

## Supporting information

### Palladium-Catalyzed Cascade $sp^2$ C-H Bond Functionalizations Allowing the One Pot Access to 4-Aryl-1,2,3,4-tetrahydroquinolines from *N*-Allyl-*N*-arylsulfonamides

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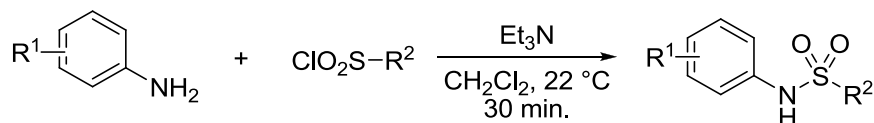
Page S29 Crystallographic Data Tables

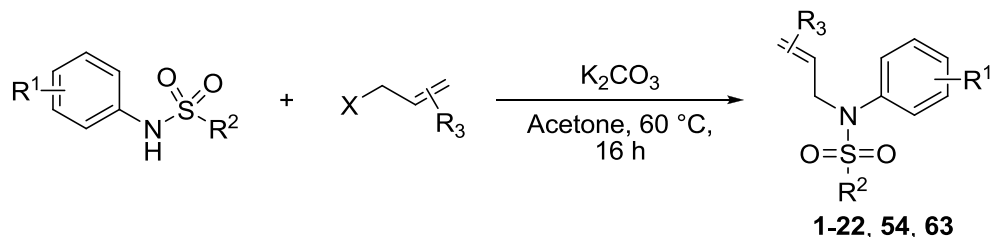
Page S31  $^1\text{H}$  and  $^{13}\text{C}$  NMR charts of new compounds

#### General remarks

All the reactions were carried out under an argon atmosphere with standard Schlenk techniques. HPLC grade solvents 1,4-dioxane, DMF, xylene,  $\text{CH}_2\text{Cl}_2$  were purchased from Acros, and used as received.  $^1\text{H}$  NMR spectra were recorded on Bruker GPX 400 MHz spectrometer. Chemical shifts ( $\delta$ ) were reported in parts per million relative to residual chloroform (7.26 ppm for  $^1\text{H}$ ; 77.0 ppm for  $^{13}\text{C}$ ), Coupling constants were reported in Hertz.  $^1\text{H}$  NMR assignment abbreviations were the following: singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m).  $^{13}\text{C}$  NMR spectra were recorded at 100 MHz on the same spectrometer and reported in ppm. All reagents were weighed and handled in air.

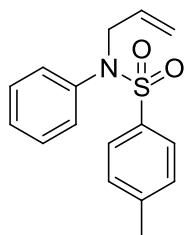
#### General procedure for the synthesis of *N*-allyl-*N*-phenylmethanesulfonamides 1-22, 54, 63:





A mixture of the aniline derivative (5 mmol) and triethylamine (0.505 g, 5 mmol) was stirred in  $\text{CH}_2\text{Cl}_2$  (15 mL) at 22 °C, then,  $\text{R}^2\text{SO}_2\text{Cl}$  (5 mmol) was slowly added to the mixture and the reaction was monitored by TLC. When a complete conversion of the starting material was observed, the mixture was concentrated then filtrated through a short silica column and evaporated to afford the desired aryl sulfamide. A mixture of this aryl sulfamide, allyl bromide derivative (7.5 mmol) and  $\text{K}_2\text{CO}_3$  (1.725 g, 12.5 mmol) in acetone (30 mL) was refluxed overnight. After reaction cooling down, the mixture was concentrated and purified by silica gel chromatography (ethyl acetate/pentane) to afford the desired products **1-22**, **54** and **63**.

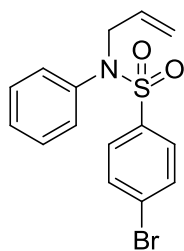
#### *N*-Allyl-4-methyl-*N*-phenylbenzenesulfonamide (**1**)<sup>1</sup>



From aniline (0.465 g, 5 mmol), 4-methylbenzene-1-sulfonyl chloride (0.950 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **1** was obtained in 93% (1.334 g) yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.48 (d,  $J$  = 8.2 Hz, 2H), 7.32-7.23 (m, 5H), 7.03 (d,  $J$  = 8.2 Hz, 2H), 5.73 (ddt,  $J$  = 16.5, 10.2, 6.3 Hz, 1H), 5.07 (d,  $J$  = 16.5 Hz, 1H), 5.03 (d,  $J$  = 10.2 Hz, 1H), 4.17 (d,  $J$  = 6.3 Hz, 2H), 2.41 (s, 3H).

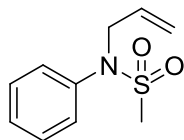
#### *N*-Allyl-4-bromo-*N*-phenylbenzenesulfonamide (**2**)<sup>2</sup>



From aniline (0.465 g, 5 mmol), 4-bromobenzene-1-sulfonyl chloride (1.275 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **2** was obtained in 87% (1.531 g) yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59 (d,  $J$  = 6.9 Hz, 2H), 7.46 (d,  $J$  = 6.9 Hz, 2H), 7.35-7.25 (m, 3H), 7.03 (d,  $J$  = 8.2 Hz, 2H), 5.73 (ddt,  $J$  = 16.5, 10.2, 6.3 Hz, 1H), 5.09 (d,  $J$  = 16.5 Hz, 1H), 5.06 (d,  $J$  = 10.2 Hz, 1H), 4.18 (d,  $J$  = 6.3 Hz, 2H).

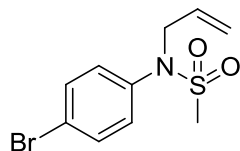
### *N*-Allyl-4-methyl-*N*-methylbenzenesulfonamide (**3**)<sup>3</sup>



From aniline (0.465 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **3** was obtained in 88% (0.928 g) yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.45-7.30 (m, 3H), 7.03 (d, *J* = 8.2 Hz, 2H), 5.84 (ddt, *J* = 16.5, 10.2, 6.3 Hz, 1H), 5.19 (d, *J* = 16.5 Hz, 1H), 5.14 (d, *J* = 10.2 Hz, 1H), 4.31 (d, *J* = 6.3 Hz, 2H), 2.92 (s, 3H).

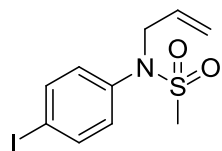
### *N*-Allyl-*N*-(4-bromophenyl)methanesulfonamide (**4**)<sup>4</sup>



From 4-bromoaniline (0.860 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **4** was obtained in 71% (1.030 g) yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 5.83 (ddt, *J* = 16.5, 10.2, 6.3 Hz, 1H), 5.23 (d, *J* = 16.5 Hz, 1H), 5.20 (d, *J* = 10.2 Hz, 1H), 4.31 (d, *J* = 6.3 Hz, 2H), 2.95 (s, 3H).

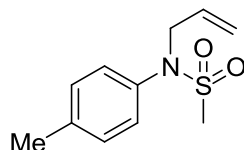
### *N*-Allyl-*N*-(4-iodophenyl)methanesulfonamide (**5**)<sup>5</sup>



From 4-iodoaniline (1.095 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **5** was obtained in 76% (1.280 g) yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.72 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 5.79 (ddt, *J* = 16.5, 10.2, 6.3 Hz, 1H), 5.17 (d, *J* = 16.5 Hz, 1H), 5.14 (d, *J* = 10.2 Hz, 1H), 4.25 (d, *J* = 6.3 Hz, 2H), 2.89 (s, 3H).

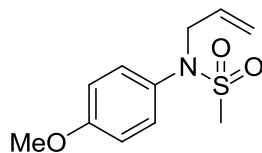
### *N*-Allyl-*N*-(4-methylphenyl)methanesulfonamide (**6**)<sup>6</sup>



From 4-methylaniline (0.535 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **6** was obtained in 81% (0.911 g) yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.28 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 5.89 (ddt, *J* = 16.5, 10.2, 6.3 Hz, 1H), 5.23 (d, *J* = 16.5 Hz, 1H), 5.19 (d, *J* = 10.2 Hz, 1H), 4.33 (d, *J* = 6.3 Hz, 2H), 2.96 (s, 3H), 2.41 (s, 3H).

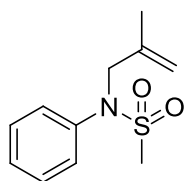
### ***N*-Allyl-*N*-(4-methoxyphenyl)methanesulfonamide (**7**)<sup>7</sup>**



From 4-methoxyaniline (0.615 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **7** was obtained in 93% (1.120 g) yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.25 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 5.83 (ddt, *J* = 16.5, 10.2, 6.3 Hz, 1H), 5.16 (d, *J* = 16.5 Hz, 1H), 5.12 (d, *J* = 10.2 Hz, 1H), 4.23 (d, *J* = 6.3 Hz, 2H), 3.79 (s, 3H), 2.90 (s, 3H).

### ***N*-(2-Methylallyl)-*N*-phenylmethanesulfonamide (**8**)**

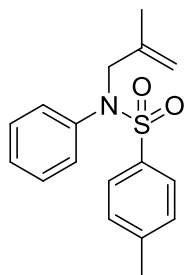


From aniline (0.465 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and 2-methylallyl chloride (0.675 g, 7.5 mmol), **8** was obtained in 85% (0.956 g) yield brown solid: mp 90-92 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.42-7.25 (m, 5H), 4.81 (s, 2H), 4.25 (s, 2H), 2.90 (s, 3H), 1.76 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 139.8, 139.0, 129.2, 128.1, 127.8, 115.0, 56.7, 37.2, 19.8.

### **4-Methyl-*N*-(2-methylallyl)-*N*-phenylbenzenesulfonamide (**9**)<sup>8</sup>**

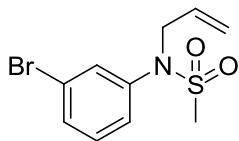


From aniline (0.465 g, 5 mmol), 4-methylbenzene-1-sulfonyl chloride (0.950 g, 5 mmol) and 2-methylallyl chloride (0.675 g, 7.5 mmol), **9** was obtained in 91% (1.369 g) yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.30-7.22 (m, 5H), 7.03 (dd, *J* = 8.2, 1.8 Hz, 2H), 4.75 (s, 1H), 4.72 (s, 1H), 4.11 (s, 2H), 2.42 (s, 3H), 1.75 (s, 3H).

### ***N*-Allyl-*N*-(3-bromophenyl)methanesulfonamide (**10**)**



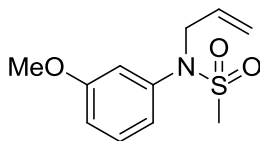


From 3-bromoaniline (0.860 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **10** was obtained in 57% (0.826 g) yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.750-7.20 (m, 4H), 5.80 (ddt,  $J = 16.5, 10.2, 6.3$  Hz, 1H), 5.20 (d,  $J = 16.5$  Hz, 1H), 5.17 (d,  $J = 10.2$  Hz, 1H), 4.27 (d,  $J = 6.3$  Hz, 2H), 2.93 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.6, 132.4, 131.2, 131.1, 130.5, 127.1, 122.5, 119.6, 53.6, 38.3.

#### ***N*-Allyl-*N*-(3-methoxyphenyl)methanesulfonamide (11)**

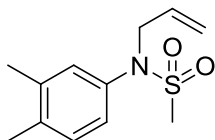


From 3-methoxyaniline (0.615 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **11** was obtained in 81% (0.976 g) yield as a brown oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.28 (t,  $J = 8.0$  Hz, 1H), 6.92-6.82 (m, 3H), 5.81 (ddt,  $J = 16.5, 10.2, 6.3$  Hz, 1H), 5.18 (d,  $J = 16.5$  Hz, 1H), 5.13 (d,  $J = 10.2$  Hz, 1H), 4.26 (d,  $J = 6.3$  Hz, 2H), 3.79 (s, 3H), 2.90 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.1, 140.4, 132.8, 129.8, 120.0, 118.9, 114.5, 113.3, 55.3, 53.5, 37.9.

#### ***N*-Allyl-*N*-(3,4-dimethylphenyl)methanesulfonamide (12)**

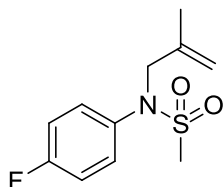


From 3,4-dimethylaniline (0.605 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **12** was obtained in 85% (1.015 g) yield as a brown oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.15-7.08 (m, 2H), 7.05 (dd,  $J = 8.2, 2.1$  Hz, 1H), 5.81 (ddt,  $J = 16.5, 10.2, 6.3$  Hz, 1H), 5.18 (d,  $J = 16.5$  Hz, 1H), 5.12 (d,  $J = 10.2$  Hz, 1H), 4.25 (d,  $J = 6.3$  Hz, 2H), 2.90 (s, 3H), 2.25 (s, 3H), 2.24 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  137.7, 136.7, 136.6, 133.0, 130.2, 129.6, 125.5, 118.6, 53.6, 37.8, 19.7, 19.2.

#### ***N*-(4-Fluorophenyl)-*N*-(2-methylallyl)methanesulfonamide (13)**

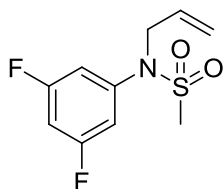


From 4-fluoroaniline (0.555 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and 2-methylallyl chloride (0.675 g, 7.5 mmol), **13** was obtained in 83% (1.008 g) yield as a yellow solid: mp 64-68 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.30 (dd,  $J = 8.5, 4.8$  Hz, 2H), 7.04 (t,  $J = 8.5$  Hz, 2H), 4.80 (s, 1H), 4.77 (s, 1H), 4.19 (s, 2H), 2.88 (s, 3H), 1.73 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.7 (d,  $J = 248.1$  Hz), 139.5, 134.7, 130.0 (d,  $J = 8.7$  Hz), 116.1 (d,  $J = 22.7$  Hz), 115.3, 56.9, 37.0, 19.6.

#### *N*-Allyl-*N*-(3,5-difluorophenyl)methanesulfonamide (**14**)

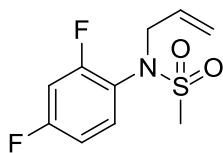


From 3,5-difluoroaniline (0.645 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **14** was obtained in 82% (1.013 g) yield as a pale yellow solid: mp 65-67 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.95-6.87 (m, 2H), 6.76 (tt,  $J = 8.7, 2.2$  Hz, 1H), 5.81 (ddt,  $J = 16.5, 10.2, 6.3$  Hz, 1H), 5.22 (d,  $J = 16.5$  Hz, 1H), 5.20 (d,  $J = 10.2$  Hz, 1H), 4.29 (d,  $J = 6.3$  Hz, 2H), 2.94 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.6 (dd,  $J = 249.5, 14.4$  Hz), 141.7 (t,  $J = 12.1$  Hz), 132.1, 119.7, 110.7 (d,  $J = 19.4$  Hz), 103.2 (t,  $J = 25.4$  Hz), 53.2, 38.4.

#### *N*-Allyl-*N*-(2,4-difluorophenyl)methanesulfonamide (**15**)

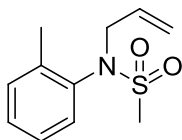


From 2,4-difluoroaniline (0.645 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **15** was obtained in 85% (1.049 g) yield as a yellow solid: mp 46-50 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35-7.29 (m, 1H), 6.90-6.82 (m, 2H), 5.77 (ddt,  $J = 16.5, 10.2, 6.3$  Hz, 1H), 5.12 (d,  $J = 16.5$  Hz, 1H), 5.07 (d,  $J = 10.2$  Hz, 1H), 4.17 (d,  $J = 6.3$  Hz, 2H), 2.94 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.3 (dd,  $J = 251.5, 11.7$  Hz), 159.5 (dd,  $J = 252.3, 12.7$  Hz), 134.1 (dd,  $J = 10.1, 2.3$  Hz), 132.3, 122.3 (dd,  $J = 12.2, 4.1$  Hz), 119.3, 111.8 (dd,  $J = 22.2, 3.7$  Hz), 104.6 (dd,  $J = 26.4, 24.4$  Hz), 53.2 (d,  $J = 2.6$  Hz), 38.9 (d,  $J = 3.4$  Hz).

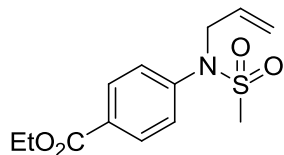
#### *N*-Allyl-*N*-(2-methylphenyl)methanesulfonamide (**16**)<sup>9</sup>



From 2-methylaniline (0.535 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **16** was obtained in 78% (0.877 g) yield as a yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.30-7.18 (m, 4H), 5.85 (ddt,  $J = 16.5, 10.2, 6.3$  Hz, 1H), 5.12 (d,  $J = 16.5$  Hz, 1H), 5.10 (d,  $J = 10.2$  Hz, 1H), 4.17 (d,  $J = 6.3$  Hz, 2H), 2.87 (s, 3H), 2.39 (s, 3H).

#### Ethyl 4-(*N*-allylmethylsulfonamido)benzoate (**17**)

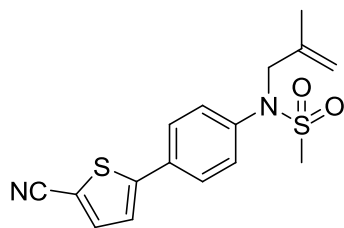


From ethyl 4-aminobenzoate (0.825 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **17** was obtained in 79% (1.117 g) yield as a brown oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.04 (d,  $J = 8.2$  Hz, 2H), 7.40 (d,  $J = 8.2$  Hz, 2H), 5.80 (ddt,  $J = 16.5, 10.2, 6.3$  Hz, 1H), 5.18 (d,  $J = 16.5$  Hz, 1H), 5.14 (d,  $J = 10.2$  Hz, 1H), 4.40-4.30 (m, 4H), 2.92 (s, 3H), 1.37 (t,  $J = 6.7$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.6, 143.4, 132.4, 130.6, 129.3, 127.0, 119.3, 61.1, 53.1, 38.3, 14.2.

#### *N*-(4-(5-Cyanothiophen-2-yl)phenyl)-*N*-(2-methylallyl)methanesulfonamide (**18**)

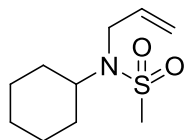


From 5-(4-aminophenyl)thiophene-2-carbonitrile (1.000 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and 2-methylallyl chloride (0.675 g, 7.5 mmol), **18** was obtained in 67% (1.112 g) yield as a yellow solid: mp 128-130 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59 (d,  $J = 8.6$  Hz, 2H), 7.58 (d,  $J = 4.4$  Hz, 1H), 7.40 (d,  $J = 8.6$  Hz, 2H), 7.25 (d,  $J = 4.4$  Hz, 1H), 4.85 (s, 2H), 4.29 (s, 2H), 2.93 (s, 3H), 1.76 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.3, 139.9, 139.5, 138.4, 131.5, 128.4, 127.2, 123.8, 115.4, 114.1, 108.8, 56.4, 37.5, 19.8.

#### *N*-Allyl-*N*-cyclohexylmethanesulfonamide (**19**)

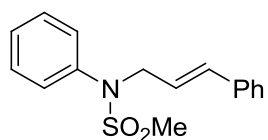


From cyclohexanamine (0.495 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **19** was obtained in 84% (0.911 g) yield as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.81 (ddt,  $J = 16.5, 10.2, 6.1$  Hz, 1H), 5.23 (d,  $J = 16.5$  Hz, 1H), 5.12 (d,  $J = 10.2$  Hz, 1H), 3.79 (d,  $J = 6.1$  Hz, 2H), 3.62-3.56 (m, 1H), 2.82 (s, 3H), 1.80-0.97 (m, 10H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  135.7, 117.4, 57.8, 45.9, 40.9, 32.0, 25.9, 25.1.

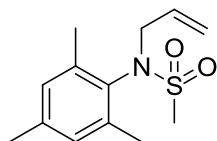
### *N*-cinnamyl-*N*-phenylmethanesulfonamide (**20**)<sup>10</sup>



From aniline (0.465 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and cinnamyl bromide (1.477 g, 7.5 mmol), **20** was obtained in 80% (1.148 g) yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.45-7.20 (m, 10H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.20 (dt, *J* = 15.8, 6.7 Hz, 1H), 4.45 (d, *J* = 6.7 Hz, 2H), 2.95 (s, 3H).

### *N*-Allyl-*N*-mesitylmethanesulfonamide (**21**)

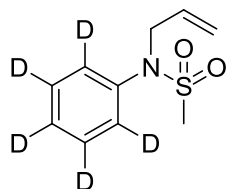


From 2,4,6-trimethylaniline (0.675 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **21** was obtained in 73% (0.923 g) yield as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.91 (s, 2H), 5.91 (ddt, *J* = 16.5, 10.2, 6.1 Hz, 1H), 5.16 (d, *J* = 16.5 Hz, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 4.12 (d, *J* = 6.1 Hz, 2H), 3.06 (s, 3H), 2.34 (s, 6H), 2.27 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 138.1, 137.9, 134.8, 132.7, 129.6, 119.4, 53.8, 41.3, 20.8, 19.2.

### *N*-Allyl-4-methyl-*N*-methylbenzenesulfonamide *d*<sub>4</sub> (**22**)

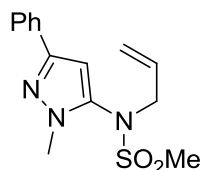


From aniline-2,3,4,5,6-*d*<sub>5</sub> (0.490 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **22** was obtained in 85% (0.918 g) yield as a white solid: mp 55-57 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.84 (ddt, *J* = 16.5, 10.2, 6.3 Hz, 1H), 5.19 (d, *J* = 16.5 Hz, 1H), 5.14 (d, *J* = 10.2 Hz, 1H), 4.31 (d, *J* = 6.3 Hz, 2H), 2.92 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 132.9, 119.0, 53.7, 38.1.

### *N*-Allyl-*N*-(1-methyl-3-phenylpyrazol-5-yl)methanesulfonamide (**54**)

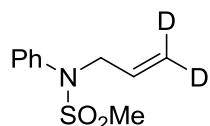


From 1-methyl-3-phenylpyrazol-5-amine (0.865 g, 5 mmol), methanesulfonyl chloride (0.570 g, 5 mmol) and allyl bromide (0.907 g, 7.5 mmol), **54** was obtained in 78% (1.135 g) yield as a yellow solid: mp 137-139 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.76 (d,  $J = 7.4$  Hz, 2H), 7.40 (t,  $J = 8.0$  Hz, 2H), 7.29 (t,  $J = 8.0$  Hz, 1H), 6.47 (s, 1H), 5.87 (ddt,  $J = 16.5, 10.2, 6.3$  Hz, 1H), 5.27-5.20 (m, 2H), 4.17 (d,  $J = 6.3$  Hz, 2H), 3.88 (s, 3H), 3.02 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.0, 138.1, 132.9, 131.2, 128.6, 127.9, 125.2, 121.2, 99.3, 54.9, 37.5, 36.0.

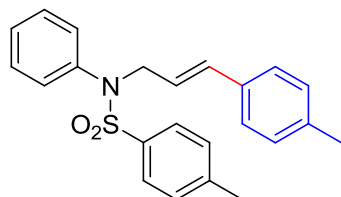
#### *N*-Allyl-4-methyl-*N*-methylbenzenesulfonamide $d_2$ (**63**)



From aniline (0.233 g, 2.5 mmol), methanesulfonyl chloride (0.285g, 2.5 mmol) and allyl-3,3-d2 methanesulfonate previously synthesized as described in a literature report<sup>12</sup> (0.518 g, 3.75 mmol), **63** was obtained in 85% (0.452 g) yield as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45-7.20 (m, 5H), 5.83-5.79 (m, 1H), 4.31-4.25 (m, 2H), 2.90 (s, 3H).

#### (*E*)-4-Methyl-*N*-phenyl-*N*-(3-*p*-tolylallyl)benzenesulfonamide (**23**)



To an oven dried 25 mL Schlenk tube under argon, *N*-allyl-*N*-phenyl-*p*-tolylsulfonamide (0.072 g, 0.25 mmol), 4-bromotoluene (0.064 g, 0.38 mmol), Pd(allyl)(dppb)Cl (3.8 mg, 0.006 mmol),  $\text{K}_2\text{CO}_3$  (0.103 g, 0.75 mmol), DMF (1.5 mL) were successively added. Then, the Schlenk tube was settled in a preheated oil bath at 140 °C for twenty hours. Upon the reaction finished, the solvent was evaporated and the crude mixture was purified by column chromatography (ethyl ether/pentane around 1/9) to afford **23** in 77% yield (0.073 g) as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.52 (d,  $J = 8.2$  Hz, 2H), 7.30-7.03 (m, 11H), 6.33 (d,  $J = 15.8$  Hz, 1H), 6.04 (dd,  $J = 15.8, 6.7$  Hz, 1H), 4.32 (d,  $J = 6.7$  Hz, 2H), 2.43 (s, 3H), 2.30 (s, 3H).

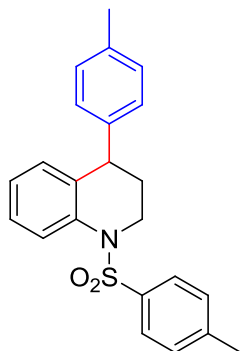
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.4, 139.2, 137.7, 135.8, 133.7, 133.6, 129.4, 129.2, 129.0, 128.9, 127.8, 127.7, 126.3, 123.0, 53.4, 21.5, 21.1.

Elemental analysis: calcd (%) for  $\text{C}_{23}\text{H}_{23}\text{NO}_2\text{S}$  (377.50): C 73.18, H 6.14; found: C 72.99, H 6.20.

#### General procedure for the synthesis of **24-53**, **55-62** and **64**:

To an oven dried 25 mL Schlenk tube under argon, *N*-allyl-*N*-phenylsulfonamides (0.5 mmol), arenesulfonyl chlorides (1.0 mmol),  $\text{PdCl}_2$  (4.4 mg, 0.0025 mmol), CuBr (0.035 g, 0.25 mmol),  $\text{Li}_2\text{CO}_3$  (0.110 g, 1.5 mmol) and 1,4-dioxane (1.5 mL) were successively added. Then, the reaction mixture was settled in a preheated (140 °C) oil bath for 20 h under stirring. Upon the reaction finished, the crude mixture was purified on silica chromatography (ethyl ether/ pentane, ethyl acetate/ pentane).

#### 4-*p*-Tolyl-1-tosyl-1,2,3,4-tetrahydroquinoline (24)



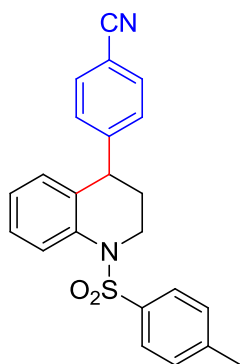
From *N*-allyl-*N*-*p*-tolylbenzenesulfonamide **1** (0.144 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **24** was obtained in 83% (0.156 g) yield as a white solid: mp 107-109 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.29-7.20 (m, 3H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.55 (d, *J* = 8.3 Hz, 2H), 4.15-4.07 (m, 1H), 3.83 (dd, *J* = 8.5, 7.0 Hz, 1H), 3.80-3.70 (m, 1H), 2.45 (s, 3H), 2.31 (s, 3H), 2.00-1.88 (m, 1H), 1.77-1.65 (m, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 143.6, 142.0, 137.0, 136.8, 136.0, 132.9, 130.3, 129.7, 129.1, 128.1, 127.4, 126.8, 125.0, 124.6, 45.5, 43.0, 30.3, 21.6, 21.0.

Elemental analysis: calcd (%) for C<sub>23</sub>H<sub>23</sub>NO<sub>2</sub>S (377.50): C 73.18, H 6.14; found: C 73.30, H 6.00.

#### 4-(1-Tosyl-1,2,3,4-tetrahydroquinolin-4-yl)benzotrile (25)



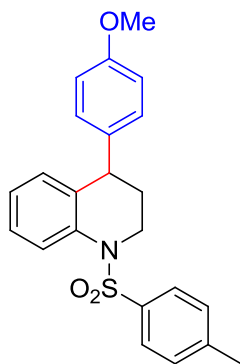
From *N*-allyl-*N*-*p*-tolylbenzenesulfonamide **1** (0.144 g, 0.5 mmol) and 4-cyanobenzene-1-sulfonyl chloride (0.202 g, 1 mmol), **25** was obtained in 72% (0.140 g) yield as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.45-7.40 (m, 4H), 7.37-7.30 (m, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.08-7.03 (m, 2H), 5.03 (dd, *J* = 8.5, 5.6 Hz, 1H), 3.80-3.50 (m, 2H), 2.42 (s, 3H), 2.30-2.10 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 146.0, 143.8, 139.1, 134.5, 132.5, 129.5, 129.3, 128.5, 128.2, 127.8, 127.7, 118.3, 112.3, 58.8, 48.0, 38.8, 21.5.

Elemental analysis: calcd (%) for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S (388.48): C 71.11, H 5.16; found: C 71.29, H 5.04.

#### 4-(4-Methoxyphenyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (26)



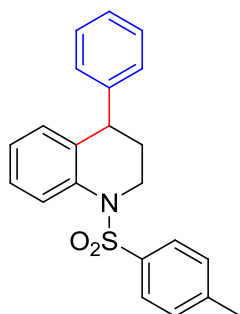
From *N*-allyl-*N*-*p*-tolylbenzenesulfonamide **1** (0.144 g, 0.5 mmol) and 4-methoxybenzene-1-sulfonyl chloride (0.207 g, 1 mmol), **26** was obtained in 95% (0.186 g) yield as a white solid: mp 127-130 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.32-7.21 (m, 3H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.60 (d, *J* = 8.6 Hz, 2H), 4.25-3.70 (m, 6H), 2.48 (s, 3H), 2.15-1.65 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 158.1, 143.6, 137.1, 137.0, 136.8, 133.0, 130.2, 129.7, 129.2, 127.4, 126.9, 125.0, 124.6, 113.8, 55.2, 45.4, 42.5, 30.4, 21.5.

Elemental analysis: calcd (%) for C<sub>23</sub>H<sub>23</sub>NO<sub>3</sub>S (393.50): C 70.20, H 5.89; found: C 70.38, H 6.05.

#### 4-Phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (27)



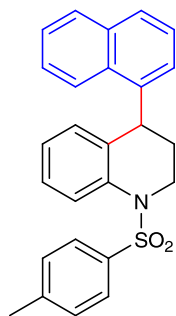
From *N*-allyl-*N*-*p*-tolylbenzenesulfonamide **1** (0.144 g, 0.5 mmol) and benzenesulfonyl chloride (0.177 g, 1 mmol), **27** was obtained in 75% (0.136 g) yield as a white solid: mp 145-148 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.30-7.10 (m, 6H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.70-6.60 (m, 2H), 4.25-4.00 (m, 1H), 3.88 (dd, *J* = 8.5, 7.0 Hz, 1H), 3.80-3.70 (m, 1H), 2.45 (s, 3H), 2.03-1.70 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 145.0, 143.7, 137.1, 136.8, 132.6, 130.3, 129.7, 128.4, 128.2, 127.4, 126.9, 126.5, 125.1, 124.7, 45.4, 43.4, 30.3, 21.5.

Elemental analysis: calcd (%) for C<sub>22</sub>H<sub>21</sub>NO<sub>2</sub>S (363.47): C 72.70, H 5.82; found: C 72.49, H 6.08.

#### 4-(Naphthalen-1-yl)-1-tosyl-1,2,3,4-tetrahydroquinoline (28)



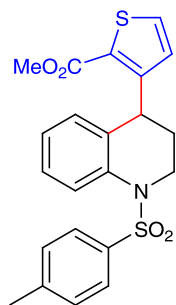
From *N*-allyl-*N*-*p*-tolylbenzenesulfonamide **1** (0.144 g, 0.5 mmol) and naphthalene-1-sulfonyl chloride (0.227 g, 1 mmol), **28** was obtained in 71% (0.146 g) yield as a white solid: mp 138-140 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.55-7.45 (m, 2H), 7.34-7.29 (m, 3H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.55 (d, *J* = 7.1 Hz, 1H), 4.61 (t, *J* = 7.7 Hz, 1H), 3.98 (t, *J* = 7.6 Hz, 2H), 2.49 (s, 3H), 2.25-1.80 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 143.7, 140.5, 137.3, 136.6, 133.8, 133.1, 131.3, 130.0, 129.7, 129.1, 127.4, 127.2, 127.1, 126.2, 126.1, 125.6, 125.3, 125.0, 124.5, 122.9, 45.1, 38.9, 29.2, 21.6.

Elemental analysis: calcd (%) for C<sub>26</sub>H<sub>23</sub>NO<sub>2</sub>S (413.53): C 75.52, H 5.61; found: C 78.41, H 5.39.

#### Methyl 3-(1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl)thiophene-2-carboxylate (**29**)



From *N*-allyl-*N*-*p*-tolylbenzenesulfonamide **1** (0.144 g, 0.5 mmol) and methyl 3-(chlorosulfonyl)thiophene-2-carboxylate (0.241 g, 1 mmol), **29** was obtained in 69% (0.147 g) yield as a light yellow solid: mp 108-110 °C.

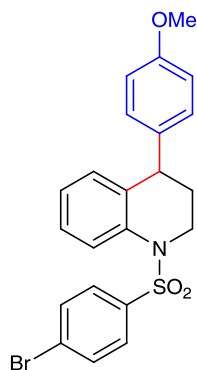
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.21-7.17 (m, 1H), 7.16 (d, *J* = 5.2 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 5.86 (d, *J* = 5.2 Hz, 1H), 5.09 (t, *J* = 7.7 Hz, 1H), 4.20-4.05 (m, 1H), 3.85 (s, 3H), 3.77-3.67 (m, 1H), 2.45 (s, 3H), 2.05-1.50 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.7, 153.4, 143.7, 136.9, 136.8, 131.7, 130.2, 130.1, 129.7, 129.4, 127.4, 127.0, 126.9, 125.1, 124.6, 51.9, 45.6, 36.6, 28.4, 21.5.

Elemental analysis: calcd (%) for C<sub>22</sub>H<sub>21</sub>NO<sub>4</sub>S<sub>2</sub> (427.54): C 61.80, H 4.95; found: C 61.60, H 4.92.

#### (4-Bromophenylsulfonyl)-4-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (**30**)





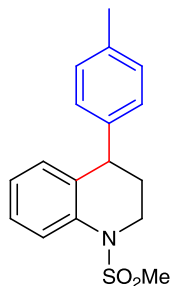
From *N*-allyl-4-bromo-*N*-phenylbenzenesulfonamide **2** (0.176 g, 0.5 mmol) and 4-methoxybenzene-1-sulfonyl chloride (0.207 g, 1 mmol), **30** was obtained in 67% (0.153 g) yield as a white solid: mp 136-138 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93 (d,  $J = 8.2$  Hz, 1H), 7.57 (d,  $J = 8.2$  Hz, 2H), 7.49 (d,  $J = 8.2$  Hz, 2H), 7.22 (t,  $J = 7.6$  Hz, 1H), 7.03 (t,  $J = 7.6$  Hz, 1H), 6.79 (d,  $J = 7.7$  Hz, 1H), 6.72 (d,  $J = 8.6$  Hz, 2H), 6.49 (d,  $J = 8.6$  Hz, 2H), 4.10-4.02 (m, 1H), 3.83 (t,  $J = 7.7$  Hz, 1H), 3.77 (s, 3H), 3.76-3.65 (m, 1H), 2.00-1.80 (m, 1H), 1.75-1.60 (m, 1H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.2, 138.5, 136.7, 136.6, 133.1, 132.3, 130.5, 129.0, 128.9, 127.9, 127.0, 125.4, 124.6, 113.9, 55.2, 45.6, 42.4, 30.4.

Elemental analysis: calcd (%) for  $\text{C}_{22}\text{H}_{20}\text{BrNO}_3\text{S}$  (458.37): C 57.65, H 4.40; found: C 57.47, H 4.28.

#### 1-(Methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (**31**)



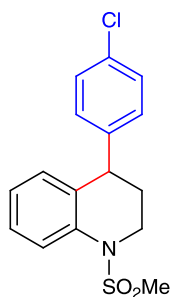
From *N*-allyl-4-methyl-*N*-methylbenzenesulfonamide **3** (0.106 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **31** was obtained in 75% (0.113 g) yield as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.81 (d,  $J = 8.2$  Hz, 1H), 7.22 (t,  $J = 7.8$  Hz, 1H), 7.13 (d,  $J = 8.0$  Hz, 2H), 7.03 (t,  $J = 7.8$  Hz, 1H), 7.02-6.93 (m, 3H), 4.17 (t,  $J = 6.7$  Hz, 1H), 3.88-3.80 (m, 2H), 2.93 (s, 3H), 2.34 (s, 3H), 2.32-2.00 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.8, 137.2, 136.4, 131.3, 130.9, 129.4, 128.2, 127.4, 124.4, 122.0, 44.3, 42.8, 38.6, 31.2, 21.0.

Elemental analysis: calcd (%) for  $\text{C}_{17}\text{H}_{19}\text{NO}_2\text{S}$  (301.40): C 67.74, H 6.35; found: C 67.99, H 6.29.

#### 4-(4-Chlorophenyl)-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinoline (**32**)



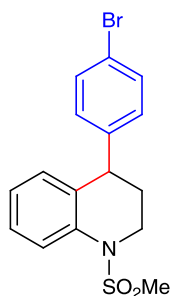
From *N*-allyl-4-methyl-*N*-methylbenzenesulfonamide **3** (0.106 g, 0.5 mmol) and 4-chlorobenzenesulfonyl chloride (0.211 g, 1 mmol), **32** was obtained in 74% (0.119 g) yield as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.81 (d,  $J = 8.2$  Hz, 1H), 7.29 (d,  $J = 8.2$  Hz, 2H), 7.27-7.25 (m, 1H), 7.10-7.07 (m, 1H), 7.06 (d,  $J = 8.2$  Hz, 2H), 6.93 (d,  $J = 7.7$  Hz, 1H), 4.21 (t,  $J = 7.7$  Hz, 1H), 3.88-3.80 (m, 2H), 2.98 (s, 3H), 2.40-2.00 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.4, 137.2, 132.6, 130.8, 130.4, 129.7, 128.8, 127.7, 124.5, 122.0, 44.2, 42.7, 38.9, 31.2.

Elemental analysis: calcd (%) for  $\text{C}_{16}\text{H}_{16}\text{ClNO}_2\text{S}$  (321.82): C 59.71, H 5.01; found: C 59.47, H 4.78.

#### 4-(4-Bromophenyl)-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinoline (**33**)



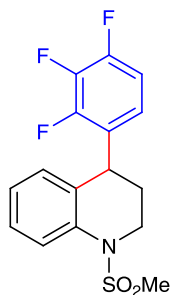
From *N*-allyl-4-methyl-*N*-methylbenzenesulfonamide **3** (0.106 g, 0.5 mmol) and 4-bromobenzenesulfonyl chloride (0.256 g, 1 mmol), **33** was obtained in 75% (0.137 g) yield as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d,  $J = 8.2$  Hz, 1H), 7.43 (d,  $J = 8.2$  Hz, 2H), 7.24 (t,  $J = 7.5$  Hz, 1H), 7.03 (t,  $J = 7.5$  Hz, 1H), 6.96 (d,  $J = 8.2$  Hz, 2H), 6.90 (d,  $J = 7.7$  Hz, 1H), 4.17 (t,  $J = 6.7$  Hz, 1H), 3.91-3.72 (m, 2H), 2.96 (s, 3H), 2.41-2.00 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.9, 137.2, 131.8, 130.8, 130.3, 130.1, 127.7, 124.5, 122.0, 120.6, 44.1, 42.8, 38.9, 31.2.

Elemental analysis: calcd (%) for  $\text{C}_{16}\text{H}_{16}\text{BrNO}_2\text{S}$  (366.27): C 52.47, H 4.40; found: C 52.29, H 4.39.

#### 1-(Methylsulfonyl)-4-(2,3,4-trifluorophenyl)-1,2,3,4-tetrahydroquinoline (**34**)



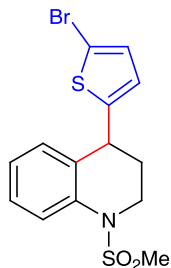
From *N*-allyl-4-methyl-*N*-methylbenzenesulfonamide **3** (0.106 g, 0.5 mmol) and 2,3,4-trifluorobenzoyl chloride (0.231 g, 1 mmol), **34** was obtained in 46% (0.079 g) yield as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (d,  $J = 8.2$  Hz, 1H), 7.27-7.22 (m, 1H), 7.05 (t,  $J = 7.6$  Hz, 1H), 6.95-6.83 (m, 2H), 6.66-6.57 (m, 1H), 4.47 (t,  $J = 7.1$  Hz, 1H), 4.00-3.70 (m, 2H), 3.00 (s, 3H), 2.35-2.05 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.9 (ddd,  $J = 249.9, 9.9, 3.2, 10.1$  Hz), 149.8 (ddd,  $J = 248.5, 10.1, 3.3$  Hz), 140.0 (dt,  $J = 252.2, 15.5$  Hz), 137.5, 130.2, 129.3 (ddd,  $J = 11.1, 3.5, 1.0$  Hz), 128.7, 127.9, 124.7, 123.6 (dt,  $J = 7.7, 5.6$  Hz), 122.3, 112.1 (dd,  $J = 17.2, 3.8$  Hz), 44.3, 39.3, 37.1, 29.4.

Elemental analysis: calcd (%) for  $\text{C}_{16}\text{H}_{14}\text{F}_3\text{NO}_2\text{S}$  (341.35): C 56.30, H 4.13; found: C 56.54, H 4.08.

#### 4-(5-Bromothiophen-2-yl)-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinoline (**35**)



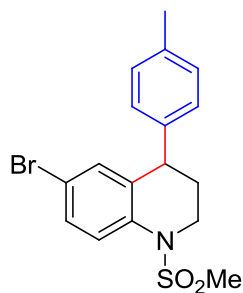
From *N*-allyl-4-methyl-*N*-methylbenzenesulfonamide **3** (0.106 g, 0.5 mmol) and 5-bromothiophene-2-sulfonyl chloride (0.262 g, 1 mmol), **35** was obtained in 78% (0.145 g) yield as a brown oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.81 (d,  $J = 8.2$  Hz, 1H), 7.24 (t,  $J = 7.6$  Hz, 1H), 7.14 (d,  $J = 6.5$  Hz, 1H), 7.08 (t,  $J = 7.6$  Hz, 1H), 6.88 (d,  $J = 3.7$  Hz, 1H), 6.48 (d,  $J = 3.7$  Hz, 1H), 4.38 (t,  $J = 5.6$  Hz, 1H), 4.00-3.80 (m, 1H), 3.80-3.70 (m, 1H), 2.88 (s, 3H), 2.40-2.10 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.0, 136.6, 130.7, 129.6, 129.3, 128.3, 125.9, 124.4, 121.9, 110.9, 43.6, 38.7, 38.3, 31.0.

Elemental analysis: calcd (%) for  $\text{C}_{14}\text{H}_{14}\text{BrNO}_2\text{S}_2$  (372.30): C 45.17, H 3.79; found: C 45.30, H 3.65.

#### 6-Bromo-1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (**36**)



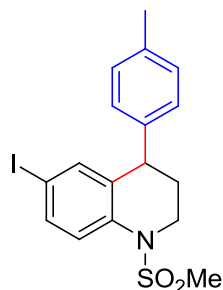
From *N*-allyl-*N*-(4-bromophenyl)methanesulfonamide **4** (0.145 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **36** was obtained in 42% (0.080 g) yield as a white solid: mp 128-130 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.33 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 2.3 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 2H), 4.12 (t, *J* = 6.5 Hz, 1H), 3.86-3.74 (m, 2H), 2.92 (s, 3H), 2.34 (s, 3H), 2.31-2.03 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 140.8, 136.7, 136.3, 133.5, 133.3, 130.5, 129.6, 128.1, 123.8, 117.6, 44.2, 42.8, 38.6, 30.9, 21.0.

Elemental analysis: calcd (%) for C<sub>17</sub>H<sub>18</sub>BrNO<sub>2</sub>S (380.30): C 53.69, H 4.77; found: C 53.47, H 4.59.

#### 6-Iodo-1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (**37**)



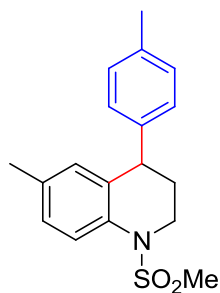
From *N*-allyl-*N*-(4-iodophenyl)methanesulfonamide **5** (0.169 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **37** was obtained in 68% (0.145 g) yield as a yellow solid: mp 106-109 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.58 (d, *J* = 8.2 Hz, 1H), 7.52 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.27 (d, *J* = 2.3 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 4.11 (t, *J* = 6.5 Hz, 1H), 3.86-3.74 (m, 2H), 2.91 (s, 3H), 2.34 (s, 3H), 2.31-2.03 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 140.9, 139.3, 137.1, 136.7, 136.4, 133.6, 129.5, 128.1, 123.8, 88.4, 44.1, 42.5, 38.6, 30.8, 21.0.

Elemental analysis: calcd (%) for C<sub>17</sub>H<sub>18</sub>INO<sub>2</sub>S (427.30): C 47.78, H 4.25; found: C 47.89, H 4.17.

#### 6-Methyl-1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (**38**)



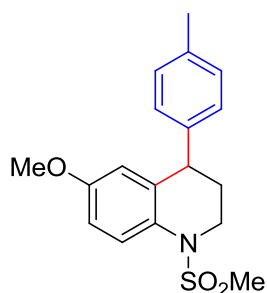
From *N*-allyl-*N*-(4-methylphenyl)methanesulfonamide **6** (0.113 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **38** was obtained in 72% (0.113 g) yield as a white solid: mp 122-126 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.69 (d, *J* = 8.2 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.76 (s, 1H), 4.13 (t, *J* = 6.5 Hz, 1H), 3.92-3.70 (m, 2H), 2.90 (s, 3H), 2.36 (s, 3H), 2.35-2.00 (m, 5H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 142.0, 136.3, 134.6, 134.1, 131.2, 131.0, 129.3, 128.2, 122.2, 44.2, 42.7, 38.4, 31.2, 21.0, 20.6.

Elemental analysis: calcd (%) for C<sub>18</sub>H<sub>21</sub>NO<sub>2</sub>S (315.43): C 68.54, H 6.71; found: C 68.40, H 6.57.

#### 6-Methoxy-1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (**39**)



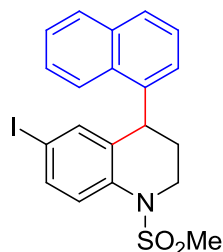
From *N*-allyl-*N*-(4-methoxyphenyl)methanesulfonamide **7** (0.121 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **39** was obtained in 69% (0.114 g) yield as a white solid: mp 108-110 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.71 (d, *J* = 8.2 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.79 (dd, *J* = 8.2, 2.9 Hz, 1H), 6.47 (d, *J* = 2.9 Hz, 1H), 4.13 (t, *J* = 6.5 Hz, 1H), 3.90-3.70 (m, 2H), 3.67 (s, 3H), 2.87 (s, 3H), 2.34 (s, 3H), 2.32-1.90 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.6, 141.6, 136.4, 133.4, 130.2, 129.4, 128.2, 124.4, 115.5, 113.0, 55.4, 44.5, 43.1, 38.4, 31.2, 21.0.

Elemental analysis: calcd (%) for C<sub>18</sub>H<sub>21</sub>NO<sub>3</sub>S (331.43): C 65.23, H 6.39; found: C 65.42, H 6.24.

#### 6-Iodo-1-(methylsulfonyl)-4-(naphthalen-1-yl)-1,2,3,4-tetrahydroquinoline (**40**)



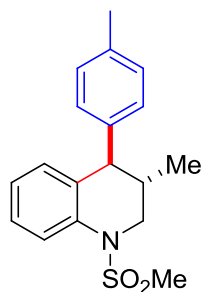
From *N*-allyl-*N*-(4-iodophenyl)methanesulfonamide **5** (0.169 g, 0.5 mmol) and naphthalene-1-sulfonyl chloride (0.227 g, 1 mmol), **40** was obtained in 67% (0.155 g) yield as a white solid: mp 226-228 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.09 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.63-7.54 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 1.6 Hz, 1H), 6.86 (d, *J* = 7.1 Hz, 1H), 5.02 (t, *J* = 6.5 Hz, 1H), 4.03-3.88 (m, 1H), 3.74-3.57 (m, 1H), 3.06 (s, 3H), 2.48-2.16 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 140.2, 139.7, 137.7, 136.5, 134.1, 133.0, 130.8, 129.3, 127.8, 126.9, 126.6, 125.9, 125.3, 123.4, 122.7, 88.3, 43.5, 39.0, 38.9, 29.1.

Elemental analysis: calcd (%) for C<sub>20</sub>H<sub>18</sub>INO<sub>2</sub>S (463.33): C 51.84, H 3.92; found: C 51.80, H 3.95.

### 3-Methyl-1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (**41**)



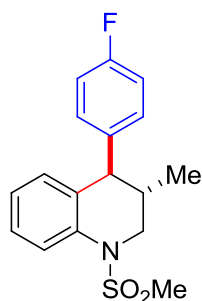
From *N*-(2-methylallyl)-*N*-phenylmethanesulfonamide **8** (0.113 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **41** was obtained in 81% (0.128 g) yield as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.20-7.05 (m, 3H), 7.02-6.88 (m, 3H), 6.83 (d, *J* = 7.7 Hz, 1H), 4.17 (dd, *J* = 13.3, 3.6 Hz, 1H), 3.62 (d, *J* = 9.5 Hz, 1H), 3.27 (dd, *J* = 13.3, 10.5 Hz, 1H), 3.04 (s, 3H), 2.35 (s, 3H), 2.25-2.10 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.0, 136.8, 136.3, 131.8, 131.1, 129.3, 128.8, 126.9, 124.3, 121.4, 51.9, 51.6, 38.9, 35.5, 21.0, 17.4.

Elemental analysis: calcd (%) for C<sub>18</sub>H<sub>21</sub>NO<sub>2</sub>S (315.43): C 68.54, H 6.71; found: C 68.36, H 6.47.

### 4-(4-Fluorophenyl)-3-methyl-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinoline (**42**)



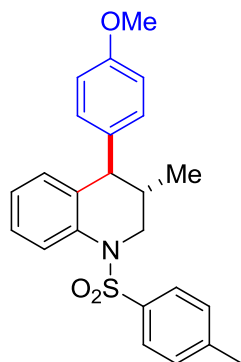
From *N*-(2-methylallyl)-*N*-phenylmethanesulfonamide **8** (0.113 g, 0.5 mmol) and 4-fluorobenzenesulfonyl chloride (0.195 g, 1 mmol), **42** was obtained in 78% (0.124 g) yield as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.08-6.92 (m, 5H), 6.77 (d, *J* = 7.7 Hz, 1H), 4.14 (dd, *J* = 13.3, 3.6 Hz, 1H), 3.63 (d, *J* = 9.5 Hz, 1H), 3.25 (dd, *J* = 13.3, 10.5 Hz, 1H), 3.04 (s, 3H), 2.25-2.10 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.6 (d,  $J = 245.3$  Hz), 139.8 (d,  $J = 3.3$  Hz), 136.8, 131.3, 131.0, 130.3 (d,  $J = 7.9$  Hz), 127.2, 124.4, 121.4, 115.4 (d,  $J = 21.3$  Hz), 51.5, 51.4, 39.1, 35.8, 17.3.

Elemental analysis: calcd (%) for  $\text{C}_{17}\text{H}_{18}\text{FNO}_2\text{S}$  (319.39): C 63.93, H 5.68; found: C 63.71, H 5.72.

#### 4-(4-Methoxyphenyl)-3-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (43)



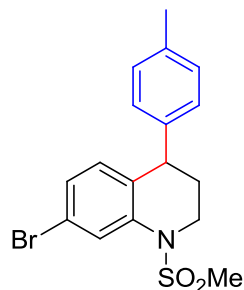
From 4-methyl-*N*-(2-methylallyl)-*N*-phenylbenzenesulfonamide **9** (0.151 g, 0.5 mmol) and 4-methoxybenzene-1-sulfonyl chloride (0.207 g, 1 mmol), **43** was obtained in 88% (0.179 g) yield as a white solid: mp 174-176 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.84 (d,  $J = 8.2$  Hz, 1H), 7.49 (d,  $J = 8.2$  Hz, 2H), 7.18 (d,  $J = 8.2$  Hz, 2H), 7.10 (t,  $J = 7.6$  Hz, 1H), 6.90 (t,  $J = 7.6$  Hz, 1H), 6.59 (d,  $J = 8.2$  Hz, 2H), 6.60-6.57 (m, 1H), 6.33 (d,  $J = 8.2$  Hz, 2H), 4.27 (dd,  $J = 14.0, 3.7$  Hz, 1H), 3.71 (s, 3H), 3.22 (d,  $J = 10.3$  Hz, 1H), 3.13 (dd,  $J = 13.9, 11.7$ , 1H), 2.38 (s, 3H), 1.75-1.50 (m, 1H), 0.71 (d,  $J = 6.5$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.2, 143.6, 137.5, 137.0, 136.0, 133.8, 130.6, 129.8, 129.7, 127.5, 126.5, 125.2, 124.5, 113.6, 55.2, 52.8, 51.5, 33.9, 21.5, 17.3.

Elemental analysis: calcd (%) for  $\text{C}_{24}\text{H}_{25}\text{NO}_3\text{S}$  (407.53): C 70.73, H 6.18; found: C 70.80, H 6.12.

#### 7-Bromo-1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (44a)



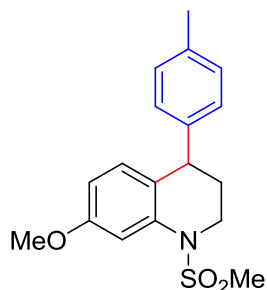
From *N*-allyl-*N*-(3-bromophenyl)methanesulfonamide **10** (0.145 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **44a** was obtained in 72% regioselectivity and 66% (0.125 g) yield as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.00 (s, 1H), 7.16-7.10 (m, 3H), 6.94 (d,  $J = 8.2$  Hz, 2H), 6.81 (d,  $J = 7.9$  Hz, 1H), 4.10 (t,  $J = 6.6$  Hz, 1H), 3.90-3.63 (m, 2H), 2.95 (s, 3H), 2.31 (s, 3H), 2.30-2.07 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.1, 138.3, 136.6, 132.1, 130.1, 129.4, 128.1, 127.3, 124.5, 120.7, 44.2, 42.5, 38.7, 30.9, 21.0.

Elemental analysis: calcd (%) for  $\text{C}_{17}\text{H}_{18}\text{BrNO}_2\text{S}$  (380.30): C 53.69, H 4.77; found: C 53.47, H 4.88.

### 7-Methoxy-1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (45a)



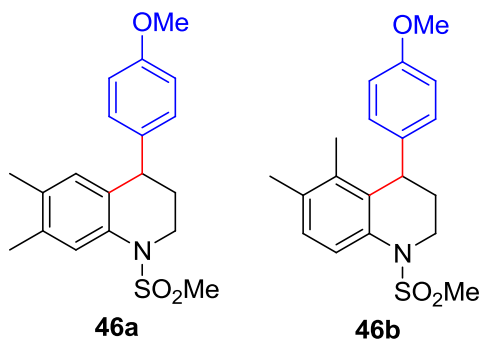
From *N*-allyl-*N*-(3-methoxyphenyl)methanesulfonamide **11** (0.121 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **45a** was obtained in 76% regioselectivity and in 80% (0.132 g) yield as a mixture of isomers as a white solid: mp 86-89 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.47 (d, *J* = 2.5 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.64 (dd, *J* = 8.6, 2.5 Hz, 1H), 4.15 (t, *J* = 6.6 Hz, 1H), 3.93-3.76 (m, 5H), 2.96 (s, 3H), 2.36 (s, 3H), 2.32-2.23 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 158.5, 142.1, 137.8, 136.2, 131.5, 129.2, 128.1, 123.1, 110.9, 106.9, 55.3, 44.2, 42.1, 38.3, 31.1, 20.9.

Elemental analysis: calcd (%) for C<sub>18</sub>H<sub>21</sub>NO<sub>3</sub>S (331.43): C 65.23, H 6.39; found: C 65.27, H 6.49.

### 4-(4-Methoxyphenyl)-6,7-dimethyl-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinoline (46a) and 4-(4-methoxyphenyl)-5,6-dimethyl-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinoline (46b)



From *N*-allyl-*N*-(3,4-dimethylphenyl)methanesulfonamide **12** (0.120 g, 0.5 mmol) and 4-methoxybenzene-1-sulfonyl chloride (0.207 g, 1 mmol), a mixture of **46a** and **46b** was obtained in 15:5 ratio and in 81% (0.140 g) yield as a yellow oil.

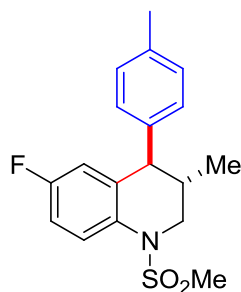
**46a**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.58 (s, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.70 (s, 1H), 4.12-4.06 (m, 1H), 3.85-3.75 (m, 5H), 2.91 (s, 3H), 2.25 (s, 3H), 2.12 (s, 3H), 2.30-2.00 (m, 2H). **46b** was also observed: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H).

Mixture of **46a** and **46b**: <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 158.2, 158.0, 137.2, 136.2, 135.9, 135.8, 135.1, 134.7, 133.0, 131.5, 129.2, 128.9, 128.8, 128.6, 123.1, 119.1, 113.9, 55.2, 55.1, 44.3, 41.9, 41.7, 38.9, 38.4, 37.9, 31.4, 30.2, 20.2, 19.7, 18.9, 15.6.

Elemental analysis: calcd (%) for C<sub>19</sub>H<sub>23</sub>NO<sub>3</sub>S (345.45): C 66.06, H 6.71; found: C 66.01, H 6.88.



### 6-Fluoro-3-methyl-1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (47)



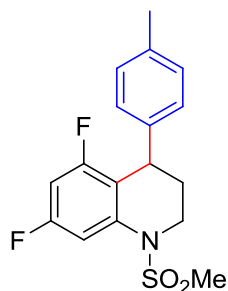
From *N*-(4-fluorophenyl)-*N*-(2-methylallyl)methanesulfonamide **13** (0.121 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **47** was obtained in 72% (0.119 g) yield as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.71 (dd, *J* = 9.2, 5.2 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.91-6.83 (m, 1H), 6.51 (dd, *J* = 9.4, 2.8 Hz, 1H), 4.18 (dd, *J* = 13.5, 3.7 Hz, 1H), 3.55 (d, *J* = 10.0 Hz, 1H), 3.22 (dd, *J* = 13.5, 11.0 Hz, 1H), 3.01 (s, 3H), 2.35 (s, 3H), 2.30-2.05 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.6 (d, *J* = 244.6 Hz), 139.9, 136.8, 134.7 (d, *J* = 7.0 Hz), 132.7 (d, *J* = 2.7 Hz), 129.5, 128.8, 124.0 (d, *J* = 8.1 Hz), 117.0 (d, *J* = 22.7 Hz), 114.1 (d, *J* = 22.6 Hz), 52.2, 51.9, 39.0, 35.2, 21.0, 17.3.

Elemental analysis: calcd (%) for C<sub>18</sub>H<sub>20</sub>FNO<sub>2</sub>S (333.42): C 64.84, H 6.05; found: C 64.21, H 6.27.

### 5,7-Difluoro-1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (48)



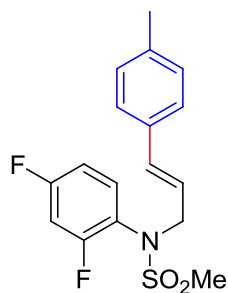
From *N*-allyl-*N*-(3,5-difluorophenyl)methanesulfonamide **14** (0.124 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **48** was obtained in 77% (0.129 g) yield as a white solid: mp 126-128 °C. Formation of Heck type product in low yield was also observed by <sup>1</sup>H NMR analysis of the crude mixture.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.55 (d, *J* = 11.4 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 7.9 Hz, 2H), 6.58 (td, *J* = 9.4, 2.4 Hz, 1H), 4.40 (bs, 1H), 4.02 (dt, *J* = 13.1, 3.6 Hz, 1H), 3.39 (td, *J* = 12.1, 3.0 Hz, 1H), 2.94 (s, 3H), 2.32 (s, 3H), 2.30-2.05 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.5 (dd, *J* = 245.2, 15.2 Hz), 161.0 (dd, *J* = 246.7, 14.1 Hz), 140.5, 139.2 (dd, *J* = 13.0, 8.8 Hz), 136.5, 129.3, 127.2, 113.4 (dd, *J* = 19.8, 4.0 Hz), 103.8 (dd, *J* = 27.3, 3.6 Hz), 99.4 (t, *J* = 26.1 Hz), 42.2, 38.4, 35.4 (d, *J* = 3.9 Hz), 29.7, 20.9.

Elemental analysis: calcd (%) for C<sub>17</sub>H<sub>17</sub>F<sub>2</sub>NO<sub>2</sub>S (337.38): C 60.52, H 5.08; found: C 60.42, H 5.22.

### (*E*)-*N*-(2,4-Difluorophenyl)-*N*-(3-*p*-tolylallyl)methanesulfonamide (49)



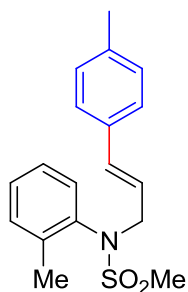
From *N*-allyl-*N*-(2,4-difluorophenyl)methanesulfonamide **15** (0.124 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **49** was obtained in 71% (0.119 g) yield as a white solid: mp 96-98 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.40-7.33 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.94-6.84 (m, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.12 (dt, *J* = 15.8, 7.0 Hz, 1H), 4.36 (d, *J* = 7.0 Hz, 2H), 3.02 (s, 3H), 2.33 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.4 (dd, *J* = 251.9, 11.7 Hz), 159.6 (dd, *J* = 252.0, 12.6 Hz), 138.0, 134.7 (d, *J* = 2.3 Hz), 134.6 (m), 133.2, 129.3, 126.4, 122.5 (dd, *J* = 12.2, 4.1 Hz), 122.3, 112.1 (dd, *J* = 22.2, 3.6 Hz), 104.9 (dd, *J* = 26.4, 24.4 Hz), 53.2 (d, *J* = 2.5 Hz), 39.4 (d, *J* = 3.5 Hz), 21.2.

Elemental analysis: calcd (%) for C<sub>17</sub>H<sub>17</sub>F<sub>2</sub>NO<sub>2</sub>S (337.38): C 60.52, H 5.08; found: C 60.39, H 5.04.

**(*E*)-*N*-*o*-Tolyl-*N*-(3-*p*-tolylallyl)methanesulfonamide (**50**)**



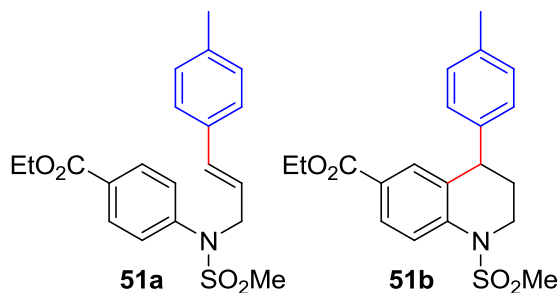
From *N*-allyl-*N*-(2-methylphenyl)methanesulfonamide **16** (0.113 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **50** was obtained in 75% (0.118 g) yield as a yellow solid: mp 92-94 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.33-7.22 (m, 4H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.15 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.35-4.25 (m, 2H), 2.97 (s, 3H), 2.38 (s, 3H), 2.30 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 139.5, 138.1, 137.9, 134.6, 133.4, 131.7, 129.3, 128.7, 128.6, 126.7, 126.4, 122.3, 54.0, 39.3, 21.2, 18.6.

Elemental analysis: calcd (%) for C<sub>18</sub>H<sub>21</sub>NO<sub>2</sub>S (315.43): C 68.54, H 6.71; found: C 68.59, H 6.91.

**(*E*)-Ethyl 4-(*N*-(3-*p*-tolylallyl)methylsulfonamido)benzoate (**51a**) and ethyl 1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline-6-carboxylate (**51b**)**



From ethyl 4-(*N*-allylmethylsulfonamido)benzoate **17** (0.142 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **51a** and **51b** were obtained in 5:1 ratio; **51a** was isolated in 74% (0.138 g) yield as a brown oil and **51b** was isolated in 15% (0.028 g) yield as a purple oil.

**51a:**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05 (d,  $J = 8.5$  Hz, 2H), 7.45 (d,  $J = 8.5$  Hz, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 7.09 (d,  $J = 8.0$  Hz, 2H), 6.47 (d,  $J = 15.8$  Hz, 1H), 6.13 (dd,  $J = 15.8, 6.7$  Hz, 1H), 4.49 (d,  $J = 6.7$  Hz, 2H), 4.37 (q,  $J = 7.1$  Hz, 2H), 2.95 (s, 3H), 2.31 (s, 3H), 1.38 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.6, 143.5, 138.0, 134.5, 133.1, 130.7, 129.4, 129.2, 127.2, 126.4, 122.2, 61.1, 53.0, 38.6, 21.1, 14.2.

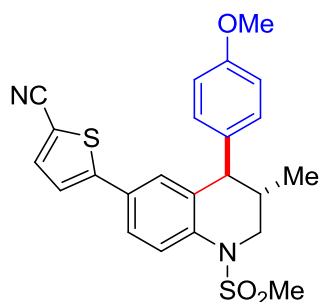
Elemental analysis: calcd (%) for  $\text{C}_{20}\text{H}_{23}\text{NO}_4\text{S}$  (373.46): C 64.32, H 6.21; found: C 64.21, H 6.28.

**51b:**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90 (s, 2H), 7.69 (s, 1H), 7.11 (d,  $J = 8.5$  Hz, 2H), 6.91 (d,  $J = 8.5$  Hz, 2H), 4.35-4.20 (m, 3H), 3.93-3.65 (m, 2H), 2.95 (s, 3H), 2.32 (s, 3H), 2.32-2.13 (m, 2H), 1.33 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.9, 141.2, 141.0, 136.4, 132.4, 130.2, 129.4, 128.7, 128.0, 125.7, 120.4, 60.8, 43.7, 42.5, 28.5, 30.5, 20.9, 14.2.

**5-(4-(4-Methoxyphenyl)-3-methyl-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinolin-6-yl)thiophene-2-carbonitrile (52)**



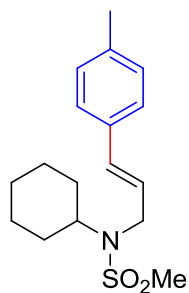
From *N*-(4-(5-cyanothiophen-2-yl)phenyl)-*N*-(2-methylallyl)methanesulfonamide **18** (0.166 g, 0.5 mmol) and 4-methoxybenzene-1-sulfonyl chloride (0.207 g, 1 mmol), **52** was obtained in 83% (0.182 g) yield as a grey oil.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.82 (d,  $J = 8.7$  Hz, 1H), 7.48 (d,  $J = 3.9$  Hz, 1H), 7.40 (dd,  $J = 8.7, 2.1$  Hz, 1H), 7.04-6.97 (m, 4H), 6.87 (d,  $J = 8.7$  Hz, 2H), 4.12 (dd,  $J = 13.1, 3.6$  Hz, 1H), 3.81 (s, 3H), 3.63 (d,  $J = 9.1$  Hz, 1H), 3.32 (d,  $J = 13.1, 10.0$  Hz, 1H), 3.07 (s, 3H), 2.25-2.15 (m, 1H), 0.98 (d,  $J = 6.6$  Hz, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.6, 150.8, 138.3, 137.9, 135.2, 132.4, 129.8, 129.0, 128.1, 125.1, 122.9, 121.7, 114.3, 114.2, 107.8, 55.2, 51.3, 51.2, 39.0, 35.3, 17.4.

Elemental analysis: calcd (%) for C<sub>23</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub> (438.56): C 62.99, H 5.06; found: C 63.14, H 5.24.

**(E)-N-Cyclohexyl-N-(3-*p*-tolylallyl)methanesulfonamide (53)**



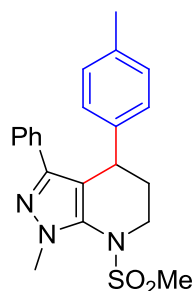
From *N*-allyl-*N*-cyclohexylmethanesulfonamide **19** (0.110 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **53** was obtained in 78% (0.120 g) yield as a white solid: mp 124-128 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.27 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.12 (dt, *J* = 15.8, 6.7 Hz, 1H), 3.99 (d, *J* = 6.7 Hz, 2H), 3.72-3.63 (m, 1H), 2.85 (s, 3H), 2.34 (s, 3H), 1.88-1.00 (m, 10H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 137.8, 133.6, 132.8, 129.3, 126.3, 125.6, 57.9, 45.7, 41.3, 32.4, 26.1, 25.3, 21.2.

Elemental analysis: calcd (%) for C<sub>17</sub>H<sub>25</sub>NO<sub>2</sub>S (307.45): C 66.41, H 8.20; found: C 66.24, H 8.32.

**1-Methyl-7-(methylsulfonyl)-3-phenyl-4-*p*-tolyl-4,5,6,7-tetrahydropyrazolo[3,4-*b*]pyridine (55)**



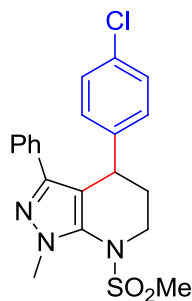
From *N*-allyl-*N*-(1-methyl-3-phenylpyrazol-5-yl)methanesulfonamide **54** (0.146 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **55** was obtained in 83% (0.158 g) yield as a white solid: mp 200-202 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.20-7.10 (m, 3H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 4.40 (t, *J* = 6.5 Hz, 1H), 4.01 (s, 3H), 3.81-3.63 (m, 2H), 3.03 (s, 3H), 2.55-2.43 (m, 1H), 2.27 (s, 3H), 2.05-1.92 (m, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 147.7, 141.4, 136.9, 136.1, 133.2, 129.3, 128.0, 127.3, 127.2, 126.7, 108.2, 46.5, 40.2, 38.4, 36.6, 31.6, 21.0.

Elemental analysis: calcd (%) for C<sub>21</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>S (381.49): C 66.12, H 6.08; found: C 66.24, H 5.89.

**4-(4-Chlorophenyl)-1-methyl-7-(methylsulfonyl)-3-phenyl-4,5,6,7-tetrahydropyrazolo[3,4-*b*]pyridine (56)**



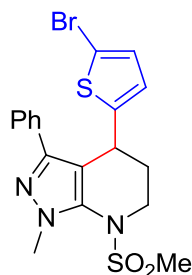
From *N*-allyl-*N*-(1-methyl-3-phenylpyrazol-5-yl)methanesulfonamide **54** (0.146 g, 0.5 mmol) and 4-chlorobenzenesulfonyl chloride (0.211 g, 1 mmol), **56** was obtained in 81% (0.162 g) yield as a yellow solid: mp 154-158 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.20-7.10 (m, 5H), 7.00 (d, *J* = 8.2 Hz, 2H), 4.43 (t, *J* = 6.5 Hz, 1H), 4.00 (s, 3H), 3.80-3.62 (m, 2H), 3.11 (s, 3H), 2.55-2.43 (m, 1H), 2.05-1.92 (m, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 147.7, 142.9, 136.9, 133.0, 132.3, 128.7, 128.6, 128.1, 127.5, 126.7, 107.5, 46.5, 40.5, 38.3, 36.5, 31.6.

Elemental analysis: calcd (%) for C<sub>20</sub>H<sub>20</sub>ClN<sub>3</sub>O<sub>2</sub>S (401.91): C 59.77, H 5.02; found: C 60.01, H 4.89.

#### 4-(5-Bromothiophen-2-yl)-1-methyl-7-(methylsulfonyl)-3-phenyl-4,5,6,7-tetrahydropyrazolo[3,4-b]pyridine (**57**)



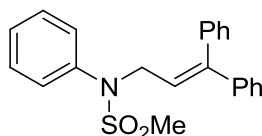
From *N*-allyl-*N*-(1-methyl-3-phenylpyrazol-5-yl)methanesulfonamide **54** (0.146 g, 0.5 mmol) and 5-bromothiophene-2-sulfonyl chloride (0.262 g, 1 mmol), **57** was obtained in 85% (0.192 g) yield as a yellow solid: mp 172-174 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.30-7.20 (m, 3H), 6.74 (d, *J* = 3.7 Hz, 1H), 6.41 (d, *J* = 3.7 Hz, 1H), 4.63 (t, *J* = 6.5 Hz, 1H), 3.97 (s, 3H), 3.88-3.60 (m, 2H), 3.06 (s, 3H), 2.55-2.43 (m, 1H), 2.10-1.98 (m, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.0, 147.6, 136.4, 133.0, 129.5, 128.3, 127.7, 126.5, 125.1, 110.1, 107.2, 45.9, 40.3, 38.3, 32.5, 31.5.

Elemental analysis: calcd (%) for C<sub>18</sub>H<sub>18</sub>BrN<sub>3</sub>O<sub>2</sub>S<sub>2</sub> (452.39): C 47.79, H 4.01; found: C 47.54, H 3.98.

#### *N*-(3,3-Diphenylallyl)-*N*-phenylmethanesulfonamide (**58**)



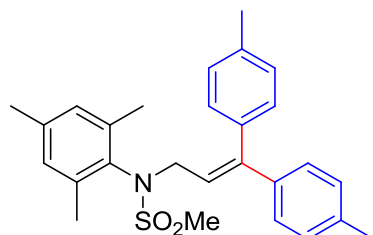
From *N*-cinnamyl-*N*-phenylmethanesulfonamide **20** (0.144 g, 0.5 mmol) and benzenesulfonyl chloride (0.177 g, 1 mmol), **58** was obtained in 57% (0.103 g) yield as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45-7.20 (m, 11H), 7.12-7.03 (m, 2H), 6.89 (dd,  $J = 7.2$  and  $3.0$  Hz, 2H), 6.09 (t,  $J = 6.9$  Hz, 1H), 4.38 (d,  $J = 6.9$  Hz, 2H), 2.87 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.3, 141.2, 138.9, 128.5, 129.5, 129.3, 128.7, 128.2, 128.1, 128.0, 127.7, 127.5, 127.3, 123.3, 49.7, 37.6.

Elemental analysis: calcd (%) for  $\text{C}_{22}\text{H}_{21}\text{NO}_2\text{S}$  (363.47): C 72.70, H 5.82; found: C 72.54, H 5.64.

### *N*-(3,3-Dip-tolylallyl)-*N*-mesitylmethanesulfonamide (**59**)



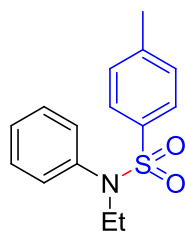
From *N*-allyl-*N*-mesitylmethanesulfonamide **21** (0.127 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **59** was obtained in 38% (0.082 g) yield as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.27-6.95 (m, 4H), 6.99 (d,  $J = 7.9$  Hz, 2H), 6.88 (s, 2H), 6.61 (d,  $J = 7.9$  Hz, 2H), 6.09 (t,  $J = 7.5$  Hz, 1H), 4.19 (d,  $J = 7.5$  Hz, 2H), 2.99 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H), 2.23 (s, 6H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.4, 138.6, 138.5, 138.0, 137.5, 137.0, 135.3, 133.8, 129.6, 129.3, 128.8, 128.7, 127.1, 121.1, 48.7, 40.7, 21.2, 21.0, 20.9, 19.3.

Elemental analysis: calcd (%) for  $\text{C}_{27}\text{H}_{31}\text{NO}_2\text{S}$  (433.60): C 74.79, H 7.21; found: C 74.60, H 7.07.

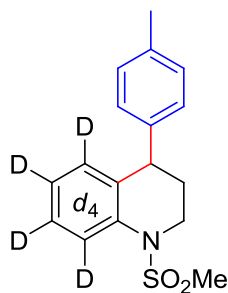
### *N*-Ethyl-4-methyl-*N*-phenylbenzenesulfonamide (**61**)<sup>11</sup>



From *N*-allyl-*N*-ethylaniline **60** (0.081 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **61** was obtained in 68% (0.093 g) yield as a yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.48 (d,  $J = 8.2$  Hz, 2H), 7.33-7.25 (m, 3H), 7.23 (d,  $J = 8.1$  Hz, 2H), 7.04 (dd,  $J = 7.6$ , 2.0 Hz, 2H), 3.59 (q,  $J = 7.1$  Hz, 2H), 2.41 (s, 3H), 1.06 (t,  $J = 7.1$  Hz, 3H).

### 1-(Methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline $d_4$ (**62**)

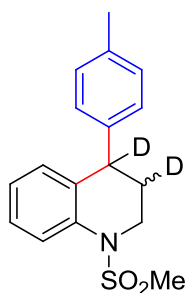


From *N*-allyl-4-methyl-*N*-methylbenzenesulfonamide  $d_4$  **22** (0.108 g, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol), **62** was obtained in 63% (0.096 g) yield as a white solid: mp 142-144 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.12 (d,  $J = 8.0$  Hz, 2H), 6.97 (d,  $J = 8.0$  Hz, 2H), 4.17 (t,  $J = 6.7$  Hz, 1H), 3.88-3.80 (m, 2H), 2.93 (s, 3H), 2.34 (s, 3H), 2.32-2.00 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.8, 137.1, 136.3, 131.1, 129.3, 128.2, 44.3, 42.8, 38.5, 31.2, 21.0.

### 1-(Methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline $d_2$ (**64**)



From *N*-allyl-4-methyl-*N*-methylbenzenesulfonamide  $d_2$  **63** (0.054 g, 0.25 mmol) and 4-methylbenzenesulfonyl chloride (0.096 g, 0.5 mmol), **64** was obtained in 57% (0.043 g) yield as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (d,  $J = 8.2$  Hz, 1H), 7.22 (t,  $J = 7.8$  Hz, 1H), 7.12 (d,  $J = 8.0$  Hz, 2H), 7.02 (t,  $J = 7.8$  Hz, 1H), 7.00-6.93 (m, 3H), 3.88-3.78 (m, 2H), 2.92 (s, 3H), 2.33 (s, 3H), 2.30-2.25 and 2.12-2.05 (m, 1H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.8, 137.2, 136.4, 131.3, 130.9, 129.4, 128.2, 127.4, 124.4, 122.0, 44.2, 42.8 (broad), 38.6, 31.2 (broad), 21.0.

HRMS  $[\text{M}+\text{Na}]^+$   $\text{C}_{17}\text{H}_{17}\text{D}_2\text{NO}_2\text{NaS}$   $m/z$  calcd: 326.11597;  $m/z$  found: 326.1157.

**1** Lim, H. J.; RajanBabu, T. V. *Org. Lett.* **2009**, *11*, 2924-2927.

**2** Ginshko, L. P.; Malinovskii, M. S.; Solomko, Z. F.; Gar, K. A.; Andreeva, E. I.; Kurochkin, A. F. *Zh. Org. Khim.* **1965**, *1*, 918-920.

**3** Corbet, M.; de Greef, M.; Zard, S. Z. *Org. Lett.* **2008**, *10*, 253-256.

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**5** Charrier, N.; Liu, Z.; Zard, S. Z. *Org. Lett.* **2012**, *14*, 2018-2021.

**6** Metayer, B.; Martin-Mingot, A.; Vullo, D.; Supuran, C. T.; Thibaudeau, S. *Org. Biomol. Chem.* **2013**, *11*, 7540-7549.

**7** Salomon, P.; Zard, S. Z. *Org. Lett.* **2014**, *16*, 2926-2929.

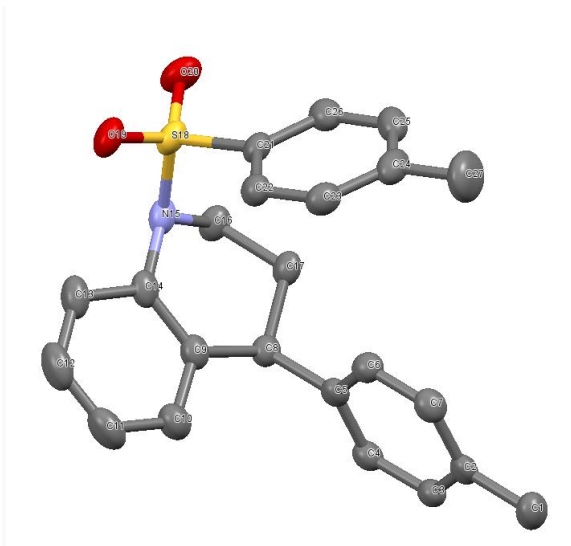
- 8** Hollmann, K.; Ecke, M.; Muehlstaedt, M. *J. Prakt. Chem.* **1991**, *333*, 711-715.
- 9** Inada, S.; Hirabayashi, S.; Taguchi, K.; Okazaki, M. *Nippon Kagaku Kaishi* **1978**, 86-92.
- 10** Barluenga, J.; Trincado, M.; Rubio, E.; Gonzalez, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 3416-3417.
- 11** Wilhelm, T.; Lautens, M. *Org. Lett.* **2005**, *7*, 4053-4056.
- 12** Stewart, I. C.; Keitz, B. K.; Kuhn, K. M.; Thomas, R. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2010**, *132*, 8534-8535.
- 13** Gryparis, C.; Efe, C.; Raptis, C.; Lykakis, I. N.; Stratakis, M. *Org. Lett.*, **2012**, *14*, 2956-2959.



## Crystallographic Data Tables

Cambridge Crystallographic Data Centre deposition numbers: CCDC 1402194 and 1402195

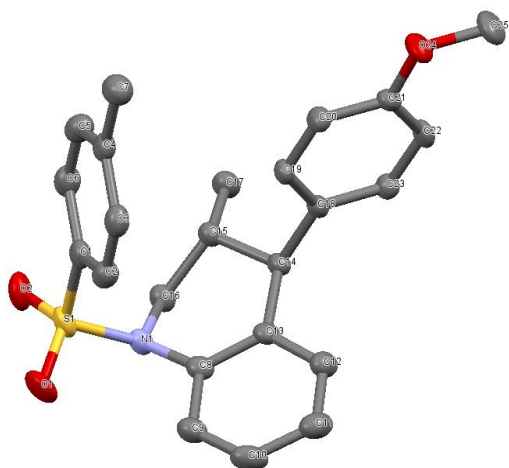
### 4-(*p*-Tolyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (**24**)



#### Crystal data and structure refinement for Compound **24**

Empirical formula	C <sub>23</sub> H <sub>23</sub> N O <sub>2</sub> S
Formula weight	377.48
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, <i>P n a 2</i> <sub>1</sub>
Unit cell dimensions	<i>a</i> = 9.7564(12) Å, $\alpha$ = 90 ° <i>b</i> = 11.2658(11) Å, $\beta$ = 90 ° <i>c</i> = 18.0254(18) Å, $\gamma$ = 90 °
Volume	1981.2(4) Å <sup>3</sup>
Z, Calculated density	4, 1.266 (g.cm <sup>-3</sup> )
Absorption coefficient	0.181 mm <sup>-1</sup>
<i>F</i> (000)	800
Crystal size	0.6 x 0.59 x 0.53 mm
Crystal color	colourless
Theta range for data collection	2.98 to 27.48 °
<i>h</i> _min, <i>h</i> _max	-12, 12
<i>k</i> _min, <i>k</i> _max	-14, 14
<i>l</i> _min, <i>l</i> _max	-22, 23
Reflections collected / unique	13866 / 4480 [R(int) <sup>a</sup> = 0.0373]
Reflections [ <i>I</i> >2 $\sigma$ ]	4031
Completeness to theta_max	0.997
Absorption correction type	multi-scan
Max. and min. transmission	0.909, 0.843
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	4480 / 1 / 246
<sup>b</sup> Goodness-of-fit	1.016
Final <i>R</i> indices [ <i>I</i> >2 $\sigma$ ]	<i>R</i> 1 <sup>c</sup> = 0.0374, <i>wR</i> 2 <sup>d</sup> = 0.0873
<i>R</i> indices (all data)	<i>R</i> 1 <sup>c</sup> = 0.0436, <i>wR</i> 2 <sup>d</sup> = 0.0905
Largest diff. peak and hole	0.235 and -0.314 e <sup>-</sup>

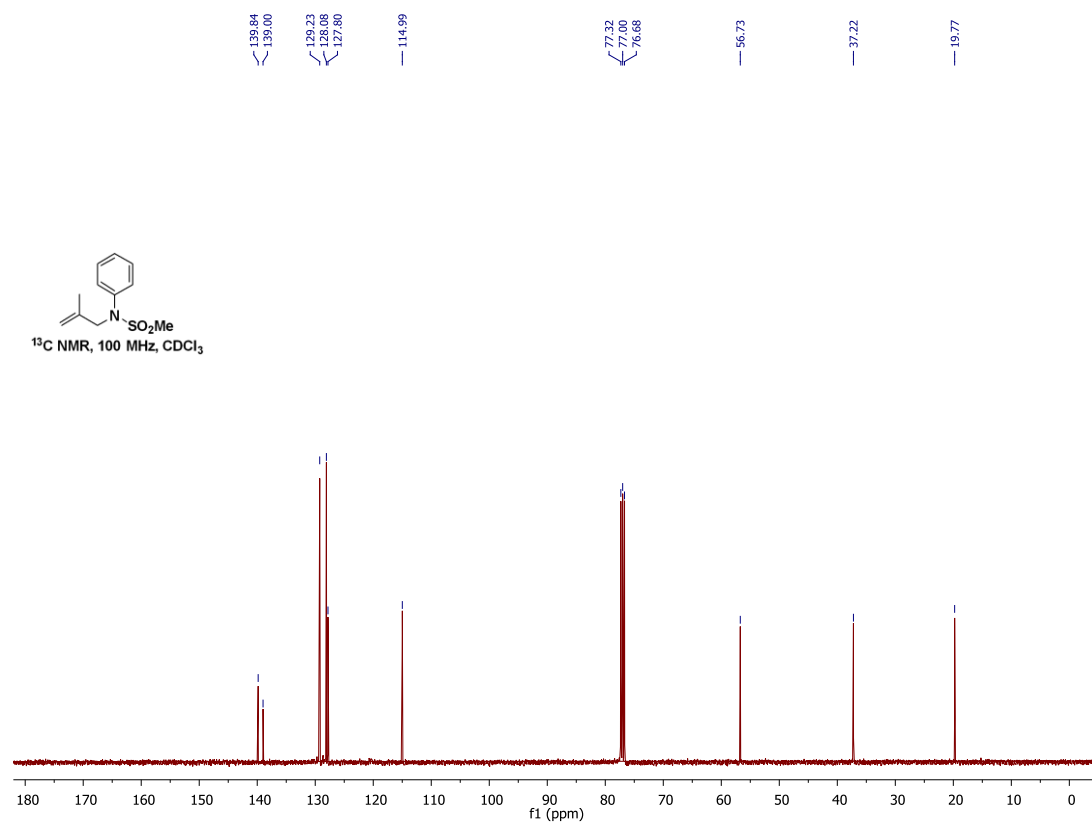
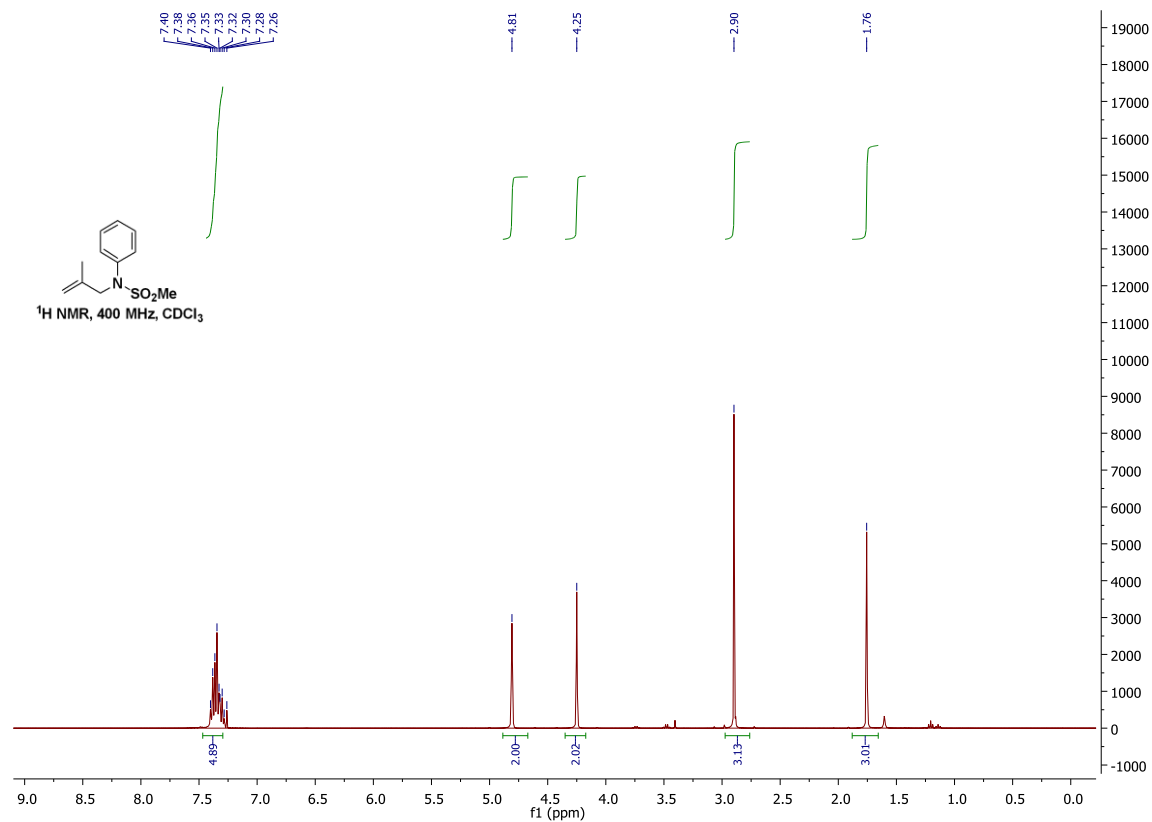
4-(4-Methoxyphenyl)-3-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (43)



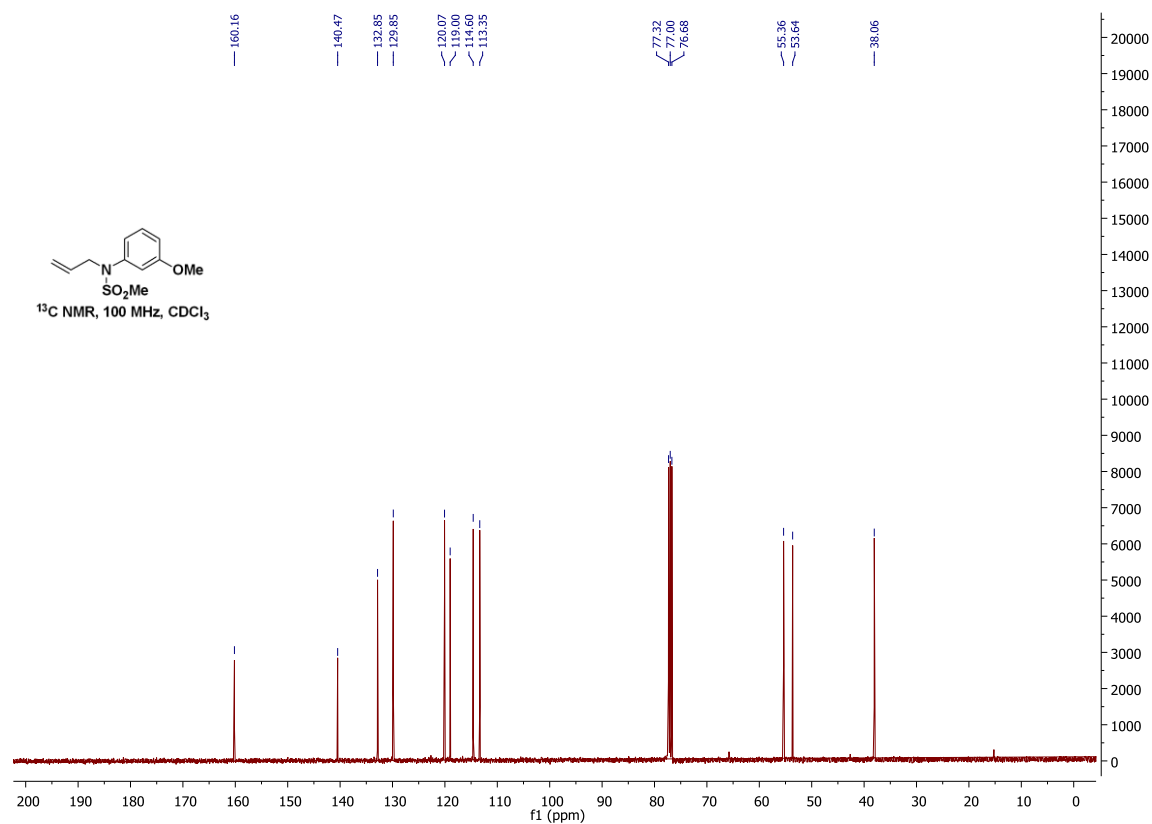
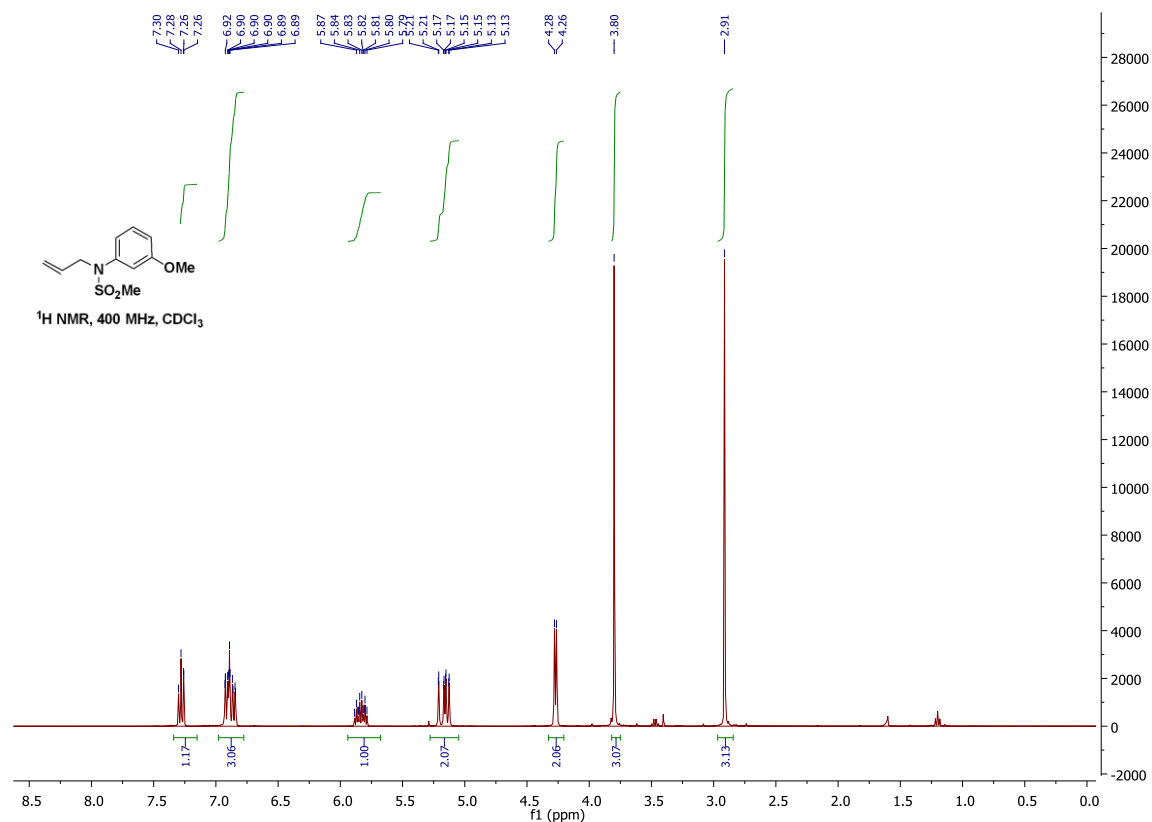
Crystal data and structure refinement for Compound **43**

Empirical formula	C <sub>24</sub> H <sub>25</sub> N O <sub>3</sub> S
Formula weight	407.51
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, <i>P</i> 2 <sub>1</sub> /c
Unit cell dimensions	a = 12.1501(9) Å, α = 90 °
	b = 14.3435(12) Å, β = 113.738(3) °
	c = 13.0096(9) Å, γ = 90 °
Volume	2075.4(3) Å <sup>3</sup>
Z, Calculated density	4, 1.304 (g.cm <sup>-3</sup> )
Absorption coefficient	0.181 mm <sup>-1</sup>
<i>F</i> (000)	864
Crystal size	0.6 x 0.59 x 0.37 mm
Crystal color	colourless
Theta range for data collection	3.29 to 27.48 °
h <sub>min</sub> , h <sub>max</sub>	-13, 15
k <sub>min</sub> , k <sub>max</sub>	-18, 18
l <sub>min</sub> , l <sub>max</sub>	-16, 11
Reflections collected / unique	15677 / 4652 [R(int) <sup>a</sup> = 0.059]
Reflections [I > 2σ]	3250
Completeness to theta <sub>max</sub>	0.976
Absorption correction type	multi-scan
Max. and min. transmission	0.935, 0.802
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	4652 / 0 / 265
<sup>b</sup> Goodness-of-fit	1.047
Final <i>R</i> indices [I > 2σ]	<i>R</i> 1 <sup>c</sup> = 0.0539, <i>wR</i> 2 <sup>d</sup> = 0.1098
<i>R</i> indices (all data)	<i>R</i> 1 <sup>c</sup> = 0.0823, <i>wR</i> 2 <sup>d</sup> = 0.1202
Largest diff. peak and hole	0.306 and -0.41 e <sup>-</sup> .Å <sup>-3</sup>

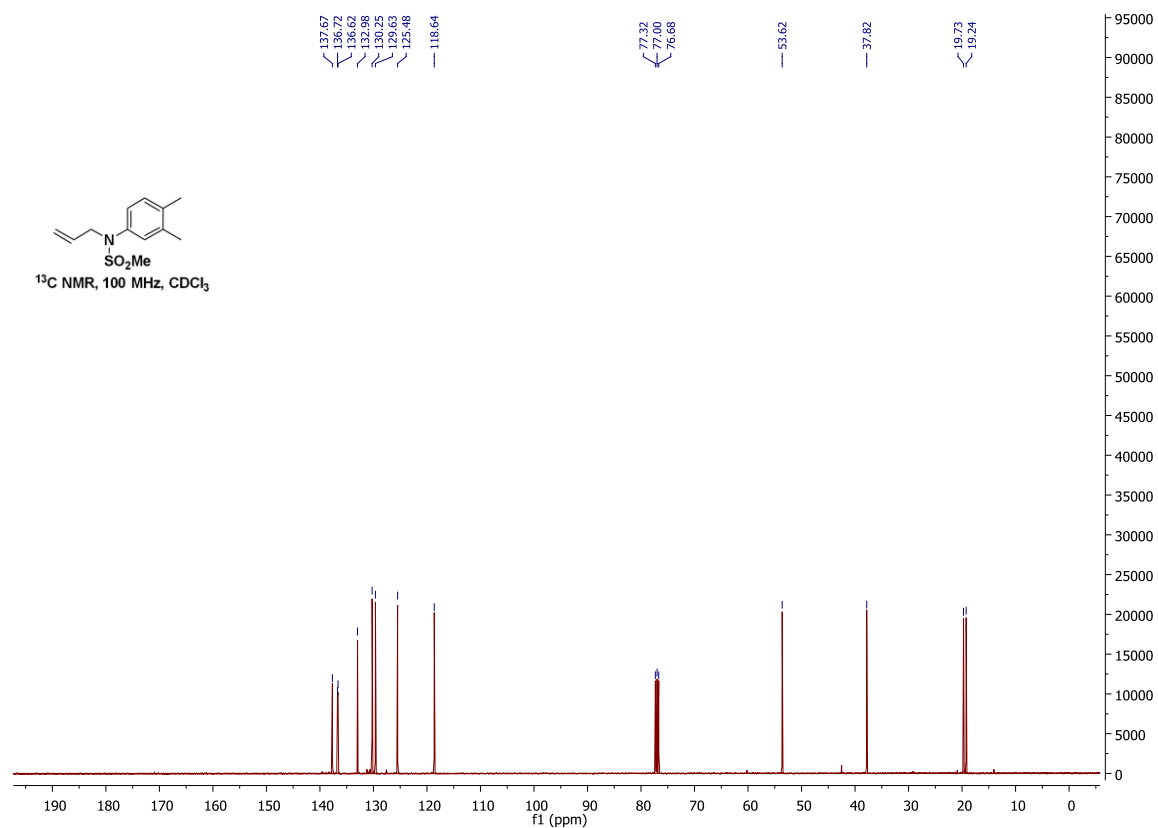
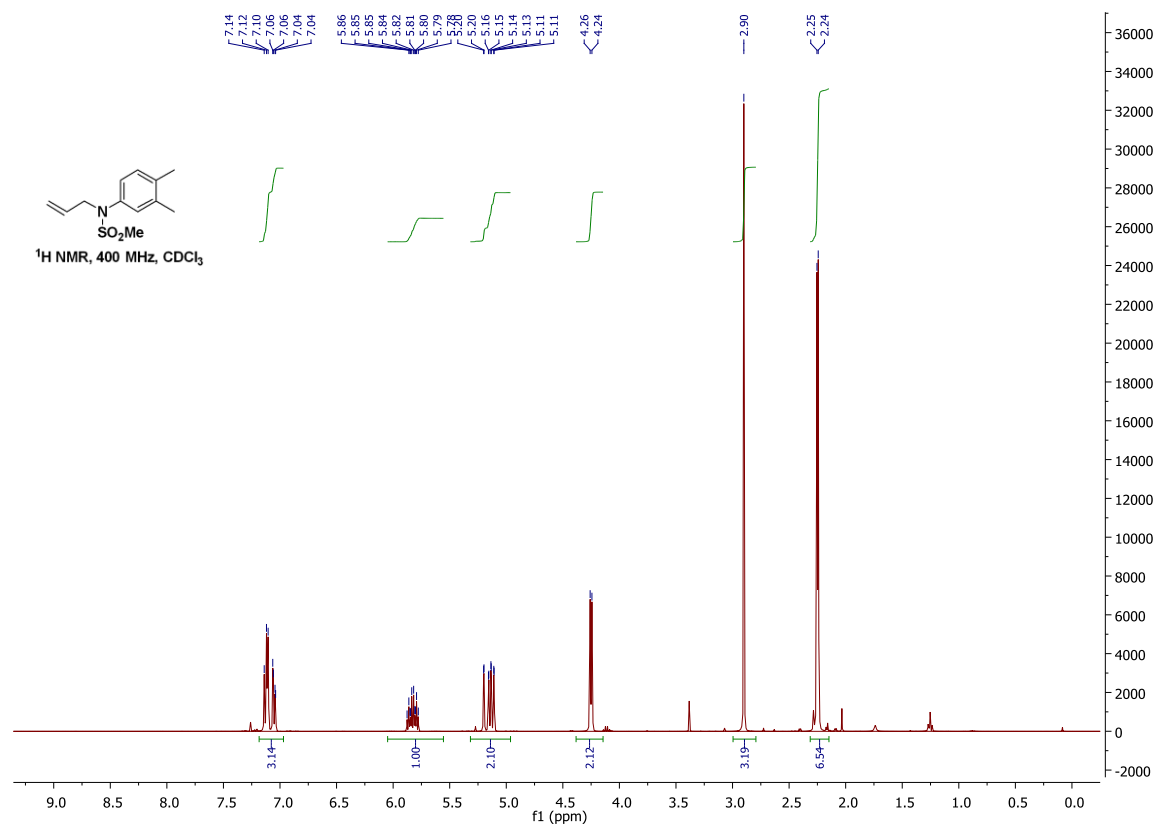
# *N*-(2-Methylallyl)-*N*-phenylmethanesulfonamide (8)



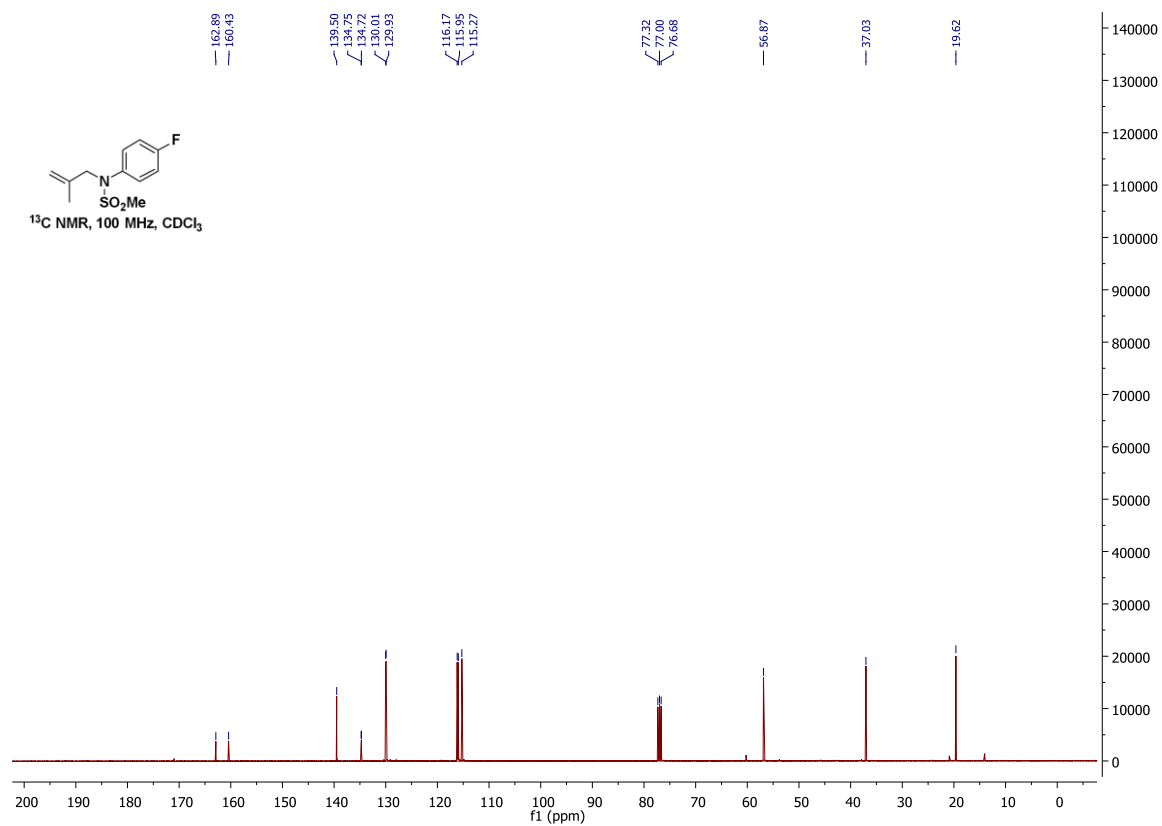
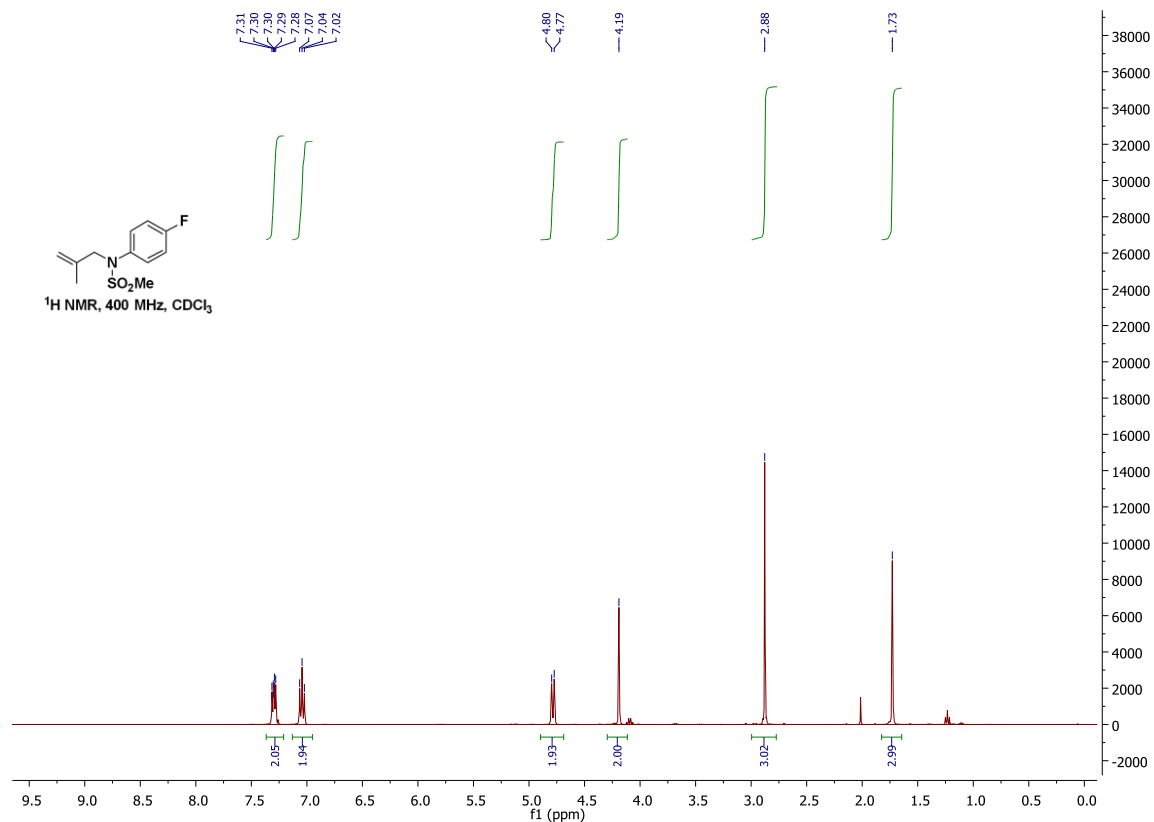
***N*-Allyl-*N*-(3-methoxyphenyl)methanesulfonamide(11)**



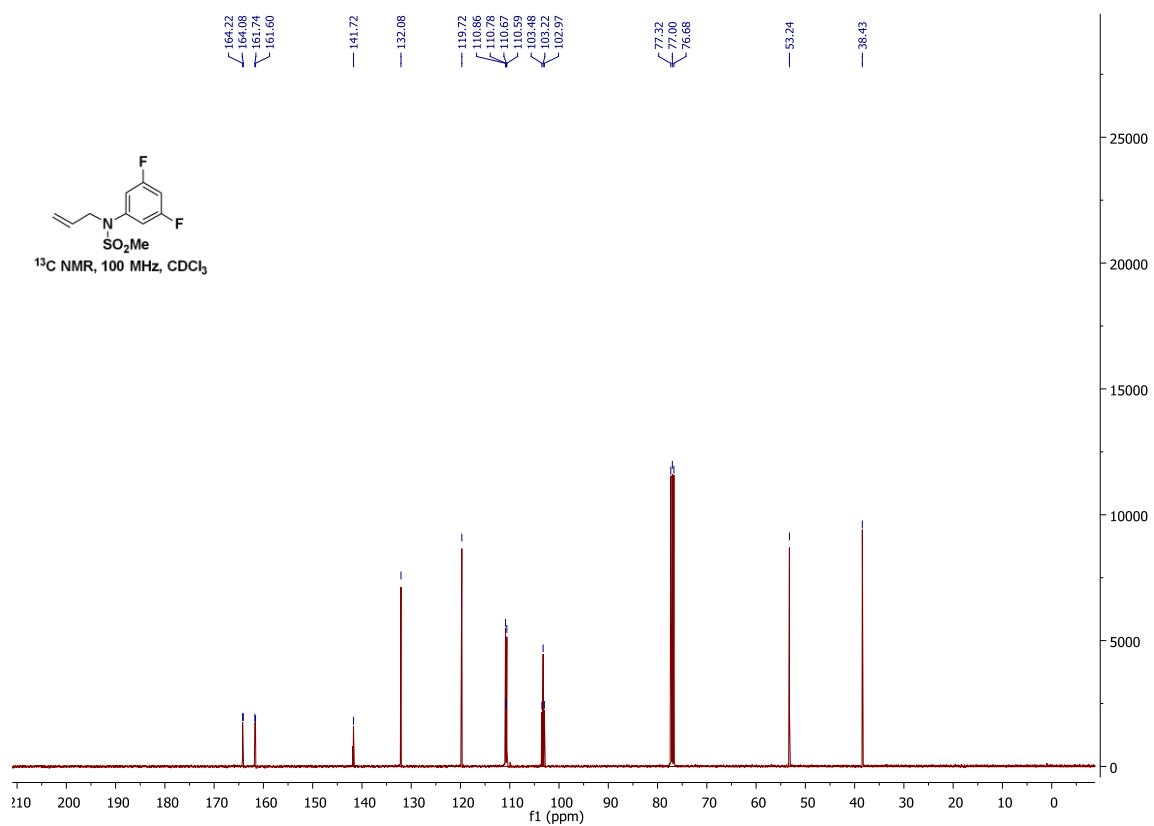
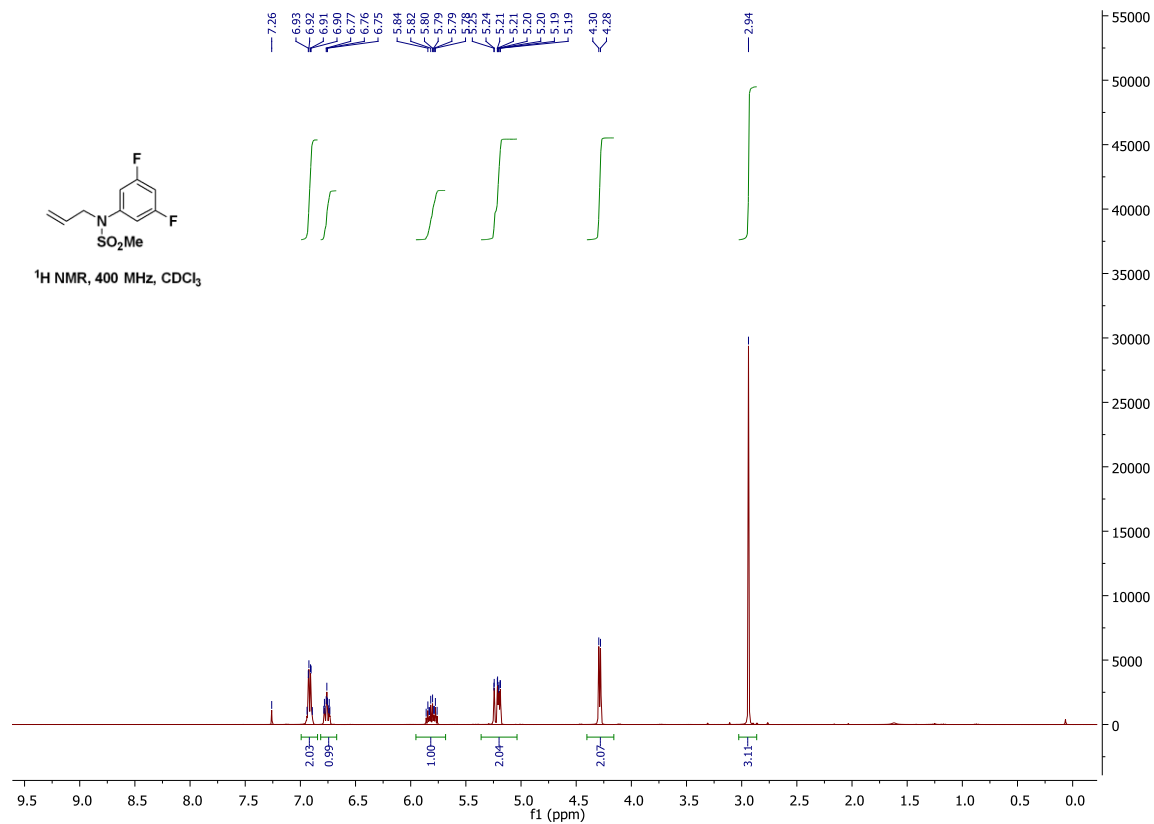
# *N*-Allyl-*N*-(3,4-dimethylphenyl)methanesulfonamide (12)



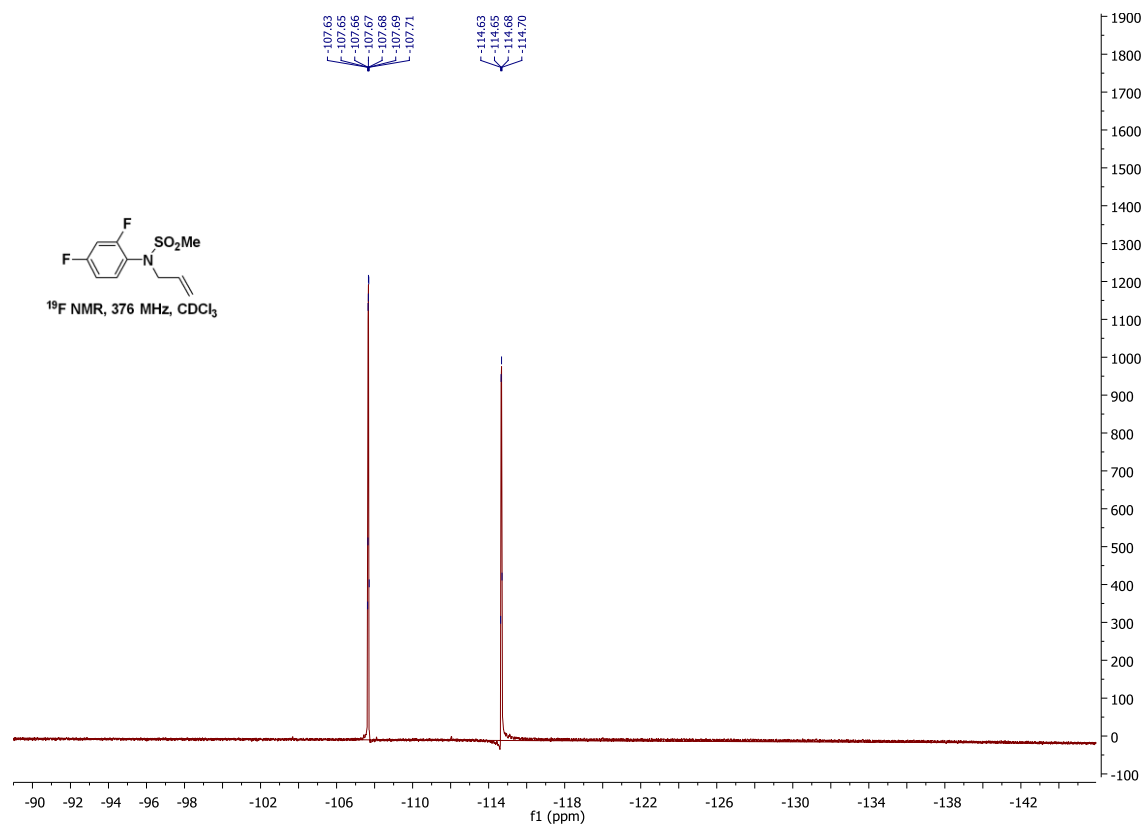
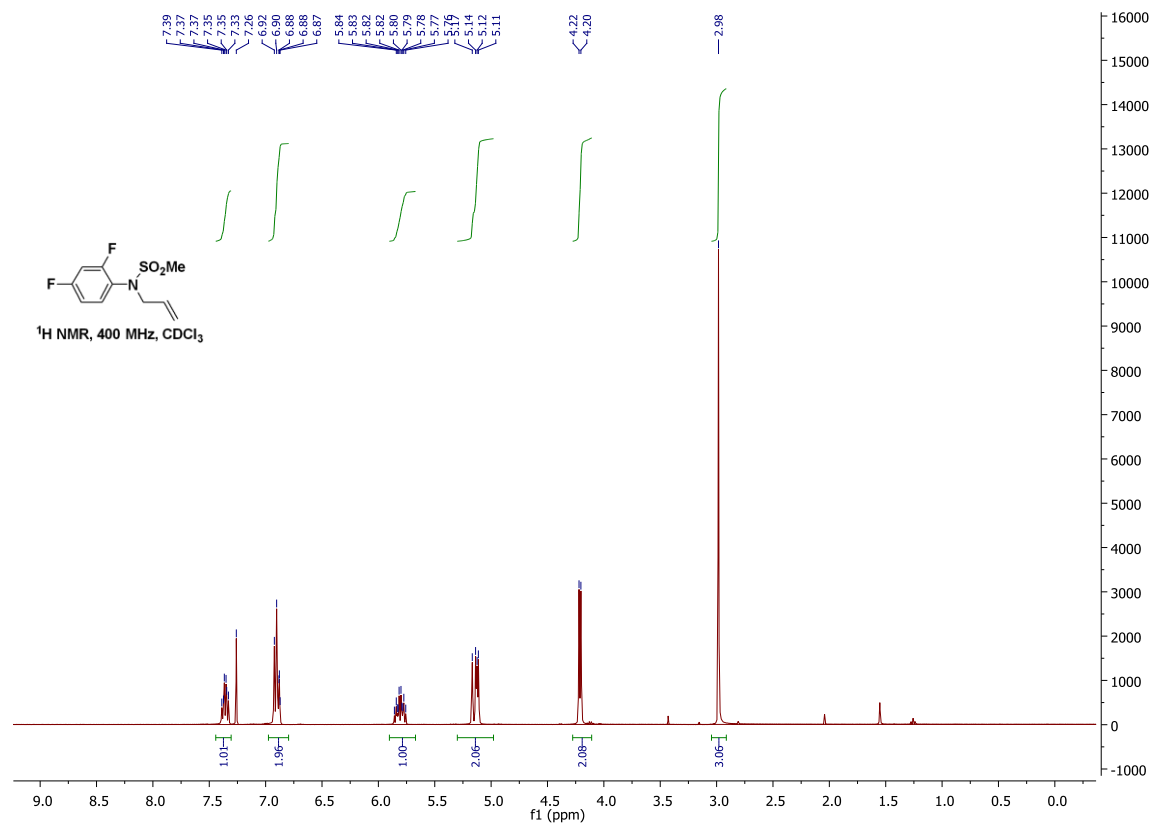
### *N*-(4-Fluorophenyl)-*N*-(2-methylallyl)methanesulfonamide (13)



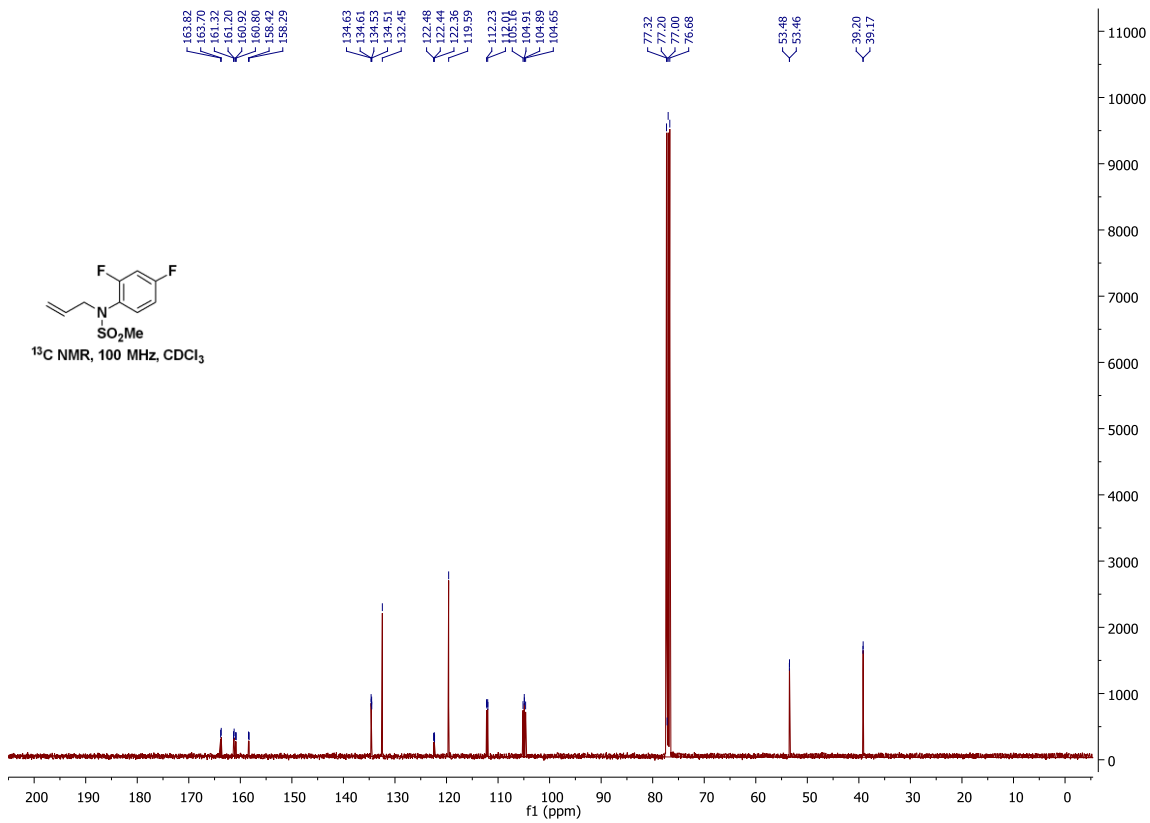
# *N*-Allyl-*N*-(3,5-difluorophenyl)methanesulfonamide (14)



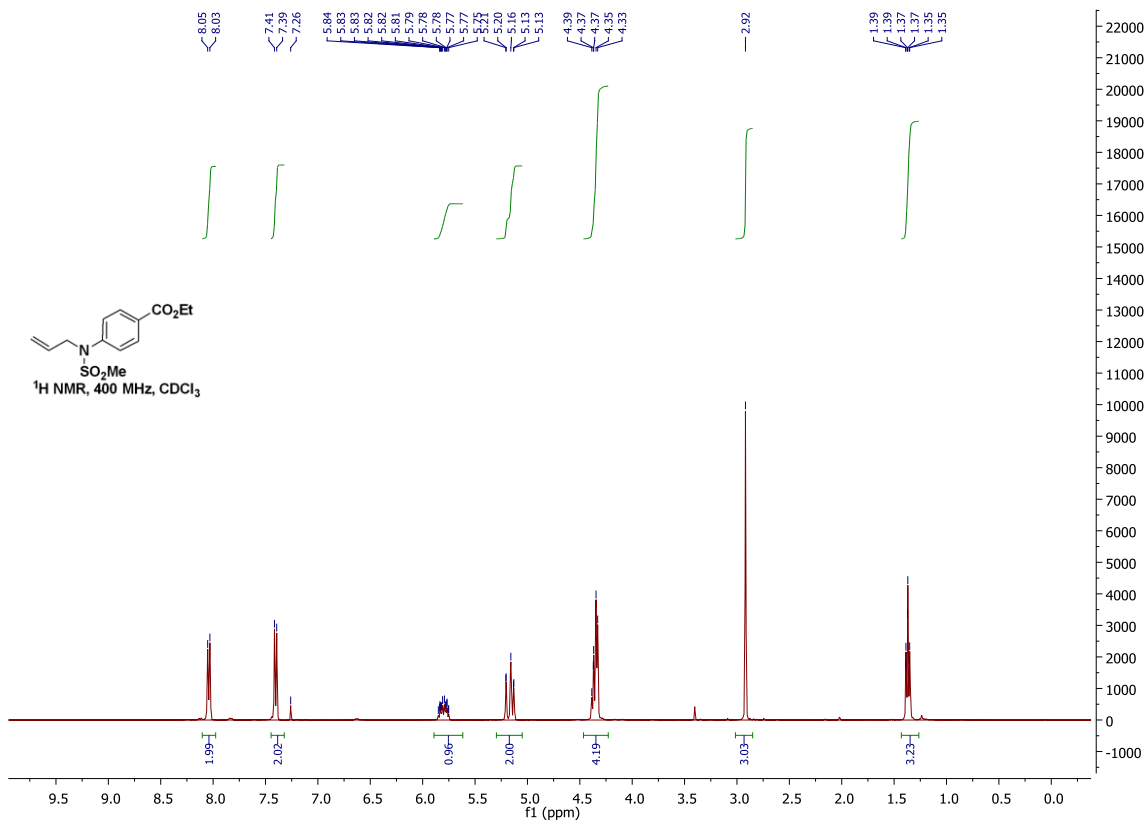
# *N*-Allyl-*N*-(2,4-difluorophenyl)methanesulfonamide (15)

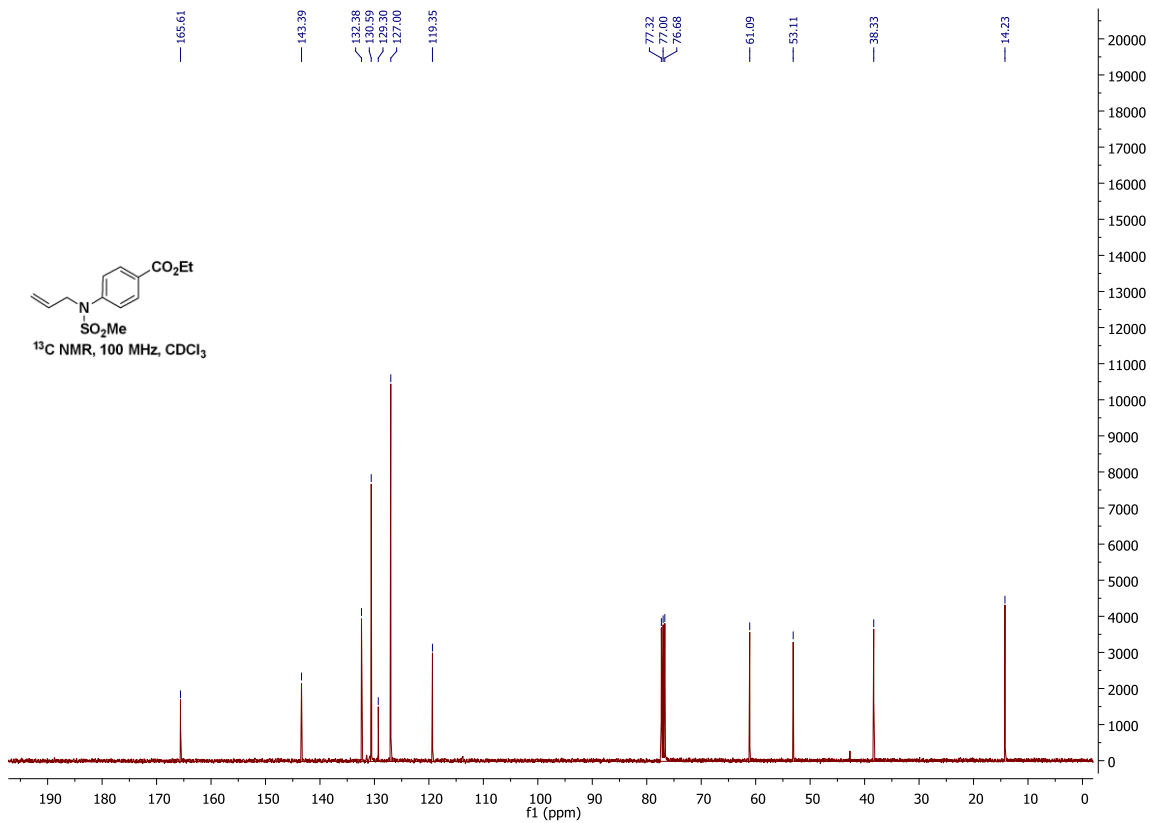




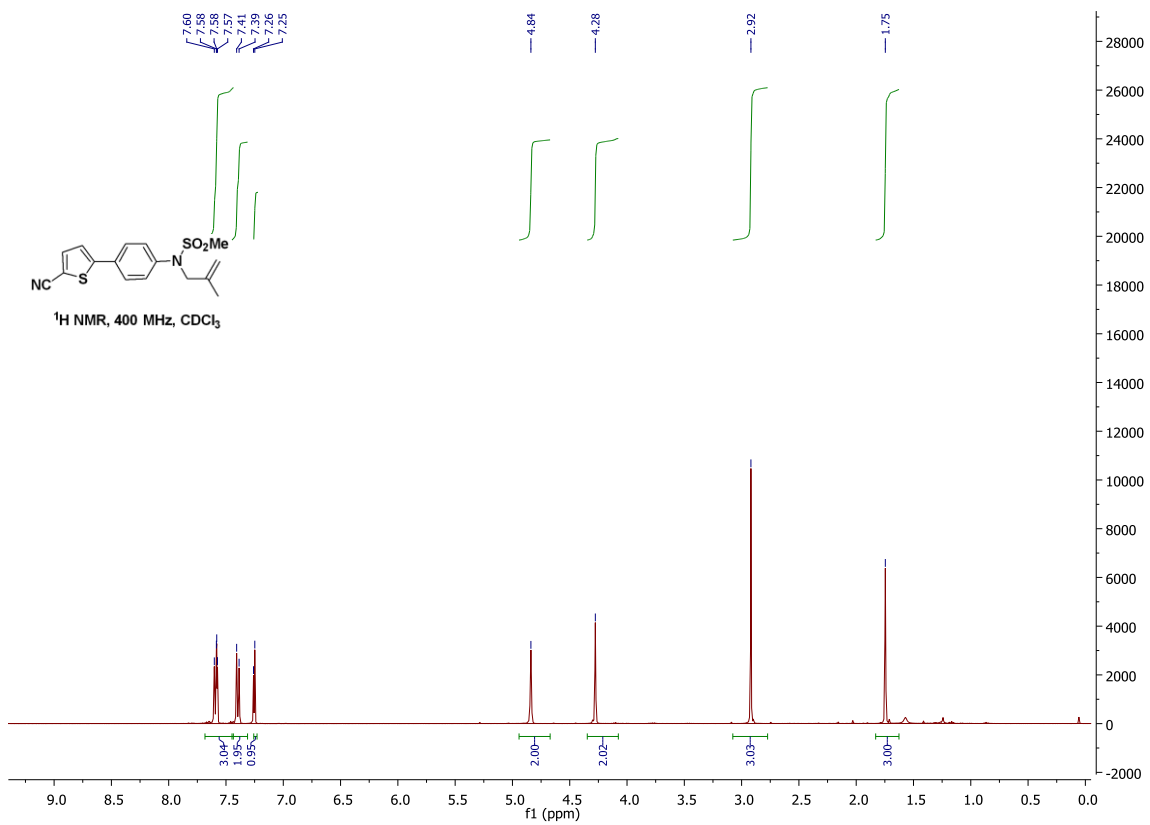


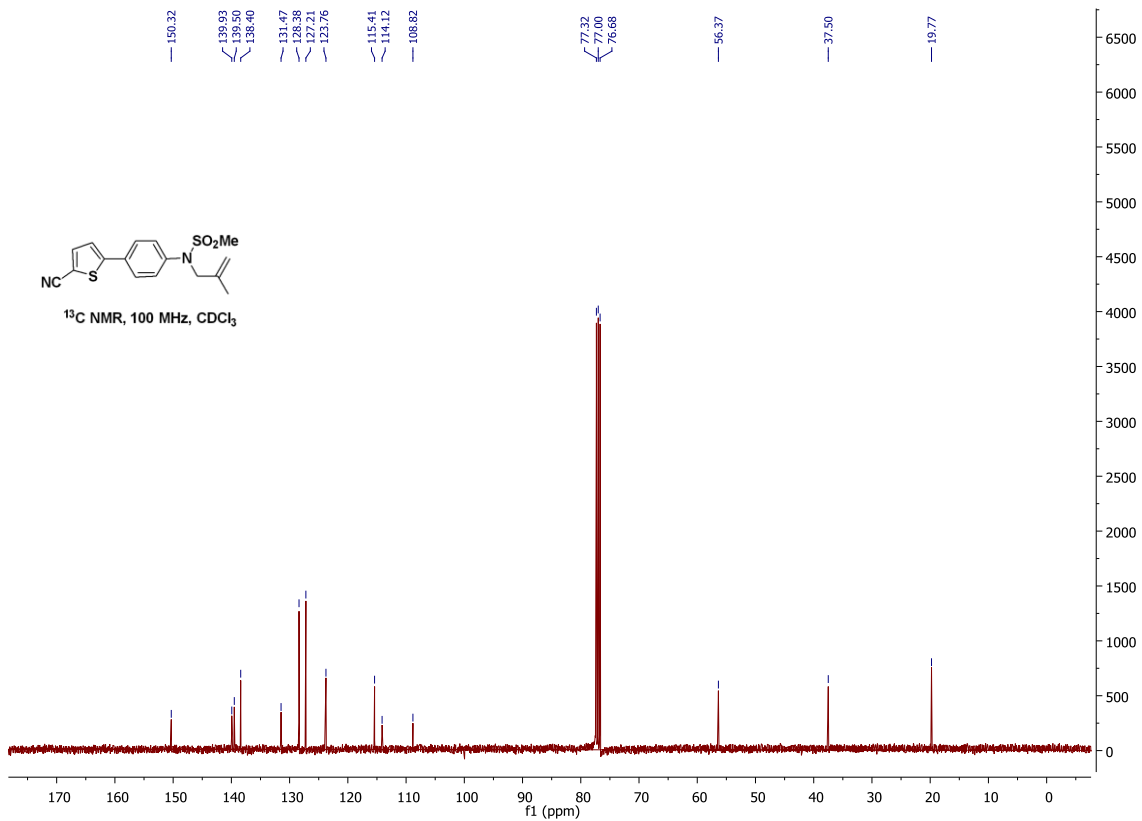
### Ethyl 4-(N-allylmethylsulfonamido)benzoate (17)



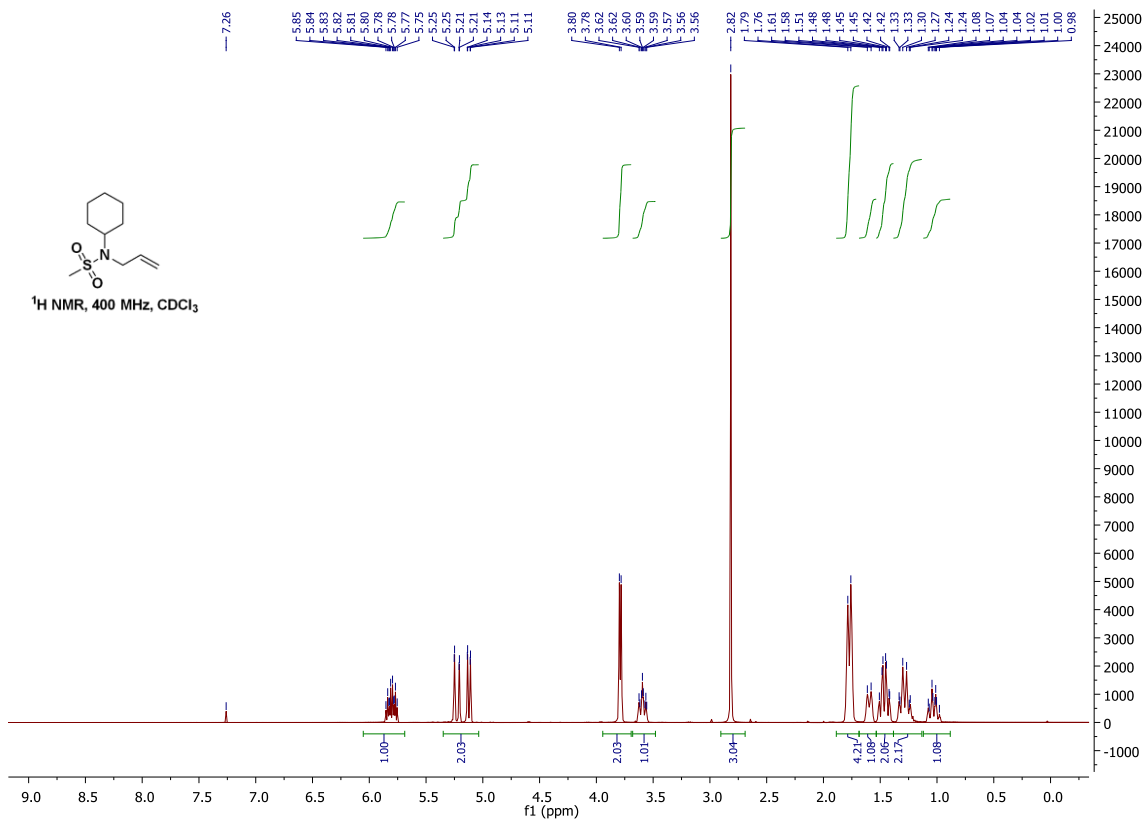


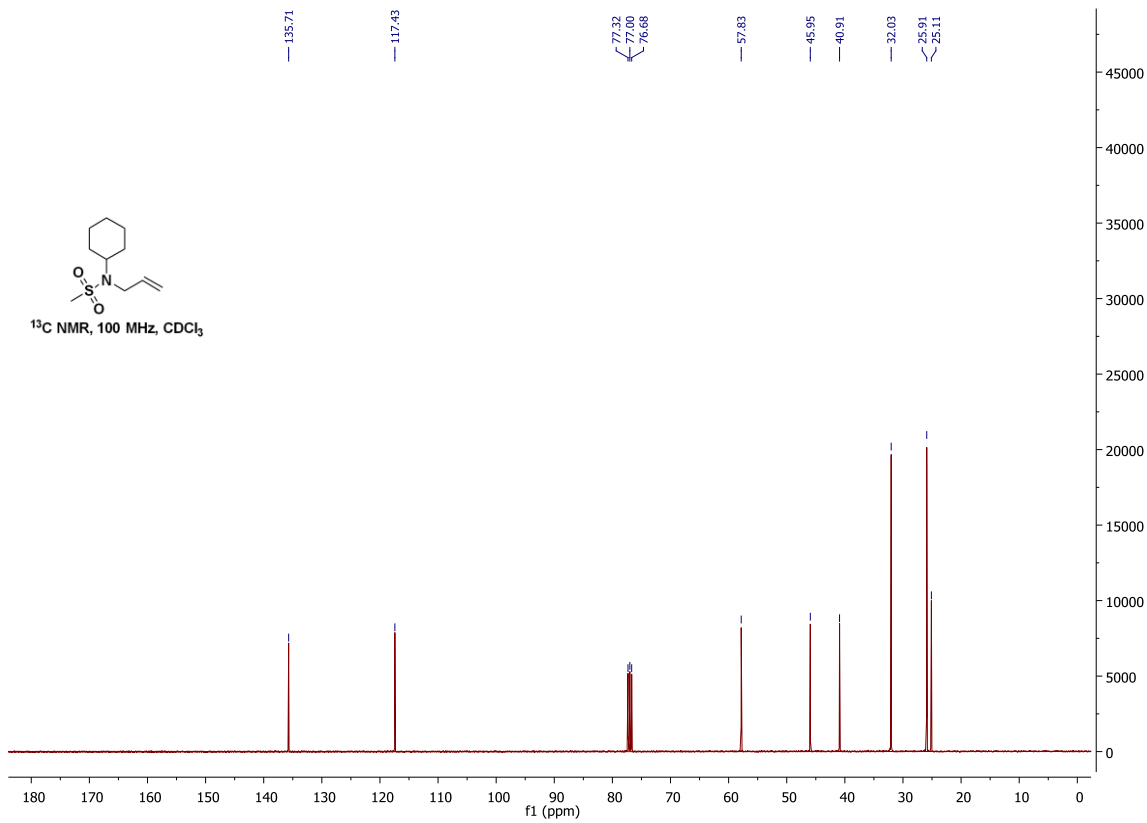
***N*-(4-(5-Cyanothiophen-2-yl)phenyl)-*N*-(2-methylallyl)methanesulfonamide (18)**



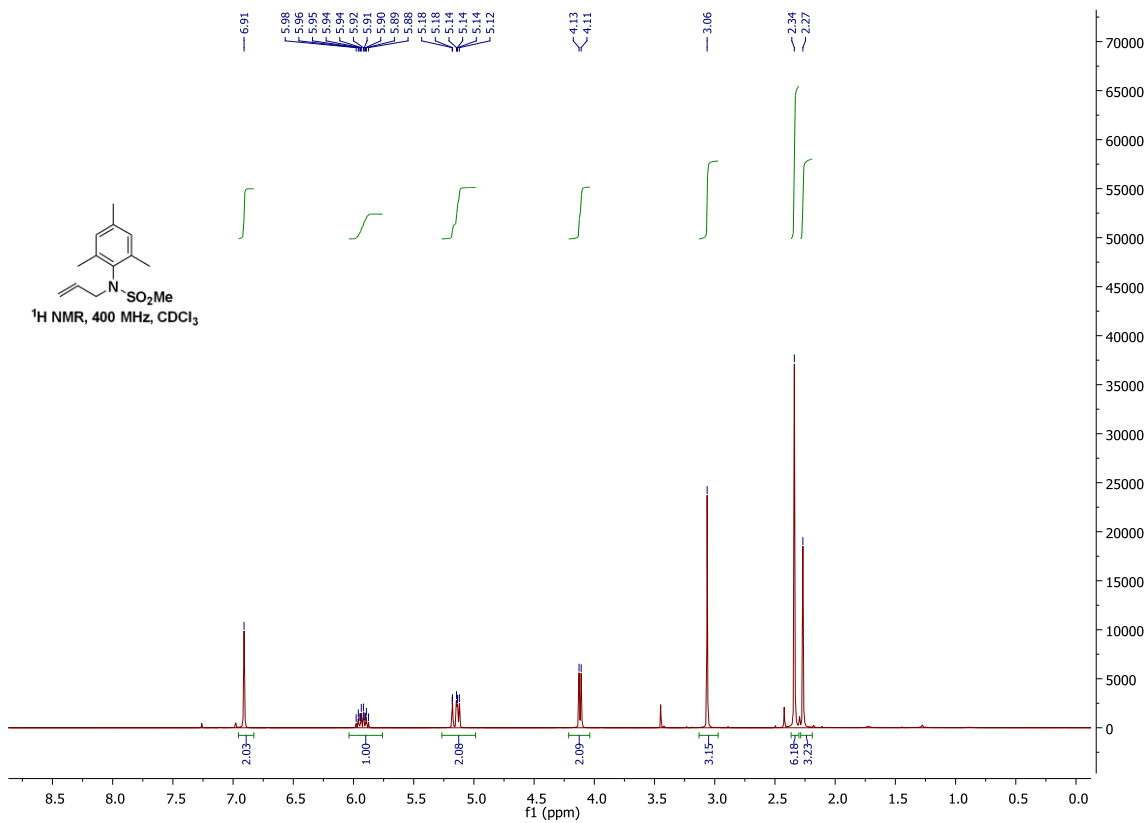


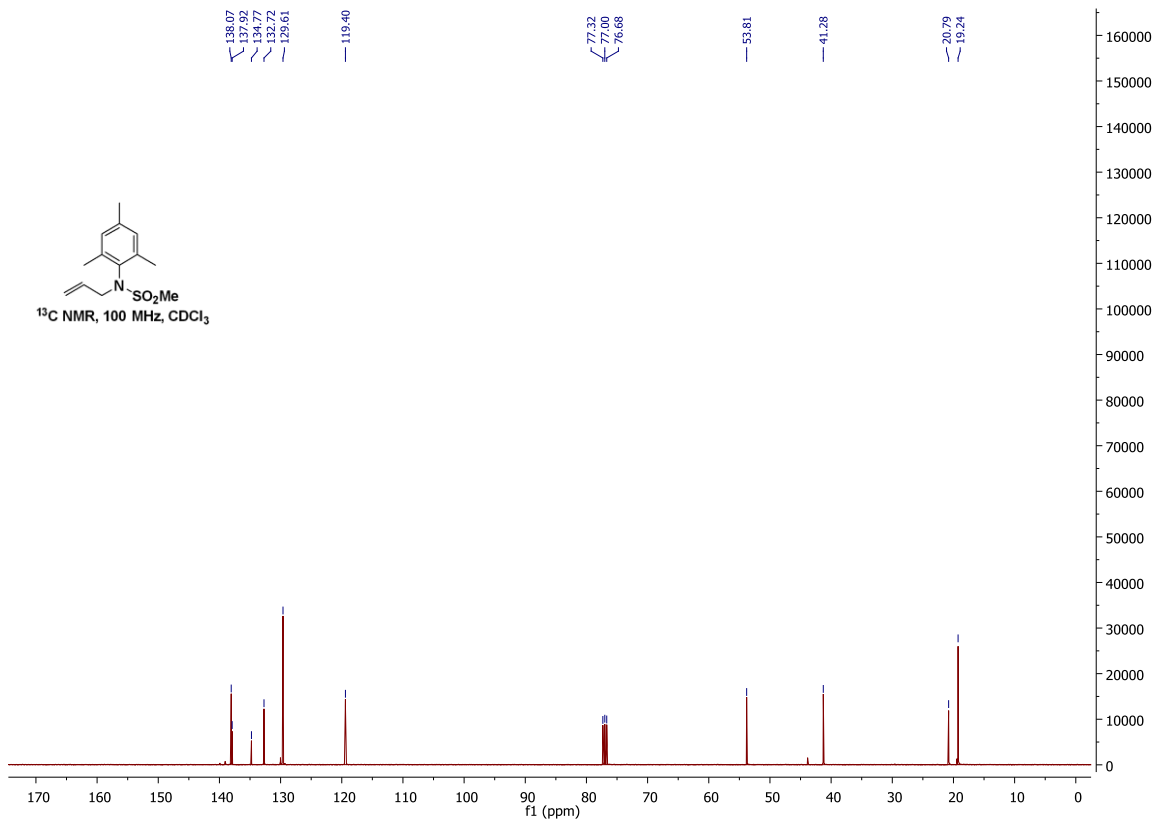
***N*-Allyl-*N*-cyclohexylmethanesulfonamide (19)**



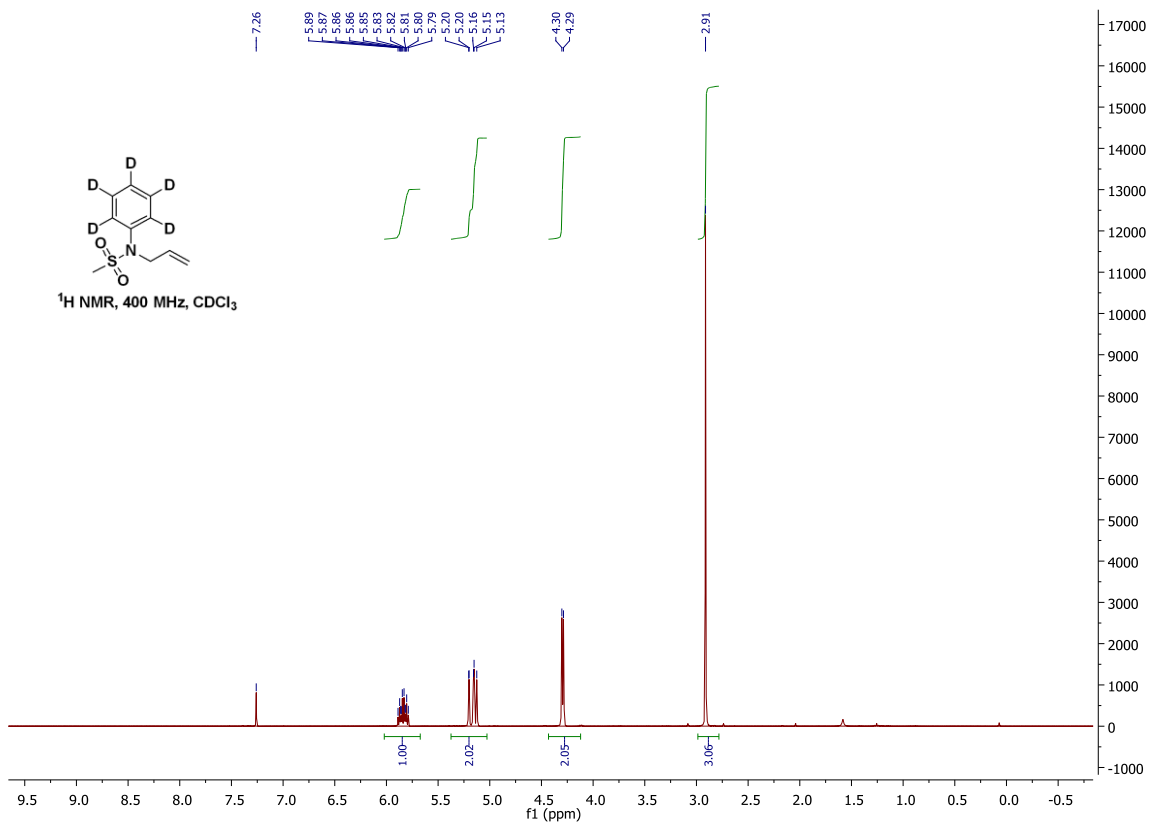


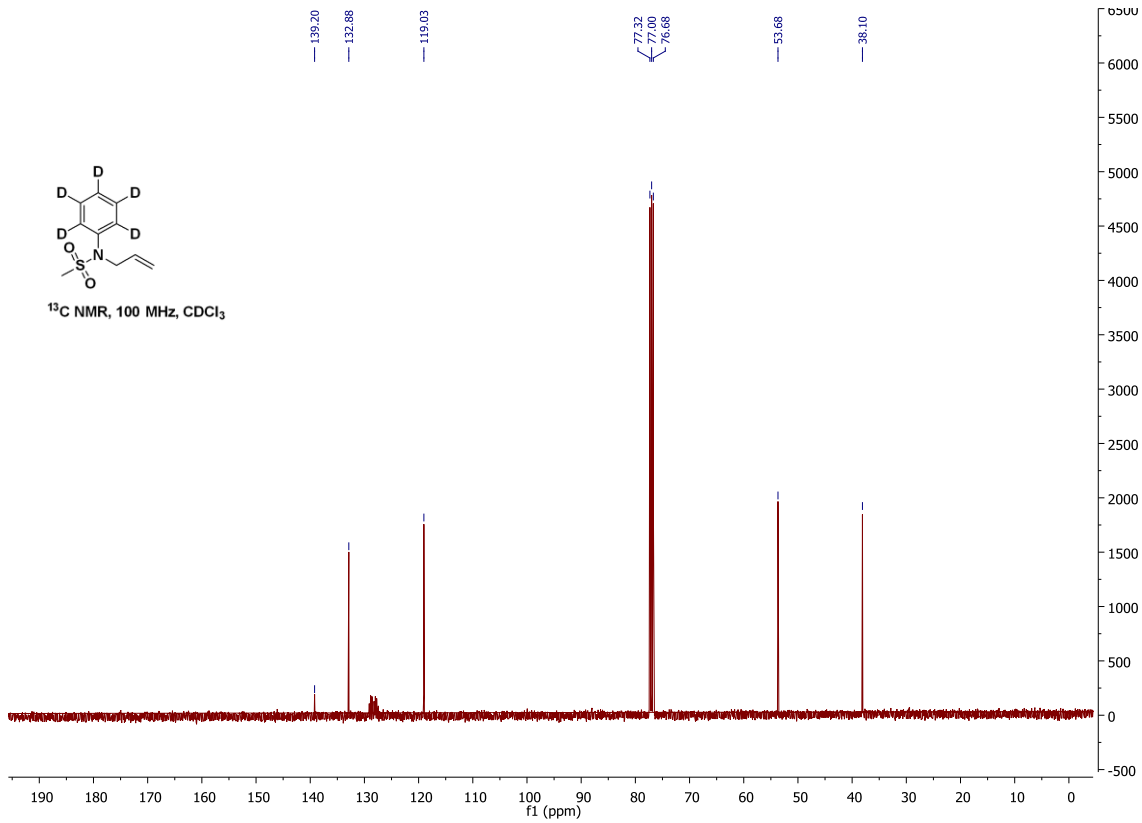
**N-Allyl-N-mesitylmethanesulfonamide (21)**



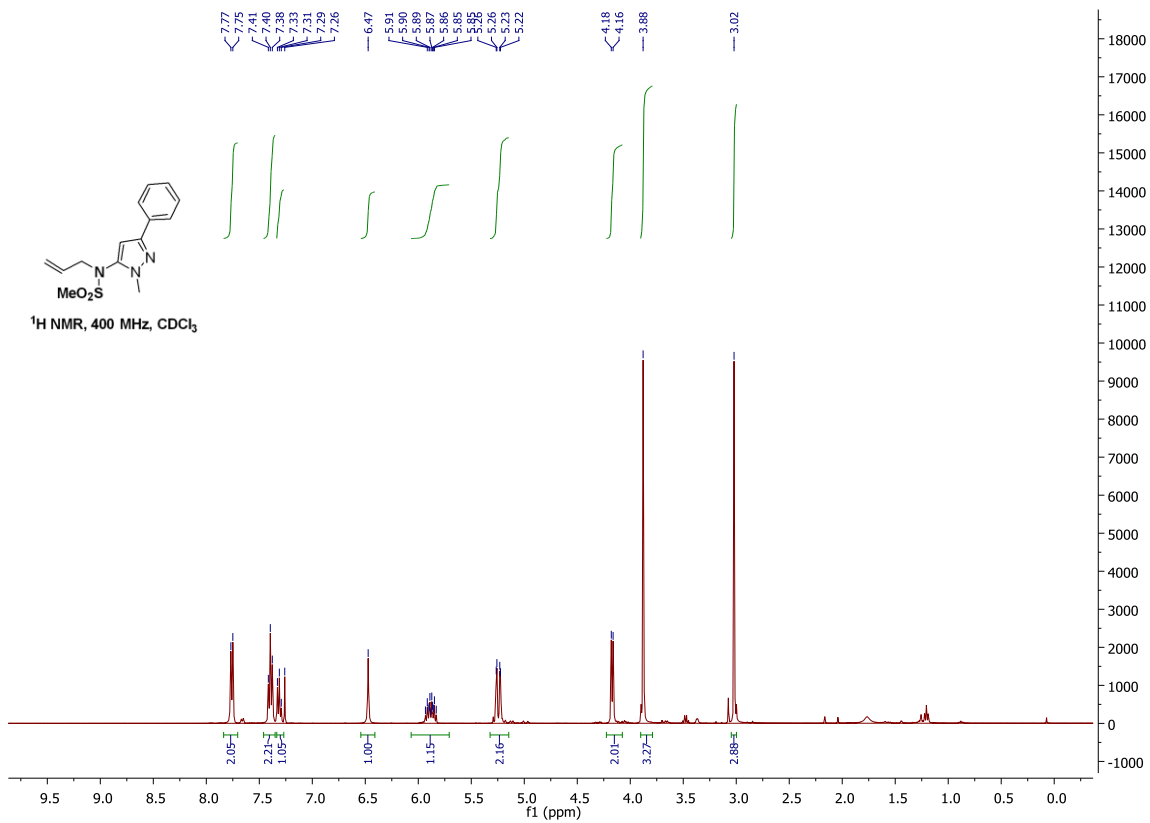


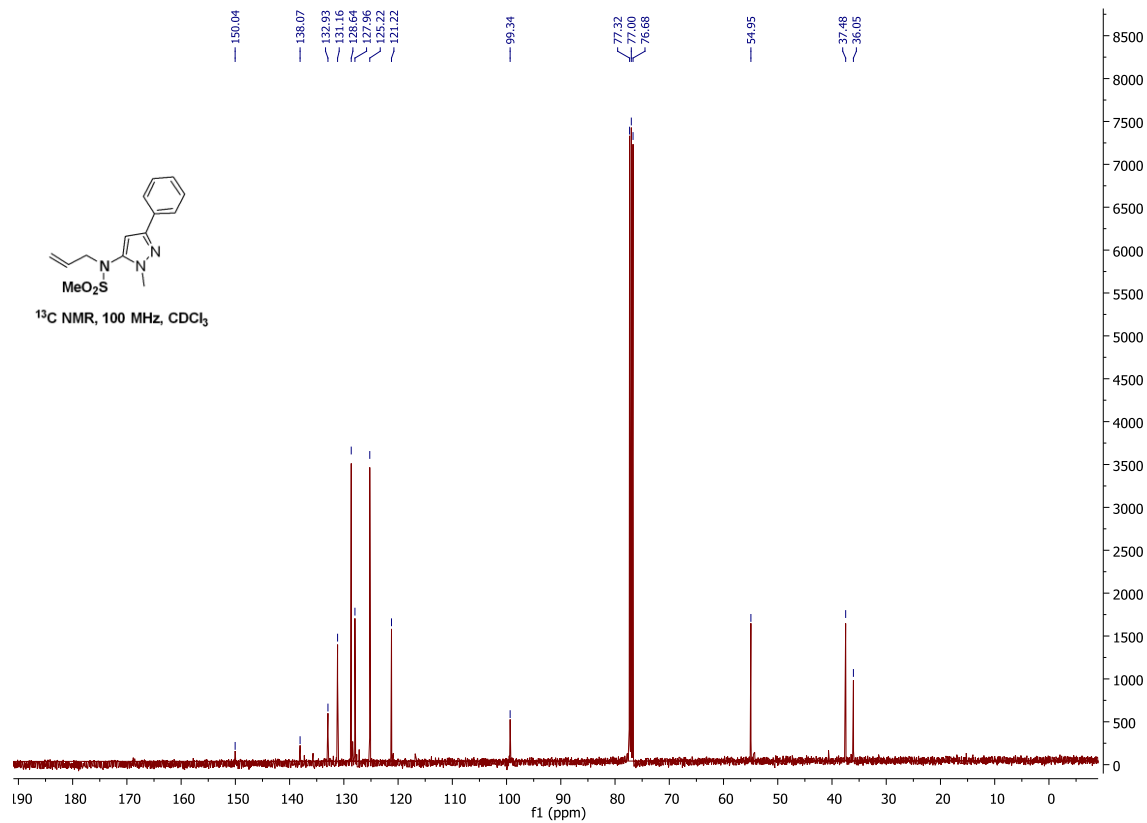
***N*-Allyl-4-methyl-*N*-methylbenzenesulfonamide *d*<sub>4</sub> (22)**



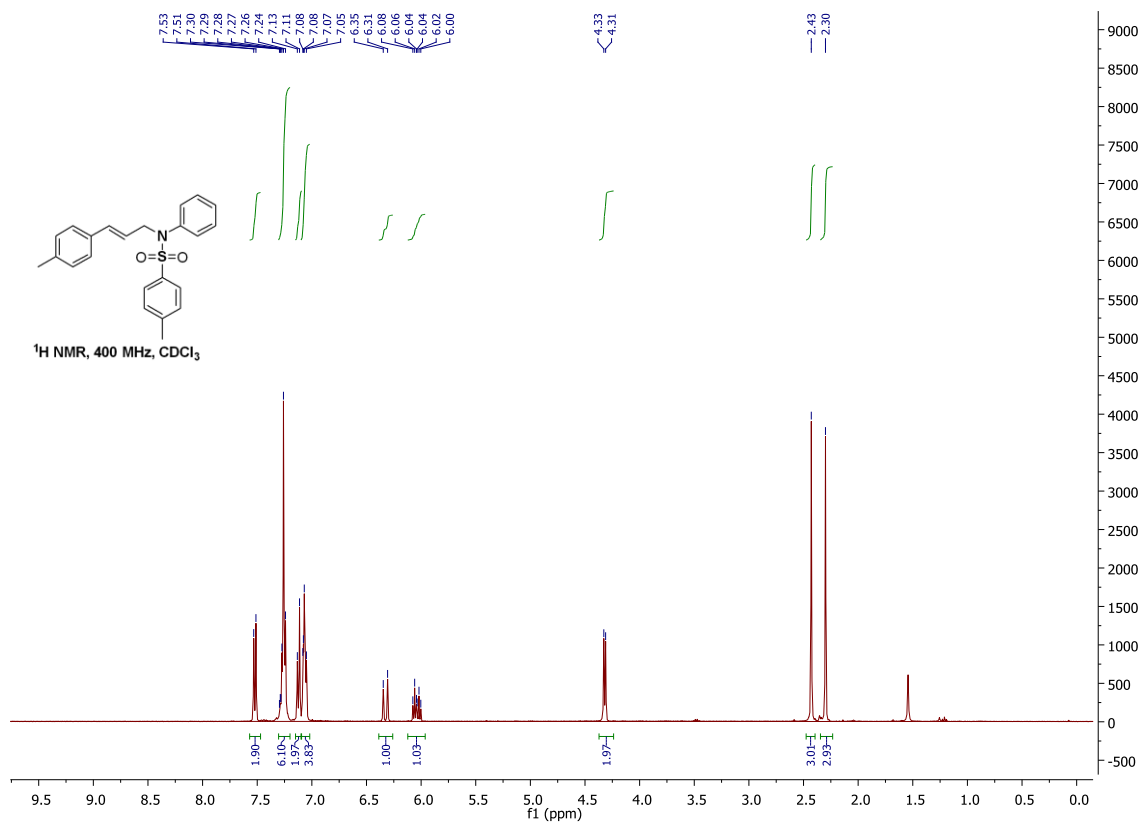


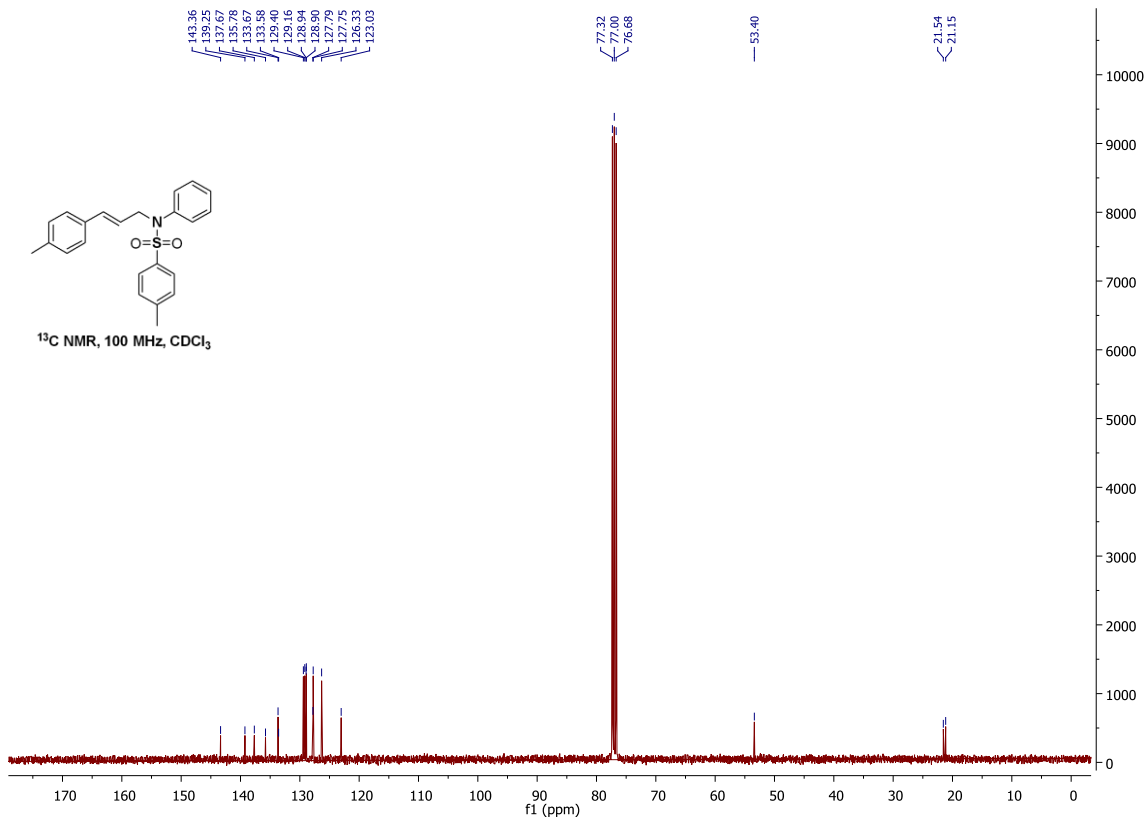
***N*-Allyl-*N*-(1-methyl-3-phenylpyrazol-5-yl)methanesulfonamide (54)**



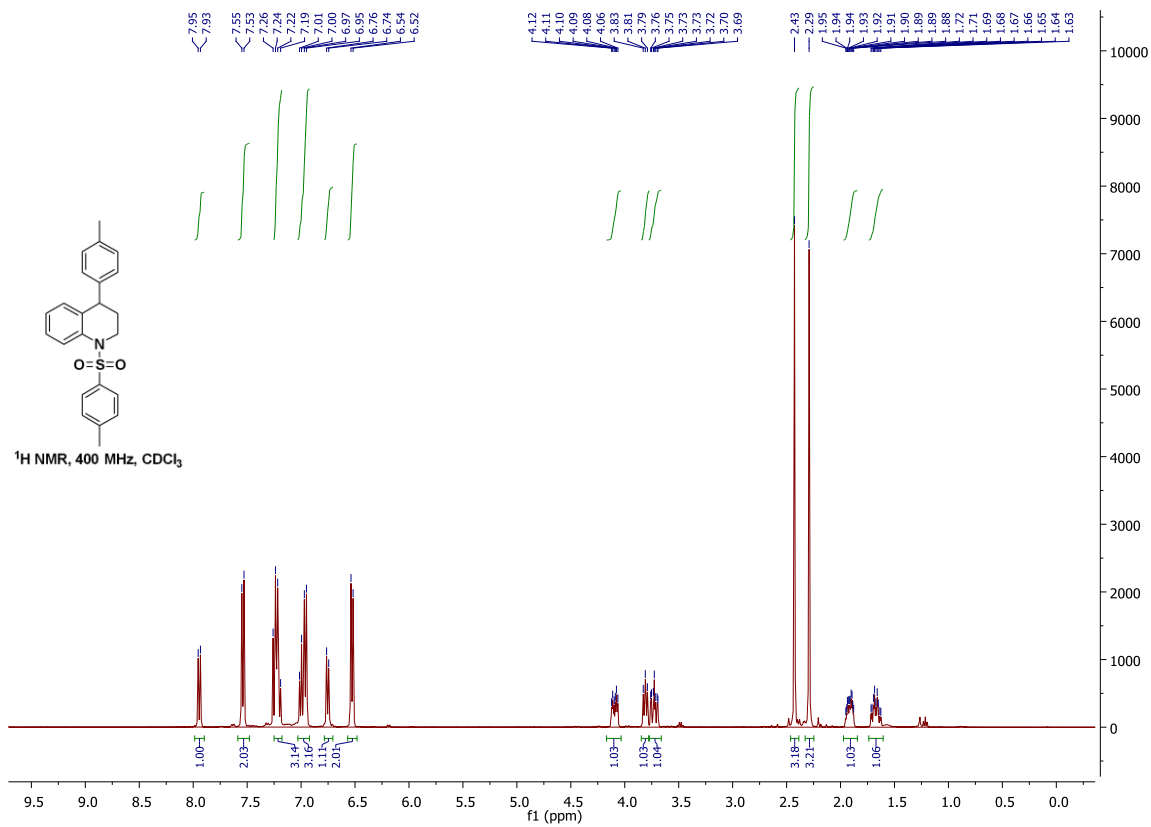


**(E)-4-Methyl-N-phenyl-N-(3-p-tolylallyl)benzenesulfonamide (23)**

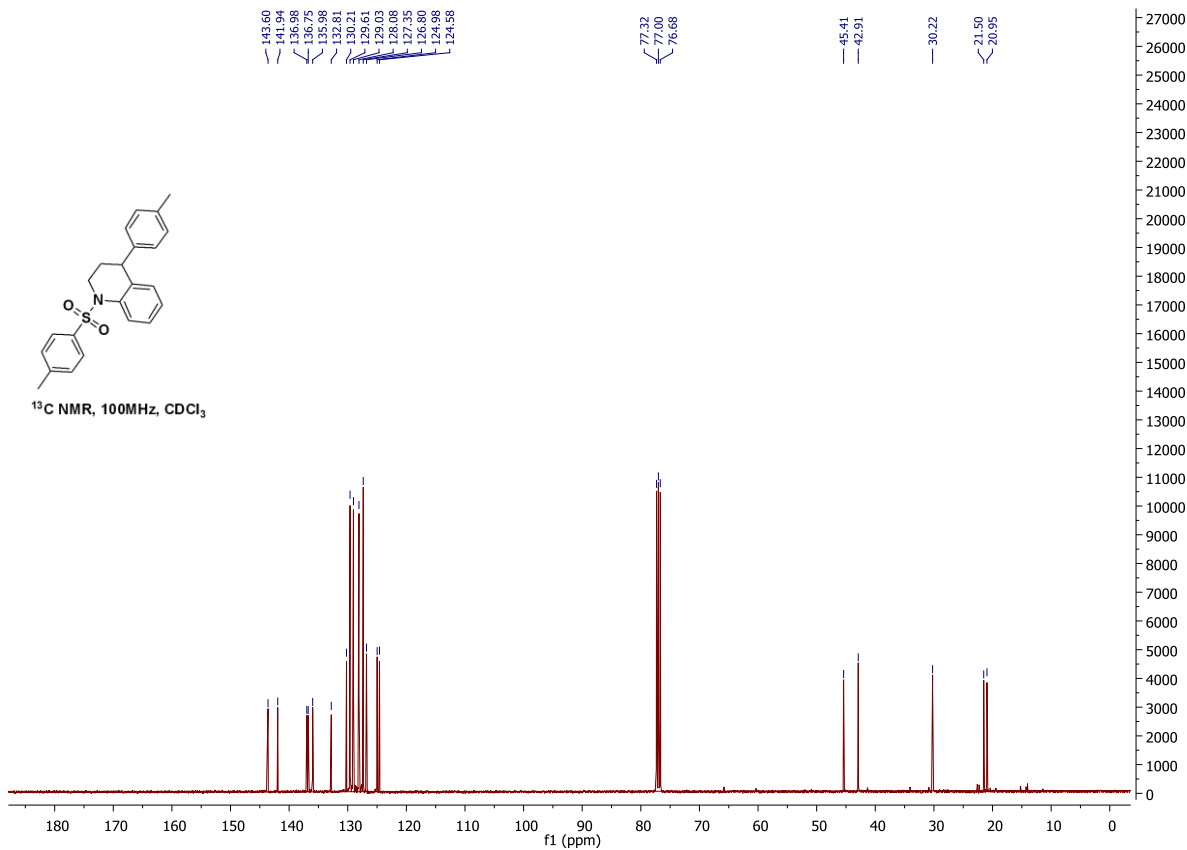




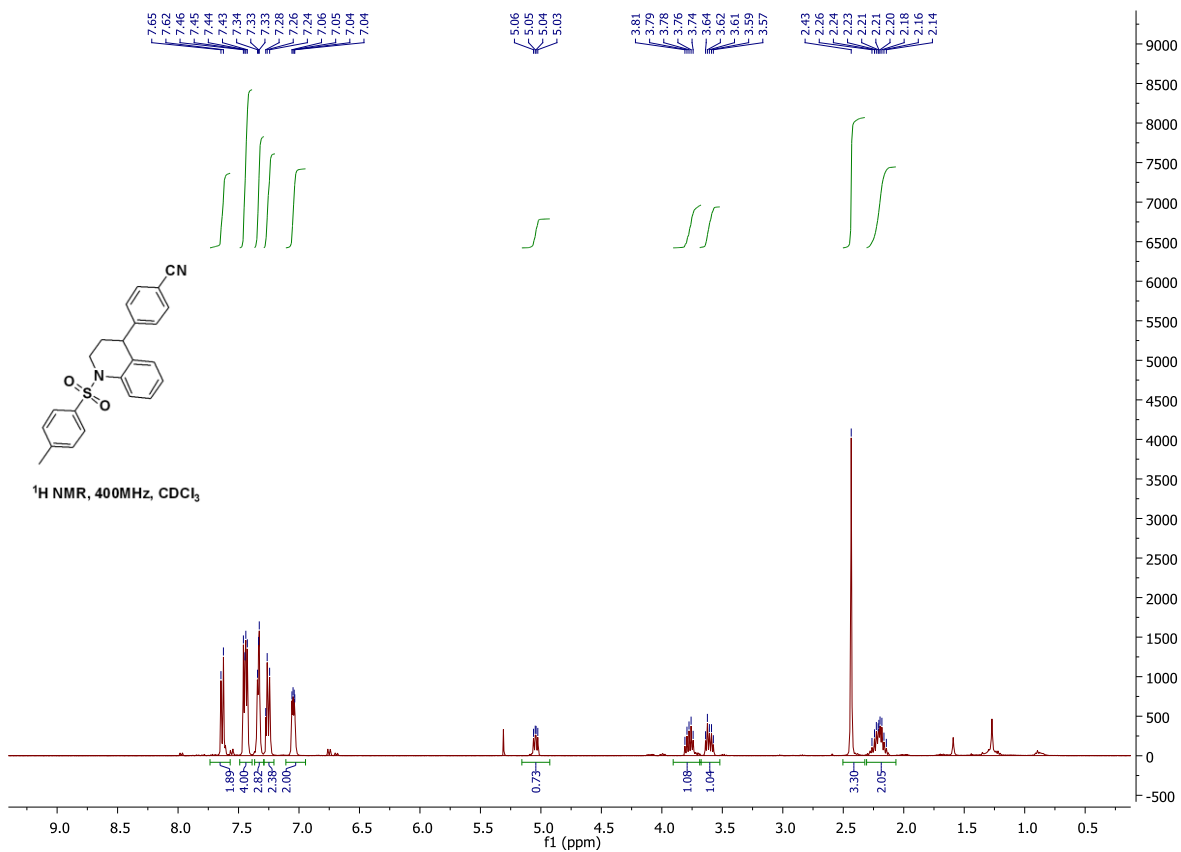
**4-p-Tolyl-1-tosyl-1,2,3,4-tetrahydroquinoline (24)**

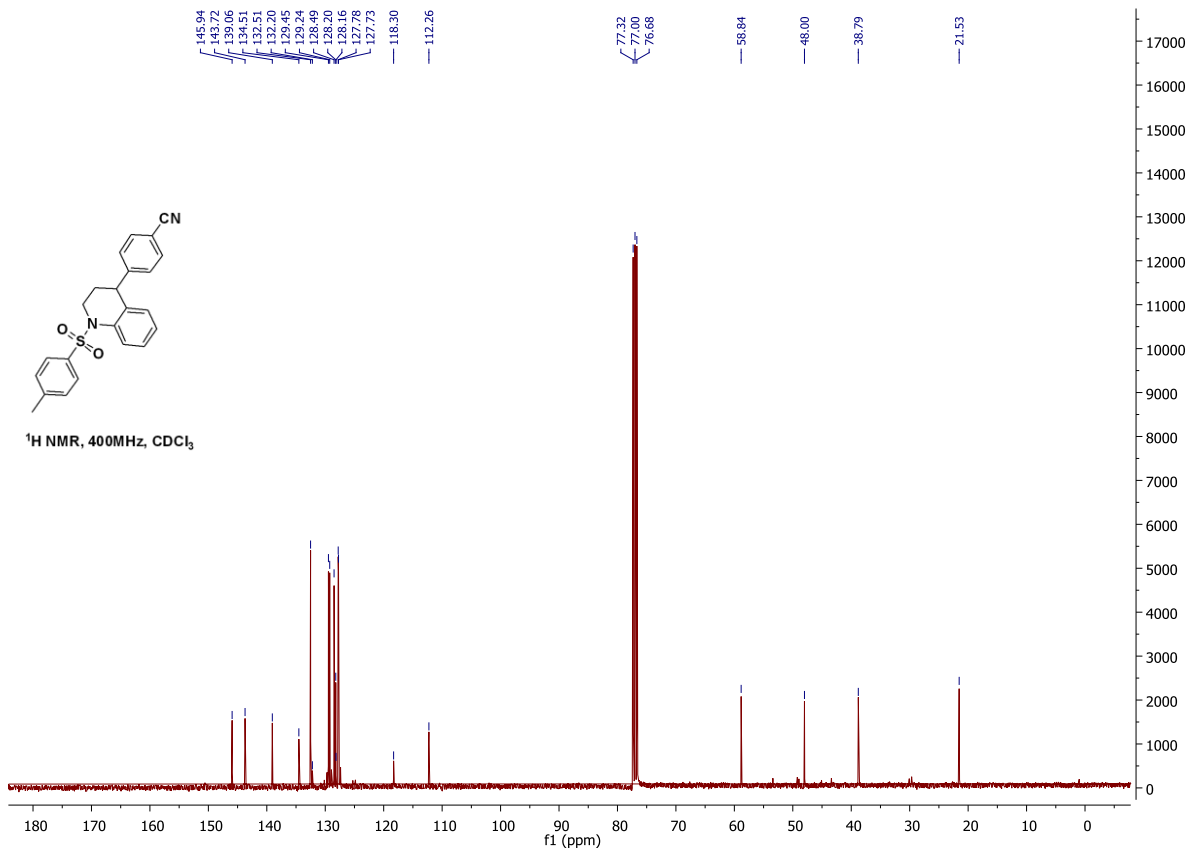




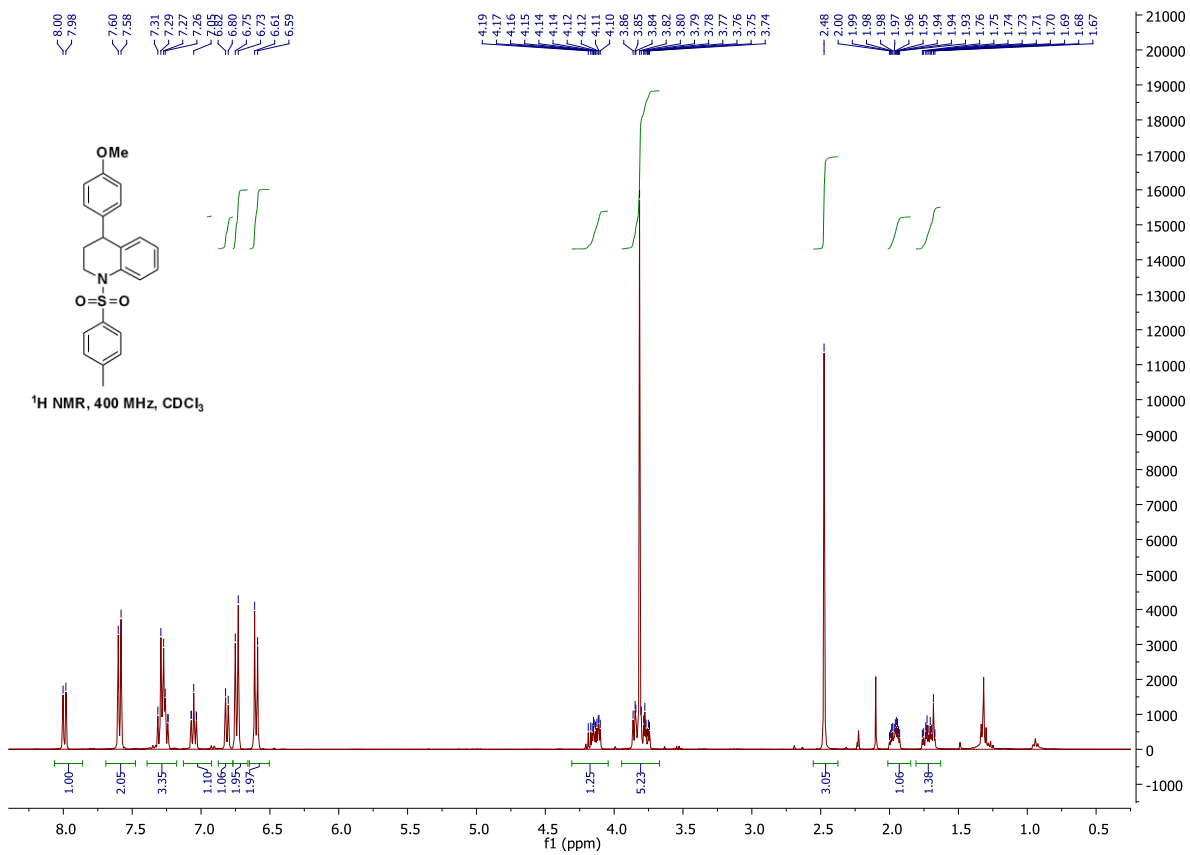


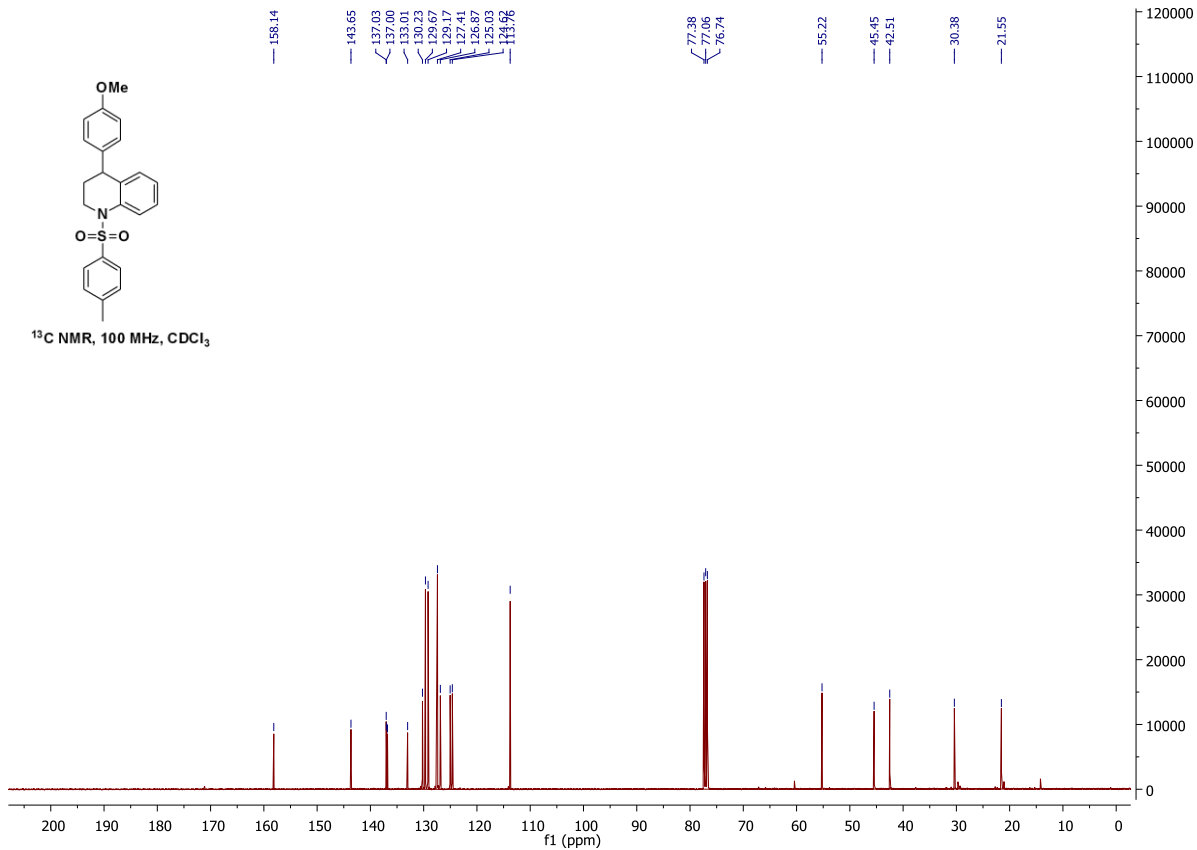
**4-(1-Tosyl-1,2,3,4-tetrahydroquinolin-4-yl)benzonitrile (25)**



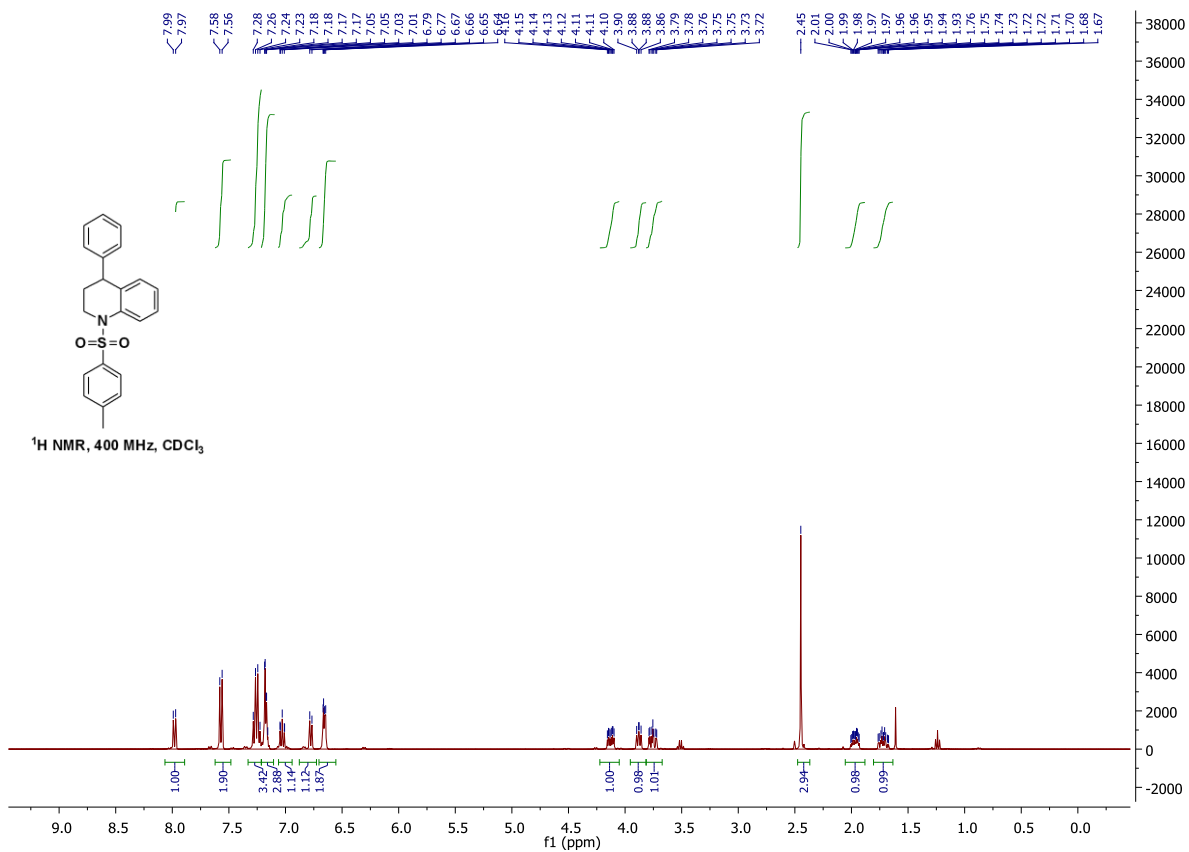


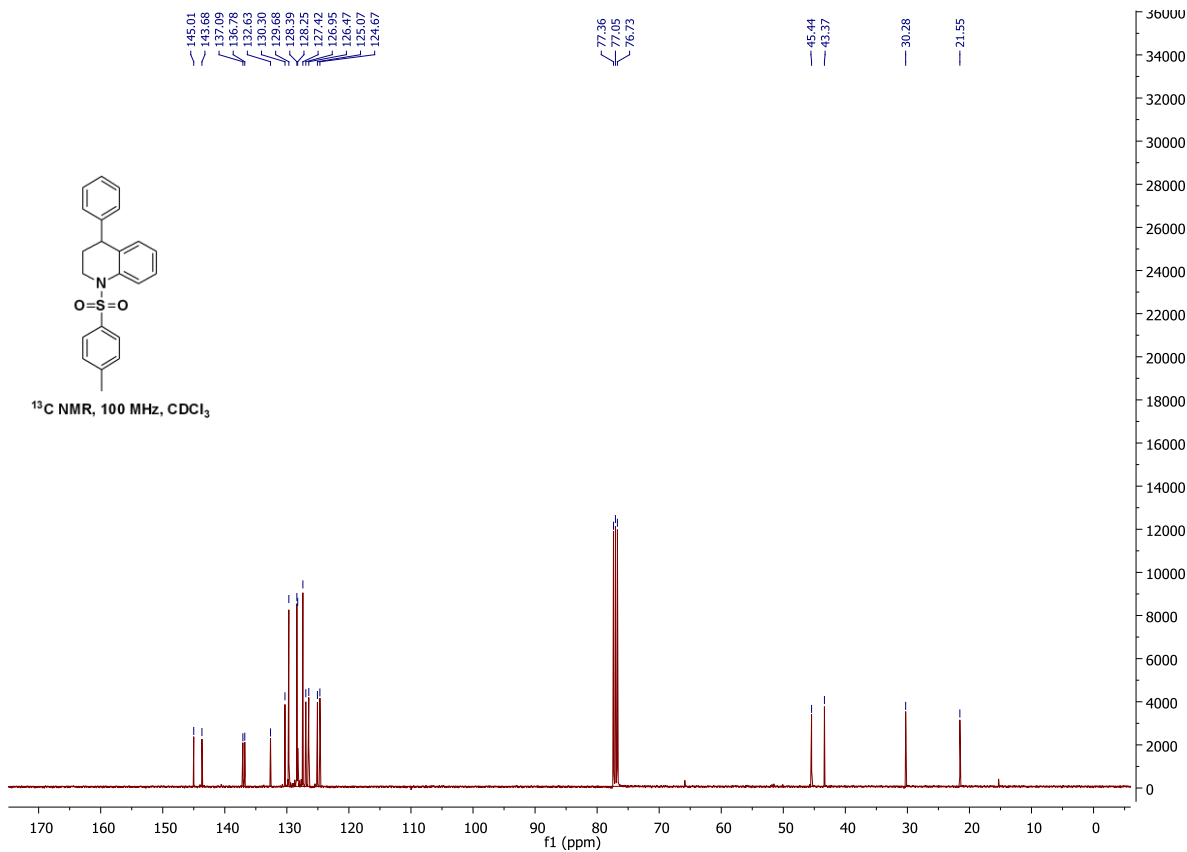
**4-(4-Methoxyphenyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (26)**



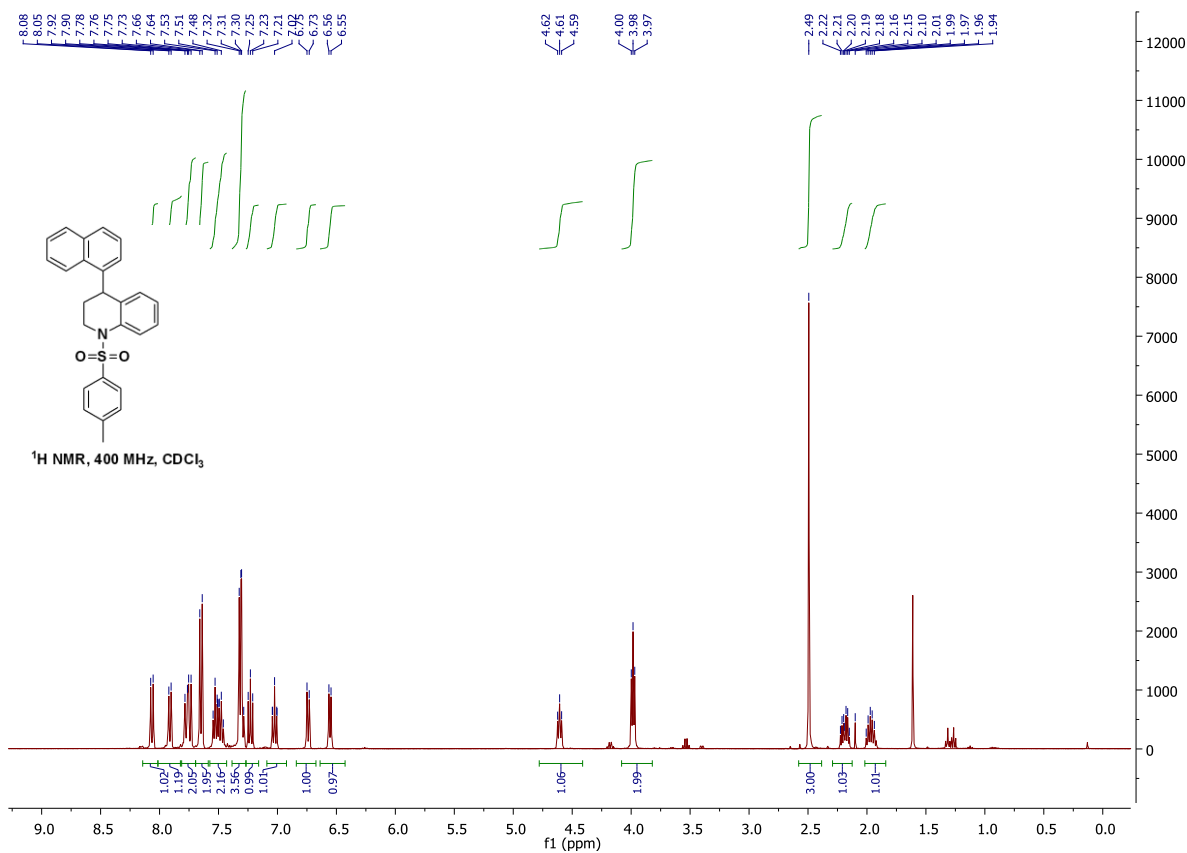


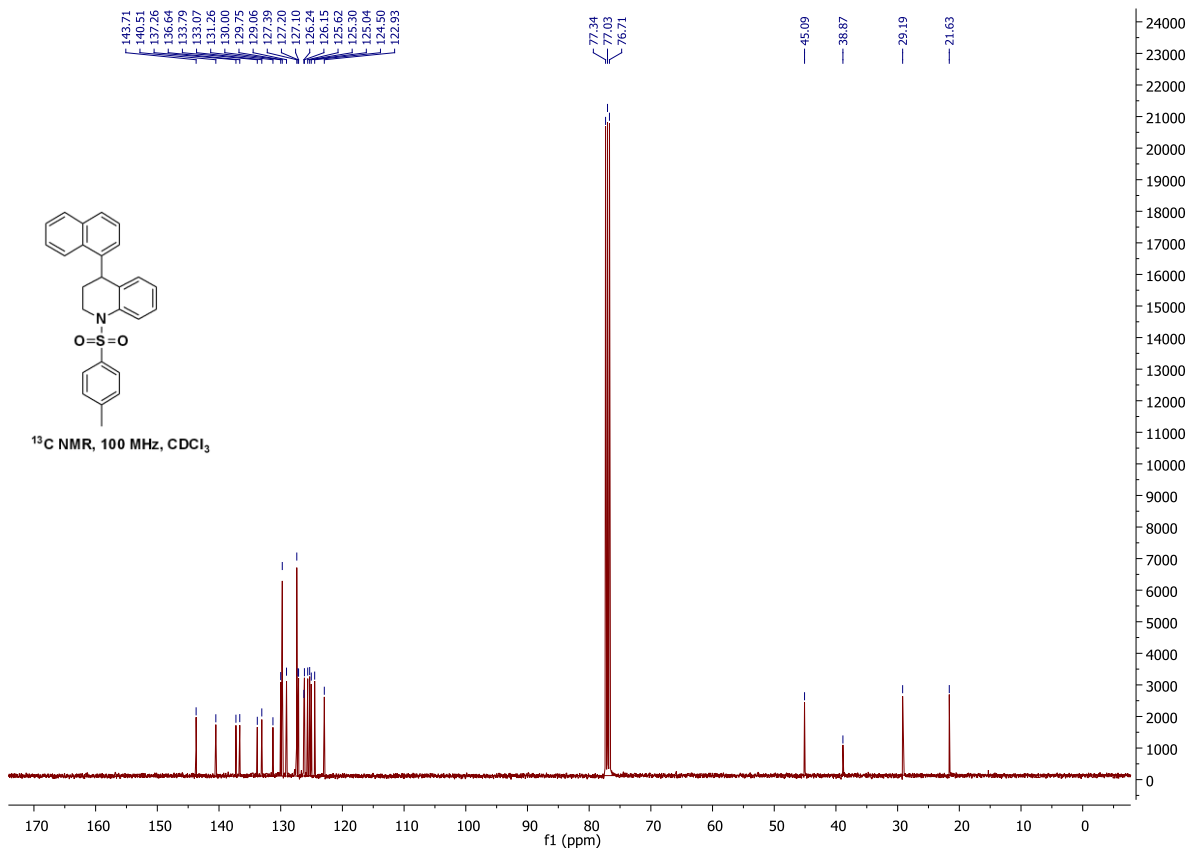
**4-Phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (27)**



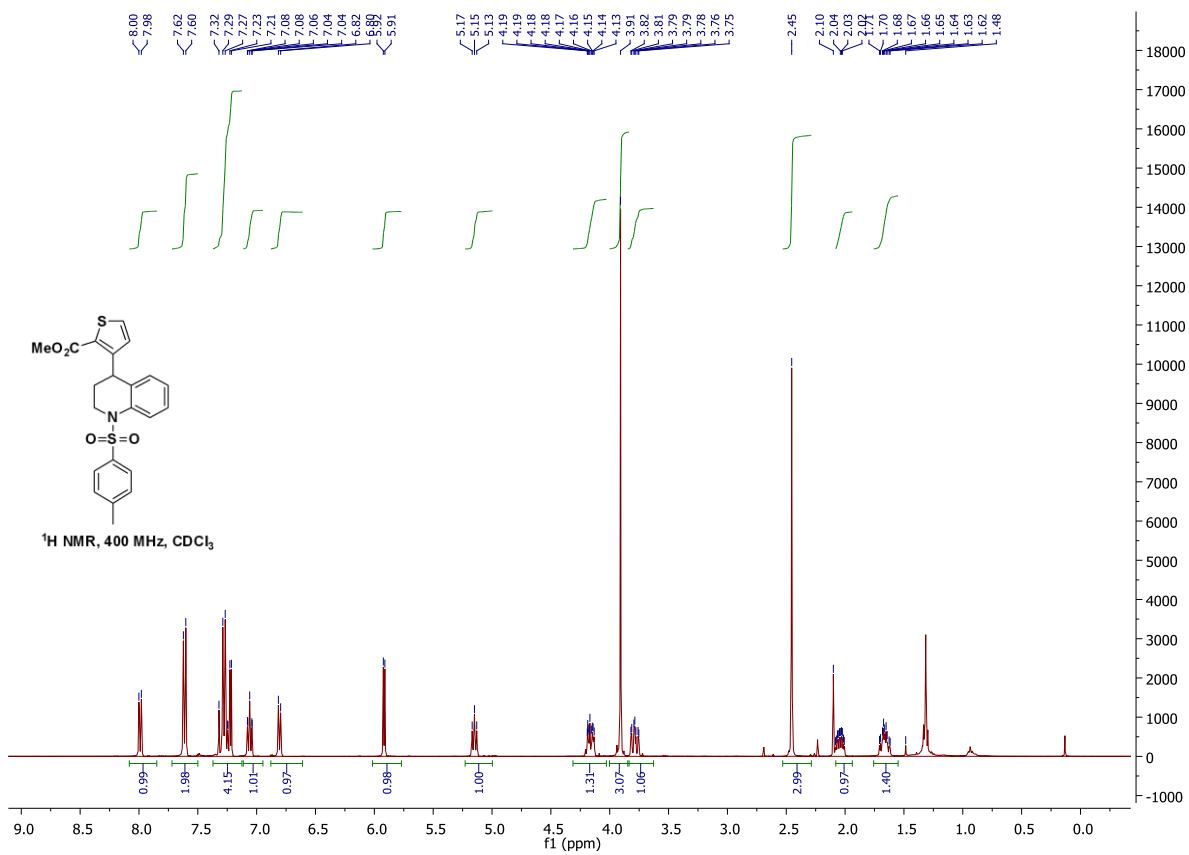


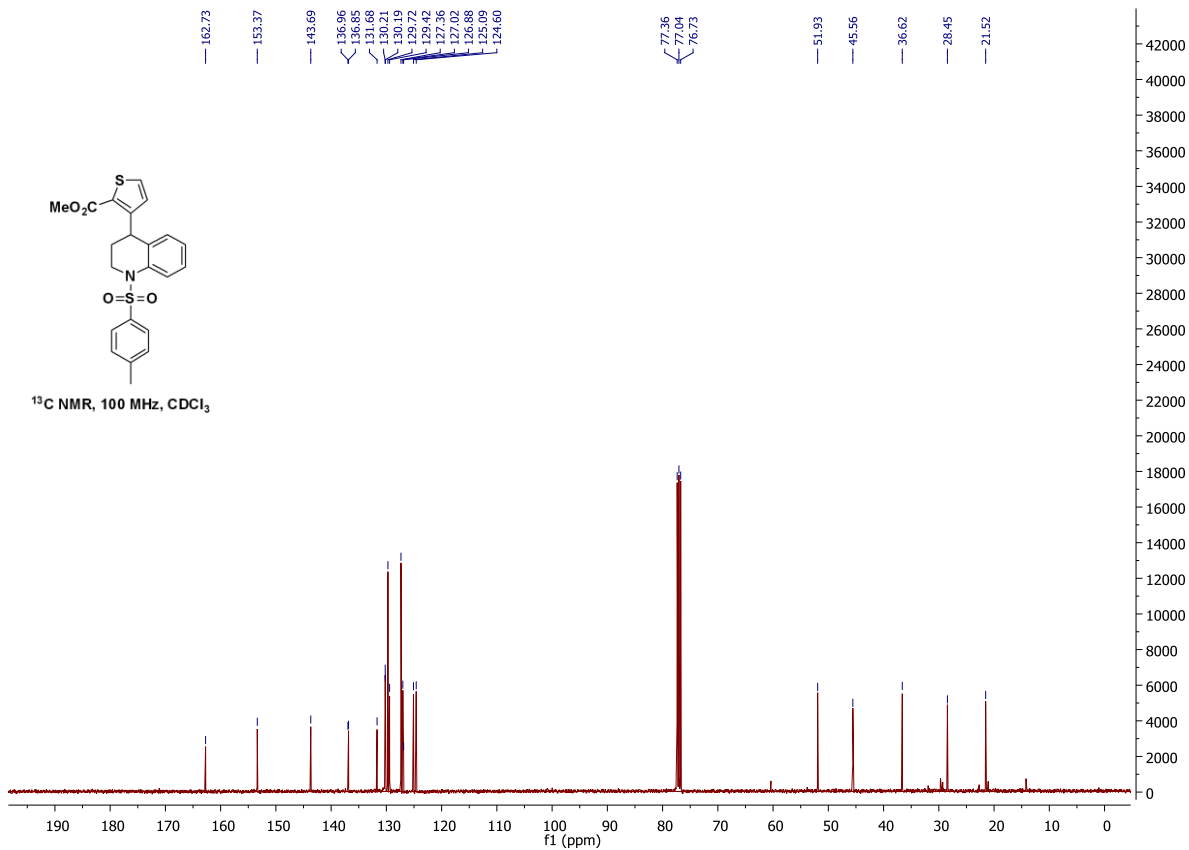
**4-(Naphthalen-1-yl)-1-tosyl-1,2,3,4-tetrahydroquinoline (28)**



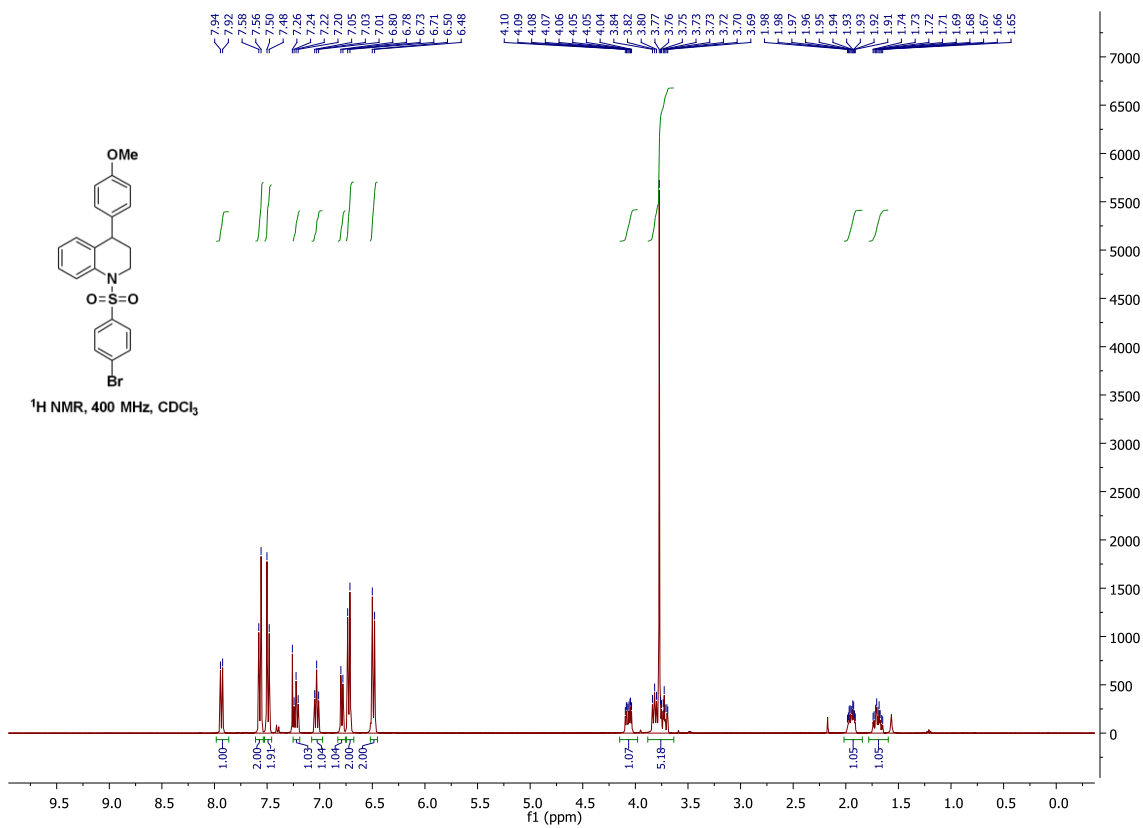


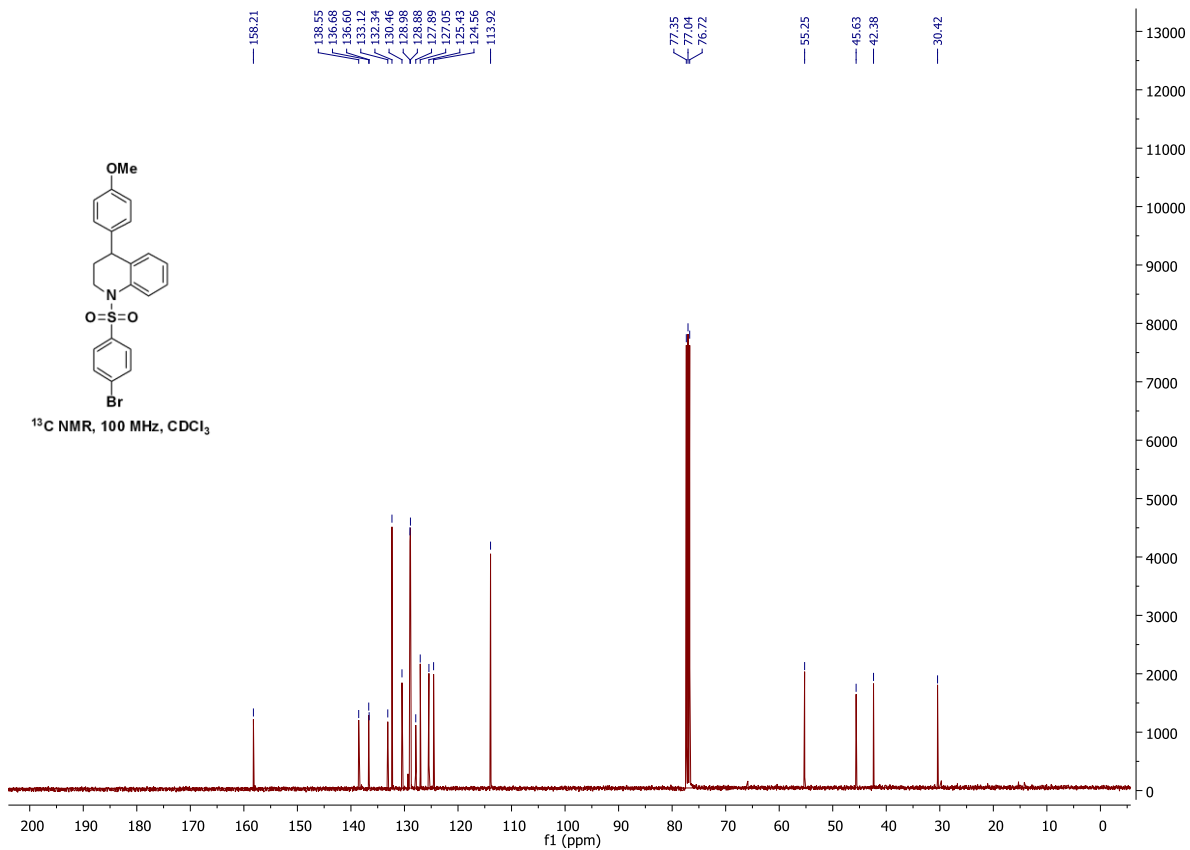
**Methyl 3-(1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl)thiophene-2-carboxylate (29)**



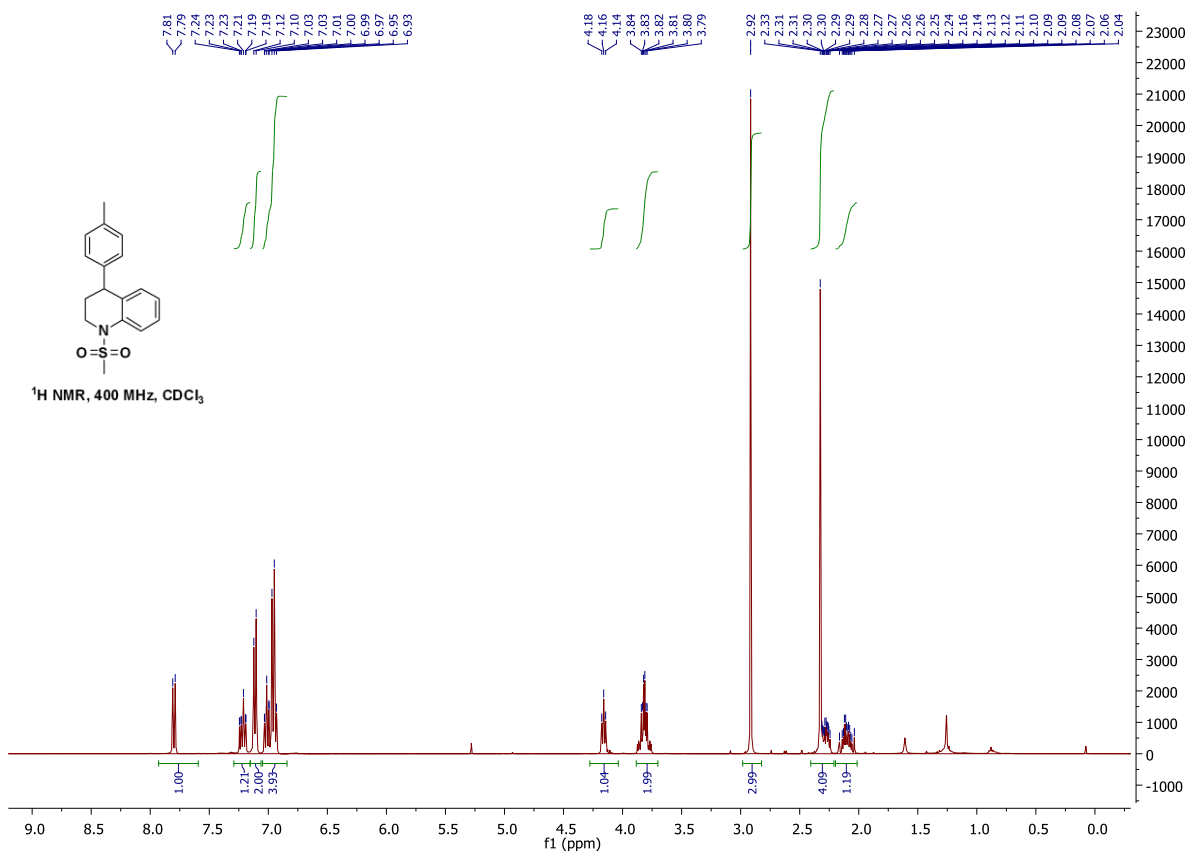


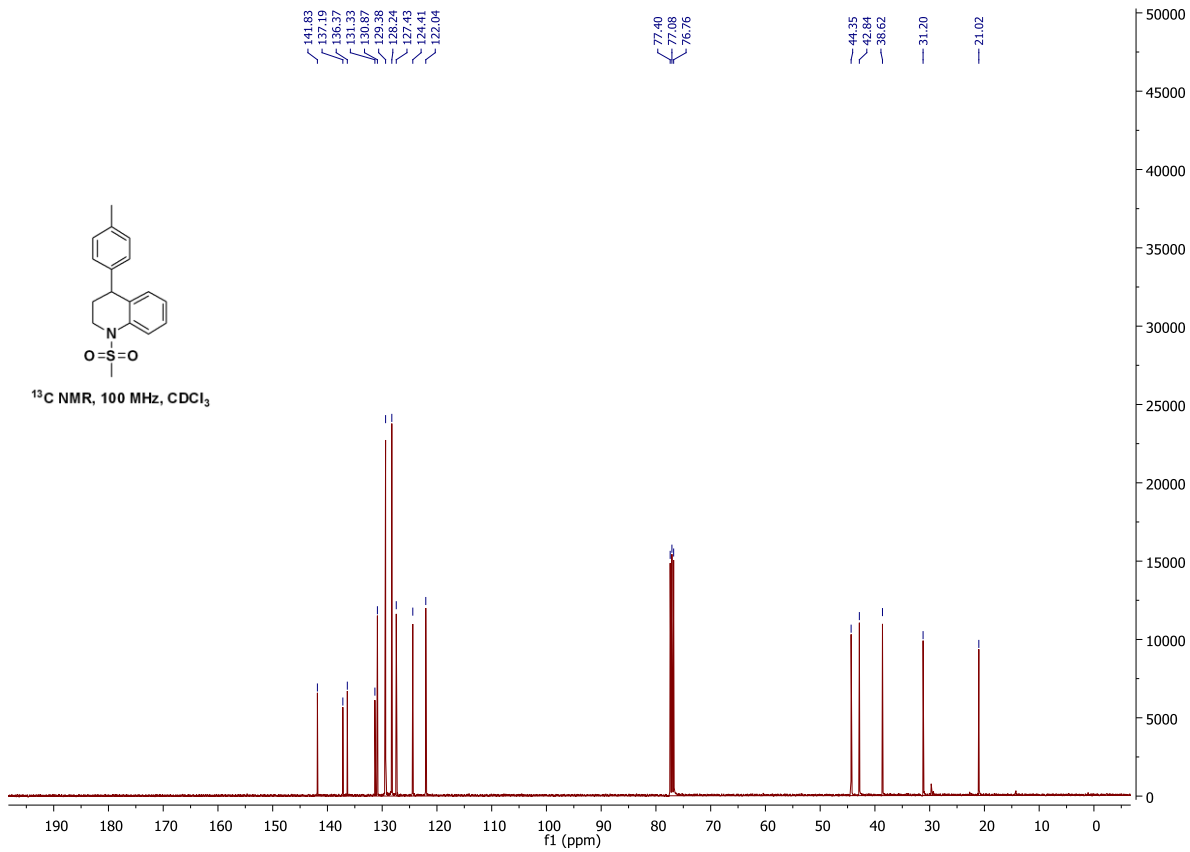
**(4-Bromophenylsulfonyl)-4-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (30)**



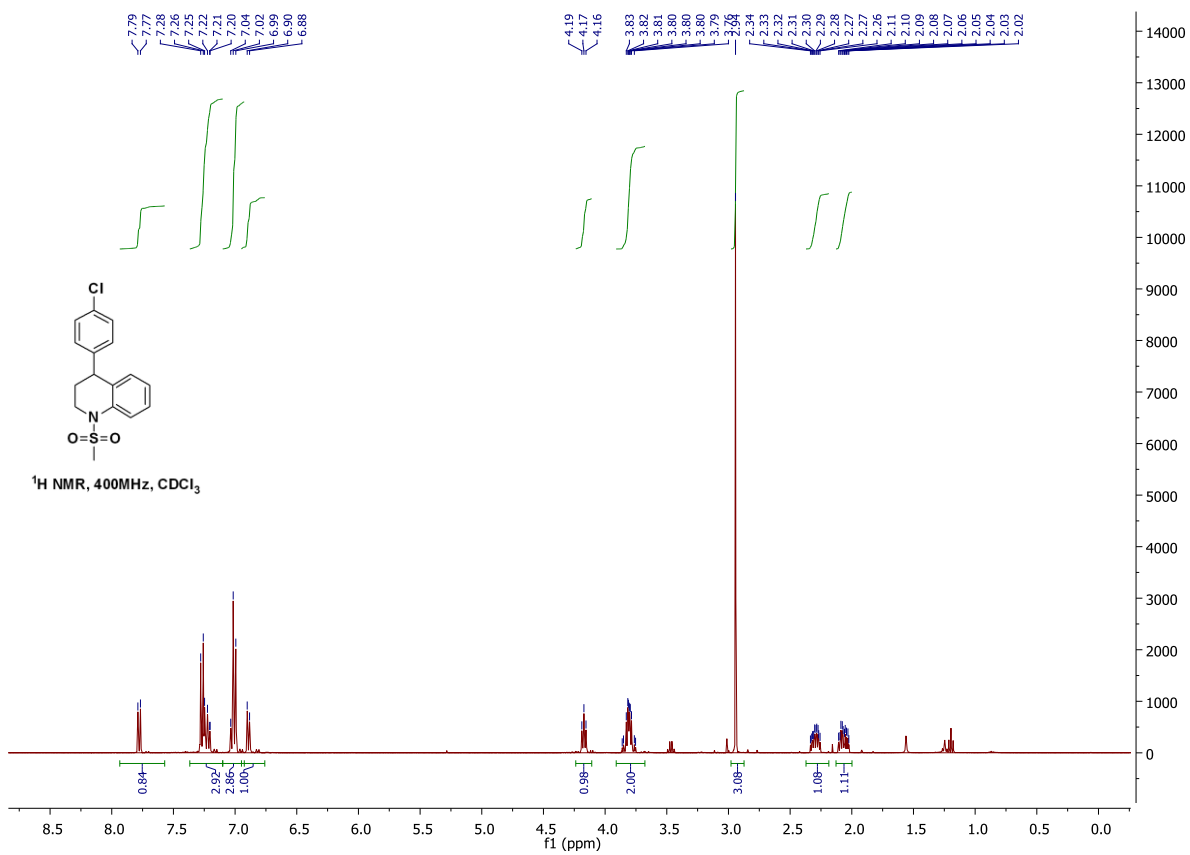


**1-(Methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (31)**

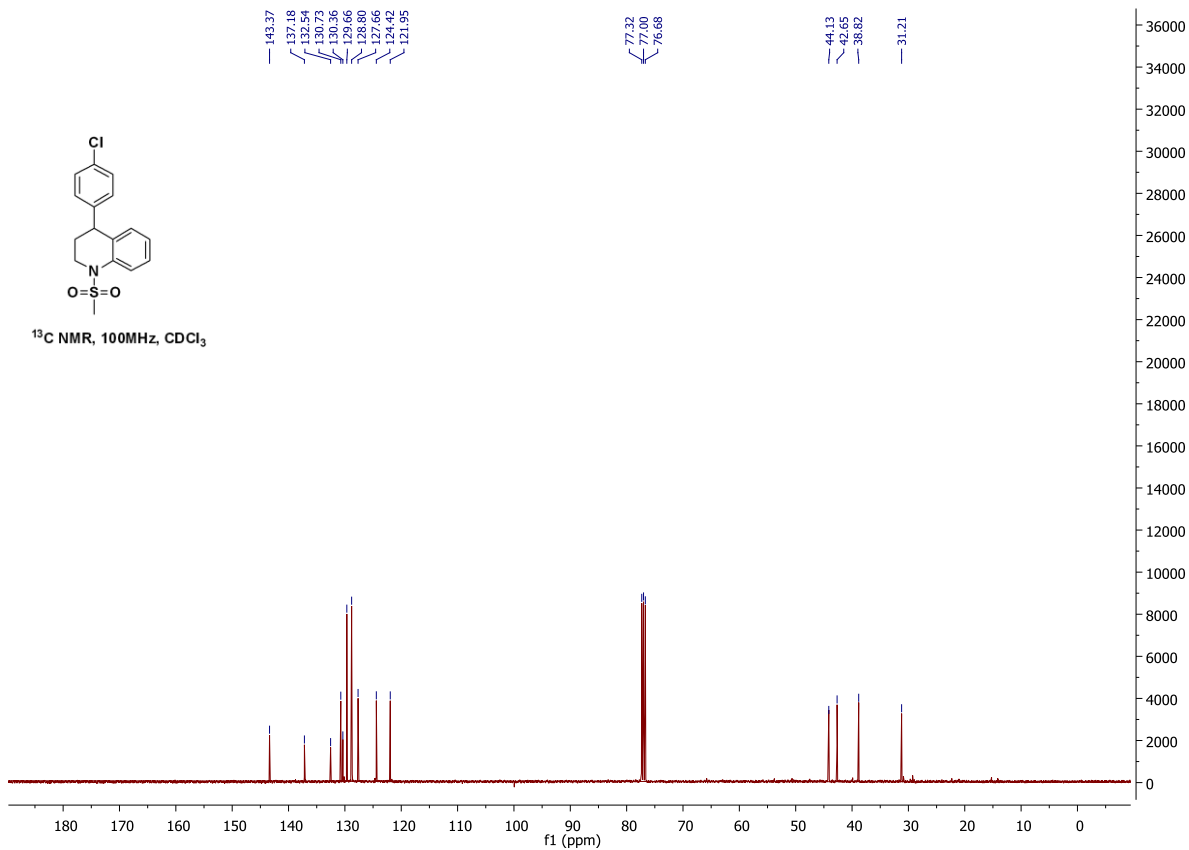




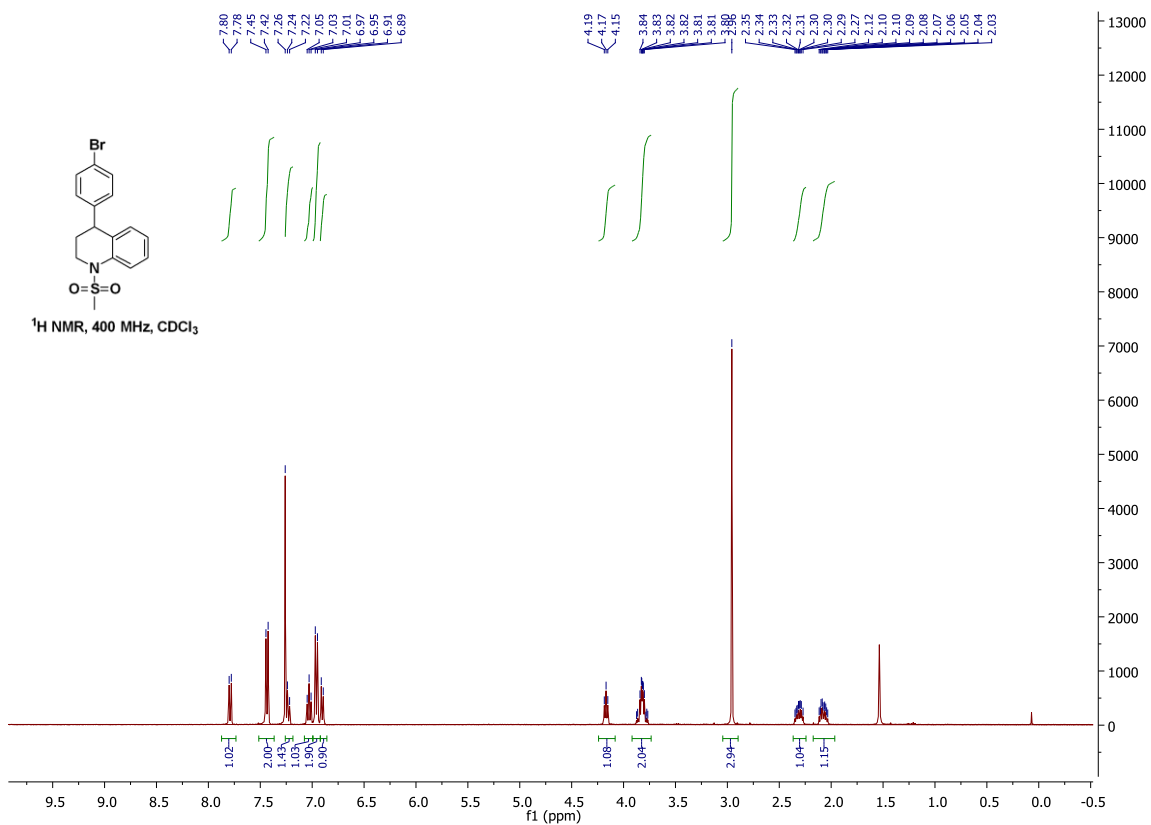
**4-(4-Chlorophenyl)-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinoline (32)**

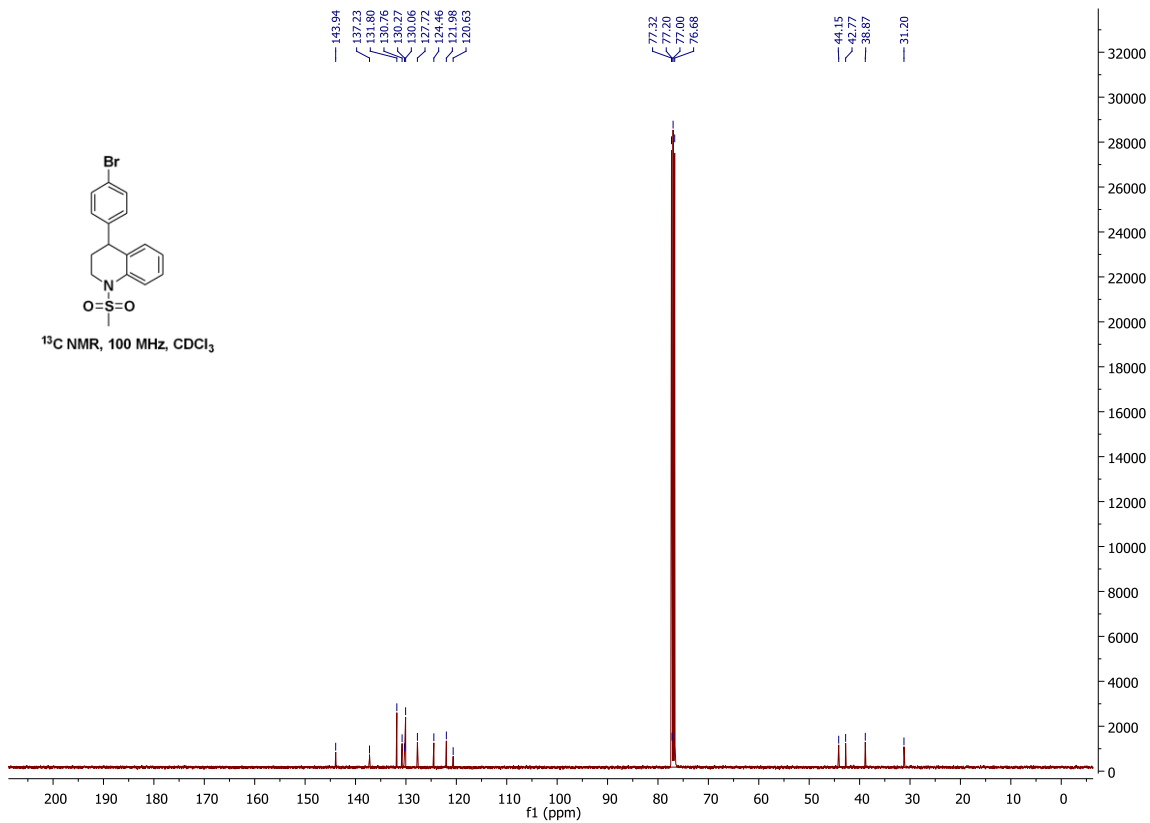




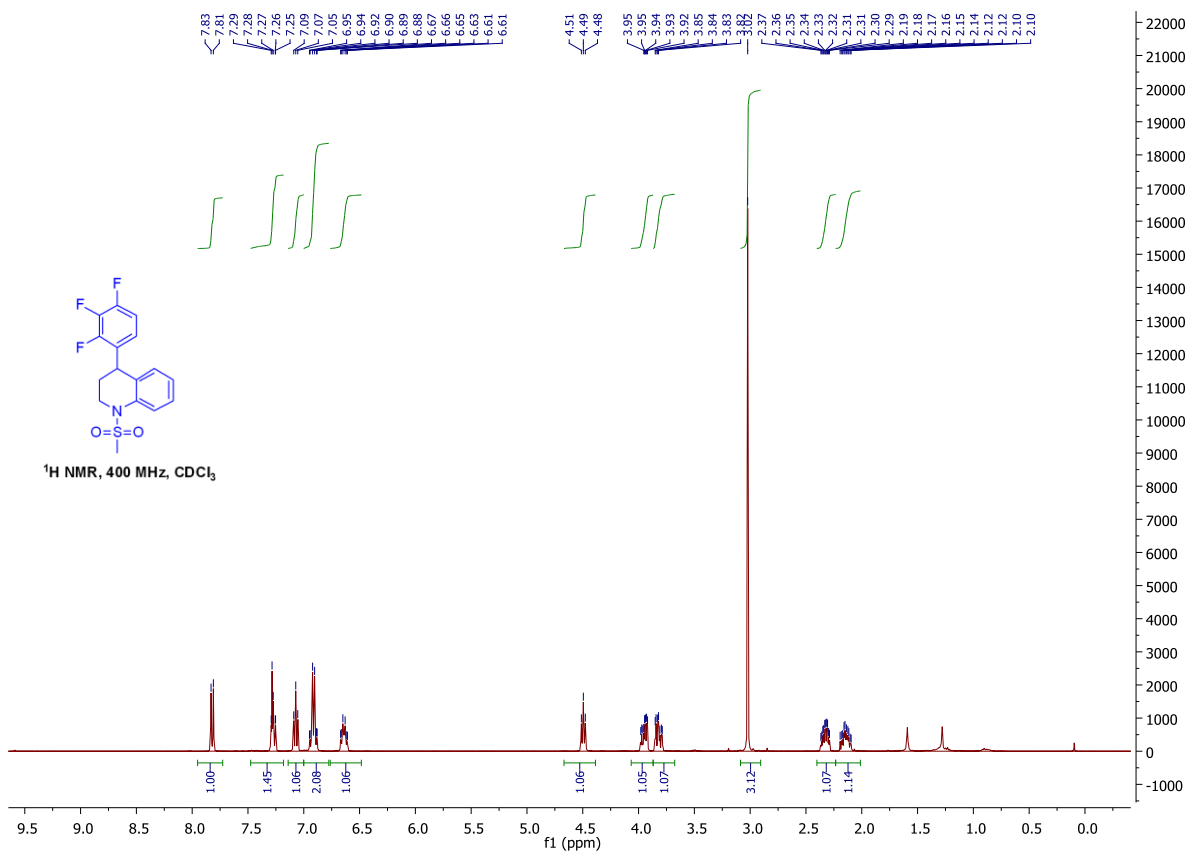


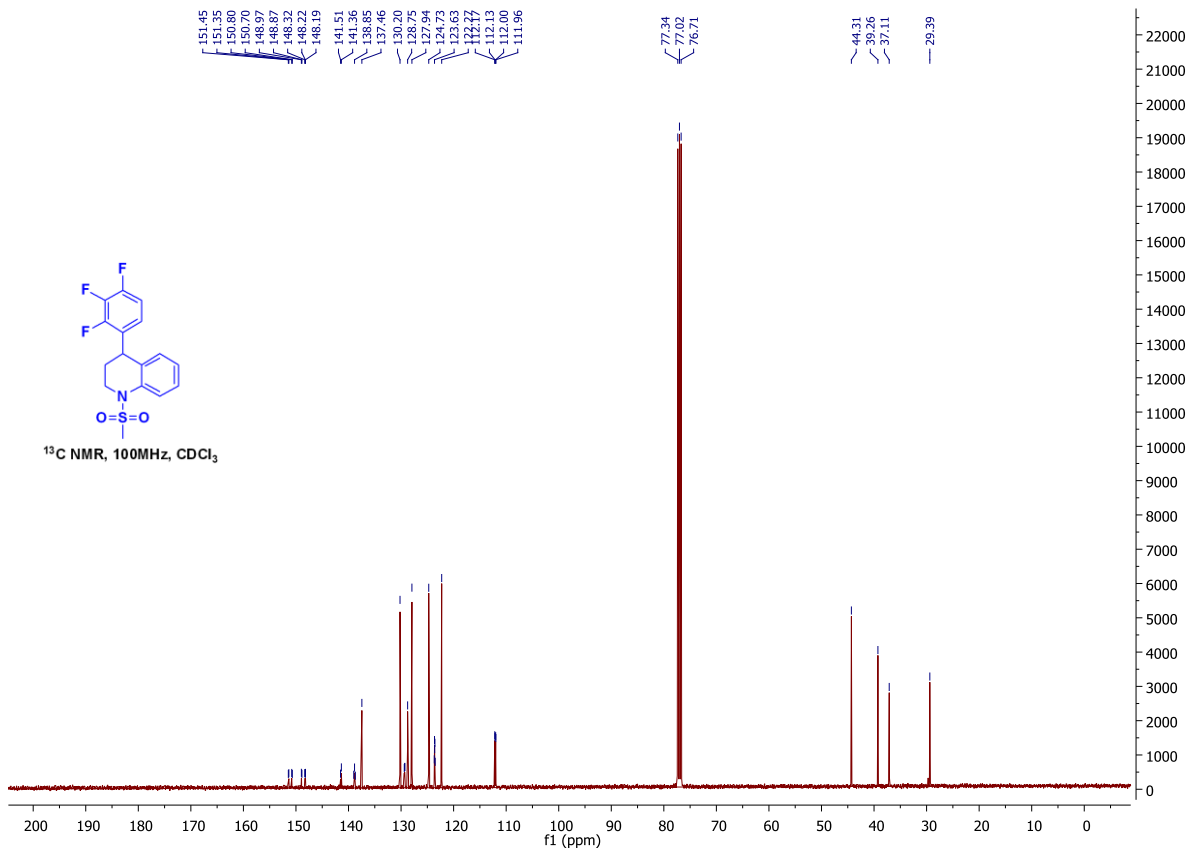
**4-(4-Bromophenyl)-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinoline (33)**



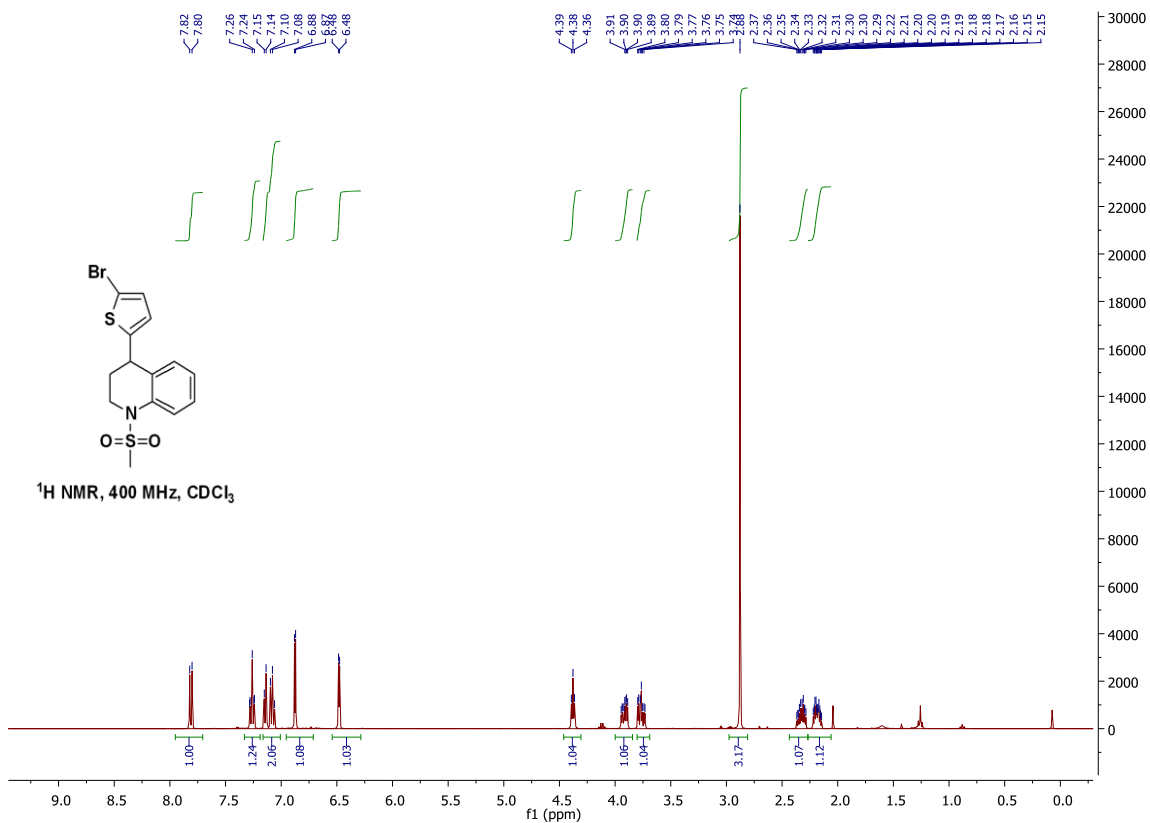


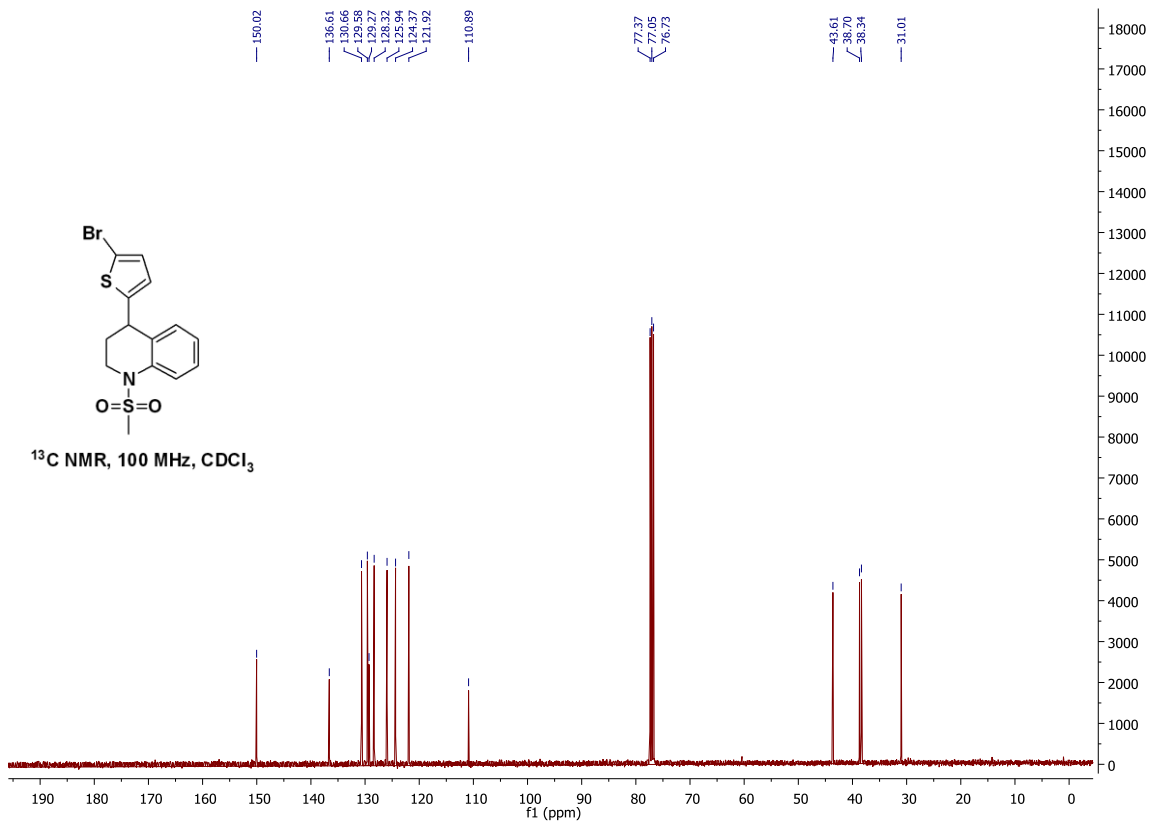
**1-(Methylsulfonyl)-4-(2,3,4-trifluorophenyl)-1,2,3,4-tetrahydroquinoline (34)**



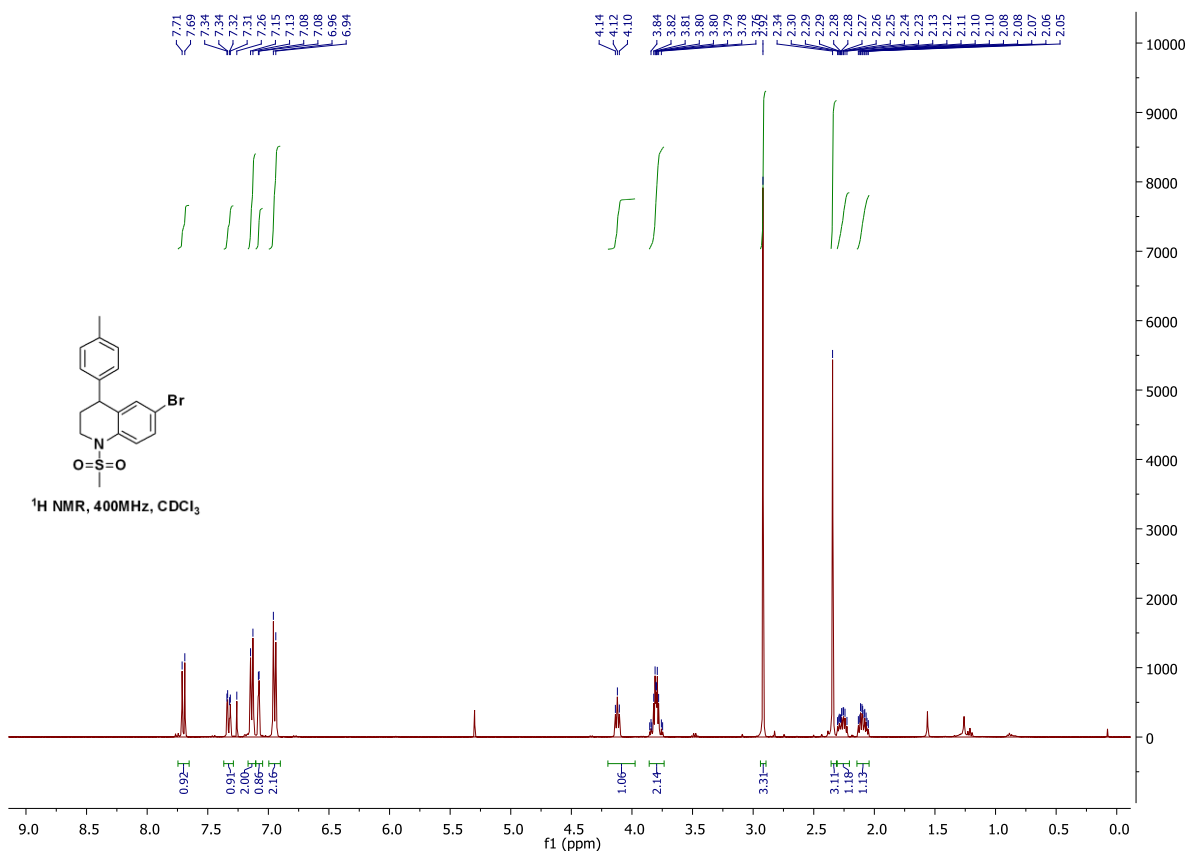


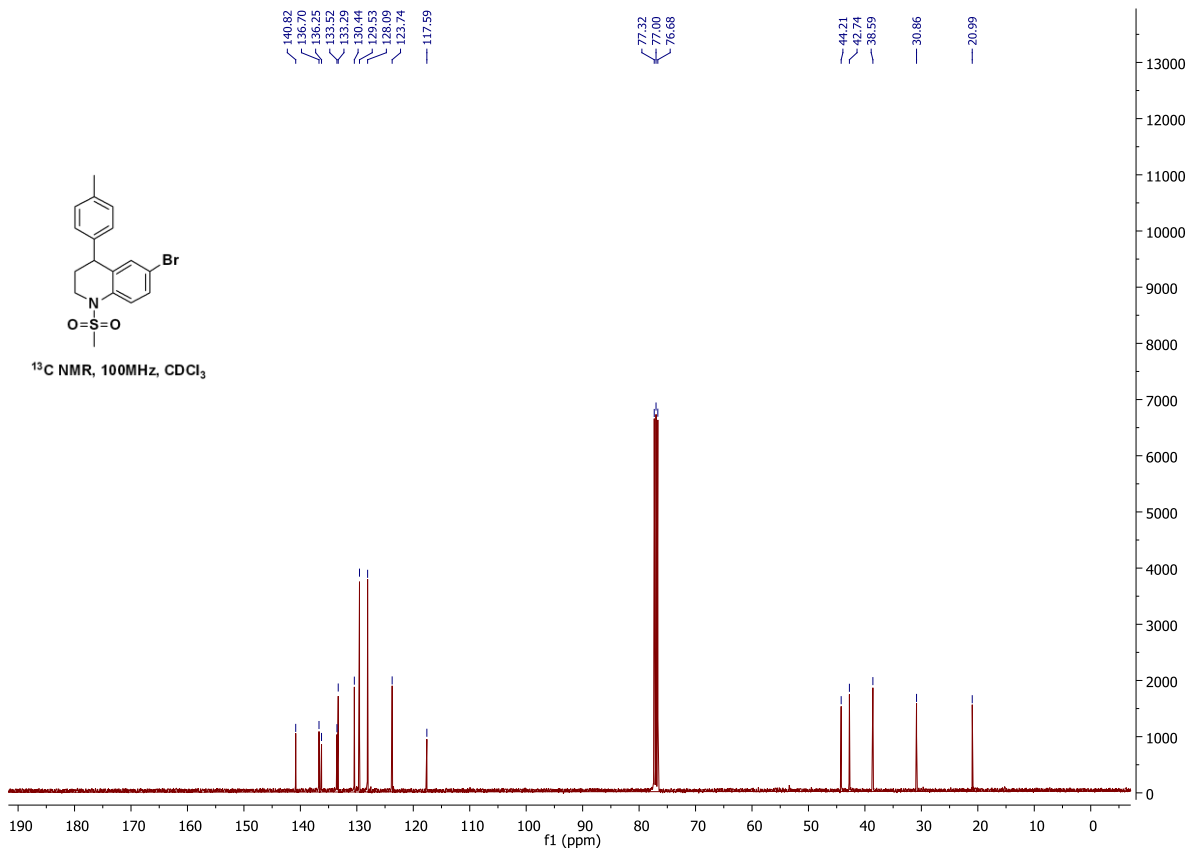
**4-(5-Bromothiophen-2-yl)-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinoline (35)**



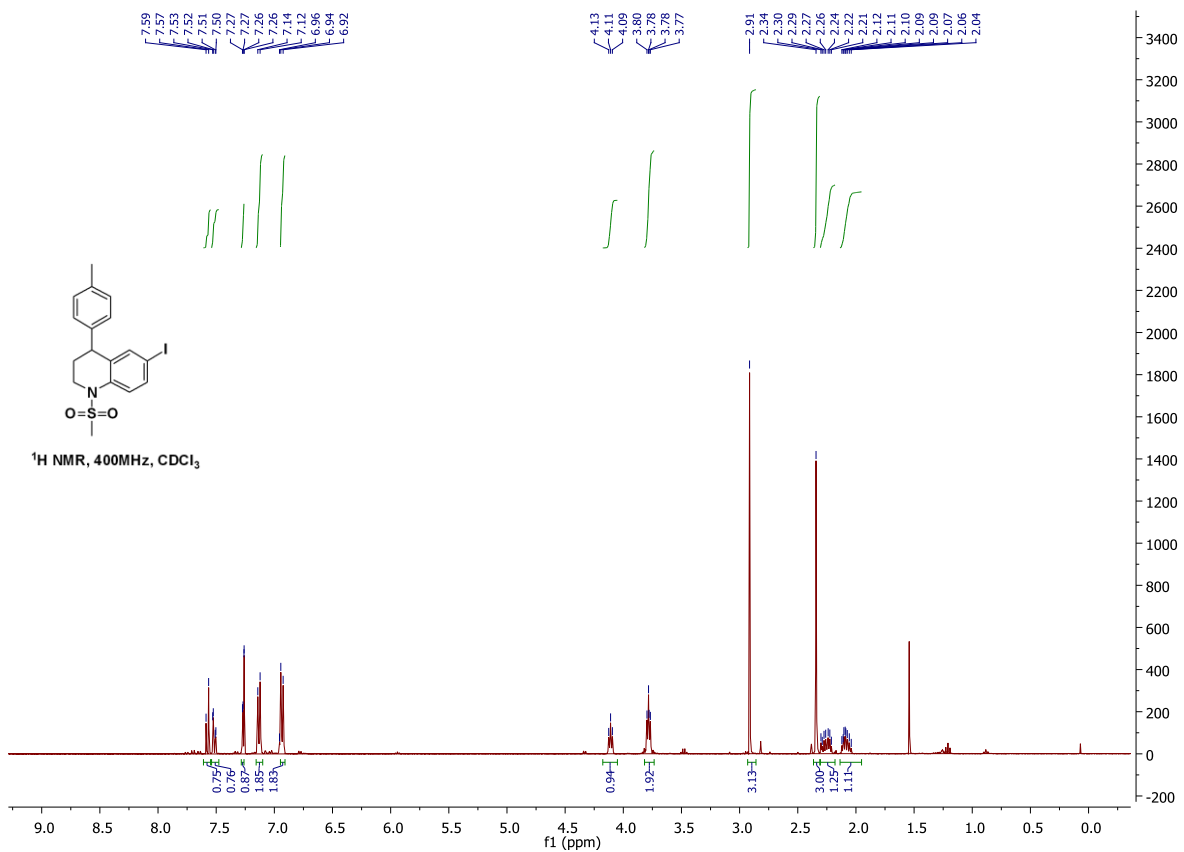


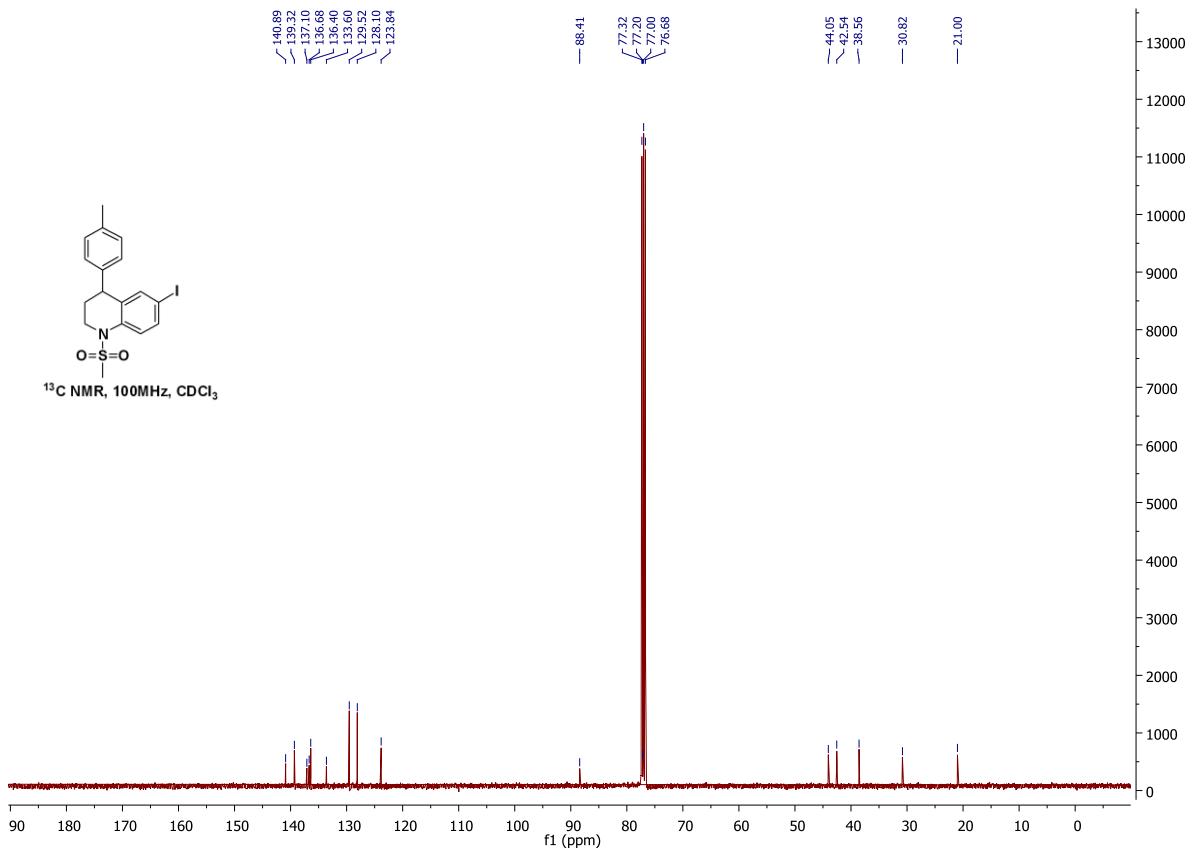
**6-Bromo-1-(methylsulfonyl)-4-p-tolyl-1,2,3,4-tetrahydroquinoline (36)**



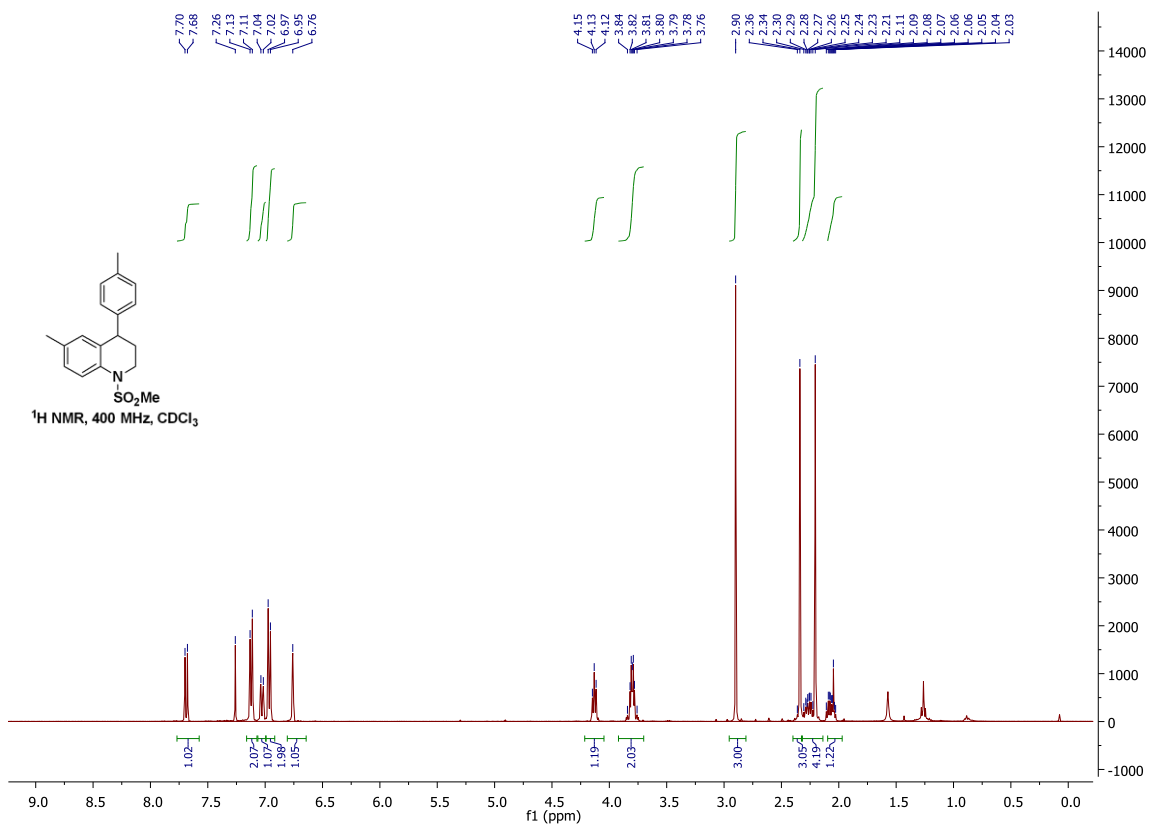


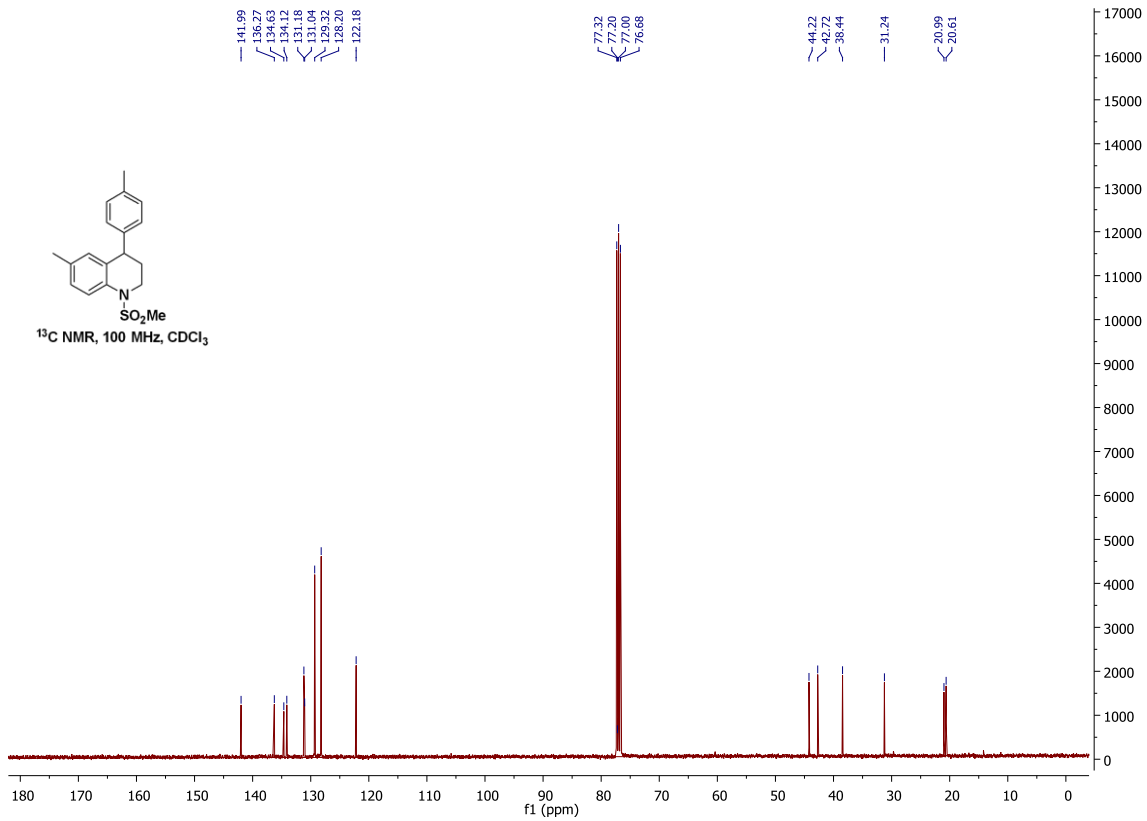
**6-Iodo-1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (37)**



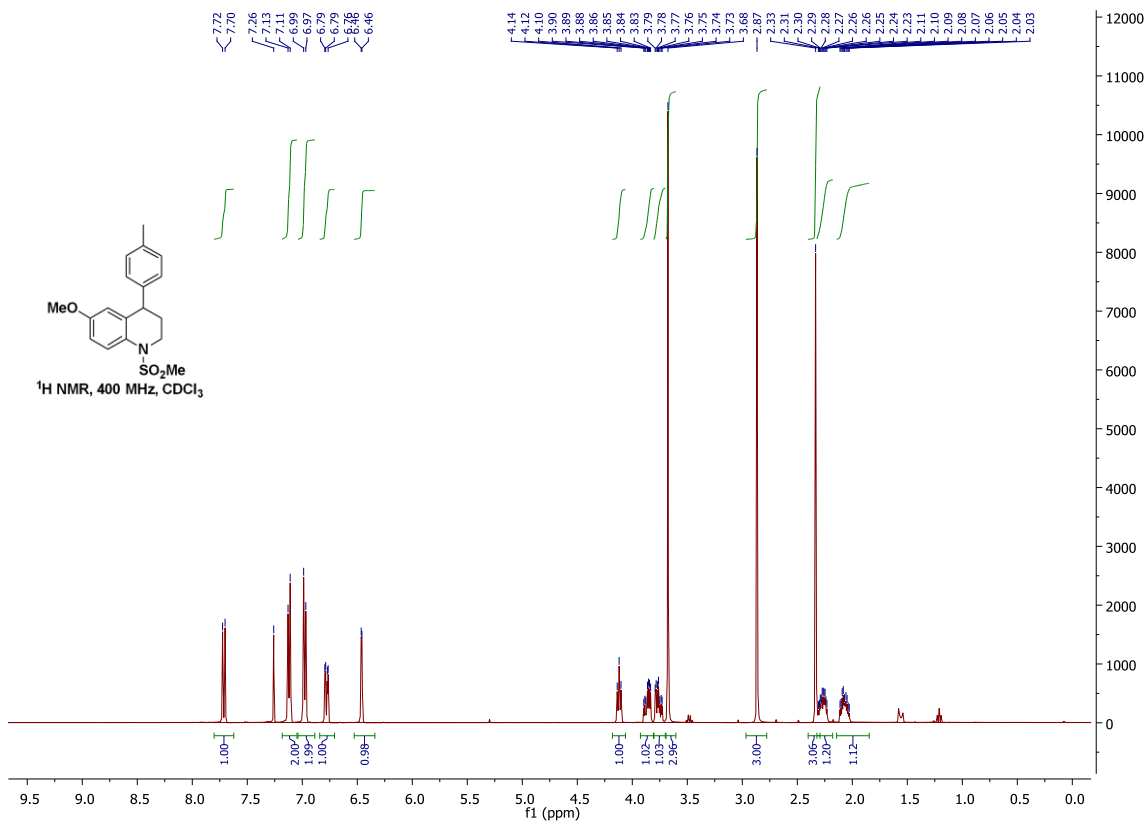


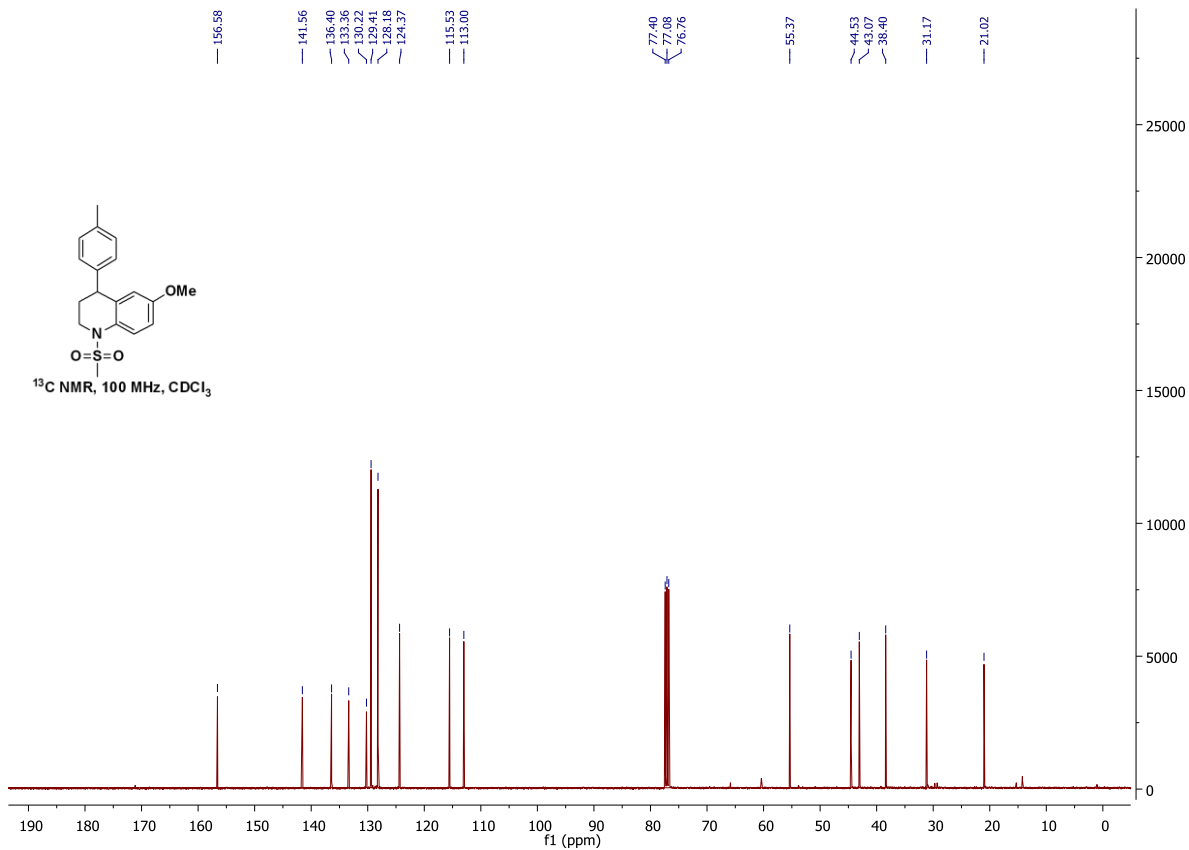
**6-Methyl-1-(methylsulfonyl)-4-p-tolyl-1,2,3,4-tetrahydroquinoline (38)**



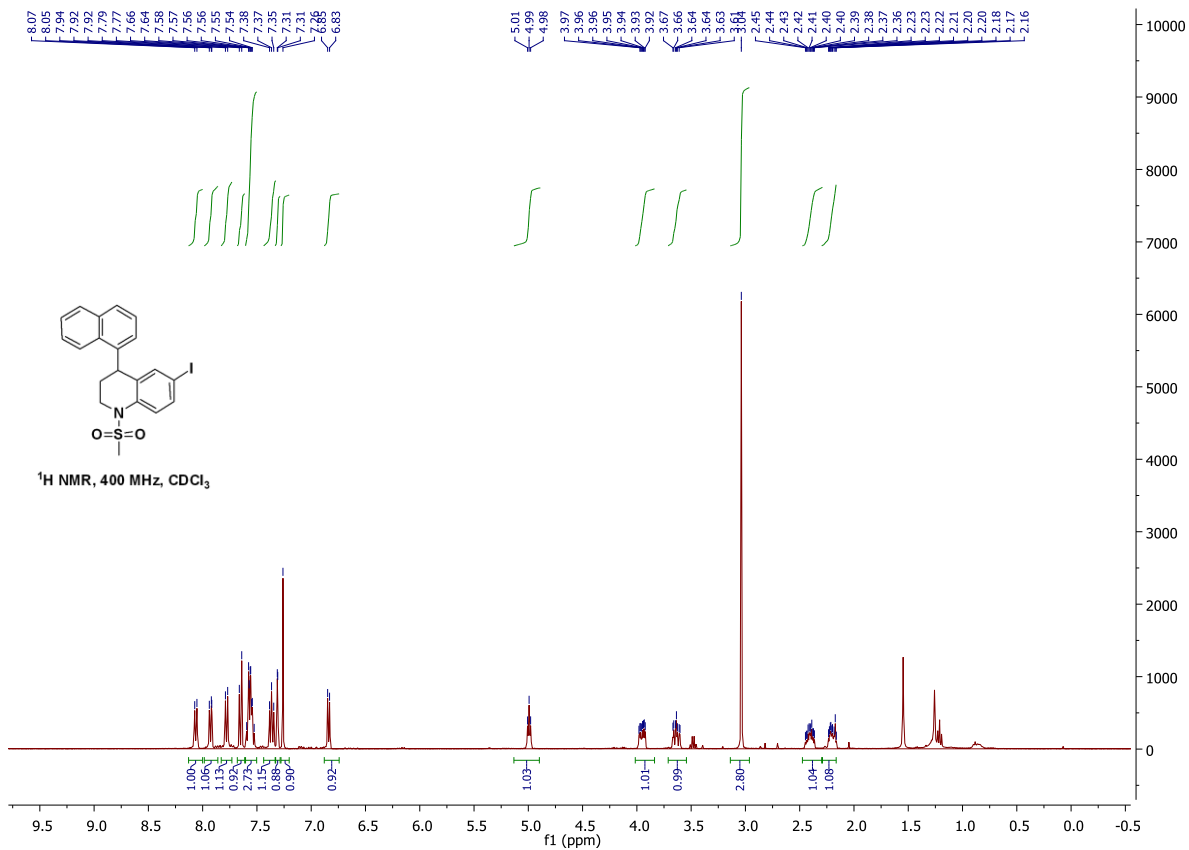


**6-Methoxy-1-(methylsulfonyl)-4-p-tolyl-1,2,3,4-tetrahydroquinoline (39)**

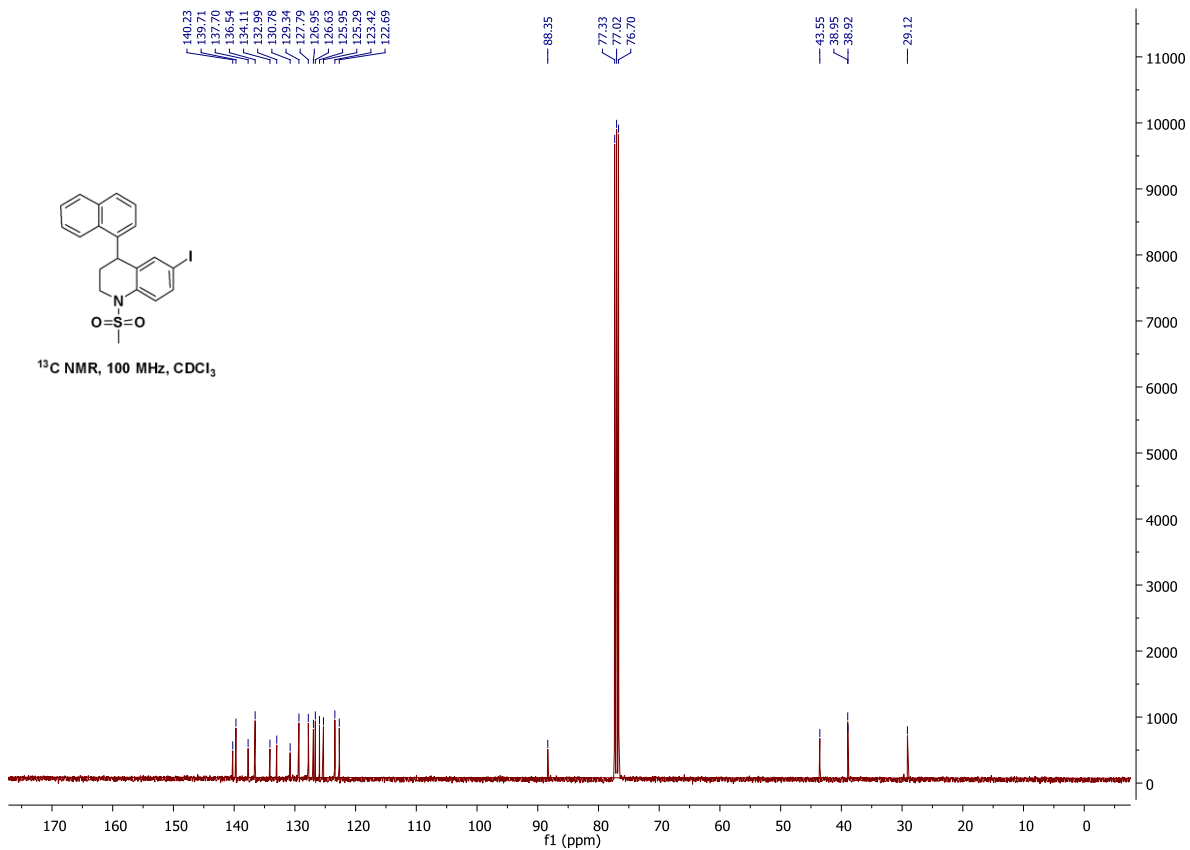




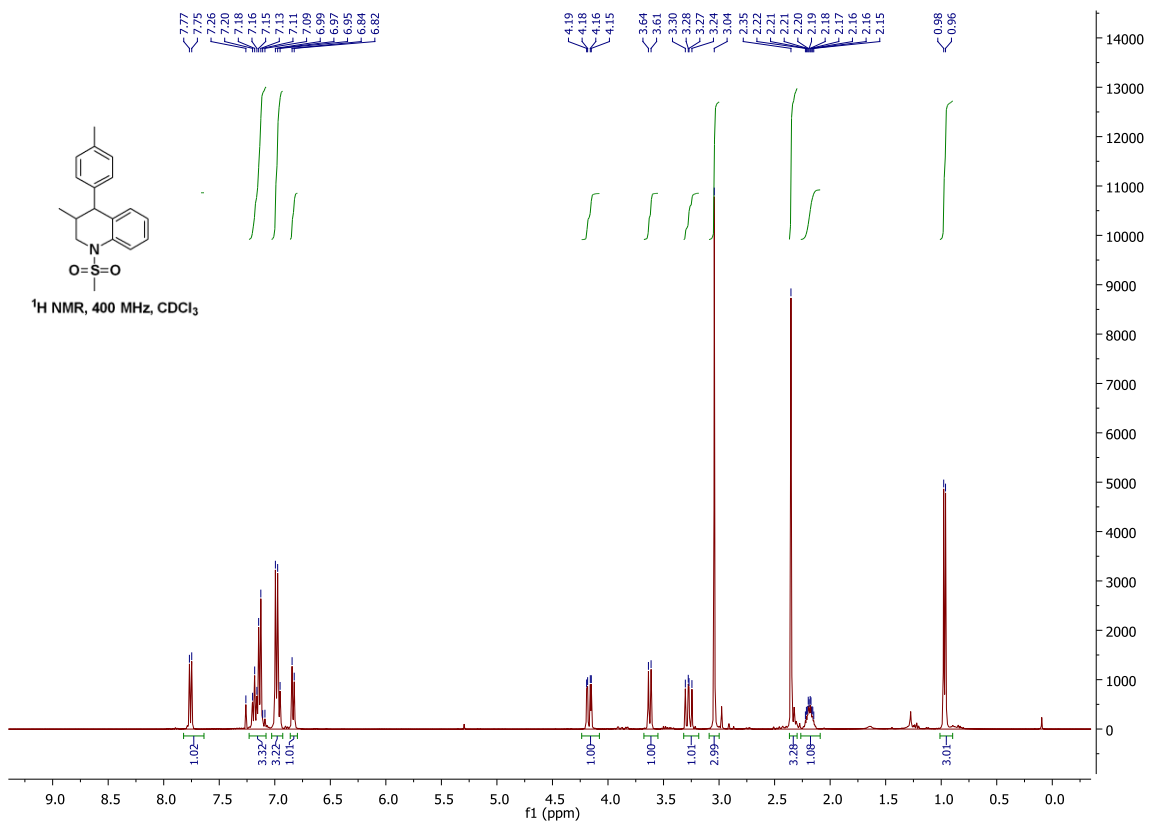
**6-Iodo-1-(methylsulfonyl)-4-(naphthalen-1-yl)-1,2,3,4-tetrahydroquinoline (40)**

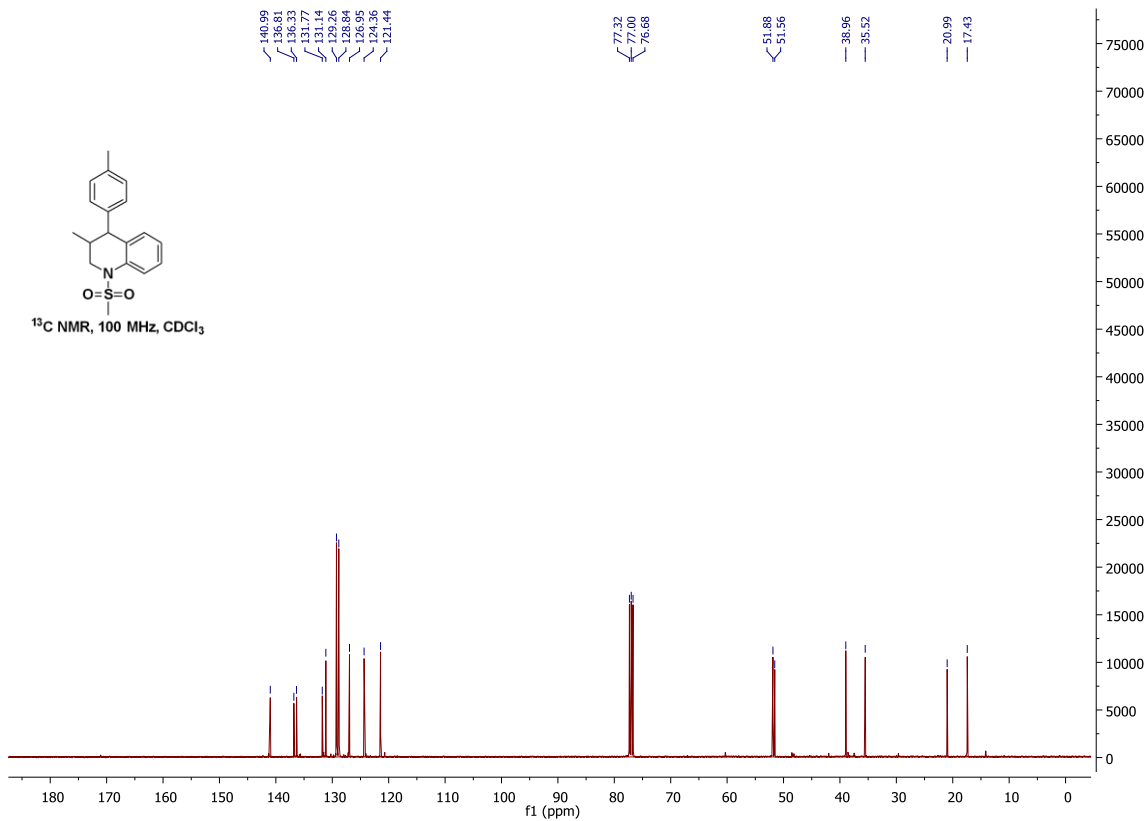




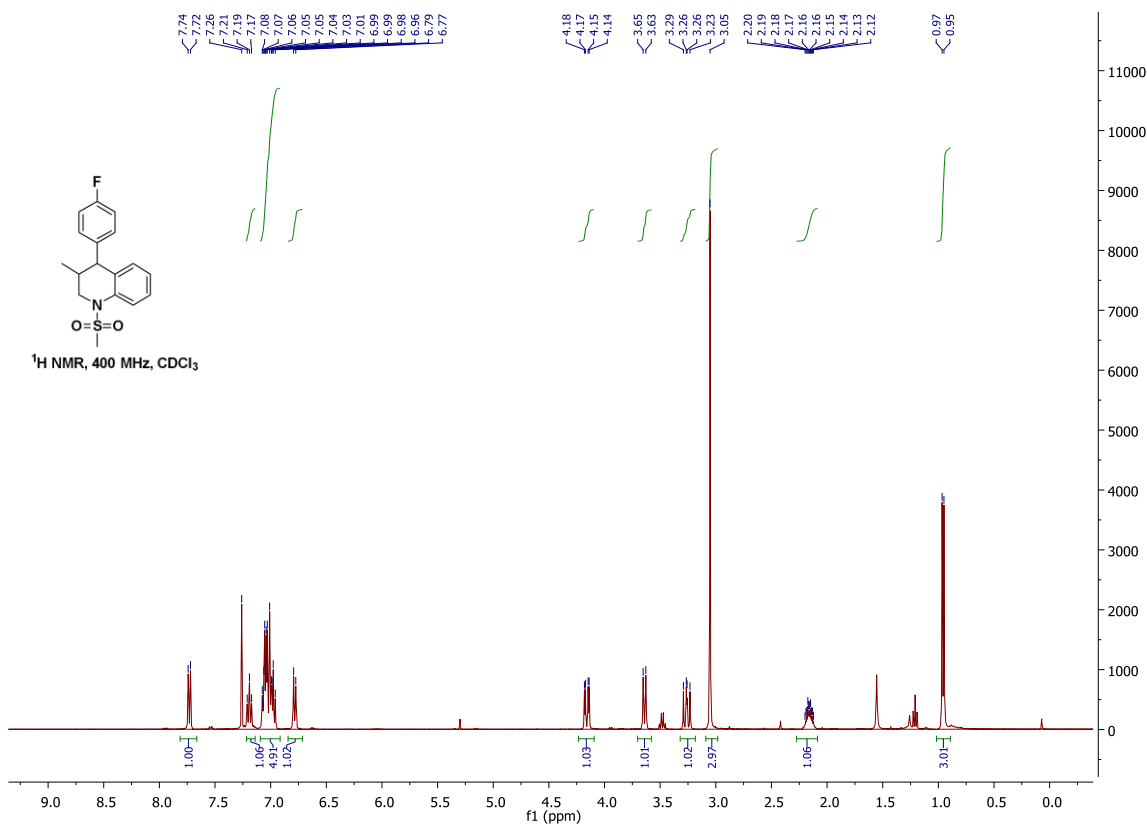


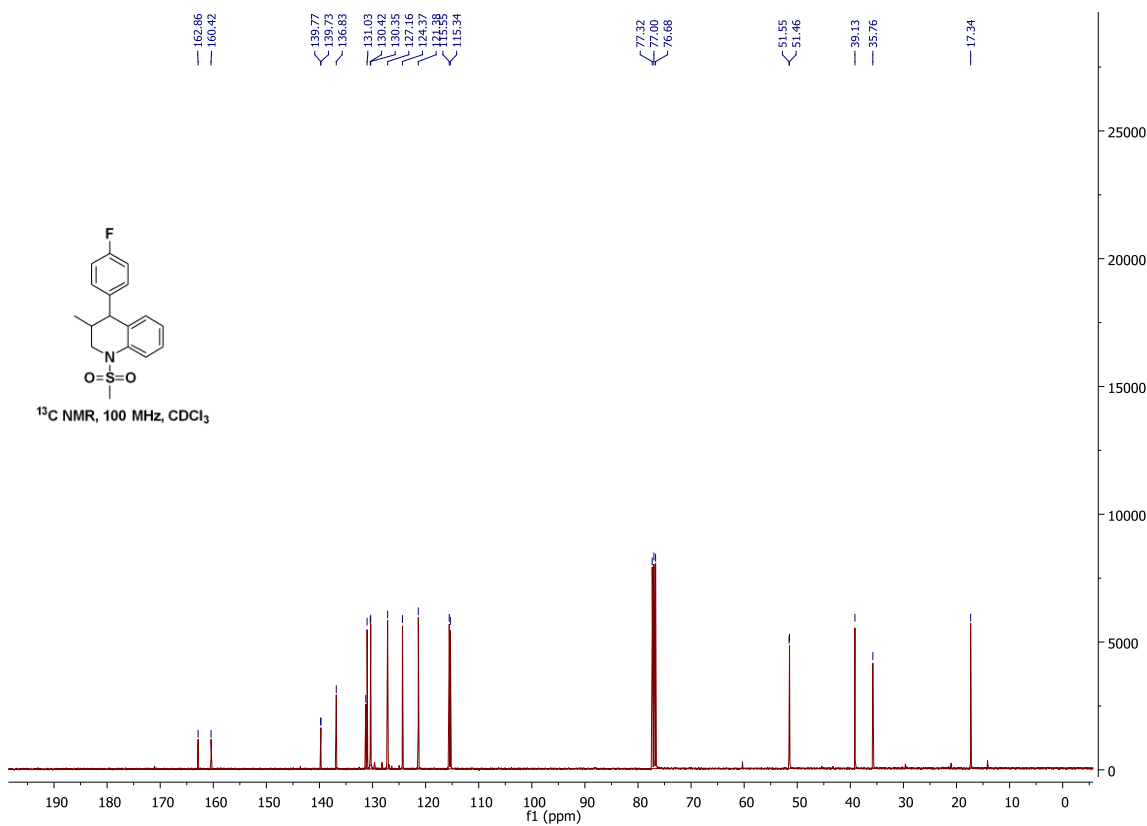
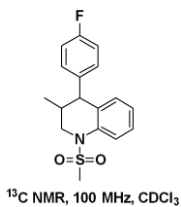
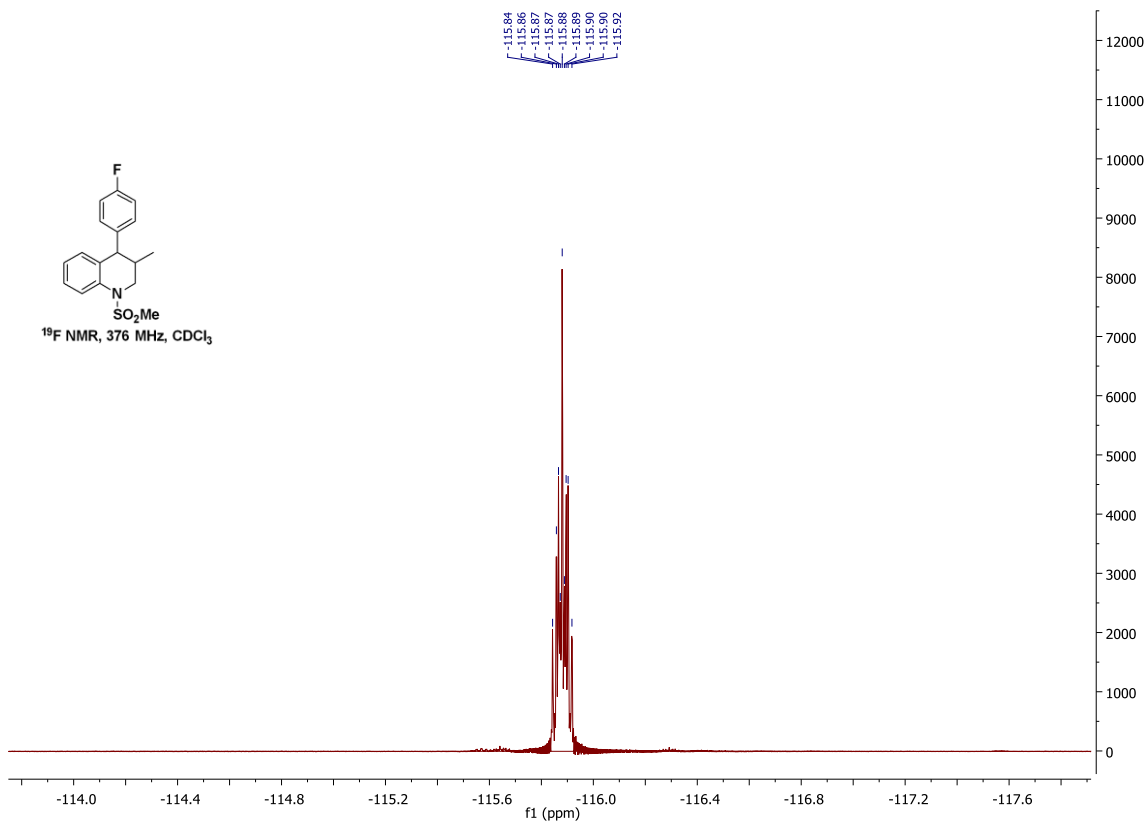
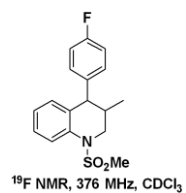
**3-Methyl-1-(methylsulfonyl)-4-p-tolyl-1,2,3,4-tetrahydroquinoline (41)**



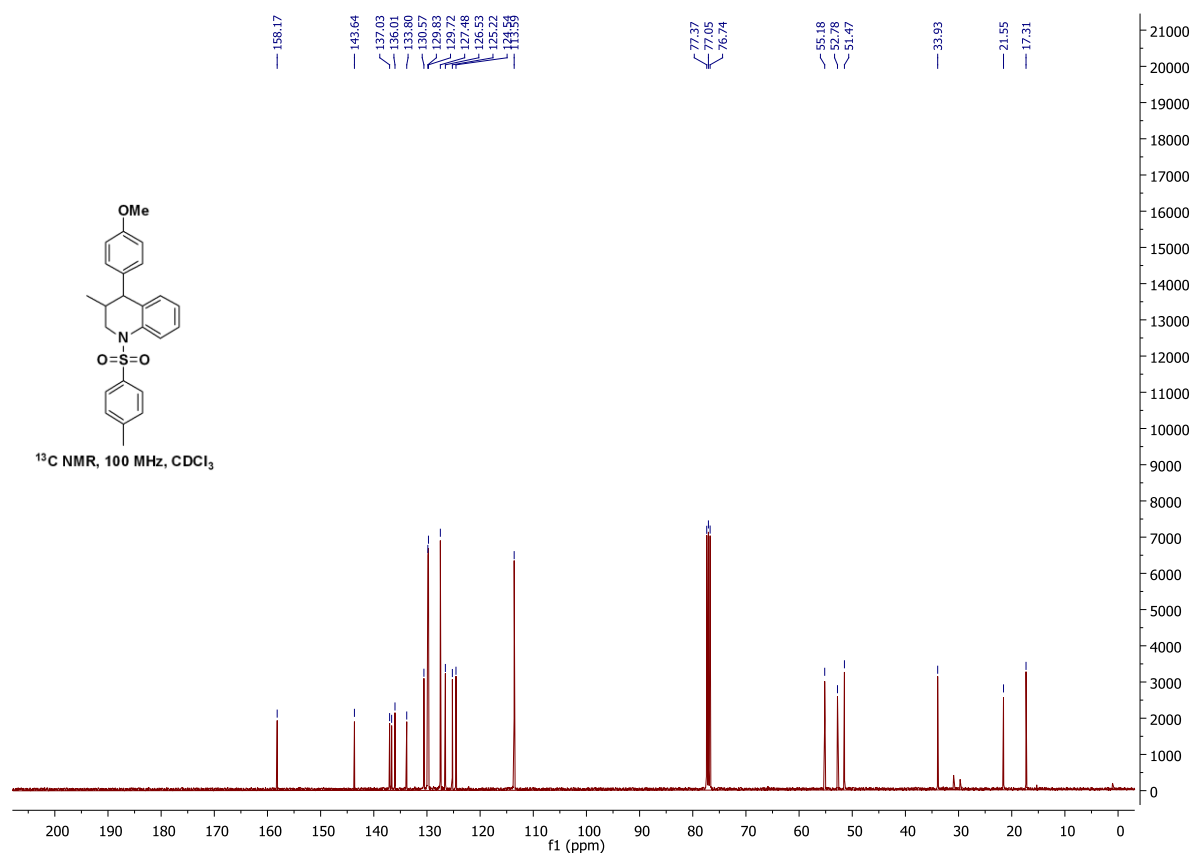
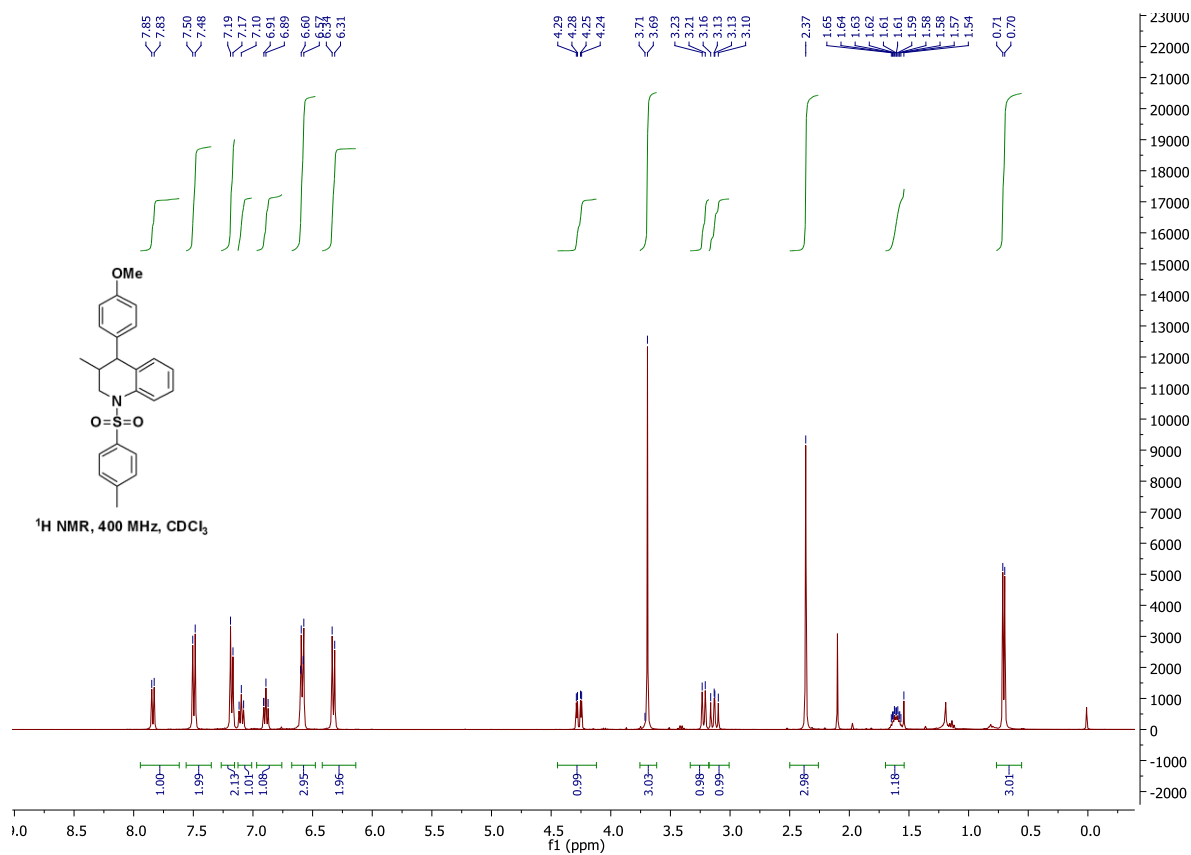


**4-(4-Fluorophenyl)-3-methyl-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinoline (42)**

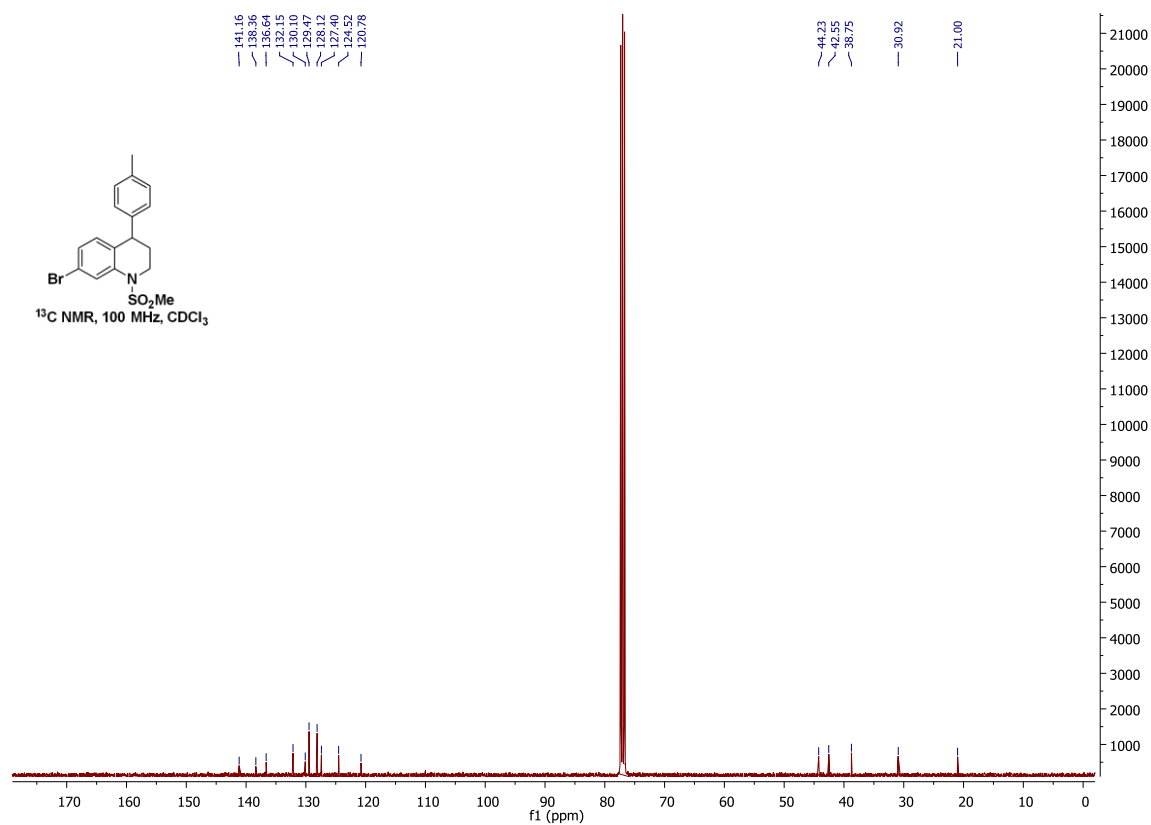
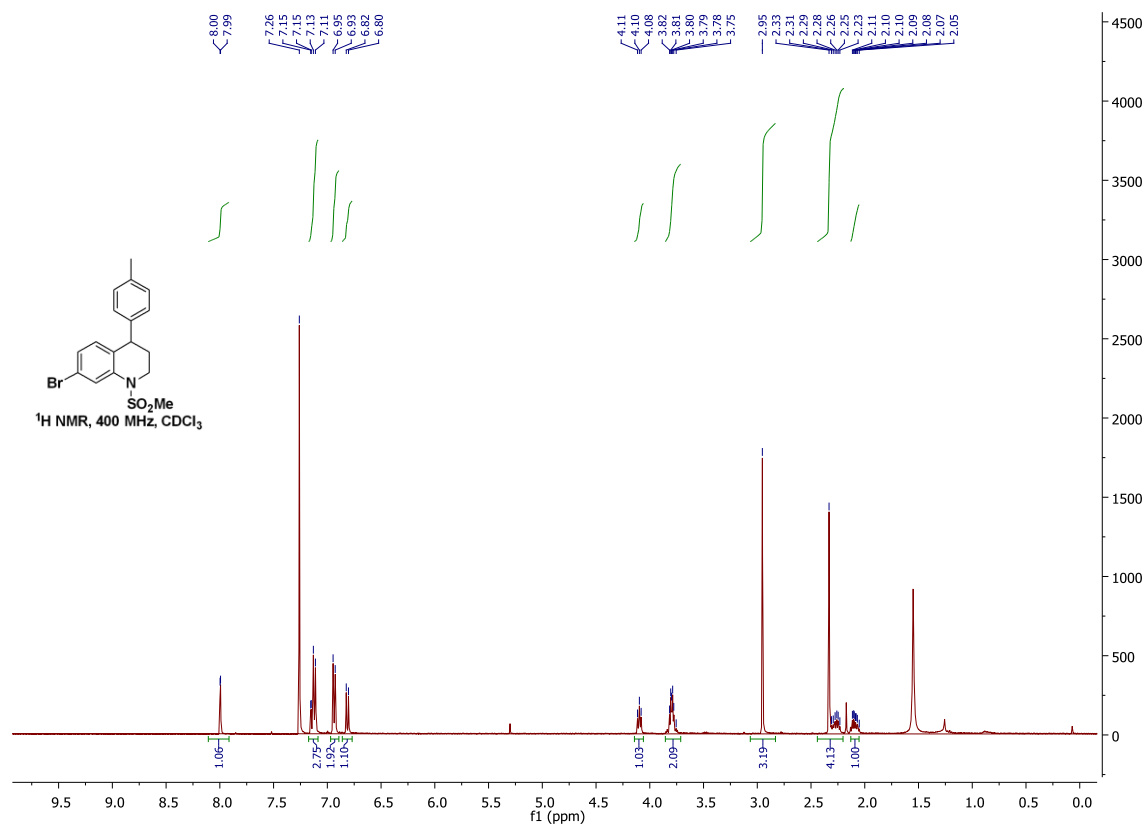




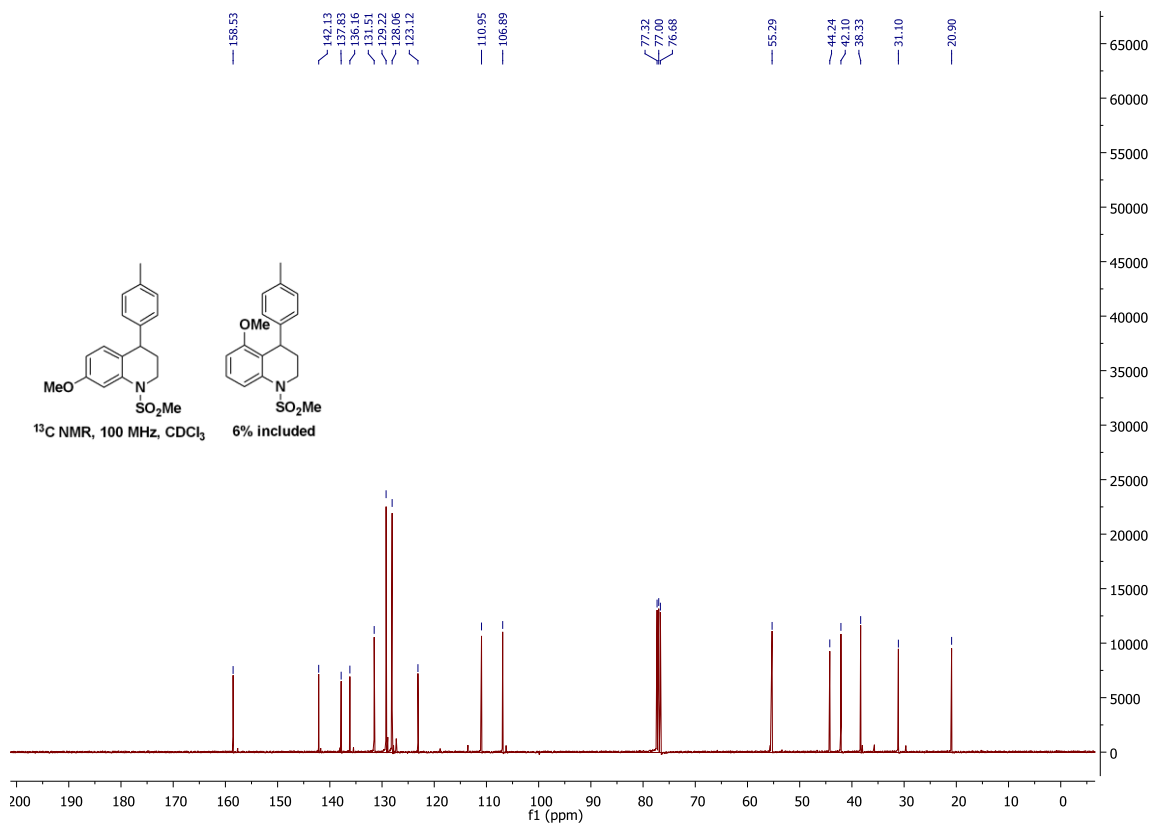
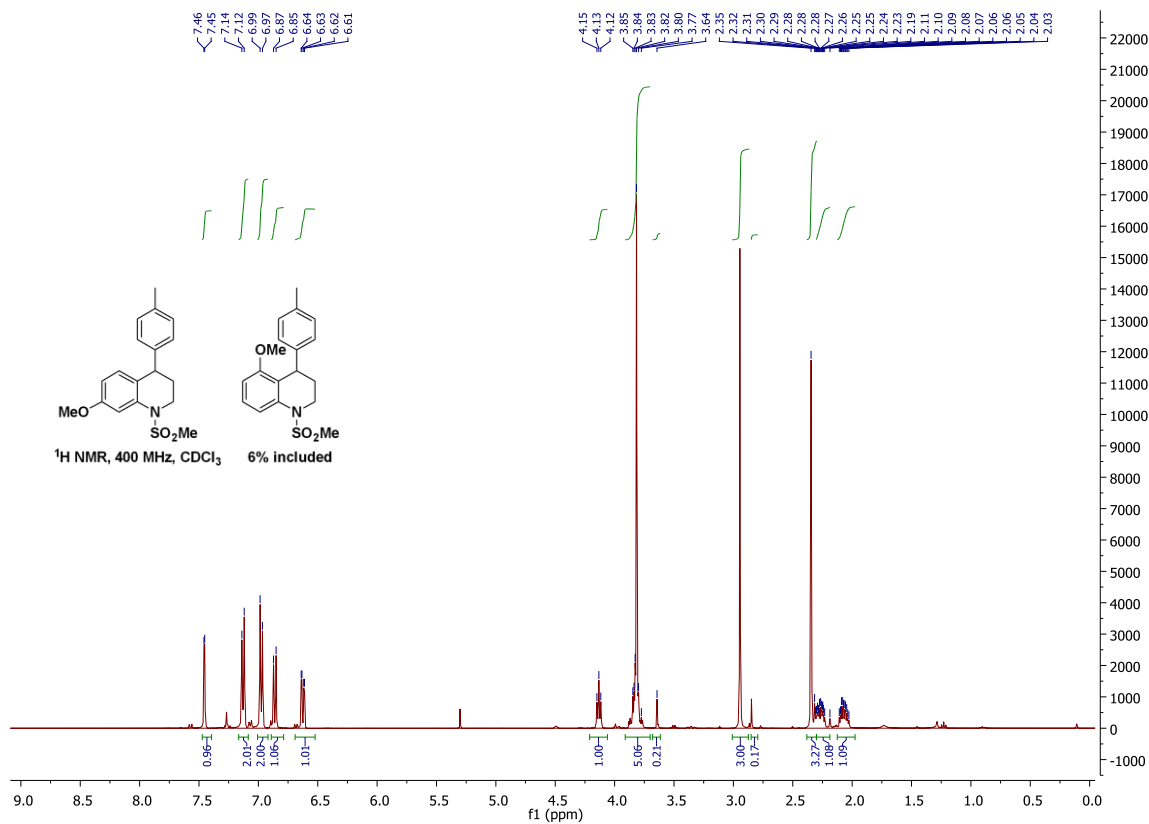
### 4-(4-Methoxyphenyl)-3-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (43)



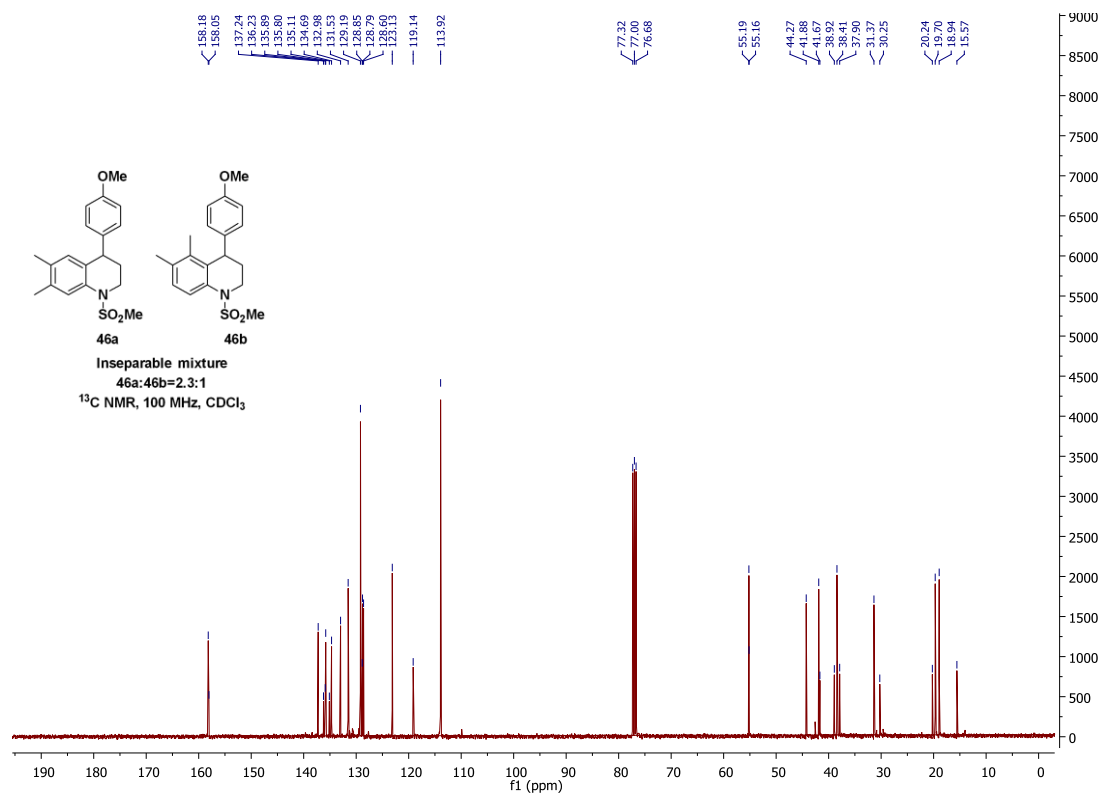
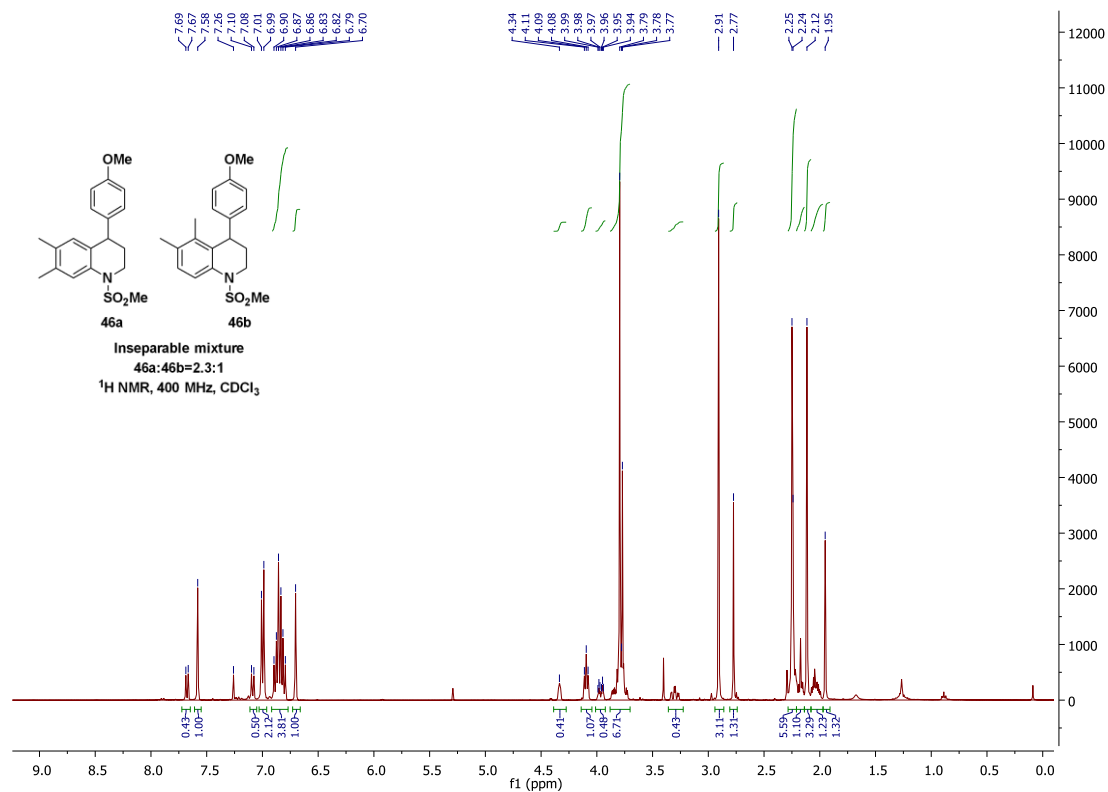
**7-Bromo-1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (44)**



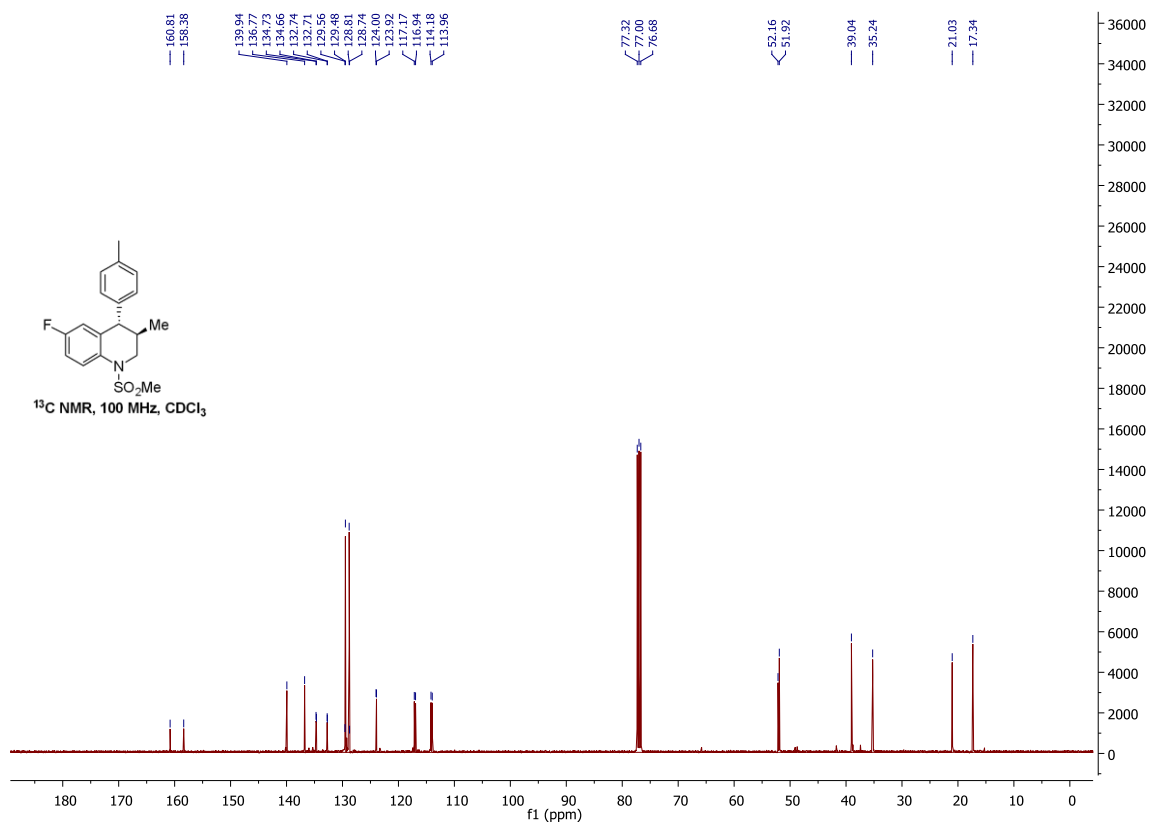
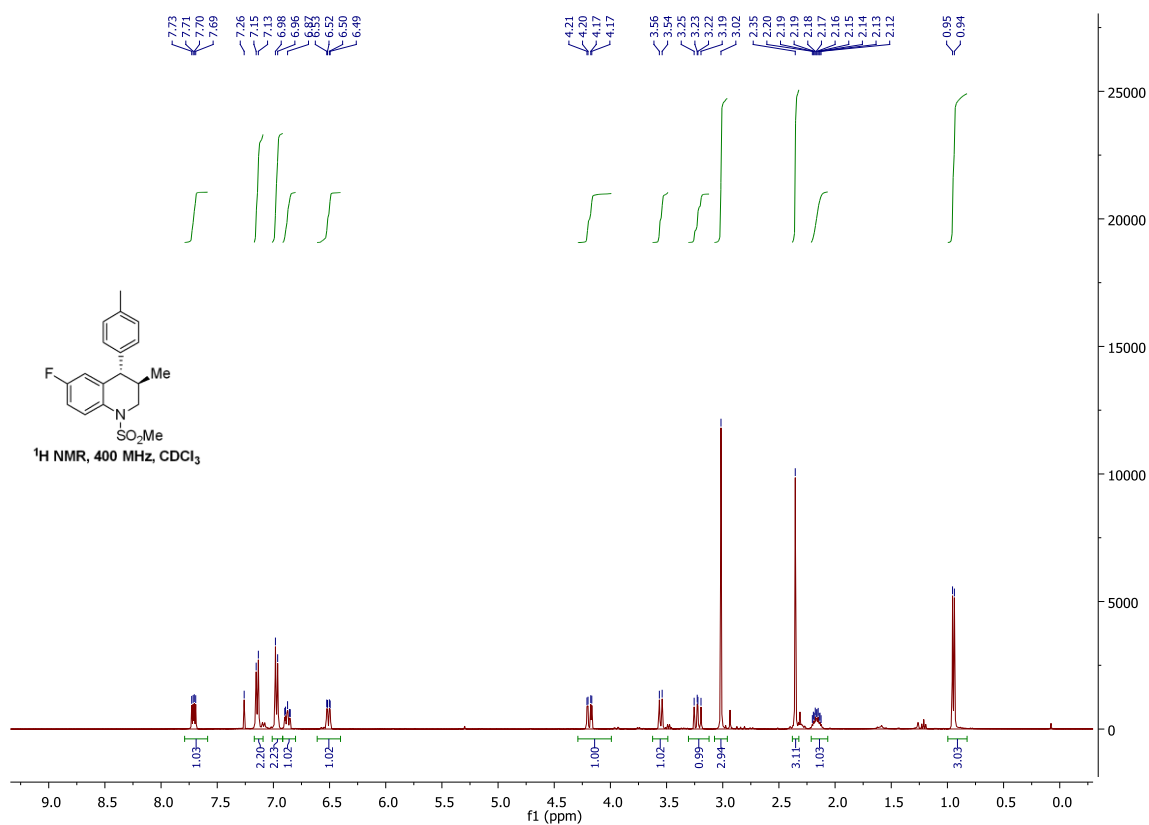
# 7-Methoxy-1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (45)



**4-(4-Methoxyphenyl)-6,7-dimethyl-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinoline (46a) and 4-(4-methoxyphenyl)-5,6-dimethyl-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinoline (46b) (46b) Mixture:46a:46=2.3:1**

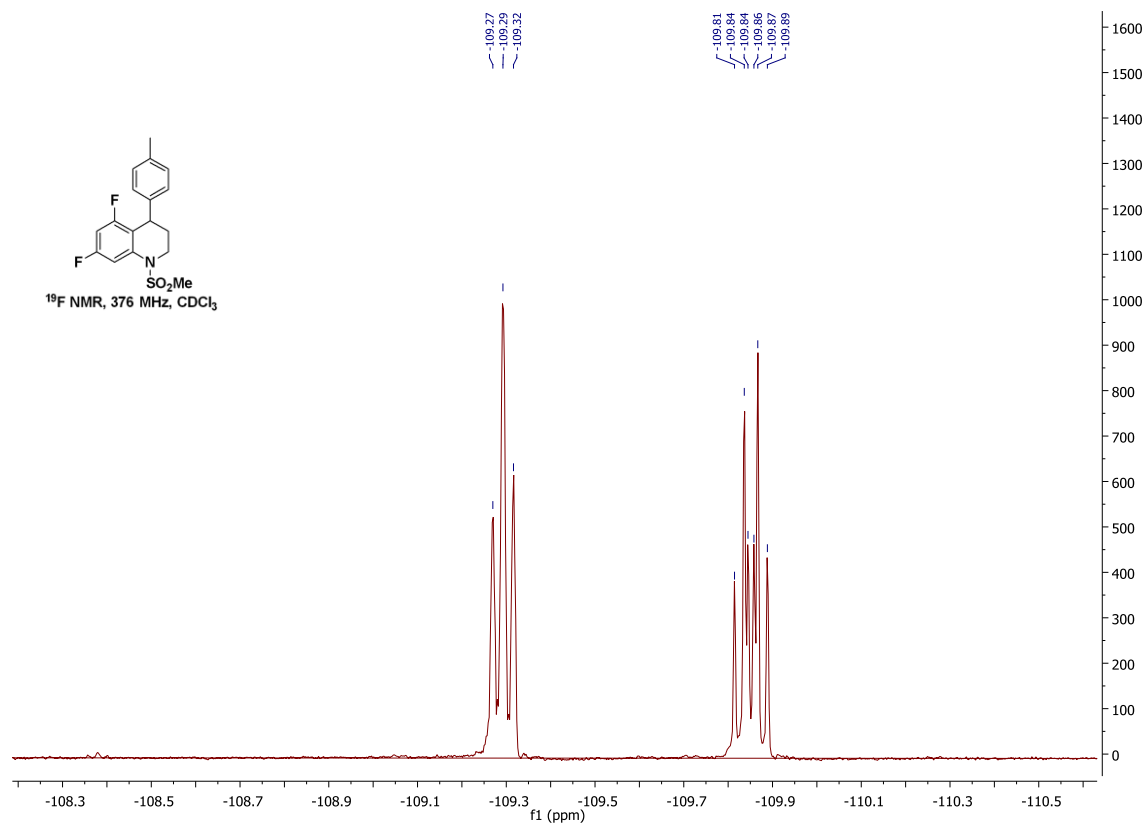
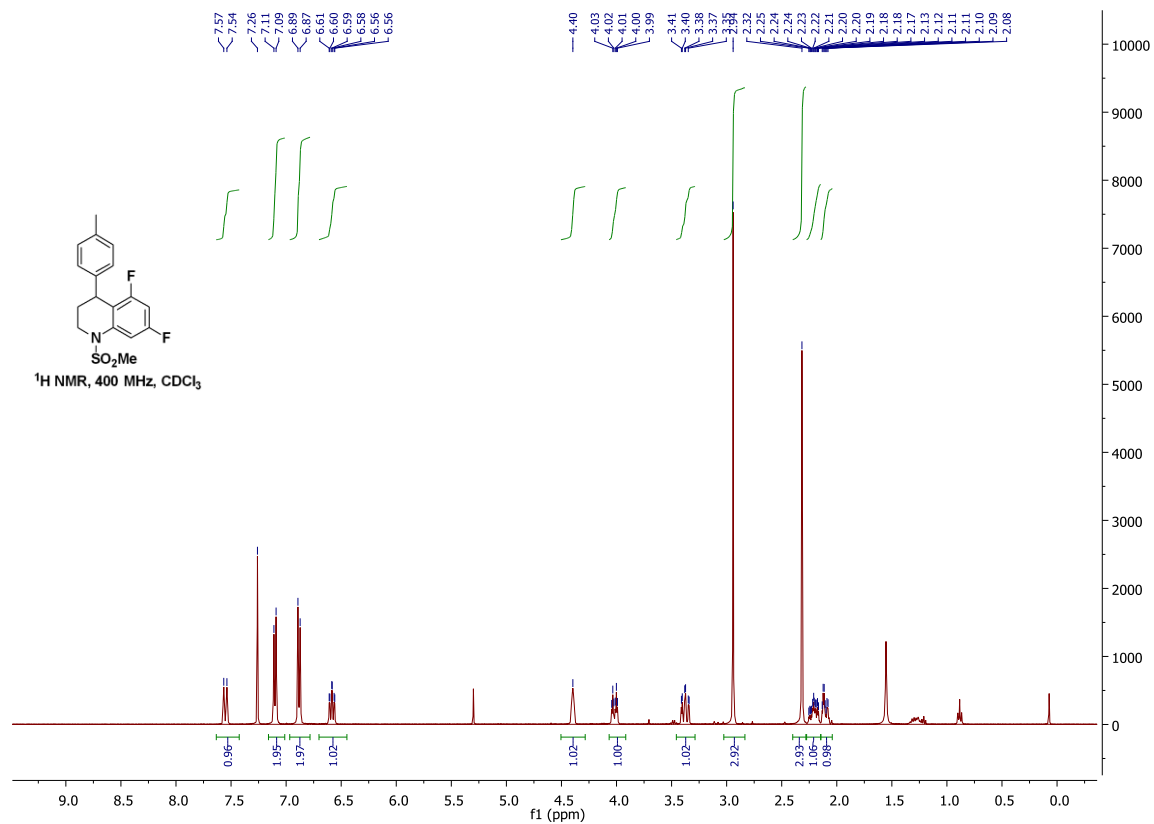


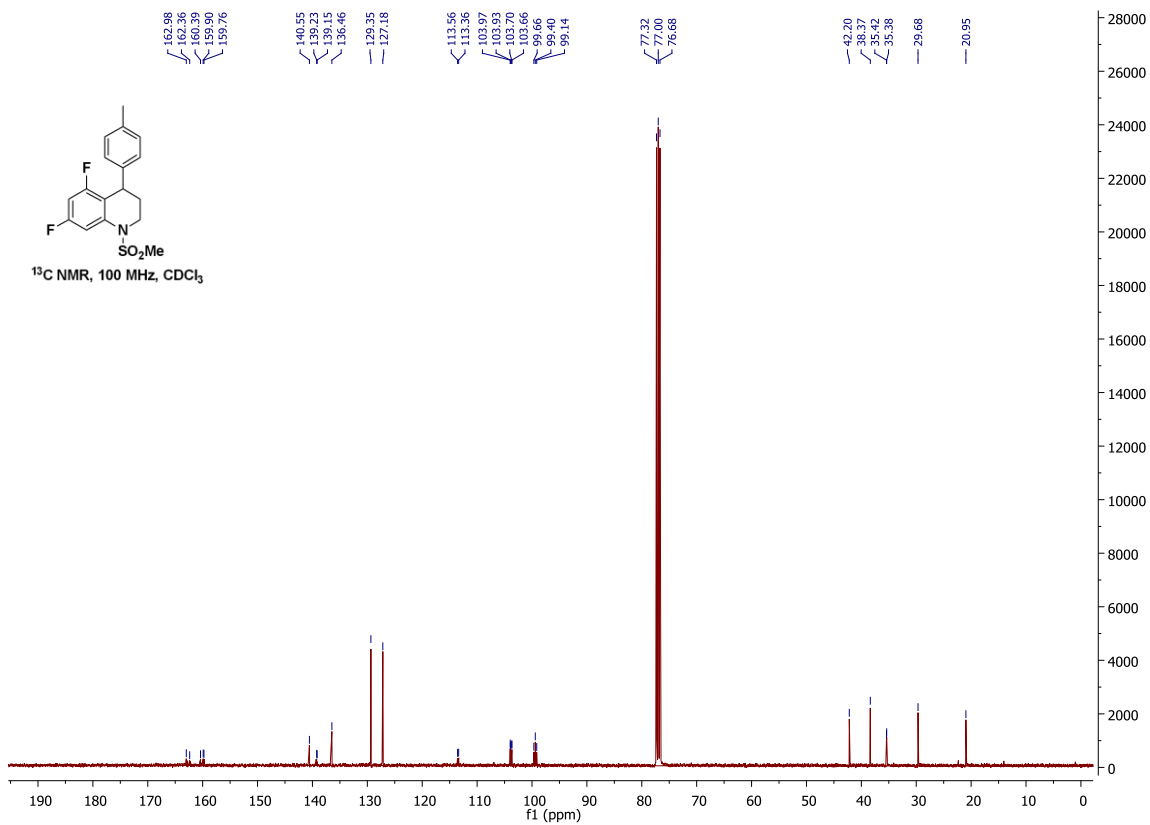
**6-Fluoro-3-methyl-1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (47)**



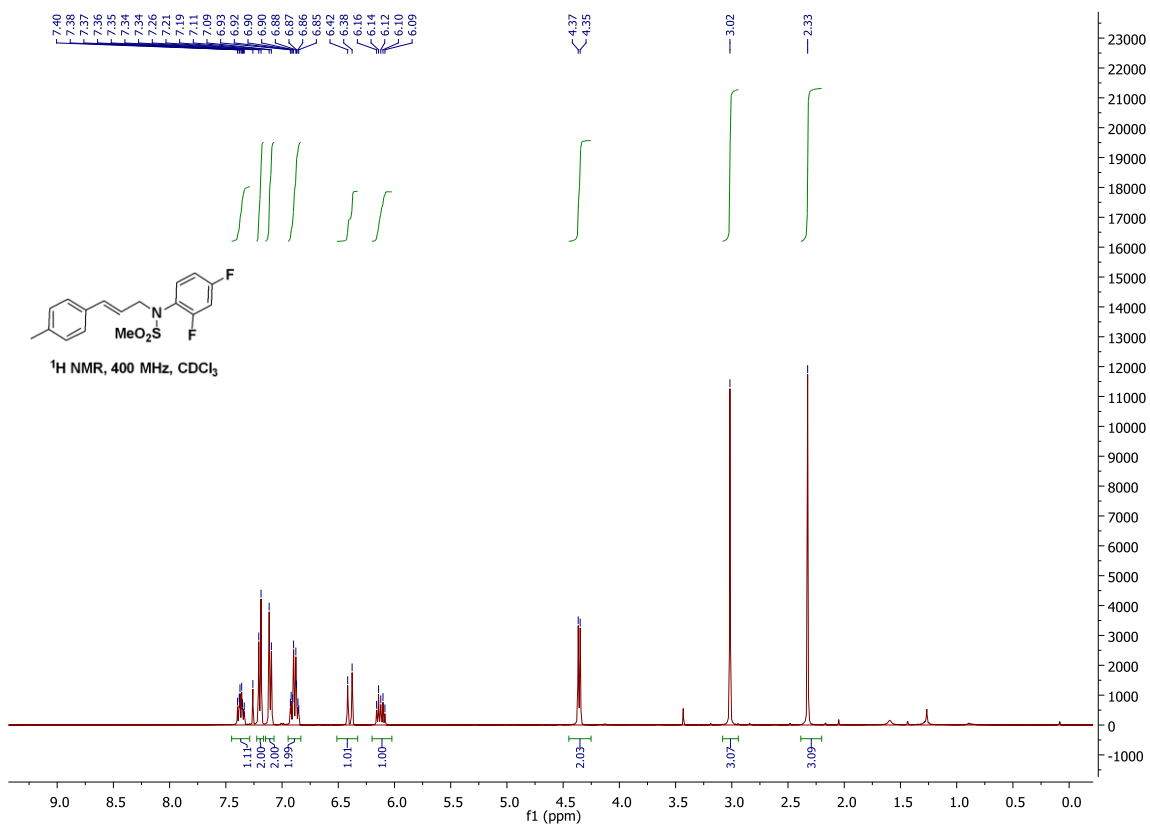


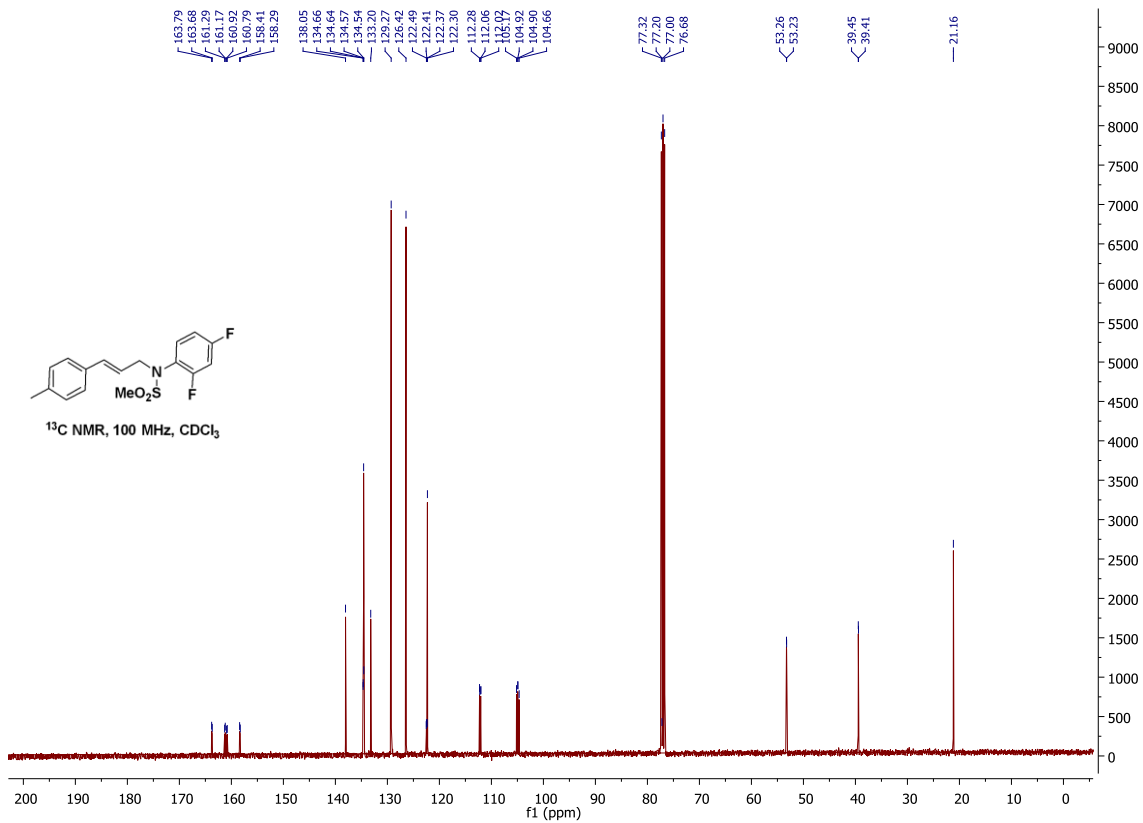
**5,7-Difluoro-1-(methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline (48)**



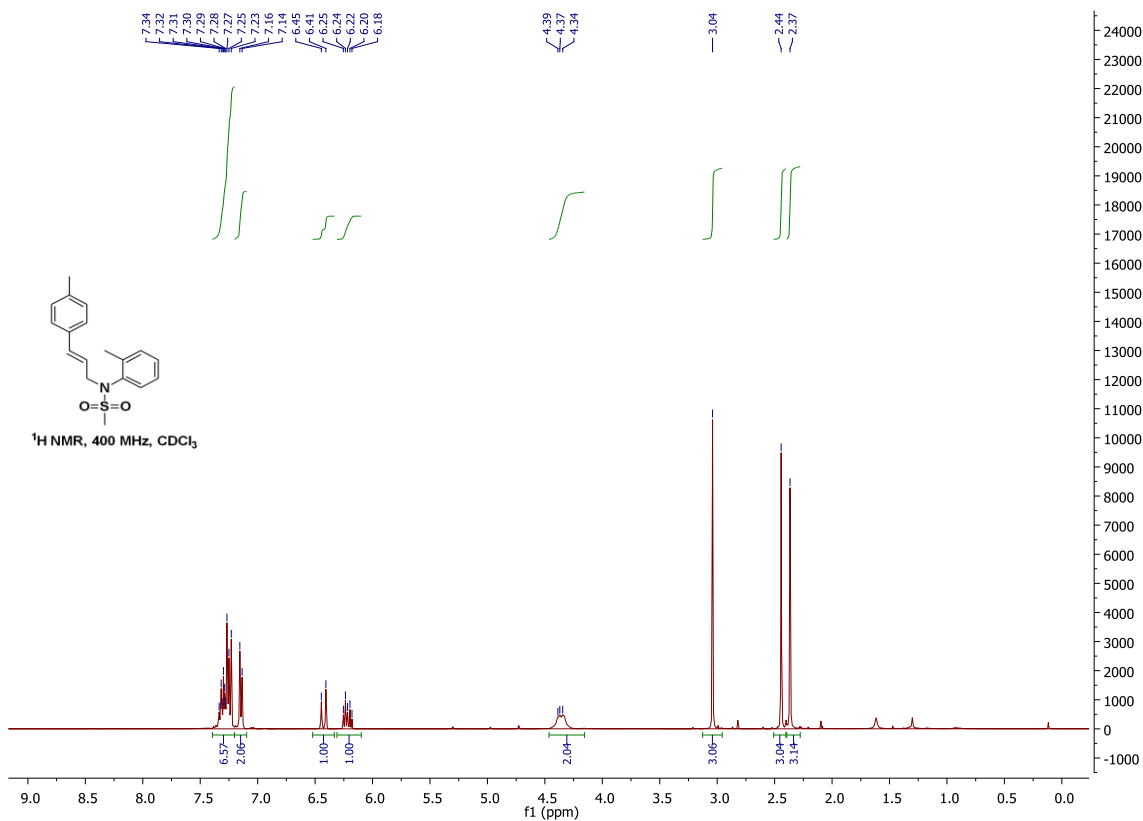


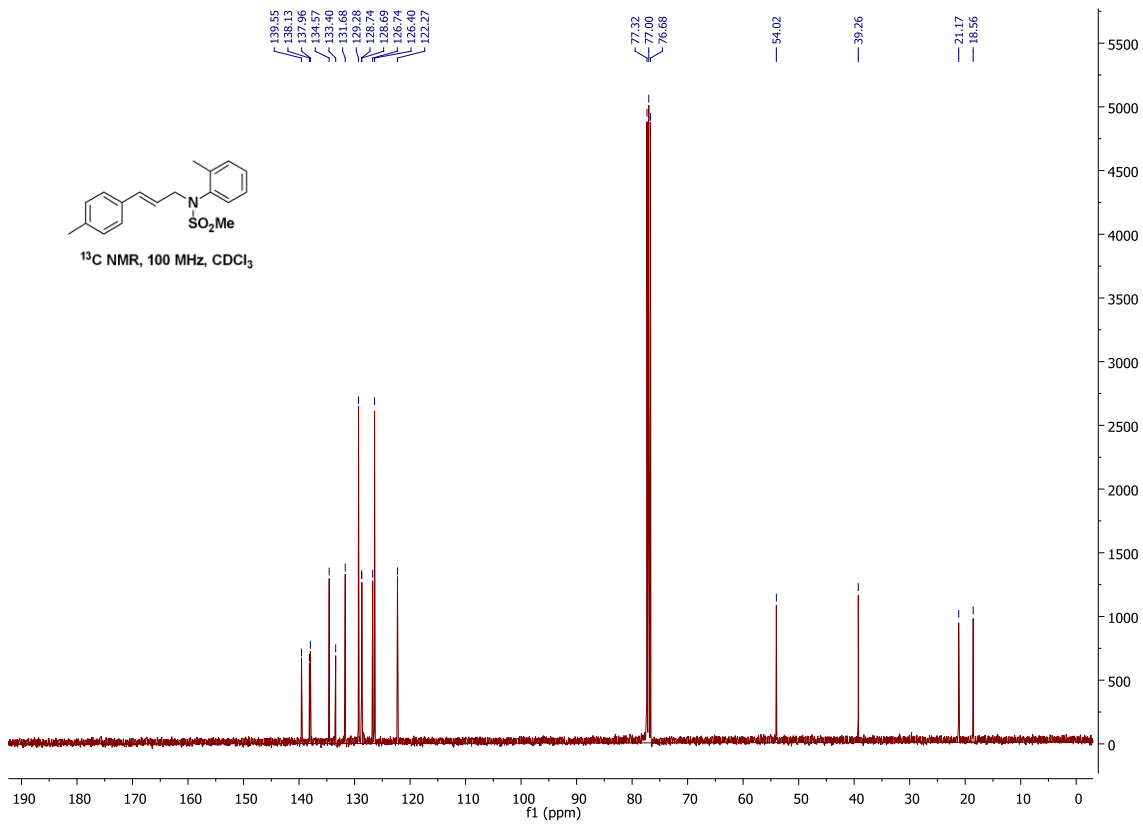
**(E)-N-(2,4-Difluorophenyl)-N-(3-p-tolylallyl)methanesulfonamide (49)**



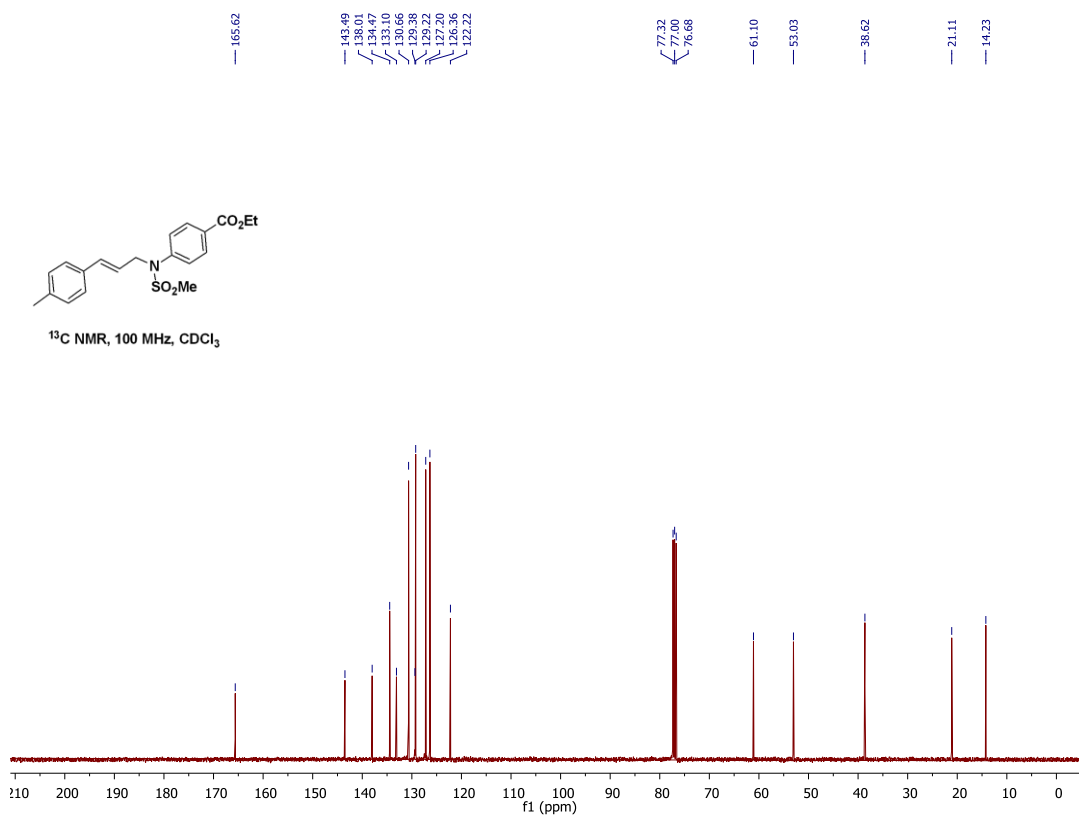
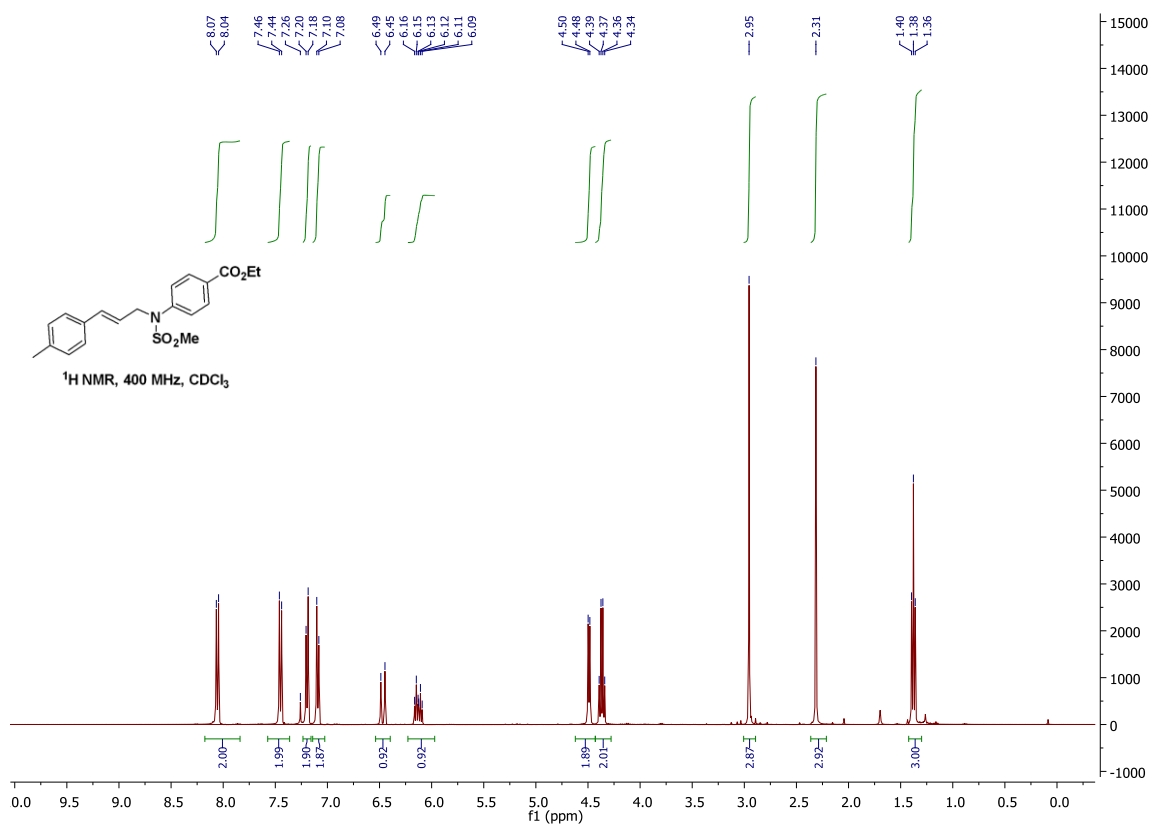


**(E)-N-*o*-Tolyl-N-(3-*p*-tolylallyl)methanesulfonamide (50)**

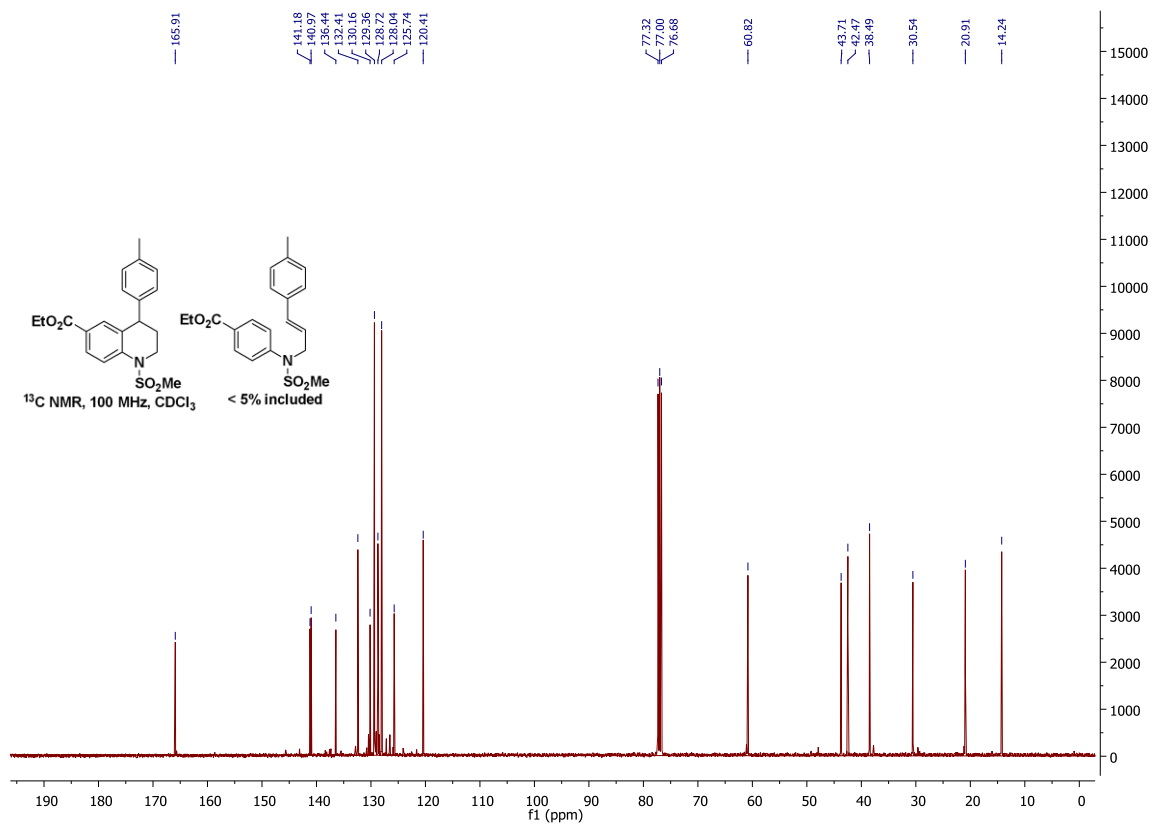
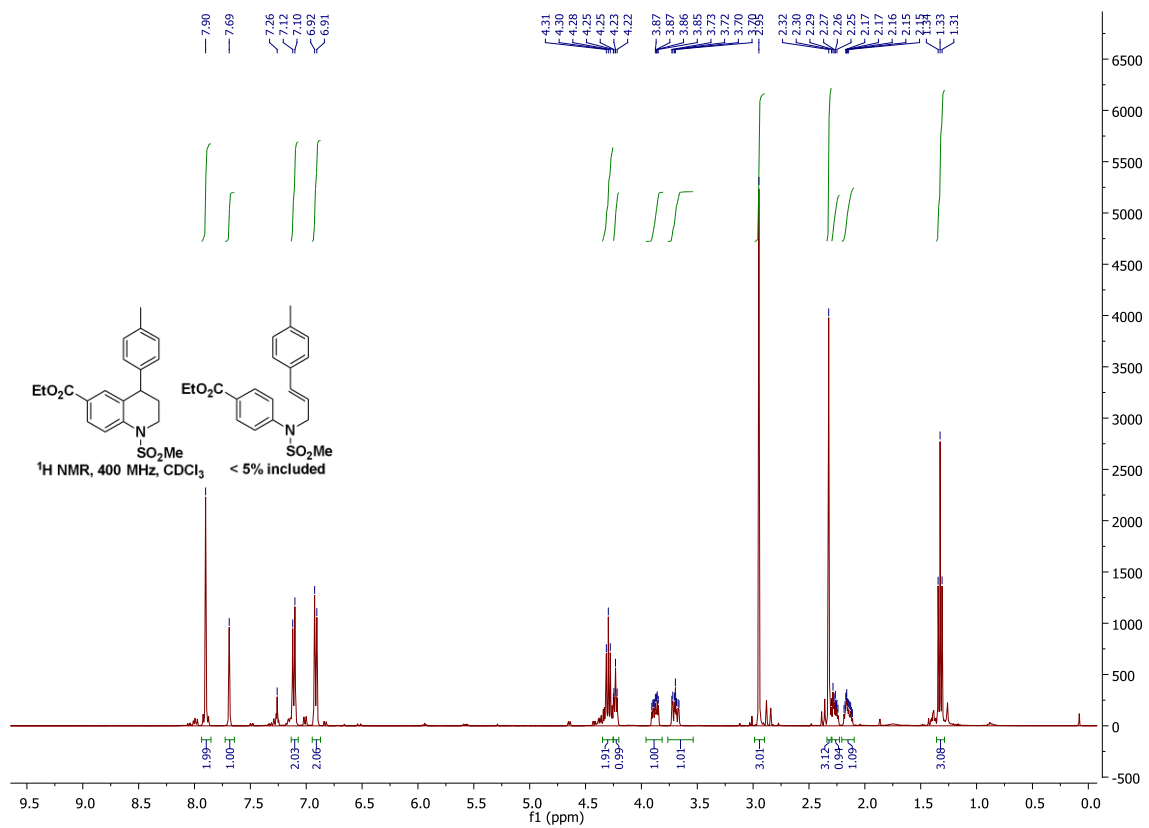




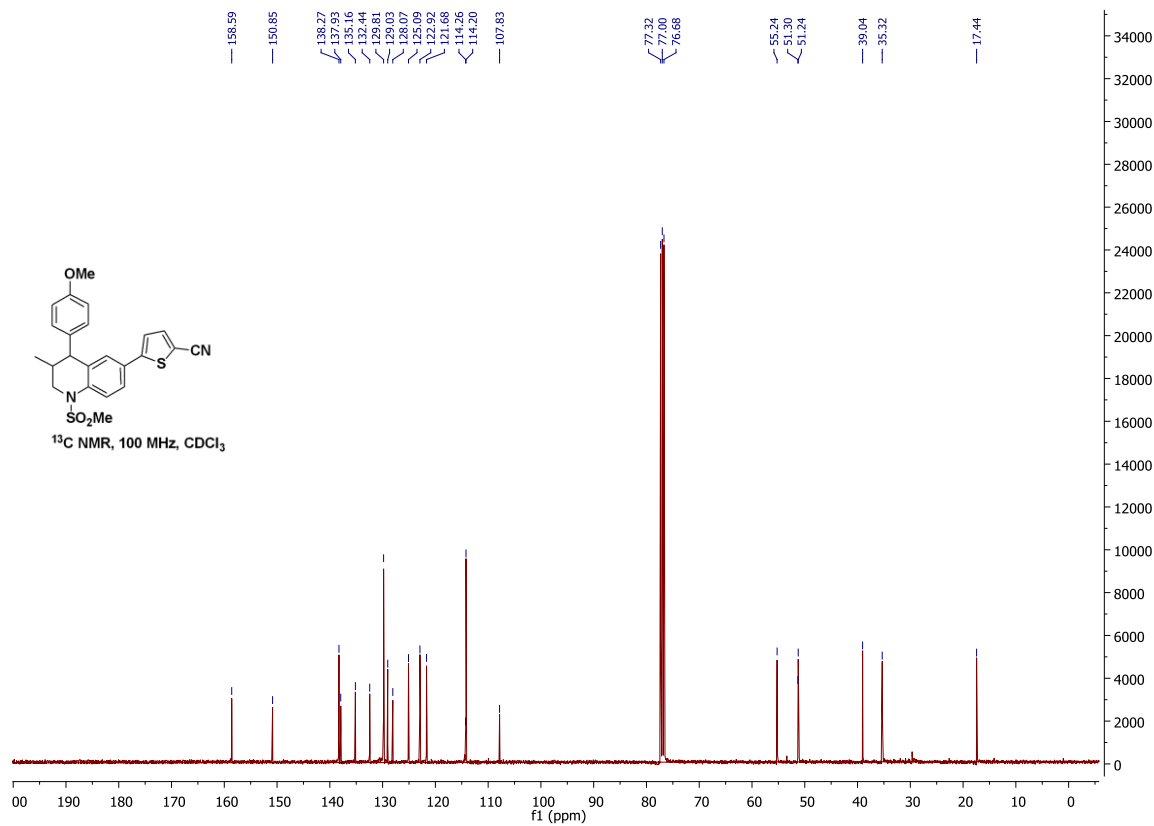
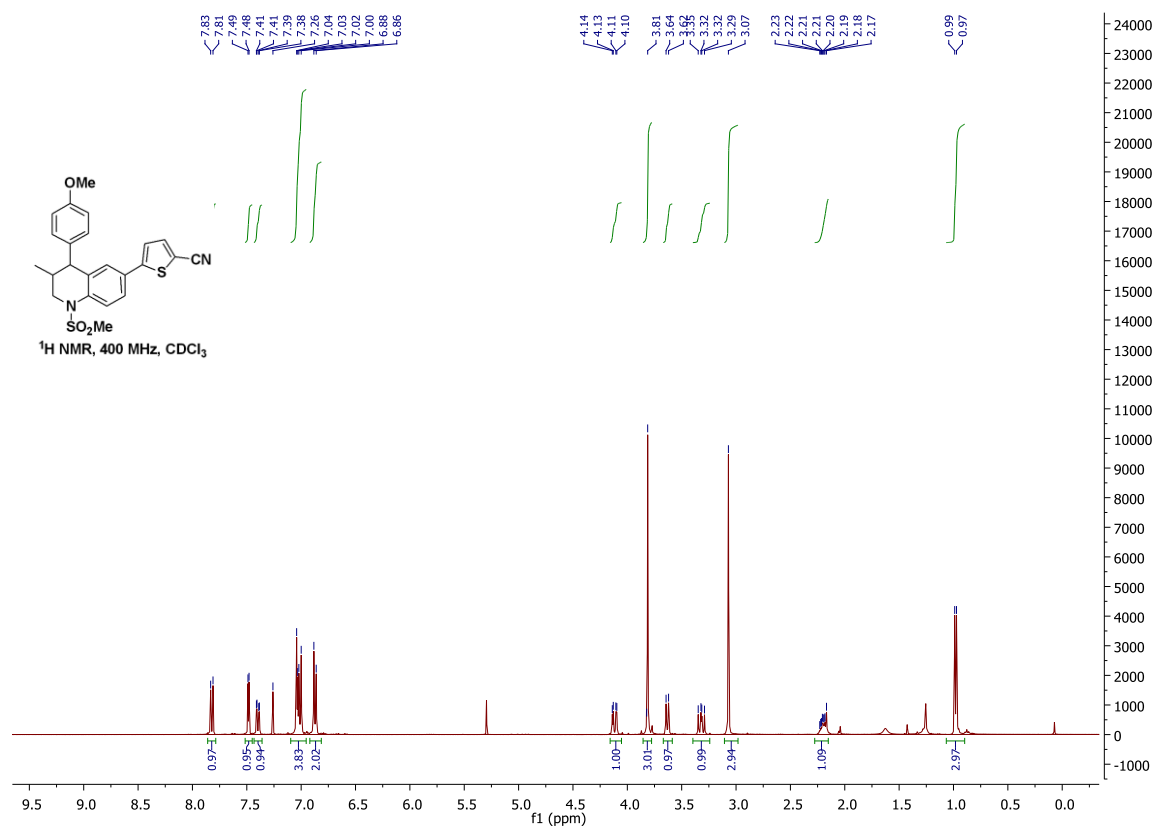
**(E)-Ethyl 4-(N-(3-*p*-tolylallyl)methylsulfonamido)benzoate (51a)**



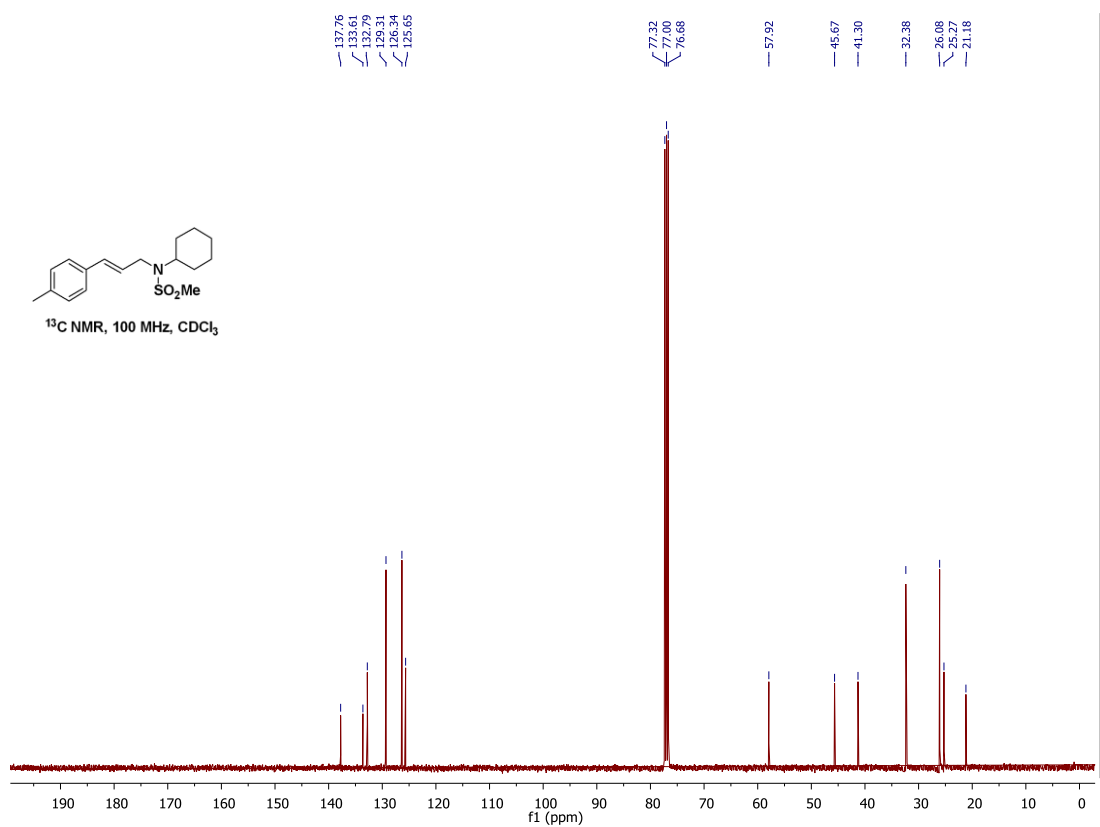
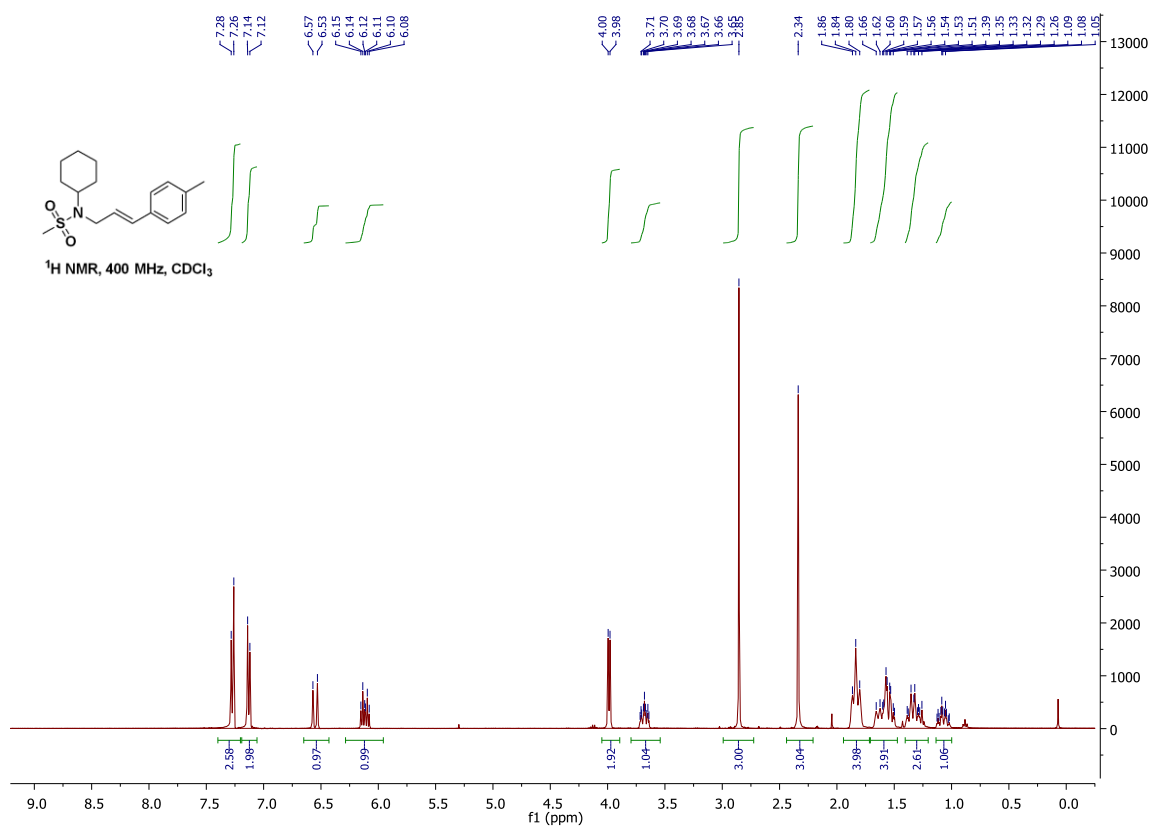
# Ethyl 1-(methylsulfonyl)-4-p-tolyl-1,2,3,4-tetrahydroquinoline-6-carboxylate (51b)



**5-(4-(4-Methoxyphenyl)-3-methyl-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinolin-6-yl)thiophene-2-carbonitrile (52)**

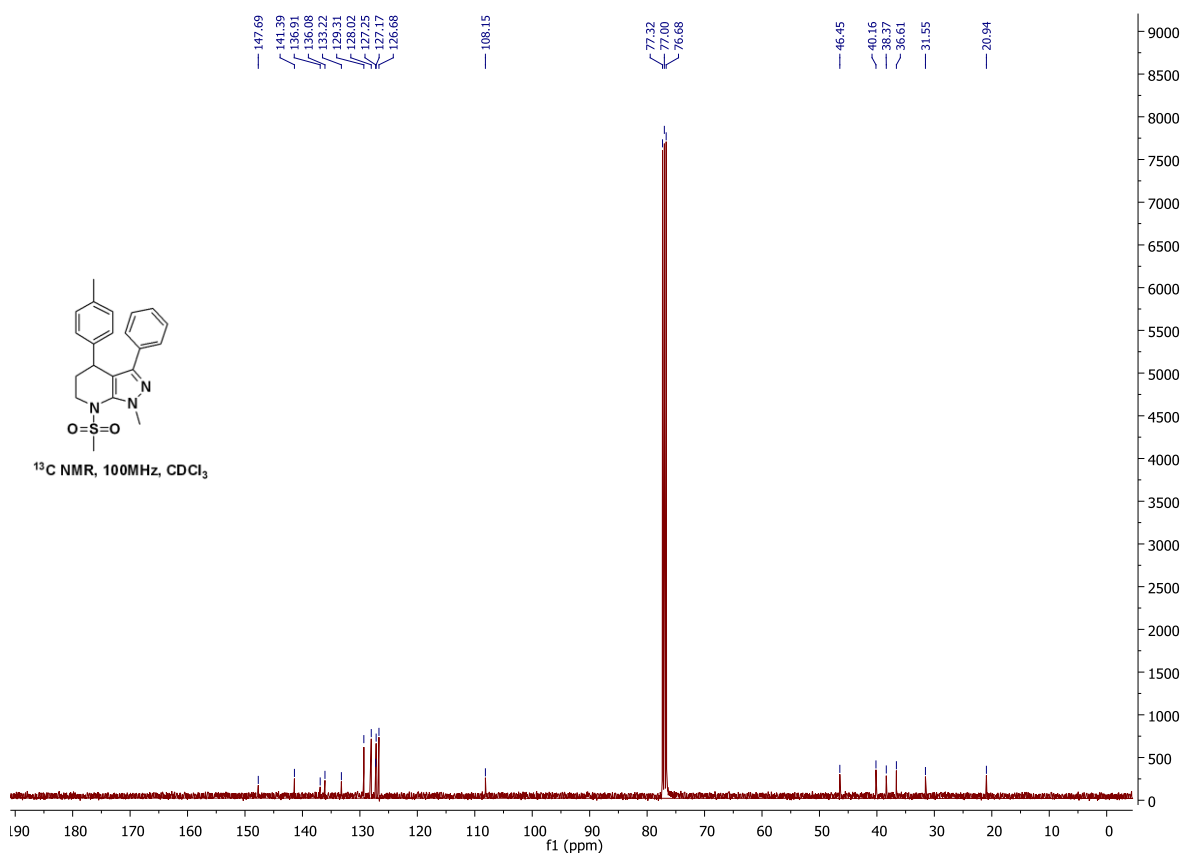
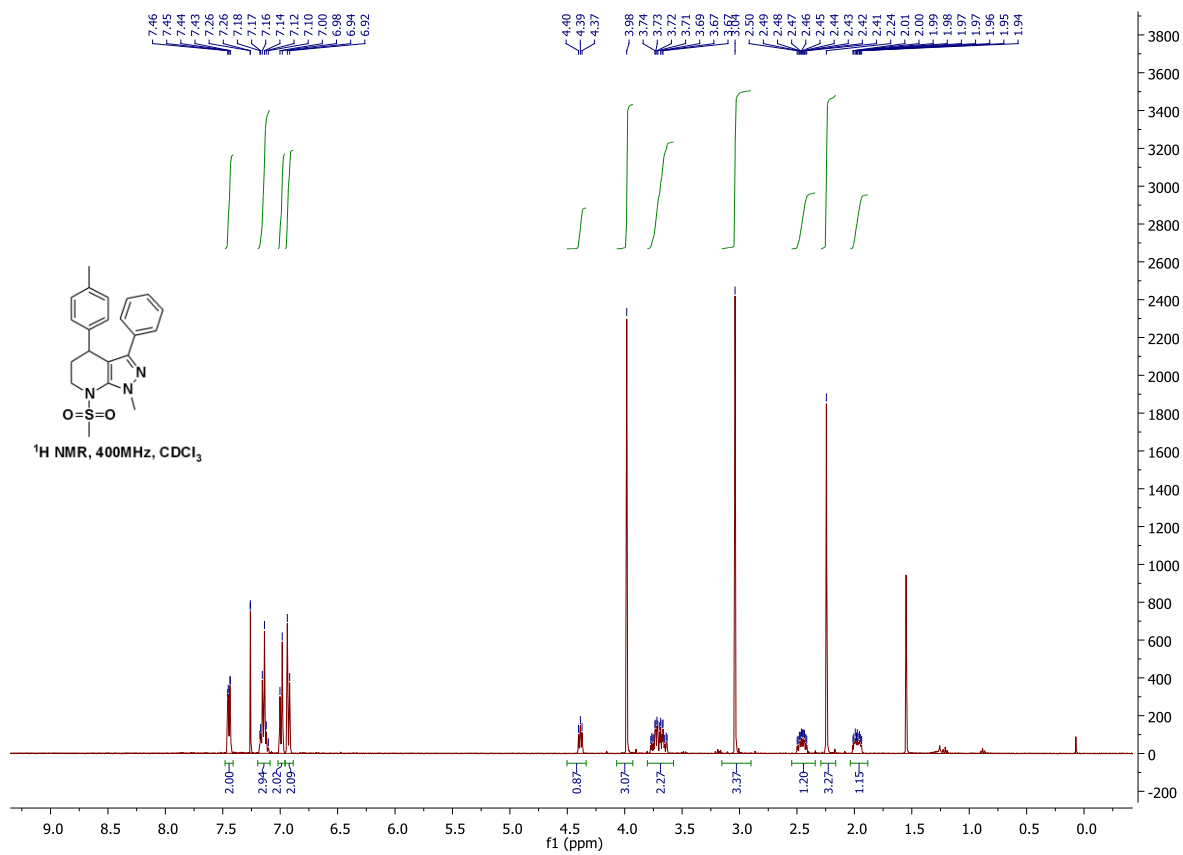


**(E)-N-Cyclohexyl-N-(3-*p*-tolylallyl)methanesulfonamide (53)**

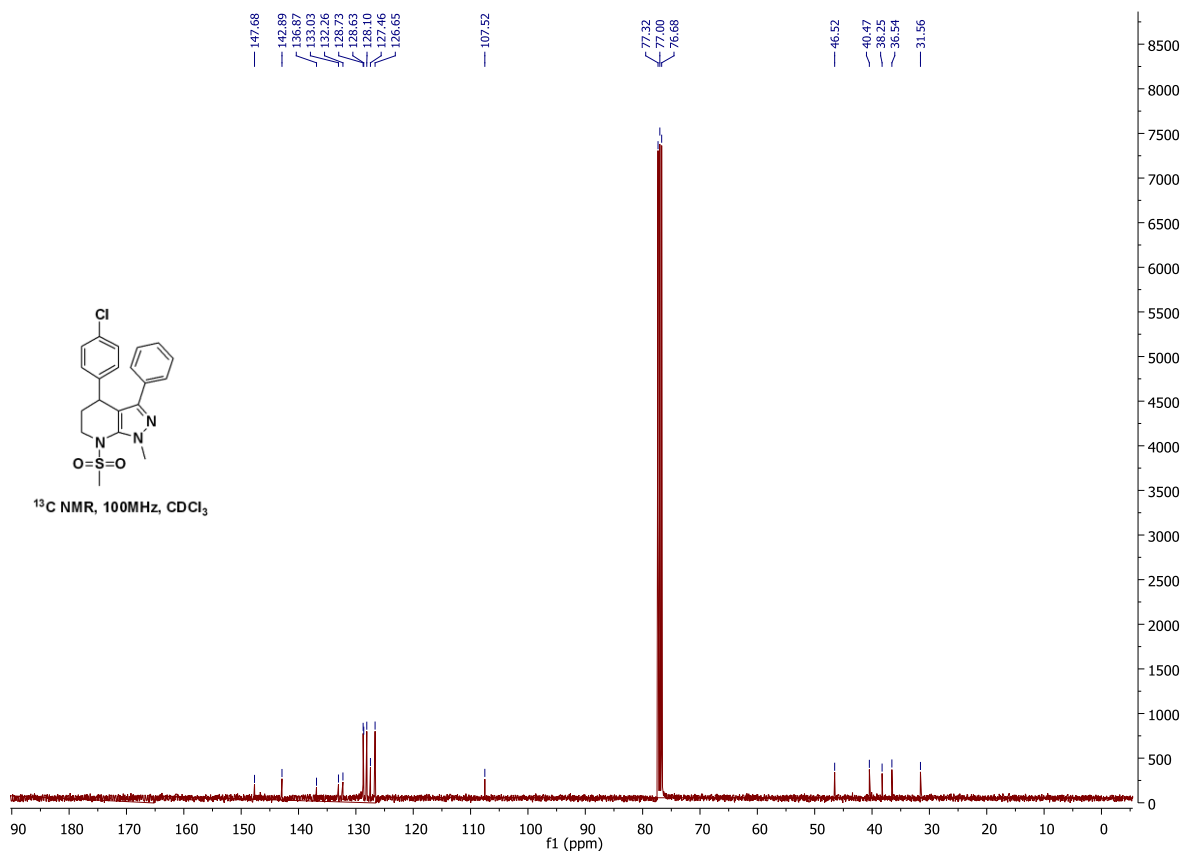
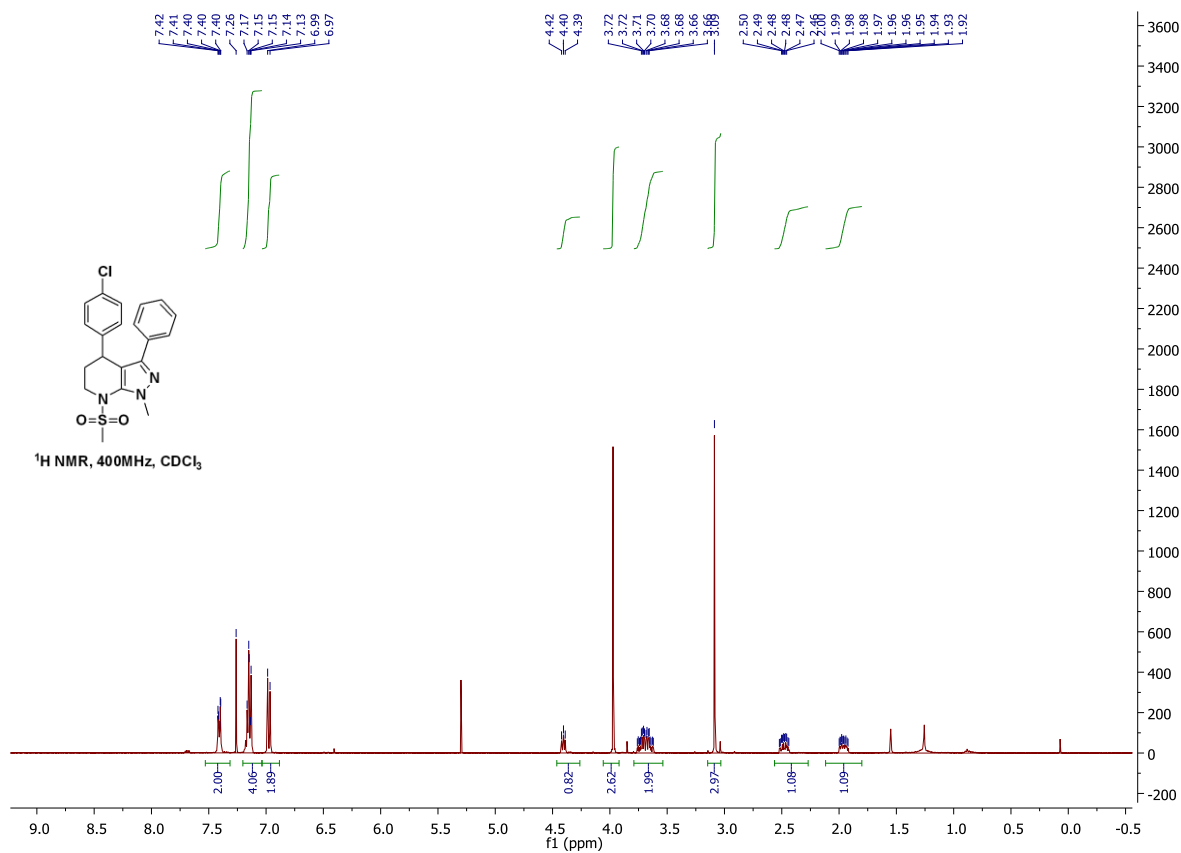




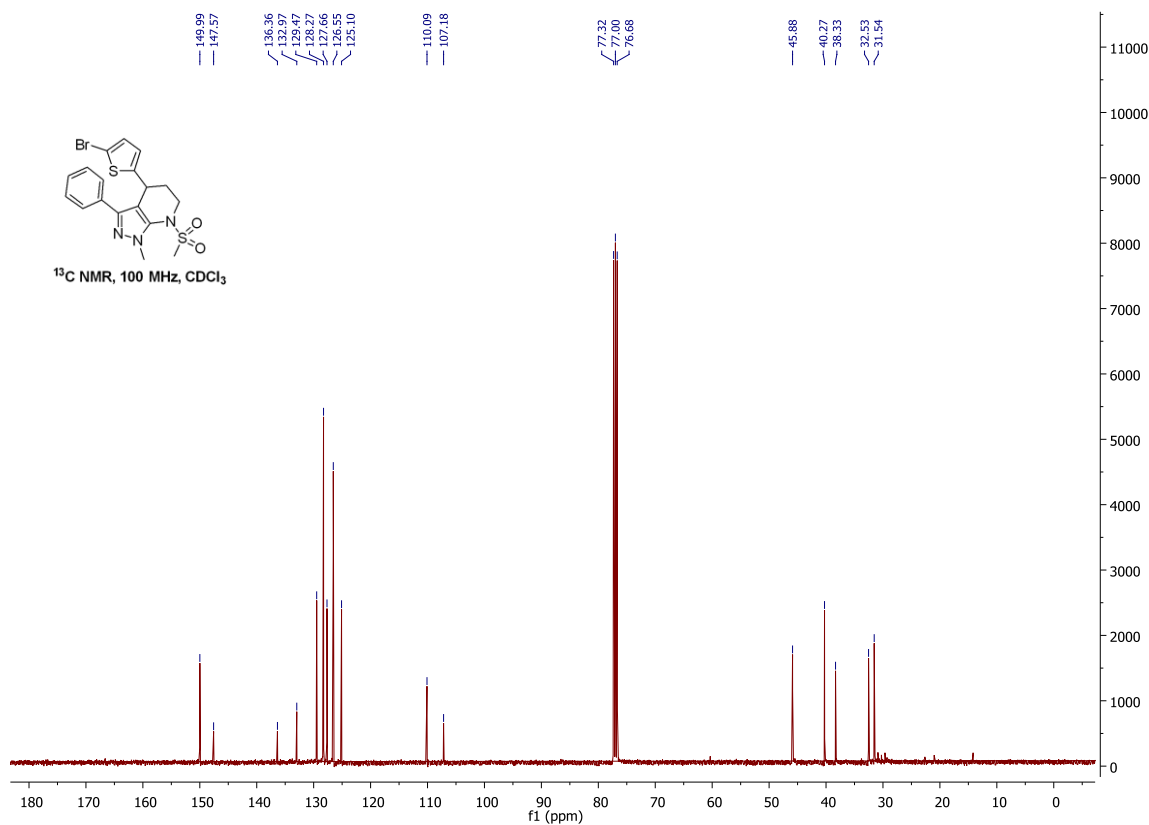
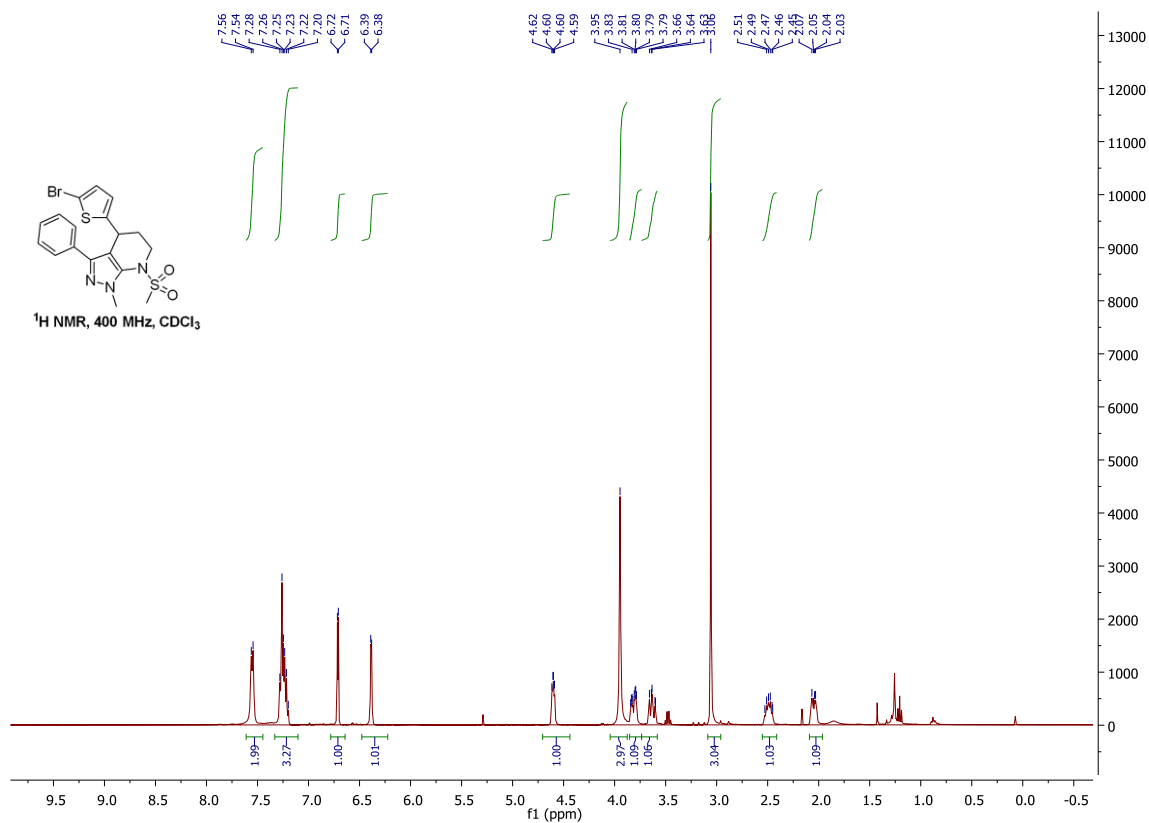
1-Methyl-7-(methylsulfonyl)-3-phenyl-4-*p*-tolyl-4,5,6,7-tetrahydropyrazolo[3,4-*b*]pyridine (55)



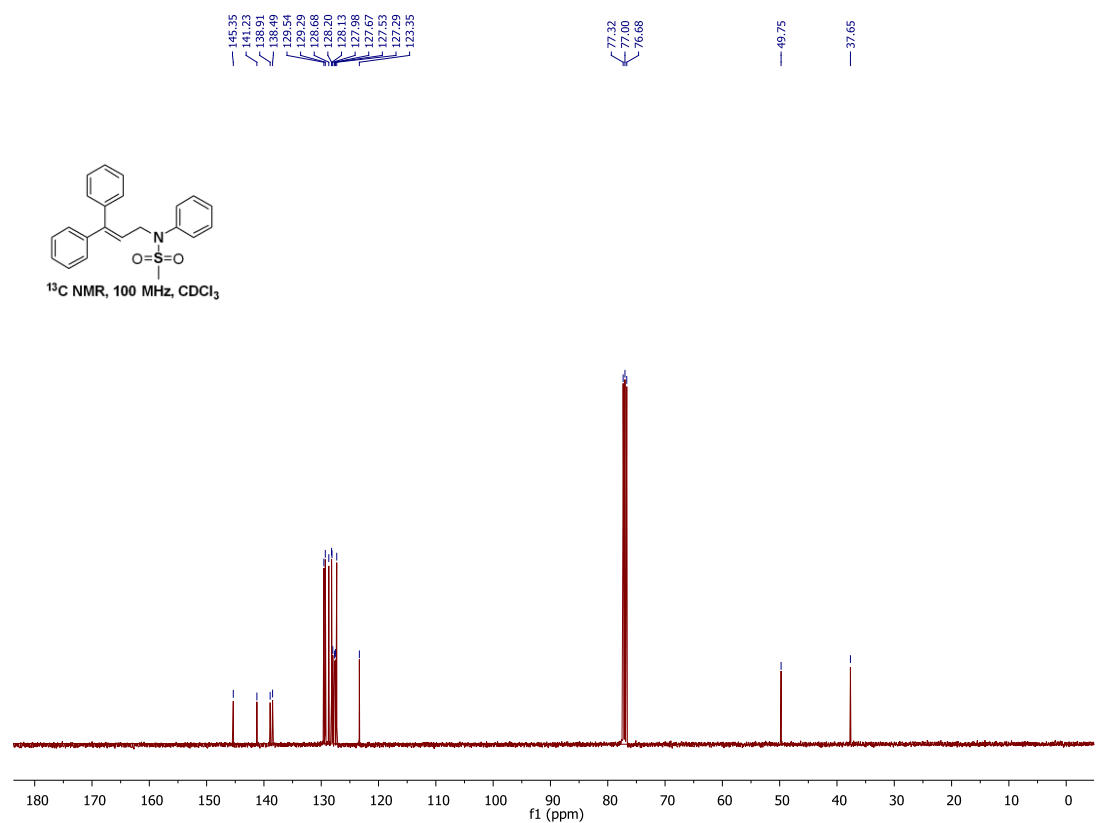
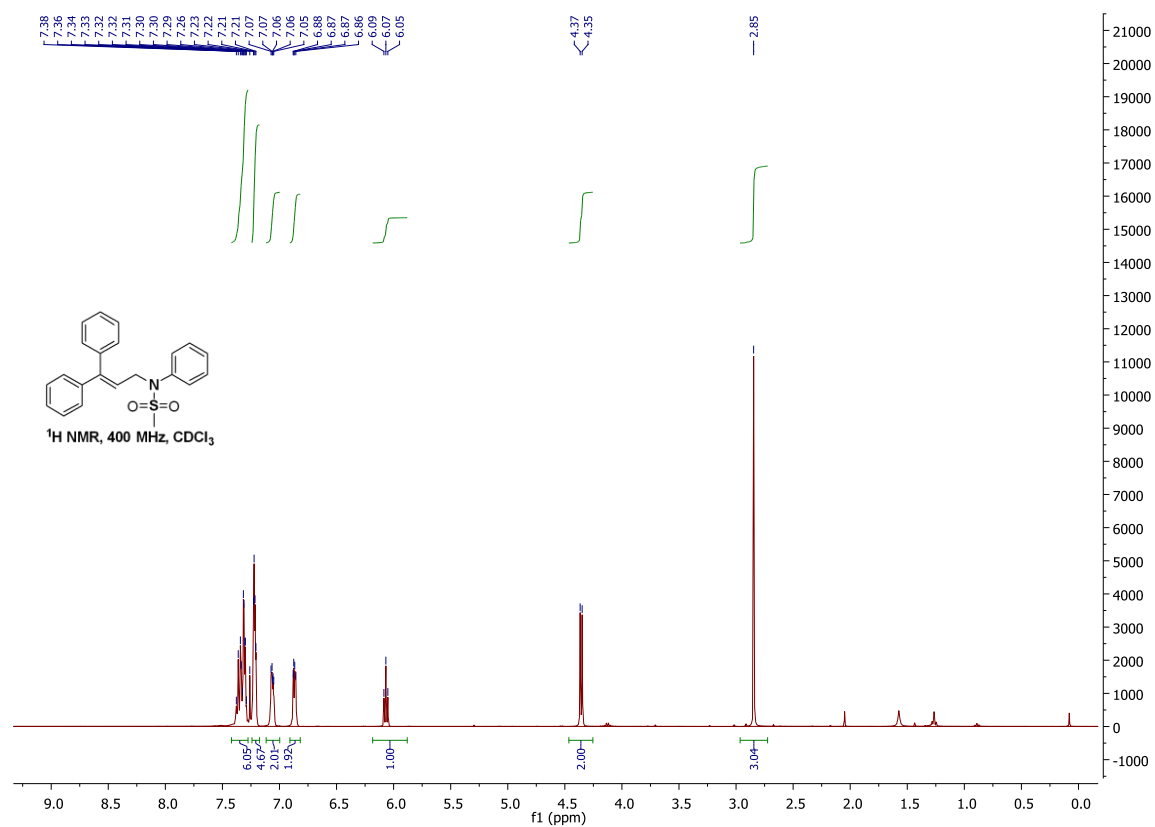
**4-(4-Chlorophenyl)-1-methyl-7-(methylsulfonyl)-3-phenyl-4,5,6,7-tetrahydropyrazolo[3,4-b]pyridine (56)**



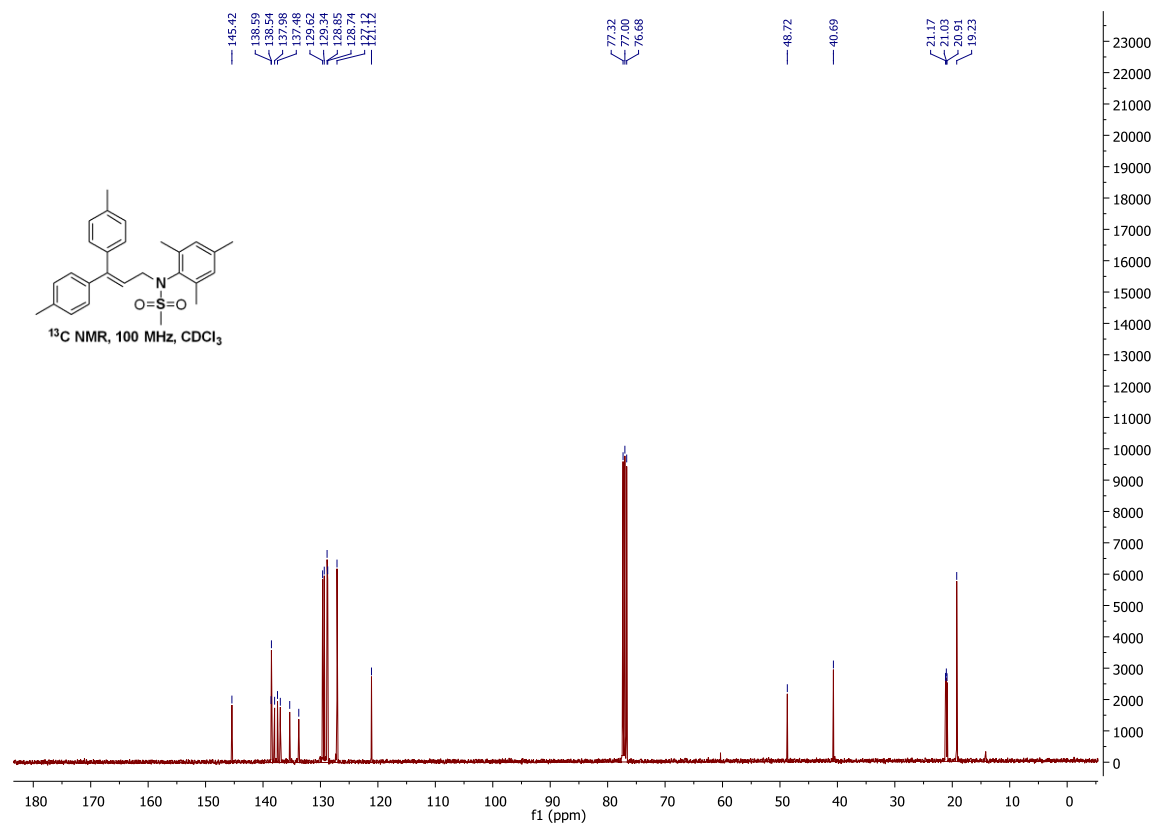
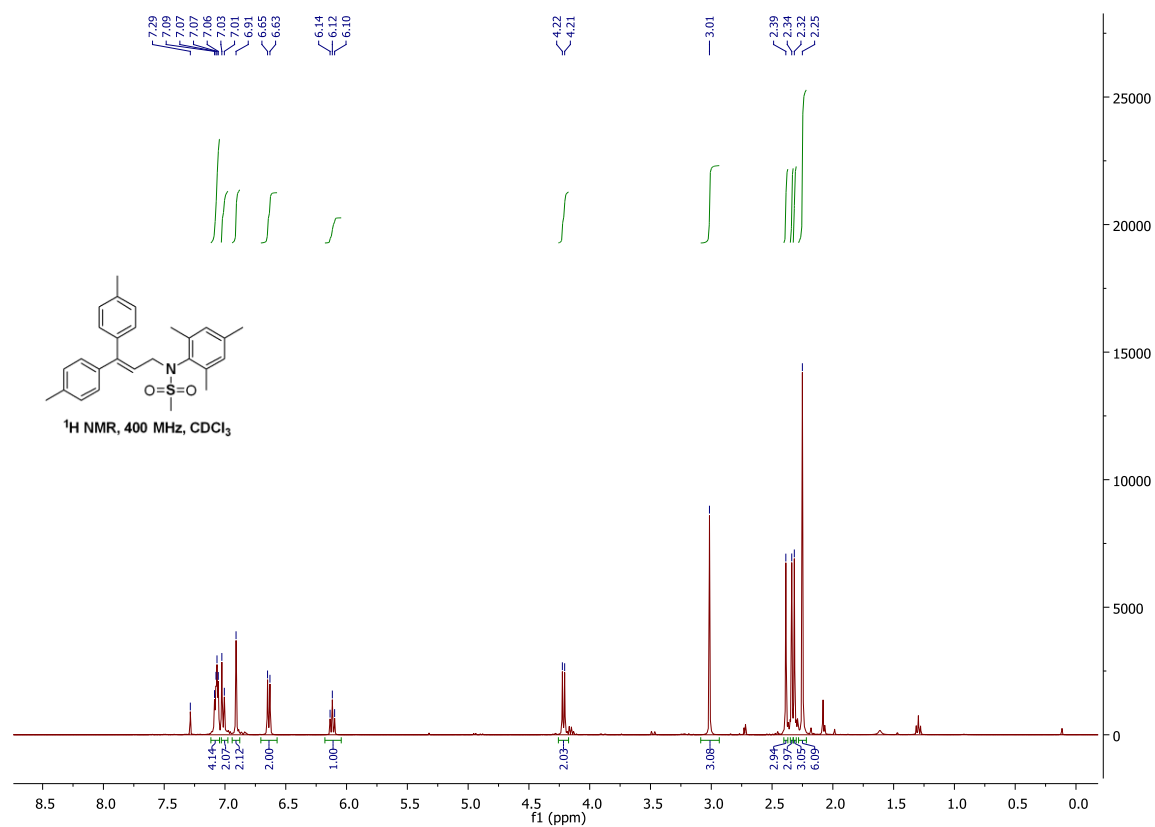
**4-(5-Bromothiophen-2-yl)-1-methyl-7-(methylsulfonyl)-3-phenyl-4,5,6,7-tetrahydropyrazolo[3,4-b]pyridine (57)**



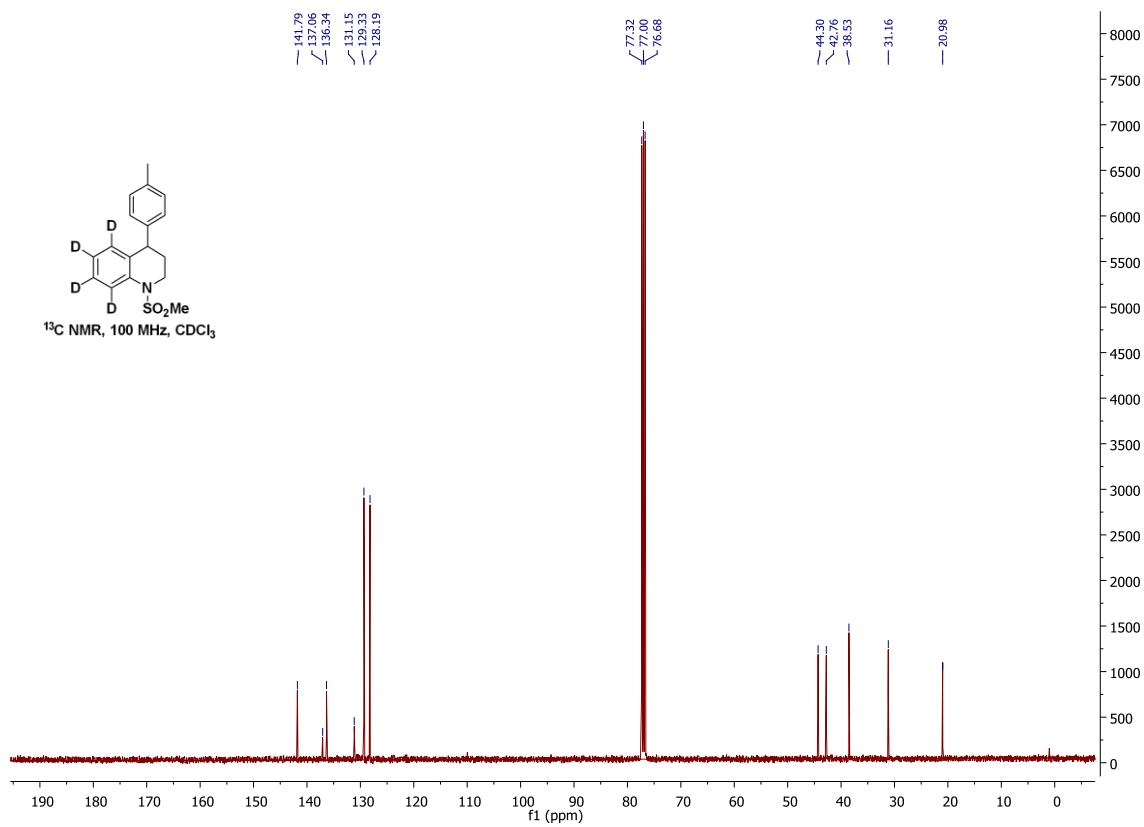
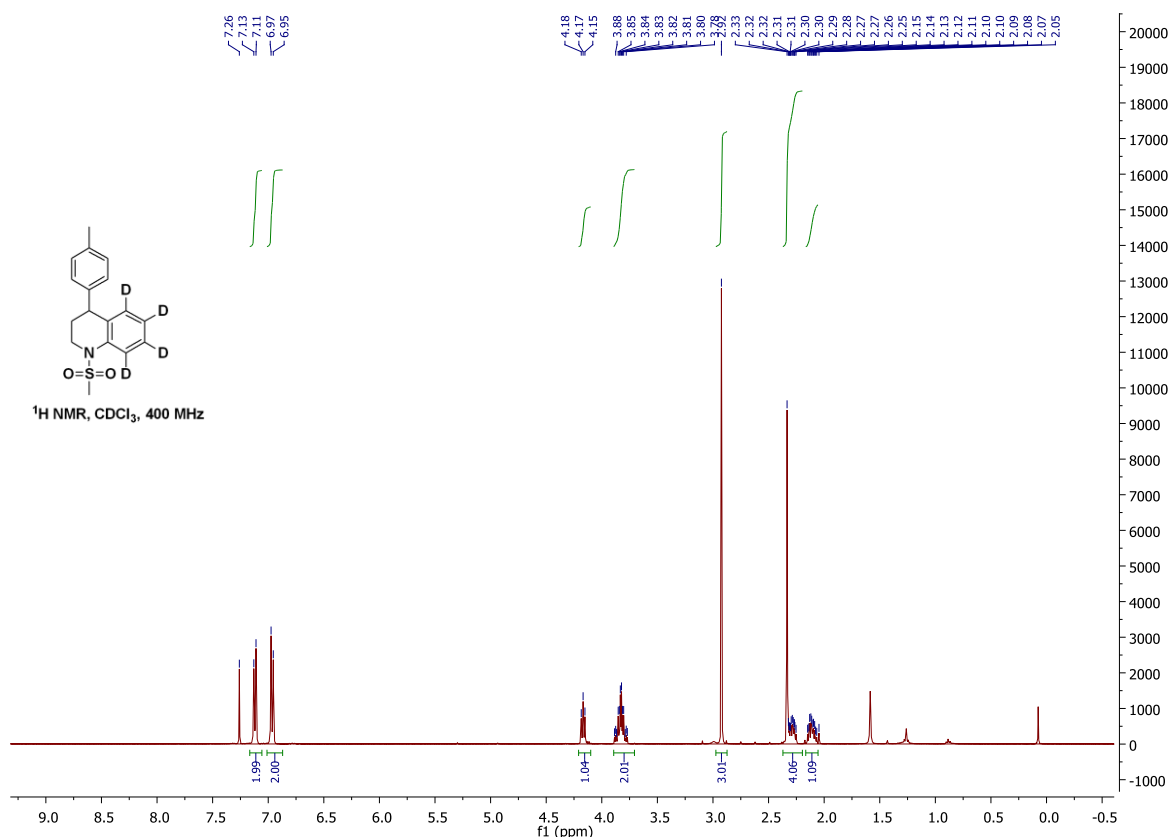
# *N*-(3,3-Diphenylallyl)-*N*-phenylmethanesulfonamide (58)



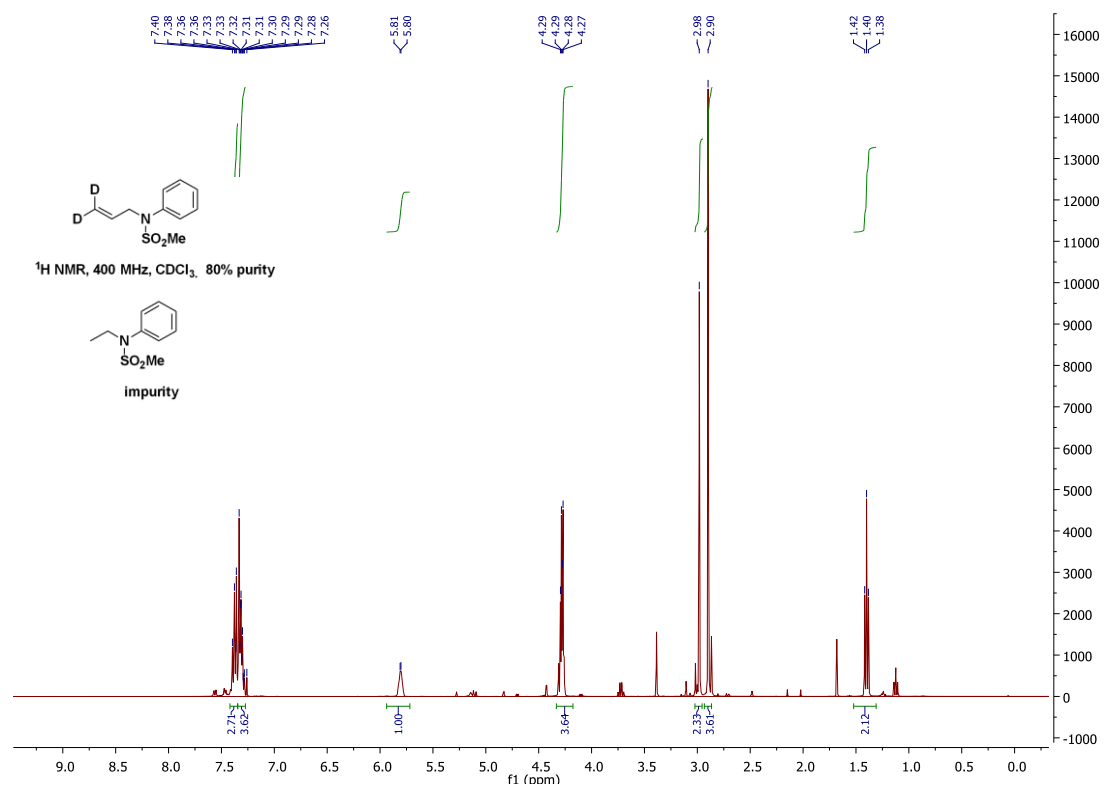
# *N*-(3,3-Dip-tolylallyl)-*N*-mesitylmethanesulfonamide (59)



**1-(Methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline *d*<sub>4</sub> (62)**



# *N*-Allyl-4-methyl-*N*-methylbenzenesulfonamide *d*<sub>2</sub> (63)



# 1-(Methylsulfonyl)-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline *d*<sub>2</sub> (64)

