Supporting Information

Regiospecific Three-Component Aminofluorination of Olefins via Photoredox Catalysis

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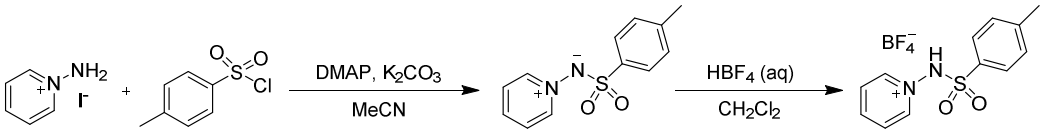
Contents

1. General information

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200−300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. The spectra were recorded in deuterochloroform ($CDCl_3$) and dimethyl-d6 sulfoxide (DMSO-d_6) as solvent at room temperature; ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm, DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.5 ppm). Data for ^{1} H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet, br = broad), integration, coupling constant (Hz), and assignment. Data for ^{13}C NMR are reported as chemical shift. HRMS spectra using ESI were recorded on an ESI-FTMS mass spectrometer.

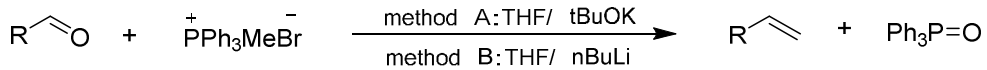
2. Preparation of substrates

(1) Preparation of the *N*-protected 1-aminopyridium salt



To a mixture of 1-aminopyridinium iodide (1 equiv) and distilled-CH_3CN (0.13 M) were added DMAP (10 mol %), K_2CO_3 (3.6 equiv) and sulfonyl chloride (1 equiv) at 0 ^oC under N_2. Then, the cooling bath was removed and the reaction mixture was stirred at R.T. for 6 h. The suspension was filtered and concentrated in vacuo. The residue was suspended in CH_2Cl_2 and filtered to remove inorganic impurities. After the solvent was removed under reduced pressure, the crude product was purified by silica gel flash column chromatography (CH_2Cl_2/MeOH = 10/1) and washed with a small amount of CH_2Cl_2 to afford aminopyridinium ylide. The ylide product (1 equiv) was diluted with CH_2Cl_2 (0.3 M) and tetrafluoroboric acid solution (40 wt.% in H_2O) (1.3 equiv) was added to the solution at R.T.. The mixture was stirred for 30 min, then the product was precipitated. The mixture was filtered, washed with diethyl ether and pentane and dried in vacuo. The pure product was obtained as a white solid.

(2) Preparation of the substituted styrene



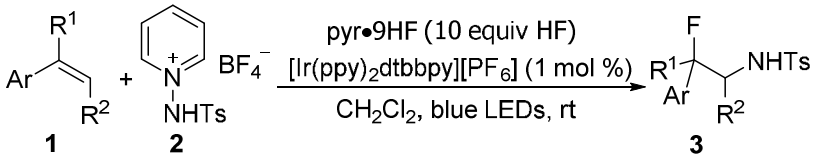
Method A: To a flame-dried round-bottomed flask were added

methyltriphenylphosphonium bromide (1.3 equiv) and THF (13 ml/mmol), *t*BuOK (1.9 equiv) was added in one portion at 0 ℃ under N_2 atomsphere, and the resulting yellow solution was stirred at room temperature for 1 h. When the starting aldehyde was consumed, the solution was filtered over a pad of celite and the residue was washed with Et_2O. The filtrate was concentrated and purified by SiO_2-gel chromatography (PE) to give the desired styrene.

Method B: To a 100 ml two-necked round-bottomed flask charged a solution of methyltriphenylphosphonium bromide (1.2 equiv) in THF (0.2 M) was added ^{n}BuLi (1.2 equiv) at 0 ℃, and the mixture was stirred at 0 ℃ for 15 min-2 h. Then the aromatic aldehyde (1.0 equiv) was added dropwise as a solution in THF (1.25 M). After allowing the solution to warm up to room temperature, the reaction mixture was stirred for another 10-16 h. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography to afford the desired vinylarene.

3. General procedure

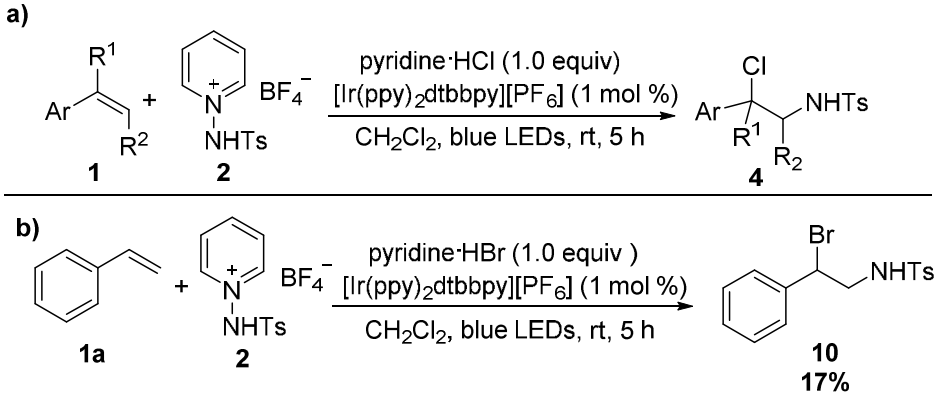
1) Aminofluorination of alkenes



Substrate **1** (0.1 mmol), pyr·9HF (10 equiv HF) and N-protected 1-aminopyridinium **2** (0.175 mmol) were added to a solution of

photocatalyst [Ir(ppy)$_2$dtbbpy][PF$_6$] (1 mol %) in CH_2Cl_2 (2 mL) in a plastic vial at room temperature. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 25 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at room temperature until the starting material was completely consumed after 5-12 h. After completion of the reaction, $NaHCO_3$ (1 mmol, 84mg) was added to the reaction mixture and stirred for 30 mins.Then the resulting mixture was evaporated under reduced pressure, and the resulting crude mixture was purified on silica gel flash column chromatography using petroleum/ethyl acetate (5:1, v/v) eluent to give the pure product **3**.

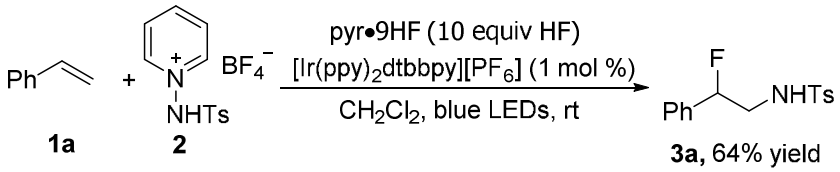
2) Aminochlorination and aminobromination of alkenes



Substrate **1** (0.1 mmol), $C_5H_5N{\cdot}HCl$ or $C_5H_5N{\cdot}HBr$ (0.1 mmol) and N-protected 1-aminopyridinium **2** (0.175 mmol) were added to a solution of photocatalyst [Ir(ppy)$_2$dtbbpy][PF$_6$] (1 mol %) inCH_2Cl_2 (2 mL) at room temperature. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped

with a 25 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at room temperature until the starting material was completely consumed after 5 h. Upon completion of the reaction, the resulting mixture was evaporated under reduced pressure, and the resulting crude mixture was purified on silica gel flash column chromatography using petroleum/ethyl acetate (5:1, v/v) eluent to give the pure product **4** (**10**).

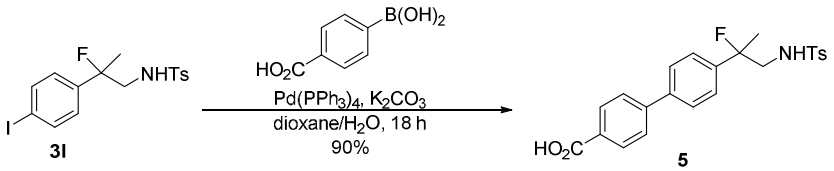
3) Aminofluorination of alkenes at 1 mmol scale (**3a**)



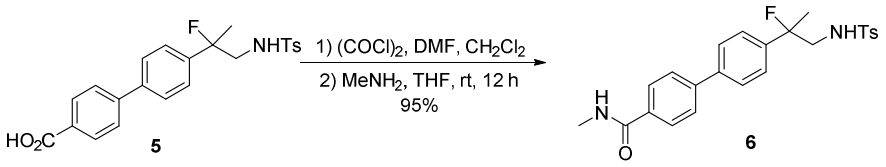
1a **2** **3a,** 64% yield

Substrate **1a** (1 mmol, 0.116ml), pyr·9HF (10 equiv HF, 0.26ml) and N-protected 1-aminopyridinium **2** (0.175 mmol, 588mg) were added to a solution of photocatalyst $[Ir(ppy)_2dtbbpy][PF_6]$ (1 mol %, 9mg) in CH_2Cl_2 (20 mL) in a plastic vial at room temperature. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 25 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at room temperature until the starting material was completely consumed after 12 h. After completion of the reaction, $NaHCO_3$ (10 mmol, 840mg) was added to the reaction mixture and stirred for 30 mins.Then the resulting mixture was evaporated under reduced pressure, and the resulting crude mixture was purified on silica gel flash column chromatography using petroleum/ethyl acetate (5:1, v/v) eluent to give the pure product **3a** (187mg, 64% yield**)**.

4. Synthesis of 6



Into a 50 mL single neck flask, **3l** (0.78 mmol, 33.7mg) 4-Carboxyphenylboronic acid (1.13 mmol, 18.7mg), K_2CO_3 (1.13 mmol, 15.6mg) and $Pd(PPh_3)_4$ (0.05 mmol, 5.8mg) were combined in dioxane/H_2O (30 ml, 3:1). The mixture was then heated at 100 ℃ with stirring for 18 h. The reaction was then cooled to room temperature and poured into H_2O. The desired product was extracted with EA and the organic layer was separated , washed twice with H_2O, dried over K_2CO_3, and concentrated under vacuum to yield the crude material as a tan solid. The crude material was purified via silica gel chromatography (DCM:MeOH = 10:1).

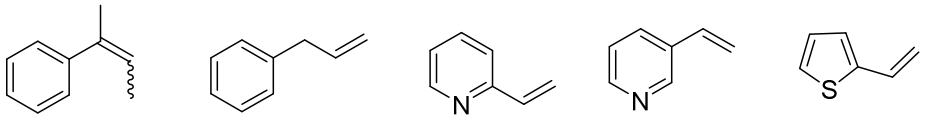


Into a 50 mL single neck flask, 1 ml $(COCl)_2$ was added by syringe to **5** (150 mg, 0.40 mmol) in CH_2Cl_2 (10 mL) while stirring under N_2 at room temperature. Immediately, 1 drop of DMF was added by pipette initiating a foaming of the mixture. The reaction was stirred for 1 h at room temperature and then concentrated under vacuum to yield a white

solid.

This material was placed to THF (10 ml) and added dropwise to a stirring solution of 40% methylamine in water (5 mL) at room temperature. The mixture was stirred overnight and the crude material was purified via silica gel chromatography (DCM:EA = 1:1).

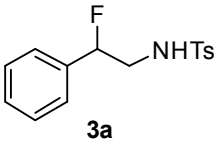
5. Unsuccessful substrates



dr=1:3.2

6. Characterization of products

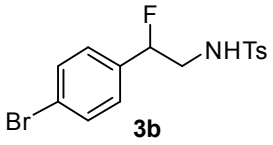
N-(2-fluoro-2-phenylethyl)-4-methylbenzenesulfonamide (3a)



3a

White solid; 24.5mg, 84% yield; reaction time 5 h, mp 54-56□;. ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.43 (s, 3H), 3.20-3.45 (m, 2H), 4.85-4.88 (m, *J* = 8 Hz, 1H), 5.48 (ddd, *J* = 48, 8, 4Hz, 1H), 7.23-7.26 (m, 2H), 7.30-7.32 (m, 2H), 7.34-7.37 (m, 3H), 7.73-7.75 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.4, 48.4 (d, *J* = 25 Hz), 92.6 (d, *J* = 173 Hz), 125.4(d, *J* = 7 Hz), 126.9, 128.5, 128.9, 129.7, 136.3(d, *J* = 19 Hz), 136.8, 143.5; ^{19}F NMR (376MHz, $CDCl_3$) δ (ppm) = -183.31. HRMS (ESI) for $C_{15}H_{16}FNO_2S$ $[M+H]^+$ calcd. 294.0959, found 294.0965.

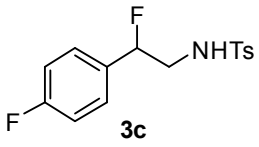
N-(2-(4-bromophenyl)-2-fluoroethyl)-4-methylbenzenesulfonamide (3b)



3b

White solid; 27.5mg, 74% yield; reaction time 5 h, mp 130-132℃; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.43 (s, 3H), 3.20-3.45 (m, 2H), 5.01 (s, 1H), 5.41-5.55 (m, 1H), 7.18 (d, *J* = 8 Hz, 2H), 7.29-7.32 (m, 4H), 7.71 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.5, 48.3 (d, *J* = 25 Hz), 92.0 (d, *J* = 174 Hz), 123.0 (d, *J* = 2.21 Hz), 126.9, 127.1(d, *J* = 7 Hz), 129.8, 131.8, 135.3(d, *J* = 20 Hz), 136.5, 143.8; ^{19}F NMR (376MHz, $CDCl_3$) δ (ppm) = -183.94. HRMS (ESI) for $C_{15}H_{15}BrFNO_2S$ $[M+H]^+$ calcd. 372.0064, found 372.0076.

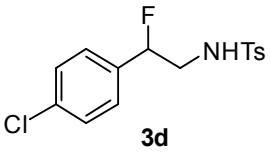
N-(2-fluoro-2-(4-fluorophenyl)ethyl)-4-methylbenzenesulfonamide (3c)



3c

White solid; 26.7mg, 86% yield; reaction time 5 h, mp 90-92℃; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.43 (s, 3H), 3.22-3.44 (m, 2H), 5.13-5.16 (m, 1H), 5.47 (ddd, *J* = 48, 8, 4Hz, 1H), 7.03 (T, *J* = 8Hz, 2H), 7.21-7.25 (m, 2H), 7.30 (d, *J* = 8Hz, 2H), 7.73 (d, *J* = 8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.5, 48.4 (d, *J* = 25 Hz), 92.1 (d, *J* = 173Hz), 115.6 (d, *J* = 21Hz), 126.9, 127.4 (dd, *J* = 7, 8Hz), 129.8, 132.1 (dd, *J* = 4, 20Hz), 136.5, 143.7, 162.9 (d, *J* = 24.5 Hz); ^{19}F NMR (376MHz, $CDCl_3$) δ (ppm) = -112.20 (d, *J* = 3.76 Hz), -181.12 (d, *J* = 3.76 Hz). HRMS (ESI) for $C_{15}H_{15}F_2NO_2S$ $[M+H]^+$ calcd. 312.0864, found 312.0870.

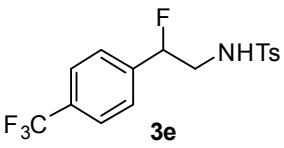
N-(2-(4-chlorophenyl)-2-fluoroethyl)-4-methylbenzenesulfonamide (3d)



3d

White solid; 23.9mg, 73% yield; reaction time 5 h mp, 124-126□;. ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.44 (s, 3H), 3.19-3.46 (m, 2H), 4.91-4.94 (m, 1H), 5.48 (ddd, *J* = 48, 8, 4Hz, 1H), 7.18 (d, *J* = 12Hz, 2H), 7.30-7.34 (m, 4H), 7.12 (d, *J* = 8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.5, 48.3 (d, *J* = 24 Hz), 92.0 (d, *J* = 174 Hz), 126.8(d, *J* = 7 Hz), 126.9, 128.8, 129.8, 134.6, 134.8 (d, *J* = 2.87 Hz), 136.5, 143.8; ^{19}F NMR (376MHz, $CDCl_3$) δ (ppm) = -183.57. HRMS (ESI) for $C_{15}H_{15}ClFNO_2S$ $[M+H]^+$ calcd. 328.0569, found 328.0579.

N-(2-fluoro-2-(4-(trifluoromethyl)phenyl)ethyl)-4-methylbenzenesulfonamide (3e)

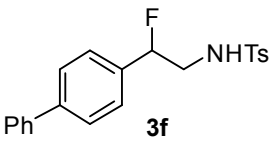


3e

White solid; 23.1mg, 64% yield; reaction time 5 h,mp 114-116□; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.43 (s, 3H), 3.23-3.52 (m, 2H), 4.91-4.94 (m, 1H), 5.58(ddd, *J* = 48, 8, 4Hz, 1H), 7.30 (d, *J* = 8Hz, 2H), 7.38 (d, *J* = 8Hz, 2H), 7.61 (d, *J* = 8Hz, 2H), 7.71 (d, *J* = 8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.5, 48.4 (d, *J* = 25Hz), 92.0 (d, *J* = 175Hz), 122.4, 125.6, 125.7, 125.7, 127.0, 129.8, 131.3, 136.7, 140.4 (d, *J* = 20.55Hz), 143.9; ^{19}F NMR (376MHz, $CDCl_3$) δ (ppm) = -62.78, -186.43. HRMS (ESI) for $C_{16}H_{15}F_4NO_2S$ $[M+H]^+$ calcd. 362.0832, found

362.0844.

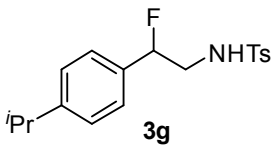
N-(2-([1,1'-biphenyl]-4-yl)-2-fluoroethyl)-4-methylbenzenesulfonamide (3f)



3f

White solid; 21.0mg, 57% yield; reaction time 5 h, mp 166-168□; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.42 (s, 3H), 3.26-3.52 (m, 2H), 4.94-4.97 (m, 1H), 5.54 (ddd, *J* = 48, 8, 4Hz, 1H), 7.30-7.33 (m, 4H), 7.37 (T, 8Hz, 1H), 7.45 (T, 8Hz, 2H), 7.55-7.59 (m, 4H), 7.75 (d, *J* = 8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.4, 48.5 (d, *J* = 26 Hz), 92.5 (d, *J* = 173Hz), 125.9 (d, *J* = 7Hz), 127.0, 127.0, 127.3, 127.6, 128.8, 129.8, 135.2(d, *J* = 20 Hz), 136.8, 140.2, 142.0 (d, *J* = 1.82Hz), 143.7; ^{19}F NMR (376MHz, $CDCl_3$) δ (ppm) = -182.85. HRMS (ESI) for $C_{21}H_{20}FNO_2S$ $[M+H]^+$ calcd. 370.1272, found 370.1281.

N-(2-fluoro-2-(4-isopropylphenyl)ethyl)-4-methylbenzenesulfonamide (3g)

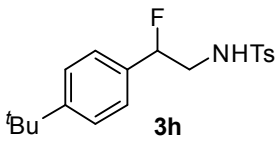


3g

White solid; 26mg, 78% yield; reaction time 5 h mp 96-98□;. ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 1.23 (d, *J* = 8Hz, 6H), 2.43 (s, 3H), 2.86-2.93 (m, 1H), 3.22-3.45 (m, 2H), 4.91-4.94 (m, 1H), 5.44 (ddd, *J* = 48, 8, 4 Hz, 1H), 7.17 (d, *J* = 8 Hz, 2H), 7.22 (d, *J* = 8 Hz, 2H), 7.31 (d, *J* = 8 Hz, 2H), 7.74 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.6, 23.9, 34.0, 48.6 (d, *J* = 25 Hz), 92.8 (d, *J* = 172Hz), 125.7 (d, *J* = 7Hz), 126.9,

127.1, 129.9, 133.7(d, J = 20 Hz), 136.8, 143.8, 150.1; ^{19}F NMR (376MHz, $CDCl_3$) δ (ppm) = -181.34. HRMS (ESI) for $C_{18}H_{22}FNO_2S$ $[M+H]^+$ calcd. 336.1428, found 336.1436.

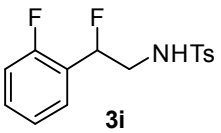
N-(2-(4-(tert-butyl)phenyl)-2-fluoroethyl)-4-methylbenzenesulfonamide (3h)



3h

White solid; 24.5mg, 70% yield; reaction time 5 h mp 122-124□;^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 1.3 (s, 9H), 2.43 (s, 3H), 3.22-3.45 (m, 2H), 5.01-5.04 (m, 1H), 5.45 (ddd, J = 48, 8, 4Hz, 1H), 7.19 (d, J = 8Hz, 2H), 7.31 (d, J = 8Hz, 2H), 7.38 (d, J = 8Hz, 2H), 7.75 (d, J = 8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.4, 31.1, 34.5, 48.4 (d, J = 25Hz), 92.6 (d, J = 172Hz), 125.3 (d, J = 7Hz), 125.5, 127.0, 129.7, 133.2 (d, J = 20Hz), 136.6, 143.6, 125.1 (d, J = 2Hz); ^{19}F NMR (376MHz, $CDCl_3$) δ (ppm) = -181.51. HRMS (ESI) for $C_{19}H_{24}FNO_2S$ $[M+H]^+$ calcd. 350.1585, found 350.1592.

N-(2-fluoro-2-(2-fluorophenyl)ethyl)-4-methylbenzenesulfonamide (3i)

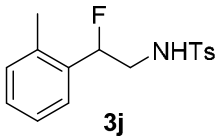


3i

White solid; 13.7mg, 44% yield; reaction time 8 h mp 52-54□;^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.43 (s, 3H), 3.27-3.58 (m, 2H), 5.00-5.03 (m, 1H), 5.70 (ddd, J = 48, 8, 3Hz, 1H), 7.03 (t, J = 12Hz, 1H), 7.16 (t, J = 4Hz, 1H), 7.30-7.35 (m, 4H), 7.75 (d, J = 8, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.5,

47.3(d, J = 25 Hz), 87.7 (dd, J = 3, 173 Hz), 115.5 (d, J = 21 Hz), 123.6 (dd, J = 13, 21 Hz), 124.4 (d, J = 3 Hz), 127.0, 127.1 (dd, J = 4, 9 Hz), 129.8, 130.6 (dd, J = 1, 9Hz), 136.7, 143.6, 159.0(dd, J = 6, 24 Hz); ^{19}F NMR (376MHz, $CDCl_3$)δ (ppm) = -117.95, -190.07. HRMS (ESI) for $C_{15}H_{15}F_2NO_2S$ $[M+H]^+$ calcd. 312.0864, found 312.0872.

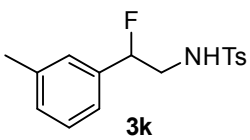
N-(2-fluoro-2-(o-tolyl)ethyl)-4-methylbenzenesulfonamide (3j)



3j

White solid; 18.7mg, 61% yield; reaction time 5 h, mp 72-74□; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.25 (s, 3H), 2.42 (s, 3H), 3.15-3.44 (m, 2H), 5.18-5.22 (m, 1H), 5.68 (ddd, J = 48, 8, 4Hz, 1H), 7.13 (d, J = 4Hz, 1H), 7.18-7.23 (m, 2H), 7.25-7.27 (m, 1H), 7.30 (d, J = 8Hz, 2H), 7.76 (d, J = 8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 18.7, 21.4, 47.6(d, J = 25 Hz), 90.4(d, J = 171 Hz), 125.0(d, J = 9 Hz), 126.2, 126.9, 128.7 (d, J = 1.67Hz), 129.7, 130.5, 134.4(d, J = 4 Hz), 134.5(d, J = 28 Hz), 136.8, 143.6; ^{19}F NMR (376MHz, $CDCl_3$) δ (ppm) =-185.31. HRMS (ESI) for $C_{16}H_{18}FNO_2S$ $[M+H]^+$ calcd. 308.1115, found 308.1123.

N-(2-fluoro-2-(m-tolyl)ethyl)-4-methylbenzenesulfonamide (3k)

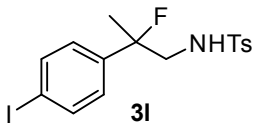


3k

White solid; 23.9mg, 78% yield; reaction time 5 h, mp 54-56□; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.32 (s, 3H), 2.42 (s, 3H), 3.21-3.45 (m, 2H), 5.13-5.16(m, 1H), 5.44 (ddd, J = 48, 8, 4Hz, 1H), 7.03 (d, J = 4Hz, 2H), 7.14 (d, J = 8Hz, 1H), 7.23 (t, J = 8Hz, 1H), 7.30 (d, J = 8Hz, 2H), 7.74 (d, J = 8Hz,

2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.4, 21.5, 48.6 (d, *J* = 25Hz), 92.8 (d, *J* = 172Hz), 122.6 (d, *J* = 7Hz), 126.2 (d, *J* = 7Hz), 127.0, 128.6, 129.8, 129.8, 136.3 (d, *J* = 19Hz), 136.8, 138.5, 142.7; ^{19}F NMR (376MHz, $CDCl_3$) δ (ppm) = -182.75. HRMS (ESI) for $C_{16}H_{18}FNO_2S$ $[M+H]^+$ calcd. 308.1115, found 308.1123.

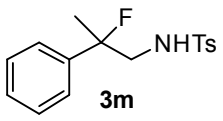
N-(2-fluoro-2-(4-iodophenyl)propyl)-4-methylbenzenesulfonamide(3l)



3l

White solid; 32.2mg, 74% yield; reaction time 5 h, mp 132-134□; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 1.65 (d, *J* = 24Hz, 3H), 2.43 (s, 3H), 3.20-3.41 (m, 2H), 4.81(t, *J* = 8Hz, 1H), 6.97 (d, *J* = 8Hz, 2H), 7.25-7.27 (m, 2H), 7.60-7.63 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.5, 24.5 (d, *J* = 24Hz), 51.7 (d, *J* = 23Hz), 93.7, 96.3 (d, *J* = 175Hz), 126.1 (d, *J* = 10Hz), 126.8, 129.7, 136.5, 137.4 (d, *J* = 1Hz), 140.9(d, *J* = 21Hz), 143.5; ^{19}F NMR (376MHz, $CDCl_3$)δ (ppm) = -153.86. HRMS (ESI) for $C_{16}H_{17}FINO_2S$ $[M+H]^+$ calcd. 434.0081, found 434.0095.

N-(2-fluoro-2-phenylpropyl)-4-methylbenzenesulfonamide (3m)

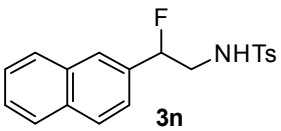


3m

White solid; 23.3mg, 76% yield; reaction time 5 h, mp 94-96□; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 1.69 (d, *J* = 24Hz , 3H), 2.41 (s, 3H), 3.21-3.42 (m, 2H), 4.84 (t, *J* = 8Hz, 1H), 7.25-7.27 (m, 4H), 7.29-7.35 (m, 3H), 7.67 (d, *J* = 12Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.4, 24.4 (d, *J* = 24Hz), 52.0 (d, *J* = 24Hz), 96.5 (d, *J* = 174Hz), 124.0 (d, *J* = 10Hz), 126.8, 127.9 (d, *J* = 1.13Hz),

128.4 (d, J = 1.46Hz), 129.6, 136.6, 141.2(d, J = 22Hz), 143.4; ^{19}F NMR (376MHz, $CDCl_3$) δ (ppm) = -153.12. HRMS (ESI) for $C_{16}H_{18}FNO_2S$ $[M+H]^+$ calcd. 308.1115, found 308.1121.

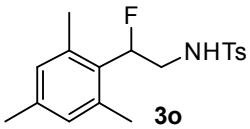
N-(2-fluoro-2-(naphthalen-2-yl)ethyl)-4-methylbenzenesulfonamide (3n)



3n

White solid; 14.1mg, 41% yield; reaction time 8 h, mp 106-108□; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.40 (s, 3H), 3.32-3.57 (m, 2H), 4.92-4.95 (m, 1H), 5.66 (ddd, J = 48, 8, 4Hz, 1H), 7.25 (s, 1H), 7.27 (s, 1H), 7.32 (d, J = 8Hz, 1H), 7.49-7.54 (m, 2H), 7.70-7.72 (m, 3H), 7.80-7.84 (m, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.5, 48.5 (d, J = 25Hz), 92.8 (d, J = 173Hz), 122.5 (d, J = 6Hz), 125.0 (d, J = 8Hz), 126.6 (d, J = 5Hz), 126.9, 127.7, 128.0, 128.6, 129.7, 132.8, 133.3, 133.5 (d, J = 20Hz), 136.6, 143.7; ^{19}F NMR (376MHz, $CDCl_3$) δ (ppm) = -183.19. HRMS (ESI) for $C_{19}H_{18}FNO_2S$ $[M+H]^+$ calcd. 344.1115, found 344.1124.

N-(2-fluoro-2-mesitylethyl)-4-methylbenzenesulfonamide (3o)

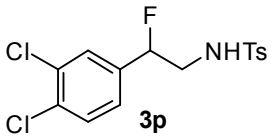


3o

White solid; 15.8mg, 47% yield; reaction time 8 h, mp 74-76□; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.23 (s, 9H), 2.43 (s, 3H), 3.17-3.32 (m, 1H), 3.41-3.51 (m, 1H), 5.04-5.07 (m, 1H), 5.81 (ddd, J = 48, 8, 4Hz, 1H), 6.80 (s, 2H), 7.31 (d, J = 8Hz, 2H), 7.76 (d, J = 8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 20.2, 20.2, 20.8, 21.5, 45.9 (d, J = 24Hz), 91.6 (d, J = 172Hz),

127.0, 129.0 (d, J = 18Hz), 129.8, 130.1, 136.0 (d, J = 4Hz), 136.9, 138.4 (d, J = 1.45Hz), 143.7; ^{19}F NMR (376MHz, $CDCl_3$) δ (ppm) = -187.76. HRMS (ESI) for $C_{18}H_{22}FNO_2S$ $[M+K]^+$ calcd. 374.0987, found 374.0997.

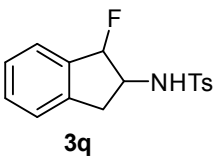
N-(2-(3,4-dichlorophenyl)-2-fluoroethyl)-4-methylbenzenesulfonamide (3p)



3p

White solid; 12.3mg, 34% yield; reaction time 8 h, mp 112-114□; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.44 (s, 3H), 3.20-3.48 (m, 2H), 5.02-5.05 (m, 1H), 5.47 (ddd, J = 48, 8, 4Hz, 1H), 7.07-7.10 (dd, J = 4, 8Hz, 1H), 7.29-7.32 (m, 3H), 7.41 (d, J = 8Hz, 1H), 7.69 (d, J = 8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.5, 48.2 (d, J = 25Hz), 91.3 (d, J = 175Hz), 124.7 (d, J = 7Hz), 126.8, 127.4 (d, J = 8Hz), 129.8, 130.6, 132.9, 133.11, 136.4(d, J = 20Hz), 136.4, 143.9; ^{19}F NMR (376MHz, $CDCl_3$) δ (ppm) = -184.86. HRMS (ESI) for $C_{15}H_{14}Cl_2FNO_2S$ $[M+H]^+$ calcd. 362.0179, found 362.0189.

N-(1-fluoro-2,3-dihydro-1H-inden-2-yl)-4-methylbenzenesulfonamide (3q)

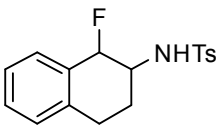


3q

White solid; 23.5mg, 77% yield; reaction time 12 h, mp 126-128□; ^{1}H NMR (400MHz, $CDCl_3$) (major isomer) δ (ppm) = 2.46 (s, 3H), 2.89-2.94(m, 1H), 3.09-3.13(m, 1H), 4.05-4.14 (m, 1H), 5.28 (dd, J = 4, 32Hz, 1H), 5.34(d, J = 4Hz, 1H), 7.21-7.23(m, 1H), 7.25(d, J = 4Hz, 1H), 7.34-7.40(m, 4H), 7.83(d, J =

4Hz, 2H); (minor isomer) δ (ppm)=2.45 (s, 3H), 2.70-2.74(m, 1H), 3.34-3.38(m, 1H), 4.07-4.15(m, 1H), 5.02(d, *J* = 4Hz, 1H), 5.73(dd, *J* = 4, 32Hz, 1H), 7.19 (d, *J* = 4Hz, 1H), 7.28 (d, *J* = 8Hz, 1H), 7.32-7.33(m, 3H), 7.38(d, *J* = 4Hz, 1H), 7.81(d, *J* = 4Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) (major isomer)δ (ppm) = 21.6, 36.8, 55.7(d, *J* = 20Hz), 93.5(d, *J* = 177Hz), 125.1(d, *J* = 3Hz), 126.4(d, *J* = 3Hz), 127.1, 127.5(d, *J* = 4Hz), 129.9, 131.0(d, *J* = 5Hz), 136.7(d, *J* = 15Hz),137.6, 142.2(d, *J* = 5Hz), 143.8; (minor isomer) δ (ppm)=21.6, 36.9, 60.1(d, *J* = 23Hz), 99.5(d, *J* = 182Hz), 125.1(d, *J* = 25Hz), 126.4(d, *J* = 3Hz), 127.2, 127.5(d, *J* = 2Hz), 129.8, 130.0(d, *J* = 3Hz), 137.0, 137.4(d, *J* = 19Hz), 140.0(d, *J* = 5Hz), 143.7; ^{19}F NMR (376MHz, $CDCl_3$) (major isomer)δ (ppm) = -177.77; (minor isomer) δ (ppm)=-171.51. HRMS (ESI) for $C_{16}H_{16}FNO_2S$ $[M+H]^+$ calcd. 306.0959, found 306.0968.

N-(1-fluoro-1,2,3,4-tetrahydronaphthalen-2-yl)-4-methylbenzenesulfonamide(3r)

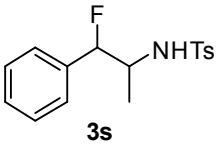


3r

White solid; 15.3mg, 48% yield; reaction time 12 h, mp 108-110□; ^{1}H NMR (400MHz, $CDCl_3$) (major isomer) δ (ppm) = 1.84-1.87(m, 1H), 1.96-2.05(m, 1H), 2.44(s, 3H), 2.77-2.84(m, 1H), 2.89-2.93(m, 1H), 3.61-3.71(m, 1H), 5.17(dd, *J* = 4, 36Hz, 1H), 5.19(d, *J* = 4Hz, 1H), 7.12(d, *J* = 4Hz, 1H), 7.19-7.22(m, 1H), 7.24(d, *J* = 4Hz, 1H), 7.29-7.33(m, 3H), 7.81(d, *J* = 8Hz, 1H); (minor isomer) δ (ppm)=1.74-1.79(m, 1H), 2.22-2.28(m, 1H),2.44(s, 3H),

2.78-2.87(m, 2H), 3.72-3.78(m, 1H), 4.86(d, *J* = 4Hz, 1H); 5.24(dd, *J* = 4, 36Hz, 1H), 7.11(d, *J* = 4Hz, 1H), 7.21-7.23(m, 1H), 7.28-7.32(m, 4H), 7.77(d, *J* = 4Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) (major isomer)δ (ppm) = 24.5, 24.7, 28.2, 52.9(d, *J* = 12Hz), 89.2(d, *J* = 113Hz), 126.4, 126.9, 128.8, 129.8, 130.0, 131.0, 131.3(d, *J* = 12Hz), 136.6, 138.2, 143.5; (minor isomer) δ (ppm) = 21.5, 24.9, 25.3, 52.7(d, *J* = 16Hz), 90.0(d, *J* = 117Hz), 126.6, 127.1, 128.7, 129.3, 129.6, 129.7, 131.2(d, *J* = 11Hz), 134.4, 136.0, 143.6; ^{19}F NMR (376MHz, $CDCl_3$) (major isomer)δ (ppm) = -168.71; (minor isomer) δ (ppm)=-163.89. HRMS (ESI) for $C_{17}H_{18}FNO_2S$ $[M+H]^+$ calcd. 320.1115, found 320.1124.

N-(1-fluoro-1-phenylpropan-2-yl)-4-methylbenzenesulfonamide (3s)

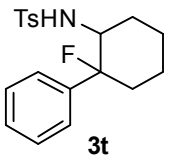


3s

Colorless liquid; 17.2 mg, 56% yield; reaction time 12 h; ^{1}H NMR (400MHz, $CDCl_3$) (major isomer)δ (ppm) = 0.95(d, *J* = 4Hz, 3H), 2.43 (s, 3H), 3.68-3.75(m, 1H), 4.78(d, *J* = 8Hz, 1H), 5.45(dd, *J* = 4, 32Hz, 1H), 7.18(d, *J* = 8Hz, 2H), 7.29-7.31(m, 3H), 7.33-7.35(m, 2H),7.77(d, *J* = 4Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) (major isomer)δ (ppm) = 14.2(d, *J* = 6Hz), 21.5, 54.0(d, *J* = 23Hz), 95.3(d, *J* = 178Hz), 125.0(d, *J* = 8Hz), 126.9, 128.3, 128.4(d, *J* = 1Hz), 129.8, 136.5(d, *J* = 20Hz), 137.9, 143.5; (minor isomer) δ (ppm) = 17.3(d, *J* = 3Hz), 21.5, 53.3(d, *J* = 25Hz), 95.1(d, *J* = 177Hz), 126.0(d, *J* = 8Hz), 126.9, 128.3, 128.6(d, *J* = 1Hz), 129.5, 135.8(d, *J* = 20Hz), 137.3, 143.3; ^{19}F NMR (376MHz, $CDCl_3$) (major isomer)δ (ppm)

=-187.64; (minor isomer) δ (ppm)=-199.84. HRMS (ESI) for $C_{16}H_{18}FNO_2S$ $[M+H]^+$ calcd. 308.1115, found 308.1122.

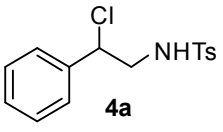
N-(2-fluoro-2-phenylcyclohexyl)-4-methylbenzenesulfonamide(3t)



3t

Brown liquid; 17.5mg, 50% yield; reaction time 12 h; ^{1}H NMR (400MHz, $CDCl_3$) (major isomer) δ (ppm) = 1.41-1.47(m, 1H), 1.59-1.84(m, 5H), 1.99-2.04(m, 1H), 2.14-2.18(m, 1H), 2.37(s, 3H), 3.46-3.60(m, 1H), 4.51(d, *J* = 8Hz, 1H), 7.02(d, *J* = 8Hz, 2H), 7.07-7.17(m, 5H), 7.23-7.26(m, 2H); (minor isomer) δ (ppm) = 1.56-1.59(m, 2H), 1.67-1.70(m, 2H), 1.86-2.13(m, 4H), 2.39(s, 3H), 3.49-3.53(m, 1H), 4.66(d, *J* = 8Hz, 1H), 7.07(d, *J* = 8Hz, 2H), 7.17-7.19(m, 4H), 7.22-7.24(m, 1H), 7.30(d, *J* = 8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) (major isomer)δ (ppm) = 18.9, 20.8(d, *J* = 1Hz), 21.5, 24.4, 31.2(d, *J* = 2Hz), 58.0(d, *J* = 21Hz), 98.0(d, *J* = 178Hz), 123.7(d, *J* = 10 Hz), 126.6, 126.8, 128.2, 129.3, 137.5, 141.7(d, *J* = 22Hz), 142.6; (minor isomer) δ (ppm) = 18.9, 20.5(d, *J* = 3.7Hz), 21.5, 27.7, 38.5(d, *J* = 23Hz), 56.5(d, *J* = 36Hz), 95.0(d, *J* = 173Hz), 125.3(d, *J* = 8Hz), 126.4, 127.2, 128.1, 129.5, 136.3, 140.8(d, *J* = 21Hz), 142.9; ^{19}F NMR (376MHz, $CDCl_3$) (major isomer)δ (ppm) =-148.22; (minor isomer) δ (ppm)=-178.22. HRMS (ESI) for $C_{19}H_{22}FNO_2S$ $[M+H]^+$ calcd. 348.1428, found 348.1435.

N-(2-chloro-2-phenylethyl)-4-methylbenzenesulfonamide (4a)

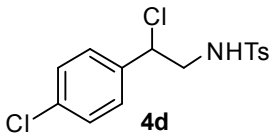


4a

White solid; 20.4mg, 66% yield; reaction time 5 h, mp

76-78□; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.44 (s, 3H), 3.39-3.52 (m, 2H), 4.79 (t, *J* = 8Hz, 1H), 4.86 (dd, *J* = 8, 8Hz, 1H), 7.27-7.29 (m, 2H), 7.31 (s, 1H), 7.33-7.36 (m, 4H), 7.73 (d, *J* = 8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.5, 50.3, 61.6, 127.0, 127.1, 128.9, 129.1, 129.8, 136.9, 137.7, 143.8. HRMS (ESI) for $C_{15}H_{16}ClNO_2S$ $[M+H]^+$ calcd. 310.0663, found 310.0672.

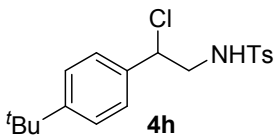
N-(2-chloro-2-(4-chlorophenyl)ethyl)-4-methylbenzenesulfonamide (4d)



4d

White solid; 19mg, 55% yield; reaction time 5 h, mp 76-78□; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.44 (s, 3H), 3.35-3.48 (m, 2H), 4.85-4.88 (m, 1H), 4.95 (t, *J* = 8Hz, 1H), 7.21-7.24 (m, 2H), 7.29-7.32 (m, 4H), 7.71 (d, *J* = 8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.5, 50.2, 60.7, 126.9, 128.5, 129.0, 129.8, 134.9, 136.2, 136.7, 143.9. HRMS (ESI) for $C_{15}H_{15}Cl_2NO_2S$ $[M+H]^+$ calcd. 344.0273, found 344.0284.

N-(2-(4-(tert-butyl)phenyl)-2-chloroethyl)-4-methylbenzenesulfonamide (4h)

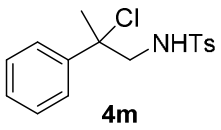


4h

White solid; 26.7mg, 55% yield; reaction time 5 h, mp 90-92□; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) =1.30 (s, 9H), 2.44 (s, 3H), 3.38-3.50 (m, 2H), 4.83-4.87 (m, 1H), 4.96 (t, *J* = 8Hz, 1H), 7.21 (d, *J* = 8Hz, 2H), 7.31-7.36 (m, 4H), 7.74 (d, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.6, 31.2,

34.7, 50.2, 61.5, 125.9, 126.9, 127.1, 129.9, 134.7, 136.9, 143.8, 152.3. HRMS (ESI) for $C_{19}H_{24}ClNO_2S$ $[M+H]^+$ calcd. 366.1289, found 366.1297.

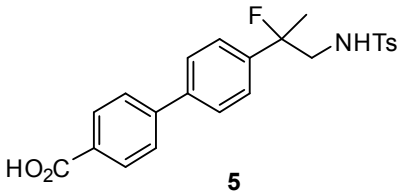
N-(2-chloro-2-phenylpropyl)-4-methylbenzenesulfonamide (4m)



4m

White solid; 26.7mg, 55% yield; reaction time 5 h, mp 66-68□; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 1.97 (s, 3H), 2.42 (s, 3H), 3.39-3.50 (m, 2H), 4.81 (t, *J* = 8Hz, 1H), 7.28-7.36 (m, 5H), 7.45-7.48 (m, 2H), 7.68 (d, *J* = 8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 21.5, 29.0, 55.4, 71.9, 126.1, 127.0, 128.3, 128.6, 129.8, 136.7, 141.7, 143.6. HRMS (ESI) for $C_{16}H_{18}ClNO_2S$ $[M+H]^+$ calcd. 324.0820, found 324.0827.

4'-(2-fluoro-1-((4-methylphenyl)sulfonamido)propan-2-yl)-[1,1'-biphenyl]-4-carboxylic acid (5)

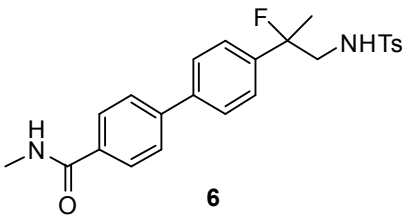


5

White solid; 38.5mg, 90% yield; reaction time 5 h, mp 183-185□; ^{1}H NMR (400MHz, d_6-DMSO) δ (ppm) = 1.63(d, *J* = 20Hz, 3H), 2.33 (s, 3H), 3.16-3.26 (m, 2H), 7.33(d, *J* = 8Hz, 2H), 7.45(d, *J* = 8Hz, 2H), 7.65(d, *J* = 8Hz, 2H), 7.71(d, *J* = 8Hz, 2H), 7.80(d, *J* = 8Hz, 2H), 7.87-7.90 (m, 1H), 8.03 (d, *J* = 8Hz, 2H); ^{13}C NMR (100MHz, d_6-DMSO) δ (ppm) =20.9, 24.4(d, *J* = 24Hz), 51.52(d, *J* = 25Hz), 96.5 (d, *J* = 174Hz), 125.2 (d, *J* = 9 Hz), 126.4, 126.7,

126.8, 129.5, 129.9, 137.9, 138.3, 141.8, 142.1, 142.5, 143.6, 167.2; ^{19}F NMR (376MHz, d_6-DMSO) δ (ppm) = -149.37. HRMS (ESI) for $C_{23}H_{22}FNO_4S$ $[M+H]^+$ calcd. 428.1326, found 428.1338.

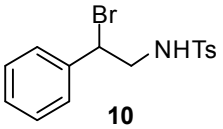
4'-(2-fluoro-1-((4-methylphenyl)sulfonamido)propan-2-yl)-N-methyl-[1,1'-biphenyl]-4-carboxamide (6)



6

White solid; 41.8mg, 90% yield; reaction time 5 h, mp 186-188□; ^{1}H NMR (400MHz, d_6-DMSO) δ (ppm) = 1.64(d, *J* = 24Hz, 3H), 2.34 (s, 3H), 2.81(d, *J* = 4Hz, 3H), 3.12-3.23 (m, 2H), 7.34 (d, *J* = 8Hz, 2H), 7.44(d, *J* = 12Hz, 2H), 7.66(d, *J* = 8Hz, 2H), 7.72 (d, *J* = 8Hz, 2H), 7.77 (d, *J* = 8Hz, 2H), 7.89(d, *J* = 4Hz, 1H), 7.94 (d, *J* = 8Hz, 2H), 8.51(q, *J* = 8Hz, 1H); ^{13}C NMR (100MHz, d_6-DMSO) δ (ppm) =21.3, 24.8 (d, *J* = 24Hz), 26.7, 52.0 (d, *J* = 24Hz), 96.9 (d, *J* = 174Hz), 125.6 (d, *J* = 9Hz), 126.9, 127.1, 128.2, 129.9, 133.8, 138.3, 138.9, 142.0, 142.2, 142.4, 142.9, 166.7; ^{19}F NMR (376MHz, d_6-DMSO) δ (ppm) = -149.32; HRMS (ESI) for $C_{24}H_{25}FN_2O_3S$ $[M+H]^+$ calcd. 441.1643, found 441.1656.

N-(2-bromo-2-phenylethyl)-4-methylbenzenesulfonamide(10)



10

White solid; 6.1mg, 17% yield, mp 94-96□; reaction time 5 h; ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 2.45 (s, 3H), 3.50-3.63 (m, 2H), 4.81 (t, *J* = 8Hz, 1H), 4.90 (t, *J* = 8Hz, 1H), 7.27-7.29 (m, 2H), 7.32-7.34 (m, 5H), 7.73 (d, *J* = 8Hz, 2H);

^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) = 24.6, 50.0, 52.6, 127.0, 127.6, 129.0, 129.2, 129.9, 136.8, 138.0, 143.9. HRMS (ESI) for $C_{15}H_{16}BrNO_2S$ $[M+H]^+$ calcd. 354.0158, found 354.0171.

7. Determination of the Quantum Yield

(1) Determination of light intensity

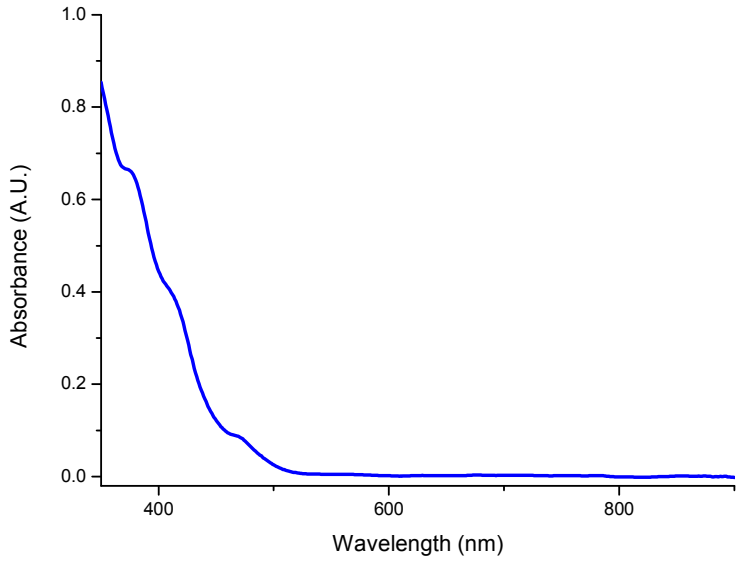


Figure S1. Absorbance of a 1.0 × 10^{-4} M solution of [Ir $(ppy)_2(dtbbpy)](PF_6)$ in CH_2Cl_2

(2) Determination of the light intensity at 420 nm

According to the procedure of Yoon[1] and Glorius,[2] the photon flux of the LED was determined by standard ferrioxalate actinometry.[3] A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (2.21 g) in H_2SO_4 (30 mL of a 0.05 M solution). A buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (50 mg) and sodium acetate (11.25 g) in H_2SO_4 (50

mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the LED, the ferrioxalate solution (2.0 mL) was placed in a Quartz tube and irradiated for 90 s at λmax = 420 nm (**figure S1**). After irradiation, the phenanthroline solution (0.35 mL) was added to the Quartz tube and the mixture was allowed to stir in the dark for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A nonirradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq. 1.

$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} \quad (1)$$

where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 $Lmol^{-1}cm^{-1}$).

The photon flux can be calculated using eq. 2.

$$\text{photo flux} = \frac{\text{mol } Fe^{2+}}{\Phi \cdot t \cdot f} \quad (2)$$

where Φ is the quantum yield for the ferrioxalate actinometer (1.12 at λex = 420 nm), t is the irradiation time (90 s), and f is the fraction of light absorbed at λex = 420 nm by the ferrioxalate actinometer. This value is calculated using eq. 3 where A(420 nm) is the absorbance of the

ferrioxalate solution at 420 nm.

$$f = 1 - 10^{-A(420\ nm)} \quad (3)$$

Sample calculation:

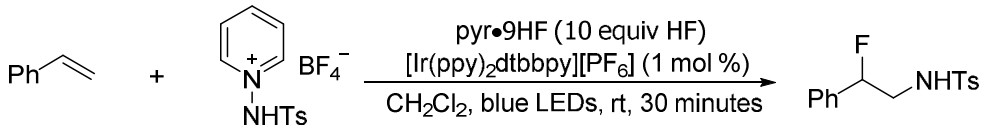
$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} = \frac{0.00235L \cdot 1.127}{1cm \cdot 11100L\ mol^{-1}\ cm^{-1}} = 2.39 \times 10^{-7} mol$$

$$f = 1 - 10^{-A(420\ nm)} = 1 - 10^{-2.403} = 0.996$$

$$\text{photo flux} = \frac{\text{mol } Fe^{2+}}{\Phi \cdot t \cdot f} = \frac{2.39 \times 10^{-7}}{1.12 \cdot 90.0s \cdot 0.99605}$$

$$= 2.38 \times 10^{-9}\ einstein \cdot s^{-1}$$

（3）Determination of the reaction quantum yield at 420 nm



1a, 1.0 equiv. **2, 1.75 equiv.** **3a, 5%**

Substrate **1a** (0.1 mmol), pyr·9HF (10 equiv HF) and N-protected 1-aminopyridinium **2** (0.175 mmol) were added to a solution of photocatalyst [Ir(ppy)$_2$dtbbpy][PF$_6$] (1 mol %) in CH_2Cl_2 (2 mL) in a flame-dried 8 mL Quartz tube at room temperature. The mixture was degassed by three cycles of freeze-pump-thaw. The mixture was stirred under nitrogen atmosphere at room temperature while irradiated by blue light (420 nm) for 30 minutes (1800 s).The reaction was irradiated in Parallel Light Reactor (WP-TEC-1020). After irradiation, the yield of the product **3a** was determined by ^{1}H NMR based on a 1,3,5-trimethoxybenzene standard and the final yield was 5% ($5 \cdot 10^{-6}$ mol).

The reaction quantum yield (Φ) was determined using eq. 4, where the photon flux is $2.38 \cdot 10^{-9}$ E s^{-1} (determined by actinometry as described above), t is the reaction time (1800 s) and f is the fraction of incident light absorbed by the reaction mixture, determined using eq. 3. An absorption spectrum of the reaction mixture gave an absorbance value of > 3 at 420 nm, indicating that essentially all the incident light (f > 0.999) is absorbed by the photocatalyst.

$$\Phi = \frac{\text{mol of product formed}}{\text{photo flux} \cdot t \cdot f} \qquad (4)$$

The reaction quantum yield (Φ) was thus determined to be 1.167.

8. References

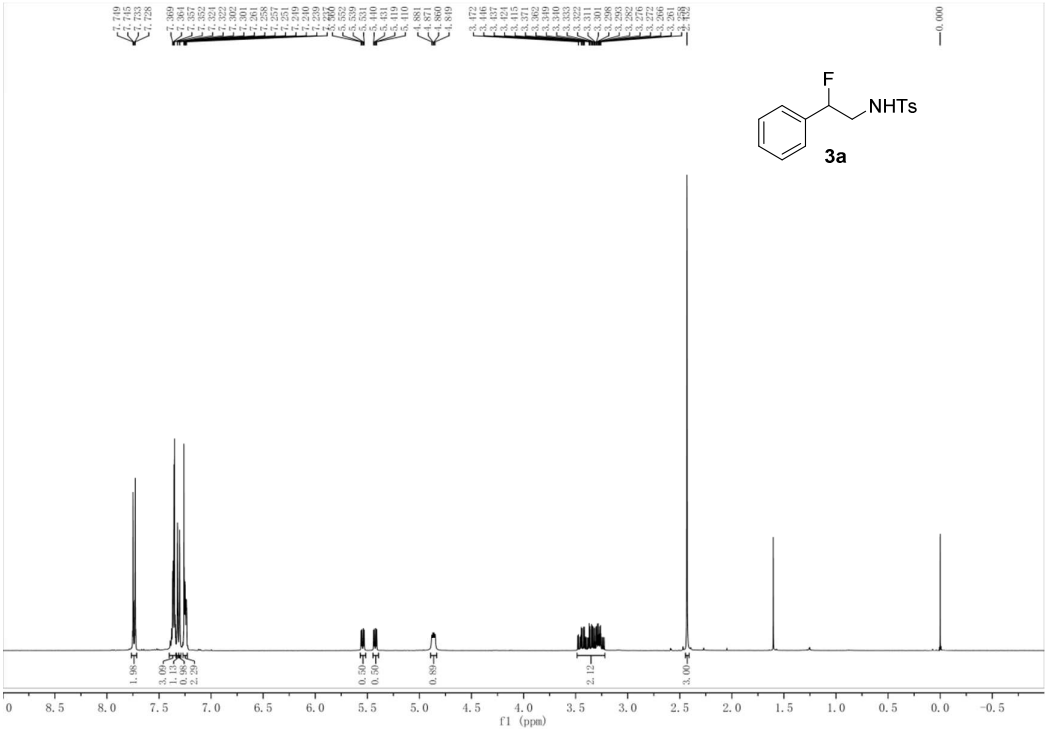
(1) Cismesia, M. A.; Yoon, T. P. *Chem. Sci.* **2015**, *6*, 5426-5434.

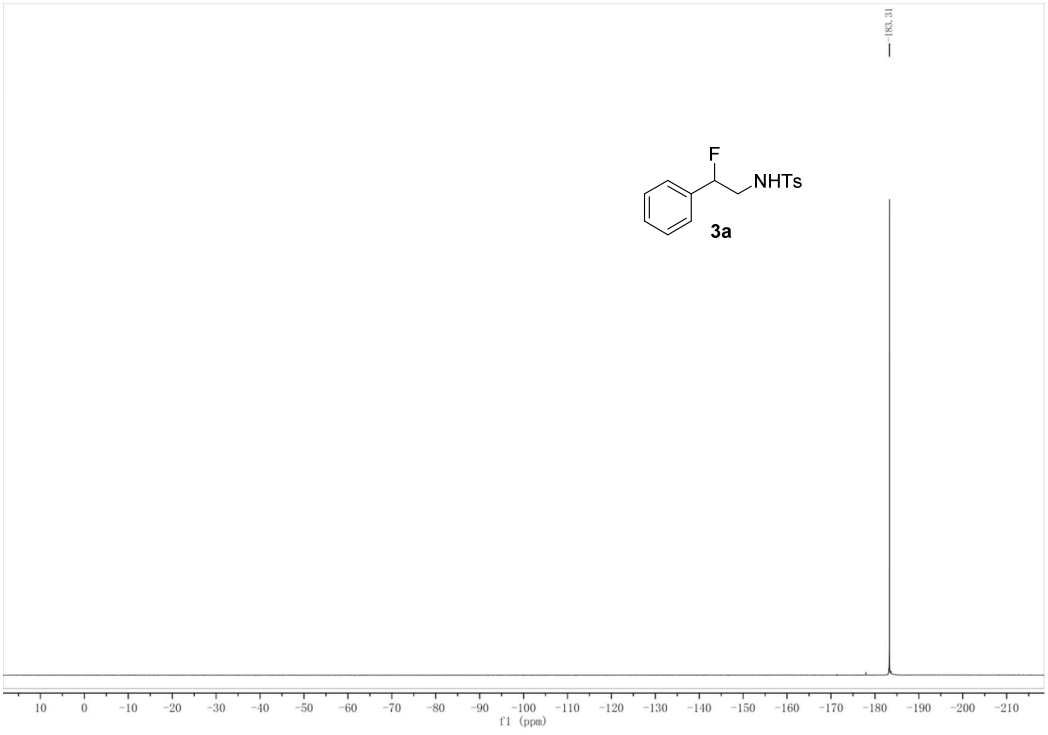
(2) (a) Garza-Sanchez, R. A.; Tlahuext-Aca, A.; Tavakoli, G.; Glorius, F. *ACS catal.* **2017**, *7*, 4057-4061. (b) Klauck, F. J. R.; James, M. J.; Glorius, F. *Angew. Chem. Int. Ed.* **2017**, *56*, 12336 –12339.

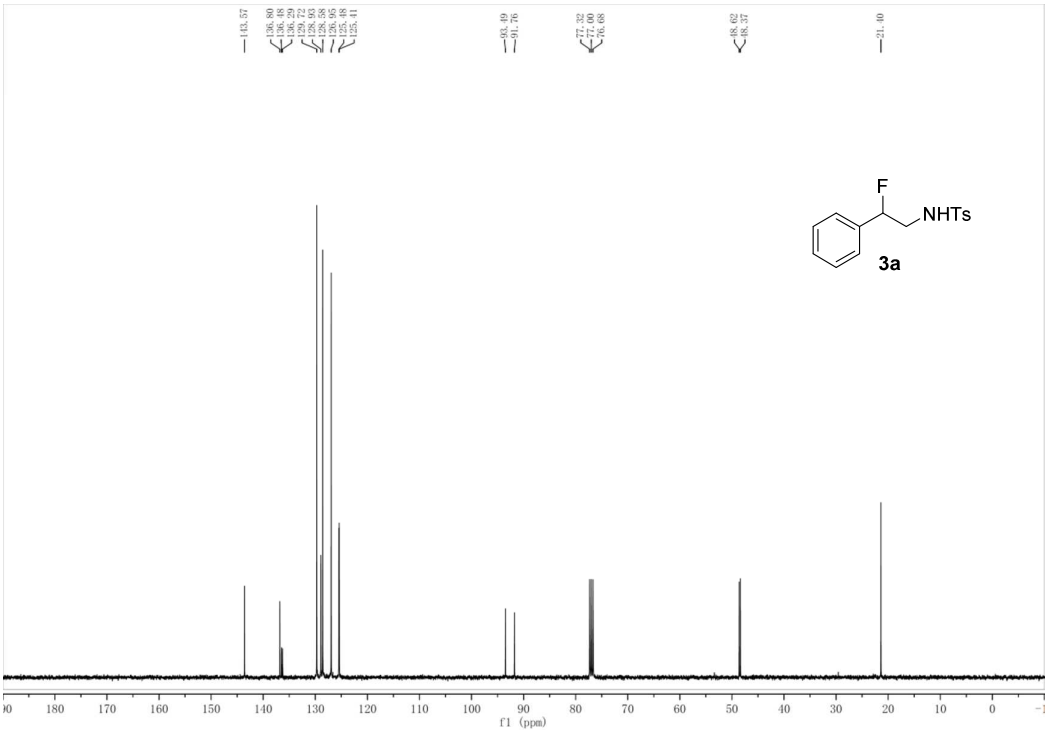
(3) Hatchard, C. G.; Parker, C. A. *Proc. Roy. Soc. (London)* **1956**, *A23*, 518-536.

9. **NMR spectra of compounds**

N-(2-fluoro-2-phenylethyl)-4-methylbenzenesulfonamide (3a)

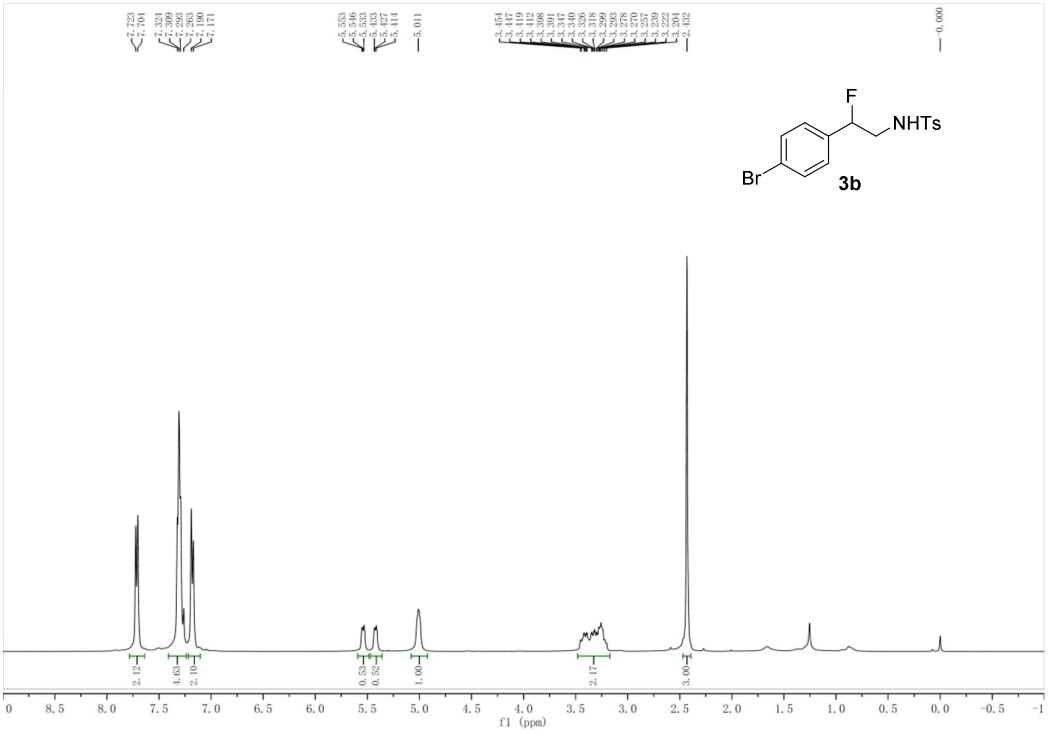

F
NHTs
3a
f1 (ppm)

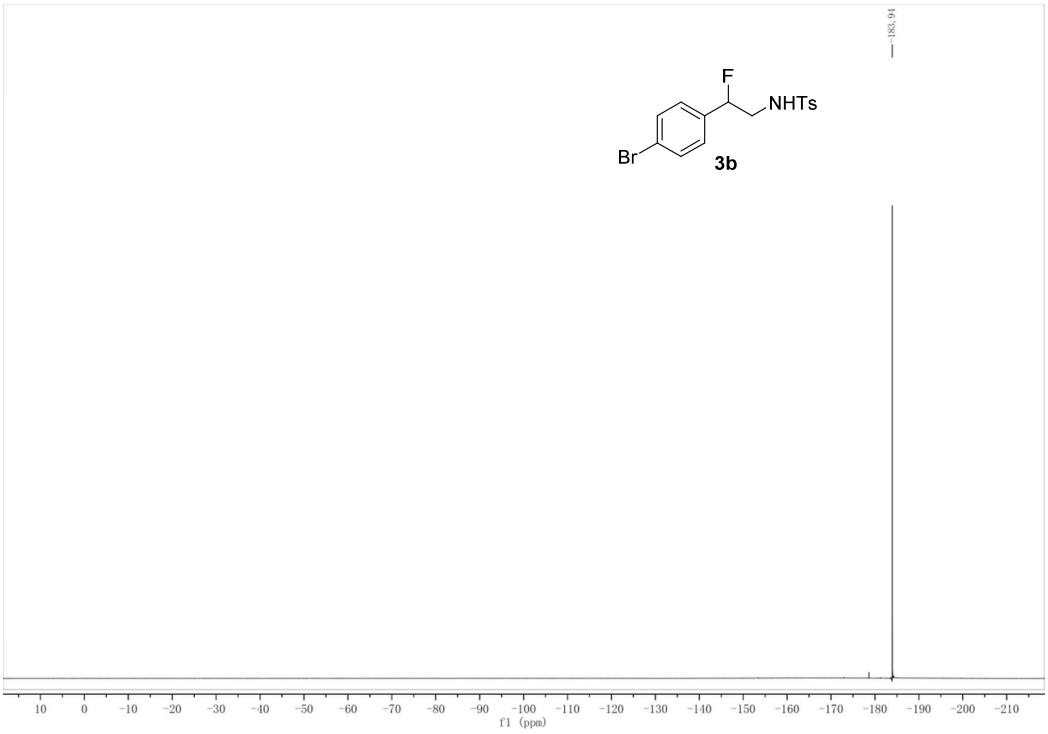

F
NHTs
3a
f1 (ppm)

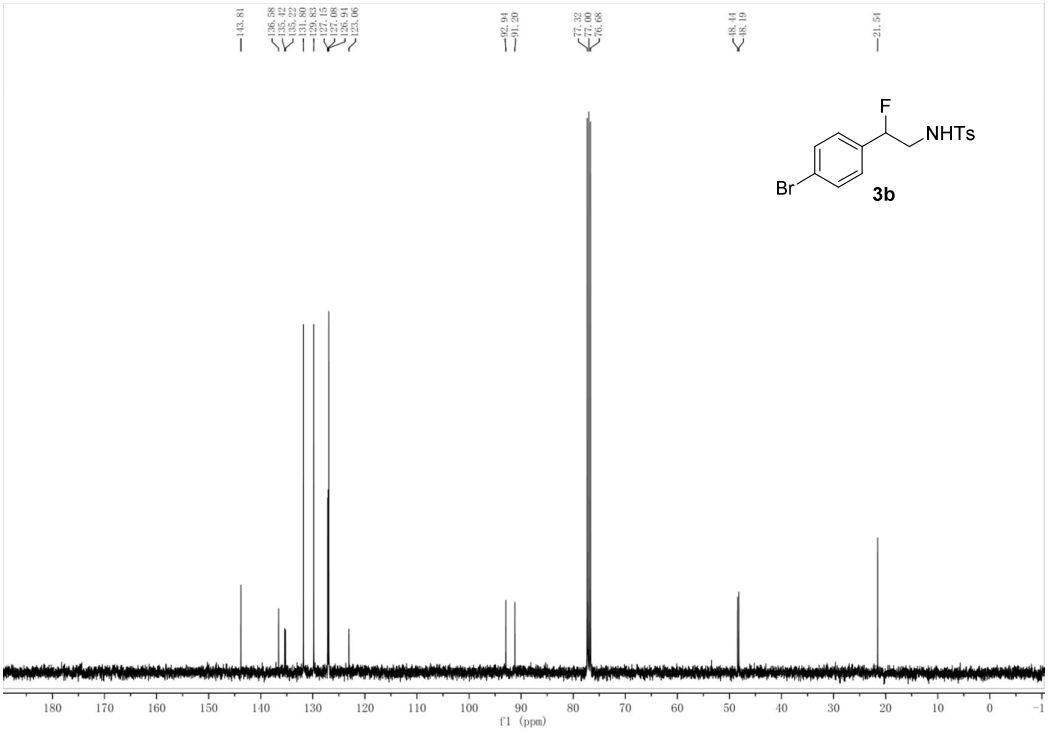


N-(2-(4-bromophenyl)-2-fluoroethyl)-4-methylbenzenesulfonamide

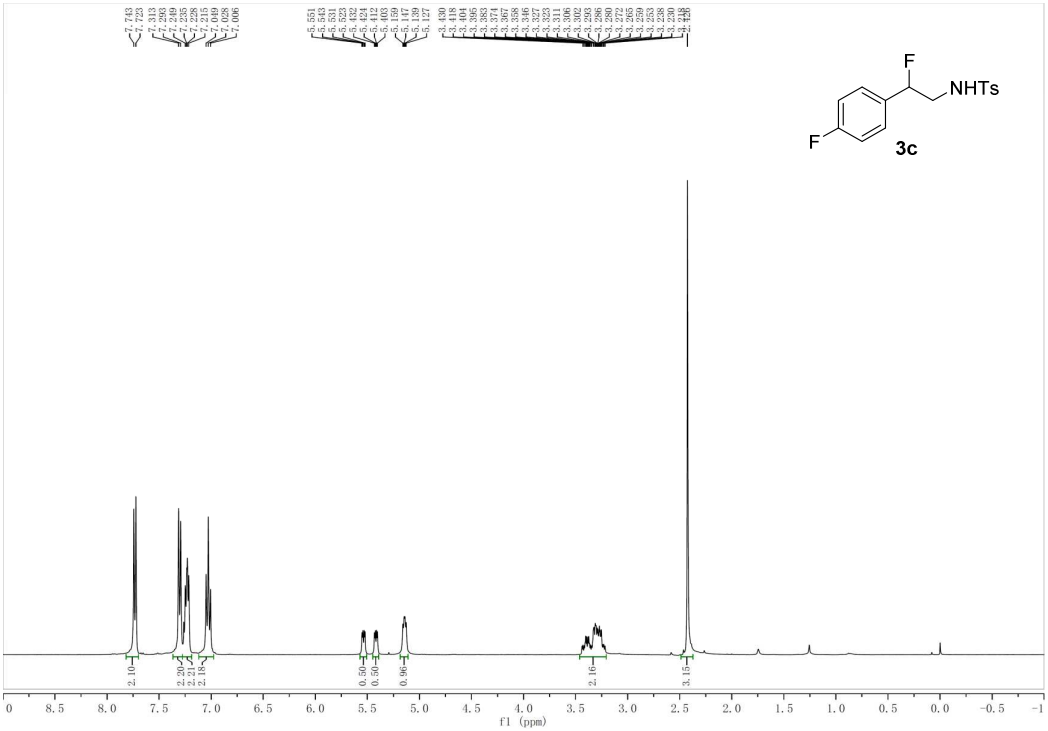
(3b)

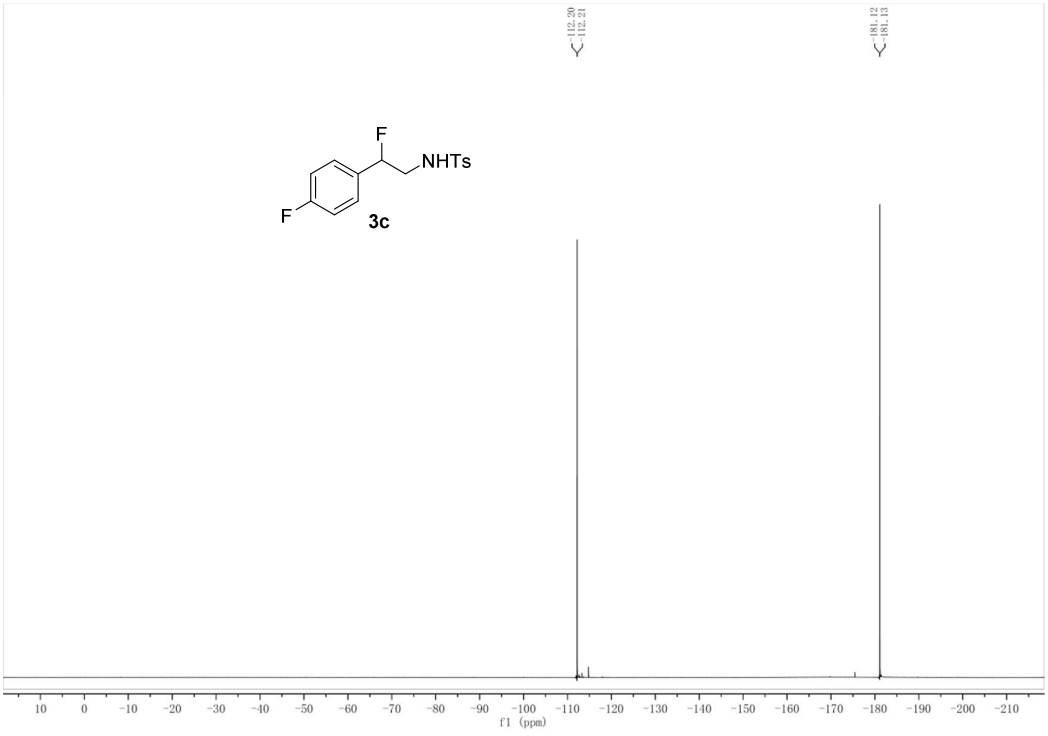


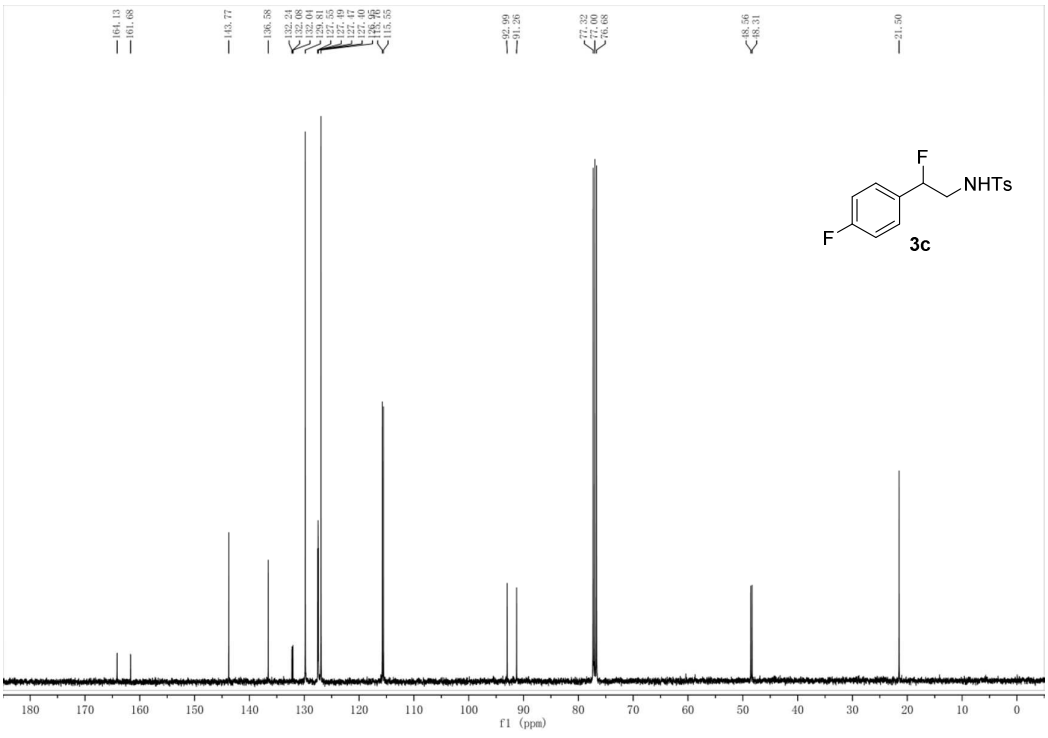

-183.94
F
NHTs
Br
3b
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


143.81
136.58
135.32
131.87
131.60
129.83
127.15
127.08
126.94
123.06
92.94
91.20
77.32
77.00
76.68
68.44
68.19
21.54
F
NHTs
Br
3b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

N-(2-fluoro-2-(4-fluorophenyl)ethyl)-4-methylbenzenesulfonamide (3c)

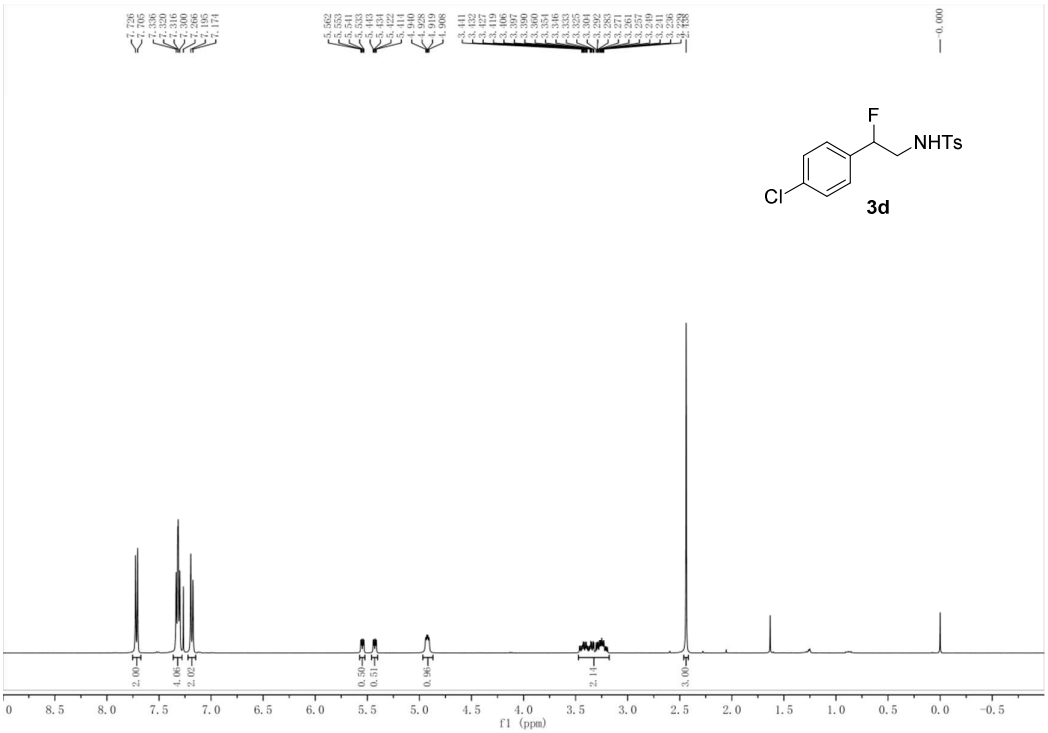


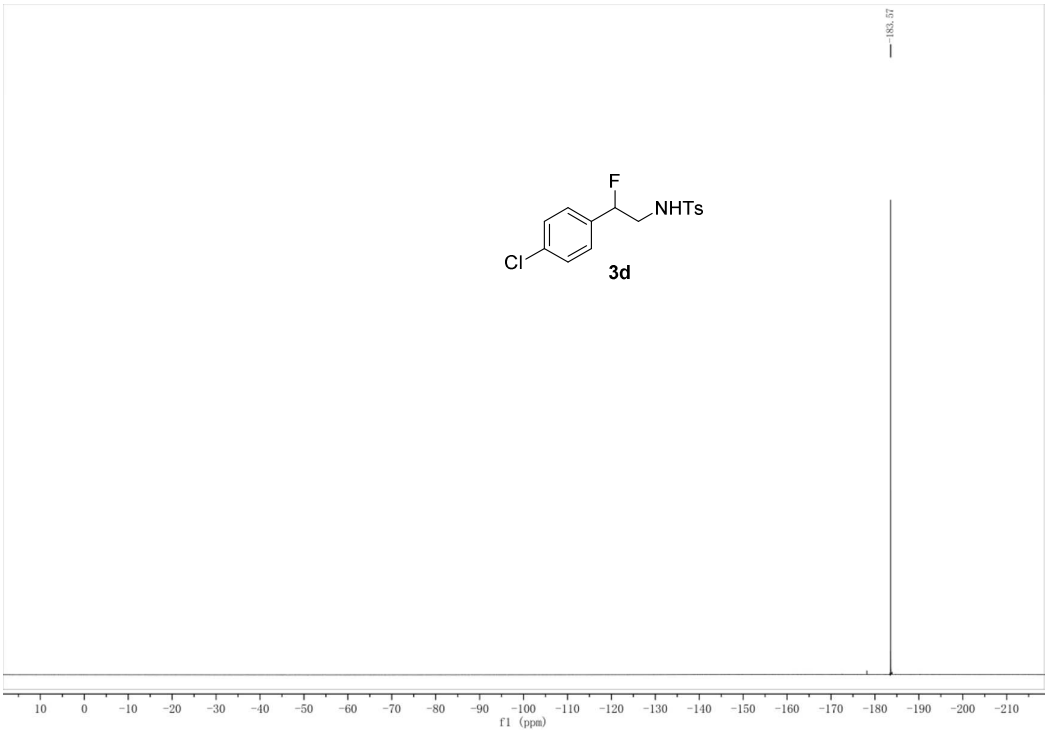


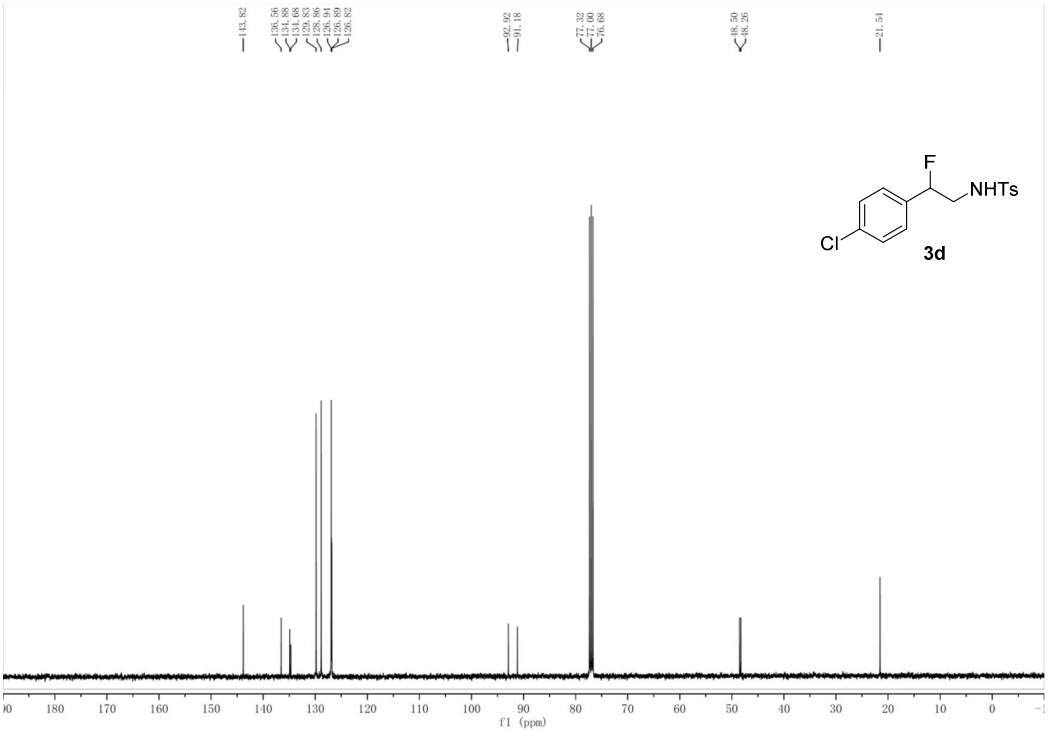


N-(2-(4-chlorophenyl)-2-fluoroethyl)-4-methylbenzenesulfonamide

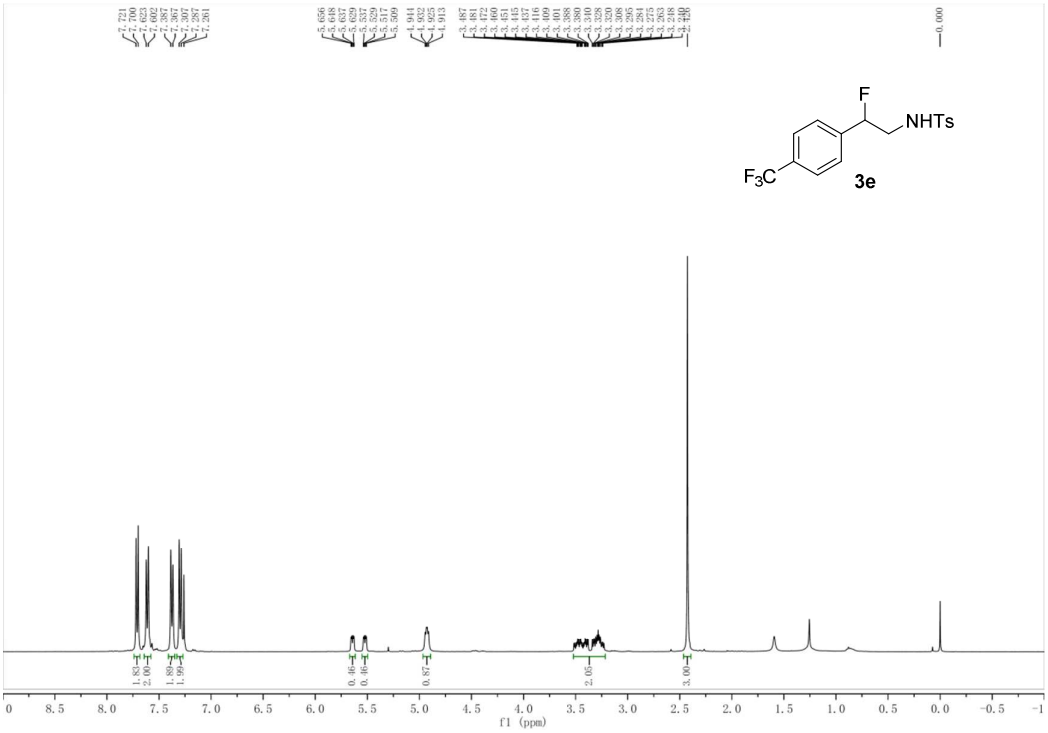
(3d)

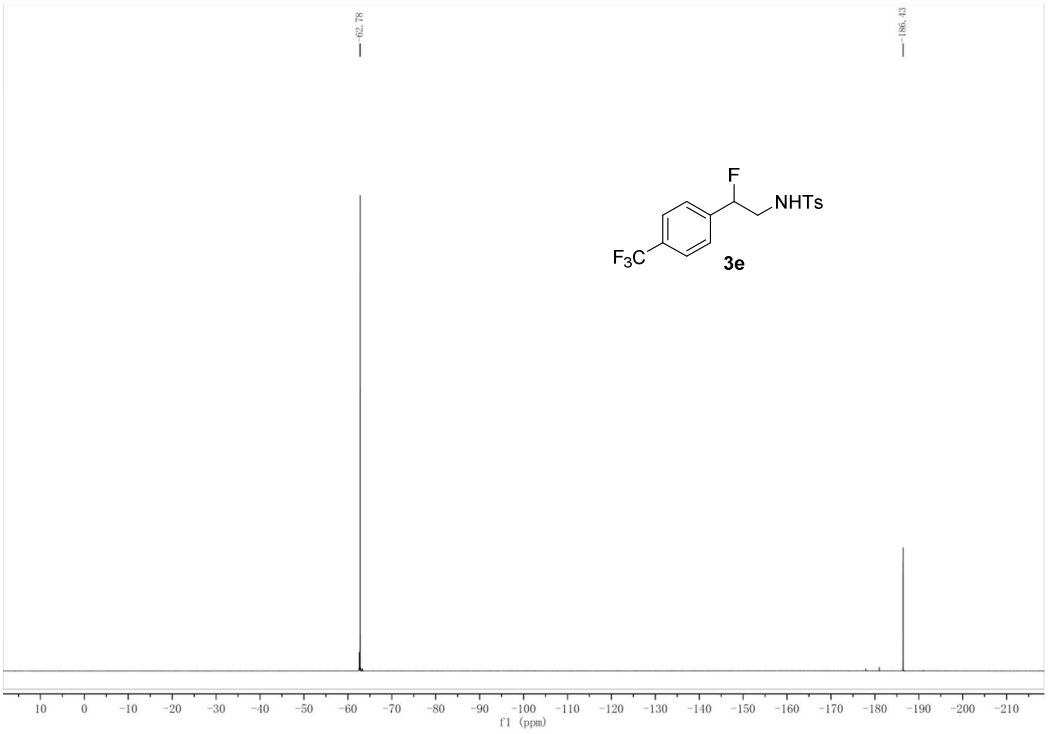


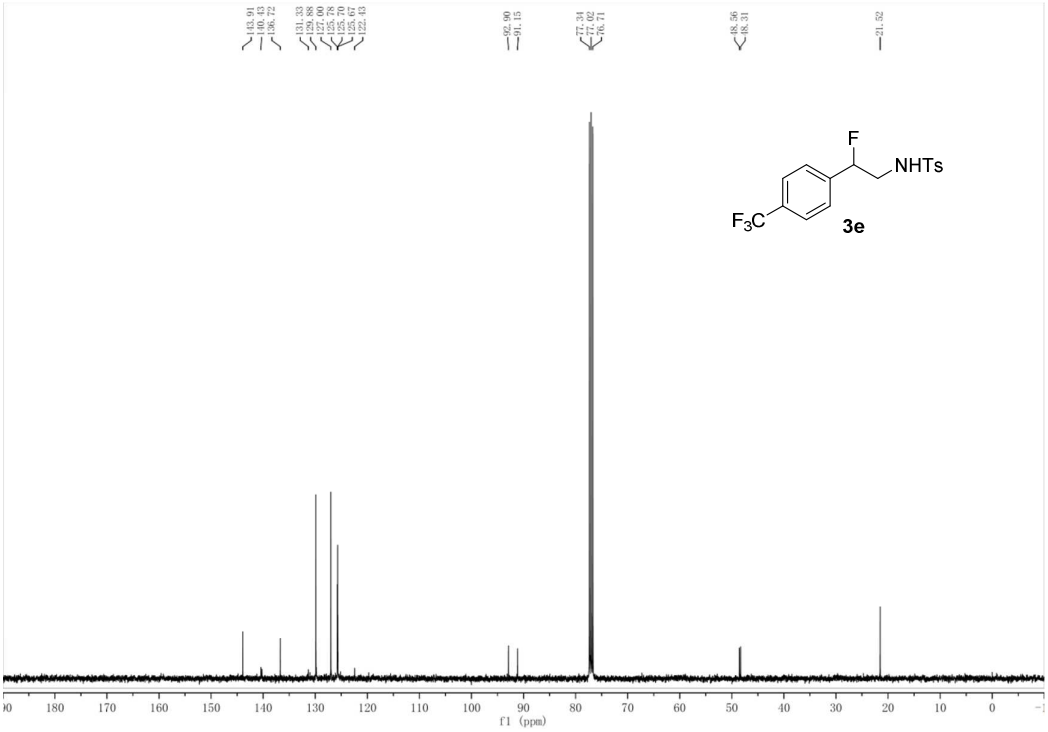

183.57
F
NHTs
Cl
3d
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)


143.82
136.56
134.88
134.68
129.55
128.86
126.94
126.89
126.82
92.92
91.18
77.32
77.00
76.68
48.50
48.26
21.54
F
NHTs
Cl
3d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

N-(2-fluoro-2-(4-(trifluoromethyl)phenyl)ethyl)-4-methylbenzenesulfonamide (3e)

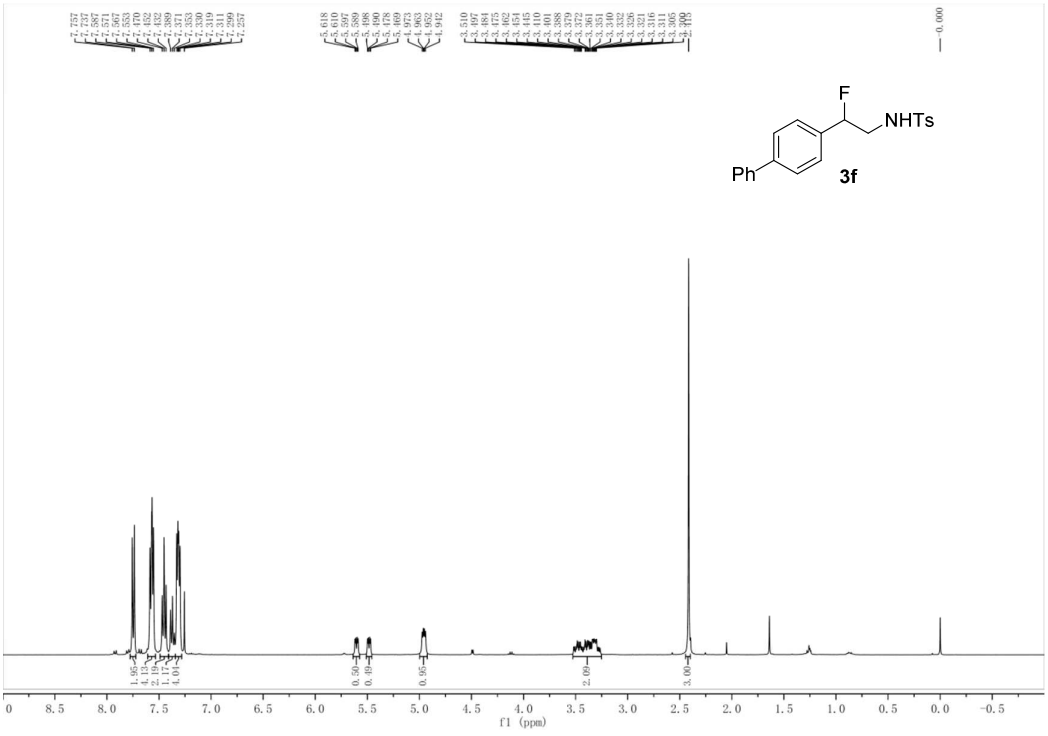


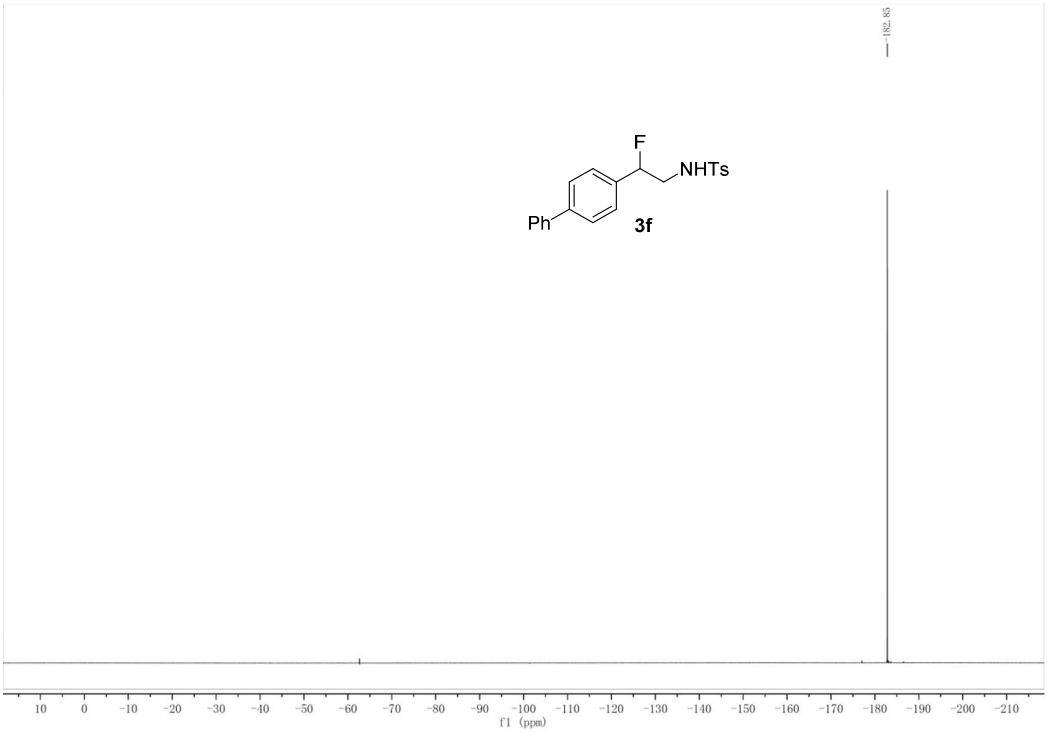


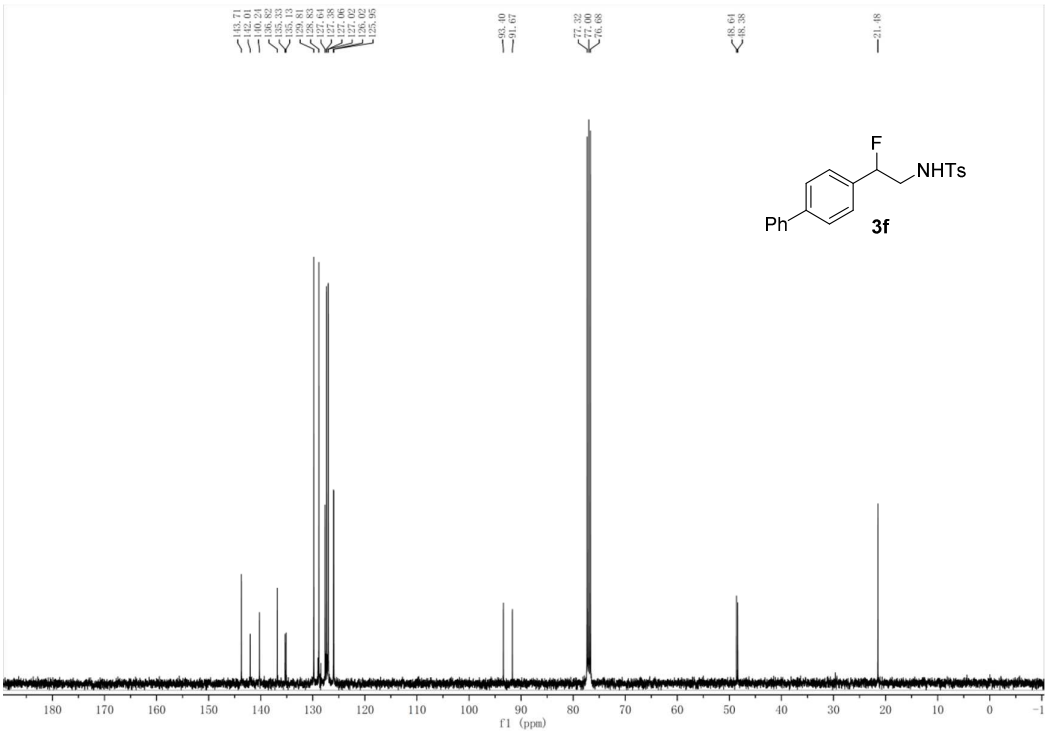


N-(2-([1,1'-biphenyl]-4-yl)-2-fluoroethyl)-4-methylbenzenesulfonamide

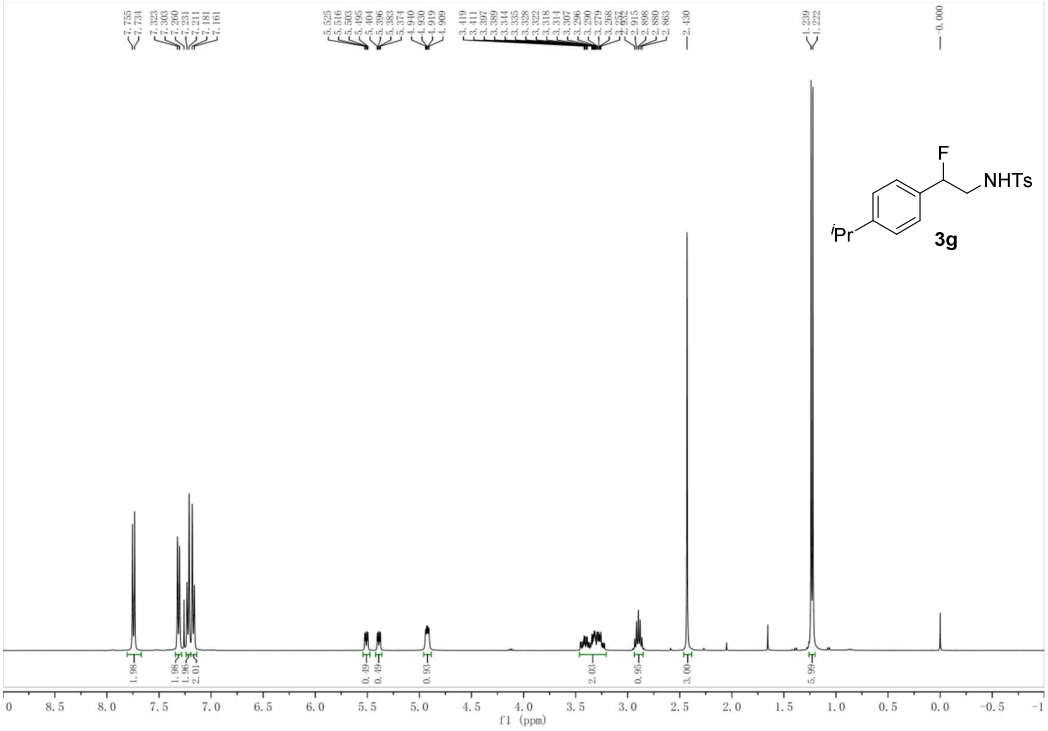
(3f)

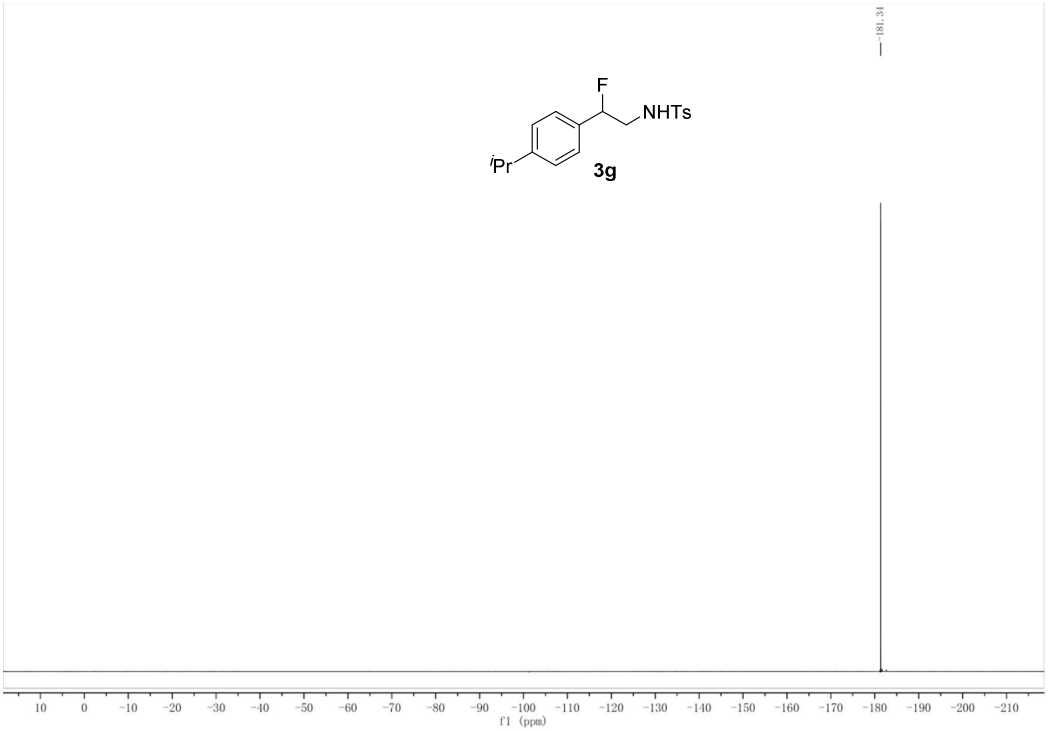


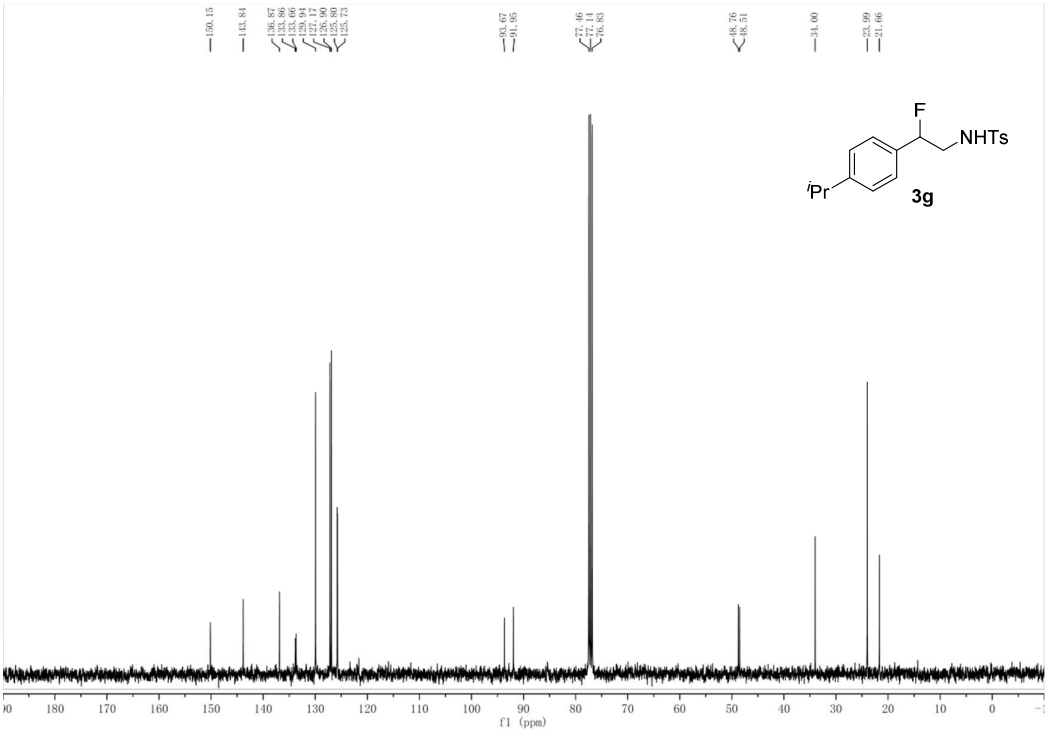

182.85
F
NHTs
Ph
3f
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)


143.71
142.01
140.24
136.82
135.73
133.13
129.81
128.83
127.64
127.38
127.06
127.02
126.02
125.95
93.40
91.67
77.32
77.00
76.68
48.64
48.38
21.48
F
NHTs
Ph
3f
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

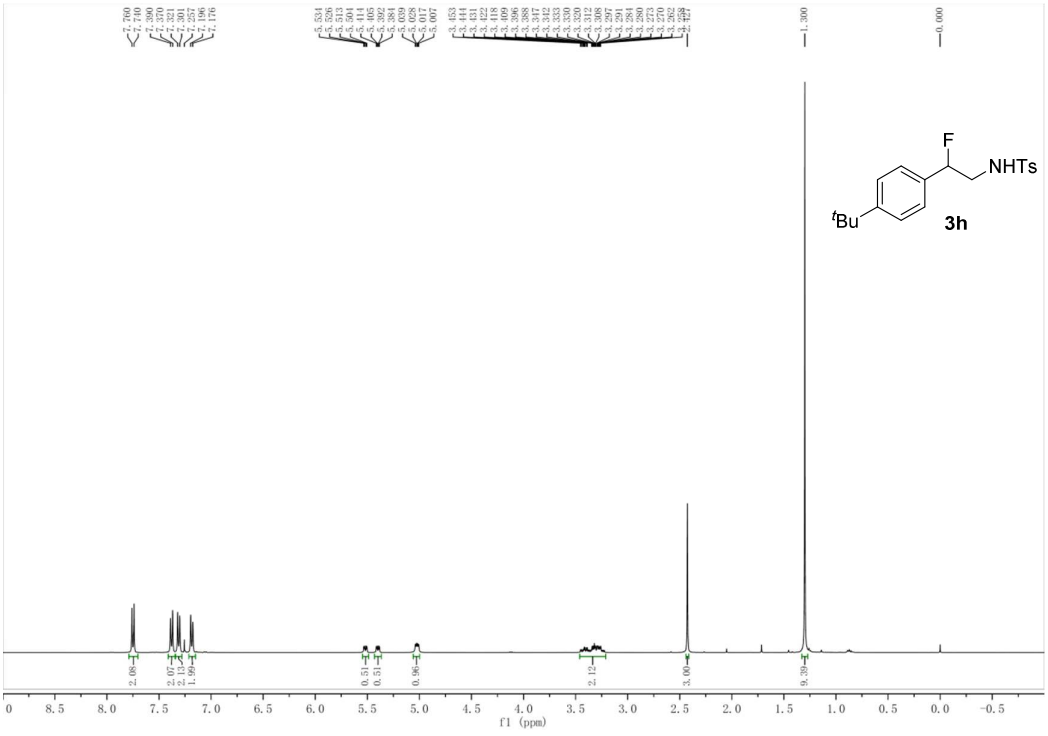
N-(2-fluoro-2-(4-isopropylphenyl)ethyl)-4-methylbenzenesulfonamide (3g)

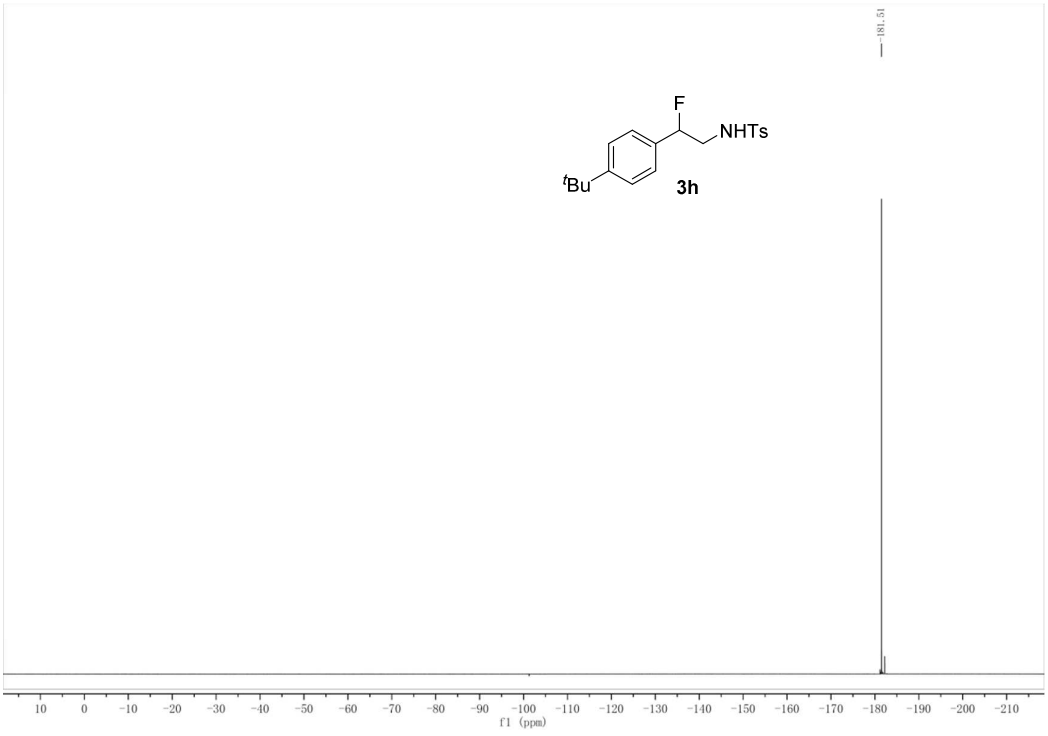


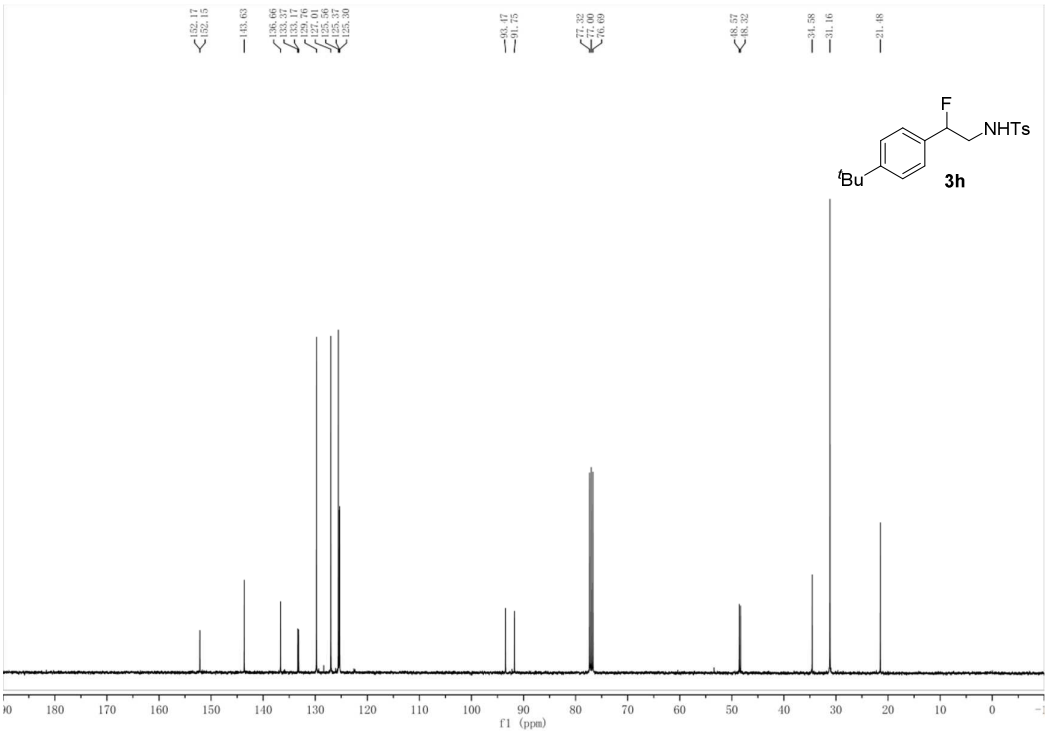




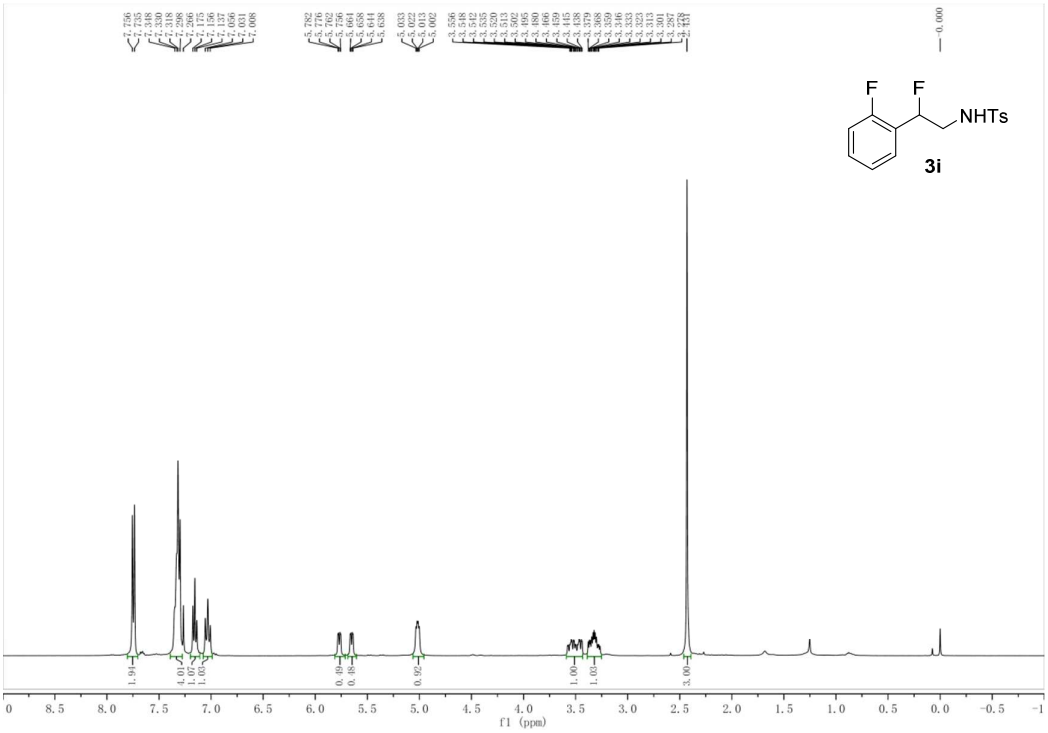
N-(2-(4-(tert-butyl)phenyl)-2-fluoroethyl)-4-methylbenzenesulfonamide (3h)

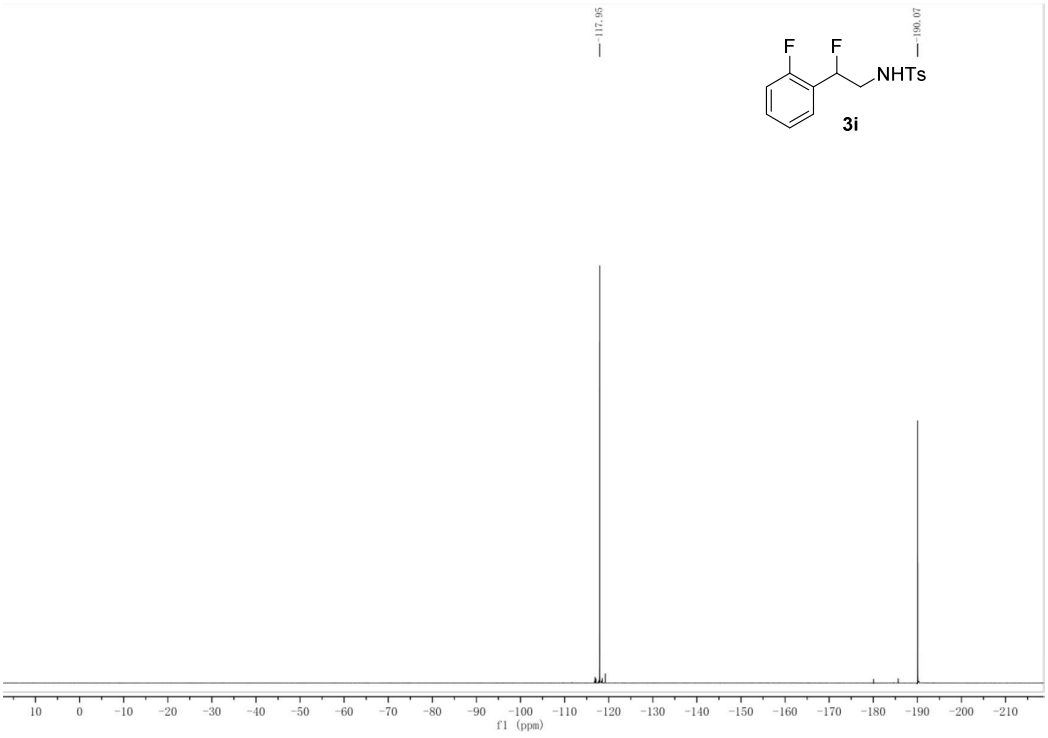


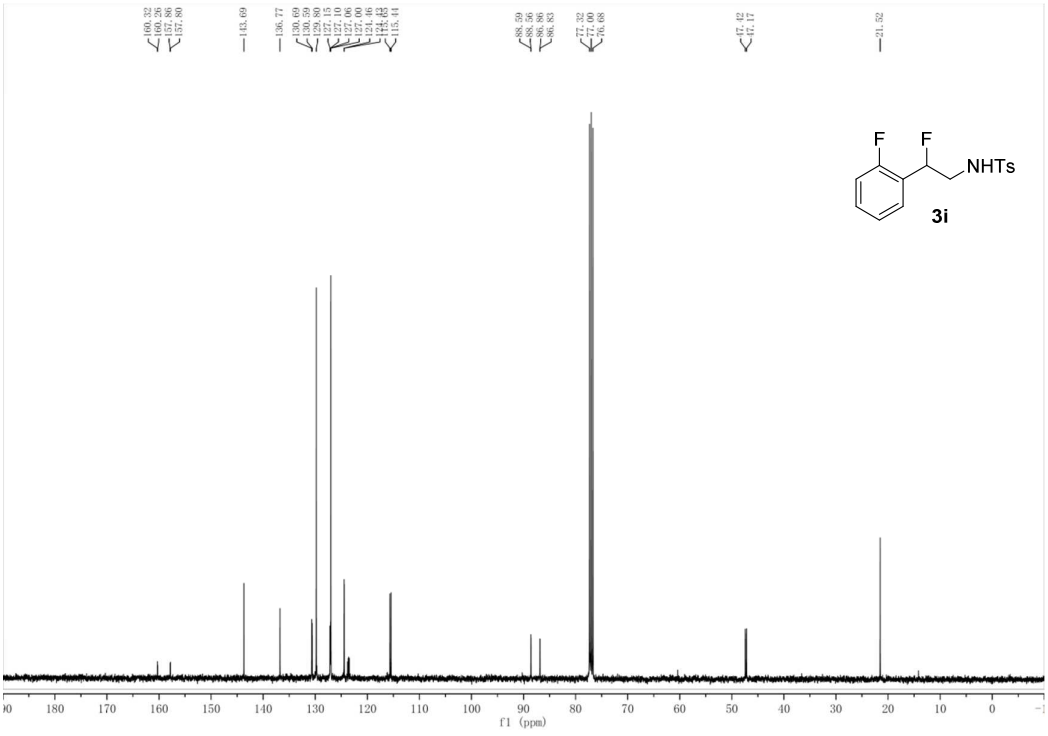

-181.54
F
NHTs
tBu
3h
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


152.17
152.15
143.63
136.66
133.37
133.17
130.76
127.01
125.56
125.37
125.30
68.47
68.25
77.32
77.00
76.69
48.57
48.32
34.58
31.16
21.48
F
NHTs
tBu
3h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

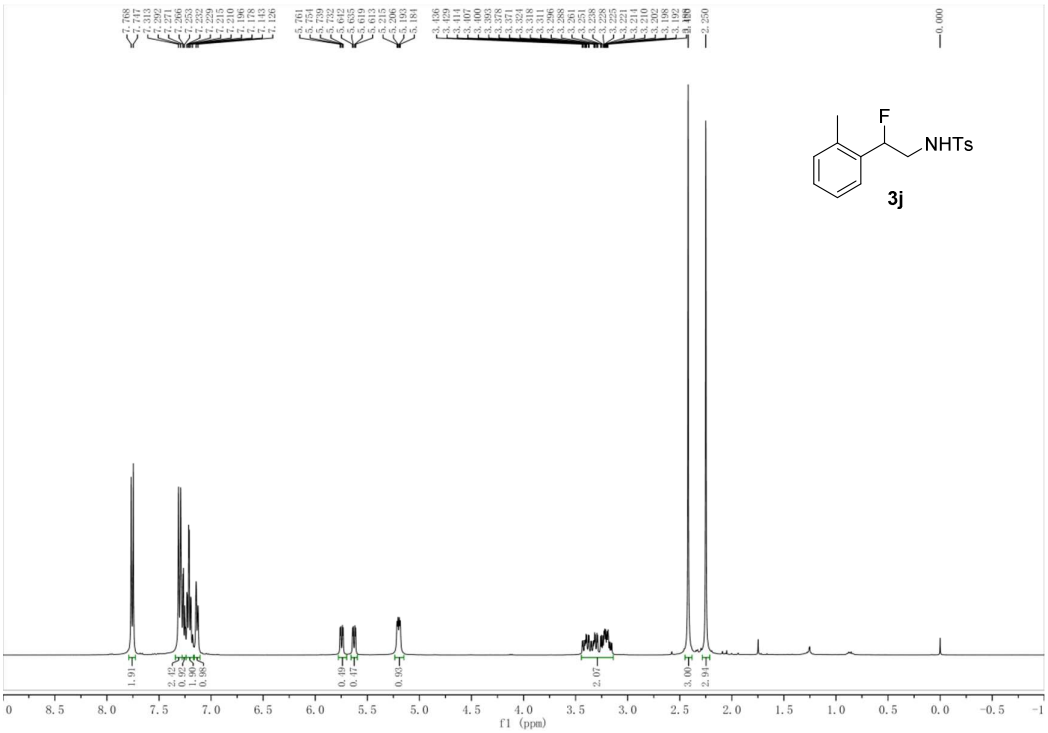
N-(2-fluoro-2-(2-fluorophenyl)ethyl)-4-methylbenzenesulfonamide (3i)

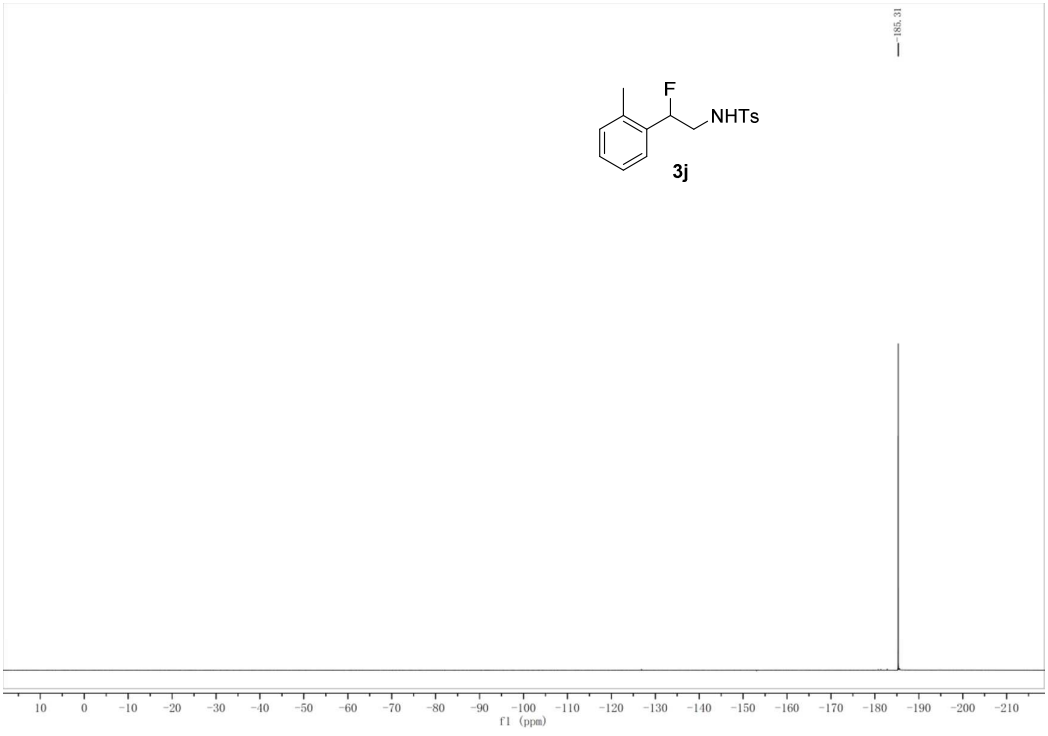


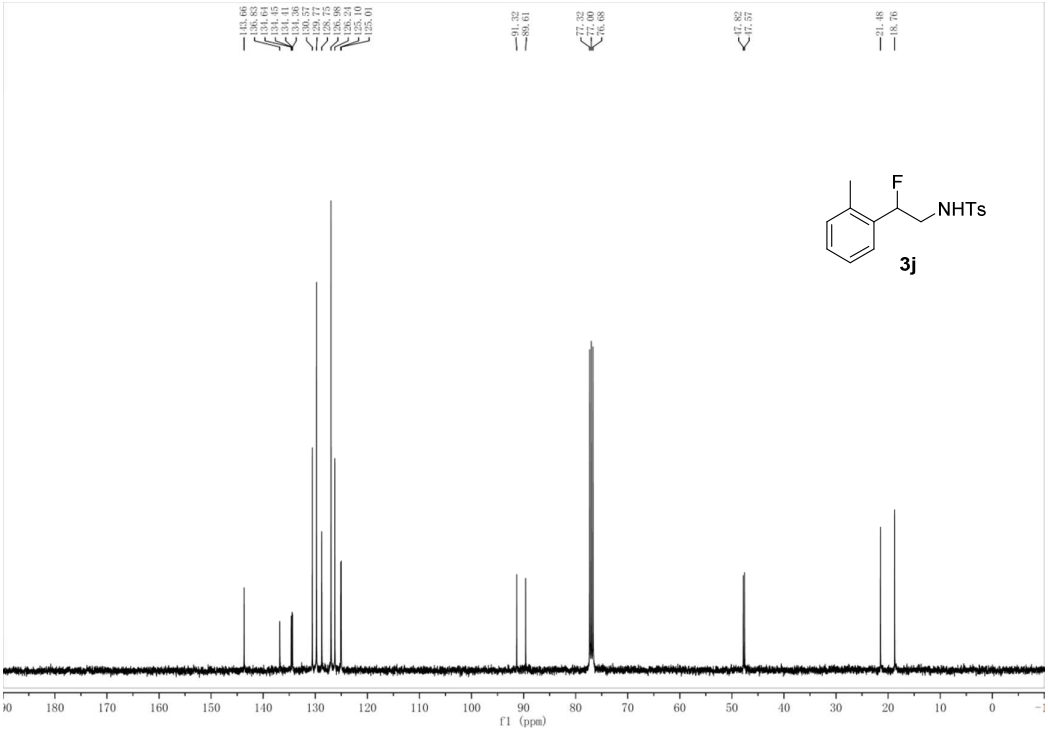




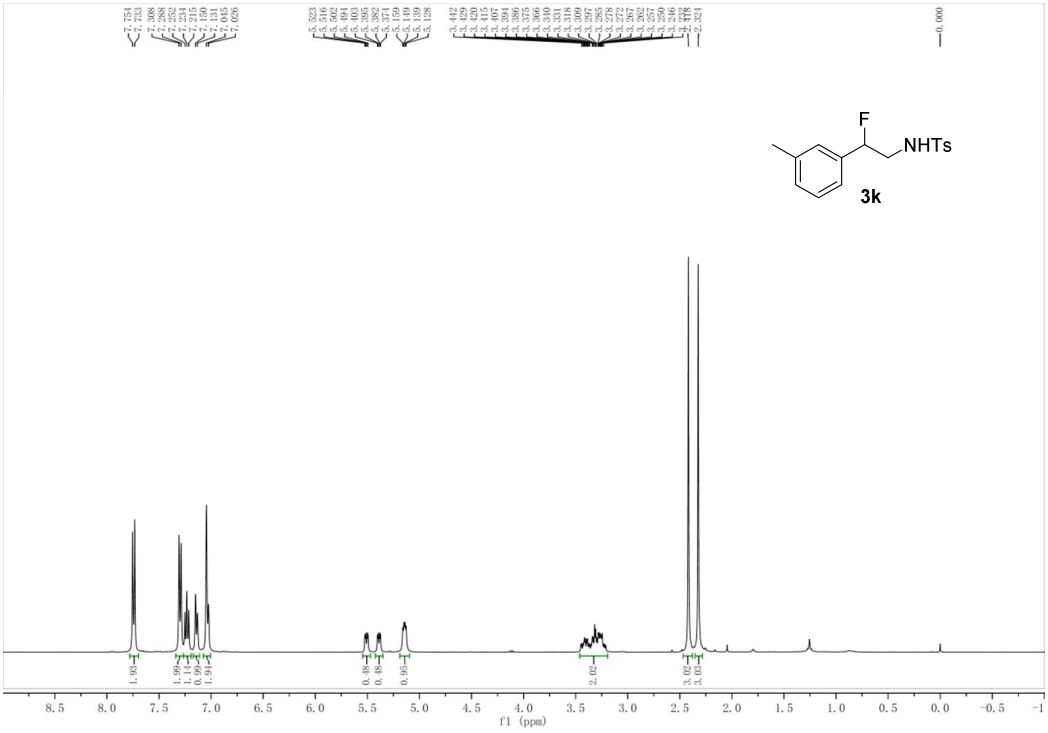
N-(2-fluoro-2-(o-tolyl)ethyl)-4-methylbenzenesulfonamide (3j)

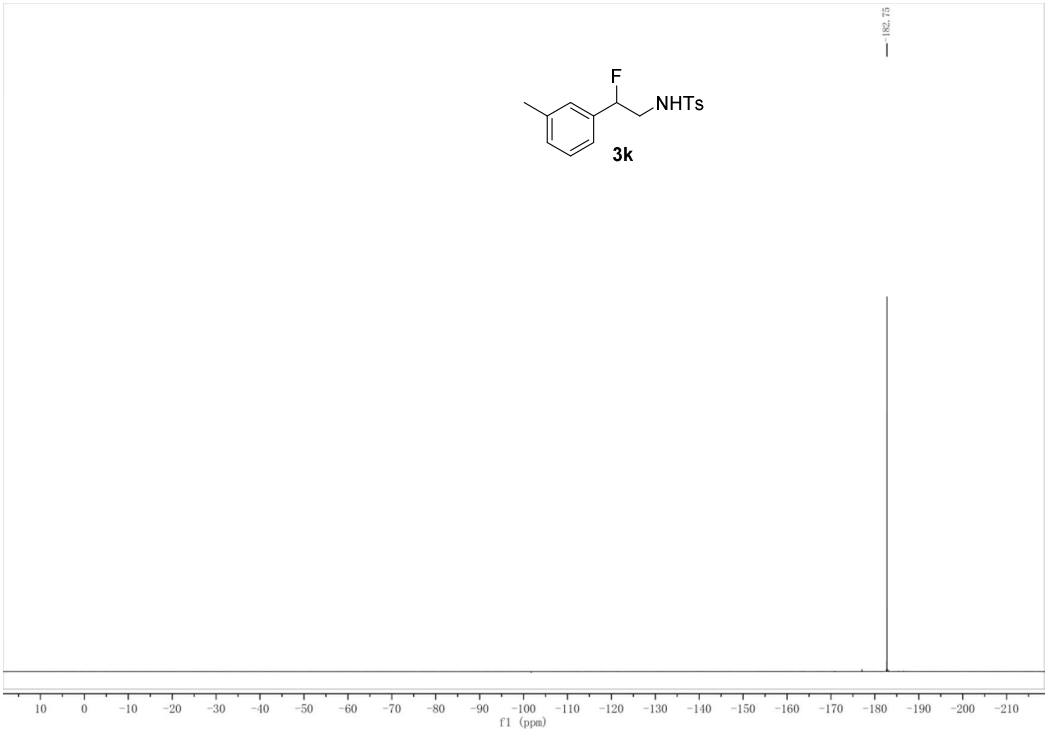


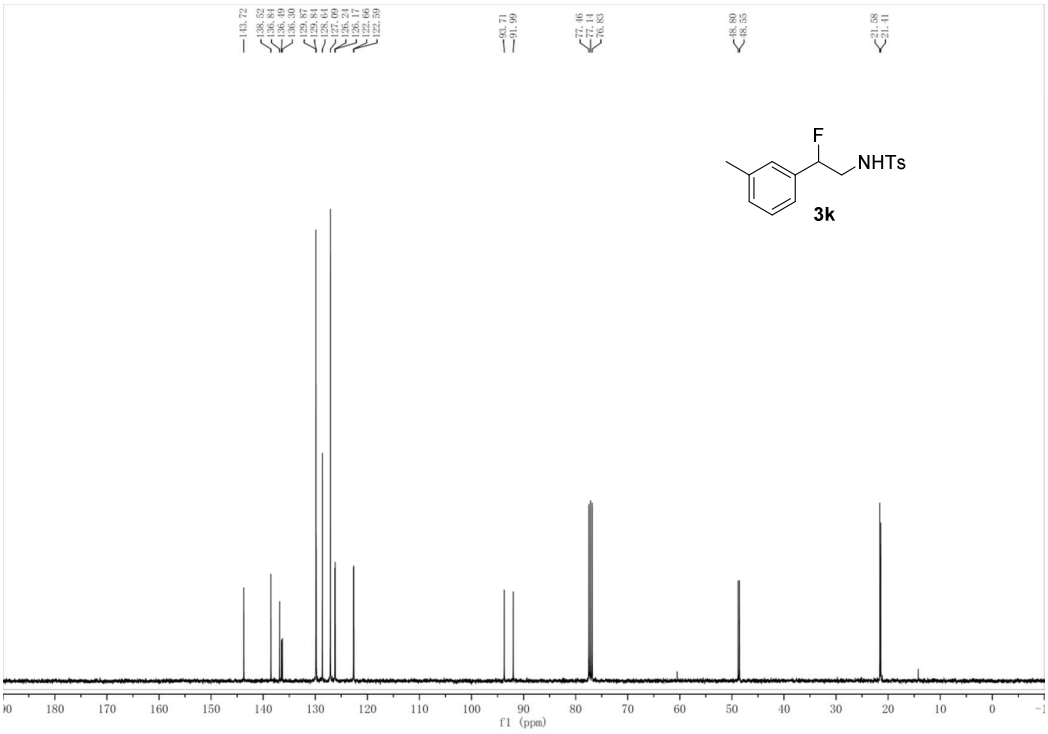

F
NHTs
3j
-185.31
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


143.66
136.83
134.64
134.45
134.41
134.36
130.57
129.77
128.75
126.98
126.31
125.10
125.01
91.32
89.61
77.32
77.00
76.68
47.82
47.57
21.48
18.76
F
NHTs
3j
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

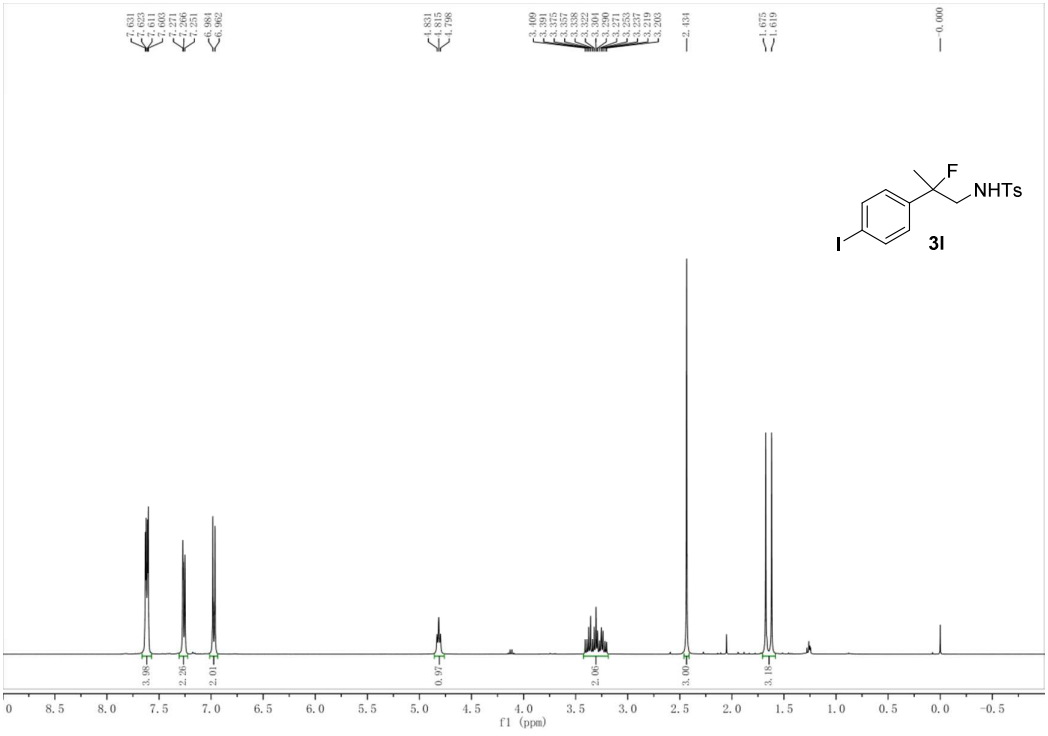
N-(2-fluoro-2-(m-tolyl)ethyl)-4-methylbenzenesulfonamide (3k)

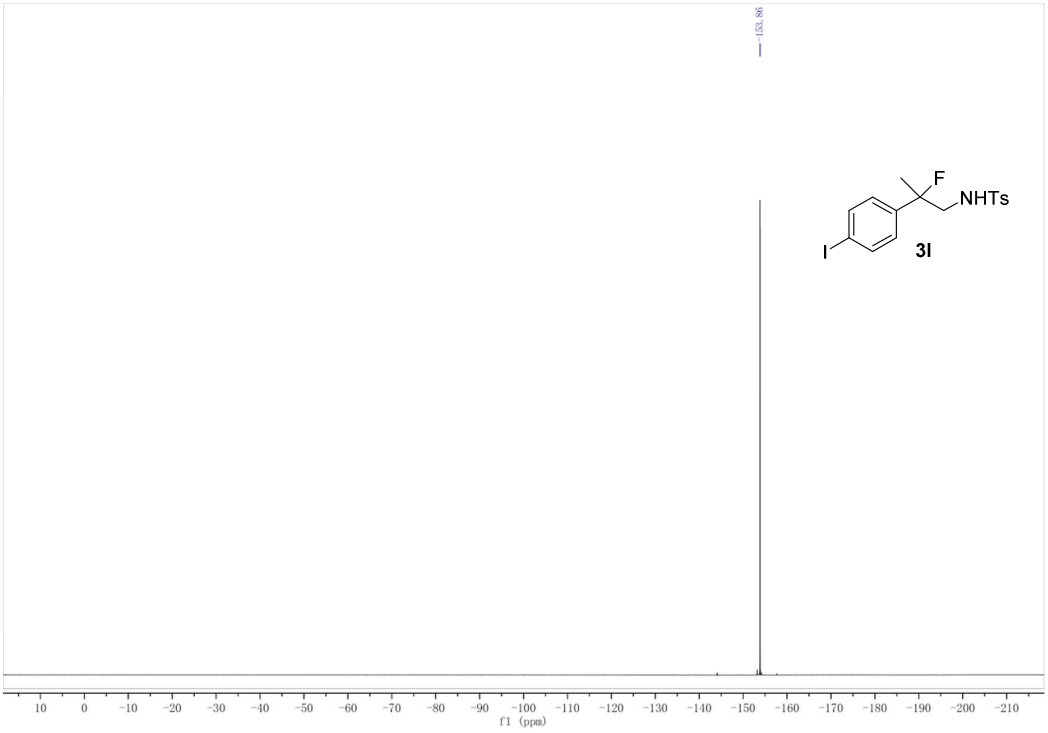


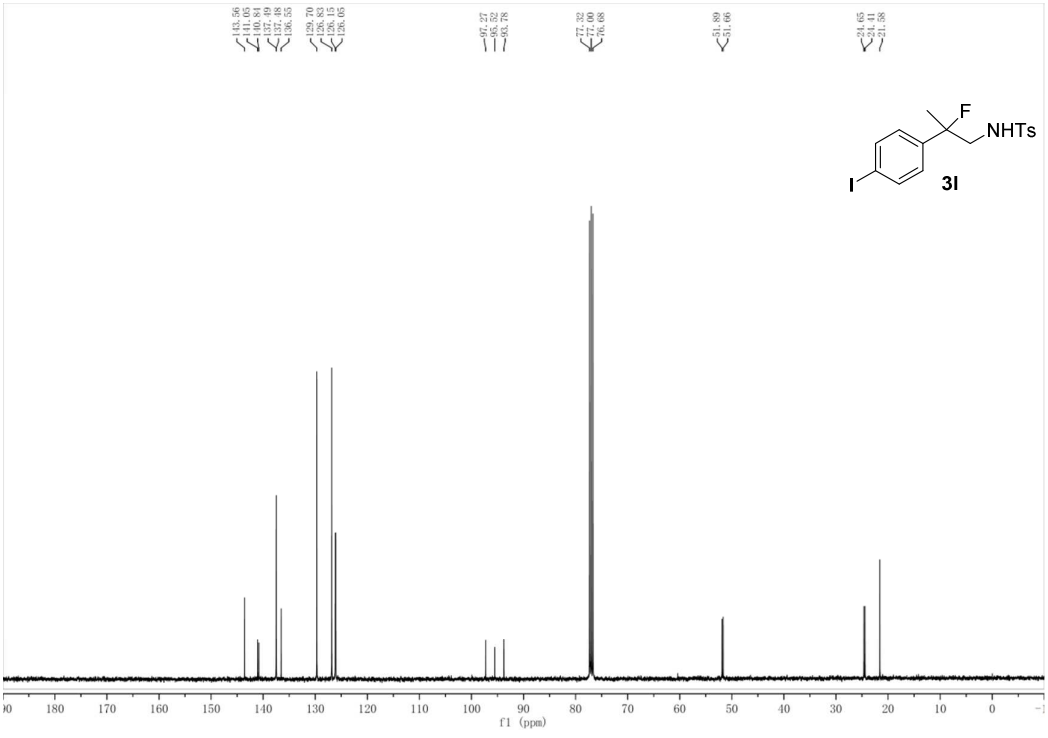




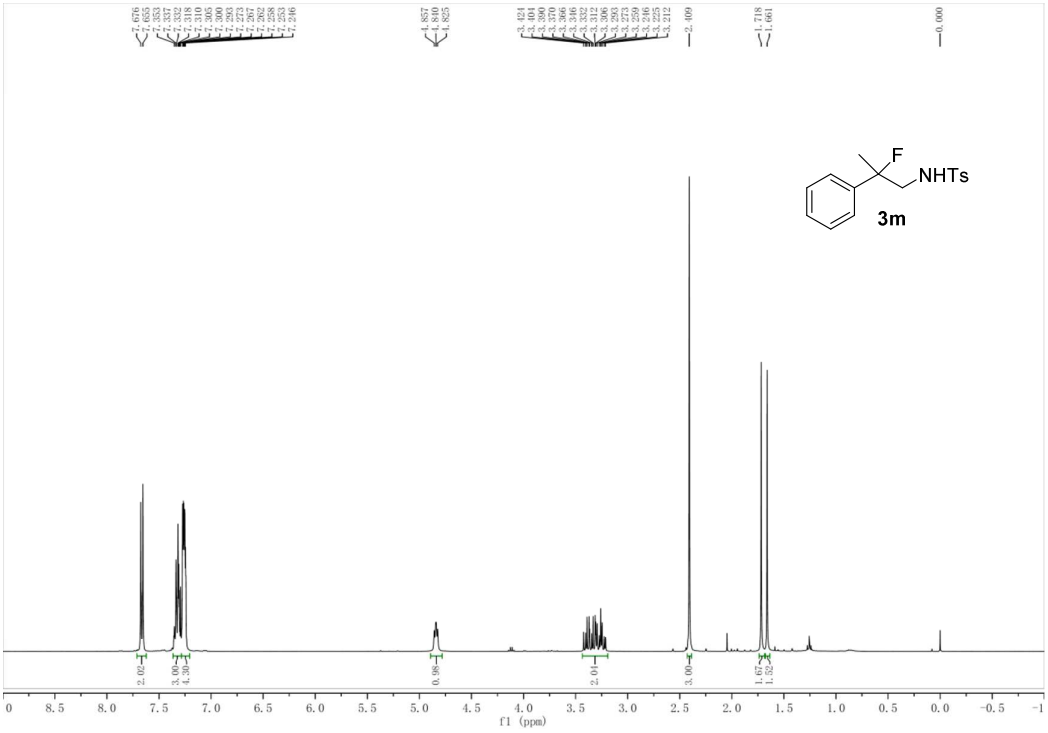
N-(2-fluoro-2-(4-iodophenyl)propyl)-4-methylbenzenesulfonamide(3l)

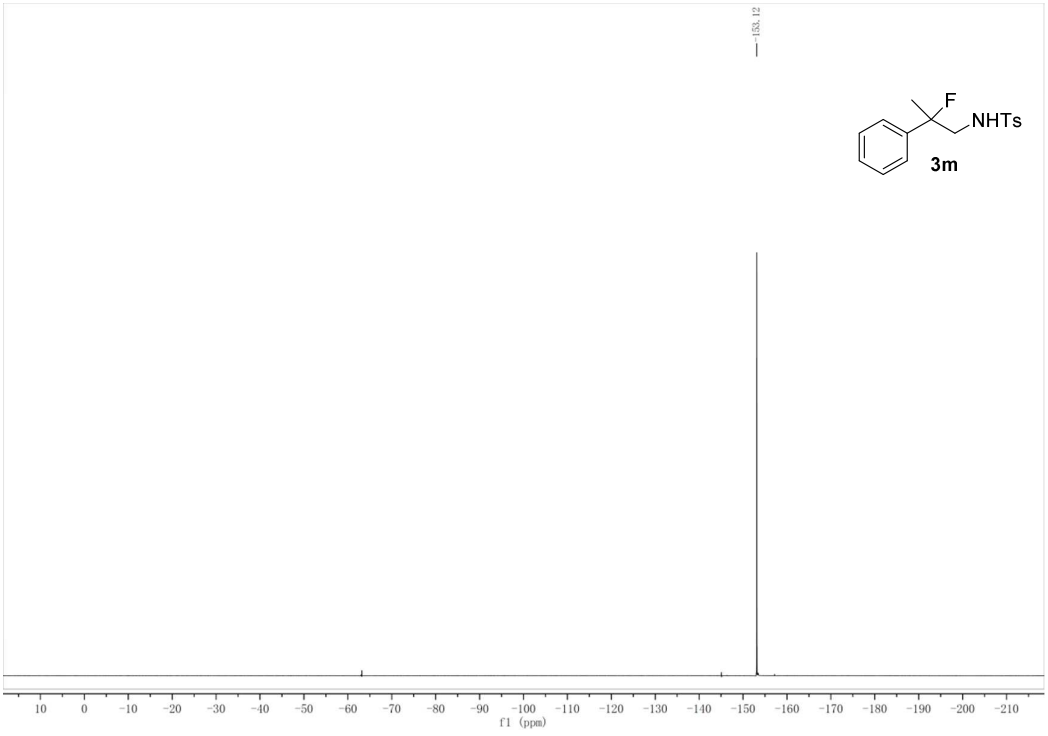


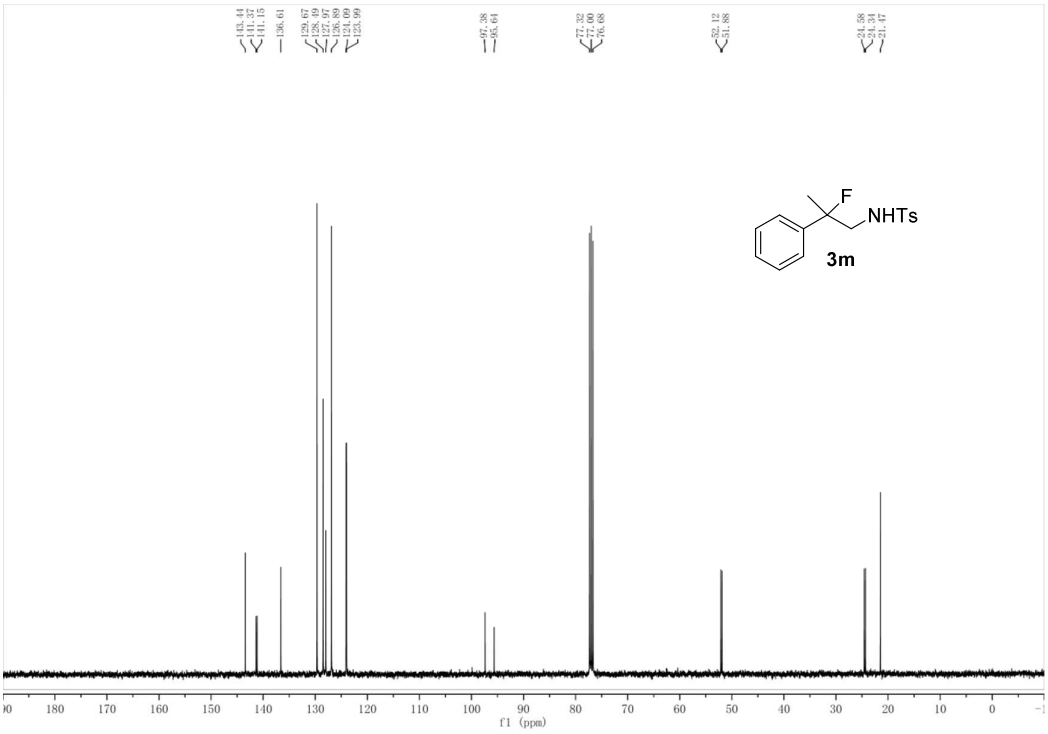

-153.86
F
NHTs
I
3l
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


143.56
141.05
140.84
137.49
135.48
130.55
129.70
128.53
128.15
126.05
97.27
95.52
93.78
77.32
77.00
76.68
51.89
51.66
24.65
24.41
21.38
F
NHTs
I
3l
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

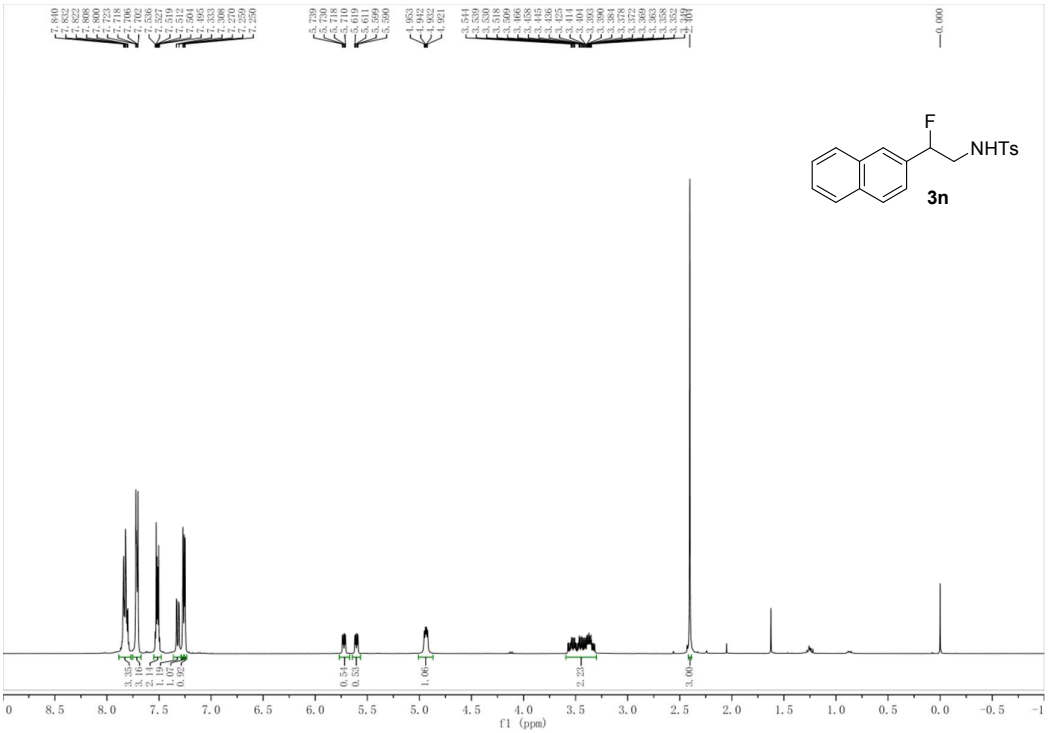
N-(2-fluoro-2-phenylpropyl)-4-methylbenzenesulfonamide (3m)

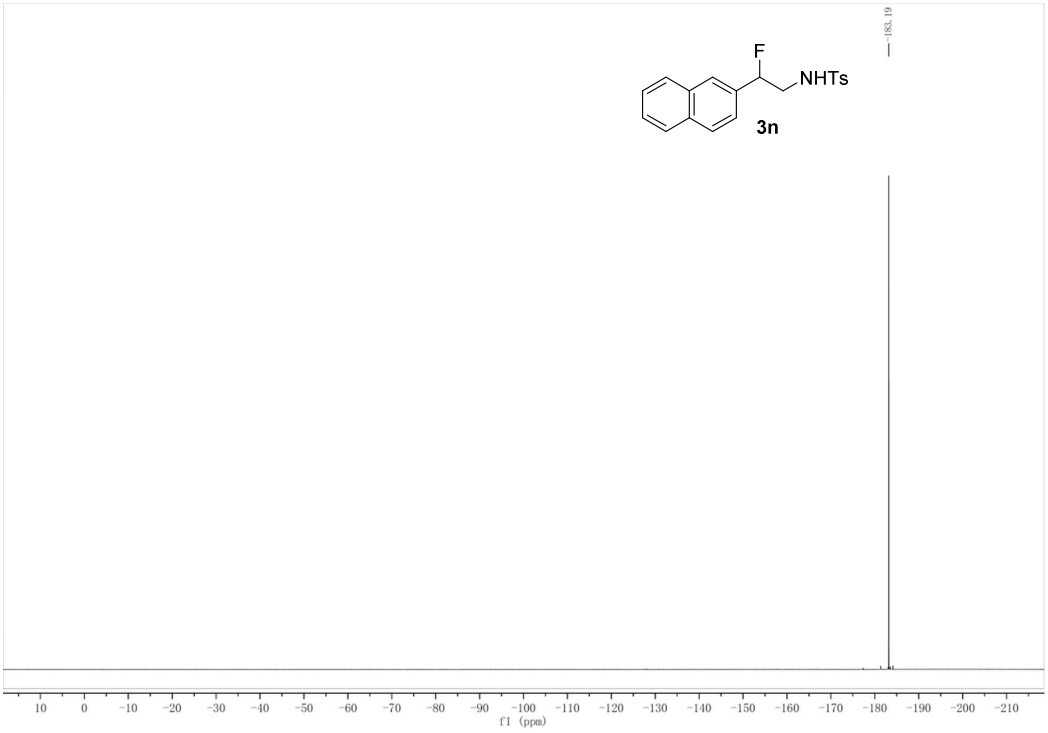


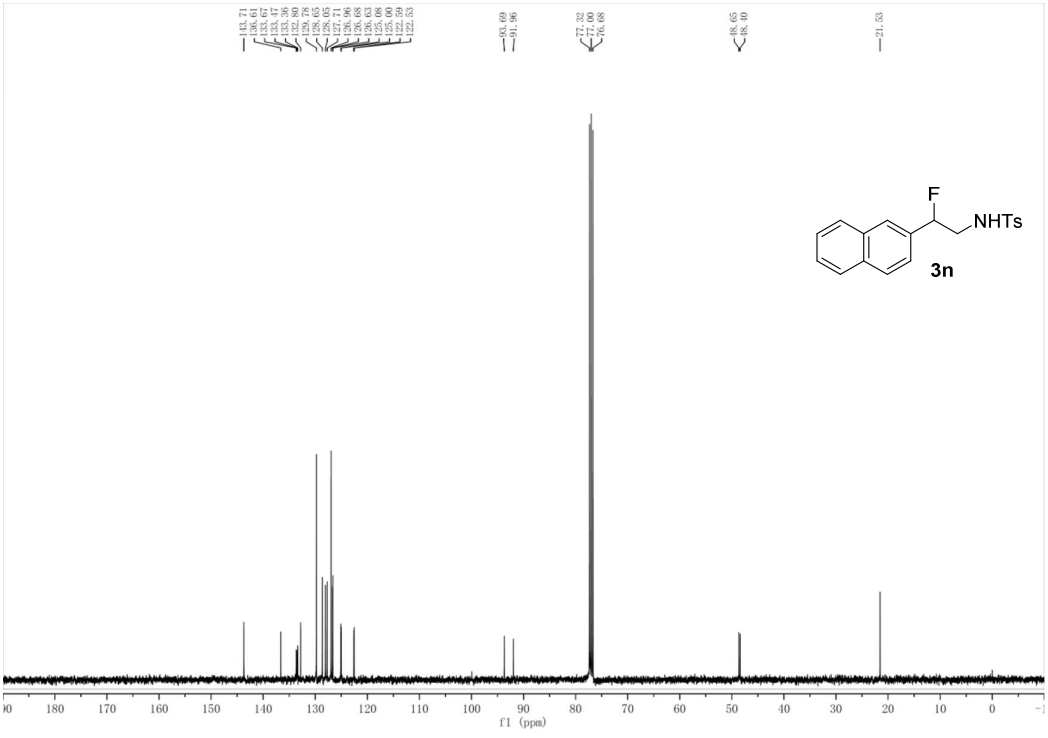




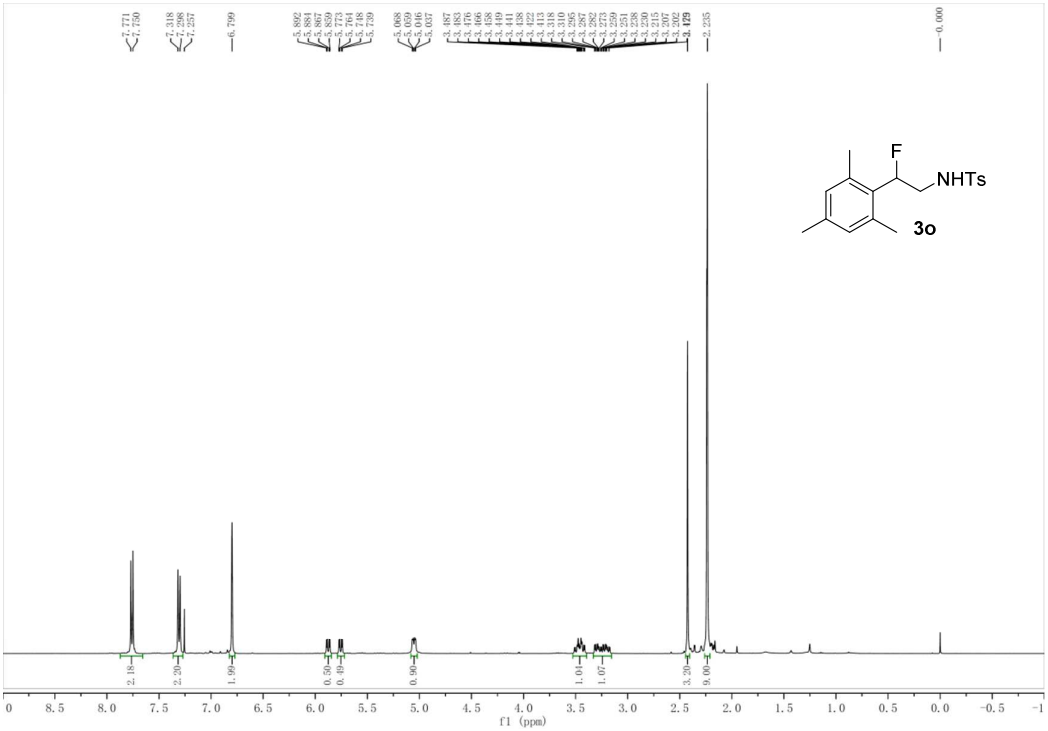
N-(2-fluoro-2-(naphthalen-2-yl)ethyl)-4-methylbenzenesulfonamide (3n)

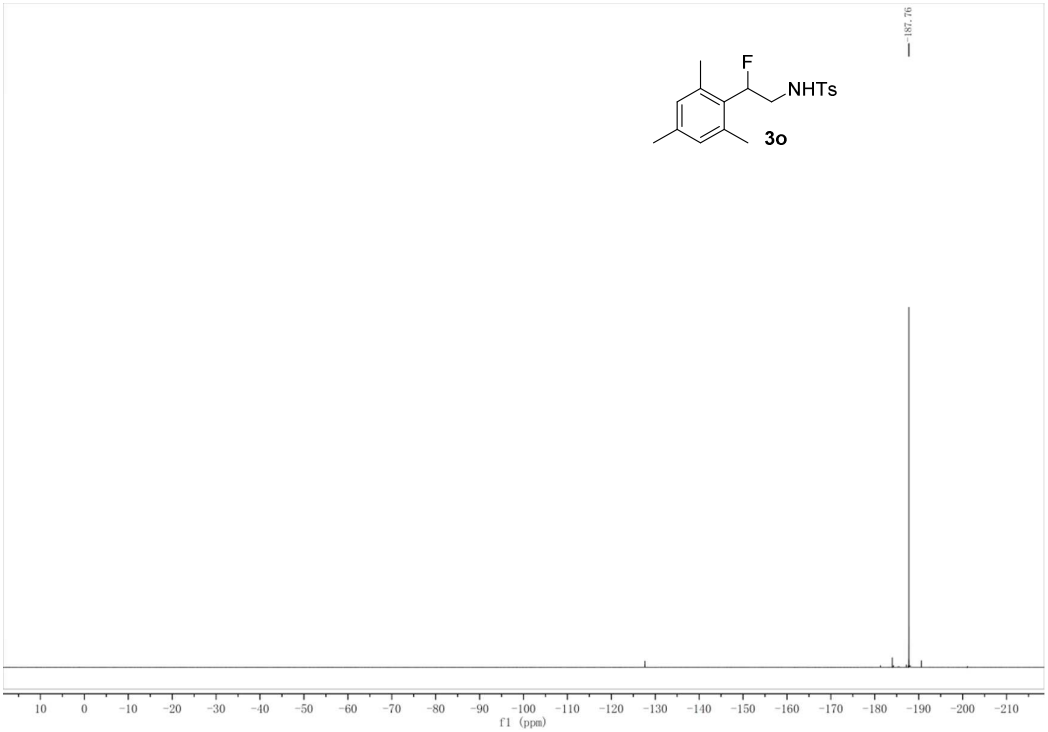


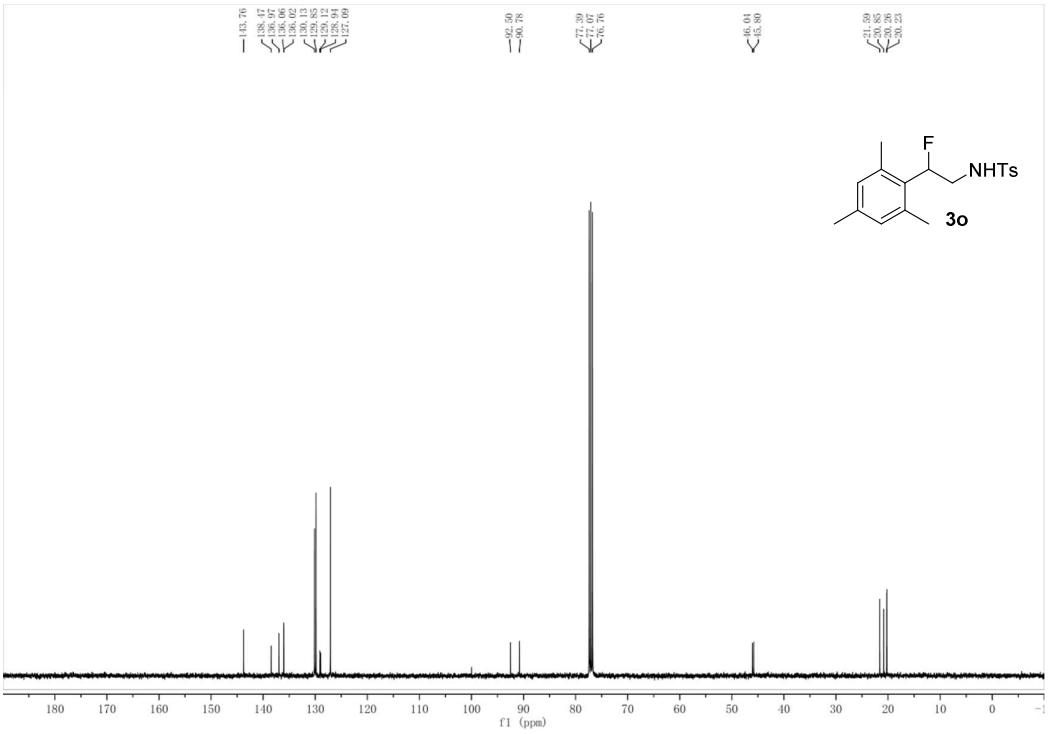

F
NHTs
3n
-183.19
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


143.71
136.61
133.57
133.47
133.36
132.89
129.78
128.65
128.05
127.71
126.98
126.68
126.63
125.08
125.00
122.59
122.53
93.69
91.96
77.32
77.00
76.68
48.65
48.40
21.53
F
NHTs
3n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

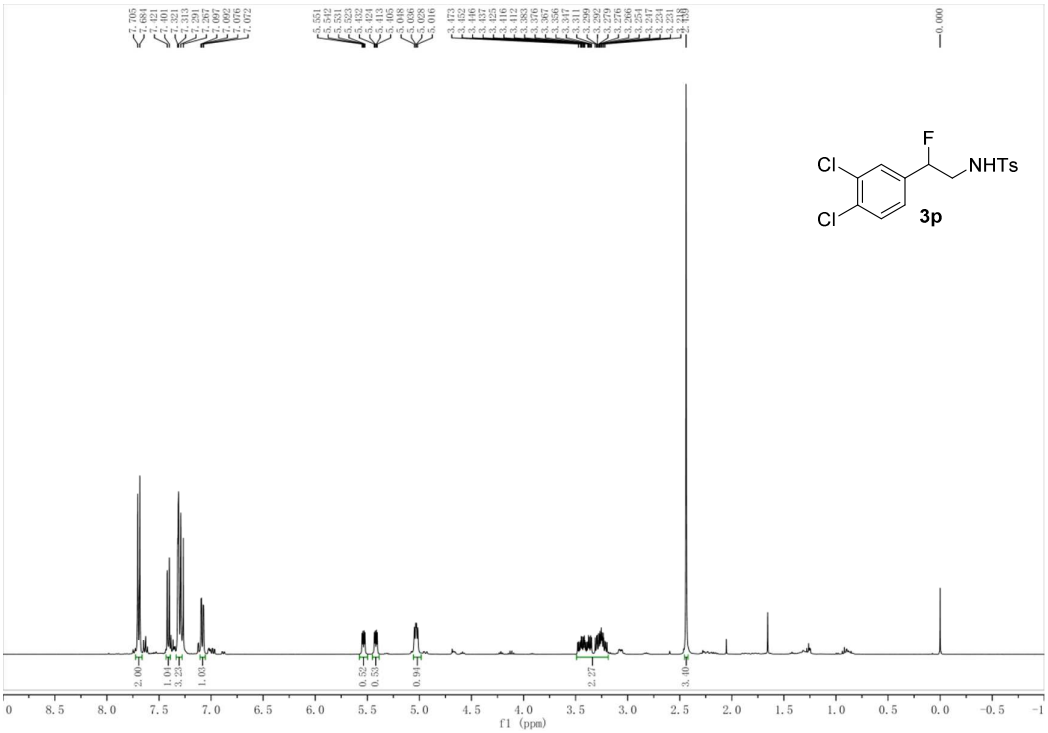
N-(2-fluoro-2-mesitylethyl)-4-methylbenzenesulfonamide (3o)

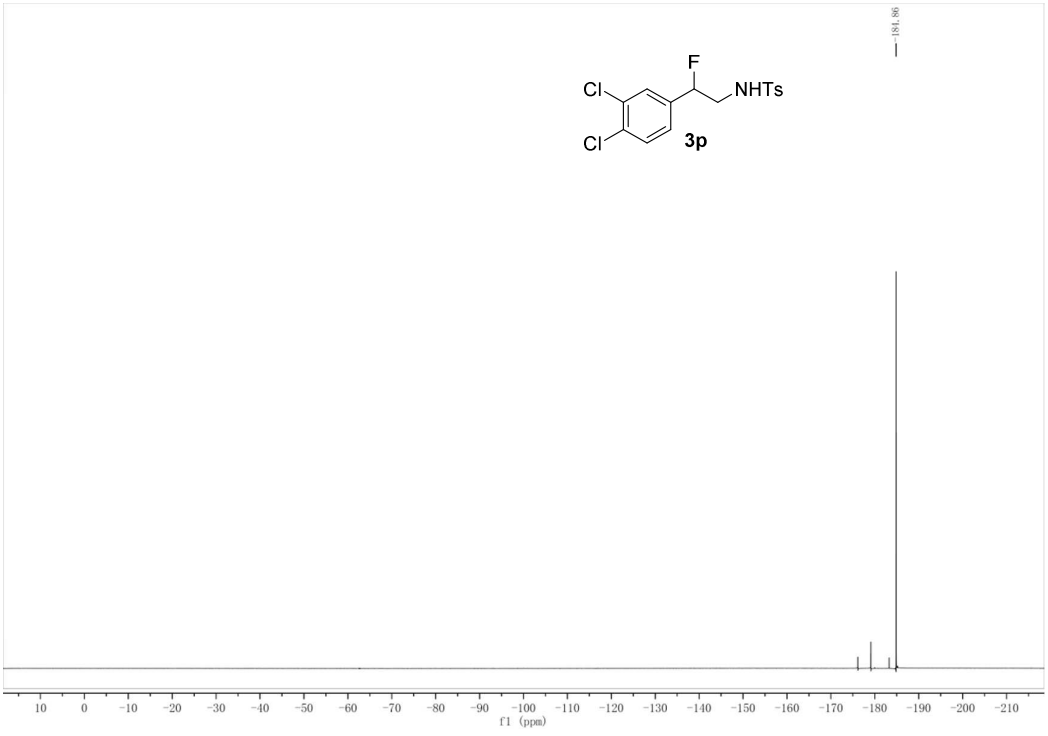


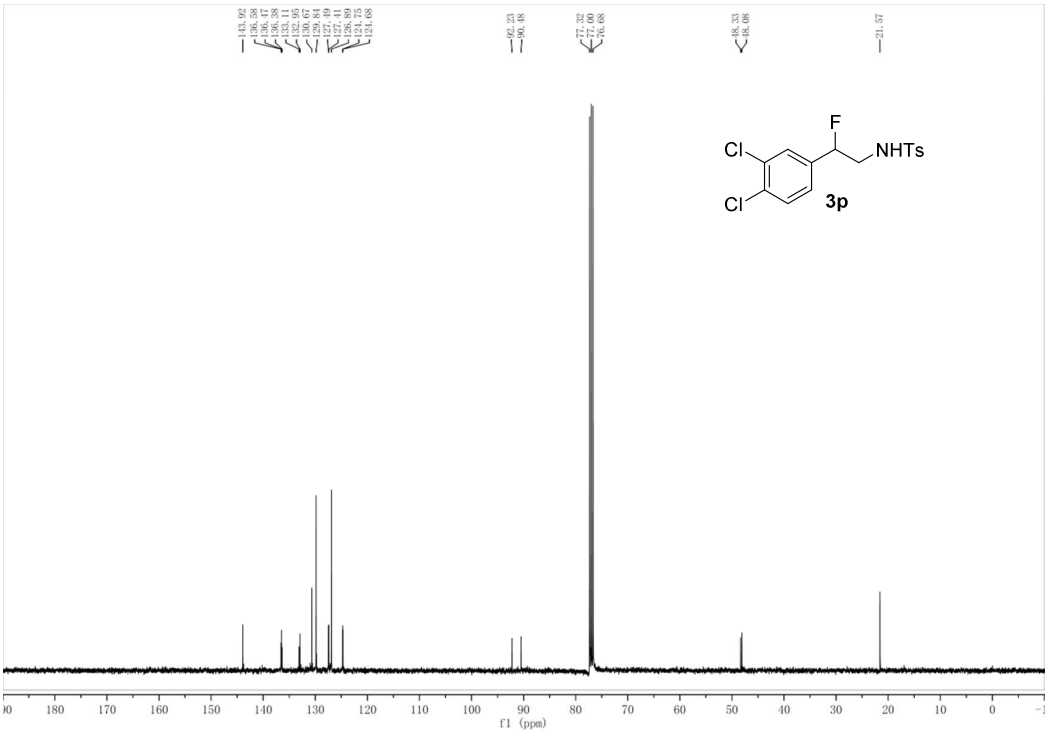




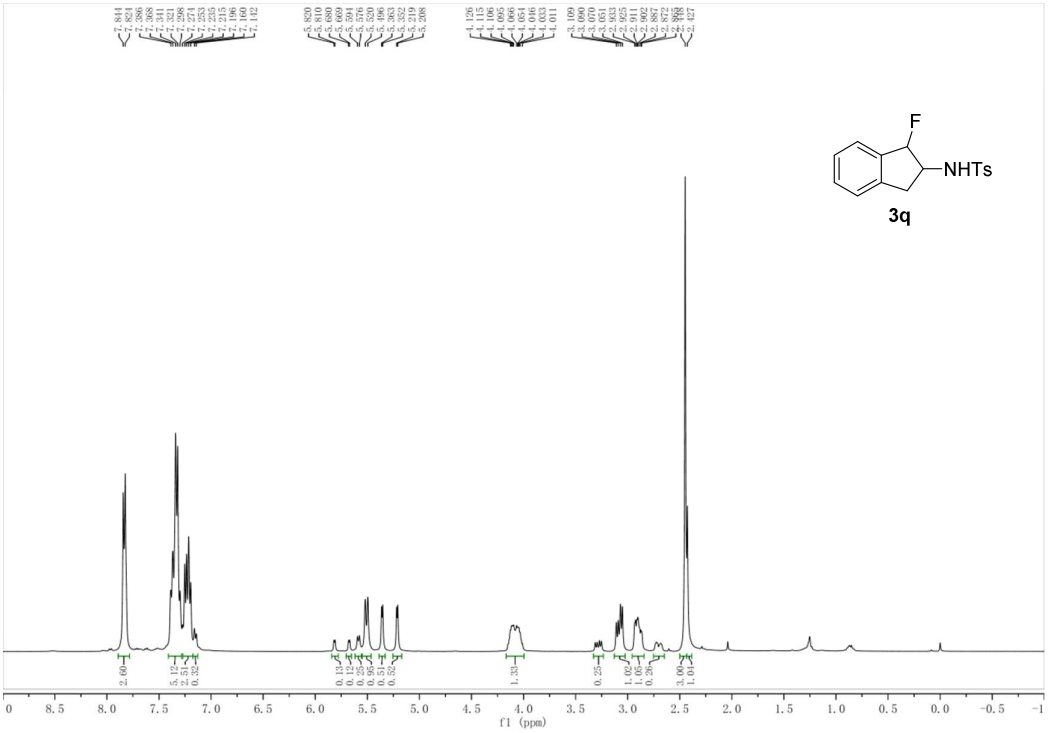
N-(2-(3,4-dichlorophenyl)-2-fluoroethyl)-4-methylbenzenesulfonamide (3p)

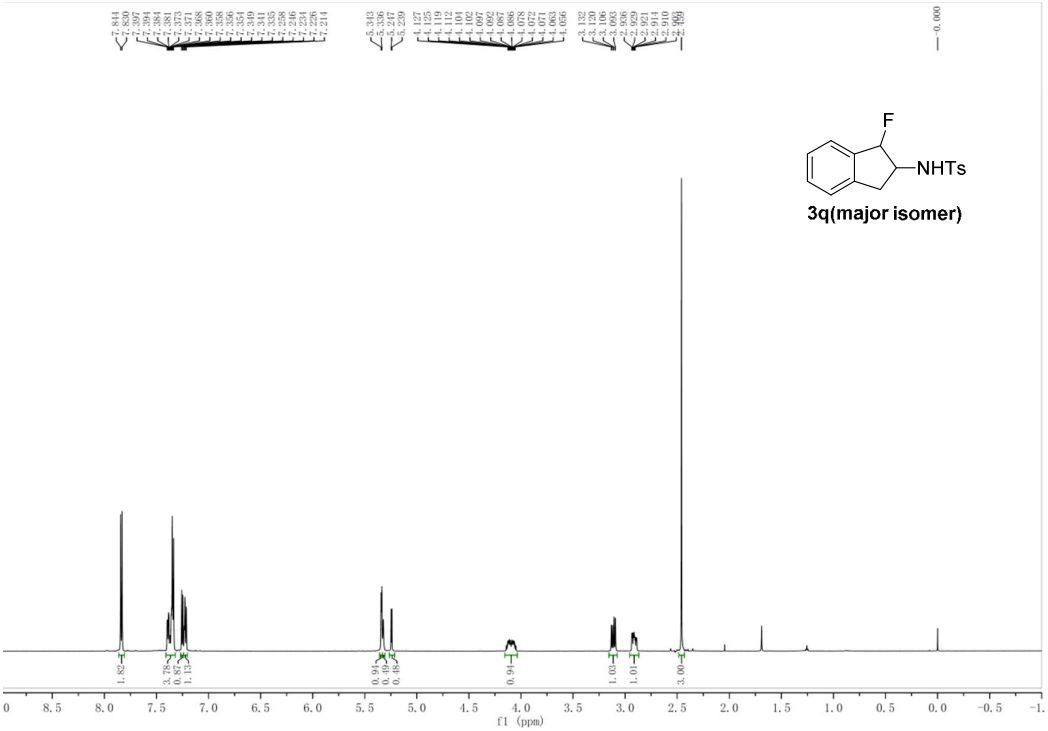


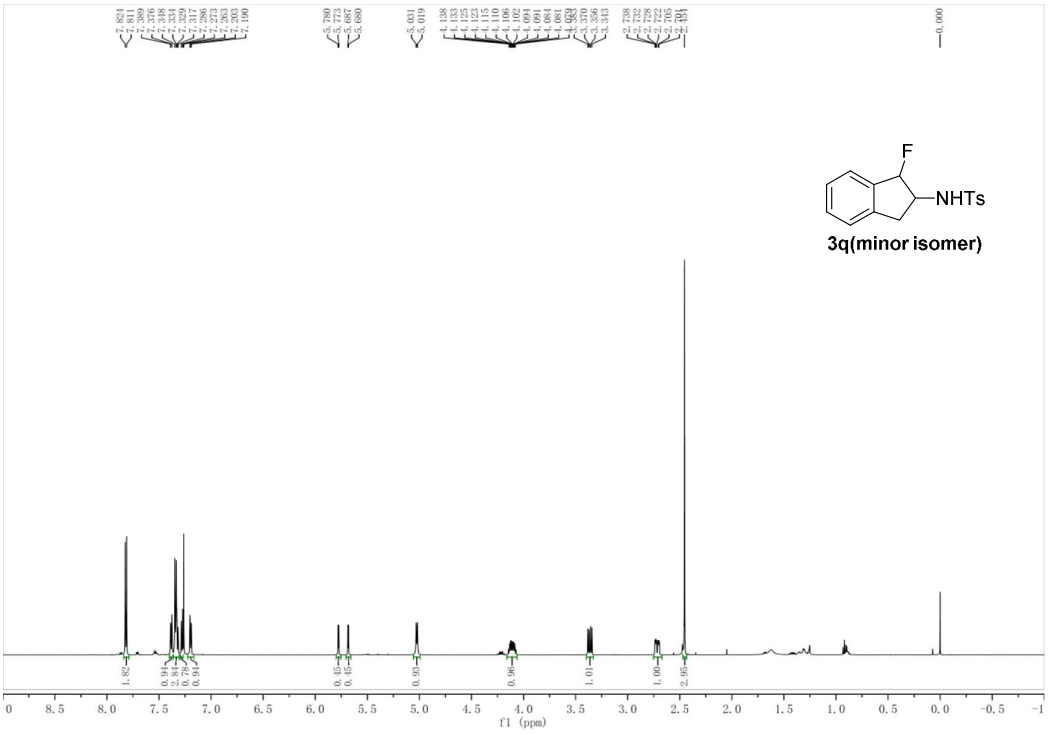

-181.86
F
Cl
NHTs
Cl
3p
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

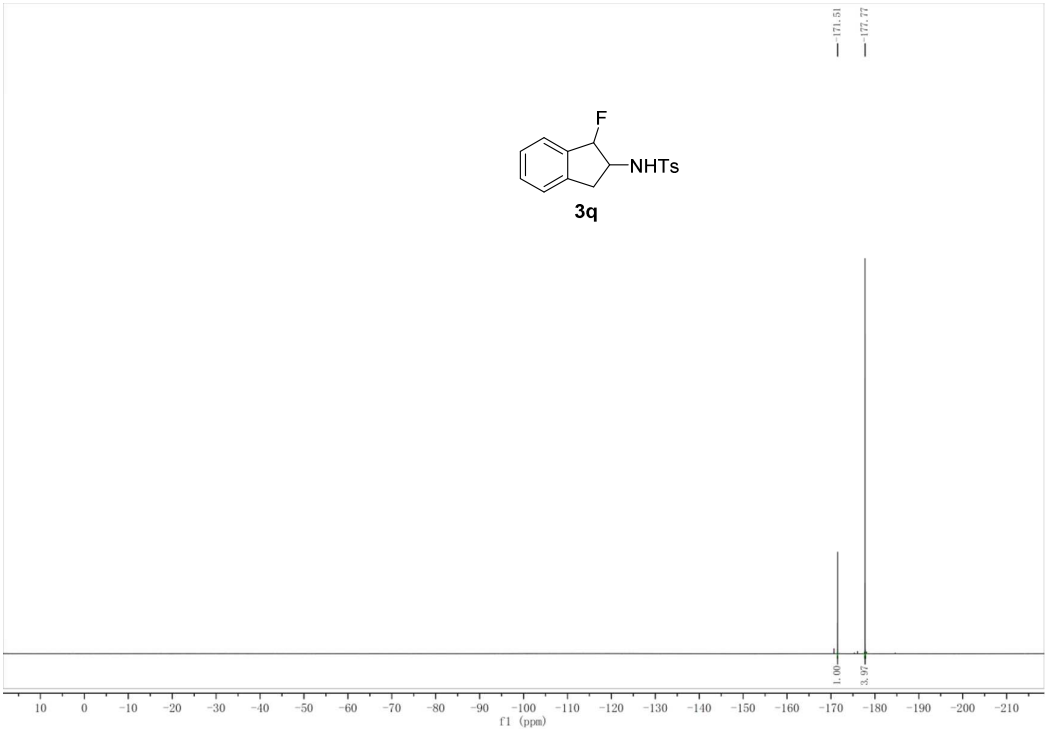

143.92
136.58
136.17
136.38
133.11
132.95
130.87
129.84
127.49
127.41
126.89
124.75
124.68
92.23
90.48
77.32
77.00
76.68
48.33
48.08
21.57
F
Cl
NHTs
Cl
3p
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

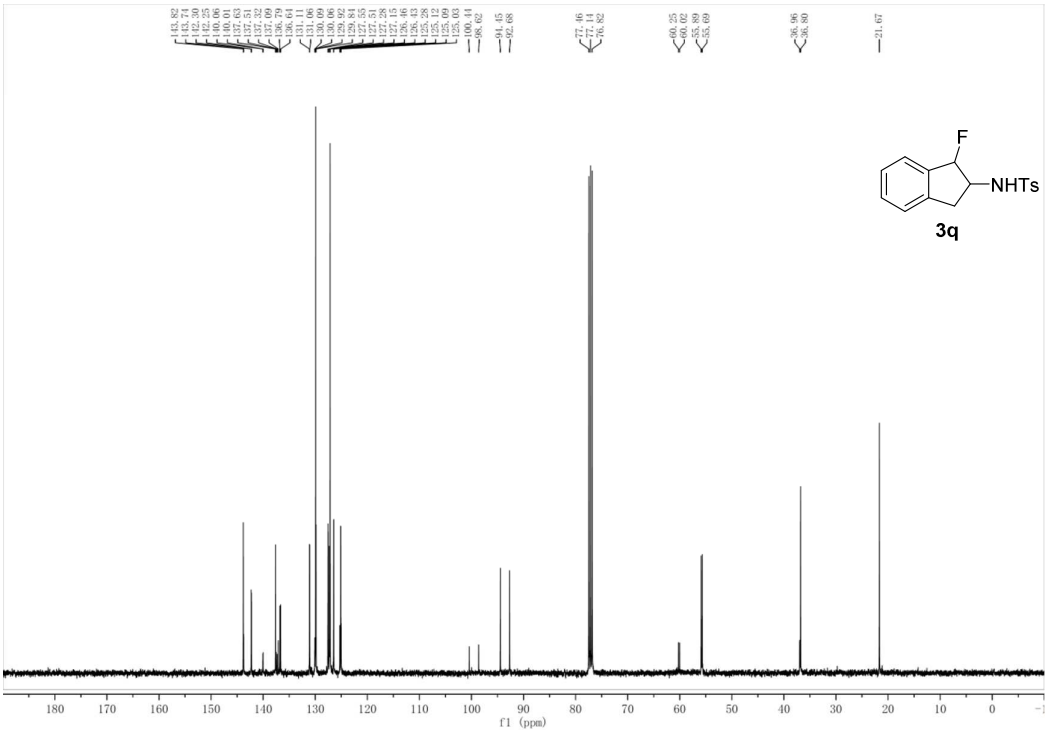
N-(1-fluoro-2,3-dihydro-1H-inden-2-yl)-4-methylbenzenesulfonamide(3q)



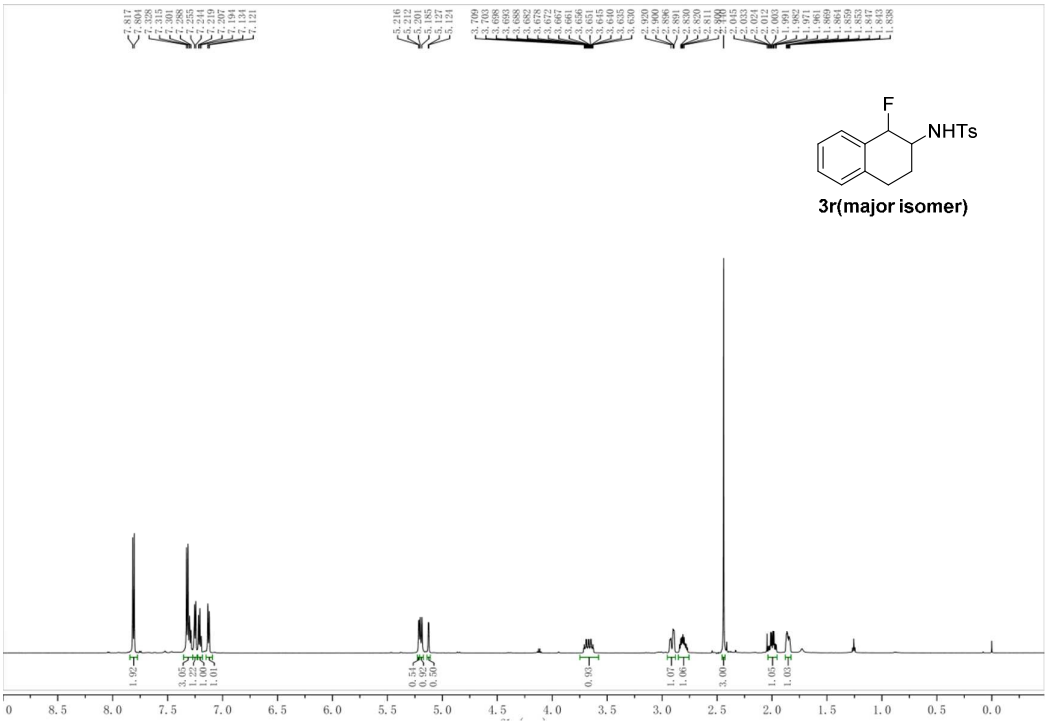


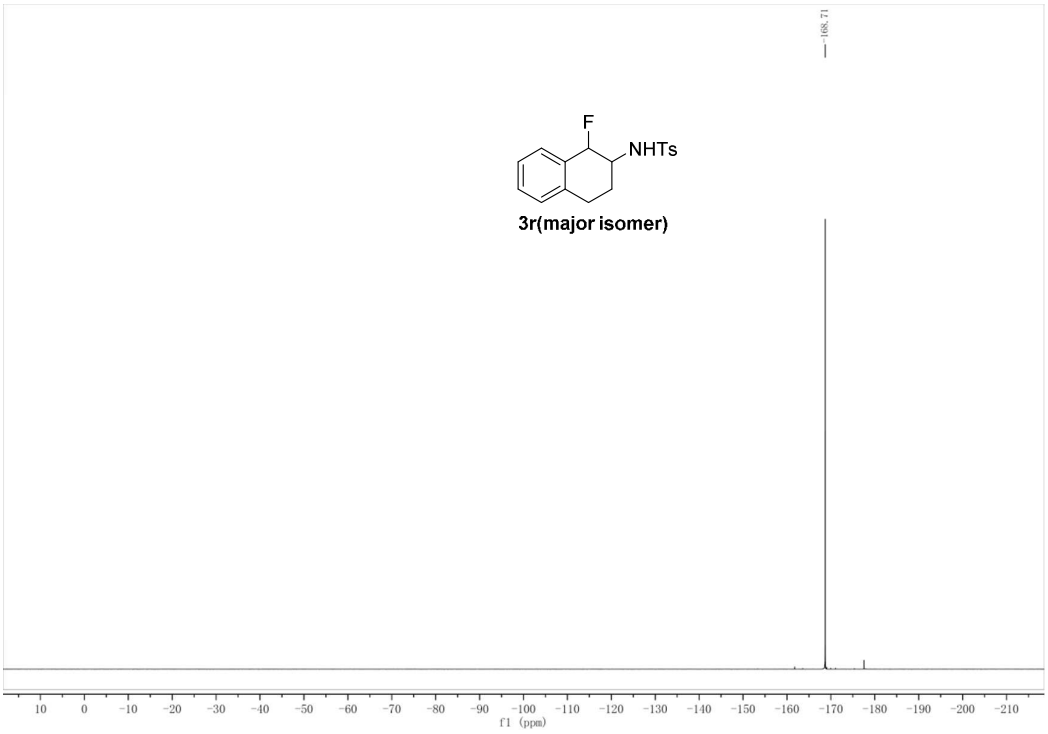

F
NHTs
3q(minor isomer)
f1 (ppm)

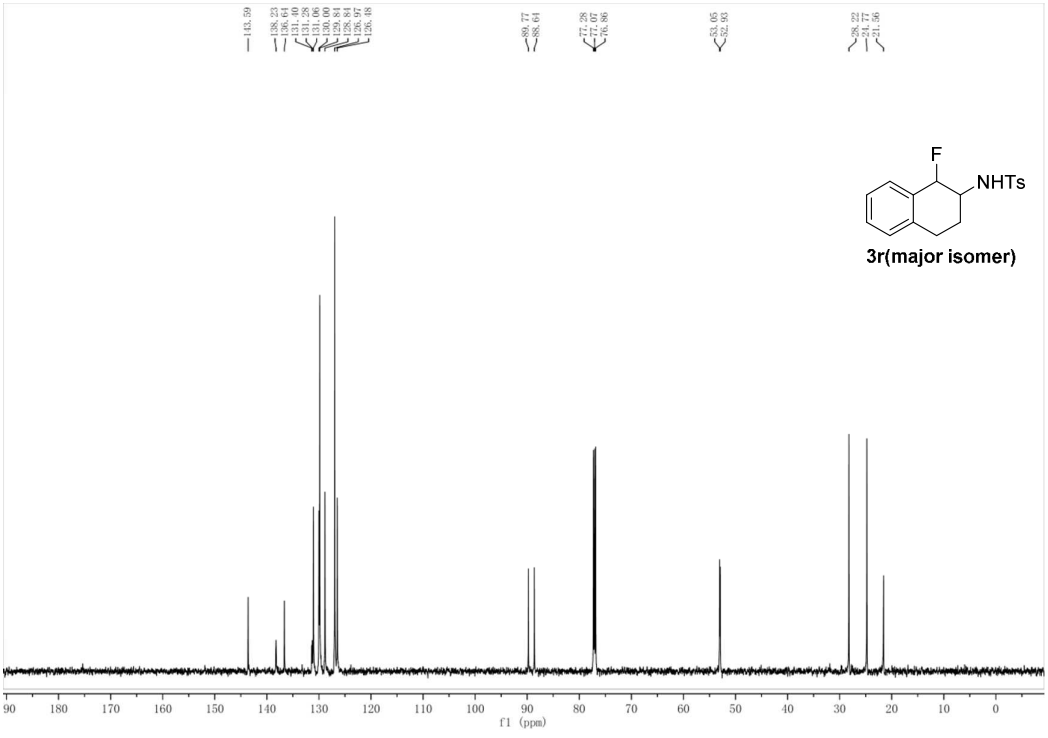

F
NHTs
3q
f1 (ppm)

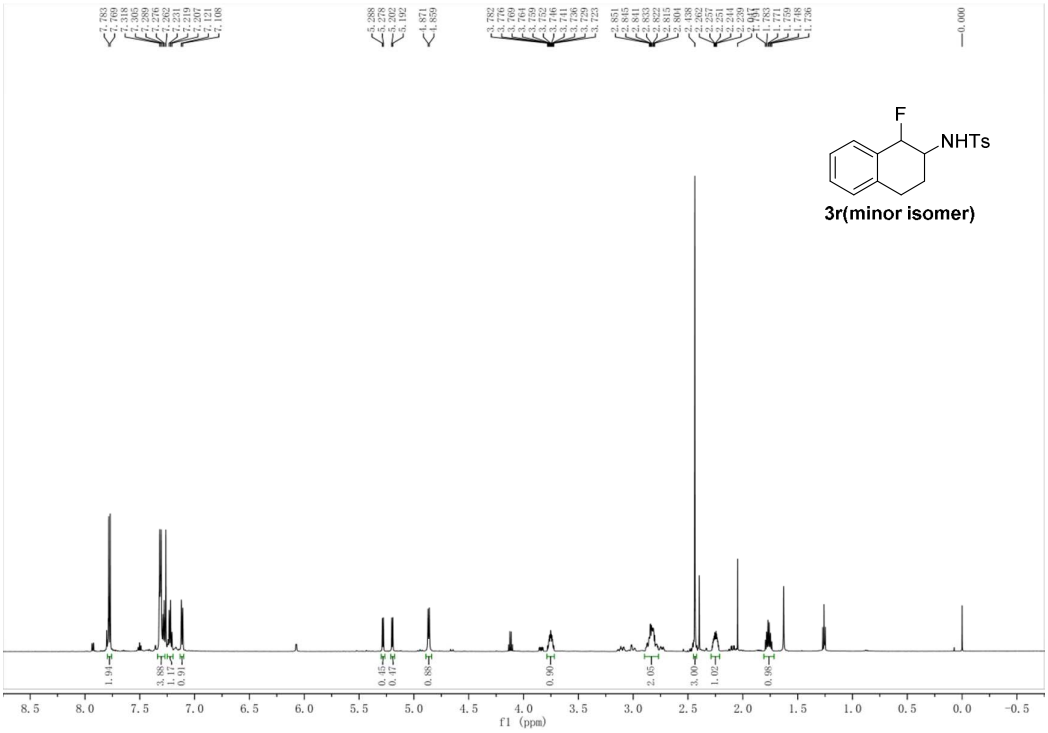


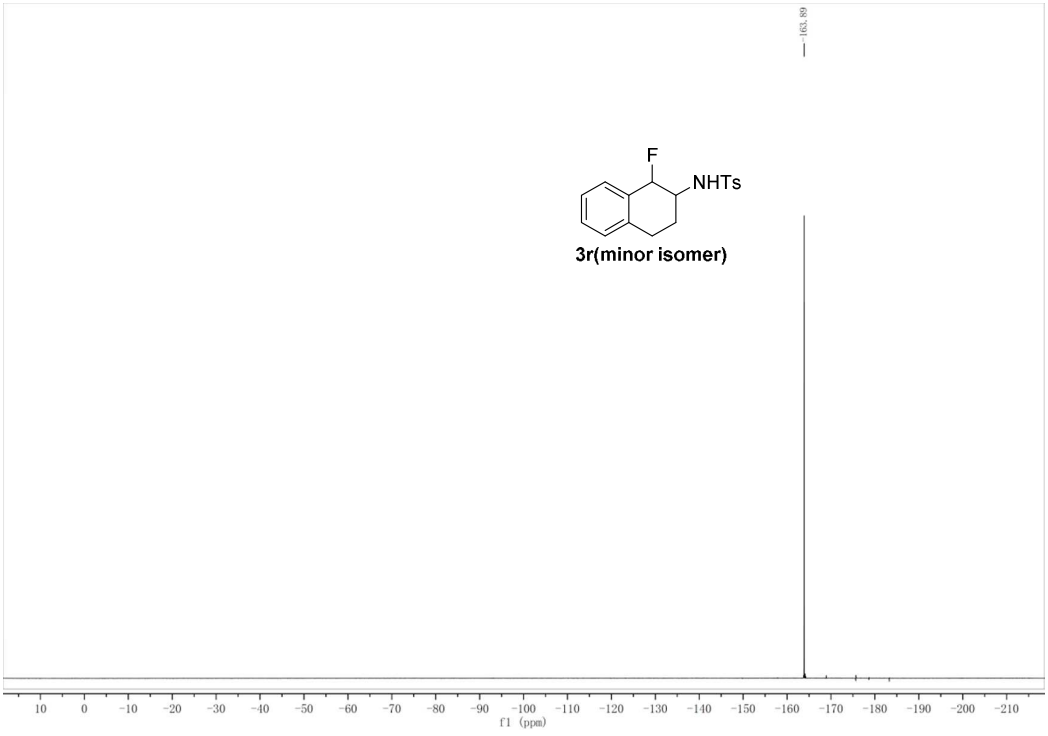
N-(1-fluoro-1,2,3,4-tetrahydronaphthalen-2-yl)-4-methylbenzenesulfonamide(3r)

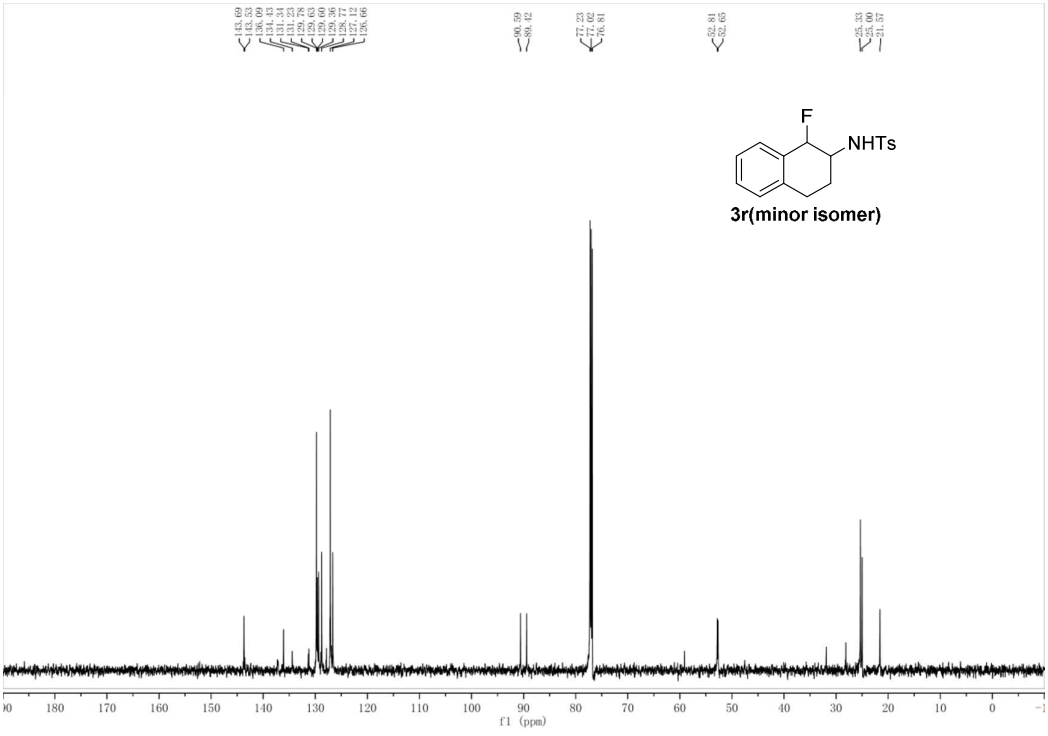


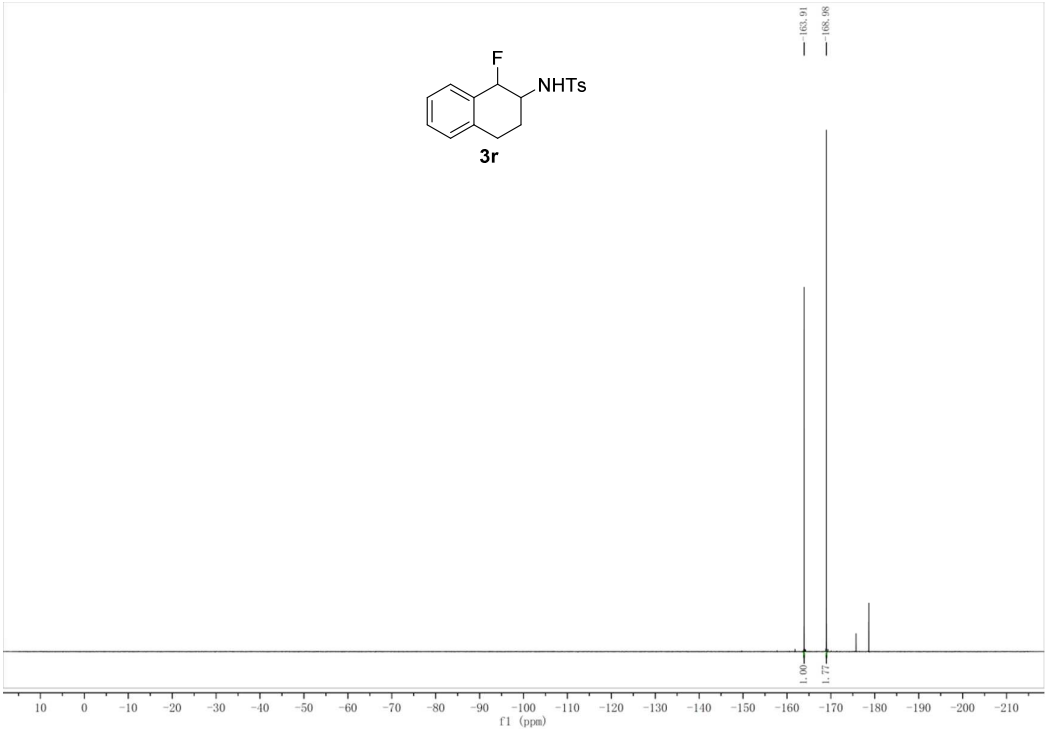

F
NHTs
3r(major isomer)
168.71
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


143.59
138.23
136.64
131.40
131.28
131.06
130.00
129.84
128.84
126.97
126.48
89.77
88.64
77.28
77.07
76.86
53.05
52.95
28.22
24.17
21.56
F
NHTs
3r(major isomer)
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

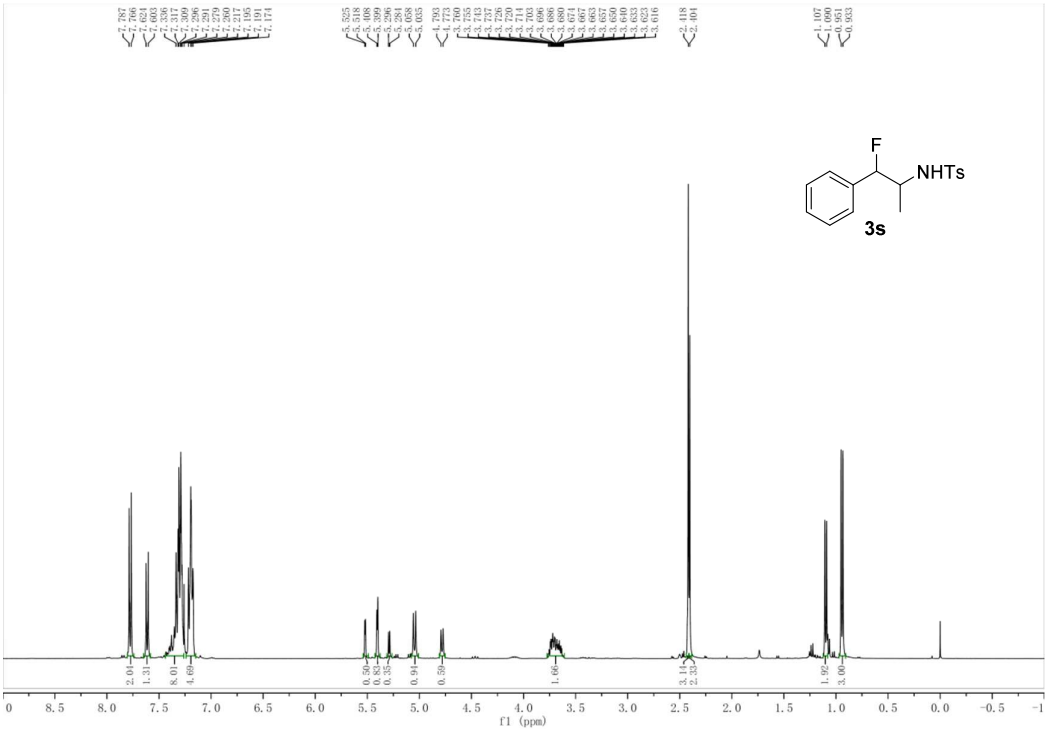

F
NHTs
3r(minor isomer)
f1 (ppm)

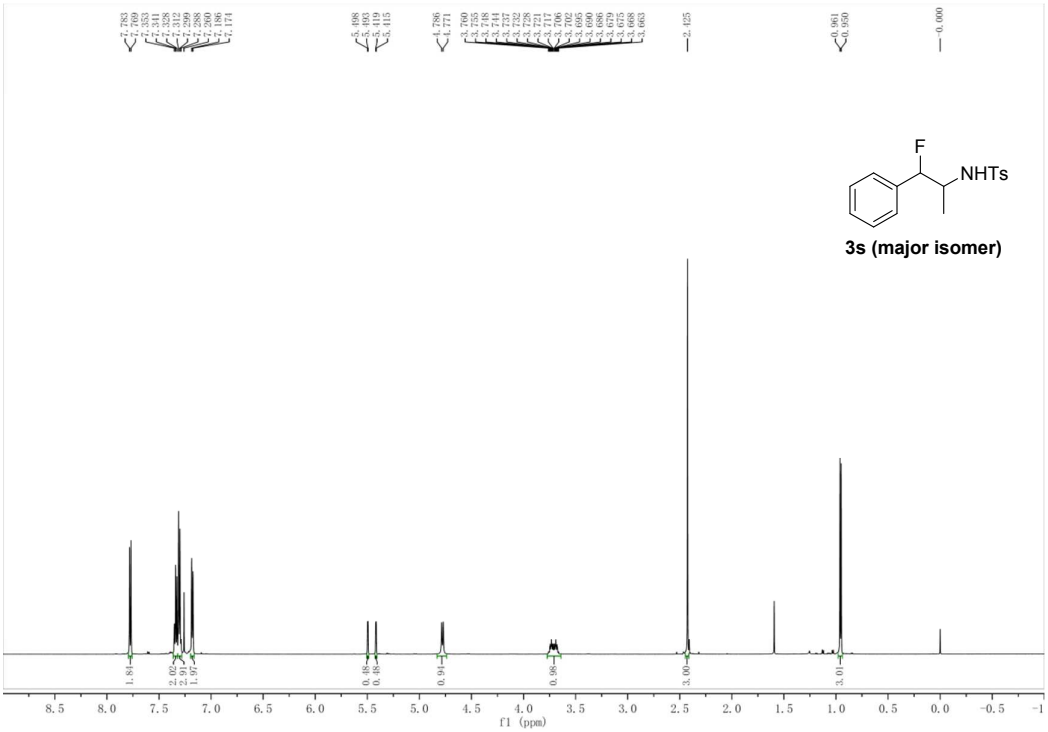

F
NHTs
3r(minor isomer)
f1 (ppm)

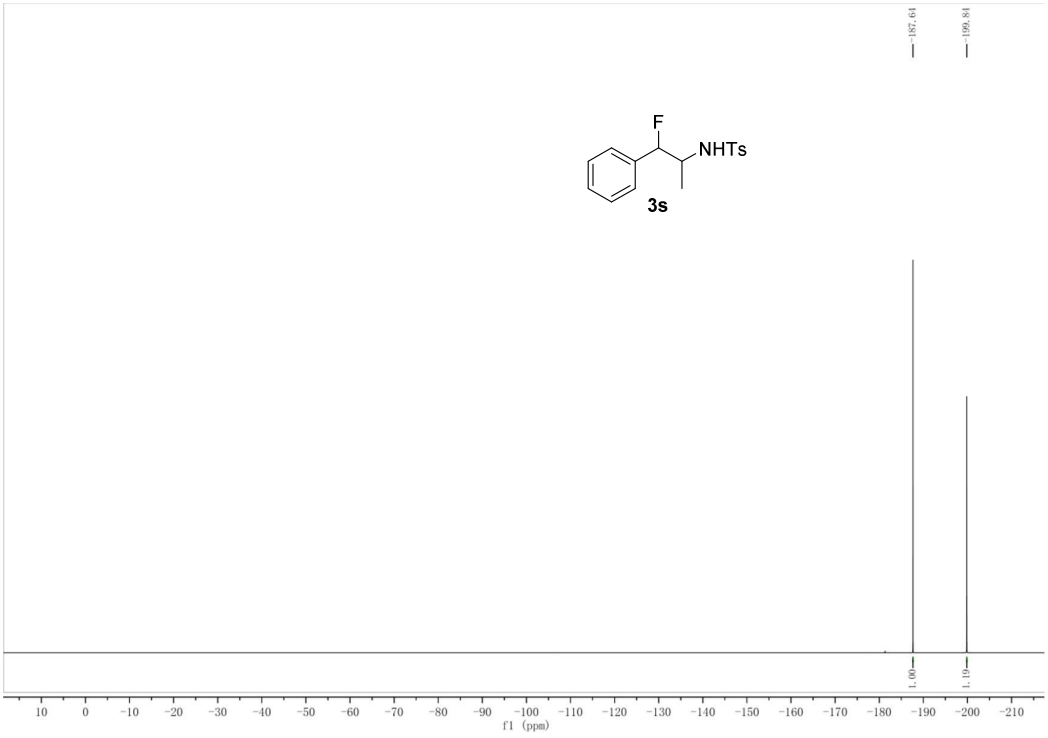

F
NHTs
3r(minor isomer)
f1 (ppm)

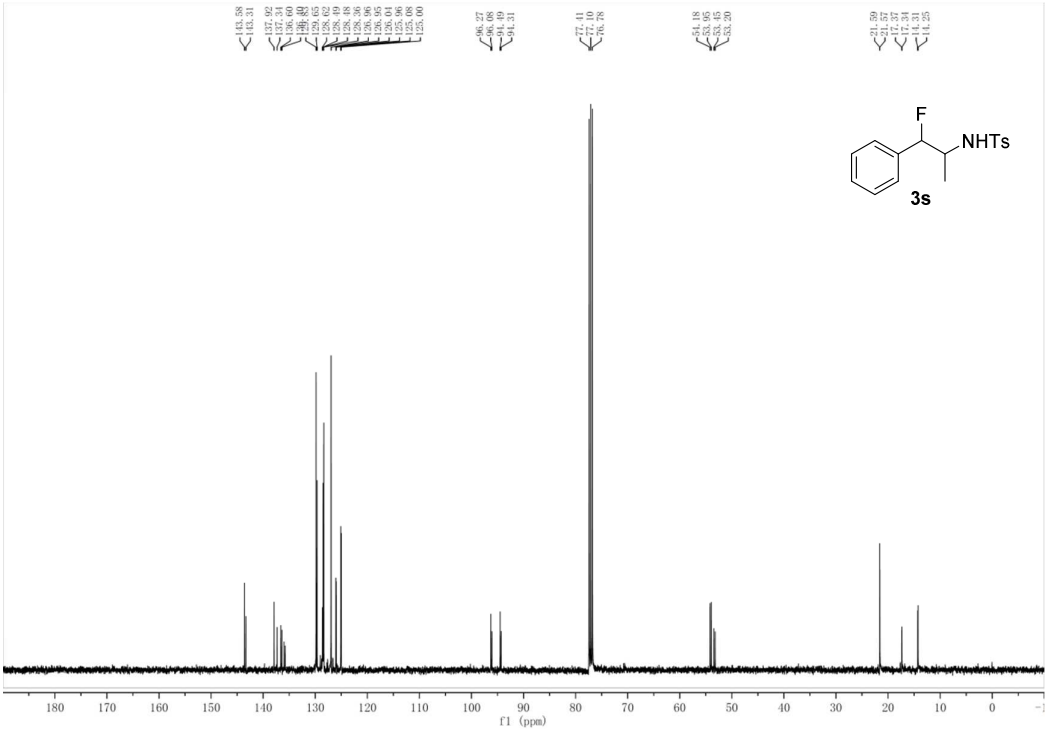

F
NHTs
3r
f1 (ppm)

N-(1-fluoro-1-phenylpropan-2-yl)-4-methylbenzenesulfonamide (3s)

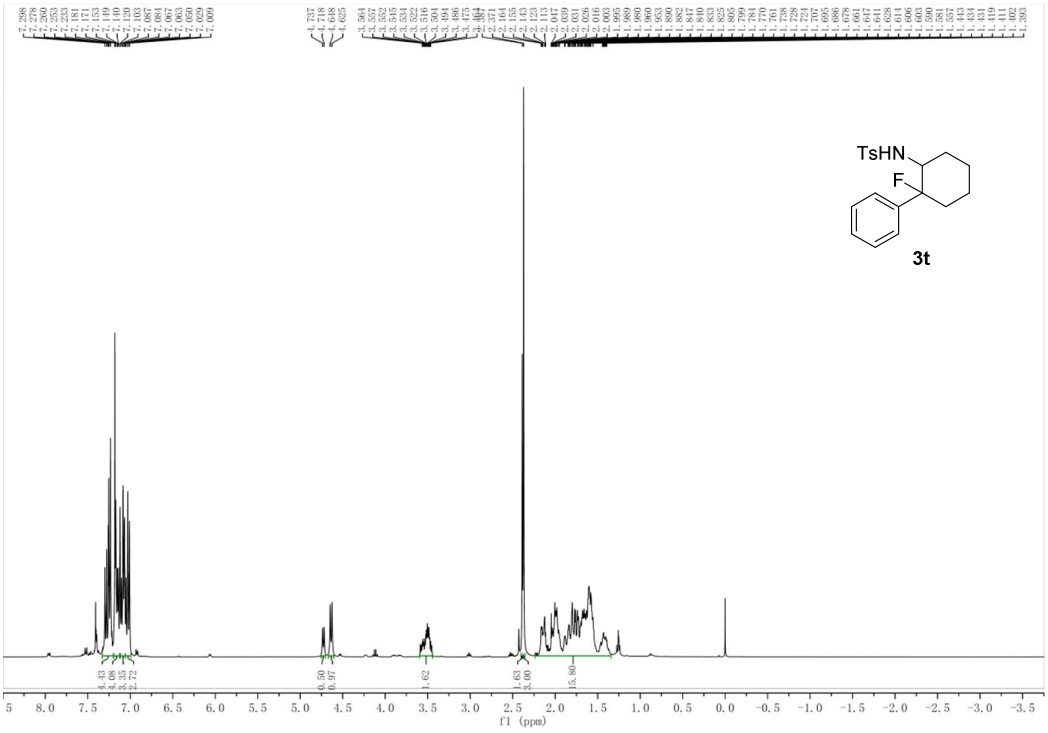


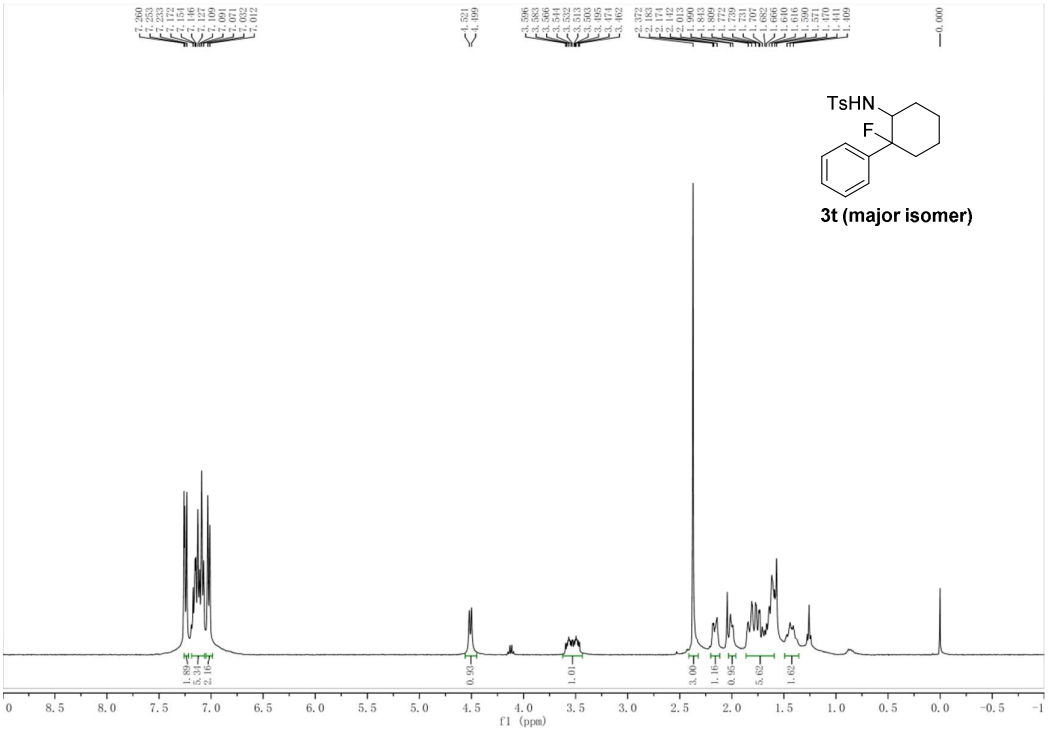


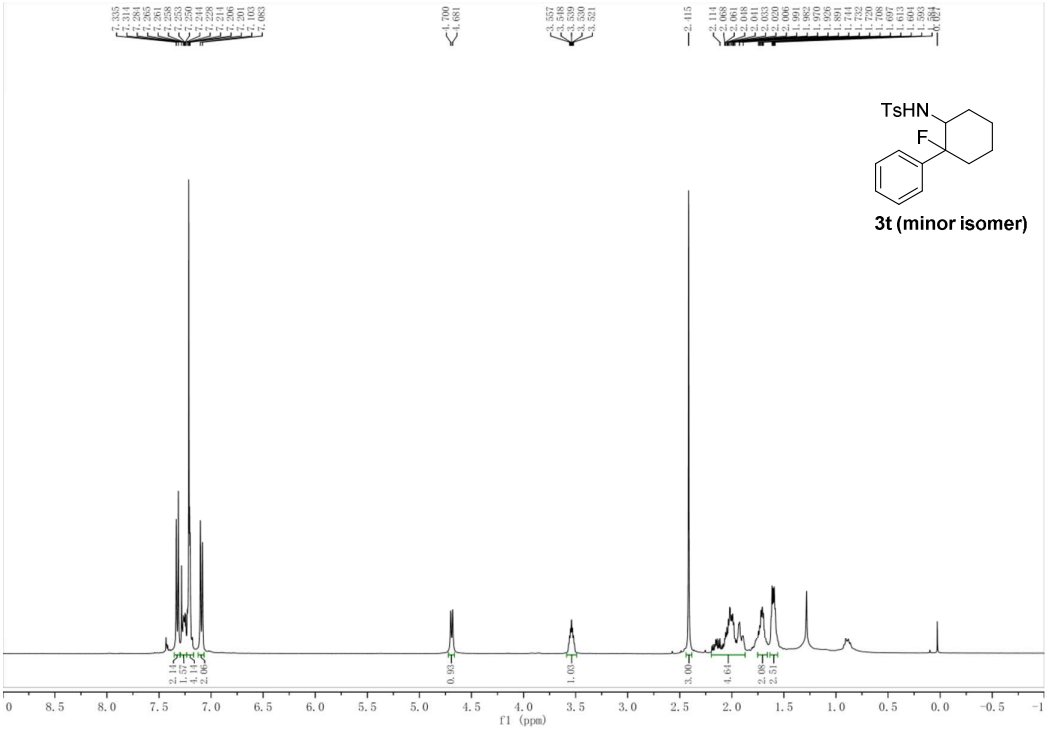

-187.61
-199.84
F
NHTs
3s
1.00
1.19
f1 (ppm)

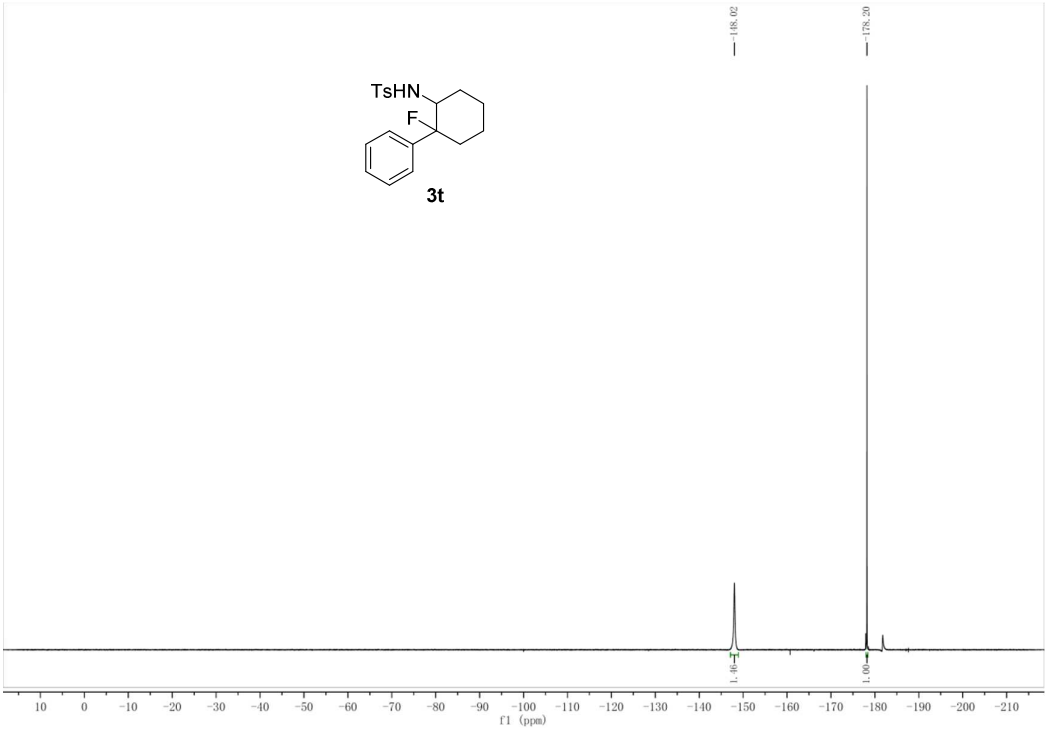

143.58
143.31
137.92
137.74
136.60
129.65
128.62
128.49
128.45
128.36
126.96
126.95
126.04
125.96
125.68
125.00
96.27
96.08
94.49
94.31
77.41
77.10
76.78
54.18
53.95
53.45
53.20
21.59
21.57
17.37
17.34
14.31
14.25
F
NHTs
3s
f1 (ppm)

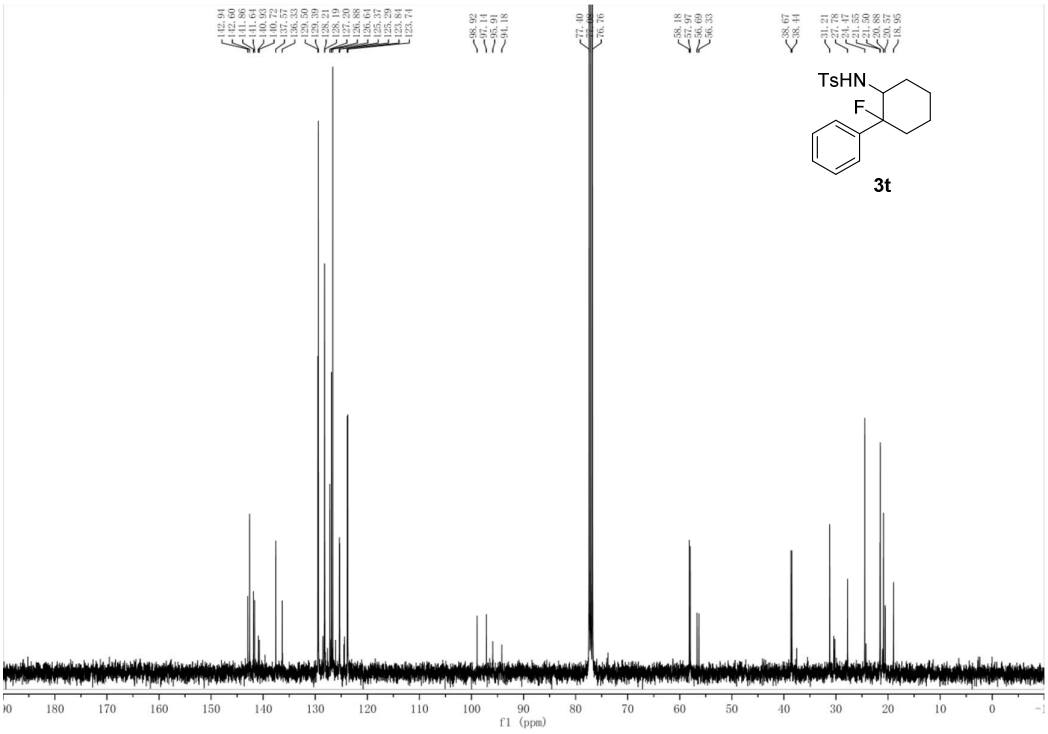
N-(2-fluoro-2-phenylcyclohexyl)-4-methylbenzenesulfonamide(3t)



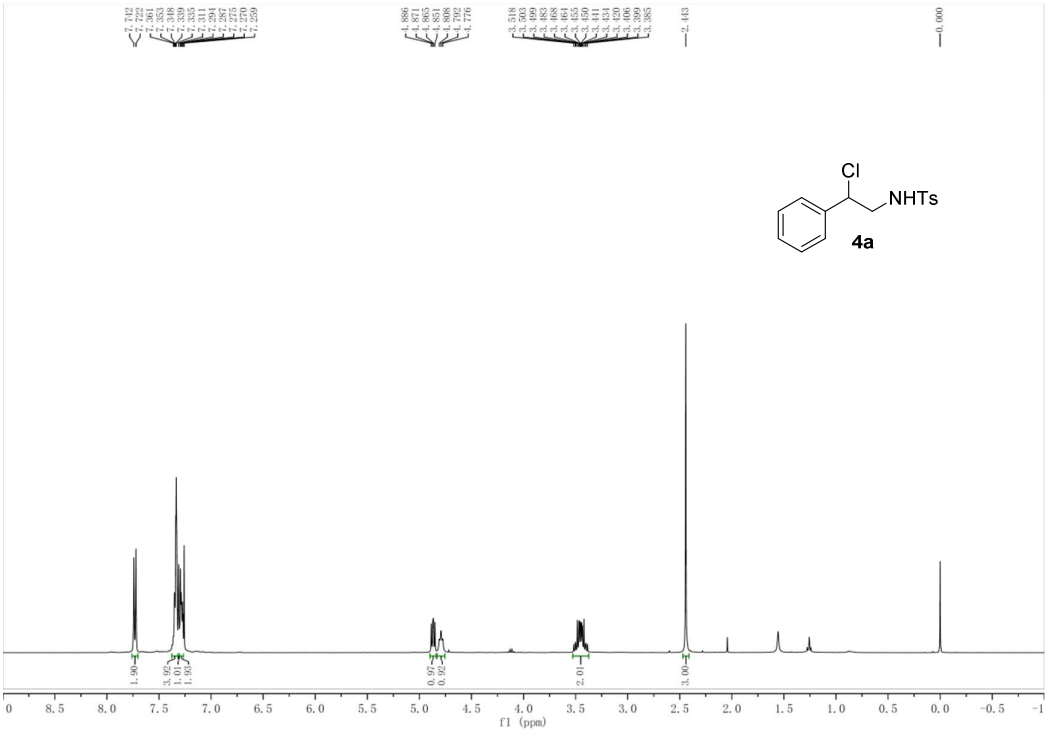


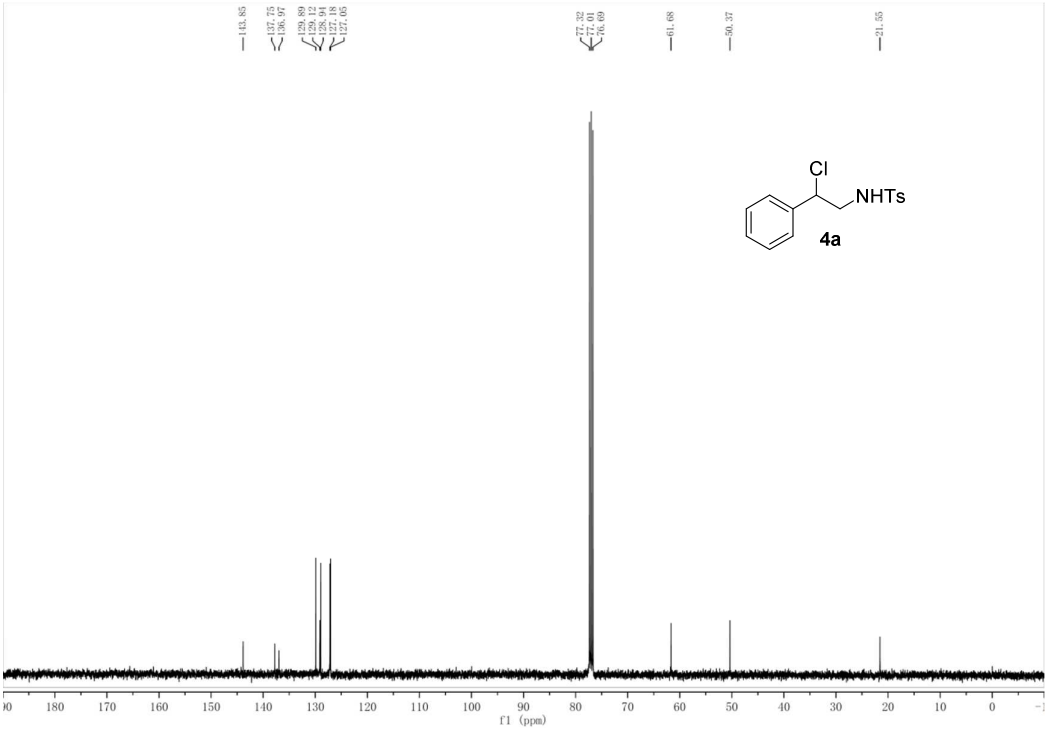

TsHN
F
3t (minor isomer)
f1 (ppm)


TsHN
F
3t
f1 (ppm)

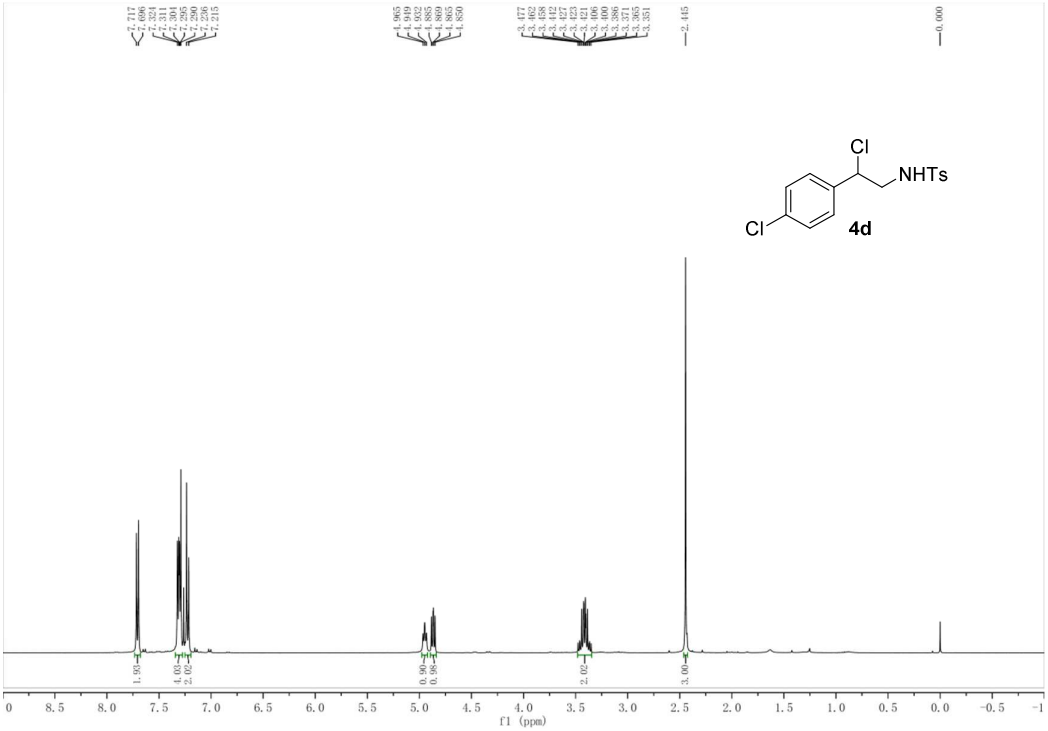


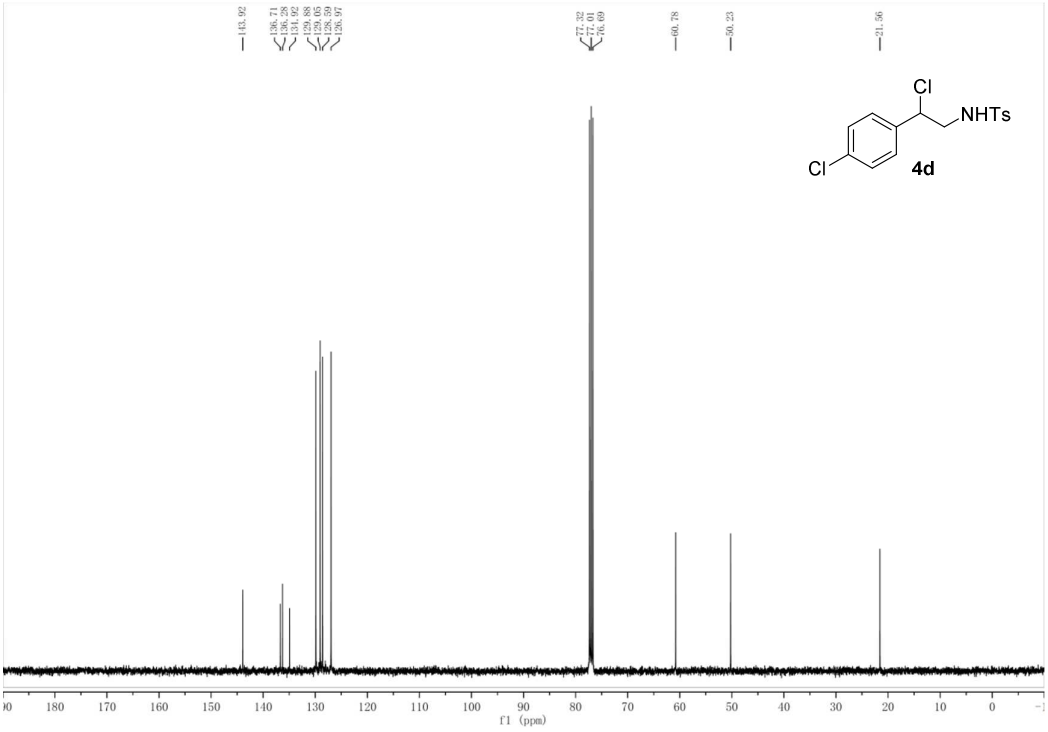
N-(2-chloro-2-phenylethyl)-4-methylbenzenesulfonamide (4a)



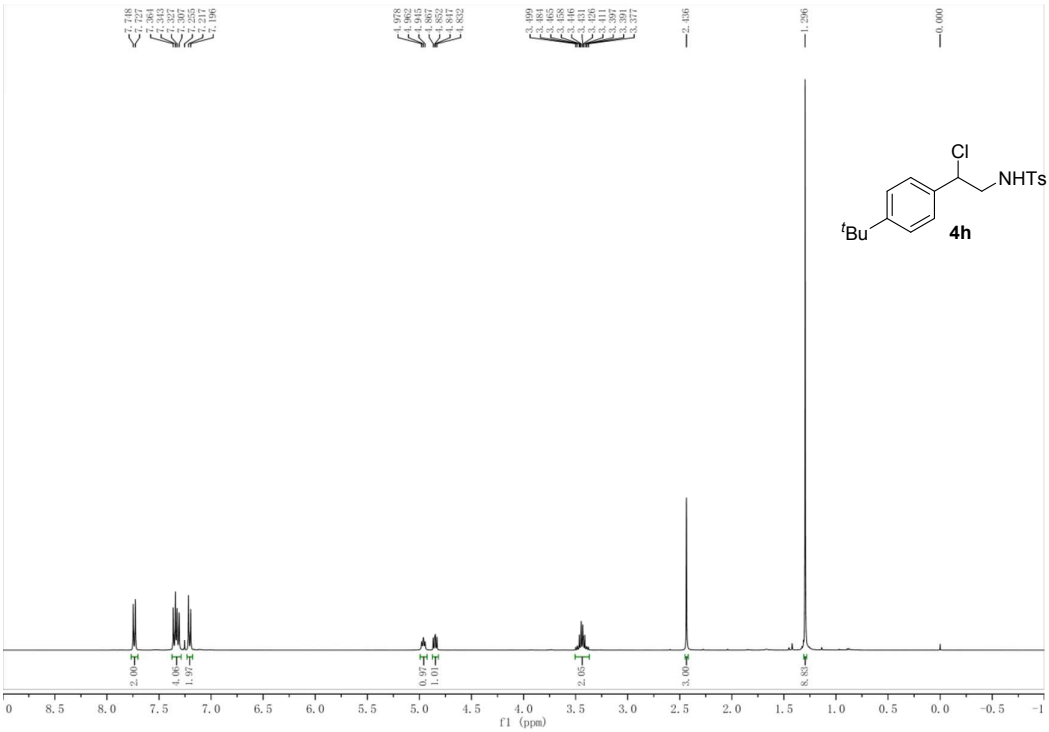


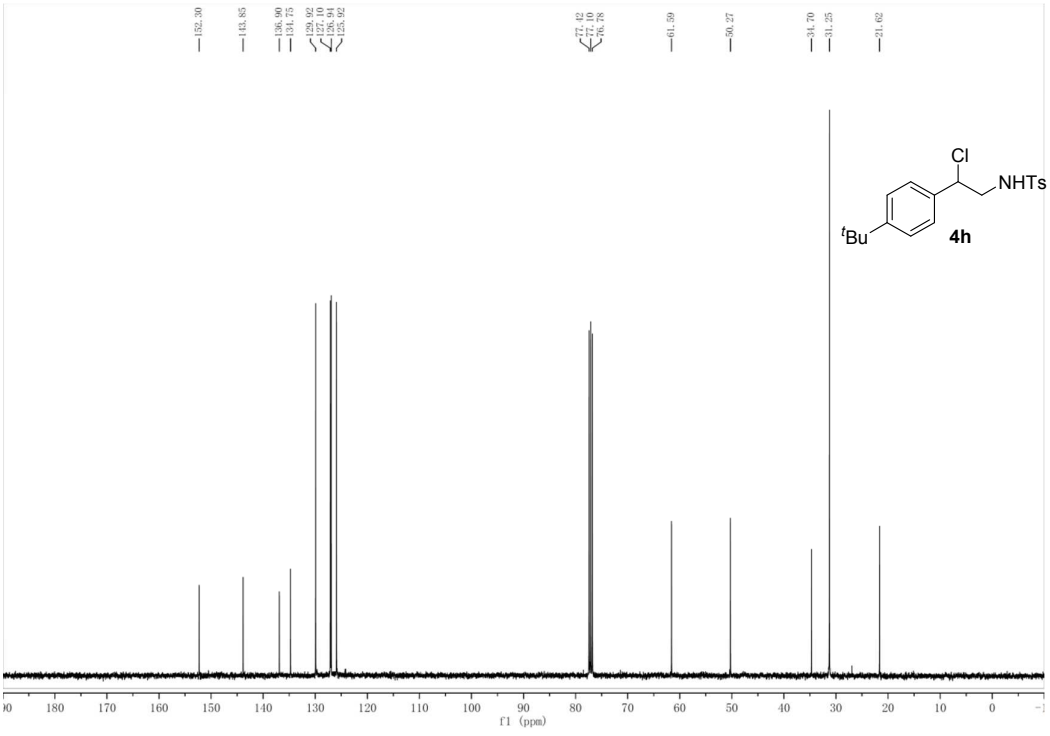
N-(2-chloro-2-(4-chlorophenyl)ethyl)-4-methylbenzenesulfonamide (4d)



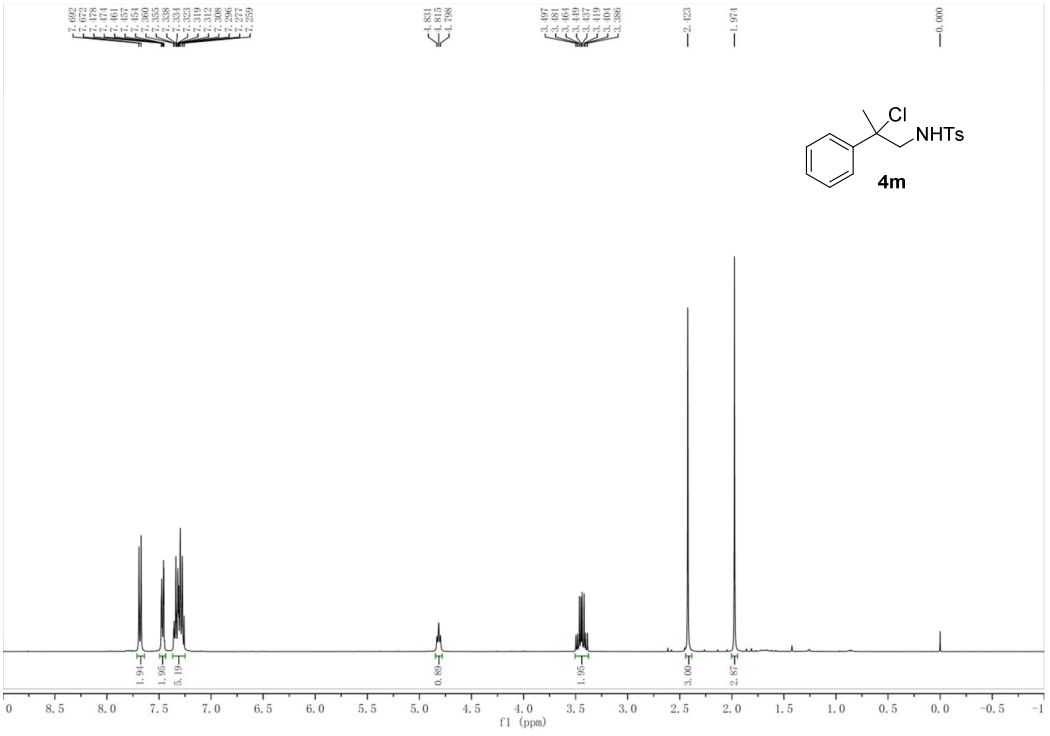


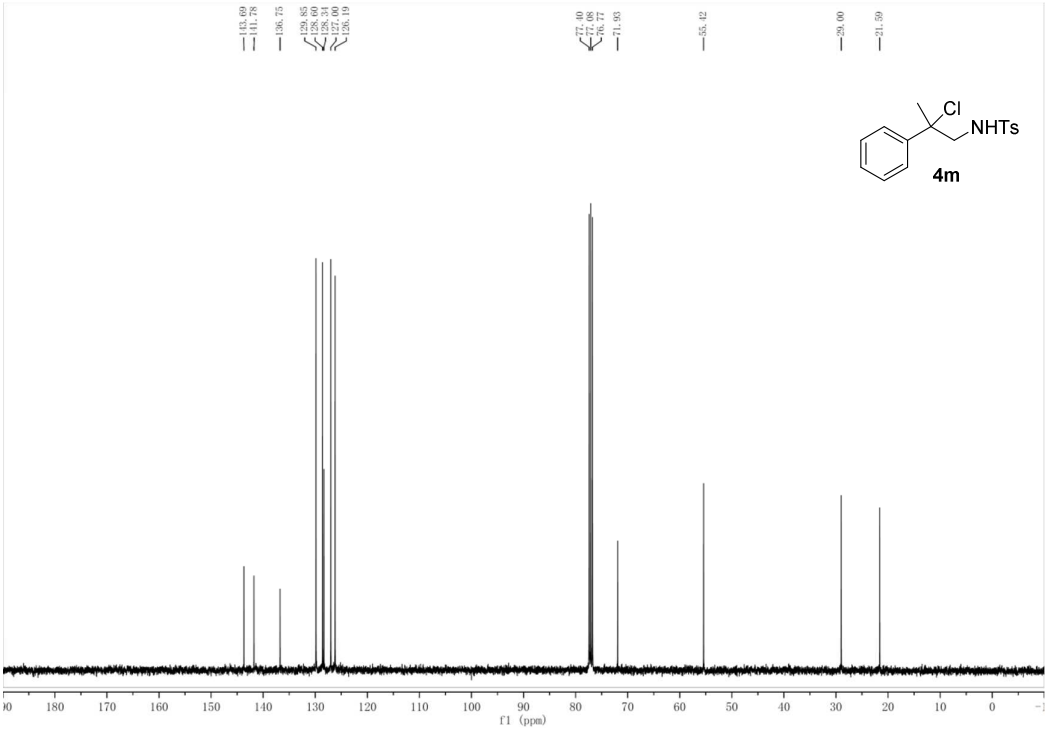
N-(2-(4-(tert-butyl)phenyl)-2-chloroethyl)-4-methylbenzenesulfonamid e (4h)



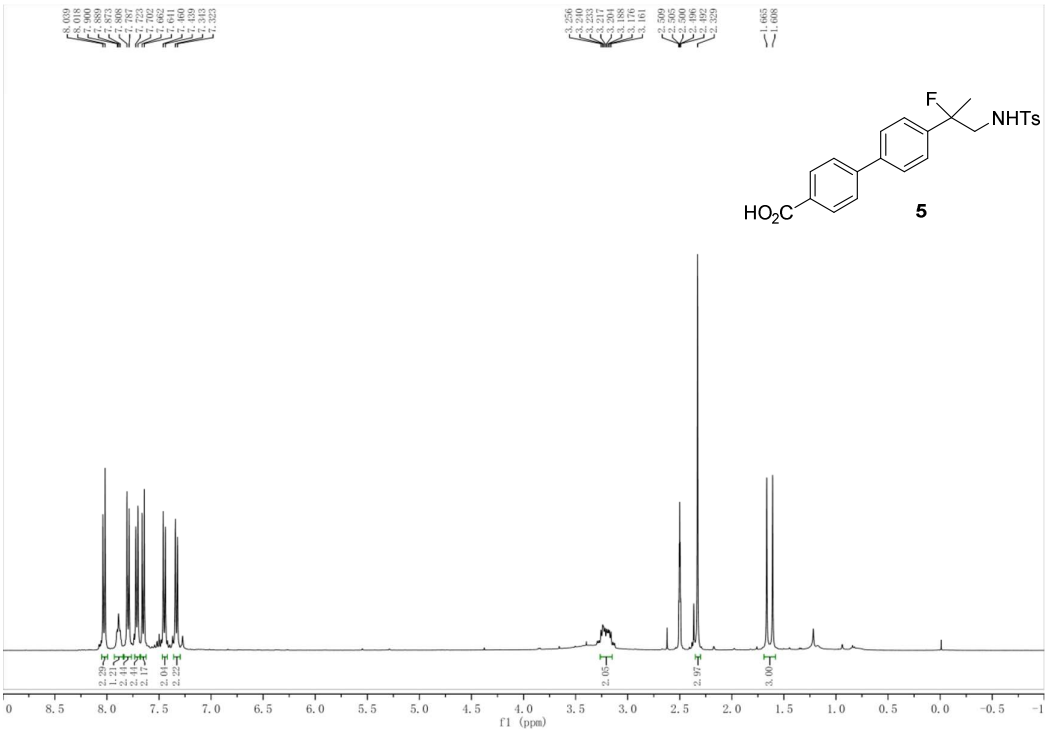


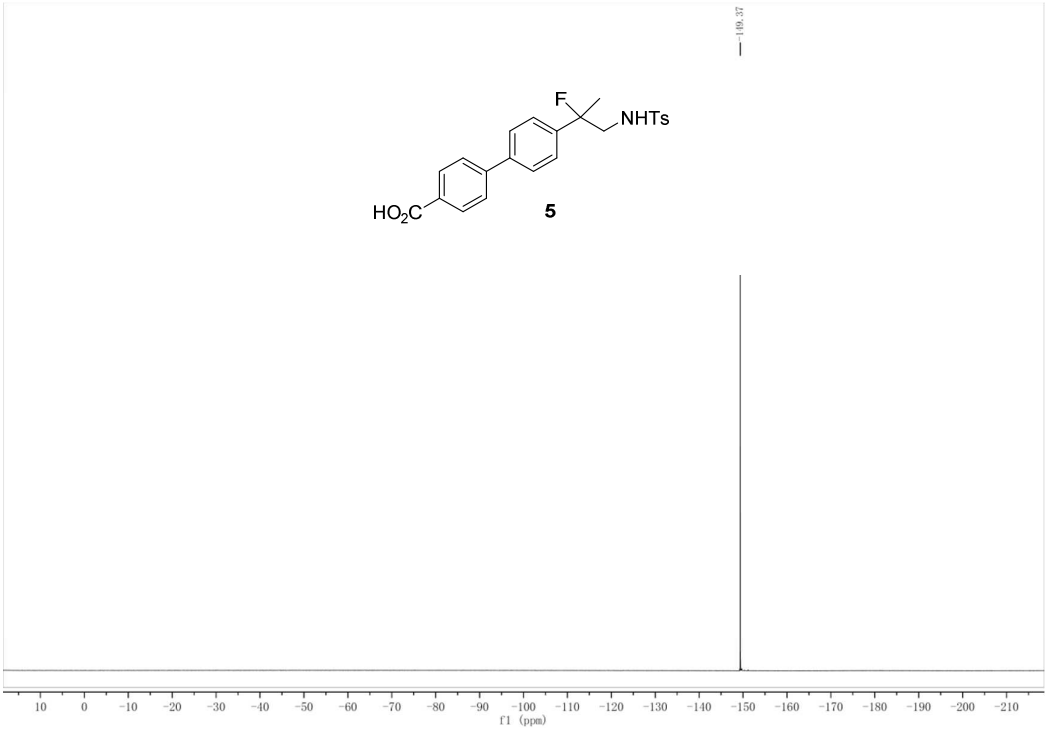
N-(2-chloro-2-phenylpropyl)-4-methylbenzenesulfonamide (4m)

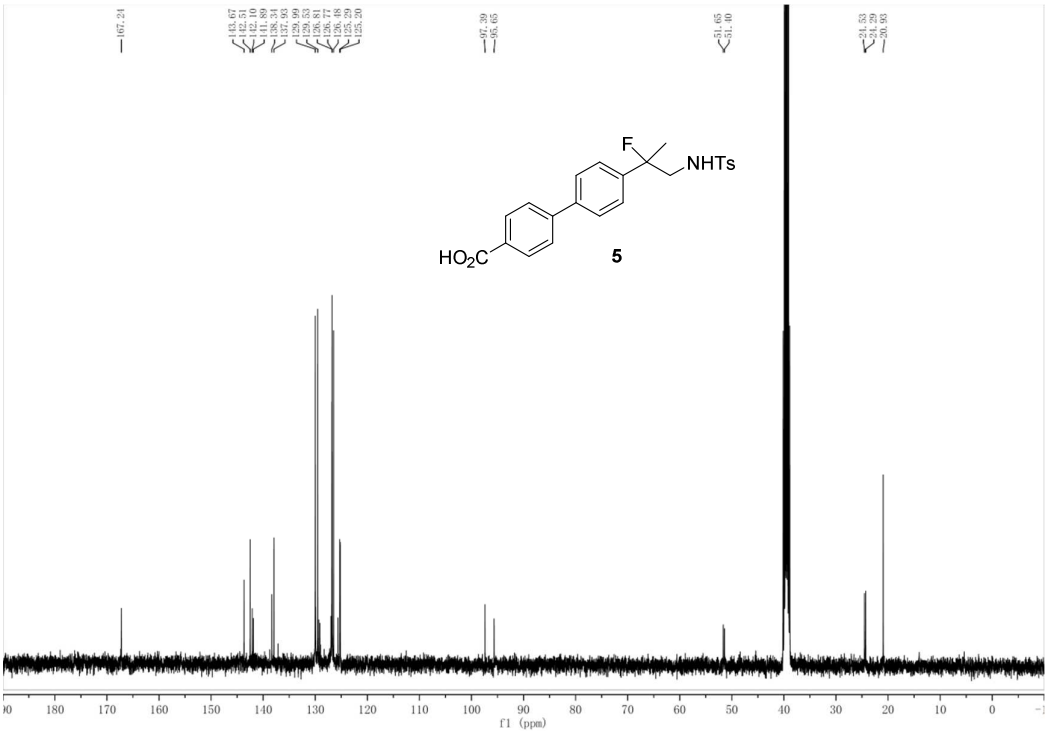




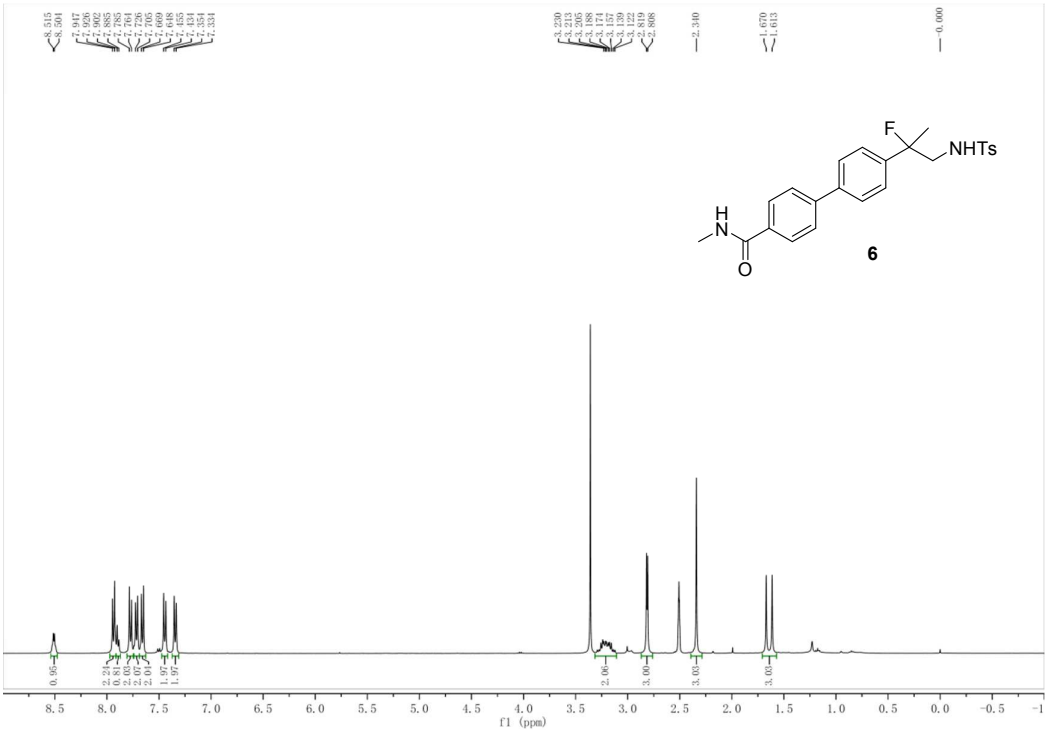
4'-(2-fluoro-1-((4-methylphenyl)sulfonamido)propan-2-yl)-[1,1'-biphenyl]-4-carboxylic acid (5)

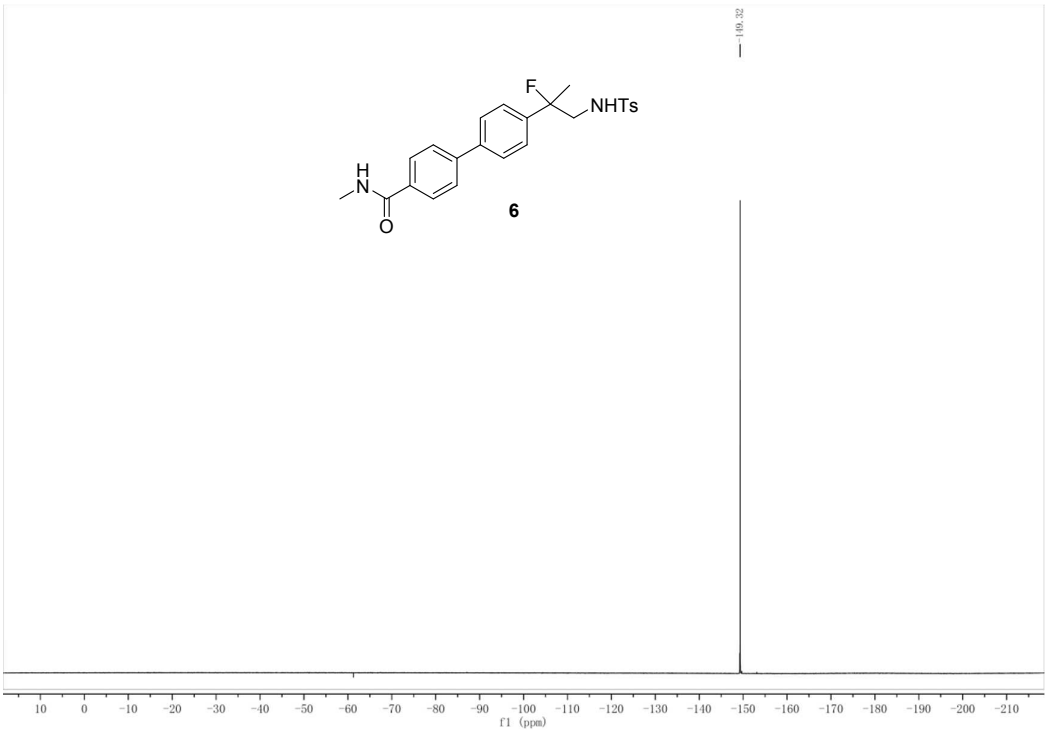


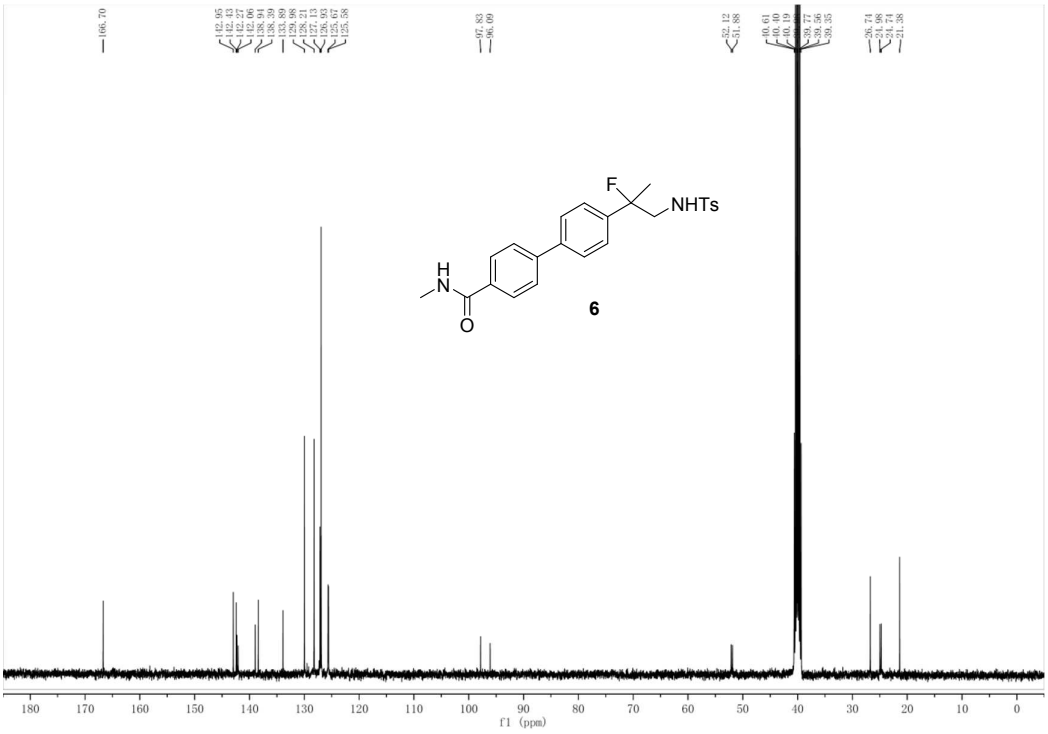

-109.37
F
NHTs
HO2C
5
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


167.24
143.67
142.51
142.10
141.89
138.34
137.93
129.99
129.53
126.81
126.77
126.48
125.39
125.20
97.39
95.65
51.65
51.40
24.53
24.29
20.93
F
NHTs
HO2C
5
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

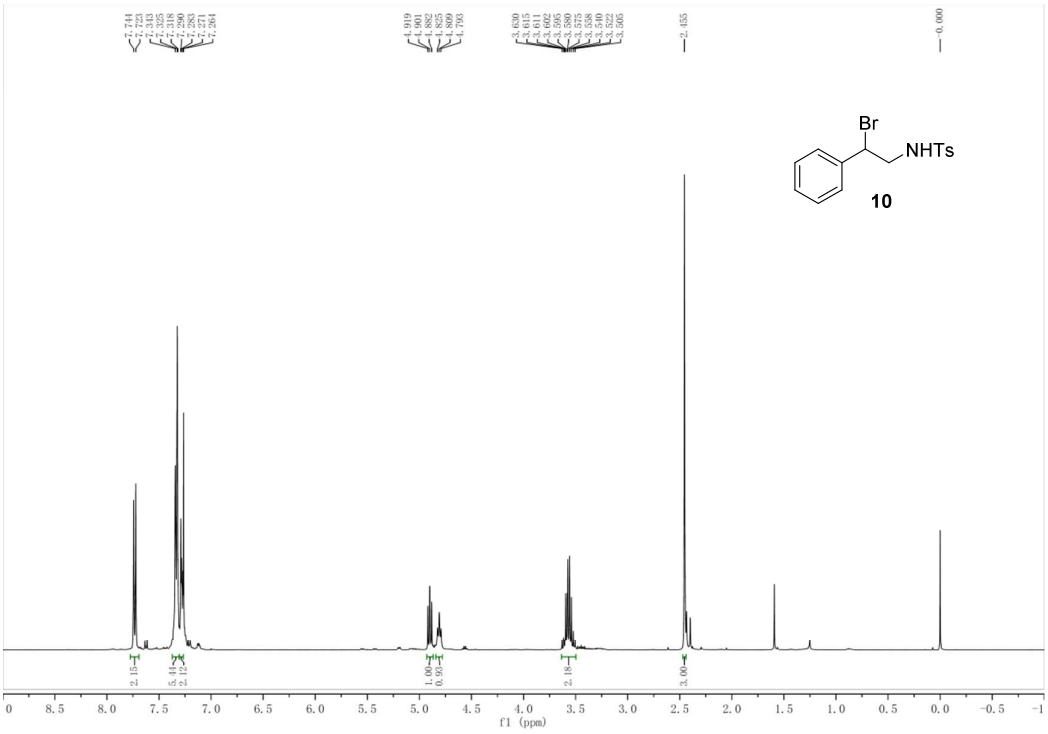
4'-(2-fluoro-1-((4-methylphenyl)sulfonamido)propan-2-yl)-N-methyl-[1, 1'-biphenyl]-4-carboxamide (6)

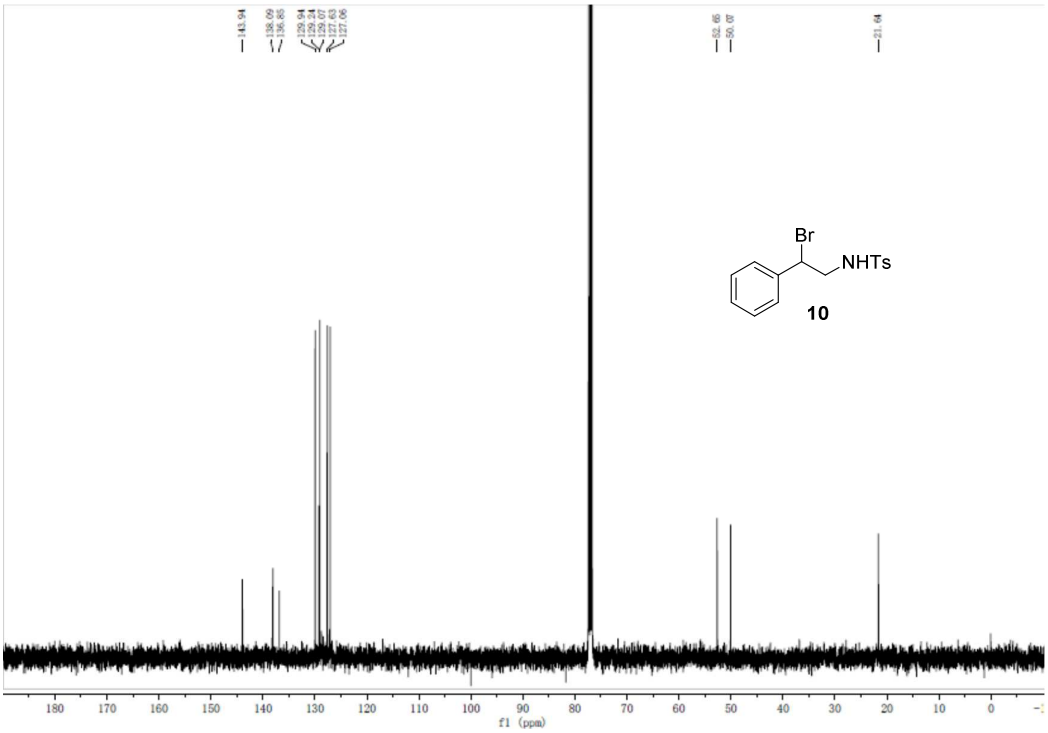






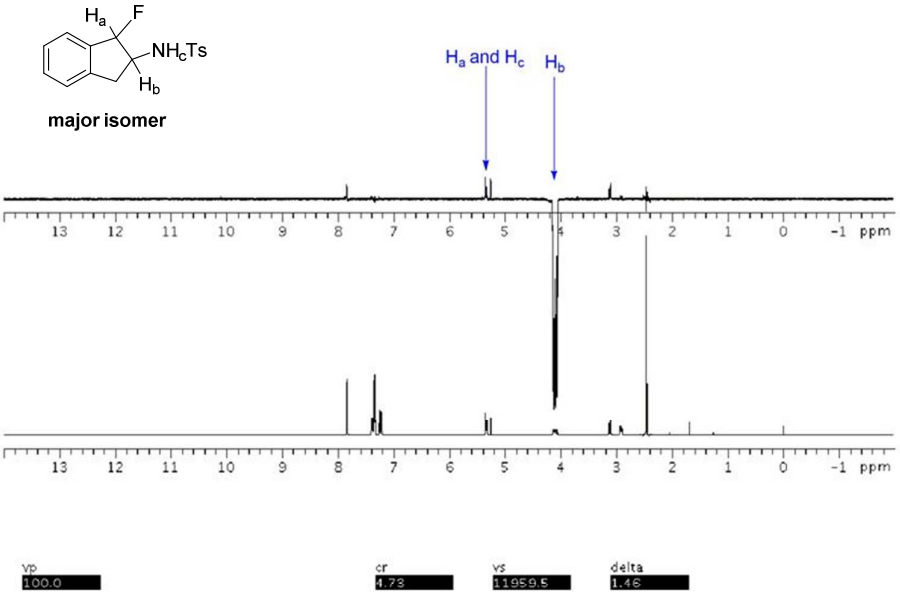
N-(2-bromo-2-phenylethyl)-4-methylbenzenesulfonamide(10)

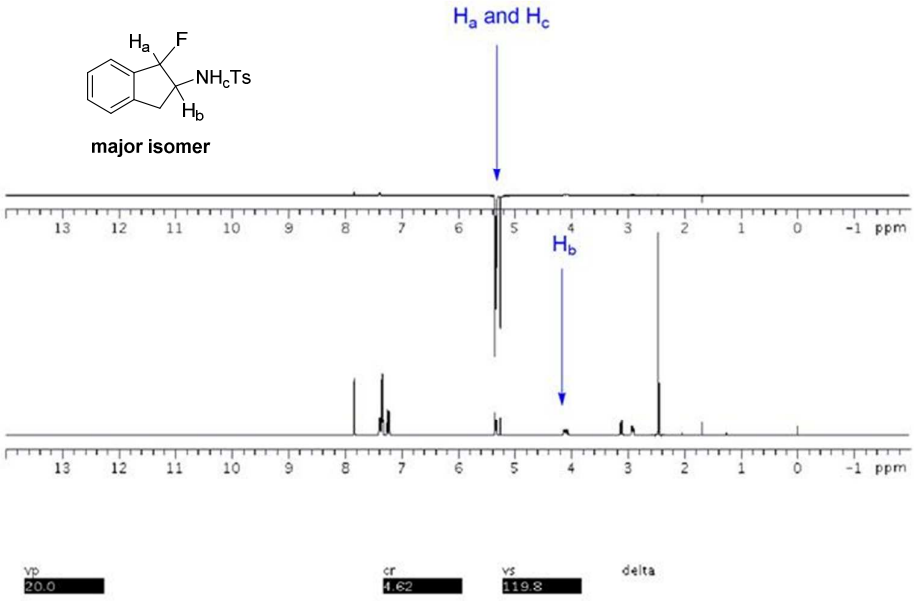




10. Determination of the configuration

NOE spectrum of compound **3q** ($CDCl_3$, 600MHz)




Ha
F
NHcTs
Hb
major isomer
Ha and Hc
Hb
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
vp
20.0
cr
4.62
vs
119.8
delta