

## Supporting information

### Palladium-catalyzed indium-mediated reductive aromatic C–H allylation of *N*-benzylsulfonimides with allyl esters

Xue-Ting Zhang and Shi-Kai Tian\*

Key Laboratory of Precision and Intelligent Chemistry and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China

#### Table of contents

General information.....	S-2
Preparation of <i>N</i> -benzylsulfonimides.....	S-2
Preparation of benzyl electrophiles.....	S-4
Preparation of allyl electrophiles.....	S-5
General procedure for the reaction of <i>N</i> -benzylsulfonimides with allyl esters.....	S-6
Analytical data for the products (Schemes 3-4) .....	S-6
References.....	S-12
Copies of NMR spectra.....	S-13

## General information

The <sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>19</sup>F NMR spectra were recorded on a Bruker AC-400 FT spectrometer (400 MHz, 100 MHz, and 376 MHz, respectively) and a Bruker AC-500 FT spectrometer (500 MHz, and 125 MHz, respectively). The chemical shifts of <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were referenced internally with tetramethylsilane ( $\delta$  H 0.00,  $\delta$  C 0.0), or residual protio solvent signals CDCl<sub>3</sub> ( $\delta$  C 77.2). The chemical shifts of <sup>19</sup>F NMR spectra were referenced to external trifluoroacetic acid. Chemical shifts ( $\delta$ ) and coupling constants (*J*) were expressed in ppm and Hz, respectively. The following abbreviations are used in reporting NMR data: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). EI-mass or ESI-mass data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an EI or an ESI source and controlled by Xcalibur software. Melting points are uncorrected.

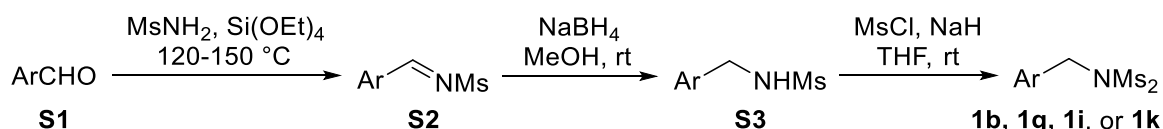
Chemicals were purchased from the Adamas, Energy Chemical, Acros, Accela, Alfa Aesar, and TCI, and used as received.

Abbreviations: Ac = acetyl, BINAP = 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthalene, Bn = benzyl, dba = dibenzylideneacetone, DBU = 1,8-diazabicyclo[5,4,0]undec-7-ene, DCM = dichloromethane, DMA = *N,N*-dimethylacetamide, DMAP = 4-dimethylaminopyridine, DME = 1,2-dimethoxyethane, DMF = *N,N*-dimethylformamide, dppb = 1,4-bis(diphenylphosphino)buthane, dppf = 1,1'-bis(diphenylphosphino)ferrocene, Ms = methanesulfonyl, Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran, TMEDA = *N,N,N',N'*-tetramethylethylenediamine, Ts = *p*-methylbenzenesulfonyl.

## Preparation of *N*-benzylsulfonimides

*N*-Benzylsulfonimides **1a**, **1c-f**, **1h**, and **1l-r** were prepared according to a literature procedure.<sup>1-2</sup>

(1) Preparation of *N*-benzylsulfonimides **1b**, **1g**, **1i**, and **1k**

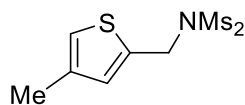


A mixture of aldehyde **S1** (5.0 mmol), methanesulfonamide (571 mg, 6.0 mmol), and tetraethoxysilane (1.0 mL) was heated at 120-150 °C (oil bath) for 24 h, and cooled to room temperature. The mixture was crystallized with petroleum ether, and filtered. The resulting solid was dried in vacuum to give imine **S2**.

To a solution of imine **S2** in methanol (10 mL) at 0 °C was added sodium borohydride (378 mg, 10.0 mmol). The mixture was stirred at room temperature for 2 h, and extracted with dichloromethane (10 mL) three times. The combined organic extracts were dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to give crude sulfonamide **S3**, which was used without further purification.

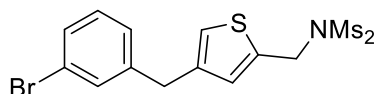
To a solution of sulfonamide **S3** in tetrahydrofuran (10 mL) at 0 °C was added sodium hydride (144 mg, 6.0 mmol). The mixture was stirred at 0 °C for 20 min, and added methanesulfonyl chloride (687 mg, 0.46 mL, 6.0 mmol). The mixture was stirred at room temperature for 2 h, quenched with ice water, and extracted with dichloromethane (10 mL) three times. The combined organic extracts were dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 4/1) to give *N*-

benzylsulfonimide **1b**, **1g**, **1i**, or **1k**.



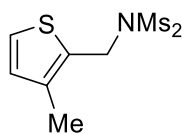
**1b**

*N*-(Methylsulfonyl)-*N*-((4-methylthiophen-2-yl)methyl)methanesulfonamide (**1b**), yellow solid (382 mg, 27% yield for three steps). m.p. 78-82 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.01 (s, 1H), 6.90 (s, 1H), 5.03 (s, 2H), 3.13 (s, 6H), 2.23 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.6, 136.8, 131.6, 122.7, 46.8, 44.1, 15.6. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>14</sub>NO<sub>4</sub>S<sub>3</sub> 284.0079; Found 284.0070.



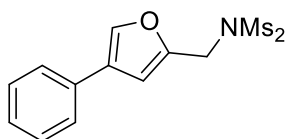
**1g**

*N*-((4-(3-Bromobenzyl)thiophen-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (**1g**), yellow solid (1.27 g, 58% yield for three steps). m.p. 94-98 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 7.21-7.08 (m, 2H), 6.99 (s, 1H), 6.95 (s, 1H), 5.02 (s, 2H), 3.88 (s, 2H), 3.11 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 142.5, 140.6, 137.8, 131.6, 130.7, 130.2, 129.5, 127.3, 123.9, 122.6, 46.8, 44.1, 36.2. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>16</sub>BrNO<sub>4</sub>S<sub>3</sub> 436.9425; Found 436.9418.



**1i**

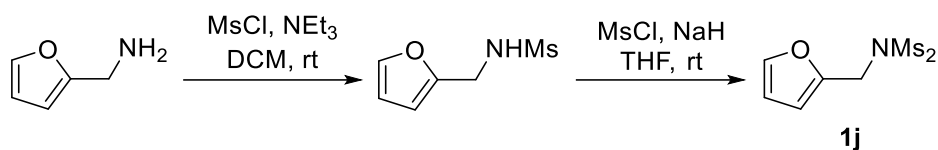
*N*-(Methylsulfonyl)-*N*-((3-methylthiophen-2-yl)methyl)methanesulfonamide (**1i**), yellow solid (495 mg, 35% yield for three steps). m.p. 73-77 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.26 (d, *J* = 4.8 Hz, 1H), 6.80 (d, *J* = 4.8 Hz, 1H), 5.08 (s, 2H), 3.12 (s, 6H), 2.30 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.8, 131.2, 130.1, 126.3, 45.5, 44.1, 13.8. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>14</sub>NO<sub>4</sub>S<sub>3</sub> 283.0007; Found 282.9997.



**1k**

*N*-(Methylsulfonyl)-*N*-((4-phenylfuran-2-yl)methyl)methanesulfonamide (**1k**), yellow solid (345 mg, 21% yield for three steps). m.p. 129-133 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.26-7.17 (m, 1H), 6.74 (s, 1H), 4.89 (s, 2H), 3.13 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.7, 139.0, 131.6, 129.0, 127.7, 127.5, 125.9, 110.1, 44.8, 43.8. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>15</sub>NO<sub>5</sub>S<sub>2</sub>Na 352.0824; Found 352.0819.

## (2) Preparation of *N*-benzylsulfonimide **1j**



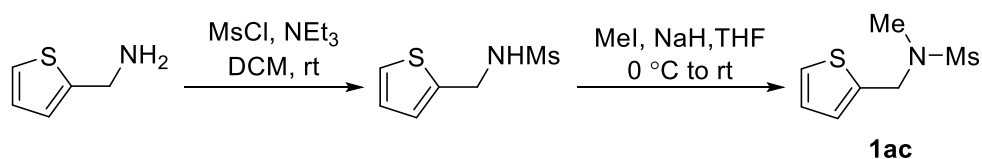
To a solution of furan-2-ylmethanamine (291 mg, 0.26 mL, 3.0 mmol) in dichloromethane (20 mL) at 0 °C was added triethylamine (455 mg, 0.63 mL, 4.5 mmol). The mixture was stirred at 0 °C for 10 min, and added methanesulfonyl chloride (481 mg, 0.33 mL, 4.2 mmol). The mixture was stirred at room temperature for 30 min, quenched with ice water, and extracted with dichloromethane (20 mL) three times. The combined organic extracts were dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give crude *N*-(furan-2-ylmethyl)methanesulfonamide, which was used without further purification.

To a solution of *N*-(furan-2-ylmethyl)methanesulfonamide in tetrahydrofuran (20 mL) under nitrogen atmosphere at 0 °C was added sodium hydride (108 mg, 4.5 mmol). The mixture was stirred at 0 °C for 10 min, and added methanesulfonyl chloride (481 mg, 0.33 mL, 4.2 mmol). The mixture was stirred at room temperature for 2 h, quenched with ice water, and extracted with dichloromethane (20 mL) three times. The combined organic extracts were dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 4/1) to give *N*-(furan-2-ylmethyl)-*N*-(methylsulfonyl)methanesulfonamide (**1j**) as a yellow solid (660 mg, 87% yield for two steps). m.p. 115-119 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47-7.45 (m, 1H), 6.48 (d, *J* = 3.2 Hz, 1H), 6.38 (dd, *J* = 3.2, 2.0 Hz, 1H), 4.94 (s, 2H), 3.16 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 148.6, 143.5, 111.1, 111.0, 44.7, 43.8. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>12</sub>NO<sub>5</sub>S<sub>2</sub> 254.0151; Found 254.0139.

## Preparation of benzyl electrophiles

Benzyl electrophiles **1ab**,<sup>3</sup> **1ad**,<sup>4</sup> **1ae**,<sup>5</sup> and **1ag**<sup>6</sup> were prepared according to literature procedures.

### (1) Preparation of sulfonimide **1ac**

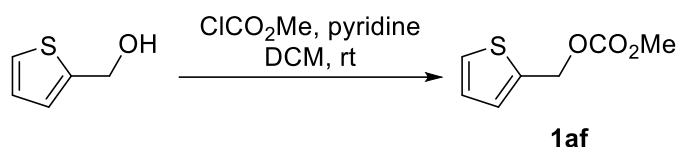


To a solution of 2-thiophenemethylamine (565 mg, 0.51 mL, 5.0 mmol) and triethylamine (758 mg, 1.04 mL, 7.5 mmol) in dichloromethane (30 mL) at 0 °C was added methanesulfonyl chloride (801 mg, 0.54 mL, 7.0 mmol). The mixture was stirred at room temperature for 30 min, quenched with ice water, and extracted with dichloromethane (20 mL) three times. The combined organic extracts were dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give crude *N*-(thiophen-2-ylmethyl)methanesulfonamide as a yellow oil, which was used without further purification.

To a solution of *N*-(thiophen-2-ylmethyl)methanesulfonamide in tetrahydrofuran (30 mL) under nitrogen atmosphere at 0 °C was added sodium hydride (180 mg, 7.5 mmol). The mixture was stirred at 0 °C for 10 min, and added methyl iodide (801 mg, 0.54 mL, 7.0 mmol). The mixture was stirred at room temperature for 2 h, and extracted with dichloromethane (30 mL) three times. The combined organic extracts were dried over anhydrous sodium sulfate, and concentrated under reduced pressure.

The residue was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 4/1), to give *N*-methyl-*N*-(thiophen-2-ylmethyl)methanesulfonamide (**1ac**) as a yellow solid (595 mg, 58% yield for two steps). m.p. 50-54 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.04 (d, *J* = 3.0 Hz, 1H), 6.99 (dd, *J* = 5.2, 3.6 Hz, 1H), 4.55 (s, 2H), 2.87 (s, 3H), 2.76 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.9, 127.7, 127.0, 126.2, 48.5, 36.9, 34.3. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>11</sub>NO<sub>2</sub>S<sub>2</sub> 205.0231; Found 205.0225.

## (2) Preparation of carbonate **1af**

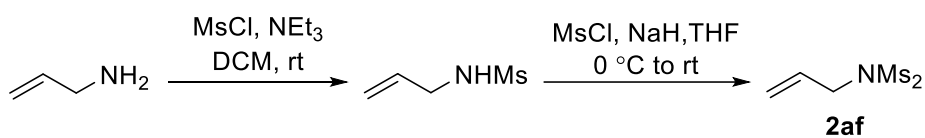


Methyl chloroformate (945 mg, 0.77 mL, 10 mmol) was added dropwise to a solution of 2-thienylmethanol (570 mg, 0.47 mL, 5.0 mmol) and pyridine (1.18 g, 1.21 mL, 15 mmol) in dichloromethane (30 mL) at 0 °C. The mixture was stirred at room temperature for 4 h, and quenched by the dropwise addition of aqueous hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (30 mL) three times. The combined organic extracts were dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 9:1) to give methyl (thiophen-2-ylmethyl) carbonate (**1af**) as a yellow oil (722 mg, 84% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.12 (d, *J* = 3.4 Hz, 1H), 6.97 (dd, *J* = 5.0, 3.4 Hz, 1H), 5.29 (s, 2H), 3.77 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.5, 136.9, 128.7, 127.2, 126.8, 63.6, 54.8. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>8</sub>O<sub>3</sub>S 172.0194; Found 172.0188.

## Preparation of allyl electrophiles

Allyl electrophiles **2ac**,<sup>7</sup> **2ad**,<sup>8</sup> and **2ae**<sup>9</sup> were prepared according to literature procedures.

### Preparation of *N*-allylsulfonamide **2af**

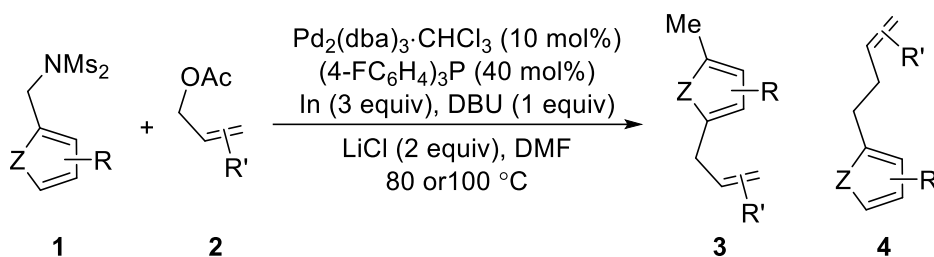


To a solution of allylamine (285 mg, 0.37 mL, 5.0 mmol) and triethylamine (758 mg, 1.04 mL, 7.5 mmol) in dichloromethane (20 mL) at 0 °C was added methanesulfonyl chloride (801 mg, 0.54 mL, 7.0 mmol). The mixture was stirred at room temperature for 30 min, and quenched with ice water. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (20 mL) three times. The combined organic extracts were dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give crude *N*-allylmethanesulfonamide, which was used without further purification.

To a solution of *N*-allylmethanesulfonamide in tetrahydrofuran (20 mL) under nitrogen atmosphere at 0 °C was added sodium hydride (180 mg, 7.5 mmol). The mixture was stirred at 0 °C for 10 min, and added methanesulfonyl chloride (801 mg, 0.54 mL, 7.0 mmol). The mixture was stirred at room temperature for 2 h, and quenched with ice water. The organic layer was separated,

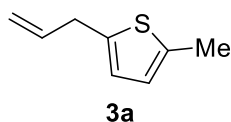
and the aqueous layer was extracted with dichloromethane (20 mL) three times. The combined organic extracts were dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 4/1) to give *N*-allyl-*N*-(methylsulfonyl)methanesulfonamide (**2af**) as a yellow oil (447 mg, 42 % yield for two steps). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 6.12-5.77 (m, 1H), 5.59-5.19 (m, 2H), 4.35 (d, *J* = 6.6 Hz, 2H), 3.29 (s, 6H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 132.4, 120.8, 51.0, 44.0. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>5</sub>H<sub>11</sub>NO<sub>4</sub>S<sub>2</sub> 213.0129; Found 213.0124.

### General procedure for the reaction of *N*-benzylsulfonimides with allyl esters

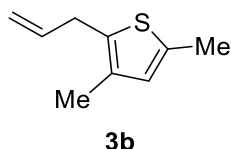


To a suspension of Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (20.7 mg, 0.020 mmol), (4-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P (25.0 mg, 0.080 mmol), In (67.5 mg, 0.60 mmol), LiCl (17.0 mg, 0.40 mmol), and *N*-benzylsulfonimide **1** (0.20 mmol) in *N,N*-dimethylformamide (1.0 mL) under nitrogen atmosphere at room temperature was added DBU (30.4 mg, 29.8 μL, 0.20 mmol) and allyl ester **2** (0.40 mmol). The mixture was heated at 80 or 100 °C (as specified in Schemes 3 and 4, oil bath) for 12 h, and cooled to room temperature. The mixture was directly purified by silica gel chromatography (eluent: petroleum ether) to give allyl(hetero)arene **3**.

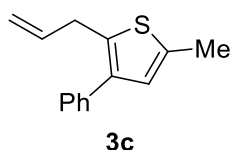
### Analytical data for the products (Schemes 3 and 4)



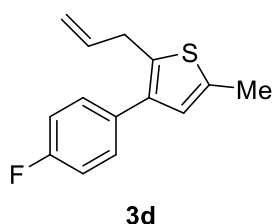
2-Allyl-5-methylthiophene (**3a**),<sup>1</sup> colorless oil (21.5 mg, 78% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.59-6.56 (m, 2H), 6.02-5.91 (m, 1H), 5.17-5.05 (m, 2H), 3.49 (d, *J* = 6.8 Hz, 2H), 2.46 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.7, 138.1, 136.8, 124.9, 124.4, 116.0, 34.5, 15.4. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>10</sub>S 138.0503; Found 138.0498.



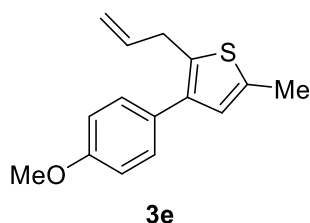
2-Allyl-3,5-dimethylthiophene (**3b**), colorless oil (27.3 mg, 90% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.45 (s, 1H), 5.96-5.85 (m, 1H), 5.16-5.05 (m, 2H), 3.39 (d, *J* = 6.4 Hz, 2H), 2.38 (s, 3H), 2.06 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 136.6, 135.9, 133.0, 132.9, 128.4, 115.6, 32.2, 15.2, 13.6. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>12</sub>S 152.0660; Found 152.0652.



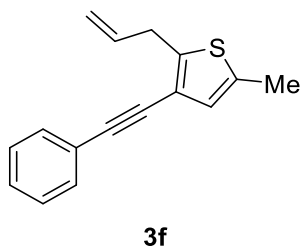
2-Allyl-5-methyl-3-phenylthiophene (**3c**)<sup>1</sup>, colorless oil (30.8 mg, 72% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38-7.33 (m, 4H), 7.29-7.25 (m, 1H), 6.70 (s, 1H), 6.02-5.92 (m, 1H), 5.15-5.06 (m, 2H), 3.53 (d, *J* = 6.4 Hz, 2H), 2.44 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.7, 137.3, 136.9, 136.9, 135.0, 128.7, 128.4, 127.4, 126.8, 116.1, 32.8, 15.3. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>14</sub>S 214.0816, Found 214.0811.



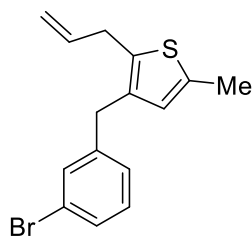
2-Allyl-3-(4-fluorophenyl)-5-methylthiophene (**3d**)<sup>1</sup>, colorless oil (36.2 mg, 78% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31-7.26 (m, 2H), 7.11-6.96 (m, 2H), 6.66 (s, 1H), 6.00-5.90 (m, 1H), 5.16-5.07 (m, 2H), 3.48 (d, *J* = 6.4 Hz, 2H), 2.44 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.8 (d, *J* = 244.3 Hz), 137.7, 137.1, 137.0, 134.9, 132.9 (d, *J* = 3.3 Hz), 130.2 (d, *J* = 7.9 Hz), 127.3, 116.2, 115.3 (d, *J* = 21.1 Hz), 32.7, 15.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -115.7. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>13</sub>FS 232.0722; Found 232.0718.



2-Allyl-3-(4-methoxyphenyl)-5-methylthiophene (**3e**)<sup>1</sup>, colorless oil (26.3 mg, 54% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30-7.25 (m, 2H), 6.94-6.89 (m, 2H), 6.68 (s, 1H), 6.03-5.93 (m, 1H), 5.13-5.04 (m, 2H), 3.82 (s, 3H), 3.51 (d, *J* = 6.0 Hz, 2H), 2.44 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.5, 138.3, 137.4, 136.7, 134.2, 129.7, 129.4, 127.5, 116.1, 113.8, 55.3, 32.8, 15.3. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>14</sub>S 244.0922; Found 244.0918.



2-Allyl-5-methyl-3-(phenylethynyl)thiophene (**3f**)<sup>1</sup>, colorless oil (23.3 mg, 49% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50-7.45 (m, 2H), 7.35-7.29 (m, 3H), 6.71 (s, 1H), 6.04-5.90 (m, 1H), 5.21-5.01 (m, 2H), 3.65 (d, *J* = 6.4 Hz, 2H), 2.40 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.4, 136.8, 136.0, 131.5, 128.4, 128.1, 127.4, 123.6, 119.0, 116.5, 91.4, 84.4, 33.6, 15.3. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>14</sub>S 238.0816; Found 238.0816.



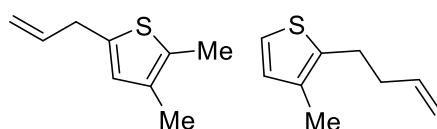
**3g**

2-Allyl-3-(3-bromobenzyl)-5-methylthiophene (**3g**), colorless oil (31.2 mg, 51% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32-7.27 (m, 2H), 7.15-7.02 (m, 2H), 6.37 (s, 1H), 5.94-5.84 (m, 1H), 5.09-5.03 (m, 2H), 3.75 (s, 2H), 3.42 (d, *J* = 6.4 Hz, 2H), 2.35 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.2, 136.8, 136.5, 135.1, 134.4, 131.6, 130.0, 129.2, 127.5, 127.2, 122.6, 116.0, 33.8, 32.2, 15.3. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>15</sub>BrS 306.0078; Found 306.0071.



**3h**

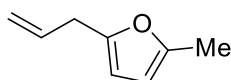
2-Allyl-3-bromo-5-methylthiophene (**3h**)<sup>1</sup>, colorless oil (13.8 mg, 32% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.58 (s, 1H), 5.95-5.86 (m, 1H), 5.16-5.06 (m, 2H), 3.45 (d, *J* = 6.4 Hz, 2H), 2.40 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.0, 135.2, 134.6, 127.8, 116.7, 107.7, 33.5, 15.5. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>9</sub>BrS 215.9608; Found 215.9604.



**3i:4i = 94:6**

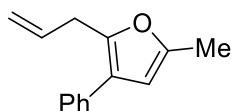
A 94:6 mixture of 5-allyl-2,3-dimethylthiophene (**3i**) and 2-(but-3-en-1-yl)-3-methylthiophene (**4i**) was obtained as a colorless oil (6.69 mg, 22 % yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) for compound **3i**: δ 6.48 (s, 1H), 6.10-5.79 (m, 1H), 5.21-4.98 (m, 2H), 3.42 (d, *J* = 6.5 Hz, 2H), 2.28 (s, 3H), 2.07 (s, 3H). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) for compound **4i**: δ 7.02 (d, *J* = 5.0 Hz, 1H), 6.78 (d, *J* = 5.0 Hz, 1H), 6.10-5.79 (m, 1H), 5.21-4.98 (m, 2H), 2.82 (dd, *J* = 8.0, 7.6 Hz, 2H), 2.44-2.34 (m, 2H), 2.16 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 138.0, 136.9, 136.6, 135.9, 132.8, 130.9, 130.0, 128.5, 127.7, 121.2, 116.0, 115.6, 34.4, 32.2, 27.6, 15.3, 13.7, 13.1. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>12</sub>S 152.0660; Found 152.0651.





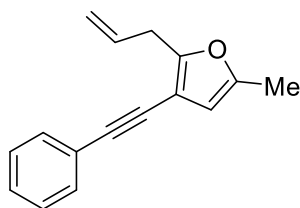
**3j**

2-Allyl-5-methylfuran (**3j**), colorless oil (14.9 mg, 61% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.00-5.85 (m, 3H), 5.17-5.07 (m, 2H), 3.34 (d,  $J = 6.8$  Hz, 2H), 2.26 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.1, 150.8, 134.5, 116.7, 106.2, 106.1, 32.8, 13.6. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_8\text{H}_{10}\text{ONa}$  145.0624; Found 145.0626.



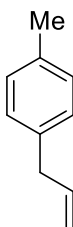
**3k**

2-Allyl-5-methyl-3-phenylfuran (**3k**), colorless oil (31.7 mg, 80% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.33 (m, 4H), 7.27-7.21 (m, 1H), 6.11 (s, 1H), 6.06-5.94 (m, 1H), 5.14-5.07 (m, 2H), 3.48 (d,  $J = 6.0$  Hz, 2H), 2.29 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.6, 147.0, 134.8, 134.3, 128.6, 127.6, 126.4, 122.5, 116.4, 107.2, 31.5, 13.6. HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{14}\text{H}_{14}\text{O}$  198.1045; Found 198.1039.



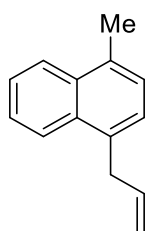
**3l**

2-Allyl-5-methyl-3-(phenylethynyl)furan (**3l**)<sup>1</sup>, colorless oil (17.8 mg, 40% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (dd,  $J = 7.6, 1.6$  Hz, 2H), 7.34-7.26 (m, 3H), 6.01-5.91 (m, 2H), 5.21-5.10 (m, 2H), 3.51 (d,  $J = 6.4$  Hz, 2H), 2.24 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 150.7, 133.6, 131.3, 128.4, 127.9, 123.7, 116.9, 108.4, 104.0, 91.8, 81.9, 31.9, 13.5. HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{16}\text{H}_{14}\text{O}$  222.1045; Found 222.1041.



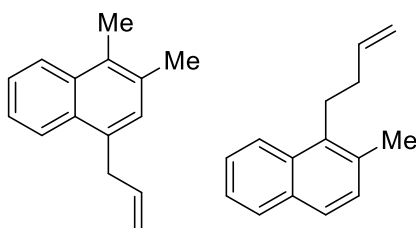
**3m**

1-Allyl-4-methylbenzene (**3m**)<sup>10</sup>, colorless oil (2.64 mg, 10% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12-7.07 (m, 4H), 6.01-5.90 (m, 1H), 5.09-5.03 (m, 2H), 3.35 (d,  $J = 6.8$  Hz, 2H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.9, 137.1, 135.7, 129.2, 128.6, 115.7, 40.0, 21.1. HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{10}\text{H}_{12}$  132.0939; Found 132.0934.



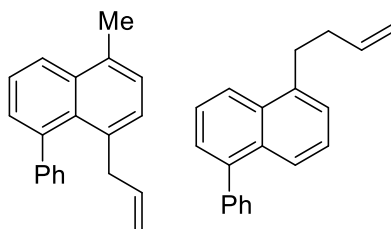
**3n**

1-Allyl-4-methylnaphthalene (**3n**)<sup>1</sup>, colorless oil (34.6 mg, 95% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05-7.99 (m, 2H), 7.53-7.48 (m, 2H), 7.25-7.21 (m, 2H), 6.15-6.05 (m, 1H), 5.10-5.05 (m, 2H), 3.80 (d, *J* = 6.4 Hz, 2H), 2.66 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.3, 134.3, 133.0, 133.0, 132.1, 126.4, 126.1, 125.5, 125.4, 124.9, 124.7, 116.1, 37.4, 19.6. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>14</sub> 182.1096; Found 182.1090.



**3o:4o** = 85:15

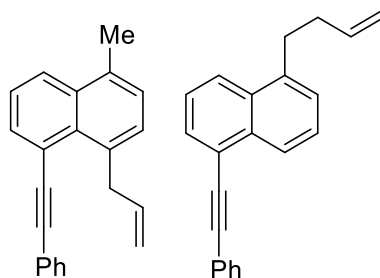
A 85:15 mixture of 4-allyl-1,2-dimethylnaphthalene (**3o**)<sup>1</sup> and 1-(but-3-en-1-yl)naphthalene (**4o**)<sup>1</sup> was obtained as a colorless oil (13.7 mg, 35% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for compound **3o**: δ 8.05 (d, *J* = 8.0 Hz, 1H), 8.00 (t, *J* = 8.0 Hz, 1H), 7.50-7.45 (m, 2H), 7.16 (s, 1H), 6.15-6.08 (m, 1H), 5.11-5.06 (m, 2H), 3.78 (d, *J* = 6.4 Hz, 2H), 2.58 (s, 3H), 2.46 (s, 3H). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for compound **4o**: 8.00 (t, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.45-7.38 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 6.04-5.95 (m, 1H), 5.11-5.06 (m, 2H), 3.18-3.14 (m, 2H), 2.50 (s, 3H), 2.40-2.34 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.5, 137.5, 135.1, 133.5, 133.4, 133.1, 132.9, 132.7, 132.2, 130.8, 129.9, 129.8, 129.3, 128.7, 126.3, 126.0, 125.5, 124.6, 124.6, 124.5, 124.5, 123.7, 116.0, 114.9, 37.3, 34.1, 28.2, 20.9, 20.3, 14.6. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>17</sub> 197.1325; Found 197.1324.



**3p:4p** = 86:14

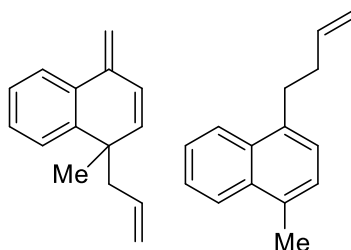
A 86:14 mixture of 4-allyl-1-methyl-5-phenylnaphthalene (**3p**)<sup>1</sup> and 1-(but-3-en-1-yl)-5-phenylnaphthalene (**4p**)<sup>1</sup> was obtained as a colorless oil (43.9 mg, 85% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for compound **3p**: δ 8.04 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.48-7.44 (m, 1H), 7.39-7.26 (m, 7H), 7.23-7.19 (m, 1H), 5.65-5.56 (m, 1H), 4.85 (dd, *J* = 10.0, 1.6 Hz, 1H), 4.67-4.62 (m, 1H), 3.07 (d, *J* = 6.4

Hz, 2H), 2.70 (s, 3H).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for compound **4p**: 8.08-8.05 (m, 1H), 7.78-7.74 (m, 1H), 7.53 (dd,  $J = 8.0, 6.8$  Hz, 1H), 7.48-7.44 (m, 3H), 7.42-7.36 (m, 5H), 6.01-5.95 (m, 1H), 5.12 (dd,  $J = 16.0, 1.6$  Hz, 1H), 5.03 (dd,  $J = 10.2, 1.6$  Hz, 1H), 3.27-3.15 (m, 2H), 2.56-2.51 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.3, 141.3, 141.2, 140.5, 138.6, 138.4, 138.2, 135.5, 134.3, 133.2, 132.2, 132.2, 130.8, 130.3, 130.0, 129.4, 128.8, 128.3, 127.9, 127.3, 126.9, 126.7, 126.1, 125.7, 125.3, 124.9, 124.7, 124.3, 123.4, 115.3, 115.1, 40.1, 35.0, 33.0, 20.4. HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{20}\text{H}_{18}$  258.1409; Found 258.1406.



**3q:4q = 90:10**

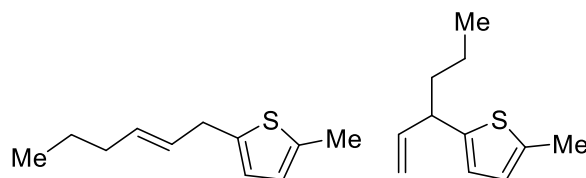
A 90:10 mixture of 4-allyl-1-methyl-5-(phenylethynyl)naphthalene (**3q**)<sup>1</sup> and 1-(but-3-en-1-yl)-5-(phenylethynyl)naphthalene (**4q**) was obtained as a colorless oil (50.8 mg, 90% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for compound **3q**:  $\delta$  8.01 (dd,  $J = 8.8, 0.8$  Hz, 1H), 7.83 (d,  $J = 6.4$  Hz, 1H), 7.58-7.54 (m, 2H), 7.44 (t,  $J = 7.6$  Hz, 1H), 7.38-7.30 (m, 3H), 7.28-7.25 (m, 2H), 6.36-6.27 (m, 1H), 5.07-4.97 (m, 2H), 4.47 (d,  $J = 6.0$  Hz, 2H), 2.65 (s, 3H).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for compound **4q**: 8.36 (d,  $J = 8.4$  Hz, 1H), 8.04-8.00 (m, 1H), 7.75 (d,  $J = 7.2$  Hz, 1H), 7.64 (dd,  $J = 8.0, 1.2$  Hz, 2H), 7.38-7.30 (m, 3H), 7.06-7.01 (m, 3H), 5.98-5.88 (m, 1H), 5.07-4.97 (m, 2H), 3.23-3.11 (m, 2H), 2.52-2.47 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.2, 138.2, 135.8, 135.7, 135.6, 135.5, 135.4, 134.6, 134.0, 133.7, 131.8, 131.5, 131.2, 130.2, 129.3, 128.6, 128.3, 127.2, 126.7, 126.5, 126.2, 125.2, 125.0, 124.6, 124.0, 119.9, 116.2, 116.1, 116.0, 115.9, 115.2, 115.1, 94.4, 93.8, 92.7, 88.0, 39.9, 35.0, 32.7, 20.3. HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{22}\text{H}_{18}$  282.1409; Found 282.1405.



**5:4r = 77:23**

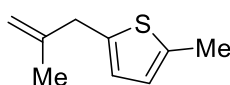
A 77:23 mixture of 1-allyl-1-methyl-4-methylene-1,4-dihydronaphthalene (**5**) and 1-(but-3-en-1-yl)-4-methylnaphthalene (**4r**) was obtained as a colorless oil (21.2 mg, 54% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for compound **5**:  $\delta$  7.75 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.36 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.29 (td,  $J = 8.0, 1.2$  Hz, 1H), 7.25-7.22 (m, 1H), 6.40 (d,  $J = 10.0$  Hz, 1H), 5.67 (d,  $J = 10.4$  Hz, 1H), 5.64 (s, 1H), 5.52-5.41 (m, 1H), 5.01 (s, 1H), 4.92-4.84 (m, 2H), 2.61-2.55 (m, 1H), 2.37-2.32 (m, 1H), 1.40 (s, 3H).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for compound **4r**: 8.07-7.96 (m, 2H), 7.53-7.49 (m, 2H), 7.21-7.18 (m, 2H), 6.01-5.89 (m, 1H), 5.09 (dd,  $J = 16.0, 1.6$  Hz, 1H), 5.06-5.02 (m, 1H), 3.16-3.11 (m, 1H), 2.67 (s,

3H), 2.61-2.55 (m, 1H), 2.52-2.45 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 142.0, 138.5, 137.9, 136.4, 136.2, 134.9, 133.1, 132.7, 132.0, 131.5, 128.2, 127.4, 126.7, 126.4, 126.2, 125.8, 125.5, 125.4, 125.0, 124.4, 123.3, 117.2, 115.0, 109.0, 48.8, 40.8, 38.7, 35.1, 32.6, 30.4. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>16</sub>Na 219.1144; Found 219.1153.



**3s:3s'** = 75:25

A 75:25 mixture of (*E*)-2-(hex-2-en-1-yl)-5-methylthiophene (**3s**) and 2-(hex-1-en-3-yl)-5-methylthiophene (**3s'**) was obtained as a colorless oil (16.6 mg, 46% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for compound **3s**: δ 6.57-6.53 (m, 2H), 5.61-5.47 (m, 2H), 3.49 (d, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 2.10 (q, *J* = 7.2 Hz, 2H), 1.46-1.37 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for compound **3s'**: δ 6.57-6.53 (m, 2H), 5.90-5.82 (m, 1H), 5.07-5.01 (m, 2H), 3.47-3.41 (m, 1H), 2.42 (s, 3H), 1.72-1.63 (m, 2H), 1.37-1.30 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 146.4, 142.0, 137.8, 137.6, 132.2, 131.2, 128.4, 127.7, 124.8, 124.7, 123.8, 123.1, 114.4, 45.2, 38.5, 29.3, 28.0, 22.9, 20.6, 15.4, 14.0, 14.0. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> Calcd for C<sub>11</sub>H<sub>16</sub>SNa 203.0865; Found 203.0884.

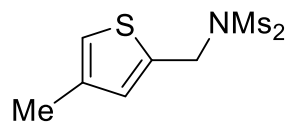


**3t**

2-Methyl-5-(2-methylallyl)thiophene (**3t**), colorless oil (14.9 mg, 49% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.75-6.40 (m, 2H), 4.82-4.80 (m, 2H), 3.42 (s, 2H), 2.43 (s, 3H), 1.73 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.8, 140.5, 138.2, 125.2, 124.8, 112.0, 38.9, 21.9, 15.5. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>12</sub>S 152.0660; Found 152.0653.

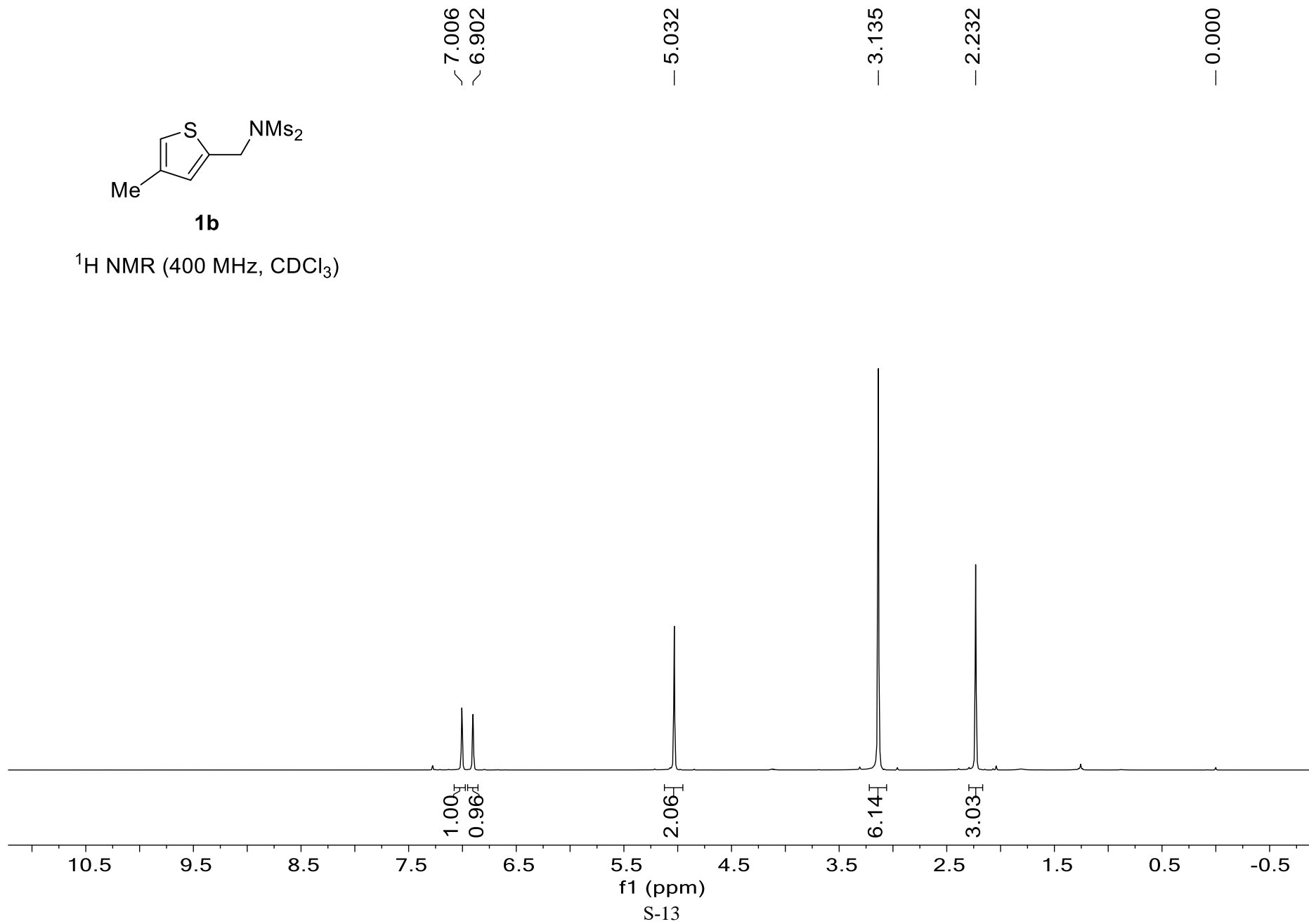
## References

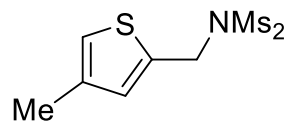
1. M.-Z. Zhu, D. Xie and S.-K. Tian, *Org. Lett.*, 2021, **23**, 6877-6881.
2. J. Dalluhm, H. Prohl and D. Henschel, *Phosphorus Sulfur; Silicon* 1996, **114**, 149-160.
3. M.-B. Li, X.-L. Tang and S.-K. Tian, *Adv. Synth. Catal.*, 2011, **353**, 1980-1984.
4. W.-J. Pan and Z.-X. Wang, *Asian J. Org. Chem.*, 2018, **7**, 1626-1634.
5. K. Zhang, O. Provot, M. Alami and C. Tran, *J. Org. Chem.*, 2022, **87**, 1249-1261.
6. F. Bavo, H. de-Jong and J. Petersen, *J. Med. Chem.*, 2021, **64**, 17795-17812.
7. J. D. V. David and J. K. Michael, *J. Am. Chem. Soc.*, 2013, **135**, 10986-10989.
8. A. F. Rodney, S. Y. Sandhya and K. Praveen, *Org. Biomol. Chem.*, 2022, **20**, 427-443.
9. B. Yang and Z.-X. Wang, *J. Org. Chem.*, 2019, **84**, 1500-1509.
10. B. M. Nestl, S. M. Glueck and M. Hall. *Eur. J. Org. Chem.* 2006, **20**, 4573-4577.



**1b**

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





**1b**

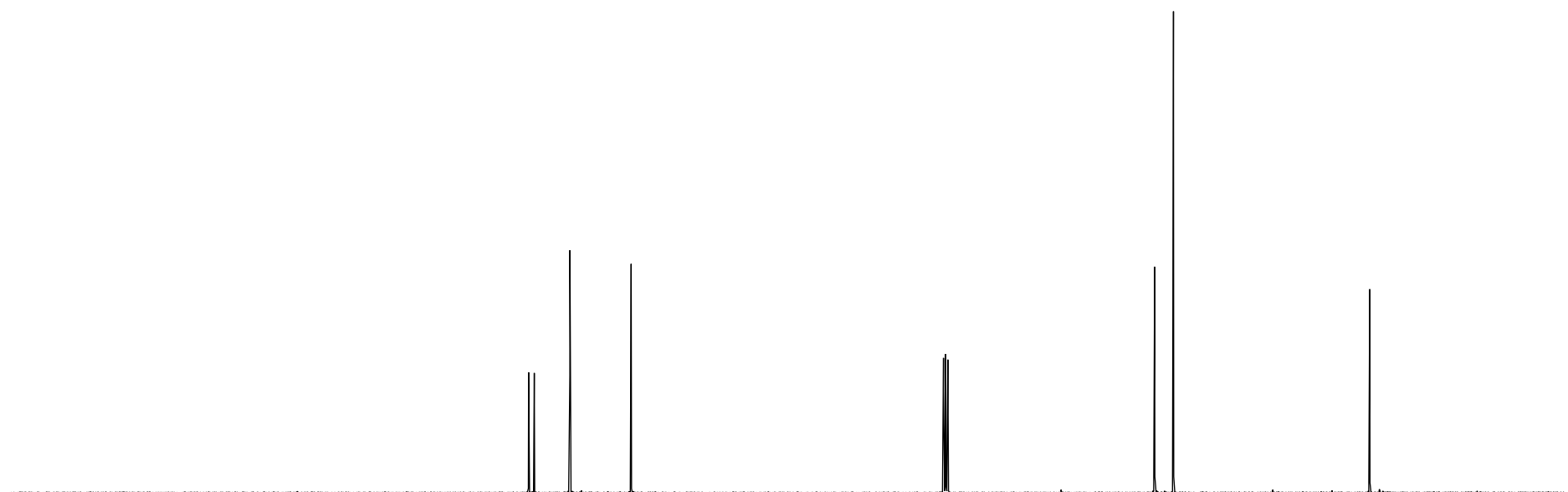
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

137.663  
136.841  
131.669  
— 122.784

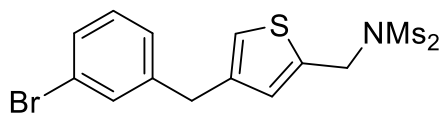
77.478  
77.160  
76.841

46.841  
44.114

— 15.636



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10  
f1 (ppm)  
S-14



**1g**

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

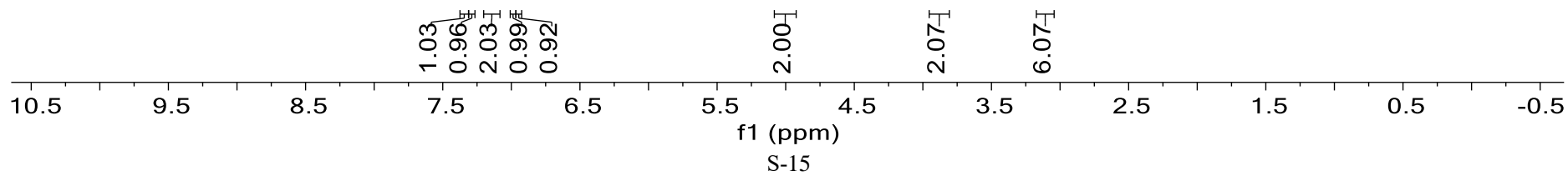
7.349  
7.330  
7.275  
7.182  
7.163  
7.144  
7.120  
7.101  
6.986  
6.951

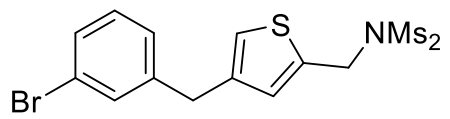
— 5.020

— 3.883

— 3.111

— 0.000





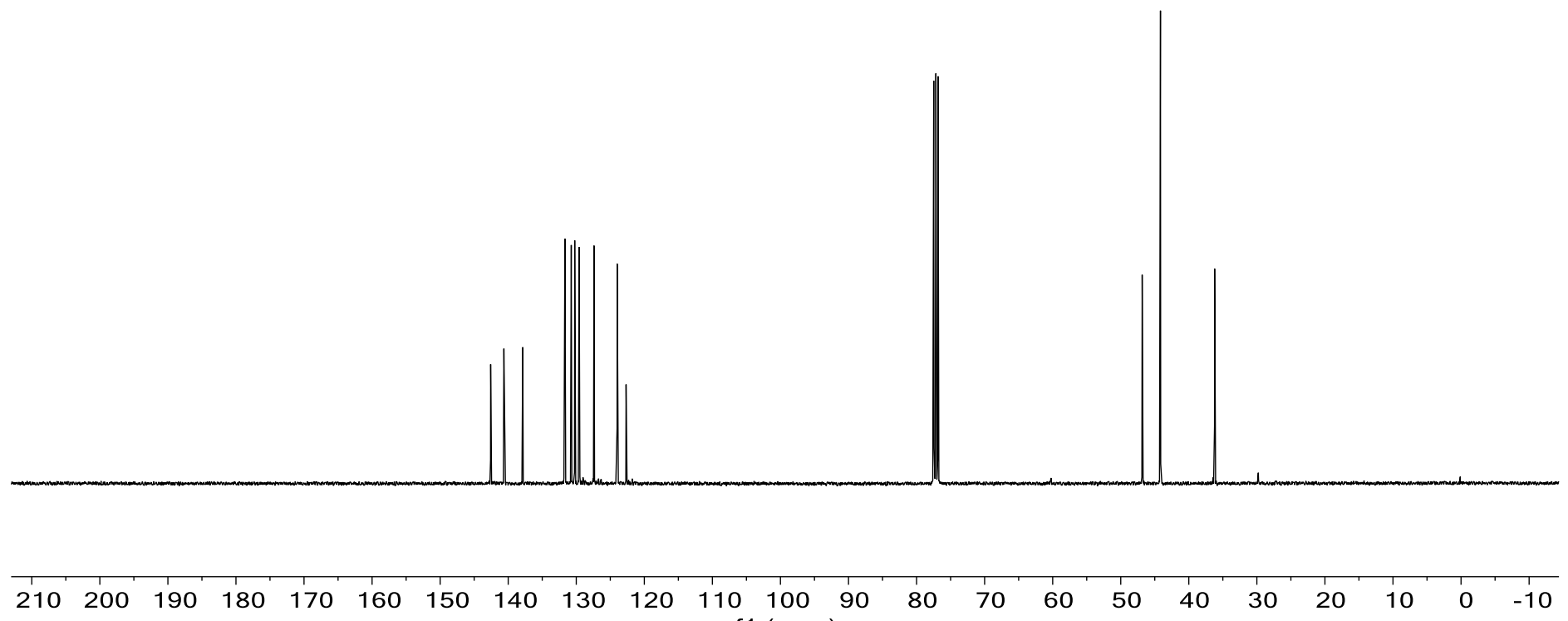
**1g**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

142.580  
140.633  
137.861  
131.664  
130.735  
130.228  
129.578  
127.388  
123.991  
122.681

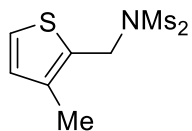
77.478  
77.160  
76.842

46.851  
44.164  
36.208



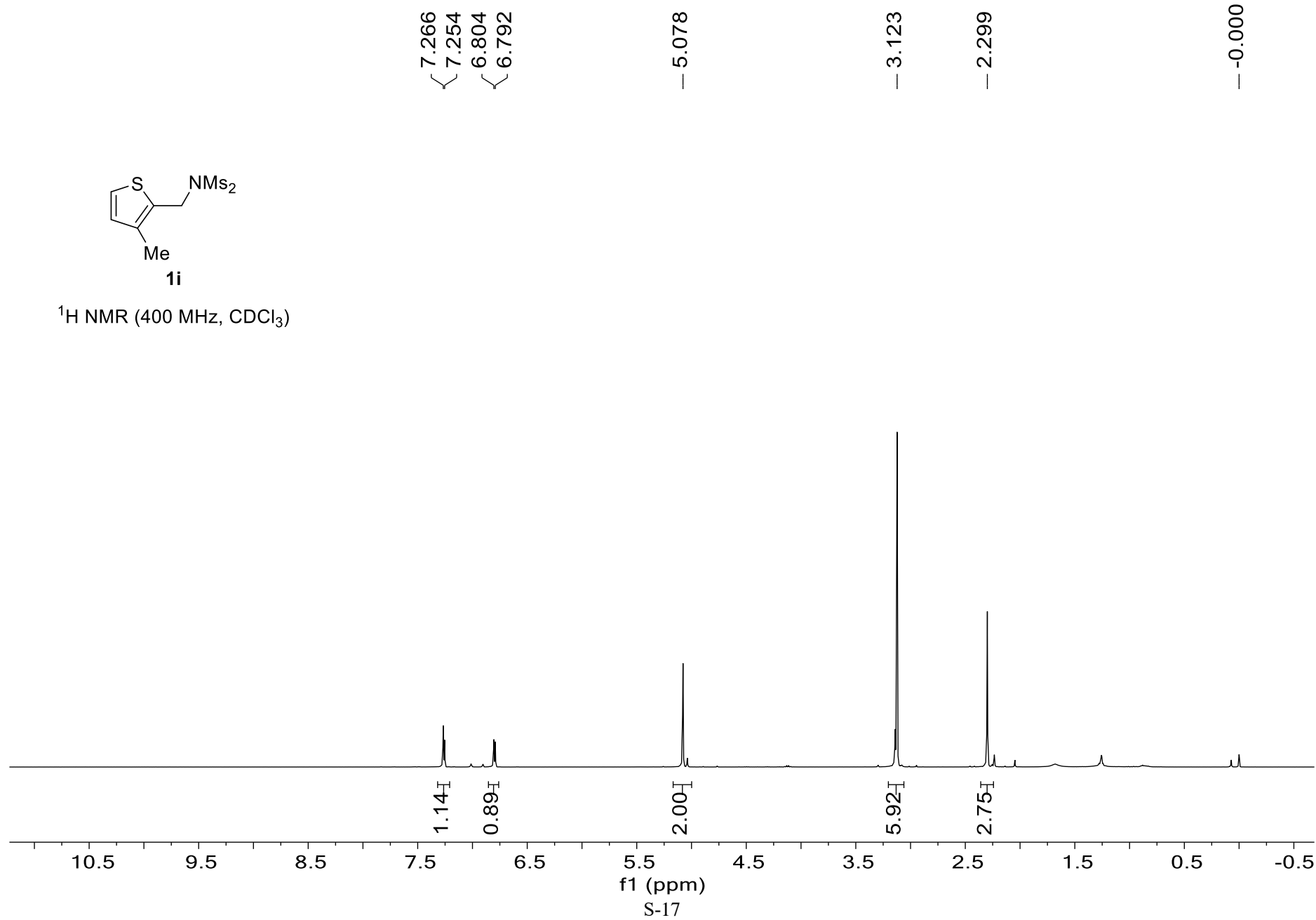
f1 (ppm)  
S-16

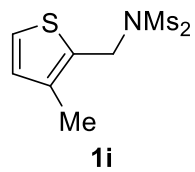




**1i**

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





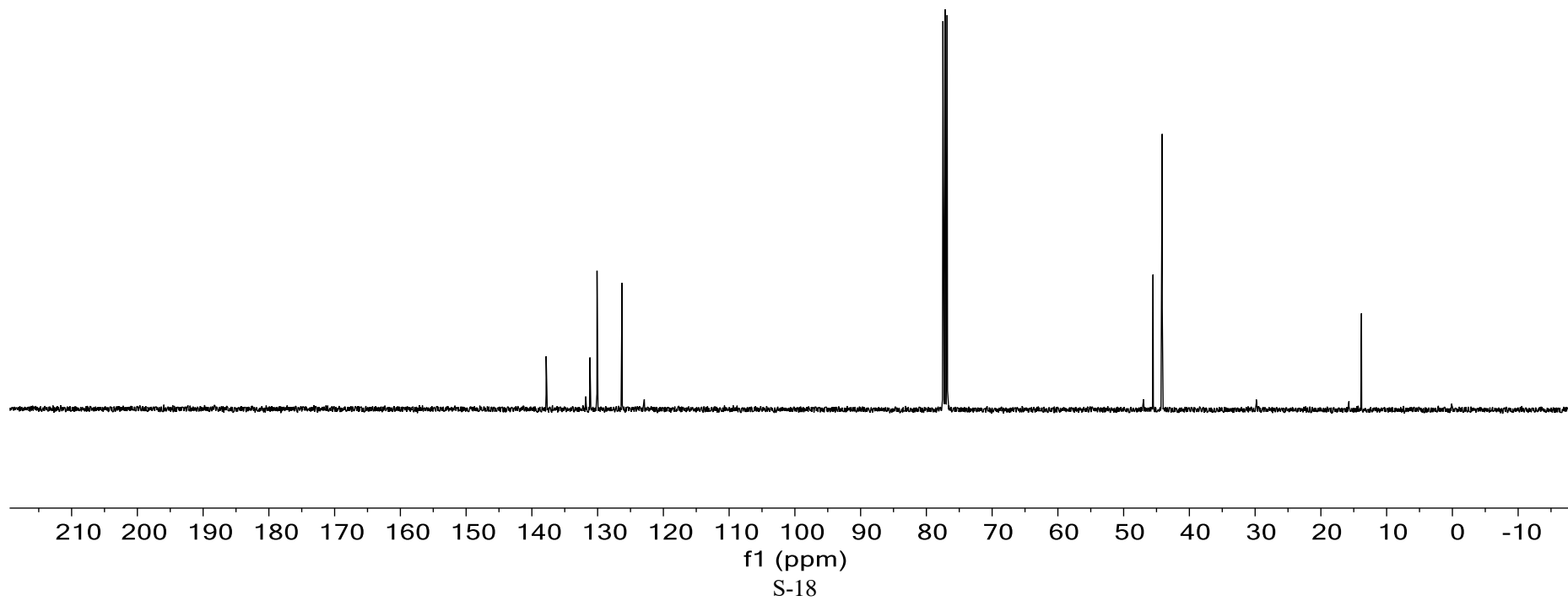
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

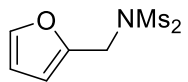
~ 137.826  
~ 131.166  
~ 130.087  
~ 126.286

{ 77.478  
{ 77.160  
{ 76.843

~ 45.526  
~ 44.136

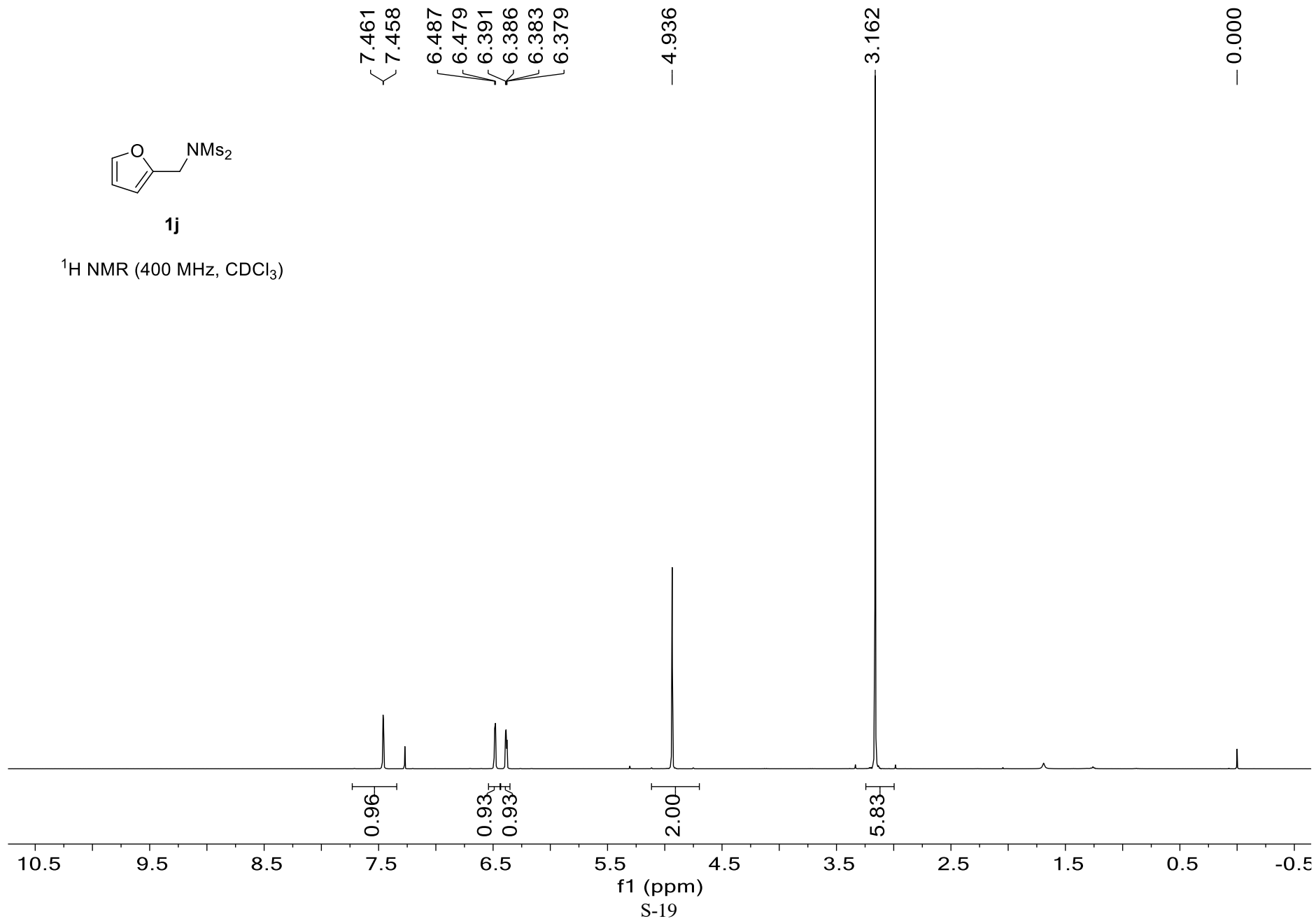
— 13.828

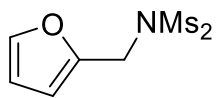




**1j**

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





**1j**

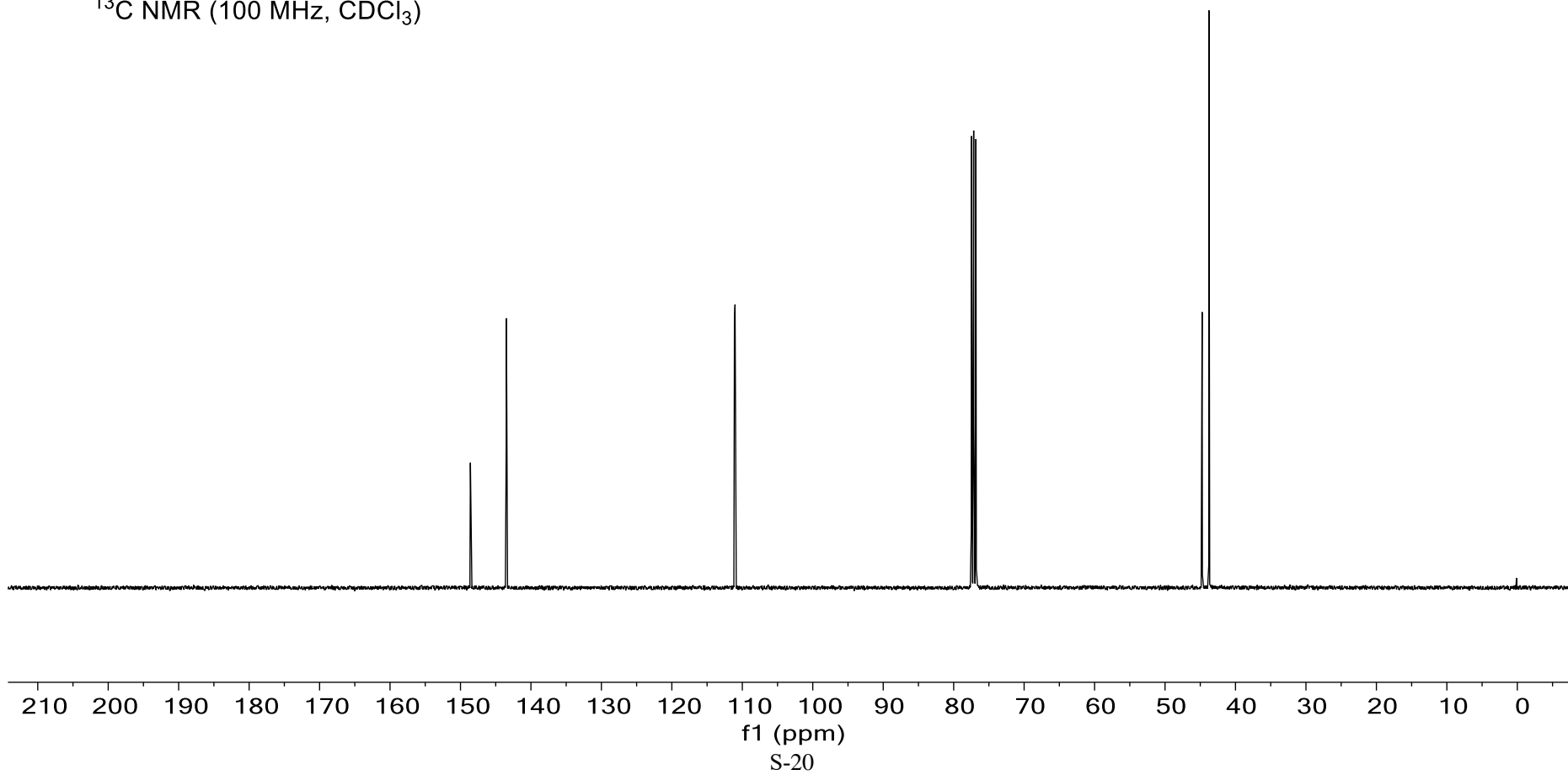
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

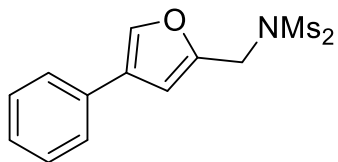
— 148.594  
— 143.478

{ 111.119  
{ 111.031

{ 77.478  
{ 77.160  
{ 76.842

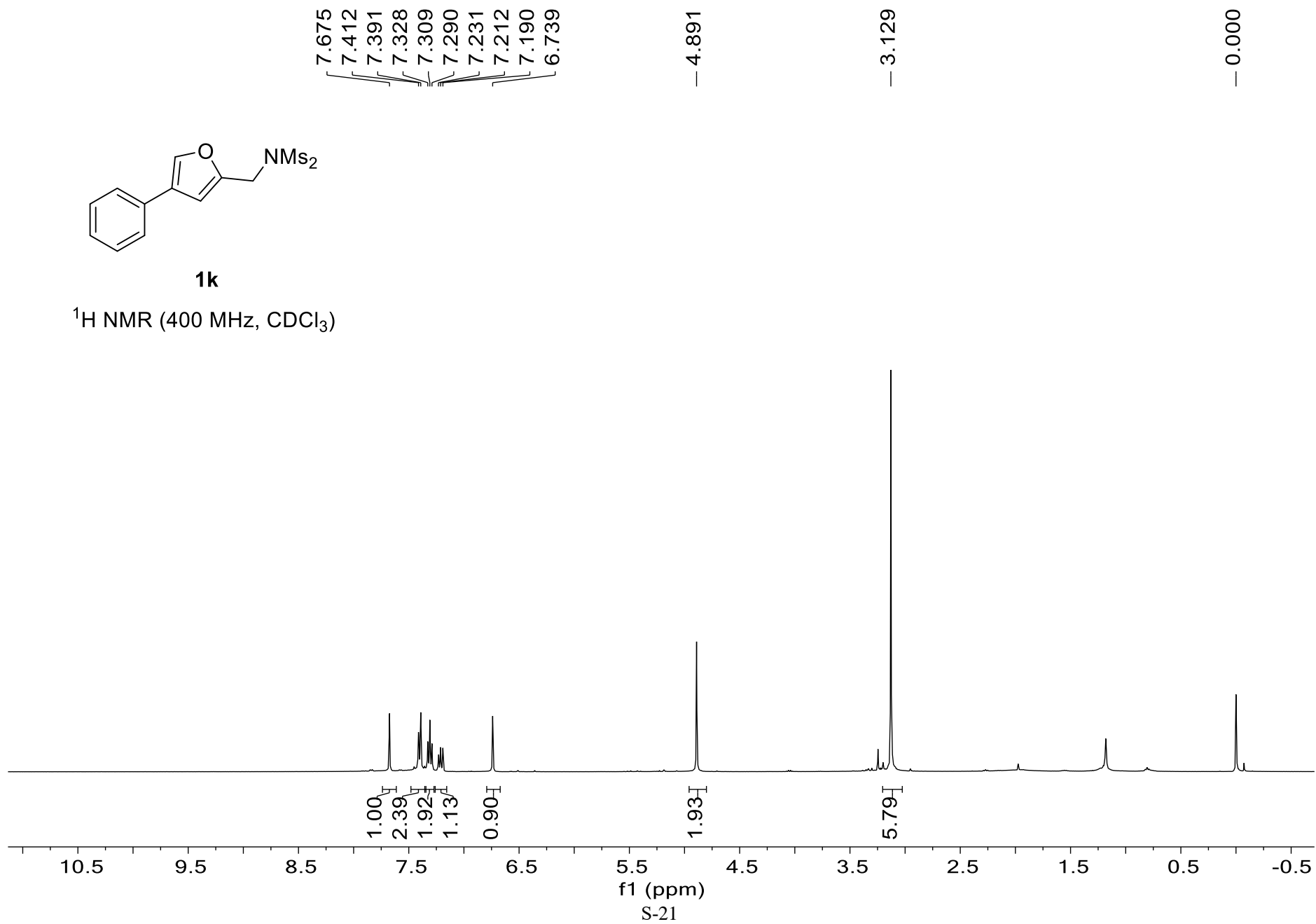
{ 44.735  
{ 43.767

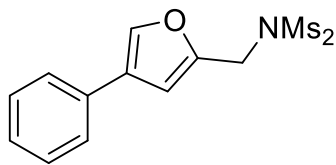




**1k**

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

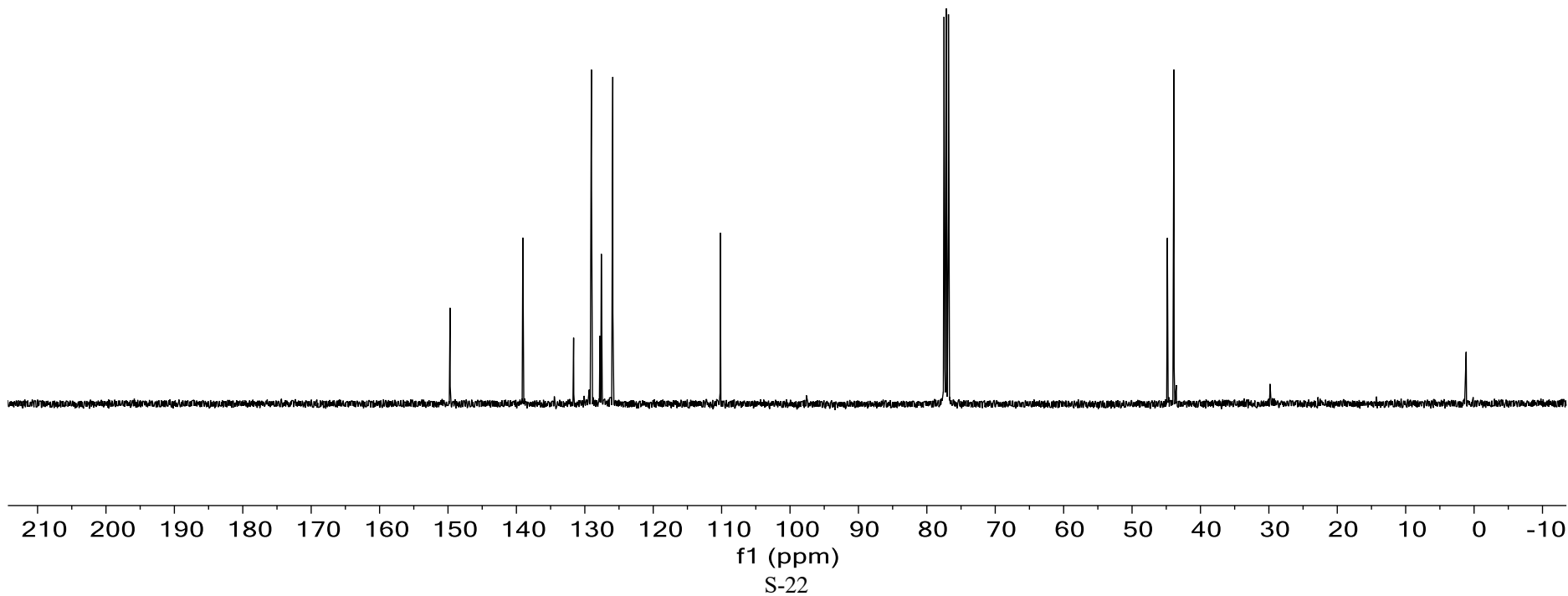


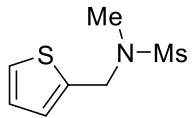


**1k**

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

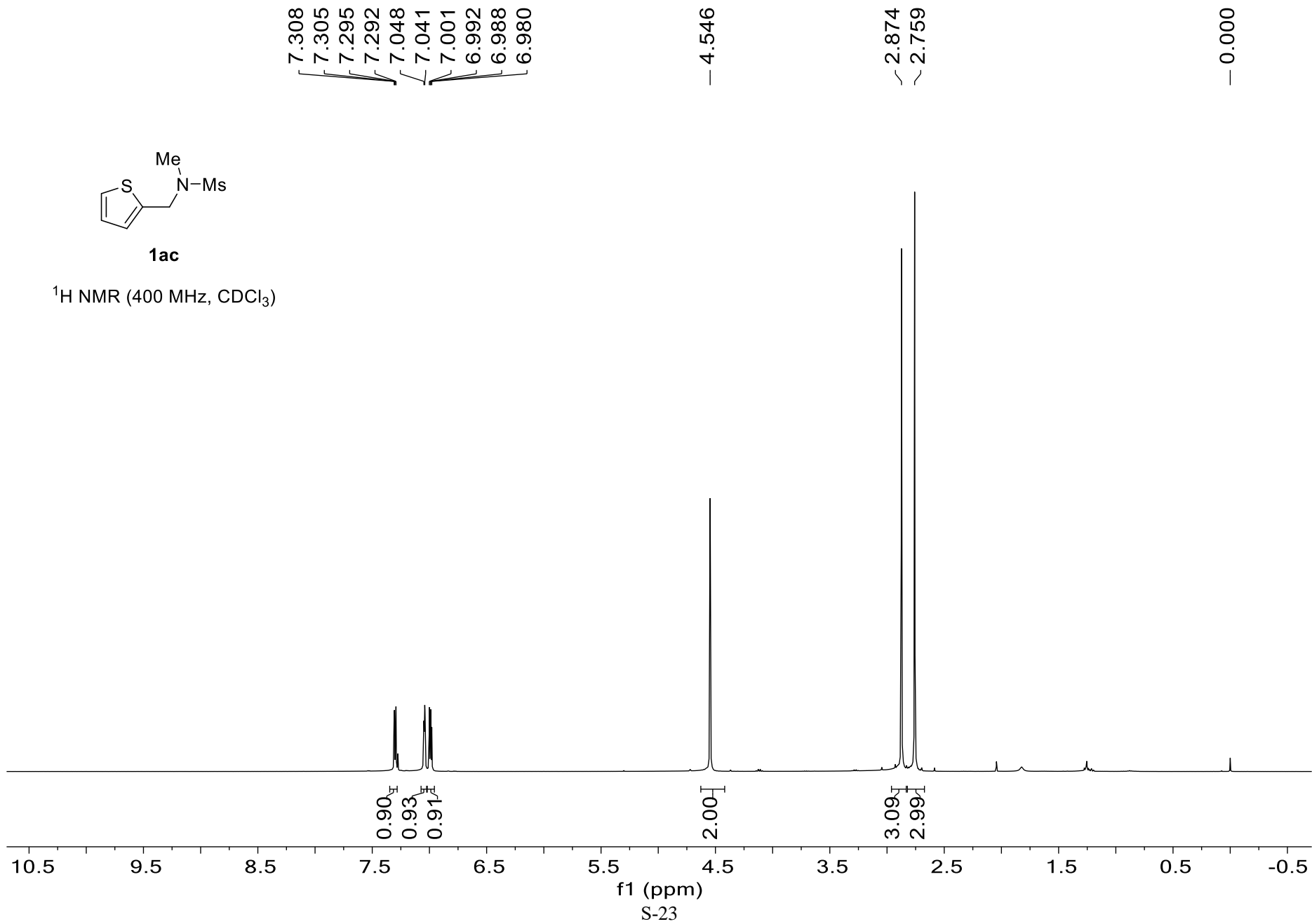
— 149.697  
139.062  
131.635  
129.037  
127.787  
127.587  
125.909  
— 110.192  
77.478  
77.160  
76.842  
44.839  
43.873

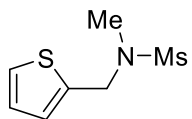




**1ac**

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





**1ac**

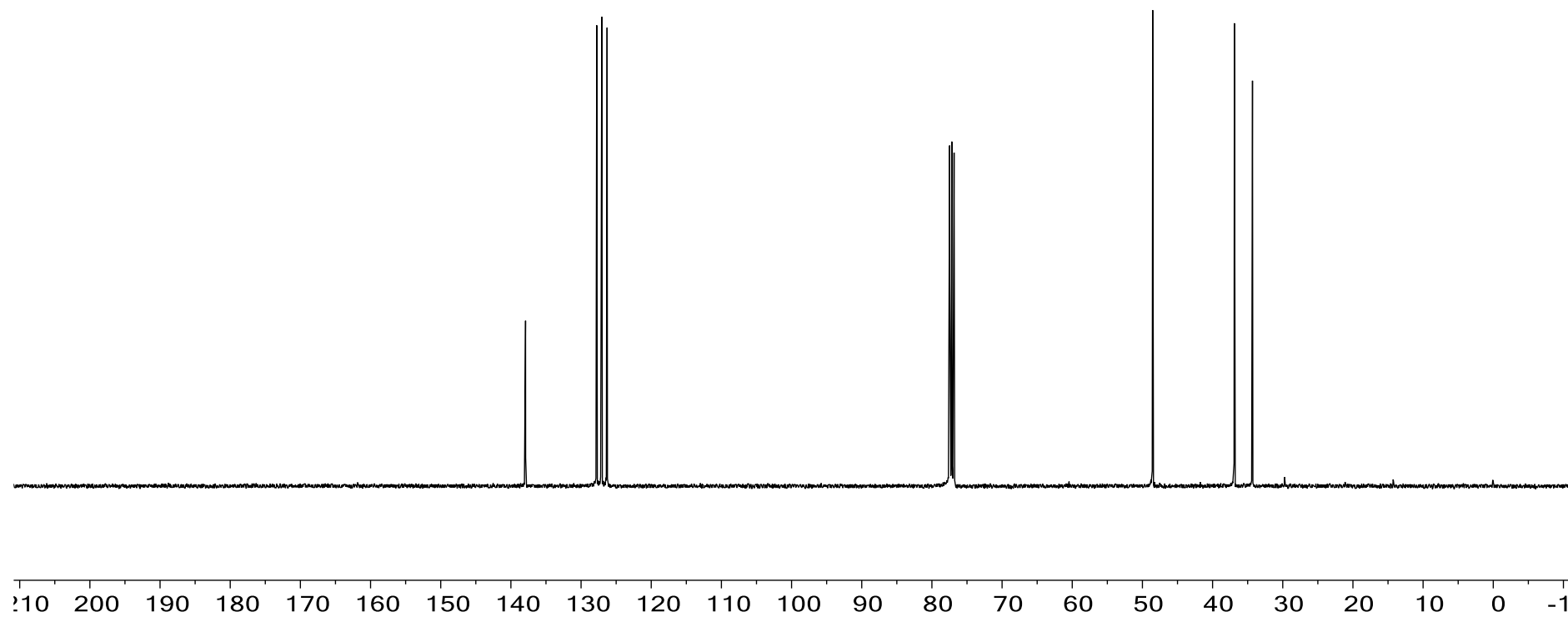
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

— 137.913  
{ 127.766  
{ 127.043  
{ 126.287

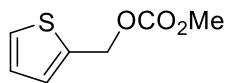
{ 77.478  
{ 77.160  
{ 76.842

— 48.538

~ 36.897  
~ 34.314

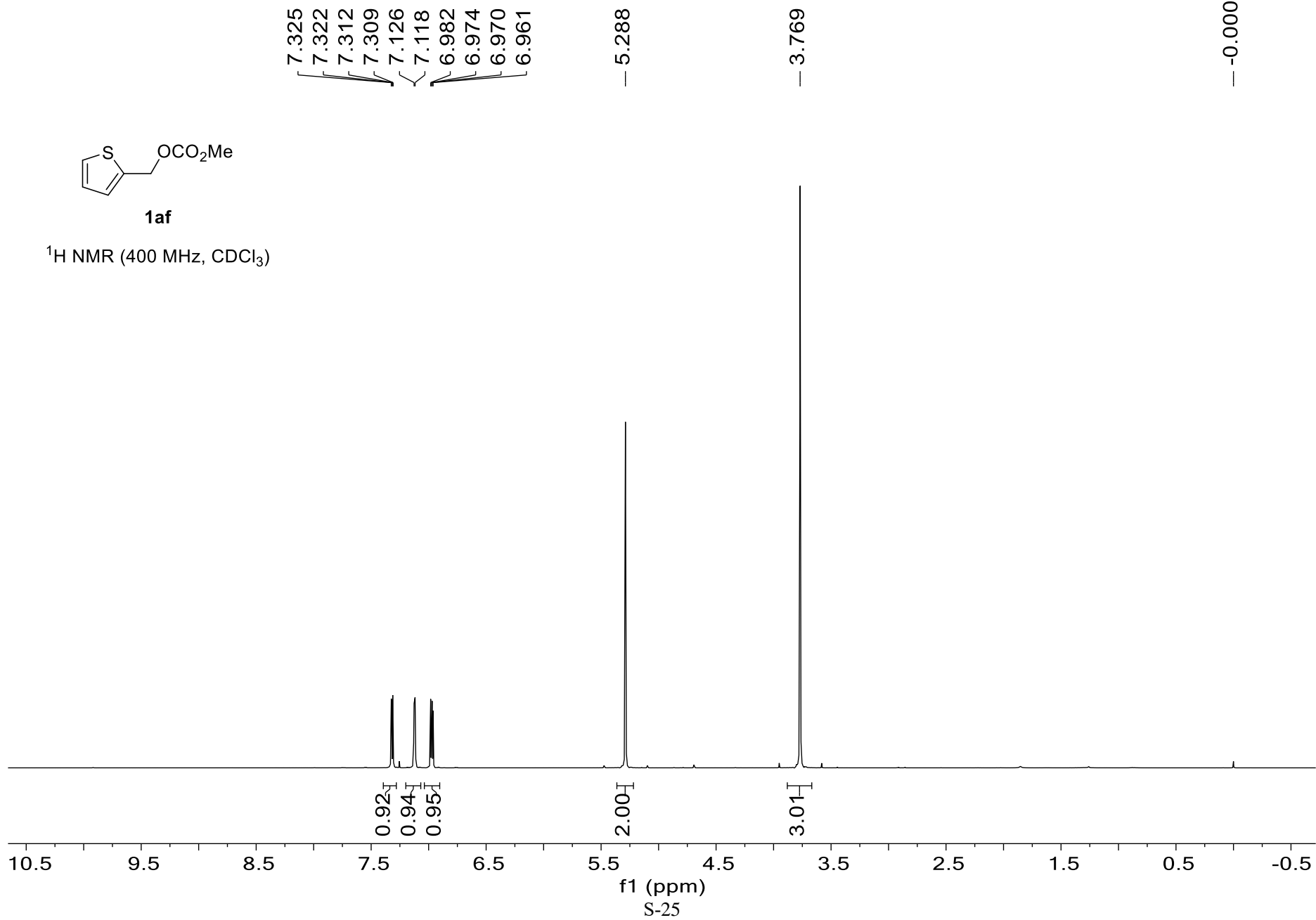


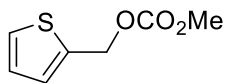




**1af**

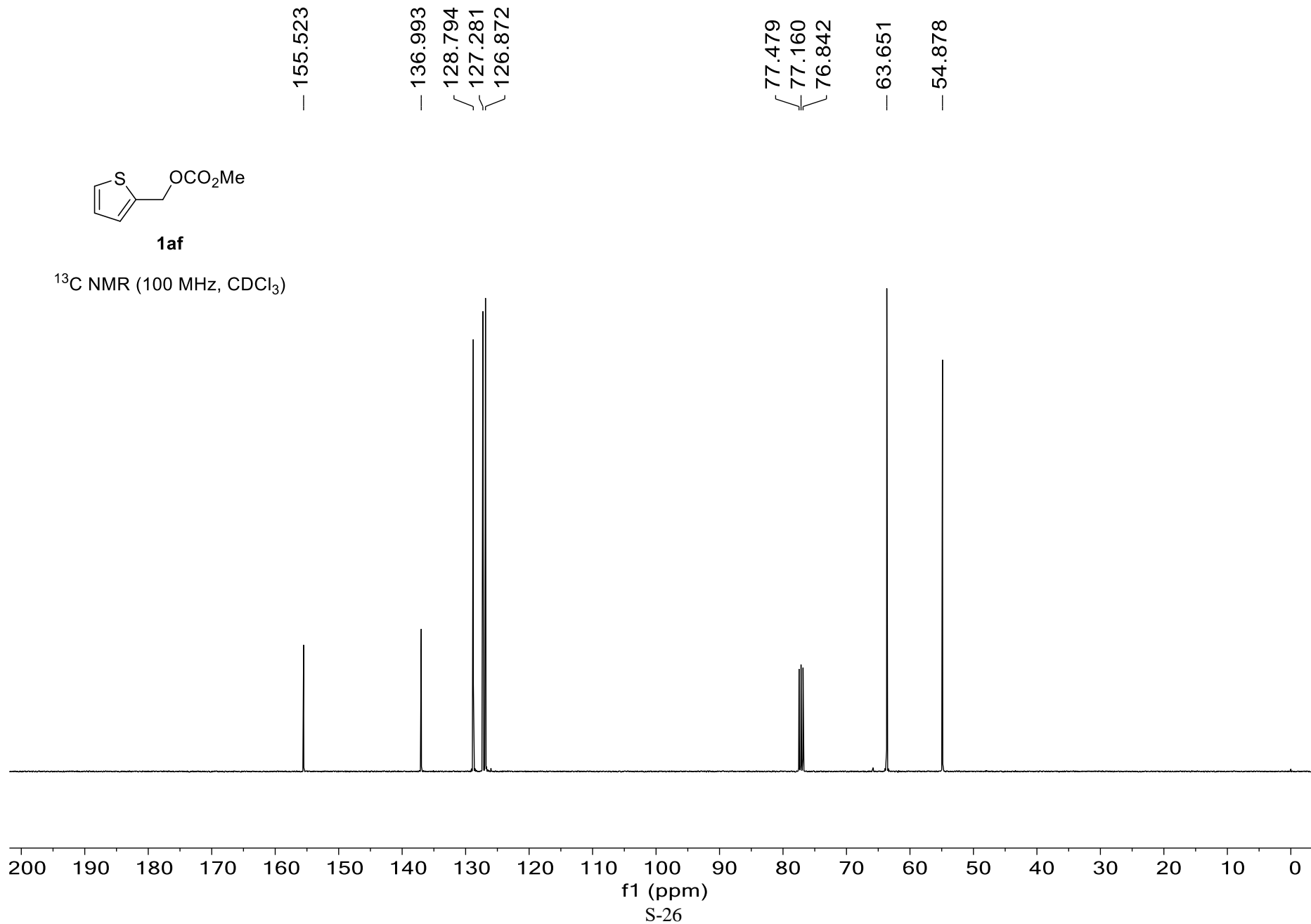
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

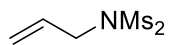




**1af**

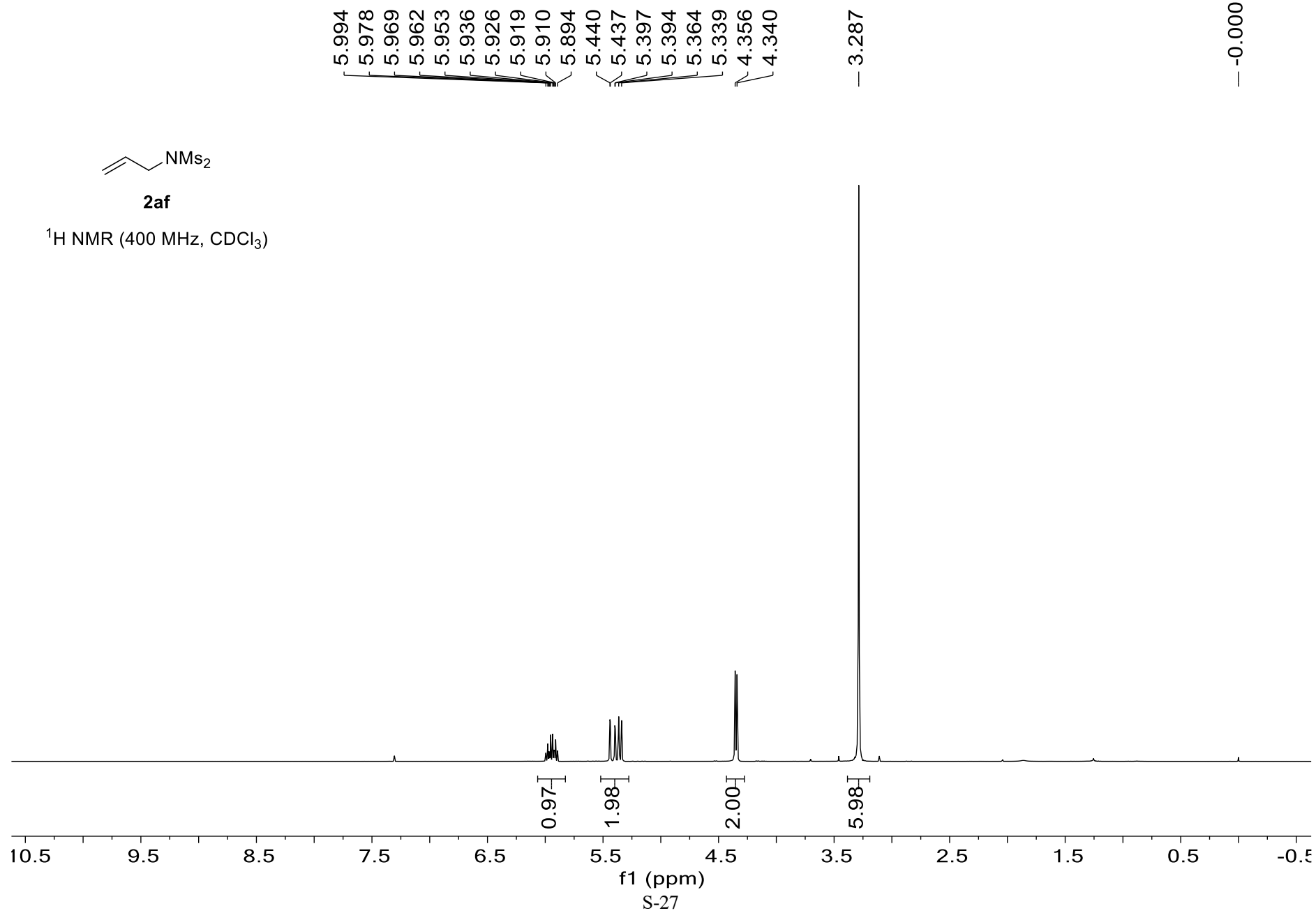
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

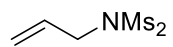




**2af**

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





**2af**

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

— 132.478

— 120.871

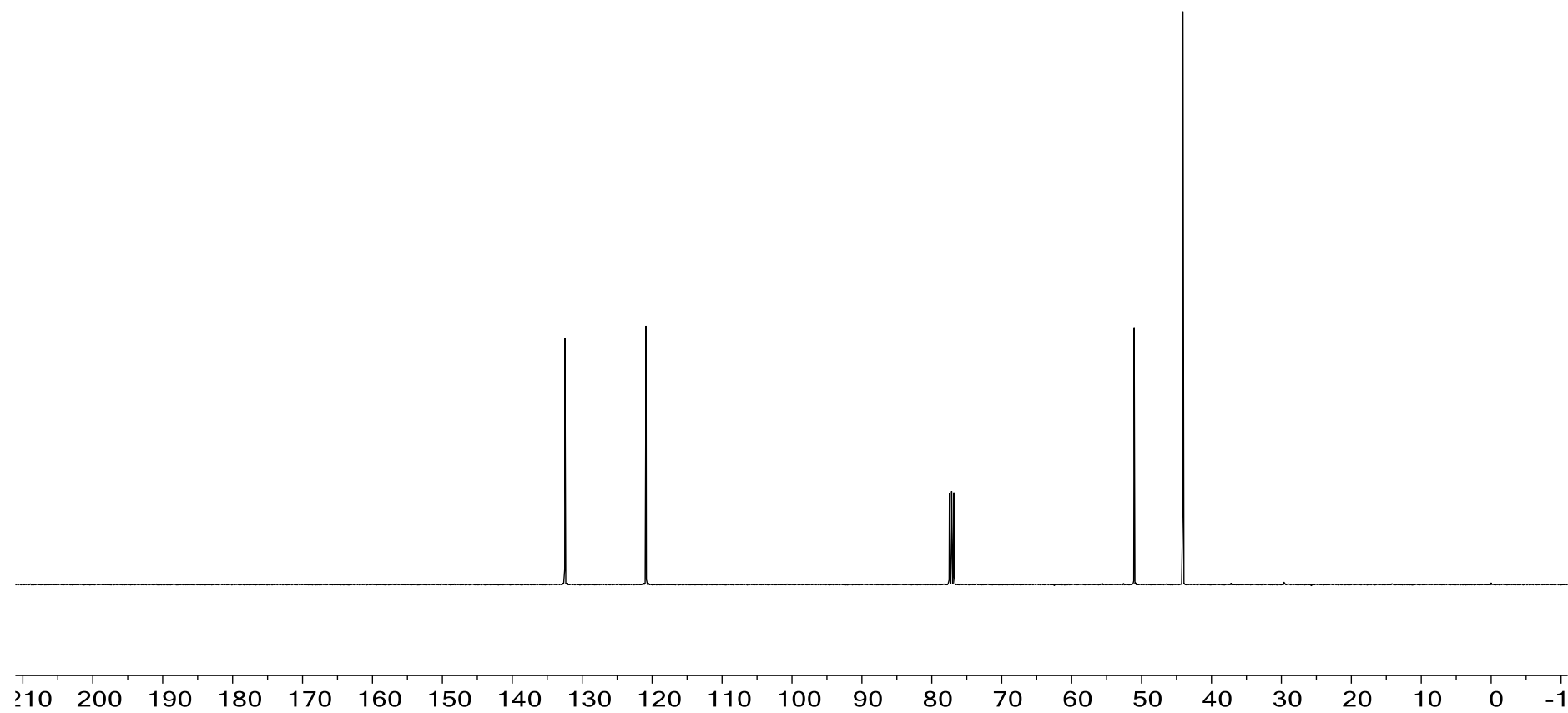
{ 77.479

{ 77.160

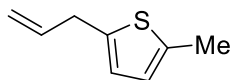
{ 76.842

— 51.058

— 44.094

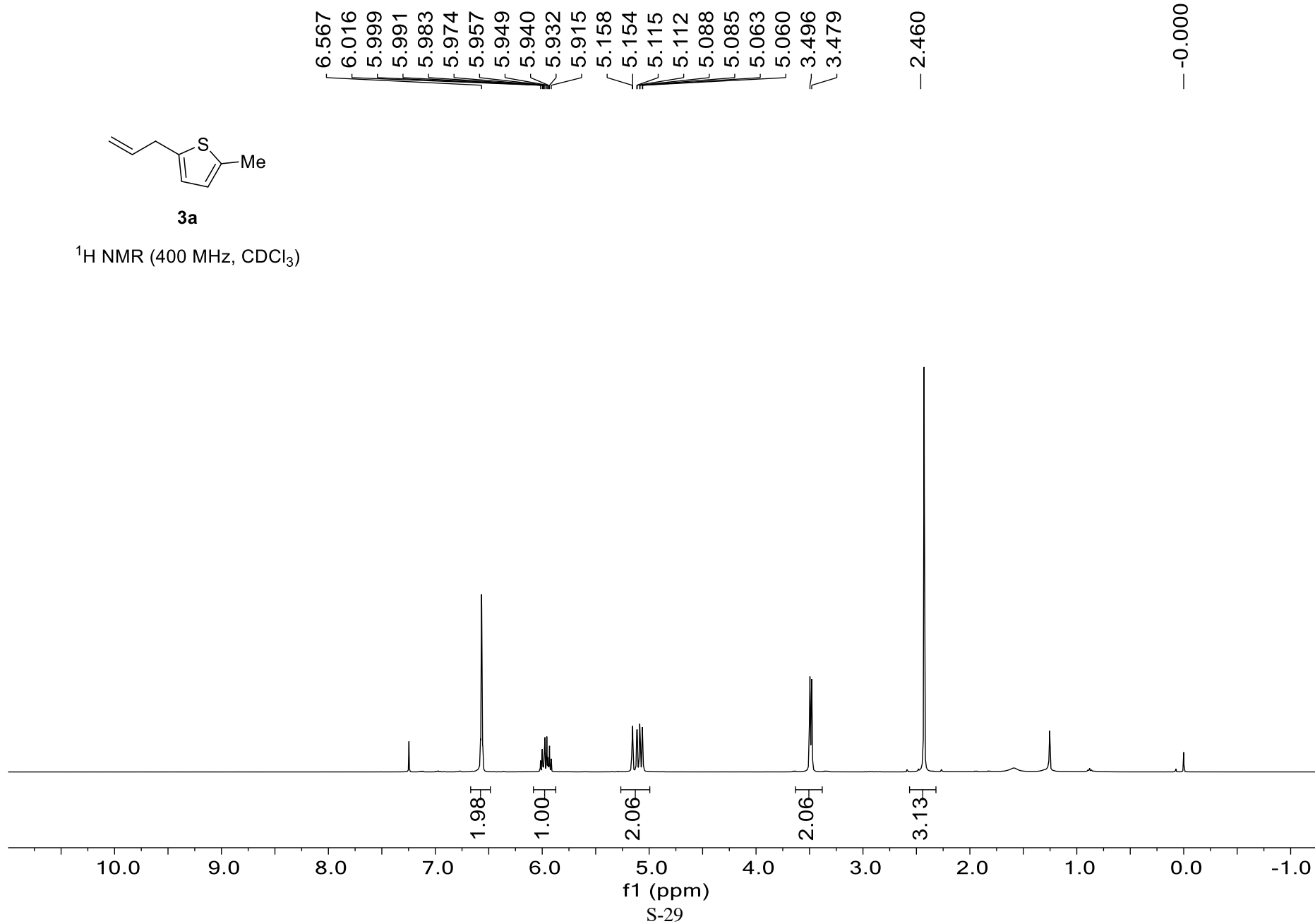


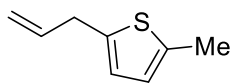
f1 (ppm)  
S-28



**3a**

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





**3a**

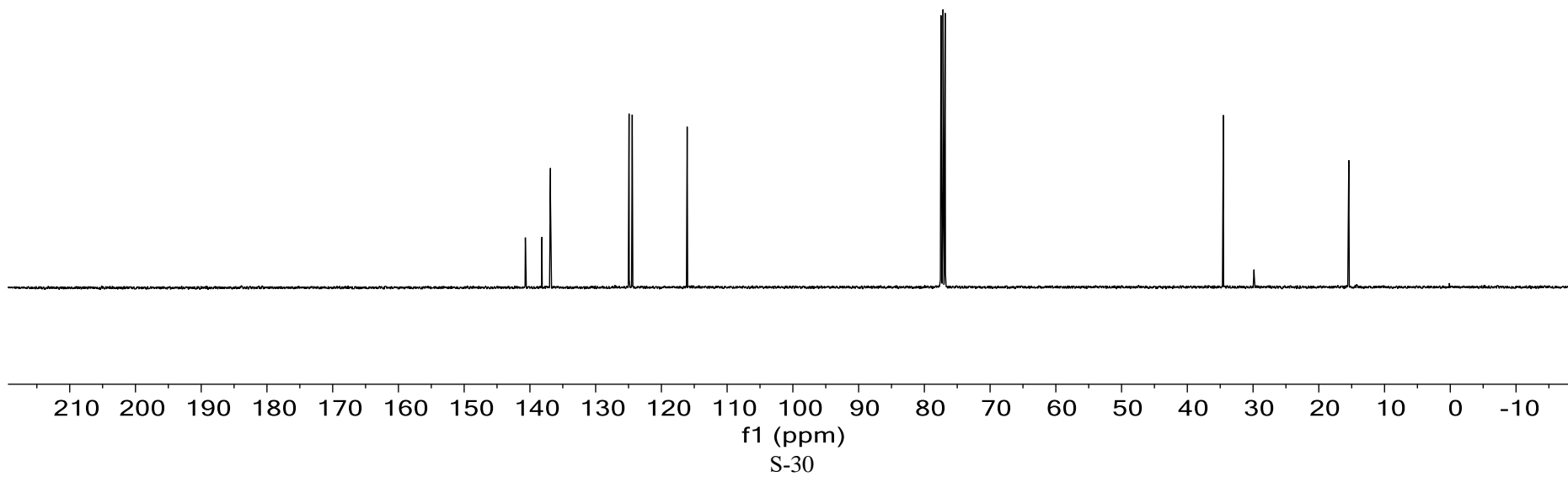
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

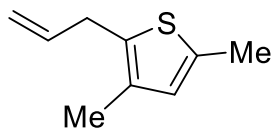
140.695  
138.180  
136.876  
124.920  
124.432  
116.081

77.478  
77.160  
76.842

34.519

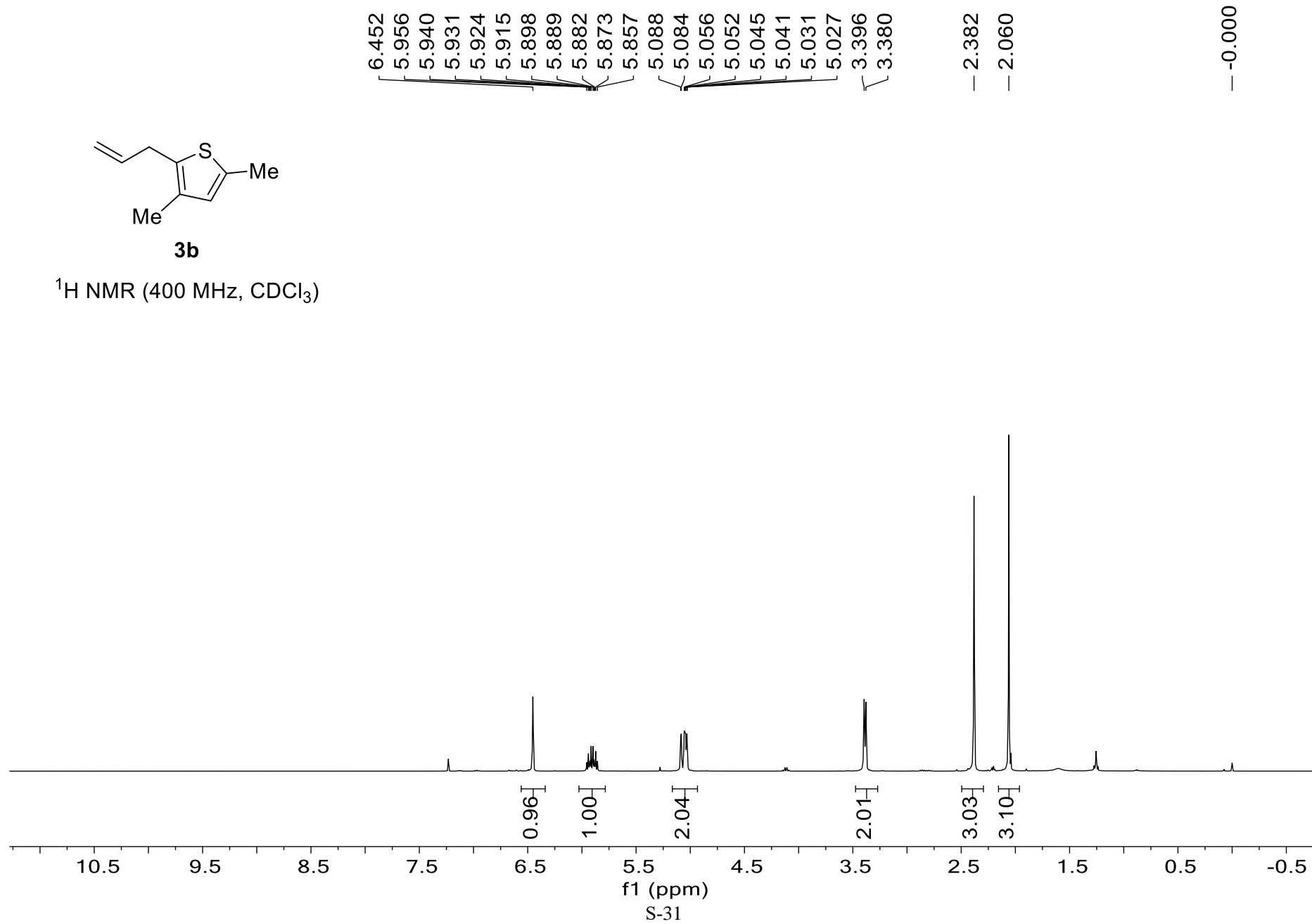
15.439

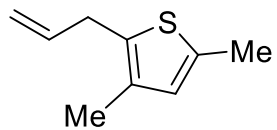




**3b**

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





**3b**

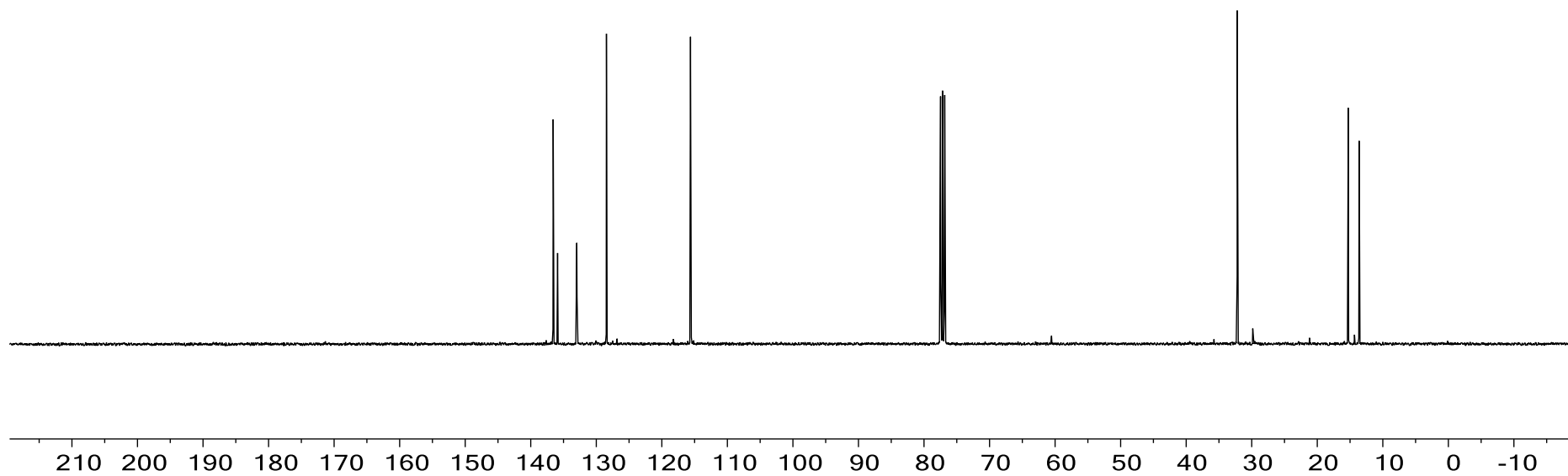
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

136.578  
135.907  
132.974  
132.941  
128.452  
— 115.628

77.477  
77.160  
76.842

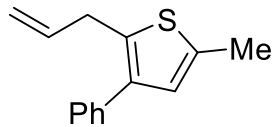
— 32.213

15.268  
13.603



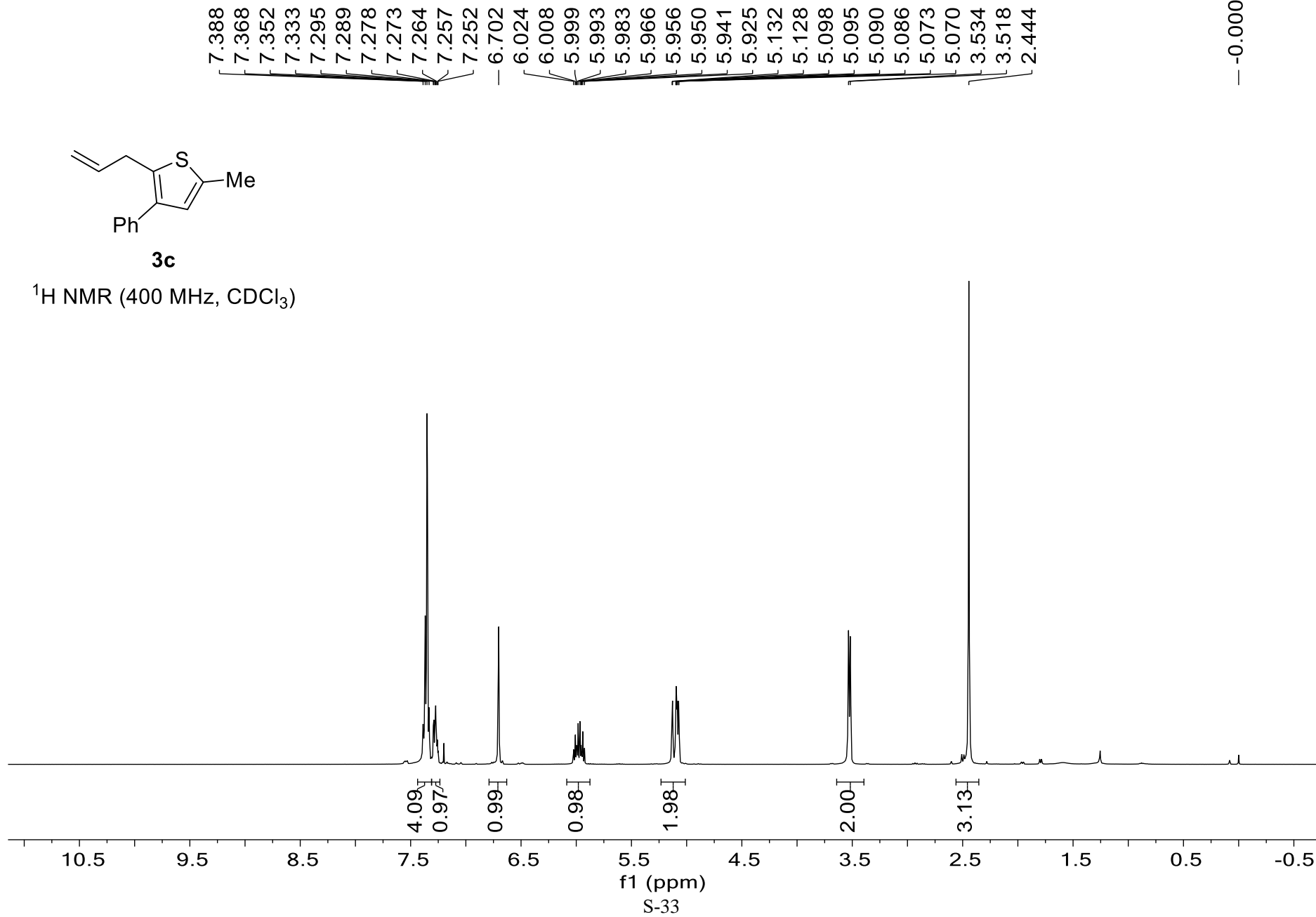
f1 (ppm)  
S-32

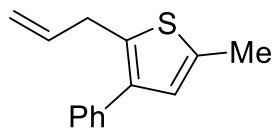




**3c**

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





**3c**

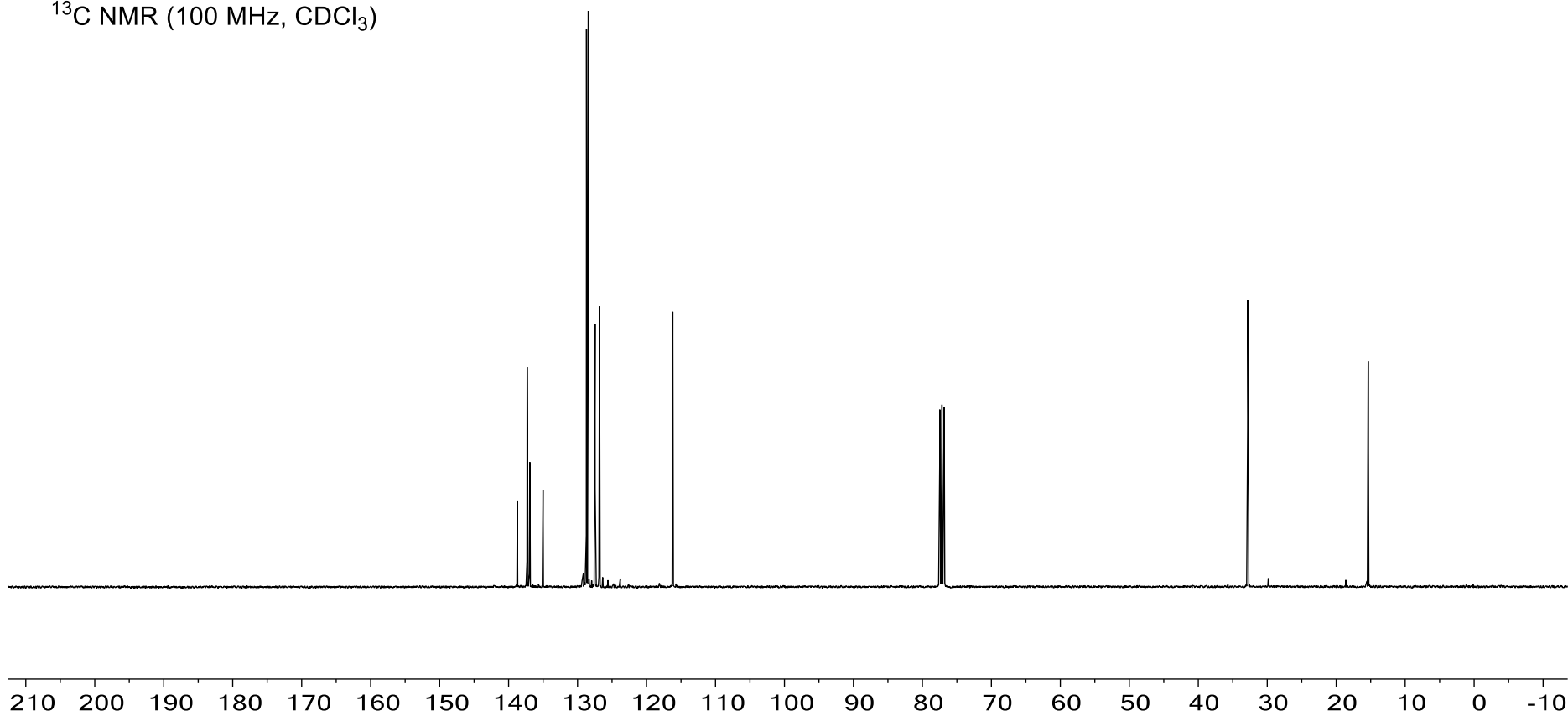
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

138.739  
137.308  
136.936  
136.912  
135.009  
128.701  
128.442  
127.456  
126.820  
— 116.189

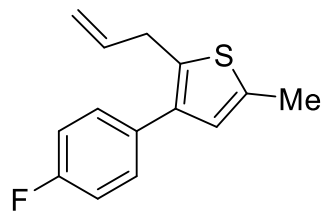
77.478  
77.160  
76.843

— 32.825

— 15.366

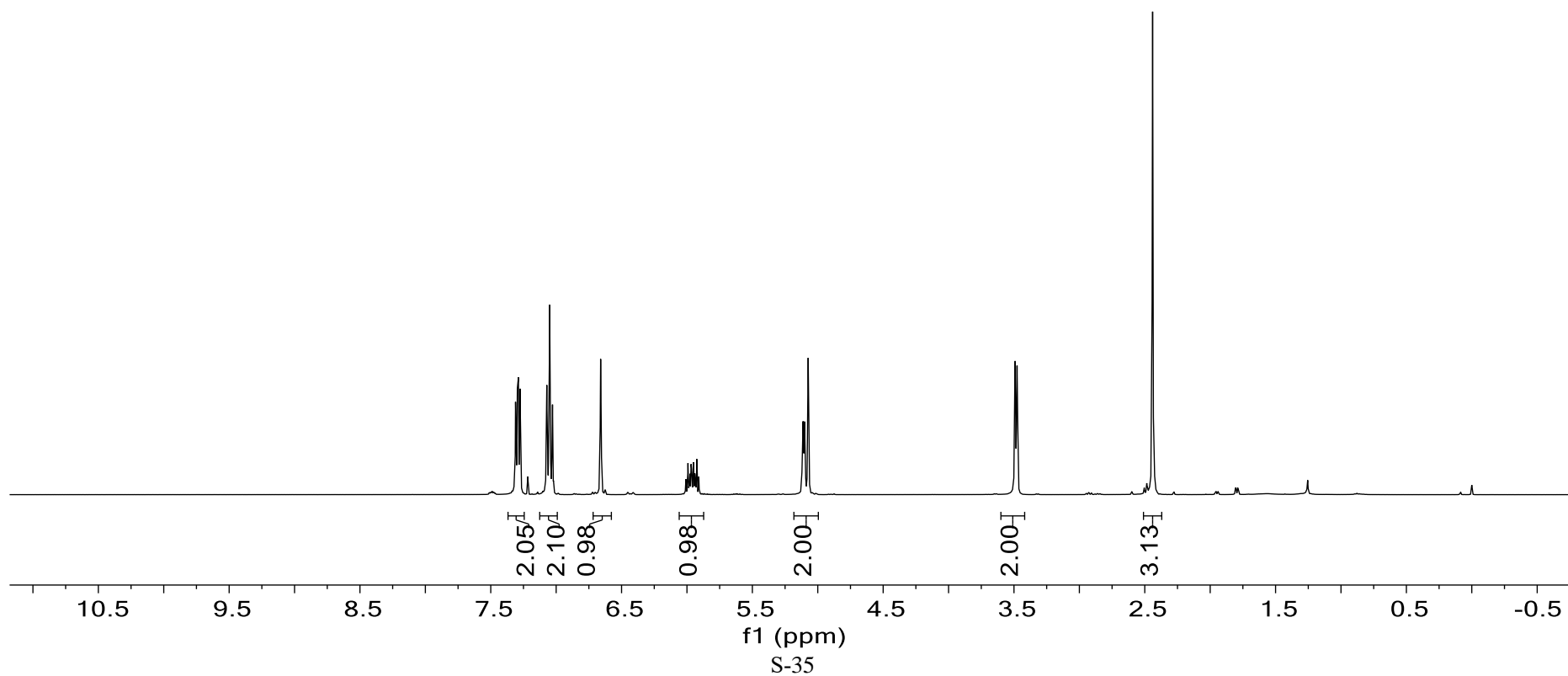


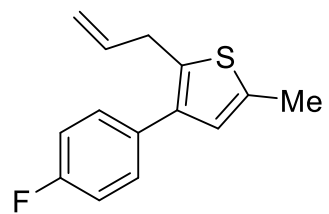
f1 (ppm)  
S-34



**3d**

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





**3d**

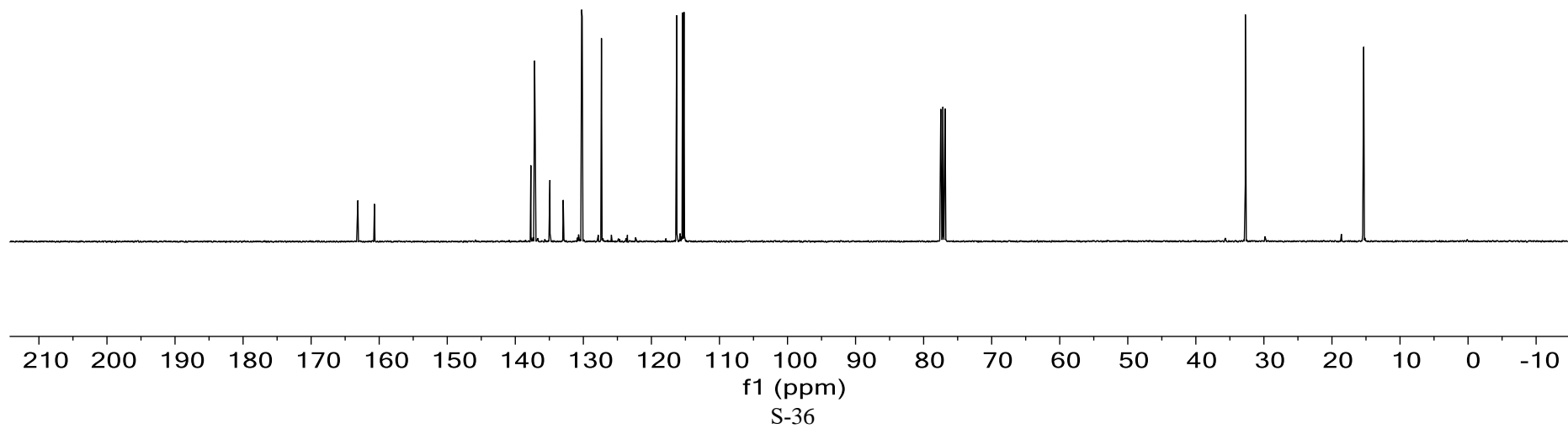
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

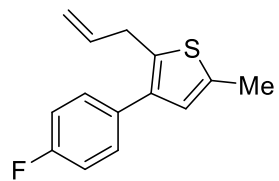
163.137  
160.694  
137.713  
137.161  
137.061  
134.914  
132.960  
132.927  
130.249  
130.171  
127.340  
116.283  
115.420  
115.209

77.478  
77.160  
76.843

— 32.724

— 15.332

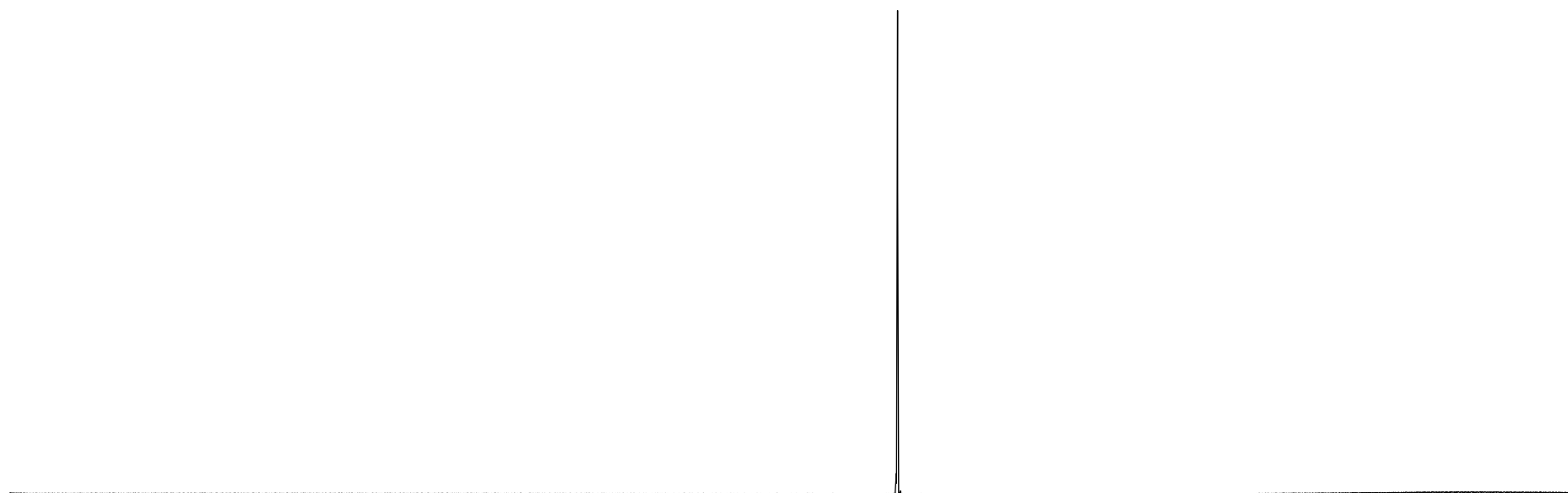




**3d**

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

— -115.720



10

-10

-30

-50

-70

-90

-110

-130

-150

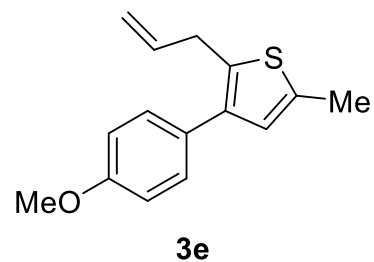
-170

-190

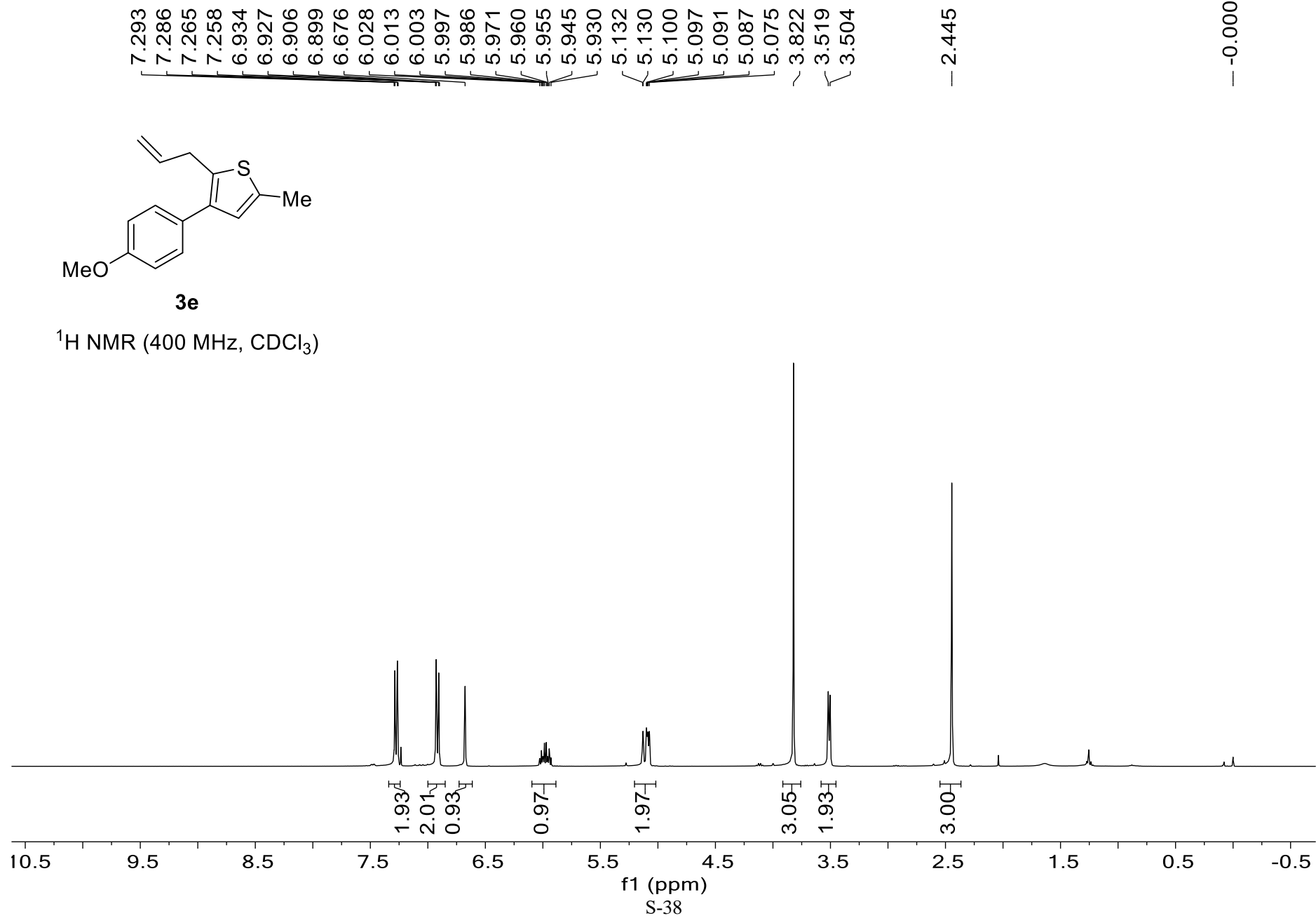
-210

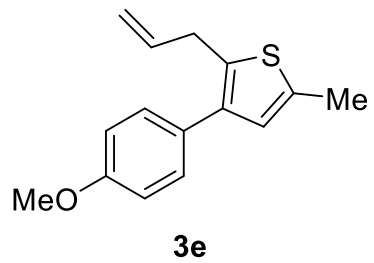
f1 (ppm)

S-37

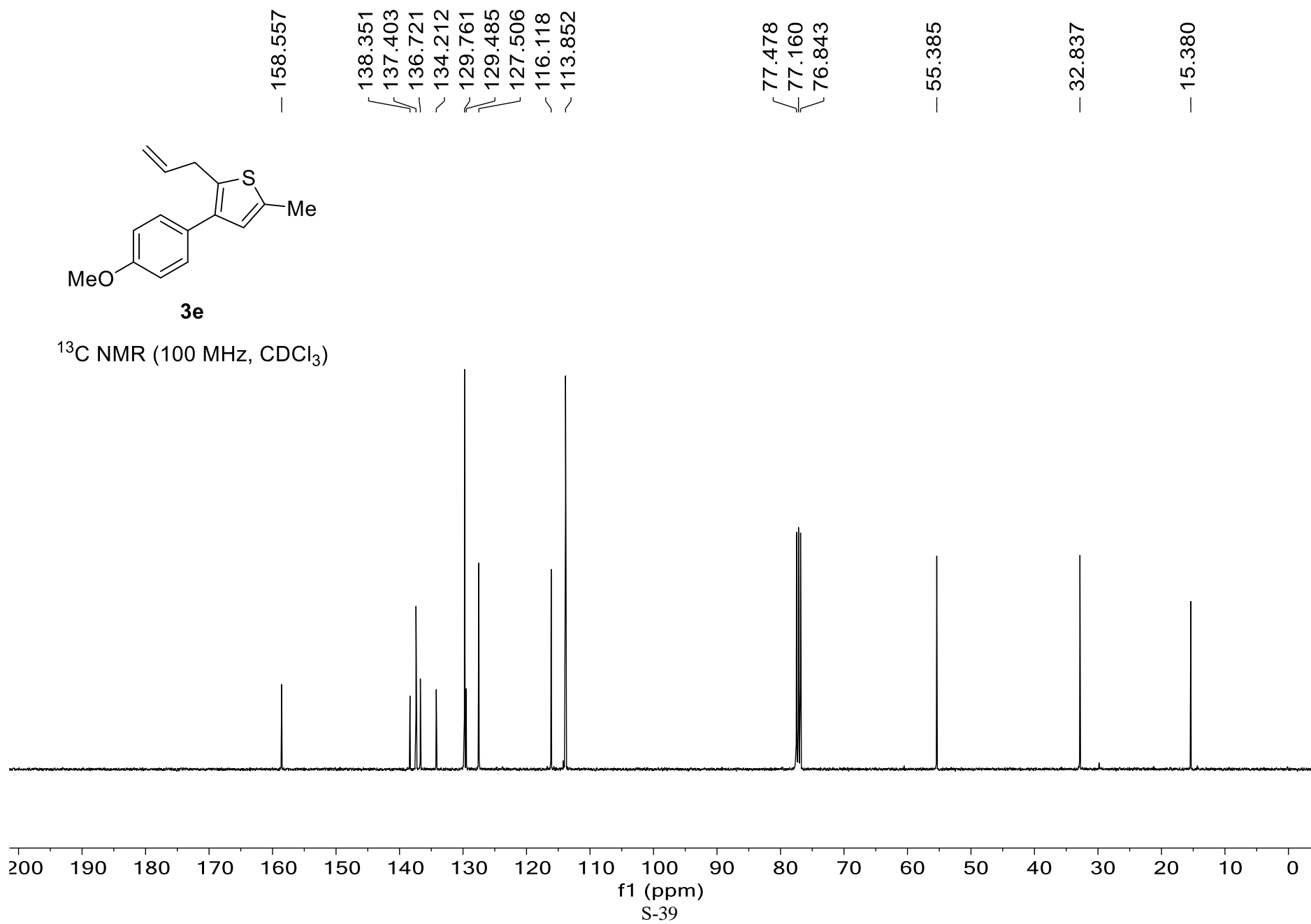


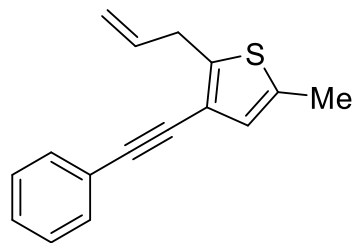
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





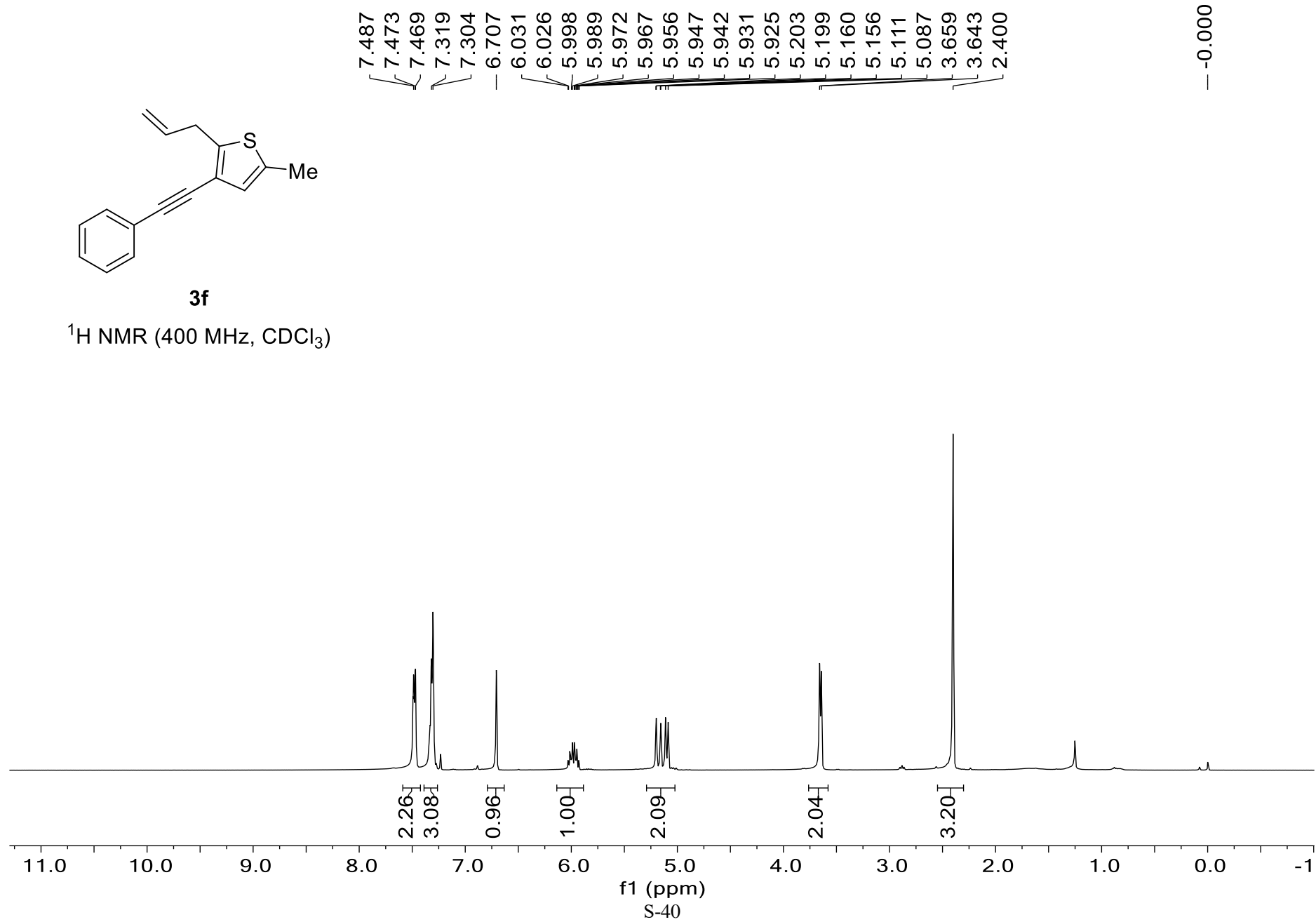
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



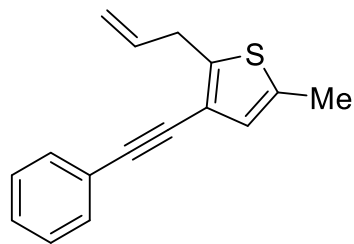


**3f**

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







**3f**

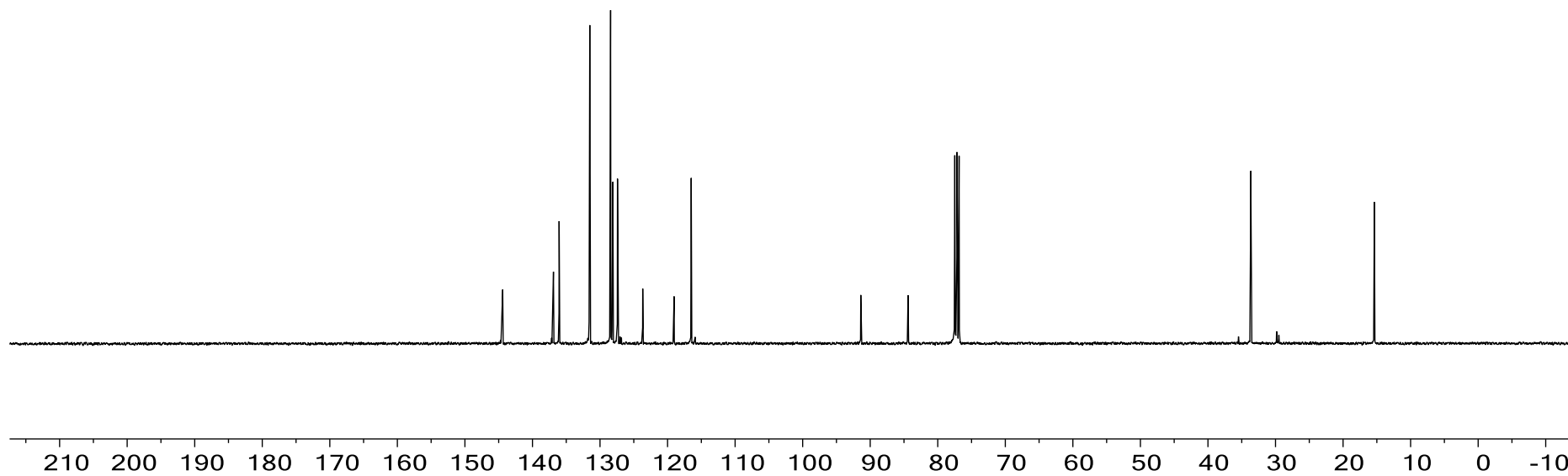
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

144.404  
136.892  
136.053  
131.516  
128.436  
128.099  
127.415  
123.679  
119.030  
116.496

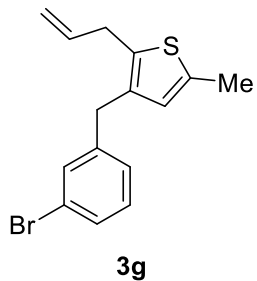
91.397  
84.397  
77.478  
77.160  
76.843

— 33.660

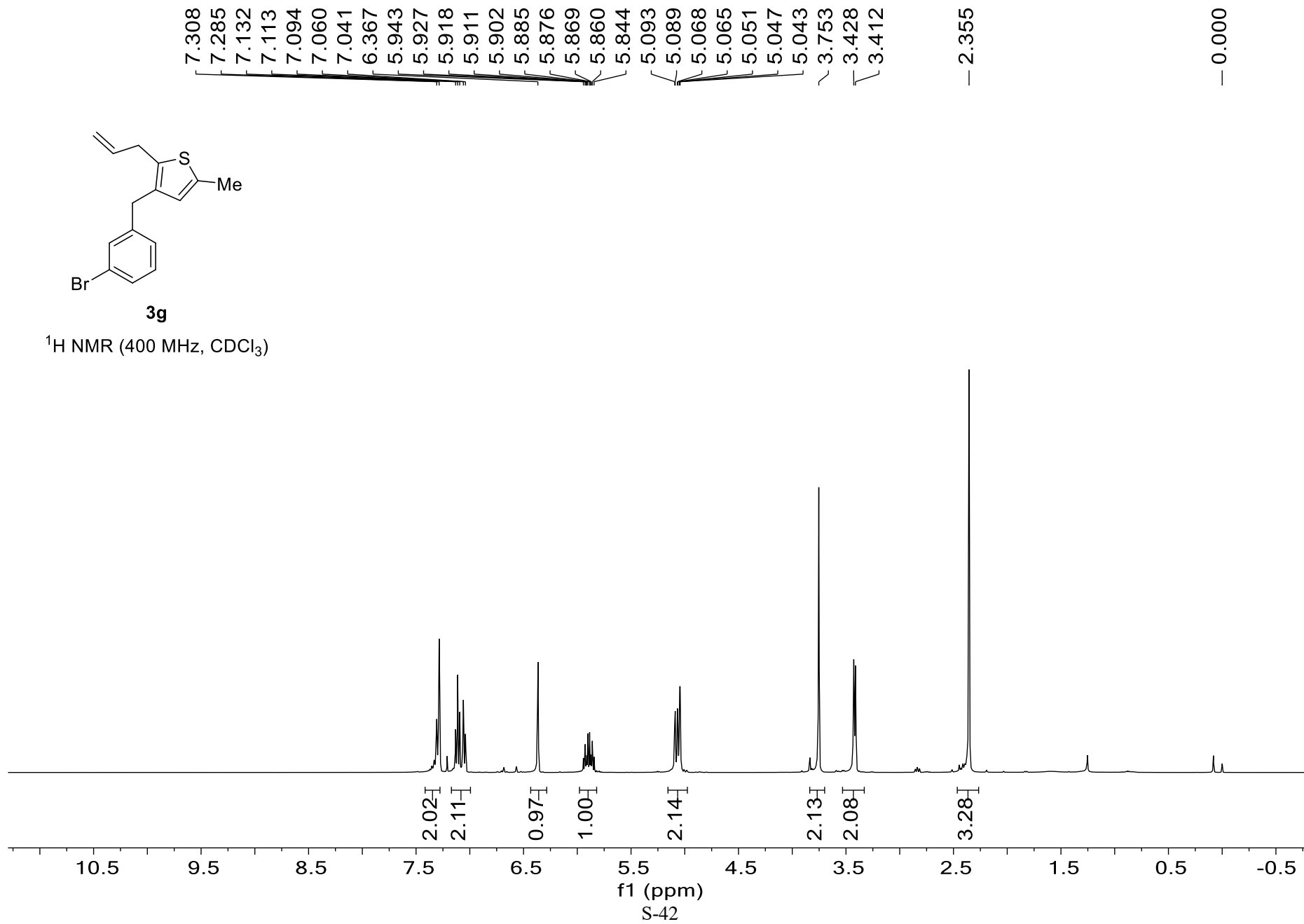
— 15.361

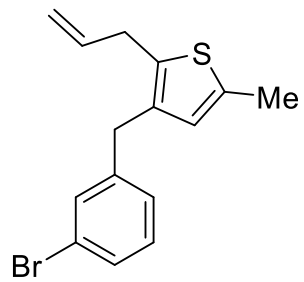


f1 (ppm)  
S-41



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





**3g**

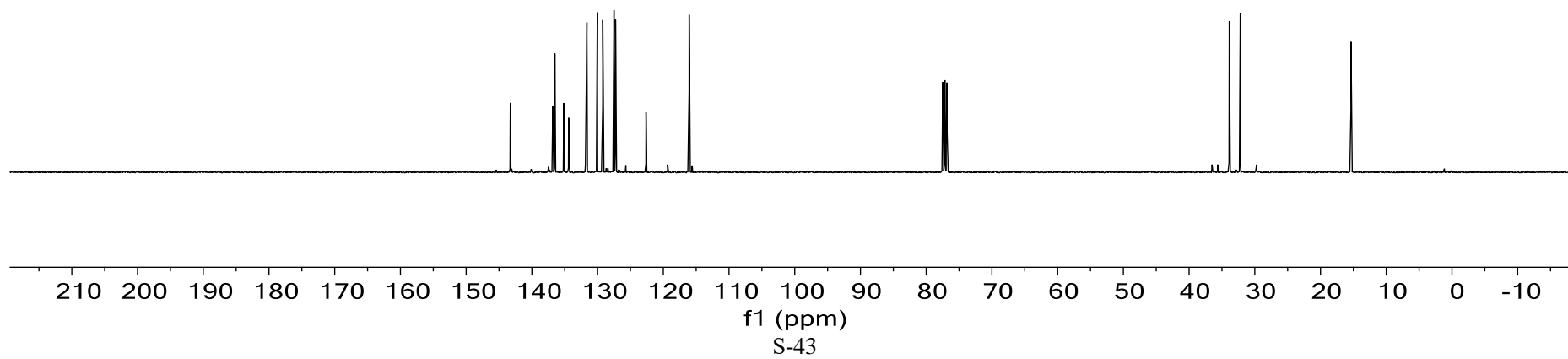
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

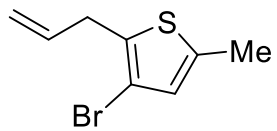
143.283  
136.811  
136.502  
135.138  
134.404  
131.622  
130.041  
129.208  
127.503  
127.264  
122.626  
116.067

77.478  
77.160  
76.843

33.884  
32.209

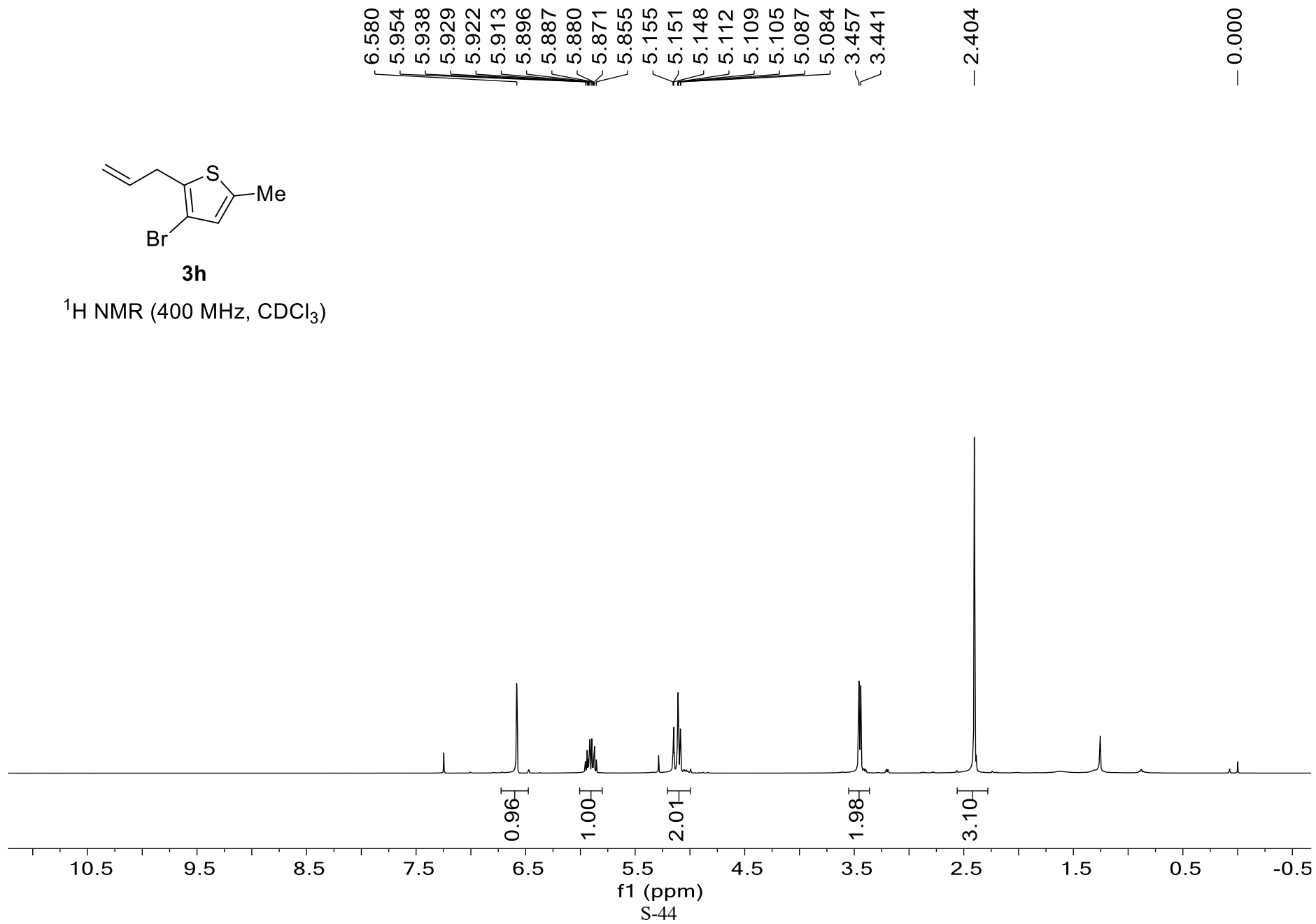
15.357

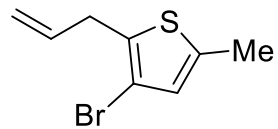




**3h**

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

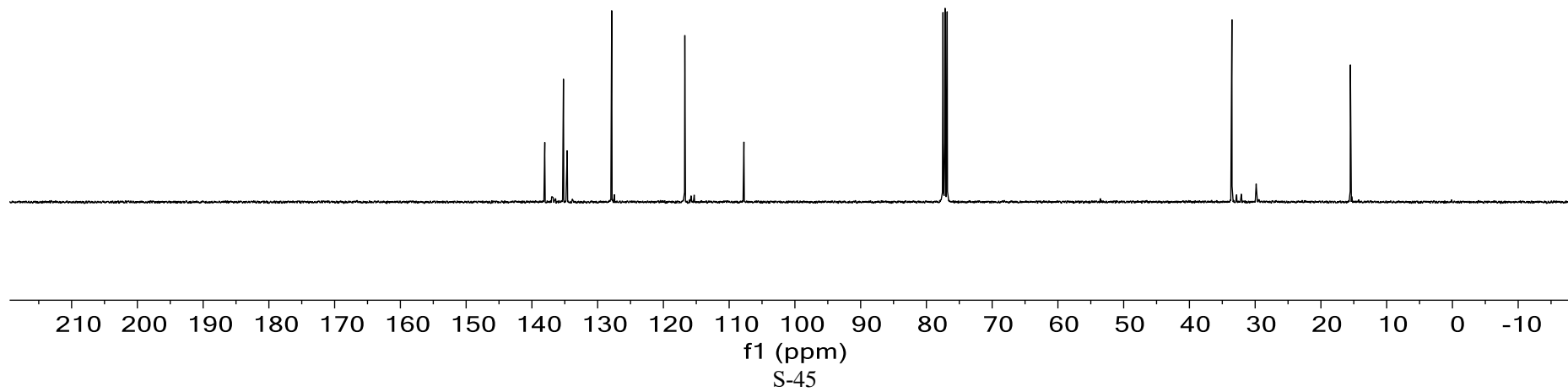


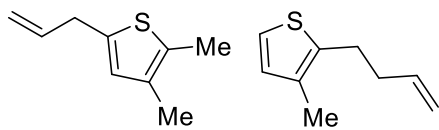


**3h**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

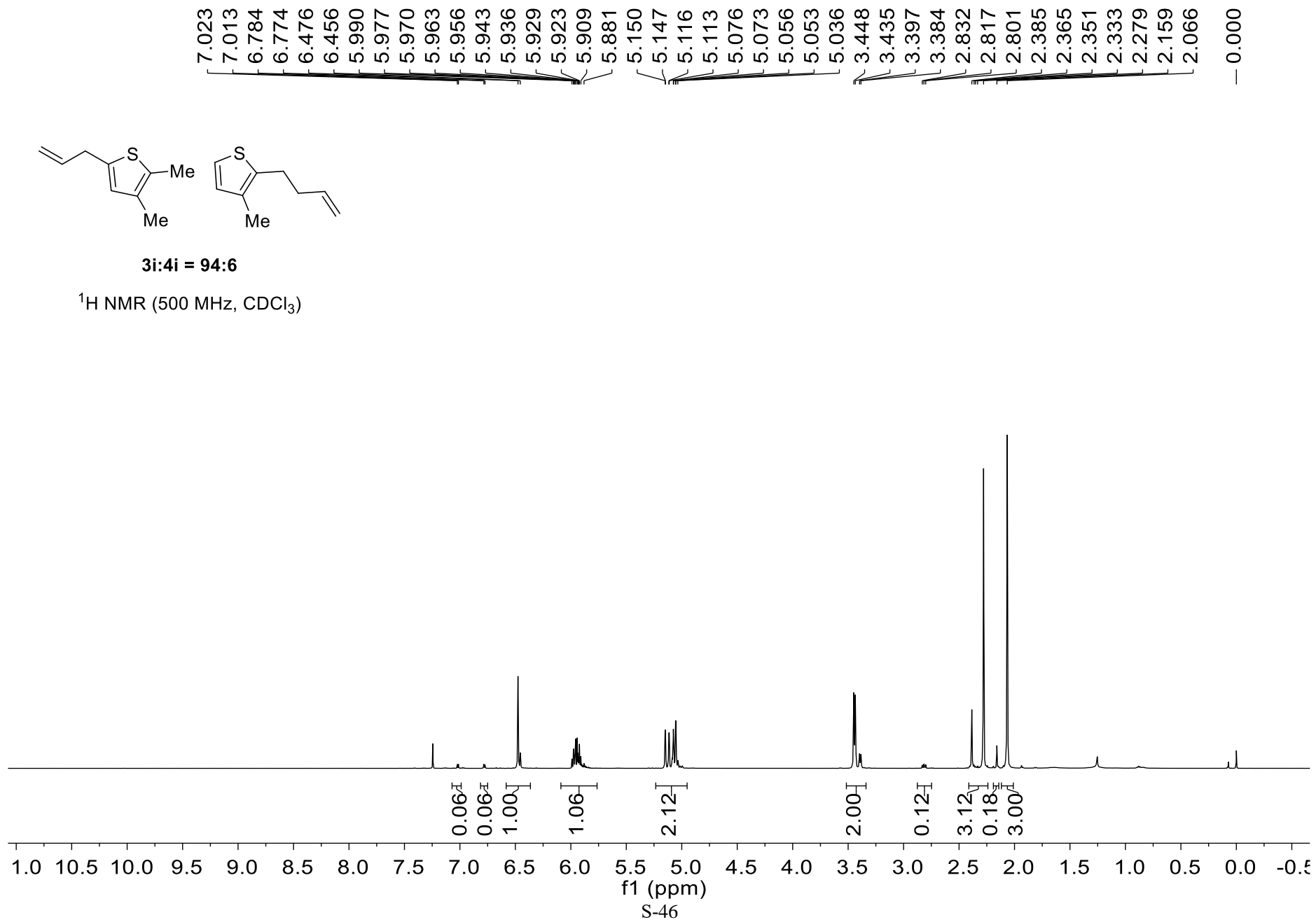
138.038  
135.202  
134.625  
127.859  
— 116.742  
— 107.753  
77.478  
77.160  
76.843  
— 33.538  
— 15.518

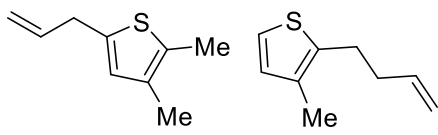




3i:4i = 94:6

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





**3i:4i = 94:6**

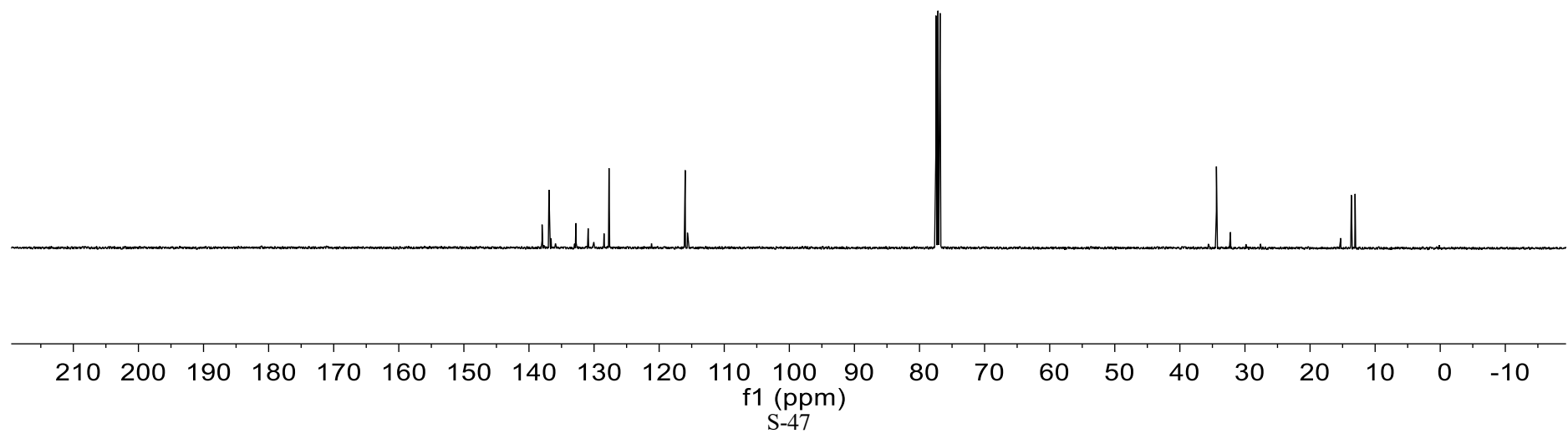
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

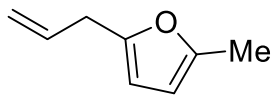
137.986  
136.929  
136.598  
135.932  
132.788  
130.910  
130.032  
128.471  
127.702  
121.168  
116.001  
115.646

77.477  
77.160  
76.842

34.384  
32.231  
27.614

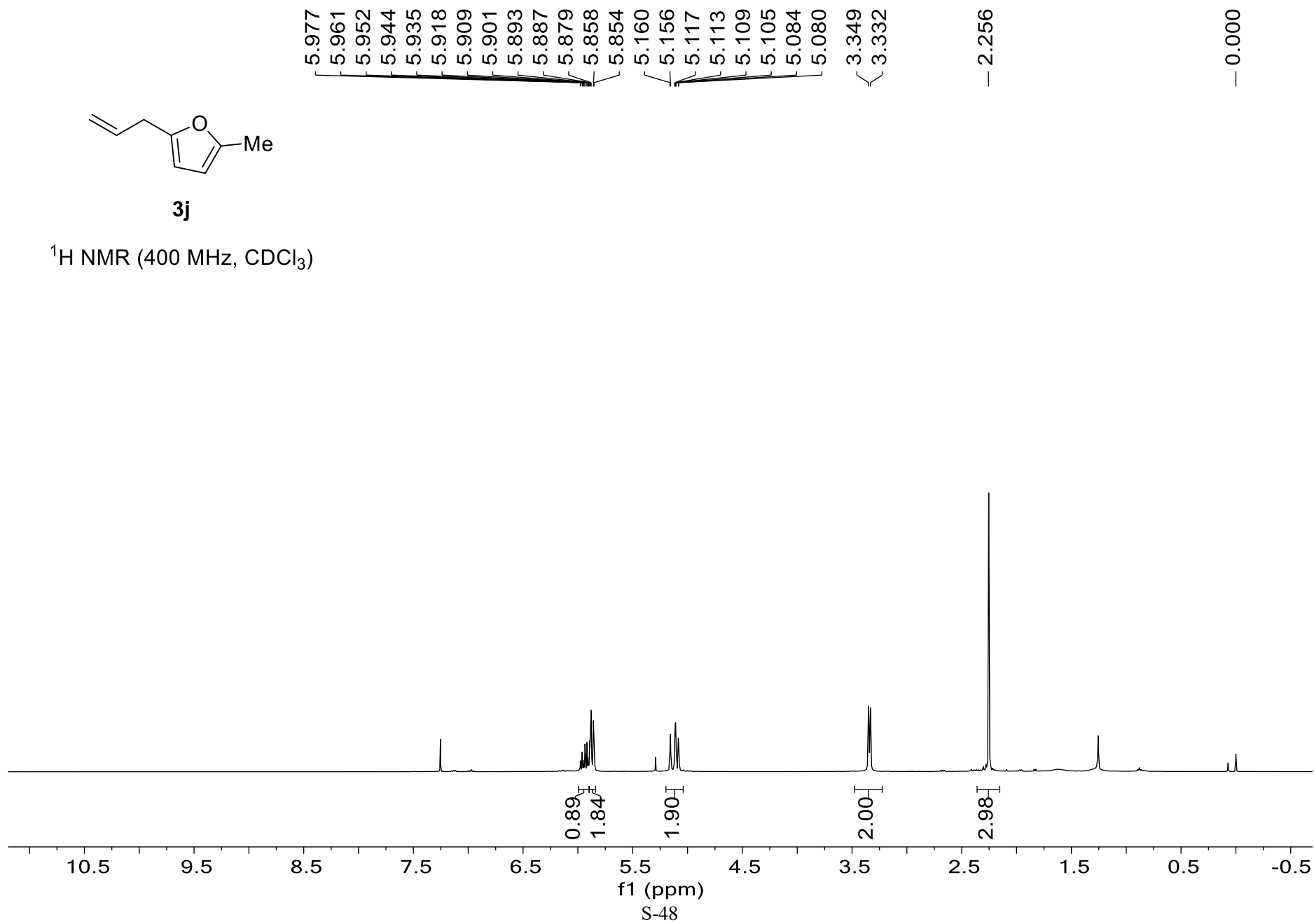
15.286  
13.657  
13.076



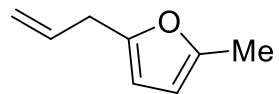


**3j**

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







**3j**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

152.154  
150.883

134.500

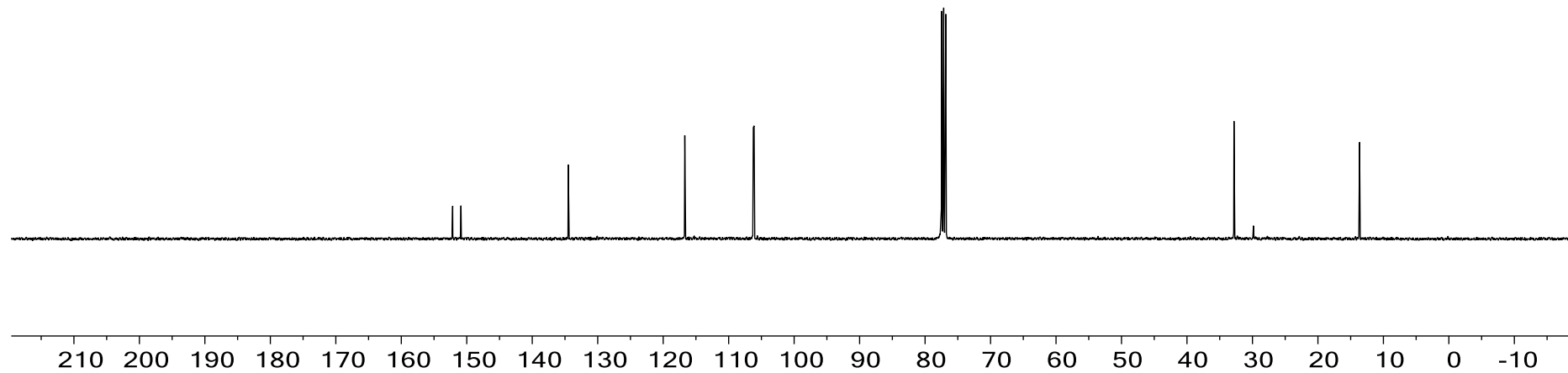
116.701

106.233  
106.113

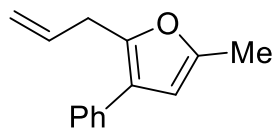
77.477  
77.160  
76.842

32.823

13.640

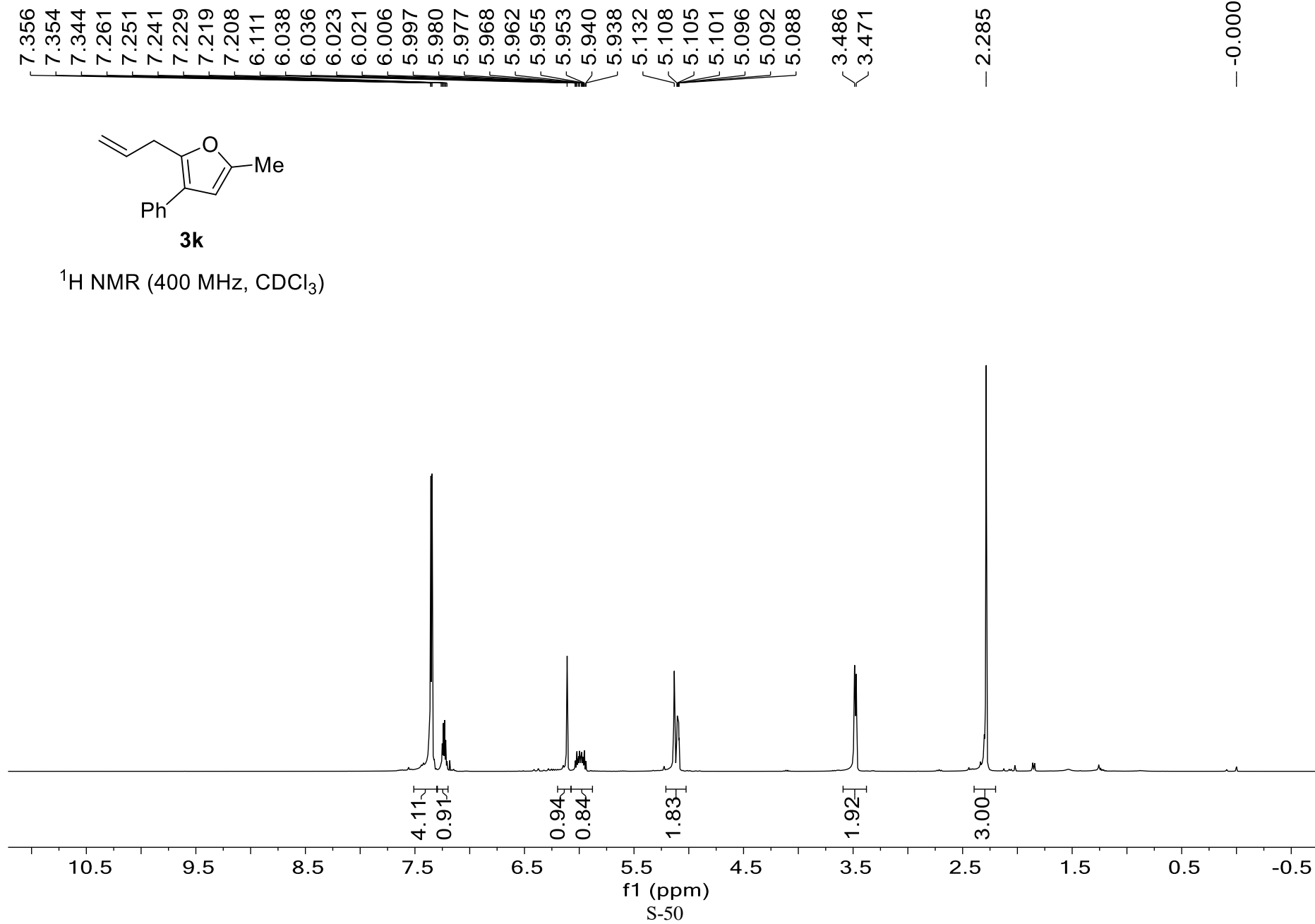


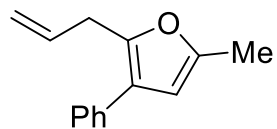
f1 (ppm)  
S-49



**3k**

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





**3k**

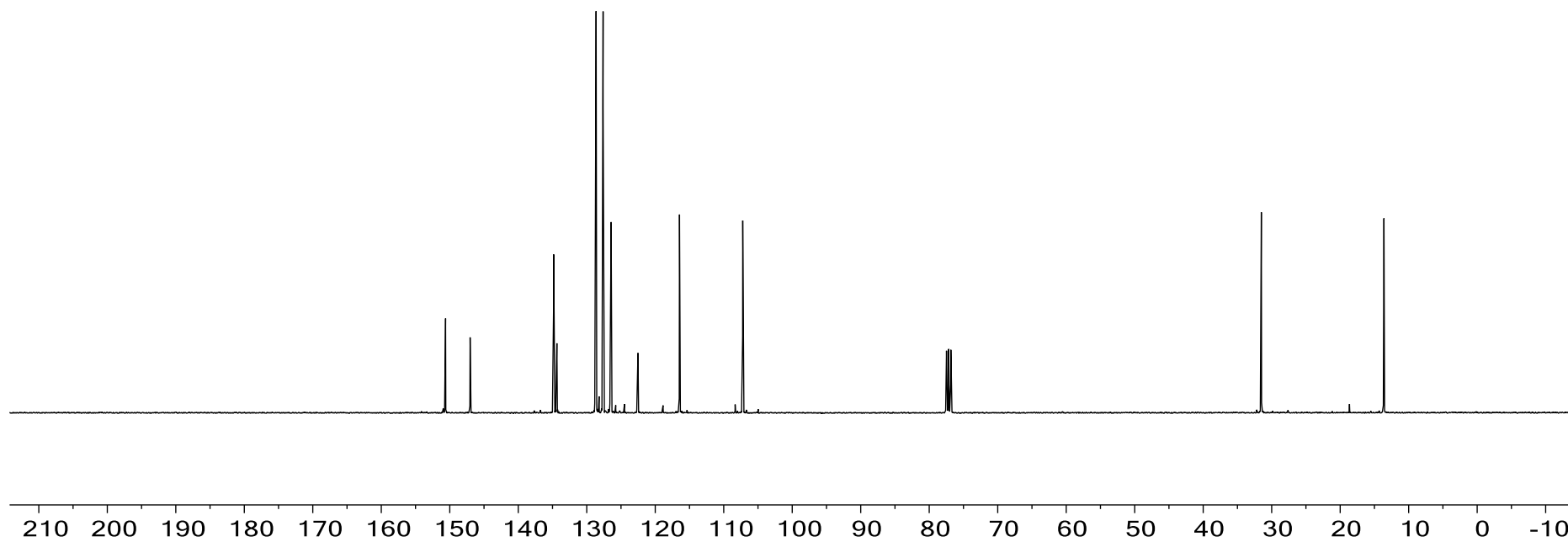
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

150.612  
147.028  
134.830  
134.362  
128.633  
127.615  
126.440  
122.521  
116.460  
107.228

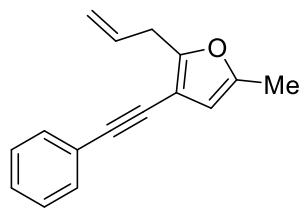
77.478  
77.160  
76.842

31.513

13.607

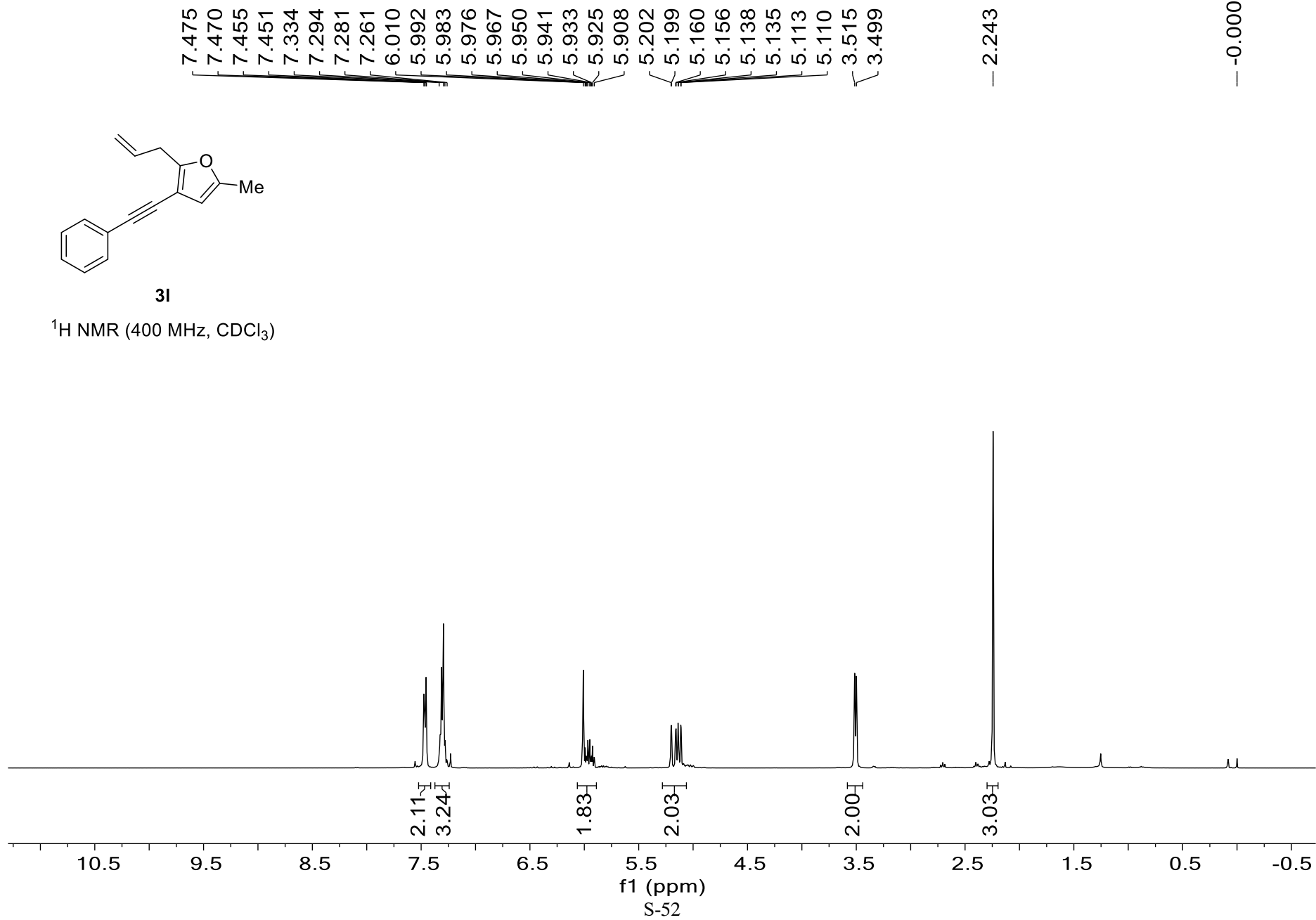


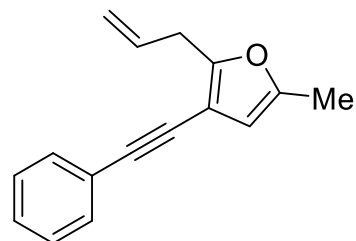
f1 (ppm)  
S-51



**3l**

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

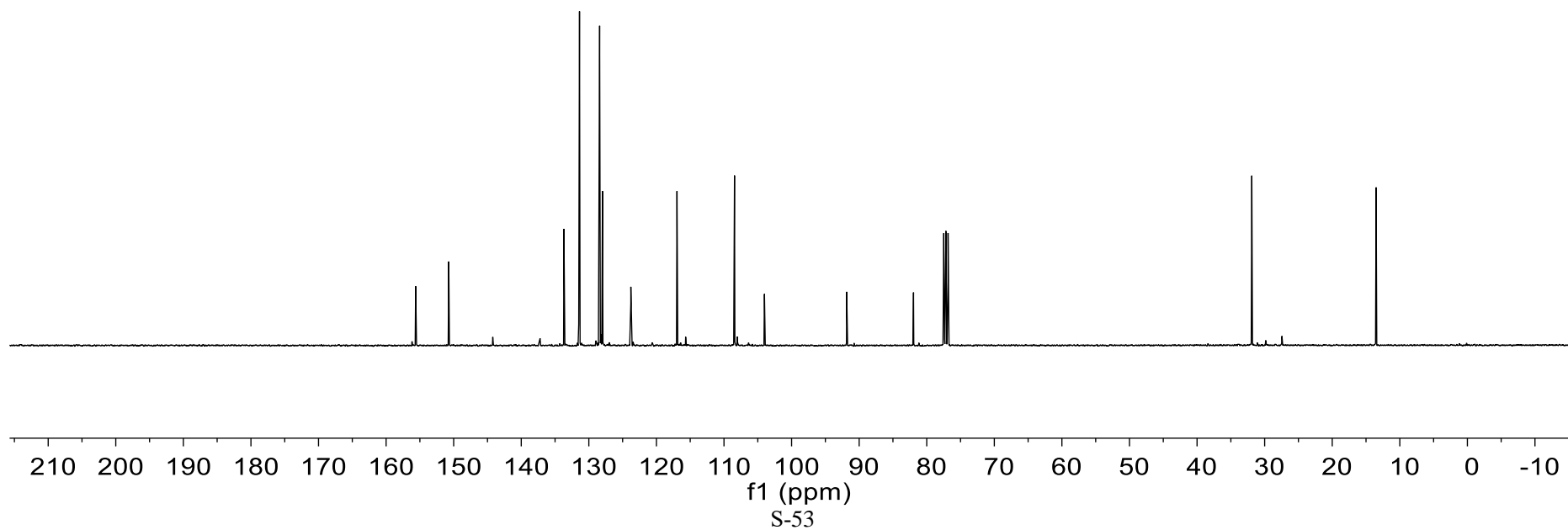


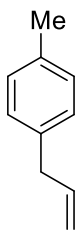


**3l**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

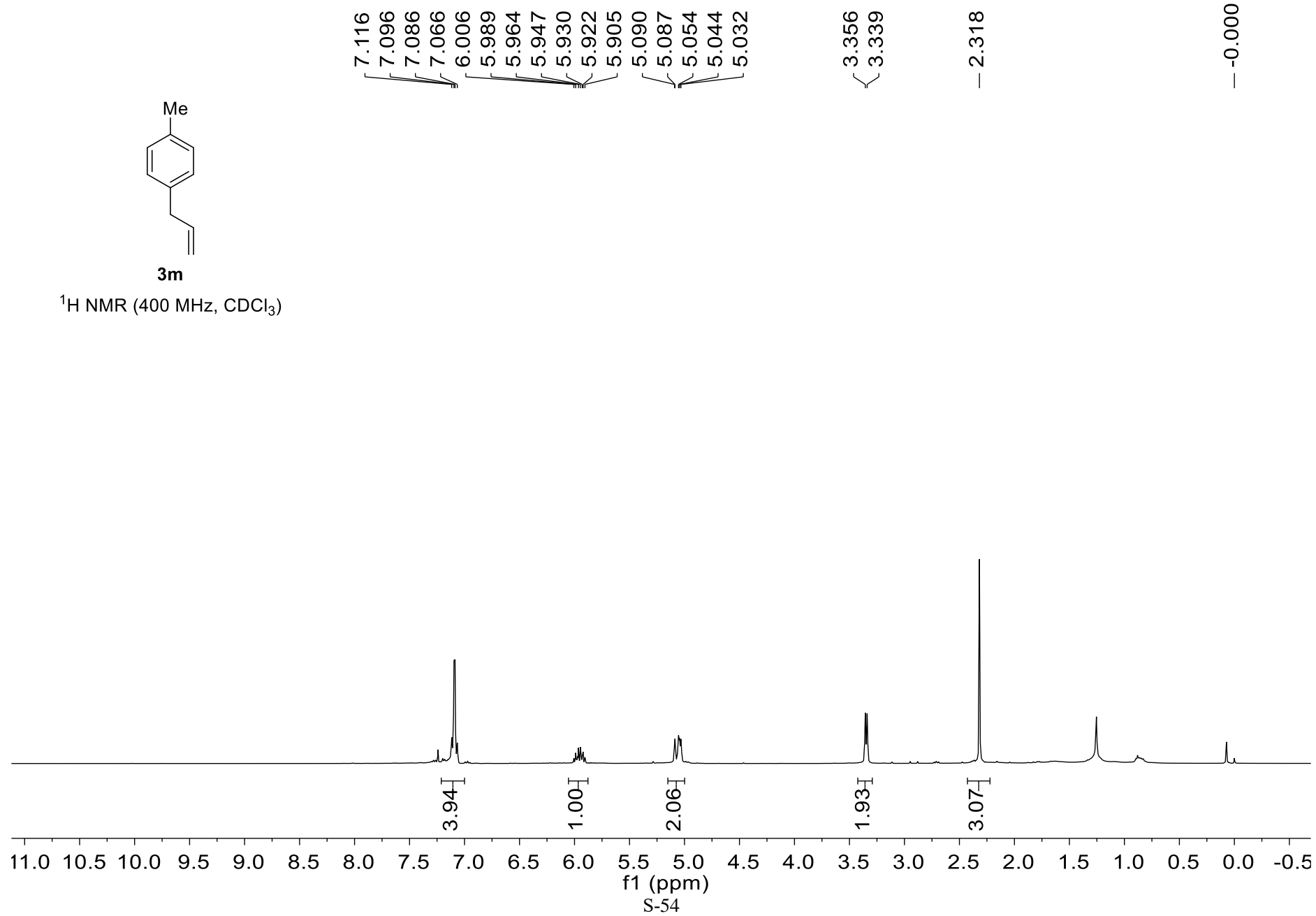
- 155.624
- 150.730
- ~ 133.684
- ~ 131.382
- ~ 128.402
- ~ 127.979
- ~ 123.783
- ~ 116.957
- ~ 108.448
- ~ 104.014
- 91.845
- ~ 81.957
- ~ 77.478
- ~ 77.160
- ~ 76.843
- 31.898
- 13.504

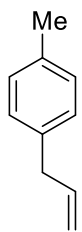




**3m**

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





**3m**

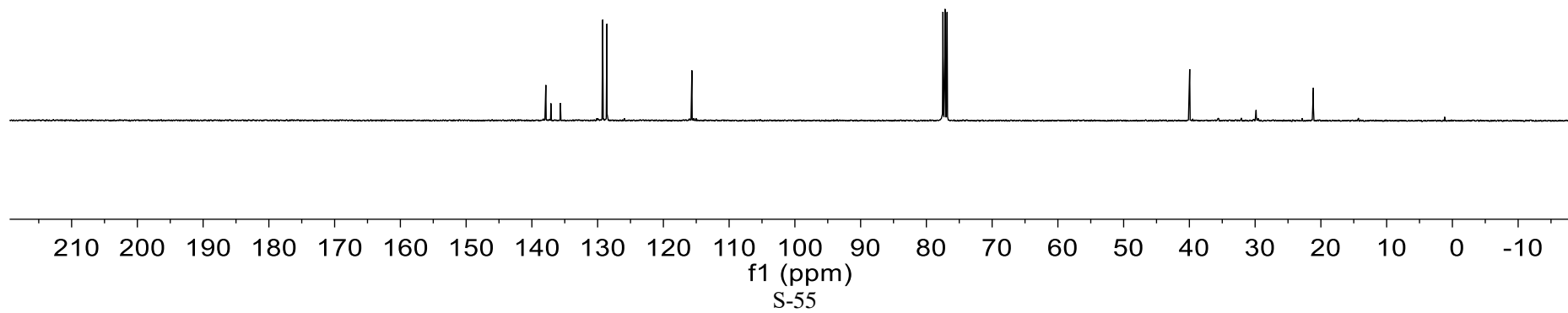
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

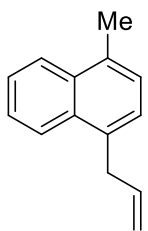
137.876  
137.109  
135.661  
129.233  
128.587  
— 115.661

77.477  
77.160  
76.842

— 39.957

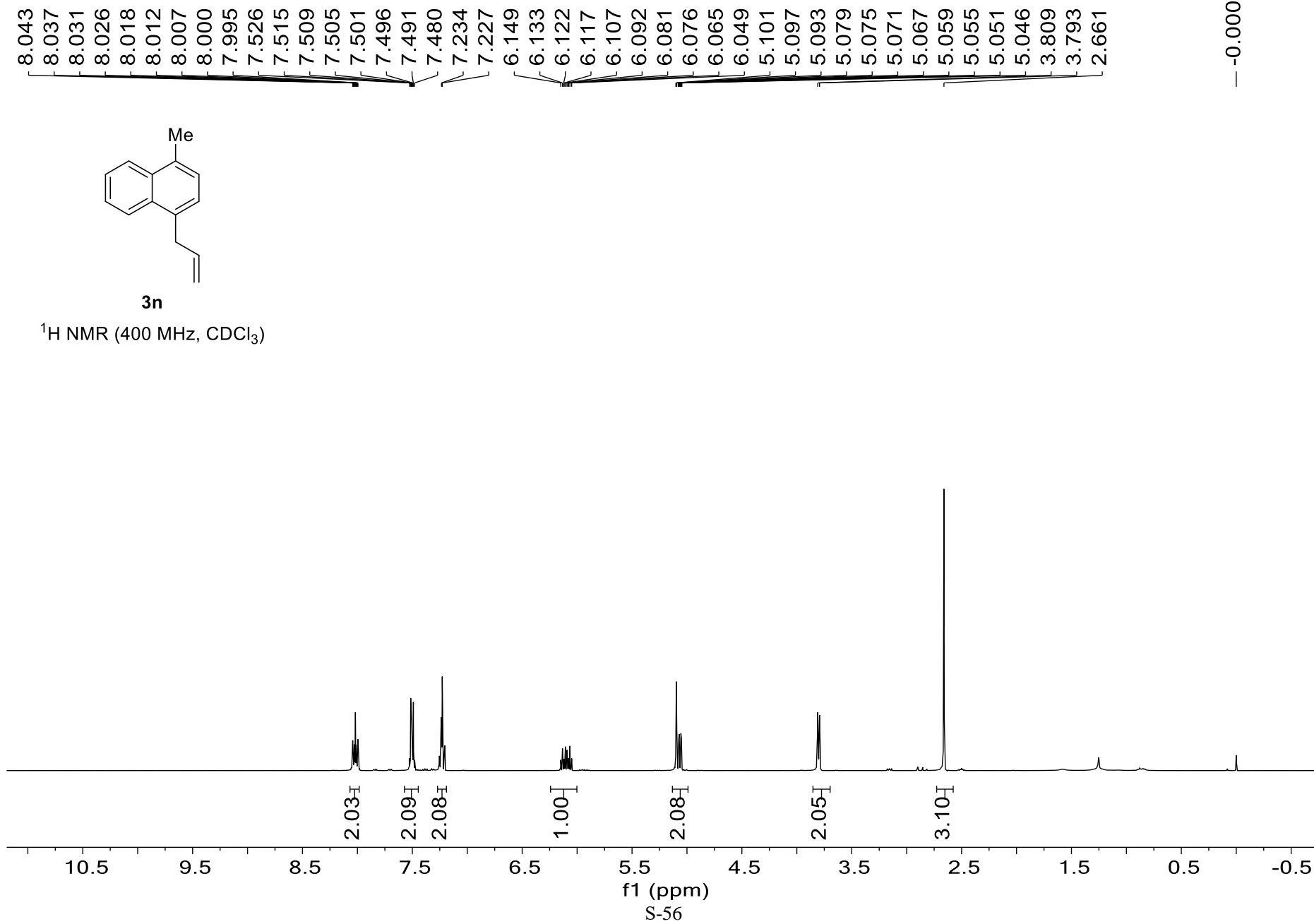
— 21.142



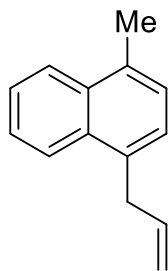


**3n**

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







**3n**

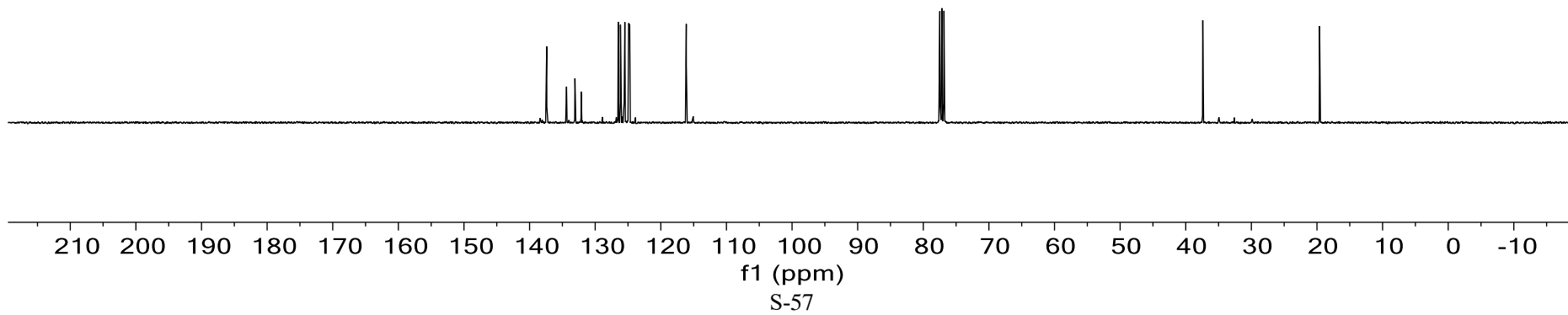
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

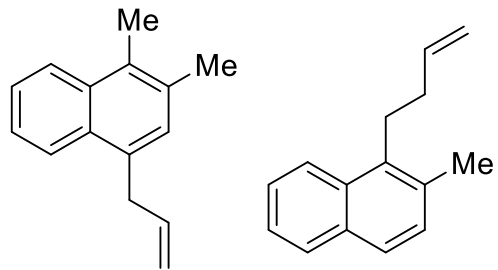
137.386  
134.370  
133.085  
133.066  
132.141  
126.494  
126.149  
125.569  
125.483  
124.911  
124.739  
116.118

77.478  
77.160  
76.843

— 37.406

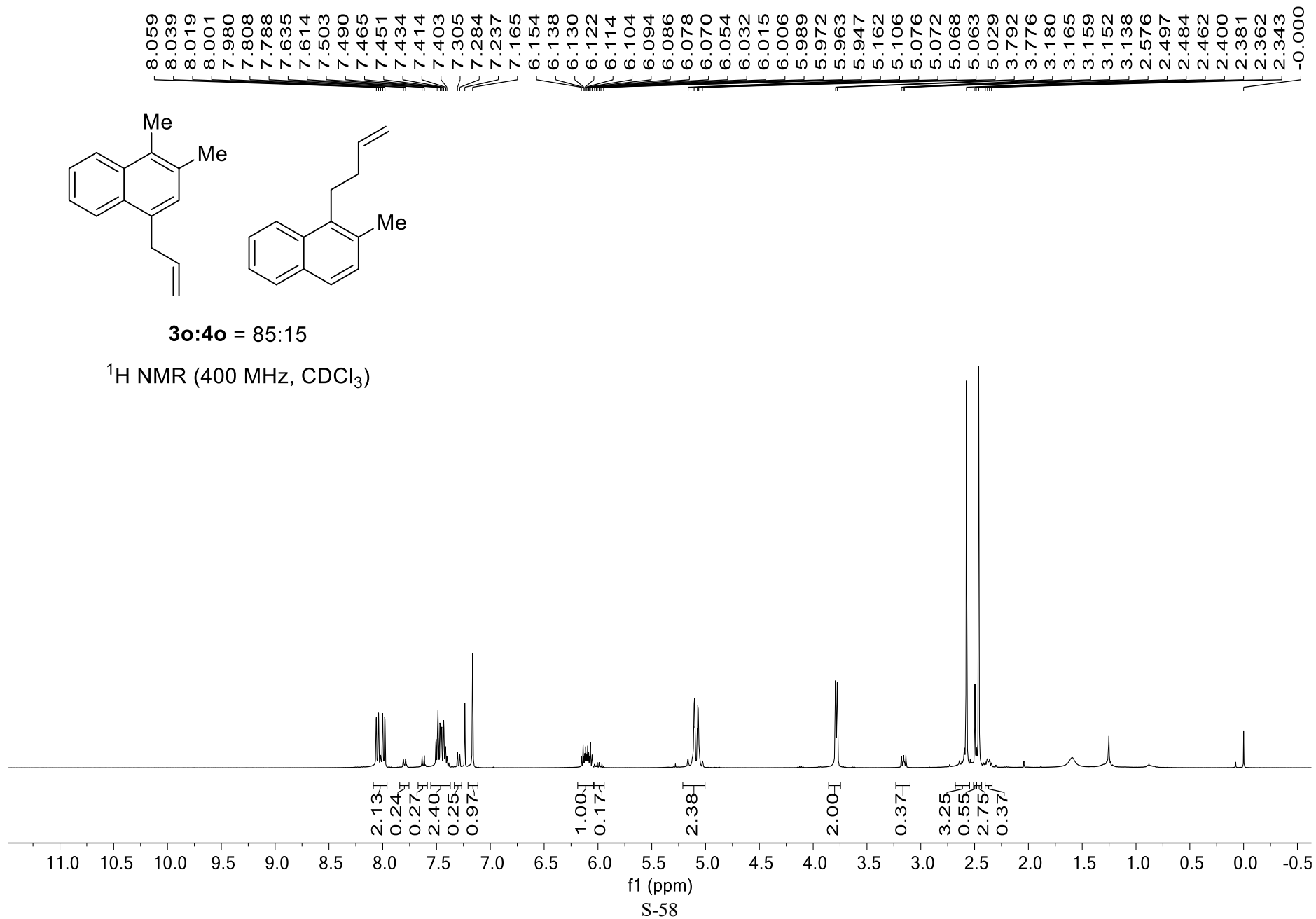
— 19.598

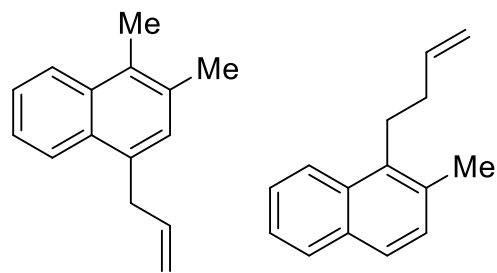




**3o:4o = 85:15**

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



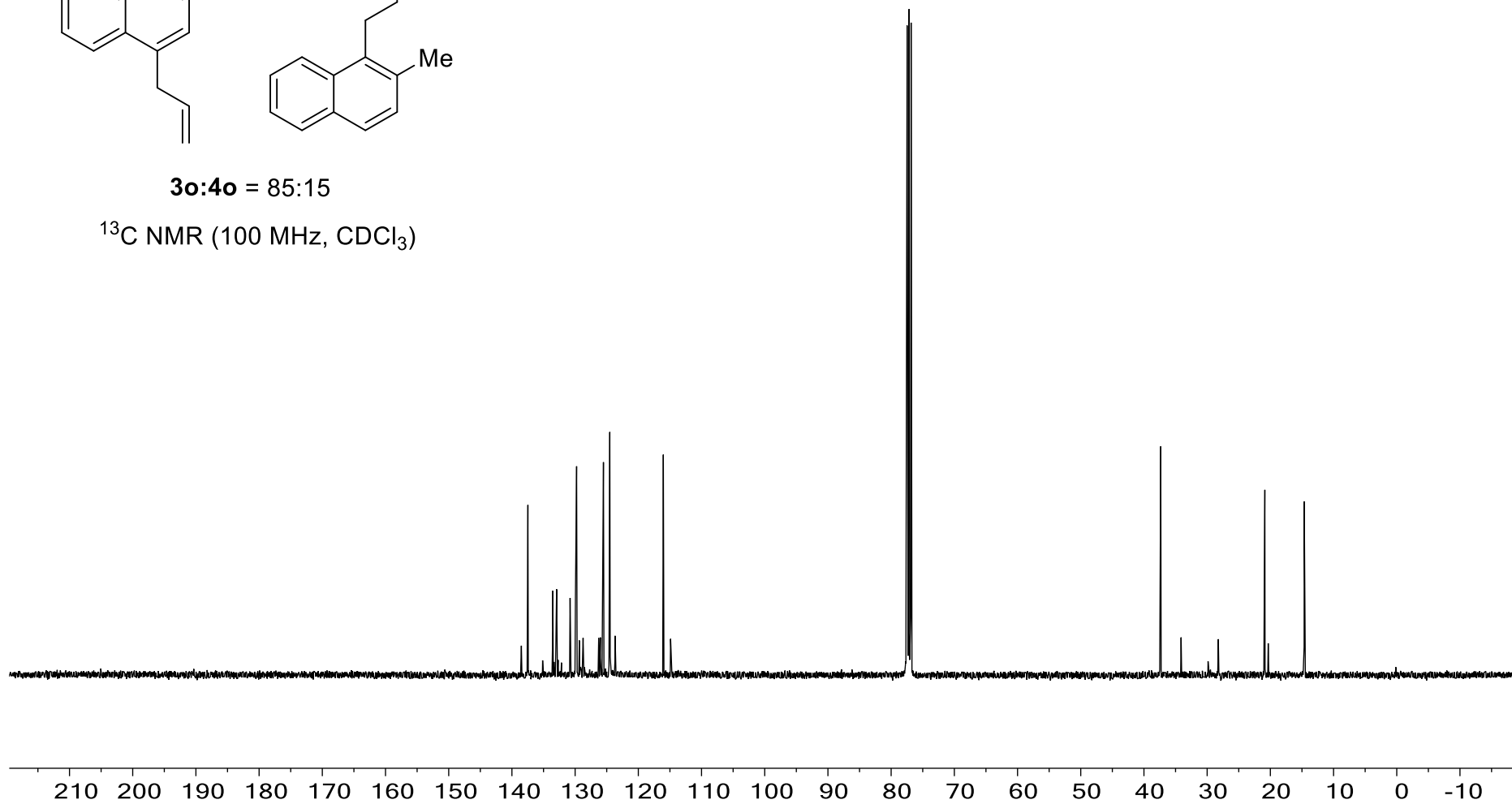


**3o:4o = 85:15**

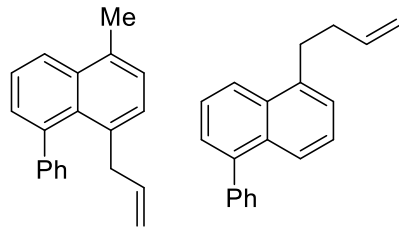
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

138.504  
 137.473  
 135.142  
 133.534  
 133.358  
 133.073  
 132.930  
 132.692  
 132.169  
 130.794  
 129.949  
 129.768  
 129.340  
 128.737  
 126.270  
 126.005  
 125.520  
 124.602  
 124.569  
 124.513  
 124.480  
 123.675  
 116.044  
 114.898  
 77.478  
 77.160  
 76.842

- 37.342  
 - 34.124  
 - 28.232  
 - 20.871  
 - 20.343  
 - 14.636

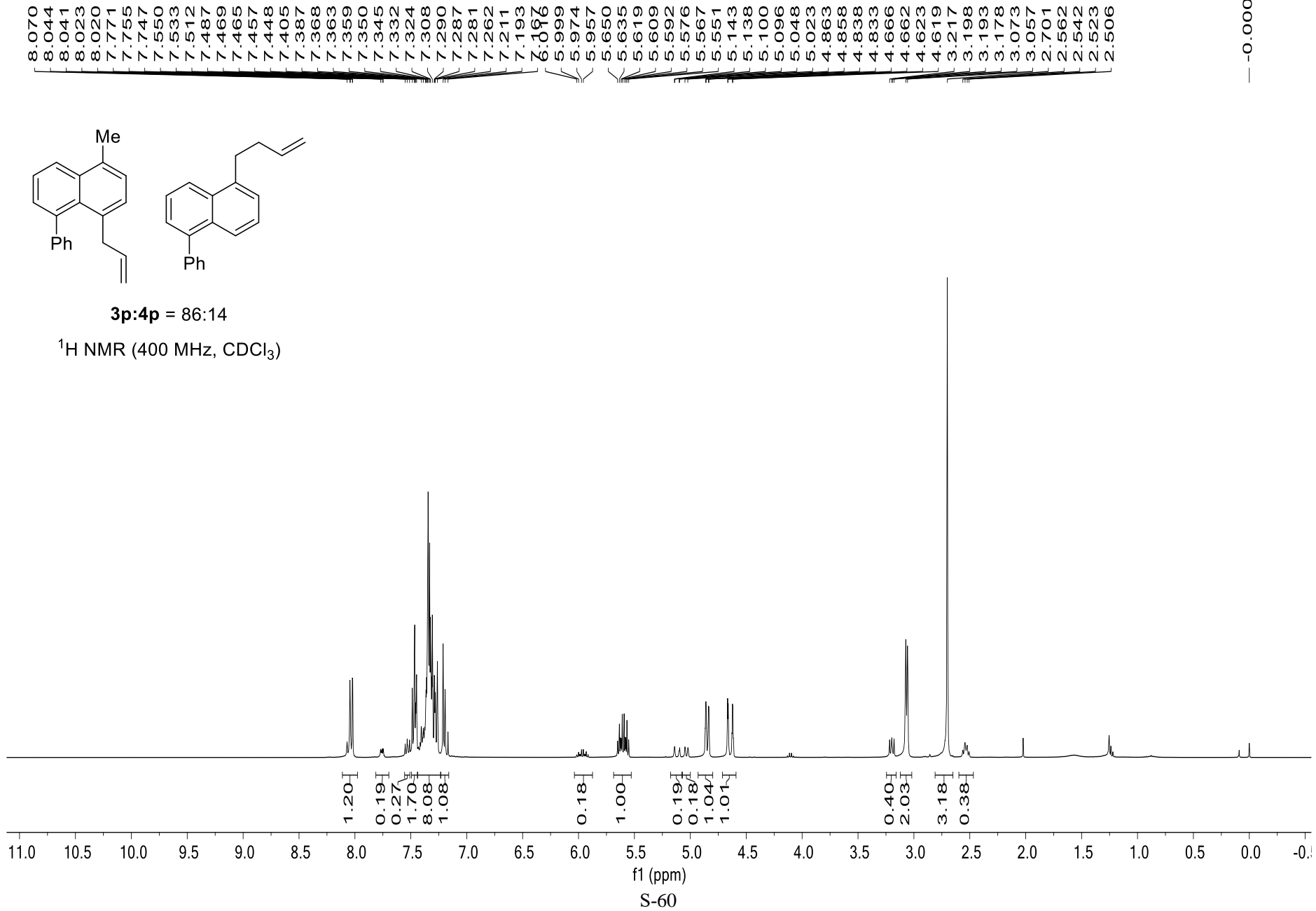


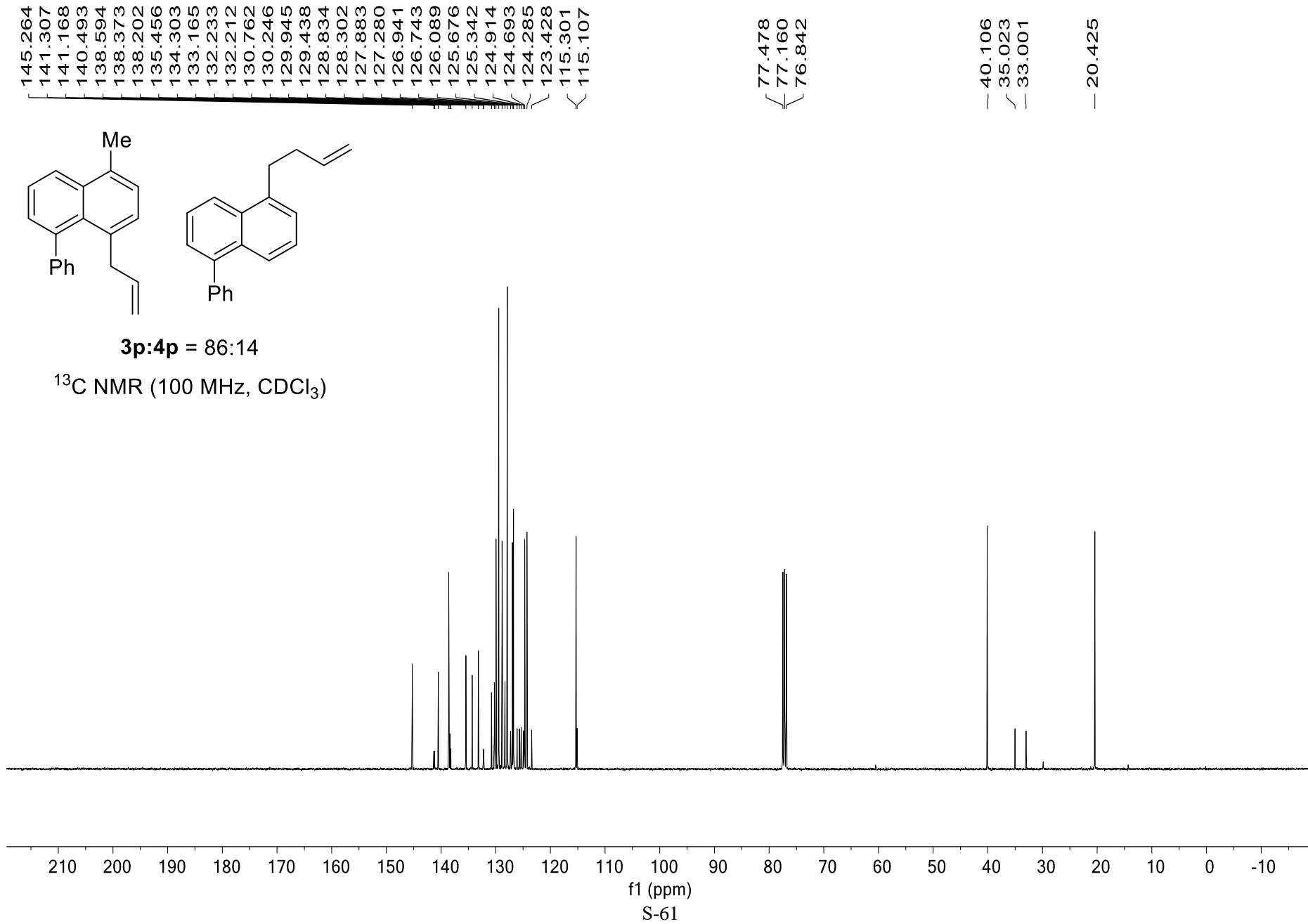
f1 (ppm)  
S-59



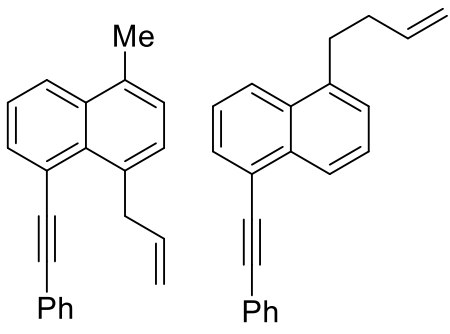
3p:4p = 86:14

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



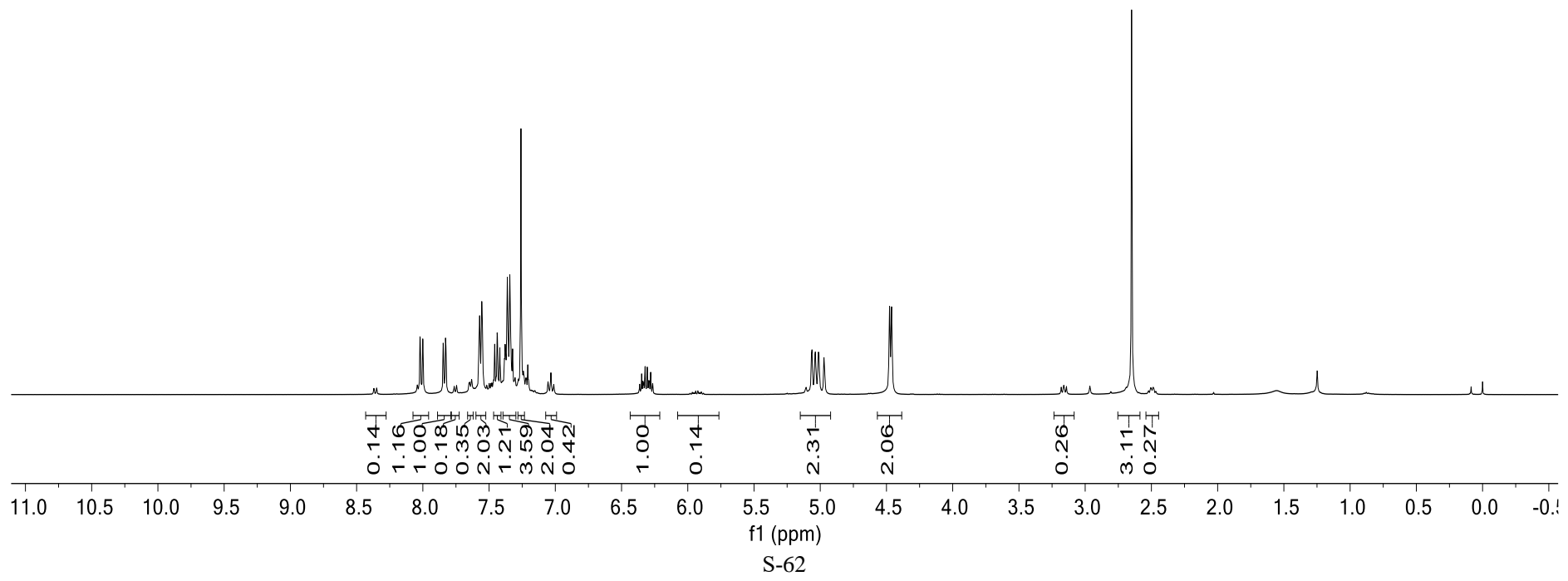


8.042  
8.022  
8.001  
7.845  
7.829  
7.763  
7.746  
7.651  
7.647  
7.631  
7.575  
7.571  
7.556  
7.518  
7.500  
7.486  
7.479  
7.458  
7.439  
7.419  
7.379  
7.362  
7.343  
7.322  
7.259  
7.241  
7.224  
7.208  
7.055  
7.033  
7.011  
6.363  
6.348  
6.338  
6.333  
6.322  
6.306  
6.295  
6.290  
6.280  
6.265  
5.065  
5.037  
5.010  
4.968  
4.477  
4.462  
3.181  
3.161  
3.141  
2.650  
2.522  
2.503  
2.486  
2.466

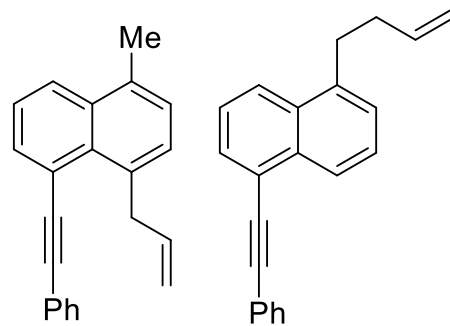


3q:4q = 90:10

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



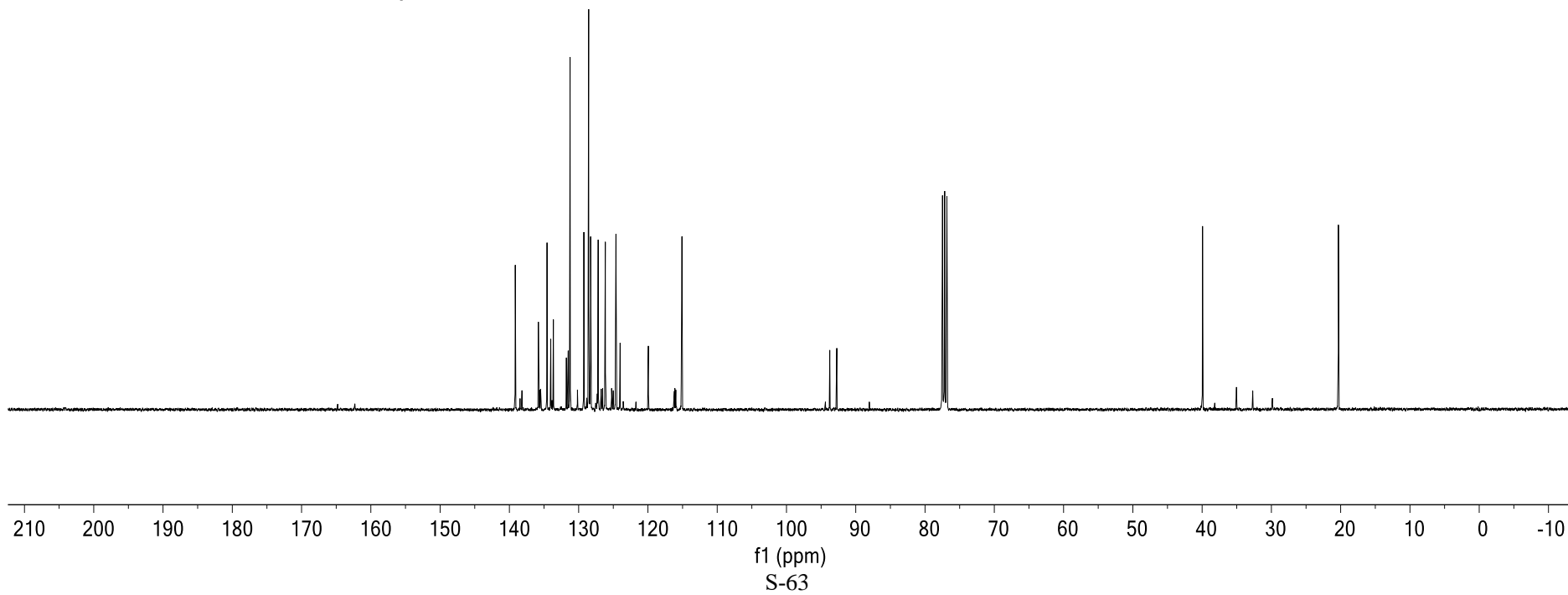
— -0.000

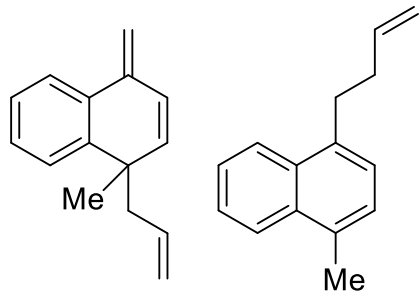


**3q:4q = 90:10**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

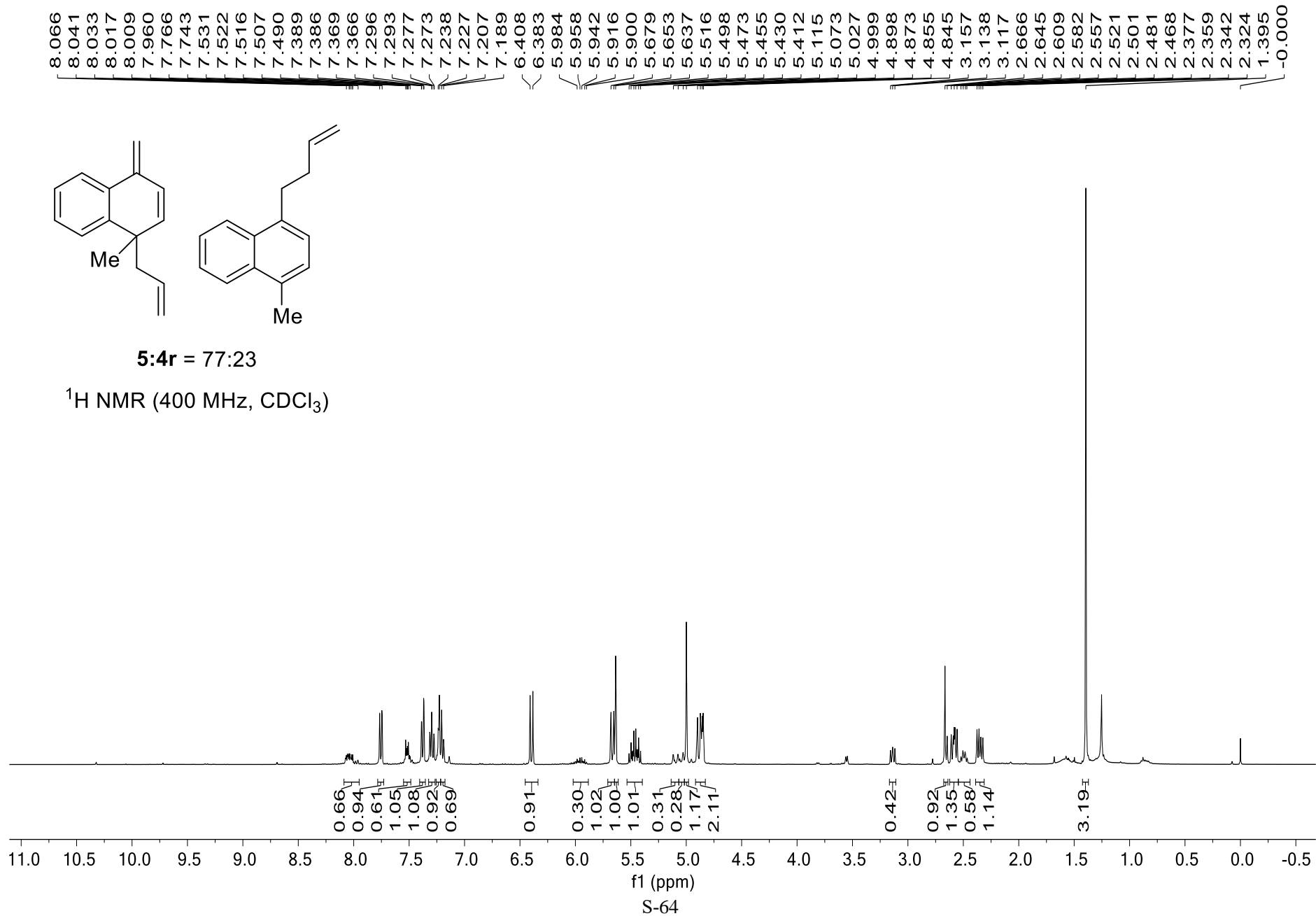
- 139.153
- 138.183
- 135.813
- 135.706
- 135.626
- 135.495
- 135.416
- 134.566
- 134.024
- 133.650
- 131.775
- 131.509
- 131.237
- 130.174
- 129.249
- 128.553
- 128.276
- 127.181
- 126.736
- 126.533
- 126.151
- 125.243
- 125.000
- 124.615
- 124.015
- 119.940
- 116.181
- 116.106
- 115.973
- 115.897
- 115.199
- 115.085
- 94.380
- 93.748
- 92.733
- 88.039
- 77.478
- 77.160
- 76.843
- 39.935
- 35.039
- 32.693
- 20.326



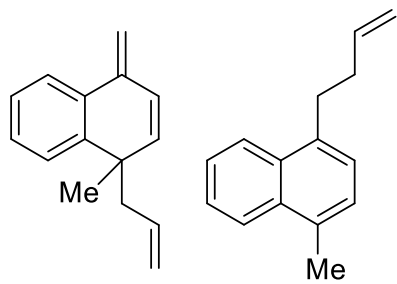


5:4r = 77:23

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





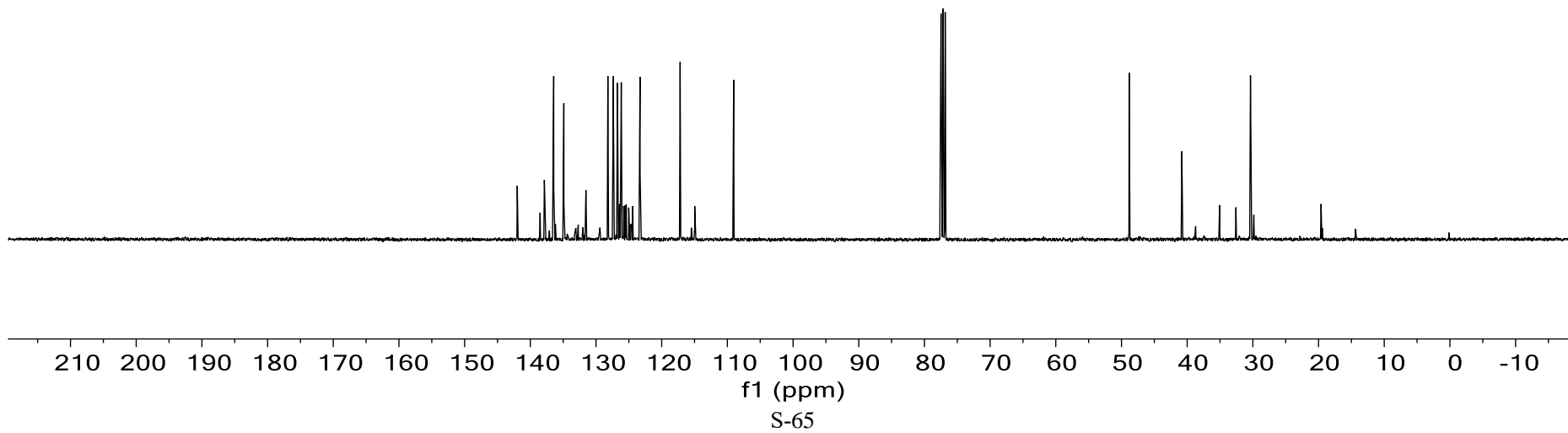


5:4r = 77:23

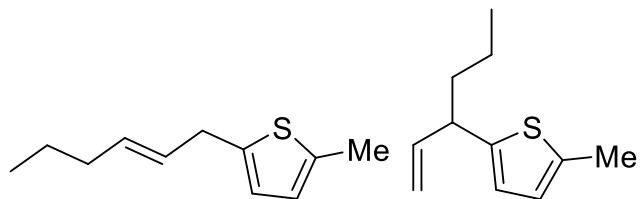
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

141.990  
138.508  
137.864  
136.442  
136.179  
134.898  
133.075  
132.709  
131.983  
131.540  
128.196  
127.350  
126.732  
126.409  
126.156  
125.785  
125.546  
125.399  
125.019  
124.409  
123.296  
117.190  
114.970  
109.046  
77.478  
77.160  
76.843

48.832  
40.806  
38.715  
35.068  
32.579  
30.366

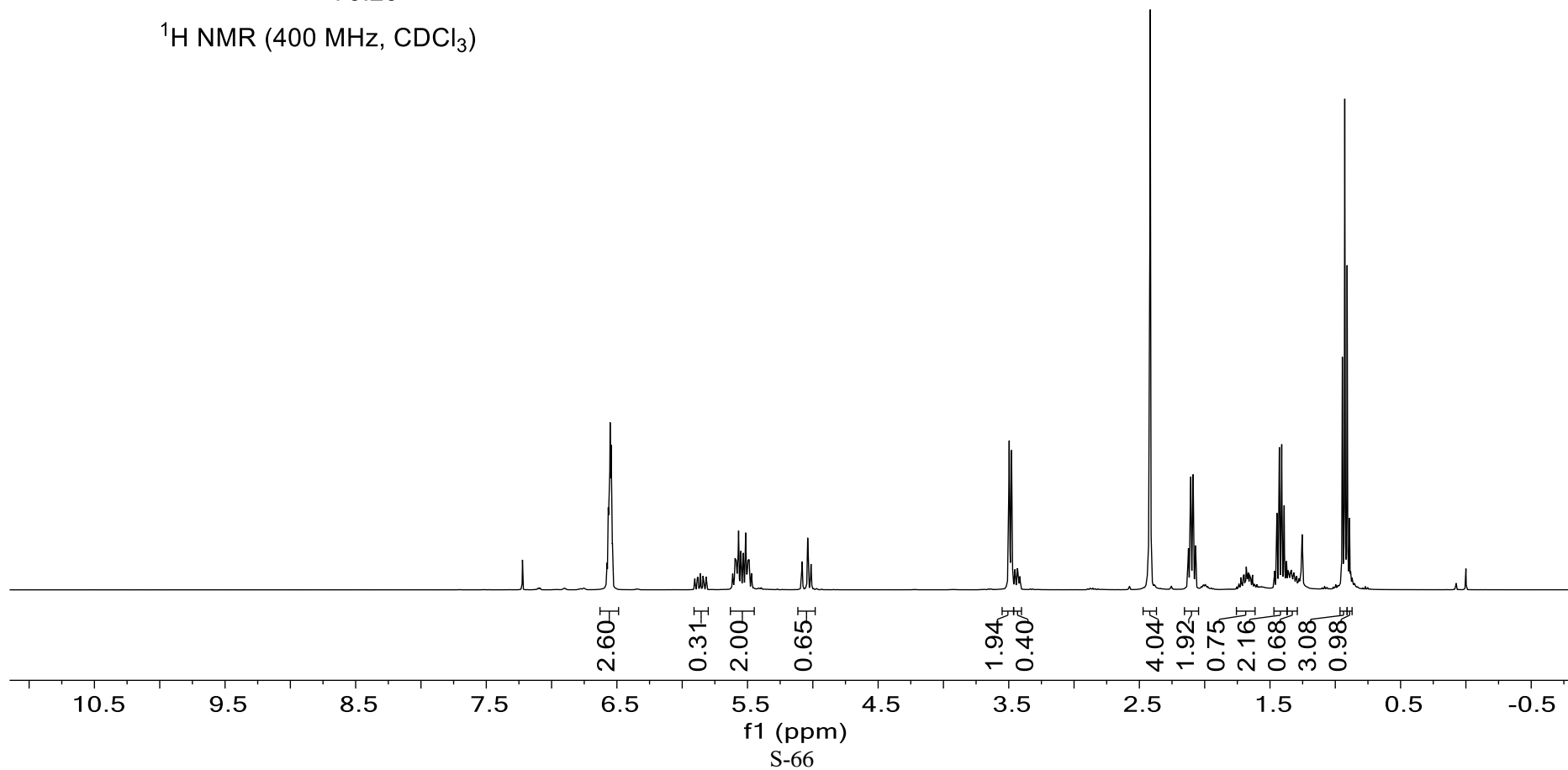


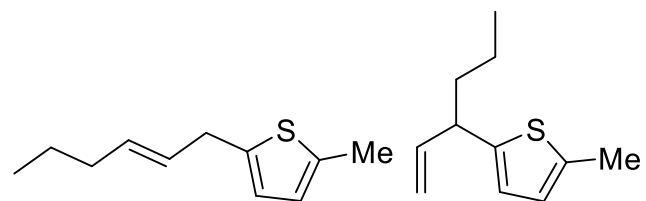
6.575  
6.566  
6.561  
6.552  
6.545  
6.534  
5.859  
5.836  
5.816  
5.613  
5.595  
5.587  
5.568  
5.551  
5.532  
5.514  
5.496  
5.487  
5.469  
5.079  
5.039  
5.014  
3.497  
3.479  
3.453  
3.433  
3.415  
2.124  
2.106  
2.088  
2.070  
1.698  
1.681  
1.665  
1.653  
1.634  
1.465  
1.447  
1.428  
1.410  
1.391  
1.373  
1.361  
1.337  
1.313  
1.295  
0.946  
0.928  
0.909  
0.891  
0.000



3s:3s' = 75:25

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





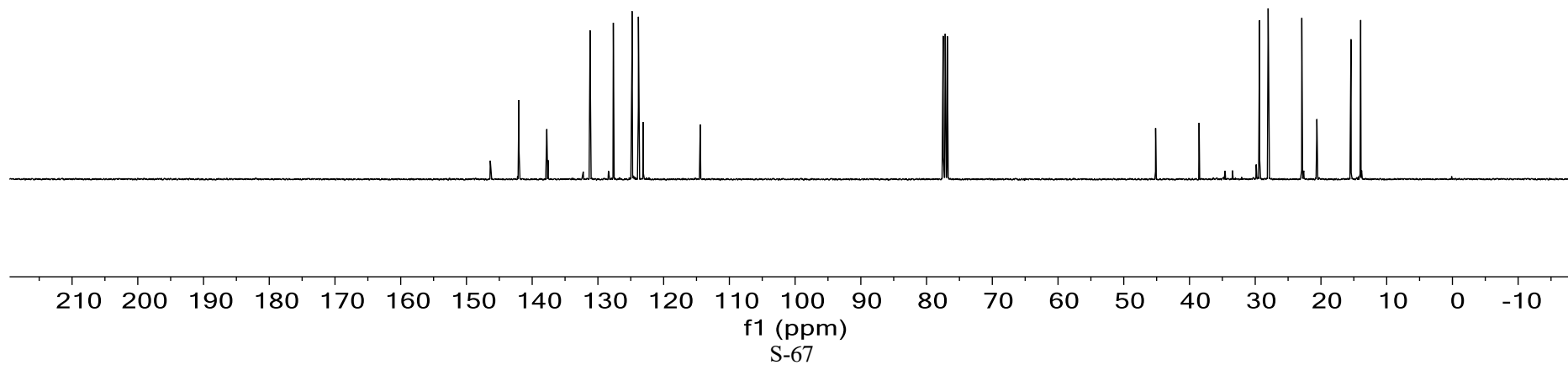
**3s:3s'** = 75:25

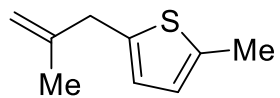
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

146.371  
142.026  
137.773  
137.586  
132.231  
131.191  
128.394  
127.656  
124.809  
124.659  
123.839  
123.091  
114.428

77.477  
77.160  
76.842

45.157  
38.540  
29.335  
28.031  
22.914  
20.620  
15.432  
14.026  
13.960





**3t**

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

6.582  
6.574  
6.559

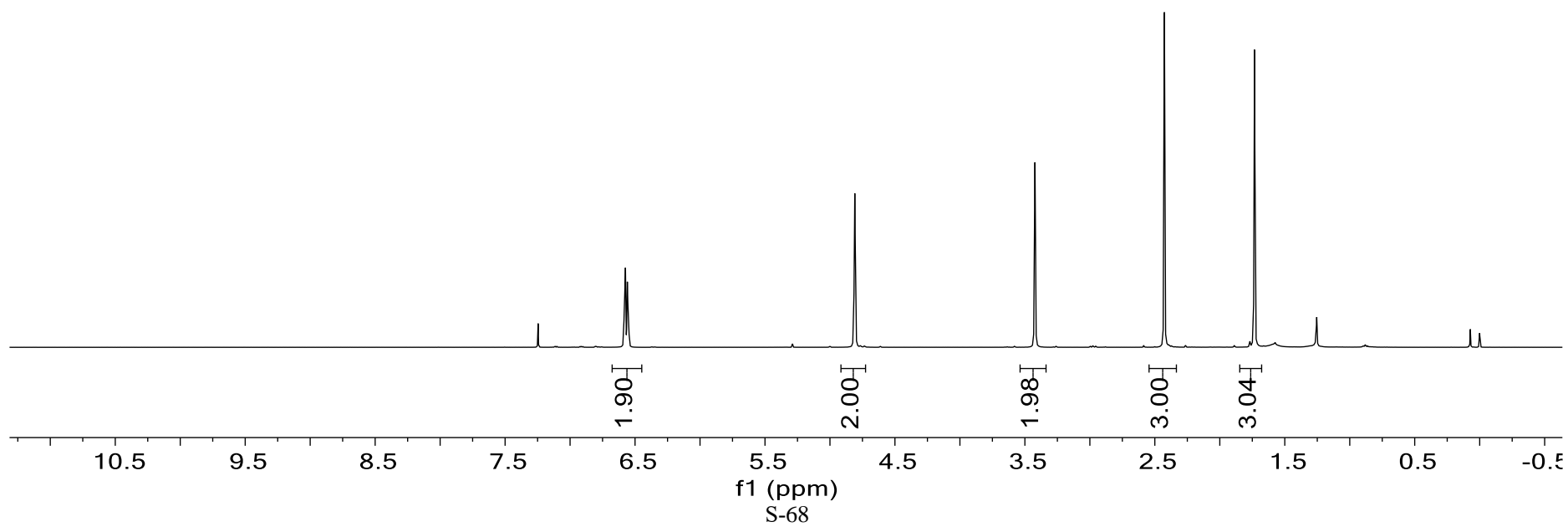
4.809

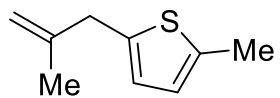
3.422

2.427

1.733

0.000





**3t**

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

144.799  
140.473  
138.195  
125.148  
124.794  
112.019  
77.477  
77.160  
76.842  
38.871  
21.907  
15.464

