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Supplementary Information

Synthesis of C3-Halo Substituted Bicyclo[1.1.1]pentylamines via Halosulfoamidation of [1.1.1]Propellane with Sodium Hypohalites and Sulfonamides

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Table of Contents

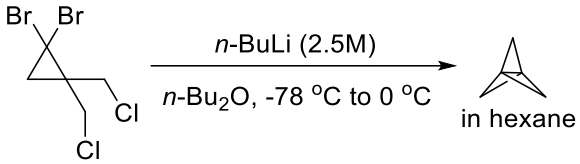
1. General information

All the commercially available reagents and solvents were used without any purification. The progress of the reactions was monitored by TLC with silica gel plates, and the visualization was carried out under UV light (254 nm). Melting points were determined using a Büchi B-540 capillary melting point apparatus. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded using a Bruker Avance III 400 MHz spectrometers. Chemical shifts of ^{1}H NMR were reported relative to the solvent signal ($CDCl_3$: δ = 7.26 ppm). Chemical shifts of ^{13}C NMR were reported relative to the solvent signal ($CDCl_3$: δ = 77.00 ppm). High-resolution mass spectra (HRMS) were recorded on Waters SYNAPT G2-S spectrometer. Column chromatography was performed on silica gel (300-400 mesh).

2. Synthesis of substrates 1

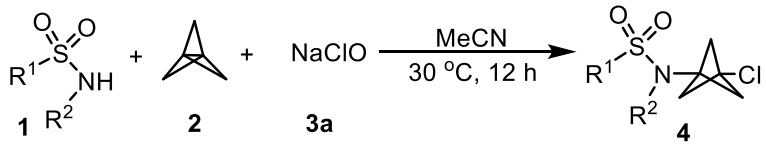
The substrates (**1a**-**1r**, **1t**),[1] and **1s**,[2] were prepared following the literature procedure, and the NMR data of all these compounds were compared with the corresponding reported data.

3. Preparation of the solution of [1.1.1]propellane in hexane

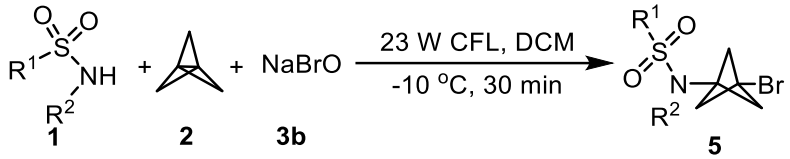


A solution of *n*-BuLi (32 mL, 80 mmol, 2.0 equiv., 2.5M in hexane) was added dropwise to a suspension of 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (40 mmol) in anhydrous dibutyl ether (40 mL) under argon at –78 °C. After the addition was complete, the mixture was allowed to warm to 0 °C and stirred for 2 h before distillation under vacuum. The concentration can be measured by ^{1}H-NMR with 1,3,5- trimethoxybenzene as an internal standard (typically concentrations are 0.4-0.7 M).

4. General method



General procedure for the synthesis of **4** (standard conditions A): A 10 mL reaction tube equipped with a magnetic stir bar was charged with **1** (0.2 mmol, 1.0 equiv.) in MeCN (1.0 mL). The sodium hypochlorite **3a** [aq., 10% available chlorine] (0.35mL, 1.0 mmol, 5.0 equiv.) and [1.1.1]propellane **2** (0.3 mmol, 1.5 equiv.) were added sequentially under stirring. After being stirred for 12 h at 30 °C, the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated and then purified by flash chromatography on silica gel with petroleum ether/ethyl acetate to afford the desired product **4**.



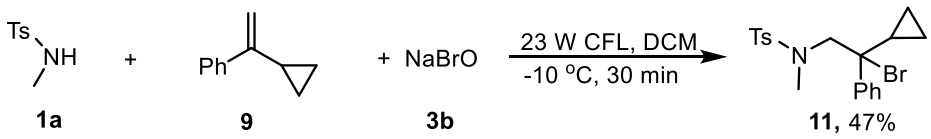
Preparation of NaBrO solution: NaOH (6 N, 1.0 mL, 6.0 mmol) was charged in a 25 mL flask equipped with a stir bar and Br_2 (100 µl, 2.0 mmol) was added at 0 °C. After stirring for 10 min, yellow transparent **3b** NaBrO (aq) was obtained. This solution was used in the following synthesis without further purification.[3]

General procedure for the synthesis of **5** (standard conditions B): A 10 mL reaction tube equipped with a magnetic stir bar was charged with **1** (0.2 mmol, 1.0 equiv.) in DCM (1.0 mL). The sodium hypobromite **3b** (0.55mL, 1.0 mmol, 5 equiv.) and [1.1.1]propellane **2** (0.3 mmol, 1.5 equiv.) were added sequentially at -10 °C under stirring. After being stirred for another 30 min at -10 °C with 23W CFL irradiation, the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated and then purified by flash chromatography on silica gel with petroleum ether/ethyl acetate to afford the desired product **5**.

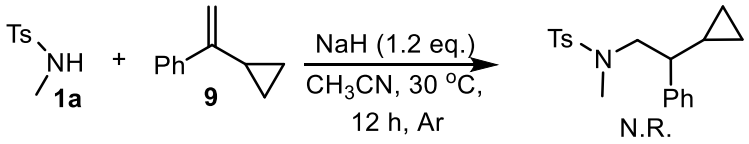
5. Mechanism research

5.1 Mechanism research for bromo-sulfonamidation reaction

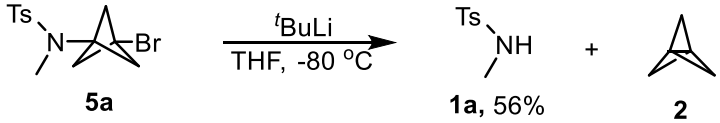
When (1-cyclopropylvinyl)-benzene **9**[4] was used instead of [1.1.1]propellane under standard bromo-sulfonamidation conditions, the addition product **11** could be obtained in 47% yield. At first, we believed that both ionic and radical pathways are involved in this transformation type.



However, the sulfonamide anion generated from NaH with sulfonamide **1a**[5], reacted with compound **9** for 12h could not obtain the desired product.



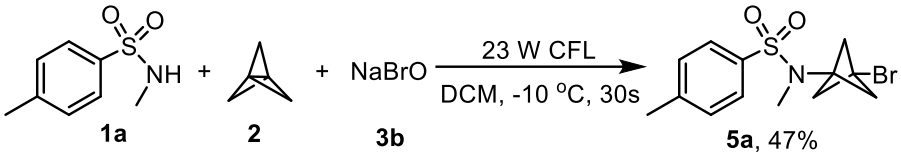
Meanwhile, the halogen-lithium exchange reaction of **5a** could afford the sulfonamides **1a** in 56% yield.



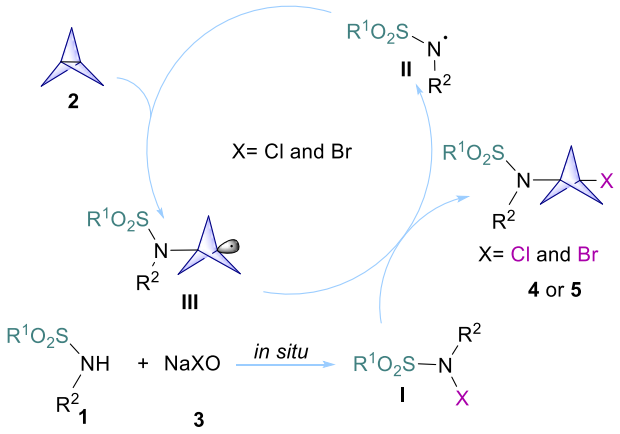
Both results indicated that the ionic addition of sulfonamide ion to compound **9** is very difficult, but the reverse ionic reaction – reformation of [1.1.1]propellane – is strongly favored.

One of the reviewers speculated that the observed phenomenon could be attributed to the rapid occurrence of bromine atom abstraction, which is significantly faster than the fragmentation of benzylic radical intermediates. Thus, we conducted a reaction under standard conditions for 30 seconds and

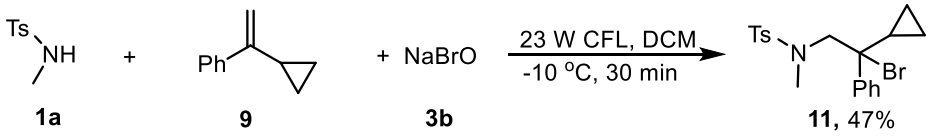
obtained the desired product **5a** in 47% yield. Therefore, we agreed that bromo-sulfonamidation is a very fast radical reaction.



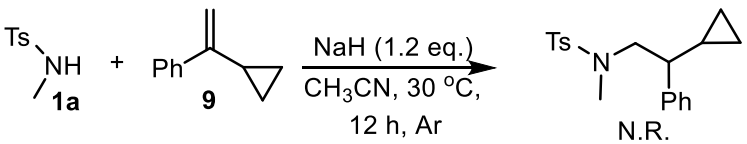
5.2 Possible mechanism of the reaction



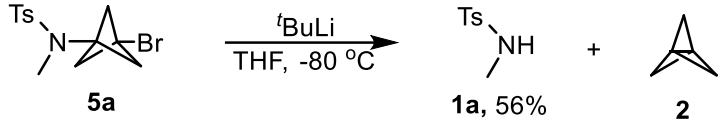
5.3 Experimental procedure for the mechanism research for bromo-sulfonamidation reaction



A 10 mL reaction tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 38.2 mg, 1.0 equiv.) in DCM (1.0 mL). The sodium hypobromite **3b** and (1-cyclopropylvinyl)benzene **9** (0.4 mmol, 61.2 mg, 2 equiv.) were added sequentially at -10 °C under stirring. After being stirred for another 30 min at -10 °C with 23W CFL irradiation, the reaction mixture was evaporated and then purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 20:1 to afford the product **11** as a white solid (39.6 mg, 47%). M.p.: 89-91 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.22 (m, 5H), 7.22 – 7.12 (m, 2H), 4.62 (d, *J* = 10.2 Hz, 1H), 4.29 (d, *J* = 10.2 Hz, 1H), 3.13 (s, 3H), 2.42 (s, 3H), 1.86 – 1.77 (m, 1H), 0.72 – 0.52 (m, 1H), 0.52 – 0.39 (m, 1H), 0.37 – 0.23 (m, 1H), -0.11 – -0.30 (m, 1H).^{13}C NMR (100 MHz, Chloroform-d) δ 142.86, 138.86, 138.35, 129.05, 127.74, 127.72, 127.56, 70.08, 43.15, 35.05, 21.47, 18.70, 4.36, 2.01. HRMS (ESI) m/z: calcd for $C_{19}H_{23}BrNO_2S^+$ $[M+H]^+$ 408.0627, found: 408.0622.

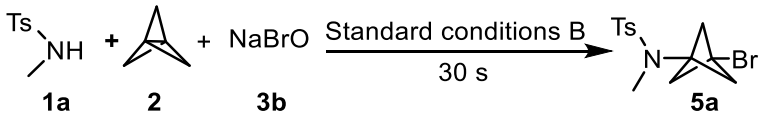


The sulfonamide salt was prepared according to the literature report.[5] A 10 mL reaction tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 37.5 mg, 1.0 equiv.) and NaH (0.24, 11.0 mg, 1.2 equiv, 60% in oil). After the tube was evacuated and backfilled with argon three times, anhydrous MeCN(1.0 mL) was added at 0 ºC. After stirring for 5 min, the (1-cyclopropylvinyl)benzene **9** (0.4 mmol, 60.0 mg, 2 equiv.) was added at 0 ºC under stirring. The resulting mixture was placed in a preheated metal block and stirred at 30 ºC for 12 h. After 2.0 mL H_2O quenching reaction, no reaction was monitored by TLC.



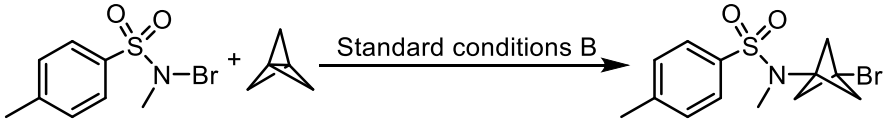
5a **1a,** 56% **2**

A 25 mL dry reaction tube equipped with a stir bar was evacuated and backfilled with argon (three times). Dissolved **5a** (0.24 mmol, 79.9 mg, 1.0 equiv) in anhydrous THF (1.5 mL) was added into a reaction tube, and stirred at -80 ºC. Slowly added *tert*-butyl lithium (1.3 M, 0.2 mL, 1.1 equiv) at -80 ºC. After the reaction was stirred for 30 min, it was quenched with CH_3OH (2 mL) at -80 ºC and then added H_2O (5 mL). The resulting mixture was extracted with ethyl acetate (10 mL × 3). The organic layers were combined, washed with brine, dried over Na_2SO_4 filtered, and then concentrated in a vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 5：1 to afford **1a** as a white solid (25.1 mg, 56%).



1a **2** **3b** **5a**

A 10 mL reaction tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 38.0 mg, 1.0 equiv.) in DCM (1.0 mL). The sodium hypobromite **3b** (0.55mL, 1.0 mmol, 5 equiv.) and [1.1.1]propellane **2** (0.3 mmol, 1.5 equiv.) were added sequentially at -10 ºC under stirring. After being stirred for another 30 s at -10 ºC with 23W CFL irradiation, the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated and then purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 20:1 to afford the desired product **5a** as a colorless oil (31.5 mg, 47%).



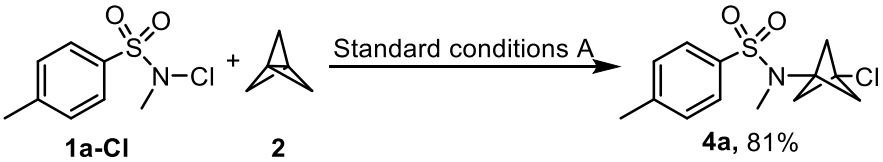
1a-Br **2** **5a,** 48%

A 10 mL reaction tube equipped with a magnetic stir bar was charged with *N*-bromo-*N,4*-dimethylbenzenesulfonamide **1a-Br**[6] (0.2 mmol, 53.0 mg, 1.0 equiv.) in DCM (1.0 mL). The [1.1.1]propellane **2** (0.3mmol, 1.5 equiv.) was added at -10 ºC under stirring. After being stirred for another 30 min at -10 ºC with 23W CFL irradiation, the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated and then purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 10:1 to afford the desired product **5a** as a colorless oil (31.8 mg, 48%).

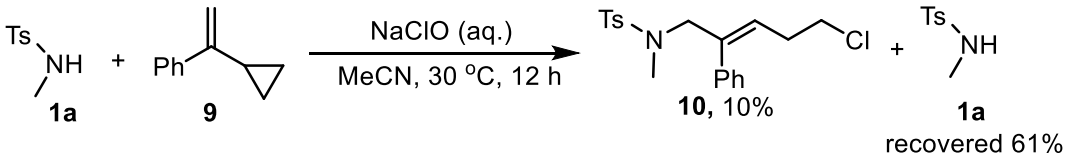
A 10 mL reaction tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 37.5 mg, 1.0 equiv.) in DCM (1.0 mL). The sodium hypobromite **3b** (0.55 mL, 1.0 mmol, 5.0 equiv.)**,** TEMPO (0.4 mmol, 65.2mg, 2.0 equiv.) and [1.1.1]propellane **2** (0.3 mmol, 1.5 equiv.) were added sequentially at -10 °C under stirring. After being stirred for another 30 min at -10 °C with 23W CFL irradiation, only trace amount of product was detected by TLC analysis.

5.4 Experimental procedure for the chloro-sulfonamidation reaction

A 10 mL reaction tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 37.0 mg, 1.0 equiv.) in MeCN (1.0 mL). The sodium hypochlorite **3a** [10% available chlorine] (0.35mL, 1.0 mmol, 5.0 equiv.), TEMPO (0.4 mmol, 62.5 mg, 2.0 equiv.) and [1.1.1]propellane **2** (0.3 mmol, 1.5 equiv.) were added sequentially under stirring. After being stirred for 12 h at 30 °C, only a trace amount of product was detected by TLC analysis.



A 10 mL reaction tube equipped with a magnetic stir bar was charged with *N*-chloro-*N,4*-dimethylbenzenesulfonamide **1a-Cl**[7] (0.2 mmol, 46.2 mg, 1.0 equiv.), **2** (0.3mmol, 1.5 equiv.), and MeCN (1.0 mL). After being stirred for 12 h at 30 °C, the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated and then purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 10:1 to afford the desired product **4a** as a colorless oil (48.9 mg, 81%).



A 10 mL reaction tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 38.1 mg, 1.0 equiv.) in MeCN (1.0 mL). The sodium hypochlorite **3a** [10% available chlorine] (0.35mL, 1.0 mmol, 5.0 equiv.) and (1-cyclopropylvinyl)benzene **9** (0.4 mmol, 59.8 mg, 2 equiv.) were added sequentially under stirring. After being stirred for 12 h at 30 °C, the reaction mixture was evaporated and then purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 20:1 to afford the product **10** as a colorless oil (7.5 mg, 10 %). After the reaction, 61% of substrate **1a** was also recovered. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 6.8 Hz, 2H), 7.39 – 7.24 (m, 5H), 5.97 (t, *J* = 7.4 Hz, 1H), 4.45 (s, 2H), 3.19 (t, *J* = 7.4 Hz, 2H), 2.80 (s, 3H), 2.63 – 2.52 (m, 2H), 2.43 (s, 3H).

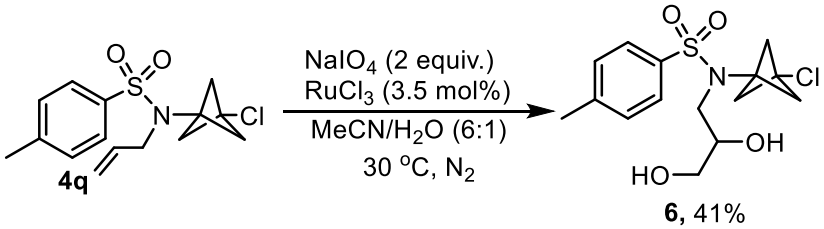
^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.40, 139.94, 138.21, 134.66, 130.12, 129.71, 128.52, 127.67, 127.39, 125.96, 49.51, 41.19, 35.09, 27.54, 21.50. HRMS (ESI) m/z: calcd for $C_{19}H_{23}ClNO_2S^+$ $[M+H]^+$ 364.1133, found: 364.1136.

6. Gram-scale synthesis of 4a and derivatization of 4q

1) Gram-scale synthesis of 4a

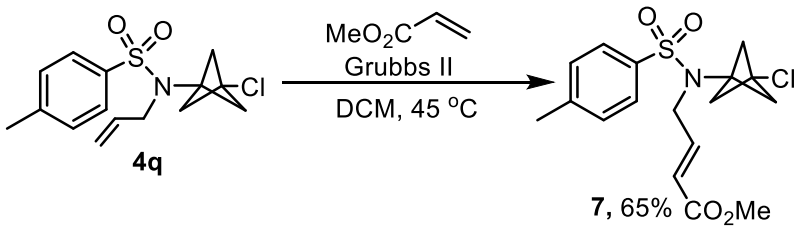
A 100 mL reaction tube equipped with a magnetic stir bar was charged with **1a** (5 mmol, 926.8 mg, 1.0 equiv.) in MeCN (25 mL). The sodium hypochlorite **3a** [10% available chlorine] (8.9 mL, 25 mmol, 5.0 equiv.) and [1.1.1]propellane **2** (7.5 mmol, 1.5 equiv.) was added sequentially at 0 °C under stirring. The mixture was stirred for 12 h at 30 °C. After the reaction was complete as monitored by TLC, it was added with H_2O (10 mL) at room temperature, and then extracted with ethyl acetate (30 mL × 3). The organic layers were combined, washed with brine, dried over Na_2SO_4 filtered, and then concentrated in a vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate to afford the desired product **4a** as a colorless oil (1.297 g, 91 %).

2) Synthesis of *N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-(2,3-dihydroxypropyl)-4-methylbenzenesulfonamide 6[8]



To a 25 mL Schlenk tube equipped with a stir bar were added **4q** (0.22 mmol, 69.7 mg, 1.0 equiv.), $NaIO_4$ (0.44 mmol, 93.9 mg, 2.0 eq.) and $RuCl_3$ (0.0077 mmol, 3.3 mg, 3.5 mol %). After the tube was evacuated and backfilled with argon three times, degassed MeCN (6.0 mL) and H_2O (1.0 mL) were added. After being stirred for 16 h at 30 °C, the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated and then purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give **6** as a colorless oil (31.6 mg, 41%);^{1}H NMR (400 MHz, Chloroform-d) δ 7.67 (d, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 3.87 – 3.76 (m, 1H), 3.72 (s, 2H), 3.39 (dd, *J* = 14.8, 6.1 Hz, 1H), 3.23 (dd, *J* = 14.8, 6.9 Hz, 1H), 2.43 (s, 3H), 2.27 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 144.21, 136.46, 129.91, 127.16, 70.48, 63.11, 58.73, 50.14, 49.61, 46.29, 21.53. HRMS (ESI) m/z: calcd for $C_{15}H_{21}ClNO_4S^+$ $[M+H]^+$ 346.0874, found: 346.0877.

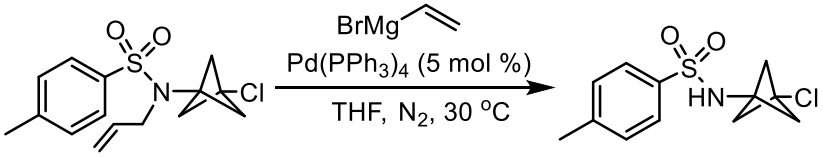
3) Synthesis of methyl (*E*)-4-((*N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-4-methyl phenyl)sulfonamido)but-2-enoate 7[9]



To a 10 mL reaction tube equipped with a stir bar were added **4q** (0.2 mmol, 63.4 mg, 1.0 equiv.),

Grubbs II catalyst (0.004mmol, 3.8 mg, 2 mol %). After the tube was evacuated and backfilled with argon three times, methyl acrylate (90μL, 1.0 mmol, 5.0 equiv.) and anhydrous DCM (2.0 mL) was added. After the reaction mixture stirring at 45 °C for 24 h, another 2 mol % of Grubbs II catalyst (0.004mmol, 3.4 mg, 2 mol %) was added. After the reaction mixture stirring for another 24 h, the reaction mixture was evaporated and then purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to give **7** as a white solid (48.9 mg, 65 %); M.p.: 84-86 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 6.95-9.73 (m, 1H), 6.01 (d, *J* = 18.0, 1H), 4.07-3.98 (m, 2H), 3.73 (s, 3H), 2.42 (s, 3H), 2.26 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 165.98, 144.01, 143.75, 137.06, 129.81, 127.10, 122.73, 58.86, 51.68, 49.25, 48.64, 46.15, 21.49. HRMS (ESI) m/z: calcd for $C_{17}H_{21}ClNO_4S^+$ $[M+H]^+$ 370.0874, found: 370.0872.

4) **Synthesis of *N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-4-methylbenzene-sulfon- amide 8**[10]

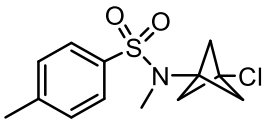


4q **8,** 54 %

A 10 mL reaction tube equipped with a stir bar was evacuated and backfilled with argon (three times). The $Pd(PPh_3)_4$ (0.01 mmol, 11.8 mg, 5 mol %), THF(3.0 mL), vinylmagnesium bromide (1.0 M solution in THF, 0.8 mmol, 4.0 eq.), and **4q** (0.2 mmol, 63.0 mg, 1.0 eq.) were then added at 0 °C under stirring. The resulting mixture was placed in a preheated metal block and stirred at 30 °C for 24 h. After the reaction was complete as monitored by TLC analysis, it was quenched with saturated $NaHCO_3$ solution (5 mL) at room temperature and then extracted with ether (10 mL × 3). The organic layers were combined, washed with brine, dried over Na_2SO_4 filtered, and then concentrated in a vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 10：1 to afford **8** as a yellow solid (29.8 mg, 54%). M.p.: 142-144 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 5.79 (s, 1H), 2.44 (s, 3H), 2.15 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.96, 137.28, 129.76, 127.23, 58.77, 46.27, 44.36, 21.55. HRMS (ESI) m/z: calcd for $C_{12}H_{15}ClNO_2S^+$ $[M+H]^+$ 272.0507, found: 272.0500.

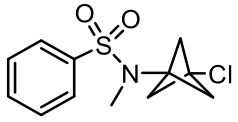
7. Characterization of products

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*,4-dimethylbenzenesulfonamide (4a)** [11]



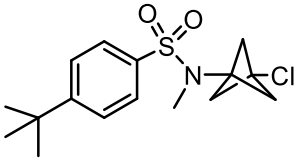
Eluent in chromatography: petroleum ether/ ethyl acetate 10:1, **4a** was isolated as a colorless oil (51.0 mg, 88 %, **4a**:**4a-S** = 96:4);^{1}H NMR (400 MHz, Chloroform-d) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 2.81 (s, 3H), 2.42 (s, 3H), 2.25 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.76, 135.52, 129.69, 127.33, 57.90, 49.68, 46.26, 34.09, 21.48.

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methylbenzenesulfonamide (4b)**



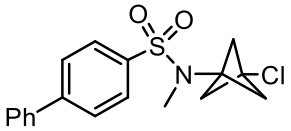
Eluent in chromatography: petroleum ether/ ethyl acetate 20:1, **4b** was isolated as a white solid (48.1 mg, 77 %, **4b**:**4b-S** = 95:5); M.p.: 66-68 ºC; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.78 (d, J = 7.8 Hz, 2H), 7.63 – 7.56 (m, 1H), 7.56 – 7.48 (m, 2H), 2.83 (s, 3H), 2.25 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 138.51, 132.89, 129.09, 127.24, 57.90, 49.65, 46.21, 34.12. HRMS (ESI) m/z: calcd for $C_{12}H_{15}ClNO_2S^+$ $[M+H]^+$ 272.0507, found: 272.0504.

4-(tert-butyl)-*N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methylbenzenesulfonamide (4c)



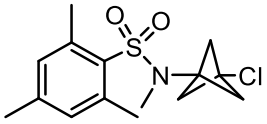
Eluent in chromatography: petroleum ether/ ethyl acetate 10:1, **4c** was isolated as a white solid (55.8 mg, 86 %, **4c**:**4c-S** = 95:5); M.p.: 96-97 ºC;^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 2.83 (s, 3H), 2.26 (s, 6H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.77, 135.48, 127.19, 126.05, 57.98, 49.73, 46.31, 35.13, 34.13, 31.04. HRMS (ESI) m/z: calcd for $C_{16}H_{23}ClNO_2S^+$ $[M+H]^+$ 328.1133, found: 328.1134.

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methyl-[1,1'-biphenyl]-4-sulfonamide (4d)**



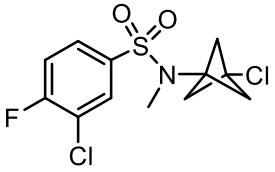
Eluent in chromatography: petroleum ether/ ethyl acetate 10:1, **4d** was isolated as a white solid (34.4 mg, 50 %); M.p.: 148-149 ºC;^{1}H NMR (400 MHz, Chloroform-d) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.53 – 7.39 (m, 3 H), 2.88 (s, 3H), 2.31 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 145.77, 138.99, 137.23, 129.03, 128.55, 127.83, 127.63, 127.23, 58.05, 49.76, 46.28, 34.13. HRMS (ESI) m/z: calcd for $C_{18}H_{19}ClNO_2S^+$ $[M+H]^+$ 348.0820, found: 348.0826.

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*,2,4,6-tetramethylbenzenesulfonamide (4e)**



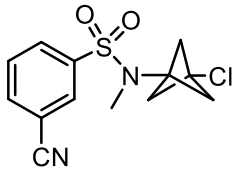
Eluent in chromatography: petroleum ether/ ethyl acetate 20:1, **4e** was isolated as a white solid (14.4 mg, 23 %, **4e**:**4e-S** = 97:3); M.p.: 71-73 ºC;^{1}H NMR (400 MHz, Chloroform-d) δ 6.94 (s, 2H), 2.75 (s, 3H), 2.57 (s, 6H), 2.30 (s, 3H), 2.26 (s, 6H).^{13}C NMR (100 MHz, Chloroform-d) δ 142.86, 140.17, 133.16, 131.95, 57.92, 49.50, 46.45, 32.31, 22.56, 20.98. HRMS (ESI) m/z: calcd for $C_{15}H_{21}ClNO_2S^+$ $[M+H]^+$ 314.0976, found: 314.0975.

3-chloro-*N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-4-fluoro-*N*-methylbenzenesulfonamide (4f)



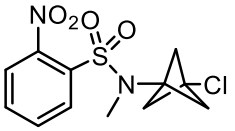
Eluent in chromatography: petroleum ether/ethyl acetate 10:1, **4f** was isolated as a white solid (47.5 mg, 78 %, **4f**:**4f-S** = 97:3); M.p.: 95-96 ºC; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.89 – 7.83 (m, 1H), 7.73 – 7.66 (m, 1H), 7.30 (t, *J* = 8.4 Hz, 1H), 2.85 (s, 3H), 2.30 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 160.66 (d, *J* = 257.6 Hz), 135.88 (d, *J* = 4.0 Hz), 130.18, 127.71 (d, *J* = 8.4 Hz), 122.54 (d, *J* = 18.8 Hz), 117.46 (d, *J* = 22.4 Hz), 58.11, 49.69, 46.13, 34.16. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -106.70. HRMS (ESI) m/z: calcd for $C_{12}H_{13}Cl_2FNO_2S^+$ $[M+H]^+$ 324.0023, found: 324.0033.

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-3-cyano-*N*-methylbenzenesulfonamide (4g)**



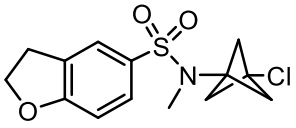
Eluent in chromatography: petroleum ether/ ethyl acetate 5:1, **4g** was isolated as a white solid (27.5 mg, 46 %); M.p.: 92-94 ºC; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.06 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.73 – 7.65 (m, 1H), 2.87 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 140.69, 135.97, 131.13, 130.74, 130.27, 116.96, 113.83, 58.10, 49.62, 46.05, 34.19. HRMS (ESI) m/z: calcd for $C_{13}H_{14}ClN_2O_2S^+$ $[M+H]^+$ 297.0459, found: 297.0473.

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methyl-2-nitrobenzenesulfonamide (4h)**



Eluent in chromatography: petroleum ether/ethyl acetate 10:1, **4h** was isolated as a yellow solid (44.3 mg, 69 %, **4h**:**4h-S** = 96:4); M.p.: 131-133 ºC; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.04 (d, *J* = 6.8 Hz, 1H), 7.76 – 7.62 (m, 3H), 2.94 (s, 3H), 2.30 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.99, 133.97, 133.42, 131.81, 130.68, 124.27, 58.08, 49.37, 46.23, 34.05. HRMS (ESI) m/z: calcd for $C_{12}H_{14}ClN_2O_4S^+$ $[M+H]^+$ 317.0357, found: 317.0365.

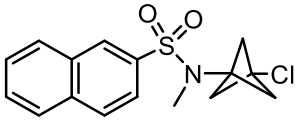
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methyl-2,3-dihydrobenzofuran-5-sulfonamide (4i)**



Eluent in chromatography: petroleum ether/ ethyl acetate 5:1, **4i** was isolated as a white solid (52.0 mg, 85 %, **4i**:**4i-S** = 95:5); M.p.: 117-118 ºC; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.62 – 7.49 (m, 2H), 6.83 (d, *J* = 8.2 Hz, 1H), 4.68 (t, *J* = 8.8 Hz, 2H), 3.27 (t, *J* = 8.8 Hz, 2H), 2.79 (s, 3H), 2.26 (s, 6H).^{13}C NMR

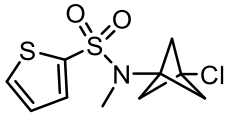
(100 MHz, Chloroform-d) δ 163.94, 129.88, 128.93, 128.34, 124.55, 109.46, 72.25, 57.92, 49.74, 46.31, 34.07, 28.97. HRMS (ESI) m/z: calcd for $C_{14}H_{17}ClNO_3S^+$ $[M+H]^+$ 314.0612, found: 314.0610.

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methylnaphthalene-2-sulfonamide (4j)**



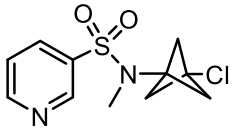
Eluent in chromatography: petroleum ether/ethyl acetate 10:1, **4j** was isolated as a white solid (48.4 mg, 75 %, **4j**:**4j-S** = 95:5); M.p.: 89-90 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.36 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), δ 7.71 – 7.60 (m, 2H), 2.90 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 135.64, 134.86, 132.15, 129.40, 129.21, 129.00, 128.85, 127.94, 127.70, 122.42, 58.10, 49.79, 46.30, 34.24. HRMS (ESI) m/z: calcd for $C_{16}H_{17}ClNO_2S^+$ $[M+H]^+$ 322.0663, found: 322.0666.

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)thiophene-2-sulfonamide (4k)**



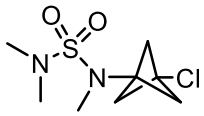
Eluent in chromatography: petroleum ether/ethyl acetate 10:1, **4k** was isolated as a colorless oil (51.0 mg, 84 %, **4k**:**4k-S** = 95:5); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.62 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.56 (dd, *J* = 3.8, 1.4 Hz, 1H), 7.11 (dd, *J* = 5.0, 3.6 Hz, 1H), 2.84 (s, 3H), 2.31 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 138.76, 132.53, 132.16, 127.45, 57.94, 49.76, 46.19, 34.15. HRMS (ESI) m/z: calcd for $C_{10}H_{13}ClNO_2S_2^+$ $[M+H]^+$ 278.0071, found: 278.0070.

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methylpyridine-3-sulfonamide (4l)**



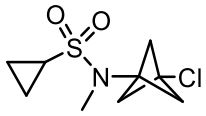
Eluent in chromatography: petroleum ether/ ethyl acetate 3:1, **4l** was isolated as a colorless oil (39.6 mg, 70 %, **4l**:**4l-S** = 96:4);^{1}H NMR (400 MHz, Chloroform-d) δ 9.00 (s, 1H), 8.82 (d, *J* = 4.8 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.41 (m, 1H), 2.87 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 153.40, 148.07, 135.39, 134.88, 123.74, 58.06, 49.62, 46.09, 34.06. HRMS (ESI) m/z: calcd for $C_{11}H_{14}ClN_2O_2S^+$ $[M+H]^+$ 273.0459, found: 273.0467.

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methyldimethylaminesulfonamide (4m)**



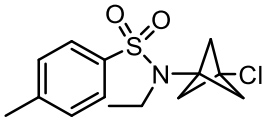
Eluent in chromatography: petroleum ether/ ethyl acetate 10:1, **4m** was isolated as a colorless oil (24.3 mg, 46 %, **4m**:**4m-S** = 96:4);^{1}H NMR (400 MHz, Chloroform-d) δ 2.80 (s, 3H), 2.77 (s, 6H), 2.38 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 58.08, 50.14, 46.32, 37.65, 34.50. HRMS (ESI) m/z: calcd for $C_8H_{16}ClN_2O_2S^+$ $[M+H]^+$ 239.0616, found: 239.0612.

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methylcyclopropanesulfonamide (4n)**



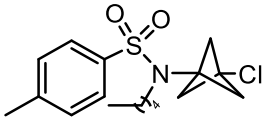
Eluent in chromatography: petroleum ether/ ethyl acetate 10:1, **4n** was isolated as a white solid (21.2 mg, 41 %); M.p.: 69-71 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 2.87 (s, 3H), 2.42 (s, 6H), 2.29 – 2.18 (m, 1H), 1.22 – 1.14 (m, 2H), 1.00 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 58.45, 49.85, 46.27, 34.26, 28.11, 5.03. HRMS (ESI) m/z: calcd for $C_9H_{15}ClNO_2S^+$ $[M+H]^+$ 236.0507, found: 236.0501.

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-ethyl-4-methylbenzenesulfonamide (4o)**



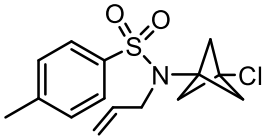
Eluent in chromatography: petroleum ether/ ethyl acetate 20:1, **4o** was isolated as a white solid (40.4 mg, 68 %, **4o**:**4o-S** = 97:3); M.p.: 53-55 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.32 (q, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 2.30 (s, 6H), 1.21 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.44, 137.80, 129.63, 126.98, 59.05, 49.00, 46.36, 43.25, 21.46, 16.12. HRMS (ESI) m/z: calcd for $C_{14}H_{19}ClNO_2S^+$ $[M+H]^+$ 300.0820, found: 300.0827.

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-4-methyl-*N*-pentylbenzenesulfonamide (4p)**



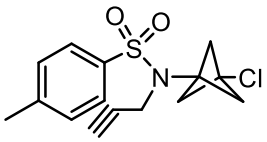
Eluent in chromatography: petroleum ether/ethyl acetate 10:1, **4p** was isolated as a colorless oil (32 mg, 45%, **4p**:**4p-S** = 98:2); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 3.28 – 3.15 (m, 2H), 2.42 (s, 3H), 2.28 (s, 6H), 1.64 – 1.55 (m, 2H), 1.35 – 1.24 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.42, 137.97, 129.62, 127.07, 59.07, 49.28, 48.56, 46.45, 30.17, 28.76, 22.24, 21.45, 13.90. HRMS (ESI) m/z: calcd for $C_{17}H_{25}ClNO_2S^+$ $[M+H]^+$ 342.1289, found: 342.1299.

***N*-allyl-*N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-4-methylbenzenesulfonamide (4q)**



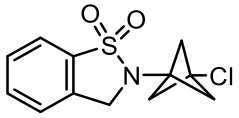
Eluent in chromatography: petroleum ether/ethyl acetate 10:1, **4q** was isolated as a colorless oil (33 mg, 52%, **4q**:**4q-S** = 95:5);^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), δ 5.86 – 5.72 (m, 1H), 5.29 – 5.12 (m, 2H), 3.91 (d, *J* = 5.0 Hz, 2H), 2.42 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.71, 137.72, 134.55, 129.76, 127.21, 117.74, 59.16, 50.79, 49.38, 46.53, 21.56. HRMS (ESI) m/z: calcd for $C_{15}H_{19}ClNO_2S^+$ $[M+H]^+$ 312.0820, found: 312.0825.

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (4r)**



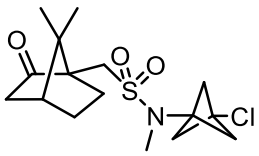
Eluent in chromatography: petroleum ether/ ethyl acetate 10:1, **4r** was isolated as a yellow oil (37.2 mg, 58 %);^{1}H NMR (400 MHz, Chloroform-d) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.16 (s, 2H), 2.42 (s, 3H), 2.37 (s, 6H), 2.19 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.98, 136.78, 129.52, 127.70, 78.49, 73.64, 59.01, 49.00, 46.20, 37.22, 21.54. HRMS (ESI) m/z: calcd for $C_{15}H_{17}ClNO_2S^+$ $[M+H]^+$ 310.0663, found: 310.0666.

2-(3-chlorobicyclo[1.1.1]pentan-1-yl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (4s)



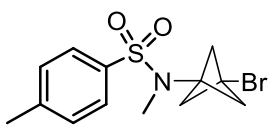
Eluent in chromatography: petroleum ether/ ethyl acetate 5:1, **4s** was isolated as a white solid (18.8 mg, 35 %, **4s**:**4s-S** = 95:5); M.p.: 151-152 ºC; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 4.35 (s, 2H), 2.58 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 135.09, 132.93, 132.50, 129.34, 124.49, 121.39, 57.90, 48.74, 46.74, 45.98. HRMS (ESI) m/z: calcd for $C_{12}H_{13}ClNO_2S^+$ $[M+H]^+$ 270.0350, found: 270.0345.

***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-1-(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-methylmethanesulfonamide (4t)**



Eluent in chromatography: petroleum ether/ethyl acetate 10:1, **4t** was isolated as a white solid (34 mg, 48%); M.p.: 84-85 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.32 (d, *J* = 14.4 Hz, 1H), 2.87 (s, 3H), 2.75 (d, *J* = 14.4 Hz, 1H), 2.55 – 2.47 (m, 1H), 2.45 (s, 6H), 2.37 (dt, *J* = 18.4, 4.2 Hz, 1H), 2.12 – 1.98 (m, 2H), 1.93 (d, *J* = 18.4 Hz, 1H), δ 1.67 – 1.57 (m, 1H), 1.47 – 1.37 (m, 1H), 1.12 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 214.89, 58.37, 49.82, 47.74, 47.17, 46.32, 42.82, 42.52, 33.84, 26.85, 25.17, 20.02, 19.76. HRMS (ESI) m/z: calcd for $C_{16}H_{25}ClNO_3S^+$ $[M+H]^+$ 346.1238, found: 346.1240.

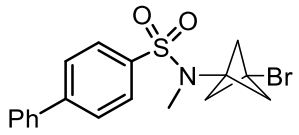
***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-*N*,4-dimethylbenzenesulfonamide (5a)**



Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **5a** was isolated as a colorless oil (47.6 mg, 70%, **5a**:**5a-S** = 98:2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.81 (s, 3H), 2.44 (s, 3H), 2.32 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.81,

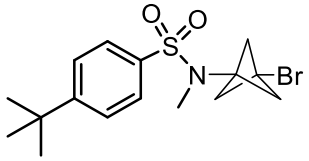
135.62, 129.74, 127.40, 59.09, 52.10, 34.01, 33.06, 21.54. HRMS (ESI) m/z: calcd for $C_{13}H_{17}BrNO_2S^+$ $[M+H]^+$ 330.0158, found: 330.0161.

***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-*N*-methyl-[1,1'-biphenyl]-4-sulfonamide (5b)**



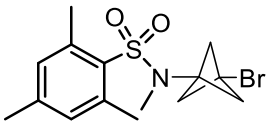
Eluent in chromatography: petroleum ether/ ethyl acetate 10:1, **5b** was isolated as a white solid (29.5 mg, 37 %); M.p.: 135-136 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.88 – 7.82 (m, 2H), 7.77 – 7.70 (m, 2H), 7.64 – 7.59 (m, 2H), 7.53 – 7.39 (m, 3H), 2.87 (s, 3H), 2.37 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 145.83, 139.00, 137.11, 129.06, 128.59, 127.86, 127.68, 127.27, 59.15, 52.11, 34.06, 33.00. HRMS (ESI) m/z: calcd for $C_{18}H_{19}BrNO_2S^+$ $[M+H]^+$ 392.0314, found: 392.0317.

***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-4-(tert-butyl)-*N*-methylbenzenesulfonamide (5c)**



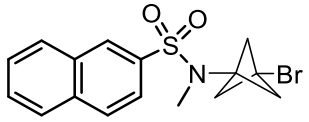
Eluent in chromatography: petroleum ether/ ethyl acetate 20:1, **5c** was isolated as a white solid (42.5 mg, 57 %); M.p.: 103-105 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.72 – 7.66 (m, 2H), 7.54 – 7.49 (m, 2H), 2.82 (s, 3H), 2.33 (s, 6H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-d) δ 156.80, 135.49, 127.20, 126.08, 59.12, 52.10, 35.15, 34.01, 33.10, 31.05. HRMS (ESI) m/z: calcd for $C_{16}H_{23}BrNO_2S^+$ $[M+H]^+$ 372.0627, found: 372.0623.

***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-*N*,2,4,6-tetramethylbenzenesulfonamide (5d)**



Eluent in chromatography: petroleum ether/ ethyl acetate 20:1, **5d** was isolated as a yellow oli (21.9 mg, 30 %);^{1}H NMR (400 MHz, Chloroform-d) δ 6.94 (s, 2H), 2.74 (s, 3H), 2.57 (s, 6H), 2.33 (s, 6H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 142.87, 140.17, 133.14, 131.96, 59.05, 51.88, 33.24, 32.18, 22.57, 20.99. HRMS (ESI) m/z: calcd for $C_{15}H_{21}BrNO_2S^+$ $[M+H]^+$ 358.0471, found: 358.0465.

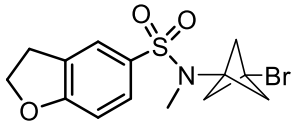
***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-*N*-methylnaphthalene-2-sulfonamide (5e)**



Eluent in chromatography: petroleum ether/ ethyl acetate 10:1, **5e** was isolated as a white solid (28.6 mg, 38 %); M.p.: 86-88 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.36 (d, J = 1.4 Hz, 1H), 8.02 – 7.95 (m, 2H), 7.93 (dd, J = 8.0, 1.4 Hz, 1H), 7.75 (dd, J = 8.6, 1.8 Hz, 1H), 7.71 – 7.60 (m, 2H), 2.89 (s, 3H), 2.34 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 135.59, 134.84, 132.12, 129.40, 129.20, 129.00, 128.82,

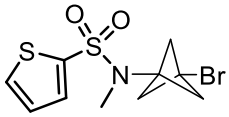
127.93, 127.70, 122.38, 59.20, 52.11, 34.11, 32.99. HRMS (ESI) m/z: calcd for $C_{16}H_{17}BrNO_2S^+$ $[M+H]^+$ 366.0158, found: 366.0151.

***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-*N*-methyl-2,3-dihydrobenzofuran-5-sulfonamide (5f)**



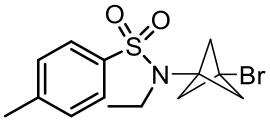
Eluent in chromatography: petroleum ether/ ethyl acetate 5:1, **5f** was isolated as a white solid (49.8 mg, 67 %, **5f**:**5f-S** = 98:2); M.p.: 115-117 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.61 – 7.53 (m, 2H), 6.84 (d, *J* = 8.4 Hz, 1H), 4.68 (t, *J* = 8.8 Hz, 2H), 3.27 (t, *J* = 8.8 Hz, 2H), 2.78 (s, 3H), 2.32 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 163.97, 129.94, 128.97, 128.35, 124.57, 109.51, 72.28, 59.08, 52.14, 33.97, 33.13, 29.01..HRMS (ESI) m/z: calcd for $C_{14}H_{17}BrNO_3S^+$ $[M+H]^+$ 358.0107, found: 358.0103.

***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-*N*-methylthiophene-2-sulfonamide (5g)**



Eluent in chromatography: petroleum ether/ ethyl acetate 10:1, **5g** was isolated as a yellow oli (15.4 mg, 23 %);^{1}H NMR (400 MHz, Chloroform-d) δ 7.62 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.57 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.13 (dd, *J* = 5.0, 3.6 Hz, 1H), 2.85 (s, 3H), 2.38 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 138.80, 132.54, 132.16, 127.46, 59.06, 52.11, 34.04, 32.86. HRMS (ESI) m/z: calcd for $C_{10}H_{13}BrNO_2S_2^+$ $[M+H]^+$ 321.9566, found: 321.9564.

***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-*N*-ethyl-4-methylbenzenesulfonamide (5h)**



Eluent in chromatography: petroleum ether/ ethyl acetate 10:1, **5h** was isolated as a yellow solid (39.8 mg, 57 %); M.p.: 74-75 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.31 (q, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 2.36 (s, 6H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.49, 137.86, 129.67, 127.02, 60.22, 51.42, 43.16, 33.17, 21.51, 16.18. HRMS (ESI) m/z: calcd for $C_{14}H_{19}BrNO_2S^+$ $[M+H]^+$ 344.0314, found: 344.0309.

8. References

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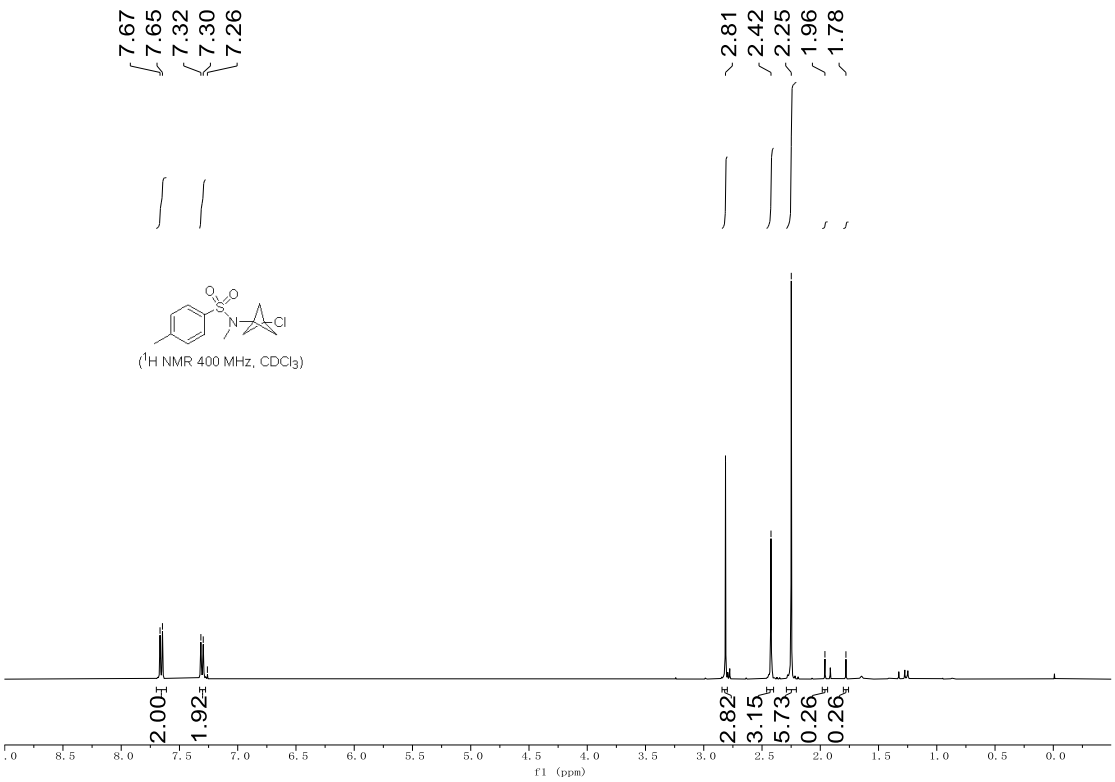
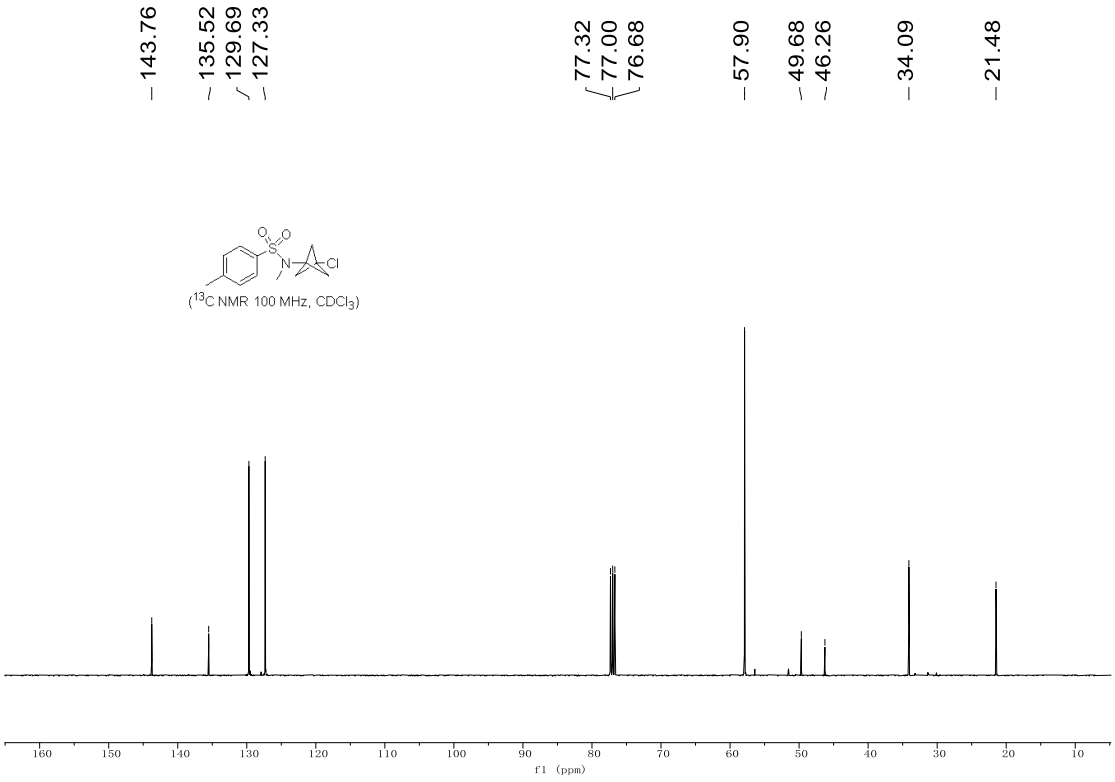
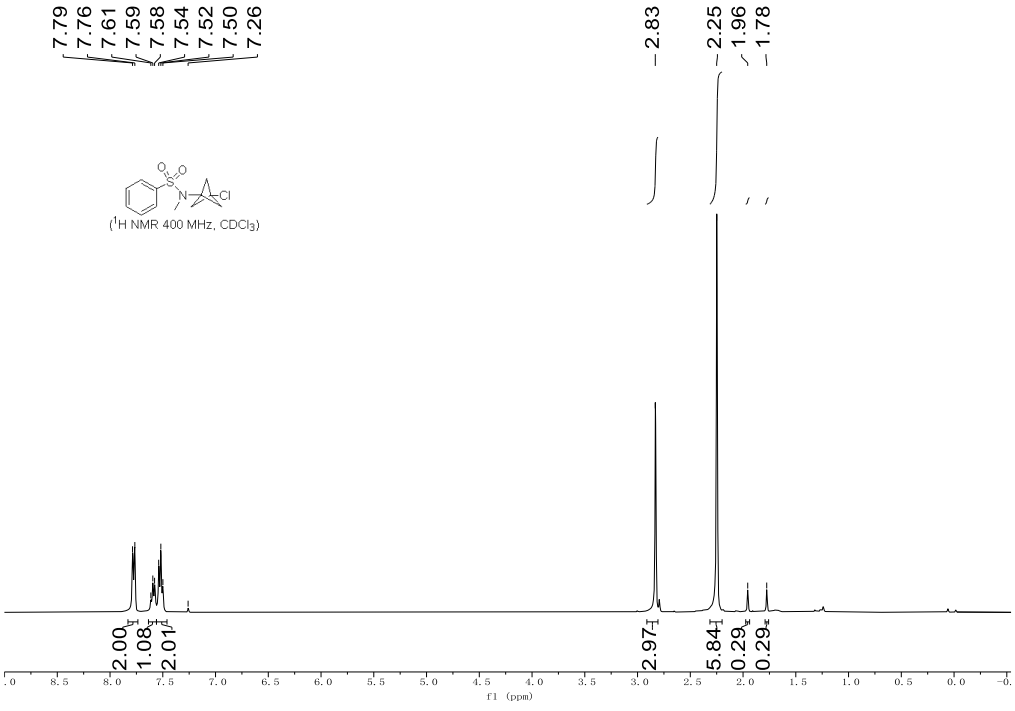
9. Copies of ^{1}H, ^{13}C NMR, and ^{19}F NMR spectra of products

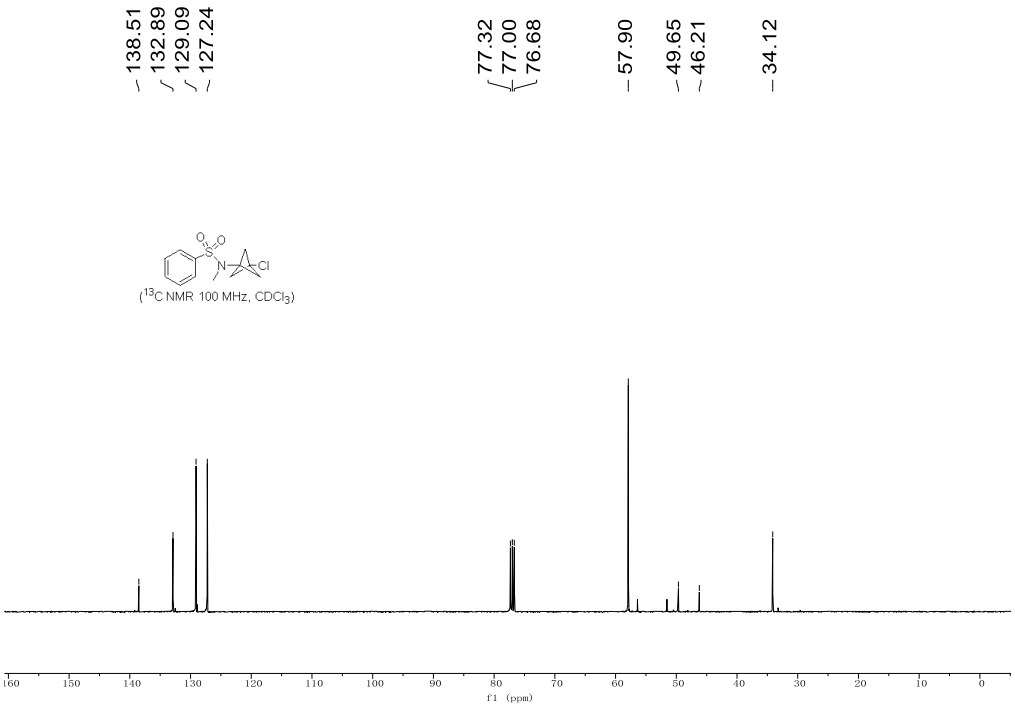
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*,4-dimethylbenzenesulfonamide (4a)**



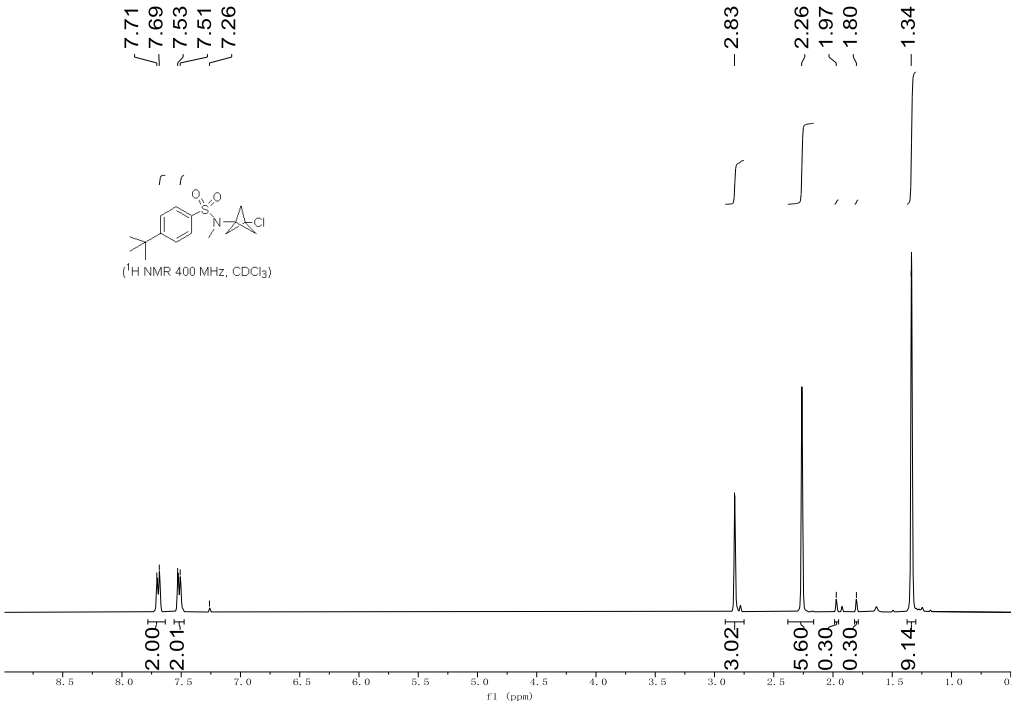


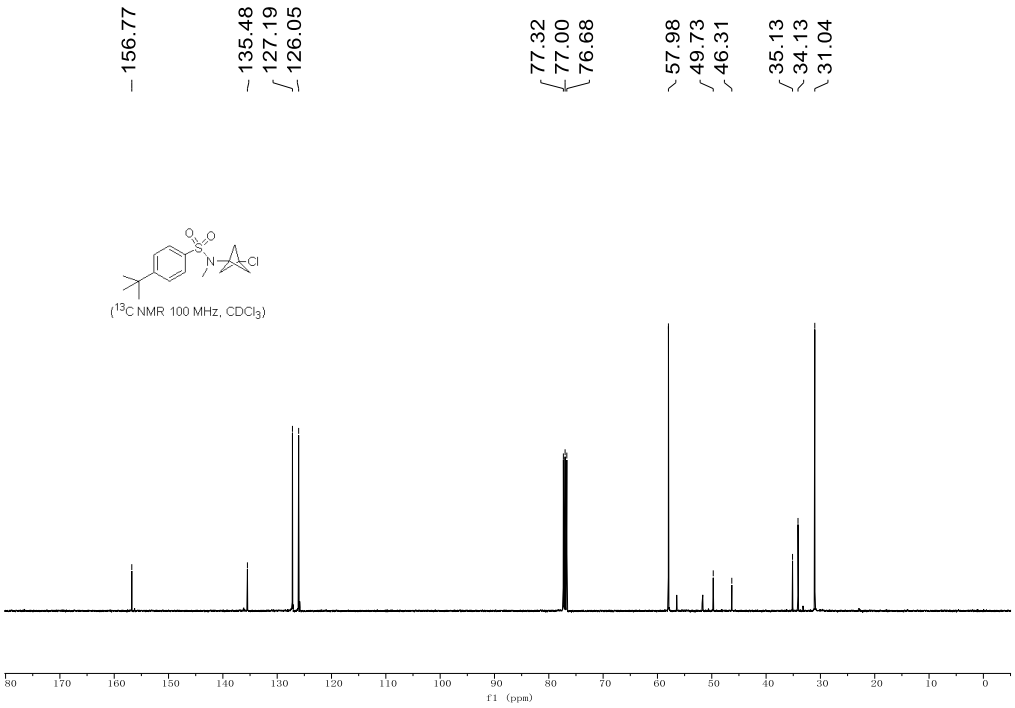
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methylbenzenesulfonamide (4b)**



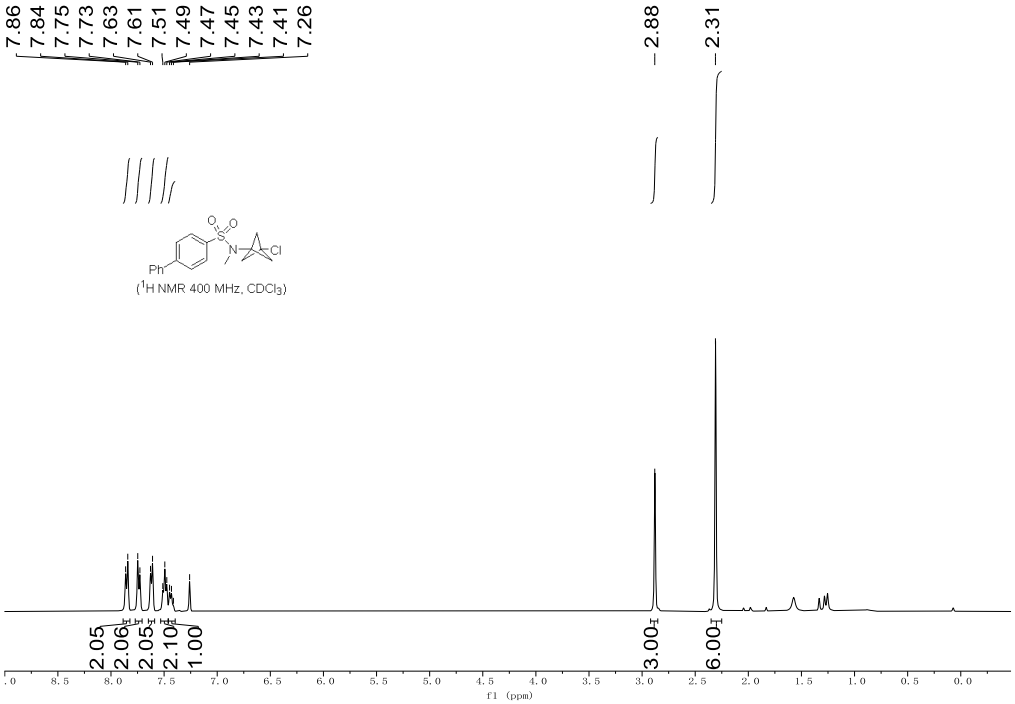


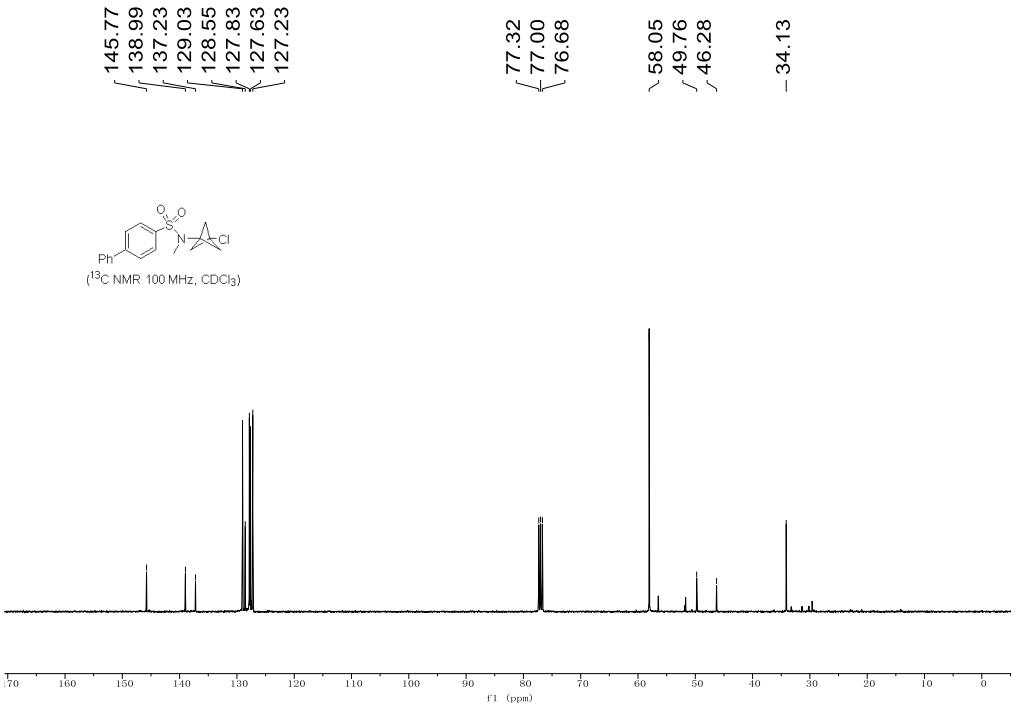
4-(tert-butyl)-*N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methylbenzenesulfonamide (4c)



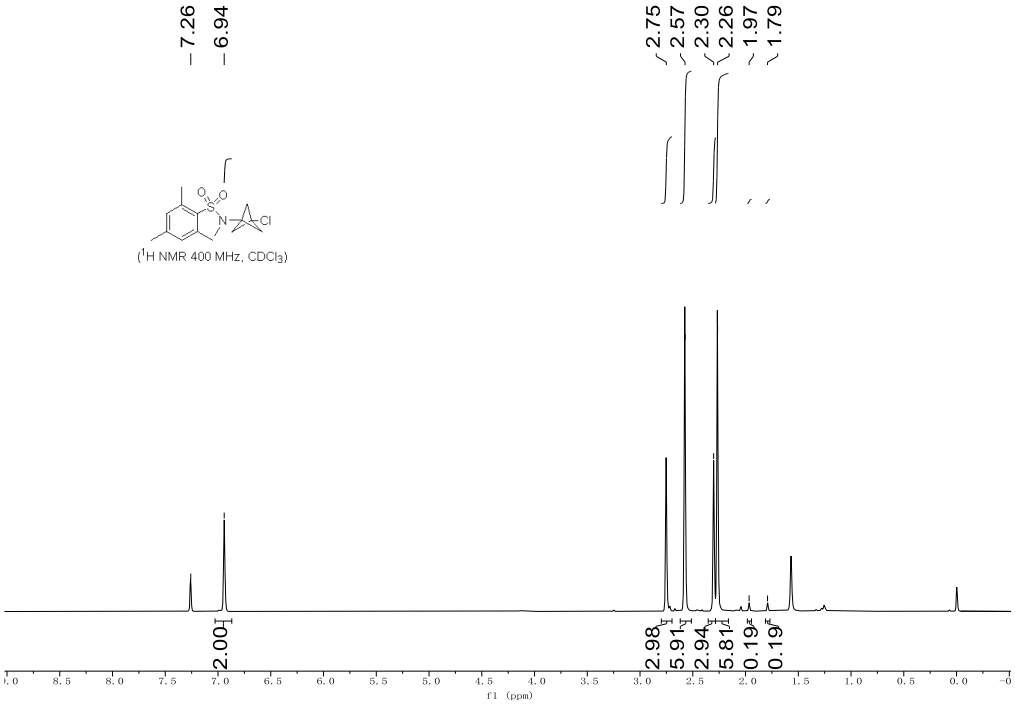


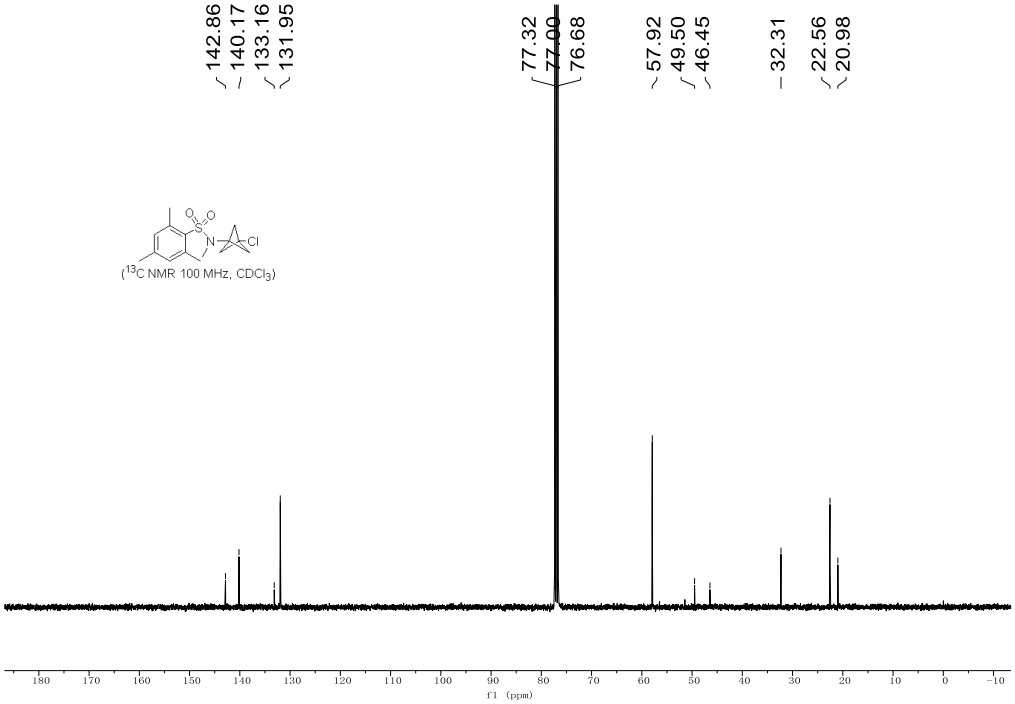
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methyl-[1,1'-biphenyl]-4-sulfonamide (4d)**



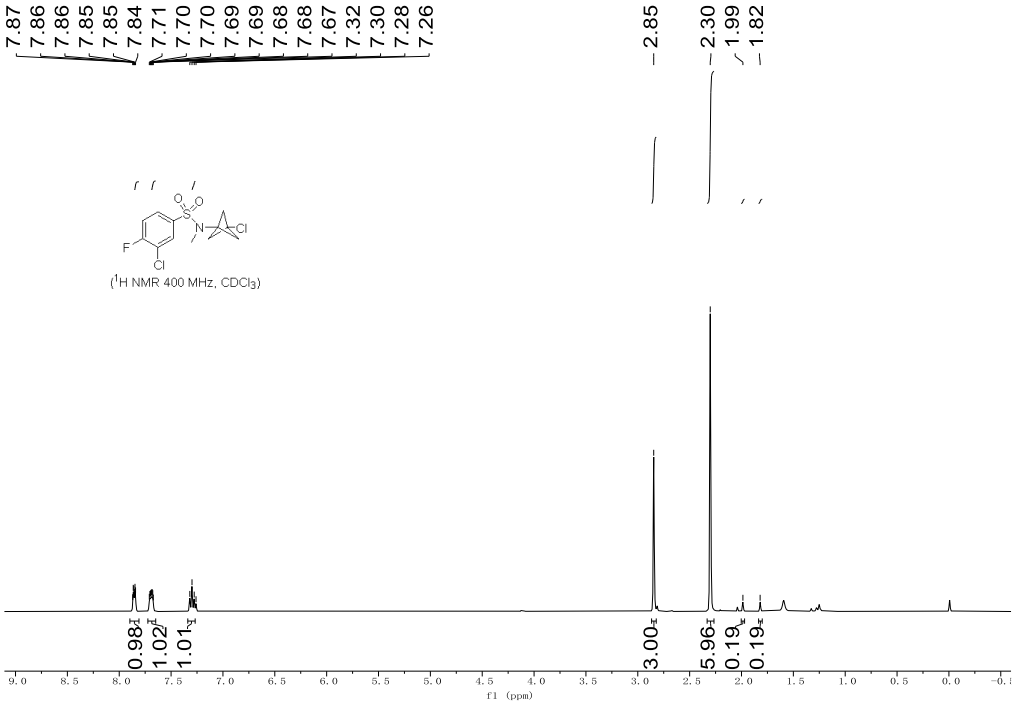


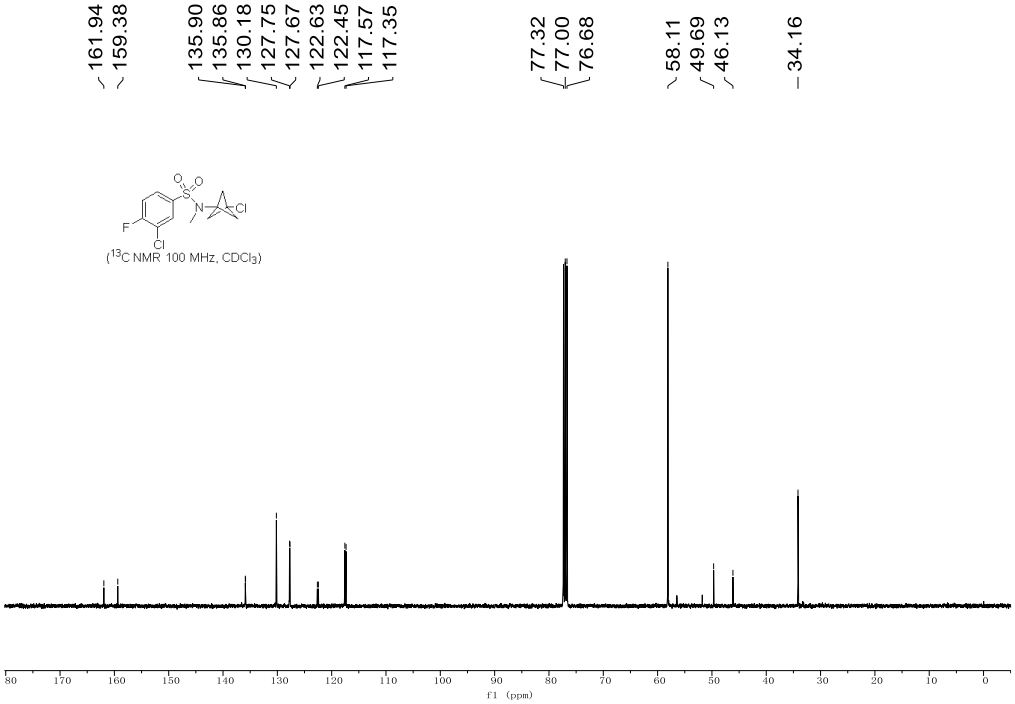
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*,2,4,6-tetramethylbenzenesulfonamide (4e)**

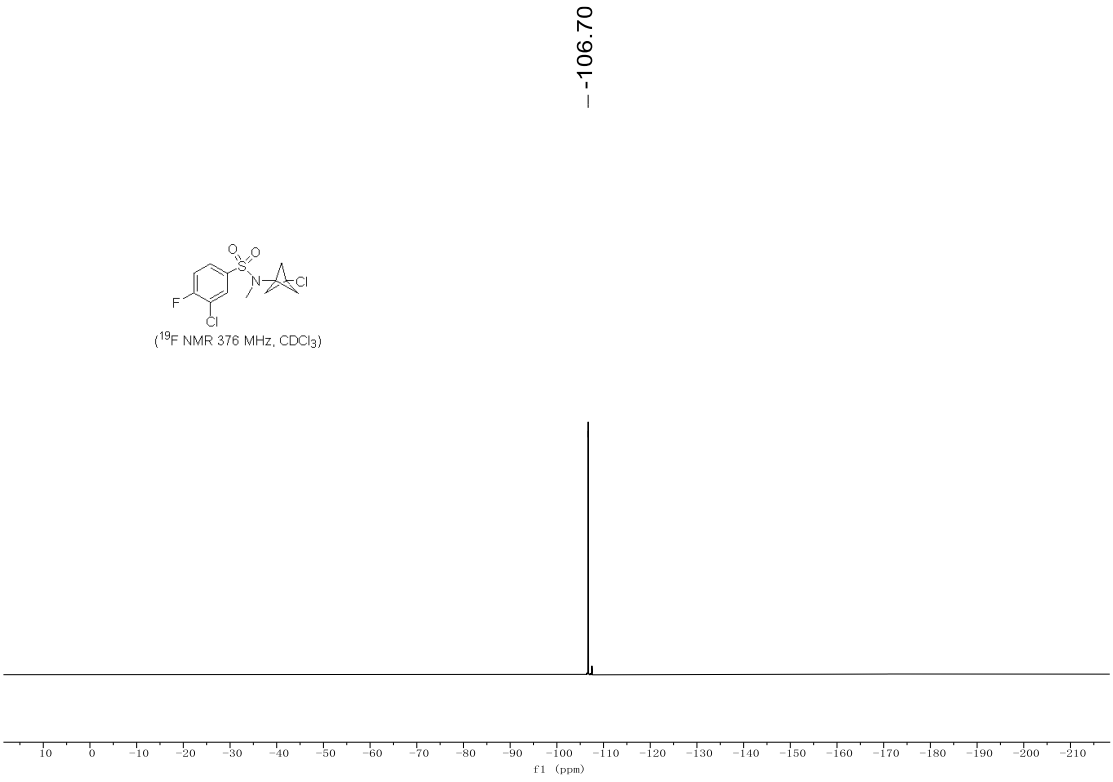




3-chloro-*N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-4-fluoro-*N*-methylbenzenesulfonamide (4f)

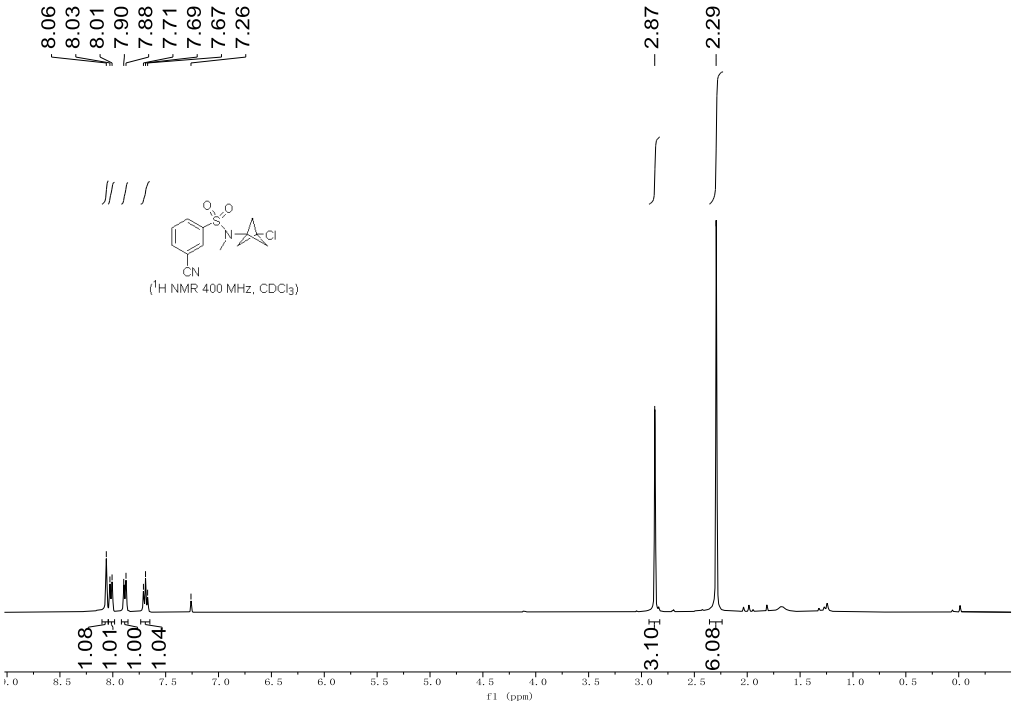


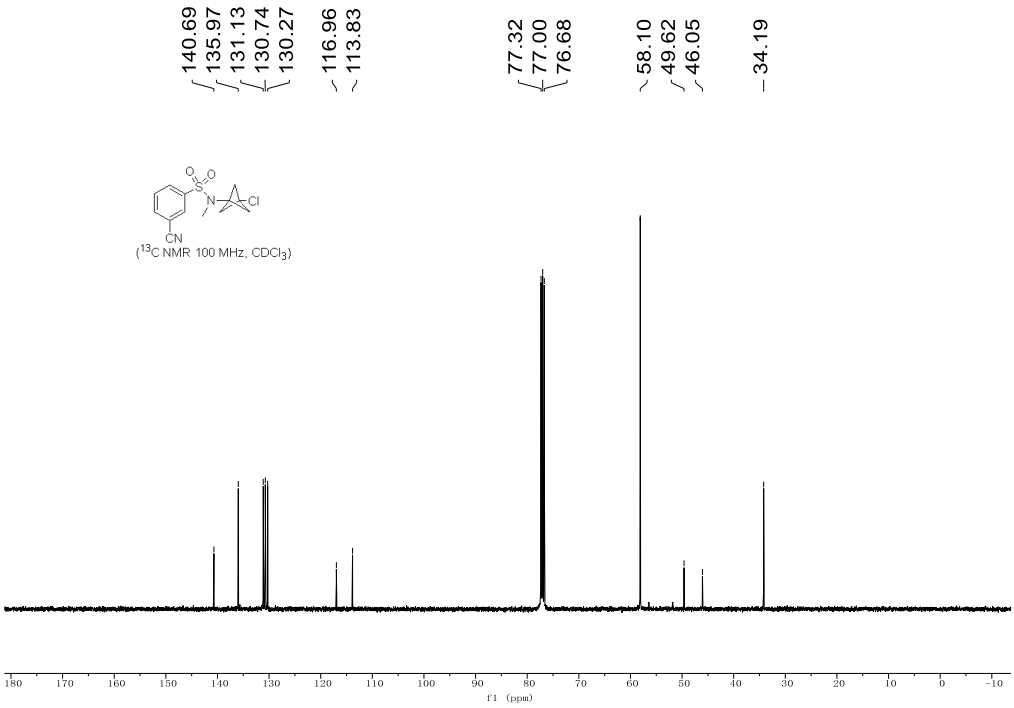




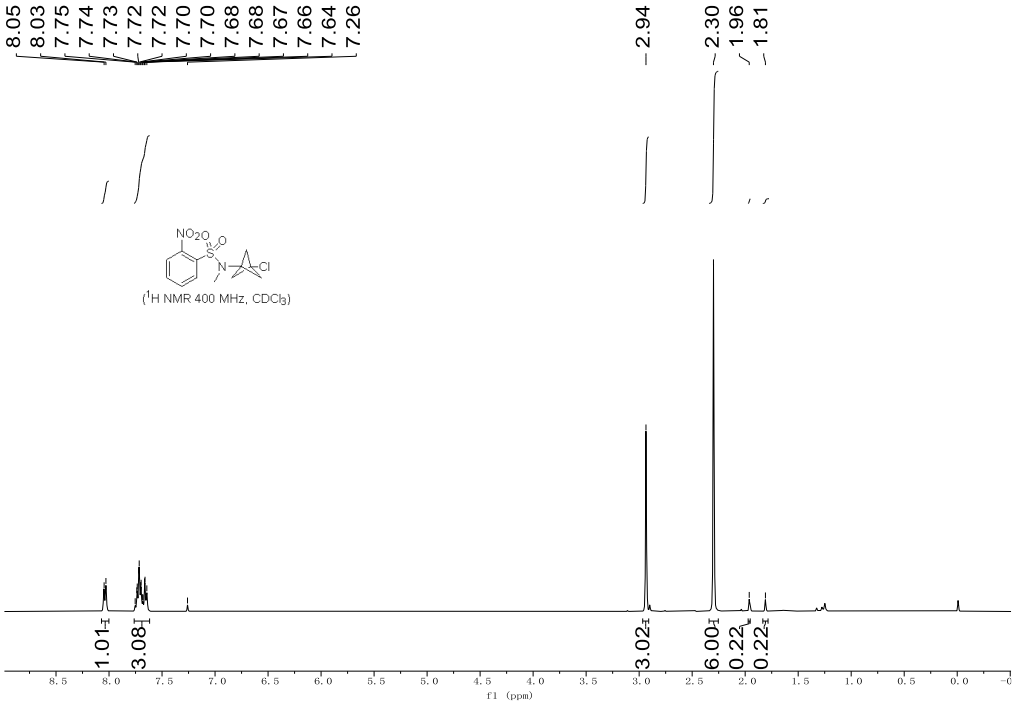
(^{19}F NMR 376 MHz, $CDCl_3$)

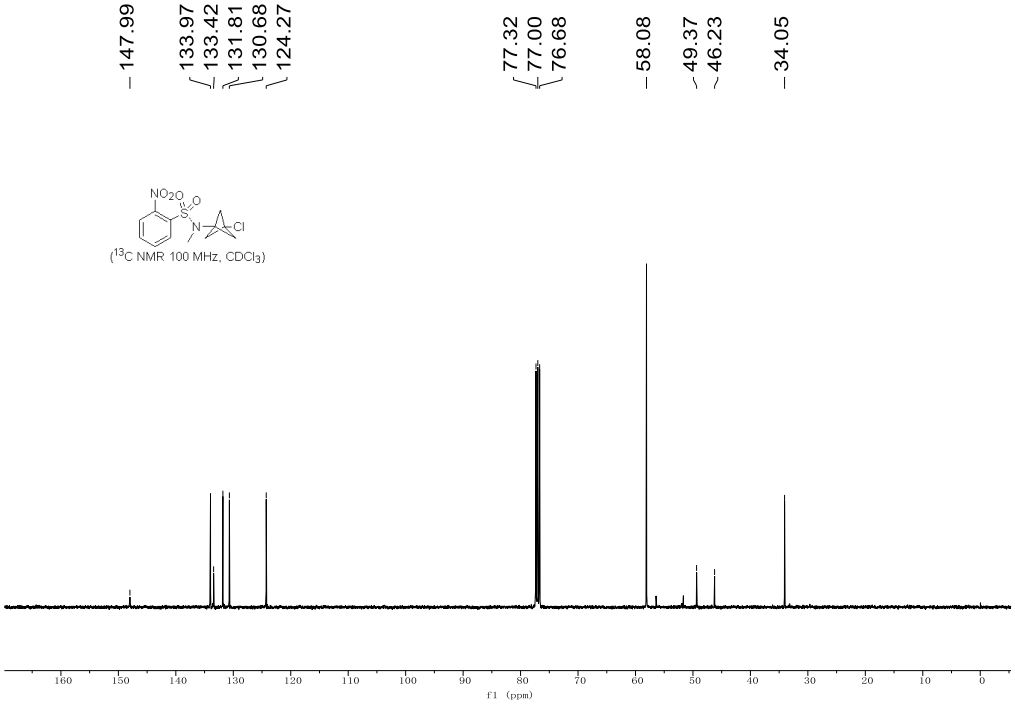
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-3-cyano-*N*-methylbenzenesulfonamide (4g)**



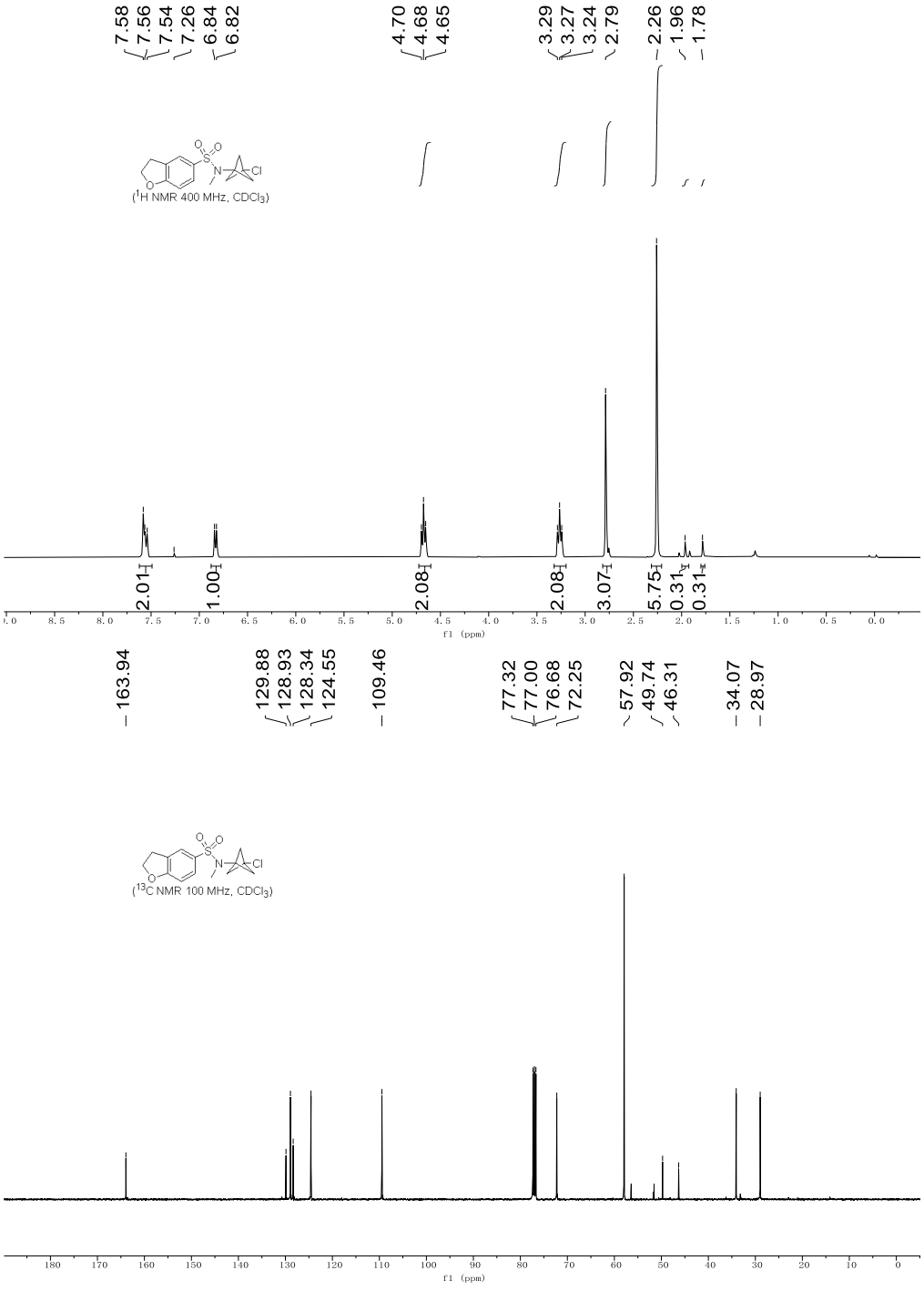


***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methyl-2-nitrobenzenesulfonamide (4h)**

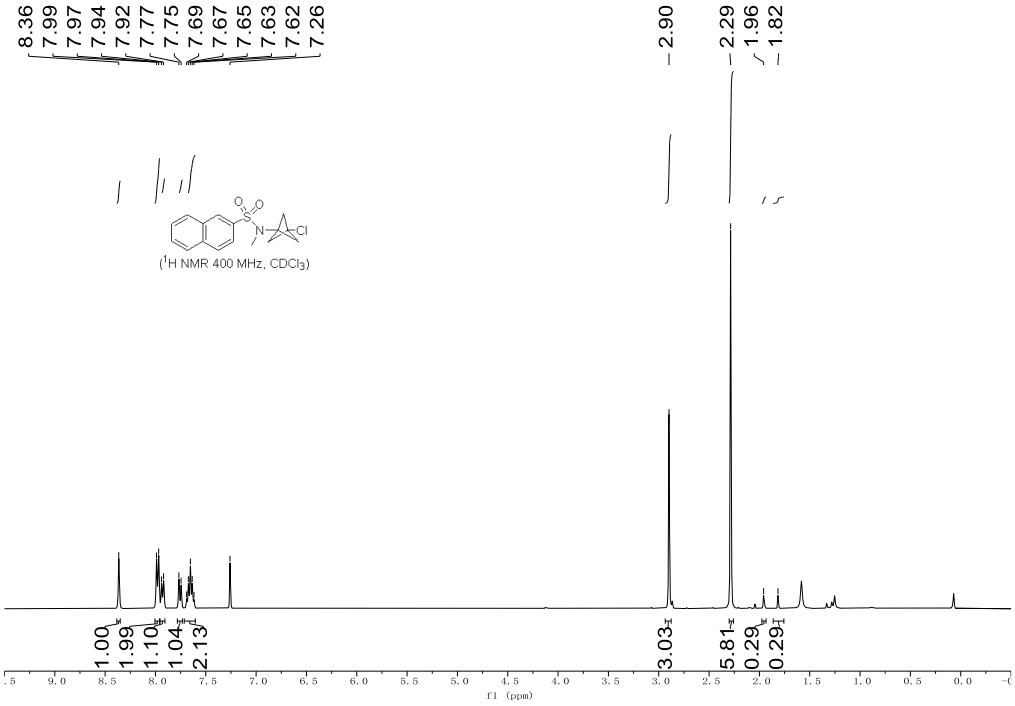


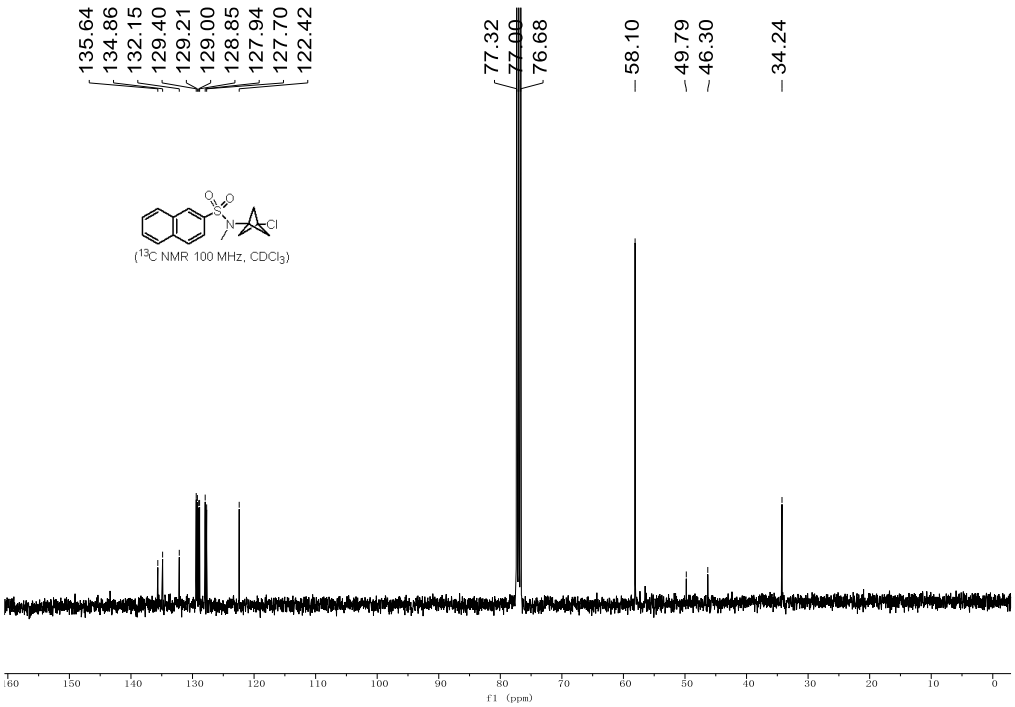


***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methyl-2,3-dihydrobenzofuran-5-sulfonamide (4i)**

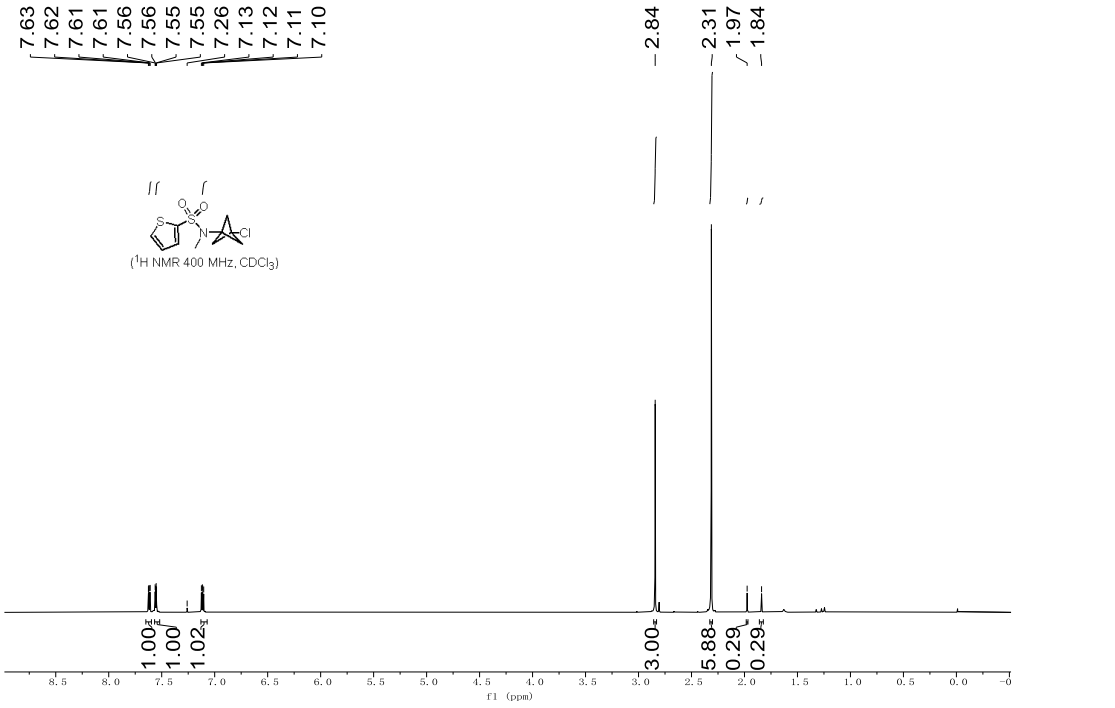


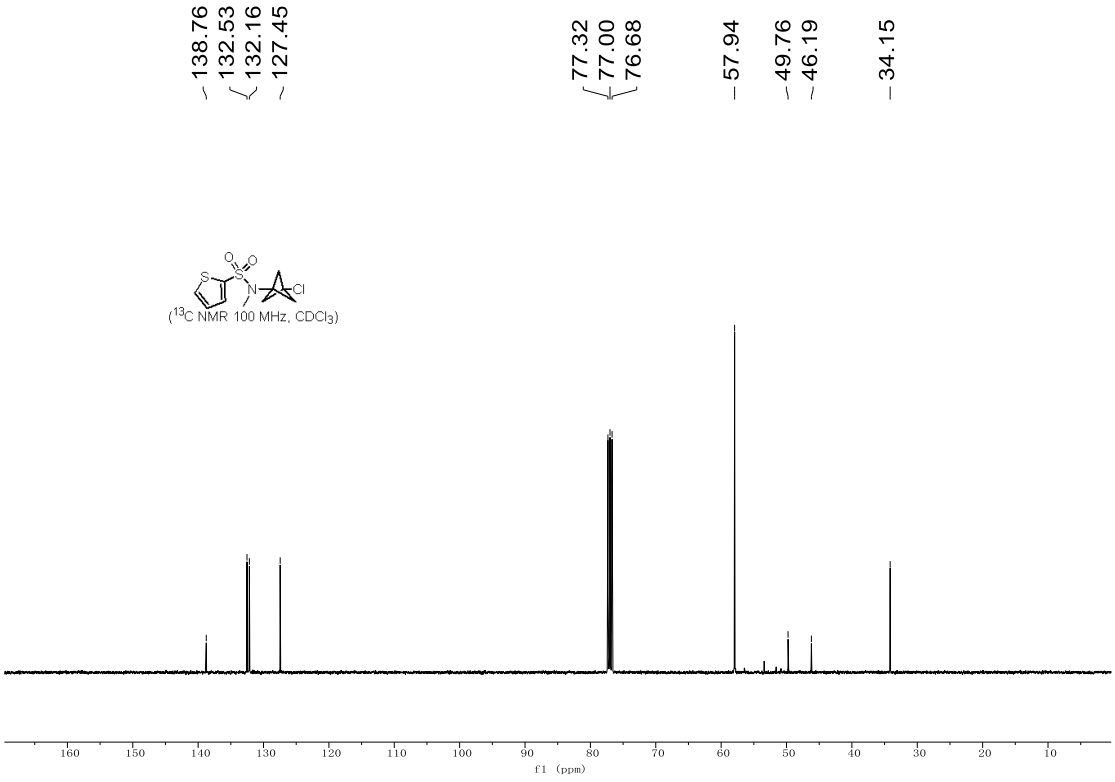
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methylnaphthalene-2-sulfonamide (4j)**



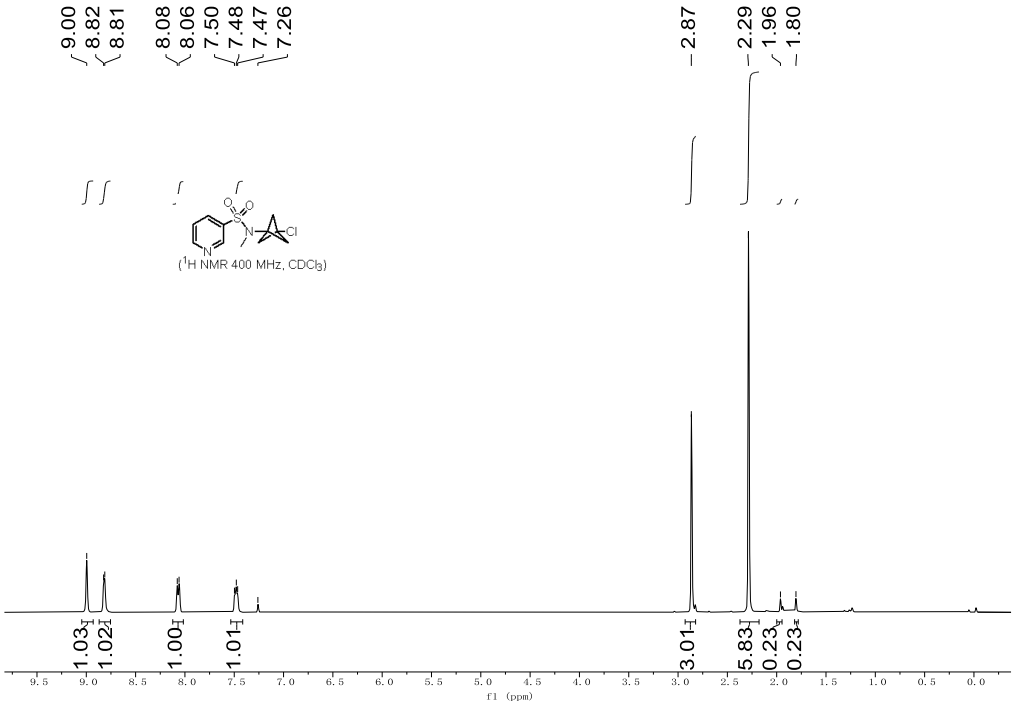


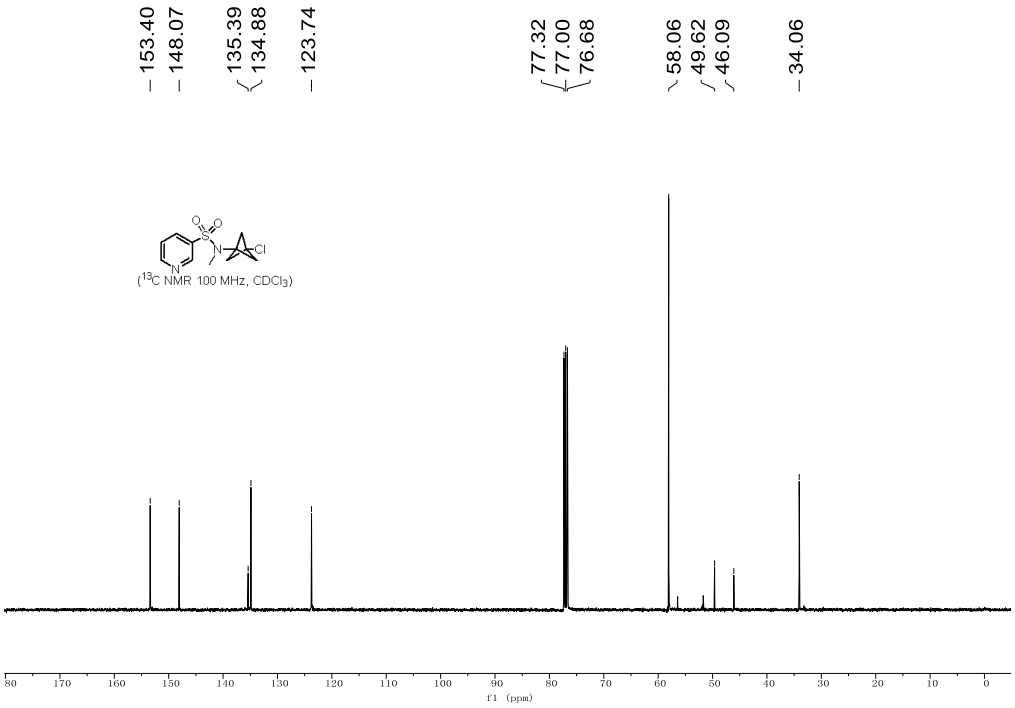
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)thiophene-2-sulfonamide (4k)**



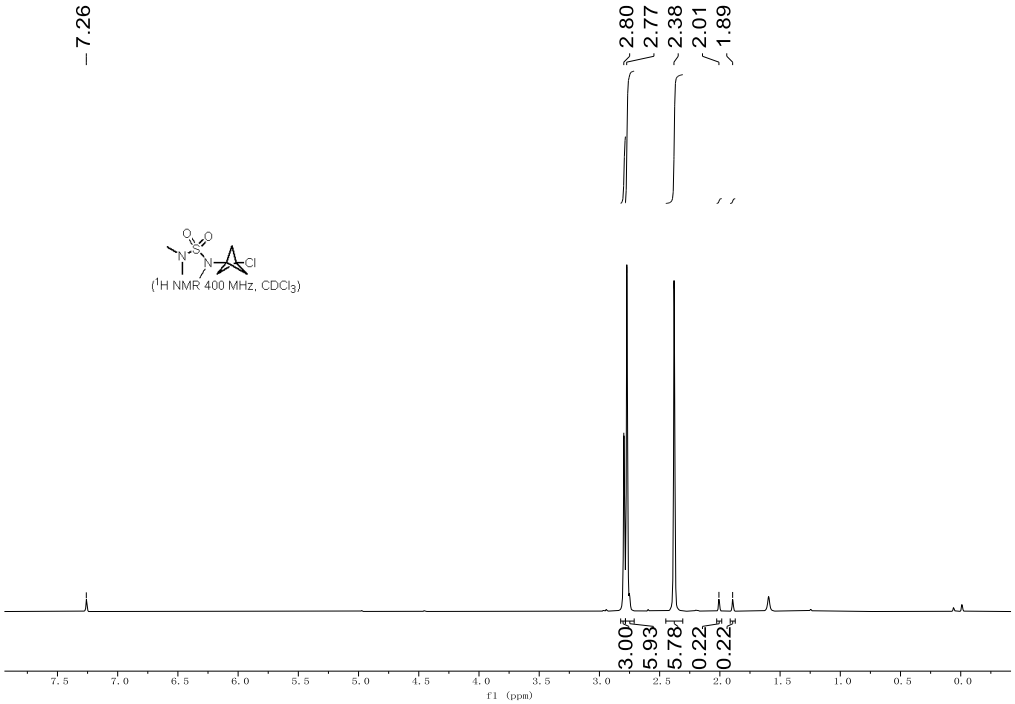


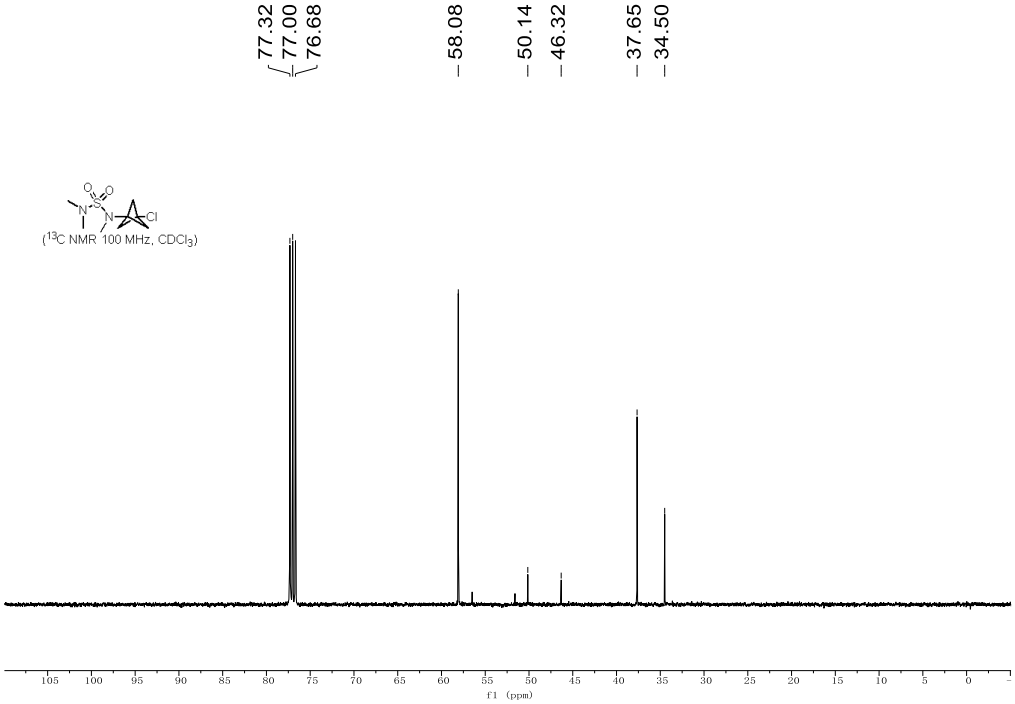
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methylpyridine-3-sulfonamide (4l)**



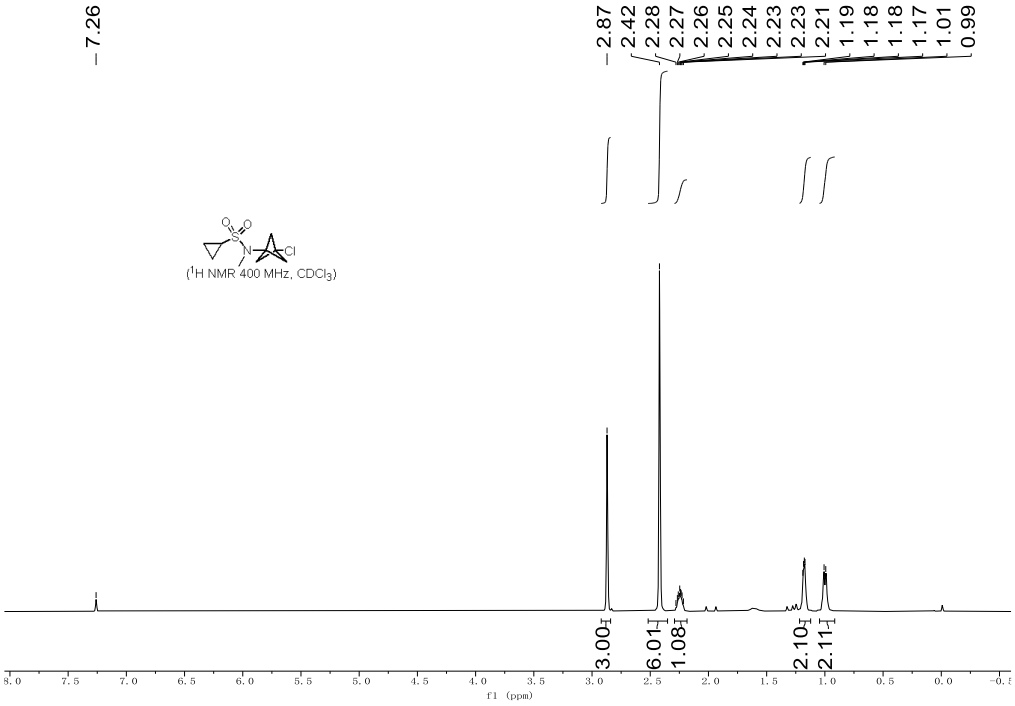


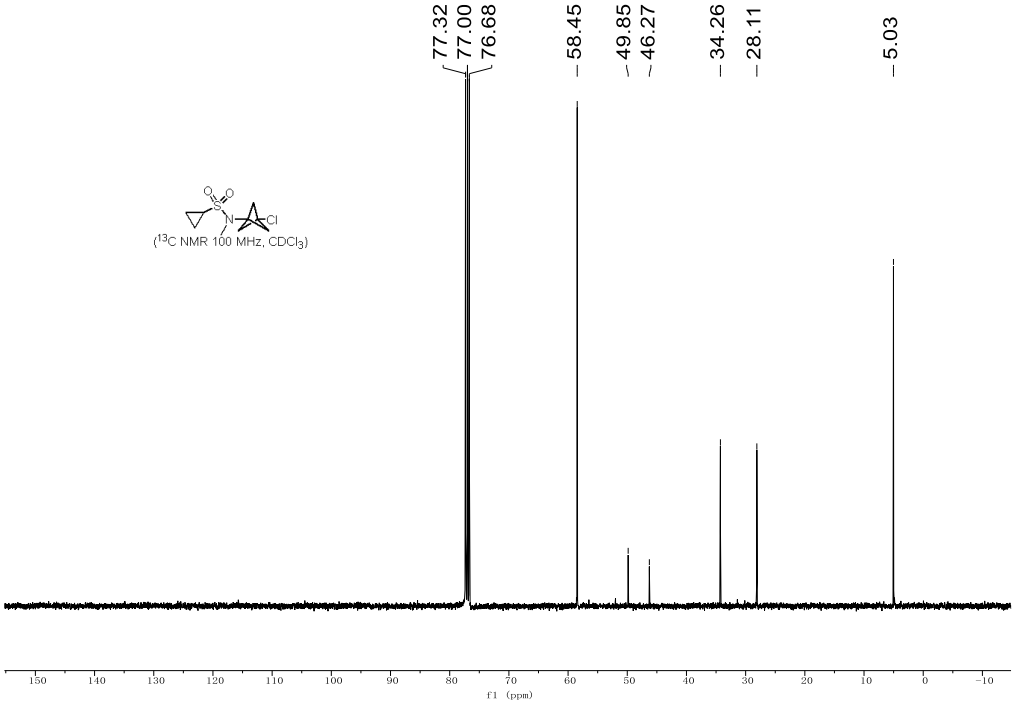
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methyldimethylaminesulfonamide (4m)**



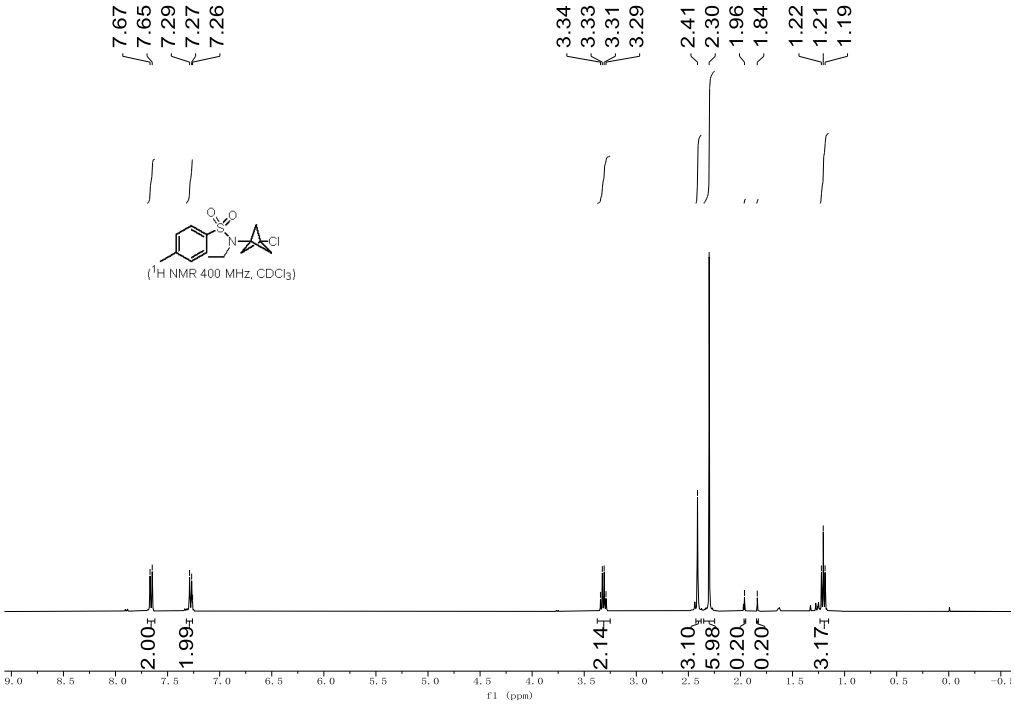


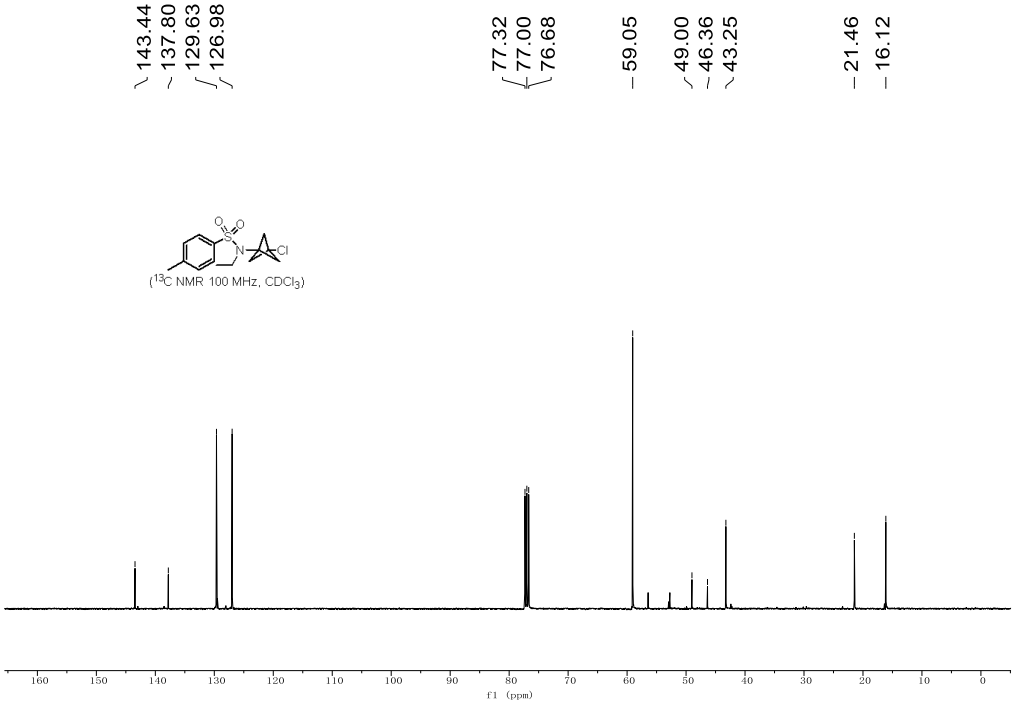
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-methylcyclopropanesulfonamide (4n)**



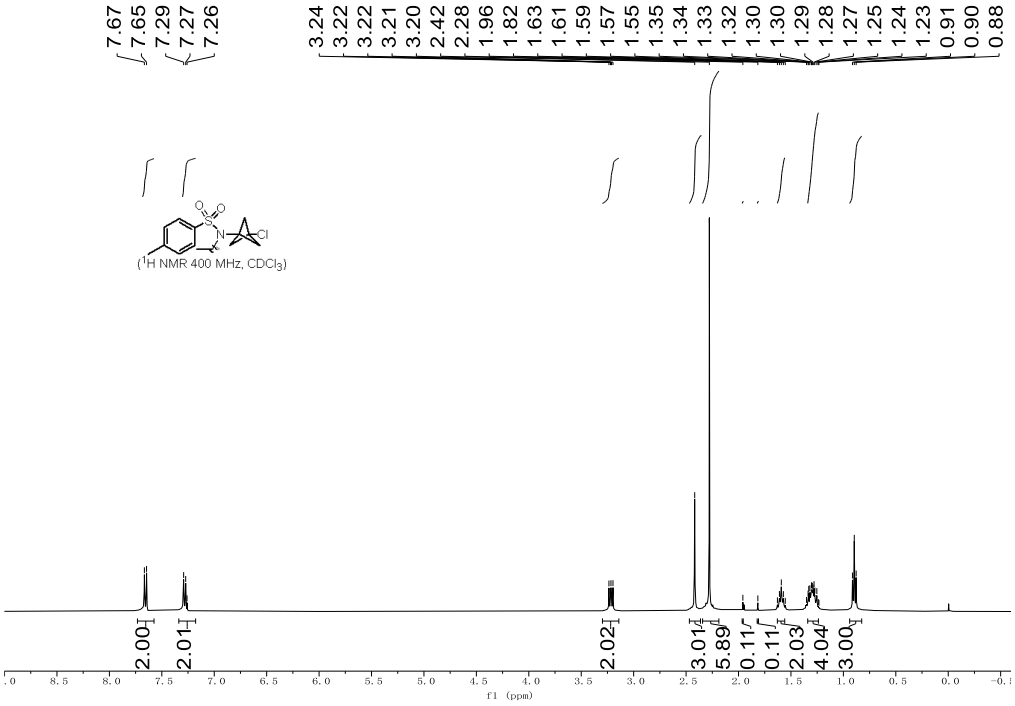


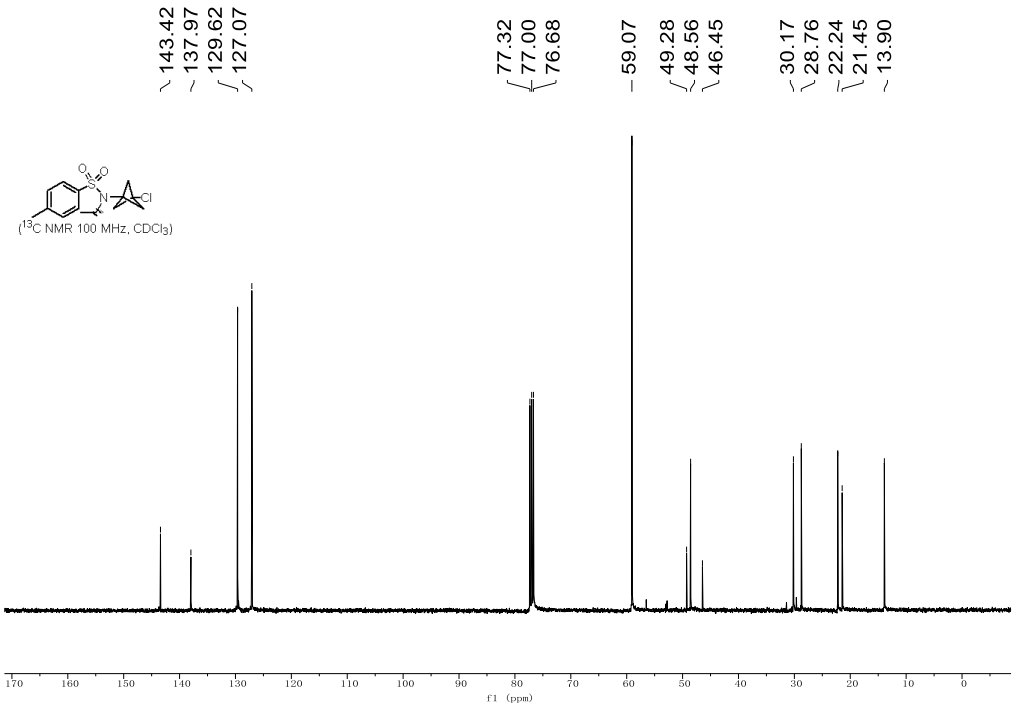
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-*N*-ethyl-4-methylbenzenesulfonamide (4o)**



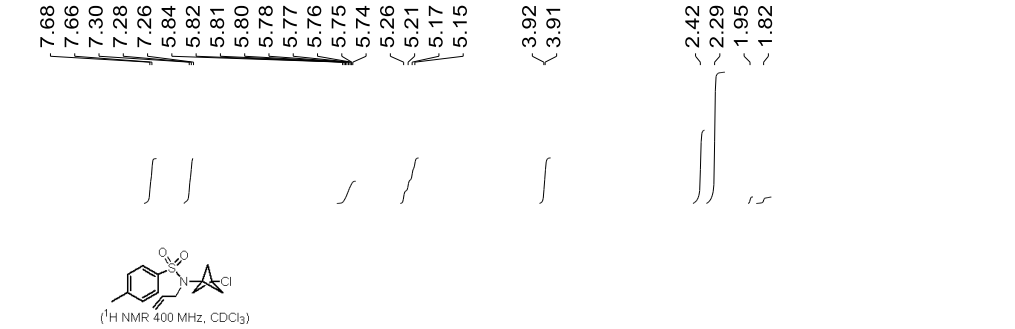


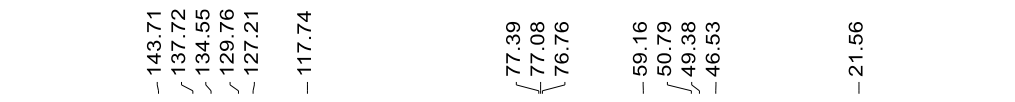
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-4-methyl-*N*-pentylbenzenesulfonamide (4p)**

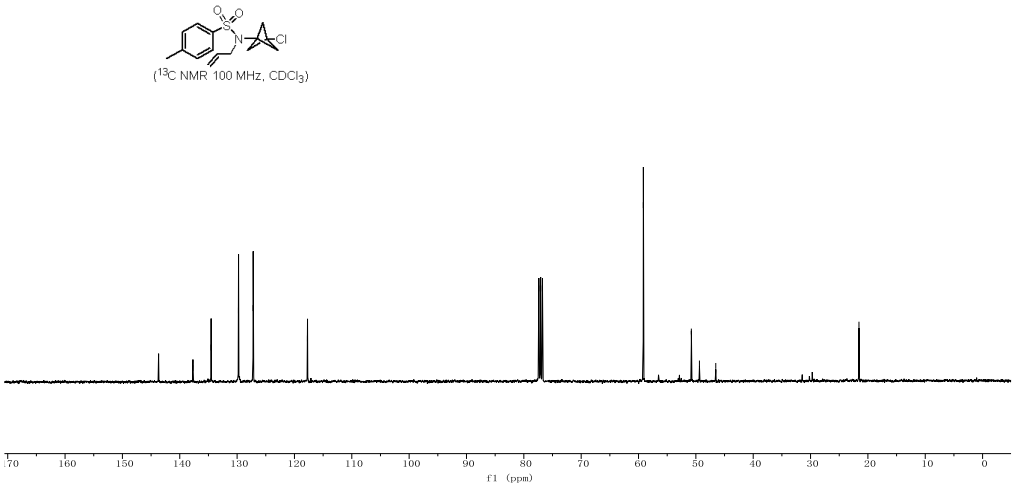




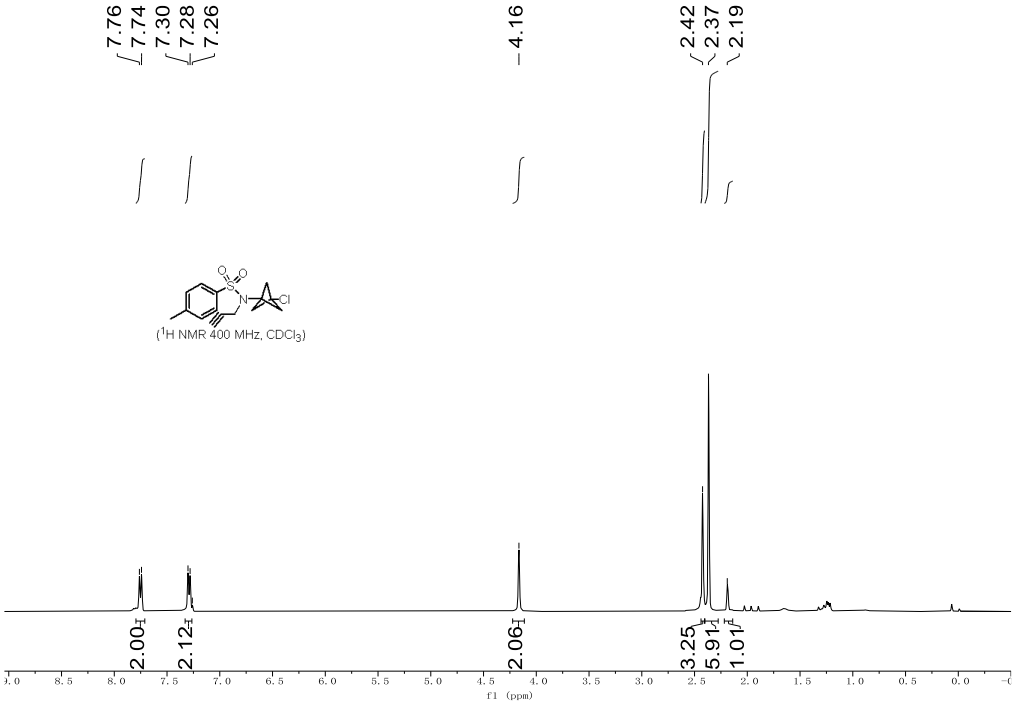
***N*-allyl-*N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-4-methylbenzenesulfonamide (4q)**

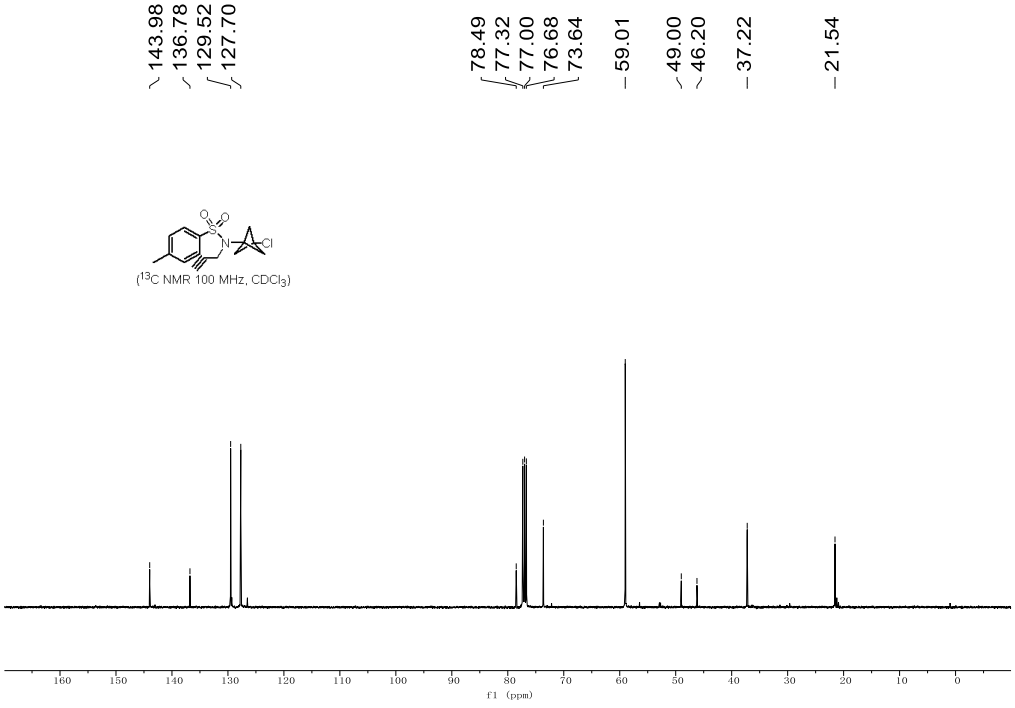




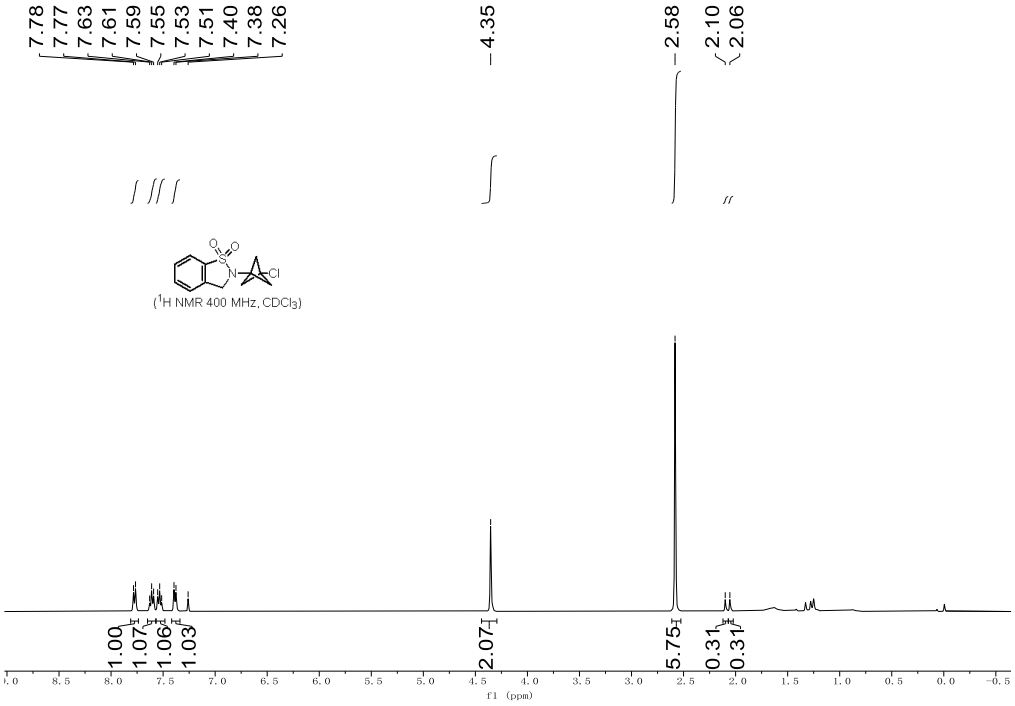


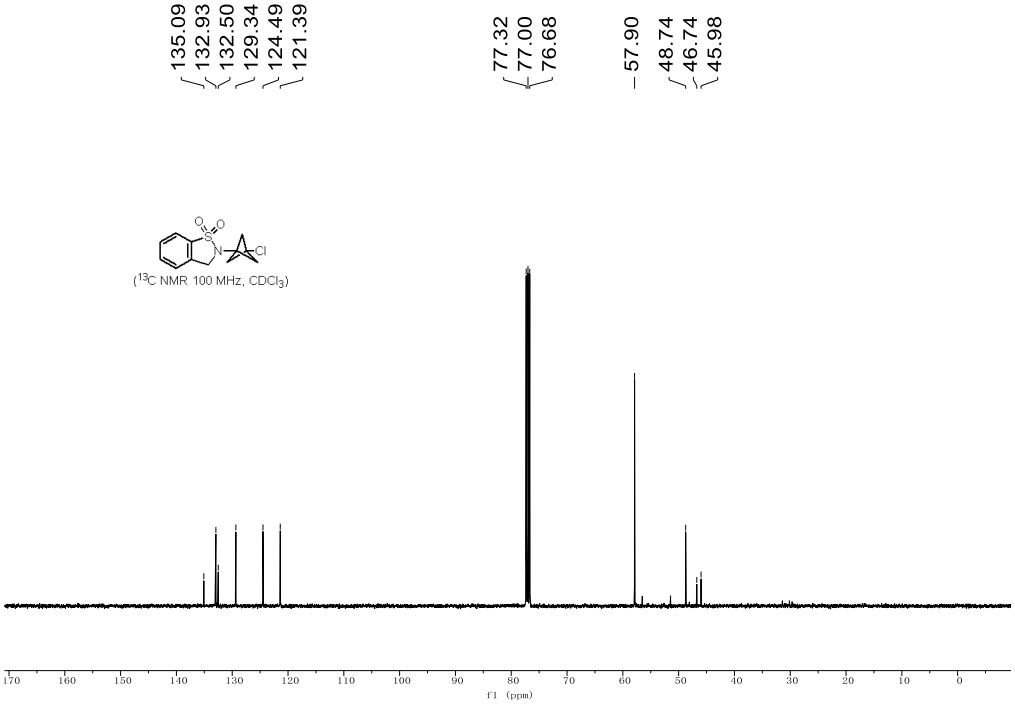
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (4r)**



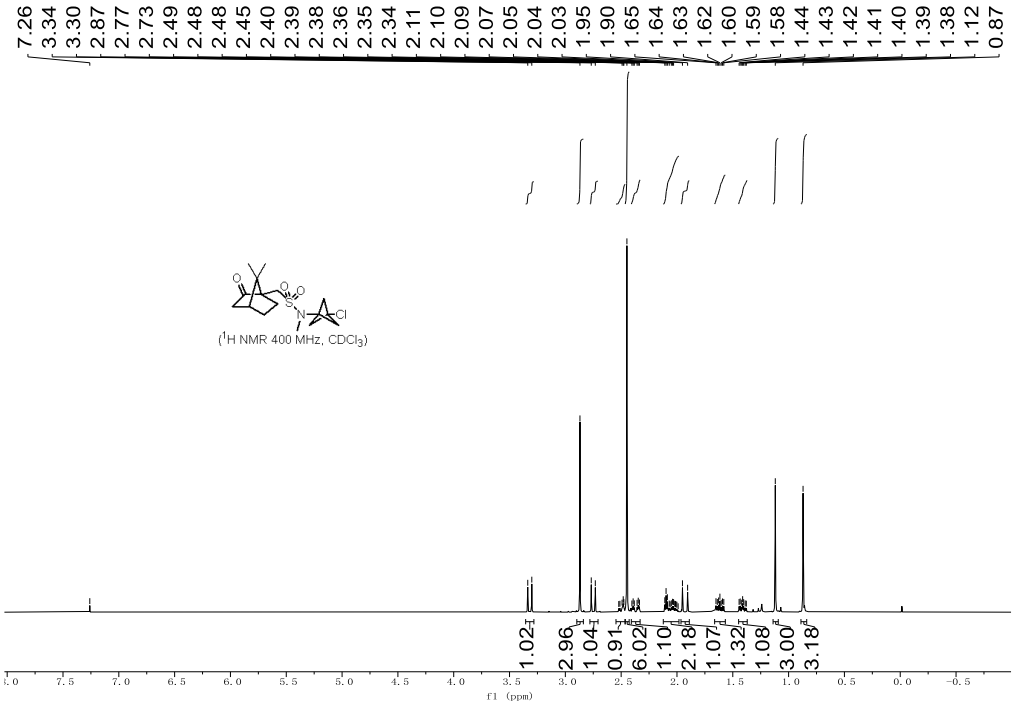


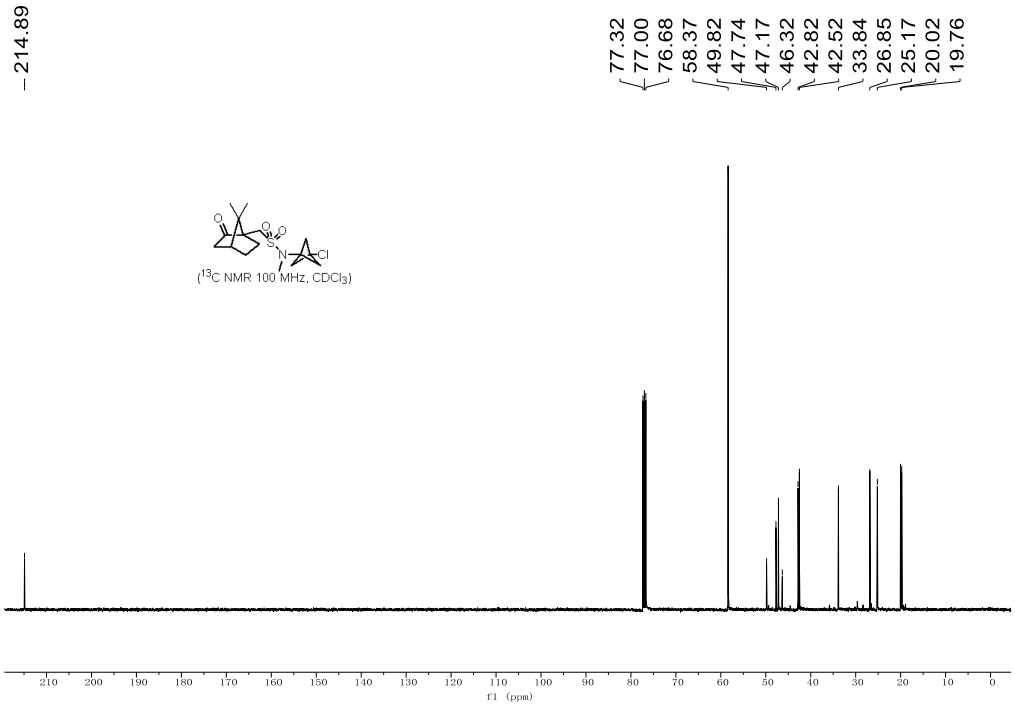
2-(3-chlorobicyclo[1.1.1]pentan-1-yl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (4s)



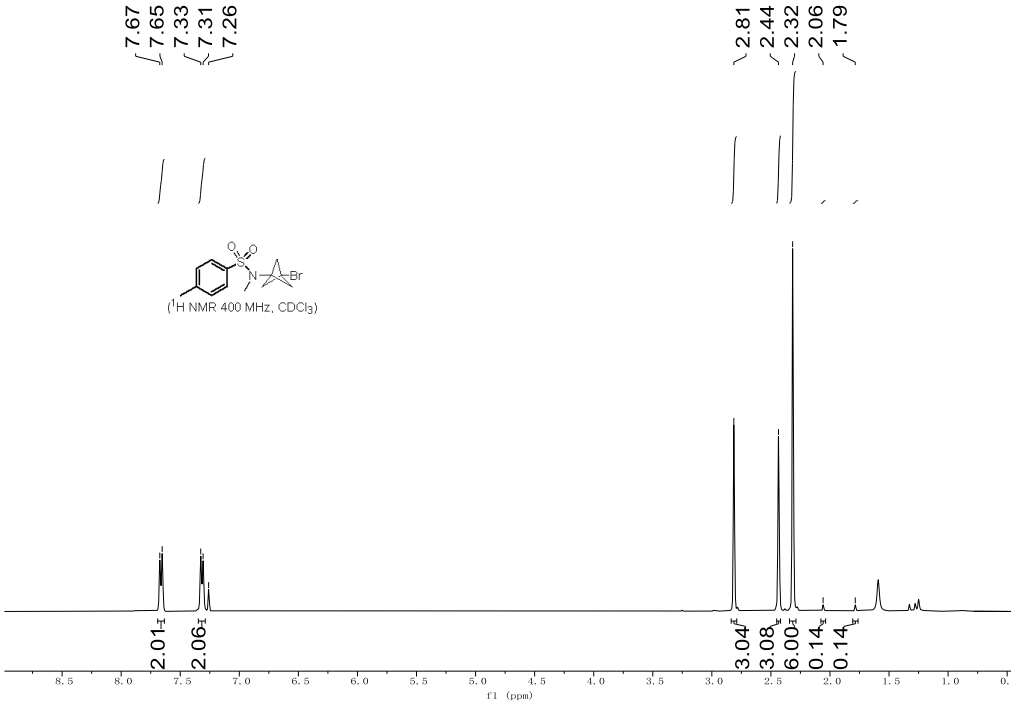


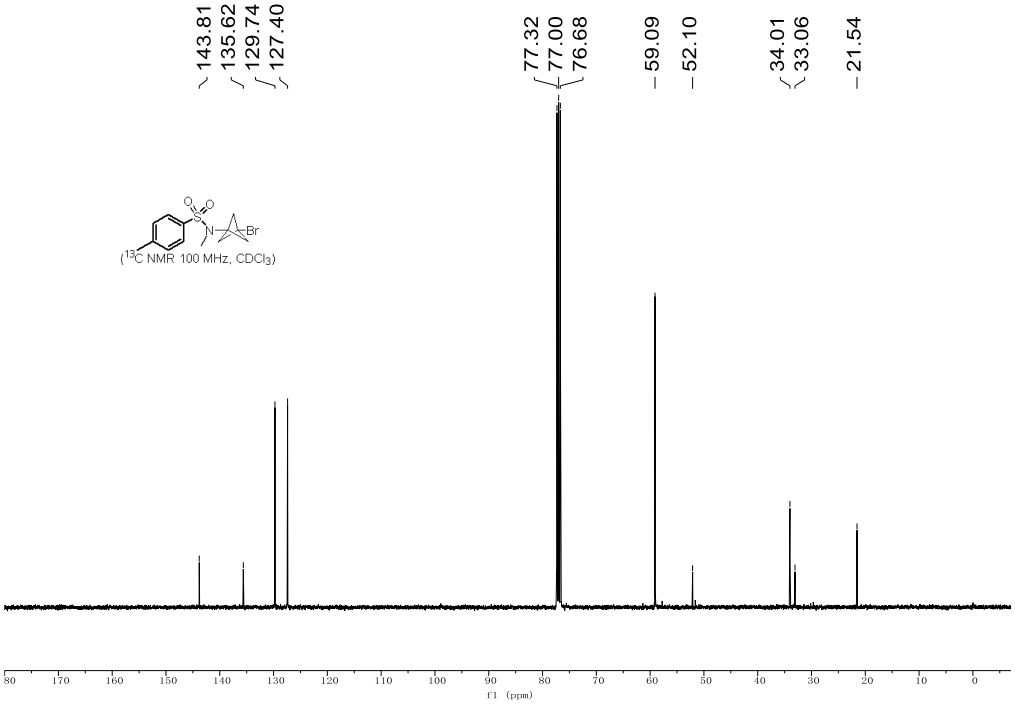
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-1-(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-methylmethanesulfonamide (4t)**



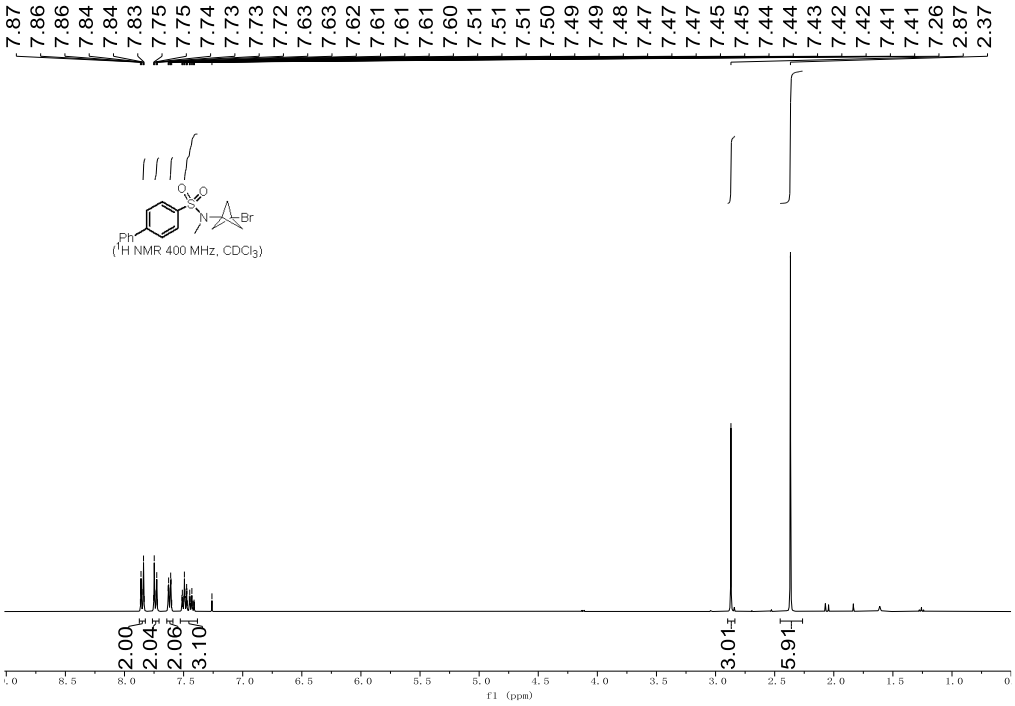


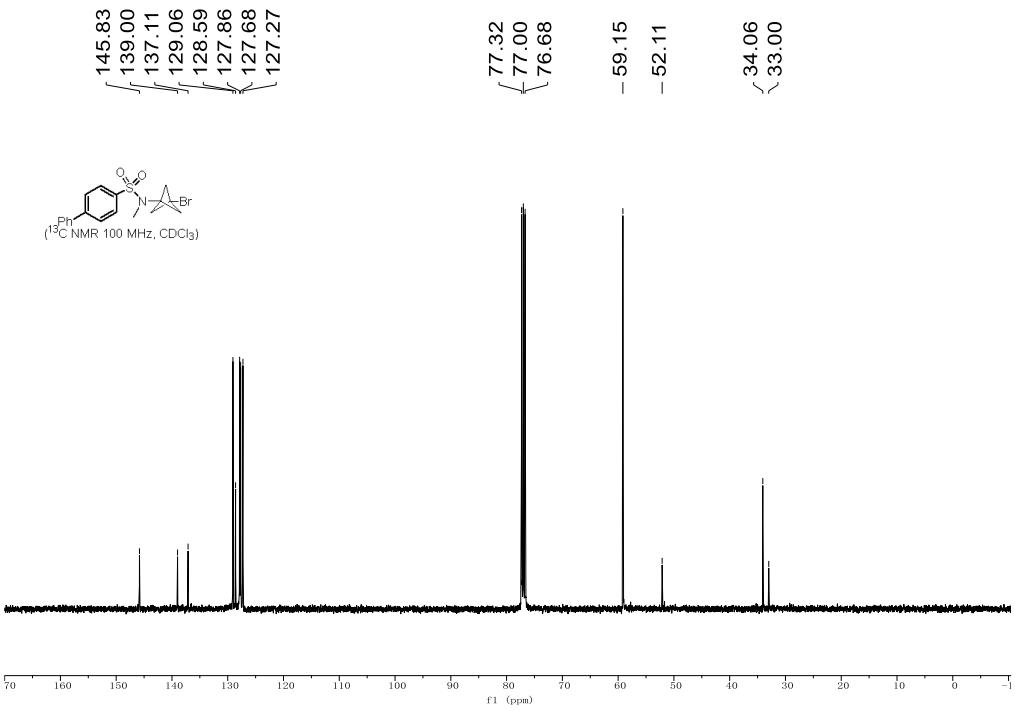
***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-*N*,4-dimethylbenzenesulfonamide (5a)**



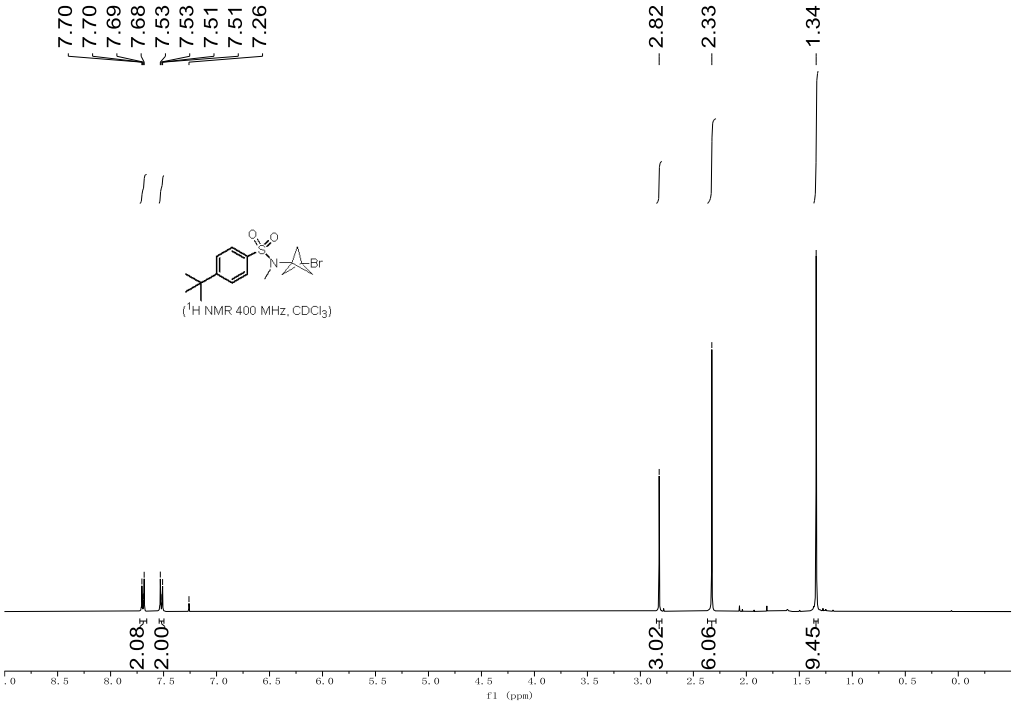


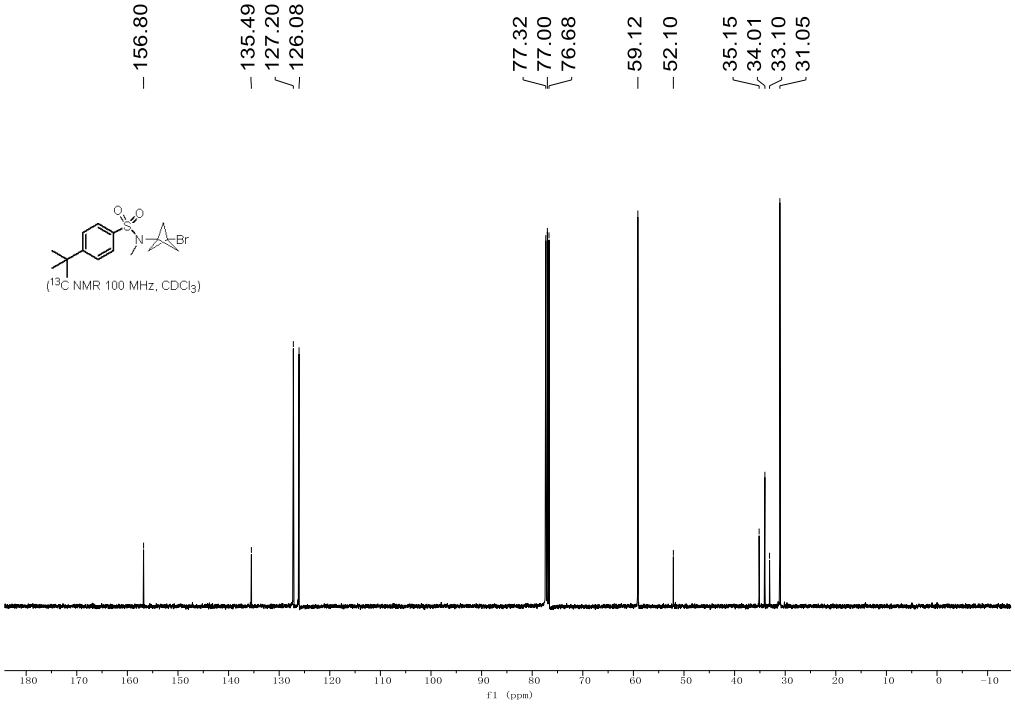
***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-*N*-methyl-[1,1'-biphenyl]-4-sulfonamide (5b)**



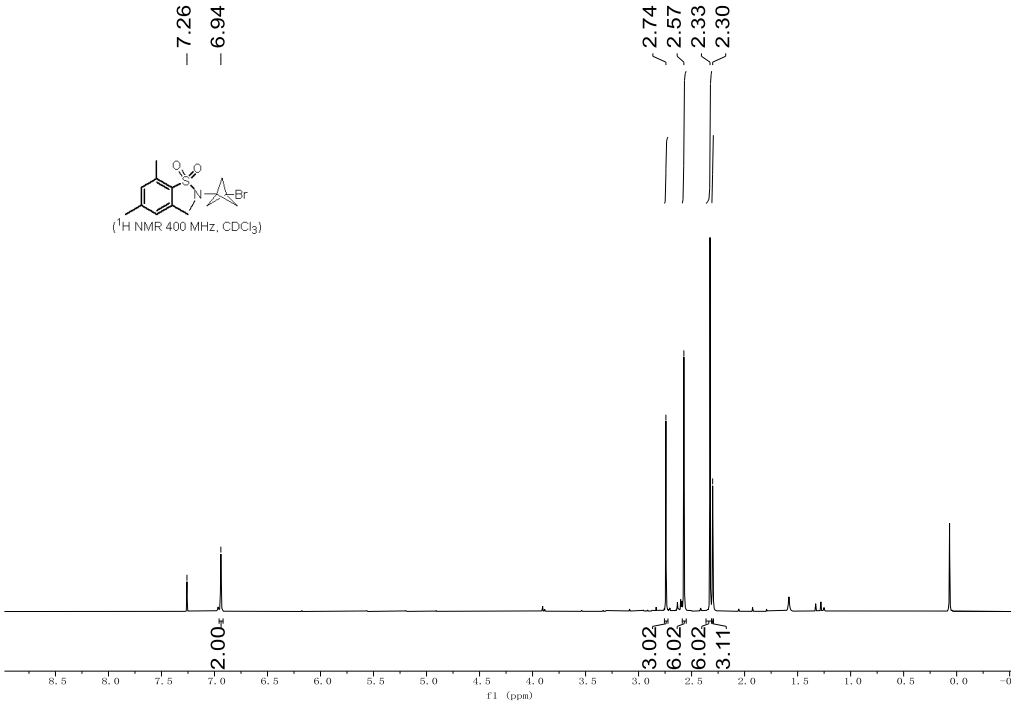


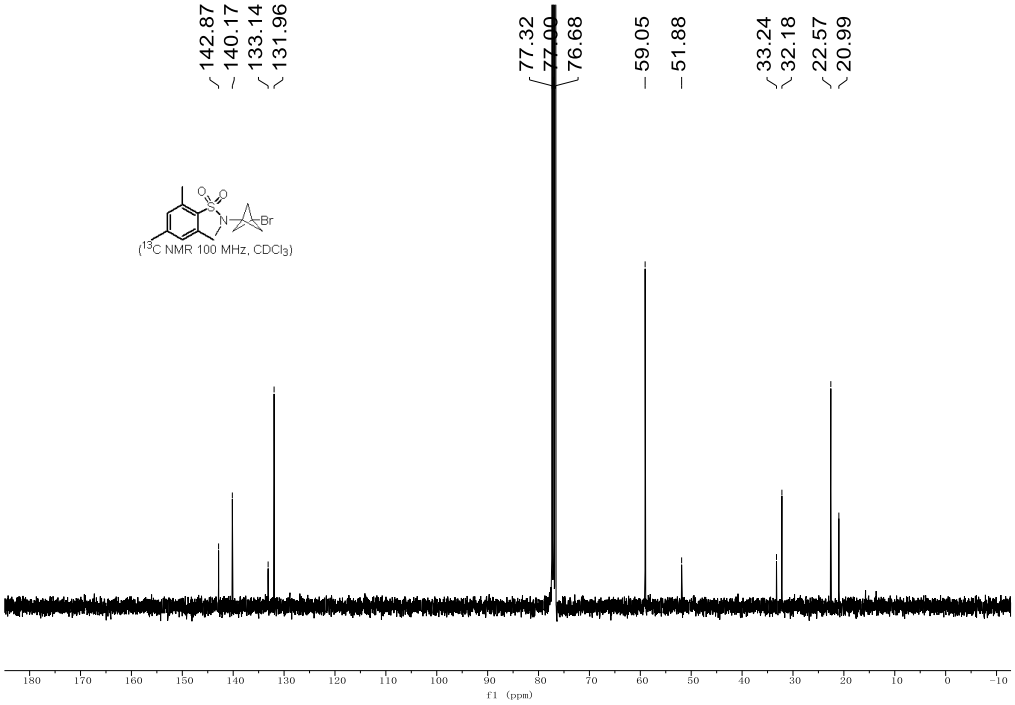
***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-4-(tert-butyl)-*N*-methylbenzenesulfonamide (5c)**



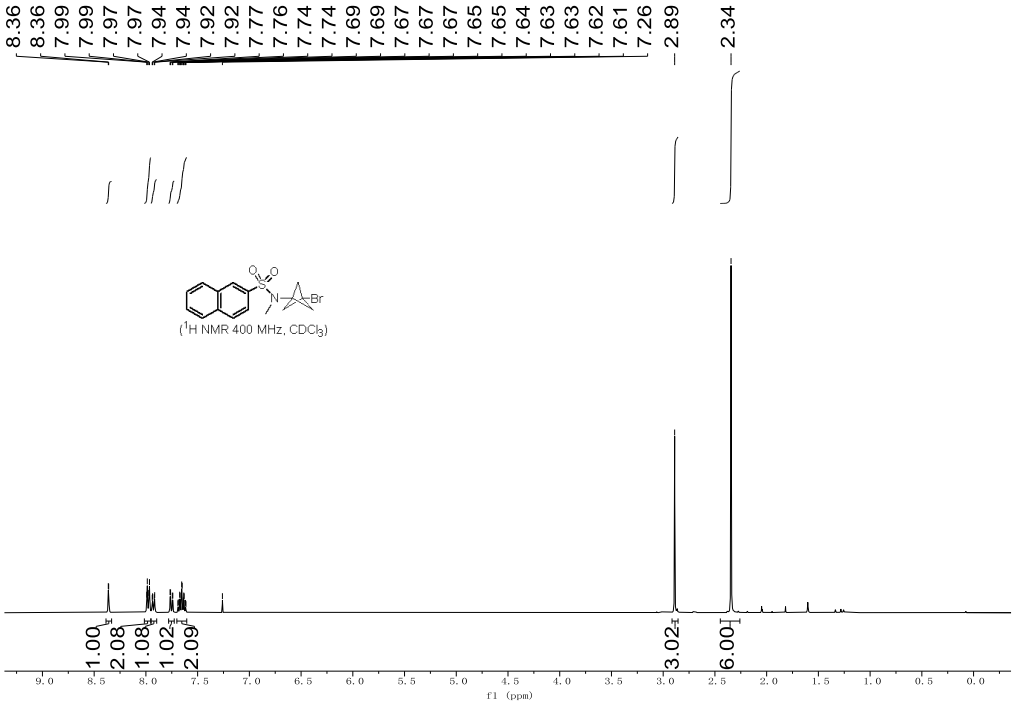


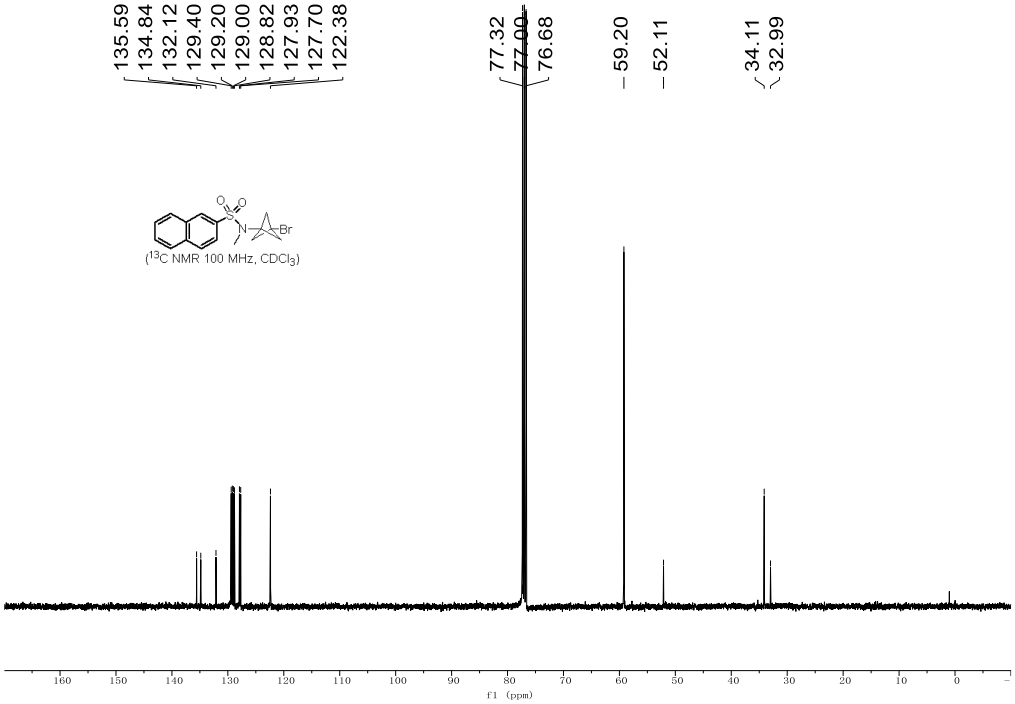
_N_-(3-bromobicyclo[1.1.1]pentan-1-yl)-_N_,2,4,6-tetramethylbenzenesulfonamide (5d)



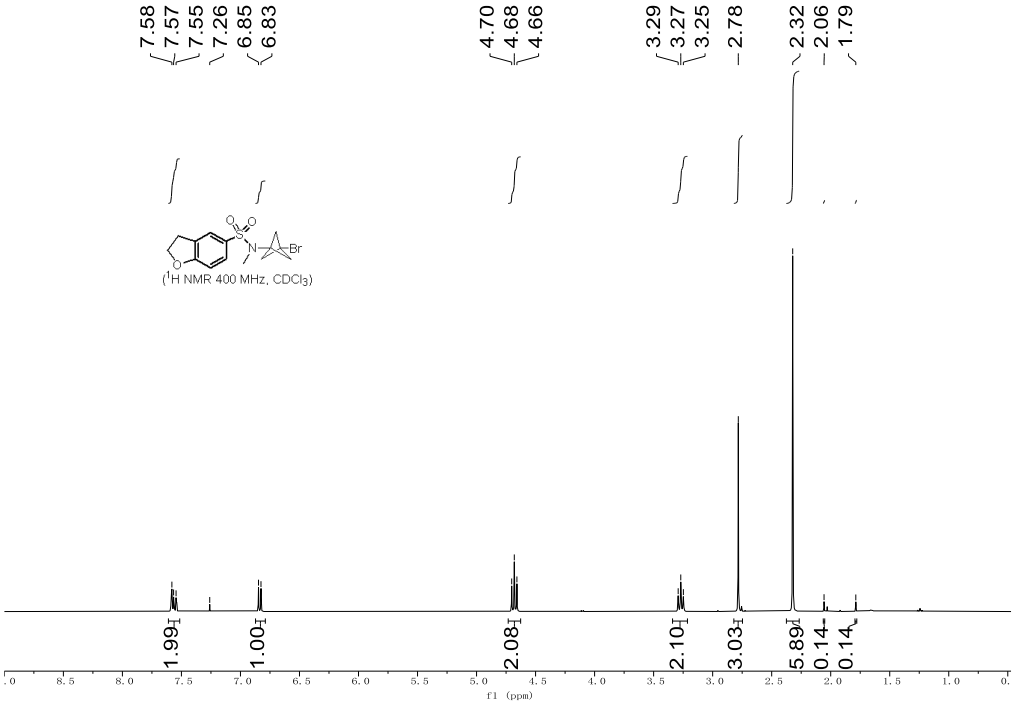


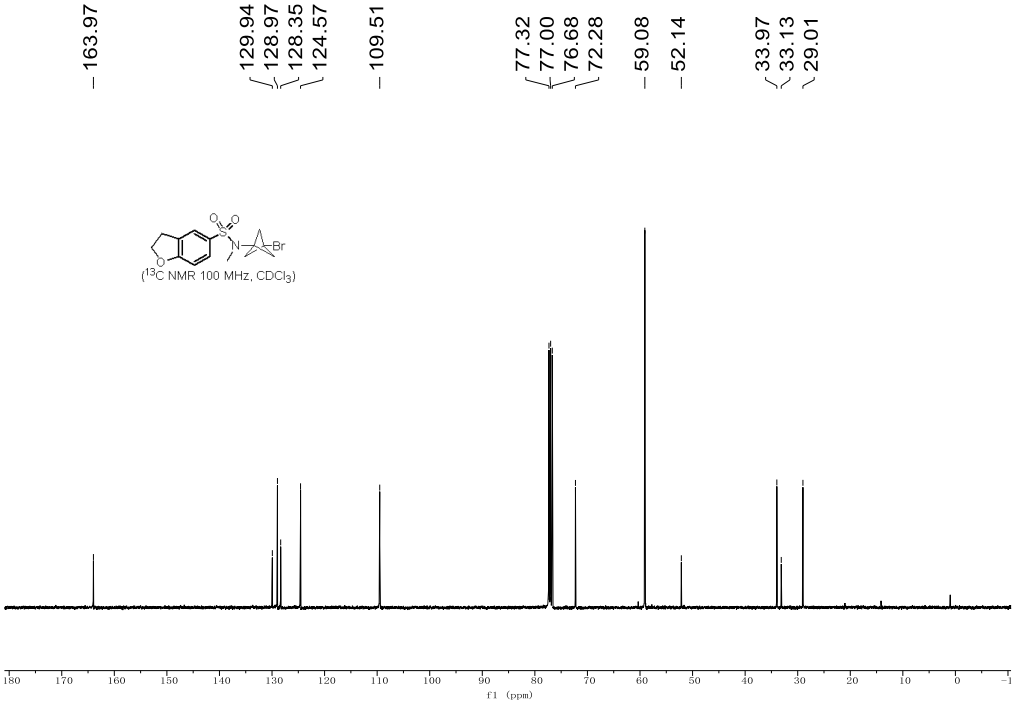
***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-*N*-methylnaphthalene-2-sulfonamide (5e)**



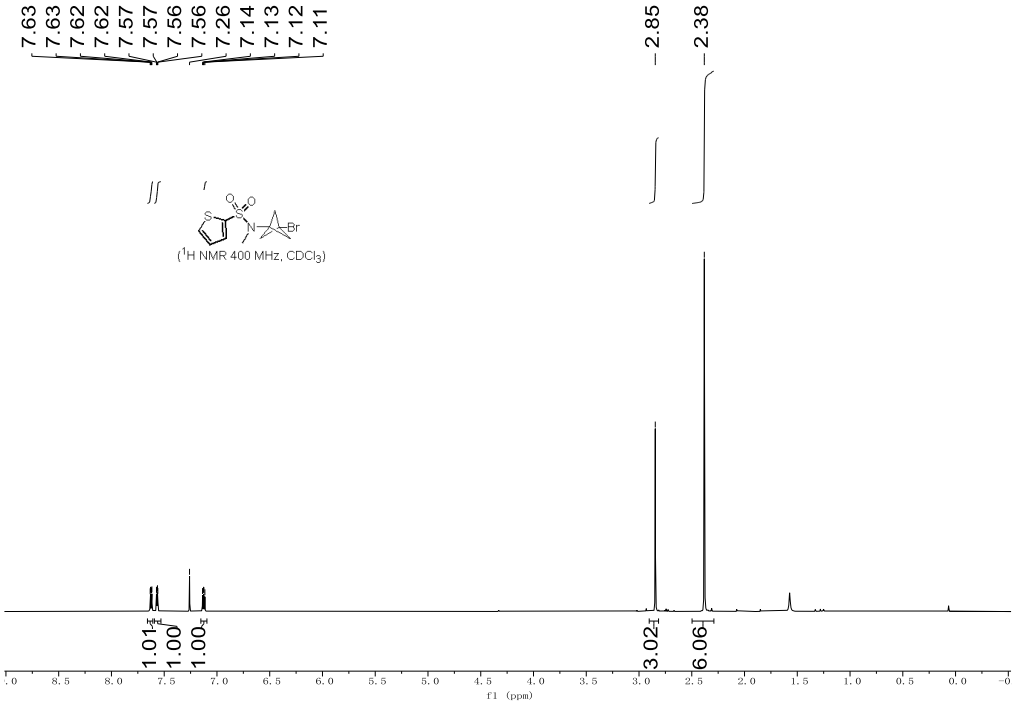


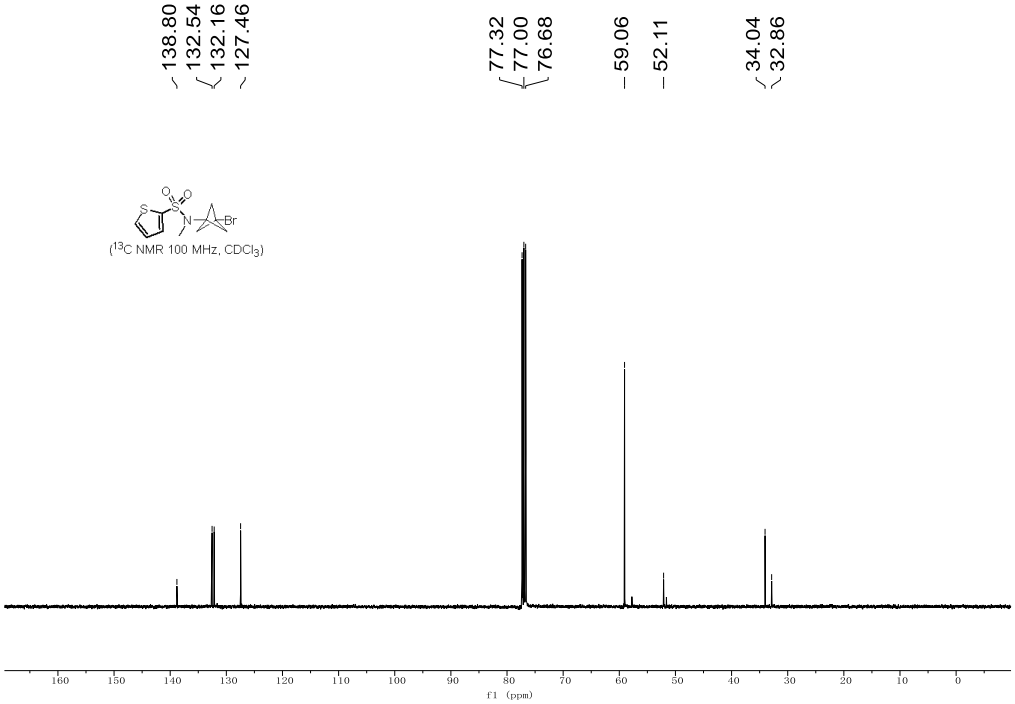
***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-*N*-methyl-2,3-dihydrobenzofuran-5-sulfonamide (5f)**



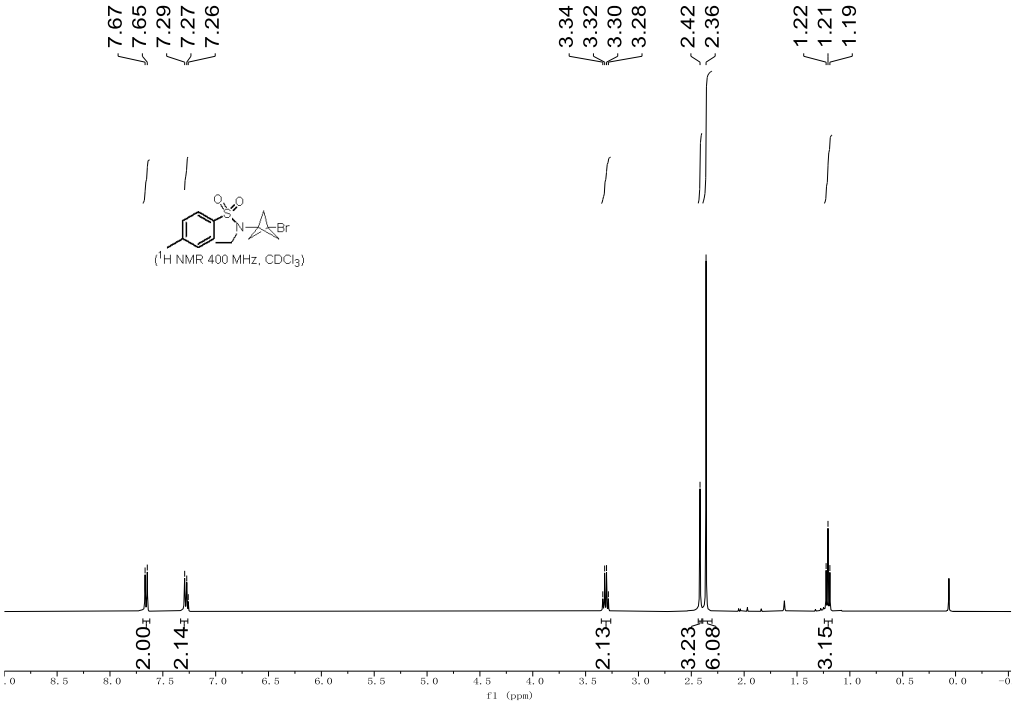


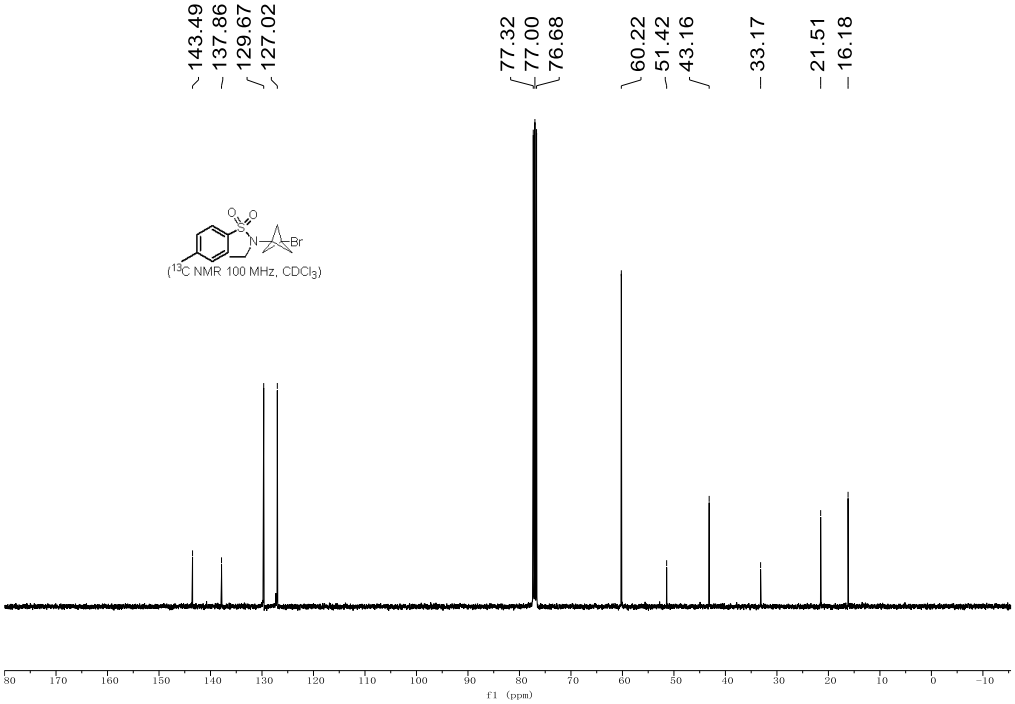
***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-*N*-methylthiophene-2-sulfonamide (5g)**



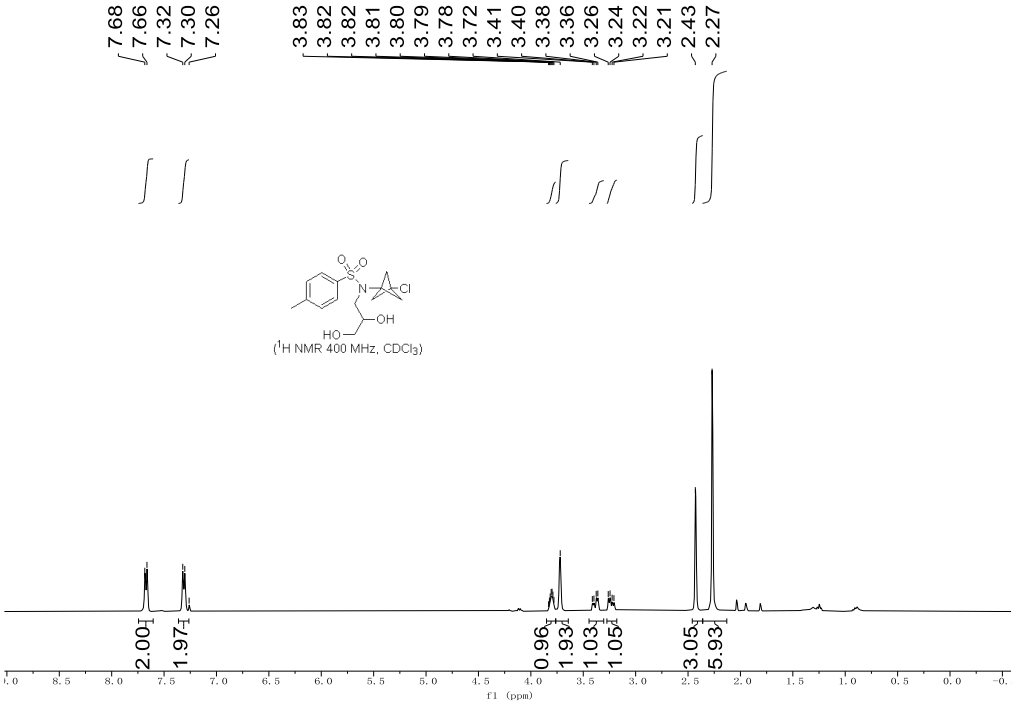


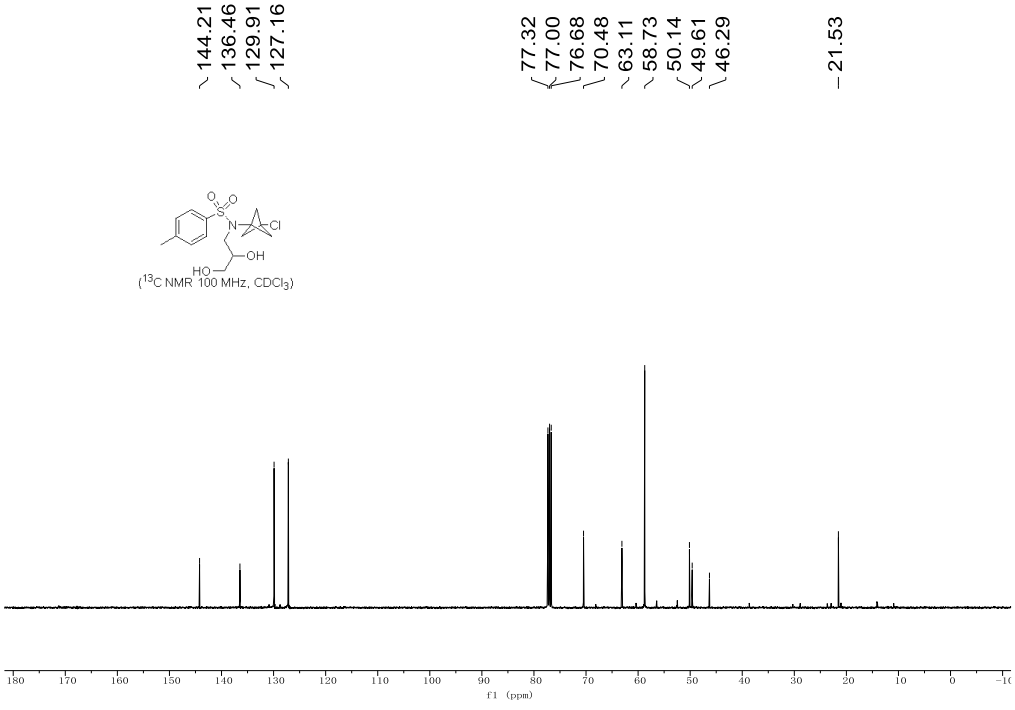
***N*-(3-bromobicyclo[1.1.1]pentan-1-yl)-*N*-ethyl-4-methylbenzenesulfonamide (5h)**



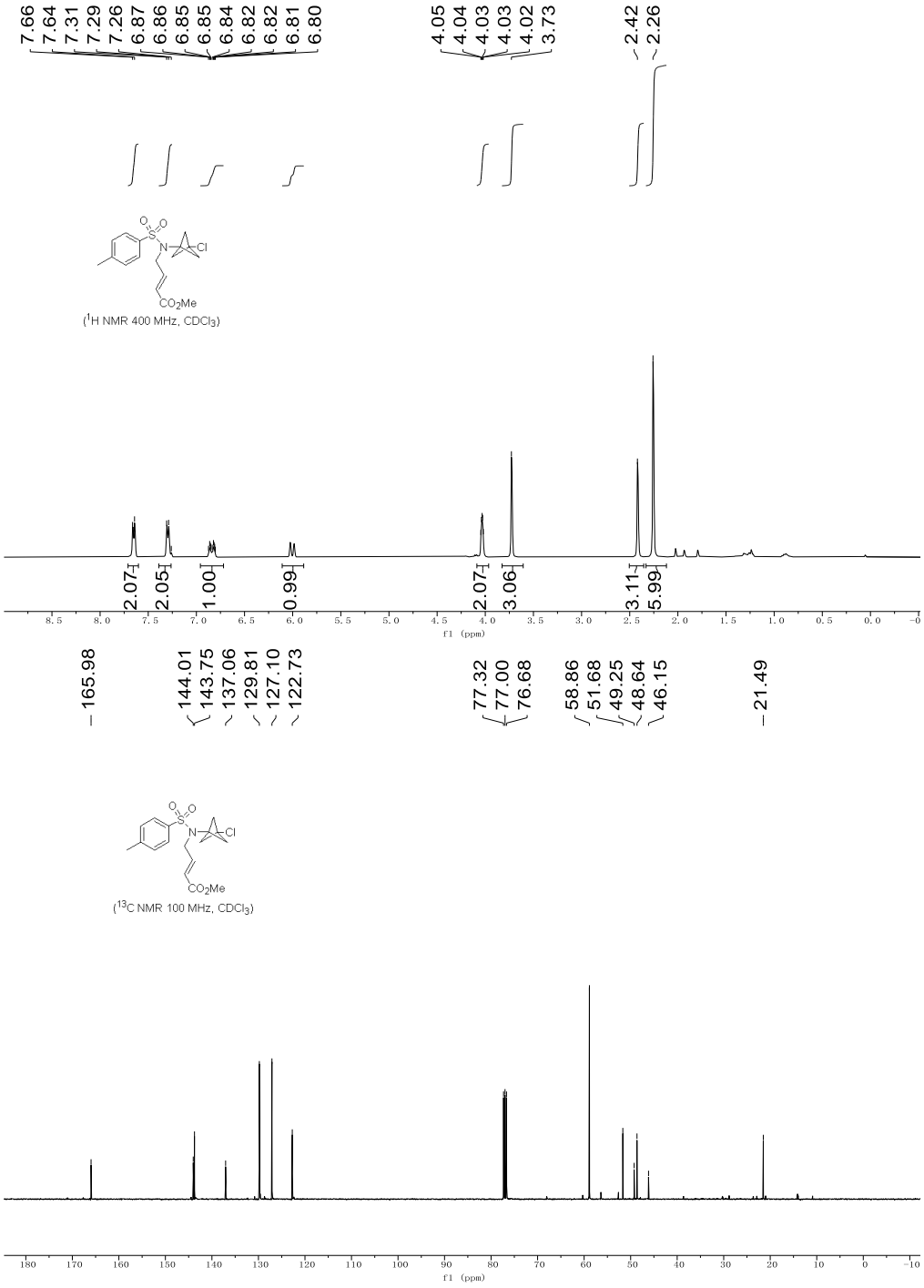


_N_-(3-chlorobicyclo[1.1.1]pentan-1-yl)-_N_-(2,3-dihydroxypropyl)-4-methylbenzenesulfonamide (6)

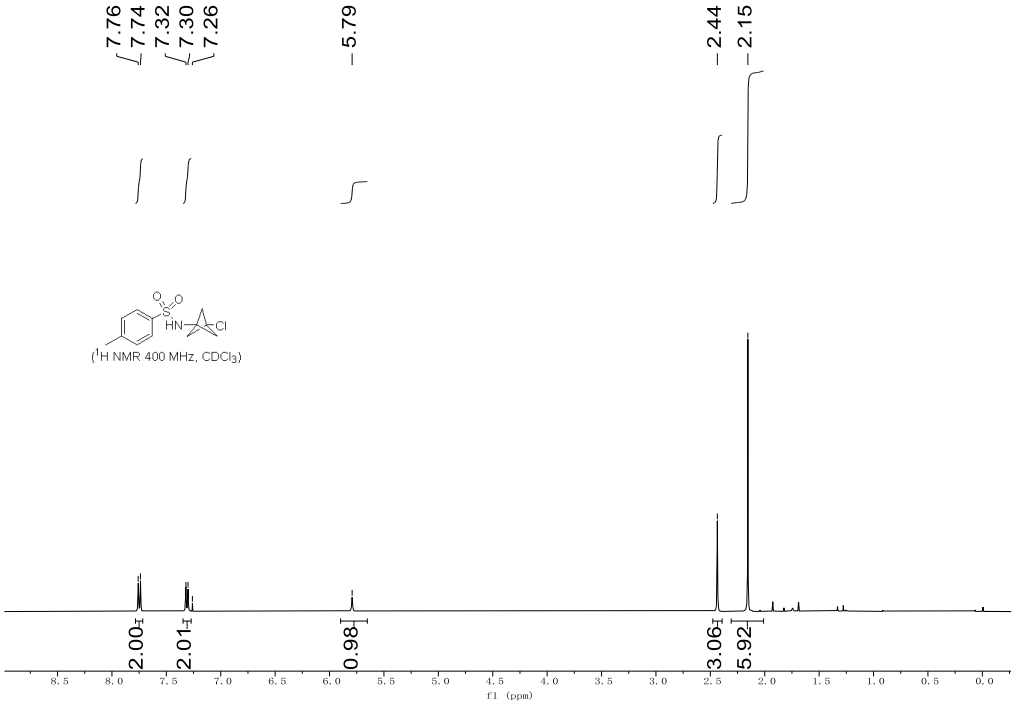


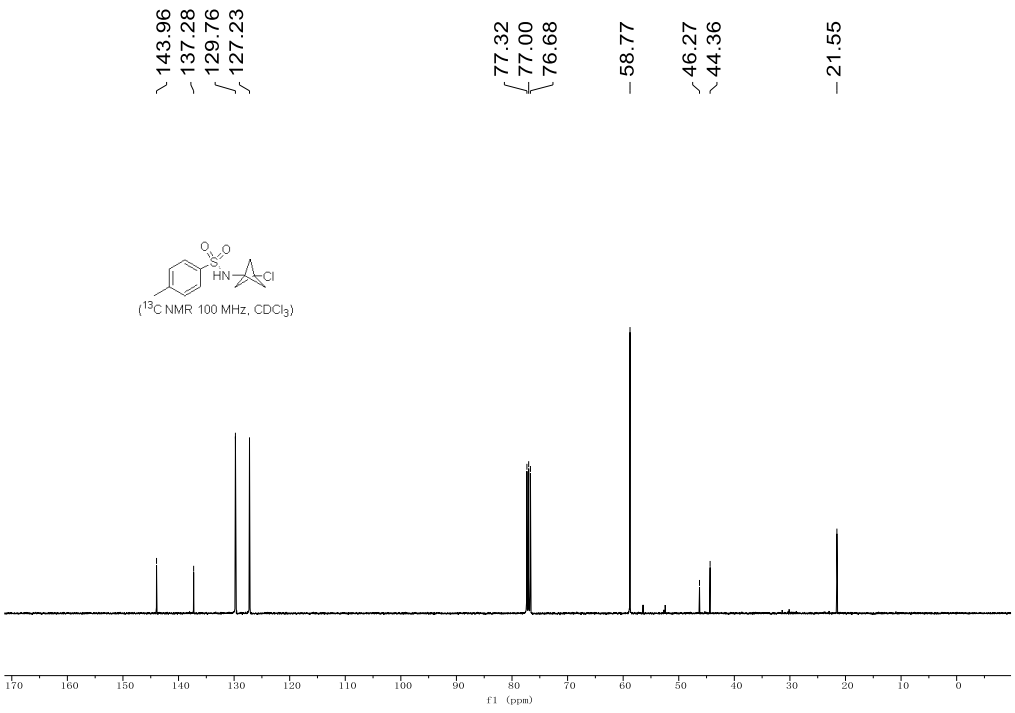


methyl (E)-4-((*N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-4-methylphenyl)sulfonamido)but-2-enoate (7)

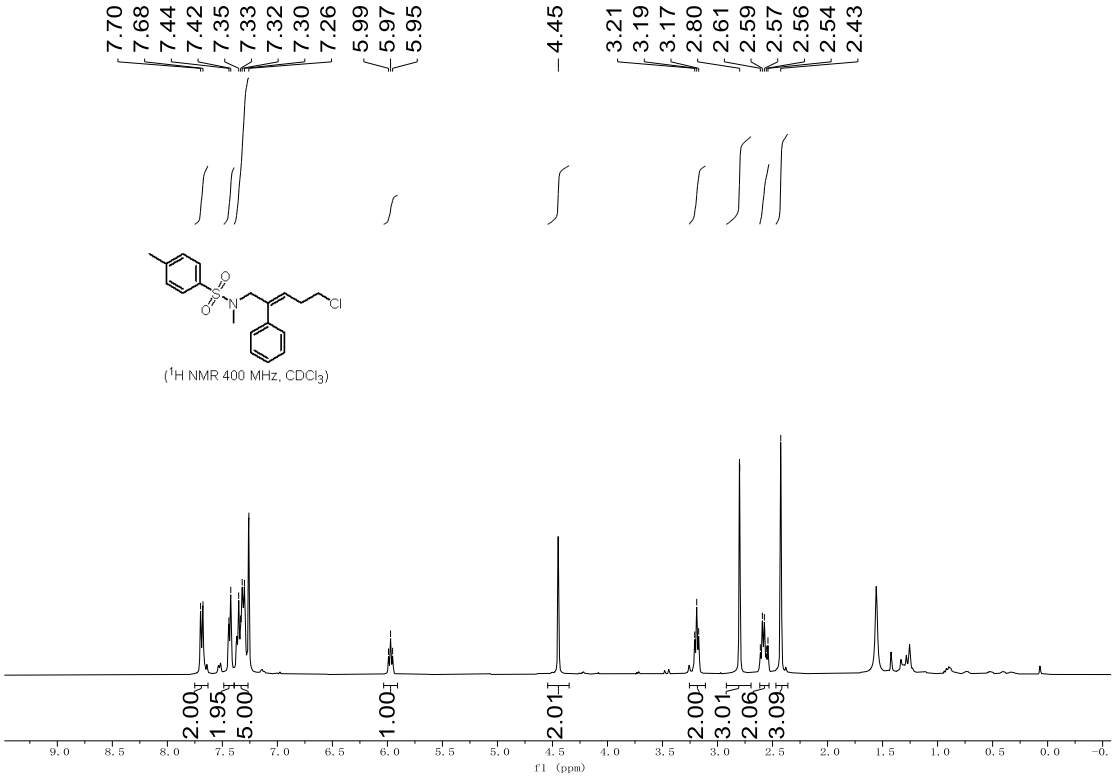


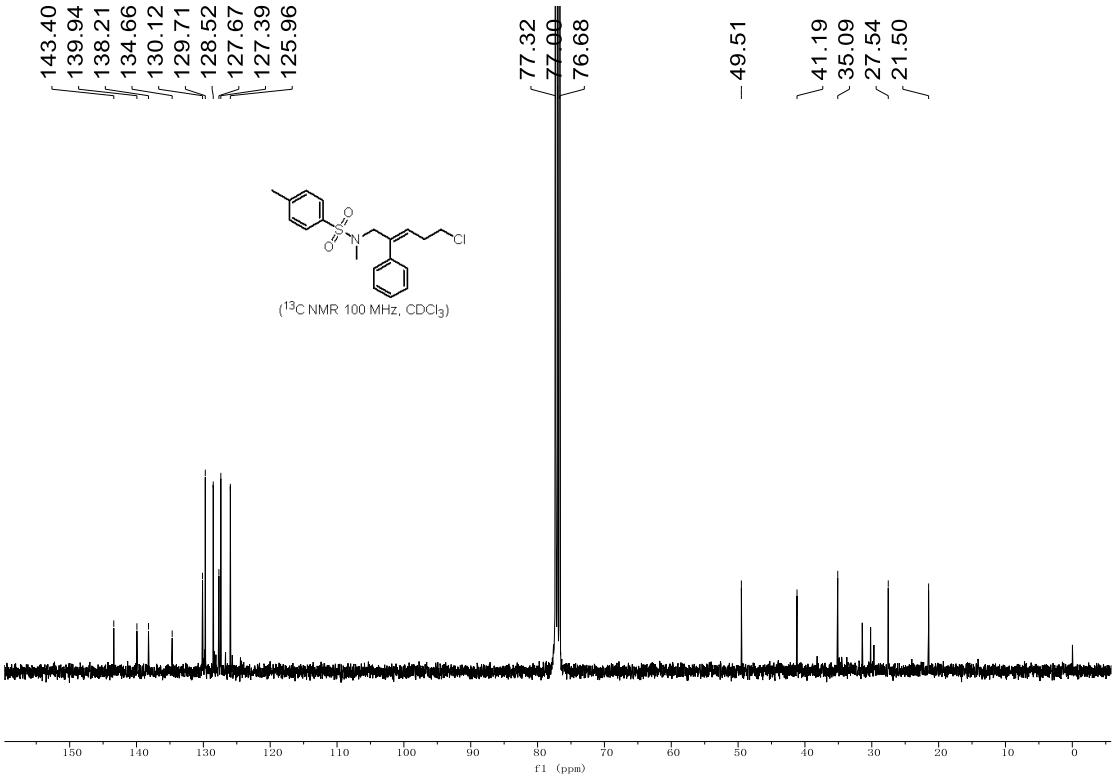
***N*-(3-chlorobicyclo[1.1.1]pentan-1-yl)-4-methylbenzenesulfonamide (8)**





(E)-*N*-(5-chloro-2-phenylpent-2-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (11)





(Z)-*N*-(5-bromo-2-phenylpent-1-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (12)