

# Mild, Redox-Neutral Alkylation of Imines Enabled by an Organic Photocatalyst

Niki R. Patel, Christopher B. Kelly, Allison P. Siegenfeld, and Gary A. Molander\*

*Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania,  
231 South 34th Street, Philadelphia, Pennsylvania 19104-6323*

\*To whom correspondence should be addressed. E-mail: gmolandr@sas.upenn.edu

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## Key to Abbreviated Terms:

4CzIPN: 2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile  
CV: Cyclic Voltammogram

Cz: Carbazole  
LED: Light-emitting diode

## General Considerations:

### General:

All chemical transformations requiring inert atmospheric conditions or vacuum distillation utilized Schlenk line techniques with a 4- or 5-port dual-bank manifold. Argon or nitrogen was used to provide such an atmosphere. LED irradiation was accomplished using the LED reactors described in our previous reports.<sup>1</sup> NMR spectra (<sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F) were obtained at 298 K. <sup>1</sup>H NMR spectra were referenced to residual non-deuterated chloroform ( $\delta$  7.26) in CDCl<sub>3</sub> or residual DMSO-*d*<sub>5</sub> ( $\delta$  2.50) in DMSO-*d*<sub>6</sub>. <sup>13</sup>C NMR spectra were referenced to CDCl<sub>3</sub> ( $\delta$  77.3) or DMSO-*d*<sub>6</sub> ( $\delta$  39.5). <sup>19</sup>F NMR spectra were referenced to hexafluorobenzene ( $\delta$  -164.9) as an internal standard.<sup>2</sup> Reactions were monitored by HPLC, GC/MS, <sup>1</sup>H NMR, and/or TLC on silica gel plates (60 Å porosity, 250 µm thickness). TLC analysis was performed using hexanes/EtOAc as the eluant and visualized using permanganate stain, Seebach's stain,<sup>3</sup> ninhydrin stain, and/or UV light. Silica plugs utilized flash silica gel (60 Å porosity, 32-63 µm). Flash chromatography was accomplished using an automated system (monitoring at 254 nm and 280 nm) with silica cartridges (60 Å porosity, 20-40 µm). Solvents were purified with drying cartridges through a solvent delivery system. Melting points (°C) are uncorrected.

### Chemicals:

Deuterated NMR solvents were either used as purchased (DMSO-*d*<sub>6</sub>) or stored over 4 Å molecular sieves and/or K<sub>2</sub>CO<sub>3</sub> (CDCl<sub>3</sub>). Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, EtOAc, pentane, hexanes, heptane, Et<sub>2</sub>O, and benzene were used as purchased. Et<sub>3</sub>N and <sup>i</sup>Pr<sub>2</sub>NH, were purchased from commercial suppliers and distilled from CaH<sub>2</sub> prior to use. THF was purchased and dried *via* a solvent delivery system. Catechol was purchased and recrystallized from refluxing hexanes or heptanes. DMF (99.8%, extra dry) was stored over 4 Å molecular sieves. Anhydrous DMSO, aldehydes, sulfonamides, and amines were purchased from commercial suppliers and used

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<sup>1</sup> For information on these reactors and their construction see the supporting information of: (a) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 764.; (b) Jouffroy, M.; Kelly, C. B.; Molander, G. *Org. Lett.* **2016**, *18*, 876.

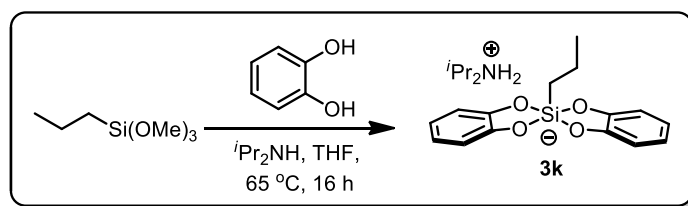
<sup>2</sup> Ravikumar, I.; Saha, S.; Ghosh, P. *Chem. Commun.* **2011**, *47*, 4721.

<sup>3</sup> Seebach, D.; Imwinkelried, R.; Stucky, G. *Helv. Chim. Acta* **1987**, *70*, 448.

without further purification. The transition metal photocatalysts  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  and  $[\text{Ir}\{\text{dFCF}_3\text{ppy}\}_2(\text{bpy})]\text{PF}_6$  were prepared in-house by the procedures outlined in our previous publications.<sup>1a,4</sup> The organic photocatalyst 4CzIPN was prepared using the procedure outlined here. New alkylsilicates (**3e-f**, **3k**) were prepared according to the representative procedure outlined below from their corresponding alkyltrimethoxysilanes. Information (preparation protocols, characterization, etc.) for all other silicates can be found in our previous reports.<sup>5</sup>

## Synthesis of Alkylbis(catecholato)silicates

### Preparation of Diisopropylammonium Bis(catecholato)propylsilicate (**3k**)



To an oven-dried, 100 mL round bottom flask equipped with a stir bar, reflux condenser, and gas inlet adapter was added catechol<sup>6</sup> (3.01 g, 27.3 mmol, 1.95 equiv) followed by anhydrous THF (28 mL) and anhydrous  $i\text{-Pr}_2\text{NH}$ <sup>7</sup> (1.70 g, 2.35 mL, 16.8 mmol, 1.2 equiv). The mixture was placed under an argon atmosphere and was allowed to stir at rt for 5 min until the solution became a pale red. After this time,  $n\text{-PrSi}(\text{OMe})_3$  (2.30 g, 14 mmol, 1.0 equiv) was added. The solution immediately lightened to a golden yellow. The solution was then heated to reflux in an oil bath and allowed to stir overnight at this temperature.<sup>8</sup> Once the reaction was judged to be complete by crude  $^1\text{H}$  NMR analysis,<sup>9</sup> the solvent was removed *in vacuo* by rotary evaporation. The resulting powder was collected *via* filtration through a medium porosity fritted funnel. The powder was washed with  $\text{Et}_2\text{O}$  (~100 mL) and pentane (~150 mL). The solid was collected and

<sup>4</sup> Tellis, J. C.; Primer, N. P.; Molander, G. A. *Science* **2014**, *345*, 433.

<sup>5</sup> (a) Jouffroy, M.; Primer, D.; Molander, G. A. *J. Am. Chem. Soc.* **2016**, *138*, 475; (b) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.*, **2016**, *18*, 764; (c) Jouffroy, M.; Davies, G. H. M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 1606.

<sup>6</sup> Recrystallized from hexane or heptane prior to use.

<sup>7</sup> A similar protocol can be used to prepare the more organic soluble triethylammonium salt. This salt works equally well for photoredox alkylation.

<sup>8</sup> Depending on the nature of the silicate and its solubility in THF, precipitation of the product would occur.

<sup>9</sup> For DIPA silicates, it is advisable to use  $\text{acetone-}d_6$  or  $\text{DMSO-}d_6$  as the NMR solvent, as these silicates have poor solubility in most other deuterated solvents.

dried further *in vacuo* to give the propylsilicate **3k** (4.20 g, 77%) as a powdery white solid (mp = 194-195 °C) that co-crystallized with ~0.25 equiv THF.<sup>10</sup>

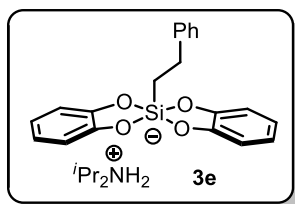
**<sup>1</sup>H NMR** δ 0.44 - 0.52 (m, 2 H), 0.73 (t, *J* = 7.3 Hz, 3 H), 1.13 - 1.26 (m, 2H), 1.18 (d, *J* = 6.4 Hz, 12H), 3.33 (sept, *J* = 6.4 Hz, 2H), 6.35 - 6.46 (m, 4 H), 6.46 - 6.54 (m, 4 H), 7.85 - 8.17 (m, 2 H).

**<sup>13</sup>C NMR** δ 17.7 (CH<sub>3</sub>), 18.0 (CH<sub>2</sub>), 18.8 (CH<sub>3</sub>), 21.1 (CH<sub>2</sub>), 46.3 (CH), 109.4 (CH), 117.0 (CH), 150.6 (CH).

**FT-IR** (cm<sup>-1</sup>, neat, ATR) 3046 (w, br), 2865 (w, br), 1484 (s), 1467 (w), 1451 (w), 1393 (vs), 810 (vs), 734 (vs).

**HRMS** (ES-) calcd for C<sub>15</sub>H<sub>15</sub>O<sub>4</sub>Si [M<sup>-i</sup>Pr<sub>2</sub>NH<sub>2</sub>]<sup>-</sup>: 287.0740, found: 287.0747.

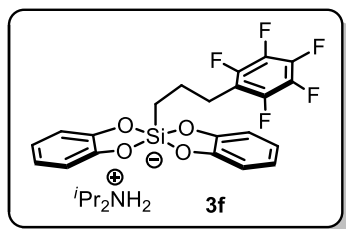
**Diisopropylammonium Bis(catecholato)(2-phenylethyl)silicate, 3e** (9.30 g, 93%) was



prepared according to the general procedure from (2-phenylethyl)trimethoxysilane (5.00 g, 22.1 mmol). The desired silicate **3e** was isolated as a off-white solid (mp = 200-201 °C). **<sup>1</sup>H NMR**

(DMSO-*d*<sub>6</sub>, 500 MHz) δ 0.72 - 0.85 (m, 2H), 1.17 (d, *J* = 6.4 Hz, 12H), 2.36 - 2.57 (m, 2H), 3.32 (sept, *J* = 6.7 Hz, 2H), 6.39 - 6.47 (m, 4H), 6.50 - 6.58 (m, 4H), 6.98 - 7.05 (m, 3H), 7.08 - 7.16 (m, 2H), 8.00 (br s, 2H). **<sup>13</sup>C NMR** (DMSO-*d*<sub>6</sub>, 125 MHz) δ 18.9 (CH<sub>3</sub>) 20.4 (CH<sub>2</sub>) 30.5 (CH<sub>2</sub>) 46.3 (CH) 109.5 (CH) 117.1 (CH) 124.8 (CH) 127.4 (CH) 127.9 (CH) 146.0 (C) 150.6 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3052 (vw, br) 2986 (vw), 2873 (vw), 1593 (w), 1485 (vs), 1239 (vs), 817 (s), 734 (vs), 700 (vs), 674 (vs), 495 (m). **HRMS** (ES-) calcd for C<sub>20</sub>H<sub>17</sub>O<sub>4</sub>Si [M<sup>-i</sup>Pr<sub>2</sub>NH<sub>2</sub>]<sup>-</sup>: 349.0896, found: 349.0908.

**Diisopropylammonium Bis(catecholato) (3-pentafluorophenylpropyl)silicate, 3f** (7.51 g,



89%) was prepared according to the general procedure from (3-pentafluorophenylpropyl)trimethoxysilane (5.02 g, 15.2 mmol).

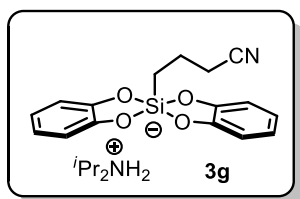
The desired silicate **3f** was isolated as a white solid (mp = 174-175 °C). **<sup>1</sup>H NMR** (DMSO-*d*<sub>6</sub>, 500 MHz) 0.45 - 0.62 (m, 2H), 1.18 (d, *J* = 7.0 Hz, 12H), 1.38 - 1.53 (m, 2H), 2.52 (t, *J* = 7.3 Hz, 2H), 3.33

<sup>10</sup> Presence of THF does not impede any photoredox process involving silicates, included alkylation.



(sept,  $J = 7.0$  Hz, 2H), 6.37 - 6.44 (m, 4H), 6.46 - 6.53 (m, 4H), 8.00 (br s, 2H).  **$^{13}\text{C}$  NMR** (DMSO- $d_6$ , 125 MHz)  $\delta$  17.9 (CH<sub>2</sub>), 18.7 (CH<sub>3</sub>), 18.8 (CH<sub>3</sub>), 24.5 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 46.4 (CH), 109.6 (CH), 116.5 (dt,  $J_{\text{C-F}} = 192.6$ ,  $J_{\text{C-C-F}} = 20.0$  Hz, CF), 117.2 (CH), 136.8 (dt,  $J_{\text{C-F}} = 243.4$ ,  $J_{\text{C-C-F}} = 14.5$  Hz, CF), 139.2 - 139.8 (m, C), 144.4 (dt,  $J_{\text{C-F}} = 242.5$ ,  $J_{\text{C-C-F}} = 11.8$  Hz, CF), 150.5 (C).  **$^{19}\text{F}$  NMR** (CDCl<sub>3</sub>, 282 MHz) -165.8 (td,  $J = 23.0$ , 6.2 Hz, 2F), -161.1 (t,  $J = 21.6$  Hz, 1F), -146.7 (dd,  $J = 22.7$ , 8.3 Hz, 2F). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3052 (vw, br.), 1485 (s), 1237 (s), 967 (w), 951 (w), 814 (s), 742 (s). **HRMS** (ES-) calcd for C<sub>21</sub>H<sub>14</sub>O<sub>4</sub>F<sub>5</sub>Si [M<sup>-i</sup>Pr<sub>2</sub>NH<sub>2</sub>]<sup>-</sup>: 453.0582, found: 453.0597.

**Diisopropylammonium Bis(catecholato)(3-cyanopropyl)silicate, 3g** (10.34 g, 95%) was



prepared according to the general procedure from 3-

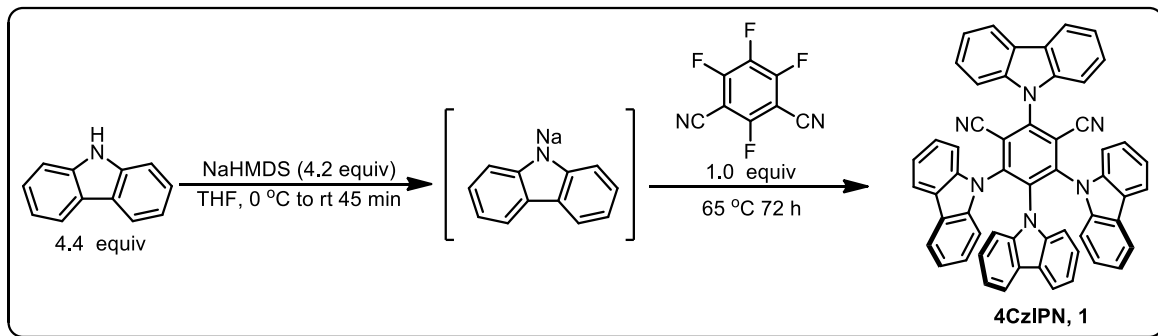
cyanopropyltrimethoxysilane (4.97 g, 26.3 mmol). The desired silicate **3g** was isolated as a light brown solid (mp = 185-186 °C).  **$^1\text{H}$  NMR**

(DMSO- $d_6$ , 500 MHz)  $\delta$  0.54 - 0.66 (m, 2H) 1.17 (d,  $J = 6.4$  Hz, 12H) 1.39 - 1.52 (m, 2H) 2.28 (t,  $J = 7.0$  Hz, 2H) 3.32 (sept,  $J = 6.4$  Hz, 2H)

6.41 - 6.48 (m, 4H) 6.51 - 6.57 (m, 4H) 8.00 (br s, 2H).  **$^{13}\text{C}$  NMR** (DMSO- $d_6$ , 125 MHz) 17.8 (CH<sub>2</sub>), 19.2 (CH<sub>3</sub>), 19.5 (CH<sub>2</sub>), 21.6 (CH<sub>2</sub>), 46.7 (CH), 110.0 (CH), 117.6 (CH), 121.3 (C), 150.8 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3110 (vw), 3052 (vw), 2974 (vw), 2235 (vw), 1485 (vs), 1237 (vs), 810 (vs), 740 (vs), 710 (vs). **HRMS** (ES-) calcd for C<sub>16</sub>H<sub>14</sub>NO<sub>4</sub>Si [M<sup>-i</sup>Pr<sub>2</sub>NH<sub>2</sub>]<sup>-</sup>: 312.0692, found: 312.0692.

## Synthesis of 4CzIPN

### Preparation of the Organic Photocatalyst



### 2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN, 1)

To a 250 mL flame-dried round bottom flask equipped with a stir bar, septum and nitrogen inlet needle was added carbazole (6.43 g, 38.5 mmol, 4.4 equiv). The system was sealed with a rubber septum and evacuated *via* an inlet needle and purged with Ar. Dry THF (77 mL) was then added, and the solution was cooled to 0 °C in an ice bath. The solution was allowed to cool for 10 min. The flask was then charged with NaHMDS in THF (2 M, 18.4 mL, 36.7 mmol, 4.2 equiv) by syringe, resulting in the solution becoming an orange-brown color. The solution was stirred for five minutes at 0 °C. After this time, the ice bath was removed, and the solution was allowed to stir at rt for 30 min. The flask was then charged with tetrafluoroisophthalonitrile (1.75 g, 8.75 mmol, 1.0 equiv) and equipped with a reflux condenser. The solution was heated at 65 °C under an Ar atmosphere and allowed to stir at this temperature for 72 h. During this time period, the solution became a very dark brown with a voluminous yellow precipitate forming over time. After the 72 h period, the flask was allowed to cool to rt and the contents of the flask were poured into a medium porosity fritted glass funnel. After the solids and liquid were separated, the solids were washed with Et<sub>2</sub>O (350 mL) to remove residual carbazole. The filtrate was discarded, and the solid was then washed with CHCl<sub>3</sub> (600 mL), to which 4CzIPN has partial solubility. The bright yellow filtrate was collected and the solvent was removed *in vacuo* by rotary evaporation. After removing residual solvent at low pressure (~0.2 mmHg), pure **1** (6.37 g, 92%) was obtained as a bright yellow solid (mp >250 °C). Characterization data for this compound matched that reported in the literature.<sup>11</sup>

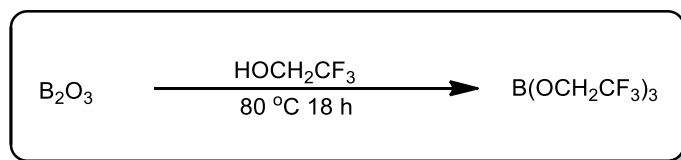
<sup>11</sup> (a) Uoyama, H. Goushi, K.; Shizu, K.; Nomura, H.; Adachi C. *Nature* **2012**, *492*, 234; (b) Luo, J.; Zhang, J. *ACS Catal.* **2016**, *6*, 873.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 6.63 (t, *J* = 7.8 Hz, 2H), 6.82 (t, *J* = 8.1 Hz, 4H), 7.04 - 7.12 (m, 8H), 7.20 - 7.24 (m, 4H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.66 - 7.73 (m, 8H), 8.22 (d, *J* = 7.8 Hz, 2H).

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 109.7 (CH), 109.8 (CH), 110.2 (CH), 111.9 (C), 116.7 (C), 119.9 (CH), 120.7 (CH), 121.3 (CH), 121.7 (CH), 122.2 (CH), 122.7 (CH), 124.1 (C), 124.8 (CH), 125.0 (C), 125.3 (C), 126.1 (CH), 127.2 (CH), 135.1 (C), 137.3 (C), 138.5 (C), 140.3 (C), 144.9 (C), 145.5 (C).

## General Procedures of Imines

### Preparation of *N*-Sulfonyl Imines



### Preparation of Sheppard's Reagent, *Tris*(2,2,2-trifluoroethyl)borate

The following procedure is a modification of the procedure described by Sheppard.<sup>12</sup> To a flame-dried 250 mL round bottom flask equipped with a reflux condenser, septum, and stir bar was added boric anhydride (51.04 g, 0.73 mol) and 2,2,2-trifluoroethanol (93 mL, 123.23 g, 1.23 mol). The reaction mixture was heated to 80 °C under argon for 18 h while stirring vigorously. After this time, the thick slurry was cooled to rt and filtered through a coarse fritted funnel. The resulting clear, pale yellow oil was fractionally<sup>13</sup> distilled (bp 119-122 °C @ 760 mmHg) through a 7 cm Vigreux column to give the desired boronate as a clear, colorless oil (46.17 g, 37%).<sup>14</sup>

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 4.22 (q, *J* = 8.5 Hz, 6H).

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 62.2 (q, *J*<sub>C-C-F</sub> = 36.3 Hz, CH<sub>2</sub>), 123.7 (q, *J*<sub>C-F</sub> = 277.0 Hz, CF<sub>3</sub>).

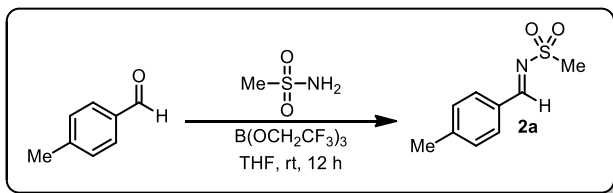
**<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz) δ -79.6 (s, 9F).

<sup>12</sup> Lanigan, R. M.; Starkov, P.; Sheppard, T. D. *J. Org. Chem.* **2013**, 78, 4512

<sup>13</sup> 2,2,2-Trifluoroethanol can azeotrope with the product, thus it is *imperative* that multiple fractions be collected.

<sup>14</sup> Sheppard's reagent should be stored in a sealed vial under an inert atmosphere to avoid hydrolysis under atmospheric conditions.

### Representative Procedure for *N*-Sulfonyl Imine Synthesis



#### *N*-(4-Methylbenzylidene)methanesulfonamide<sup>15</sup> (**2a**)

The following procedure is a modification of the procedure described by Reeves.<sup>16</sup> To a 50 mL round bottom flask equipped with a stir bar was added methanesulfonamide (1.71 g, 18 mmol, 1.2 equiv), THF (15 mL), and *p*-tolualdehyde (1.80 g, 15 mmol, 1 equiv). The reaction mixture was stirred for 5 min. The flask was then charged with Sheppard's reagent (4.04 mL, 5.77 g, 18.25 mmol, 1.25 equiv), and was sealed with a rubber septum. The reaction mixture was stirred at rt overnight. After judged to be complete by <sup>1</sup>H NMR analysis,<sup>17</sup> the reaction mixture was diluted with ~20 mL of EtOAc and transferred to a separatory funnel. Saturated aq NaHCO<sub>3</sub> (~50 mL) and an additional 20 mL of EtOAc were added, and the layers were separated. The aq layer was extracted with additional EtOAc (3 × 30 mL) and the combined organic layers were washed with saturated aq NaHCO<sub>3</sub> (~75 mL), deionized H<sub>2</sub>O (~100 mL) and finally brine (~100 mL). The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was removed *in vacuo* by rotary evaporation. Upon solvent removal, a crude solid was obtained. The solid was washed with pentane (5 × 15 mL) and dried *in vacuo* to afford pure **2a** (2.34 g, 79%) as a white solid (mp = 110-111 °C).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 2.46 (s, 3H), 3.12 (s, 3H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 2H), 8.98 (s, 1H).

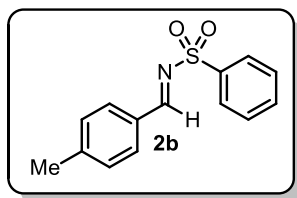
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 22.3 (CH<sub>3</sub>), 40.6 (CH<sub>3</sub>), 129.9 (C), 130.3 (CH), 131.7 (CH), 147.0 (C), 171.7 (CH).

<sup>15</sup> Shaghafi, M. B.; Grote, R. E.; Jarvo, E. R. *Org. Lett.* **2011**, *13*, 5188.

<sup>16</sup> Reeves, J. T.; Visco, M. D.; Marsini, M. A.; Grinberg, N.; Busacca, C. A.; Mattson, A. E.; Senanayake, C. H. *Org. Lett.* **2015**, *17*, 2442.

<sup>17</sup> In several cases with other aldehydes, the reaction required longer reaction times. If the reaction did not reach completion after 24 h, an additional 0.5 equiv of Sheppard's reagent and 0.25 equiv of the sulfonamide were added. Typically the reaction reached completion within 24 h of this addition. If no progression of the reaction was observed after this time, the reaction was halted and workup commenced.

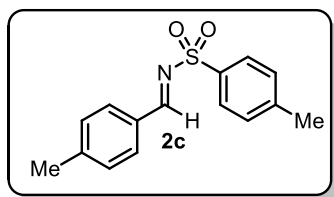
**N-(4-Methylbenzylidene)benzenesulfonamide**,<sup>18</sup> **2b** (2.09 g, 81%) was prepared according to



the general procedure from *p*-tolualdehyde (1.32 g, 11 mmol, 1.1 equiv) **with the following modification**: Benzenesulfonamide (1.57 g, 10 mmol, 1 equiv) was used in place of methanesulfonamide and served as the limiting reagent. The desired imine **2b** was isolated as a

white solid (mp = 113-114 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 2.43 (s, 3H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.54 (t, *J* = 7.9 Hz, 2H), 7.62 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 8.01 (dd, *J* = 8.4, 1.1 Hz, 2H), 9.02 (s, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 22.3 (CH<sub>3</sub>), 128.2 (CH), 129.4 (CH), 130.1 (C), 130.2 (CH), 131.8 (CH), 133.7 (CH), 138.8 (C), 146.8 (C), 170.7 (CH).

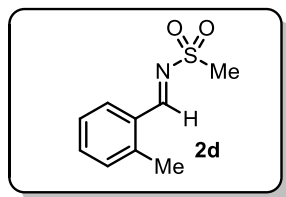
**4-Methyl-N-(4-methylbenzylidene)benzenesulfonamide**,<sup>19</sup> **2c** (1.01 g, 74%) was prepared



according to the general procedure from *p*-tolualdehyde (0.721 g, 6 mmol, 1.2 equiv) **with the following modification**: Benzenesulfonamide (0.856 g, 5 mmol, 1 equiv) was used in place of methanesulfonamide and served as the limiting reagent. The

desired imine **2c** was isolated as a white solid (mp = 114-115 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 2.43 (s, 3H), 2.44 (s, 3H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 8.99 (s, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 21.9 (CH<sub>3</sub>), 22.3 (CH<sub>3</sub>), 126.8 (C), 128.3 (CH), 130.0 (CH), 130.2 (CH), 131.7 (CH), 135.7 (C), 144.7 (C), 146.7 (C), 170.2 (CH).

**N-(2-Methylbenzylidene)methanesulfonamide**,<sup>20</sup> **2d** (2.28 g, 71%) was prepared according to



the general procedure from *o*-tolualdehyde (1.80 g, 0.015 mol). The desired imine **2d** was obtained as a light yellow solid (mp = 103 °C).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 2.62 (s, 3H), 3.13 (s, 3H), 7.25 - 7.36 (m, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 9.32 (s, 1H).

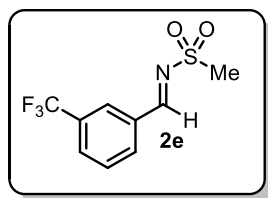
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 19.8 (CH<sub>3</sub>), 40.6 (CH<sub>3</sub>), 126.9 (CH), 130.3 (C), 130.7 (CH), 131.9 (CH), 135.0 (CH), 142.7 (C), 170.3 (CH).

<sup>18</sup> Cui, X.; Shi, F.; Deng, Y. *Chem. Commun.* **2012**, 48, 7586.

<sup>19</sup> Boulwood, T.; Affron, D. P.; Trowbridge, A. D.; Bull, J. A. *J. Org. Chem.* **2013**, 78, 6632.

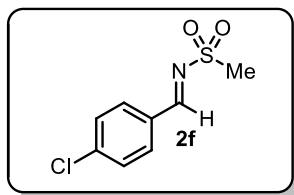
<sup>20</sup> Uruguchi, D.; Kinoshita, N.; Kizu, T.; Ooi, T. *J. Am. Chem. Soc.* **2015**, 137, 13768.

**N-(3-(Trifluoromethyl)benzylidene)methanesulfonamide**,<sup>21</sup> **2e** (2.67 g, 71%) was prepared



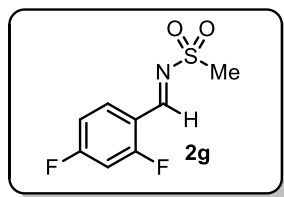
according to the general procedure from 3-(trifluoromethyl)benzaldehyde (2.61 g, 0.015 mol). The desired imine **2e** was obtained as a white solid (mp = 90-92 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 3.17 (s, 3H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 8.26 (s, 1H), 9.09 (s, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 40.3 (CH<sub>3</sub>), 123.5 (q, *J*<sub>C-F</sub> = 273.4 Hz, CF<sub>3</sub>), 127.5 (q, *J*<sub>C-C-F</sub> = 3.6 Hz, CH), 130.1 (C), 131.4 (q, *J*<sub>C-C-F</sub> = 2.7 Hz, CH), 132.1 (q, *J*<sub>C-C-F</sub> = 33.6 Hz, C), 133.0 (CH), 134.7 (CH), 170.3 (CH). **<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz) -66.2 (s, 3F). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3072 (vw), 3050 (vw), 2951 (w), 1602 (m), 1301 (vs), 1146 (vs), 968 (m), 802 (vs), 702 (m), 502 (s). **HRMS** (ES<sup>+</sup>) calcd for C<sub>9</sub>H<sub>9</sub>F<sub>3</sub>NO<sub>2</sub>S [M+H]<sup>+</sup>: 252.0306, found: 252.0298.

**N-(4-Chlorobenzylidene)methanesulfonamide**,<sup>22</sup> **2f** (2.51 g, 77%) was prepared according to



the general procedure from 4-chlorobenzaldehyde (2.11 g, 0.015 mol). The desired imine **2f** was obtained as a white solid (mp = 100-102 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 3.13 (s, 3H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 2H), 8.99 (s, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 40.5 (CH<sub>3</sub>), 130.0 (CH), 130.8 (C), 132.6 (CH), 142.0 (C), 170.5 (CH).

**N-(2,4-Difluorobenzylidene)methanesulfonamide**, **2g** (2.63 g, 71%) was prepared according to



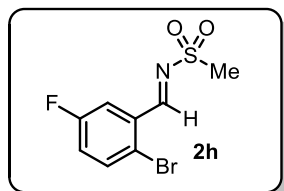
the general procedure from 2,4-difluorobenzaldehyde (2.61 g, 0.015 mol). The desired imine **2g** was obtained as an off-white solid (mp = 119-121 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 3.14 (s, 3H), 6.95 (ddd, *J* = 10.4, 8.4, 2.3 Hz, 1H), 7.01 - 7.07 (m, 1H), 8.10 - 8.21 (m, 1H), 9.29 (s, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 40.4 (CH<sub>3</sub>), 105.2 (dd, *J*<sub>C-C-F</sub> = 26.0, *J*<sub>C-C-F</sub> = 24.0 Hz, CH), 113.4 (dd, *J*<sub>C-C-F</sub> = 22.0, *J*<sub>C-C-C-F</sub> = 3.7 Hz, CH), 117.2 (dd, *J*<sub>C-C-F</sub> = 8.7, *J*<sub>C-C-C-F</sub> = 3.2 Hz, C), 131.5 (dd, *J*<sub>C-C-C-F</sub> = 11.0, *J*<sub>C-C-C-F</sub> = 2.8 Hz, CH), 165.6 (dd, *J*<sub>C-F</sub> = 317.1, *J*<sub>C-C-C-F</sub> = 12.8 Hz, CF), 164.29 (d, *J*<sub>C-C-C-F</sub> = 5.5 Hz, CH), 167.6 (dd, *J*<sub>C-F</sub> = 317.1, *J*<sub>C-C-C-F</sub> = 12.8 Hz, CF). **<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz) -114.1 (d, *J* = 12.4 Hz, 1F), -99.2 (d, *J* = 12.4 Hz, 1F). **FT-IR** (cm<sup>-1</sup>, neat,

<sup>21</sup> Marques, C. S.; Burke, A. J. *Eur. J. Org. Chem.* **2012**, 4232.

<sup>22</sup> Marques, C. S.; Burke, A. J. *Eur. J. Org. Chem.* **2012**, 4232.

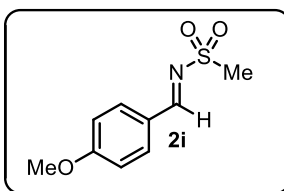
ATR) 3112 (vw), 3023 (vw), 2927 (vw), 1607(s), 1583 (s), 1498 (m), 1431 (w), 1298 (s), 1270 (vs), 1134 (s), 1092 (m), 975 (m), 809 (s), 750 (m). **HRMS** (CI+) calcd for C<sub>8</sub>H<sub>8</sub>F<sub>2</sub>NO<sub>2</sub>S [M+H]<sup>+</sup>: 220.0238, found: 220.0335.

**N-(2-Bromo-5-fluorobenzylidene)methanesulfonamide, 2h** (2.69 g, 64%) was prepared



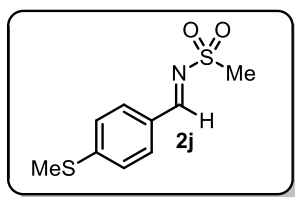
according to the general procedure from 2-bromo-5-fluorobenzaldehyde (3.05 g, 0.015 mol). The desired imine **2h** was obtained as an off-white white solid (mp = 128-129 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 3.17 (s, 3H), 7.23 (ddd, *J* = 8.9, 7.5, 3.2 Hz, 1H), 7.68 (dd, *J* = 8.9, 4.9 Hz, 1H), 7.90 (dd, *J* = 8.7, 3.2 Hz, 1H), 9.41 (d, *J* = 2.1 Hz, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 40.4 (CH<sub>3</sub>), 117.1 (d, *J*<sub>C-C-F</sub> = 24.5 Hz, CH), 123.5 (d, *J*<sub>C-C-C-F</sub> = 3.6 Hz, C), 123.6 (d, *J*<sub>C-C-F</sub> = 22.7 Hz, CH), 132.8 (d, *J*<sub>C-C-F</sub> = 7.3 Hz, C), 135.6 (d, *J*<sub>C-C-F</sub> = 8.2 Hz, CH), 162.1 (d, *J*<sub>C-F</sub> = 250.7 Hz, CF), 170.1 (CH). **<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz) -115.2 (s, 1F). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3062 (vw), 3010 (vw), 2931 (vw), 1596 (vs), 1456 (m), 1411 (w), 1308 (vs), 1137 (vs), 967 (s), 814 (vs), 786 (s), 516 (s), 505 (vs). **HRMS** (ES+) calcd for C<sub>8</sub>H<sub>8</sub>BrFNO<sub>2</sub>S [M+H]<sup>+</sup>: 279.9443, found: 279.9429.

**N-(4-Methoxybenzylidene)methanesulfonamide, 2i** (2.53 g, 79%) was prepared according to



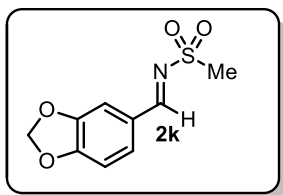
the general procedure from *p*-anisaldehyde (2.04 g, 0.015 mol). The desired imine **2i** was obtained as a white solid (mp = 86-87 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 3.11 (s, 3H), 3.91 (s, 3H), 7.01 (d, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 8.93 (s, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 40.7 (CH<sub>3</sub>), 56.0 (CH<sub>3</sub>), 115.1 (CH), 125.2 (C), 134.0 (CH), 165.7 (C), 170.8 (CH). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3032 (vw), 2935 (vs), 2847 (vw), 1594 (s), 1510 (s), 1421 (s), 1294 (s), 1249 (s), 1134 (vs), 1023 (s), 810 (m), 742 (s), 511 (s), 493 (s). **HRMS** (CI+) calcd for C<sub>9</sub>H<sub>12</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>: 214.0532, found: 214.0534.

*N*-(4-(Methylthio)benzylidene)methanesulfonamide,<sup>23</sup> **2j** (3.05 g, 77%) was prepared



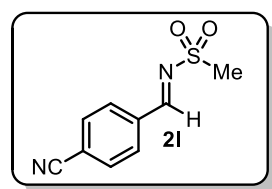
according to the general procedure from 4-(methylthio)benzaldehyde (2.28 g, 0.015 mol). The desired imine **2j** was obtained as a white solid (mp = 121-123 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 2.55 (s, 3H), 3.12 (s, 3H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 2H), 8.95 (s, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 14.9 (CH<sub>3</sub>), 40.7 (CH<sub>3</sub>), 125.6 (CH), 128.5 (C), 131.7 (CH), 149.7 (C), 170.9 (CH).

*N*-(Benzo[*d*][1,3]dioxol-5-ylmethylene)methanesulfonamide, **2k** (2.49 g, 73%) was prepared



according to the general procedure from piperonal (2.25 g, 0.015 mol). The desired imine **2k** was obtained as a light brown solid (mp = 102-104 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 3.09 (s, 3 H), 6.09 (s, 2H), 6.91 (d, *J* = 7.9 Hz, 1H), 7.40 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.46 (d, *J* = 1.5 Hz, 1H), 8.85 (s, 1 H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 40.6 (CH<sub>3</sub>), 102.6 (CH<sub>2</sub>), 108.1 (CH), 108.9 (CH), 127.1 (C), 131.1 (CH), 149.1 (C), 154.3 (C), 170.6 (CH). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3021 (vw), 2915 (vw), 1579 (m), 1452 (s), 1262 (vs), 1140 (vs), 1104 (s), 929 (m), 810 (vs), 487 (m). **HRMS** (CI+) calcd for C<sub>9</sub>H<sub>10</sub>NO<sub>4</sub>S [M+H]<sup>+</sup>: 228.0331, found: 228.0334.

*N*-(4-Cyanobenzylidene)methanesulfonamide,<sup>24</sup> **2l** (1.04 g, 62%) was prepared according to



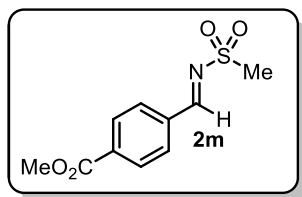
the general procedure from 4-formylbenzocyanide (1.05 g, 0.015 mol). The desired imine **2l** was obtained as white solid (mp = 170-171 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 3.18 (s, 3H), 7.84 (d, *J* = 8.24 Hz, 2H), 8.08 (d, *J* = 8.24 Hz, 2H), 9.08 (s, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 40.5 (CH<sub>3</sub>), 117.8 (C), 118.3 (C), 131.6 (CH), 133.2 (CH), 135.9 (C), 169.8 (CH). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3025 (vw), 3007 (vw), 2931 (vw), 2226 (m), 1604 (m), 1557 (m), 1301 (s), 1142 (s), 840 (m), 771 (s), 526 (vs). **HRMS** (CI+) calcd for C<sub>9</sub>H<sub>9</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup>: 209.0385, found: 209.0409.

<sup>23</sup> Uraguchi, D.; Kinoshita, N.; Kizu, T.; Ooi, T. *J. Am. Chem. Soc.* **2015**, *137*, 13768.

<sup>24</sup> Marques, C. S.; Burke, A. J. *Eur. J. Org. Chem.*, **2012**, 4232.

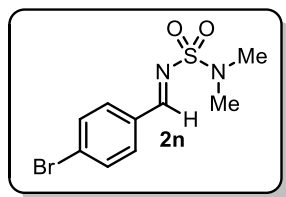


**Methyl 4-(((Methylsulfonyl)imino)methyl)benzoate, 2m** (2.83 g, 78%) was prepared



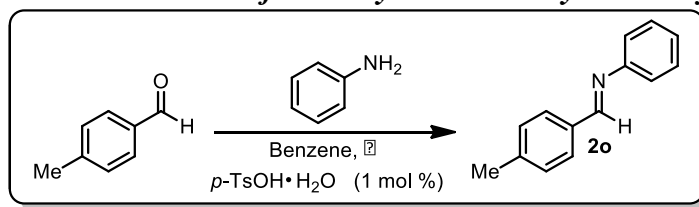
according to the general procedure from methyl 4-formylbenzoate (2.46 g, 0.015 mol). The desired imine **2m** was obtained as a white solid (mp = 136-137 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 3.16 (s, 3H), 3.96 (s, 3H), 8.03 (d, *J* = 8.5 Hz, 2H), 8.18 (d, *J* = 8.5 Hz, 2H), 9.08 (s, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 40.5 (CH<sub>3</sub>), 52.9 (CH<sub>3</sub>), 130.5 (CH), 131.3 (CH), 135.9 (C × 2), 166.1 (C), 170.8 (CH). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3023 (vw), 2951 (vw), 1716 (m), 1612 (m), 1298 (s), 1142 (vs), 1106 (m), 972 (m), 809 (m), 695 (m), 490 (m). **HRMS** (ES<sup>+</sup>) calcd for C<sub>10</sub>H<sub>12</sub>NO<sub>4</sub>S [M+H]<sup>+</sup>: 242.0487, found: 242.0488.

***N'*-(4-Bromobenzylidene)-*N,N*-dimethylsulfamide, <sup>25</sup> 2n** (1.94 g, 89%) was prepared according



to the general procedure from 4-bromobenzaldehyde (1.39 g, 7.5 mmol) **with the following modification:** *N,N*-dimethylsulfamide (1.12 g, 10 mmol) was used in place of methanesulfonamide. The desired imine **2n** was isolated as a white solid (mp = 119-120 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 2.89 (s, 6H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 8.85 (s, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 38.6 (CH<sub>3</sub>), 130.0 (C), 131.6 (C), 132.3 (CH), 132.8 (CH), 169.5 (CH).

#### ***Representative Procedure for N-Aryl/N-Heteroaryl Imine Synthesis***



***N*-(4-Methylbenzylidene)aniline<sup>26</sup>, 2o**

The following procedure is a modification of the procedure outlined by Leadbeater and Tilley.<sup>27</sup>

To a 100 mL flask equipped with a stir bar was added *p*-tolualdehyde (6.01 g, 50 mmol, 1 equiv),

<sup>25</sup> Reeves, J. T.; Visco, M. D.; Marsini, M. A.; Grinberg, N.; Busacca, C. A.; Mattson, A. E.; Senanayake, C. H. *Org. Lett.* **2015**, *17*, 2442.

<sup>26</sup> Perez, J. M.; Cano, R.; Yus, M.; Ramon, D. J. *Eur. J. Org. Chem.* **2012**, 4548.

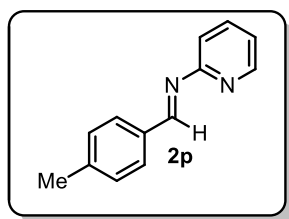
<sup>27</sup> Mercadante, M. A.; Kelly, C. B.; Hamlin, T. A.; Delle Chiaie, K. R.; Drago, M. D.; Duffy, K. K.; Dumas, M. T.; Fager, D. C.; Glod, B. L. C.; Hansen, K. E.; Hill, C. R.; Leising, R. M.; Lynes, C. L.; MacInnis, A. E.; McGohey, M. R.; Murray, S. A.; Piquette, M. C.; Roy, S. L.; Smith, R. M.; Sullivan, K. R.; Truong, B. H.; Vailonis, K. M.; Gorbatyuk, V.; Leadbeater, N. E.; Tilley L. J. *Chem. Sci.* **2014**, *5*, 3983.

aniline (4.89 g, 52.5 mmol, 1.05 equiv), and benzene (50 mL). The solution was allowed to stir for 5 min at rt and *p*-TsOH · H<sub>2</sub>O (0.095 g, 0.5 mmol, 0.01 equiv) was then added all at once. The flask was equipped with a graduated Dean-Stark trap along with a reflux condenser. The Dean-Stark trap was back-filled with ~15 mL of benzene to ensure constant volume throughout the reaction. The reaction mixture was heated to reflux in a 120 °C oil bath and stirred via a magnetic stir plate. To ensure that the vapor made it to the condenser, the arm of the Dean-Stark trap was insulated with a layer of glass wool. The reaction mixture was allowed to reflux until ~1 equivalent of H<sub>2</sub>O was observed in the trap (~0.9 mL). Upon completion the reaction mixture was cooled to room temperature and the benzene was removed *in vacuo* by rotary evaporation. To remove *p*-TsOH, pentane (~ 50 mL) was added resulting in the precipitation of a white powder. The fine precipitate was filtered and discarded. The filtrate was dried by rotary evaporation. The resulting crude imine was then purified *via* vacuum distillation (bp 118-120 °C @ 0.1 mmHg) giving the pure imine **2o** (8.09 g, 83%) as a clear, pale yellow oil that solidified on standing (mp = 45-47 °C).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 2.44 (s, 3H), 7.21 - 7.27 (m, 3H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.38 - 7.44 (m, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 8.44 (s, 1H).

**<sup>13</sup>C NMR** (DMSO-*d*<sub>6</sub>, 125 MHz) δ 21.9 (CH<sub>3</sub>), 121.1 (CH), 126.0 (CH), 129.1 (CH), 129.4 (CH), 129.8 (CH), 134.0 (C), 142.1 (C), 152.5 (C), 160.6 (CH).

*N*-(4-Methylbenzylidene)pyridin-2-amine,<sup>28</sup> **2p** (4.40 g, 89%) was prepared according to the



general procedure from *p*-tolualdehyde (3.15 g, 26.25 mmol, 1.05 equiv) **with the following modifications**: 1) 2-aminopyridine (2.35 g, 25 mmol, 1 equiv) was used in place of aniline and was the limiting reagent; 2) The crude product was washed twice with pentane; 3) The crude material was washed with a minimal amount of Et<sub>2</sub>O in addition

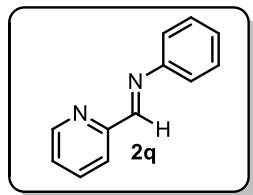
to the pentane washes. The desired imine **2p** was isolated as a light brown solid (mp = 79-81 °C).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 2.43 (s, 3H), 7.16 (ddd, *J* = 7.3, 4.9, 0.9 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.31 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.74 (td, *J* = 7.6, 1.8 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 8.49 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 9.11 (s, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 21.9 (CH<sub>3</sub>),

<sup>28</sup> Meiswinkel, A.; Werner, H. *Inorg. Chim. Acta* **2004**, 357, 2855.

119.8 (CH), 121.8 (C), 129.7 (2 × CH), 133.6 (CH), 138.2 (CH), 142.7 (CH), 149.0 (C), 161.6 (C), 163.0 (CH).

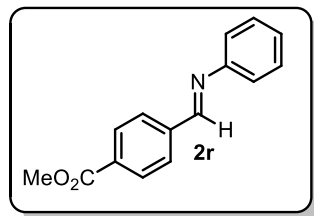
***N*-(Pyridin-2-ylmethylene)aniline**,<sup>29</sup> **2q** (3.53 g, 77%) was prepared according to the general



procedure from 2-pyridinecarboxaldehyde (2.68 g, 0.025 mol) *with the following modifications*: 1) No *p*-TsOH · H<sub>2</sub>O was utilized; 2) Further purification was accomplished by vacuum distillation (100-103 °C @ 0.1 mmHg). The desired imine **2q** was isolated as a clear, pale yellow oil. **<sup>1</sup>H**

**NMR** (CDCl<sub>3</sub>, 500 MHz) δ 7.23 - 7.30 (m, 3 H), 7.33 (dd, *J* = 7.0, 5.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.77 (td, *J* = 7.7, 1.1 Hz, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 8.60 (s, 1H), 8.69 (d, *J* = 4.6 Hz, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 121.3 (CH), 122.1 (CH), 125.3 (CH), 126.9 (CH), 129.4 (CH), 136.8 (CH), 149.9 (CH), 151.2 (C), 154.8 (C), 160.8 (CH).

**Methyl 4-((Phenylimino)methyl)benzoate**,<sup>30</sup> **2r** (4.58 g, 77%) was prepared according to the



general procedure from methyl 4-formylbenzoate (4.10 g, 0.025 mol) *with the following modifications*: 1) The crude product was washed twice with pentane; 2) The crude material was washed with a minimal amount of Et<sub>2</sub>O in addition to the pentane washes. The desired imine **2r** was isolated as a pale yellow solid (mp = 126-127

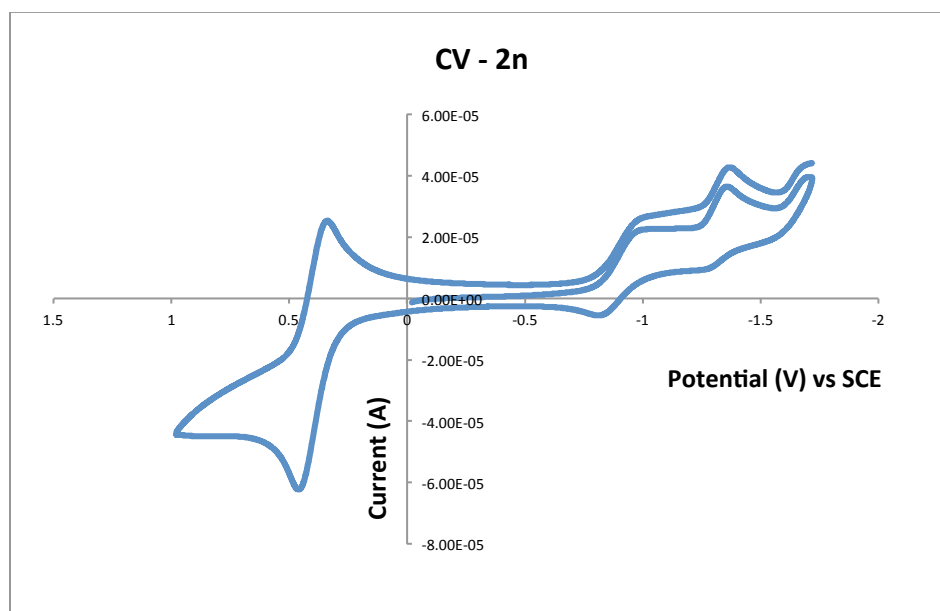
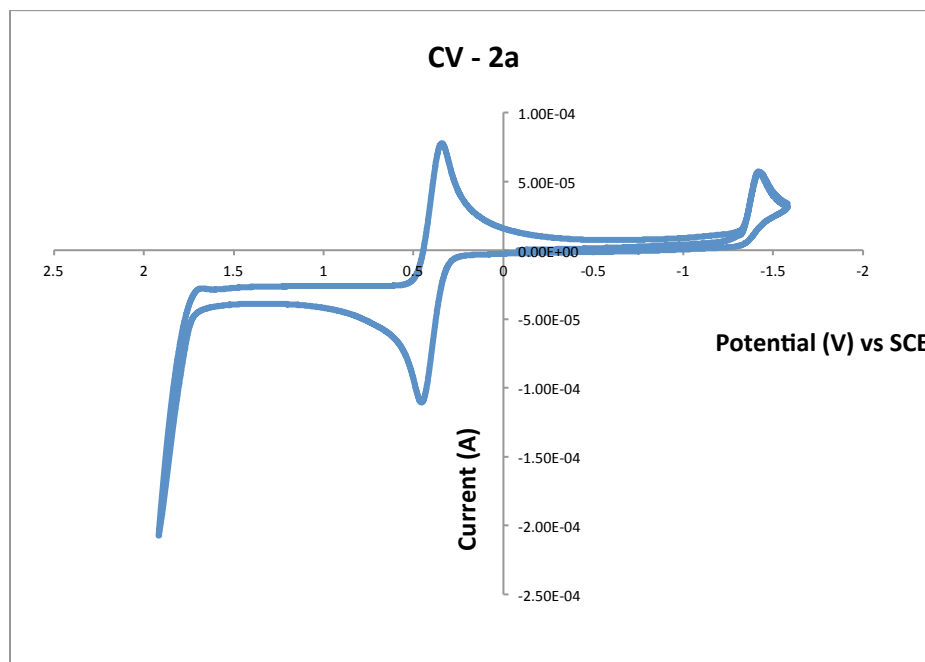
°C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 3.96 (s, 3H), 7.22 - 7.26 (m, 2H), 7.27 (dt, *J* = 7.3, 1.4 Hz, 1H), 7.39 - 7.44 (m, 2H), 7.98 (d, *J* = 8.5 Hz, 2H), 8.14 (d, *J* = 8.5 Hz, 2H), 8.51 (s, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 52.6 (CH<sub>3</sub>), 121.2 (CH), 126.8 (CH), 128.9 (CH), 129.5 (CH), 130.3 (s, 6 C), 132.6 (C), 140.3 (C), 151.8 (C), 159.3 (CH), 166.9 (C).

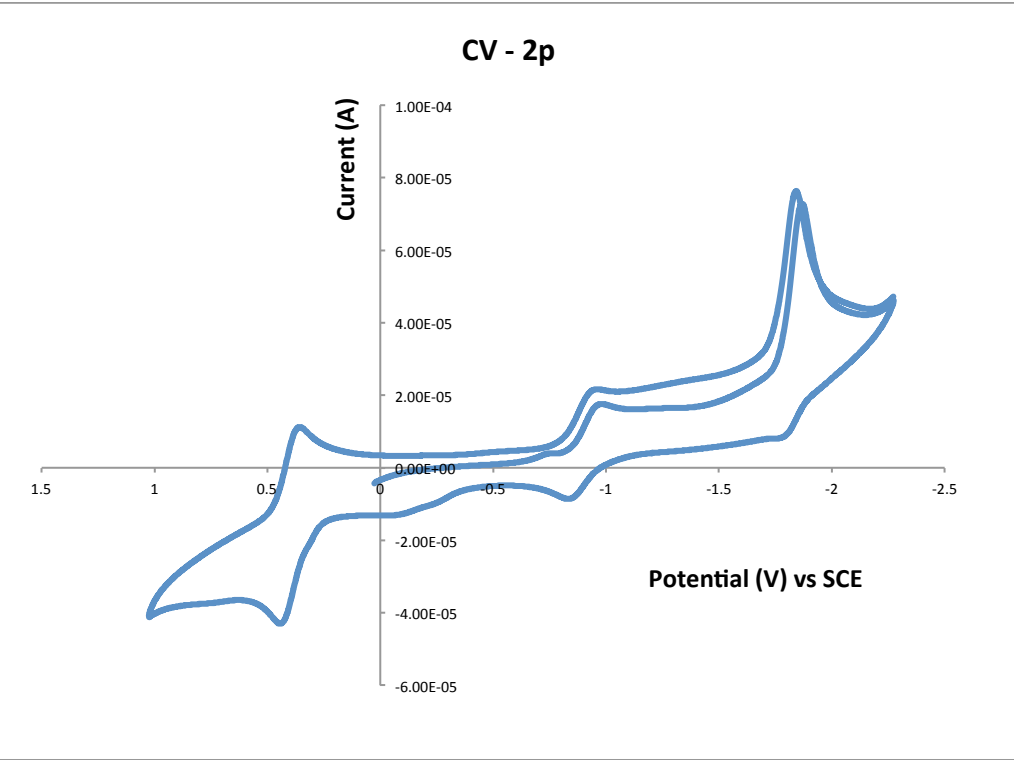
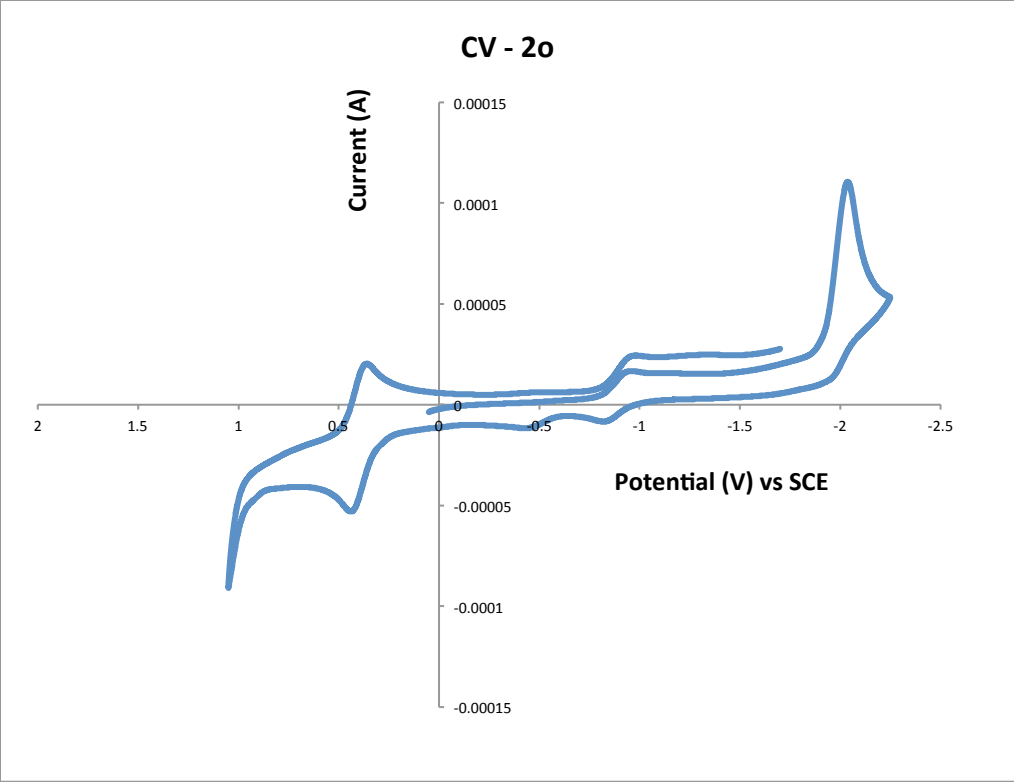
<sup>29</sup> Fan, M.; Zhou, W.; Jiang, Y.; Ma, D. *Angew. Chem., Int. Ed.* **2016**, *55*, 6211.

<sup>30</sup> Naka, H.; Koseki, D.; Kondo, Y. *Adv. Synth. Catal.* **2008**, *350*, 1901.

## Cyclic Voltammogram of Representative Imines

Voltammetric measurements were recorded on a CH Instruments: Model 600E Series Electrochemical Analyzer using a standard three electrodes setup in dry and degassed MeCN (10 mL), with ferrocene as an internal reference ( $E_{1/2}^0 = + 0.40$  V vs SCE) and  $\text{Bu}_4\text{NPF}_6$  as the electrolyte (0.10 mmol). Cyclic voltammograms were recorded with a step potential of 0.002 V at a scan rate of 0.1 V/s.



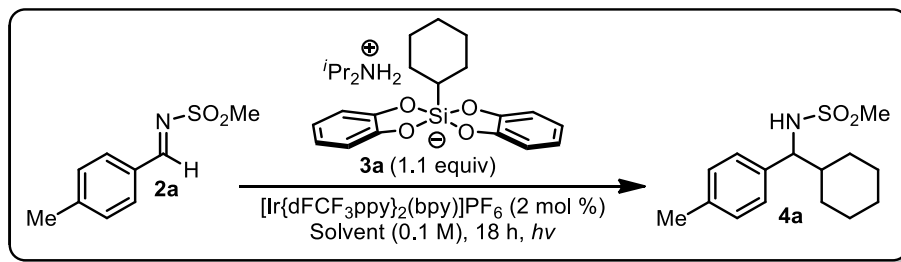


## Control and Optimization Studies

### Procedure for optimization and control studies:

To a 4 mL reaction vial equipped with a stir bar, was added diisopropylammonium bis(catecholato)cyclohexylsilicate **2a** (0.0473 g, 0.11 mmol, 1.1 equiv), *N*-(4-methylbenzylidene)methanesulfonamide, **2a** (0.0197 g, 0.1 mmol, 1 equiv) and the appropriate photocatalyst (0.002 mmol, 0.02 equiv). The vial was sealed with a cap containing a TFE lined silicone septa and was evacuated and purged with argon three times *via* an inlet needle. The vial was then charged with the appropriate anhydrous solvent (1 mL). After this, the cap was sealed with Parafilm<sup>®</sup> and the vial was irradiated in the aforementioned LED reactor for 18 h. The temperature of the reaction was maintained at approximately 27 °C *via* a fan. After 18 h, reaction progress was evaluated by GC/MS.

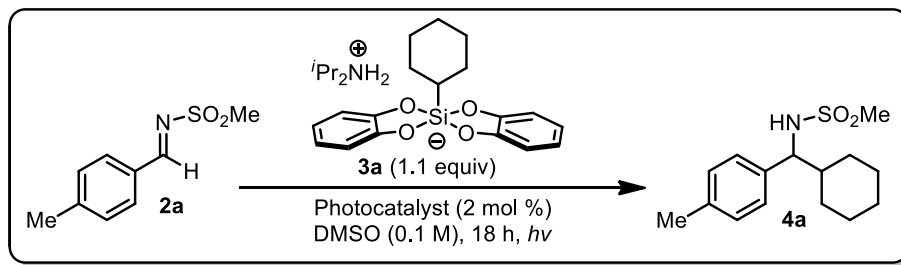
**Table S1: Solvent Screen of Photoredox-Mediated Alkylation of Imines<sup>a</sup>**



| Entry    | Solvent     | Conversion to <b>4a</b> |
|----------|-------------|-------------------------|
| 1        | Toluene     | 4%                      |
| 2        | MeCN        | 10%                     |
| 3        | THF         | 28%                     |
| 4        | Dioxane     | 39%                     |
| 5        | DMF         | 90%                     |
| <b>6</b> | <b>DMSO</b> | <b>97%</b>              |

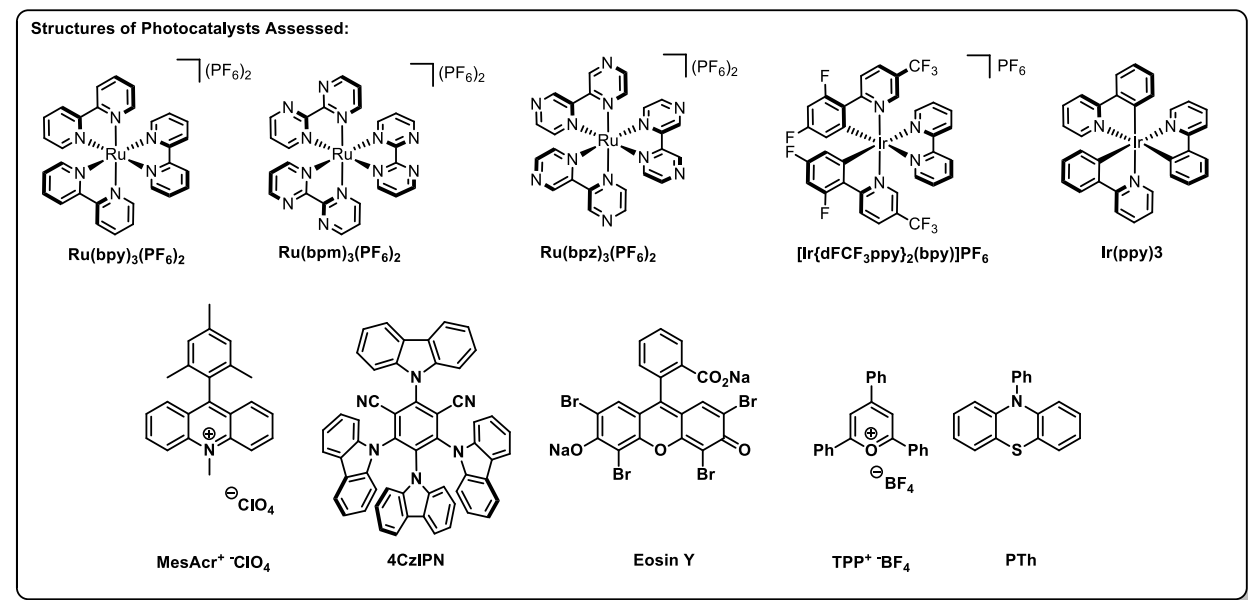
<sup>a</sup> Percent conversion was approximated based upon relative areas from the GC/MS trace of a given run. Conversion = 100 × (area of alkylated product)/(area of imine **2a** + area of alkylated product)

**Table S2: Assessment of Various Photoredox Catalysts<sup>a</sup>**

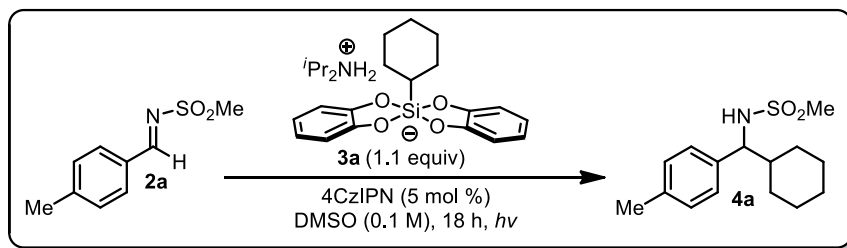


| Entry     | Photocatalyst   | Conversion to <b>4a</b> |
|-----------|---|-------------------------|
| 1         | Ru(bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub>          | 94%                     |
| 2         | Ru(bpm) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub>          | 48%                     |
| 3         | Ru(bpz) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub>          | 62%                     |
| 4         | [Ir{dFCF <sub>3</sub> ppy} <sub>2</sub> (bpy)]PF <sub>6</sub> | 97%                     |
| 5         | Ir(ppy) <sub>3</sub>  | 98%                     |
| 6         | MesAcr <sup>+</sup> ClO <sub>4</sub> <sup>-</sup>             | 8%                      |
| 7         | Eosin Y   | 74%                     |
| 8         | TPP <sup>+</sup> BF <sub>4</sub> <sup>-</sup>                 | Trace                   |
| 9         | PTh   | 0%                      |
| <b>10</b> | <b>4CzIPN</b>   | <b>100%</b>             |

<sup>a</sup> Percent conversion was approximated based upon relative areas from the GC/MS trace of a given run. Conversion = 100 × (area of alkylated product)/(area of imine **2a** + area of alkylated product)



**Table S3: Control Studies using Imine 2a**

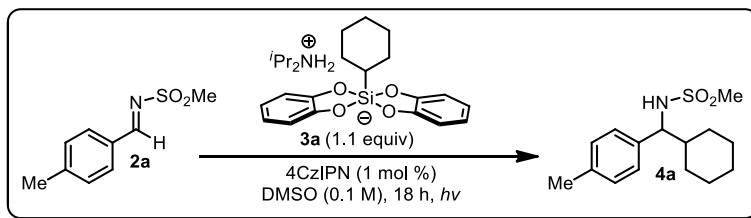


| Entry          | Deviation from procedure  | Conversion to 4a <sup>a</sup> |
|----------------|---------------------------|-------------------------------|
| 1              | None                      | 100%                          |
| 2              | No photocatalyst (4CzIPN) | 0%                            |
| 3              | No light                  | 0%                            |
| 4 <sup>b</sup> | No Silicate               | 0%                            |

<sup>a</sup>Percent conversion was approximated based upon relative areas from the GC/MS trace of a given run. Conversion =  $100 \times (\text{area of alkylated product}) / (\text{area of imine } \mathbf{2a} + \text{area of alkylated product})$ . <sup>b</sup>No consumption or hydrolysis of the imine was observed



## General Procedure for Imine Alkylation Mediated by 4CzIPN



### *N*-(Cyclohexyl(*p*-tolyl)methyl)methanesulfonamide (**4a**)

To an 8 mL reaction vial equipped with a stir bar were added 4CzIPN (4 mg, 0.005 mmol, 0.01 equiv), imine **2a** (99 mg, 0.5 mmol, 1 equiv), and alkylsilicate **3a** (257 mg, 0.6 mmol, 1.1 equiv). The vial was sealed with a cap containing a TFE lined silicone septa and placed under an argon atmosphere *via* an inlet needle. The vial was evacuated three times *via* an inlet needle then purged with argon. The vial was then charged with anhyd DMSO (5 mL) *via* a syringe. The cap was sealed with Parafilm<sup>®</sup>, and the now bright yellow solution was irradiated by blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at approximately 27 °C *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by HPLC and/or GC/MS. Once judged to be complete, the now yellow-brown solution was transferred to a separatory funnel and diluted with deionized H<sub>2</sub>O (20 mL) and EtOAc (~20 mL). The layers were separated,<sup>31</sup> and the aq layer was extracted with EtOAc (3 × ~20 mL). The combined organic layers were washed with aq 2 M NaOH (2 × ~100 mL)<sup>32</sup> followed by brine (~100 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO<sub>2</sub> column chromatography (gradient hexane/EtOAc containing 1% Et<sub>3</sub>N) to give the desired sulfonamide, **4a**, (110 mg, 78%) as an off-white solid (mp = 143-142 °C).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 0.88 - 0.98 (m, 1H), 1.04 (qd, *J* = 12.5, 3.2 Hz, 1H), 1.09 - 1.28 (m, 3H), 1.34 - 1.42 (m, 1H), 1.55 - 1.71 (m, 3H), 1.74 - 1.82 (m, 1H), 1.99 - 2.06 (m, 1H), 2.35 (s, 3 H), 2.52 (s, 3H), 4.14 (t, *J* = 8.4 Hz, 1H), 5.15 (d, *J* = 8.8 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H).

<sup>31</sup> Occasionally an emulsion would form, thus requiring the addition of a small amount (~ 5 mL) of brine to assist in layer separation.

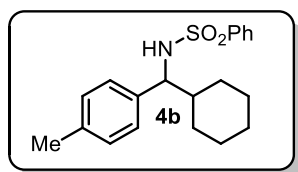
<sup>32</sup> Note that the aq layer will turn dark brown and become warm likely due to the reaction between catechol (or the orthosilicate byproduct) and hydroxide.

**$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  21.3 ( $\text{CH}_3$ ), 26.1 ( $\text{CH}_2$ ), 26.2 ( $\text{CH}_2$ ), 26.4 ( $\text{CH}_2$ ), 29.9 ( $\text{CH}_2$ ), 30.1 ( $\text{CH}_2$ ), 41.9 ( $\text{CH}_3$ ), 43.9 ( $\text{CH}$ ), 63.4 ( $\text{CH}$ ), 127.3 ( $\text{CH}$ ), 129.6 ( $\text{CH}$ ), 137.6 ( $\text{C}$ ), 137.9 ( $\text{C}$ ).

**FT-IR** ( $\text{cm}^{-1}$ , neat, ATR) 3251 (w, br), 2933 (w), 1448 (m), 1313 (vs), 1159 (vs), 975 (m), 771 (m), 515 (vs).

**HRMS** (ES-) calcd for  $\text{C}_{15}\text{H}_{22}\text{NO}_2\text{S}$   $[\text{M}-\text{H}]^-$ : 280.1377, found: 280.1352.

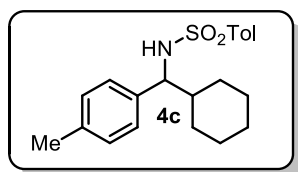
***N*-(Cyclohexyl(*p*-tolyl)methyl)benzenesulfonamide, 4b** (157 mg, 91%) was prepared



according to the general procedure from 2b (130 mg, 0.5 mmol). The desired sulfonamide **4b** was isolated as an off-white semisolid.  **$^1\text{H}$**

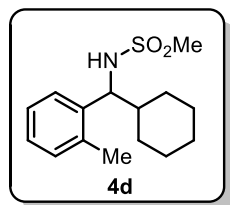
**NMR** ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  0.78 - 0.89 (m, 1H), 0.93 (qd,  $J = 12.3$ , 3.5 Hz, 1H), 1.00 - 1.19 (m, 3H), 1.22 - 1.34 (m, 1H), 1.48 - 1.63 (m, 3H), 1.65 - 1.76 (m, 1H), 1.90 - 2.00 (m, 1H), 2.22 (s, 3H), 4.01 (t,  $J = 7.8$  Hz, 1H), 5.45 (d,  $J = 8.2$  Hz, 1H), 6.80 (d,  $J = 7.9$  Hz, 2H), 6.88 (d,  $J = 7.9$  Hz, 2H), 7.18 - 7.28 (m, 2H), 7.37 (t,  $J = 7.3$  Hz, 1H), 7.60 (dd,  $J = 8.4$ , 1.1 Hz, 2H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  21.2 ( $\text{CH}_3$ ), 26.2 ( $\text{CH}_2$ ), 26.4 ( $\text{CH}_2$ ), 29.8 ( $\text{CH}_2$ ), 30.0 ( $\text{CH}_2$ ), 44.0 ( $\text{CH}$ ), 63.6 ( $\text{CH}$ ), 127.1 ( $\text{CH}$ ), 127.2 ( $\text{CH}$ ), 128.7 ( $\text{CH}$ ), 129.0 ( $\text{CH}$ ), 132.1 ( $\text{CH}$ ), 136.8 ( $\text{C}$ ), 137.1 ( $\text{C}$ ), 141.0 ( $\text{C}$ ). **FT-IR** ( $\text{cm}^{-1}$ , neat, ATR) 3251 (w), 2917 (w), 2849 (w), 1447 (w), 1325 (m), 1261 (s), 1041 (m), 822 (w), 608 (m), 546 (m). **HRMS** (ES+) calcd for  $\text{C}_{20}\text{H}_{25}\text{NNaO}_2\text{S}$   $[\text{M}+\text{Na}]^+$ : 366.1504, found: 366.1500.

***N*-(Cyclohexyl(*p*-tolyl)methyl)benzenesulfonamide, 4c** (154 mg, 86%) was prepared according



to the general procedure from 2c (137 mg, 0.5 mmol). The desired sulfonamide **4c** was isolated as a off-white semisolid.  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  0.78 - 0.89 (m, 1H), 0.93 (qd,  $J = 12.1$ , 2.9 Hz, 1H), 1.01 - 1.20 (m, 3H), 1.25 - 1.33 (m, 1H), 1.50 - 1.64 (m, 3H), 1.68 - 1.76 (m, 1H), 1.91 - 1.99 (m, 1H), 2.25 (s, 3H), 2.33 (s, 3H), 3.99 (t,  $J = 8.1$  Hz, 1H), 5.32 (d,  $J = 8.1$  Hz, 1H), 6.80 (d,  $J = 7.8$  Hz, 2H), 6.90 (d,  $J = 7.8$  Hz, 2H), 7.04 (d,  $J = 8.1$  Hz, 2H), 7.48 (d,  $J = 8.1$  Hz, 2H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  21.2 ( $\text{CH}_3$ ), 21.6 ( $\text{CH}_3$ ), 26.2 ( $\text{CH}_2$ ), 26.4 ( $\text{CH}_2$ ), 29.8 ( $\text{CH}_2$ ), 30.0 ( $\text{CH}_2$ ), 44.0 ( $\text{CH}$ ), 63.5 ( $\text{CH}$ ), 127.2 ( $\text{CH}$ ), 127.3 ( $\text{CH}$ ), 128.9 ( $\text{CH}$ ), 129.3 ( $\text{CH}$ ), 136.8 ( $\text{C}$ ), 137.2 ( $\text{C}$ ), 138.1 ( $\text{C}$ ), 142.8 ( $\text{C}$ ). **FT-IR** ( $\text{cm}^{-1}$ , neat, ATR) 3249 (w), 2921 (m), 2853 (w), 1440 (m), 1320 (s), 1307 (w), 1158 (vs), 808 (m), 722 (m), 672 (vs), 582 (s) 545 (vs). **HRMS** (ES+) calcd for  $\text{C}_{21}\text{H}_{27}\text{NNaO}_2\text{S}$   $[\text{M}+\text{Na}]^+$ : 380.1660, found: 380.1657.

**N-(Cyclohexyl(o-tolyl)methyl)methanesulfonamide, 4d** (90 mg, 64%) was prepared according



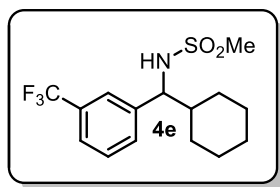
to the general procedure from **2d** (99 mg, 0.5 mmol). The desired

sulfonylamine **4d** was isolated as an off-white solid (mp = 103-104 °C). **<sup>1</sup>H**

**NMR** (CDCl<sub>3</sub>, 500 MHz) δ 0.99 - 1.24 (m, 5H), 1.38 (s, 1H), 1.53 - 1.63 (m, 1H), 1.63 - 1.70 (m, 2H), 1.78 - 1.86 (m, 1H), 2.07 - 2.13 (m, 1H), 2.41 (s, 3H), 2.45 (s, 3H), 4.51 (t, *J* = 8.4 Hz, 1H), 4.96 (d, *J* = 8.3 Hz, 1H), 7.15 -

7.19 (m, 2H), 7.19 - 7.26 (m, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 19.9 (CH<sub>3</sub>), 26.2 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 26.5 (CH<sub>2</sub>), 29.9 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 41.9 (CH<sub>3</sub>), 44.0 (CH<sub>2</sub>), 59.1 (br, CH), 126.4 (br, C), 126.9 (CH), 127.6 (CH), 131.0 (CH), 136.0 (CH), 139.7 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3273 (w, br), 2940 (m), 2853 (w), 1427 (m), 1327 (s), 1315 (vs), 1154 (vs), 1042 (m), 981 (s), 756 (s), 519 (s). **HRMS** (ES<sup>+</sup>) calcd for C<sub>15</sub>H<sub>23</sub>NNaO<sub>2</sub>S [M+Na]<sup>+</sup>: 304.1347, found: 301.1343.

**N-(Cyclohexyl(3-(trifluoromethyl)phenyl)methyl)methanesulfonamide, 4e** (114 mg, 68%)

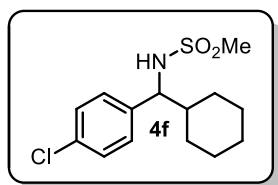


was prepared according to the general procedure from **2e** (126 mg, 0.5 mmol). The desired sulfonylamine **4e** was isolated as a light yellow oil.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 0.92 - 1.08 (m, 2H), 1.09 - 1.24 (m, 3H), 1.34 - 1.42 (m, 1H), 1.58 - 1.73 (m, 3H), 1.75 - 1.82 (m, 1H), 1.91 -

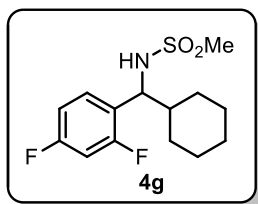
2.01 (m, 1H), 2.60 (s, 3H), 4.29 (t, *J* = 7.9 Hz, 1H), 5.49 (d, *J* = 8.1 Hz, 1H), 7.44 - 7.52 (m, 2H), 7.53 (s, 1H), 7.56 (d, *J* = 7.3 Hz, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 26.1 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>), 42.0 (CH<sub>3</sub>), 43.9 (CH), 63.2 (CH), 124.2 (q, *J*<sub>C-F</sub> = 272.2 Hz, CF<sub>3</sub>), 124.1 (q, *J*<sub>C-C-F</sub> = 3.8 Hz, CH), 124.8 (q, *J*<sub>C-C-F</sub> = 3.8 Hz, CH), 129.5 (CH), 130.9 (CH), 131.3 (q, *J*<sub>C-C-F</sub> = 32.5 Hz, C), 142.3 (C). **<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz) -65.8 (s, 3F). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3283 (w, br), 2929 (m), 2854 (w), 1451 (w), 1326 (vs), 1152 (vs), 1074 (s), 978 (m), 705 (m), 516 (m). **HRMS** (ES<sup>+</sup>) calcd for C<sub>15</sub>H<sub>20</sub>F<sub>3</sub>NNaO<sub>2</sub>S [M+Na]<sup>+</sup>: 358.1065, found: 358.1069.

**N-((4-Chlorophenyl)(cyclohexyl)methyl)methanesulfonamide, 4f** (136 mg, 90%) was



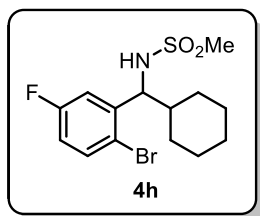
prepared according to the general procedure from **2f** (109 mg, 0.5 mmol). The desired sulfonamide **4f** was isolated as an off-white solid (mp = 170-171 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 0.88 - 0.97 (m, 1H), 1.01 (qd, *J* = 11.9, 3.4 Hz, 1H), 1.06 - 1.26 (m, 3H), 1.33 - 1.41 (m, 1H), 1.52 - 1.72 (m, 3H), 1.75 - 1.82 (m, 1H), 1.93 - 1.99 (m, 1H), 2.58 (s, 3H), 4.19 (t, *J* = 7.9 Hz, 1H), 4.85 (d, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 26.1 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 29.8 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>), 42.1 (CH<sub>3</sub>), 43.9 (CH), 63.0 (CH), 128.8 (CH), 129.1 (CH), 133.7 (C), 139.6 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3247 (w), 2936 (w), 2856 (w), 1451 (m), 1309 (vs), 1160 (vs), 1091 (m), 977 (m), 761 (s), 555 (s), 517 (vs). **HRMS** (ES<sup>+</sup>) calcd for C<sub>14</sub>H<sub>20</sub>ClNNaO<sub>2</sub>S [M+Na]<sup>+</sup>: 324.0801, found: 324.0792.

**N-(Cyclohexyl(2,4-difluorophenyl)methyl)methanesulfonamide, 4g** (130 mg, 85%) was



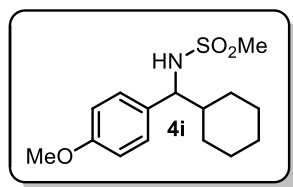
prepared according to the general procedure from **2g** (110 mg, 0.5 mmol). The desired sulfonamide **4g** was isolated as an off-white semisolid. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 0.90 - 1.09 (m, 2H), 1.10 - 1.27 (m, 3H), 1.32 - 1.39 (m, 1H), 1.61 - 1.73 (m, 3H), 1.76 - 1.83 (m, 1H), 2.02 - 2.10 (m, 1H), 2.66 (s, 3H), 4.36 (t, *J* = 8.8 Hz, 1H), 5.18 (d, *J* = 9.0 Hz, 1H), 6.84 (ddd, *J* = 10.9, 8.7, 2.4 Hz, 1H), 6.89 (td, *J* = 8.3, 2.4 Hz, 1H), 7.23 (td, *J* = 8.4, 6.4 Hz, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 26.0 (CH<sub>2</sub>), 26.1 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 30.2 (CH<sub>2</sub>), 41.7 (CH<sub>3</sub>), 42.9 (CH), 58.8 (CH), 104.7 (t, *J*<sub>C-C-F</sub> = 25.7 Hz, CH), 111.9 (dd, *J*<sub>C-C-F</sub> = 21.1, *J*<sub>C-C-C-F</sub> = 2.8 Hz, 2 C), 124.3 (dd, *J*<sub>C-C-F</sub> = 12.8, *J*<sub>C-C-C-F</sub> = 3.7 Hz, C), 130.3 (dd, *J*<sub>C-C-C-F</sub> = 9.3, 7.3 Hz, CH), 161.6 (td, *J*<sub>C-F</sub> = 249.3, *J*<sub>C-C-C-F</sub> = 11.9 Hz, 2 × CF). **<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz) -116.6 (d, *J* = 7.2 Hz, 1F), -113.50 (d, *J* = 8.3 Hz, 1F). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3281 (w, br), 2929 (m), 2854 (w), 1604 (w), 1504 (m), 1449 (w), 1314 (s), 1153 (vs), 1093 (m), 967 (vs), 848 (m), 755 (m), 511 (vs). **HRMS** (ES<sup>+</sup>) calcd for C<sub>14</sub>H<sub>19</sub>F<sub>2</sub>NNaO<sub>2</sub>S [M+Na]<sup>+</sup>: 326.1002, found: 326.1003.

***N*-(2-Bromo-5-fluorophenyl)(cyclohexyl)methyl)methanesulfonamide, 4h** (120 mg, 66%)



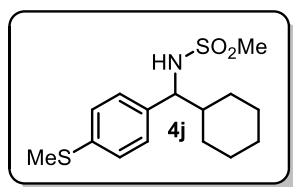
was prepared according to the general procedure from **2h** (140 mg, 0.5 mmol). The desired sulfonamide **4h** was isolated as a powdery white solid (mp = 165-166 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 1.02 - 1.25 (m, 5H), 1.34 - 1.47 (m, 1H), 1.60 - 1.76 (m, 3H), 1.77 - 1.86 (m, 1H), 1.96 (br s, 1H), 2.71 (s, 3H), 4.68 (br s, 1H), 5.33 (d, *J* = 7.6 Hz, 1H), 6.91 (ddd, *J* = 8.7, 7.6, 2.9 Hz, 1H), 7.04 (dd, *J* = 9.3, 2.9 Hz, 1H), 7.54 (dd, *J* = 8.8, 5.1 Hz, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 26.1 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 28.7 (br, CH<sub>2</sub>), 30.0 (br, CH<sub>2</sub>), 41.7 (CH<sub>3</sub>), 43.3 (br, CH), 61.6 (br, CH), 115.4 (br, C), 116.6 (d, *J*<sub>C-F</sub> = 21.8 Hz, CH), 117.5 (br, C), 134.7 (br, CH), 143.1 (br, C), 162.4 (d, *J*<sub>C-F</sub> = 248.0 Hz, CF). **<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz) - 116.3 (s, 1F). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3255 (w, br), 2945 (w), 2851 (w), 1471 (w), 1329 (m), 1313 (m), 1153 (vs), 980 (w), 774 (m), 480 (vs). **HRMS** (ES<sup>+</sup>) calcd for C<sub>14</sub>H<sub>19</sub>BrFNNaO<sub>2</sub>S [M+Na]<sup>+</sup>: 386.0202, found: 386.0205.

***N*-(Cyclohexyl(4-methoxyphenyl)methyl)methanesulfonamide, 4i** (128 mg, 86%) was



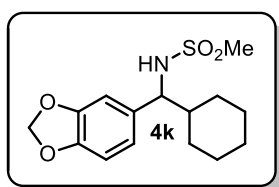
prepared according to the general procedure from **2i** (108 mg, 0.5 mmol). The desired sulfonamide **4i** was isolated as an off-white solid (mp = 126-128 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 0.85 - 0.95 (m, 1H), 1.02 (qd, *J* = 11.9, 2.7 Hz, 1H), 1.08 - 1.27 (m, 3H), 1.32 - 1.40 (m, 1H), 1.50 - 1.70 (m, 3H), 1.72 - 1.80 (m, 1H), 1.96 - 2.06 (m, 1H), 2.51 (s, 3H), 3.80 (s, 3H), 4.12 (t, *J* = 8.4 Hz, 1H), 4.77 - 5.07 (m, 1H), 6.88 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 26.1 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>), 42.0 (CH<sub>3</sub>), 44.0 (CH), 55.5 (CH<sub>3</sub>), 63.2 (CH), 114.3 (CH), 128.5 (CH), 132.9 (C), 159.3 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3248 (w), 2938 (m), 2851 (w), 1613 (w), 1513 (s), 1443 (m), 1311 (vs), 1249 (s), 1156 (vs), 1132 (s), 1029 (s), 833 (s), 752 (s), 514 (vs). **HRMS** (ES<sup>+</sup>) calcd for C<sub>15</sub>H<sub>23</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 320.1296, found: 320.1291.

***N*-(Cyclohexyl(4-(methylthio)phenyl)methyl)methanesulfonamide 4j** (125 mg, 80%) was



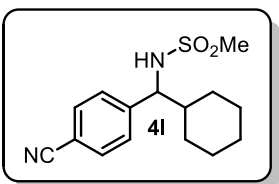
prepared according to the general procedure from **2j** (115 mg, 0.5 mmol). The desired sulfonamide **4j** was isolated as an off-white solid (mp = 108-110 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 0.87 - 0.96 (m, 1H), 1.01 (qd, *J* = 12.2, 3.4 Hz, 1H), 1.06 - 1.27 (m, 3H), 1.32 - 1.42 (m, 1H), 1.52 - 1.70 (m, 3H), 1.72 - 1.80 (m, 1H), 1.92 - 2.03 (m, 1H), 2.47 (s, 3H), 2.54 (s, 3H), 4.13 (t, *J* = 8.2 Hz, 1H), 5.28 (d, *J* = 8.5 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 15.8 (CH<sub>3</sub>), 26.1 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 29.8 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>), 42.0 (CH<sub>3</sub>), 43.9 (CH), 63.2 (CH), 126.8 (CH), 127.9 (CH), 137.6 (C), 138.2 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3299 (w), 2932 (w), 2917 (w), 2849 (w), 1418 (w), 1311 (s), 1151 (s), 986 (m), 514 (s). **HRMS** (ES<sup>+</sup>) calcd for C<sub>15</sub>H<sub>23</sub>NNaO<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup>: 336.1068, found: 336.1068.

***N*-(Benzo[d][1,3]dioxol-5-yl(cyclohexyl)methyl)methanesulfonamide, 4k** (107 mg, 69%) was



prepared according to the general procedure from **2k** (114 mg, 0.5 mmol). The desired sulfonamide **4k** was isolated as an off-white solid (mp = 137-139 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 0.84 - 0.96 (m, 1H), 1.03 (qd, *J* = 12.0, 2.4 Hz, 1H), 1.09 - 1.28 (m, 3H), 1.34 - 1.40 (m, 1H), 1.47 - 1.58 (m, 1H), 1.59 - 1.71 (m, 2 H), 1.78 (s, 1H), 1.97 - 2.06 (m, 1H), 2.58 (s, 3H), 4.08 (t, *J* = 8.3 Hz, 1H), 5.13 (d, *J* = 8.3 Hz, 1H), 5.97 (s, 2H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.74 (s, 1H), 6.78 (d, *J* = 7.8 Hz, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 26.1 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>), 30.2 (CH<sub>2</sub>), 42.1 (CH<sub>3</sub>), 43.9 (CH), 63.5 (CH), 101.5 (CH<sub>2</sub>), 107.4 (CH), 108.5 (CH), 121.0 (CH), 135.0 (C), 147.3 (C), 148.4 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3246 (w), 2928 (w), 2877 (w), 1487 (m), 1325 (m), 1316 (s), 1240 (s), 1154 (vs), 1037 (s), 982 (m), 785 (m), 763 (s), 506 (s). **HRMS** (ES<sup>-</sup>) calcd for C<sub>15</sub>H<sub>20</sub>NO<sub>4</sub>S [M-H]<sup>-</sup>: 310.1119, found: 310.1111.

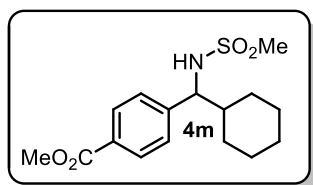
***N*-(4-Cyanophenyl)(cyclohexyl)methyl)methanesulfonamide, 4l** (100 mg, 68%) was prepared



according to the general procedure from **2l** (104 mg, 0.5 mmol). The desired sulfonamide **4l** was isolated as an off-white solid (mp = 144-145 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 0.91 - 1.06 (m, 2H), 1.09 - 1.23 (m, 3H), 1.32 - 1.40 (m, 1H), 1.57 - 1.73 (m, 3H), 1.74 - 1.82 (m, 1H), 1.87 - 1.96 (m, 1H), 2.65 (s, 3H), 4.27 (t, *J* = 8.0 Hz, 1H), 5.43 (br s, 1H), 7.39 (d, *J* = 8.3 Hz,

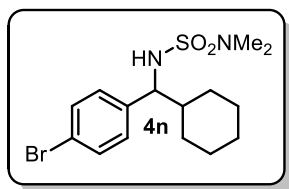
2H), 7.67 (d,  $J = 8.3$  Hz, 2H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  26.0 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 30.2 (CH<sub>2</sub>), 42.1 (CH<sub>3</sub>), 43.8 (CH), 63.2 (CH), 111.9 (C), 118.7 (C), 128.2 (CH), 132.7 (CH), 146.7 (CH). FT-IR (cm<sup>-1</sup>, neat, ATR) 3252 (w, br.), 2932 (w), 2852 (w), 2232 (w), 1451 (m), 1310 (vs), 1159 (vs), 1062 (m), 977 (s), 764 (s), 564 (s), 514 (s). HRMS (ES+) calcd for C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>2</sub>S [M-Na]<sup>+</sup>: 315.1143, found: 315.1144.

**Methyl 4-(Cyclohexyl(methylsulfonamido)methyl)benzoate, 4m** (125 mg, 77%) was prepared



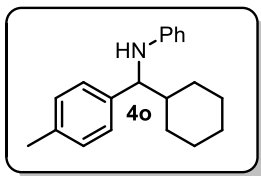
according to the general procedure from **2m** (121 mg, 0.5 mmol). The desired sulfonamide **4m** was isolated as an off-white solid (mp = 85-86 °C).  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  0.90 - 1.08 (m, 2H), 1.08 - 1.27 (m, 3H), 1.31 - 1.40 (m, 1H), 1.57 - 1.71 (m, 3H), 1.73 - 1.82 (m, 1H), 1.93 - 2.02 (m, 1H), 2.56 (s, 3H), 3.92 (s, 3H), 4.26 (t,  $J = 8.2$  Hz, 1H), 5.45 (d,  $J = 8.3$  Hz, 1H), 7.34 (d,  $J = 8.3$  Hz, 2H), 8.04 (d,  $J = 8.3$  Hz, 2H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  26.1 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 29.7 (CH<sub>2</sub>), 30.2 (CH<sub>2</sub>), 42.1 (CH<sub>3</sub>), 43.9 (CH), 52.4 (CH<sub>3</sub>), 63.3 (CH), 127.5 (CH), 129.9 (C), 130.3 (CH), 146.3 (C), 166.9 (C). FT-IR (cm<sup>-1</sup>, neat, ATR) 3297 (w), 2945 (w), 2847 (w), 1722 (s), 1448 (w), 1312 (s), 1260 (vs), 1147 (s), 1113 (s), 1020 (vs), 982 (s), 799 (vs), 757 (s), 707 (s), 514 (vs). HRMS (ES-) calcd for C<sub>16</sub>H<sub>22</sub>NO<sub>4</sub>S [M-H]<sup>-</sup>: 324.1275, found: 324.1271.

**N'-((4-Bromophenyl)(cyclohexyl)methyl)-N,N-dimethylsulfamide, 4n** (152 mg, 80%) was



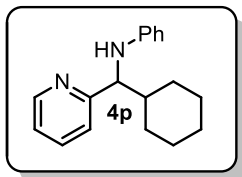
prepared according to the general procedure from **2n** (131 mg, 0.5 mmol). The desired sulfamide **4n** was isolated as a yellow semisolid.  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  0.89 (qd,  $J = 12.0, 3.4$  Hz, 1H), 1.01 (qd,  $J = 12.2, 3.4$  Hz, 1H), 1.06 - 1.23 (m, 3H), 1.30 - 1.37 (m, 1H), 1.47 - 1.57 (m, 1H), 1.57 - 1.70 (m, 2H), 1.73 - 1.79 (m, 1H), 1.93 - 2.00 (m, 1H), 2.49 (s, 6H), 4.01 (t,  $J = 7.9$  Hz, 1H), 5.15 (d,  $J = 6.4$  Hz, 1H), 7.10 (d,  $J = 8.5$  Hz, 2H), 7.45 (d,  $J = 8.5$  Hz, 2H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  26.1 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 29.9 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>), 37.8 (CH<sub>3</sub>), 44.1 (CH), 63.3 (CH), 121.4 (C), 129.3 (CH), 131.7 (CH), 141.0 (C). FT-IR (cm<sup>-1</sup>, neat, ATR) 3291 (w, br.), 2924 (m), 2852 (w), 1447 (m), 1317 (s), 1147 (vs), 1009 (m), 1062 (m), 954 (s), 826 (m), 706 (s), 572 (vs). HRMS (ES+) calcd for C<sub>15</sub>H<sub>24</sub>BrN<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup>: 375.0742, found: 375.0741.

***N*-(Cyclohexyl(*p*-tolyl)methyl)aniline, 4o** (72 mg, 51%) was prepared according to the general



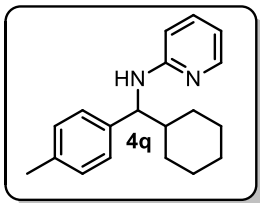
procedure from **2o** (98 mg, 0.5 mmol). The desired amine **4o** was isolated as a yellow oil. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 1.05 - 1.36 (m, 5H), 1.54 - 1.61 (m, 1H), 1.63 - 1.71 (m, 2H), 1.72 - 1.83 (m, 2H), 1.88 - 1.97 (m, 1H), 2.35 (s, 3H), 4.08 - 4.19 (m, 2H), 6.53 (d, *J* = 8.3 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 7.09 (t, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 21.3 (CH<sub>3</sub>), 26.6 (CH<sub>2</sub>), 26.7 (2 × CH<sub>2</sub>), 29.8 (CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 45.2 (CH), 63.4 (CH), 113.4 (CH), 117.1 (CH), 127.4 (CH), 129.2 (CH), 129.3 (CH), 136.4 (C), 139.9 (C), 148.1 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3279 (w, br), 2918 (w), 2886 (w), 1447 (w), 1325 (m), 1315 (vs), 1156 (s), 1041 (w), 981 (s), 725 (m), 607 (m) 546 (vs). **HRMS** (CI<sup>+</sup>) calcd for C<sub>20</sub>H<sub>26</sub>N [M+H]<sup>+</sup>: 280.2060, found: 280.2055.

***N*-(Cyclohexyl(pyridin-2-yl)methyl)aniline, 4p** (105 mg, 78%) was prepared according to the



general procedure from **2p** (91 mg, 0.5 mmol). The desired amine **4p** was isolated as an off-white powdery solid (mp = 83-84 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 1.04 - 1.31 (m, 5H), 1.47 - 1.55 (m, 1H), 1.62 - 1.79 (m, 3H), 1.82 - 1.93 (m, 2H), 4.30 (d, *J* = 5.2 Hz, 1H), 4.54 (br. s., 1H), 6.57 (d, *J* = 7.9 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 7.06 - 7.14 (m, 3H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 8.59 (d, *J* = 4.6 Hz, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 26.5 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 26.7 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 44.0 (CH), 64.5 (CH), 113.5 (CH), 117.3 (CH), 122.1 (CH), 122.3 (CH), 129.4 (CH), 136.3 (CH), 148.1 (C), 149.5 (CH), 162.3 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3267 (w, br), 2927 (m), 2847 (w), 1592 (m), 1498 (m), 1323 (m), 744 (vs), 691 (s), 570 (m). **HRMS** (ES<sup>+</sup>) calcd for C<sub>18</sub>H<sub>23</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 267.1856, found: 267.1870.

***N*-(Cyclohexyl(*p*-tolyl)methyl)pyridin-2-amine, 4q** (108 mg, 76%) was prepared according to

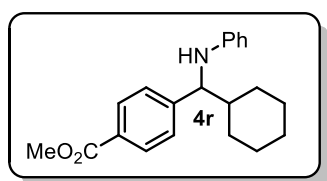


the general procedure from **2q** (98 mg, 0.5 mmol). The desired amine **4q** was isolated as an off-white solid (mp = 93-94 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 1.01 - 1.26 (m, 5H), 1.50 - 1.58 (m, 1H), 1.60 - 1.78 (m, 4H), 1.85 - 1.93 (m, 1H), 2.31 (s, 3H), 4.29 (t, *J* = 6.9 Hz, 1H), 5.15 (d, *J* = 6.7 Hz, 1H), 6.16 (d, *J* = 8.5 Hz, 1H), 6.49 (dd, *J* = 7.0, 4.9 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.25 - 7.29 (m, 1H), 8.04 (d, *J* = 3.7 Hz, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz)



$\delta$  21.3 (CH<sub>3</sub>), 26.5 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 44.8 (CH), 61.8 (CH), 106.4 (CH), 113.0 (CH), 127.3 (CH), 129.2 (CH), 136.6 (C), 137.7 (CH), 139.3 (C), 148.4 (CH), 158.8 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3237 (w, br), 2916 (m), 2850 (w), 1597 (vs), 1575 (s), 1530 (s), 1440 (vs), 768 (vs), 607 (w), 515 (w). **HRMS** (ES<sup>+</sup>) calcd for C<sub>19</sub>H<sub>25</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 281.2012, found: 281.2019.

**Methyl 4-(Cyclohexyl(phenylamino)methyl)benzoate, 4r** (104 mg, 64%) was prepared



according to the general procedure from **2r** (120 mg, 0.5 mmol). The

desired amine **4r** was isolated as a clear, colorless semisolid. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz)  $\delta$  0.99 - 1.33 (m, 5H), 1.48 - 1.57 (m, 1H),

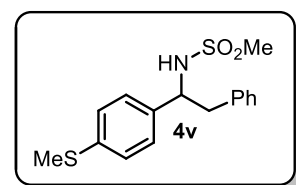
1.58 - 1.81 (m, 4H), 1.81 - 1.91 (m, 1H), 3.90 (s, 3H), 4.18 (d,  $J$  = 3.1

Hz, 2H), 6.47 (d,  $J$  = 8.7 Hz, 2H), 6.62 (t,  $J$  = 7.3 Hz, 1H), 7.06 (t,  $J$  = 8.2 Hz, 2H), 7.38 (d,  $J$  = 8.2 Hz, 2H), 7.98 (d,  $J$  = 8.2 Hz, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz)  $\delta$  26.5 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>),

29.6 (CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 45.0 (CH), 52.3 (CH<sub>3</sub>), 63.6 (CH), 113.4 (CH), 117.5 (CH), 127.5 (CH), 129.1 (C), 129.4 (CH), 129.9 (CH), 147.6 (C), 148.6 (C), 167.3 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR)

3401 (vw, br), 2925 (w), 2852 (w), 1713 (m), 1600 (m), 1503 (m), 1277 (vs), 1103 (m), 747 (m), 691 (m). **HRMS** (ES<sup>+</sup>) calcd for C<sub>21</sub>H<sub>26</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 324.1958, found: 324.1961.

**N-(1-(4-(Methylthio)phenyl)-2-phenylethyl)methanesulfonamide, 4v** (116 mg, 72%) was



prepared according to the general procedure from **2j** (115 mg, 0.5 mmol) *with the following modifications*: 1) 1.3 equiv of diisopropylammonium bis(catecholato)benzylsilicate **3b** (284 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were

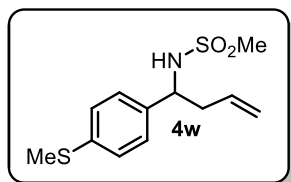
used. The desired sulfonamide **4v** was isolated as a yellow solid (mp = 119-120 °C). **<sup>1</sup>H NMR**

(CDCl<sub>3</sub>, 500 MHz)  $\delta$  2.40 (s, 3H), 2.48 (s, 3H), 3.00 (dd,  $J$  = 13.7, 8.2 Hz, 1H), 3.09 (dd,  $J$  = 13.4, 6.4 Hz, 1H), 4.69 (q,  $J$  = 7.2 Hz, 1H), 4.92 (d,  $J$  = 7.0 Hz, 1H), 7.11 (d,  $J$  = 7.0 Hz, 2H),

7.18 - 7.25 (m, 4H), 7.25 - 7.30 (m, 3H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz)  $\delta$  15.9 (CH<sub>3</sub>), 41.9 (CH<sub>3</sub>), 44.1 (CH<sub>2</sub>), 59.2 (CH), 126.9 (CH), 127.4 (CH), 127.6 (CH), 129.0 (CH), 129.8 (CH), 136.8 (C),

137.9 (C), 138.7 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3326 (w, br), 2924 (vw), 1421 (w), 1311 (s), 1145(vs), 1081 (m), 990 (s), 819 (m), 748 (m), 701 (s), 524 (vs). **HRMS** (ES<sup>-</sup>) calcd for C<sub>16</sub>H<sub>18</sub>NO<sub>2</sub>S<sub>2</sub> [M-H]<sup>-</sup>: 320.0777, found: 320.0775.

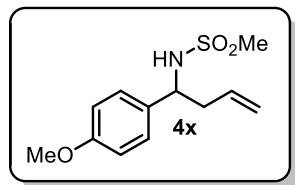
***N***-(1-(4-(Methylthio)phenyl)but-3-en-1-yl)methanesulfonamide, **4w** (99 mg, 73%) was



prepared according to the general procedure from **2j** (115 mg, 0.5 mmol) *with the following modifications*: 1) 1.3 equiv of triethylammonium bis(catecholato)allylsilicate **3c** (252 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were used. The

desired sulfonamide **4w** was isolated as a clear viscous oil that solidified upon standing to give a white powder (mp = 70-71 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 2.45 - 2.58 (m, 2H), 2.48 - 2.50 (s, 3H), 2.61 (s, 3H), 4.53 (q, *J* = 7.3 Hz, 1H), 4.66 (d, *J* = 5.5 Hz, 1H), 5.15 - 5.20 (m, 2H), 5.62 - 5.73 (m, 1H), 7.22 - 7.26 (m, 4H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 15.9 (CH<sub>3</sub>), 42.2 (CH<sub>3</sub>), 42.3 (CH<sub>2</sub>), 57.1 (CH), 119.9 (CH<sub>2</sub>), 127.0 (CH), 127.5 (CH), 133.3 (CH), 137.8 (C), 138.8 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3268 (w, br), 2931 (vw), 1448 (w), 1317 (s), 1151(vs), 1081 (m), 980 (m), 817 (m), 759 (m), 516 (vs). **HRMS** (ES-) calcd for C<sub>12</sub>H<sub>16</sub>NO<sub>2</sub>S<sub>2</sub> [M-H]<sup>-</sup>: 270.0622, found: 270.0614.

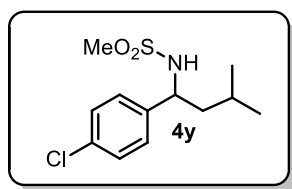
***N***-(1-(4-(Methoxy)phenyl)but-3-en-1-yl)methanesulfonamide, **4x** (79 mg, 61%) was



prepared according to the general procedure from **2i** (107 mg, 0.5 mmol) *with the following modifications*: 1) 1.3 equiv of triethylammonium bis(catecholato)allylsilicate **3c** (252 mg, 0.65 mmol) were used; 2) 3 mol % of Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (13 mg, 0.015 mol) were

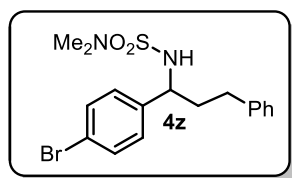
used in place of 4CzIPN. The desired sulfonamide **4x** was isolated as a pale brown oil. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 2.49 - 2.54 (m, 2H), 2.56 (s, 3H), 3.80 (s, 3H), 4.49 (q, *J* = 6.7 Hz, 1H), 5.02 (d, *J* = 6.4 Hz, 1H), 5.08 - 5.17 (m, 2H), 5.61 - 5.74 (m, 1H), 6.89 (d, *J* = 8.9 Hz, 2H), 7.24 (d, *J* = 8.9 Hz, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 42.2 (CH<sub>3</sub>), 42.3 (CH<sub>2</sub>), 55.5 (CH<sub>3</sub>), 57.1 (CH), 114.4 (CH<sub>2</sub>), 119.4 (CH), 128.2 (CH), 133.1 (C), 133.6 (CH), 159.5 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3278 (w, br), 2941 (vw), 1513 (m), 1442 (w), 1311 (s), 1246 (s), 1148 (vs), 980 (s), 831 (s), 516 (vs). **HRMS** (CI<sup>+</sup>) calcd for C<sub>12</sub>H<sub>18</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>: 256.1007, found: 256.1009.

**N-(1-(4-(Methylthio)phenyl)but-3-en-1-yl)methanesulfonamide, 4y** (90 mg, 65%) was



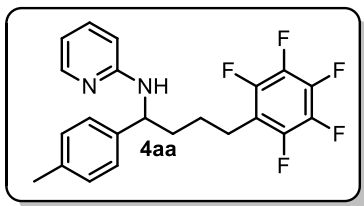
prepared according to the general procedure from **2f** (109 mg, 0.5 mmol) *with the following modifications*: 1) 1.3 equiv of diisopropylammonium bis(catecholato)isobutylsilicate **3d** (262 mg, 0.65 mmol) were used; 2) 3 mol % of Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (13 mg, 0.015 mol) were used in place of 4CzIPN. The desired sulfonamide **4y** was isolated as a pale brown oil. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 0.93 (d, *J* = 6.1 Hz, 6H), 1.50 - 1.58 (m, 2H), 1.62 - 1.72 (m, 1H), 2.55 (s, 3H), 4.49 (q, *J* = 6.8 Hz, 1H), 4.98 (d, *J* = 6.7 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 22.5 (CH<sub>3</sub>), 22.6 (CH<sub>3</sub>), 25.0 (CH), 42.3 (CH<sub>3</sub>), 47.0 (CH), 56.2 (CH), 128.3 (CH), 129.4 (CH), 134.0 (C), 140.7 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3267 (w, br), 2958 (w), 1492 (w), 1311 v(s), 1151 (vs), 1135 (s), 1091 (m), 979 (m), 829 (w), 734 (vs), 516 (vs). **HRMS** (CI<sup>+</sup>) calcd for C<sub>12</sub>H<sub>19</sub>ClNO<sub>2</sub>S [M+H]<sup>+</sup>: 276.0825, found: 276.0811.

**N'-(1-(4-Bromophenyl)-3-phenylpropyl)-N,N-dimethylsulfamide, 4z** (115 mg, 57%) was



prepared according to the general procedure from **2n** (146 mg, 0.5 mmol) *with the following modifications*: 1) 1.3 equiv of diisopropylammonium bis(catecholato)(2-phenylethyl)silicate **3e** (294 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were used. The desired sulfamide **4z** was isolated as a yellow semisolid. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 1.97 - 2.06 (m, 1H), 2.11 - 2.20 (m, 1H), 2.48 - 2.65 (m, 2H), 2.53 (s, 6H), 4.31 (q, *J* = 7.0 Hz, 1H), 4.72 (d, *J* = 7.0 Hz, 1H), 7.13 (d, *J* = 7.02 Hz, 2H), 7.15 - 7.21 (m, 3H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 32.5 (CH<sub>2</sub>) 37.8 (CH<sub>3</sub>) 39.3 (CH<sub>2</sub>) 57.9 (CH) 121.9 (C) 126.5 (CH) 128.6 (CH) 128.8 (CH) 128.8 (CH) 132.1 (CH) 140.8 (C) 141.3 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3285 (w, br), 3034 (vw), 2925 (w), 2851 (w), 1454 (m), 1317 (m), 1144 (vs), 1071 (m), 956 (m), 699 (vs), 523 (m). **HRMS** (ES<sup>+</sup>) calcd for C<sub>17</sub>H<sub>22</sub>BrN<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup>: 397.0580, found: 397.0588.

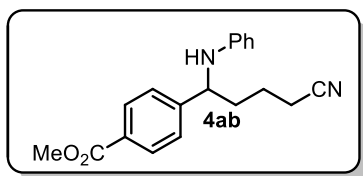
**N-(4-(Perfluorophenyl)-1-(p-tolyl)butyl)pyridin-2-amine, 4aa** (114 mg, 57%) was prepared



according to the general procedure from **2p** (98 mg, 0.5 mmol) *with the following modifications*: 1) 1.3 equiv of diisopropylammonium bis(catecholato) (3-pentafluorophenylpropyl)silicate **3f** (361 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol)

were used. The desired amine **4aa** was isolated as a yellow semisolid. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 1.55 - 1.68 (m, 1H), 1.69 - 1.77 (m, 1H), 1.77 - 1.93 (m, 2H), 2.32 (s, 3H), 2.70 (t, *J* = 7.3 Hz, 2H), 4.56 (q, *J* = 7.0 Hz, 1H), 5.07 (d, *J* = 6.7 Hz, 1H), 6.20 (d, *J* = 8.5 Hz, 1H), 6.52 (t, *J* = 6.1 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 4.6 Hz, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 21.3 (CH<sub>3</sub>), 22.3 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>), 37.8 (CH<sub>2</sub>), 56.1 (CH), 106.9 (CH), 114.2 (dt, *J*<sub>C-F</sub> = 207.1, *J*<sub>C-C-F</sub> = 18.3 Hz, CF), 113.4 (CH), 126.5 (CH), 129.6 (CH), 137.6 (dt, *J*<sub>C-C-F</sub> = 252.0, *J*<sub>C-F</sub> = 14.7 Hz, CF), 137.1 (C), 137.7 (CH), 140.1 - 140.6 (m, C), 140.3 (C), 145.3 (dt, *J*<sub>C-F</sub> = 240.1, *J*<sub>C-C-F</sub> = 11.9 Hz, CF), 148.4 (CH), 158.4 (C). **<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz) -166.0 (td, *J* = 21.6, 8.3 Hz, 2F), -161.0 (t, *J* = 20.6 Hz, 1F), -147.2 (dd, *J* = 22.7, 8.3 Hz, 2F). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3255 (vw, br.), 2937 (vw), 2851 (vw), 1600 (m), 1573 (n), 1501 (vs), 1444 (m), 1265 (m), 1121 (m), 962 (m), 734 (vs). **HRMS** (ES<sup>+</sup>) calcd for C<sub>22</sub>H<sub>20</sub>F<sub>5</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 407.1541, found: 407.1531.

**Methyl 4-(4-Cyano-1-(phenylamino)butyl)benzoate, 4ab** (96 mg, 62%) was prepared

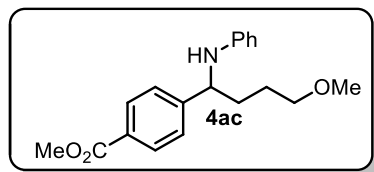


according to the general procedure from **2r** (120 mg, 0.5 mmol) *with the following modifications*: 1) 1.3 equiv of diisopropylammonium bis(catecholato)(3-cyanopropyl)silicate **3g** (273 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg,

0.015 mol) were used. The desired amine **ab** was isolated as a clear yellow oil. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 1.66 - 1.76 (m, 1H), 1.78 - 1.89 (m, 1H), 1.90 - 2.04 (m, 2H), 2.29 - 2.43 (m, 2H), 3.91 (s, 3H), 4.43 (t, *J* = 6.7 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 8.01 (d, *J* = 8.3 Hz, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 17.3 (CH<sub>3</sub>), 22.6 (CH<sub>2</sub>), 37.5 (CH<sub>2</sub>), 52.3 (CH<sub>3</sub>), 57.6 (CH), 113.7 (CH), 118.3 (CH), 119.4 (C), 126.6 (CH), 129.5 (CH), 129.6 (C), 130.4 (CH), 146.8 (C), 148.7 (C), 167.0 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3281 (w, br.), 3052 (vw), 2949 (w), 2852 (vw), 2242 (w), 1715 (s),

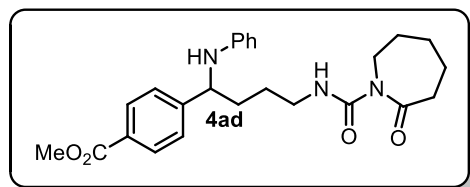
1601 (m), 1504 (m), 1434 (m), 1278 (vs), 1112 (m), 750 (s), 693 (m). **HRMS** (ES+) calcd for C<sub>19</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 309.1598, found: 309.1609.

**Methyl 4-(4-Methoxy-1-(phenylamino)butyl)benzoate, 4ac** (108 mg, 69%) was prepared



according to the general procedure from **2r** (120 mg, 0.5 mmol) **with the following modifications:** 1) 1.3 equiv of diisopropylammonium bis(catecholato)(3-methoxypropyl)silicate **3h** (291 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were used. The desired amine **4ac** was isolated as a clear yellow oil. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 1.57 - 1.76 (m, 2H), 1.89 (q, *J* = 7.4 Hz, 2H), 3.34 (s, 3H), 3.36 - 3.43 (m, 2H), 3.85 - 3.92 (m, 3H), 4.33 (br s, 1H), 4.37 (t, *J* = 6.7 Hz, 1H), 6.47 (d, *J* = 8.2 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 26.7 (CH<sub>2</sub>), 35.7 (CH<sub>2</sub>), 52.3 (CH<sub>3</sub>), 58.3 (CH), 58.9 (CH<sub>3</sub>), 72.4 (CH<sub>3</sub>), 113.5 (CH), 117.7 (CH), 126.7 (CH), 129.2 (C), 129.4 (CH), 130.2 (CH), 147.4 (C), 150.0 (C), 167.2 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3392 (vw, br), 2925 (w), 2851 (w), 1717 (s), 1601 (s), 1504 (m), 1276 (vs), 1111 (s), 735 (s), 707 (m). **HRMS** (ES+) calcd for C<sub>19</sub>H<sub>23</sub>NNaO<sub>3</sub> [M+Na]<sup>+</sup>: 336.1576, found: 336.1565.

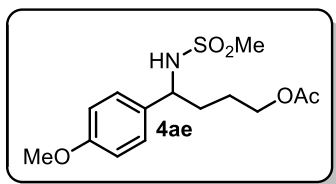
**Methyl 4-(4-(2-Oxazepane-1-carboxamido)-1-(phenylamino)butyl)benzoate, 4ad** (127 mg,



58%) was prepared according to the general procedure from **2r** (120 mg, 0.5 mmol) **with the following modifications:** 1) 1.3 equiv of diisopropylammonium bis(catecholato)(2-oxo-propyl-azepanyl-1-carboxamidyl)silicate **3i** (353 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were used. The desired sulfonamide **4ad** was isolated as a clear yellow oil. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 1.70 (m, *J* = 0.6 Hz, 10H), 2.60 - 2.72 (m, 2H), 3.31 (q, *J* = 6.2 Hz, 2H), 3.88 (s, 3H), 3.91 - 4.00 (m, 2H), 4.14 - 4.32 (m, br, 1H), 4.39 (t, *J* = 6.7 Hz, 1H), 6.47 (d, *J* = 7.9 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 2H), 9.30 (t, *J* = 5.2 Hz, 1H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 23.7 (CH<sub>2</sub>), 26.7 (CH<sub>2</sub>), 28.5 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 36.0 (CH<sub>2</sub>), 39.9 (CH<sub>2</sub>), 40.4 (CH<sub>2</sub>), 44.0 (CH<sub>2</sub>), 52.2 (CH<sub>3</sub>), 58.0 (CH), 113.5 (CH), 117.7 (CH), 126.6 (CH), 129.2

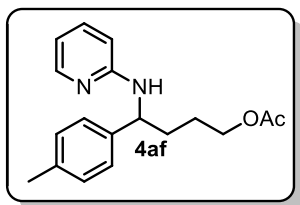
(CH), 129.3 (CH), 130.0 (C), 130.2 (CH), 147.2 (C), 149.7 (C), 155.2 (C), 167.1 (C), 179.7 (C). **FT-IR** ( $\text{cm}^{-1}$ , neat, ATR) 3373 (vw, br), 3262 (vw, br.), 3050 (vw), 2943 (w), 2851 (vw) 1692 (vs), 1601 (m), 1527 (m), 1435 (m), 1277 (vs), 1178 (m), 969 (w), 733 (vs), 693 (s). **HRMS** (ES+) calcd for  $\text{C}_{25}\text{H}_{32}\text{N}_3\text{O}_4$   $[\text{M}+\text{H}]^+$ : 438.2393, found: 438.2399.

**4-(4-Methoxyphenyl)-4-(methylsulfonamido)butyl Acetate, 4ae** (68 mg, 43%) was prepared



according to the general procedure from **2i** (107 mg, 0.5 mmol) *with the following modifications*: 1) 1.3 equiv of diisopropylammonium bis(catecholato)(3-acetoxypropyl)silicate **3j** (291 mg, 0.65 mmol) were used; 2) 3 mol % of  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  (13 mg, 0.015 mol) were used in place of 4CzIPN. The desired sulfonamide **4ae** was isolated as a pale brown oil.  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  1.50 - 1.99 (m, 4H), 2.05 (s, 3H), 2.57 (s, 3H), 3.83 (s, 3H), 4.07 (t,  $J = 6.2$  Hz, 2H), 4.42 (q,  $J = 7.4$  Hz, 1H), 4.86 (d,  $J = 7.6$  Hz, 1H), 6.92 (d,  $J = 8.7$  Hz, 2H), 7.24 (d,  $J = 8.9$  Hz, 2H).  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  21.2 ( $\text{CH}_2$ ), 25.8 ( $\text{CH}_2$ ), 34.4 ( $\text{CH}_2$ ), 42.2 ( $\text{CH}_3$ ), 55.6 ( $\text{CH}_3$ ), 57.9 (CH), 64.0 ( $\text{CH}_2$ ), 114.7 ( $\text{CH}_2$ ), 128.1 ( $\text{CH}_2$ ), 133.2 (C), 159.7 (C), 171.4 (C). **FT-IR** ( $\text{cm}^{-1}$ , neat, ATR) 3277 (w, br), 2949 (w), 1732 (s), 1513 (s), 1314(s), 1243 (vs), 1148 (vs), 1031 (vs), 976 (s), 833 (s), 757 (m), 518 (s). **HRMS** (ES-) calcd for  $\text{C}_{14}\text{H}_{20}\text{NO}_5\text{S}$   $[\text{M}-\text{H}]^-$ : 314.1062, found: 314.1065.

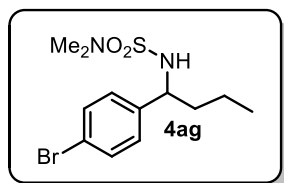
**4-(Pyridin-2-ylamino)-4-(*p*-tolyl)butyl Acetate, 4af** (100 mg, 67%) was prepared according to



the general procedure from **2f** (98 mg, 0.5 mmol) *with the following modifications*: 1) 1.3 equiv of diisopropylammonium bis(catecholato)(3-acetoxypropyl)silicate **3j** (291 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were used. The desired amine **4af** was isolated as a clear yellow oil.  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  1.60 - 1.71 (m, 1H), 1.72 - 1.81 (m, 1H), 1.82 - 1.96 (m, 2H), 2.02 (s, 3H), 2.32 (s, 3H), 4.06 (td,  $J = 6.4, 1.8$  Hz, 2H), 4.57 (q,  $J = 6.7$  Hz, 1H), 5.03 (d,  $J = 6.7$  Hz, 1H), 6.21 (d,  $J = 8.2$  Hz, 1H), 6.52 (dd,  $J = 6.9, 5.3$  Hz, 1H), 7.13 (d,  $J = 7.9$  Hz, 2H), 7.23 (d,  $J = 8.2$  Hz, 2H), 7.30 (ddd,  $J = 8.5, 7.1, 1.8$  Hz, 1H), 8.05 (dd,  $J = 4.7, 1.4$  Hz, 1H).  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  21.2 ( $\text{CH}_3$ ), 21.3 ( $\text{CH}_3$ ), 25.8 ( $\text{CH}_2$ ), 34.9 ( $\text{CH}_2$ ), 56.1 (CH), 64.3 ( $\text{CH}_2$ ), 106.9 (CH), 113.4 (CH), 126.5 (CH), 129.6 (CH), 137.1 (C), 137.7 (CH), 140.4 (C), 148.4 (CH), 158.4 (C), 171.4

(C). **FT-IR** ( $\text{cm}^{-1}$ , neat, ATR) 3253 (vw, br), 2951 (w), 2849 (vw), 1734 (s), 1599 (s), 1510 (m), 1443 (m), 1237 (vs), 1040 (m), 771 (m), 734(m). **HRMS** (ES+) calcd for  $\text{C}_{18}\text{H}_{22}\text{N}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 321.1579, found: 321.1589.

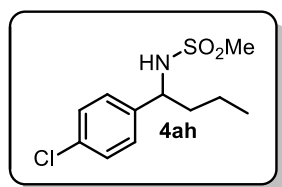
***N'*-(1-(4-Bromophenyl)butyl)-*N,N*-dimethylsulfamide, 4ag** (102 mg, 61%) was prepared



according to the general procedure from **2n** (146 mg, 0.5 mmol) *with the following modifications*: 1) 1.3 equiv of diisopropylammonium bis(catecholato)propylsilicate **3k** (253 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were used. The desired sulfamide

**4ag** was isolated as a pale yellow semisolid.  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  0.90 (t,  $J = 7.3$  Hz, 3H), 1.17 - 1.27 (m, 1H), 1.29 - 1.40 (m, 1H), 1.60 - 1.70 (m, 1H), 1.77 (br s, 1H), 2.53 (s, 6H), 4.27 (q,  $J = 7.3$  Hz, 1H), 4.97 (d,  $J = 6.4$  Hz, 1H), 7.17 (d,  $J = 8.3$  Hz, 2H), 7.47 (d,  $J = 8.3$  Hz, 2H).  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  13.9 ( $\text{CH}_3$ ), 19.5 ( $\text{CH}_2$ ), 37.8 ( $\text{CH}_3$ ), 40.1 ( $\text{CH}_2$ ), 58.0 ( $\text{CH}$ ), 121.6 (C), 128.7 (CH), 131.9 (CH), 141.9 (C). **FT-IR** ( $\text{cm}^{-1}$ , neat, ATR) 3284 (w, br), 2989 (m), 2856 (w), 1456 (m), 1318 (s), 1448 (vs), 1128 (s), 1071 (s), 1113 (s), 957 (s), 720 (s), 706 (vs), 556 (vs). **HRMS** (ES+) calcd for  $\text{C}_{12}\text{H}_{20}\text{BrN}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 335.0423, found: 335.0424.

***N*-(1-(4-(Methylthio)phenyl)but-3-en-1-yl)methanesulfonamide, 4ah** (89 mg, 68%) was



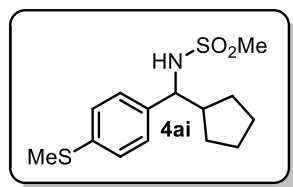
prepared according to the general procedure from **2f** (109 mg, 0.5 mmol) *with the following modifications*: 1) 1.3 equiv of diisopropylammonium bis(catecholato)propylsilicate **3k** (253 mg, 0.65 mmol) were used; 2) 3 mol % of Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (13 mg, 0.015 mol)

were used in place of 4CzIPN. The desired sulfonamide **4ah** was isolated as a pale brown oil.

**$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  0.91 (t,  $J = 7.5$  Hz, 3H), 1.17 - 1.31 (m, 1H), 1.30 - 1.42 (m, 1H), 1.58 - 1.73 (m, 1H), 1.73 - 1.84 (m, 1H), 2.59 (s, 3H), 4.42 (t,  $J = 7.3$  Hz, 1H), 5.04 (br s, 1H), 7.24 (d,  $J = 8.2$  Hz, 2H), 7.34 (d,  $J = 8.5$  Hz, 2H).  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  13.8 ( $\text{CH}_3$ ), 19.5 ( $\text{CH}_2$ ), 39.9 ( $\text{CH}_2$ ), 42.2 ( $\text{CH}_3$ ), 57.7 (CH), 128.3 (CH), 129.3 (CH), 133.9 (C), 140.6 (C). **FT-IR** ( $\text{cm}^{-1}$ , neat, ATR) 3277 (w, br), 2961 (w), 1492 (w), 1311 v(s), 1151 (vs), 1127 (s), 1090 (s), 976 (s), 732 (vs), 516 (vs). **HRMS** (CI+) calcd for  $\text{C}_{11}\text{H}_{17}\text{ClO}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 262.0669, found: 262.0659.



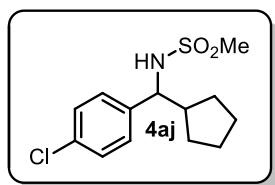
**N-(Cyclopentyl(4-(methylthio)phenyl)methyl)methanesulfonamide, 4ai** (105 mg, 70%) was



prepared according to the general procedure from **2j** (115 mg, 0.5 mmol) *with the following modifications*: 1) 1.3 equiv of diisopropylammonium bis(catecholato)cyclopentylsilicate **3I** (270 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were

used. The desired sulfonamide **4ai** was isolated as a viscous yellow oil. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 1.05 - 1.16 (m, 1H), 1.31 - 1.40 (m, 1H), 1.43 - 1.53 (m, 2H), 1.53 - 1.64 (m, 2H), 1.64 - 1.74 (m, 1H), 1.84 - 1.94 (m, 1H), 2.10 - 2.22 (m, 1H), 2.48 (s, 3H), 2.49 (s, 3H), 4.14 (dd, *J* = 9.6, 7.5 Hz, 1H), 4.94 (d, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 15.9 (CH<sub>3</sub>), 25.5 (2 × CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 42.2 (CH<sub>3</sub>), 46.7 (CH), 62.9 (CH), 126.9 (C,CH), 127.8 (CH), 138.5 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3275(w, br), 2952 (w), 2867 (w), 1439 (m), 1309 (s), 1147 (vs), 1048 (m), 977 (m), 751 (m), 516 (s). **HRMS** (CI+) calcd for C<sub>14</sub>H<sub>22</sub>NO<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 300.1092, found: 300.1090.

**N-((4-Chlorophenyl)(cyclopentyl)methyl)methanesulfonamide, 4aj** (105 mg, 73%) was

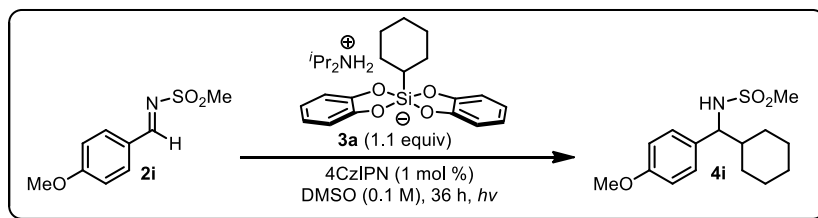


prepared according to the general procedure from **2f** (109 mg, 0.5 mmol) *with the following modifications*: 1) 1.3 equiv of diisopropylammonium bis(catecholato)cyclopentylsilicate **3I** (270 mg, 0.65 mmol) were used; 2) 3 mol% of Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (13 mg, 0.015 mol) were used in place of

4CzIPN. The desired sulfonamide **4aj** was isolated as a crystalline, pale yellow solid (mp = 94-95 °C). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 1.09 (dq, *J* = 12.9, 8.3 Hz, 1H), 1.29 - 1.39 (m, 1H), 1.41 - 1.52 (m, 2H), 1.52 - 1.62 (m, 2H), 1.63 - 1.71 (m, 1H), 1.85 - 1.94 (m, 1H), 2.09 - 2.20 (m, 1H), 2.51 (s, 3H), 4.15 (t, *J* = 8.4 Hz, 1H), 5.41 (d, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 25.4 (2 × CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 42.1 (CH<sub>3</sub>), 46.6 (CH), 62.7 (CH), 128.7 (CH), 129.2 (CH), 133.8 (C), 140.5 (C). **FT-IR** (cm<sup>-1</sup>, neat, ATR) 3265 (w, br), 2953 (w), 2868 (w), 1447 (w), 1308 (vs), 1155 (vs), 1090 (m), 978 (m), 517 (s). **HRMS** (ES-) calcd for C<sub>13</sub>H<sub>17</sub>ClNO<sub>2</sub>S [M-H]<sup>-</sup>: 286.0669, found: 286.0664.



## Representative Procedure for Large Scale Alkylation



### ***N*-(Cyclohexyl(4-methoxyphenyl)methyl)methanesulfonamide (**4i**)**

To an oven dried, 100 mL round bottom flask equipped with a stir bar were added diisopropylammonium bis(catecholato)cyclohexylsilicate **3a** (3.07 g, 7.15 mmol, 1.3 equiv), imine **2i** (1.07 g, 5 mmol, 1 equiv), and 4CzIPN (0.0394 g, 0.05 mmol, 0.01 equiv). The flask was sealed with a rubber septum and was evacuated and purged with argon three times *via* an inlet needle. The flask was then charged with anhyd DMSO (50 mL) *via* a syringe. The now bright yellow solution was irradiated by blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at approximately 27 °C *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by GC/MS. Once complete (~36 h), the now yellow-brown solution was transferred to a separatory funnel and diluted with deionized H<sub>2</sub>O (~150 mL) and EtOAc (~100 mL). The layers were separated,<sup>33</sup> and the aq layer was extracted with EtOAc (3 × ~100 mL). The combined organic layers were washed with 2 M NaOH (2 × ~150 mL), followed by brine (~150 mL). The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO<sub>2</sub> column chromatography (gradient hexane/EtOAc containing 1% Et<sub>3</sub>N) to give the desired sulfonamide **4a** (1.15 g, 77%) as a light brown solid (mp = 126-127 °C).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 0.85 - 0.95 (m, 1H), 1.02 (qd, *J* = 11.9, 2.7 Hz, 1H), 1.08 - 1.27 (m, 3H), 1.32 - 1.40 (m, 1H), 1.50 - 1.70 (m, 3H), 1.72 - 1.80 (m, 1H), 1.96 - 2.06 (m, 1H), 2.51 (s, 3H), 3.80 (s, 3H), 4.12 (t, *J* = 8.4 Hz, 1H), 4.77 - 5.07 (m, 1H), 6.88 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 2H).

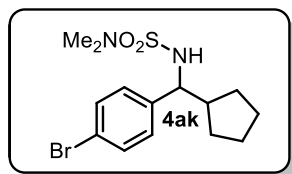
<sup>33</sup> In the event that an emulsion forms, addition of a small amount (~30 mL) of brine can be used to assist in layer separation.

**$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 125 MHz) 26.1 ( $\text{CH}_2$ ), 26.2 ( $\text{CH}_2$ ), 26.4 ( $\text{CH}_2$ ), 30.0 ( $\text{CH}_2$ ), 30.1 ( $\text{CH}_2$ ), 42.0 ( $\text{CH}_3$ ), 44.0 ( $\text{CH}$ ), 55.5 ( $\text{CH}_3$ ), 63.2 ( $\text{CH}$ ), 114.3 ( $\text{CH}$ ), 128.5 ( $\text{CH}$ ), 132.9 ( $\text{C}$ ), 159.3 ( $\text{C}$ ).

**FT-IR** ( $\text{cm}^{-1}$ , neat, ATR) 3248 (w), 2938 (m), 2851 (w), 1613 (w), 1513 (s), 1443 (m), 1311 (vs), 1249 (s), 1156 (vs), 1132 (s), 1029 (s), 833 (s), 752 (s), 514 (vs).

**HRMS** (ES+) calcd for  $\text{C}_{15}\text{H}_{23}\text{NNaO}_3\text{S}$   $[\text{M}+\text{Na}]^+$ : 320.1296, found: 320.1291.

***N'*-((4-Bromophenyl)(cyclopentyl)methyl)-*N,N*-dimethylsulfamide 4ak** (1.14 g, 63%) was

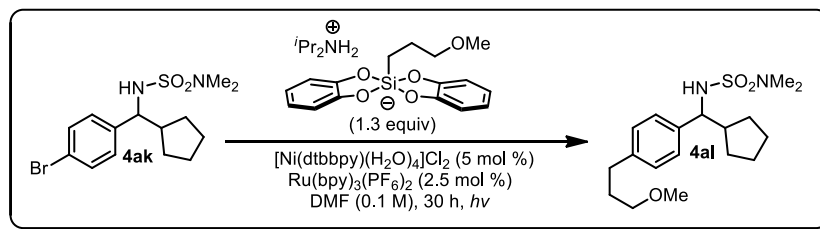


prepared according to the general procedure from **2n** (1.46 g, 5 mmol) *with the following modifications*: 1) 1.2 equiv of

diisopropylammonium bis(catecholato)cyclopentylsilicate **3l** (2.49 g, 6 mmol) were used; 2) the reaction was complete in 24 h. The desired

sulfamide **4ak** was isolated as a viscous yellow oil that solidified upon standing to give a yellow solid (mp = 86-87 °C).  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  1.03 - 1.15 (m, 1H), 1.26 - 1.36 (m, 1H), 1.41 - 1.53 (m, 2H), 1.53 - 1.64 (m, 2H), 1.64 - 1.75 (m, 1H), 1.84 - 1.94 (m, 1H), 2.02 - 2.15 (m, 1H), 2.46 (s, 6H), 4.01 (dd,  $J$  = 9.6, 6.6 Hz, 1H), 4.84 (d,  $J$  = 6.4 Hz, 1H), 7.14 (d,  $J$  = 8.2 Hz, 2H), 7.46 (d,  $J$  = 8.2 Hz, 2H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  25.4 ( $2 \times \text{CH}_2$ ), 30.4 ( $\text{CH}_2$ ), 30.5 ( $\text{CH}_2$ ), 37.7 ( $\text{CH}_3$ ), 47.0 ( $\text{CH}$ ), 63.0 ( $\text{CH}$ ), 121.5 ( $\text{C}$ ), 129.1 ( $\text{CH}$ ), 131.8 ( $\text{CH}$ ), 141.9 ( $\text{C}$ ). **FT-IR** ( $\text{cm}^{-1}$ , neat, ATR) 3260 (w, br), 2948 (w), 2856 (w), 1449 (w), 1317 (m), 1142 (vs), 1070 (w), 954 (w), 705 (m), 576 (m). **HRMS** (ES+) calcd for  $\text{C}_{14}\text{H}_{22}\text{BrN}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 361.0585, found: 361.0590.

## Procedure for Ni/Photoredox Cross-Coupling of **4ak**



### *N'*-(Cyclopentyl(4-(3-methoxypropyl)phenyl)methyl)-*N,N*-dimethylsulfamide, **4al**

To an 8 mL reaction vial equipped with a stir bar were added the diisopropylammonium bis(catecholato)(3-methoxypropyl)silicate **3h** (273 mg, 0.65 mmol, 1.3 equiv), [Ni(dtbbpy)(H<sub>2</sub>O)<sub>4</sub>]Cl<sub>2</sub> (11.8 mg, 0.025 mmol, 0.05 equiv),<sup>34</sup> and Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (10.8 mg, 0.0125 mmol, 0.025 equiv). The vial was sealed with a cap containing a TFE-lined silicone septa. The vial was evacuated three times *via* an inlet needle then purged with argon. The vial was then charged *via* a syringe with sulfamide **4ak** (181 mg, 0.5 mmol, 1 equiv) dissolved in anhyd, degassed DMF (5 mL). The cap was sealed with Parafilm, and the now bright red solution was irradiated in the aforementioned LED reactor. The temperature of the reaction was maintained at approximately 27 °C *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by HPLC. Once judged to be complete, the now opaque, milky-brown solution was transferred to a separatory funnel and diluted with deionized H<sub>2</sub>O (~20 mL) and EtOAc (~20 mL). The layers were separated,<sup>35</sup> and the aq layer was extracted with EtOAc (3 × ~20 mL). The combined organic layers were washed with 2 M NaOH (2 × ~30 mL), 2 M HCl (~30 mL), deionized H<sub>2</sub>O (~30 mL), and brine (~50 mL). The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by flash column chromatography (gradient hexane/EtOAc containing 1% Et<sub>3</sub>N) to give the desired coupling product, **4al**, (129 mg, 73%) as a clear, colorless oil that solidified upon standing (mp = 84–85 °C).

<sup>34</sup> In previous reports, we either pre-complexed the dtbbpy ligand to nickel *in situ* or conducted the reaction without pre-complexation. We recently found that preparation of [Ni(dtbbpy)(H<sub>2</sub>O)<sub>4</sub>]Cl<sub>2</sub> simplifies the process entirely. This complex can easily be prepared by reacting dtbbpy (1.05 equiv) with NiCl<sub>2</sub> • 6H<sub>2</sub>O in refluxing ethanol (0.1 M) for 12 h. Once cooled to rt the solvent can be removed *in vacuo* by rotary evaporation, and the resulting mint green solid can be washed with Et<sub>2</sub>O followed by pentane to remove any residual ligand. This complex can be stored on the bench for an indefinite period of time.

<sup>35</sup> Note that a precipitate will often form and rest at the interface between the organic and aq layers. It can be discarded during the washes without compromising yield.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 1.07 - 1.17 (m, 1 H), 1.27 - 1.37 (m, 1 H), 1.41 - 1.52 (m, 2 H), 1.53 - 1.63 (m, 2 H), 1.64 - 1.74 (m, 1 H), 1.82 - 1.94 (m, 3 H), 2.06 - 2.18 (m, 1 H), 2.42 (s, 6 H), 2.63 - 2.70 (m, 2 H), 3.33 (s, 3 H), 3.37 (t, *J* = 6.4 Hz, 2 H), 4.02 (dd, *J* = 9.5, 7.0 Hz, 1 H), 4.69 (d, *J* = 6.4 Hz, 1 H), 7.11 - 7.18 (m, 4 H).

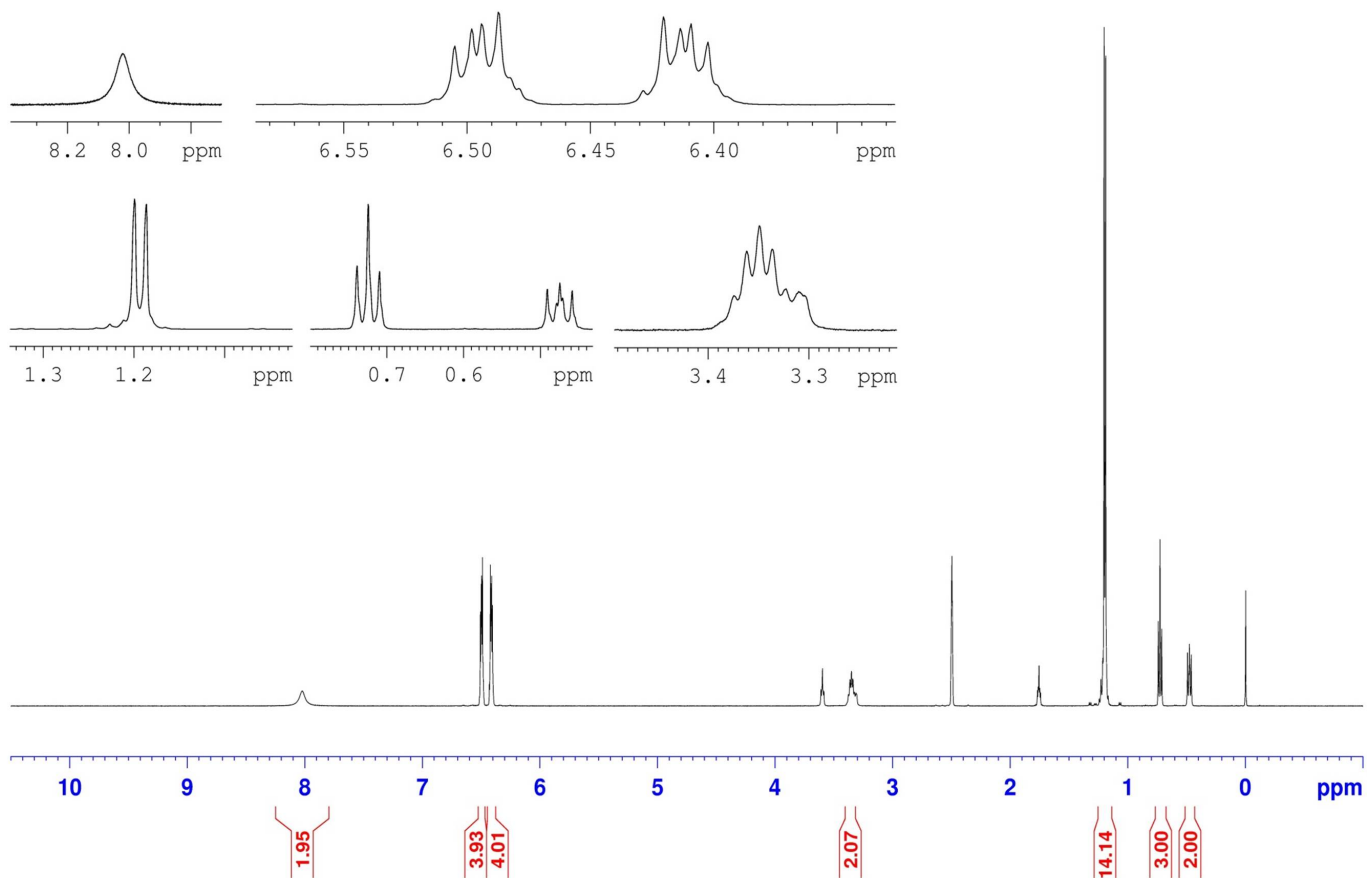
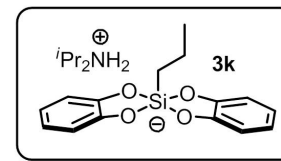
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) 25.4 (2 × CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 31.4 (CH<sub>2</sub>), 32.2 (CH<sub>2</sub>), 37.6 (CH<sub>3</sub>), 47.1 (CH), 58.8 (CH<sub>3</sub>), 63.3 (CH), 72.1 (CH<sub>2</sub>), 127.3 (CH), 128.7 (CH), 140.2 (C), 141.5 (C).

**FT-IR** (cm<sup>-1</sup>, neat, ATR) 3284(w, br), 2942 (w), 2867 (w), 1448 (m), 1338 (s), 1151 (vs), 1116 (s), 953 (s), 705 (vs), 563 (vs).

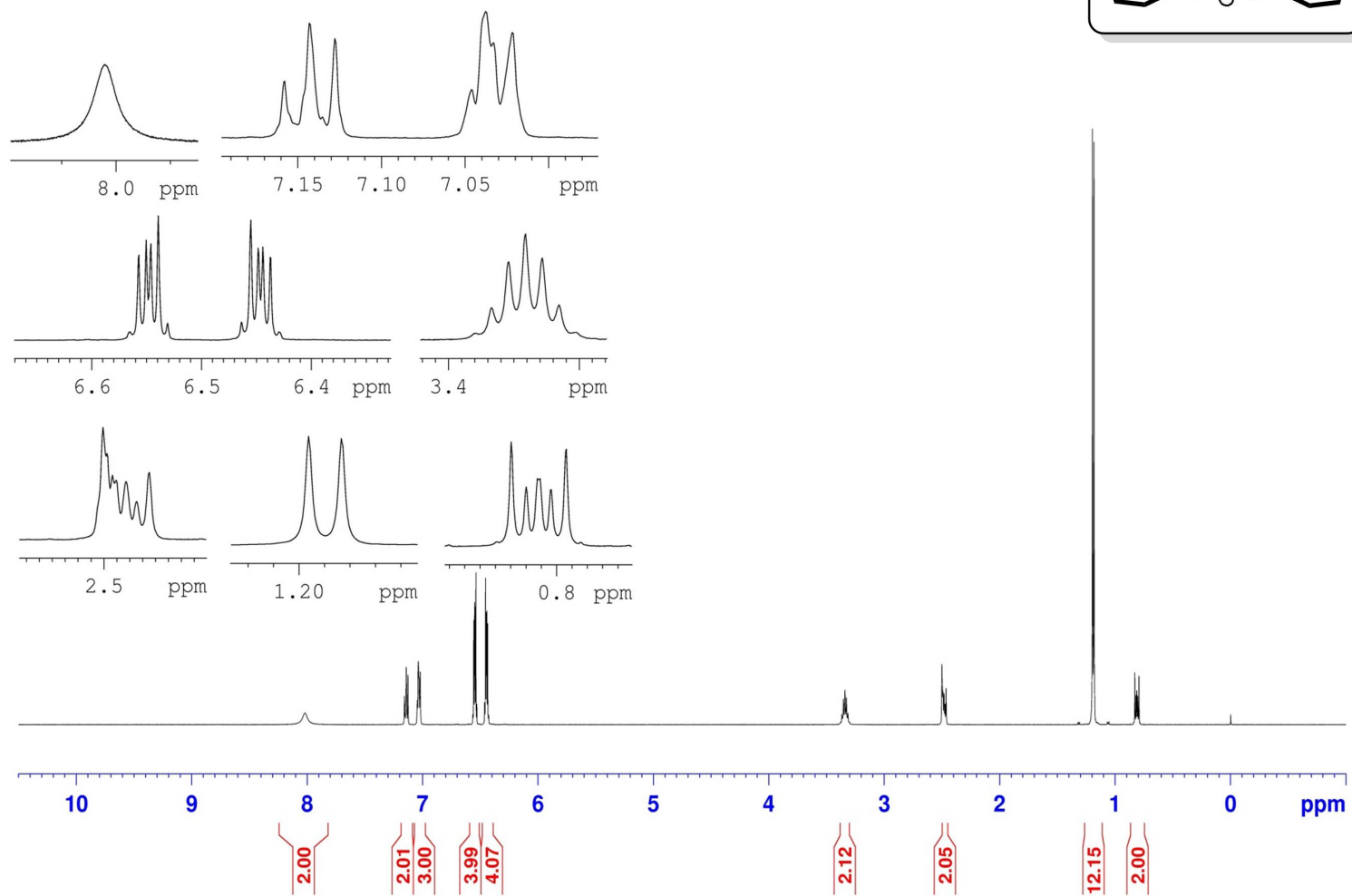
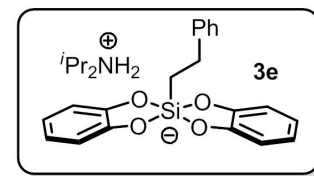
**HRMS** (ES<sup>+</sup>) calcd for C<sub>18</sub>H<sub>31</sub>N<sub>2</sub>O<sub>3</sub>S [M+H]<sup>+</sup>: 355.2050, found: 355.2046.

# $^1\text{H}$ NMR Spectra of Synthesized Compounds

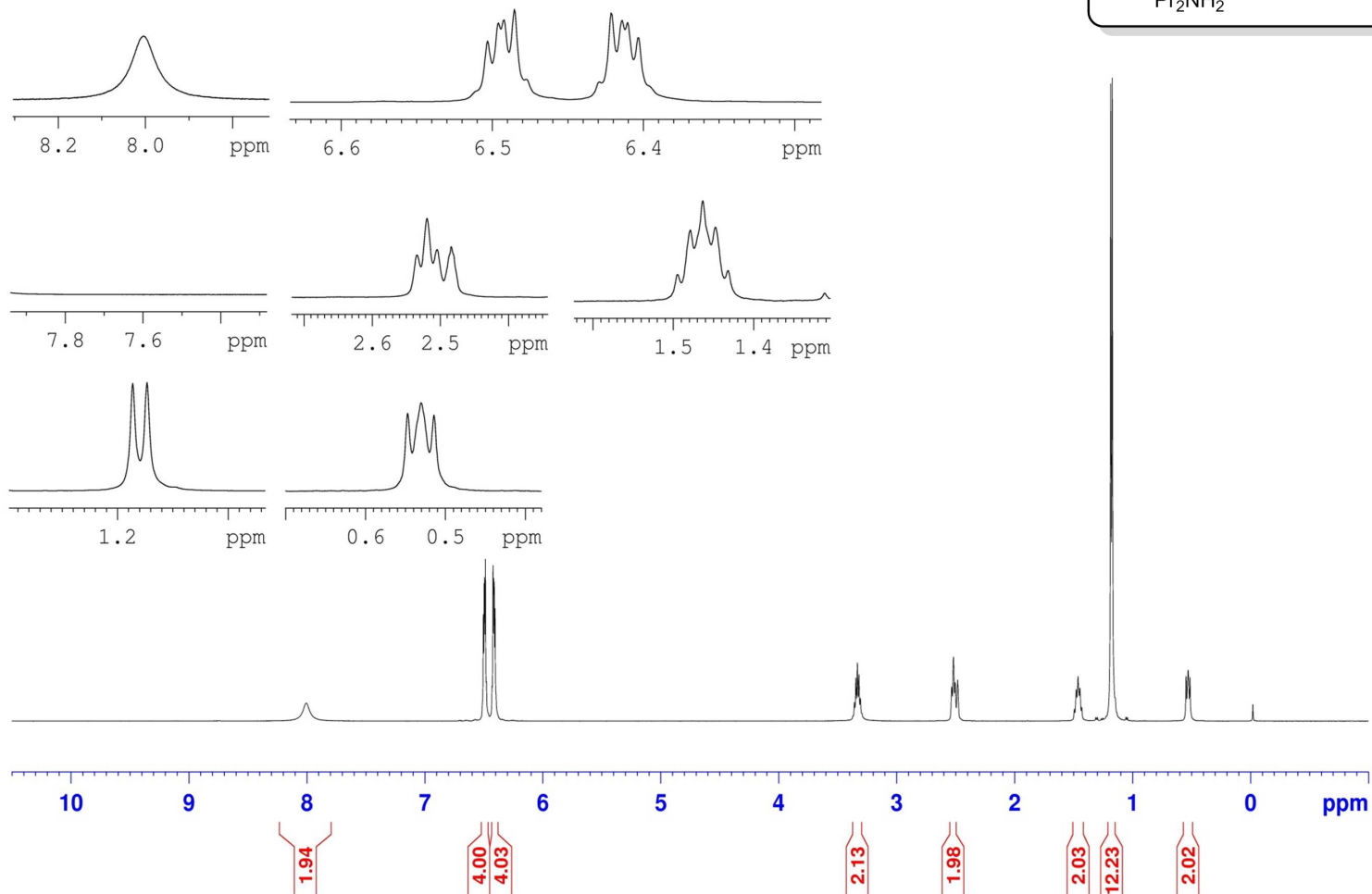
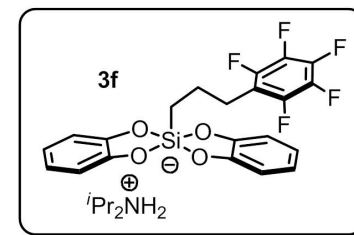
Diisopropylammonium Bis(catecholato)propylsilicate  
500 MHz, DMSO-d<sub>6</sub>



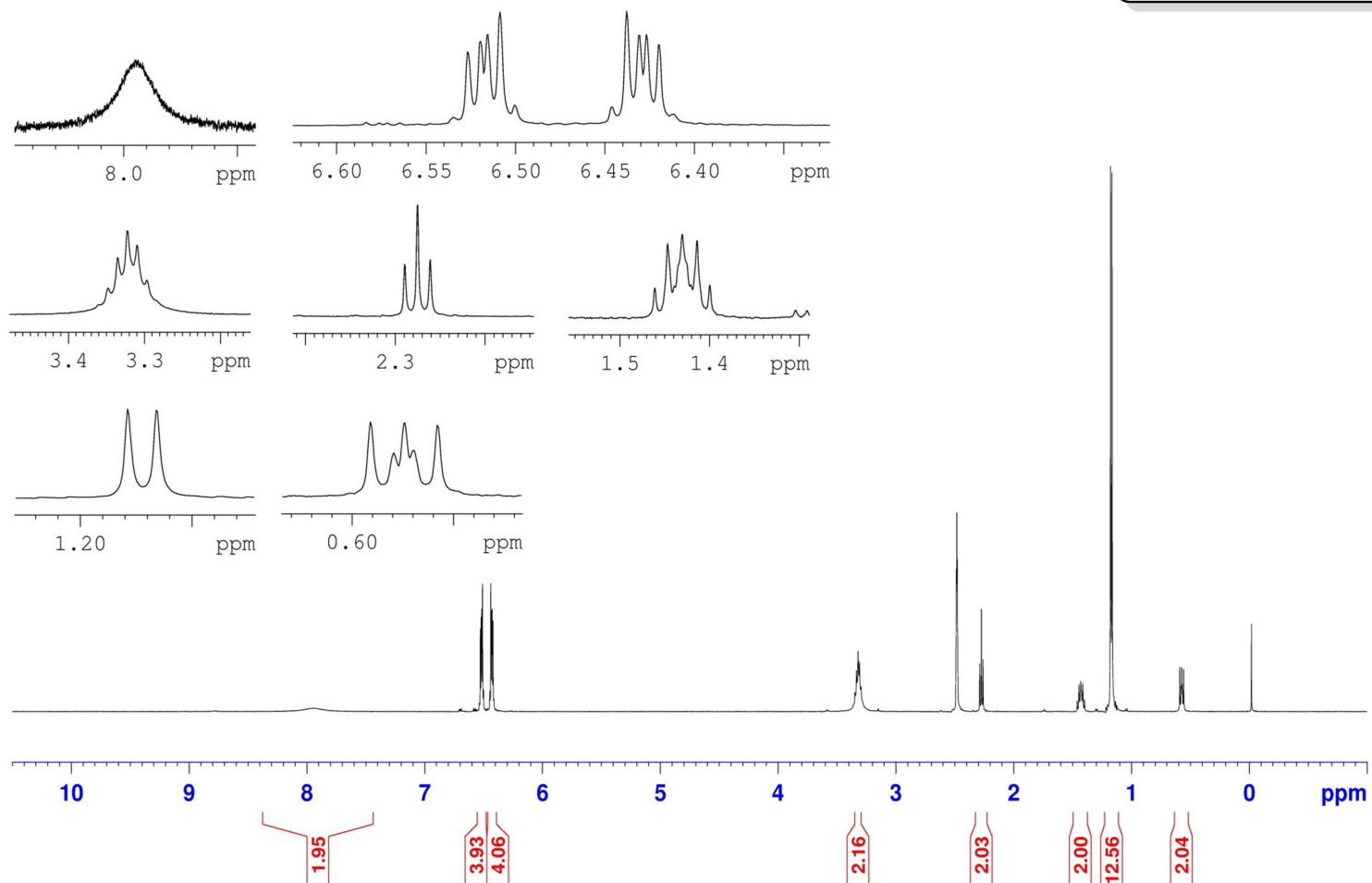
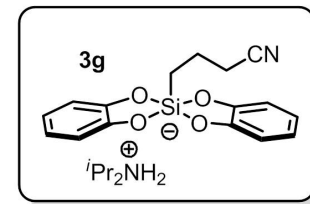
**Diisopropylammonium Bis(catecholato)(2-phenylethyl)silicate**  
500 MHz, CDCl<sub>3</sub>



**Diisopropylammonium Bis(catecholato) (3-pentafluorophenylpropyl)silicate**  
500 MHz, DMSO-d<sub>6</sub>

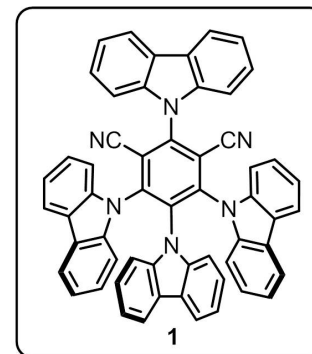
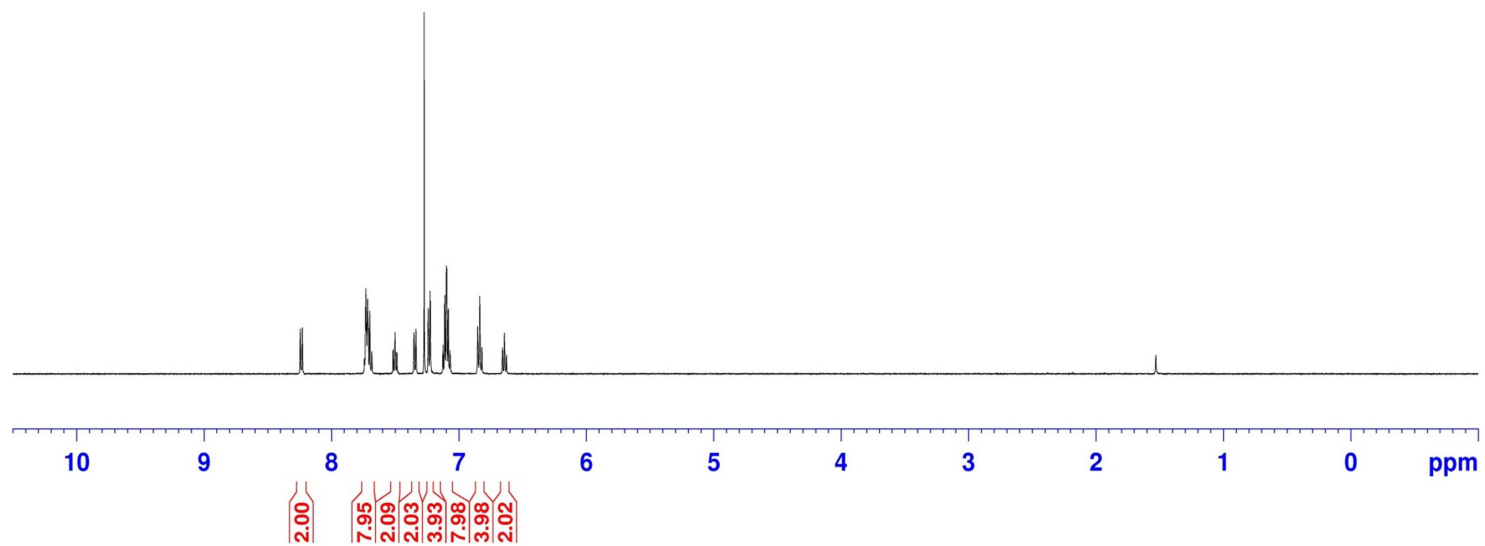
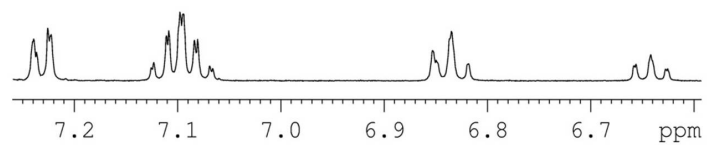
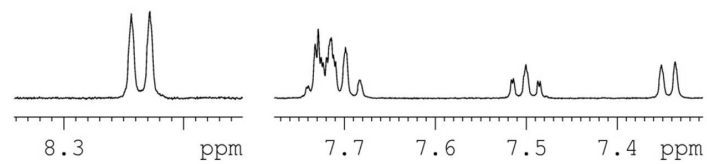


**Diisopropylammonium Bis(catecholato)(3-cyanopropyl)silicate**  
500 MHz, DMSO-d<sub>6</sub>

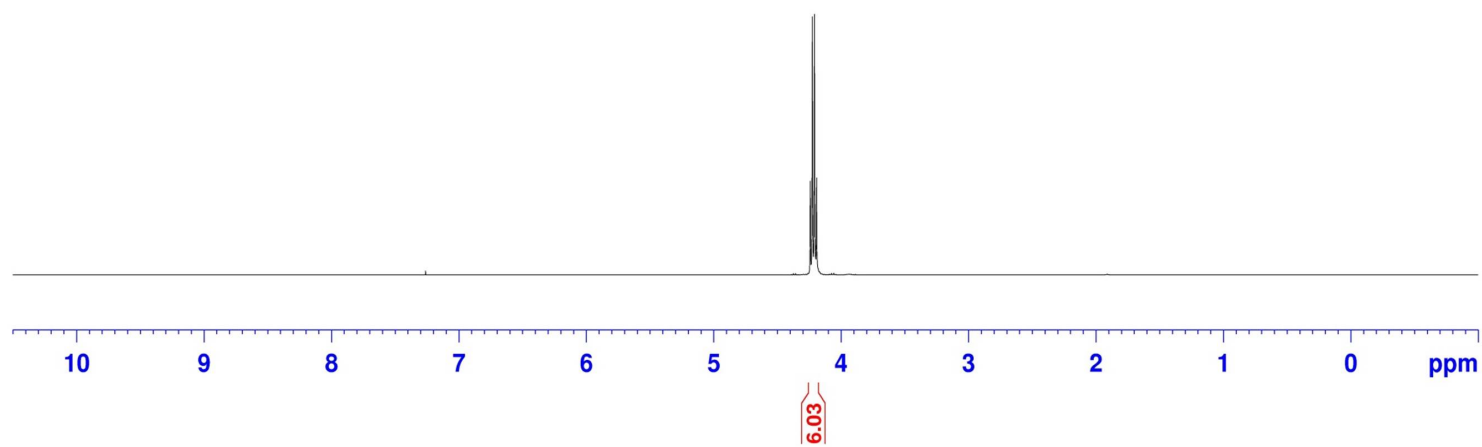
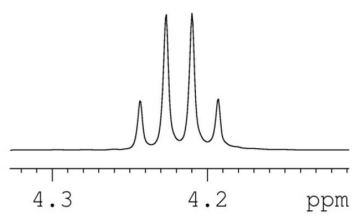
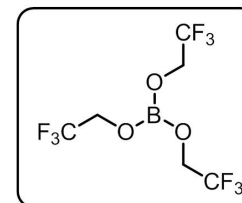




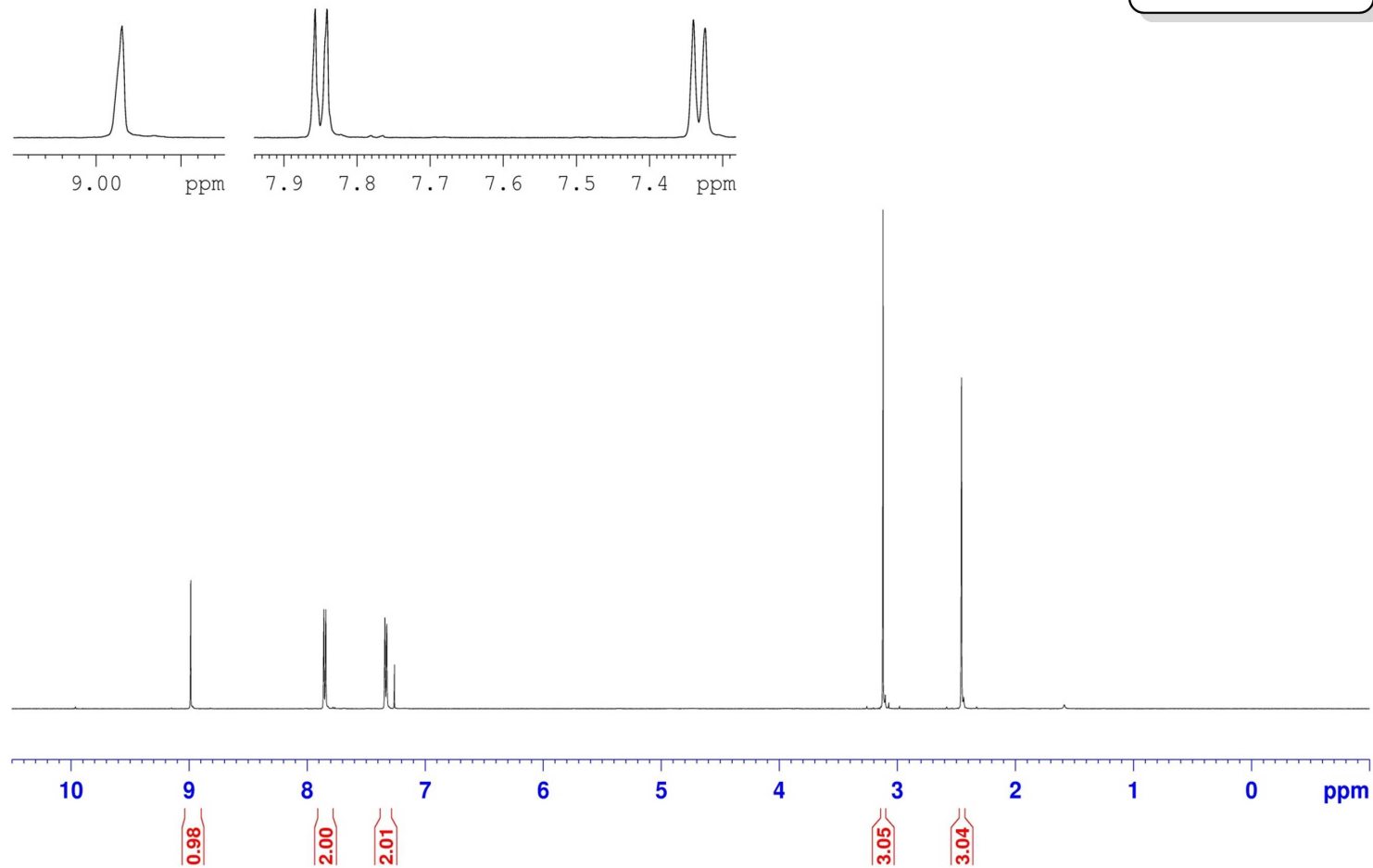
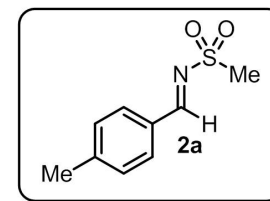
(4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile  
500 MHz, CDCl<sub>3</sub>



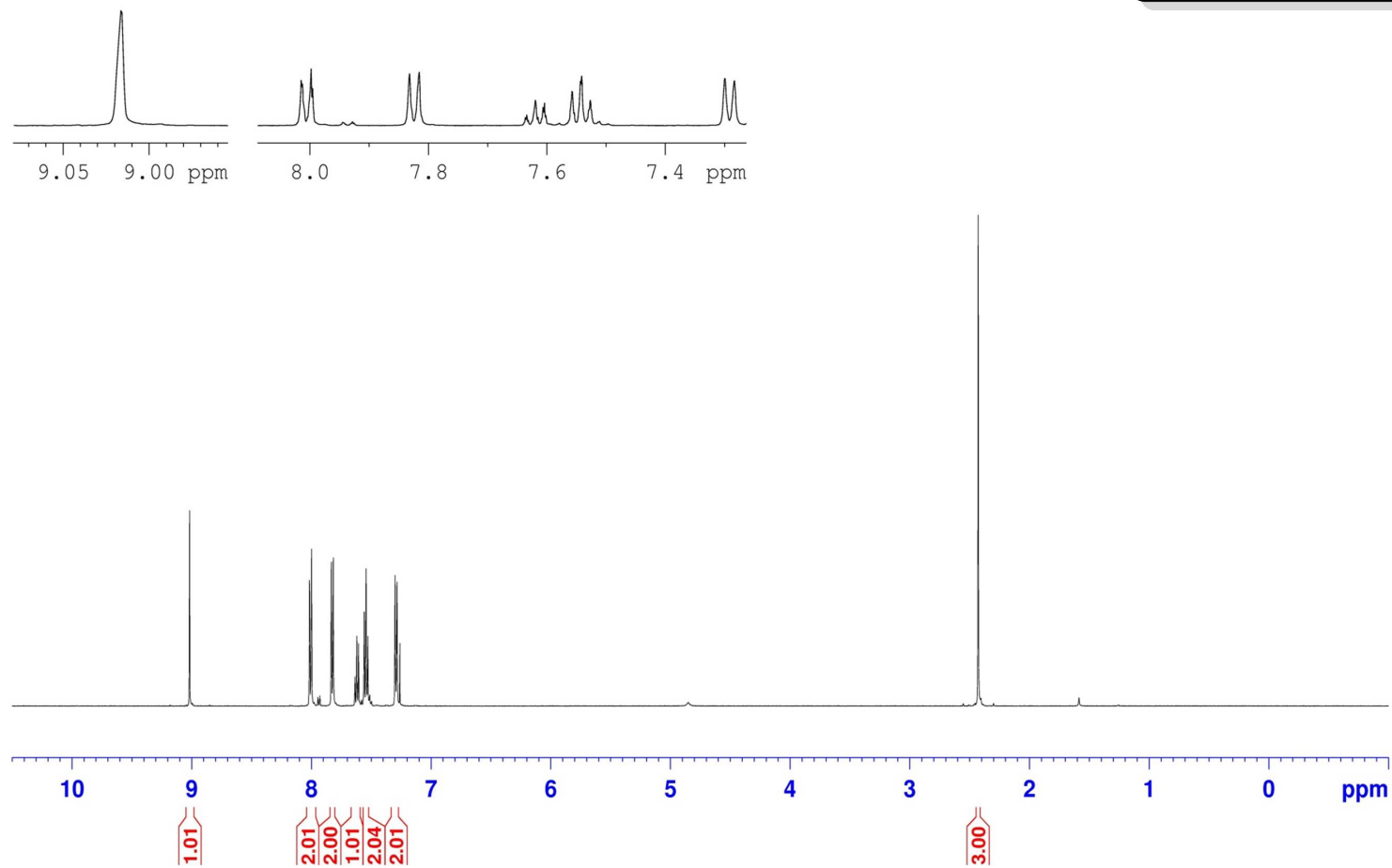
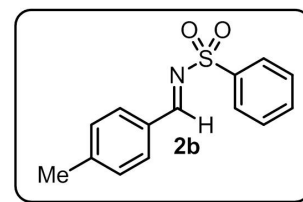
Tris(2,2,2-trifluoroethyl) borate  
500 MHz, CDCl<sub>3</sub>



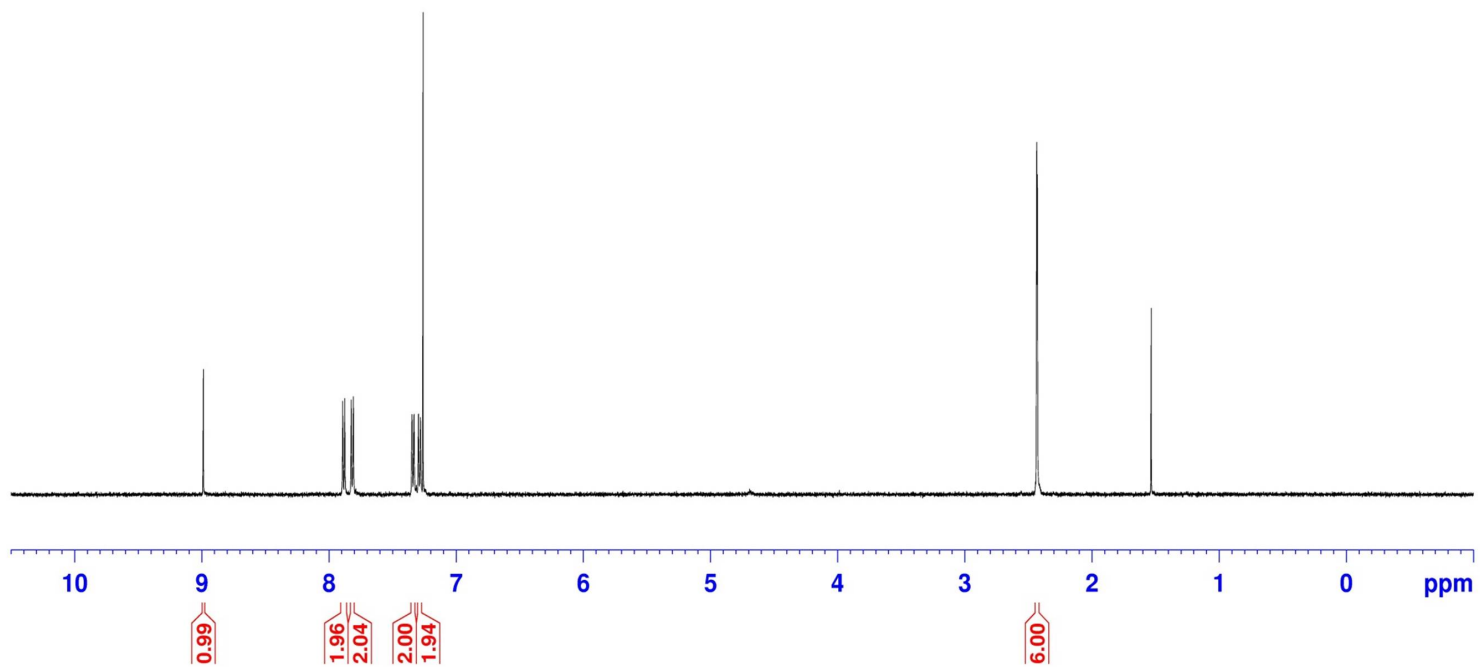
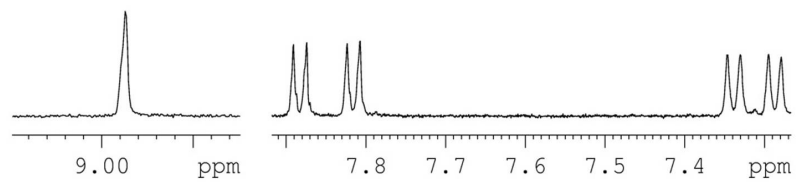
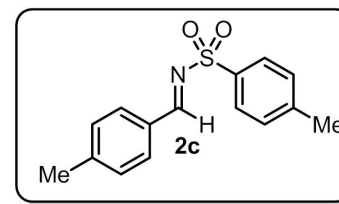
**N-(4-methylbenzylidene)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



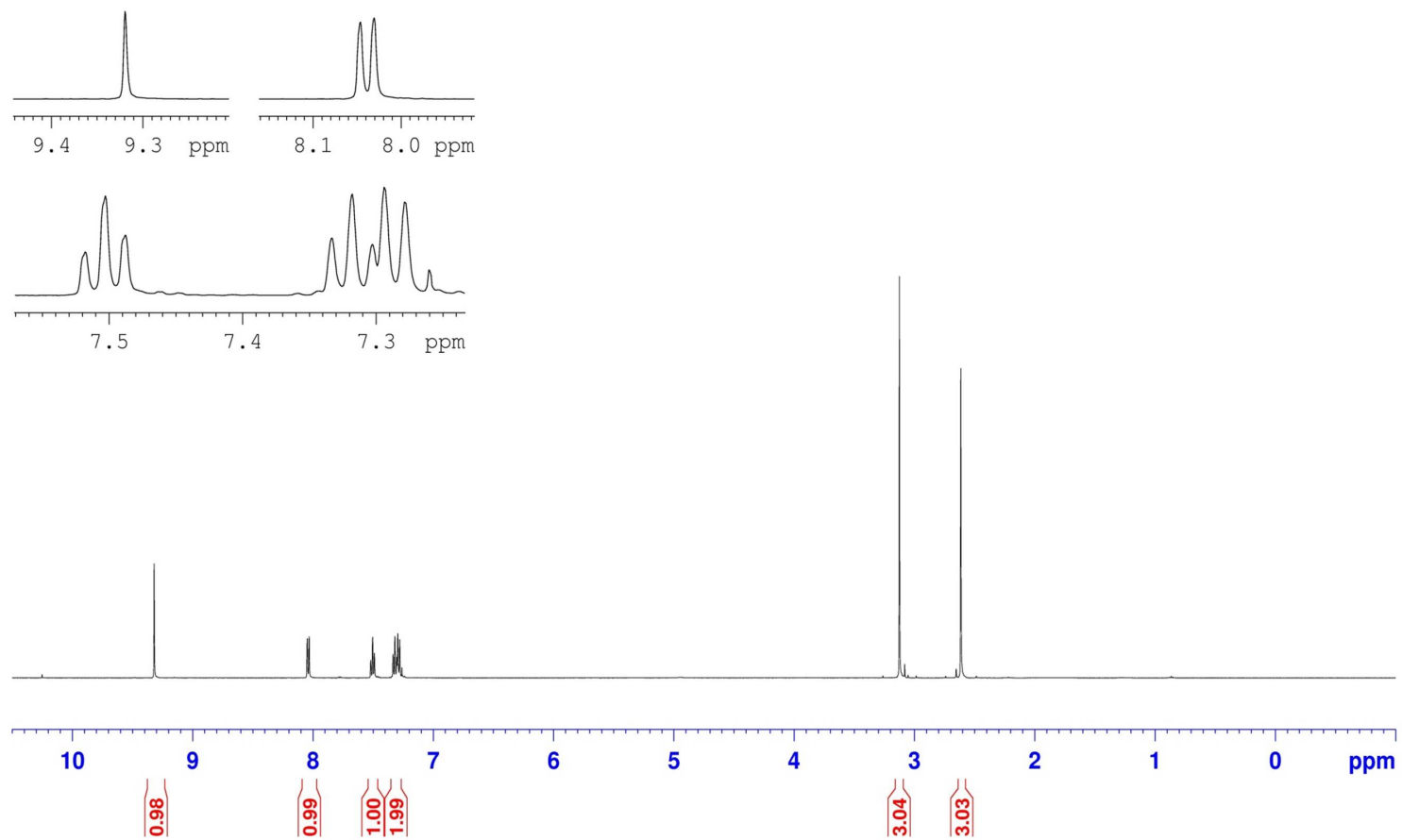
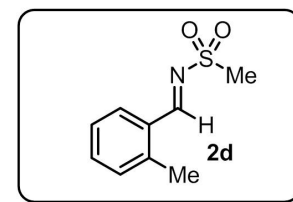
**N-(4-methylbenzyl)benzenesulfonamide**  
500 MHz, CDCl<sub>3</sub>



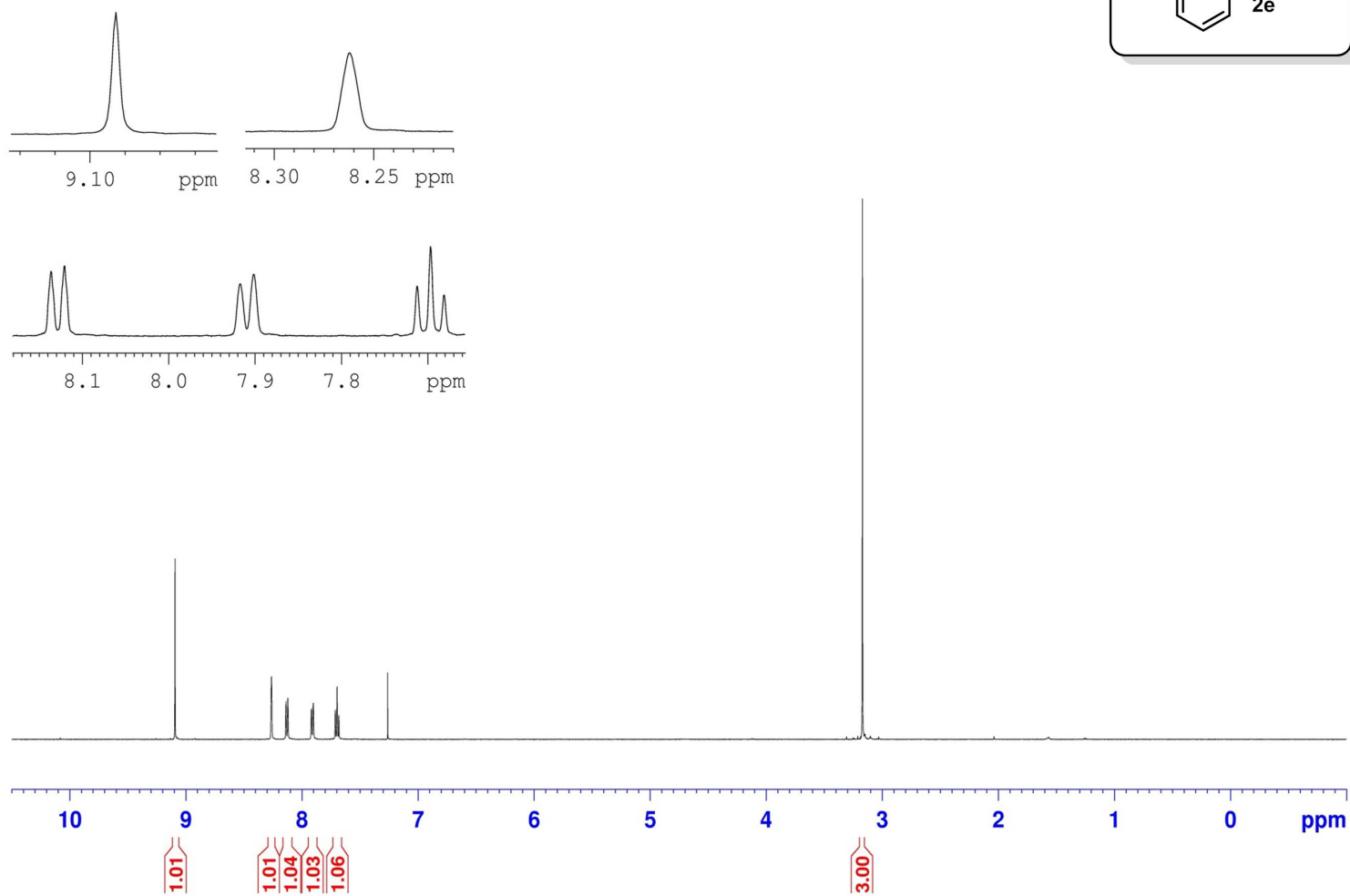
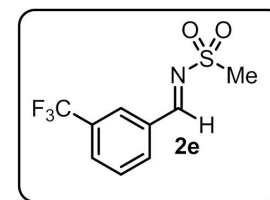
4-methyl-N-(4-methylbenzylidene)benzenesulfonamide  
500 MHz, CDCl<sub>3</sub>



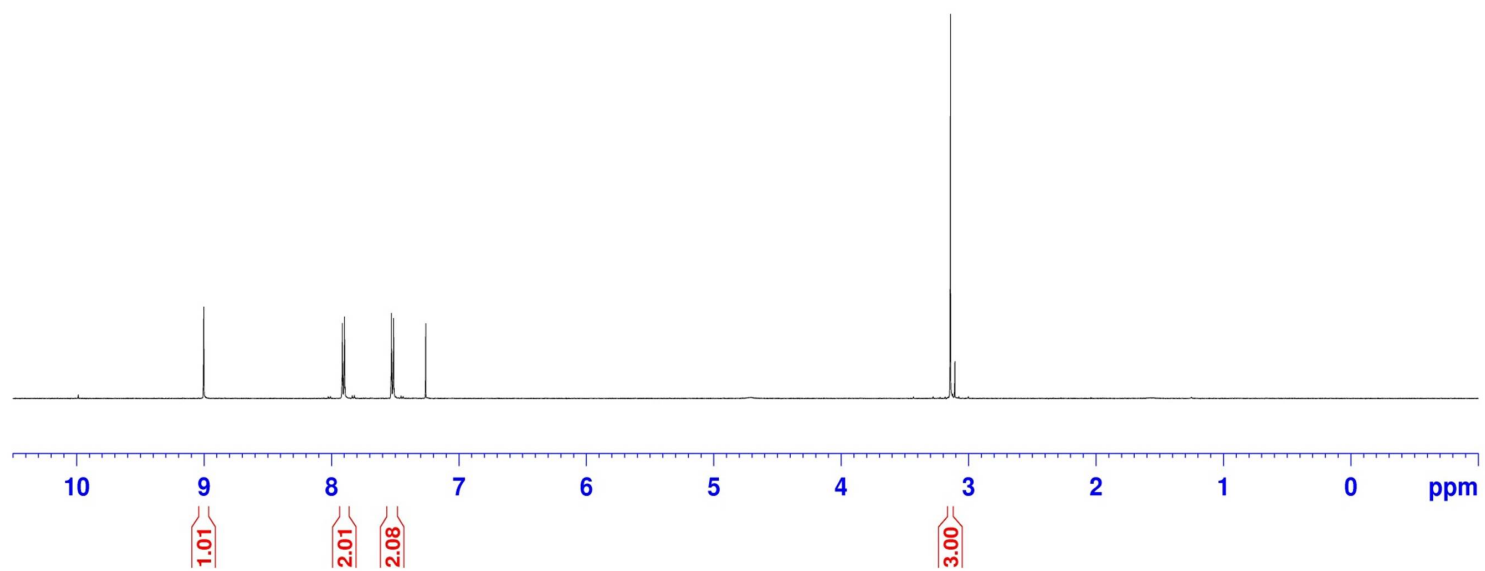
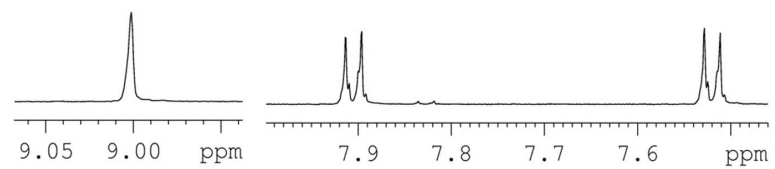
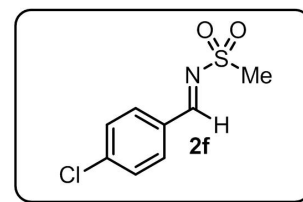
N-(2-methylbenzylidene)methanesulfonamide  
500 MHz, CDCl<sub>3</sub>



**N-(3-(trifluoromethyl)benzylidene)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>

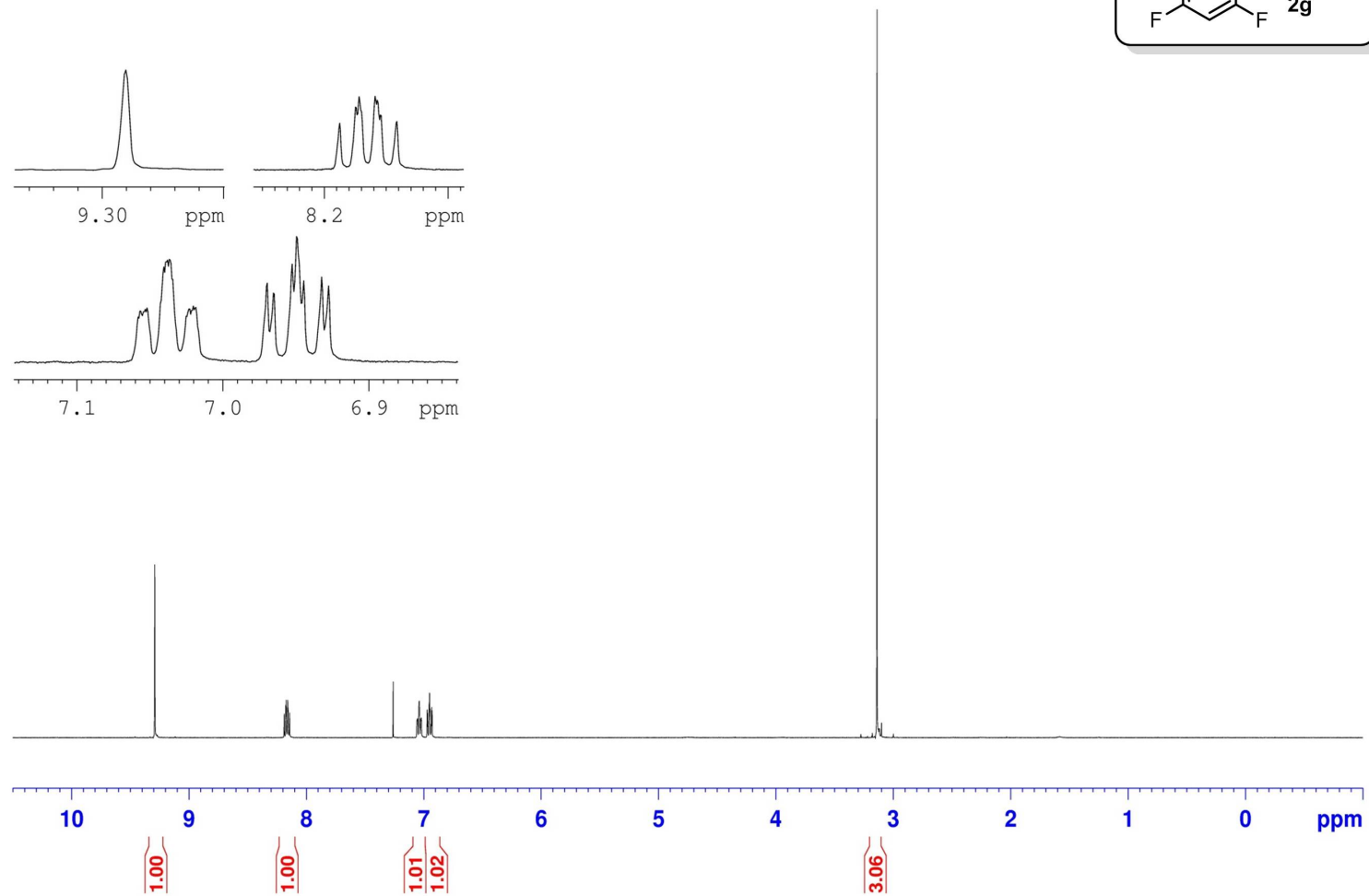
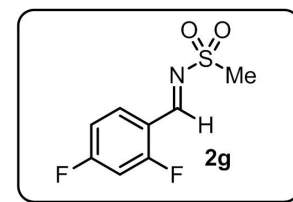


**N-(4-chlorobenzylidene)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>

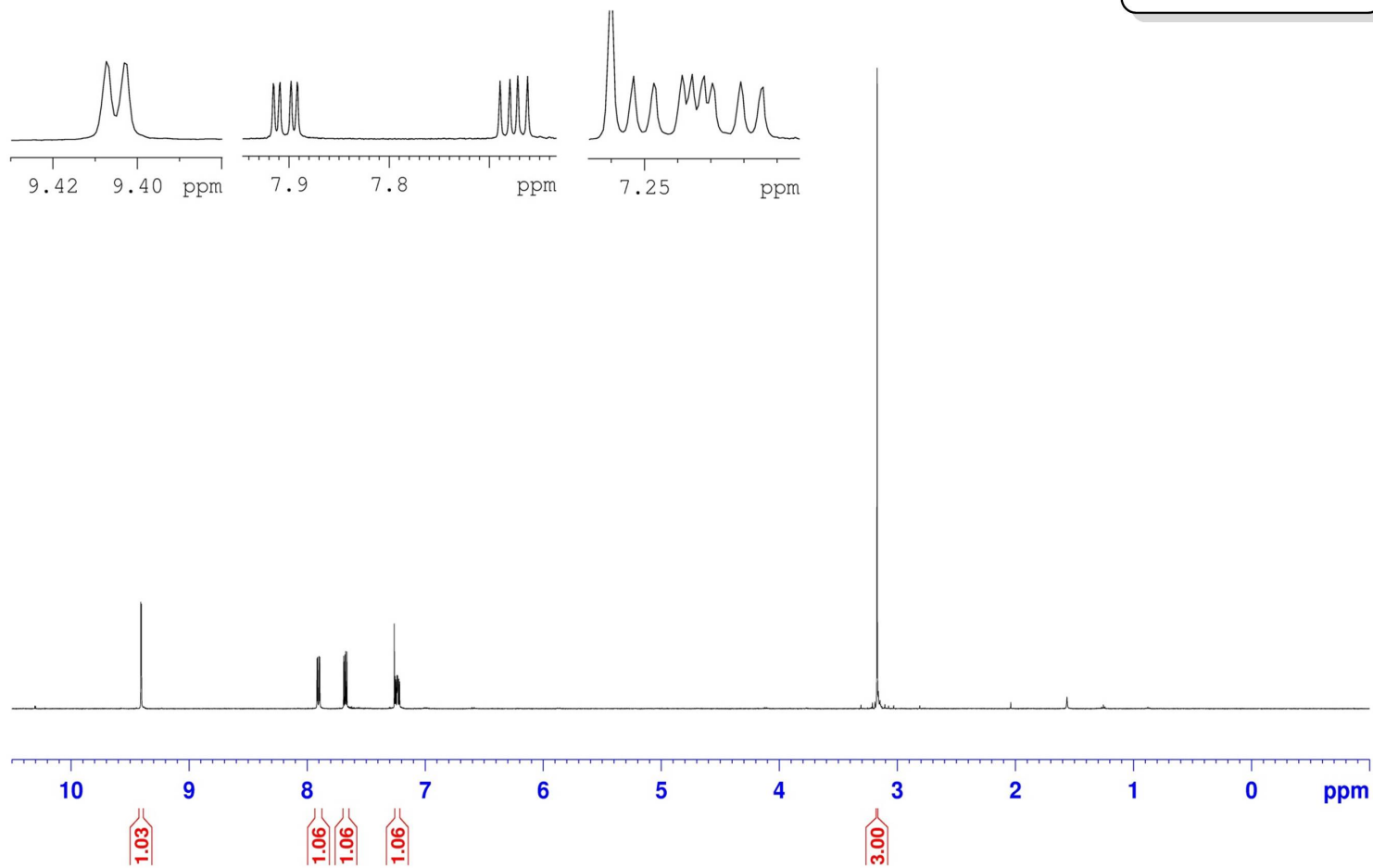
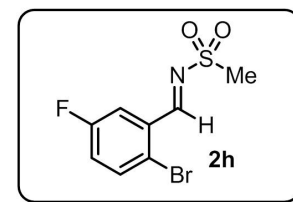




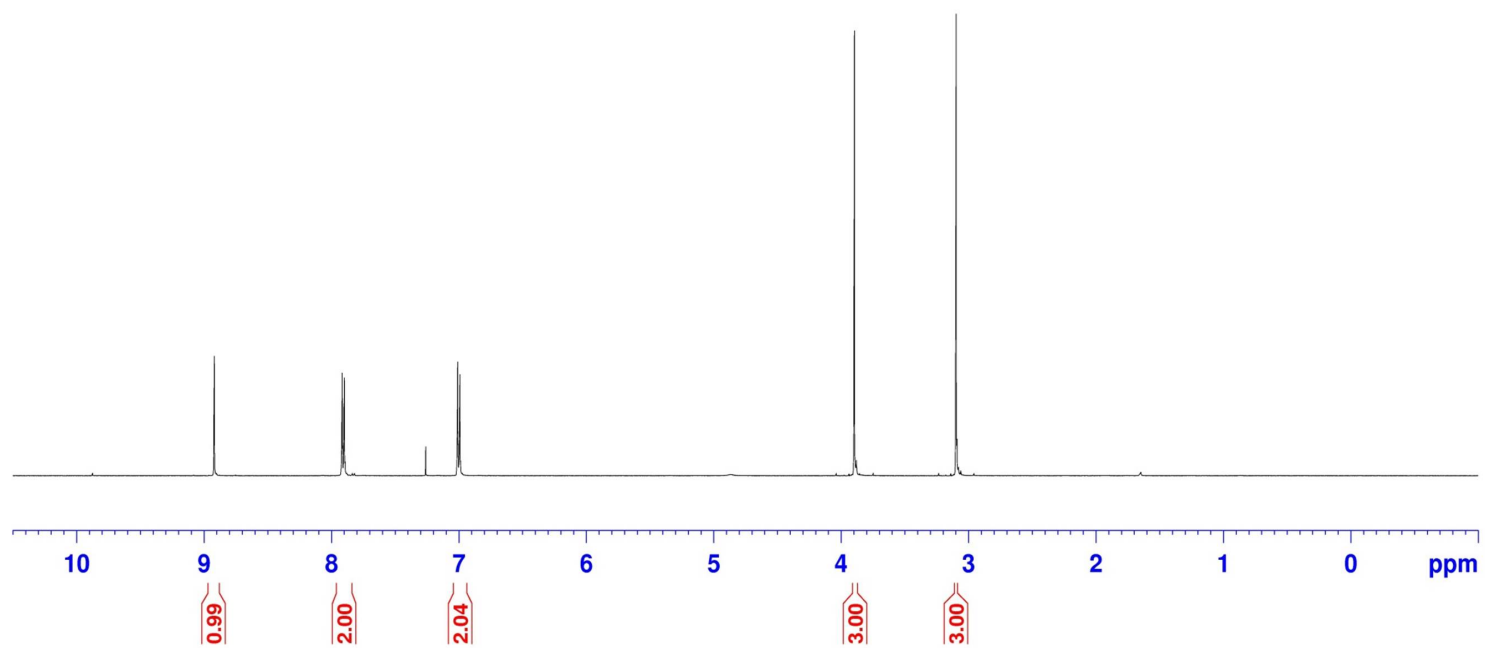
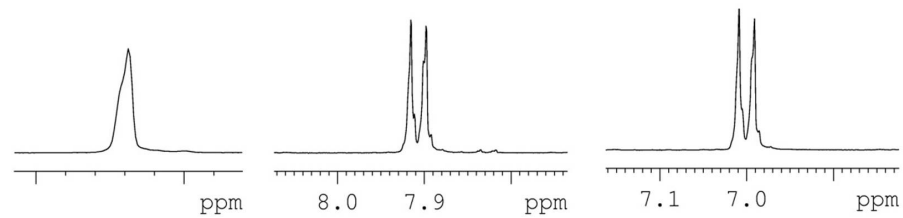
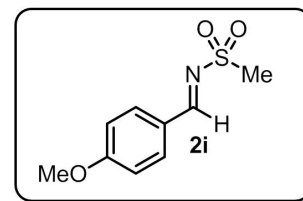
**N-(2,4-difluorobenzylidene)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



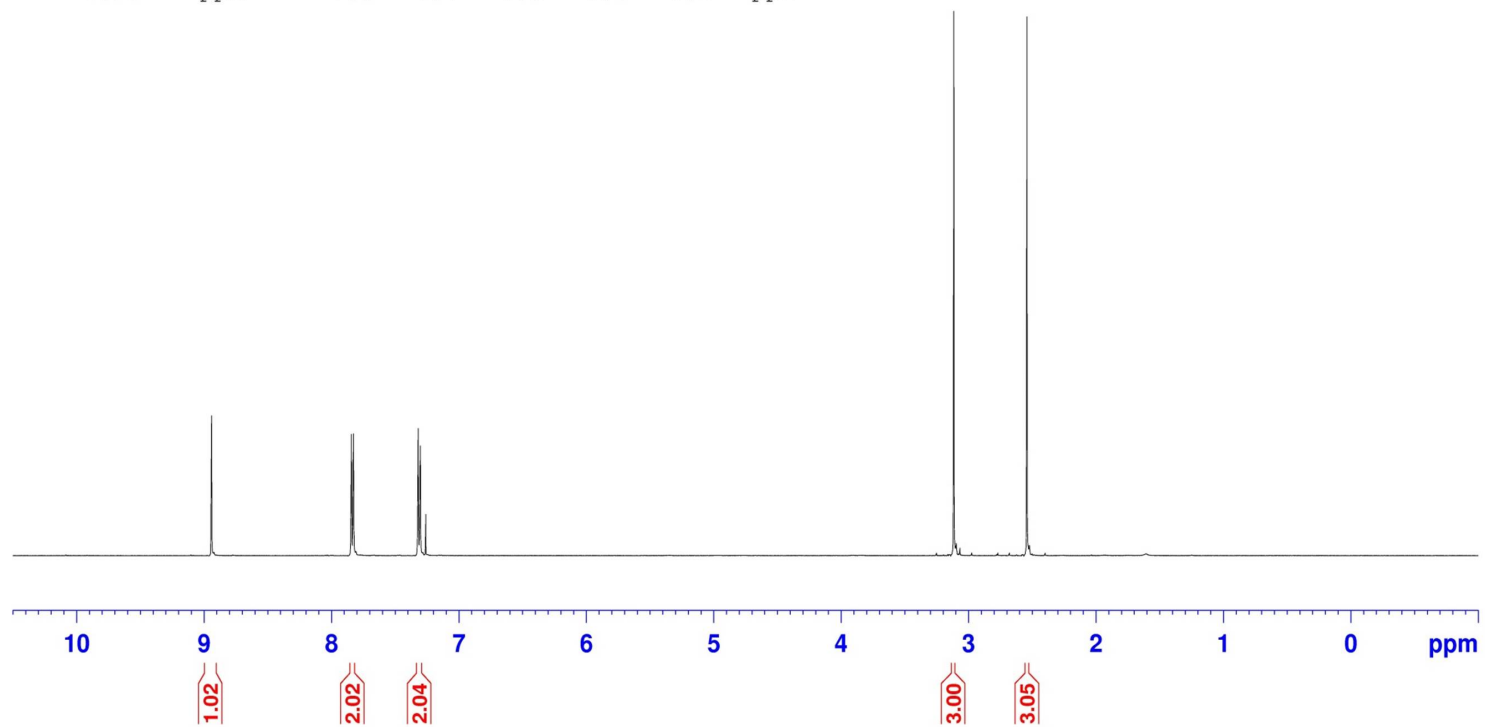
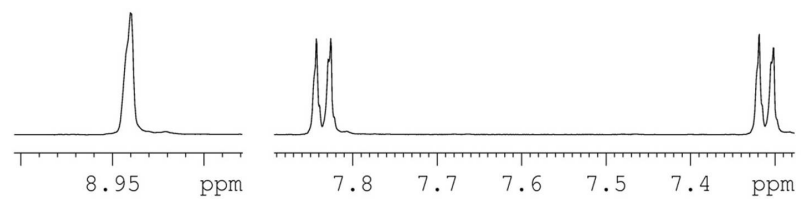
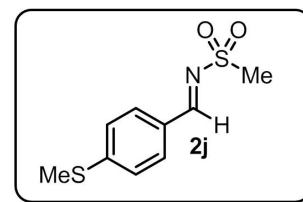
**N-(2-bromo-5-fluorobenzylidene)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



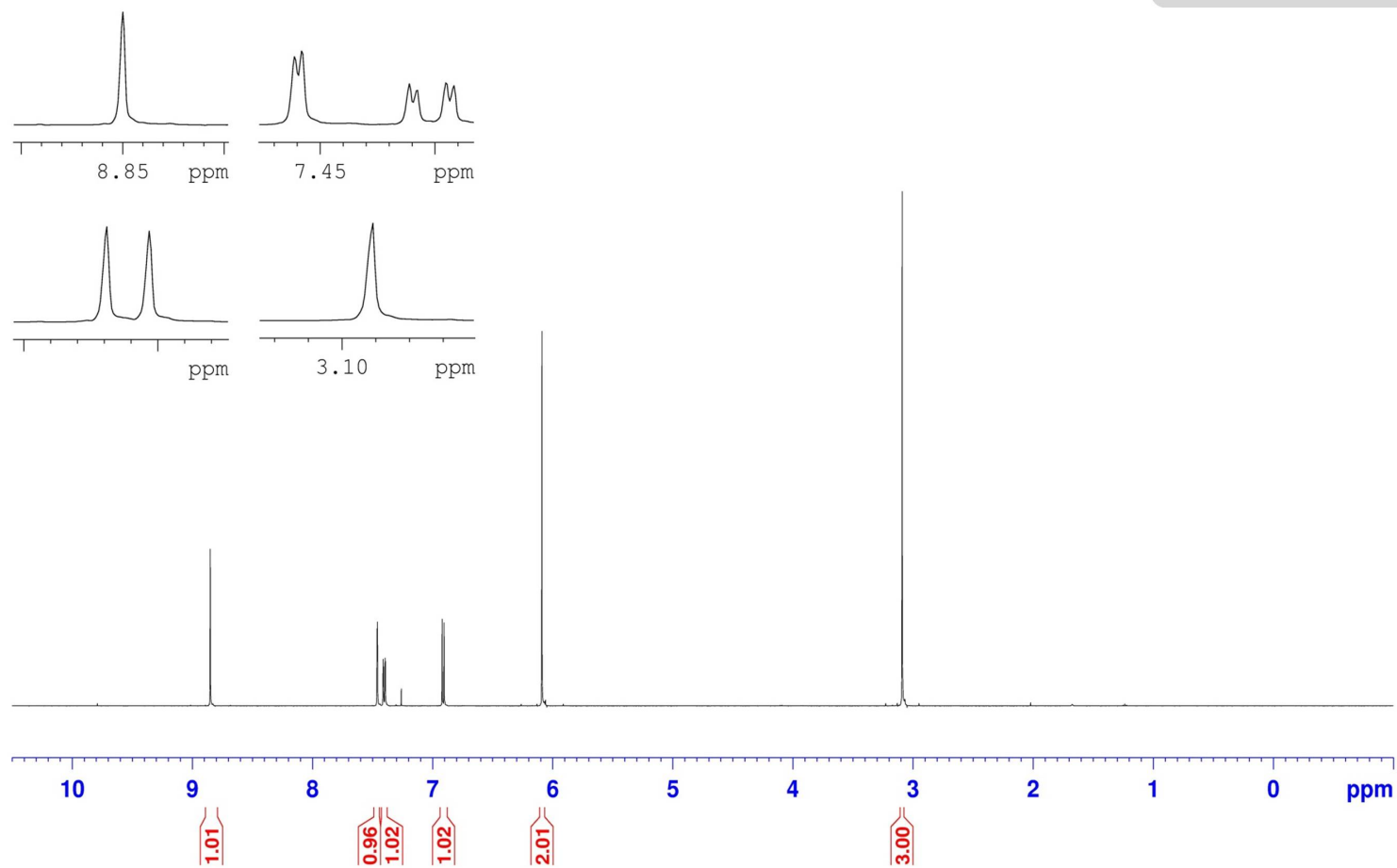
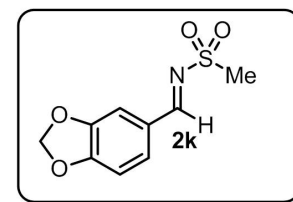
**N-(4-methoxybenzylidene)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



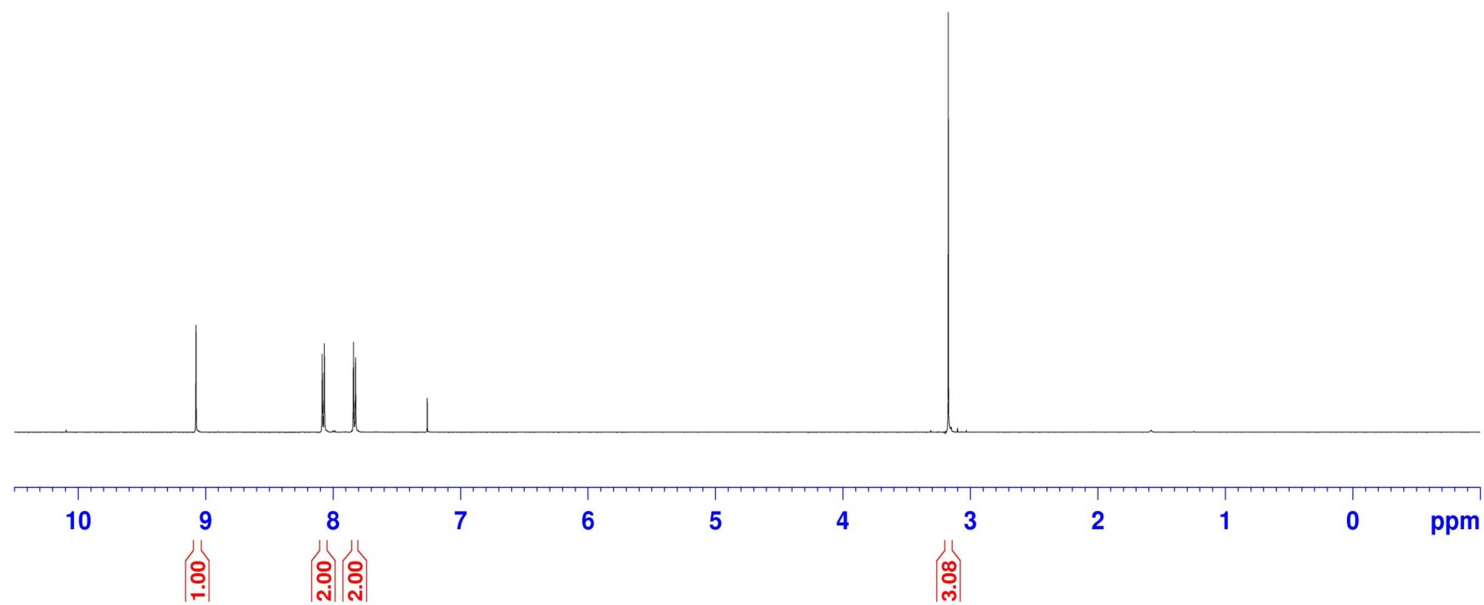
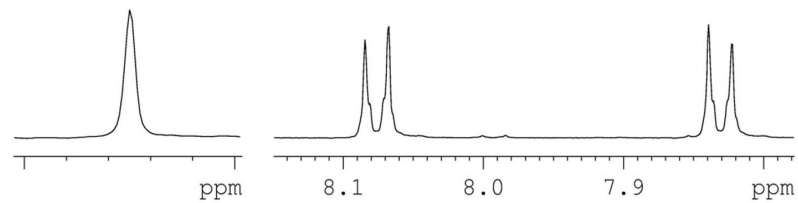
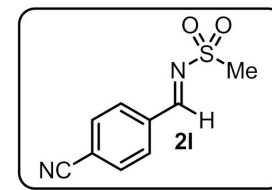
N-(4-(methylthio)benzylidene)methanesulfonamide  
500 MHz, CDCl<sub>3</sub>



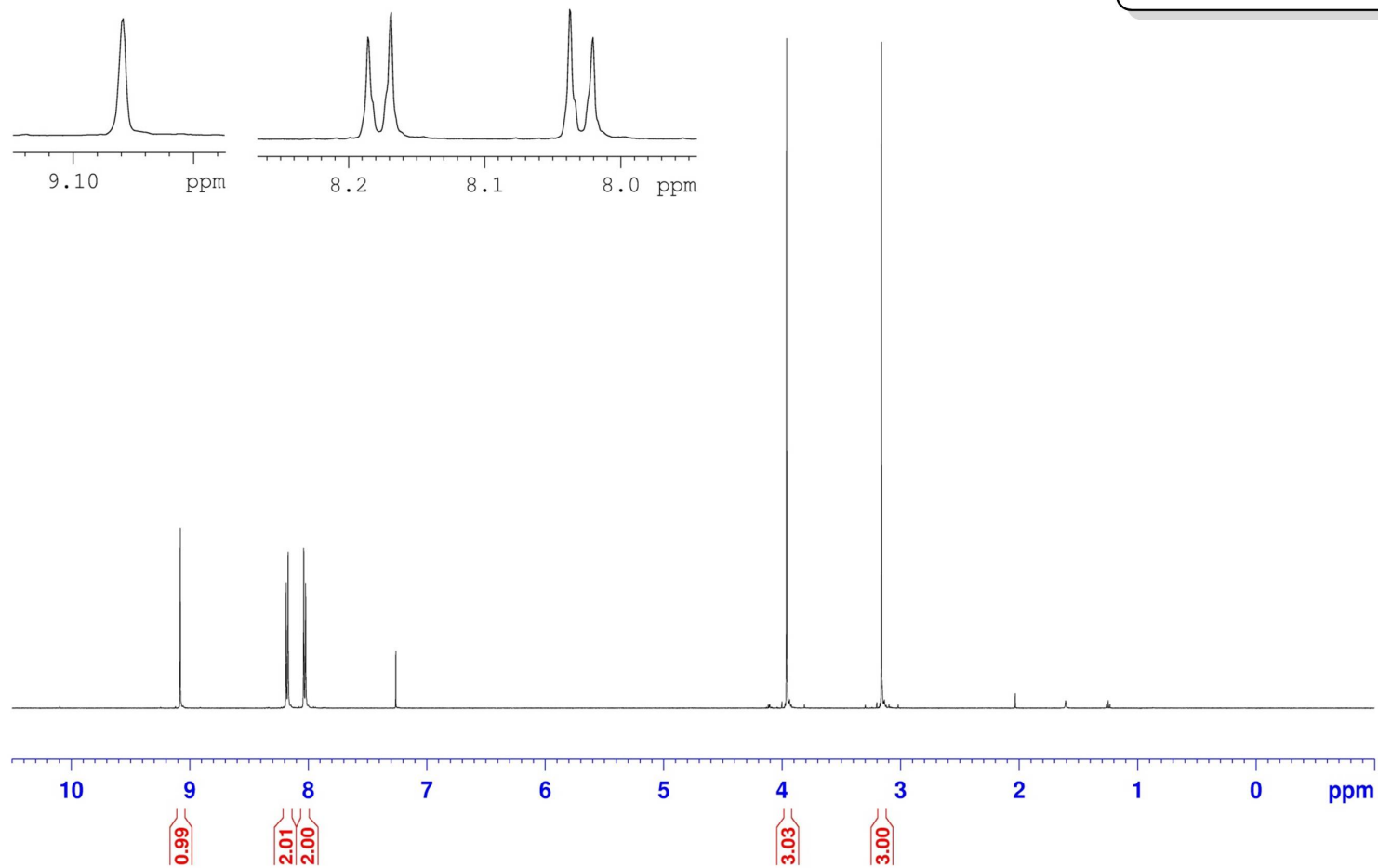
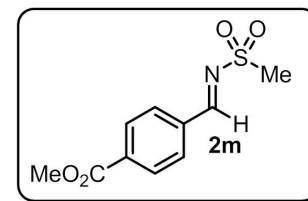
N-(benzo[d][1,3]dioxol-5-ylmethylene)methanesulfonamide  
500 MHz, CDCl<sub>3</sub>



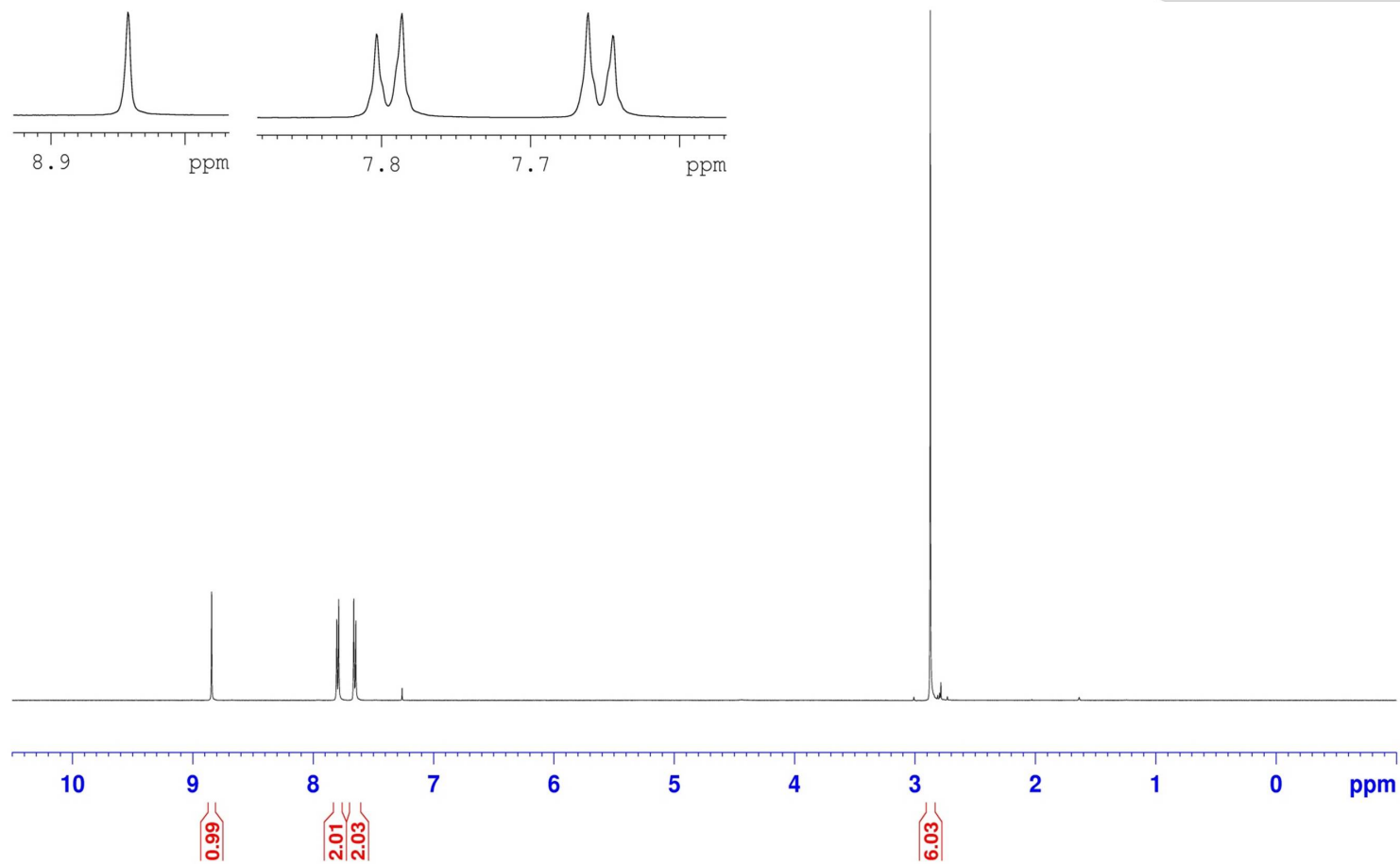
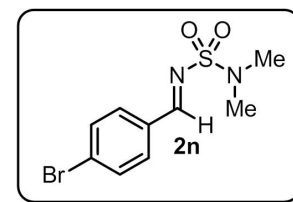
**N-(4-cyanobenzylidene)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



methyl 4-(((methylsulfonyl)imino)methyl)benzoate  
500 MHz, CDCl<sub>3</sub>

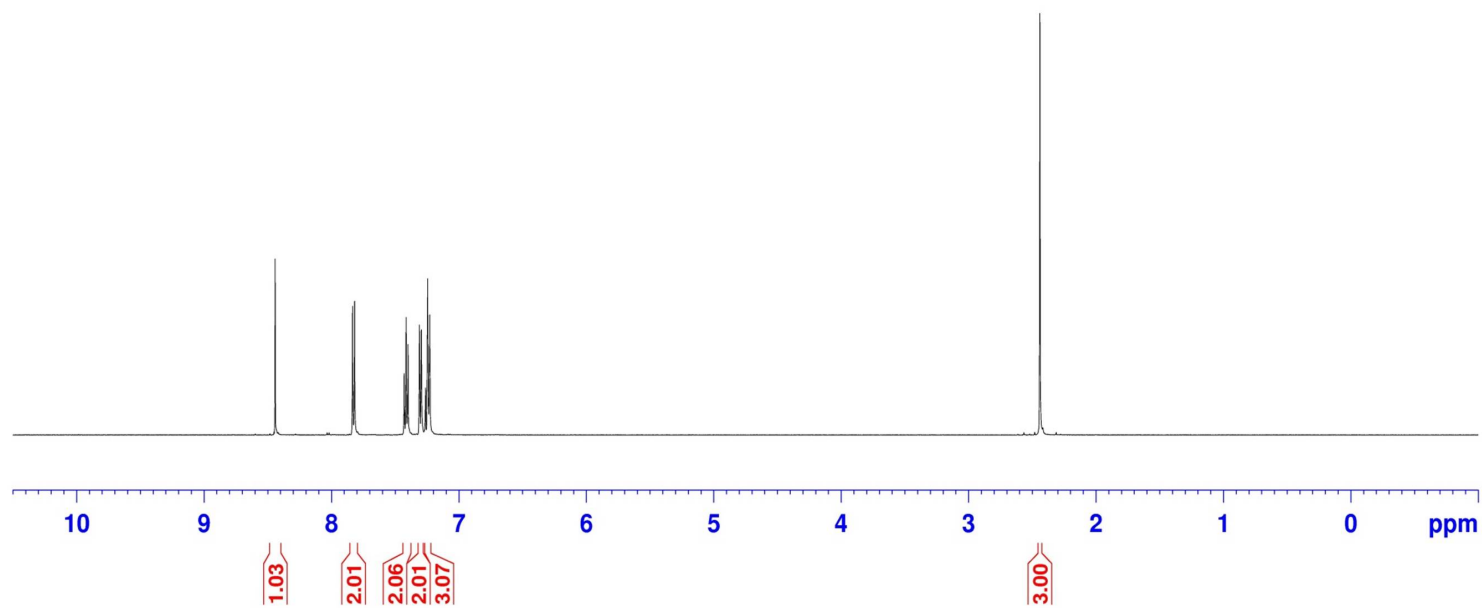
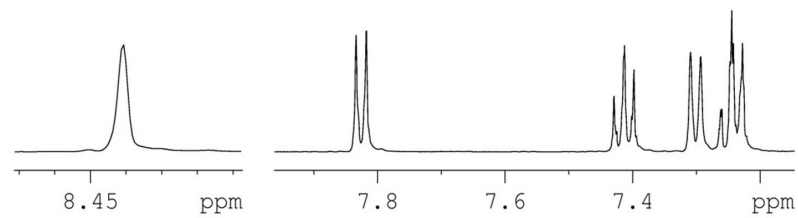
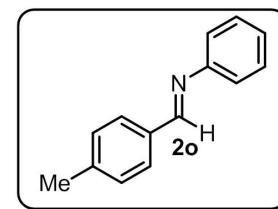


**N-(4-bromobenzylidene)-N,N-dimethylsulfamide**  
500 MHz, CDCl<sub>3</sub>

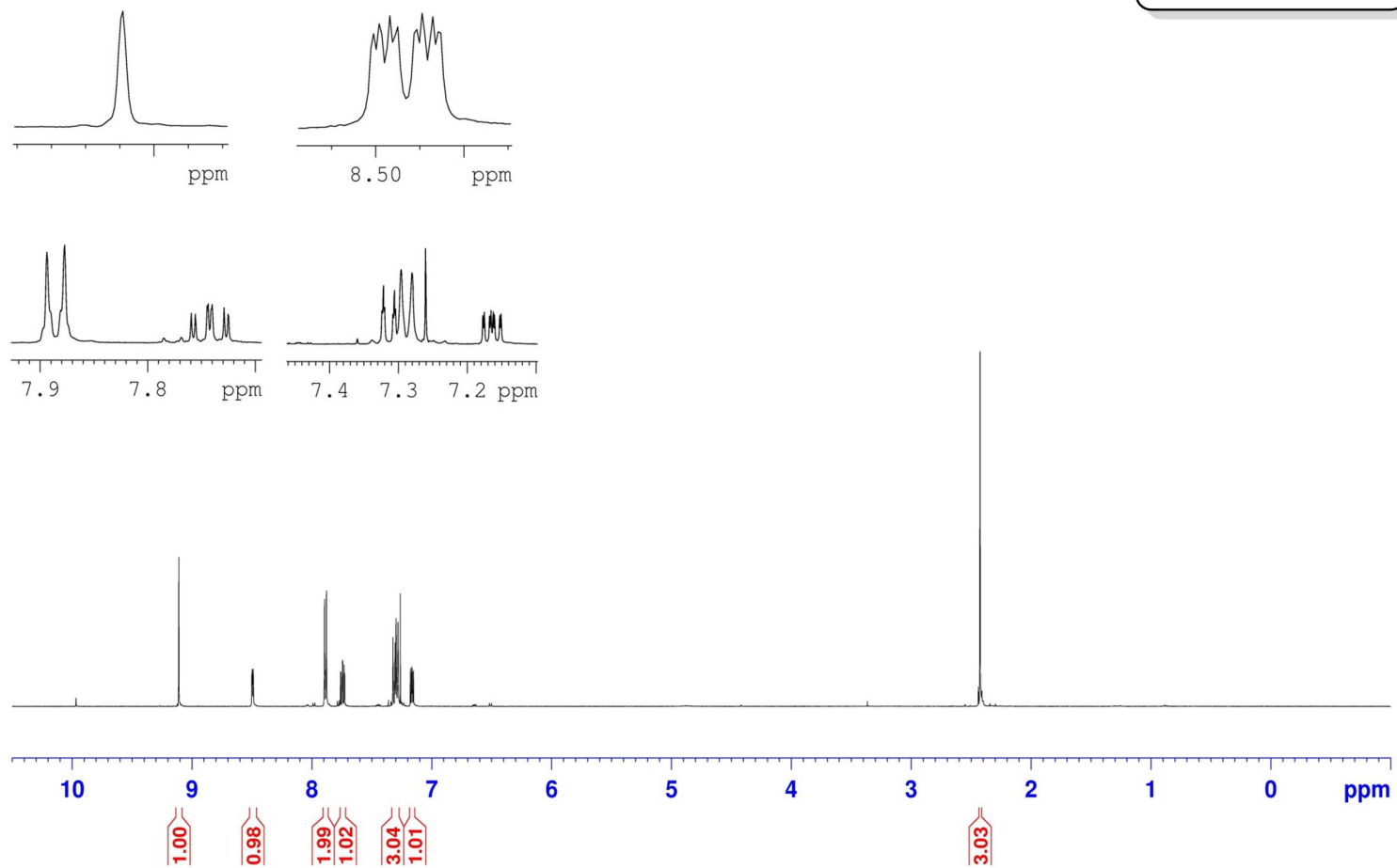
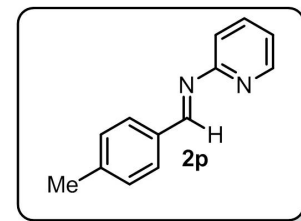




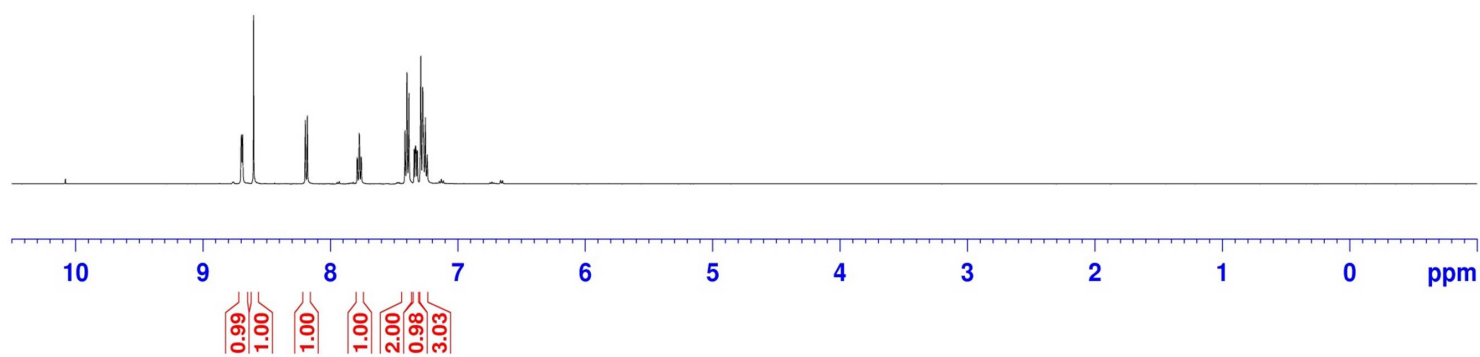
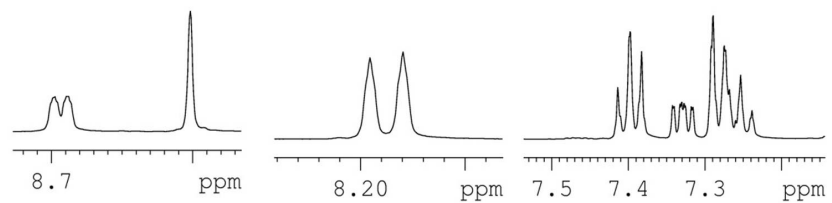
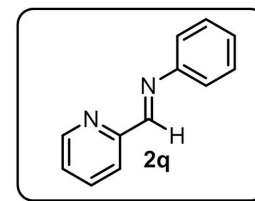
**N-(4-methylbenzylidene)aniline**  
500 MHz, CDCl<sub>3</sub>



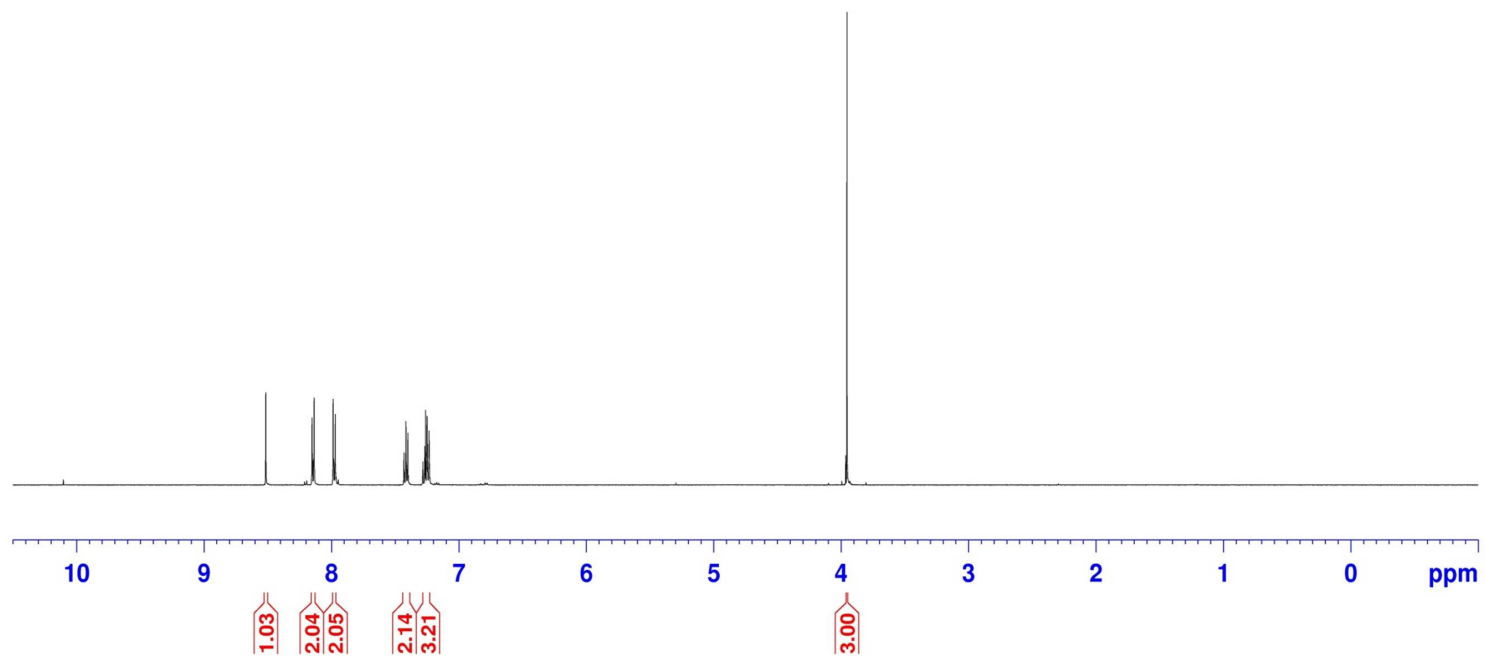
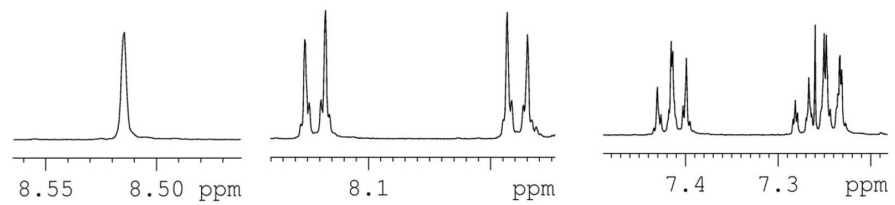
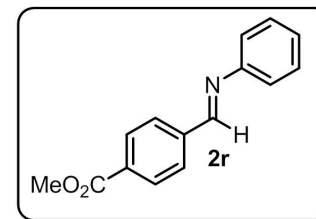
**N-(4-methylbenzylidene)pyridin-2-amine**  
500 MHz, CDCl<sub>3</sub>



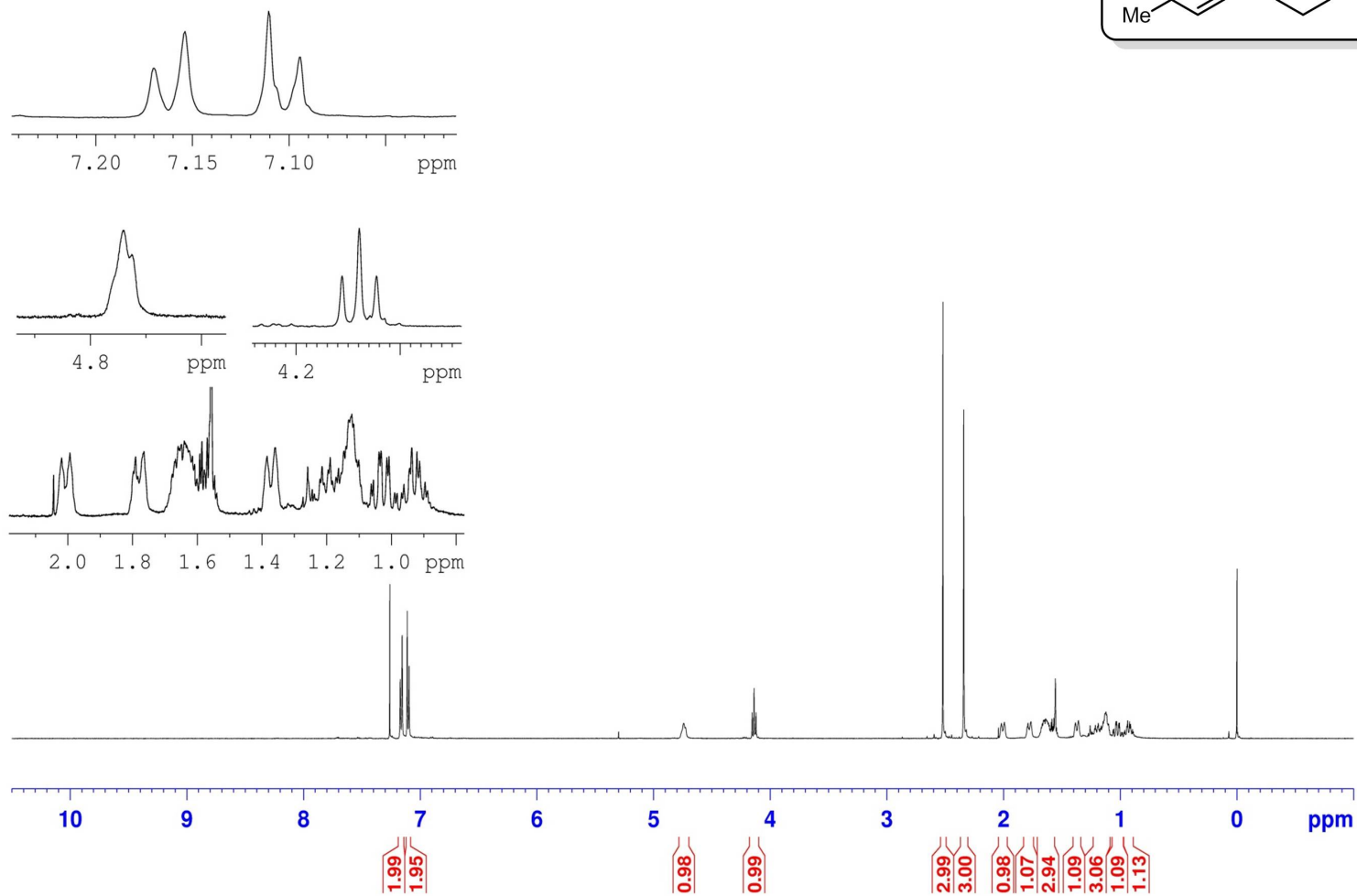
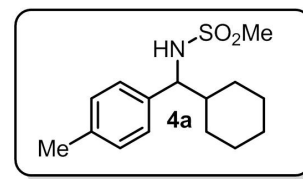
**N-(pyridin-2-ylmethylene)aniline**  
500 MHz, CDCl<sub>3</sub>



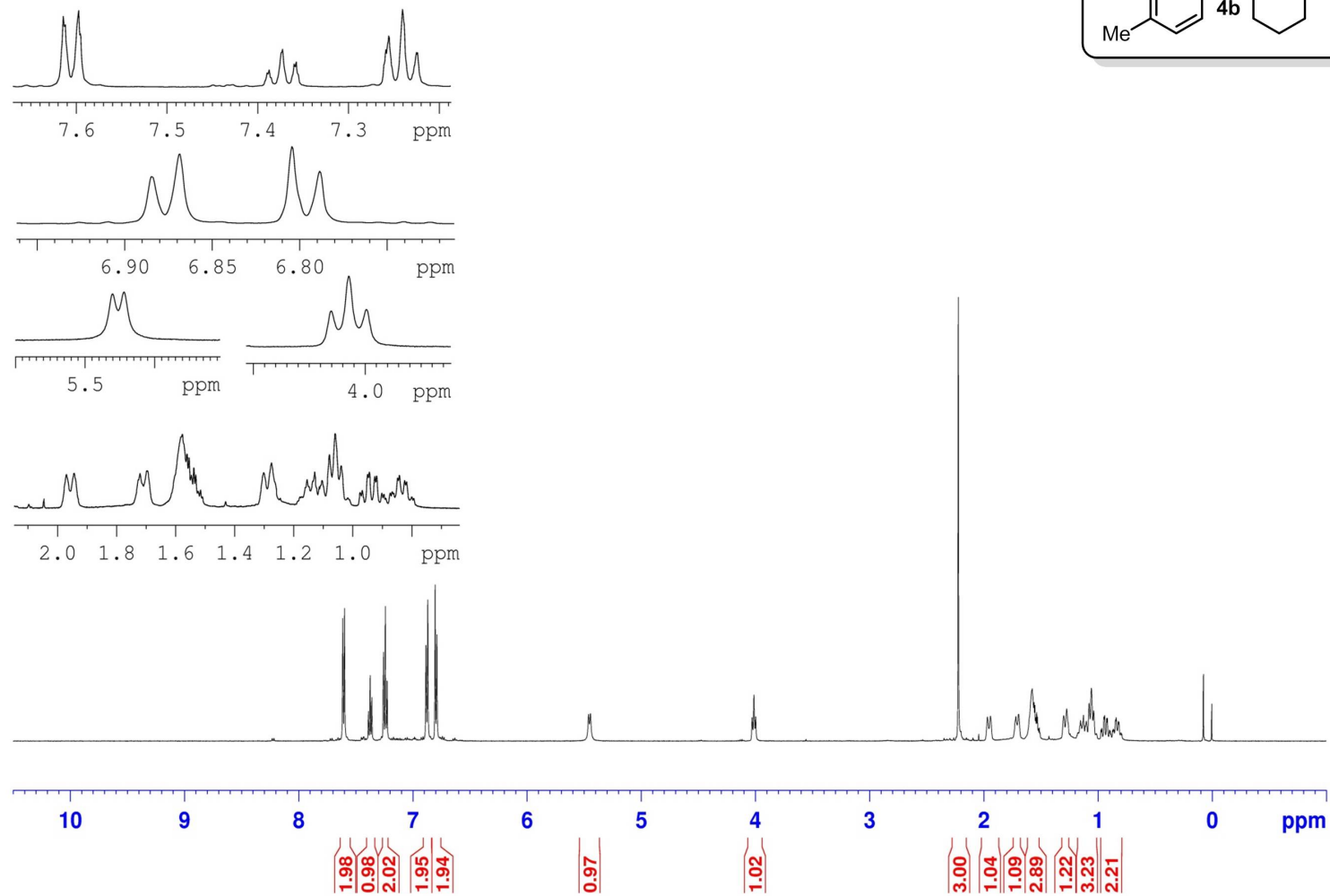
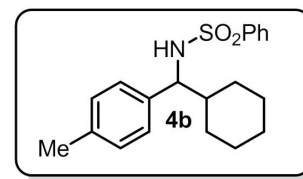
methyl 4-((phenylimino)methyl)benzoate  
500 MHz, CDCl<sub>3</sub>



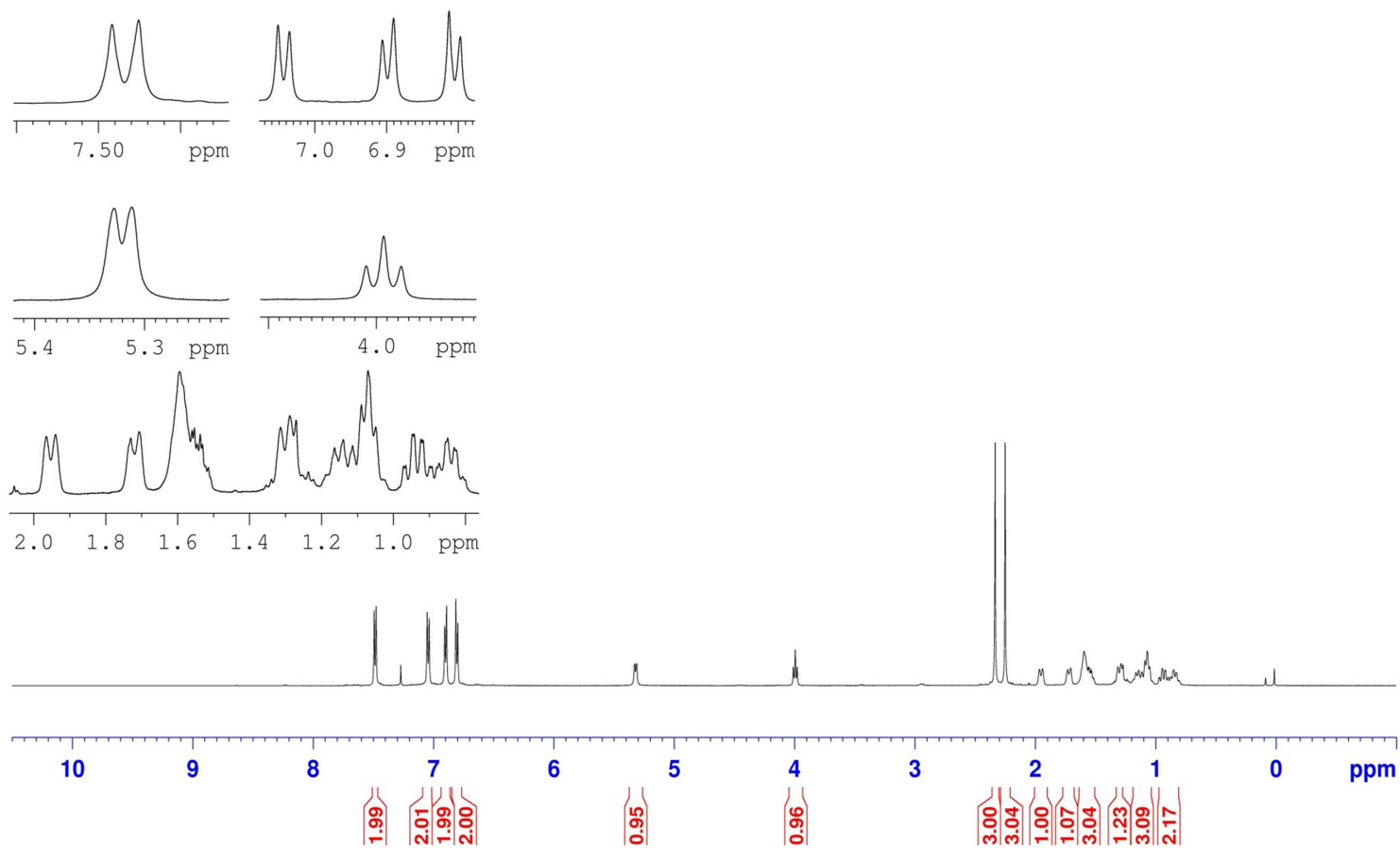
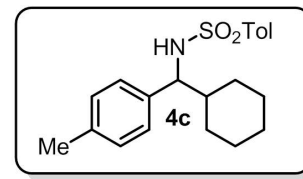
**N-(cyclohexyl(p-tolyl)methyl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



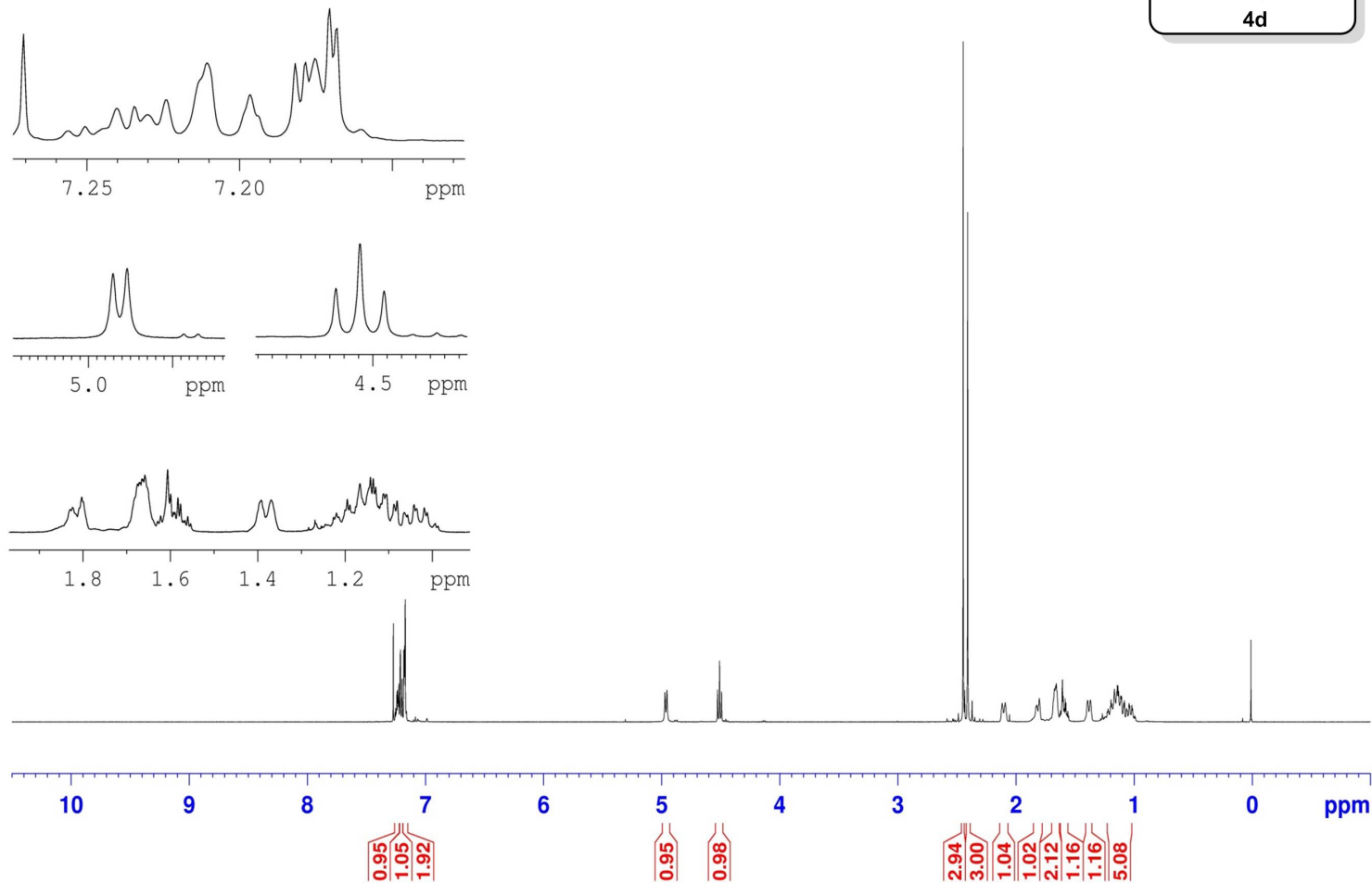
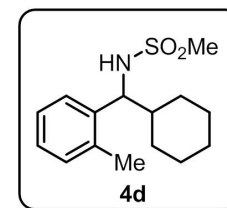
**N-(cyclohexyl(p-tolyl)methyl)benzenesulfonamide**  
500 MHz, CDCl<sub>3</sub>



**N-(cyclohexyl(p-tolyl)methyl)-4-methylbenzenesulfonamide**  
500 MHz, CDCl<sub>3</sub>

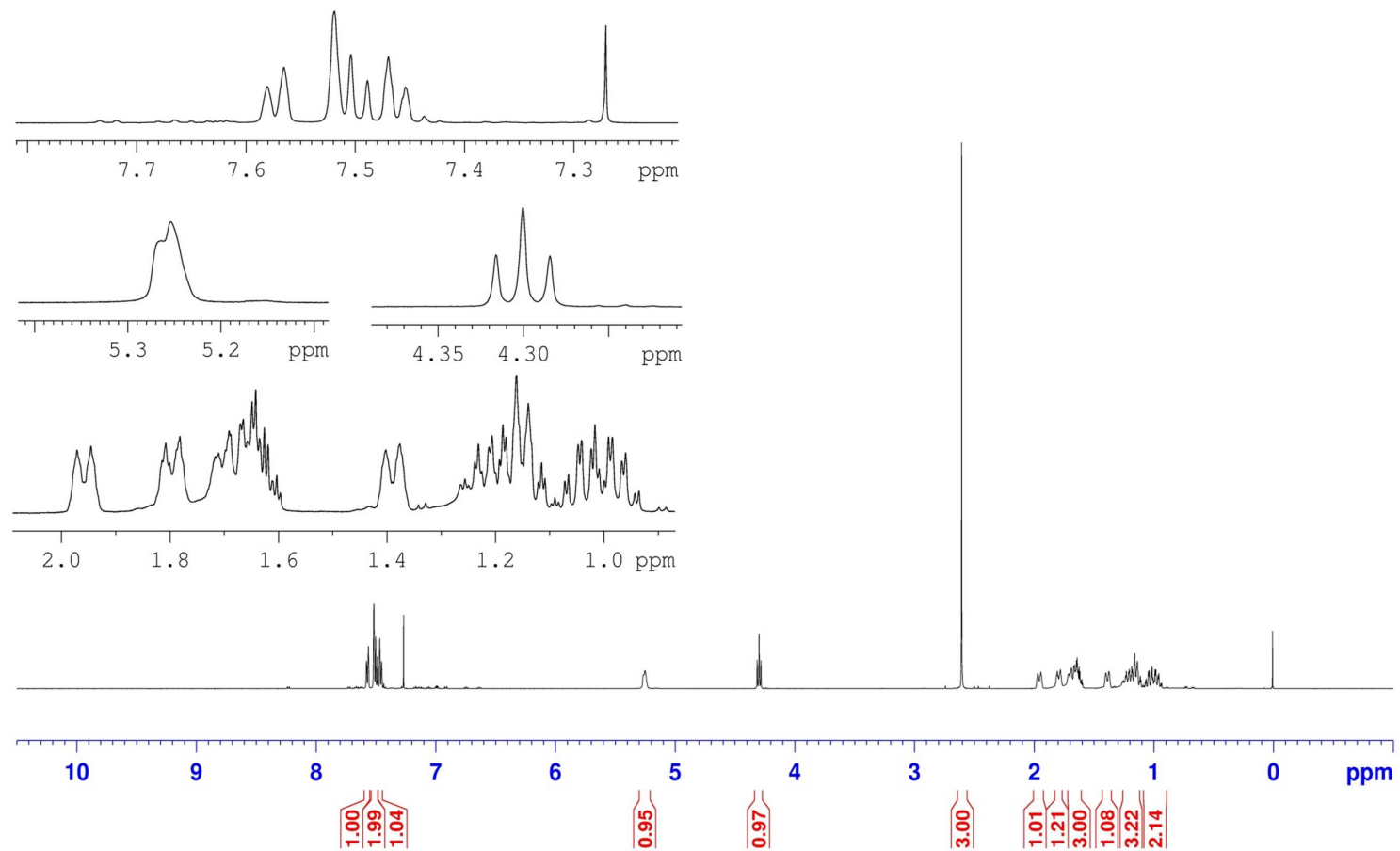
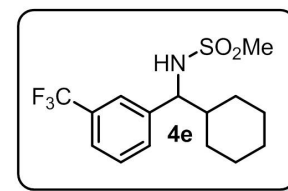


**N-(cyclohexyl(o-tolyl)methyl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>

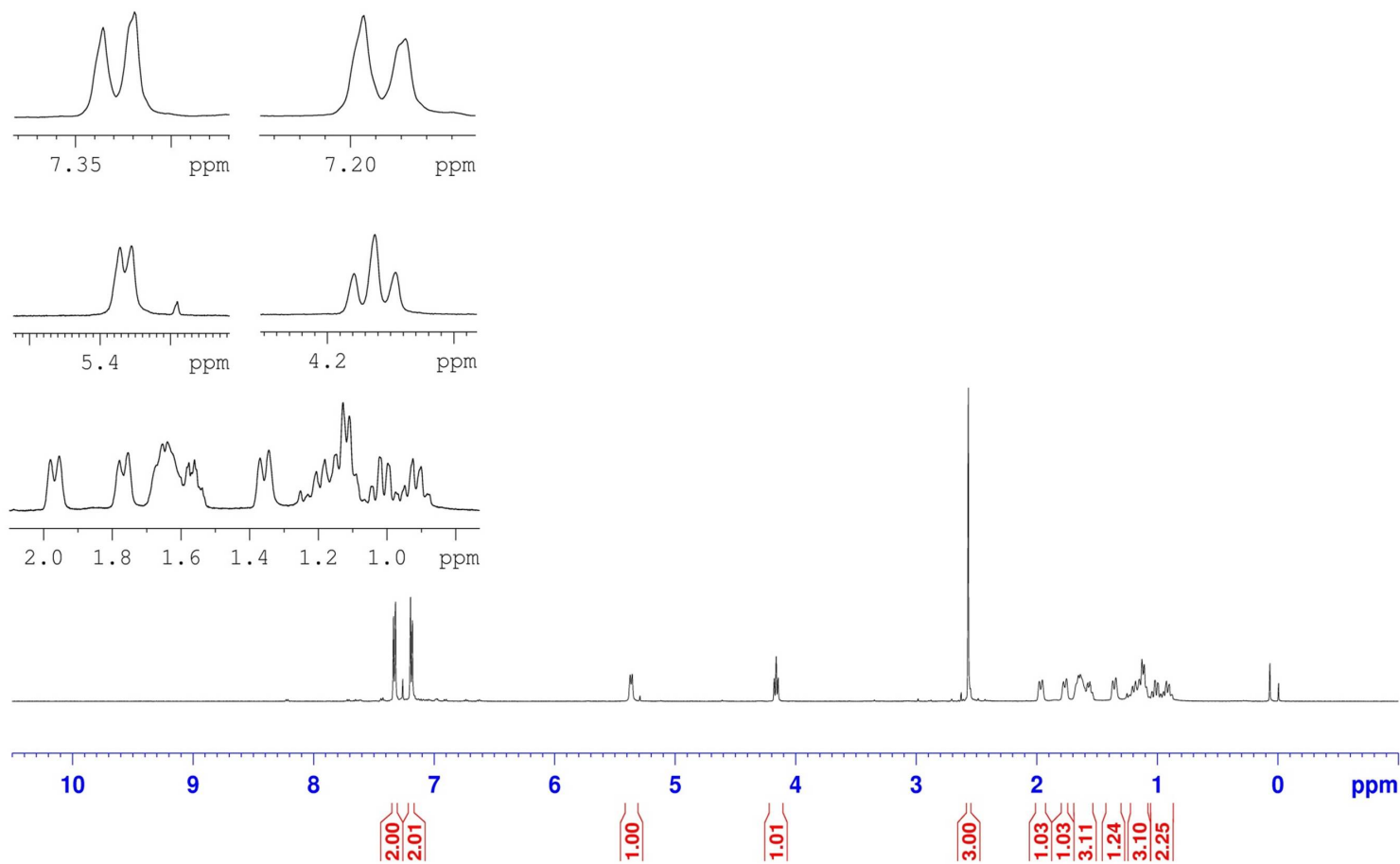
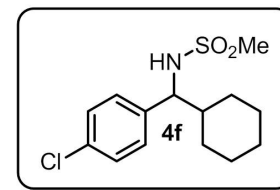




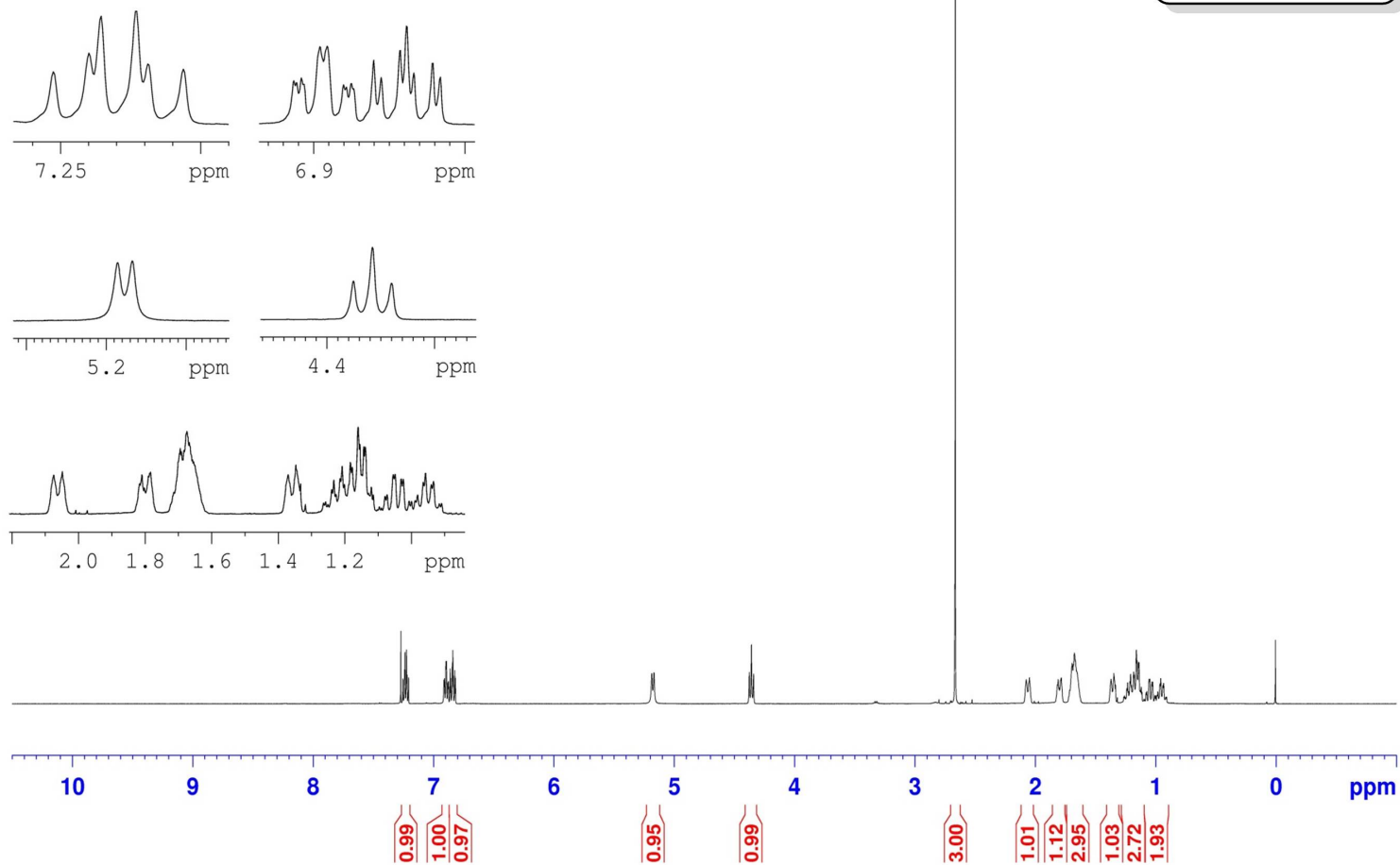
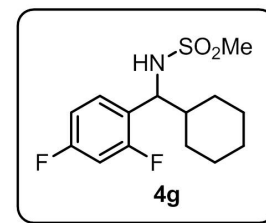
**N-(cyclohexyl(3-(trifluoromethyl)phenyl)methyl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



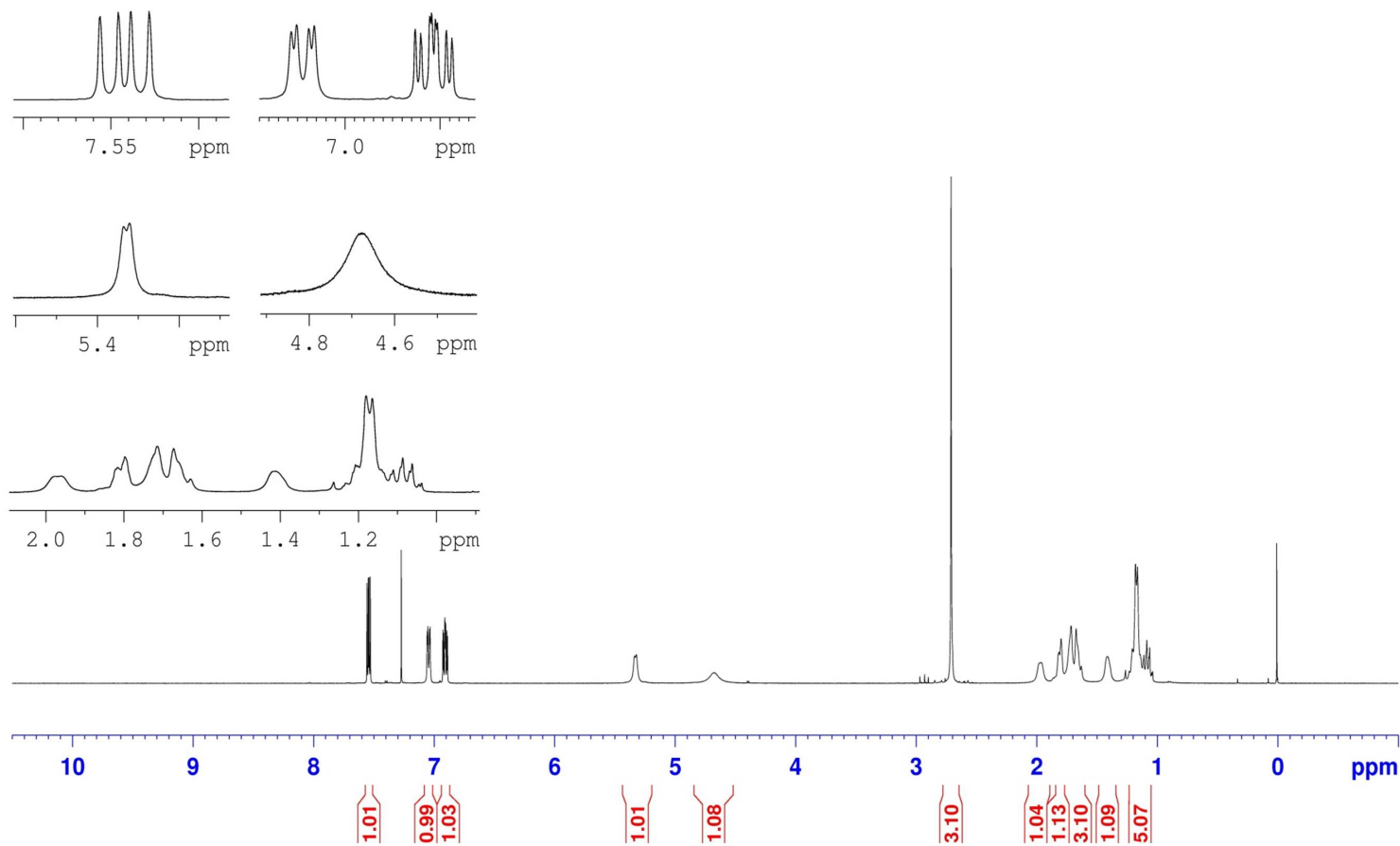
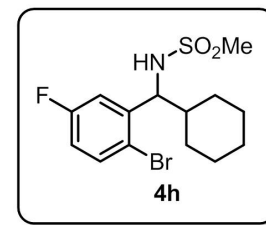
**N-((4-chlorophenyl)(cyclohexyl)methyl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



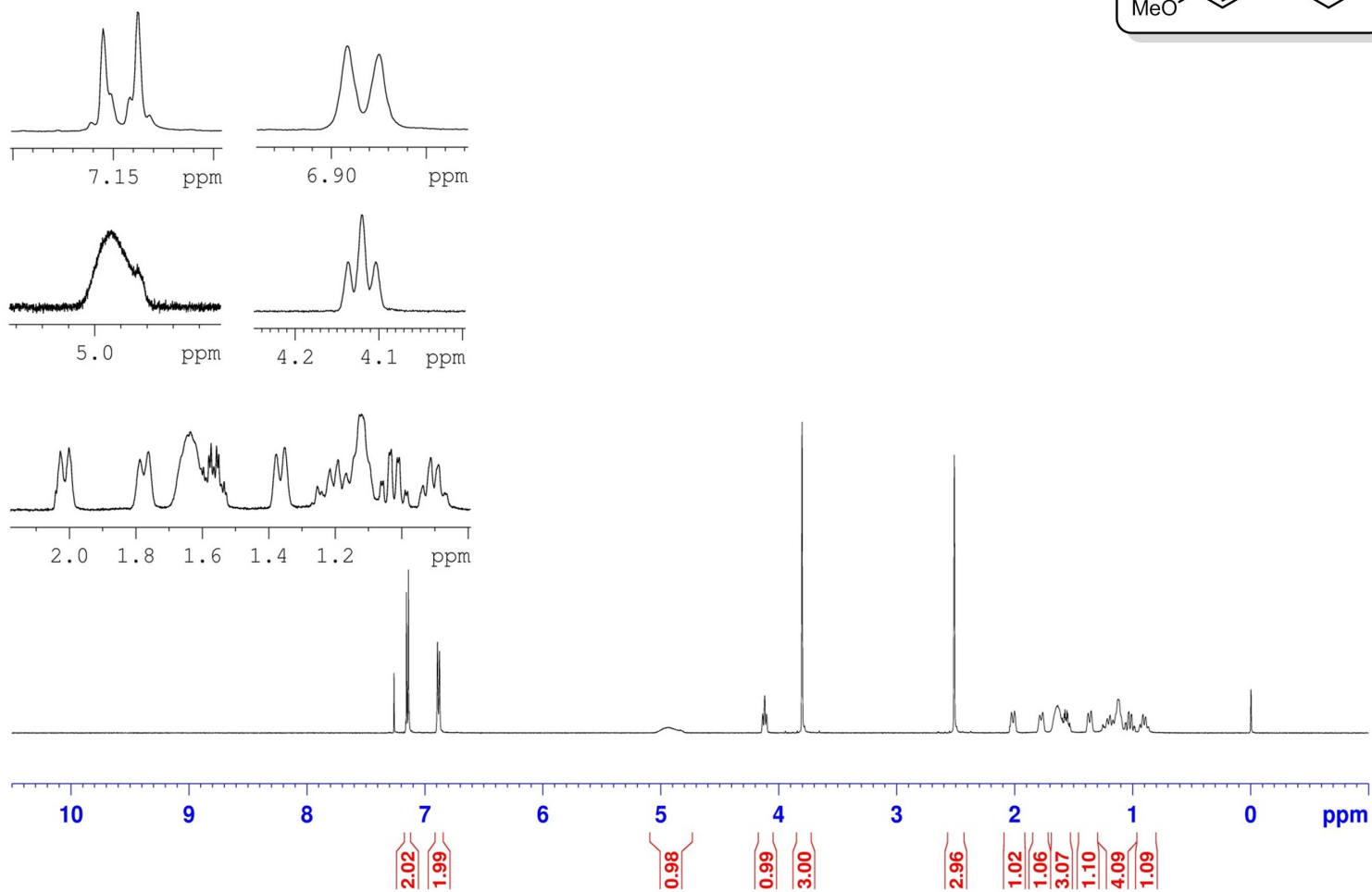
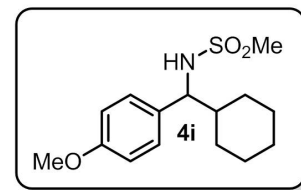
N-(cyclohexyl(2,4-difluorophenyl)methyl)methanesulfonamide  
500 MHz, CDCl<sub>3</sub>



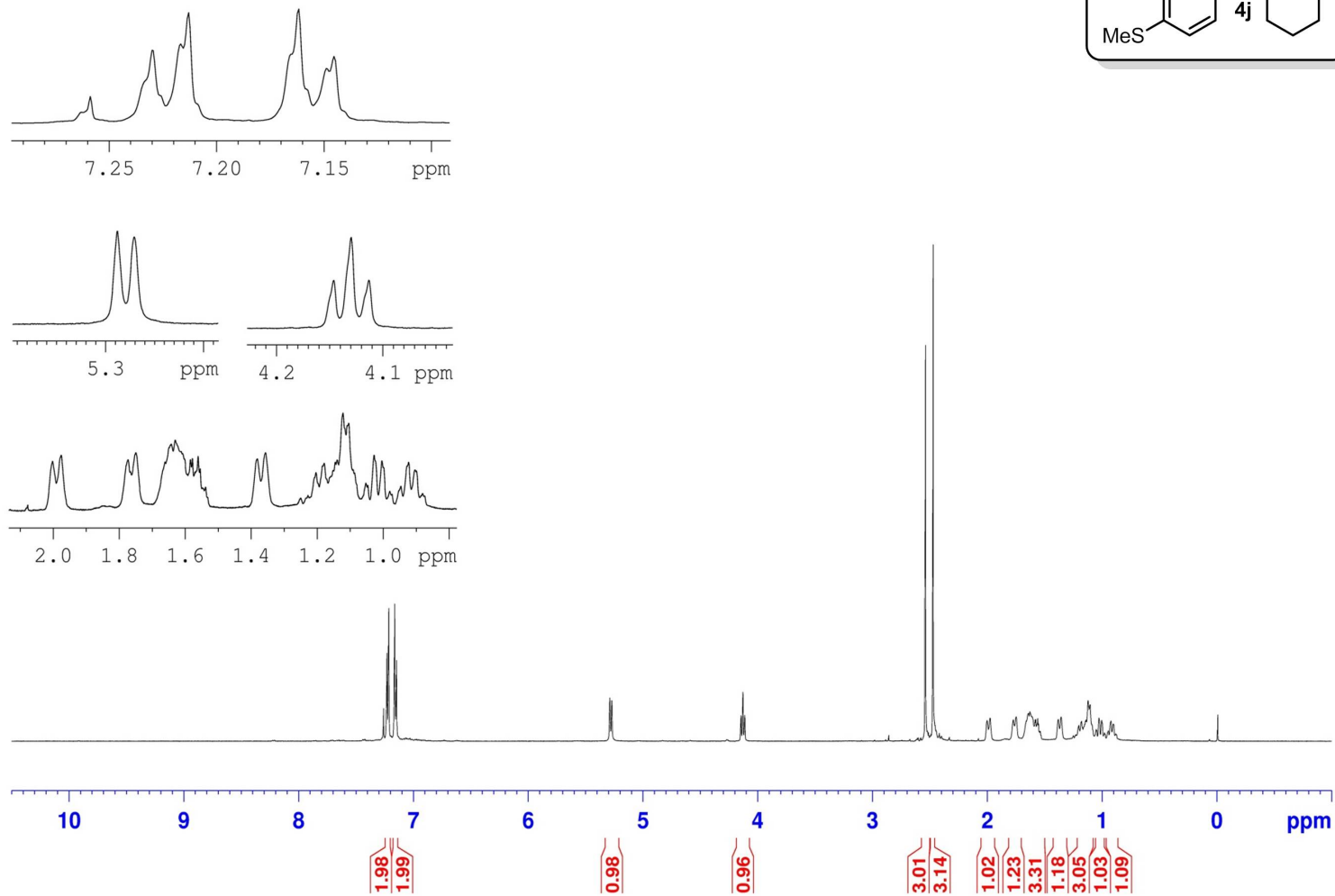
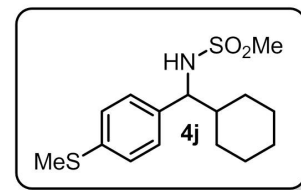
**N-((2-bromo-5-fluorophenyl)(cyclohexyl)methyl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



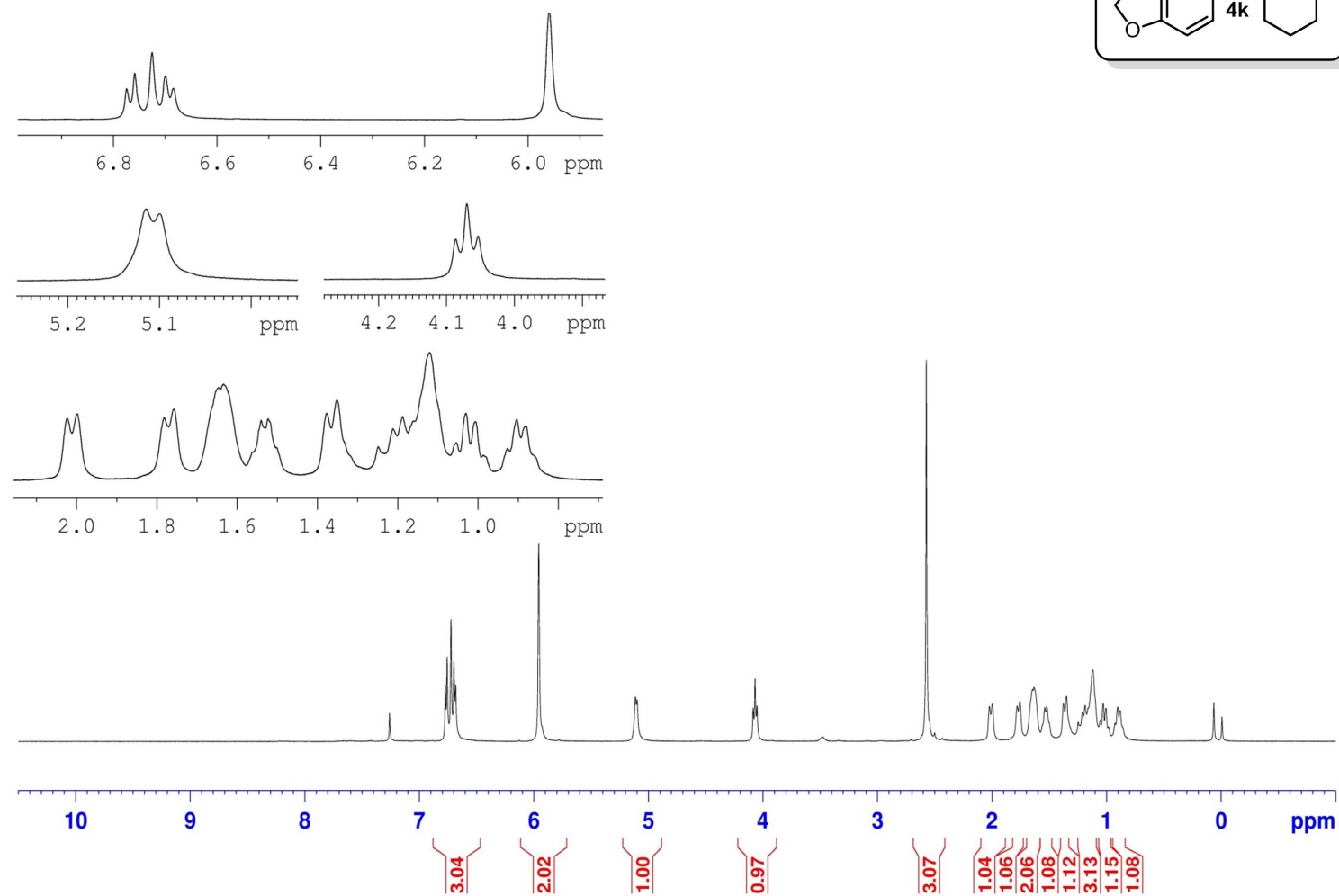
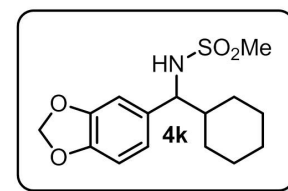
**N-(cyclohexyl(4-methoxyphenyl)methyl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



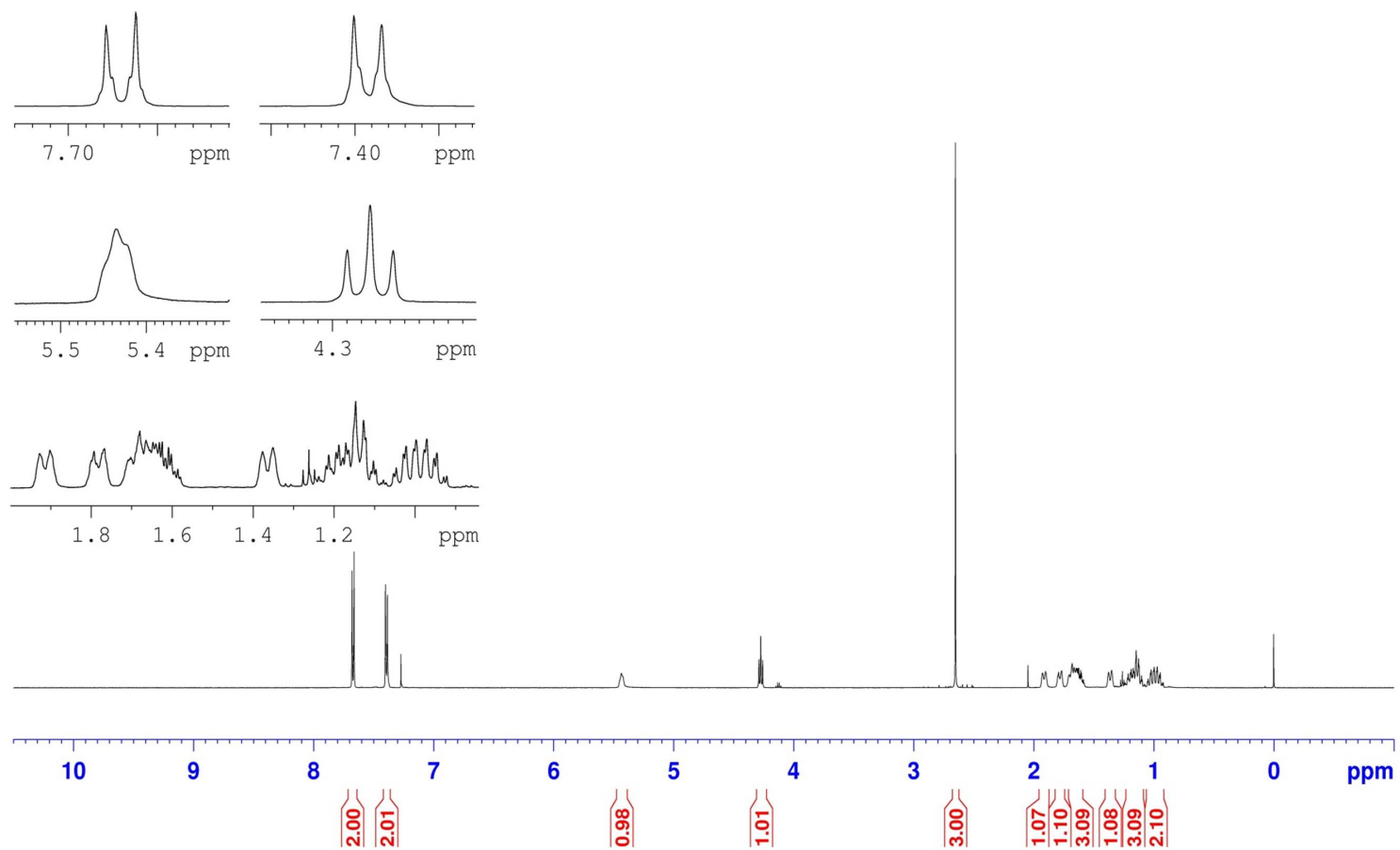
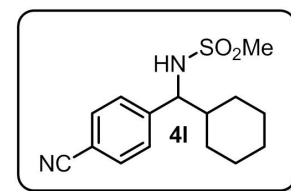
**N-(cyclohexyl(4-(methylthio)phenyl)methyl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



**N-(benzo[d][1,3]dioxol-5-yl(cyclohexyl)methyl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>

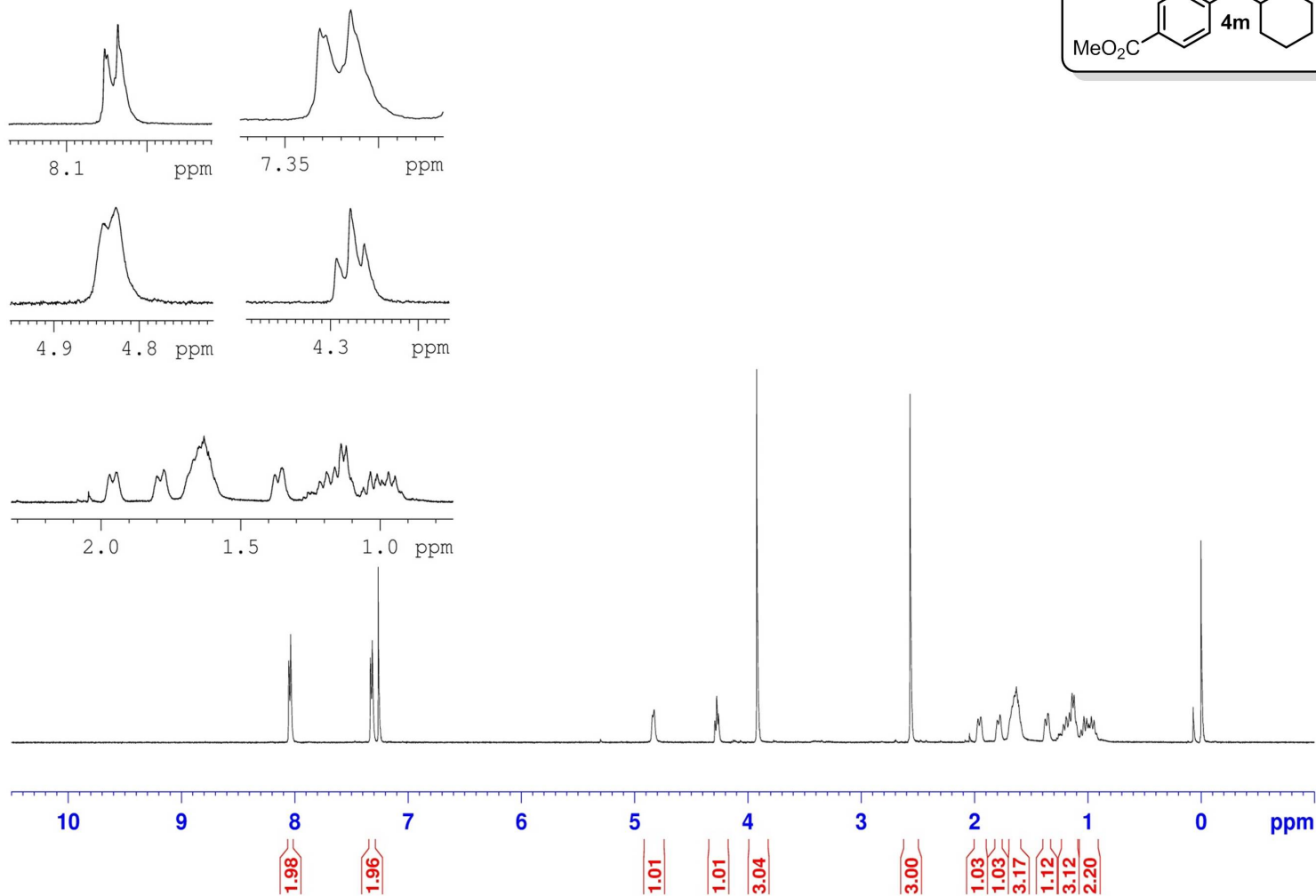
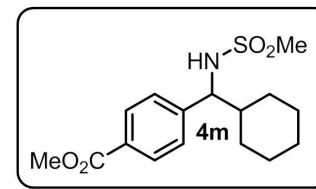


**N-((4-цyанопpены)(cyclohexyl)метил)метанесуфонамиде**  
**500 MHz, CDCl<sub>3</sub>**

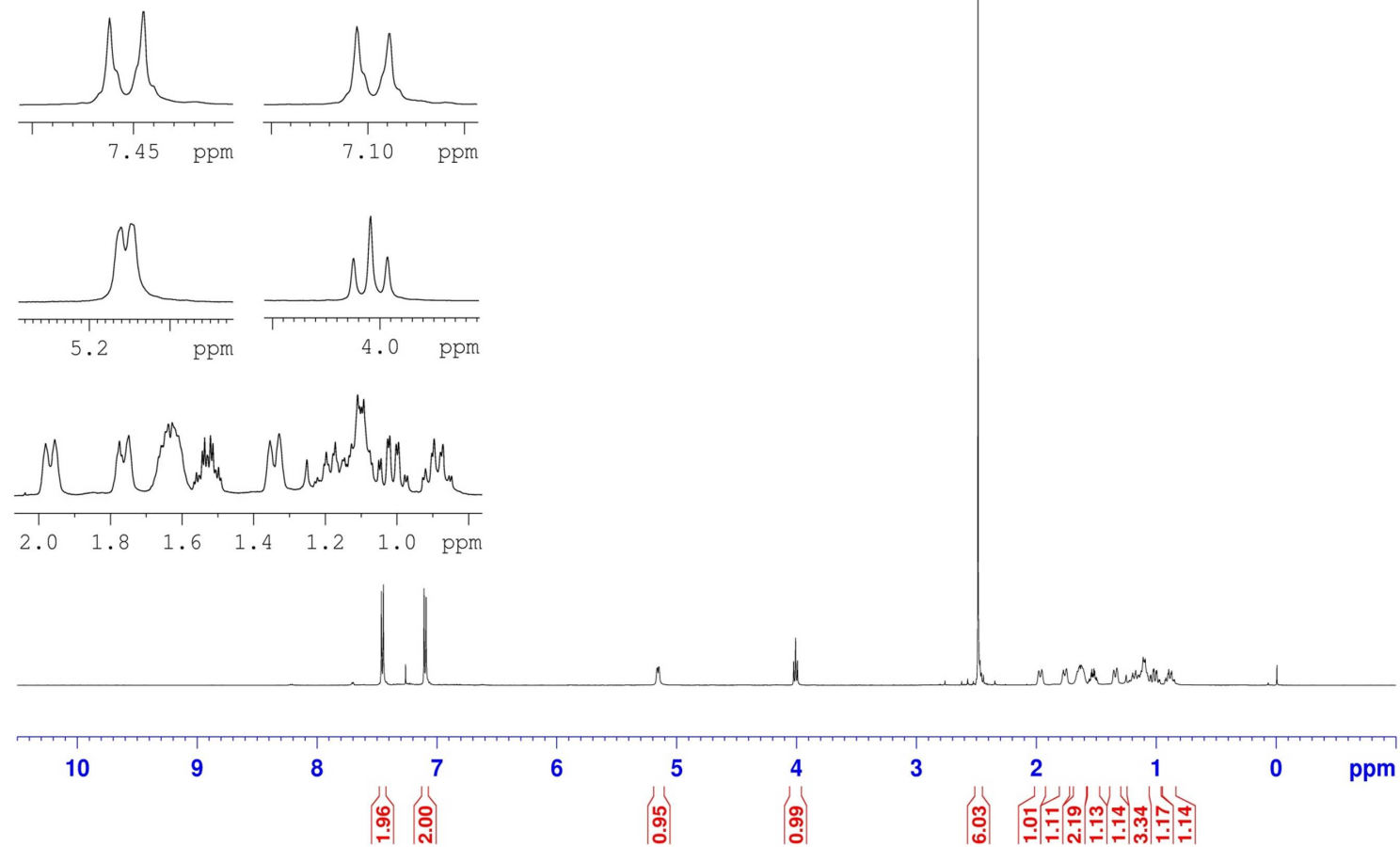
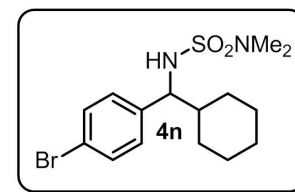




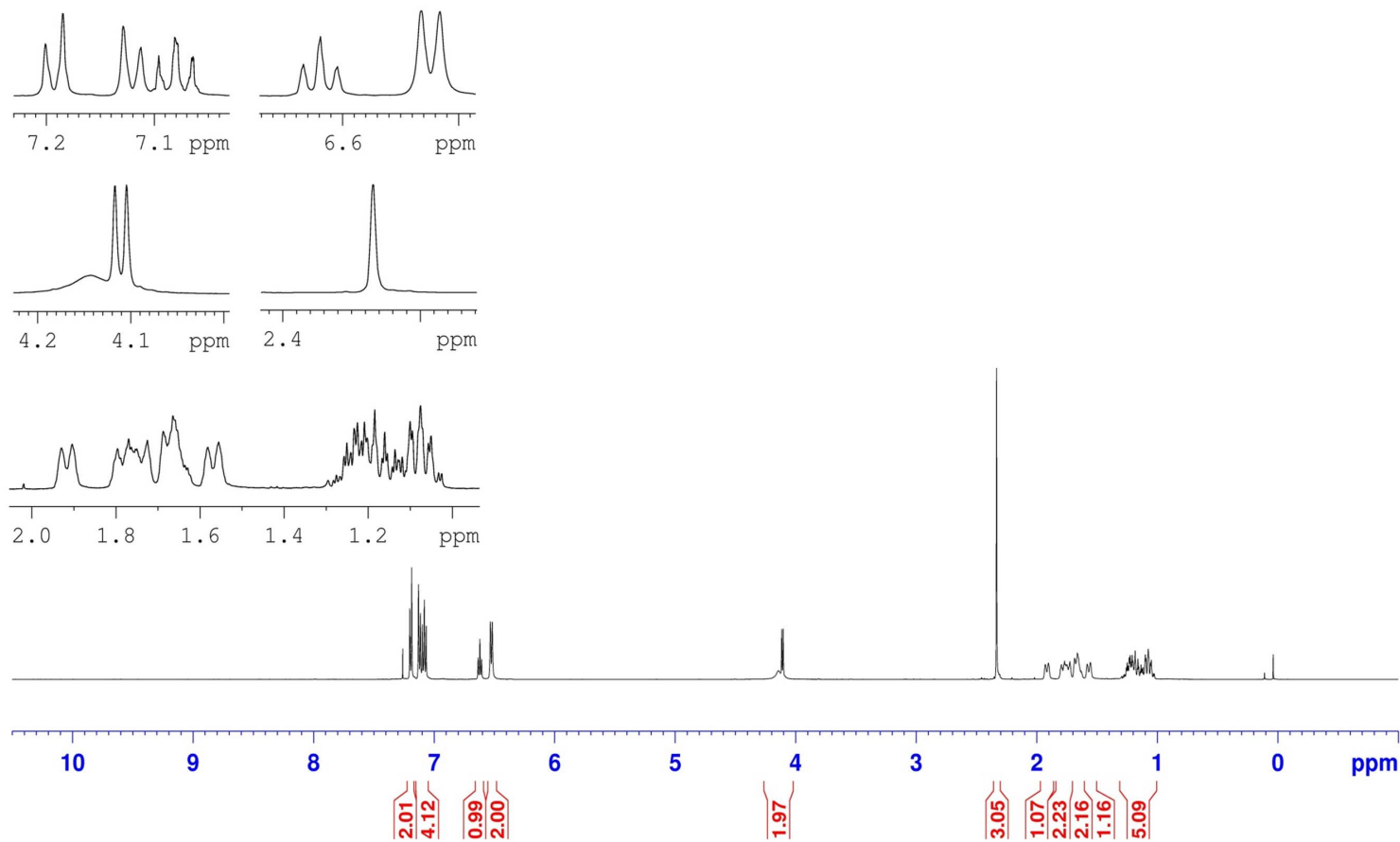
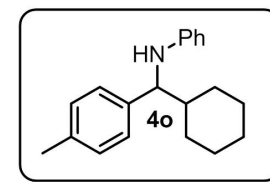
methyl 4-(cyclohexyl(methylsulfonamido)methyl)benzoate  
500 MHz, CDCl<sub>3</sub>



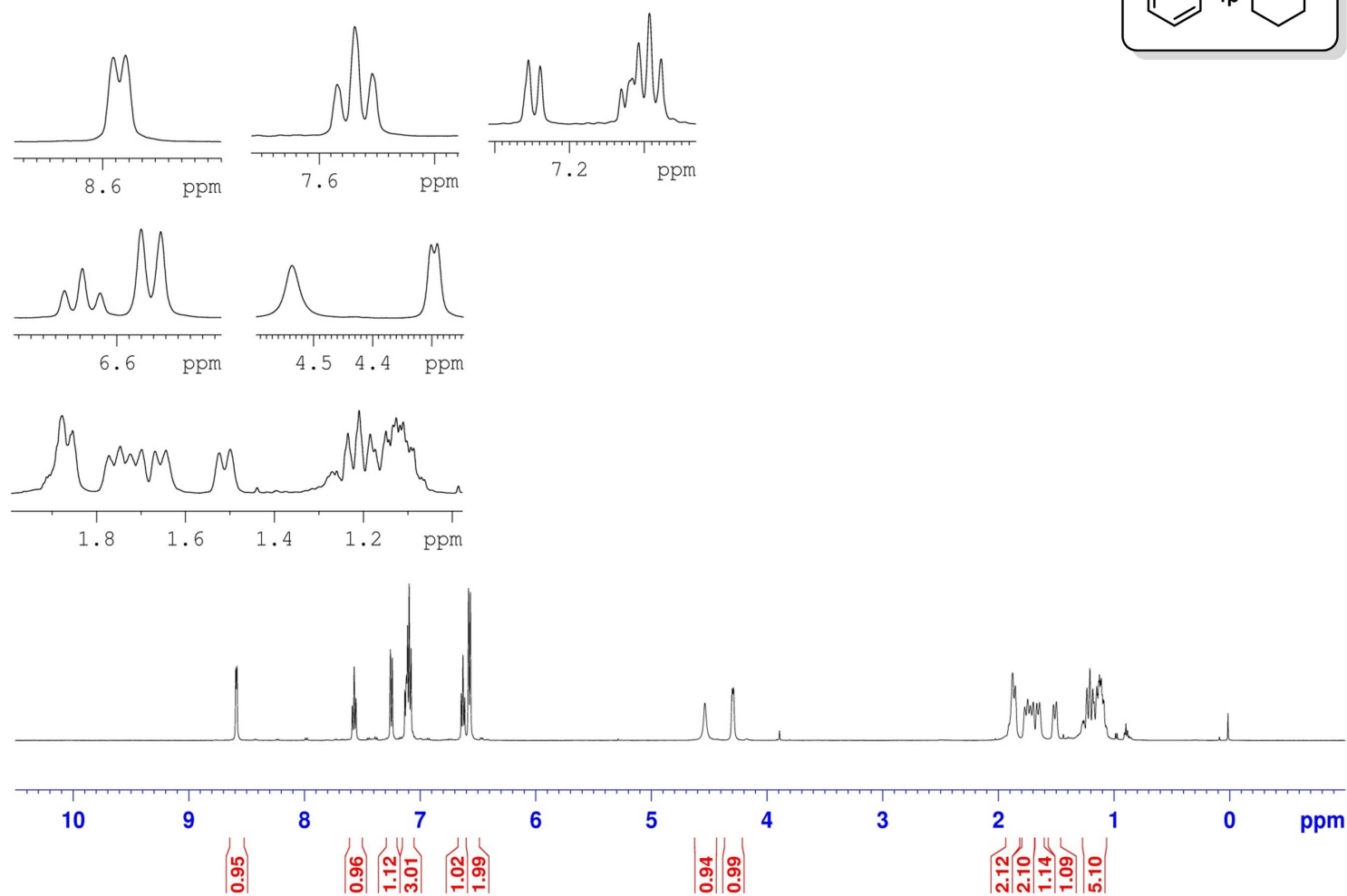
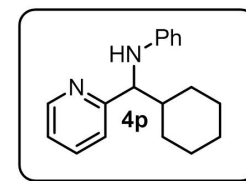
**N-((4-bromophenyl)(cyclohexyl)methyl)-N,N-dimethylsulfamide**  
500 MHz, CDCl<sub>3</sub>



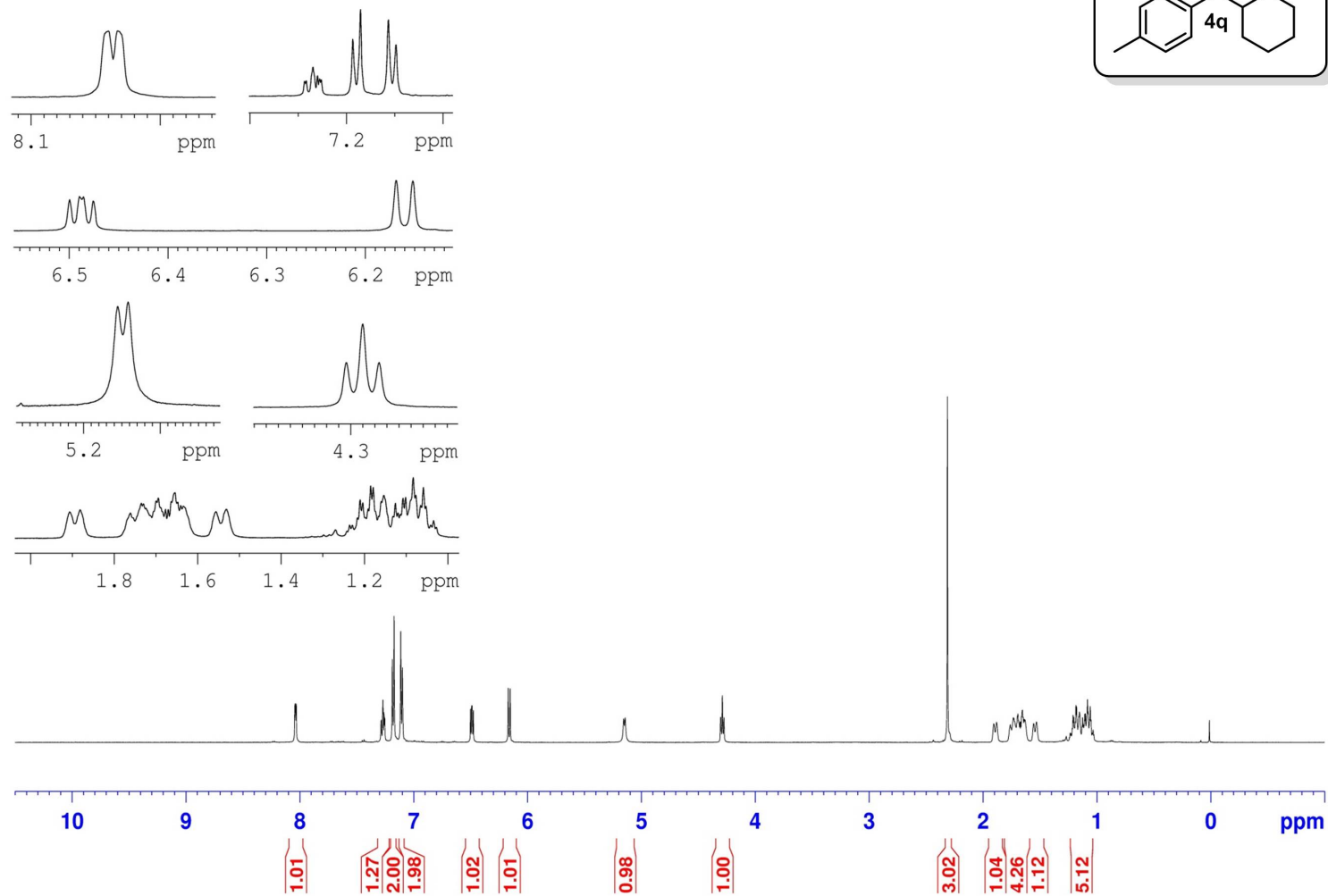
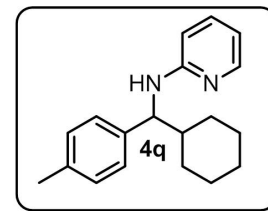
**N-(cyclohexyl(p-tolyl)methyl)aniline**  
500 MHz, CDCl<sub>3</sub>



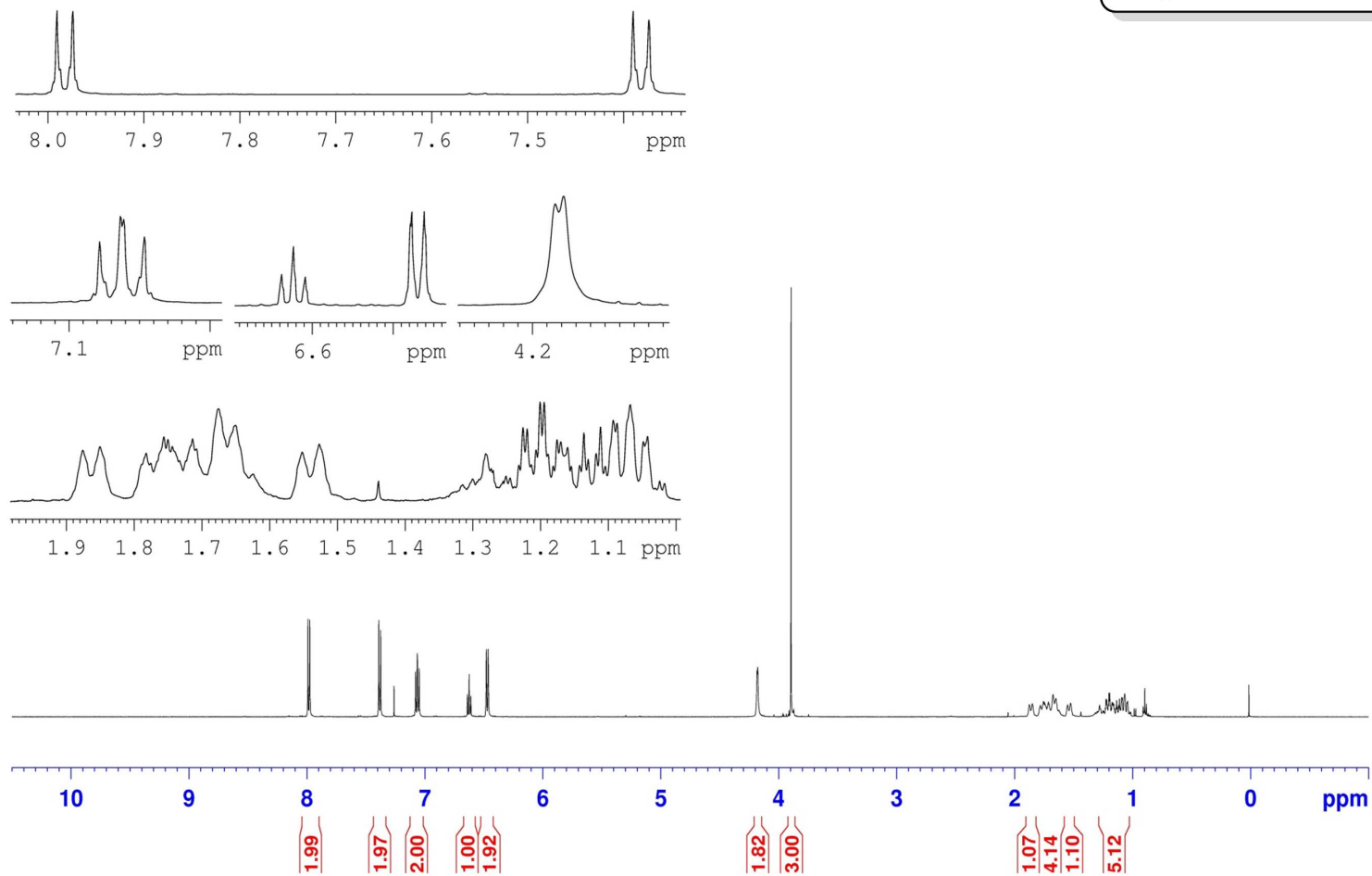
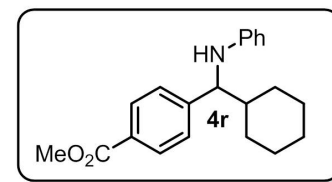
**N-(cyclohexyl(pyridin-2-yl)methyl)aniline**  
500 MHz, CDCl<sub>3</sub>



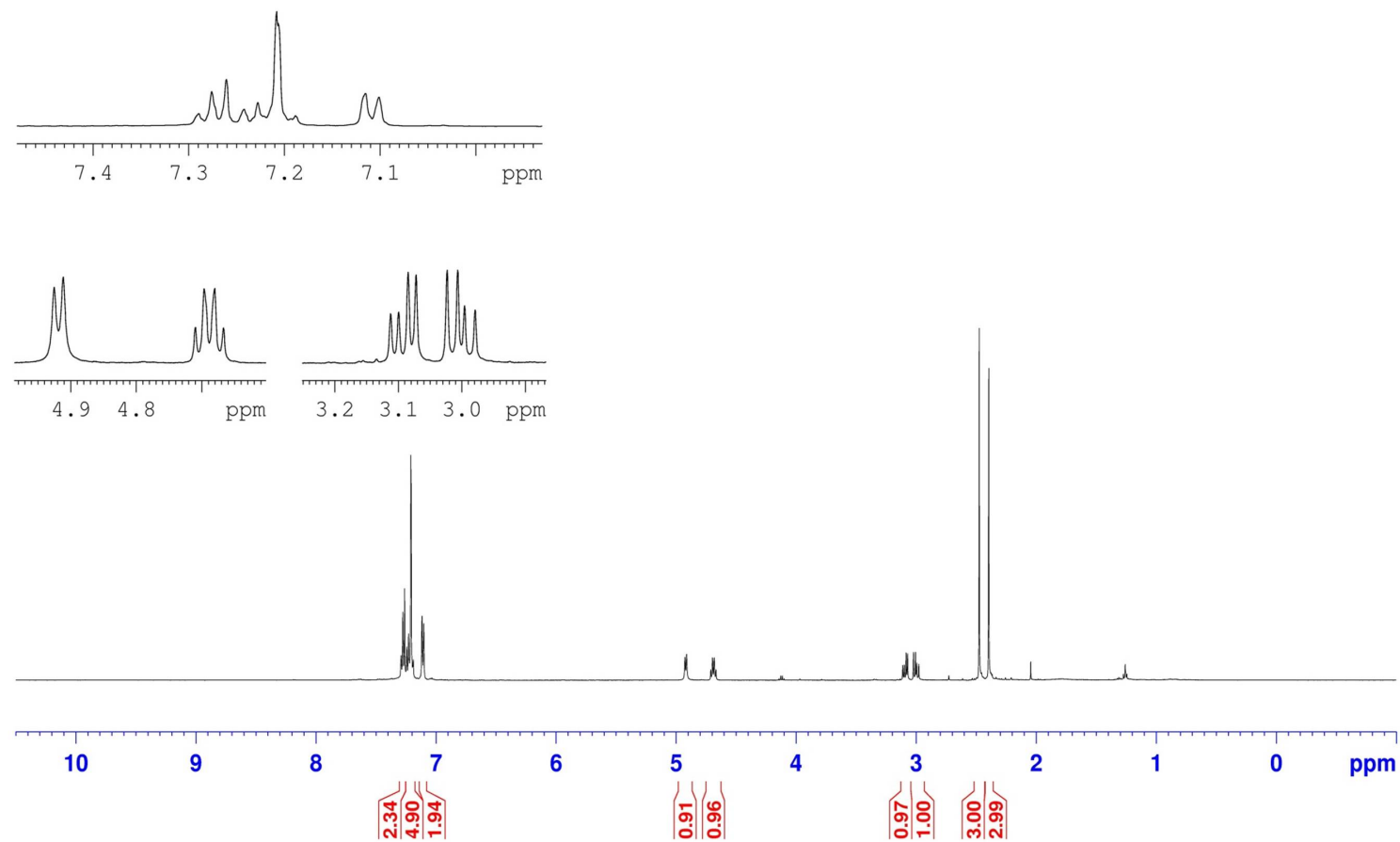
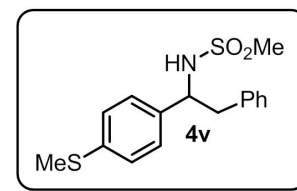
**N-(cyclohexyl(p-tolyl)methyl)pyridin-2-amine**  
500 MHz, CDCl<sub>3</sub>



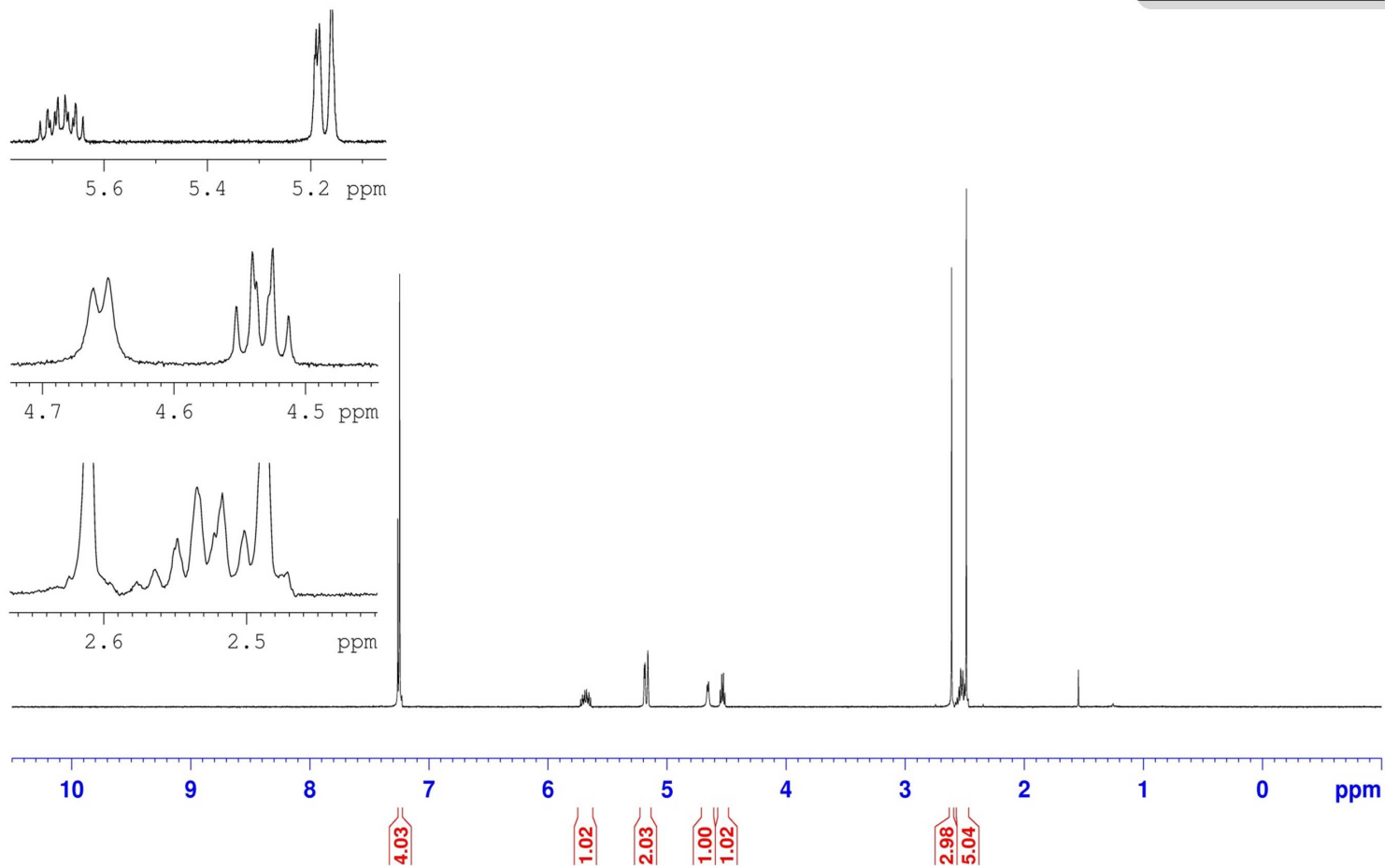
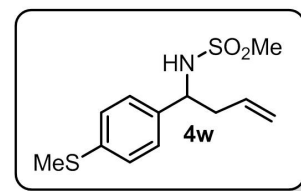
methyl 4-(cyclohexyl(phenylamino)methyl)benzoate  
500 MHz, CDCl<sub>3</sub>



**N-(1-(4-(methylthio)phenyl)-2-phenylethyl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>

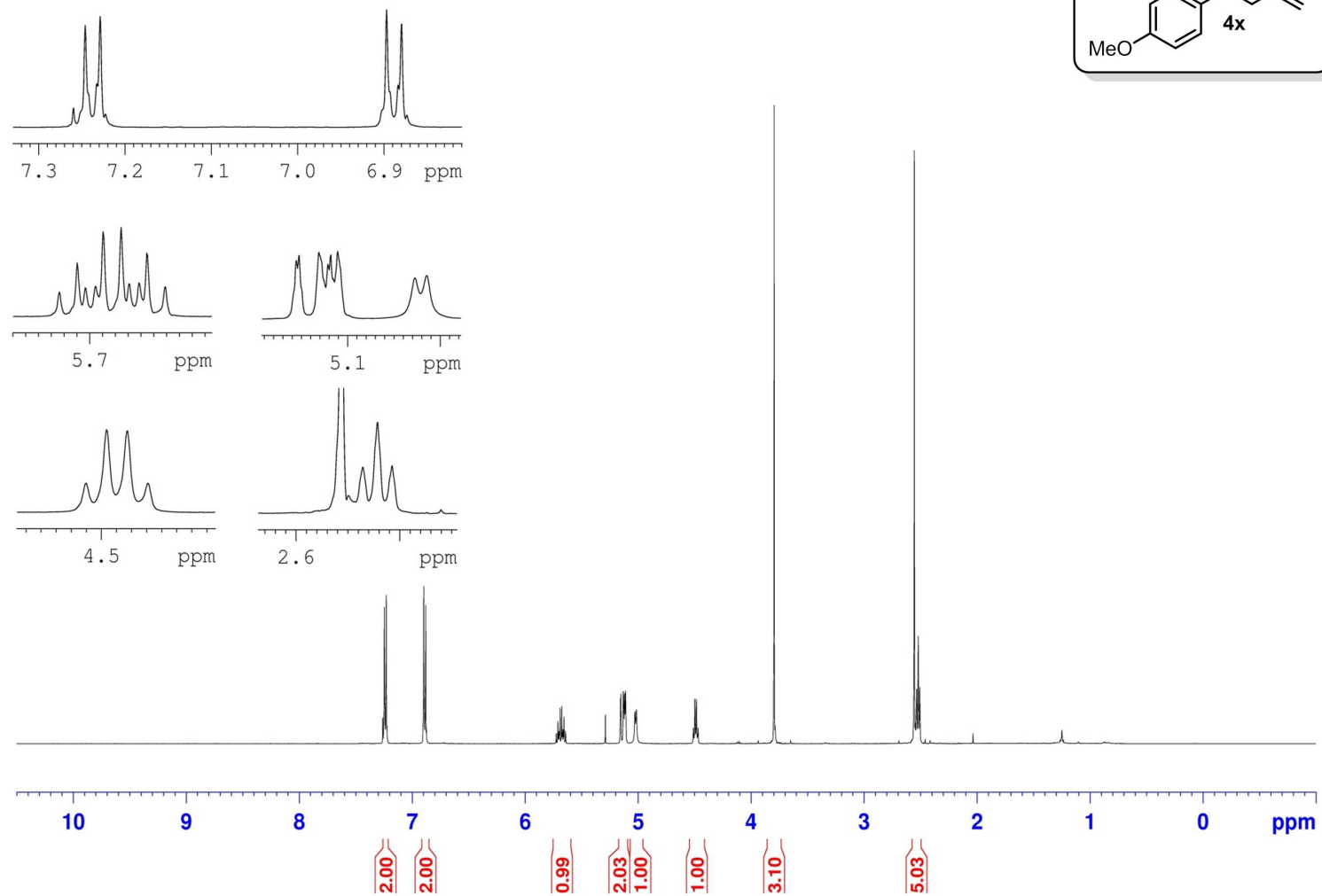
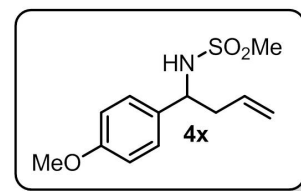


**N-(1-(4-(methylthio)phenyl)but-3-en-1-yl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>

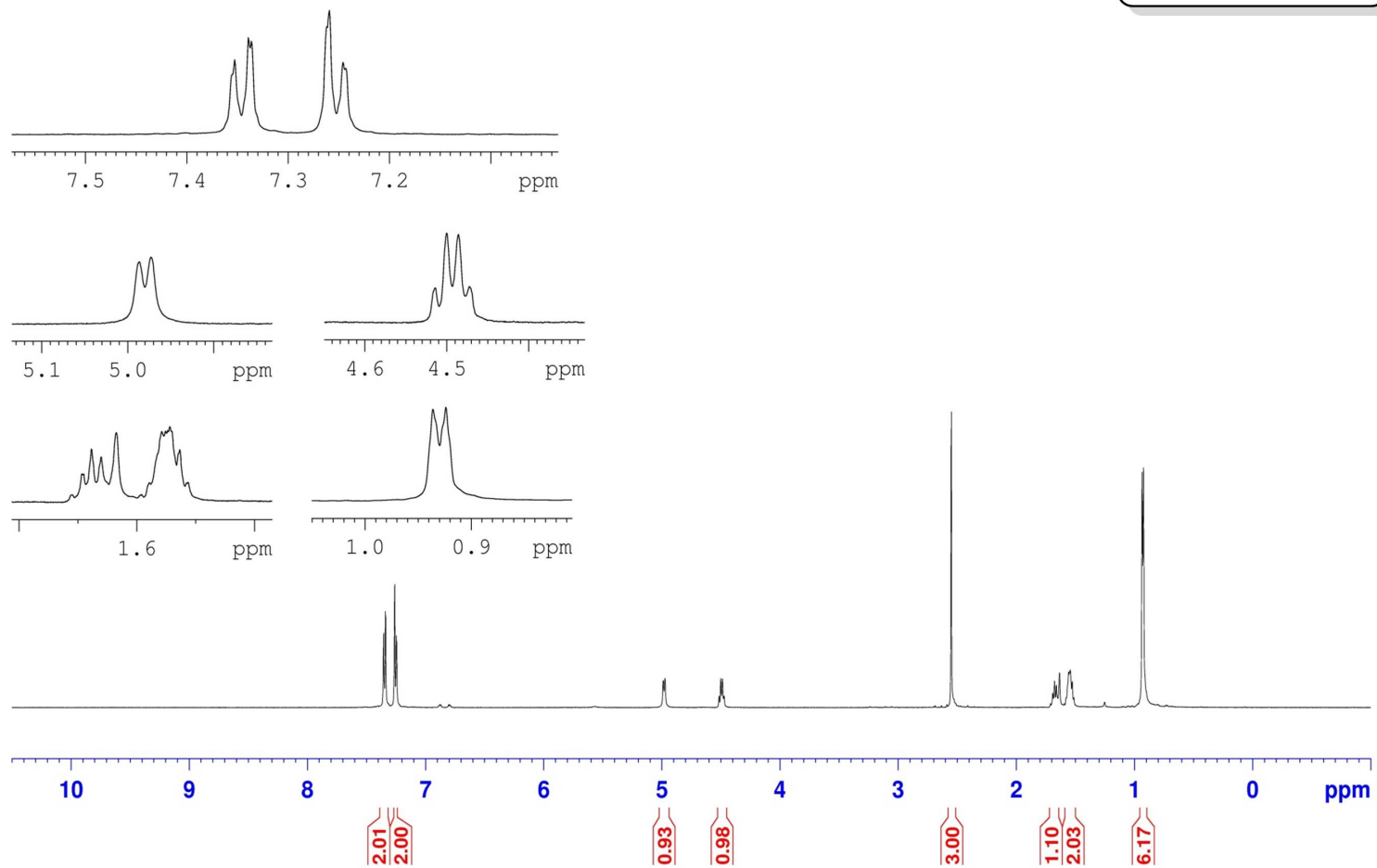
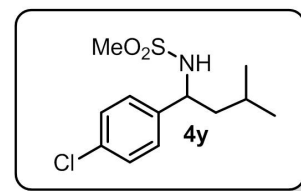




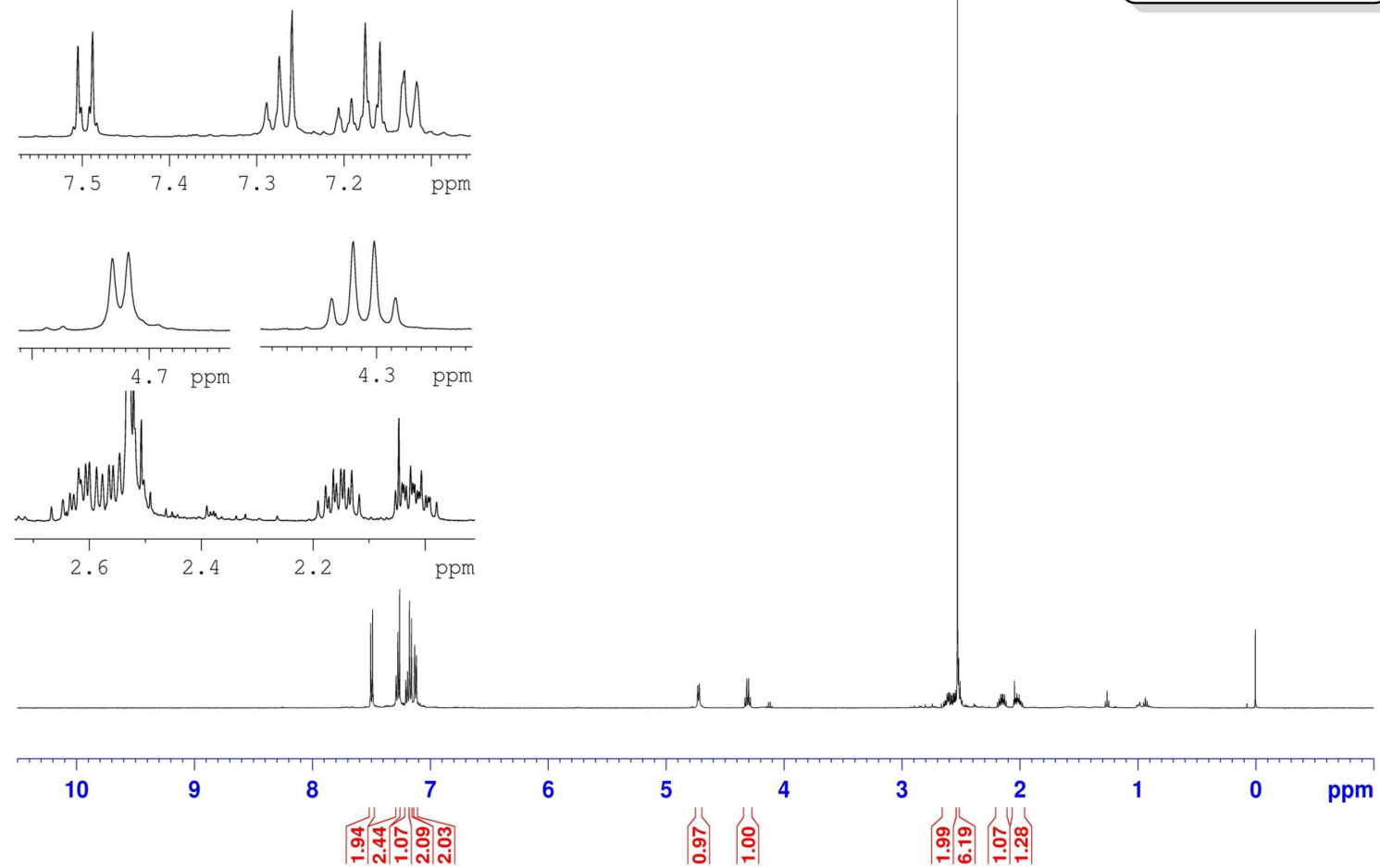
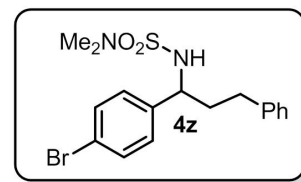
**N-(1-(4-methoxyphenyl)but-3-en-1-yl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



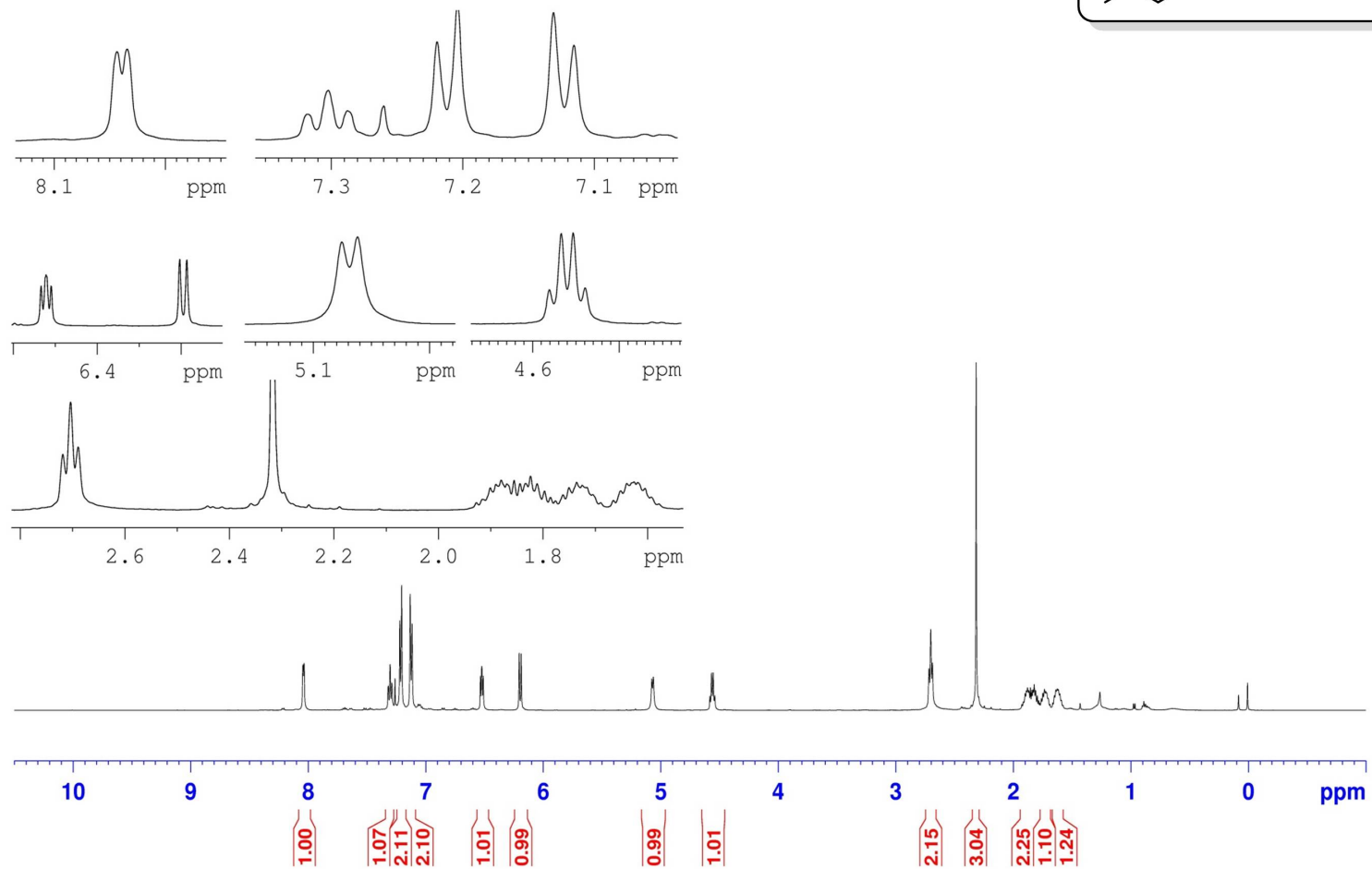
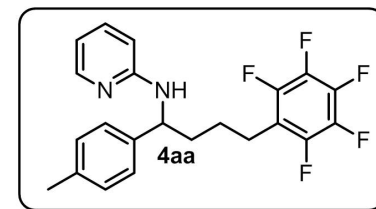
**N-(1-(4-chlorophenyl)-3-methylbutyl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



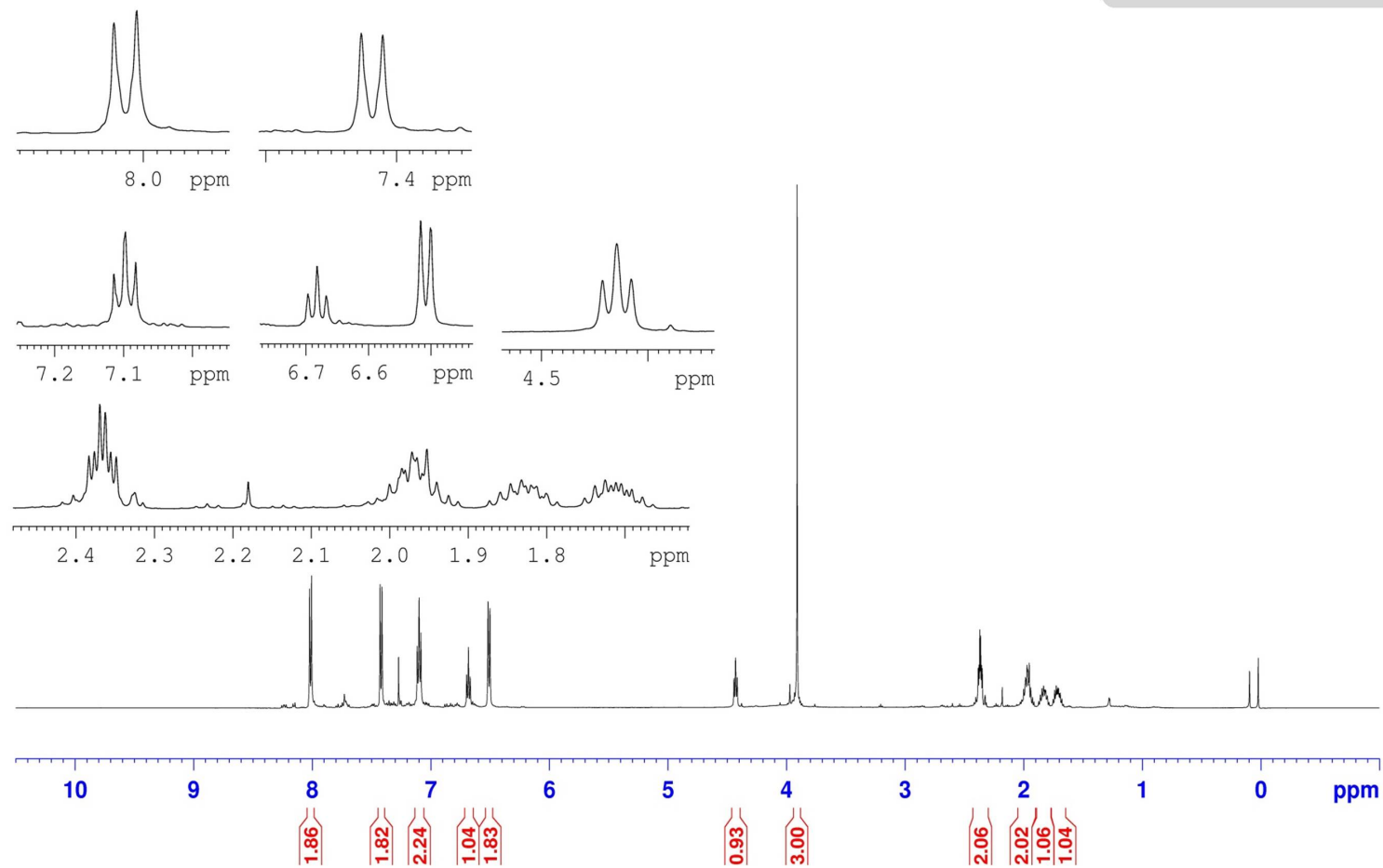
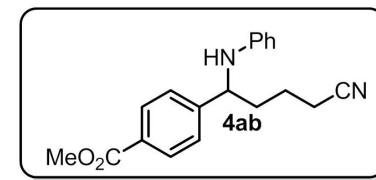
**N'-(1-(4-bromophenyl)-3-phenylpropyl)-N,N-dimethylsulfamide**  
500 MHz, CDCl<sub>3</sub>



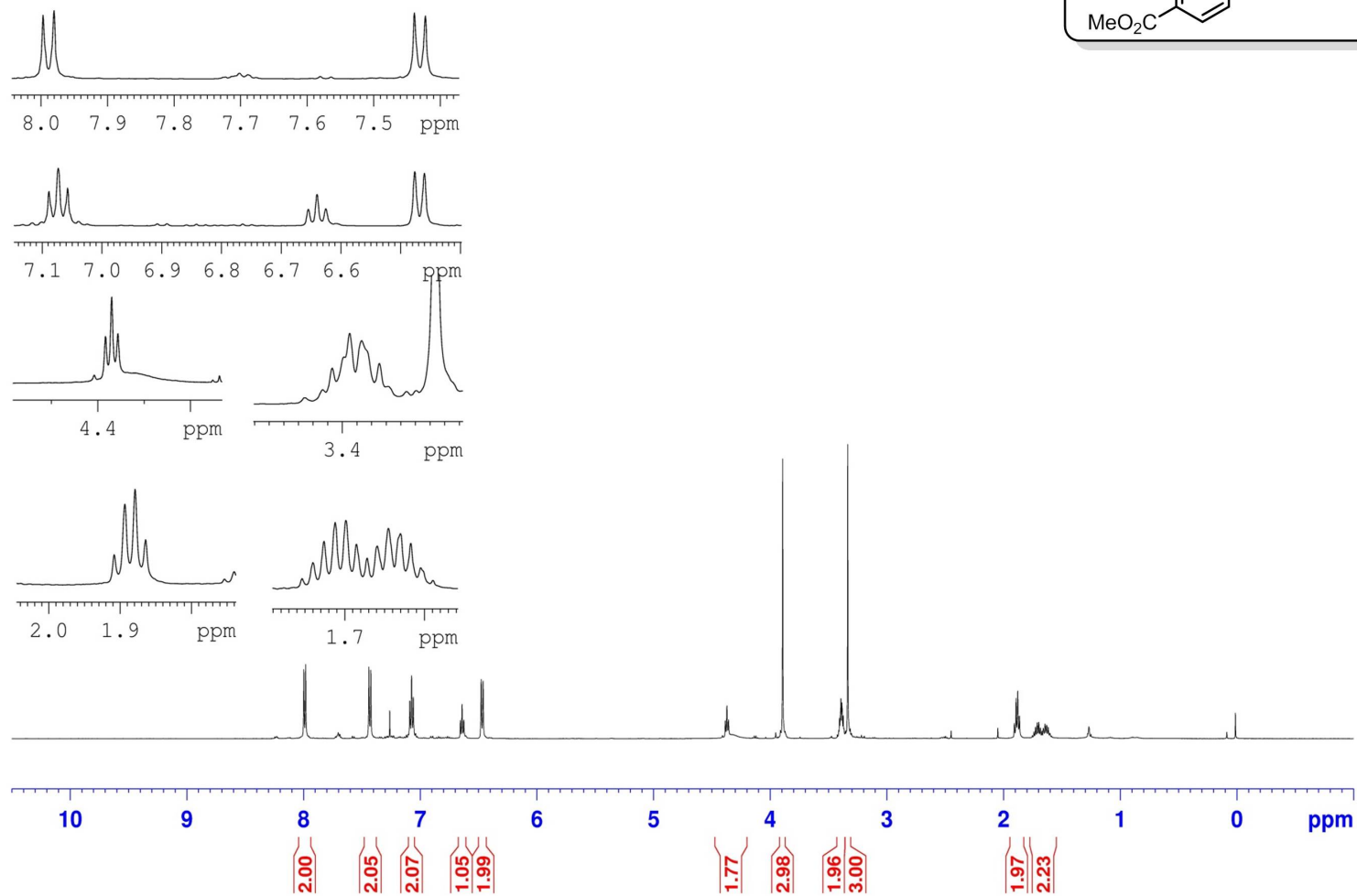
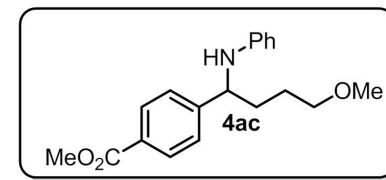
**N-(4-(perfluorophenyl)-1-(p-tolyl)butyl)aniline**  
500 MHz, CDCl<sub>3</sub>



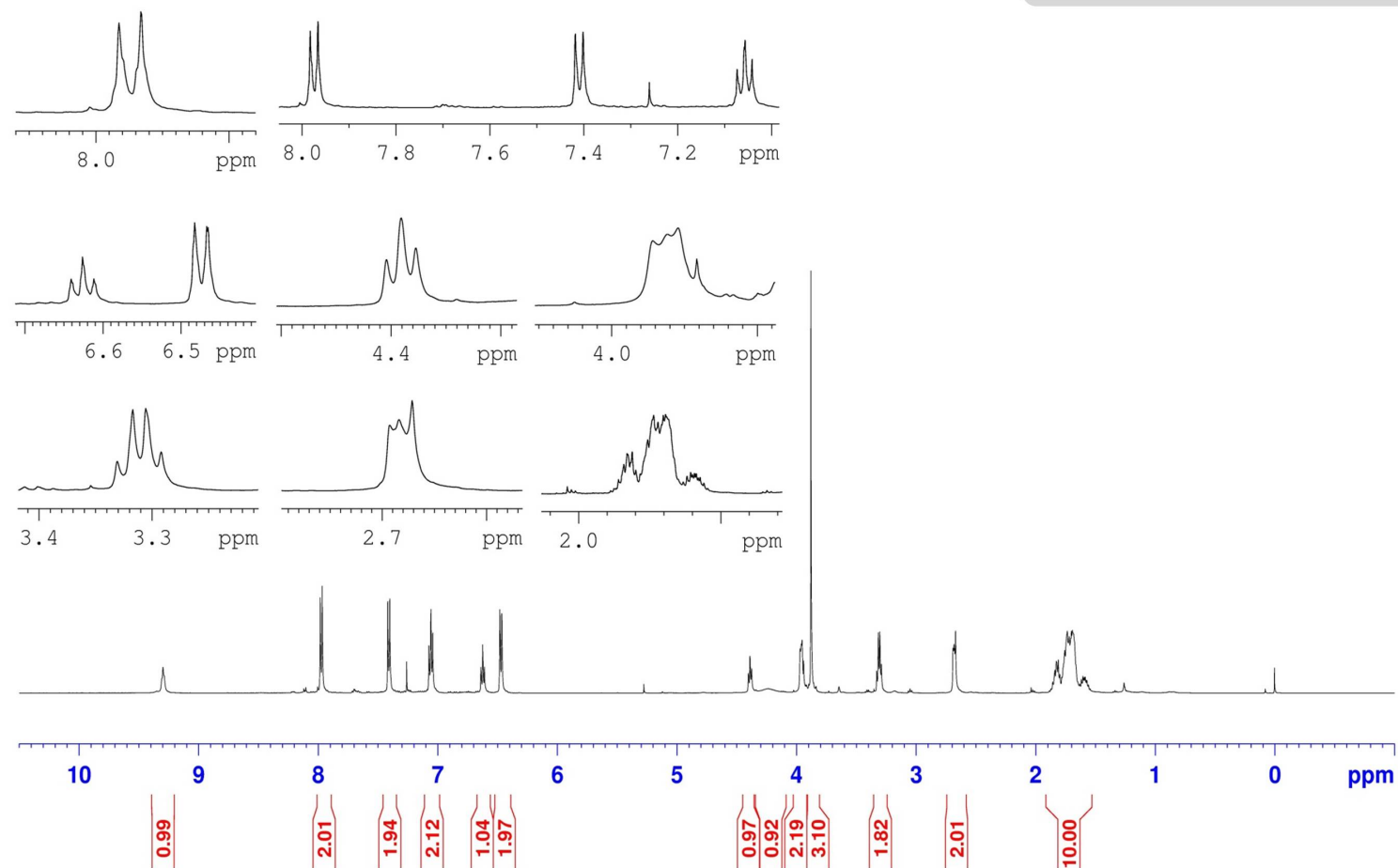
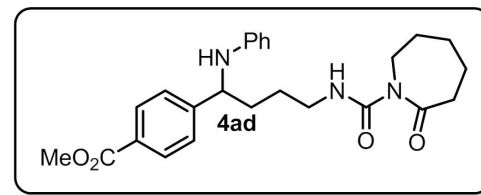
methyl 4-(4-cyano-1-(phenylamino)butyl)benzoate  
500 MHz, CDCl<sub>3</sub>



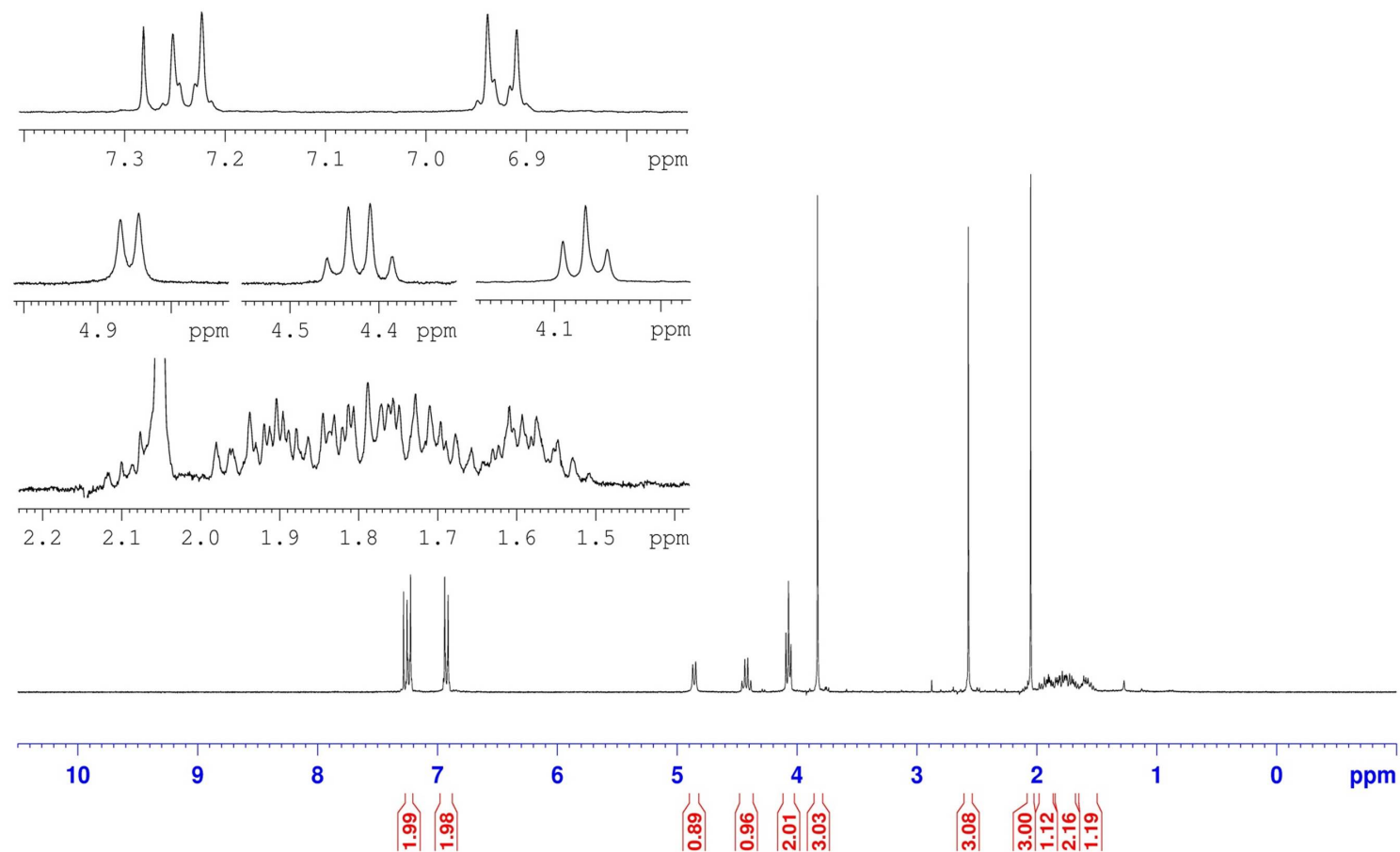
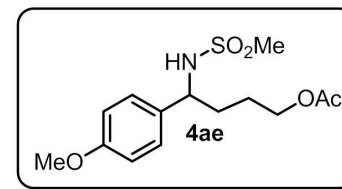
**methyl 4-(4-methoxy-1-(phenylamino)butyl)benzoate**  
500 Mhz, CDCl<sub>3</sub>



methyl 4-(4-(2-oxoazepane-1-carboxamido)-1-(phenylamino)butyl)benzoate  
500 MHz, CDCl<sub>3</sub>

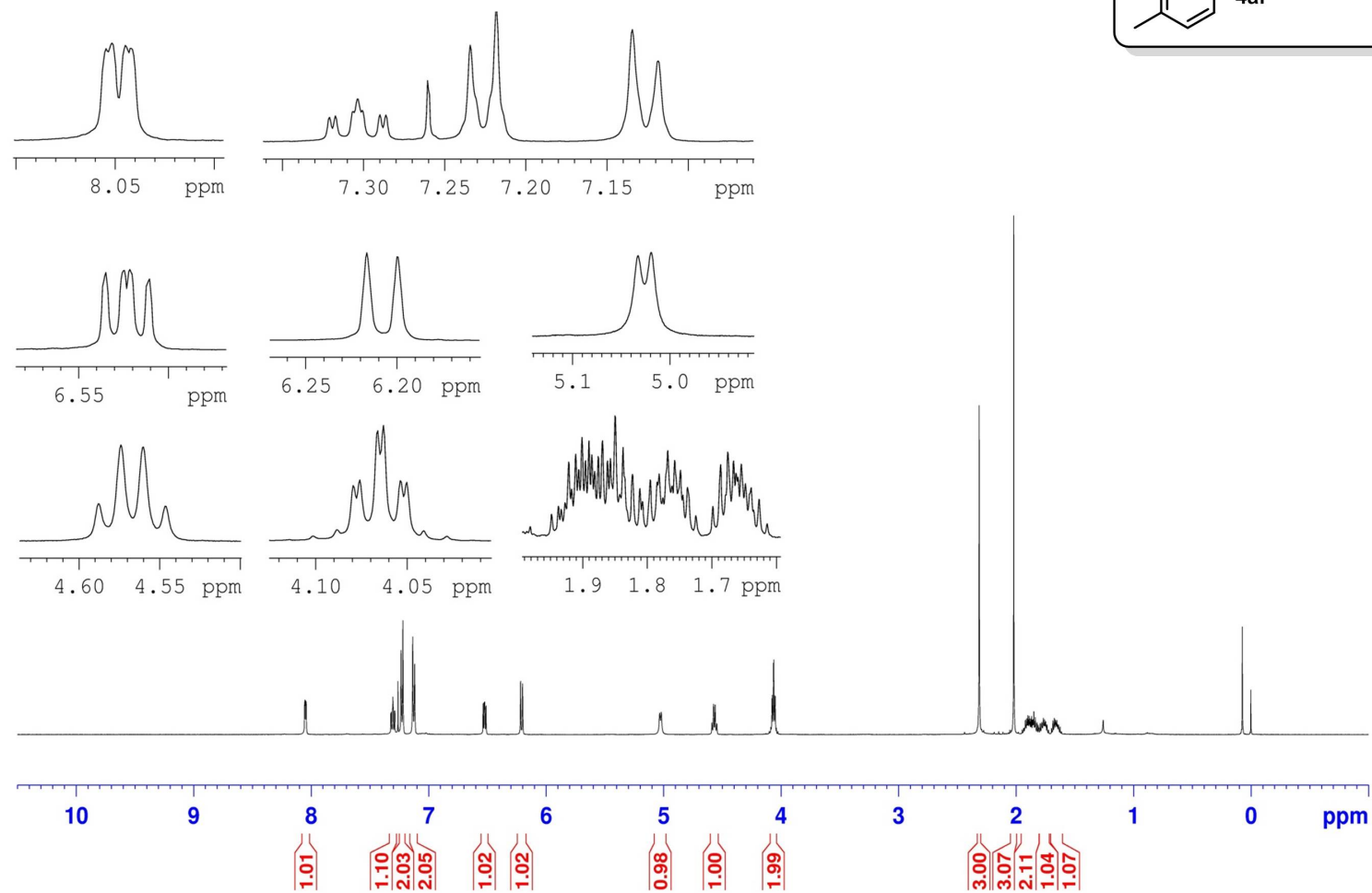
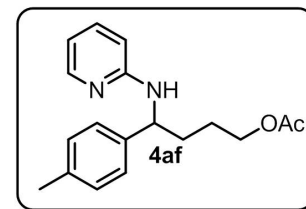


4-(4-methoxyphenyl)-4-(methylsulfonamido)butyl acetate  
300 MHz, CDCl<sub>3</sub>

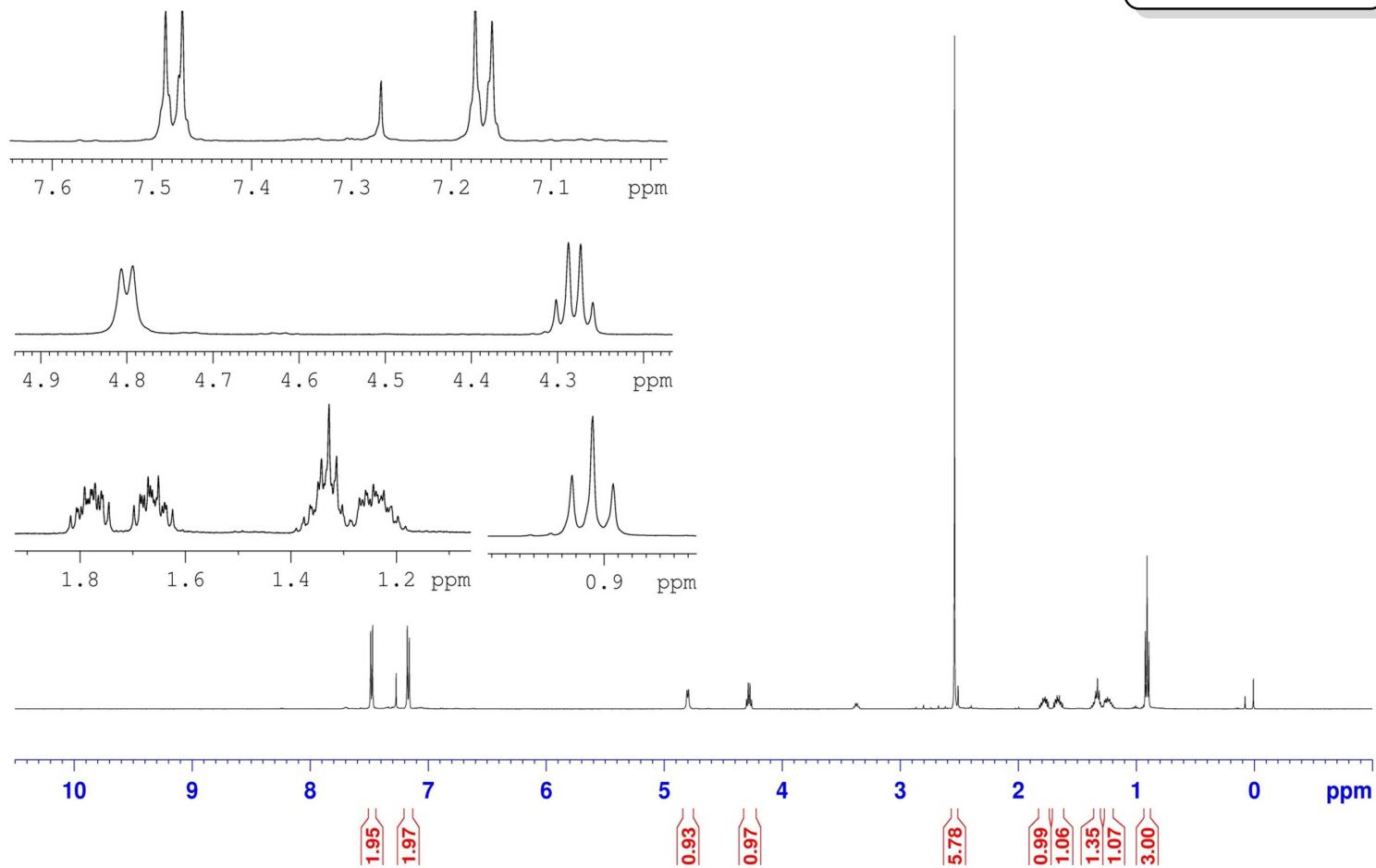
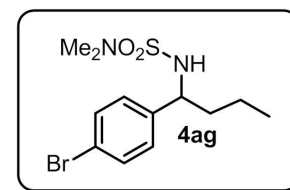




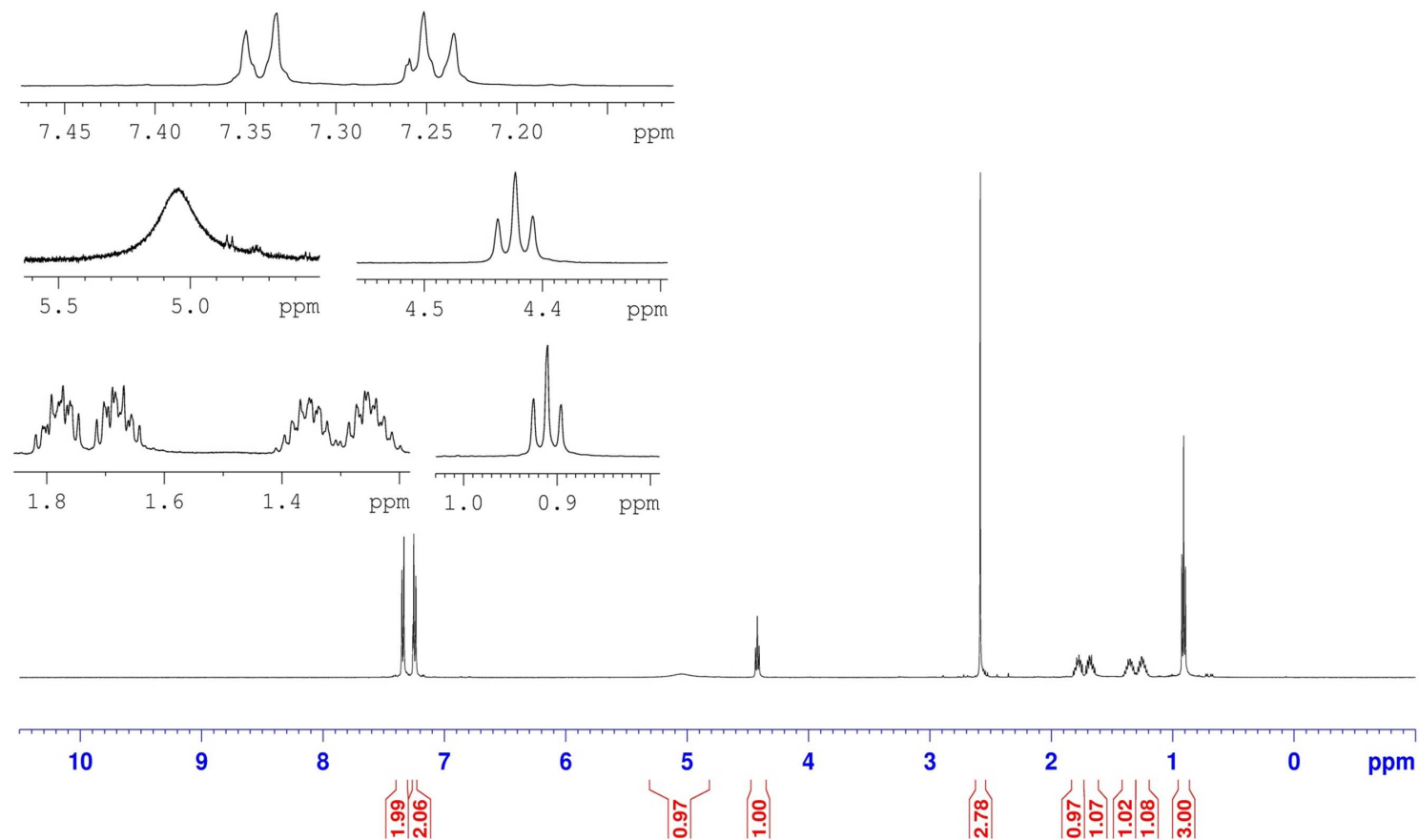
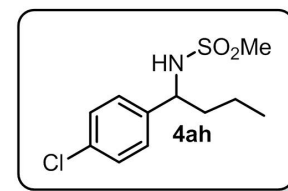
4-(pyridin-2-ylamino)-4-(p-tolyl)butyl acetate  
500 MHz, CDCl<sub>3</sub>



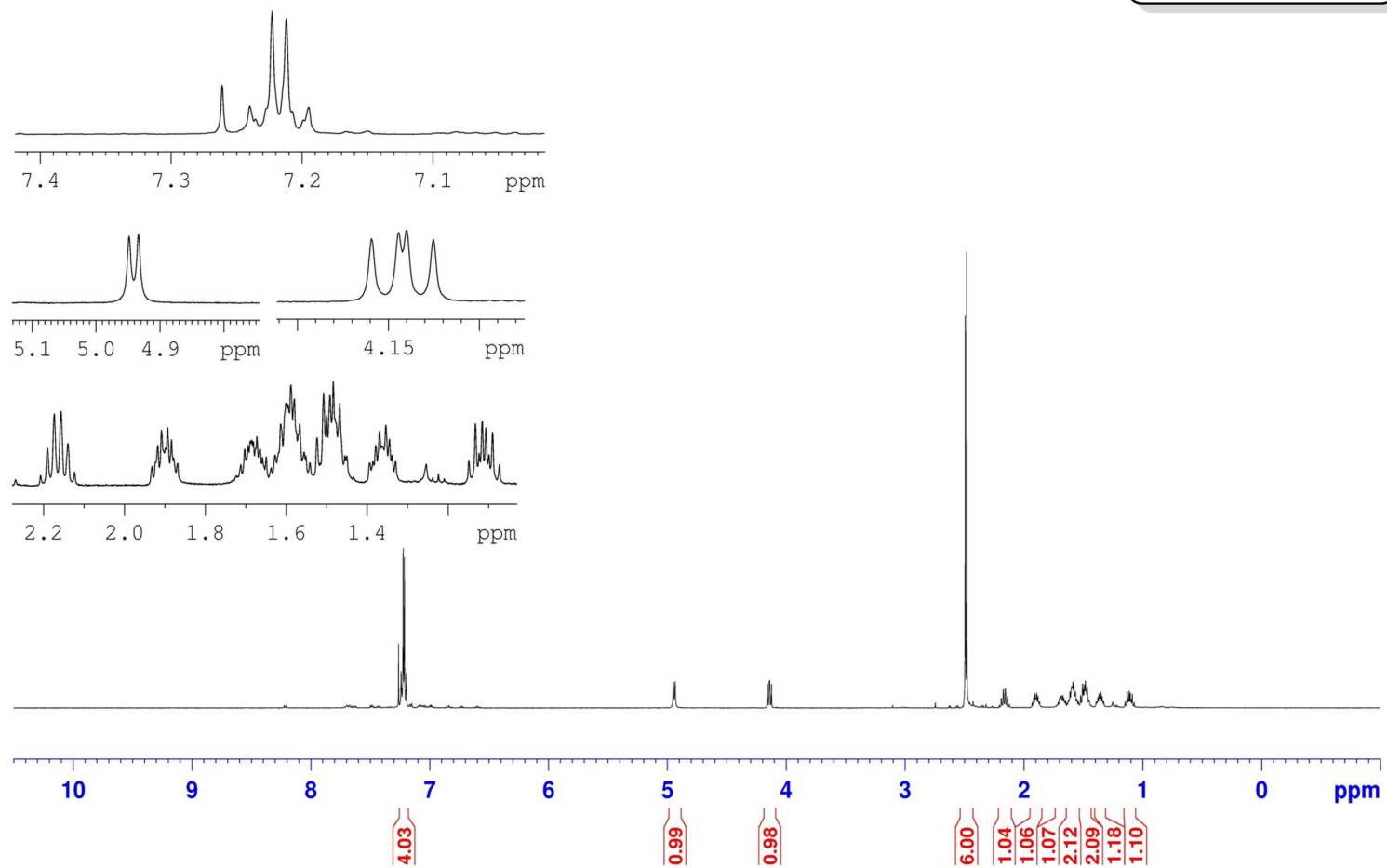
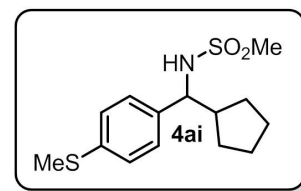
**N'-(1-(4-bromophenyl)-3-phenylpropyl)-N,N-dimethylsulfamide**  
500 MHz, CDCl<sub>3</sub>



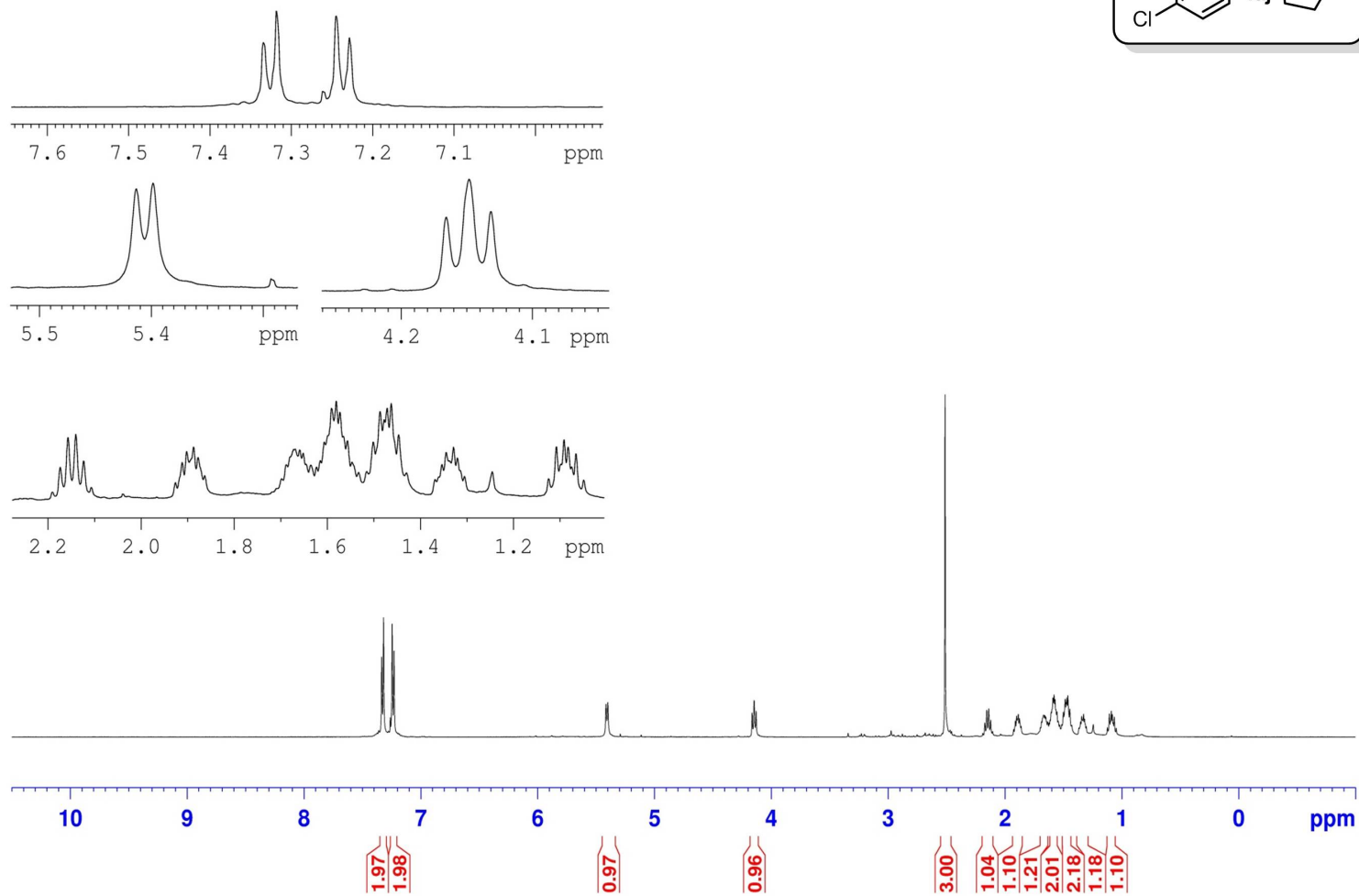
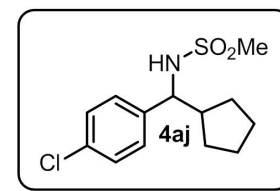
**N-(1-(4-chlorophenyl)butyl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



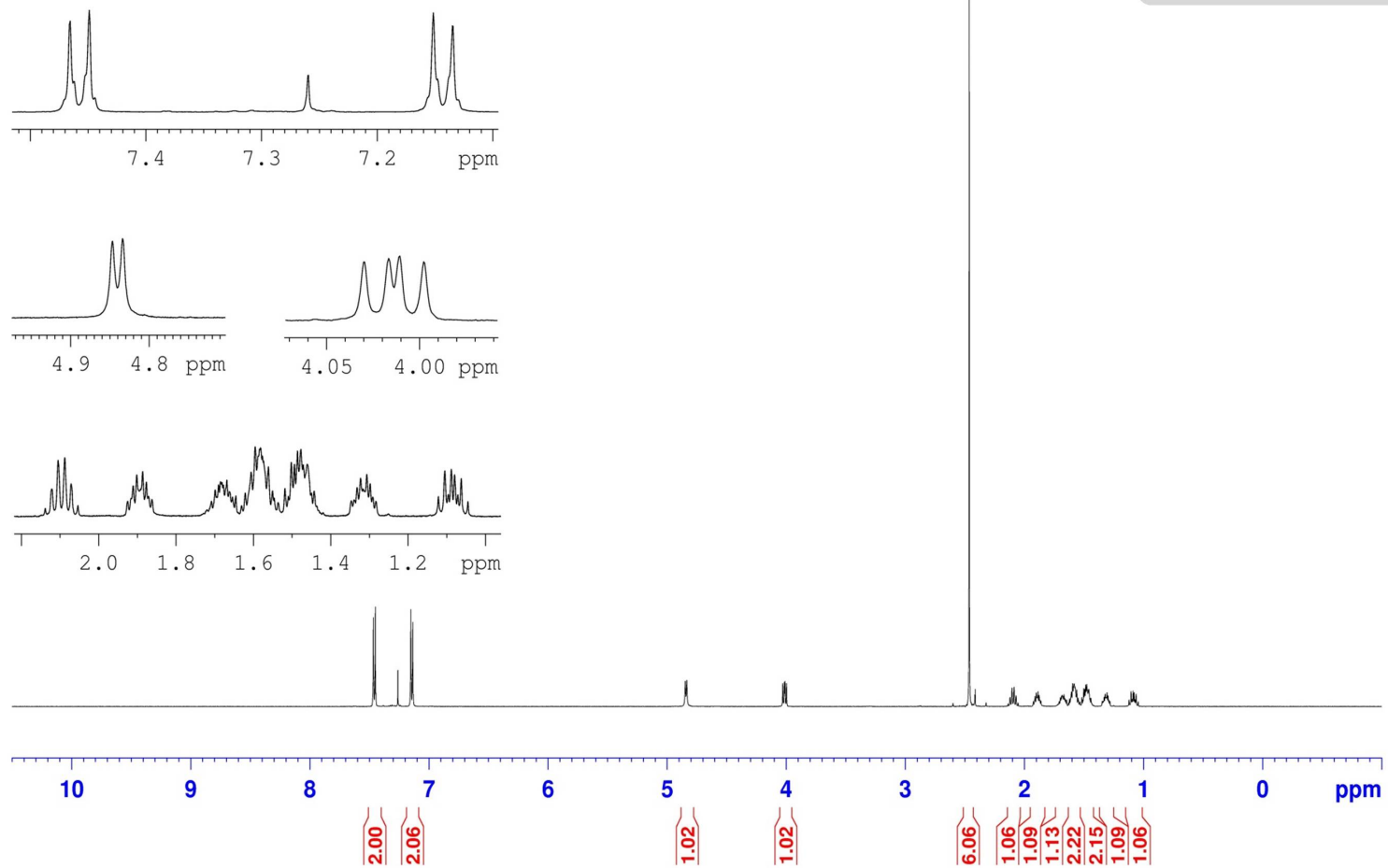
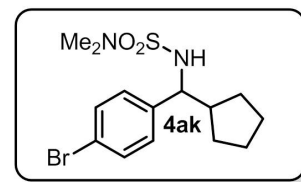
**N-(cyclopentyl(4-(methylthio)phenyl)methyl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



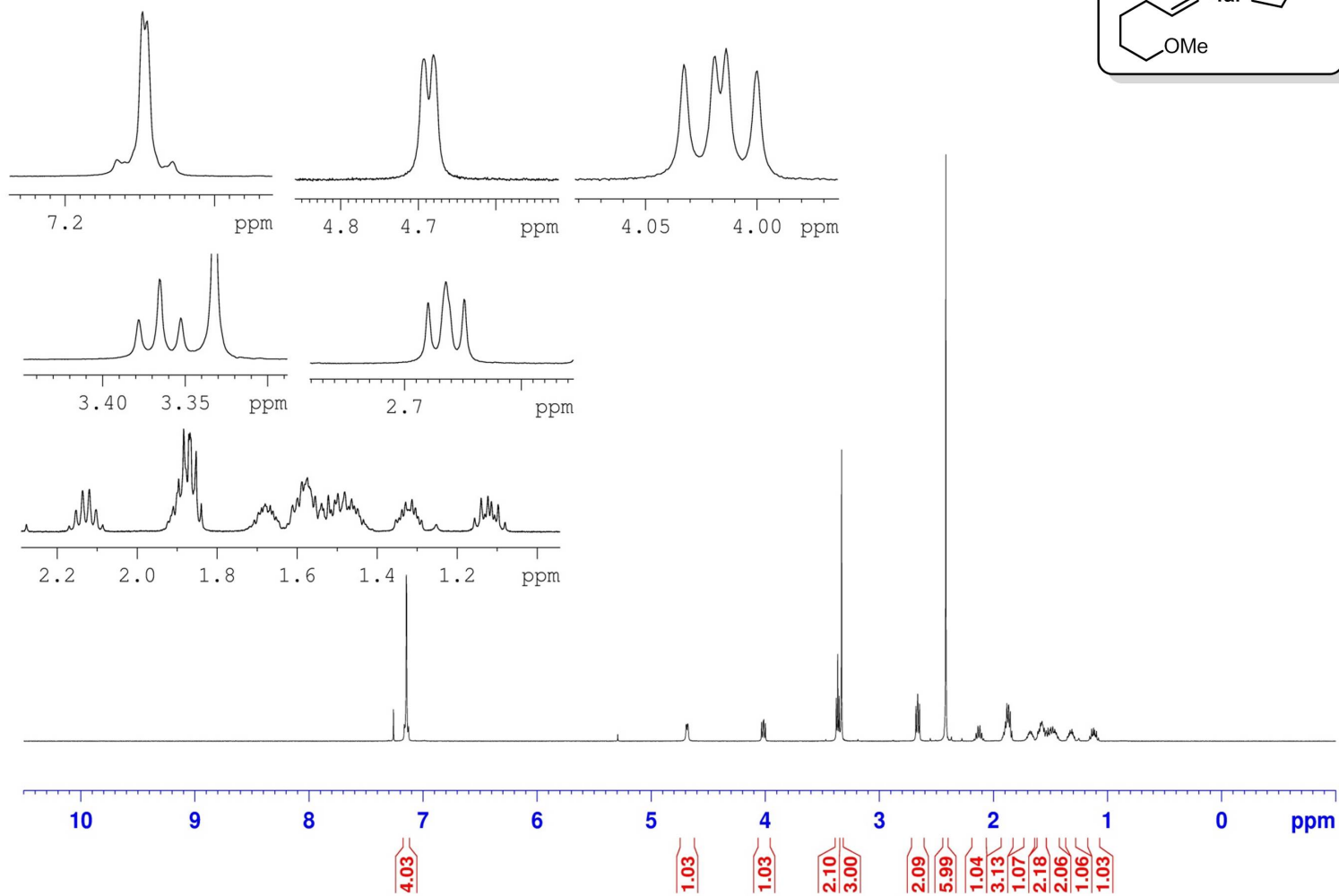
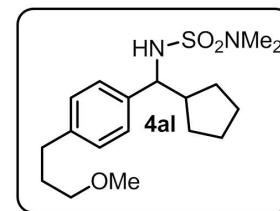
**N-((4-chlorophenyl)(cyclopentyl)methyl)methanesulfonamide**  
500 MHz, CDCl<sub>3</sub>



**N'-(4-bromophenyl)(cyclopentyl)methyl)-N,N-dimethylsulfamide**  
500 MHz, CDCl<sub>3</sub>

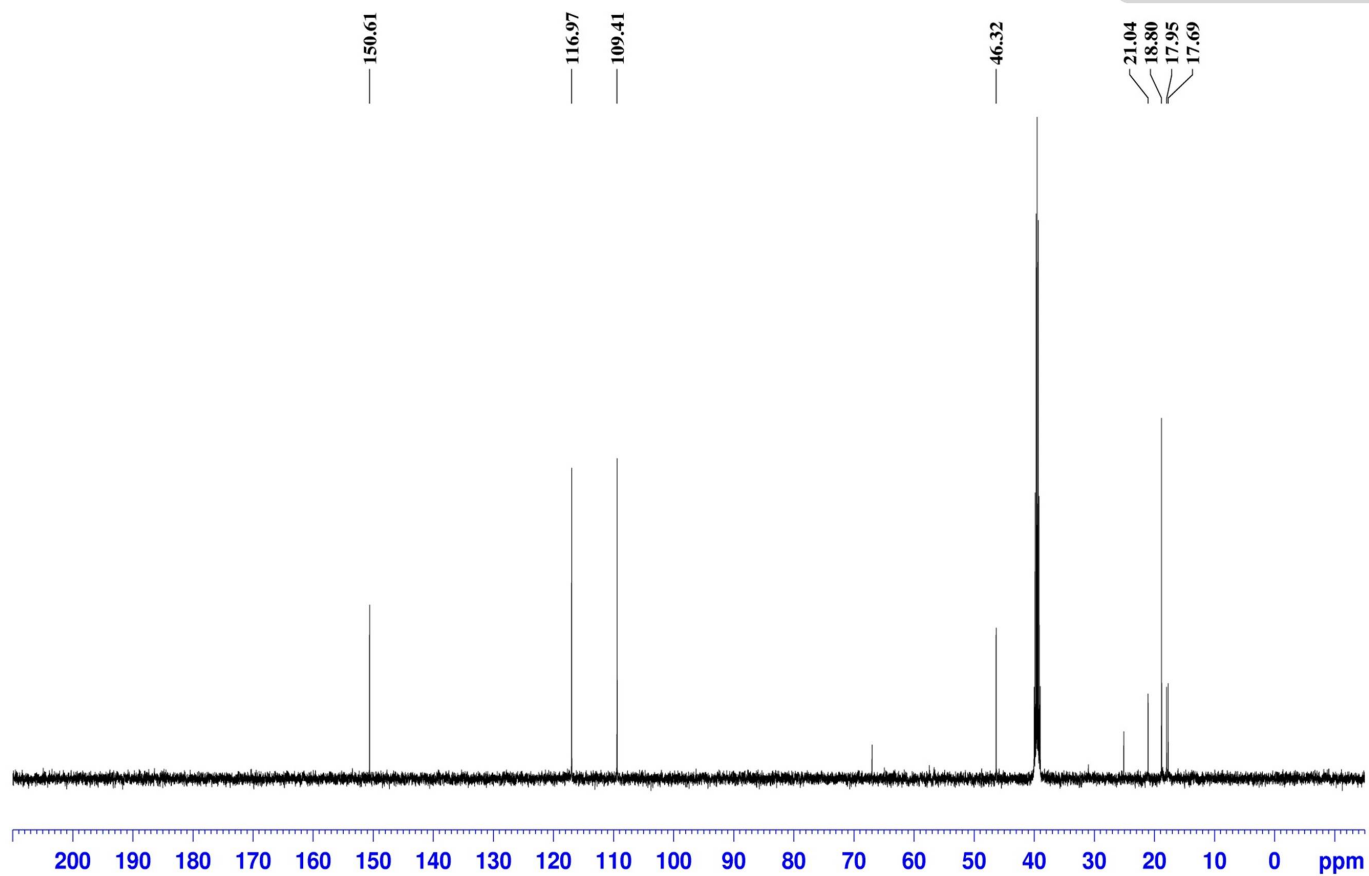
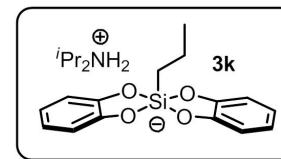


**N'-(cyclopentyl(4-(3-methoxypropyl)phenyl)methyl)-N,N-dimethylsulfamide**  
500 MHz, CDCl<sub>3</sub>



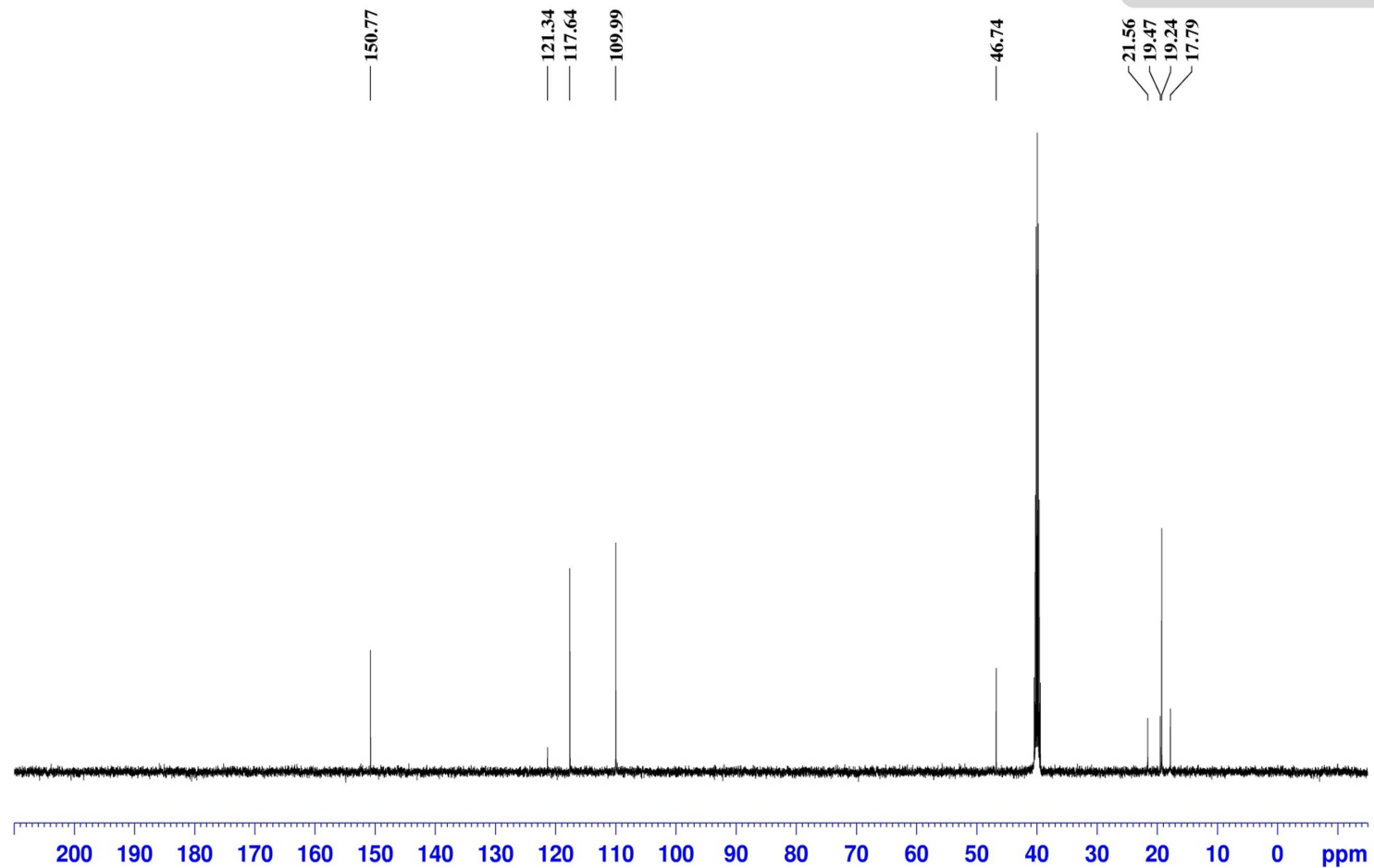
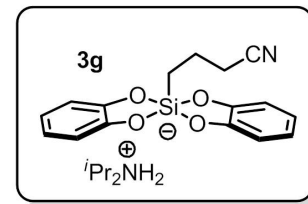
# $^{13}\text{C}$ NMR Spectra of Synthesized Compounds

Diisopropylammonium Bis(catecholato)propylsilicate  
125 MHz, DMSO-d6

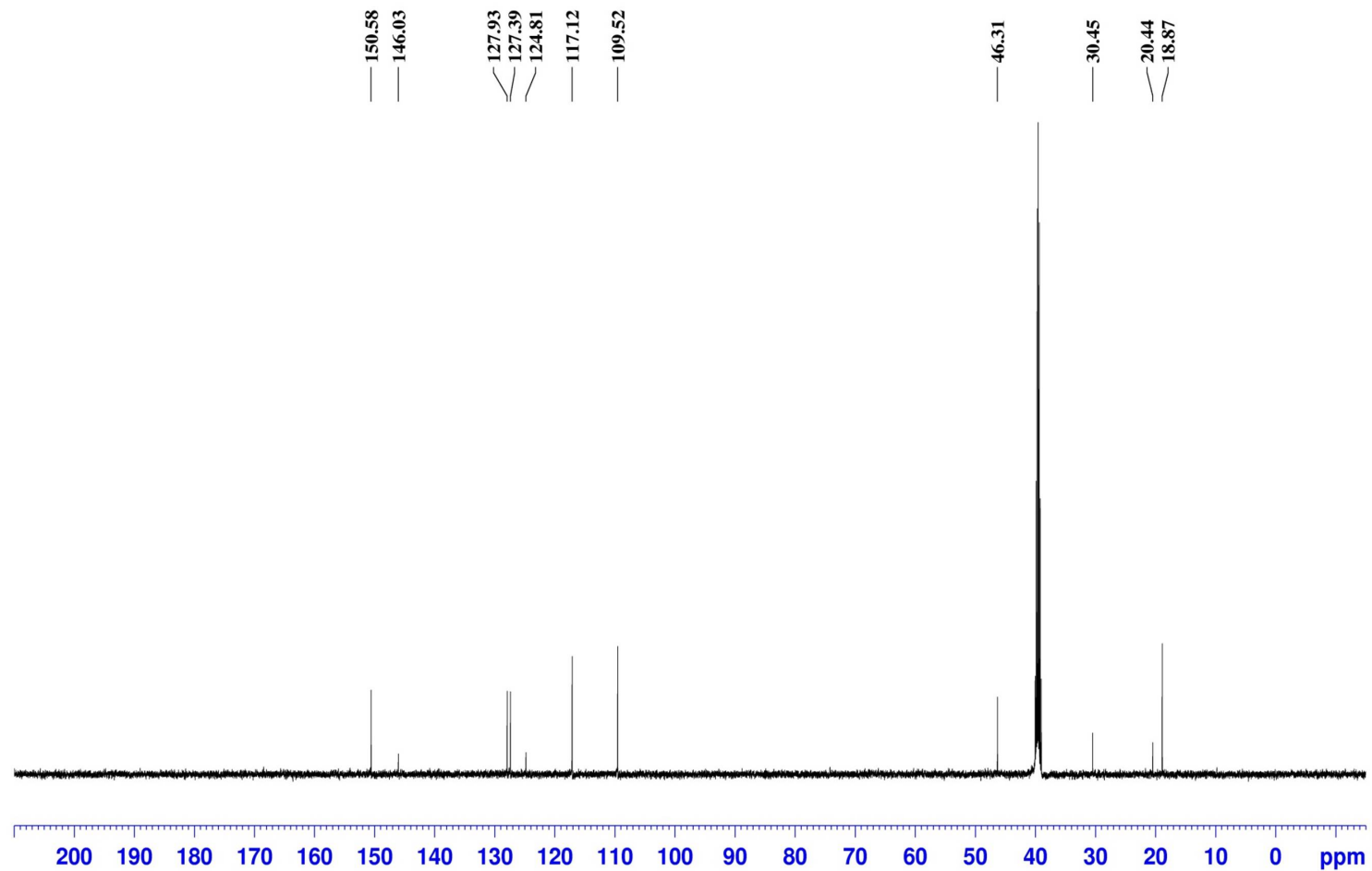
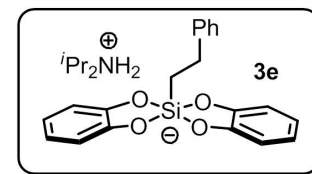




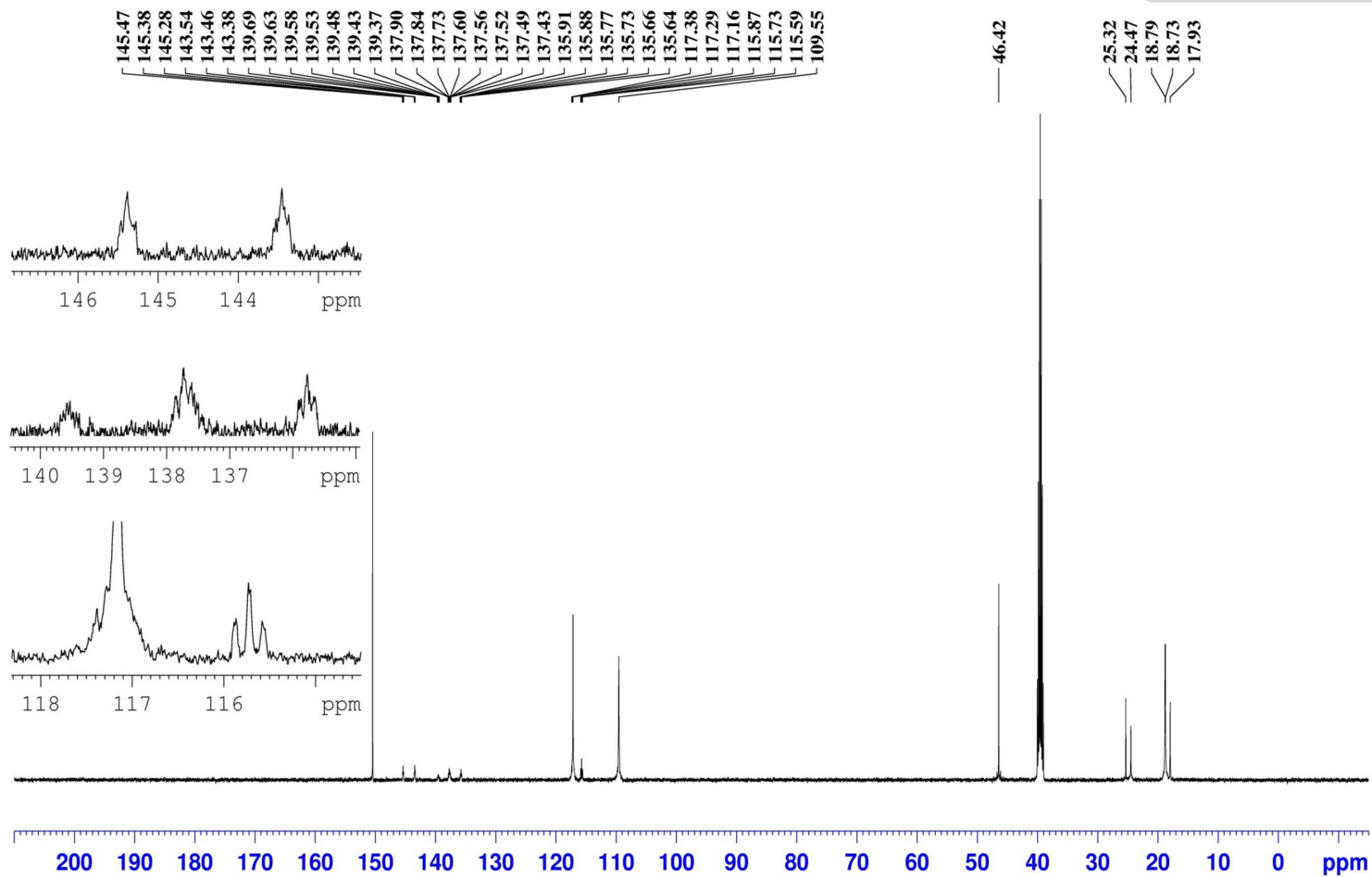
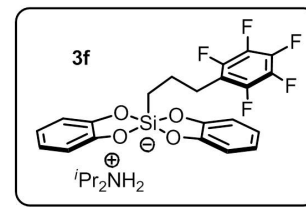
Diisopropylammonium Bis(catecholato)(3-cyanopropyl)silicate  
125 MHz, DMSO-d6



Diisopropylammonium Bis(catecholato)(2-phenylethyl)silicate  
125 MHz, DMSO-d6

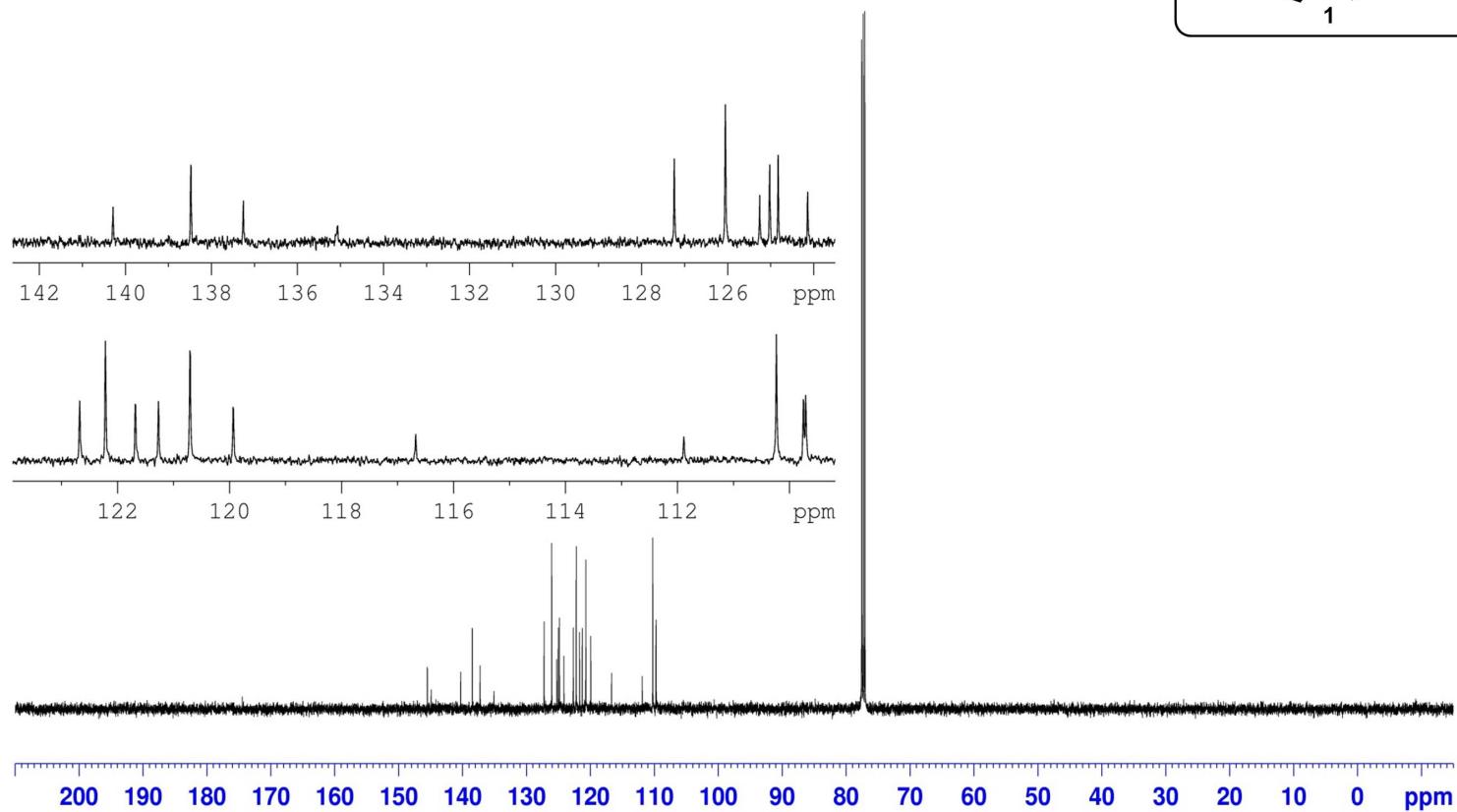


Diisopropylammonium Bis(catecholato) (3-pentafluorophenylpropyl)silicate  
125 MHz, DMSO-d6

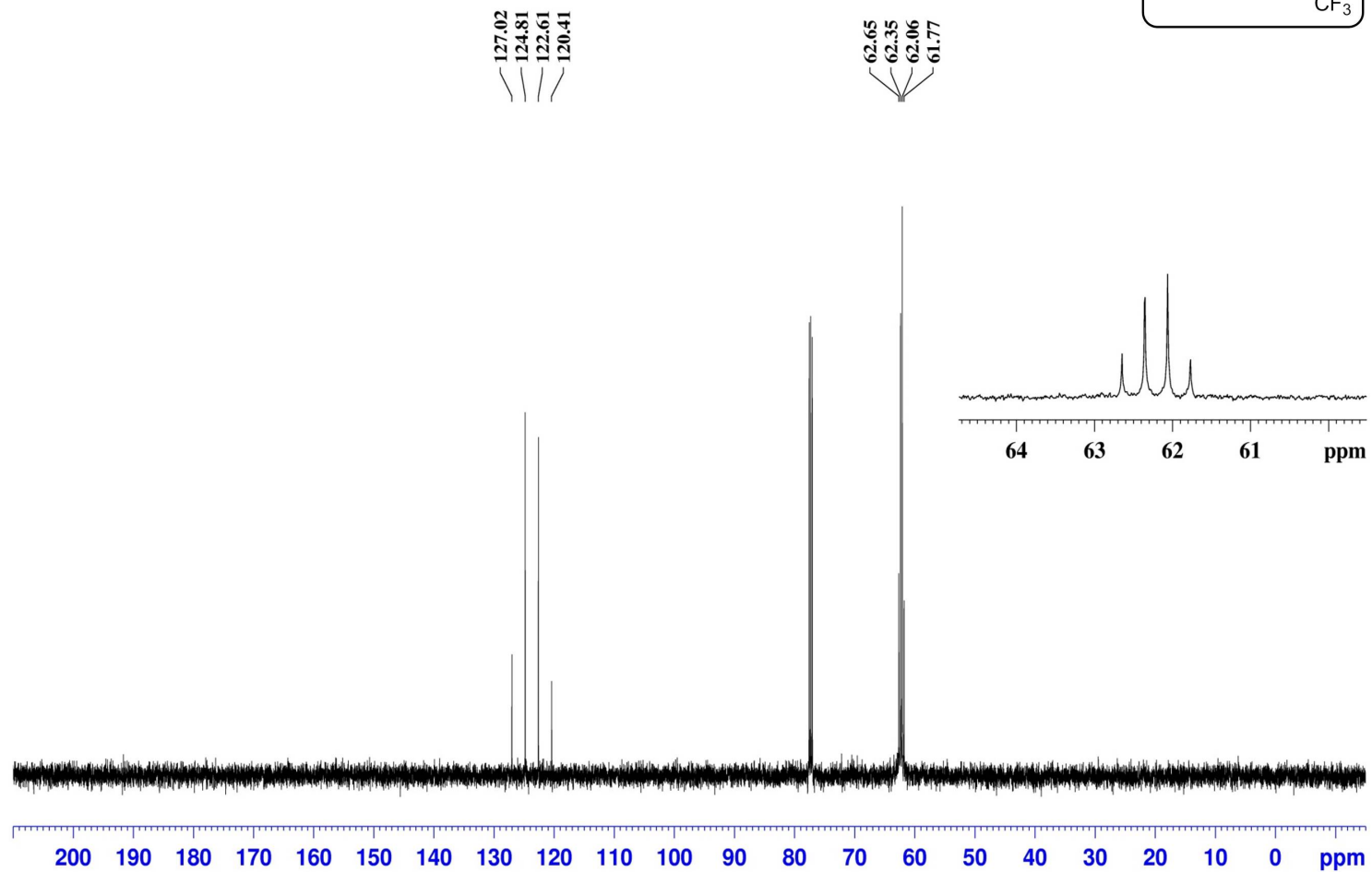
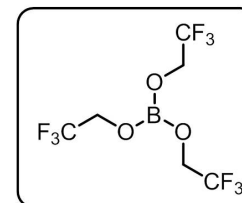


2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile  
125 MHz, CDCl<sub>3</sub>

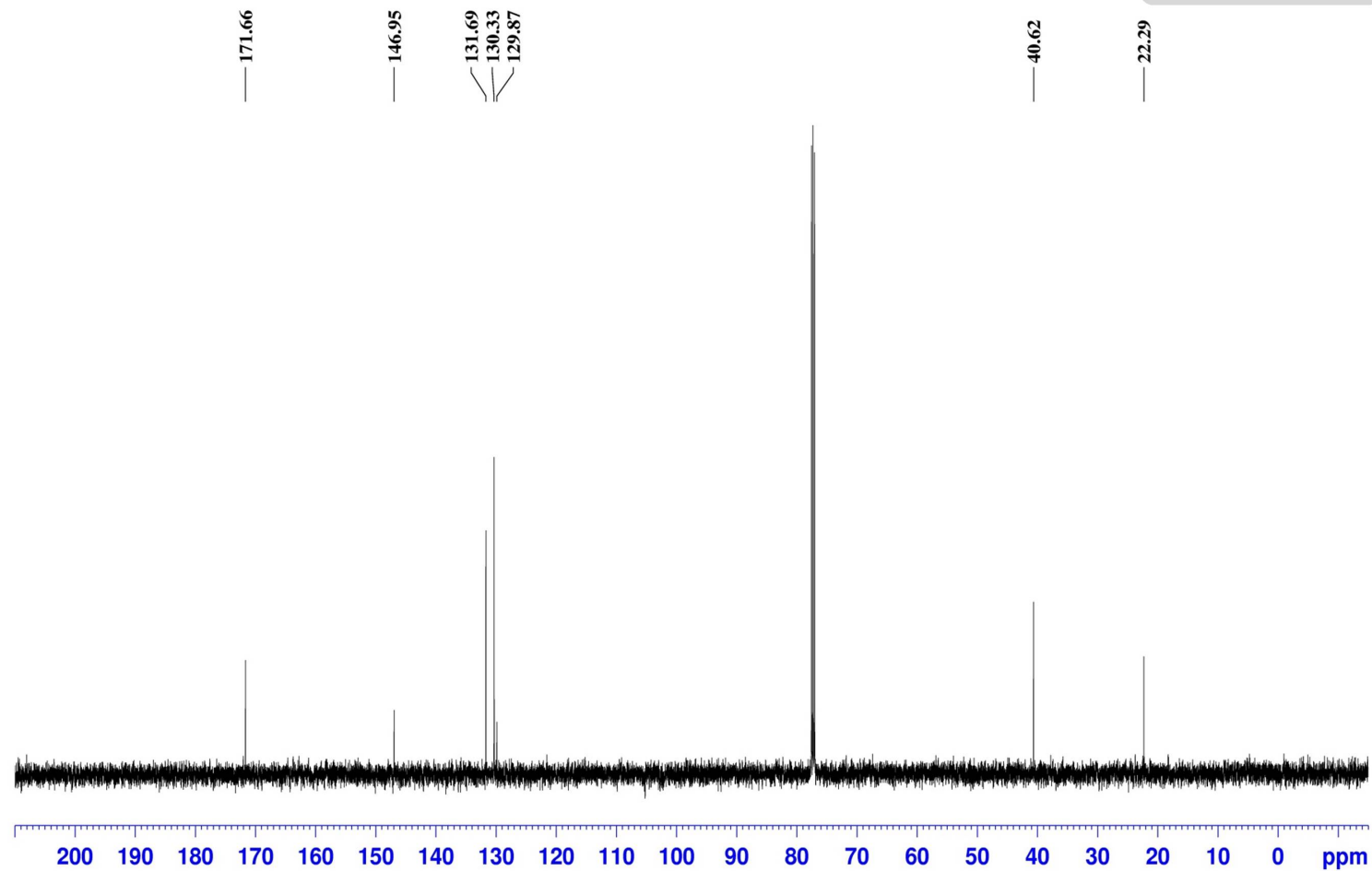
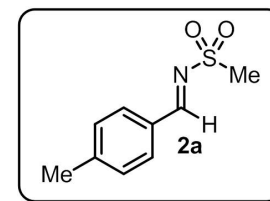
145.51  
144.91  
140.29  
138.48  
137.26  
135.07  
127.24  
126.05  
125.25  
125.02  
124.83  
124.14  
122.67  
122.21  
121.68  
121.27  
120.70  
119.93  
116.67  
111.89  
110.23  
109.75  
109.71



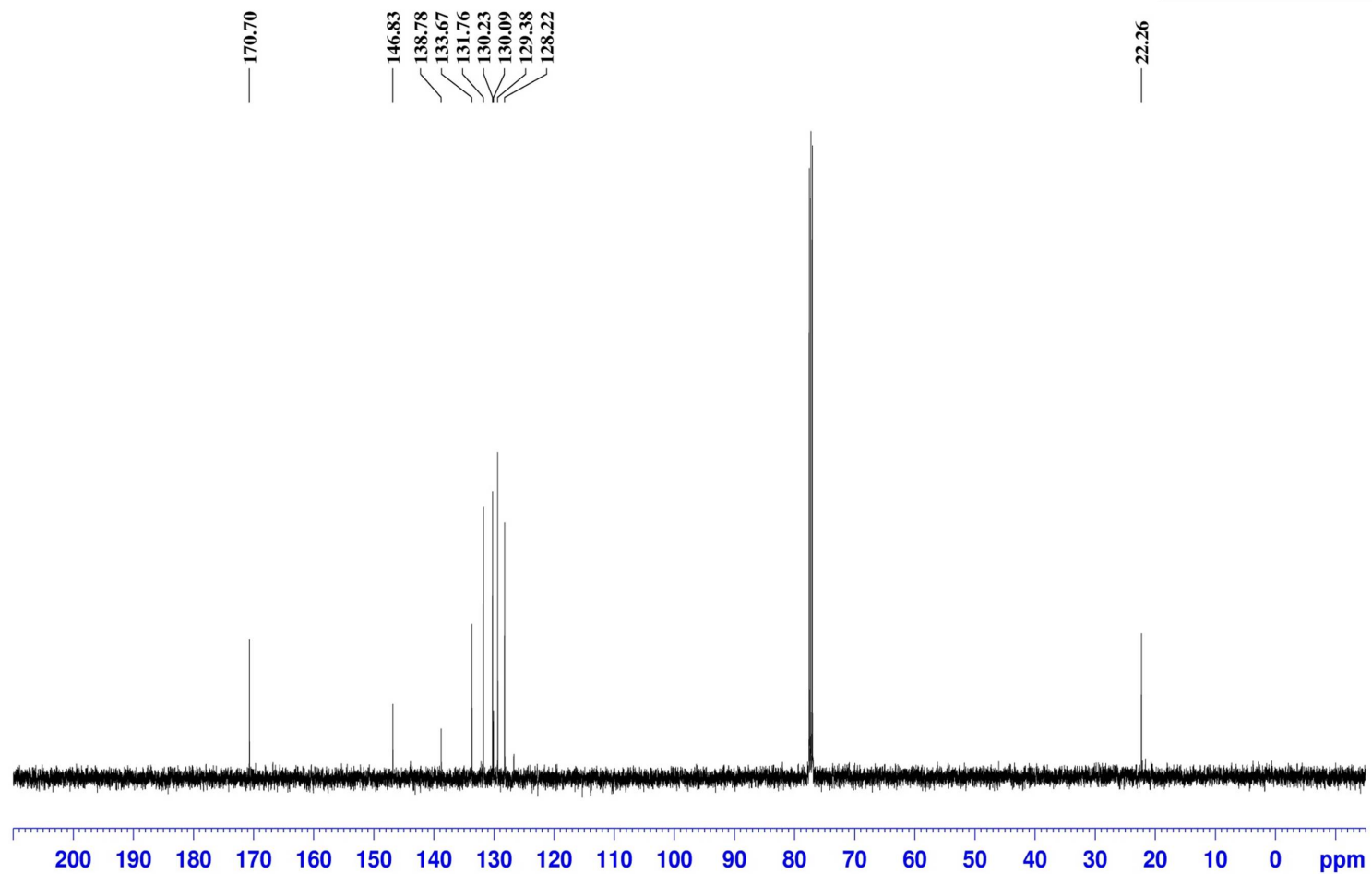
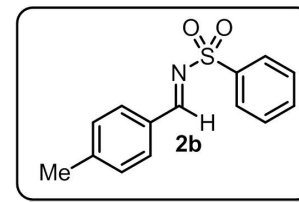
Tris(2,2,2-trifluoroethyl) borate  
125 MHz, CDCl<sub>3</sub>



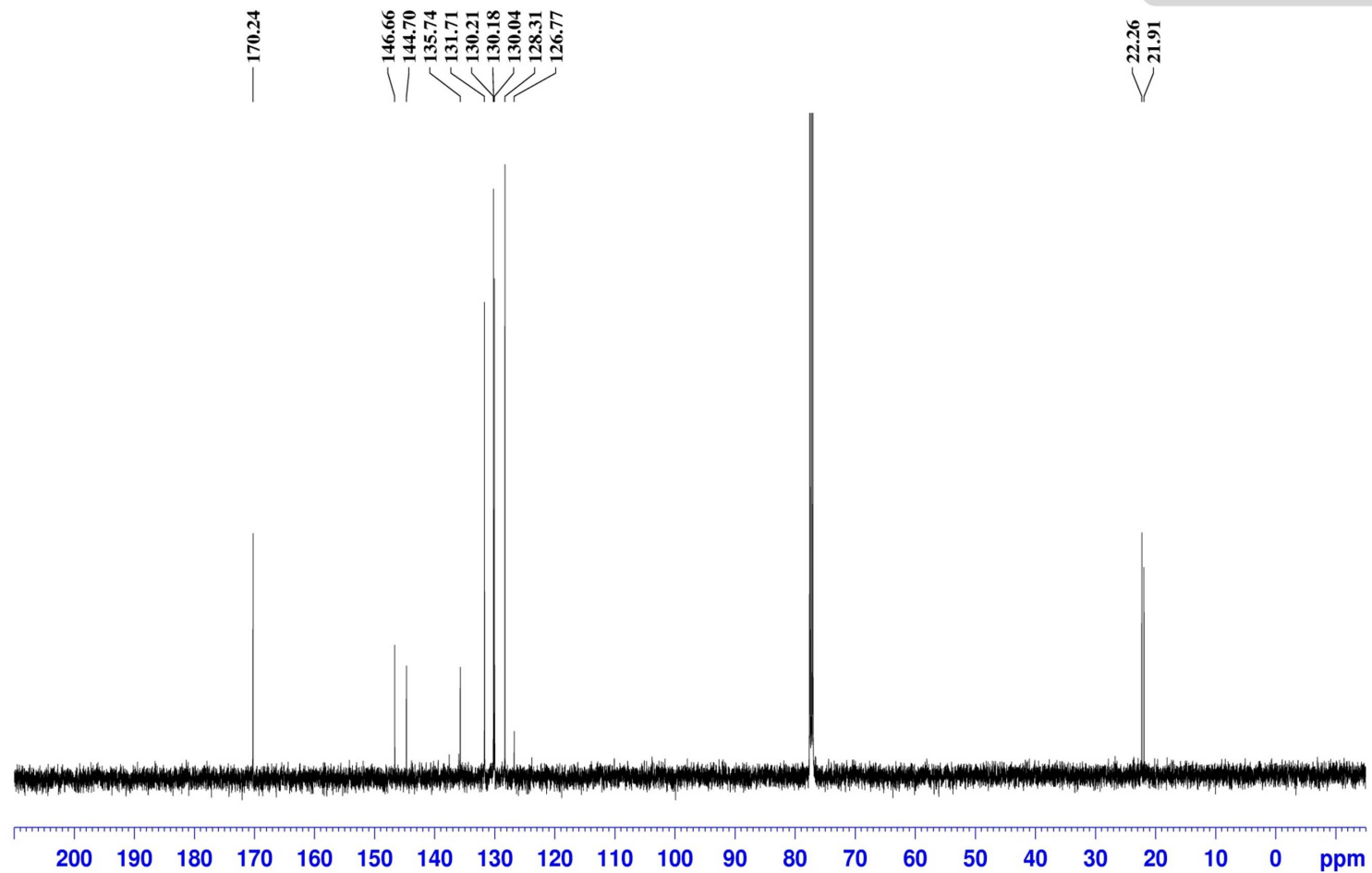
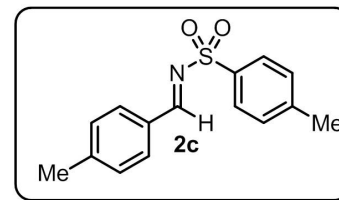
N-(4-methylbenzylidene)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



N-(4-methylbenzylidene)aniline  
125 MHz, CDCl<sub>3</sub>

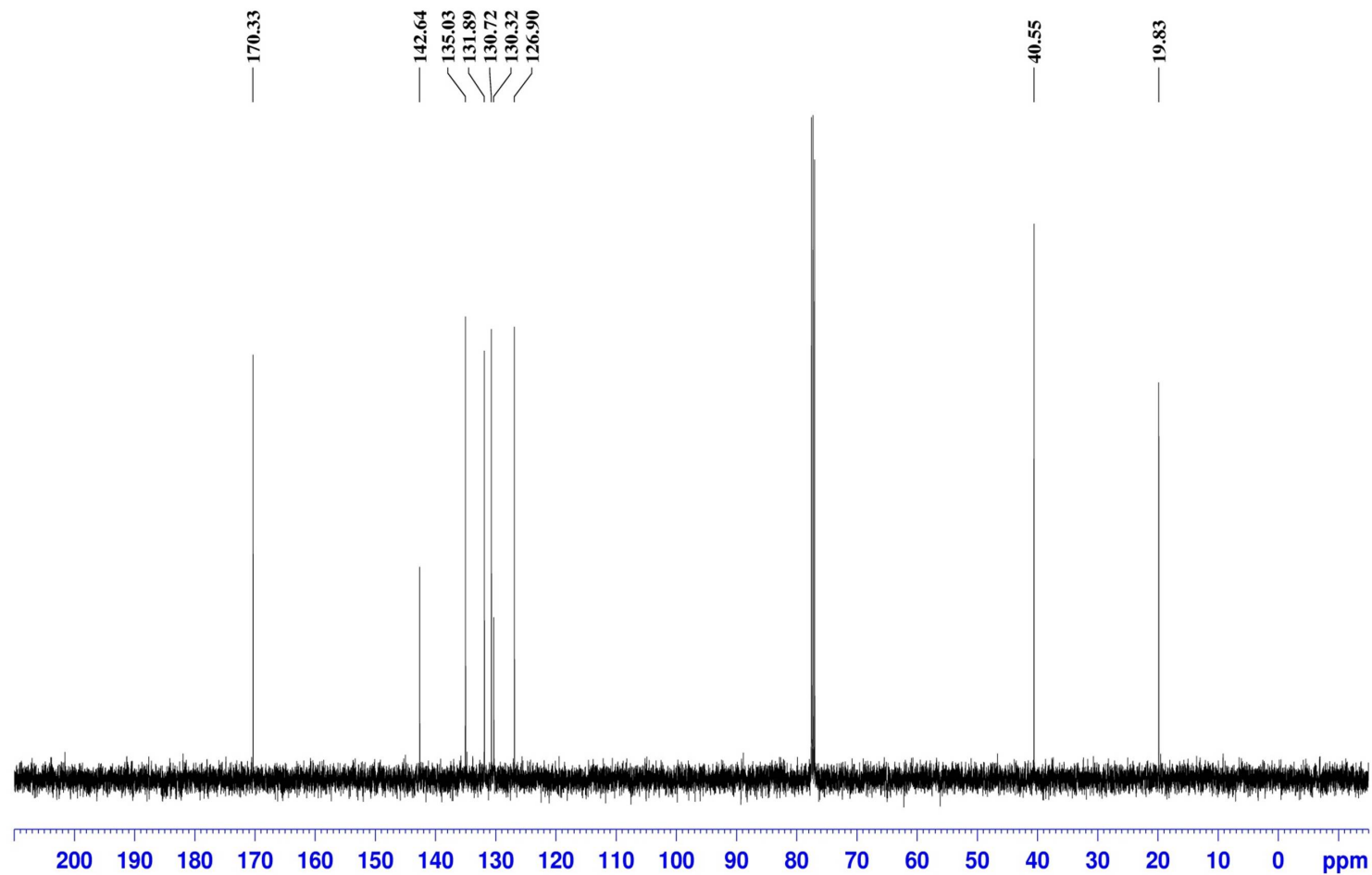
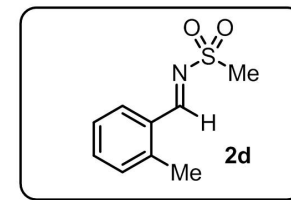


4-methyl-N-(4-methylbenzylidene)benzenesulfonamide  
125 MHz, CDCl<sub>3</sub>

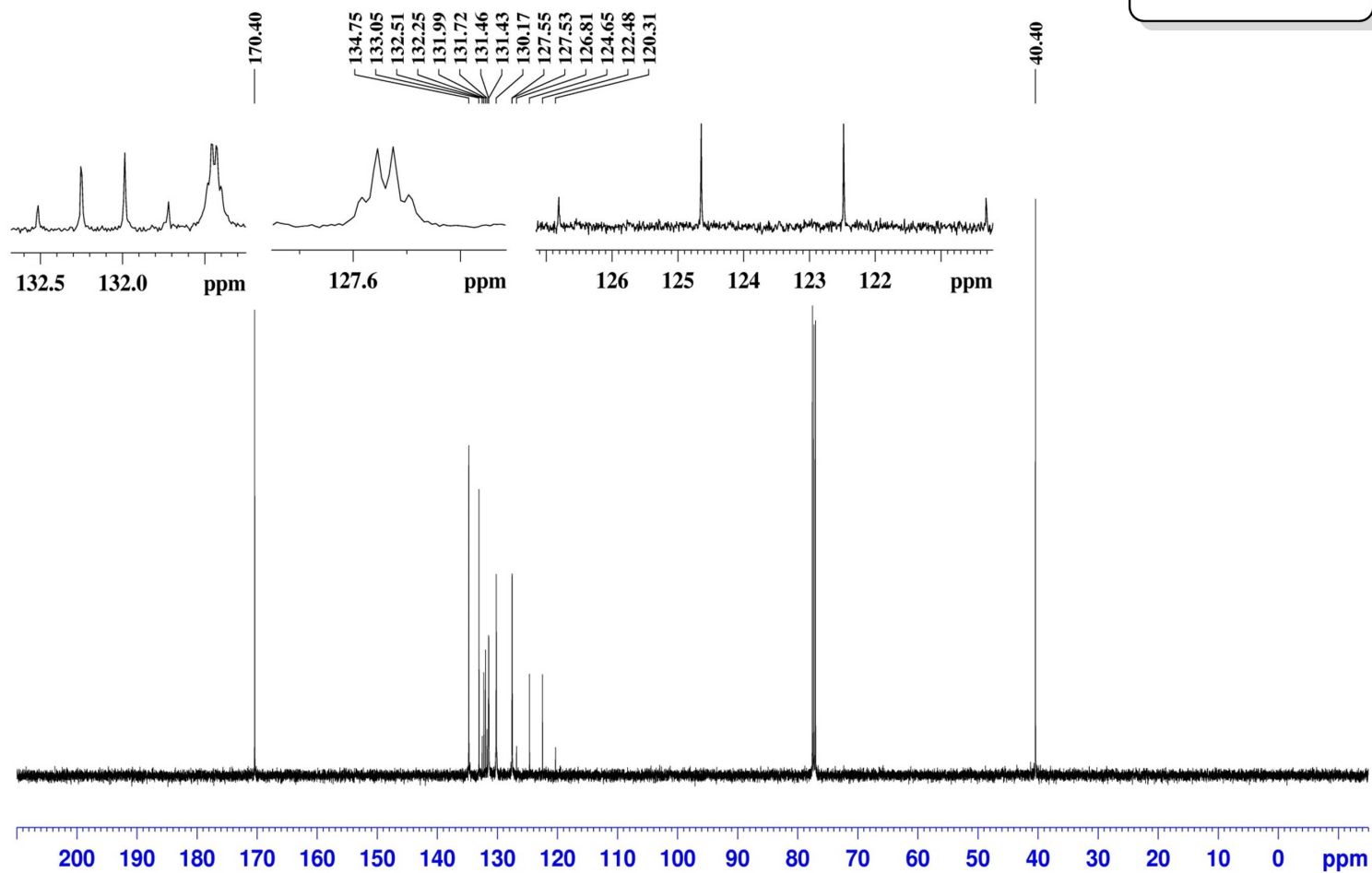
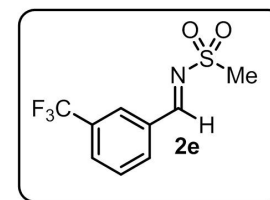




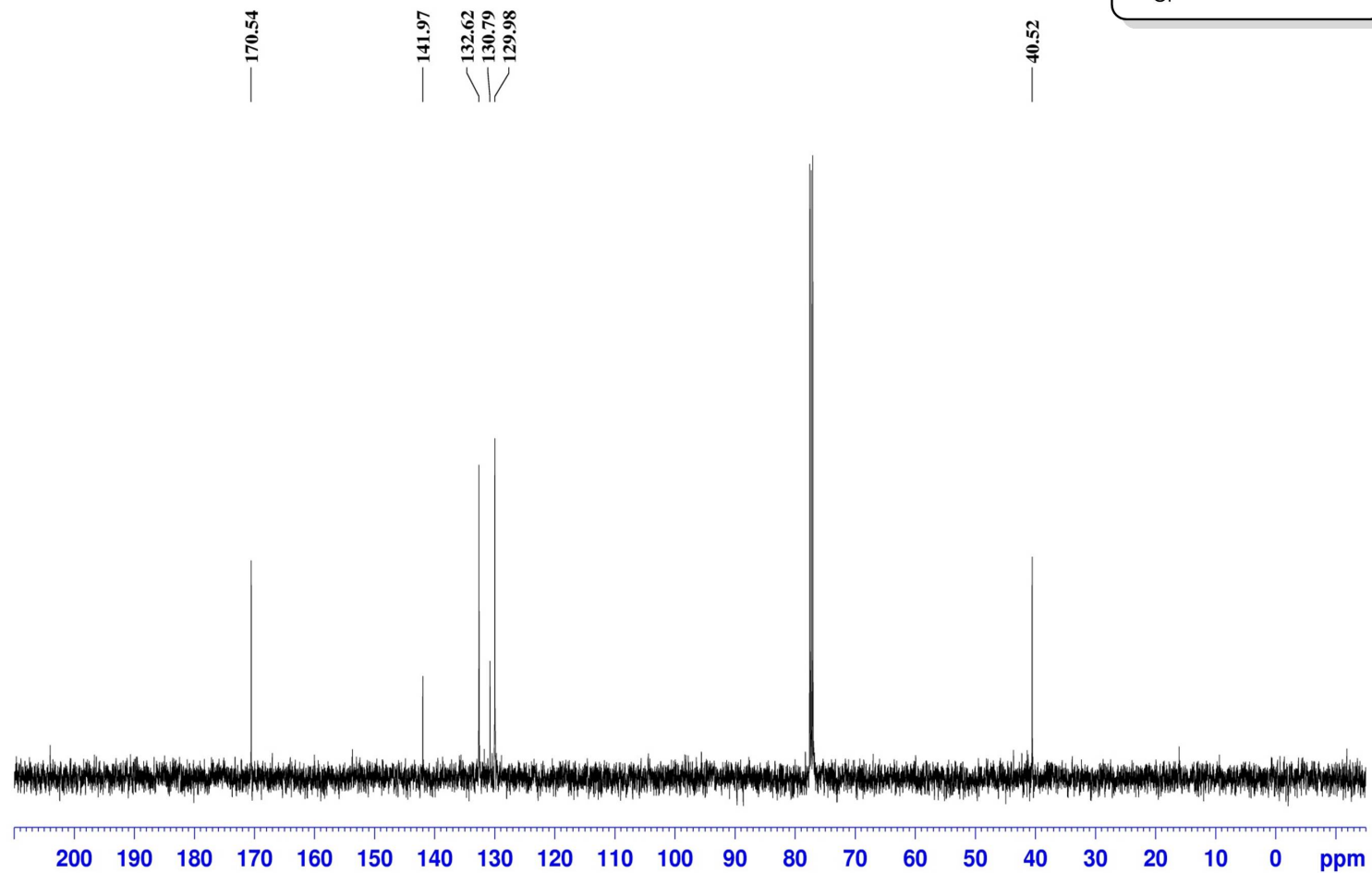
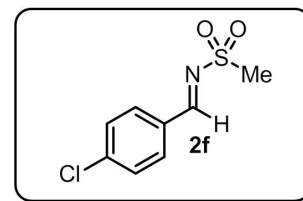
N-(2-methylbenzylidene)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



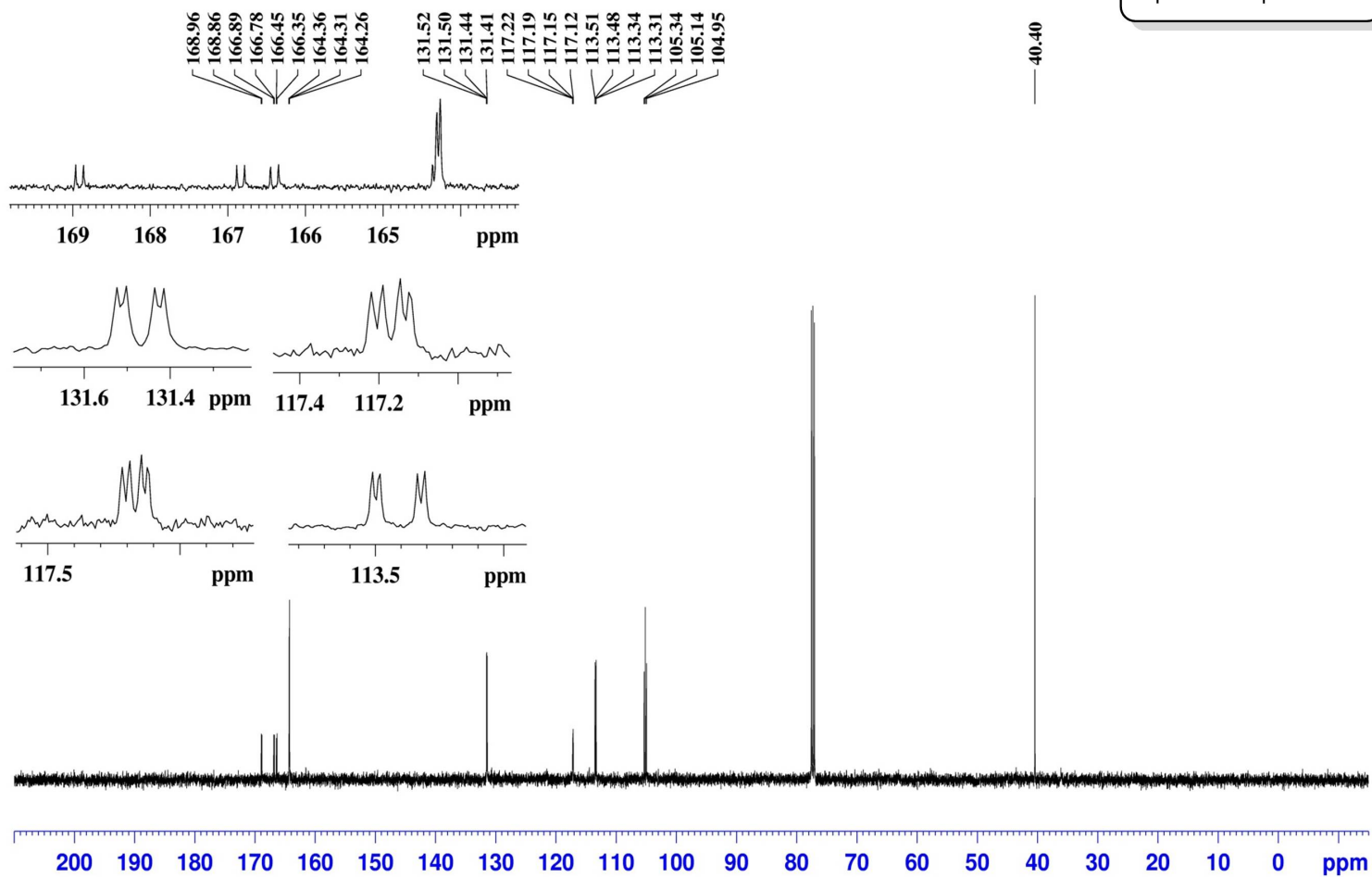
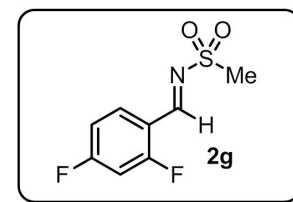
N-(3-(trifluoromethyl)benzylidene)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



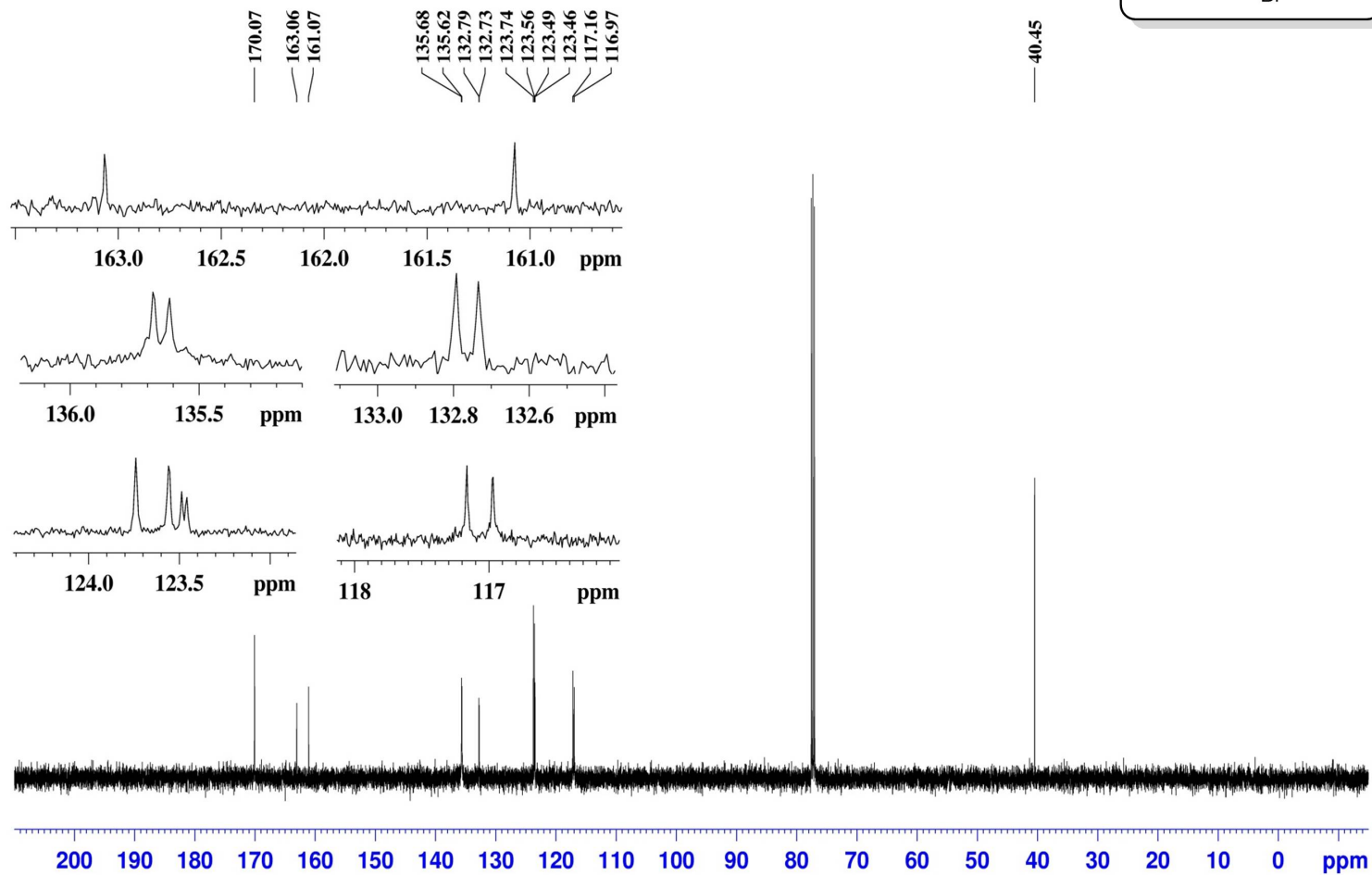
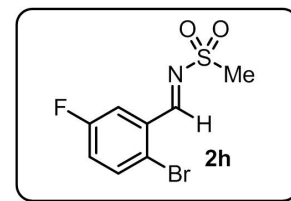
N-(4-chlorobenzylidene)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



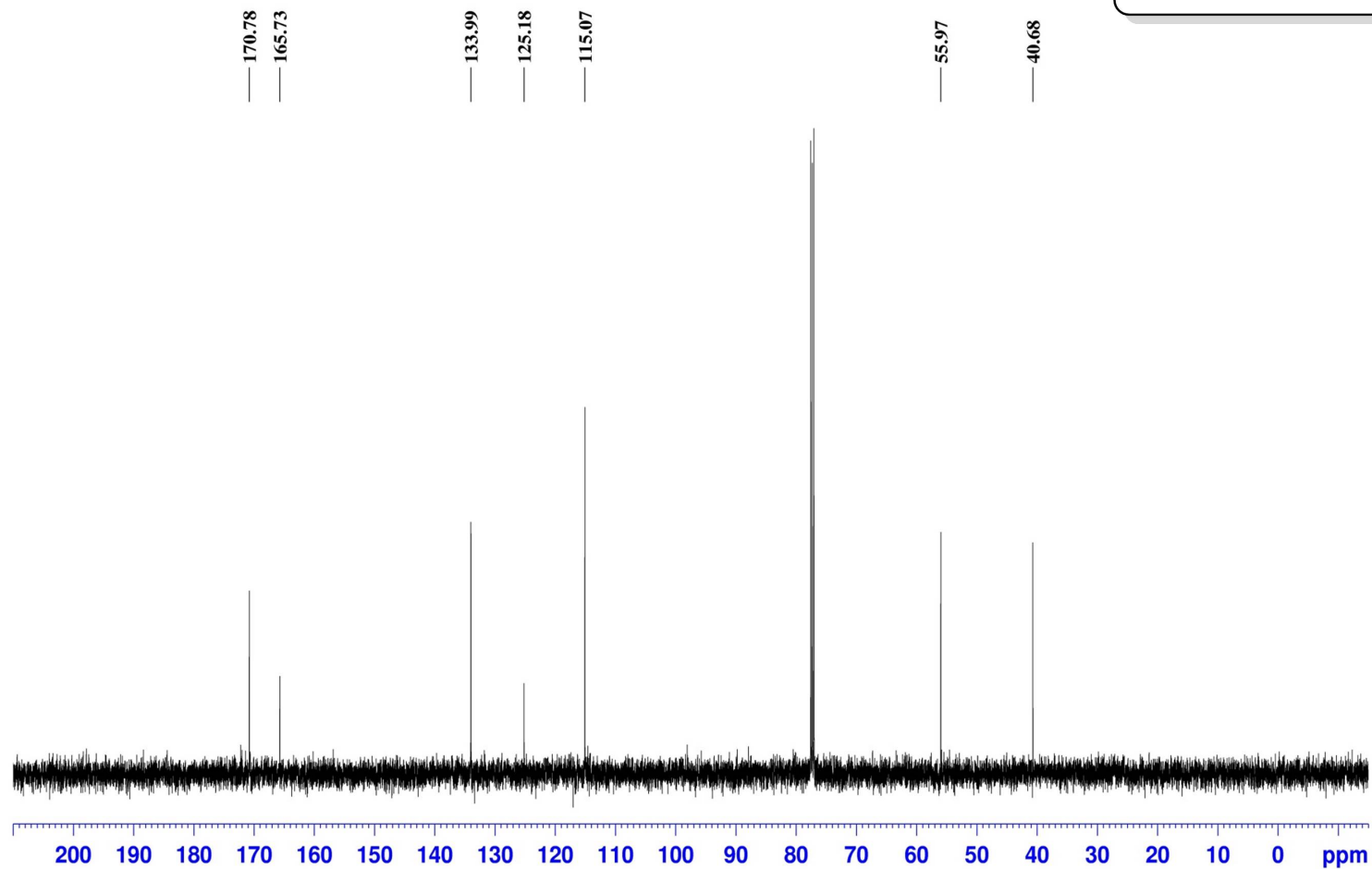
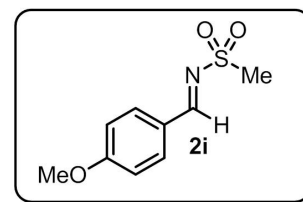
N-(2,4-difluorobenzylidene)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



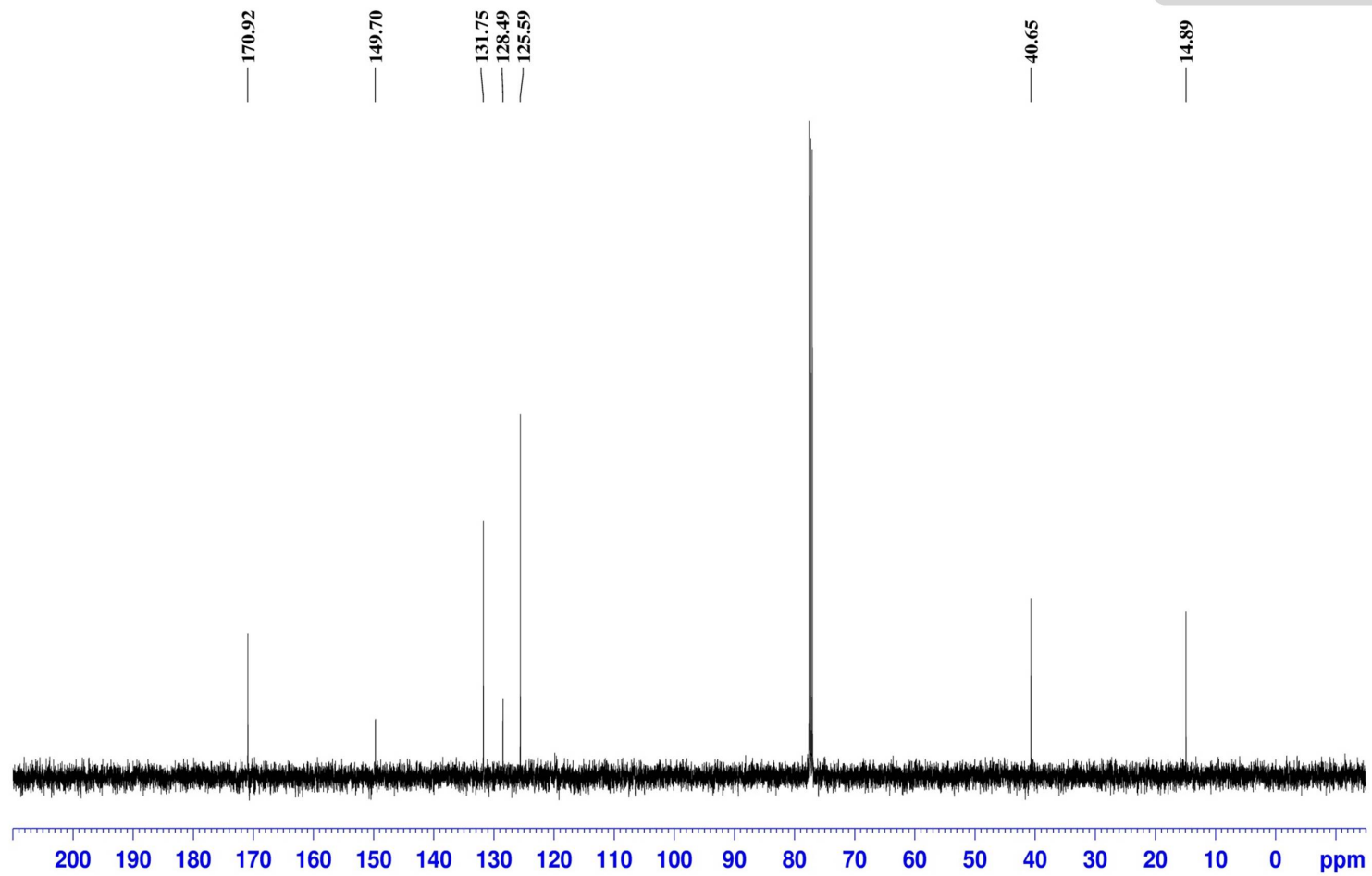
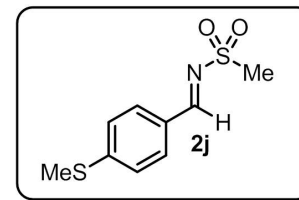
N-(2-bromo-5-fluorobenzylidene)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



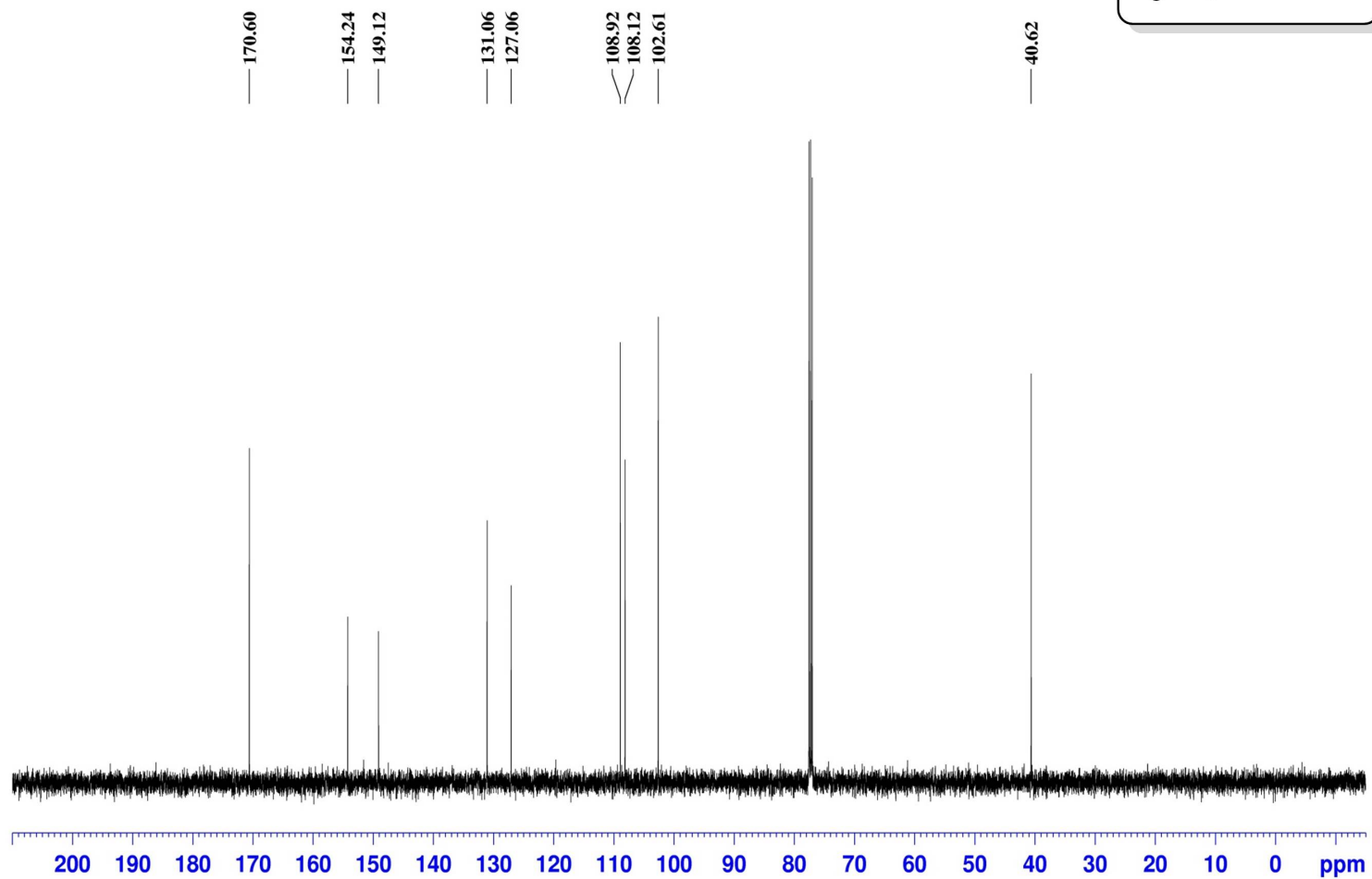
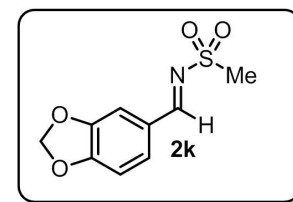
N-(4-methoxybenzylidene)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



N-(4-(methylthio)benzylidene)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>

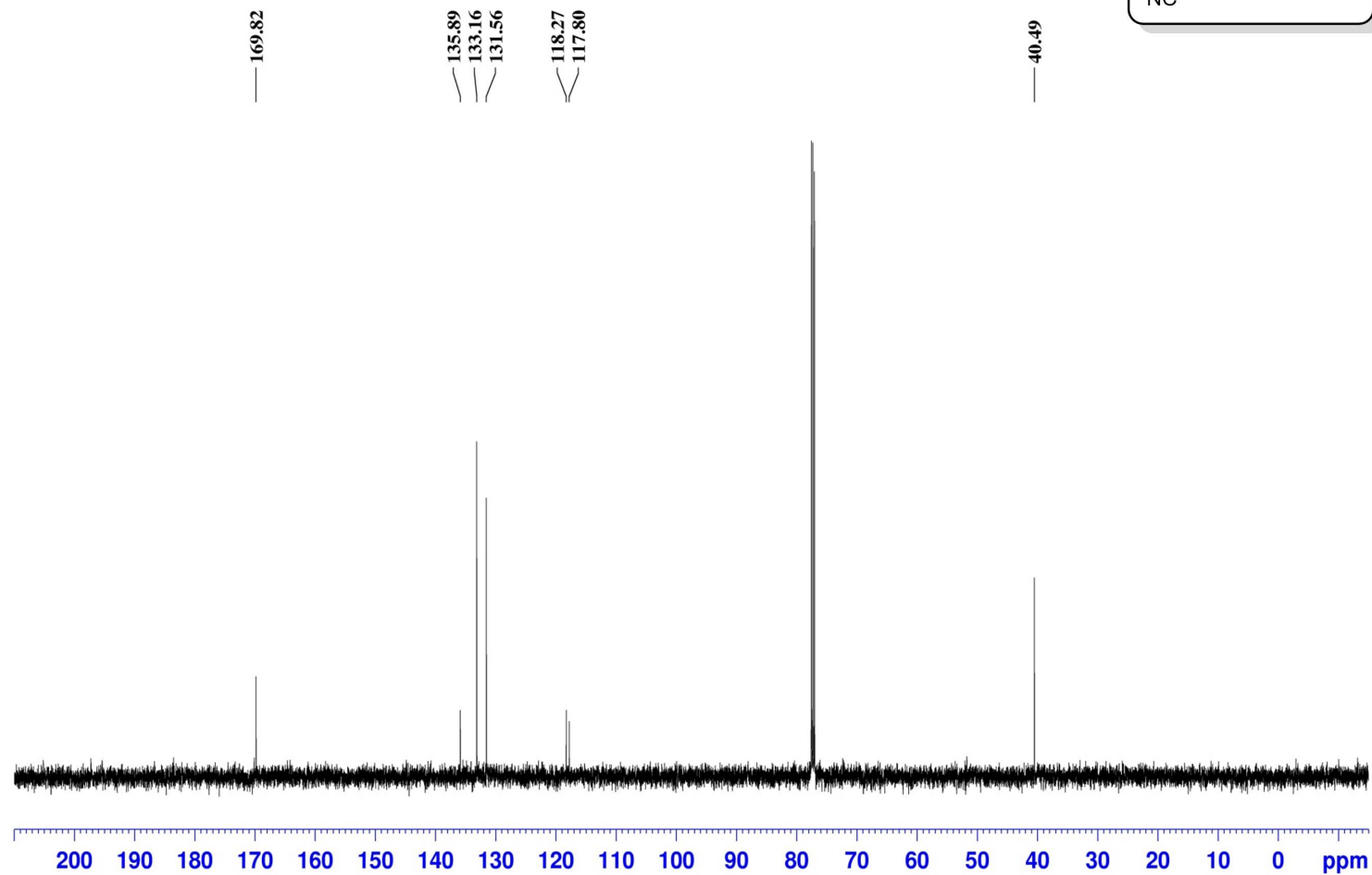
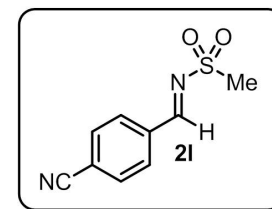


N-(benzo[d][1,3]dioxol-5-ylmethylene)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>

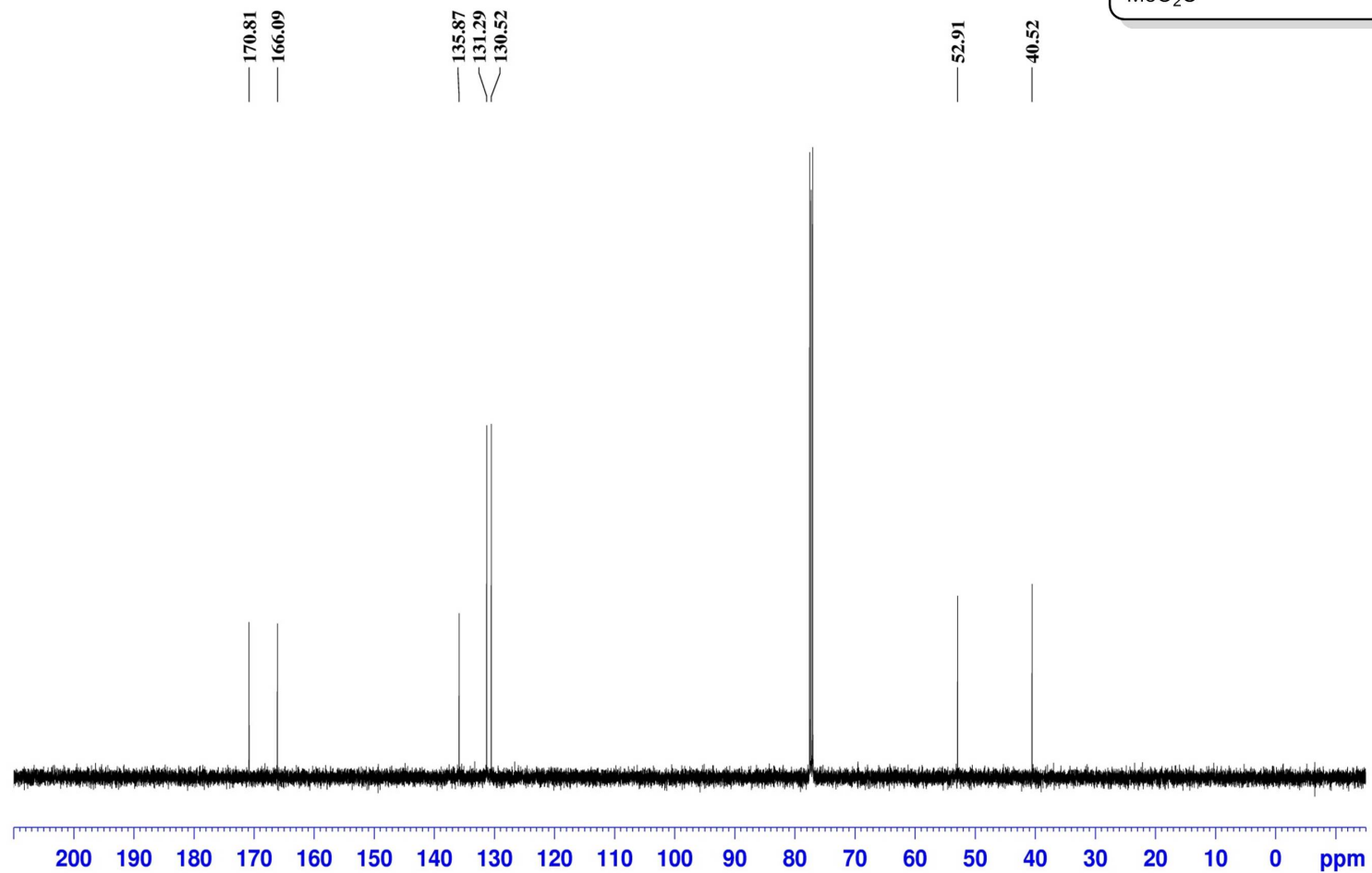
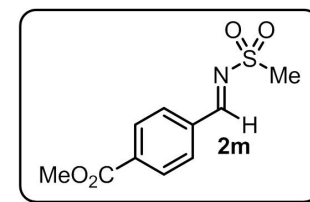




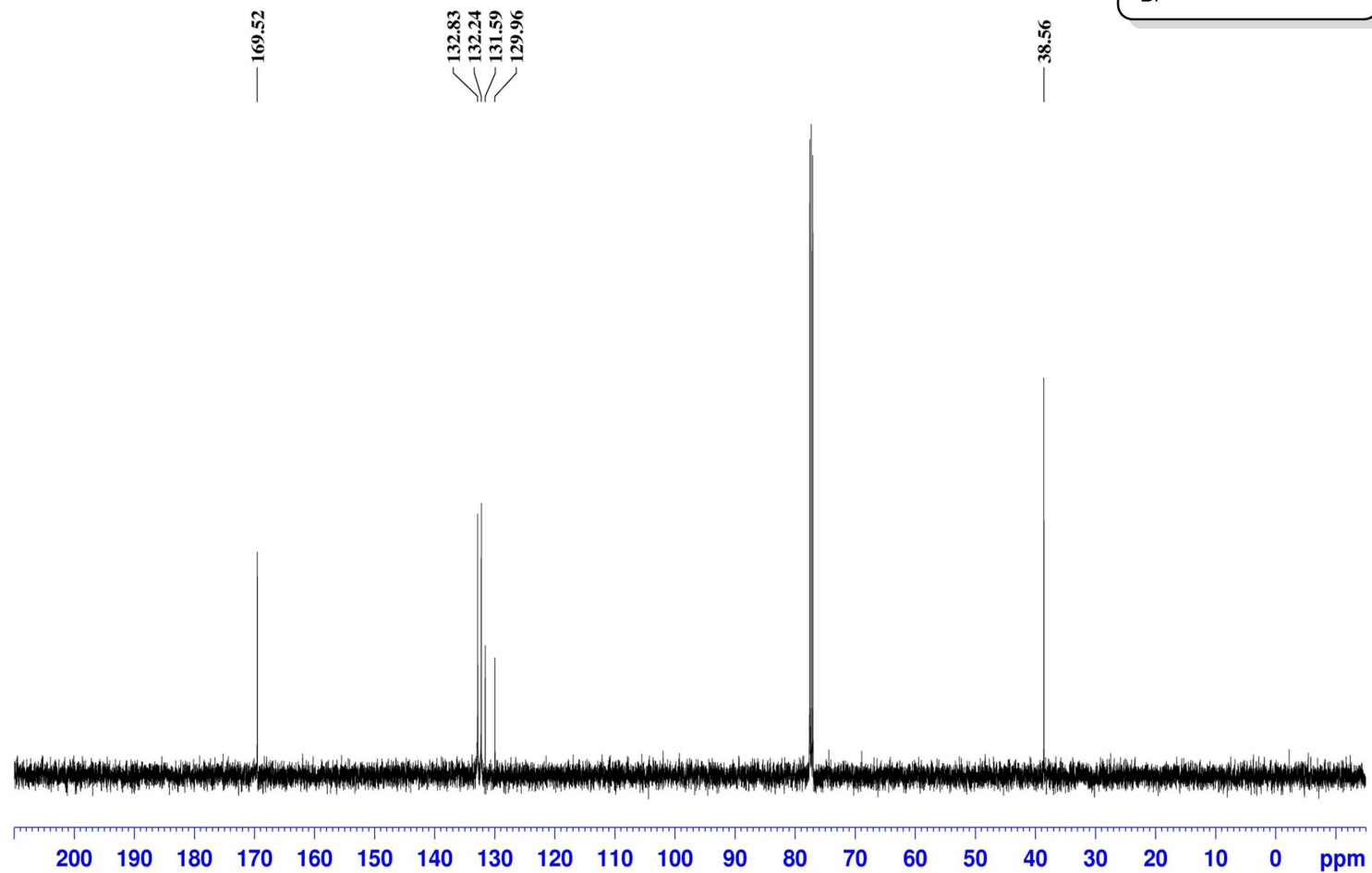
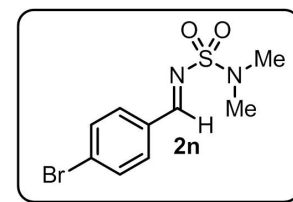
N-(4-cyanobenzylidene)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



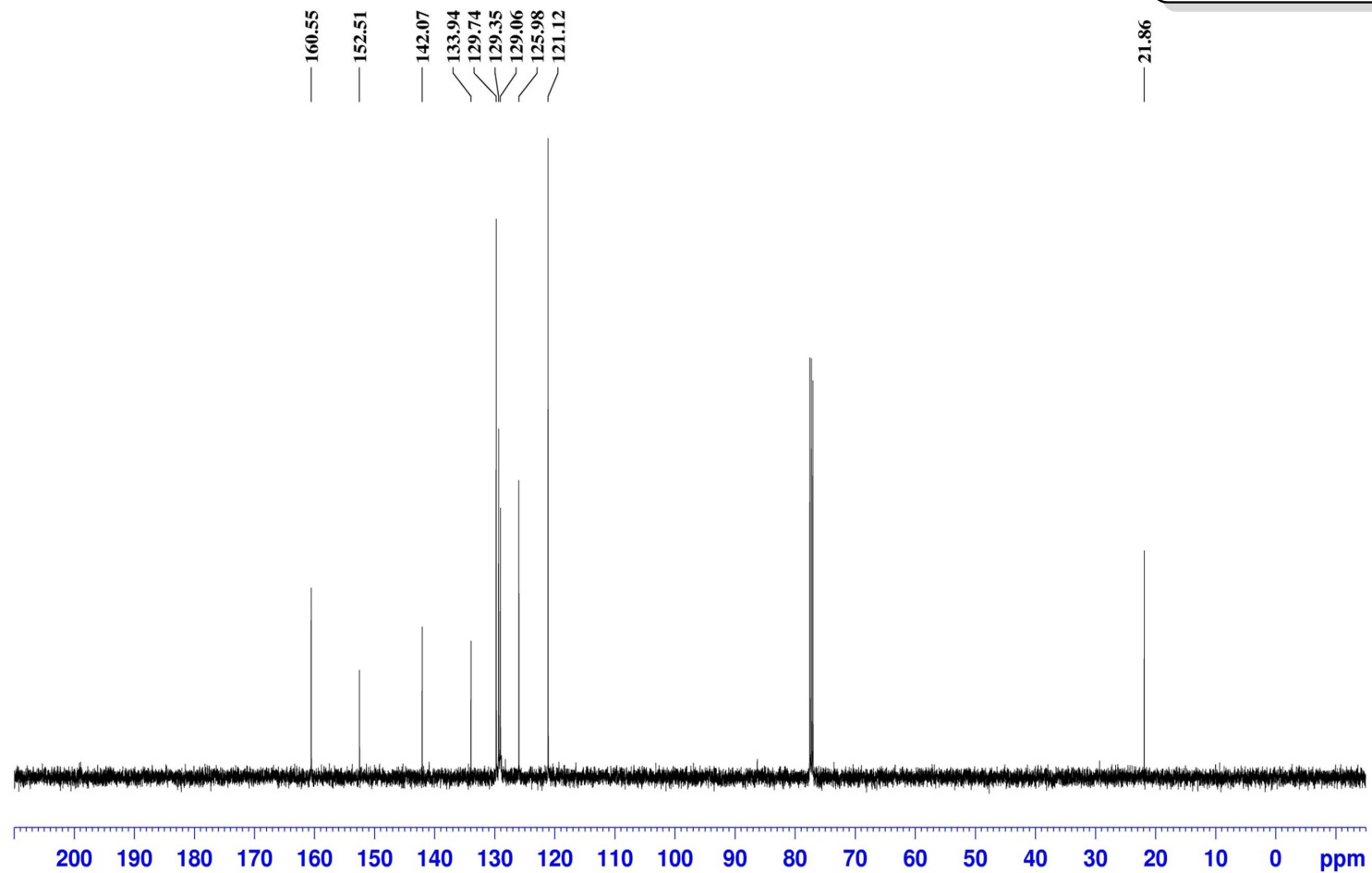
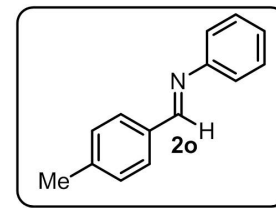
methyl 4-(((methylsulfonyl)imino)methyl)benzoate  
125 MHz, CDCl<sub>3</sub>



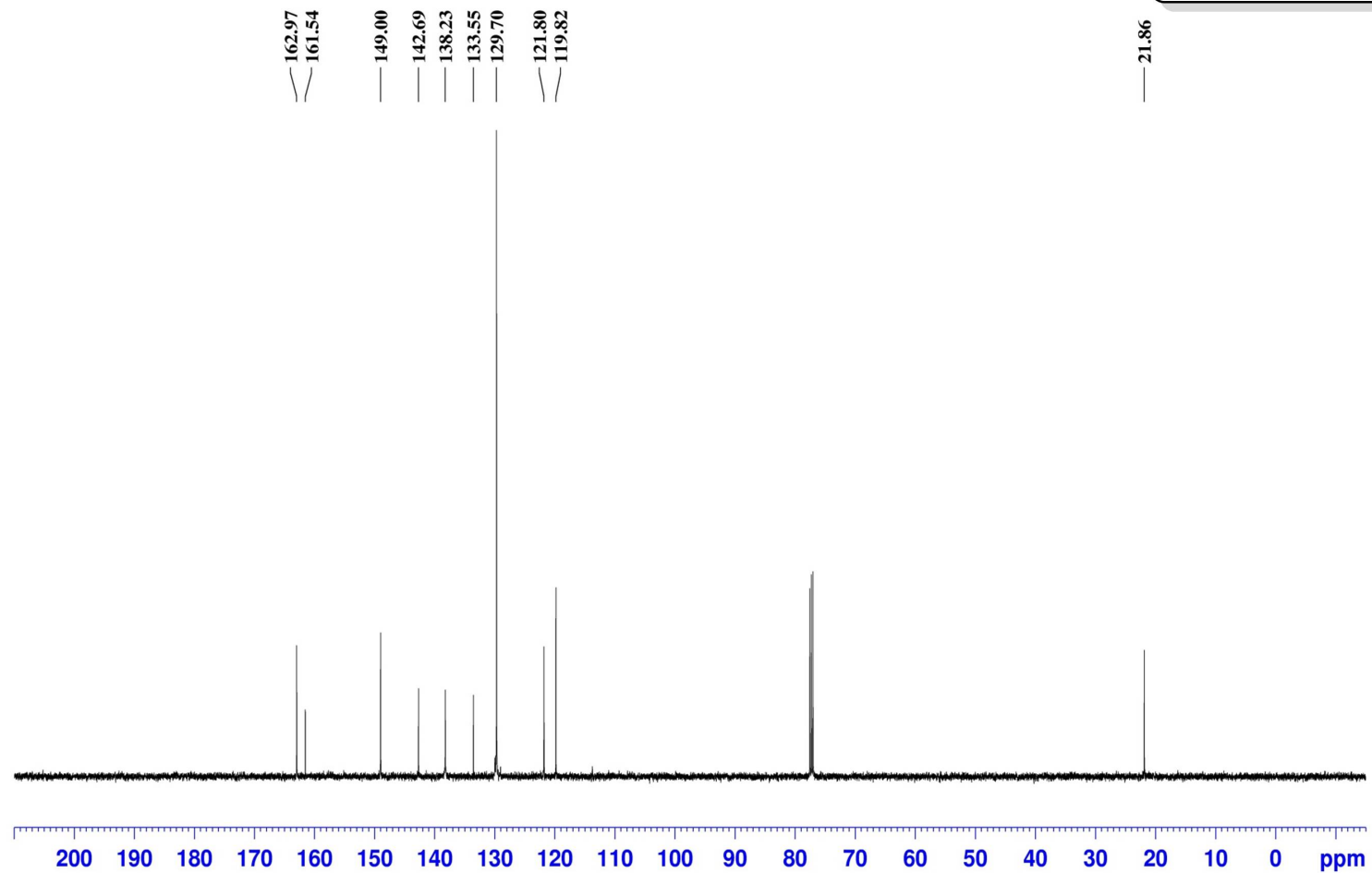
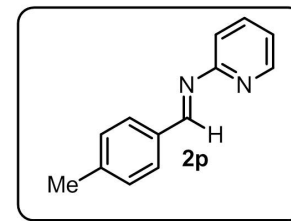
N'-(4-Bromobenzylidene)-N,N-dimethylsulfamide  
125 MHz, CDCl<sub>3</sub>



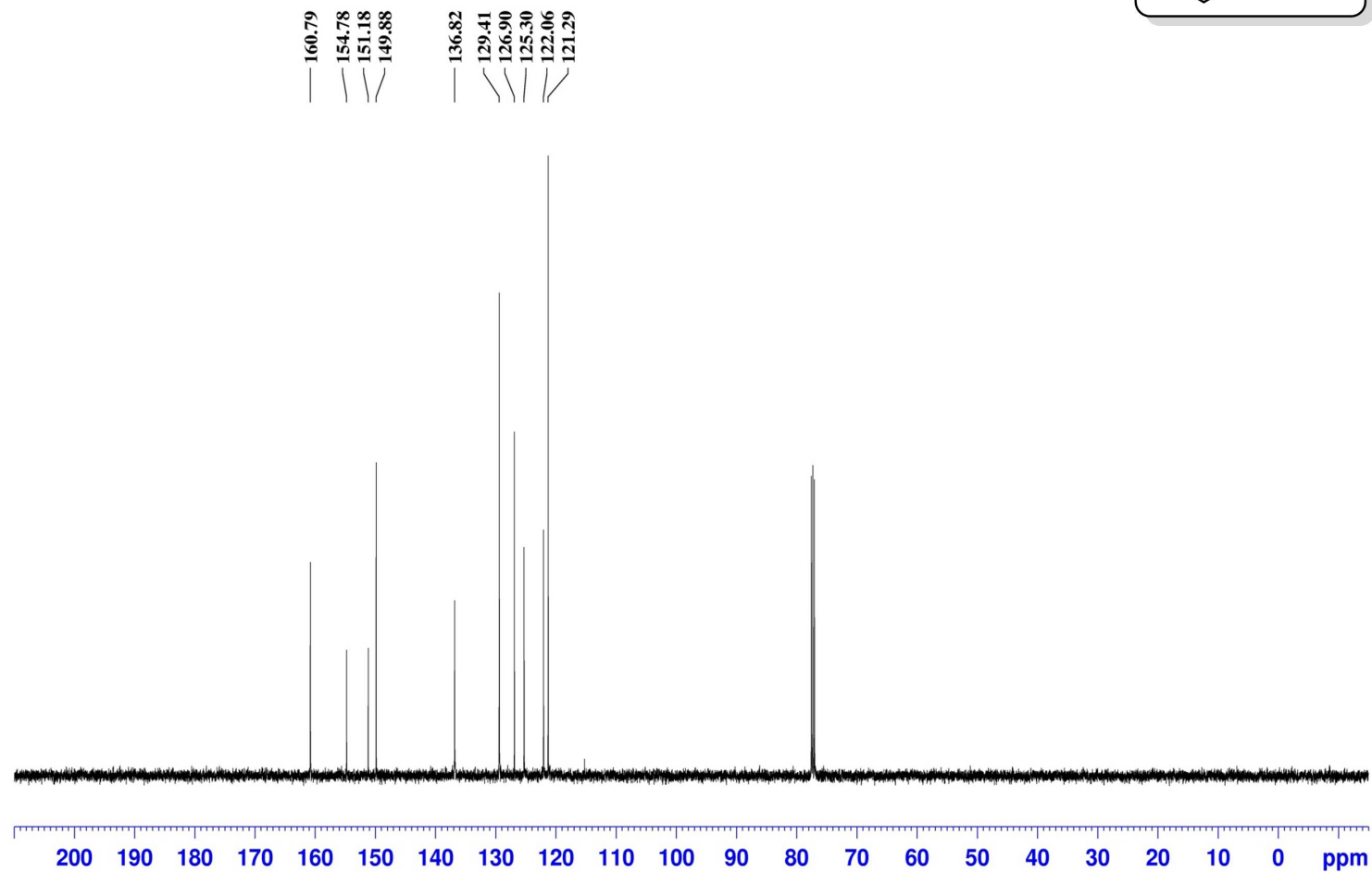
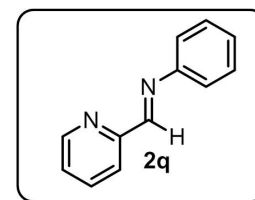
N-(4-methylbenzylidene)aniline  
125 MHz, CDCl<sub>3</sub>



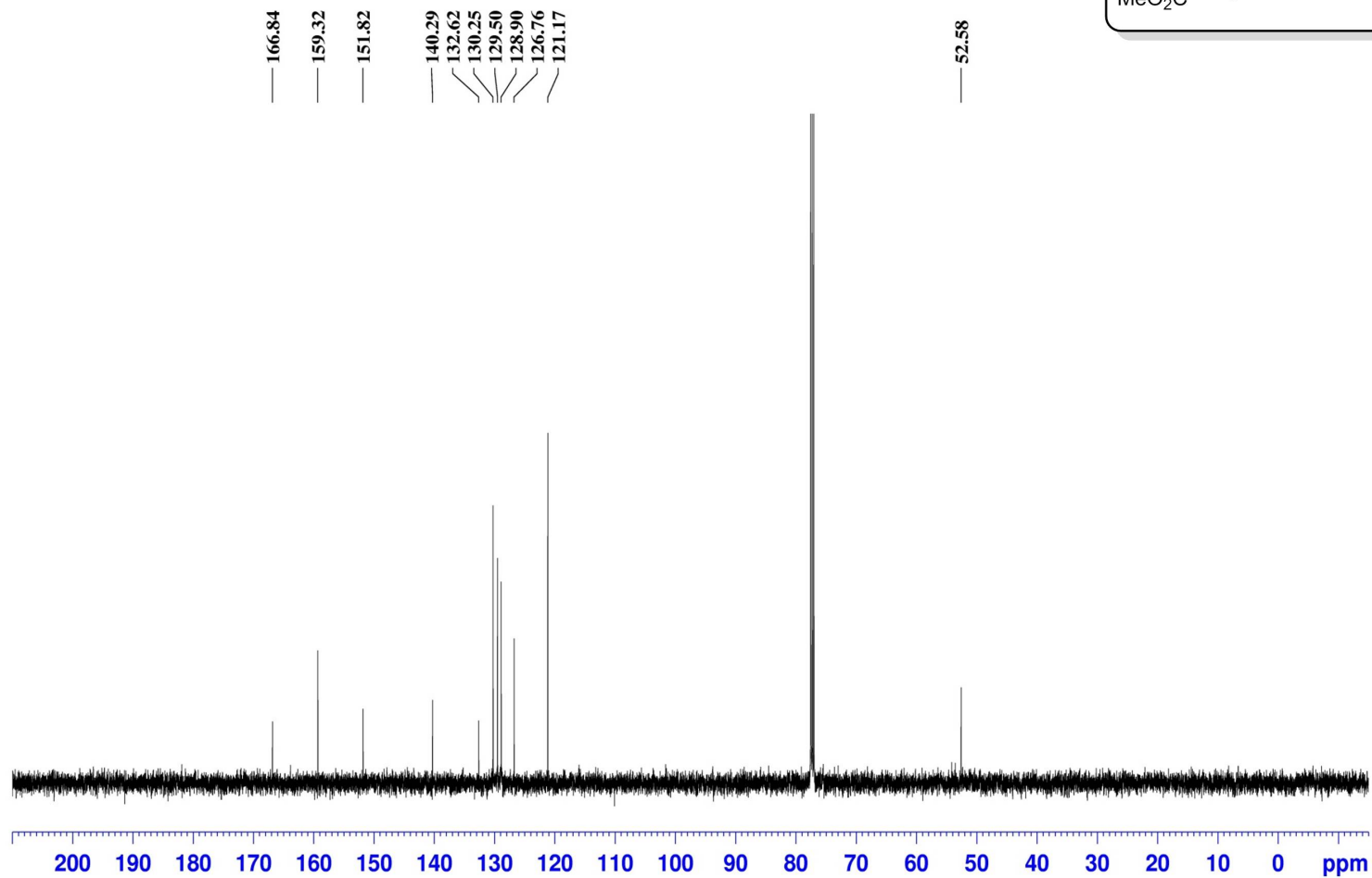
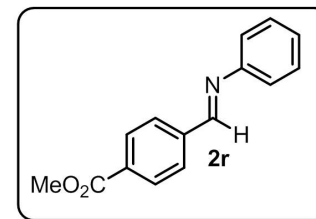
N-(4-methylbenzylidene)pyridin-2-amine  
125 MHz, CDCl<sub>3</sub>



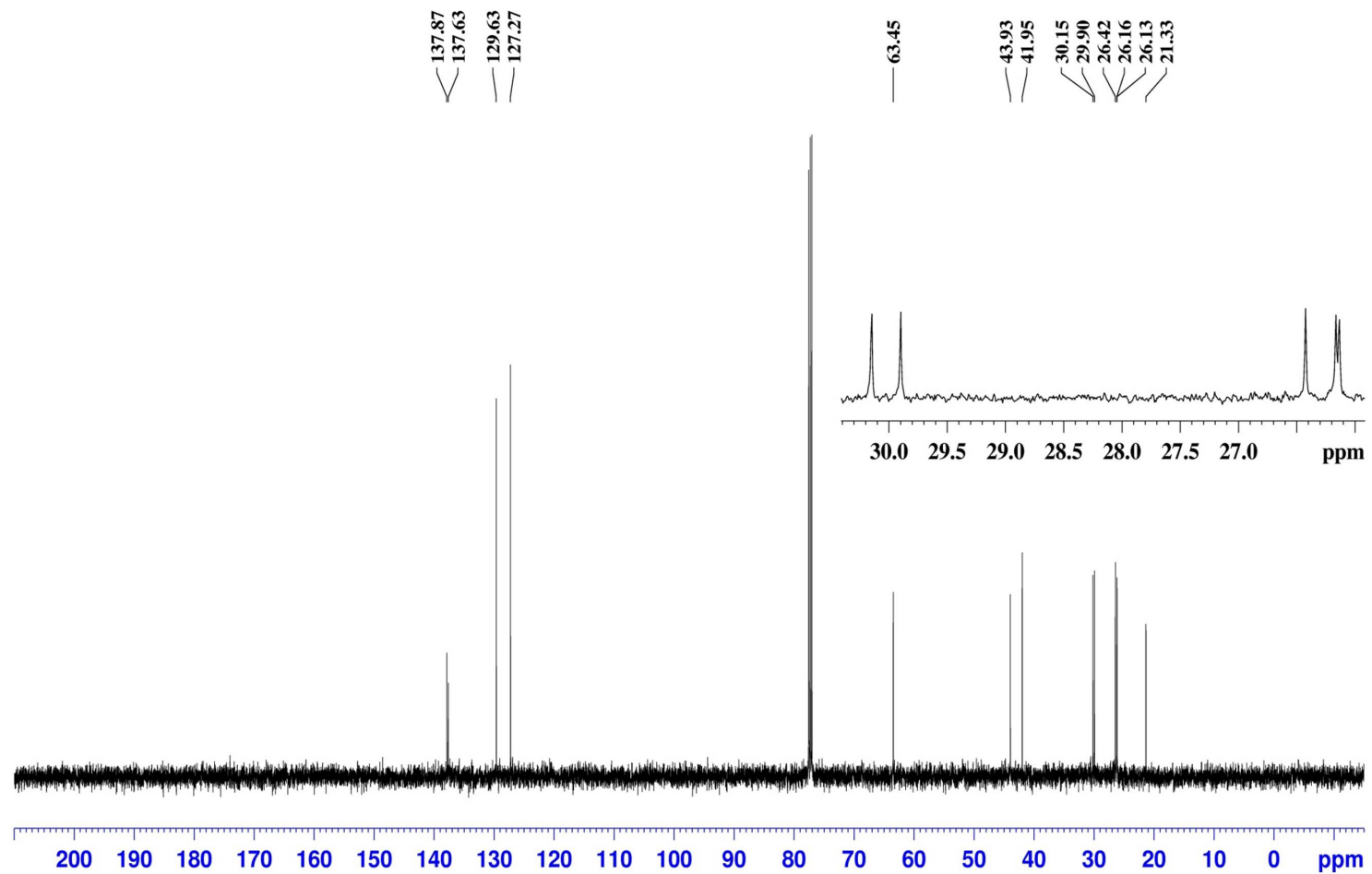
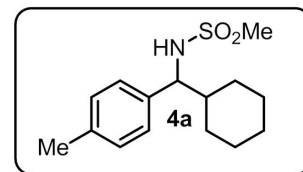
N-(pyridin-2-ylmethylene)aniline  
125 MHz, CDCl<sub>3</sub>



methyl 4-((phenylimino)methyl)benzoate  
125 MHz, CDCl<sub>3</sub>

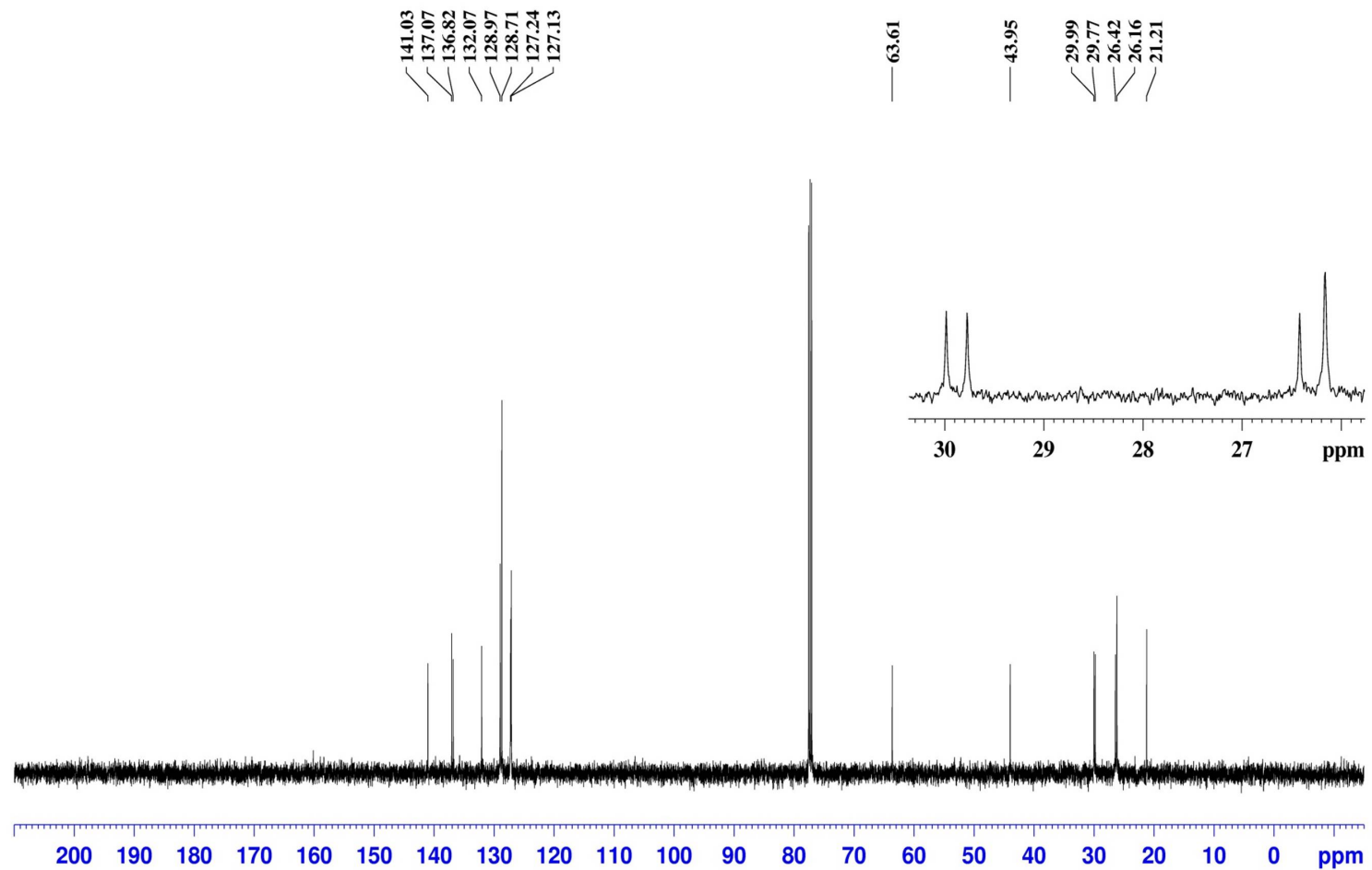
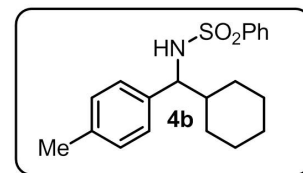


N-(cyclohexyl(p-tolyl)methyl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>

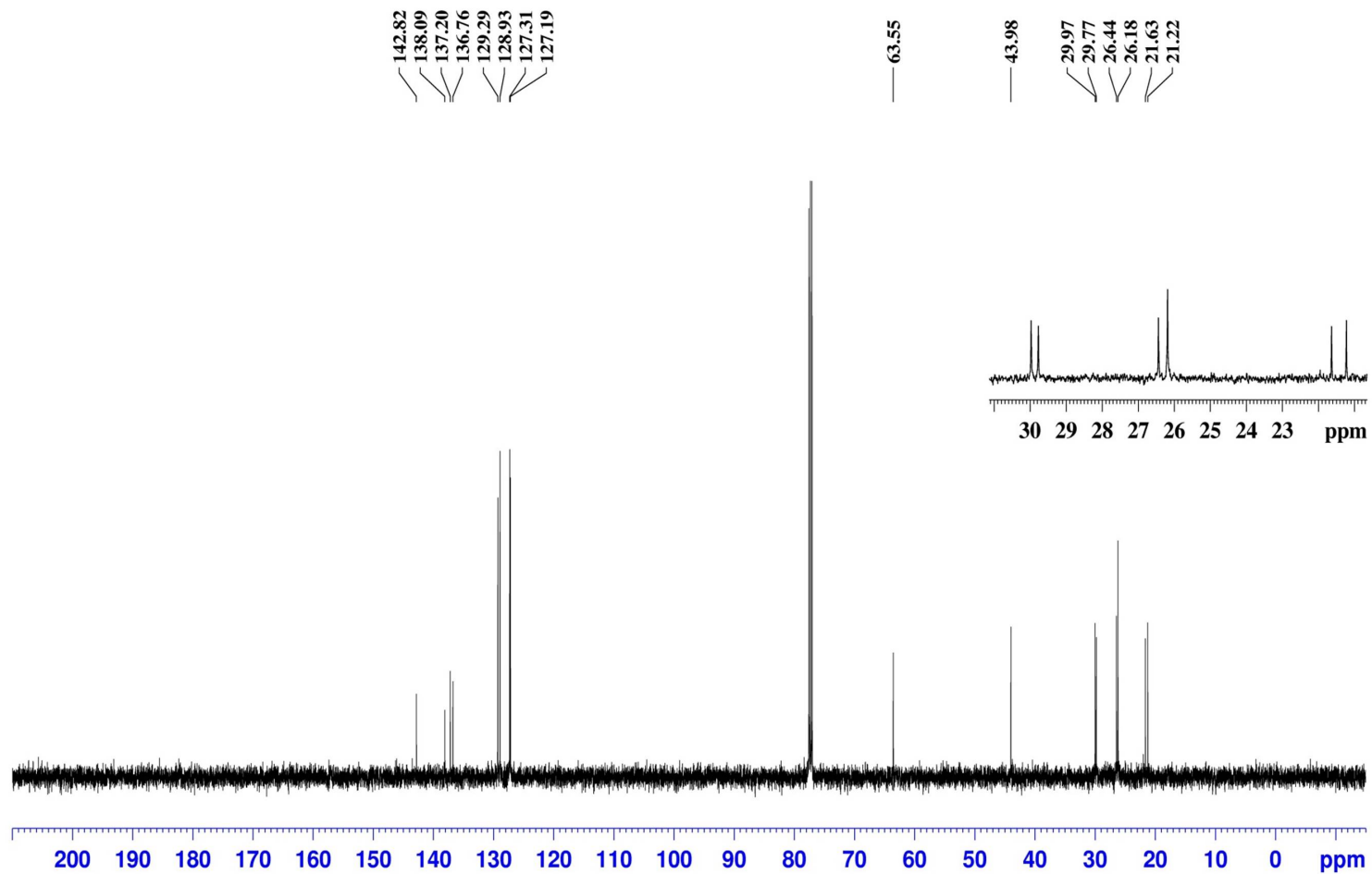
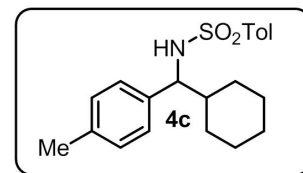




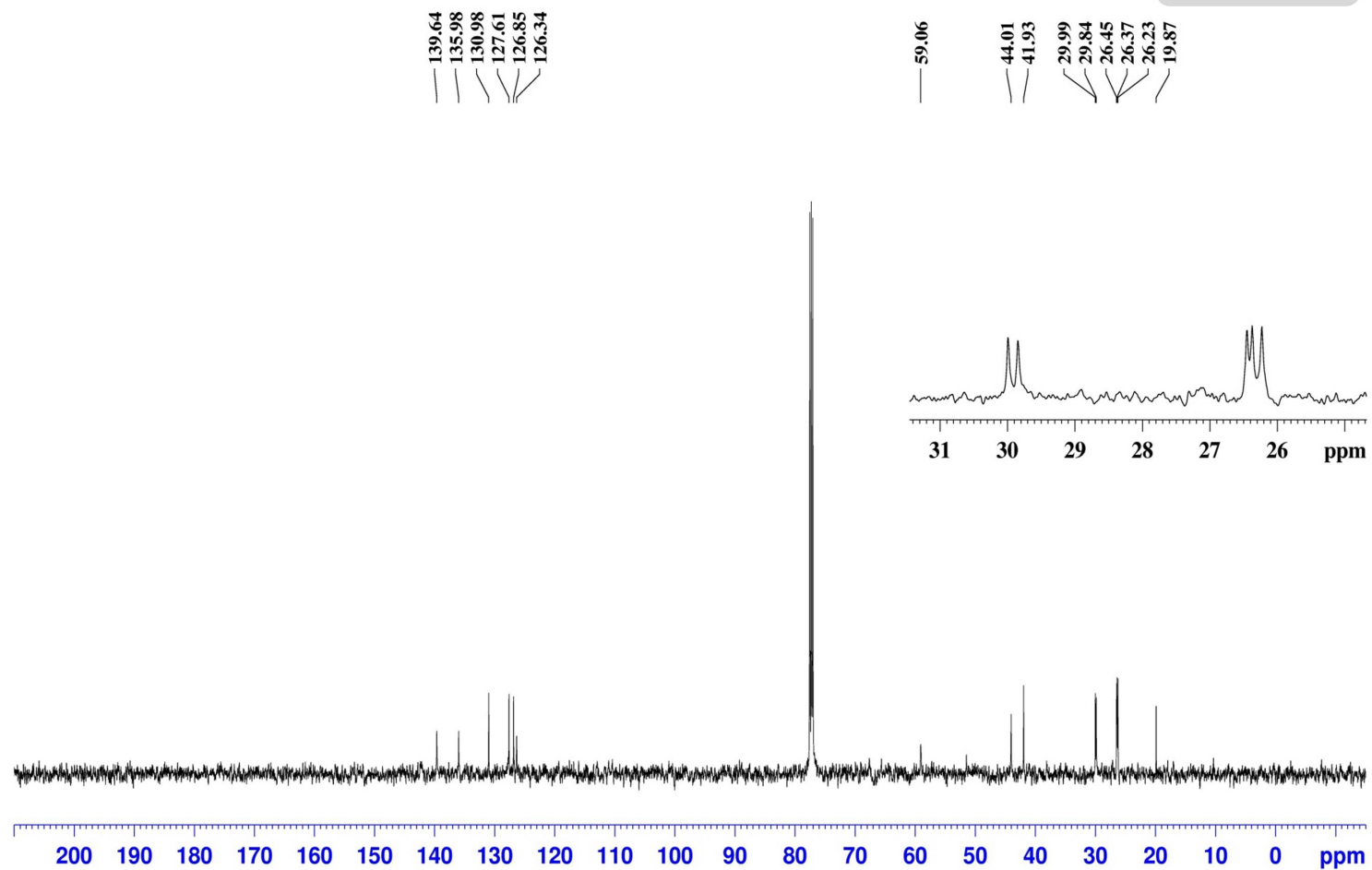
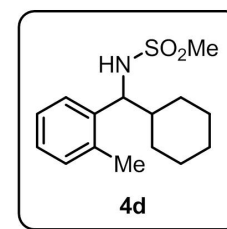
N-(cyclohexyl(p-tolyl)methyl)benzenesulfonamide  
125 MHz, CDCl<sub>3</sub>



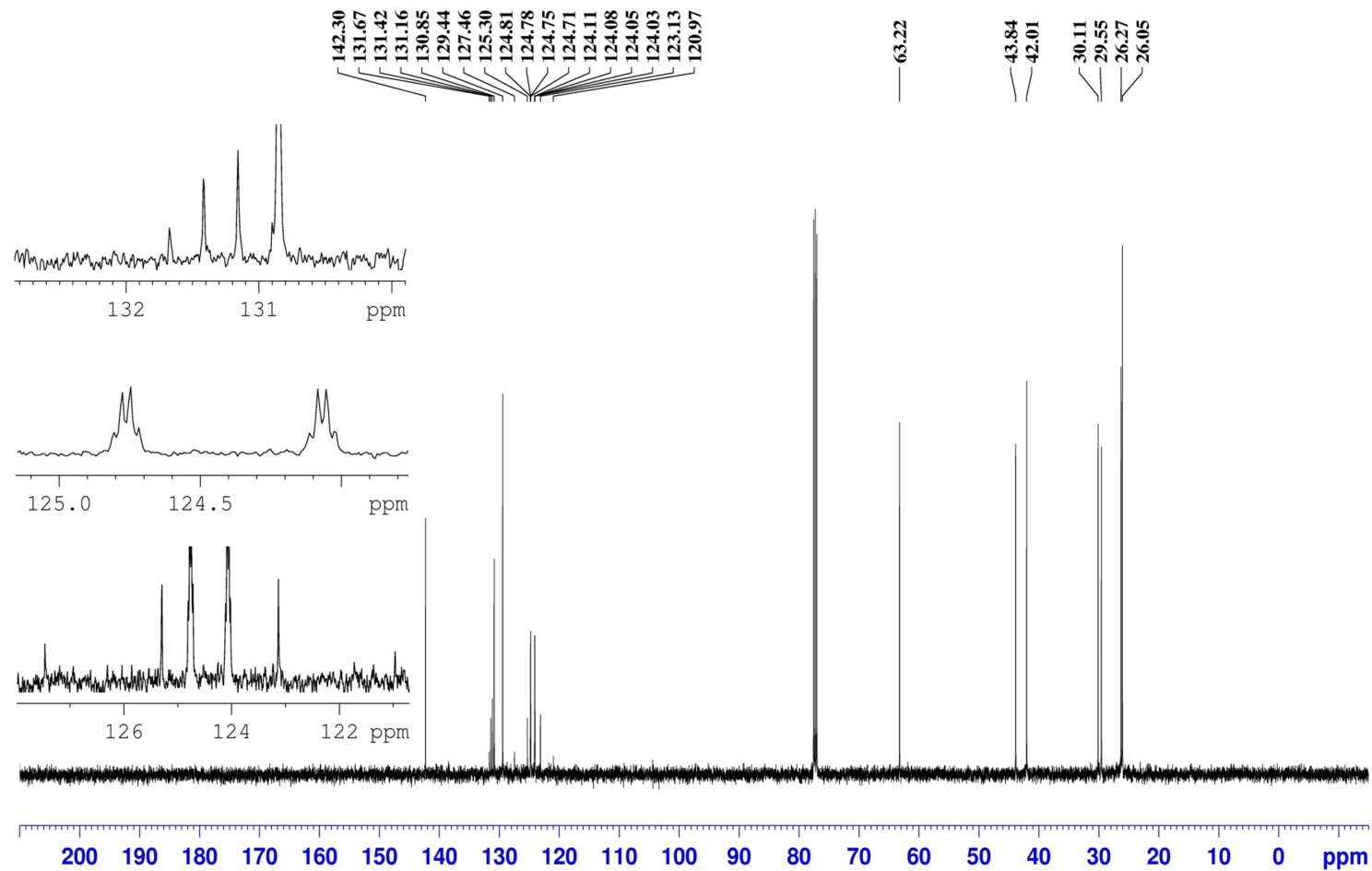
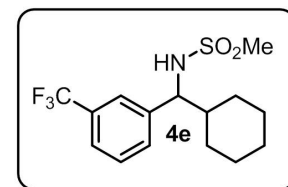
N-(cyclohexyl(p-tolyl)methyl)-4-methylbenzenesulfonamide  
125 MHz, CDCl<sub>3</sub>



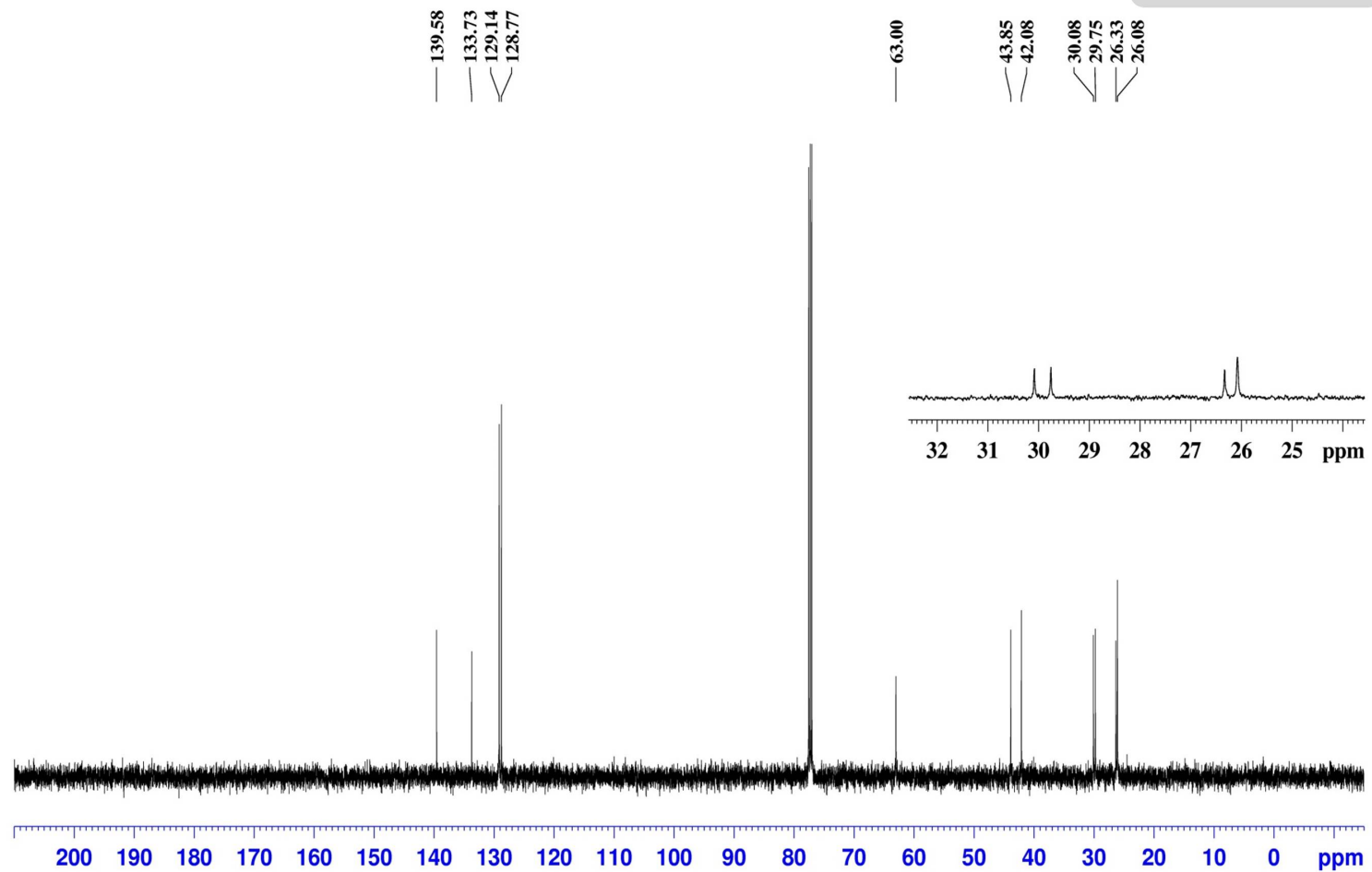
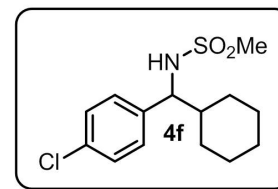
N-(cyclohexyl(o-tolyl)methyl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



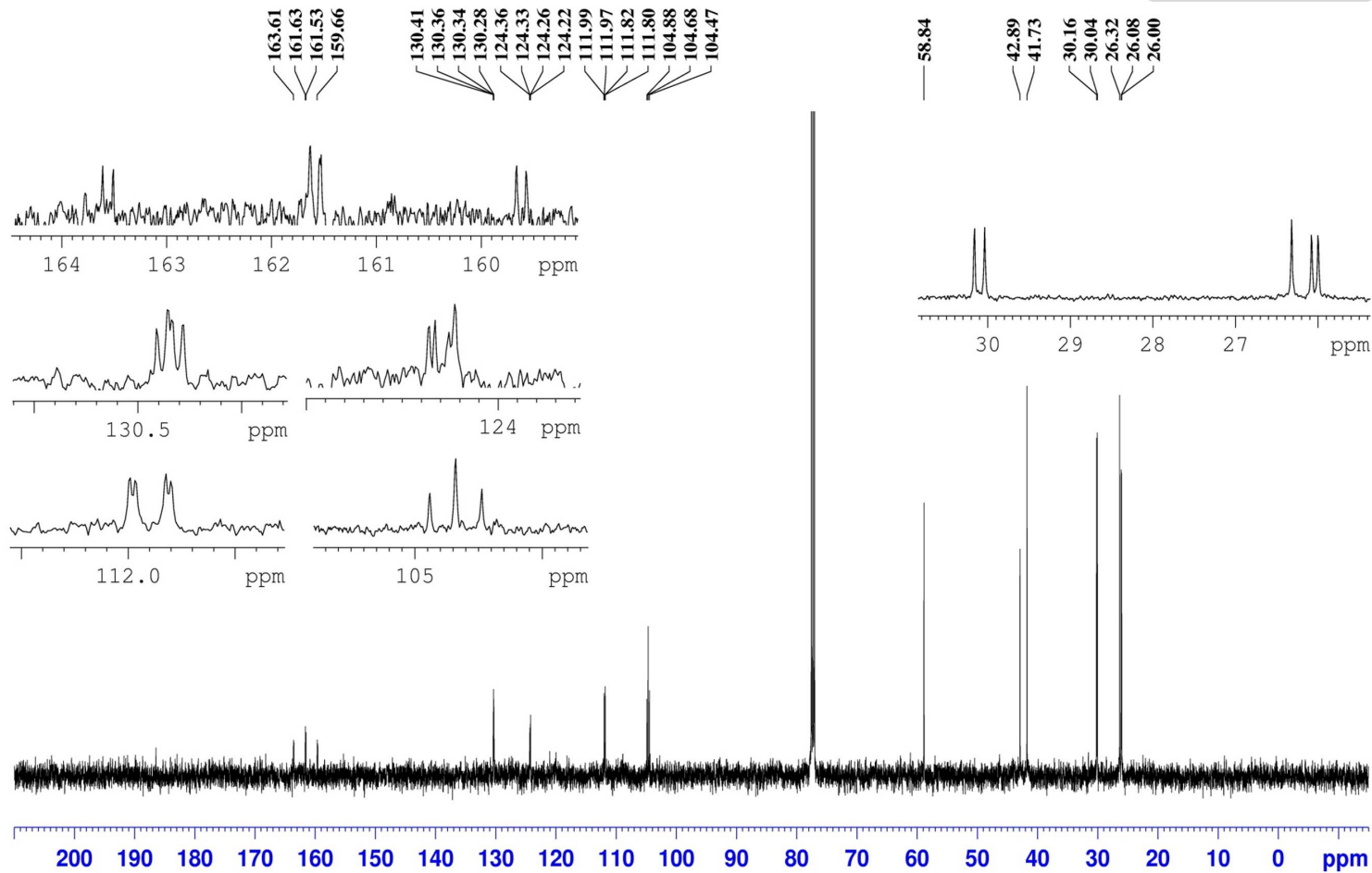
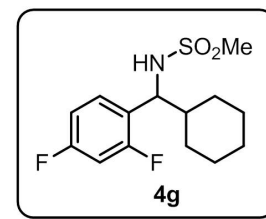
**N-(cyclohexyl(3-(trifluoromethyl)phenyl)methyl)methanesulfonamide**  
125 MHz, CDCl<sub>3</sub>



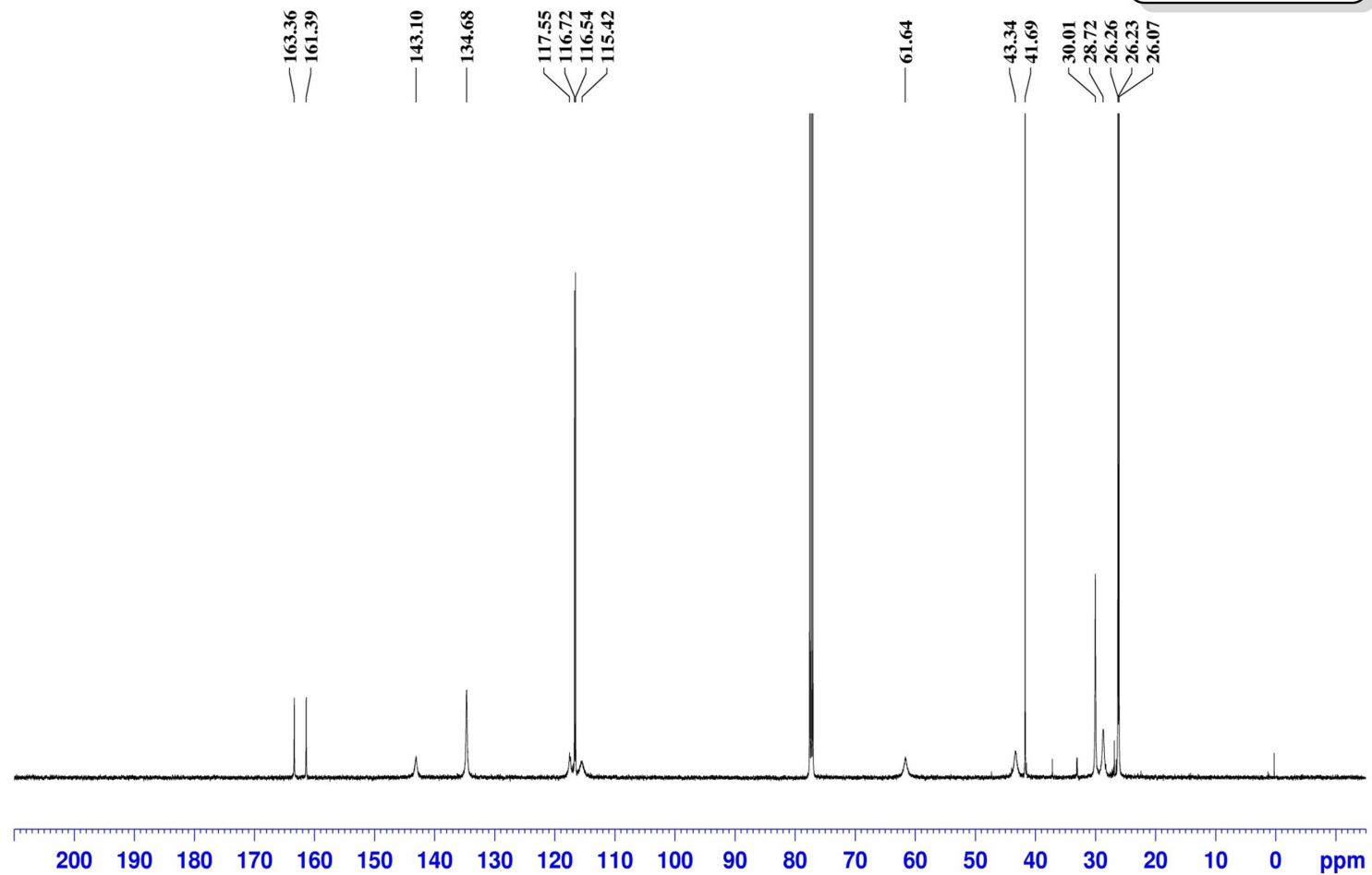
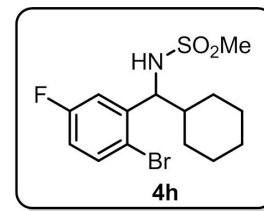
N-((4-chlorophenyl)(cyclohexyl)methyl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



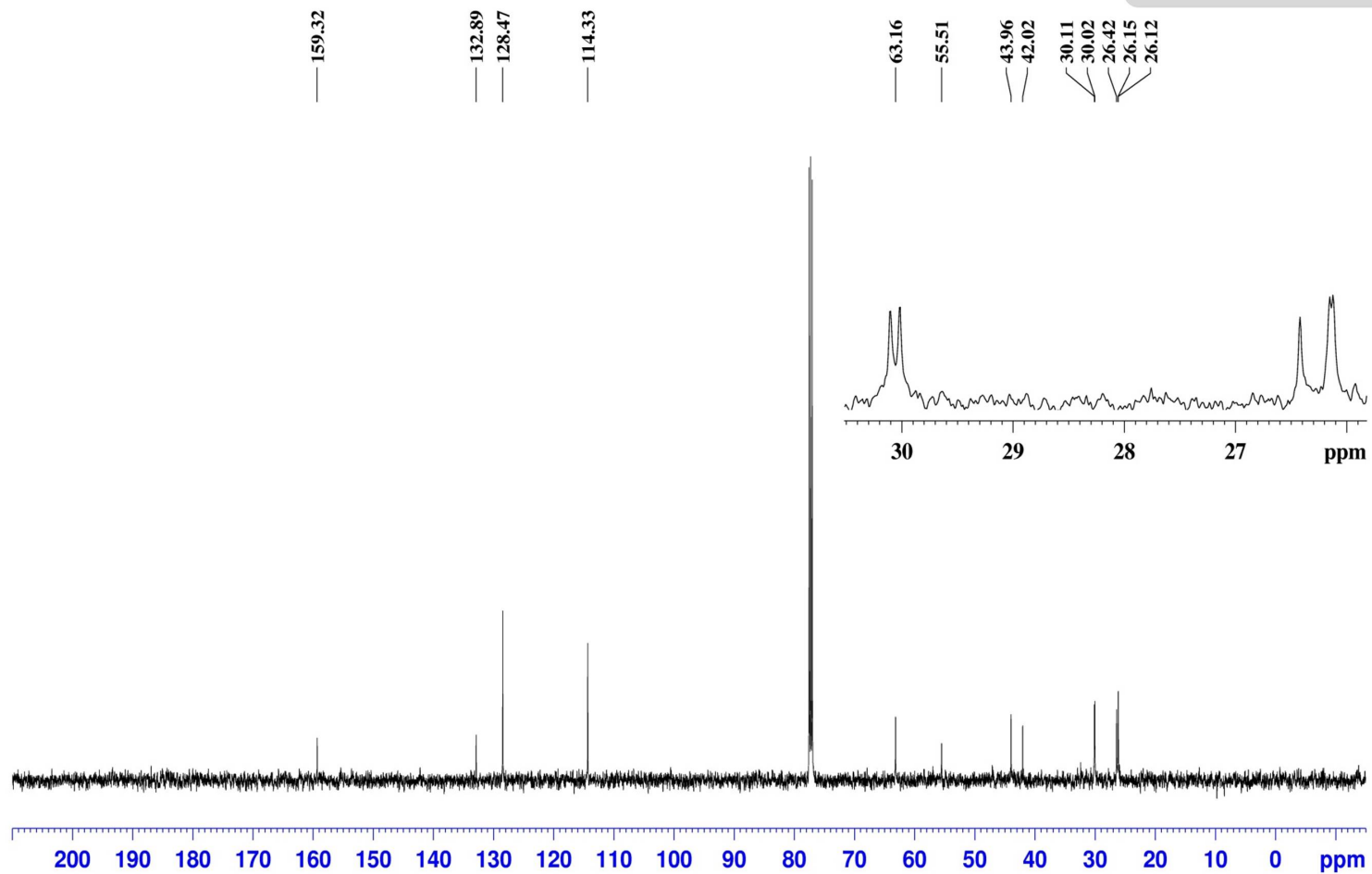
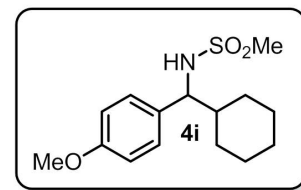
**N-(cyclohexyl(2,4-difluorophenyl)methyl)methanesulfonamide**  
125 Mhz, CDCl<sub>3</sub>



N-((2-bromo-5-fluorophenyl)(cyclohexyl)methyl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>

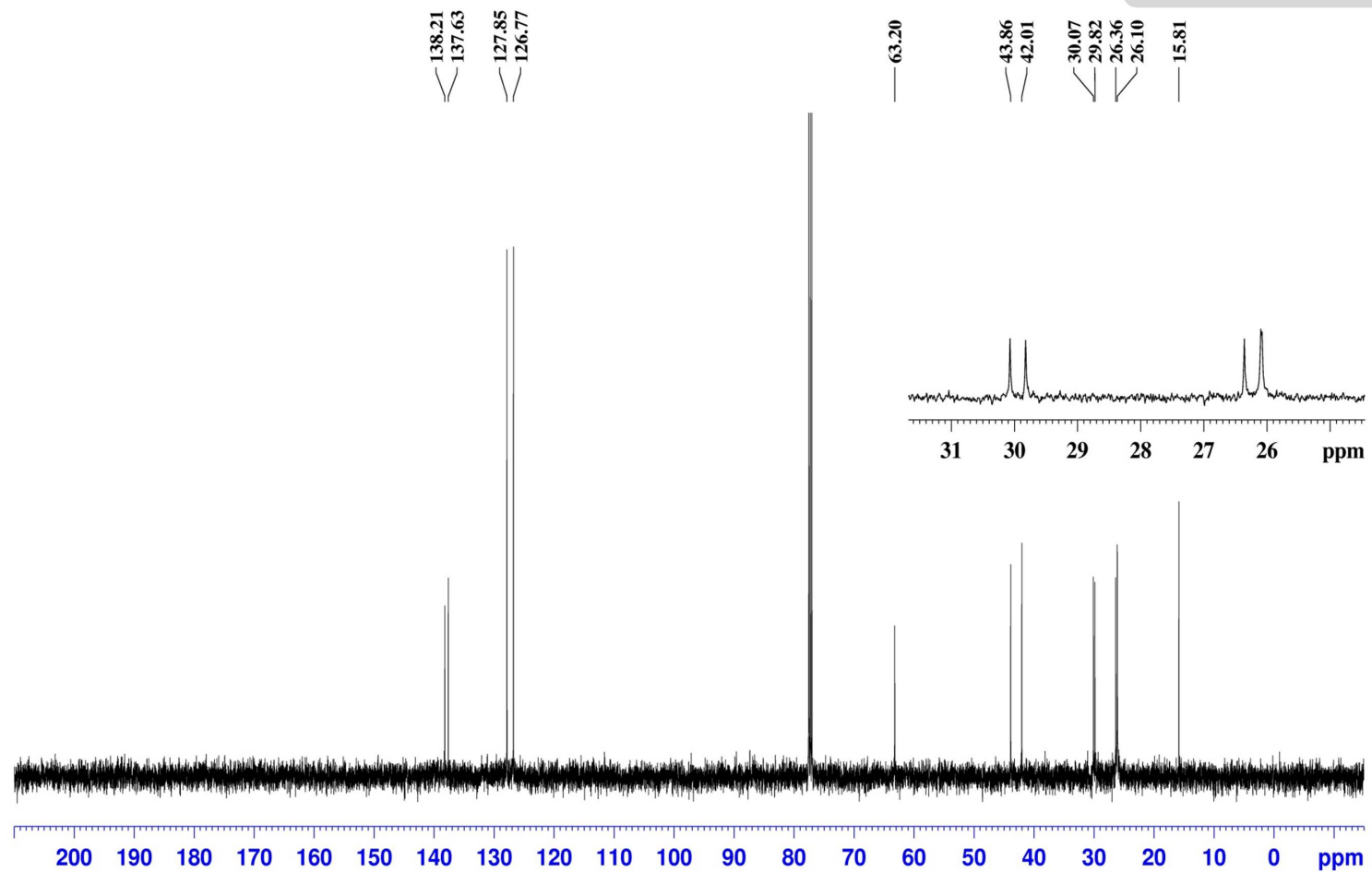
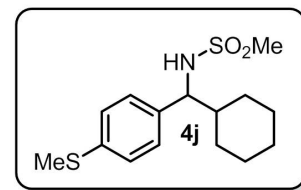


N-(cyclohexyl(4-methoxyphenyl)methyl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>

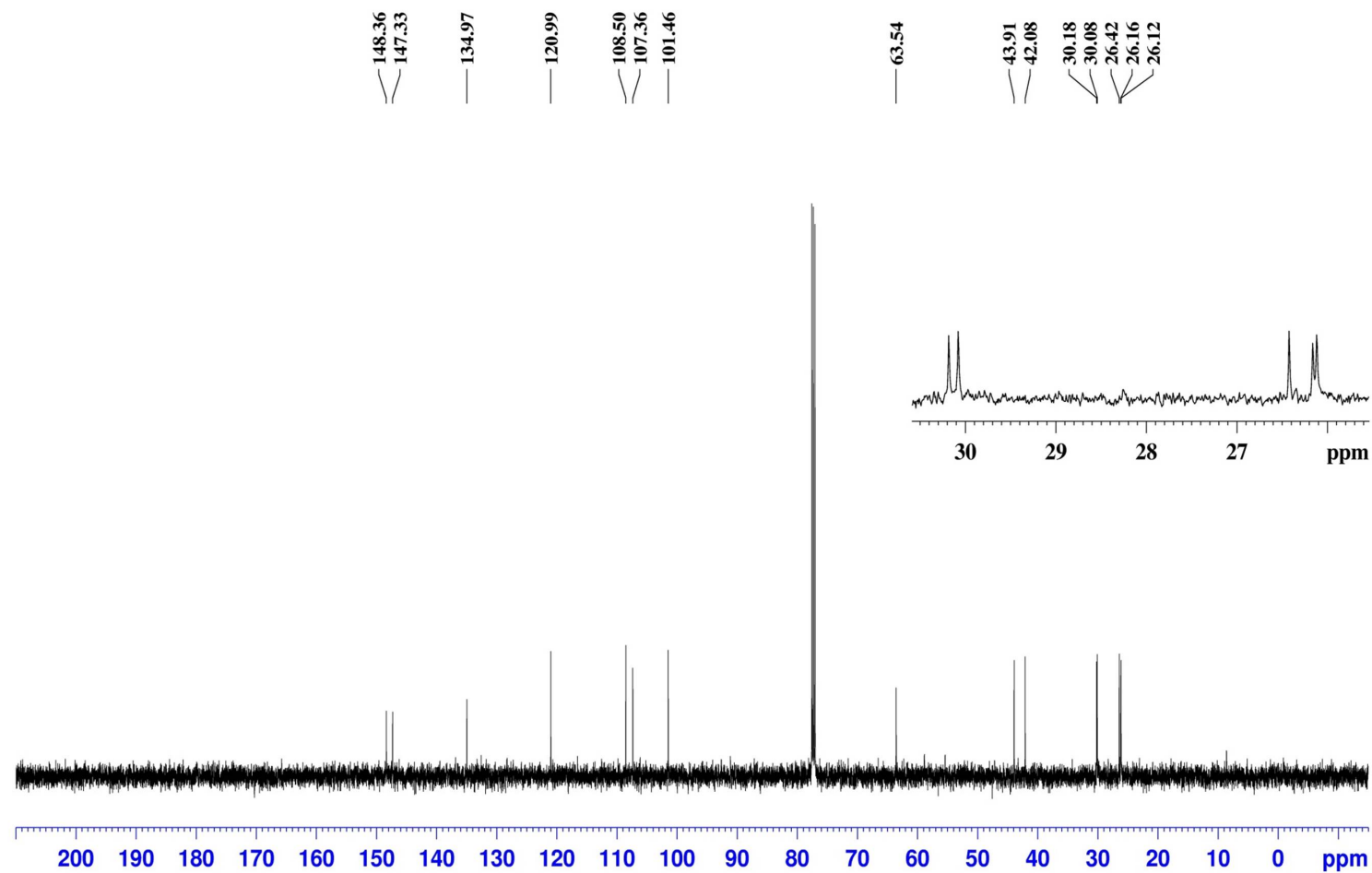
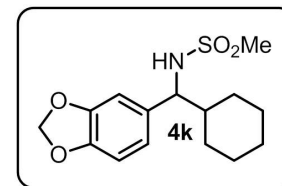




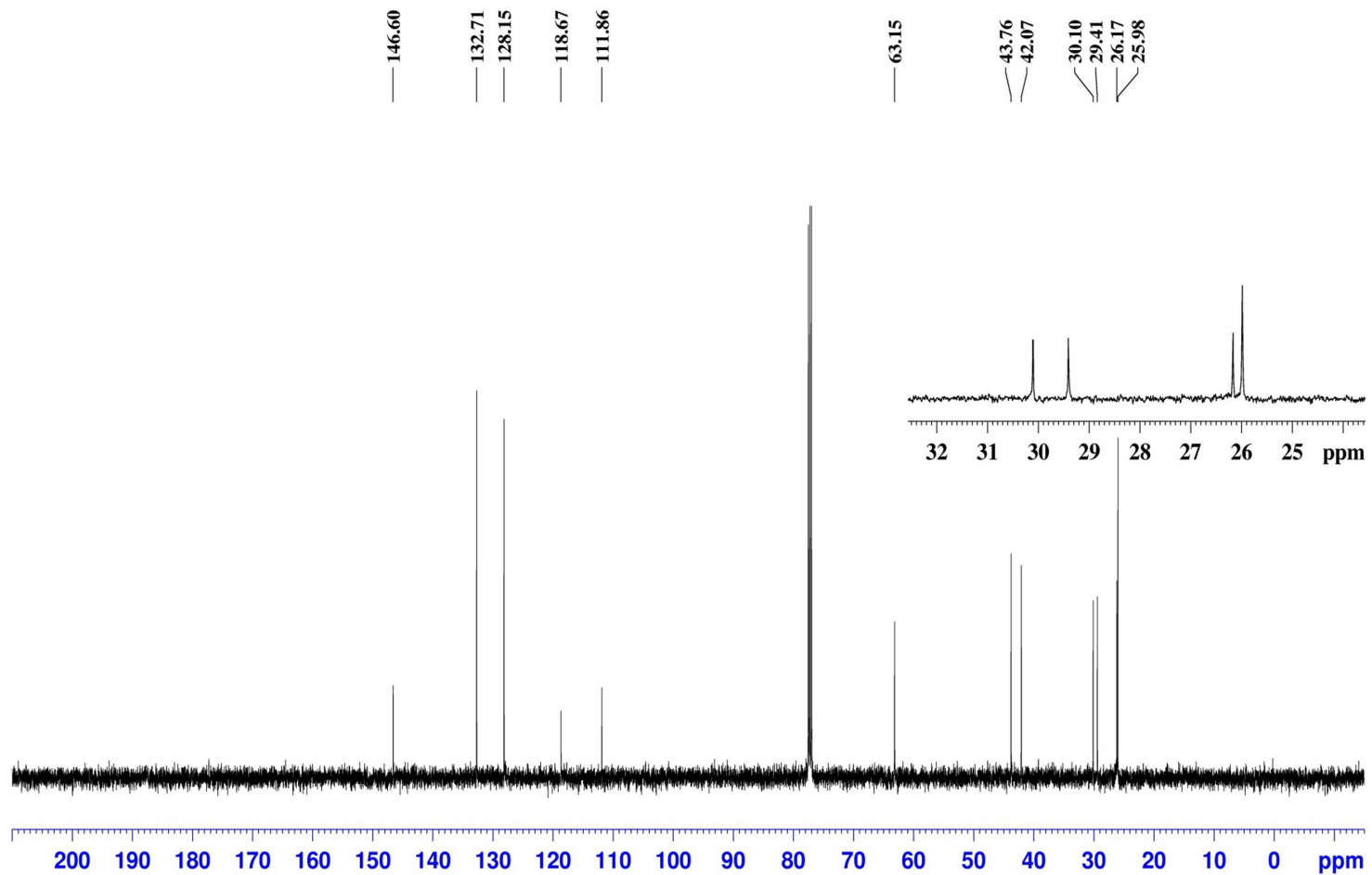
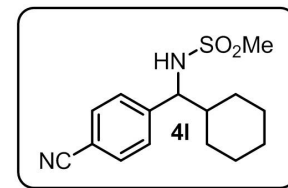
N-(cyclohexyl(4-(methylthio)phenyl)methyl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



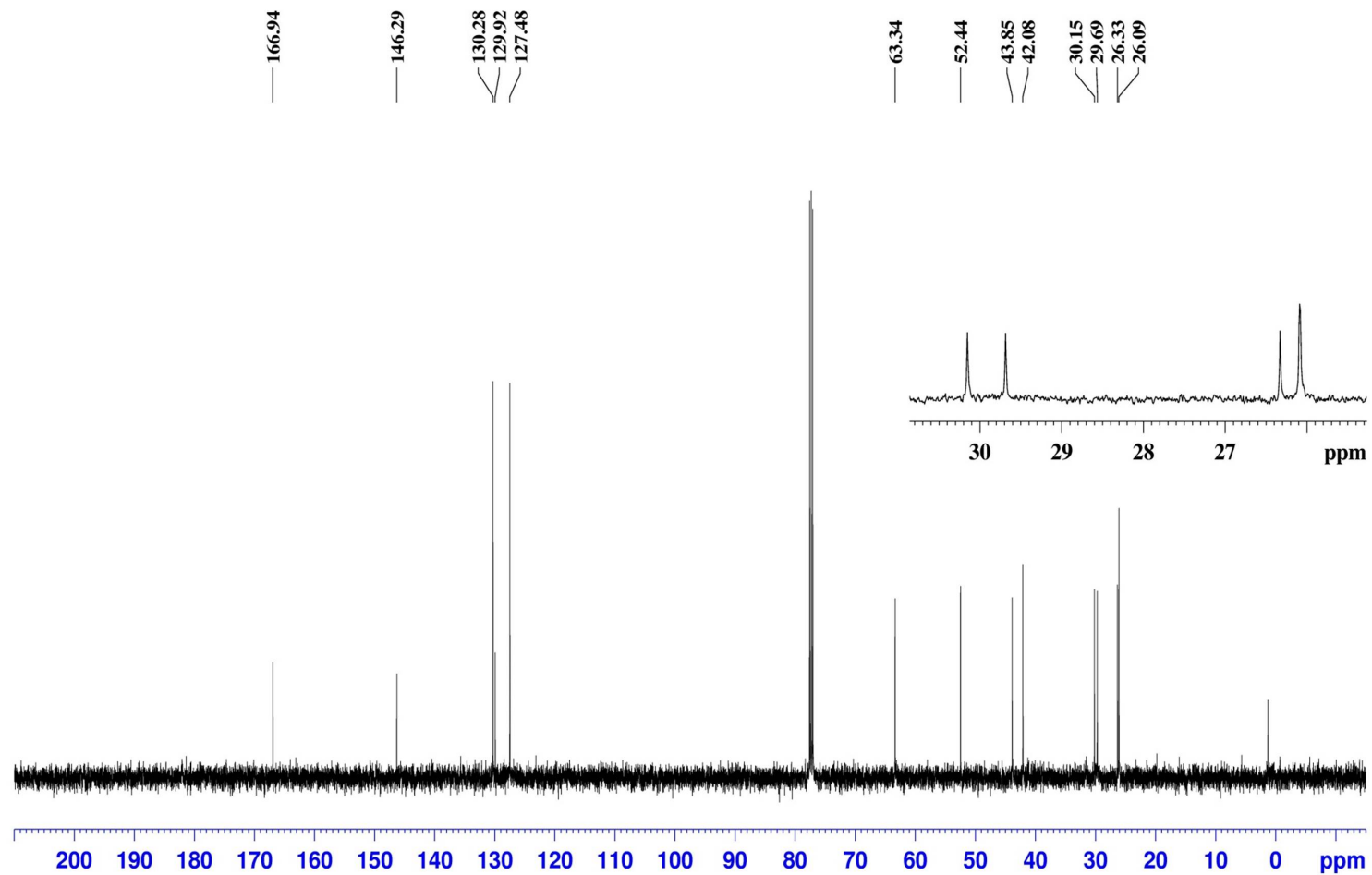
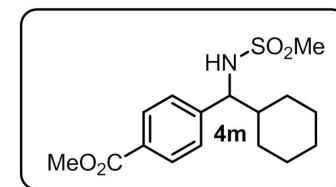
N-(benzo[d][1,3]dioxol-5-yl(cyclohexyl)methyl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



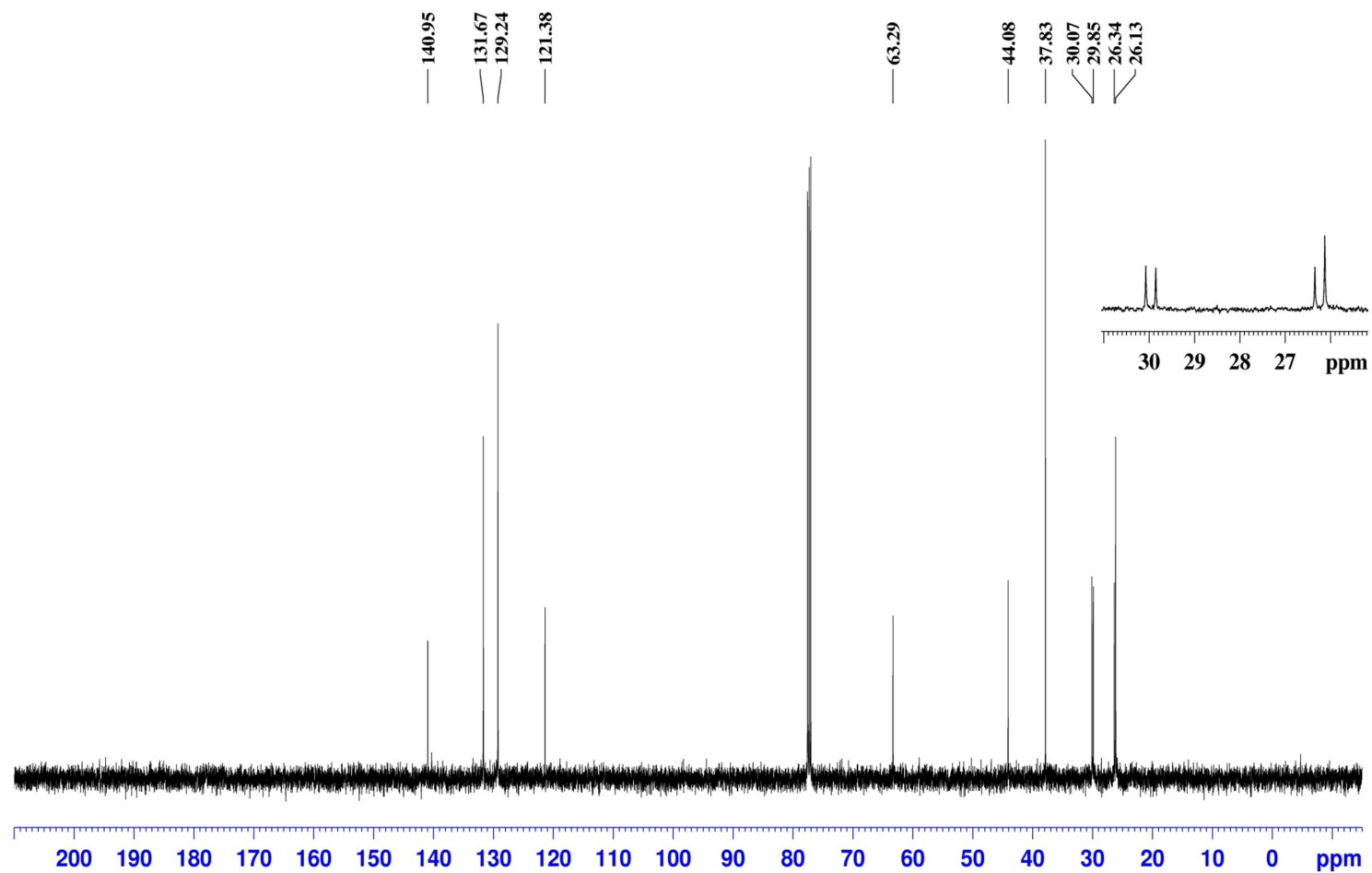
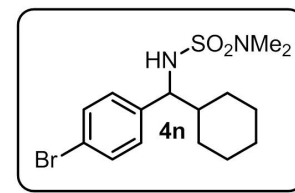
N-((4-cyanophenyl)(cyclohexyl)methyl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



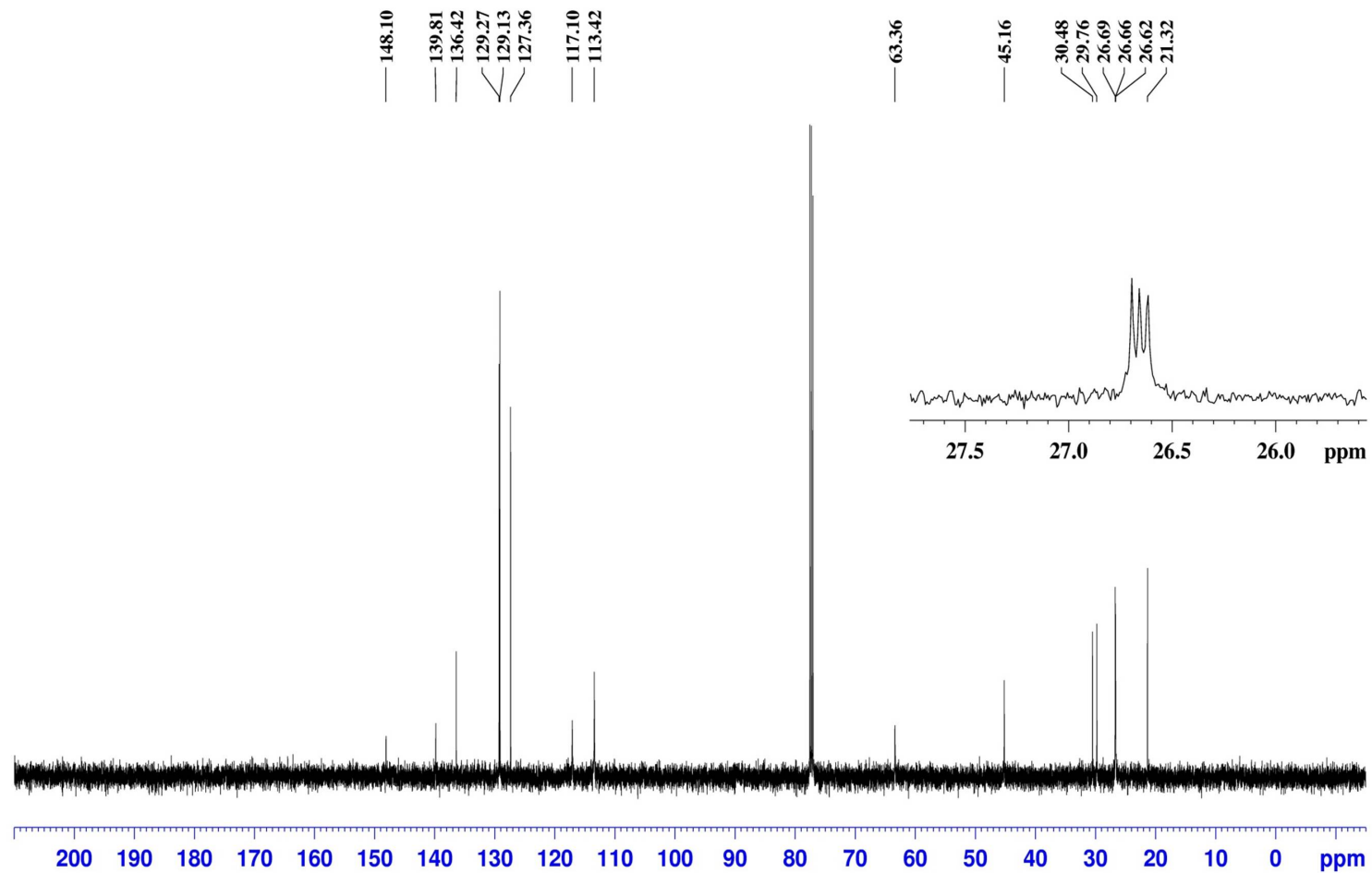
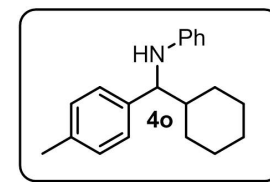
methyl 4-(cyclohexyl(methylsulfonamido)methyl)benzoate  
125 MHz, CDCl<sub>3</sub>



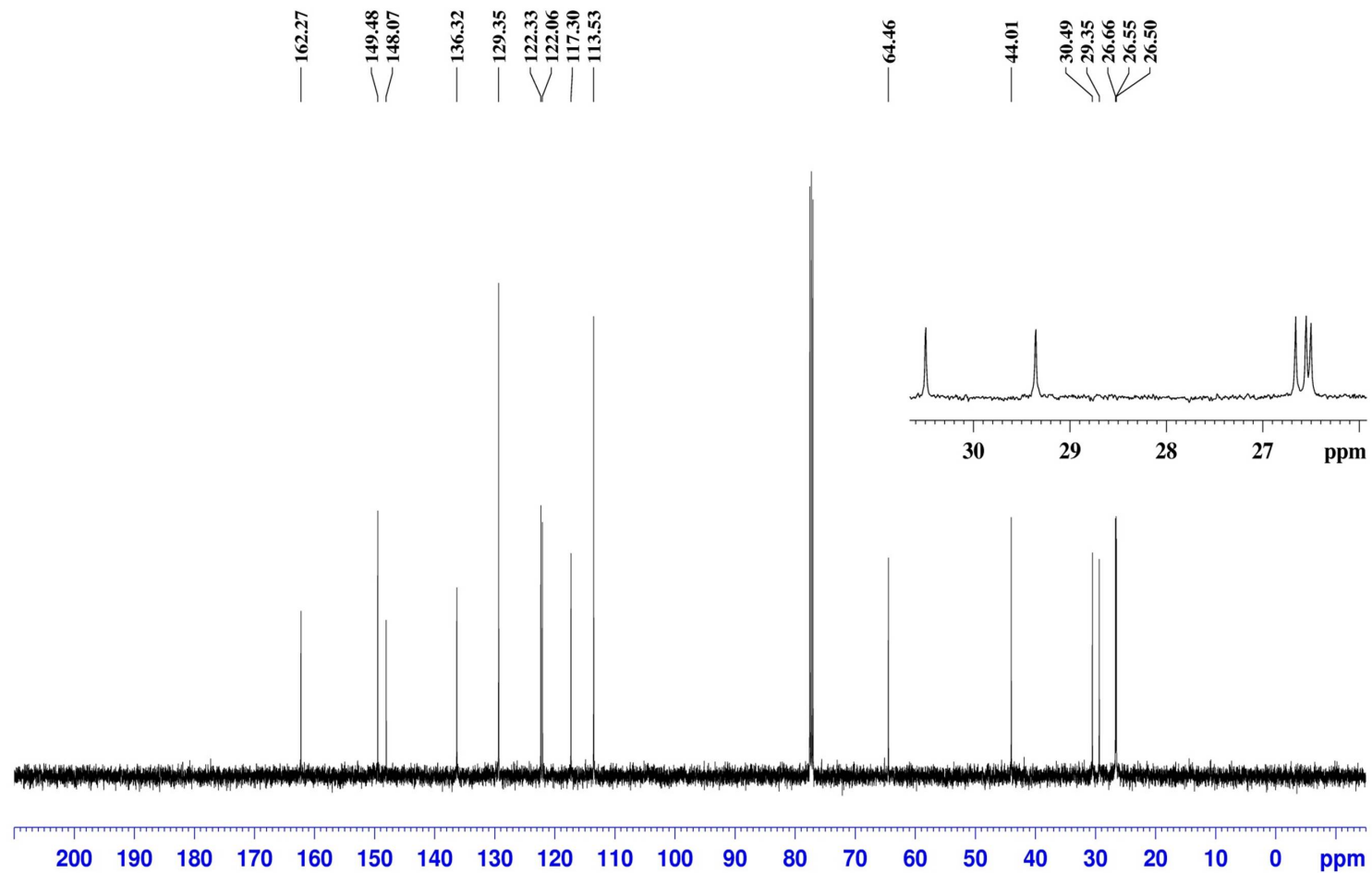
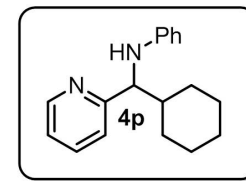
N'-((4-bromophenyl)(cyclohexyl)methyl)-N,N-dimethylsulfamide  
125 MHz, CDCl<sub>3</sub>



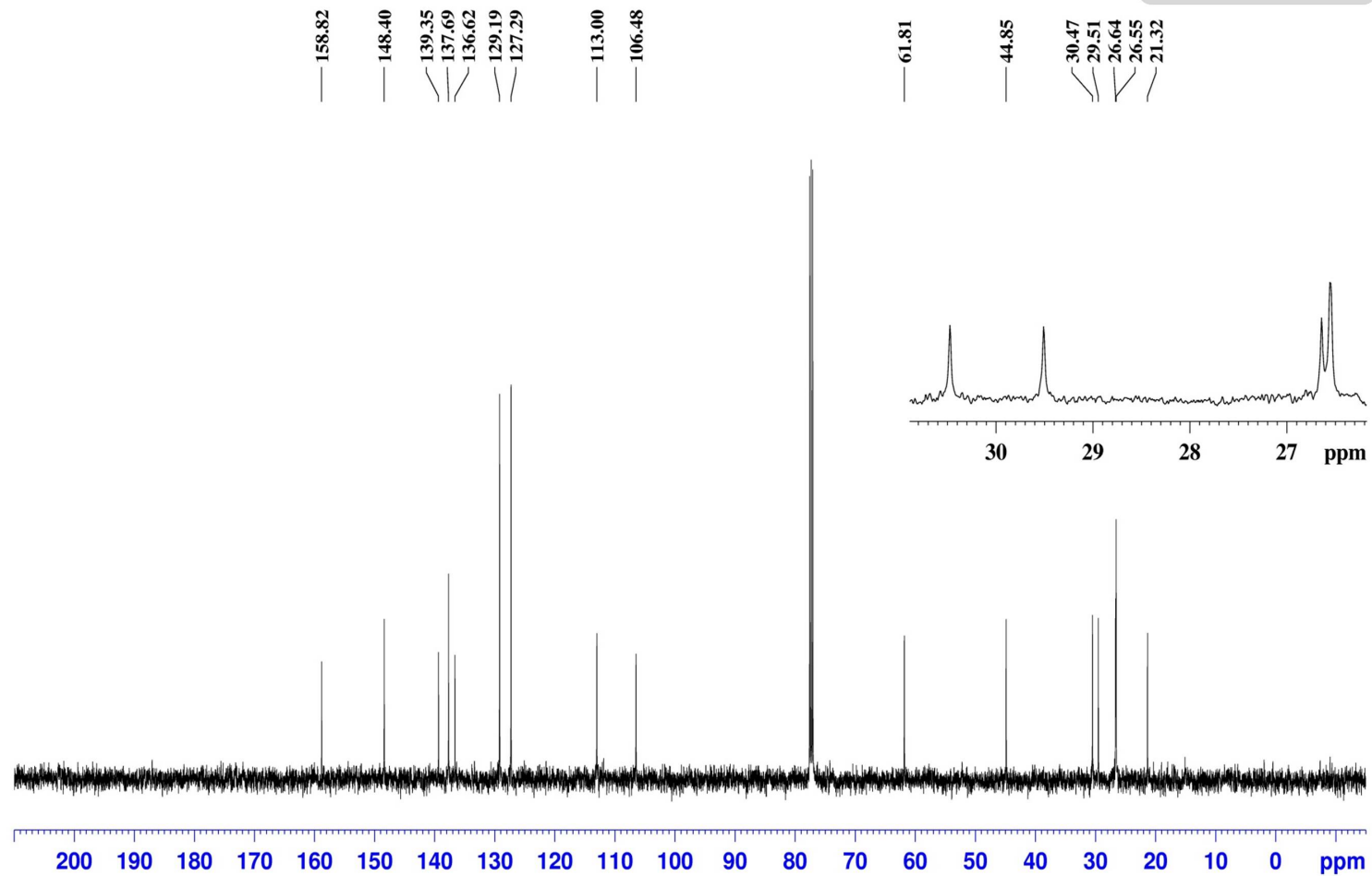
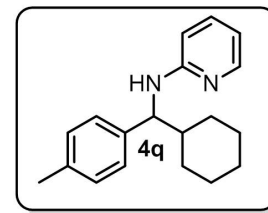
N-(cyclohexyl(p-tolyl)methyl)aniline  
125 MHz, CDCl<sub>3</sub>



N-(cyclohexyl(pyridin-2-yl)methyl)aniline  
125 MHz, CDCl<sub>3</sub>

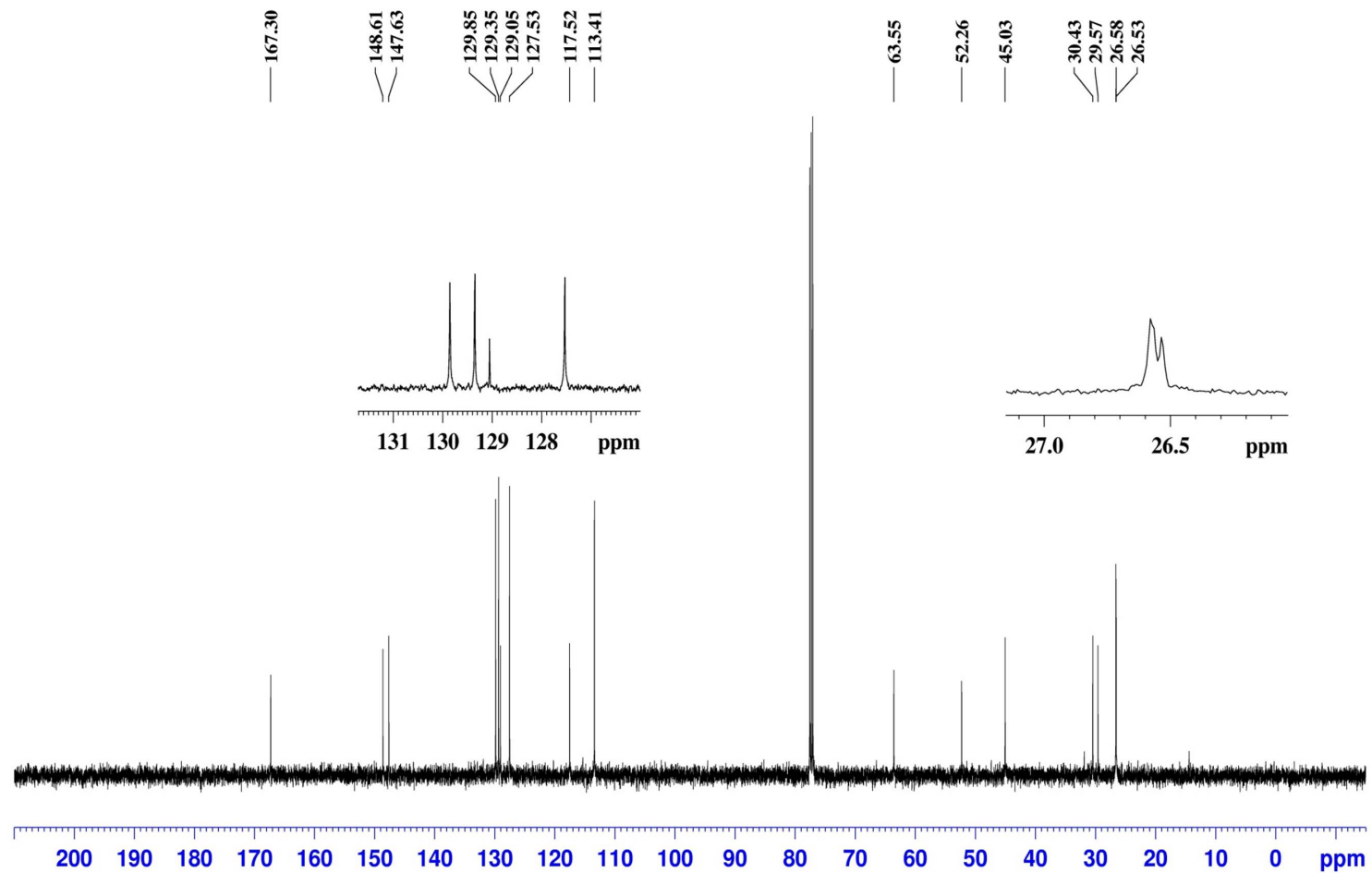
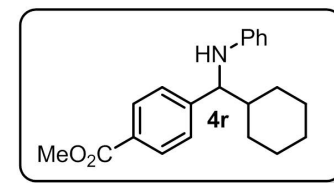


N-(cyclohexyl(p-tolyl)methyl)pyridin-2-amine  
125 MHz, CDCl<sub>3</sub>

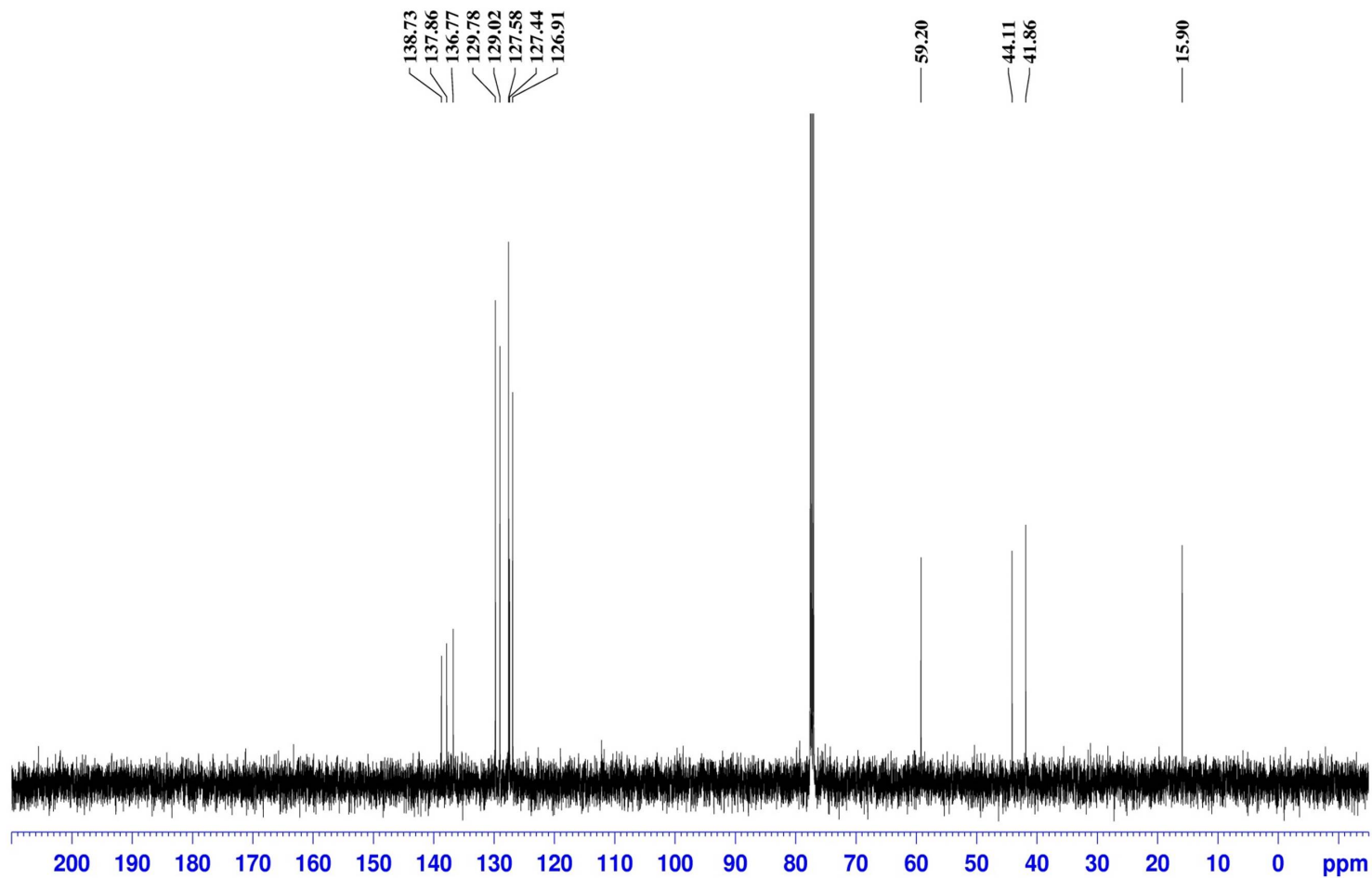
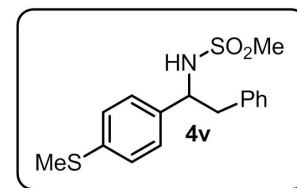




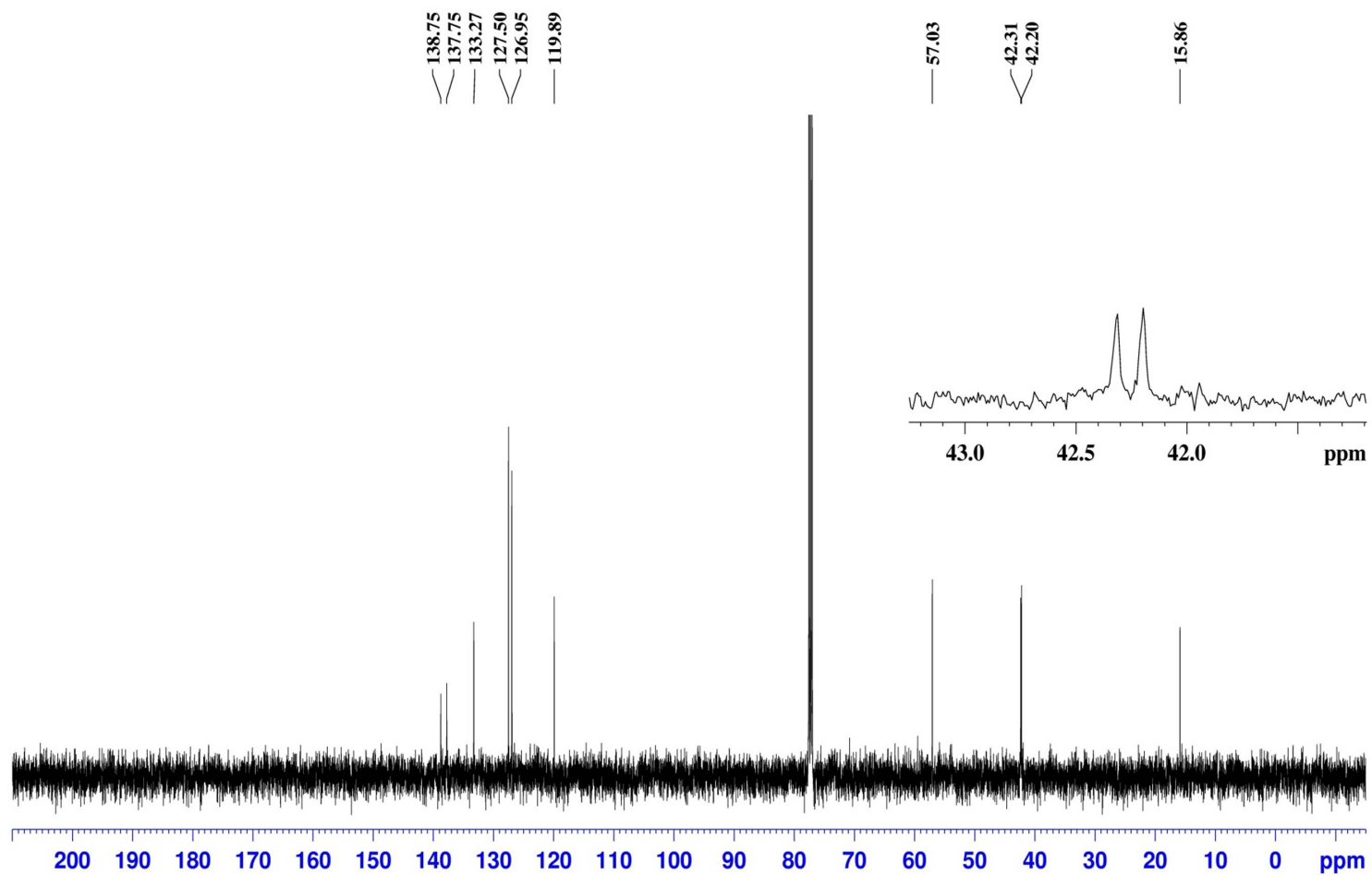
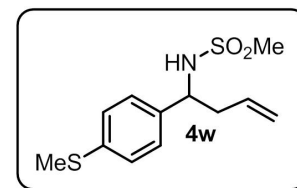
methyl 4-(cyclohexyl(phenylamino)methyl)benzoate  
125 MHz, CDCl<sub>3</sub>



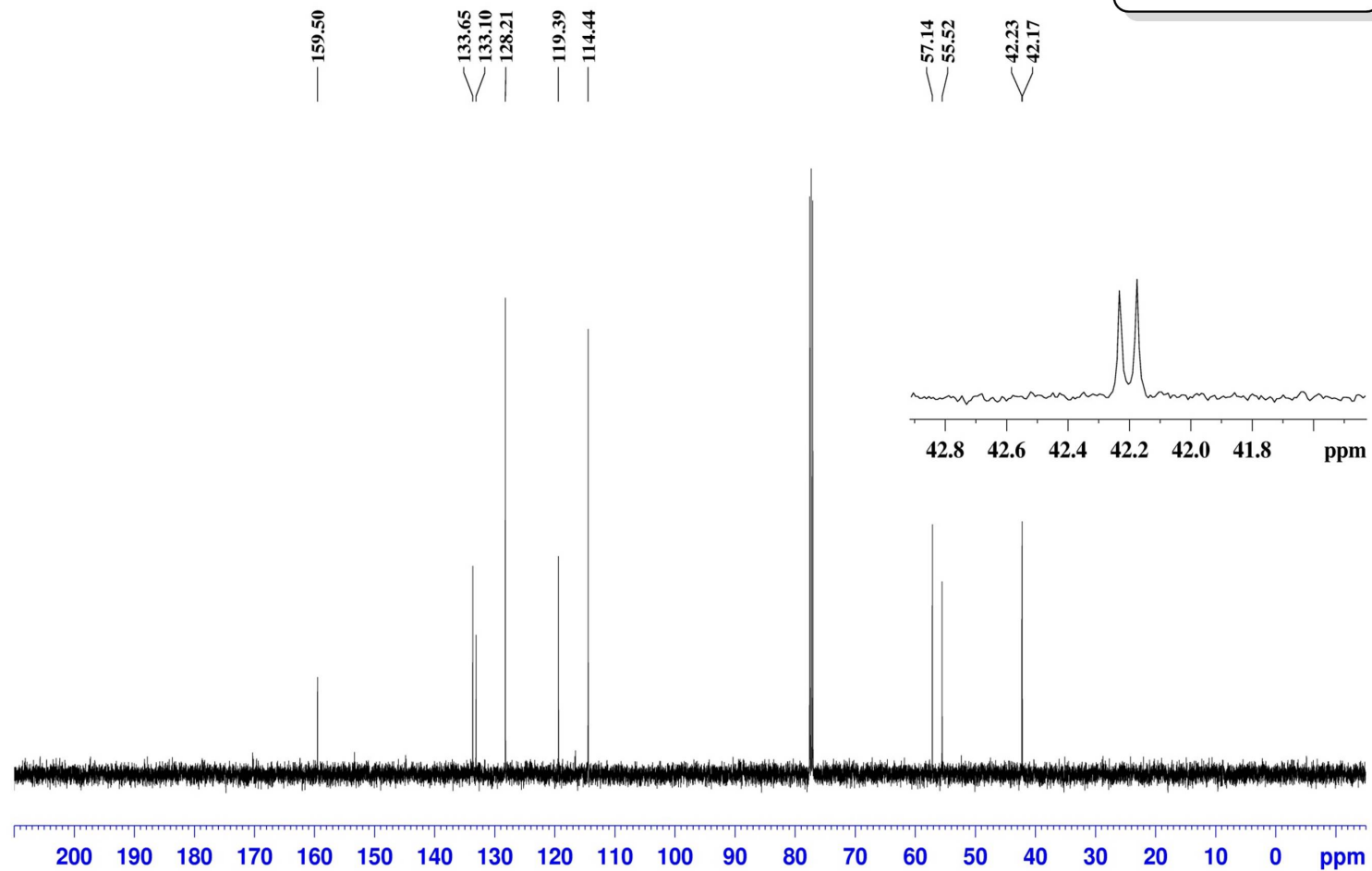
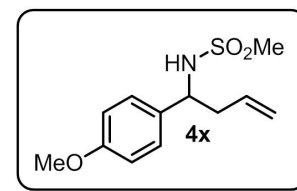
N-(1-(4-(methylthio)phenyl)-2-phenylethyl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



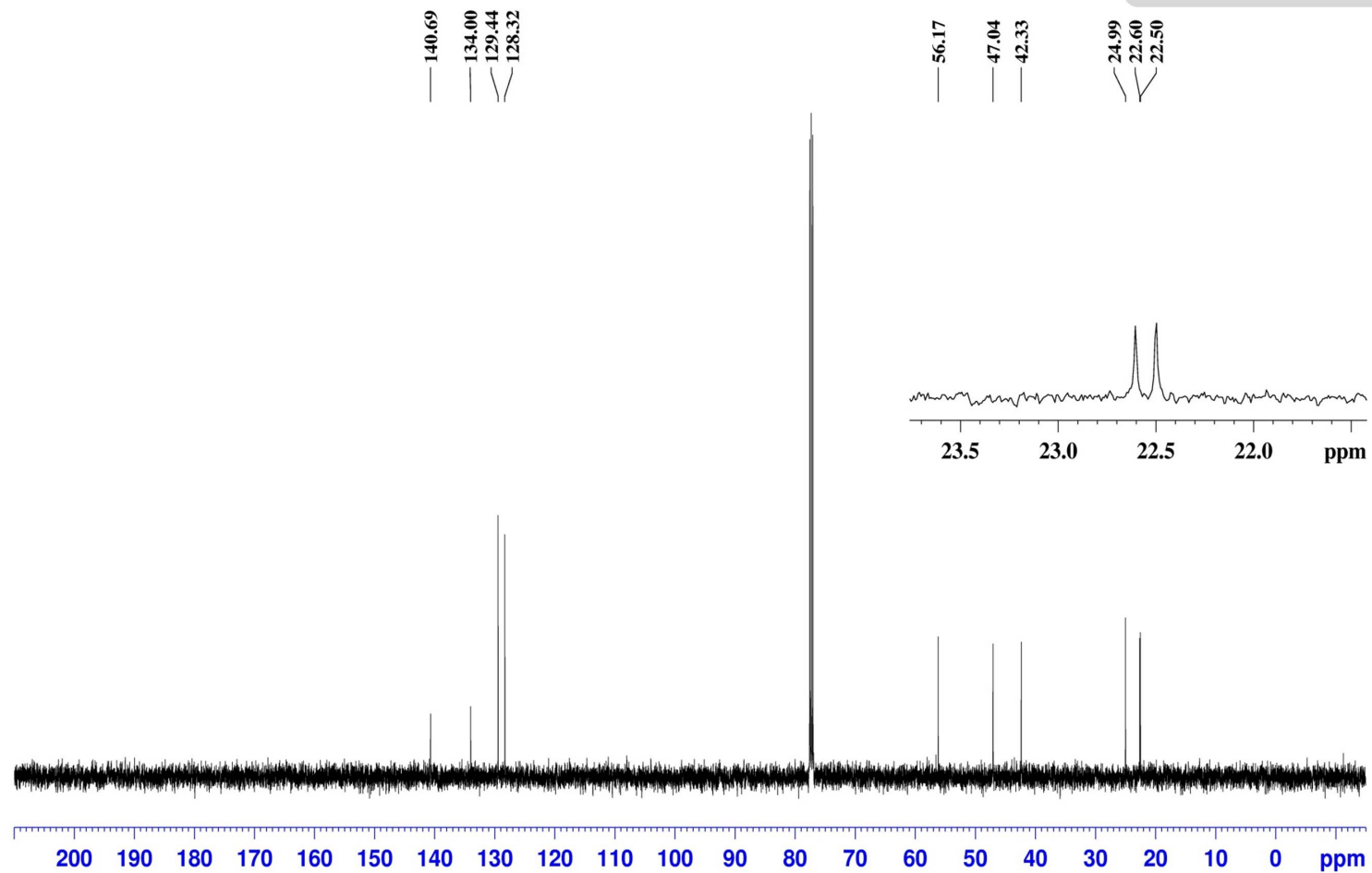
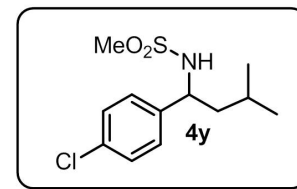
N-(1-(4-(methylthio)phenyl)but-3-en-1-yl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



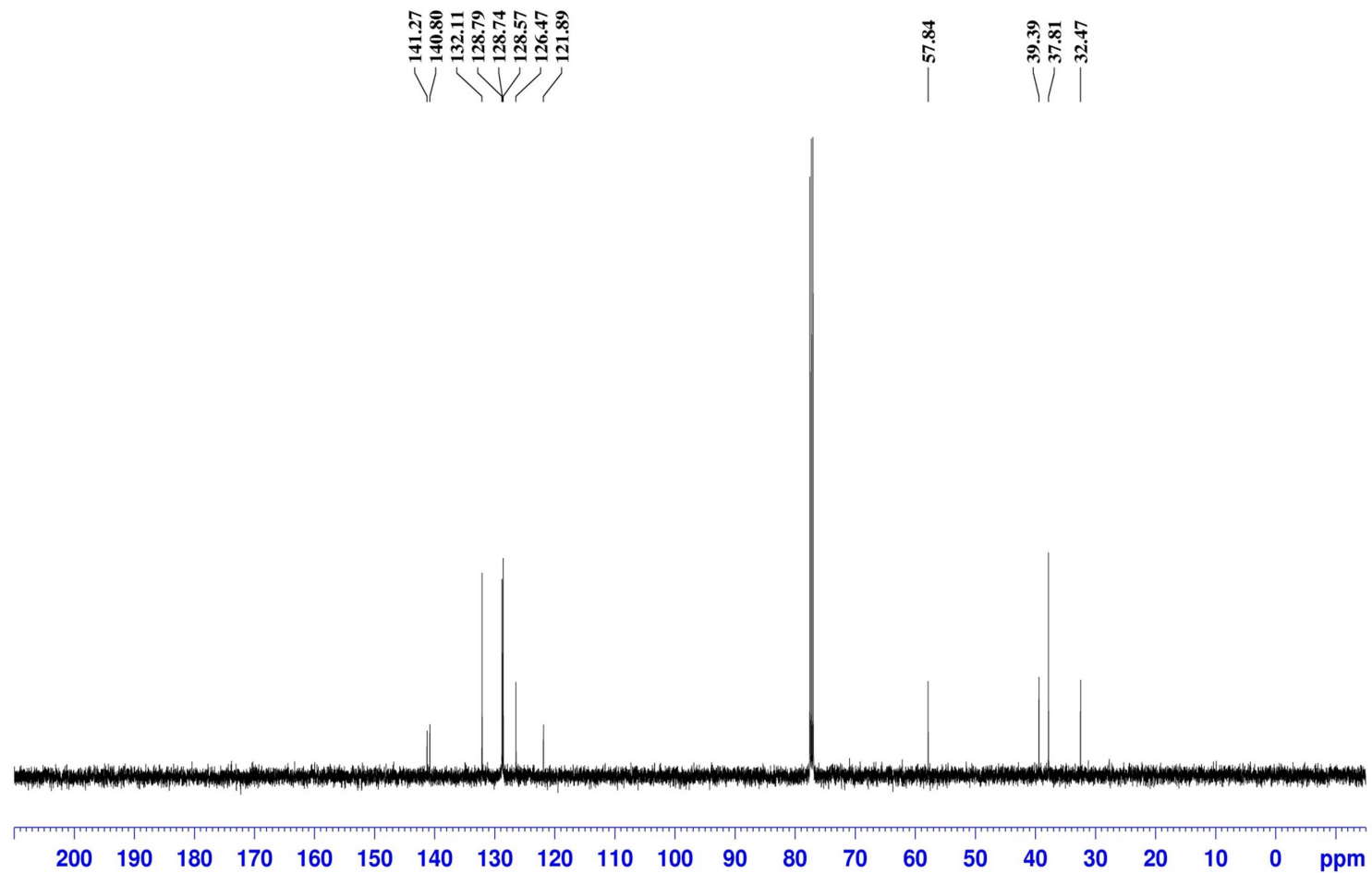
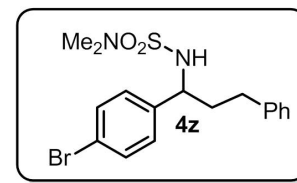
N-(1-(4-methoxyphenyl)but-3-en-1-yl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



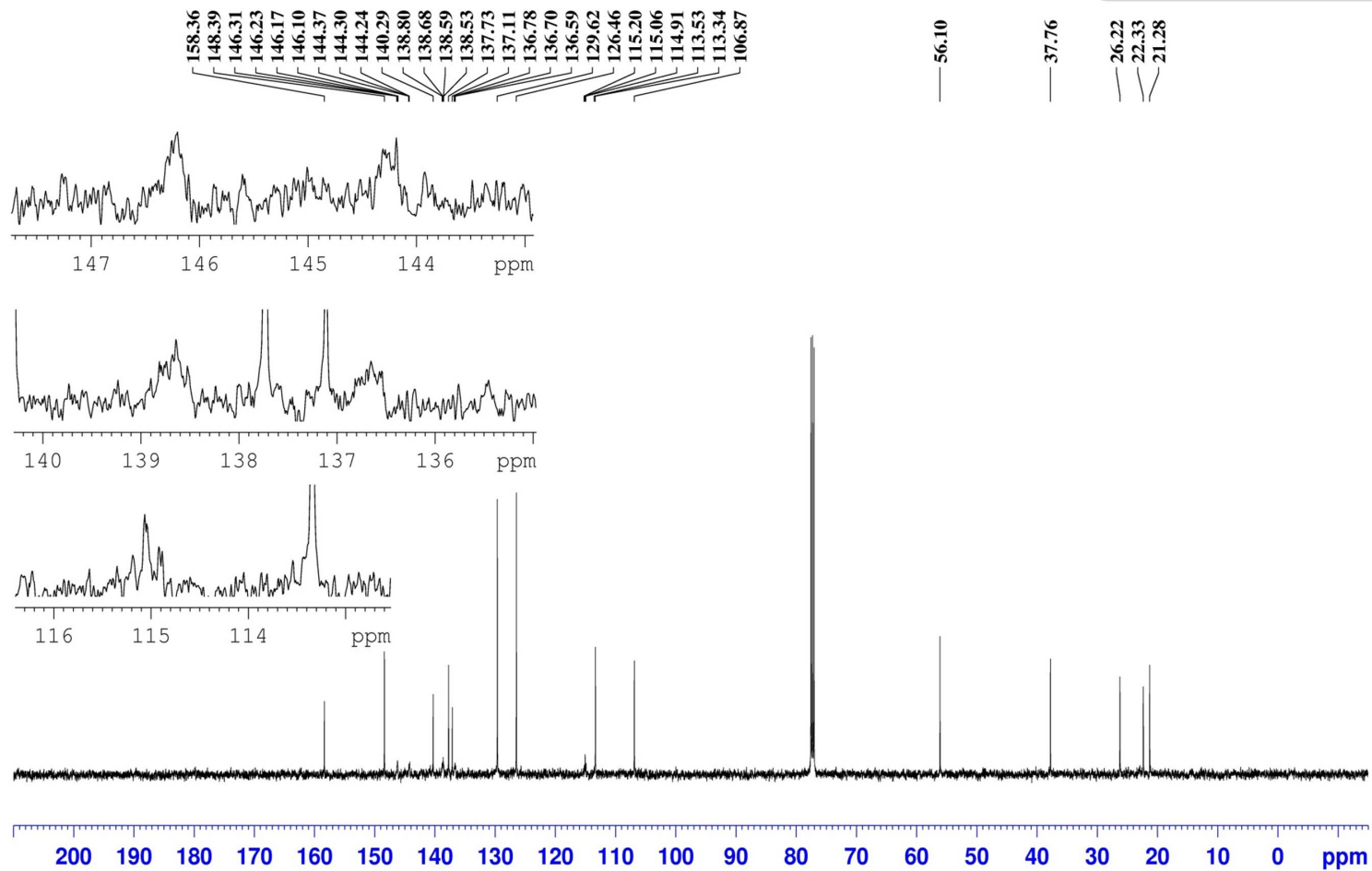
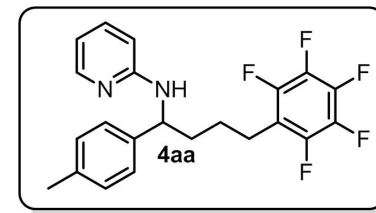
N-(1-(4-chlorophenyl)-3-methylbutyl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



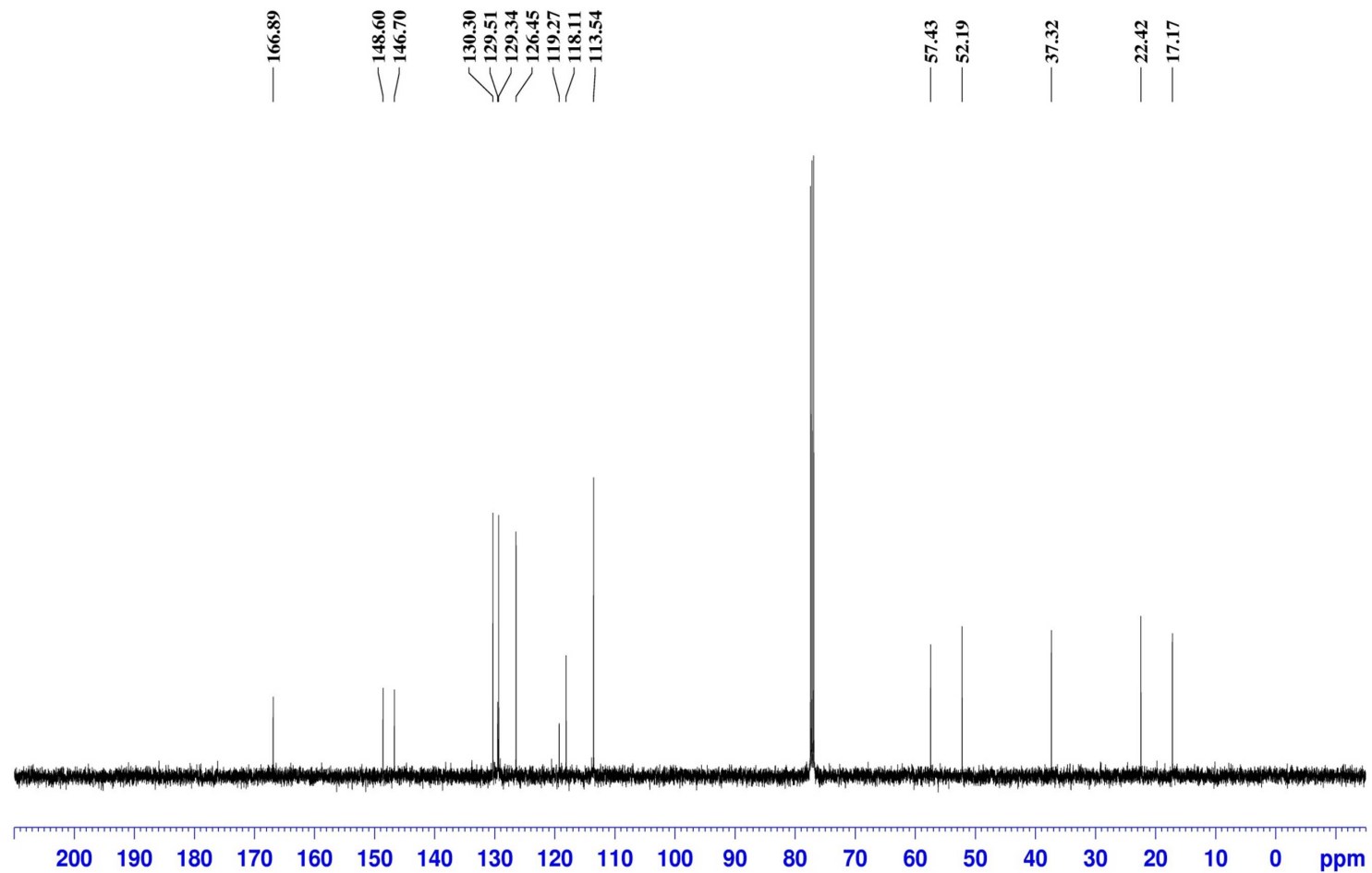
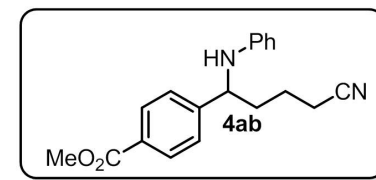
**N<sup>2</sup>-(1-(4-bromophenyl)-3-phenylpropyl)-N,N-dimethylsulfamide**  
125 MHz, CDCl<sub>3</sub>



**N-(4-(perfluorophenyl)-1-(p-tolyl)butyl)pyridin-2-amine**  
125 MHz, CDCl<sub>3</sub>

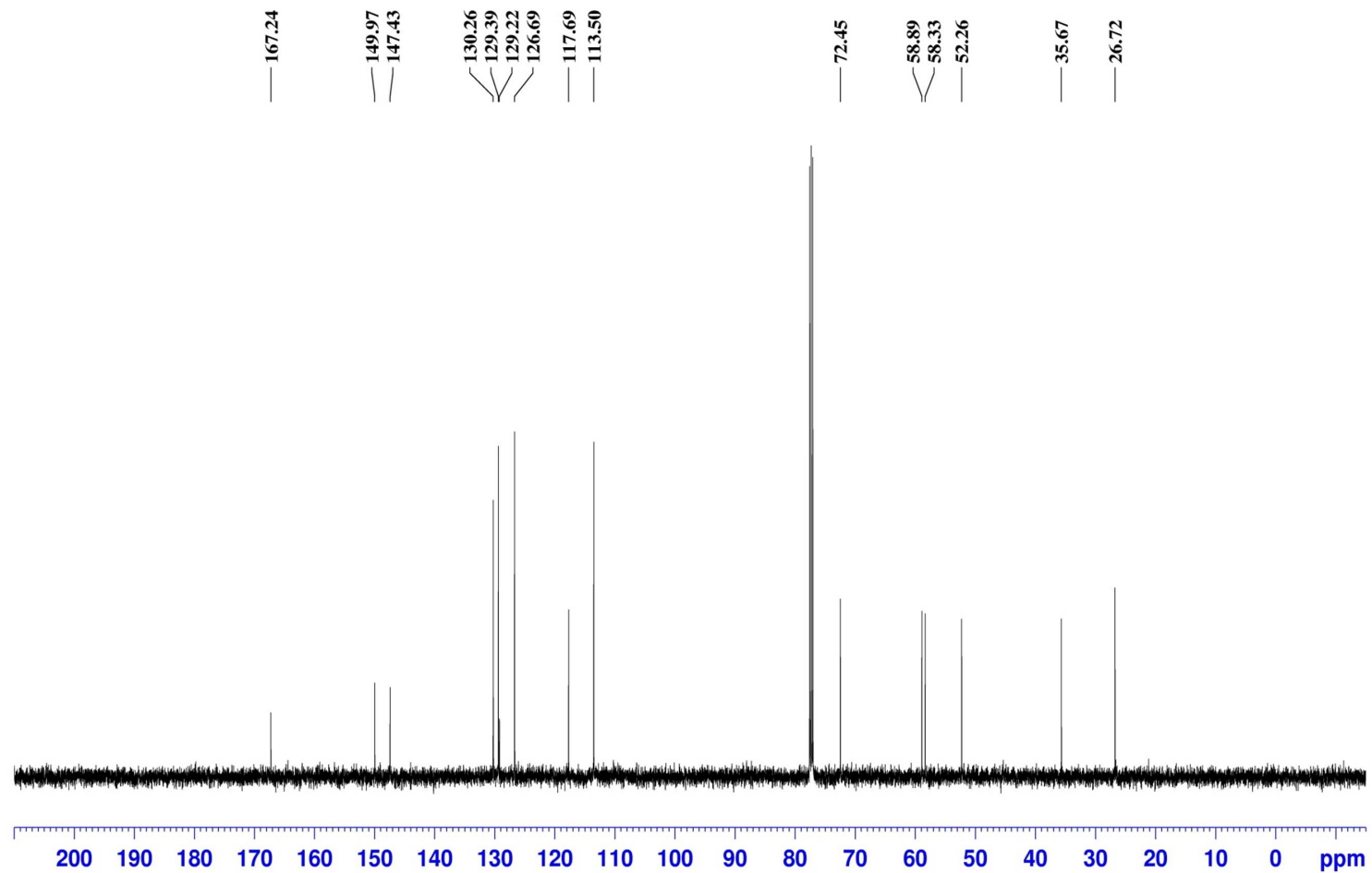
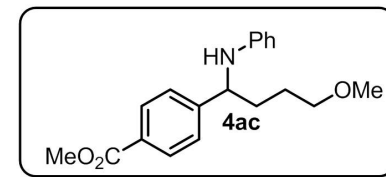


methyl 4-(4-cyano-1-(phenylamino)butyl)benzoate  
125 MHz, CDCl<sub>3</sub>

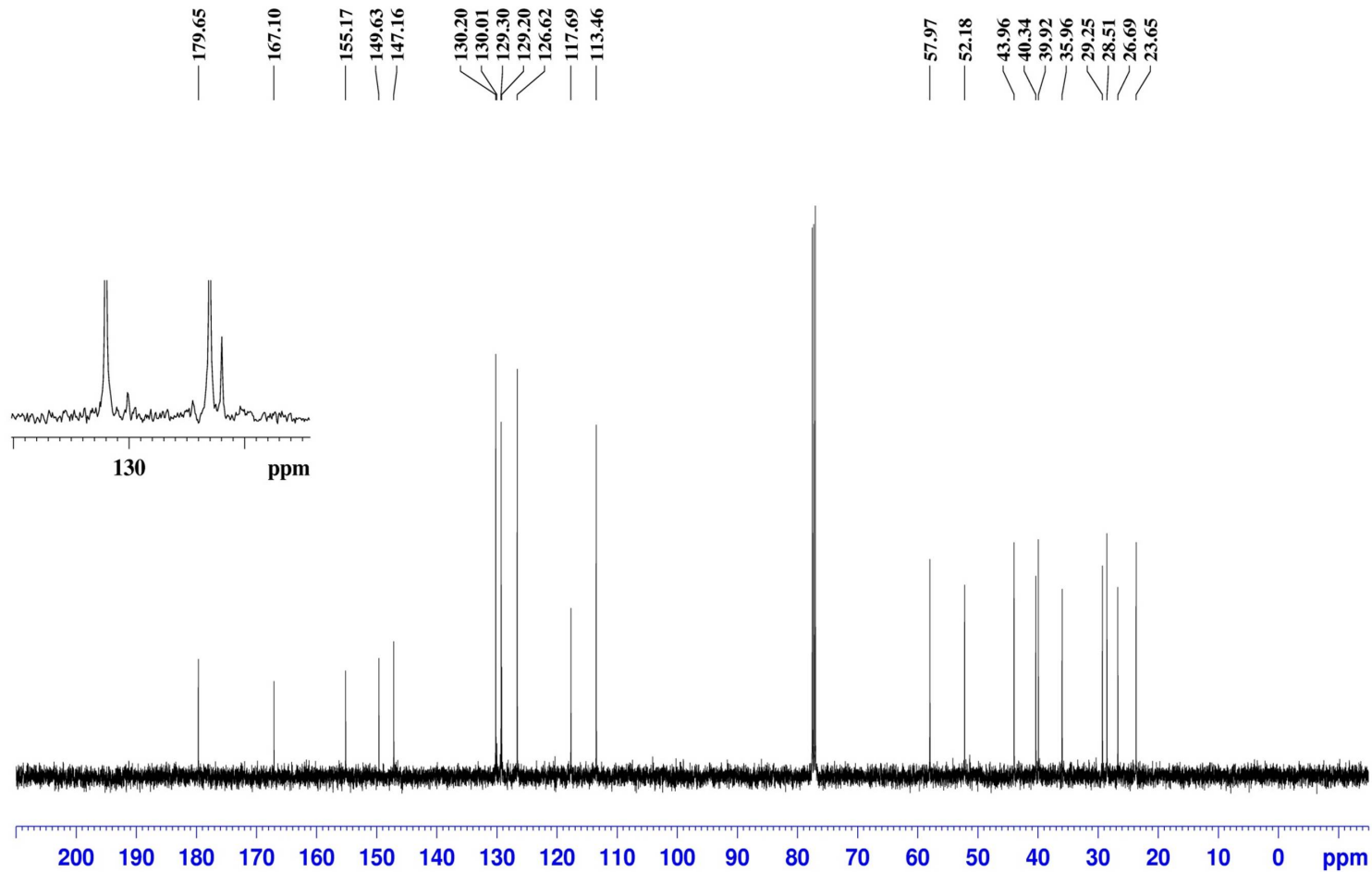
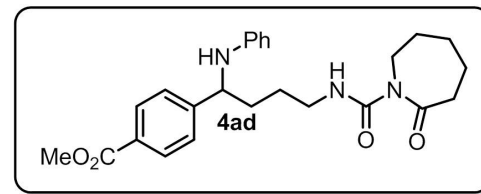




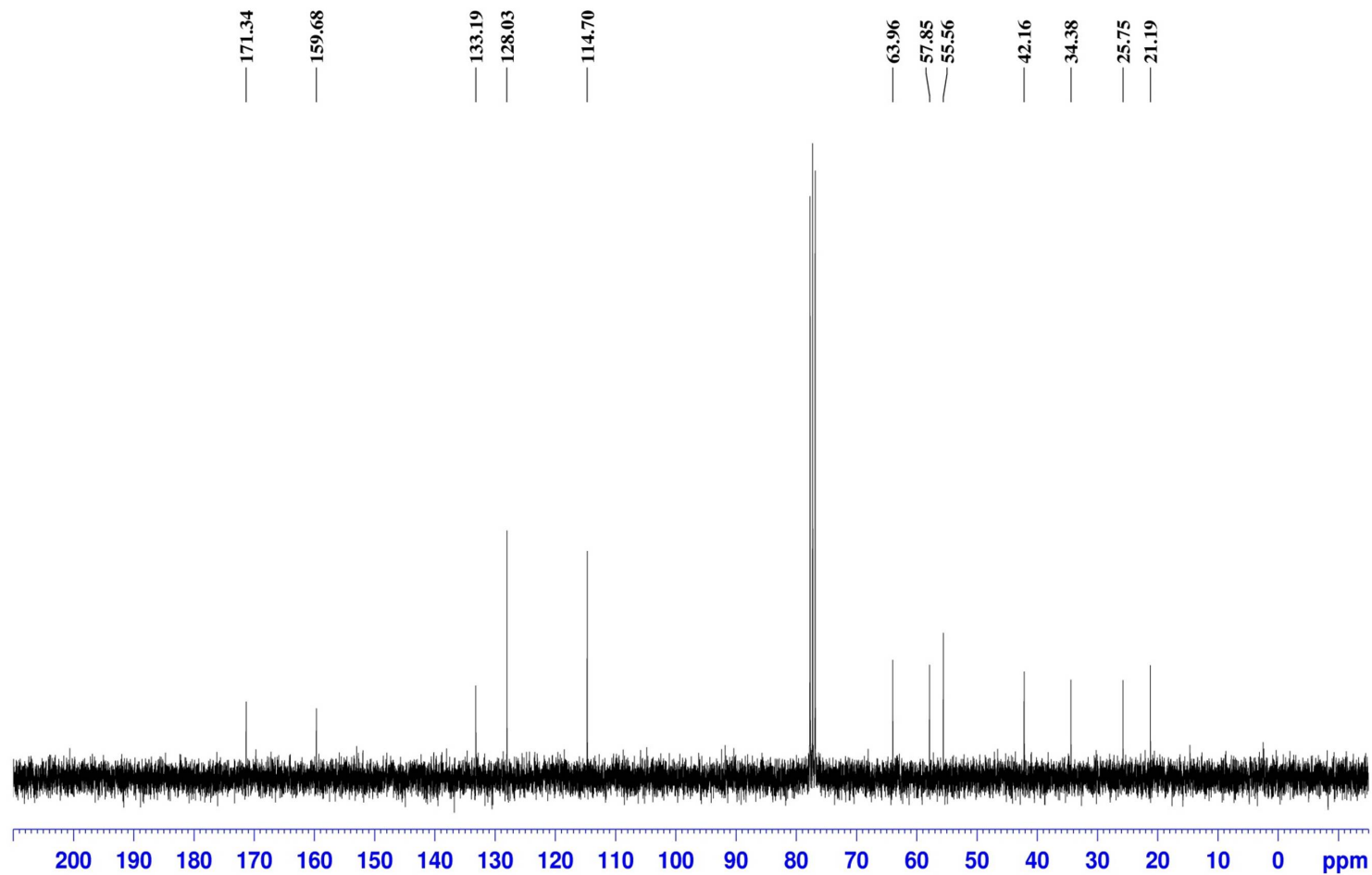
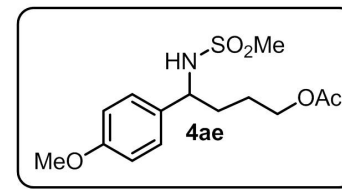
methyl 4-(4-methoxy-1-(phenylamino)butyl)benzoate  
125 MHz, CDCl<sub>3</sub>



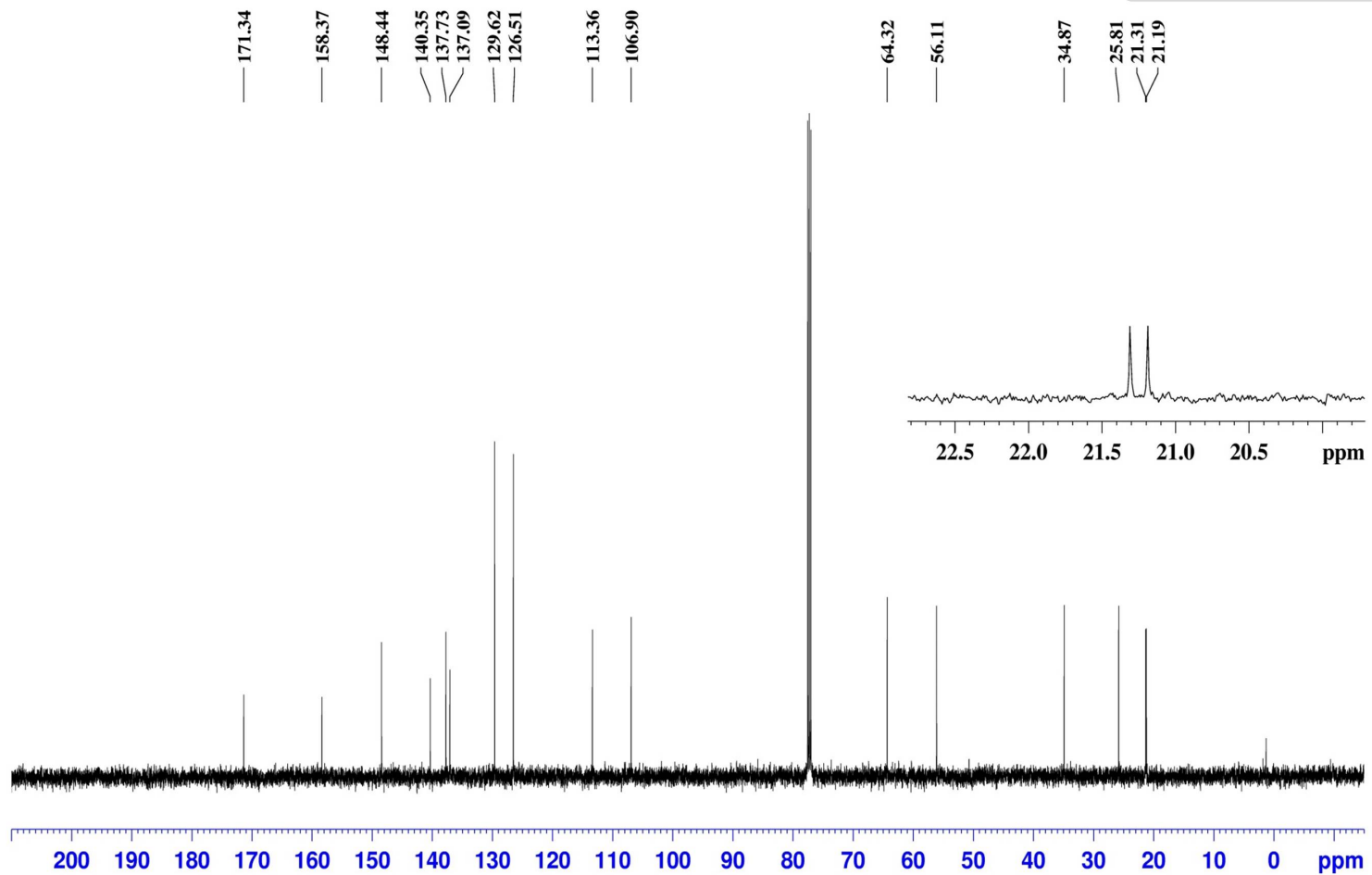
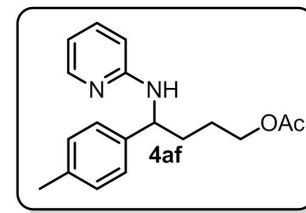
methyl 4-(4-(2-oxoazepane-1-carboxamido)-1-(phenylamino)butyl)benzoate  
125 MHz, CDCl<sub>3</sub>



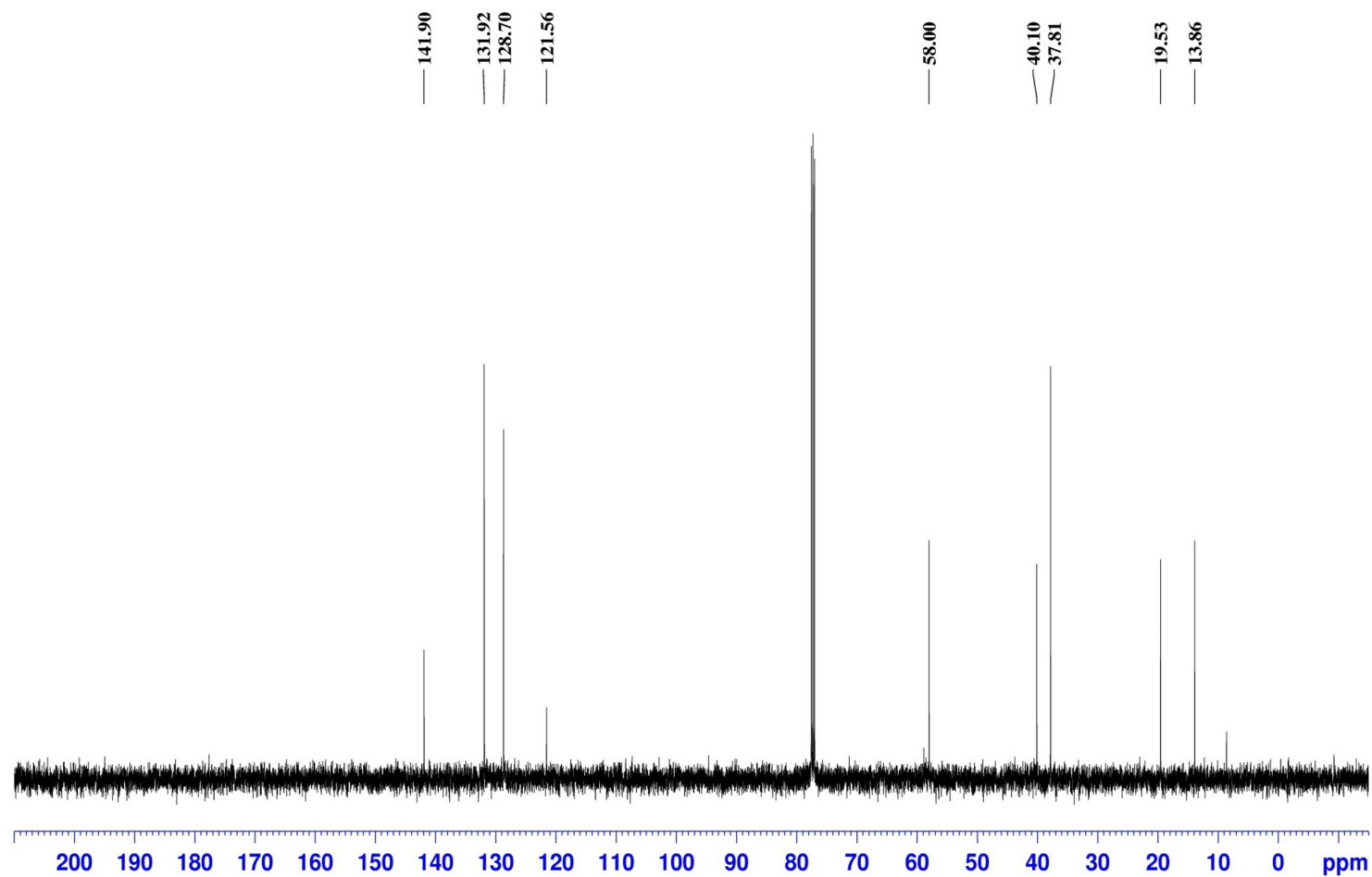
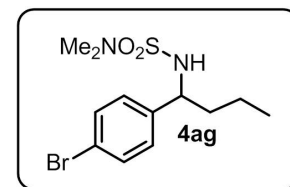
4-(4-methoxyphenyl)-4-(methylsulfonamido)butyl acetate  
75 MHz, CDCl<sub>3</sub>



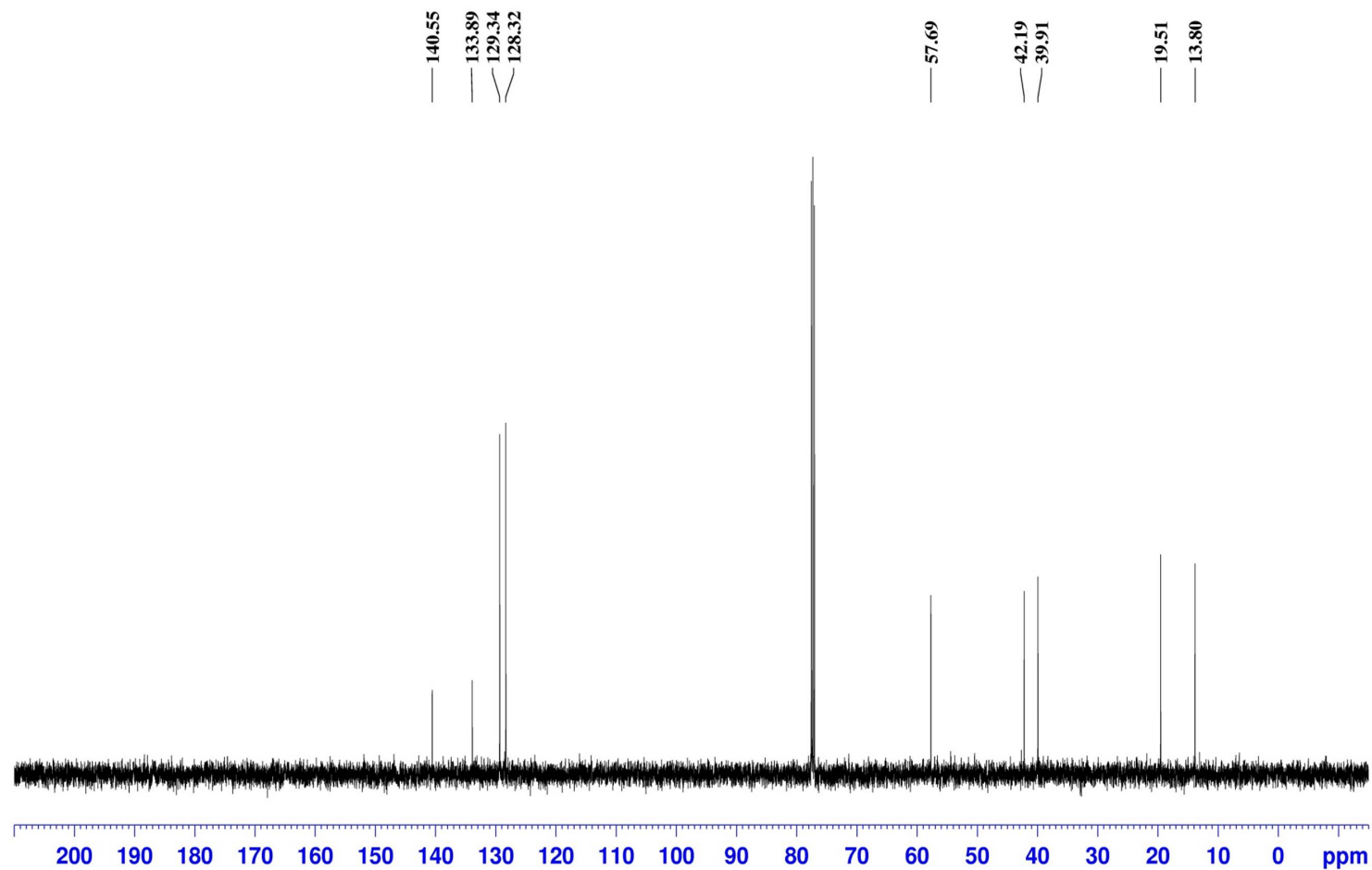
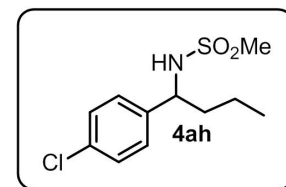
4-(pyridin-2-ylamino)-4-(p-tolyl)butyl acetate  
125 MHz, CDCl<sub>3</sub>



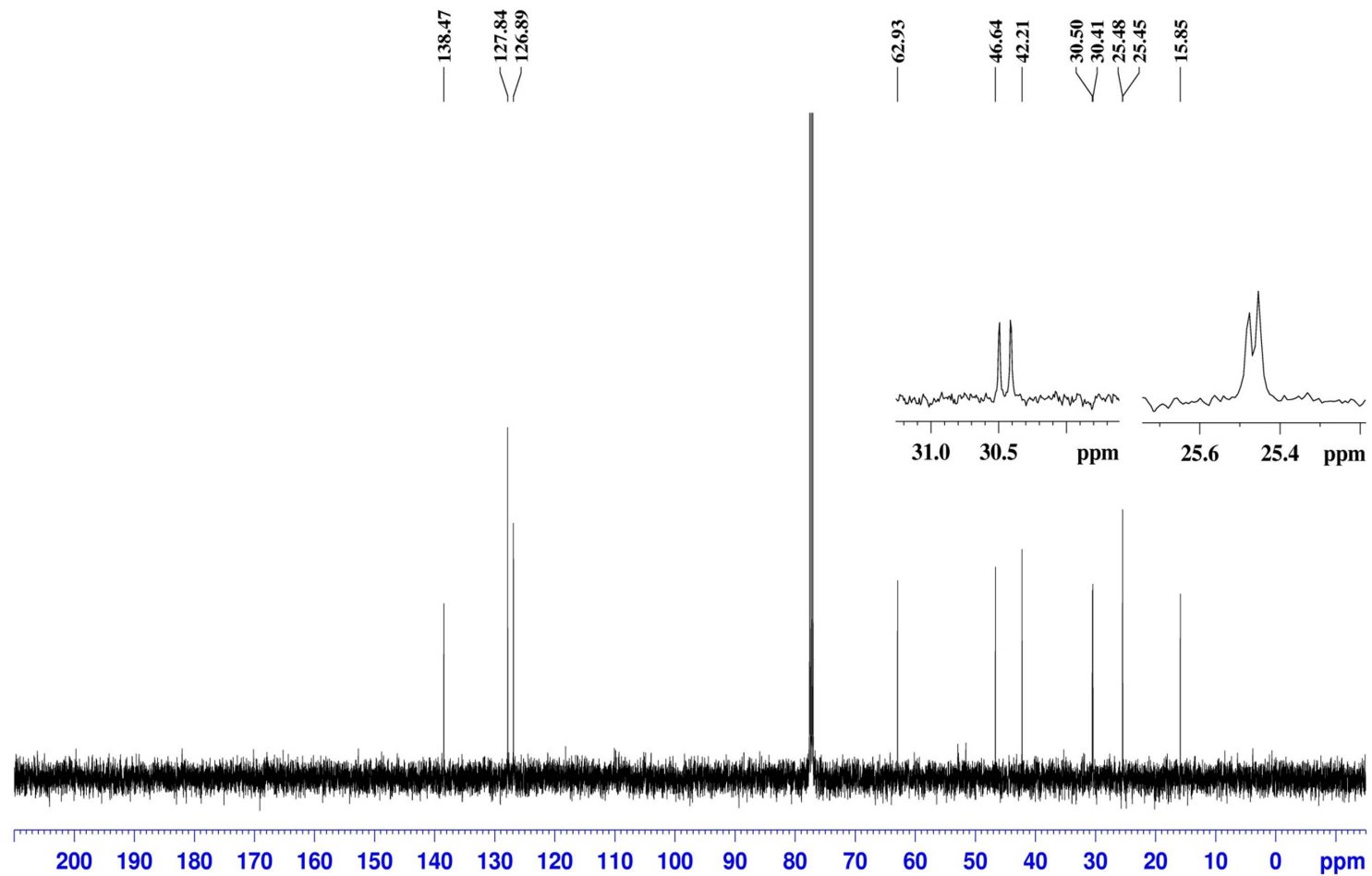
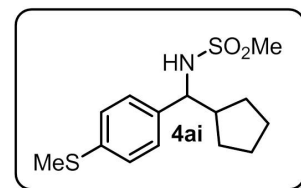
N'-(1-(4-bromophenyl)butyl)-N,N-dimethylsulfamide  
125 MHz, CDCl<sub>3</sub>



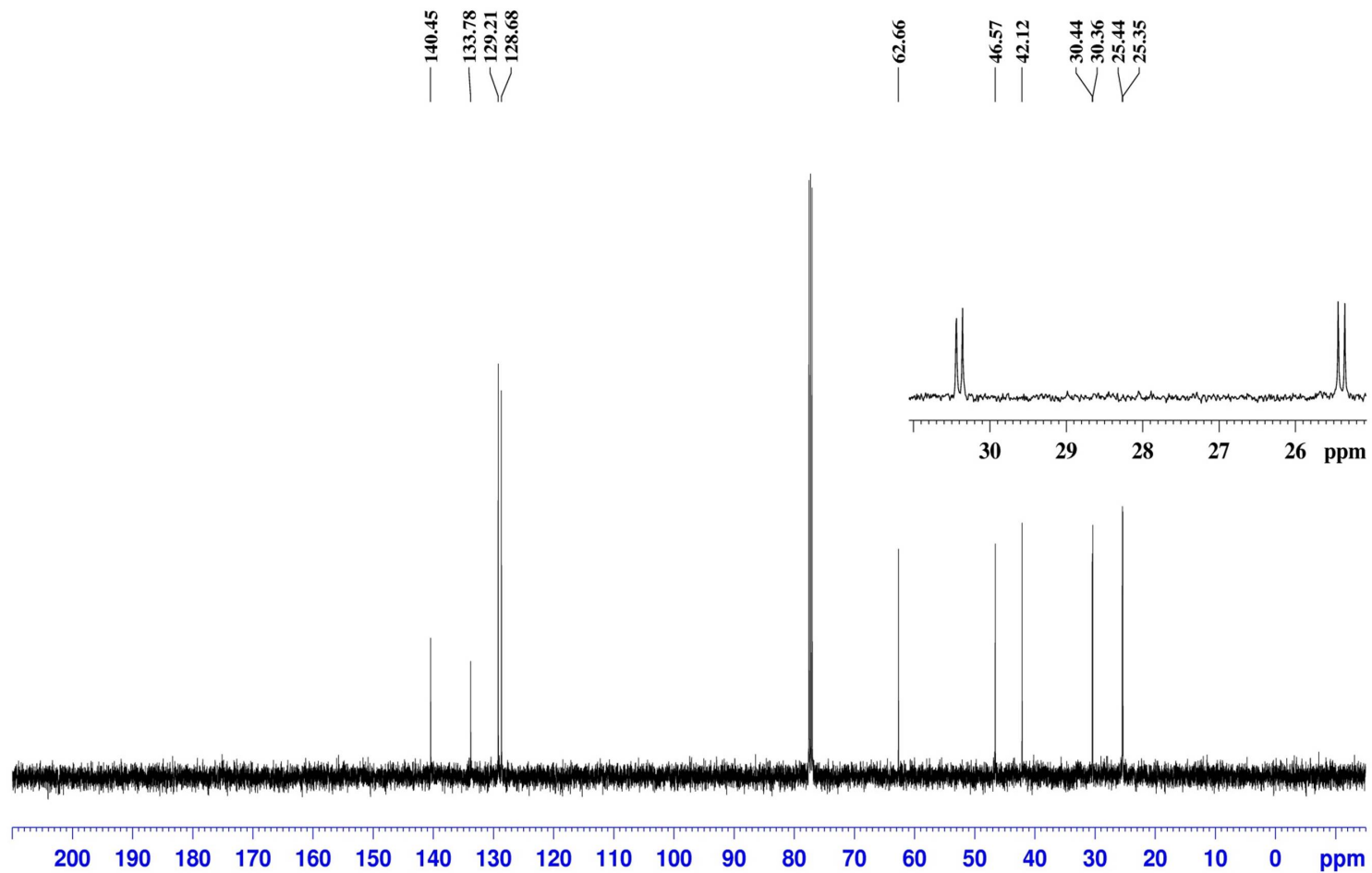
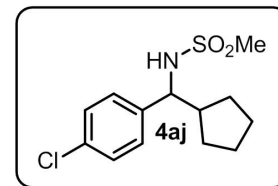
N-(1-(4-chlorophenyl)butyl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>



N-(cyclopentyl(4-(methylthio)phenyl)methyl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>

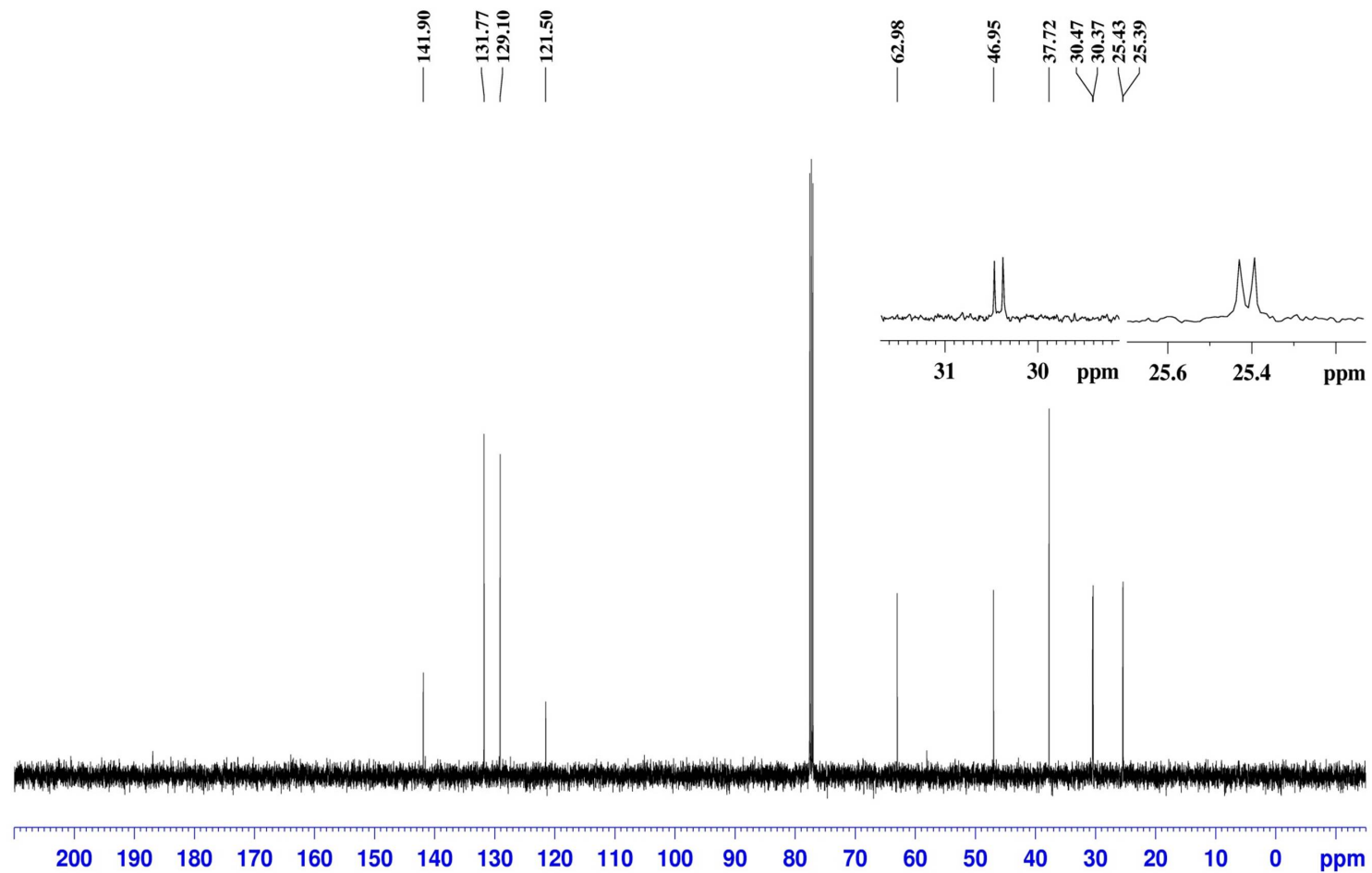
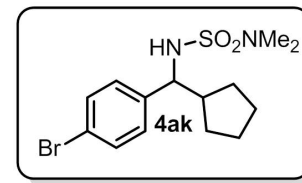


N-((4-chlorophenyl)(cyclopentyl)methyl)methanesulfonamide  
125 MHz, CDCl<sub>3</sub>

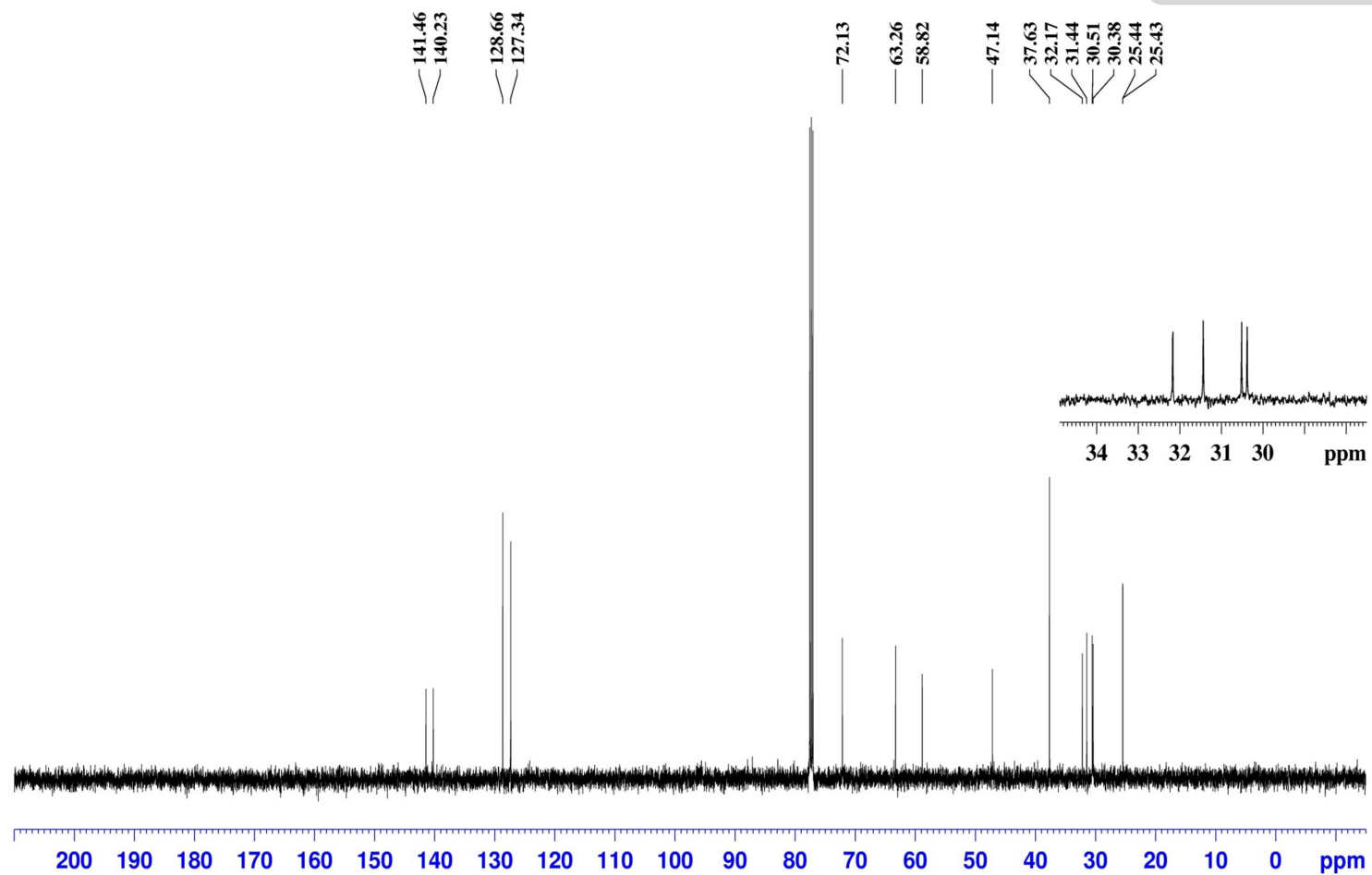
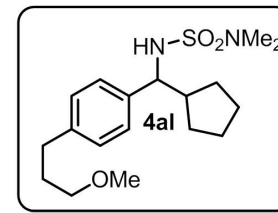




**N'-((4-bromophenyl)(cyclopentyl)methyl)-N,N-dimethylsulfamide**  
125 MHz, CDCl<sub>3</sub>

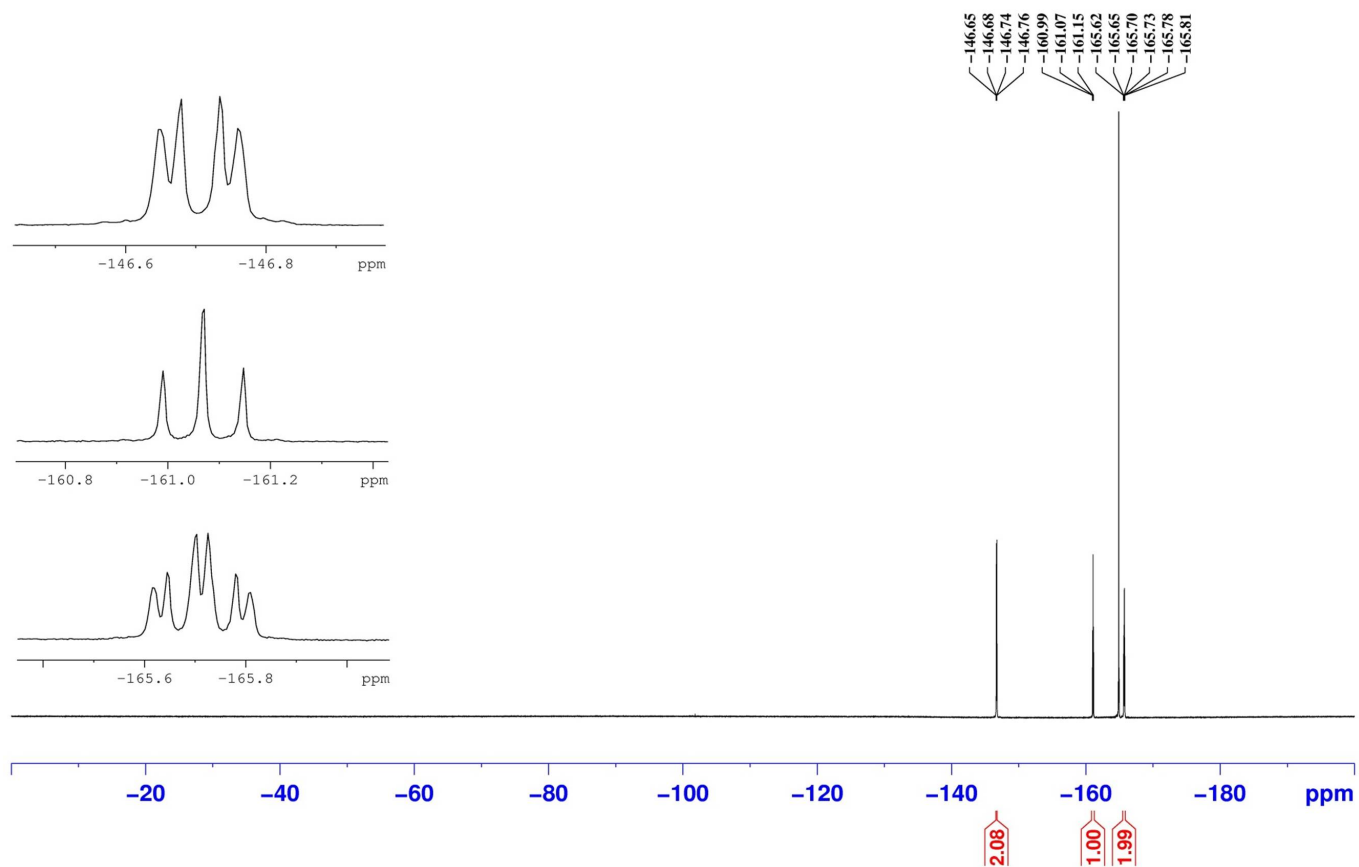
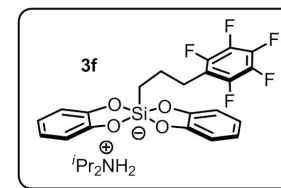


N'-(cyclopentyl(4-(3-methoxypropyl)phenyl)methyl)-N,N-dimethylsulfamide  
500 MHz, CDCl<sub>3</sub>

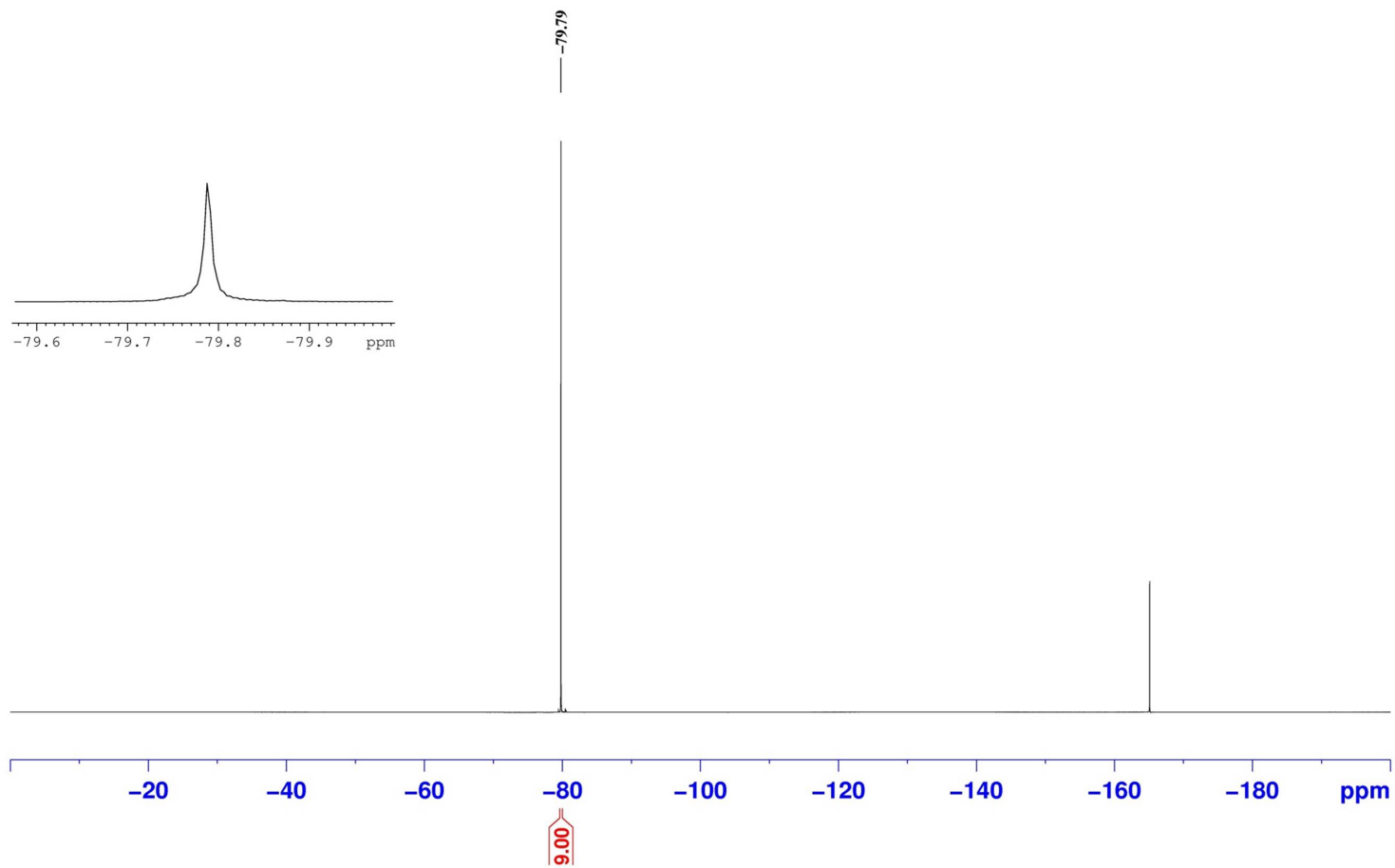
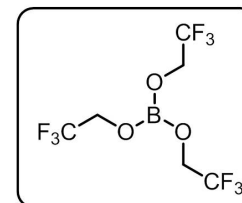


# <sup>19</sup>F NMR Spectra of Synthesized Compounds

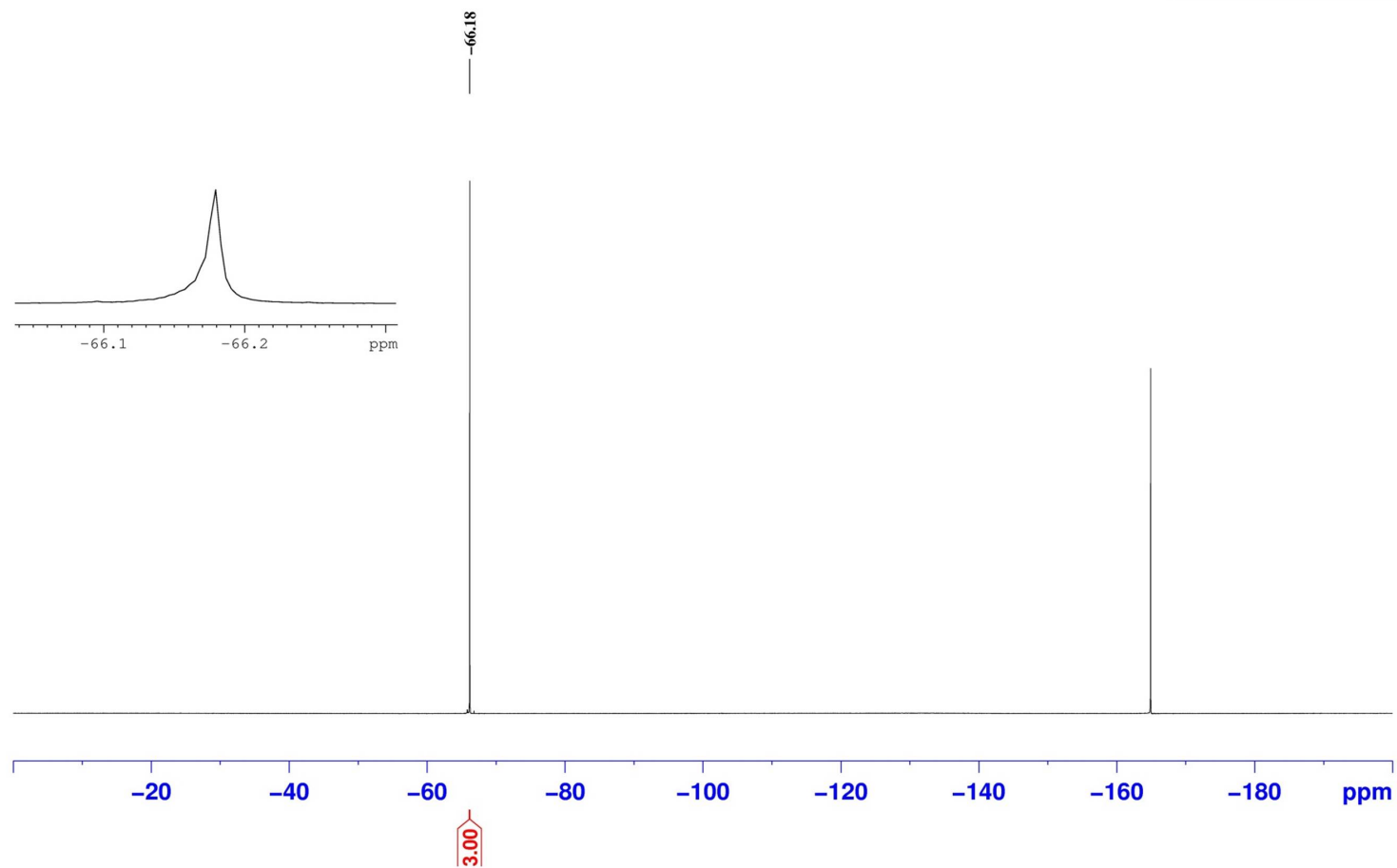
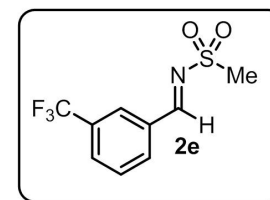
Diisopropylammonium Bis(catecholato) (3-pentafluorophenylpropyl)silicate  
282 MHz, CDCl<sub>3</sub>



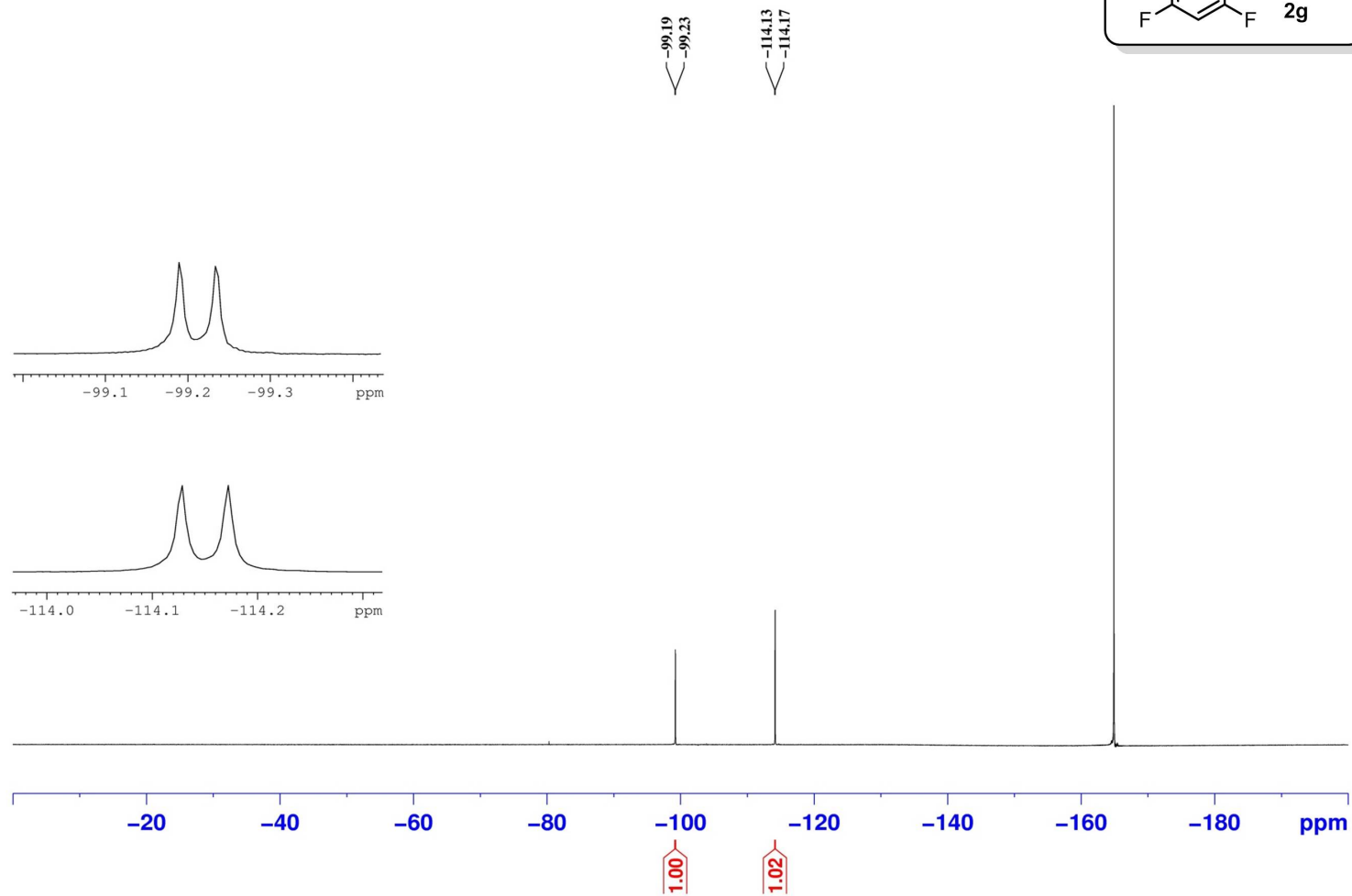
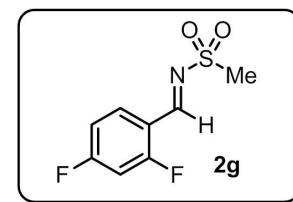
Tris(2,2,2-trifluoroethyl)borate  
282 MHz, CDCl<sub>3</sub>



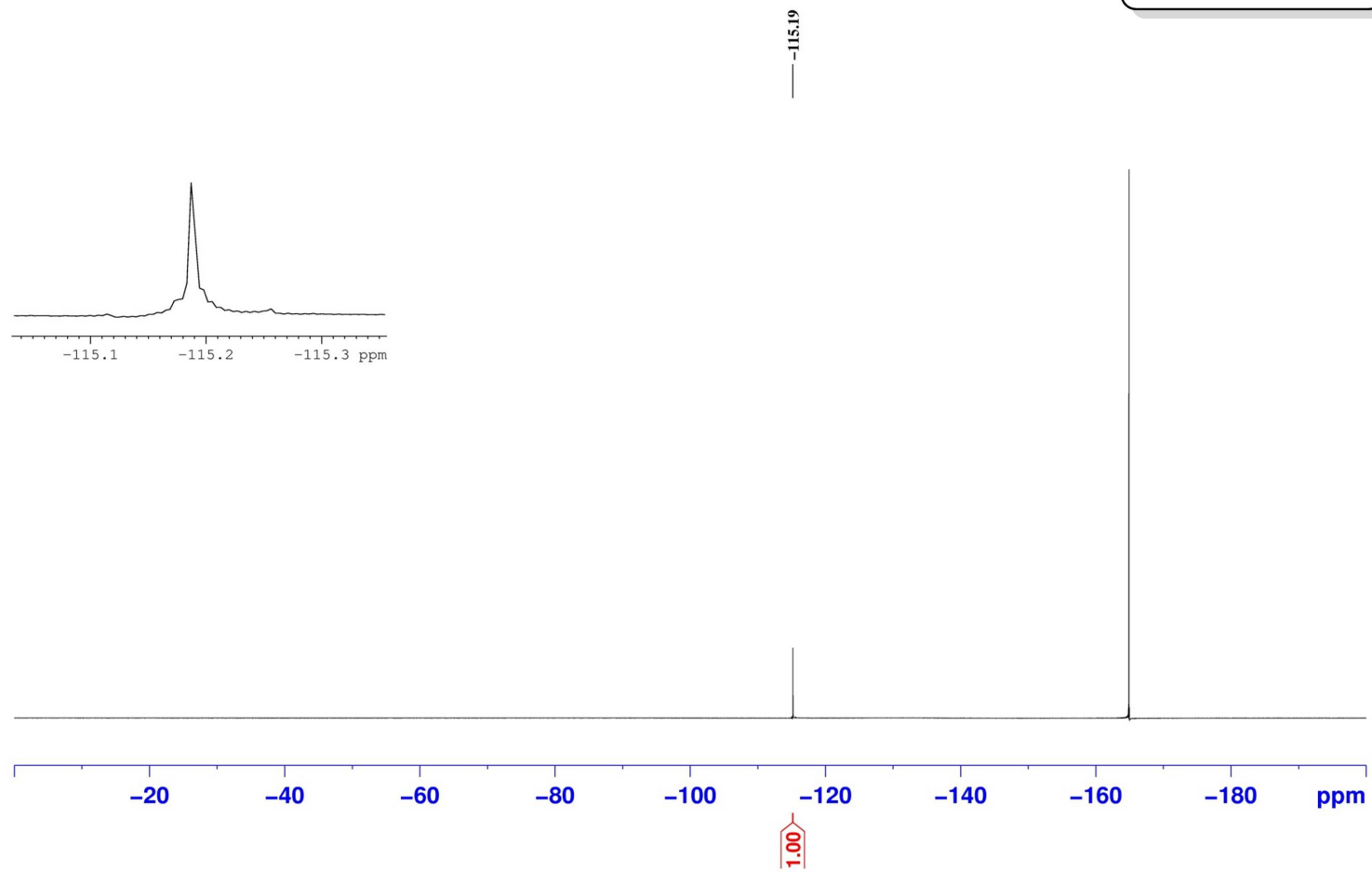
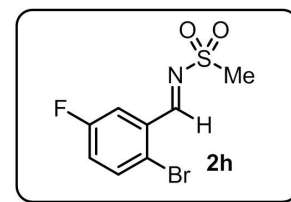
N-(3-(trifluoromethyl)benzylidene)methanesulfonamide  
282 MHz, CDCl<sub>3</sub>



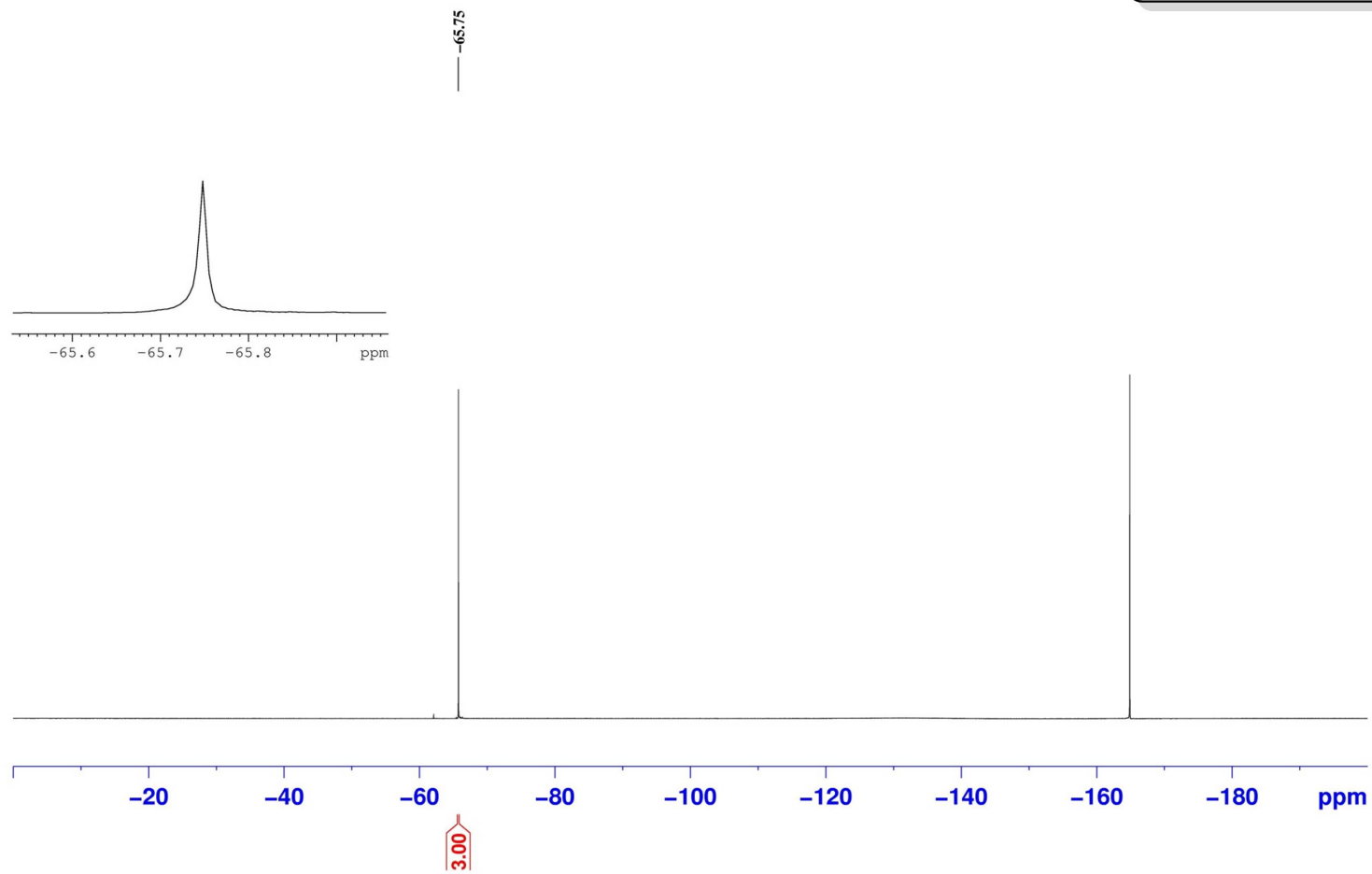
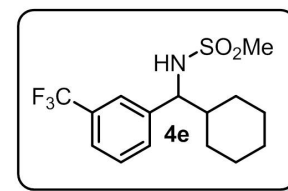
N-(2,4-difluorobenzylidene)methanesulfonamide  
282 MHz, CDCl<sub>3</sub>



**N-(2-bromo-5-fluorobenzylidene)methanesulfonamide**  
282 MHz, CDCl<sub>3</sub>

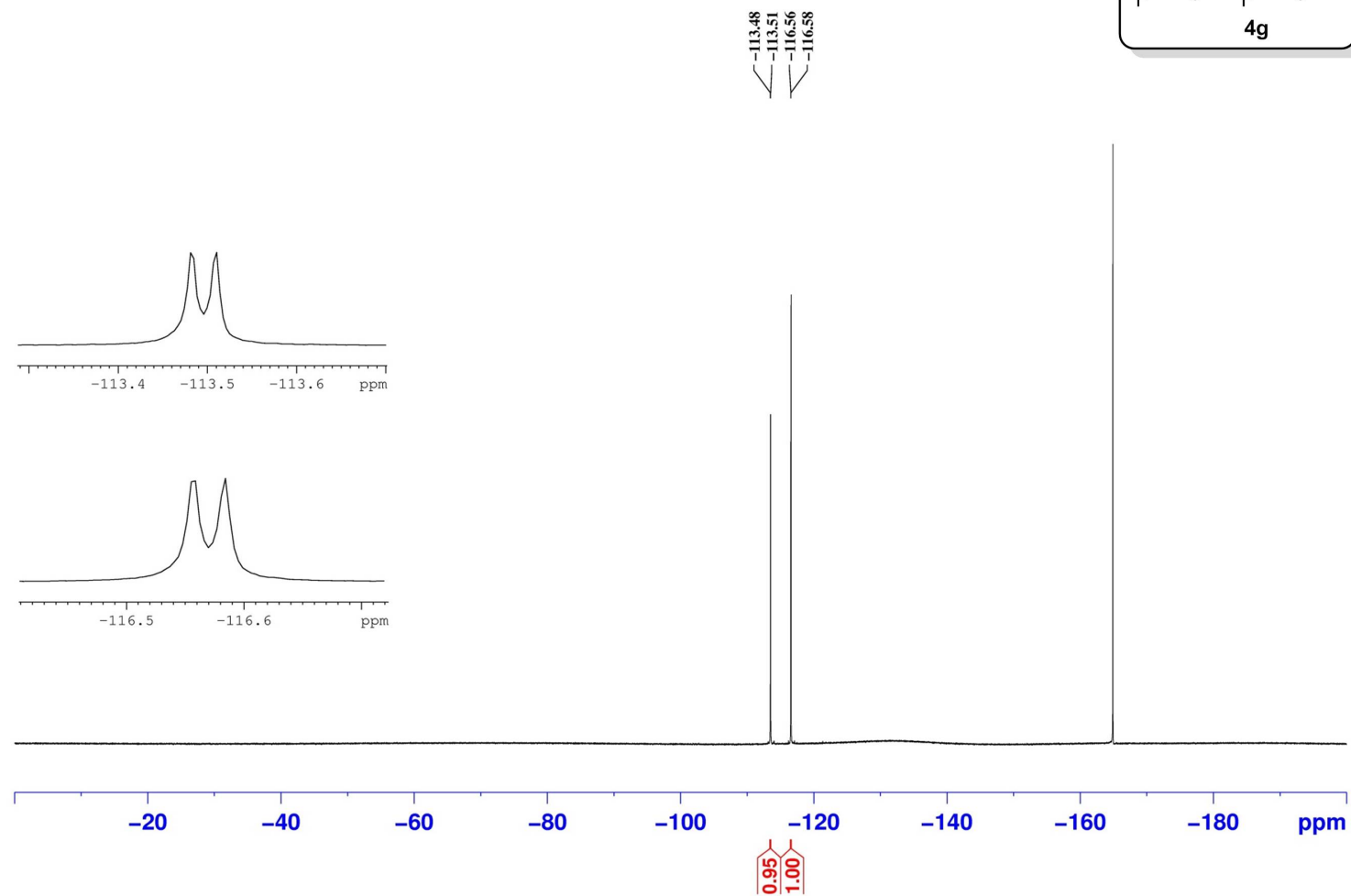
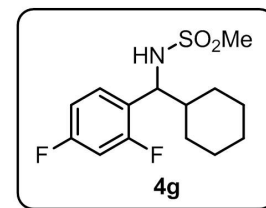


N-(cyclohexyl(3-(trifluoromethyl)phenyl)methyl)methanesulfonamide  
282 MHz, CDCl<sub>3</sub>

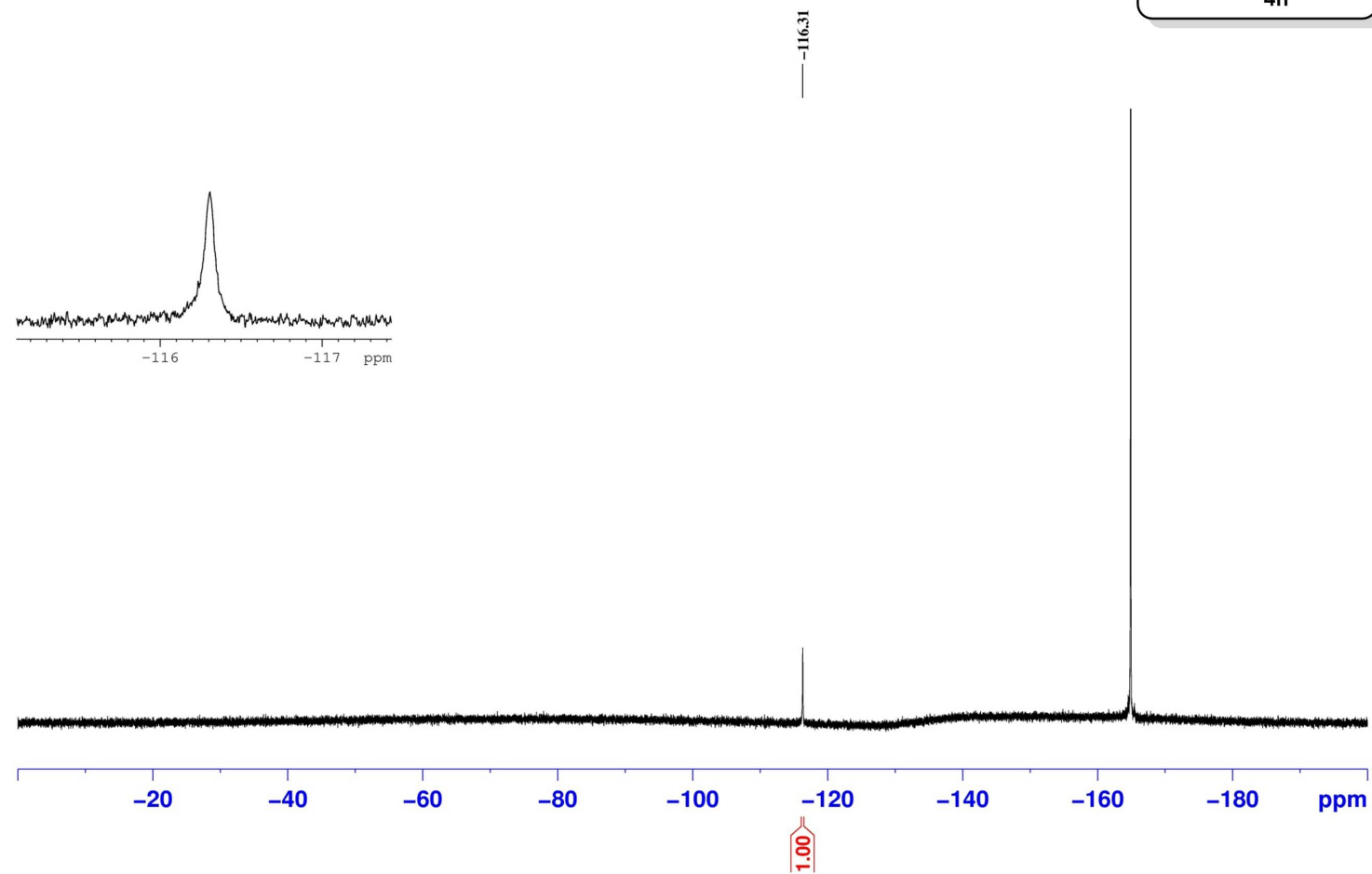
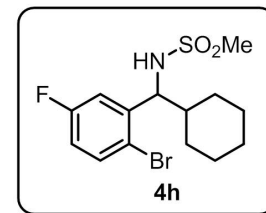




N-(cyclohexyl(2,4-difluorophenyl)methyl)methanesulfonamide  
282 MHz, CDCl<sub>3</sub>



N-((2-bromo-5-fluorophenyl)(cyclohexyl)methyl)methanesulfonamide  
282 MHz, CDCl<sub>3</sub>



**N-(4-(perfluorophenyl)-1-(p-tolyl)butyl)pyridin-2-amine**  
282 MHz, CDCl<sub>3</sub>

