

## Supporting information

# Tandem 1,2-Sulfur Migration and (Aza)-Diels-Alder Reaction of $\beta$ -Thio- $\alpha$ -Diazoimines: Rhodium Catalyzed Synthesis of (Fused)-Polyhydropyridines, and Cyclohexenes

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## Table of contents

1. General Comments	2
2. Analytical Methods	2
3. General procedure for the synthesis of thio-tethered <i>N</i> -sulfonyl-1,2,3-triazoles <b>1</b>	3
4. Rhodium catalyzed 1,2-sulfur migration and aza-Diels-Alder reaction of <b>1a</b> : Optimization	13
5. General procedure for the synthesis of tetrahydropyridines <b>3</b>	14
6. General procedure for the synthesis of fused tetrahydropyridines <b>5</b>	24
7. General procedure for the synthesis of tetrahydropyridines ( <b>6-11, 16</b> ), dihydropyridines ( <b>14</b> and <b>15</b> ) and cyclohexenes ( <b>18</b> )	33
8. One-pot synthesis of compound <b>3a</b> from phenylpropargyl sulfide	42
9. One-pot synthesis of compound <b>5a</b> from phenylpropargyl sulfide	43
10. Synthesis of compound <b>24</b>	43
11. Synthesis of compound <b>25</b>	44
12. Synthesis of 3-(4-methoxyphenyl)-5-(phenylthio)pyridine <b>26</b>	45
13. NMR spectra of isolated compounds	46
14. Crystallographic Data and Structure Refinements Summary for Compound <b>3a</b>	109

## **1. General Comments:**

All reactions were carried out under an atmosphere of dry nitrogen using reaction tubes. Dry 1,2-DCE was prepared by distilling over CaH<sub>2</sub> and stored over using molecular sieves 4Å under N<sub>2</sub> atmosphere. [Rh<sub>2</sub>(OAc)<sub>4</sub>], [Rh<sub>2</sub>(Oct)<sub>4</sub>], [Rh<sub>2</sub>(DOSP)<sub>4</sub>] and [Rh<sub>2</sub>(TBSP)<sub>4</sub>] were obtained from Aldrich and they were used as received.

Column chromatography was performed using Rankem Silicagel (100-200 mesh) and the solvent system used unless otherwise specified, was ethyl acetate-hexanes with various percentage of polarity depending on the nature of the substrate.

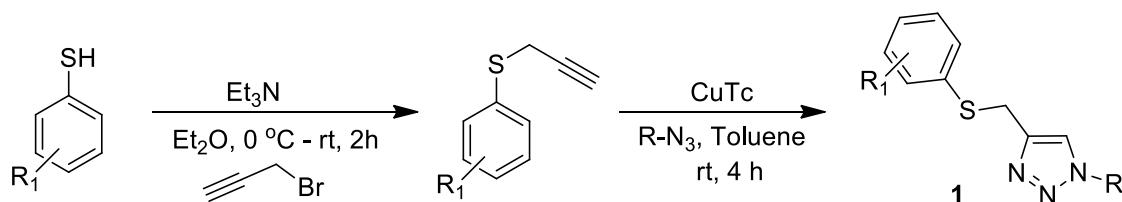
It is important to note that purity of both triazoles and dienophiles significantly affect the reactions.

## **2. Analytical Methods:**

NMR data were recorded on 400 and 500 MHz spectrometers. <sup>13</sup>C and <sup>1</sup>H NMR spectra were referenced to signals of deutero solvents and residual protonated solvents, respectively. Infrared spectra were recorded on a Thermo Nicolet iS10 FT spectrometer. HRMS were recorded by electron spray ionization (ESI) method on a Q-TOF Micro with lock spray source. Melting points are corrected. The crystal data were collected and integrated using a Bruker Axs kappa apex2 CCD diffractometer, with graphite monochromated Mo-Kα radiation.

### 3. General procedure for the synthesis of thio-tethered *N*-sulfonyl-1,2,3-triazoles

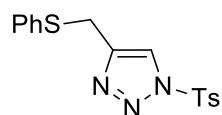
**1:**<sup>1</sup>



Step-1: To the mixture of propargyl bromide (0.95 mL, 10.74 mmol, 1.1 equiv) and triethylamine (2.71 mL, 19.54 mmol, 2 equiv) in Et<sub>2</sub>O (15 mL) at 0 °C, aryl thiols (9.77 mmol, 1 equiv) was added dropwise over 5 min. The reaction mixture was stirred at 0 °C for 15 minutes then warmed to room temperature and stirred for 2 h. The progress of the reaction was monitored by TLC analysis. After the completion of the reaction, the reaction mixture was quenched with H<sub>2</sub>O (10 mL), extracted with diethyl ether (2 x 15 mL) and the organic layer was washed with 10% NaOH (2 x 10 mL). The organic layer was dried over (Na<sub>2</sub>SO<sub>4</sub>), filtered and the solvent was removed under reduced pressure. The resultant aryl propargyl sulfide was used in the next step without further purification.

Step-2: To a stirred solution of crude aryl propargyl sulfide (1 equiv) and CuTc (0.1 equiv) in toluene (15 mL), sulfonyl azide (1 equiv) was added at room temperature under N<sub>2</sub> atmosphere. The resulting solution was stirred for 4 h and monitored by TLC analysis. After the completion of the reaction, the reaction mixture was quenched with saturated NH<sub>4</sub>Cl solution (25 mL), extracted with EtOAc (2 x 25 mL) and dried over (Na<sub>2</sub>SO<sub>4</sub>). Evaporation of solvent under reduced pressure followed by purification by column chromatography afforded the thio-tethered *N*-sulfonyl-1,2,3-triazoles **1** in good yields.

#### 4-((Phenylthio)methyl)-1-tosyl-1,2,3-triazole (**1a**) :



According to the general procedure the product was isolated in 90% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

<sup>1</sup> J. Raushel, V. V. Fokin, *Org. Lett.* **2010**, *12*, 4952.

mp: 95-97 °C.

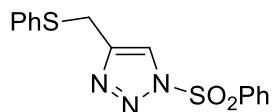
FTIR (KBr): 3128, 3085, 2981, 1641, 1582, 1549, 1479, 1434, 1390, 1368, 1304, 1233, 1191, 1171, 1087, 1008, 968, 807, 743, 670, 577, 537 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.90 (d, 2H, *J* = 8.5 Hz), 7.81 (s, 1H), 7.36 (d, 2H, *J* = 8.1 Hz), 7.28-7.20 (m, 5H), 4.17 (s, 2H), 2.45 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 147.3, 145.1, 134.6, 133.1, 130.5, 130.4, 129.2, 128.7, 127.2, 121.9, 28.9, 21.9.

HRMS: calcd.for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>+H: 346.0678; found: 346.0679.

### 1- (Phenylsulfonyl)-4-((phenylthio)methyl)-1,2,3-triazole (1b) :



According to the general procedure the product was isolated in 83% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

mp: 68-70 °C.

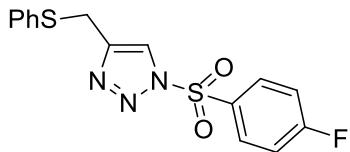
FTIR (KBr): 3152, 3056, 2985, 1583, 1479, 1446, 1396, 1310, 1265, 1195, 1090, 1011, 971, 895, 736, 706, 625, 592, 563 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.04-8.01 (m, 2H), 7.83 (s, 1H), 7.74-7.70 (m, 1H), 7.60-7.56 (m, 2H), 7.28-7.20 (m, 5H), 4.18 (s, 2H),

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 145.2, 136.2, 135.7, 134.5, 130.5, 129.9, 129.2, 128.6, 127.2, 122.0, 28.9.

HRMS: calcd.for C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>+H: 332.0522; found: 332.0527.

**1-((4-Fluorophenyl)sulfonyl)-4-((phenylthio)methyl)-1,2,3-triazole (1c) :**



According to the general procedure the product was isolated in 70% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

mp: 94-96 °C.

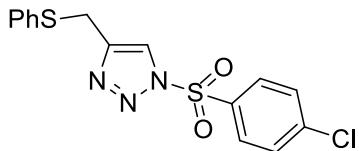
FTIR (KBr): 3153, 3062, 2926, 1588, 1491, 1398, 1264, 1192, 1090, 1011, 970, 837, 750, 679, 582, 539 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.08-8.04 (m, 2H), 7.83 (s, 1H), 7.29-7.20 (m, 7H), 4.18 (s, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 167.0 (d, *J* = 261.1 Hz), 145.3, 134.5, 132.1, 131.8 (d, *J* = 10.1 Hz), 130.4, 129.2, 129.2, 127.2, 121.9, 117.5 (d, *J* = 23.2 Hz), 28.8.

HRMS: calcd. for C<sub>15</sub>H<sub>12</sub>N<sub>3</sub>O<sub>2</sub>FS<sub>2</sub>+H: 350.0428; found: 350.0430.

**1-((4-Chlorophenyl)sulfonyl)-4-((phenylthio)methyl)-1,2,3-triazole (1d) :**



According to the general procedure the product was isolated in 70% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

mp: 114-116 °C.

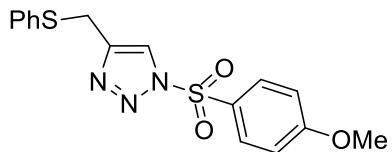
FTIR (KBr): 3131, 3091, 1579, 1476, 1437, 1398, 1369, 1308, 1274, 1262, 1239, 1191, 1090, 1011, 970, 823, 748, 690, 640, 610, 571 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.95 (d, 2H, *J* = 8.7 Hz), 7.82 (s, 1H), 7.54 (d, 2H, *J* = 8.7 Hz), 7.28-7.20 (m, 5H), 4.18 (s, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 145.4, 142.9, 134.6, 134.5, 130.4, 130.3, 130.0, 129.2, 127.2, 122.0, 28.9.

HRMS: calcd.for C<sub>15</sub>H<sub>12</sub>ClN<sub>3</sub>O<sub>2</sub>S<sub>2</sub>+H: 366.0132; found: 366.0138.

**1-((4-Methoxyphenyl)sulfonyl)-4-((phenylthio)methyl)-1,2,3-triazole (1e) :**



According to the general procedure the product was isolated in 72% yield using the mixture of ethyl acetate/hexanes (12:88) as an eluent for column chromatography.

mp: 93-95 °C.

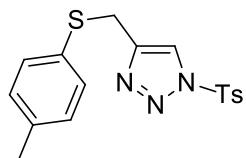
FTIR (KBr): 3148, 3059, 2978, 2942, 2843, 1591, 1497, 1391, 1310, 1269, 1195, 1170, 1092, 1015, 975, 835, 805, 743, 678, 583, 552 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.96 (d, 2H, *J*= 9.1 Hz), 7.81 (s, 1H), 7.28-7.20 (m, 5H), 7.00 (d, 2H, *J*= 9.1 Hz), 4.17 (s, 2H), 3.88 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 165.4, 145.0, 134.6, 131.2, 130.3, 129.2, 127.1, 127.0, 121.8, 115.1, 56.0, 28.9.

HRMS: calcd.for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub>+H: 362.0628; found: 362.0633.

**4-((*p*-Tolylthio)methyl)-1-tosyl-1,2,3-triazole (1f) :**



According to the general procedure the product was isolated in 68% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

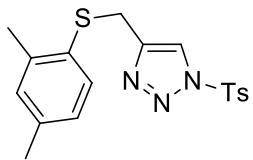
mp: 101-103 °C.

FTIR (KBr): 3150, 3055, 2983, 2924, 1594, 1493, 1395, 1307, 1264, 1192, 1181, 1091, 1011, 972, 809, 747, 701, 671, 583, 541 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.91 (d, 2H, *J* = 8.4 Hz), 7.78 (s, 1H), 7.36 (d, 2H, *J* = 7.9 Hz), 7.16 (d, 2H, *J* = 8.2 Hz), 7.04 (d, 2H, *J* = 7.9 Hz), 4.11 (s, 2H), 2.45 (s, 3H), 2.31 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, 24 °C): δ 147.3, 145.3, 137.5, 133.2, 131.3, 130.8, 130.5, 130.0, 128.7, 121.9, 29.6, 21.9, 21.1.

**4-((2,4-Dimethylphenyl)thio)methyl-1-tosyl-1,2,3-triazole (1g) :**



According to the general procedure the product was isolated in 72% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

mp: 63-65 °C.

FTIR (KBr): 3128, 2981, 2921, 1592, 1548, 1479, 1392, 1306, 1236, 1190, 1124, 1088, 1011, 964, 876, 747, 671, 539 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.92 (d, 2H, *J* = 8.2 Hz), 7.71 (s, 1H), 7.37 (d, 2H, *J* = 8.2 Hz), 7.10 (d, 1H, *J* = 7.7 Hz), 6.97 (s, 1H), 6.87 (d, 2H, *J* = 8.0 Hz), 4.07 (s, 2H), 2.45 (s, 3H), 2.28 (s, 3H), 2.23 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, 24 °C): δ 147.3, 145.3, 139.4, 137.5, 133.2, 131.6, 131.4, 130.4, 129.9, 128.7, 127.4, 121.8, 28.8, 21.9, 21.0, 20.3.

**4-((4-Methoxyphenyl)thio)methyl-1-tosyl-1H-1,2,3-triazole (1h) :**



According to the general procedure the product was isolated in 70% yield using the mixture of ethyl acetate/hexanes (12:88) as an eluent for column chromatography.

mp: 92-94 °C.

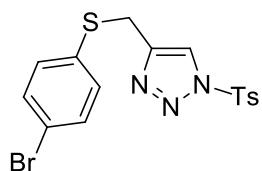
FTIR (KBr): 3141, 2962, 2896, 1592, 1494, 1388, 1309, 1287, 1252, 1194, 1175, 1088, 1011, 973, 818, 677, 580, 537 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.90 (d, 2H, *J* = 8.4 Hz), 7.72 (s, 1H), 7.36 (d, 2H, *J* = 8.1 Hz), 7.20 (d, 2H, *J* = 8.8 Hz), 6.75 (d, 2H, *J* = 8.8 Hz), 4.04 (s, 2H), 3.78 (s, 3H), 2.44 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 159.7, 147.3, 145.2, 134.4, 133.2, 130.5, 128.6, 124.5, 121.8, 114.8, 55.4, 30.8, 21.9.

HRMS: calcd.for C<sub>17</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub>+H: 376.0784; found: 376.0789.

**4-(((4-Bromophenyl)thio)methyl)-1-tosyl-1,2,3-triazole (1i) :**



According to the general procedure the product was isolated in 63% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

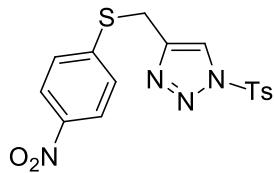
mp: 101-103 °C.

FTIR (KBr): 3129, 3059, 2962, 2923, 1591, 1540, 1469, 1440, 1388, 1301, 1236, 1196, 1174, 1091, 1036, 1003, 969, 894, 804, 719, 667, 624, 579, 540, 510 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.90 (d, 2H, *J* = 8.2 Hz), 7.85 (s, 1H), 7.38 (d, 2H, *J* = 8.2 Hz), 7.32 (d, 2H, *J* = 8.5 Hz), 7.11 (d, 2H, *J* = 8.4 Hz), 4.15 (s, 2H), 2.46 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, 24 °C): δ 147.5, 144.7, 133.7, 133.0, 132.2, 131.9, 130.5, 128.7, 122.0, 121.2, 28.8, 22.0.

**4-(((4-Nitrophenyl)thio)methyl)-1-tosyl-1,2,3-triazole (1j) :**



According to the general procedure the product was isolated in 32% yield using the mixture of ethyl acetate/hexanes (13:87) as an eluent for column chromatography.

mp: 148-150 °C.

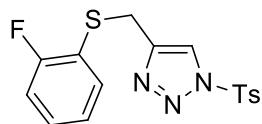
FTIR (KBr): 3156, 2925, 2851, 1586, 1512, 1396, 1338, 1264, 1182, 1118, 1090, 1013, 975, 853, 744, 668, 579, 543 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.06 (d, 2H, *J* = 9.0 Hz), 8.01 (s, 1H), 7.92 (d, 2H, *J* = 8.5 Hz), 7.36-7.33 (m, 4H), 4.31 (s, 2H), 2.44 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 147.8, 145.0, 143.9, 132.8, 130.6, 128.8(4), 128.8(0), 127.2, 124.1, 122.1, 26.9, 21.9.

HRMS: calcd. for C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>+Na: 413.0349; found: 413.0354.

**4-(((2-Fluorophenyl)thio)methyl)-1-tosyl-1,2,3-triazole (1k) :**



According to the general procedure the product was isolated in 90% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

mp: 83-85 °C.

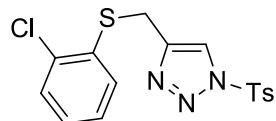
FTIR (KBr): 3142, 3083, 2925, 1592, 1471, 1394, 1259, 1188, 1013, 971, 814, 754, 670, 583, 540 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.90 (d, 2H, *J* = 8.3 Hz), 7.84 (s, 1H), 7.36 (d, 2H, *J* = 8.1 Hz), 7.25-7.21 (m, 2H), 7.05-6.97 (m, 2H), 4.16 (s, 2H), 2.44 (s, 3H).

$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C):  $\delta$  161.9 (d,  $J = 246.1$  Hz), 147.4, 144.7, 133.7, 133.1, 130.5, 129.8 (d,  $J = 8.0$  Hz), 128.7, 124.7 (d,  $J = 3.7$  Hz), 121.9, 121.1 (d,  $J = 18.5$  Hz), 116.0 (d,  $J = 22.7$  Hz), 28.3, 21.9.

HRMS: calcd. for  $\text{C}_{16}\text{H}_{14}\text{N}_3\text{O}_2\text{FS}_2+\text{H}$ : 364.0584; found: 364.0584.

**4-((2-Chlorophenyl)thio)methyl-1-tosyl-1,2,3-triazole (1l) :**



According to the general procedure the product was isolated in 82% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

mp: 112-114 °C.

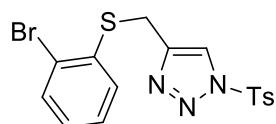
FTIR (KBr): 3150, 3055, 2986, 2926, 1594, 1452, 1395, 1308, 1265, 1193, 1118, 1091, 1012, 973, 811, 750, 670, 583, 542  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 24 °C):  $\delta$  7.92 (d, 2H,  $J = 8.4$  Hz), 7.90 (s, 1H), 7.37-7.35 (m, 3H), 7.25-7.22 (m, 1H), 7.14-7.12 (m, 2H), 4.22 (s, 2H), 2.45 (s, 3H).

$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C):  $\delta$  147.5, 144.5, 134.7, 133.0, 130.6, 130.5, 130.4, 130.0, 128.8, 127.9, 127.4, 122.1, 27.5, 21.9.

HRMS: calcd. for  $\text{C}_{16}\text{H}_{14}\text{N}_3\text{O}_2\text{S}_2\text{Cl}+\text{H}$ : 380.0289; found: 380.0309.

**4-((2-Bromophenyl)thio)methyl-1-tosyl-1,2,3-triazole (1m) :**



According to the general procedure the product was isolated in 70% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

mp: 113-115 °C.

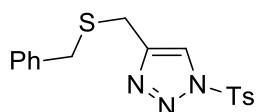
FTIR (KBr): 3147, 3026, 2925, 1593, 1449, 1394, 1261, 1191, 1090, 1013, 972, 812, 749, 669, 582, 539 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.95-7.90 (m, 3H), 7.54-7.52 (m, 1H), 7.36 (d, 2H, *J* = 8.1 Hz), 7.23-7.15 (m, 2H), 7.07-7.03 (m, 1H), 4.22 (s, 2H), 2.45 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 147.5, 144.4, 135.9, 133.2, 133.0, 130.5, 129.9, 128.8, 128.0, 127.9, 124.6, 122.1, 27.9, 21.9.

HRMS: calcd.for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>Br+H: 423.9784; found: 423.9774.

#### 4-((Benzylthio)methyl)-1-tosyl-1,2,3-triazole (1n) :



According to the general procedure the product was isolated in 70% yield using the mixture of ethyl acetate/hexanes (8:92) as an eluent for column chromatography.

mp: 93-95 °C.

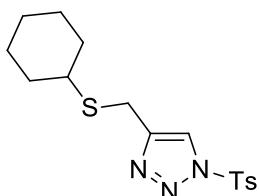
FTIR (KBr): 3130, 3022, 2990, 1593, 1546, 1492, 1451, 1384, 1299, 1233, 1180, 1014, 975, 816, 738, 681, 574, 537 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.98 (d, 2H, *J* = 8.5 Hz), 7.88 (s, 1H), 7.38 (d, 2H, *J* = 8.0 Hz), 7.29-7.23 (m, 5H), 3.71 (s, 2H), 3.65 (s, 2H), 2.45 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 147.4, 145.9, 137.6, 133.1, 130.5, 129.1, 128.8, 128.7, 127.4, 121.6, 36.3, 25.1, 21.9.

HRMS: calcd.for C<sub>17</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>+H: 360.0835; found: 360.0839.

#### 4- ((Cyclohexylthio)methyl)-1-tosyl-1,2,3-triazole (1o) :



According to the general procedure the product was isolated in 60% yield using the mixture of ethyl acetate/hexanes (6:94) as an eluent for column chromatography.

mp: 86-88 °C.

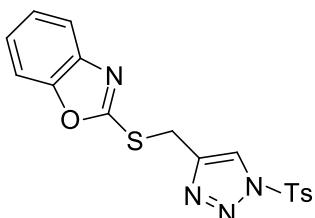
FTIR (KBr): 3135, 3053, 2925, 2849, 1592, 1549, 1446, 1387, 1304, 1242, 1191, 1180, 1091, 1011, 964, 814, 744, 676, 584, 540 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.02 (s, 1H), 7.97 (d, 2H, *J* = 8.3 Hz), 7.37 (d, 2H, *J* = 8.0 Hz), 3.79 (s, 2H), 2.66-2.44 (m, 1H), 2.44 (s, 3H), 1.92-1.90 (m, 2H), 1.74-1.71 (m, 2H), 1.31-1.21 (m, 6H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 147.2, 146.5, 133.0, 130.3, 128.6, 121.5, 43.5, 33.2, 25.8, 25.6, 24.1, 21.7.

HRMS: calcd.for C<sub>16</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>+H: 352.1148; found: 352.1142.

### 2-(((1-Tosyl-1,2,3-triazol-4-yl)methyl)thio)benzo[d]oxazole (1p) :



According to the general procedure the product was isolated in 64% yield using the mixture of ethyl acetate/hexanes (12:88) as an eluent for column chromatography.

mp: 155-157 °C.

FTIR (KBr): 3113, 3071, 2993, 2923, 1594, 1555, 1500, 1447, 1388, 1310, 1239, 1127, 1091, 1019, 927, 807, 744, 671, 539 cm<sup>-1</sup>.

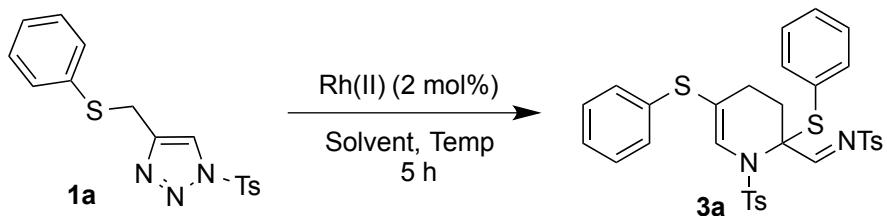
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.26 (s, 1H), 7.92 (d, 2H, *J* = 8.5 Hz), 7.64-7.62 (m, 1H), 7.44-7.42 (m, 1H), 7.33-7.24 (m, 4H), 4.58 (s, 2H), 2.40 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 163.7, 152.2, 147.5, 143.6, 141.7, 132.9, 130.5, 128.8, 124.6, 124.3, 122.9, 118.6, 110.1, 26.3, 21.9.

HRMS: calcd.for C<sub>17</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>+H: 387.0580; found: 387.0570.

#### 4. Rhodium catalyzed tandem 1,2-sulfur migration and aza-Diels-Alder reaction of

##### 1a: Optimization.

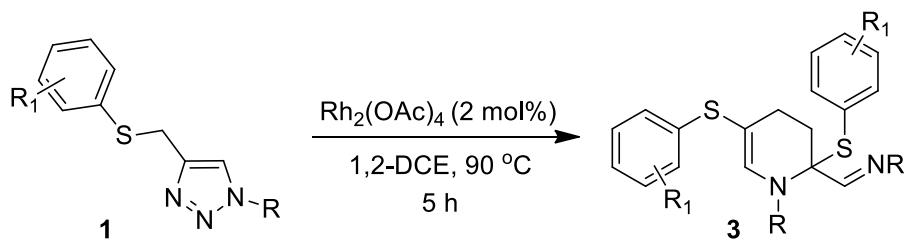


4-((Phenylthio)methyl)-1-tosyl-1,2,3-triazole **1a** (50 mg, 0.144 mmol) and Rh(II)-catalyst (0.0028 mmol, 2 mol%) were added under nitrogen atmosphere to an oven dried 10 mL reaction tube equipped with stir bar. Solvent (1 mL, as mentioned in the table) was introduced through syringe, subsequently; the reaction tube was sealed and kept at temperature mentioned in the table for 5 h. After the TLC analysis, it was cooled to room temperature and purified by column chromatography using hexane/ethyl acetate mixture as eluent to afford tetrahydropyridine **3a**.

Entry	Rh(II) (2 mol%)	Solvent	Temp (°C)	Yield of <b>3a</b> (%) <sup>a</sup>
1	Rh <sub>2</sub> (OAc) <sub>4</sub>	CHCl <sub>3</sub>	75	43
2	Rh <sub>2</sub> (OAc) <sub>4</sub>	CHCl <sub>3</sub>	90	55
3	Rh <sub>2</sub> (OAc) <sub>4</sub>	Toluene	90	80
4	Rh <sub>2</sub> (OAc) <sub>4</sub>	1,2-DCE	90	94
5	Rh <sub>2</sub> (Oct) <sub>4</sub>	1,2-DCE	90	85
6	Rh <sub>2</sub> (DOSP) <sub>4</sub>	1,2-DCE	90	93
7	Rh <sub>2</sub> (TBSP) <sub>4</sub>	1,2-DCE	90	94
8	Rh <sub>2</sub> (OAc) <sub>4</sub>	1,2-DCE	90	83 <sup>b</sup>

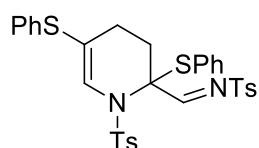
<sup>a</sup> Isolated yields. <sup>b</sup> 3 h.

## 5. General procedure for the synthesis of tetrahydropyridines 3:



*N*-Sulfonyl-1,2,3-triazole **1** (0.144 mmol) and  $\text{Rh}_2(\text{OAc})_4$  (1.28 mg, 0.0028 mmol, 2 mol%) were added under nitrogen atmosphere to an oven dried 10 mL reaction tube equipped with stir bar. 1,2-DCE (1 mL) was introduced through syringe and the reaction tube was sealed and stirred at 90 °C for 5 h. After the TLC analysis, it was cooled to room temperature and purified by column chromatography using hexane/ethyl acetate mixture as eluent to afford tetrahydropyridines **3** in high yield and purity.

### *N*-(**(2,5-Bis(phenylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene**-4-methylbenzenesulfonamide (**3a**) :



According to the general procedure the product was isolated in 94% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

mp: 131-133 °C.

FTIR (KBr): 3101, 2956, 1620, 1595, 1472, 1439, 1331, 1163, 1088, 1040, 960, 835, 812, 787, 743, 691, 664, 566, 538, 502  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C):  $\delta$  8.71 (s, 1H), 7.87 (d, 2H,  $J$  = 8.2 Hz), 7.44-7.34 (m, 7H), 7.32-7.25 (m, 6H), 7.22-7.20 (m, 3H), 7.13 (s, 1H), 2.49 (s, 3H), 2.44 (s, 1H), 2.41 (s, 3H), 2.05 (dd, 1H,  $J$  = 6.1, 18.1 Hz), 1.92 (dd, 1H,  $J$  = 6.9, 14.6 Hz), 1.66-1.61 (m, 1H).

$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C):  $\delta$  168.7, 145.2, 144.9, 137.5, 135.3, 134.8, 133.1, 130.6, 130.0, 129.4, 129.3, 129.2, 129.1, 128.6, 127.7, 127.0, 126.7, 119.0, 71.8, 28.0, 25.3, 21.8, 21.7.

HRMS: calcd. for  $\text{C}_{32}\text{H}_{30}\text{N}_2\text{O}_4\text{S}_4+\text{H}$ : 635.1161; found: 635.1152.

**N-((1-(Phenylsulfonyl)-2,5-bis(phenylthio)-1,2,3,4-tetrahydropyridin-2-yl)methylene)benzenesulfonamide (3b) :**



According to the general procedure the product was isolated in 80% yield using the mixture of ethyl acetate/hexanes (8:92) as an eluent for column chromatography.

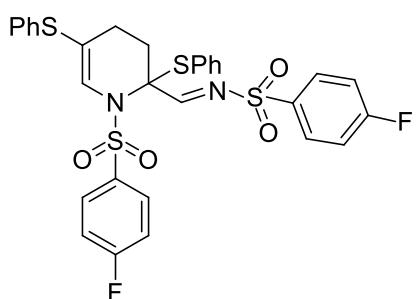
FTIR (CHCl<sub>3</sub>): 3065, 2924, 1619, 1444, 1338, 1167, 1085, 838, 797, 743, 691, 586 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.77 (s, 1H), 8.01-7.99 (m, 2H), 7.72-7.68 (m, 1H), 7.61-7.54 (m, 3H), 7.47-7.39 (m, 4H), 7.37-7.24 (m, 9H), 7.22-7.20 (m, 1H), 7.12 (t, 1H, *J* = 1.5 Hz), 2.48-2.38 (m, 1H), 2.04 (dd, 1H, *J* = 6.1, 18.3 Hz), 1.92 (dd, 1H, *J* = 6.1, 14.8 Hz), 1.63-1.56 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 169.1, 138.2, 137.5, 136.3, 134.6, 134.1, 133.8, 130.8, 129.5, 129.4, 129.3, 129.2, 129.1, 128.2, 127.6, 126.9, 126.8, 119.6, 71.8, 28.0, 25.3.

HRMS: calcd. for C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>S<sub>4</sub>+Na: 629.0668; found: 629.0660.

**4-Fluoro-N-((1-((4-fluorophenyl)sulfonyl)-2,5-bis(phenylthio)-1,2,3,4-tetrahydropyridin-2-yl)methylene)benzenesulfonamide (3c) :**



According to the general procedure the product was isolated in 75% yield using the mixture of ethyl acetate/hexanes (8:92) as an eluent for column chromatography.

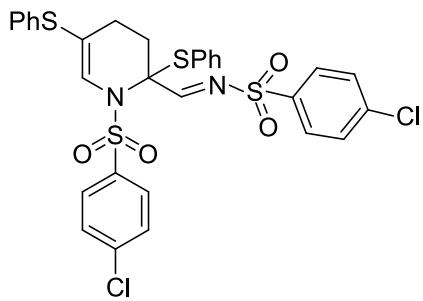
FTIR (CHCl<sub>3</sub>): 3057, 2983, 2929, 1621, 1585, 1476, 1348, 1265, 1169, 1089, 1017, 894, 740, 621, 564, 483 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.70 (s, 1H), 8.00-7.97 (m, 2H), 7.57-7.54 (m, 2H), 7.45-7.41 (m, 1H), 7.36-7.22 (m, 11H), 7.12-7.08 (m, 3H), 2.45 (dddd, 1H, *J* = 1.2, 7.1, 12.1, 18.3 Hz), 2.08 (dd, 1H, *J* = 6.4, 18.3 Hz), 1.92 (dd, 1H, *J* = 6.5, 14.3 Hz), 1.65 (ddd, 1H, *J* = 6.4, 12.3, 18.8 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 169.1, 166.2 (d, *J* = 257.1 Hz), 165.7 (d, *J* = 257.5 Hz), 137.4, 134.3, 134.3, 132.1, 132.0 (d, *J* = 9.5 Hz), 130.8, 130.6 (d, *J* = 9.5 Hz), 129.5, 129.5, 129.2, 128.3, 127.6, 127.0, 126.7, 125.4, 120.1, 116.9, 116.6, 71.7, 28.2, 25.2.

HRMS: calcd. for C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>F<sub>2</sub>S<sub>4</sub>+Na: 665.0479; found: 665.0468.

**4-Chloro-N-((1-((4-chlorophenyl)sulfonyl)-2,5-bis(phenylthio)-1,2,3,4-tetrahydropyridin-2-yl)methylene)benzenesulfonamide (3d) :**



According to the general procedure the product was isolated in 76% yield using the mixture of ethyl acetate/hexanes (8:92) as an eluent for column chromatography.

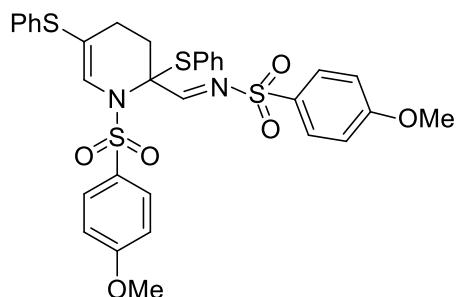
FTIR (CHCl<sub>3</sub>): 3060, 2927, 2856, 1626, 1580, 1474, 1345, 1265, 1165, 1088, 1015, 909, 829, 740, 619, 558, 481 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.65 (s, 1H), 7.89 (d, 2H, *J* = 8.7 Hz), 7.54 (d, 2H, *J* = 8.7 Hz), 7.47-7.38 (m, 5H), 7.33-7.28 (m, 7H), 7.24-7.22 (m, 2H), 7.06 (s, 1H), 2.44 (dddd, 1H, *J* = 1.4, 7.1, 12.2, 18.3 Hz), 2.09 (dd, 1H, *J* = 6.3, 18.3 Hz), 1.92 (dd, 1H, *J* = 6.4, 14.7 Hz), 1.66 (ddd, 1H, *J* = 6.5, 12.4, 18.8 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 169.1, 141.1, 140.6, 137.4, 136.7, 134.5, 134.3, 130.9, 130.5, 129.8, 129.6, 129.5, 129.3, 129.1, 128.3, 127.5, 127.1, 126.6, 120.3, 71.7, 28.3, 25.3.

HRMS: calcd. for C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>Cl<sub>2</sub>S<sub>4</sub>+H: 675.0069; found: 675.0082.

**4-Methoxy-N-((1-((4-methoxyphenyl)sulfonyl)-2,5-bis(phenylthio)-1,2,3,4-tetrahydropyridin-2-yl)methylene)benzenesulfonamide (3e) :**



According to the general procedure the product was isolated in 85% yield using the mixture of ethyl acetate/hexanes (11:89) as an eluent for column chromatography.

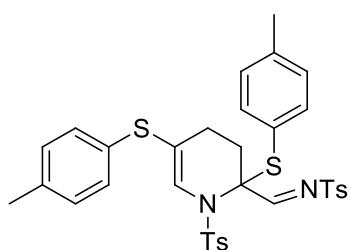
FTIR (CHCl<sub>3</sub>): 3058, 2970, 2928, 2255, 1593, 1494, 1343, 1264, 1163, 1092, 1028, 908, 736, 568 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.54 (s, 1H), 7.83 (d, 2H, *J* = 8.9 Hz), 7.37 (d, 2H, *J* = 9.0 Hz), 7.32-7.30 (m, 1H), 7.26-7.17 (m, 8H), 7.13-7.12 (m, 1H), 7.04 (t, 1H, *J* = 1.3 Hz), 6.96 (d, 2H, *J* = 9.0 Hz), 6.78 (d, 2H, *J* = 8.9 Hz), 3.81 (s, 3H), 3.77 (s, 3H), 2.35 (dd, 1H, *J* = 1.4, 7.1, 12.2, 18.1 Hz), 1.98 (dd, 1H, *J* = 6.2, 18.1 Hz), 1.83 (dd, 1H, *J* = 6.3, 14.8 Hz), 1.58-1.50 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 168.1, 164.2, 163.7, 137.4, 134.8, 131.4, 130.5, 129.9, 129.6, 129.3, 129.2, 129.1, 128.7, 127.0, 126.9, 126.7, 119.0, 114.6, 114.5, 71.6, 55.8, 55.7, 28.0, 25.3.

HRMS: calcd. for C<sub>32</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>S<sub>4</sub>+H: 667.1059; found: 667.1083.

**N-((2,5-Bis(*p*-tolylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3f) :**



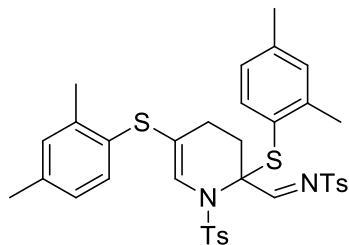
According to the general procedure the product was isolated in 87% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

FTIR (CHCl<sub>3</sub>): 3056, 2975, 2933, 1614, 1439, 1344, 1264, 1168, 1087, 1047, 907, 813, 733, 567 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.67 (s, 1H), 7.94-7.81 (m, 2H), 7.39-7.34 (m, 4H), 7.22 (d, 4H, *J* = 8.1 Hz), 7.18-7.15 (m, 2H), 7.09 (d, 4H, *J* = 8.0 Hz), 7.06-7.02 (m, 1H), 2.48 (s, 3H), 2.45-2.34 (m, 1H), 2.41 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H), 2.00 (dd, 1H, *J* = 6.2, 17.8 Hz), 1.87 (dd, 1H, *J* = 6.3, 14.7 Hz), 1.52 (ddd, 1H, *J* = 6.4, 12.1, 18.5 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 168.7, 145.1, 144.7, 141.0, 137.3, 137.0, 135.2, 133.2, 130.6, 130.1, 130.0, 129.9(7), 129.9(4), 129.8, 129.1, 127.7, 127.4, 123.3, 120.5, 71.6, 27.5, 25.2, 21.8, 21.7, 21.5, 21.4.

**N-((2,5-Bis((2,4-dimethylphenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3g) :**



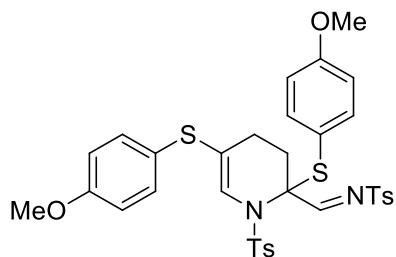
According to the general procedure the product was isolated in 89% yield using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography.

FTIR (CHCl<sub>3</sub>): 3056, 2982, 2927, 1612, 1439, 1340, 1260, 1166, 1089, 1046, 817, 737, 669, 569 cm<sup>-1</sup>.  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.53 (s, 1H), 7.84 (d, 2H, *J* = 8.1 Hz), 7.32 (d, 2H, *J* = 8.1 Hz), 7.22-7.22 (m, 2H), 7.16-7.08 (m, 5H), 7.0 (s, 1H), 6.97-6.87 (m, 3H), 2.43 (s, 3H), 2.41 (s, 3H), 2.38 (s, 3H), 2.37-2.33 (m, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 2.28 (s, 3H), 2.02-1.91 (m, 2H), 1.55 (ddd, 1H, *J* = 6.5, 12.2, 19.0 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 169.4, 145.0, 144.5, 144.1, 141.0, 139.0, 138.0, 137.5, 135.3, 133.5, 131.9, 131.5, 131.2, 129.8, 129.1, 129.0, 128.3, 127.6, 127.3, 125.8, 125.3, 122.6, 121.2, 72.5, 28.4, 25.1, 21.7, 21.7, 21.6, 21.4, 21.0, 20.4.

HRMS: calcd.for C<sub>36</sub>H<sub>38</sub>N<sub>2</sub>O<sub>4</sub>S<sub>4</sub>+Na: 713.1607; found: 713.1612.

**N-((2,5-bis((4-methoxyphenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3h) :**



According to the general procedure the product was isolated in 96% yield using the mixture of ethyl acetate/hexanes (11:89) as an eluent for column chromatography.

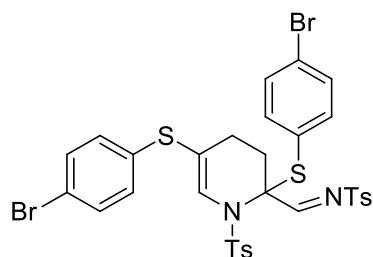
FTIR (CHCl<sub>3</sub>): 3020, 2964, 2929, 1615, 1592, 1492, 1347, 1290, 1249, 1215, 1164, 1090, 1031, 760, 667, 568, 543, 416 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.67 (s, 1H), 7.87 (d, 2H, *J* = 8.3 Hz), 7.38 (d, 2H, *J* = 8.3 Hz), 7.32-7.28 (m, 4H), 7.23 (d, 2H, *J* = 8.8 Hz), 7.14 (d, 2H, *J* = 8.3 Hz), 6.95 (s, 1H), 6.83 (d, 2H, *J* = 8.8 Hz) 6.79 (d, 2H, *J* = 8.7 Hz), 3.80 (s, 3H), 3.79 (s, 3H), 2.47 (s, 3H), 2.39 (s, 3H), 2.38-2.28 (m, 1H), 1.95 (dd, 1H, *J* = 6.5, 18.2 Hz), 1.83 (dd, 1H, *J* = 6.8, 14.6 Hz), 1.47 (ddd, 1H, *J* = 6.8, 12.3, 19.0 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 168.8, 161.6, 159.4, 145.1, 144.7, 139.1, 135.2, 132.9, 129.9, 129.8, 129.1, 128.3, 127.7, 125.7, 124.1, 122.2, 117.4, 114.9, 114.8, 71.7, 55.4, 55.4, 27.2, 25.0, 21.8, 21.7.

HRMS: calcd.for C<sub>34</sub>H<sub>34</sub>N<sub>2</sub>O<sub>6</sub>S<sub>4</sub>+Na: 717.1192; found: 717.1197.

**N-((2,5-Bis((4-bromophenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3i) :**



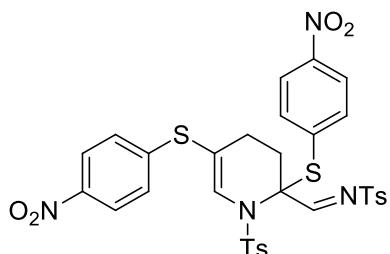
According to the general procedure the product was isolated in 55% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

FTIR (CHCl<sub>3</sub>): 3063, 2923, 2853, 1638, 1597, 1565, 1470, 1386, 1338, 1161, 1087, 1007, 909, 813, 731, 667, 564, 483 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.64 (s, 1H), 7.84 (d, 2H, *J* = 8.1 Hz), 7.40-7.36 (m, 8H), 7.21-7.12 (m, 7H), 2.49 (s, 3H), 2.42 (s, 3H), 2.40-2.33 (m, 1H), 2.04 (dd, 1H, *J* = 6.4, 18.3 Hz), 1.93 (dd, 1H, *J* = 6.4, 14.7 Hz), 1.64 (ddd, 1H, *J* = 6.4, 12.1, 18.7 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 168.3, 145.5, 145.2, 138.7, 135.3, 134.1, 132.9, 132.6, 132.3, 130.6, 130.1, 130.1, 129.2, 129.1, 127.6, 126.0, 125.8, 120.7, 117.9, 71.9, 28.3, 25.1, 21.9, 21.8.

**N-((2,5-Bis((4-nitrophenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3j) :**



According to the general procedure the product was isolated in 44% yield using the mixture of ethyl acetate/hexanes (11:89) as an eluent for column chromatography.

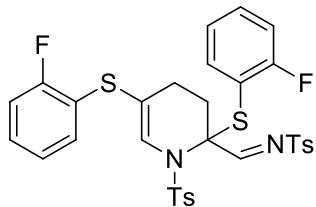
FTIR (CHCl<sub>3</sub>): 3053, 2986, 1597, 1580, 1522, 1343, 1265, 1167, 1089, 853, 750, 650, 543 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.63 (s, 1H), 8.06 (d, 2H, *J* = 9.0 Hz), 7.98 (d, 2H, *J* = 8.7 Hz), 7.79 (d, 2H, *J* = 8.3 Hz), 7.48 (d, 2H, *J* = 8.8 Hz), 7.42 (d, 2H, *J* = 8.3 Hz), 7.35 (d, 2H, *J* = 8.0 Hz), 7.30-7.28 (m, 3H), 7.22 (d, 2H, *J* = 8.3 Hz), 2.52-2.43 (m, 1H), 2.47 (s, 3H), 2.40 (s, 3H), 2.15 (dd, 1H, *J* = 6.1, 18.5 Hz), 2.04 (dd, 1H, *J* = 6.2, 14.7 Hz), 1.83 (ddd, 1H, *J* = 6.4, 12.6, 18.9 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 168.1, 148.9, 145.9, 145.7, 137.9, 135.3(5), 135.3(2), 132.9, 132.2, 130.4, 130.1, 129.1, 128.3, 127.8, 127.5, 126.8, 124.3, 124.0, 113.2, 72.9, 29.7, 25.2, 21.8.

HRMS: calcd.for C<sub>32</sub>H<sub>28</sub>N<sub>4</sub>O<sub>8</sub>S<sub>4</sub>+Na: 747.0682; found: 747.0688.

**N-((2,5-Bis((2-fluorophenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3k) :**



According to the general procedure the product was isolated in 82% yield using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography.

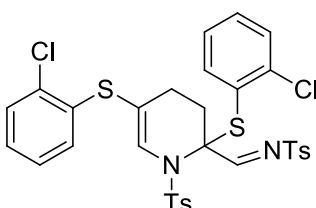
FTIR (CHCl<sub>3</sub>): 2981, 2933, 1630, 1458, 1375, 1254, 1095, 1046, 909, 735, 652 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.75 (s, 1H), 7.86 (d, 2H, *J* = 8.3 Hz), 7.48-7.31 (m, 7H), 7.25-7.16 (m, 3H), 7.15-7.02 (m, 5H), 2.57-2.44 (m, 1H), 2.47 (s, 3H), 2.40 (s, 3H), 2.05 (dd, 1H, *J* = 6.2, 18.1 Hz), 1.96 (dd, 1H, *J* = 6.4, 14.8 Hz), 1.67 (ddd, 1H, *J* = 6.4, 12.4, 18.8 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 168.7, 164.1 (d, *J* = 251.2 Hz), 160.9 (d, *J* = 245.9 Hz), 145.2, 144.9, 139.8, 135.2, 133.4 (d, *J* = 8.0 Hz), 132.9, 131.7, 130.0, 129.9, 129.2, 129.1 (d, *J* = 7.9 Hz), 128.9, 128.8, 128.3, 127.6, 125.3, 125.0 (d, *J* = 3.7 Hz), 124.7 (d, *J* = 3.6 Hz), 121.6 (d, *J* = 16.5 Hz), 116.9, 116.5 (d, *J* = 23.6 Hz), 115.9 (d, *J* = 22.0 Hz), 114.3 (d, *J* = 18.3 Hz), 72.5, 28.4, 25.1, 21.8, 21.7.

HRMS: calcd.for C<sub>32</sub>H<sub>28</sub>F<sub>2</sub>N<sub>2</sub>O<sub>4</sub>S<sub>4</sub>+H: 671.0973; found: 671.0984.

**N-((2,5-Bis((2-chlorophenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3l) :**



According to the general procedure the product was isolated in 83% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

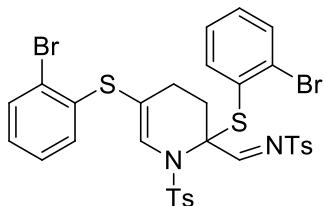
FTIR (CHCl<sub>3</sub>): 3061, 2923, 2857, 1622, 1596, 1450, 1429, 1368, 1346, 1329, 1164, 1090, 1033, 841, 812, 754, 737, 660, 570, 554, cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.73 (s, 1H), 7.86 (d, 2H, *J* = 8.3 Hz), 7.52-7.43 (m, 4H), 7.40-7.35 (m, 4H), 7.28-7.19 (m, 5H), 7.14-7.12 (m, 2H), 2.56 (dd, 1H, *J* = 1.7, 6.8, 12.1, 18.0 Hz), 2.46 (s, 3H), 2.42 (s, 3H), 2.16-2.09 (m, 2H), 1.81 (ddd, 1H, *J* = 6.6, 12.6, 18.8 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 168.9, 145.2, 145.0, 141.2, 139.6, 135.5, 134.8, 133.2, 133.1, 132.1, 130.8, 130.6, 130.1, 130.0, 129.9, 129.1, 128.9, 127.7, 127.6, 127.3, 127.2, 126.5, 115.7, 73.2, 29.4, 25.3, 21.8, 21.7.

HRMS: calcd. for C<sub>32</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>Cl<sub>2</sub>S<sub>4</sub>+H: 703.0382; found: 703.0391.

**N-((2,5-Bis((2-bromophenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3m) :**



According to the general procedure the product was isolated in 77% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

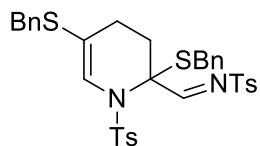
mp: 155-157 °C.

FTIR (KBr): 3053, 2985, 2924, 2855, 1580, 1460, 1446, 1423, 1375, 1265, 1169, 909, 741, 650, 492, 458, 439 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.72 (s, 1H), 7.86 (d, 2H, *J* = 8.0 Hz), 7.69-7.63 (m, 1H), 7.56-7.49 (m, 2H), 7.46-7.39 (m, 2H), 7.38-7.27 (m, 4H), 7.24-7.14 (m, 5H), 7.07-6.99 (m, 1H), 2.63-2.49 (m, 1H), 2.45 (s, 3H), 2.41 (s, 3H), 2.20-2.08 (m, 2H), 1.88-1.76 (m, 1H).

$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C):  $\delta$  168.9, 145.2, 145.0, 139.1, 136.9, 135.5, 134.0, 133.3(4), 133.3(0), 132.4, 132.0, 131.1, 130.1, 129.9, 129.1, 128.8, 128.6, 128.2, 127.8, 127.7, 127.4, 122.8, 116.0, 73.3, 29.5, 25.3, 21.8, 21.7.

***N-((2,5-Bis(benzylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3n) :***



According to the general procedure the product was isolated in 68% yield using the mixture of ethyl acetate/hexanes (8:92) as an eluent for column chromatography.

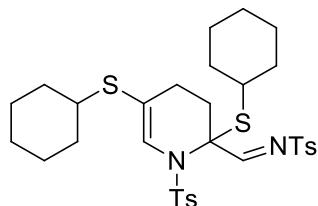
FTIR ( $\text{CHCl}_3$ ): 3057, 2932, 2855, 1654, 1439, 1348, 1265, 1169, 1110, 1034, 905, 809, 756, 667, 567  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 24 °C):  $\delta$  8.80 (s, 1H), 7.81 (d, 2H,  $J$  = 8.3 Hz), 7.33 (d, 2H,  $J$  = 8.0 Hz), 7.30-7.26 (m, 4H), 7.25-7.19 (m, 6H), 7.08 (d, 2H,  $J$  = 8.3 Hz), 7.02 (d, 2H,  $J$  = 8.1 Hz), 6.48 (t, 1H,  $J$  = 1.3 Hz), 3.80 & 3.77 (ABq, 2H,  $J$  = 13.8 Hz), 3.73 & 3.68 (ABq, 2H,  $J$  = 12.9 Hz), 2.41 (s, 3H), 2.33 (s, 3H), 2.23 (dd, 1H,  $J$  = 1.4, 7.3, 12.1, 17.9 Hz), 1.91 (dd, 1H,  $J$  = 6.3, 17.8 Hz), 1.81 (dd, 2H,  $J$  = 6.4, 14.8 Hz), 1.32 (dd, 1H,  $J$  = 6.6, 12.1, 18.7 Hz).

$^{13}\text{C}\{\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 24 °C):  $\delta$  167.6, 145.1, 144.7, 137.6, 136.1, 134.9, 133.8, 129.9(9), 129.9(2), 129.3, 128.8(9), 128.8(5), 128.7, 128.7, 127.6(5), 127.6(3), 127.3, 123.5, 121.1, 70.6, 37.1, 34.0, 27.4, 25.5, 21.8, 21.7.

HRMS: calcd. for  $\text{C}_{34}\text{H}_{34}\text{N}_2\text{O}_4\text{S}_4+\text{H}$ : 663.1474; found: 663.1472.

**N-((2,5-Bis(cyclohexylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3o) :**



According to the general procedure the product was isolated in 85% yield using the mixture of ethyl acetate/hexanes (6:94) as an eluent for column chromatography.

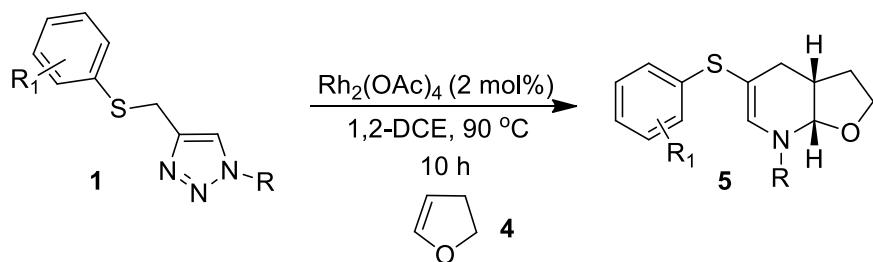
FTIR (CHCl<sub>3</sub>): 3054, 2986, 2933, 2855, 1598, 1447, 1422, 1347, 1265, 1164, 1091, 1044, 895, 744, 705, 660, 566 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.66 (s, 1H), 7.90 (d, 2H, *J* = 8.3 Hz), 7.39 (d, 2H, *J* = 8.0 Hz), 7.33 (d, 2H, *J* = 8.3 Hz), 7.13 (d, 2H, *J* = 8.1 Hz), 6.80 (s, 1H), 2.91-2.82 (m, 2H), 2.46 (s, 3H), 2.37 (s, 3H), 2.37-2.28 (m, 1H), 2.04-1.90 (m, 2H), 1.86-1.61 (m, 9H), 1.42-1.37 (m, 1H), 1.35-1.23 (m, 11H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 167.0, 145.1, 144.8, 134.9, 133.2, 130.0, 129.9, 129.2, 127.8, 126.6, 121.4, 70.9, 44.5, 42.8, 35.8, 34.6, 33.4, 33.3, 27.5, 27.1, 25.8, 25.4, 21.8, 21.7.

HRMS: calcd. for C<sub>32</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub>S<sub>4</sub>+Na: 669.1920; found: 669.1921.

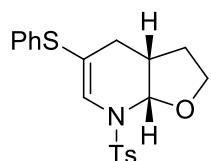
## 6. General procedure for the synthesis of fused tetrahydropyridines 5:



*N*-Sulfonyl-1,2,3-triazole **1** (50 mg, 0.144 mmol), Rh<sub>2</sub>(OAc)<sub>4</sub> (1.28 mg, 0.0028 mmol, 2 mol%) and 1,2-DCE (1 mL) were added under nitrogen atmosphere to an oven dried 10 mL reaction tube equipped with stir bar. Next, 2,3-dihydrofuran **4** (40 mg, 0.576 mmol) was introduced through syringe, the reaction tube was sealed and stirred at 90 °C for 10 h. After the TLC analysis, it was cooled to room

temperature and purified by column chromatography using hexane/ethyl acetate mixture as eluent to afford fused tetrahydropyridines **5** in high yield and purity.

**5-(Phenylthio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5a) :**



According to the general procedure the product was isolated in 90% yield using the mixture of ethyl acetate/hexanes (8:92) as an eluent for column chromatography.

mp: 121-123 °C.

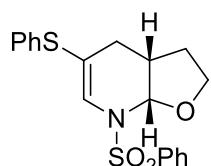
FTIR (KBr): 2941, 2889, 1640, 1598, 1475, 1436, 1404, 1351, 1240, 1106, 1027, 967, 862, 803, 746, 695, 667, 587, 549 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.83 (d, 2H, *J* = 8.2 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 7.29-7.26 (m, 2H), 7.23-7.17 (m, 3H), 7.15-7.13 (m, 1H), 5.55 (d, 1H, *J* = 4.4 Hz), 3.84 (dt, 1H, *J* = 4.5, 8.9 Hz), 3.78 (q, 1H, *J* = 8.0 Hz), 2.45 (s, 3H), 2.35-2.32 (m, 1H), 2.22 (dd, 1H, *J* = 6.6, 17.1 Hz), 2.13-2.08 (m, 1H), 1.95 (ddd, 1H, *J* = 1.4, 8.4, 17.0 Hz), 1.74-1.70 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 144.4, 136.8, 135.5, 129.8, 129.1, 128.7, 128.6, 127.6, 126.3, 108.9, 83.9, 64.4, 35.8, 29.9, 28.4, 21.7.

HRMS: calcd. for C<sub>20</sub>H<sub>21</sub>NO<sub>3</sub>S<sub>2</sub>+H: 388.1036; found: 388.1056.

**7-(Phenylsulfonyl)-5-(phenylthio)-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5b) :**



According to the general procedure the product was isolated in 97% yield using the mixture of ethyl acetate/hexanes (8:92) as an eluent for column chromatography.

mp: 106-108 °C.

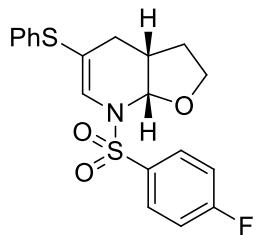
FTIR (KBr): 3055, 2982, 2928, 1638, 1595, 1431, 1369, 1263, 1169, 1043, 908, 735, 653, 415 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.95-7.92 (m, 2H), 7.62-7.58 (m, 1H), 7.55-7.51 (m, 2H), 7.28-7.17 (m, 5H), 7.13-7.13 (m, 1H), 5.55 (d, 1H, *J* = 4.4 Hz), 3.82 (dt, 1H, *J* = 4.7, 8.9, 13.4 Hz), 3.73 (q, 1H, *J* = 7.8 Hz), 2.38-2.30 (m, 1H), 2.22 (dd, 1H, *J* = 6.7, 6.5 Hz), 2.13-2.04 (m, 1H), 1.94 (ddd, 1H, *J* = 1.7, 8.2, 17.0 Hz), 1.74-1.69 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 139.8, 135.4, 133.2, 129.2, 129.1, 128.7, 128.5, 127.6, 126.4, 109.2, 83.9, 64.5, 36.0, 29.9, 28.7.

HRMS: calcd. for C<sub>19</sub>H<sub>19</sub>NO<sub>3</sub>S<sub>2</sub>+H: 374.0879; found: 374.0881.

**7-((4-Fluorophenyl)sulfonyl)-5-(phenylthio)-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5c) :**



According to the general procedure the product was isolated in 78% yield using the mixture of ethyl acetate/hexanes (08:92) as an eluent for column chromatography.

mp: 118-120 °C.

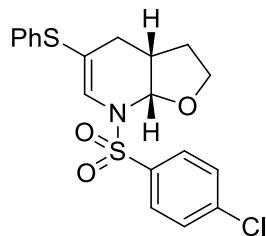
FTIR (KBr): 3061, 2985, 2941, 2907, 1464, 1447, 1374, 1299, 1240, 1098, 1046, 938, 847, 737, 703, 634, 608 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.97-7.94 (m, 2H), 7.28-7.15 (m, 7H), 7.07-7.07 (m, 1H), 5.56 (d, 1H, *J* = 4.4 Hz), 3.81 (dt, 1H, *J* = 4.6, 8.7 Hz), 3.73 (q, 1H, *J* = 8.0 Hz), 2.39-2.33 (m, 1H), 2.22 (dd, 1H, *J* = 6.9, 17.3 Hz), 2.14-2.03 (m, 1H), 1.93 (ddd, 1H, *J* = 1.8, 8.4, 17.1 Hz), 1.73-1.66 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 165.4 (d, *J* = 253.6 Hz), 135.9 (d, *J* = 3.1 Hz), 135.2, 130.5 (d, *J* = 9.7 Hz), 129.1, 128.8, 128.0, 126.5, 116.4 (d, *J* = 22.3 Hz), 109.6, 83.9, 64.4, 36.0, 29.9, 28.3.

HRMS: calcd. for C<sub>19</sub>H<sub>18</sub>FNO<sub>3</sub>S<sub>2</sub>+Na: 414.0604; found: 428.0610.

**7-((4-Chlorophenyl)sulfonyl)-5-(phenylthio)-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5d) :**



According to the general procedure the product was isolated in 79% yield using the mixture of ethyl acetate/hexanes (8:92) as an eluent for column chromatography.

mp: 140-142 °C.

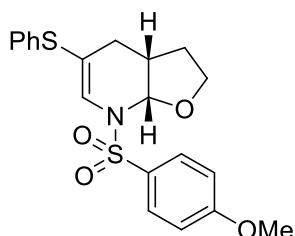
FTIR (KBr): 3086, 2924, 1638, 1580, 1467, 1357, 1169, 1094, 1029, 969, 859, 804, 750, 699, 624, 561 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.87 (d, 2H, *J* = 8.7 Hz), 7.49 (d, 2H, *J* = 8.7 Hz), 7.28-7.16 (m, 5H), 7.06-7.06 (m, 1H), 5.56 (d, 1H, *J* = 4.4 Hz), 3.82 (dt, 1H, *J* = 4.6, 8.8 Hz), 3.73 (q, 1H, *J* = 8.1 Hz), 2.41-2.33 (m, 1H), 2.22 (dd, 1H, *J* = 6.7, 17.1 Hz), 2.14-2.05 (m, 1H), 1.93 (ddd, 1H, *J* = 1.8, 8.4, 17.2 Hz), 1.74-1.66 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 139.8, 138.3, 135.2, 129.4, 129.2, 129.1, 128.8, 127.9, 126.5, 109.9, 84.0, 64.5, 36.0, 29.9, 28.3.

HRMS: calcd. for C<sub>19</sub>H<sub>18</sub>NO<sub>3</sub>ClS<sub>2</sub>+H: 408.0489; found: 408.0498.

**7-((4-Methoxyphenyl)sulfonyl)-5-(phenylthio)-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5e) :**



According to the general procedure the product was isolated in 80% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

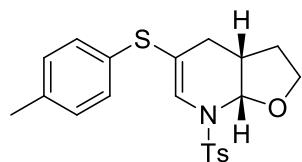
FTIR (CHCl<sub>3</sub>): 3056, 2982, 2930, 1592, 1494, 1430, 1352, 1265, 1164, 1100, 1033, 896, 737, 568 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.84 (d, 2H, *J* = 8.9 Hz), 7.25-7.12 (m, 5H), 7.07 (t, 1H, *J* = 0.9 Hz), 6.95 (d, 2H, *J* = 8.9 Hz), 5.50 (d, 1H, *J* = 4.2 Hz), 3.84 (s, 3H), 3.80 (dt, 1H, *J* = 4.6, 9.1 Hz), 3.75 (q, 1H, *J* = 8.0 Hz), 2.33-2.26 (s, 1H), 2.17 (dd, 1H, *J* = 6.8, 17.0 Hz), 2.11-2.04 (m, 1H), 1.90 (ddd, 1H, *J* = 1.9, 6.7, 17.2 Hz), 1.71-1.64 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 163.4, 135.6, 131.4, 129.9, 129.1, 128.8, 128.6, 126.3, 114.3, 108.7, 83.9, 64.4, 55.8, 35.8, 30.9, 28.4.

HRMS: calcd. for C<sub>20</sub>H<sub>21</sub>NO<sub>4</sub>S<sub>2</sub>+H: 404.0985; found: 404.0981.

### 5-(*p*-Tolylthio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5f) :



According to the general procedure the product was isolated in 84% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

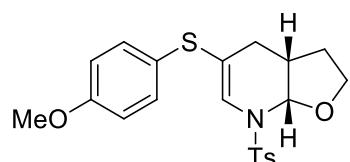
FTIR (CHCl<sub>3</sub>): 3055, 2977, 1637, 1598, 1436, 1357, 1265, 1169, 1101, 1040, 909, 804, 736, 664 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.80 (d, 2H, *J* = 8.3 Hz), 7.30 (d, 2H, *J* = 8.0 Hz), 7.14-7.06 (m, 5H), 5.51 (d, 1H, *J* = 4.4 Hz), 3.80 (dt, 1H, *J* = 4.8, 8.8 Hz), 3.73 (q, 1H, *J* = 7.9 Hz), 2.42 (s, 3H), 2.31-2.28 (m, 1H), 2.30 (s, 3H), 2.17 (dd, 1H, *J* = 6.7, 17.1 Hz), 2.08-2.03 (m, 1H), 1.90 (ddd, 1H, *J* = 1.8, 10.1, 18.7 Hz), 1.71-1.63 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 144.0, 136.7, 136.5, 131.4, 129.7, 129.6, 129.3, 127.5, 127.4, 109.9, 83.9, 64.3, 35.8, 29.8, 28.1, 21.6, 21.0.

HRMS: calcd. for C<sub>21</sub>H<sub>23</sub>NO<sub>3</sub>S<sub>2</sub>+H: 402.1192; found: 402.1201.

### 5-((4-Methoxyphenyl)thio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5h) :



According to the general procedure the product was isolated in 72% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

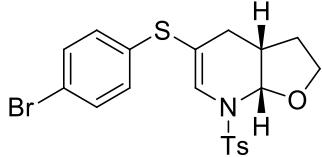
FTIR (CHCl<sub>3</sub>): 2985, 2941, 2909, 1465, 1448, 1373, 1299, 1240, 1170, 1098, 1045, 937, 918, 847, 735, 634, 608 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.71 (d, 2H, *J* = 8.3 Hz), 7.21 (d, 2H, *J* = 8.2 Hz), 7.14 (d, 2H, *J* = 6.9 Hz), 6.93 (s, 1H), 6.73 (d, 2H, *J* = 8.8 Hz), 5.42 (d, 1H, *J* = 4.5 Hz), 3.69 (s, 3H), 3.74-3.68 (m, 1H), 3.64 (q, 1H, *J* = 7.9 Hz), 2.34 (s, 3H), 2.22-2.16 (m, 1H), 2.06 (dd, 1H, *J* = 6.4, 17.0 Hz), 2.01-1.92 (m, 1H), 1.78 (ddd, 1H, *J* = 1.6, 8.1, 17.0 Hz), 1.59-1.54 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 159.1, 143.9, 136.7, 132.1, 129.6, 127.4, 126.2, 124.9, 114.6, 114.4, 83.9, 64.4, 55.3, 35.9, 29.8, 27.9, 21.6.

HRMS: calcd. for C<sub>21</sub>H<sub>23</sub>NO<sub>4</sub>S<sub>2</sub>+H: 418.1141; found: 418.1132.

### 5-((4-Bromophenyl)thio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5i) :



According to the general procedure the product was isolated in 78% yield using the mixture of ethyl acetate/hexanes (9:91) as an eluent for column chromatography.

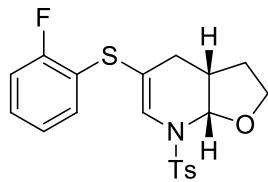
FTIR (CHCl<sub>3</sub>): 3055, 2980, 1636, 1598, 1467, 1425, 1362, 1264, 1170, 1097, 1043, 898, 737 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.80 (d, 2H, *J* = 8.3 Hz), 7.40-7.34 (m, 2H), 7.33-7.29 (m, 2H), 7.13-7.13 (m, 1H), 7.07-7.05 (m, 2H), 5.53 (d, 1H, *J* = 4.3 Hz), 3.81 (dt, 1H, *J* = 4.6, 8.9 Hz), 3.75 (q, 1H, *J* = 8.0 Hz), 2.43 (s, 3H), 2.35-2.27 (m, 1H), 2.17 (dd, 1H, *J* = 6.7, 17.0 Hz), 2.13-2.05 (m, 1H), 1.90 (ddd, 1H, *J* = 1.9, 10.4, 19.0 Hz), 1.73-1.65 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 144.2, 137.5, 135.0, 132.1, 130.0, 129.8, 129.3, 127.6, 120.1, 108.0, 83.7, 64.3, 35.7, 29.9, 28.3, 21.7.

HRMS: calcd. for C<sub>20</sub>H<sub>20</sub>NO<sub>3</sub>BrS<sub>2</sub>+H: 466.0141; found: 466.0140.

**5-((2-Fluorophenyl)thio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5k) :**



According to the general procedure the product was isolated in 76% yield using the mixture of ethyl acetate/hexanes (9:91) as an eluent for column chromatography.

mp: 150-152 °C

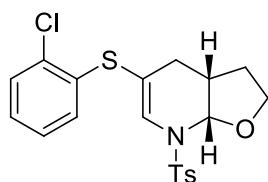
FTIR (KBr): 3057, 2960, 2255, 1639, 1466, 1362, 1258, 1172, 1103, 1043, 910, 744, 663 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.80 (d, 2H, *J* = 8.3 Hz), 7.31 (d, 2H, *J* = 8.1 Hz), 7.20-7.13 (m, 3H), 7.07-7.00 (m, 2H), 5.52 (d, 1H, *J* = 4.4 Hz), 3.82 (dt, 1H, *J* = 4.6, 8.8 Hz), 3.74 (q, 1H, *J* = 8.0 Hz), 2.43 (s, 3H), 2.35-2.29 (m, 1H), 2.20 (dd, 1H, *J* = 6.5, 16.9 Hz), 2.13-2.04 (m, 1H), 1.93 (ddd, 1H, *J* = 1.7, 8.3, 17.0 Hz), 1.73-1.66 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 160.6 (d, *J* = 245.9 Hz), 159.4, 144.1, 136.7, 130.6, 129.8, 129.3, 128.3 (d, *J* = 7.5 Hz), 127.5, 124.6 (d, *J* = 3.6 Hz), 122.8 (d, *J* = 17.3 Hz), 115.8 (d, *J* = 21.7 Hz), 107.1, 83.8, 64.4, 35.8, 29.9, 28.4, 21.7.

HRMS: calcd. for C<sub>20</sub>H<sub>20</sub>FNO<sub>3</sub>S<sub>2</sub>+Na: 428.0761; found: 428.0766.

**5-((2-Chlorophenyl)thio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5l) :**



According to the general procedure the product was isolated in 88% yield using the mixture of ethyl acetate/hexanes (1:9) as an eluent for column chromatography.

mp: 135-137 °C.

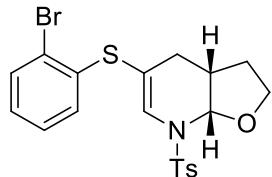
FTIR (KBr): 2924, 2895, 2852, 1636, 1597, 1450, 1431, 1366, 1348, 1247, 1168, 1103, 1032, 968, 752, 664 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.80 (d, 2H, *J* = 8.3 Hz), 7.33-7.30 (m, 3H), 7.17-7.03 (m, 4H), 5.55 (d, 1H, *J* = 4.2 Hz), 3.84 (dt, 1H, *J* = 4.4, 8.7 Hz), 3.78 (q, 1H, *J* = 8.0 Hz), 2.43 (s, 3H), 2.39-2.32 (m, 1H), 2.23 (dd, 1H, *J* = 6.8, 17.2 Hz), 2.17-2.08 (m, 1H), 1.97 (ddd, 1H, *J* = 1.8, 8.7, 17.1 Hz), 1.76-1.69 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 144.3, 136.7, 135.6, 132.4, 130.9, 129.9, 129.8, 127.8, 127.6, 127.2, 126.7, 106.4, 83.7, 64.3, 35.6, 30.0, 28.5, 21.7.

HRMS: calcd. for C<sub>20</sub>H<sub>20</sub>NO<sub>3</sub>ClS<sub>2</sub>+H: 422.0646; found: 422.0669.

### 5-((2-Bromophenyl)thio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5m) :



According to the general procedure the product was isolated in 80% yield using the mixture of ethyl acetate/hexanes (9:91) as an eluent for column chromatography.

mp: 125-127 °C.

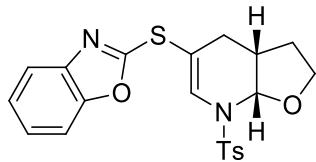
FTIR (KBr): 3054, 2982, 2958, 2930, 1637, 1599, 1446, 1367, 1265, 1217, 1168, 1102, 1044, 909, 740, 664, 650 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.80 (d, 2H, *J* = 8.3 Hz), 7.51-7.48 (m, 1H), 7.31 (d, 2H, *J* = 8.0 Hz), 7.22-7.18 (m, 2H), 7.02-6.98 (m, 2H), 5.55 (d, 1H, *J* = 4.2 Hz), 3.85 (dt, 1H, *J* = 4.4, 8.8 Hz), 3.78 (q, 1H, *J* = 8.2 Hz), 2.43 (s, 3H), 2.37-2.32 (m, 1H), 2.24 (dd, 1H, *J* = 6.8, 17.2 Hz), 2.18-2.09 (m, 1H), 1.98 (ddd, 1H, *J* = 1.9, 8.7, 17.0 Hz), 1.77-1.70 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 144.3, 137.7, 136.7, 133.2, 131.0, 129.8(5), 129.8(2), 127.8, 127.6, 126.9, 122.1, 106.8, 83.7, 64.2, 35.6, 30.0, 28.5, 21.7.

HRMS: calcd. for C<sub>20</sub>H<sub>20</sub>NO<sub>3</sub>BrS<sub>2</sub>+H: 466.0141; found: 466.0138.

**2-((7-Tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridin-5-yl)thio)benzo[d]oxazole (5p) :**



According to the general procedure the product was isolated in 91% yield using the mixture of ethyl acetate/hexanes (8:92) as an eluent for column chromatography.

mp: 169-171 °C.

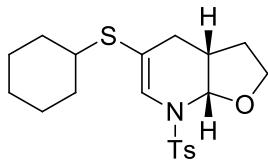
FTIR (KBr): 3057, 2985, 1450, 1375, 1248, 1088, 1049, 932, 848, 737, 613 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.82 (d, 2H, *J* = 8.3 Hz), 7.35-7.33 (m, 3H), 7.28-7.26 (m, 2H), 7.12 (s, 1H), 7.01-6.99 (m, 1H), 5.60 (d, 1H, *J* = 4.3 Hz), 3.87 (dt, 1H, *J* = 5.4, 8.5 Hz), 3.71 (q, 1H, *J* = 8.5 Hz), 2.66-2.62 (m, 2H), 2.45 (s, 3H), 2.41-2.36 (m, 1H), 2.25-2.16 (m, 1H), 2.12-2.04 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 180.2, 147.6, 144.4, 136.6, 133.0, 129.8, 127.5, 126.7, 125.2, 124.6, 112.2, 110.6, 109.8, 84.6, 65.1, 36.1, 29.6, 23.8, 21.7.

HRMS: calcd. for C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>+H: 429.0937; found: 429.0929.

**5-(Cyclohexylthio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5o) :**



According to the general procedure the product was isolated in 86% yield using the mixture of ethyl acetate/hexanes (6:94) as an eluent for column chromatography.

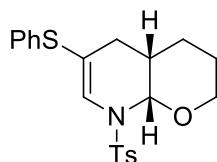
FTIR (CHCl<sub>3</sub>): 2985, 2938, 1462, 1447, 1374, 1299, 1243, 1168, 1100, 1047, 913, 738, 647 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.77 (d, 2H, *J* = 8.3 Hz), 7.28 (d, 2H, *J* = 8.3 Hz), 6.86 (s, 1H), 5.48 (d, 2H, *J* = 4.5 Hz), 3.81 (dt, 1H, *J* = 4.8, 8.6 Hz), 3.76 (q, 1H, *J* = 7.6 Hz), 2.75-2.71 (m, 1H), 2.41 (s, 3H), 2.34-2.23 (m, 2H), 2.13-2.07 (m, 1H), 1.97 (ddd, 1H, *J* = 1.6, 7.7, 16.5 Hz), 1.85-1.83 (m, 2H), 1.77-1.71 (m, 3H), 1.36-1.12 (m, 6H).

$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C):  $\delta$  143.8, 136.8, 129.6, 127.4, 126.8, 109.8, 84.0, 64.5, 44.3, 36.0, 33.4, 33.2, 29.9, 25.9, 25.8, 21.6.

HRMS: calcd. for  $\text{C}_{20}\text{H}_{28}\text{NO}_3\text{S}_2+\text{H}$ : 394.1505; found: 394.1506.

### 6-(Phenylthio)-8-tosyl-3,4,4a,5,8,8a-hexahydro-2H-pyrano[2,3-b]pyridine (5a') :



According to the general procedure the product was isolated in 30% yield using the mixture of ethyl acetate/hexanes (3:97) as an eluent for column chromatography.

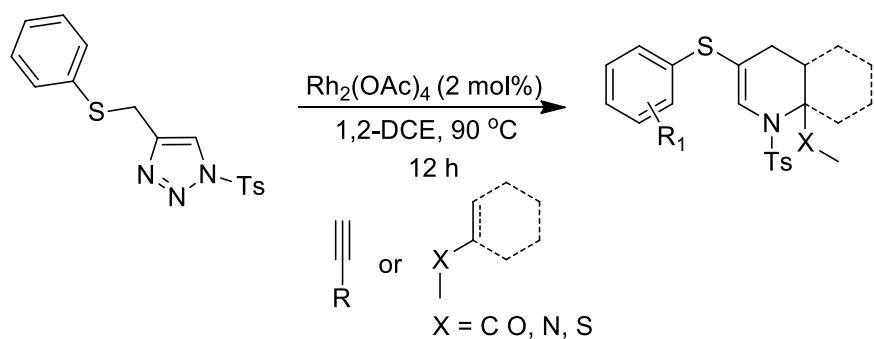
FTIR ( $\text{CHCl}_3$ ): 3058, 2925, 2855, 1636, 1596, 1582, 1473, 1443, 1360, 1305, 1267, 1230, 1167, 1071, 1026, 986, 870, 667  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C):  $\delta$  7.70 (d, 2H,  $J = 8.2$  Hz), 7.25-7.06 (m, 7H), 6.93 (s, 1H), 5.20 (s, 1H), 3.88-3.84 (m, 1H), 3.57-3.51 (m, 1H), 2.54-2.38 (m, 1H), 2.34 (s, 1H), 1.93-1.47 (m, 8H).

$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C):  $\delta$  144.1, 141.7, 137.0, 136.0, 129.7, 129.0, 128.2, 127.6, 126.0, 109.2, 82.0, 68.3, 32.6, 27.2, 26.5, 21.7, 20.2.

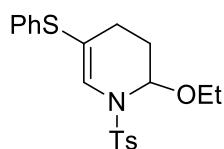
HRMS: calcd. for  $\text{C}_{21}\text{H}_{23}\text{NO}_3\text{S}_2+\text{H}$ : 402.1192; found: 402.1188.

## 7. General procedure for the synthesis of tetrahydropyridines (6-11, 16), dihydropyridine (14 and 15) and cyclohexenes (18):



4-((Phenylthio)methyl)-1-tosyl-1,2,3-triazole (50 mg, 0.144 mmol) and Rh<sub>2</sub>(OAc)<sub>4</sub> (1.28 mg, 0.0028 mmol, 2 mol%) and 1,2-DCE (1 mL) were added under nitrogen atmosphere to an oven dried 10 mL reaction tube equipped with stir bar. The dienophile (0.576 mmol) was introduced through syringe; next, the reaction tube was sealed and stirred at 90 °C for 12 h. After the TLC analysis, it was cooled to room temperature and purified by column chromatography using hexane/ethyl acetate mixture as eluent to afford products in high yield and purity.

### **2-Ethoxy-5-(phenylthio)-1-tosyl-1,2,3,4-tetrahydropyridine (6) :**



According to the general procedure the product was isolated in 84% yield using the mixture of ethyl acetate/hexanes (8:92) as an eluent for column chromatography.

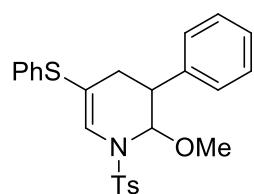
FTIR (CHCl<sub>3</sub>): 3056, 2981, 2928, 1595, 1427, 1359, 1265, 1169, 1103, 738, 564 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.69 (d, 2H, *J* = 7.9 Hz), 7.33 (d, 2H, *J* = 8.2 Hz), 7.23-7.20 (m, 2H), 7.15-7.12 (m, 3H), 7.07 (s, 1H), 5.24 (s, 1H), 3.87-3.80 (m, 1H), 3.66-3.60 (m, 1H), 2.45 (s, 1H), 2.39-2.31 (m, 1H), 1.93-1.83 (m, 2H), 1.20 (t, 3H, *J* = 7.0 Hz), 1.05-0.98 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, 24 °C): δ 144.1, 136.4, 136.1, 130.0, 129.0, 128.9, 127.7, 127.0, 125.8, 114.1, 80.7, 63.2, 26.7, 22.6, 21.7, 15.0.

HRMS: calcd. for C<sub>20</sub>H<sub>23</sub>NO<sub>3</sub>S<sub>2</sub>+K: 428.0751; found: 428.0760.

### **2-Methoxy-3-phenyl-5-(phenylthio)-1-tosyl-1,2,3,4-tetrahydropyridine (7) :**



According to the general procedure the product was isolated in 60% yield using the mixture of ethyl acetate/hexanes (5:95) as an eluent for column chromatography.

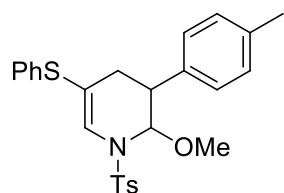
FTIR (CHCl<sub>3</sub>): 3054, 2985, 2928, 1632, 1597, 1583, 1440, 1423, 1362, 1343, 1265, 1189, 1168, 1103, 1070, 943, 909, 739, 650 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.30-7.23 (m, 4H), 7.20-7.18 (m, 1H), 7.11-7.06 (m, 4H), 6.97-6.93 (m, 4H), 6.89 (d, 1H, *J* = 7.3 Hz), 5.32-5.30 (m, 1H), 3.57 (s, 3H), 3.36 (dd, 1H, *J* = 2.3, 7.1 Hz), 2.82 (ddd, 1H, *J* = 2.1, 7.4, 17.9 Hz), 2.36 (s, 3H), 2.24 (d, 1H, *J* = 17.8 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 143.3, 139.0, 136.4, 135.3, 129.7, 129.4, 129.0, 128.5, 128.1, 127.5, 126.8, 126.6, 111.7, 87.2, 55.9, 41.3, 27.8, 21.6.

HRMS: calcd. for C<sub>25</sub>H<sub>25</sub>NO<sub>3</sub>S<sub>2</sub>+Na: 474.1168; found: 474.1174.

### 2-Methoxy-5-(phenylthio)-3-(p-tolyl)-1-tosyl-1,2,3,4-tetrahydropyridine (8) :



According to the general procedure the product was isolated in 70% yield using the mixture of ethyl acetate/hexanes (5:95) as an eluent for column chromatography.

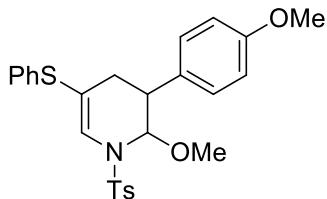
FTIR (CHCl<sub>3</sub>): 3055, 2983, 2929, 1632, 1595, 1357, 1265, 1169, 1099, 909, 736, 657 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.30-7.22 (m, 4H), 7.19-7.15 (m, 1H), 7.11-7.06 (m, 3H), 6.94 (d, 2H, *J* = 8.0 Hz), 6.75-6.70 (m, 4H), 5.26-5.25 (m, 1H), 3.55 (s, 3H), 3.30 (dd, 1H, *J* = 2.4, 7.2 Hz), 2.79 (ddd, 1H, *J* = 2.1, 7.5, 17.9 Hz), 2.36 (s, 3H), 2.24 (s, 3H), 2.20 (d, 1H, *J* = 17.9 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 143.0, 136.5, 136.4, 136.0, 135.3, 129.5, 129.4, 129.0(3), 129.0(1), 128.0, 127.2, 126.6, 112.0, 87.3, 55.8, 41.0, 27.8, 21.6, 21.1.

HRMS: calcd. for C<sub>26</sub>H<sub>27</sub>NO<sub>3</sub>S<sub>2</sub>+Na: 488.1325; found: 488.1330.

**2-Methoxy-3-(4-methoxyphenyl)-5-(phenylthio)-1-tosyl-1,2,3,4-tetrahydropyridine (9) :**



According to the general procedure the product was isolated in 72% yield using the mixture of ethyl acetate/hexanes (6:94) as an eluent for column chromatography.

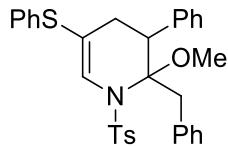
FTIR (CHCl<sub>3</sub>): 2984, 2924, 1646, 1583, 1450, 1404, 1375, 1095, 1049, 931, 848, 737, 612 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.21-7.13 (m, 4H), 7.09-7.06 (m, 4H), 7.11-7.06 (m, 2H), 6.85 (d, 2H, *J* = 8.0 Hz), 6.66 (d, 2H, *J* = 8.5 Hz), 6.33 (d, 2H, *J* = 8.7 Hz), 5.14-5.13 (m, 1H), 3.62 (s, 3H), 3.46 (s, 3H), 3.18 (dd, 1H, *J* = 2.4, 7.1 Hz), 2.79 (ddd, 1H, *J* = 2.0, 7.4, 17.9 Hz), 2.25 (s, 3H), 2.09 (d, 1H, *J* = 17.9 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 158.5, 143.2, 136.4, 135.2, 130.9, 129.4, 128.9, 128.2, 127.9, 126.5, 113.6, 111.7, 87.3, 55.7, 55.0, 40.4, 27.8, 21.4.

HRMS: calcd. for C<sub>26</sub>H<sub>27</sub>NO<sub>4</sub>S<sub>2</sub>+Na: 504.1274; found: 504.1279.

**2-Benzyl-2-methoxy-3-phenyl-5-(phenylthio)-1-tosyl-1,2,3,4-tetrahydropyridine (10) :**



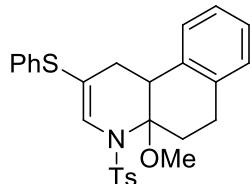
According to the general procedure the product was isolated in 36% yield using the mixture of ethyl acetate/hexanes (5:95) as an eluent for column chromatography.

FTIR (CHCl<sub>3</sub>): 3060, 2923, 2852, 1636, 1593, 1492, 1476, 1454, 1440, 1354, 1265, 1168, 1086, 1067, 1004, 910, 741, 662, 566, 408 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.82 (d, 2H, *J* = 8.3 Hz), 7.39-7.27 (m, 7H), 7.22 (d, 1H, *J* = 2.1 Hz), 7.17-7.09 (m, 8H), 6.98-6.96 (m, 2H), 4.11 (d, 1H, *J* = 14.1 Hz), 3.29 (s, 3H), 3.11-3.04 (m, 2H), 2.57-2.51 (m, 1H), 2.50 (s, 3H), 2.0 (dd, 1H, *J* = 4.6, 16.3 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 143.6, 139.5, 139.0, 135.9, 135.5, 131.7, 131.0, 129.7, 129.4, 128.9, 128.6, 128.3, 128.1, 127.5, 127.2, 126.7, 126.1, 114.3, 94.6, 53.3, 50.4, 39.8, 33.3, 21.7. HRMS: calcd. for C<sub>32</sub>H<sub>31</sub>NO<sub>3</sub>S<sub>2</sub>+Na: 564.1638; found: 564.1643.

**4a-Methoxy-2-(phenylthio)-4-tosyl-1,4,4a,5,6,10b-hexahydrobenzo[f]quinolone (11) :**

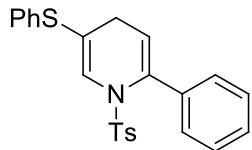


According to the general procedure the product was isolated in 46% yield using the mixture of ethyl acetate/hexanes (5:95) as an eluent for column chromatography.

FTIR (CHCl<sub>3</sub>): 3053, 2972, 1580, 1534, 1436, 1352, 1267, 1177, 1070, 1039, 899, 856, 736 cm<sup>-1</sup>.  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.78 (d, 2H, J = 8.3 Hz), 7.50 (d, 1H, J = 1.5 Hz), 7.30-7.27 (m, 3H), 7.25-7.22 (m, 2H), 7.19-7.07 (m, 3H), 7.04-7.00 (m, 2H), 6.89 (d, 1H, J = 7.8 Hz), 3.35-3.31 (m, 1H), 3.08-2.98 (m, 1H), 2.80 (s, 3H), 2.58-2.52 (m, 1H), 2.42 (s, 3H), 2.36-2.17 (m, 2H), 2.05 (s, 1H), 2.01 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 143.8, 138.7, 136.2, 135.9, 134.6, 133.1, 129.5, 129.1, 128.8, 128.5, 128.2, 127.7, 126.9, 126.3, 126.0, 106.6, 92.6, 50.5, 41.1, 36.3, 28.7, 26.3, 21.7.  
HRMS: calcd. for C<sub>27</sub>H<sub>27</sub>NO<sub>3</sub>S<sub>2</sub>+K: 516.1064; found: 516.1078.

**2-Phenyl-5-(phenylthio)-1-tosyl-1,4-dihydropyridine (14) :**



According to the general procedure the product was isolated in 23% yield using the mixture of ethyl acetate/hexanes (4:96) as an eluent for column chromatography.

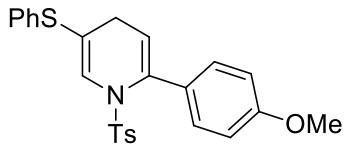
FTIR (CHCl<sub>3</sub>): 3069, 2965, 2895, 1639, 1584, 1476, 1439, 1357, 1293, 1074, 911, 735, 650 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.62 (d, 2H, *J* = 8.3 Hz), 7.49-7.47 (m, 2H), 7.37-7.26 (m, 8H), 7.23-7.20 (m, 2H), 5.40 (t, 1H, *J* = 4.5 Hz), 2.48 (s, 3H), 2.31 (d, 2H, *J* = 4.4 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, 24 °C): δ 144.4, 138.9, 137.4, 130.8, 130.0, 129.8, 129.5, 129.3, 129.2, 129.0, 128.4, 128.1, 127.9, 127.4, 127.0, 117.6, 29.1, 21.8.

HRMS: calcd.for C<sub>24</sub>H<sub>21</sub>NO<sub>2</sub>S<sub>2</sub>+H: 420.1086; found: 420.1081.

### 2-(4-Methoxyphenyl)-5-(phenylthio)-1-tosyl-1,4-dihdropyridine (15) :



According to the general procedure the product was isolated in 27% yield using the mixture of ethyl acetate/hexanes (4:96) as an eluent for column chromatography.

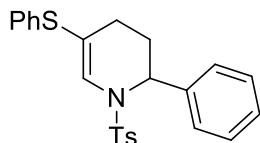
FTIR (CHCl<sub>3</sub>): 3056, 2967, 2878, 1592, 1484, 1460, 1387, 1265, 1164, 1187, 1053, 876, 765 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.59 (d, 2H, *J* = 8.3 Hz), 7.39 (d, 2H, *J* = 8.8 Hz), 7.31-7.20 (m, 7H), 6.92 (s, 1H), 6.88 (d, 2H, *J* = 8.8 Hz), 5.29 (t, 1H, *J* = 4.5 Hz), 3.82 (s, 3H), 2.46 (s, 3H), 2.27 (d, 2H, *J* = 4.4 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, 24 °C): δ 159.8, 144.3, 138.5, 133.6, 132.7, 130.8, 130.0, 129.8, 129.4, 129.1, 128.2, 128.0, 127.4, 124.7, 116.0, 113.5, 55.3, 29.0, 21.8.

HRMS: calcd.for C<sub>25</sub>H<sub>23</sub>NO<sub>3</sub>S<sub>2</sub>+H: 450.1192; found: 450.1186.

### 2-Phenyl-5-(phenylthio)-1-tosyl-1,2,3,4-tetrahydropyridine (16) :



According to the general procedure the product was isolated in 25% yield using the mixture of ethyl acetate/hexanes (4:96) as an eluent for column chromatography.

FTIR (CHCl<sub>3</sub>): 3055, 2960, 2927, 2855, 1623, 1597, 1584, 1363, 1340, 1265, 1169, 1105, 1083, 955, 738, 704, 666 cm<sup>-1</sup>.

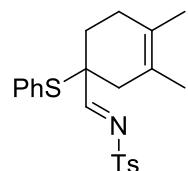
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.65 (d, 2H, *J* = 8.4 Hz), 7.49-7.49 (m, 1H), 7.29-7.09 (m, 12H), 5.24-5.23 (m, 1H), 2.43 (s, 3H), 2.03-1.97 (m, 1H), 1.86-1.73 (m, 2H), 1.57-1.53 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 144.0, 139.5, 136.2, 136.0, 131.1, 129.8, 128.9, 128.5, 128.0, 127.4, 127.1, 126.0, 125.9, 111.4, 55.4, 27.7, 23.0, 21.7.

HRMS: calcd. for C<sub>24</sub>H<sub>23</sub>NO<sub>2</sub>S<sub>2</sub>+H: 422.1243; found: 422.1253.

**N-((3,4-Dimethyl-1-(phenylthio)cyclohex-3-en-1-yl)methylene)-4-methylbenzenesulfonamide**

**(18a) :**



According to the general procedure (reaction was performed at 120 °C) the product was isolated in 46% yield using the mixture of ethyl acetate/hexanes (3:97) as an eluent for column chromatography.

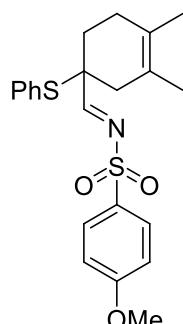
FTIR (CHCl<sub>3</sub>): 2920, 2861, 1610, 1442, 1324, 1267, 1161, 1091, 909, 804, 734 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.31 (s, 1H), 7.65 (d, 2H, *J* = 8.3 Hz), 7.25 (d, 2H, *J* = 8.1 Hz), 7.22-7.18 (m, 1H), 7.16-7.14 (m, 2H), 2.40 (s, 3H), 2.23-2.08 (m, 3H), 1.87-1.78 (m, 3H), 1.53 (s, 3H), 1.49 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 174.7, 144.4, 137.5, 135.4, 129.7, 129.6, 128.8, 128.2, 128.0, 125.7, 122.1, 53.8, 38.0, 28.8, 21.7, 19.0, 18.7.

HRMS: calcd. for C<sub>22</sub>H<sub>25</sub>NO<sub>2</sub>S<sub>2</sub>+H: 400.1399; found: 400.1398.

**N-((3,4-dimethyl-1-(phenylthio)cyclohex-3-en-1-yl)methylene)-4-methoxybenzenesulfonamide  
(18b) :**



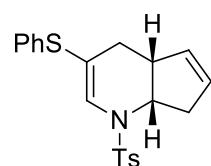
According to the general procedure (reaction was performed at 120 °C) the product was isolated in 35% yield using the mixture of ethyl acetate/hexanes (3:97) as an eluent for column chromatography.

FTIR (CHCl<sub>3</sub>): 3056, 2983, 2926, 1594, 1495, 1437, 1331, 1264, 1161, 1092, 1031, 908, 737 cm<sup>-1</sup>.  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.33 (s, 1H), 7.74 (d, 2H, *J* = 9.0 Hz), 7.25-7.23 (m, 1H), 7.21-7.18 (m, 2H), 7.11-7.07 (m, 2H), 6.96 (d, 2H, *J* = 8.9 Hz), 3.86 (s, 3H), 2.27-2.21 (m, 3H), 1.93-1.81 (m, 3H), 1.57 (s, 3H), 1.54 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 174.1, 163.6, 137.4, 130.0, 129.7, 129.5, 128.7, 128.1, 125.6, 122.0, 114.3, 55.7, 53.6, 37.9, 28.8, 28.7, 19.0, 18.6.

HRMS: calcd. for C<sub>22</sub>H<sub>25</sub>NO<sub>3</sub>S<sub>2</sub>+H: 417.1349; found: 417.1345.

**3-(Phenylthio)-1-tosyl-4a,7,7a-tetrahydro-1*H*-cyclopenta[b]pyridine (20a) :**



According to the general procedure the product was isolated in 28% yield using the mixture of ethyl acetate/hexanes (3:97) as an eluent for column chromatography.

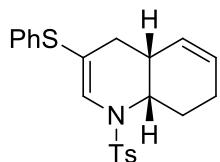
FTIR (CHCl<sub>3</sub>): 3057, 2932, 2855, 1635, 1437, 1358, 1265, 1169, 1101, 1007, 903, 806, 738, 666 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.73 (d, 2H, *J* = 8.3 Hz), 7.35-7.23 (m, 3H), 7.26-7.22 (m, 2H), 7.16-7.13 (m, 3H), 5.84-5.82 (m, 1H), 5.79-5.74 (m, 1H), 4.63-4.61 (m, 1H), 2.46 (s, 3H), 2.43-2.40 (m, 1H), 2.22-2.15 (m, 1H), 1.97-1.84 (m, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 144.2, 136.2, 135.7, 134.0, 131.3, 130.9, 130.0, 129.0, 128.1, 127.2, 126.0, 109.6, 61.1, 38.0, 34.8, 30.3, 21.7.

HRMS: calcd.for C<sub>21</sub>H<sub>21</sub>NO<sub>2</sub>S<sub>2</sub>+H: 384.1086; found: 384.1089.

### 3-(Phenylthio)-1-tosyl-1,4,4a,7,8,8a-hexahydroquinoline (20b) :



According to the general procedure the product was isolated in 26% yield using the mixture of ethyl acetate/hexanes (3:97) as an eluent for column chromatography.

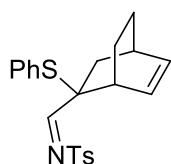
FTIR (CHCl<sub>3</sub>): 3053, 2984, 2927, 2856, 1631, 1598, 1583, 1476, 1355, 1265, 1169, 1026, 910, 805, 792, 671, 652 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.63 (d, 2H, *J* = 8.3 Hz), 7.24 (d, 2H, *J* = 8.0 Hz), 7.17-7.12 (m, 3H), 7.06-7.03 (m, 3H), 5.59-5.56 (m, 1H), 5.39-5.36 (m, 1H), 4.38 (m, 1H), 2.36 (s, 3H), 2.09 (ddd, 1H, *J* = 2.0, 11.0, 17.3 Hz), 1.89-1.85 (m, 2H), 1.71-1.53 (m, 4H).

<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, 24 °C): δ 144.2, 136.4, 136.3, 130.1, 130.0, 129.4, 129.0, 128.0, 127.7, 127.1, 125.8, 110.5, 52.7, 29.1, 27.0, 25.2, 21.7, 20.4.

HRMS: calcd.for C<sub>22</sub>H<sub>23</sub>NO<sub>2</sub>S<sub>2</sub>+H: 398.1243; found: 398.1239.

### 4-Methyl-N-((2-(phenylthio)bicyclo[2.2.2]oct-5-en-2yl)methylene)benzenesulfonamide (22) :



According to the general procedure the product was isolated in 56% (dr; 1.5:1) yield using the mixture of ethyl acetate/hexanes (4:96) as an eluent for column chromatography.

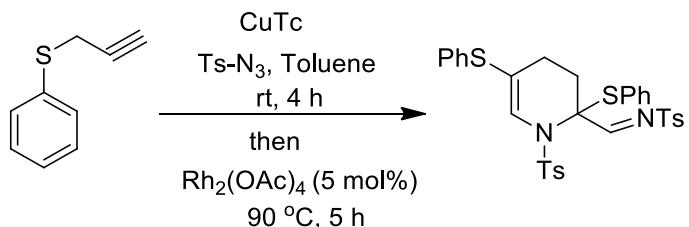
FTIR (CHCl<sub>3</sub>): 3050, 2928, 2864, 1602, 1473, 1439, 1324, 1306, 1291, 1160, 1090, 1019, 813, 780, 750, 703, 694, 668 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C): δ 8.37 (s, 0.65H), 8.11 (s, 1H), 7.67 (d, 1.5H, *J* = 8.3 Hz), 7.59 (d, 2H, *J* = 8.2 Hz), 7.24-7.09 (m, 8H), 7.02-6.98 (m, 3.4H), 6.36-6.27 (s, 1.3H), 6.14-6.10 (m, 1H), 6.00-5.97 (m, 1H), 2.64-2.54 (m, 3H), 2.46-2.41 (m, 1H), 2.37 (s, 2H), 2.36 (s, 3H), 2.23 (dd, 1H, *J* = 2.5, 13.9 Hz), 2.04 (td, 1H, *J* = 3.3, 13.6 Hz), 1.68-1.60 (m, 1H), 1.47 (dd, 1H, *J* = 2.1, 11.6 Hz), 1.38-1.20 (m, 4H).

<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, 24 °C): δ 176.0, 175.6, 144.5, 144.2, 136.6, 136.5, 135.9, 135.4, 135.3, 134.9, 132.9, 132.8, 131.3, 129.8, 129.6, 129.4, 129.3, 129.2, 128.9, 128.0, 127.9, 127.1, 58.9, 58.5, 36.9, 36.1, 34.7, 33.5, 30.2, 30.0, 25.5, 22.9, 22.8, 21.7, 21.7, 20.0.

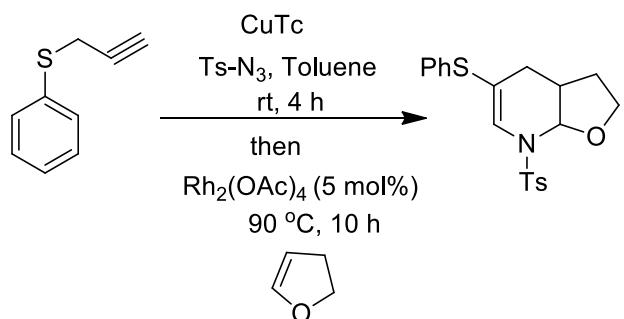
HRMS: calcd. for C<sub>22</sub>H<sub>23</sub>NO<sub>2</sub>S<sub>2</sub>+H: 398.1243; found: 398.1265.

## 8. One-pot synthesis of compound 3a from phenylpropargyl sulfide:



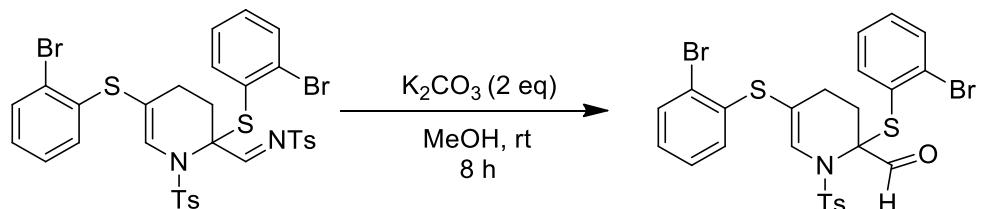
Phenylpropargyl sulfide (96 mg, 0.649 mmol, 1 equiv) and CuTc (12 mg, 0.1 equiv) in toluene (4 mL) was added tosyl azide (128 mg, 0.649 mmol, 1 equiv) at room temperature under N<sub>2</sub> atmosphere. The reaction mixture was stirred at room temperature for 4 h. After the consumption of starting material, Rh<sub>2</sub>(OAc)<sub>4</sub> (14.34 mg, 0.0324 mmol, 5 mol%) was added to the reaction tube and stirred at 90 °C for 5 h. After the TLC analysis, it was cooled to room temperature and purified by column chromatography using hexane/ethyl acetate mixture as eluent to afford tetrahydropyridine **3a** in 66% yield.

## 9. One-pot synthesis of compound **5a** from phenylpropargyl sulfide:



Phenylpropargyl sulfide (96 mg, 0.649 mmol, 1 equiv) and CuTc (12 mg, 0.1 equiv) in toluene (4 mL) was added tosyl azide (128 mg, 0.649 mmol, 1 equiv) at room temperature under  $\text{N}_2$  atmosphere. The reaction mixture was stirred at room temperature for 4 h. After the consumption of starting material,  $\text{Rh}_2(\text{OAc})_4$  (14.34 mg, 0.0324 mmol, 5 mol%) and 2,3-dihydrofuran (181 mg, 2.596 mmol) were added to the reaction tube and stirred at 90 °C for 10 h. After the TLC analysis, it was cooled to room temperature and purified by column chromatography using hexane/ethyl acetate mixture as eluent to afford fused tetrahydropyridine **5a** in 69% yield.

## 10. Synthesis of compound **24**:



Compound **3m** (50 mg, 0.063 mmol) and  $\text{K}_2\text{CO}_3$  (0.126 mmol, 2 equiv) were added under nitrogen atmosphere to an oven dried 10 mL reaction tube equipped with stir bar. 4 mL of MeOH was introduced through syringe and the reaction mixture was stirred at room temperature for 8 h. After the TLC analysis, the reaction mixture was dilute with water (10 mL) and extracted with DCM (2 x 5 mL). The combined organic layer was dried over ( $\text{Na}_2\text{SO}_4$ ) and filtered. Evaporation of solvent under reduced pressure followed by column chromatography of the crude product afforded the aldehyde **24** in 70% yield.

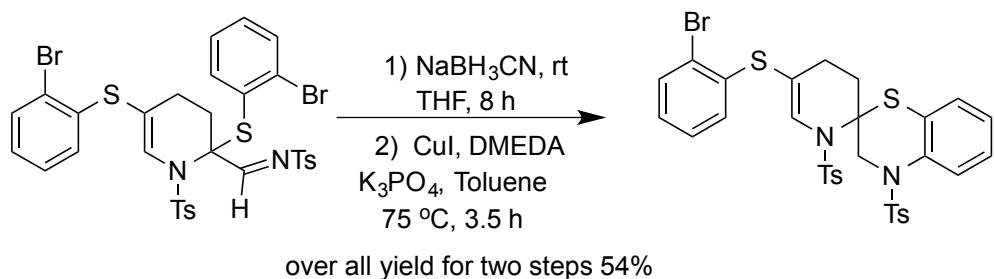
FTIR ( $\text{CHCl}_3$ ): 2925, 2855, 1748, 1623, 1596, 1424, 1371, 1264, 1169, 1100, 1020, 910, 744, 653  $\text{cm}^{-1}$ .

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 9.90 (s, 1H), 7.72-7.61 (m, 4H), 7.54-7.52 (m, 1H), 7.36-7.28 (m, 4H), 7.22-7.18 (m, 3H), 7.06-6.99 (m, 1H), 2.53-2.46 (m, 1H), 2.44 (s, 3H), 2.13 (dd, 2H, *J* = 5.9, 18.1 Hz), 2.02-1.82 (m, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C): δ 189.9, 145.1, 139.4, 137.2, 136.9, 136.0, 133.9, 133.3, 131.7, 131.3, 130.1, 128.4, 128.3, 127.9, 127.7, 127.3, 126.8, 122.7, 113.7, 76.2, 28.6, 24.9, 21.7.

HRMS: calcd. for C<sub>25</sub>H<sub>21</sub>NO<sub>3</sub>Br<sub>2</sub>S<sub>3</sub>+Na: 659.8943; found: 659.8948.

## 11. Synthesis of compound 25:



Sodium cyanoborohydride (0.189, 1.5 equiv) was added to a solution of compound **3m** (100 mg, 0.126 mmol) in dry THF (5 mL) at room temperature. The reaction mixture was stirred at rt for 8 h. After the TLC analysis, the reaction mixture was quenched with addition of water (10 mL) and extracted with EtOAc (2 x 5 mL). The combined organic layer was dried over (Na<sub>2</sub>SO<sub>4</sub>) and filtered. Evaporation of solvent resulted in the amide, which was used in the next step without further purification.

The amide obtained above was dissolved in 2 mL of toluene in reaction tube, subsequently, CuI (5 mol%), *N,N'*-dimethylethylenediamine (DMEDA) (10 mol%) and K<sub>3</sub>PO<sub>4</sub> (2 equiv) were added under nitrogen atmosphere. The reaction tube was sealed and stirred at 75 °C for 1.5 h. After the TLC analysis, the reaction mixture was cooled to room temperature and purified by column chromatography using ethyl acetate hexane/ hexane (1:9) mixture as eluent to afford benzo[b][1,4]thiazine-2,2'-pyridine **25** in overall yield of 54% for two steps.

FTIR (CHCl<sub>3</sub>): 2955, 2865, 1709, 1575, 1362, 1294, 1175, 1079, 1028, 967, 924, 660, 569, 428 cm<sup>-1</sup>.

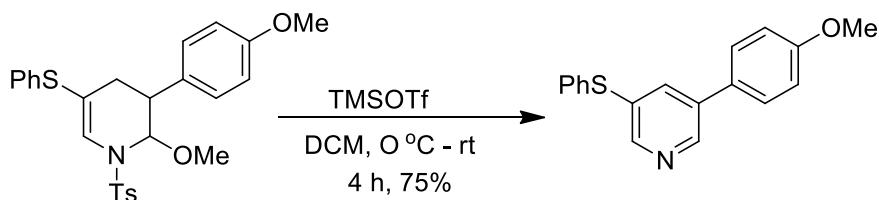
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C): δ 7.76 (d, 2H, *J* = 8.3 Hz), 7.68 (d, 2H, *J* = 8.4 Hz), 7.53 (dd, 1H, *J* = 1.1, 7.9 Hz), 7.40 (s, 1H), 7.35 (d, 2H, *J* = 8.1 Hz), 7.30-7.23 (m, 4H), 7.11 (dd, 1H, *J* = 1.5, 7.9

Hz), 7.07-6.95 (m, 4H), 4.70 (d, 1H,  $J$  = 13.7 Hz), 4.39 (d, 1H,  $J$  = 13.7 Hz), 2.73 (s, 1H), 2.58-2.47 (s, 2H), 2.45 (s, 6H).

$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C):  $\delta$  144.7, 144.3, 138.3, 137.6, 137.4, 137.3, 133.4, 133.3, 130.2, 129.8, 128.0, 127.9, 127.7, 127.2, 127.1(8), 127.1(3), 127.0, 126.9, 125.7, 125.3, 121.4, 110.0, 71.6, 55.6, 37.6, 24.3, 21.7, 21.7.

HRMS: calcd. for  $\text{C}_{32}\text{H}_{29}\text{N}_2\text{O}_4\text{BrS}_4+\text{H}$ : 713.0266; found: 713.0278.

## 12. Synthesis of 3-(4-methoxyphenyl)-5-(phenylthio)pyridine 26 :



Compound 9 (50 mg, 0.1 mmol, 1 equiv) in dichloromethane (2 mL) at 0 °C was added TMSOTf (0.259 mmol, 2.5 equiv) drop wise over 5 min. The reaction mixture was then slowly allowed to come to room temperature over 4 h and an aqueous solution of saturated bicarbonate (3 mL) was added. The reaction was extracted with DCM (3 x 5 mL) and the combined organic part was dried over  $\text{Na}_2\text{SO}_4$ , filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using hexane/ethyl acetate (9:91) mixture as eluent to afford 3-(4-methoxyphenyl)-5-(phenylthio)pyridine 26 in 75% yield.

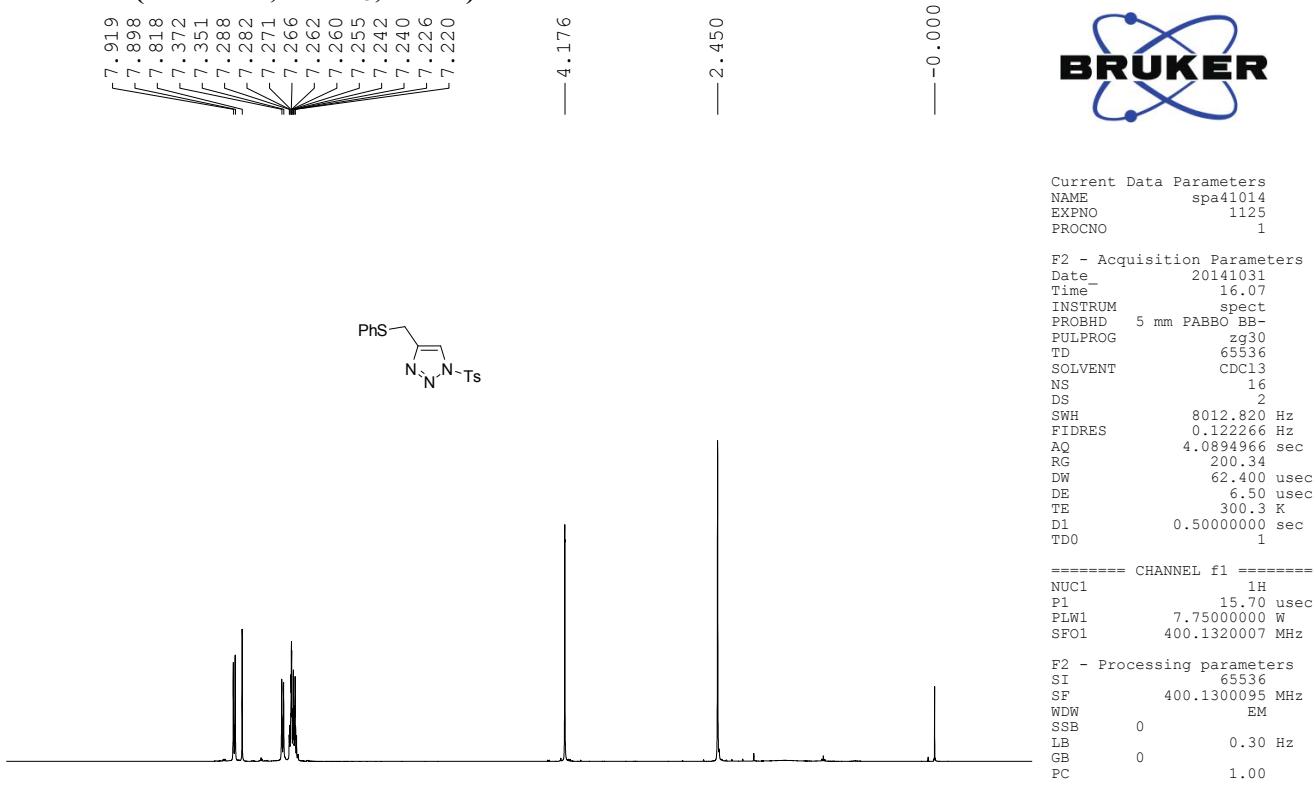
FTIR ( $\text{CHCl}_3$ ): 3057, 2959, 2924, 2852, 1609, 1578, 1513, 1475, 1462, 1439, 1421, 1322, 1216, 1107, 1083, 1047, 829, 808, 743, 705, 691, 663  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C):  $\delta$  8.58 (d, 1H,  $J$  = 2.1 Hz), 8.39 (d, 1H,  $J$  = 2.1 Hz), 7.68 (t, 1H,  $J$  = 2.1 Hz), 7.40-7.33 (m, 4H), 7.29-7.26 (m, 2H), 7.19 (s, 1H), 6.91 (d, 2H,  $J$  = 8.8 Hz), 3.78 (s, 3H).

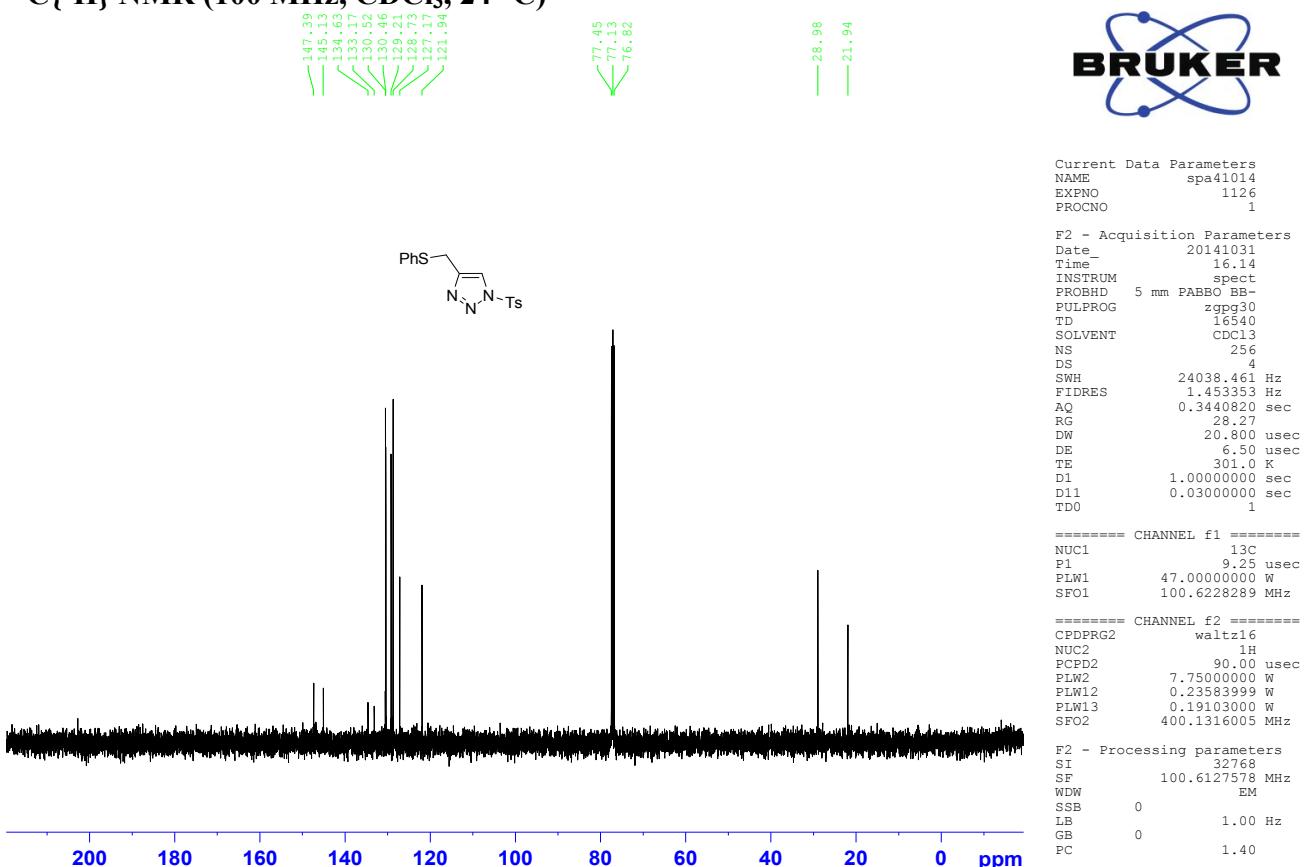
$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C):  $\delta$  160.1, 149.1, 146.2, 136.8, 135.8, 134.1, 133.5, 131.8, 129.6, 129.5, 128.4, 128.0, 114.7, 55.5.

HRMS: calcd. for  $\text{C}_{18}\text{H}_{15}\text{NOS}+\text{H}$ : 294.0947; found: 294.0951.

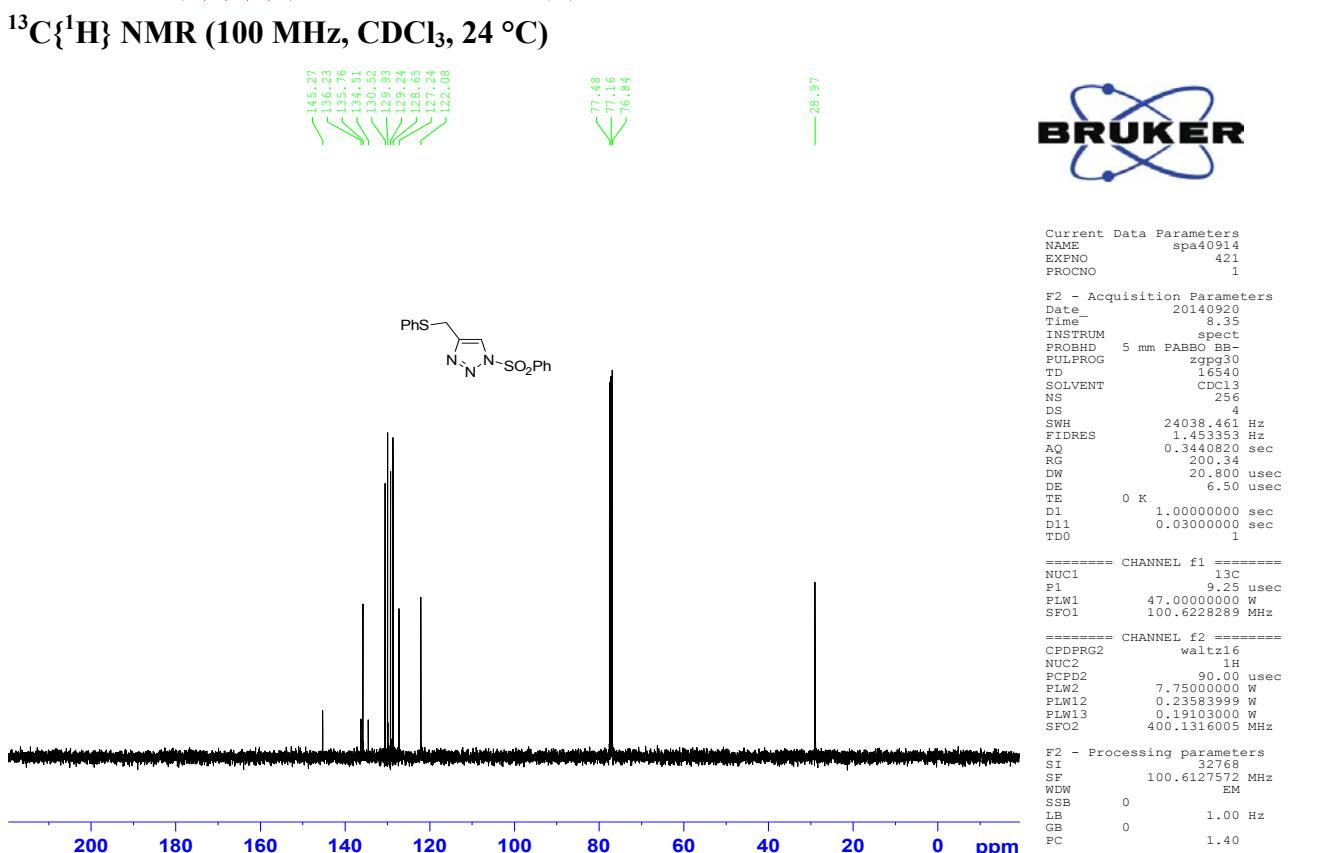
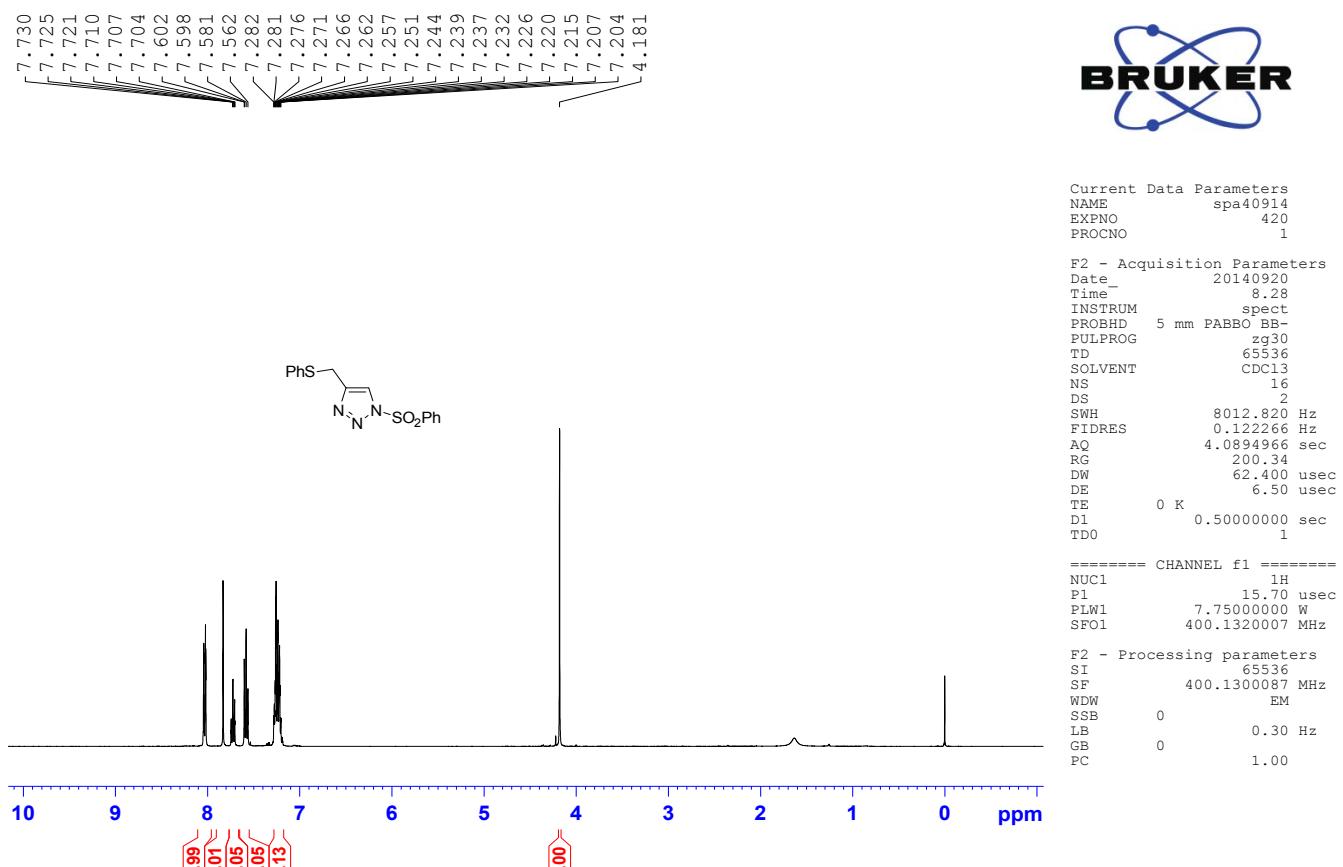
**13. NMR spectra of isolated compounds:**  
**4-((Phenylthio)methyl)-1-tosyl-1,2,3-triazole (1a) :**  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)



<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)

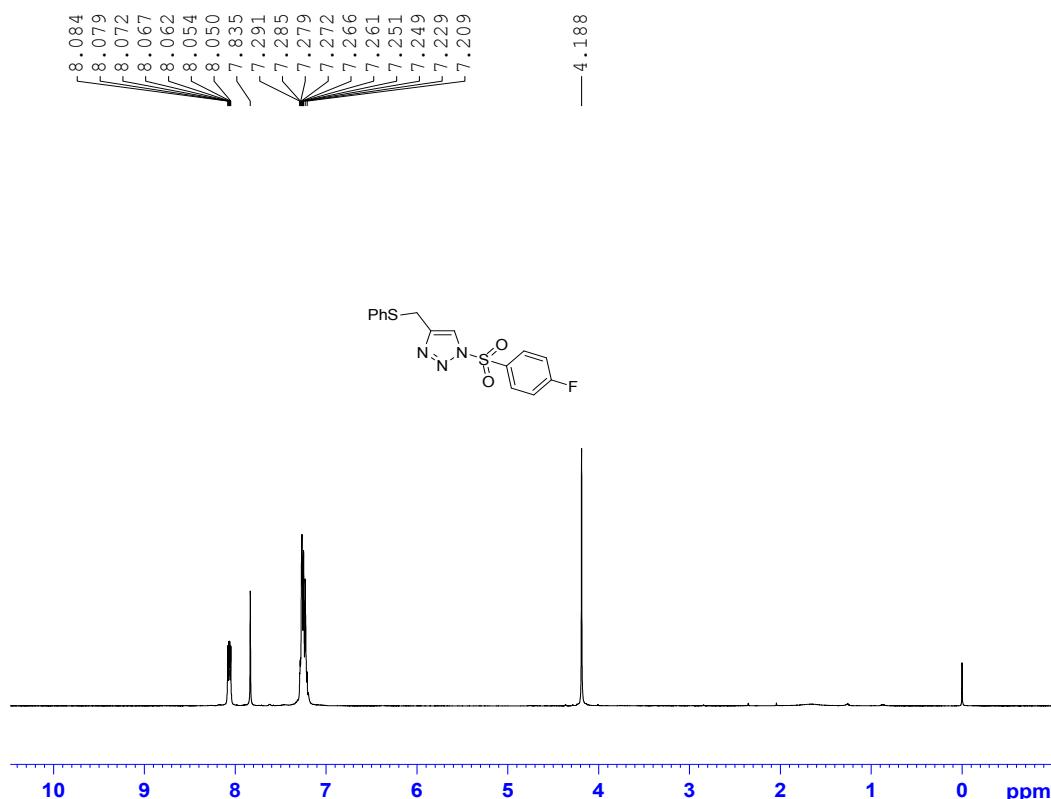


**1- (Phenylsulfonyl)-4- ((phenylthio)methyl)-1,2,3-triazole (1b) :**  
 **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



**1-((4-Fluorophenyl)sulfonyl)-4-((phenylthio)methyl)-1,2,3-triazole (1c) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



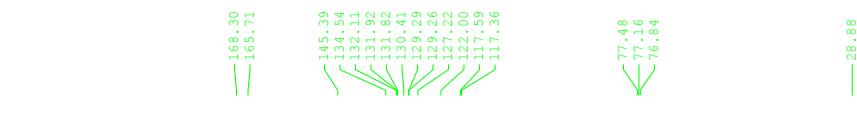
Current Data Parameters  
NAME spa41014  
EXPNO 184  
PROCNO 1

F2 - Acquisition Parameters  
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Time 20.27  
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PULPROG zpg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 200.34  
DW 62.400 usec  
DE 6.50 usec  
TE 299.1 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SFO1 400.1320007 MHz

F2 - Processing parameters  
SI 65536  
SF 400.1300090 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa41014  
EXPNO 185  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20141006  
Time\_ 20.34  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zpg30  
TD 16540  
SOLVENT CDCl3  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 299.6 K  
D1 1.0000000 sec  
D11 0.03000000 sec  
TDO 1

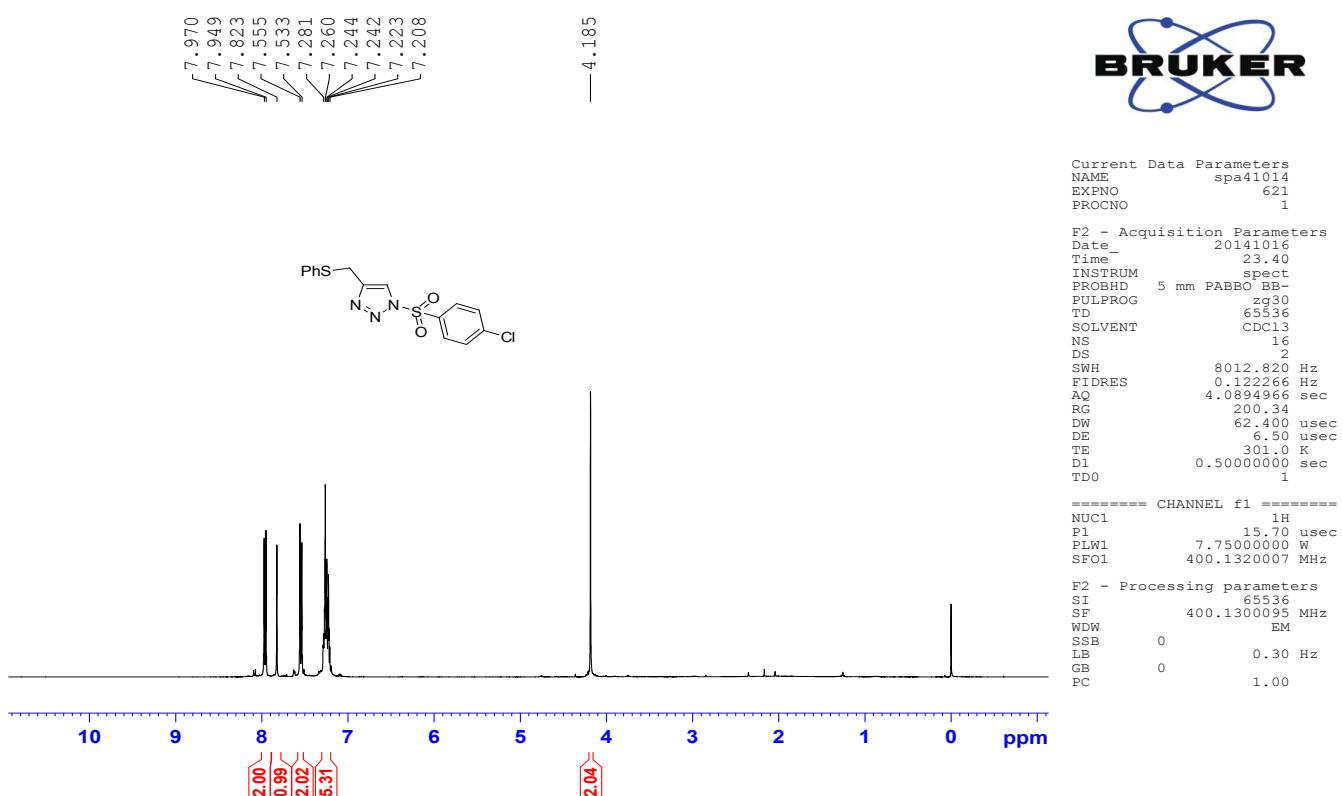
===== CHANNEL f1 ======  
NUC1 13C  
P1 9.25 usec  
PLW1 47.0000000 W  
SFO1 100.6228289 MHz

===== CHANNEL f2 ======  
CPDPG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.2358399 W  
PLW13 0.1910300 W  
SFO2 400.1316005 MHz

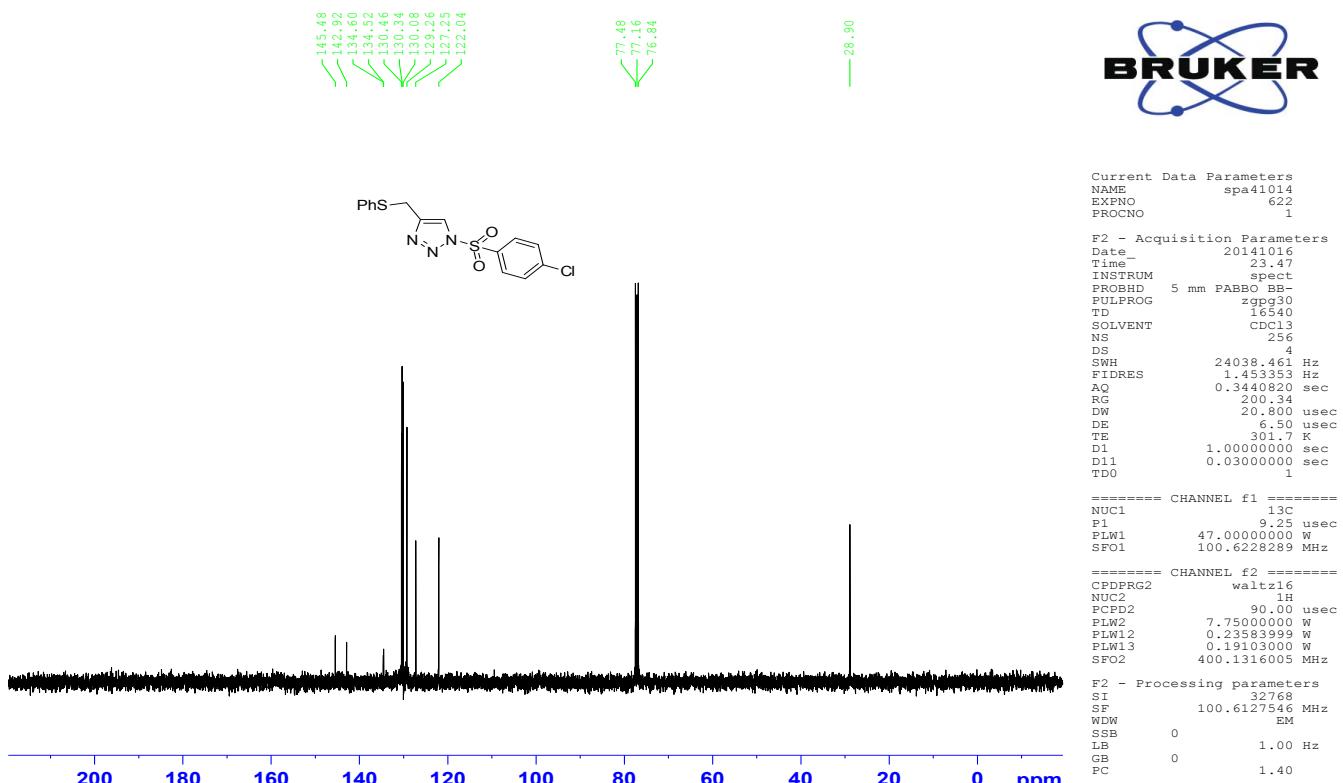
F2 - Processing parameters  
SI 32768  
SF 100.6127558 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**1-((4-Chlorophenyl)sulfonyl)-4-((phenylthio)methyl)-1,2,3-triazole (1d) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

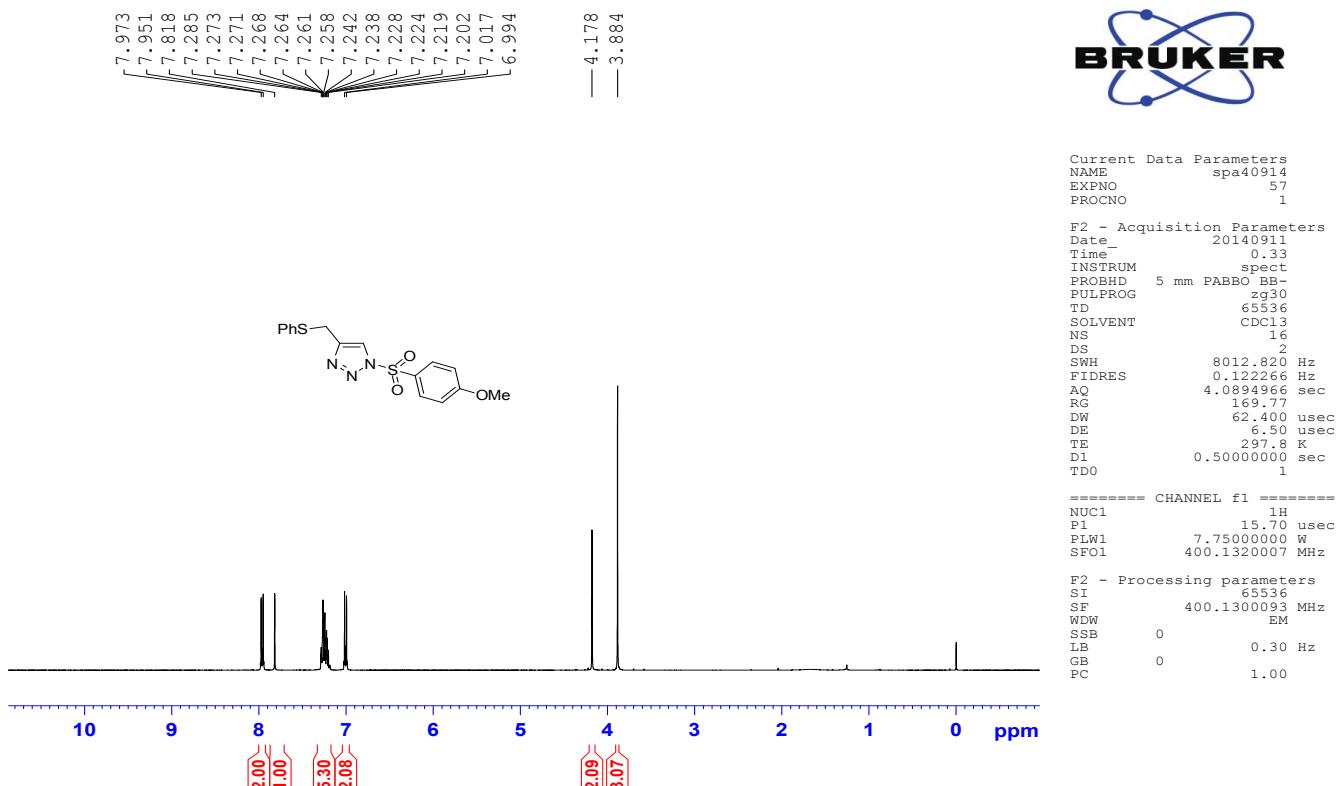


**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**

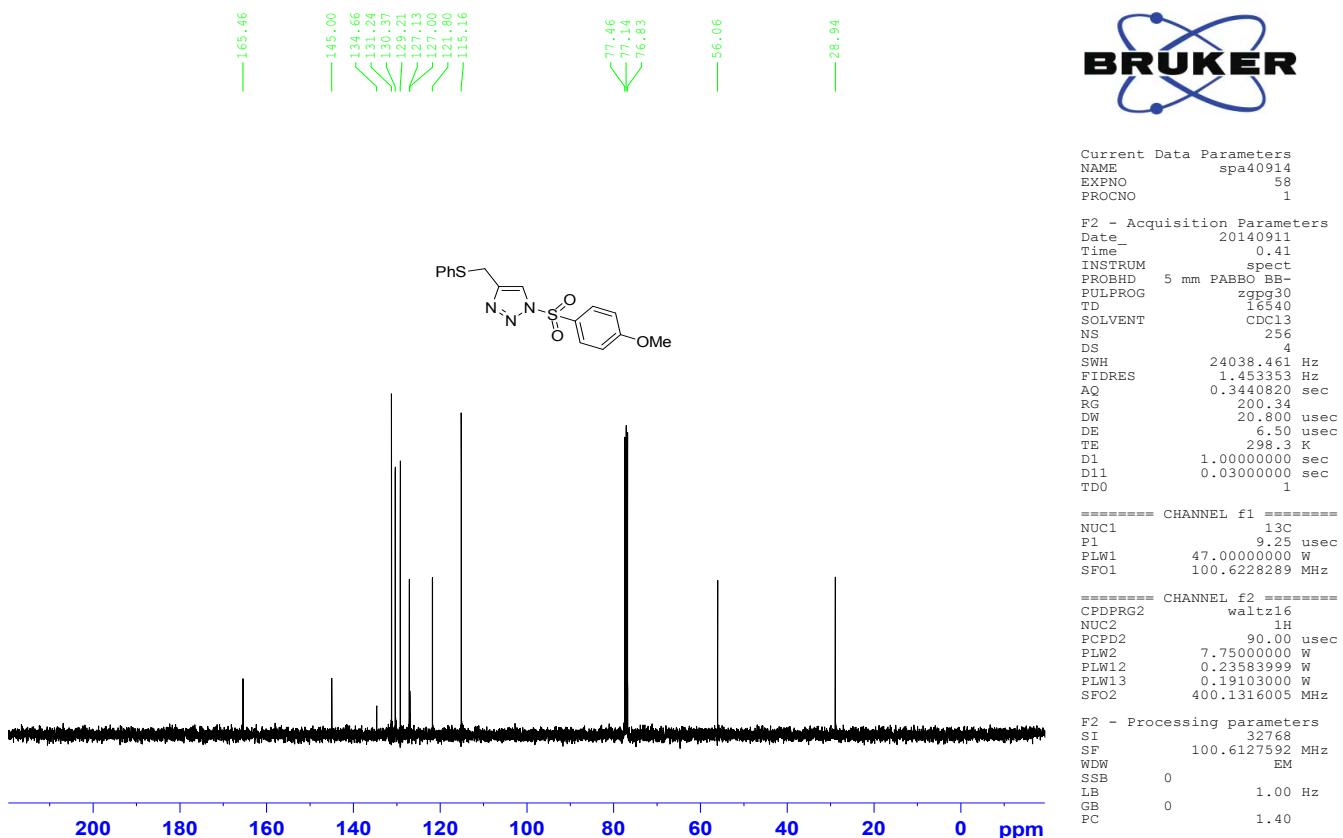


**1-((4-Methoxyphenyl)sulfonyl)-4-((phenylthio)methyl)-1,2,3-triazole (1e) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

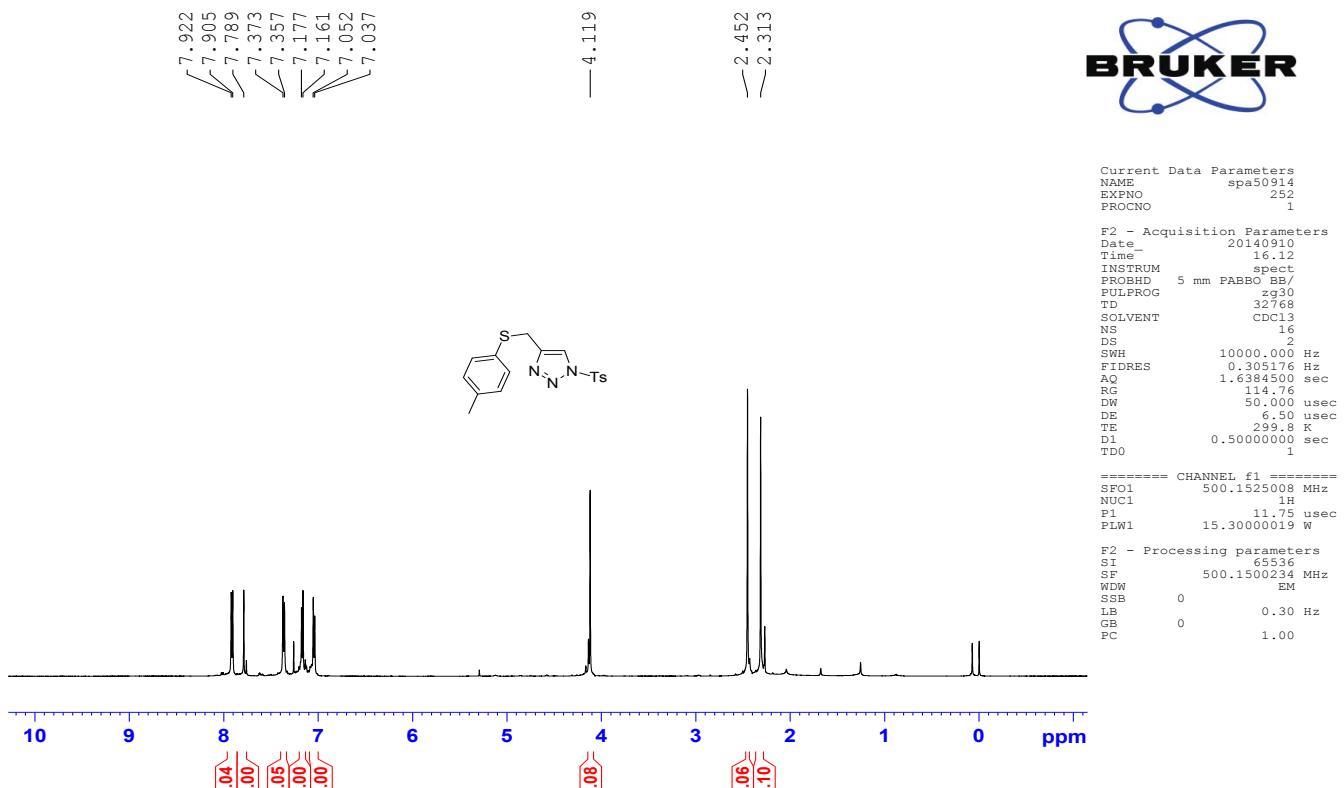


**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**

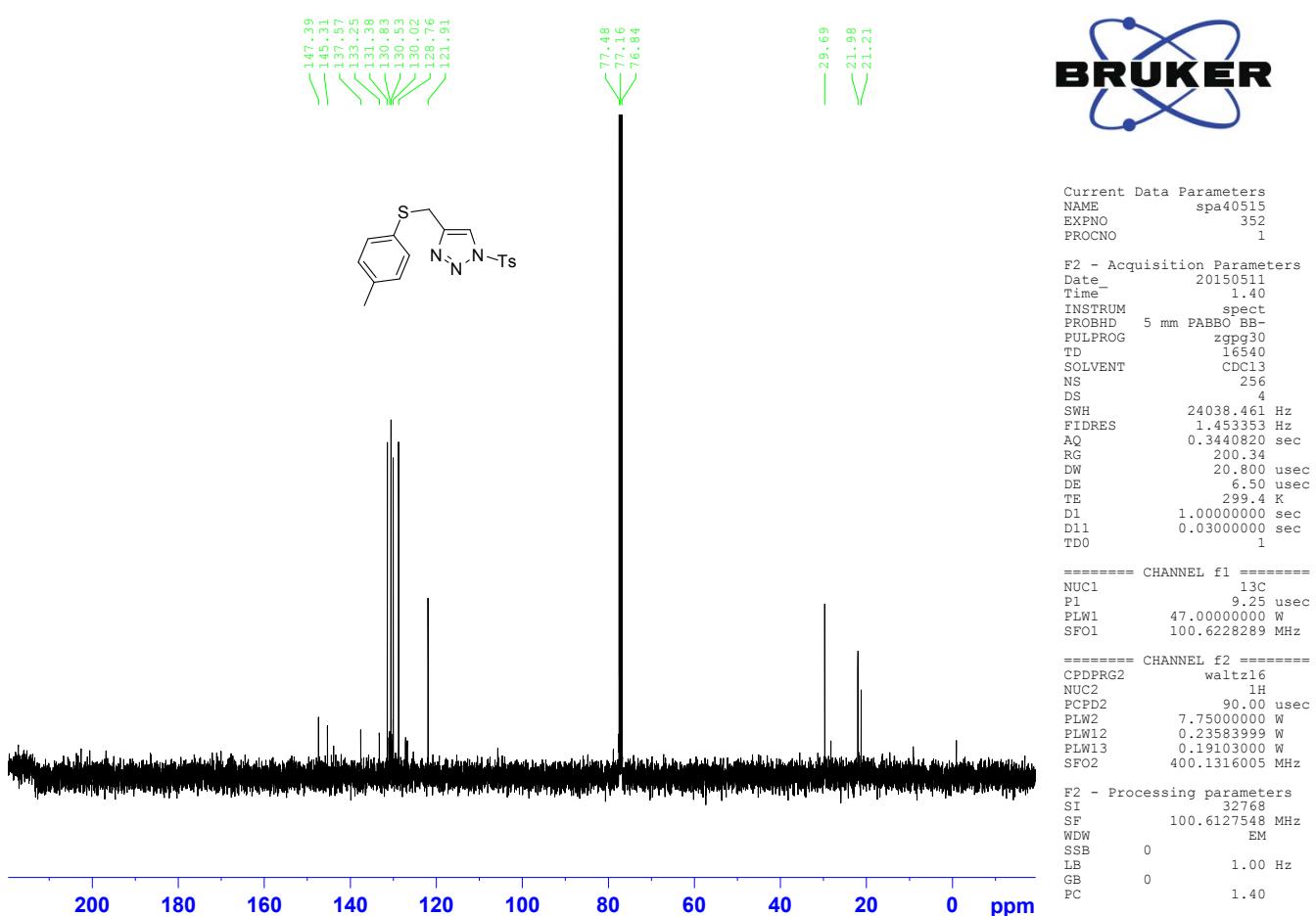


**4-((*p*-tolylthio)methyl)-1-tosyl-1,2,3-triazole (**1f**) :**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C)

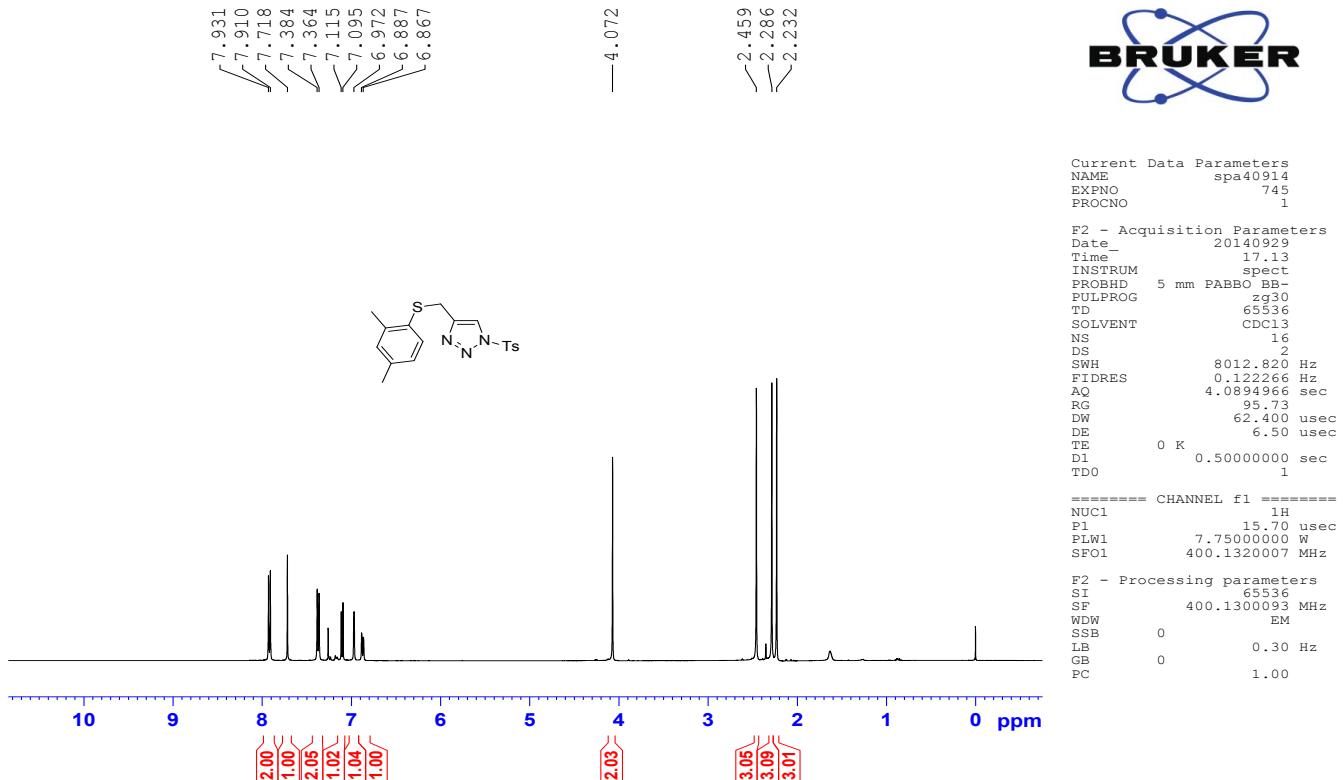


<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, 24 °C)

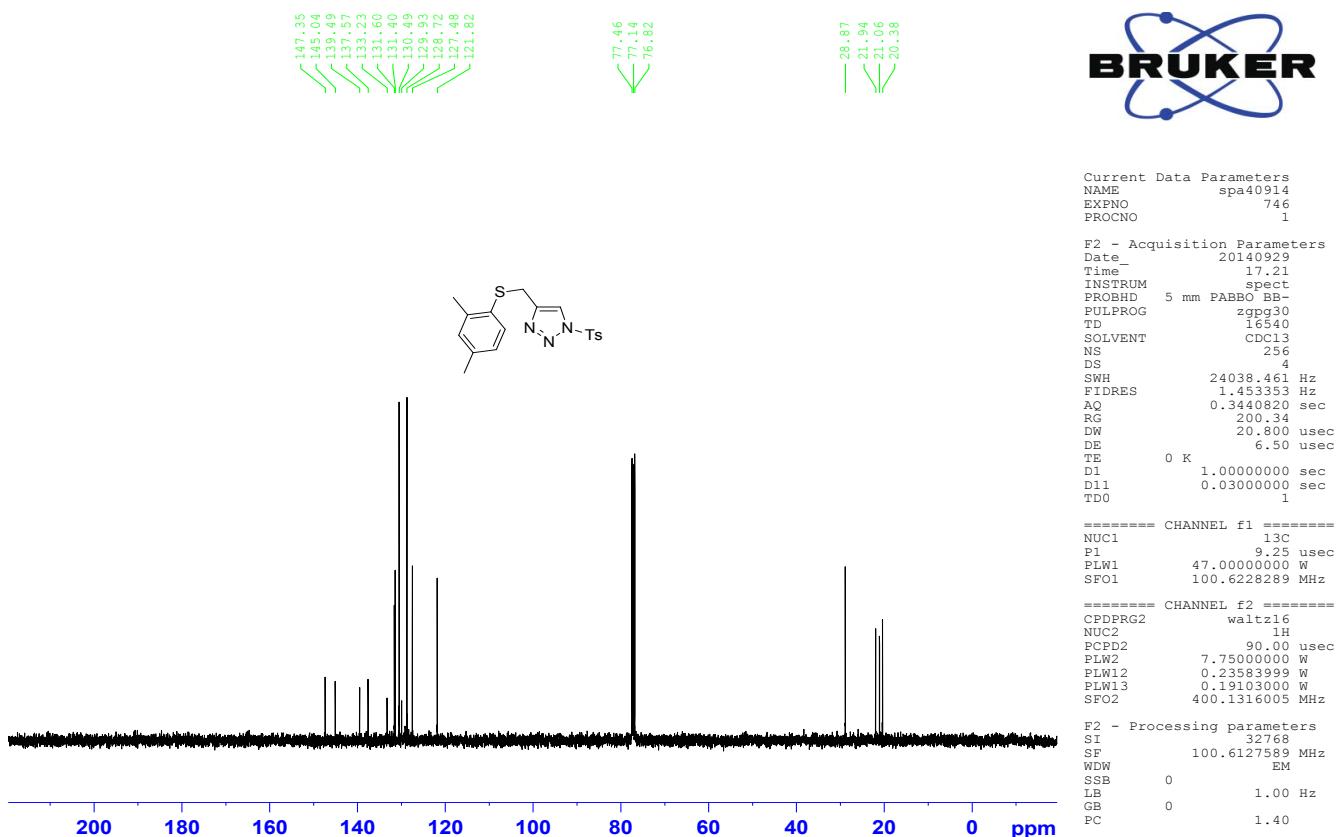


**4-(((2,4-dimethylphenyl)thio)methyl)-1-tosyl-1,2,3-triazole (1g) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

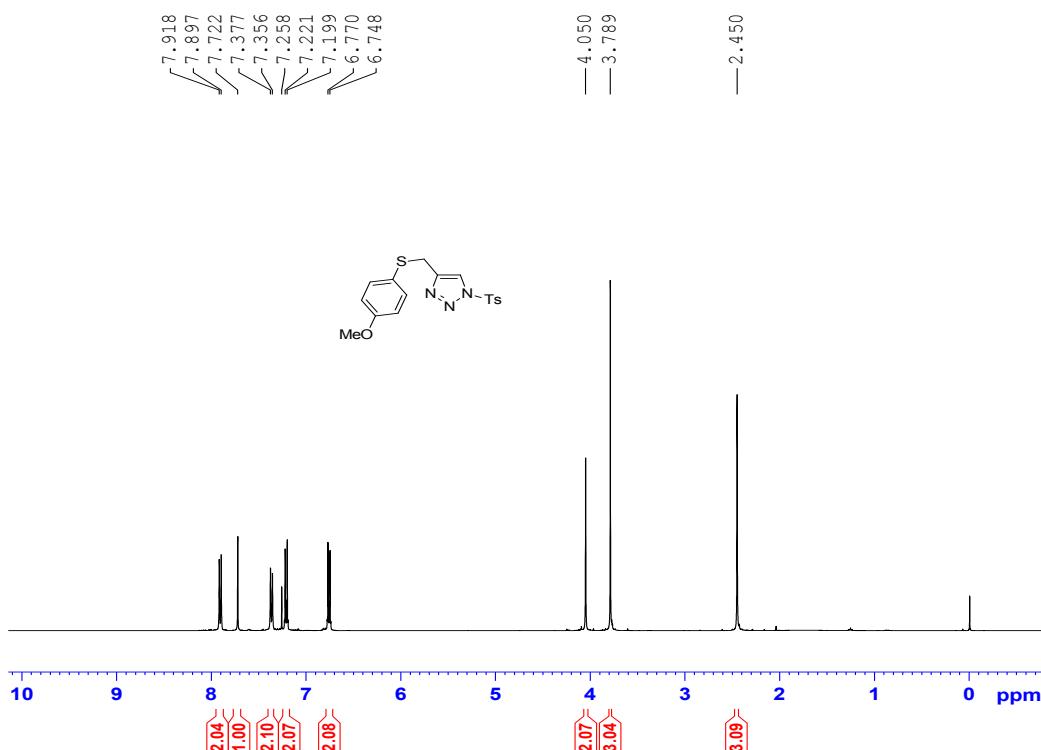


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**

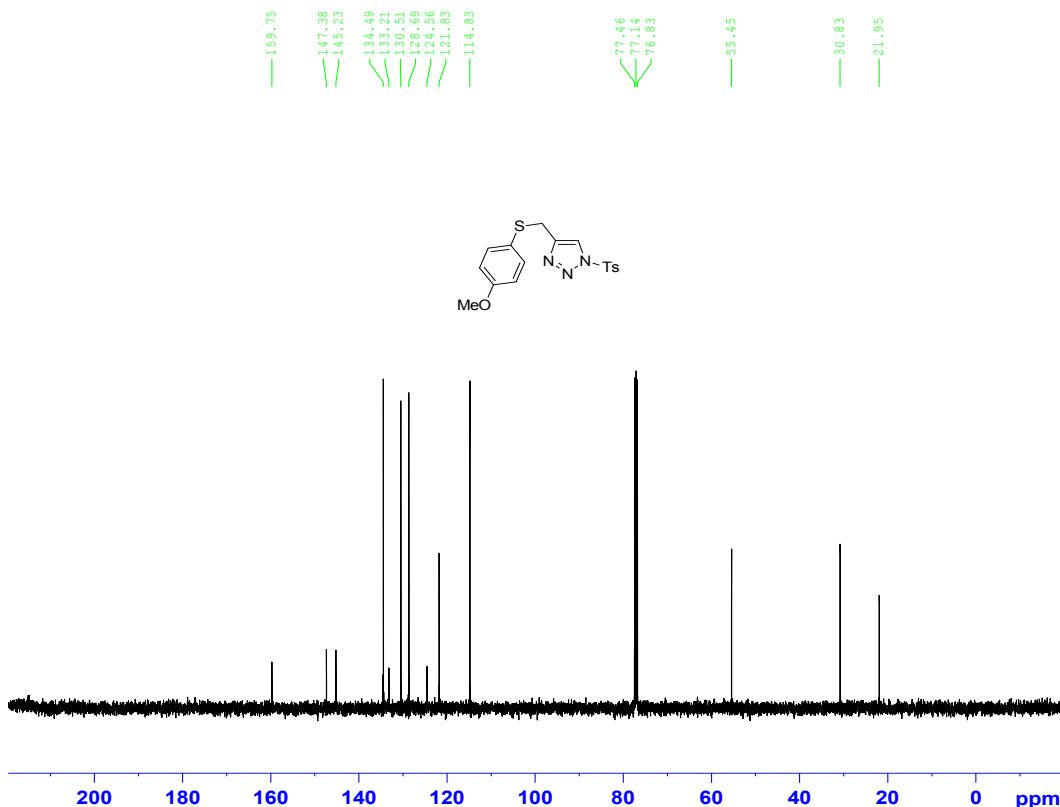


**4-(((4-Methoxyphenyl)thio)methyl)-1-tosyl-1,2,3-triazole (1h) :**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C)

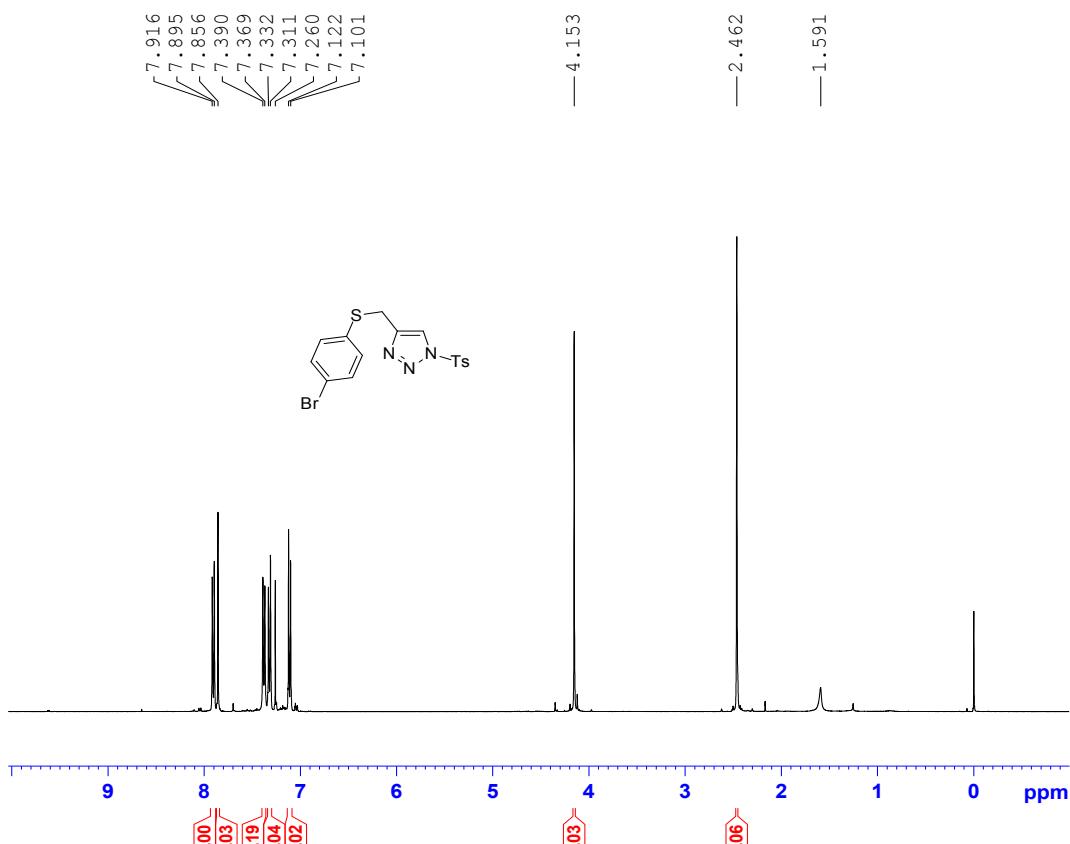


<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)

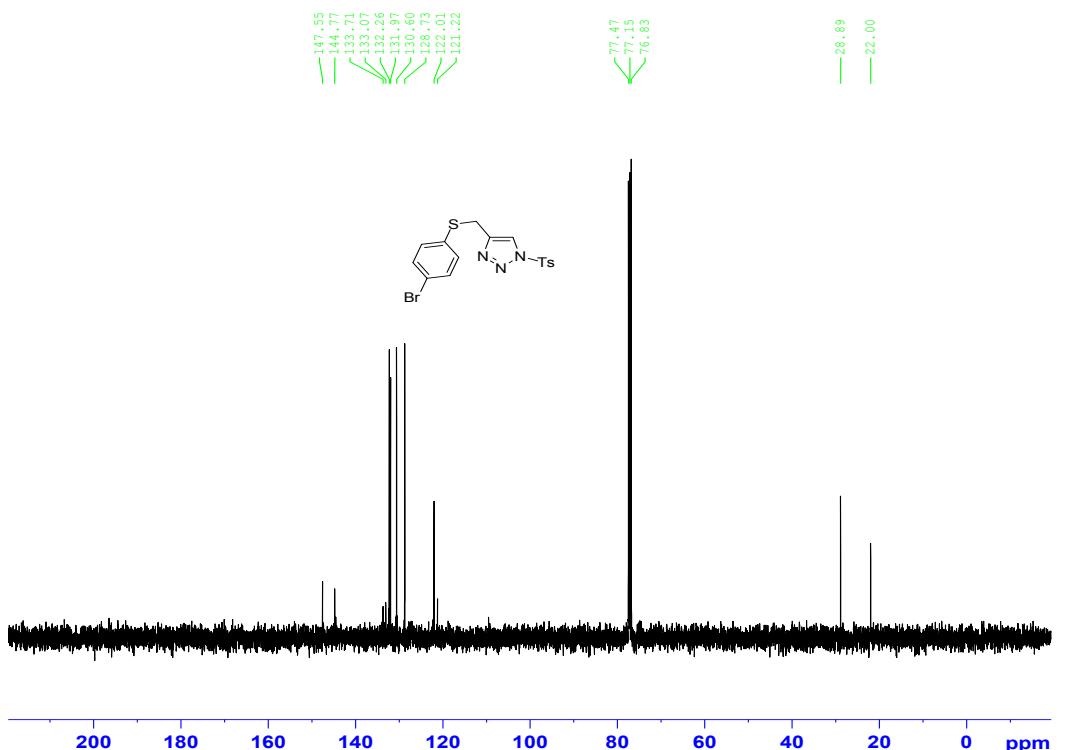


**4-(((4-bromophenyl)thio)methyl)-1-tosyl-1,2,3-triazole (1i) :**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)**

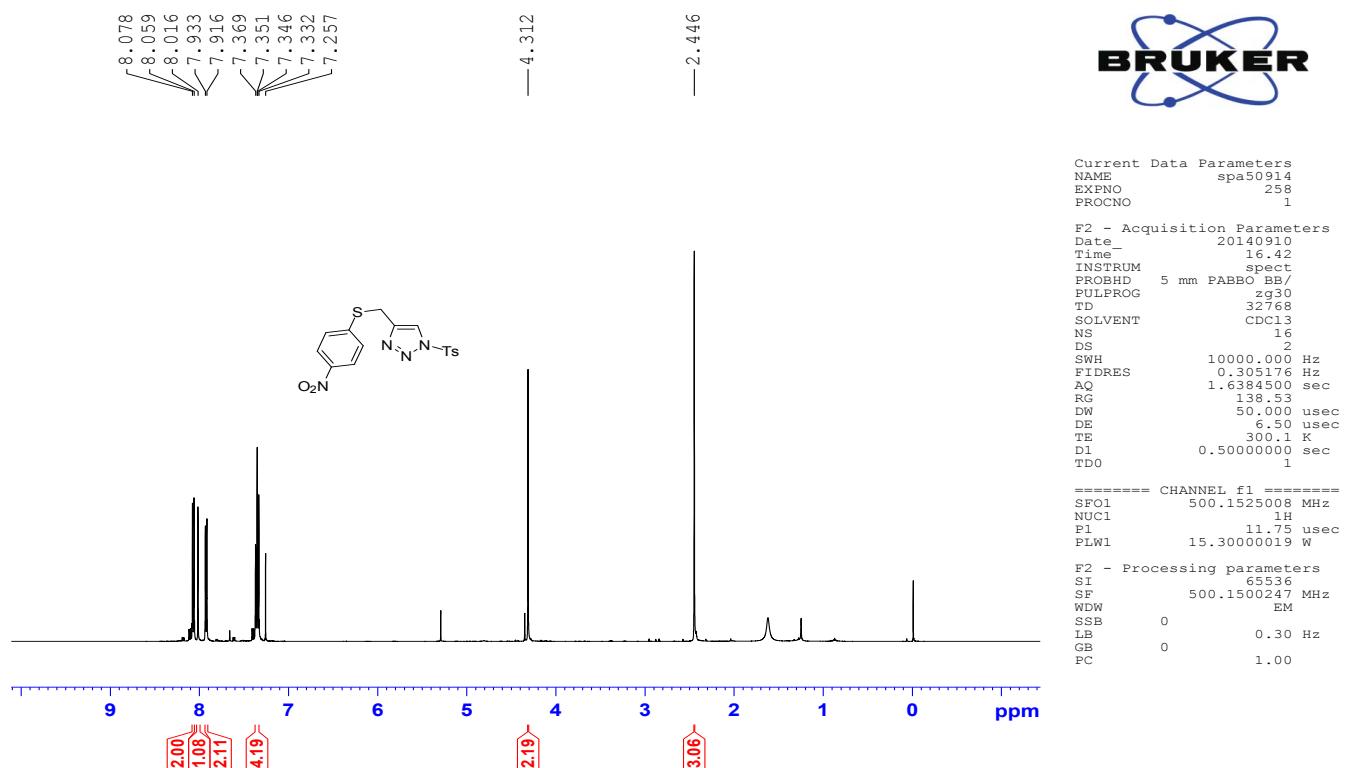


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)**

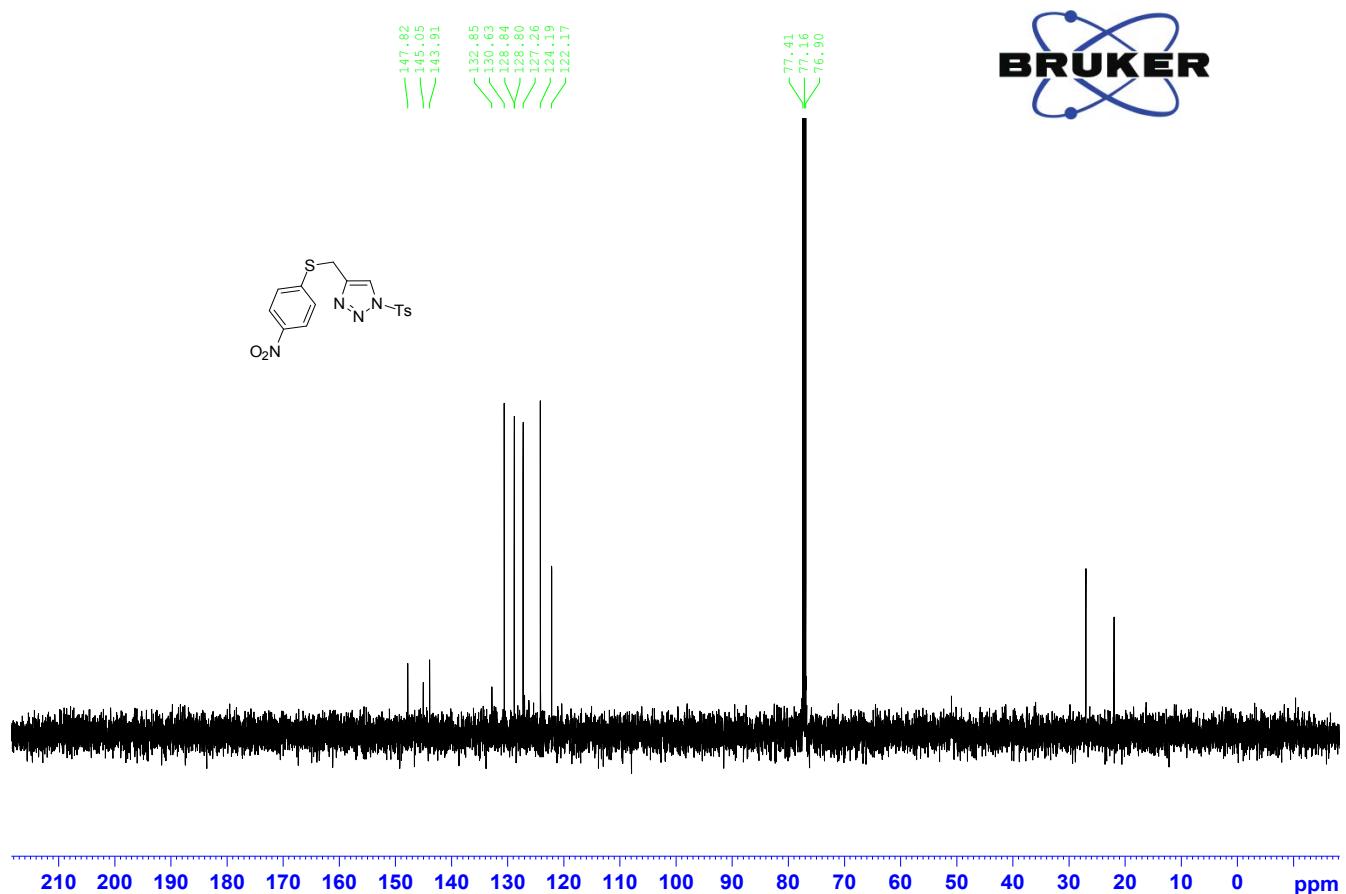


**4-(((4-Nitrophenyl)thio)methyl)-1-tosyl-1,2,3-triazole (1j) :**

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 24 °C)**

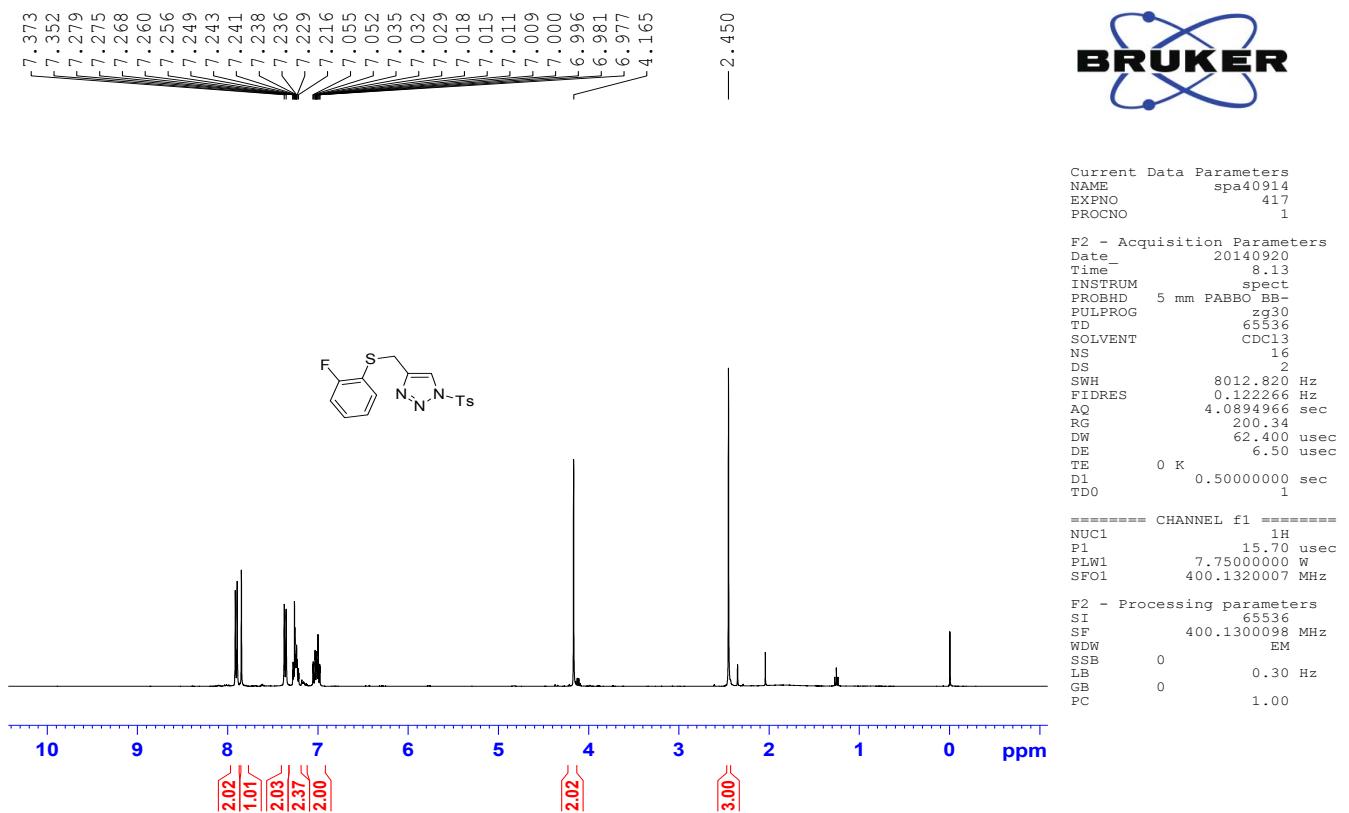


**$^{13}\text{C}\{\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 24 °C)**

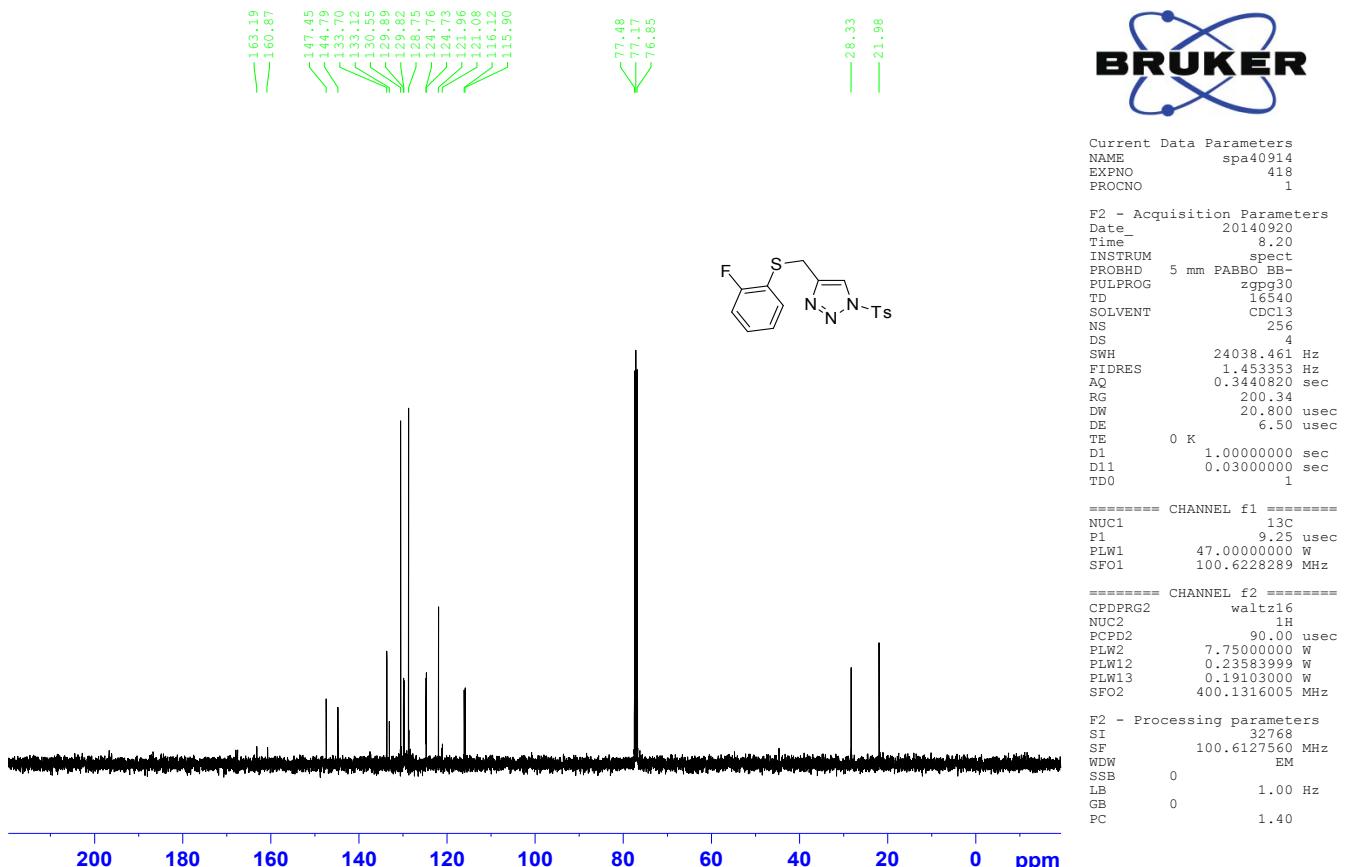


**4-(((2-Fluorophenyl)thio)methyl)-1-tosyl-1,2,3-triazole (1k) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

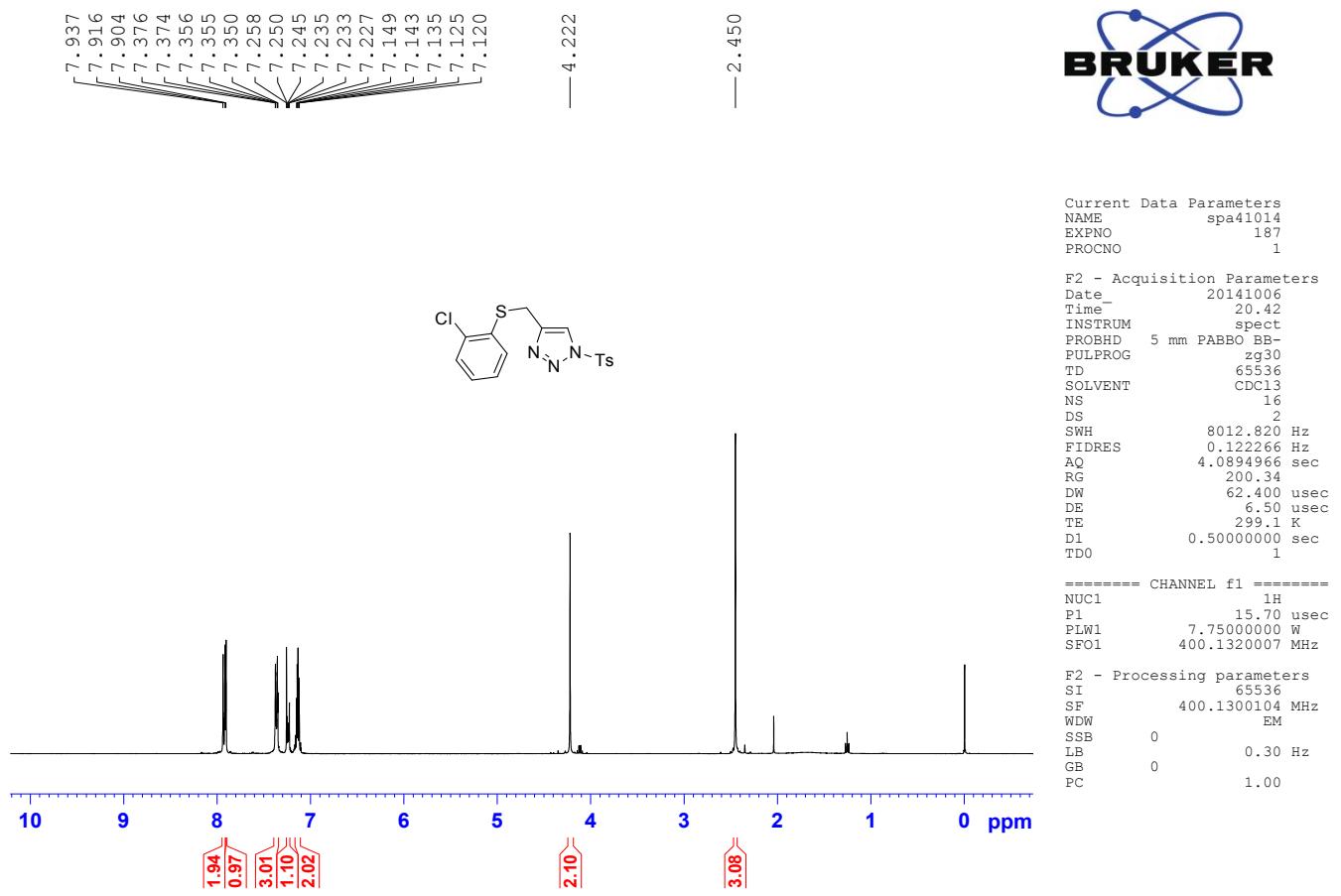


**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**

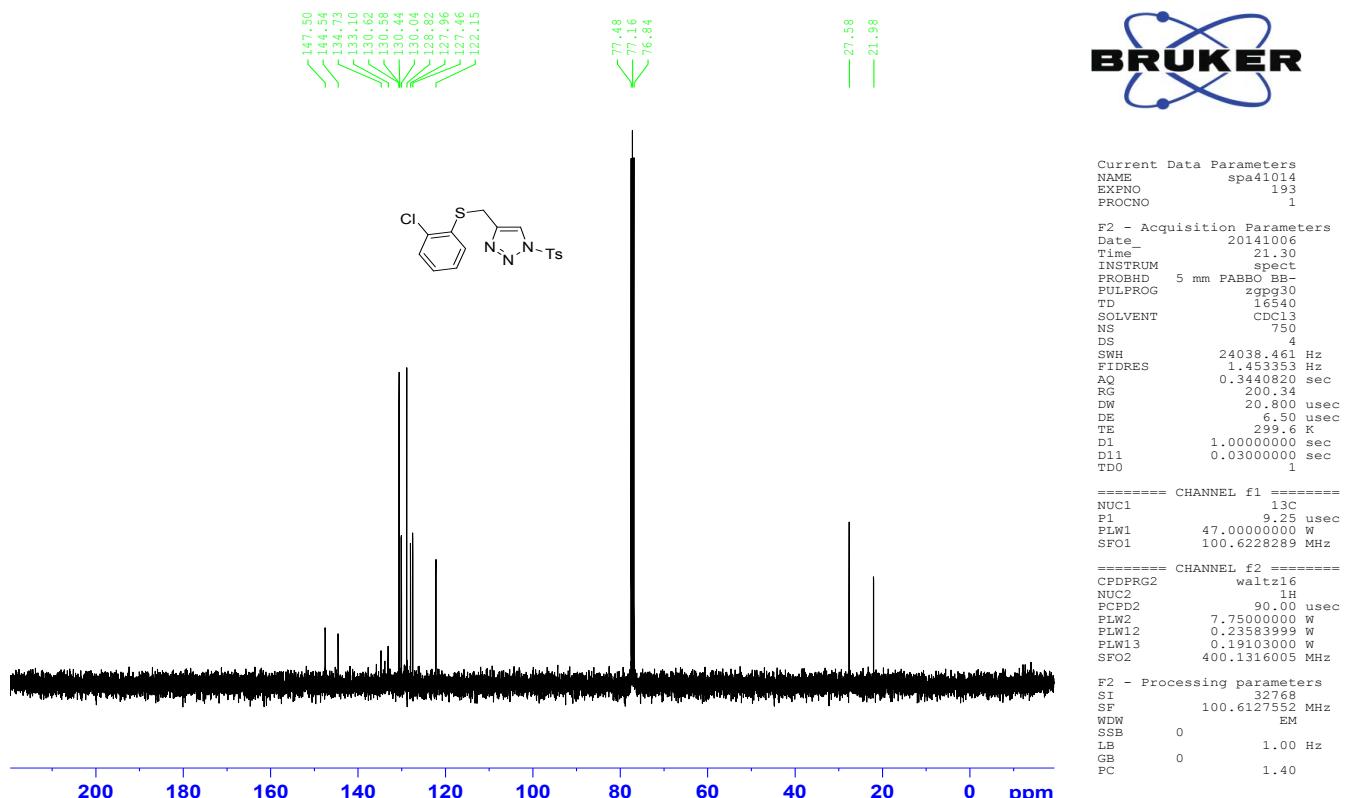


**4-(((2-Chlorophenyl)thio)methyl)-1-tosyl-1,2,3-triazole (1l) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

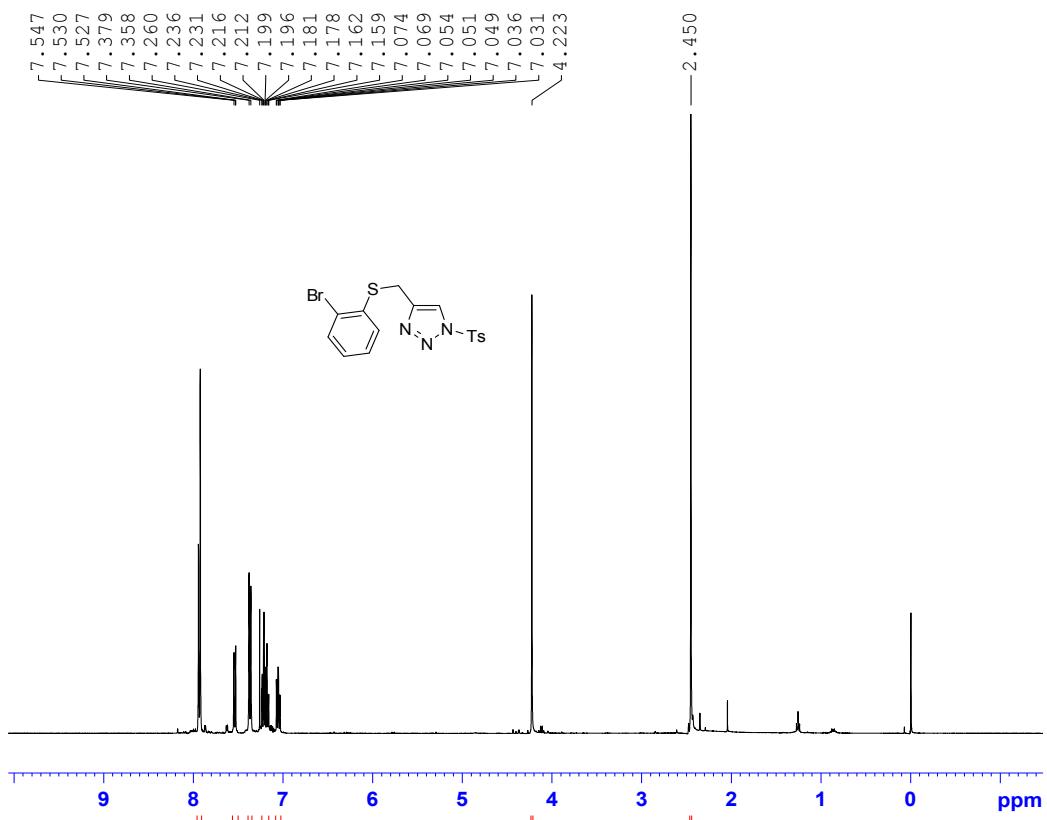


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



**4-(((2-Bromophenyl)thio)methyl)-1-tosyl-1,2,3-triazole (1m) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



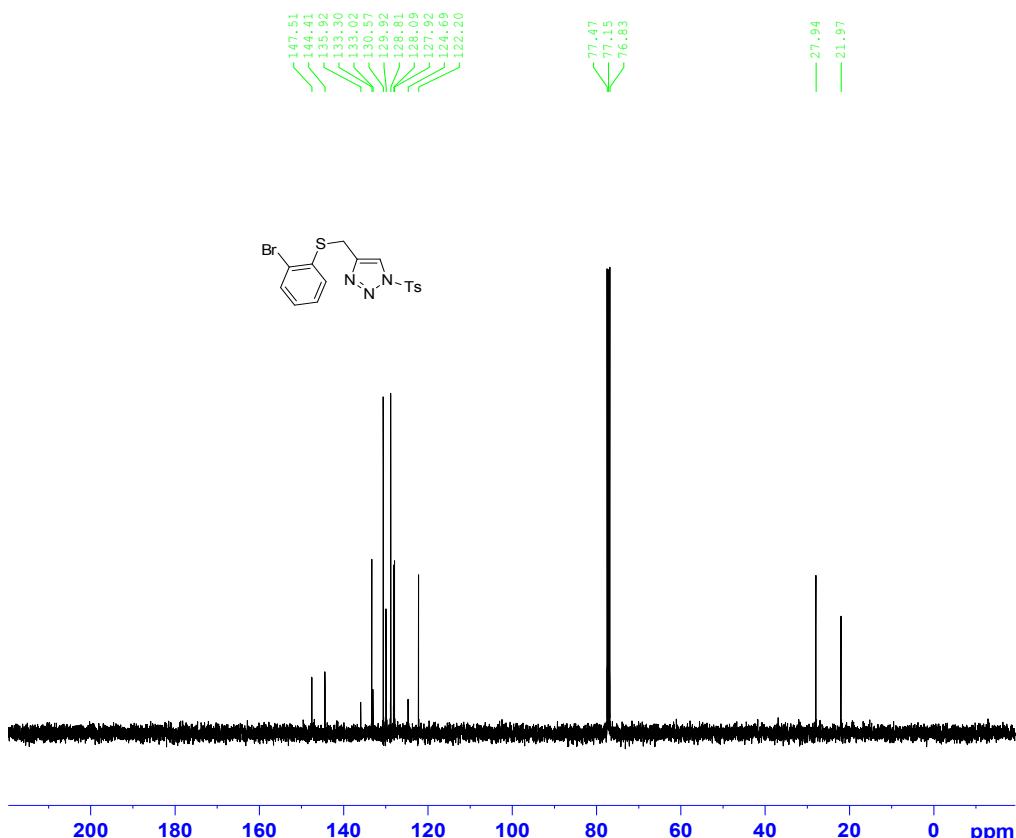
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EXPNO 414  
PROCNO 1

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PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 200.34  
DW 62,400 usec  
DE 6.50 usec  
TE 0 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SFO1 400.1320007 MHz

F2 - Processing parameters  
SI 65536  
SF 400.1300098 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa40914  
EXPNO 415  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20140920  
Time\_ 8.05  
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PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 16540  
SOLVENT CDCl3  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20,800 usec  
DE 6.50 usec  
TE 0 K  
D1 1.0000000 sec  
D11 0.0300000 sec  
TDO 1

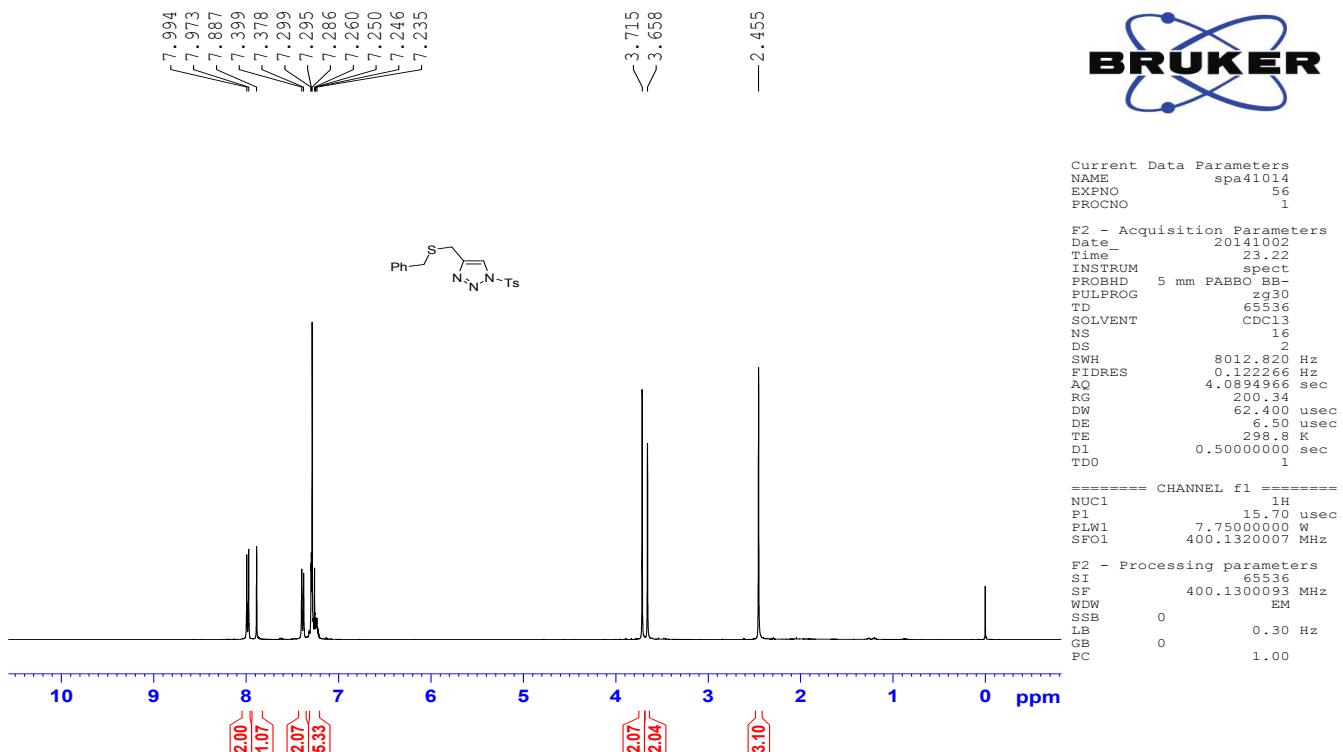
===== CHANNEL f1 =====  
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P1 9.25 usec  
PLW1 47.0000000 W  
SFO1 100.6228289 MHz

===== CHANNEL f2 =====  
CPDPG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.2358399 W  
PLW13 0.1910300 W  
SFO2 400.1316005 MHz

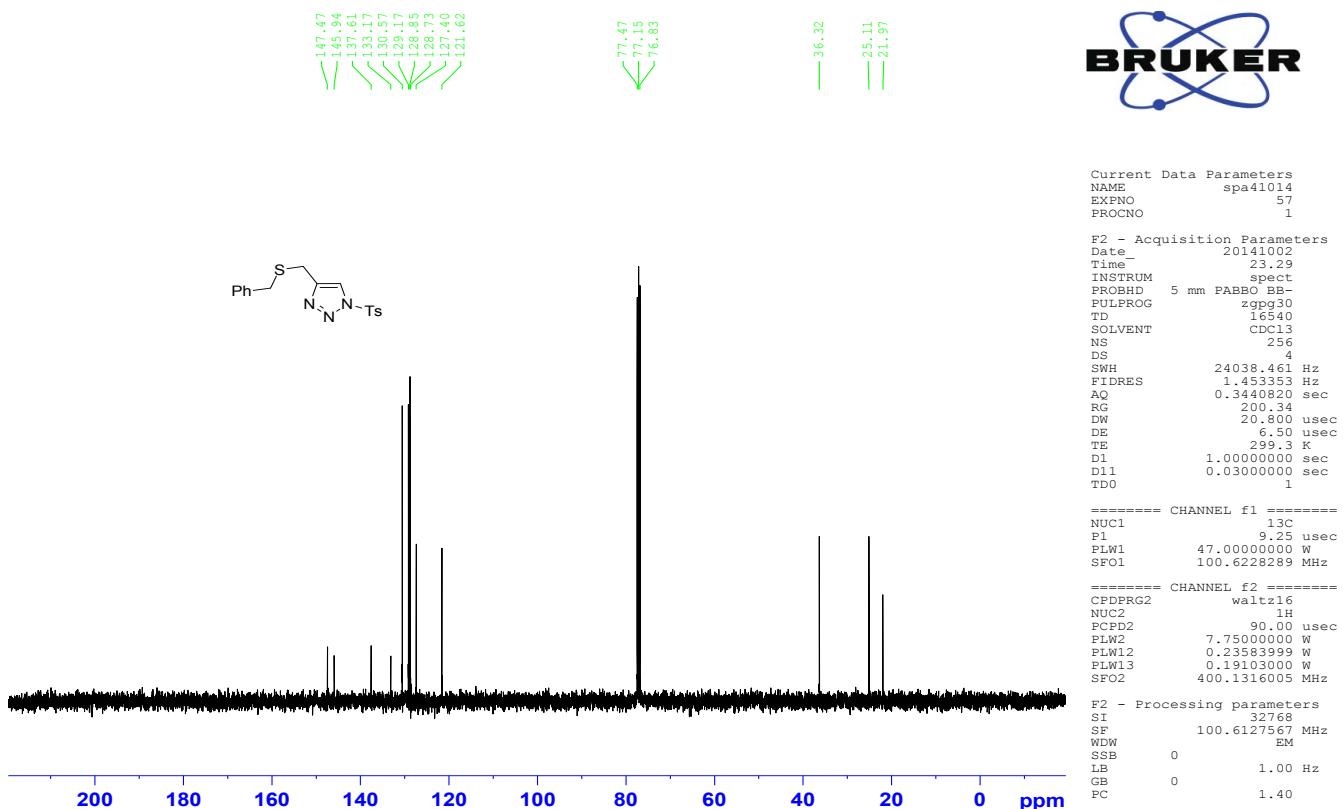
F2 - Processing parameters  
SI 32768  
SF 100.6127581 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**4-((Benzylthio)methyl)-1-tosyl-1,2,3-triazole (1n) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

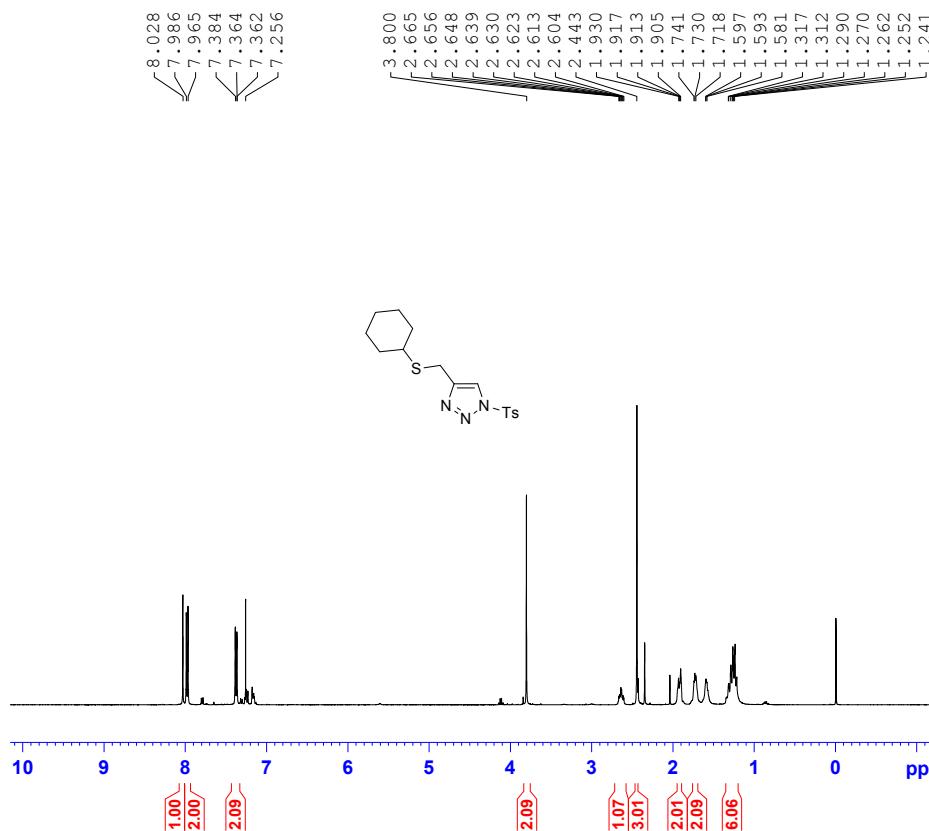


**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**

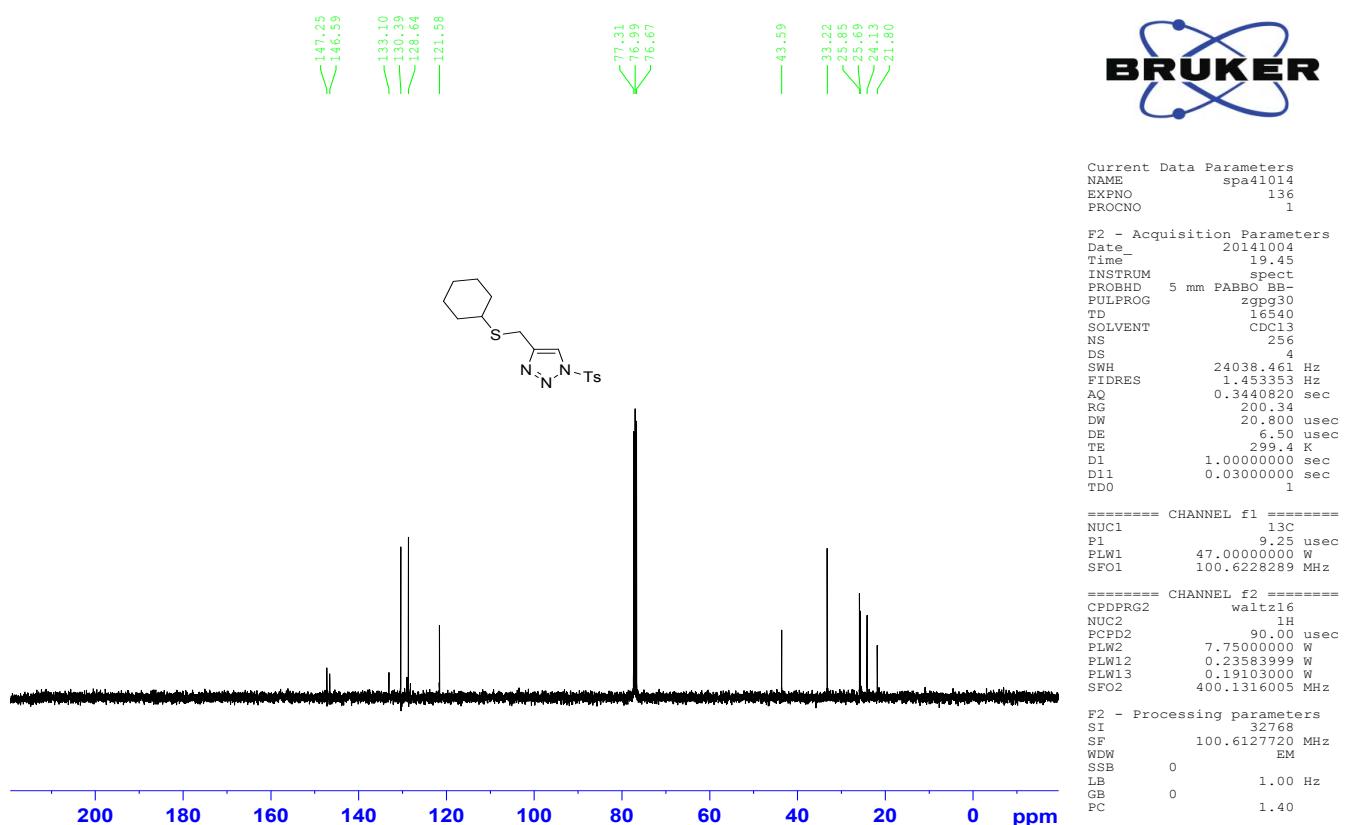


**4-((Cyclohexylthio)methyl)-1-tosyl-1,2,3-triazole (1o) :**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)

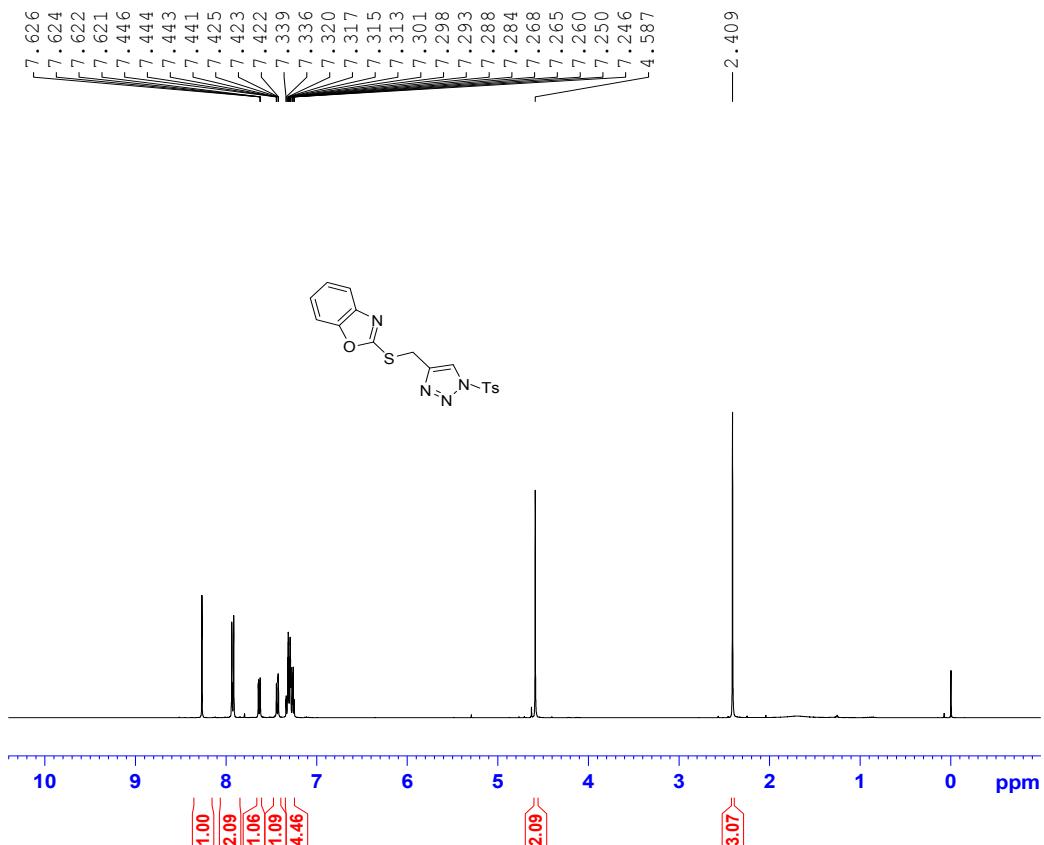


<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)



**2-(((1-Tosyl-1,2,3-triazol-4-yl)methyl)thio)benzo[d]oxazole (1p) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



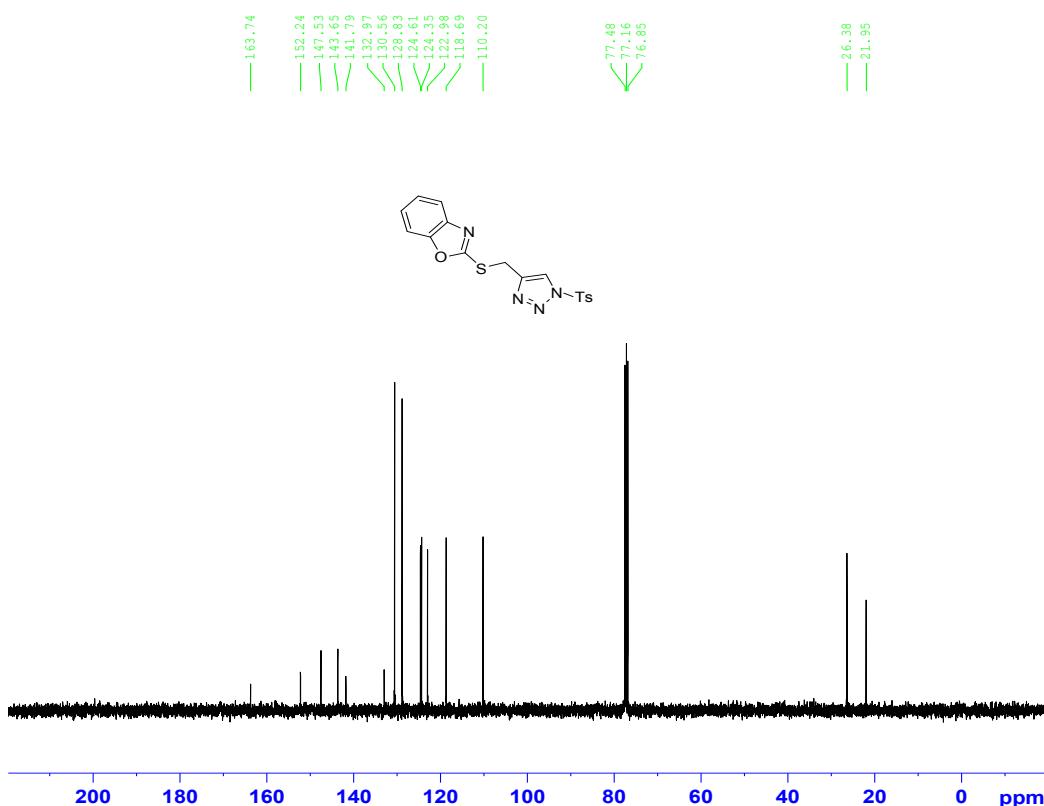
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EXPNO 86  
PROCNO 1

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SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 200.34  
DW 62,400 usec  
DE 6.50 usec  
TE 0 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SFO1 400.1320007 MHz

F2 - Processing parameters  
SI 65536  
SF 400.1300098 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa40914  
EXPNO 87  
PROCNO 1

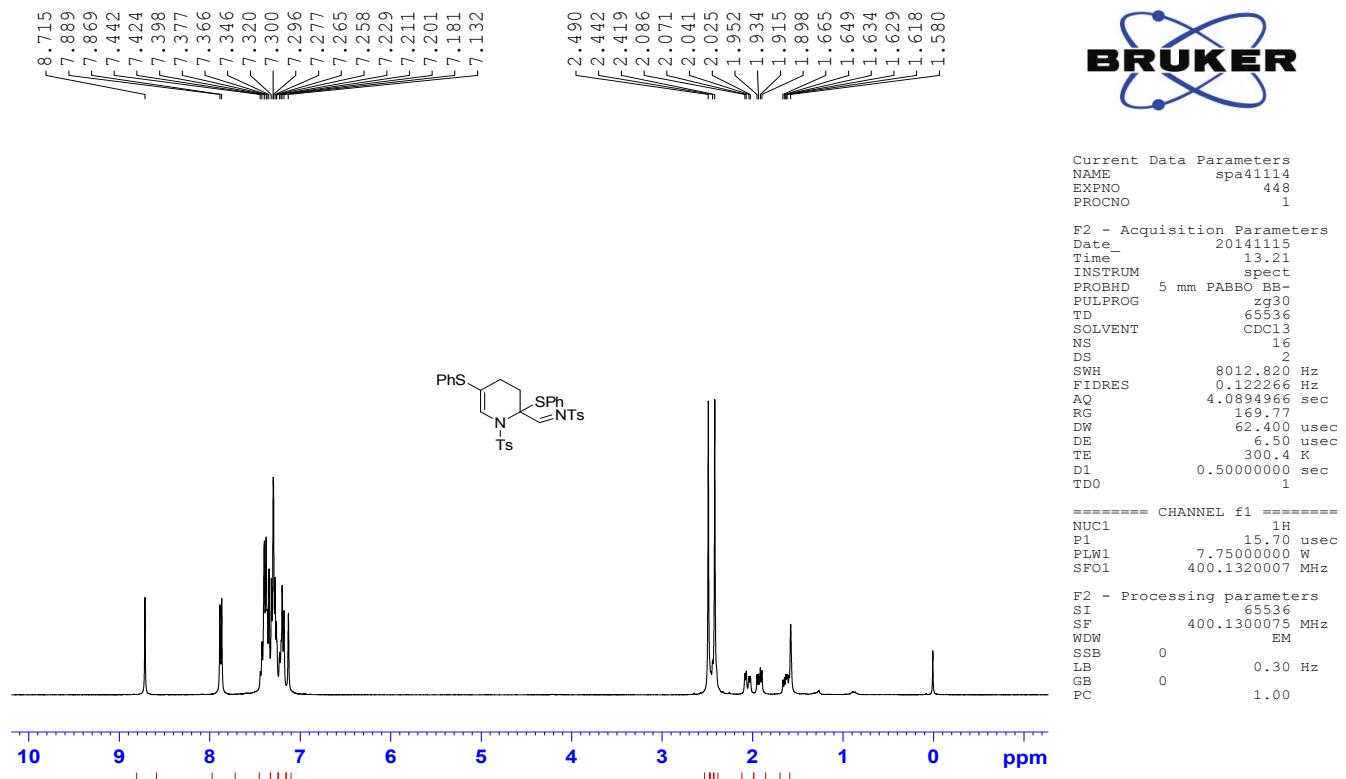
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PULPROG zgpg30  
TD 16540  
SOLVENT CDCl3  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440800 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 0 K  
D1 1.0000000 sec  
D11 0.0300000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 13C  
P1 9.25 usec  
PLW1 47.0000000 W  
SFO1 100.6228289 MHz

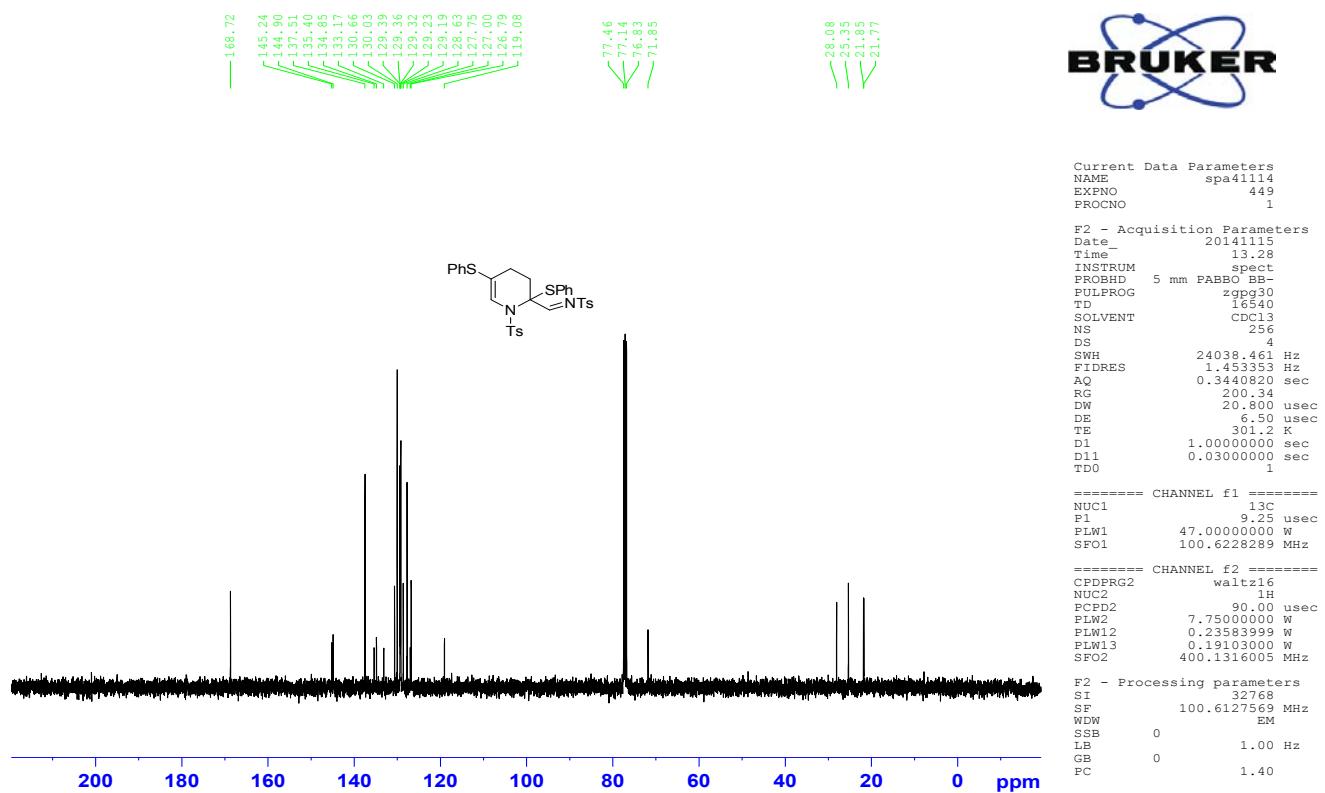
===== CHANNEL f2 ======  
CPDPG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127561 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**N-((2,5-Bis(phenylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3a) :**  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)

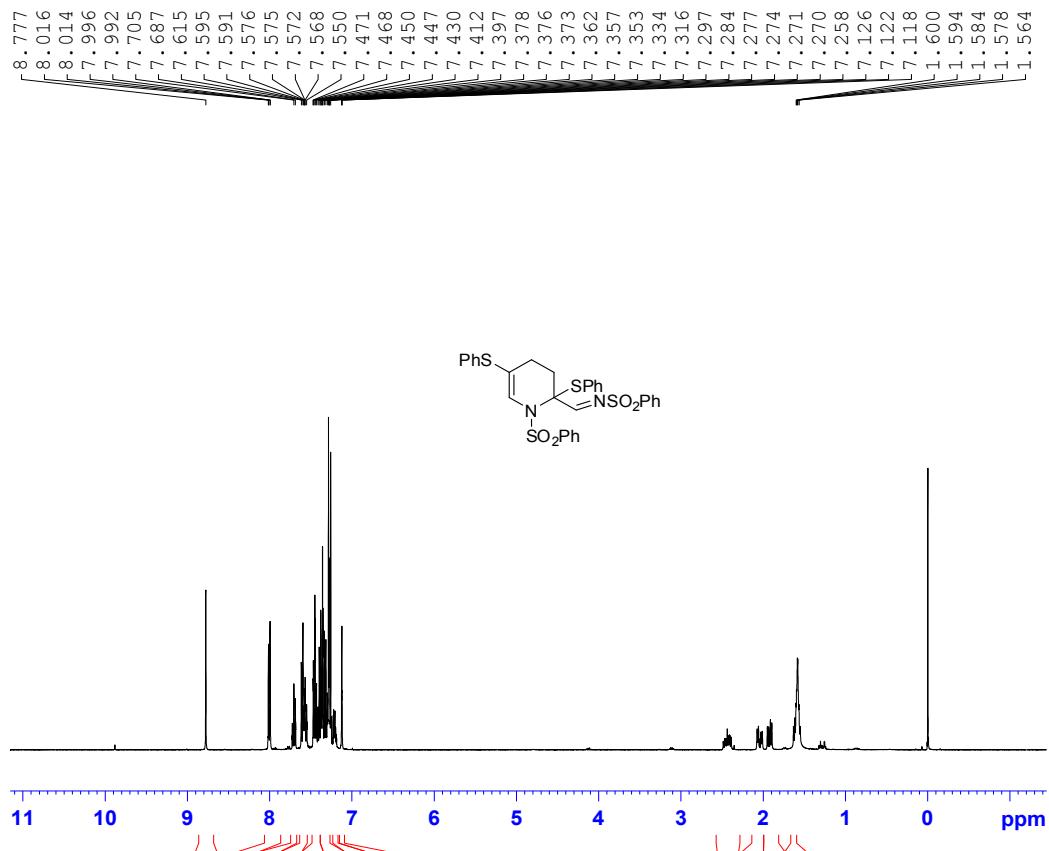


<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)

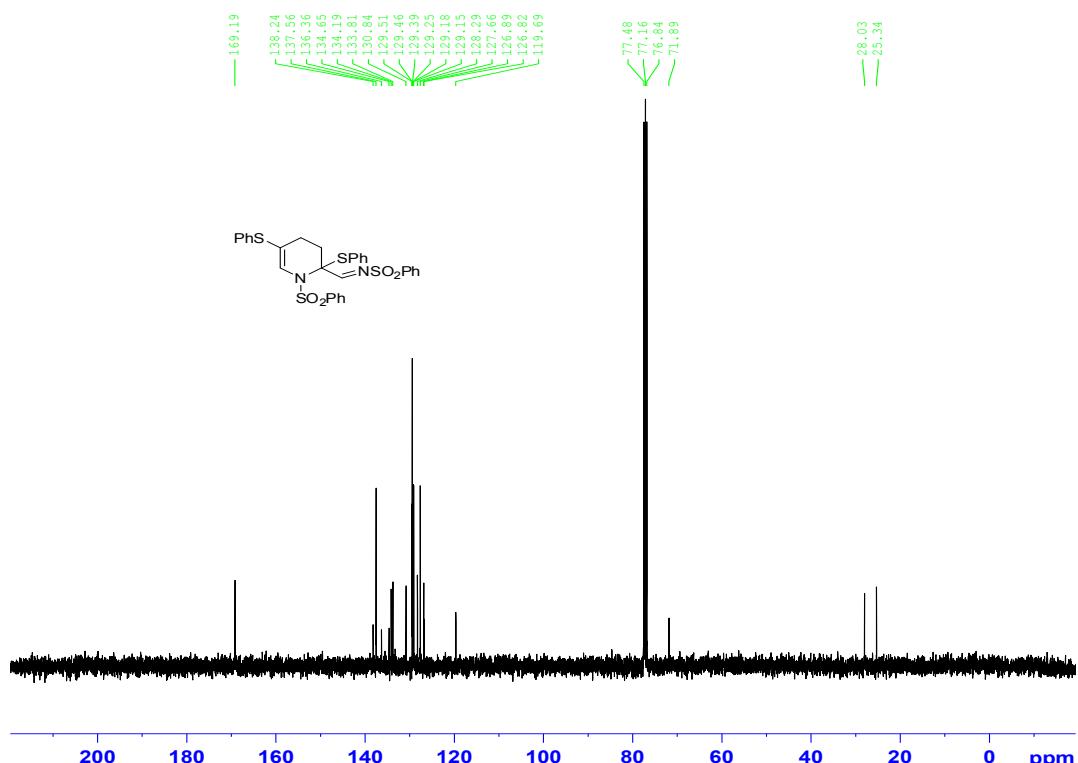


**N-((1-(Phenylsulfonyl)-2,5-bis(phenylthio)-1,2,3,4-tetrahydropyridin-2-yl)methylene)benzenesulfonamide (3b) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

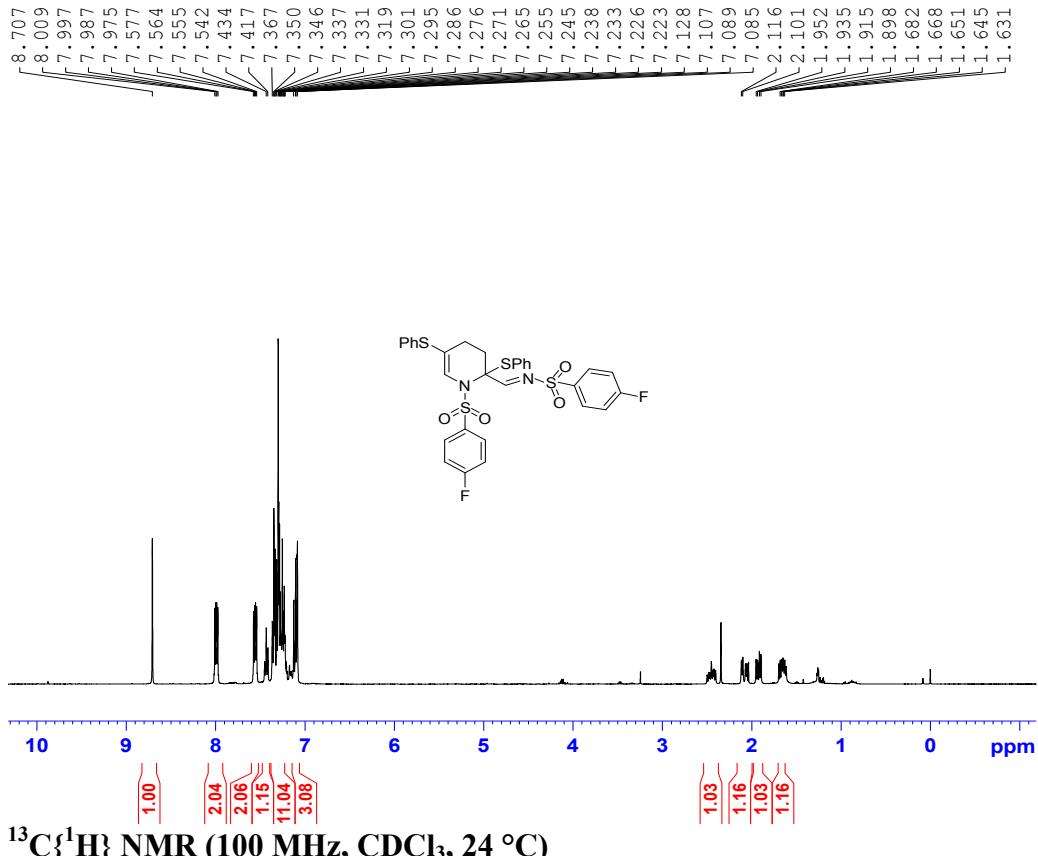


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



**(E)-4-Fluoro-N- ( (1- ( (4-fluorophenyl)sulfonyl)-2,5-bis (phenylthio)-1,2,3,4-tetrahydropyridin-2-yl)methylene)benzenesulfonamide (3c) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



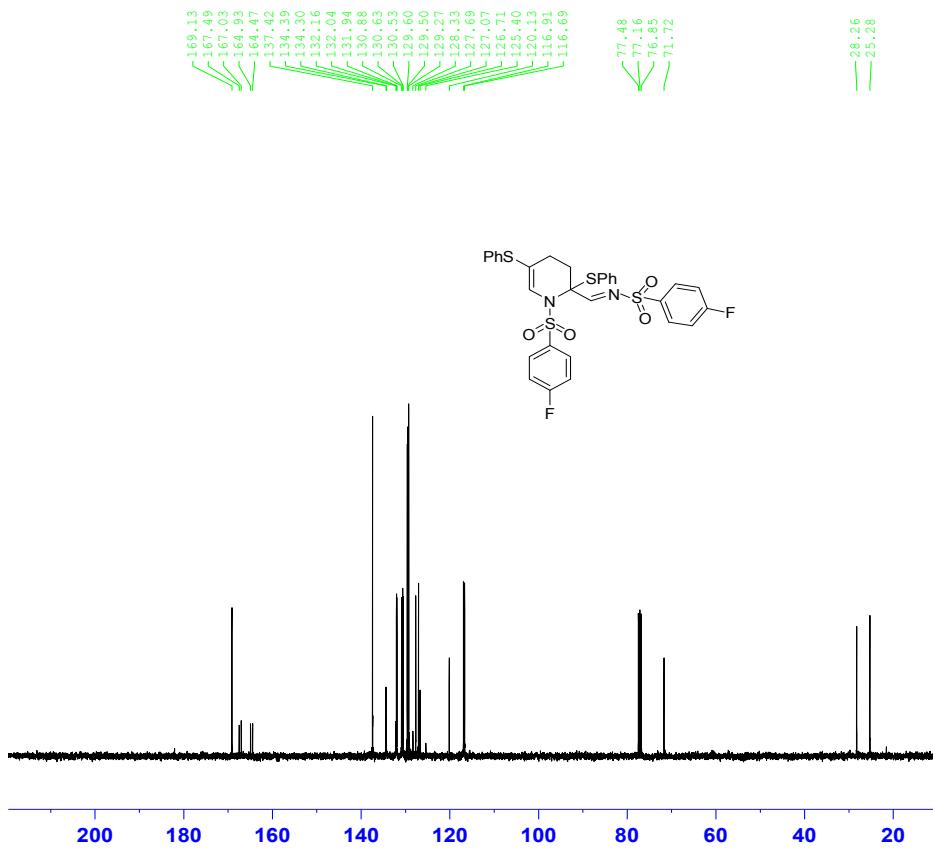
Current Data Parameters  
NAME spa41014  
EXPNO 615  
PROCNO 1

F2 - Acquisition Parameters  
Date 20141016  
Time 22.34  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDC13  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 88.51  
DW 62.400 usec  
DE 6.50 usec  
TE 301.0 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SFO1 400.1320007 MHz

F2 - Processing parameters  
SI 65536  
SF 400.1300126 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa41014  
EXPNO 616  
PROCNO 1

F2 - Acquisition Parameters  
Date 20141016  
Time 22.42  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 16540  
SOLVENT CDC13  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 301.8 K  
D1 1.0000000 sec  
D11 0.0300000 sec  
TDO 1

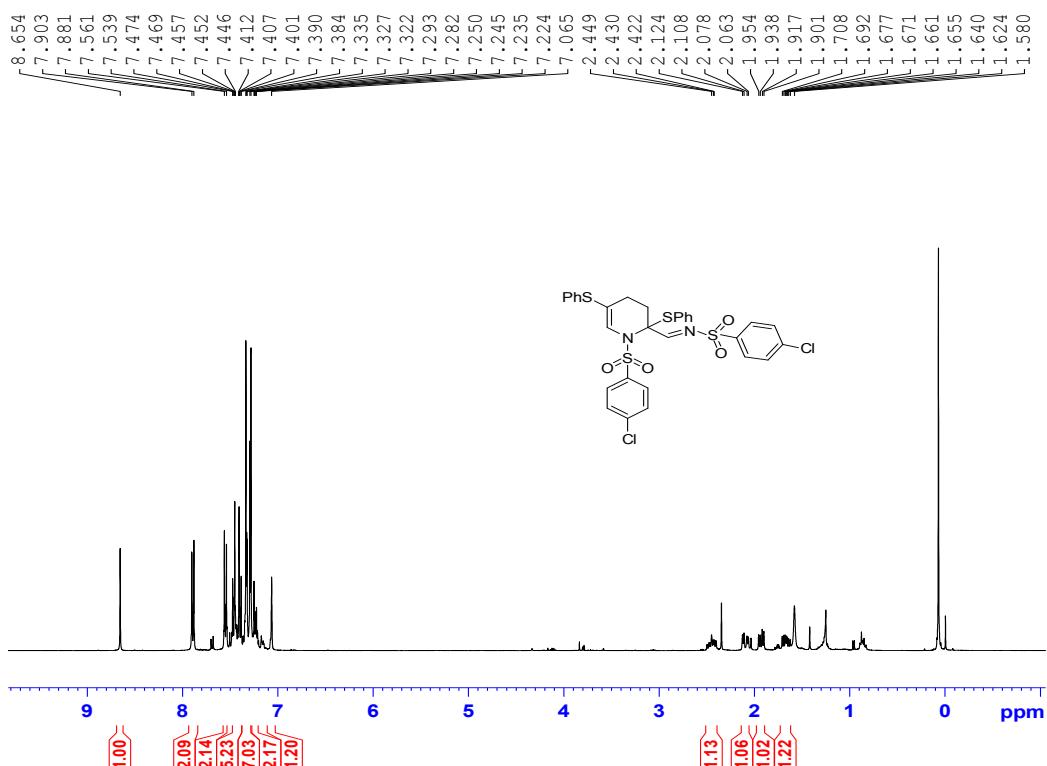
===== CHANNEL f1 ======  
NUC1 13C  
P1 9.25 usec  
PLW1 47.0000000 W  
SFO1 100.6228289 MHz

===== CHANNEL F2 ======  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127600 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**(E)-4-Chloro-N- ( (1- ( (4-chlorophenyl)sulfonyl)-2,5-bis (phenylthio)-1,2,3,4-tetrahydropyridin-2-yl)methylene)benzenesulfonamide (3d) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



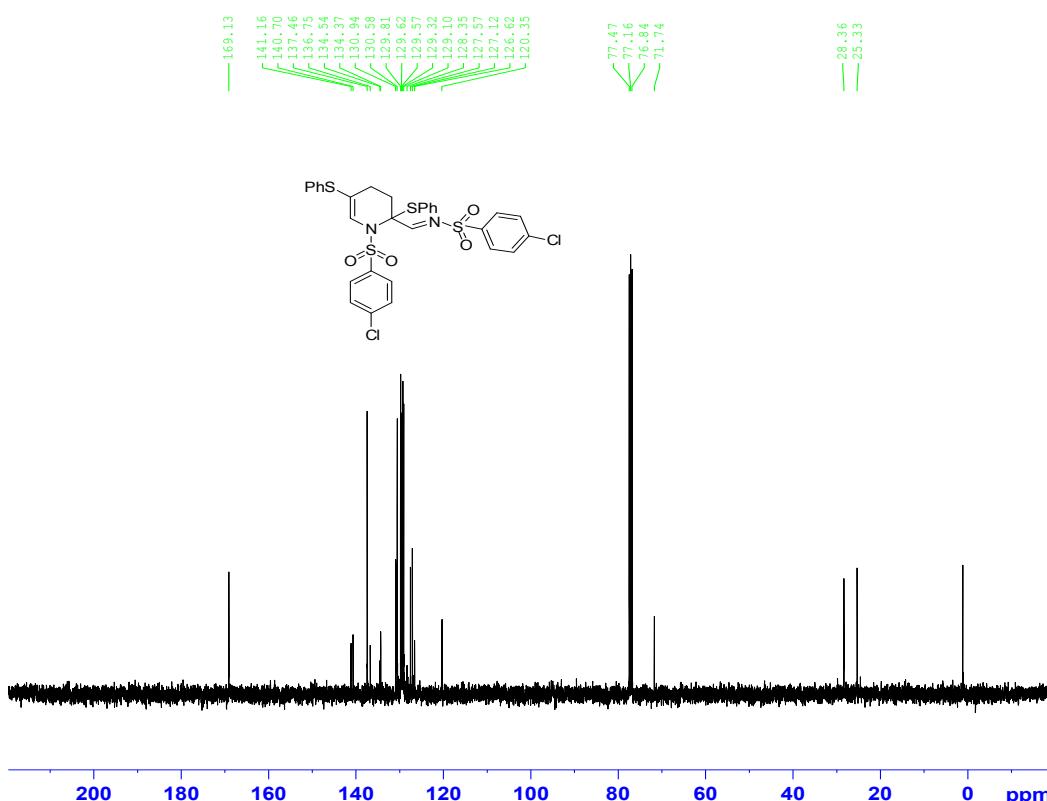
Current Data Parameters  
NAME spa41014  
EXPNO 712  
PROCNO 1

F2 - Acquisition Parameters  
Date 20141012  
Time 20:51  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 138.85  
DW 62.400 usec  
DE 6.50 usec  
TE 300.3 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SFOL 400.1320007 MHz

F2 - Processing parameters  
SI 65536  
SF 400.1300136 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa41014  
EXPNO 713  
PROCNO 1

F2 - Acquisition Parameters  
Date 20141018  
Time 20:58  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 16540  
SOLVENT CDCl3  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440824 sec  
RG 20.84  
DW 20.800 usec  
DE 6.50 usec  
TE 301.0 K  
D1 1.0000000 sec  
D11 0.03000000 sec  
TDO 1

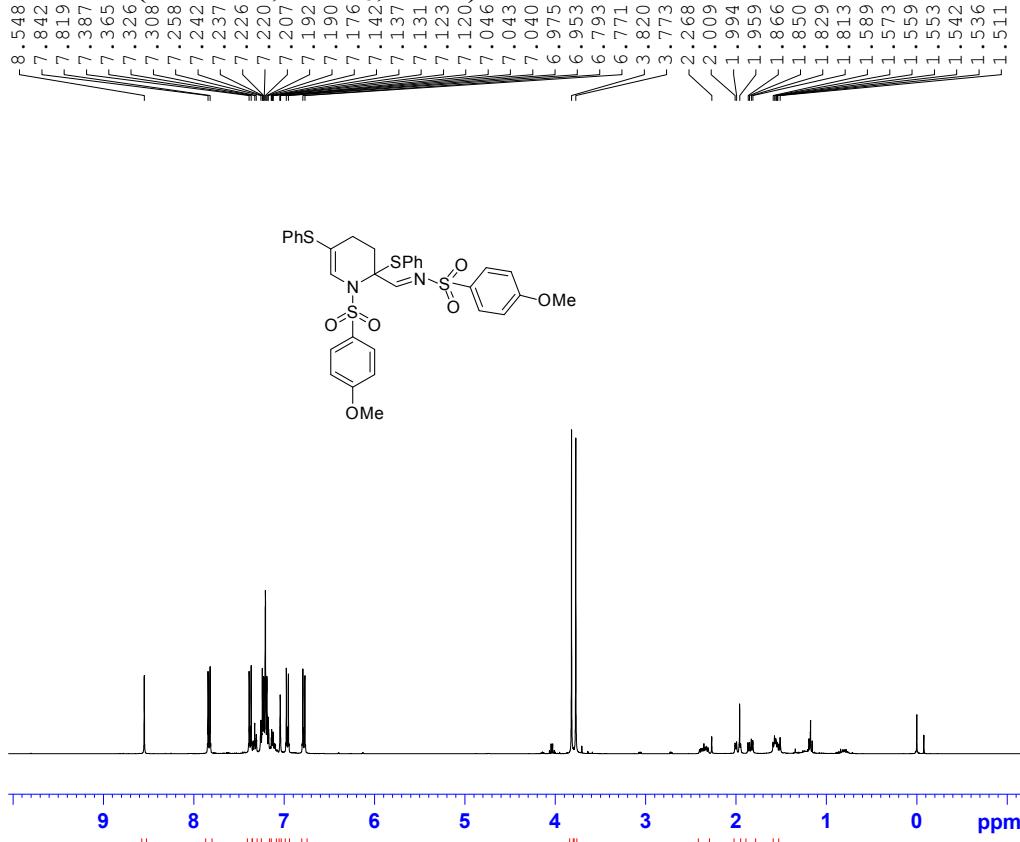
===== CHANNEL f1 ======  
NUC1 13C  
P1 9.25 usec  
PLW1 47.0000000 W  
SFOL 100.6228289 MHz

===== CHANNEL f2 ======  
CPDPG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SFOL 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127562 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**(E)-4-Methoxy-N- ( (1- ( (4-methoxyphenyl)sulfonyl)-2,5-bis (phenylthio)-1,2,3,4-tetrahydropyridin-2-yl)methylene)benzenesulfonamide (3e) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



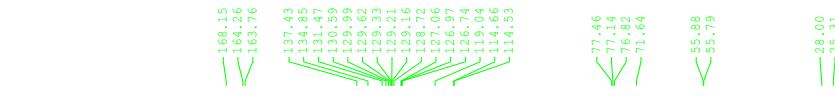
Current Data Parameters  
NAME spa40914  
EXPNO 214  
PROCNO 1

F2 - Acquisition Parameters  
Date 20140914  
Time 15.57  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 88.51  
DW 62,400 usec  
DE 6.50 usec  
TE 0 K  
D1 0.50000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 1H  
P1 15.70 usec  
PLW1 7.75000000 W  
SF01 400.1320007 MHz

F2 - Processing parameters  
SI 65536  
SF 400.1300431 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa40914  
EXPNO 215  
PROCNO 1

F2 - Acquisition Parameters  
Date 20140914  
Time 16.04  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 16540  
SOLVENT CDCl3  
NS 256  
DS 4  
SWH 24038.46 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 0 K  
D1 1.00000000 sec  
D11 0.03000000 sec  
TDO 1

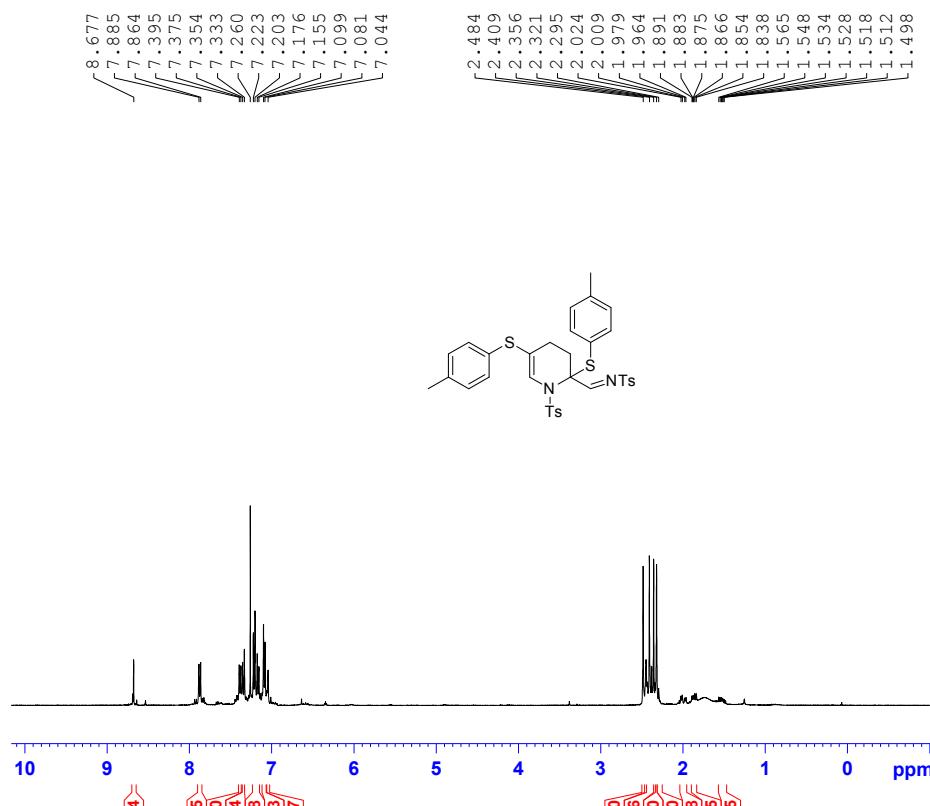
===== CHANNEL f1 ======  
NUC1  $^{13}\text{C}$   
P1 9.25 usec  
PLW1 47.00000000 W  
SF01 100.6228289 MHz

===== CHANNEL f2 ======  
CPDPG2 waltz16  
NUC2  $^1\text{H}$   
PCPD2 90.00 usec  
PLW2 7.75000000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SF02 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127621 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**N- ( (2,5-Bis (p-tolylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3f) :**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)**



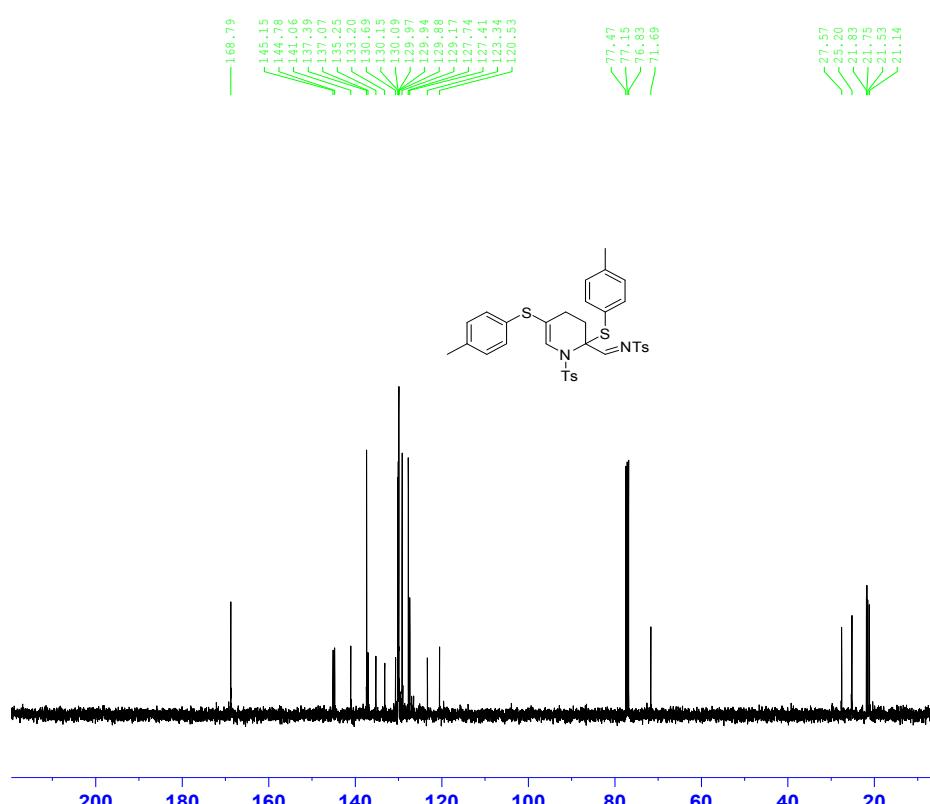
Current Data Parameters  
NAME spa40515  
EXPNO 504  
PROCNO 1

F2 - Acquisition Parameters  
Date 20150514  
Time 21.03  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 200.34  
DW 62.400 usec  
DE 6.50 usec  
TE 295.7 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 1H  
P1 15.49 usec  
PLW1 7.7500000 W  
SF01 400.1320007 MHz

F2 - Processing parameters  
SI 65536  
SF 400.1300094 MHz  
WDW EM  
SSB 0 0.30 Hz  
LB 0 1.00  
GB 0  
PC 1.00

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)**



Current Data Parameters  
NAME spa40914  
EXPNO 212  
PROCNO 1

F2 - Acquisition Parameters  
Date 20140914  
Time 15.49  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 16540  
SOLVENT CDCl<sub>3</sub>  
NS 107  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.4530533 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 0 K  
D1 1.00000000 sec  
D11 0.03000000 sec  
TDO 1

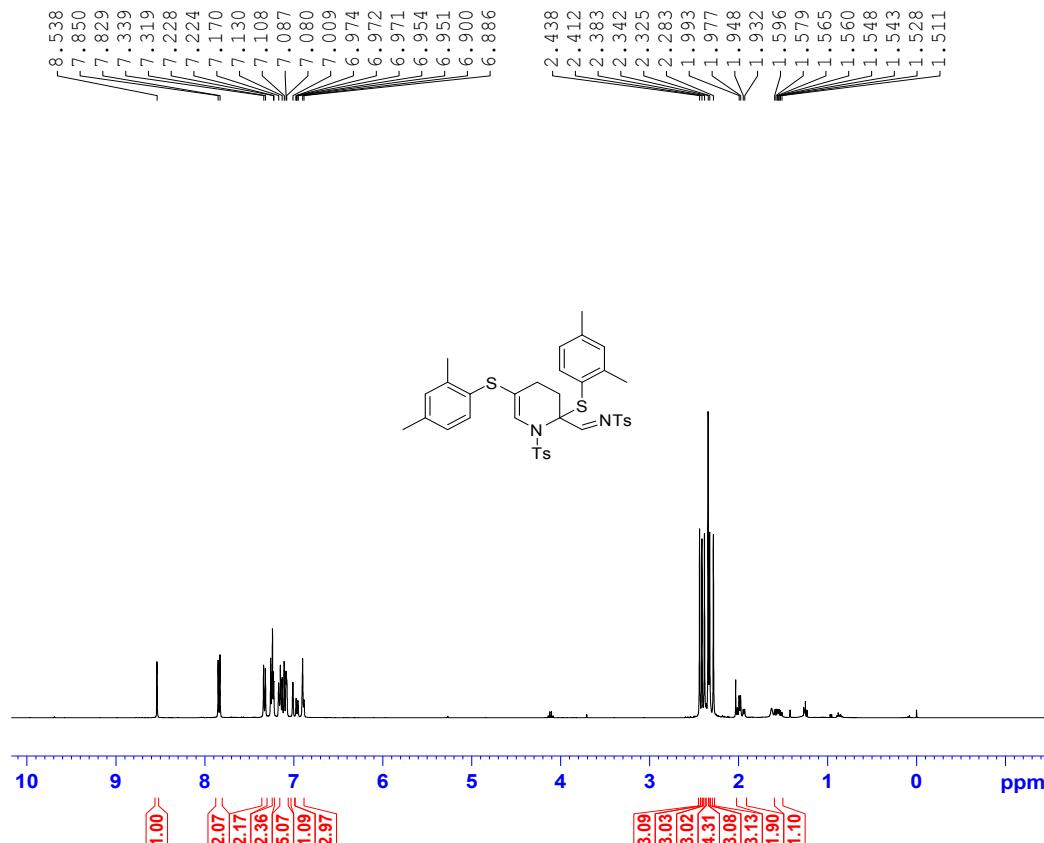
===== CHANNEL f1 ======  
NUC1 <sup>13</sup>C  
P1 9.25 usec  
PLW1 47.00000000 W  
SF01 100.6228289 MHz

===== CHANNEL f2 ======  
CPDPFG2 waltz16  
NUC2 <sup>1</sup>H  
PCPD2 90.00 usec  
PLW2 7.75000000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SF02 400.1316005 MHz

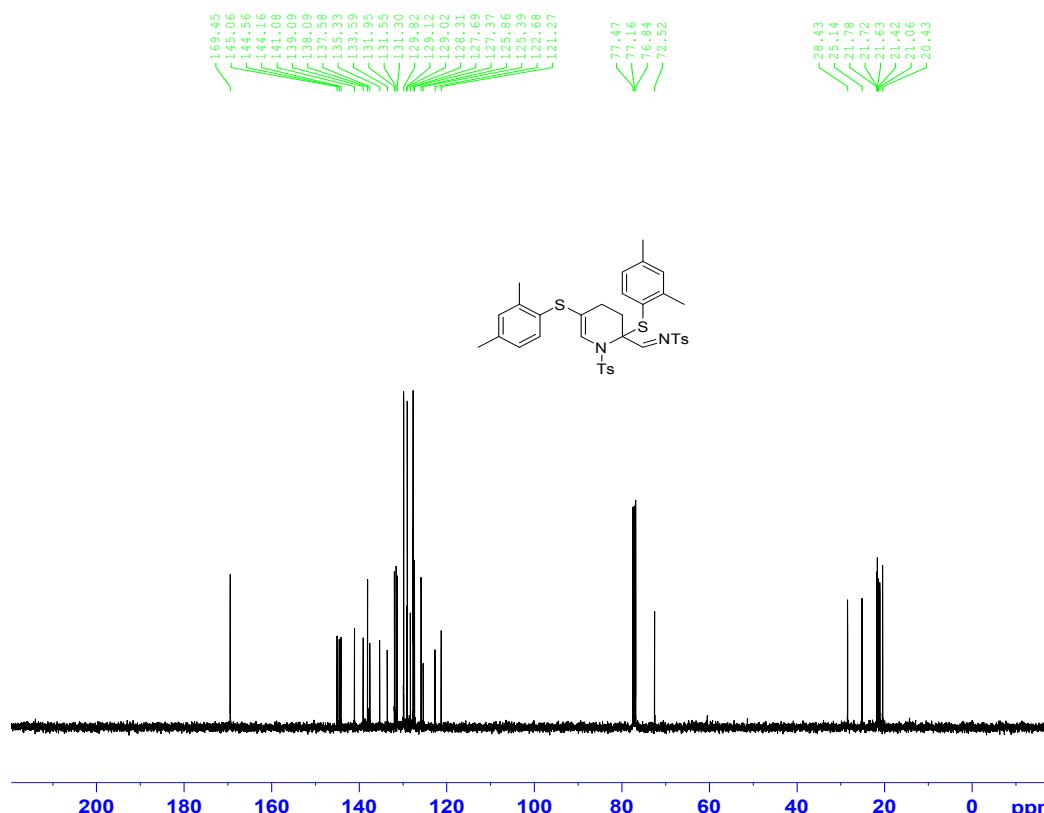
F2 - Processing parameters  
SI 32768  
SF 100.6127616 MHz  
WDW EM  
SSB 0 1.00 Hz  
LB 0 1.40  
GB 0  
PC

**N-((2,5-Bis((2,4-dimethylphenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2yl)methylene)-4-methylbenzenesulfonamide (3g) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

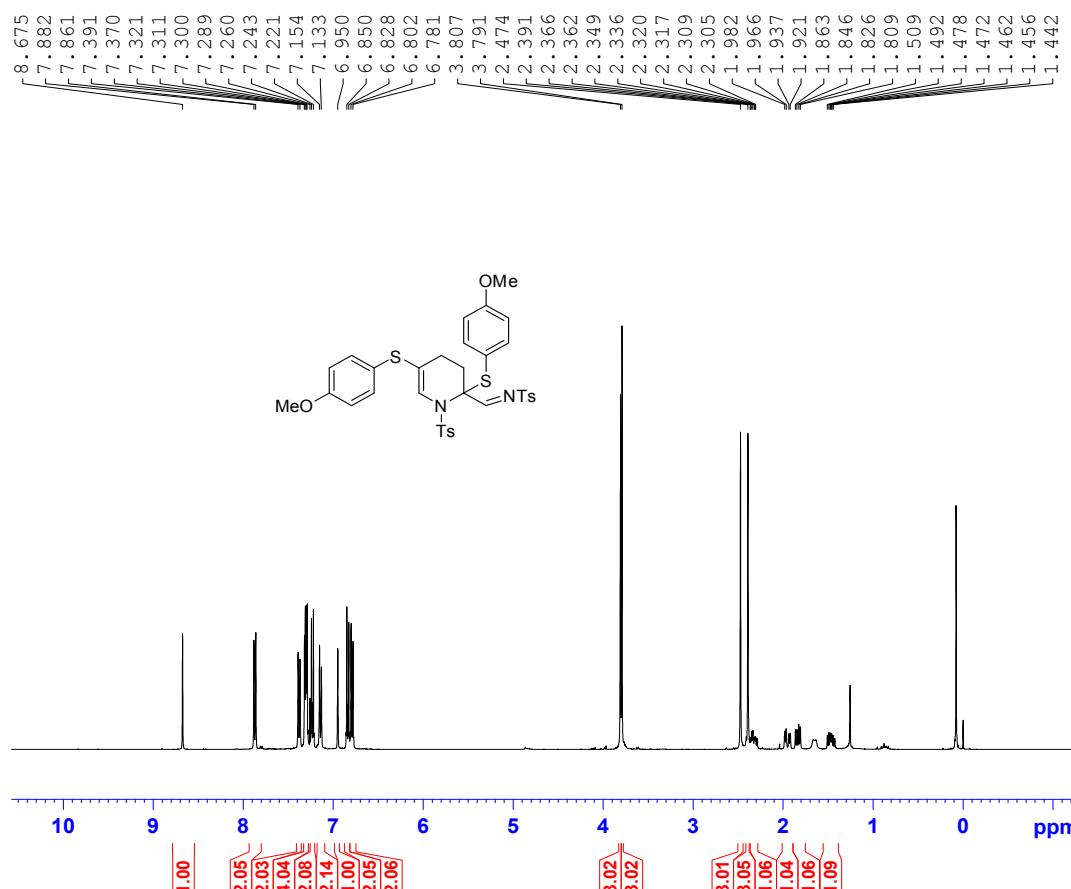


**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**

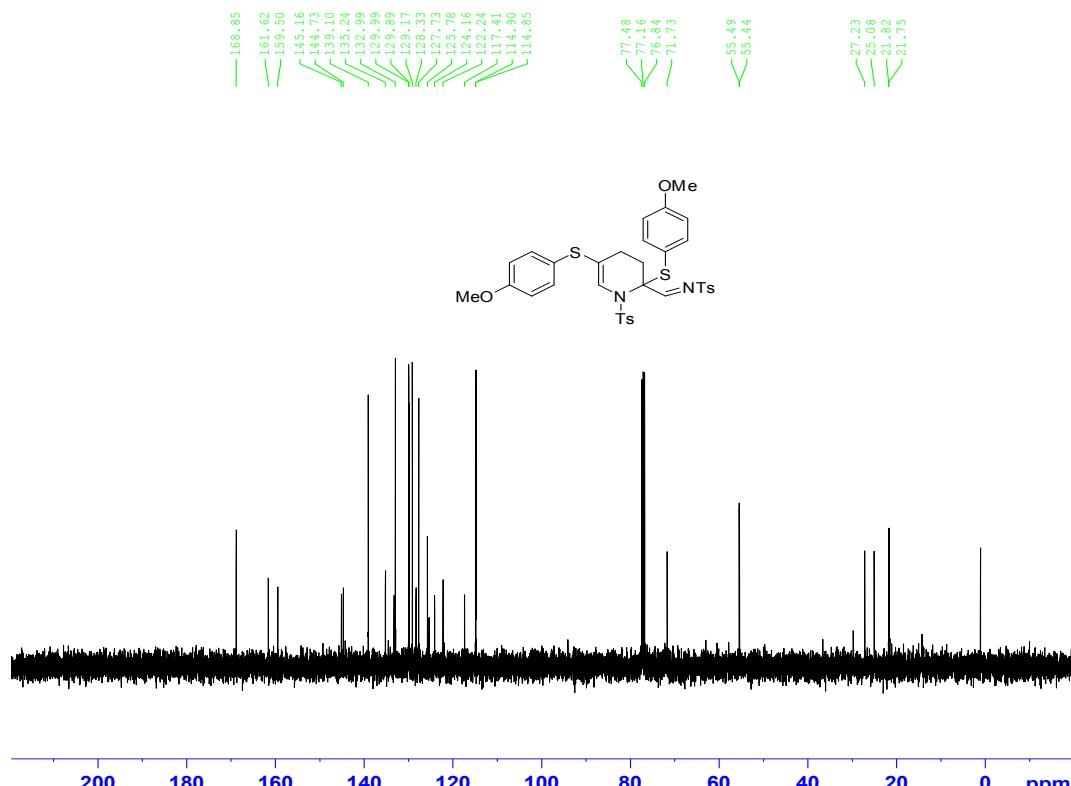


**N-((2,5-Bis((4-methoxyphenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3h) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

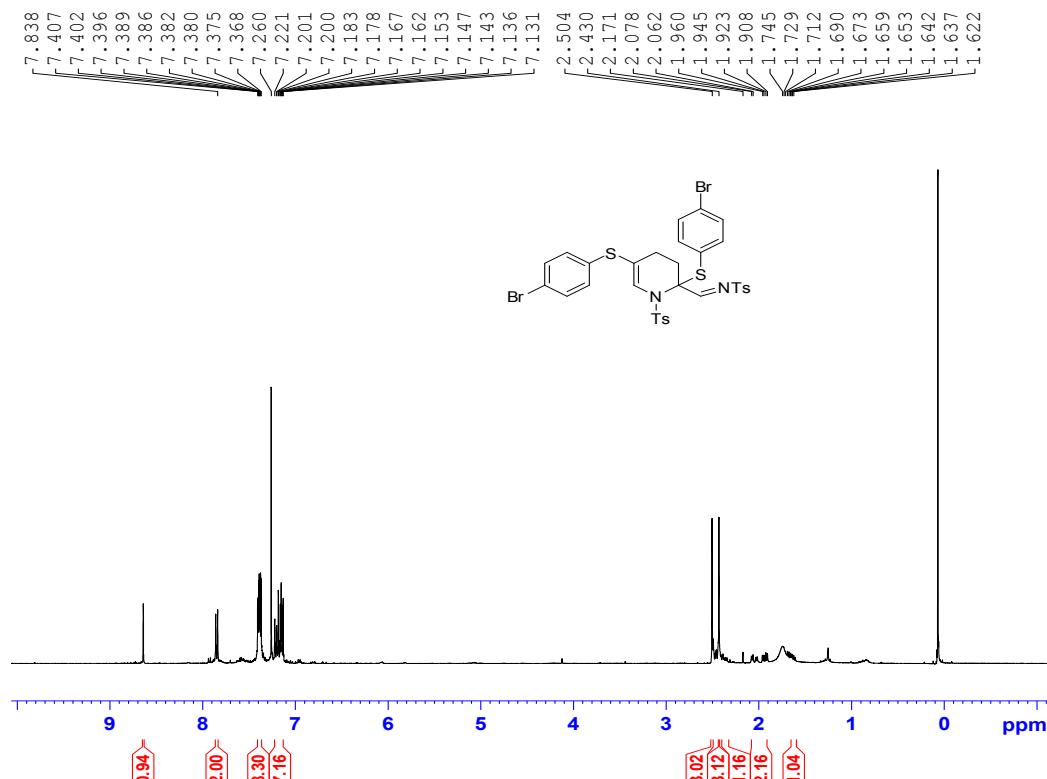


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



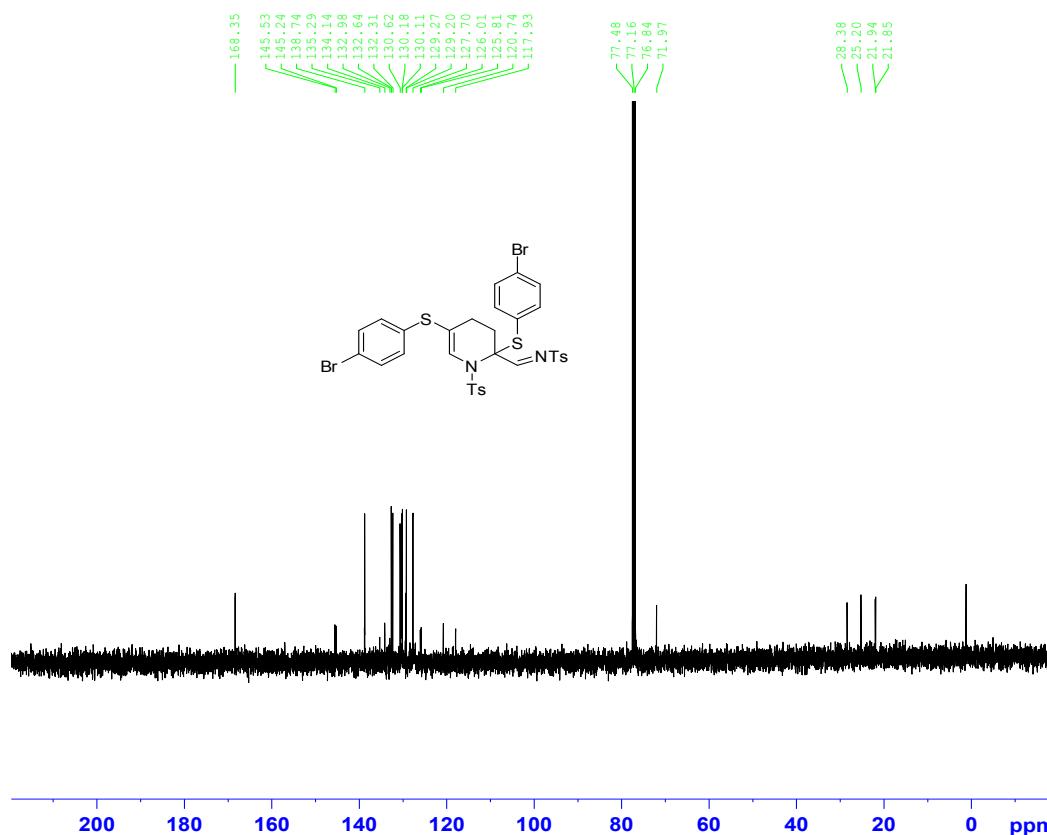
**N-((2,5-Bis((4-bromophenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3i) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa40515  
EXPNO 502  
PROCNO 1  
F2 - Acquisition Parameters  
Date\_ 20150514  
Time 20.08  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 200.34  
DW 62.400 usec  
DE 6.50 usec  
TE 296.0 K  
D1 0.5000000 sec  
TDO 1  
===== CHANNEL f1 ======  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SF01 400.1320007 MHz  
F2 - Processing parameters  
SI 65536  
SF 400.1300095 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

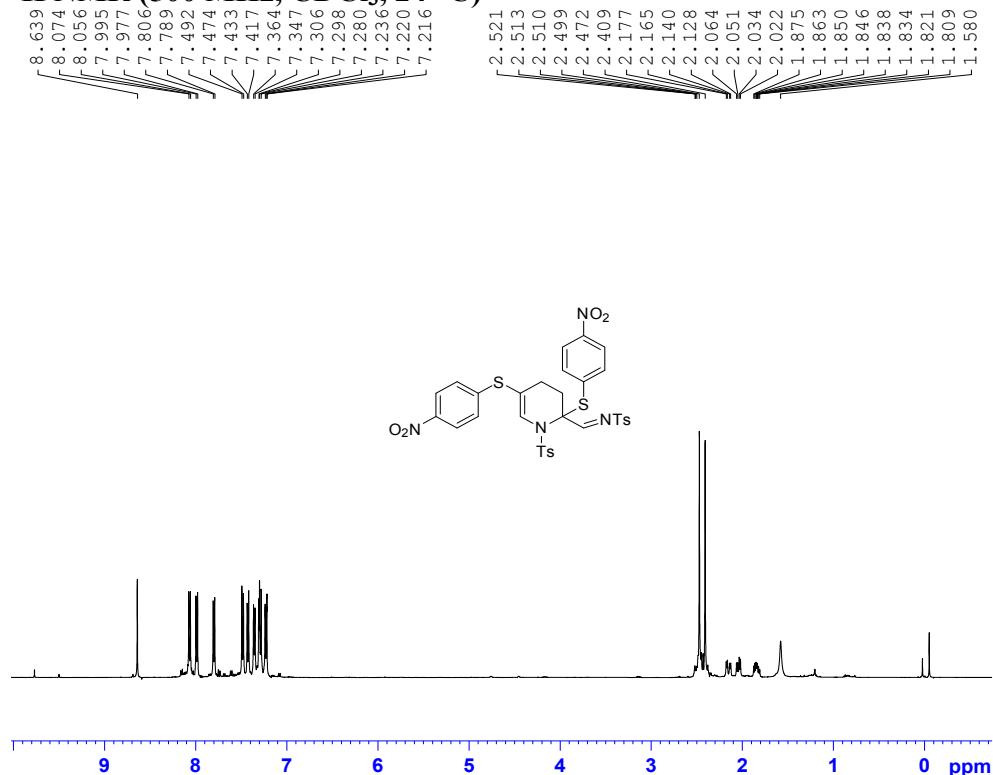
**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa40515  
EXPNO 426  
PROCNO 1  
F2 - Acquisition Parameters  
Date\_ 20150513  
Time 12.28  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 16540  
SOLVENT CDCl3  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 296.5 K  
D1 1.0000000 sec  
D11 0.0300000 sec  
TDO 1  
===== CHANNEL f1 ======  
NUC1 13C  
P1 9.25 usec  
PLW1 47.0000000 W  
SF01 100.6228289 MHz  
===== CHANNEL f2 ======  
CPDPG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SF02 400.1316005 MHz  
F2 - Processing parameters  
SI 32768  
SF 100.6127551 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**N-((2,5-Bis ((4-nitrophenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3j) :**

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 24 °C)**

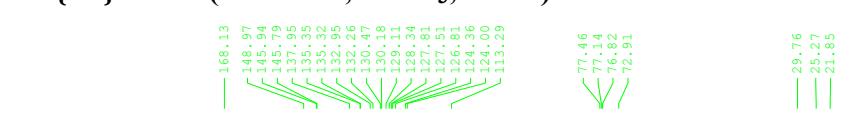


Current Data Parameters  
NAME spa50515  
EXPNO 78  
PROCNO 1  
  
F2 - Acquisition Parameters  
Date\_ 20150518  
Time\_ 15.58  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zg30  
TD 32768  
SOLVENT CDCl3  
NS 32  
DS 2  
SWH 10000.000 Hz  
FIDRES 0.305176 Hz  
AQ 1.6384500 sec  
RG 114.76  
DW 50.000 usec  
DE 6.50 usec  
TE 295.4 K  
D1 0.5000000 sec  
TDO 0.5000000 sec  
1

===== CHANNEL f1 =====  
SFO1 500.1525008 MHz  
NUC1 1H  
P1 11.75 usec  
PLW1 15.3000019 W

F2 - Processing parameters  
SI 65536  
SF 500.1500445 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

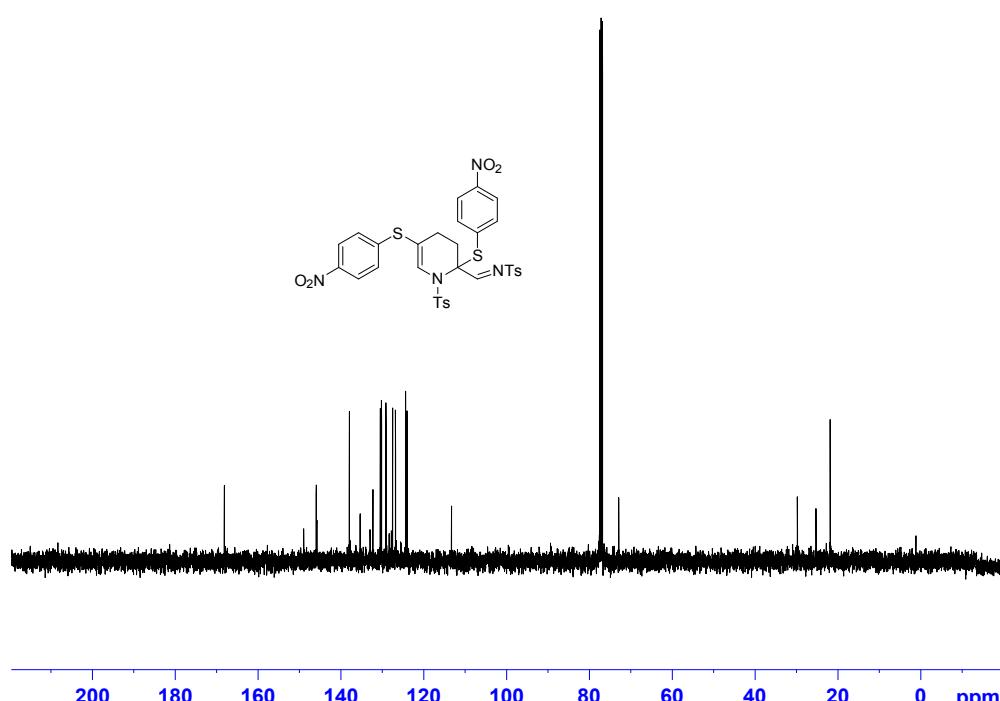
**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa40914  
EXPNO 90  
PROCNO 1  
  
F2 - Acquisition Parameters  
Date\_ 20140911  
Time\_ 22.33  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 16540  
SOLVENT CDCl3  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453253 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 0 K  
D1 1.0000000 sec  
D11 0.0300000 sec  
TDO 1

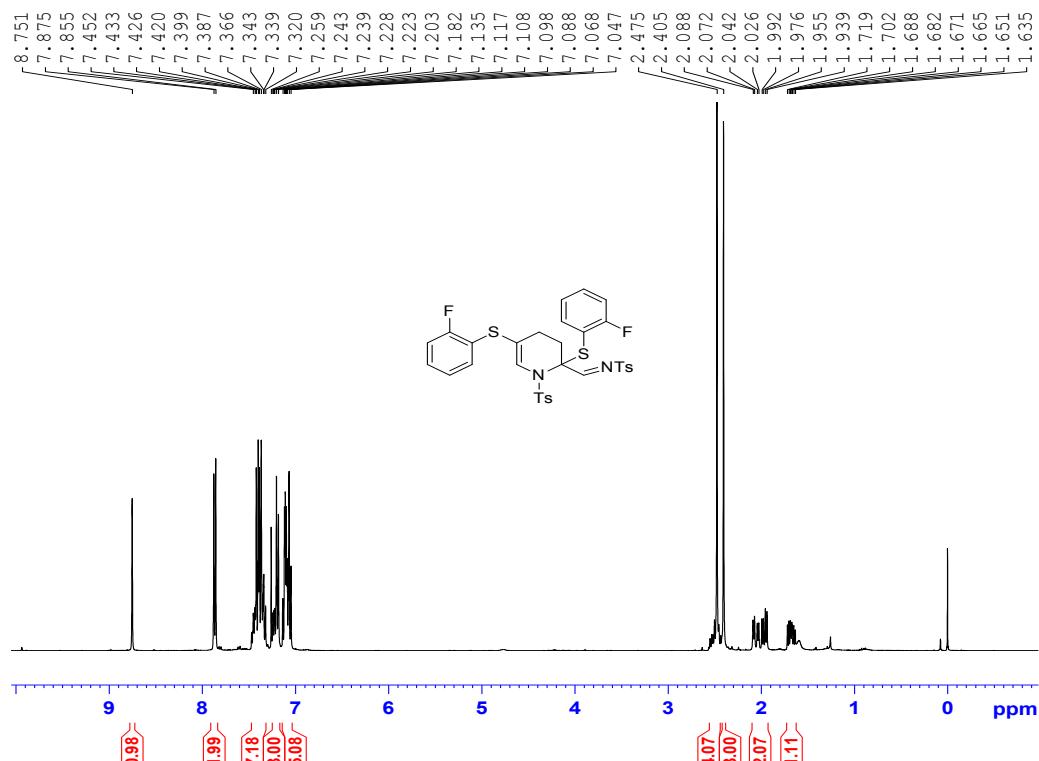
===== CHANNEL f1 =====  
NUC1 13C  
P1 9.25 usec  
PLW1 47.0000000 W  
SFO1 100.6228289 MHz  
  
===== CHANNEL f2 =====  
CPDPG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.2358399 W  
PLW13 0.1910300 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127574 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40



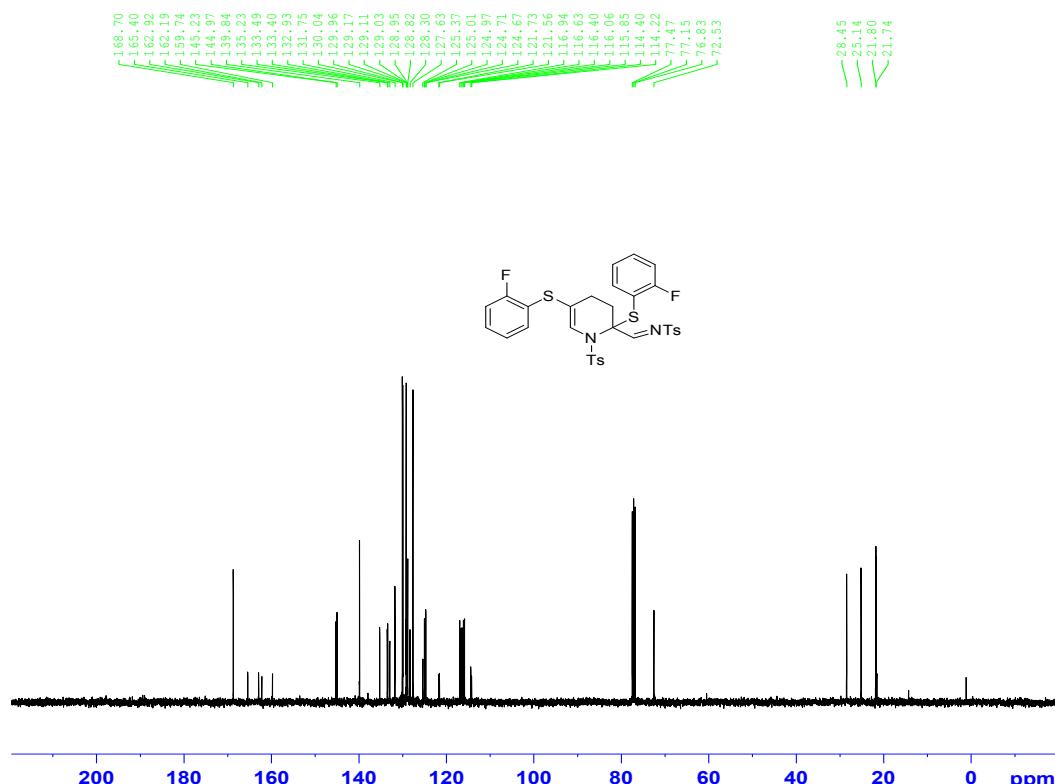
**N-((2,5-bis ((2-fluorophenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3k) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa40415  
EXPNO 927  
PROCNO 1  
  
F2 - Acquisition Parameters  
Date 20150429  
Time 14.39  
INSTRUM spect  
PROBHD 5 mm PABBI 1H/  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 88.51  
DW 62.400 usec  
DE 6.50 usec  
TE 298.3 K  
D1 0.5000000 sec  
TDO 1  
  
===== CHANNEL f1 ======  
NUC1 1H  
P1 9.00 usec  
PLW1 8.5000000 W  
SFO1 400.1320007 MHz  
  
F2 - Processing parameters  
SI 65536  
SF 400.1300104 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

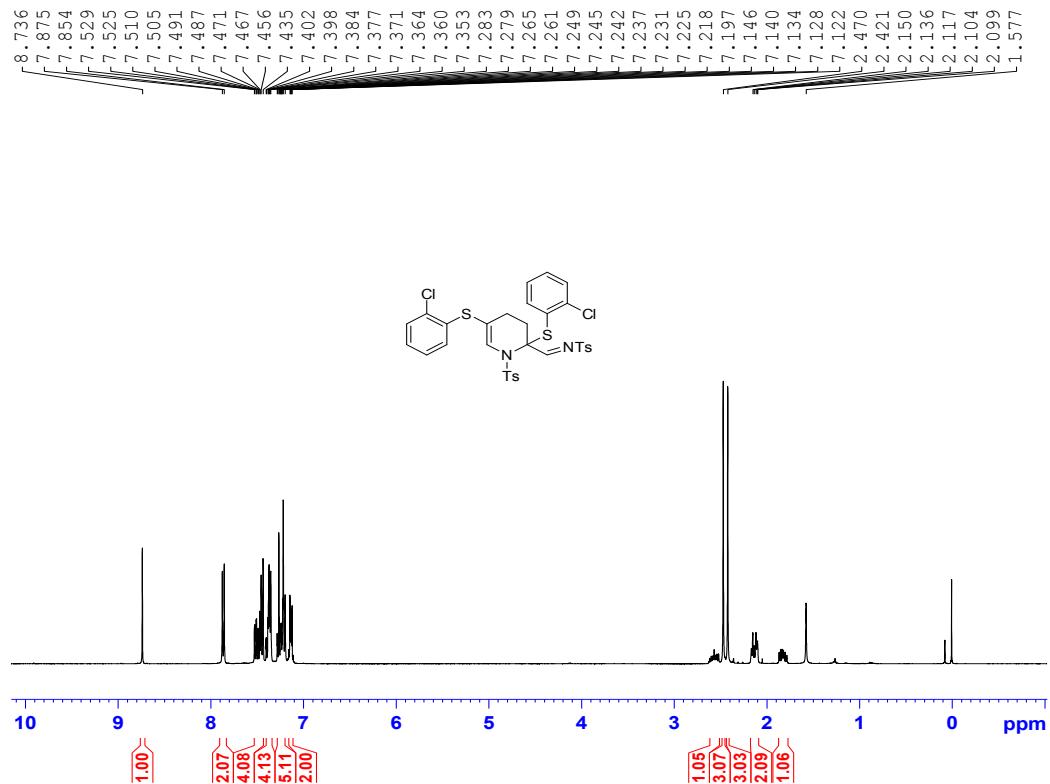
**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



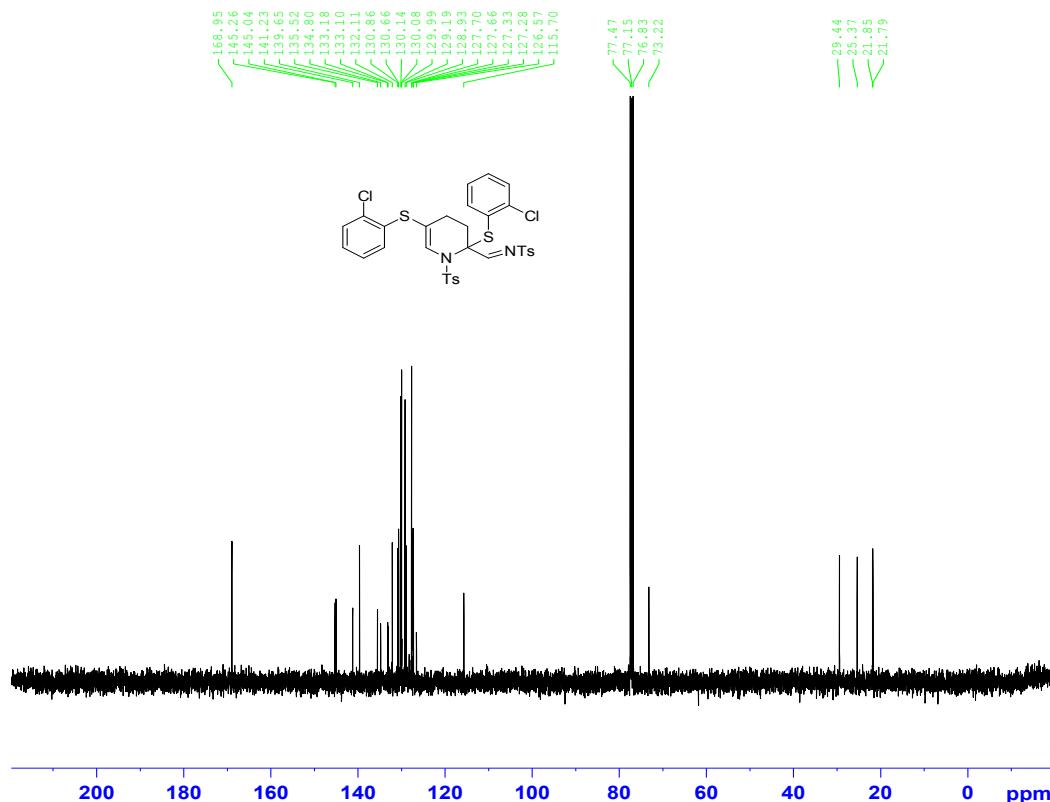
Current Data Parameters  
NAME spa40914  
EXPNO 496  
PROCNO 1  
  
F2 - Acquisition Parameters  
Date 20140923  
Time 1.43  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 16540  
SOLVENT CDCl3  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 0 K  
D1 1.0000000 sec  
D11 0.03000000 sec  
TDO 1  
  
===== CHANNEL f1 ======  
NUC1 13C  
P1 9.25 usec  
PLW1 47.0000000 W  
SFO1 100.6228289 MHz  
  
===== CHANNEL f2 ======  
CPDPRG2 waltz16  
NUC2 1H  
P1 30.00 usec  
PLW2 7.7500000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SFO2 400.1316005 MHz  
  
F2 - Processing parameters  
SI 32768  
SF 100.6127634 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**N-((2,5-bis ((2-chlorophenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3l) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

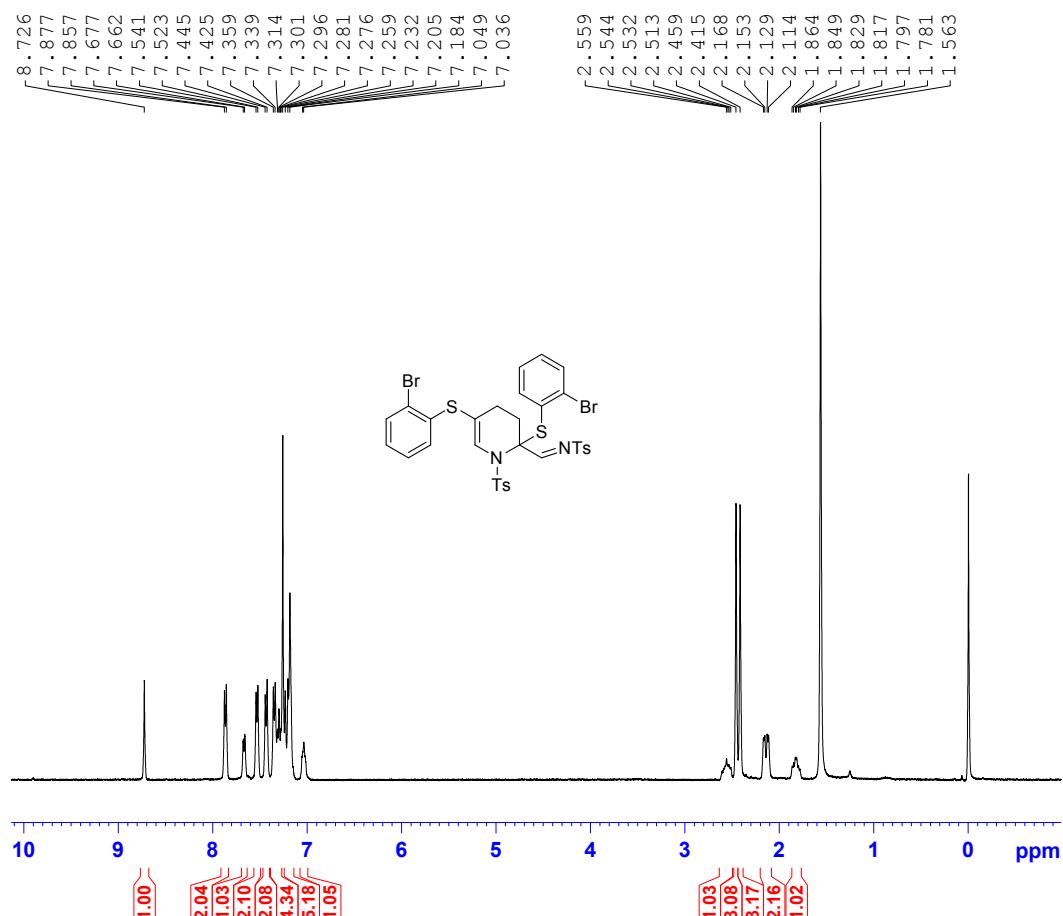


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



**N-((2,5-Bis((2-bromophenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3m) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



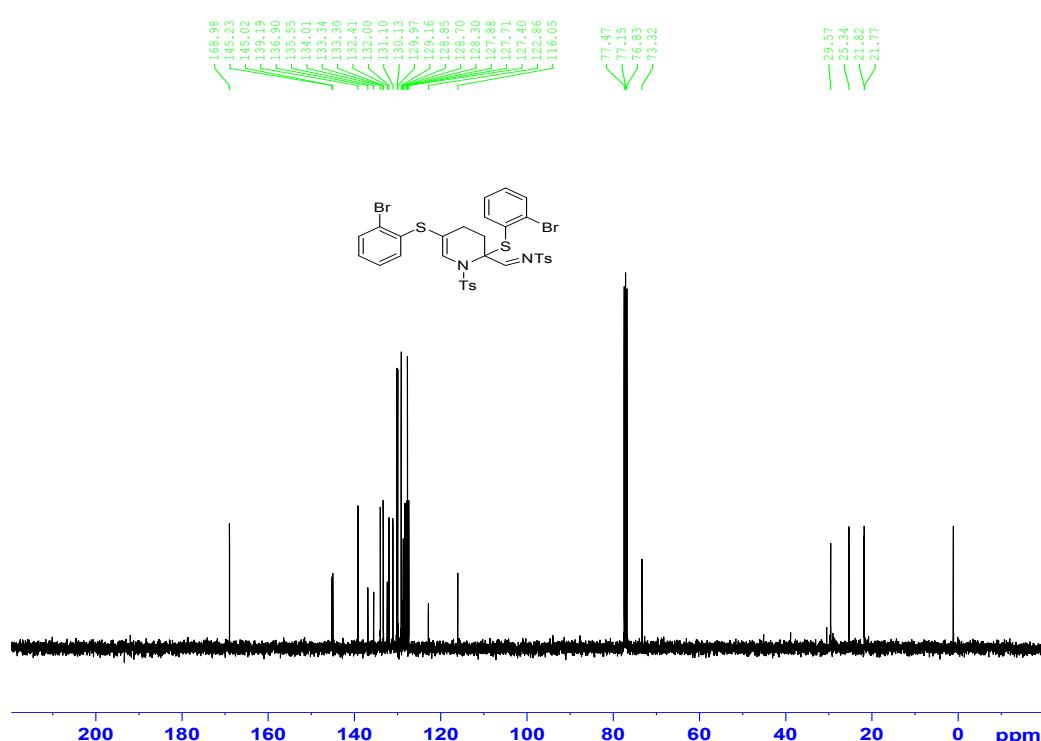
Current Data Parameters  
NAME spa40515  
EXPNO 472  
PROCNO 1

F2 - Acquisition Parameters  
Date 20150514  
Time 10.53  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDC13  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 200.34  
DW 62.400 usec  
DE 6.50 usec  
TE 295.6 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SF01 400.1320007 MHz

F2 - Processing parameters  
SI 65536  
SF 400.1300097 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa41114  
EXPNO 557  
PROCNO 1

F2 - Acquisition Parameters  
Date 20141119  
Time 14.59  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 16540  
SOLVENT CDC13  
NS 25  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20.800 usec  
DE 301.7 usec  
TE 301.7 K  
D1 1.0000000 sec  
D11 0.03000000 sec  
TDO 1

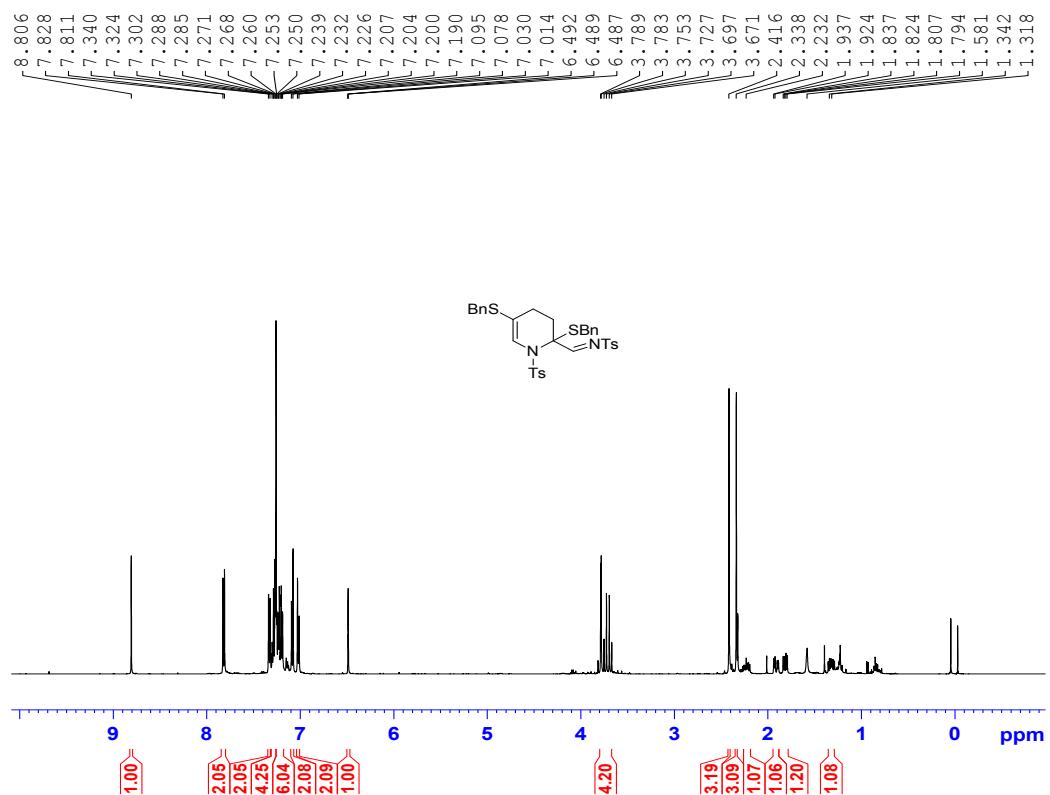
===== CHANNEL f1 ======  
NUC1 13C  
P1 9.25 usec  
PLW1 47.0000000 W  
SF01 100.6228289 MHz

===== CHANNEL f2 ======  
CPDRG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SFO2 400.1316005 MHz

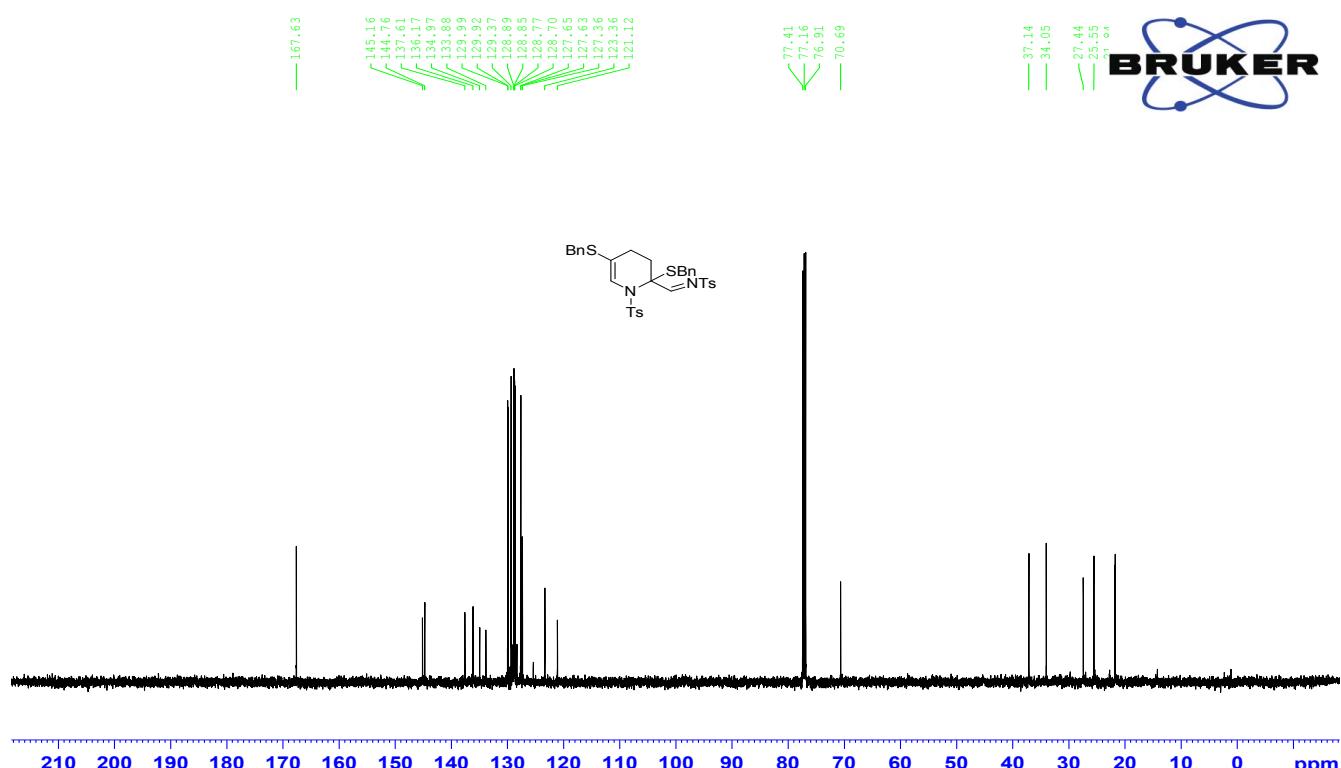
F2 - Processing parameters  
SI 32768  
SF 100.6127576 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**N-((2,5-Bis (benzylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3n) :**

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 24 °C)**

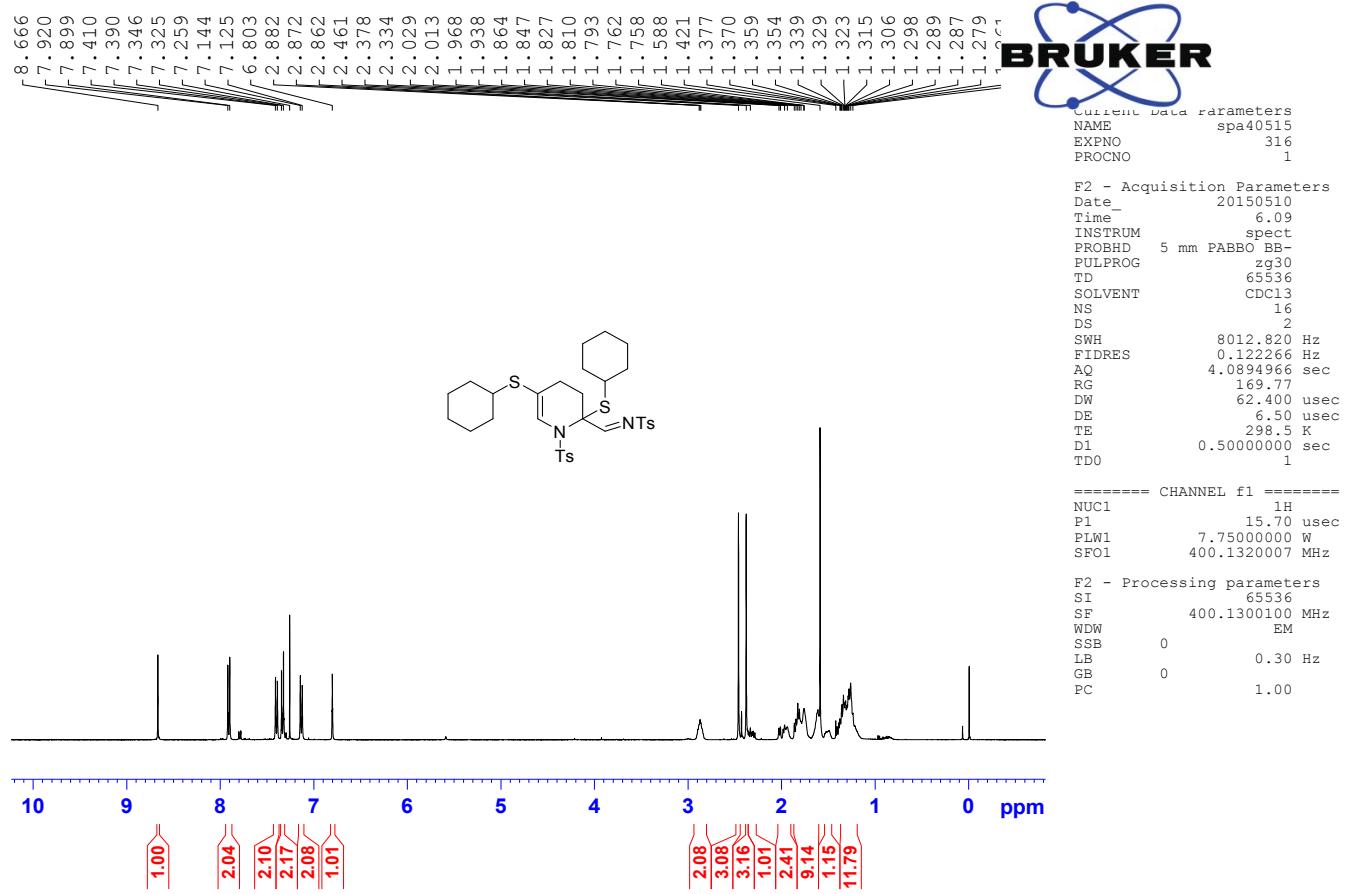


**$^{13}\text{C}\{\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 24 °C)**

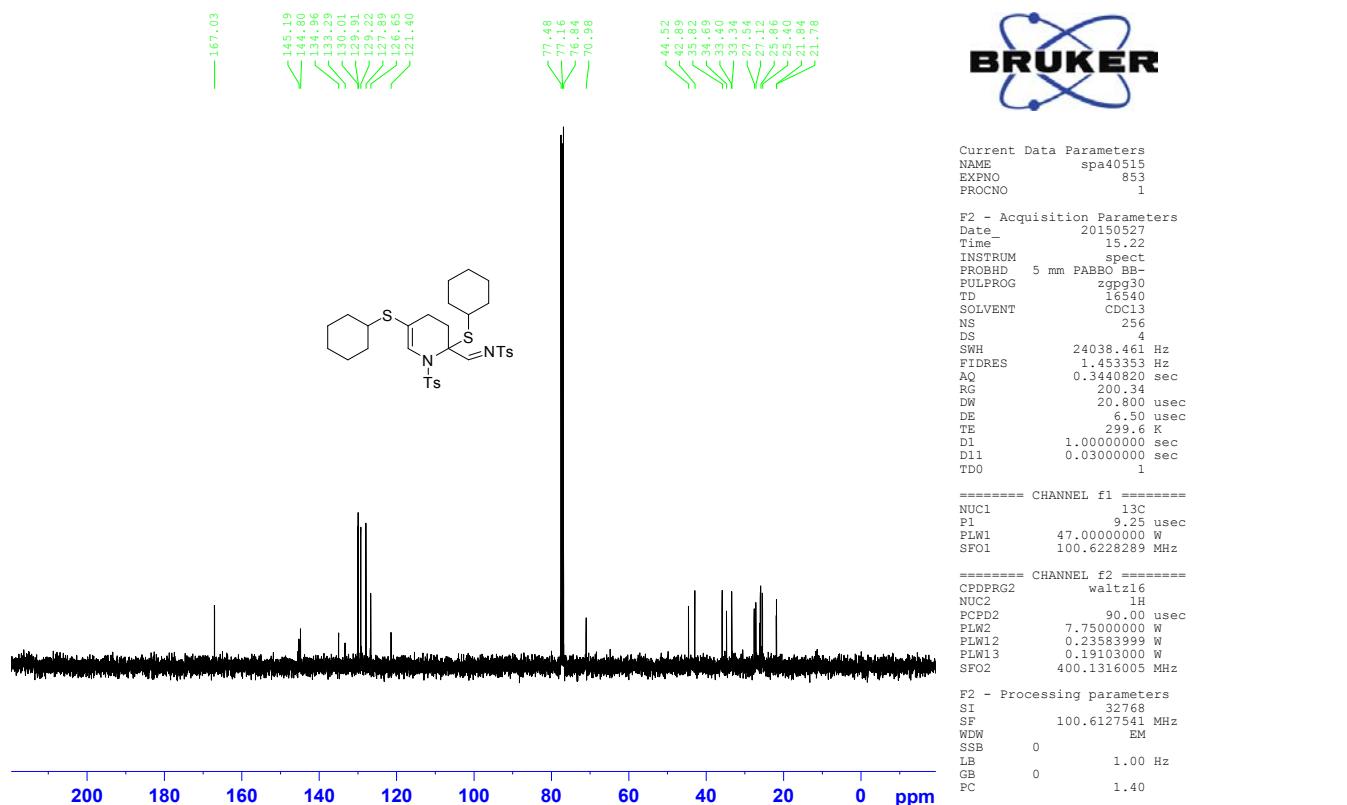


**N-((2,5-bis(cyclohexylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide (3o) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

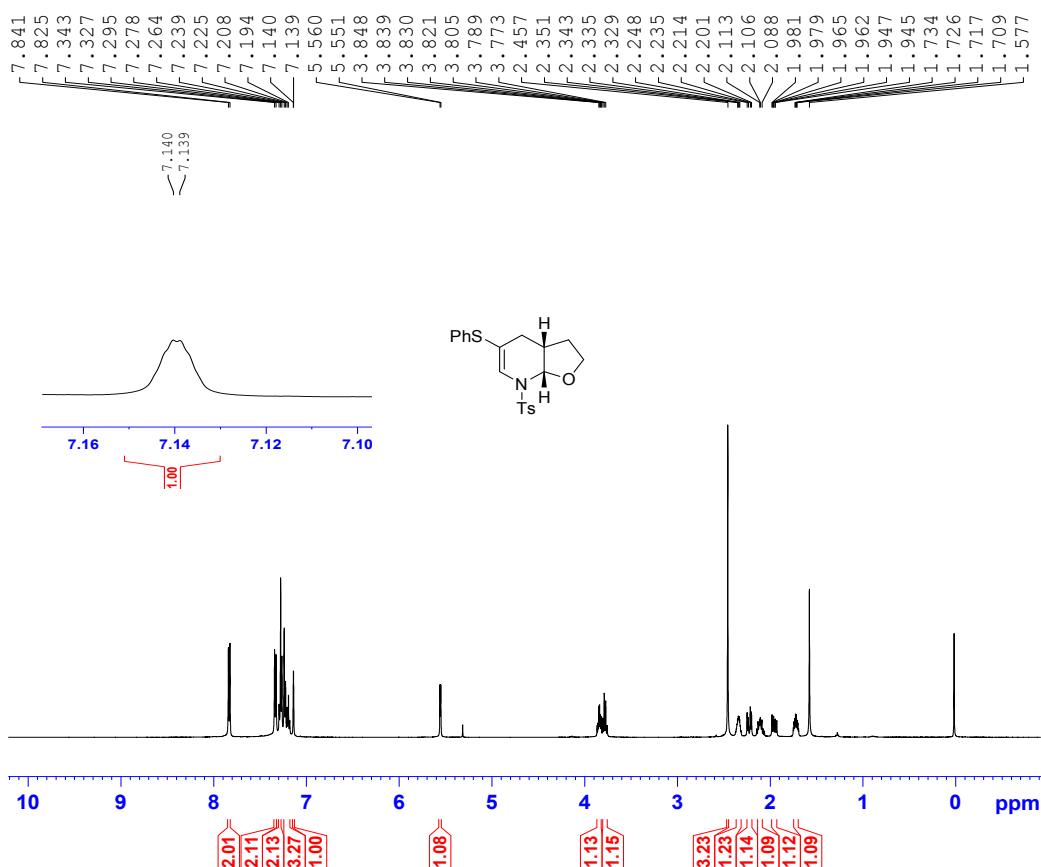


**$^{13}\text{C}\{\text{1H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**

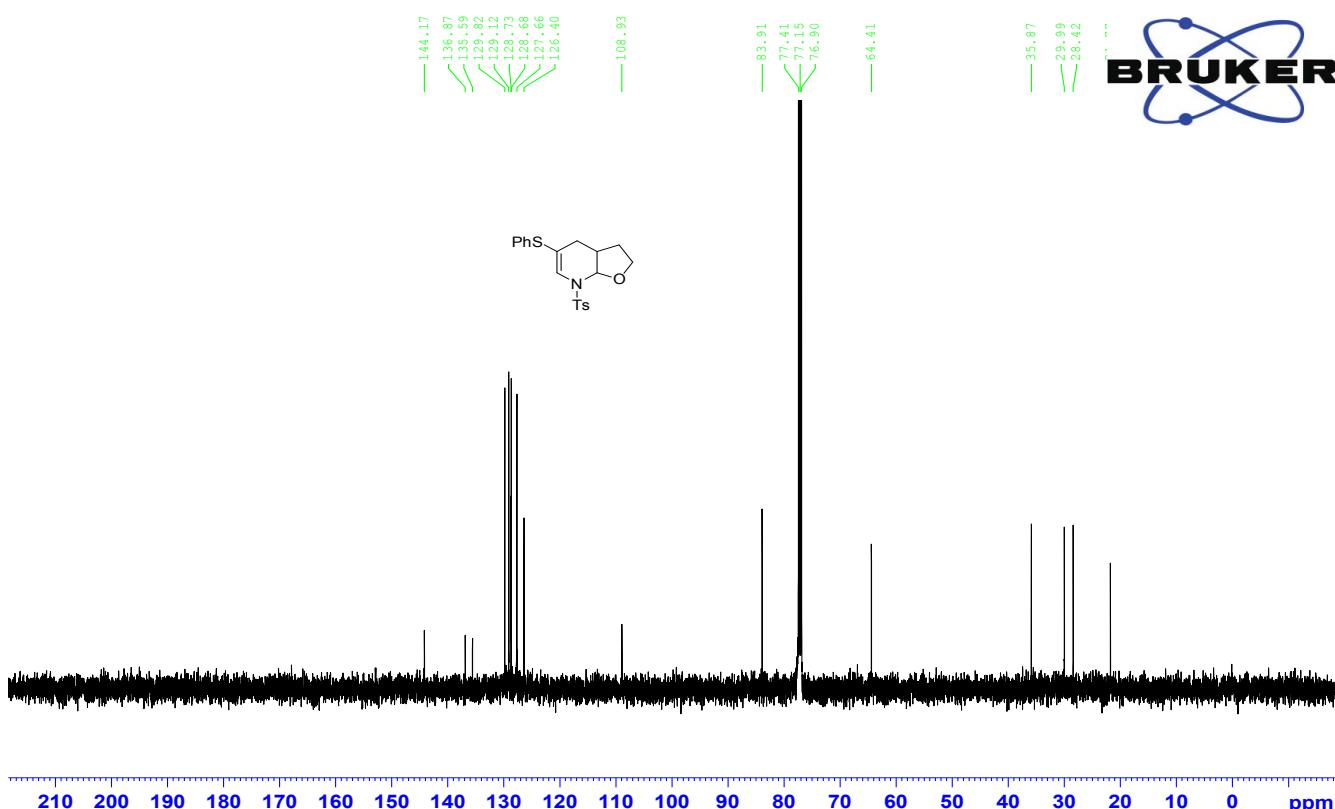


**5- (Phenylthio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5a) :**

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 24 °C)**

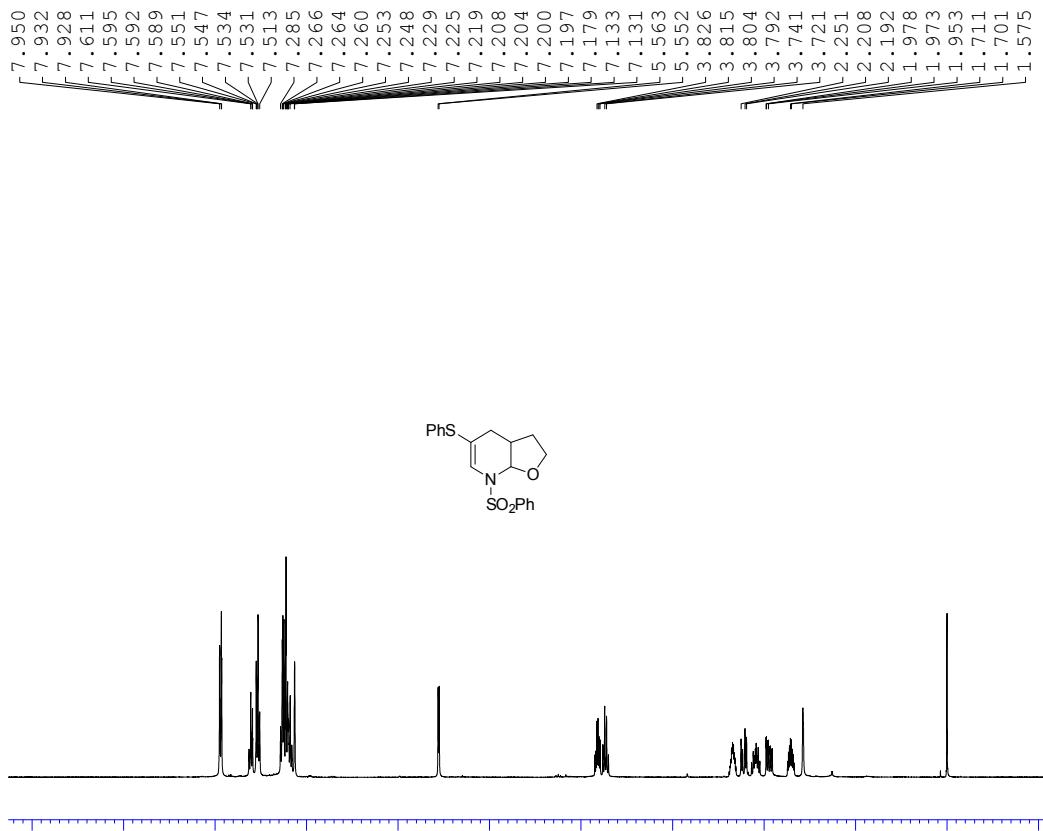


**$^{13}\text{C}\{\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 24 °C)**



**7-(Phenylsulfonyl)-5-(phenylthio)-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5b) :**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)**

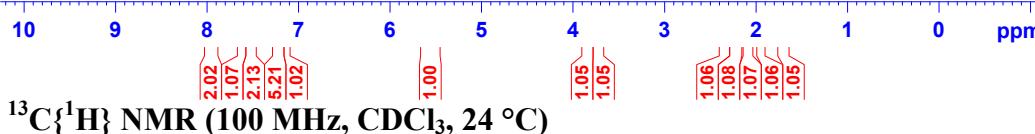


Current Data Parameters  
NAME spa40914  
EXPNO 544  
PROCNO 1

F2 - Acquisition Parameters  
Date 20140923  
Time 21.59  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDC13  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 200.34  
DW 62.400 usec  
DE 6.50 usec  
TE 0 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SFO1 400.1320007 MHz

F2 - Processing parameters  
SI 65536  
SF 400.1300096 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)**



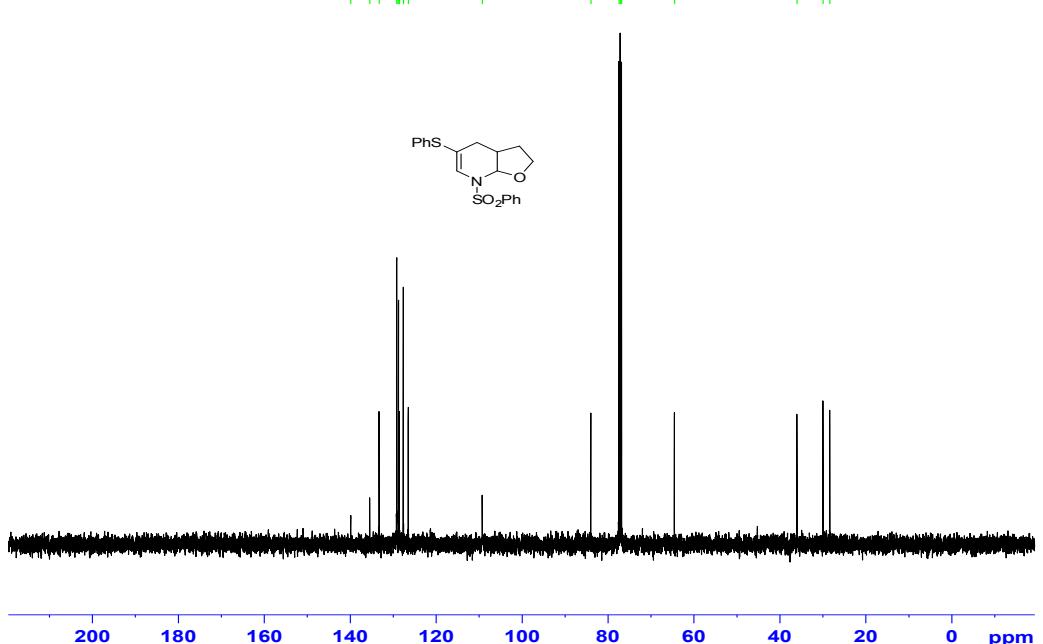
Current Data Parameters  
NAME spa40914  
EXPNO 549  
PROCNO 1

F2 - Acquisition Parameters  
Date 20140923  
Time 22.06  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 163840  
SOLVENT CDC13  
NS 256  
DS 4  
SWH 24038.468 Hz  
FIDRES 1.451213.3 sec  
AQ 0.3440820 sec  
RG 200.34  
DW 20,800 usec  
DE 6.50 usec  
TE 0 K  
D1 1.0000000 sec  
D11 0.03000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 13C  
P1 9.25 usec  
PLW1 47.00000000 W  
SFO1 100.6228289 MHz

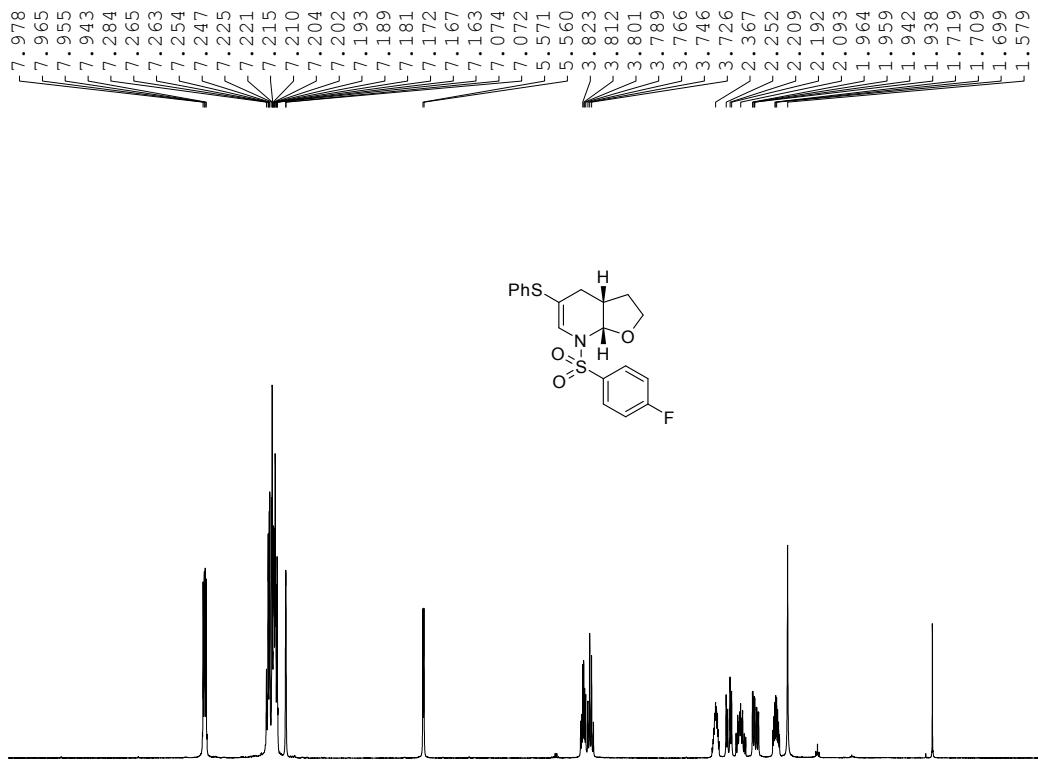
===== CHANNEL f2 ======  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SFO2 400.1316000 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127559 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

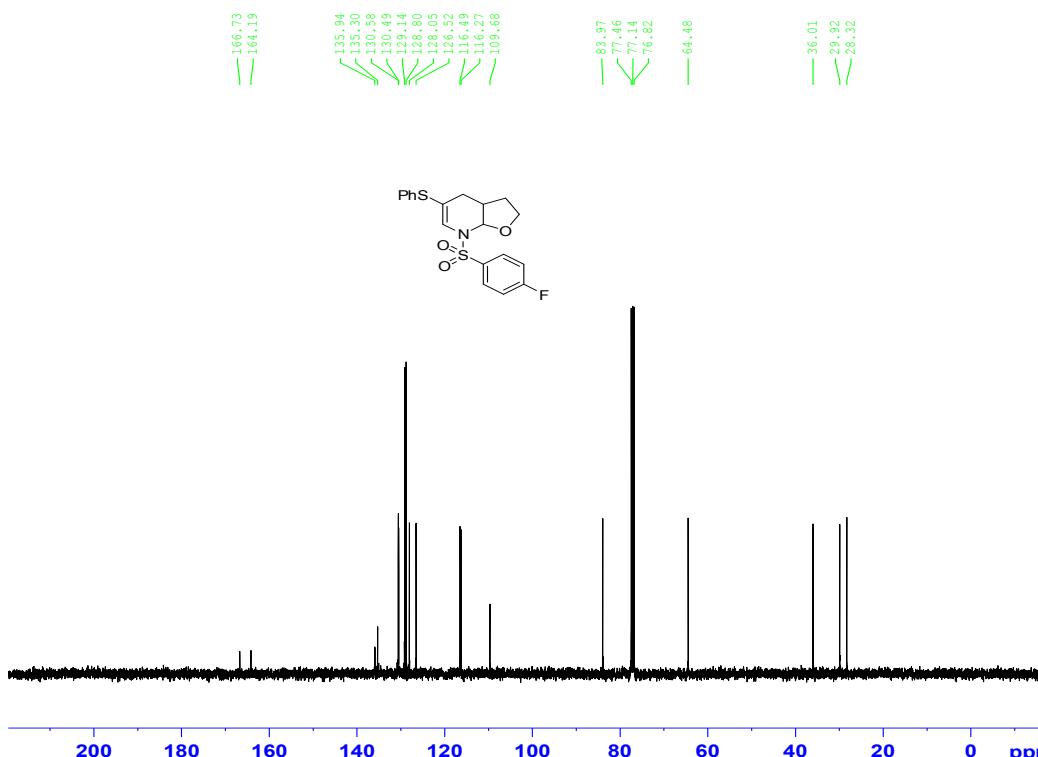


**7-(4-Fluorophenyl)sulfonyl)-5-(phenylthio)-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5c) :**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)**

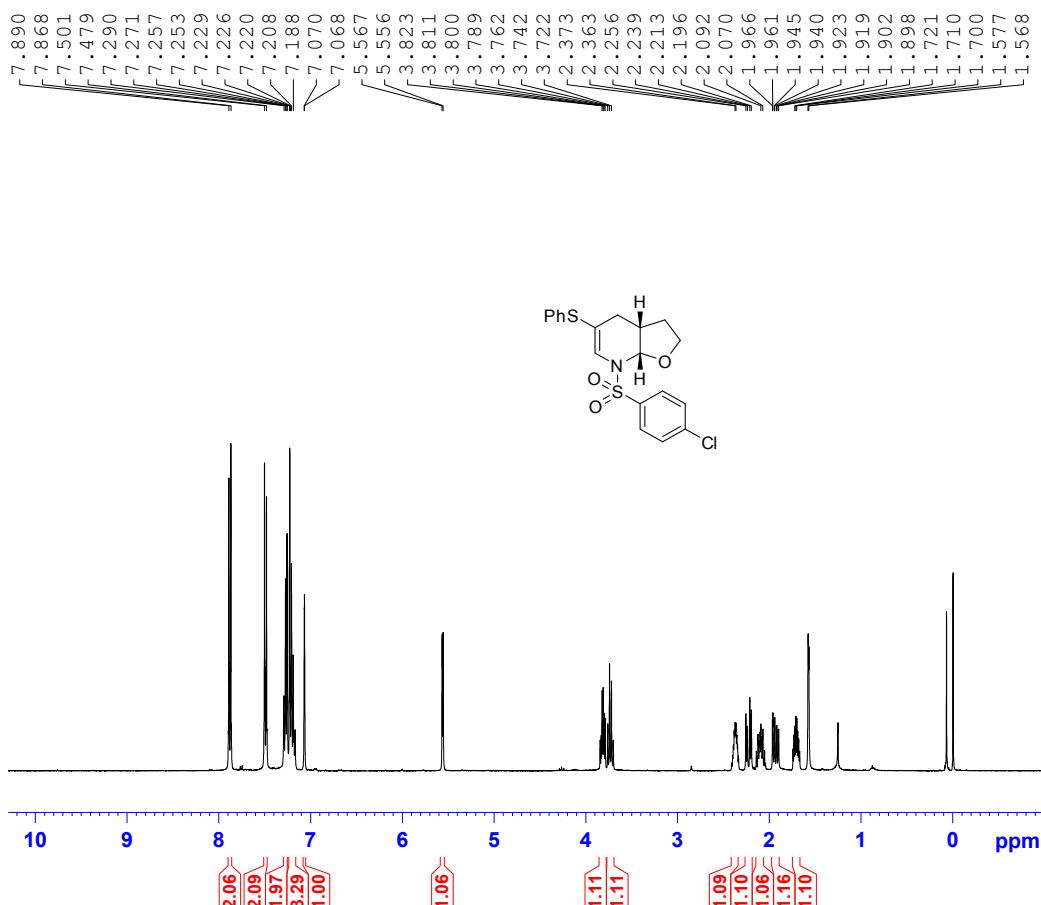


**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)**

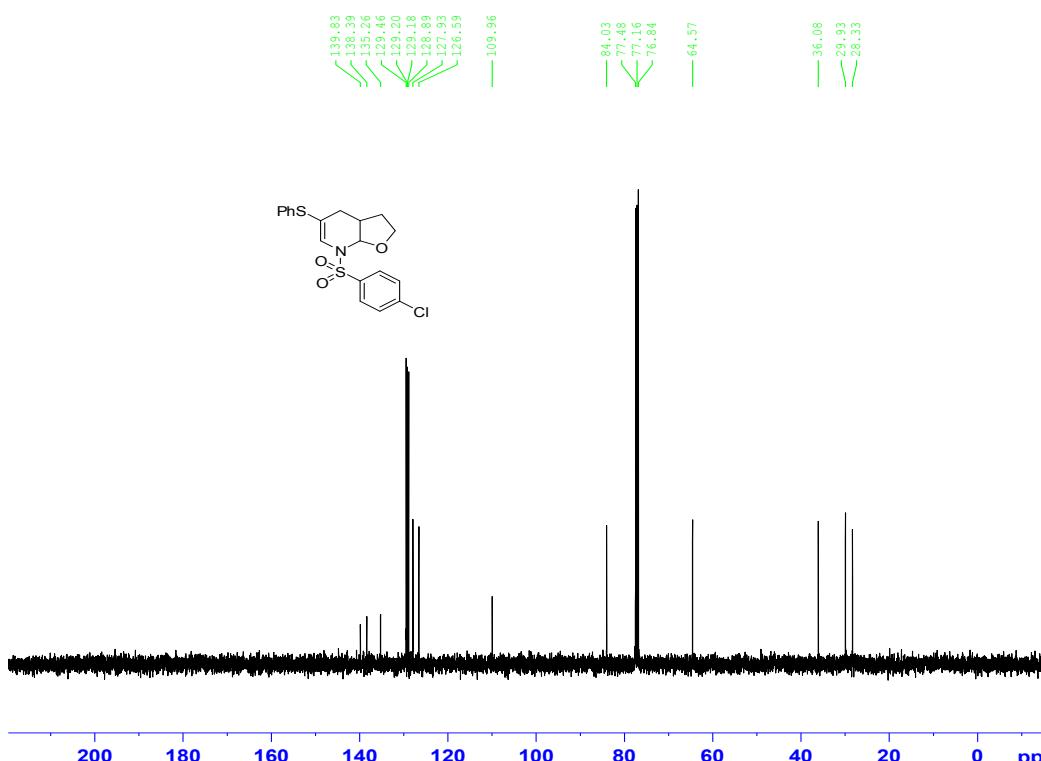


**7-((4-Chlorophenyl)sulfonyl)-5-(phenylthio)-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5d) :**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)**

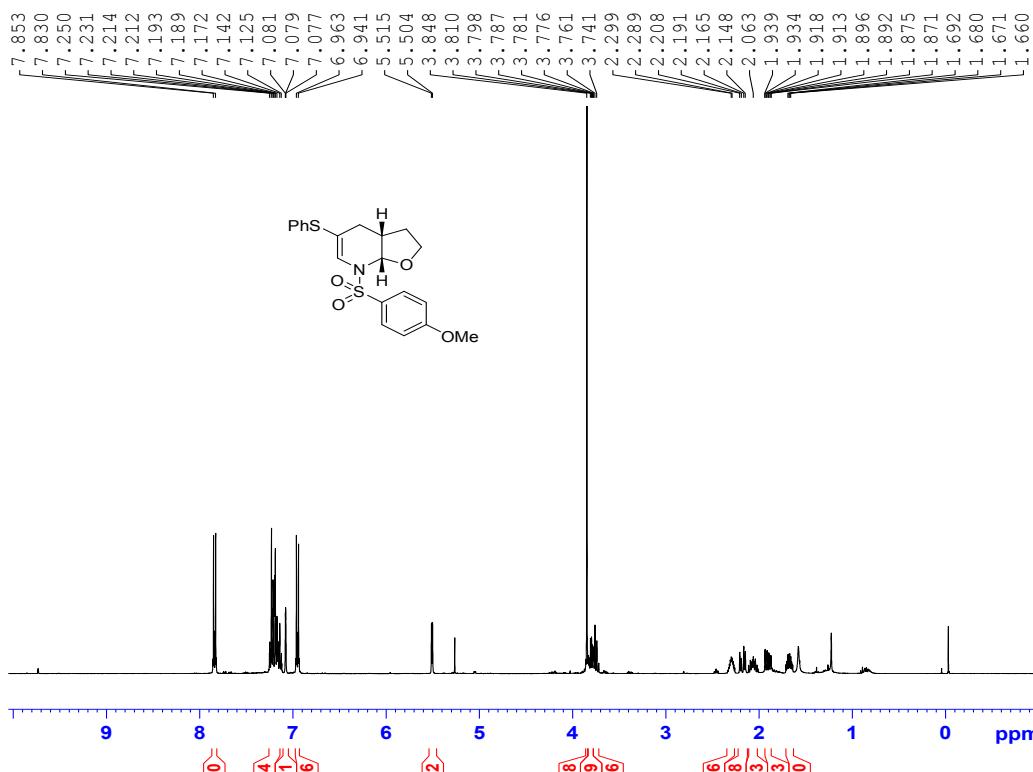


**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)**

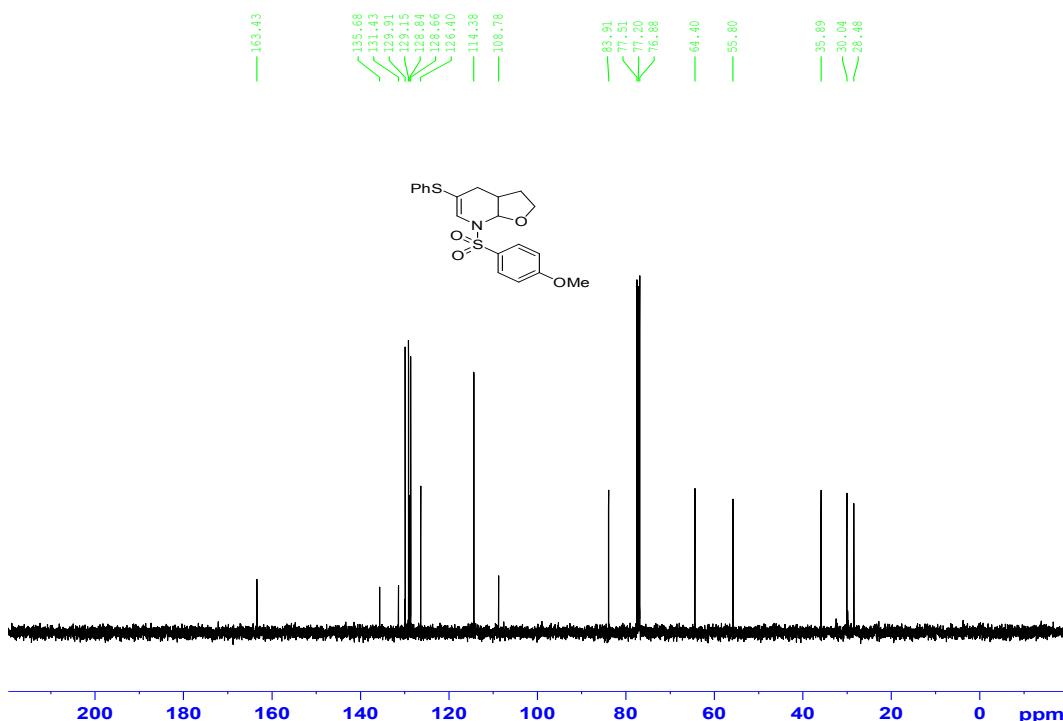


**7-((4-Methoxyphenyl)sulfonyl)-5-(phenylthio)-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5e) :**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)**

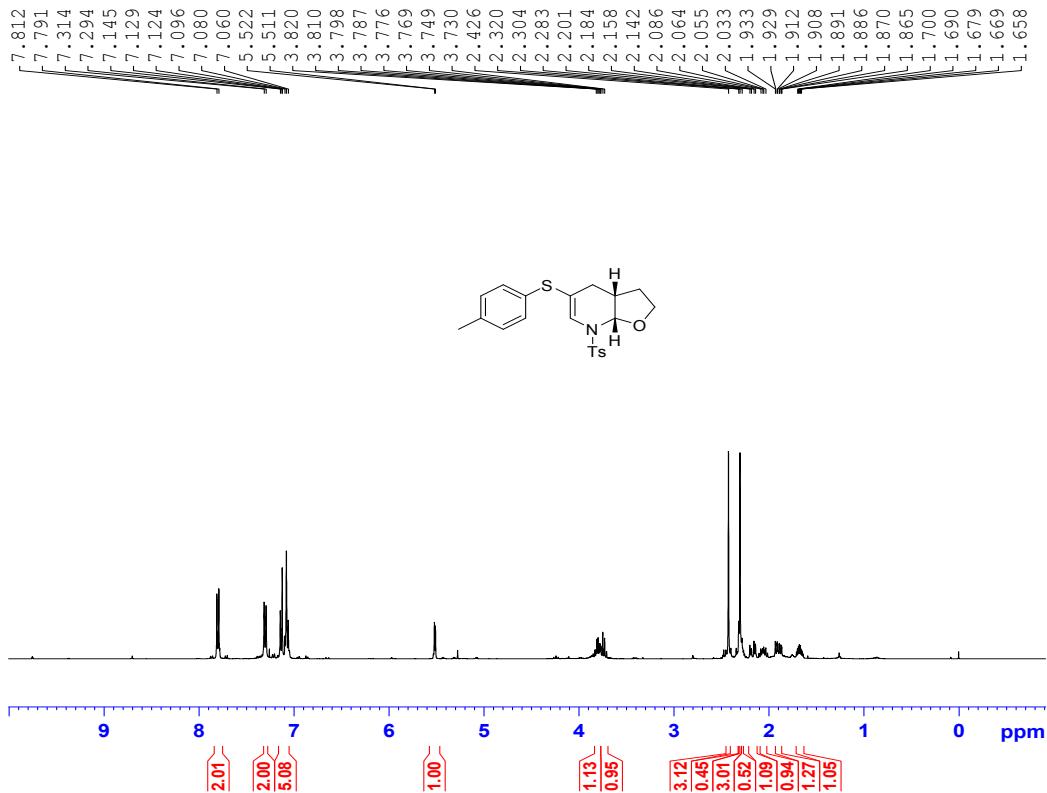


**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)**



**5- (*p*-Tolylthio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-*b*]pyridine (5f) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



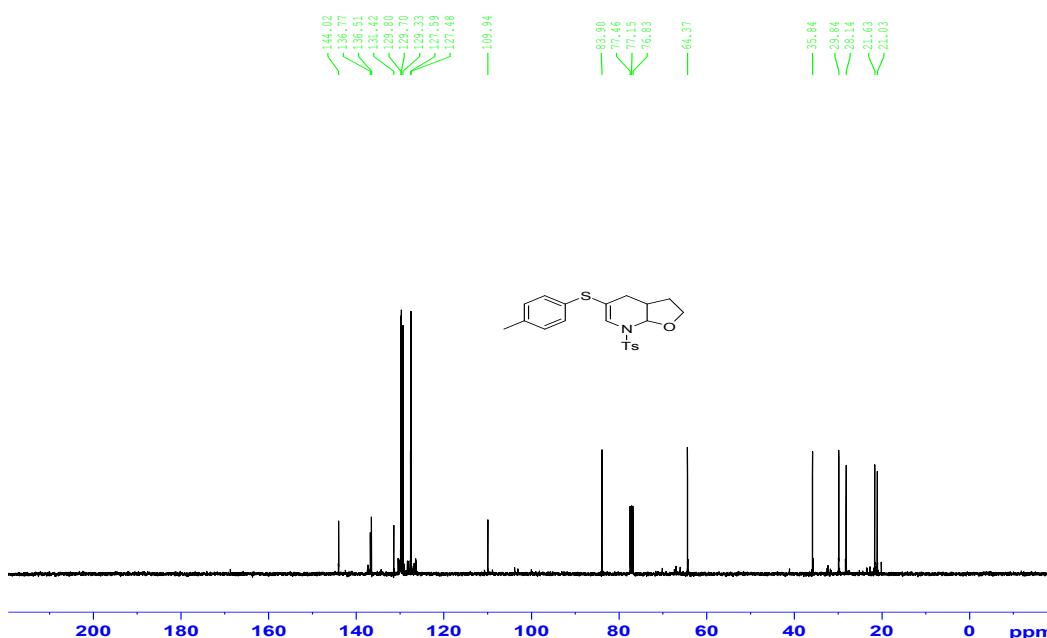
Current Data Parameters  
NAME spa40914  
EXPNO 237  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20140915  
Time 15.15  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 50.04  
DW 62,400 usec  
DE 6.50 usec  
TE 0 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SFO1 400.1320007 MHz

F2 - Processing parameters  
SI 65536  
SF 400.1300096 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa40914  
EXPNO 238  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20140915  
Time 10.23  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3400000 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 0 K  
D1 1.0000000 sec  
D11 0.03000000 sec  
TDO 1

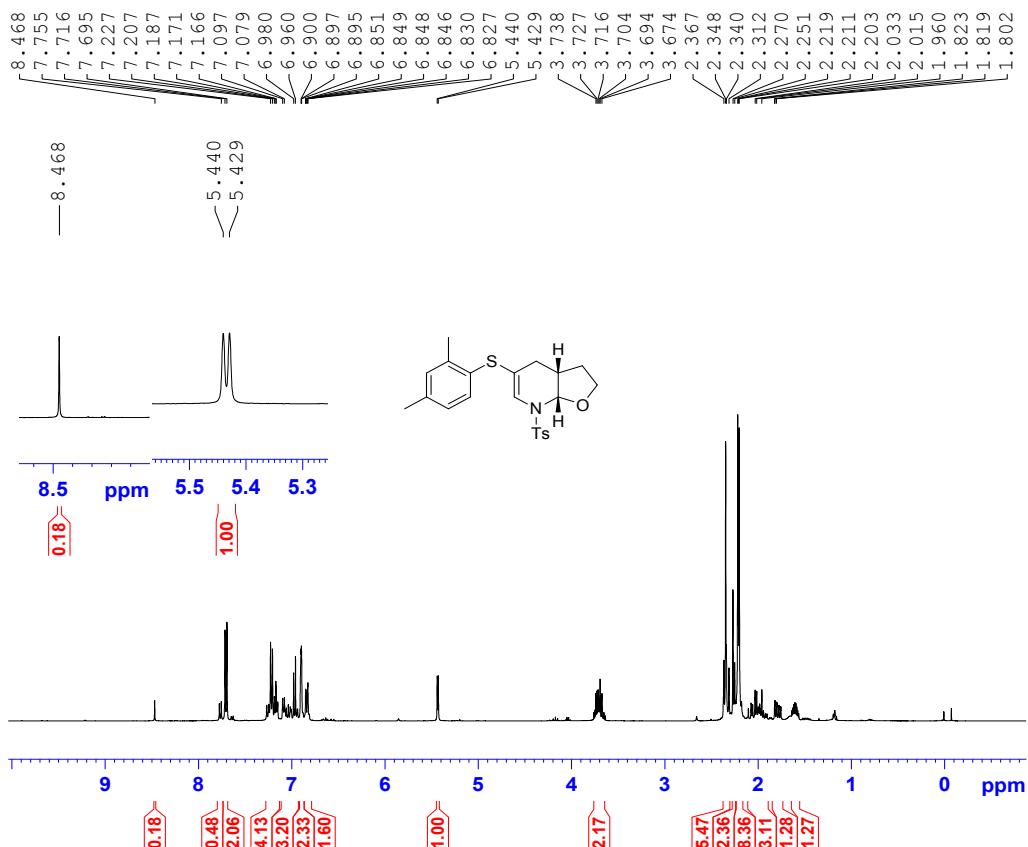
===== CHANNEL f1 =====  
NUC1 13C  
P1 9.00 usec  
PLW1 47.0000000 W  
SFO1 100.6228289 MHz

===== CHANNEL f2 =====  
CPDPFRG2 waltz16  
NUC2 1H  
DPP2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127644 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**5-((2,4-Dimethylphenyl)thio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5g) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



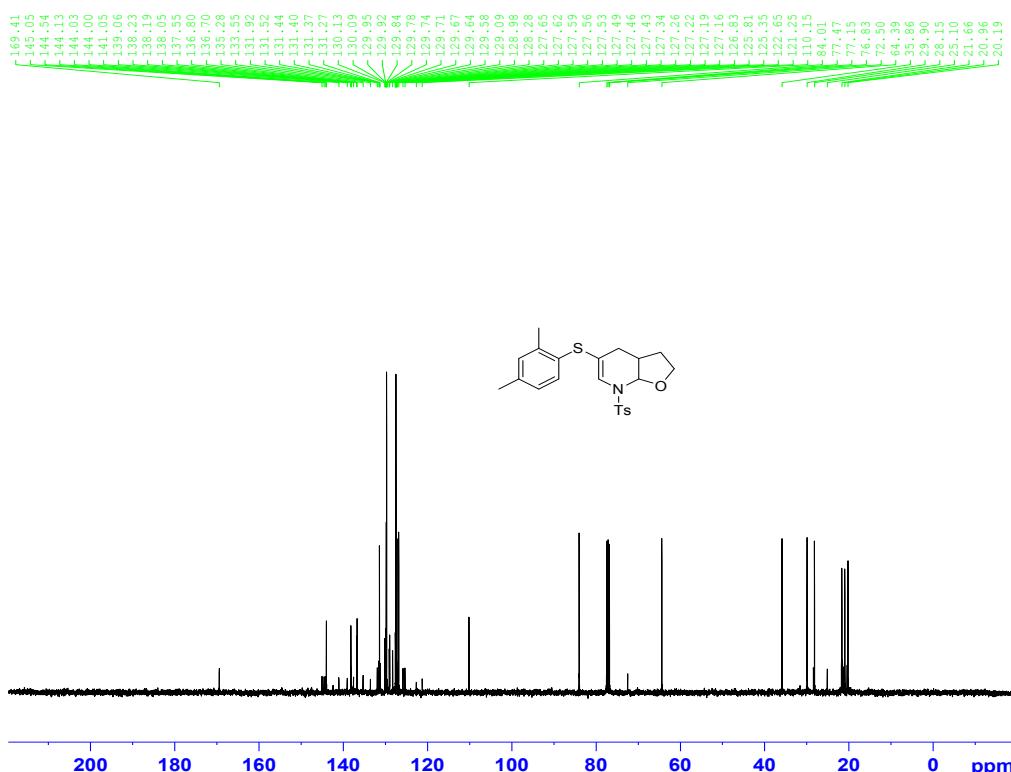
Current Data Parameters  
NAME spa40914  
EXPNO 794  
PROCNO 1

F2 - Acquisition Parameters  
Date 20140930  
Time 19.12  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 60.89  
DW 62.400 usec  
DE 6.50 usec  
TE 298.7 K  
D1 0.5000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SFO1 400.1320007 MHz

F2 - Processing parameters  
SI 65536  
SF 400.1300449 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa40914  
EXPNO 795  
PROCNO 1

F2 - Acquisition Parameters  
Date 20140930  
Time 19.20  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 16540  
SOLVENT CDCl3  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 299.1 K  
D1 1.0000000 sec  
D11 0.0300000 sec  
TD0 1

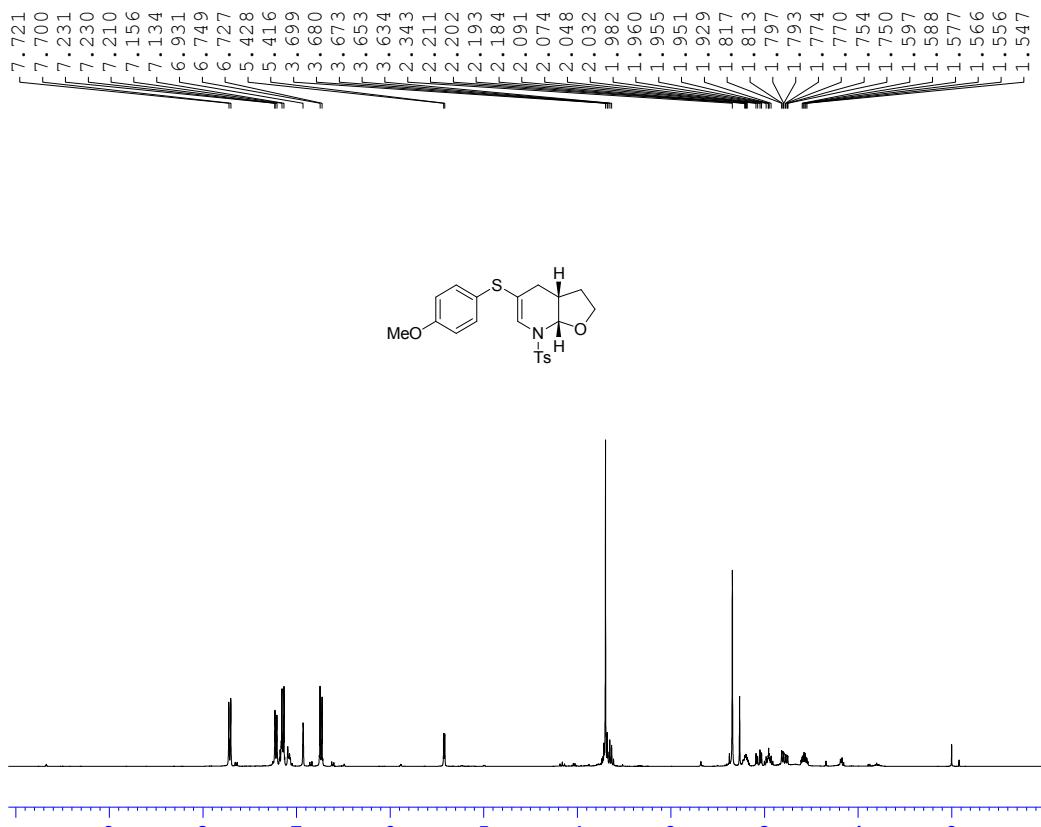
===== CHANNEL f1 =====  
NUC1 13C  
P1 9.25 usec  
PLW1 47.0000000 W  
SFO1 100.6228289 MHz

===== CHANNEL f2 =====  
CPDPG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.2358399 W  
PLW13 0.19103000 W  
SFO2 400.1316005 MHz

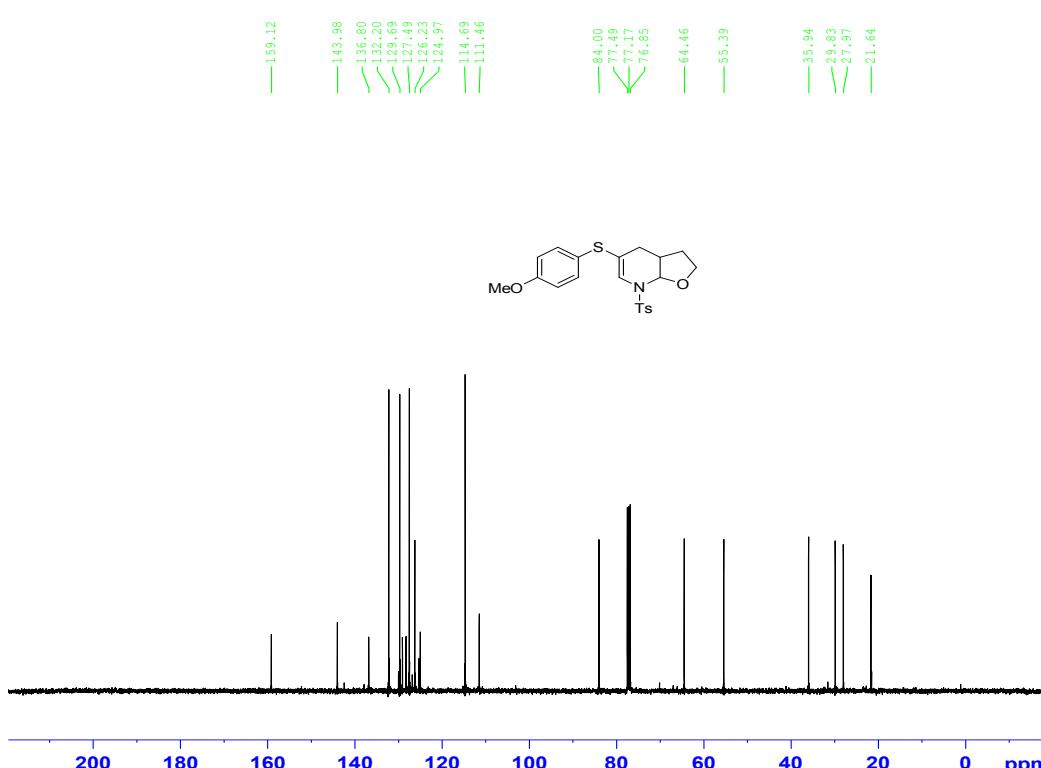
F2 - Processing parameters  
SI 32768  
SF 100.6127656 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**5-((4-Methoxyphenyl)thio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5h) :**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)**

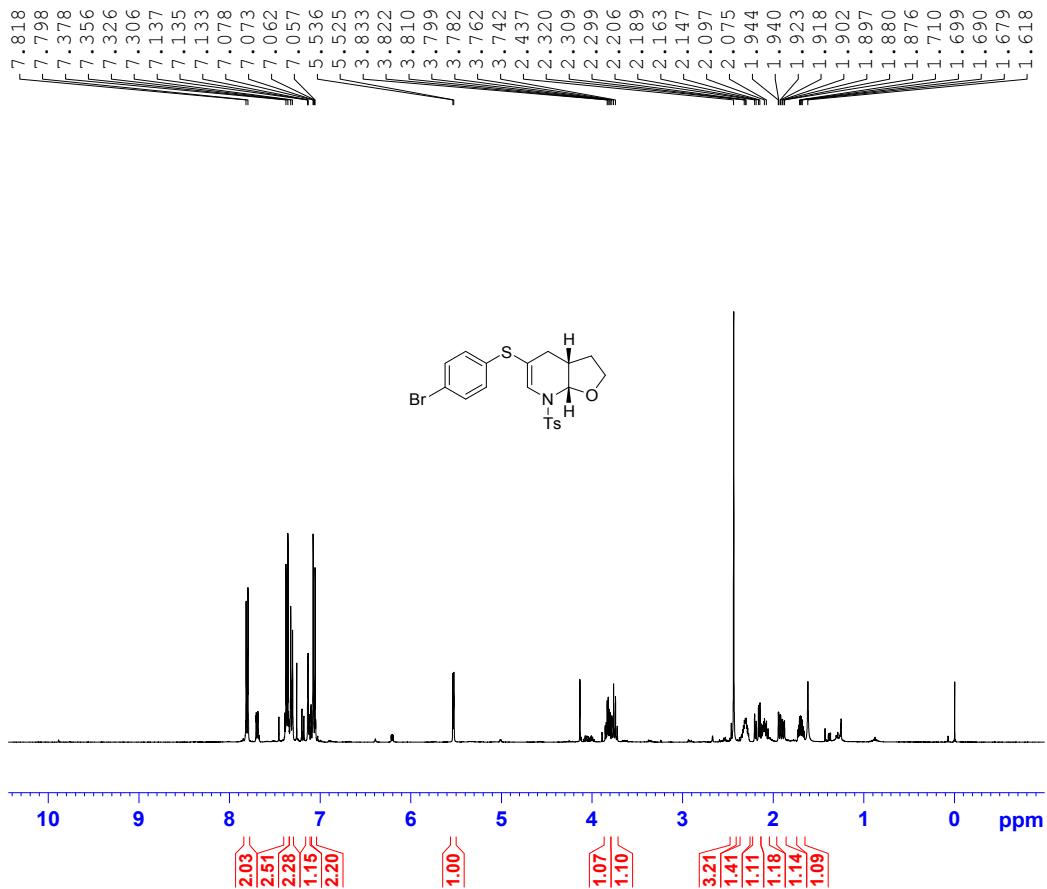


**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)**

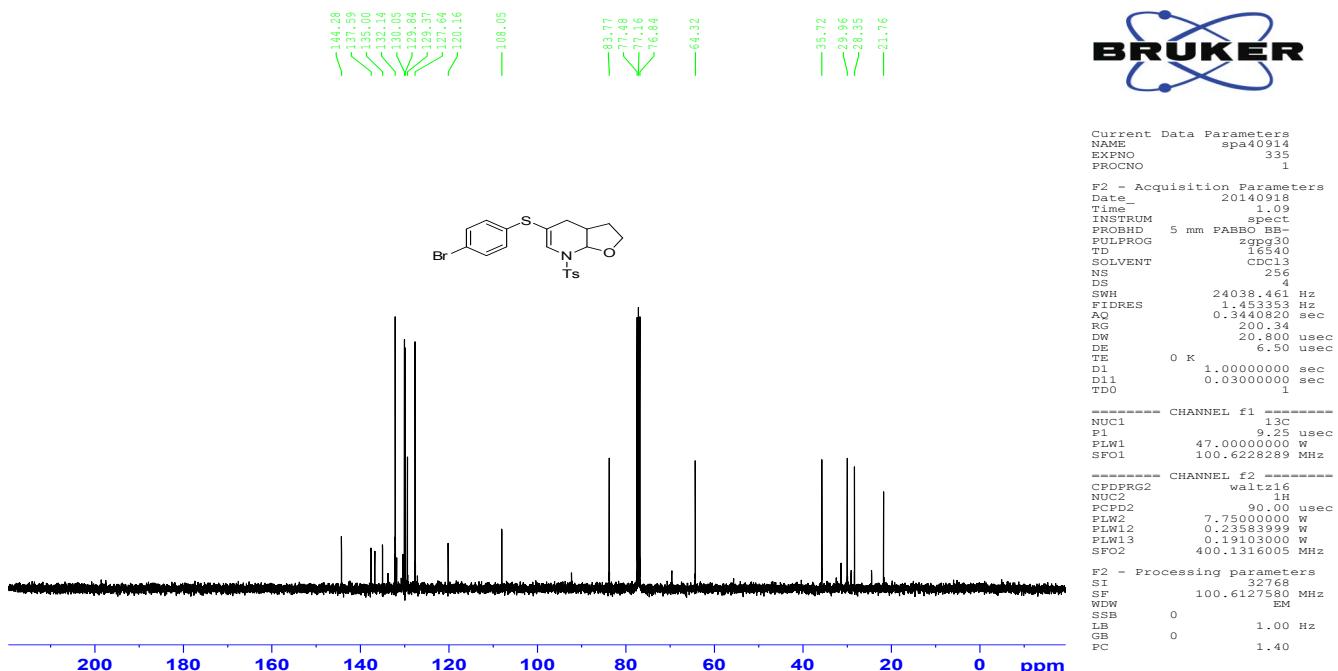


**5-((4-Bromophenyl)thio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5i) :**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)**

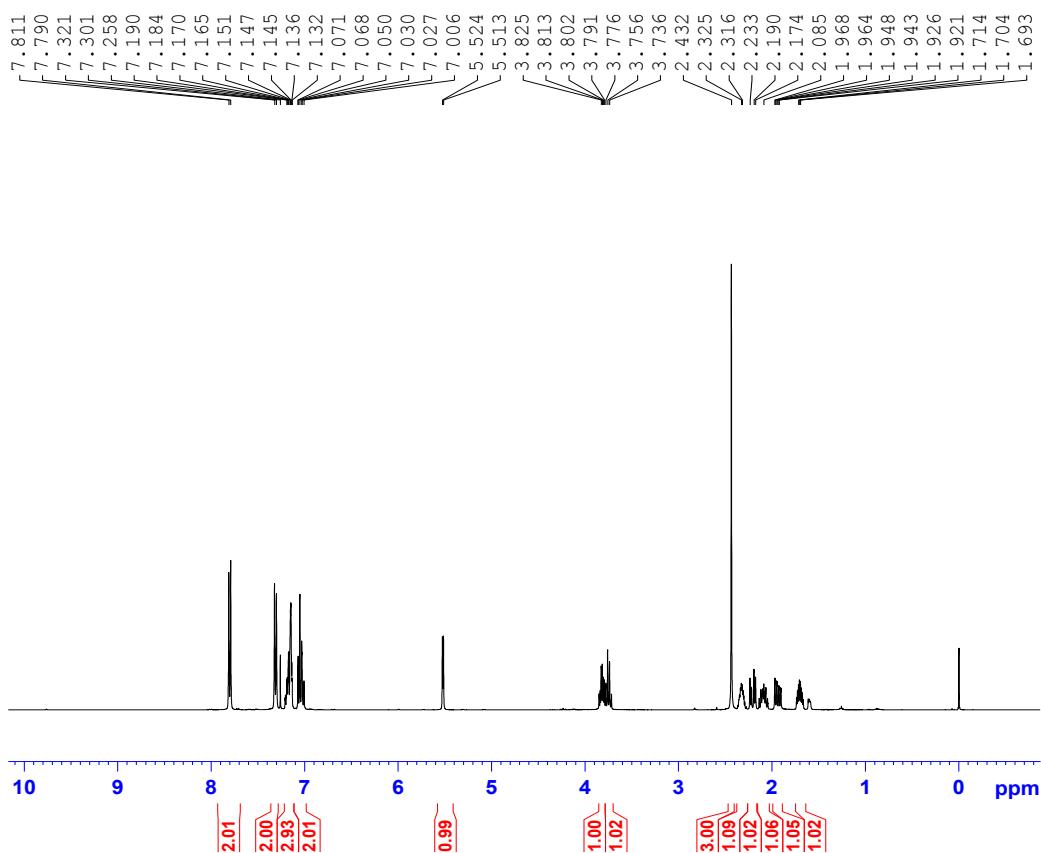


**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)**

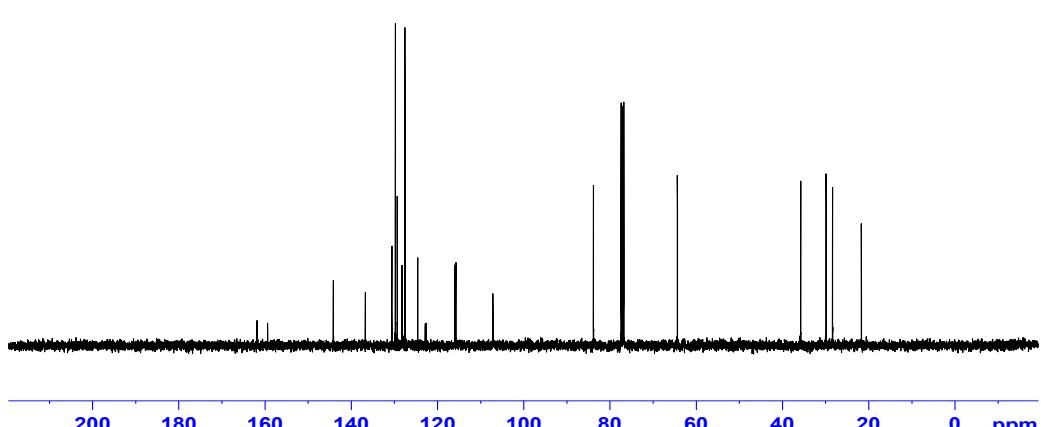
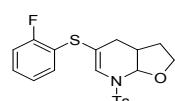
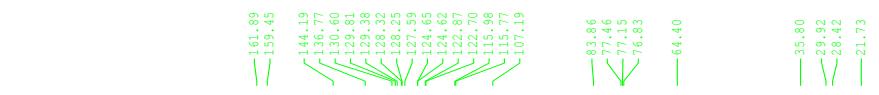


**5-((2-Fluorophenyl)thio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5k) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

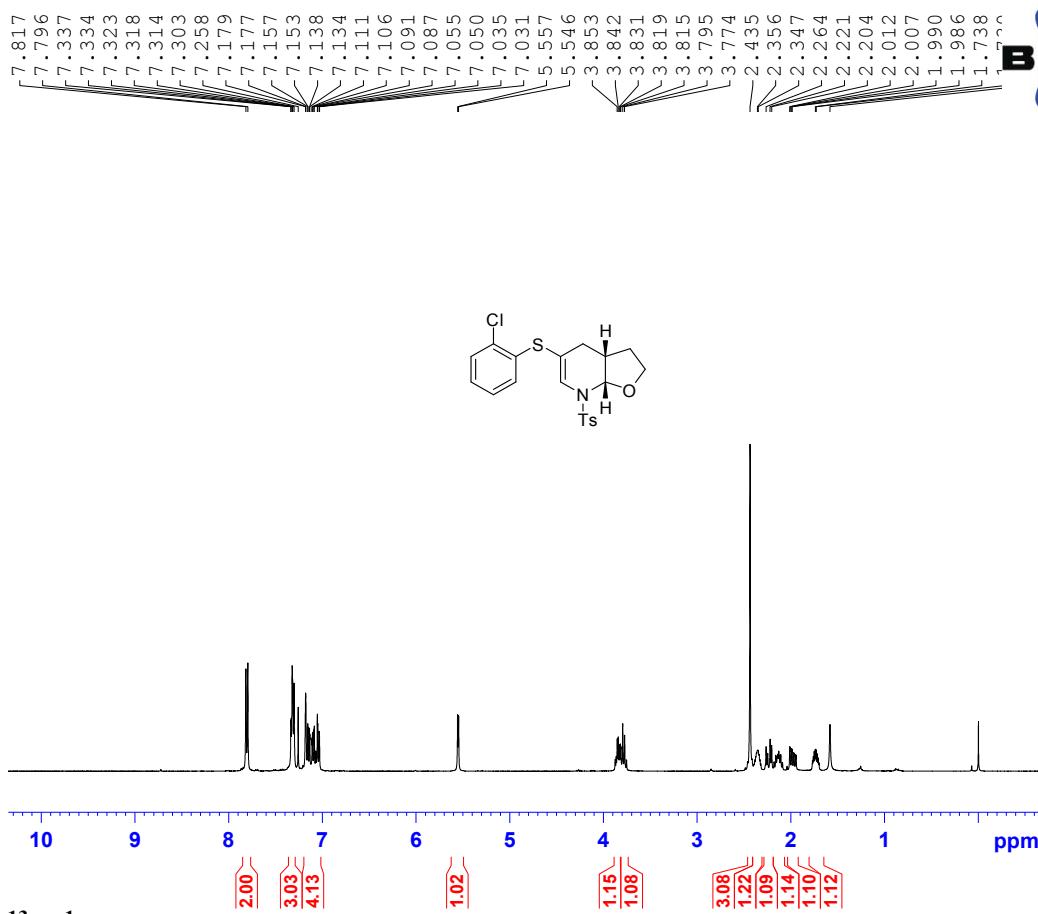


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



**5-((2-Chlorophenyl)thio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5l) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



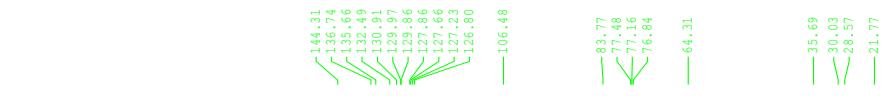
Current Data Parameters  
NAME spa41014  
EXPNO 312  
PROCNO 1

F2 - Acquisition Parameters  
Date 20141009  
Time 14.11  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 169.77  
DW 62.400 usec  
DE 6.50 usec  
TE 298.1 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SFO1 400.1320007 MHz

F2 - Processing parameters  
SI 65536  
SF 400.1300101 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa41014  
EXPNO 313  
PROCNO 1

F2 - Acquisition Parameters  
Date 20141009  
Time 14.18  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 16384  
SOLVENT CDCl3  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 298.1 K  
D1 1.00000000 sec  
D11 0.03000000 sec  
TDO 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 9.25 usec  
PLW1 47.00000000 W  
SFO1 100.6228289 MHz

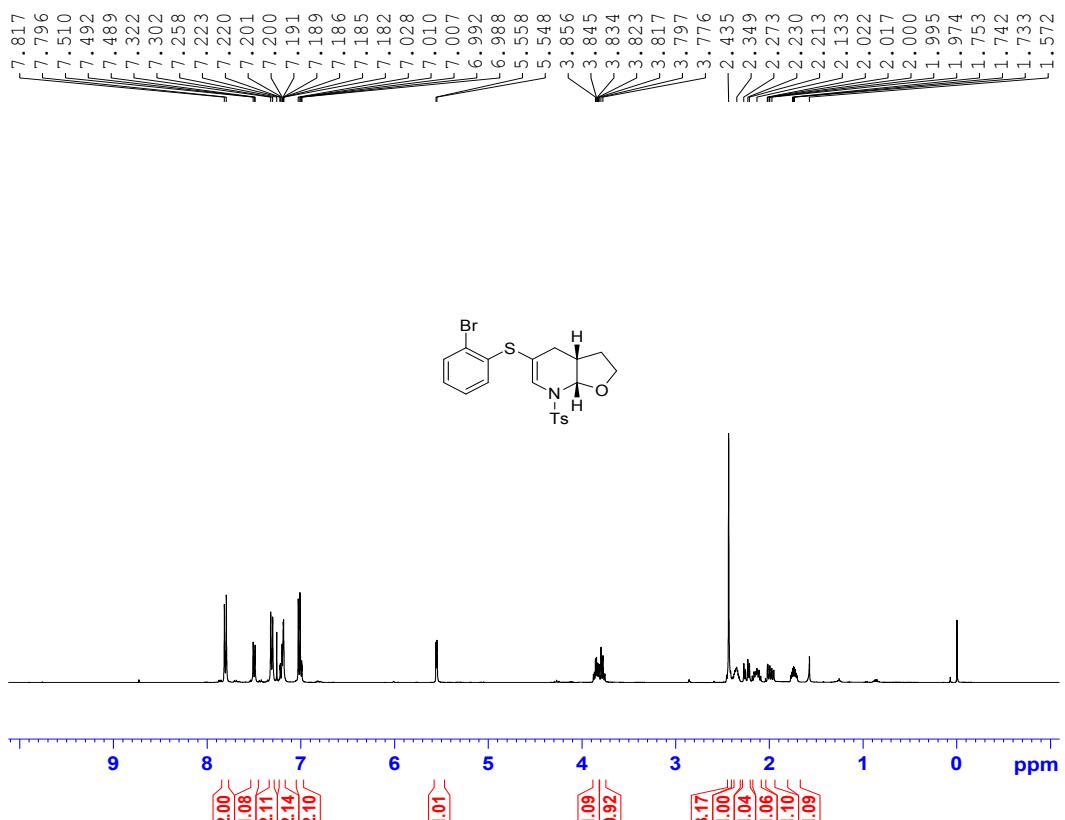
===== CHANNEL f2 =====  
CPDPG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127561 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

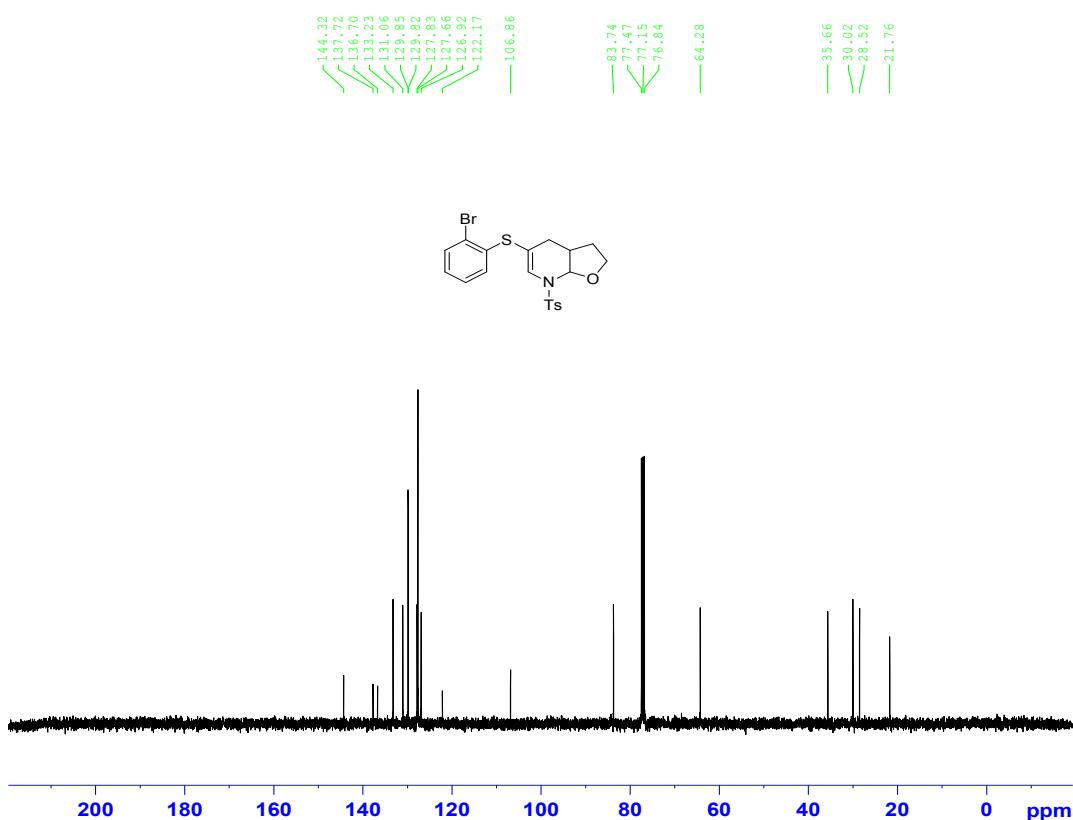


**5-((2-Bromophenyl)thio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5m) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

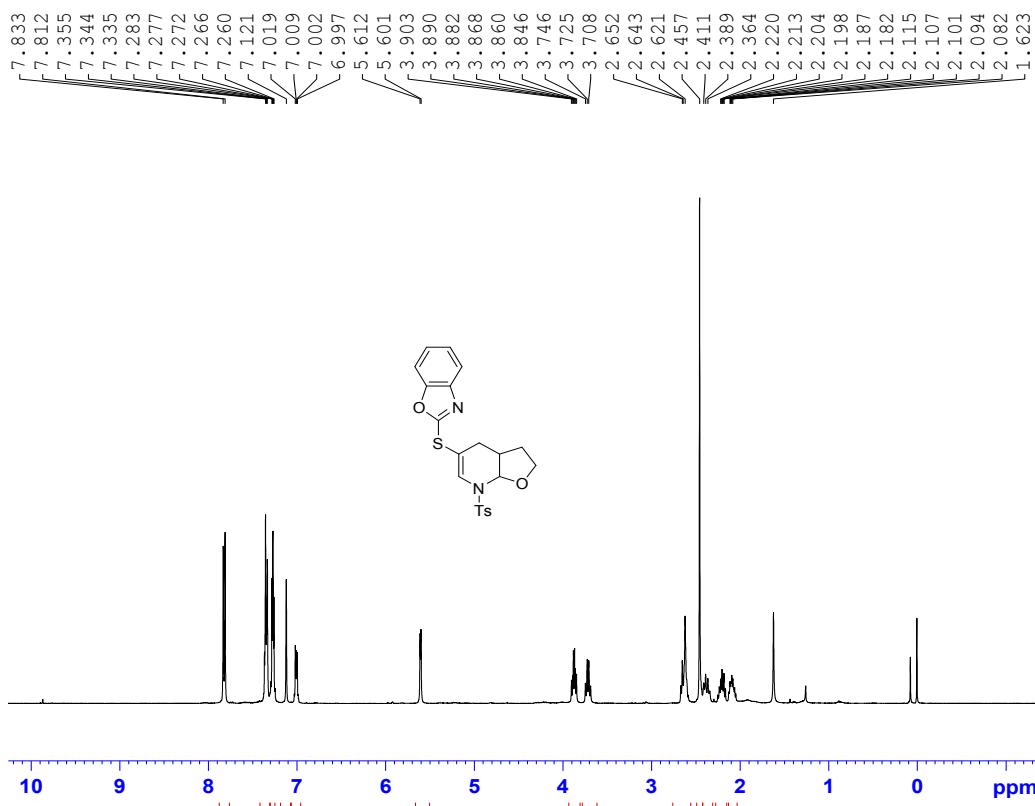


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



**2-((7-Tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridin-5-yl)thio)benzo[d]oxazole (5p) :**

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24 °C)**



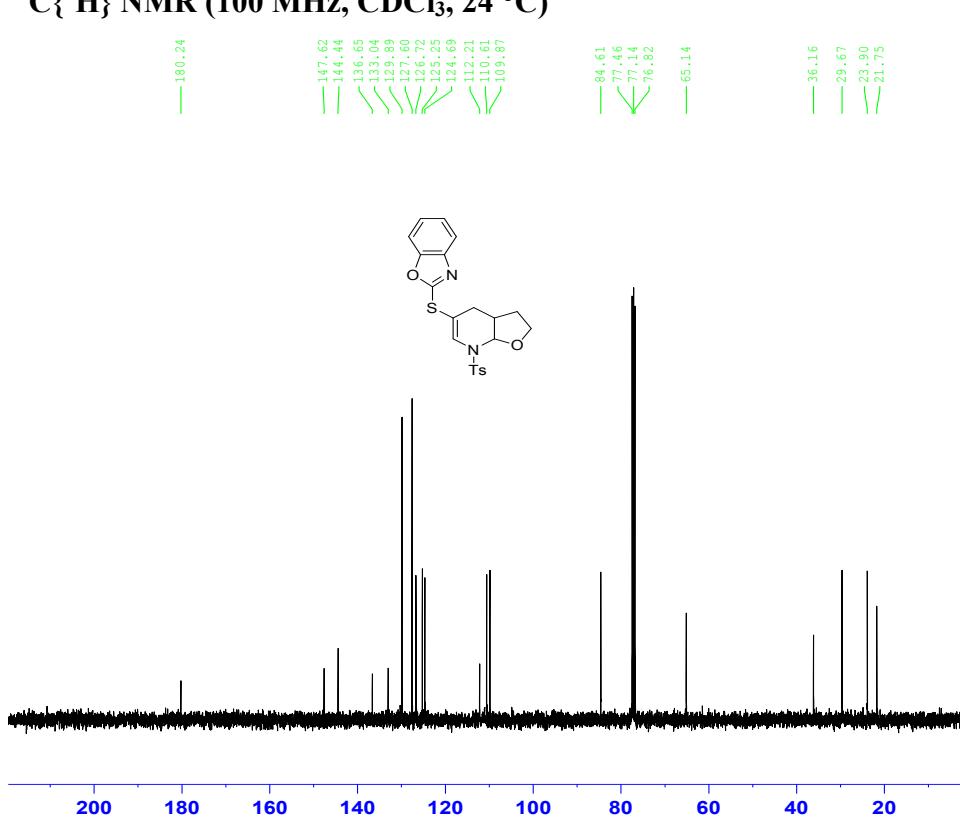
Current Data Parameters  
NAME spa40914  
EXPNO 379  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20140918  
Time\_ 21.58  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 169.77  
DW 62.400 usec  
DE 6.00 usec  
TE 0 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SFO1 400.1320007 MHz

F2 - Processing parameters  
SI 65536  
SF 400.1300048 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)**



Current Data Parameters  
NAME spa40914  
EXPNO 380  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20140918  
Time\_ 22.06  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 16540  
SOLVENT CDCl<sub>3</sub>  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.450551 Hz  
AQ 0.340800 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 0 K  
D1 1.00000000 sec  
D11 0.03000000 sec  
TDO 1

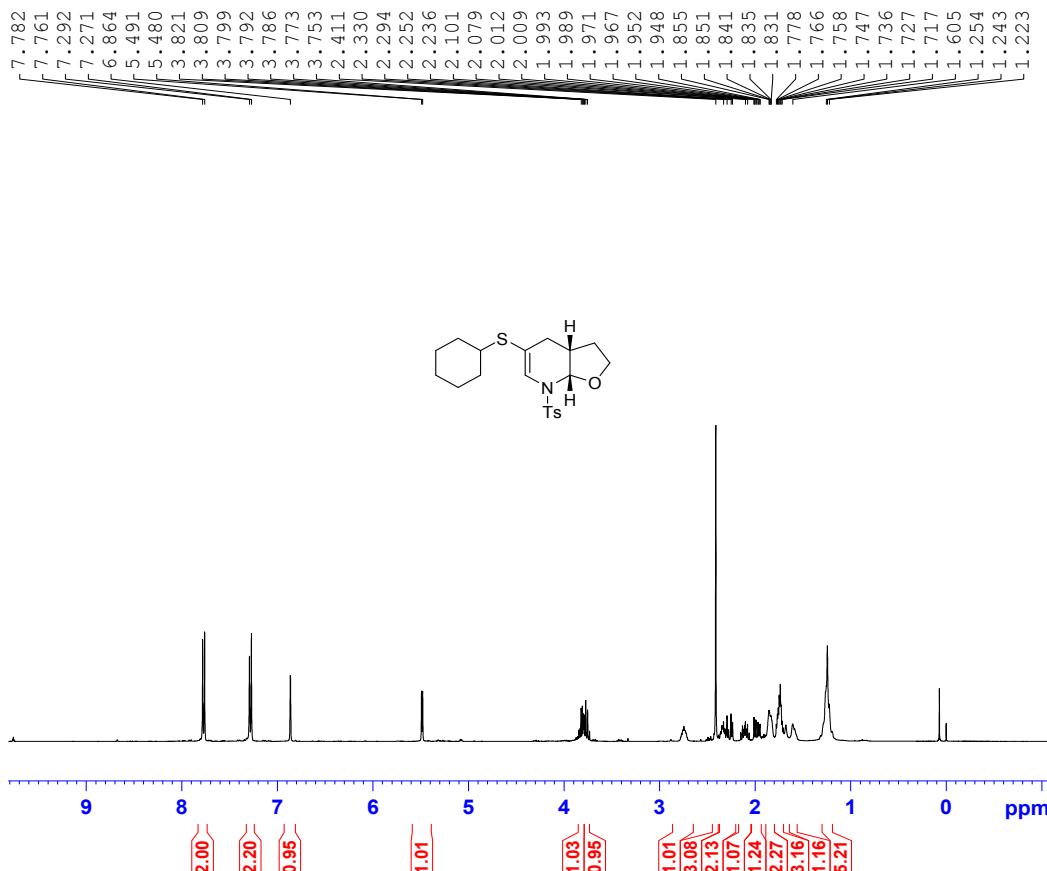
===== CHANNEL f1 ======  
NUC1 13C  
P1 9.25 usec  
PLW1 47.0000000 W  
SFO1 100.6228289 MHz

===== CHANNEL f2 ======  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SFO2 400.1316005 MHz

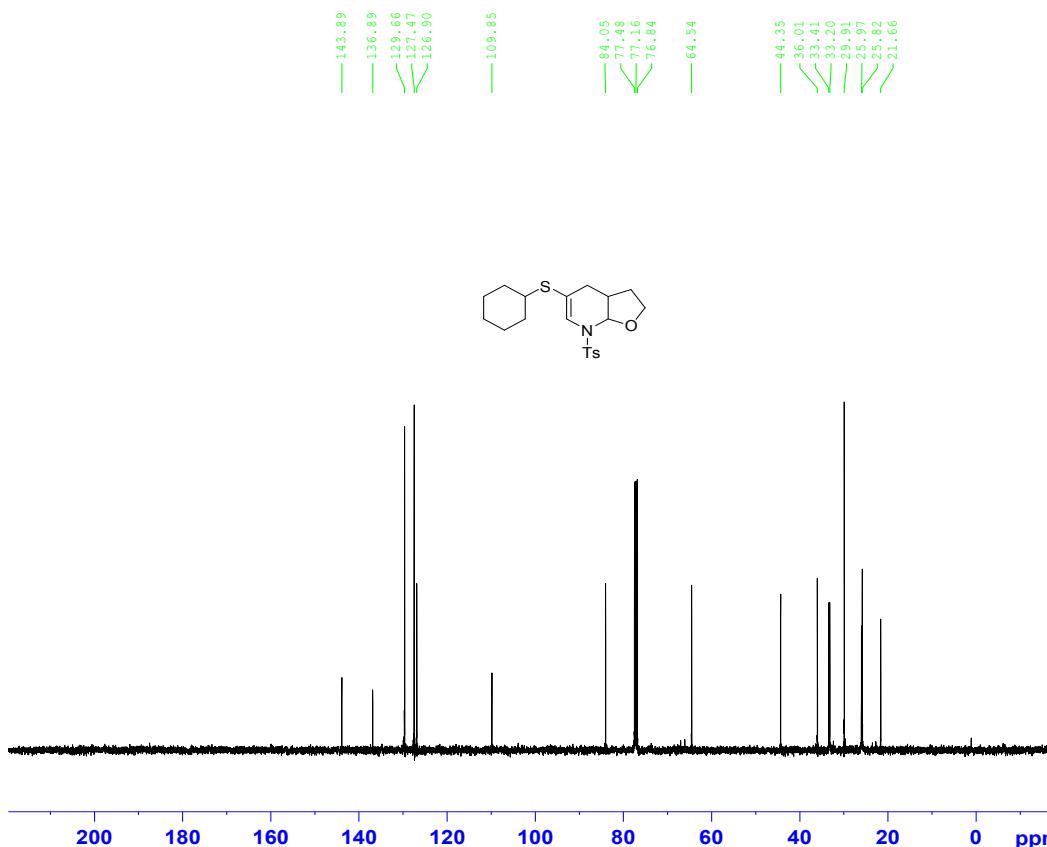
F2 - Processing parameters  
SI 32768  
SF 100.6127593 MHz  
NDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**5-(Cyclohexylthio)-7-tosyl-2,3,3a,4,7,7a-hexahydrofuro[2,3-b]pyridine (5o) :**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)**

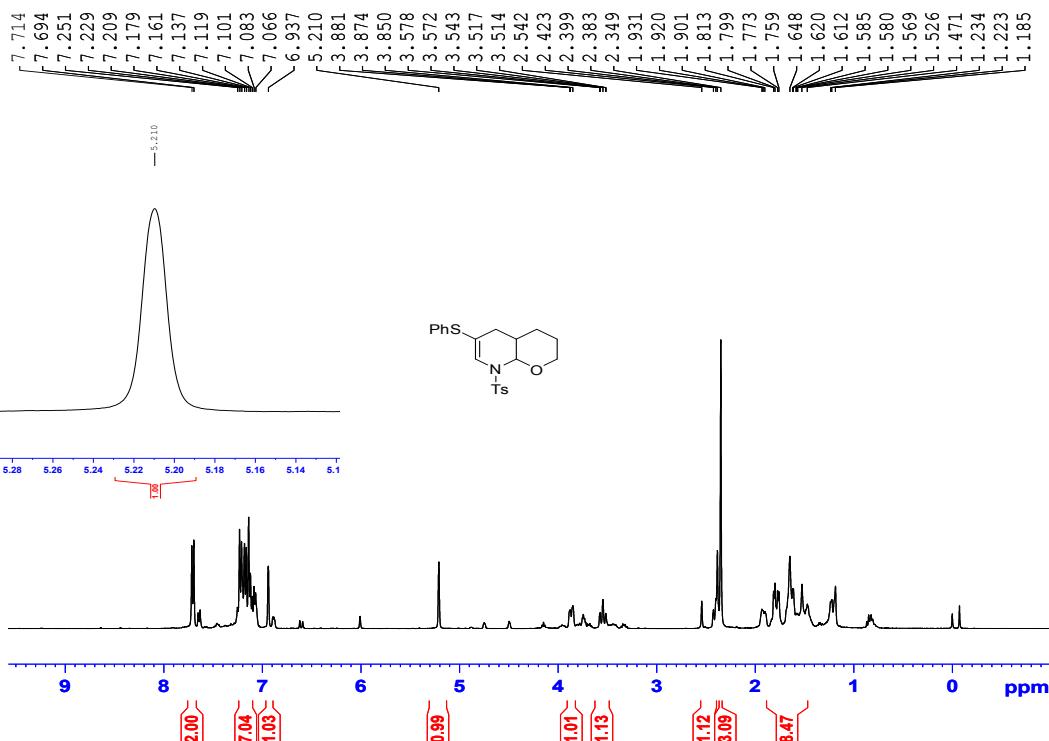


**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)**

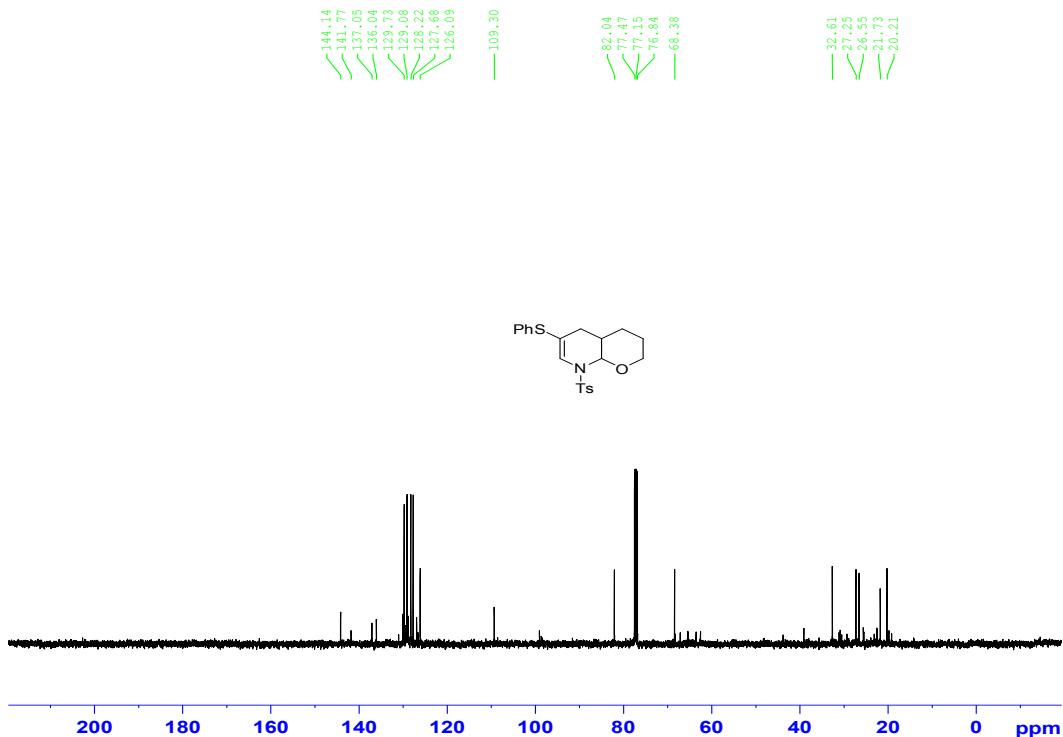


**6-(Phenylthio)-8-tosyl-3,4,4a,5,8,8a-hexahydro-2H-pyrano[2,3-b]pyridine (5a') :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

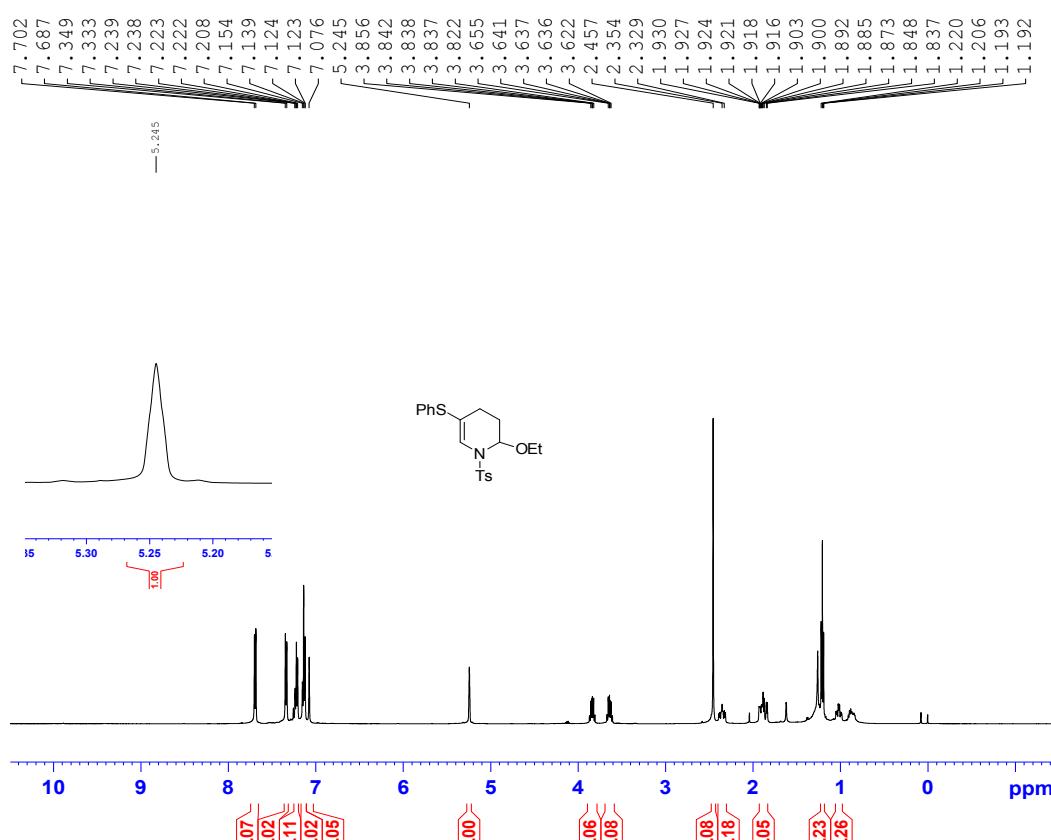


**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**

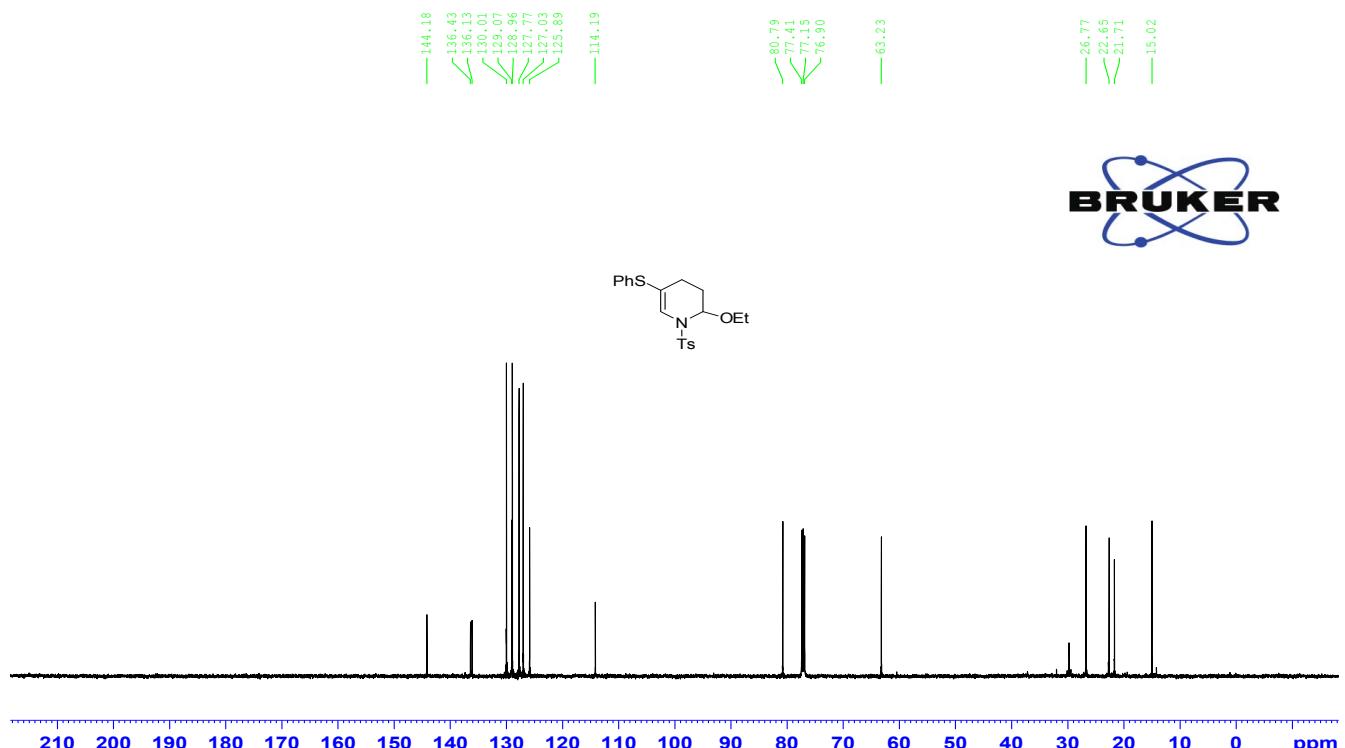


**2-Ethoxy-5-(phenylthio)-1-tosyl-1,2,3,4-tetrahydropyridine (6) :**

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 24 °C)**

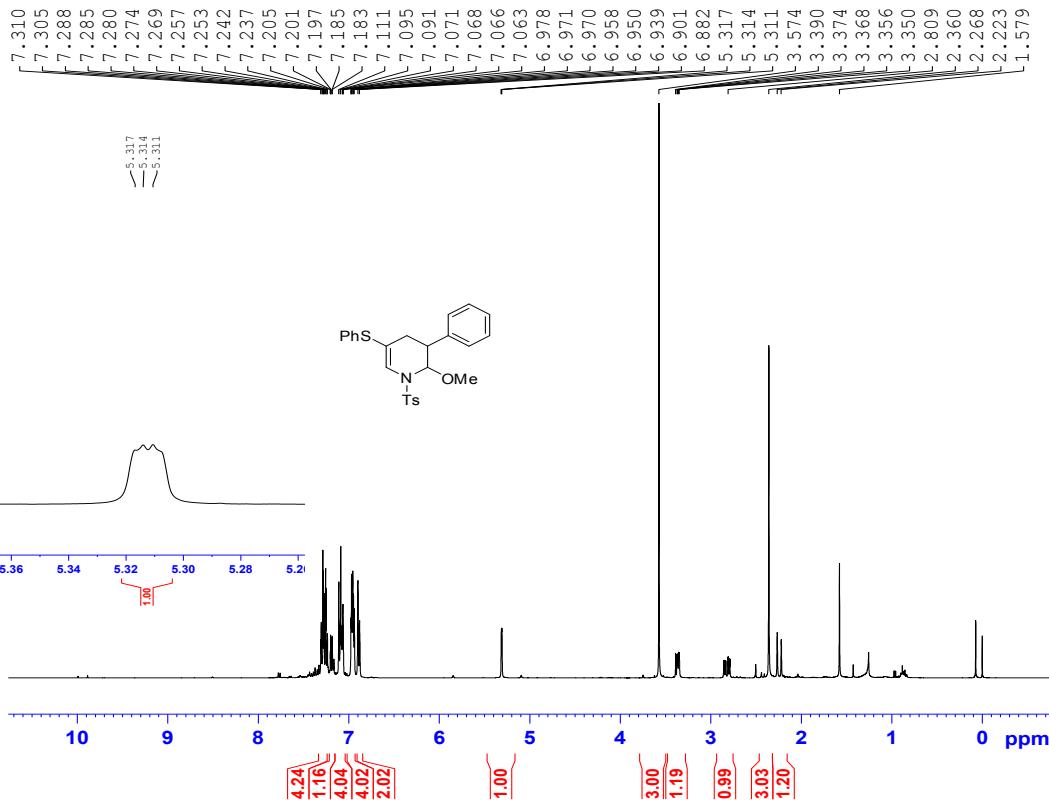


**$^{13}\text{C}\{\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 24 °C)**

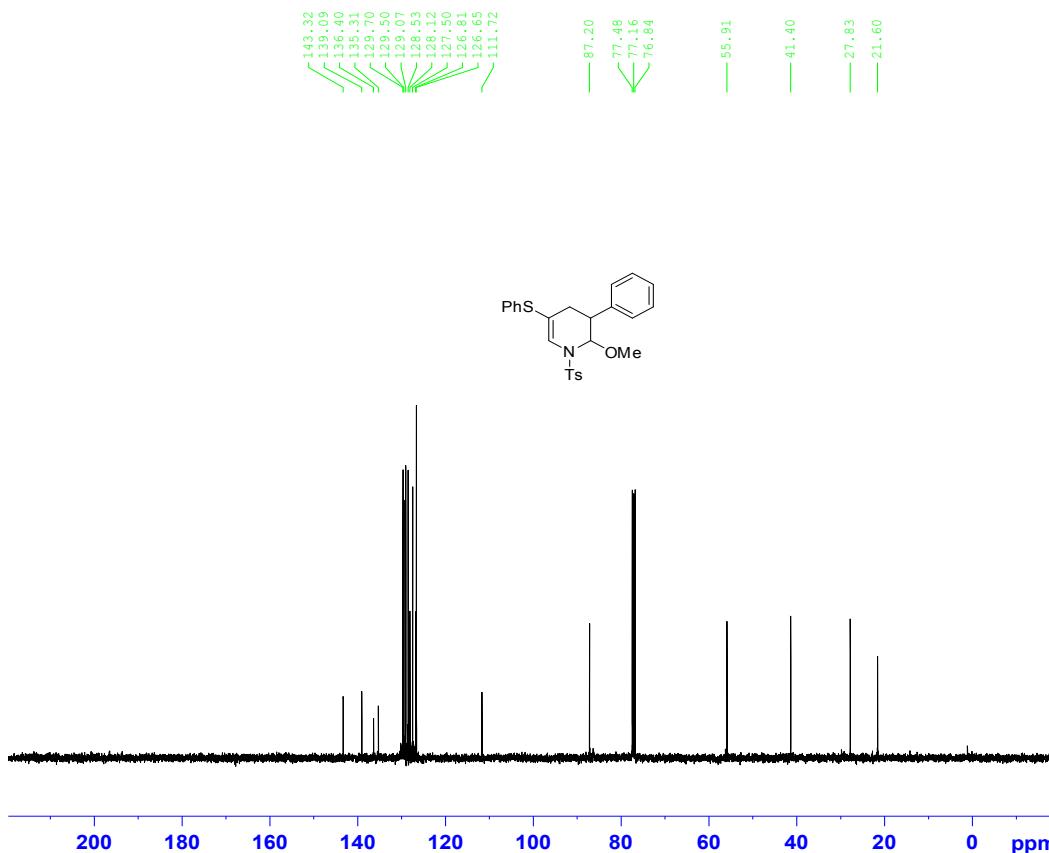


**2-Methoxy-3-phenyl-5-(phenylthio)-1-tosyl-1,2,3,4-tetrahydropyridine (7) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

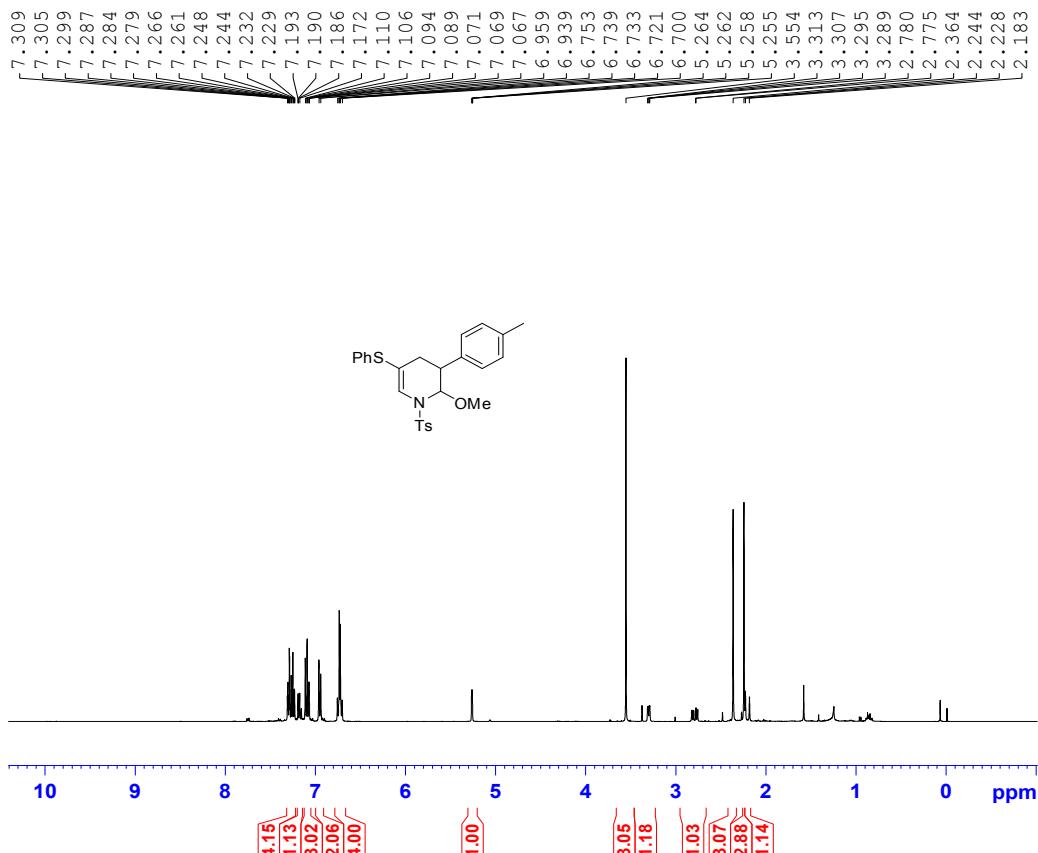


**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**

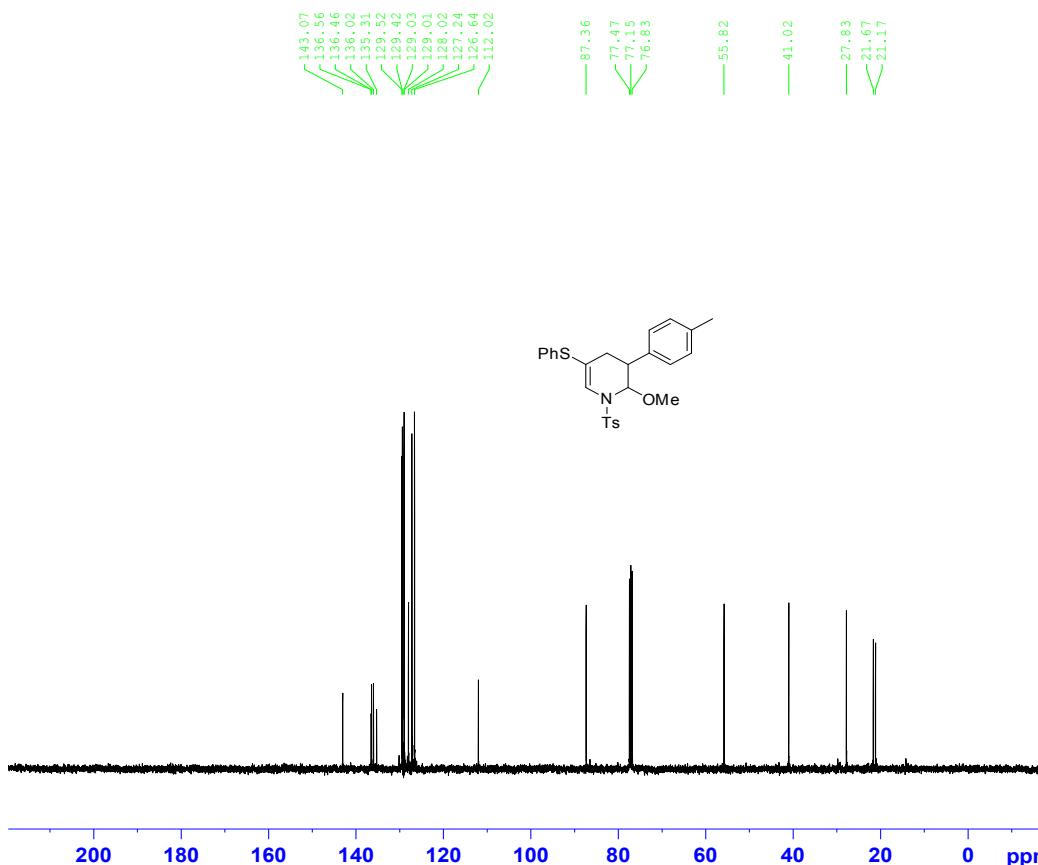


**2-Methoxy-5- (phenylthio)-3- (p-tolyl)-1-tosyl-1,2,3,4-tetrahydropyridine (8) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

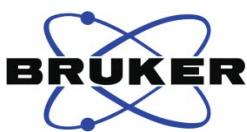
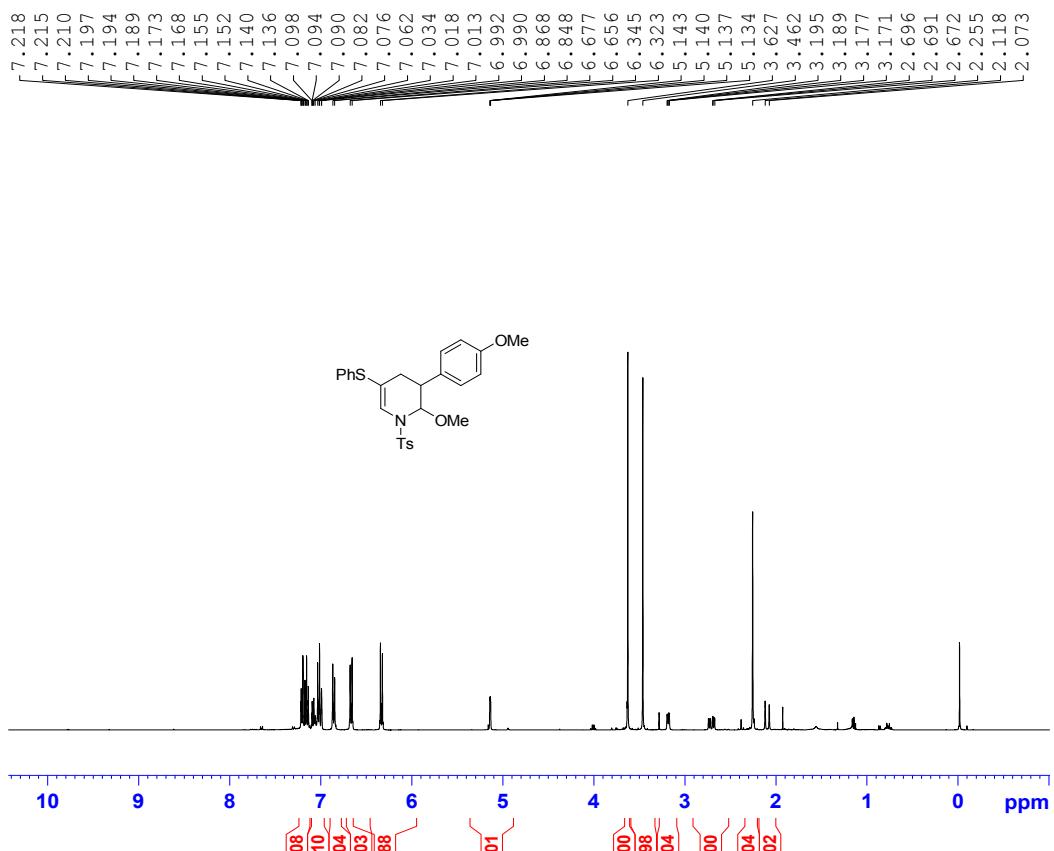


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**

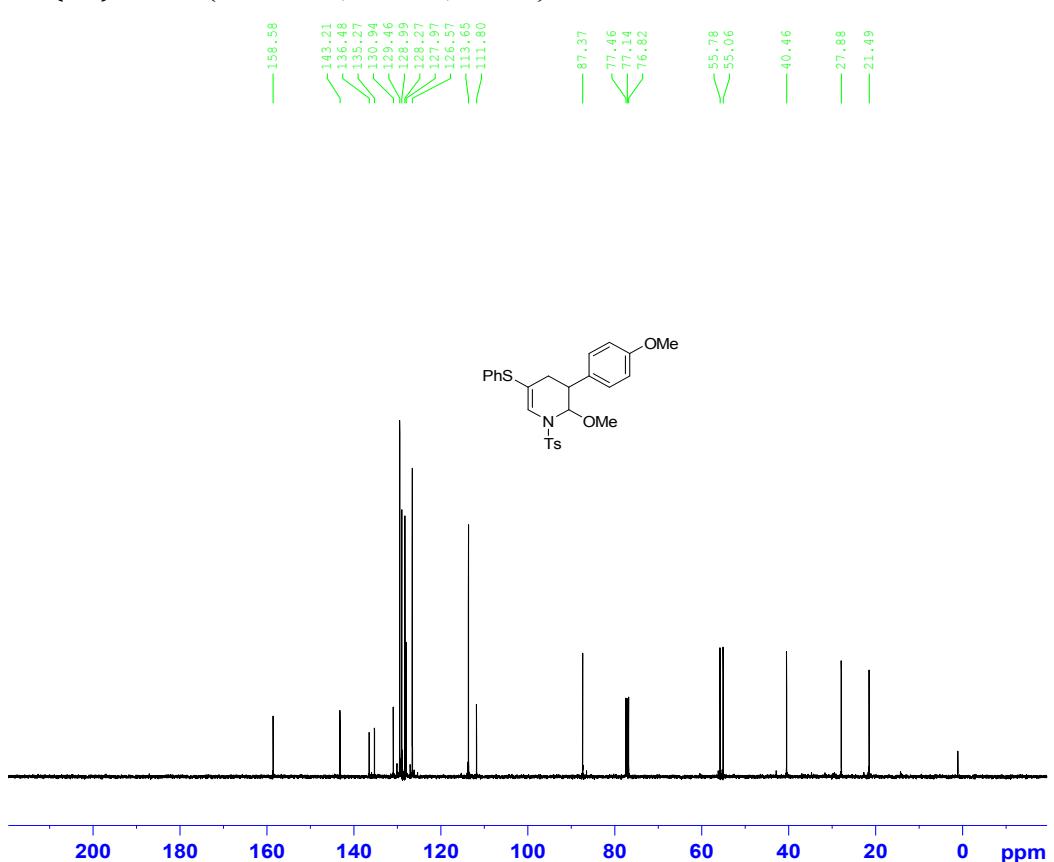


**2-Methoxy-3-(4-methoxyphenyl)-5-(phenylthio)-1-tosyl-1,2,3,4-tetrahydropyridine (9) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

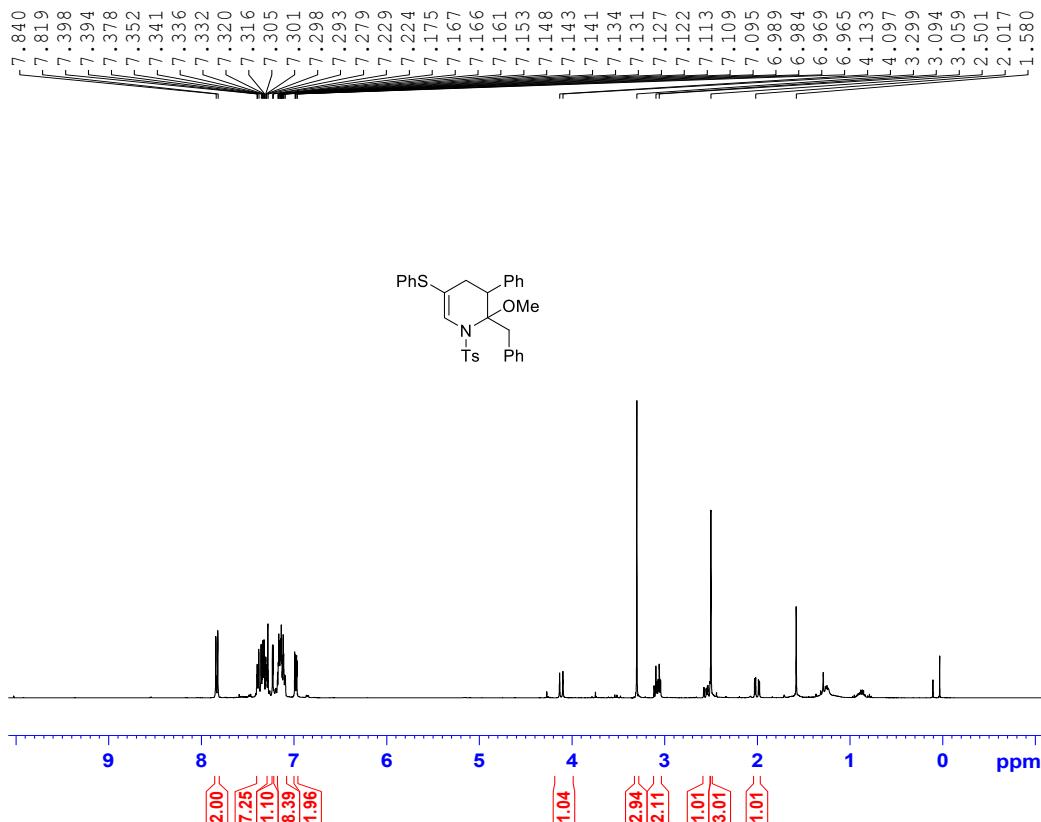


**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



**2-Benzyl-2-methoxy-3-phenyl-5-(phenylthio)-1-tosyl-1,2,3,4-tetrahydropyridine (10) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



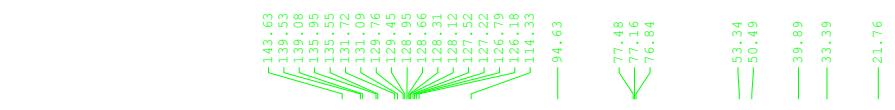
Current Data Parameters  
NAME spa40515  
EXPNO 673  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150521  
Time\_ 15.41  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 138.85  
DW 62.400 usec  
DE 6.50 usec  
TE 301.1 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SFO1 400.1320007 MHz

F2 - Processing parameters  
SI 65536  
SF 400.1300018 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa40515  
EXPNO 851  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150527  
Time\_ 15.09  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 16540  
SOLVENT CDCl3  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20,800 usec  
DE 6.50 usec  
TE 299.5 K  
D1 1.0000000 sec  
D11 0.03000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 13C  
P1 9.25 usec  
PLW1 47.0000000 W  
SFO1 100.6228289 MHz

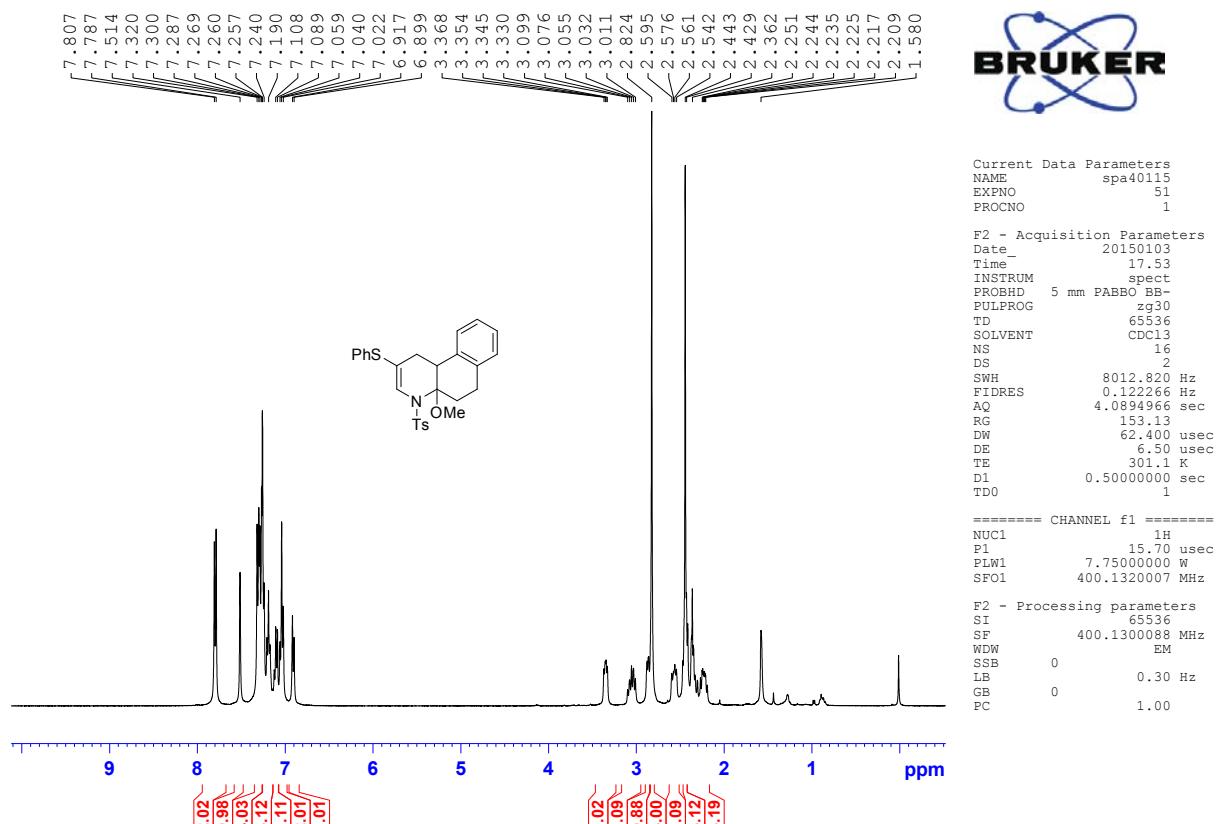
===== CHANNEL f2 ======  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127550 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

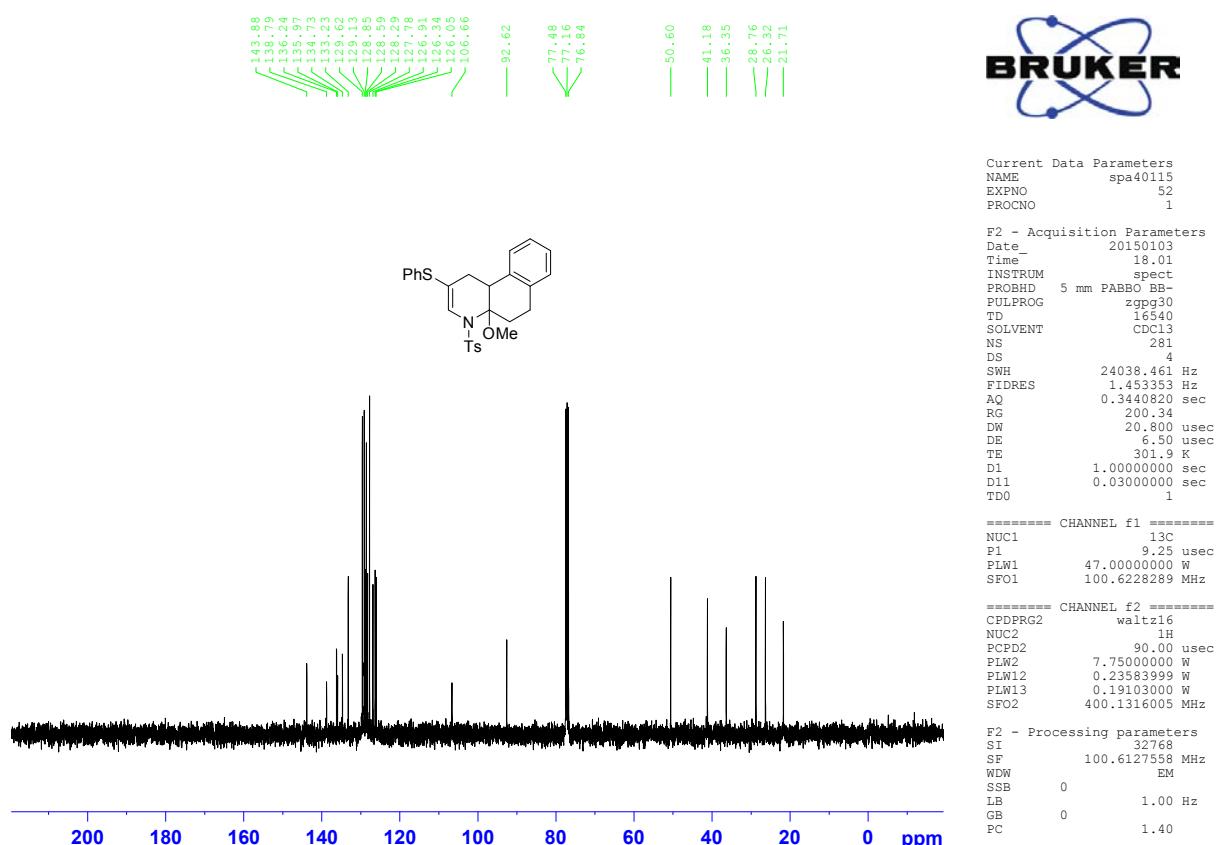


**4a-Methoxy-2-(phenylthio)-4-tosyl-1,4,4a,5,6,10b-hexahydrobenzo[f]quinolone (11) :**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)**

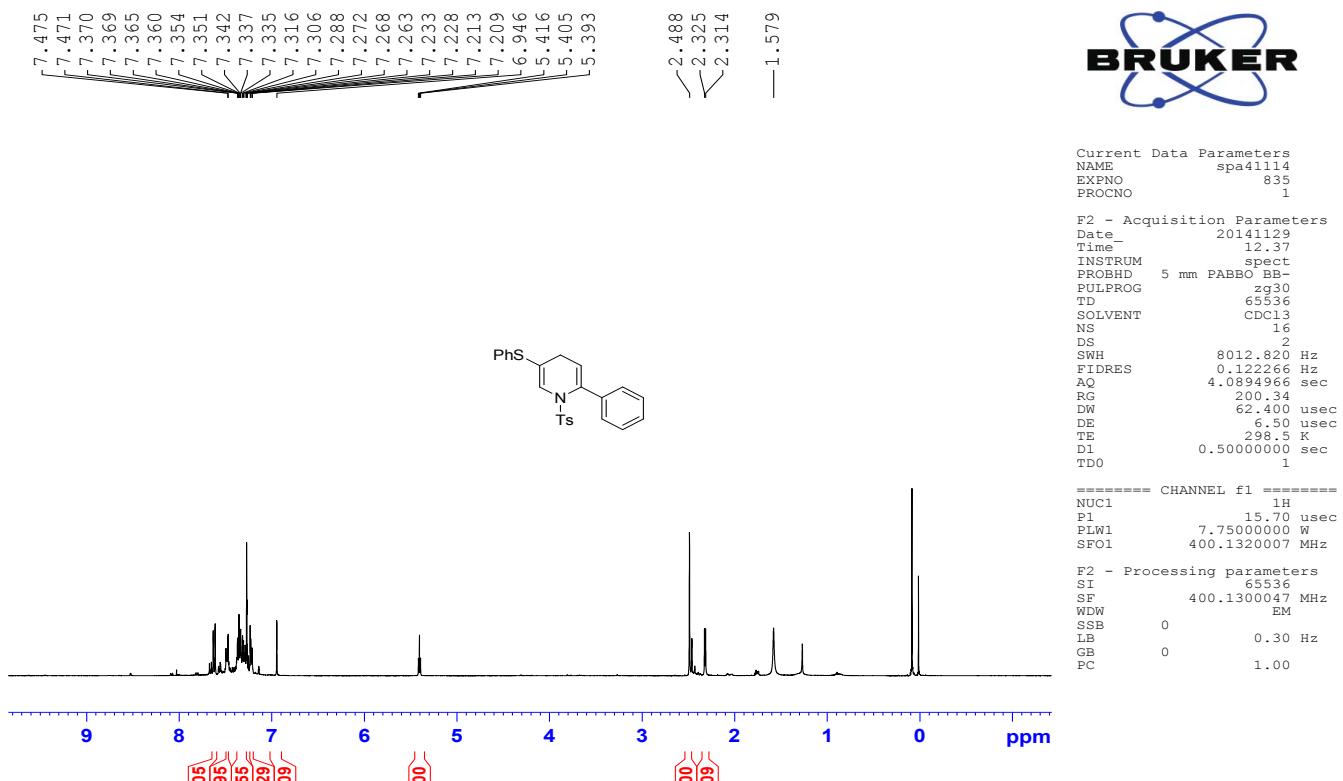


**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)**

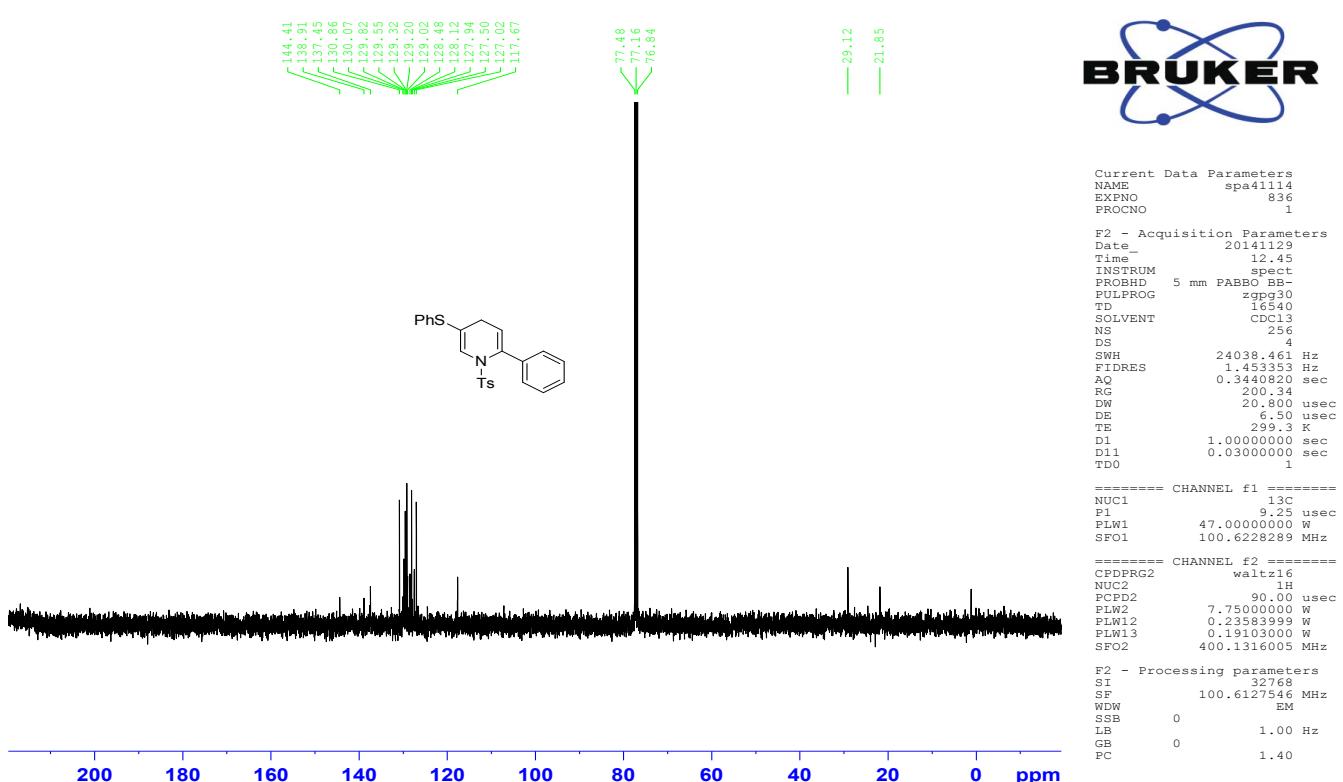


**2-Phenyl-5-(phenylthio)-1-tosyl-1,4-dihdropyridine (14) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

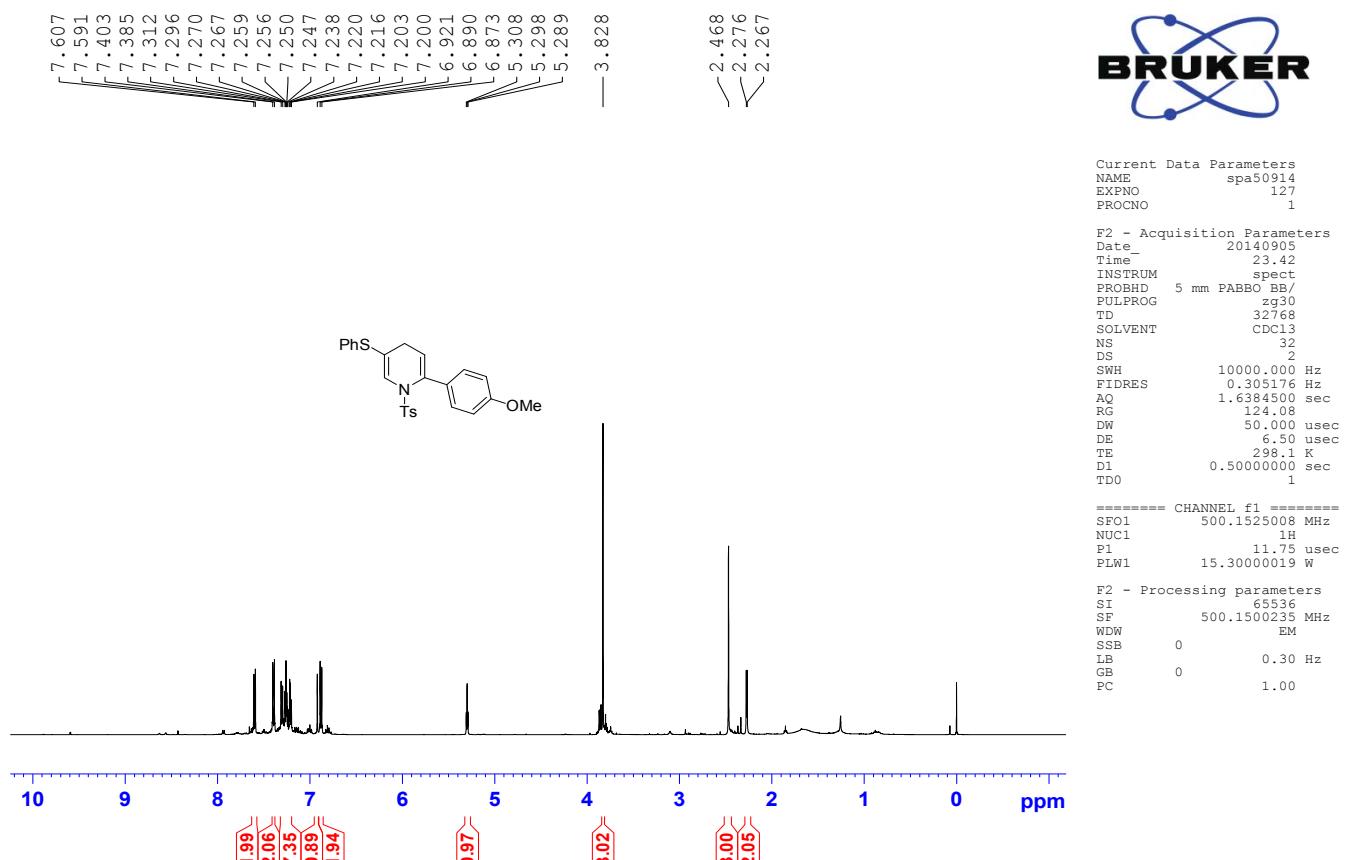


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**

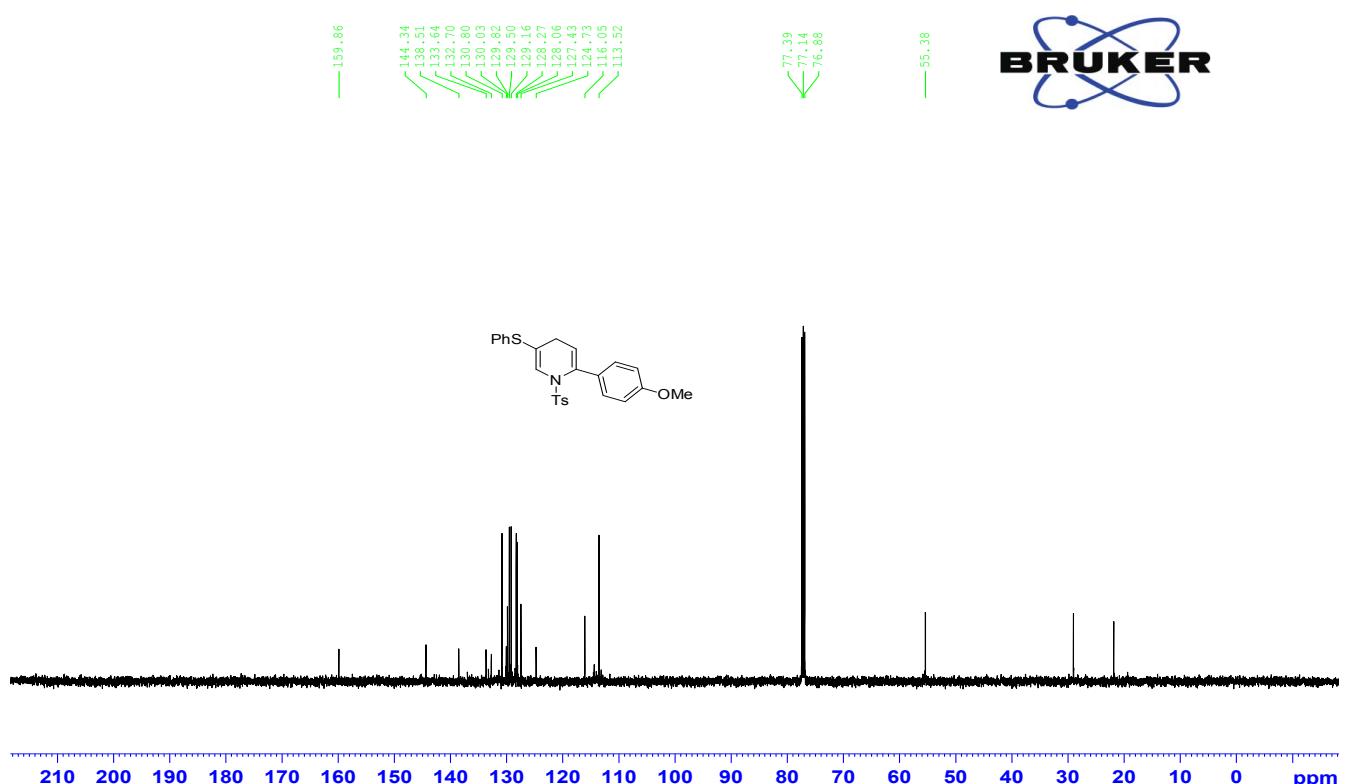


**2-(4-Methoxyphenyl)-5-(phenylthio)-1-tosyl-1,4-dihdropyridine (15) :**

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 24 °C)**

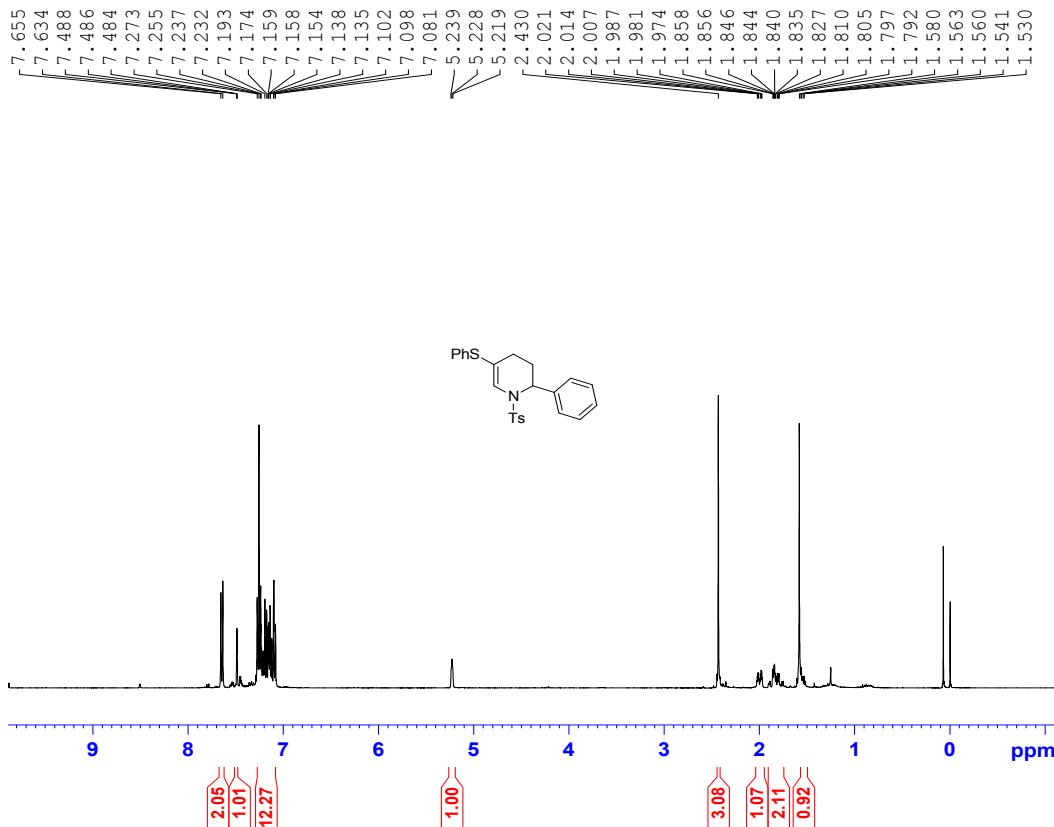


**$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 24 °C)**

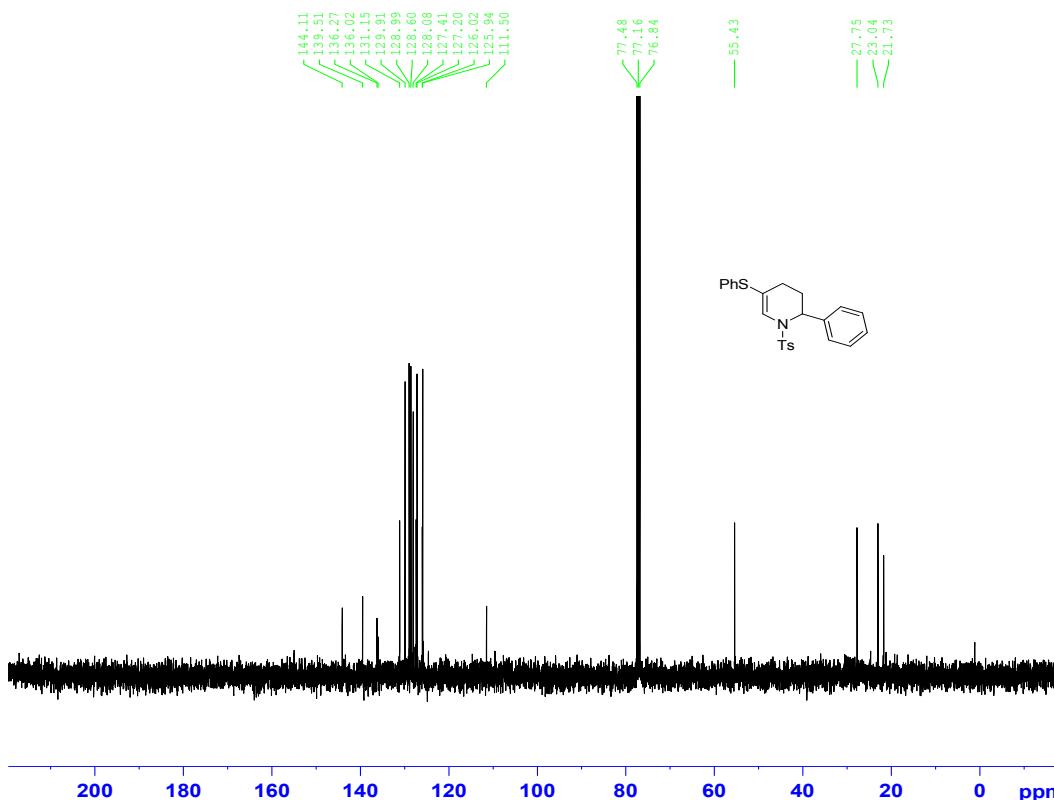


**2-Phenyl-5- (phenylthio)-1-tosyl-1,2,3,4-tetrahydropyridine (16) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

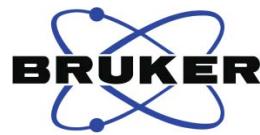
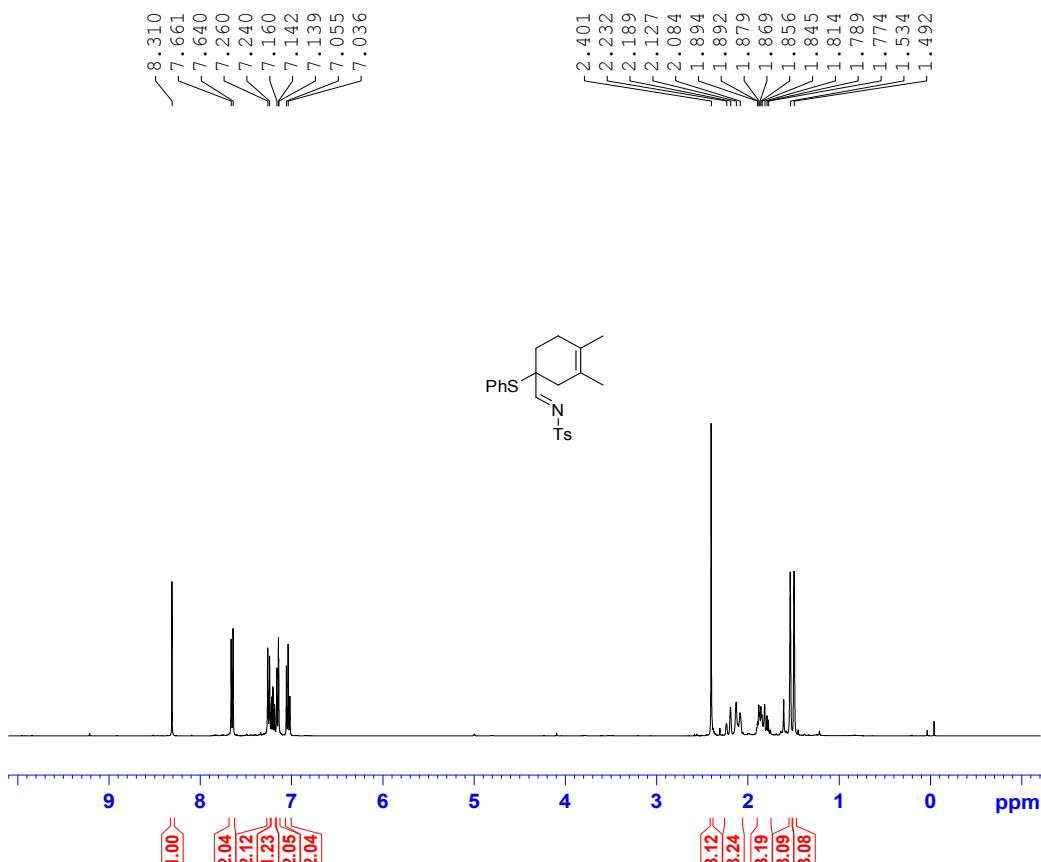


**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



***N*-(3,4-Dimethyl-1-(phenylthio)cyclohex-3-en-1-yl)methylene)-4-methylbenzenesulfonamide  
(18a) :**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)

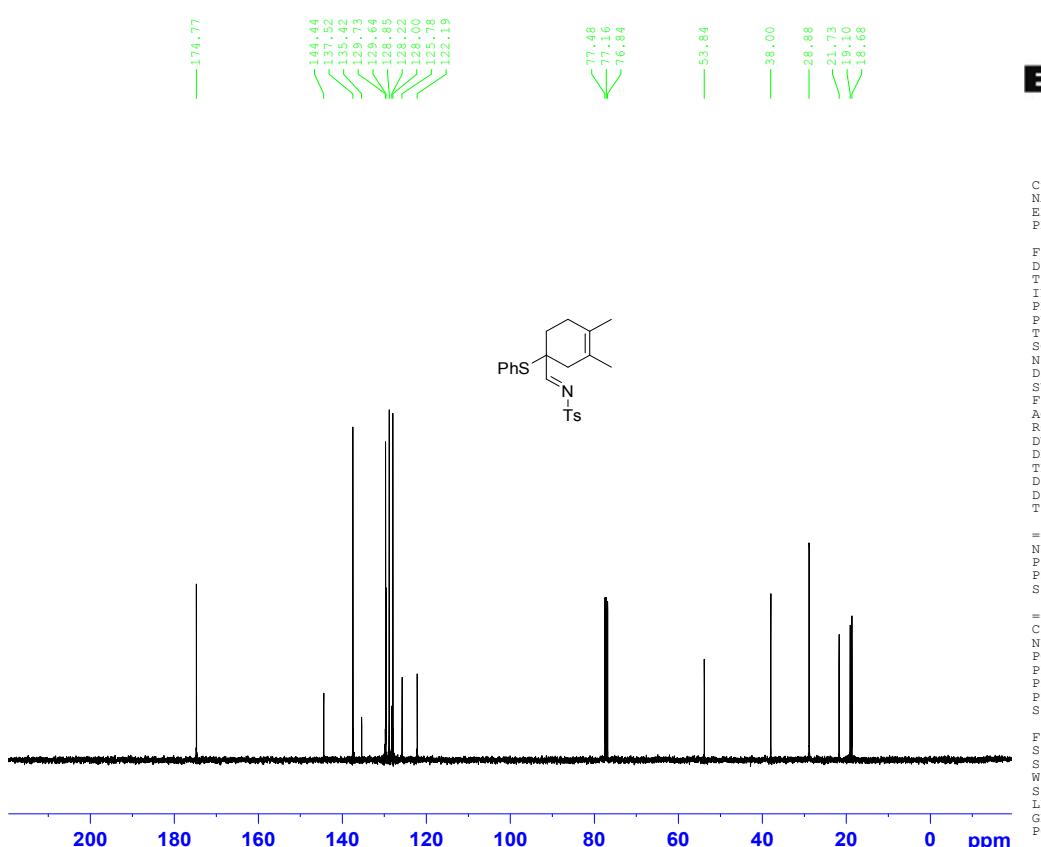


Current Data Parameters  
NAME spa40515  
EXPNO 319  
PROCNO 1

F2 - Acquisition Parameters  
Date 20150510  
Time 6.42  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 79.8  
DW 62.400 usec  
DE 6.50 usec  
TE 299.7 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SF01 400.1320007 MHz  
F2 - Processing parameters  
SI 65536  
SF 400.1300261 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)



Current Data Parameters  
NAME spa40515  
EXPNO 320  
PROCNO 1

F2 - Acquisition Parameters  
Date 20150510  
Time 6.49  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 16540  
SOLVENT CDCl<sub>3</sub>  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 299.4 K  
D1 1.0000000 sec  
D11 0.03000000 sec  
TDO 1

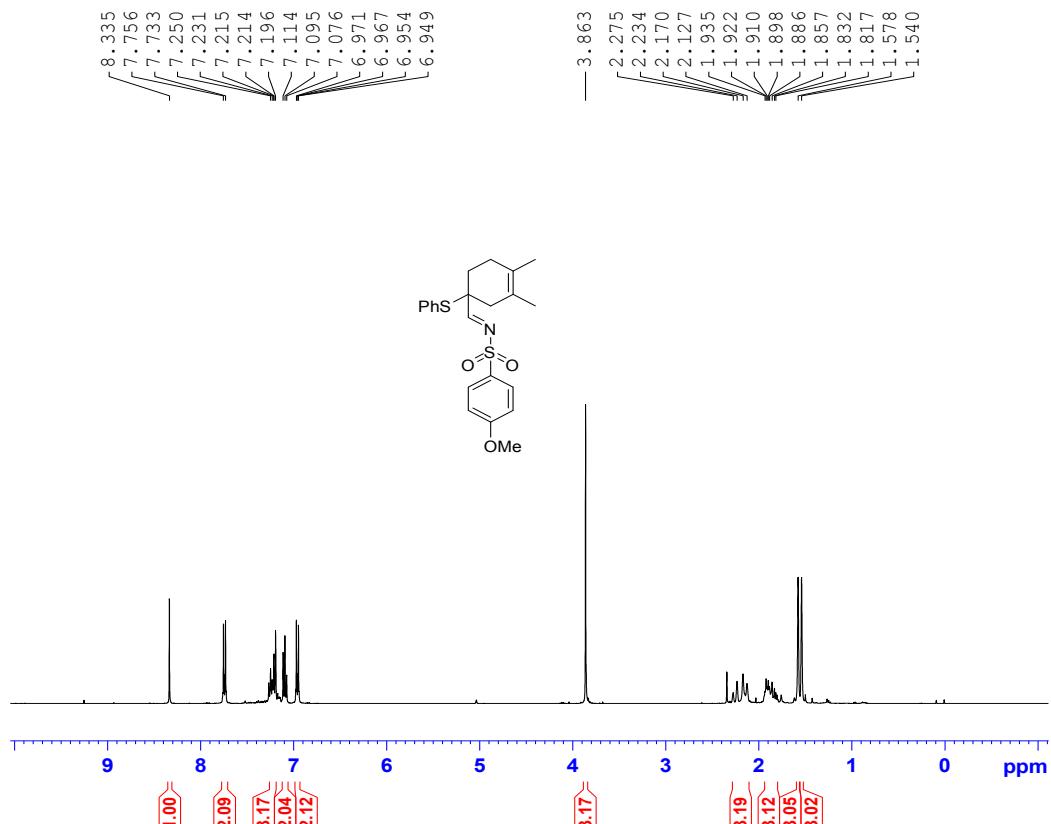
===== CHANNEL f1 ======  
NUC1 <sup>13</sup>C  
P1 9.25 usec  
PLW1 47.0000000 W  
SF01 100.6228289 MHz  
===== CHANNEL f2 ======  
CPDPG2 waltz16  
NUC2 <sup>1</sup>H  
PCPD2 90.0 usec  
PLW2 7.7500000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SF02 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127596 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**N-((3,4-Dimethyl-1-(phenylthio)cyclohex-3-en-1-yl)methylene)-4-methoxybenzenesulfonamide**

(18b) :

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

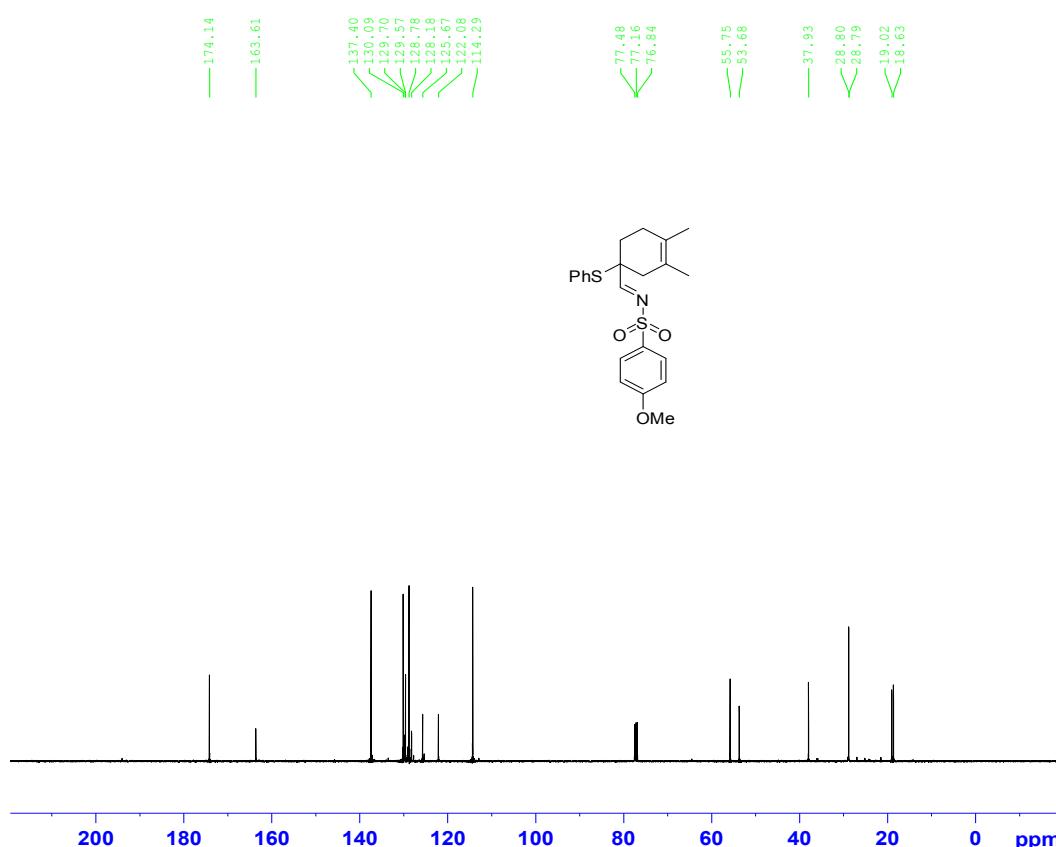


Current Data Parameters  
NAME spa40515  
EXPNO 322  
PROCNO 1

F2 - Acquisition Parameters  
Date 20150510  
Time 6.57  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 31.9  
DW 62.400 usec  
DE 6.50 usec  
TE 298.7 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SFO1 400.1320007 MHz  
  
F2 - Processing parameters  
SI 65536  
SF 400.1300056 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa40515  
EXPNO 323  
PROCNO 1

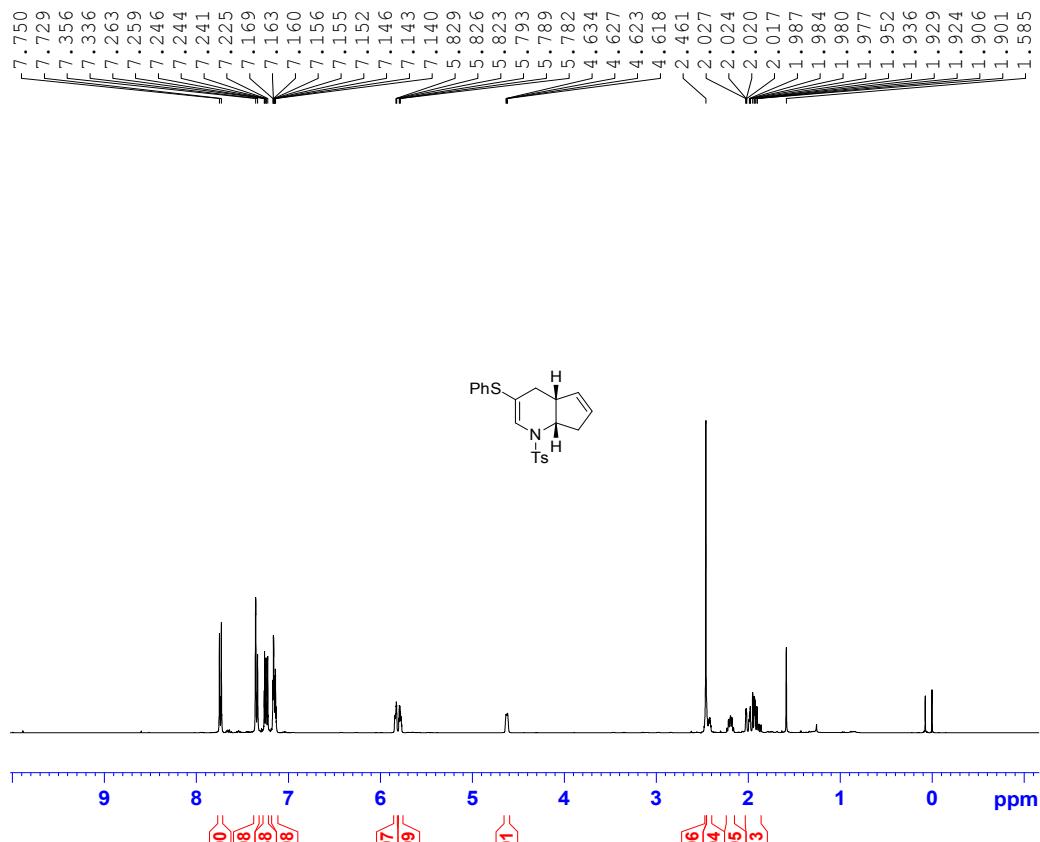
F2 - Acquisition Parameters  
Date 20150510  
Time 7.04  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 16540  
SOLVENT CDCl3  
NS 256  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 299.4 K  
D1 1.0000000 sec  
D11 0.03000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 13C  
P1 9.25 usec  
PLW1 47.0000000 W  
SFO1 100.6228289 MHz  
  
===== CHANNEL f2 ======  
CPDPG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 7.7500000 W  
PLW12 0.23583999 W  
PLW13 0.19103000 W  
SFO2 400.1316005 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127688 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**3-(Phenylthio)-1-tosyl-4,4a,7,7a-tetrahydro-1*H*-cyclopenta[b]pyridine (20a) :**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24 °C)**

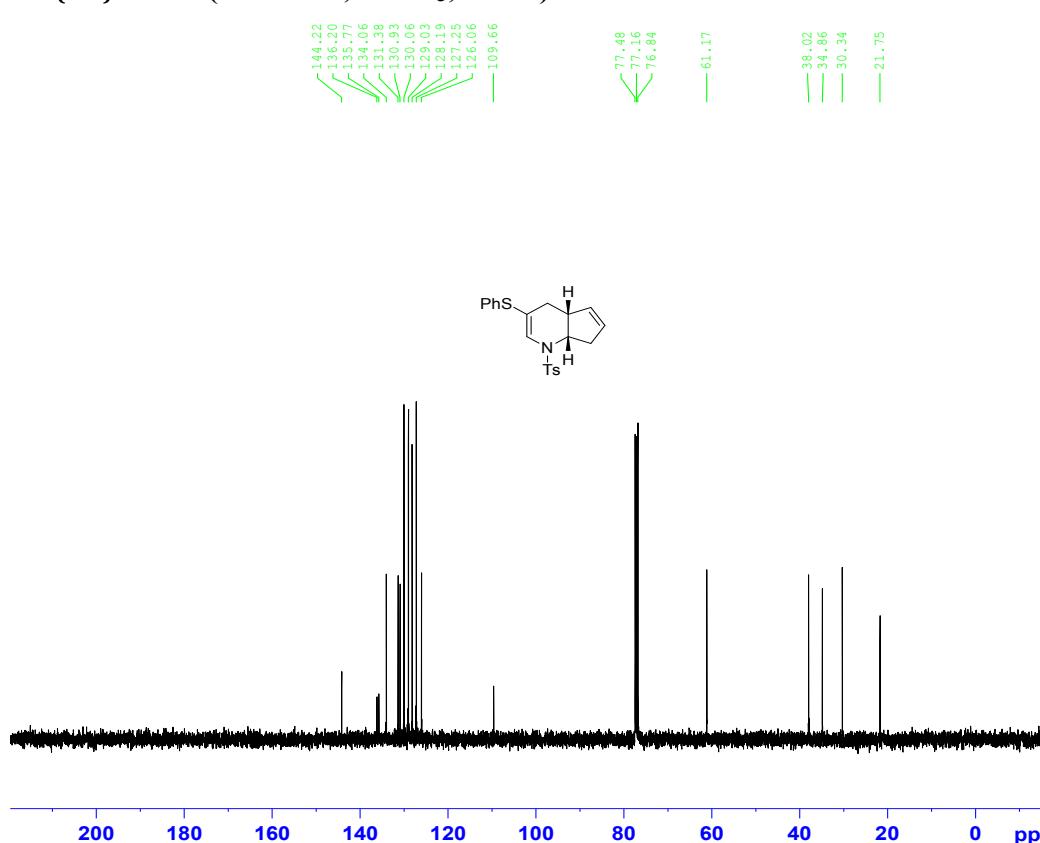


Current Data Parameters  
NAME spa40415  
EXPNO 988  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150430  
Time 23.18  
INSTRUM spect  
PROBHD 5 mm PABBI 1H/  
PULPROG zg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 95.73  
DW 62.400 usec  
DE 6.50 usec  
TE 298.7 K  
D1 0.5000000 sec  
TDO 1

===== CHANNEL f1 ======  
NUC1 1H  
P1 9.00 usec  
PLW1 8.5000000 W  
SFO1 400.1320007 MHz  
  
F2 - Processing parameters  
SI 65536  
SF 400.1300105 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 24 °C)**



Current Data Parameters  
NAME spa40415  
EXPNO 989  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150430  
Time 23.28  
INSTRUM spect  
PROBHD 5 mm PABBI 1H/  
PULPROG zgpg30  
TD 16340  
SOLVENT CDCl<sub>3</sub>  
NS 412  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 299.0 K  
D1 1.0000000 sec  
D11 0.0300000 sec  
TDO 1

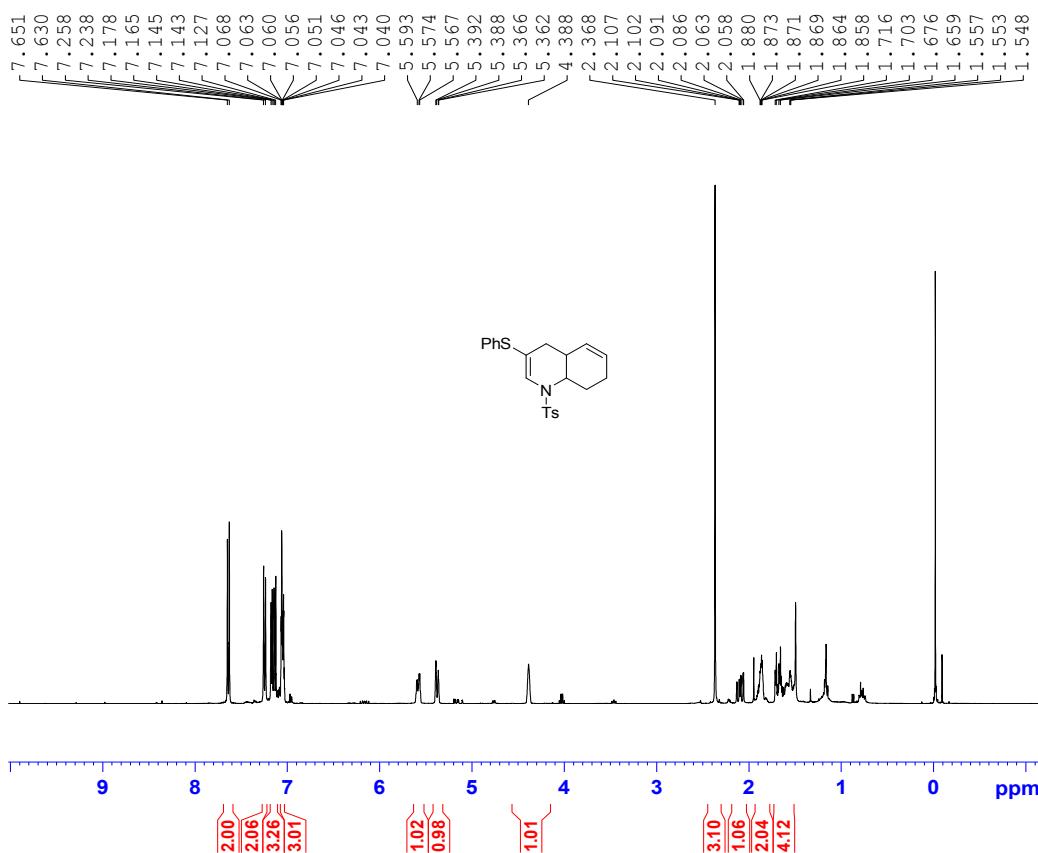
===== CHANNEL f1 ======  
NUC1 13C  
P1 15.00 usec  
PLW1 76.0000000 W  
SFO1 100.6228289 MHz

===== CHANNEL f2 ======  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PLW2 8.5000000 W  
PLW12 0.0850000 W  
PLW13 0.06885000 W  
SFO2 400.1316005 MHz

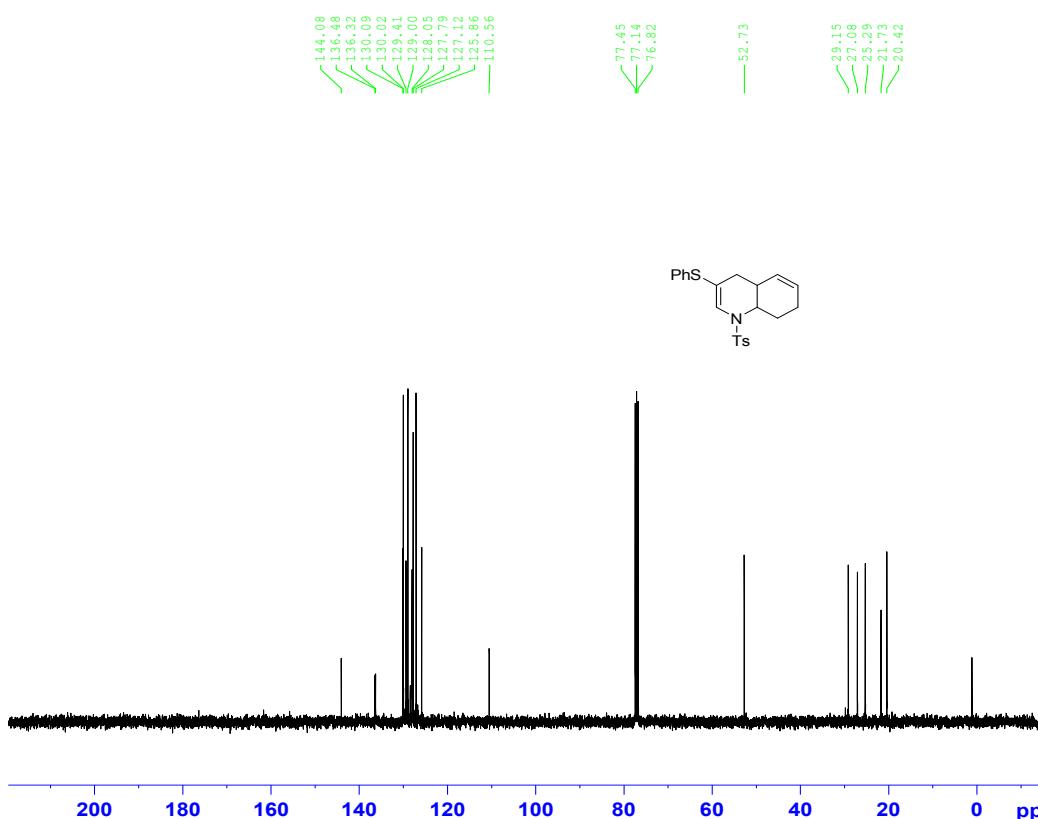
F2 - Processing parameters  
SI 32768  
SF 100.6127563 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**3-(Phenylthio)-1-tosyl-1,4,4a,7,8,8a-hexahydroquinoline (20b) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

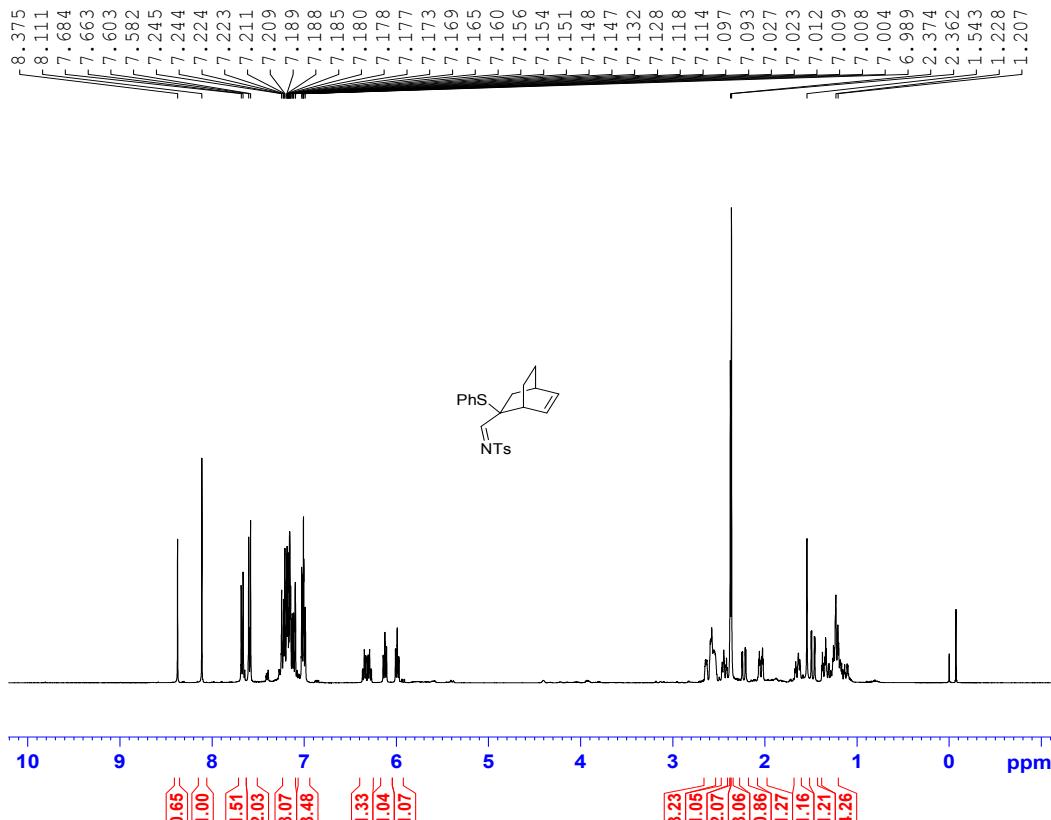


**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**

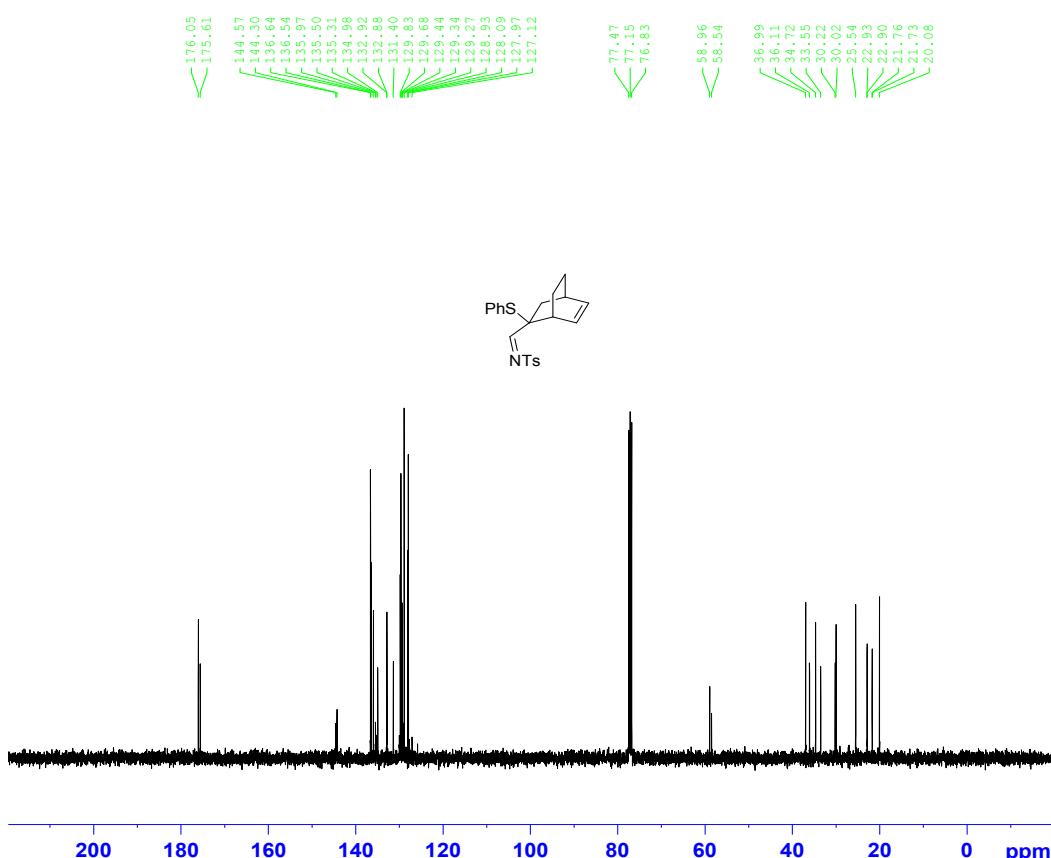


**4-Methyl-N-((*1R,2S,4R*)-2-(phenylthio)bicyclo[2.2.2]oct-5-en-2-yl)methylene)benzenesulfonamide (22) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

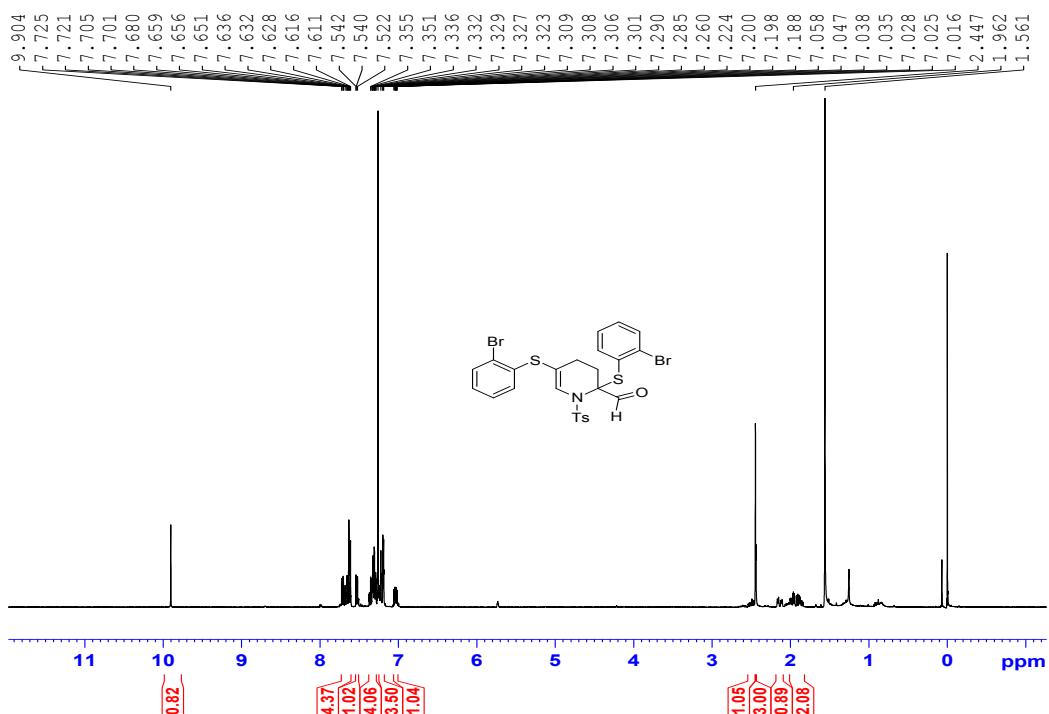


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



**2,5-Bis((2-bromophenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridine-2-carbaldehyde (24) :**

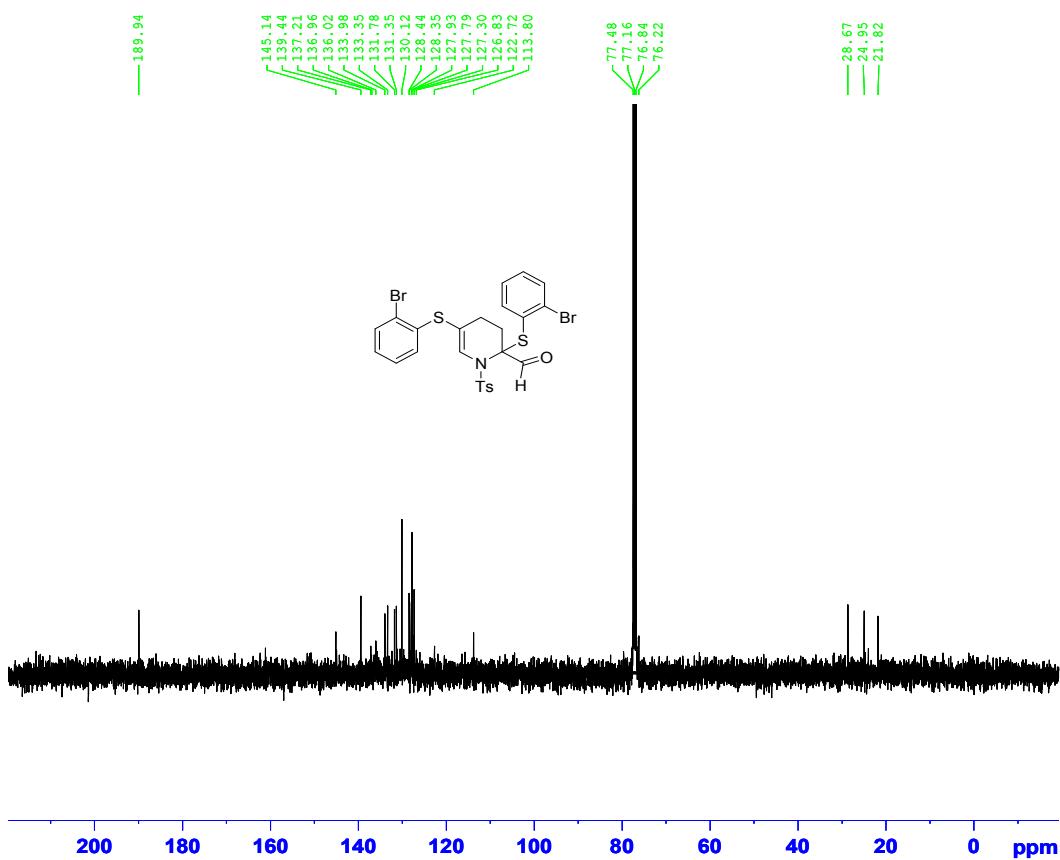
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa40515  
EXPNO 315  
PROCNO 1

F2 - Acquisition Parameters  
Date 20150510  
Time 6.05  
INSTRUM spect  
PROBHD 5 mm PABBO\_BI  
PULPROG zg30  
TD 6536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.1522260 Hz  
AQ 4.089456 sec  
RG 200.34  
DW 62.400 usec  
DE 6.50 usec  
TE 298.5 K  
D1 0.5000000 sec  
TDO 0.5000000 sec  
===== CHANNEL f1 =====  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 W  
SFO1 400.1320007 MHz  
F2 - Processing parameters  
SI 65536  
SF 400.1300095 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



Current Data Parameters  
NAME spa40415  
EXPNO 947  
PROCNO 1

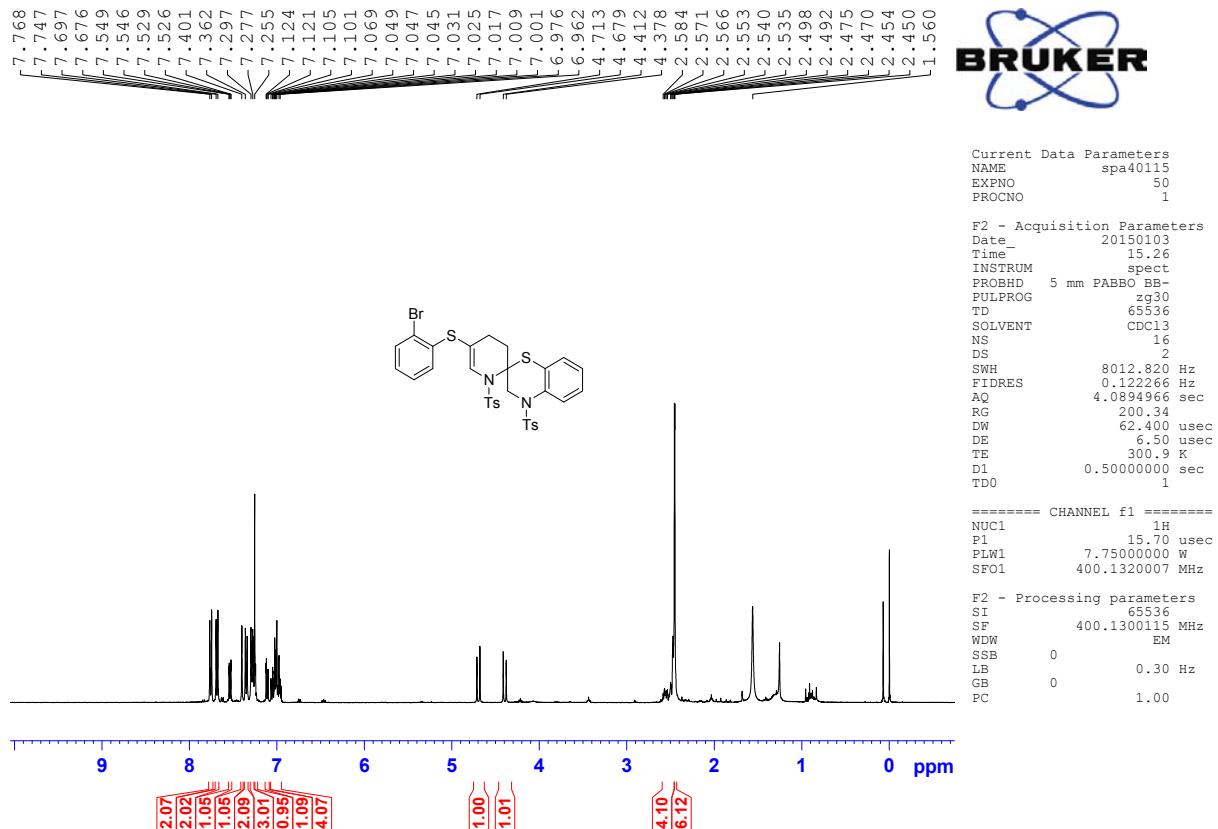
F2 - Acquisition Parameters  
Date 20150430  
Time 1.18  
INSTRUM spect  
PROBHD 5 mm PABBI 1H/  
PULPROG zgpg30  
TD 16540  
SOLVENT CDCl3  
NS 2500  
DS 4  
SWH 24038.461 Hz  
FIDRES 1.453353 Hz  
AQ 0.3440820 sec  
RG 200.34  
DW 20.800 usec  
DE 6.50 usec  
TE 298.9 K  
D1 1.0000000 sec  
D11 0.0300000 sec  
TDO 1

===== CHANNEL f1 =====  
NUC1 13C  
P1 15.00 usec  
PLW1 76.0000000 W  
SFO1 100.6228289 MHz  
===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
FCPD2 90.00 usec  
PLW2 8.5000000 W  
PLW12 0.0850000 W  
PLW13 0.06885000 W  
SFO2 400.1316005 MHz

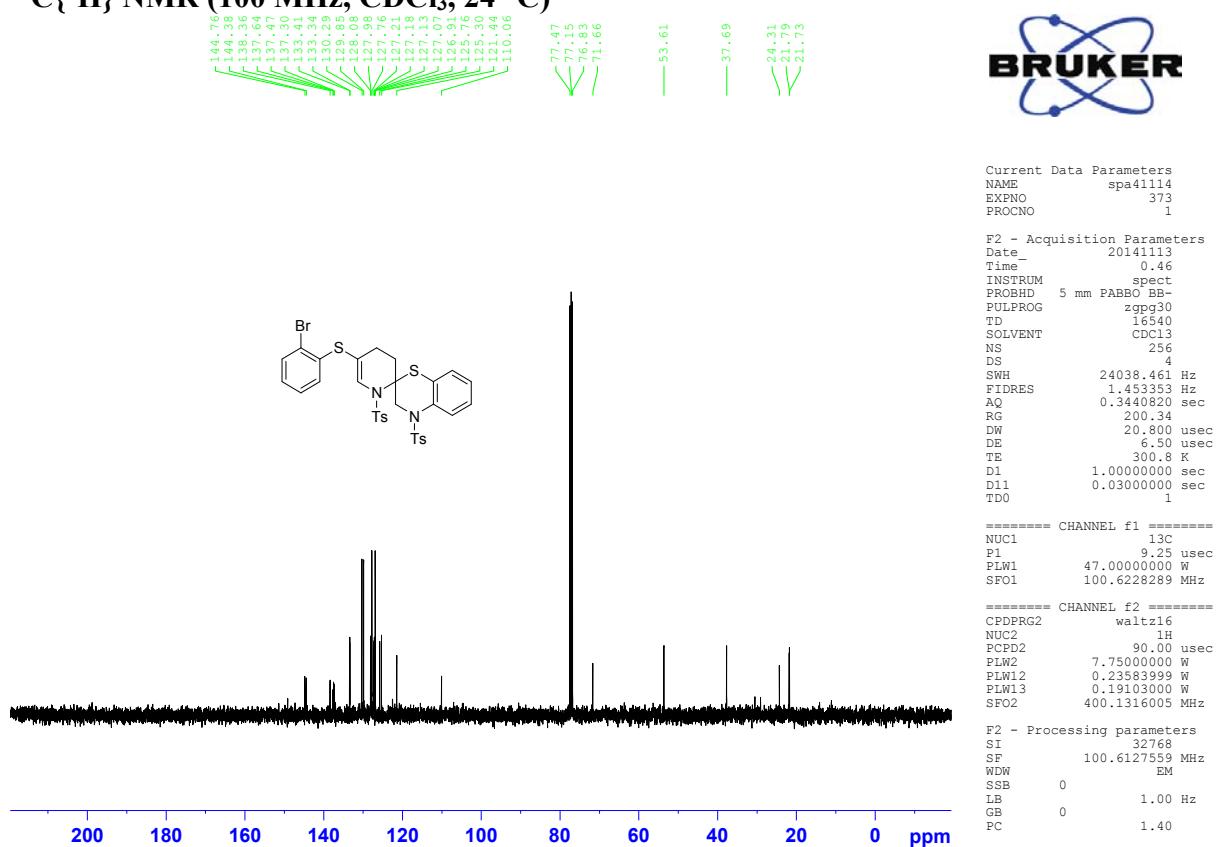
F2 - Processing parameters  
SI 32768  
SF 100.6127537 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

**5'-(2-bromophenyl)thio)-1',4-ditosyl-3,3',4,4'-tetrahydro-1'H-spiro[benzo[b][1,4]thiazine-2,2'-pyridine] (25) :**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**

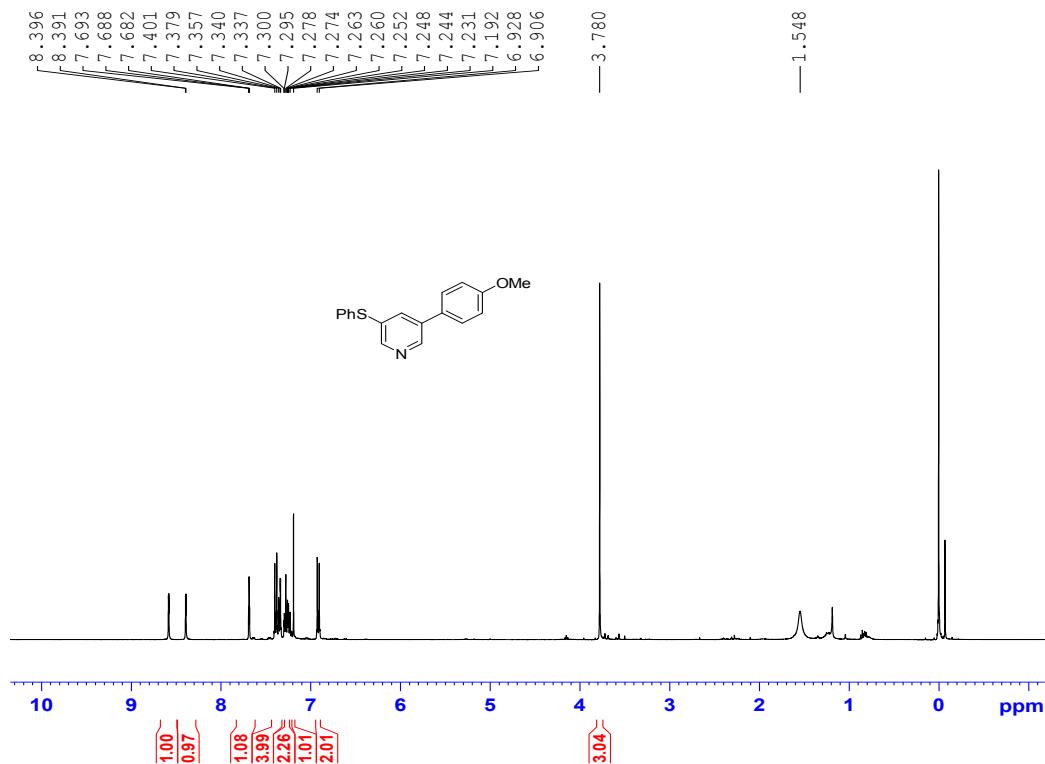


**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**

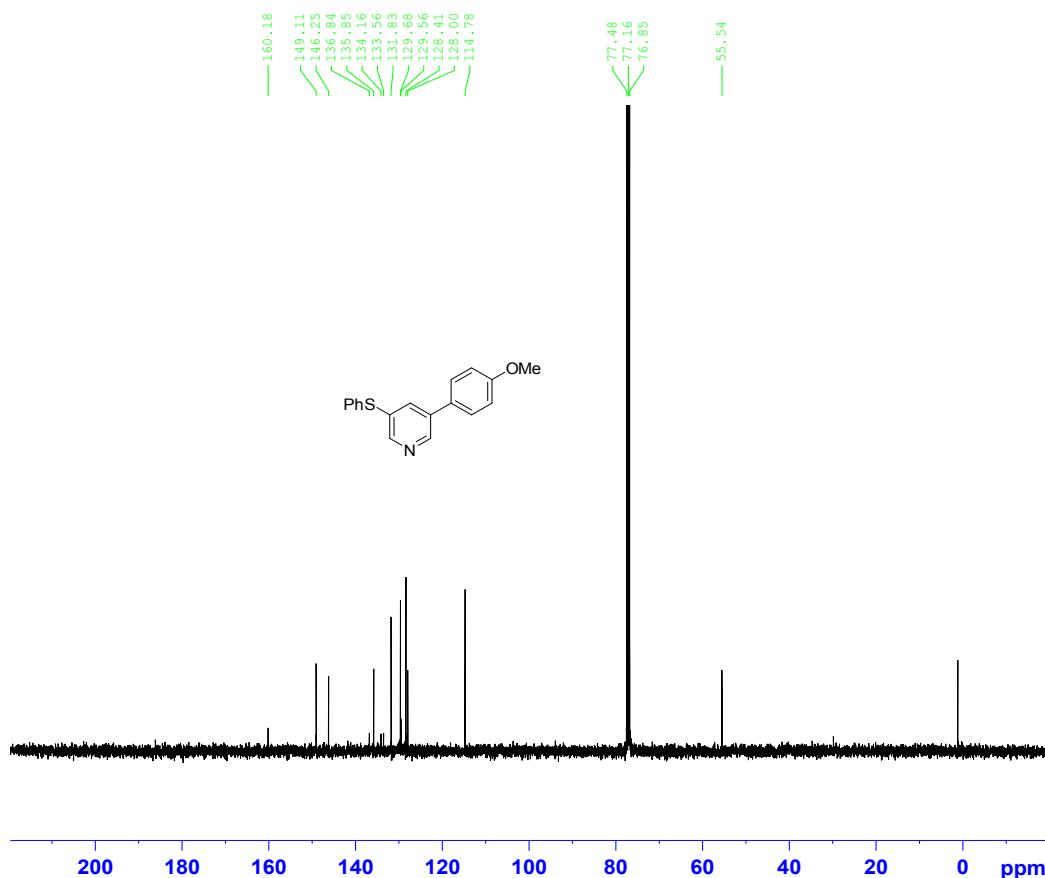


**3- (4-Methoxyphenyl)-5- (phenylthio)pyridine (26) :**

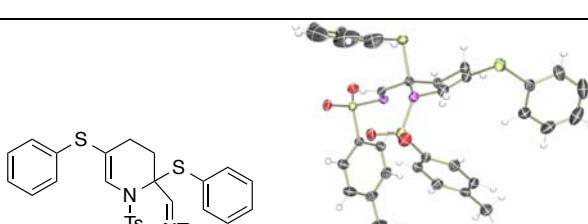
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C)**



**$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 24 °C)**



## 14. Crystallographic Data and Structure Refinements Summary for Compound 3a.

DATA	3a
Molecular Structure (Ortep Structure)	
CCDC number	1040728
Formula	C <sub>32</sub> H <sub>30</sub> N <sub>2</sub> O <sub>4</sub> S <sub>4</sub>
Formula weight	634.86
Color	Colorless
Temperature/K	296(2)
Radiation	Mo K $\alpha$
Wavelength/ $\text{\AA}$	0.71073
Crystal system	Triclinic
Space group	P -1
a ( $\text{\AA}$ )	11.2966(2)
b ( $\text{\AA}$ )	12.1022(3)
c ( $\text{\AA}$ )	12.7036(3)
$\alpha$ ( $^{\circ}$ )	85.244(1)
$\beta$ ( $^{\circ}$ )	70.619(1)
$\gamma$ ( $^{\circ}$ )	77.661(1)
Volume ( $\text{\AA}^3$ )	1600.36(6)
Z	2
Density (g/ml)	1.317
$\mu$ (1/mm)	0.335
F (000)	664
$\theta$ (min, max)	1.723, 25
No. of unique reflns	5632
No. of parameters	381
$R_{\text{obs}}$ , $wR_{2\text{-obs}}$	0.035, 0.092
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ (e $\text{\AA}^{-3}$ )	-0.306, 0.282
GooF	1.029