Electronic Supplementary Information

Asymmetric hydrogenation of α,β-unsaturated sulfones by a rhodium/thiourea-bisphosphine complex

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Contents

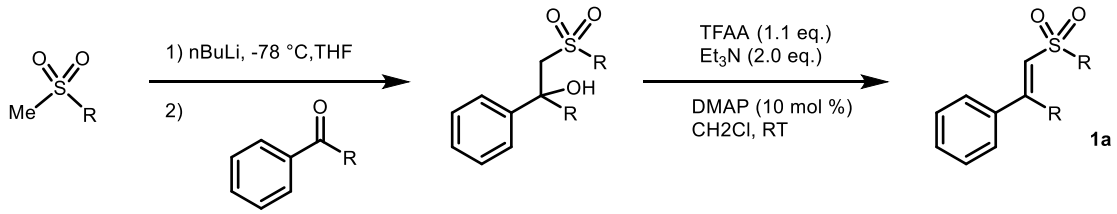
1. General remarks.

All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under an argon atmosphere or in an argon-filled glove box. Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers without further purification. Anhydrous solvents were purchased from J&K Chemical and degassed by bubbling argon over a period of 30 min. Purification of products was carried out by flash chromatography using silica gel (200-300 mesh). Thin layer chromatography was carried out using silica gel plates from Merck (GF254). $[Rh(NBD)Cl]_2$ and other metal precursors were purchased from Heraeus.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance 400 MHz or on a Bruker Avance 500 MHz spectrometer with tetramethylsilane as the internal standard. Chemical shifts are reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.27 ppm for ^{1}H NMR or 77.0 ppm for ^{13}C NMR. Data is reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz) and signal area integration in natural numbers. ^{13}C NMR analyses were recorded with ^{1}H decoupling. Enantiomeric excess values were determined Agilent 1290 Series HPLC instrument. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Rudolph Autopol I polarimeter at 589 nm.

2. Synthesis of unsaturated sulfone substrates

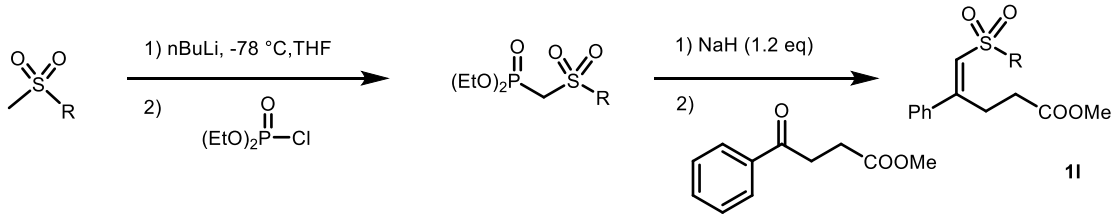
Method A[1]:



To solution of methyl phenyl sulfone (5 mmol, 0.85 g) in THF (50 mL), cooled to -78 ℃, a solution of *n*-BuLi in hexane (2.4 M, 5.5 mmol, 2.29 mL) was added. The mixture was stirred at -78 ℃ for 30 min before acetophenone (5.5 mmol, 0.61 mL) was added. The resulting solution was stirred at -78 ℃ for another 90 min and then was treated with aqueous saturated NH_4Cl (20 mL). The aqueous layer was extracted with EtOAc twice (2 × 30 mL). The combined organic layers were dried over $NaSO_4$, filtered and concentrated.

The crude resulting alcohol and DAMP (0.5 mmol, 66.7 mg) were dissolved in CH_2Cl_2 (30 mL). The mixture was cooled to 0 ℃ before Et_3N (10 mmol, 1.39 mL) and TFAA (5.5 mmol, 0.73 mL) were successively added. The reaction mixture was stirred at 0 ℃ for 30 min and was warmed up to room temperature. After stirring overnight, the mixture was hydrolyzed with aqueous saturated NH_4Cl (20 mL). The organic layer was separated and aqueous layer extracted with CH_2Cl_2 twice (2 × 20 mL). The combined layers were dried over $NaSO_4$, filtered and concentrated. The residue was purified by flash chromatography to afford the sulfone **1a** as a white solid; yield: 62%, 843 mg (for 2 steps).

Method B[2]:



Under a nitrogen atmosphere, to the solution of methyl phenyl sulfone (5 mmol, 0.85 g) in THF (50 mL), cooled to -78 ℃, a solution of *n*-BuLi in hexane (2.4 M, 5.5 mmol, 2.29 mL) was added.

The resulting mixture was then stirred at 0 ℃ for 30 min, then cooled back to -78 ℃, diethyl chlorophosphate (4.75 mmol, 0.69 mL) was added. The temperature naturally reached to rt and the mixture was stirred for another 2 h before NaH (6 mmol, 0.26 g) was added. After stirring for 1 h, methyl 4-oxo-4-phenylbutanoate (4.8 mmol, 0.81 mL) was added and the mixture stirred overnight. After quenching with NH_4Cl (20 mL), the aqueous layer was extracted with CH_2Cl_2 twice (2 × 30 mL). The combined layers were dried over $NaSO_4$, filtered and concentrated. The residue was purified by flash chromatography to afford the sulfone **1l** as a white solid; yield: 40%, 724 mg (for 2 steps).

(*E*)-1-methyl-4-((2-phenylprop-1-en-1-yl)sulfonyl)benzene (**1a**)

Synthesized with method A.

White solid, yield: 62%, 843 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.83 (m, 2H), 7.42 – 7.32 (m, 7H), 6.62 – 6.58 (m, 1H), 2.52 (d, *J* = 1.2 Hz, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.02, 144.19, 140.23, 139.27, 129.89, 129.86, 128.74, 127.80, 127.33, 126.34, 21.66, 17.19. *m/z* (ESI–MS): calc. 273.0944 $[M+H]^+$, found 273.0938 $[M+H]^+$.

(*E*)-1-fluoro-4-(1-tosylprop-1-en-2-yl)benzene (**1b**)

Synthesized with method A.

White solid, yield: 65%, 942 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.82 (m, 2H), 7.42 – 7.31 (m, 4H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.56 (d, *J* = 1.2 Hz, 1H), 2.51 (d, *J* = 1.2 Hz, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ163.64 (d, *J* = 250.6 Hz), 151.71, 144.29, 139.15, 136.23, 136.20, 129.93, 128.29 (d, *J* = 8.4 Hz), 127.77 (d, *J* = 1.3 Hz), 127.34, 115.78 (d, *J* = 21.7 Hz), 21.66, 17.24. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.86. *m/z* (ESI–MS): calc. 291.0850 $[M+H]^+$, found 391.0843 $[M+H]^+$.

(*E*)-1-chloro-4-(1-tosylprop-1-en-2-yl)benzene (**1c**)

Synthesized with method A.

White solid, yield: 60%, 918 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.81 (m, 2H), 7.39 – 7.31 (m, 6H), 6.58 (q, *J* = 1.2 Hz, 1H), 2.50 (d, *J* = 1.2 Hz, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.52, 144.37, 139.03, 138.59, 135.93, 129.96, 128.96, 128.21, 127.68, 127.37, 21.67, 17.10. *m/z* (ESI–MS): calc. 307.0554 $[M+H]^+$, found 307.0548 $[M+H]^+$.

(*E*)-1-bromo-4-(1-tosylprop-1-en-2-yl)benzene (**1d**)

Synthesized with method A.

White solid, yield: 63%, 1.1g.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.22 (m, 2H), 6.58 (d, *J* = 1.2 Hz, 1H), 2.50 (d, *J* = 1.0 Hz, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.59, 144.39, 139.09, 139.00, 131.93, 129.96, 128.24, 127.92, 127.37, 124.21, 21.68, 17.06. *m/z* (ESI–MS): calc.353.0028 $[M+H]^+$, found 353.0016 $[M+H]^+$.

(*E*)-1-methyl-4-((2-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)sulfonyl)benzene (**1e**)

Synthesized with method A.

White solid, yield: 50%, 850 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.82 (m, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.61 (d, *J* = 1.3 Hz, 1H), 2.55 (d, *J* = 1.3 Hz, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.28, 144.57, 143.88, 138.76, 131.57 (q, *J* = 32.8 Hz), 130.02, 129.66, 127.10 (q, *J* = 66.6 Hz), 125.73 (q, *J* = 3.7 Hz), 123.74 (q, *J* = 272.3 Hz), 21.68, 17.25. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -62.85. *m/z* (ESI–MS): calc. 341.0818 $[M+H]^+$, found 341.0810 $[M+H]^+$.

(*E*)-1-methyl-4-((2-(p-tolyl)prop-1-en-1-yl)sulfonyl)benzene (**1f**)

Synthesized with method A.

White solid, yield: 54%, 772 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.80 (m, 2H), 7.37 – 7.27 (m, 4H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.59 (d, *J* = 1.2 Hz, 1H), 2.49 (d, *J* = 1.2 Hz, 3H), 2.44 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.95, 144.07, 140.23, 139.43, 137.19, 129.85, 129.42, 127.29, 126.87, 126.26, 21.65, 21.26, 17.05. *m/z* (ESI–MS): calc. 287.1100 $[M+H]^+$, found 287.1093 $[M+H]^+$.

(*E*)-1-methyl-3-(1-tosylprop-1-en-2-yl)benzene (**1g**)

Synthesized with method A.

White solid, yield: 46%, 657 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.15 (m, 4H), 6.59 (d, *J* = 1.2 Hz, 1H), 2.50 (d, *J* = 1.2 Hz, 3H), 2.44 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.27, 144.13, 140.24, 139.34, 138.47, 130.61, 129.87, 128.62, 127.56, 127.31, 127.01, 123.46, 21.66, 21.43, 17.22. *m/z* (ESI–MS): calc. 287.1100 $[M+H]^+$, found 287.1093 $[M+H]^+$.

(*E*)-1-methyl-2-(1-tosylprop-1-en-2-yl)benzene (**1h**)

Synthesized with method A.

White solid, yield: 40%, 572 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.80 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.11 (m, 3H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.25 (q, *J* = 1.3 Hz, 1H), 2.45 (s, 3H), 2.41 (d, *J* = 1.4 Hz, 3H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.20, 144.24, 141.70, 139.18, 133.81, 130.63, 129.90, 129.74, 128.37, 127.24, 126.82, 125.94, 21.68, 19.82, 19.51. *m/z* (ESI–MS): calc. 287.1100 $[M+H]^+$, found 287.1093 $[M+H]^+$.

(*E*)-1-methoxy-4-(1-tosylprop-1-en-2-yl)benzene (**1i**)

Synthesized with method A.

White solid, yield: 68%, 1.03 g.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.30 (m, 4H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 1.1 Hz, 1H), 3.84 – 3.78 (m, 3H), 2.51 – 2.46 (m, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.07, 152.40, 144.00, 139.58, 132.10, 129.84, 127.82, 127.24, 125.81, 114.05, 55.42, 21.64, 16.91. *m/z* (ESI–MS): calc. 303.1049 $[M+H]^+$, found 303.1043 $[M+H]^+$.

(*E*)-1-methoxy-3-(1-tosylprop-1-en-2-yl)benzene (**1j**)

Synthesized with method A.

White solid, yield: 57%, 861 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.31 – 7.23 (m, 1H), 6.99 – 6.86 (m, 3H), 6.60 (d, *J* = 1.2 Hz, 1H), 3.87 – 3.77 (m, 3H), 2.50 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.70, 152.91, 144.22, 141.71, 139.21, 129.90, 129.78, 127.94, 127.33, 118.73, 115.09, 112.17, 55.41, 21.66, 17.27. *m/z* (ESI–MS): calc. 303.1049 $[M+H]^+$, found 303.1042 $[M+H]^+$.

(*E*)-1-methoxy-2-(1-tosylprop-1-en-2-yl)benzene (**1k**)

Synthesized with method A.

White solid, yield: 41%, 619 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.82 (m, 2H), 7.39 – 7.27 (m, 3H), 7.07 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.95 – 6.84 (m, 2H), 6.43 (q, *J* = 1.2 Hz, 1H), 3.78 (s, 3H), 2.44 (d, *J* = 1.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.34, 153.60, 143.97, 139.44, 130.65, 130.29, 129.78, 129.33, 128.72, 127.26, 120.58, 111.16, 55.47, 21.66, 18.75. *m/z* (ESI–MS): calc. 303.1049 $[M+H]^+$, found 303.1043 $[M+H]^+$.

methyl (*E*)-4-phenyl-5-tosylpent-4-enoate (**1l**)

Synthesized with method B.

White solid, yield: 40%, 724 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.83 (m, 2H), 7.36 (dddd, *J* = 8.6, 5.0, 3.2, 1.5 Hz, 7H), 6.51 (s, 1H), 3.62 (s, 3H), 3.41 – 3.27 (m, 2H), 2.45 (s, 3H), 2.41 – 2.35 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.57, 155.44, 144.40, 139.01, 138.32, 129.97, 129.95, 129.07, 128.91, 127.39, 126.84, 51.76, 32.71, 25.67, 21.64. *m/z* (ESI–MS): calc. 362.1421 $[M+H]^+$, found 362.1410 $[M+H]^+$.

(*E*)-(1-(methylsulfonyl)prop-1-en-2-yl)benzene (**1m**)

Synthesized with method B.

Origin oil, yield: 31%, 31 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.38 (m, 5H), 6.55 (d, *J* = 1.3 Hz, 1H), 3.06 (s, 3H), 2.58 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.39, 139.88, 130.07, 128.85, 126.55, 126.29, 43.99, 17.29. *m/z* (ESI–MS): calc. 197.0631 $[M+H]^+$, found 197.0629 $[M+H]^+$.

(*E*)-2-(1-tosylprop-1-en-2-yl)thiophene (**1n**)

Synthesized with method B.

White solid, yield: 20%, 279 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ7.91 – 7.79 (m, 2H), 7.38 – 7.31 (m, 3H), 7.29 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.03 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.71 (q, *J* = 1.2 Hz, 1H), 2.53 (d, *J* = 1.2 Hz, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.17, 144.14, 143.19, 139.48, 129.88, 128.35, 128.13, 127.63, 127.25, 124.58, 21.62, 16.68. *m/z* (ESI–MS): calc. 279.0508 $[M+H]^+$, found 279.0501 $[M+H]^+$.

(*E*)-1-(tosylmethylene)-1,2,3,4-tetrahydronaphthalene (**1o**)

Synthesized with method A.

White solid, yield: 15%, 224 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.81 (m, 2H), 7.51 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.37 – 7.24 (m, 3H), 7.22 – 7.09 (m, 2H), 6.78 (t, *J* = 1.7 Hz, 1H), 3.05 (ddd, *J* = 7.3, 5.5, 1.8 Hz, 2H), 2.77 (t, *J* = 6.2 Hz, 2H), 2.43 (s, 3H), 1.82 (p, *J* = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.07, 143.99, 140.31, 139.63, 132.39, 130.40, 129.79, 129.47, 127.22, 126.54, 125.08, 123.39, 29.74, 26.85, 22.25, 21.62. *m/z* (ESI–MS): calc. 299.1100 $[M+H]^+$, found 299.1092 $[M+H]^+$.

(*E*)-1-methoxy-4-(2-methyl-3-tosylallyl)benzene(**1p**)

Synthesized with method B.

White solid, yield: 32%, 270 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.47 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.12 (q, *J* = 1.3 Hz, 1H), 3.79 (s, 3H), 3.33 (d, *J* = 1.3 Hz, 2H), 2.43 (s, 3H), 2.08 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.67, 156.39, 143.92, 139.43, 130.19, 129.76, 128.21, 127.55, 127.12, 114.16, 55.28, 45.71, 21.62, 17.72. *m/z* (ESI–MS): calc. 316.11 , found 317.1204 $[M+H]^+$.

(*Z*)-2-(1-phenyl-2-tosylvinyl)thiophene(**1q**)

Synthesized with method A.

White solid, yield: 2.9%, 100 mg.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.54 (m, 2H), 7.48 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.43 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.33 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 2H), 7.28 (d, *J* = 1.2 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.07 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.87 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.67, 143.91, 139.85, 138.22, 136.09, 133.01, 130.43, 129.93, 129.64, 129.37, 128.50, 128.46, 127.65, 126.84, 21.60. *m/z* (ESI–MS): calc. 340.06, found 341.1661 $[M+H]^{+}$.

3. General procedures for hydrogenation of unsaturated sulfones.

In an argon-filled glovebox, a solution of $[Rh(NBD)Cl]_2$ (6.7 mg, 0.01 mmol) and (*S*,*R*)-Zhaophos (2.1 eq.) in 2.0 ml CH_3CH_2OH was stirred at room temperature for 30 min. Sulfone (0.10 mmol) was dissolved in 0.5 mL CF_3CH_2OH in a 5-ml score-break ampule. A specified volume of the catalyst solution (0.10 ml, 1% Rh catalyst) and 0.4 mL CH_3CH_2OH were transferred by syringes to this ampule successively. This mixture was gently stirred to homogeneity. The ampule was place in a Parr autoclave which was pressurized with hydrogen gas to 60 atm H_2 afterwards. The autoclave was placed on a stir plate (600 rpm) for 48 hours at 40 ℃. The hydrogen gas was carefully released in a fume hood and the reaction mixture was concentrated *in vacuo*. The residue was purified by flash chromatography (on silica, petroleum ether/ethyl acetate) to afford chiral sulfone. Enantiomeric excess was determined by HPLC on a stationary phase.

4. Linear dependence of the product ee on the ligand ee.

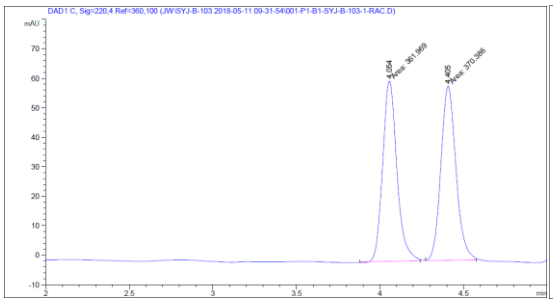
Hydrogenation reactions were conducted under the optimized condition with 0.10 mmol 1a and 1% catalyst. Ligand with different ee was prepared by mixing two enantiomers in a specific ratio.

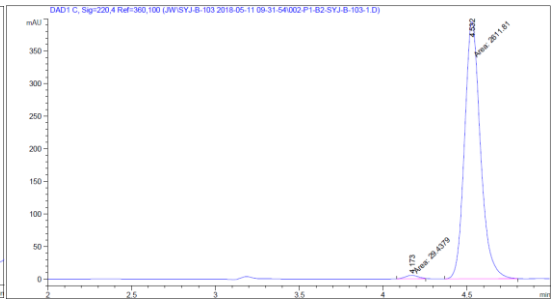
ee of ligand	20	40	60	80	100
ee of product	24	38	61	85	98

5. Characterization data for chiral sulfones.

(*S*)-methyl-4-((2-phenylpropyl)sulfonyl)benzene (**2a**)

White solid, mp = 76-78 ℃, 98% yield, 26.85 mg, 98% ee, $[\alpha]^{25}_{D}$ -16.80 (*c* 1.28, MeOH). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.64 (m, 2H), 7.31 – 7.14 (m, 5H), 7.10 – 7.04 (m, 2H), 3.45 – 3.27 (m, 3H), 2.42 (s, 3H), 1.44 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.46, 144.16, 136.92, 129.79, 128.73, 127.90, 126.81, 126.72, 63.44, 35.07, 22.16, 21.63. *m/z* (ESI–MS): calc. 275.1100 $[M+H]^+$, found 275.1092 $[M+H]^+$. HPLC (Daicel Chiralpak IA, hexanes/i-PrOH = 90/10, flow rate = 0.5 mL/min, UV = 220 nm): t_1 =4.01 min, t_2 = 4.41 min.





Signal 1: DAD1 C, Sig=220,4 Ref=360,100

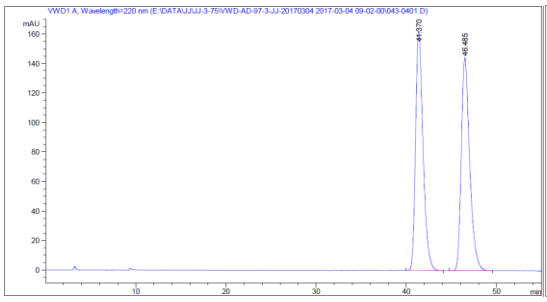
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.054	MM	0.0984	361.96887	61.32983	49.4253
2	4.405	MM	0.1041	370.38611	59.27185	50.5747

Signal 1: DAD1 C, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.173	MM	0.0905	29.43792	5.42044	1.1145
2	4.532	MM	0.1100	2611.81177	395.61856	98.8855

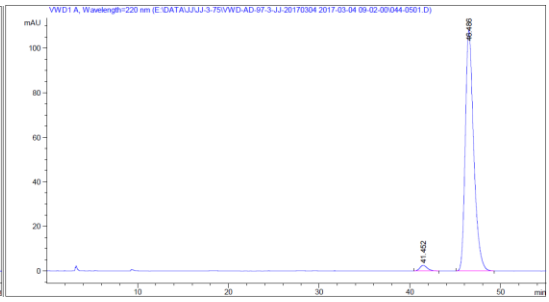
(*S*)-1-fluoro-4-(1-tosylpropan-2-yl)benzene (**2b**)

White solid, mp = 57-58 ℃, 97% yield, 28.32 mg, 96% ee, $[\alpha]^{25}_{D}$ -13.54 (*c* 0.96, MeOH). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.27 (t, *J* = 4.0 Hz, 3H), 7.09 – 6.99 (m, 2H), 6.89 (t, *J* = 8.7 Hz, 2H), 3.45 – 3.25 (m, 3H), 2.42 (s, 3H), 1.40 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.61 (d, *J* = 245.1 Hz), 144.55, 139.68 (d, *J* = 3.2 Hz), 136.86, 129.79, 128.25 (d, *J* = 7.9 Hz), 127.87, 115.47 (d, *J* = 21.3 Hz), 63.46, 34.47, 22.44, 21.62. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -116.00. *m/z* (ESI–MS): calc. 293.1006 $[M+H]^+$, found 293.0996 $[M+H]^+$. HPLC (Daicel Chiralpak AD, hexanes/i-PrOH = 97/3, flow rate = 1.0 mL/min, UV = 220 nm): t_1 = 41.37 min, t_2 = 46.49 min.



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.370	BB	0.8774	9335.07129	162.20813	49.9796
2	46.485	BB	0.9807	9342.67383	144.22763	50.0204

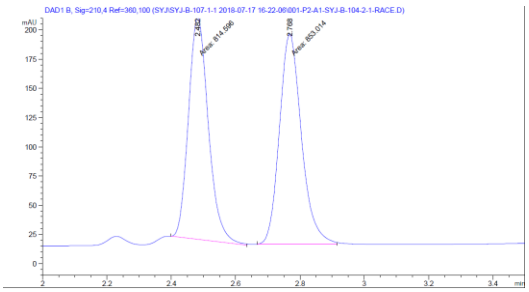


Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.452	BB	0.7043	141.81207	2.51694	1.9999
2	46.486	BB	0.9733	6949.00635	108.05723	98.0001

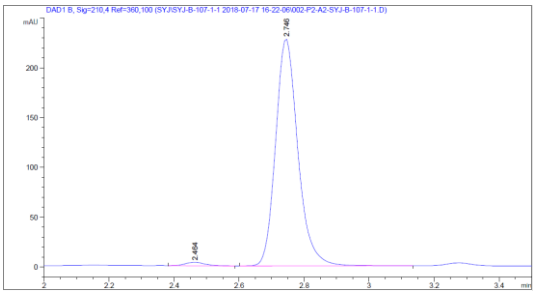
(*S*)-1-chloro-4-(1-tosylpropan-2-yl)benzene (**2c**)

White solid, mp = 89-92 °C, 97% yield, 29.88 mg, 98% ee, $[\alpha]^{25}_{D}$ -13.46 (*c* 1.27, MeOH). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.19 – 7.12 (m, 2H), 7.02 – 6.96 (m, 2H), 3.42 – 3.25 (m, 3H), 2.43 (s, 3H), 1.39 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.61, 142.29, 136.74, 132.56, 129.78, 128.77, 128.17, 127.86, 63.20, 34.68, 22.37, 21.63. *m/z* (ESI–MS): calc. 309.0711 $[M+H]^{+}$, found 309.0702 $[M+H]^{+}$. HPLC (Daicel Chiralpak IA, hexanes/i-PrOH = 70/30, flow rate = 0.5 mL/min, UV = 210 nm): t_1 = 2.48 min, t_2 = 2.77 min.



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.482	MM	0.0709	814.59631	191.37947	48.8481
2	2.768	MM	0.0787	853.01422	180.54153	51.1519



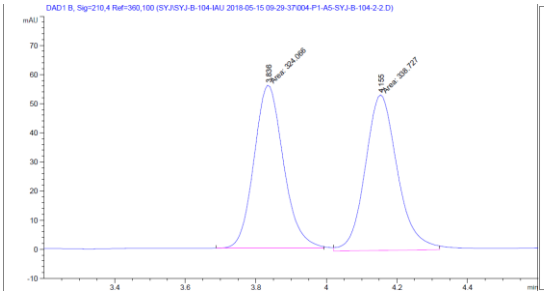
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.464	BB	0.0643	14.12001	3.40961	1.2860
2	2.746	BB	0.0714	1083.87378	228.07515	98.7140

(*S*)-1-bromo-4-(1-tosylpropan-2-yl)benzene (**2d**)

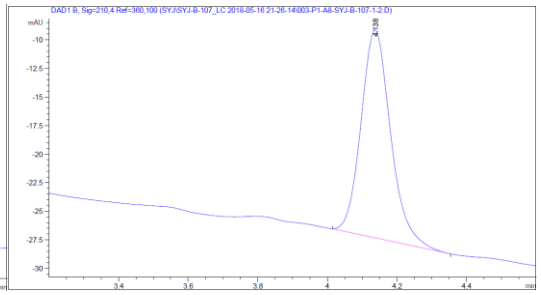
White solid, mp = 94-96 °C, 65% yield, 22.88 mg, >99% ee, $[\alpha]^{25}_{D}$ -6.62 (*c* 1.45, MeOH).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.13 (m, 4H), 7.07 (dd, *J* = 6.9, 1.9 Hz, 2H), 3.50 – 3.18 (m, 3H), 2.42 (s, 3H), 1.44 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz,

Chloroform-*d*) δ 144.41, 144.17, 136.97, 129.76, 128.70, 127.88, 126.78, 126.70, 63.47, 35.07, 22.13, 21.60. *m/z* (ESI–MS): calc. 353.0205 $[M+H]^+$, found 353.0199 $[M+H]^+$. HPLC (Daicel Chiralpak IA, hexanes/i-PrOH = 90/10, flow rate = 0.5 mL/min, UV = 210 nm): t_1 = 3.84 min, t_2 = 4.16 min.



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.836	MM	0.0964	324.06641	56.00245	48.8941
2	4.155	MM	0.1056	338.72656	53.44873	51.1059

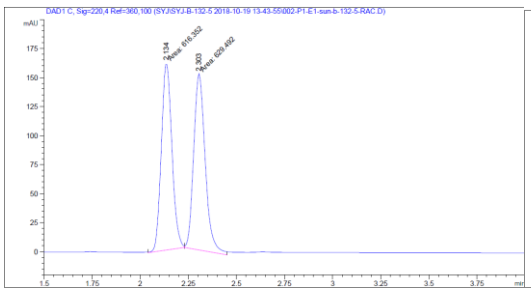


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.138	BB	0.0886	107.12025	18.21458	100.0000

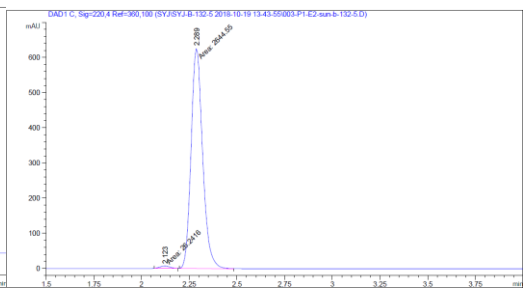
(*S*)-1-methyl-4-((2-(4-(trifluoromethyl)phenyl)propyl)sulfonyl)benzene (**2e**)

White solid, mp = 71-74 ℃, 98% yield, 33.52 mg, 98% ee, $[\alpha]^{25}_D$ -9.60 (*c* 1.24, MeOH). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.18 (dd, *J* = 17.1, 8.0 Hz, 4H), 3.56 – 3.25 (m, 3H), 2.39 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.60, 144.62, 136.54, 129.74, 129.06 (q, *J* = 32.5 Hz), 127.55 (q, *J* = 57.9 Hz), 125.57 (q, *J* = 3.8 Hz), 124.03 (q, *J* = 271.9 Hz), 62.85, 35.26, 22.52, 21.51. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -62.55. *m/z* (ESI–MS): calc. 343.0974, found 343.0969 $[M+H]^+$. HPLC (Daicel Chiralpak IA, hexanes/i-PrOH = 70/30, flow rate = 0.5 mL/min, UV = 220 nm): t_1 = 2.13 min, t_2 = 2.30 min.



Signal 1: DAD1 C, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.134	MM	0.0635	616.35223	161.75171	49.4726
2	2.303	MM	0.0690	629.49237	152.14188	50.5274

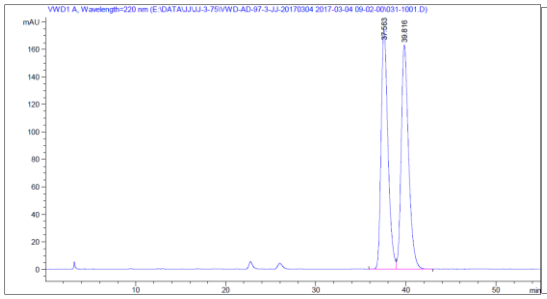


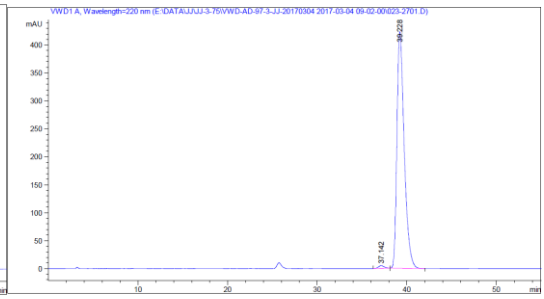
Signal 1: DAD1 C, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.123	MM	0.0616	26.24158	7.10269	0.9825
2	2.289	MM	0.0701	2644.55127	628.43427	99.0175

(*S*)-1-methyl-4-((2-(p-tolyl)propyl)sulfonyl)benzene (**2f**)

White solid, mp = 80-81 °C, 98% yield, 28.22 mg, 98% ee, $[\alpha]^{25}_{D}$ -18.81 (*c* 1.35, MeOH). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.23 (m, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 3.42 – 3.22 (m, 3H), 2.42 (s, 3H), 2.28 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.38, 141.15, 136.98, 136.44, 129.74, 129.35, 127.89, 126.58, 63.54, 34.67, 22.21, 21.63, 21.00. *m/z* (ESI–MS): calc. 289.1257 $[M+H]^{+}$, found 289.1249 $[M+H]^{+}$. HPLC (Daicel Chiralpak AD, hexanes/i-PrOH = 97/3, flow rate = 1.0 mL/min, UV = 220 nm): t_1 = 37.56 min, t_2 = 39.82 min.





Signal 1: VWD1 A, Wavelength=220 nm

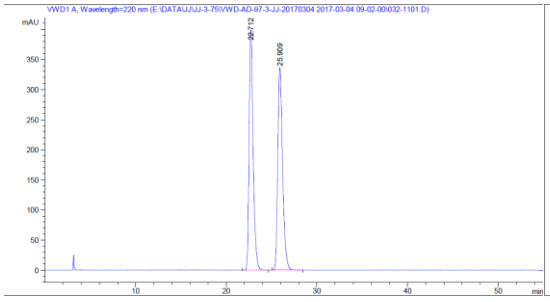
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.563	BV	0.8085	9206.09375	174.21312	49.7637
2	39.816	VB	0.8626	9293.50879	163.13707	50.2363

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.142	BB	0.6840	221.83301	4.92971	0.9202
2	39.228	BB	0.8561	2.38858e4	423.41760	99.0798

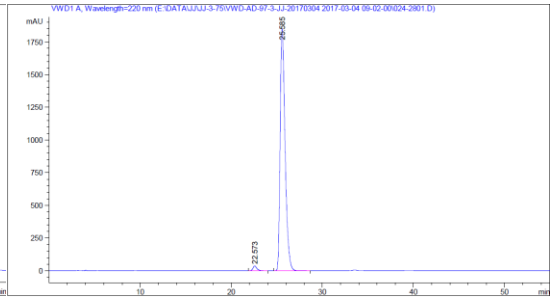
(*S*)-1-methyl-3-(1-tosylpropan-2-yl)benzene (**2g**)

Colorless oil, 97% yield, 27.93 mg, 97% ee, $[\alpha]^{25}_{D}$ -15.52 (*c* 1.45, MeOH). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.64 (m, 2H), 7.29 – 7.23 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.96 (ddt, *J* = 7.6, 1.8, 0.9 Hz, 1H), 6.87 (dt, *J* = 7.7, 1.5 Hz, 1H), 6.83 (d, *J* = 1.8 Hz, 1H), 3.45 – 3.25 (m, 3H), 2.41 (s, 3H), 2.25 (s, 3H), 1.47 – 1.37 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.36, 144.05, 138.28, 136.95, 129.70, 128.63, 127.89, 127.51, 127.46, 123.77, 63.41, 35.03, 22.22, 21.61, 21.37. *m/z* (ESI–MS): calc. 289.1257 $[M+H]^{+}$, found 289.1251 $[M+H]^{+}$. HPLC (Daicel Chiralpak AD, hexanes/i-PrOH = 97/3, flow rate = 1.0 mL/min, UV = 220 nm): t_1 = 22.71 min, t_2 = 25.91 min.



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.712	BB	0.4726	1.24134e4	399.43887	49.9875
2	25.909	BB	0.5640	1.24197e4	336.18179	50.0125

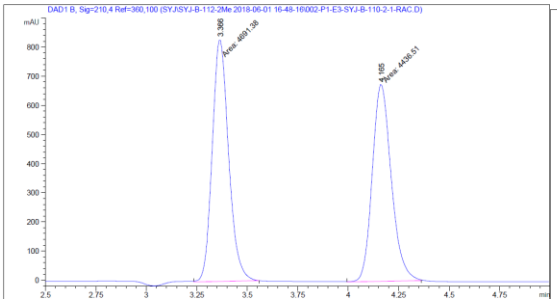


Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.573	BB	0.4355	1055.57397	36.49348	1.4917
2	25.585	BB	0.5769	6.97093e4	1848.73633	98.5083

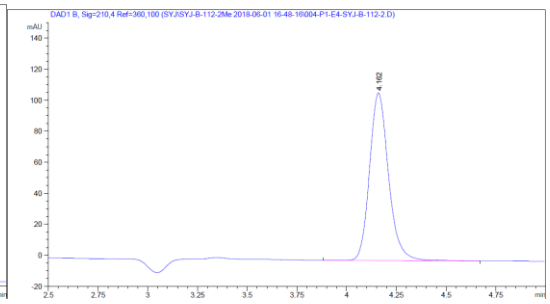
(*S*)-1-methyl-2-(1-tosylpropan-2-yl)benzene (**2h**)

White solid, mp = 57-60 °C, 53% yield (87 h), 15.26 mg, >99% ee, $[\alpha]^{25}_{D}$ -1.67 (*c* 0.36, MeOH). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.62 (m, 2H), 7.36 – 7.20 (m, 2H), 7.15 – 6.93 (m, 4H), 3.77 – 3.56 (m, 1H), 3.39 – 3.23 (m, 2H), 2.41 (s, 3H), 2.24 (s, 3H), 1.41 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.47, 142.38, 136.91, 134.97, 130.64, 129.78, 127.85, 126.52, 126.46, 125.33, 63.00, 29.97, 21.63, 21.49, 19.33. *m/z* (ESI–MS): calc. 289.1257 $[M+H]^{+}$, found 289.1250 $[M+H]^{+}$. HPLC (Daicel Chiralpak IA, hexanes/i-PrOH = 90/10, flow rate = 0.5 mL/min, UV = 210 nm): t_1 = 3.37 min, t_2 = 4.17 min.



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.366	MM	0.0940	4691.38037	831.90210	51.3961
2	4.165	MM	0.1091	4436.50977	677.53351	48.6039



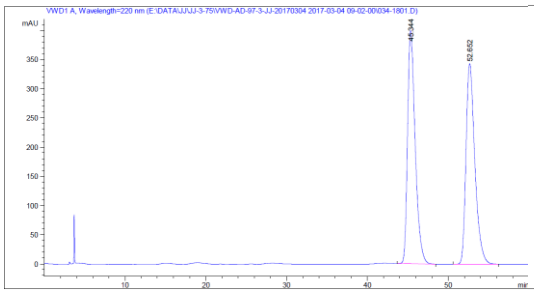
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.162	BB	0.1015	719.21942	108.26273	100.0000

(*S*)-1-methoxy-4-(1-tosylpropan-2-yl)benzene (**2i**)

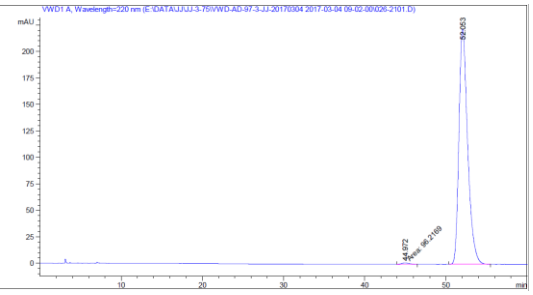
White solid, mp = 63-65 °C, 98% yield, 29.79 mg, 99% ee, $[\alpha]^{25}_{D}$ -15.31 (*c* 1.47, MeOH). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.19 (m, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 3H), 3.43 – 3.22 (m, 3H), 2.42 (s, 3H), 1.40 (d, *J* = 6.7

Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.36, 144.36, 137.01, 136.19, 129.75, 127.88, 127.70, 114.02, 63.68, 55.27, 34.31, 22.30, 21.62. *m/z* (ESI–MS): calc. 305.1206 $[M+H]^+$, found 305.1199 $[M+H]^+$. HPLC (Daicel Chiralpak AD, hexanes/i-PrOH = 96/4, flow rate = 1.0 mL/min, UV = 220 nm): t_1 = 45.34 min, t_2 = 52.65 min.



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.344	BB	0.9970	2.61616e4	398.97507	50.0259
2	52.652	BB	1.1606	2.61346e4	343.52042	49.9741

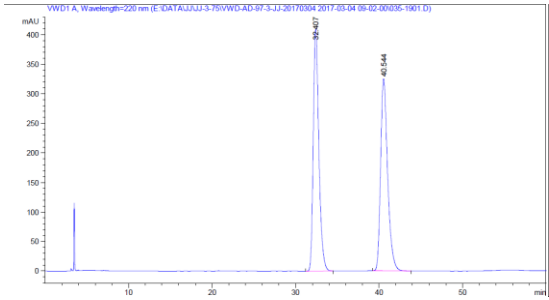


Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.972	MM	1.0925	96.21690	1.46788	0.5781
2	52.053	BB	1.1265	1.65472e4	222.01666	99.4219

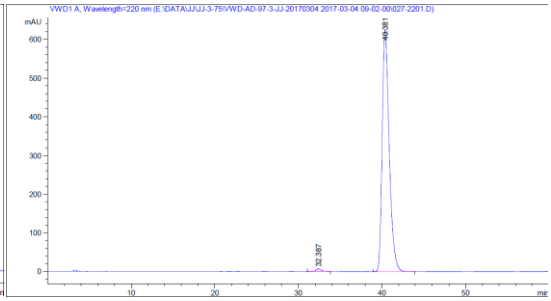
(*S*)-1-methoxy-3-(1-tosylpropan-2-yl)benzene (**2j**)

Colorless oil, 97% yield, 29.48 mg, 98% ee, $[\alpha]^{25}_D$ -23.60 (*c* 1.36, MeOH). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.60 (m, 2H), 7.37 – 7.19 (m, 2H), 7.14 (t, *J* = 7.9 Hz, 1H), 6.76 – 6.62 (m, 2H), 6.61 – 6.53 (m, 1H), 3.74 (s, 3H), 3.44 – 3.24 (m, 3H), 2.42 (s, 3H), 1.42 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.72, 145.76, 144.45, 136.89, 129.76, 127.90, 119.04, 112.68, 111.83, 63.36, 55.16, 35.14, 22.09, 21.62. *m/z* (ESI–MS): calc. 305.1206 $[M+H]^+$, found 305.1199 $[M+H]^+$. HPLC (Daicel Chiralpak AD, hexanes/i-PrOH = 96/4, flow rate = 1.0 mL/min, UV = 220 nm): t_1 = 32.41 min, t_2 = 40.54 min.



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.407	BB	0.6977	1.89091e4	409.49890	49.9850
2	40.544	BB	0.8825	1.89204e4	324.83124	50.0150

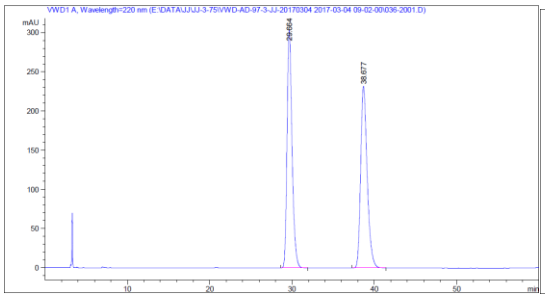


Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.387	BB	0.6865	332.61484	7.25983	0.9025
2	40.381	BB	0.8911	3.65230e4	625.63574	99.0975

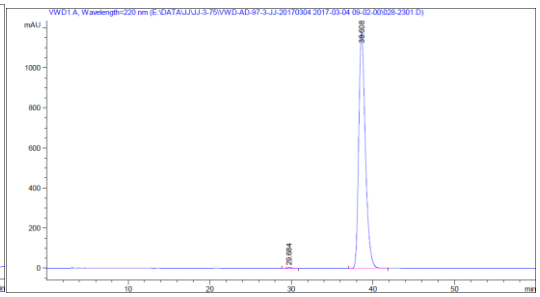
(*S*)-1-methoxy-2-(1-tosylpropan-2-yl)benzene (**2k**)

Colorless oil, 98% yield, 29.79 mg, >99% ee, $[\alpha]^{25}_{D}$ -15.62 (*c* 1.46, MeOH). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.62 (m, 2H), 7.28 – 7.21 (m, 2H), 7.17 – 7.02 (m, 2H), 6.83 (td, *J* = 7.5, 1.0 Hz, 1H), 6.75 – 6.62 (m, 1H), 3.65 (s, 3H), 3.63 – 3.51 (m, 2H), 3.38 – 3.21 (m, 1H), 2.41 (s, 3H), 1.42 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.57, 144.08, 136.89, 131.48, 129.48, 128.01, 127.95, 127.87, 120.63, 110.47, 61.65, 54.96, 30.60, 21.62, 19.80. *m/z* (ESI–MS): calc. 305.1206 $[M+H]^+$, found 305.1199 $[M+H]^+$. HPLC (Daicel Chiralpak AD, hexanes/i-PrOH = 96/4, flow rate = 1.0 mL/min, UV = 220 nm): t_1 = 29.66 min, t_2 = 38.68 min.



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.664	BB	0.6384	1.27939e4	303.73413	49.9781
2	38.677	BB	0.8367	1.28051e4	232.07457	50.0219

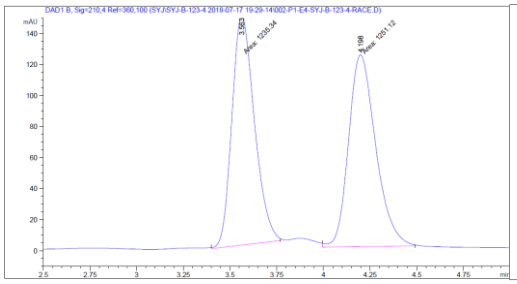


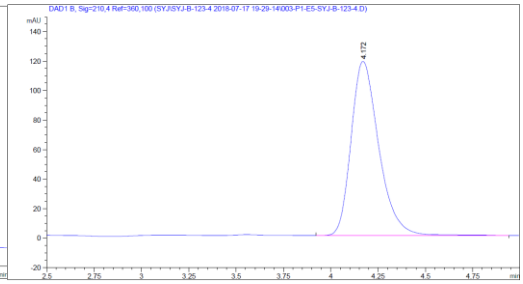
Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.684	BB	0.6070	148.62306	3.64258	0.2240
2	38.608	BB	0.8645	6.61888e4	1176.32947	99.7760

(*S*)-methyl-4-phenyl-5-tosylpentanoate (**2l**)

Colorless oil, 90% yield, 32.67 mg, >99% ee, $[\alpha]^{25}_{D}$ +10.98 (*c* 0.82, MeOH). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.58 (m, 2H), 7.19 (ddd, *J* = 10.1, 8.6, 6.4 Hz, 5H), 7.04 – 6.96 (m, 2H), 3.59 (s, 3H), 3.49 – 3.34 (m, 2H), 3.23 (dtd, *J* = 10.9, 6.6, 4.3 Hz, 1H), 2.40 (s, 3H), 2.30 (dddd, *J* = 13.6, 9.5, 6.5, 4.4 Hz, 1H), 2.25 – 1.85 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.18, 144.39, 140.80, 136.76, 129.70, 128.77, 127.88, 127.52, 127.17, 62.25, 51.59, 40.07, 31.66, 31.23, 21.57. *m/z* (ESI–MS): calc. 364.1577 $[M+H]^+$, found 364.1567 $[M+H]^+$. HPLC (Daicel Chiralpak IB, hexanes/i-PrOH = 70/30, flow rate = 0.5 mL/min, UV = 210 nm): t_1 = 3.56 min, t_2 = 4.20 min.





Signal 1: DAD1 B, Sig=210,4 Ref=360,100

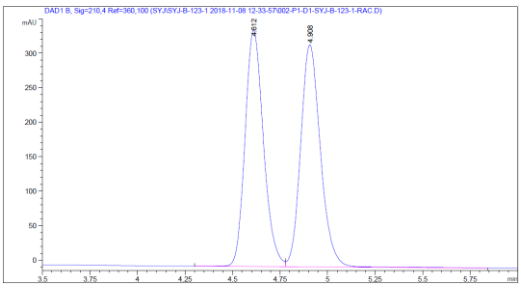
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.563	MM	0.1392	1235.34106	147.89131	49.6827
2	4.198	MM	0.1685	1251.11914	123.78474	50.3173

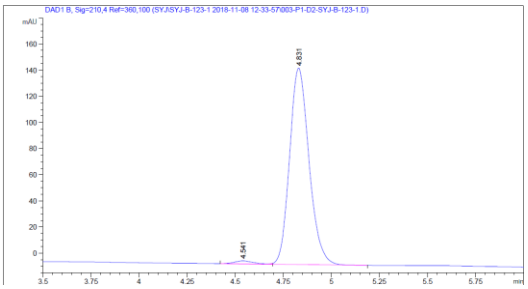
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.172	BB	0.1549	1203.50208	118.12947	100.0000

(*S*)- (1-(methylsulfonyl)propan-2-yl)benzene (**2m**)

White solid, mp = 65-69 ℃, 88% yield (87 h), 17.42 mg, 97% ee, $[\alpha]^{25}_{D}$ -25.13 (*c* 1.15, MeOH). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.32 (m, 2H), 7.30 – 7.24 (m, 3H), 3.48 (h, *J* = 7.0 Hz, 1H), 3.37 (dd, *J* = 14.3, 7.8 Hz, 1H), 3.23 (ddd, *J* = 14.4, 6.0, 1.0 Hz, 1H), 2.47 (s, 3H), 1.47 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.52, 129.11, 127.41, 127.00, 62.46, 41.87, 35.41, 22.46. *m/z* (ESI–MS): calc. 199.0787 $[M+H]^+$, found 199.0788 $[M+H]^+$. HPLC (Daicel Chiralpak IC, hexanes/i-PrOH = 70/30, flow rate = 0.5 mL/min, UV = 210 nm): t_1 = 4.61 min, t_2 = 4.91 min.





Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.612	BV	0.1022	2301.70239	343.29276	49.7018
2	4.908	VB	0.1104	2329.32324	322.12741	50.2982

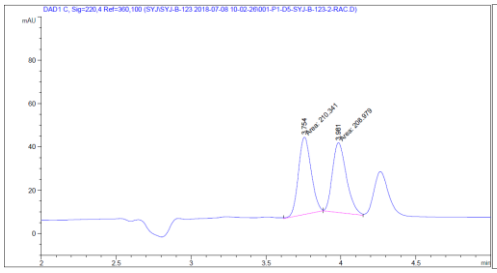
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

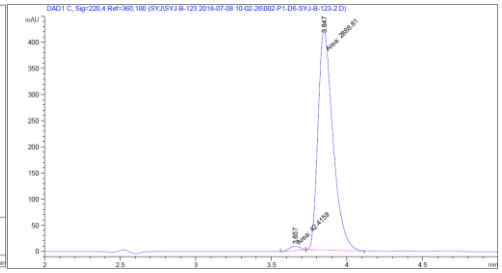
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.541	BV E	0.1032	15.13534	2.28818	1.4126
2	4.831	VB R	0.1099	1056.34839	150.43857	98.5874

(*S*)-2-(1-tosylpropan-2-yl)thiophene (**2n**)

Colorless oil, 98% yield, 29.10 mg, 97% ee, $[\alpha]^{25}_{D}$ -21.44 (*c* 1.25, MeOH). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.62 (m, 2H), 7.35 – 7.27 (m, 2H), 7.09 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.84 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.75 (dt, *J* = 3.5, 1.0 Hz, 1H)，3.84 – 3.64 (m, 1H), 3.44 (dd, *J* = 14.2, 4.9 Hz, 1H), 3.31 (dd, *J* = 14.2, 8.3 Hz, 1H), 2.43 (s, 3H), 1.52 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz,

Chloroform-*d*) δ 147.92, 144.61, 136.89, 129.86, 127.89, 126.71, 123.65, 123.64, 64.17, 30.71, 22.99, 21.63. *m/z* (ESI–MS): calc. 298.0930 $[M+H]^+$, found 298.0923 $[M+H]^+$. HPLC (Daicel Chiralpak IA, hexanes/i-PrOH = 90/10, flow rate = 0.5 mL/min, UV = 220 nm): t_1 = 3.75 min, t_2 = 3.98 min.





Signal 1: DAD1 C, Sig=220,4 Ref=360,100

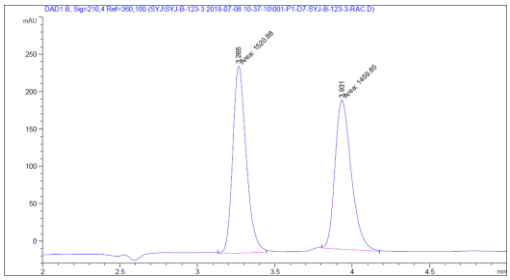
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.754	MM	0.0978	210.34056	35.86115	50.1624
2	3.981	MM	0.1076	208.97890	32.38361	49.8376

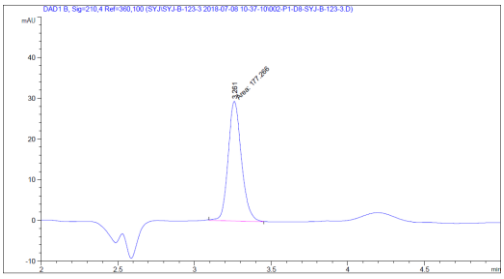
Signal 1: DAD1 C, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.657	MM	0.0833	42.41594	8.48949	1.4470
2	3.847	MM	0.1147	2888.81323	419.77029	98.5530

(*S*)-1-(tosylmethyl)-1,2,3,4-tetrahydronaphthalene (**2o**)

White solid, mp = 102-103 ℃, 91% yield, 28.85 mg, >99% ee, $[\alpha]^{25}_D$ -25.29 (*c* 0.34, MeOH). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.12 – 6.99 (m, 3H), 6.98 – 6.92 (m, 1H), 3.55 – 3.43 (m, 1H), 3.44 – 3.19 (m, 2H), 2.82 – 2.66 (m, 2H), 2.46 (s, 3H), 2.16 – 2.05 (m, 1H), 2.00 – 1.87 (m, 1H), 1.77 (dddd, *J* = 13.9, 9.0, 6.8, 3.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.68, 137.69, 137.29, 136.98, 130.00, 129.44, 128.64, 127.98, 126.49, 126.21, 62.92, 32.85, 29.11, 27.52, 21.67, 18.89. *m/z* (ESI–MS): calc. 318.1522 $[M+H]^+$, found 318.1514 $[M+H]^+$. HPLC (Daicel Chiralpak IB, hexanes/i-PrOH = 90/10, flow rate = 0.5 mL/min, UV = 220 nm): t_1 = 3.27 min, t_2 = 3.93 min.





Signal 1: DAD1 B, Sig=210,4 Ref=360,100

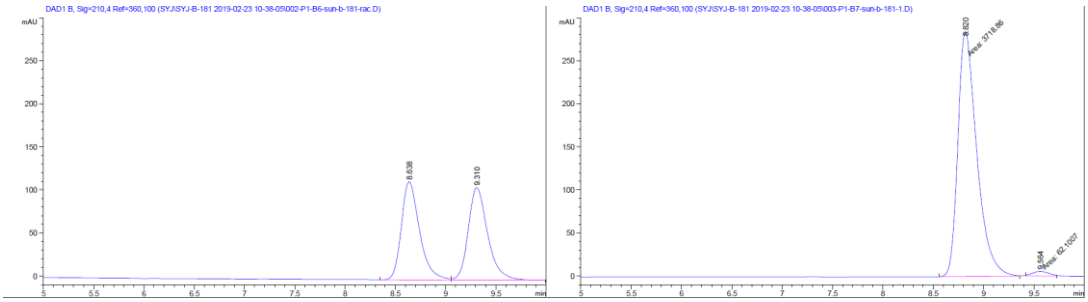
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.265	MM	0.1010	1520.87585	250.92654	51.0237
2	3.931	MM	0.1215	1459.84607	200.24019	48.9763

Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.261	MM	0.1003	177.26637	29.44426	100.0000

(*S*)-1-methoxy-4-(2-methyl-3-tosylpropyl)benzene(**2p**)

White solid, 84% yield, 26.72 mg, 97% ee, $[\alpha]^{25}_{D}$ 9.44 (*c* 1.25, MeOH). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 1H), 3.78 (s, 3H), 3.09 (dd, *J* = 14.2, 4.5 Hz, 1H), 2.87 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.68 – 2.48 (m, 2H), 2.45 (s, 3H), 2.28 (pd, *J* = 7.0, 4.5 Hz, 1H), 1.07 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.12, 144.40, 137.01, 130.83, 130.08, 129.83, 127.83, 113.79, 61.34, 55.24, 41.85, 30.62, 21.62, 19.86. *m/z* (ESI–MS): calc. 318.13, found 319.1362 $[M+H]^{+}$. HPLC (Daicel Chiralpak IA, hexanes/i-PrOH = 95/5, flow rate = 0.5 mL/min, UV = 210 nm): t_1 = 8.82 min, t_2 = 9.56 min.



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

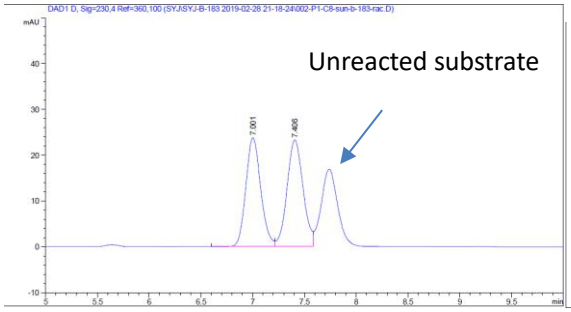
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.638	BV	0.1904	1427.93262	113.80331	49.8605
2	9.310	VBA	0.2042	1435.92126	107.24236	50.1395

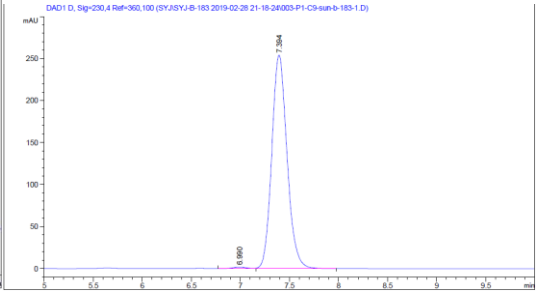
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.820	MM	0.2178	3718.86401	284.62509	98.3575
2	9.564	MM	0.1897	62.10070	5.45595	1.6425

(+)-2-(1-phenyl-2-tosylethyl)thiophene(**2q**)

Yellow solid, 98% yield, 33.52 mg, >99% ee, $[\alpha]^{25}_{D}$ 19.28 (c 1.15, CH_3Cl). 1H NMR (600 MHz, Chloroform-d) δ 7.67 – 7.40 (m, 2H), 7.22 – 7.11 (m, 7H), 7.09 (dd, J = 5.1, 1.2 Hz, 1H), 4.85 (t, J = 7.0 Hz, 1H), 3.88 (h, J = 7.8 Hz, 2H), 2.37 (s, 3H). 13C NMR (151 MHz, Chloroform-d) δ 145.53, 144.28, 141.04, 136.56, 129.56, 128.76, 127.96, 127.58, 127.27, 126.74, 124.76, 124.63, 62.71, 41.95, 21.57. m/z (ESI–MS): calc. 342.07, found 365.0639 $[M+Na]^{+}$. HPLC (Daicel Chiralpak IC, hexanes/i-PrOH = 70/30, flow rate = 0.5 mL/min, UV = 230 nm): t_1 = 7.00 min, t_2 = 7.41 min.





Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.001	BV	0.1547	237.85483	23.77395	48.6873
2	7.406	VV	0.1674	250.68117	23.31941	51.3127

Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.990	BV E	0.1483	17.45443	1.84640	0.6314
2	7.394	VB R	0.1661	2746.91382	254.17796	99.3686

6. Kinetic studies

6.1 Reaction in optimized condition (CF_3CH_2OH/EtOH):

Hydrogenation reactions under pressurized condition were carried out on a Mettler-Toledo EasyMax 102 station with a 100-mL pressure vessel. Experiment procedure: The vessel was dried by a heat gun and sealed afterwards. After 3 vacuum-argon-back-fill cycles, a mixture of **1a** (3.75 mmol), zhaophos (35.9 mg) and $[Rh(NBD)Cl]_2$ (8.6 mg) in anhydrous trifluoroethanol/ethanol (1:1, v/v) was transferred into the vessel via a syringe. The vessel was pressurized with 20 atm hydrogen gas and stirred at 300 rpm. The temperature was maintained at 40°C and the IR spectra were collected with such time intervals: every 15 seconds for the first hour; every 30 seconds for the next 2h, every 2 minutes for the rest of time. The reaction was monitored by tracing the consumption of **1a** at 828 cm^{-1} and formation of **2a** at 767 cm^{-1}. A baseline correction was applied for analysing the peak intensities. Reaction parameters were summarized as follow:

temp	total vol.	conc. **1a**	conc. cat.	S/C
40 °C	15.0 mL	0.25 M	$2.5*10^{-3}$ M	100

The data were manipulated guided by Blackmond's tutorial review. The raw absorption intensity data obtained from ReactIR 15 were converted to concentration (M) vs time (s).

The date were fitted to a 9th order polynomial equation using unweighted least-square fit:

$$[\mathbf{1a}] = \quad f(t) = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + a_5 t^5 + a_6 t^6 + a_7 t^7 + a_8 t^8 + a_9 t^9$$

The rate of consumption of **1a** was obtained from the deviation of *f(t)*:

$$v = -\frac{\mathrm{d}[\mathbf{1a}]}{\mathrm{dt}} = -(a_1 + 2a_2t^1 + 3a_3t^2 + 4a_4t^3 + 5a_5t^4 + 6a_6t^5 + 7a_7t^6 + 8a_8t^7 + 9a_9t^8)$$

For the formation of **2a**, similar operation was performed:

$$[\mathbf{2a}] = f(t) = a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4 + a_5t^5 + a_6t^6 + a_7t^7 + a_8t^8 + a_9t^9$$

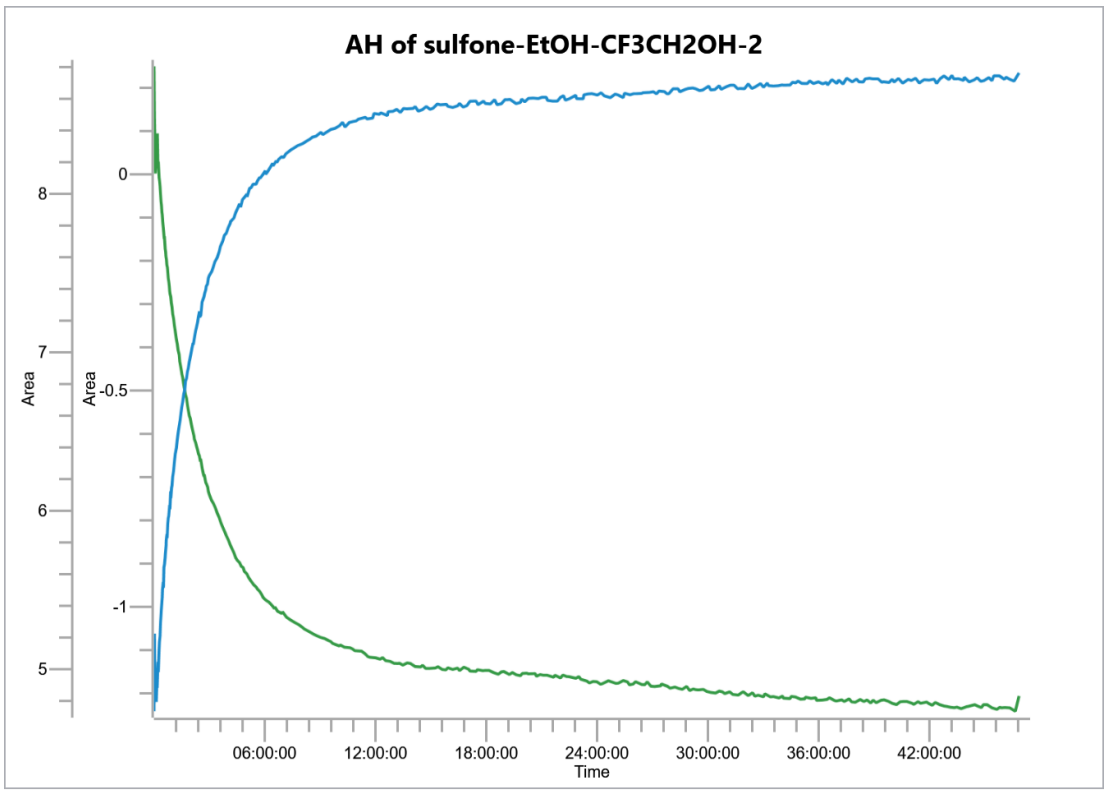
$$v = \frac{\mathrm{d}[\mathbf{2a}]}{\mathrm{dt}} = a_1 + 2a_2t^1 + 3a_3t^2 + 4a_4t^3 + 5a_5t^4 + 6a_6t^5 + 7a_7t^6 + 8a_8t^7 + 9a_9t^8$$

Data fitting was carried out with Origin 2017™. Plotting **1a** consumption rate $-\frac{\mathrm{d}[\mathbf{1a}]}{\mathrm{dt}}$ *vs* substrate concentration [**1a**] and **2a** formation reaction rate $\frac{\mathrm{d}[\mathbf{2a}]}{\mathrm{dt}}$ *vs* [**1a**] gave graphical reaction equations.

Fitting parameters of the two sets of data:

consumption of **1a**		formation of **2a**	
a_0	0.24038	a_0	0.01222
a_1	$-2.49264*10^{-5}$	a_1	$2.83522*10^{-5}$
a_2	$1.46183*10^{-9}$	a_2	$-1.80638*10^{-9}$
a_3	$-5.16157*10^{-14}$	a_3	$6.70572*10^{-14}$
a_4	$1.12643*10^{-18}$	a_4	$-1.5086*10^{-18}$
a_5	$-1.54258*10^{-23}$	a_5	$2.1078*10^{-23}$
a_6	$1.32326*10^{-28}$	a_6	$-1.83505*10^{-28}$
a_7	$-6.89041*10^{-34}$	a_7	$9.66982*10^{-34}$
a_8	$1.98908*10^{-39}$	a_8	$-2.8199*10^{-39}$
a_9	$-2.44045*10^{-45}$	a_9	$3.49084*10^{-45}$
R-Square(COD)	0.9997	R-Square(COD)	0.9992

Raw data:



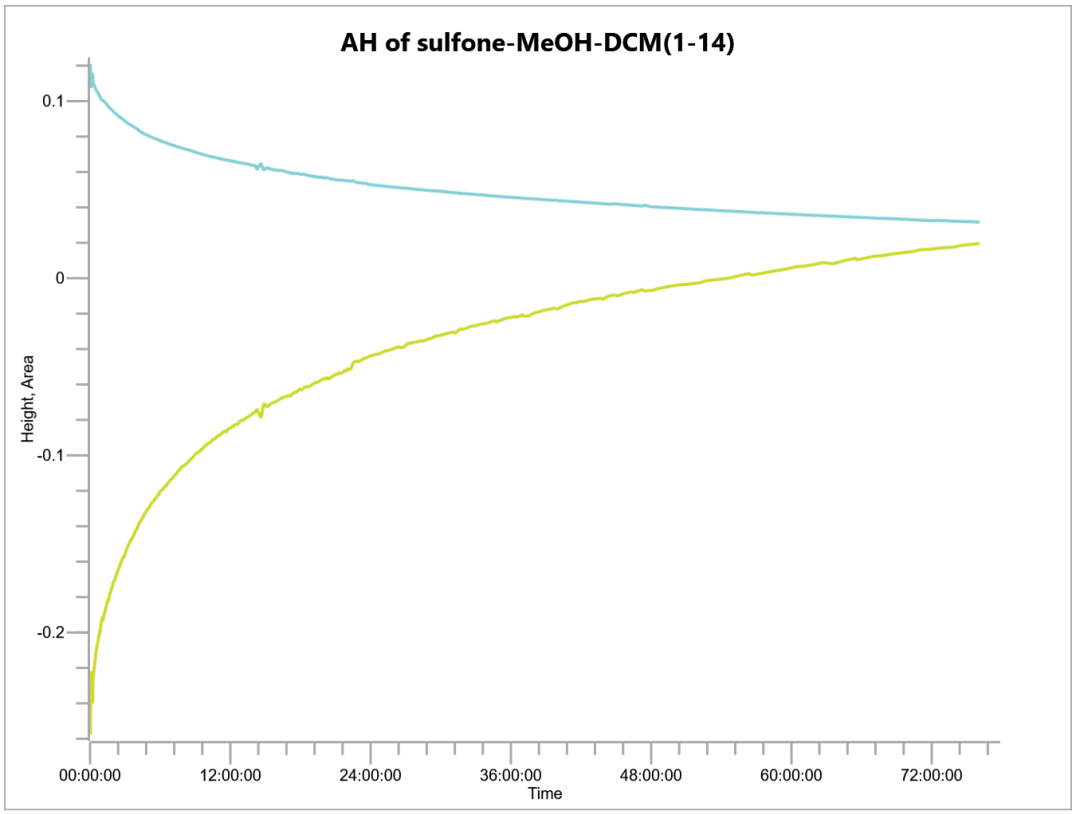
6.2 Reaction in DCM:

The reaction was monitored by tracing the consumption of **1a** at 828 cm^{-1} and formation of **2a** at 846 cm^{-1}. Complex was prepared by mixing ligand and metal precursor in methanol, which made the reaction solvent a mixture of MeOH/DCM = 1:14 (v/v). Data manipulation was the same with the scenario in the optimized condition.

consumption of **1a**		formation of **2a**	
a_0	0.24519	a_0	0.0064
a_1	$-7.27472*10^{-6}$	a_1	$7.29611*10^{-6}$
a_2	$2.53566*10^{-10}$	a_2	$-2.49106*10^{-10}$
a_3	$-5.751*10^{-15}$	a_3	$5.54163*10^{-15}$
a_4	$7.93646*10^{-20}$	a_4	$-7.56917*10^{-20}$
a_5	$-6.7845*10^{-25}$	a_5	$6.4511*10^{-25}$
a_6	$3.61227*10^{-30}$	a_6	$-3.44008*10^{-30}$
a_7	$-1.16517*10^{-35}$	a_7	$1.11399*10^{-35}$
a_8	$2.08258*10^{-41}$	a_8	$-2.00081*10^{-41}$

a_9	$-1.58197*10^{-47}$	a_9	$1.52743*10^{-47}$
R-Square(COD)	0.9997	R-Square(COD)	0.9997

Raw data:



7. Crystal data for 2a

Crystal data and structure refinement for cxy0541_0m.

Identification code	cxy0541_0m
Empirical formula	$C_{16}H_{18}O_2S$
Formula weight	274.36
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.712(4)
b/Å	15.280(13)
c/Å	8.280(5)
α/°	90
β/°	104.192(15)
γ/°	90
Volume/Å^3	700.6(9)
Z	2
ρ_{calc}g/cm^3	1.301
μ/mm^{-1}	0.226
F(000)	292.0
Crystal size/mm^3	0.45 × 0.42 × 0.32
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.074 to 55.088
Index ranges	$-7 \le h \le 7$, $-19 \le k \le 19$, $-10 \le l \le 10$
Reflections collected	14818
Independent reflections	3221 [R_{int} = 0.0392, R_{sigma} = 0.0289]
Data/restraints/parameters	3221/1/175
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0246, wR_2 = 0.0619
Final R indexes [all data]	R_1 = 0.0256, wR_2 = 0.0623
Largest diff. peak/hole / e Å^{-3}	0.27/-0.18
Flack parameter	-0.01(2)

Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for cxy0541_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
S1	5765.6(7)	5436.3(3)	5645.1(5)	13.58(12)
O1	5664(3)	6051.7(11)	6947.9(17)	21.5(3)
O2	8086(2)	5082.4(10)	5572.5(17)	20.8(3)
C1	1014(4)	6988.4(14)	-1062(2)	19.5(4)
C2	2271(3)	6649.6(12)	629(2)	14.8(4)
C3	4412(4)	6180.9(12)	859(2)	15.1(4)
C4	5503(3)	5820.6(13)	2398(2)	14.2(4)
C5	4453(3)	5935.9(12)	3719(2)	12.6(3)
C6	3849(3)	4550.6(13)	5876(2)	13.5(4)
C7	3911(3)	3732.6(12)	4821(2)	14.6(4)
C8	3018(3)	3879.1(12)	2965(2)	12.1(3)
C9	4337(4)	3560.4(13)	1887(2)	16.1(4)
C10	3504(4)	3663.5(13)	184(2)	18.5(4)
C11	1348(4)	4096.1(13)	-479(2)	17.4(4)
C12	832(3)	4298.2(12)	2287(2)	14.4(4)
C13	8(4)	4416.3(13)	583(2)	16.9(4)
C14	1286(4)	6782.4(13)	1997(3)	17.1(4)
C15	2357(3)	6429.3(13)	3537(2)	15.6(4)
C16	2408(4)	3014.7(13)	5386(3)	21.1(4)

Anisotropic Displacement Parameters ($Å^2×10^3$) for cxy0541_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
S1	10.60(19)	19.6(2)	10.34(19)	-0.20(17)	2.21(14)	-1.46(19)
O1	23.3(7)	26.2(8)	14.8(6)	-6.2(6)	4.4(6)	-7.1(6)
O2	10.6(6)	33.6(8)	17.7(7)	6.4(6)	2.4(5)	2.8(6)
C1	18.5(10)	19.8(10)	17.9(10)	5.0(8)	0.5(8)	0.0(8)
C2	16.3(9)	10.1(8)	17.1(9)	1.1(7)	2.3(7)	-3.2(7)
C3	17.0(9)	15.1(9)	14.6(9)	0.1(7)	6.3(7)	-0.3(7)
C4	11.0(8)	15.9(8)	16.4(8)	0.6(7)	4.8(7)	2.0(7)
C5	11.7(8)	14.0(9)	11.7(8)	0.9(7)	1.9(6)	-0.8(7)
C6	12.7(8)	18.7(9)	9.7(8)	0.9(7)	3.7(7)	-1.3(7)
C7	14.9(9)	16.1(9)	12.9(8)	1.6(7)	3.5(7)	3.9(7)
C8	12.8(8)	12.3(8)	11.2(8)	-0.8(6)	2.8(7)	-1.2(7)
C9	14.9(9)	15.8(9)	18.5(9)	-0.1(7)	6.1(7)	1.9(7)

C10	21.8(10)	19.1(10)	17.1(9)	-3.1(7)	9.9(8)	-0.6(8)
C11	23.0(10)	19.1(9)	10.1(9)	-0.8(7)	4.0(8)	-3.6(8)
C12	14.0(8)	15.2(9)	15.1(9)	-1.9(7)	5.5(7)	0.9(7)
C13	14.9(8)	17.6(9)	16.8(9)	1.4(7)	0.9(7)	0.2(7)
C14	13.8(9)	14.4(9)	24.2(10)	-0.1(8)	6.5(8)	2.6(7)
C15	14.0(9)	16.1(9)	18.4(9)	-2.7(7)	7.3(7)	0.5(7)
C16	30.3(11)	15.7(9)	18.0(9)	3.5(7)	7.3(8)	-1.1(8)

Bond Lengths for cxy0541_0m.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
S1	O1	1.4429(17)	C6	C7	1.530(3)
S1	O2	1.4463(17)	C7	C8	1.513(3)
S1	C5	1.761(2)	C7	C16	1.535(3)
S1	C6	1.780(2)	C8	C9	1.389(3)
C1	C2	1.501(3)	C8	C12	1.393(3)
C2	C3	1.389(3)	C9	C10	1.383(3)
C2	C14	1.397(3)	C10	C11	1.387(3)
C3	C4	1.387(3)	C11	C13	1.389(3)
C4	C5	1.382(3)	C12	C13	1.386(3)
C5	C15	1.391(3)	C14	C15	1.382(3)

Bond Angles for cxy0541_0m.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O1	S1	O2	118.69(9)	C7	C6	S1	117.29(13)
O1	S1	C5	107.95(11)	C6	C7	C16	108.47(16)
O1	S1	C6	106.04(10)	C8	C7	C6	114.20(16)
O2	S1	C5	108.39(9)	C8	C7	C16	109.91(16)
O2	S1	C6	108.32(11)	C9	C8	C7	119.97(17)
C5	S1	C6	106.88(9)	C9	C8	C12	118.45(18)
C3	C2	C1	120.62(18)	C12	C8	C7	121.53(16)
C3	C2	C14	118.65(18)	C10	C9	C8	120.65(19)
C14	C2	C1	120.72(18)	C9	C10	C11	120.54(18)
C4	C3	C2	120.84(18)	C10	C11	C13	119.42(18)
C5	C4	C3	119.46(18)	C13	C12	C8	121.15(17)

C4	C5	S1	119.38(15)	C12	C13	C11	119.77(19)
C4	C5	C15	120.80(17)	C15	C14	C2	121.07(18)
C15	C5	S1	119.81(14)	C14	C15	C5	119.10(17)

Torsion Angles for cxy0541_0m.

A	**B**	**C**	**D**	**Angle**/°	**A**	**B**	**C**	**D**	**Angle**/°
S1	C5	C15	C14	-176.94(15)	C5	S1	C6	C7	74.20(16)
S1	C6	C7	C8	-64.7(2)	C6	S1	C5	C4	-106.97(17)
S1	C6	C7	C16	172.36(14)	C6	S1	C5	C15	72.02(17)
O1	S1	C5	C4	139.33(15)	C6	C7	C8	C9	133.12(18)
O1	S1	C5	C15	-41.68(17)	C6	C7	C8	C12	-49.6(2)
O1	S1	C6	C7	-170.82(13)	C7	C8	C9	C10	177.83(18)
O2	S1	C5	C4	9.57(19)	C7	C8	C12	C13	-178.88(18)
O2	S1	C5	C15	-171.44(15)	C8	C9	C10	C11	0.7(3)
O2	S1	C6	C7	-42.40(16)	C8	C12	C13	C11	1.4(3)
C1	C2	C3	C4	-176.04(18)	C9	C8	C12	C13	-1.5(3)
C1	C2	C14	C15	176.21(18)	C9	C10	C11	C13	-0.9(3)
C2	C3	C4	C5	-0.5(3)	C10	C11	C13	C12	-0.2(3)
C2	C14	C15	C5	0.1(3)	C12	C8	C9	C10	0.5(3)
C3	C2	C14	C15	-2.4(3)	C14	C2	C3	C4	2.6(3)
C3	C4	C5	S1	177.12(14)	C16	C7	C8	C9	-104.7(2)
C3	C4	C5	C15	-1.9(3)	C16	C7	C8	C12	72.6(2)
C4	C5	C15	C14	2.0(3)					

Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for cxy0541_0m.

Atom	***x***	***y***	***z***	**U(eq)**
H1A	-535.08	6711.57	-1425.01	29
H1B	1971.27	6860.49	-1837.51	29
H1C	801.36	7609.97	-1005.99	29
H3	5122.18	6107.66	-29.04	18
H4	6929.47	5504.03	2538.75	17
H6A	4260.86	4376.81	7038.61	16
H6B	2200.51	4765.44	5620.04	16

H7	5587.11	3529.33	5045.26	18
H9	5795.41	3274.98	2316.53	19
H10	4397.25	3440.95	-523.41	22
H11	804.57	4170.98	-1624.9	21
H12	-89.67	4502.44	2991.06	17
H13	-1437.84	4709	151.21	20
H14	-113.56	7113.77	1868.19	21
H15	1686.13	6520.24	4439.27	19
H16A	787.3	3220.79	5271.49	32
H16B	3112.72	2871.15	6530.67	32
H16C	2382.34	2503.24	4708.55	32

Experimental

Single crystals of $C_{16}H_{18}O_2S$ [cxy0541_0m] were []. A suitable crystal was selected and [] on a BrukerD8 venture microsource diffractometer. The crystal was kept at 100 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the XL [3] refinement package using Least Squares minimisation.

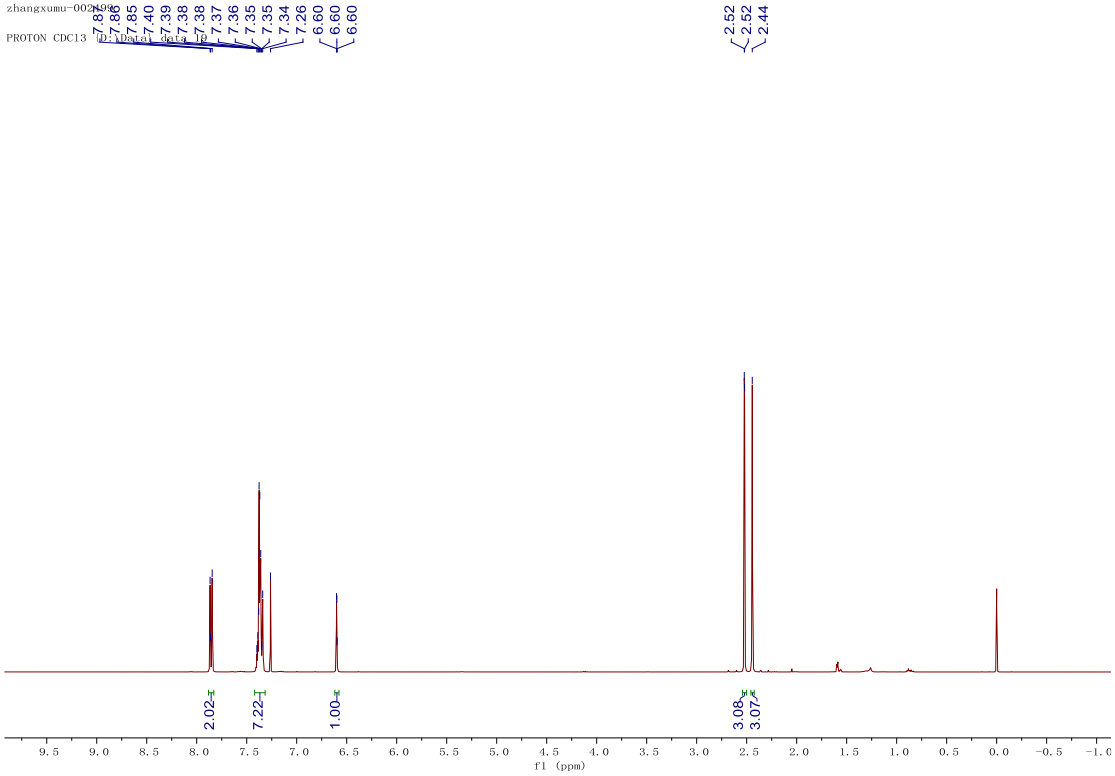
1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

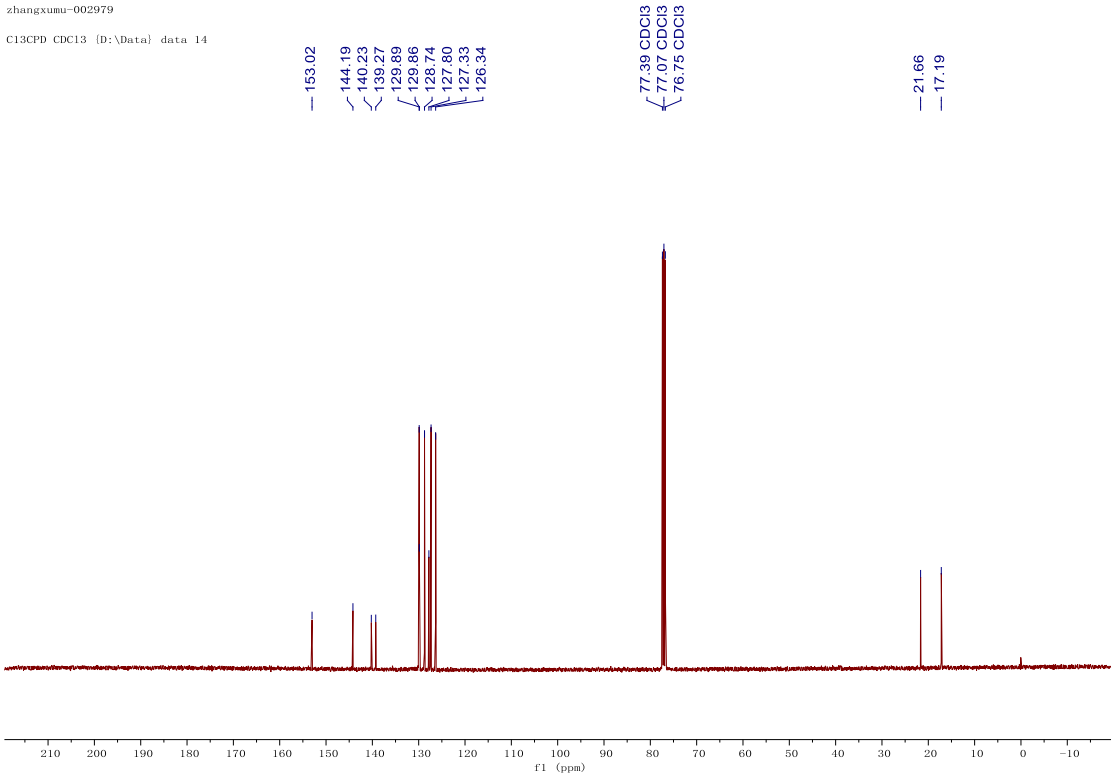
Crystal structure determination

Crystal Data for $C_{16}H_{18}O_2S$ (M =274.36 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 5.712(4) Å, b = 15.280(13) Å, c = 8.280(5) Å, β = 104.192(15)°, V = 700.6(9) Å^3, Z = 2, T = 100 K, μ(MoKα) = 0.226 mm^{-1}, *Dcalc* = 1.301 g/cm^3, 14818 reflections measured ($5.074° \leq 2\Theta \leq 55.088°$), 3221 unique ($R_{int}$ = 0.0392, R_{sigma} = 0.0289) which were used in all calculations. The final R_1 was 0.0246 ($I > 2\sigma(I)$) and wR_2 was 0.0623 (all data).

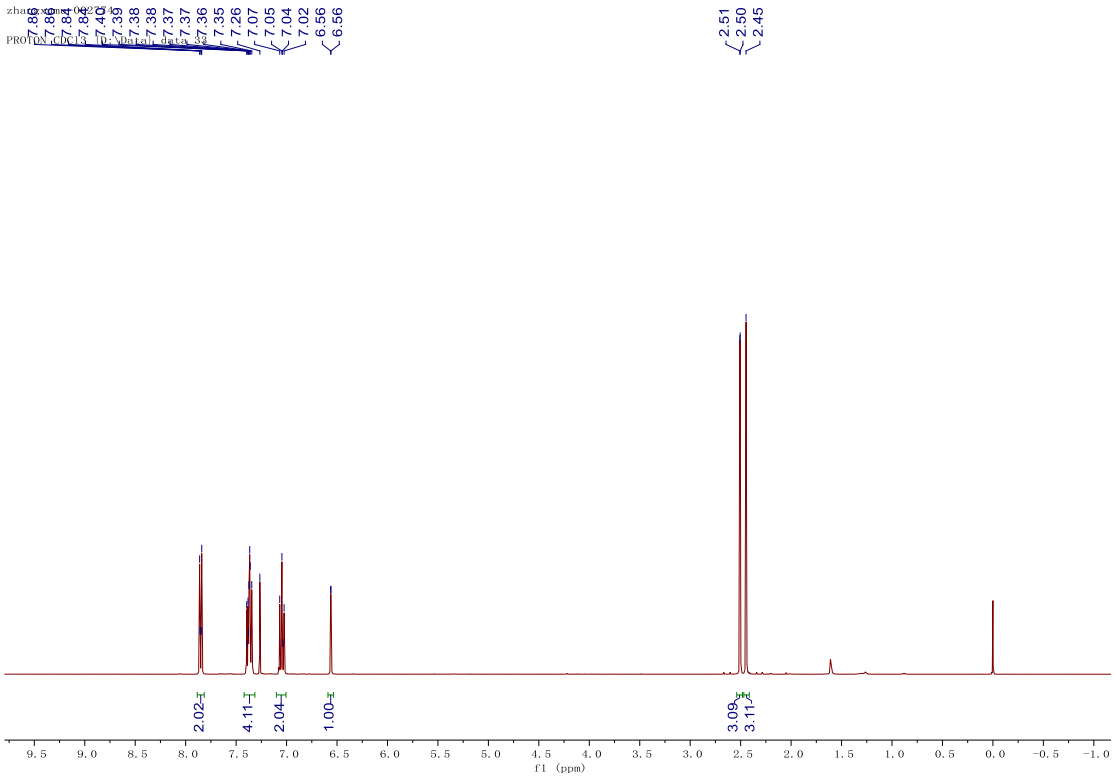
8. NMR spectra

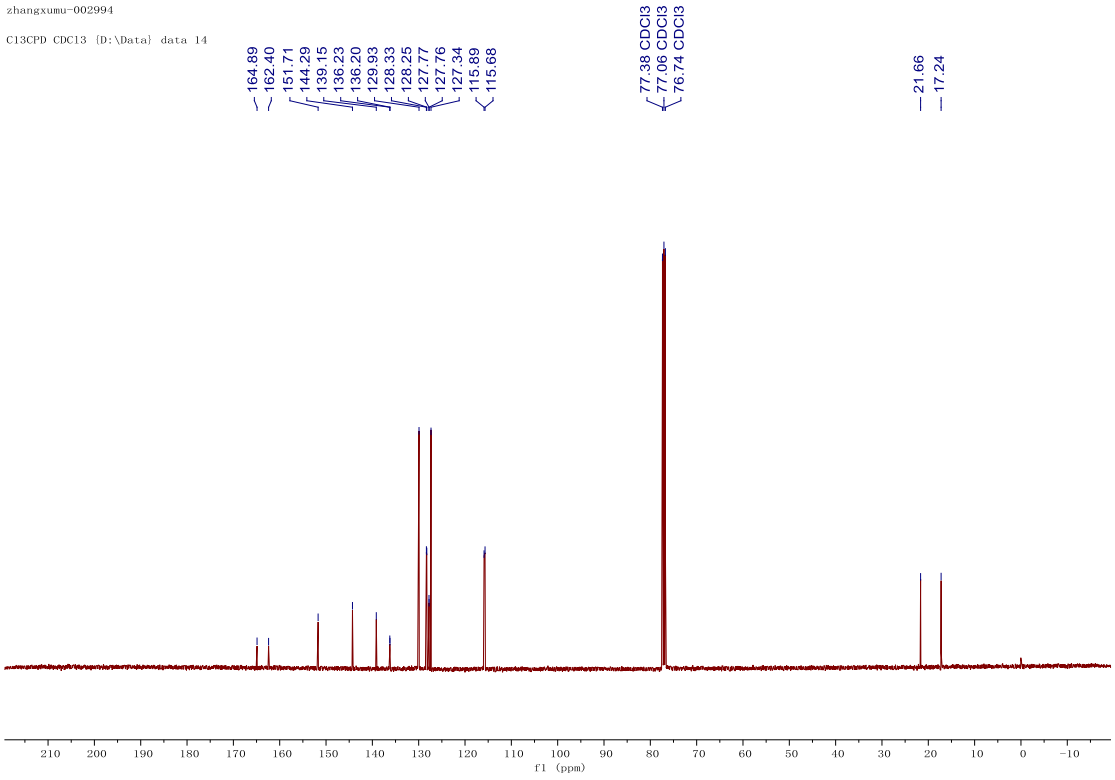
(E)-1-methyl-4-((2-phenylprop-1-en-1-yl)sulfonyl)benzene (**1a**)

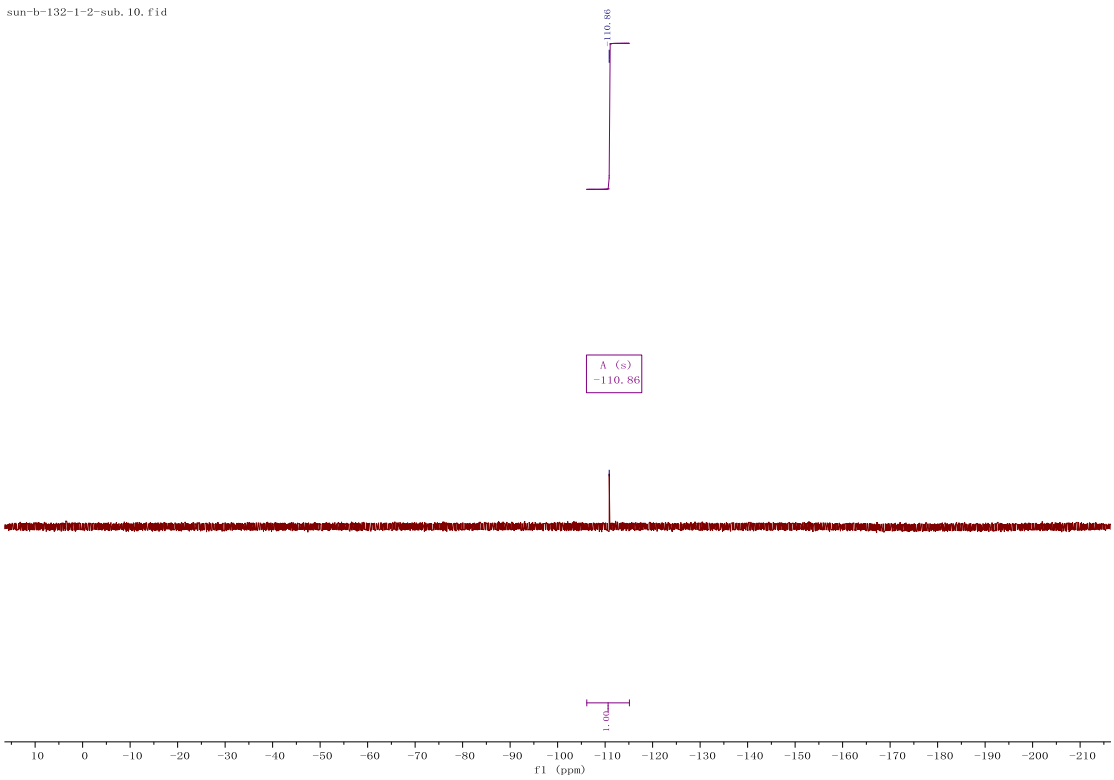




(E)-1-fluoro-4-(1-tosylprop-1-en-2-yl)benzene (**1b**)



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1.00
10
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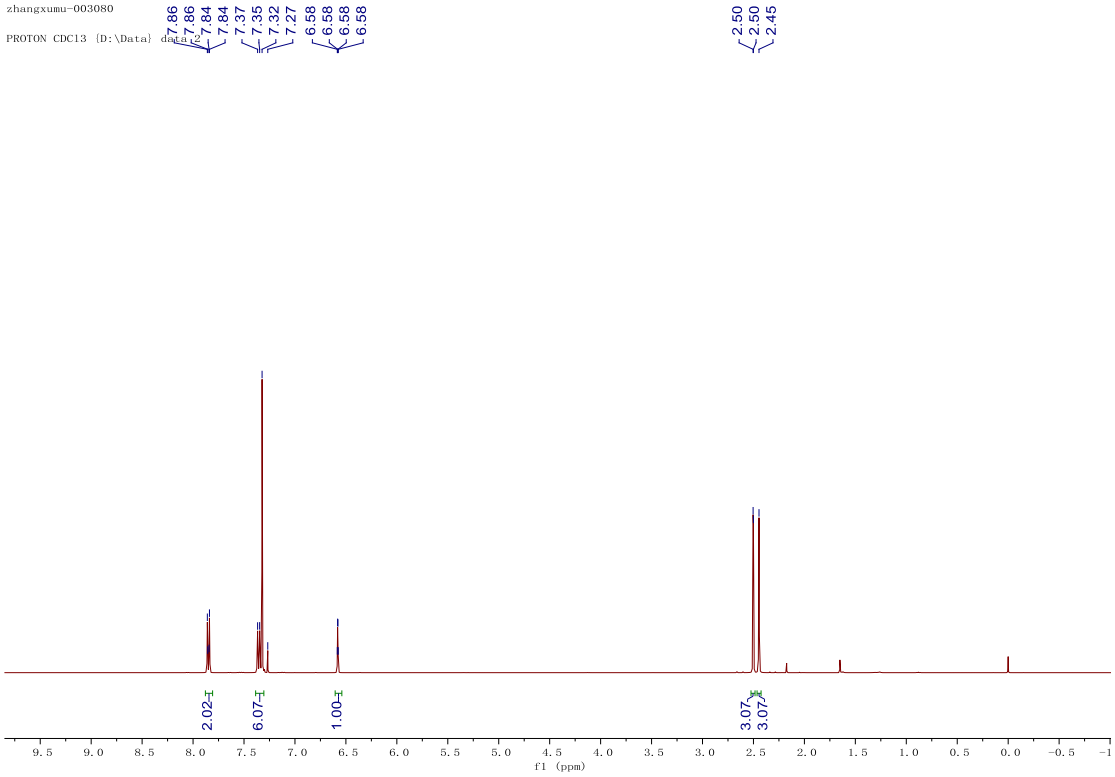
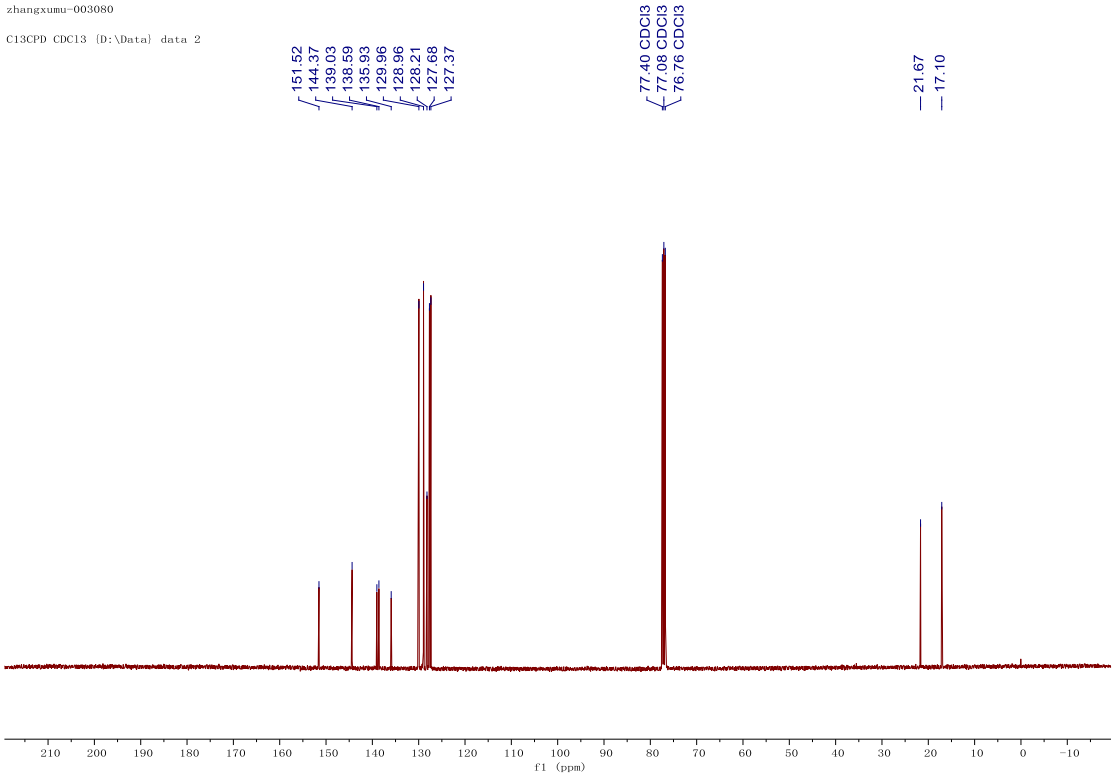
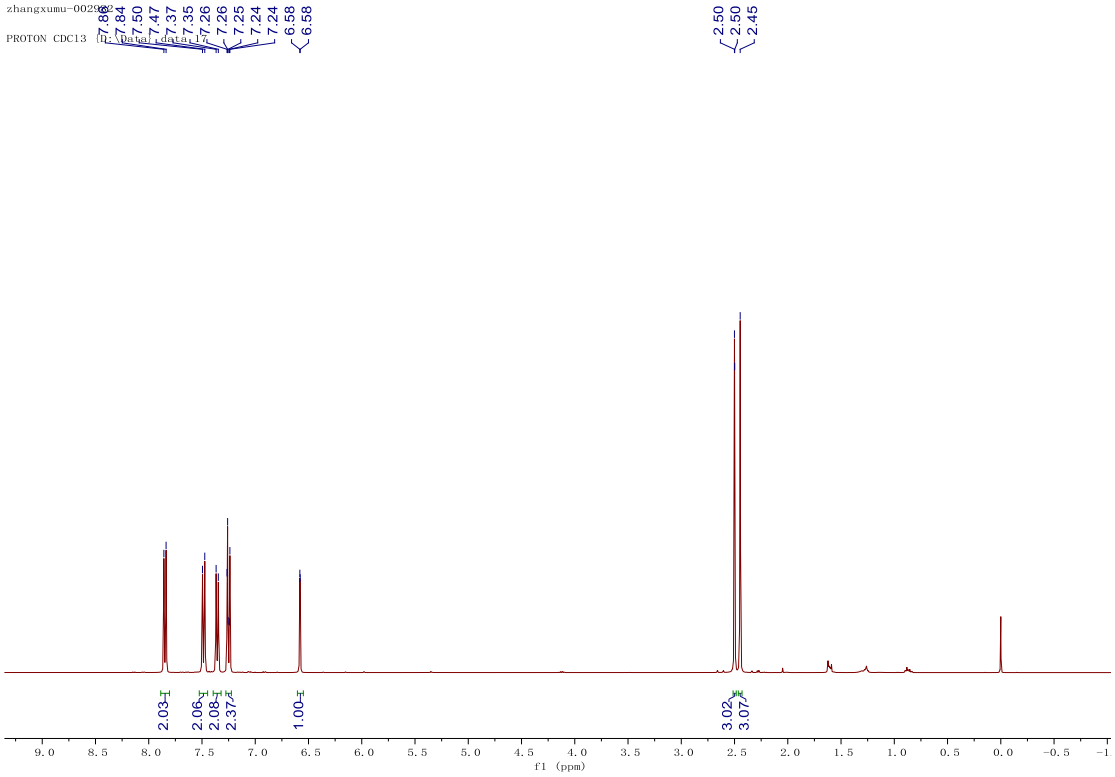
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

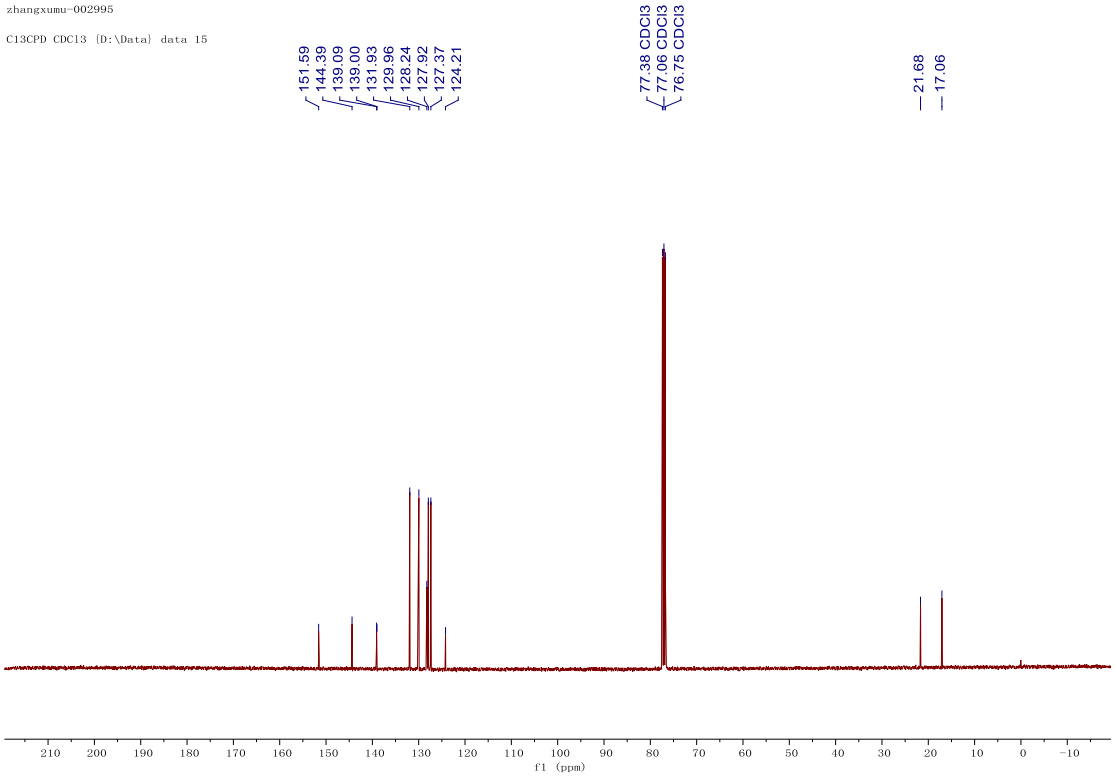
(E)-1-chloro-4-(1-tosylprop-1-en-2-yl)benzene (**1c**)



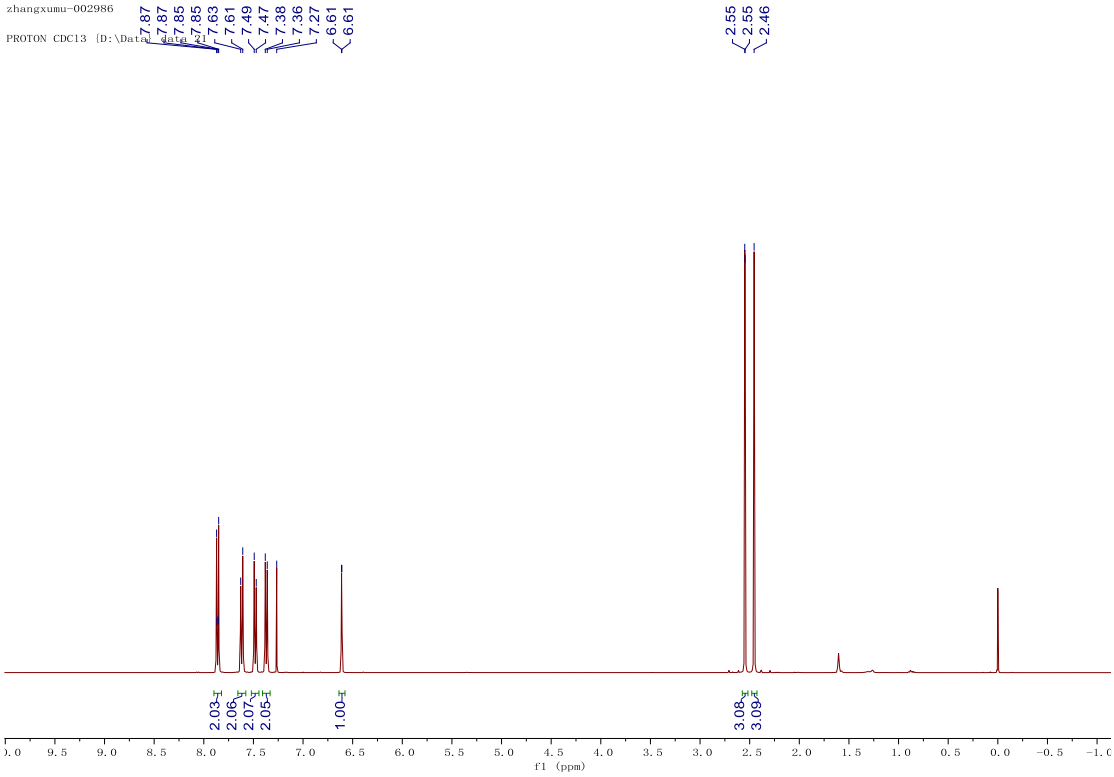


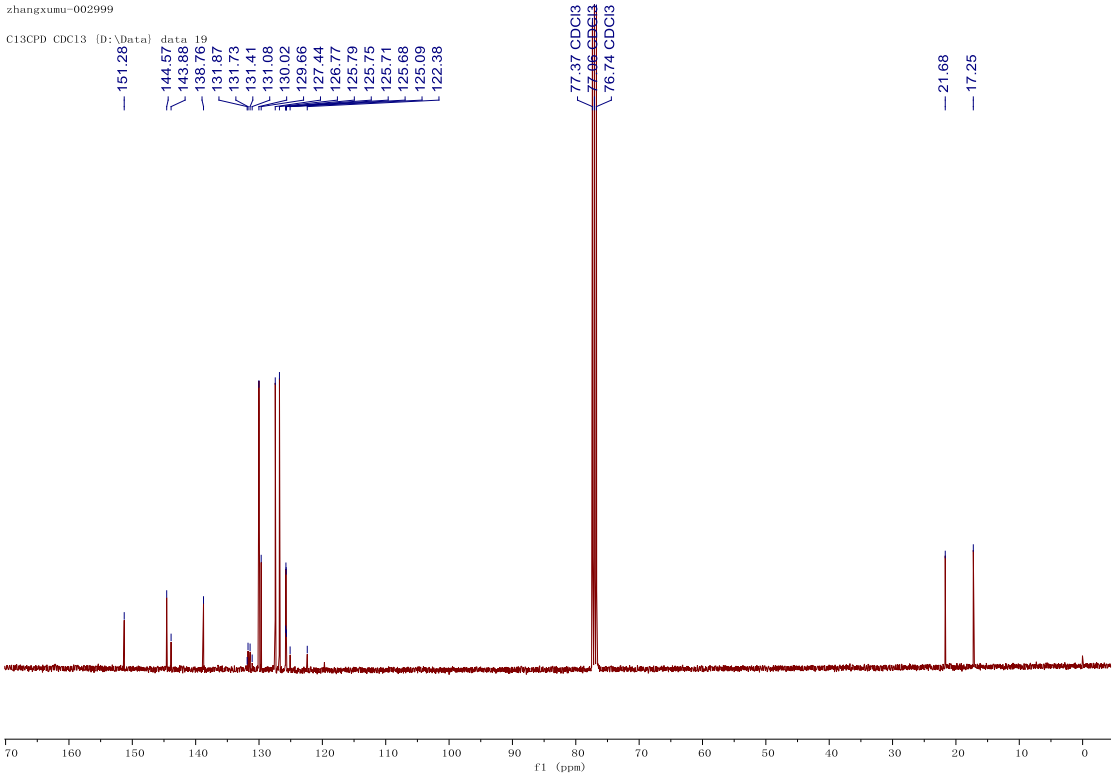
(E)-1-bromo-4-(1-tosylprop-1-en-2-yl)benzene (**1d**)

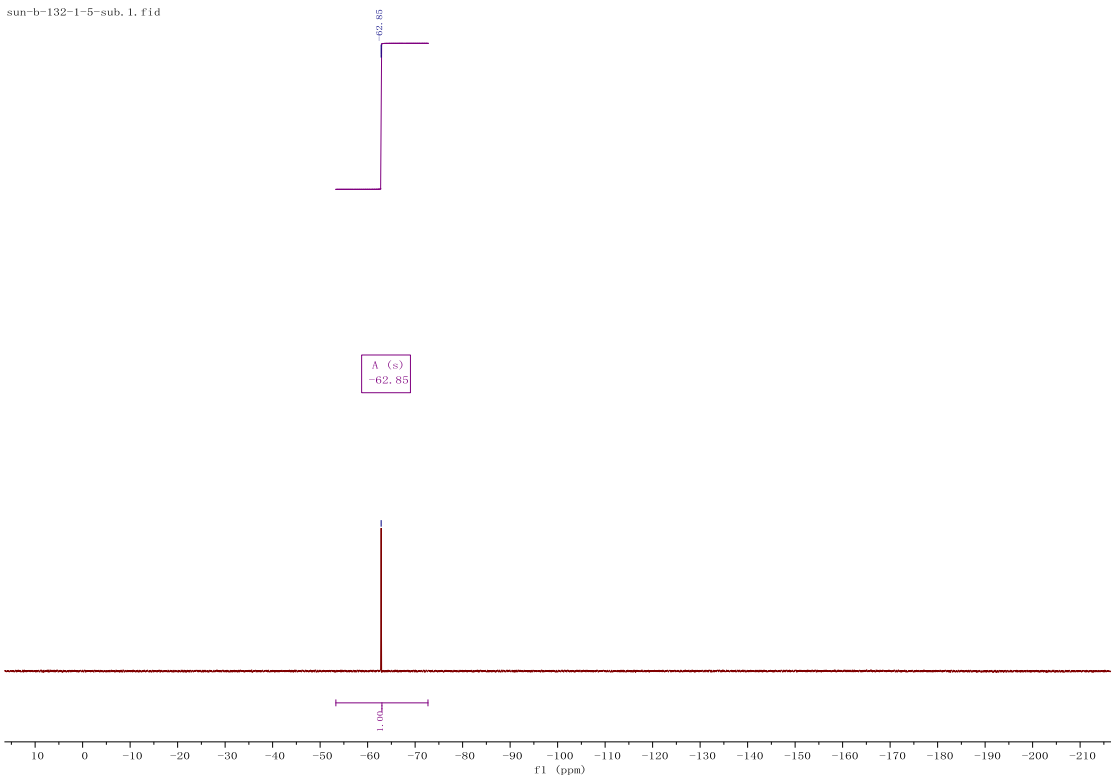




(E)-1-methyl-4-((2-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)sulfonyl)benzene (**1e**)



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-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
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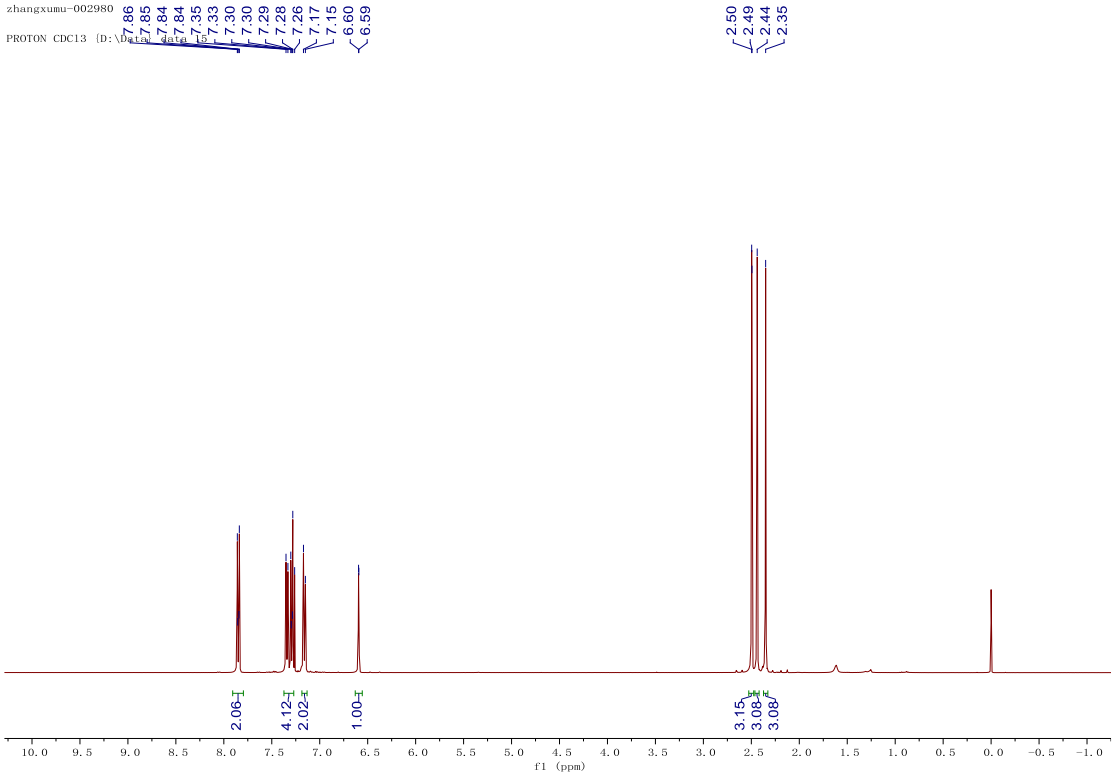
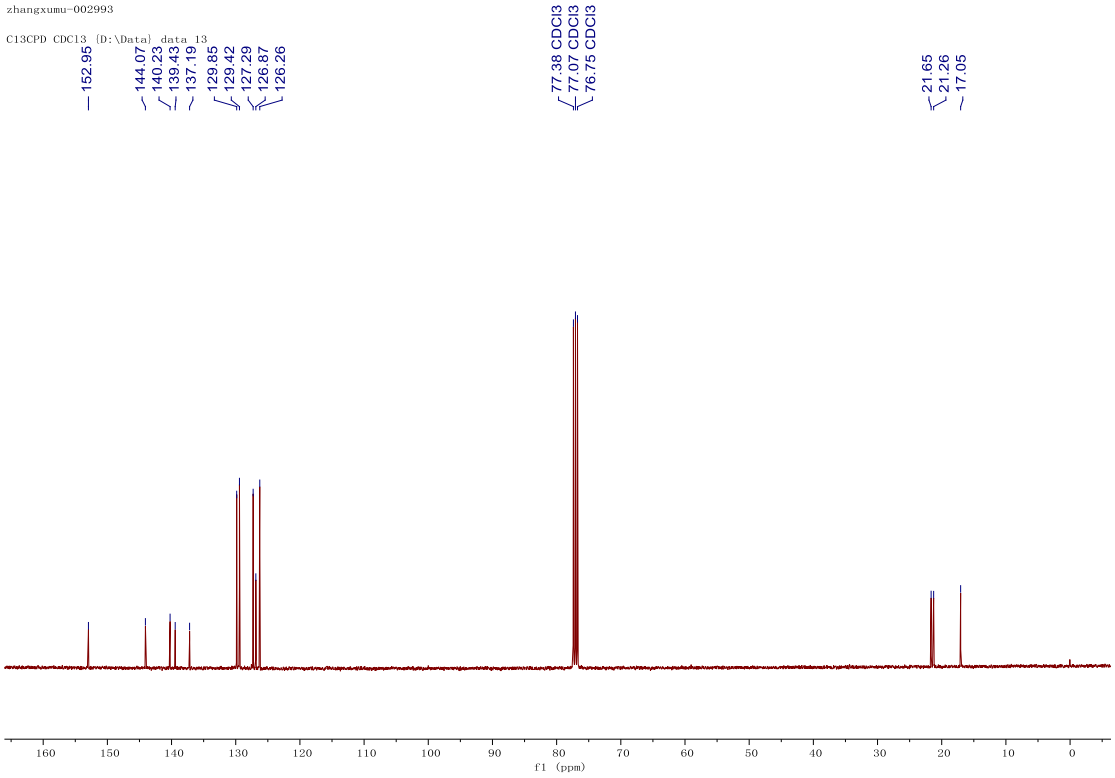
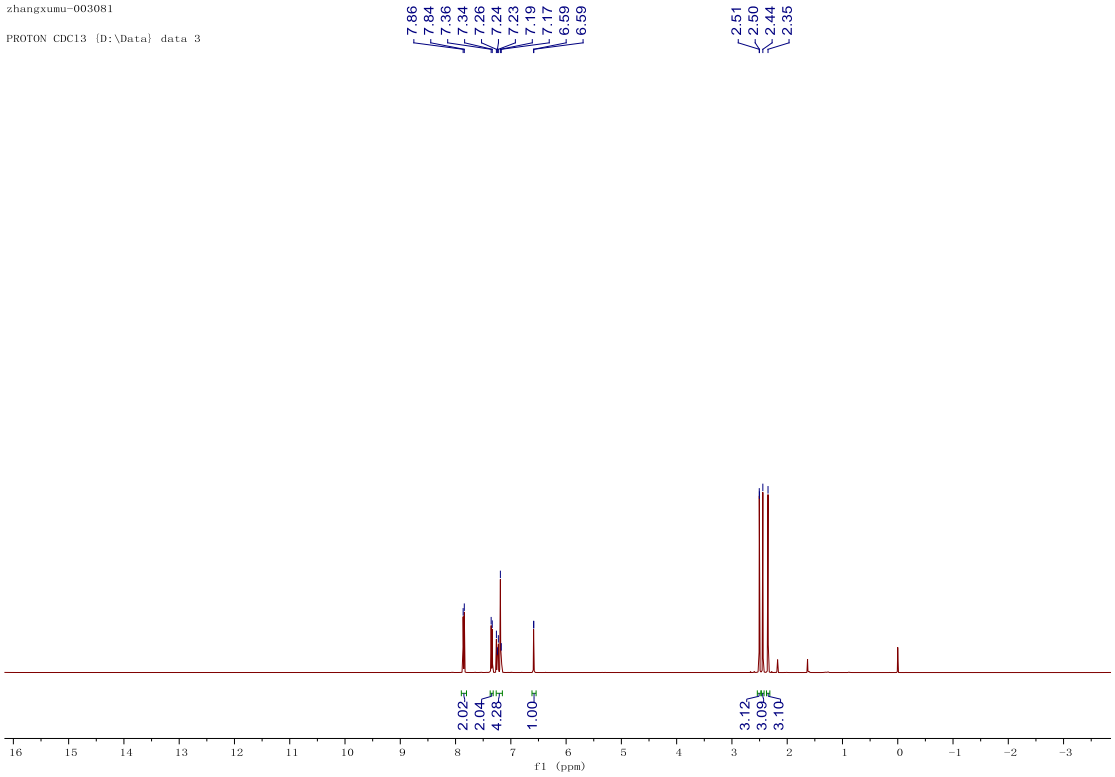
-210
f1 (ppm)

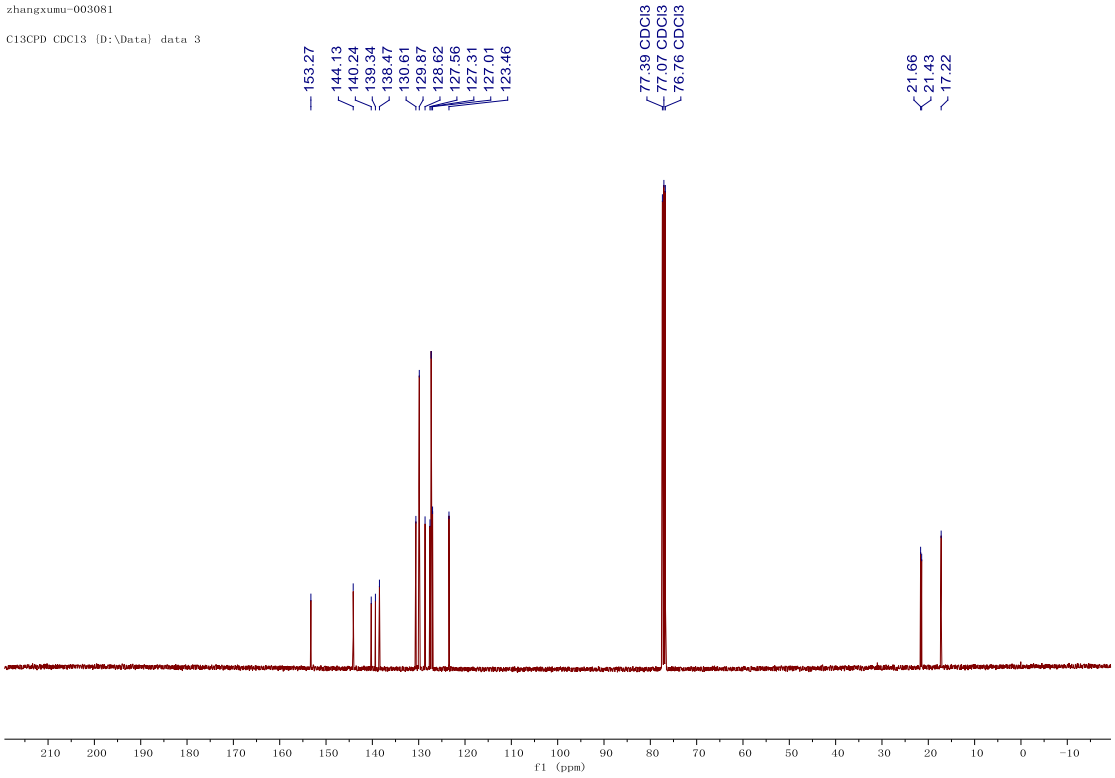
(E)-1-methyl-4-((2-(p-tolyl)prop-1-en-1-yl)sulfonyl)benzene (**1f**)



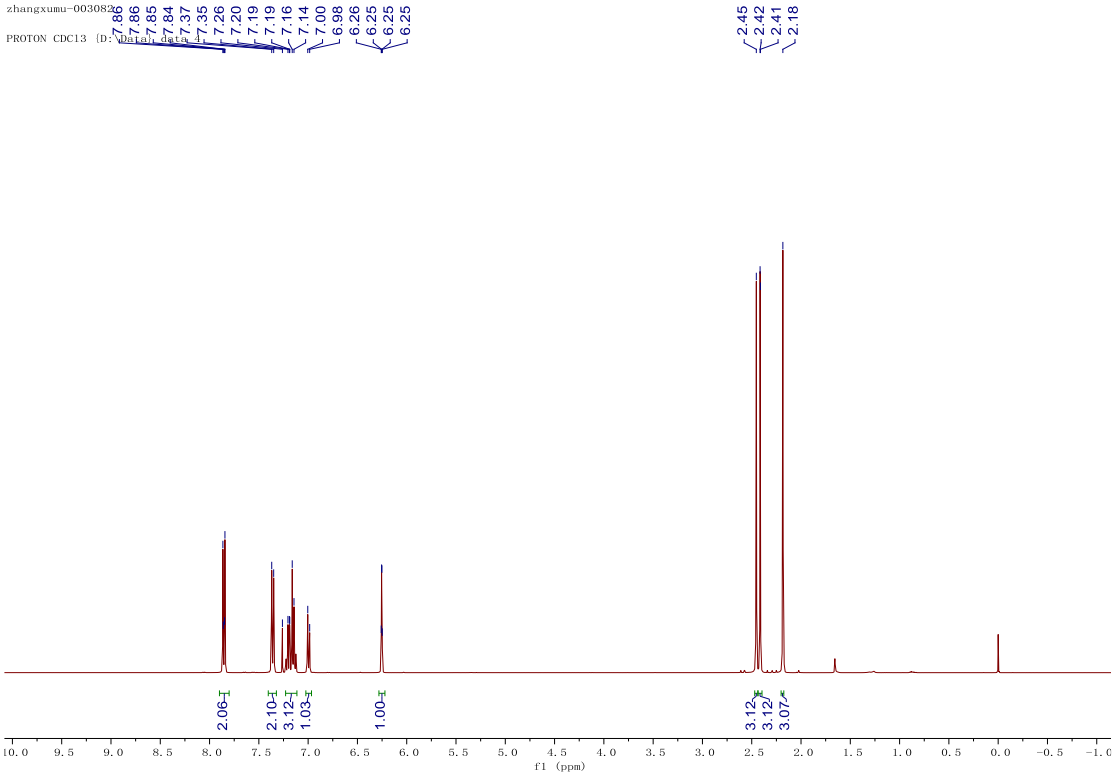


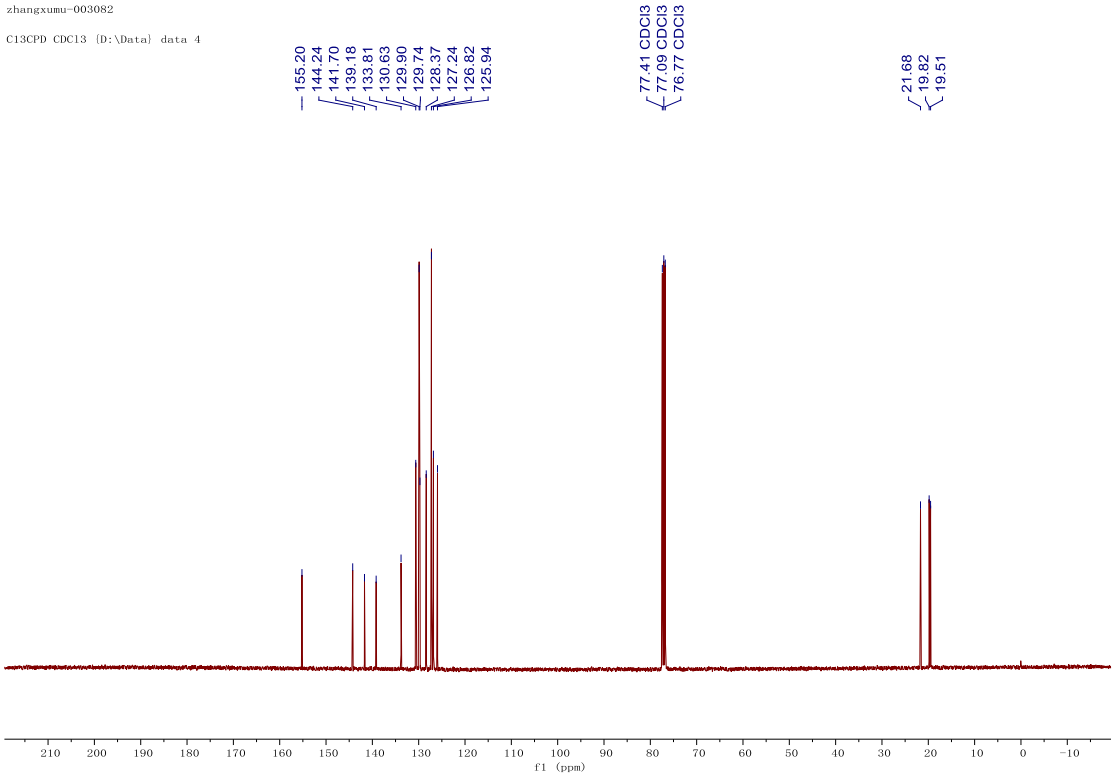
(E)-1-methyl-3-(1-tosylprop-1-en-2-yl)benzene (**1g**)



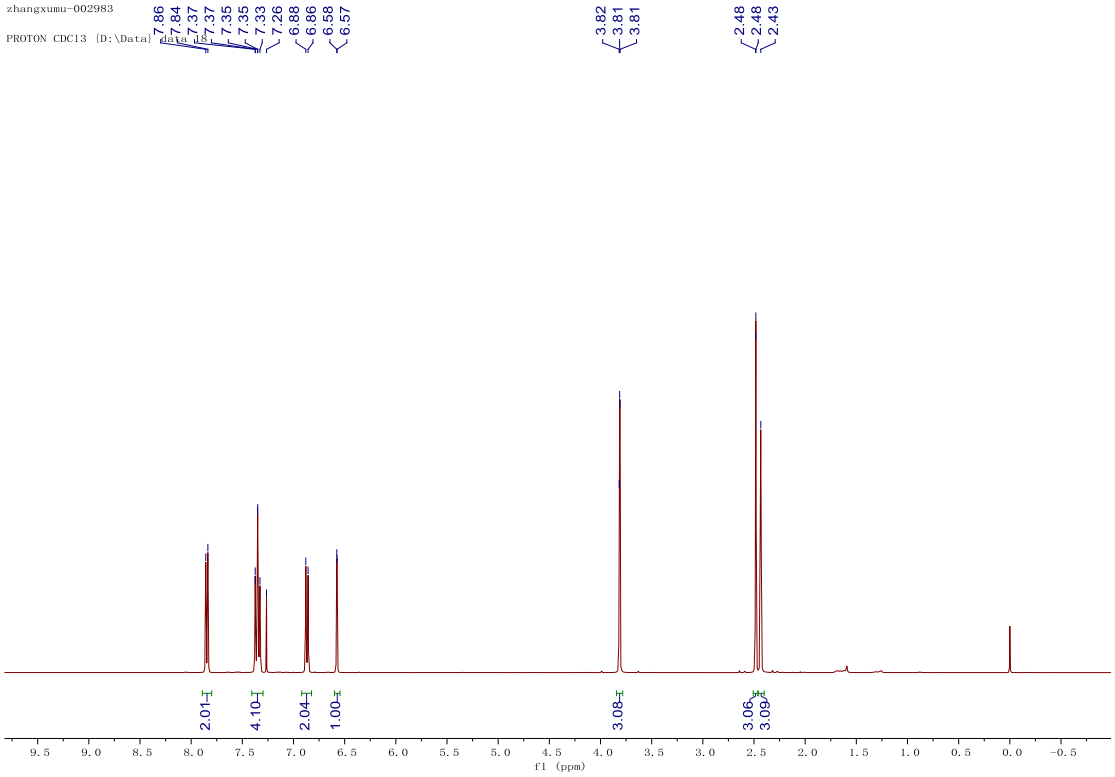


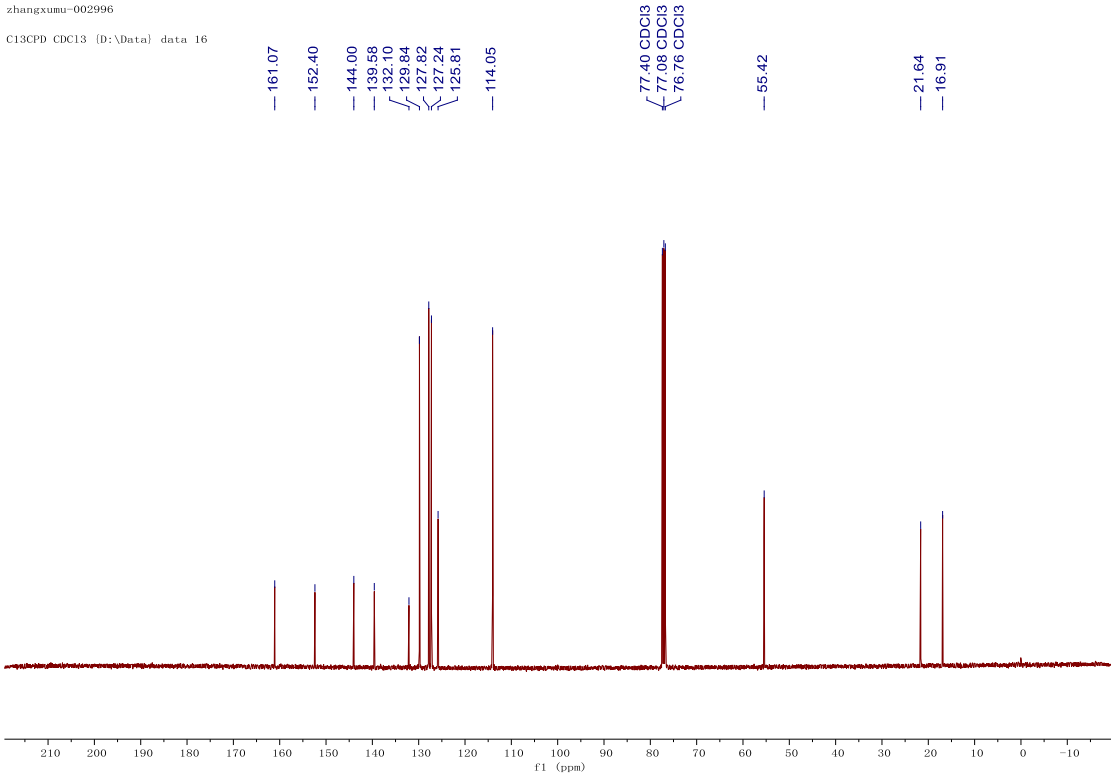
(E)-1-methyl-2-(1-tosylprop-1-en-2-yl)benzene (**1h**)



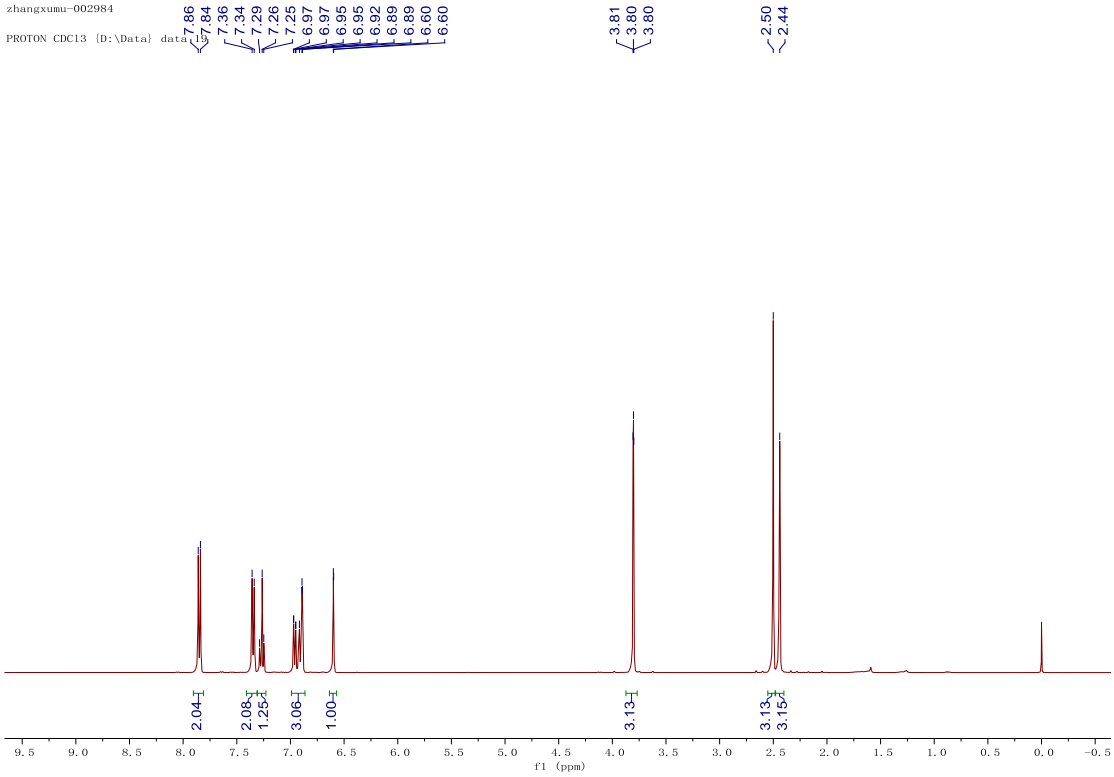


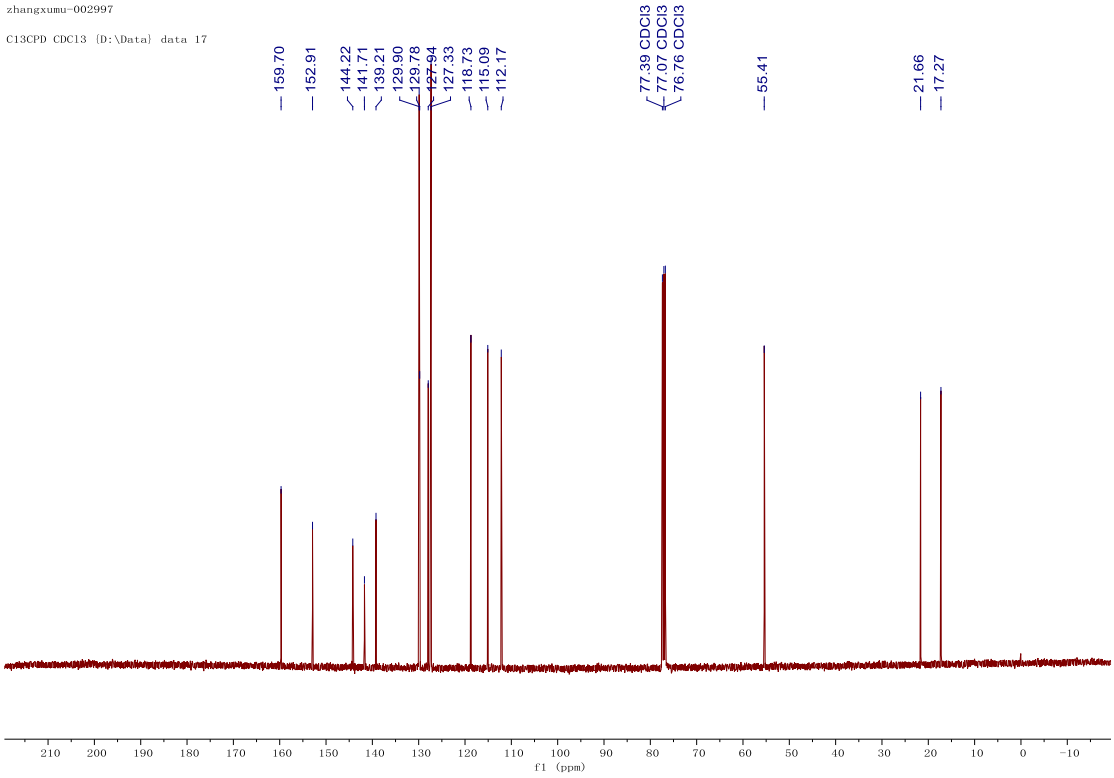
(E)-1-methoxy-4-(1-tosylprop-1-en-2-yl)benzene (**1i**)



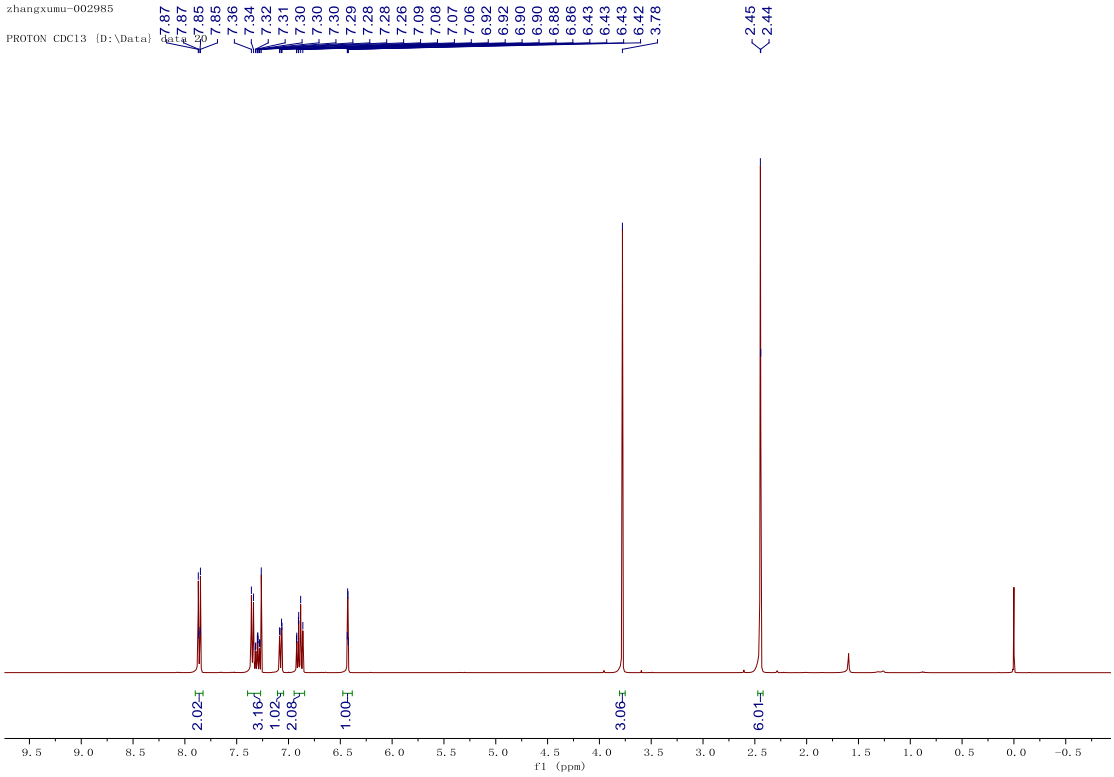


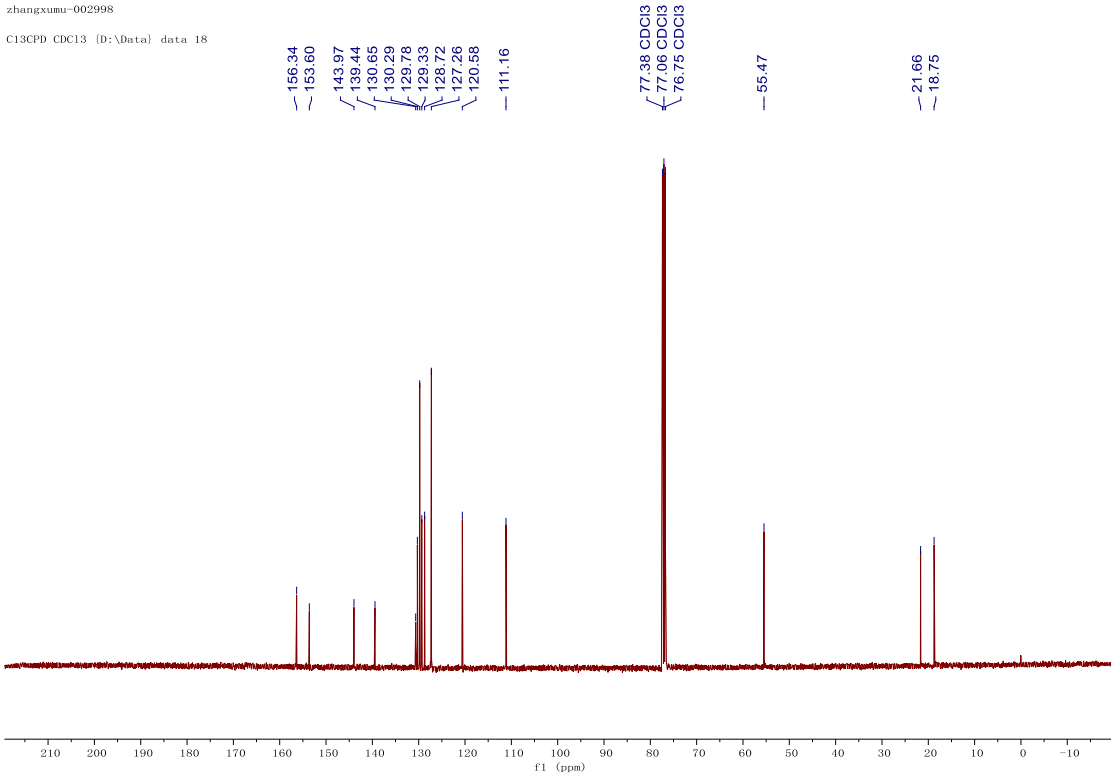
(E)-1-methoxy-3-(1-tosylprop-1-en-2-yl)benzene (**1j**)



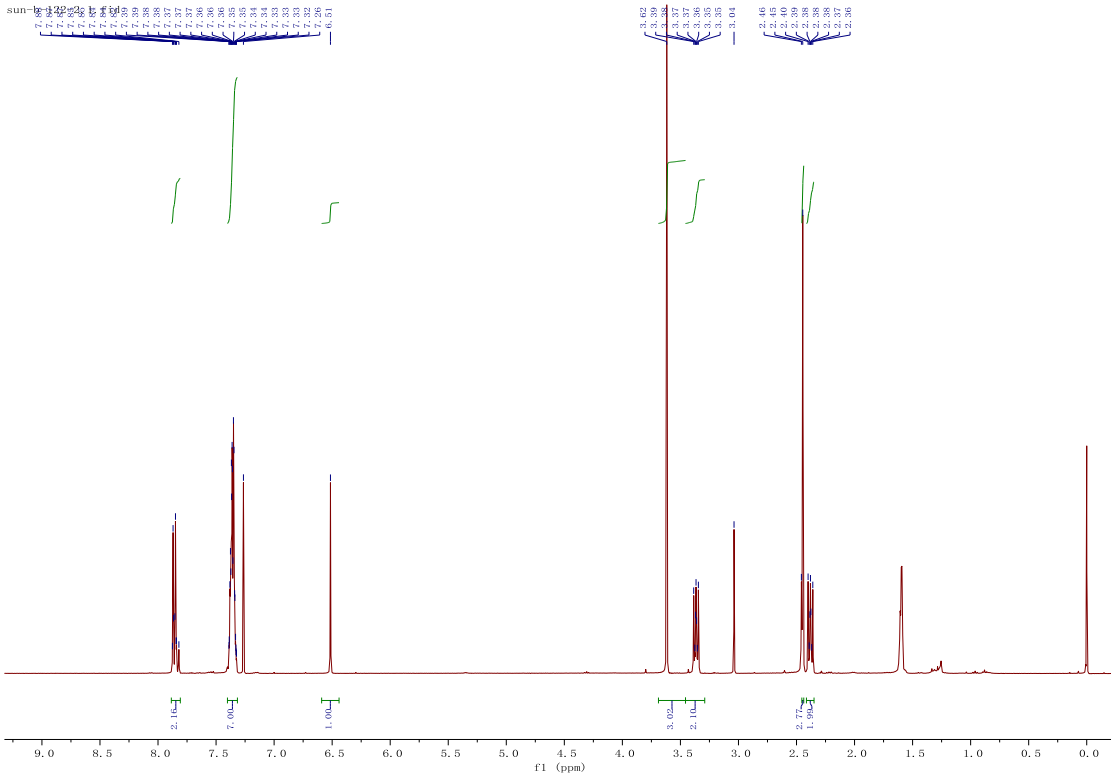


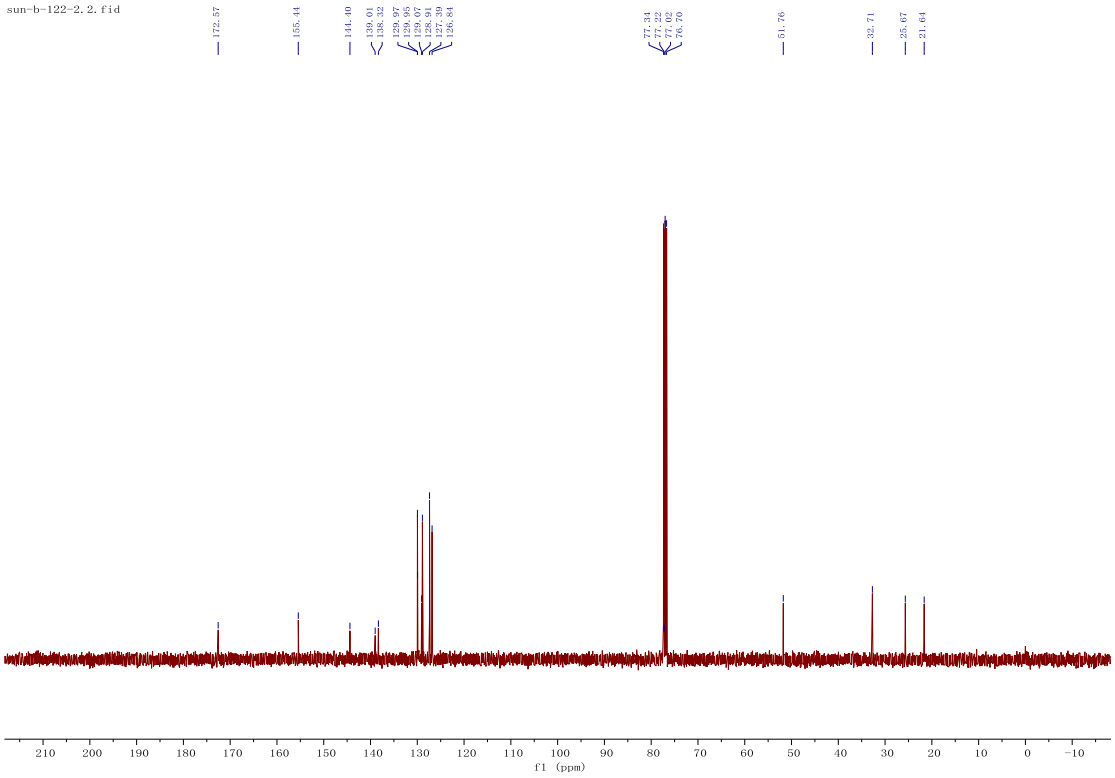
(E)-1-methoxy-2-(1-tosylprop-1-en-2-yl)benzene (**1k**)



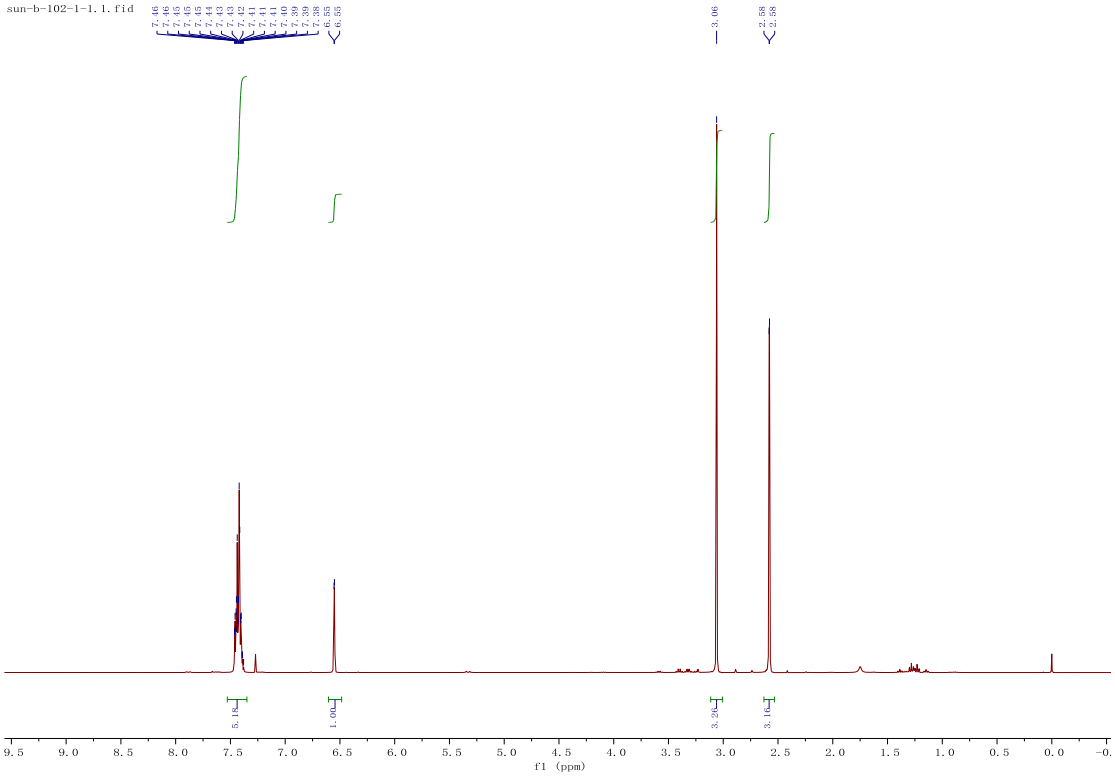


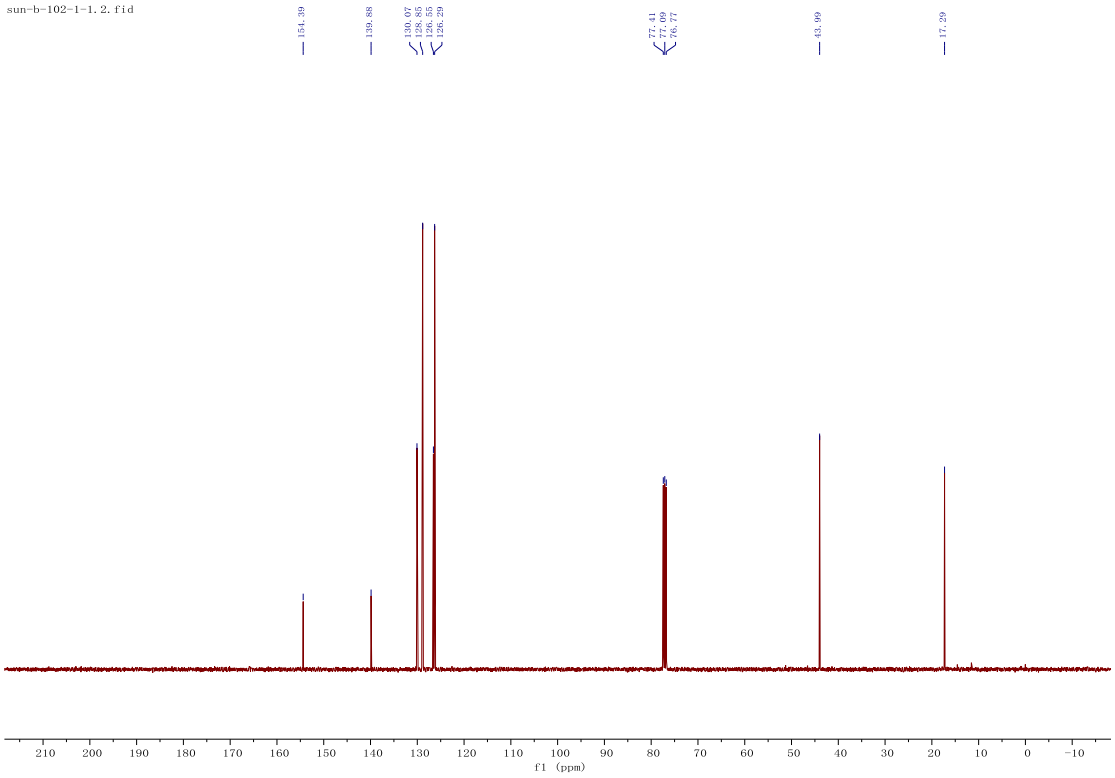
methyl (E)-4-phenyl-5-tosylpent-4-enoate (**1l**)



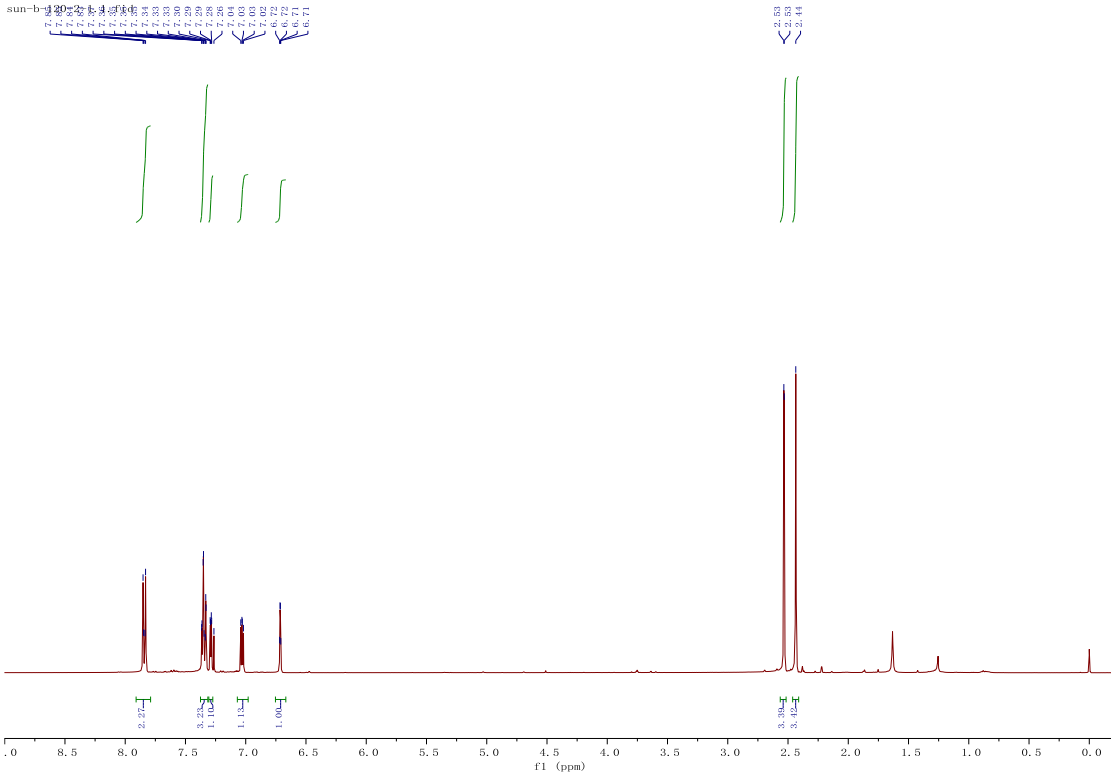


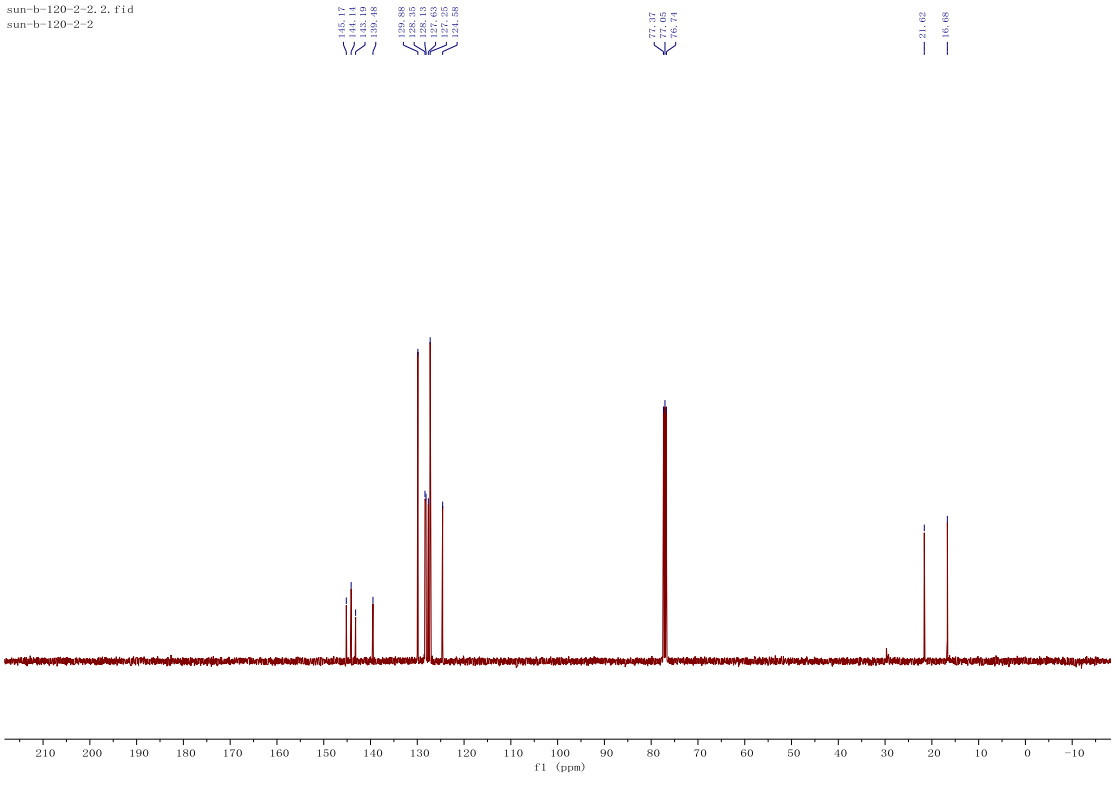
(E)-(1-(methylsulfonyl)prop-1-en-2-yl)benzene (**1m**)



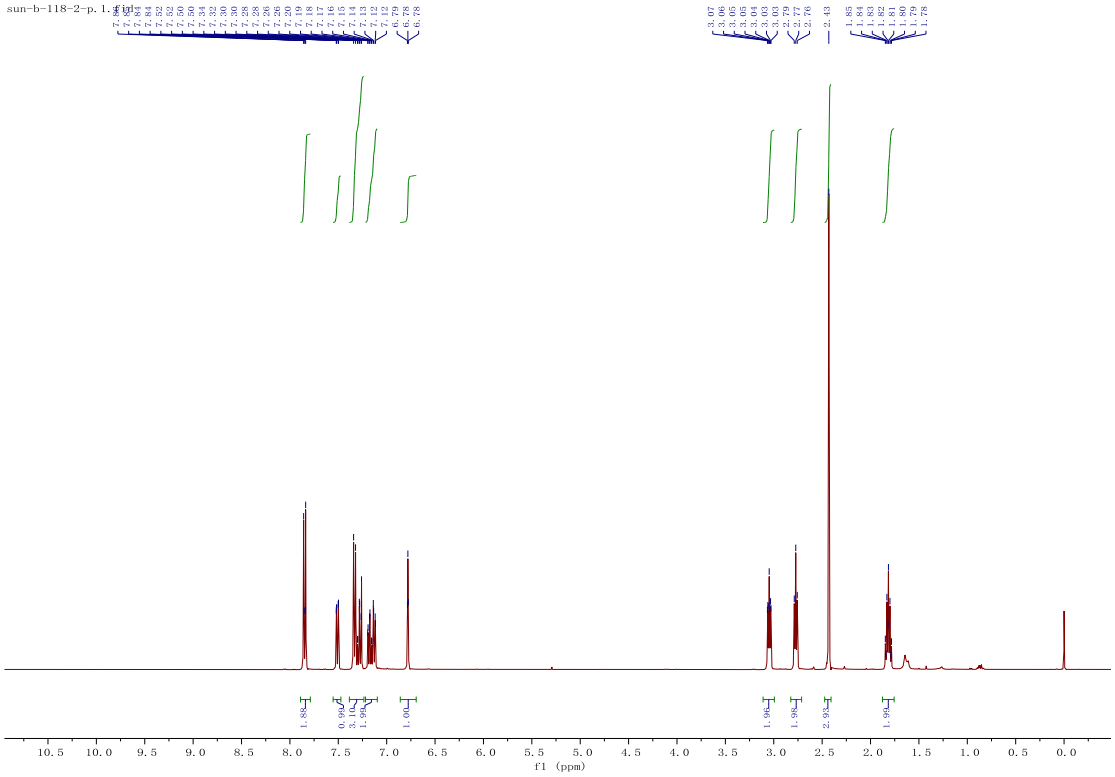


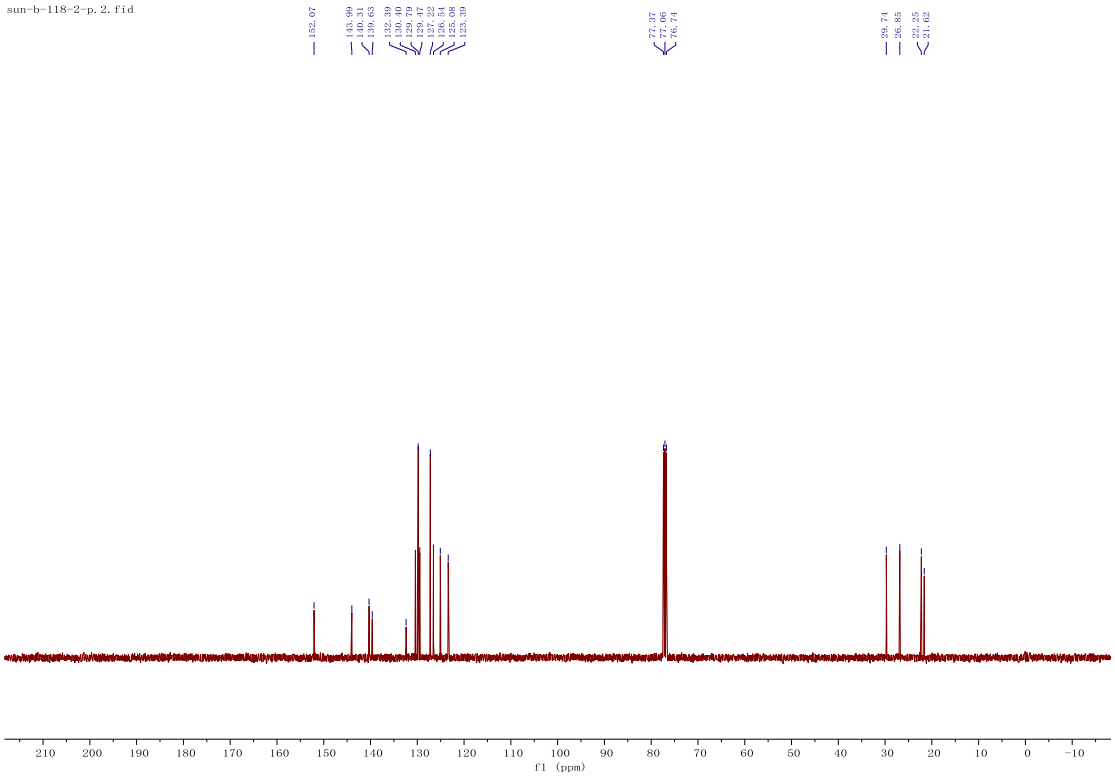
(E)-2-(1-tosylprop-1-en-2-yl)thiophene (**1n**)



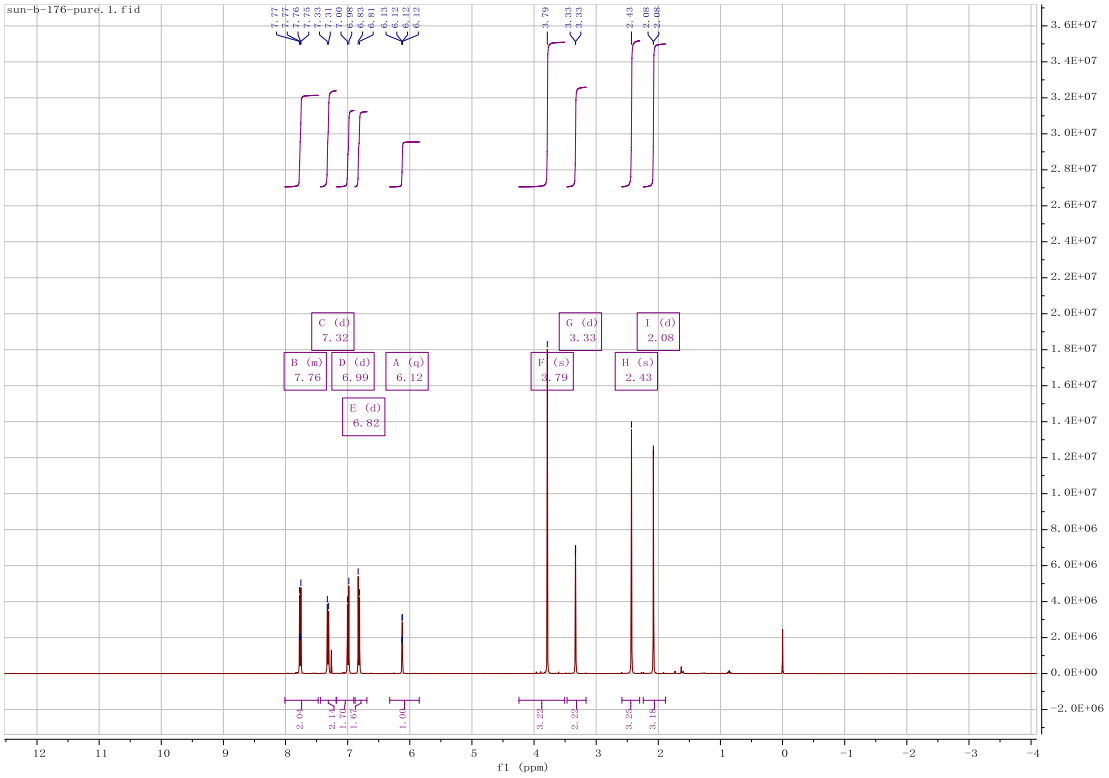


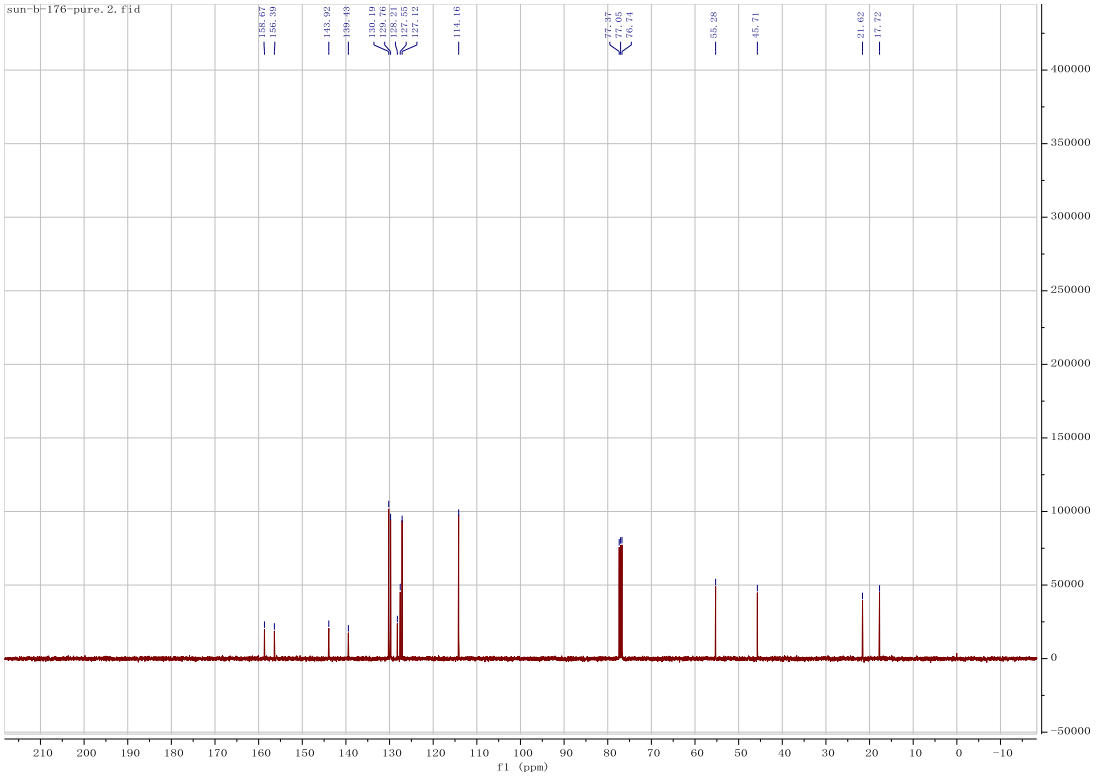
(E)-1-(tosylmethylene)-1,2,3,4-tetrahydronaphthalene (**1o**)



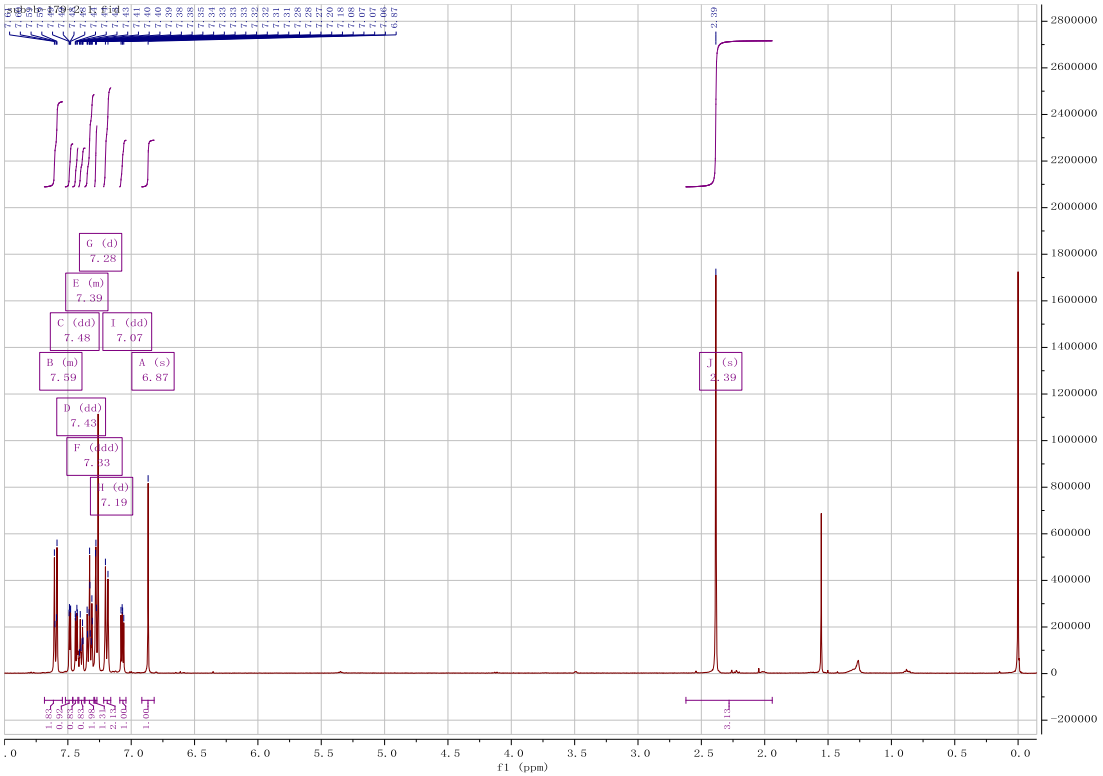


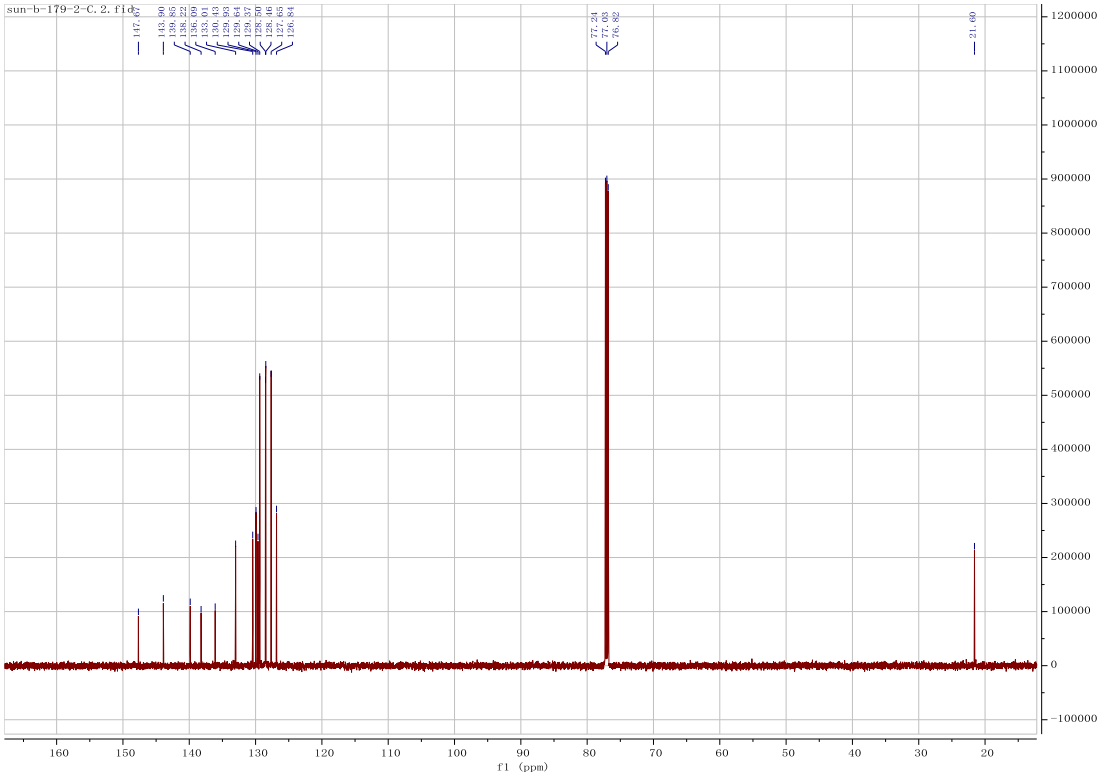
(E)-1-methoxy-4-(2-methyl-3-tosylallyl)benzene(**1p**)



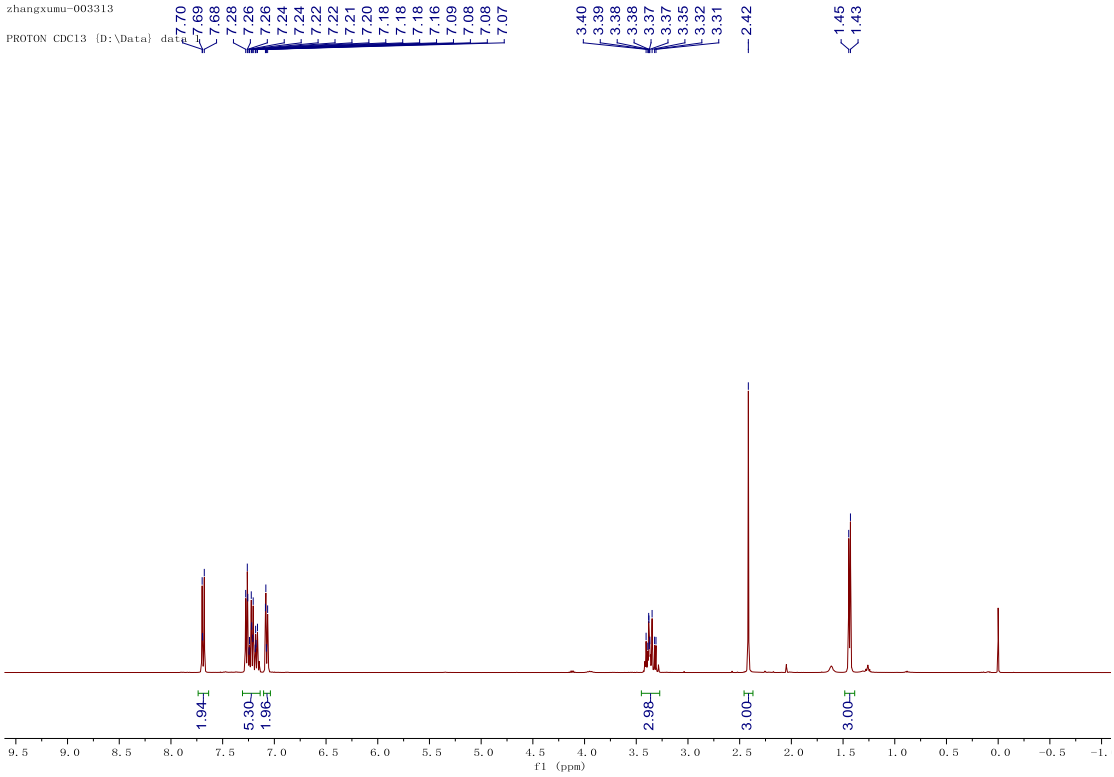


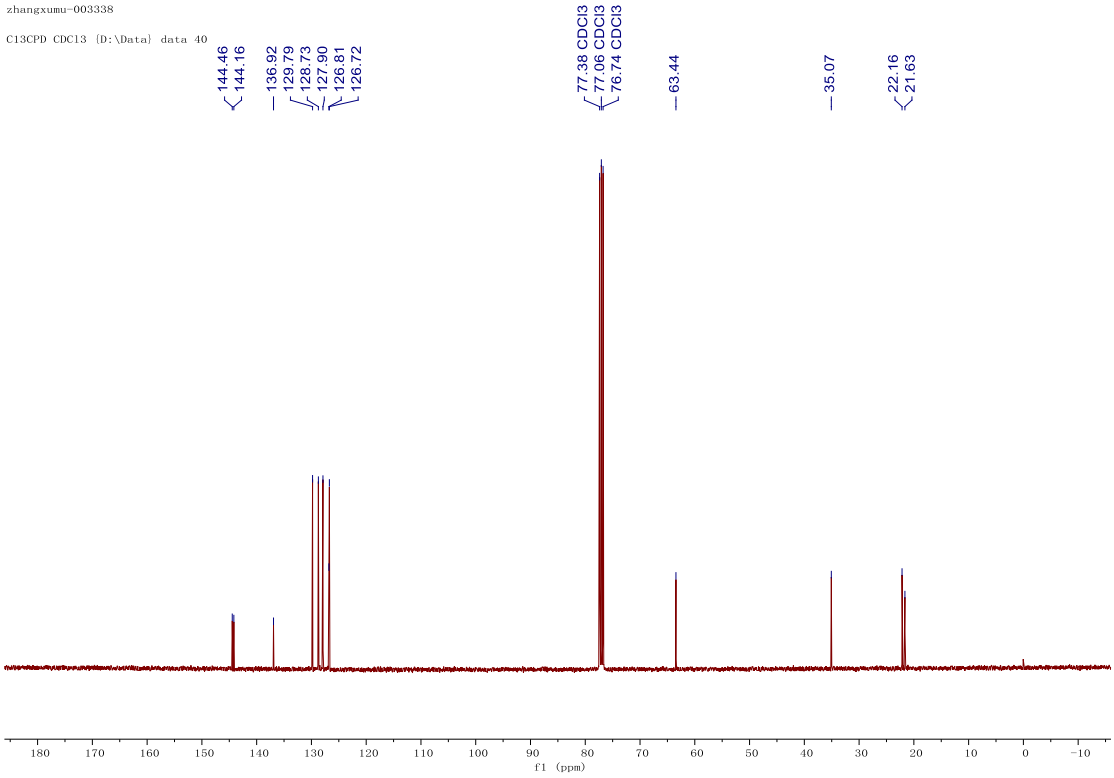
(Z)-2-(1-phenyl-2-tosylvinyl)thiophene(**1q**)



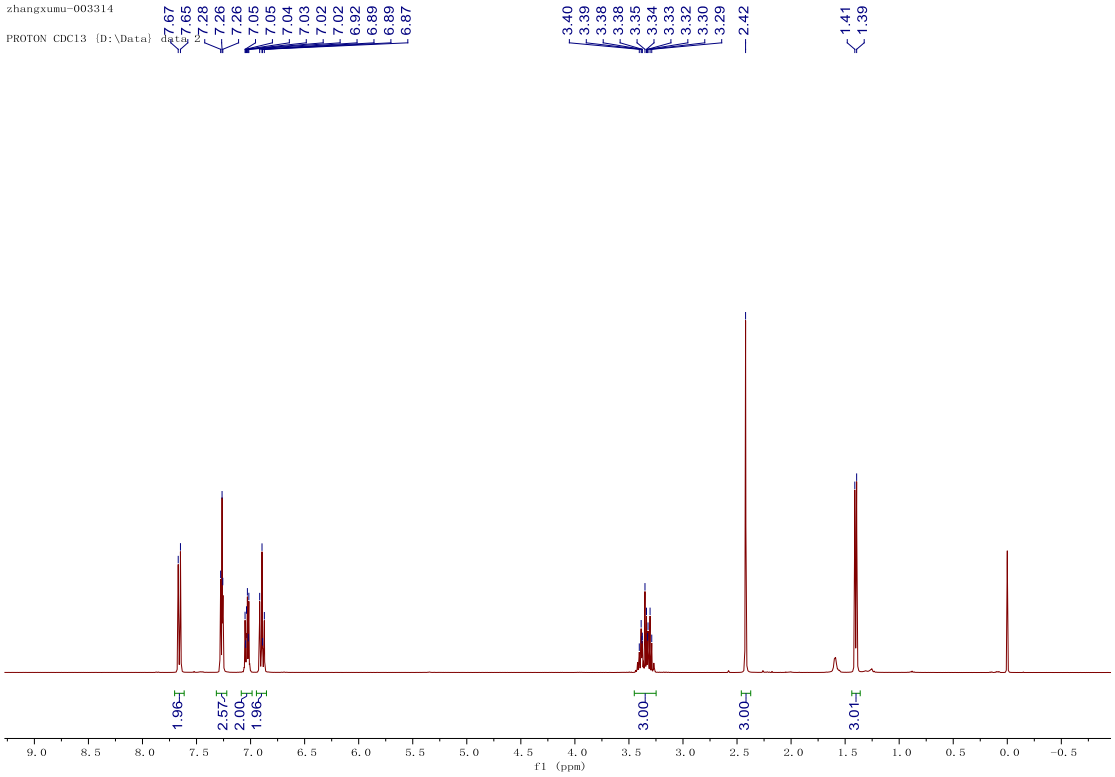


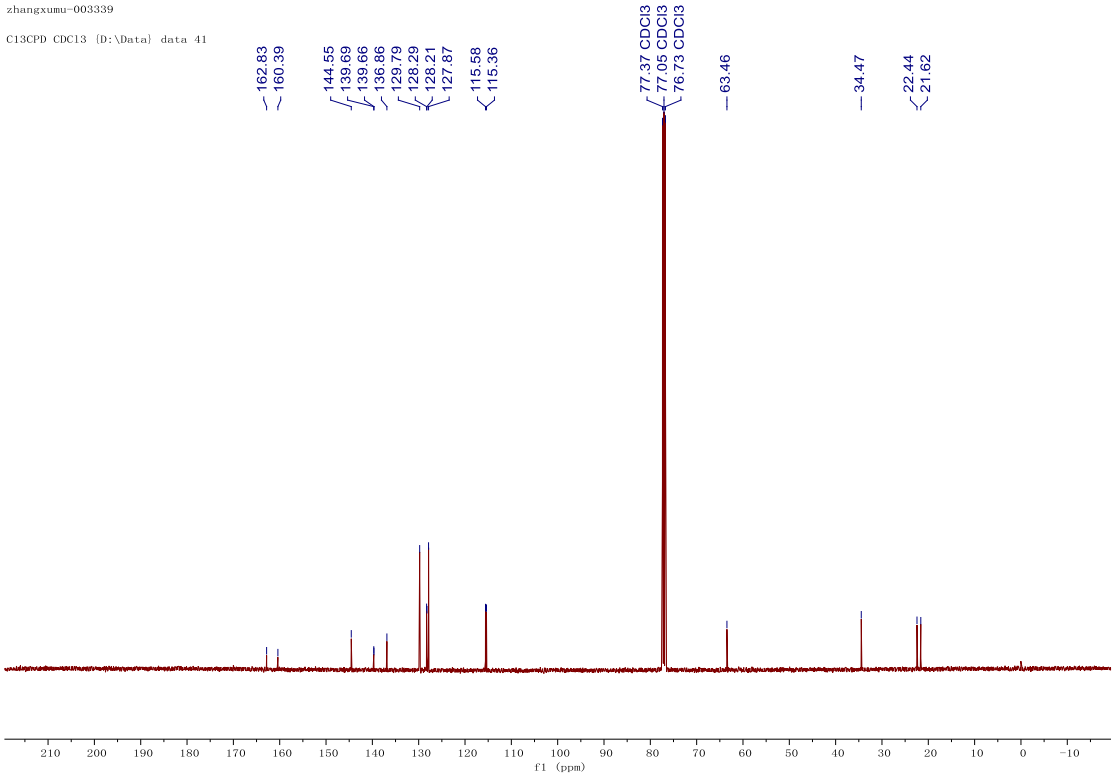
methyl-4-((2-phenylpropyl)sulfonyl)benzene (**2a**)

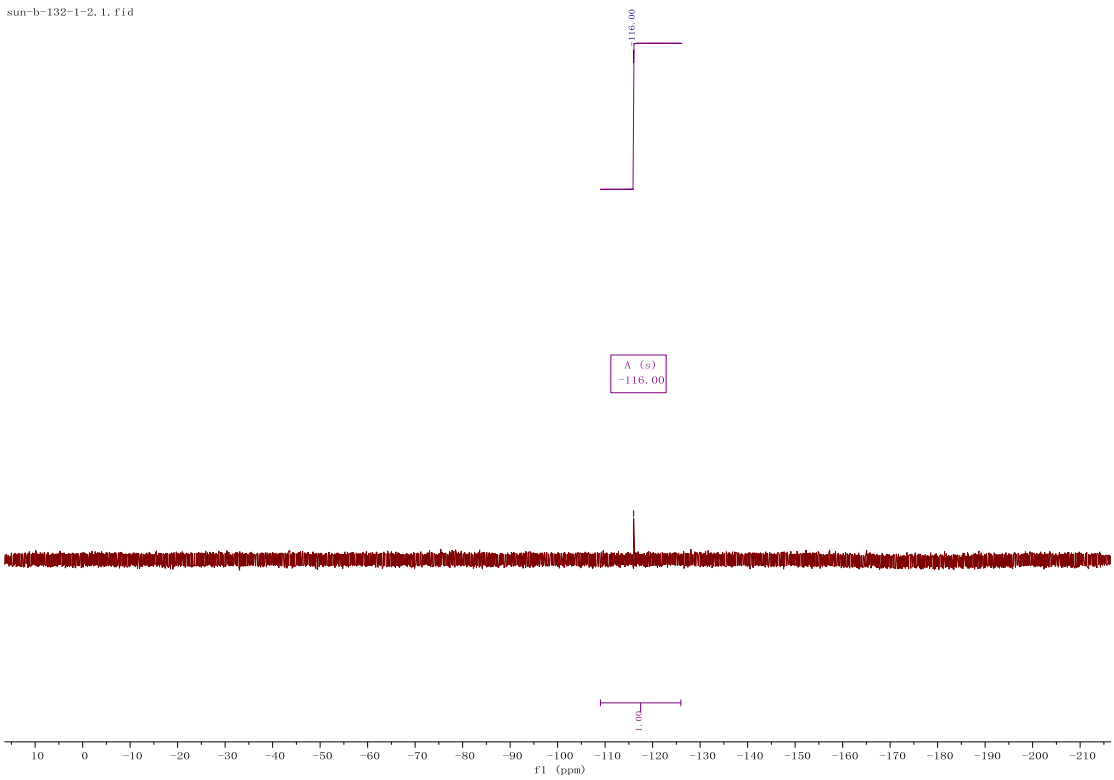




1-fluoro-4-(1-tosylpropan-2-yl)benzene (**2b**)



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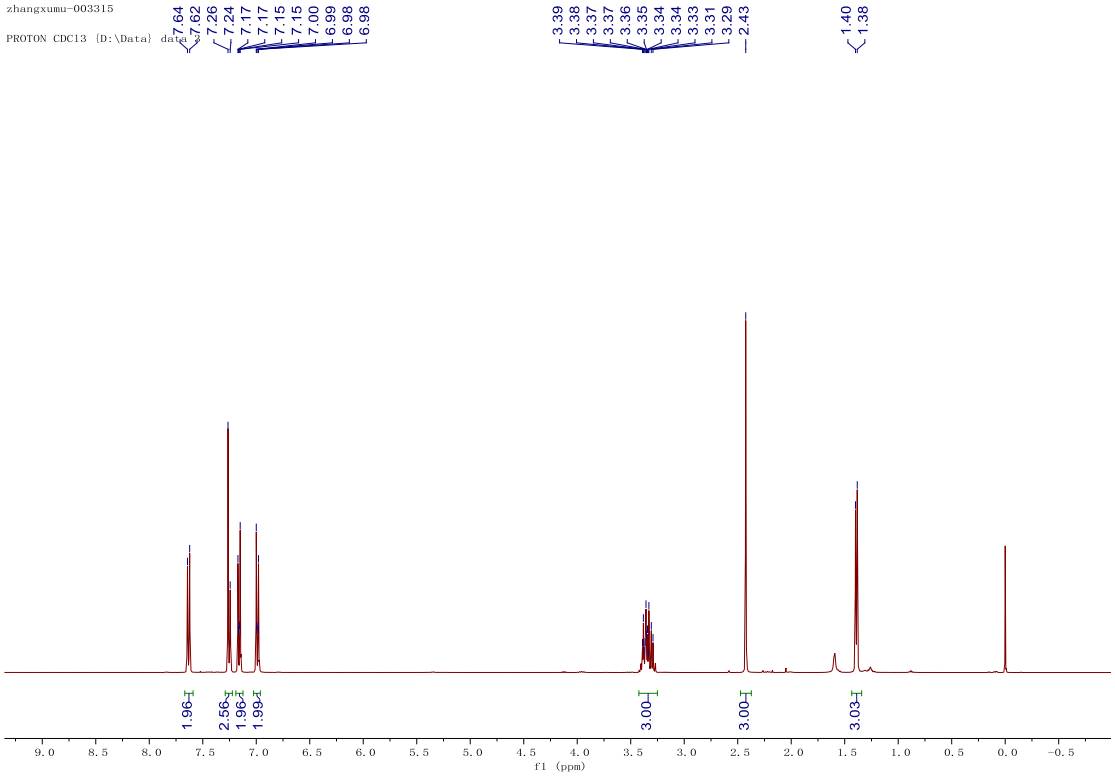
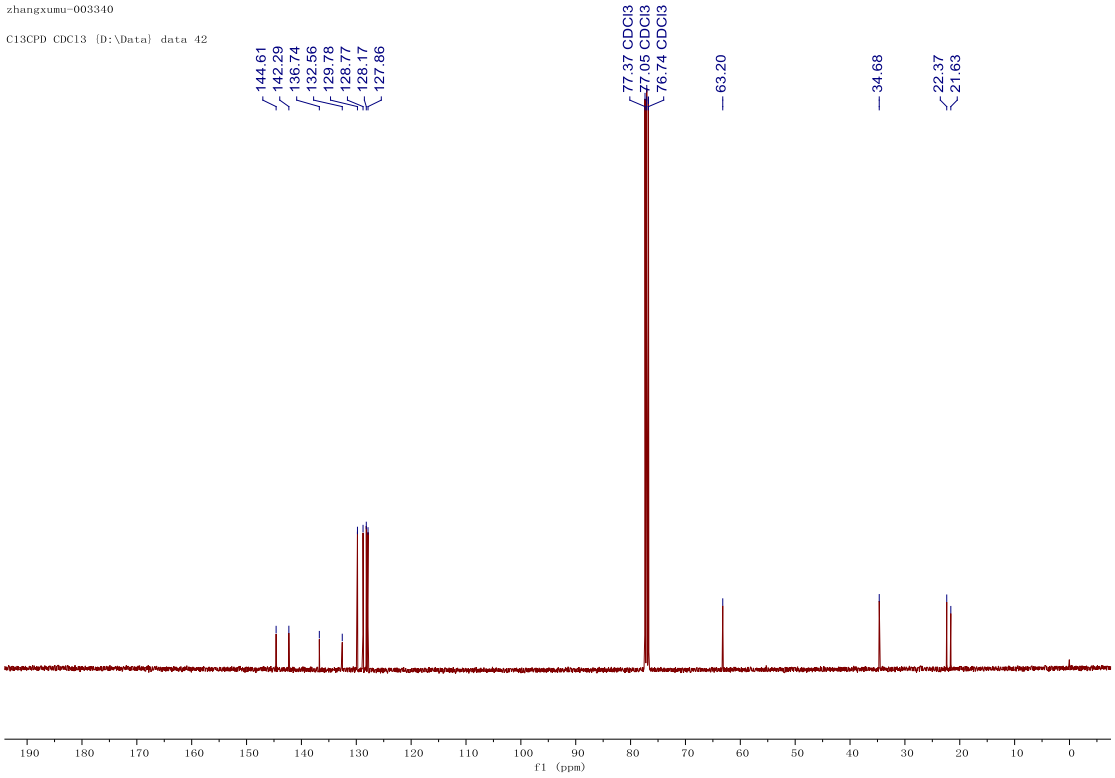
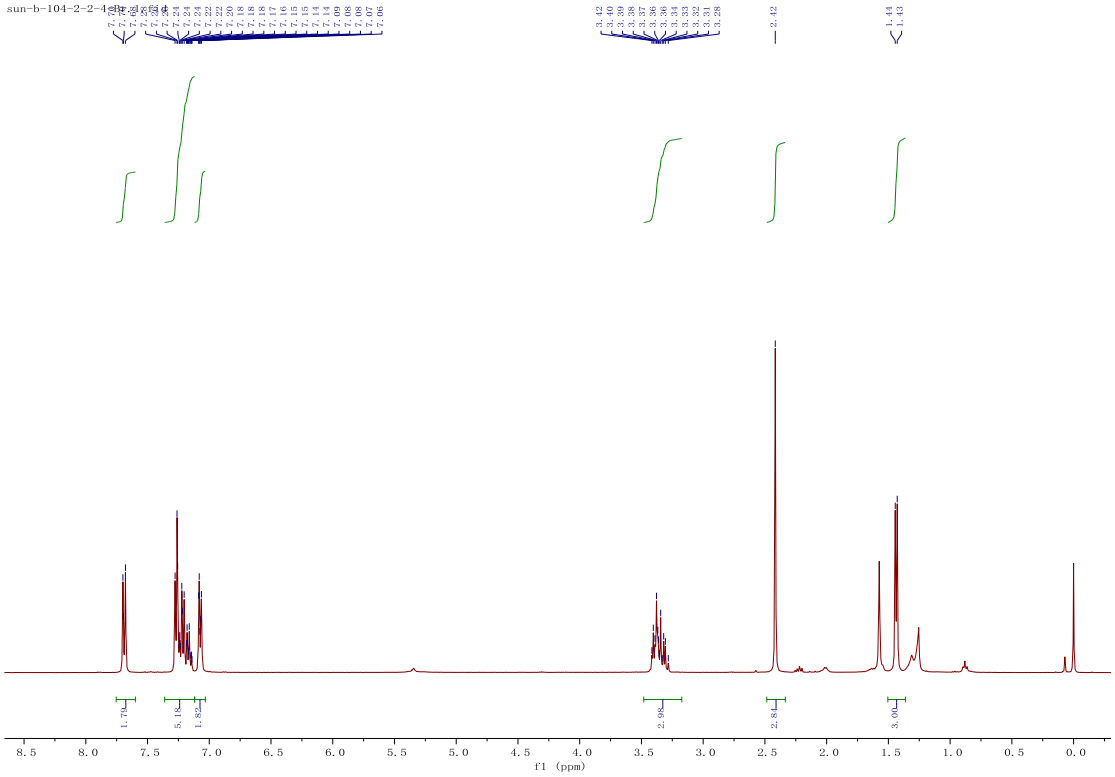
A (s)
-116.00
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

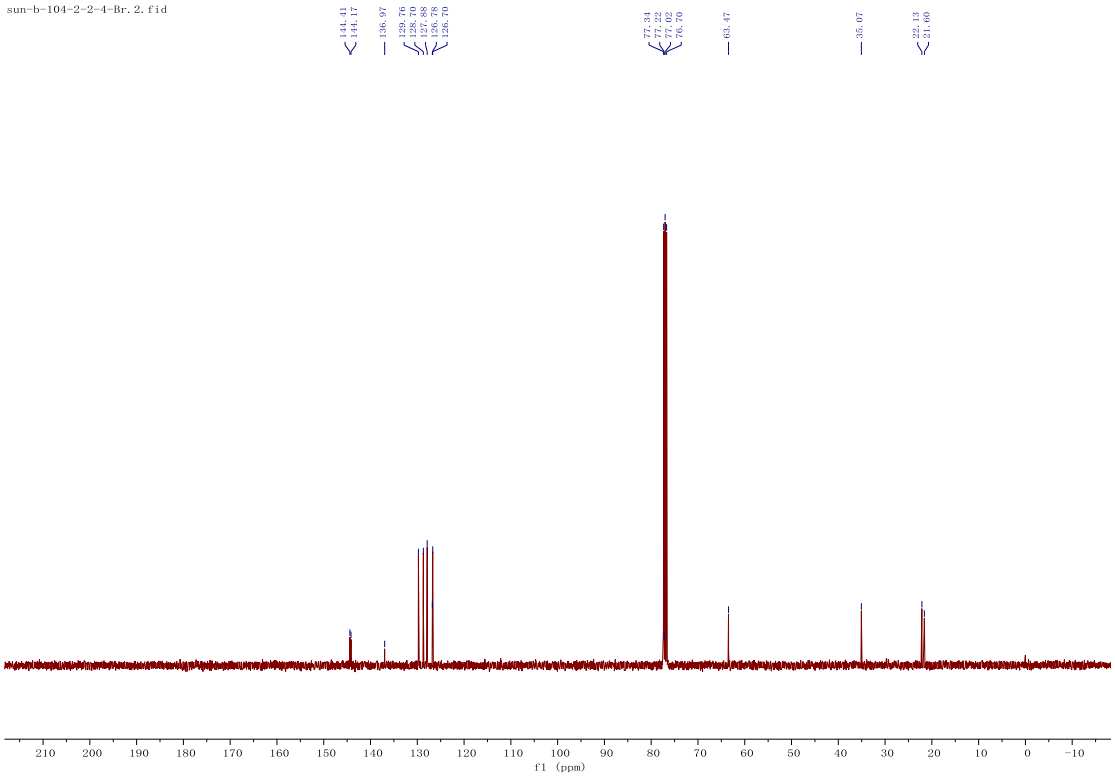
1-chloro-4-(1-tosylpropan-2-yl)benzene (**2c**)



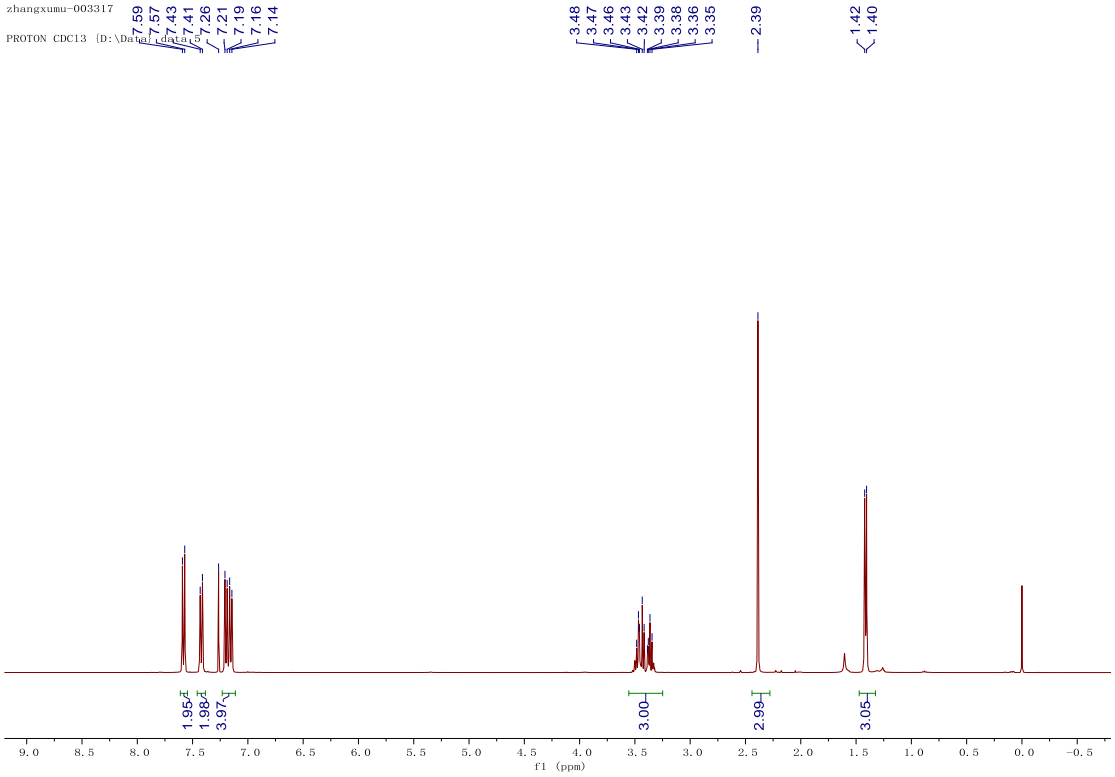


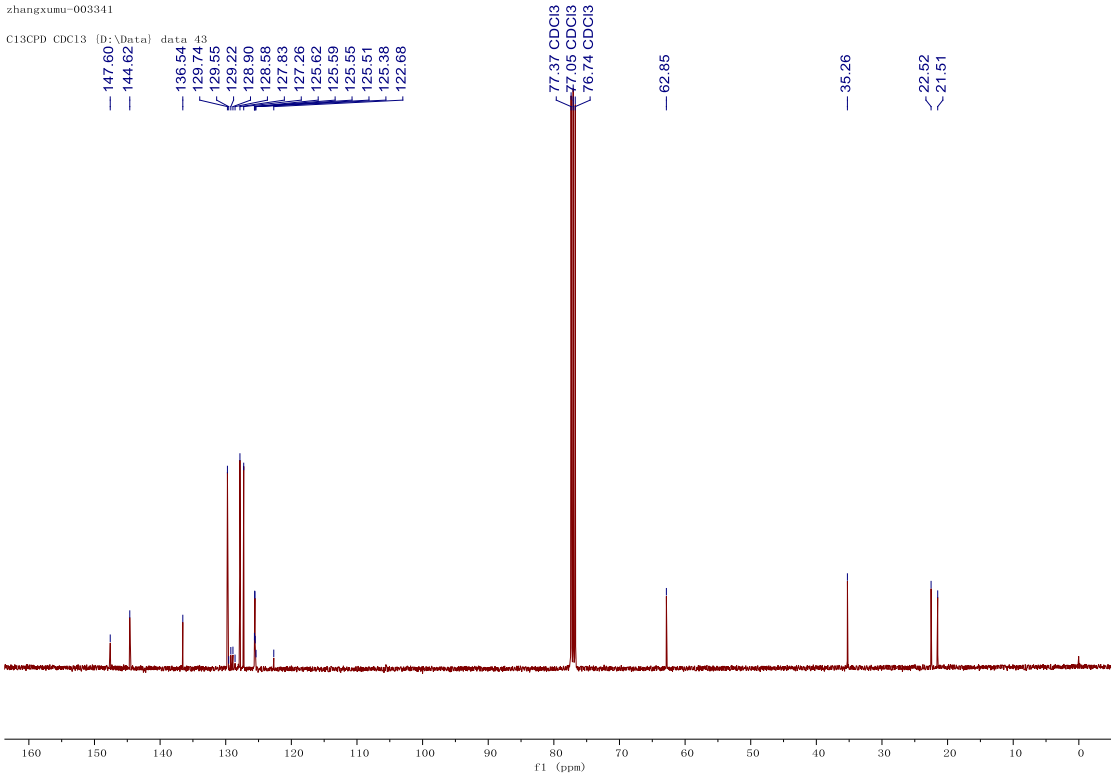
1-bromo-4-(1-tosylpropan-2-yl)benzene (**2d**)

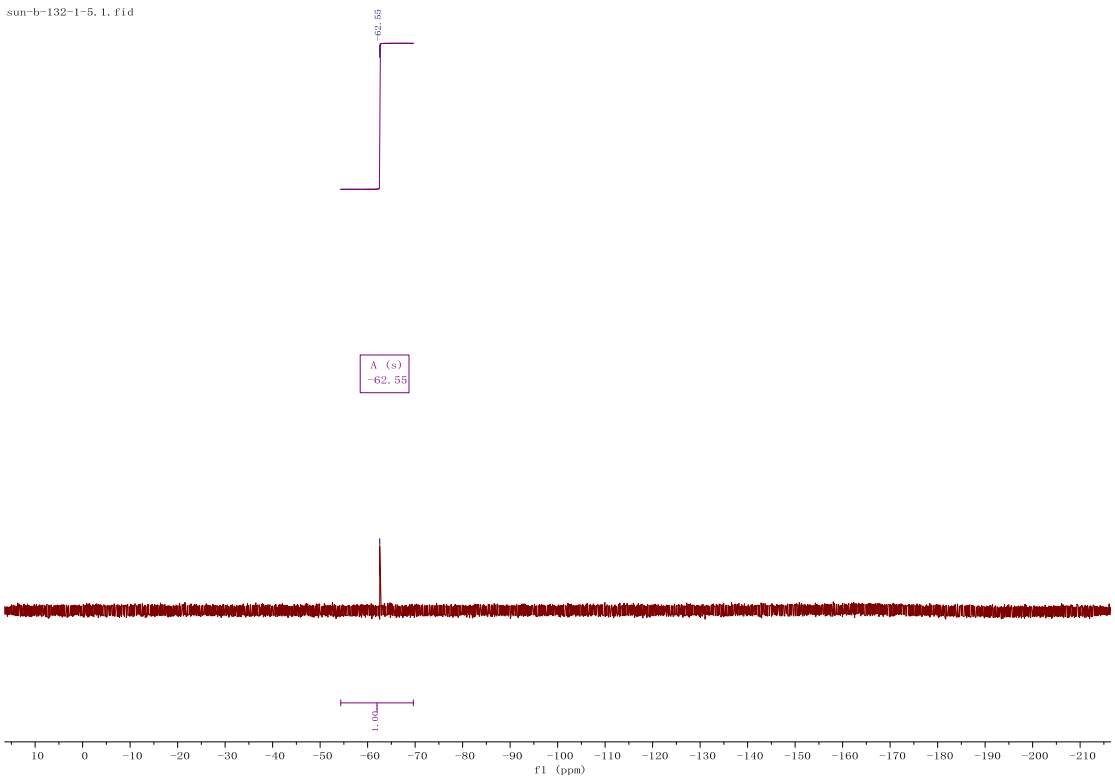




1-methyl-4-((2-(4-(trifluoromethyl)phenyl)propyl)sulfonyl)benzene (**2e**)



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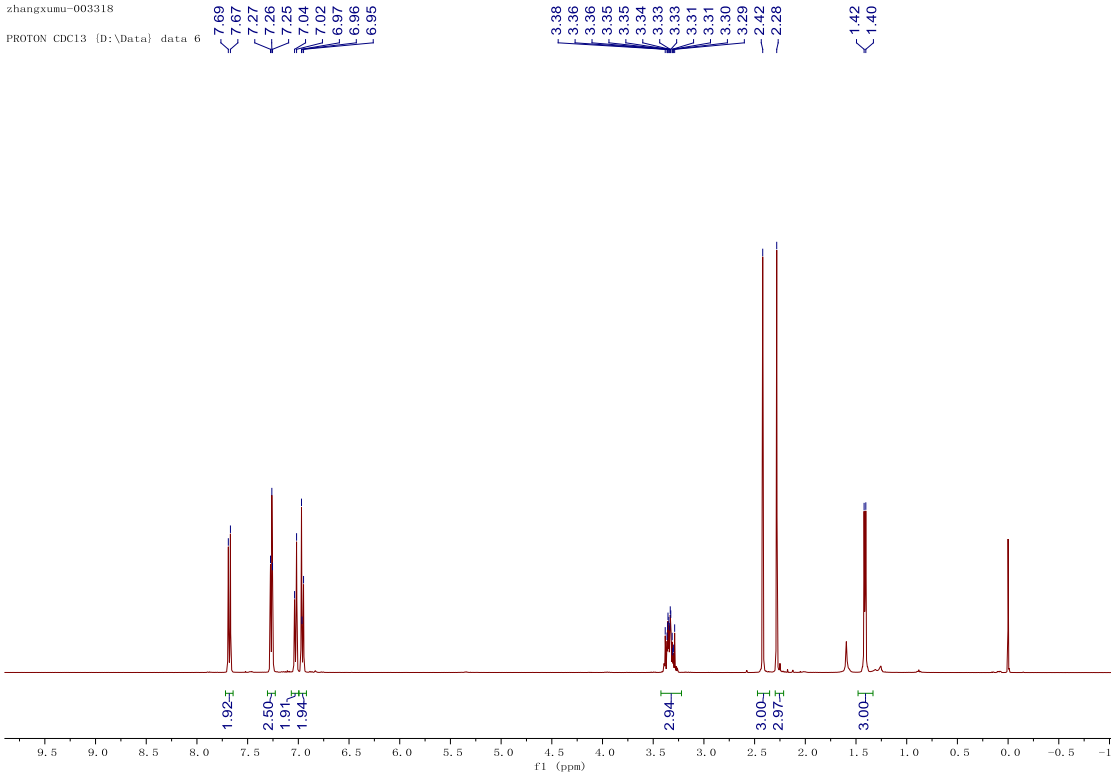
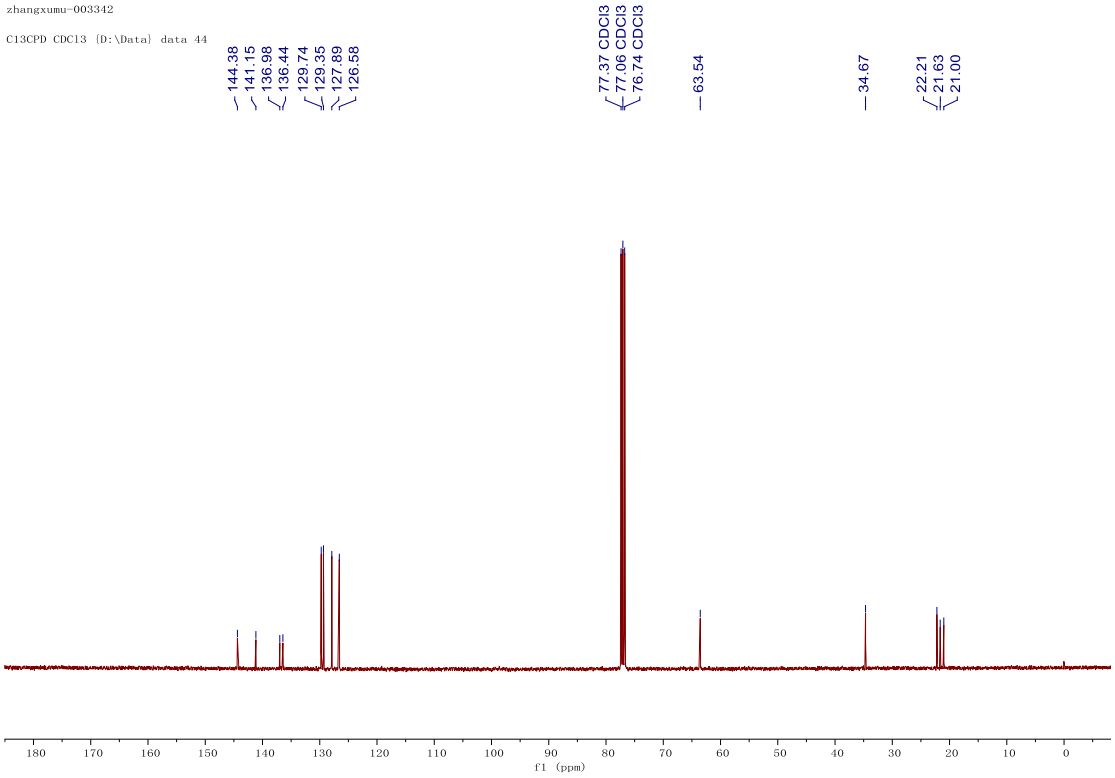
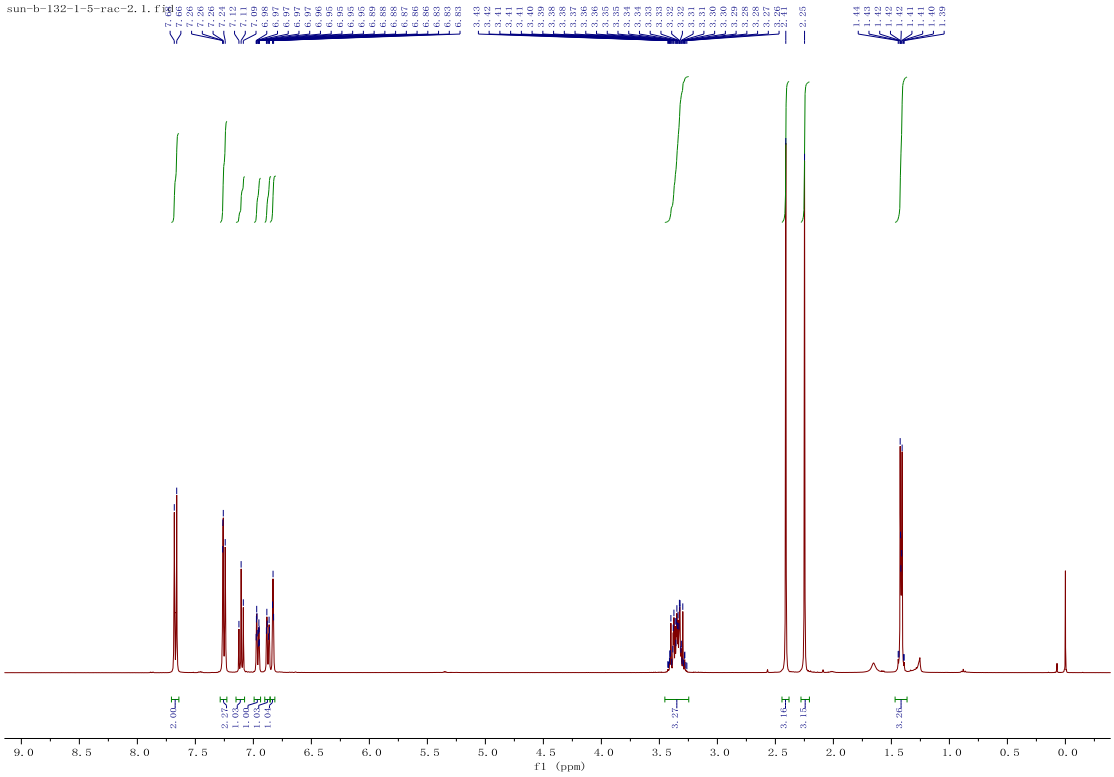
A (s)
-62.55
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

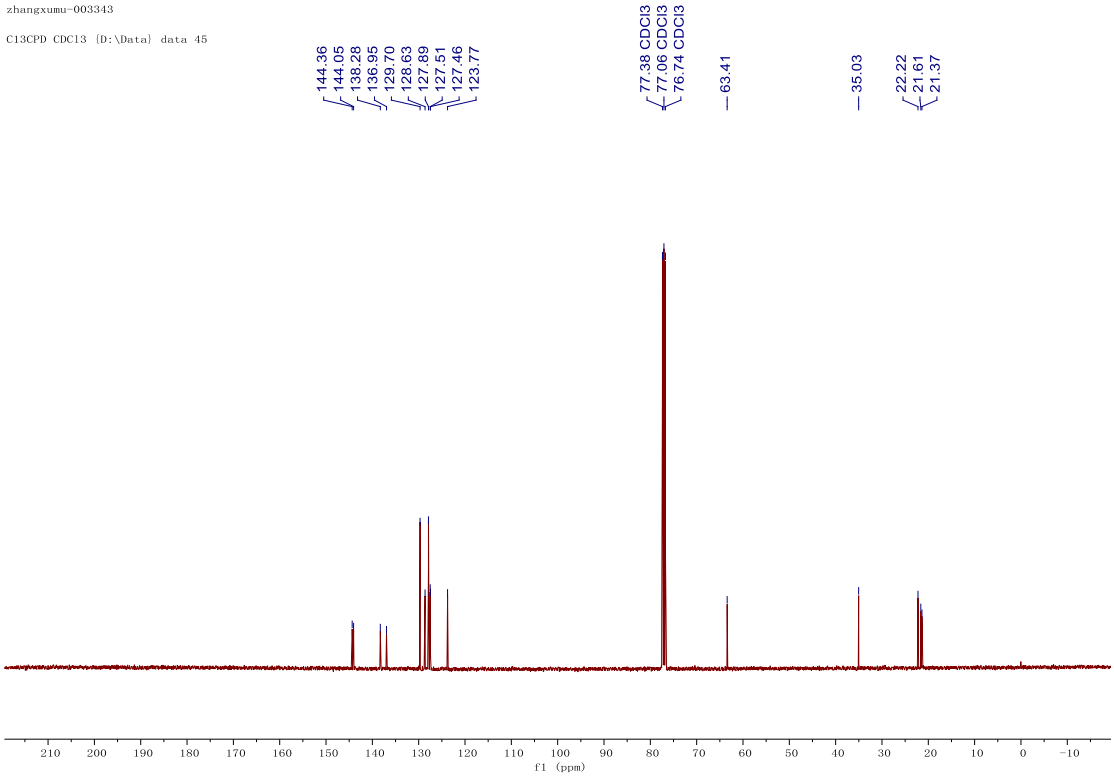
1-methyl-4-((2-(p-tolyl)propyl)sulfonyl)benzene (**2f**)



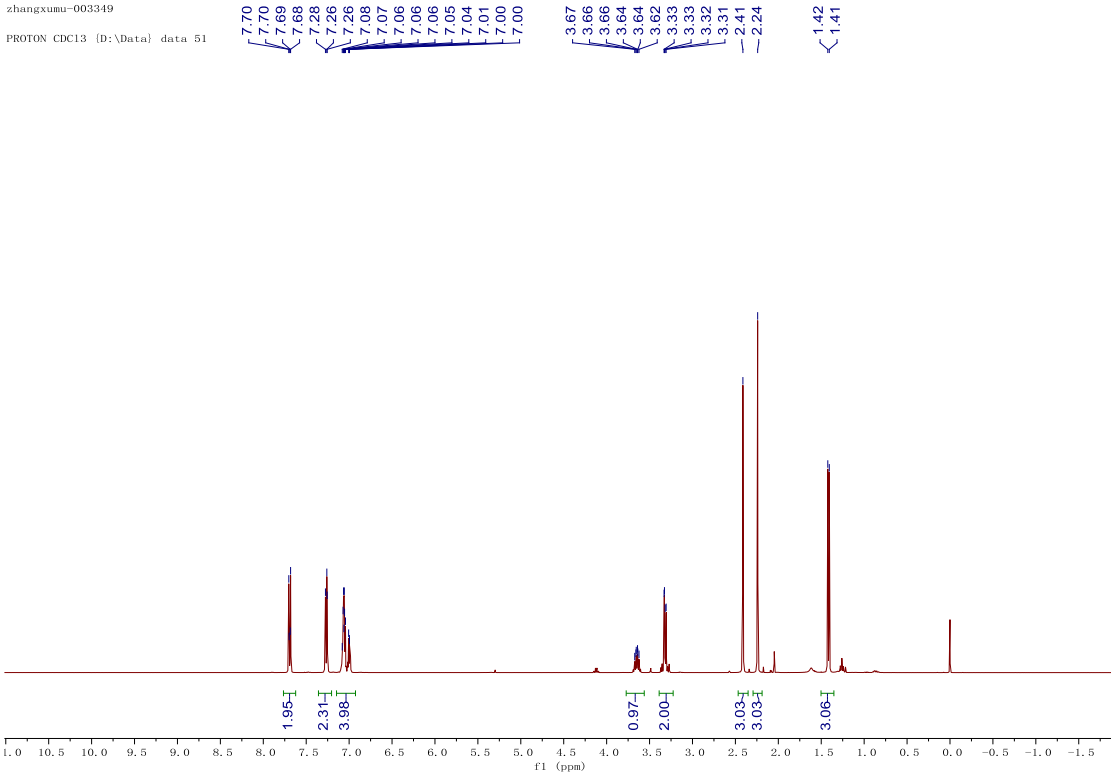


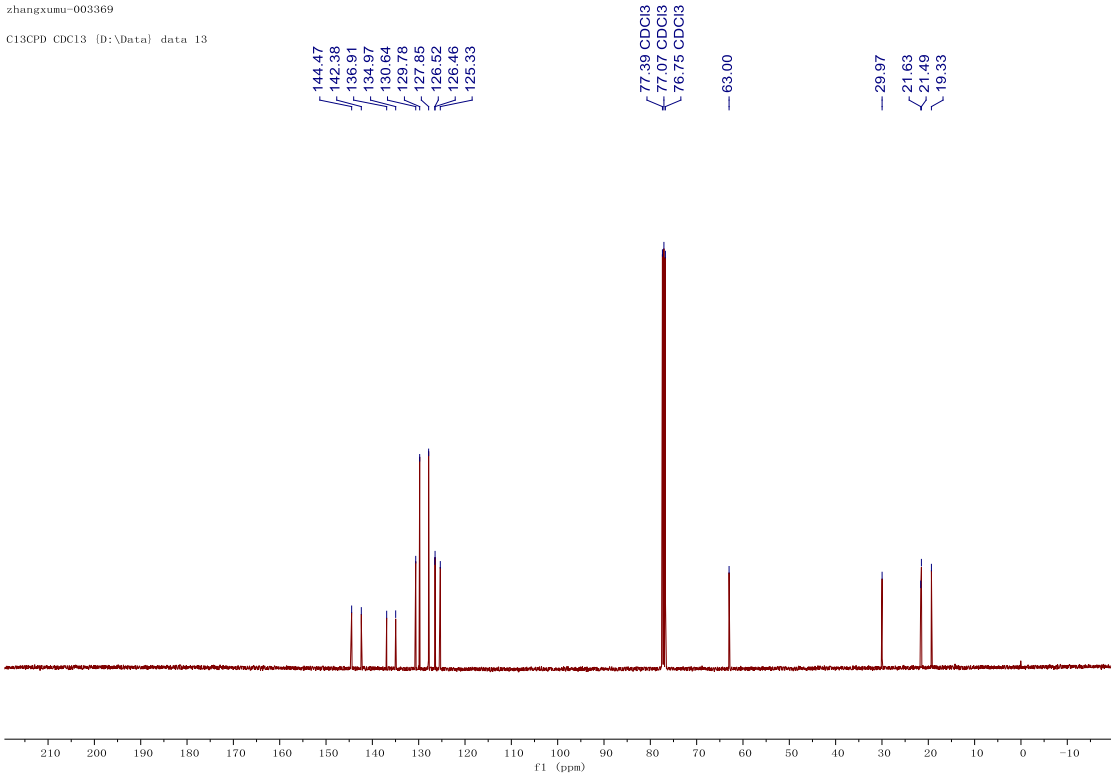
1-methyl-3-(1-tosylpropan-2-yl)benzene (**2g**)



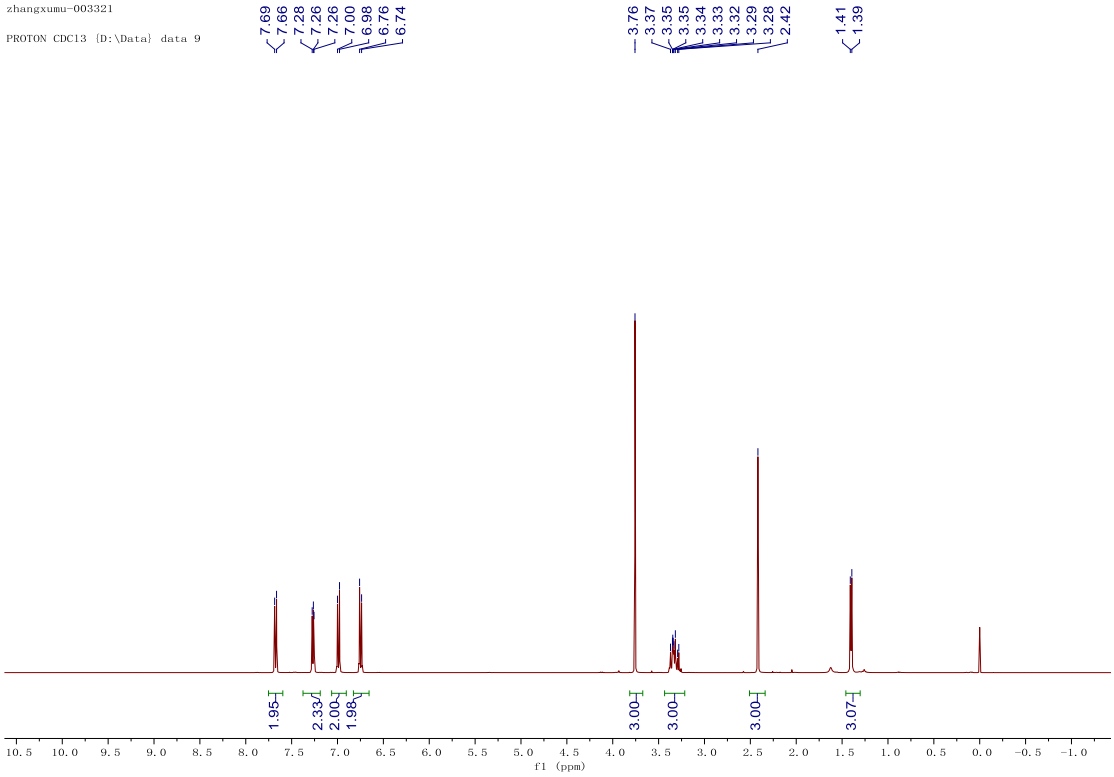


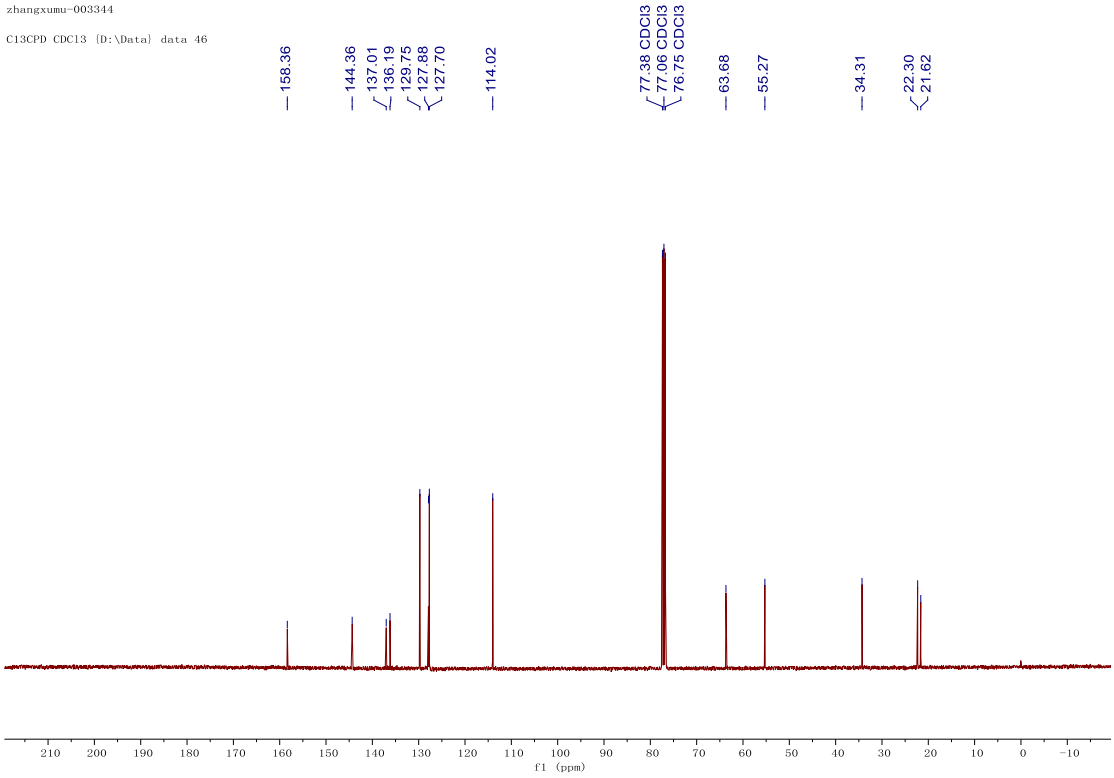
1-methyl-2-(1-tosylpropan-2-yl)benzene (**2h**)



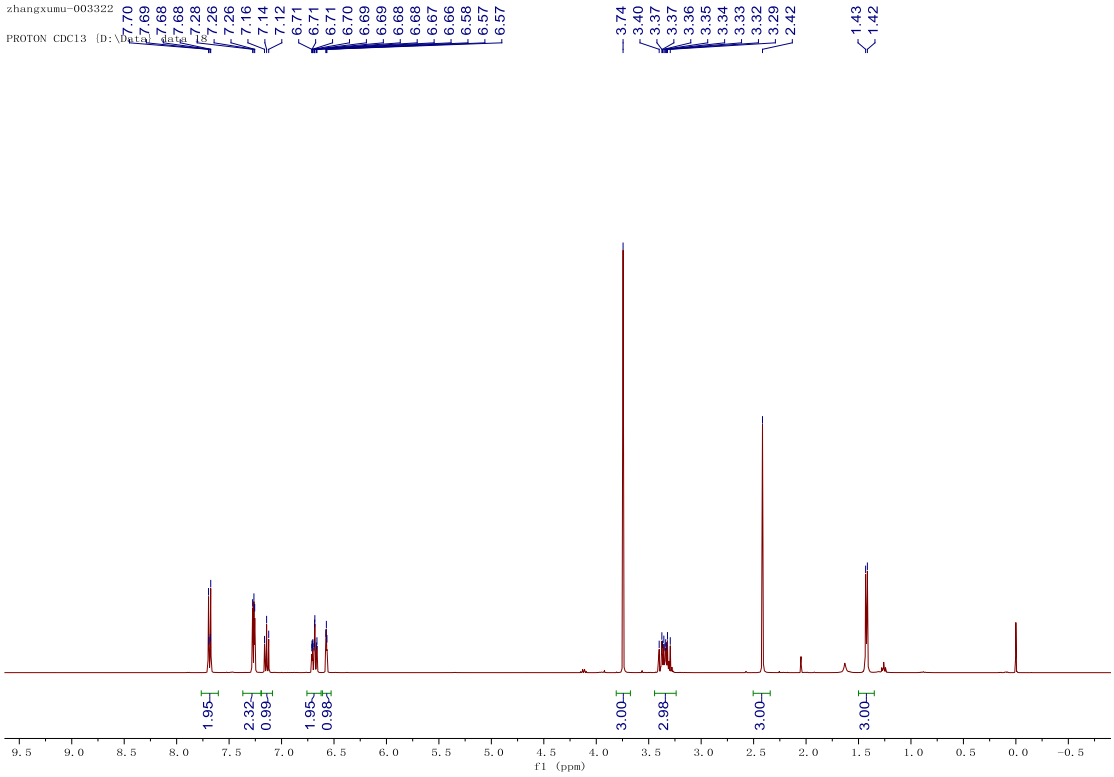


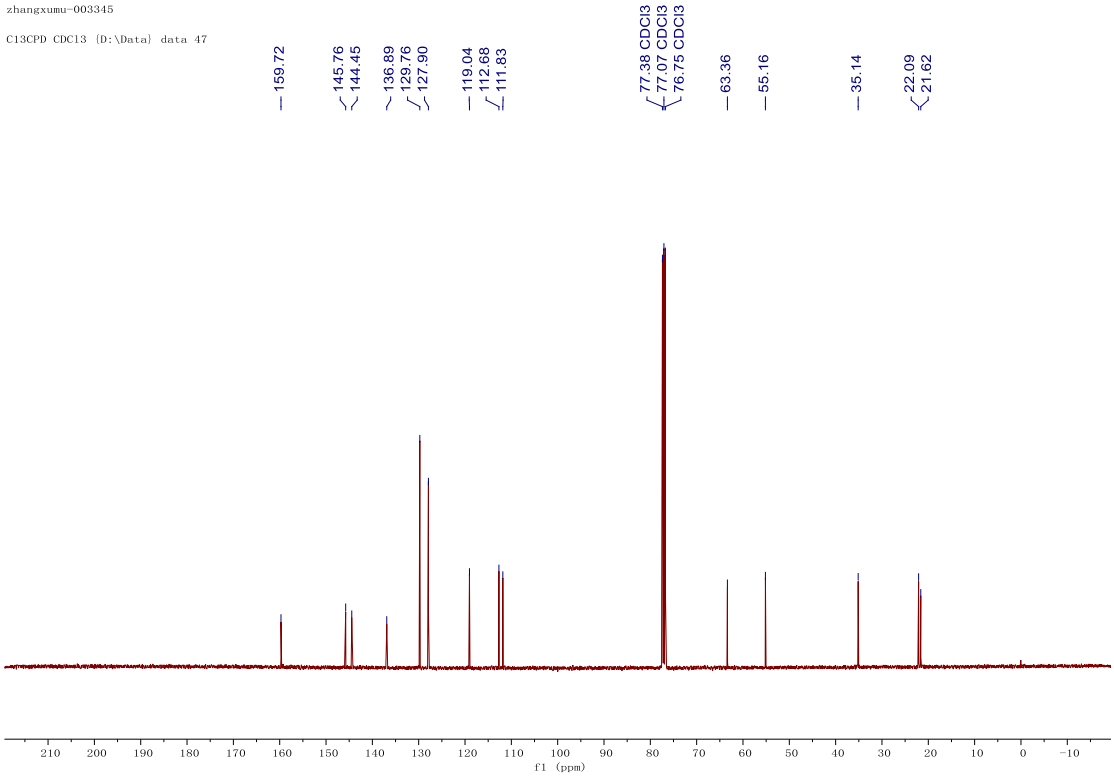
1-methoxy-4-(1-tosylpropan-2-yl)benzene (**2i**)



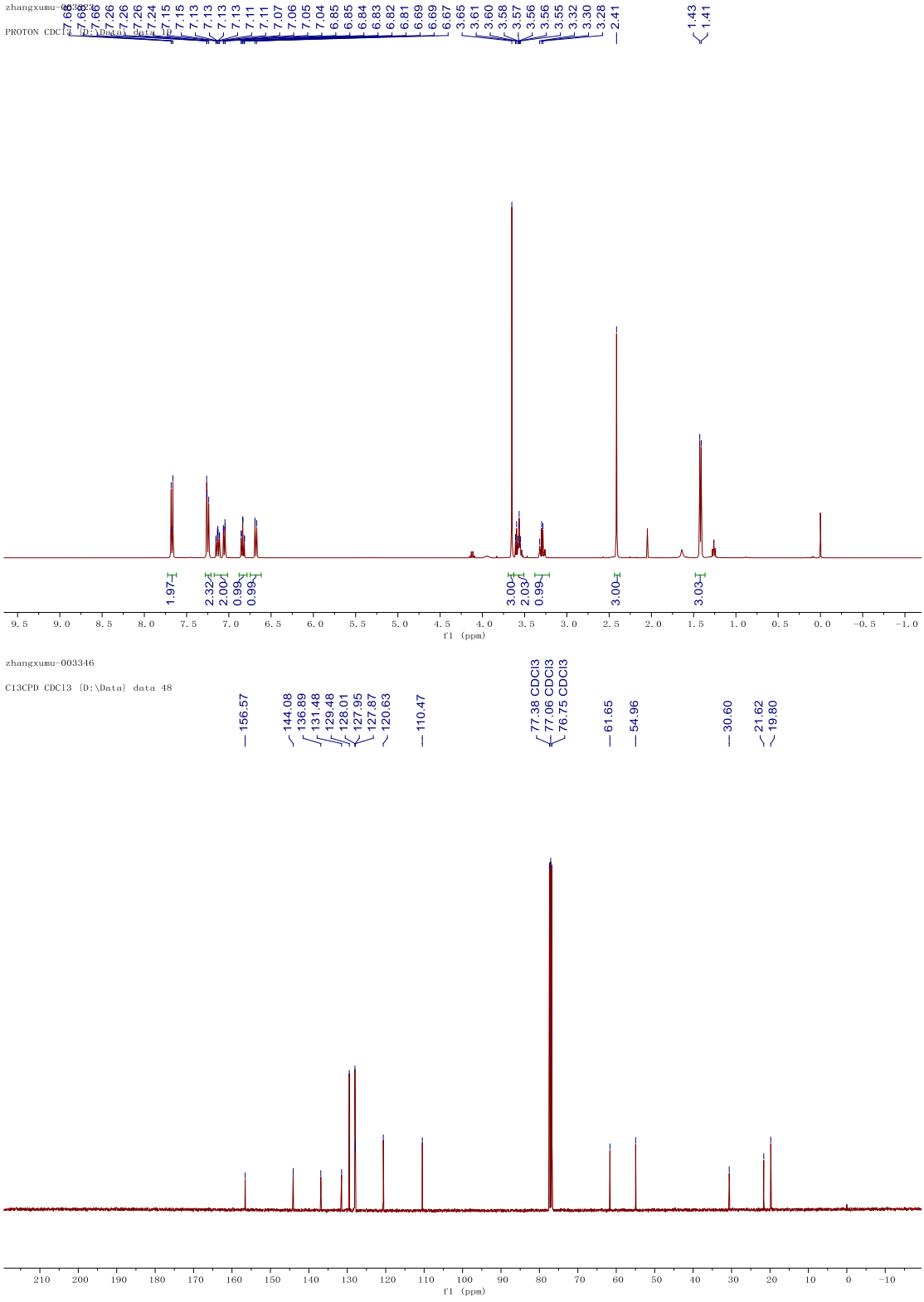


1-methoxy-3-(1-tosylpropan-2-yl)benzene (**2j**)

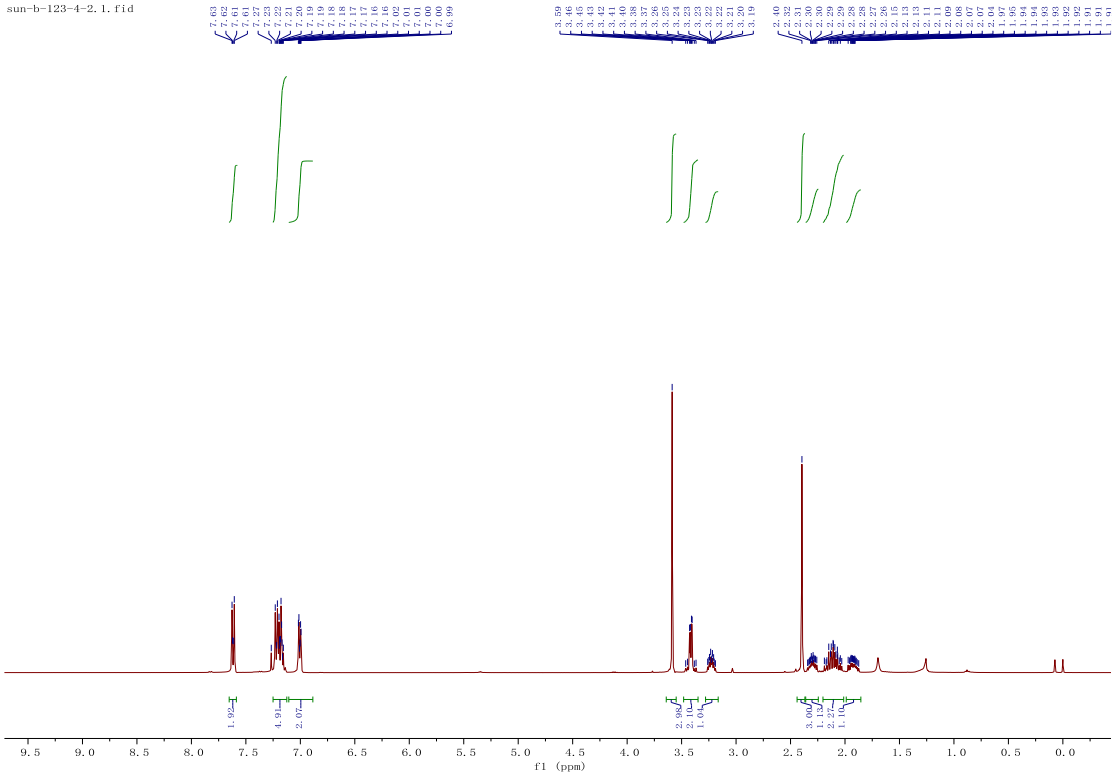


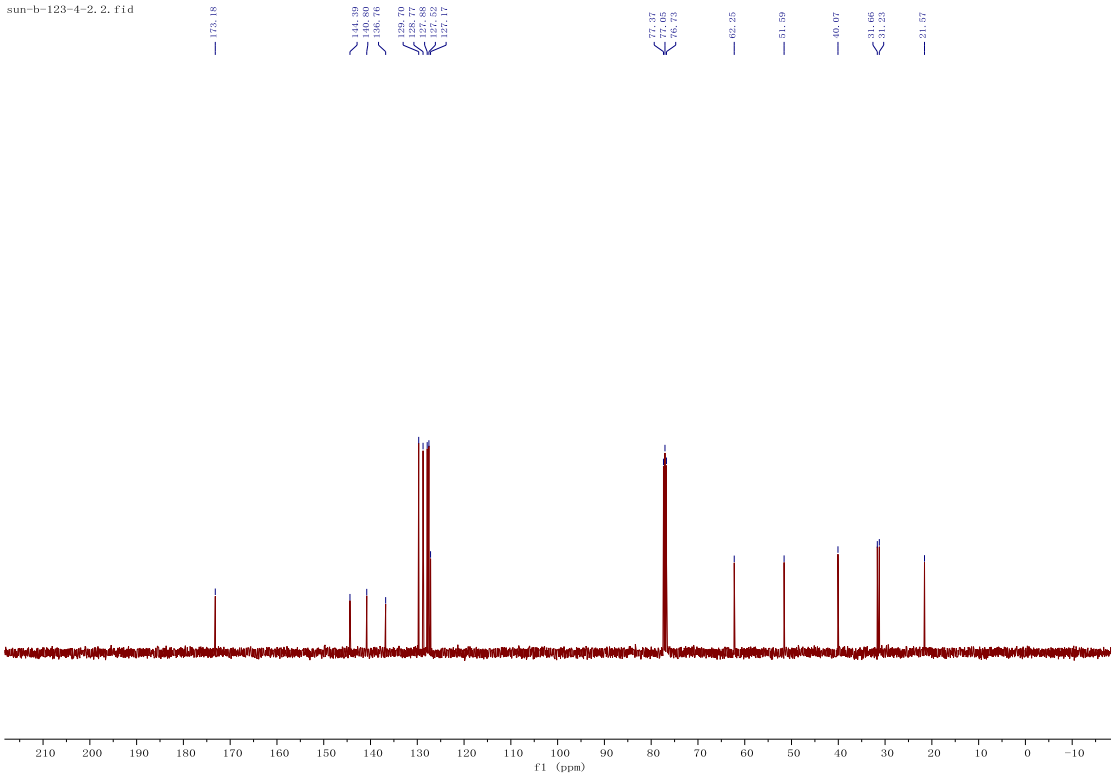


1-methoxy-2-(1-tosylpropan-2-yl)benzene (**2k**)

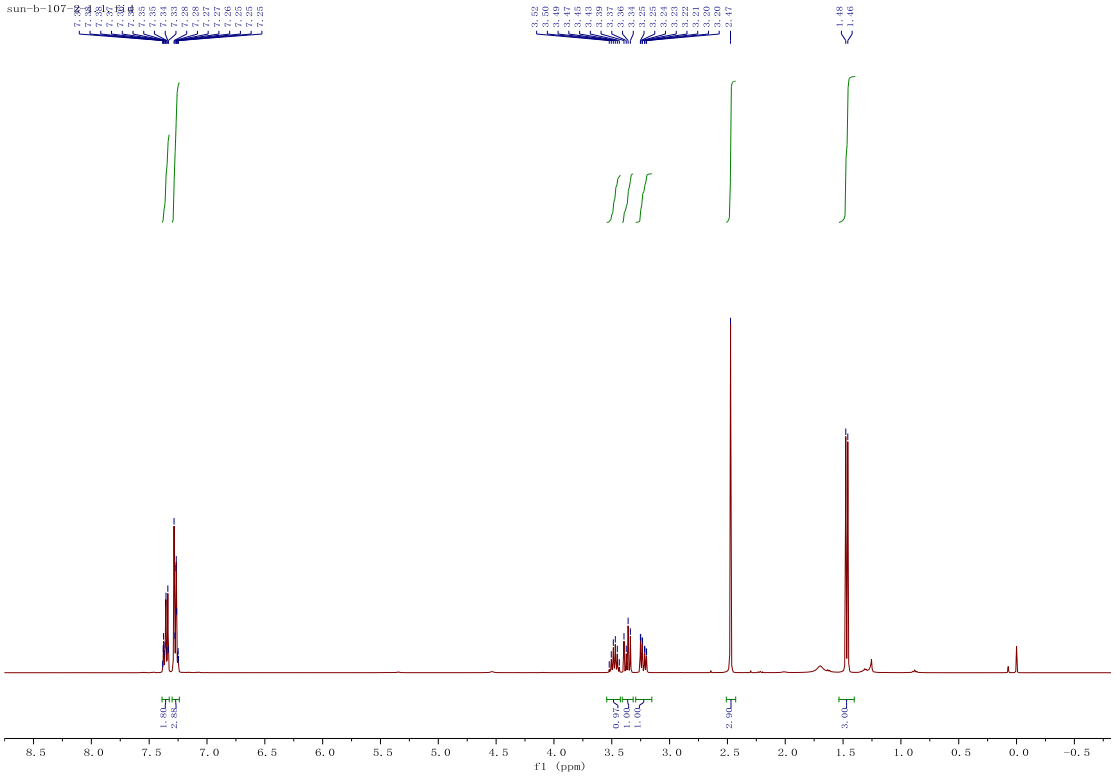


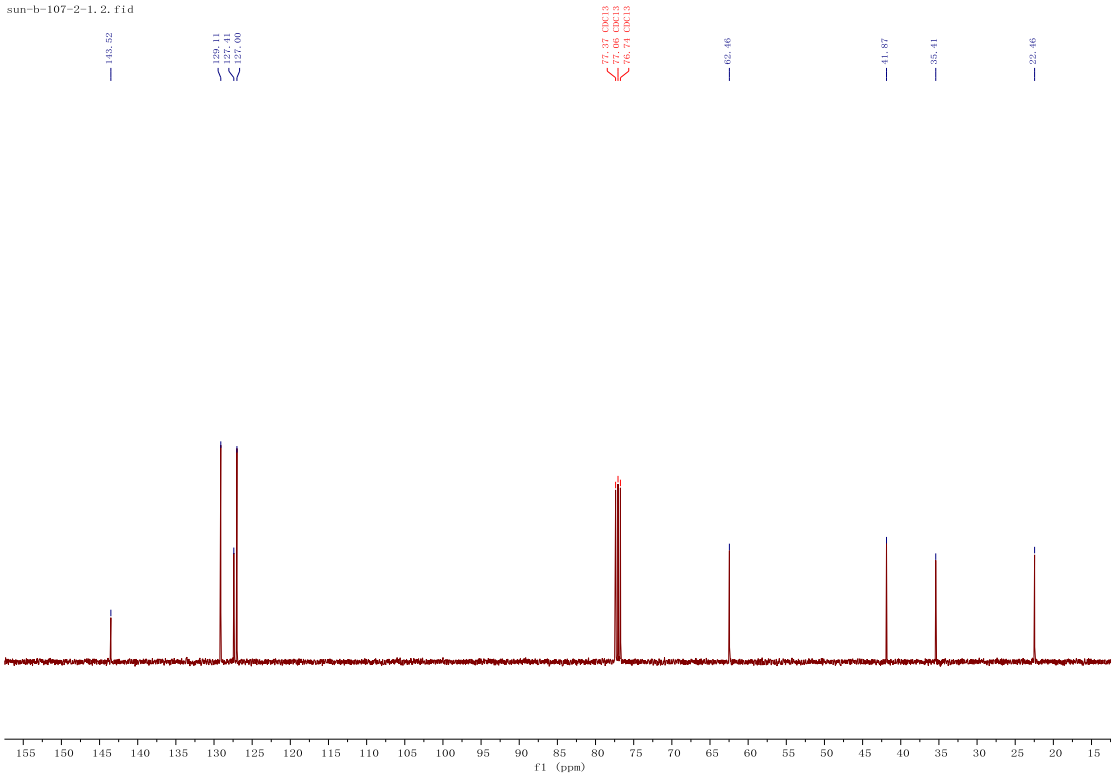
methyl-4-phenyl-5-tosylpentanoate (**2l**)



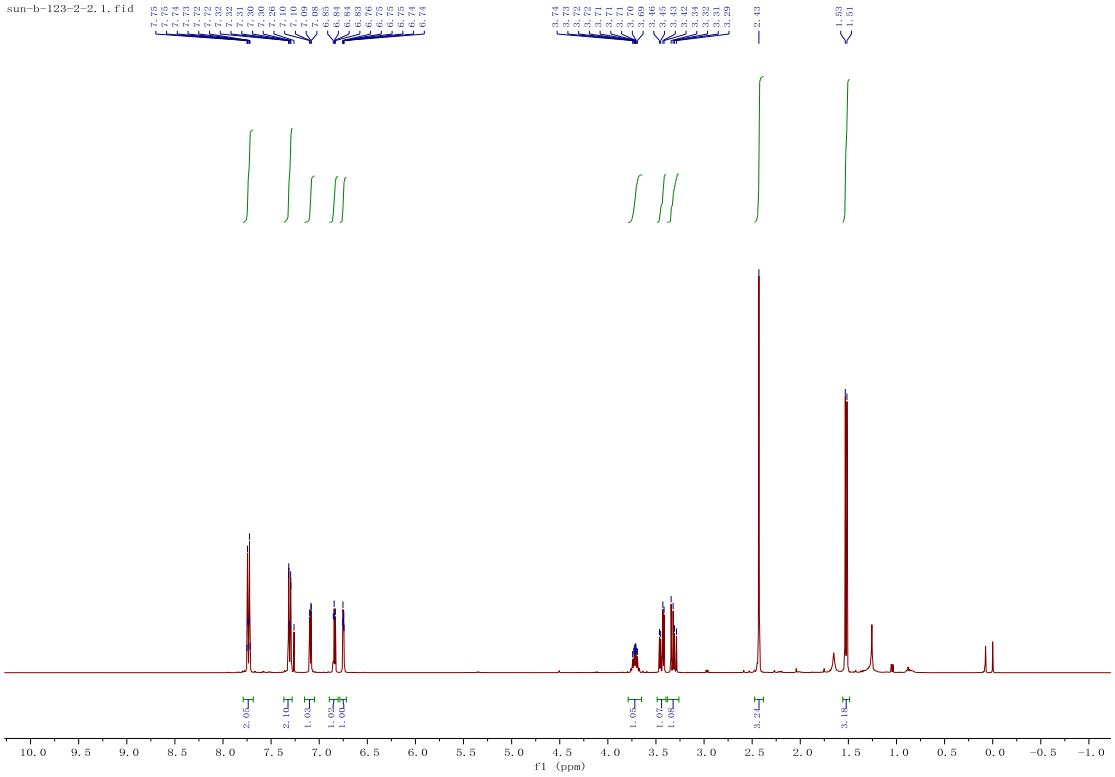


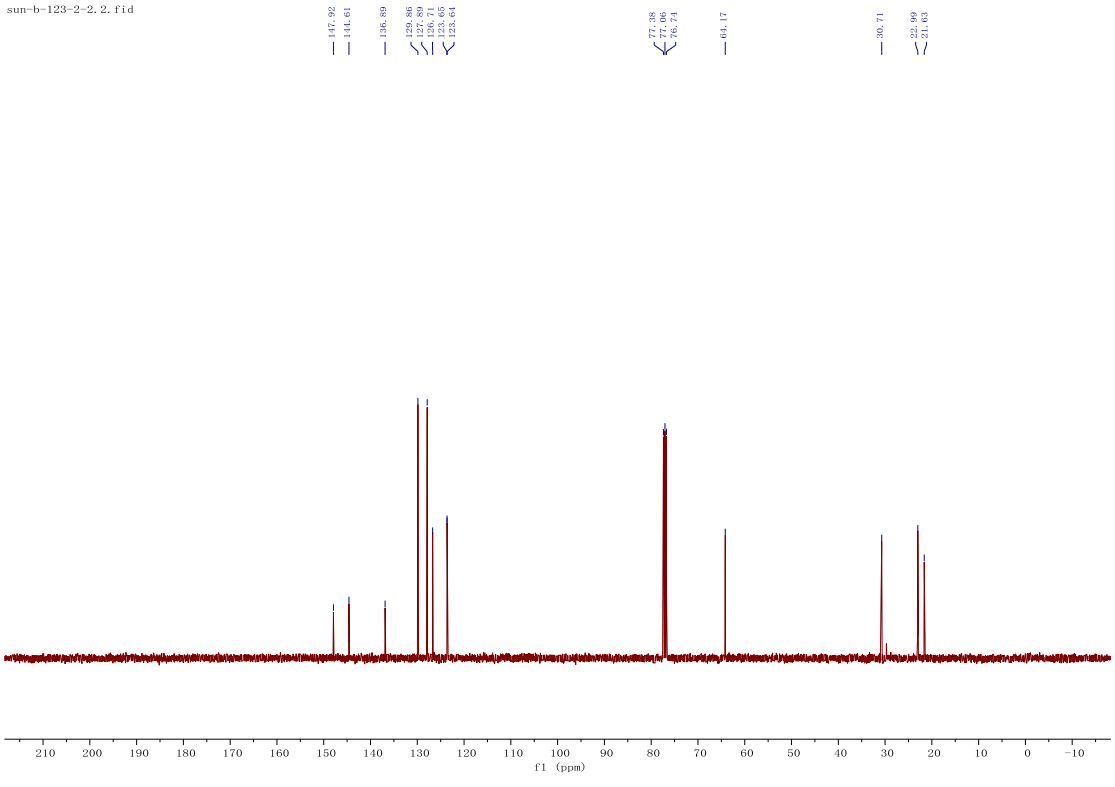
(1-(methylsulfonyl)propan-2-yl)benzene (**2m**)



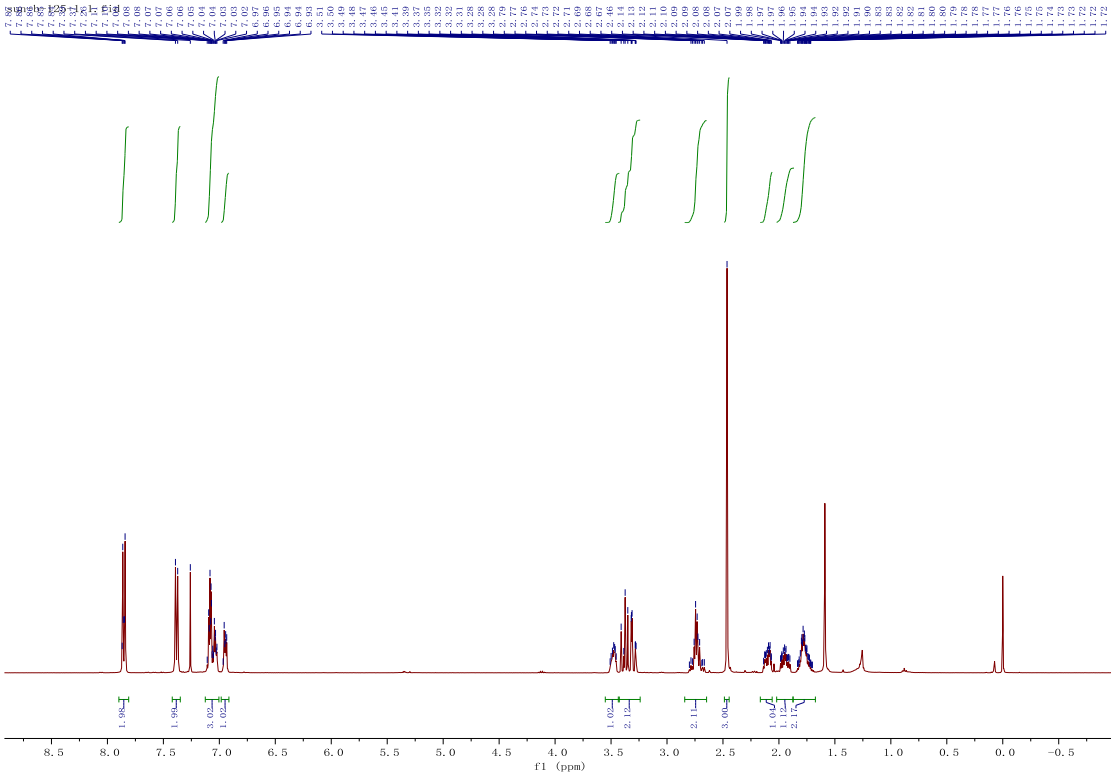


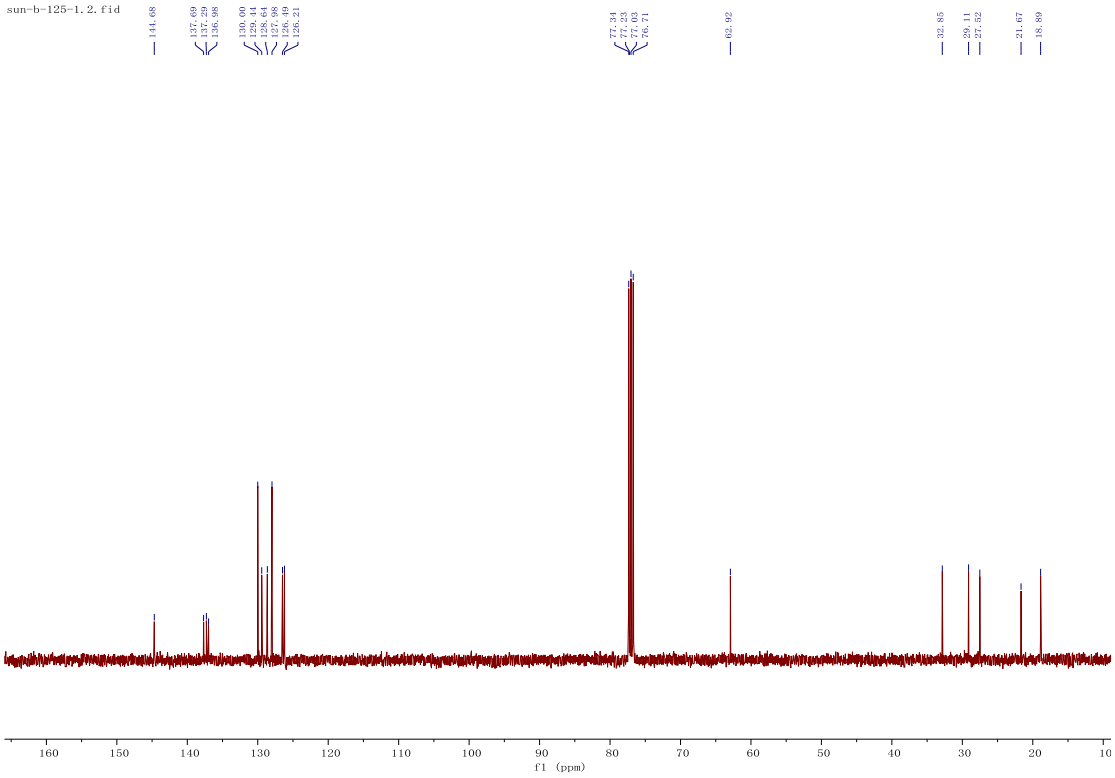
2-(1-tosylpropan-2-yl)thiophene (**2n**)



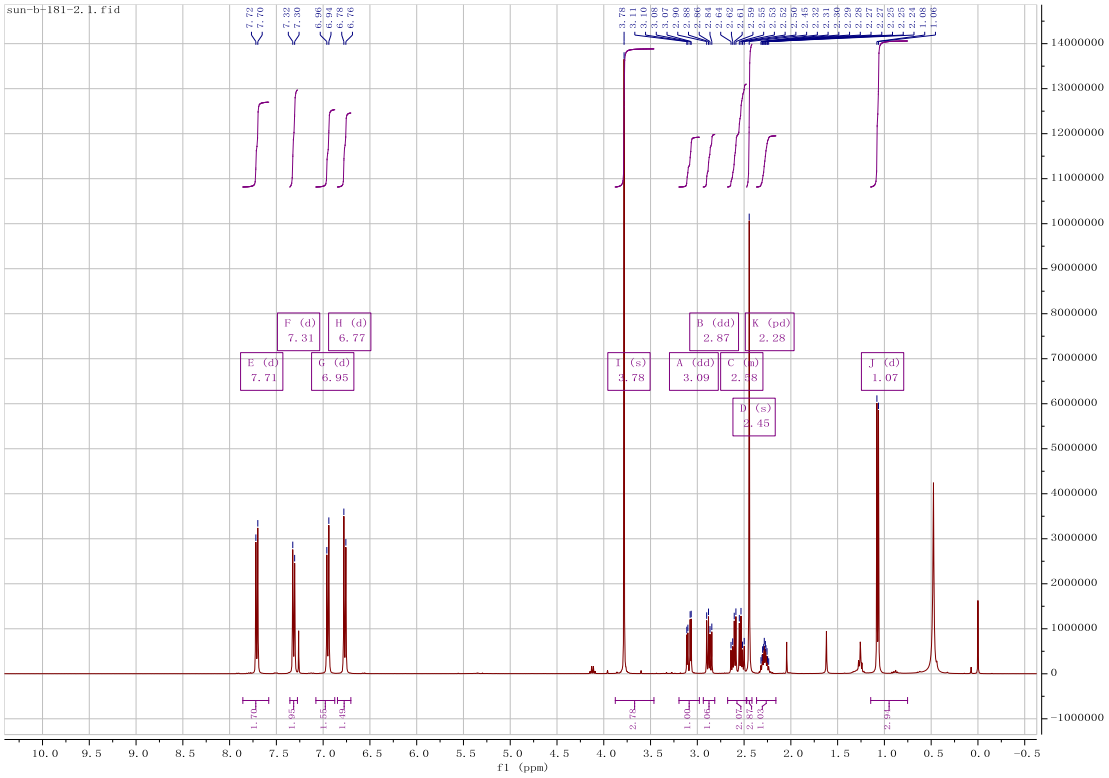


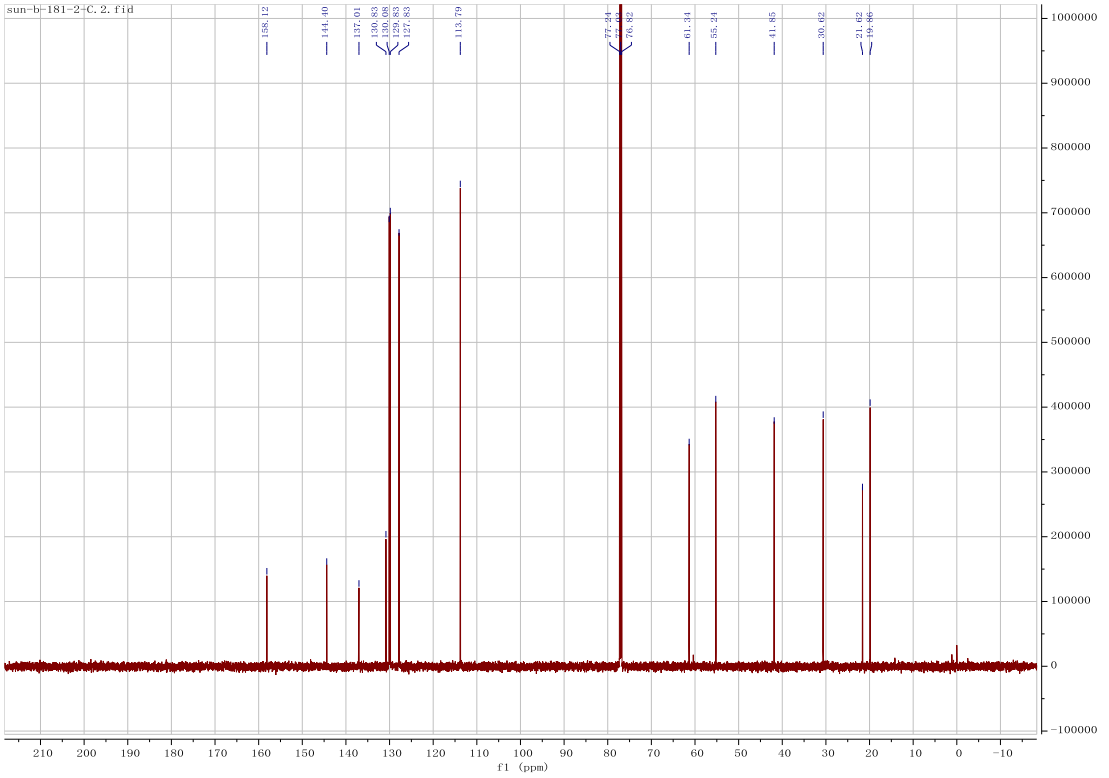
1-(tosylmethyl)-1,2,3,4-tetrahydronaphthalene (**2o**)



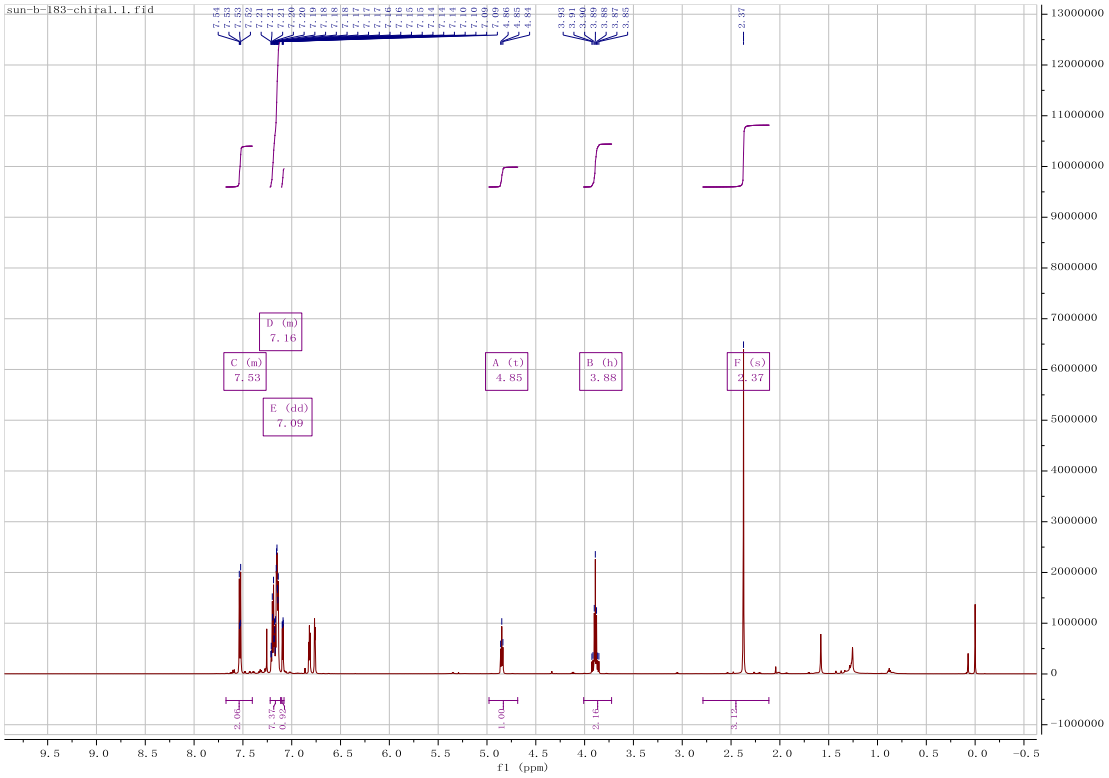


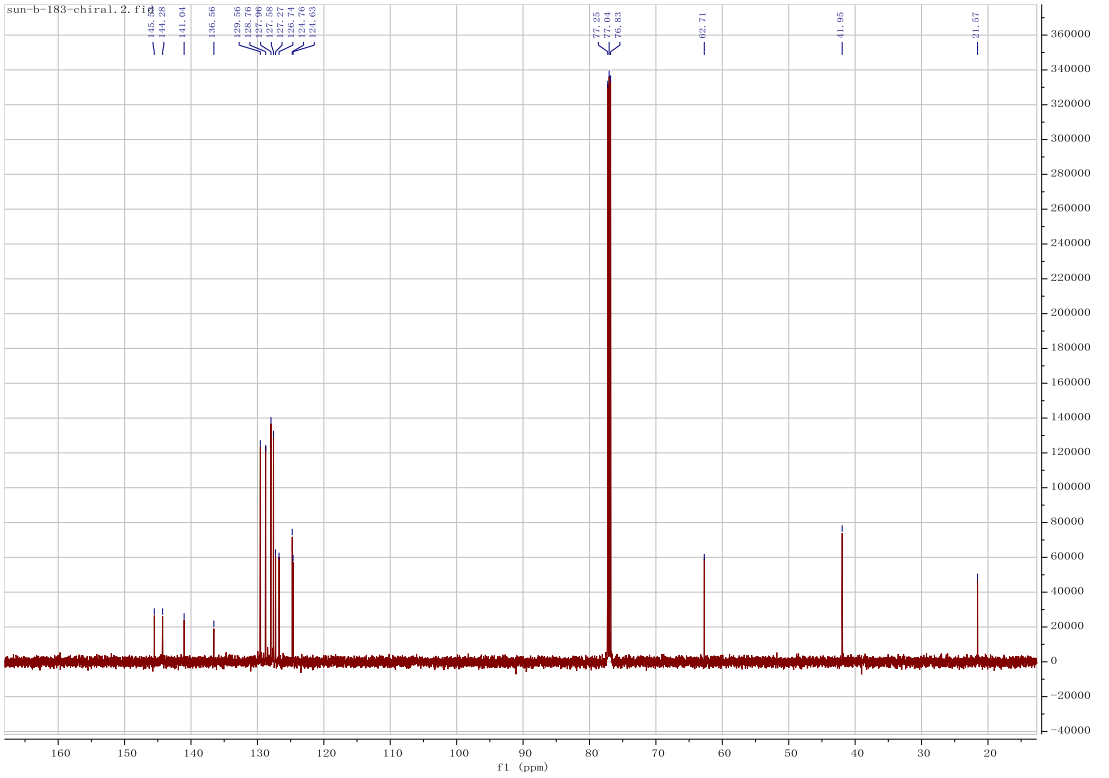
(*S*)-1-methoxy-4-(2-methyl-3-tosylpropyl)benzene(**2p**)





(+)-2-(1-phenyl-2-tosylethyl)thiophene(**2q**)





Reference:
[1] Juan C. Carretero, et al. *Angew. Chem. Int. Ed.* **2007**, *46*, 3329-3332.
[2] Takashi Takahashi, et al. *Eur. J. Org. Chem.* **2015**, 4756-4764;
Houda Fillion, et al. *Tetrahedron Letters*, **1992**, *33*, (34), 4909-4910.