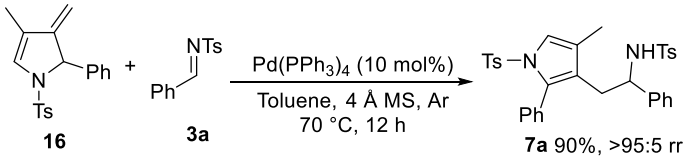


Synthesis of 6b: To an oven-dried 100 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-(1-phenylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **5b** (488.1 mg, 1.500 mmol), $Pd(OAc)_2$ (16.8 mg, 0.0748 mmol, 5 mol%) and PPh_3 (39.0 mg, 0.149 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (15.0 mL) was added via syringe. The mixture was stirred at 60 °C for 2 h, and monitored by TLC (EtOAc/petroleum ether = 1/10). After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give 3,4-dimethylene-2-phenyl-1-tosylpyrrolidine **6b**: 268.5 mg (0.8249 mmol), as a white solid, 55% yield, mp 93–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52 (d, J = 8.2 Hz, 2H), 7.29–7.24 (m, 5H), 7.19 (d, J = 8.0 Hz, 2H), 5.54–5.33 (m, 2H), 5.23 (s, 1H), 5.00 (s, 1H), 4.71 (s, 1H), 4.34–4.17 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 146.8, 143.4, 141.3, 141.1, 134.7, 129.4, 128.4, 127.7, 127.6, 127.4, 108.2, 105.9 , 67.9, 52.8, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{19}NO_2SNa^+$ 348.1029 Found 348.1036.



Isomerization of 6b to 16: To an oven-dried 50 mL Schlenk tube equipped with a stirring bar were added 3,4-dimethylene-2-phenyl-1-tosylpyrrolidine **6b** (162.7 mg, 0.5000 mmol), $Pd(PPh_3)_4$ (28.9 mg, 0.0248 mmol, 5 mol%), and **A1** (12.2 mg, 0.0998 mmol, 100 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (5.0 mL) was added via syringe. The mixture was stirred at 60 °C for 2 h, and monitored by ^{1}H-NMR analysis. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give **16**: 100.8 mg (0.3097 mmol), as a white solid, 62% yield, mp 138–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (d, J = 8.2 Hz, 2H), 7.33–7.20 (m, 7H), 6.73 (s, 1H), 5.05 (d, J = 3.0 Hz, 1H), 4.65 (d, J = 3.0 Hz, 1H), 4.38 (t, J = 2.2 Hz, 1H), 2.41 (s, 3H), 1.73 (d, J = 1.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.2, 143.8, 140.7, 133.9, 132.5, 129.7, 128.5, 127.9, 127.6, 127.3, 121.6, 101.3, 67.9, 21.6, 9.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{19}NO_2SNa^+$ 348.1029; Found 348.1036

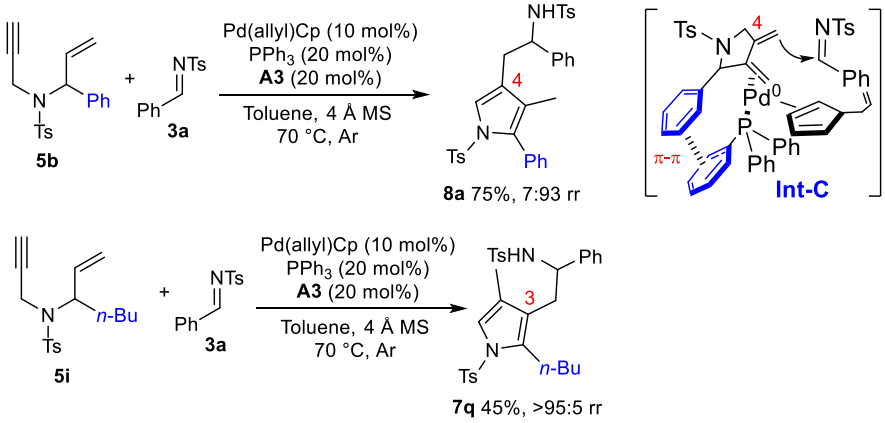
About 60% conversion was determined by ^{1}H-NMR analysis in the presence of **A1** (20 mol%) in 2 h. *These results clearly demonstrated that increasing the loadings of acid additive could facilitate the isomerization of **6b** to **16**.*



Synthesis of 7a from the reaction of 16 and 3a: To an oven-dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-3-methylene-2-phenyl-1-tosyl-2,3-dihydro-1*H*-pyrrole **16** (39.0 mg, 0.120 mmol), *N*-benzylidene-4-methyl benzenesulfonamide **3a** (25.9 mg, 0.100 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol, 10 mol%) and 4 Å MS (40 mg). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred at 70 °C for 12 h, and monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **7a**: 52.6 mg (0.0900 mmol), as a yellow solid, 90% yield; >95:5 rr.

*In conclusion, increasing the amounts of acid additive could improve the formation of 3-pyrrolylmethylated product **7a** by rapid generation of **16**.*

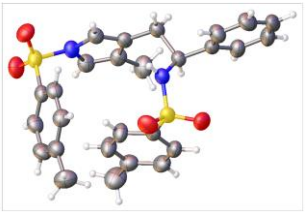
11.3 Rationale for regioselective 4-pyrrolylmethylation

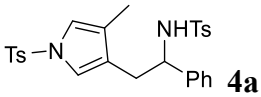


As outlined above, the reaction of *n*-butyl substituted enyne **5i** with **3a** still delivered 3-pyrrolylmethylated product **7q** exclusively under the catalysis of Pd(allyl)Cp, PPh_3 and acid **A3**, but using phenyl-subsituted enyne **5b** gave 4-pyrrolylmethylated product **8a** exclusively under the same catalytic conditions. *The results indicated that a phenyl group on **5b** was crucial for the formation of 4-pyrrolylmethylated **8a**, probably a π-π stacking between intermediate **6b** and ligand PPh_3, as outlined in **Int-C**, might help direct and stabilize the η^2-Pd^0-diene complex, which would result in the generation of 4-pyrrolylmethylated **8a**. Menawhile, allyl cyclopentadiene formed in situ might also play a significant role as a ligand,*

12. Crystal data, ECD spectra and structural refinement

Procedure for the recrystallization of 4a: to a 10 mL tube containing **4a** (20 mg) was added petroleum ether (3.6 mL) and *i*-PrOH (2.4 mL). The mixture was heated until a clear solution was formed, which was kept aside overnight at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the structure of **4a**. The data were collected by an Agilent Gemini equipped with a Cu radiation source (K = 1.54184 Å) at 296.9 K. CCDC 2184605 (**4a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.





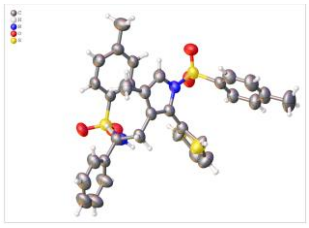
4a

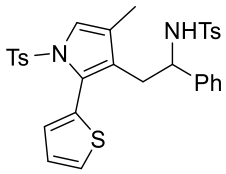
(ellipsoid contour probability 50%)

Identification code	**4a**
Empirical formula	$C_{27}H_{28}N_2O_4S_2$
Formula weight	508.63
Temperature/K	296.87(12)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.4288(3)
b/Å	10.4362(3)
c/Å	26.2815(7)
α/°	90
β/°	96.065(3)
γ/°	90
Volume/Å^3	2571.67(13)
Z	4
ρ_{calc}g/cm^3	1.314
μ/mm^{-1}	2.169
F(000)	1072.0
Crystal size/mm^3	0.5 × 0.35 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.764 to 142.66
Index ranges	$-11 \leq h \leq 11$, $-8 \leq k \leq 12$, $-31 \leq l \leq 27$
Reflections collected	14349
Independent reflections	4931 [R_{int} = 0.0507, R_{sigma} = 0.0434]
Data/restraints/parameters	4931/0/319
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0639, wR_2 = 0.1703
Final R indexes [all data]	R_1 = 0.0749, wR_2 = 0.1898
Largest diff. peak/hole / e Å^{-3}	0.46/-0.29

Procedure for the recrystallization of 7o: To a 10 mL tube containing **7o** (40 mg) was added petroleum ether, EtOAc and DCM (10:3:1, about 6.0 mL). The mixture was heated until a clear

solution was formed, which was kept aside overnight at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the structure of **7o**. The data were collected by an Agilent Gemini equipped with a Mo radiation source (K = 0.71073 Å) at 302.0 K. CCDC 2184606 (**7o**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.





7o

(ellipsoid contour probability 50%)

Identification code	**7o**
Empirical formula	$C_{31}H_{30}N_2O_4S_3$
Formula weight	590.75
Temperature/K	302.0
Crystal system	monoclinic
Space group	C2/c
a/Å	29.5374(19)
b/Å	9.7700(5)
c/Å	24.882(3)
α/°	90
β/°	122.932(2)
γ/°	90
Volume/Å^3	6026.6(8)
Z	8
ρ_{calc}g/cm^3	1.302
μ/mm^{-1}	0.284
F(000)	2480.0
Crystal size/mm^3	0.35 × 0.28 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.9 to 54.992
Index ranges	-38 ≤ h ≤ 38, -12 ≤ k ≤ 10, -32 ≤ l ≤ 32

Reflections collected	37923
Independent reflections	6899 [R_{int} = 0.0619, R_{sigma} = 0.0388]
Data/restraints/parameters	6899/0/378
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0497, wR_2 = 0.1164
Final R indexes [all data]	R_1 = 0.0920, wR_2 = 0.1404
Largest diff. peak/hole / e $Å^{-3}$	0.31/-0.32

ECD spectra and structural refinement for enantioenriched 7a and 8b

Computation details

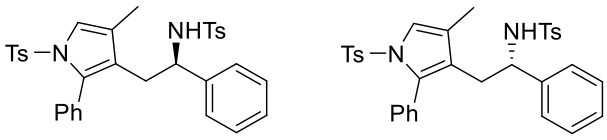
Conformational search of investigated compounds has been carried out by using Molclus software (version 1.9.9.4) together with Gaussian 09 software package.[5] All stable conformations obtained are then optimized using DFT at the PBE1PBE /6-31G(d) level, and the harmonic vibrational frequencies of each conformation were calculated at the same level. The self-consistent reaction field (SCRF) and SMD[6] solvation model was adopted to evaluate the effect of solvent (Methanol). The energy of each conformer and Boltzmann distribution was calculated. Based on the Boltzmann distribution of each conformer, the ECD of each represent conformer was calculated by TDDFT at the pbe1pbe/def2tzvp level and the weighted ECD spectrums were plotted by Multiwfn software.[7]

(5) L. Tian, Molclus program, Version 1.9.9.4, http://www.keinsci.com/research/ molclus.html

(6) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem*. 2011, **32**, 1456.

(7) T. Lu, and F. Chen, *J. Comput. Chem.* 2012, **33**, 580.

Results:



(*R*)-**7a** (*S*)-**7a**

The Boltzmann distribution of molecule (*S*)-**7a** and weighted ECD spectrum were given in **Table S12.1** and **Figure S12.1** respectively. The experimental ECD spectrum of (*S*)-**7a** is opposite to the predicted ECD spectrum, which means the experimental ECD of molecule **7a** is in *R*-configuration.

Table 12.1 The Boltzmann distribution of the investigated molecule (*S*)-**7a**.

(*S*)-**7a**	Index	DG(kcal/mol)	$Q_{i(Relat)}$	Percent
S-cluster6.log	1	0	1	59.47%
S-cluster4.log	2	0.70532124	0.304084886	18.08%
S-cluster8.log	3	0.96322785	0.196764875	11.70%
S-cluster5.log	4	1.066767	0.165216222	9.83%
S-cluster10.log	6	2.88340845	0.007699143	0.46%
S-cluster9.log	7	3.23544156	0.004250106	0.25%
S-cluster3.log	8	3.35466846	0.003475407	0.21%
S-cluster7.log	9	14.22941676	3.71315E-11	0.00%

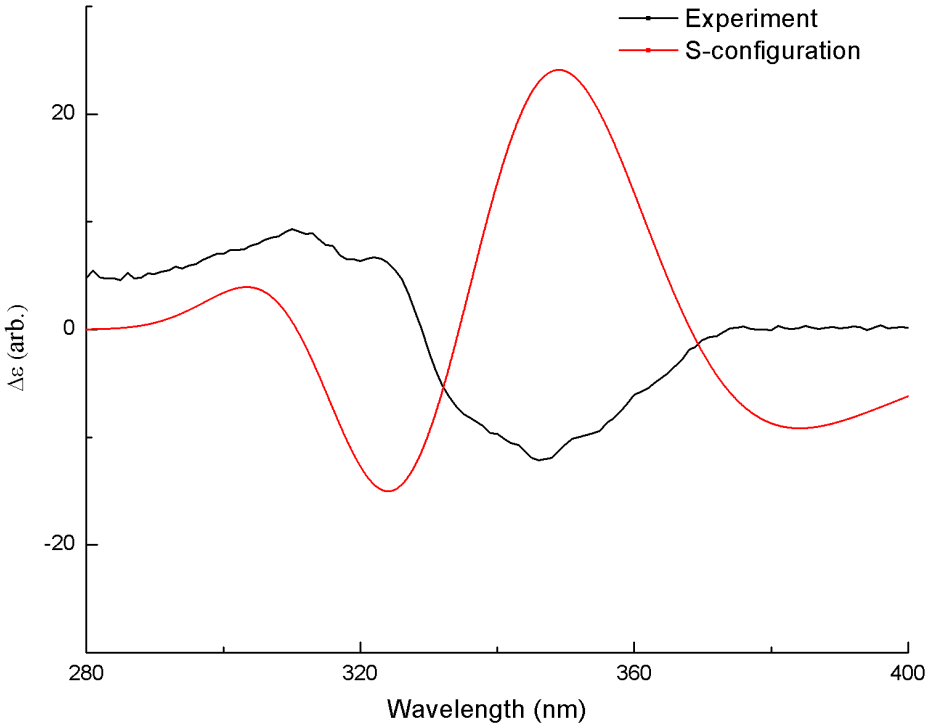
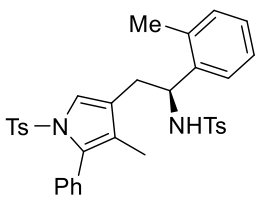
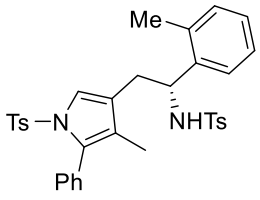


Figure S12.1. The experimental and predicted ECD of (*S*)-**7a**.



(*S*)-**8b**



(*R*)-**8b**

The molecule of (*S*)-**8b** may have different conformers in solvents and each conformer owns different ECD absorbing spectra. Hence, the ECD spectrum of experimental results is the average ECD spectrum of each conformer.

Conformational search shows that (*S*)-**8b** have 9 different conformer clusters, and 9 representative

conformers were chosen from each cluster. The Boltzmann distribution of 9 representative conformers was given in **Table S12.2**. The proportion of each conformer ranges from 2.14% to 41.69%. Hence, the ECD of 9 representative conformers were predicted and the weighted ECD spectrum was given in **Figure S12.2**.

The predicted ECD spectrum of (*S*)-**8b** is opposite to the experimental results in 300 nm wavelength, which means that the experimental product is in *R*-configuration.

Table S12.2. The Boltzmann distribution of the investigated molecule (*S*)-**8b**.

(*S*)-**8b**	Index	DG(kcal/mol)	$Q_{i(Relat)}$	Percent
conf26.log	1	0	1	41.69%
conf18.log	2	0.44929716	0.468449	19.53%
conf22.log	3	0.65072787	0.333436	13.90%
conf17.log	4	0.94000998	0.204629	8.53%
conf10.log	5	1.08998487	0.158867	6.62%
conf13.log	6	1.56626496	0.071108	2.96%
conf9.log	7	1.69866957	0.056867	2.37%
conf14.log	8	1.73067258	0.053877	2.25%
conf12.log	9	1.75891053	0.05137	2.14%

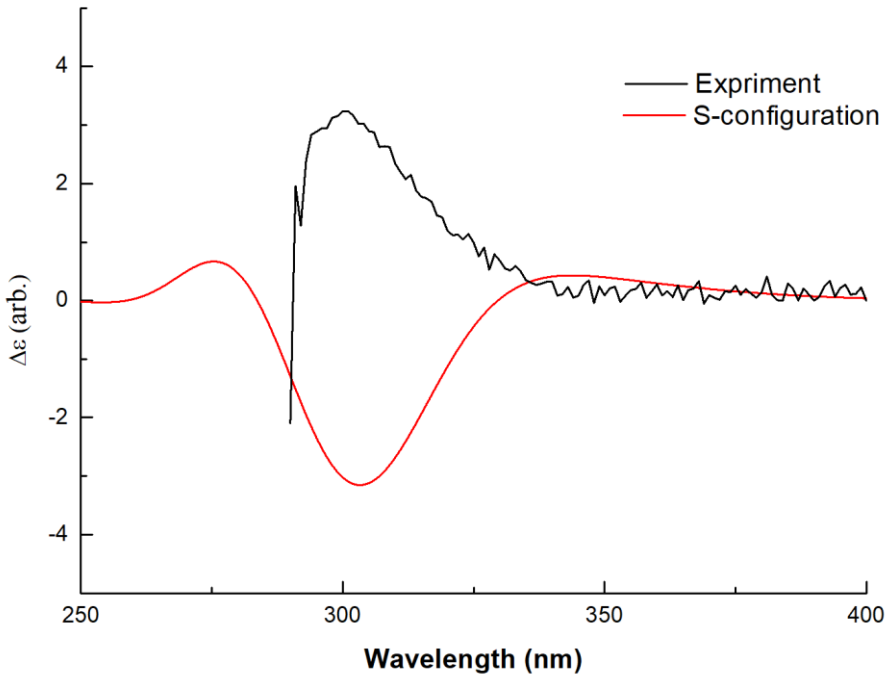
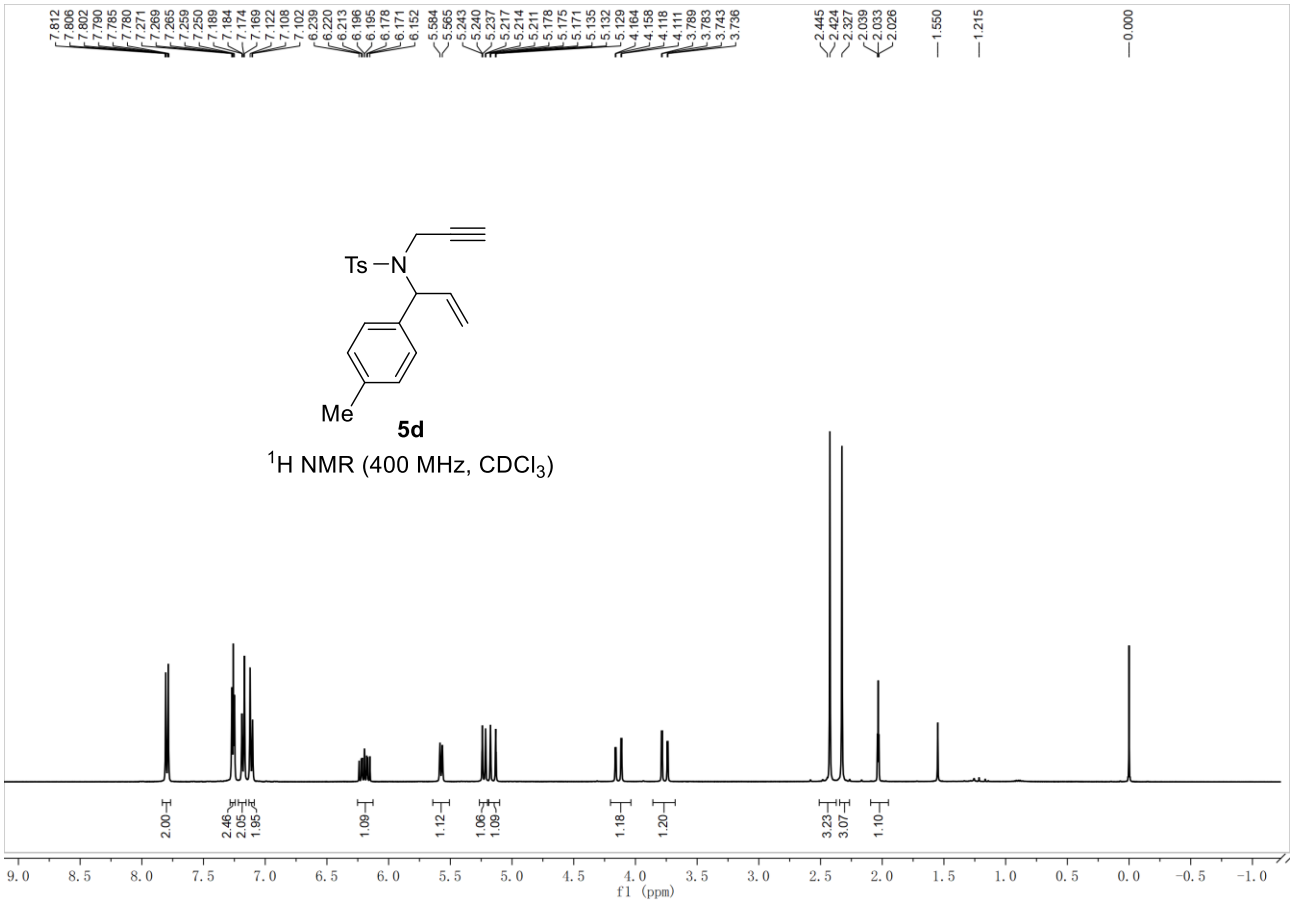
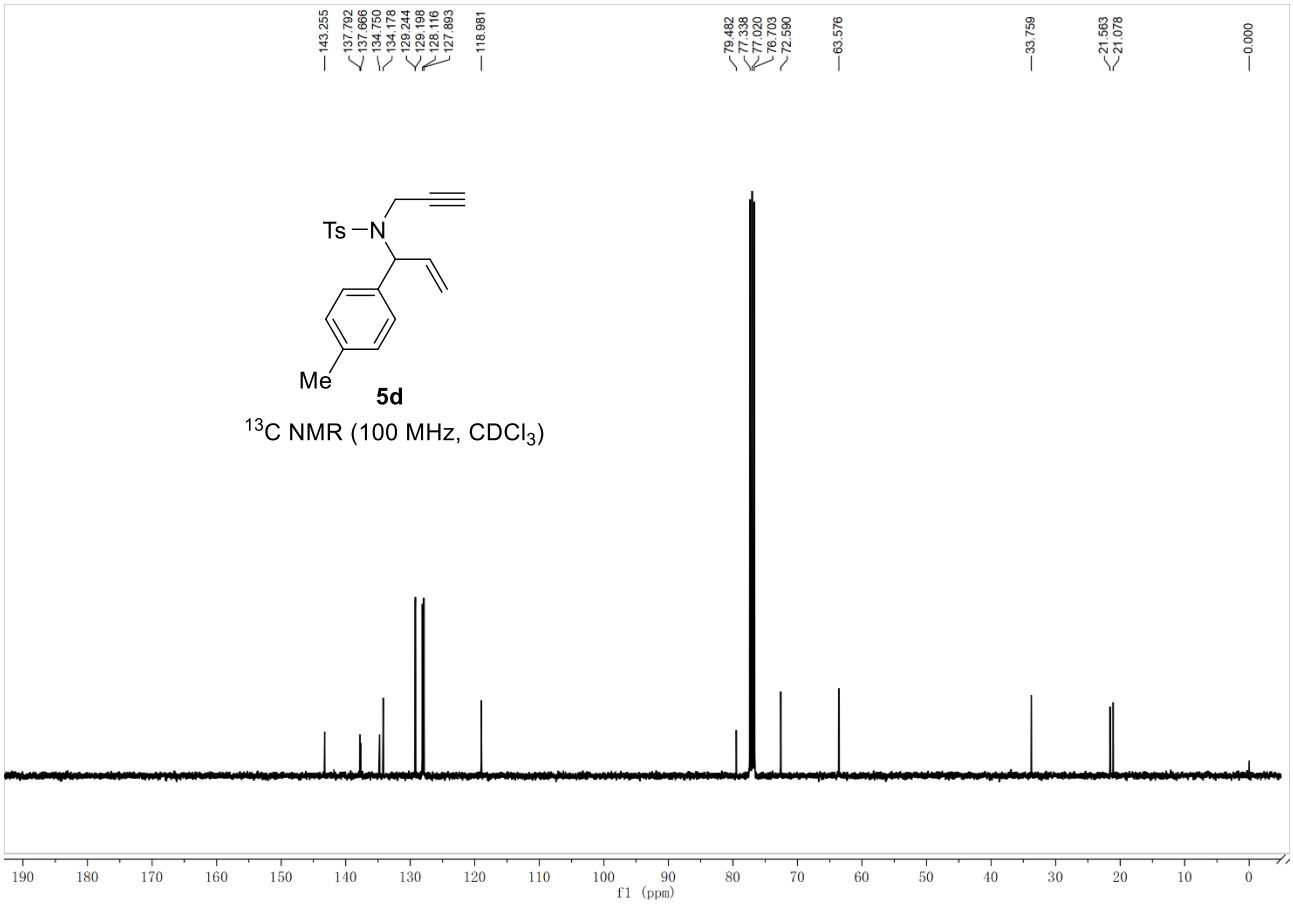
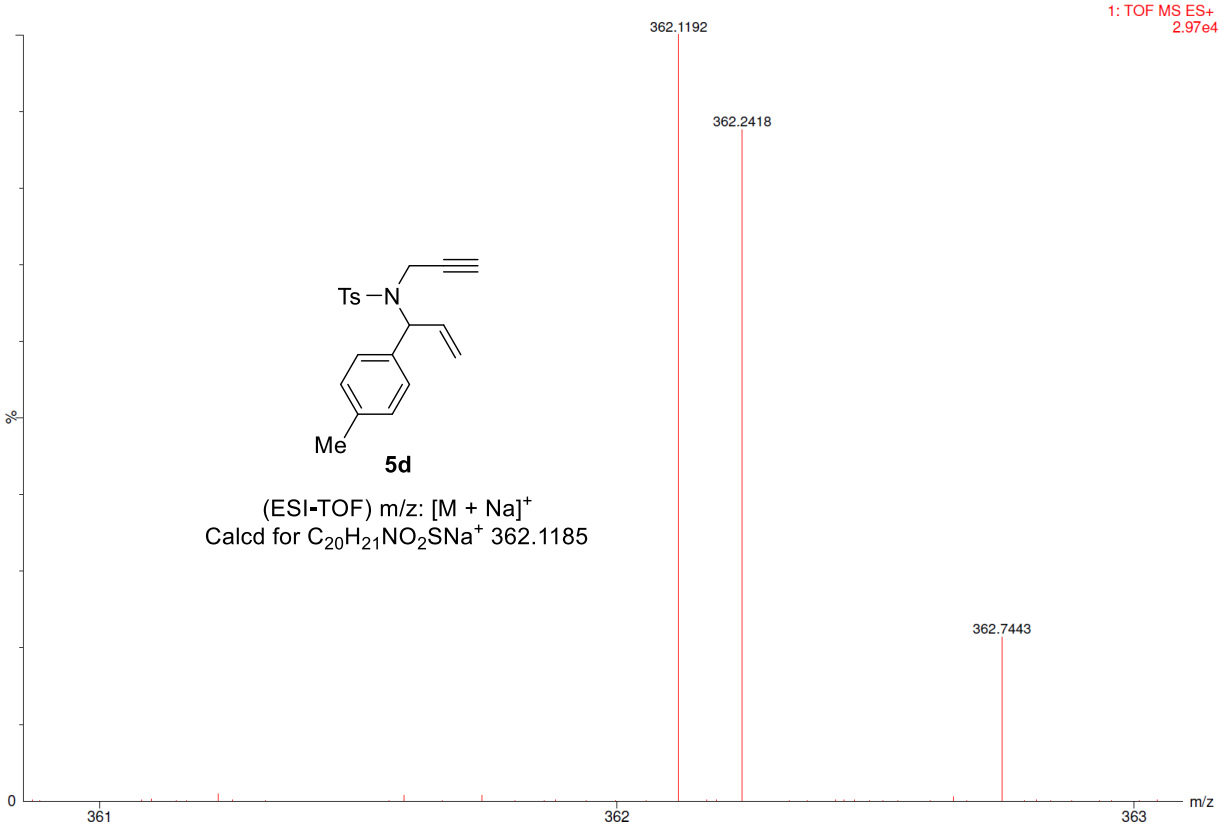


Figure S12.2. The experimental and predicted ECD of (*S*)-**8b**.

13. NMR, HRMS spectra and HPLC chromatograms

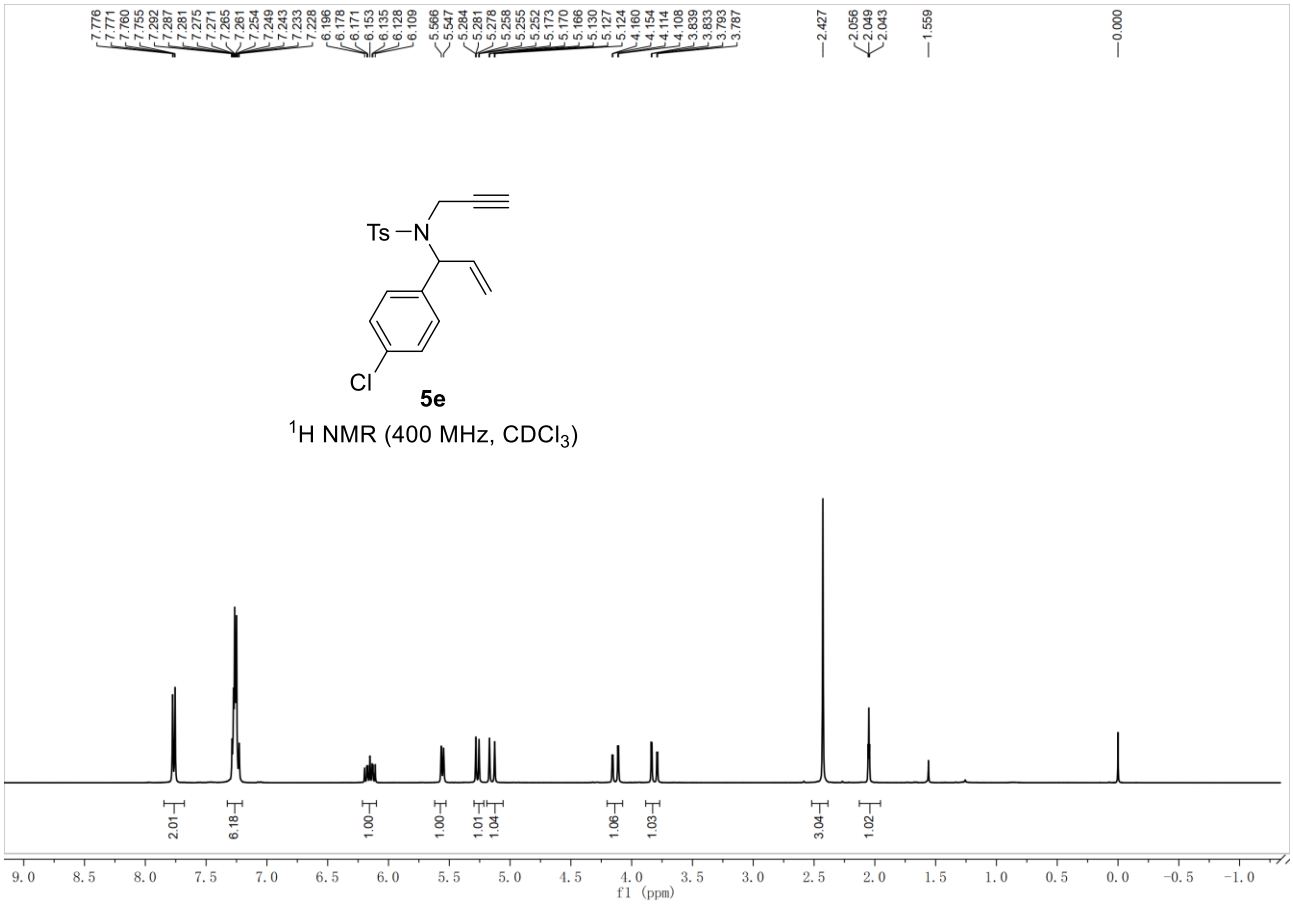






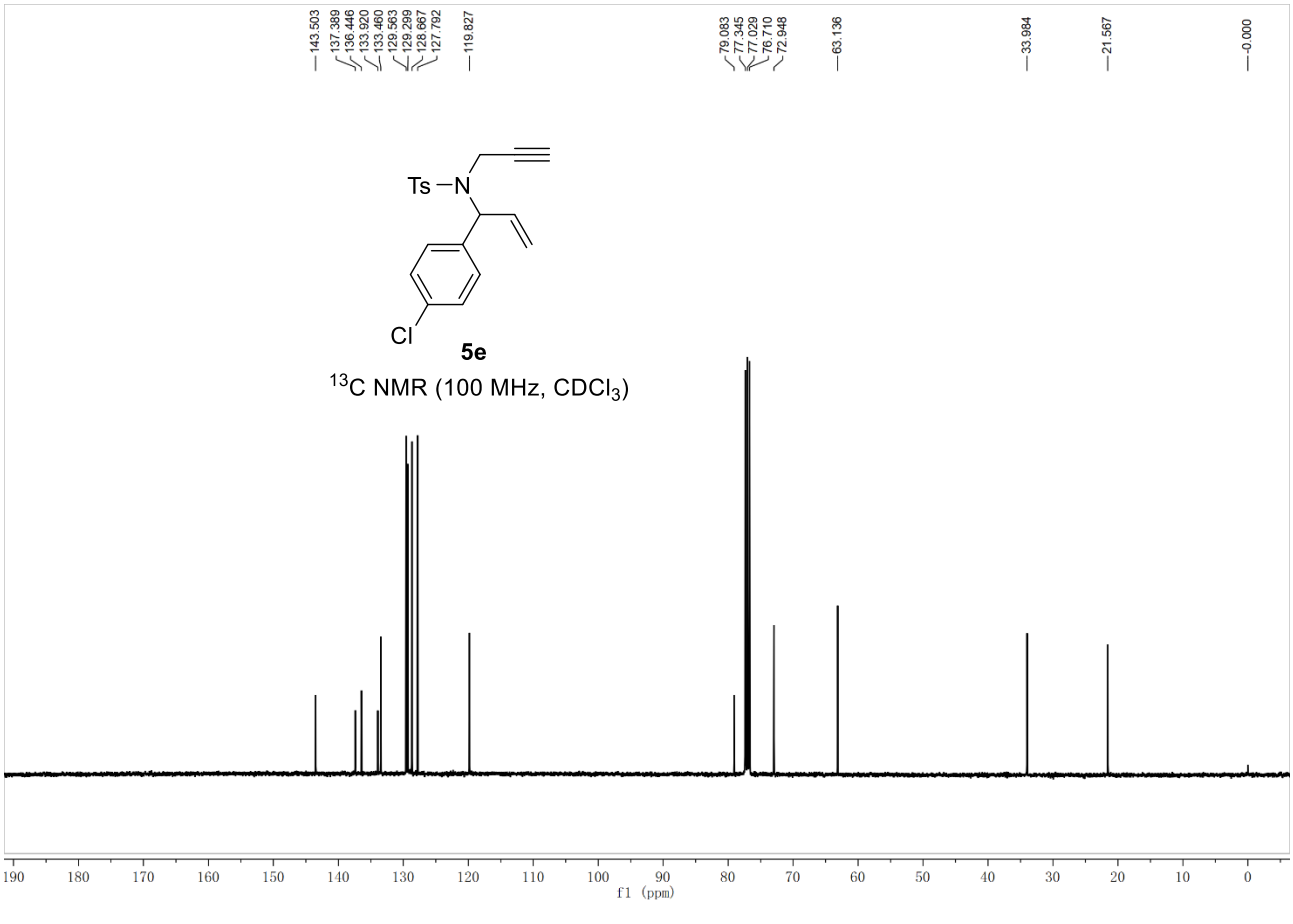
5d

(ESI-TOF) m/z: $[M + Na]^+$
Calcd for $C_{20}H_{21}NO_2SNa^+$ 362.1185



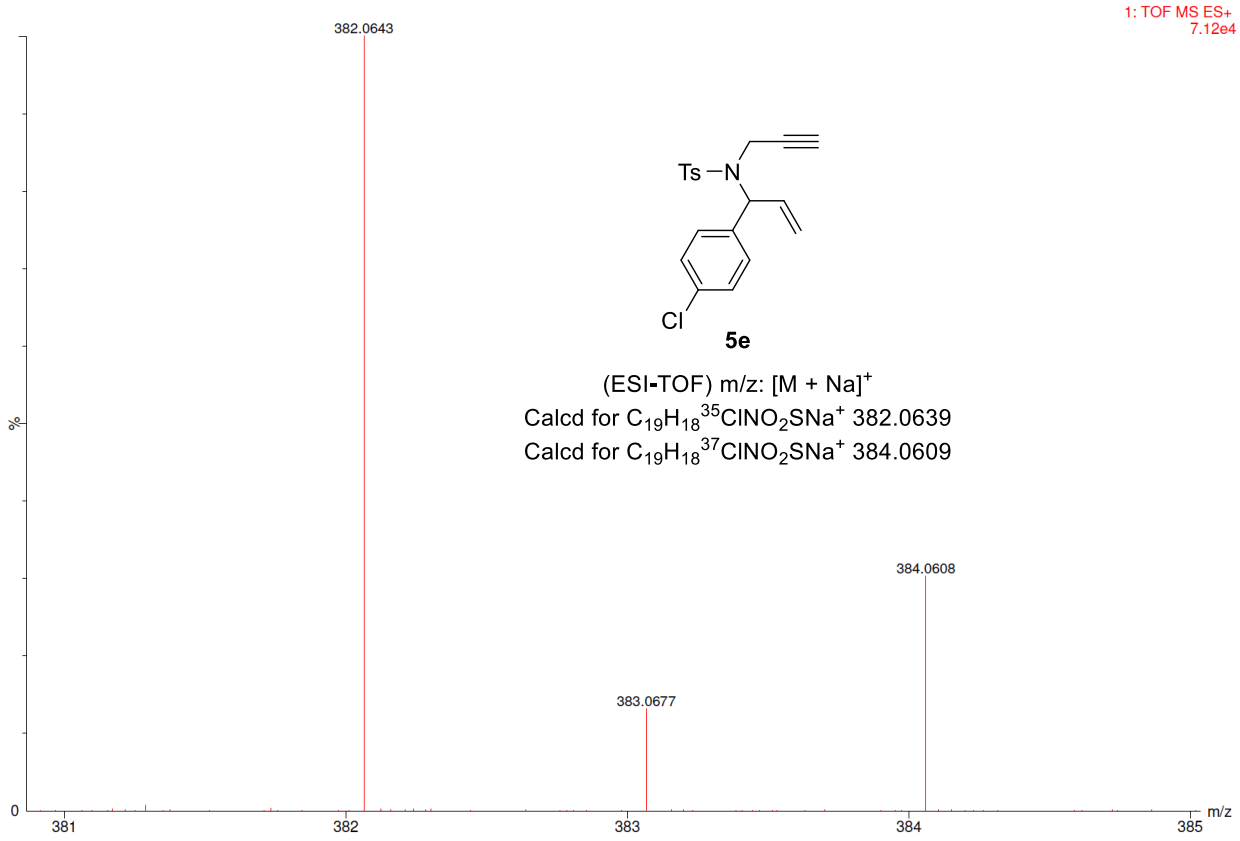
5e

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



5e

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

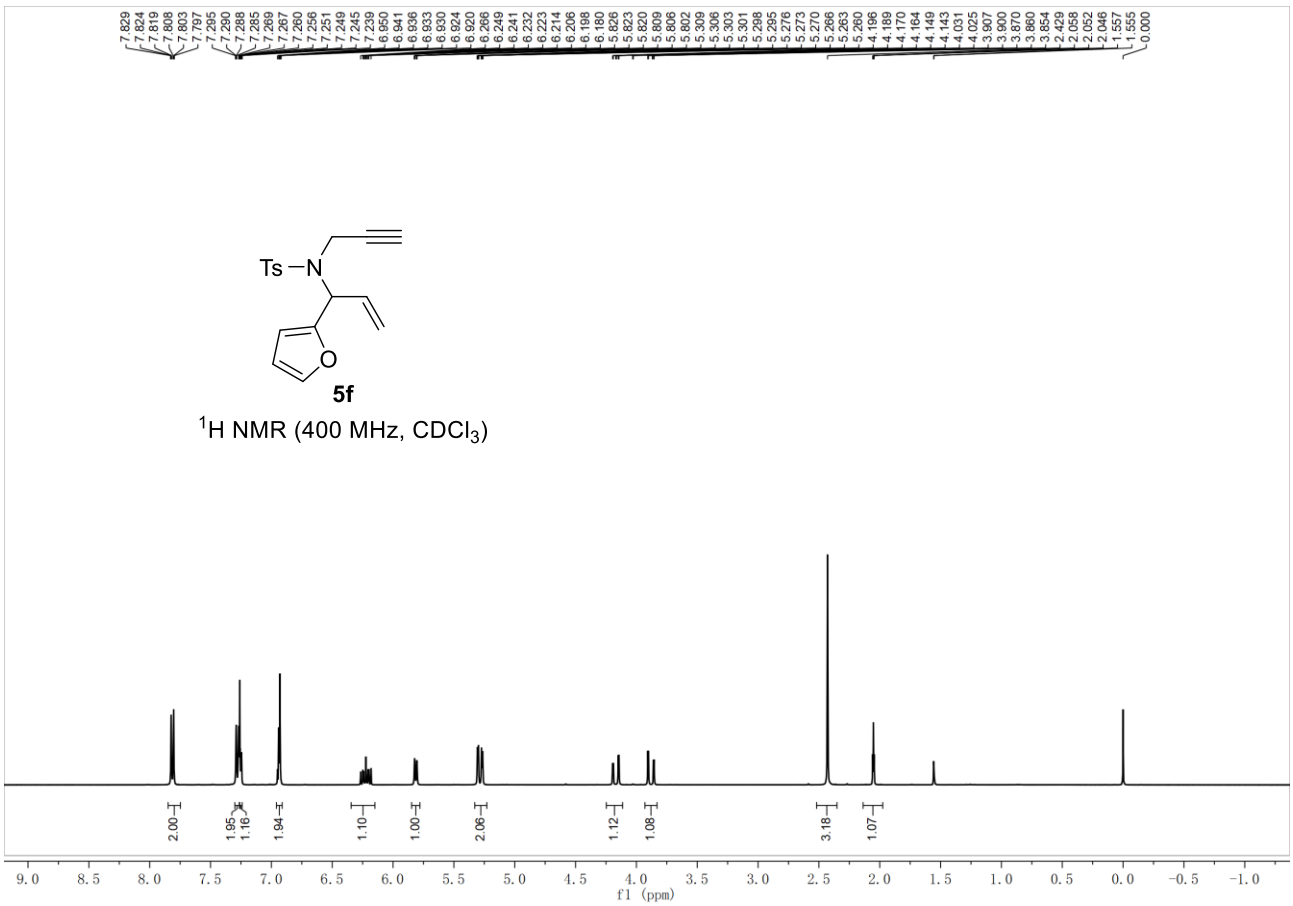


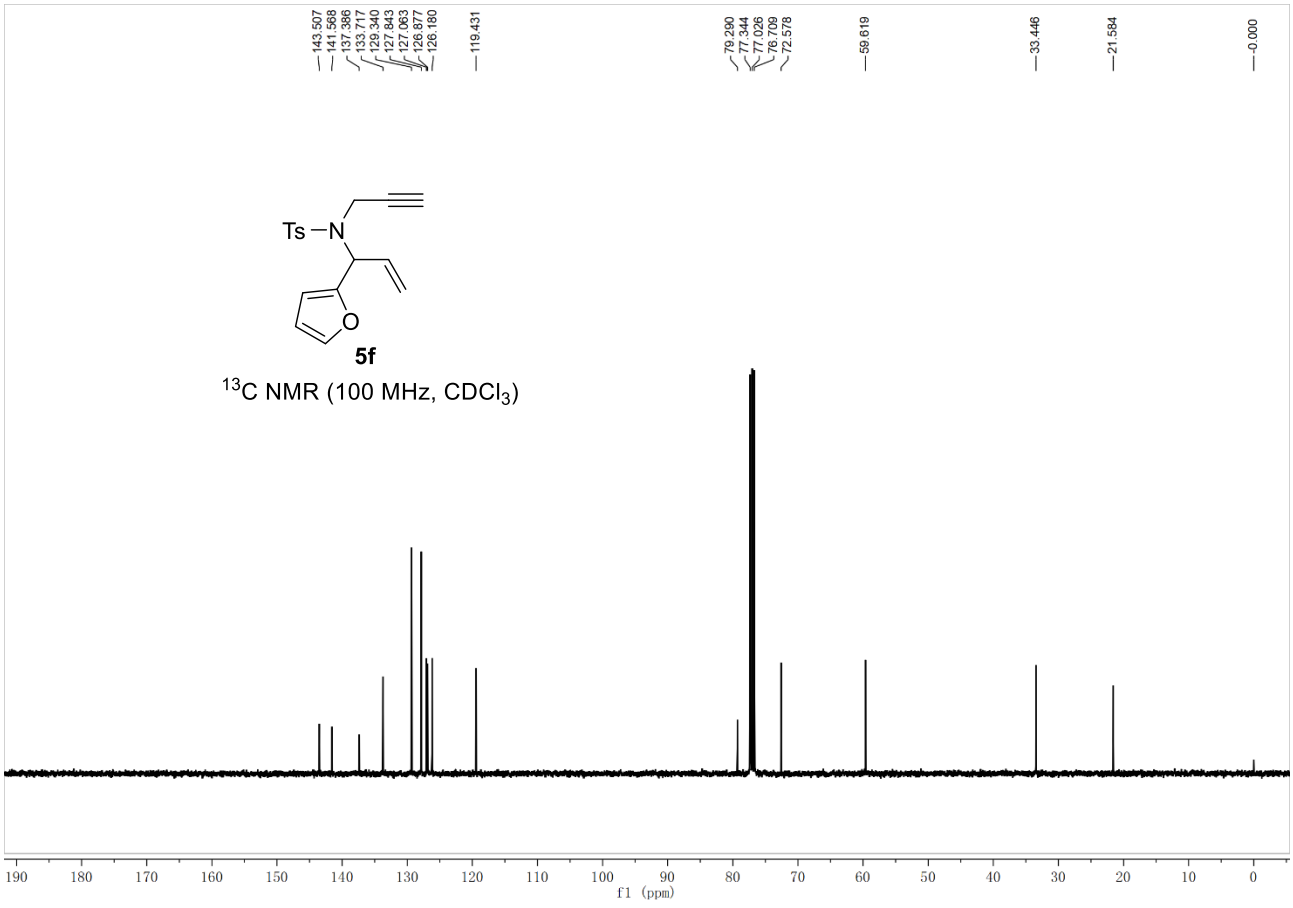
5e

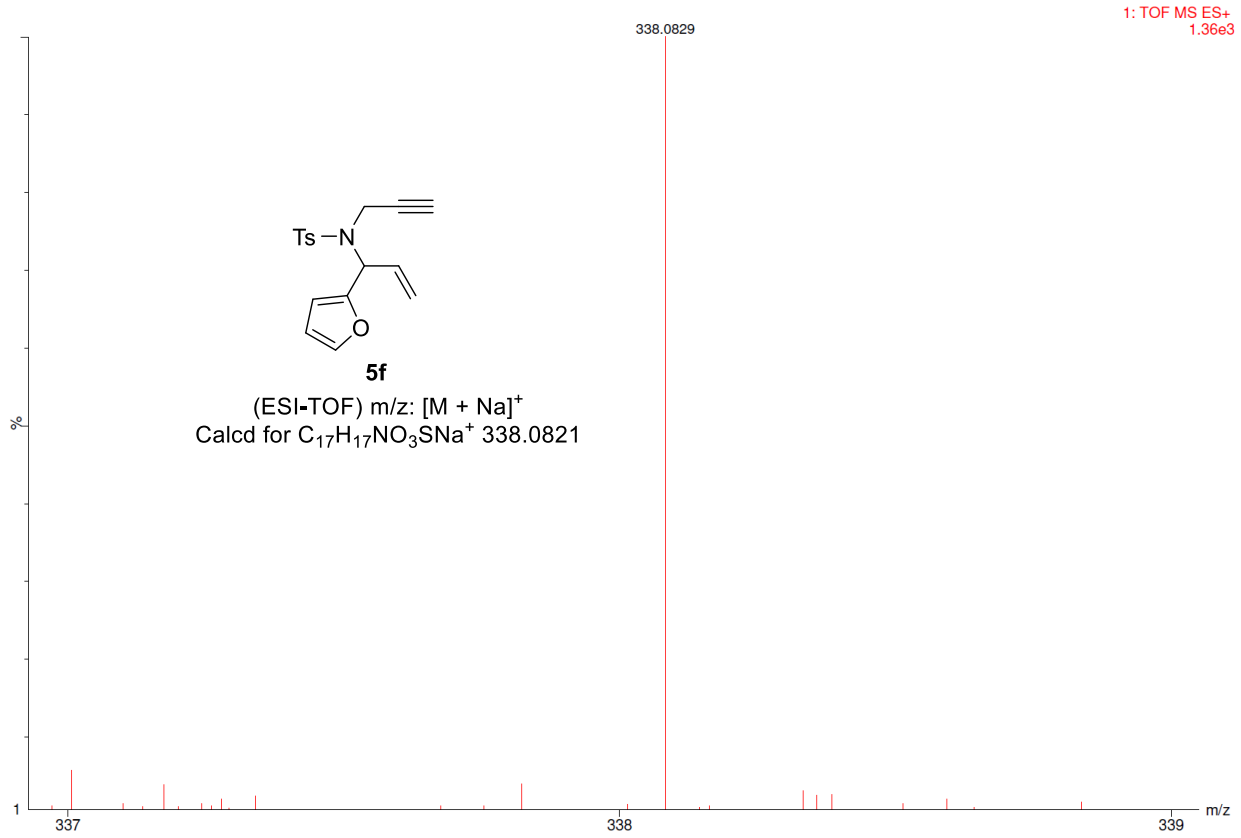
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{19}H_{18}{}^{35}ClNO_2SNa^+$ 382.0639

Calcd for $C_{19}H_{18}{}^{37}ClNO_2SNa^+$ 384.0609


7.829
7.824
7.819
7.808
7.803
7.797
7.295
7.290
7.288
7.285
7.269
7.267
7.260
7.256
7.251
7.249
7.245
7.239
6.950
6.941
6.936
6.933
6.930
6.924
6.920
6.266
6.249
6.241
6.232
6.223
6.214
6.206
6.198
6.180
5.826
5.823
5.820
5.809
5.806
5.802
5.309
5.306
5.303
5.301
5.298
5.285
5.276
5.273
5.270
5.266
5.263
5.260
4.196
4.189
4.170
4.164
4.149
4.143
4.031
4.025
3.907
3.900
3.870
3.860
3.854
2.429
2.058
2.052
2.046
1.557
1.555
0.000
Ts
N
O
5f
1H NMR (400 MHz, CDCl3)
2.00
1.95
1.16
1.94
1.10
1.00
2.06
1.12
1.08
3.18
1.07
f1 (ppm)

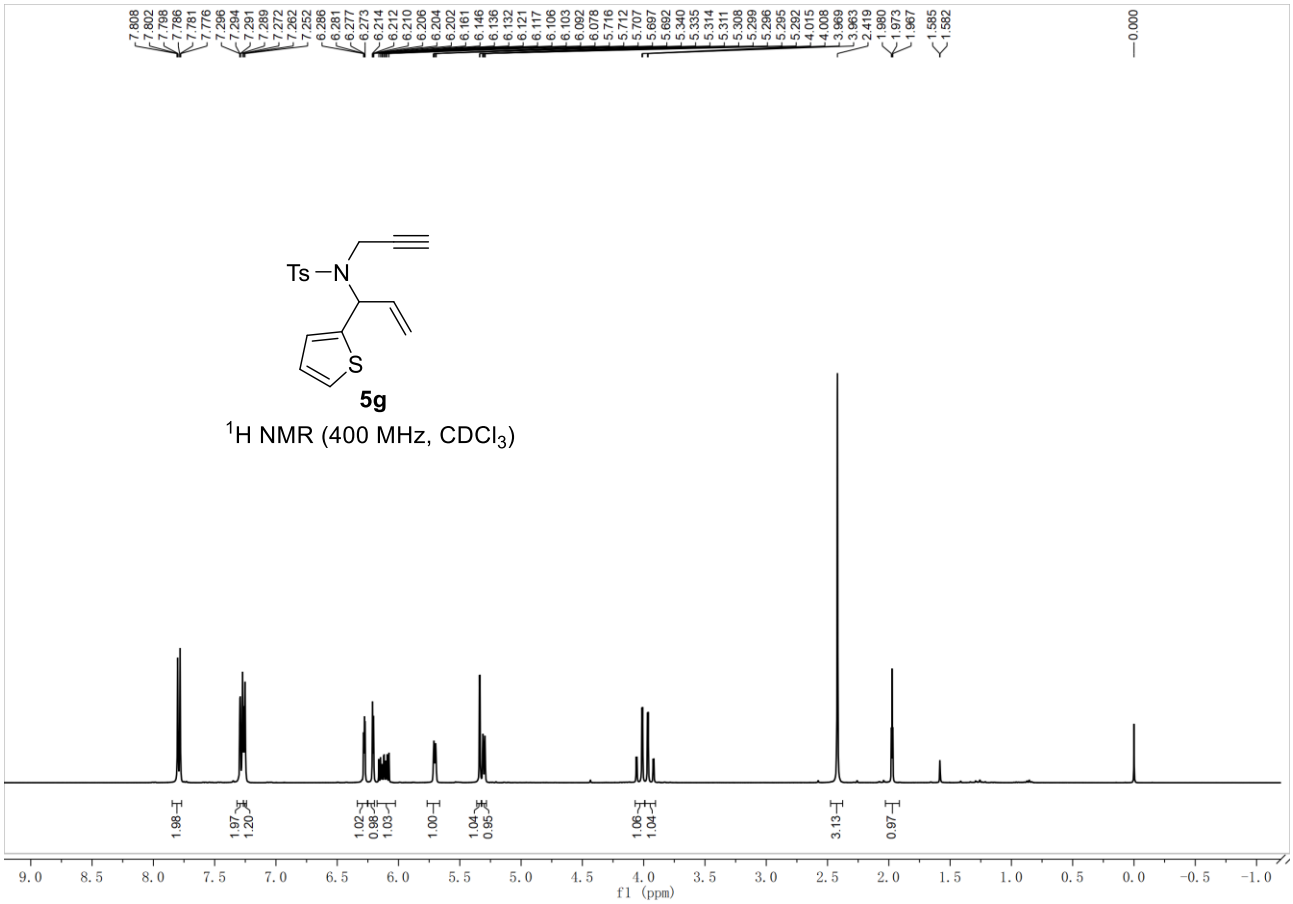

143.507
141.588
137.386
133.717
129.340
127.843
127.063
126.877
126.180
119.431
79.290
77.344
77.026
76.709
72.578
59.619
33.446
21.584
0.000
Ts
N
O
5f
13C NMR (100 MHz, CDCl3)
f1 (ppm)



5f

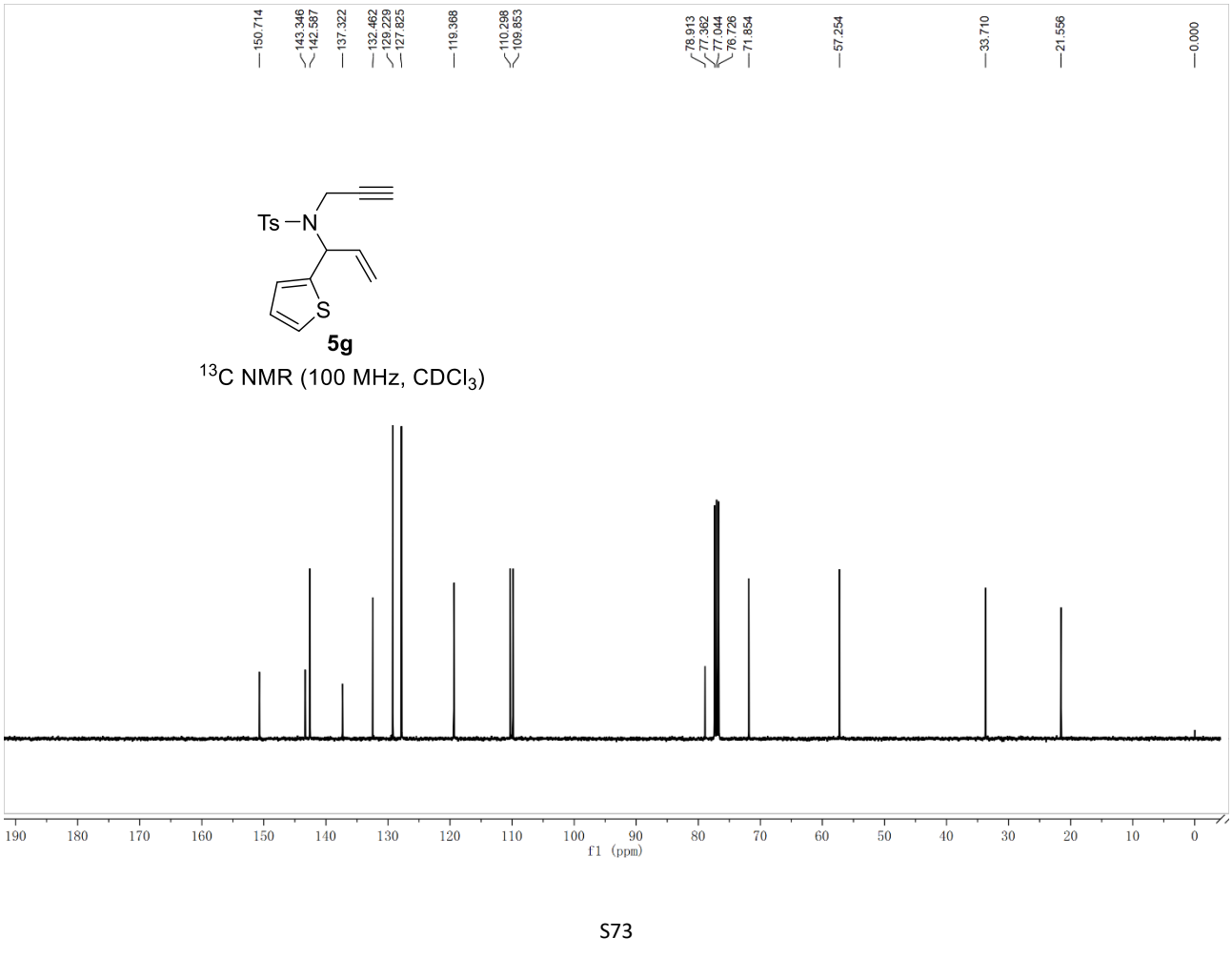
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{17}H_{17}NO_3SNa^+$ 338.0821



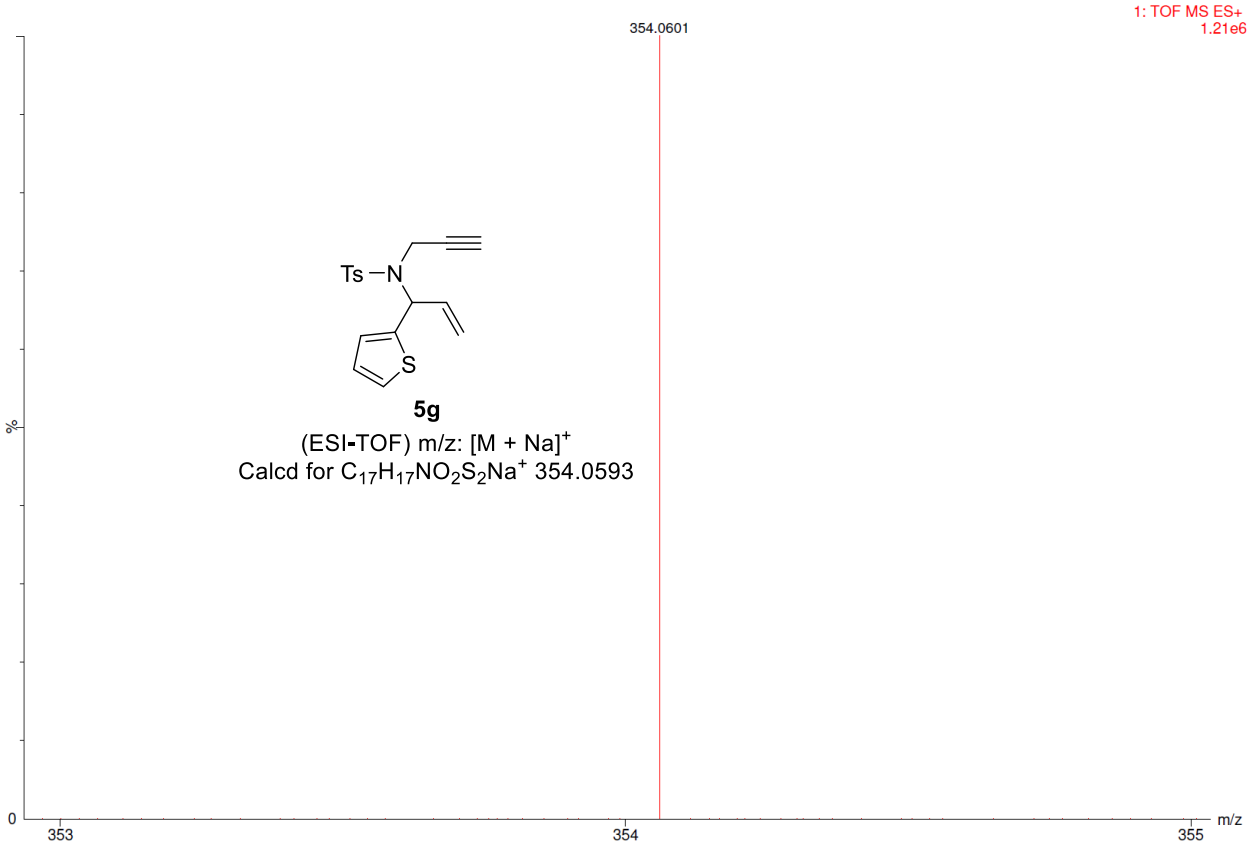
5g

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



5g

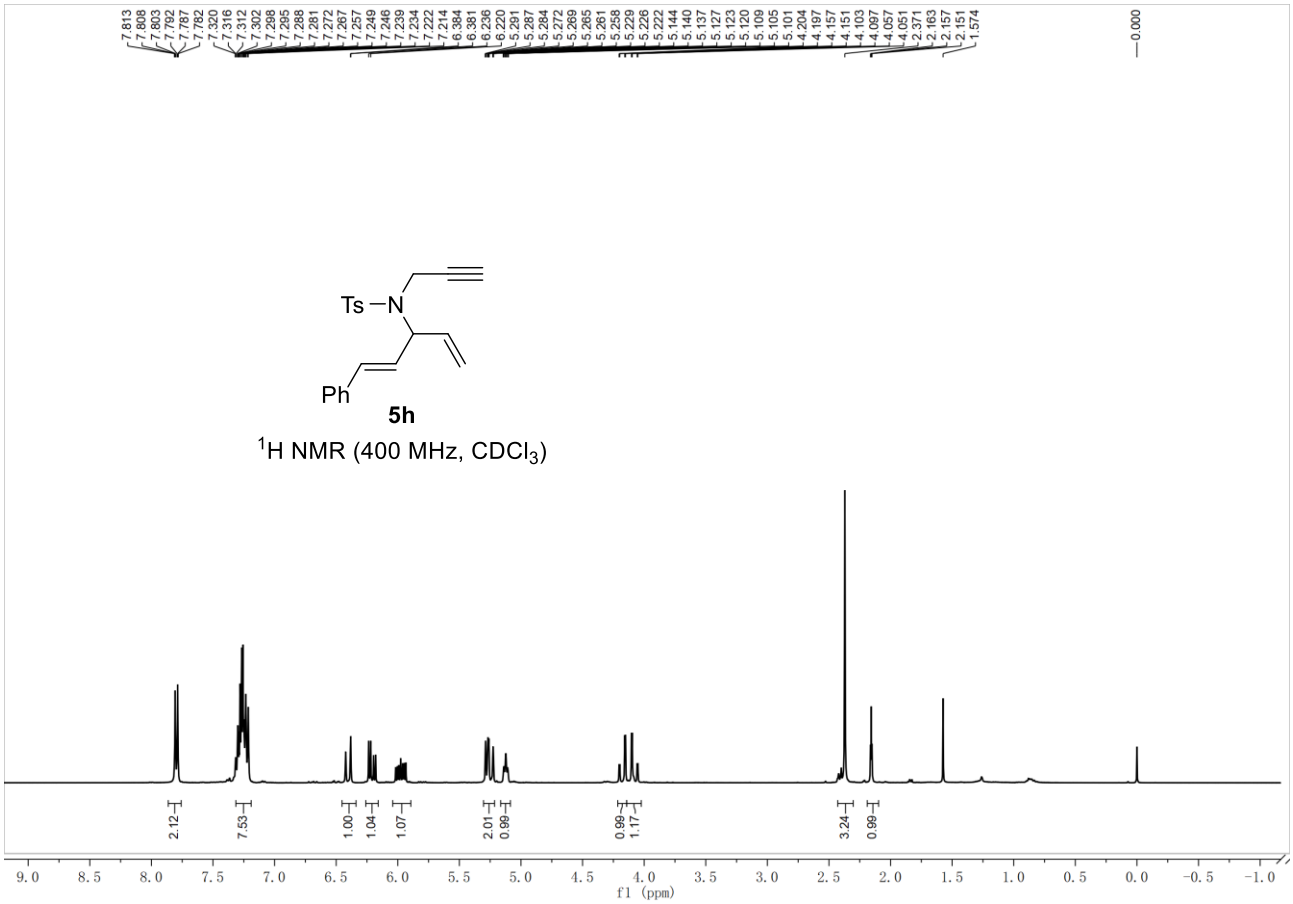
^{13}C NMR (100 MHz, $CDCl_3$)



5g

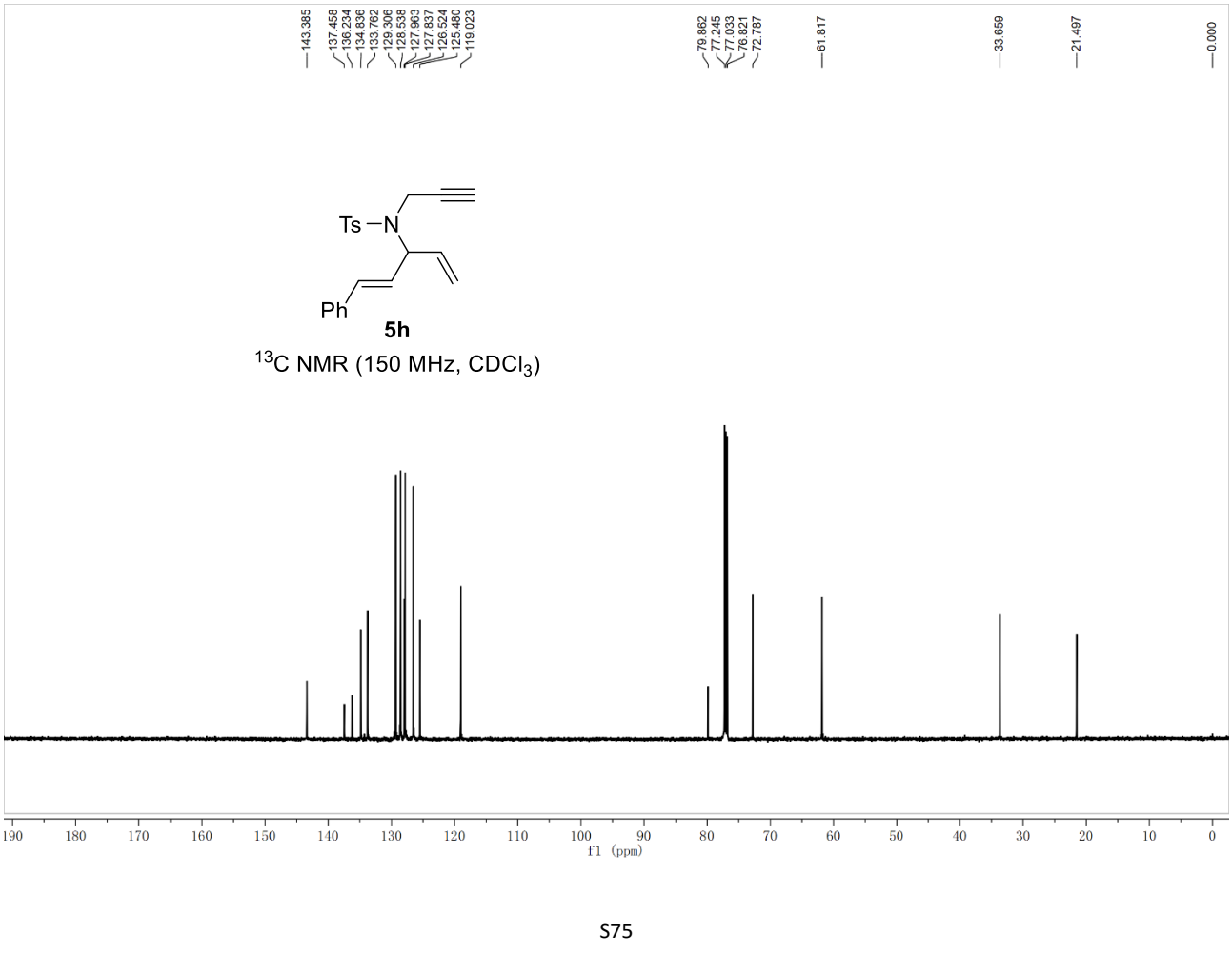
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{17}H_{17}NO_2S_2Na^+$ 354.0593



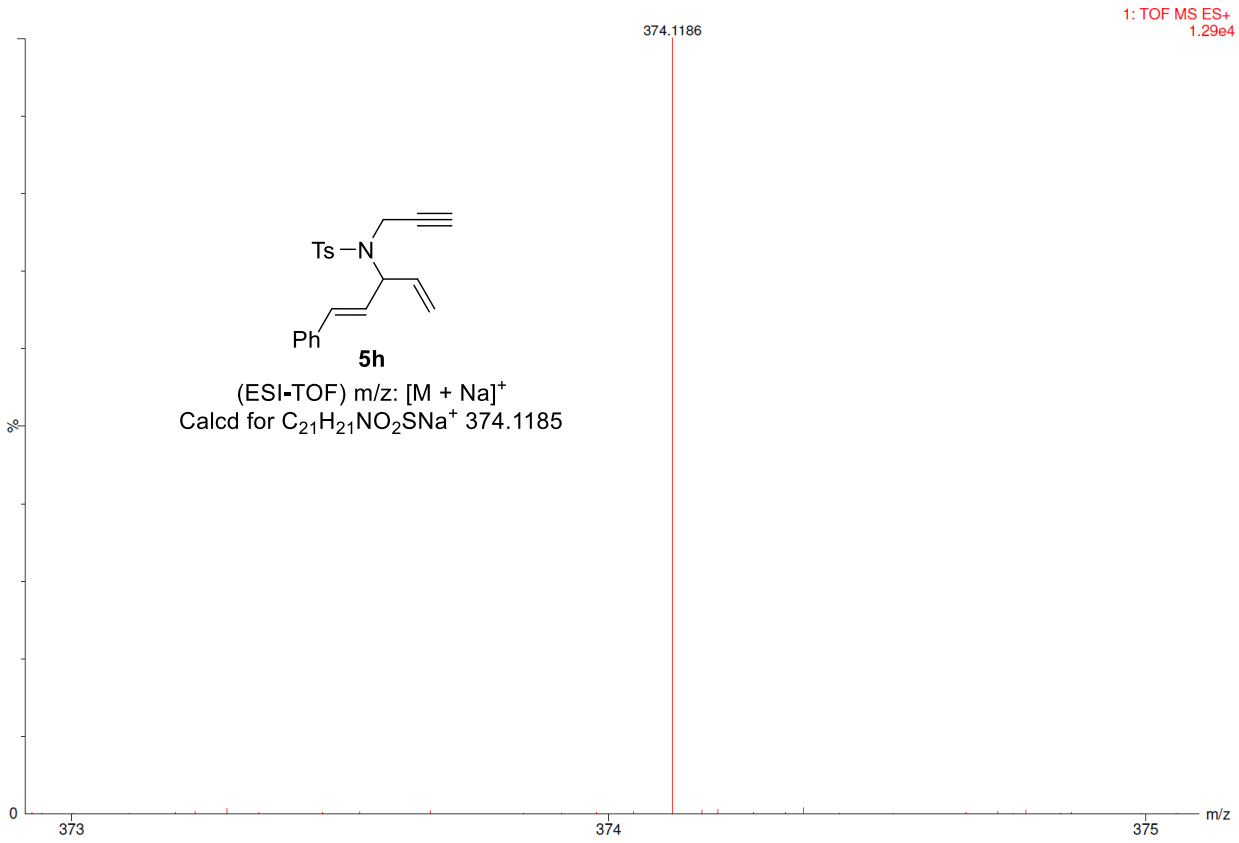
5h

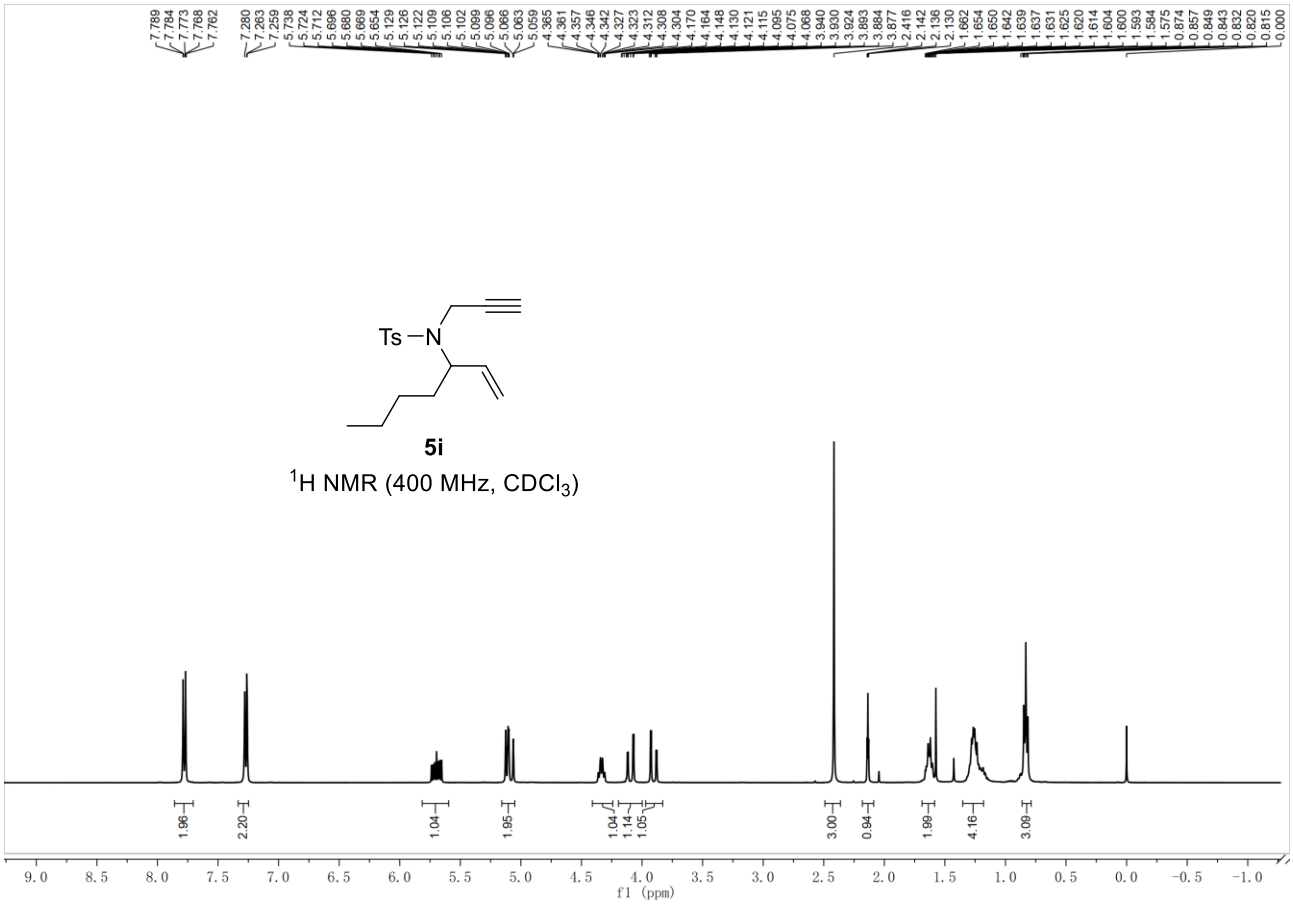
^{1}H NMR (400 MHz, $CDCl_3$)



5h

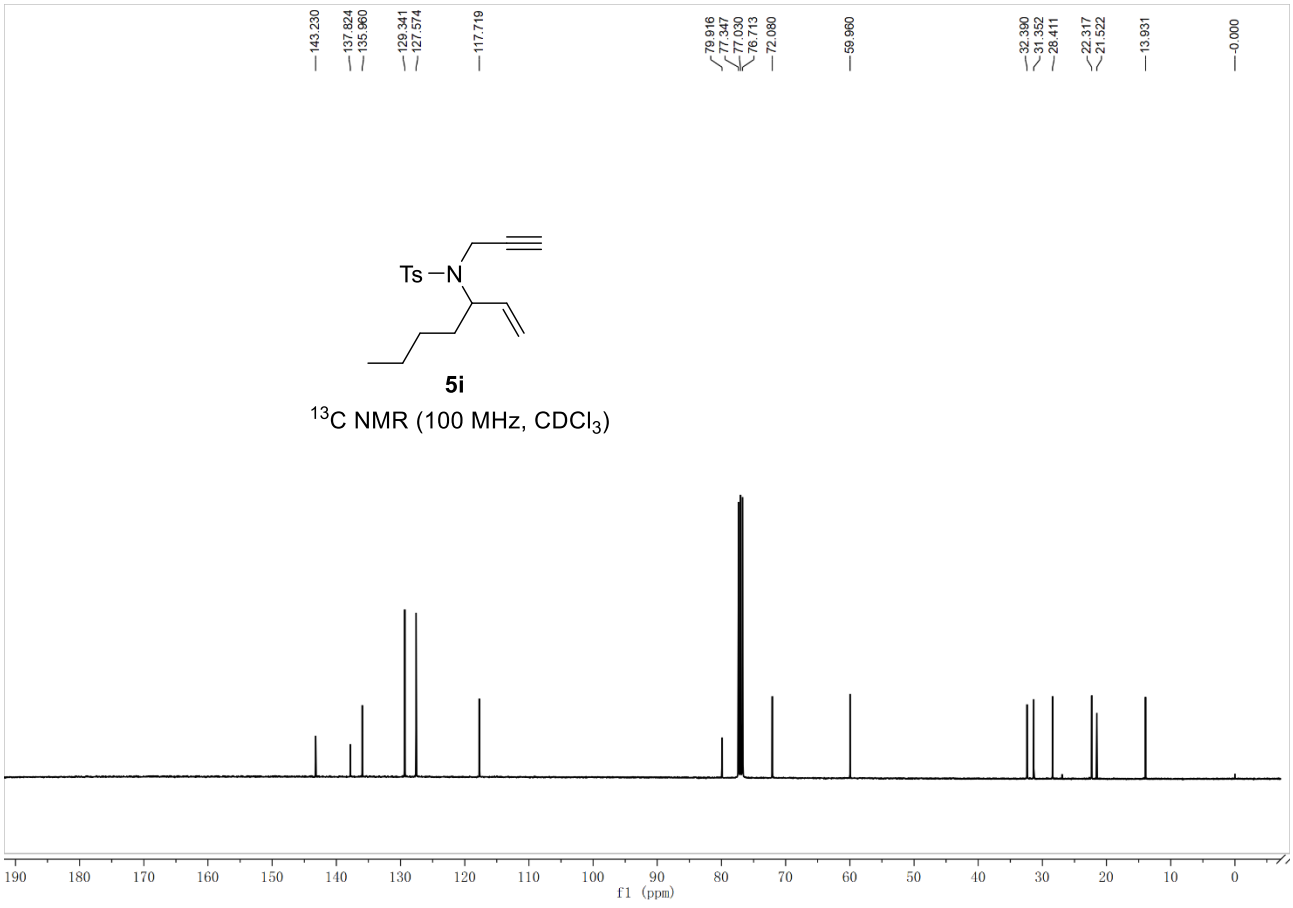
^{13}C NMR (150 MHz, $CDCl_3$)


1: TOF MS ES+
1.29e4
374.1186
Ts
N
Ph
5h
(ESI-TOF) m/z: [M + Na]+
Calcd for C21H21NO2SNa+ 374.1185
%
0
373
374
375
m/z



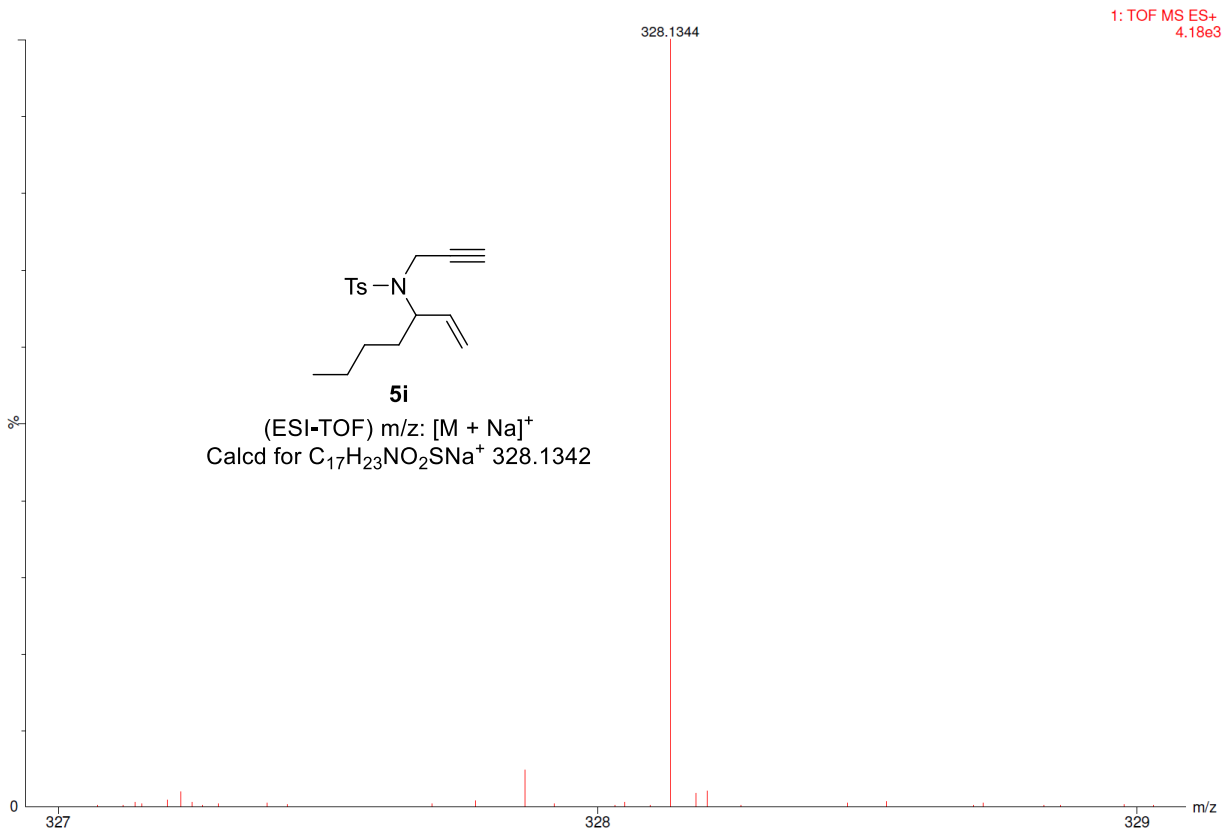
5i

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



5i

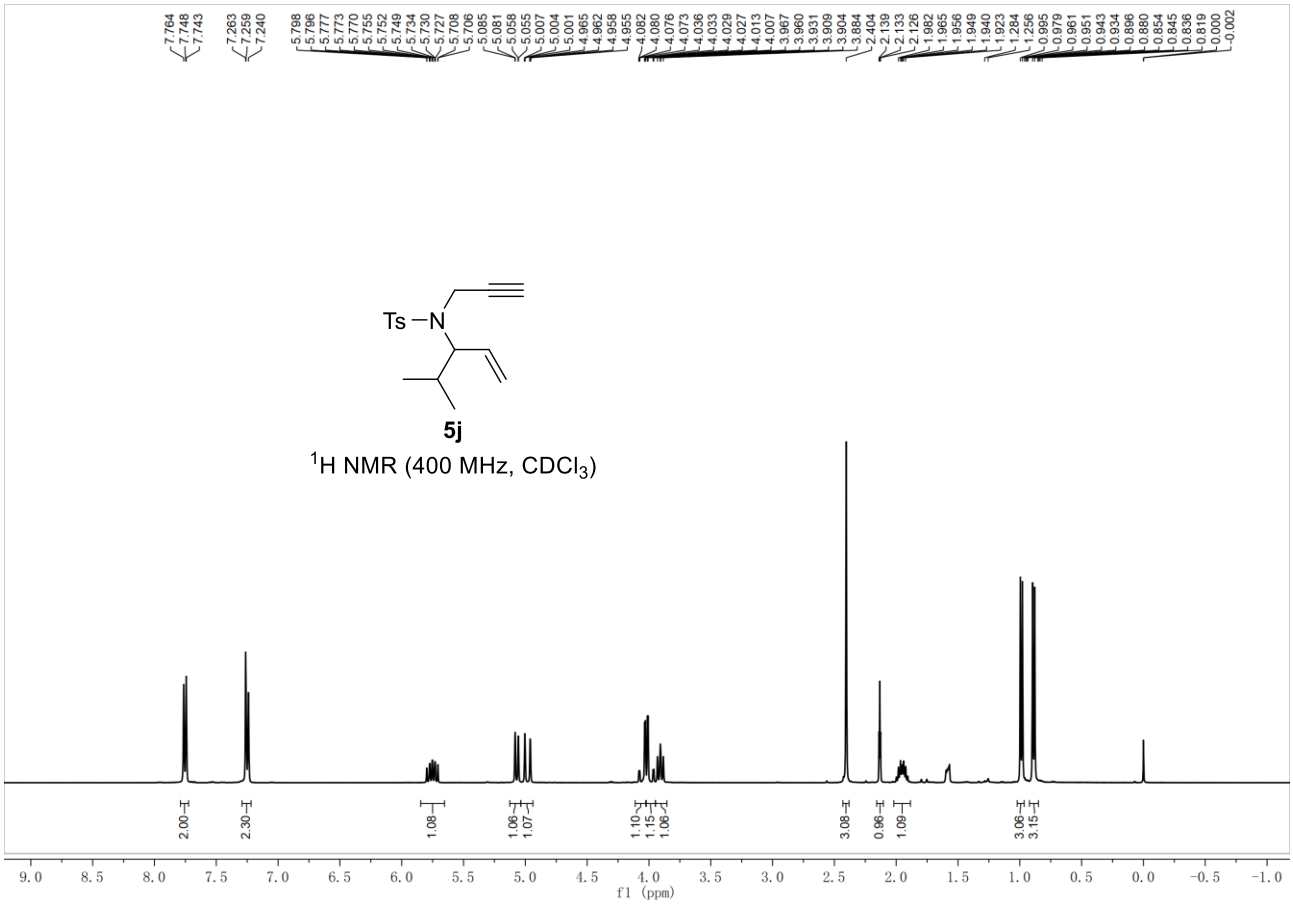
^{13}C NMR (100 MHz, $CDCl_3$)

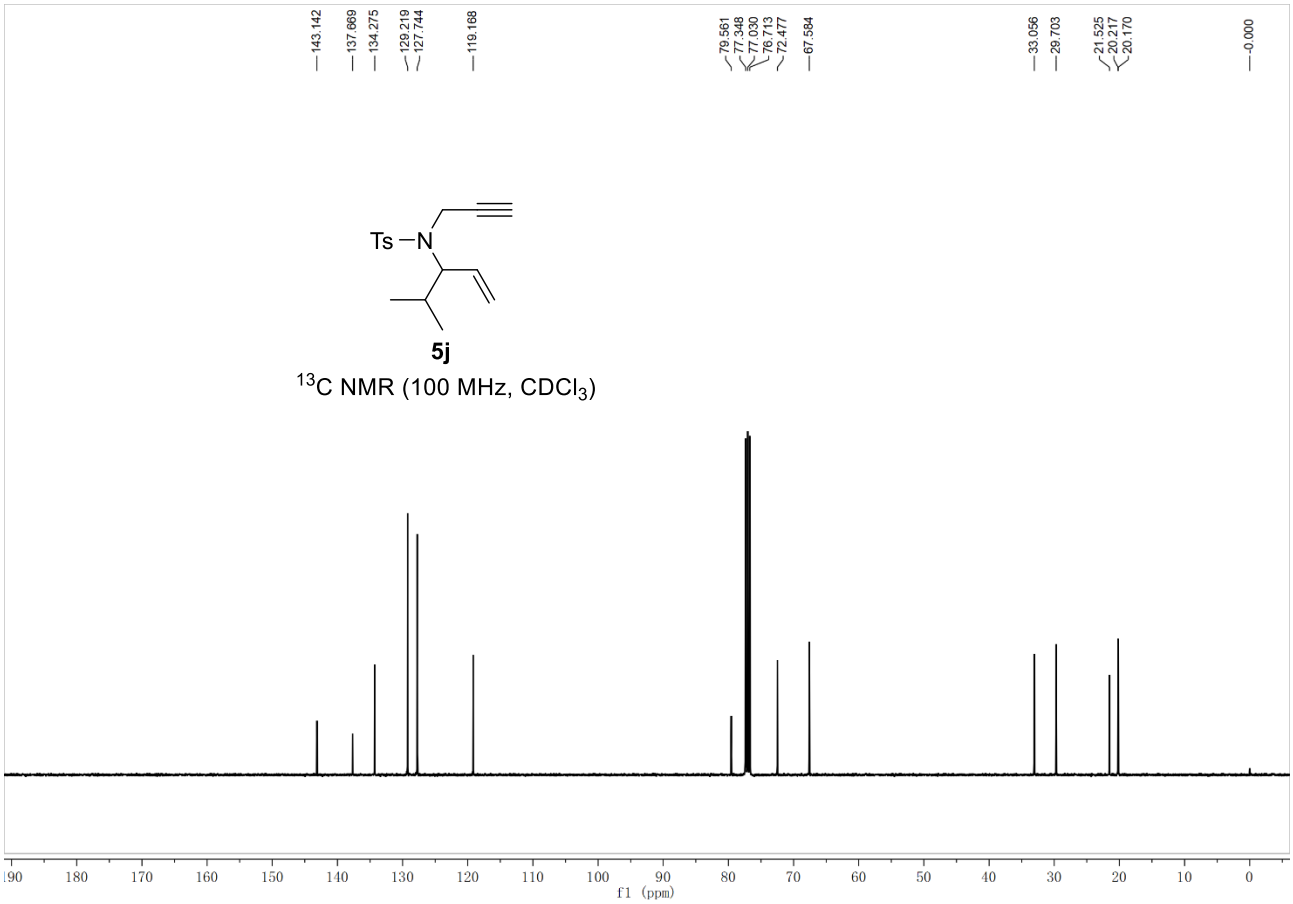


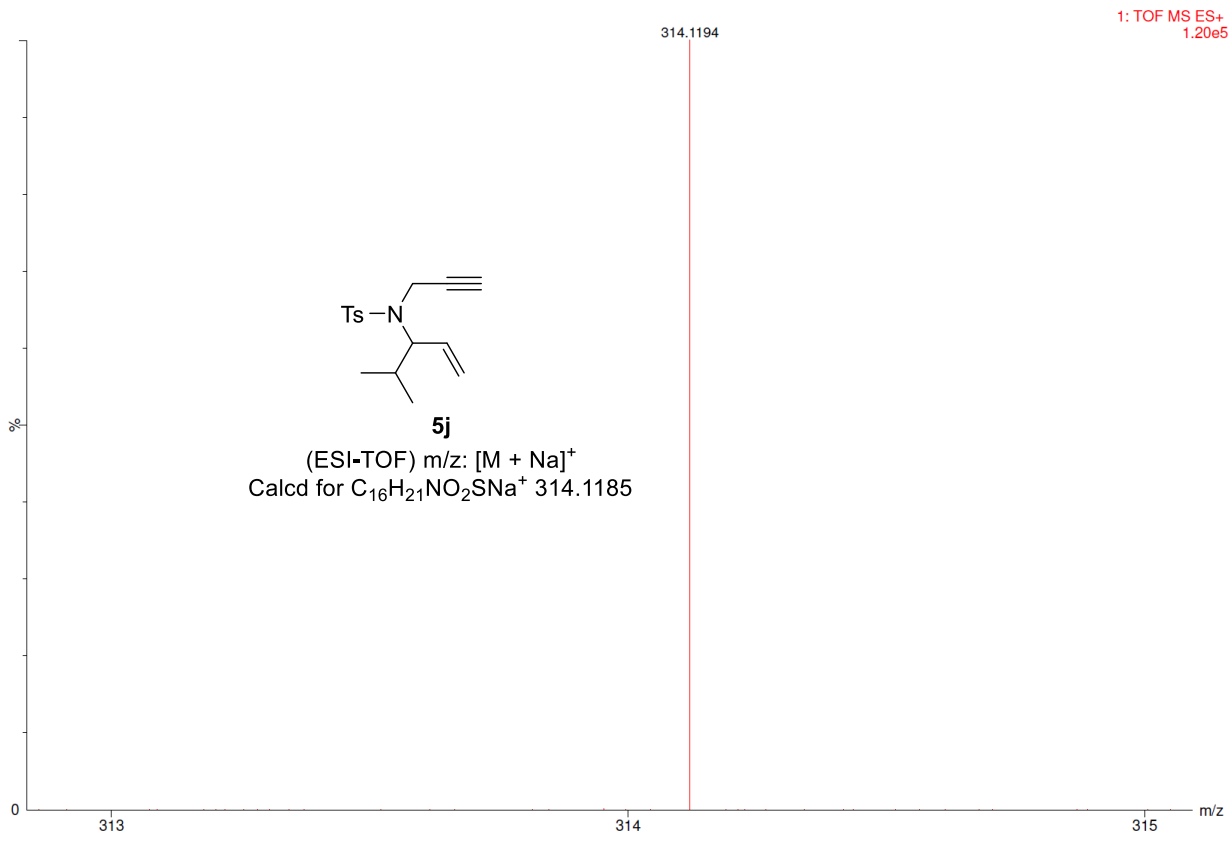
5i

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{17}H_{23}NO_2SNa^+$ 328.1342


Ts—N
5j
1H NMR (400 MHz, CDCl3)
f1 (ppm)

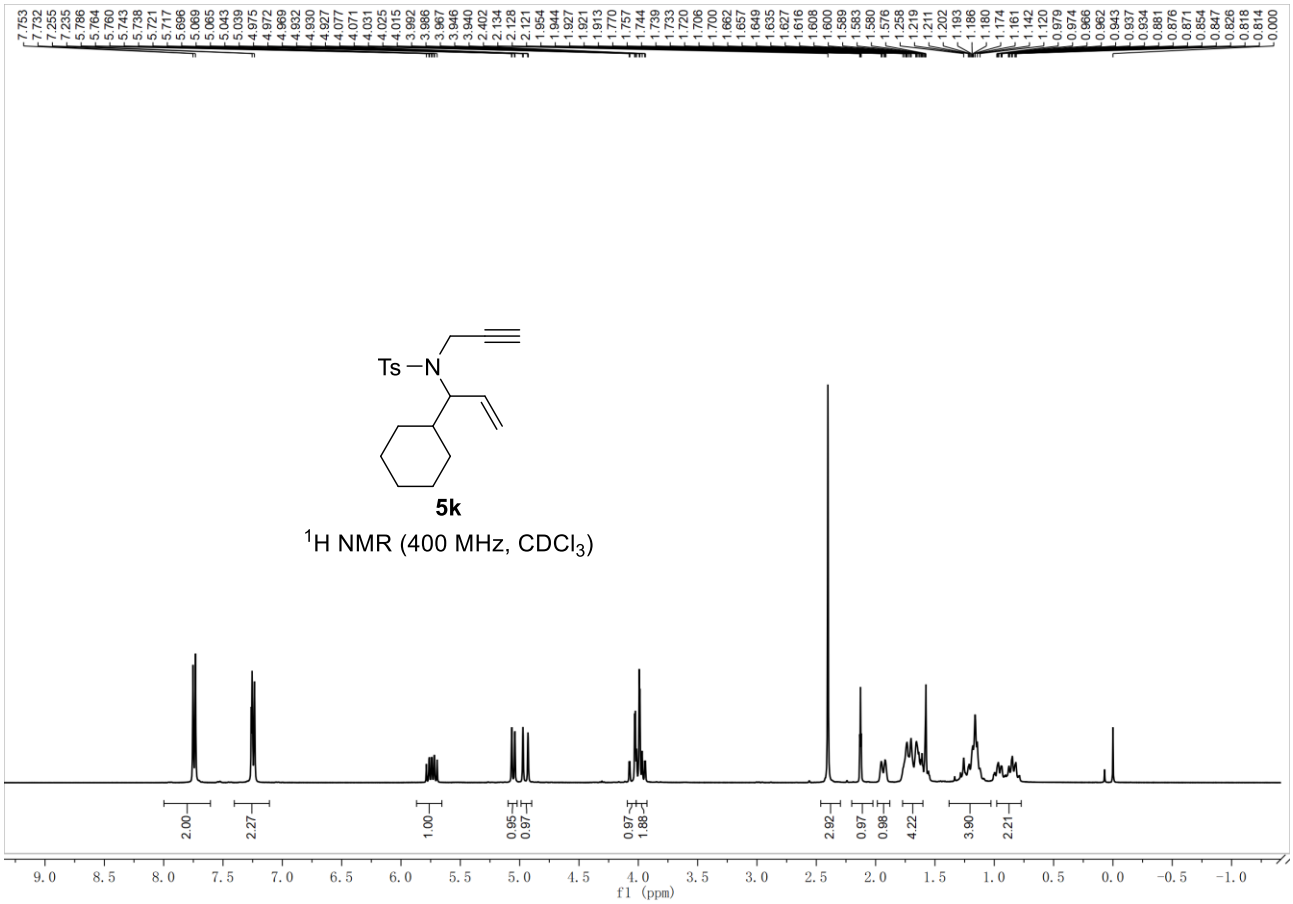

Ts—N
5j
13C NMR (100 MHz, CDCl3)
f1 (ppm)

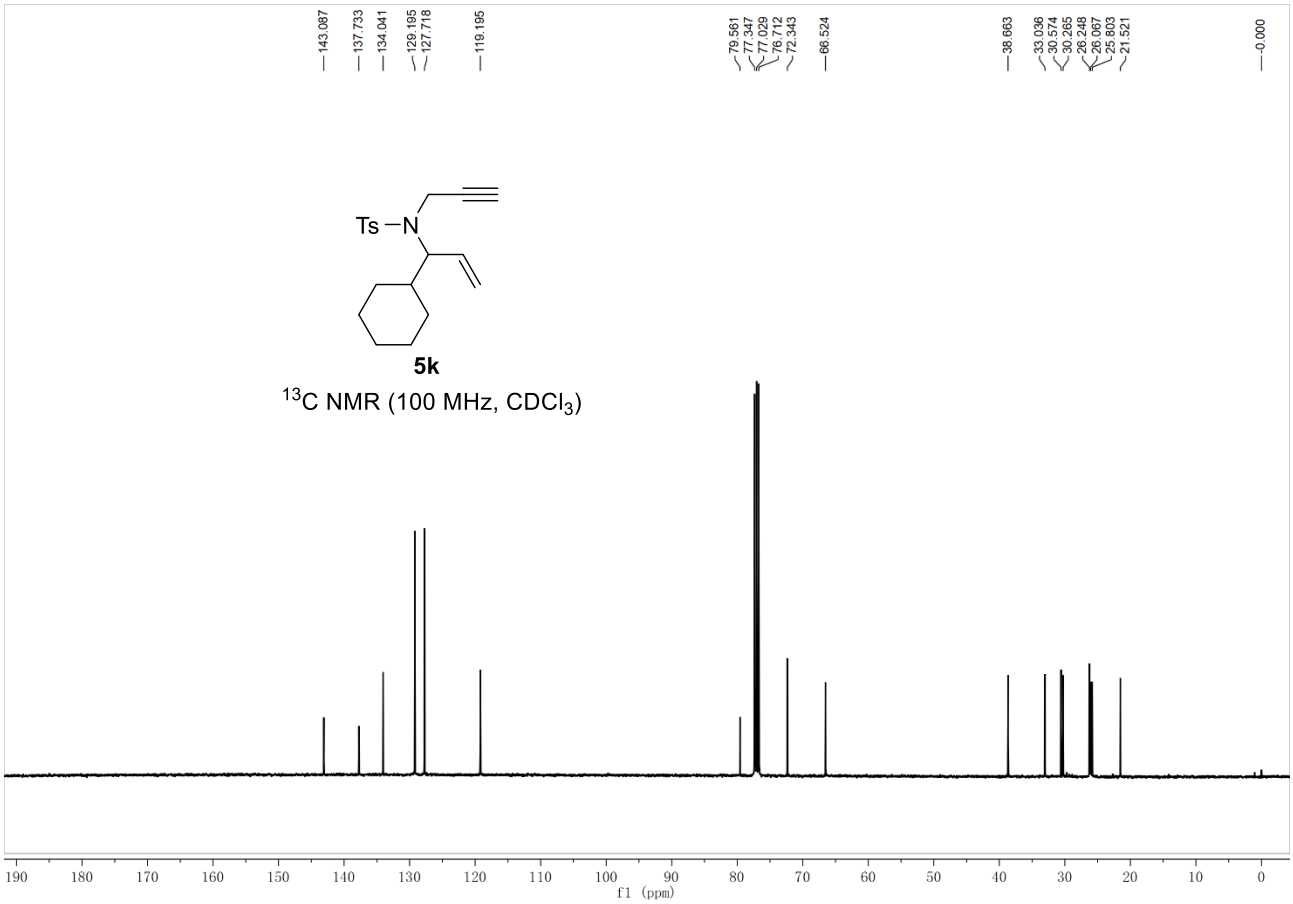


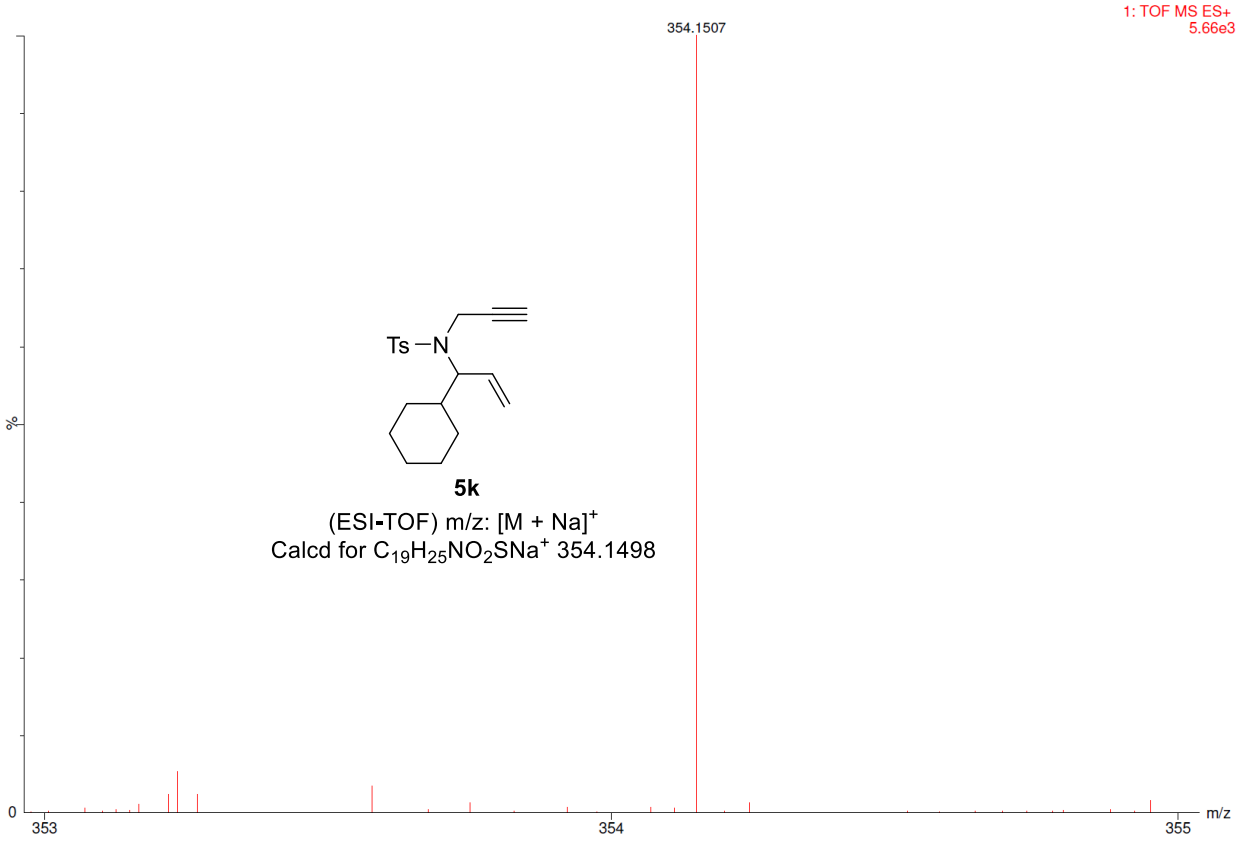
5j

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{16}H_{21}NO_2SNa^+$ 314.1185


Ts
N
5k
1H NMR (400 MHz, CDCl3)
f1 (ppm)

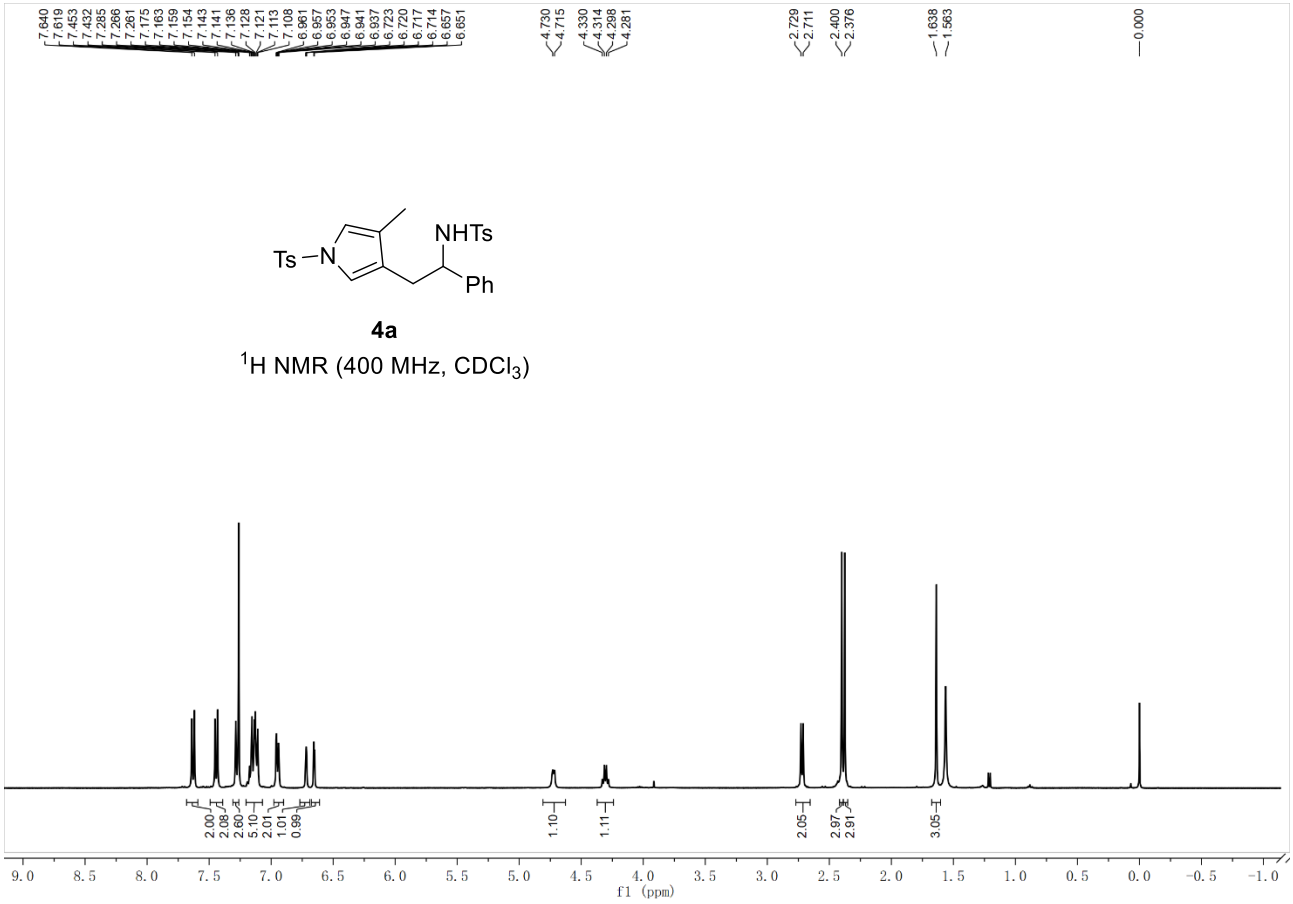

Ts
N
5k
13C NMR (100 MHz, CDCl3)
f1 (ppm)



5k

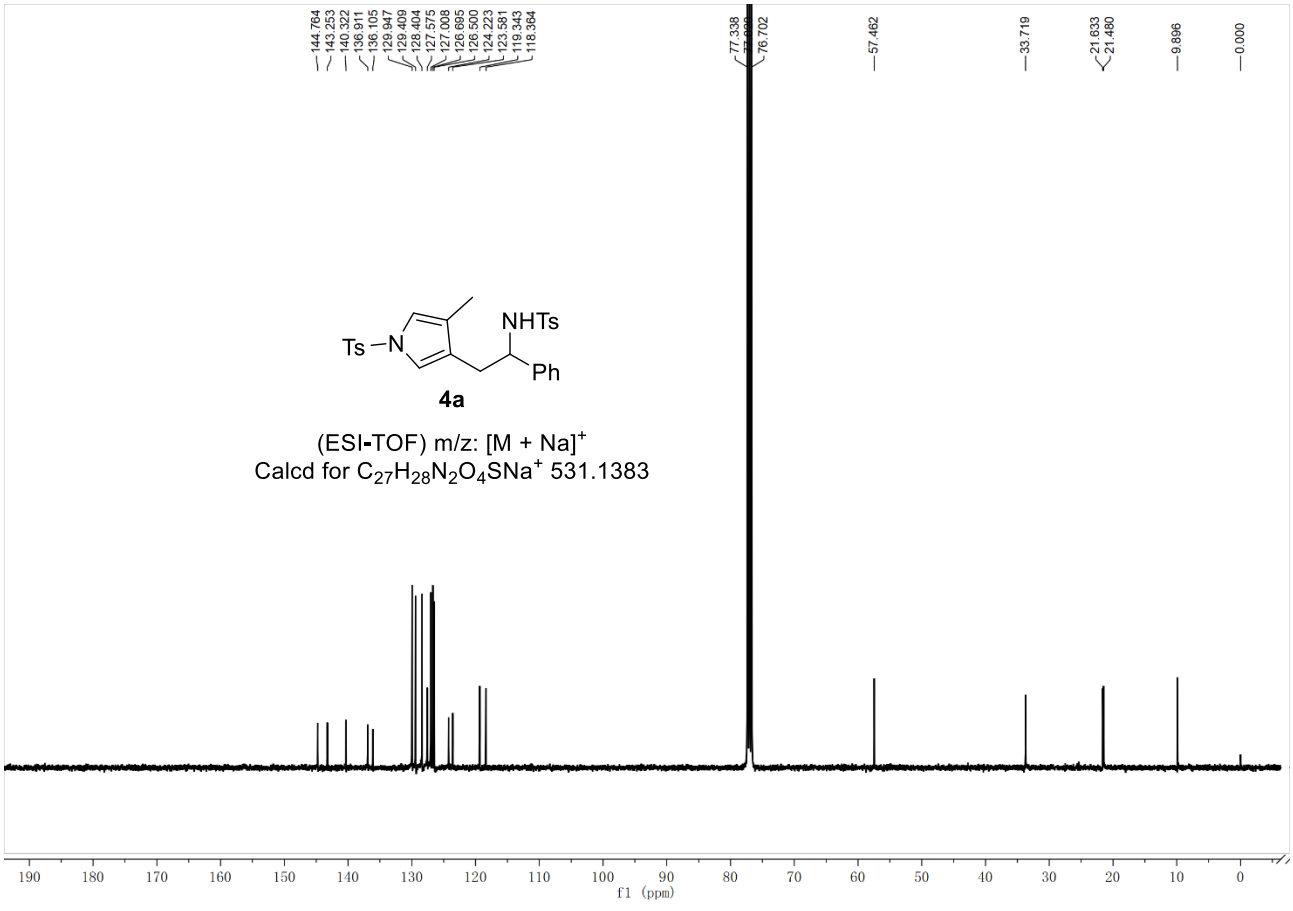
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{19}H_{25}NO_2SNa^+$ 354.1498



4a

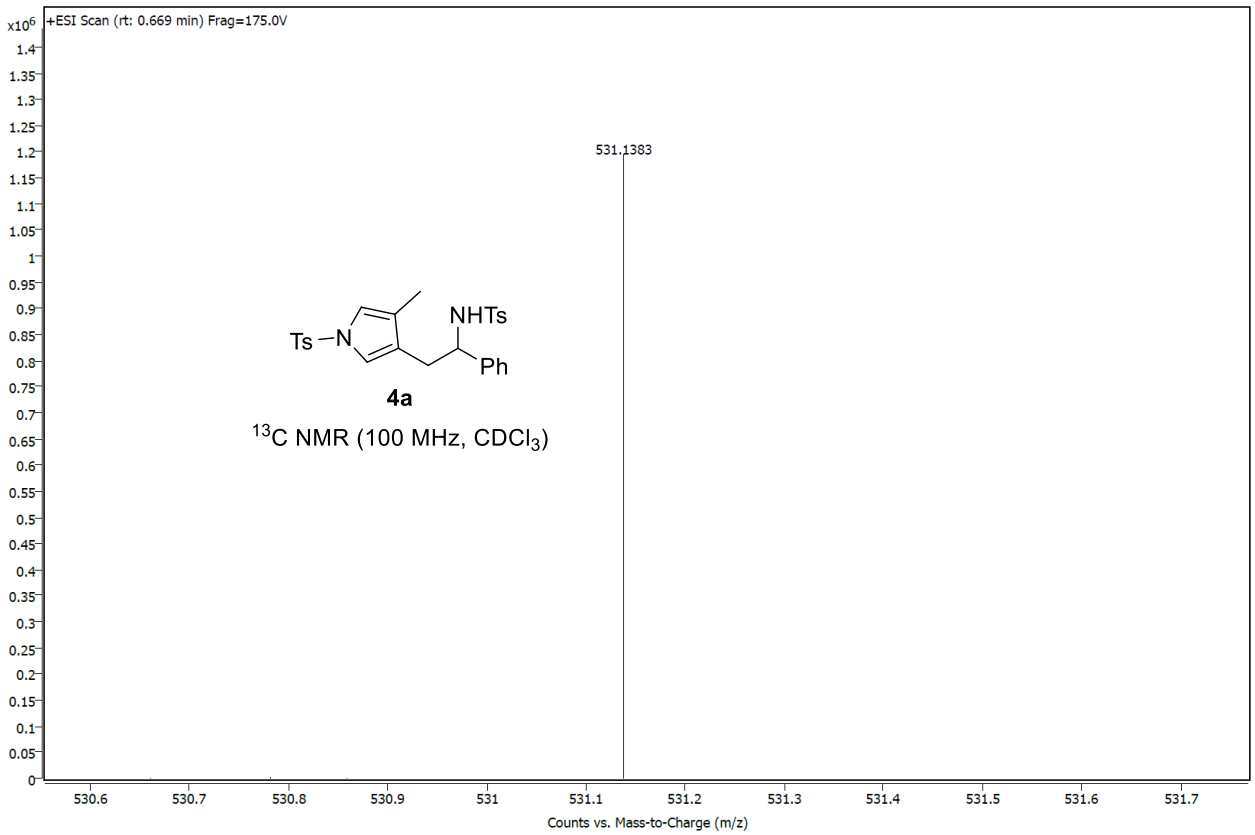
^{1}H NMR (400 MHz, $CDCl_3$)

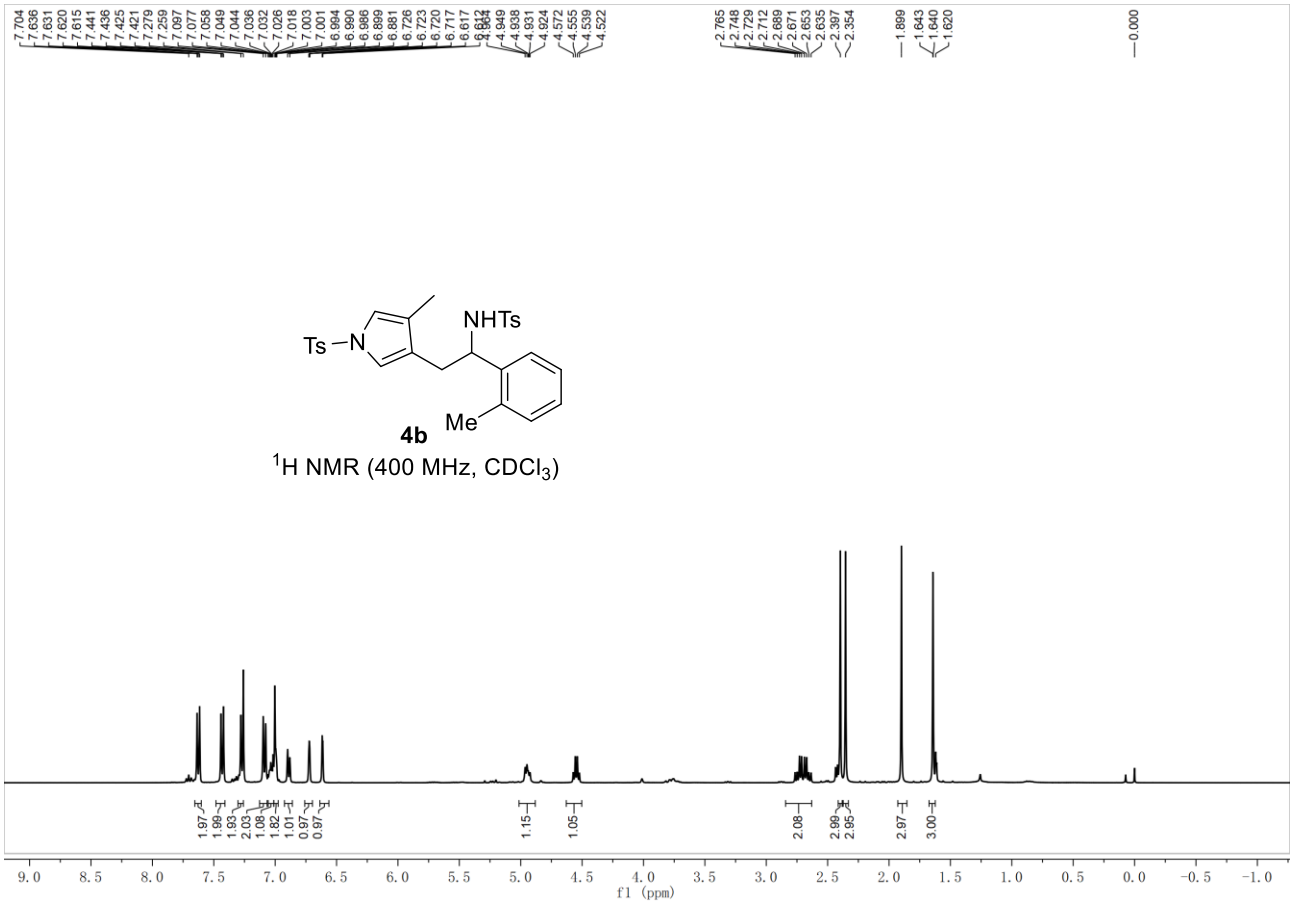


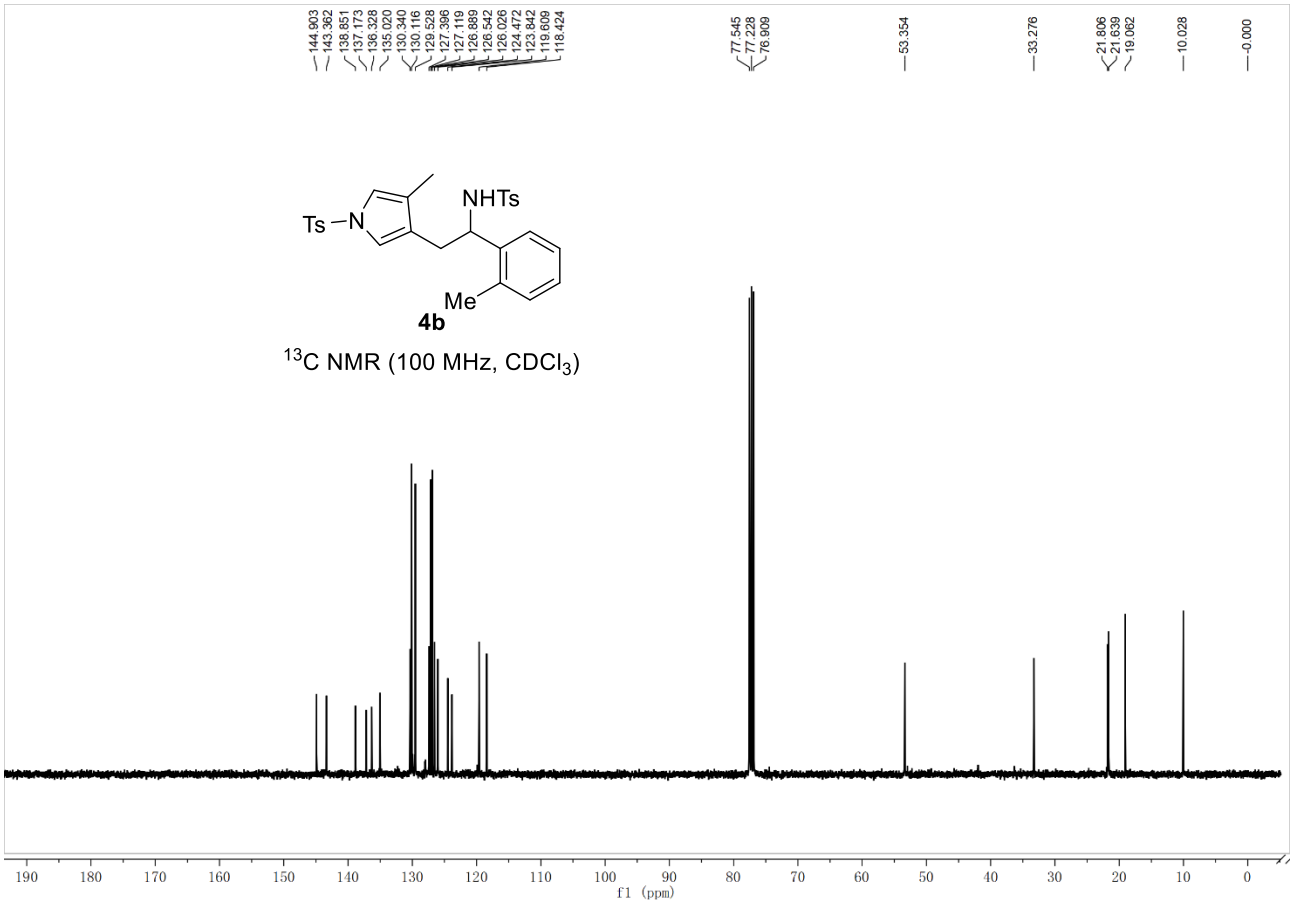
4a

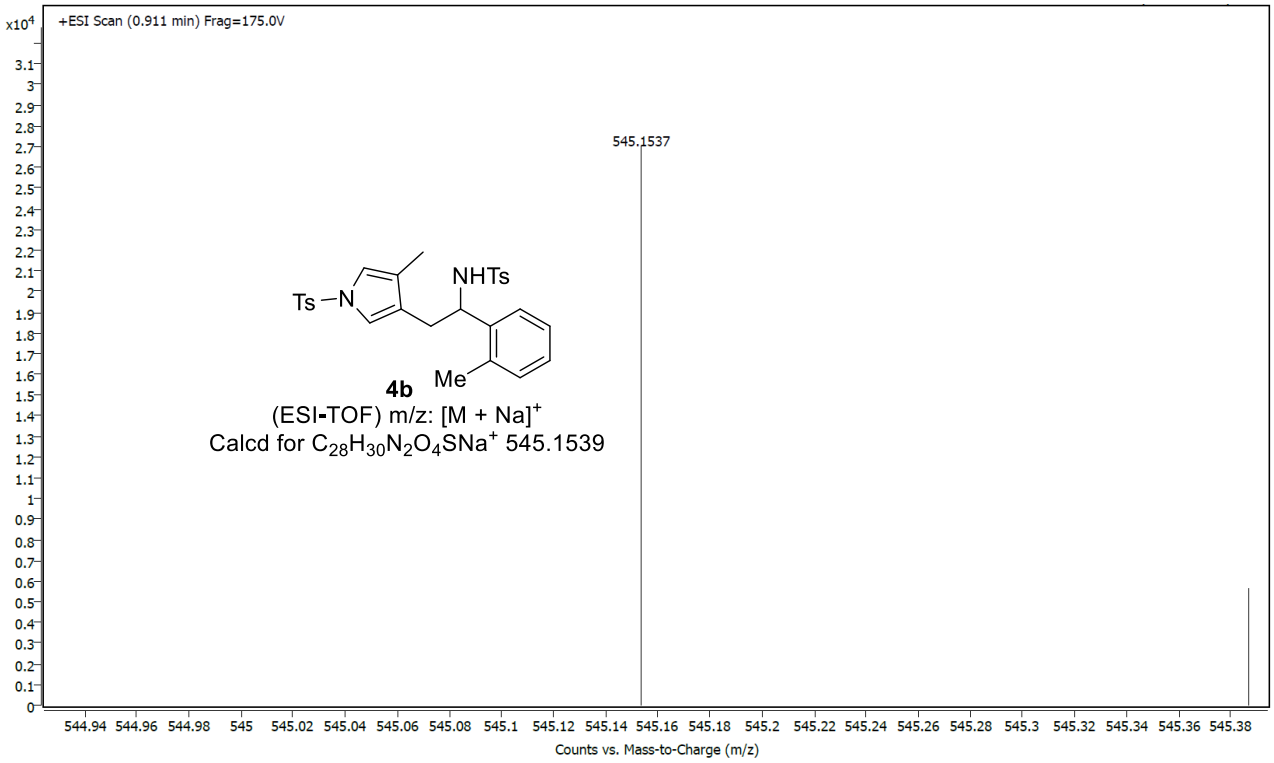
(ESI-TOF) m/z: $[M + Na]^+$

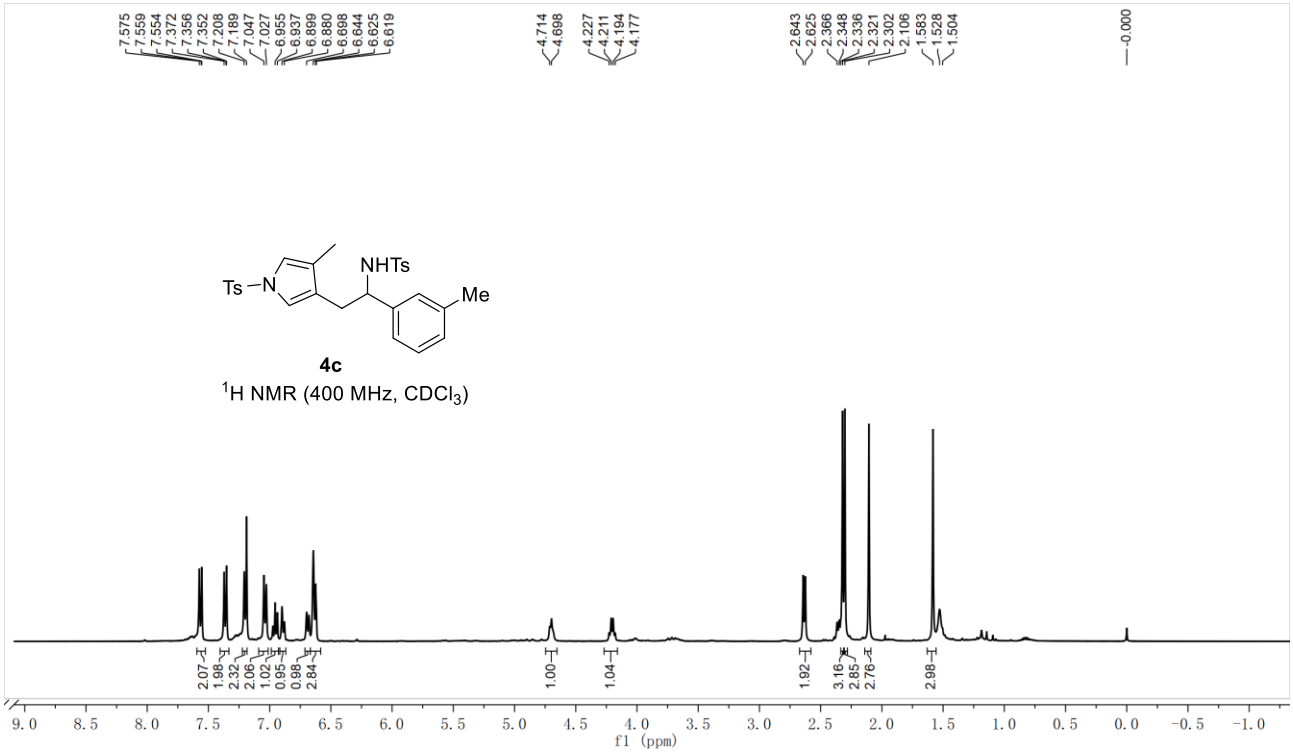
Calcd for $C_{27}H_{28}N_2O_4SNa^+$ 531.1383


x10^6
+ESI Scan (rt: 0.669 min) Frag=175.0V
531.1383
Ts
N
NHTs
Ph
4a
13C NMR (100 MHz, CDCl3)
Counts vs. Mass-to-Charge (m/z)


7.704
7.636
7.631
7.620
7.615
7.441
7.436
7.425
7.421
7.279
7.259
7.097
7.077
7.058
7.049
7.044
7.036
7.032
7.026
7.018
7.003
7.001
6.994
6.890
6.886
6.899
6.881
6.726
6.723
6.720
6.717
6.617
4.949
4.938
4.931
4.924
4.572
4.555
4.539
4.522
2.765
2.748
2.729
2.712
2.689
2.671
2.653
2.635
2.397
2.354
1.899
1.643
1.640
1.620
0.000
NHTs
Ts
N
Me
4b
1H NMR (400 MHz, CDCl3)
1.97
1.99
1.93
2.03
1.08
1.82
1.01
0.97
0.97
1.15
1.05
2.08
2.99
2.95
2.97
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

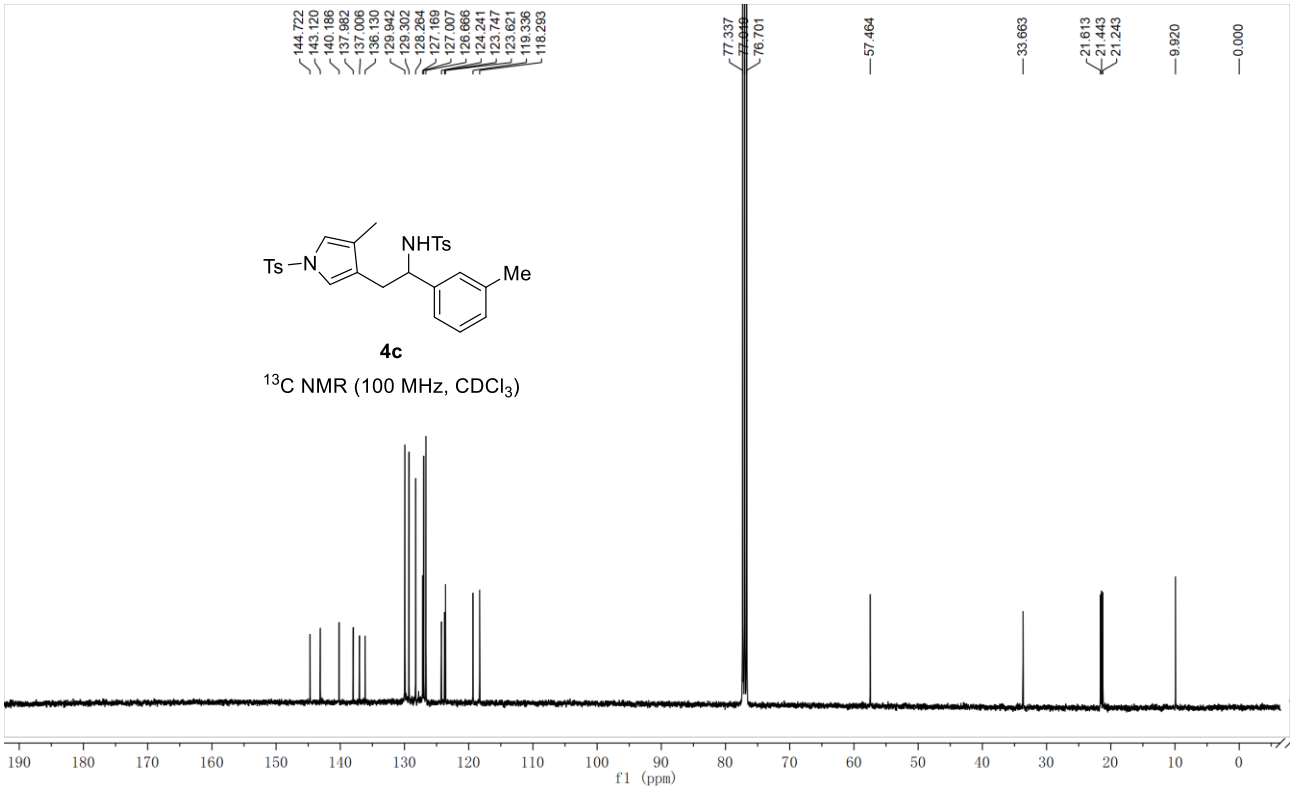

144.903
143.362
138.851
137.173
136.328
135.020
130.340
130.116
129.528
127.396
127.119
126.889
126.542
126.026
124.472
123.842
119.609
118.424
77.545
77.228
76.909
53.354
33.276
21.806
21.639
19.062
10.028
0.000
NHTs
Ts
N
Me
4b
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


+ESI Scan (0.911 min) Frag=175.0V
x10^4
545.1537
NHTs
Ts
N
Me
4b
(ESI-TOF) m/z: [M + Na]+
Calcd for C28H30N2O4SNa+ 545.1539
Counts vs. Mass-to-Charge (m/z)



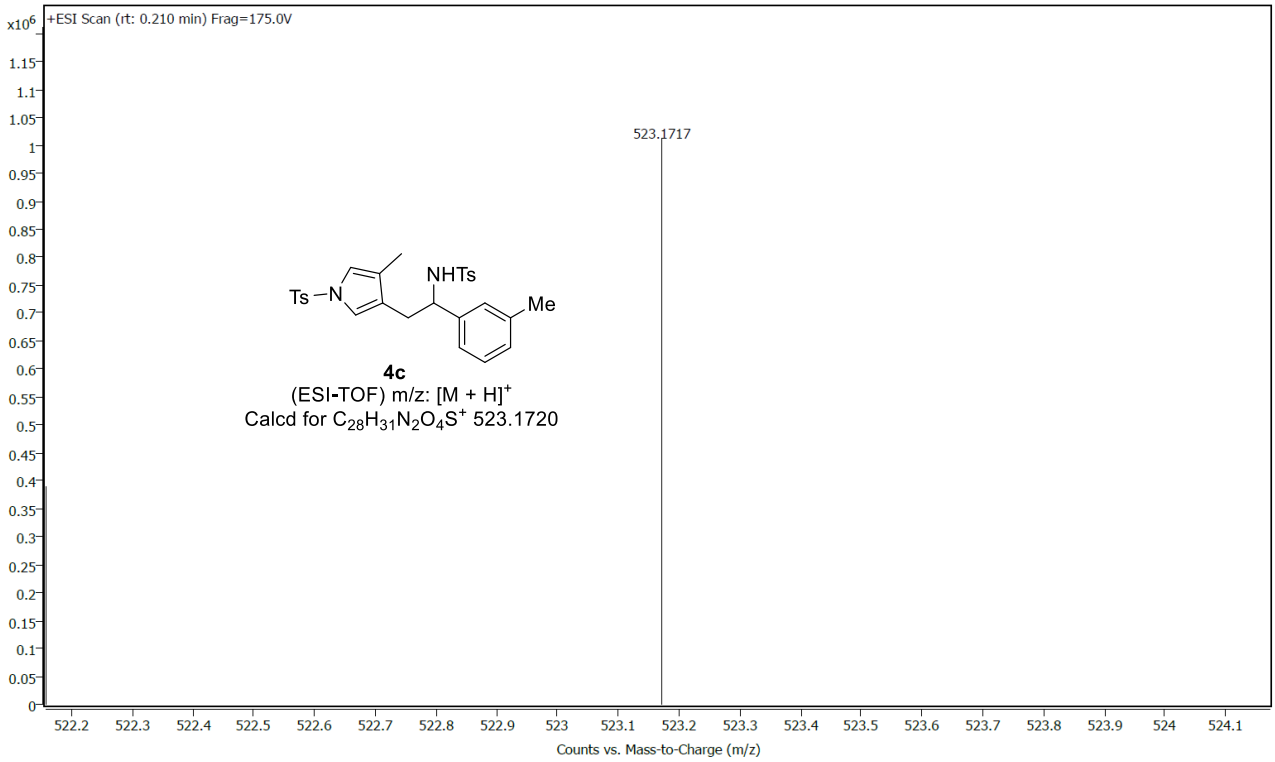
4c

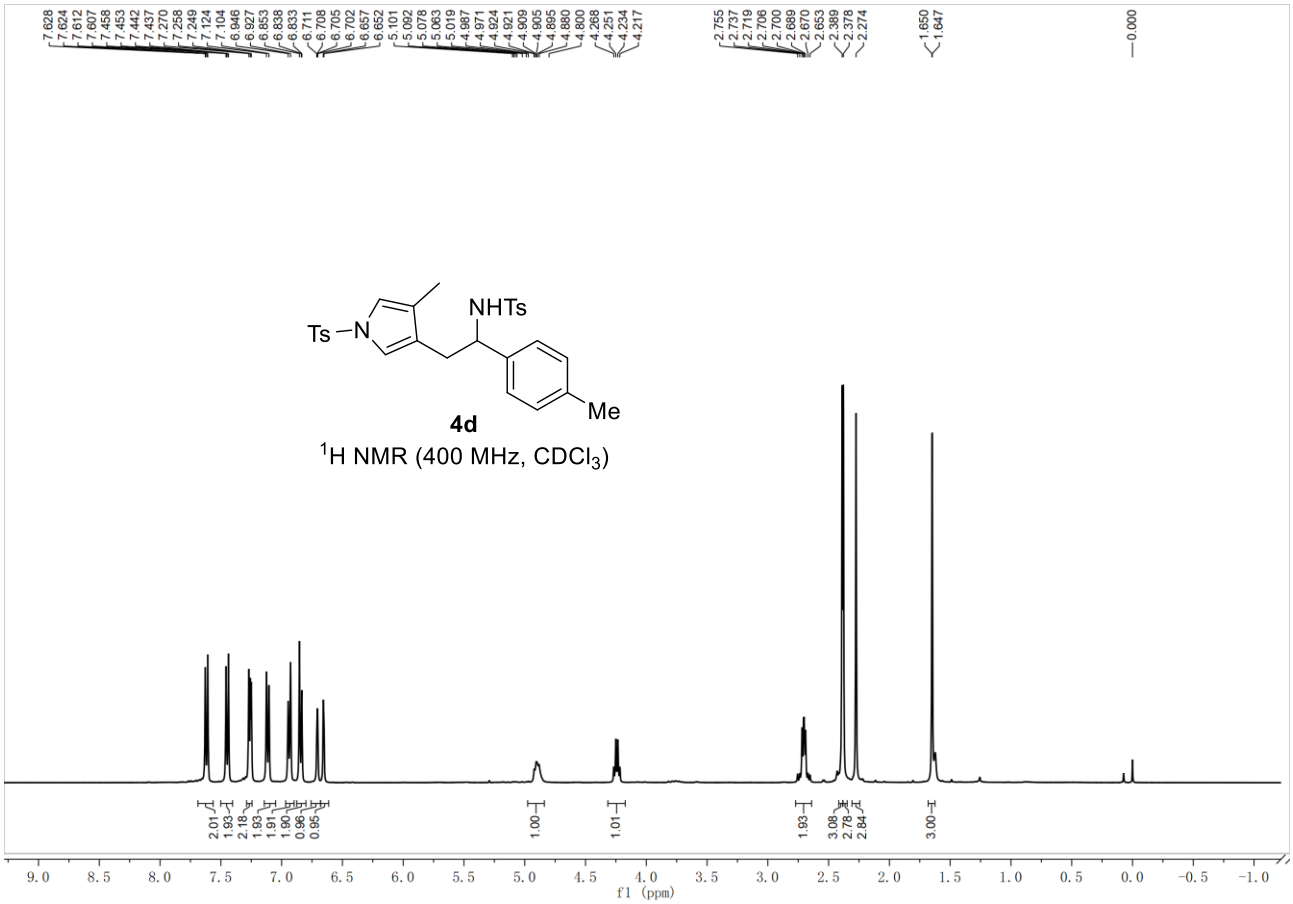
^{1}H NMR (400 MHz, $CDCl_3$)

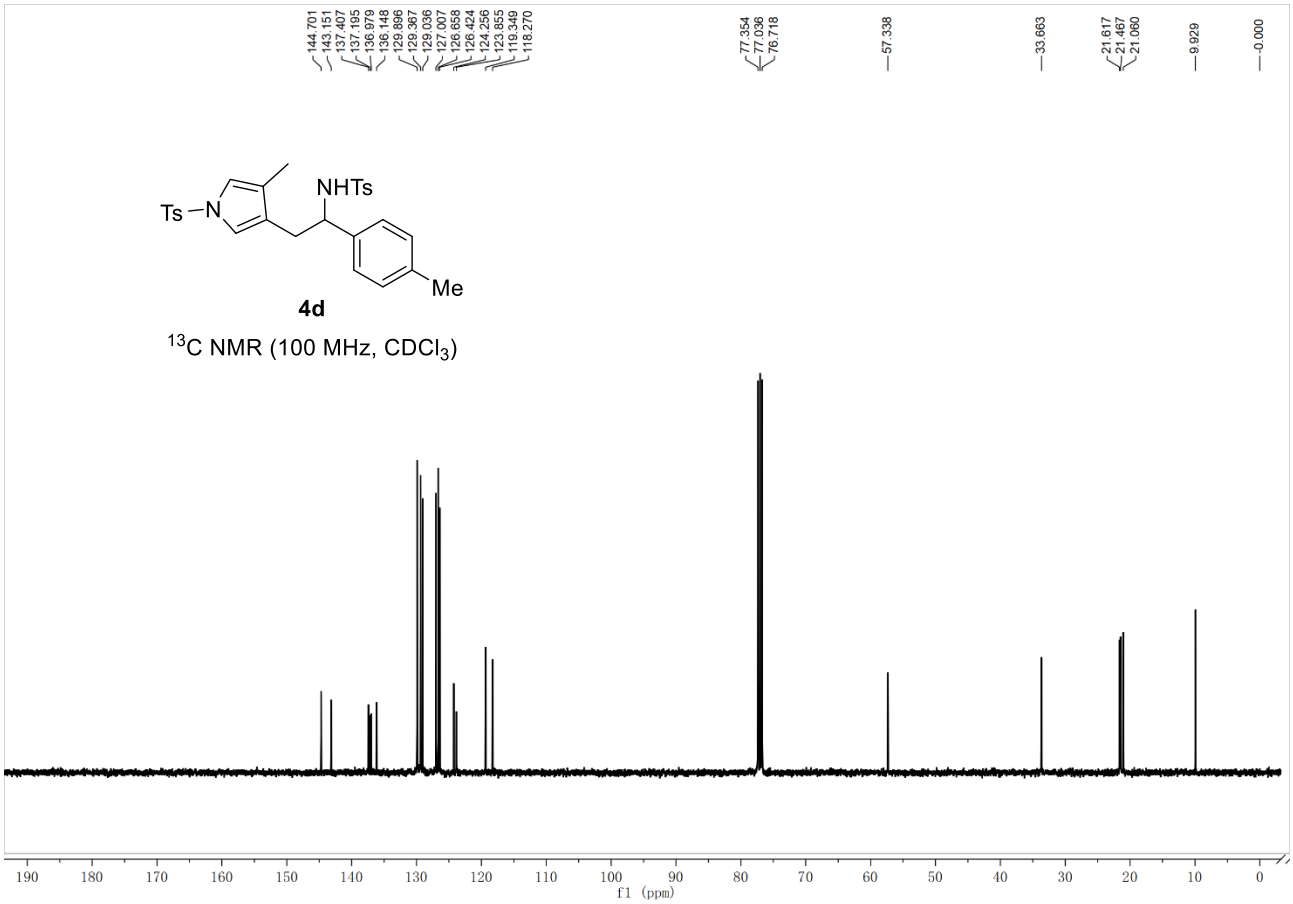


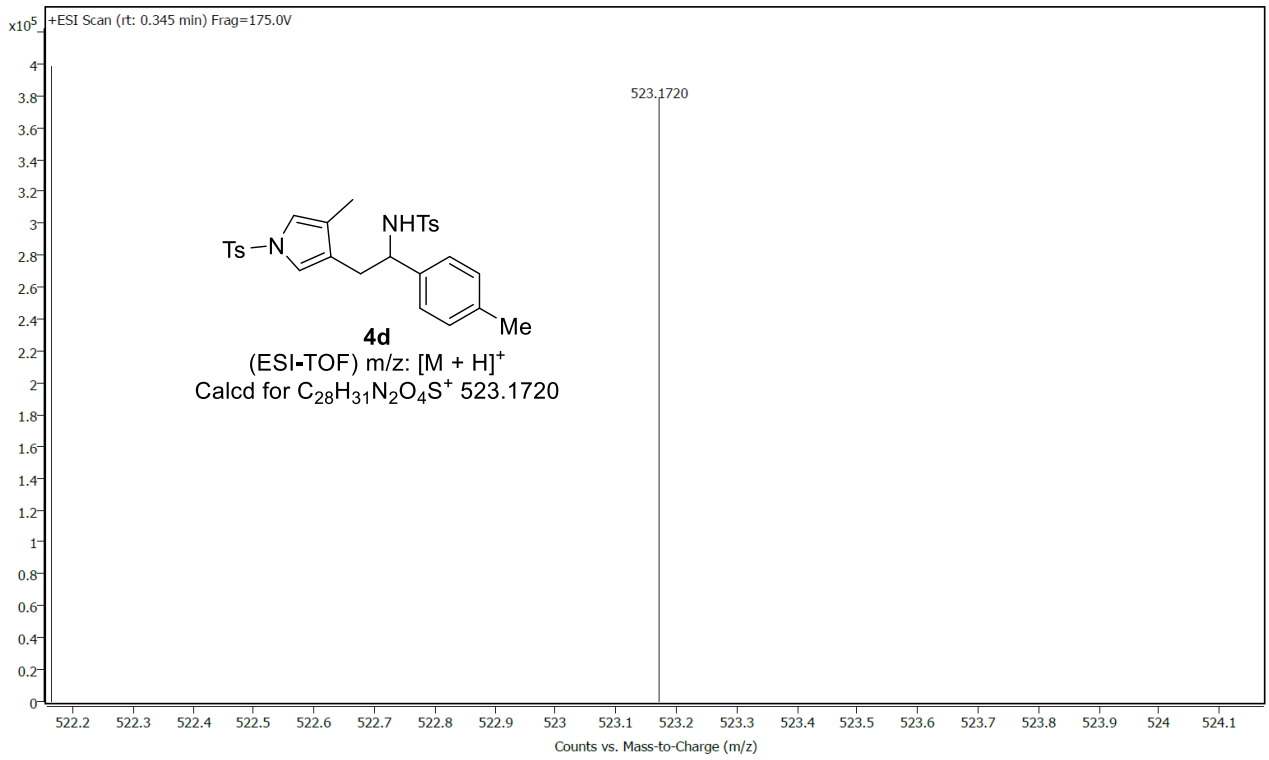
4c

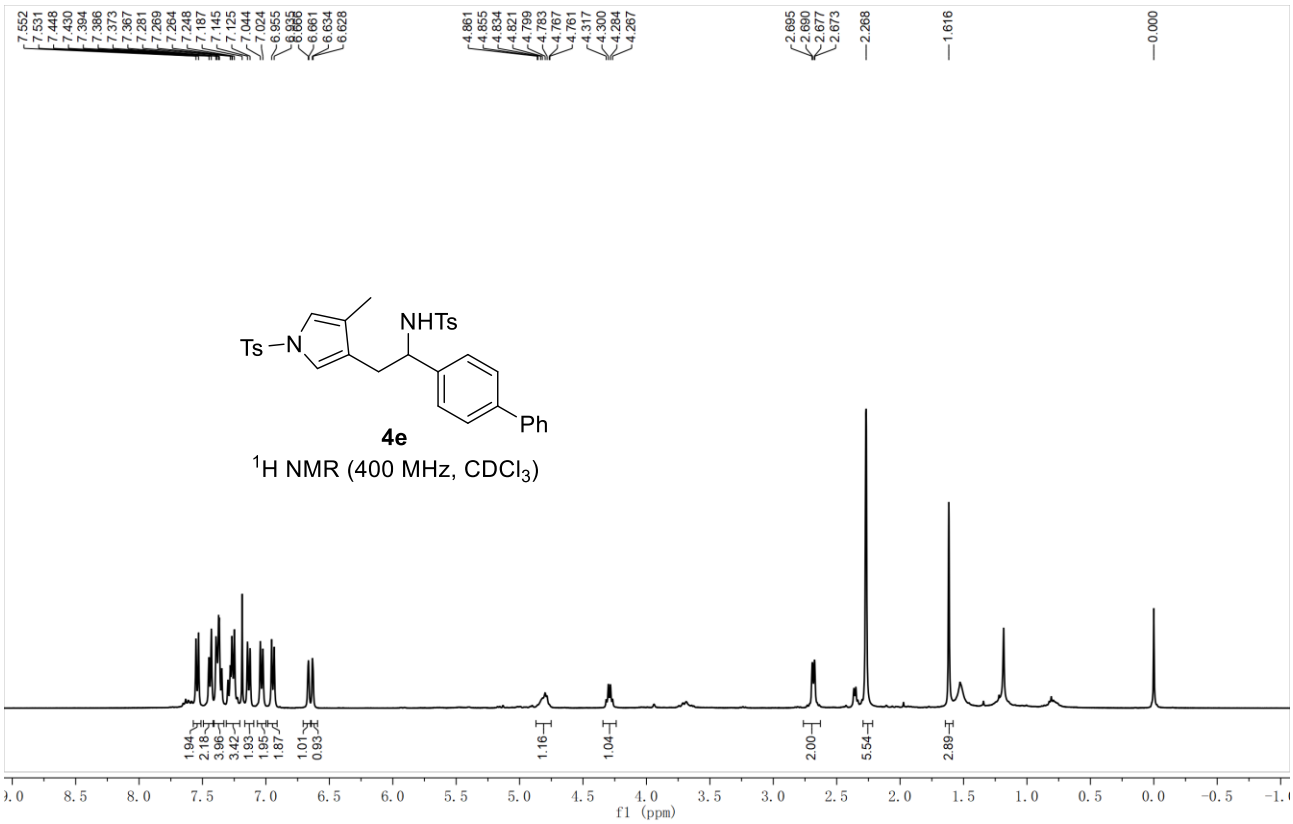
^{13}C NMR (100 MHz, $CDCl_3$)

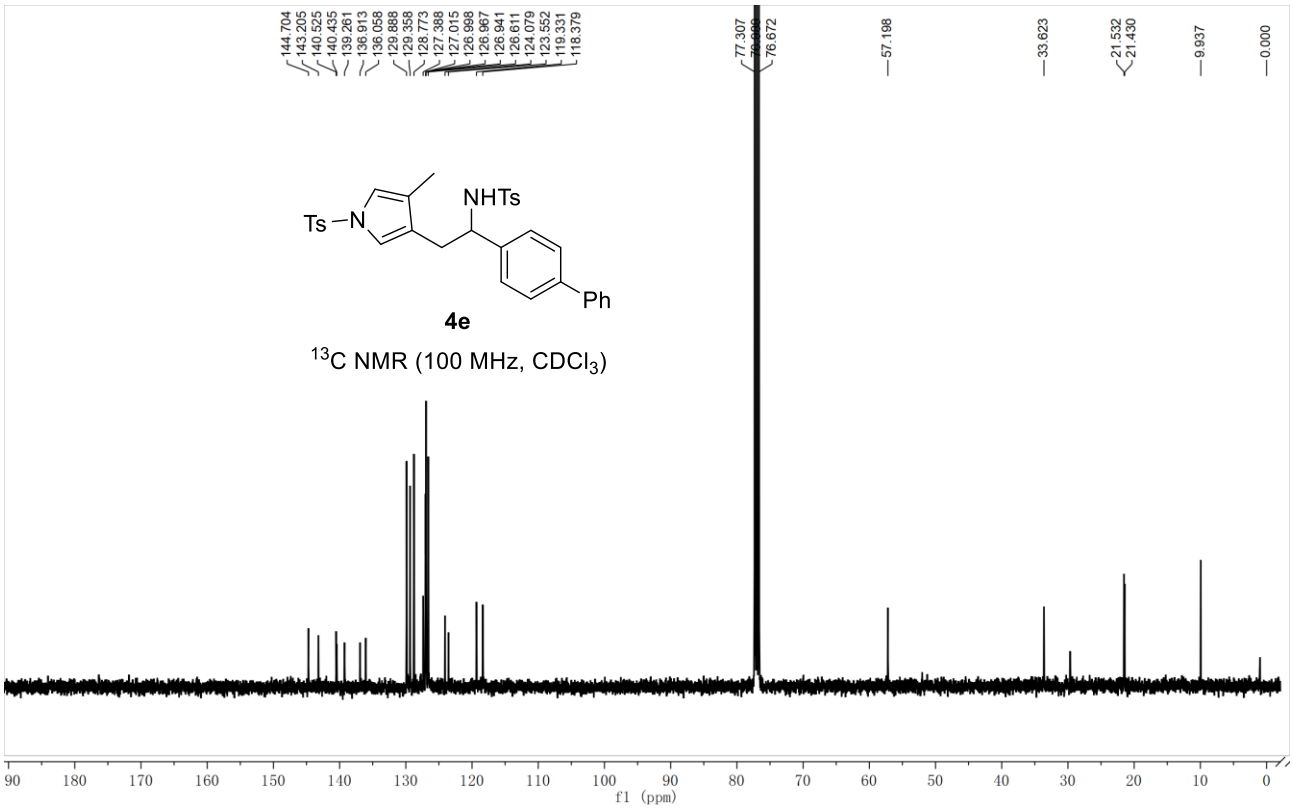

+ESI Scan (rt: 0.210 min) Frag=175.0V
x10^6
523.1717
NHTs
Ts
N
Me
4c
(ESI-TOF) m/z: [M + H]+
Calcd for C28H31N2O4S+ 523.1720
Counts vs. Mass-to-Charge (m/z)

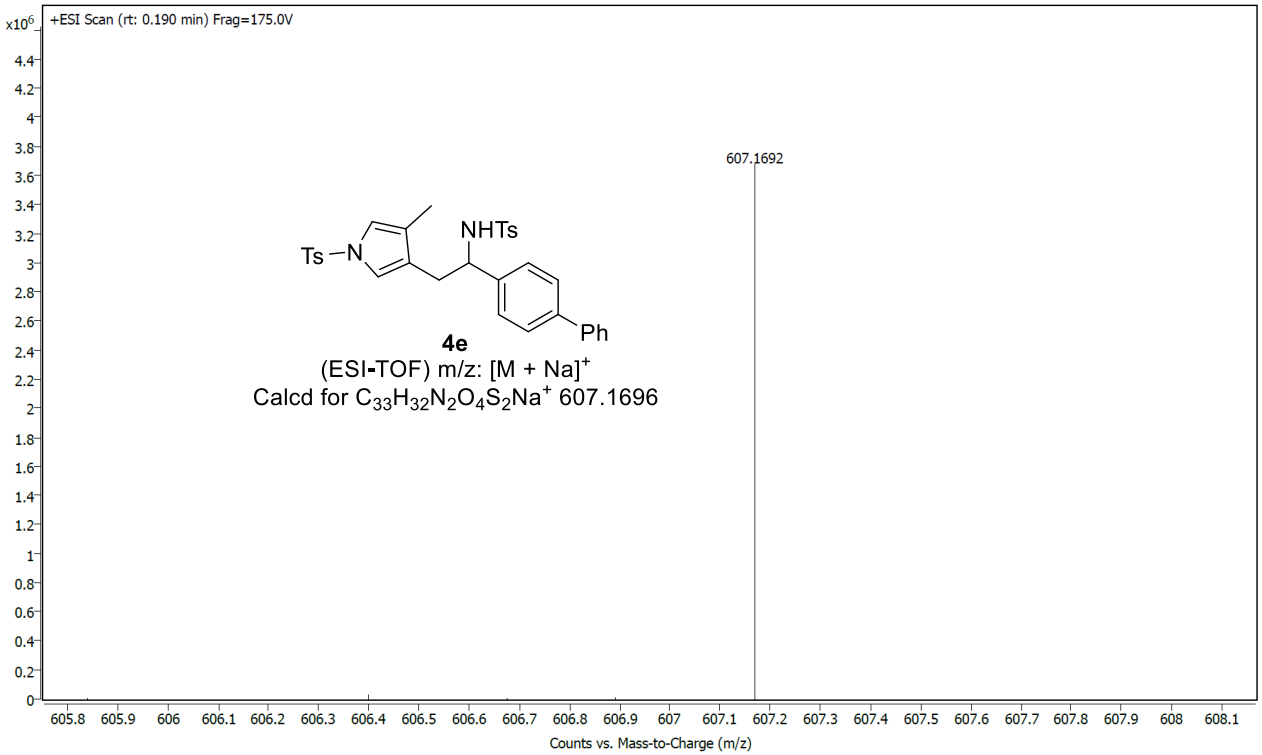

NHTs
Ts
N
Me
4d
1H NMR (400 MHz, CDCl3)
f1 (ppm)

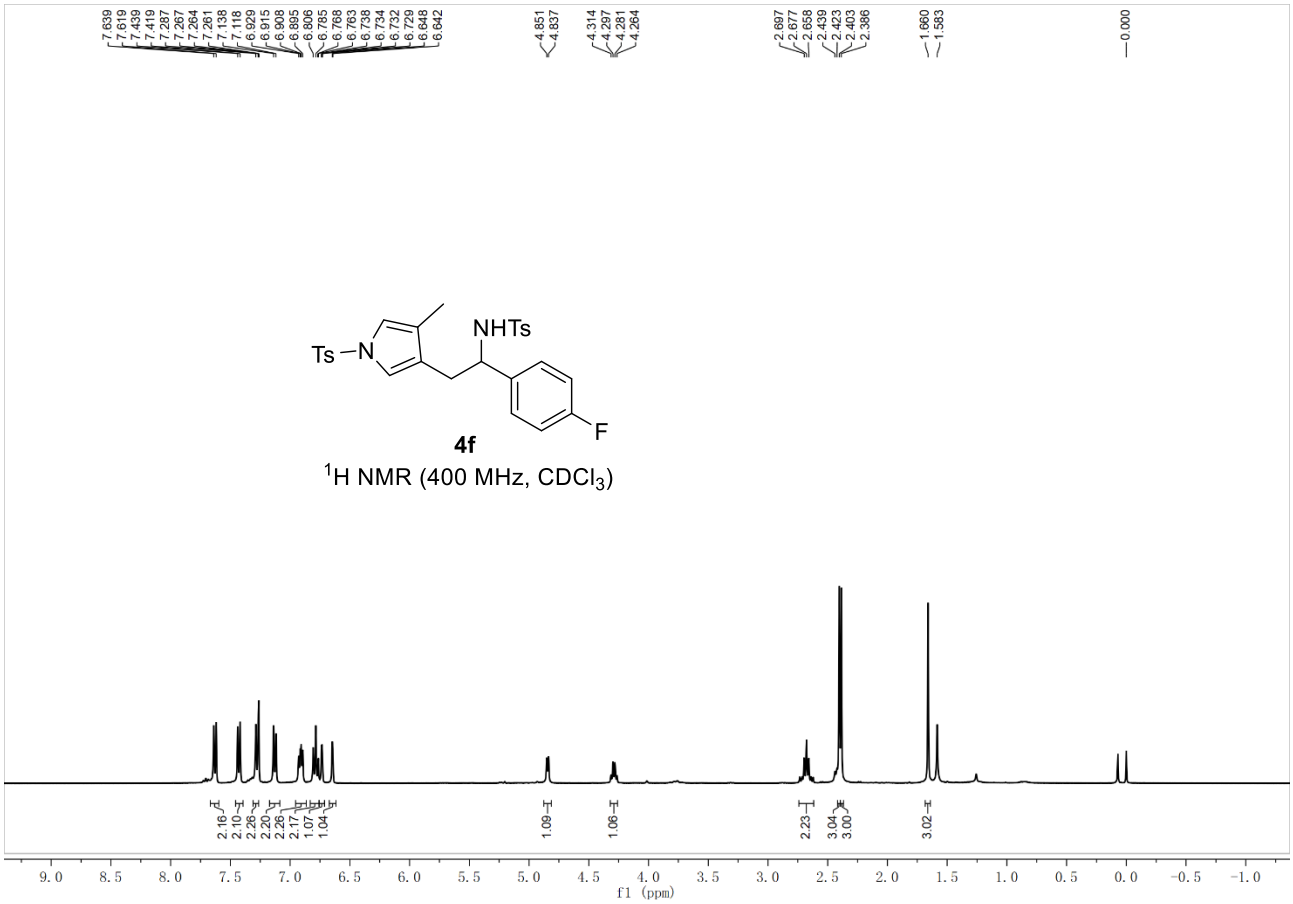

NHTs
Ts
N
Me
4d
13C NMR (100 MHz, CDCl3)
f1 (ppm)


x10^5
+ESI Scan (rt: 0.345 min) Frag=175.0V
523.1720
NHTs
Ts
N
Me
4d
(ESI-TOF) m/z: [M + H]+
Calcd for C28H31N2O4S+ 523.1720
Counts vs. Mass-to-Charge (m/z)


NHTs
Ts
N
Ph
4e
1H NMR (400 MHz, CDCl3)
f1 (ppm)

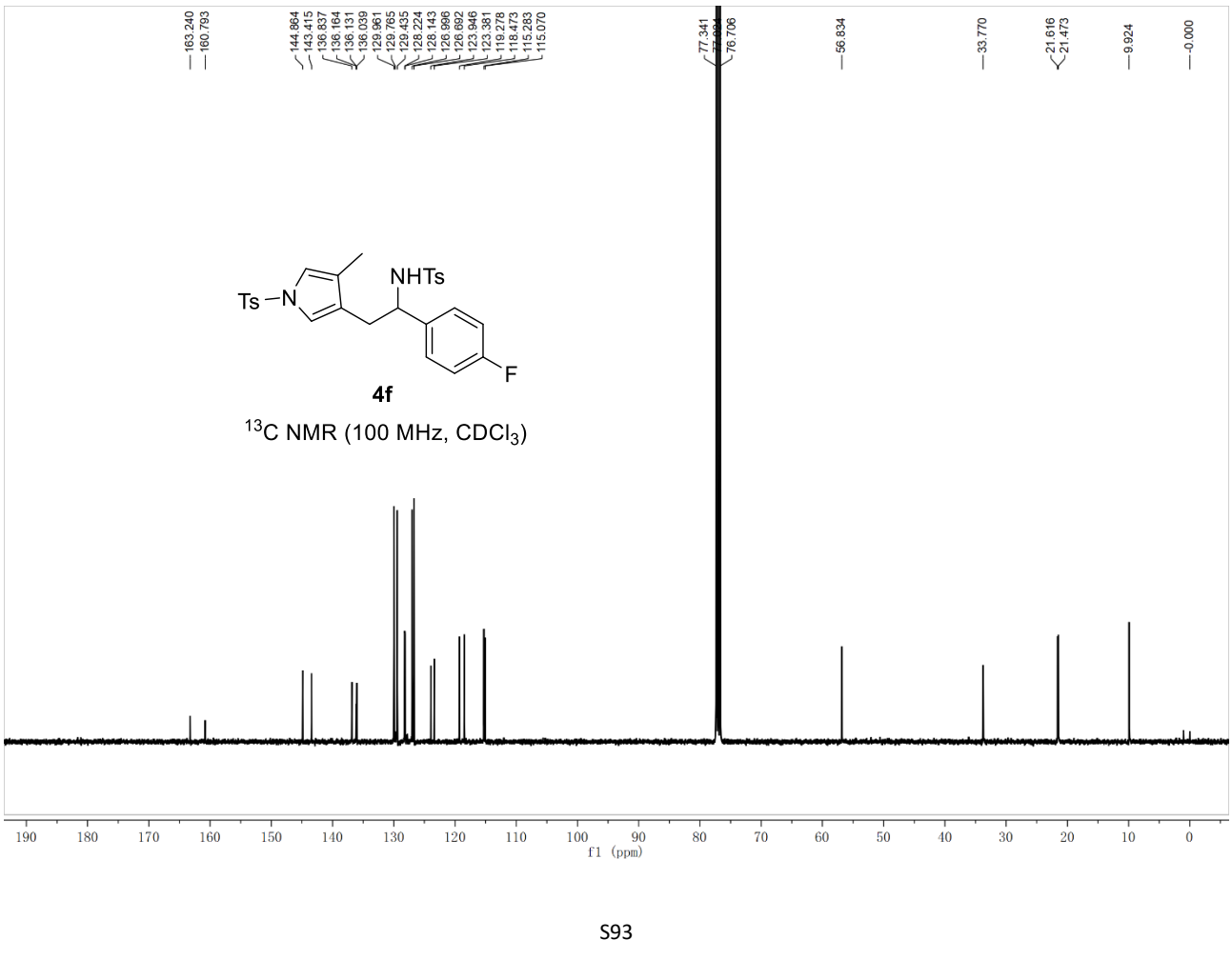

NHTs
Ts
N
Ph
4e
13C NMR (100 MHz, CDCl3)
f1 (ppm)


+ESI Scan (rt: 0.190 min) Frag=175.0V
x10^6
607.1692
NHTs
Ts
N
Ph
4e
(ESI-TOF) m/z: [M + Na]+
Calcd for C33H32N2O4S2Na+ 607.1696
Counts vs. Mass-to-Charge (m/z)



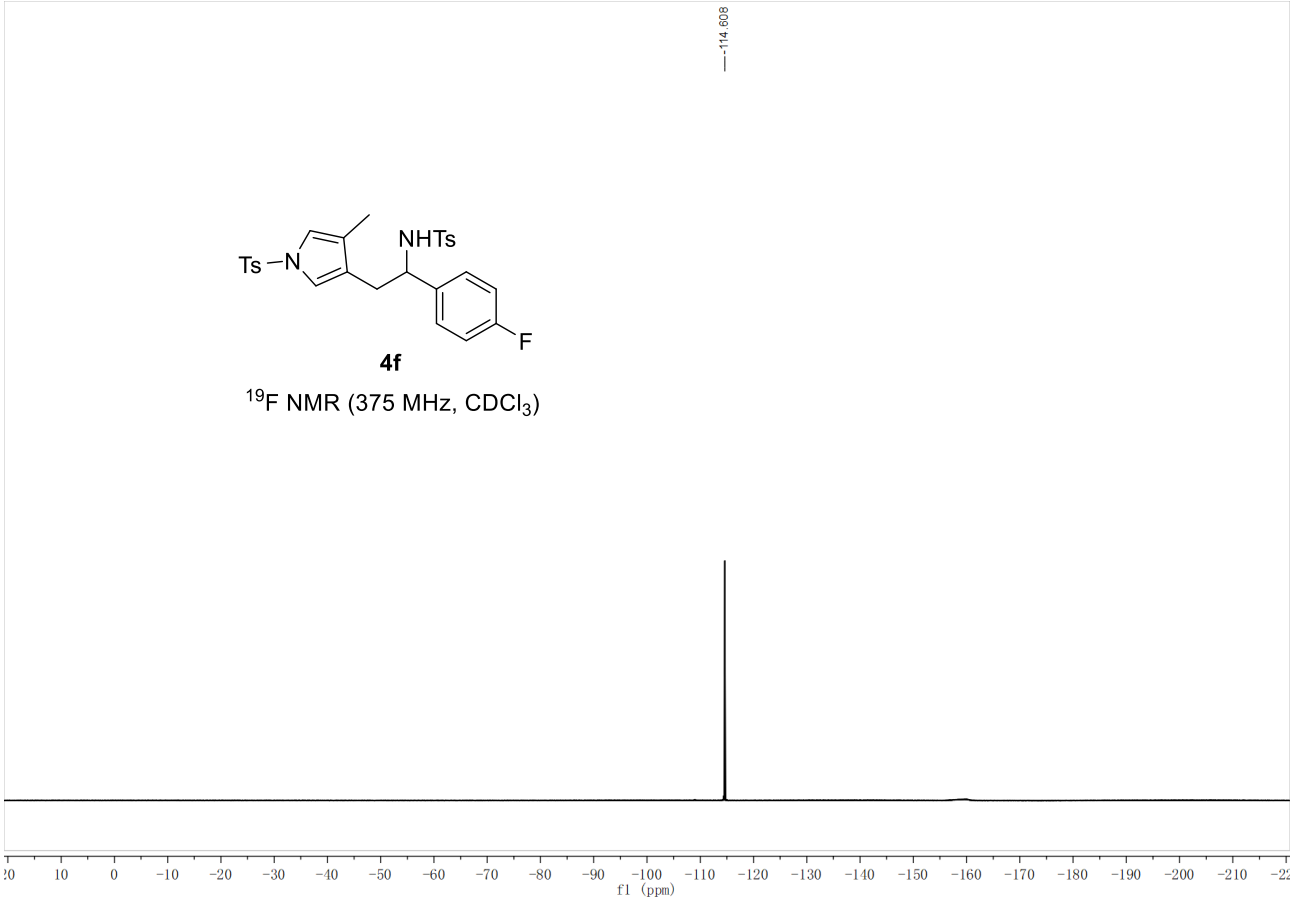
4f

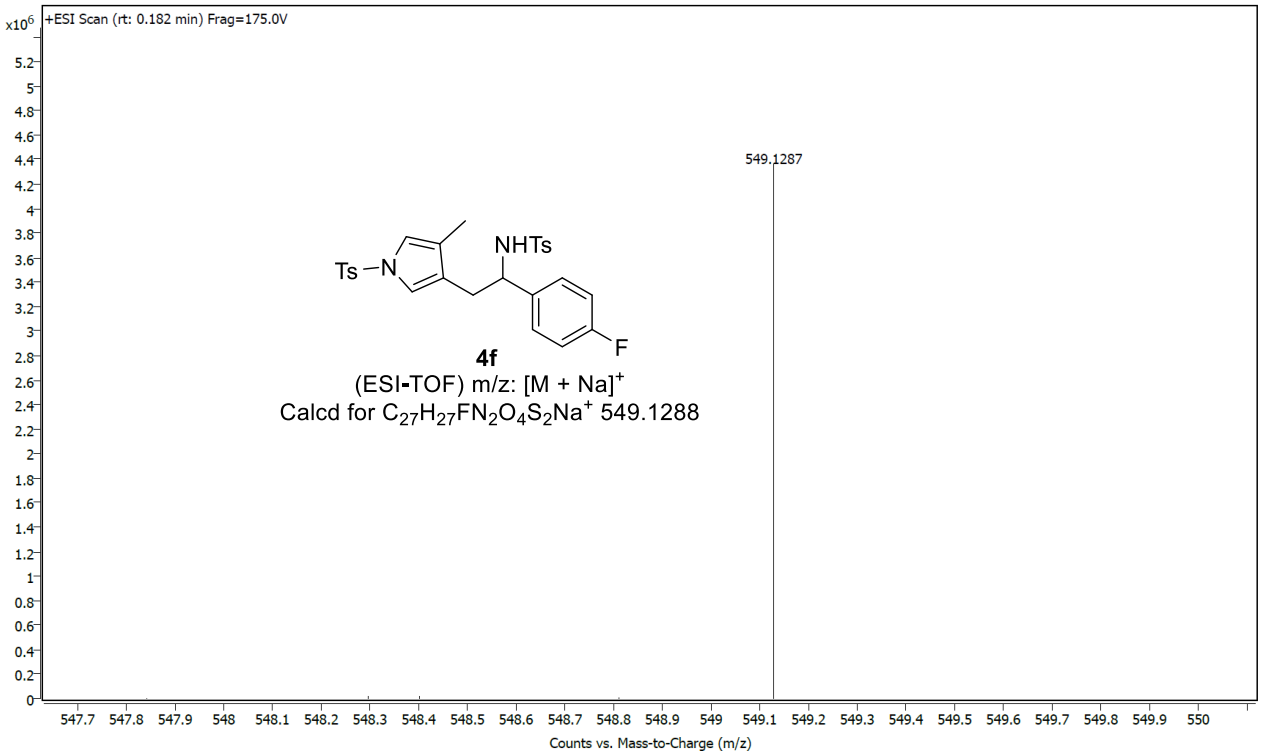
^{1}H NMR (400 MHz, $CDCl_3$)

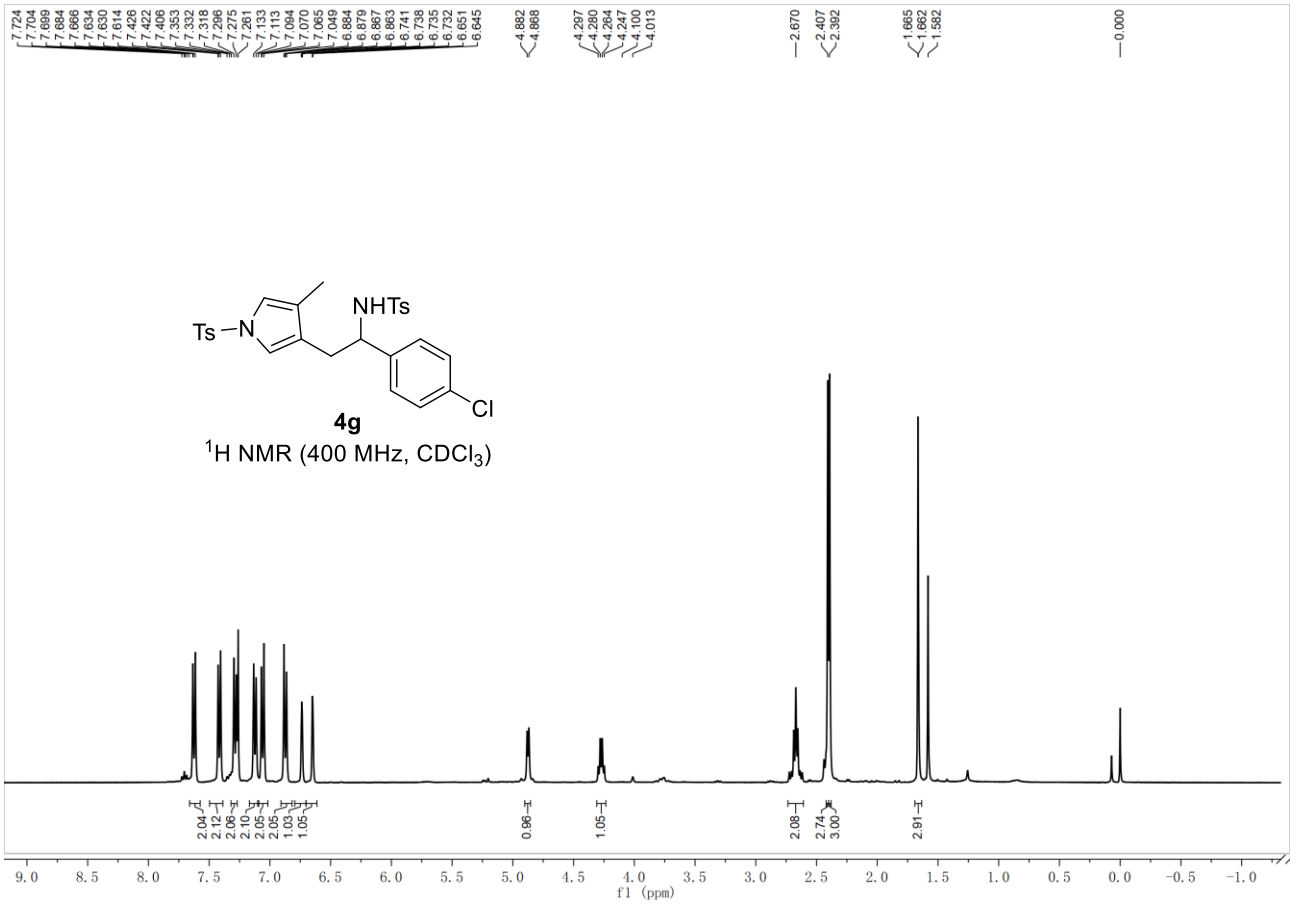


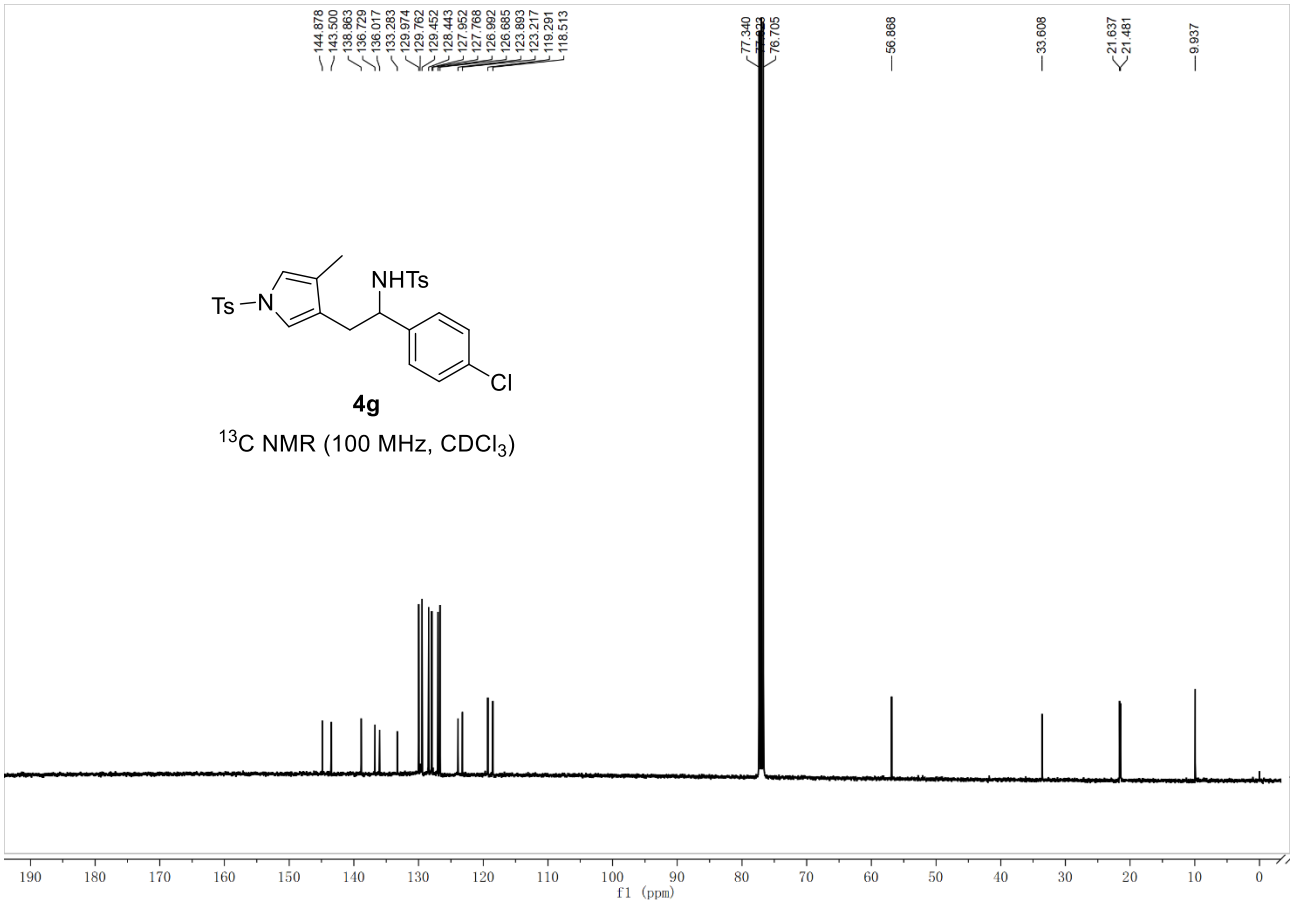
4f

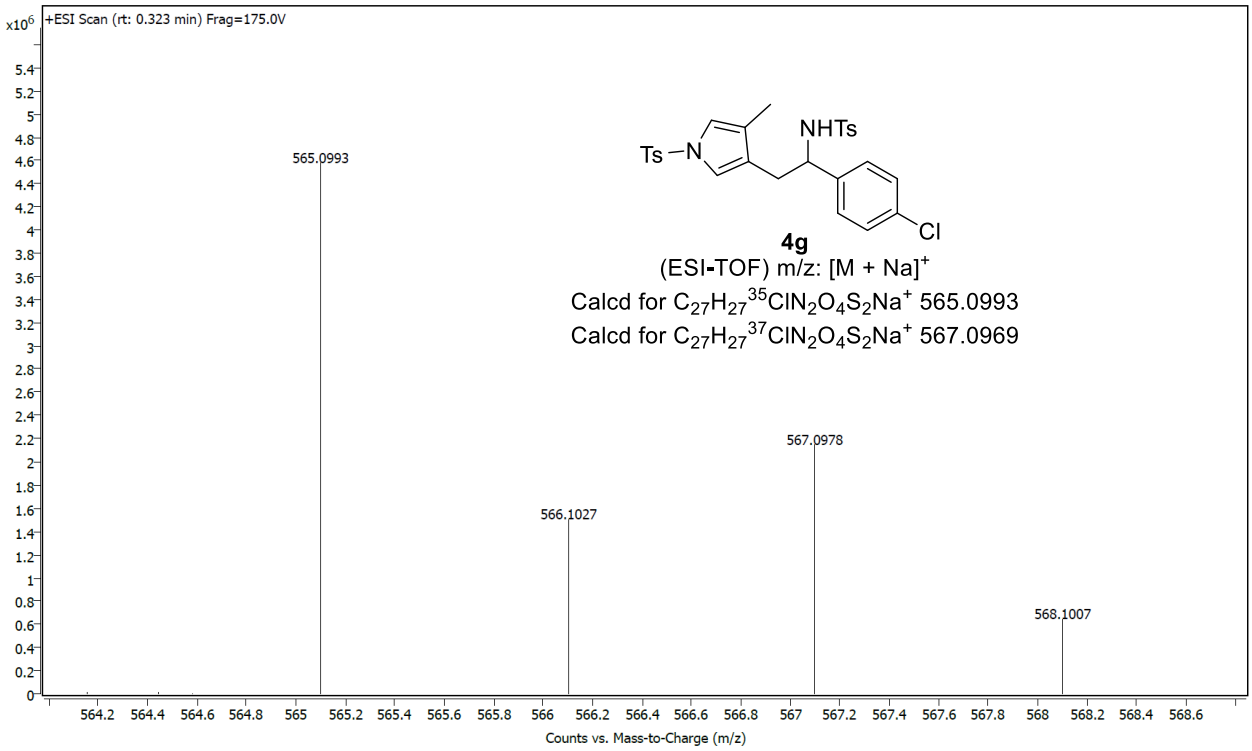
^{13}C NMR (100 MHz, $CDCl_3$)


-114.608
Ts
N
NHTs
F
4f
19F NMR (375 MHz, CDCl3)
f1 (ppm)


x10^6
+ESI Scan (rt: 0.182 min) Frag=175.0V
549.1287
Ts
N
NHTs
F
4f
(ESI-TOF) m/z: [M + Na]+
Calcd for C27H27FN2O4S2Na+ 549.1288
Counts vs. Mass-to-Charge (m/z)


NHTs
Ts
N
Cl
4g
1H NMR (400 MHz, CDCl3)
f1 (ppm)


NHTs
Ts
N
Cl
4g
13C NMR (100 MHz, CDCl3)
f1 (ppm)

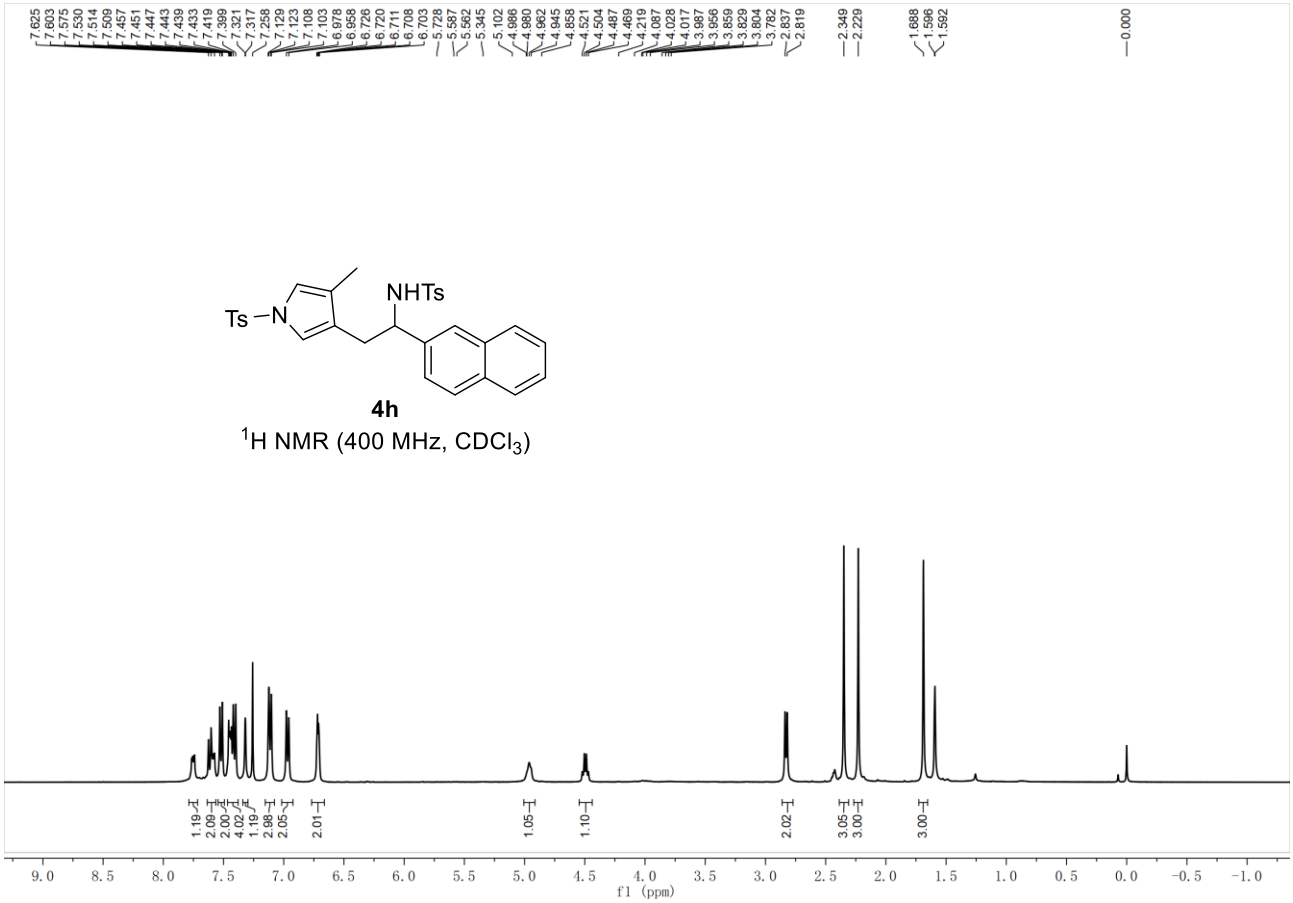


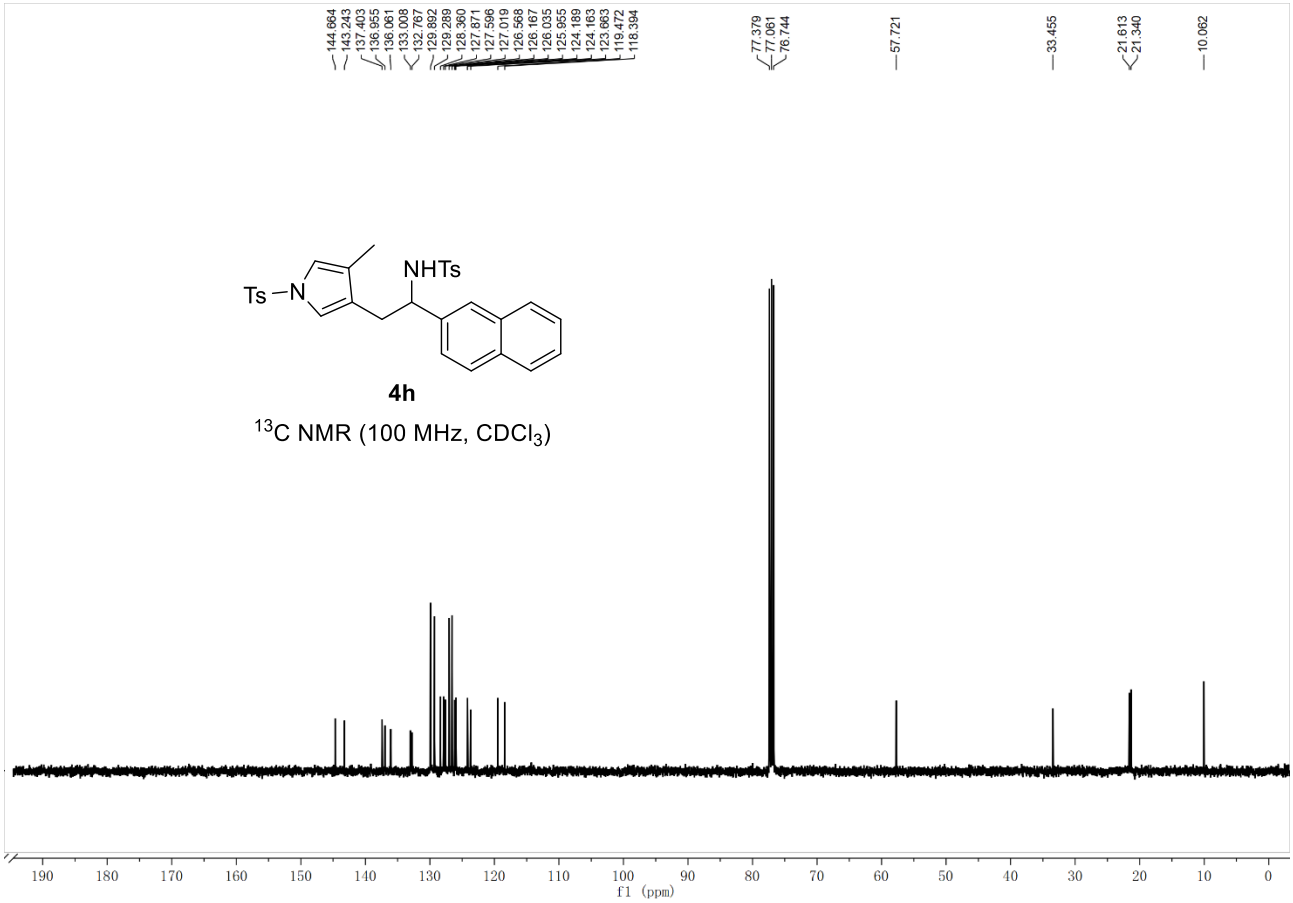
4g

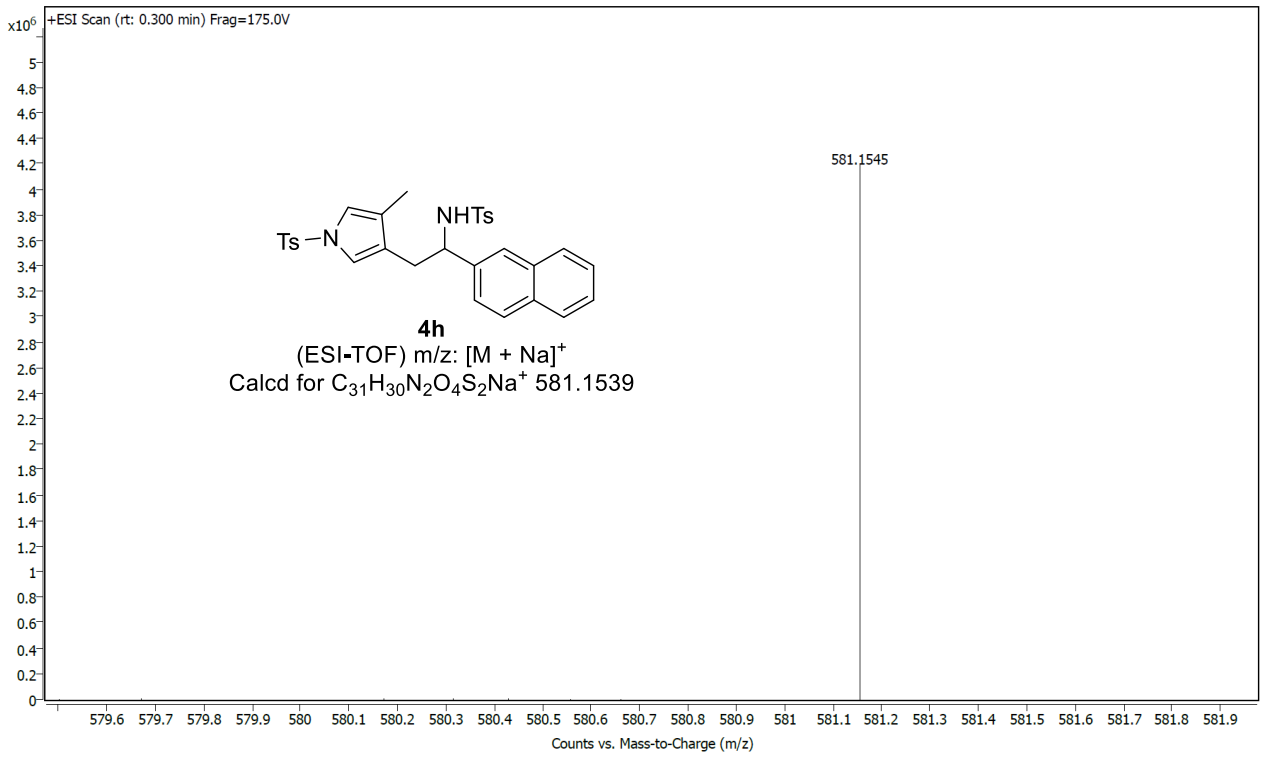
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{27}H_{27}{}^{35}ClN_2O_4S_2Na^+$ 565.0993

Calcd for $C_{27}H_{27}{}^{37}ClN_2O_4S_2Na^+$ 567.0969


7.625
7.603
7.575
7.530
7.514
7.509
7.457
7.451
7.447
7.443
7.439
7.433
7.419
7.399
7.321
7.317
7.258
7.129
7.123
7.108
7.103
6.978
6.958
6.726
6.720
6.711
6.708
6.703
5.728
5.587
5.562
5.345
5.102
4.886
4.880
4.862
4.945
4.858
4.521
4.504
4.487
4.469
4.219
4.087
4.028
4.017
3.987
3.956
3.859
3.829
3.804
3.782
2.837
2.819
2.349
2.229
1.688
1.596
1.592
0.000
Ts
N
NHTs
4h
1H NMR (400 MHz, CDCl3)
1.19
2.09
2.00
4.02
1.19
2.98
2.05
2.01
1.05
1.10
2.02
3.05
3.00
3.00
f1 (ppm)

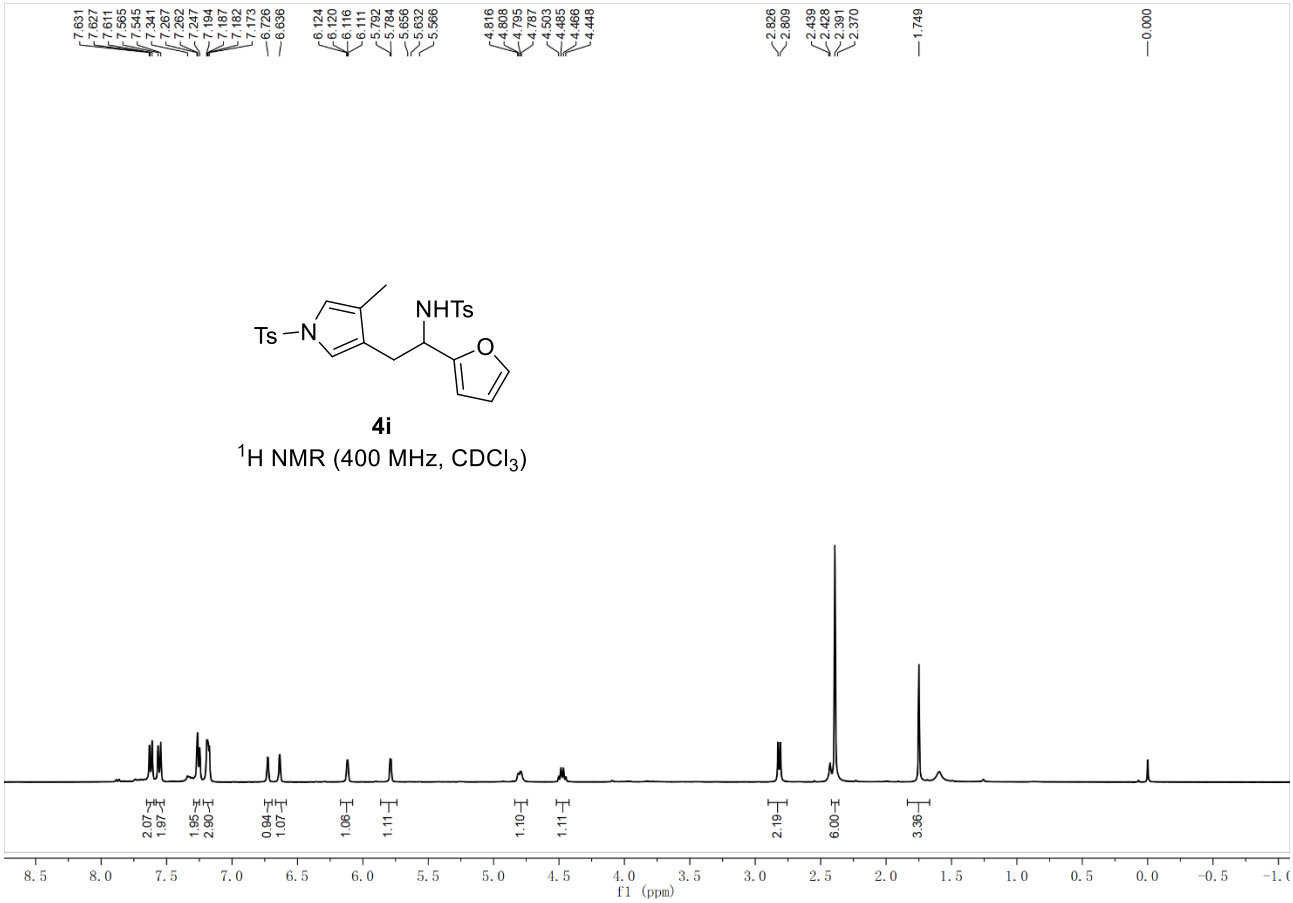

144.664
143.243
137.403
136.955
136.081
133.008
132.767
129.892
129.289
128.360
127.871
127.596
127.019
126.568
126.167
126.035
125.955
124.189
124.163
123.663
119.472
118.394
77.379
77.061
76.744
57.721
33.455
21.613
21.340
10.062
Ts
N
NHTs
4h
13C NMR (100 MHz, CDCl3)
f1 (ppm)



4h

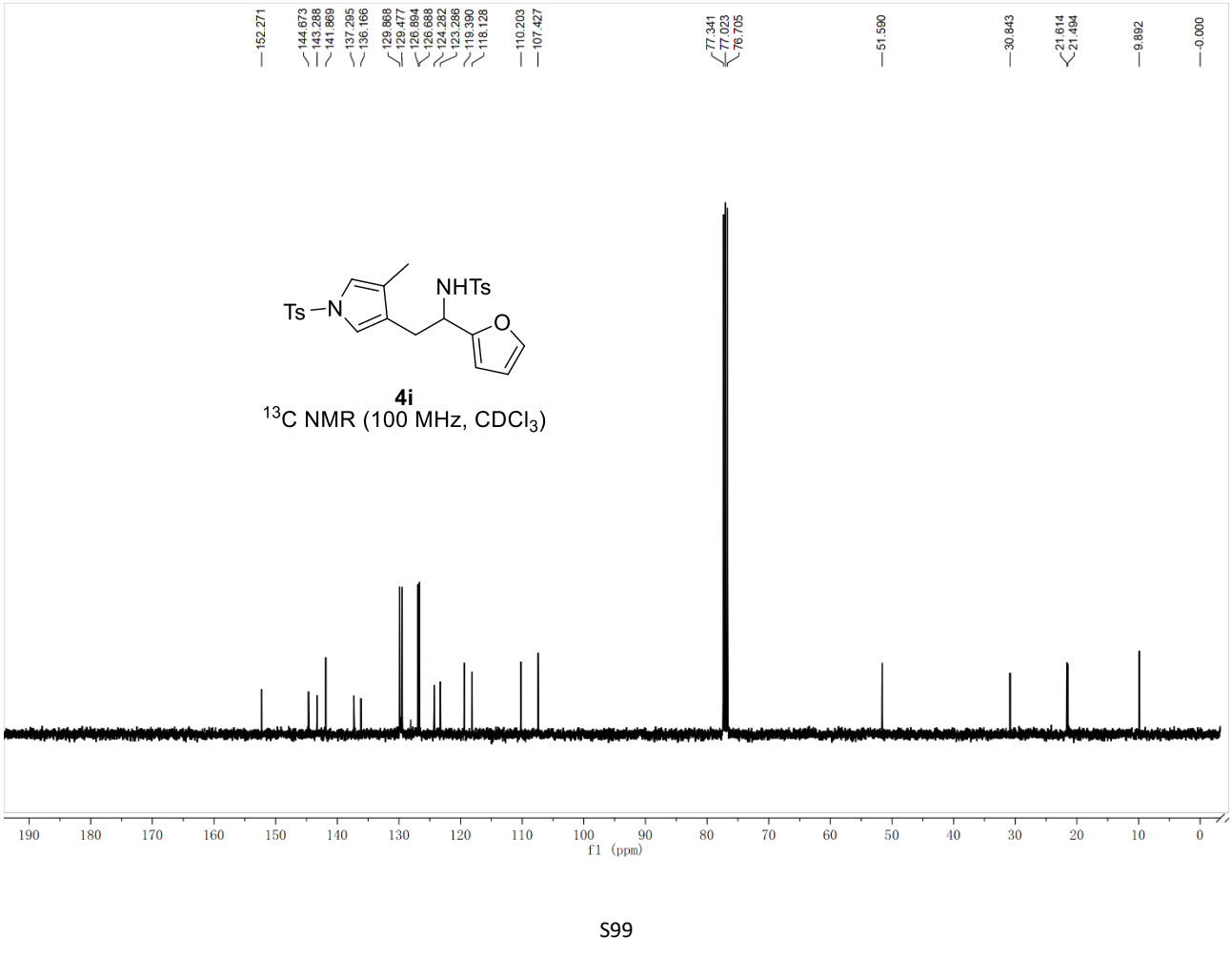
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{31}H_{30}N_2O_4S_2Na^+$ 581.1539



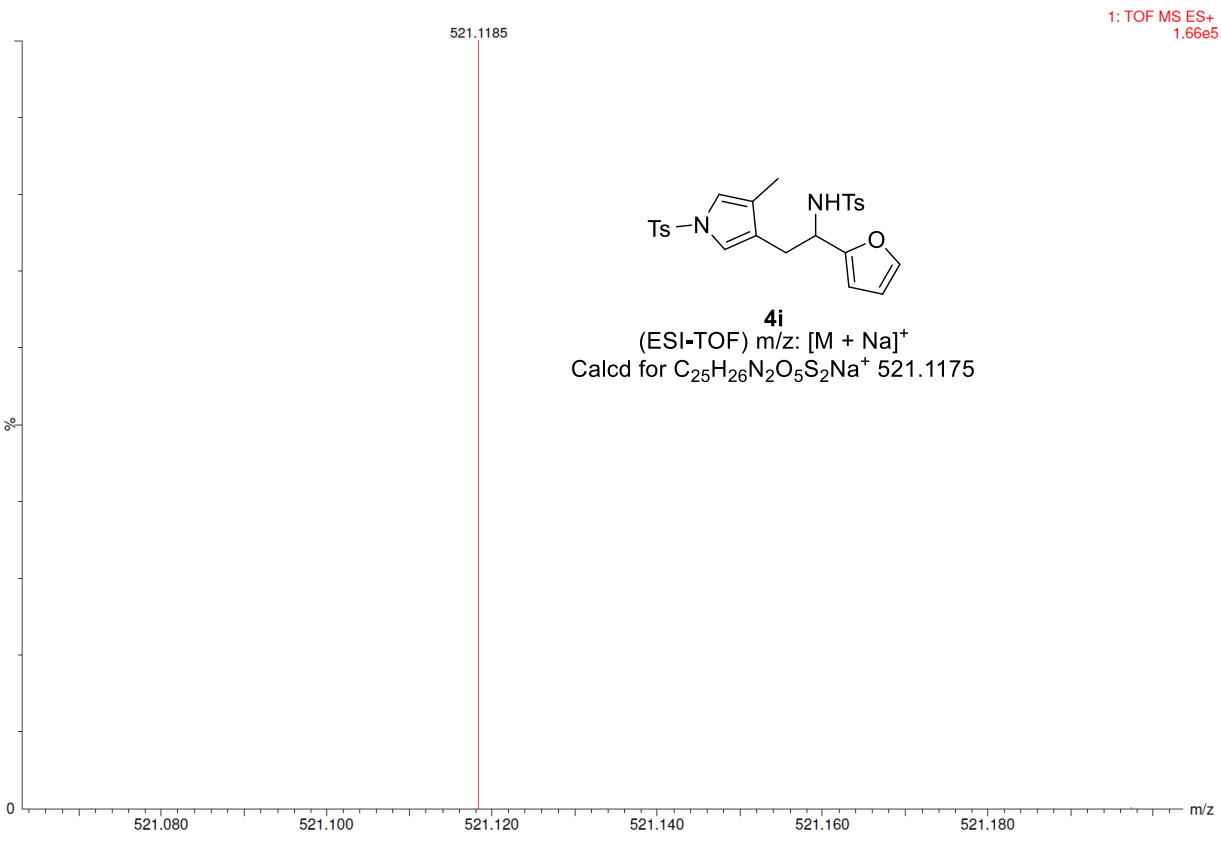
4i

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



4i

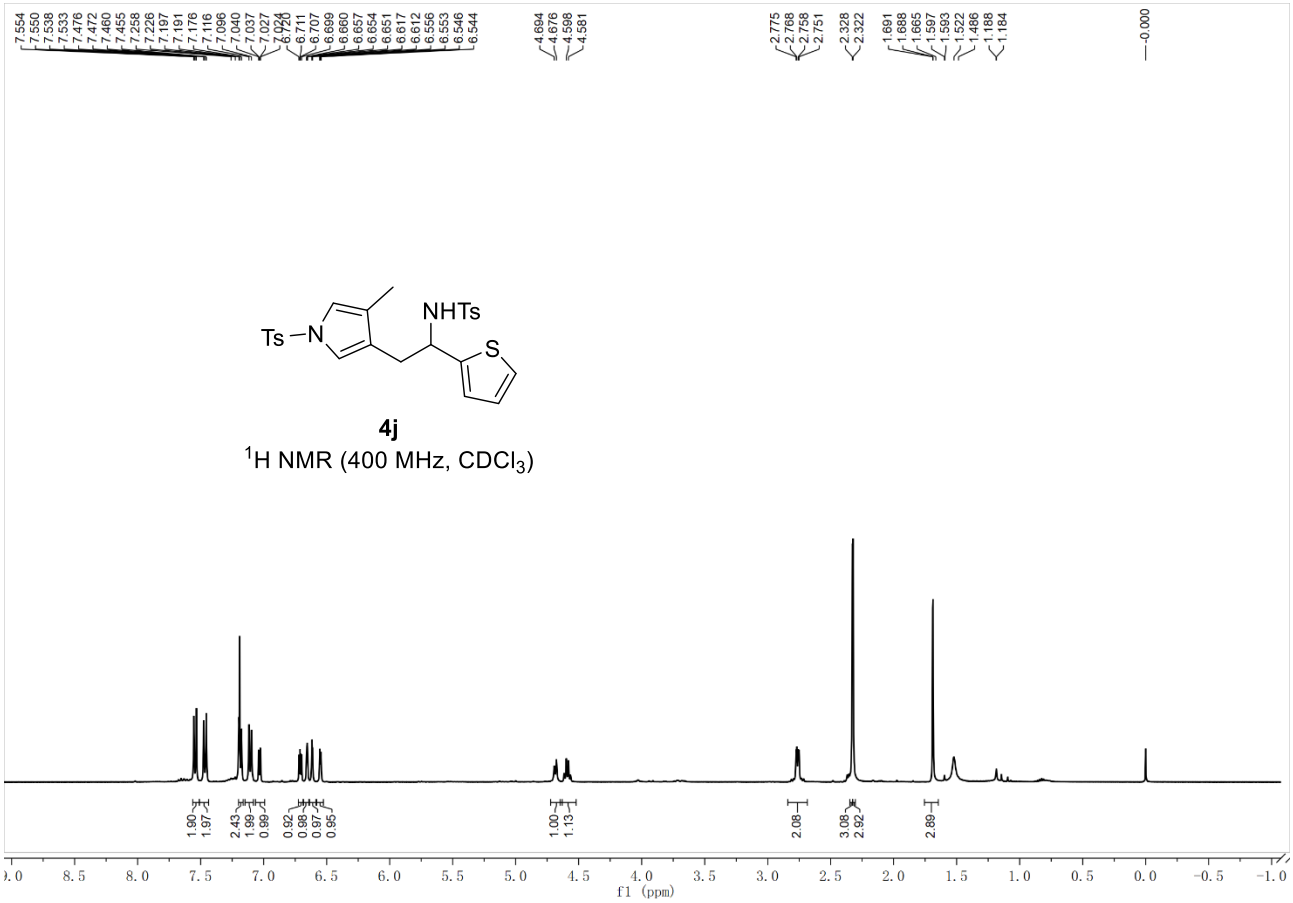
^{13}C NMR (100 MHz, $CDCl_3$)



4i

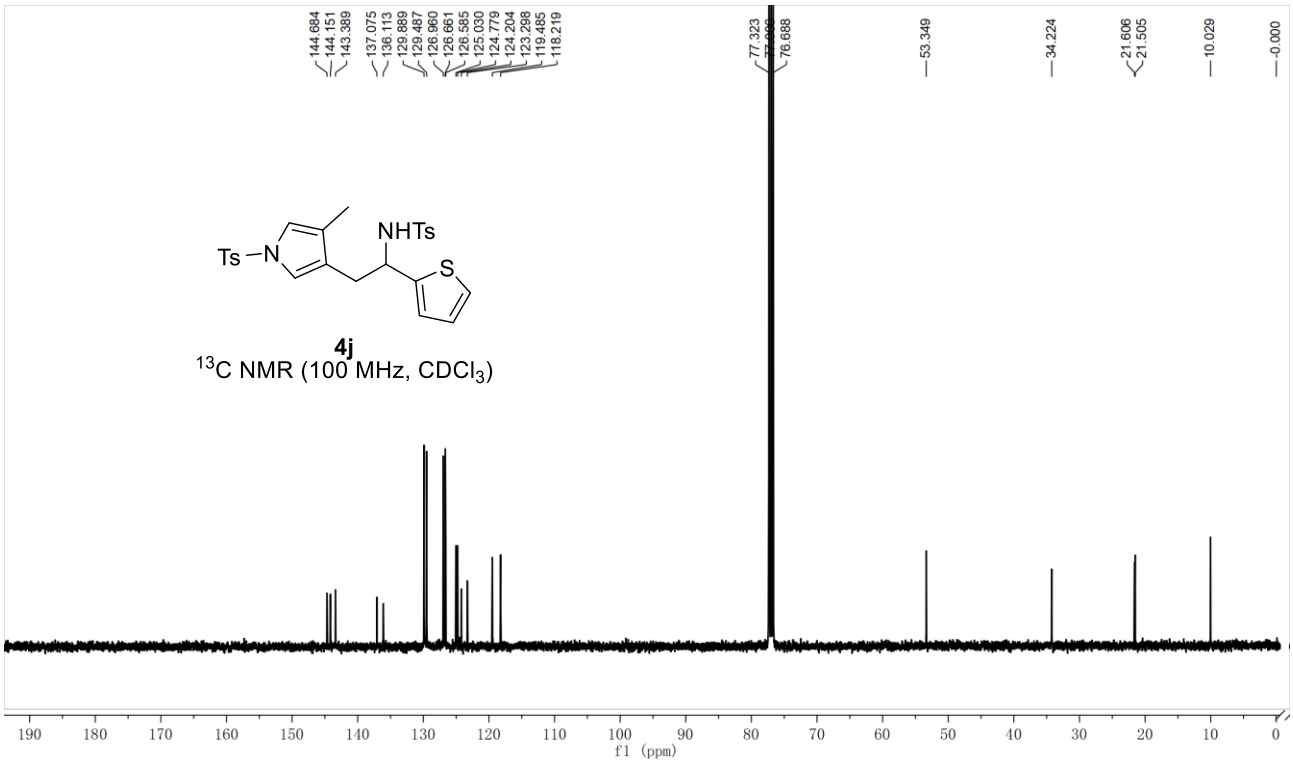
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{25}H_{26}N_2O_5S_2Na^+$ 521.1175



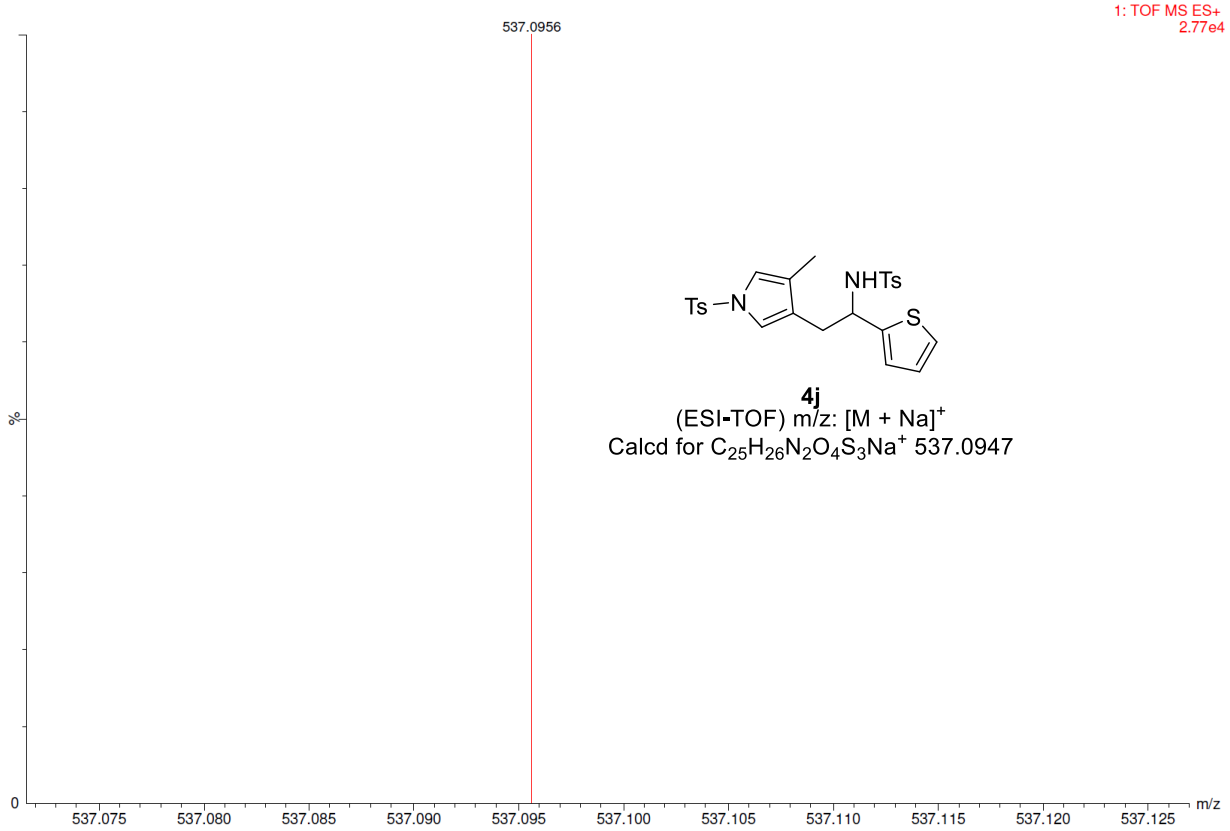
4j

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



4j

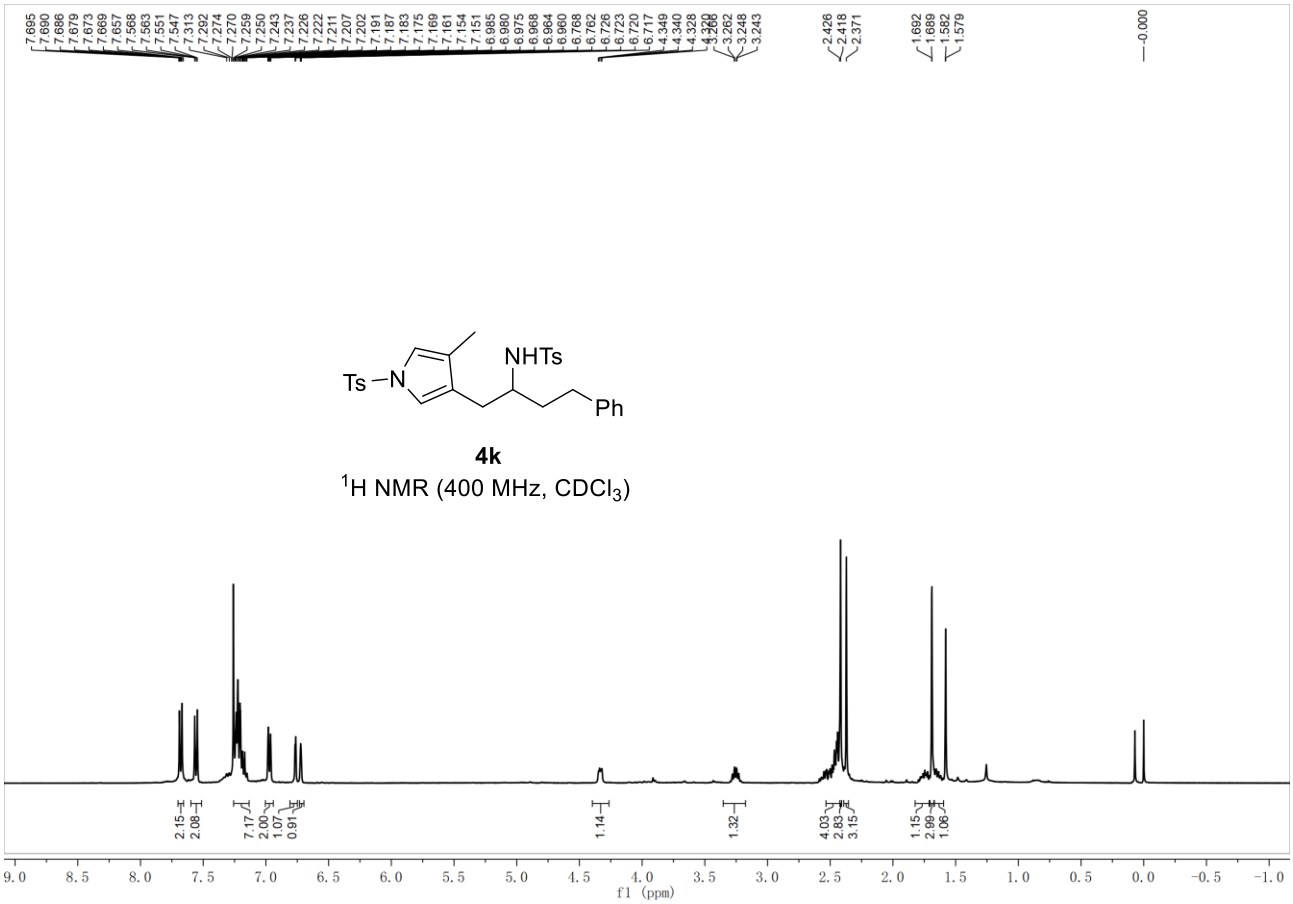
^{13}C NMR (100 MHz, $CDCl_3$)

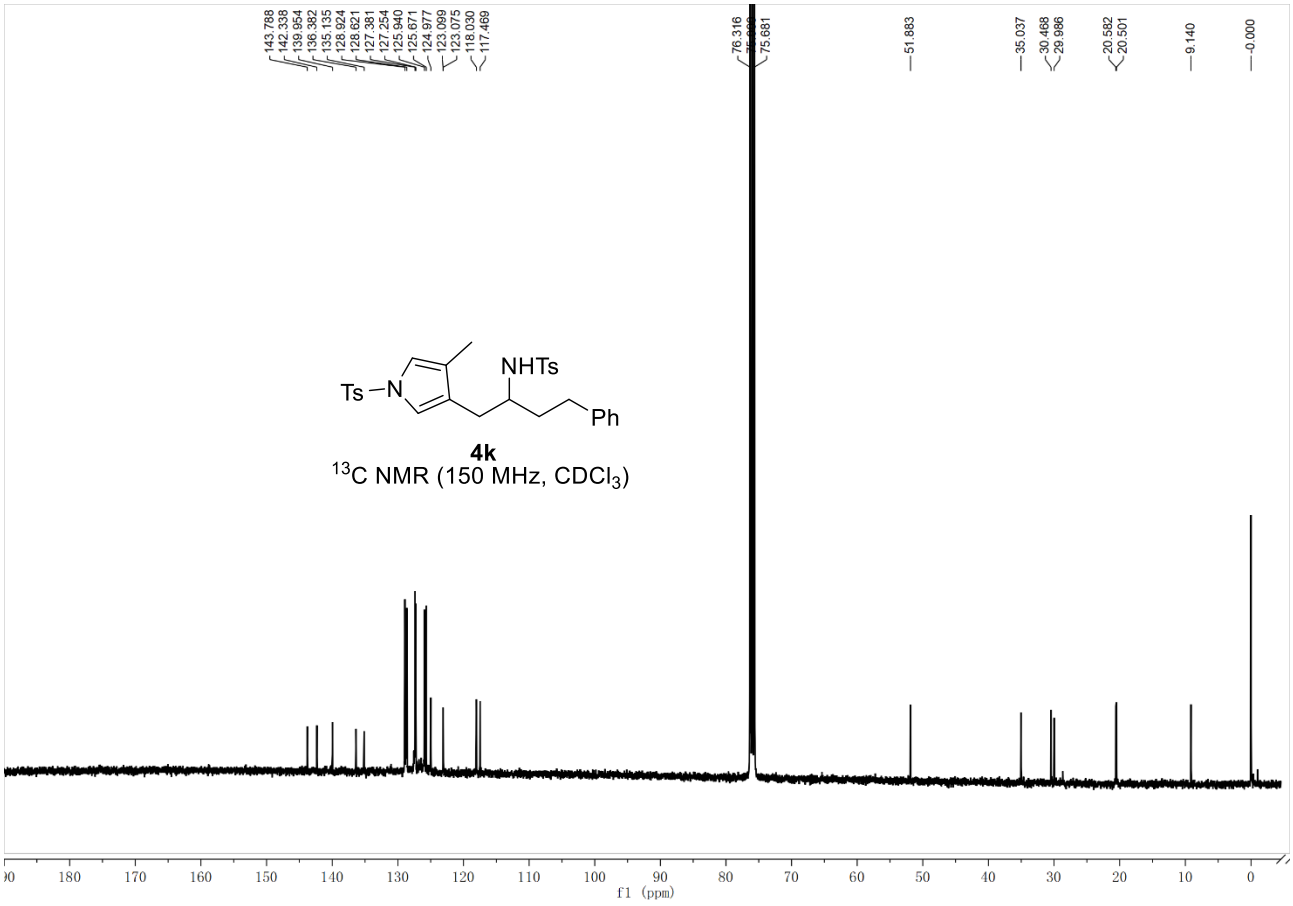


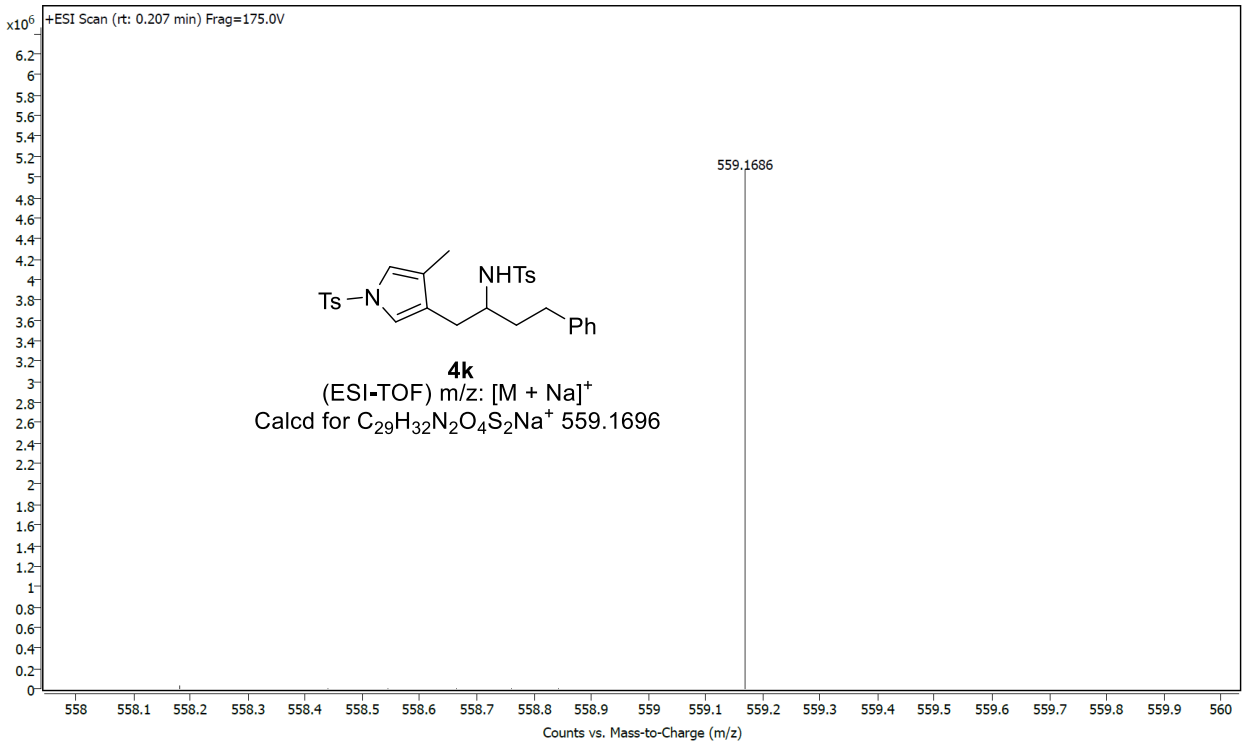
4j

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{25}H_{26}N_2O_4S_3Na^+$ 537.0947


NHTs
Ts
N
Ph
4k
1H NMR (400 MHz, CDCl3)
f1 (ppm)

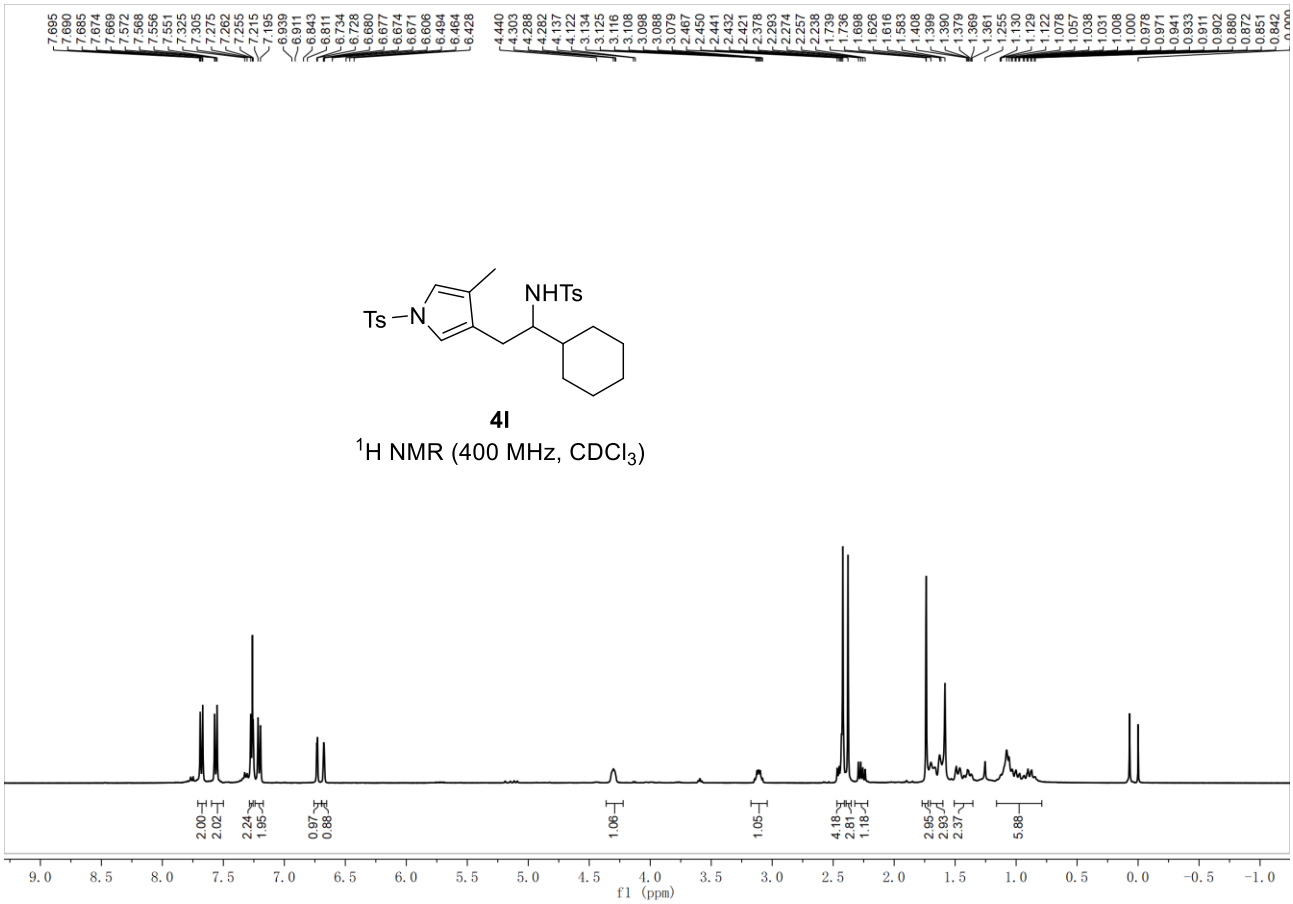

NHTs
Ts
N
Ph
4k
13C NMR (150 MHz, CDCl3)
f1 (ppm)



4k

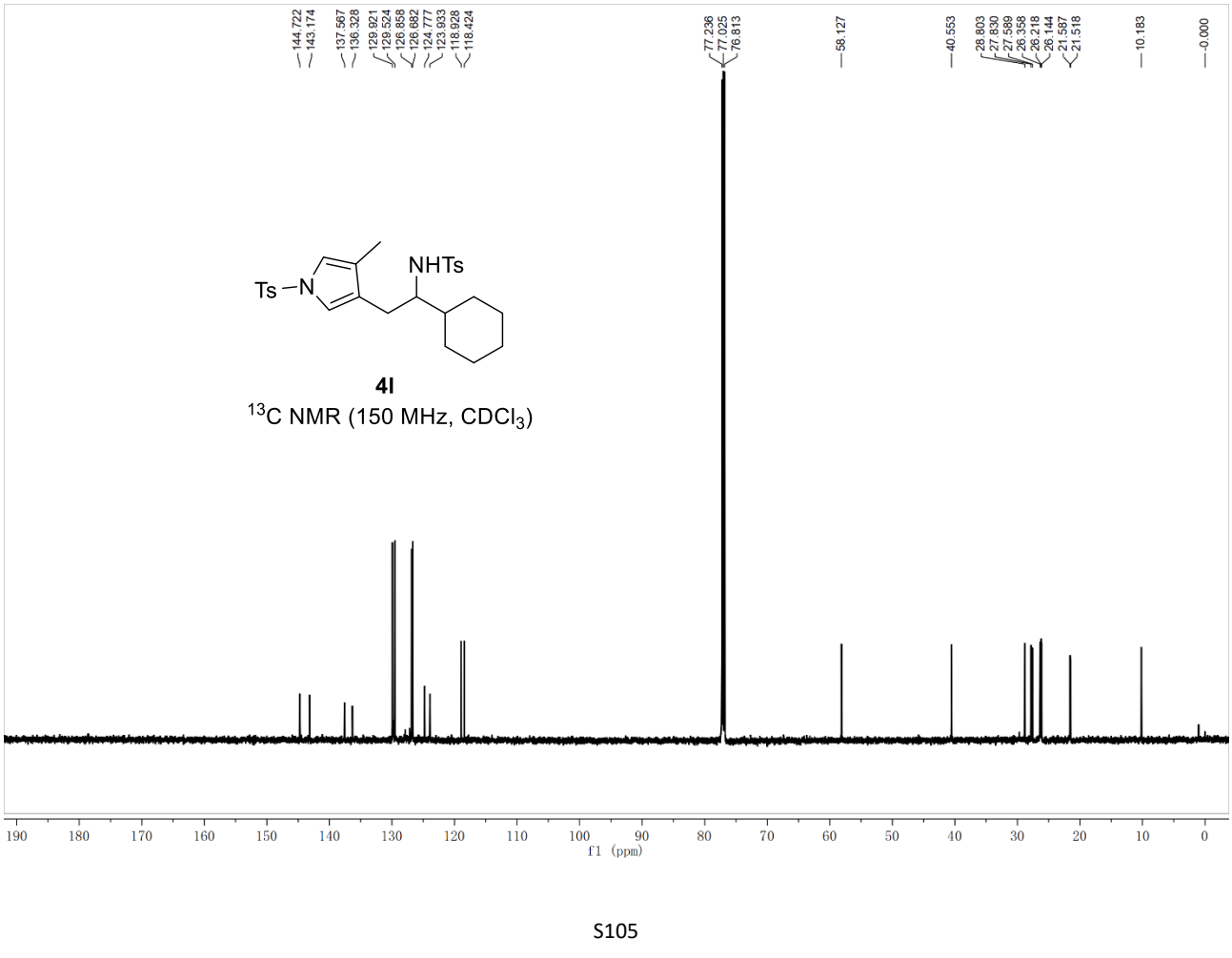
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{29}H_{32}N_2O_4S_2Na^+$ 559.1696



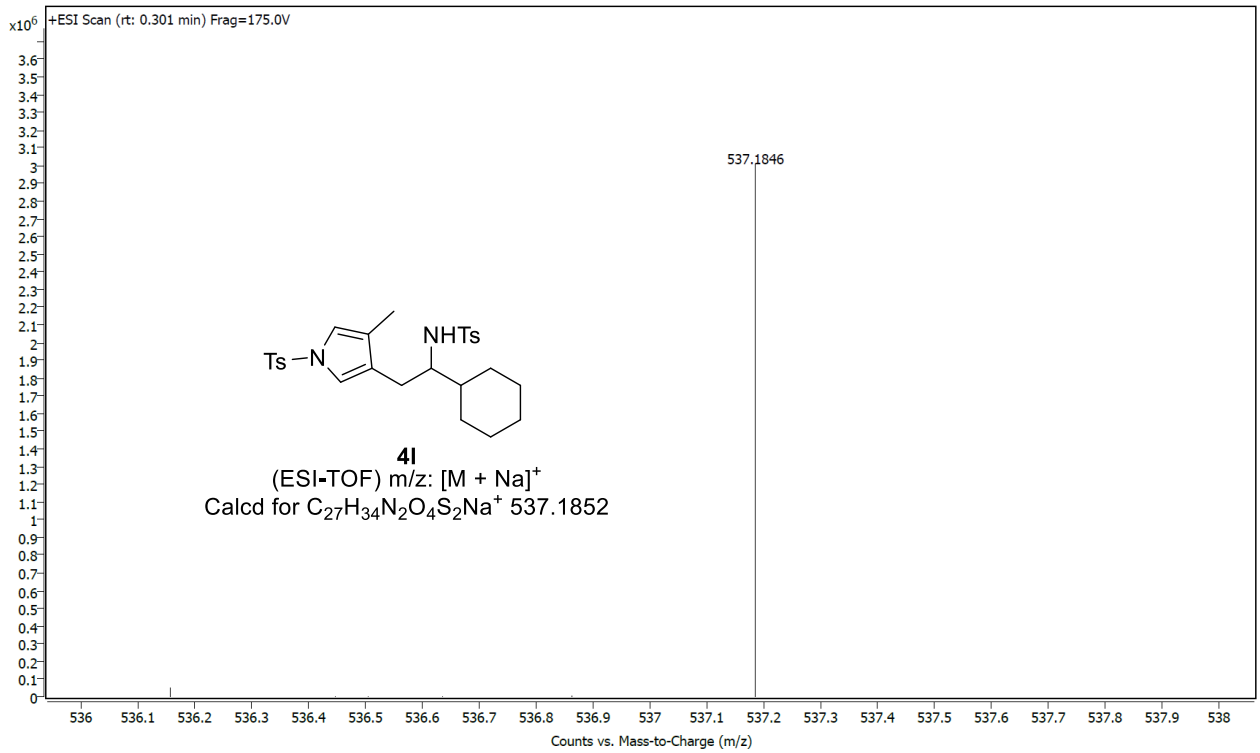
4l

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



4l

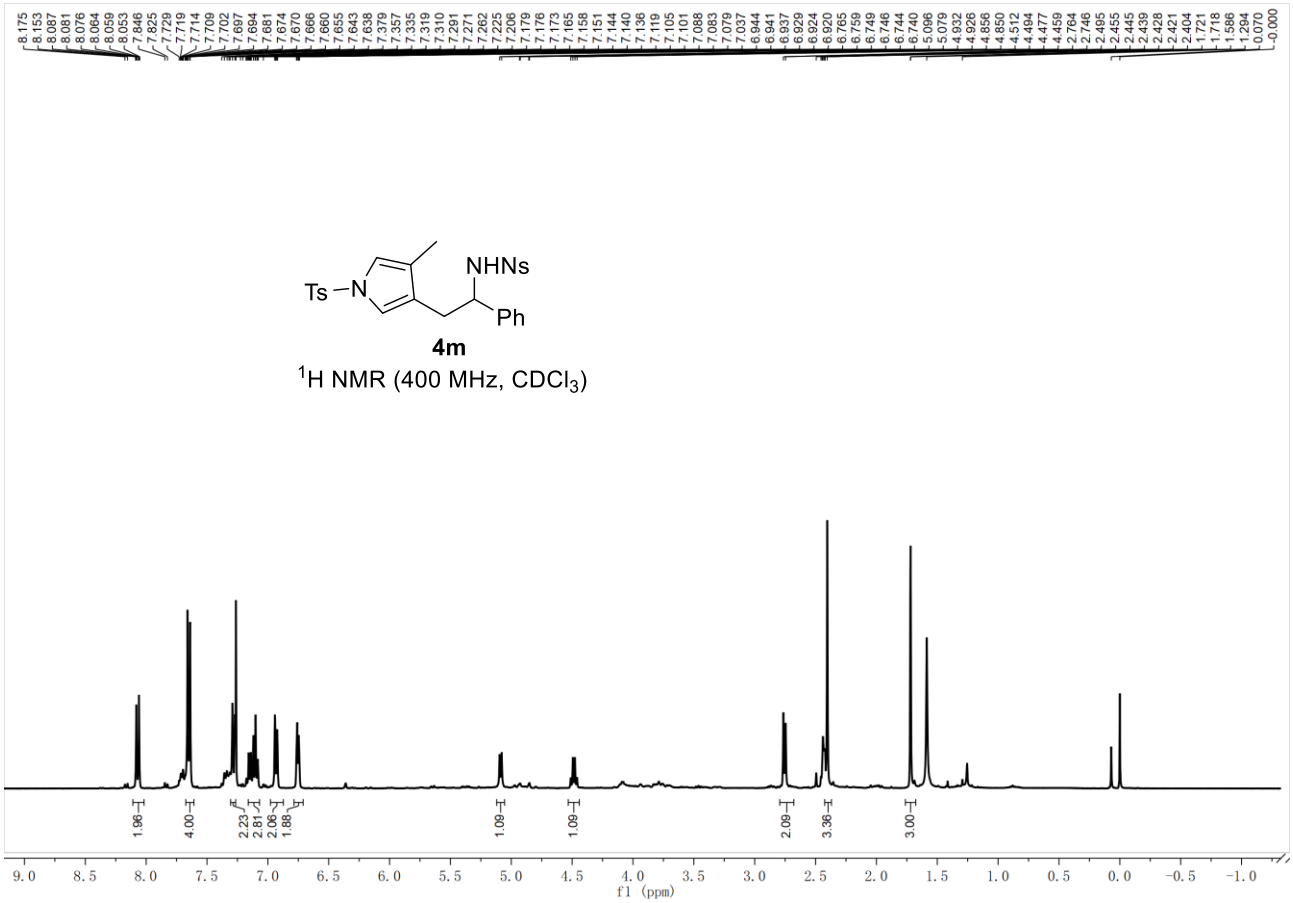
^{13}C NMR (150 MHz, $CDCl_3$)

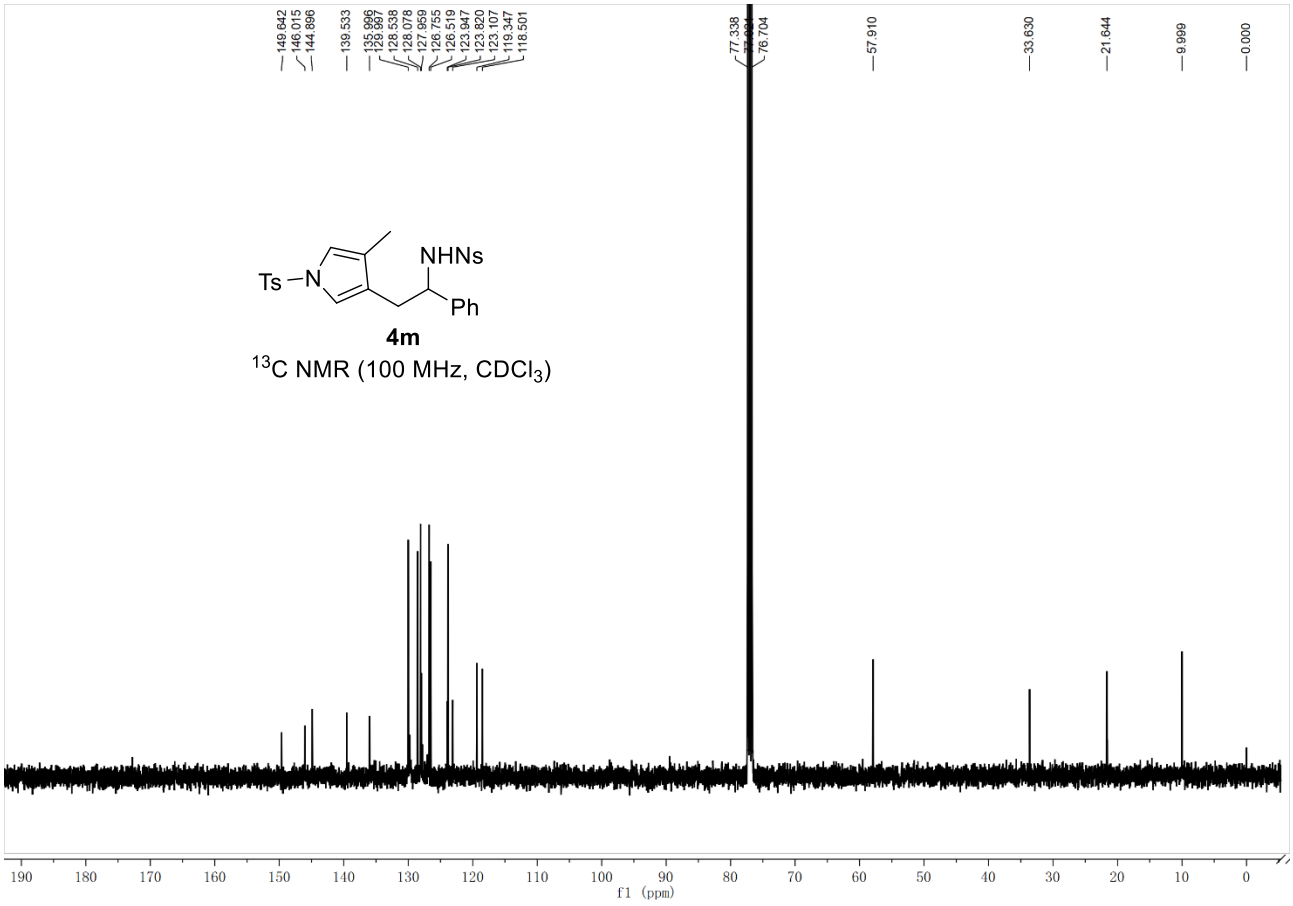


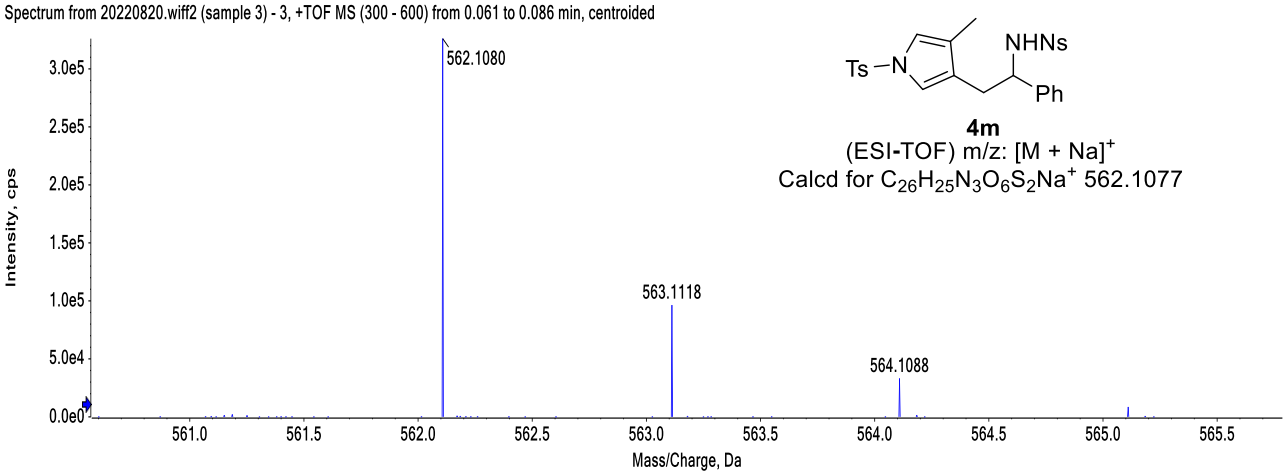
4l

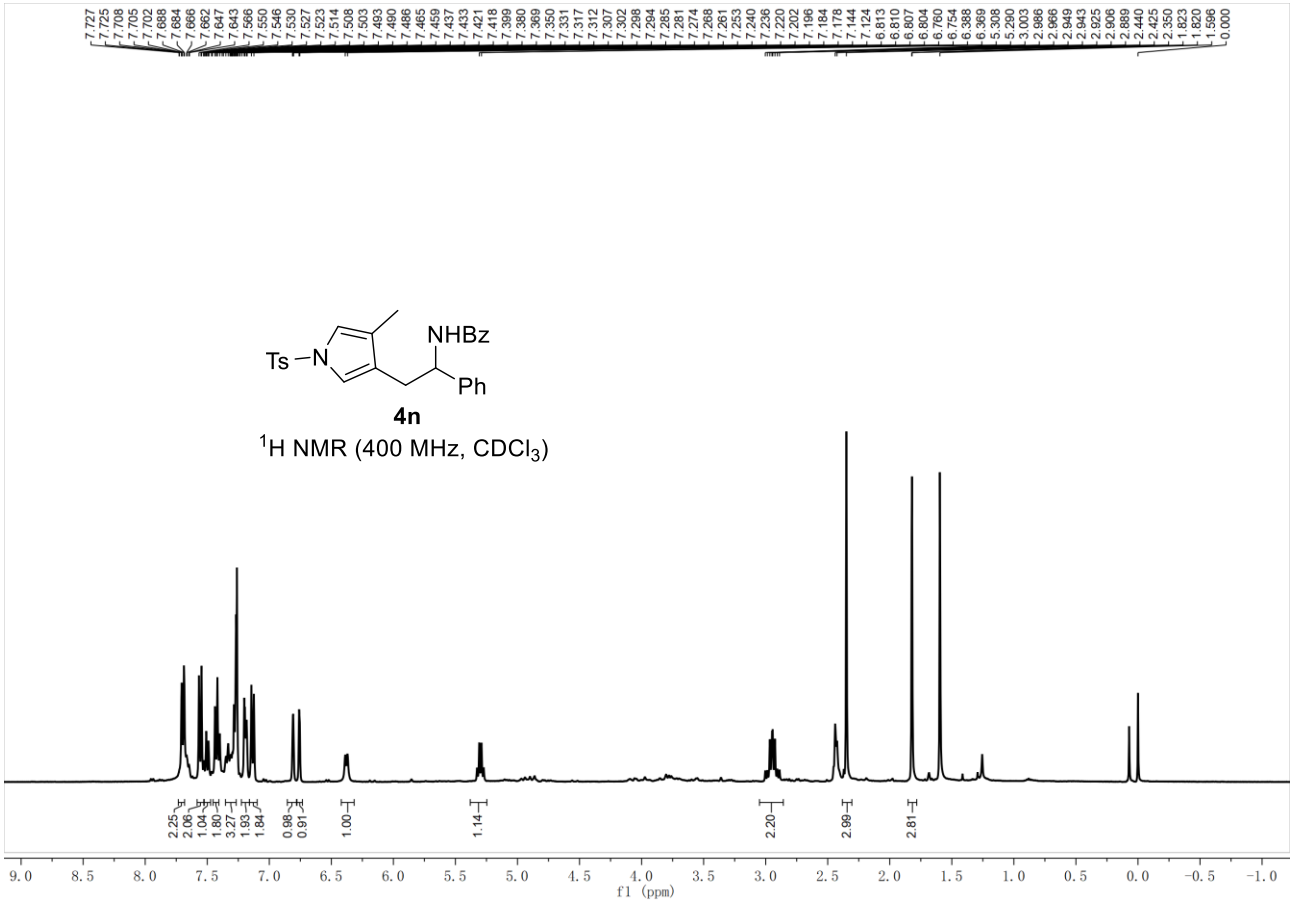
(ESI-TOF) m/z: $[M + Na]^+$

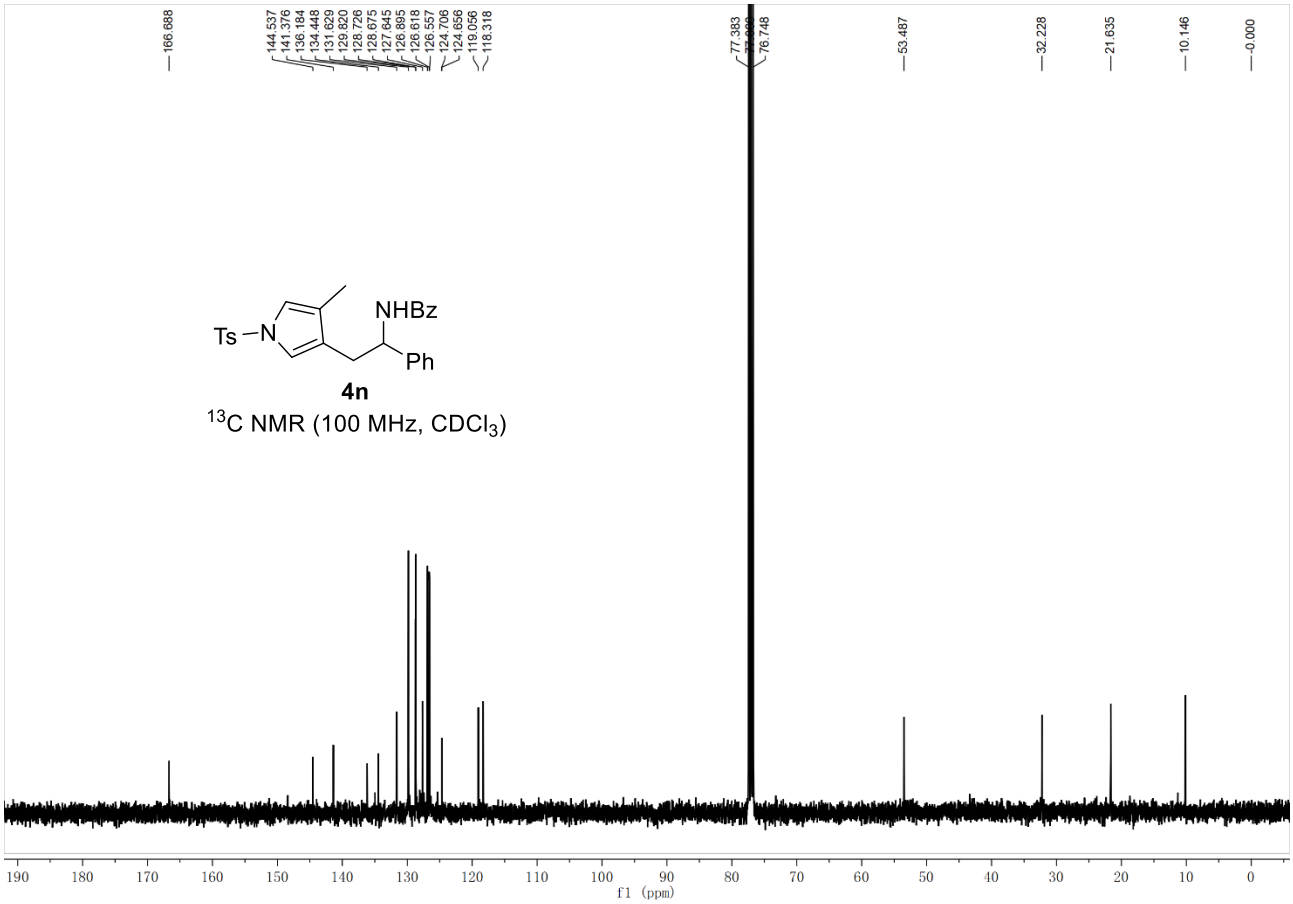
Calcd for $C_{27}H_{34}N_2O_4S_2Na^+$ 537.1852


NHNs
Ts
N
Ph
4m
1H NMR (400 MHz, CDCl3)
f1 (ppm)

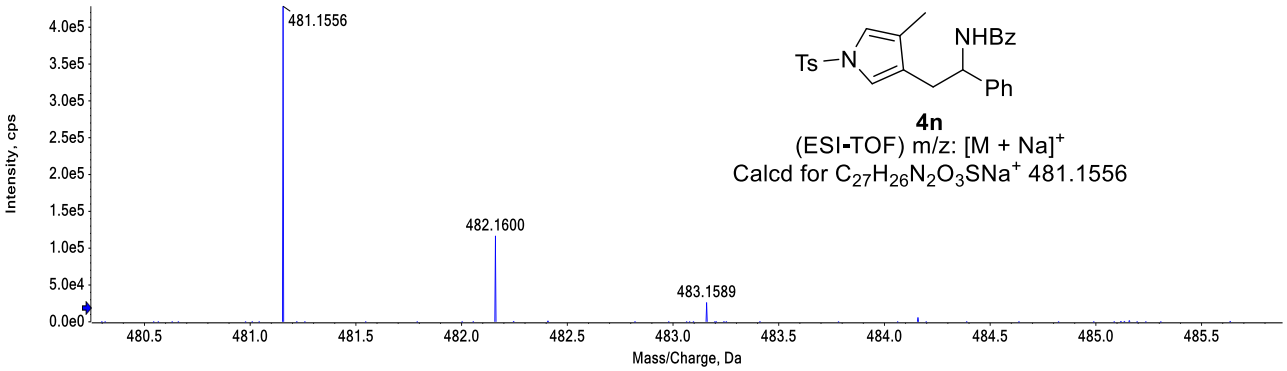

NHNs
Ts
N
Ph
4m
13C NMR (100 MHz, CDCl3)
f1 (ppm)


Spectrum from 20220820.wiff2 (sample 3) - 3, +TOF MS (300 - 600) from 0.061 to 0.086 min, centroided
562.1080
563.1118
564.1088
Intensity, cps
Mass/Charge, Da
Ts
N
NHNs
Ph
4m
(ESI-TOF) m/z: [M + Na]+
Calcd for C26H25N3O6S2Na+ 562.1077


NHBz
Ts
N
Ph
4n
1H NMR (400 MHz, CDCl3)
f1 (ppm)


NHBz
Ts
N
Ph
4n
13C NMR (100 MHz, CDCl3)
f1 (ppm)

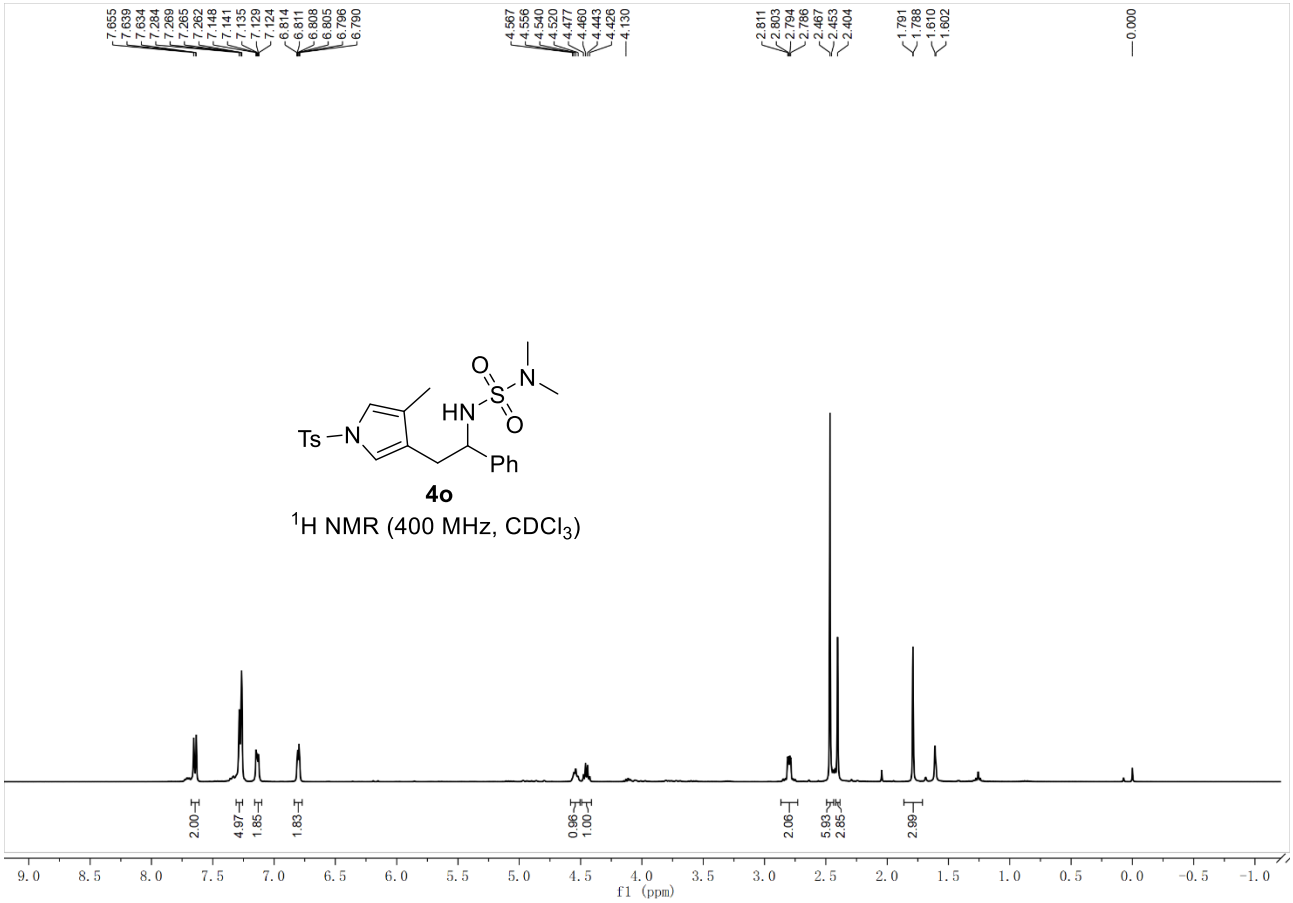
Spectrum from 20220820.wiff2 (sample 2) - 2, +TOF MS (300 - 600) from 0.061 to 0.086 min, Recalibrated, centroided



4n

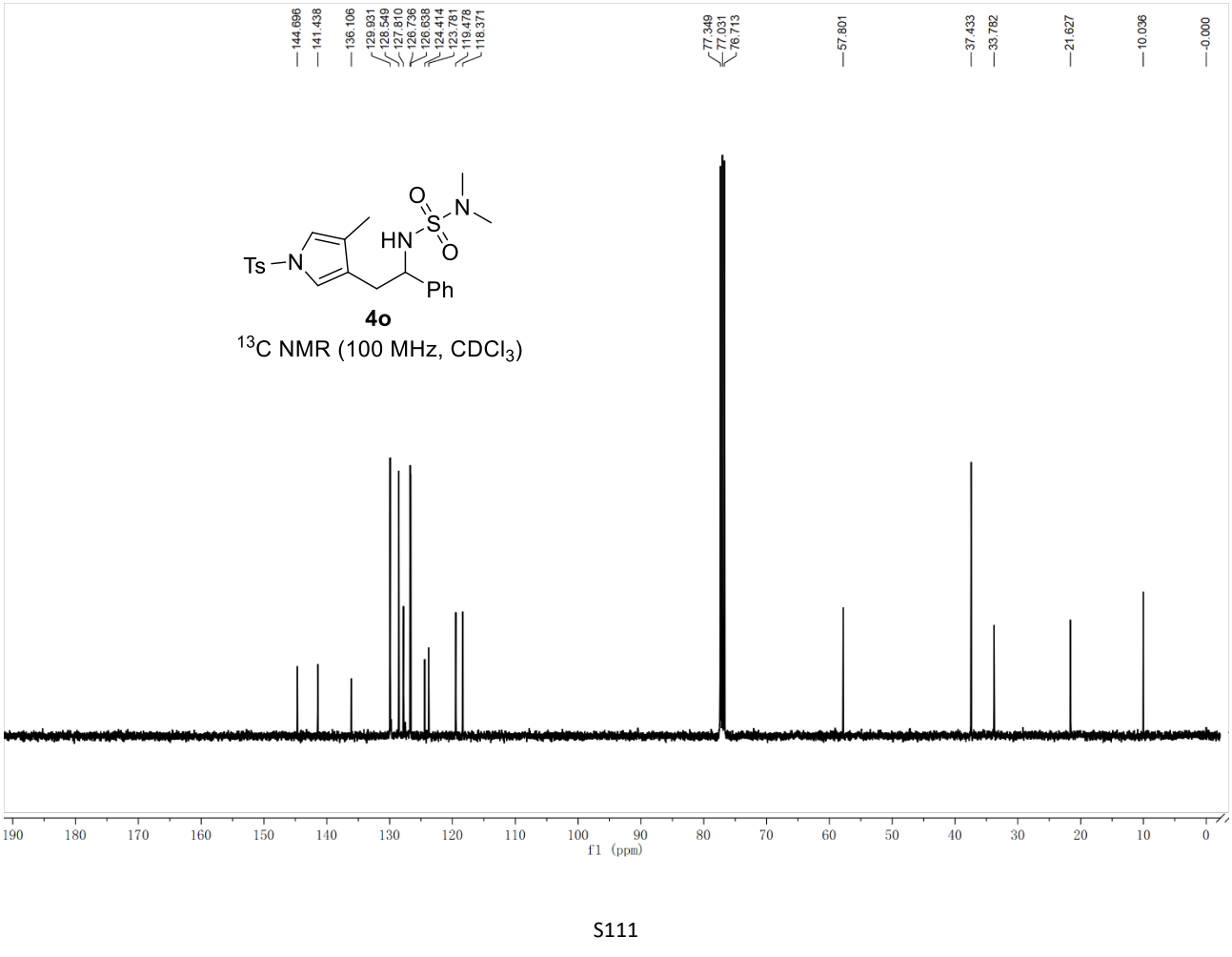
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{27}H_{26}N_2O_3SNa^+$ 481.1556



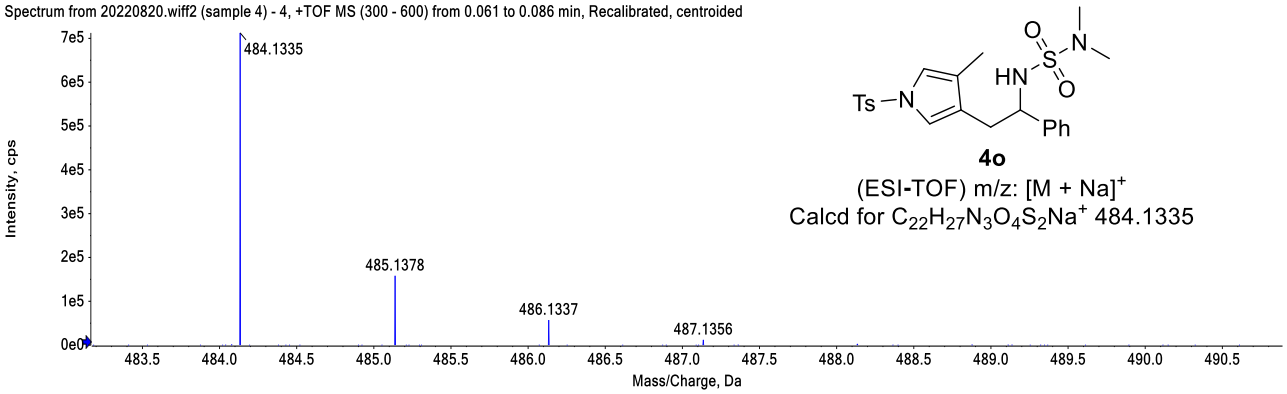
4o

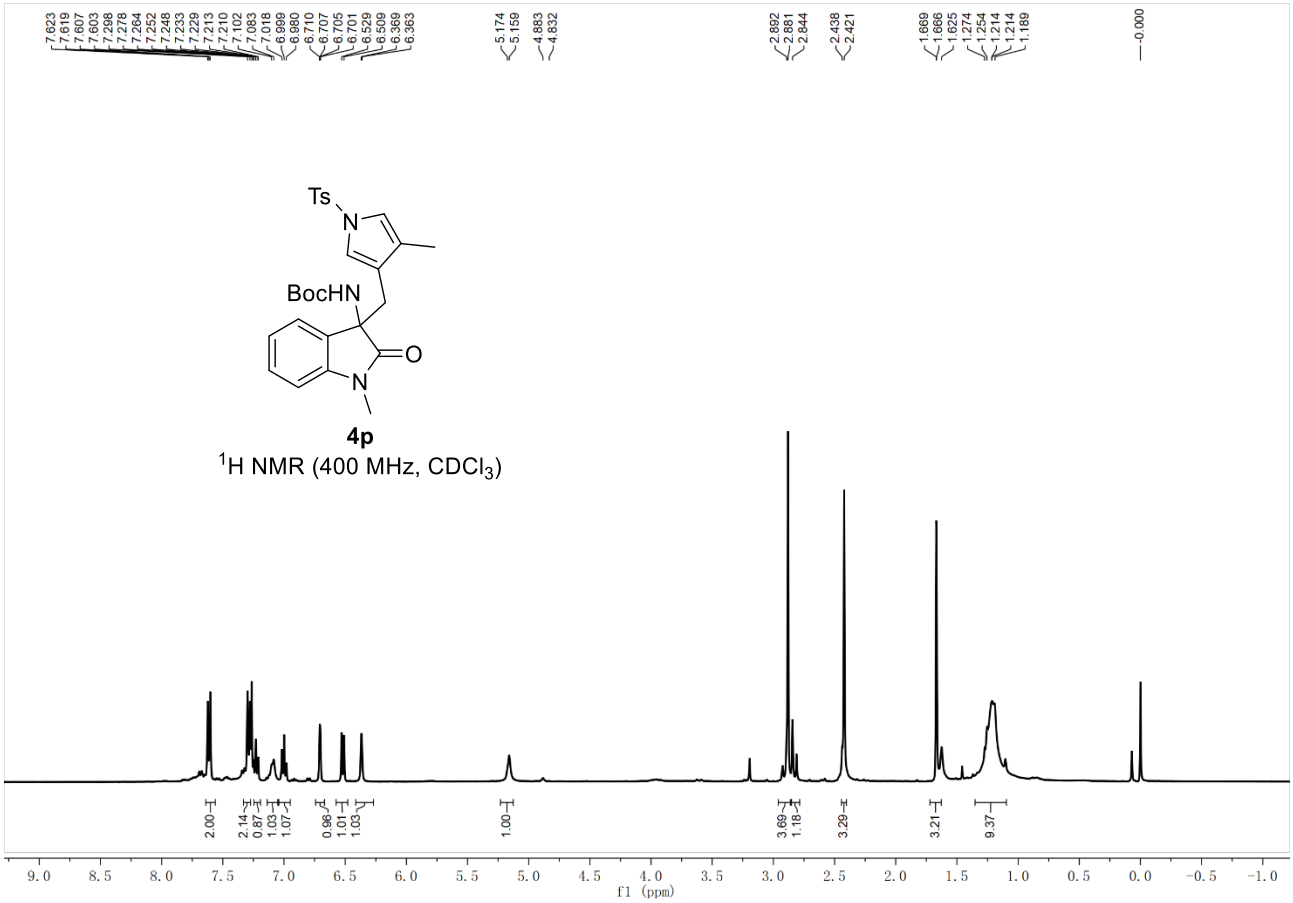
^{1}H NMR (400 MHz, $CDCl_3$)

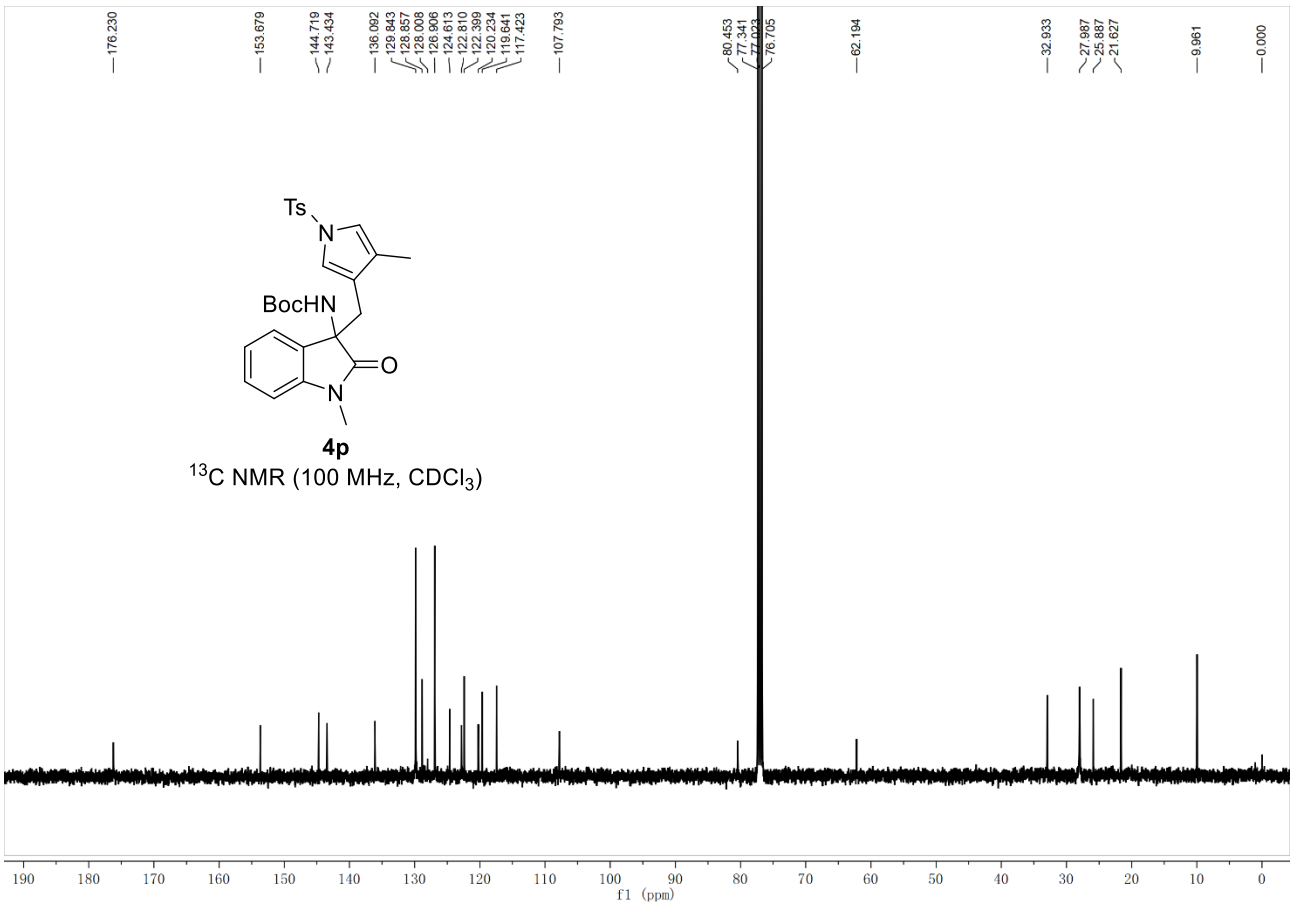


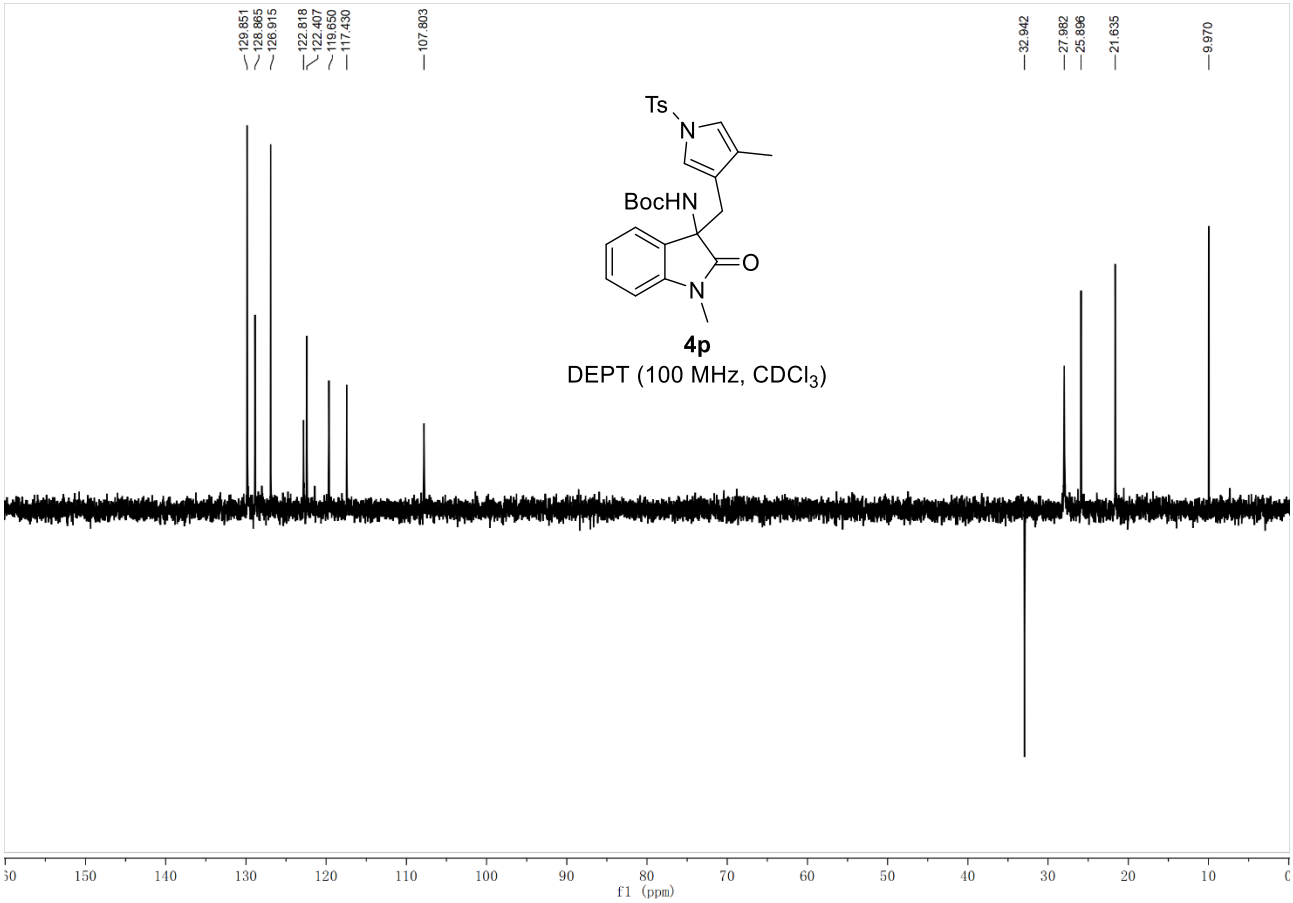
4o

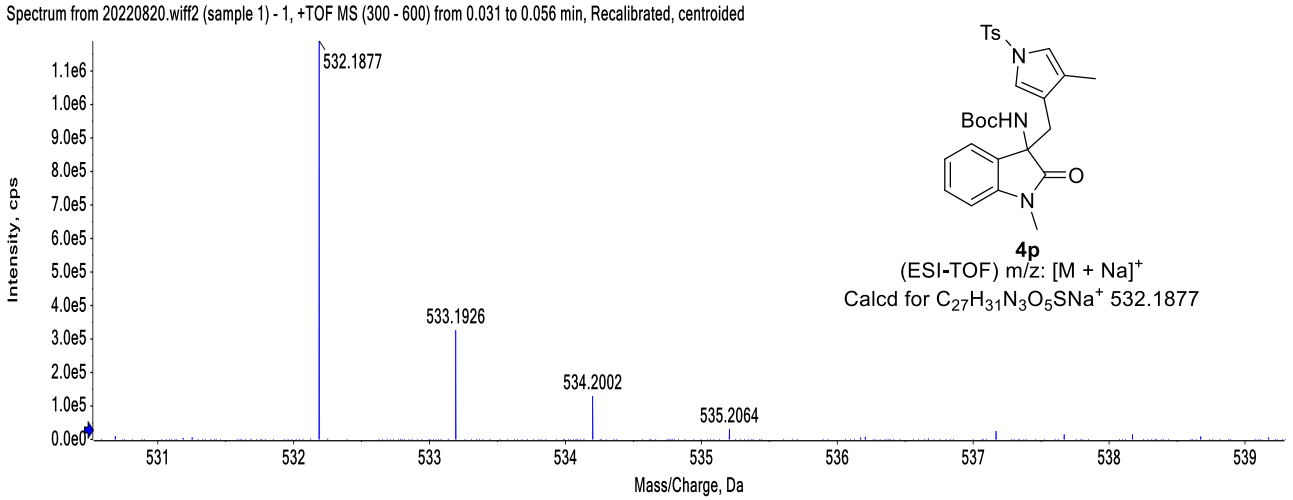
^{13}C NMR (100 MHz, $CDCl_3$)

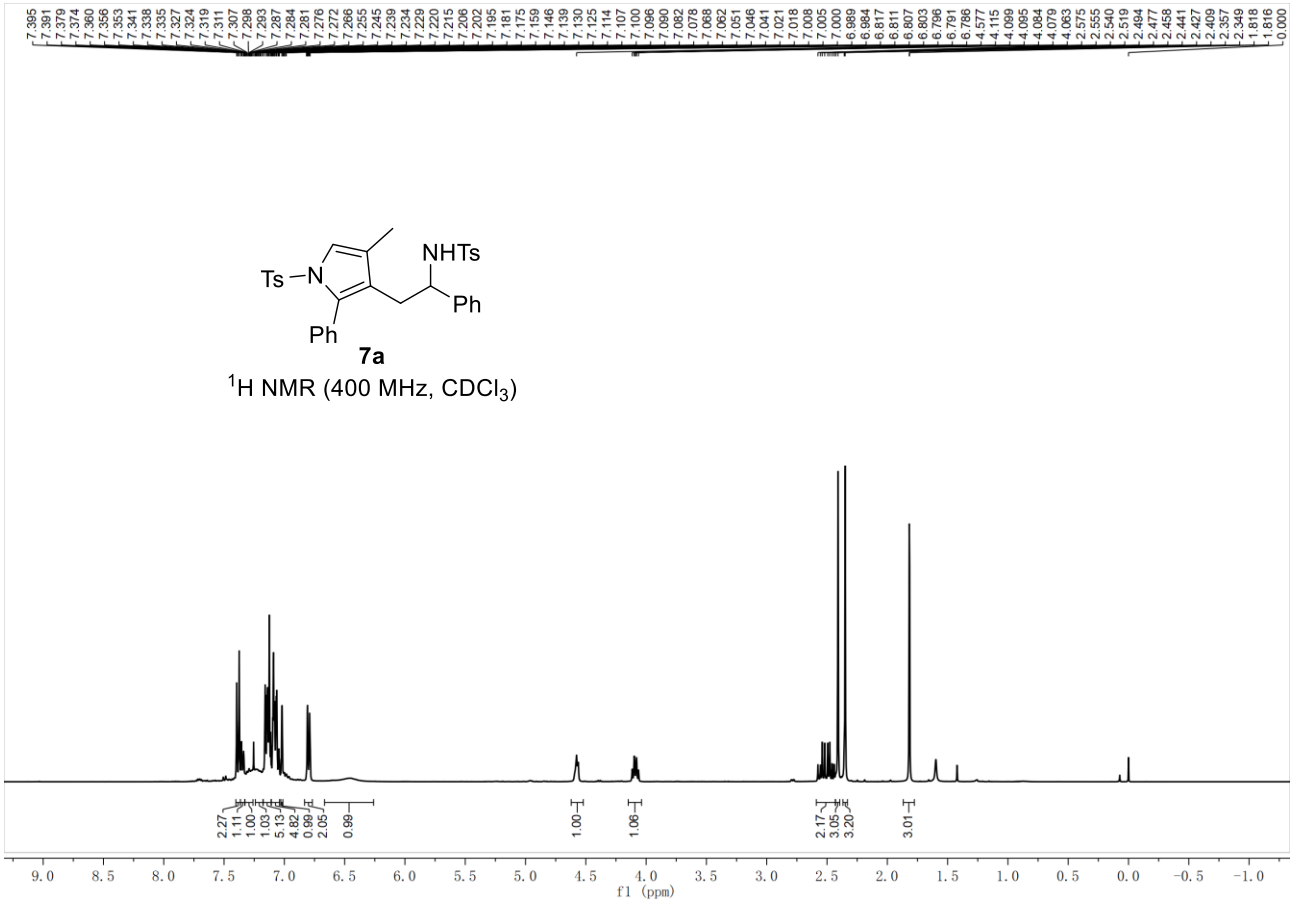

Spectrum from 20220820.wiff2 (sample 4) - 4, +TOF MS (300 - 600) from 0.061 to 0.086 min, Recalibrated, centroided
Intensity, cps
7e5
6e5
5e5
4e5
3e5
2e5
1e5
0e0
484.1335
485.1378
486.1337
487.1356
483.5
484.0
484.5
485.0
485.5
486.0
486.5
487.0
487.5
488.0
488.5
489.0
489.5
490.0
490.5
Mass/Charge, Da
O
N
S
HN
O
Ts
N
Ph
4o
(ESI-TOF) m/z: [M + Na]+
Calcd for C22H27N3O4S2Na+ 484.1335


Ts
N
BocHN
O
N
4p
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Ts
N
BocHN
O
N
4p
13C NMR (100 MHz, CDCl3)
f1 (ppm)

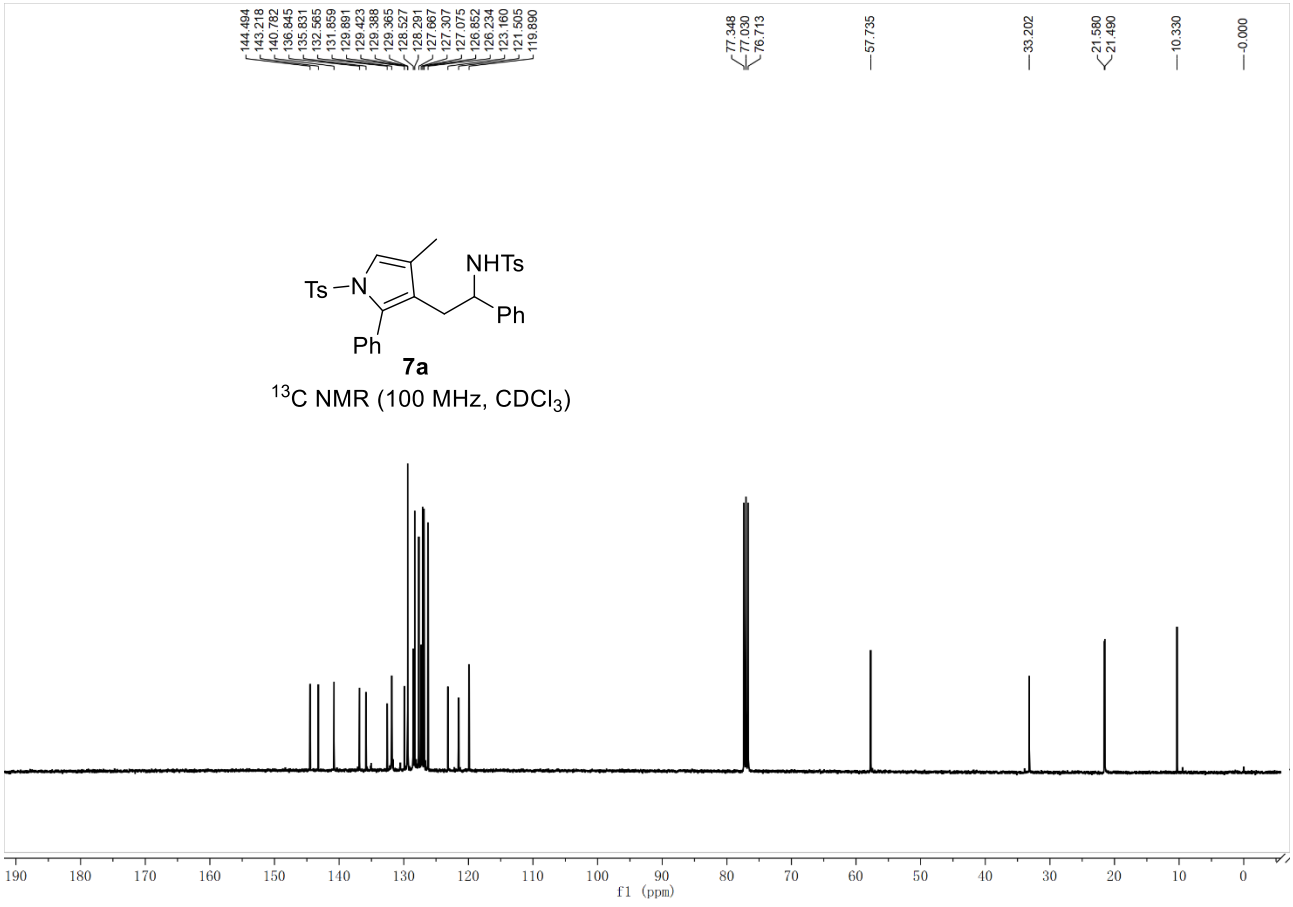

129.851
128.865
128.915
122.818
122.407
119.650
117.430
107.803
32.942
27.982
25.896
21.635
9.970
Ts
N
BocHN
O
N
4p
DEPT (100 MHz, CDCl3)
f1 (ppm)


Spectrum from 20220820.wiff2 (sample 1) - 1, +TOF MS (300 - 600) from 0.031 to 0.056 min, Recalibrated, centroided
Intensity, cps
Mass/Charge, Da
532.1877
533.1926
534.2002
535.2064
Ts
N
BocHN
O
N
4p
(ESI-TOF) m/z: [M + Na]+
Calcd for C27H31N3O5SNa+ 532.1877



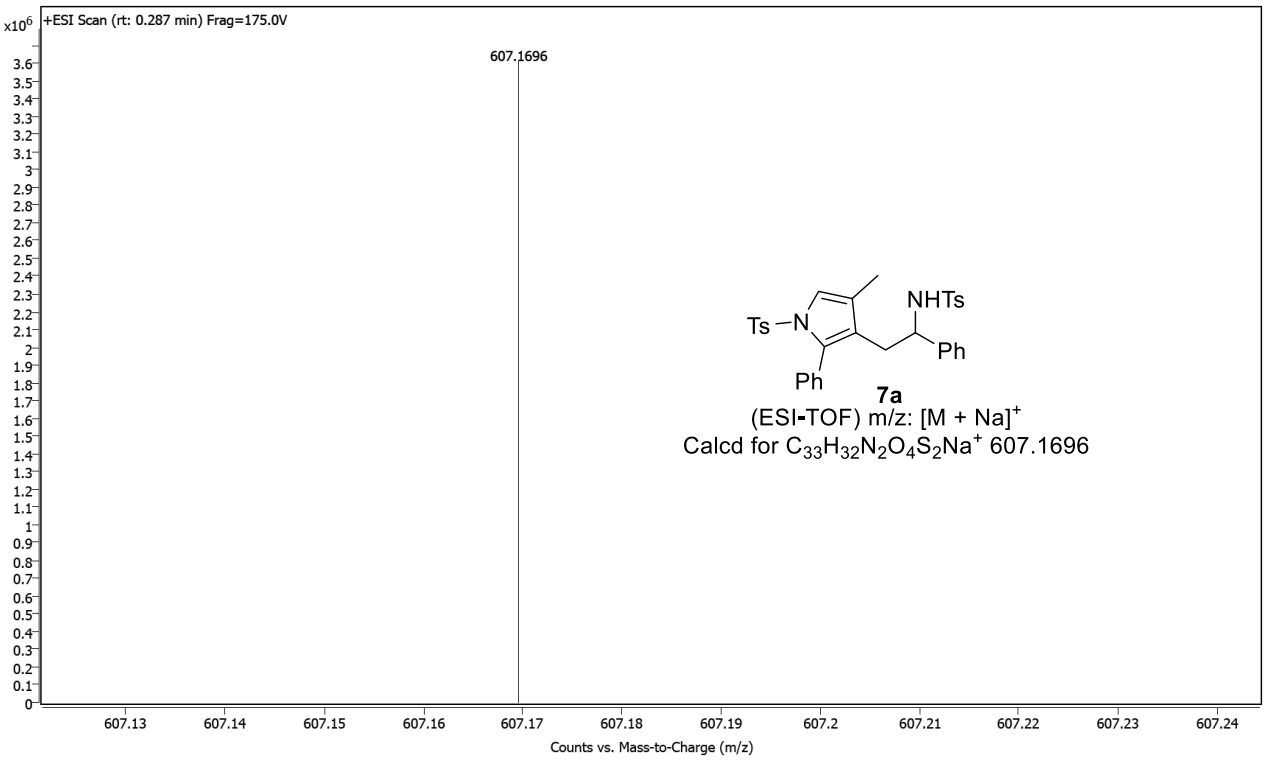
7a

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



7a

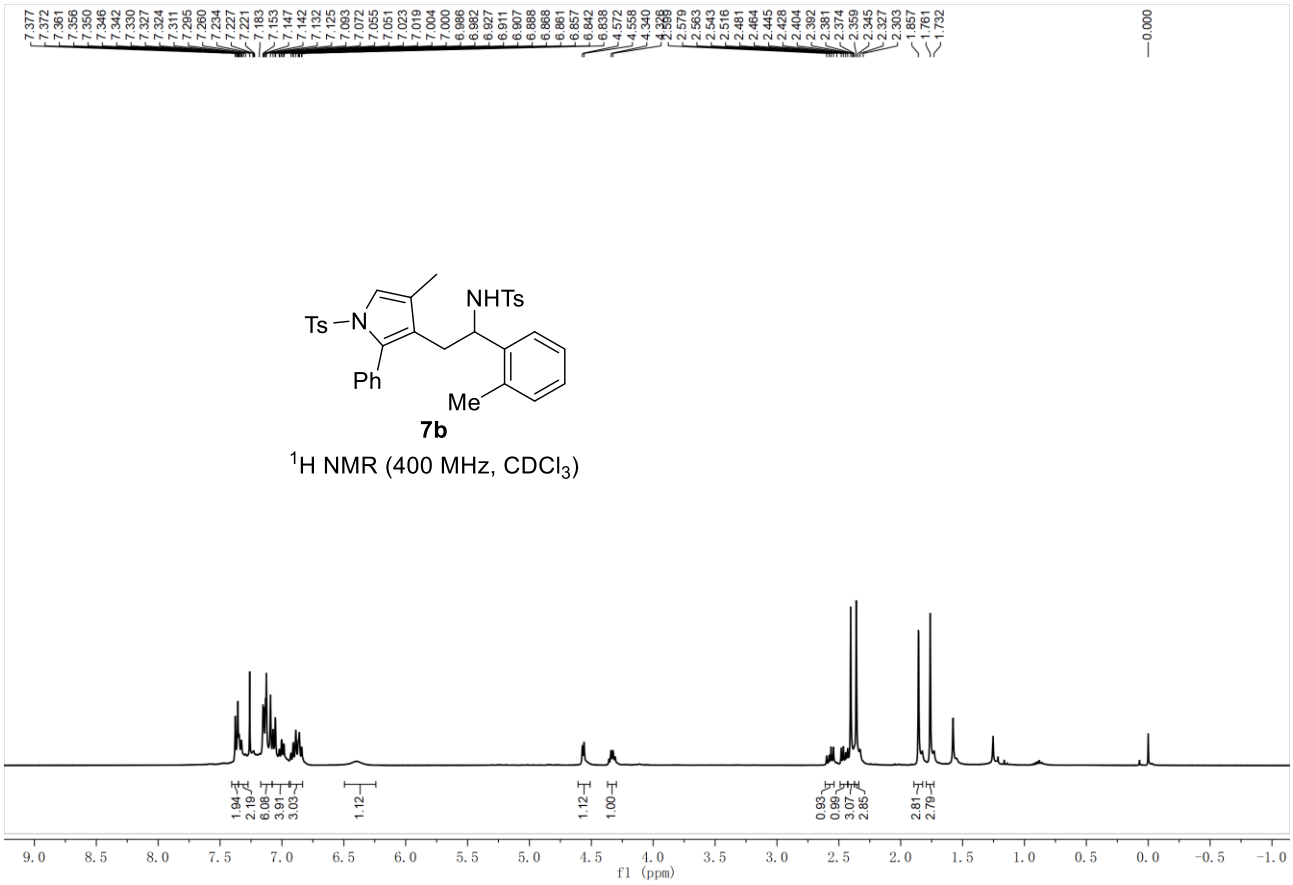
^{13}C NMR (100 MHz, $CDCl_3$)

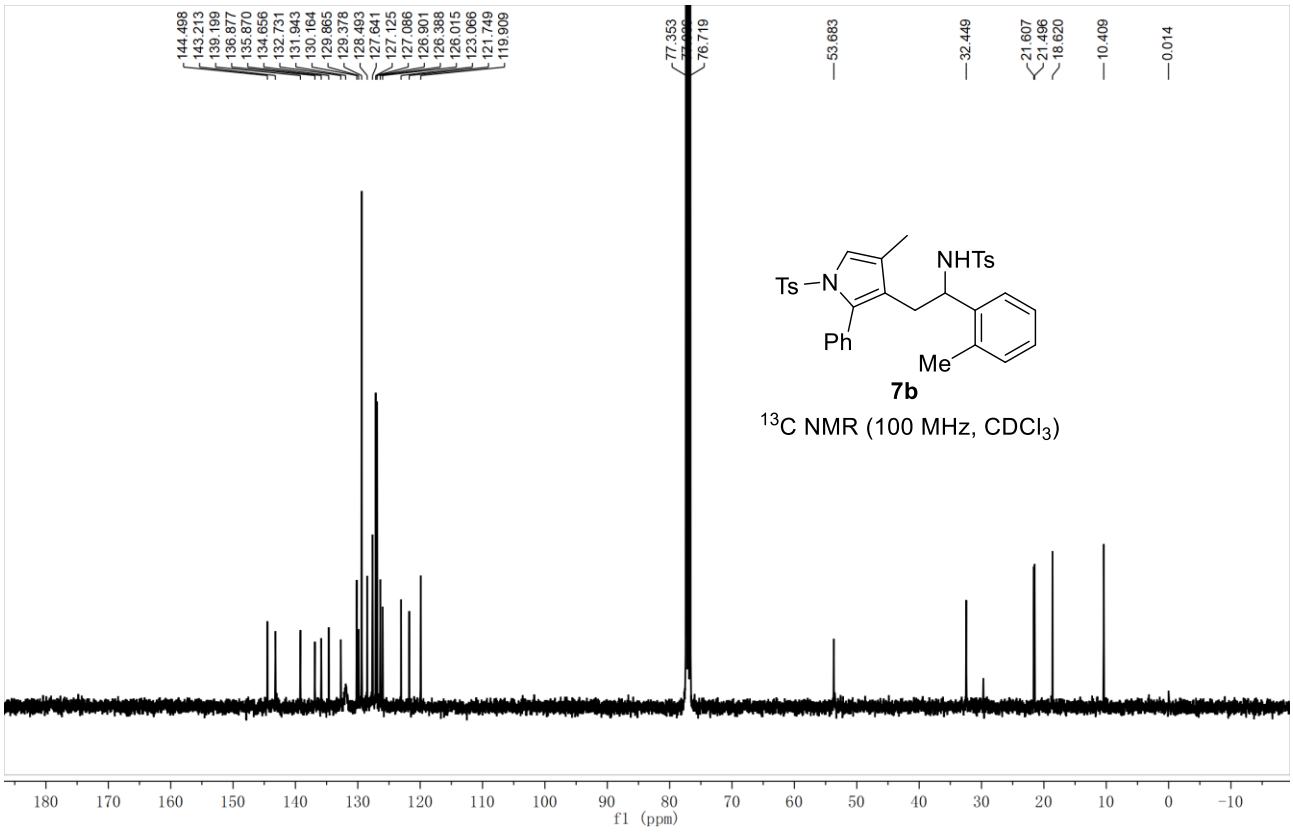


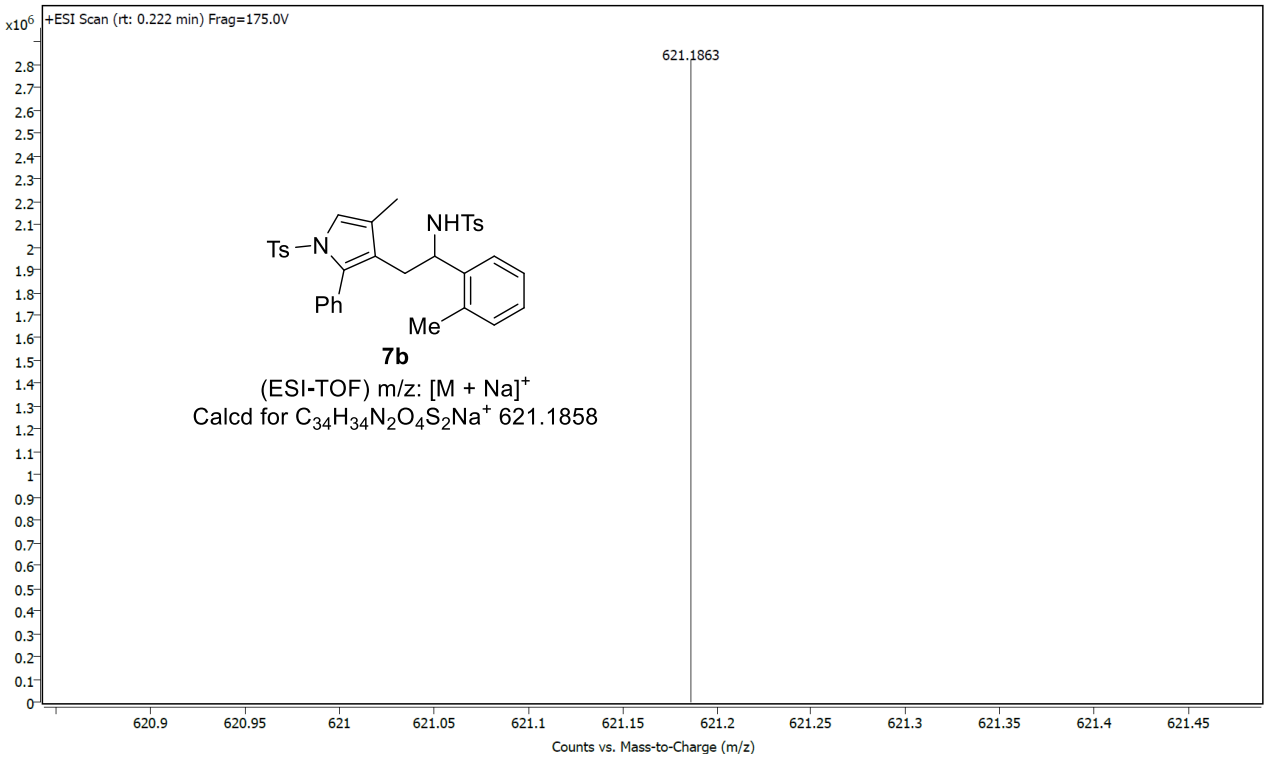
7a

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{33}H_{32}N_2O_4S_2Na^+$ 607.1696


NHTs
Ts
N
Ph
Me
7b
1H NMR (400 MHz, CDCl3)
f1 (ppm)

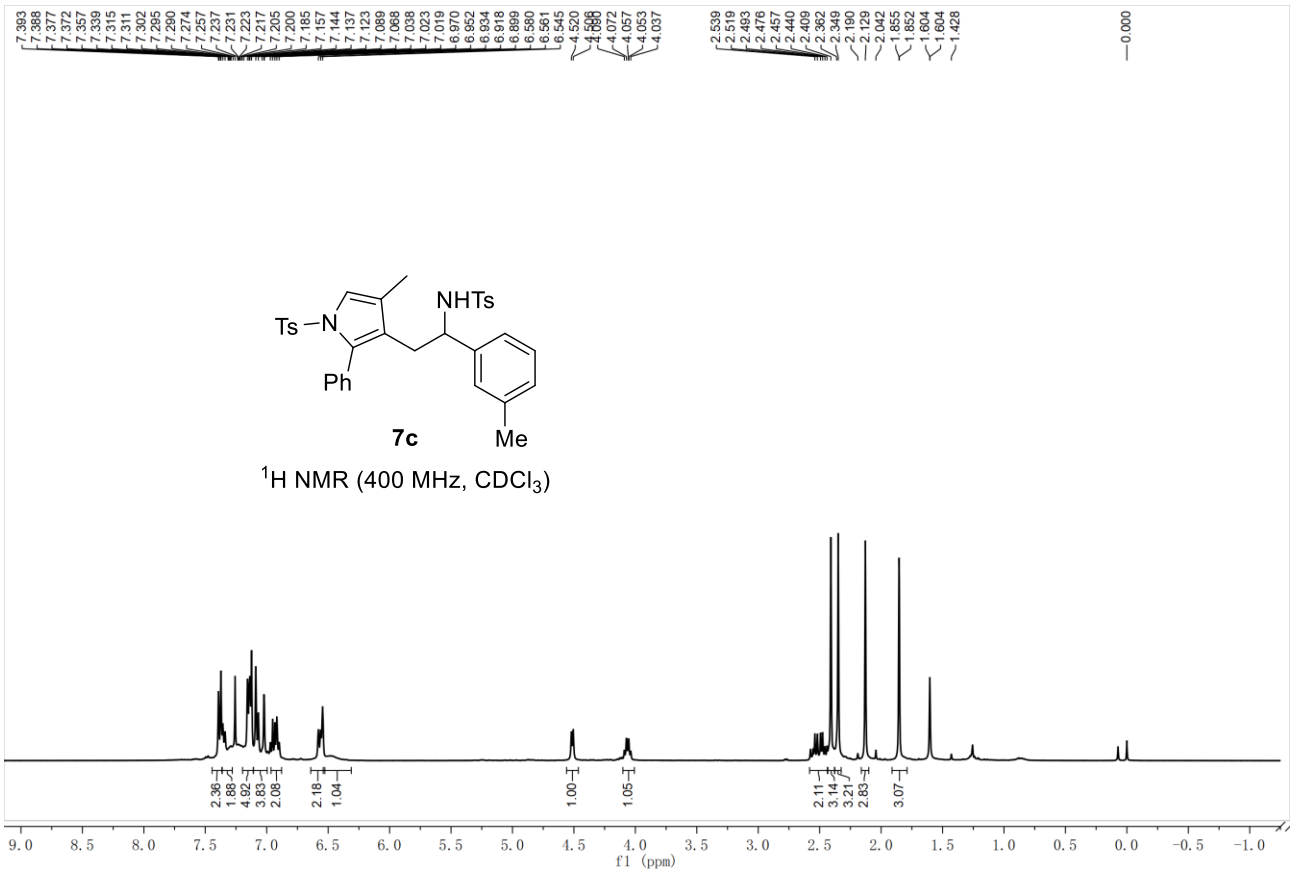

NHTs
Ts
N
Ph
Me
7b
13C NMR (100 MHz, CDCl3)
f1 (ppm)



7b

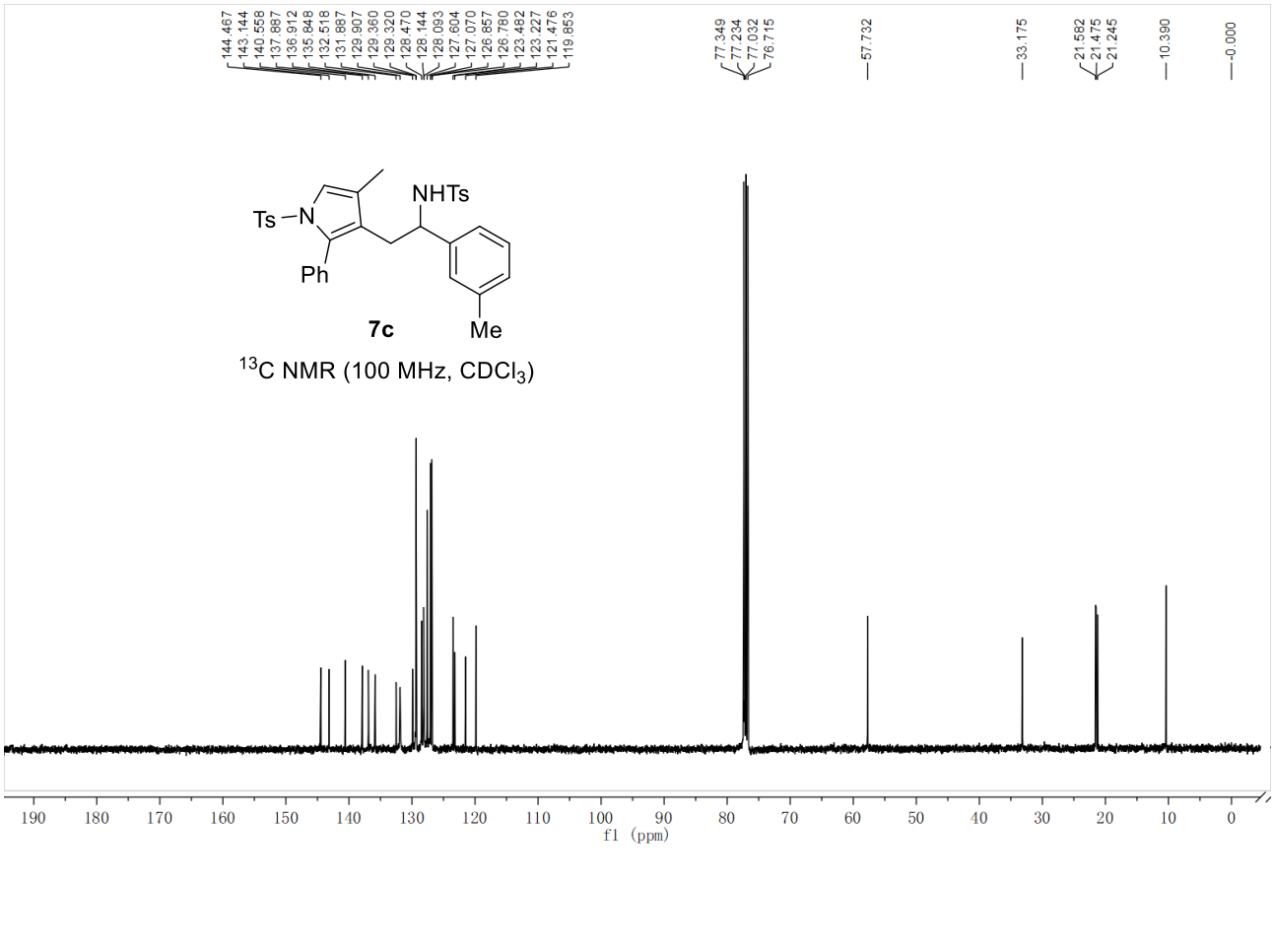
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858



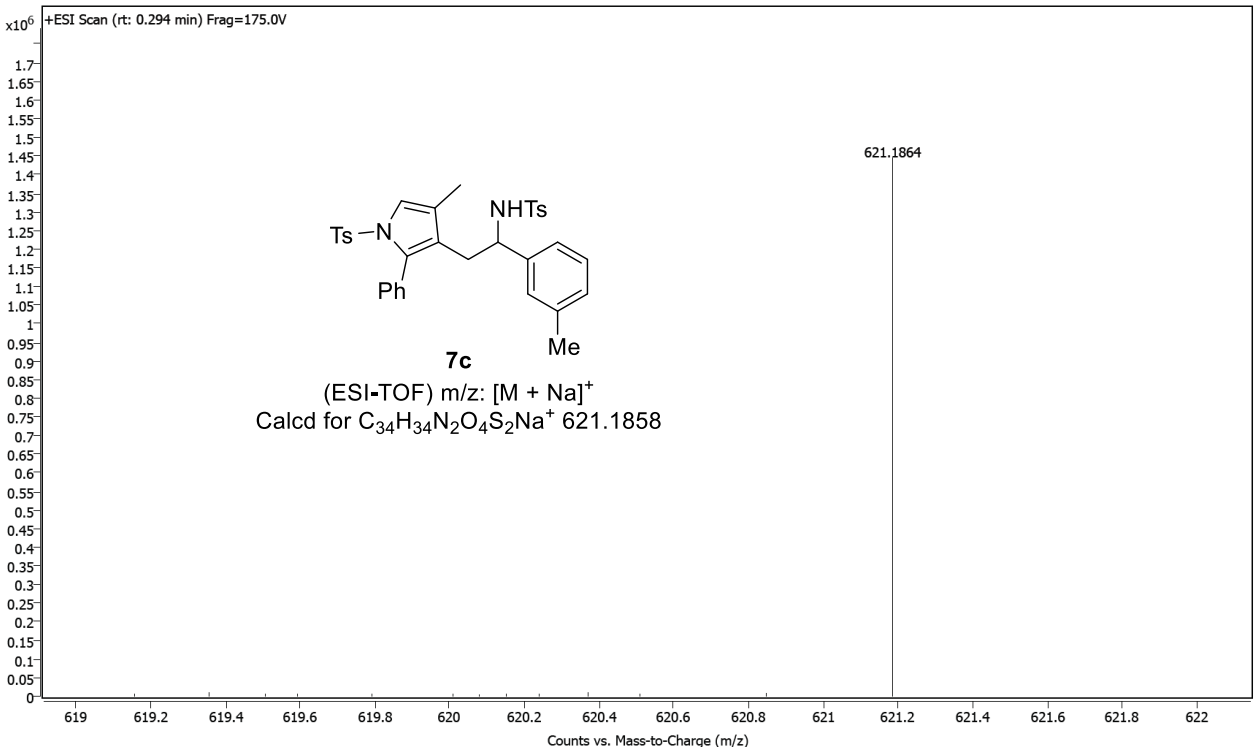
7c

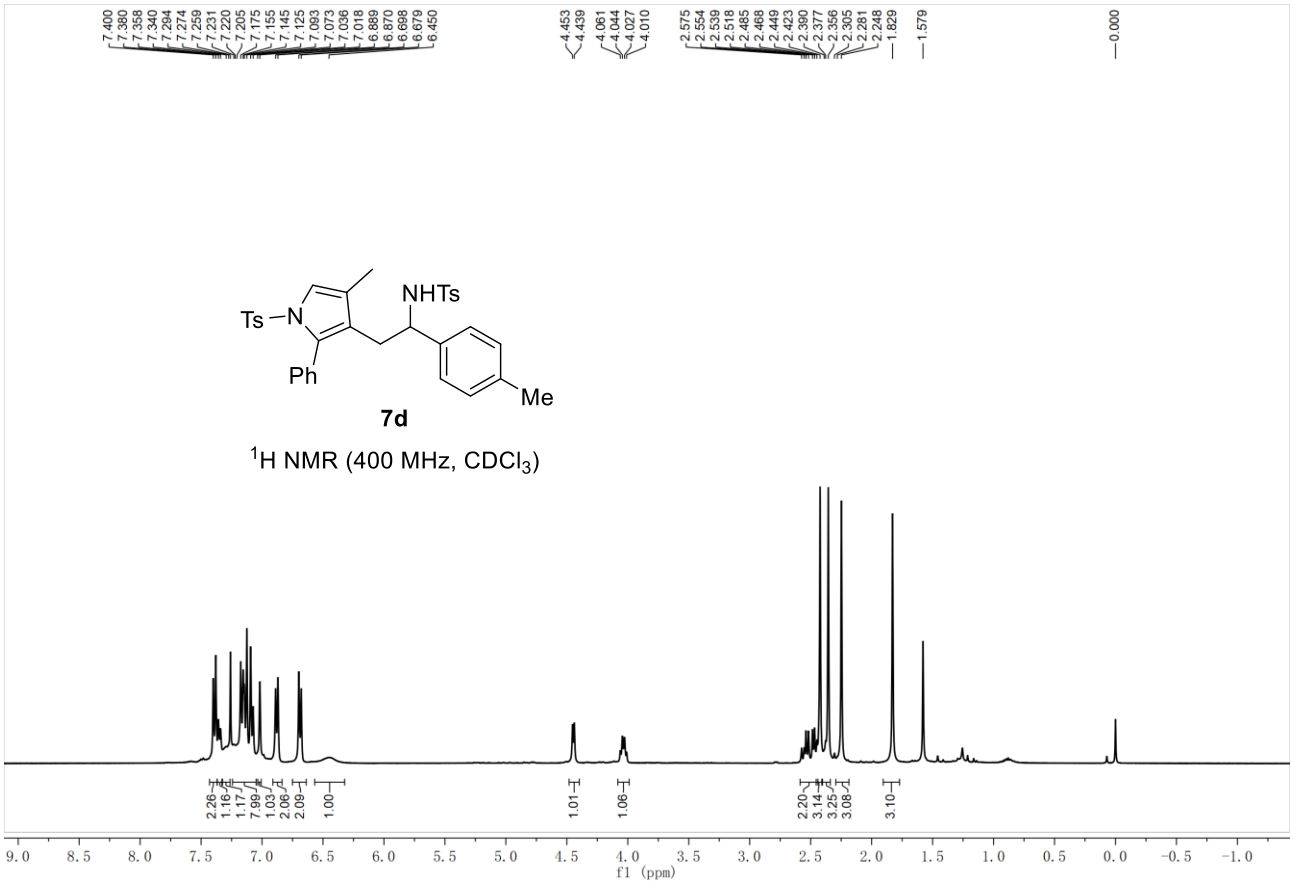
^{1}H NMR (400 MHz, $CDCl_3$)



7c

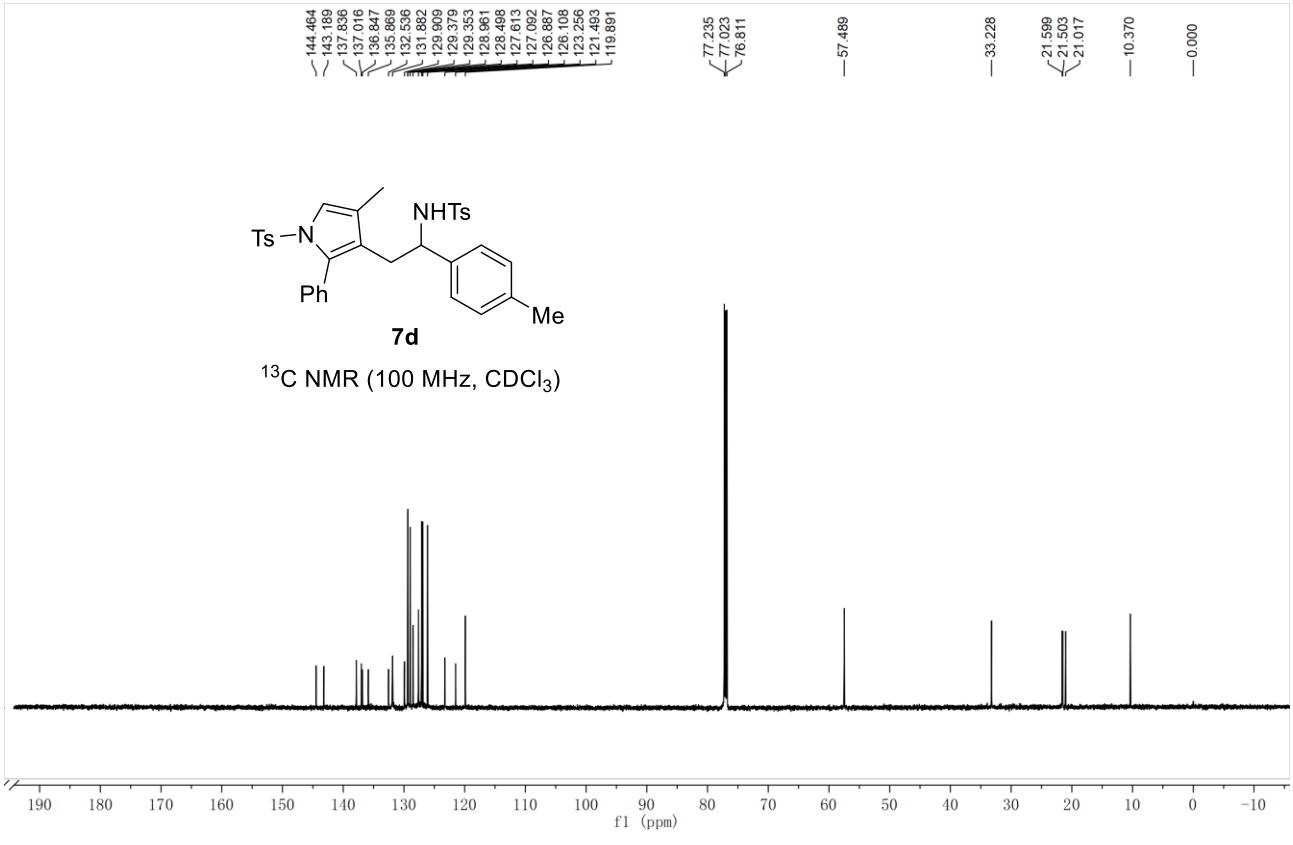
^{13}C NMR (100 MHz, $CDCl_3$)


+ESI Scan (rt: 0.294 min) Frag=175.0V
x10^6
621.1864
NHTs
Ts
N
Ph
Me
7c
(ESI-TOF) m/z: [M + Na]+
Calcd for C34H34N2O4S2Na+ 621.1858
Counts vs. Mass-to-Charge (m/z)



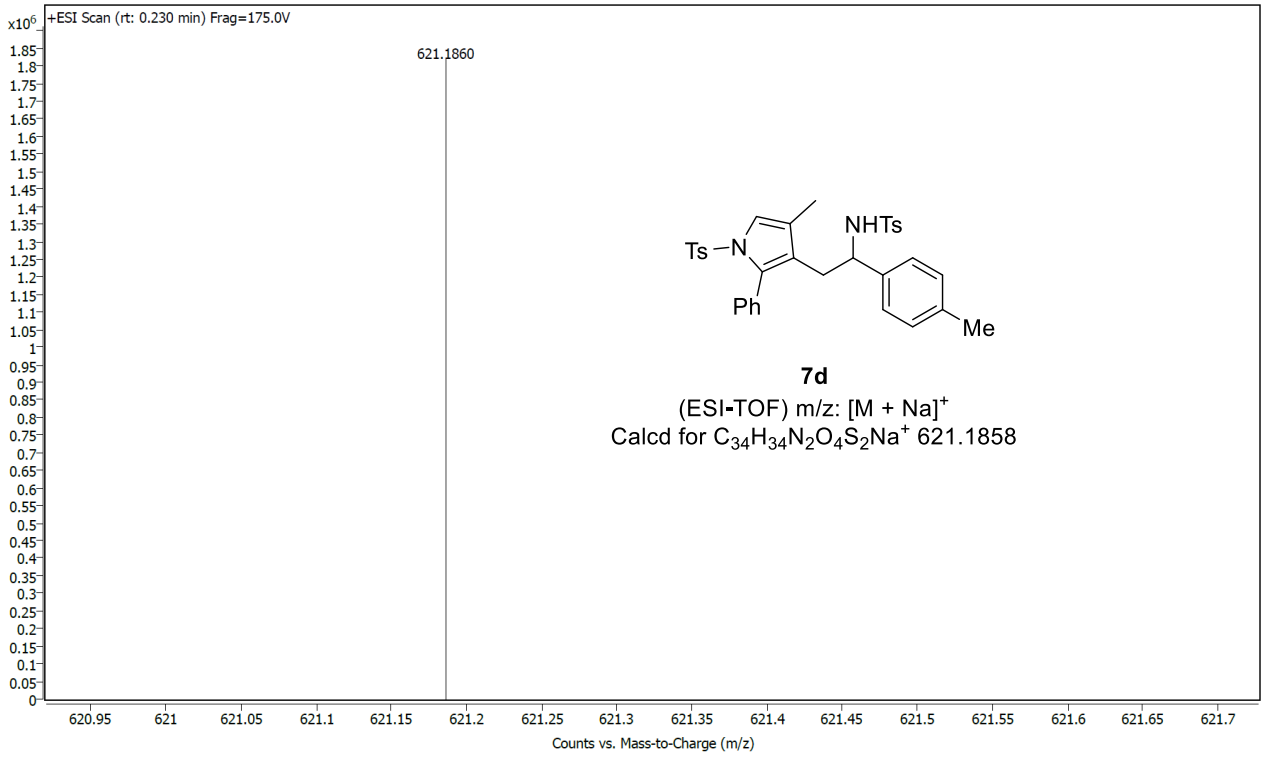
7d

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



7d

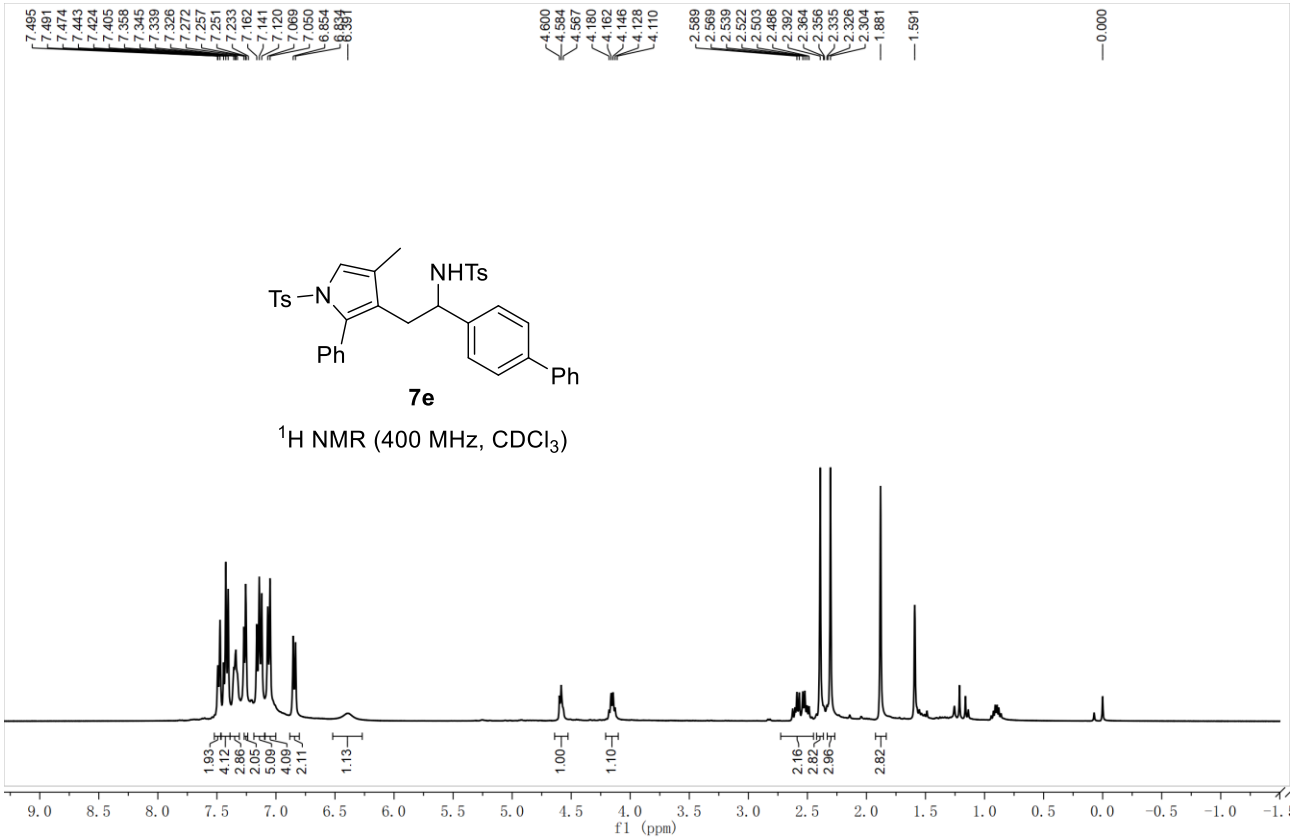
^{13}C NMR (100 MHz, $CDCl_3$)

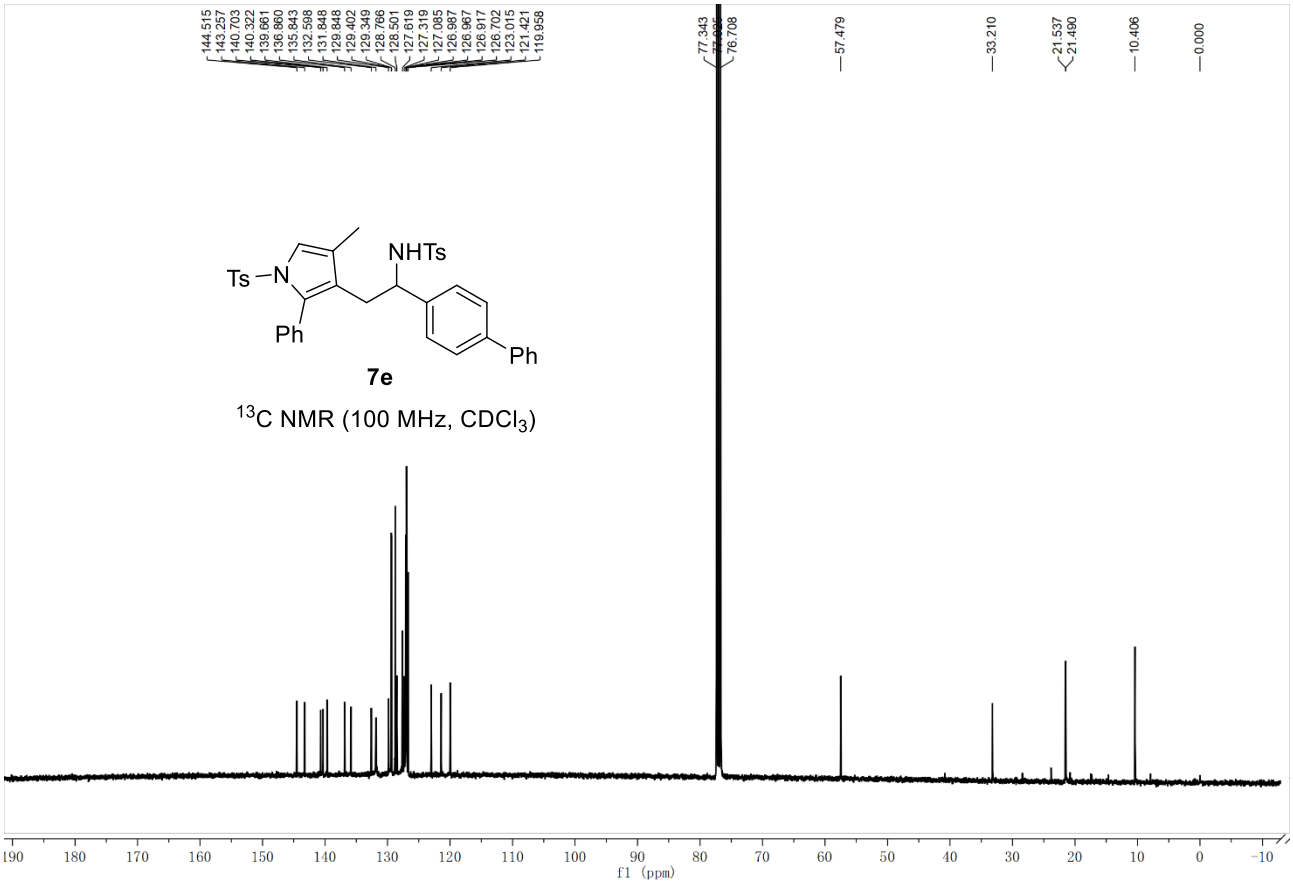


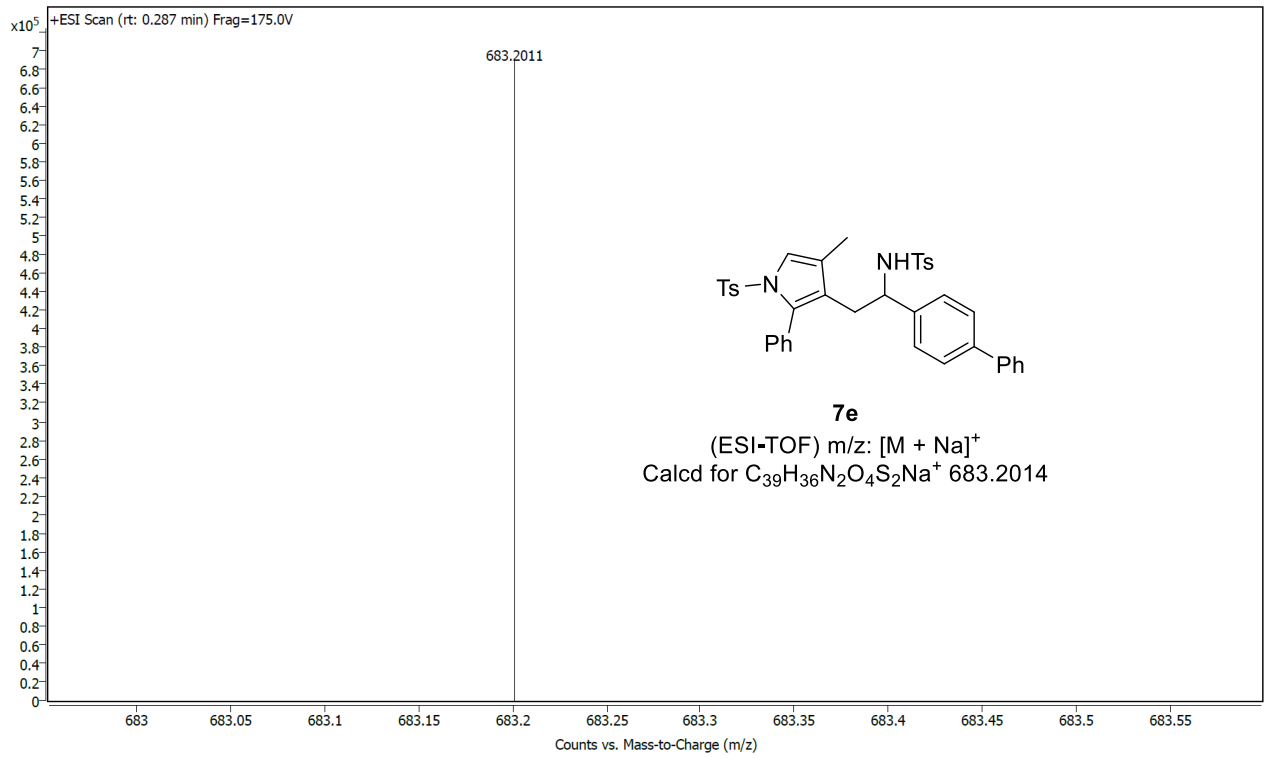
7d

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858


7.495
7.491
7.474
7.443
7.424
7.405
7.358
7.345
7.339
7.326
7.272
7.257
7.251
7.233
7.162
7.141
7.120
7.069
7.050
6.854
6.834
6.391
4.600
4.584
4.567
4.180
4.162
4.146
4.128
4.110
2.589
2.569
2.539
2.522
2.503
2.486
2.392
2.364
2.356
2.335
2.326
2.304
1.881
1.591
0.000
NHTs
Ts
N
Ph
Ph
7e
1H NMR (400 MHz, CDCl3)
1.93
4.12
2.86
2.05
5.09
4.09
2.11
1.13
1.00
1.10
2.16
2.82
2.96
2.82
f1 (ppm)

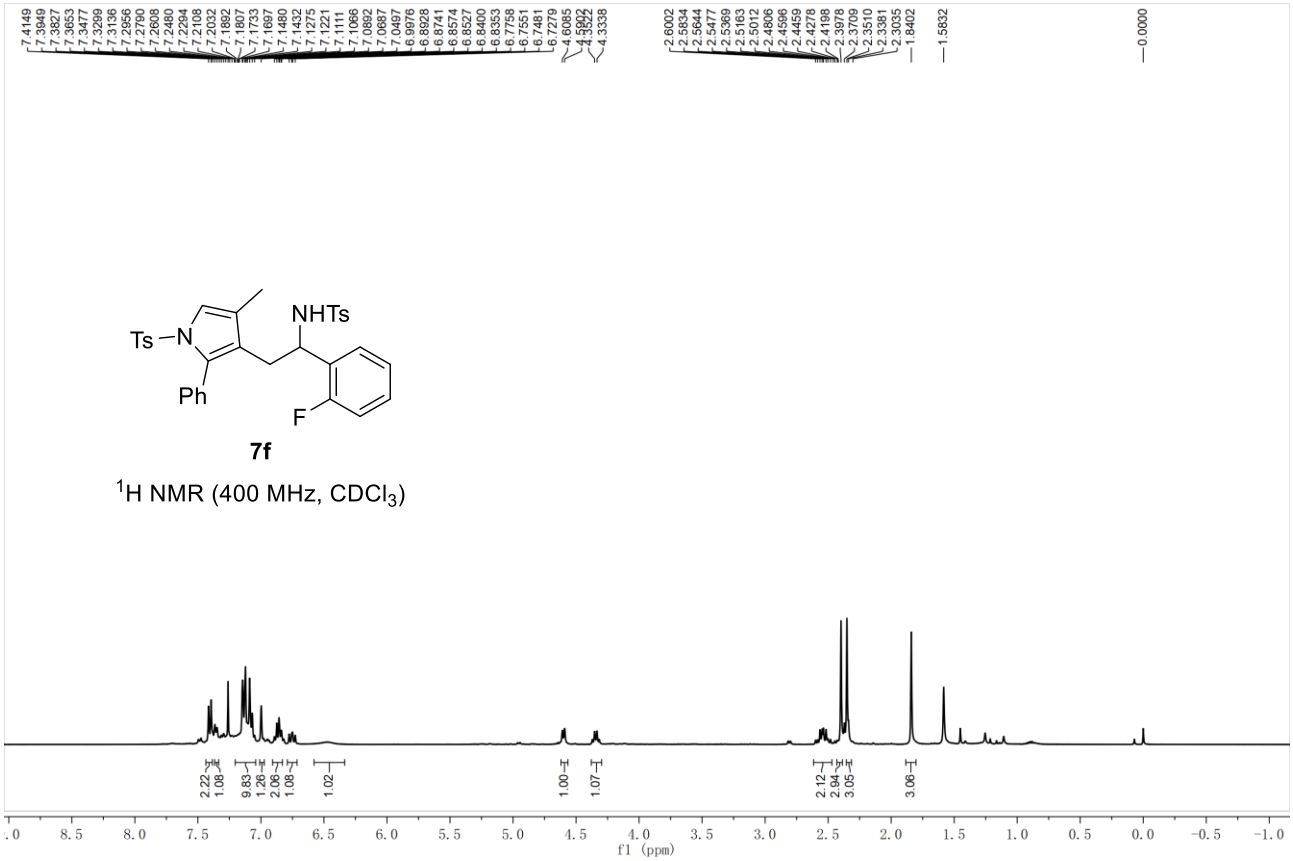

144.515
143.257
140.703
140.322
139.661
136.860
135.843
132.598
131.848
129.848
129.402
129.349
128.786
128.501
127.619
127.319
127.085
126.987
126.967
126.917
126.702
123.015
121.421
119.958
77.343
77.025
76.708
57.479
33.210
21.537
21.490
10.406
0.000
NHTs
Ts
N
Ph
Ph
7e
13C NMR (100 MHz, CDCl3)
f1 (ppm)

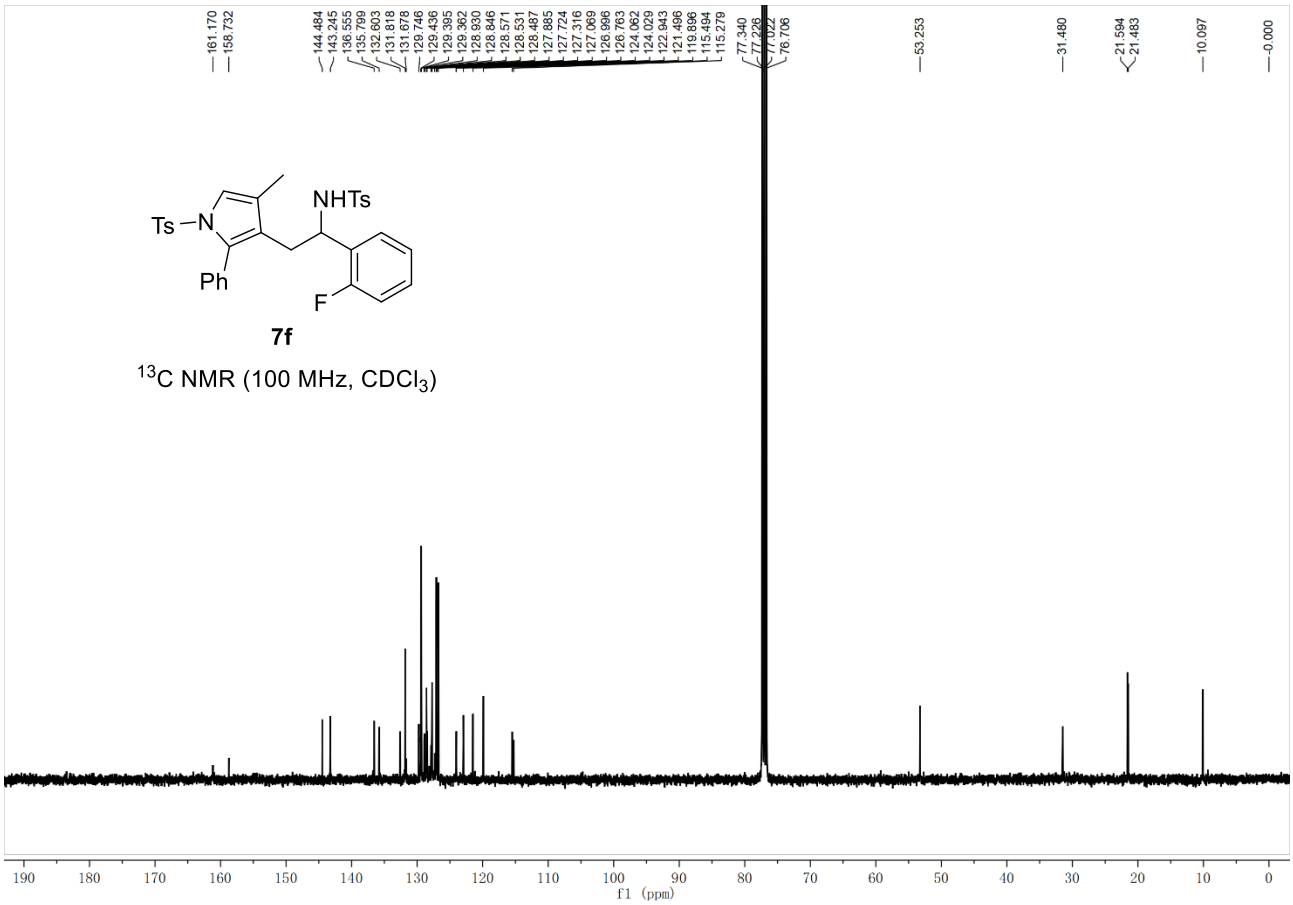


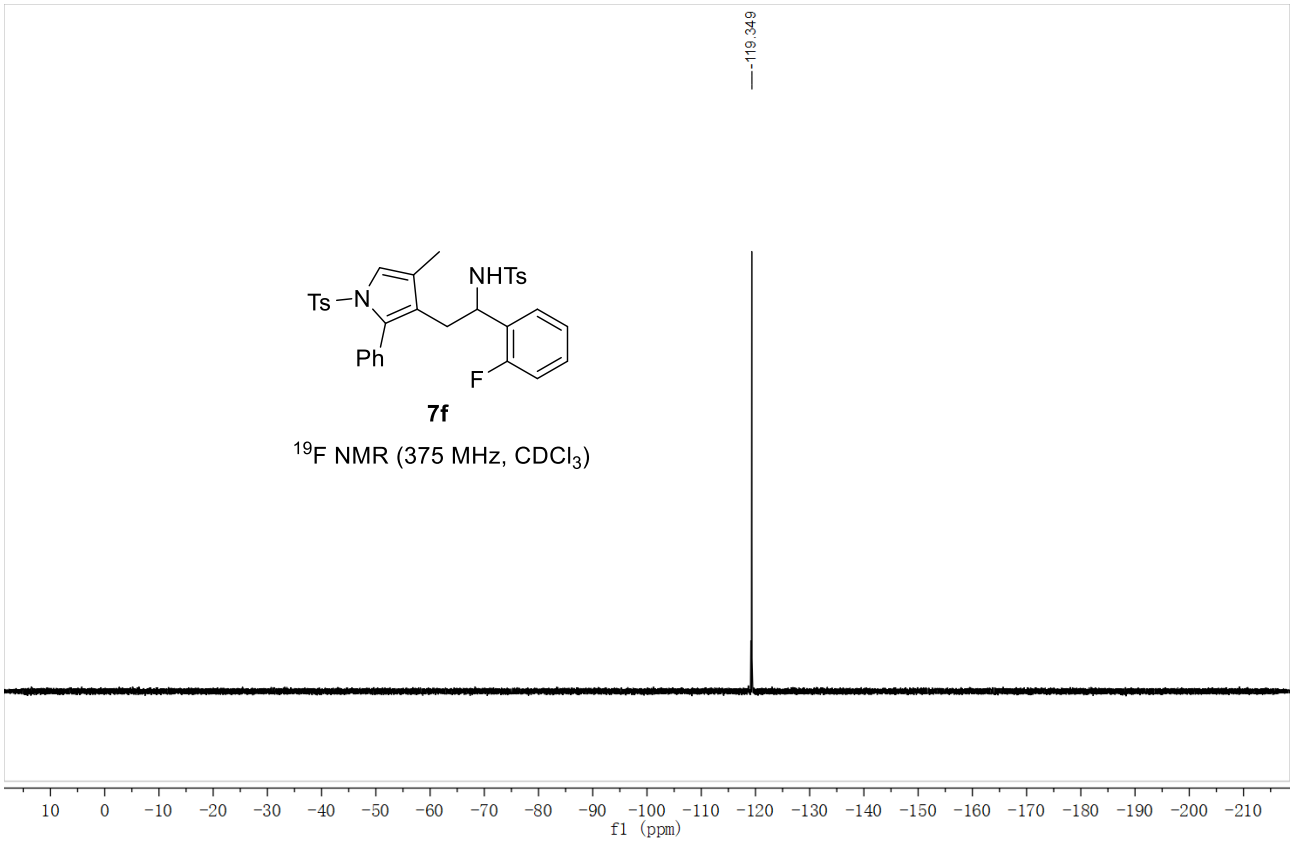
7e

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{39}H_{36}N_2O_4S_2Na^+$ 683.2014

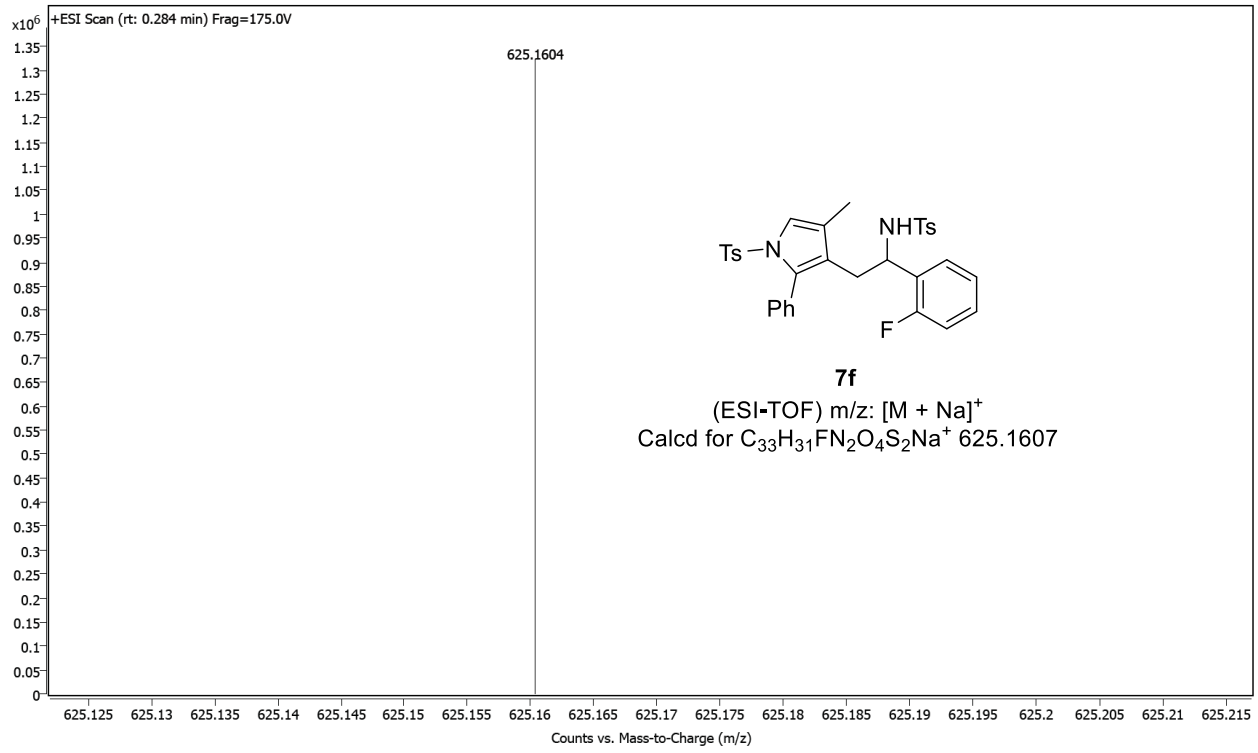

NHTs
Ts
N
Ph
F
7f
1H NMR (400 MHz, CDCl3)
f1 (ppm)


NHTs
Ts
N
Ph
F
7f
13C NMR (100 MHz, CDCl3)
f1 (ppm)



7f

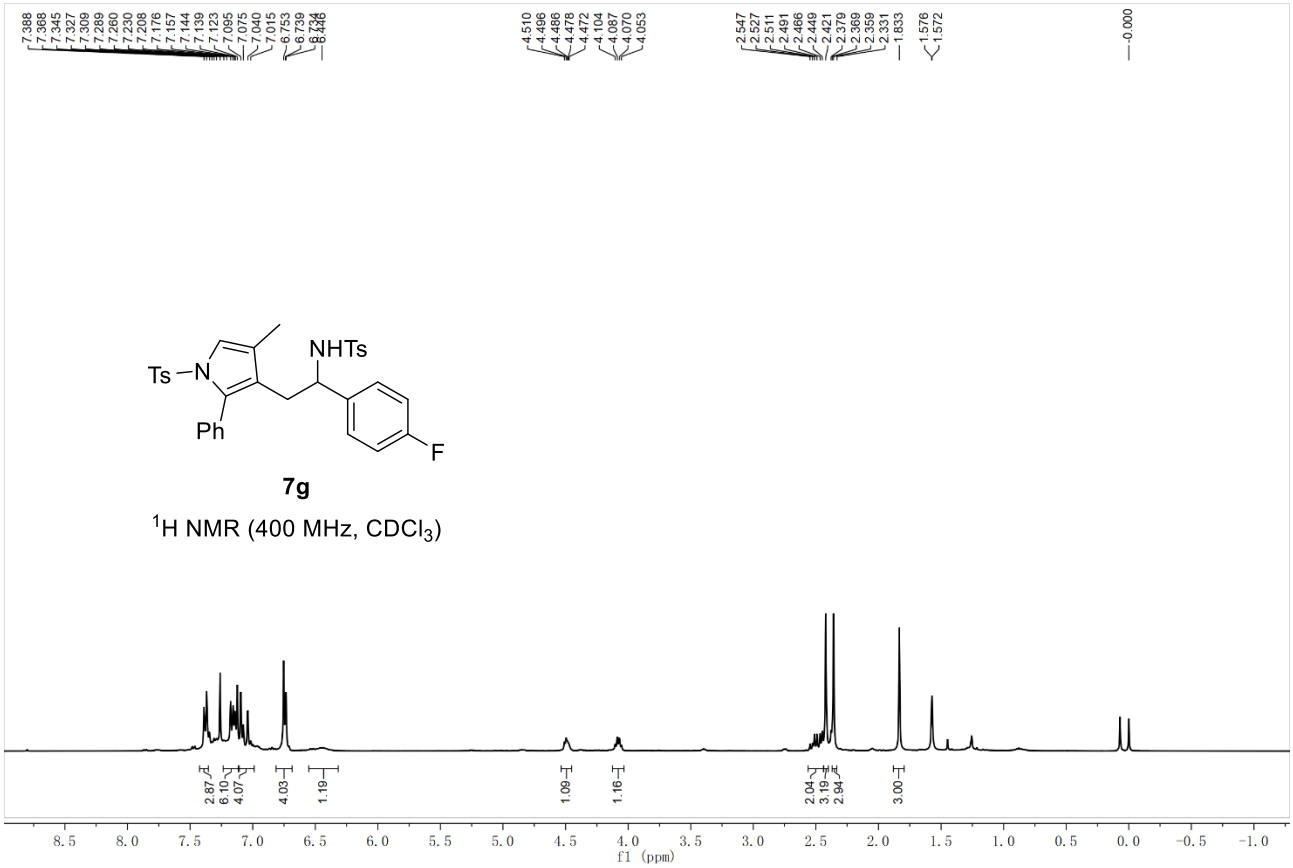
^{19}F NMR (375 MHz, $CDCl_3$)

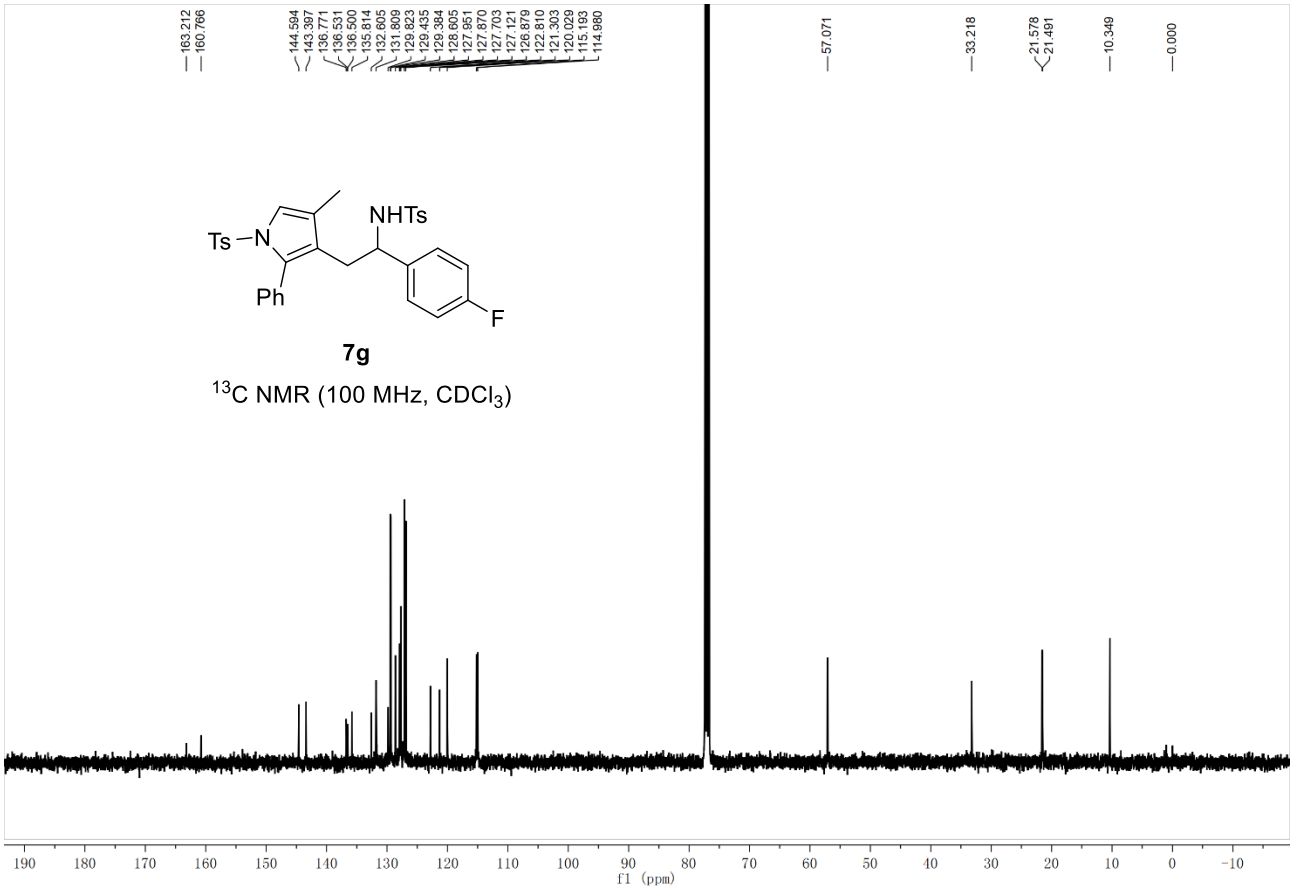


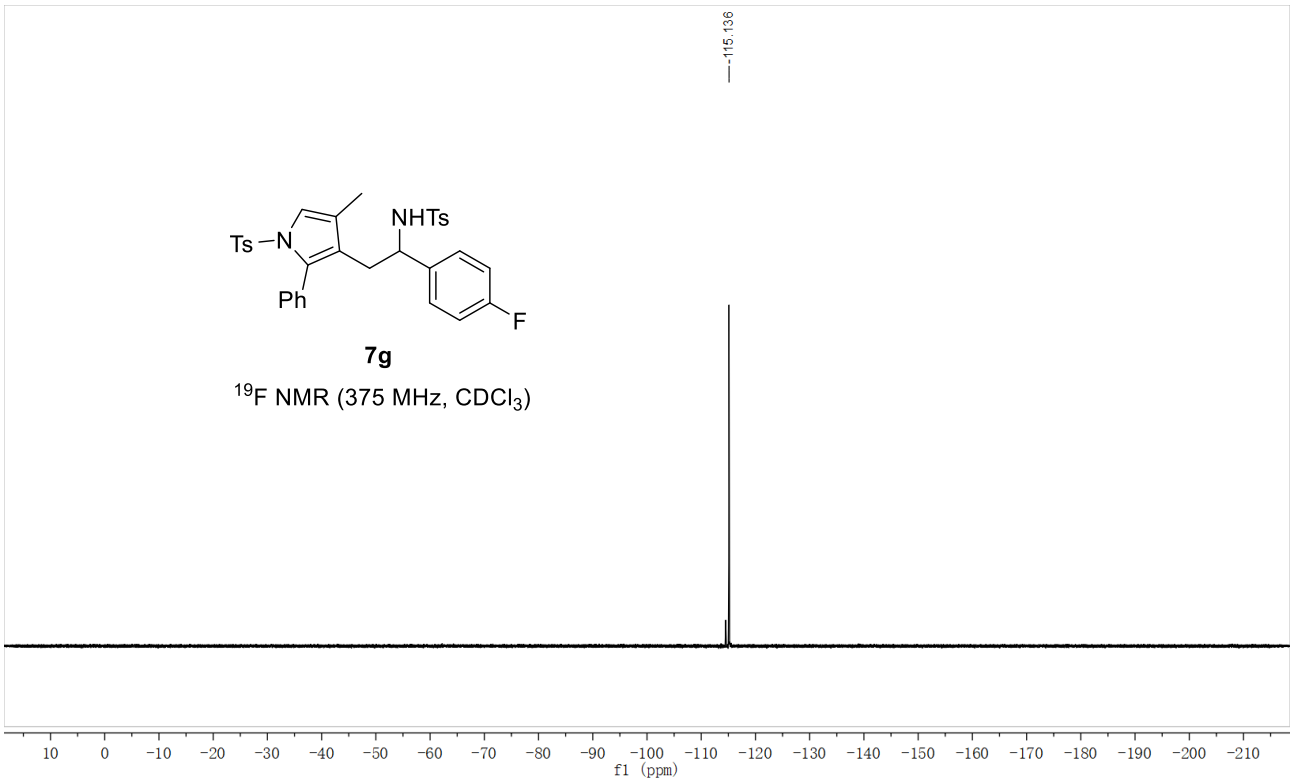
7f

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{33}H_{31}FN_2O_4S_2Na^+$ 625.1607

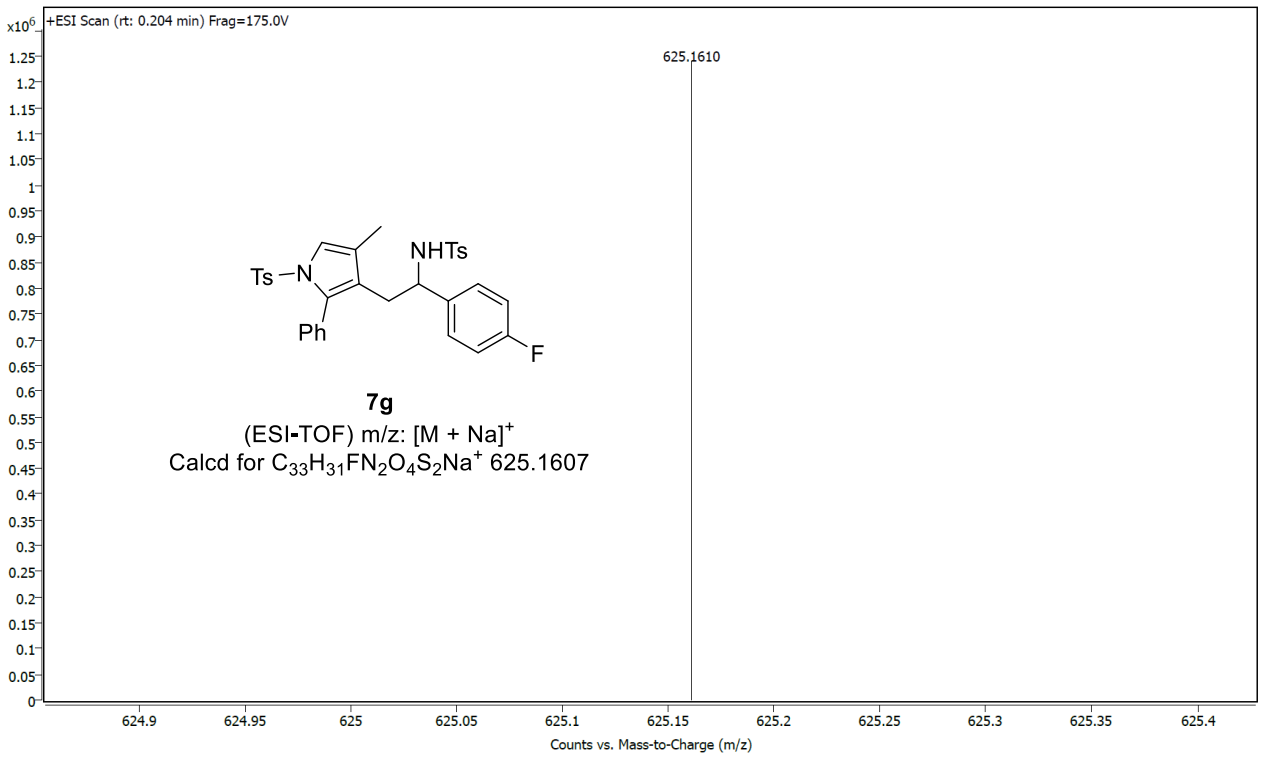

NHTs
Ts
N
Ph
F
7g
1H NMR (400 MHz, CDCl3)
f1 (ppm)


NHTs
Ts
N
Ph
F
7g
13C NMR (100 MHz, CDCl3)
f1 (ppm)



7g

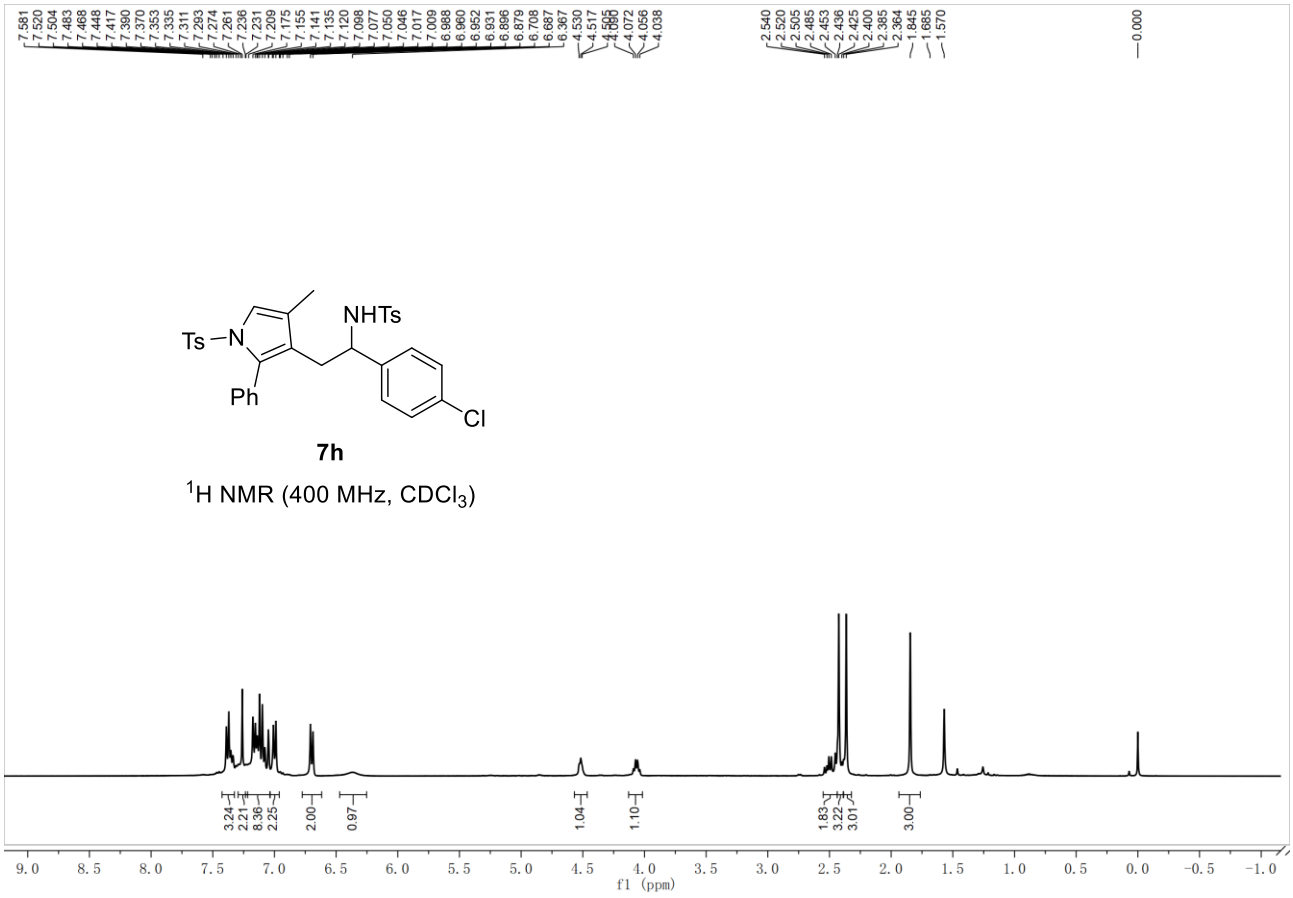
^{19}F NMR (375 MHz, $CDCl_3$)

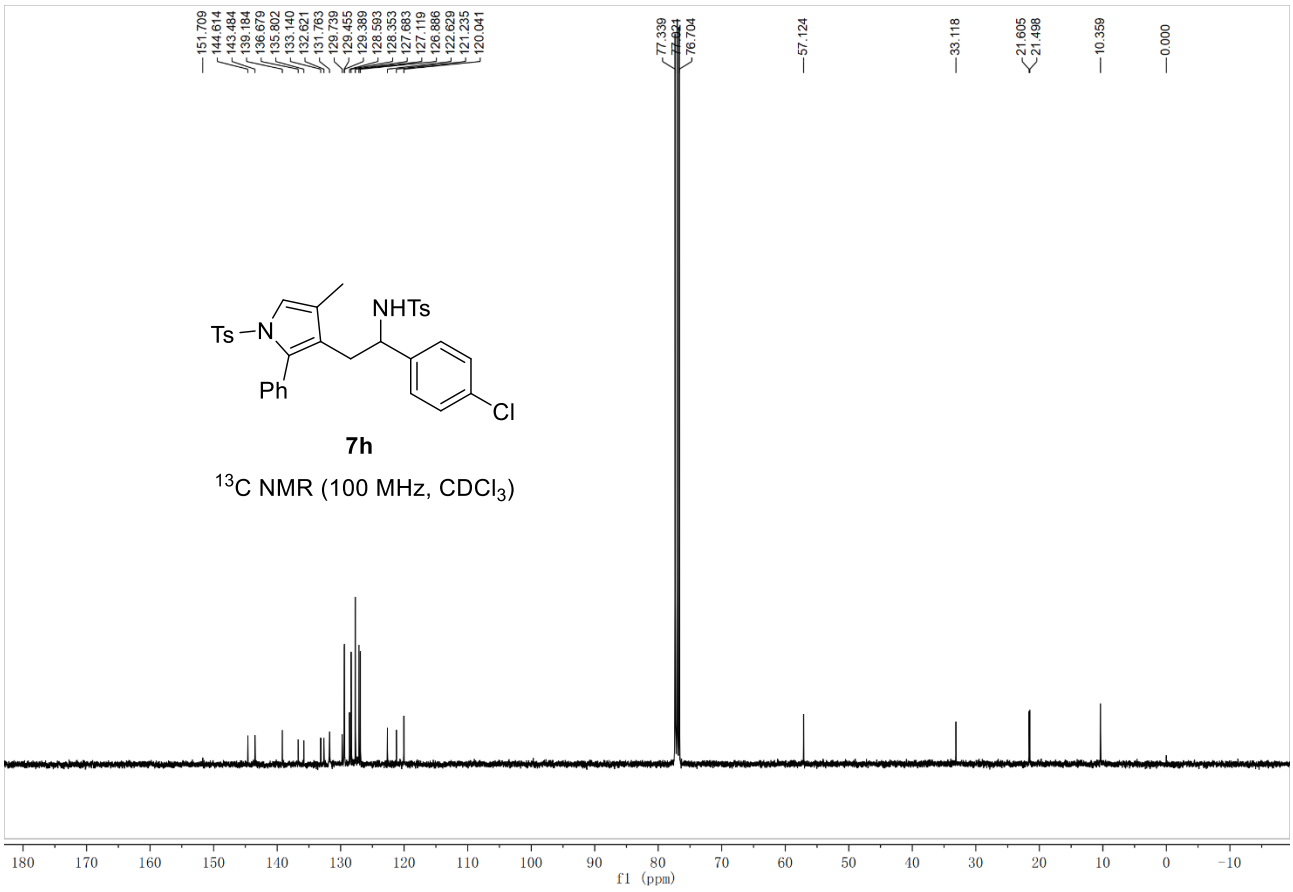


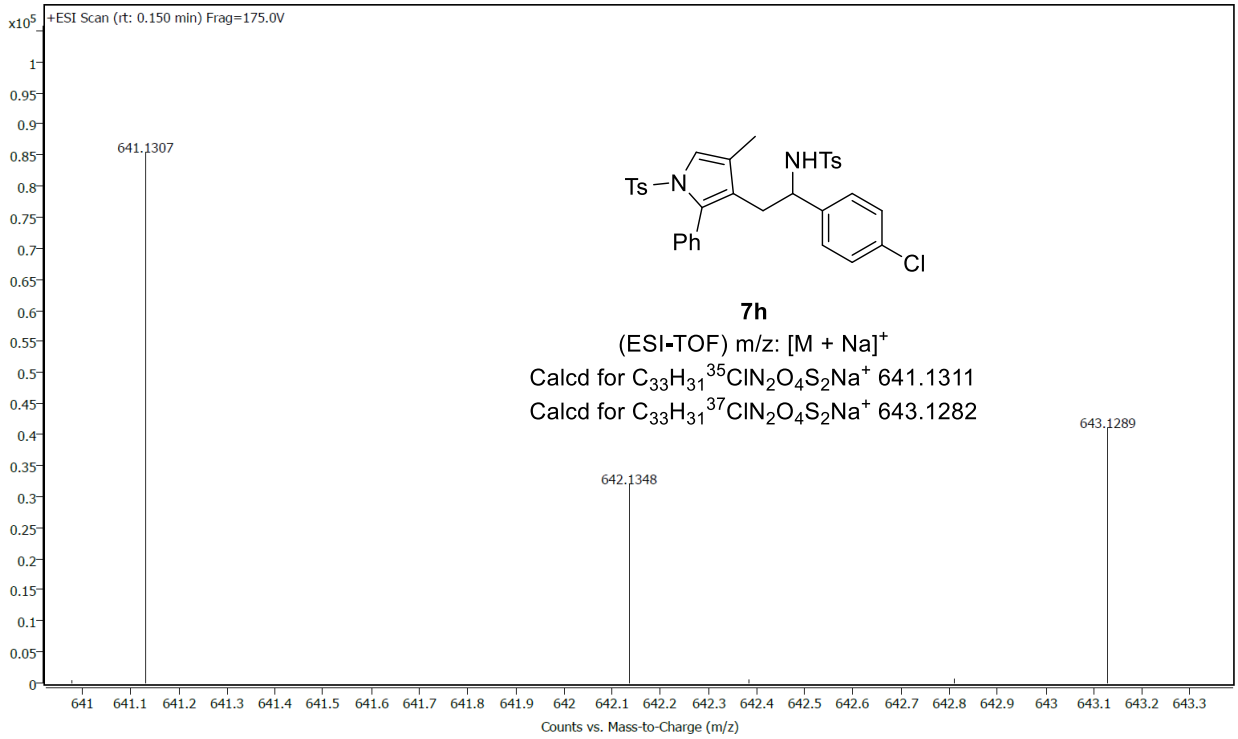
7g

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{33}H_{31}FN_2O_4S_2Na^+$ 625.1607


NHTs
Ts
N
Ph
Cl
7h
1H NMR (400 MHz, CDCl3)
f1 (ppm)


NHTs
Ts
N
Ph
Cl
7h
13C NMR (100 MHz, CDCl3)
f1 (ppm)

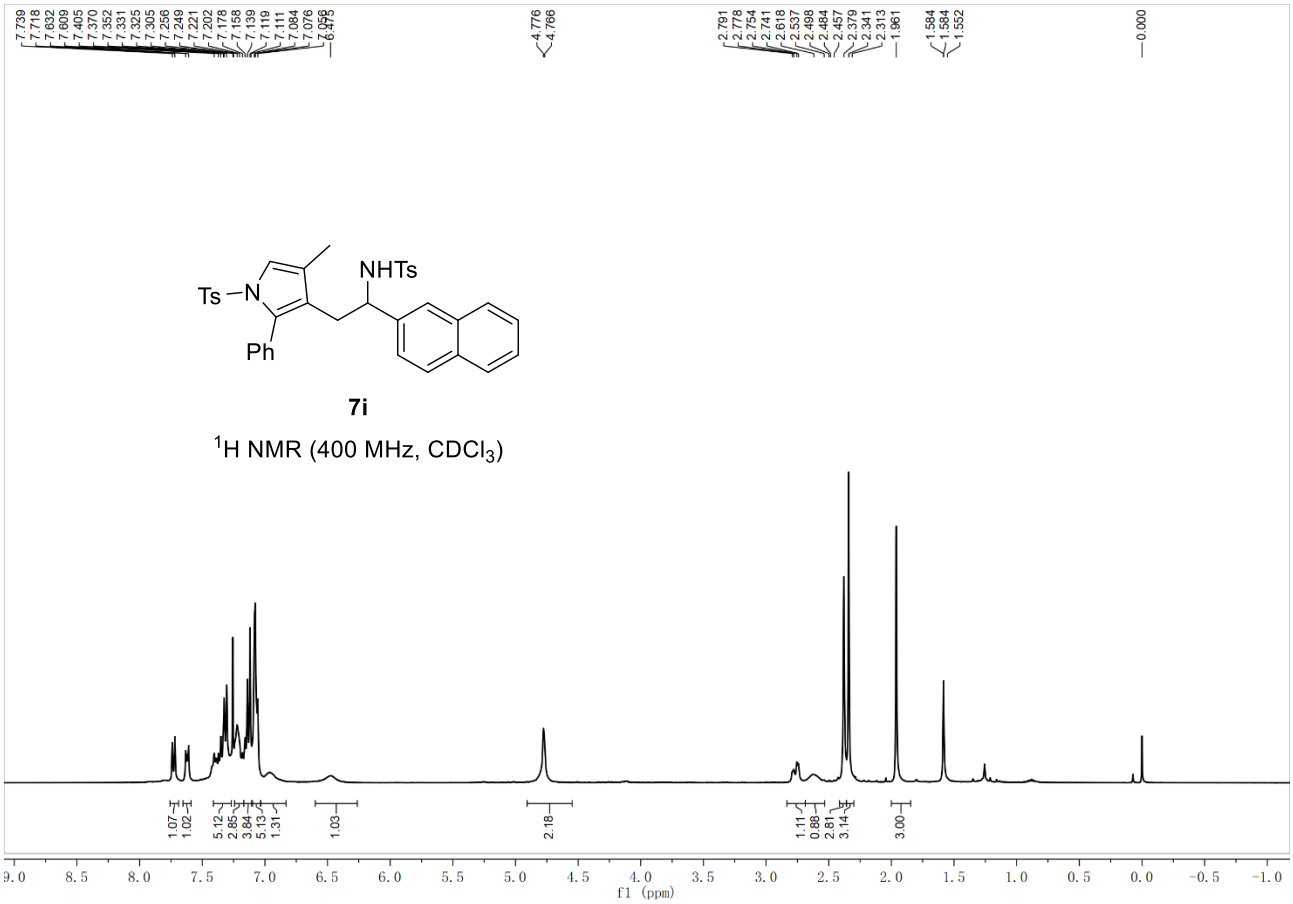


7h

(ESI-TOF) m/z: $[M + Na]^+$

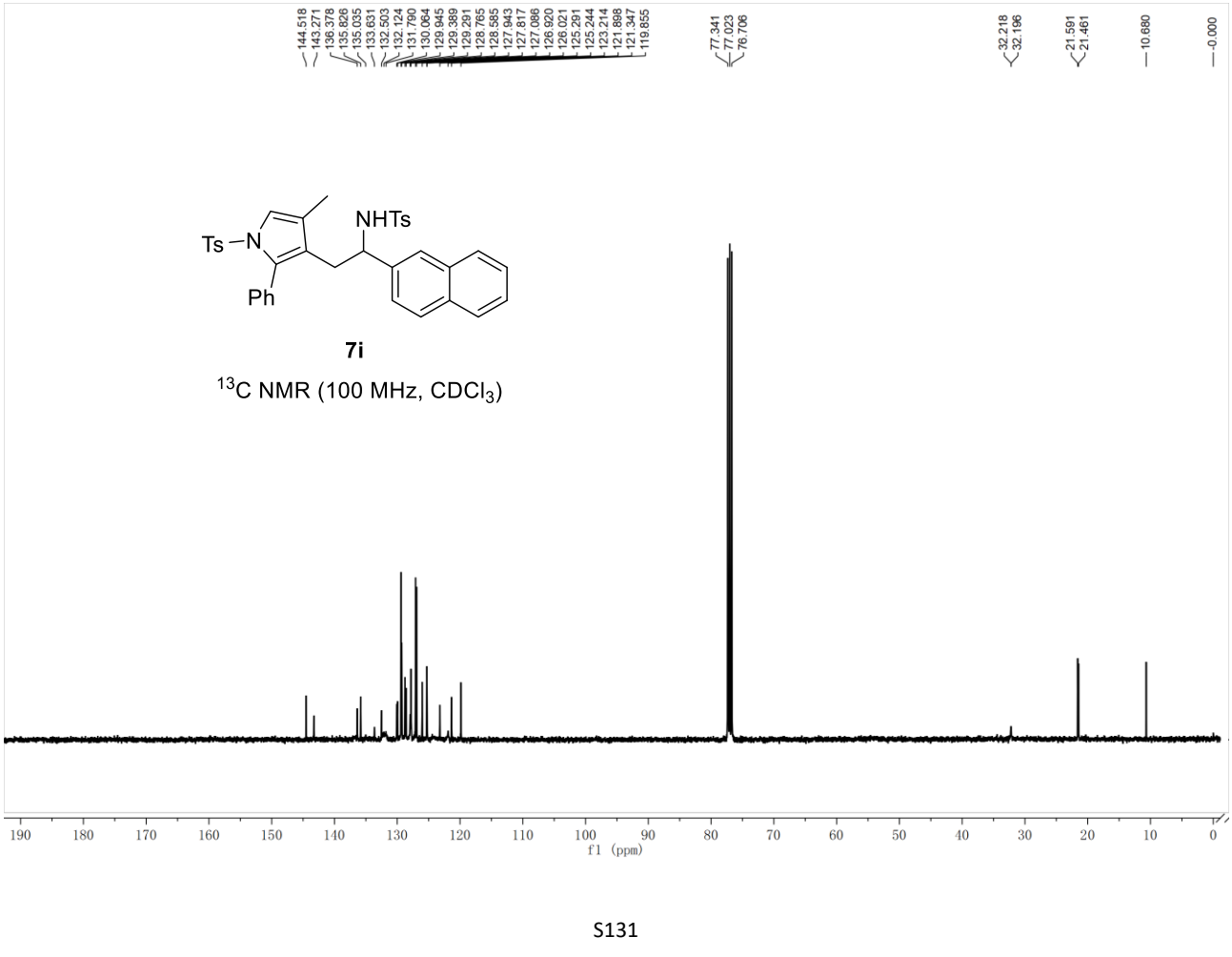
Calcd for $C_{33}H_{31}{}^{35}ClN_2O_4S_2Na^+$ 641.1311

Calcd for $C_{33}H_{31}{}^{37}ClN_2O_4S_2Na^+$ 643.1282



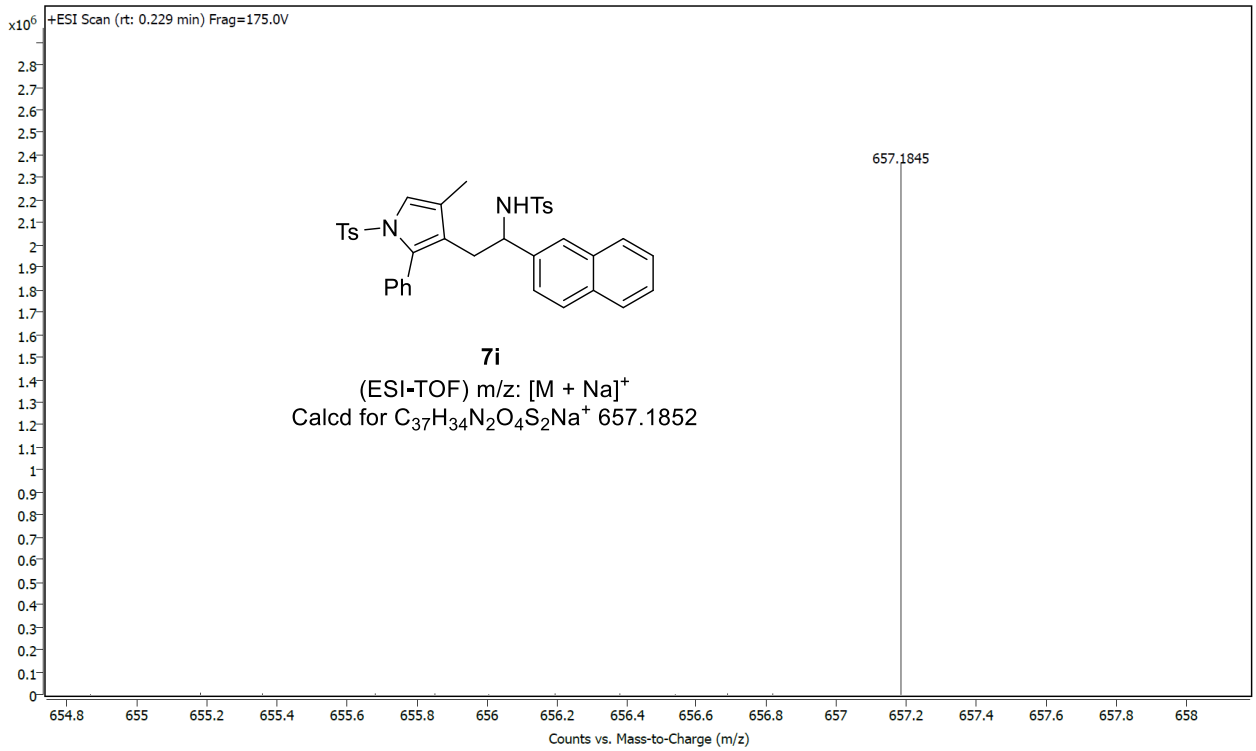
7i

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



7i

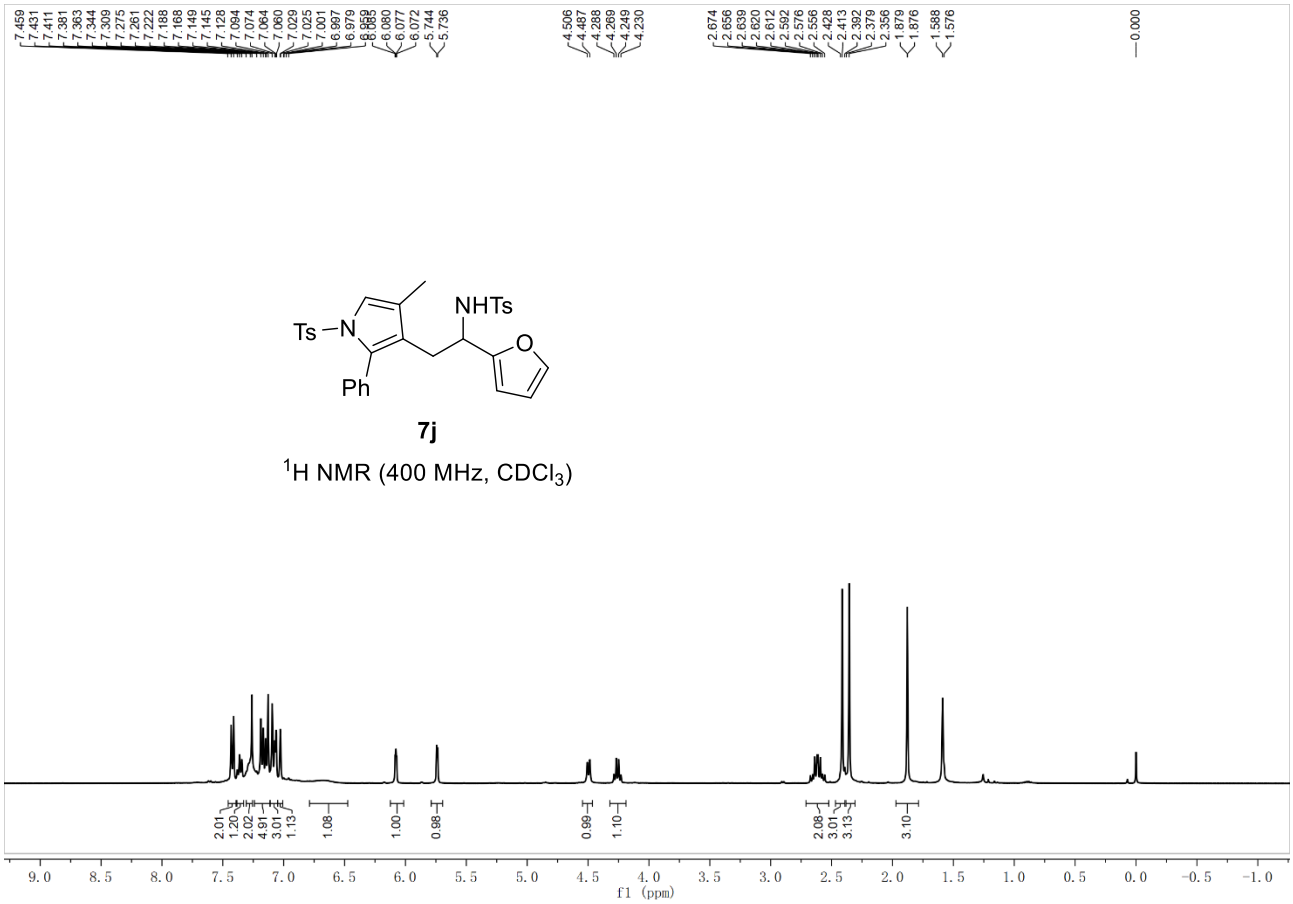
^{13}C NMR (100 MHz, $CDCl_3$)



7i

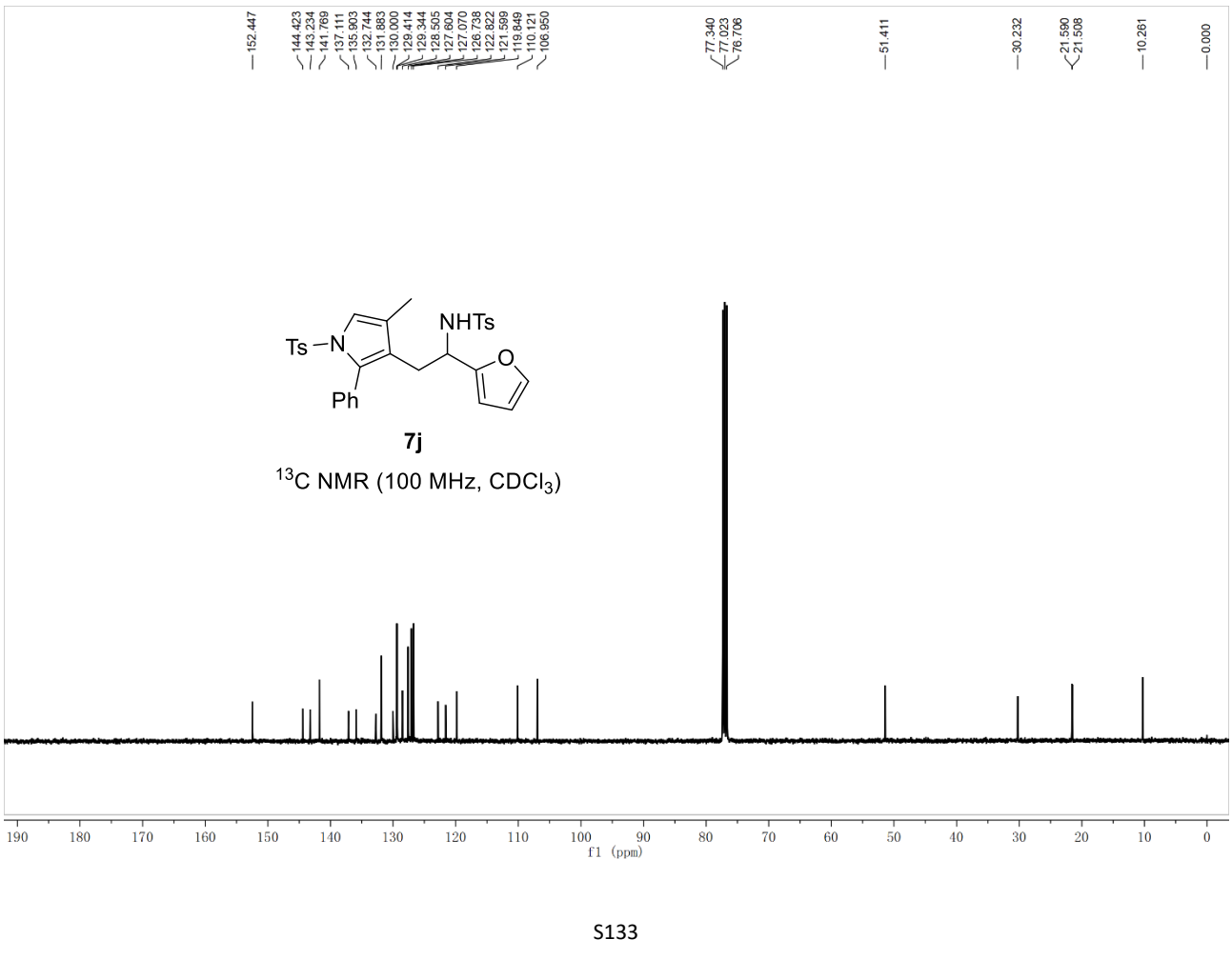
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{37}H_{34}N_2O_4S_2Na^+$ 657.1852



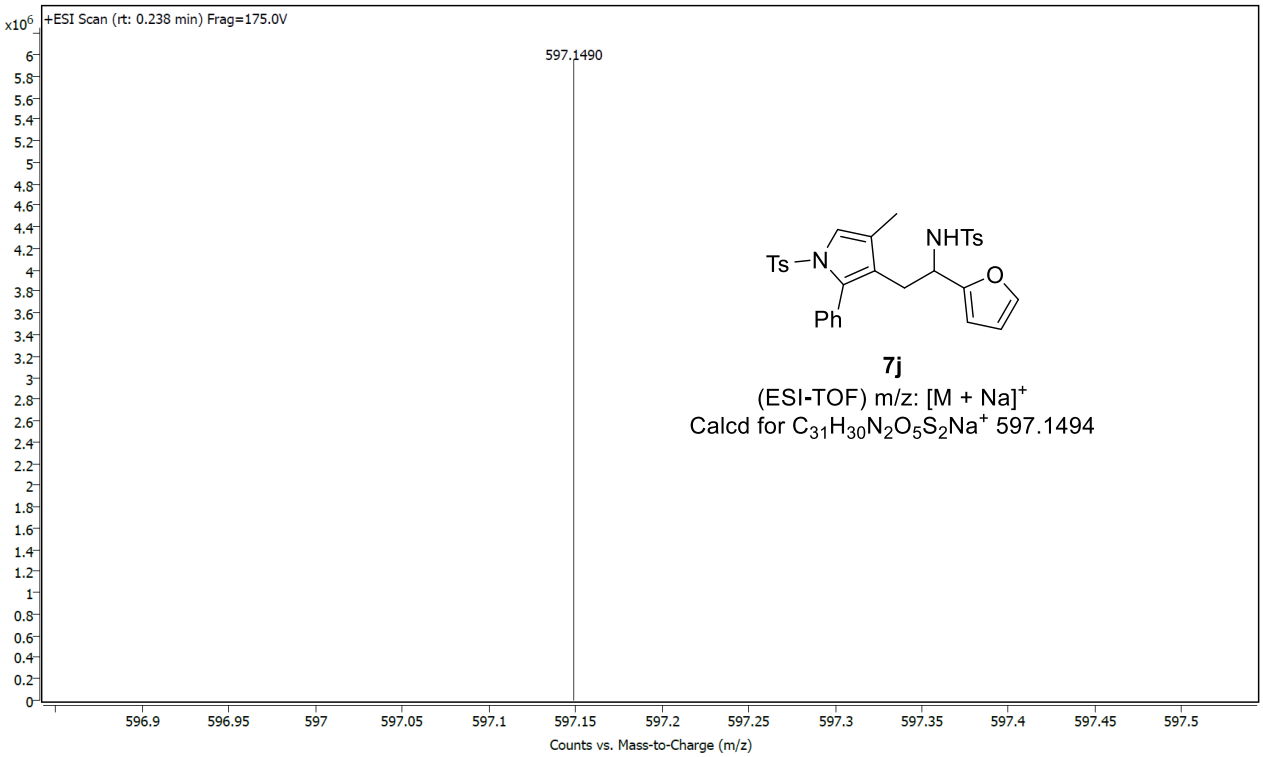
7j

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



7j

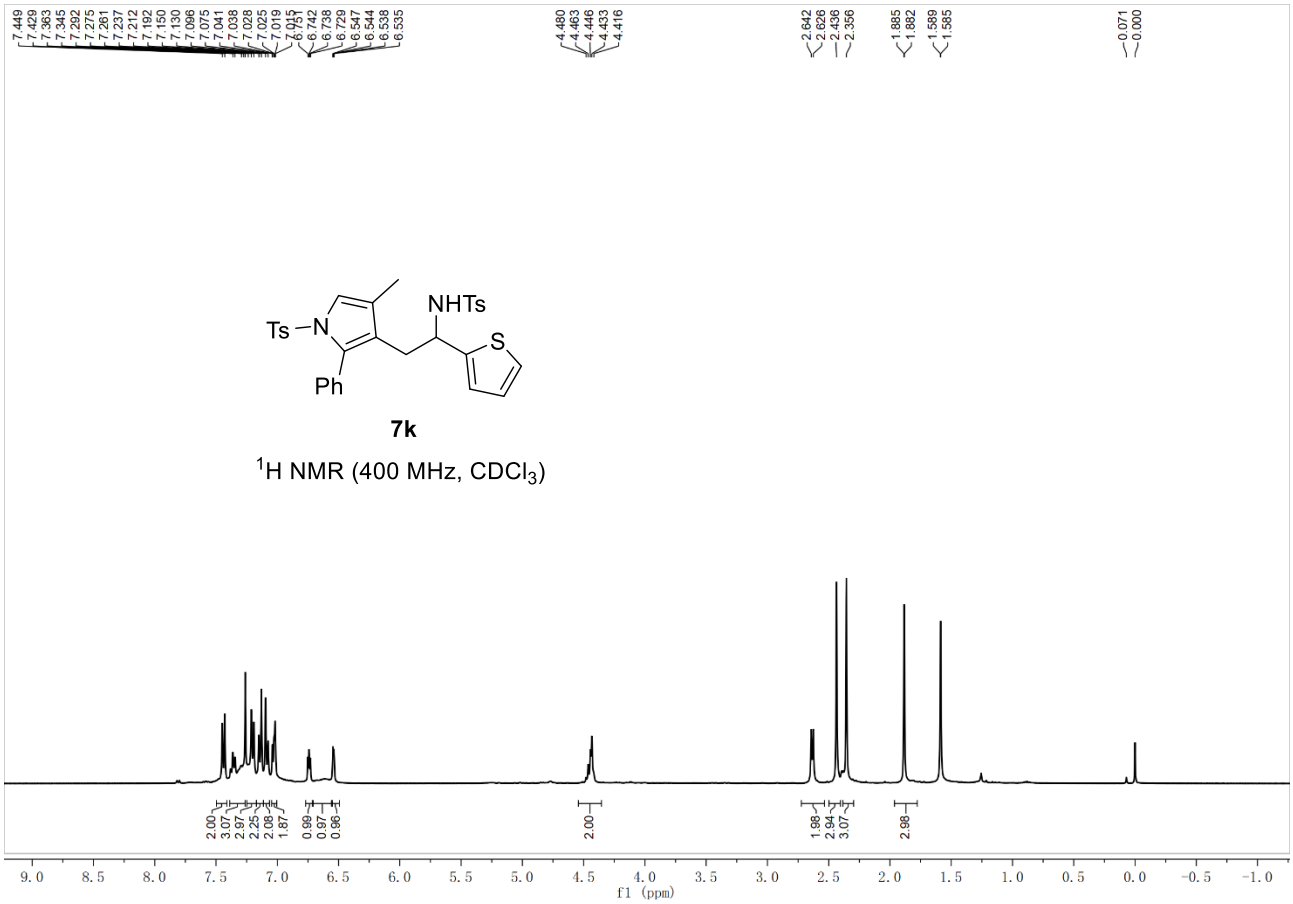
^{13}C NMR (100 MHz, $CDCl_3$)



7j

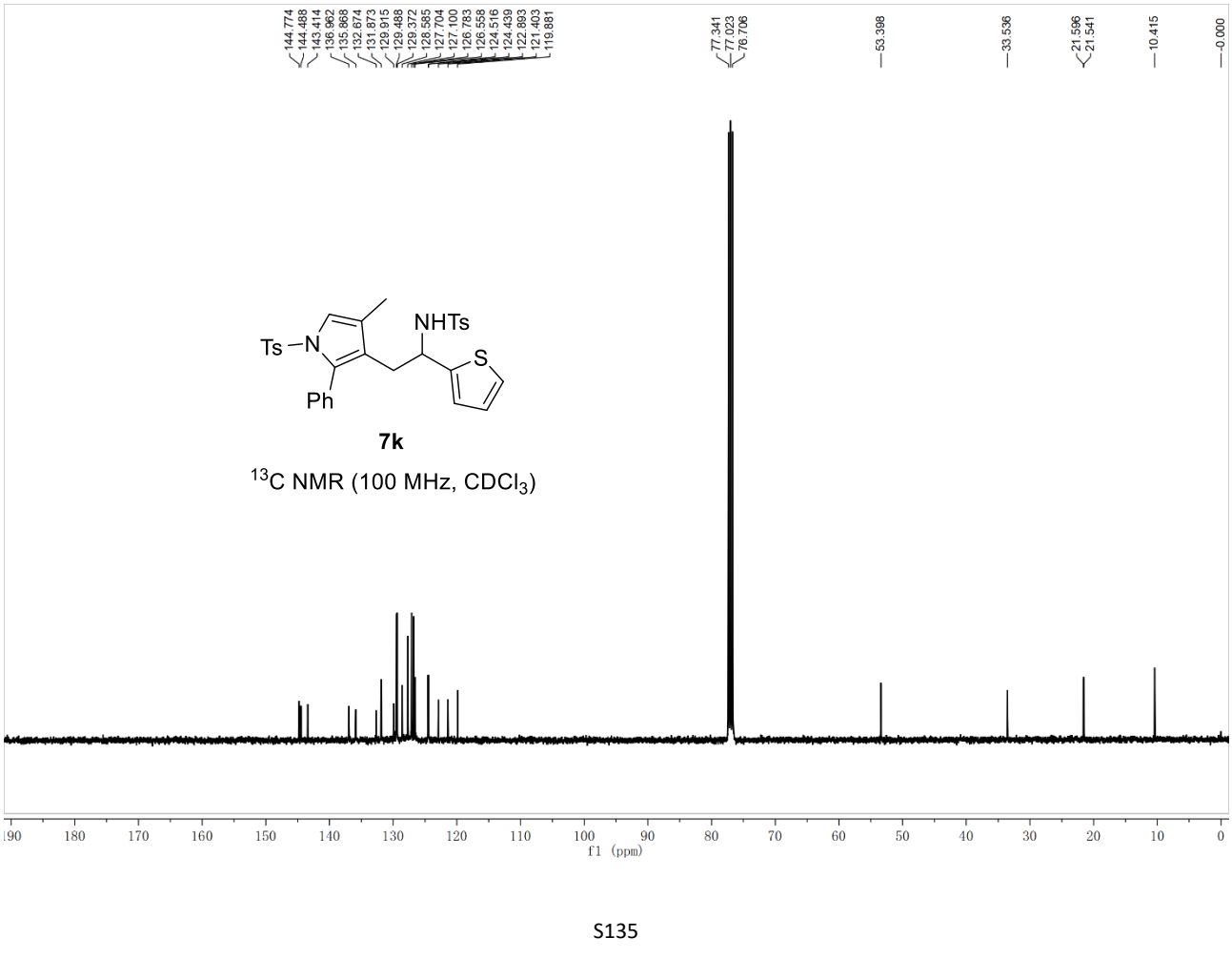
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{31}H_{30}N_2O_5S_2Na^+$ 597.1494



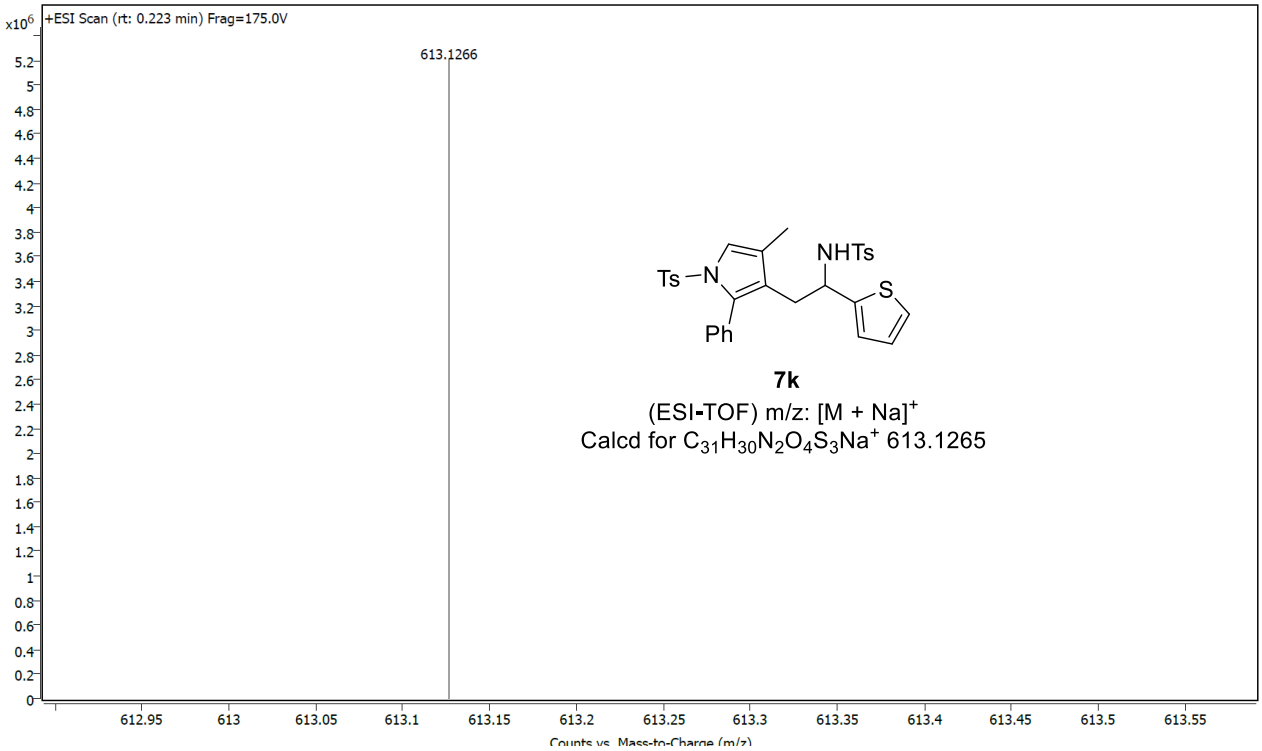
7k

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



7k

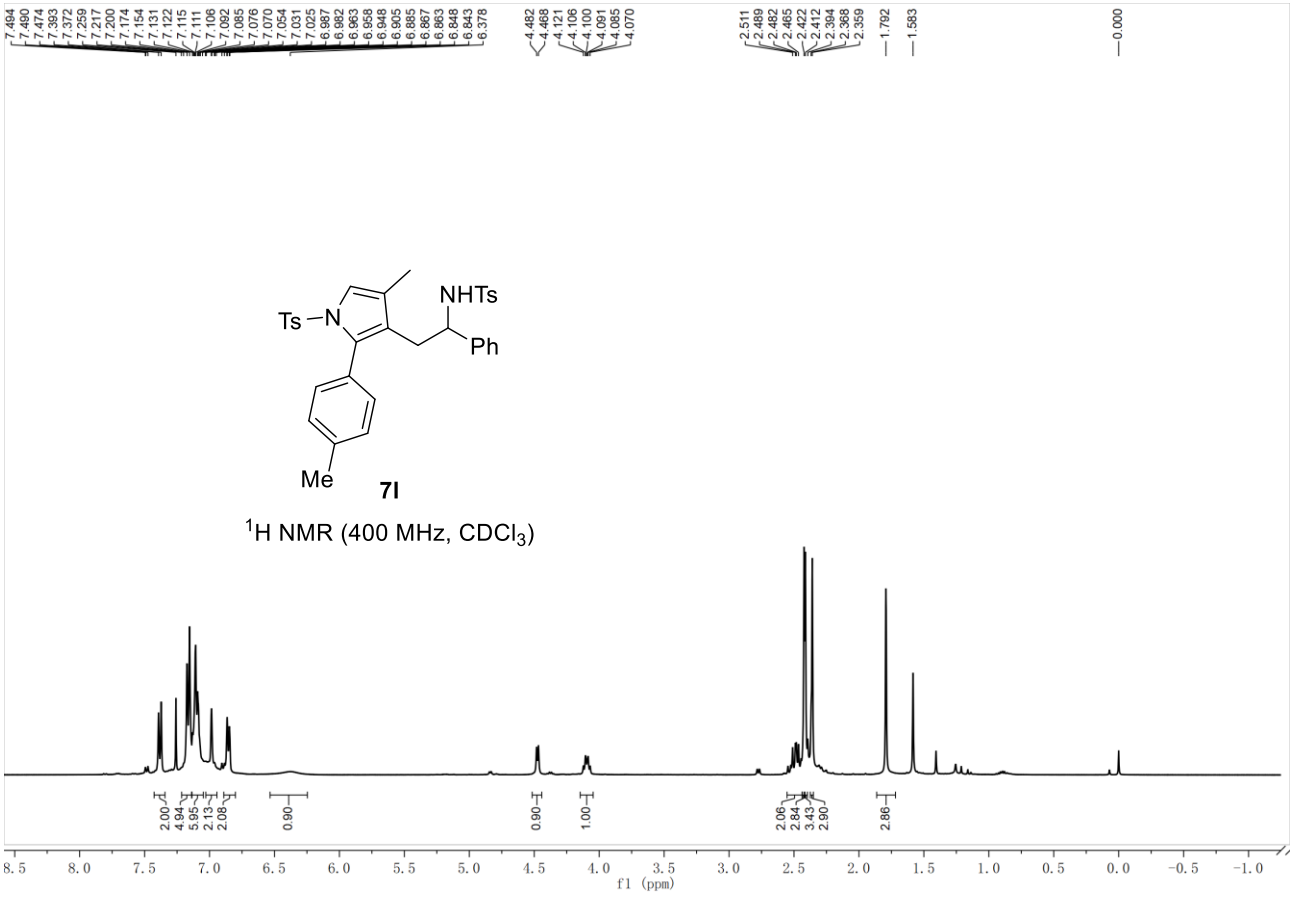
^{13}C NMR (100 MHz, $CDCl_3$)



7k

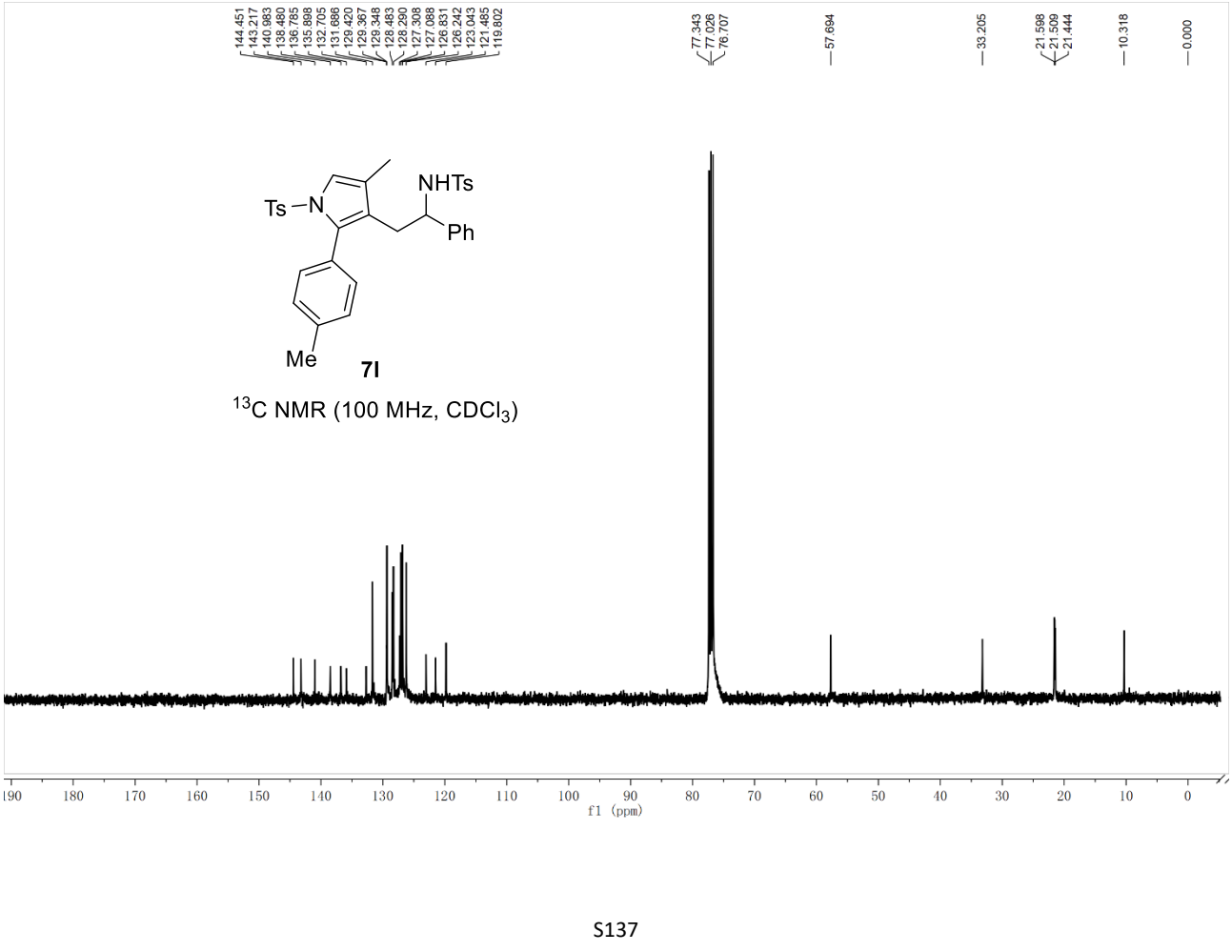
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{31}H_{30}N_2O_4S_3Na^+$ 613.1265



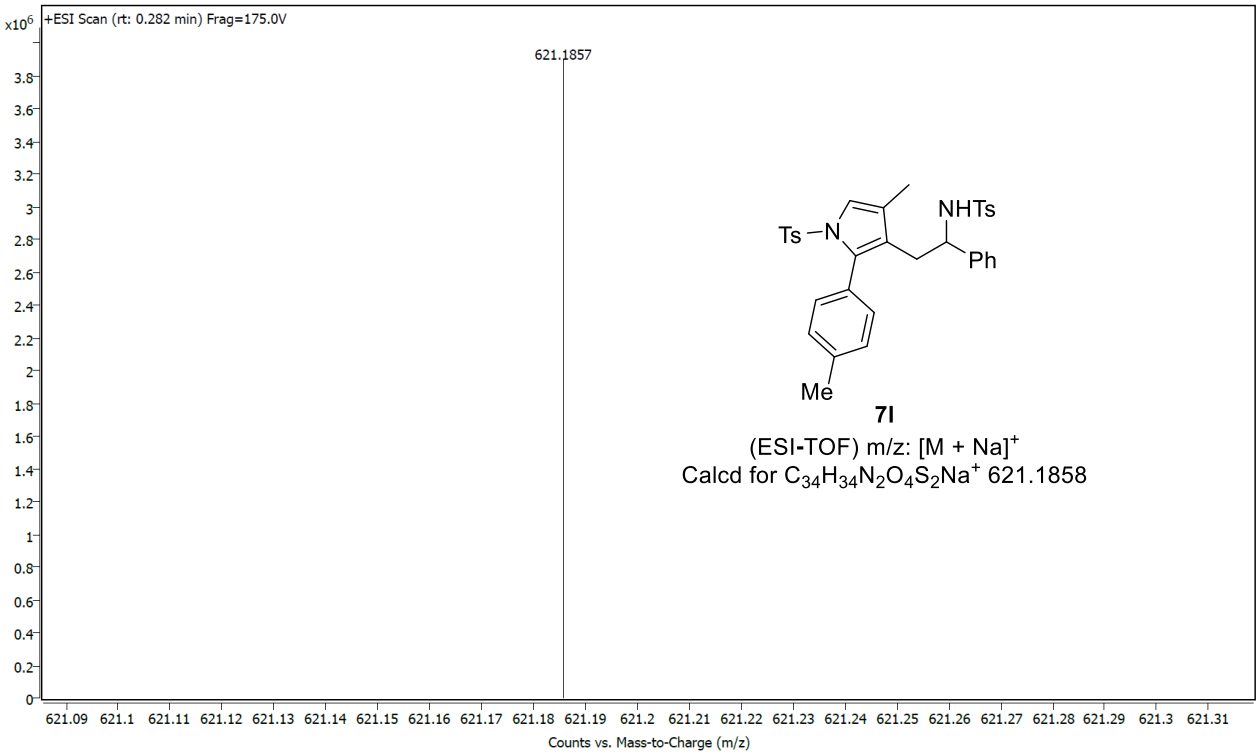
7l

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



7l

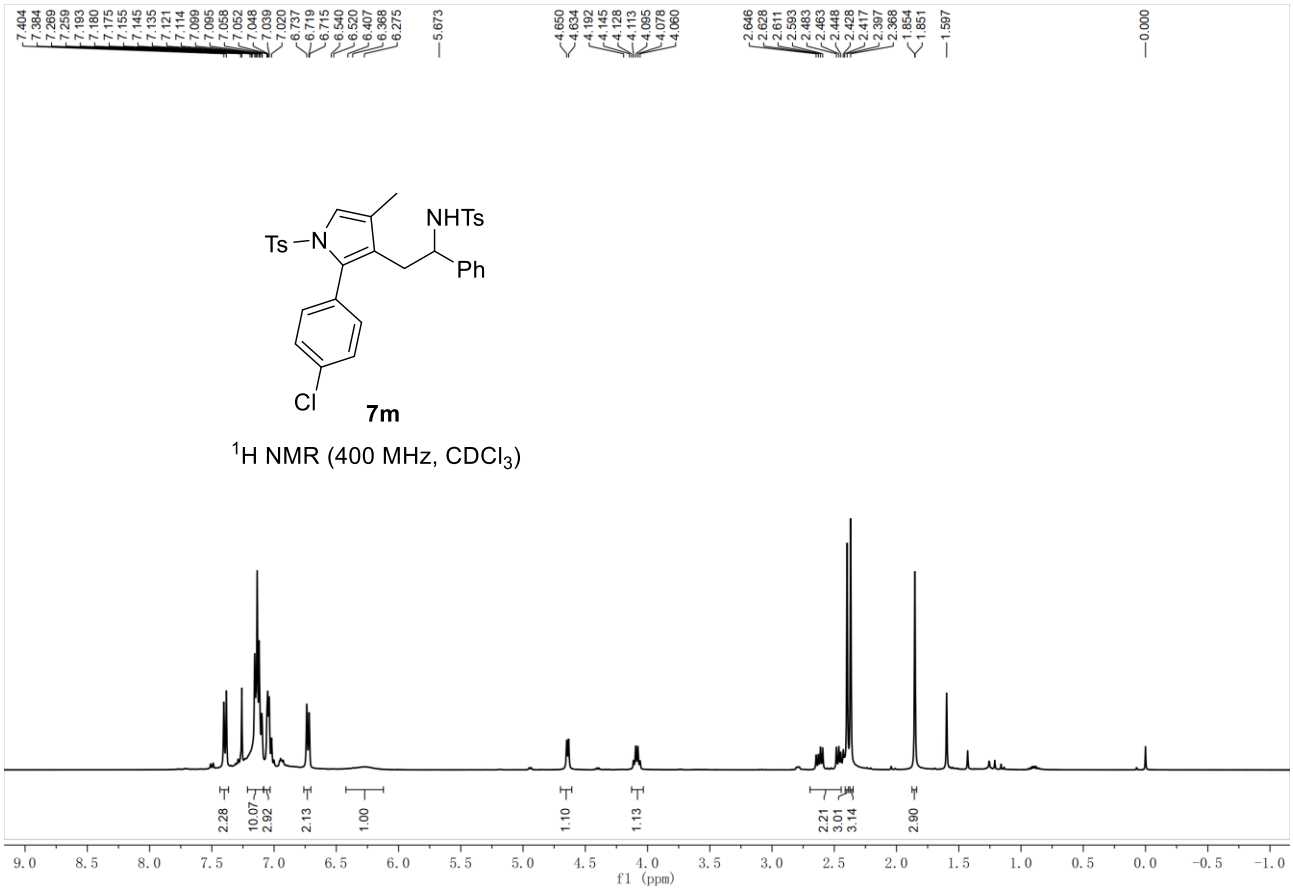
^{13}C NMR (100 MHz, $CDCl_3$)

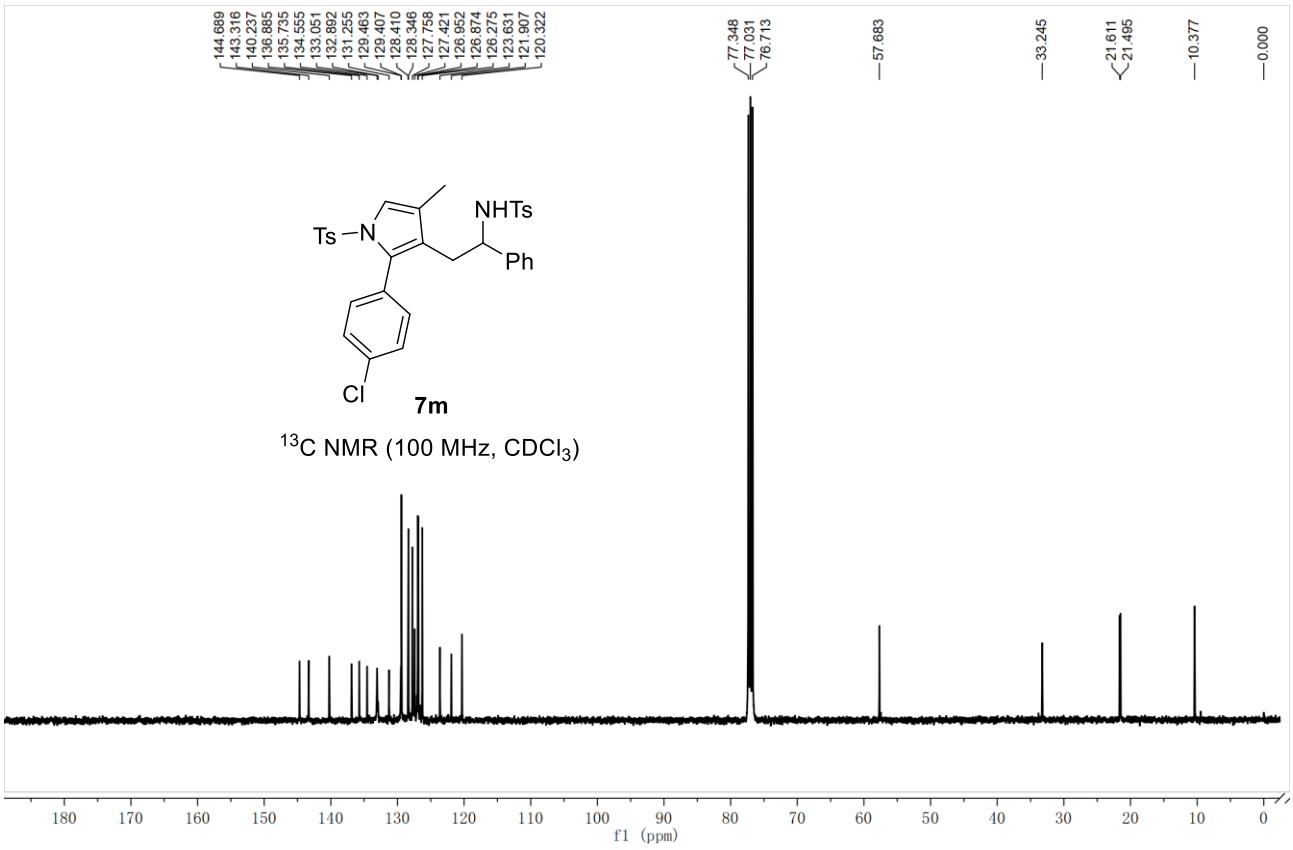


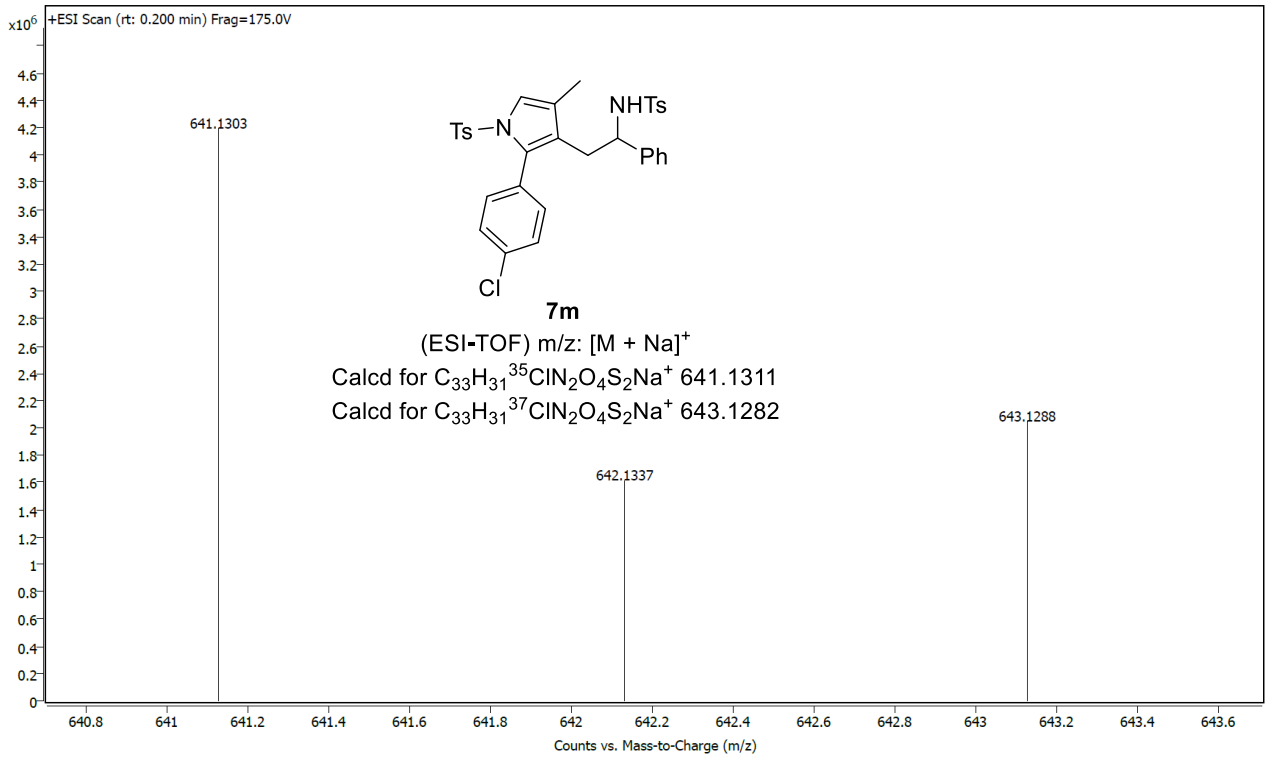
7l

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858


7.404
7.384
7.269
7.259
7.193
7.180
7.175
7.155
7.145
7.135
7.121
7.114
7.099
7.085
7.058
7.052
7.048
7.039
7.020
6.737
6.719
6.715
6.540
6.520
6.407
6.368
6.275
5.673
4.650
4.634
4.192
4.145
4.128
4.113
4.095
4.078
4.060
2.646
2.628
2.611
2.593
2.483
2.463
2.448
2.428
2.417
2.397
2.368
1.854
1.851
1.597
0.000
NHTs
Ts
N
Ph
Cl
7m
1H NMR (400 MHz, CDCl3)
2.28
10.07
2.92
2.13
1.00
1.10
1.13
2.21
3.01
3.14
2.90
f1 (ppm)


144.689
143.316
140.237
136.885
135.735
134.555
133.051
132.892
131.255
129.463
129.407
128.410
128.346
127.758
127.421
126.952
126.874
126.275
123.631
121.907
120.322
77.348
77.031
76.713
57.683
33.245
21.611
21.495
10.377
0.000
NHTs
Ts
N
Ph
Cl
7m
13C NMR (100 MHz, CDCl3)
f1 (ppm)

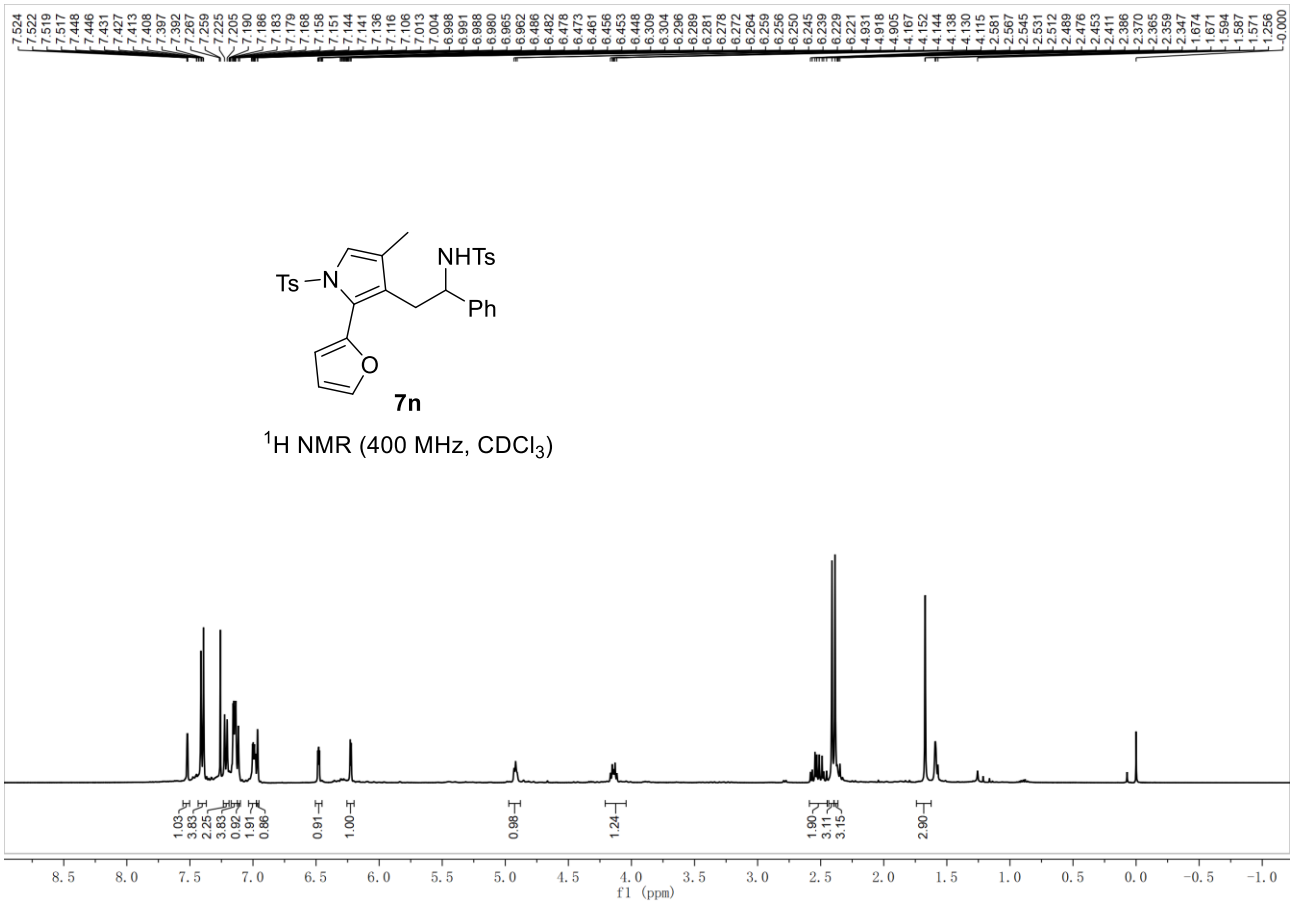


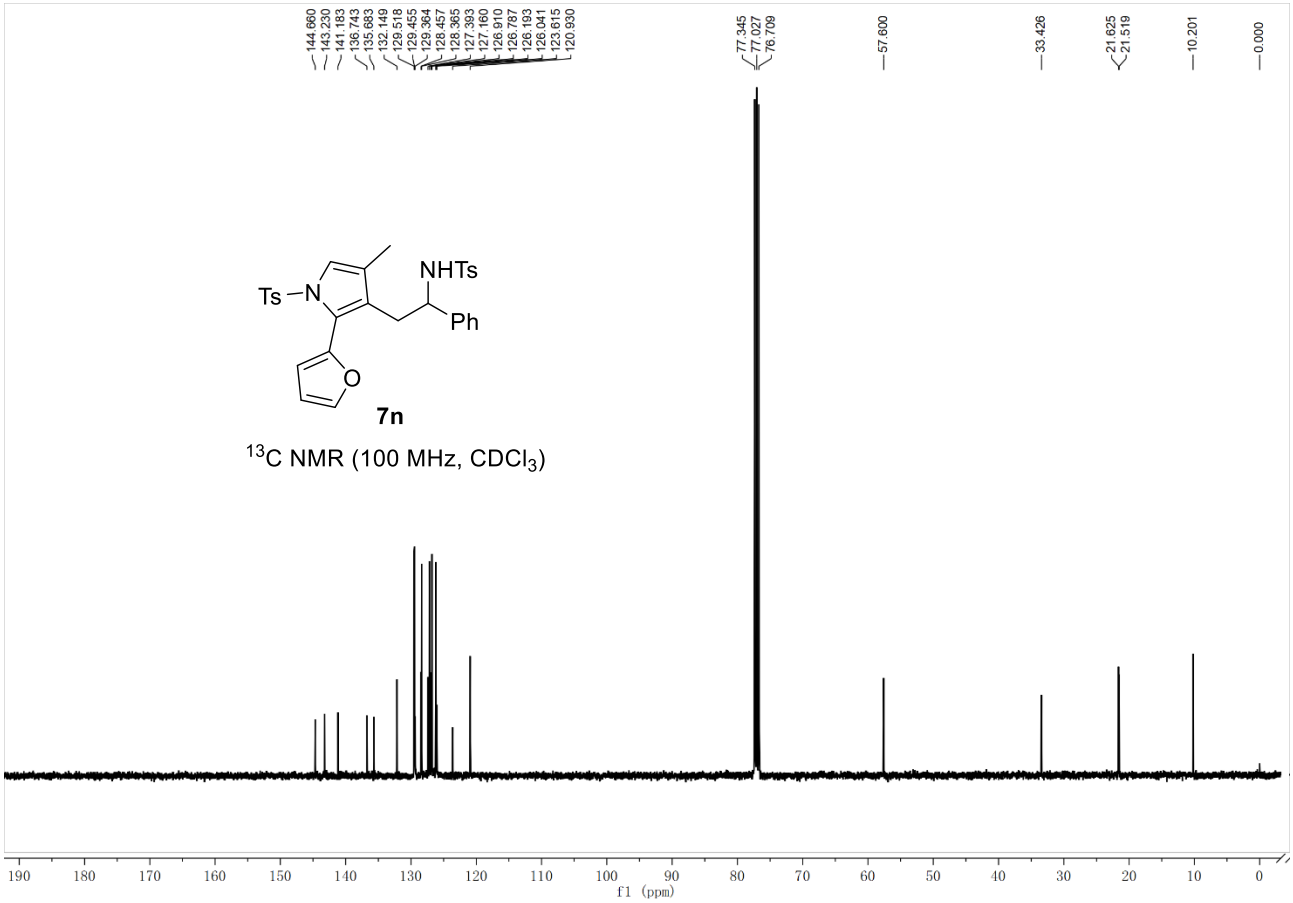
7m

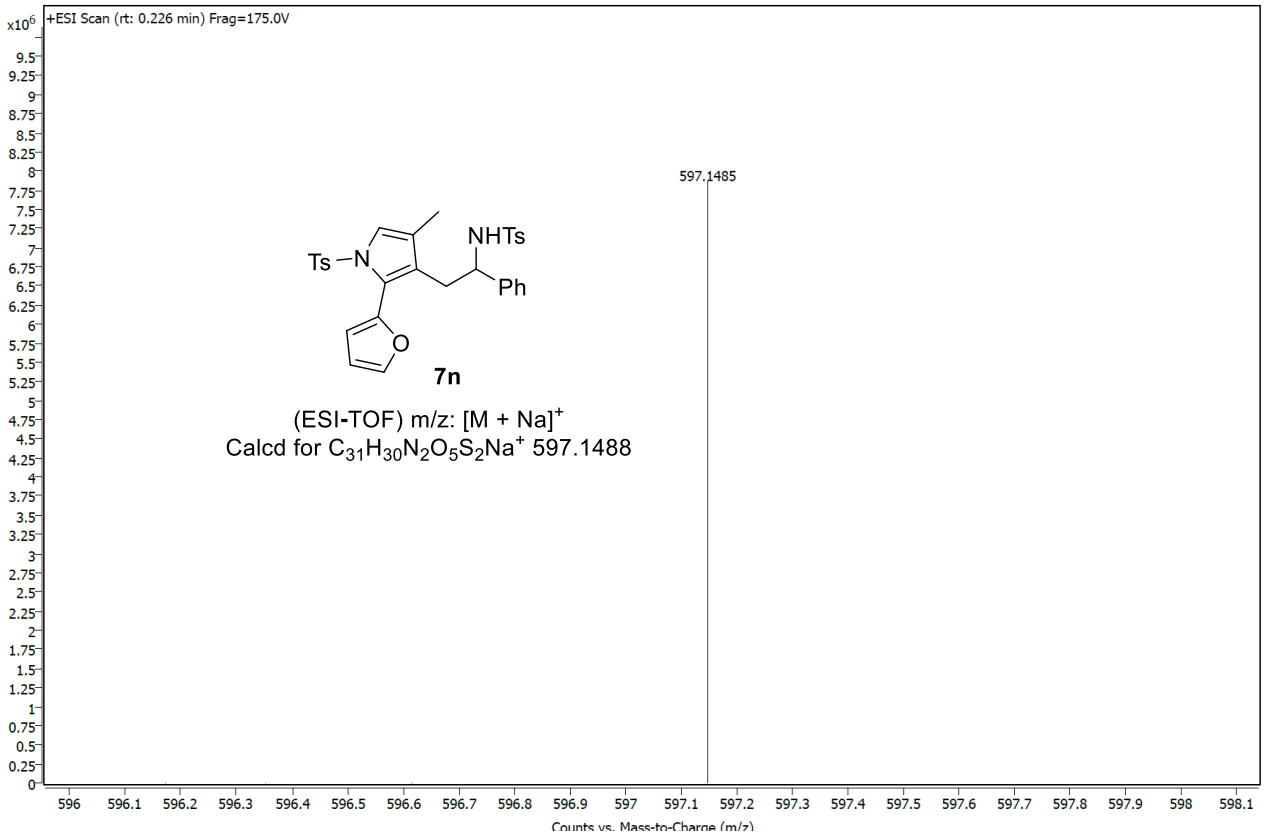
(ESI-TOF) m/z: $[M + Na]^+$

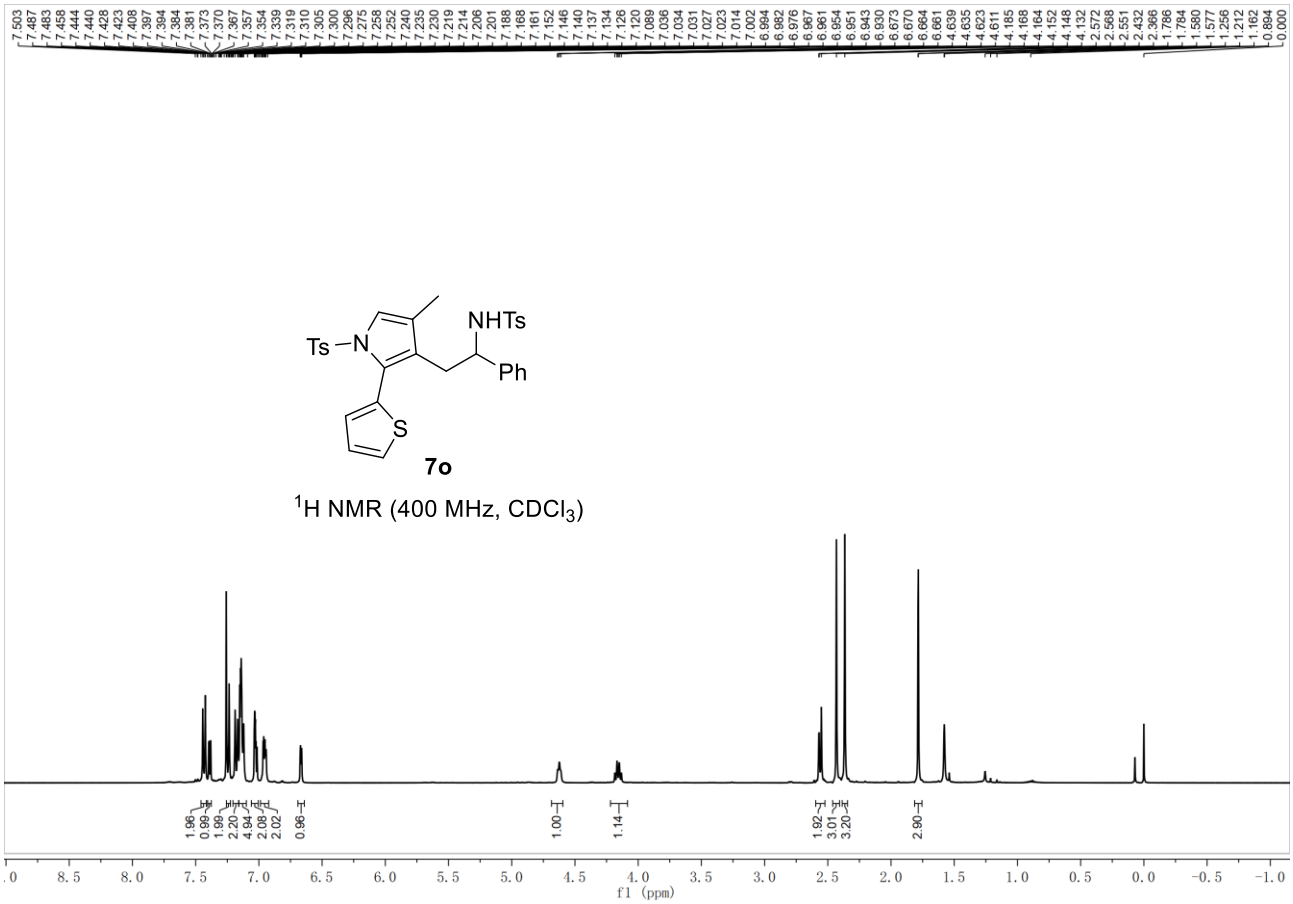
Calcd for $C_{33}H_{31}{}^{35}ClN_2O_4S_2Na^+$ 641.1311

Calcd for $C_{33}H_{31}{}^{37}ClN_2O_4S_2Na^+$ 643.1282


NHTs
Ts
N
Ph
O
7n
1H NMR (400 MHz, CDCl3)
f1 (ppm)

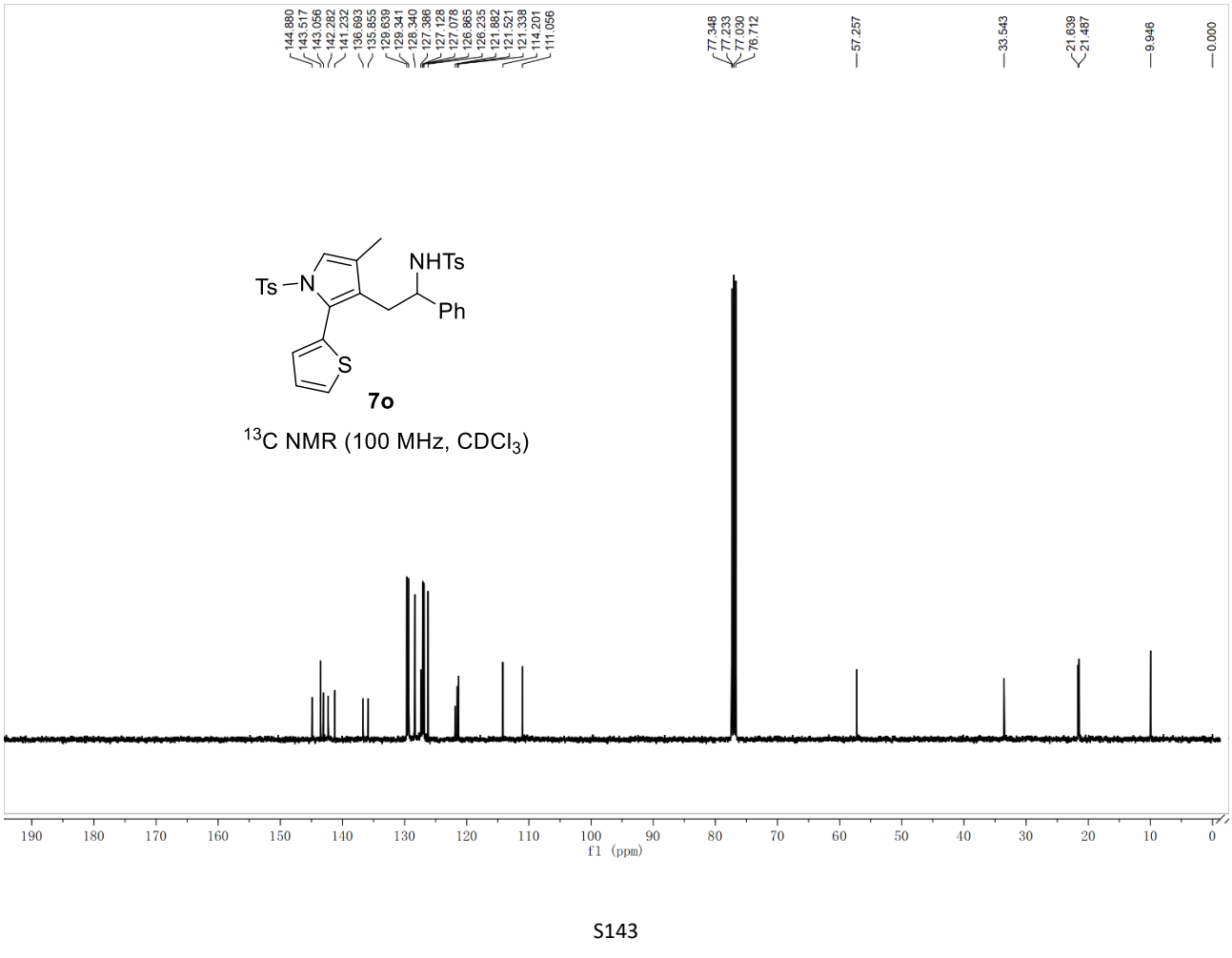

NHTs
Ts
N
Ph
O
7n
13C NMR (100 MHz, CDCl3)
f1 (ppm)


+ESI Scan (rt: 0.226 min) Frag=175.0V
x10^6
597.1485
NHTs
Ts
N
Ph
O
7n
(ESI-TOF) m/z: [M + Na]+
Calcd for C31H30N2O5S2Na+ 597.1488
Counts vs. Mass-to-Charge (m/z)



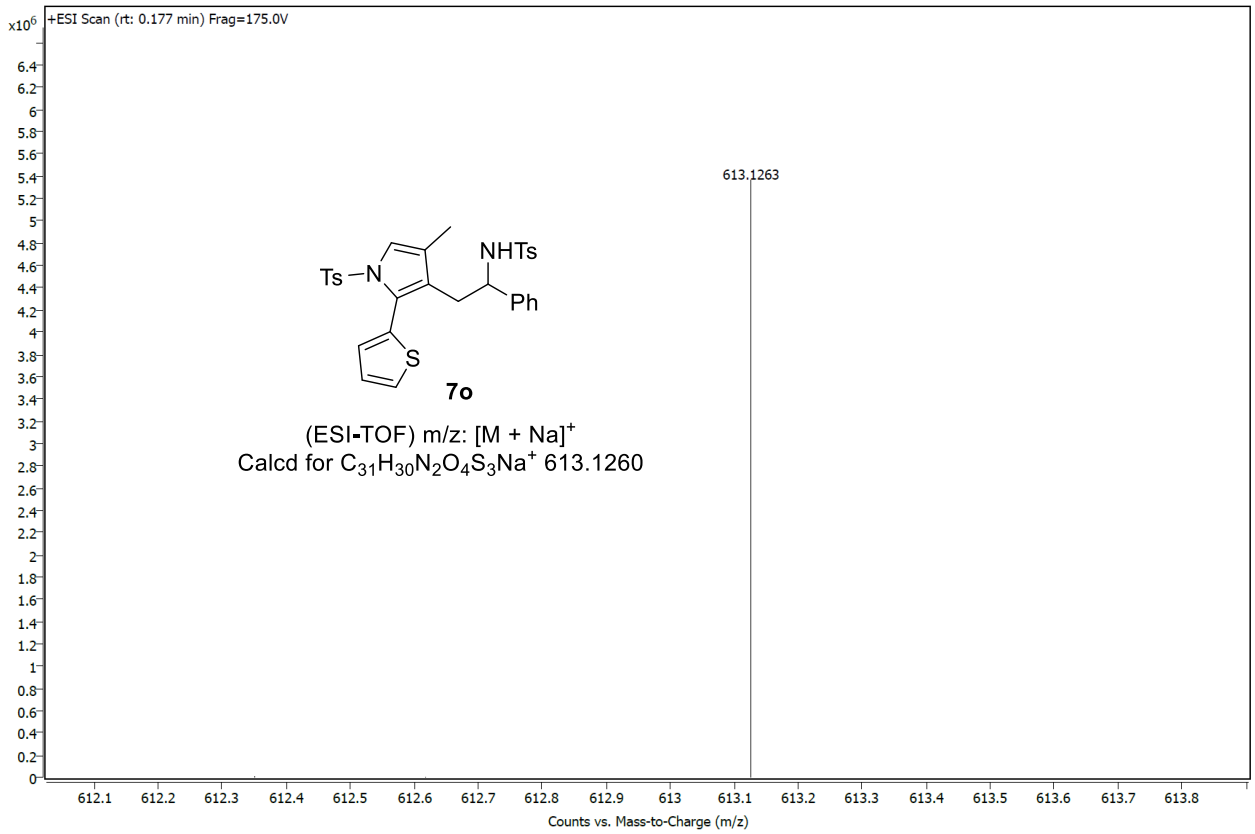
7o

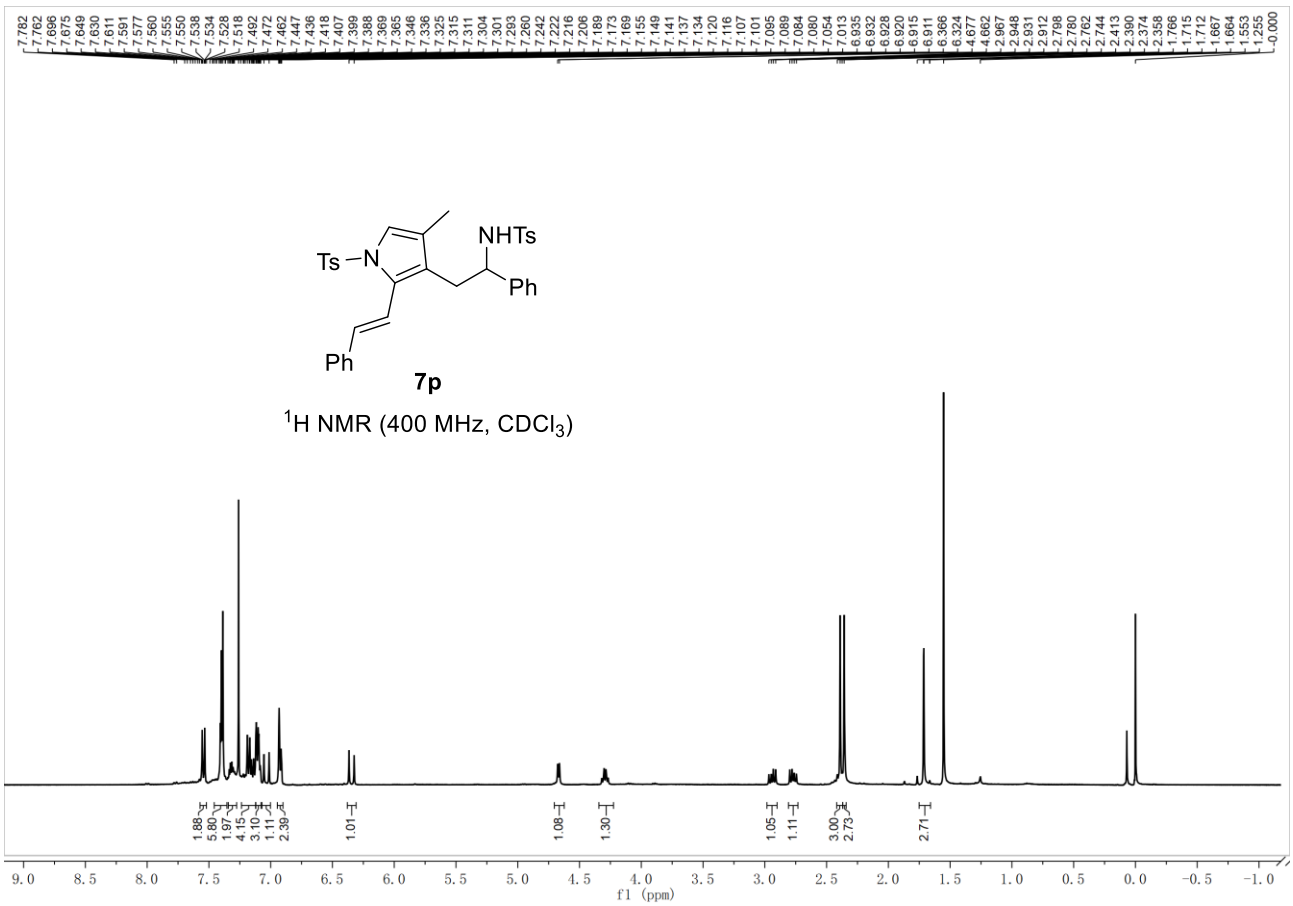
^{1}H NMR (400 MHz, $CDCl_3$)



7o

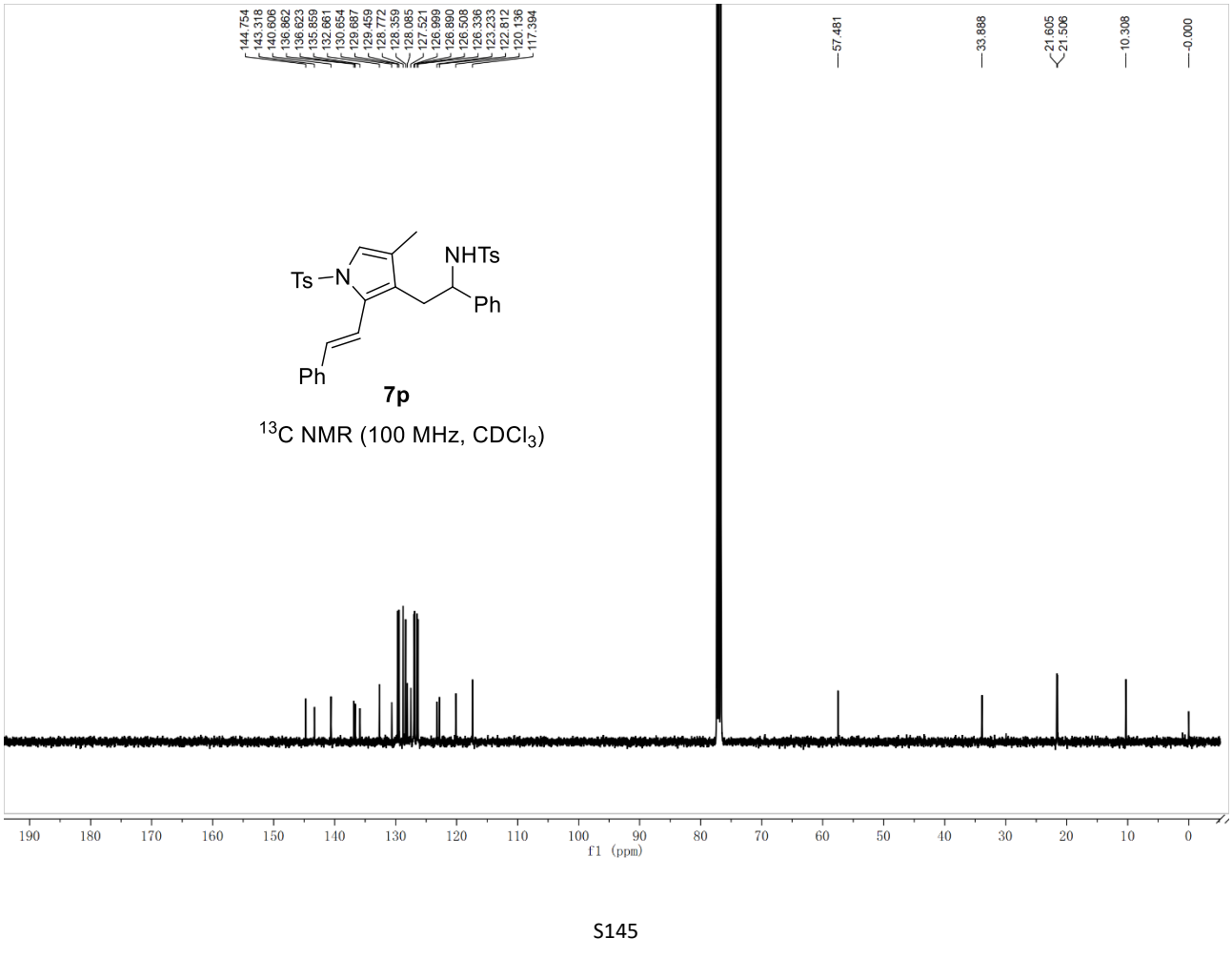
^{13}C NMR (100 MHz, $CDCl_3$)


+ESI Scan (rt: 0.177 min) Frag=175.0V
x10^6
613.1263
Ts
N
NHTs
Ph
S
7o
(ESI-TOF) m/z: [M + Na]+
Calcd for C31H30N2O4S3Na+ 613.1260
Counts vs. Mass-to-Charge (m/z)



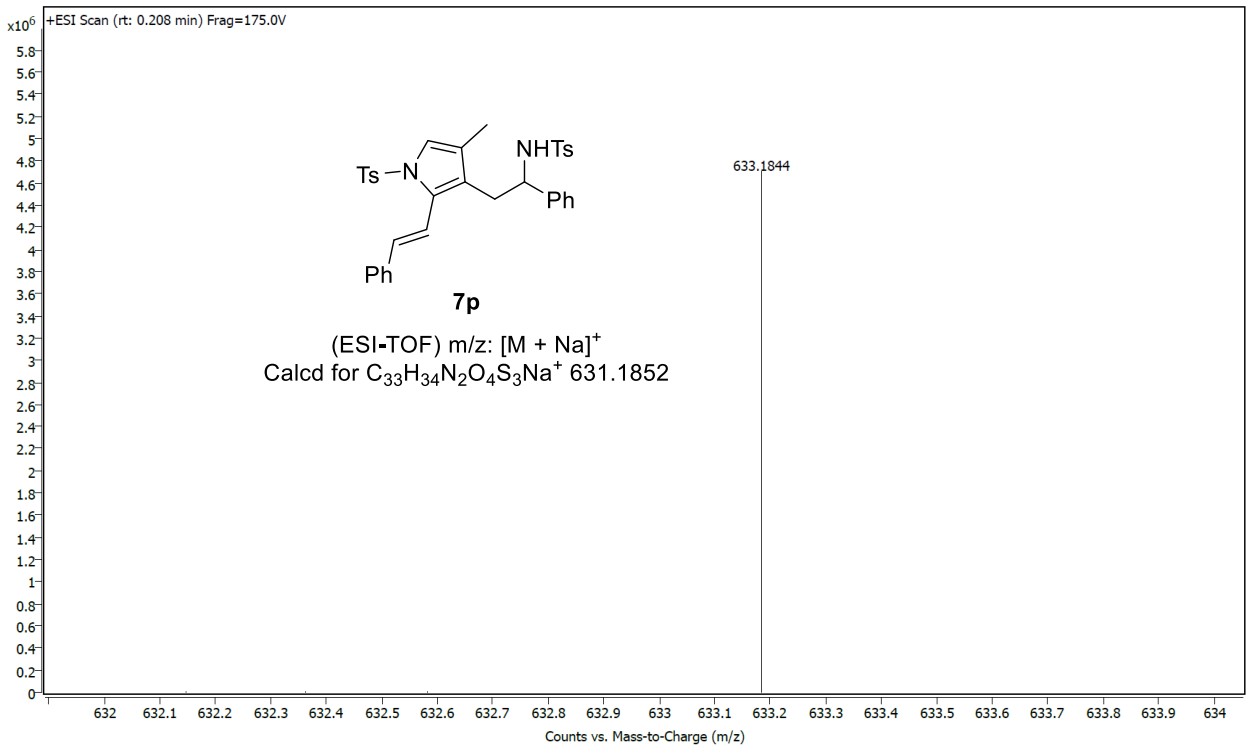
7p

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



7p

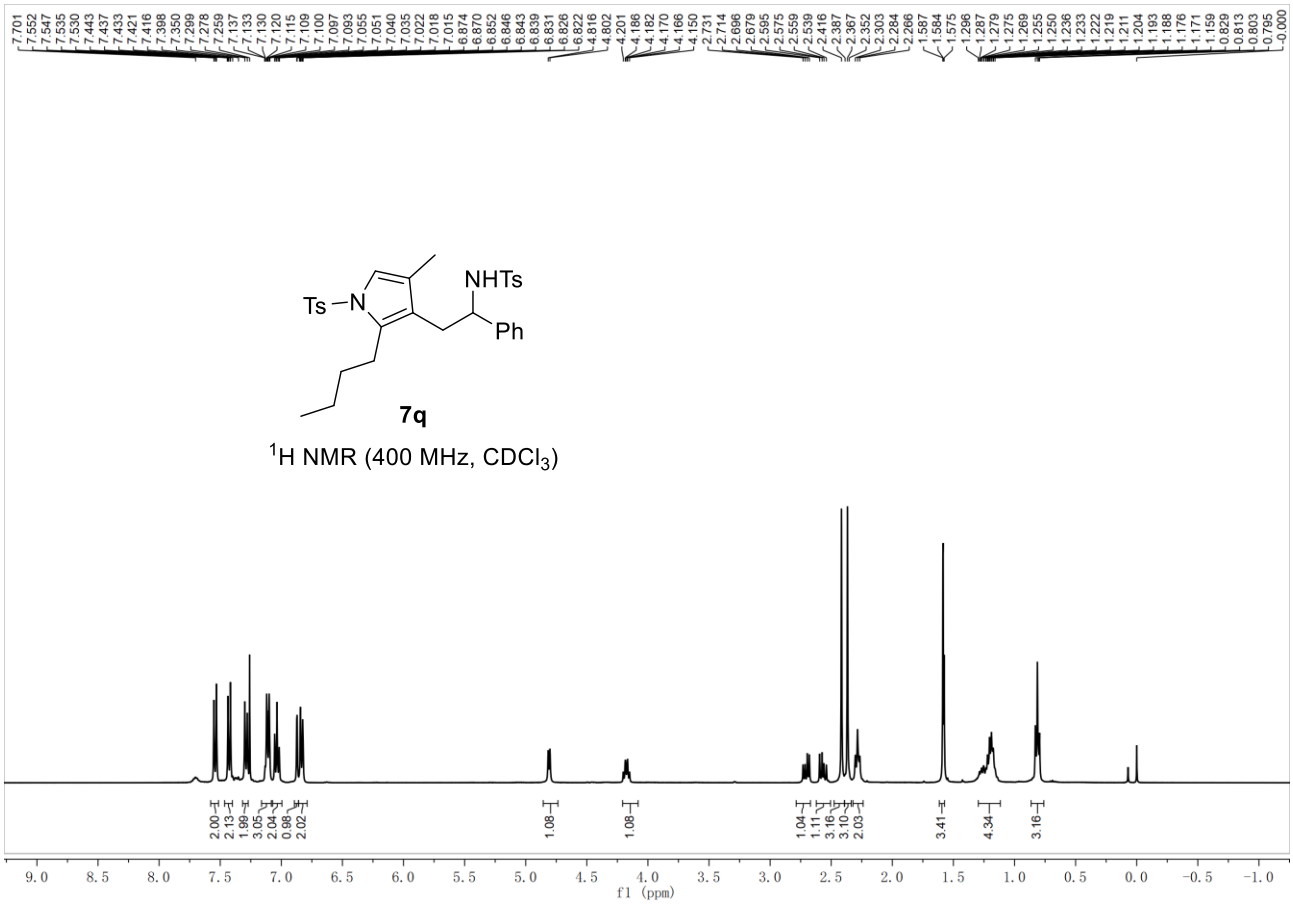
^{13}C NMR (100 MHz, $CDCl_3$)



7p

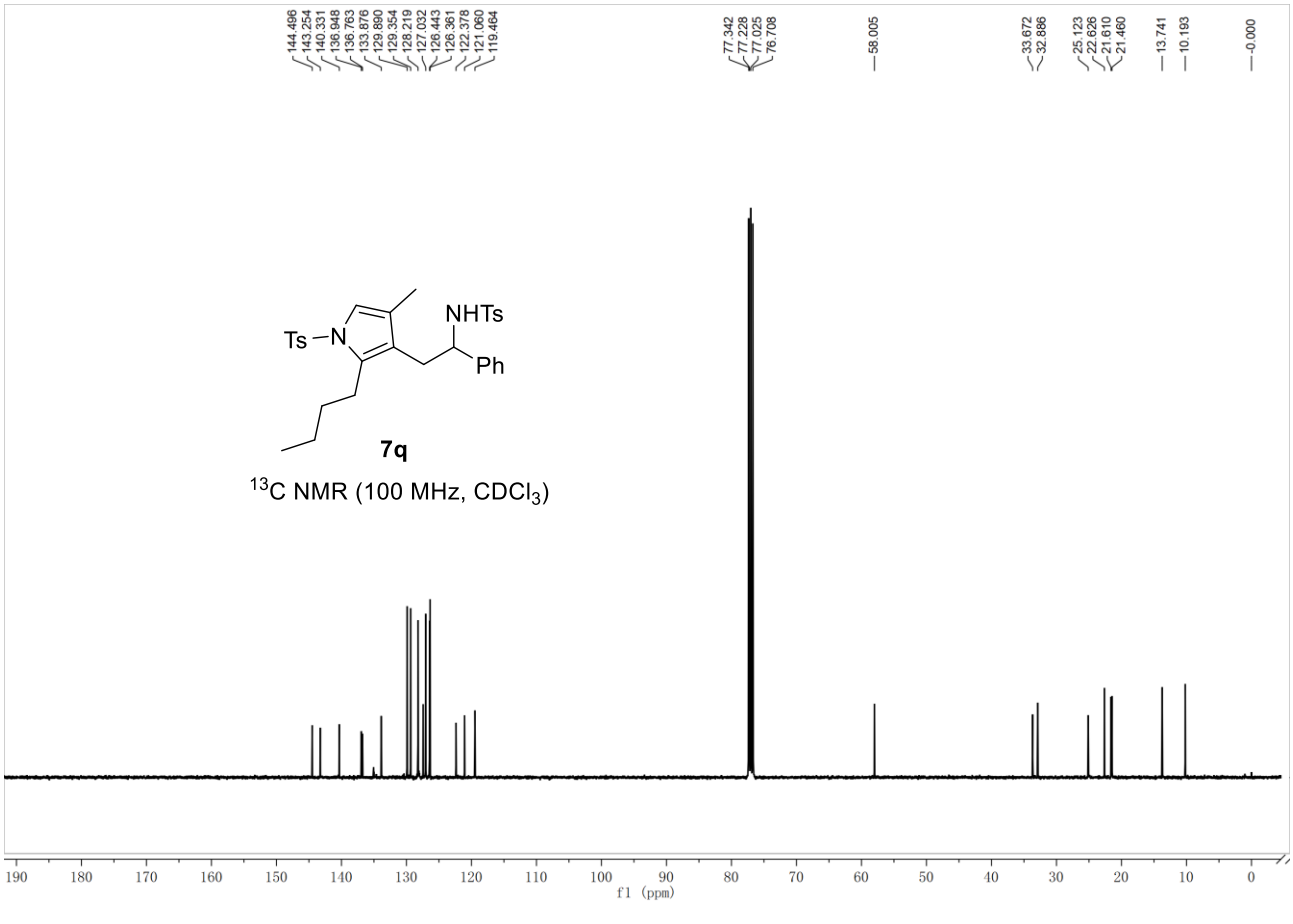
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{33}H_{34}N_2O_4S_3Na^+$ 631.1852



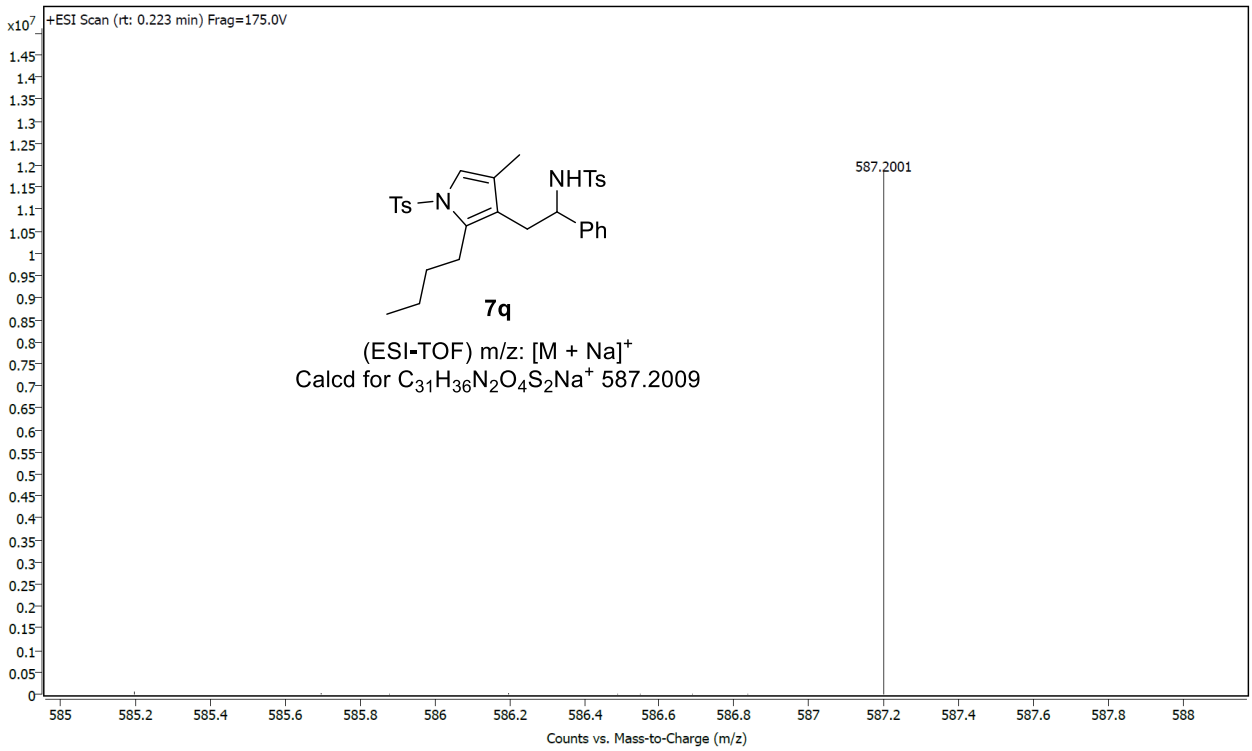
7q

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



7q

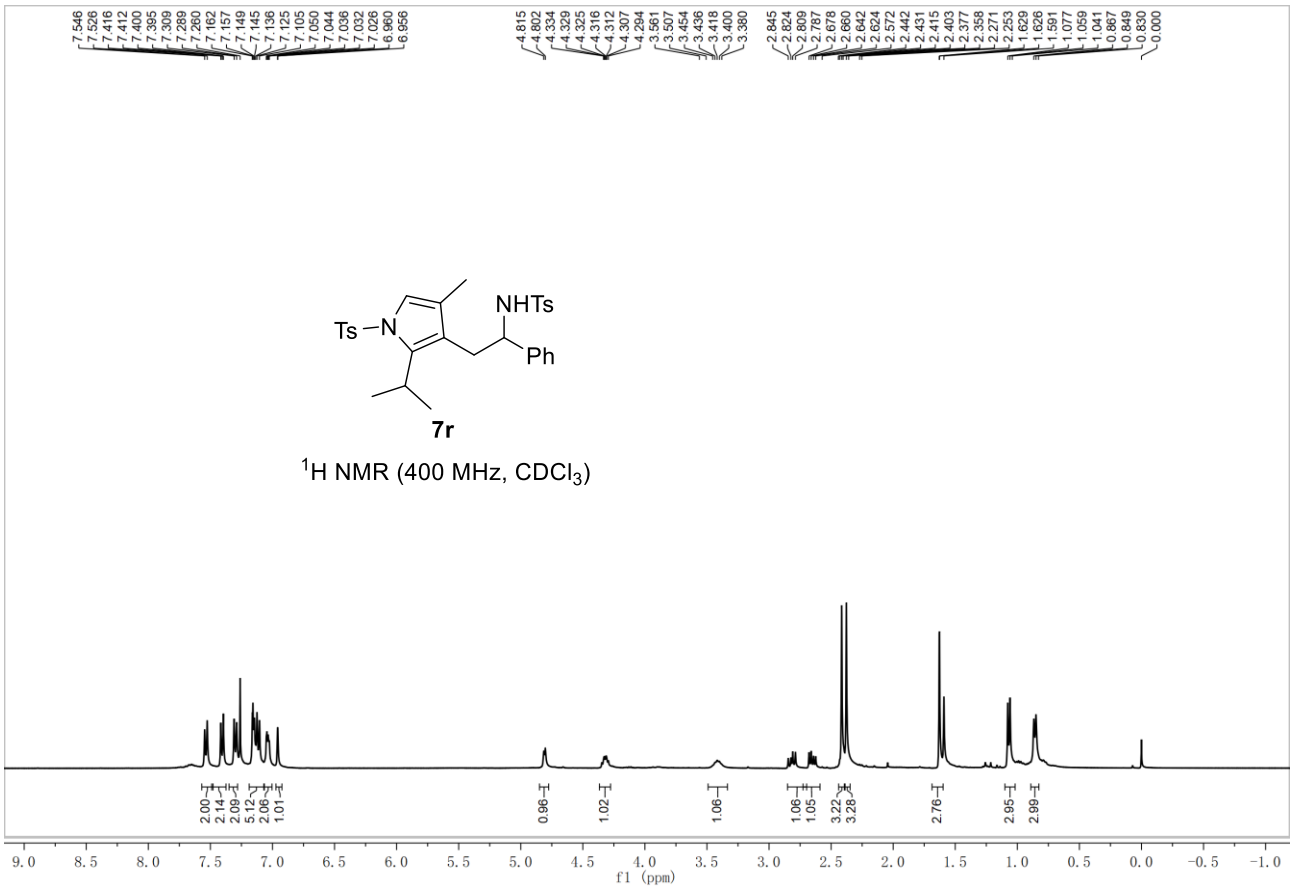
^{13}C NMR (100 MHz, $CDCl_3$)



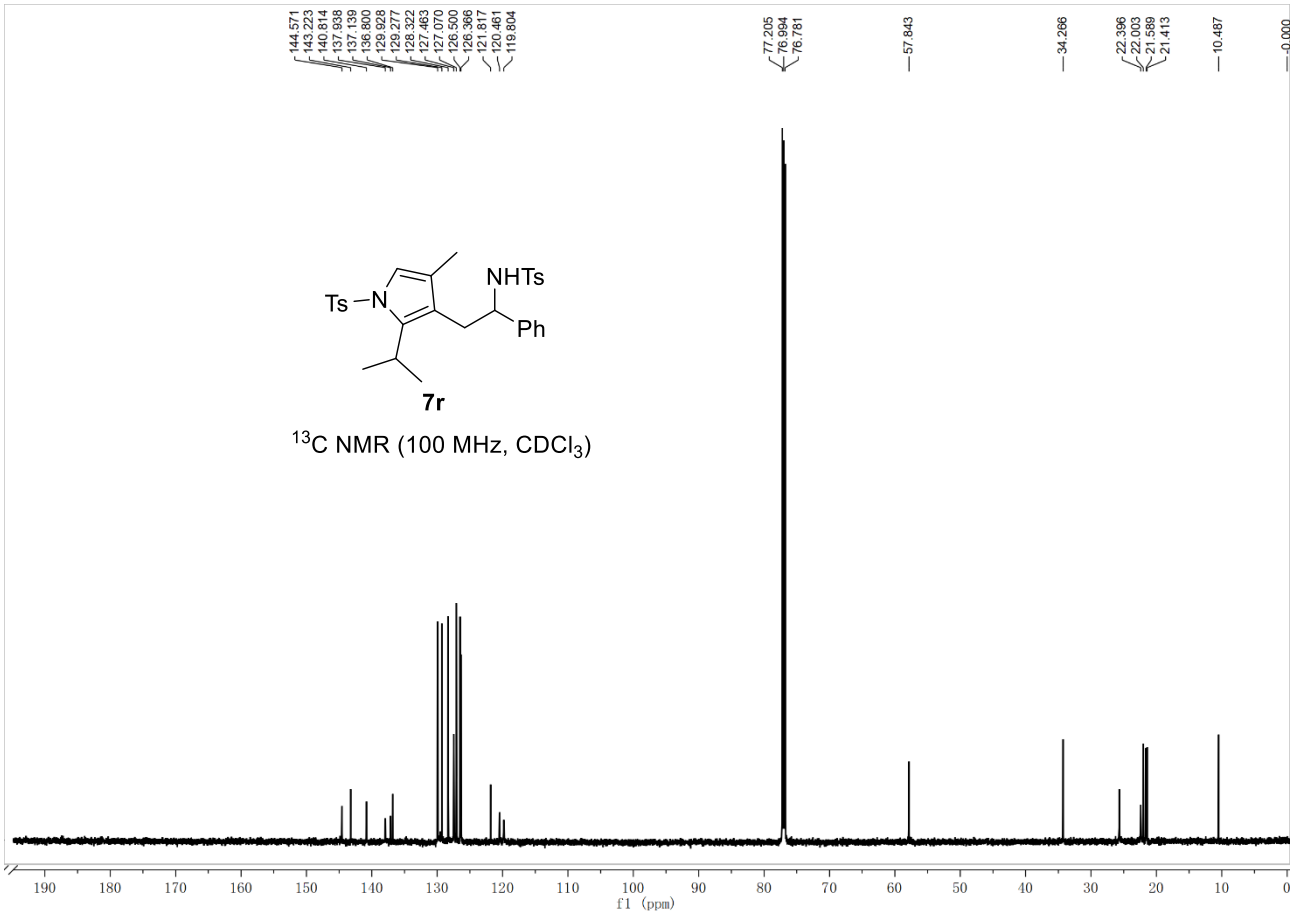
7q

(ESI-TOF) m/z: $[M + Na]^+$

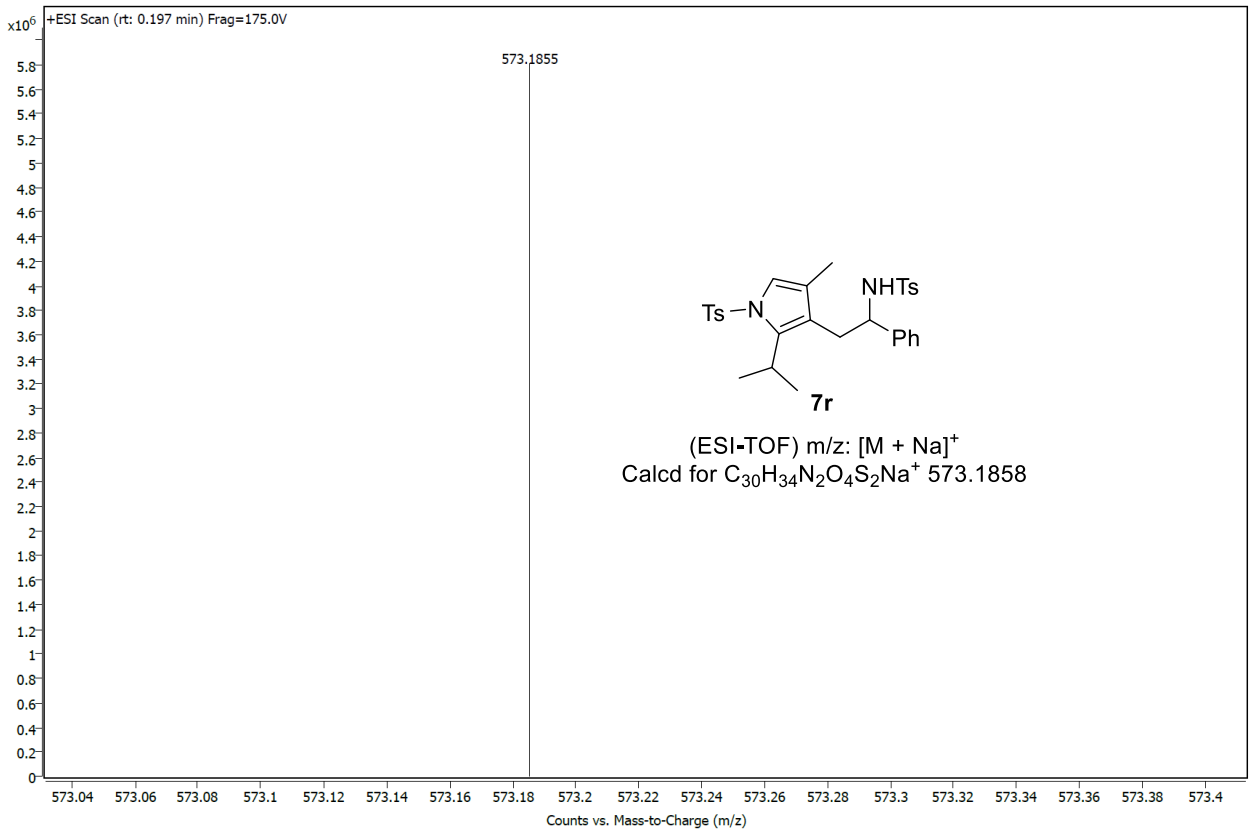
Calcd for $C_{31}H_{36}N_2O_4S_2Na^+$ 587.2009



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



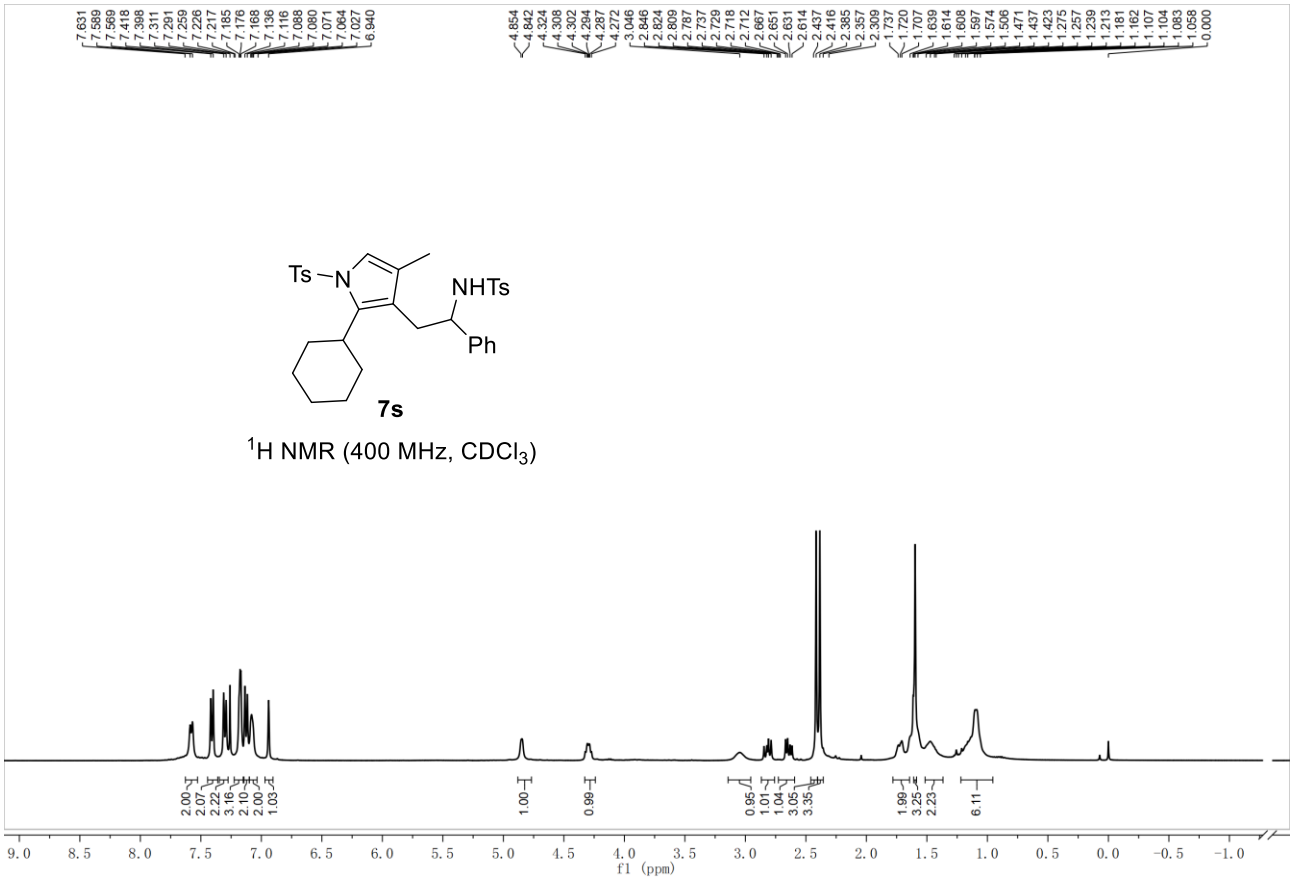
^{13}C NMR (100 MHz, $CDCl_3$)

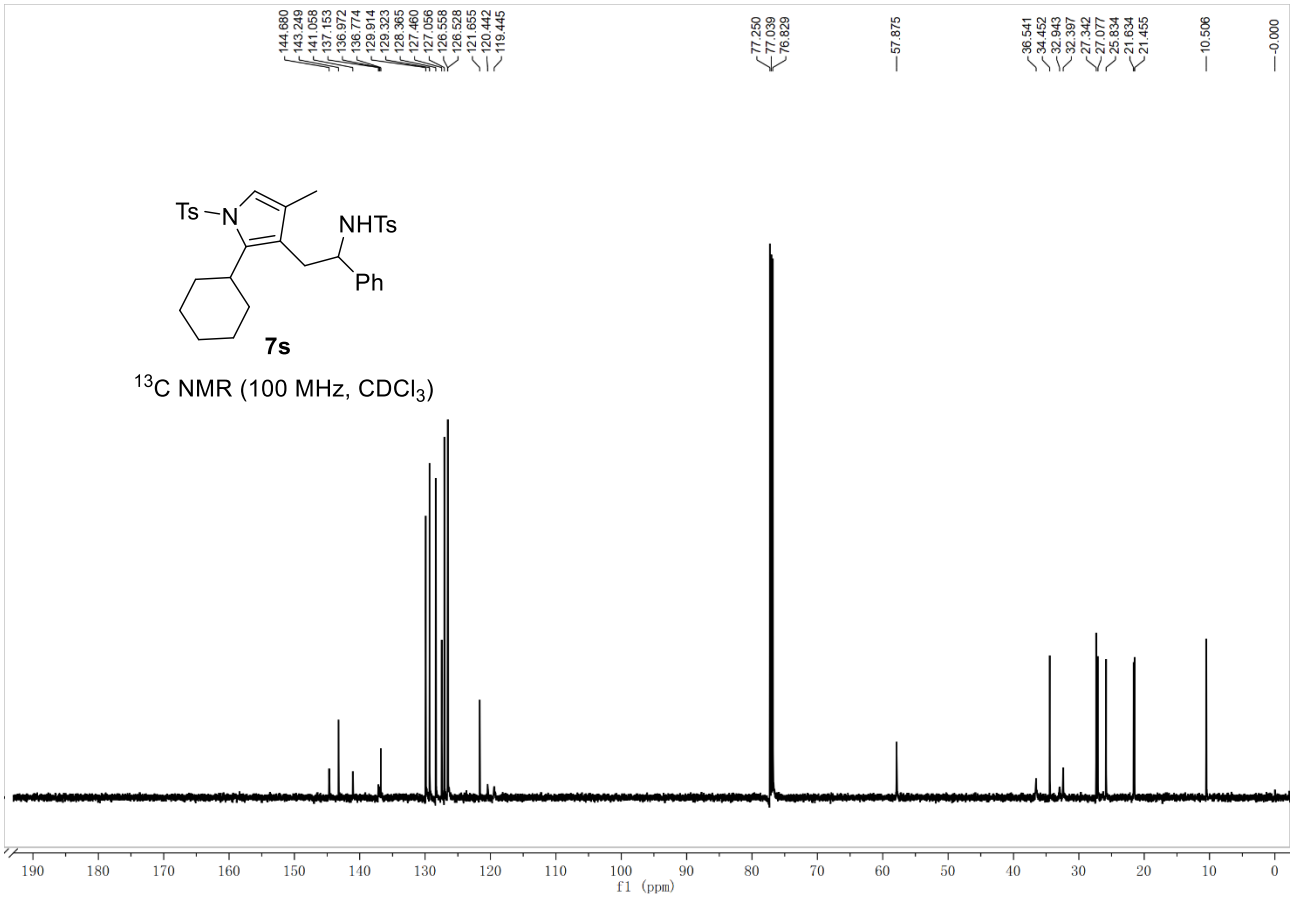


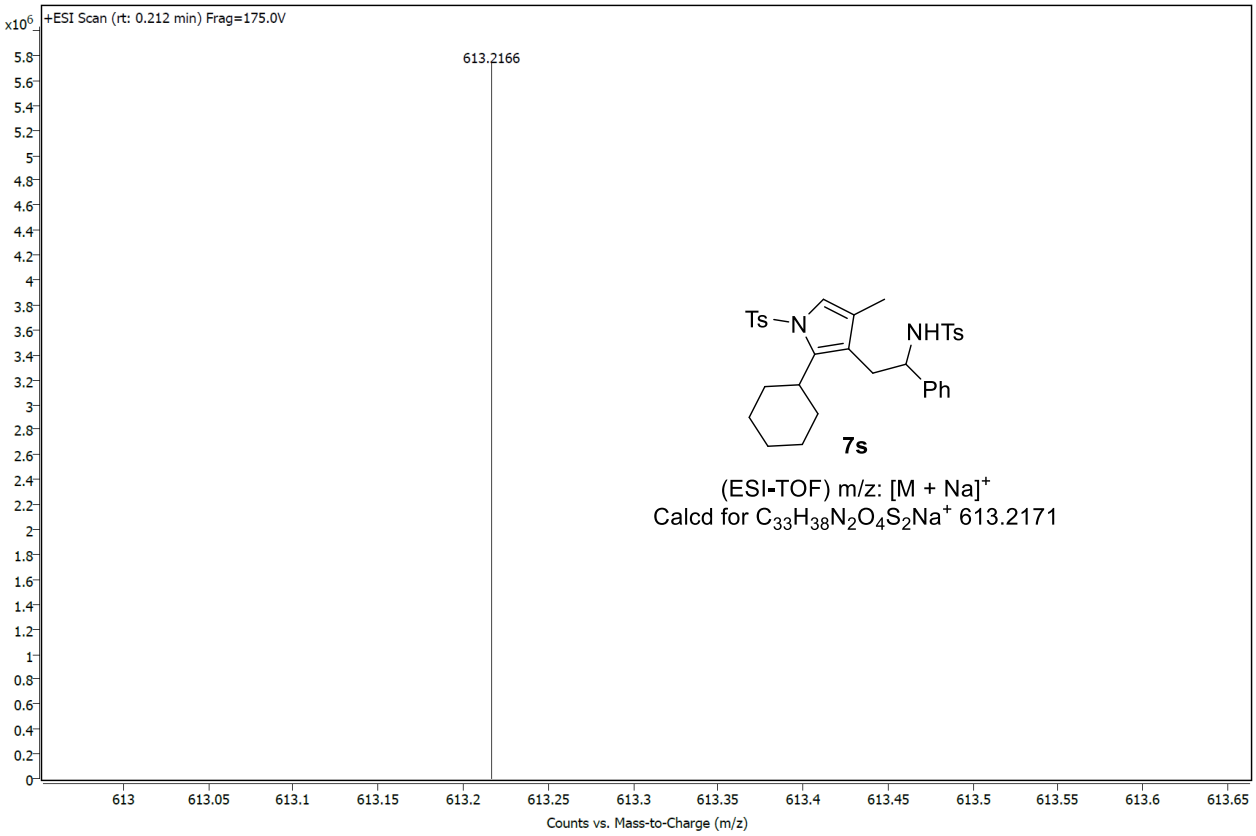
7r

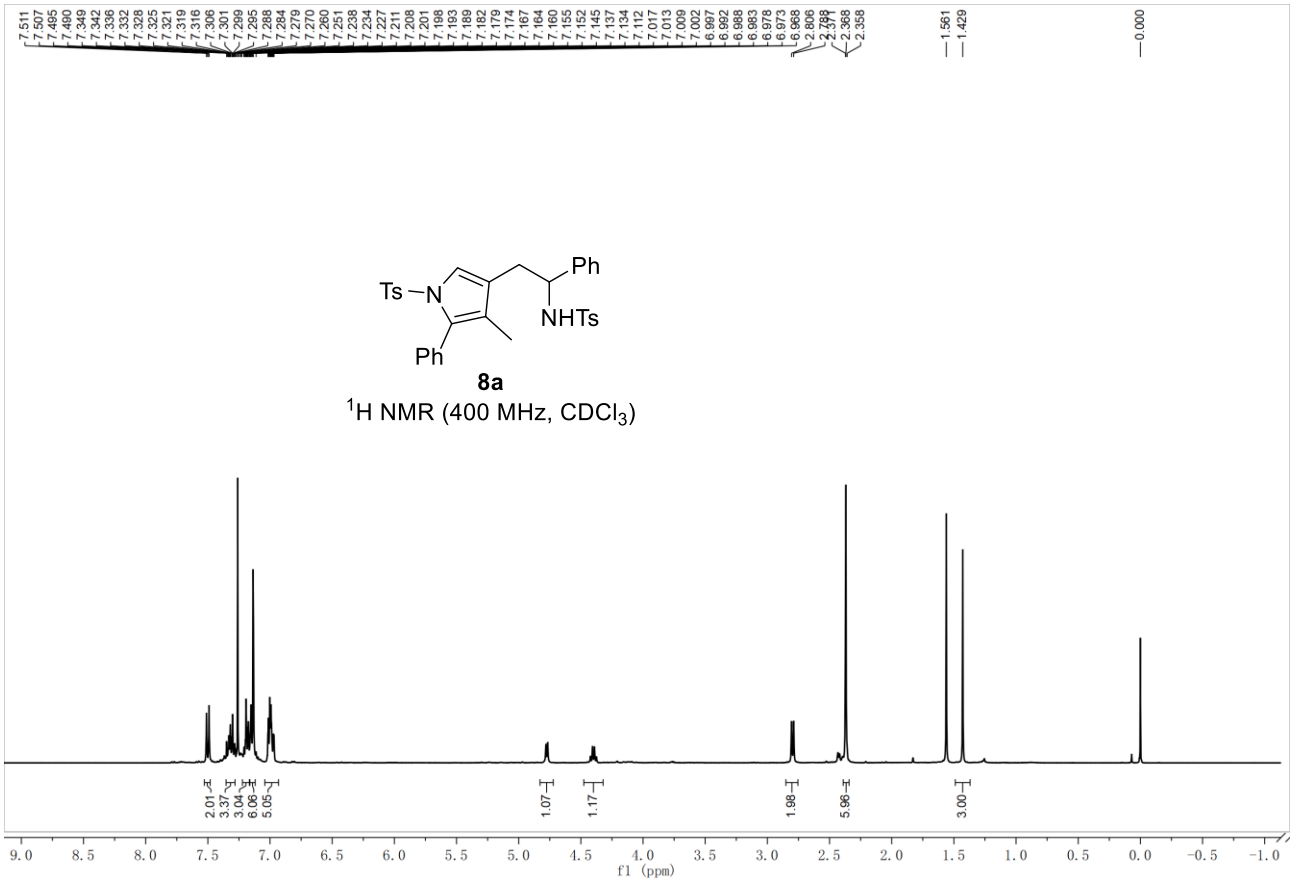
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{30}H_{34}N_2O_4S_2Na^+$ 573.1858


Ts
N
NHTs
Ph
7s
1H NMR (400 MHz, CDCl3)
f1 (ppm)

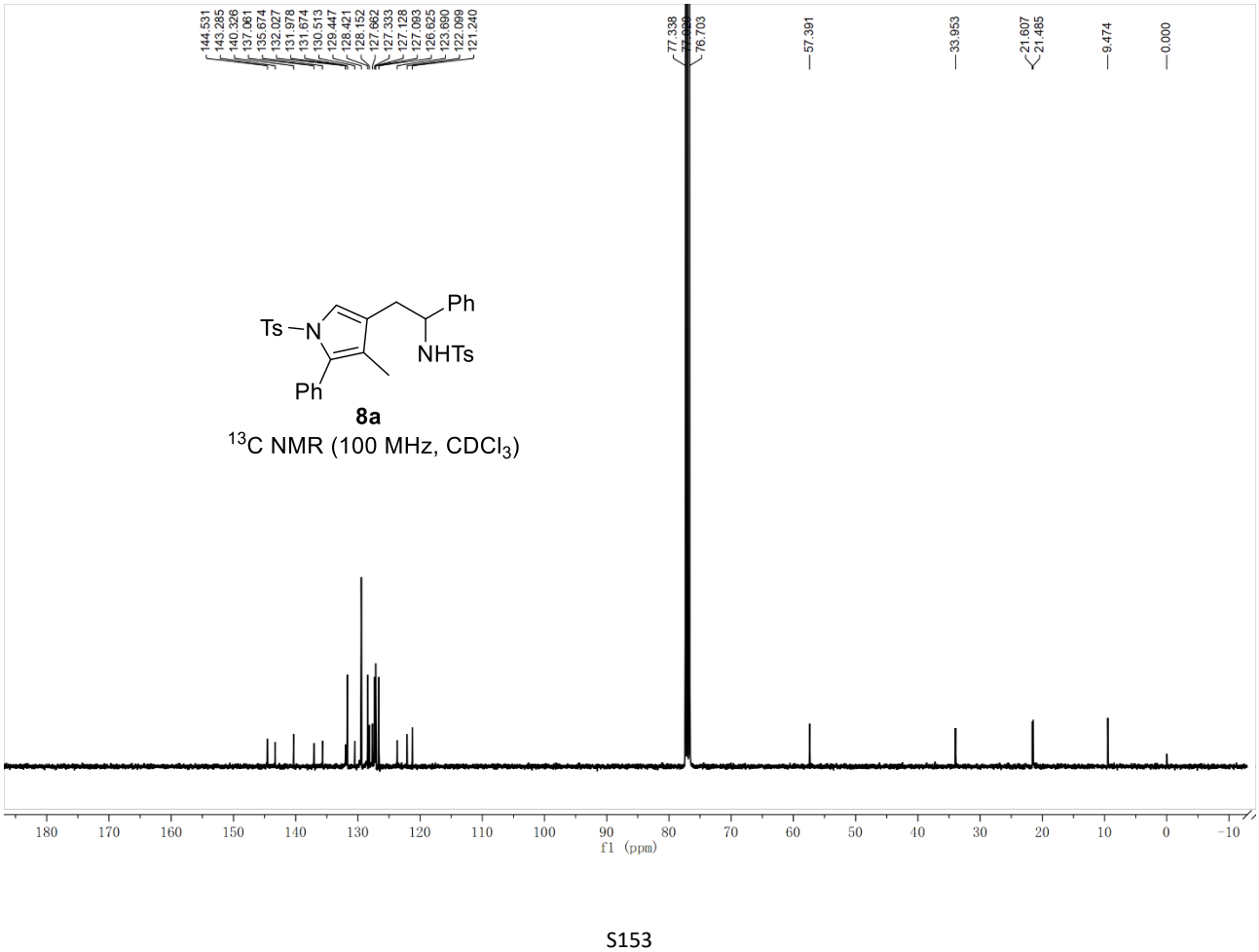

Ts
N
NHTs
Ph
7s
13C NMR (100 MHz, CDCl3)
f1 (ppm)


+ESI Scan (rt: 0.212 min) Frag=175.0V
x10^6
613.2166
Counts vs. Mass-to-Charge (m/z)
Ts
N
NHTs
Ph
7s
(ESI-TOF) m/z: [M + Na]+
Calcd for C33H38N2O4S2Na+ 613.2171



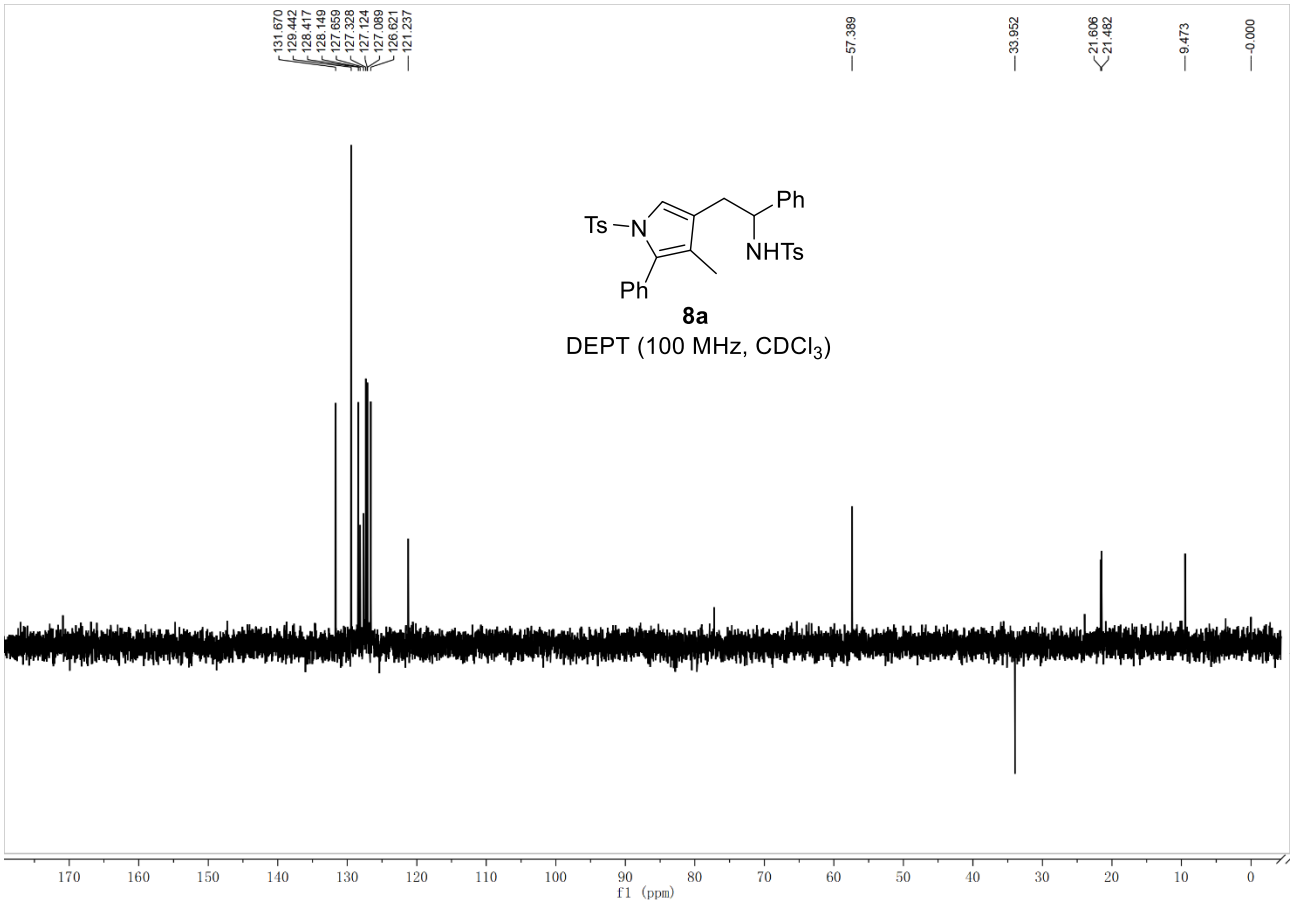
8a

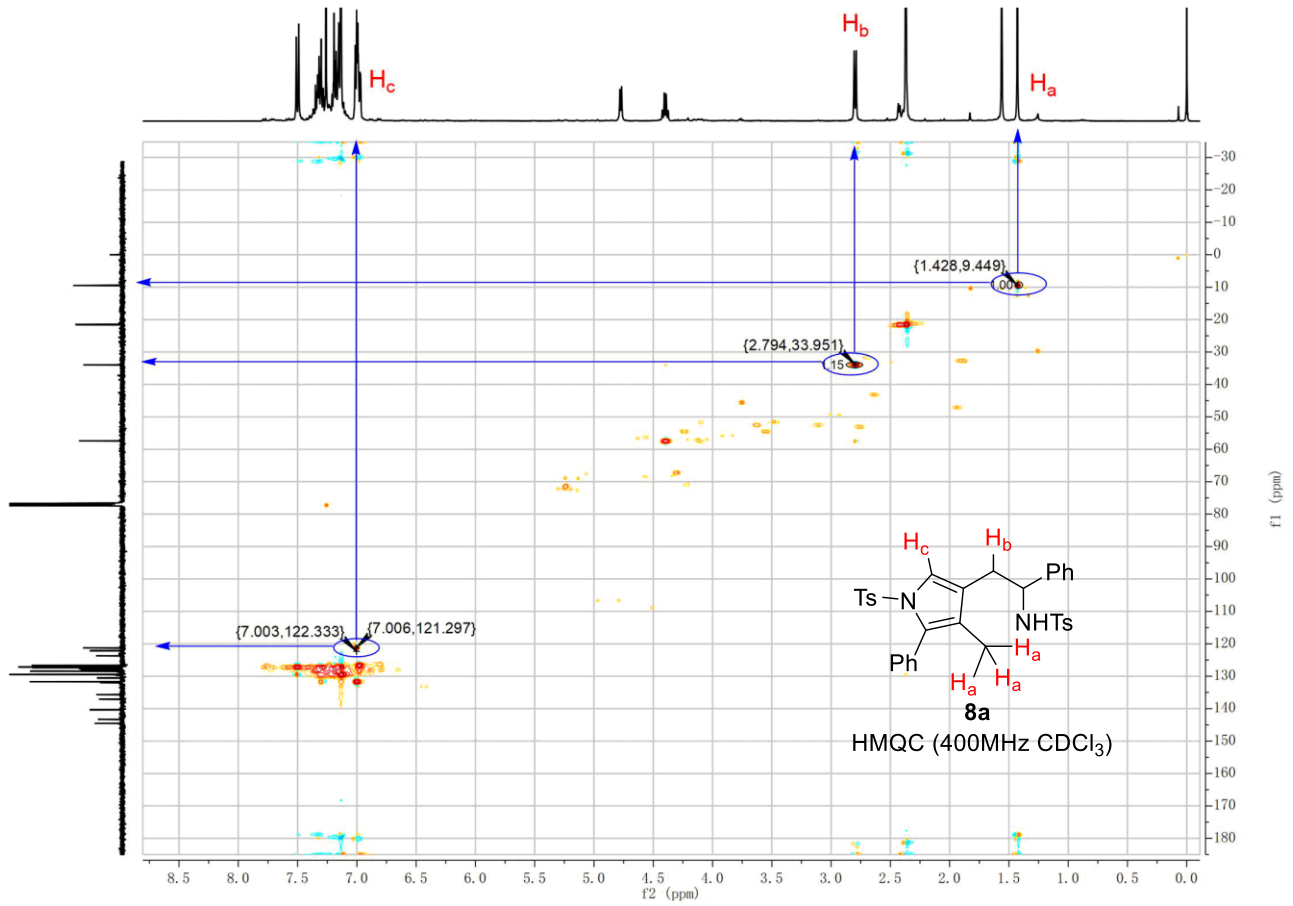
^{1}H NMR (400 MHz, $CDCl_3$)

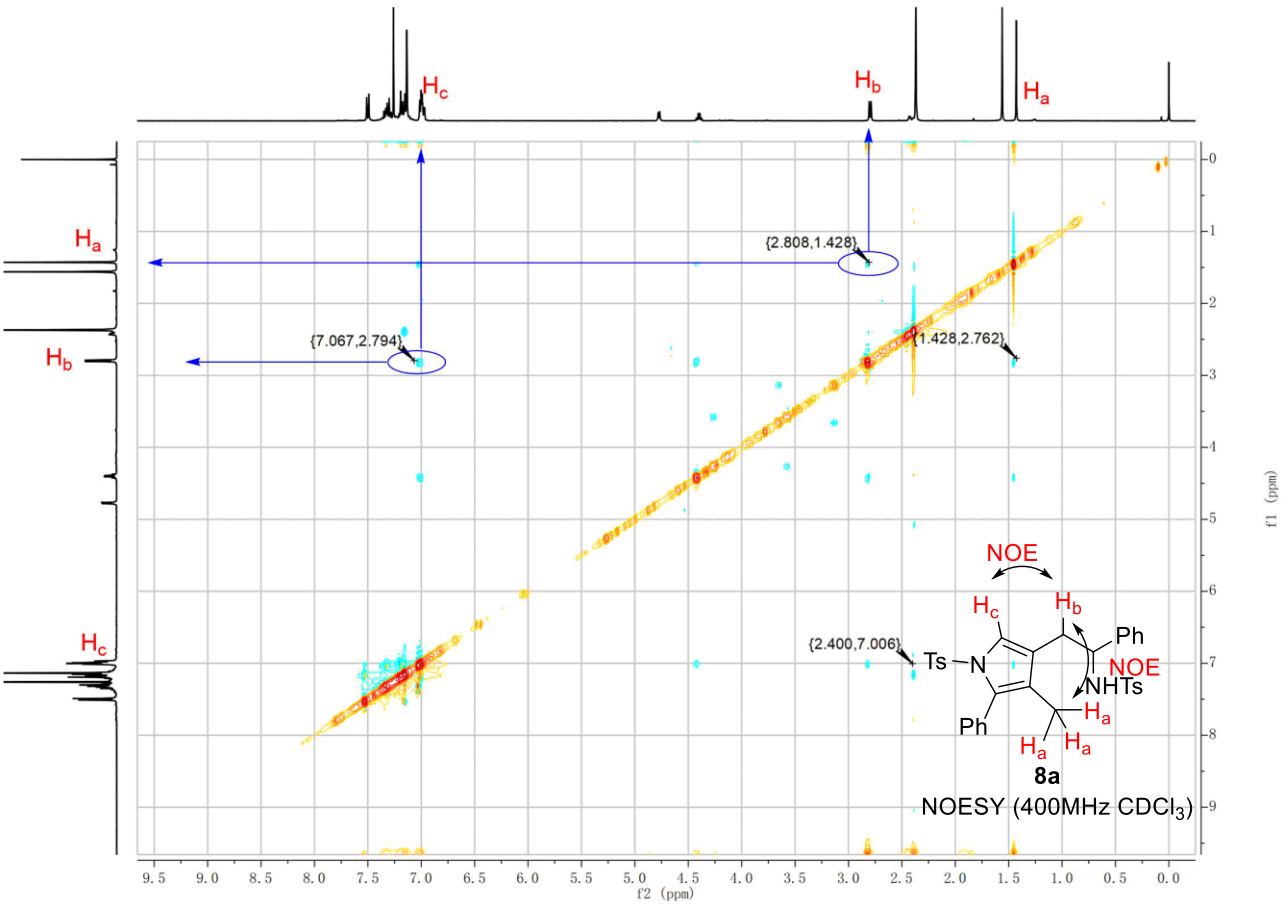


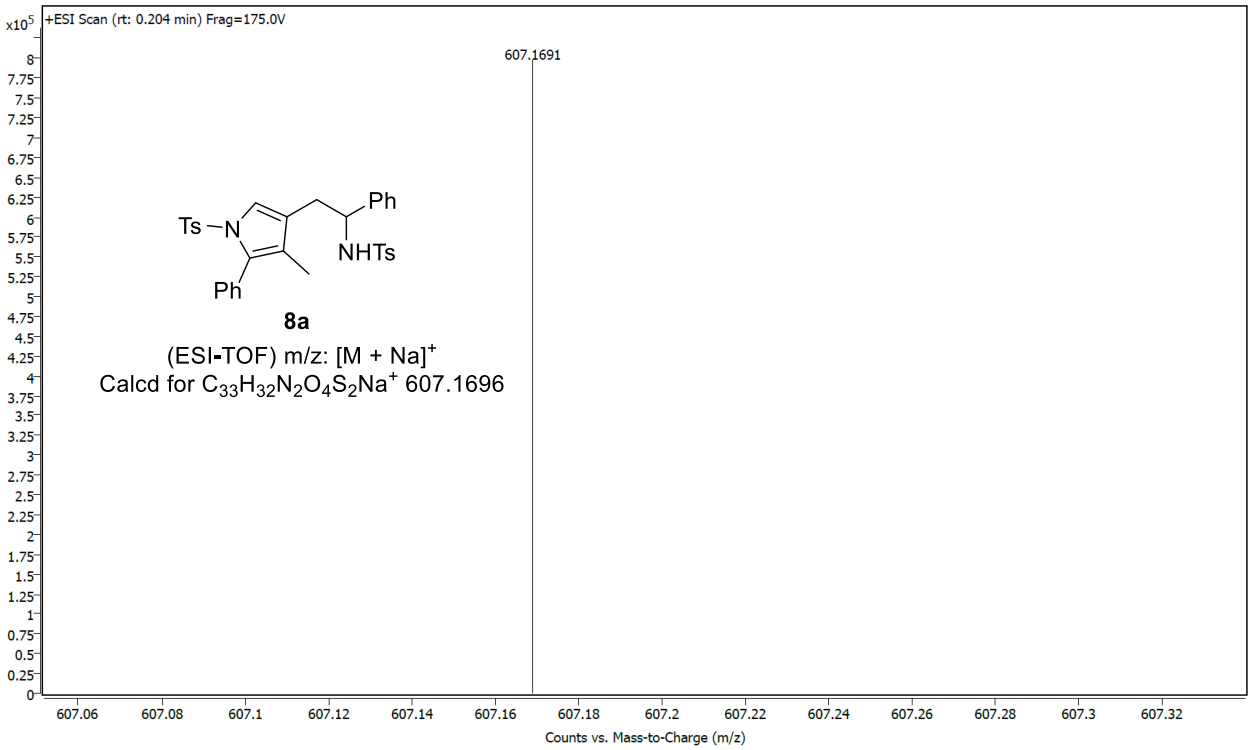
8a

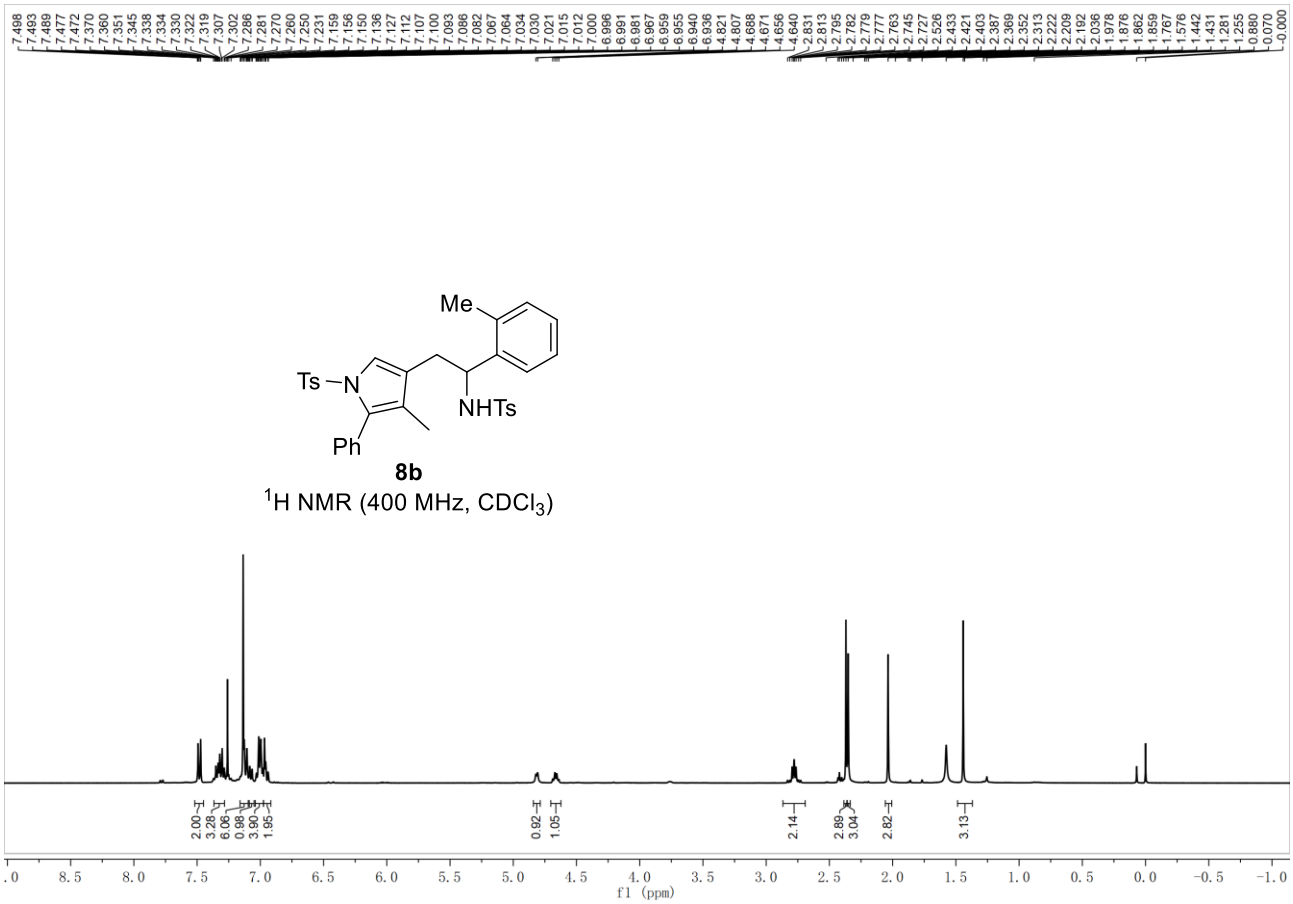
^{13}C NMR (100 MHz, $CDCl_3$)


131.670
129.442
128.417
128.149
127.659
127.328
127.124
127.089
126.621
121.237
57.389
33.952
21.606
21.482
9.473
0.000
Ts
N
Ph
NHTs
Ph
8a
DEPT (100 MHz, CDCl3)
f1 (ppm)


Hb
Hc
Ha
{1.428,9.449}
{2.794,33.951}
{7.003,122.333}
{7.006,121.297}
Hc
Hb
Ts
N
Ph
NHTs
Ph
Ha
Ha
Ha
8a
HMQC (400MHz CDCl3)
f2 (ppm)
f1 (ppm)

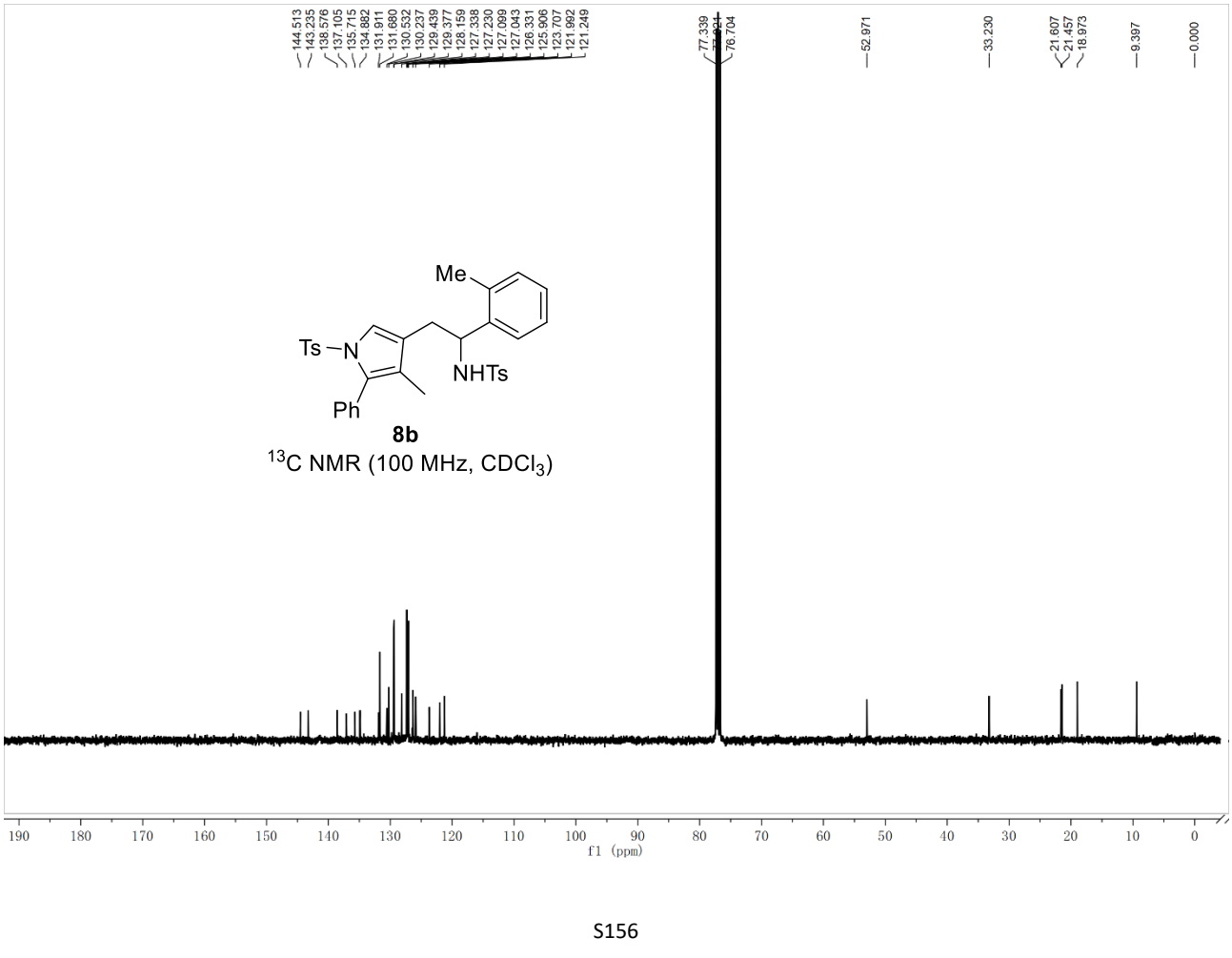

Hc
Hb
Ha
{2.808,1.428}
{7.067,2.794}
{1.428,2.762}
{2.400,7.006}
NOE
Ts
N
Ph
NHTs
f2 (ppm)
f1 (ppm)
8a
NOESY (400MHz CDCl3)


+ESI Scan (rt: 0.204 min) Frag=175.0V
607.1691
Ts
N
Ph
NHTs
Ph
8a
(ESI-TOF) m/z: [M + Na]+
Calcd for C33H32N2O4S2Na+ 607.1696
Counts vs. Mass-to-Charge (m/z)



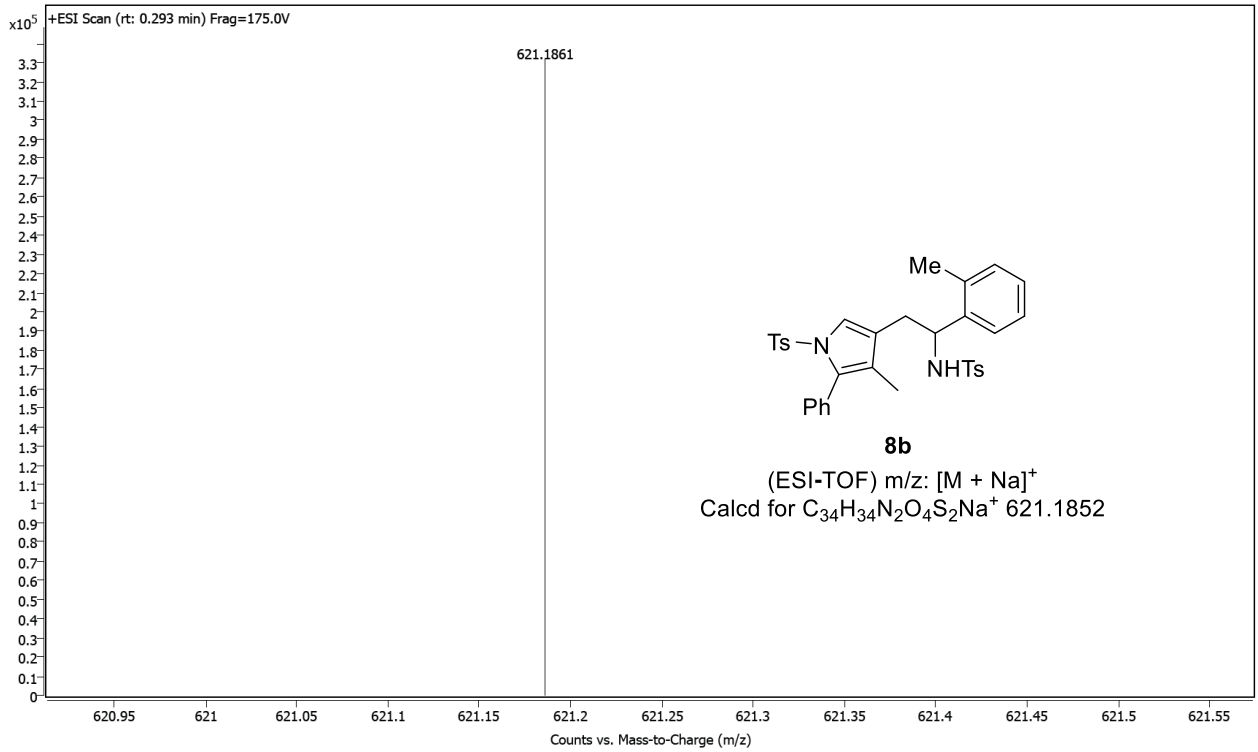
8b

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



8b

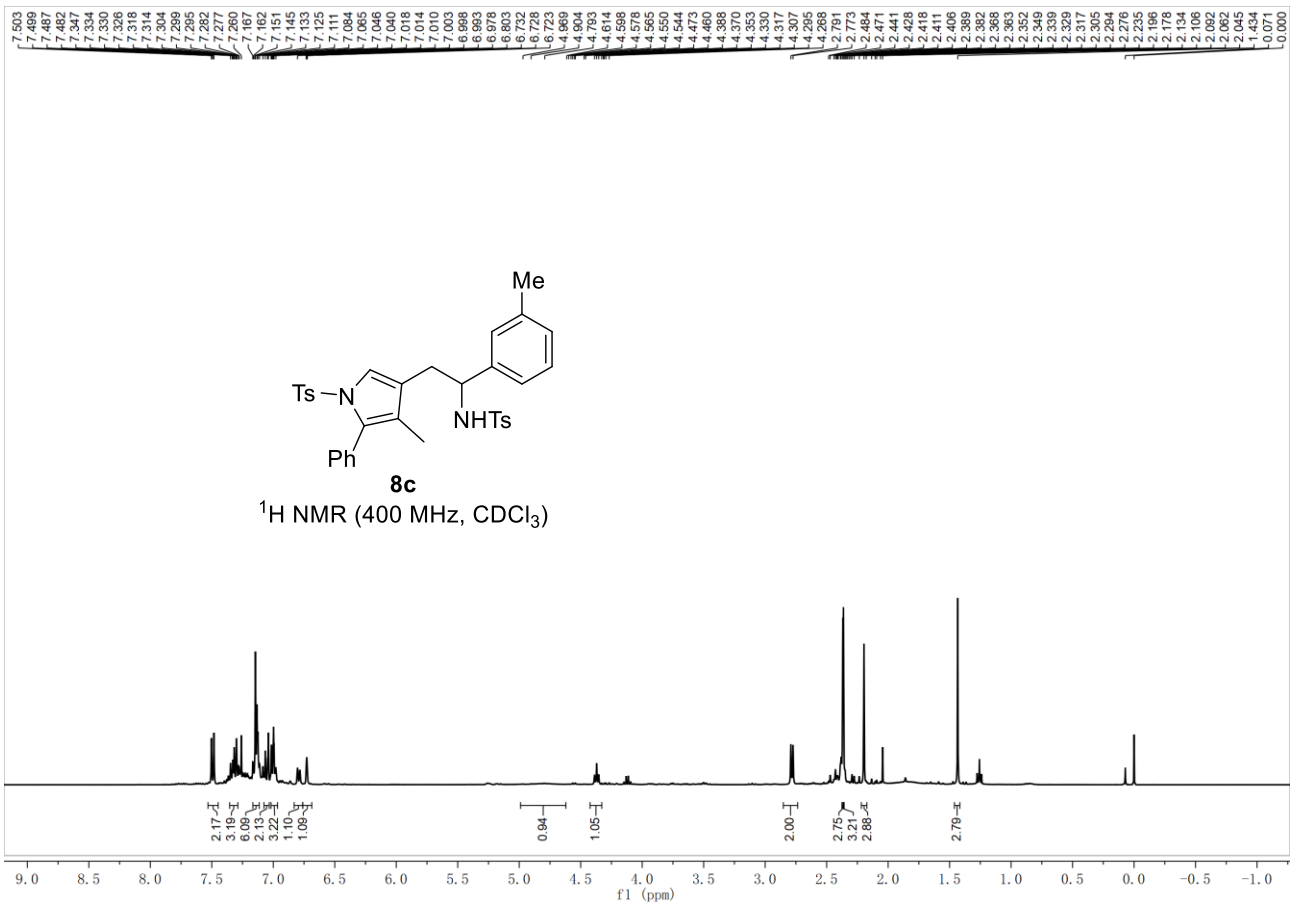
^{13}C NMR (100 MHz, $CDCl_3$)



8b

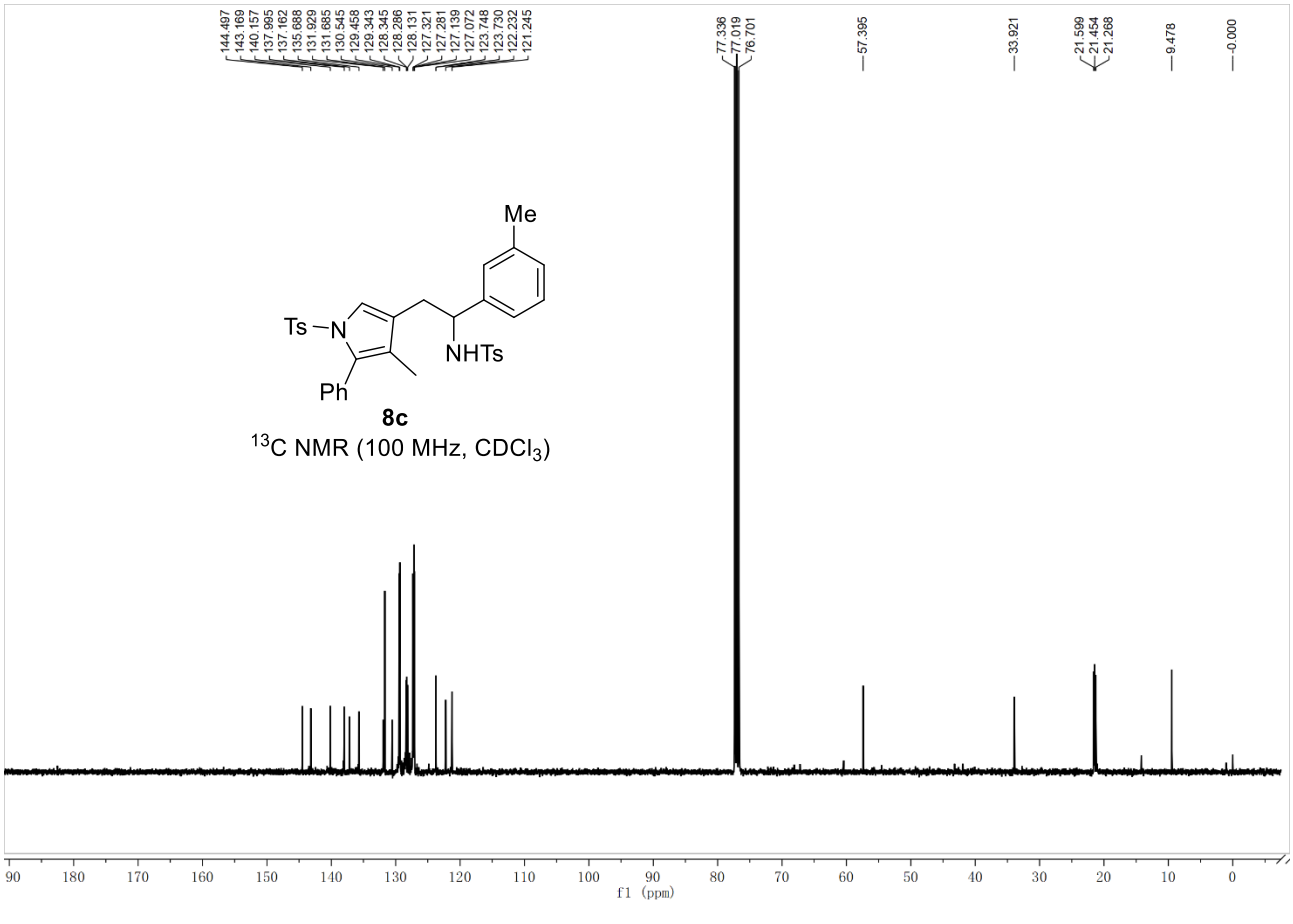
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1852



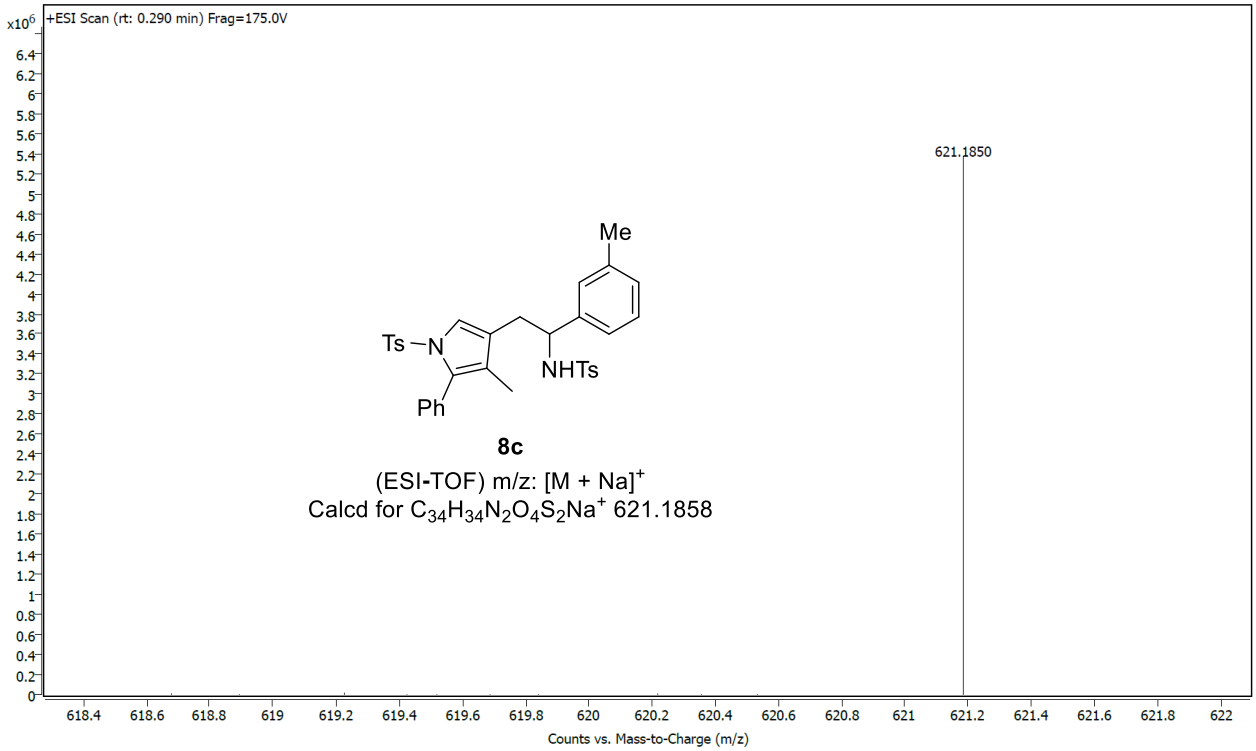
8c

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



8c

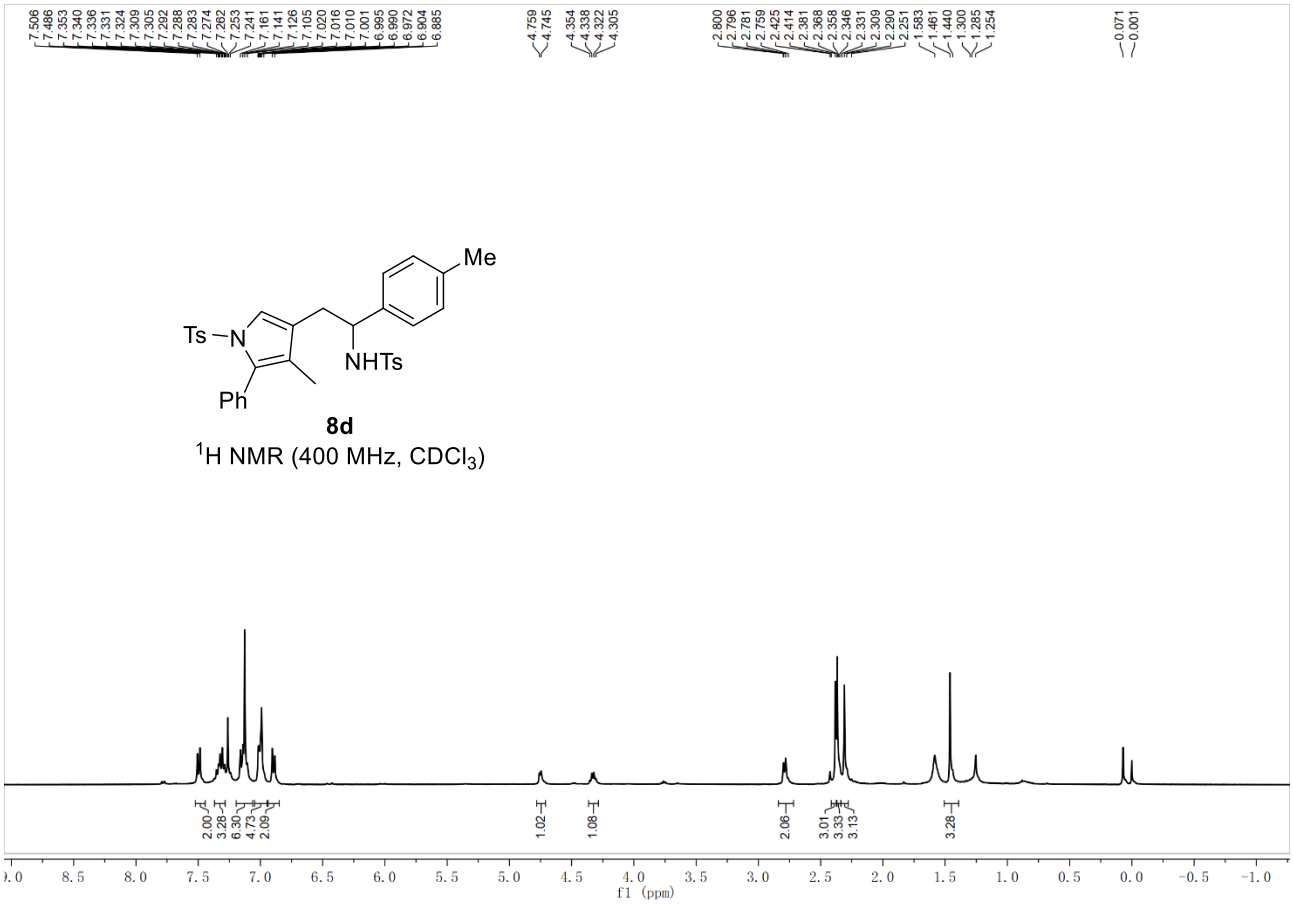
^{13}C NMR (100 MHz, $CDCl_3$)



8c

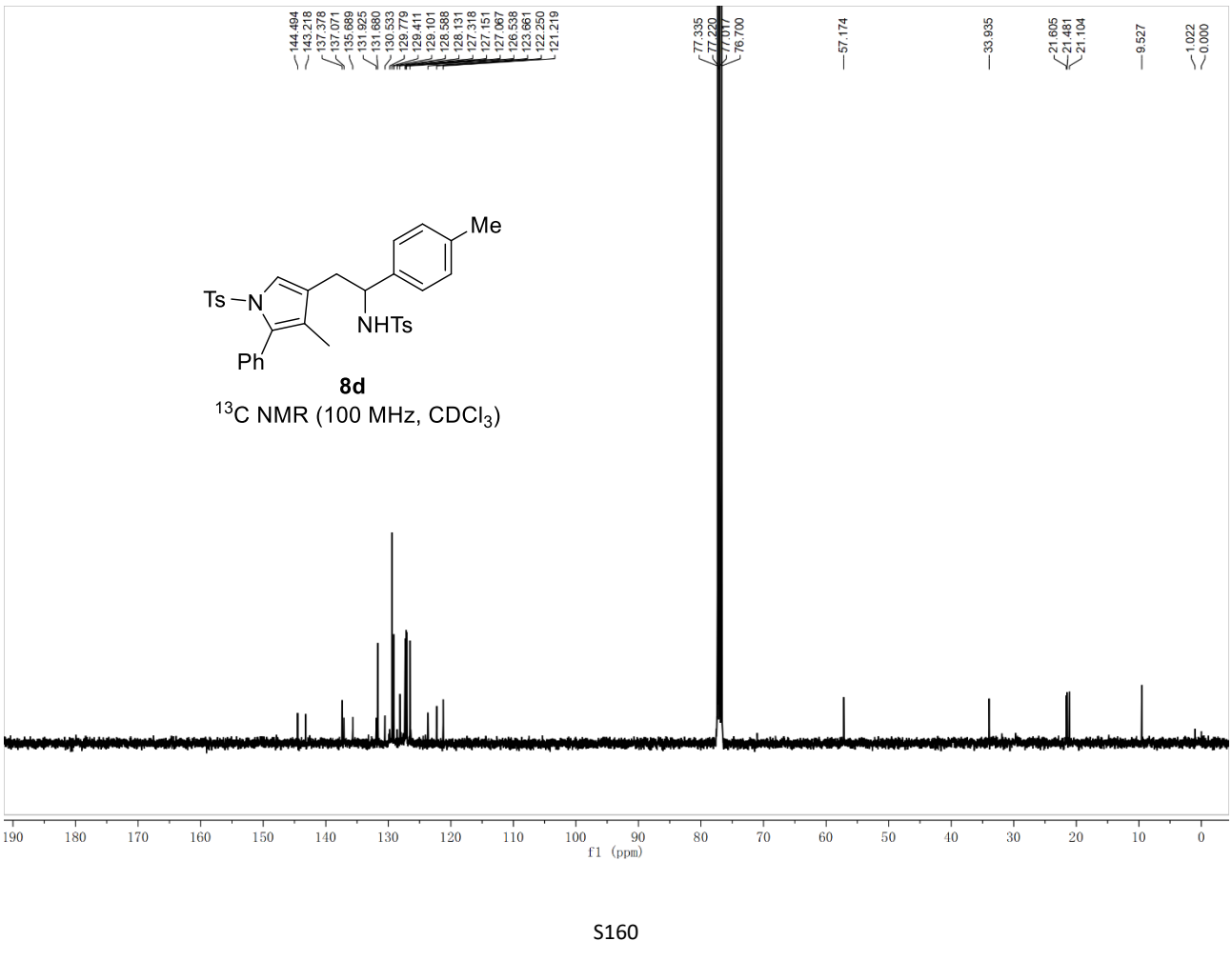
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858



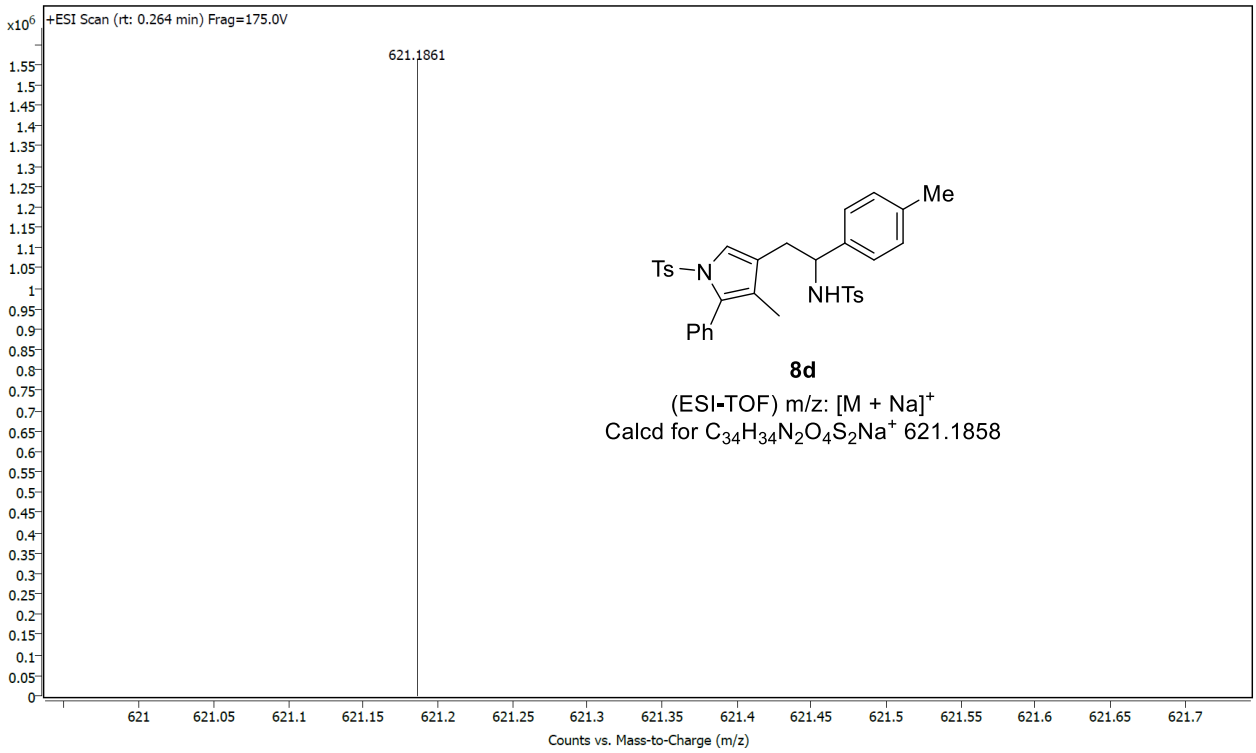
8d

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



8d

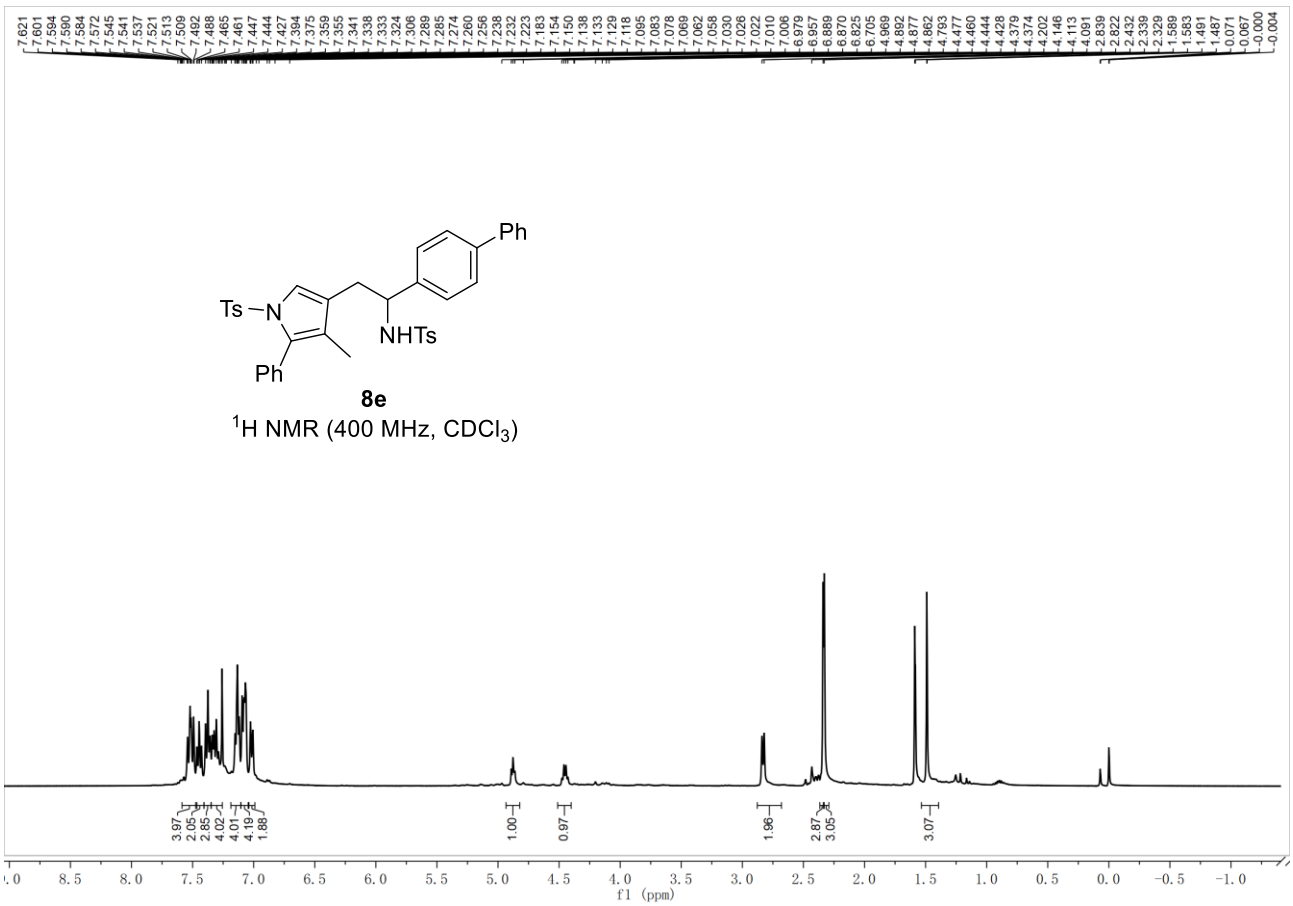
^{13}C NMR (100 MHz, $CDCl_3$)



8d

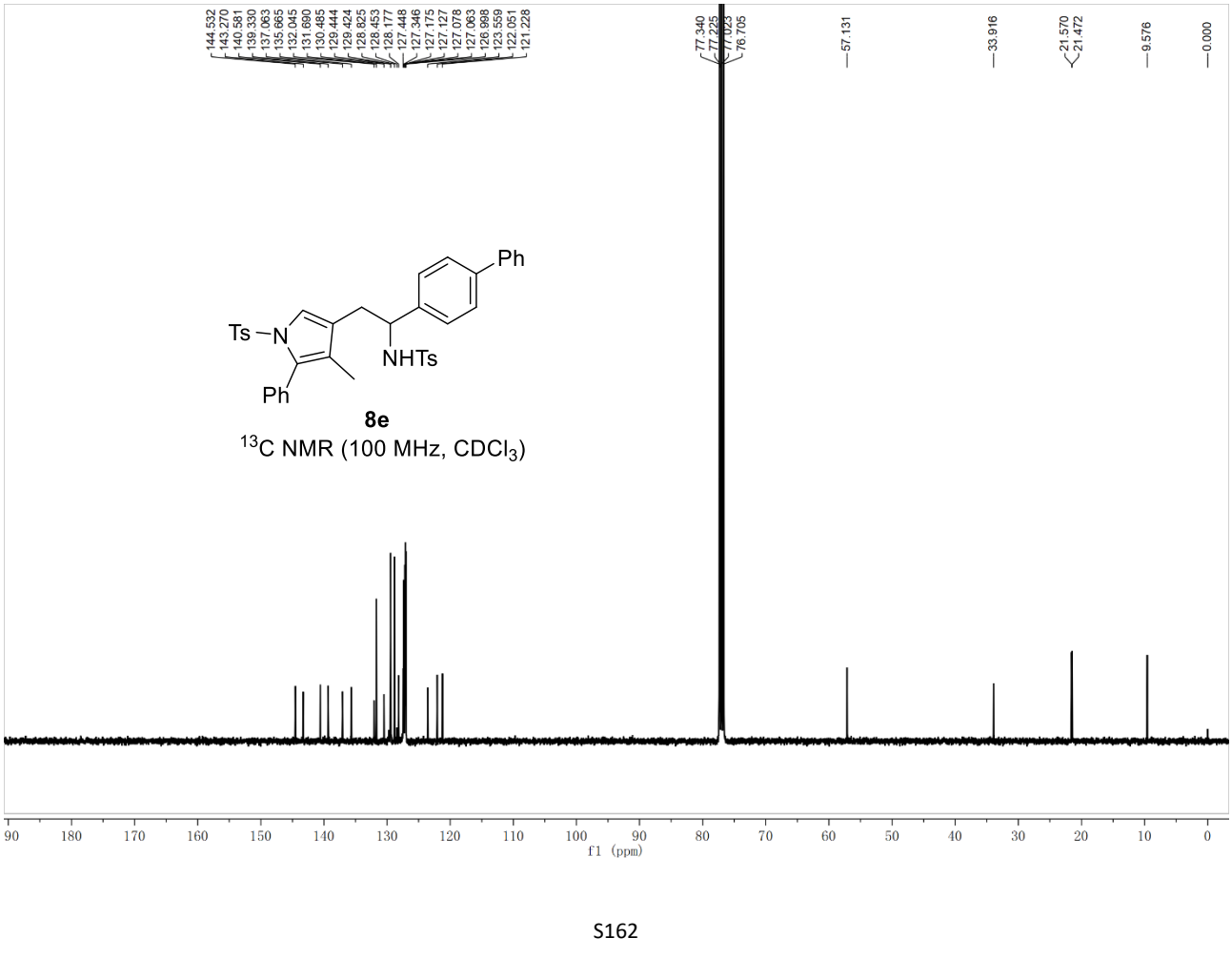
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858



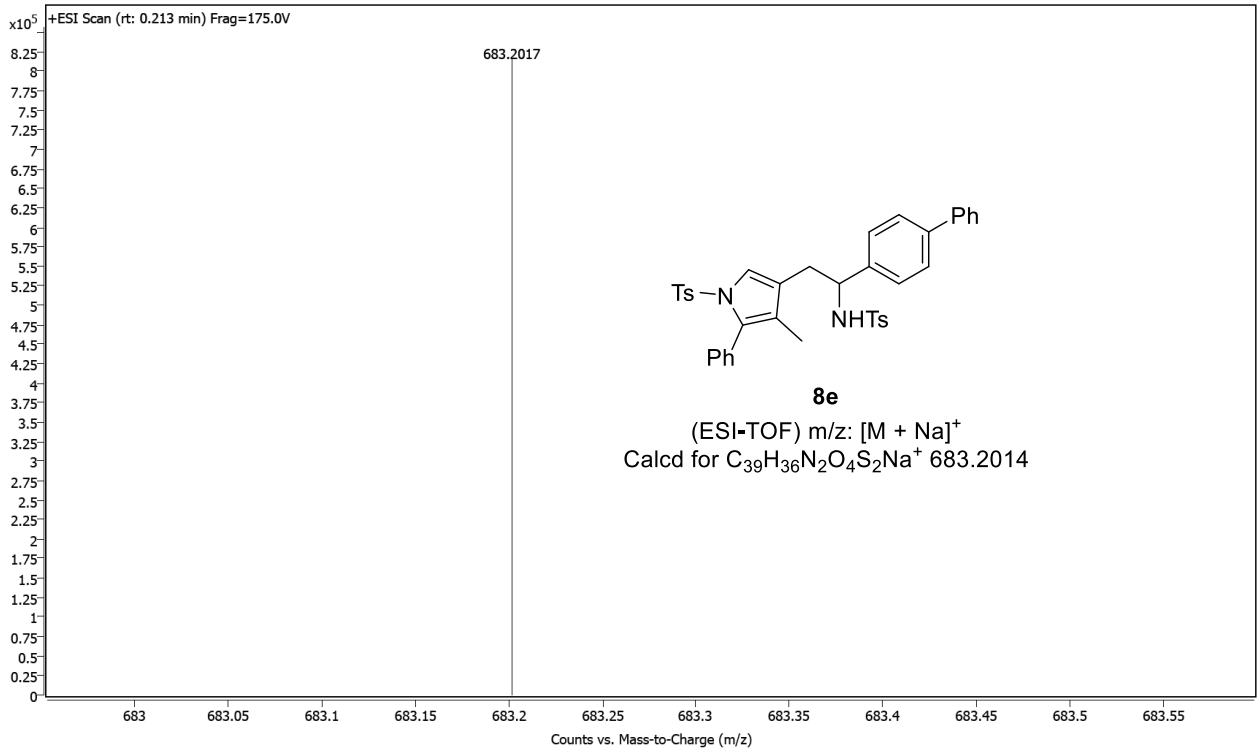
8e

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



8e

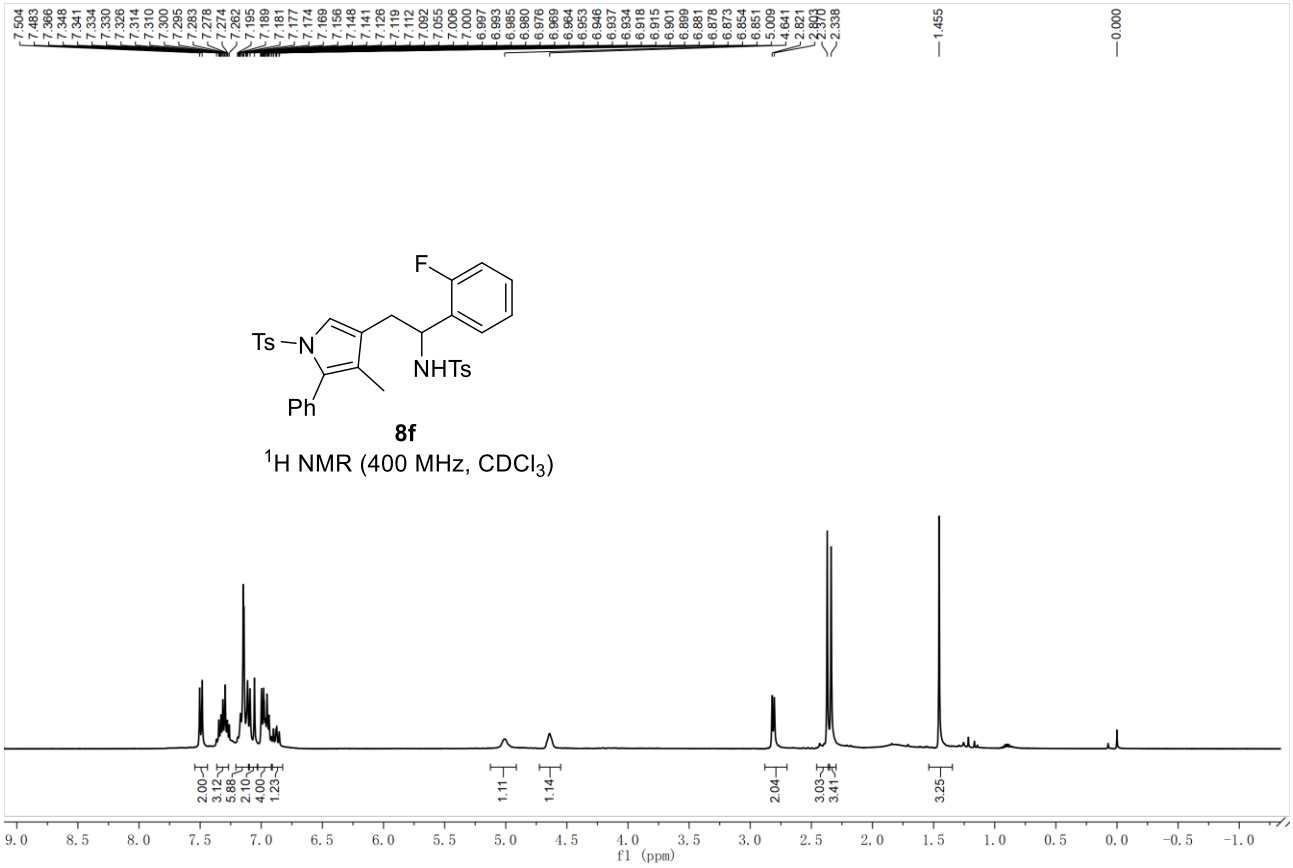
^{13}C NMR (100 MHz, $CDCl_3$)

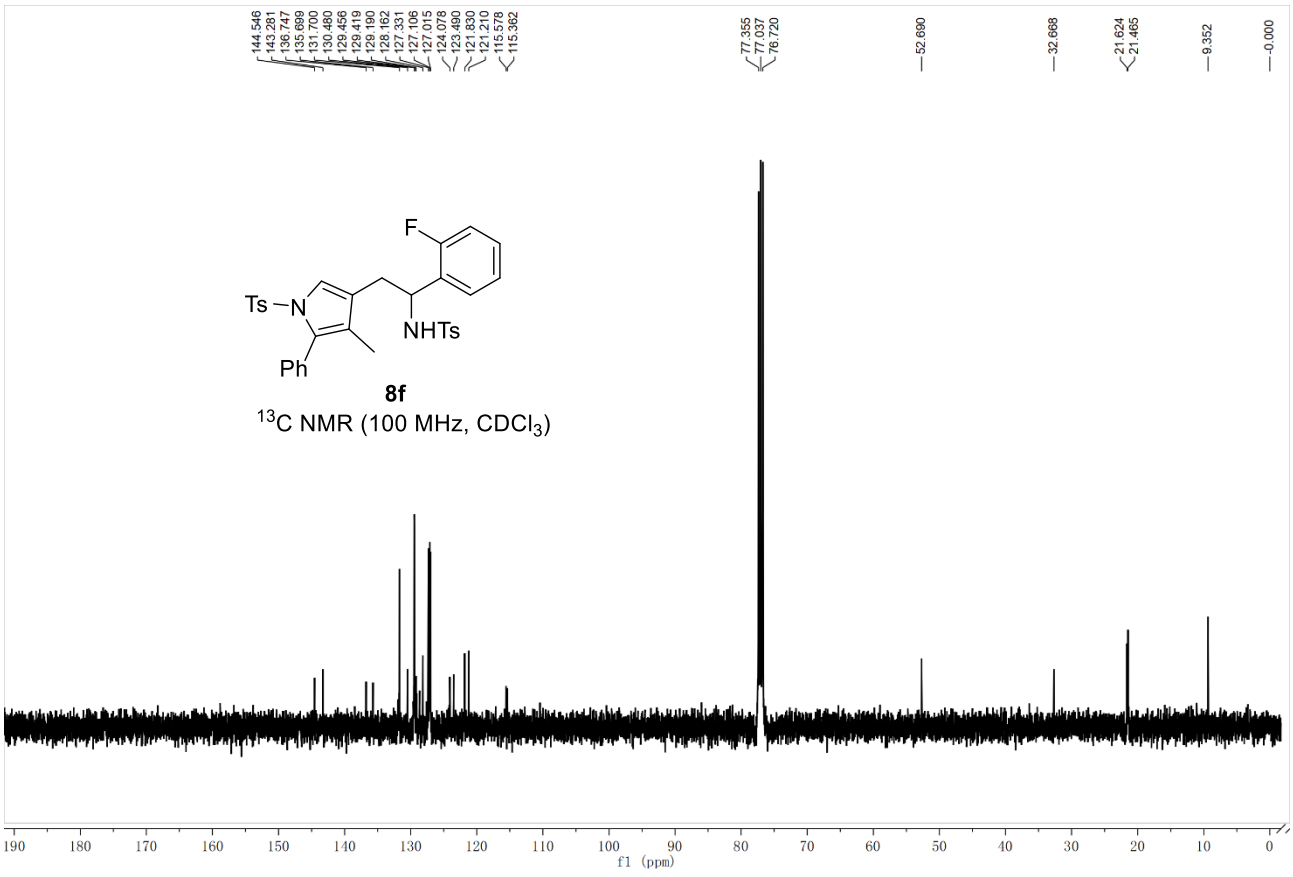


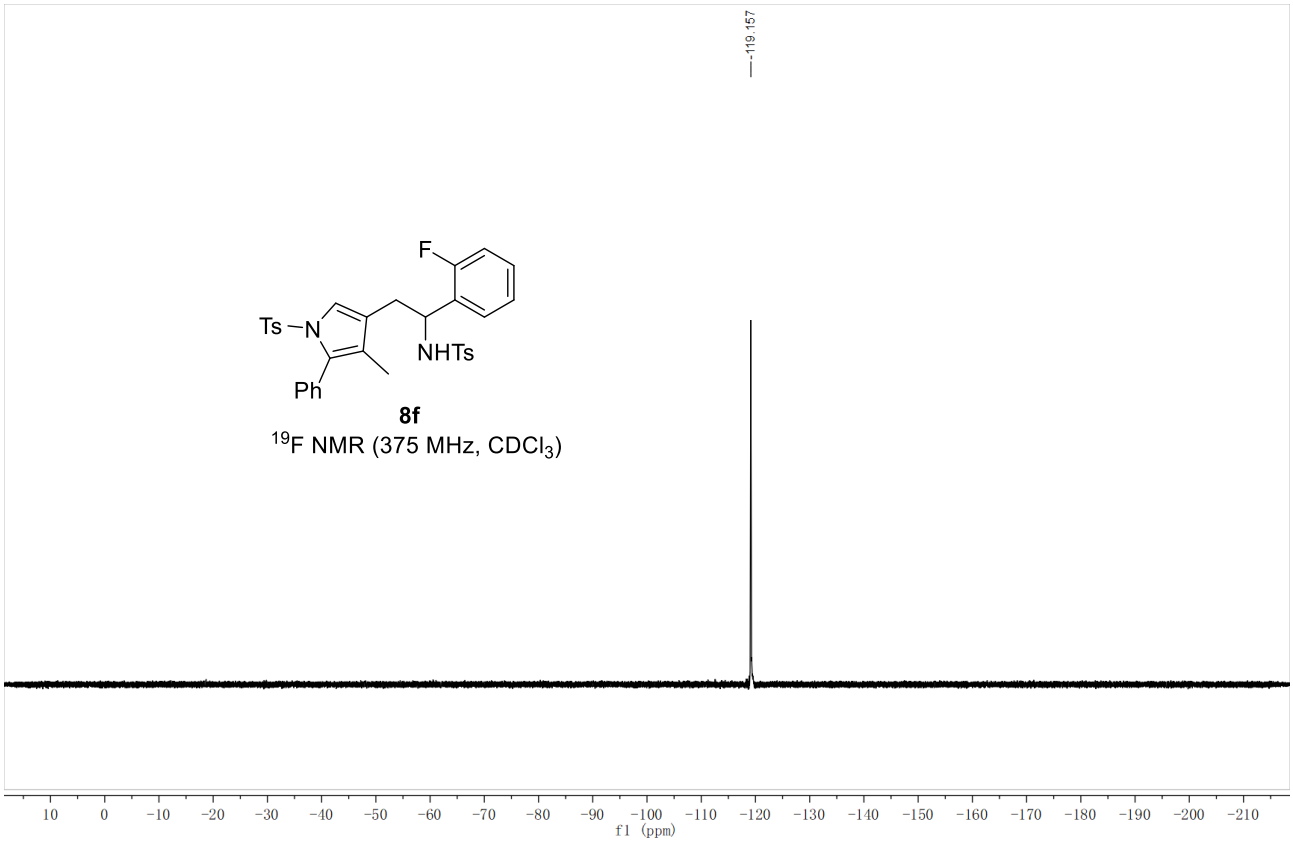
8e

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{39}H_{36}N_2O_4S_2Na^+$ 683.2014

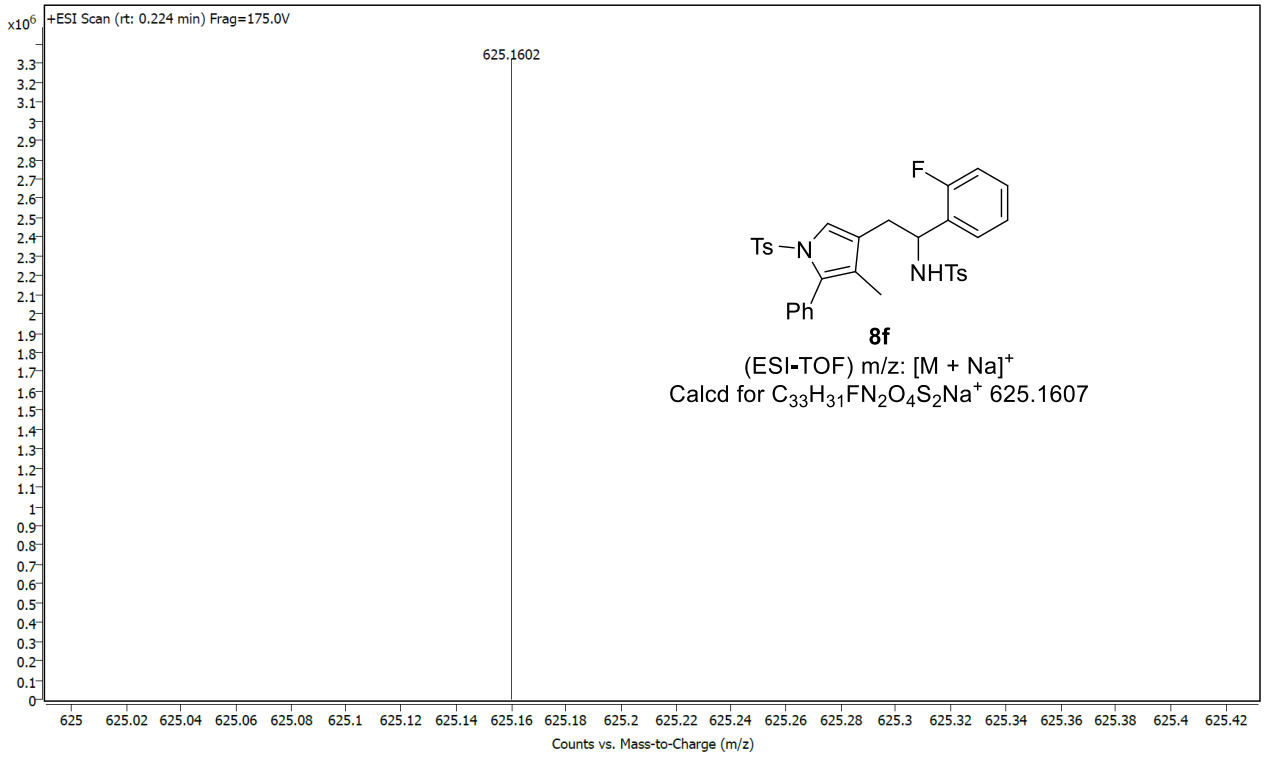

F
Ts
N
NHTs
Ph
8f
1H NMR (400 MHz, CDCl3)
f1 (ppm)


F
Ts
N
NHTs
Ph
8f
13C NMR (100 MHz, CDCl3)
f1 (ppm)



8f

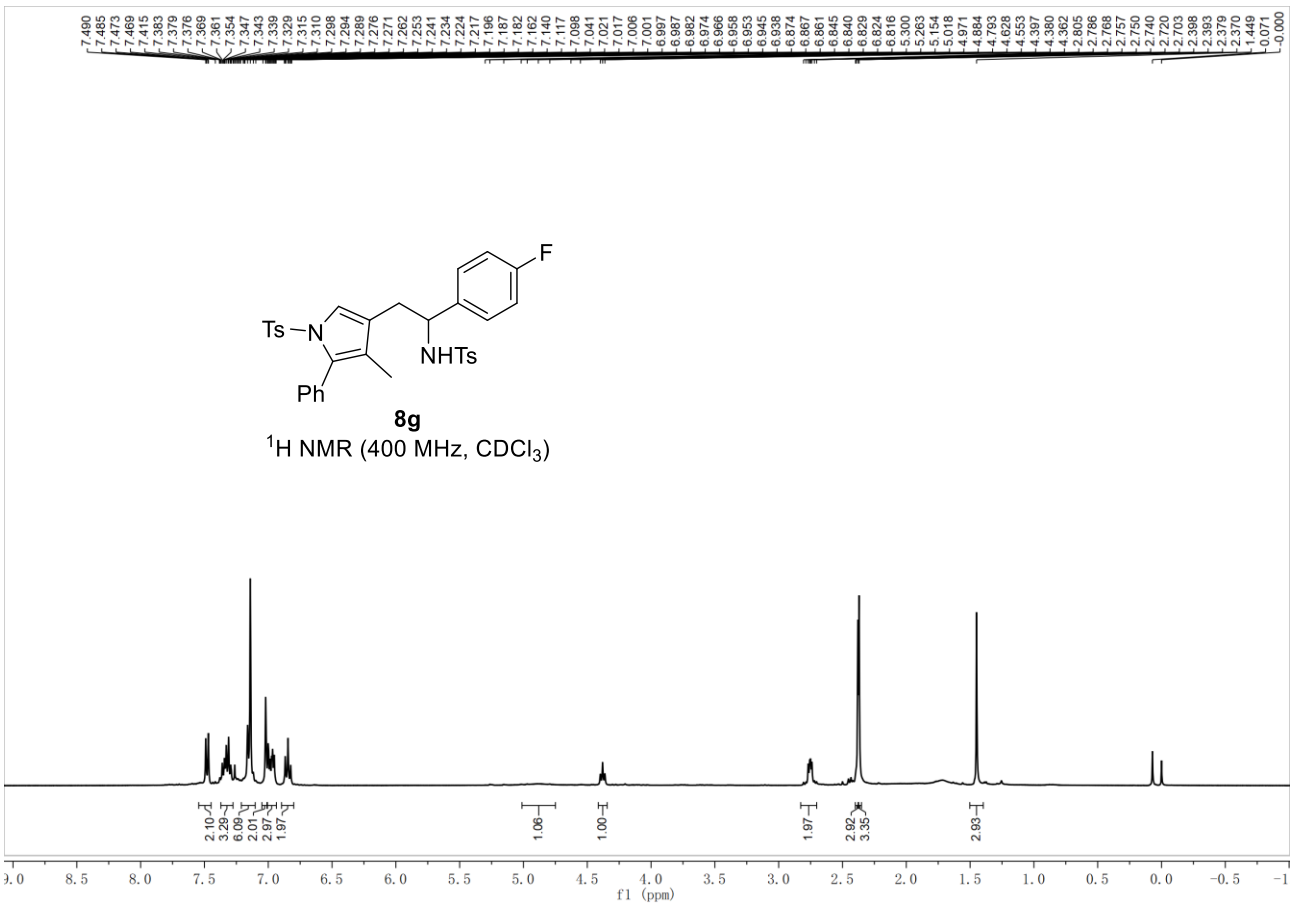
^{19}F NMR (375 MHz, $CDCl_3$)



8f

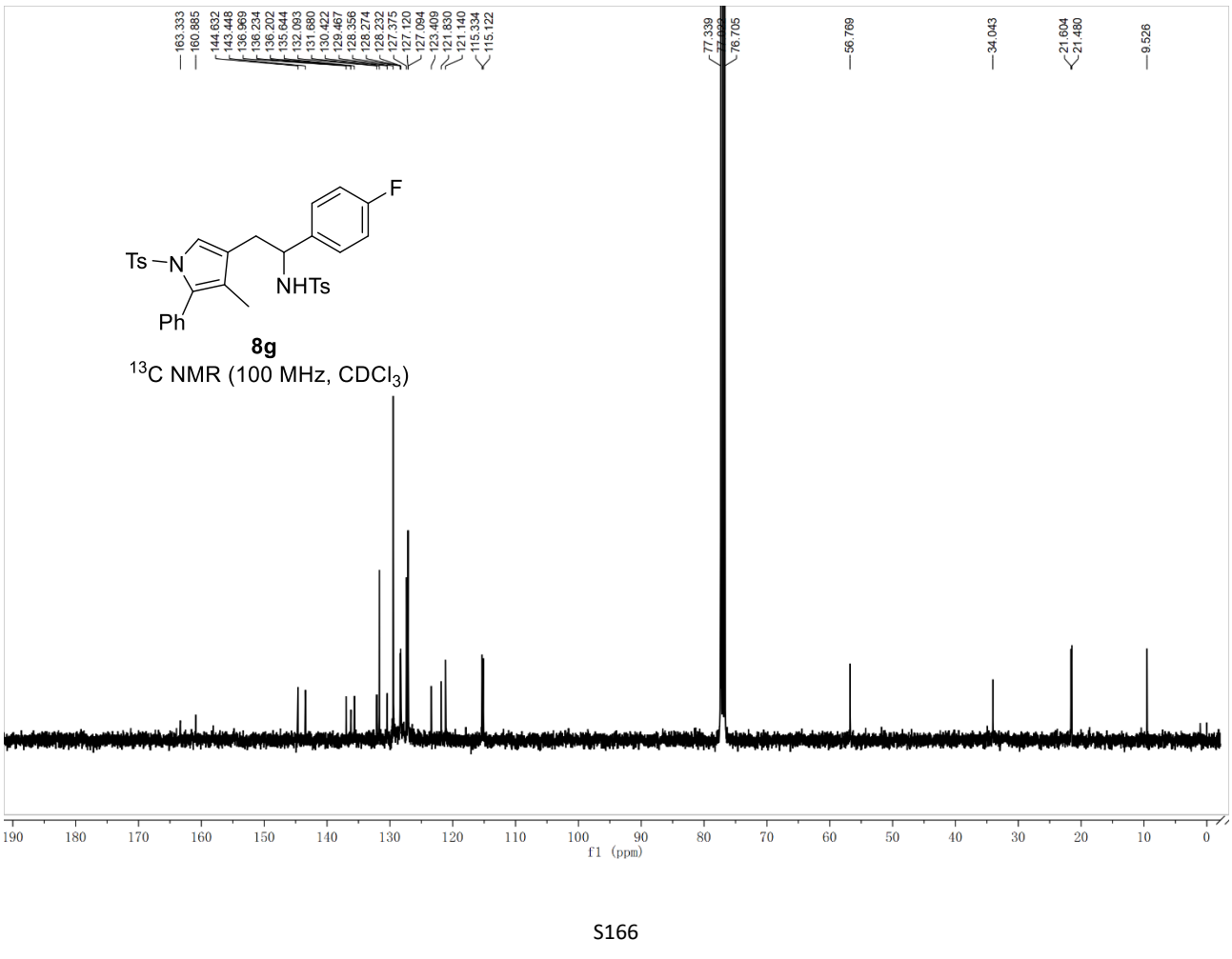
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{33}H_{31}FN_2O_4S_2Na^+$ 625.1607



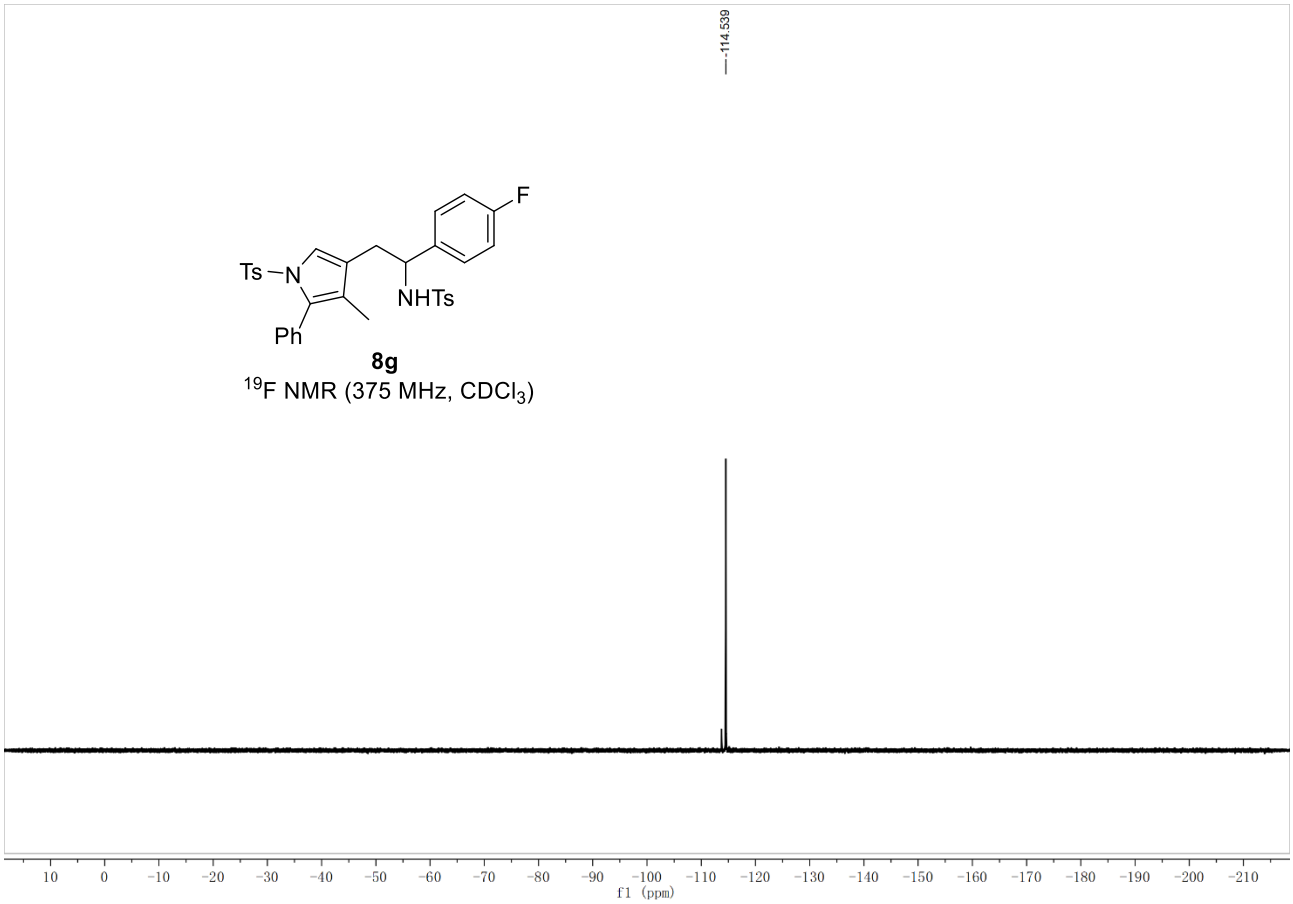
8g

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



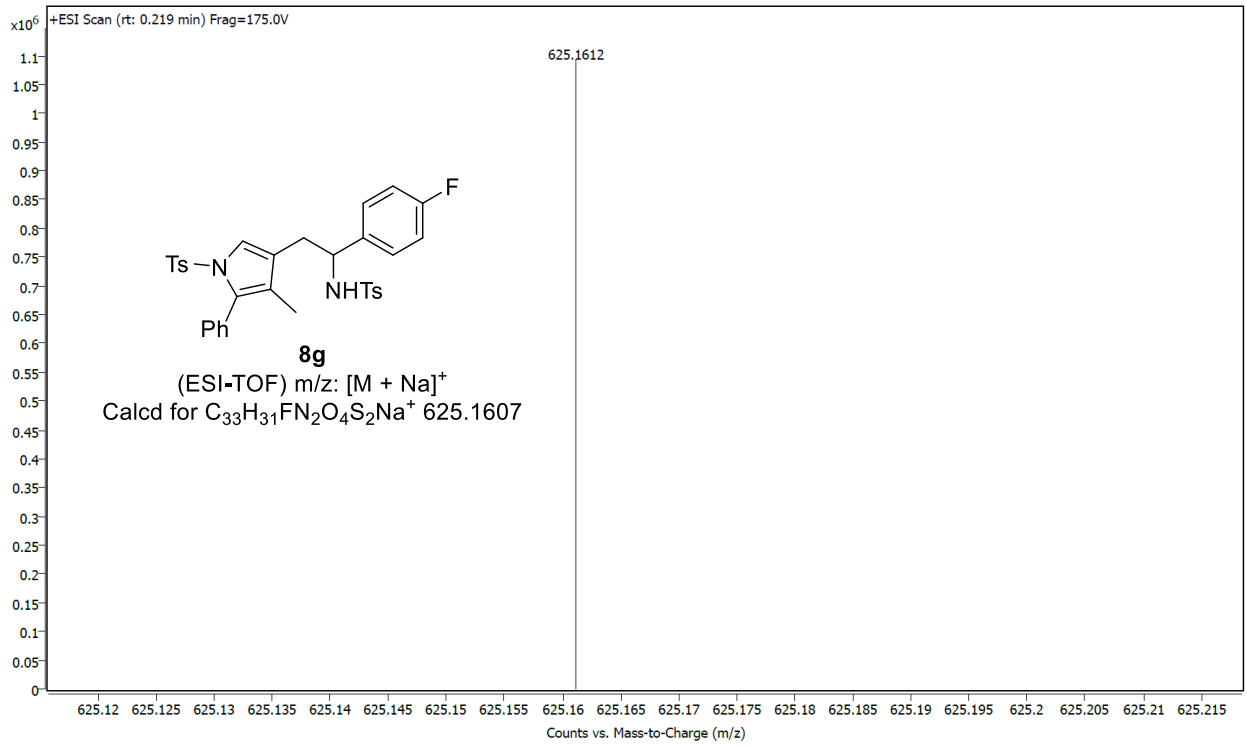
8g

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



8g

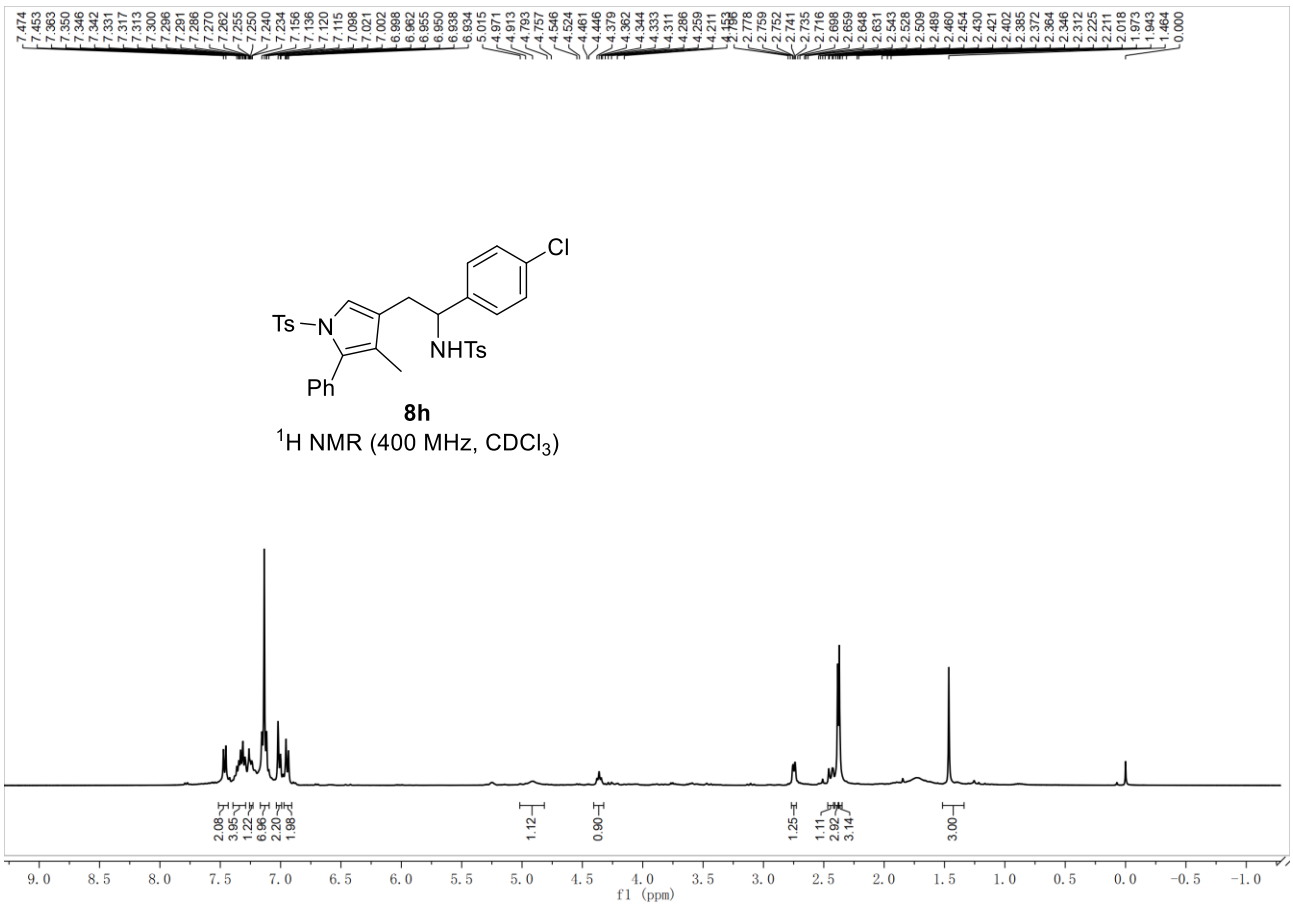
^{19}F NMR (375 MHz, $CDCl_3$)



8g

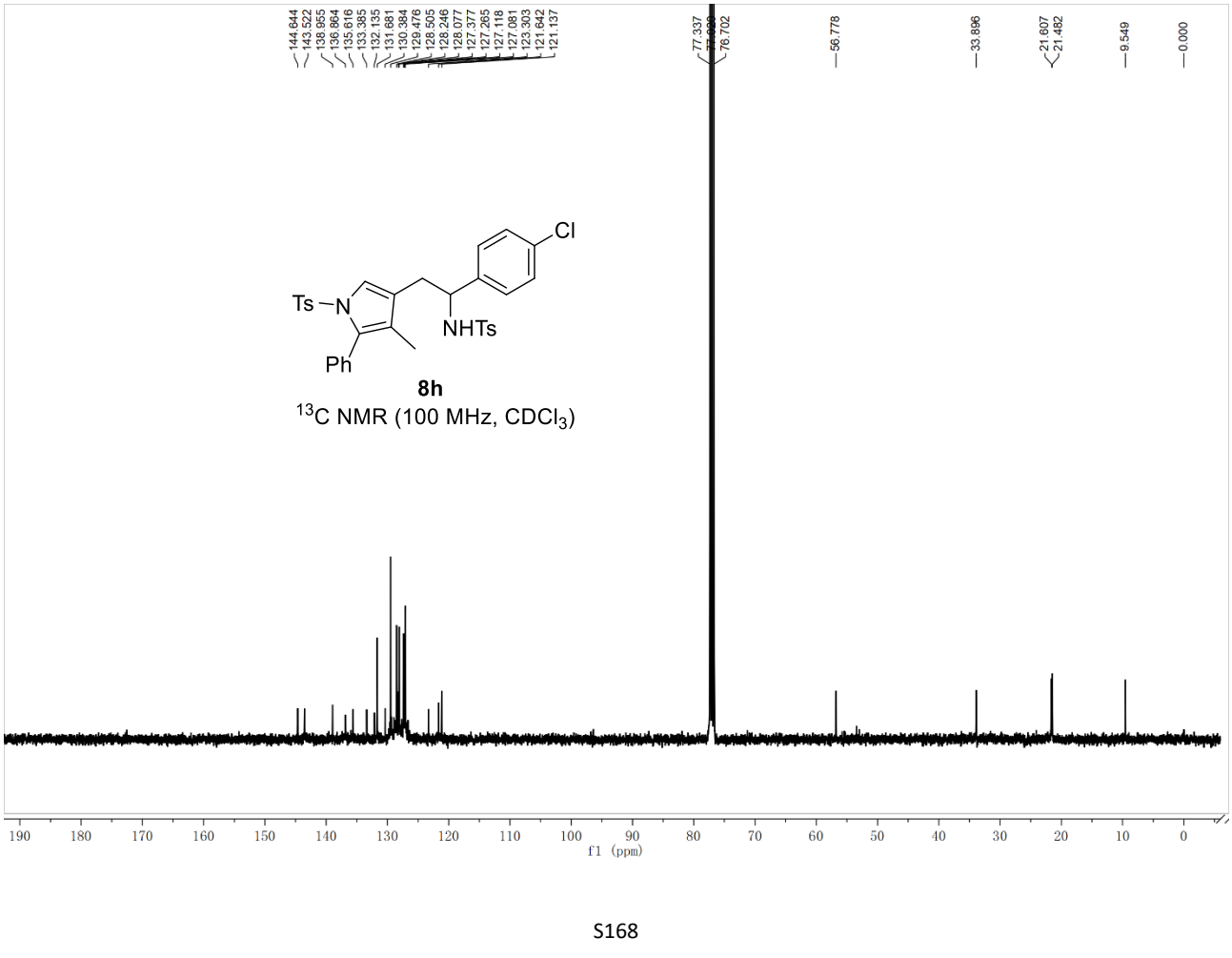
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{33}H_{31}FN_2O_4S_2Na^+$ 625.1607



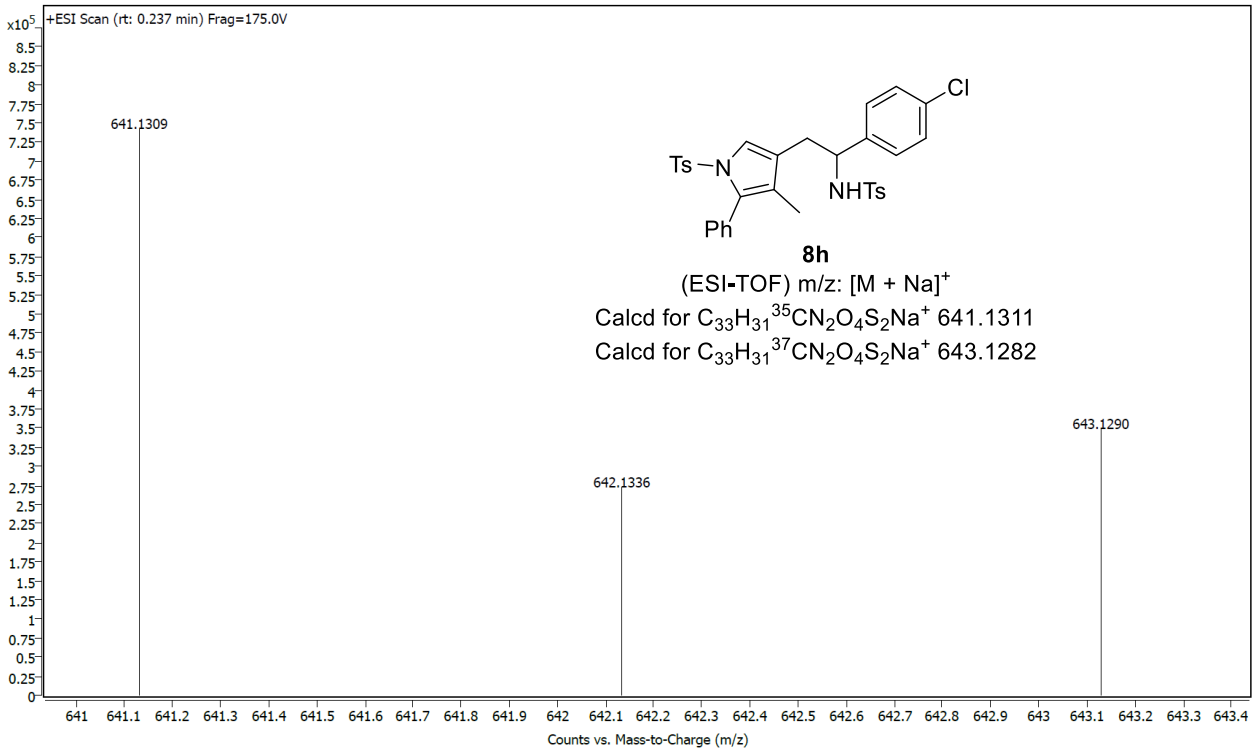
8h

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



8h

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

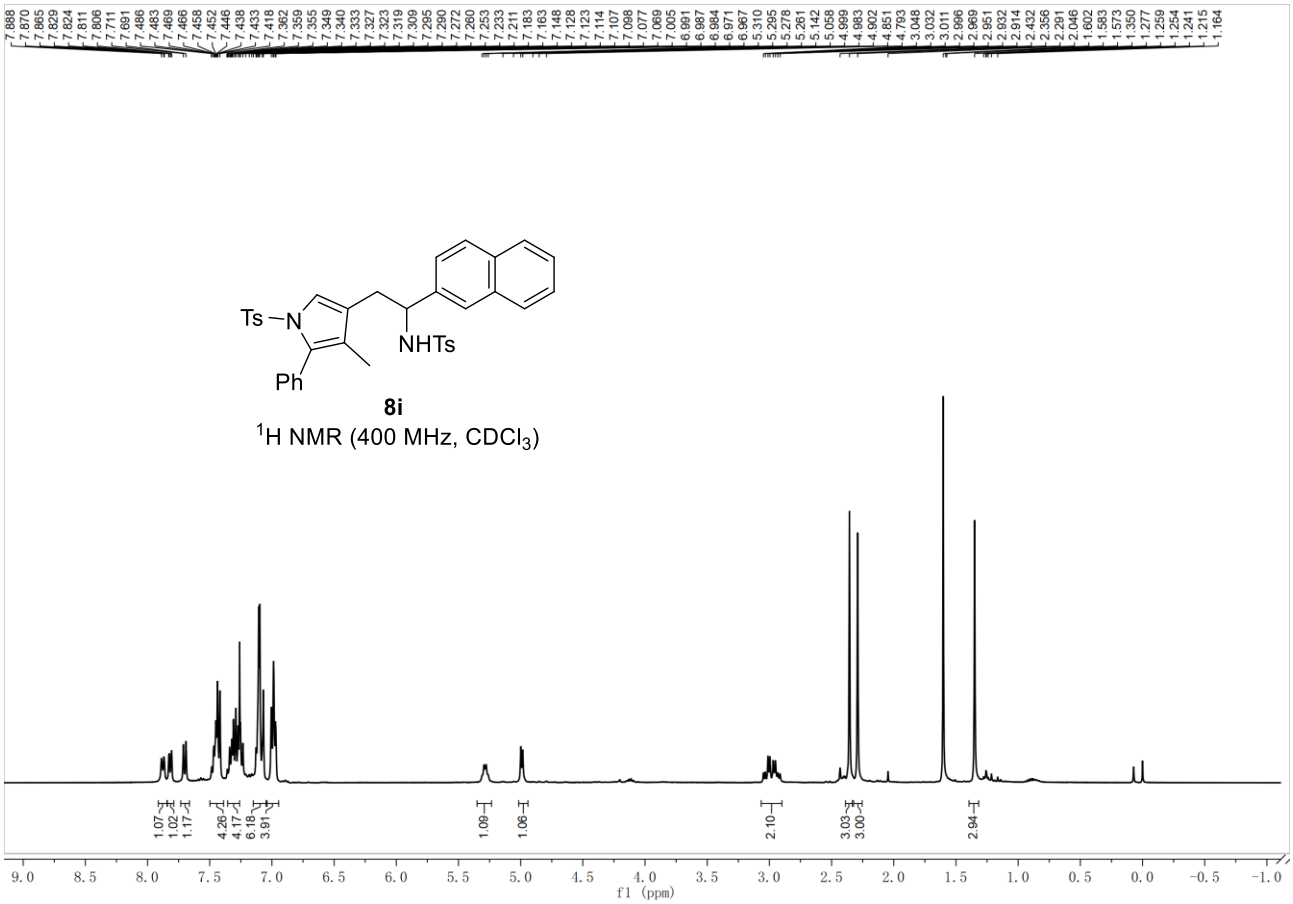


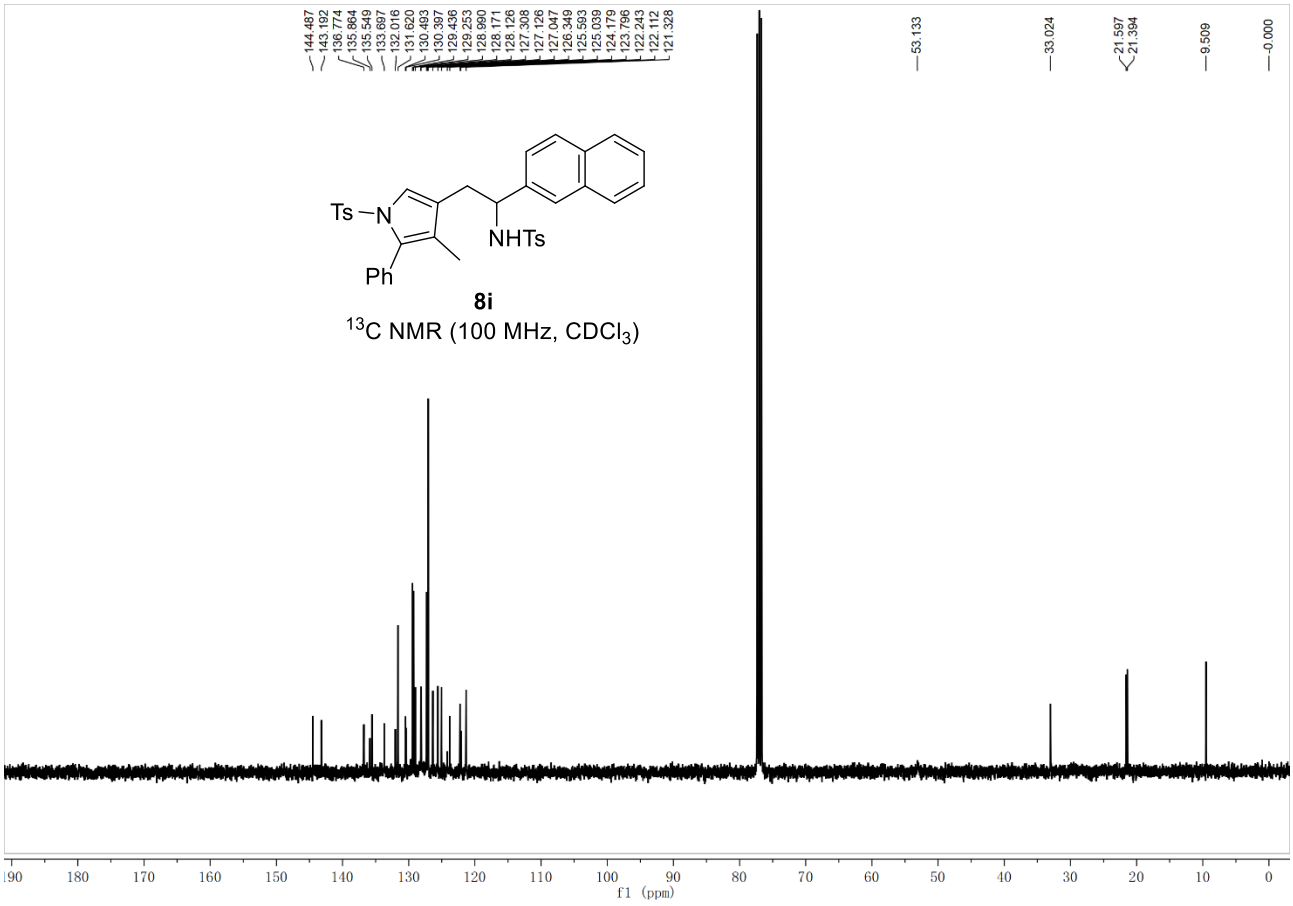
8h

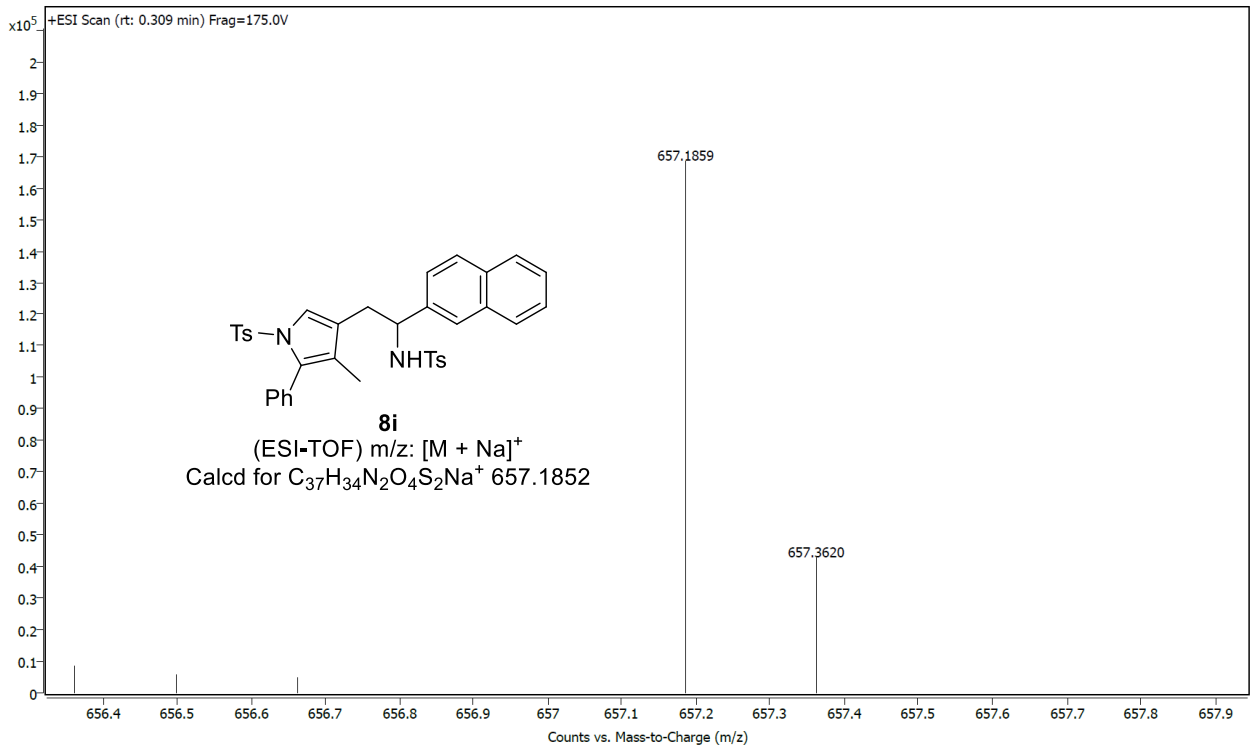
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{33}H_{31}{}^{35}CN_2O_4S_2Na^+$ 641.1311

Calcd for $C_{33}H_{31}{}^{37}CN_2O_4S_2Na^+$ 643.1282


Ts
N
NHTs
Ph
8i
1H NMR (400 MHz, CDCl3)
f1 (ppm)

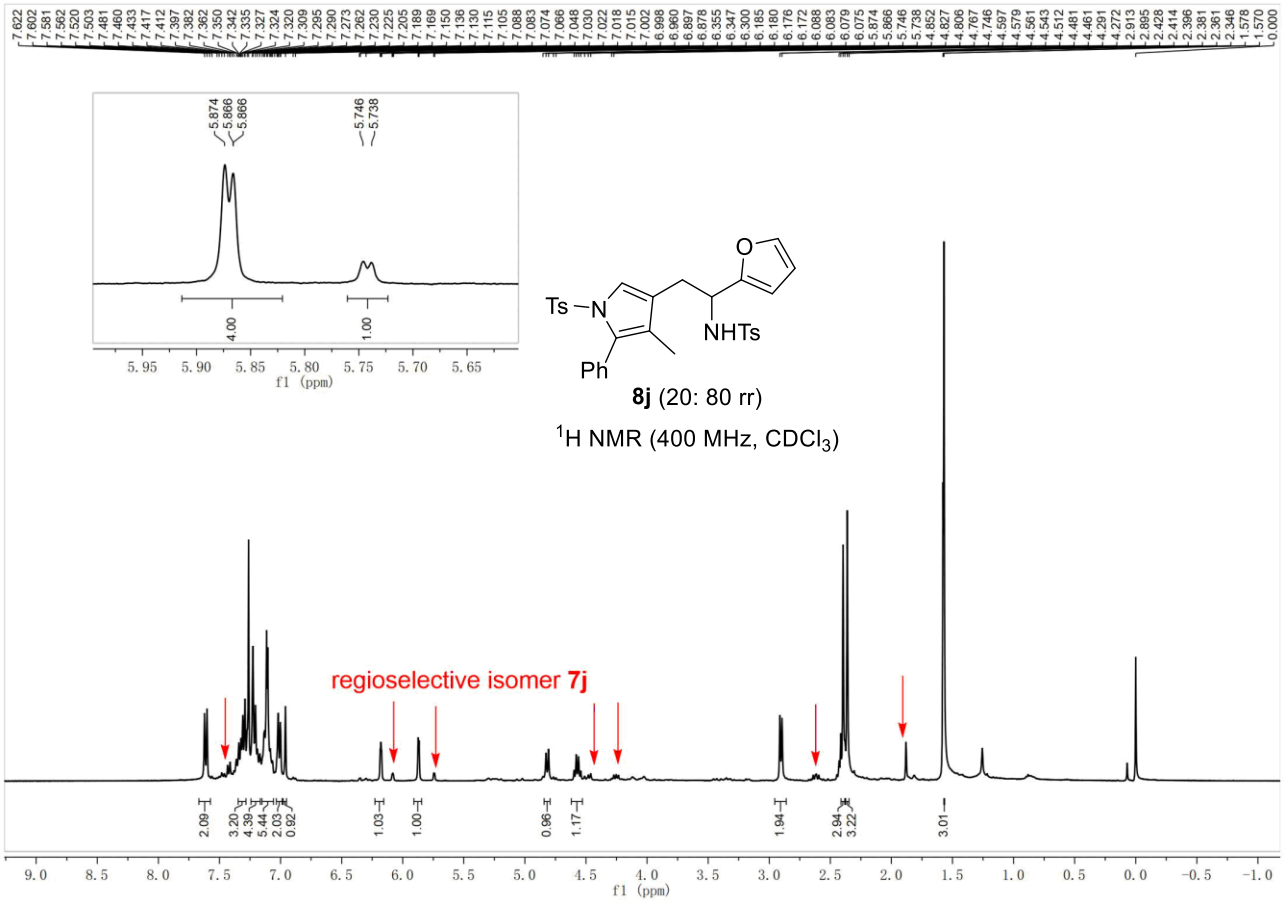

Ts
N
NHTs
Ph
8i
13C NMR (100 MHz, CDCl3)
f1 (ppm)



8i

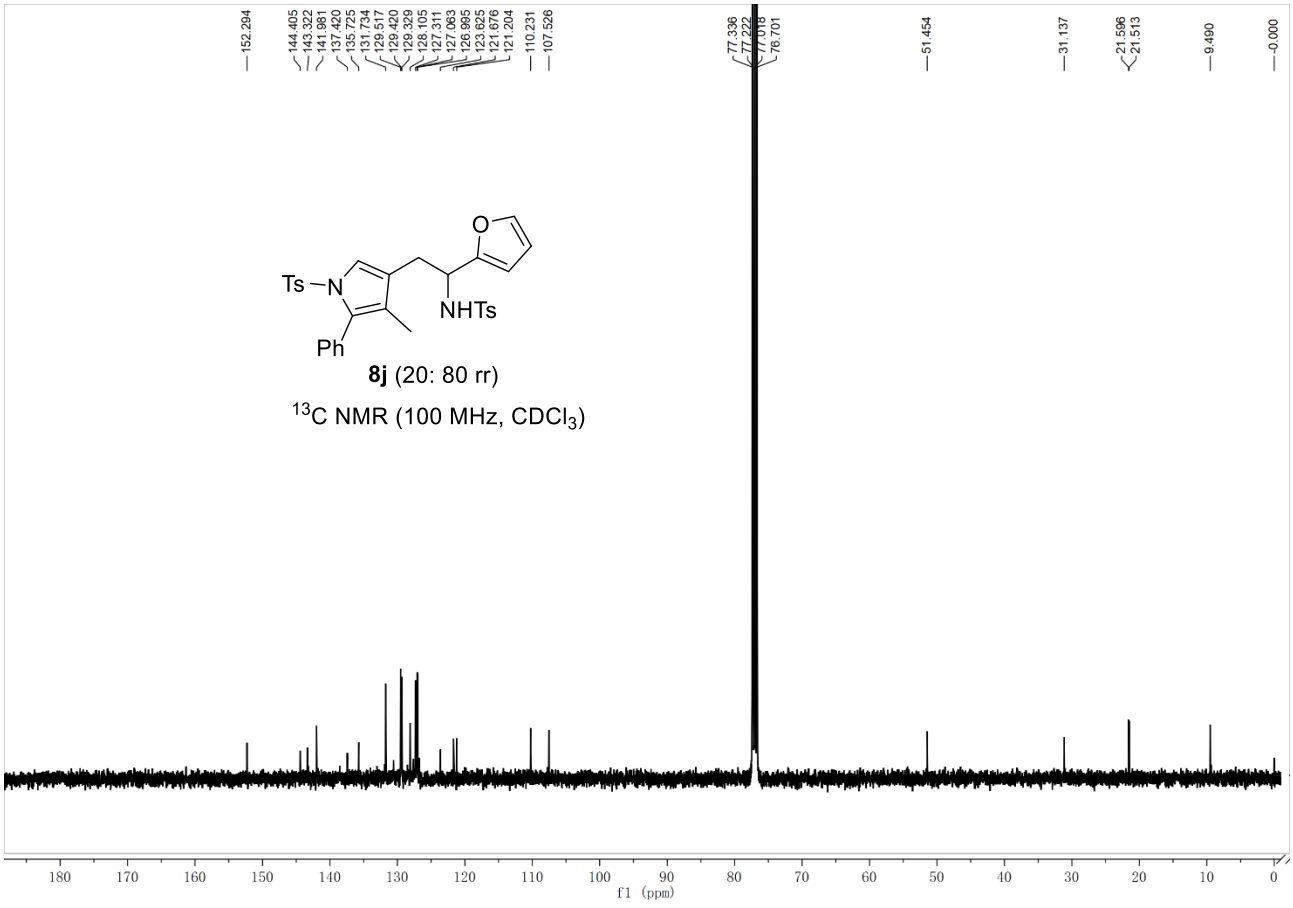
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{37}H_{34}N_2O_4S_2Na^+$ 657.1852



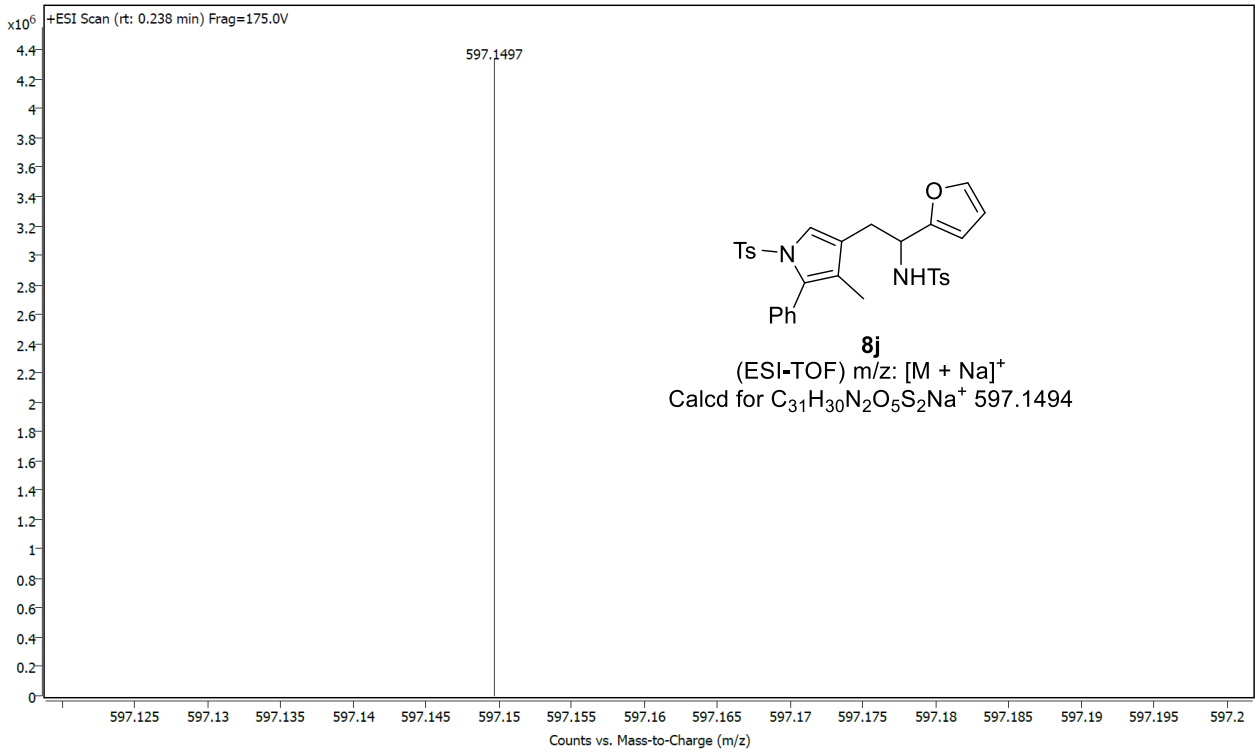
8j (20: 80 rr)

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



8j (20: 80 rr)

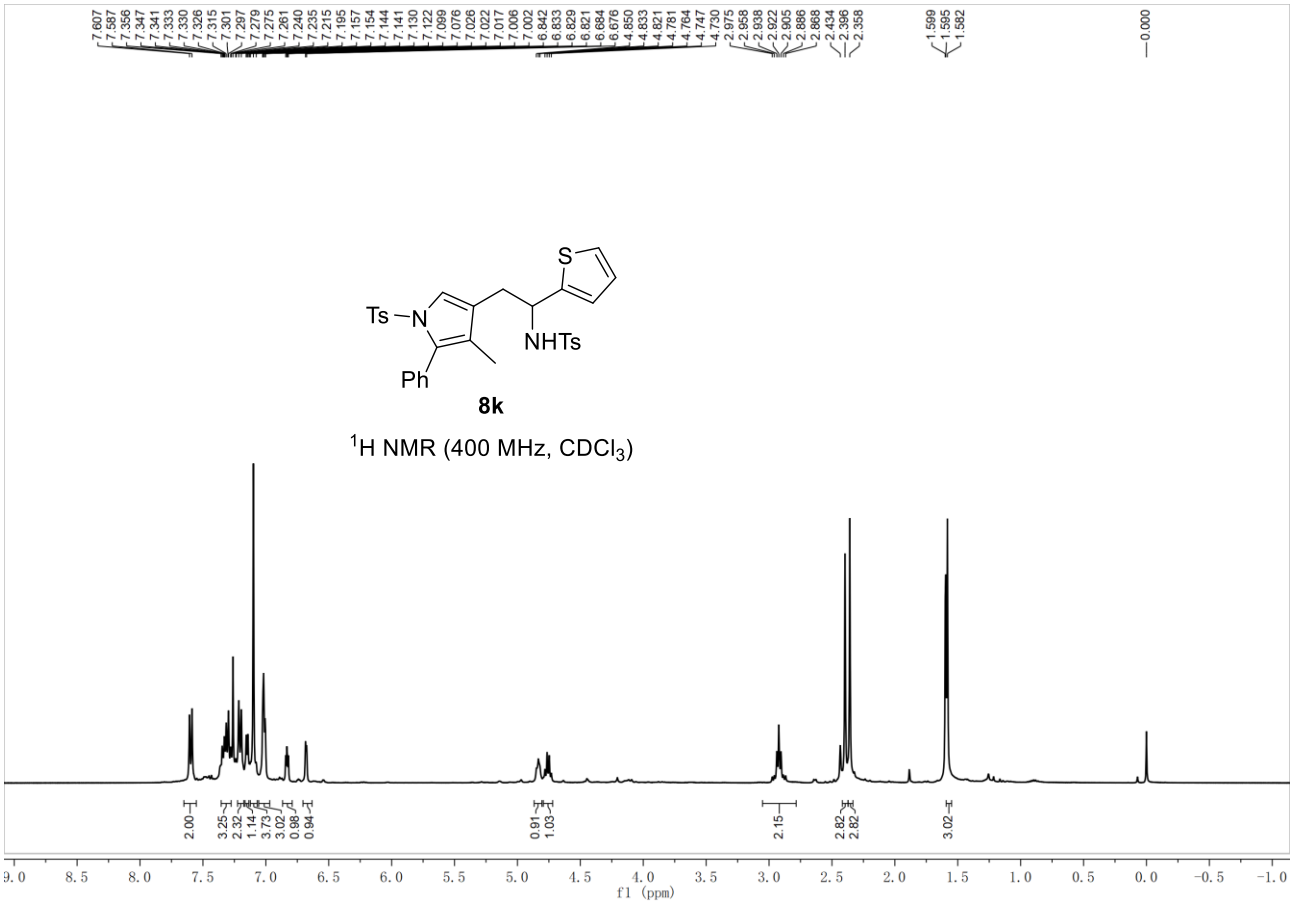
^{13}C NMR (100 MHz, $CDCl_3$)



8j

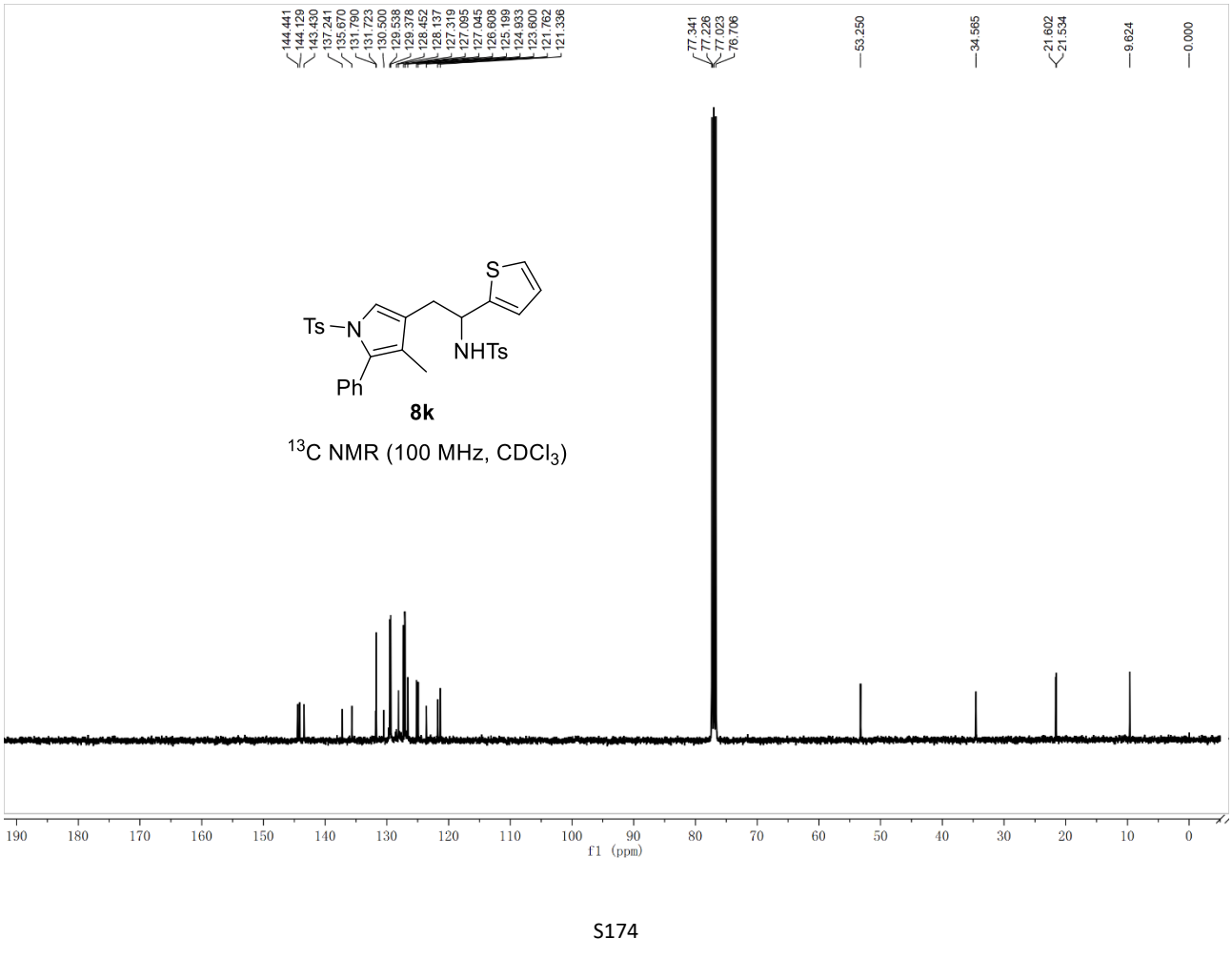
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{31}H_{30}N_2O_5S_2Na^+$ 597.1494



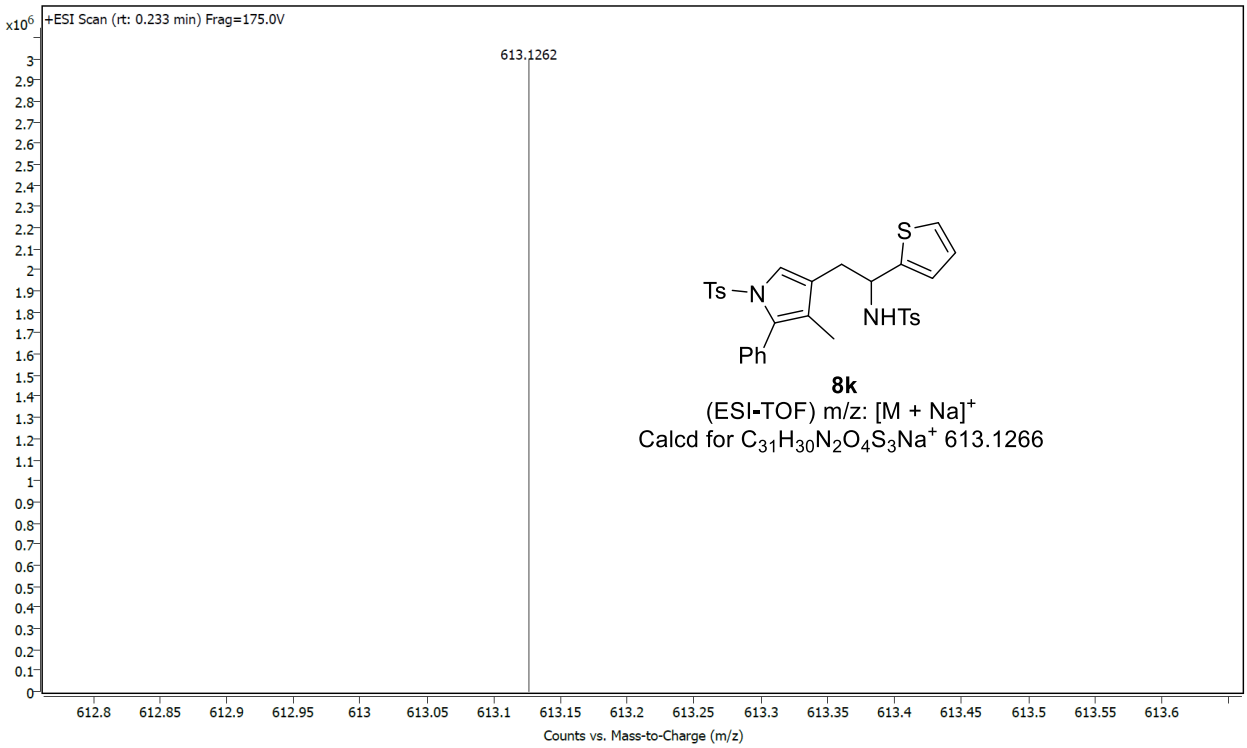
8k

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



8k

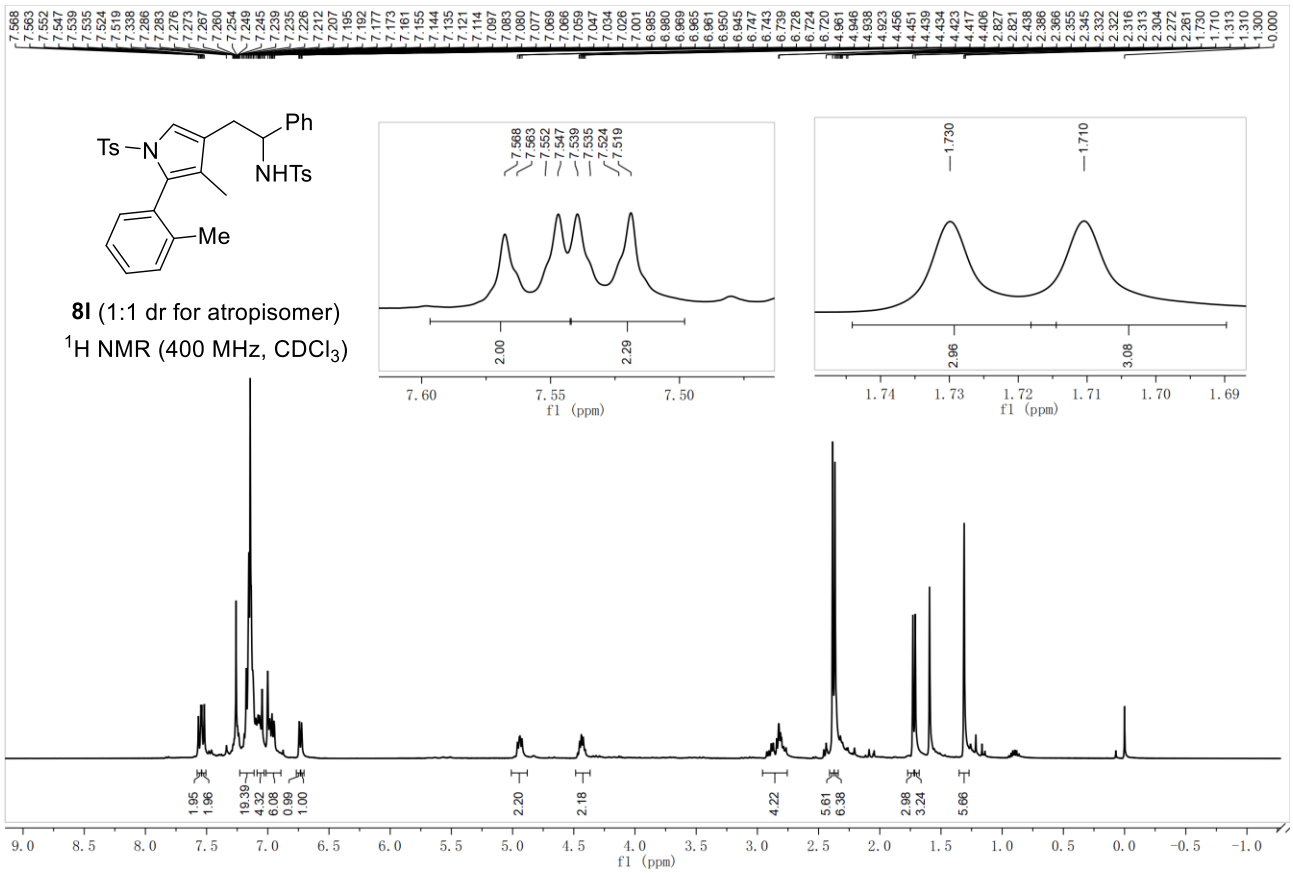
^{13}C NMR (100 MHz, $CDCl_3$)

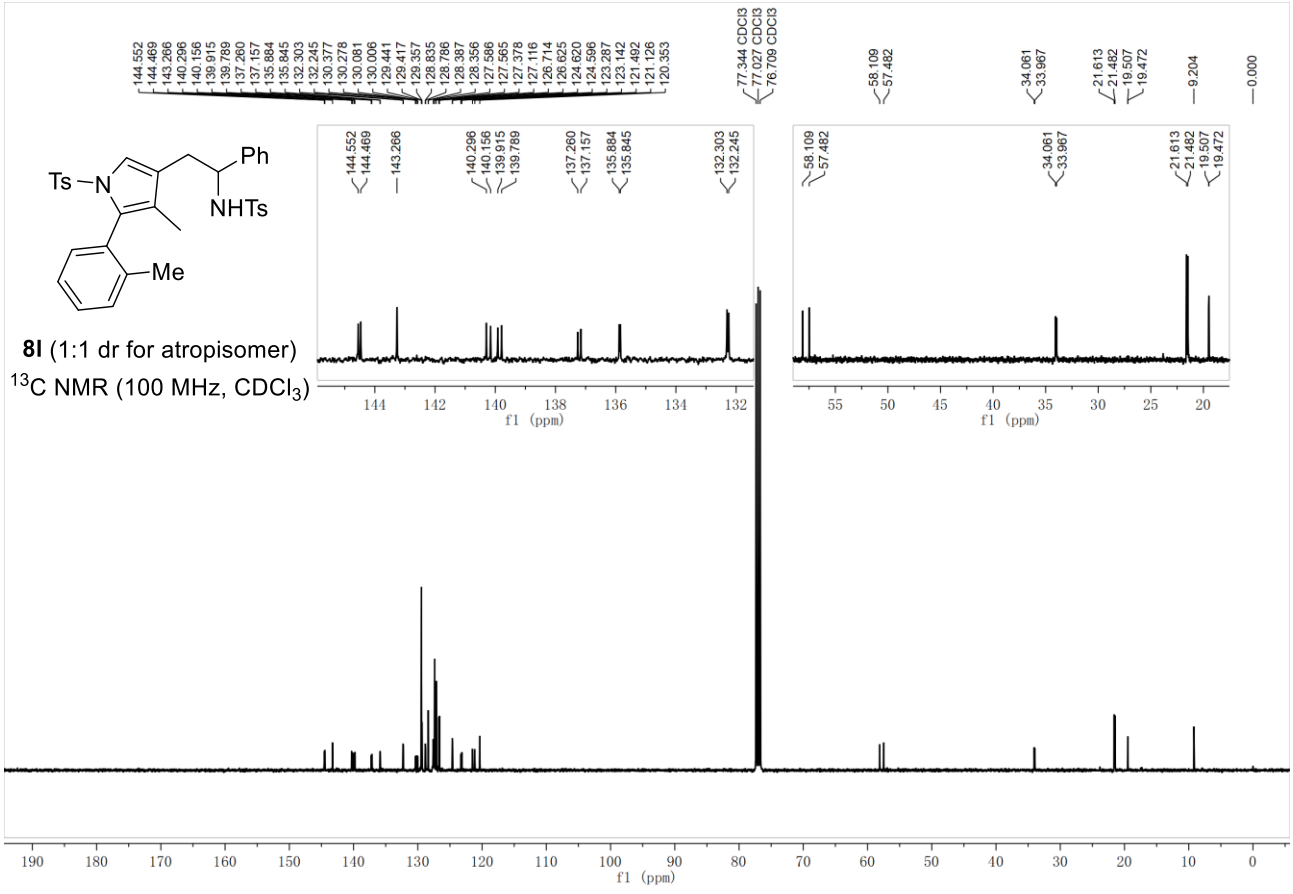


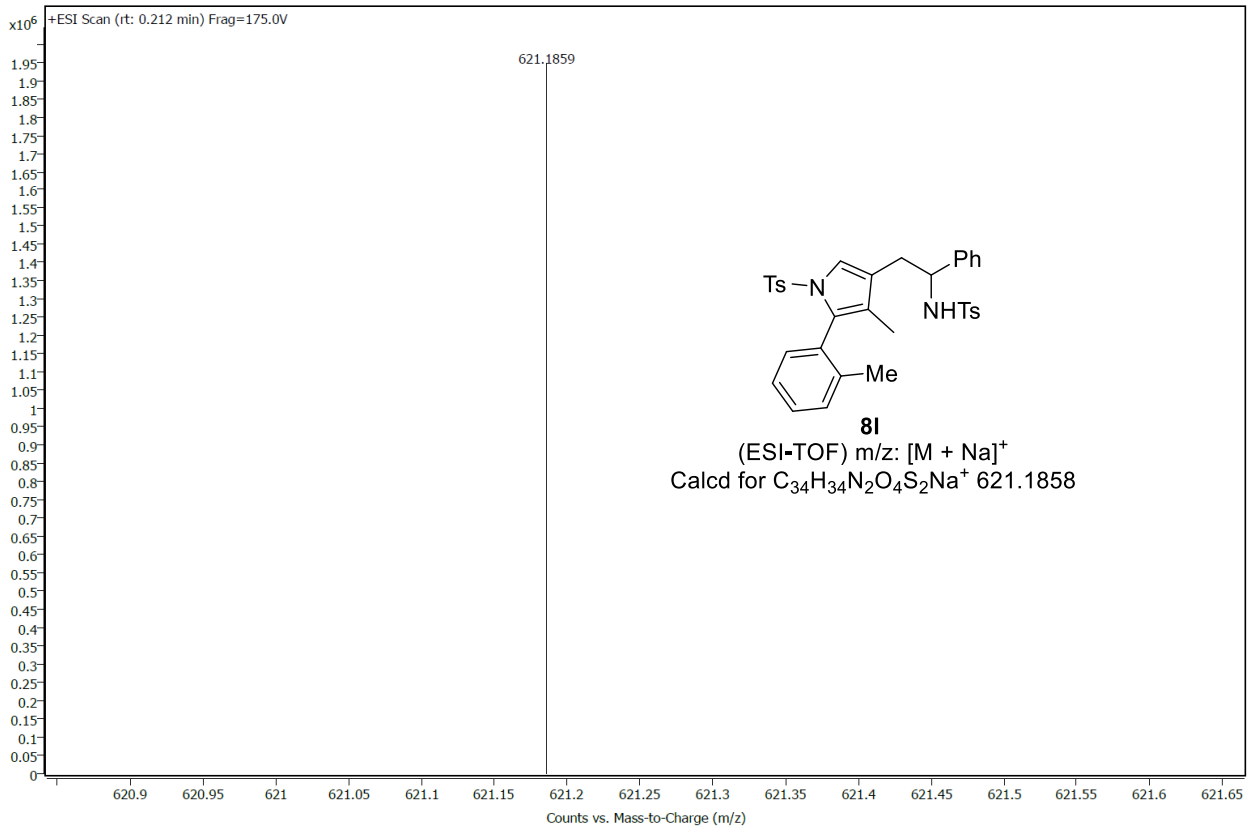
8k

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{31}H_{30}N_2O_4S_3Na^+$ 613.1266


Ts
N
Ph
NHTs
Me
8l (1:1 dr for atropisomer)
1H NMR (400 MHz, CDCl3)
f1 (ppm)

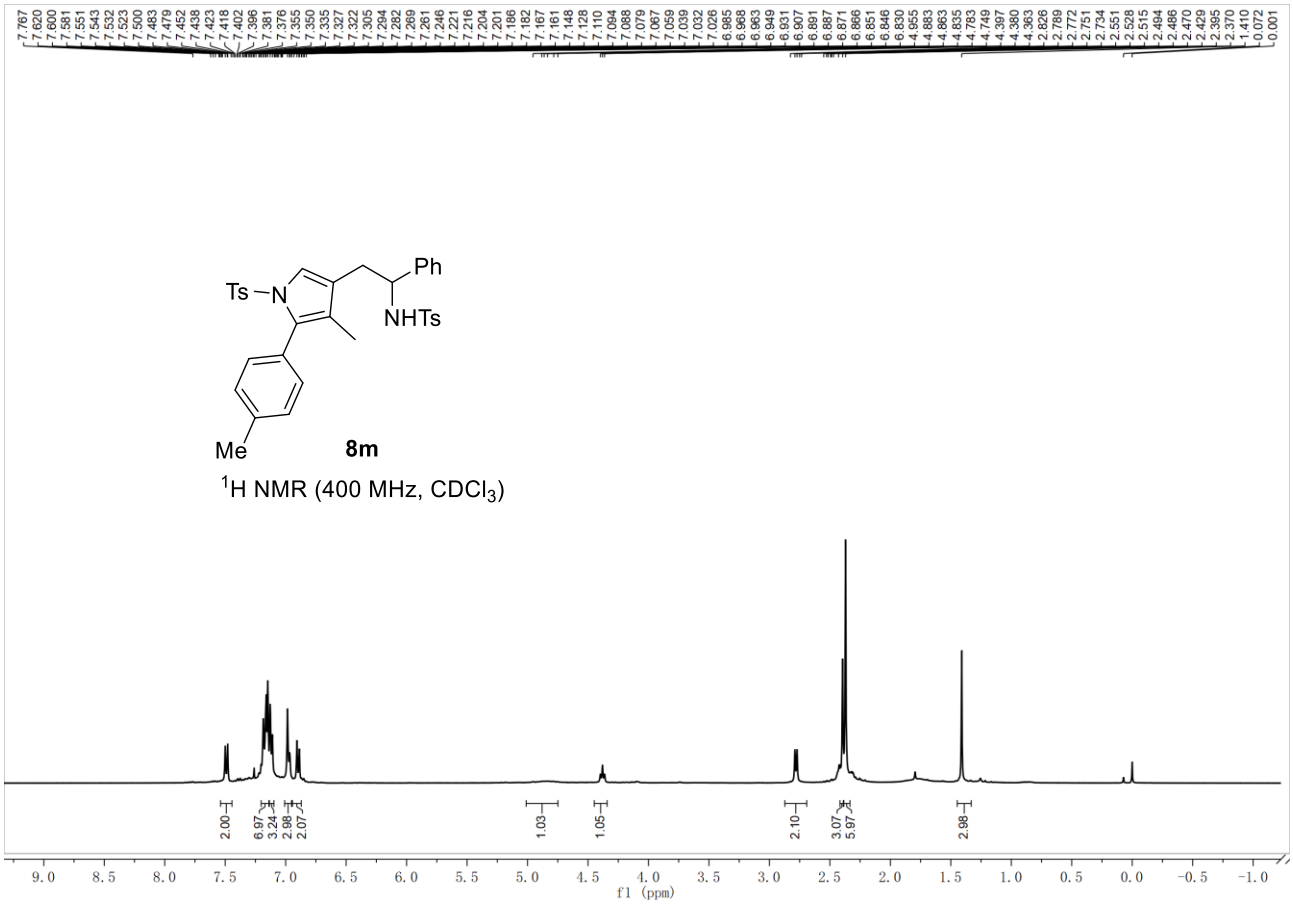

Ts
N
Ph
NHTs
Me
8l (1:1 dr for atropisomer)
13C NMR (100 MHz, CDCl3)
f1 (ppm)

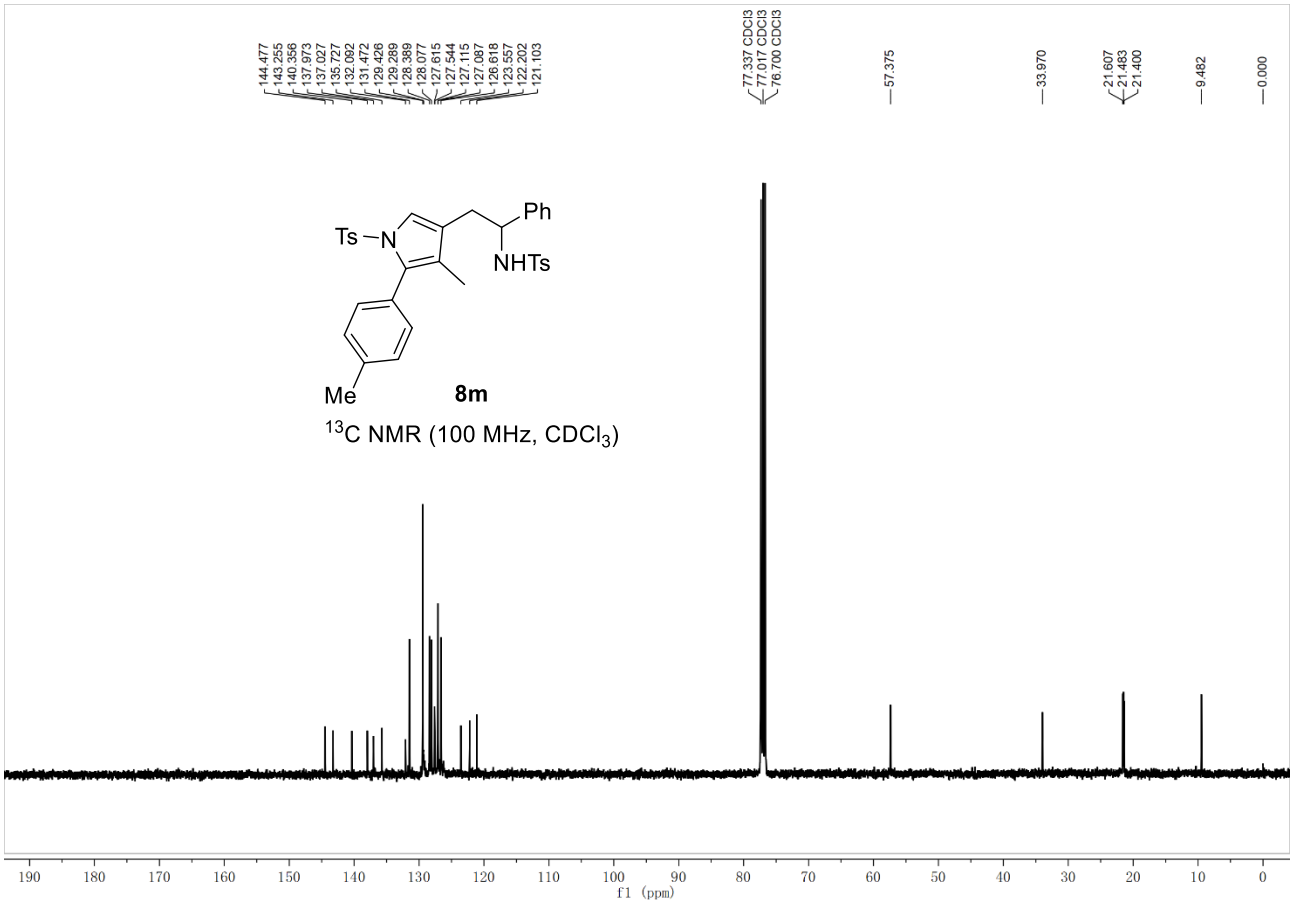


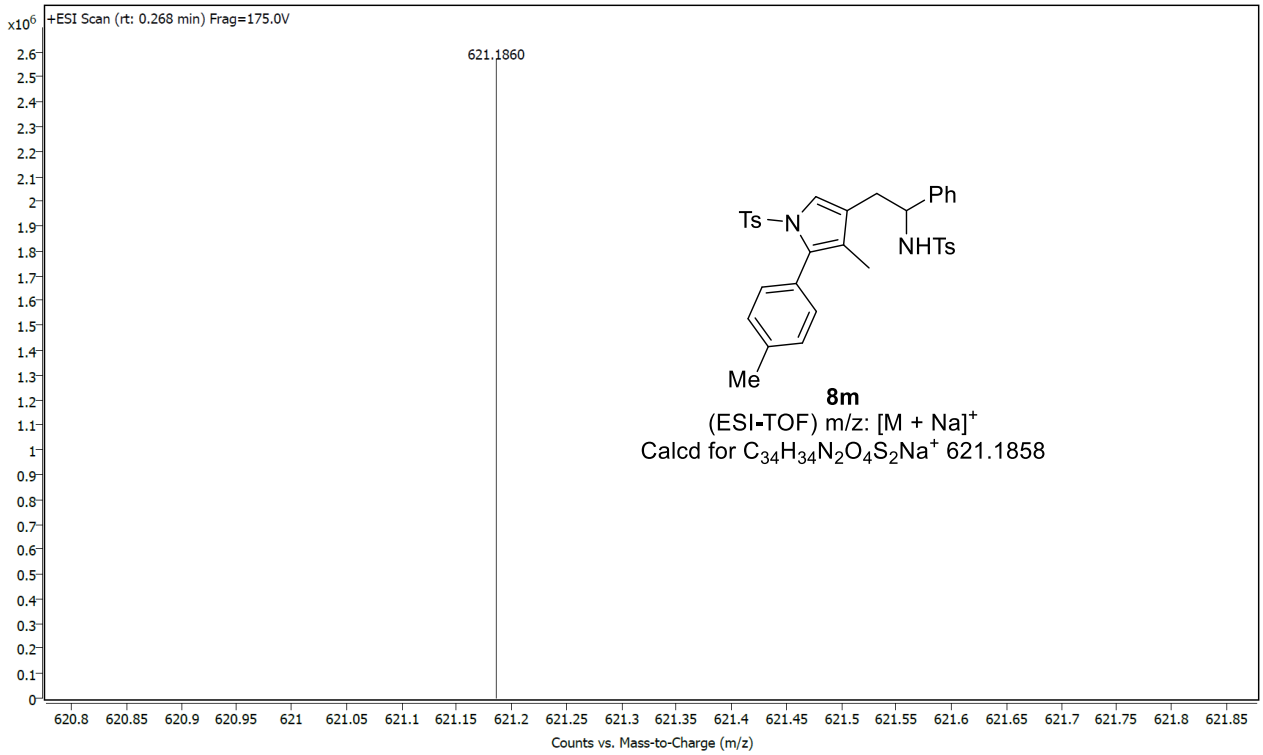
8l

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858


Ts
N
Ph
NHTs
Me
8m
1H NMR (400 MHz, CDCl3)
f1 (ppm)

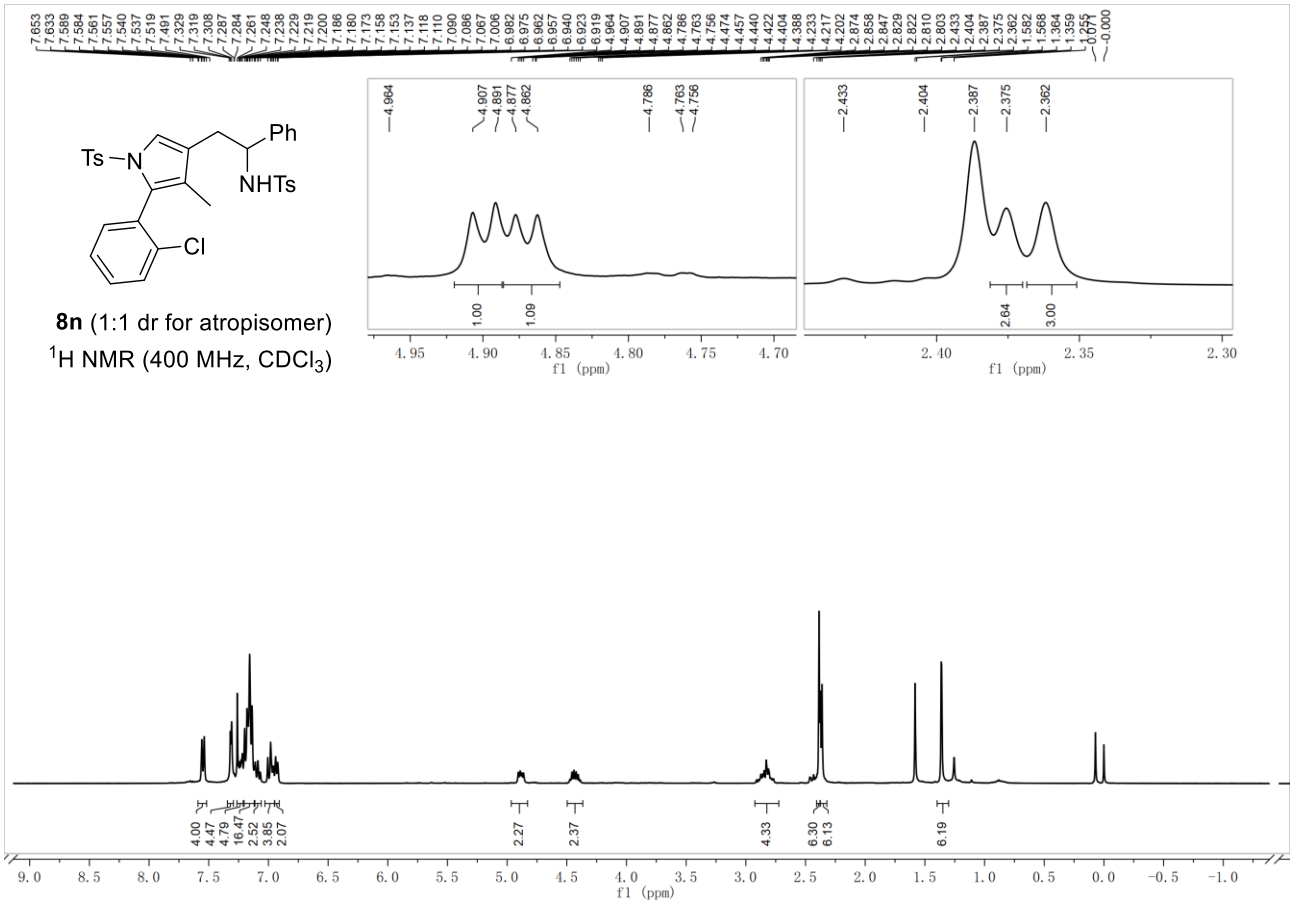

Ts
N
Ph
NHTs
Me
8m
13C NMR (100 MHz, CDCl3)
f1 (ppm)



8m

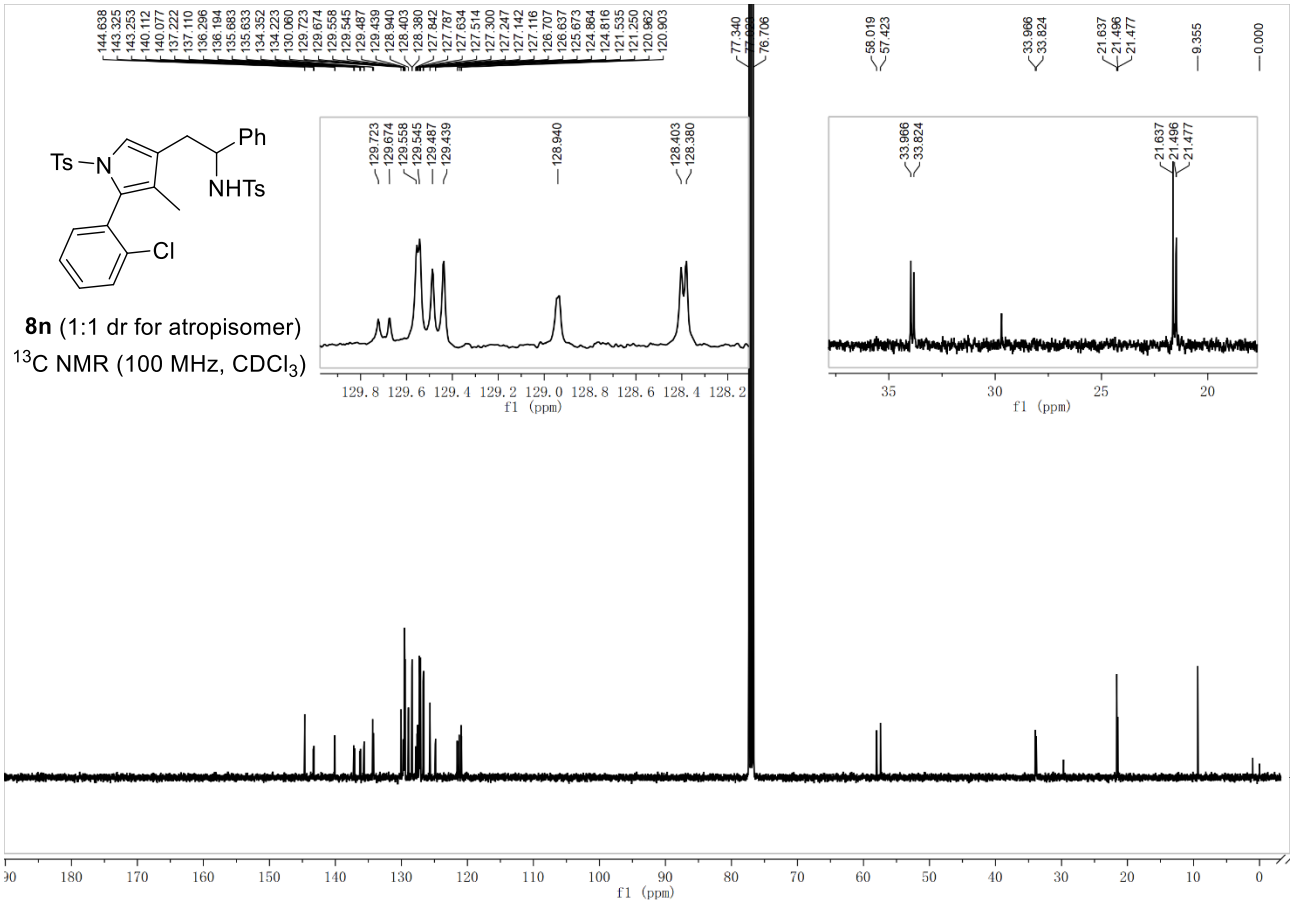
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{34}H_{34}N_2O_4S_2Na^+$ 621.1858



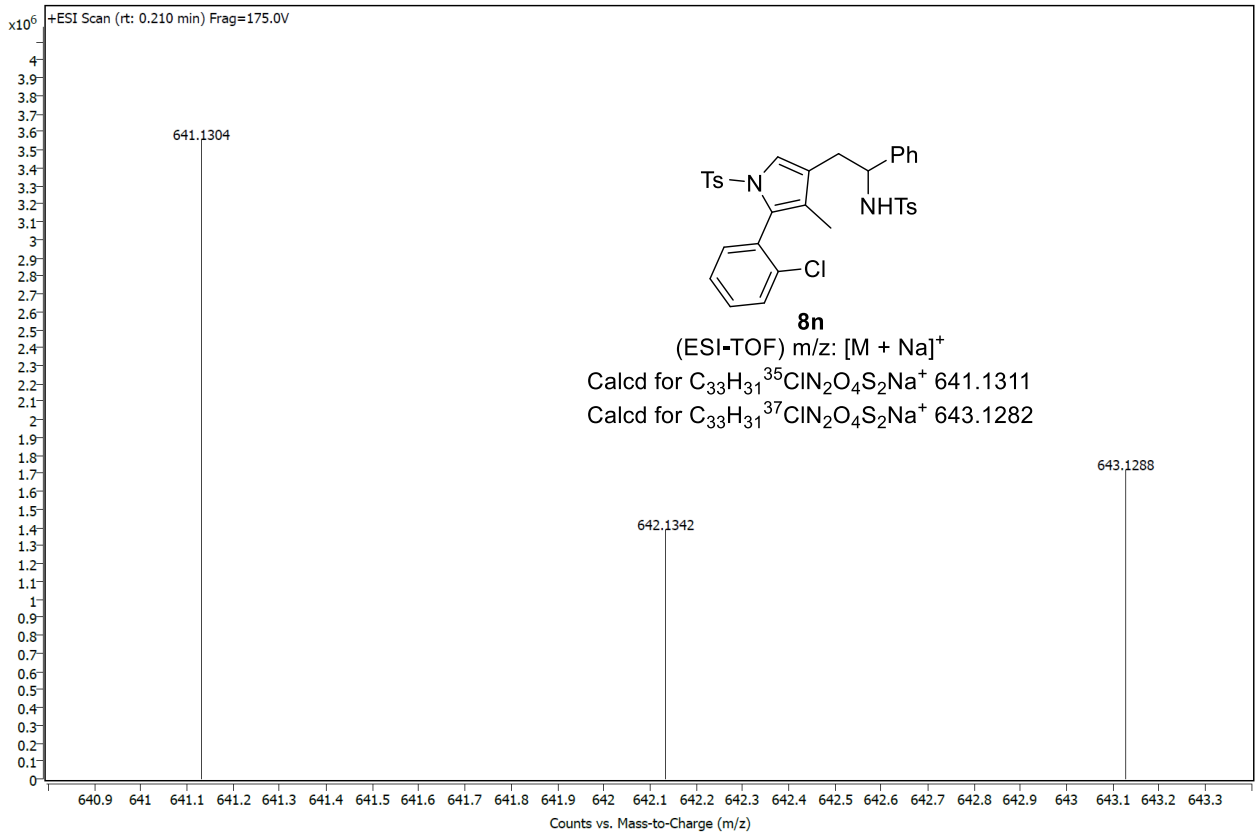
8n (1:1 dr for atropisomer)

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



8n (1:1 dr for atropisomer)

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

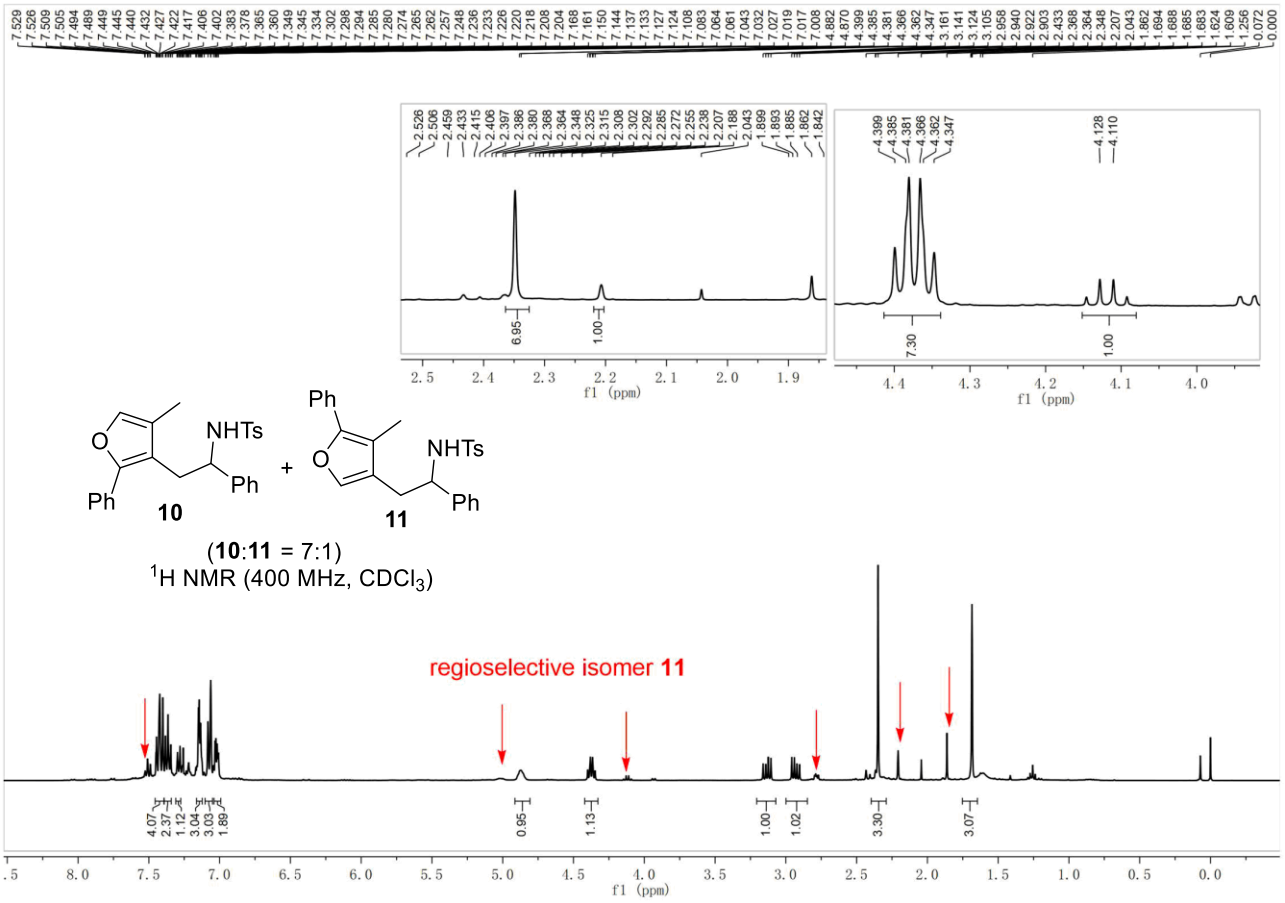


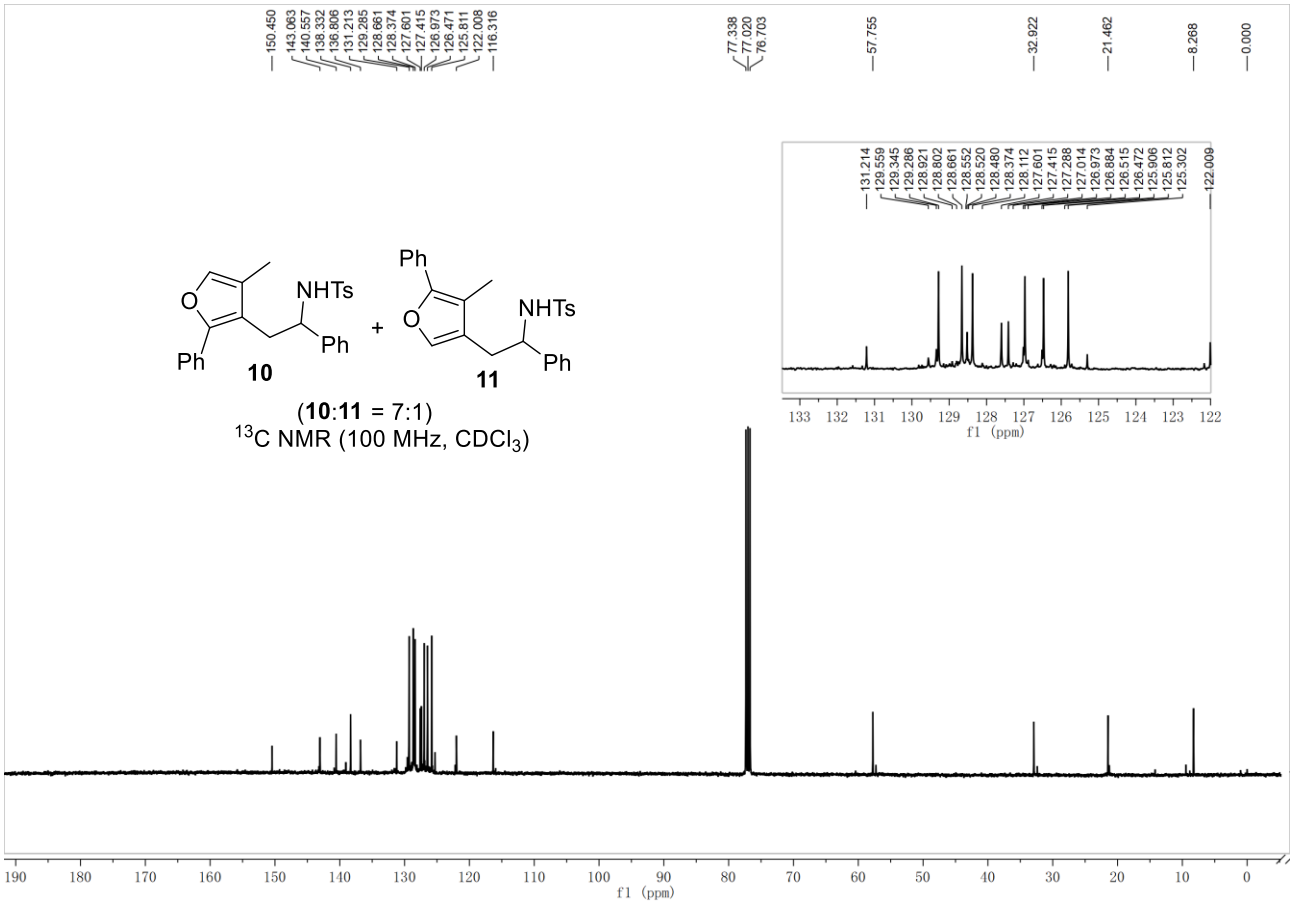
8n

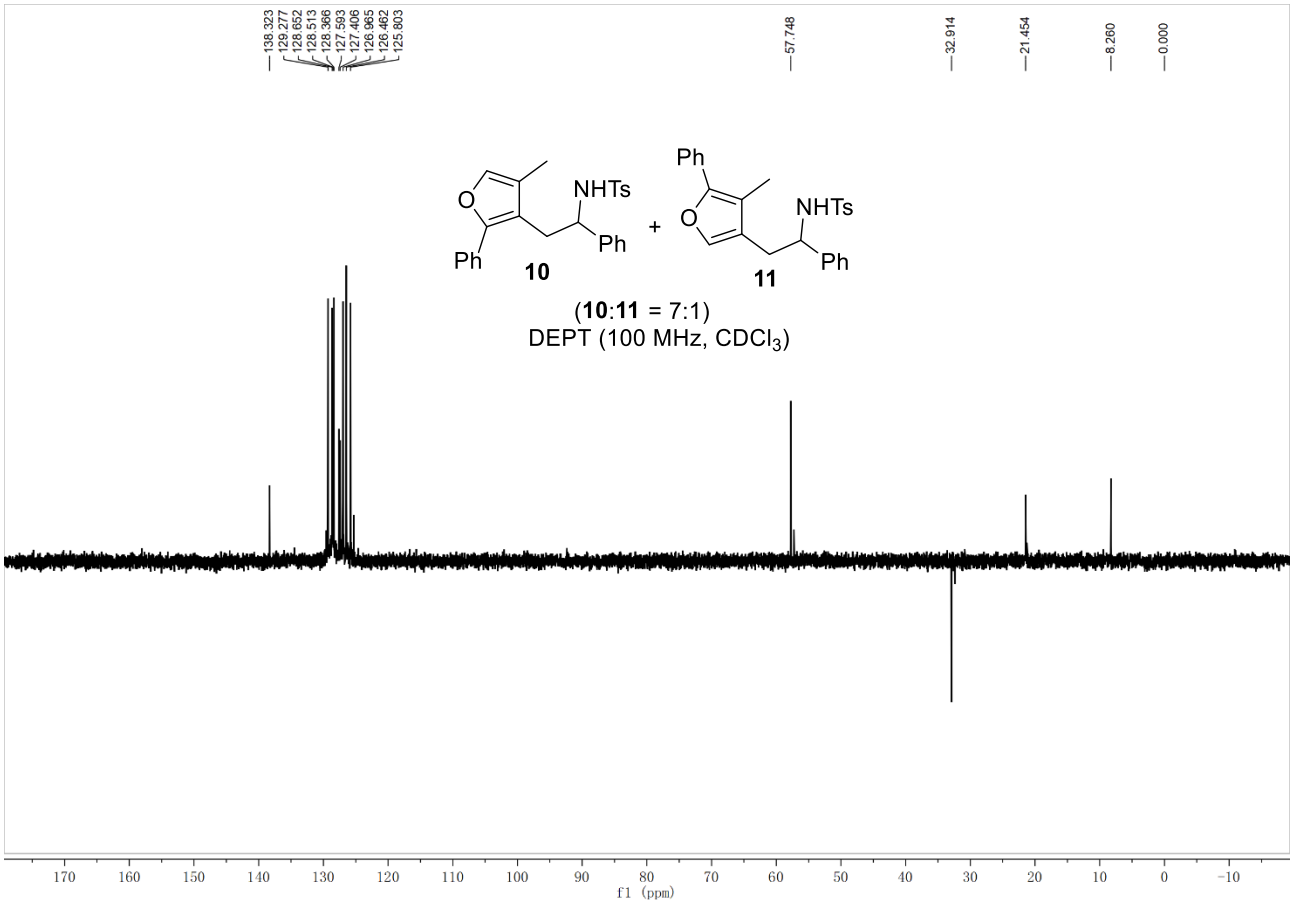
(ESI-TOF) m/z: $[M + Na]^+$

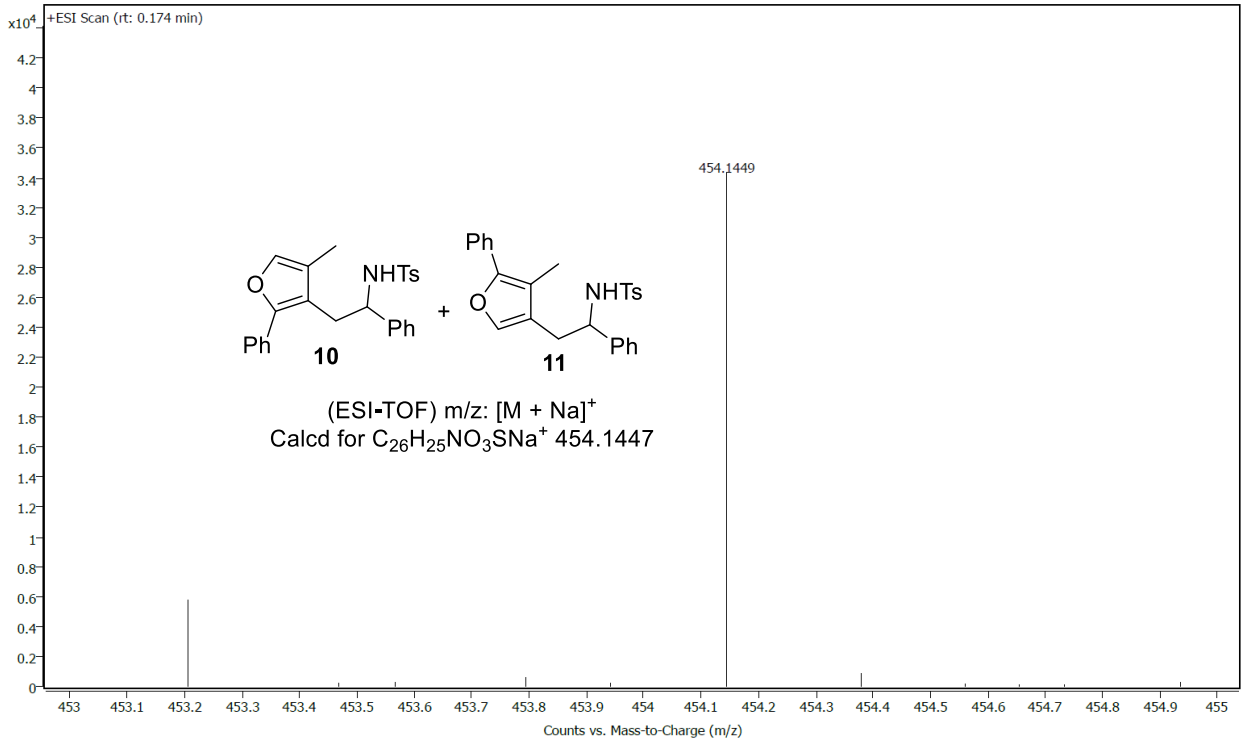
Calcd for $C_{33}H_{31}{}^{35}ClN_2O_4S_2Na^+$ 641.1311

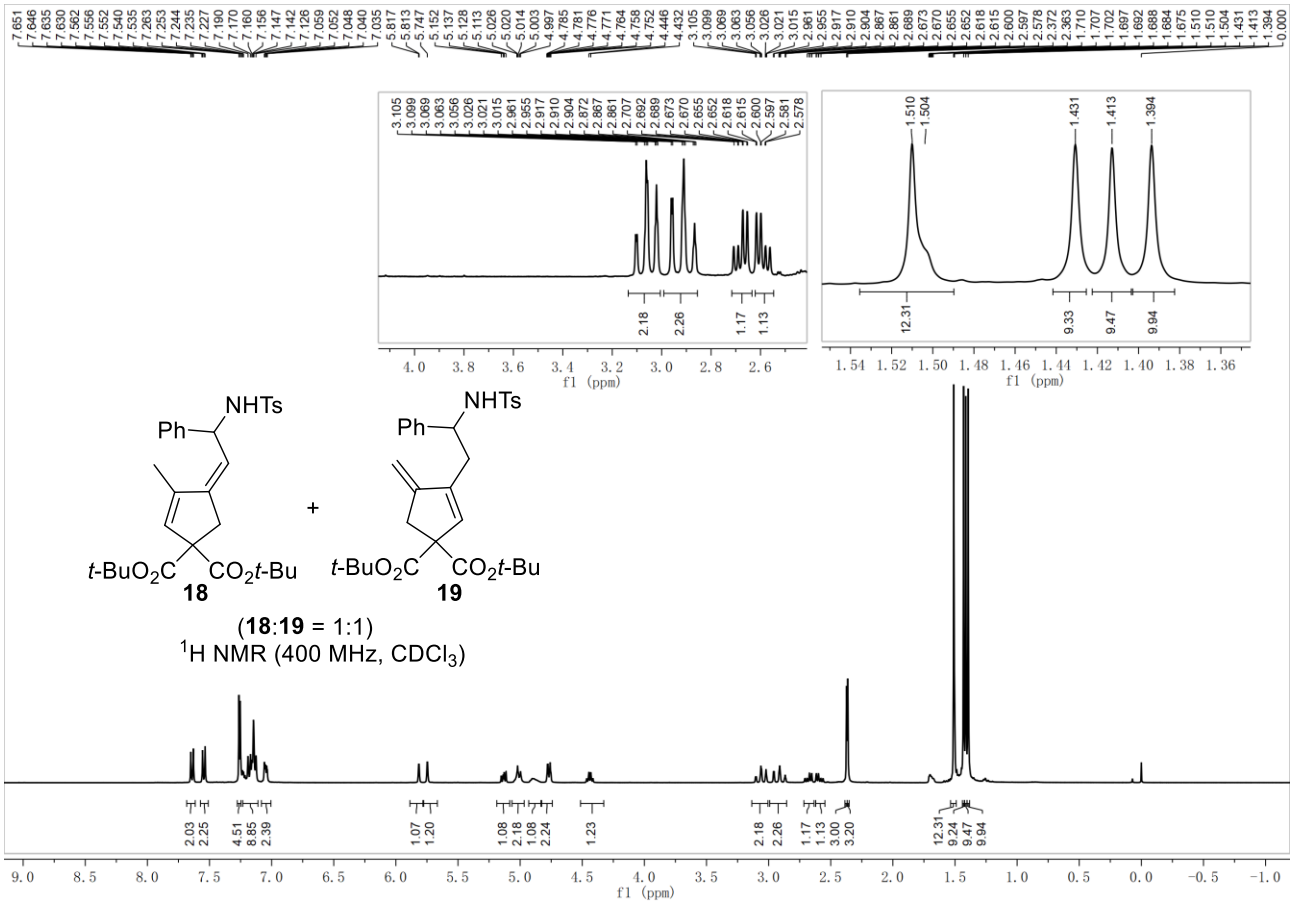
Calcd for $C_{33}H_{31}{}^{37}ClN_2O_4S_2Na^+$ 643.1282

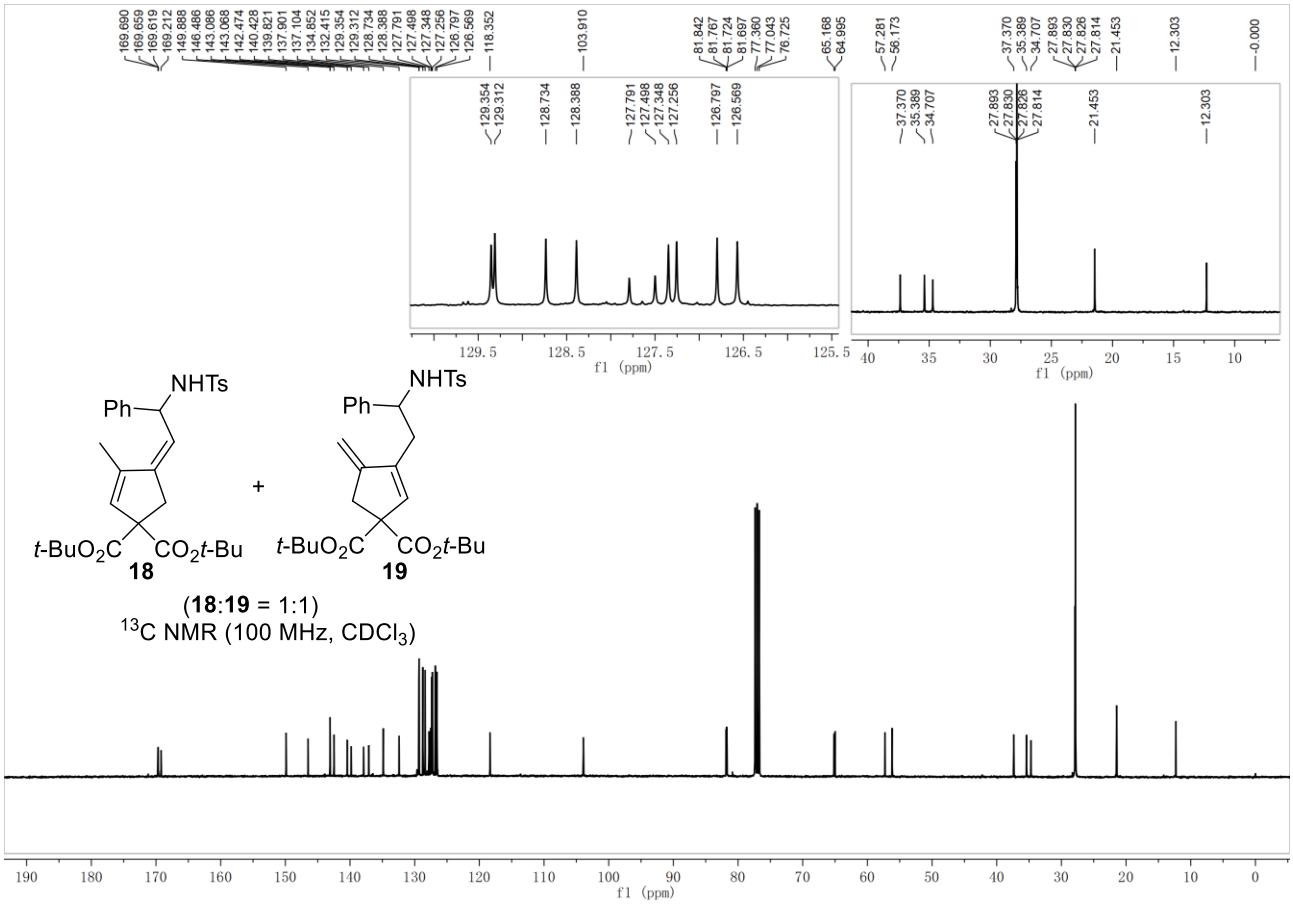

NHTs
Ph
Ph
10
NHTs
Ph
Ph
11
(10:11 = 7:1)
1H NMR (400 MHz, CDCl3)
regioselective isomer 11
f1 (ppm)

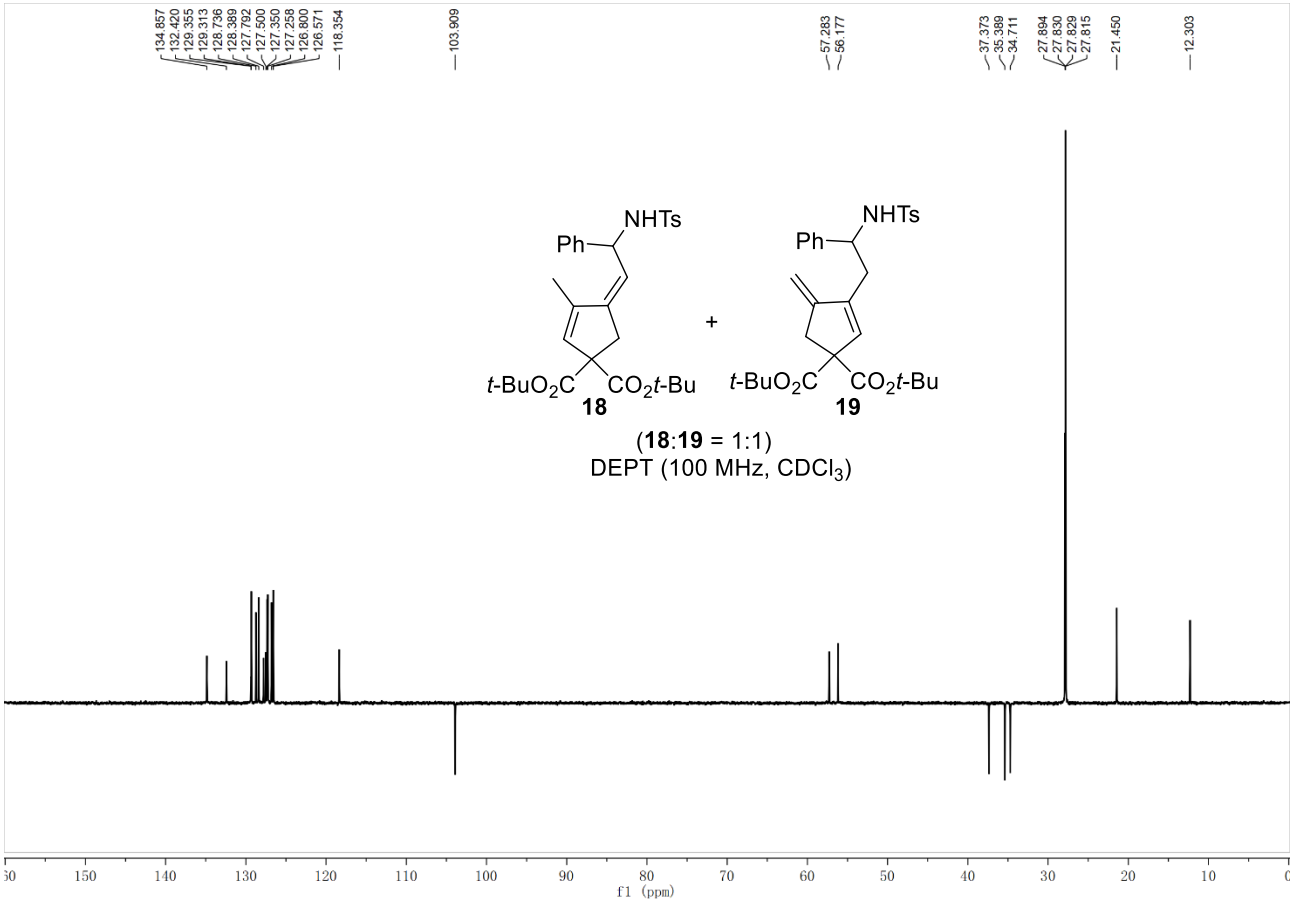

NHTs
Ph
Ph
10
NHTs
Ph
Ph
11
(10:11 = 7:1)
13C NMR (100 MHz, CDCl3)
f1 (ppm)

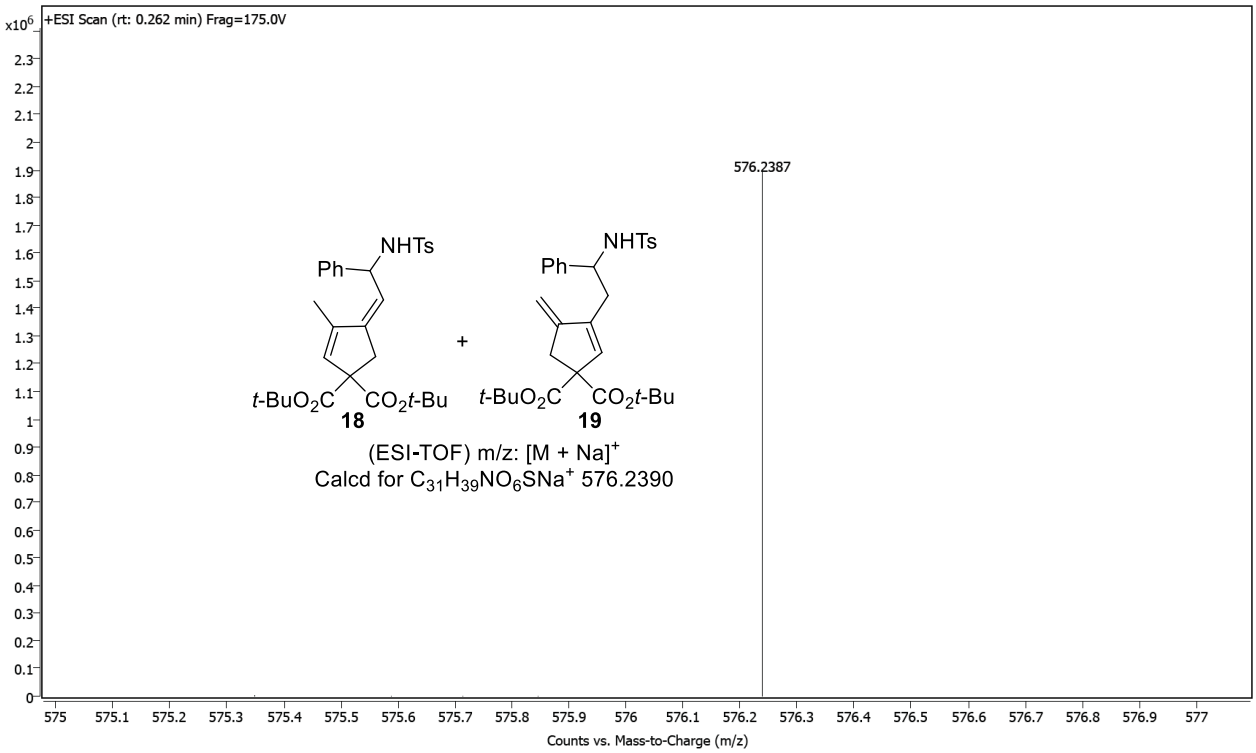

138.323
129.277
128.652
128.513
128.366
127.593
127.406
126.965
126.462
125.803
57.748
32.914
21.454
8.280
0.000
NHTs
Ph
Ph
10
Ph
NHTs
O
Ph
11
(10:11 = 7:1)
DEPT (100 MHz, CDCl3)
f1 (ppm)

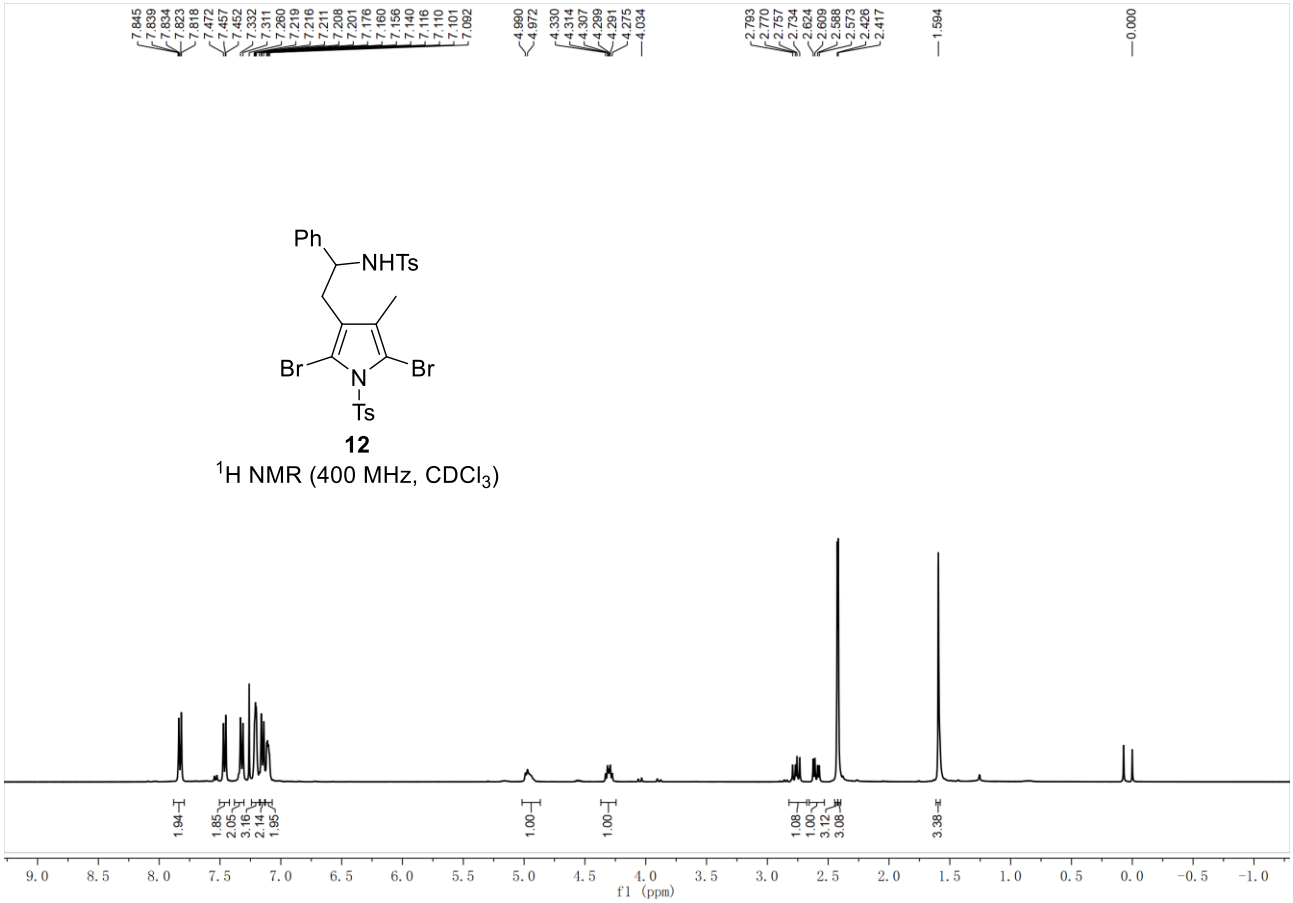

x10^4
+ESI Scan (rt: 0.174 min)
454.1449
NHTs
Ph
Ph
10
Ph
NHTs
O
Ph
11
(ESI-TOF) m/z: [M + Na]+
Calcd for C26H25NO3SNa+ 454.1447
Counts vs. Mass-to-Charge (m/z)

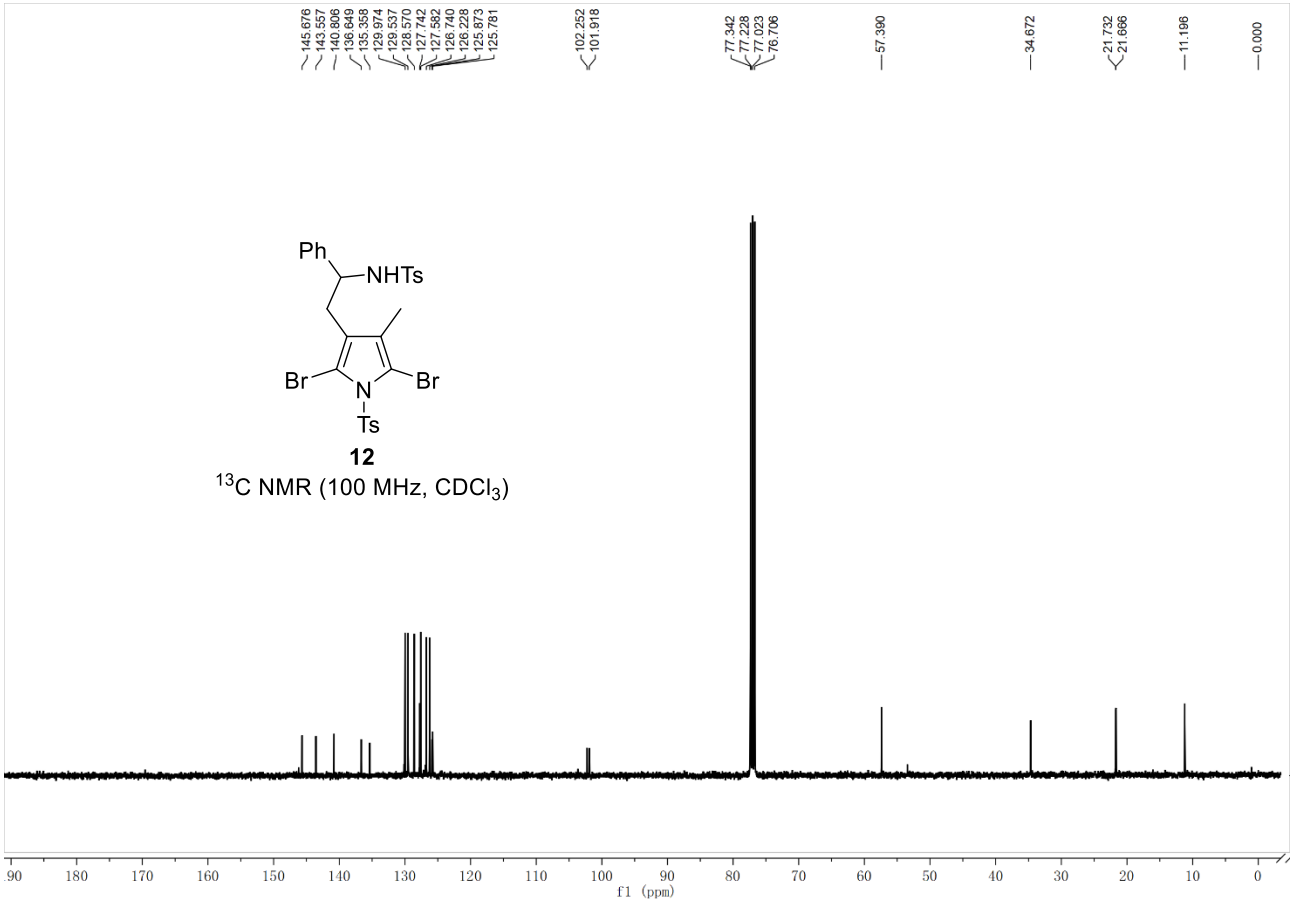

NHTs
Ph
t-BuO2C
CO2t-Bu
18
19
+
(18:19 = 1:1)
1H NMR (400 MHz, CDCl3)
f1 (ppm)

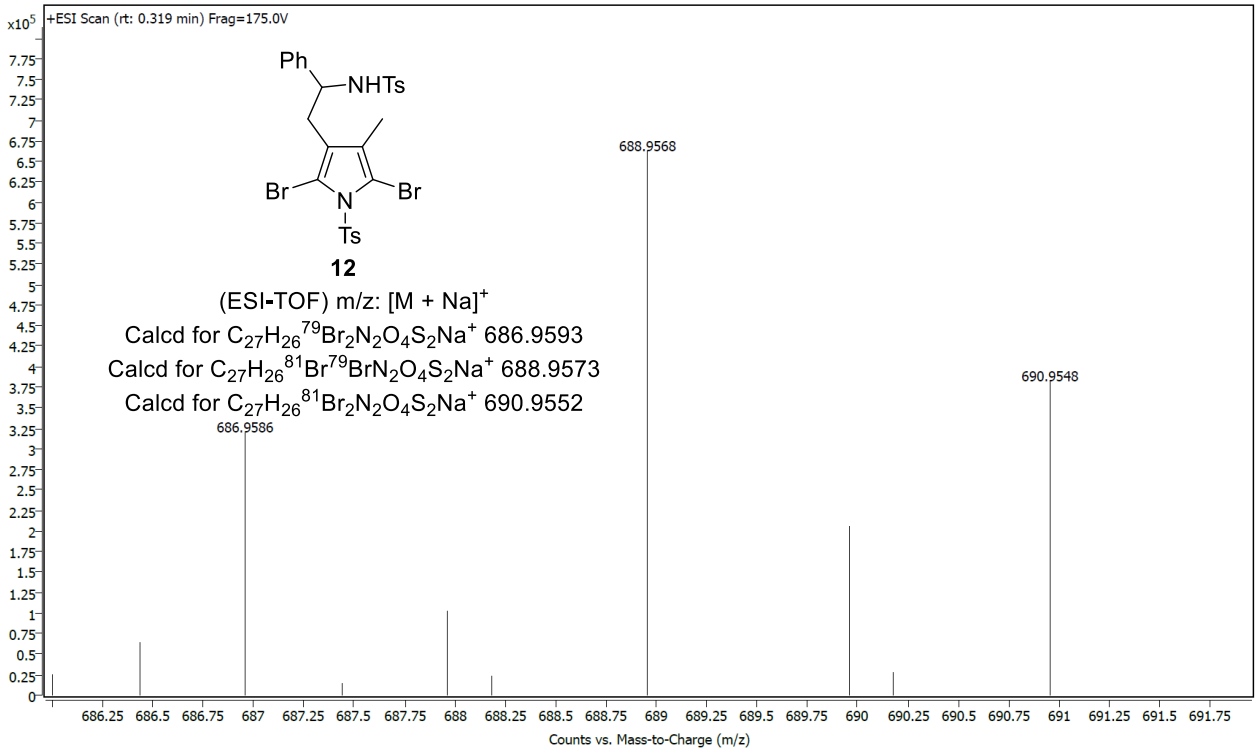

NHTs
Ph
t-BuO2C
CO2t-Bu
18
19
+
(18:19 = 1:1)
13C NMR (100 MHz, CDCl3)
f1 (ppm)

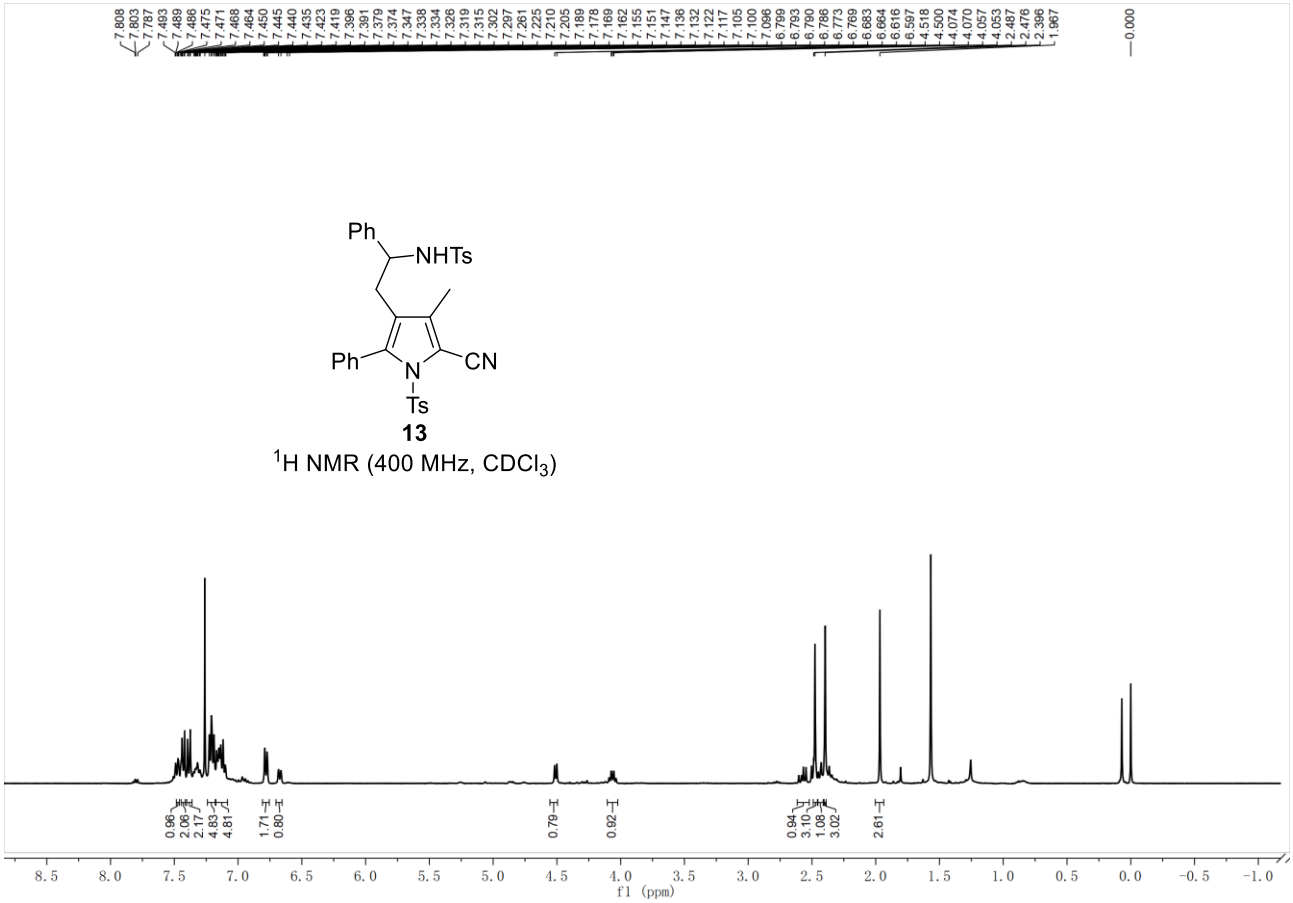

134.857
132.420
129.455
129.313
128.736
128.389
127.792
127.500
127.350
127.258
126.800
126.571
118.354
103.909
57.283
56.177
37.373
35.389
34.711
27.894
27.830
27.829
27.815
21.450
12.303
NHTs
Ph
t-BuO2C
CO2t-Bu
18
+
NHTs
Ph
t-BuO2C
CO2t-Bu
19
(18:19 = 1:1)
DEPT (100 MHz, CDCl3)
f1 (ppm)


+ESI Scan (rt: 0.262 min) Frag=175.0V
x10^6
576.2387
NHTs
Ph
t-BuO2C
CO2t-Bu
18
+
NHTs
Ph
t-BuO2C
CO2t-Bu
19
(ESI-TOF) m/z: [M + Na]+
Calcd for C31H39NO6SNa+ 576.2390
Counts vs. Mass-to-Charge (m/z)


7.845
7.839
7.834
7.823
7.818
7.472
7.457
7.452
7.332
7.311
7.280
7.219
7.216
7.211
7.208
7.201
7.176
7.160
7.156
7.140
7.116
7.110
7.101
7.092
4.990
4.972
4.330
4.314
4.307
4.299
4.291
4.275
4.034
2.793
2.770
2.757
2.734
2.624
2.609
2.588
2.573
2.426
2.417
1.594
0.000
Ph
NHTs
Br
Br
N
Ts
12
1H NMR (400 MHz, CDCl3)
1.94
1.85
2.05
3.16
2.14
1.95
1.00
1.00
1.08
1.00
3.12
3.08
3.38
f1 (ppm)

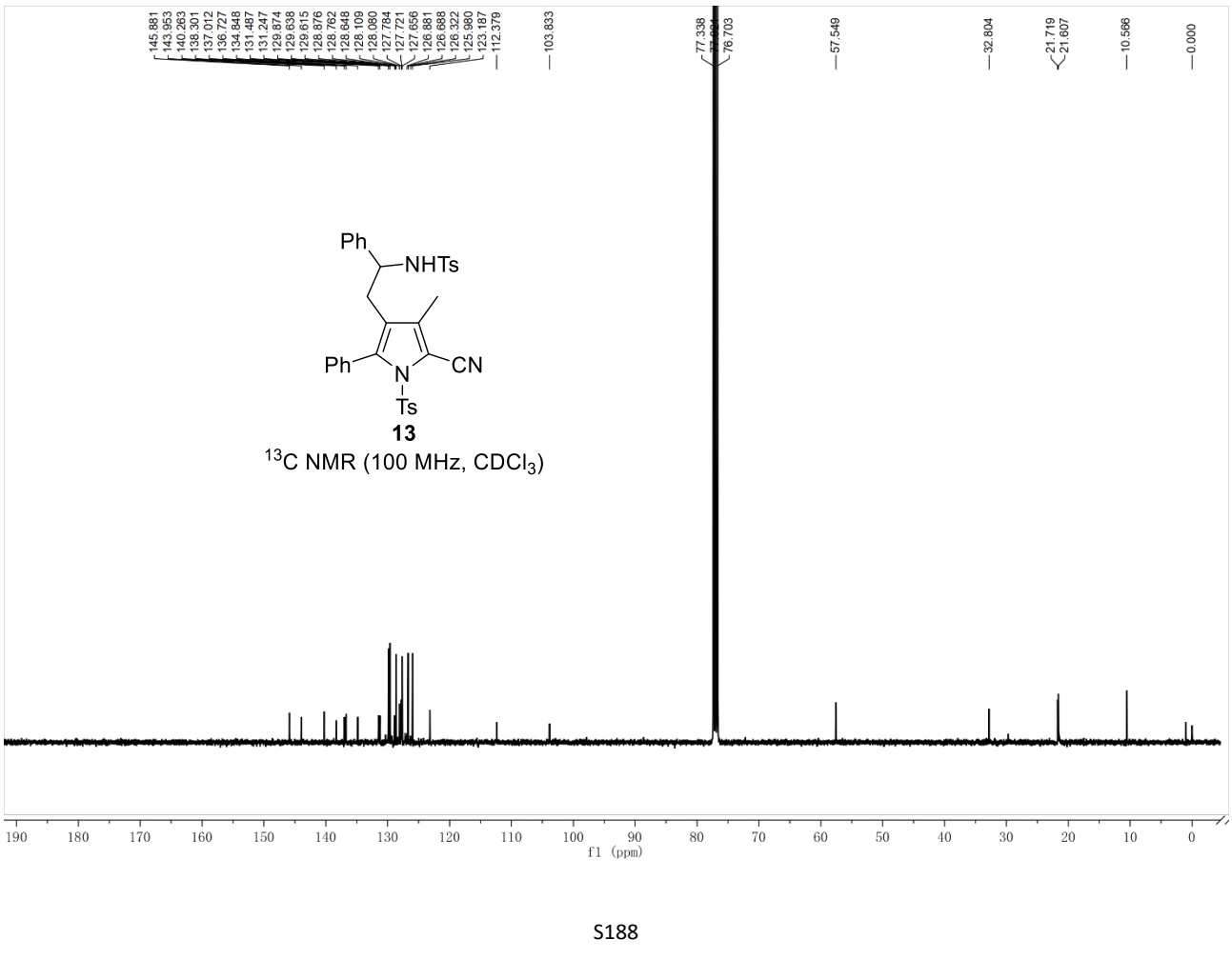

145.676
143.557
140.806
136.649
135.358
129.974
129.537
128.570
127.742
127.582
126.740
126.228
125.873
125.781
102.252
101.918
77.342
77.228
77.023
76.706
57.390
34.672
21.732
21.666
11.196
0.000
Ph
NHTs
Br
Br
N
Ts
12
13C NMR (100 MHz, CDCl3)
f1 (ppm)


+ESI Scan (rt: 0.319 min) Frag=175.0V
x10^5
Ph
NHTs
Br
Br
N
Ts
12
(ESI-TOF) m/z: [M + Na]+
Calcd for C27H26 79Br2N2O4S2Na+ 686.9593
Calcd for C27H26 81Br 79BrN2O4S2Na+ 688.9573
Calcd for C27H26 81Br2N2O4S2Na+ 690.9552
686.9586
688.9568
690.9548
Counts vs. Mass-to-Charge (m/z)



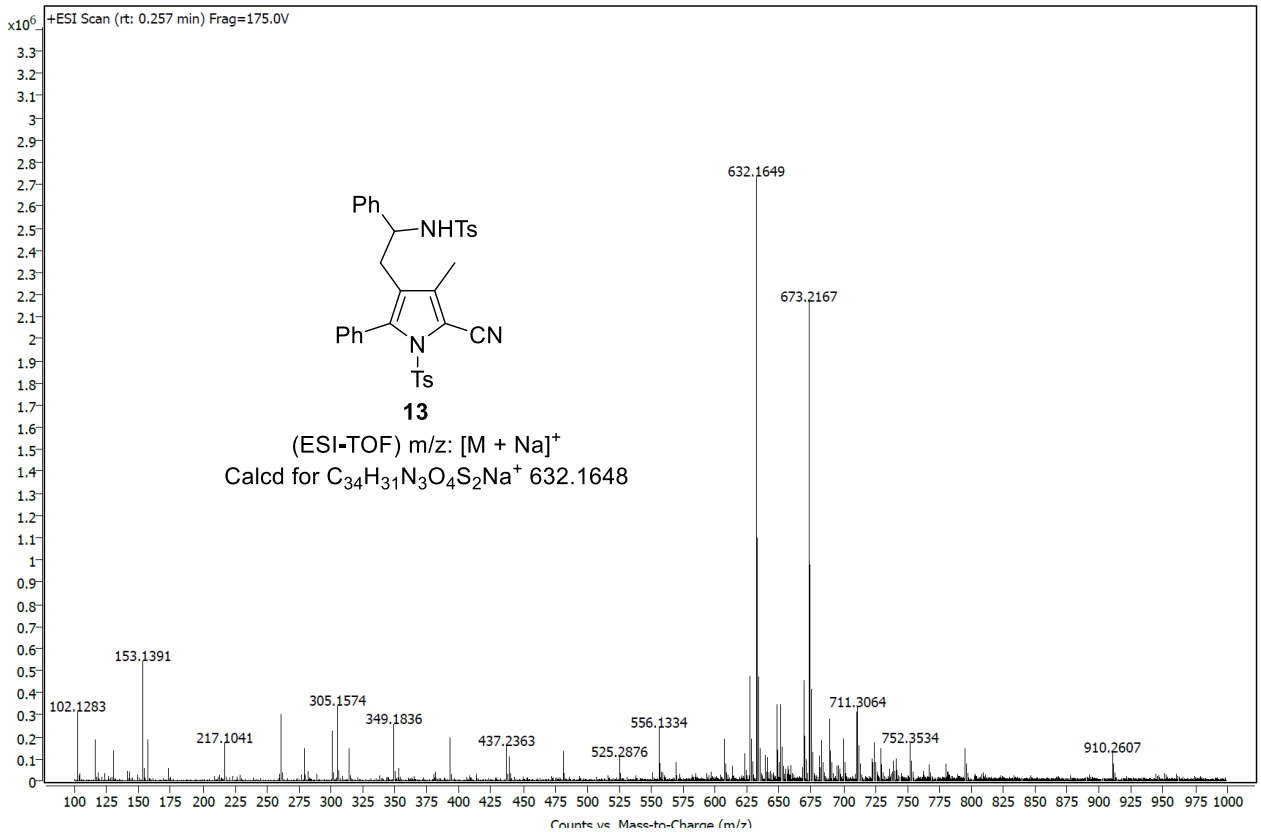
13

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



13

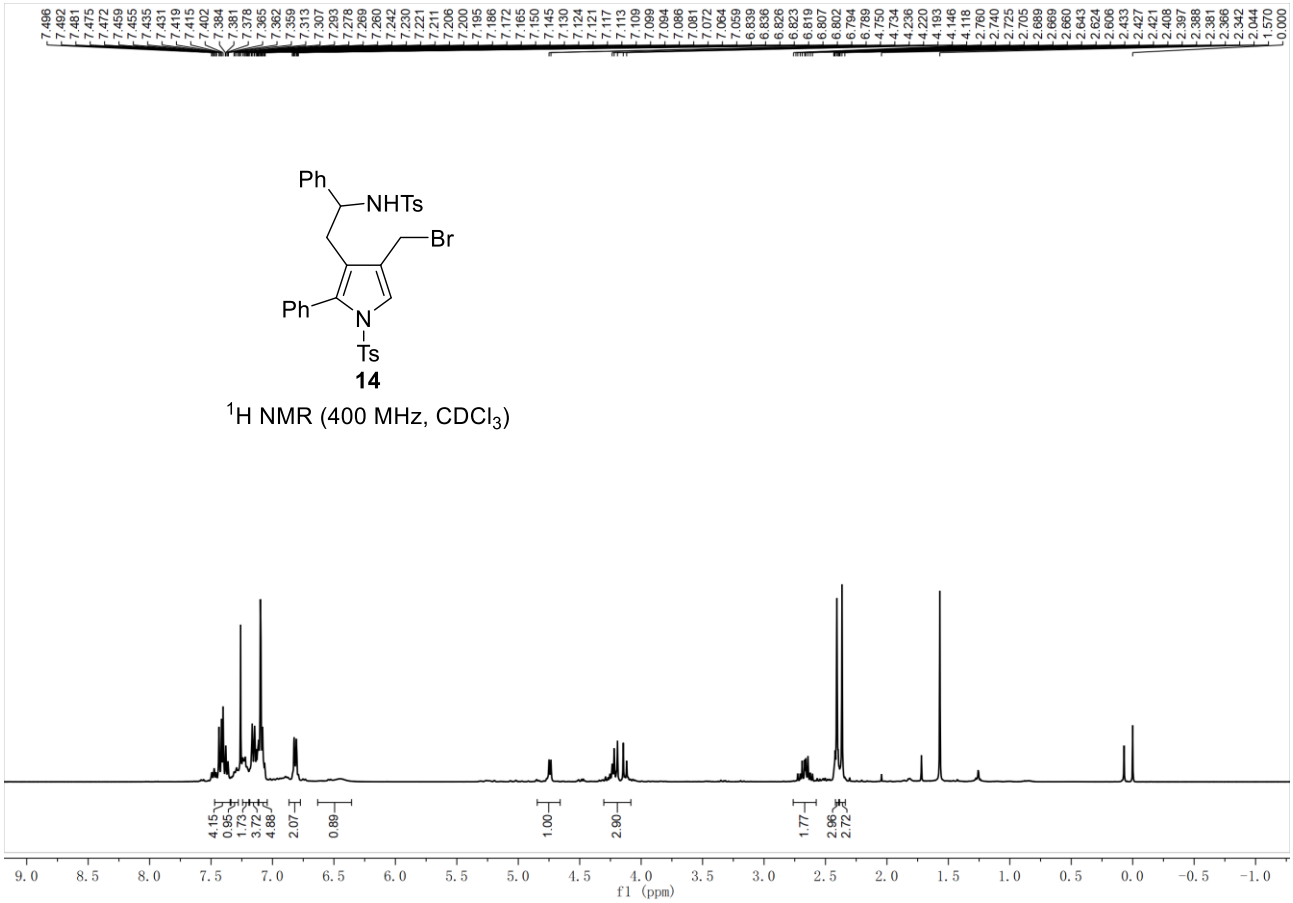
^{13}C NMR (100 MHz, $CDCl_3$)

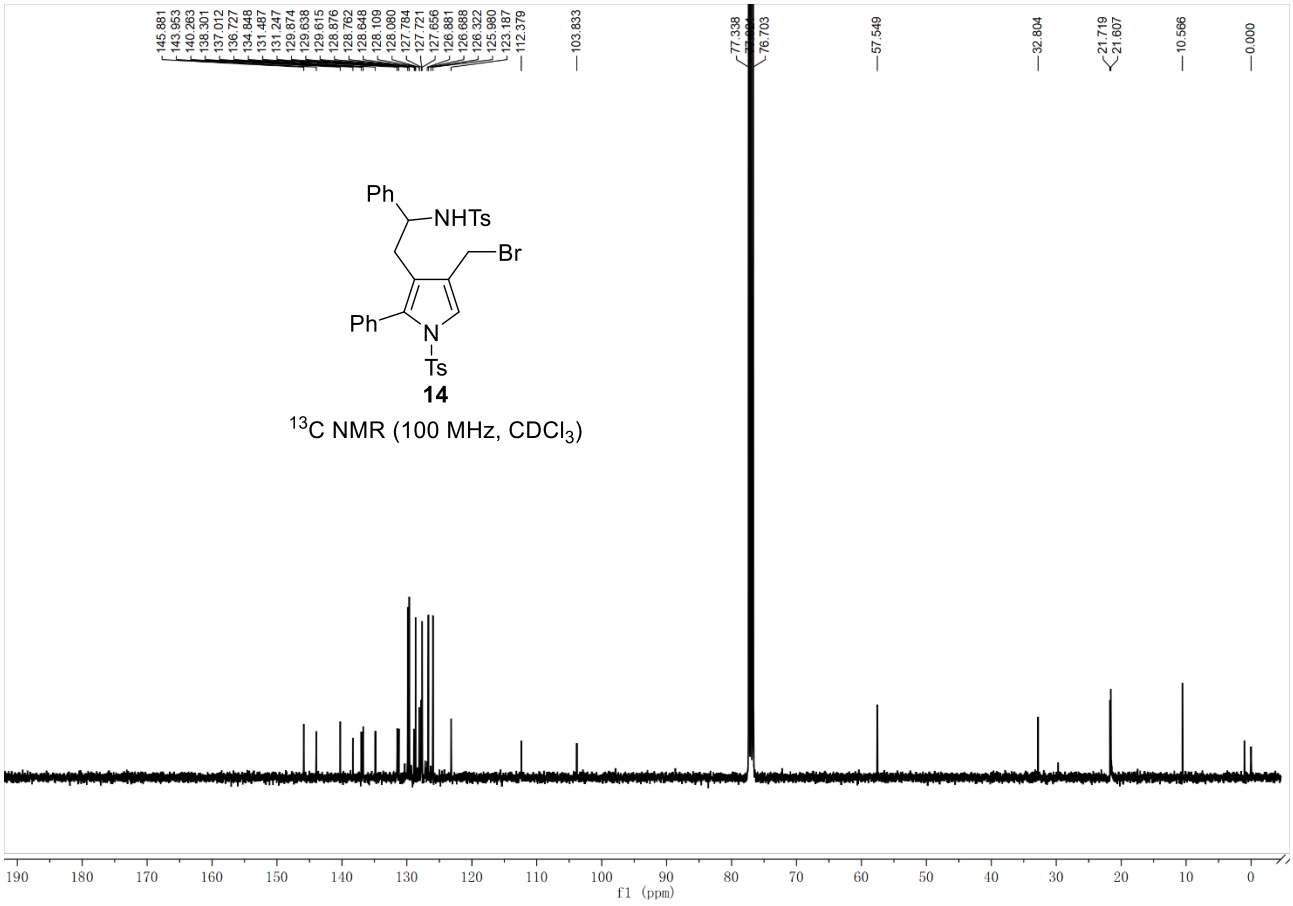


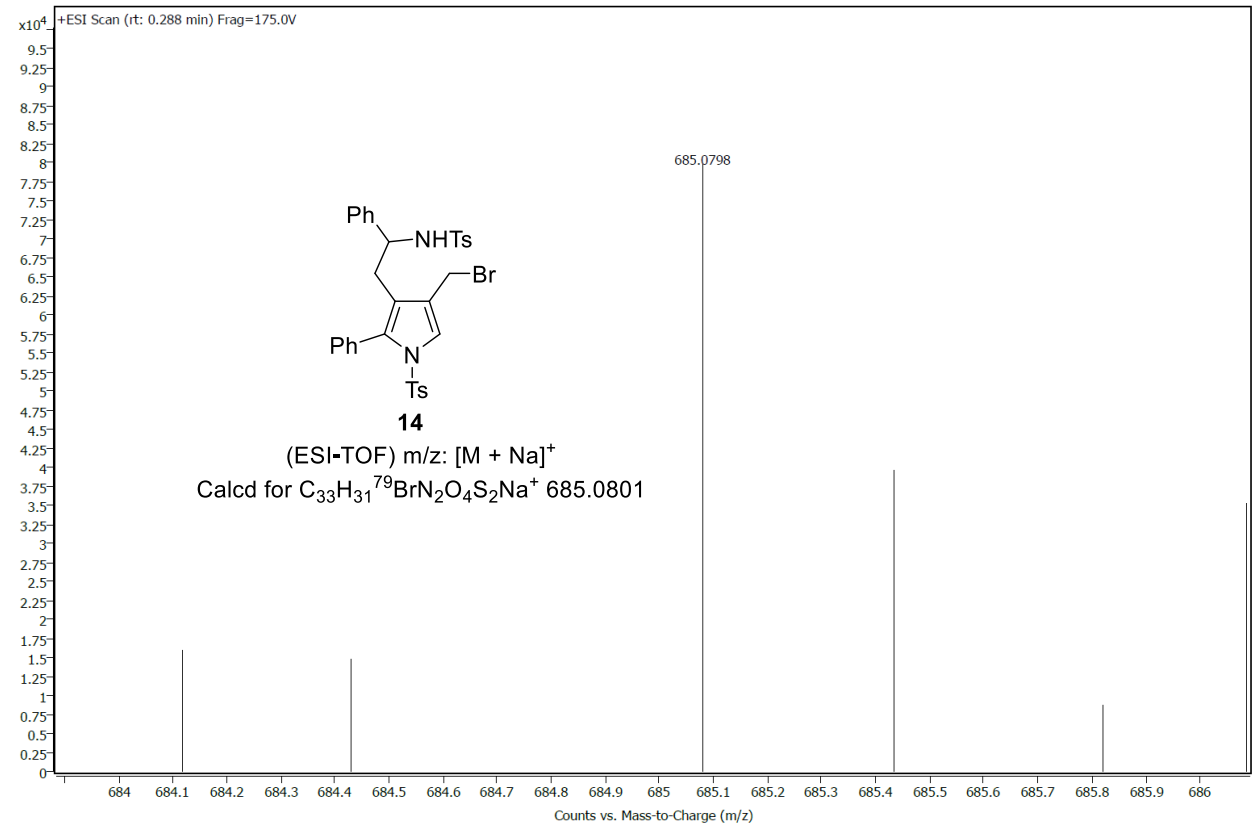
13

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{34}H_{31}N_3O_4S_2Na^+$ 632.1648


Ph
NHTs
Br
Ph
N
Ts
14
1H NMR (400 MHz, CDCl3)
f1 (ppm)

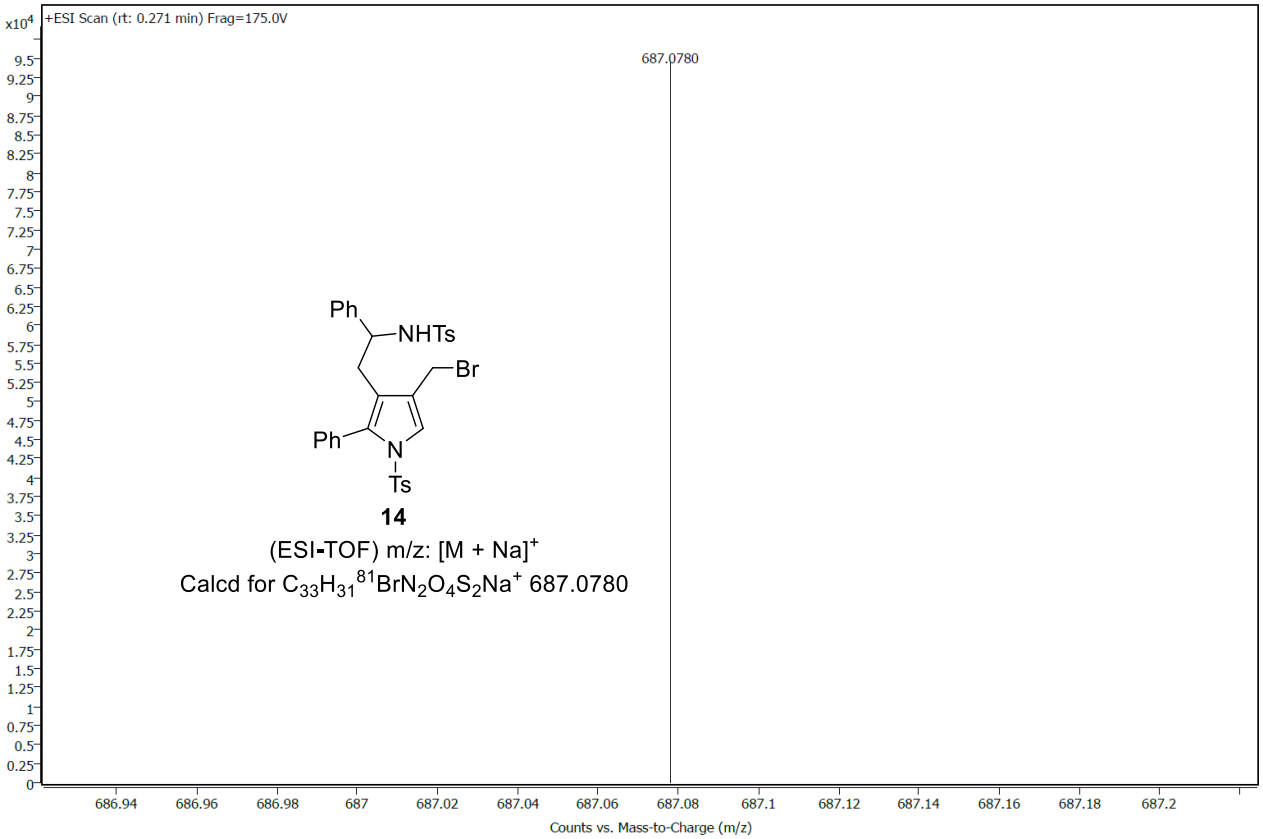

Ph
NHTs
Br
Ph
N
Ts
14
13C NMR (100 MHz, CDCl3)
f1 (ppm)



14

(ESI-TOF) m/z: $[M + Na]^+$

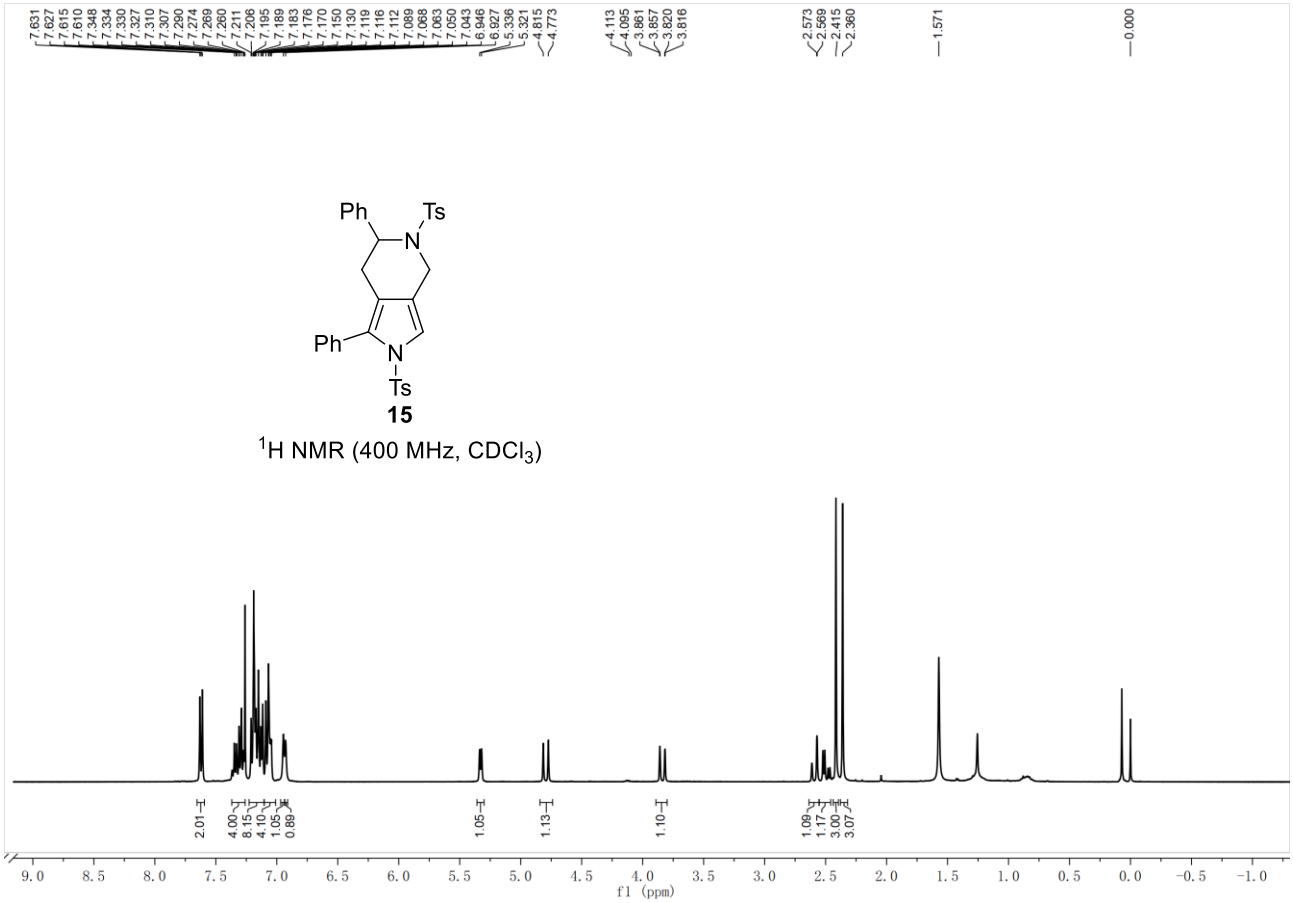
Calcd for $C_{33}H_{31}{}^{79}BrN_2O_4S_2Na^+$ 685.0801

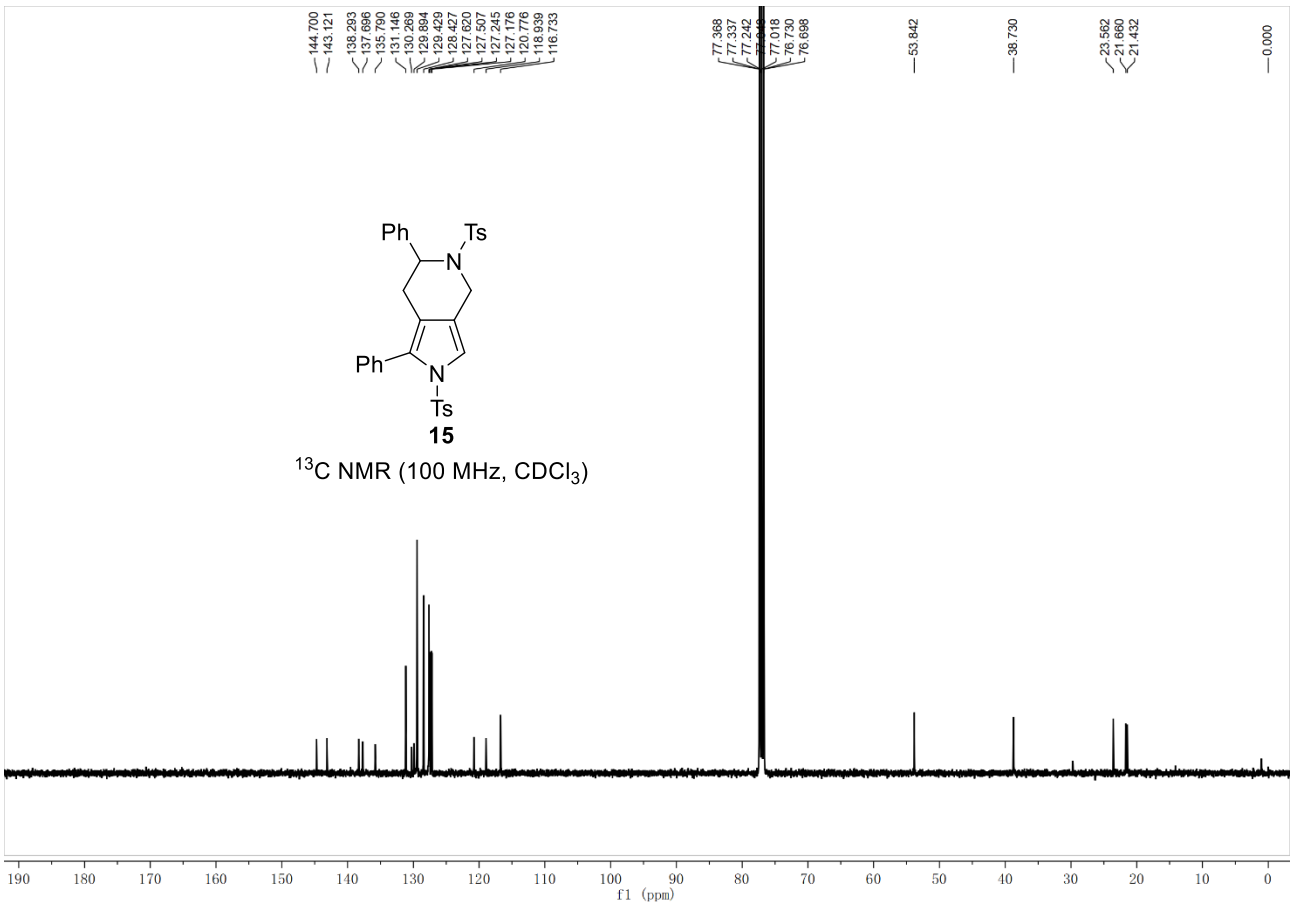


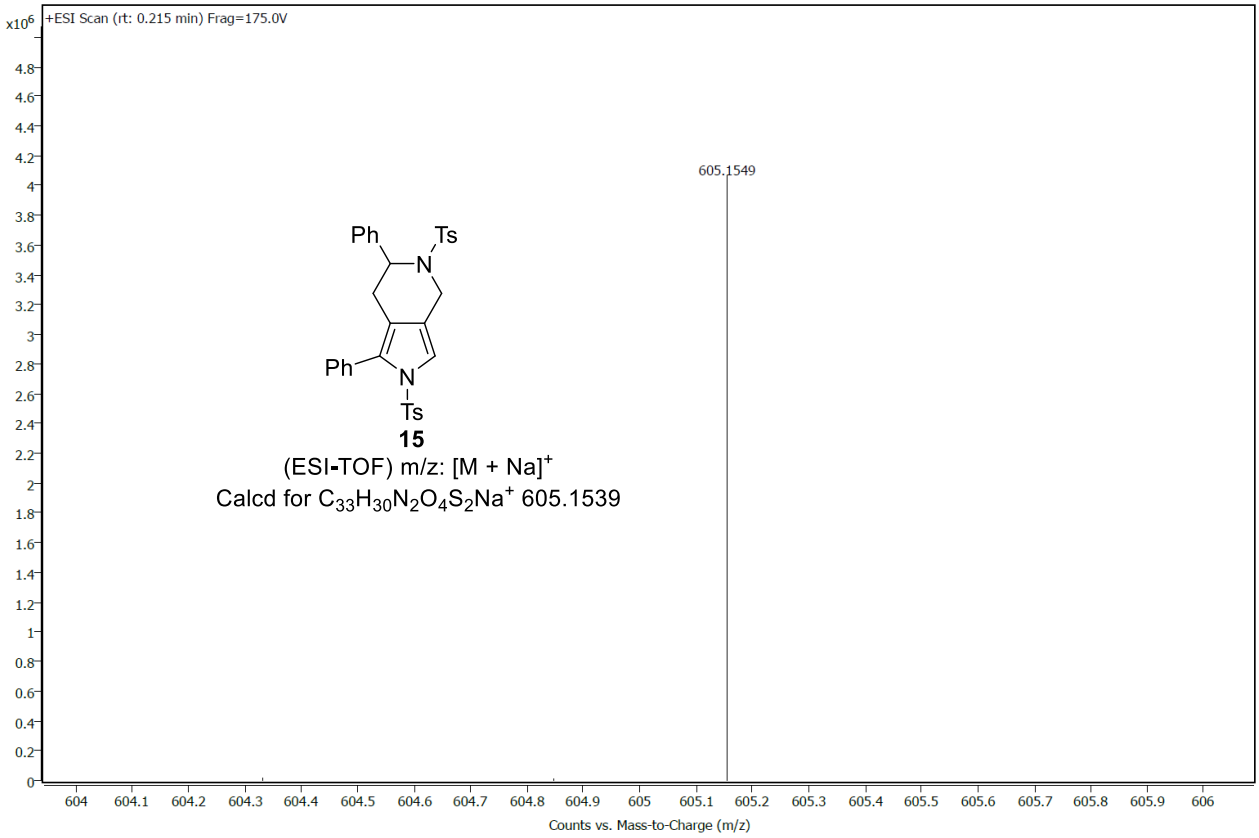
14

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{33}H_{31}{}^{81}BrN_2O_4S_2Na^+$ 687.0780


7.631
7.627
7.615
7.610
7.348
7.334
7.330
7.327
7.310
7.307
7.290
7.274
7.269
7.260
7.211
7.206
7.195
7.189
7.183
7.176
7.170
7.150
7.130
7.119
7.116
7.112
7.089
7.068
7.063
7.050
7.043
6.946
6.927
5.336
5.321
4.815
4.773
4.113
4.095
3.861
3.857
3.820
3.816
2.573
2.569
2.415
2.360
1.571
0.000
Ph
Ts
N
Ph
N
Ts
15
1H NMR (400 MHz, CDCl3)
2.01
4.00
8.15
4.10
1.05
0.89
1.05
1.13
1.10
1.09
1.17
3.00
3.07
f1 (ppm)

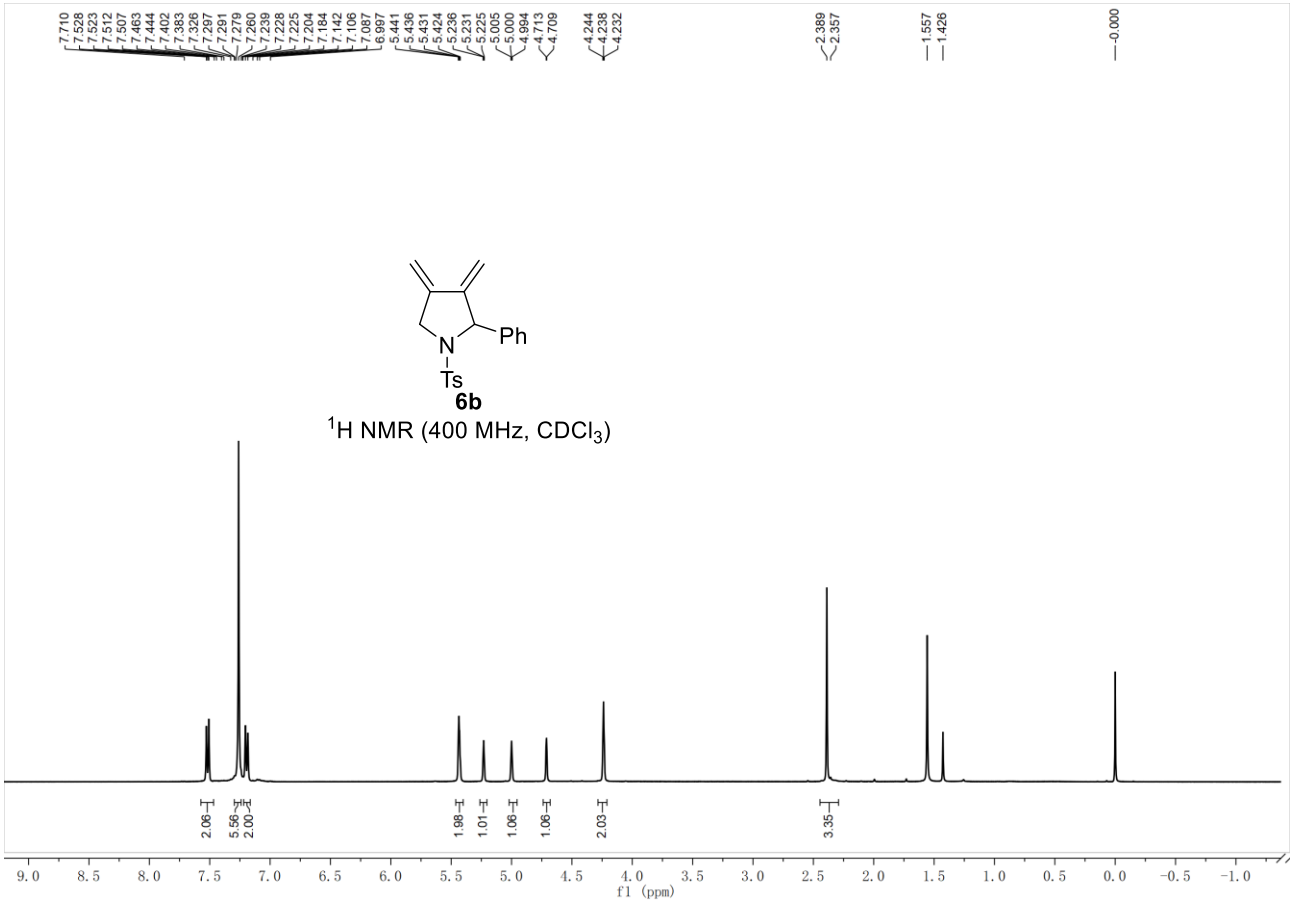

144.700
143.121
138.293
137.696
135.790
131.146
130.269
129.894
129.429
128.427
127.620
127.507
127.245
127.176
120.776
118.939
116.733
77.368
77.337
77.242
77.018
76.730
76.698
53.842
38.730
23.562
21.660
21.432
0.000
Ph
Ts
N
Ph
N
Ts
15
13C NMR (100 MHz, CDCl3)
f1 (ppm)

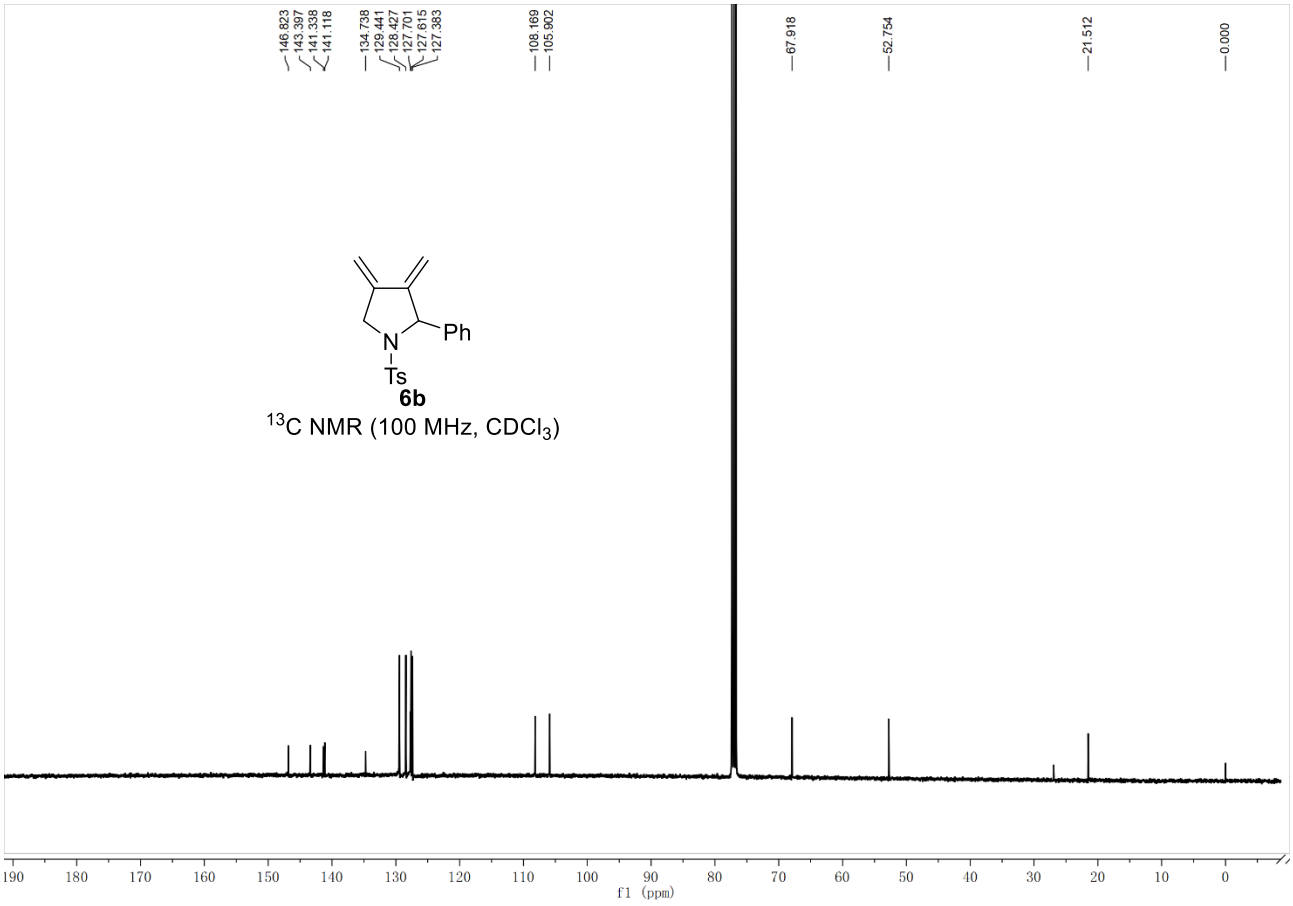


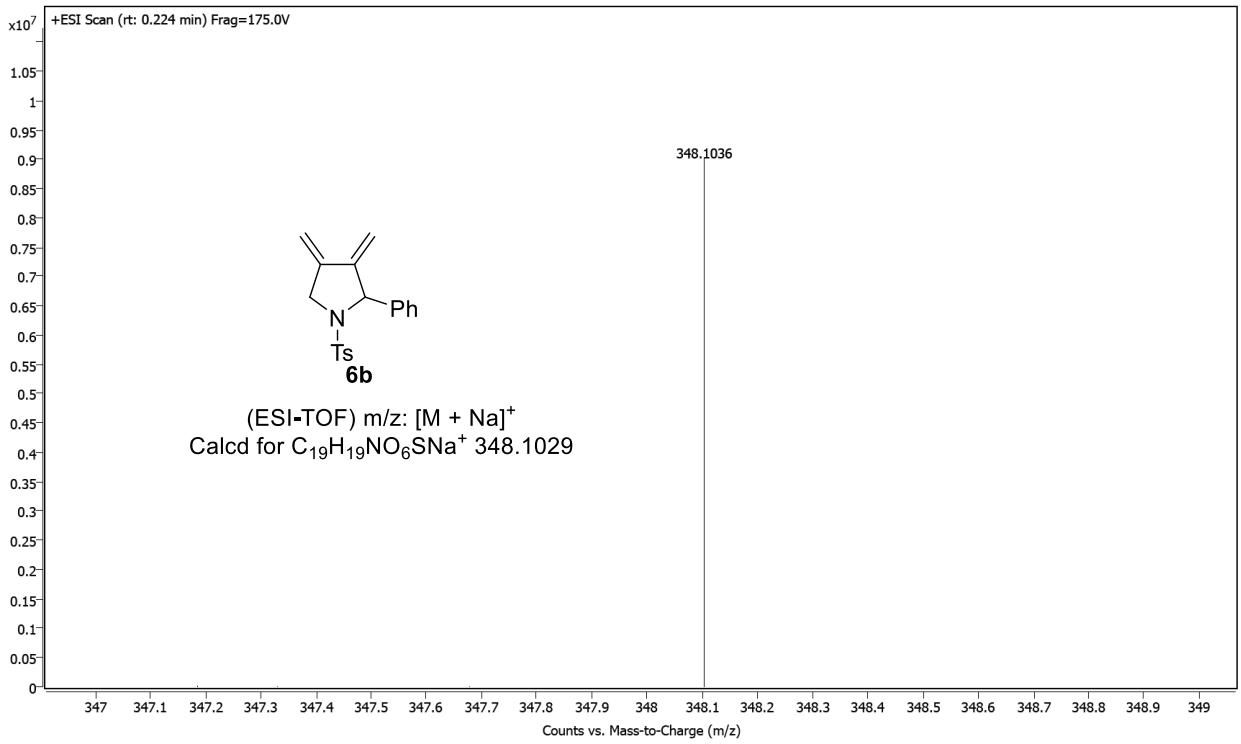
15

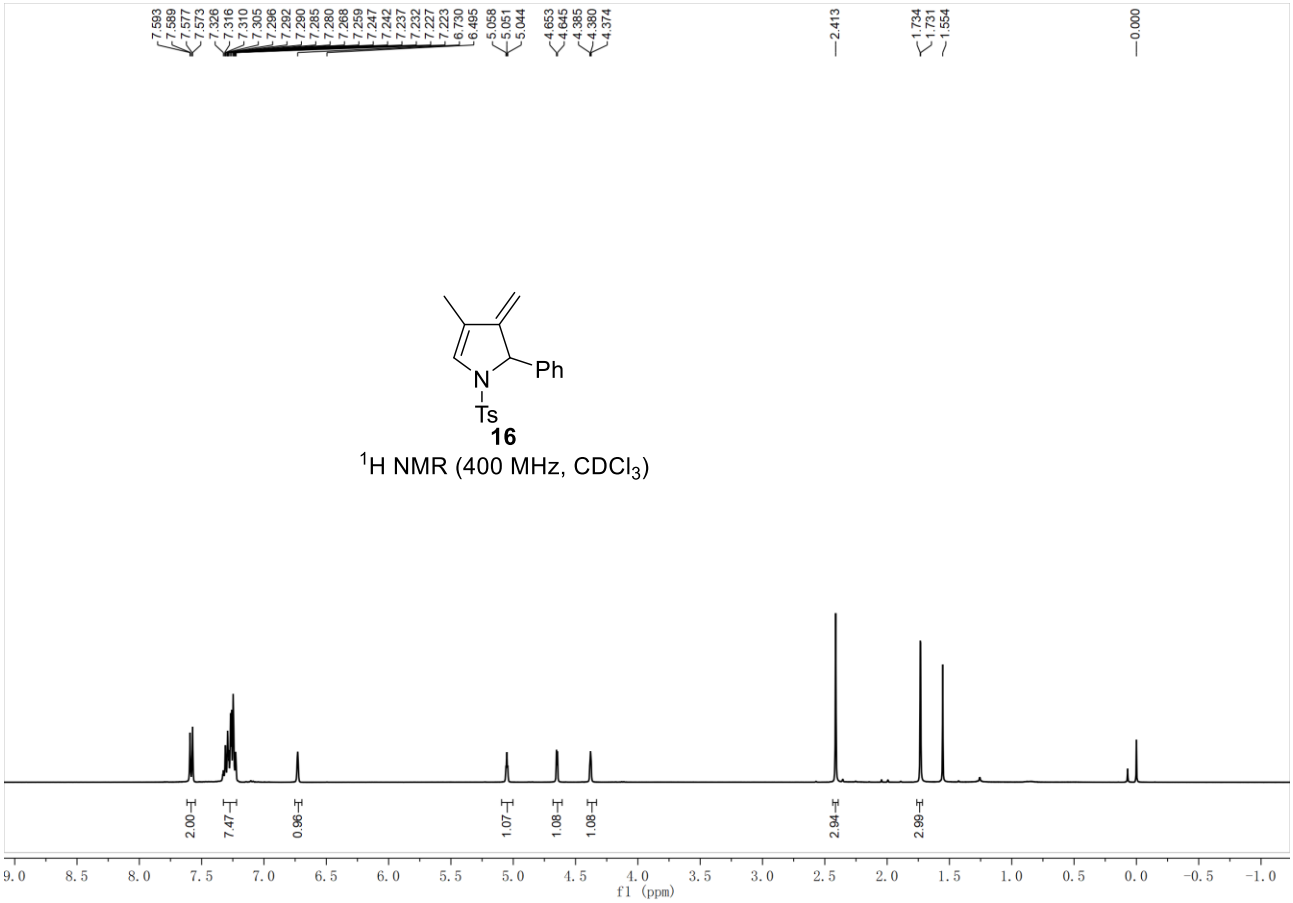
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{33}H_{30}N_2O_4S_2Na^+$ 605.1539

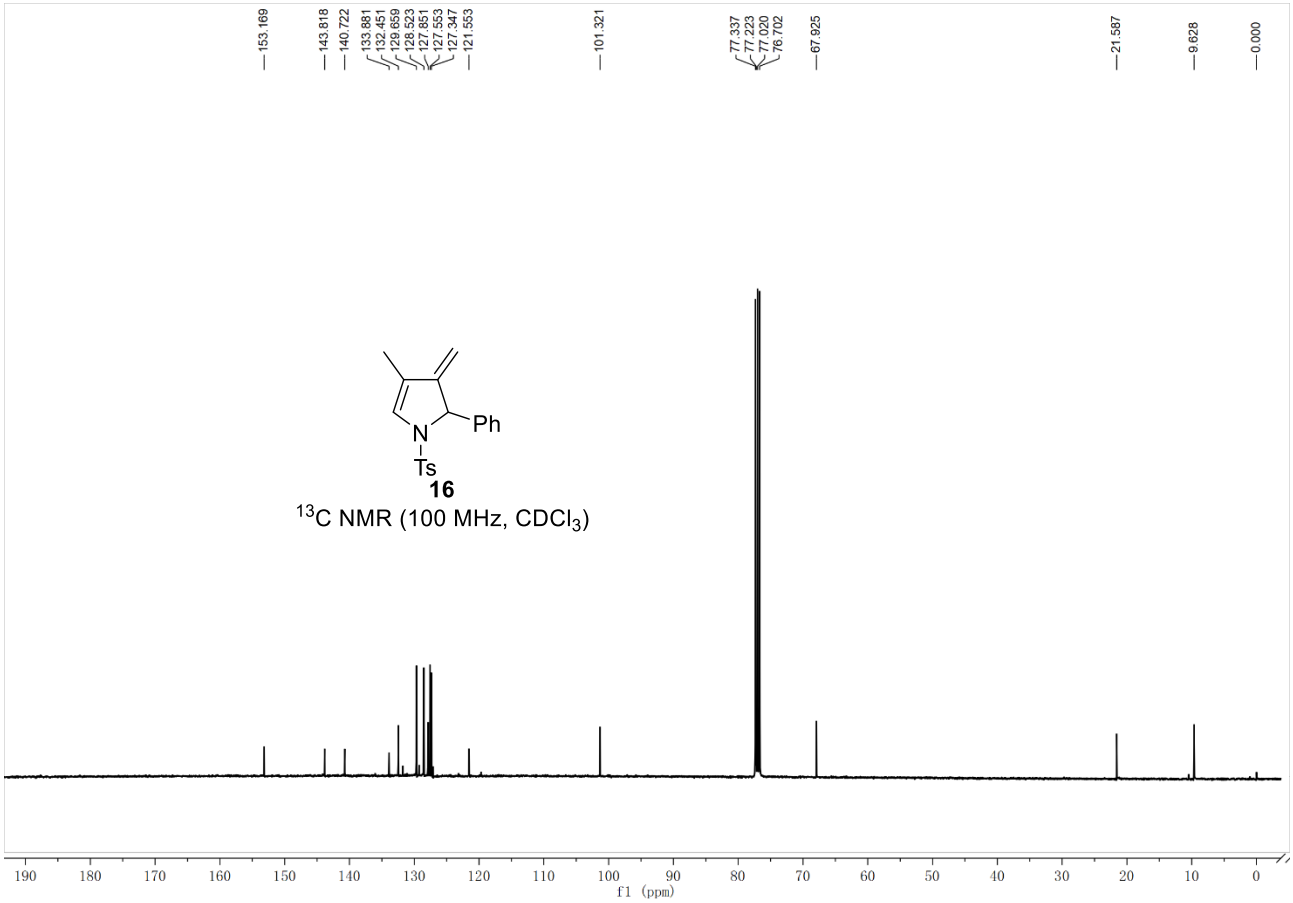

7.710
7.528
7.523
7.512
7.507
7.463
7.444
7.402
7.383
7.326
7.297
7.291
7.279
7.260
7.239
7.228
7.225
7.204
7.184
7.142
7.106
7.087
6.997
5.441
5.436
5.431
5.424
5.236
5.231
5.225
5.005
5.000
4.994
4.713
4.709
4.244
4.238
4.232
2.389
2.357
1.557
1.426
0.000
Ph
N
Ts
6b
1H NMR (400 MHz, CDCl3)
2.06
5.56
2.00
1.98
1.01
1.08
1.06
2.03
3.35
f1 (ppm)


146.823
143.397
141.338
141.118
134.738
129.441
128.427
127.701
127.615
127.383
108.169
105.902
67.918
52.754
21.512
0.000
Ph
N
Ts
6b
13C NMR (100 MHz, CDCl3)
f1 (ppm)

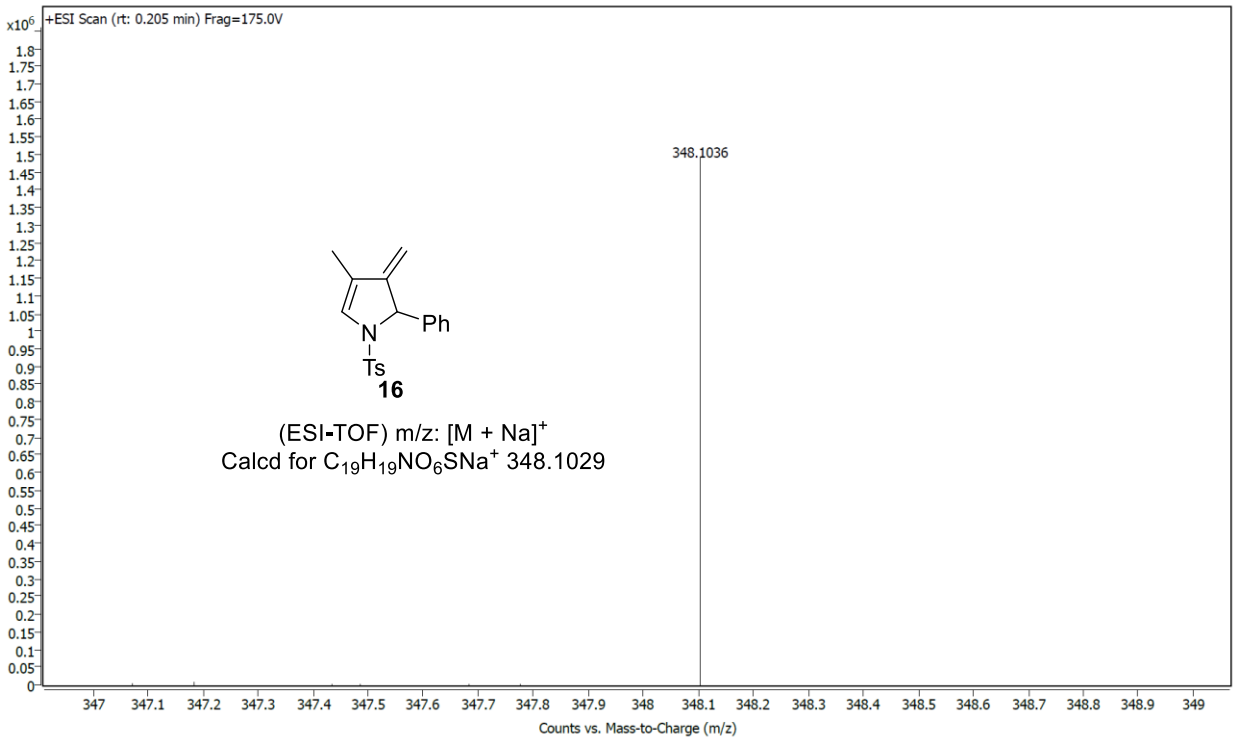

+ESI Scan (rt: 0.224 min) Frag=175.0V
x10^7
348.1036
Ph
N
Ts
6b
(ESI-TOF) m/z: [M + Na]+
Calcd for C19H19NO6SNa+ 348.1029
Counts vs. Mass-to-Charge (m/z)



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



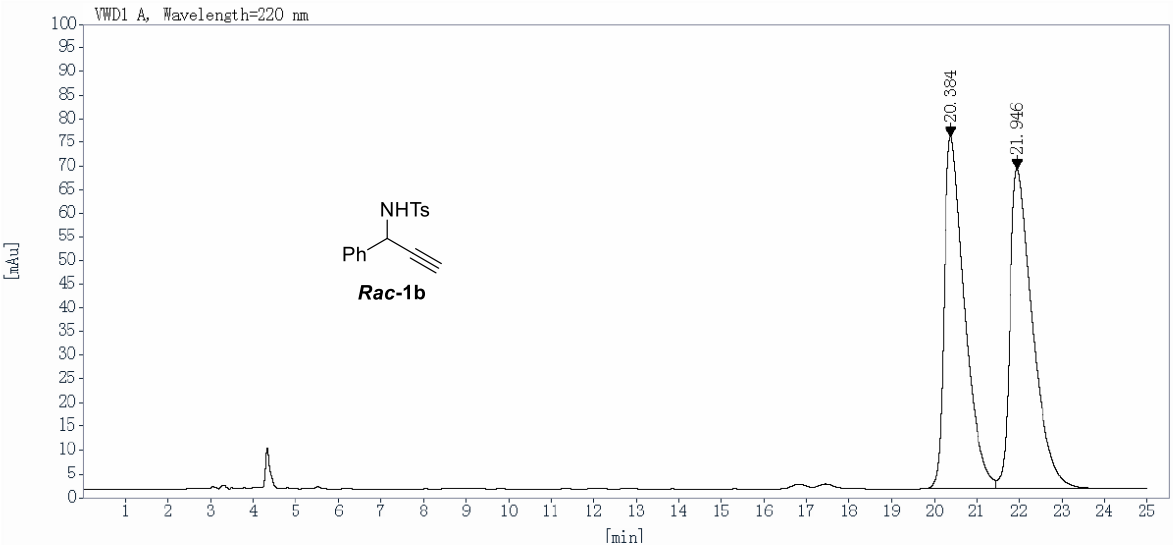
^{13}C NMR (100 MHz, $CDCl_3$)



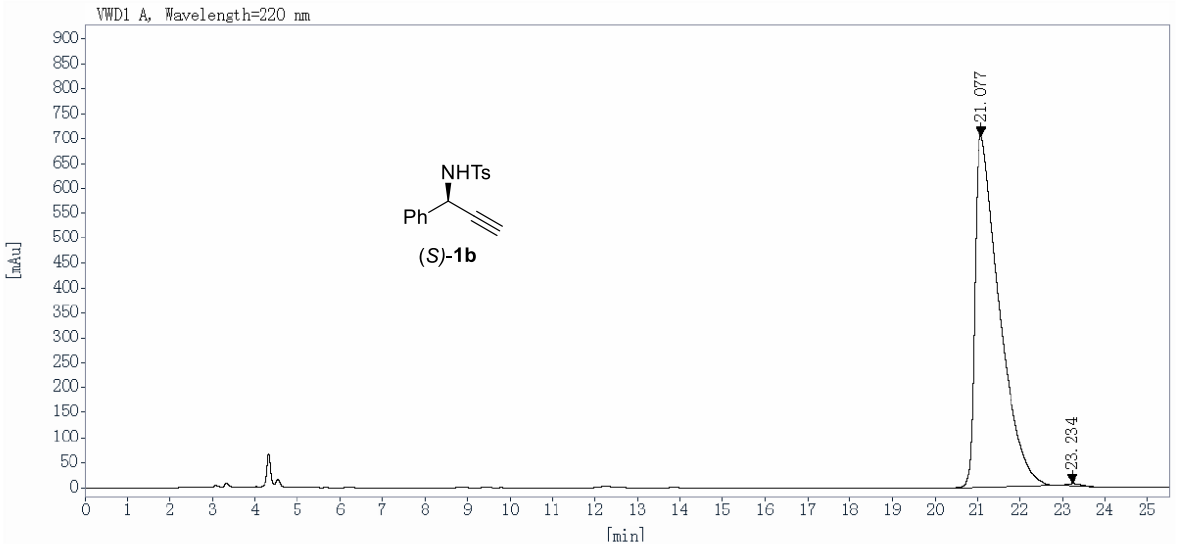
16

(ESI-TOF) m/z: $[M + Na]^+$

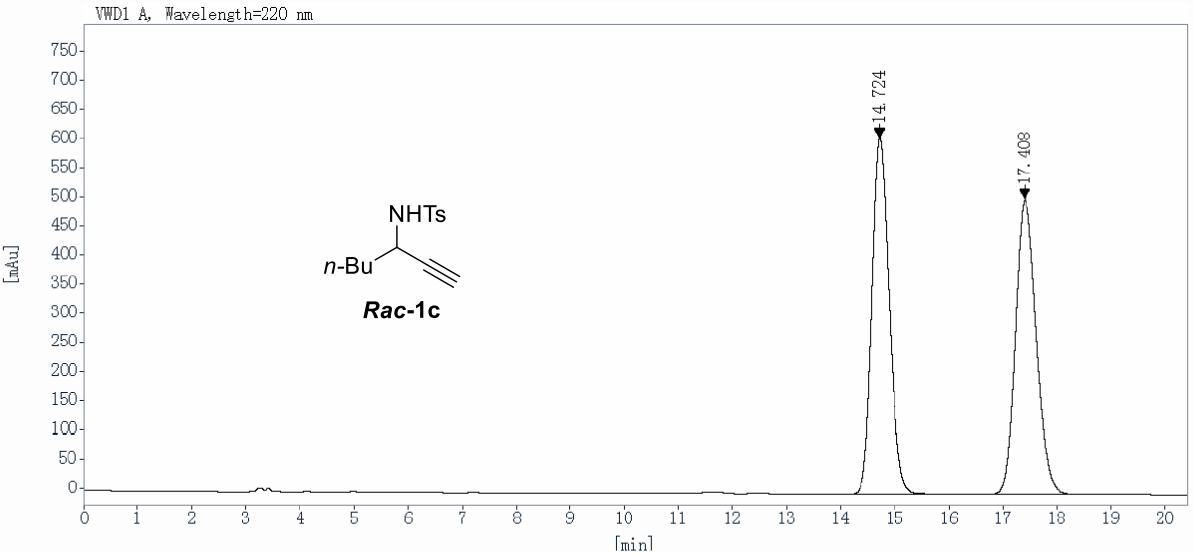
Calcd for $C_{19}H_{19}NO_6SNa^+$ 348.1029



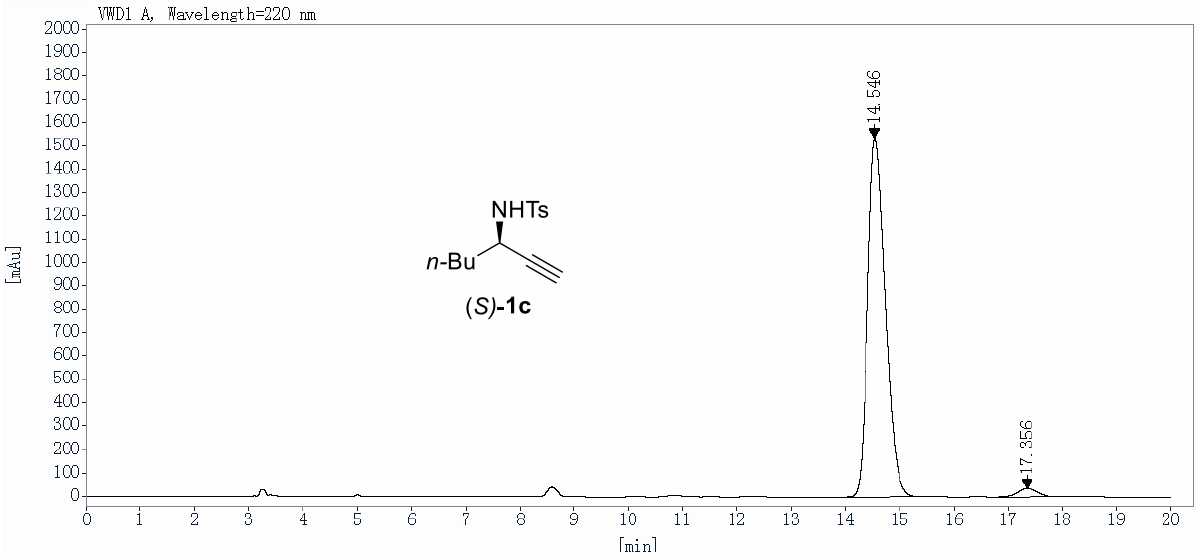
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
20.384	BV	0.49	410.7130	13615.7227	49.8288
21.946	VBA	0.54	373.1350	13709.2813	50.1712
			Totals:	27325.0039	100.0000



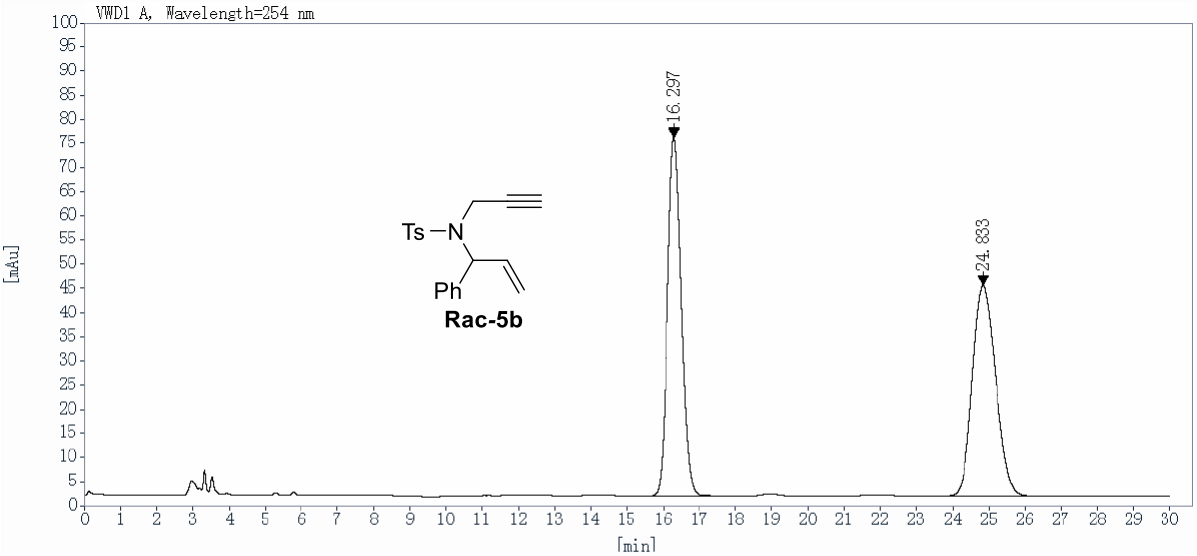
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
21.077	BBA	0.58	703.4344	27920.5313	99.5732
23.234	BBA	0.41	4.5840	119.6806	0.4268
			Totals:	28040.2118	100.0000



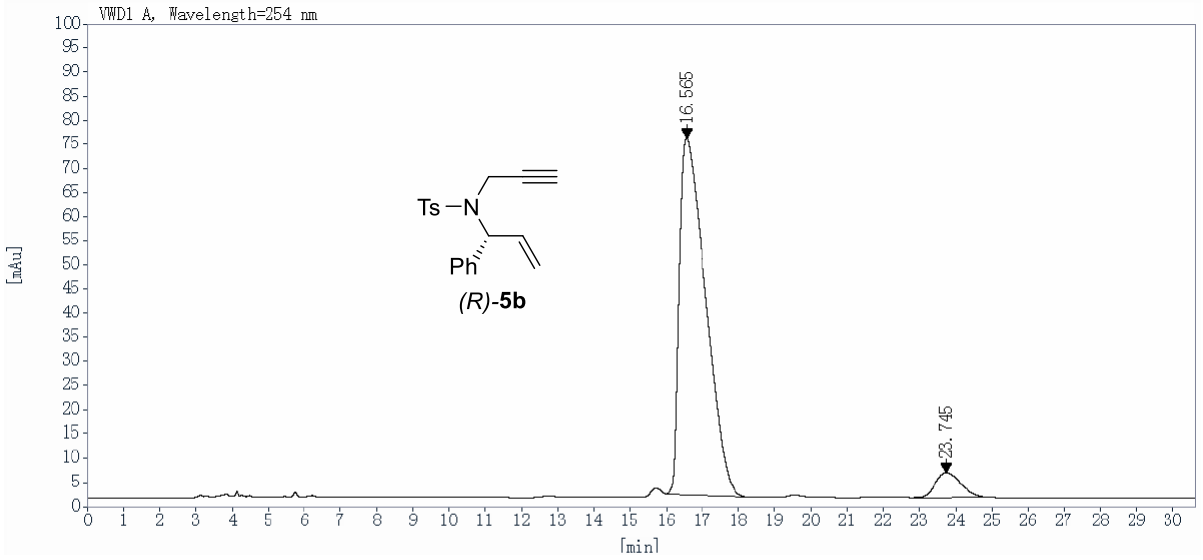
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
14.724	BB	0.34	611.7380	13476.1807	49.9546
17.408	BBA	0.41	506.6285	13500.6982	50.0454
			Totals:	26976.8789	100.0000



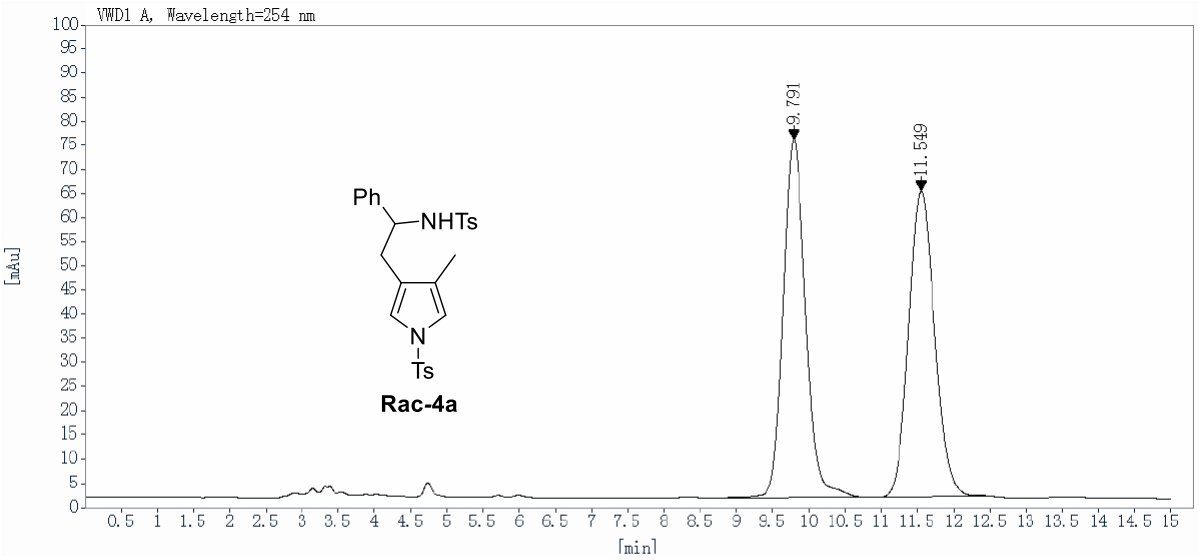
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
14.546	BBA	0.35	1531.5427	34613.7383	97.3773
17.356	BB	0.40	36.3731	932.2530	2.6227
			Totals:	35545.9913	100.0000



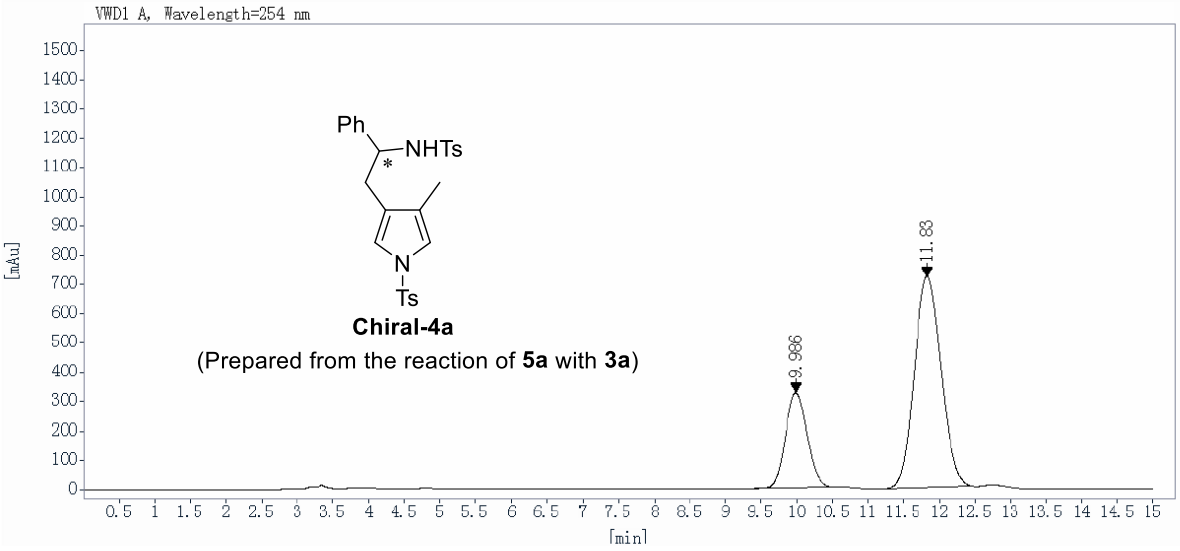
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
16.297	BBA	0.41	55.6605	1454.3594	49.9389
24.833	BBA	0.70	32.6445	1457.9210	50.0611
			Totals:	2912.2804	100.0000



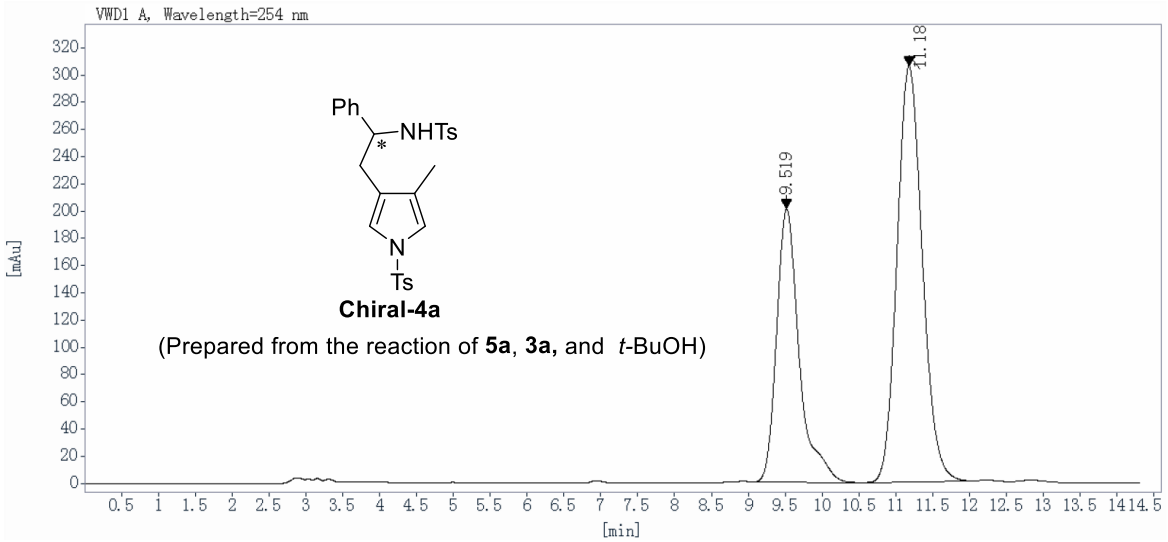
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
16.565	BBA	0.81	984.4285	49063.5547	93.5542
23.745	BBA	0.78	68.7986	3380.4258	6.4458
			Totals:	52443.9805	100.0000



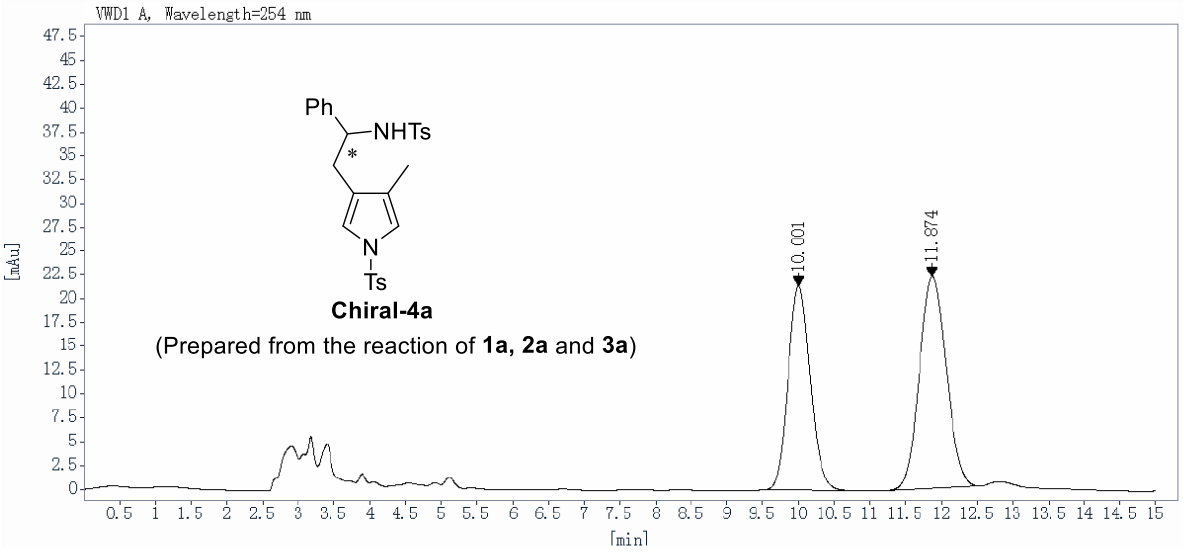
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
9.791	BBA	0.33	132.7070	2838.5107	50.0555
11.549	BBA	0.39	113.2538	2832.2109	49.9445
			Totals:	5670.7217	100.0000



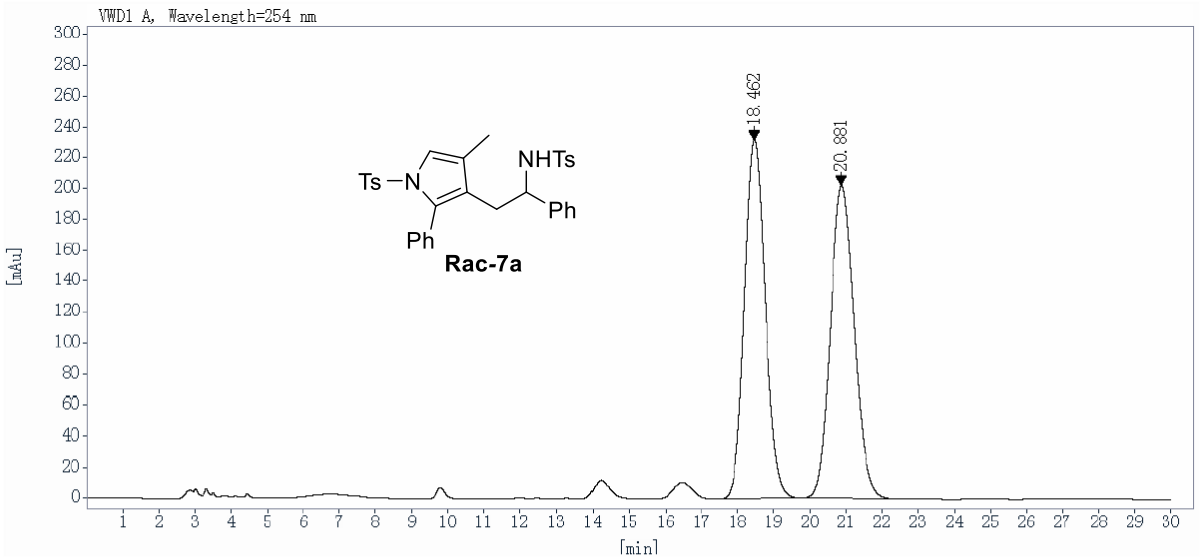
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
9.986	BBA	0.33	323.2359	6849.2271	26.6323
11.830	BBA	0.41	721.5989	18868.4961	73.3677
			Totals:	25717.7231	100.0000



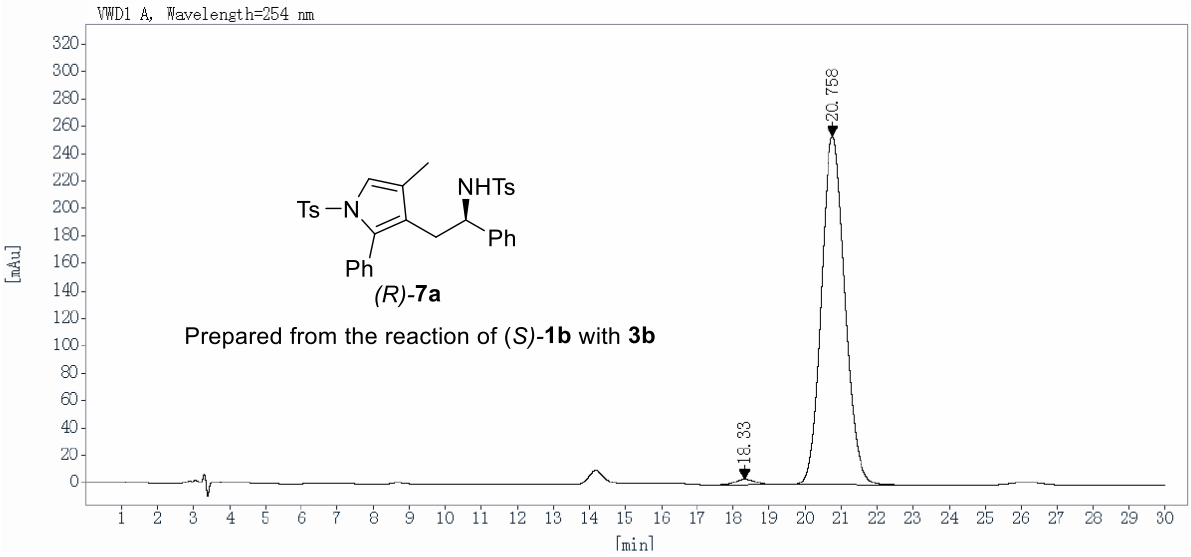
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
9.519	BB	0.32	200.5821	4283.0273	37.0362
11.180	BB	0.37	305.6908	7281.3979	62.9638
			Totals:	11564.4253	100.0000



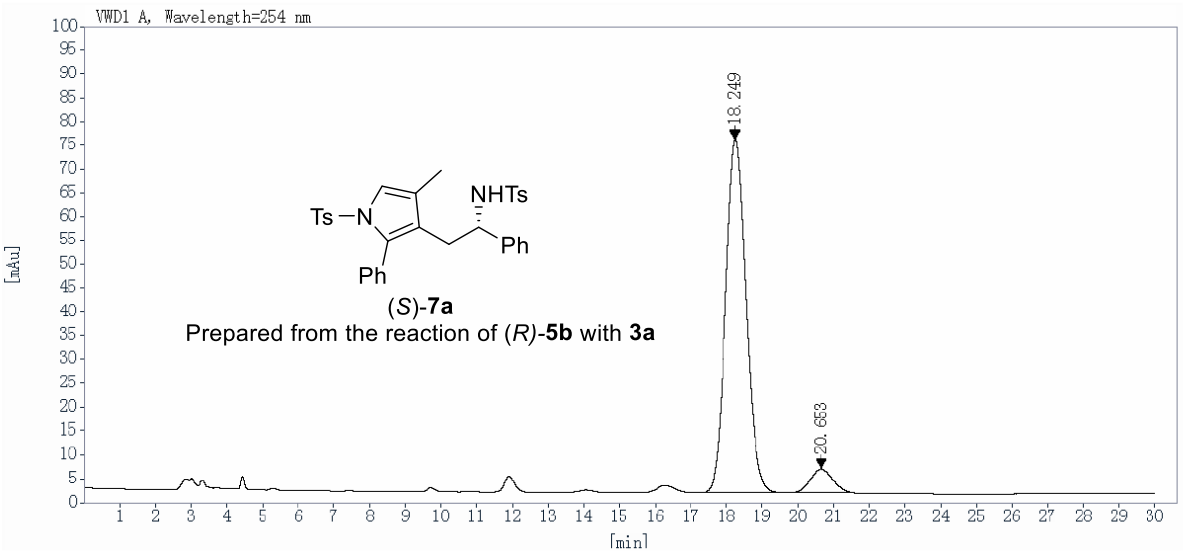
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
10.001	BBA	0.34	21.3849	464.2442	44.4765
11.874	BB	0.41	22.1611	579.5522	55.5235
			Totals:	1043.7964	100.0000



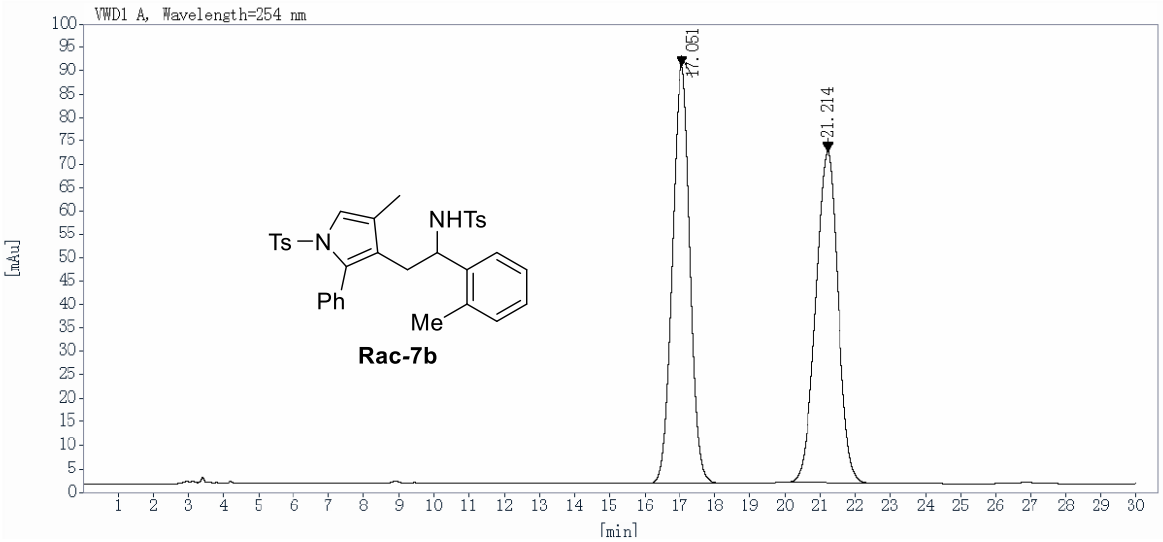
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
18.462	BB	0.62	231.6297	9252.9609	49.9753
20.881	BB	0.71	201.8466	9262.1123	50.0247
			Totals:	18515.0732	100.0000



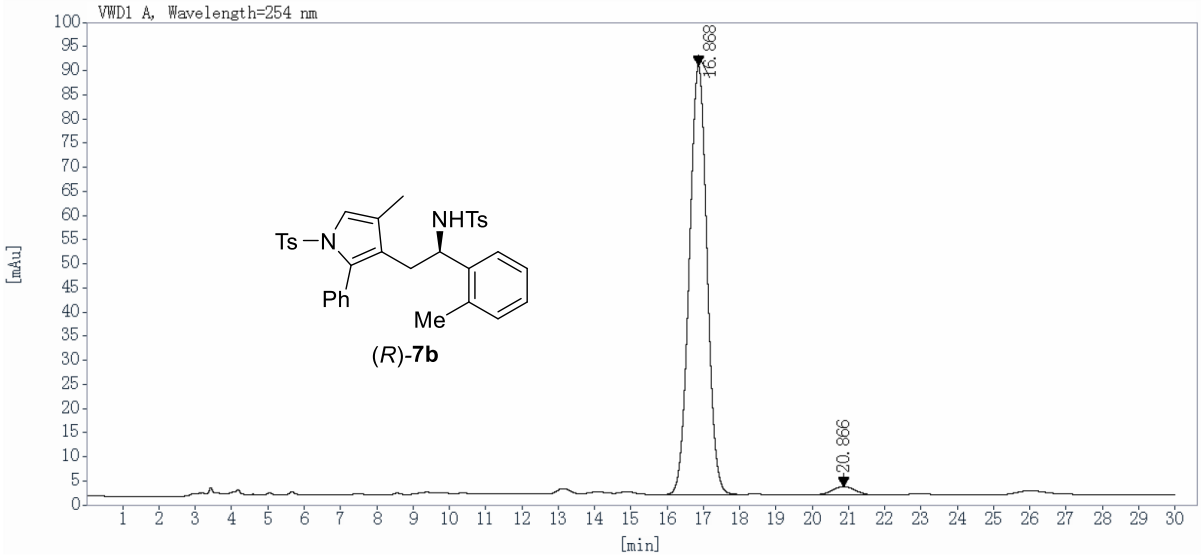
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
18.330	BB	0.59	4.4236	170.3662	1.4507
20.758	BB	0.71	254.5995	11573.5928	98.5493
			Totals:	11743.9590	100.0000



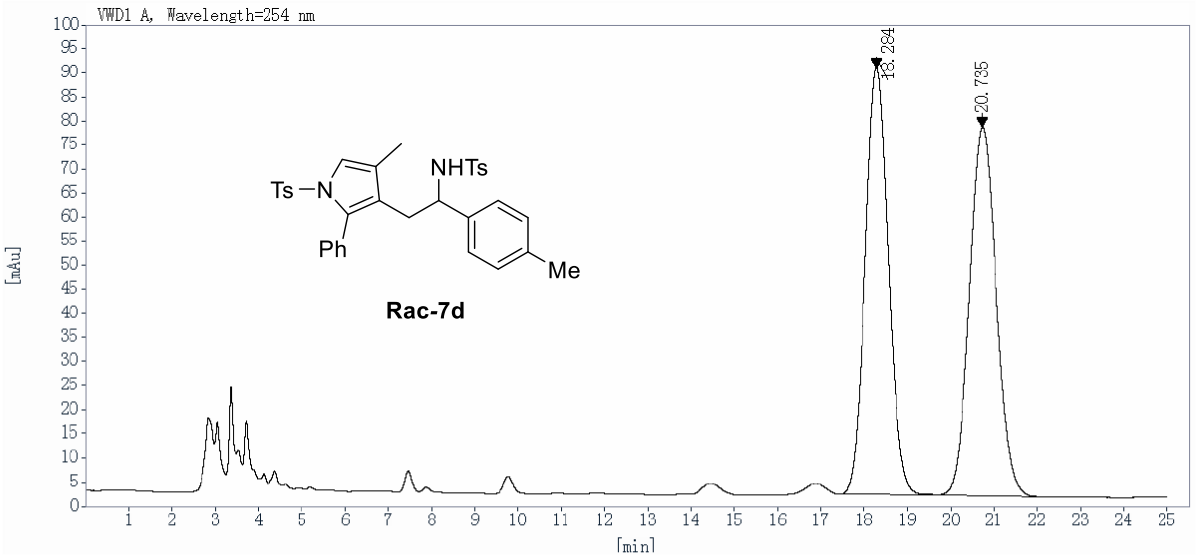
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
18.249	BBA	0.61	40.1458	1584.7935	93.2275
20.653	BBA	0.64	2.6916	115.1271	6.7725
			Totals:	1699.9205	100.0000



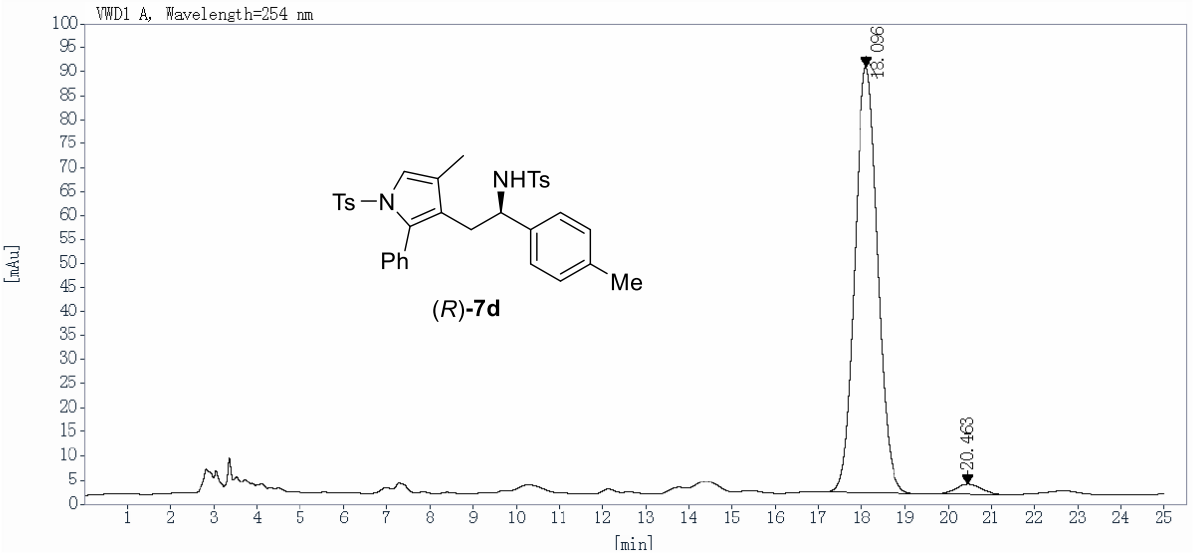
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
17.051	BB	0.54	819.1260	28545.9863	50.0740
21.214	BB	0.68	649.0676	28461.5820	49.9260
			Totals:	57007.5684	100.0000



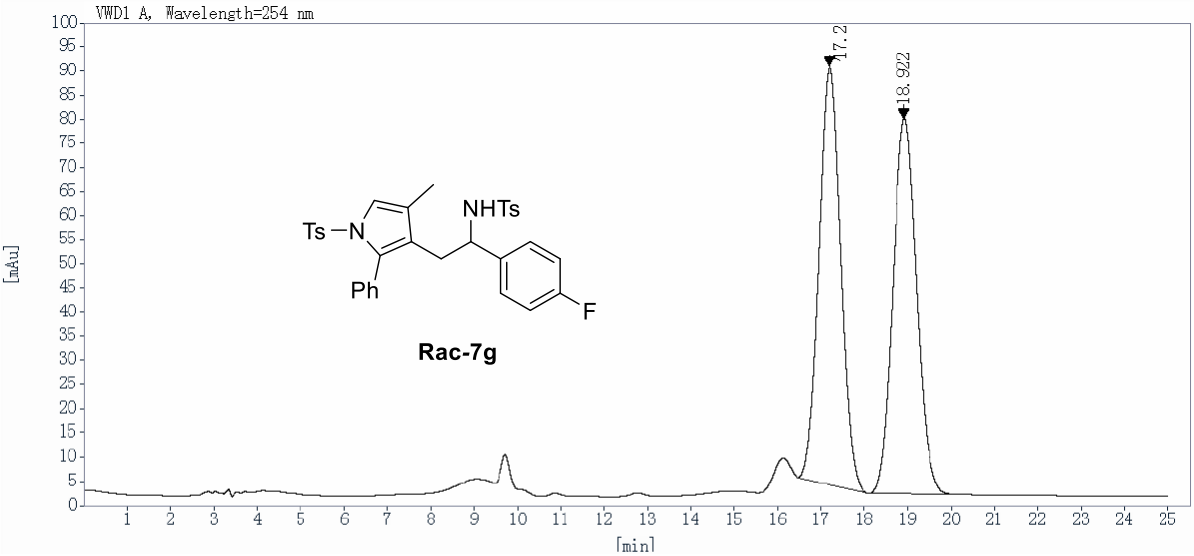
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
16.868	BB	0.53	733.2902	24794.3203	97.7492
20.866	BBA	0.65	13.8482	570.9182	2.2508
			Totals:	25365.2385	100.0000



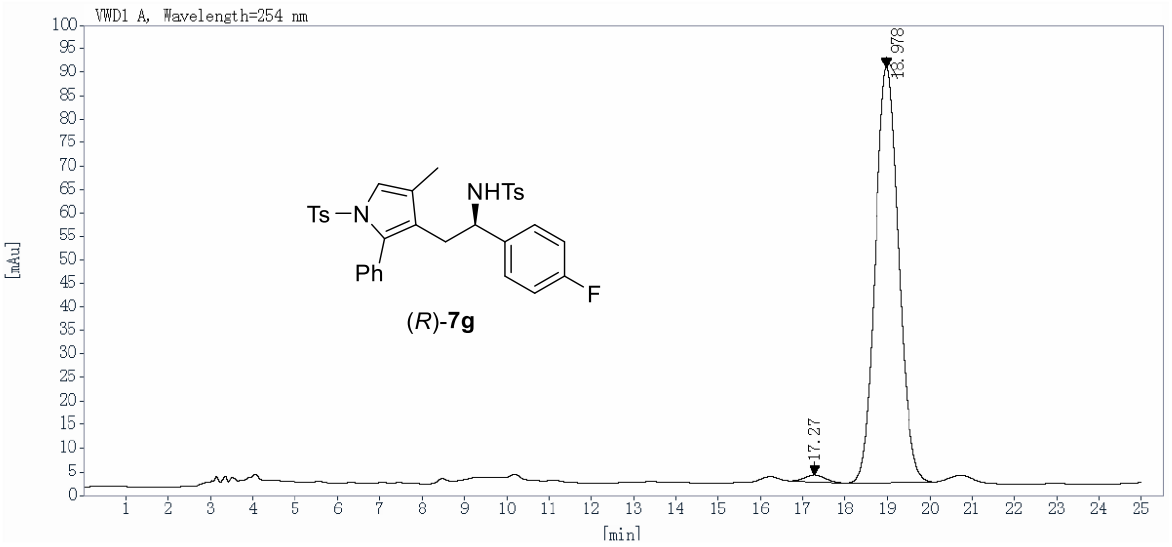
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
18.284	BB	0.58	26.2000	967.5932	49.9677
20.735	BB	0.66	22.6299	968.8438	50.0323
			Totals:	1936.4370	100.0000



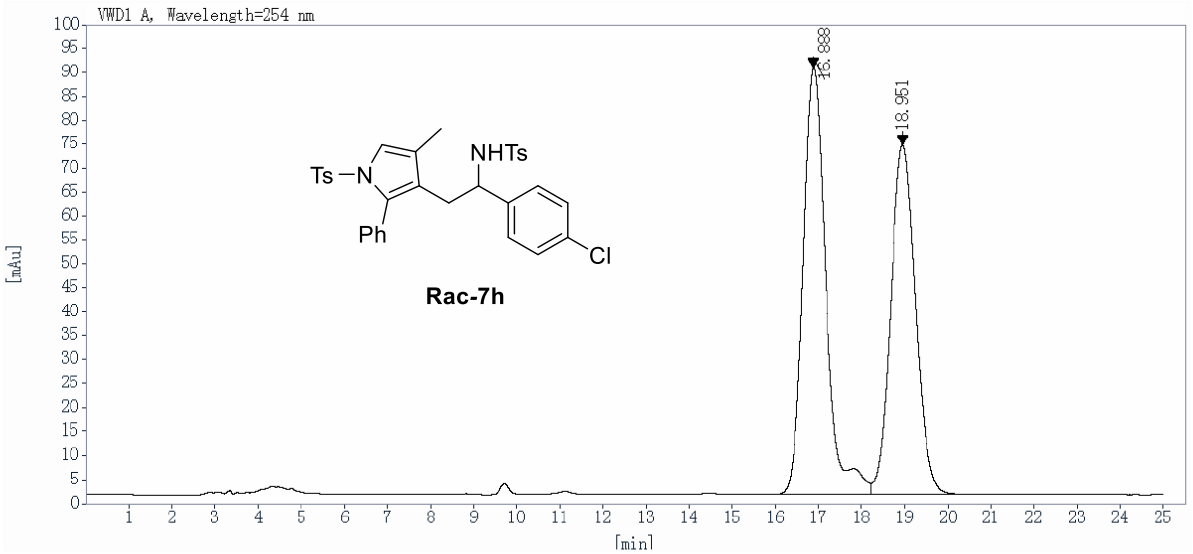
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
18.096	BB	0.57	63.8802	2341.9404	97.4086
20.463	BBA	0.66	1.4872	62.3047	2.5914
			Totals:	2404.2451	100.0000



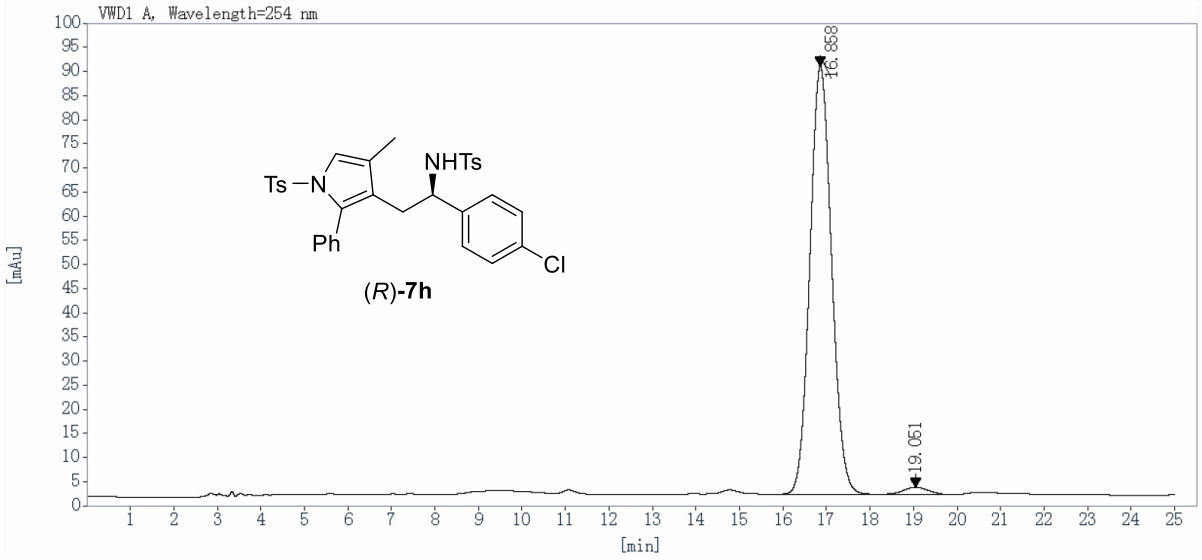
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
17.200	BB	0.55	225.2283	7882.7695	50.7076
18.922	BB	0.59	201.7345	7662.7690	49.2924
			Totals:	15545.5386	100.0000



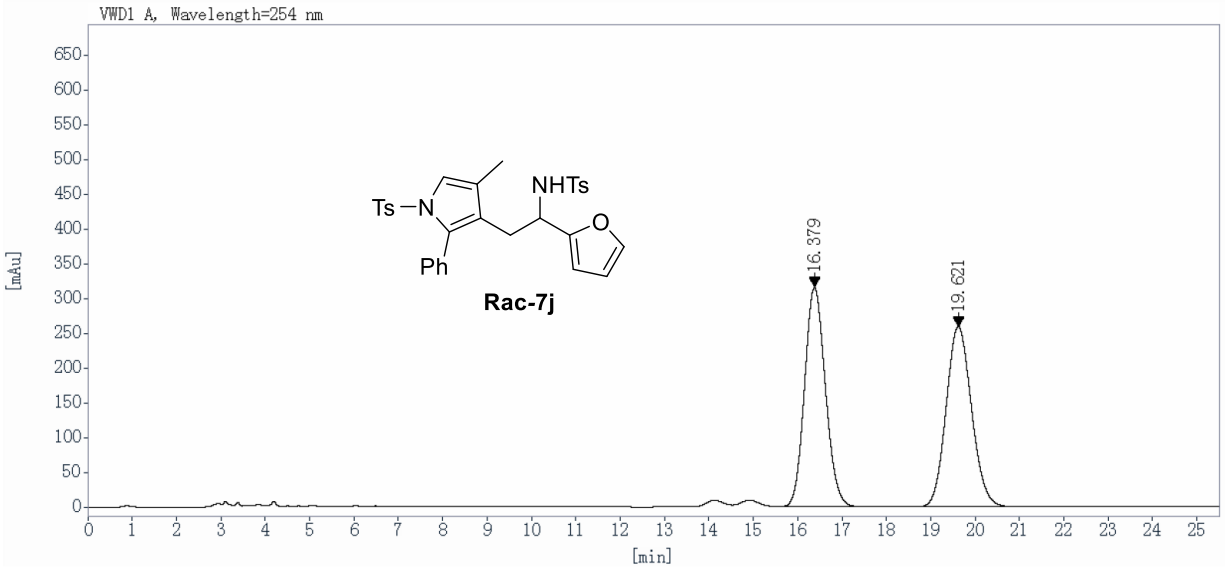
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
17.270	BB	0.51	3.4593	114.2187	1.3739
18.978	BB	0.60	213.5724	8198.9922	98.6261
			Totals:	8313.2109	100.0000



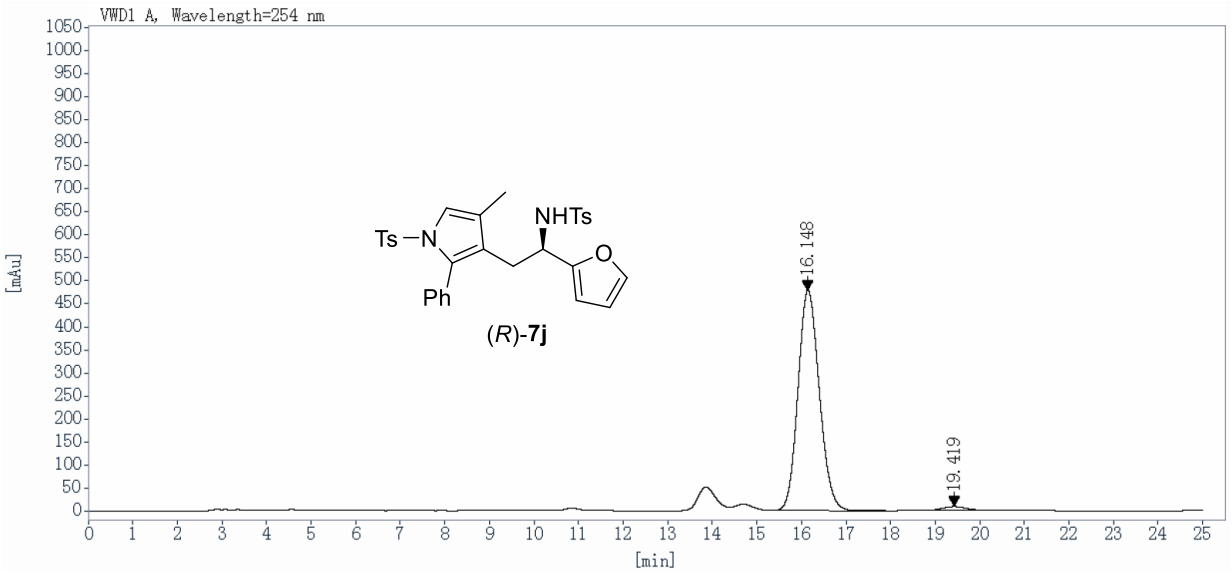
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
16.888	BV R	0.54	204.0264	7477.3335	52.8772
18.951	VB	0.62	166.9891	6663.6089	47.1228
			Totals:	14140.9424	100.0000



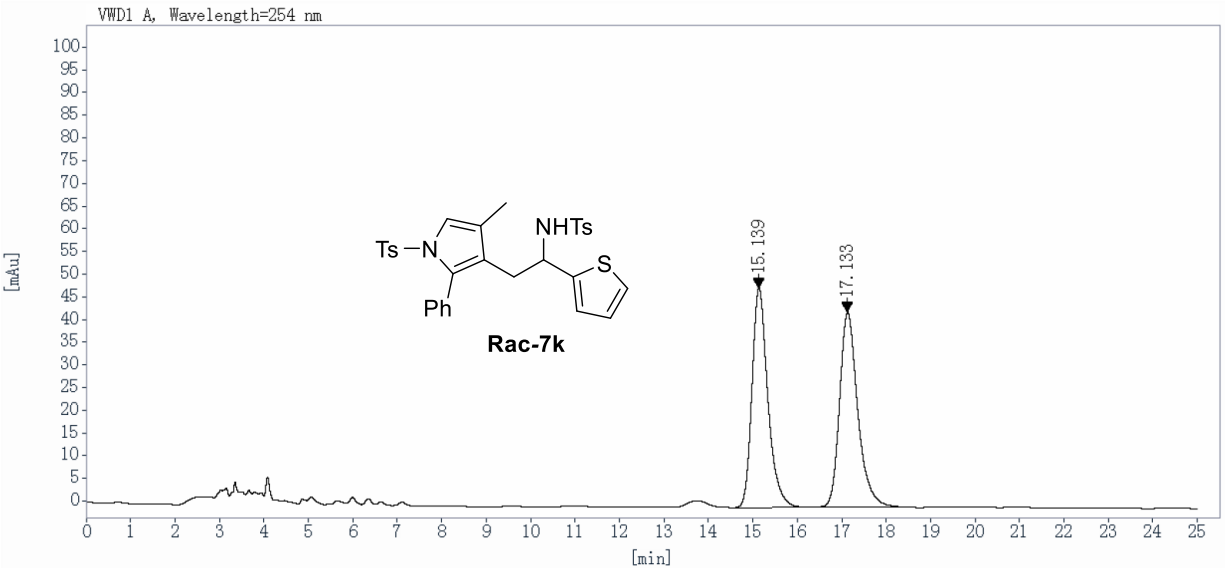
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
16.858	BB	0.54	168.9910	5843.0757	98.1324
19.051	BB	0.59	2.8021	111.2027	1.8676
			Totals:	5954.2784	100.0000



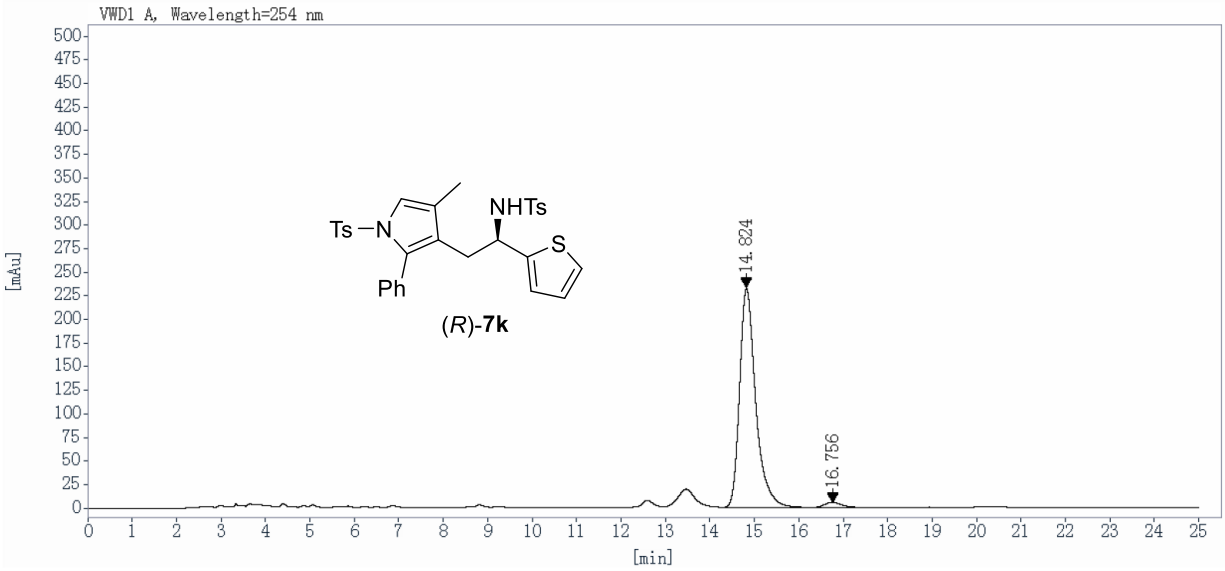
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
16.379	BBA	0.51	315.9218	10308.7559	49.9784
19.621	BBA	0.62	260.1114	10317.6748	50.0216
			Totals:	20626.4307	100.0000



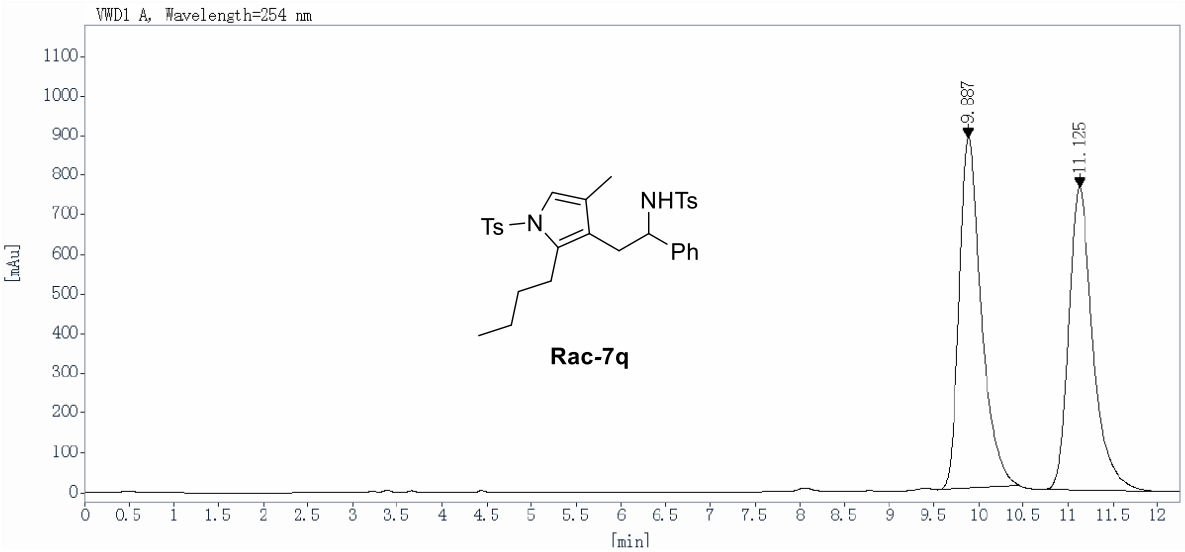
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
16.148	BB	0.51	479.6103	15890.9863	97.9198
19.419	BB	0.60	8.7166	337.5786	2.0802
			Totals:	16228.5649	100.0000



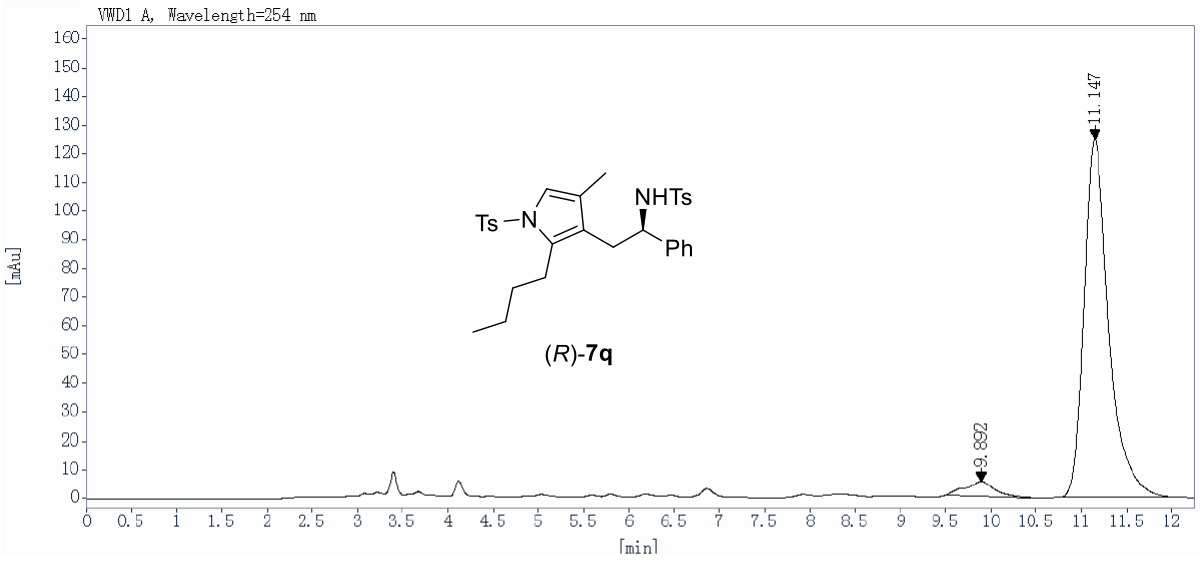
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
15.139	BB	0.37	48.3045	1194.7423	49.5461
17.133	BBA	0.43	42.9382	1216.6317	50.4539
			Totals:	2411.3740	100.0000



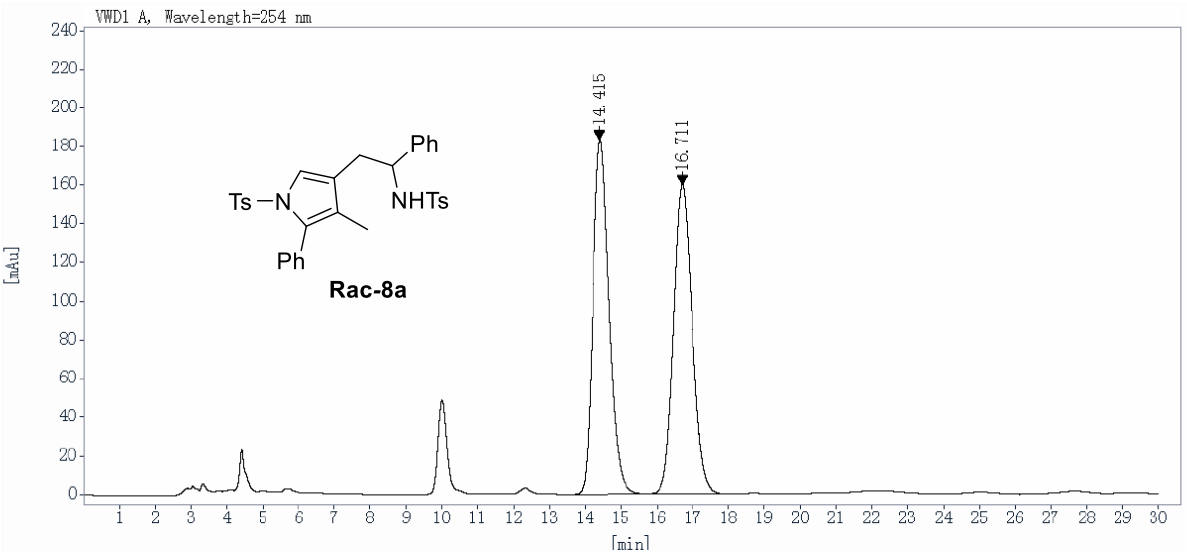
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
14.824	BB	0.38	232.6911	5829.2886	97.5254
16.756	BBA	0.41	5.4741	147.9142	2.4746
			Totals:	5977.2028	100.0000



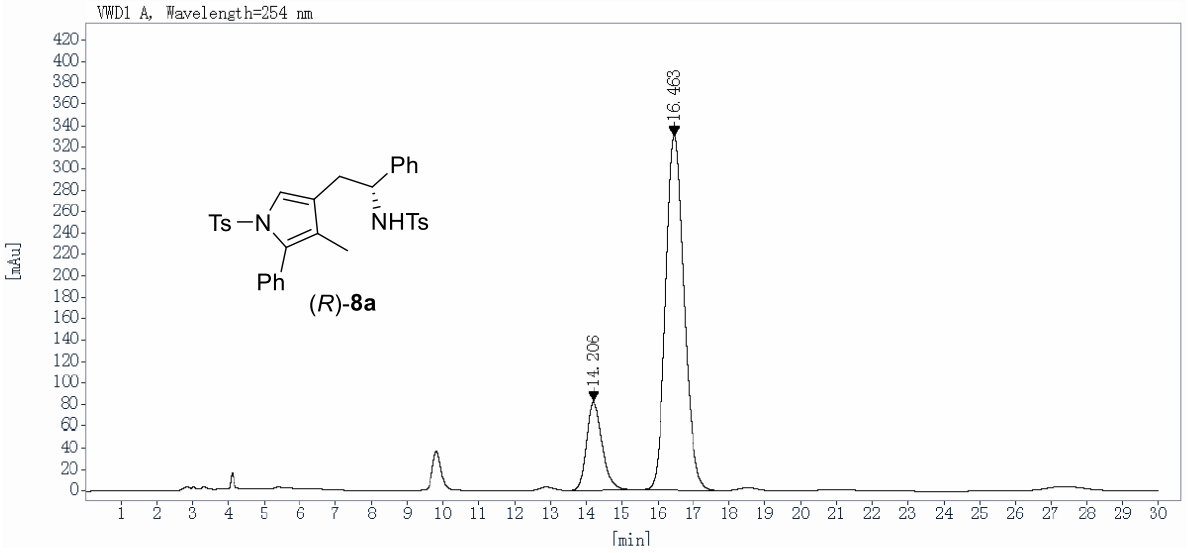
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
9.887	BBA	0.25	884.7026	15068.9658	51.4267
11.125	BBA	0.28	762.0808	14232.8711	48.5733
			Totals:	29301.8369	100.0000



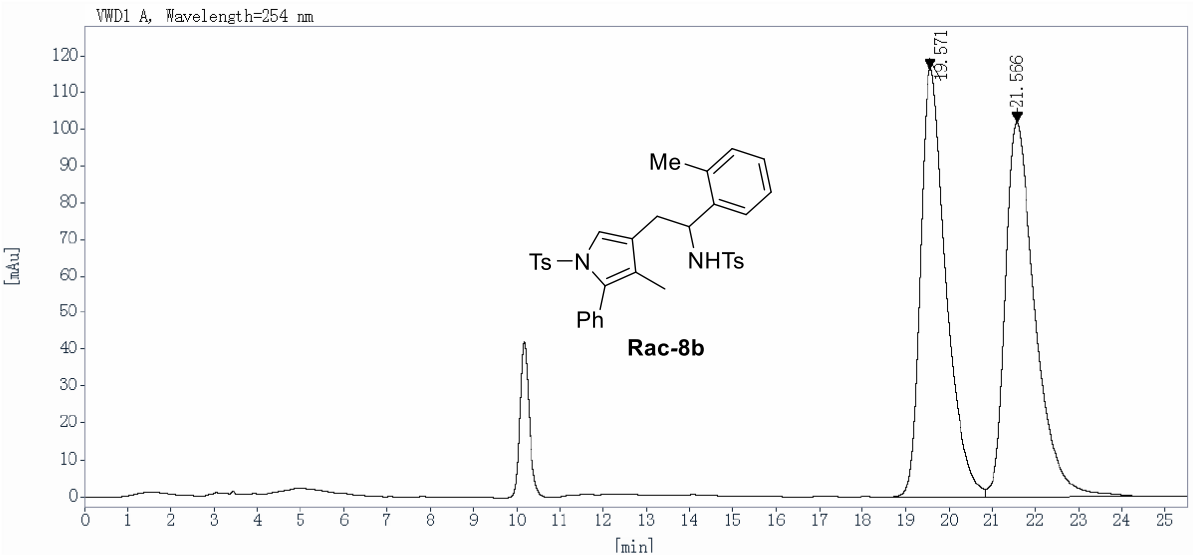
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
9.892	BBA	0.31	5.2062	118.1341	4.7788
11.147	BBA	0.28	124.6378	2353.9263	95.2212
			Totals:	2472.0604	100.0000



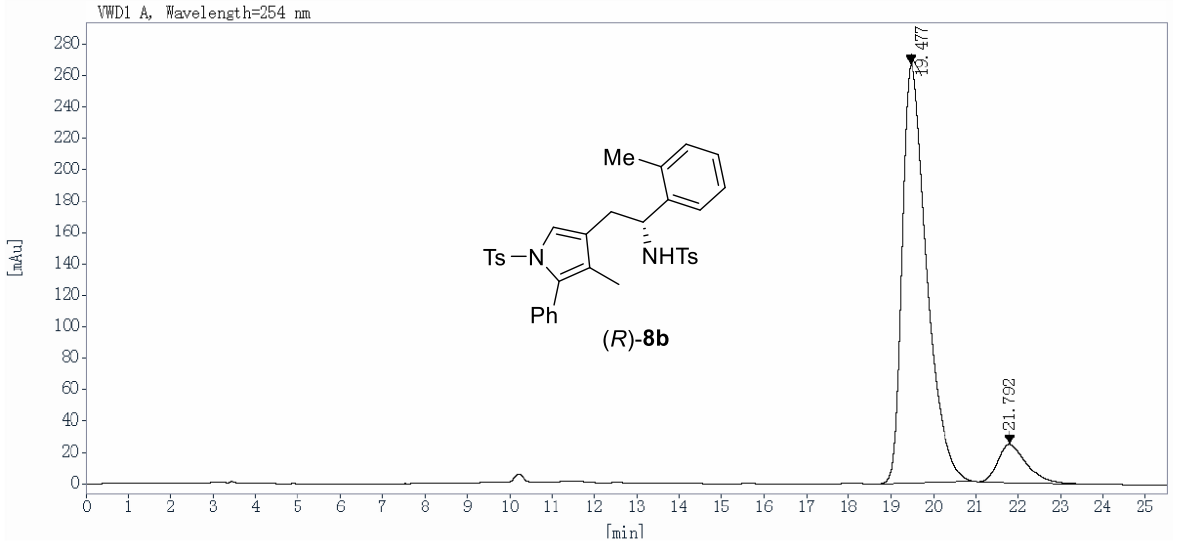
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
14.415	BB	0.48	182.9412	5669.3901	49.7027
16.711	BB	0.56	159.5419	5737.2061	50.2973
			Totals:	11406.5962	100.0000



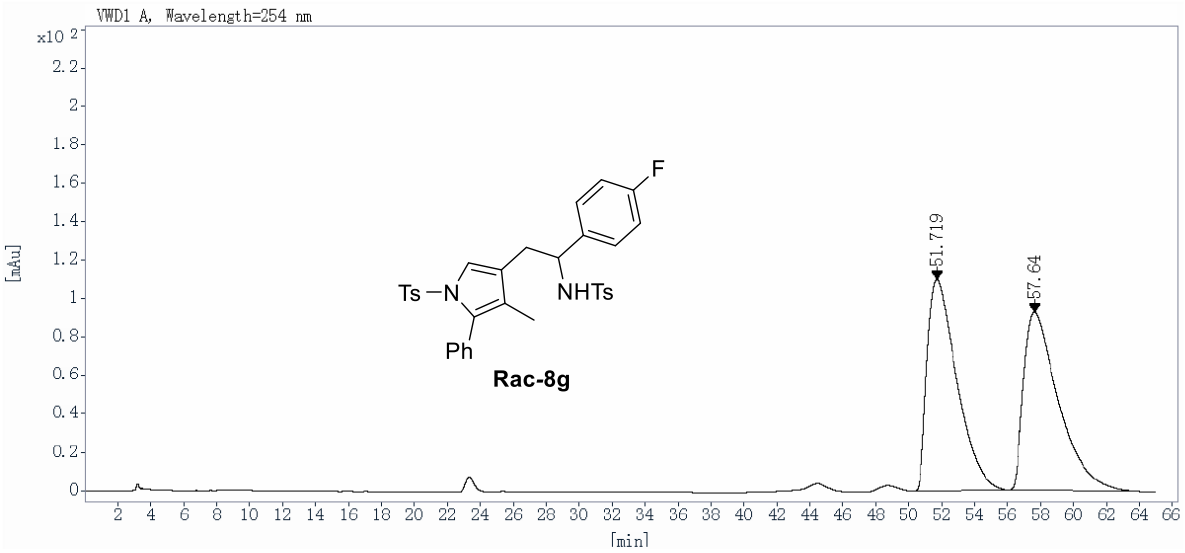
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
14.206	BB	0.47	81.9122	2508.2964	17.6404
16.463	BBA	0.55	329.7209	11710.7334	82.3596
			Totals:	14219.0298	100.0000



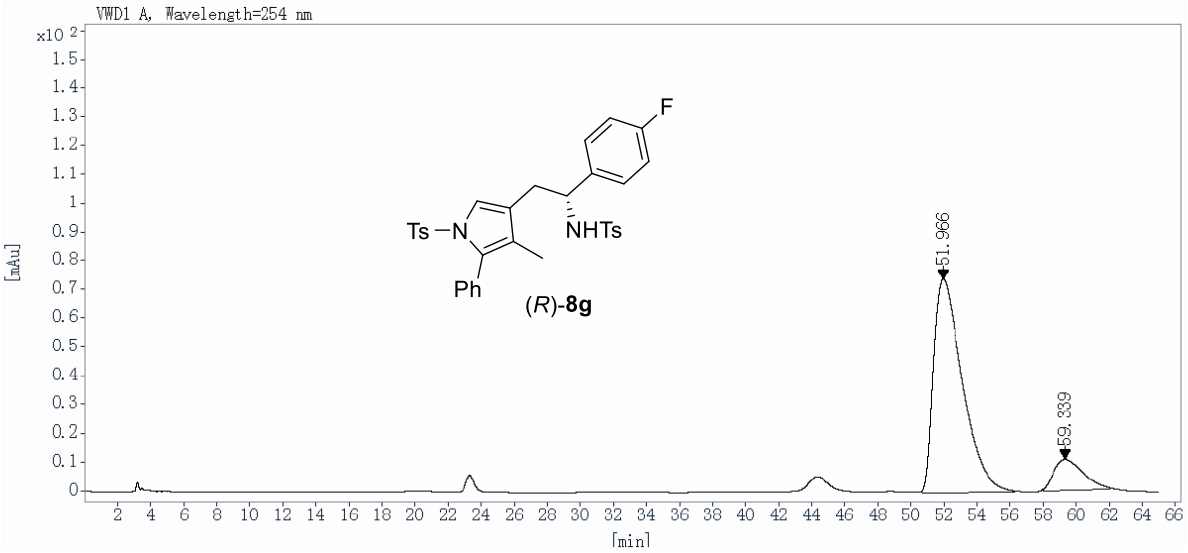
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
19.571	BV	0.61	116.5011	4758.4785	49.5538
21.566	VBA	0.72	101.7727	4844.1816	50.4462
			Totals:	9602.6602	100.0000



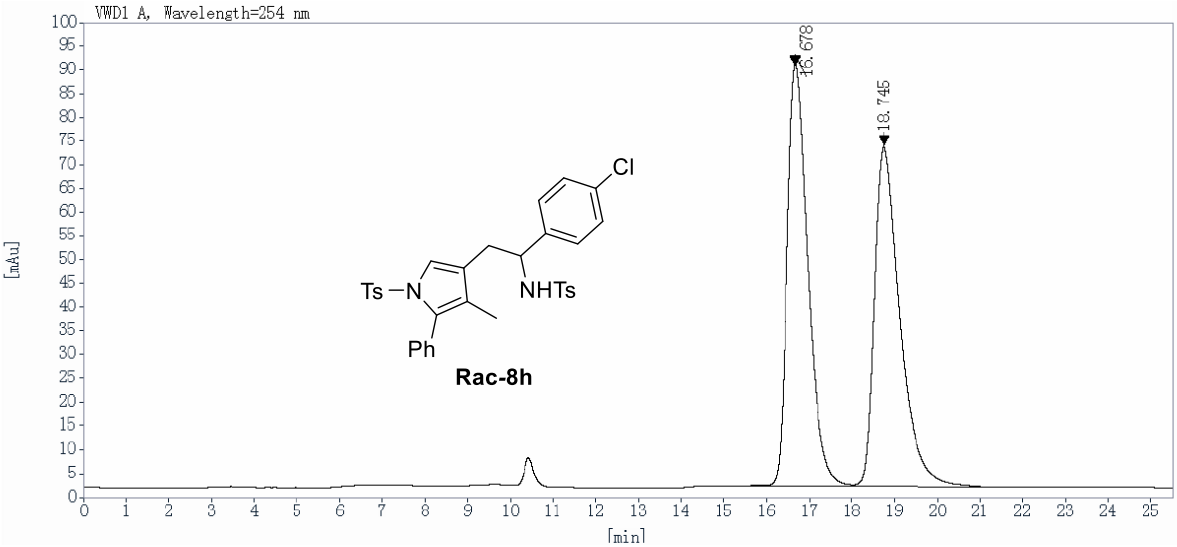
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
19.477	BBA	0.61	266.5908	10715.5400	90.4177
21.792	BBA	0.71	24.2748	1135.6184	9.5823
			Totals:	11851.1584	100.0000



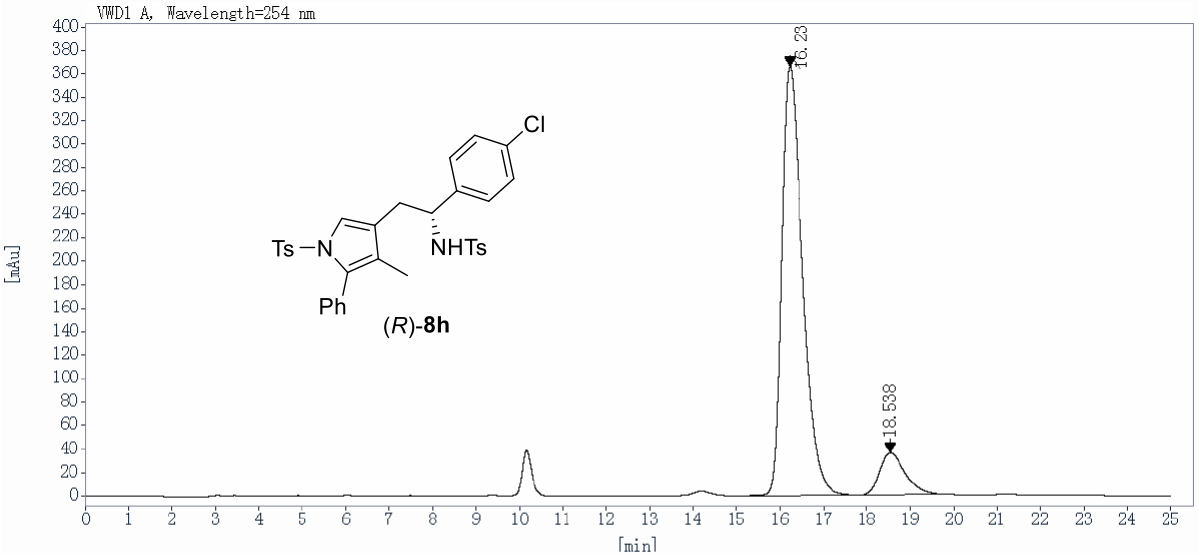
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
51.719	BB	1.87	109.6363	13736.9482	50.2929
57.640	BBA	2.17	92.2946	13576.9326	49.7071
			Totals:	27313.8809	100.0000



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
51.966	MM	2.01	74.1474	8934.3047	86.8233
59.339	MM	2.10	10.7680	1355.9113	13.1767
			Totals:	10290.2159	100.0000



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
16.678	BV	0.51	264.9188	8883.4336	50.0244
18.745	VBA	0.63	214.0126	8874.7598	49.9756
			Totals:	17758.1934	100.0000



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
16.230	BB	0.51	365.9899	12054.0117	89.0774
18.538	BBA	0.62	36.0112	1478.0463	10.9226
			Totals:	13532.0580	100.0000