

## Supporting Information for:

### Visible-light-induced tandem ring opening/1,6-conjugate addition of cyclobutanols with *p*-quinone methides under metal- and additive-free conditions

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## 1. General Information

Flash column chromatography was performed using silica gel from Qingdao Haiyang. Anhydrous solvents [tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), toluene, ethyl acetate (EtOAc), acetonitrile (CH<sub>3</sub>CN), methanol (CH<sub>3</sub>OH), dichloromethane (DCM), and 1,4-dioxane] were purchased from Adamas, Energy Chemicals, or Innochem, and used as received. All commercial reagents were purchased from Bidepharm, Energy Chemical, Aladdin, and Adamas of the highest purity grade. Photosensitizers were purchased from laajoo, Adamas, Alfa, or Aldrich, and used as received.

## General Analytical Information

All new compounds were characterized by NMR spectroscopy, high-resolution mass spectroscopy, and melting point (if solids). NMR spectra were recorded on a Bruker Ascend™ 400 spectrometer and were calibrated using TMS or residual deuterated solvent as an internal reference (Chloroform-*d*: 7.26 ppm for <sup>1</sup>H NMR and 77.16 ppm for <sup>13</sup>C NMR, DMSO-*d*<sub>6</sub>: 2.50 ppm for <sup>1</sup>H NMR and 39.52 ppm for <sup>13</sup>C NMR). HRMS spectra were recorded on a Waters Acquity UPLC/Xevo TQD MSMS. Melting points (Mp) were recorded on a MP450 melting point apparatus.

## Experimental Set-up

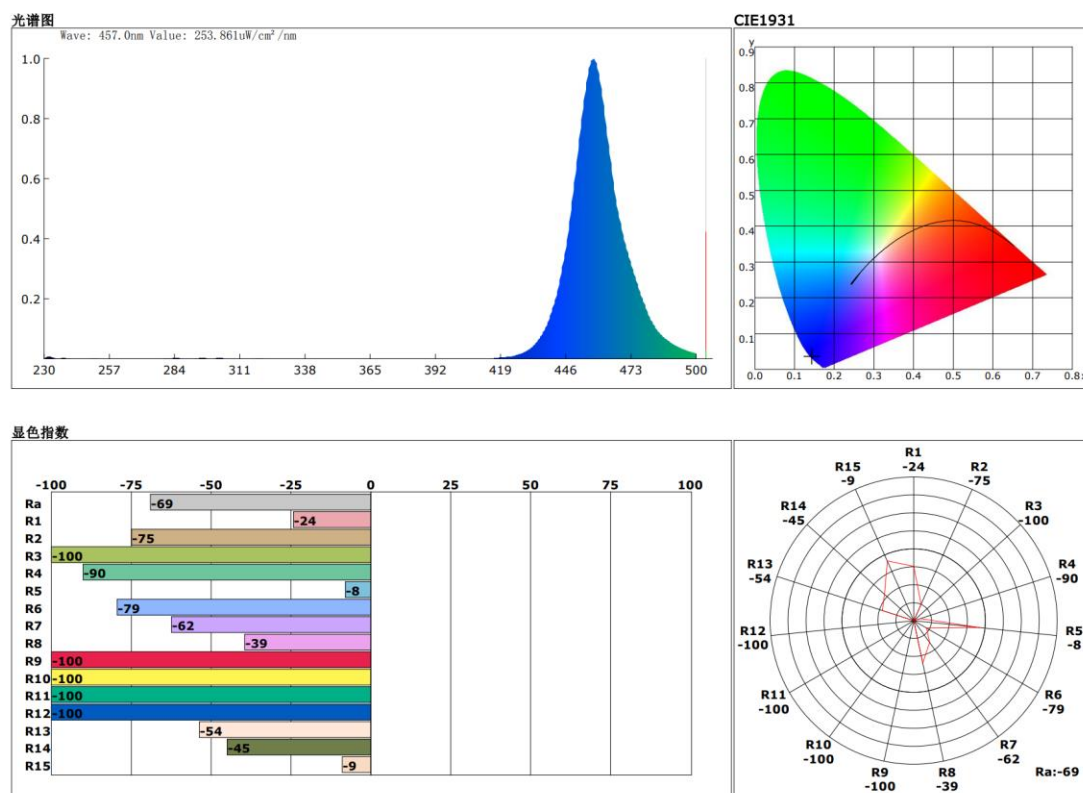


Figure S1. The emission spectra and spectral distribution of the blue LEDs

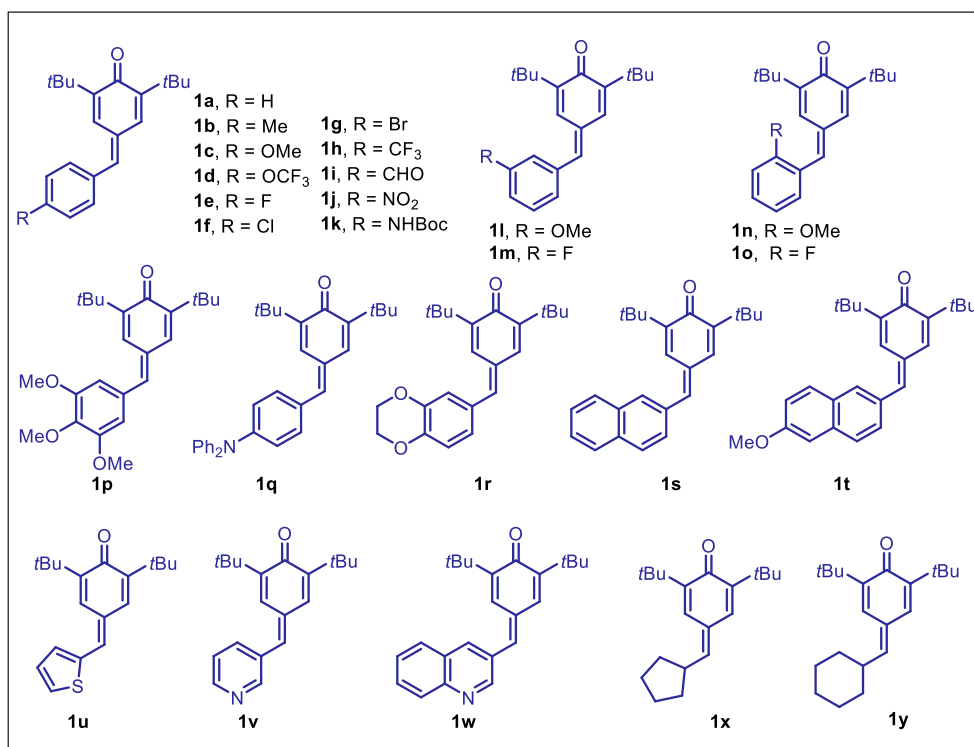
The Material of the Irradiation Vessel  
 Manufacturer: GeAo Chemical  
 Model: 24 W, blue LEDs  
 Broadband source:  $\lambda = 450\text{-}460\text{ nm}$  ( $\lambda_{\text{max}} = 457.0\text{ nm}$ )  
 Material of the irradiation vessel: borosilicate reaction tube  
 Distance from the light source to the irradiation vessel: 3.0 cm  
 Not use any filters

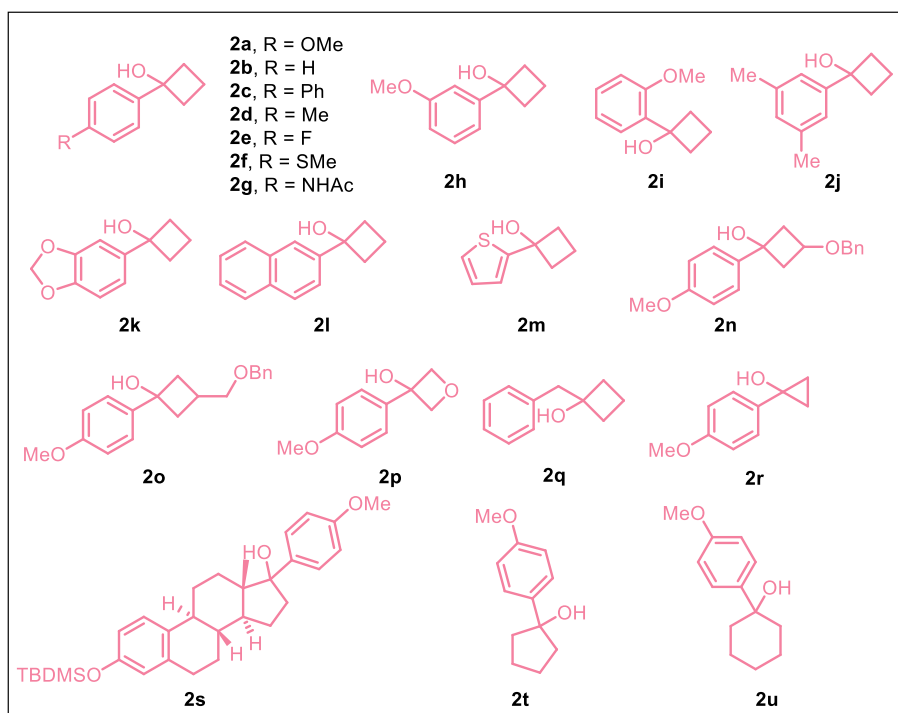


Figure S2. The set-up for the reaction

## 2. Product Synthesis and Characterization

### 2.1 List of Substrates

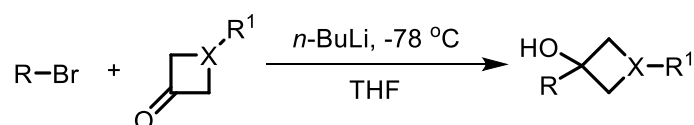




The *p*-quinone methides **1a-1y**<sup>[1]</sup> and all cyclobutanols **2a-2u** were prepared according to reported literature procedures.

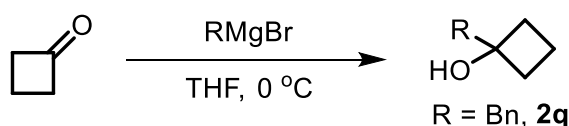
## 2.2 General procedure for the preparation of cyclobutanols

Cyclobutanols **2a-2p**, **2t**, **2u** were prepared according to **procedure A**:



**Procedure A:** **2a-2p**, **2t**, **2u** were synthesized according to the reported procedure<sup>[2]</sup>. *n*BuLi (2.5M in THF, 5.2 mL, 13 mmol, 1.3 equiv.) was added dropwise over 5 min to a solution of bromide (13 mmol, 1.3 equiv.) in THF (20 mL) at -78 °C. The reaction mixture was stirred at -78 °C for a further 10 min. Cyclobutanone (10mmol, 1.0 equiv.) was added dropwise as a solution in THF (5 mL) to the reaction mixture. Following a further 10 min at -78 °C the reaction mixture was warmed to rt then quenched with water (20 mL). The filtrate was extracted with ethyl acetate (3 × 20 mL), washed with saturated NaCl solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the cyclobutanols **2a-2p**, **2t**, **2u**.

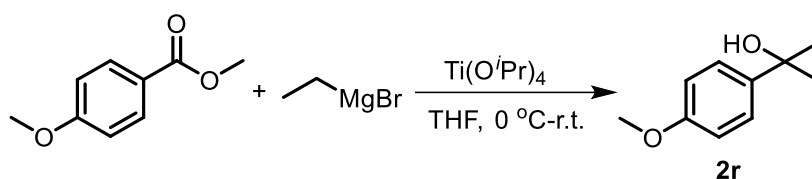
Cyclobutanol **2q** was prepared according to **procedure B**:





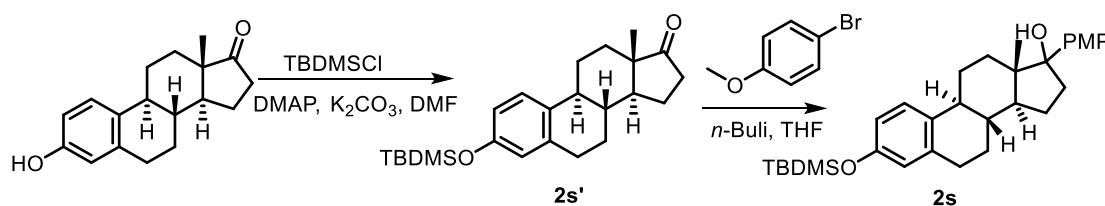
**Procedure B:** **2q** was synthesized according to the reported procedure<sup>[3]</sup>. To an oven-dried round bottom flask (100 mL) equipped, the cyclobutanone (10 mmol, 1.0 equiv.) was dissolved in dry diethyl ether (15 mL) and stirred for 5 min at 0 °C under argon. Then benzylmagnesium bromide (13 mmol, 13 mL, 1 mol/L in THF, 1.0 equiv.) was added dropwise to the solution. Following a further 2 h at 0 °C, the reaction mixture was warmed to rt. The reaction was quenched with water (15 mL). The filtrate was extracted with ethyl acetate (3 × 20 mL), washed with saturated NaCl solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the cyclobutanol **2q**.

Cyclopropanol **2r** was prepared according to **procedure C**:



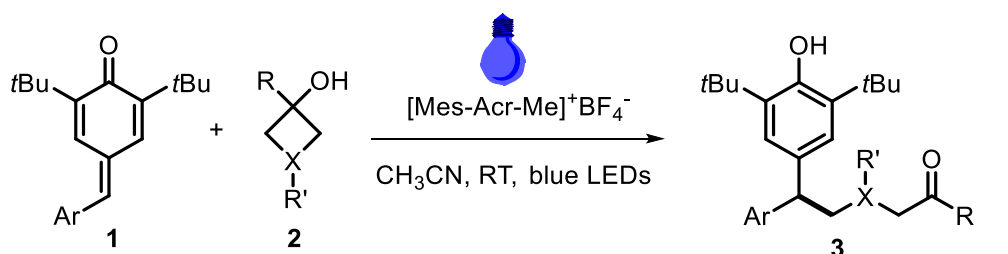
**Procedure C:** **2r** was synthesized according to the reported procedure<sup>[4]</sup>. To an oven-dried round bottom flask (100 mL) equipped, the ester (10 mmol) was dissolved in dry diethyl ether (15 mL). Ti(*i*PrO)<sub>4</sub> (14 mmol, 1.4 equiv.) was added to the solution and stirred for 5 min at 0 °C under argon. Then ethylmagnesium bromide (28 mmol, 28 mL, 1.0 mol/L in THF) was added dropwise to the solution. The mixture was warmed to room temperature and stirred overnight. The reaction was quenched with water (15 mL). The filtrate was extracted with ethyl acetate (3 × 20 mL), washed with saturated NaCl solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the cyclopropanols **2r**.

**2s** was prepared according to **procedure D**:

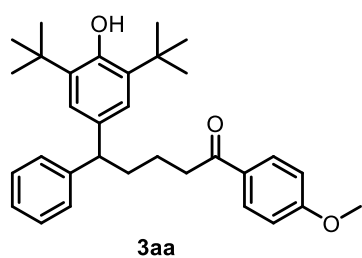


**Procedure D:** **2s** was synthesized by the natural estrogen Estrone through a two-step reaction, according to the reported procedure<sup>[5]</sup>. To a flame-dried round-bottom flask (100 mL), estrone (1.0 equiv.), DMAP (0.5 equiv.), K<sub>2</sub>CO<sub>3</sub> (1.0 equiv.) were added in DMF (20 mL). TBDMSCl was added dropwise to the solution. The mixture stirred overnight until starting material was consumed by TLC. The reaction was washed with semi-saturated NaCl solution (3 × 100 mL) and the aqueous layer was then extracted ethyl acetate (3 × 20 mL), The organic layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the intermediates **2s'**. **2s** was prepared according to procedure **A** by **2s'**.

## 2.3 General procedure for visible-light-promoted tandem ring opening/1,6-conjugate addition of cyclobutanols with *p*-quinone methides

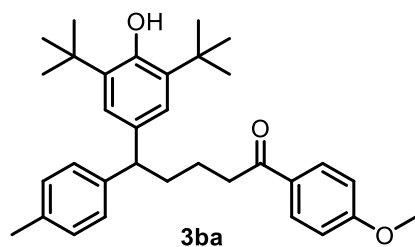


To an oven-dried quartz tube, *p*-quinone methides **1** (0.1 mmol), cyclobutanols **2** (0.1 mmol) and [Mes-Acr-Me]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (0.025 mmol) were added in an argon-filled glove-box. CH<sub>3</sub>CN (1.0 mL) was added into the tube via a syringe. The tube was sealed with a rubber plug wrapped with plastic film, removed from the glove box. The mixture was irradiated by 24 W 460 nm LEDs at room temperature for 24 h. After removal of solvents, the crude mixture was purified by flash chromatography (petroleum ether/ethyl acetate) to afford the pure products **3aa-3wa**, **3ab-3as**.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-5-phenylpentan-1-one (3aa).** General Procedure was used to prepare the desired product **3aa**.

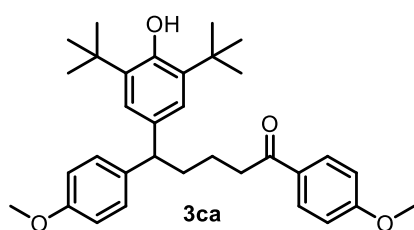
Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded **3aa** as a yellow solid (44.9 mg, 0.095 mmol, 95%); Mp: 101.3-103.5 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.9 Hz, 2H), 7.24 – 7.13 (m, 4H), 7.11 – 7.04 (m, 1H), 6.95 (s, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 4.93 (s, 1H), 3.78 (s, 3H), 3.76 (dd, *J* = 8.0 Hz, 1H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.02 (qd, *J* = 7.4, 4.3 Hz, 2H), 1.63 (p, *J* = 7.6 Hz, 2H), 1.32 (s, 18H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 198.9, 163.3, 152.0, 145.5, 135.7, 135.5, 130.3, 130.1, 128.4, 127.9, 125.9, 124.2, 113.7, 55.4, 51.4, 38.3, 36.0, 34.4, 30.4, 23.4. HRMS (DART-TOF) calculated for C<sub>32</sub>H<sub>39</sub>O<sub>5</sub> [M-H]<sup>-</sup> *m/z* 471.2905, found 471.2900. IR (KBr, cm<sup>-1</sup>): 3634, 2956, 1675, 1600, 1510, 1486, 1435, 1363, 1259, 1170, 1073, 1009, 884, 832, 718.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-5-(*p*-tolyl) pentan-1-one (3ba).** General Procedure was used to prepare the desired product **3ba**.

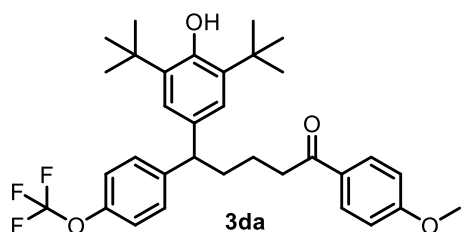
Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3ba** as yellow oil (42.3 mg, 0.087 mmol, 87%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.9 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 2.3 Hz, 2H), 6.81 (dd, *J* = 9.1, 2.3 Hz, 2H), 4.91 (s, 1H), 3.77 (s, 3H), 3.72 (t, *J* = 7.9 Hz, 1H), 2.81 (t, *J* = 7.4 Hz, 2H),

2.21 (s, 3H), 1.99 (qd,  $J = 7.3, 3.9$  Hz, 2H), 1.62 (p,  $J = 7.6$  Hz, 2H), 1.32 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.9, 163.3, 151.9, 142.5, 135.7, 135.6, 135.3, 130.3, 130.1, 129.0, 127.7, 124.1, 113.6, 55.4, 51.0, 38.3, 36.0, 34.3, 30.4, 23.5, 21.0. HRMS (DART-TOF) calculated for  $\text{C}_{33}\text{H}_{41}\text{O}_3^-$  [M-H] $^-$   $m/z$  485.3061, found 485.3058. IR (KBr,  $\text{cm}^{-1}$ ): 3636, 2959, 1676, 1600, 1511, 1436, 1363, 1261, 1170, 1028, 809.



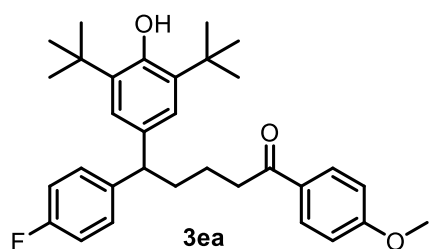
**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1,5-bis(4-methoxyphenyl) pentan-1-one (3ca).** General Procedure was used to prepare the desired product **3ca**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3ca** as an orange oil (39.2 mg, 0.078 mmol, 78%).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.84 – 7.72 (m, 2H), 7.11 – 7.06 (m, 2H), 6.93 (s, 2H), 6.84 – 6.79 (m, 2H), 6.76 – 6.71 (m, 2H), 4.91 (s, 1H), 3.77 (s, 3H), 3.73 (dd,  $J = 7.8$  Hz, 1H), 3.69 (s, 3H), 2.81 (t,  $J = 7.4$  Hz, 2H), 2.03 – 1.91 (m, 2H), 1.62 (dp,  $J = 14.1, 7.5, 6.9$  Hz, 2H), 1.32 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.9, 163.3, 157.8, 151.9, 137.6, 135.9, 135.6, 130.3, 130.2, 128.7, 124.1, 113.8, 113.7, 55.4, 55.2, 50.5, 38.2, 36.2, 34.3, 30.4, 23.4. HRMS (DART-TOF) calculated for  $\text{C}_{33}\text{H}_{41}\text{O}_4^-$  [M-H] $^-$   $m/z$  501.3010, found 501.3007. IR (KBr,  $\text{cm}^{-1}$ ): 3633, 2956, 1675, 1601, 1511, 1436, 1363, 1250, 1172, 1032, 834.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-5-(4-(trifluoromethoxy) phenyl) pentan-1-one (3da).** General Procedure was used to prepare the desired product **3da**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded **3da** as yellow oil

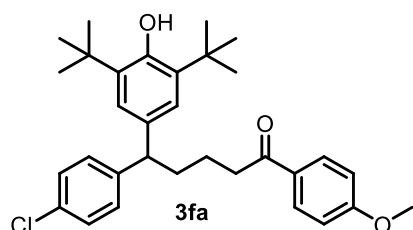
(37.9 mg, 0.068 mmol, 68%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.79 (d,  $J = 8.9$  Hz, 2H), 7.18 (d,  $J = 2.2$  Hz, 2H), 7.07 – 7.01 (m, 2H), 6.92 (s, 2H), 6.86 – 6.80 (m, 2H), 4.97 (s, 1H), 3.78 (s, 3H), 3.78 (t, 1H), 2.83 (t,  $J = 7.3$  Hz, 2H), 2.11 – 1.86 (m, 2H), 1.62 (dq,  $J = 10.4, 7.4$  Hz, 2H), 1.33 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.7, 163.4, 152.1, 147.4, 144.2, 135.8, 134.8, 130.3, 130.1, 129.0, 124.1, 120.8, 120.5 (q,  $J = 256.6$  Hz), 113.7, 55.4, 50.8, 38.1, 35.9, 34.4, 30.3, 23.2.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -57.86. HRMS (DART-TOF) calculated for  $\text{C}_{33}\text{H}_{38}\text{F}_3\text{O}_4^-$  [M-H] $^-$   $m/z$  555.2727, found 555.2725. IR (KBr,  $\text{cm}^{-1}$ ): 3638, 2958, 1676, 1601, 1510, 1436, 1261, 1169, 1172, 1031, 835.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-(4-fluorophenyl)-1-(4-methoxyphenyl) pentan-1-one (3ea).** General Procedure was used to prepare the desired product **3ea**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded **3ea** as yellow oil (45.1 mg, 0.092 mmol, 92%).

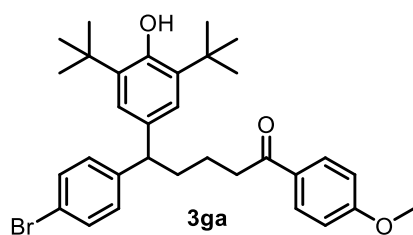
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.79 (d,  $J = 8.9$  Hz, 2H), 7.13 (dd,  $J = 8.6, 5.5$  Hz, 2H), 6.96 – 6.75 (m, 6H), 4.95 (s, 1H), 3.78 (s, 3H), 3.78 (dd,  $J = 8.0$  Hz, 1H) 2.82 (t,  $J = 7.3$  Hz, 2H), 2.04 – 1.93 (m, 2H), 1.71 – 1.55 (m, 2H),

1.32 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.7, 163.3, 161.2 (d,  $J = 243.6$  Hz), 152.0, 141.1 (d,  $J = 3.2$  Hz), 135.7, 135.3, 130.3, 130.1, 129.2 (d,  $J = 7.8$  Hz), 124.1, 115.1 (d,  $J = 21.0$  Hz), 113.7, 55.4, 50.6, 38.2, 36.1, 34.4, 30.3, 23.3.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -117.73. HRMS (DART-TOF) calculated for  $\text{C}_{32}\text{H}_{38}\text{FO}_3^-$  [M-H] $^-$   $m/z$  489.2810, found 489.2807. IR (KBr,  $\text{cm}^{-1}$ ): 3635, 2956, 1676, 1603, 1509, 1436, 1258, 1175, 1026, 979, 832, 815.



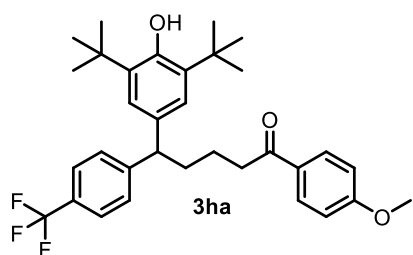
**5-(4-Chlorophenyl)-5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl) pentan-1-one (3fa).** General Procedure was used to prepare the desired product **3fa**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3fa** as yellow oil (45.1 mg, 0.089 mmol, 89%).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.78 (d,  $J = 8.9$  Hz, 2H), 7.18 – 7.08 (m, 4H), 6.91 (s, 2H), 6.82 (d,  $J = 8.9$  Hz, 2H), 4.95 (s, 1H), 3.77 (s, 3H), 3.76 – 3.70 (t,  $J = 7.8$  Hz, 1H), 2.82 (t,  $J = 7.3$  Hz, 2H), 2.04 – 1.91 (m, 2H), 1.61 (p,  $J = 7.3$  Hz, 2H), 1.32 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  197.7, 162.3, 151.1, 143.0, 134.8, 133.9, 130.5, 129.2, 129.0, 128.2, 127.4, 123.0, 112.7, 54.4, 49.8, 37.1, 34.8, 33.3, 29.3, 22.2. HRMS (DART-TOF) calculated for  $\text{C}_{32}\text{H}_{38}\text{ClO}_3^-$  [M-H] $^-$   $m/z$  505.2514, found 505.2512. IR (KBr,  $\text{cm}^{-1}$ ): 3635, 2958, 1676, 1600, 1510, 1490, 1435, 1362, 1260, 1170, 1092, 1014, 833.



**5-(4-Bromophenyl)-5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl) pentan-1-one (3ga).** General Procedure was used to prepare the desired product **3ga**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3ga** as orange oil (49.1 mg, 0.089 mmol, 89%).

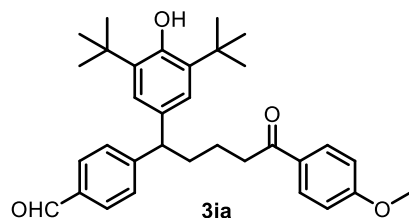
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.78 (d,  $J = 8.9$  Hz, 2H), 7.31 (d,  $J = 8.4$  Hz, 2H), 7.05 (d,  $J = 8.5$  Hz, 2H), 6.91 (s, 2H), 6.82 (d,  $J = 8.9$  Hz, 2H), 4.95 (s, 1H), 3.78 (s, 3H), 3.72 (t,  $J = 7.8$  Hz, 1H), 2.82 (t,  $J = 7.3$  Hz, 2H), 2.05 – 1.92 (m, 2H), 1.68 – 1.57 (m, 2H), 1.32 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.7, 163.3, 152.1, 144.5, 135.8, 134.8, 131.4, 130.3, 130.1, 129.6, 124.0, 119.6, 113.7, 55.4, 50.9, 38.1, 35.7, 34.4, 30.3, 23.2. HRMS (DART-TOF) calculated for  $\text{C}_{32}\text{H}_{38}\text{BrO}_3^-$  [M-H] $^-$   $m/z$  549.2009, found 549.2004. IR (KBr,  $\text{cm}^{-1}$ ): 3634, 2956, 1675, 1600, 1510, 1486, 1435, 1363, 1259, 1170, 1073, 1009, 884, 832, 718.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-5-(4-(trifluoromethyl)phenyl) pentan-1-one (3ha).** General Procedure was used to prepare the desired product **3ha**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded **3ha** as orange oil (51.4 mg, 0.095 mmol, 95%).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.79 (d,  $J = 8.9$  Hz, 2H), 7.45 (d,  $J = 8.1$  Hz, 2H), 7.29 (d,  $J = 8.1$  Hz, 2H), 6.93 (s, 2H), 6.82 (d,  $J = 8.9$  Hz, 2H), 4.97 (s, 1H), 3.83 (t,  $J = 7.8$  Hz, 1H), 3.78 (s, 3H), 2.83

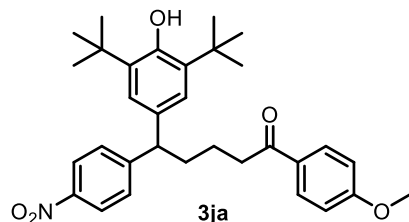
(t,  $J = 7.2$  Hz, 2H), 2.03 (q,  $J = 7.8, 7.3$  Hz, 2H), 1.63 (qd,  $J = 9.4, 8.8, 4.5$  Hz, 2H), 1.33 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  198.6, 163.4, 152.3, 149.6, 135.9, 134.4, 130.3, 130.0, 128.2 (q,  $J = 32.3$  Hz), 128.1, 125.3 (q,  $J = 3.8$  Hz), 125.1 (q,  $J = 292.2$  Hz), 124.1, 113.7, 55.4, 51.4, 38.1, 35.6, 34.4, 30.3, 23.2.  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -62.33. HRMS (DART-TOF) calculated for  $\text{C}_{33}\text{H}_{38}\text{F}_3\text{O}_3^-$   $[\text{M}-\text{H}]^-$   $m/z$  539.2778, found 539.2777. IR (KBr,  $\text{cm}^{-1}$ ): 3636, 2958, 1676, 1601, 1511, 1436, 1326, 1260, 1169, 1121, 1068, 1017, 838.



**4-(1-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-(4-methoxyphenyl)-5-oxopentyl)benzaldehyde (3ia).**

**General Procedure** was used to prepare the desired product **3ia**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded **3ia** as yellow oil (28.1 mg, 0.056 mmol, 56%).

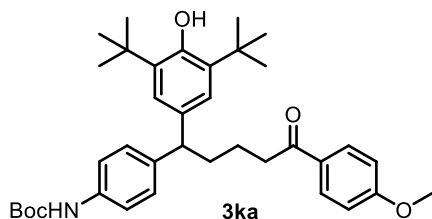
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  9.95 (s, 1H), 7.94 – 7.81 (m, 2H), 7.79 (d,  $J = 8.2$  Hz, 2H), 7.43 (d,  $J = 8.2$  Hz, 2H), 7.01 (s, 2H), 6.90 (d,  $J = 8.9$  Hz, 2H), 5.07 (s, 1H), 3.93 (t,  $J = 7.8$  Hz, 1H), 3.85 (s, 3H), 2.92 (t,  $J = 7.2$  Hz, 2H), 2.12 (tdd,  $J = 8.6, 5.0, 2.2$  Hz, 2H), 1.70 (q,  $J = 9.5, 8.5$  Hz, 2H), 1.40 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  198.6, 192.0, 163.4, 152.9, 152.3, 135.9, 134.6, 134.3, 130.3, 130.1, 130.0, 128.5, 124.2, 113.7, 55.5, 51.7, 38.1, 35.5, 34.4, 30.3, 23.2. HRMS (DART-TOF) calculated for  $\text{C}_{33}\text{H}_{40}\text{NaO}_4^+$   $[\text{M}+\text{Na}]^+$   $m/z$  523.2819, found 523.2826. IR (KBr,  $\text{cm}^{-1}$ ): 3633, 2956, 1700, 1602, 1574, 1510, 1435, 1362, 1307, 1260, 1170, 1029, 909, 839, 731.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-5-(4-nitrophenyl)pentan-1-one (3ja).**

**General Procedure** was used to prepare the desired product **3ja**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (20/1) as eluent afforded **3ja** as yellow oil (33.1 mg, 0.064 mmol, 64%).

$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.13 (d,  $J = 8.7$  Hz, 2H), 7.88 (d,  $J = 8.9$  Hz, 2H), 7.41 (d,  $J = 8.6$  Hz, 2H), 6.99 (s, 2H), 6.90 (d,  $J = 8.8$  Hz, 2H), 5.10 (s, 1H), 3.96 (t,  $J = 7.7$  Hz, 1H), 3.85 (s, 3H), 2.93 (t,  $J = 7.1$  Hz, 2H), 2.12 (q,  $J = 7.8$  Hz, 2H), 1.71 (td,  $J = 7.5, 3.3$  Hz, 2H), 1.40 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  198.4, 163.4, 153.4, 152.5, 146.3, 136.1, 133.7, 130.3, 128.6, 126.3, 124.1, 123.7, 113.7, 55.5, 51.4, 37.9, 35.4, 34.4, 30.3, 23.0. HRMS (DART-TOF) calculated for  $\text{C}_{32}\text{H}_{40}\text{NO}_5^+$   $[\text{M}+\text{H}]^+$   $m/z$  518.2901, found 518.2891. IR (KBr,  $\text{cm}^{-1}$ ): 3442, 2956, 1674, 1600, 1516, 1435, 1345, 1257, 1171, 1030, 828, 704.

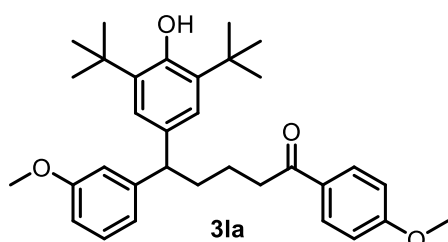


**Tert-butyl (4-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5-(4-methoxyphenyl)-5-oxopentyl)phenyl)carbamate (3ka).**

**General Procedure** was used to prepare the desired product **3ka**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (20/1) as eluent afforded

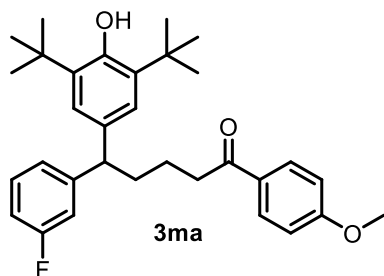
**3ka** as yellow oil (21.1 mg, 0.036 mmol, 36%).  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.85 (d,  $J = 8.6$  Hz, 2H), 7.25 (d,  $J = 8.1$  Hz, 2H), 7.17 (d,  $J = 8.1$  Hz, 2H), 7.00 (s, 2H), 6.89 (d,  $J$

= 8.5 Hz, 2H), 6.39 (s, 1H), 5.01 (s, 1H), 3.85 (s, 3H), 3.79 (t,  $J = 7.8$  Hz, 1H), 2.89 (t,  $J = 7.4$  Hz, 2H), 2.05 (dt,  $J = 10.1, 5.1$  Hz, 2H), 1.68 (p,  $J = 7.5$  Hz, 2H), 1.50 (s, 9H), 1.39 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.9, 163.3, 152.9, 151.9, 149.3, 140.2, 136.1, 135.6, 130.3, 130.1, 128.3, 124.1, 118.7, 113.6, 55.4, 50.7, 38.2, 35.9, 34.3, 30.3, 28.4, 28.3, 23.4. HRMS (DART-TOF) calculated for  $\text{C}_{37}\text{H}_{49}\text{NNaO}_5^+$   $[\text{M}+\text{Na}]^+$   $m/z$  610.3503, found 610.3515. IR (KBr,  $\text{cm}^{-1}$ ): 3441, 2957, 1670, 1600, 1523, 1436, 1367, 1314, 1235, 1160, 839.



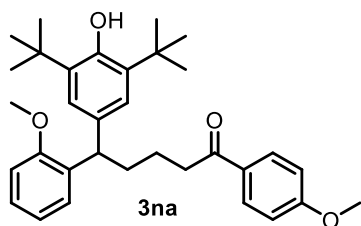
**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-(3-methoxyphenyl)-1-(4-methoxyphenyl) pentan-1-one (3la).** General Procedure was used to prepare the desired product **3la**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3la** as yellow oil (40.7 mg, 0.081 mmol, 81%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$

7.81 – 7.73 (m, 2H), 7.11 (t,  $J = 7.9$  Hz, 1H), 6.96 (s, 2H), 6.86 – 6.77 (m, 3H), 6.73 (t,  $J = 2.1$  Hz, 1H), 6.62 (dd,  $J = 8.1, 2.7$  Hz, 1H), 4.93 (s, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 3.69 (t, 1H), 2.81 (t,  $J = 7.4$  Hz, 2H), 2.01 (dtd,  $J = 14.5, 7.2, 4.8$  Hz, 2H), 1.63 (p,  $J = 7.6$  Hz, 2H), 1.32 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.8, 163.3, 159.6, 152.0, 147.2, 135.7, 135.3, 130.3, 130.2, 129.2, 124.2, 120.3, 113.9, 113.7, 111.0, 55.4, 55.1, 51.5, 38.2, 35.9, 34.4, 30.4, 23.4. HRMS (DART-TOF) calculated for  $\text{C}_{33}\text{H}_{41}\text{O}_4^-$   $[\text{M}-\text{H}]^-$   $m/z$  501.3010, found 501.3009. IR (KBr,  $\text{cm}^{-1}$ ): 3635, 2956, 1675, 1600, 1510, 1434, 1362, 1260, 1170, 1031, 831, 700.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-(3-fluorophenyl)-1-(4-methoxyphenyl) pentan-1-one (3ma).**

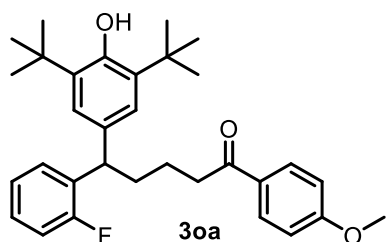
General Procedure was used to prepare the desired product **3ma**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded **3ma** as yellow oil (44.7 mg, 0.091 mmol, 91%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.79 (d,  $J = 8.9$  Hz, 2H), 7.15 (td,  $J = 8.1, 6.2$  Hz, 1H), 6.97 (dt,  $J = 7.7, 1.2$  Hz, 1H), 6.93 (s, 2H), 6.89 – 6.74 (m, 4H), 4.96 (s, 1H), 3.78 (s, 3H), 3.78 (p, 1H), 2.83 (t,  $J = 7.3$  Hz, 2H), 2.06 – 1.93 (m, 2H), 1.62 (p,  $J = 7.4$  Hz, 2H), 1.33 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.7, 163.3, 163.0 (d,  $J = 245.1$  Hz), 152.2, 148.2 (d,  $J = 6.7$  Hz), 135.8, 134.8, 130.3, 130.1, 129.7 (d,  $J = 8.3$  Hz), 124.1, 123.5 (d,  $J = 2.7$  Hz), 114.6 (d,  $J = 21.1$  Hz), 113.7, 112.8 (d,  $J = 21.2$  Hz), 55.4, 51.2 (d,  $J = 1.6$  Hz), 38.1, 35.7, 34.4, 30.3, 23.2.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -113.56. HRMS (DART-TOF) calculated for  $\text{C}_{32}\text{H}_{38}\text{FO}_3^-$   $[\text{M}-\text{H}]^-$   $m/z$  489.2810, found 489.2808. IR (KBr,  $\text{cm}^{-1}$ ): 3636, 2957, 1676, 1601, 1511, 1435, 1363, 1259, 1171, 1030, 883, 783, 698.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-(2-methoxyphenyl)-1-(4-methoxyphenyl) pentan-1-one (3na).**

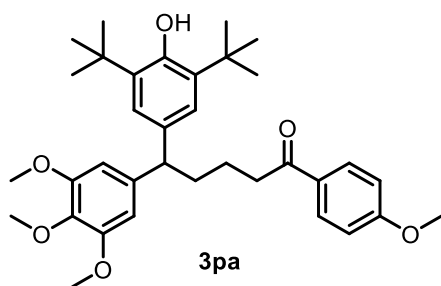
General Procedure was used to prepare the desired product **3na**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3na** as yellow oil (40.2 mg, 0.08 mmol, 80%).  $^1\text{H}$  NMR (400 MHz,

**Chloroform-*d***)  $\delta$  7.85 – 7.69 (m, 2H), 7.13 (dd,  $J = 7.6, 1.7$  Hz, 1H), 7.05 (ddd,  $J = 8.2, 7.4, 1.7$  Hz, 1H), 7.01 (s, 2H), 6.84 – 6.78 (m, 3H), 6.75 (dd,  $J = 8.2, 1.1$  Hz, 1H), 4.89 (s, 1H), 4.29 (t,  $J = 7.9$  Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 2.82 (dd,  $J = 8.2, 6.8$  Hz, 2H), 2.08 – 1.91 (m, 2H), 1.62 (p,  $J = 7.2$  Hz, 2H), 1.32 (s, 18H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  199.1, 163.2, 157.0, 151.8, 135.3, 135.2, 134.0, 130.3, 130.2, 127.7, 126.7, 124.6, 120.6, 113.6, 110.8, 55.4, 55.4, 42.8, 38.3, 34.8, 34.3, 30.4, 23.5. **HRMS (DART-TOF)** calculated for  $\text{C}_{33}\text{H}_{41}\text{O}_4^-$  [M-H] $^-$   $m/z$  501.3010, found 501.3007. **IR (KBr,  $\text{cm}^{-1}$ ):** 3635, 2955, 1676, 1600, 1510, 1490, 1436, 1362, 1240, 1170, 1113, 1029, 833, 753.



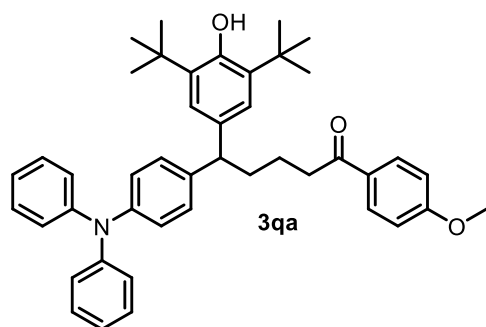
**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-(2-fluorophenyl)-1-(4-methoxyphenyl) pentan-1-one (3oa).**

**General Procedure** was used to prepare the desired product **3oa**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded **3oa** as yellow oil (44.2 mg, 0.09 mmol, 90%).  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.79 (d,  $J = 8.9$  Hz, 2H), 7.23 – 7.18 (m, 1H), 7.10 – 7.02 (m, 1H), 7.02 – 6.96 (m, 3H), 6.90 (ddd,  $J = 10.5, 8.0, 1.4$  Hz, 1H), 6.82 (d,  $J = 8.9$  Hz, 2H), 4.95 (s, 1H), 4.15 (t,  $J = 7.9$  Hz, 1H), 3.78 (s, 3H), 2.84 (t,  $J = 7.4$  Hz, 2H), 2.12 – 1.95 (m, 2H), 1.64 (p,  $J = 7.5$  Hz, 2H), 1.32 (s, 18H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  198.8, 163.3, 160.7 (d,  $J = 244.5$  Hz), 152.1, 135.6, 134.2, 132.3 (d,  $J = 14.4$  Hz), 130.3, 130.1, 128.7 (d,  $J = 4.7$  Hz), 127.3 (d,  $J = 8.4$  Hz), 124.3, 124.1 (d,  $J = 3.5$  Hz), 115.4 (d,  $J = 23.0$  Hz), 113.7, 55.4, 43.4 (d,  $J = 2.1$  Hz), 38.1, 34.8, 34.4, 30.3, 23.2.  **$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)**  $\delta$  -118.00. **HRMS (DART-TOF)** calculated for  $\text{C}_{32}\text{H}_{38}\text{FO}_3^-$  [M-H] $^-$   $m/z$  489.2810, found 489.2806. **IR (KBr,  $\text{cm}^{-1}$ ):** 3636, 2955, 1671, 1602, 1511, 1487, 1455, 1434, 1360, 1261, 1223, 1175, 1024, 977, 886, 842, 813, 753.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-5-(3,4,5-trimethoxyphenyl) pentan-1-one (3pa).**

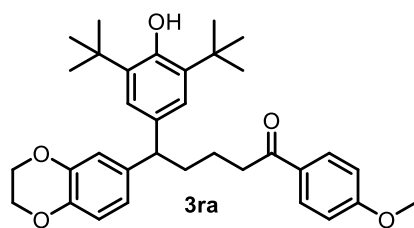
**General Procedure** was used to prepare the desired product **3pa**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3pa** as yellow oil (50.6 mg, 0.09 mmol, 90%).  **$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.79 (d,  $J = 8.9$  Hz, 2H), 6.97 (s, 2H), 6.82 (d,  $J = 8.9$  Hz, 2H), 6.42 (s, 2H), 4.95 (s, 1H), 3.78 (s, 3H), 3.75 (s, 6H), 3.73 (s, 3H), 3.68 (t,  $J = 7.9$  Hz, 1H), 2.83 (t,  $J = 7.3$  Hz, 2H), 1.97 (dtt,  $J = 12.9, 8.8, 5.0$  Hz, 2H), 1.73 – 1.59 (m, 2H), 1.34 (s, 18H).  **$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  198.8, 163.3, 153.0, 152.1, 141.1, 136.4, 135.7, 135.2, 130.3, 130.1, 124.1, 113.7, 105.1, 60.8, 56.1, 55.4, 51.8, 38.2, 36.4, 34.4, 30.4, 23.4. **HRMS (DART-TOF)** calculated for  $\text{C}_{35}\text{H}_{45}\text{O}_6^-$  [M-H] $^-$   $m/z$  561.3221, found 561.3215. **IR (KBr,  $\text{cm}^{-1}$ ):** 3635, 2957, 1675, 1600, 1509, 1461, 1322, 1260, 1171, 1127, 1010, 833.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-(4-(diphenylamino)phenyl)-1-(4-methoxyphenyl)pentan-1-one (3qa).**

**General Procedure** was used to prepare the desired product **3qa**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3qa** as orange oil (25.0 mg, 0.039 mmol, 39%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.9 Hz, 2H), 7.17 – 7.11 (m, 4H), 7.08 – 7.03

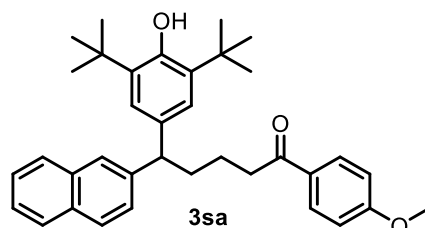
(m, 2H), 7.00 – 6.95 (m, 4H), 6.95 – 6.87 (m, 6H), 6.85 – 6.81 (m, 2H), 4.96 (s, 1H), 3.78 (s, 3H), 3.73 (t, *J* = 7.8 Hz, 1H), 2.84 (t, *J* = 7.4 Hz, 2H), 2.08 – 1.90 (m, 2H), 1.66 (dtt, *J* = 13.2, 9.4, 4.6 Hz, 2H), 1.34 (s, 18H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 199.0, 163.3, 151.9, 148.0, 145.6, 139.9, 135.7, 135.6, 130.3, 130.1, 129.1, 128.7, 124.4, 124.3, 123.9, 122.3, 113.7, 55.4, 50.8, 38.3, 36.3, 34.4, 30.4, 23.5. **HRMS (DART-TOF)** calculated for C<sub>44</sub>H<sub>48</sub>NO<sub>3</sub><sup>-</sup> [M-H]<sup>-</sup> *m/z* 638.3639, found 638.3633. **IR (KBr, cm<sup>-1</sup>):** 3443, 2959, 1675, 1599, 1492, 1261, 1169, 1109, 1027, 806, 752, 695.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-1-(4-methoxyphenyl)pentan-1-one (3ra).**

**General Procedure** was used to prepare the desired product **3ra**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded

**3ra** as yellow oil (40.9 mg, 0.077 mmol, 77%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.80 (m, 2H), 7.01 (s, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 3.1 Hz, 3H), 5.00 (s, 1H), 4.21 (s, 4H), 3.85 (s, 3H), 3.72 (t, *J* = 7.8 Hz, 1H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.03 (ddq, *J* = 11.4, 7.1, 3.9, 3.0 Hz, 2H), 1.77 – 1.64 (m, 2H), 1.40 (s, 18H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 198.9, 163.3, 152.0, 143.2, 141.7, 139.0, 135.6, 135.6, 130.3, 130.1, 124.0, 120.7, 117.0, 113.6, 64.4, 64.3, 55.4, 50.7, 38.3, 36.0, 34.4, 30.4, 30.3, 23.4. **HRMS (DART-TOF)** calculated for C<sub>34</sub>H<sub>41</sub>O<sub>5</sub><sup>-</sup> [M-H]<sup>-</sup> *m/z* 529.2959, found 529.2955. **IR (KBr, cm<sup>-1</sup>):** 3627, 2957, 1675, 1600, 1506, 1434, 1362, 1286, 1258, 1170, 1068, 882, 810.



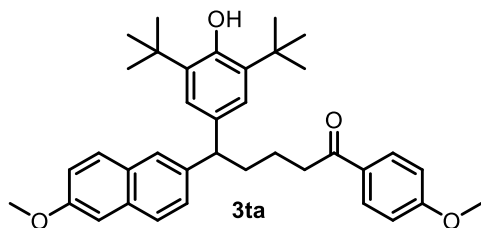
**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-5-(naphthalen-2-yl)pentan-1-one (3sa).**

**General Procedure** was used to prepare the desired product **3sa**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3sa** as orange oil (39.2 mg, 0.075 mmol,

75%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 8.10 (m, 1H), 7.82 – 7.70 (m, 3H), 7.61 (dt, *J* = 7.3, 3.7 Hz, 1H), 7.44 – 7.30 (m, 4H), 7.03 (s, 2H), 6.83 – 6.69 (m, 2H), 4.92 (s, 1H), 4.63 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 2.83 (t, *J* = 7.3 Hz, 2H), 2.27 – 2.04 (m, 2H), 1.81 – 1.62 (m, 2H), 1.29 (s, 18H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 198.9, 163.3, 151.9, 141.1, 135.6, 134.9, 134.1, 132.0, 130.3, 130.1, 128.8, 126.6, 125.8, 125.5, 125.2, 124.5, 124.2, 123.7, 113.7, 55.4, 45.9, 38.3, 36.4, 34.4, 30.4, 23.6. **HRMS (DART-TOF)** calculated for C<sub>36</sub>H<sub>41</sub>O<sub>3</sub><sup>-</sup>

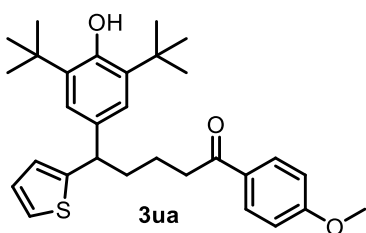


[M-H]<sup>-</sup> m/z 521.3061, found 521.3057. **IR (KBr, cm<sup>-1</sup>):** 3626, 2956, 1674, 1600, 1510, 1434, 1362, 1259, 1169, 1028, 778.



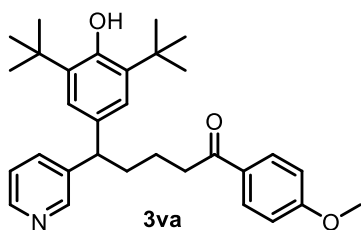
**5-(3,5-Di-tert-butyl-4-hydroxyphenyl)-5-(6-methoxynaphthalen-2-yl)-1-(4-methoxyphenyl)pentan-1-one (3ta).** General Procedure was used to prepare the desired product **3ta**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent

afforded **3ta** as yellow oil (27.6 mg, 0.05 mmol, 50%). **<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.88 – 7.79 (m, 2H), 7.72 – 7.59 (m, 3H), 7.36 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.13 – 7.05 (m, 4H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.01 (s, 1H), 3.97 (t, *J* = 7.8 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 2.94 – 2.88 (t, 2H), 2.27 – 2.07 (m, 2H), 1.85 – 1.68 (m, 2H), 1.39 (s, 18H). **<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 198.9, 163.3, 157.2, 152.0, 140.6, 135.6, 135.6, 133.1, 130.3, 130.1, 129.2, 129.1, 127.1, 126.9, 125.9, 124.2, 118.5, 113.6, 105.6, 55.4, 55.3, 51.2, 38.3, 35.8, 34.4, 30.4, 23.5. **HRMS (DART-TOF)** calculated for C<sub>37</sub>H<sub>43</sub>O<sub>4</sub><sup>-</sup> [M-H]<sup>-</sup> m/z 551.3166, found 551.3163. **IR (KBr, cm<sup>-1</sup>):** 3442, 2957, 1673, 1601, 1509, 1435, 1362, 1261, 1169, 1029, 808.



**5-(3,5-Di-tert-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-5-(thiophen-2-yl)pentan-1-one (3ua).** General Procedure was used to prepare the desired product **3ua**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3ua** as yellow oil (41.2 mg, 0.086 mmol, 86%). **<sup>1</sup>H NMR (400**

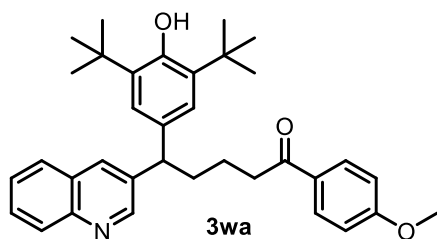
**MHz, Chloroform-*d*)** δ 7.83 – 7.75 (m, 2H), 7.14 (dd, *J* = 4.9, 2.9 Hz, 1H), 6.94 – 6.87 (m, 4H), 6.84 – 6.79 (m, 2H), 4.95 (s, 1H), 3.84 (t, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 2.81 (dd, *J* = 8.2, 7.0 Hz, 2H), 2.09 – 1.84 (m, 2H), 1.73 – 1.56 (m, 2H), 1.32 (s, 18H). **<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 198.9, 163.3, 152.0, 146.4, 135.7, 135.2, 130.3, 130.1, 127.7, 125.2, 124.2, 120.0, 113.7, 55.4, 46.9, 38.2, 36.5, 34.4, 30.4, 23.3. **HRMS (DART-TOF)** calculated for C<sub>30</sub>H<sub>37</sub>O<sub>3</sub>S<sup>-</sup> [M-H]<sup>-</sup> m/z 477.2468, found 477.2466. **IR (KBr, cm<sup>-1</sup>):** 3443, 2957, 1675, 1600, 1510, 1434, 1360, 1257, 1170, 1028, 837.



**5-(3,5-Di-tert-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-5-(pyridin-3-yl)pentan-1-one (3va).** General Procedure was used to prepare the desired product **3va**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3va** as yellow oil (29.4 mg, 0.062 mmol, 62%). **<sup>1</sup>H NMR (400 MHz,**

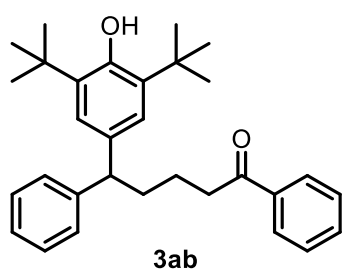
**Chloroform-*d*)** δ 8.45 (d, *J* = 2.3 Hz, 1H), 8.34 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.84 – 7.76 (m, 2H), 7.49 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.13 (dd, *J* = 7.9, 4.8 Hz, 1H), 6.93 (s, 2H), 6.86 – 6.79 (m, 2H), 5.00 (s, 1H), 3.78 (t, 1H), 3.78 (s, 3H), 2.85 (td, *J* = 7.1, 1.6 Hz, 2H), 2.03 (q, *J* = 7.9 Hz, 2H), 1.71 – 1.59 (m, 2H), 1.33 (s, 18H). **<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 198.5, 163.4, 152.3, 149.6, 147.4, 140.8, 136.0, 135.1, 134.2, 130.3, 130.0, 124.1, 123.4, 113.7, 55.4, 49.0, 38.0,

35.5, 34.4, 30.3, 23.1. **HRMS (DART-TOF)** calculated for  $C_{31}H_{38}NO_3^-$   $[M-H]^-$   $m/z$  472.2857, found 472.2852. **IR (KBr,  $cm^{-1}$ ):** 3443, 2958, 1675, 1601, 1511, 1434, 1363, 1260, 1170, 1027, 808, 715.

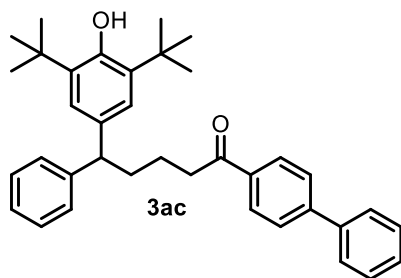


**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-5-(quinolin-3-yl) pentan-1-one (3wa).** General Procedure was used to prepare the desired product **3wa**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3wa** as orange oil (39.8 mg, 0.076

mmol, 76%).  **$^1H$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  8.76 (d,  $J = 2.3$  Hz, 1H), 7.98 (d,  $J = 8.4$  Hz, 1H), 7.92 (d,  $J = 2.2$  Hz, 1H), 7.80 (d,  $J = 8.9$  Hz, 2H), 7.71 (dd,  $J = 8.2, 1.4$  Hz, 1H), 7.57 (ddd,  $J = 8.4, 6.9, 1.5$  Hz, 1H), 7.44 (dd,  $J = 8.1, 6.8$  Hz, 1H), 7.00 (s, 2H), 6.81 (d,  $J = 8.9$  Hz, 2H), 5.00 (s, 1H), 3.98 (t,  $J = 7.8$  Hz, 1H), 3.77 (s, 3H), 2.95 – 2.77 (m, 2H), 2.15 (qd,  $J = 8.1, 3.1$  Hz, 2H), 1.76 – 1.61 (m, 2H), 1.32 (s, 18H).  **$^{13}C$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  198.5, 163.4, 152.4, 151.7, 146.6, 138.2, 136.1, 134.0, 133.5, 130.3, 130.0, 128.9, 128.8, 128.2, 127.6, 126.6, 124.2, 113.7, 55.4, 49.2, 38.0, 35.4, 34.4, 30.3, 23.2. **HRMS (DART-TOF)** calculated for  $C_{35}H_{40}NO_3^-$   $[M-H]^-$   $m/z$  522.3013, found 522.3010. **IR (KBr,  $cm^{-1}$ ):** 3445, 2955, 1674, 1600, 1510, 1435, 1363, 1260, 1170, 1029, 788, 752.

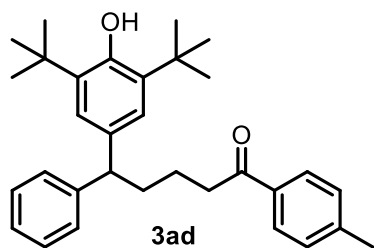


**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1,5-diphenylpentan-1-one (3ab).** General Procedure was used to prepare the desired product **3ab**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded **3ab** as yellow oil (17.7 mg, 0.04 mmol, 40%).  **$^1H$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.81 (dd,  $J = 8.1, 1.4$  Hz, 2H), 7.46 (t,  $J = 7.4$  Hz, 1H), 7.35 (t,  $J = 7.7$  Hz, 2H), 7.23 – 7.16 (m, 4H), 7.09 (qd,  $J = 7.2, 6.1, 4.2$  Hz, 1H), 6.96 (s, 2H), 4.94 (s, 1H), 3.78 (d,  $J = 7.8$  Hz, 1H), 2.88 (t,  $J = 7.3$  Hz, 2H), 2.03 (qd,  $J = 7.3, 4.6$  Hz, 2H), 1.65 (p,  $J = 7.6$  Hz, 2H), 1.32 (s, 18H).  **$^{13}C$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  200.2, 152.0, 145.4, 137.0, 135.6, 135.4, 132.8, 128.5, 128.4, 128.0, 127.8, 125.9, 124.2, 53.4, 51.4, 38.5, 35.9, 34.4, 30.4, 23.2. **HRMS (DART-TOF)** calculated for  $C_{31}H_{37}O_2^-$   $[M-H]^-$   $m/z$  441.2799, found 441.2795. **IR (KBr,  $cm^{-1}$ ):** 3636, 2956, 1685, 1598, 1435, 1363, 1234, 752, 700.



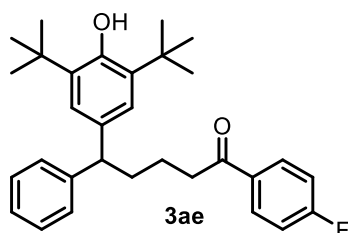
**1-([1,1'-Biphenyl]-4-yl)-5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5-phenylpentan-1-one (3ac).** General Procedure was used to prepare the desired product **3ac**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3ac** as yellow oil (34.2mg, 0.066 mmol, 66%).  **$^1H$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.87 (d,  $J = 8.4$  Hz, 2H), 7.61 – 7.48 (m, 4H), 7.39 (t,  $J = 7.8$  Hz, 2H), 7.35 – 7.29 (m, 1H), 7.26 – 7.15 (m, 4H), 7.08 (tq,  $J =$

7.6, 3.9 Hz, 1H), 6.97 (s, 2H), 4.94 (s, 1H), 3.78 (t,  $J = 7.8$  Hz, 1H), 2.90 (t,  $J = 7.3$  Hz, 2H), 2.04 (qd,  $J = 7.3, 4.3$  Hz, 2H), 1.68 (q,  $J = 7.5$  Hz, 2H), 1.32 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  199.9, 152.0, 145.6, 145.4, 140.0, 135.7, 135.6, 135.4, 128.9, 128.7, 128.4, 128.2, 127.9, 127.3, 127.2, 125.9, 124.2, 51.5, 38.6, 35.9, 34.4, 30.4, 23.3. HRMS (DART-TOF) calculated for  $\text{C}_{37}\text{H}_{41}\text{O}_2^-$   $[\text{M}-\text{H}]^-$   $m/z$  517.3112, found 517.3107. IR (KBr,  $\text{cm}^{-1}$ ): 3627, 2953, 1671, 1602, 1433, 1360, 1287, 1233, 1144, 1116, 1008, 752, 697.



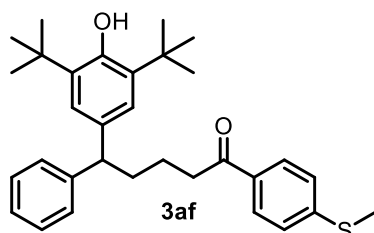
**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1,5-diphenylpentan-1-one (3ad).** General Procedure was used to prepare the desired product **3ad**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded **3ad** as yellow oil (25.3 mg, 0.057 mmol, 57%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.78 (d,  $J = 8.0$  Hz, 2H), 7.26 (q,  $J = 2.1$  Hz, 4H), 7.21 (d,  $J = 8.0$  Hz,

2H), 7.16 (dq,  $J = 5.7, 3.0$  Hz, 1H), 7.02 (d,  $J = 5.6$  Hz, 2H), 5.01 (s, 1H), 3.84 (t,  $J = 7.8$  Hz, 1H), 2.92 (t,  $J = 7.4$  Hz, 2H), 2.39 (s, 3H), 2.08 (q,  $J = 7.2, 6.8$  Hz, 2H), 1.74 – 1.63 (m, 2H), 1.39 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  200.0, 152.0, 145.4, 143.6, 135.6, 135.5, 134.5, 129.2, 128.4, 128.2, 127.9, 125.9, 124.2, 51.4, 38.5, 36.0, 34.4, 30.4, 23.3, 21.6. HRMS (DART-TOF) calculated for  $\text{C}_{32}\text{H}_{40}\text{NaO}_2^+$   $[\text{M}+\text{Na}]^+$   $m/z$  479.2921, found 479.2923. IR (KBr,  $\text{cm}^{-1}$ ): 3441, 2957, 1680, 1606, 1435, 1232, 1119, 807, 701.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(4-fluorophenyl)-5-phenylpentan-1-one (3ae).** General Procedure was used to prepare the desired product **3ae**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (100/1) as eluent afforded **3ae** as yellow oil (27.2 mg, 0.059 mmol, 59%).

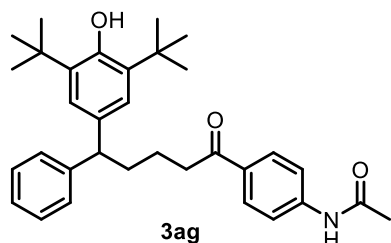
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.85 – 7.78 (m, 2H), 7.18 (s, 4H), 7.08 (tt,  $J = 5.4, 2.4$  Hz, 1H), 7.01 (t,  $J = 8.6$  Hz, 2H), 6.95 (s, 2H), 4.93 (s, 1H), 3.76 (t,  $J = 7.8$  Hz, 1H), 2.84 (t,  $J = 7.3$  Hz, 2H), 2.02 (qd,  $J = 7.4, 3.8$  Hz, 2H), 1.64 (p,  $J = 7.5$  Hz, 2H), 1.32 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  197.6, 164.6 (d,  $J = 254.3$  Hz), 151.0, 144.3, 134.7, 134.4, 132.4 (d,  $J = 3.1$  Hz), 129.6 (d,  $J = 9.2$  Hz), 127.4, 126.8, 124.9, 123.2, 114.6 (d,  $J = 21.8$  Hz), 50.4, 37.5, 34.9, 33.4, 29.4, 22.2.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -105.80. HRMS (DART-TOF) calculated for  $\text{C}_{31}\text{H}_{36}\text{FO}_2^-$   $[\text{M}-\text{H}]^-$   $m/z$  459.2704, found 459.2704. IR (KBr,  $\text{cm}^{-1}$ ): 3638, 2959, 1686, 1598, 1435, 1365, 1230, 1156, 806, 701.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(4-(methylthio)phenyl)-5-phenylpentan-1-one (3af).**

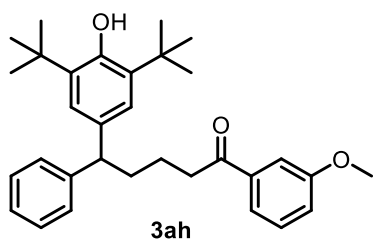
General Procedure was used to prepare the desired product **3af**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded **3af** as yellow oil (21.0 mg, 0.043 mmol, 43%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.77 – 7.65 (m, 2H), 7.23 – 7.11 (m, 6H), 7.07 (dd,  $J = 6.5, 5.7$  Hz, 1H), 6.95

(s, 2H), 4.93 (s, 1H), 3.76 (t,  $J = 7.8$  Hz, 1H), 2.82 (t,  $J = 7.4$  Hz, 2H), 2.42 (s, 3H), 2.01 (qd,  $J = 7.3, 3.9$  Hz, 2H), 1.63 (p,  $J = 7.5$  Hz, 2H), 1.32 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.2, 151.0, 144.5, 144.4, 134.7, 134.4, 132.4, 127.5, 127.3, 126.8, 124.9, 124.1, 123.2, 50.4, 37.4, 34.9, 33.4, 29.4, 22.3, 13.8. HRMS (DART-TOF) calculated for  $\text{C}_{32}\text{H}_{39}\text{O}_2\text{S}^-$  [ $\text{M}-\text{H}$ ] $^-$   $m/z$  487.2676, found 487.2673. IR (KBr,  $\text{cm}^{-1}$ ): 3636, 2955, 1673, 1591, 1555, 1433, 1398, 1359, 1236, 1145, 1093, 886, 810, 754, 700.



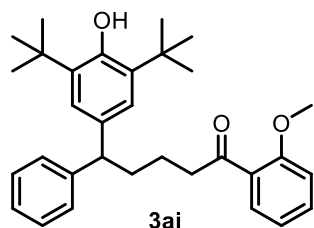
***N*-(4-(5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-phenylpentanoyl)phenyl)acetamide (3ag).** General Procedure was used to prepare the desired product 3ag. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded 3ag as yellow solid (34.2 mg, 0.068 mmol, 68%); **Mp:** 186.8-187.4.  $^1\text{H}$

NMR (400 MHz, Chloroform-*d*)  $\delta$  7.94 – 7.75 (m, 3H), 7.58 (d,  $J = 8.4$  Hz, 2H), 7.33 – 7.21 (m, 4H), 7.21 – 7.08 (m, 1H), 7.03 (s, 2H), 5.03 (s, 1H), 3.83 (t,  $J = 7.8$  Hz, 1H), 2.92 (t,  $J = 7.4$  Hz, 2H), 2.17 (s, 3H), 2.14 – 2.00 (m, 2H), 1.76 – 1.64 (m, 2H), 1.39 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  199.3, 168.8, 152.0, 145.3, 142.3, 135.7, 135.4, 132.6, 129.4, 128.4, 127.8, 126.0, 124.2, 118.9, 51.4, 38.4, 35.9, 34.4, 30.4, 24.7, 23.3. HRMS (DART-TOF) calculated for  $\text{C}_{33}\text{H}_{41}\text{NNaO}_3^+$  [ $\text{M}+\text{Na}$ ] $^+$   $m/z$  522.2979, found 522.2985. IR (KBr,  $\text{cm}^{-1}$ ): 3632, 3328, 2948, 1673, 1595, 1531, 1408, 1315, 1235, 1178, 705.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(3-methoxyphenyl)-5-phenylpentan-1-one (3ah).** General Procedure was used to prepare the desired product 3ah. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded 3ah as yellow oil (21.7 mg, 0.046 mmol, 46%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.44 – 7.35 (m, 2H), 7.25 (t,  $J = 8.1$  Hz,

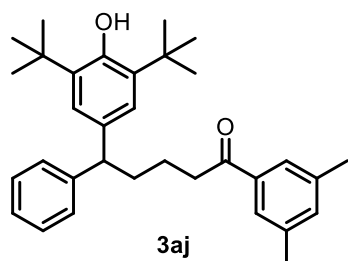
1H), 7.19 (d,  $J = 5.9$  Hz, 4H), 7.08 (dp,  $J = 8.6, 2.7$  Hz, 1H), 7.02 – 6.98 (m, 1H), 6.95 (s, 2H), 4.93 (s, 1H), 4.93 (t, 1H), 4.93 (s, 3H), 2.86 (t,  $J = 7.3$  Hz, 2H), 2.06 – 1.98 (m, 2H), 1.64 (p,  $J = 7.0, 6.6$  Hz, 2H), 1.32 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  200.0, 159.8, 152.0, 145.4, 138.4, 135.7, 135.4, 129.5, 128.4, 127.8, 125.9, 124.2, 120.7, 119.3, 112.4, 55.4, 51.4, 38.7, 35.9, 34.4, 30.4, 23.2. HRMS (DART-TOF) calculated for  $\text{C}_{32}\text{H}_{39}\text{O}_3^-$  [ $\text{M}-\text{H}$ ] $^-$   $m/z$  471.2904, found 471.2901. IR (KBr,  $\text{cm}^{-1}$ ): 3452, 2955, 1684, 1597, 1433, 1362, 1258, 1044, 882, 767, 701.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(2-methoxyphenyl)-5-phenylpentan-1-one (3ai).** General Procedure was used to prepare the desired product 3ai. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded 3ai as yellow oil (45.4 mg, 0.096 mmol, 96%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.60 (dd,  $J = 7.7, 1.8$  Hz, 1H), 7.41 (td,  $J = 7.8, 1.8$  Hz, 1H), 7.25 (d,  $J = 6.2$  Hz, 4H), 7.14 (td,  $J = 6.0,$

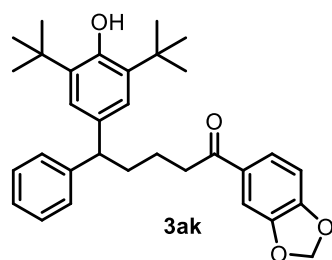
2.8 Hz, 1H), 7.01 (s, 2H), 7.00 – 6.86 (m, 2H), 4.99 (s, 1H), 3.85 – 3.78 (m, 4H), 2.96 (t,  $J =$

7.3 Hz, 2H), 2.05 (qd,  $J = 7.2, 4.3$  Hz, 2H), 1.65 (p,  $J = 7.6$  Hz, 2H), 1.39 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  202.9, 158.3, 151.9, 145.5, 135.8, 135.6, 133.1, 130.2, 128.8, 128.3, 127.9, 125.9, 124.2, 120.7, 111.5, 55.5, 51.5, 43.8, 36.1, 34.4, 30.4, 23.2. HRMS (DART-TOF) calculated for  $\text{C}_{32}\text{H}_{39}\text{O}_3^-$  [M-H] $^-$   $m/z$  471.2904, found 471.2901. IR (KBr,  $\text{cm}^{-1}$ ): 3452, 2955, 1684, 1597, 1433, 1362, 1258, 1044.



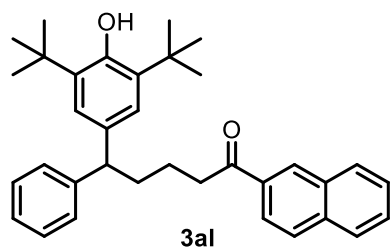
**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-(2-methoxyphenyl)-1-(4-methoxyphenyl) pentan-1-one (3aj).**

**General Procedure** was used to prepare the desired product **3aj**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded **3aj** as yellow oil (25.9 mg, 0.055 mmol, 55%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.42 (s, 2H), 7.19 (d,  $J = 5.6$  Hz, 4H), 7.11 – 7.05 (m, 2H), 6.95 (s, 2H), 4.92 (s, 1H), 3.76 (t,  $J = 7.8$  Hz, 1H), 2.88 – 2.81 (m, 2H), 2.27 (s, 6H), 2.07 – 1.96 (m, 2H), 1.63 (p,  $J = 7.5$  Hz, 2H), 1.32 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  200.7, 151.9, 145.5, 138.1, 137.2, 135.6, 135.5, 134.4, 128.3, 127.8, 125.9, 125.8, 124.2, 51.5, 38.7, 35.9, 34.3, 30.4, 23.2, 21.2. HRMS (DART-TOF) calculated for  $\text{C}_{33}\text{H}_{41}\text{O}_2^-$  [M-H] $^-$   $m/z$  469.3112, found 469.3103. IR (KBr,  $\text{cm}^{-1}$ ): 3450, 2956, 1681, 1605, 1435, 1363, 1310, 1158, 701.



**1-(Benzo[*d*][1,3]dioxol-5-yl)-5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5-phenylpentan-1-one (3ak).**

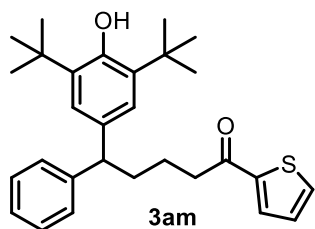
**General Procedure** was used to prepare the desired product **3ak**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3ak** as yellow oil (39.9 mg, 0.082 mmol, 82%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.38 (dd,  $J = 8.2, 1.7$  Hz, 1H), 7.30 (d,  $J = 1.7$  Hz, 1H), 7.18 (d,  $J = 2.9$  Hz, 4H), 7.11 – 7.02 (m, 1H), 6.95 (s, 2H), 6.72 (d,  $J = 8.1$  Hz, 1H), 5.93 (s, 2H), 4.92 (s, 1H), 3.76 (t,  $J = 7.8$  Hz, 1H), 2.78 (t,  $J = 7.4$  Hz, 2H), 2.01 (qd,  $J = 7.3, 4.1$  Hz, 2H), 1.62 (p,  $J = 7.6$  Hz, 2H), 1.32 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.3, 152.0, 151.5, 148.1, 145.4, 135.7, 135.4, 132.0, 128.3, 127.8, 125.9, 124.2, 107.9, 107.8, 101.7, 51.4, 38.3, 35.9, 34.4, 30.4, 29.6, 23.4. HRMS (DART-TOF) calculated for  $\text{C}_{32}\text{H}_{37}\text{O}_4^-$  [M-H] $^-$   $m/z$  485.2697, found 485.2693. IR (KBr,  $\text{cm}^{-1}$ ): 3634, 2956, 1675, 1603, 1488, 1438, 1362, 1250, 1110, 1038, 934, 884, 807, 769, 701.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(naphthalen-2-yl)-5-phenylpentan-1-one (3al).**

**General Procedure** was used to prepare the desired product **3al**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3al** as yellow oil (39.9 mg, 0.081 mmol, 81%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.30 (d,  $J = 1.7$  Hz, 1H), 7.92 – 7.81 (m, 2H), 7.77 (d,  $J = 8.6$  Hz, 2H), 7.55 – 7.40 (m, 2H), 7.19 (d,  $J = 4.4$  Hz, 4H), 7.08 (h,  $J = 4.3$  Hz, 1H), 6.96 (s, 2H), 4.92

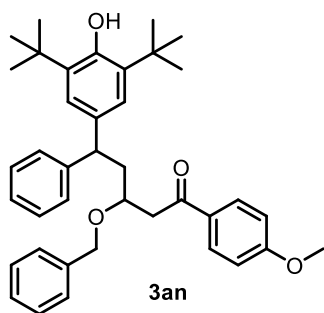
(s, 1H), 3.79 (t,  $J = 7.8$  Hz, 1H), 3.00 (t,  $J = 7.3$  Hz, 2H), 2.07 (qd,  $J = 7.4, 4.0$  Hz, 2H), 1.71 (p,  $J = 7.5$  Hz, 2H), 1.32 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  200.2, 152.0, 145.4, 135.7, 135.5, 135.5, 134.4, 132.6, 129.6, 129.5, 128.4, 128.4, 128.3, 127.9, 127.7, 126.7, 125.9, 124.2, 124.0, 51.5, 38.7, 36.0, 34.4, 30.4, 23.3. HRMS (DART-TOF) calculated for  $\text{C}_{35}\text{H}_{39}\text{O}_2^-$  [M-H] $^-$   $m/z$  491.2955, found 491.2955. IR (KBr,  $\text{cm}^{-1}$ ): 3528, 2958, 1675, 1436, 1354, 1306, 1240, 1117, 827, 758, 704.



**5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-phenyl-1-(thiophen-2-yl) pentan-1-one (3am).**

**General Procedure** was used to prepare the desired product **3am**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3am** as a yellow oil (17.9 mg, 0.04 mmol, 40%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.58 (d,  $J = 4.4$  Hz, 2H), 7.31 – 7.21 (m, 4H), 7.15 (tt,  $J = 5.4, 2.4$  Hz, 1H), 7.08 (t,  $J = 4.4$  Hz,

1H), 7.02 (s, 2H), 5.00 (s, 1H), 3.83 (t,  $J = 7.8$  Hz, 1H), 2.88 (t,  $J = 7.4$  Hz, 2H), 2.09 (qd,  $J = 7.4, 4.5$  Hz, 2H), 1.72 (p,  $J = 7.5$  Hz, 2H), 1.39 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  193.1, 152.0, 145.3, 144.4, 135.7, 135.3, 133.2, 131.6, 128.4, 128.0, 127.8, 125.9, 124.2, 51.4, 39.4, 35.9, 34.3, 30.4, 23.6. HRMS (DART-TOF) calculated for  $\text{C}_{29}\text{H}_{35}\text{O}_2\text{S}^-$  [M-H] $^-$   $m/z$  447.2363, found 447.2360. IR (KBr,  $\text{cm}^{-1}$ ): 3635, 2956, 1662, 1435, 1415, 1362, 1235, 724, 701.



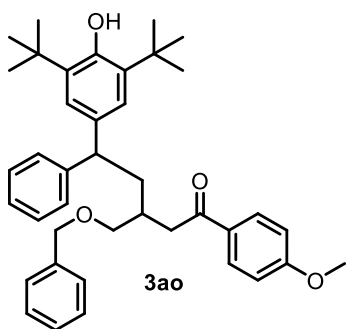
**3-(Benzyloxy)-5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-5-phenylpentan-1-one (3an).**

**General Procedure** was used to prepare the desired product **3an**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3an** as red oil (37.6 mg, 0.065 mmol, 65%, 1:1 dr).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.72 (dd,  $J = 8.8, 1.6$  Hz, 2H), 7.24 – 7.14 (m, 7H), 7.14 – 7.03 (m, 3H), 6.96 (d,  $J = 10.1$  Hz, 2H), 6.84 – 6.75 (m, 2H), 4.94 (d,  $J = 8.0$  Hz, 1H), 4.38 – 4.18 (m, 2H), 4.10 (dt,

$J = 8.0, 6.5$  Hz, 1H), 3.96 – 3.83 (m, 1H), 3.78 (s, 3H), 3.14 (dd,  $J = 15.8, 6.4$  Hz, 1H), 2.89 (dd,  $J = 18.7, 15.6$  Hz, 1H), 2.26 (qd,  $J = 6.9, 6.0, 1.8$  Hz, 2H), 1.31 (d,  $J = 6.4$  Hz, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*) 197.4, 197.1, 163.4, 152.1, 152.0, 145.8, 144.5, 138.5, 135.8, 135.7, 135.7, 134.2, 130.5, 130.5, 130.4, 130.3, 128.5, 128.4, 128.3, 128.2, 127.8, 127.8, 127.7, 127.5, 127.5, 126.1, 125.9, 124.6, 124.3, 113.7, 74.8, 74.8, 71.9, 71.9, 55.5, 47.6, 47.4, 44.0, 44.0, 42.0, 41.9, 34.4, 30.4, 30.3. HRMS (DART-TOF) calculated for  $\text{C}_{39}\text{H}_{45}\text{O}_4^-$  [M-H] $^-$   $m/z$  577.3323, found 577.3321. IR (KBr,  $\text{cm}^{-1}$ ): 3623, 2955, 1664, 1603, 1577, 1510, 1432, 1358, 1254, 1178, 1024, 839, 817, 780, 758, 699.

**3-((Benzyloxy)methyl)-5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-5-phenylpentan-1-one (3ao).**

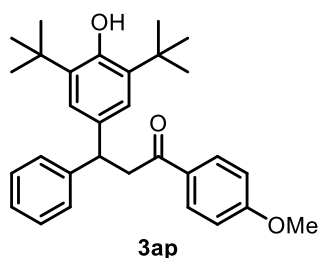
**General Procedure** was used to prepare the desired product **3ao**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3ao** as green oil (37.9 mg, 0.064 mmol, 64%, 1.1:1 dr).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.79 – 7.63 (m, 2H), 7.31 – 7.12 (m, 9H), 7.07 (tdd,  $J = 6.7, 4.3, 2.2$  Hz, 1H),



6.93 (d,  $J = 1.7$  Hz, 2H), 6.77 (d,  $J = 8.7$  Hz, 2H), 4.93 (d,  $J = 10.9$  Hz, 1H), 4.38 – 4.25 (m, 2H), 3.85 (q,  $J = 8.7, 8.2$  Hz, 1H), 3.76 (s, 3H), 3.34 (dd,  $J = 7.1, 5.1$  Hz, 2H), 2.94 (dd,  $J = 15.6, 7.3$  Hz, 1H), 2.80 (dd,  $J = 15.8, 10.3$  Hz, 1H), 2.30 – 2.18 (m, 1H), 2.14 (dd,  $J = 14.0, 7.6$  Hz, 1H), 2.08 – 1.98 (m, 1H), 1.30 (d,  $J = 1.3$  Hz, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.7, 198.5, 163.2, 152.0, 152.0, 145.6, 144.9, 138.6, 138.6, 135.7, 135.6, 135.4, 134.9, 130.4, 130.4, 128.4, 128.4, 128.3, 128.0, 127.9, 127.6, 127.6, 127.4, 126.0, 125.9, 124.3, 113.6,

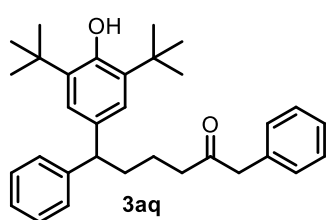
113.6, 73.0, 72.9, 72.6, 72.2, 55.4, 49.0, 48.8, 41.1, 40.9, 38.3, 38.3, 34.4, 34.3, 34.0, 33.8, 30.4.

**HRMS (DART-TOF)** calculated for  $\text{C}_{40}\text{H}_{47}\text{O}_4^-$  [M-H] $^-$   $m/z$  591.3479, found 591.3475. **IR (KBr,  $\text{cm}^{-1}$ ):** 3578, 2952, 1670, 1602, 1578, 1434, 1362, 1306, 1255, 1118, 1031, 981, 889, 835, 774, 703.



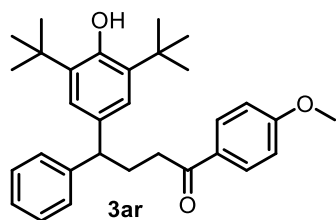
**3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-3-phenylpropan-1-one (3ap).** General Procedure was used to prepare the desired product **3ap**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3ap** as yellow oil (26.6 mg, 0.06 mmol, 60%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.80 (d,  $J = 8.9$  Hz, 2H), 7.18 (dd,  $J = 3.7, 2.1$  Hz, 4H), 7.07 (tt,  $J = 5.7, 2.9$  Hz, 1H), 6.93 (s, 2H), 6.81

(d,  $J = 8.9$  Hz, 2H), 4.93 (s, 1H), 4.64 (t,  $J = 7.4$  Hz, 1H), 3.77 (s, 3H), 3.54 (dd,  $J = 7.4, 1.7$  Hz, 2H), 1.47 (s, 2H), 1.29 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  197.3, 163.3, 152.1, 144.7, 135.7, 134.8, 130.5, 130.3, 128.4, 127.9, 126.1, 124.4, 113.6, 55.4, 46.5, 45.1, 34.3, 30.3. **HRMS (DART-TOF)** calculated for  $\text{C}_{30}\text{H}_{35}\text{O}_3^-$  [M-H] $^-$   $m/z$  443.2592, found 443.2590. **IR (KBr,  $\text{cm}^{-1}$ ):** 3434, 2955, 1673, 1600, 1510, 1435, 1363, 1258, 1170, 1115, 1029, 831, 741, 700.

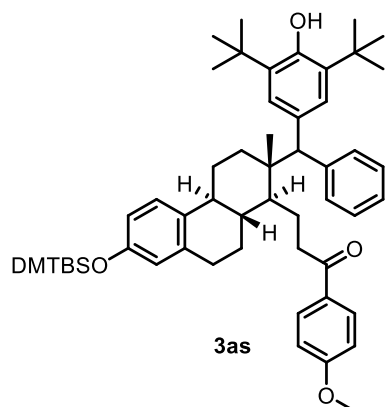


**6-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1,6-diphenylhexan-2-one (3aq).** General Procedure was used to prepare the desired product **3aq**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (50/1) as eluent afforded **3aq** as a yellow oil (8.2 mg, 0.018 mmol, 18%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34 – 7.27 (m, 3H), 7.25 – 7.08 (m, 7H), 6.97

(s, 2H), 5.00 (s, 1H), 3.73 (t,  $J = 7.8$  Hz, 1H), 3.62 (s, 2H), 2.43 (t,  $J = 7.3$  Hz, 2H), 2.01 – 1.84 (m, 2H), 1.54 – 1.47 (m, 2H), 1.39 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  208.2, 151.9, 145.3, 135.6, 135.4, 134.3, 129.4, 128.7, 128.3, 127.8, 126.9, 125.9, 124.1, 51.4, 50.1, 41.8, 35.7, 34.3, 30.4, 22.4. **HRMS (DART-TOF)** calculated for  $\text{C}_{32}\text{H}_{39}\text{O}_2^-$  [M-H] $^-$   $m/z$  455.2955, found 455.2951. **IR (KBr,  $\text{cm}^{-1}$ ):** 3636, 2959, 1676, 1600, 1511, 1436, 1363, 1261, 1170, 1028, 809.



**4-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-4-phenylbutan-1-one (3ar).**<sup>[4b]</sup> **General Procedure** was used to prepare the desired product **3ar**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **3ar** as yellow oil (32.6 mg, 0.71 mmol, 71%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.82 (d, *J* = 8.9 Hz, 2H), 7.28 (d, *J* = 4.3 Hz, 4H), 7.20 – 7.14 (m, 1H), 7.04 (s, 2H), 6.90 – 6.83 (m, 2H), 5.03 (s, 1H), 3.89 (t, *J* = 7.9 Hz, 1H), 3.84 (s, 3H), 2.92 – 2.75 (m, 2H), 2.51 – 2.35 (m, 2H), 1.39 (s, 18H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  198.9, 163.3, 152.1, 145.0, 135.7, 135.1, 130.3, 130.2, 128.4, 127.9, 126.1, 124.3, 113.6, 55.4, 50.8, 36.8, 34.4, 31.0, 30.4. **HRMS (DART-TOF)** calculated for C<sub>31</sub>H<sub>37</sub>O<sub>3</sub><sup>-</sup> [M-H]<sup>-</sup> *m/z* 457.2748, found 457.2745. **IR (KBr, cm<sup>-1</sup>):** 3619, 2958, 1676, 1602, 1574, 1510, 1364, 1306, 1260, 1236, 1206, 1173, 1121, 1027, 987, 833, 699.

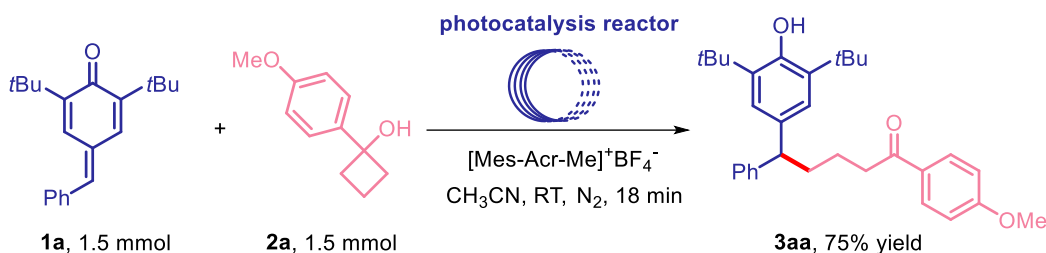


**3-((1*S*,2*S*,4*aS*,10*aS*)-7-((*Tert*-butyldimethylsilyl)oxy)-2-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)-2-methyl-1,2,3,4,4*a*,9,10,10*a*-octahydrophenanthren-1-yl)-1-(4-methoxyphenyl)propan-1-one (3as).** **General Procedure** was used to prepare the desired product **3as**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (15/1) as eluent afforded **3as** as brown oil (18.1 mg, 0.023 mmol, 23%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.57 (dd, *J* = 9.0, 7.4 Hz, 2H), 7.40 – 7.31 (m, 1H), 7.16 (d, *J* = 7.1 Hz, 1H), 7.12 – 6.92 (m, 6H), 6.71 (dd, *J* = 15.7, 8.9 Hz, 2H), 6.44 (dt, *J* = 8.5, 2.3 Hz, 1H), 6.39 – 6.31 (m, 1H), 4.81 (d, *J* = 14.7 Hz, 1H), 3.92 (d, *J* = 2.1 Hz, 1H), 3.69 (d, *J* = 9.5 Hz, 3H), 2.68 – 2.35 (m, 3H), 2.19 – 1.66 (m, 6H), 1.24 (s, 12H), 1.13 (s, 12H), 0.84 (d, *J* = 33.1 Hz, 12H), 0.00 (d, *J* = 2.3 Hz, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) 199.2, 198.7, 163.3, 153.4, 153.3, 151.9, 151.8, 143.9, 142.7, 137.7, 137.6, 135.4, 134.6, 133.5, 132.9, 132.8, 131.8, 130.8, 130.5, 130.3, 130.1, 130.0, 128.3, 127.4, 127.4, 126.9, 126.5, 126.5, 125.8, 125.60 119.6, 119.5, 117.4, 117.4, 113.5, 61.9, 61.6, 55.4, 46.8, 46.6, 43.9, 43.5, 43.1, 43.0, 41.9, 41.5, 39.6, 39.5, 35.9, 35.0, 34.3, 34.2, 30.5, 30.4, 27.8, 27.5, 27.4, 25.7, 25.7, 22.6, 22.5, 19.9, 19.5, 18.2, 18.2, -4.39. **HRMS (DART-TOF)** calculated for C<sub>52</sub>H<sub>69</sub>O<sub>4</sub>Si<sup>-</sup> [M-H]<sup>-</sup> *m/z* 785.4971 found 785.4968. **IR (KBr, cm<sup>-1</sup>):** 3639, 2955, 1677, 1601, 1497, 1437, 1361, 1257, 1170, 1032, 976, 840, 781, 703.



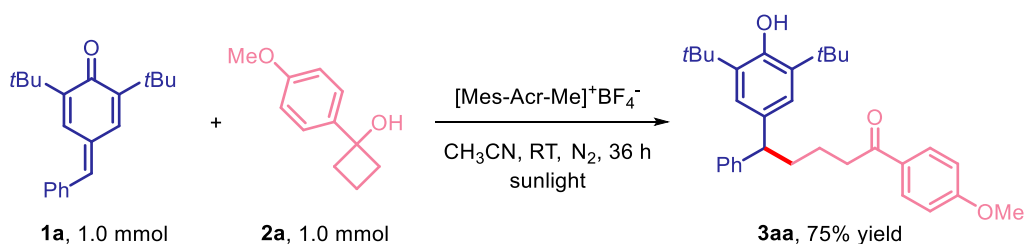
### 3. Scale-up and Transformation of Product

#### 3.1 Gram-scale synthesis in continuous flow



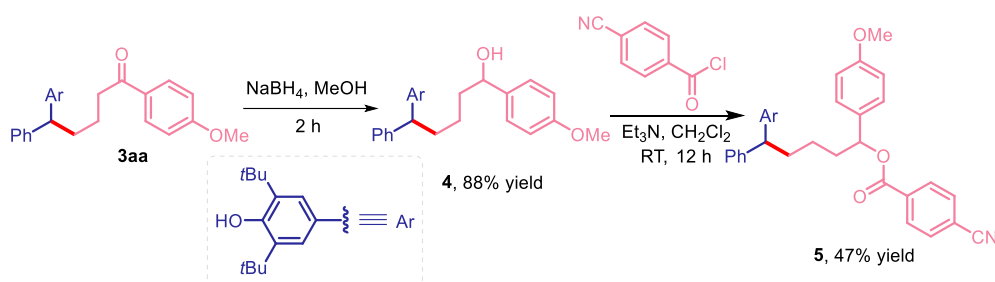
To an oven-dried round bottom flask (50 ml), *p*-quinone methide **1a** (1.5 mmol), cyclobutanol **2a** (1.5 mmol) and  $[\text{Mes-Acr-Me}]^+\text{BF}_4^-$  (0.0375mmol) were added in an argon-filled glove-box.  $\text{CH}_3\text{CN}$  (15 mL) was added into the flask via a syringe. The reaction mixture was dissolved completely. Acetonitrile flowed in the continuous flow apparatus until the air was completely discharged and the temperature was controlled at 23 °C. The reaction mixture was aspirated through coiled tube with the flow rates of 1 mL/min. The peristaltic pump worked before the solution entered the photoreactor to fully mix the mixture. The residence time of 15 ml reaction mixture was 18 minutes after entering the continuous flow photoreaction apparatus. After completion of the reaction, the crude mixture was purified by flash chromatography (petroleum ether/ethyl acetate) to afford the product **3aa** (531.2 mg, 75% yield).

#### 3.2 Sunlight driven experiment

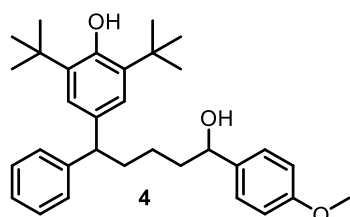


To an oven-dried quartz tube, *p*-quinone methide **1a** (1.0 mmol), cyclobutanol **2a** (1.0 mmol) and  $[\text{Mes-Acr-Me}]^+\text{BF}_4^-$  (0.025 mmol) was added in an argon-filled glove-box.  $\text{CH}_3\text{CN}$  (5 mL) was added into the tube via a syringe. The tube was sealed with a rubber plug wrapped with plastic film, removed from the glove box. The resulting mixture was irradiated by sunlight for 36 h (as an on/off visible light irradiation experiment, the reaction solution was kept in dark place at night). After completion of the reaction, the crude mixture was purified by flash chromatography (petroleum ether/ethyl acetate) to afford the product **3aa** (354.5 mg, 75% yield).

### 3.3 Synthetic applications

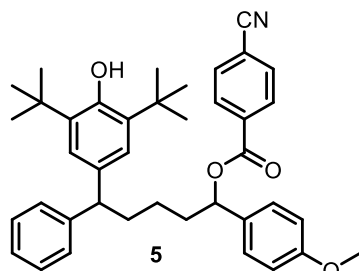


Adapted from a literature procedure<sup>[6]</sup>. To a solution of **3aa** (0.2 mmol) in MeOH (2.0 mL) was added NaBH<sub>4</sub> slowly (0.6 mmol). After 2 h the mixture was concentrated under reduced pressure and purified by flash chromatography (petroleum ether/ethyl acetate) directly to afford the pure product **4** (83.4 mg, 88% yield). To an oven-dried round bottom flask (10 mL) equipped, product **4** (0.1 mmol), 4-Cyanobenzoyl chloride (0.2 mmol), Et<sub>3</sub>N (0.5 mmol) were added in DCM (2 mL) in an argon-filled glove-box. After the reaction tube was sealed, the mixture was stirred at rt for 12 h. Then quenched with saturated NaHCO<sub>3</sub> (2 mL) solution and the aqueous layer was extracted DCM (3×5 mL). The organic layers were combined, washed with saturated NaCl solution, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford **5** (56.8 mg, 47% yield).



**2,6-Di-tert-butyl-4-(5-hydroxy-5-(4-methoxyphenyl)-1-phenylpentyl) phenol (4)**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **4** as yellow oil (83.4 mg, 0.176 mmol, 88%, 1:1 dr). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.09 (m, 8H), 6.98 (s, 2H), 6.87 – 6.81 (m, 2H), 5.00 (d, *J* = 2.8 Hz, 1H),

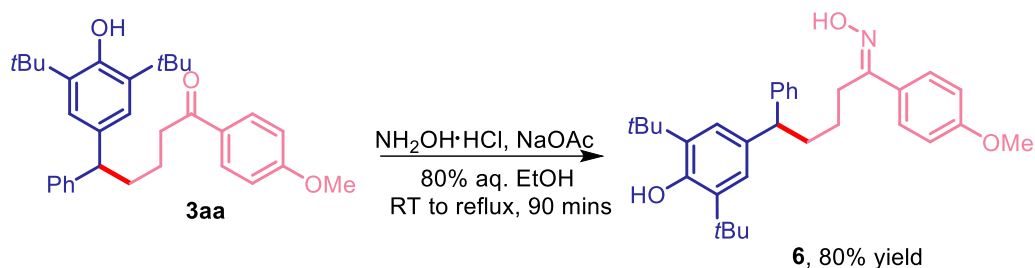
4.59 – 4.50 (m, 1H), 3.79 (s, 3H), 3.79 (t, 1H), 2.01 (m, 2H), 1.89 – 1.58 (m, 4H), 1.39 (d, *J* = 1.5 Hz, 18H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 159.0, 159.0, 151.9, 145.6, 145.5, 137.0, 136.9, 135.7, 135.7, 135.5, 128.3, 127.9, 127.1, 127.1, 125.8, 124.2, 124.2, 74.1, 74.0, 55.3, 51.3, 51.3, 38.9, 38.8, 36.3, 36.2, 34.4, 30.4, 24.5, 24.4. HRMS (DART-TOF) calculated for C<sub>32</sub>H<sub>41</sub>O<sub>3</sub><sup>-</sup> [M-H]<sup>-</sup> *m/z* 473.3061, found 473.3057. IR (KBr, cm<sup>-1</sup>): 3407, 2954, 1611, 1513, 1435, 1363, 1247, 1175, 1033, 832, 701.



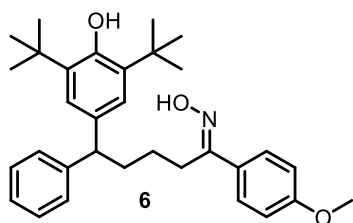
**5-(3,5-Di-tert-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-5-phenylpentyl 4-cyanobenzoate (5)**. Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **5** as transparent oil (28.4 mg, 0.047 mmol, 47%, 1:1 dr). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.00 (m, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.17 (m, 6H), 7.16 – 7.09 (m, 1H), 6.97 (s, 2H), 6.85

(d, *J* = 8.7 Hz, 2H), 5.91 – 5.84 (m, 1H), 5.01 (d, *J* = 1.6 Hz, 1H), 3.82 – 3.70 (s, 3H), 3.70 (m, 1H), 2.16 – 1.87 (m, 4H), 1.37 (d, *J* = 2.2 Hz, 18H), 1.32 – 1.22 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 164.2, 159.5, 159.5, 152.0, 151.9, 145.3, 135.6, 135.4, 134.5, 134.4, 132.2,

132.1, 132.0, 130.1, 128.3, 128.0, 128.0, 127.9, 127.8, 125.9, 125.9, 124.2, 118.0, 116.2, 114.0, 55.2, 51.1, 35.9, 35.9, 35.8, 34.35, 30.4, 24.1, 24.1. **HRMS (DART-TOF)** calculated for  $C_{40}H_{44}NO_4^-$   $[M-H]^-$   $m/z$  602.3275, found 602.3270. **IR (KBr,  $cm^{-1}$ ):** 3636, 2954, 1700, 1610, 1512, 1432, 1289, 1247, 1180, 1105, 1036, 931, 865, 831, 769, 701.



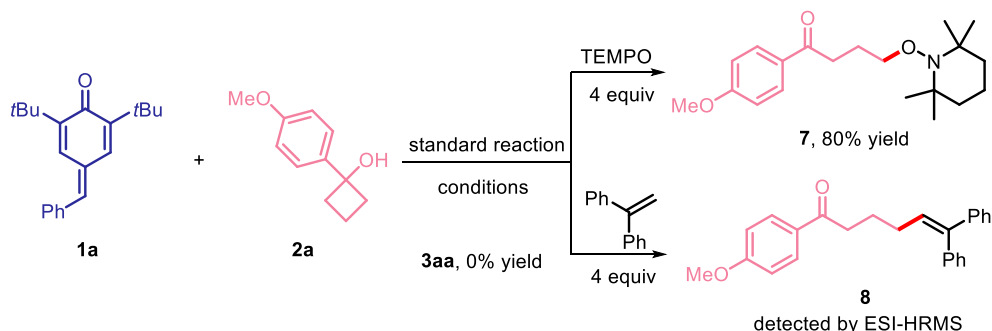
Adapted from a literature procedure<sup>[7][6]</sup>. To an oven-dried three-necked flash (50 mL) equipped, hydroxylamine hydrochloride (0.32 mmol) and sodium acetate trihydrate (0.4 mmol) were dissolved in 80% ethanol aqueous solution (20 mL). The mixture was allowed to stir at room temperature for 30 minutes. Then **3aa** (0.2 mmol) was added and the reaction mixture was refluxed at 80 °C for 1 h. When the reaction was complete (TLC monitoring). reduce the pressure to concentrate part of the reaction solvent and the aqueous layer extracted with DCM (3×5 mL). The organic layers were combined, washed with saturated NaCl solution, dried over  $Na_2SO_4$  and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford **6** (77.9 mg, 80% yield).



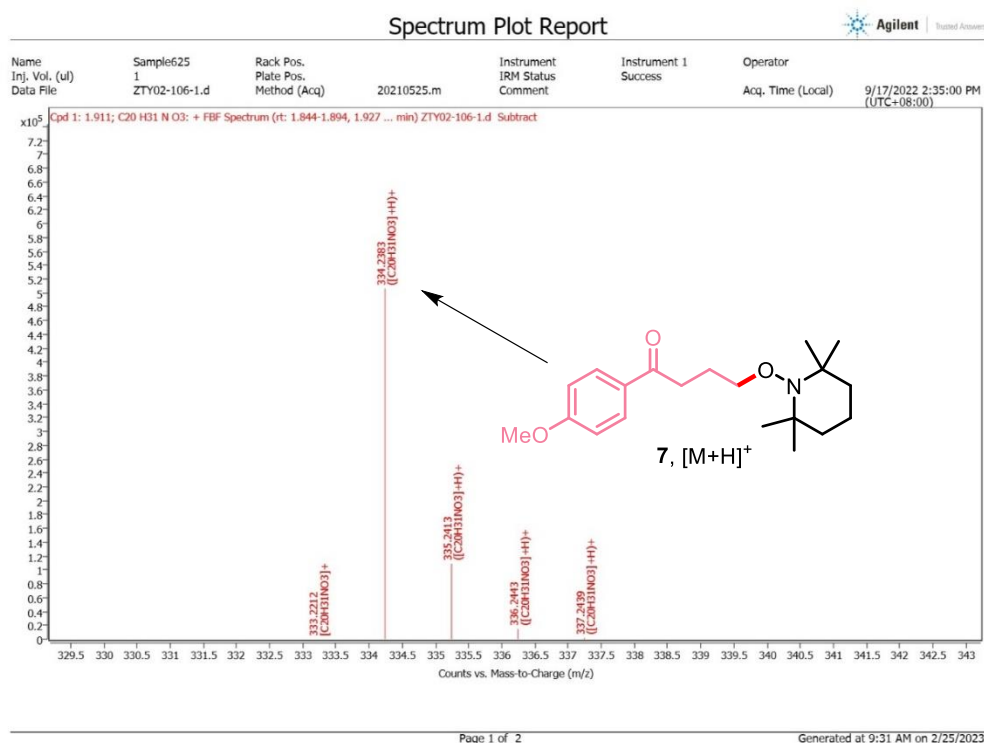
**(E)-5-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-5-phenylpentan-1-one oxime (6).**

Chromatographic purification on silica gel using petroleum ether/ethyl acetate (30/1) as eluent afforded **6** as transparent solid (77.9 mg, 0.16 mmol, 80%). Mp: 148.3-148.9 °C. **<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  8.04 (s, 1H), 7.42 (d,  $J = 8.9$  Hz, 2H), 7.29 – 7.19 (m, 4H), 7.17 – 7.10 (m, 1H), 6.99 (s, 2H), 6.84 (d,  $J = 8.9$  Hz, 2H), 5.00 (s, 1H), 3.81 (t, 1H), 3.81 (s, 3H), 2.85 – 2.65 (m, 2H), 2.08 (qd,  $J = 8.0, 2.1$  Hz, 2H), 1.53 (dd,  $J = 9.0, 6.7$  Hz, 2H), 1.38 (s, 18H). **<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**.  $\delta$  160.3, 159.2, 151.9, 145.5, 135.5, 135.3, 128.3, 128.1, 127.9, 127.5, 125.8, 124.2, 113.9, 55.3, 50.8, 36.1, 34.3, 30.4, 25.5, 24.9. **HRMS (DART-TOF)** calculated for  $C_{32}H_{42}NO_3^+$   $[M+H]^+$   $m/z$  488.3159, found 488.3170. **IR (KBr,  $cm^{-1}$ ):** 3624, 3208, 2956, 1675, 1510, 1486, 1435, 1363, 1259, 1170, 1073, 1009, 884, 832, 718.

## 4. Mechanistic Experiments

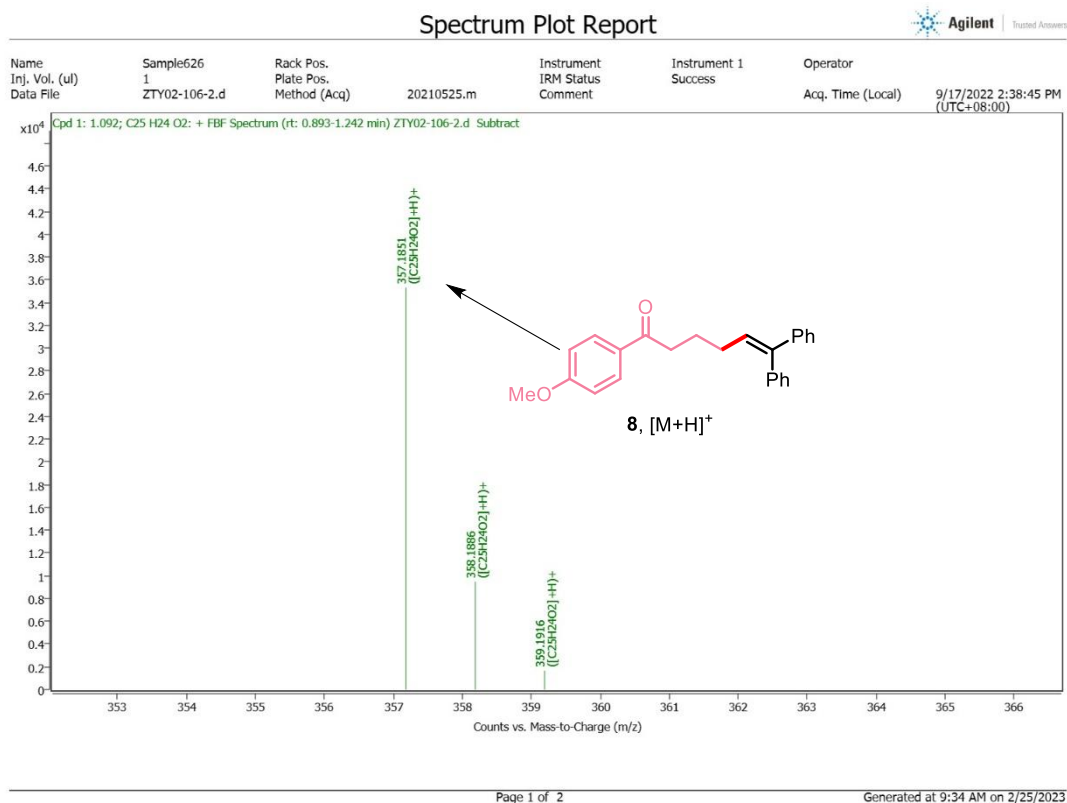


To an oven-dried quartz tube, *p*-quinone methide **1a** (0.1 mmol), cyclobutanol **2a** (0.1 mmol), [Mes-Acr-Me]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (0.025 mmol) and TEMPO (0.4 mmol) were added in an argon-filled glove-box. CH<sub>3</sub>CN (1.0 mL) was added into the tube via a syringe. The tube was sealed with a rubber plug wrapped with plastic film, removed from the glove box. The mixture was irradiated by 24 W 460 nm LEDs at room temperature for 24 h. After removal of solvents, the crude mixture was purified by flash chromatography (petroleum ether/ethyl acetate) to afford the pure products **7** (0.08 mmol, 80%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 3.84 (t, *J* = 6.3 Hz, 2H), 3.17 – 2.92 (m, 2H), 1.99 (dq, *J* = 7.8, 6.3 Hz, 2H), 1.51 – 1.44 (m, 4H), 1.32 (dd, *J* = 26.0, 4.3 Hz, 2H), 1.16 (s, 6H), 1.12 (s, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 198.8, 163.3, 130.3, 130.2, 113.7, 75.6, 59.7, 55.5, 39.6, 35.2, 33.1, 23.9, 20.1, 17.1. HRMS (DART-TOF) compound **7** calculated for C<sub>20</sub>H<sub>32</sub>NO<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup> *m/z* 334.2377, found 334.2383.



**Figure S3** *p*-Quinone methide **1a** and cyclobutanol **2a** under standard conditions with TEMPO

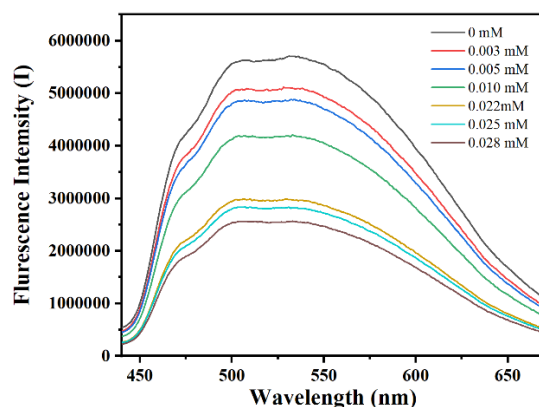
To an oven-dried quartz tube, *p*-quinone methide **1a** (0.1 mmol), cyclobutanol **2a** (0.1 mmol), [Mes-Acr-Me]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (0.025 mmol) and ethene-1,1-diyldibenzene (0.4 mmol) were added in an argon-filled glove-box. CH<sub>3</sub>CN (1.0 mL) was added into the tube via a syringe. The tube was sealed with a rubber plug wrapped with plastic film, removed from the glove box. The mixture was irradiated by 24 W 460 nm LEDs at room temperature for 24 h. HRMS (DART-TOF) compound **8** calculated for C<sub>25</sub>H<sub>25</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 357.1850, found 357.1851.



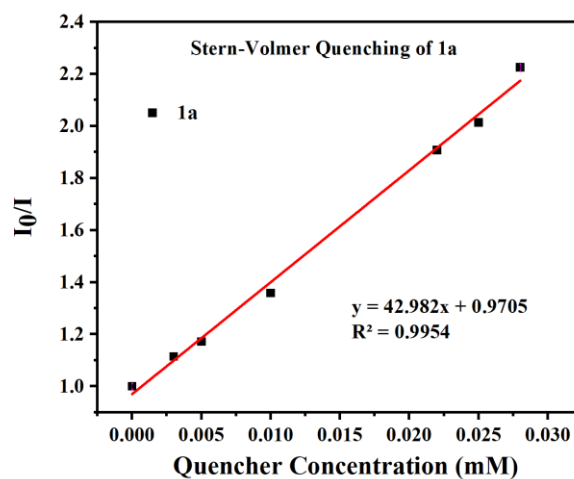
**Figure S4** *p*-Quinone methide **1a** and cyclobutanol **2a** under standard conditions with ethene-1,1-diyldibenzene

## 5. Stern-Volmer fluorescence quenching experiments

All fluorescence measurements were recorded by a F-4600 FL Spectrophotometer. Six sets of light intensity changes were measured in 3 mL of [Mes-Acr-Me]<sup>+</sup>BF<sub>4</sub><sup>-</sup> in acetonitrile solution at a concentration of 6.25×10<sup>-5</sup> mol/L, and 10 μL-200 μL of 0.5 mM of **1a** acetonitrile solution were added sequentially dropwise to each of the six sets of light intensity changes by fluorescence testing of the gradient solution.

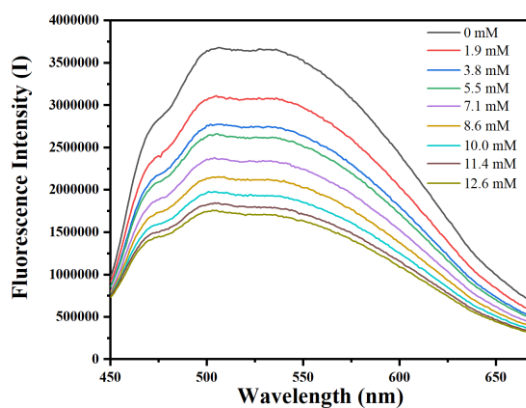


**Figure S5** The fluorescence emission spectra of  $[\text{Mes-Acr-Me}]^+\text{BF}_4^-$  with different concentration of **1a** in  $\text{CH}_3\text{CN}$  (excitation wavelength: 460 nm)

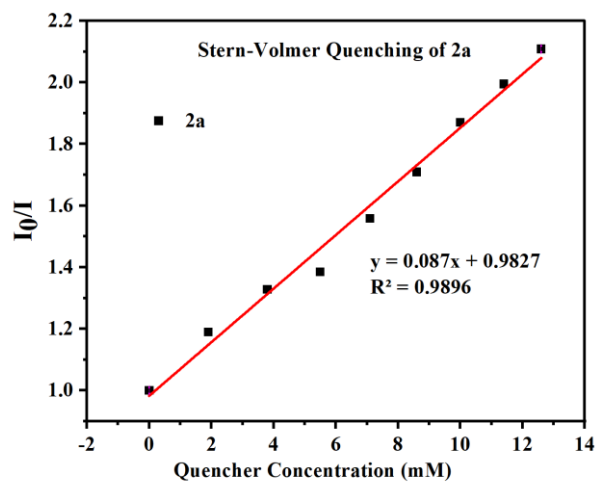


**Figure S6** Stern-Volmer fluorescence quenching plot

In 3 mL of acetonitrile solution of  $[\text{Mes-Acr-Me}]^+\text{BF}_4^-$  at a concentration of  $6.25 \times 10^{-5}$  mol/L, 100  $\mu\text{L}$ -800  $\mu\text{L}$  of 60 mM of **2a** acetonitrile solution was added dropwise in sequence to test the change of light intensity by fluorescence of the gradient solution respectively, and eight groups were measured.



**Figure S7** The fluorescence emission spectra of  $[\text{Mes-Acr-Me}]^+\text{BF}_4^-$  with different concentration of **2a** in  $\text{CH}_3\text{CN}$  (excitation wavelength: 460 nm)



**Figure S8** Stern-Volmer fluorescence quenching plot

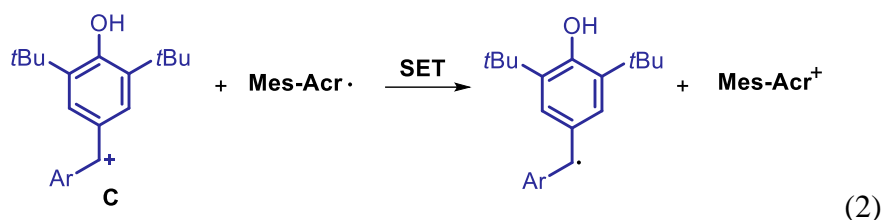
## 6. DFT Computational Study

All the species are fully optimized at the  $\omega$ B97X-D/cc-pVDZ level<sup>8-9</sup>. Frequency analyses are performed at the same level to confirm that the characteristics of the structures are minima (without imaginary frequencies) or transition states (only one imaginary frequency). Calculations of the intrinsic reaction coordinates (IRC)<sup>10-11</sup> are calculated to ensure that the transition states indeed have connected two minima. The single-point energies calculated at the  $\omega$ B97X-D/aug-cc-pVTZ level is added to the Gibbs free energy correction to obtain the Gibbs free energies. All these calculations are performed with Gaussian 16 program.<sup>12</sup>

### Modified Marcus theory

The activation free energies of the outer-sphere single electron transfer reactions were calculated using modified Marcus theory<sup>13</sup>. According to the Marcus equation, the solvent reorganization energy  $\lambda_0$  may be calculated from equation (1):

$$\lambda_0 = (332 \text{kcal/mol}) \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right) \left( \frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon} \right) \quad (1)$$



$a_1$  and  $a_2$  are the radii of **C** and Mes-Acr<sup>•</sup>,  $R = a_1 + a_2$ ,  $\epsilon_{\text{op}}$  is the optical dielectric constant ( $\epsilon_{\text{op}} = 1.81$ ),  $\epsilon$  is the static dielectric constant for the DMF solvent ( $\epsilon = 35.69$ ). We estimate the inner reorganization energy for the reactants  $\lambda_i = 0$ . Thus, the total reorganization energy  $\lambda = \lambda_i + \lambda_0$ .

According to Marcus theory,  $\Delta G_r$  is the reaction energy, and  $\Delta G_0^\ddagger$  is the intrinsic barrier.

$$\Delta G_{\text{ET}'}^\ddagger = \Delta G_0^\ddagger \left( 1 + \frac{\Delta G_r}{4\Delta G_0^\ddagger} \right)^2 \quad \Delta G_0^\ddagger = \frac{\lambda}{4} \quad (3)$$

### Cartesian coordinates together with the electronic energies for all the complexes calculated in this study

**A**

**E = -577.394688**

C	2.78322800	0.37847000	1.08645700
C	3.80284900	0.78758900	-0.00005300
C	2.78315200	0.37850200	-1.08650700
C	1.93347900	-0.38165700	0.00000300
H	3.11835500	-0.28680500	1.89403900



H	2.25589900	1.23212300	1.53295900
H	4.70628600	0.16274200	-0.00010300
H	4.11626100	1.83819100	-0.00003700
H	3.11823900	-0.28679300	-1.89409000
H	2.25579200	1.23213400	-1.53301400
C	0.46780600	-0.12922100	0.00004400
C	-0.04349200	1.20123400	0.00004900
C	-0.45063800	-1.22222300	0.00007900
C	-1.38833700	1.43000800	0.00004700
H	0.64309800	2.04846500	0.00005300
C	-1.80406000	-1.01586100	0.00007100
H	-0.04250200	-2.23136300	0.00011300
C	-2.30027200	0.32172200	0.00002900
H	-1.80956500	2.43553400	0.00004900
H	-2.48738400	-1.86395700	0.00012100
O	2.12714200	-1.76797800	-0.00004600
O	-3.56125800	0.64749700	0.00002300
C	-4.59871300	-0.35353700	-0.00012400
H	-4.52418900	-0.96834800	0.90697200
H	-5.53527400	0.21029900	-0.00040700
H	-4.52377600	-0.96857600	-0.90702900
H	3.07167800	-1.95994100	-0.00001200

**1a**

**E = -890.515066**

C	-0.67157200	1.23681500	-0.07905900
C	-1.96289700	0.49312600	0.07338800
C	-1.94191200	-1.00295200	0.02406100
C	-0.74618900	-1.62567200	-0.04202400
C	0.52479800	-0.91699000	-0.06053600
C	0.48054000	0.53474900	-0.13008000
H	-0.68657800	-2.71482700	-0.05704600
H	1.42968200	1.04910000	-0.26493900
O	-3.01972800	1.09977900	0.21713700
C	1.67900700	-1.63450000	-0.04007100

H	1.58370300	-2.72444200	-0.10401500
C	3.05887500	-1.13349500	0.03908700
C	3.42974500	-0.07184100	0.88029100
C	4.05788300	-1.76633200	-0.71818600
C	4.75041200	0.36677500	0.92898100
H	2.68162000	0.39117700	1.52566400
C	5.37503900	-1.32152500	-0.67542700
H	3.78937000	-2.60871100	-1.35986100
C	5.72494100	-0.24922600	0.14553000
H	5.02130100	1.18969600	1.59271800
H	6.13473500	-1.81722200	-1.28225200
H	6.75933700	0.09642500	0.18475500
C	-0.70444000	2.76686800	-0.17351100
C	-1.57932400	3.20124300	-1.36621700
C	-1.26549700	3.35581300	1.13666700
C	0.70131700	3.34692300	-0.38622100
C	-3.27193400	-1.76485600	0.06721200
H	-0.64003600	3.05955300	1.99408500
H	-1.26340400	4.45633200	1.08045900
H	-2.29224400	3.01704200	1.31745300
H	-2.61677500	2.86813000	-1.24345600
H	-1.57407300	4.29978100	-1.45030100
H	-1.18470900	2.78826000	-2.30844800
H	1.37857300	3.11215500	0.45019400
H	1.16246700	2.98437600	-1.31833800
H	0.63373700	4.44306500	-0.45531700
C	-4.15742300	-1.33516900	-1.11963400
C	-3.05492100	-3.28134300	-0.03536100
C	-3.99607600	-1.48008900	1.39831100
H	-5.09965000	-1.90609400	-1.10622300
H	-4.39903400	-0.26678200	-1.07186100
H	-3.65123400	-1.54031200	-2.07658900
H	-4.93787900	-2.05075500	1.43865500
H	-3.37421000	-1.79240000	2.25255200
H	-4.22903400	-0.41416600	1.50466800

H	-4.03125300	-3.78869200	-0.01768400
H	-2.55248800	-3.56461200	-0.97381500
H	-2.46631700	-3.67422500	0.80863500

**TS**

**E = -1467.923097**

C	2.87191600	1.44595800	-1.37327900
C	3.18369500	2.67153600	-0.49056100
C	3.42021300	1.87236000	0.77059600
C	3.27487000	0.35876700	-0.36464100
H	1.80284200	1.34912500	-1.59162800
H	3.43652900	1.38451800	-2.31272800
H	2.34268300	3.37180200	-0.40282300
H	4.07663400	3.22145900	-0.81263900
H	2.55887400	1.68688500	1.42057300
H	4.37416900	1.93577900	1.30062100
C	4.64023400	-0.13980600	-0.28011700
C	5.72092000	0.50643500	-0.93469600
C	4.91551300	-1.28387800	0.50360500
C	6.99923400	0.02067900	-0.82337400
H	5.54842300	1.39320300	-1.54580400
C	6.19776600	-1.78019300	0.62180900
H	4.09105300	-1.78240900	1.01209100
C	7.25916400	-1.13087500	-0.04218700
H	7.83736100	0.49627700	-1.33234000
H	6.37441000	-2.67007900	1.22363400
O	2.35284300	-0.47892800	0.08299100
O	8.52741700	-1.51600700	0.00037400
C	8.88886000	-2.66870100	0.75682100
H	8.38171800	-3.56567700	0.36996400
H	9.97063400	-2.77520500	0.63034700
H	8.65389900	-2.52739600	1.82279900
H	1.42347500	-0.10367800	-0.00296100
C	-1.90553900	-0.64426500	0.09618100
C	-1.17978500	0.64611100	0.06258100

C	-1.93632400	1.91274600	0.18216600
C	-3.28964800	1.84703200	0.23878800
C	-4.02616900	0.60646500	0.16259500
C	-3.26162500	-0.61767600	0.13298500
H	-3.88216100	2.75867200	0.31513600
H	-3.81866600	-1.54932800	0.18884900
O	0.06709800	0.69130100	-0.04325400
C	-5.39221800	0.65024900	0.15261000
H	-5.84690500	1.63300400	0.32356300
C	-6.34301900	-0.44241800	-0.03744400
C	-7.56105900	-0.39749800	0.66366700
C	-6.11160000	-1.51052900	-0.92269200
C	-8.49166800	-1.42124400	0.53342600
H	-7.76668800	0.44192600	1.33149400
C	-7.05377200	-2.52375800	-1.06475400
H	-5.21110400	-1.52071500	-1.53837800
C	-8.23778500	-2.48882800	-0.32844700
H	-9.42444100	-1.38249700	1.09750500
H	-6.86931600	-3.33963100	-1.76504700
H	-8.97409000	-3.28606700	-0.44115000
C	-1.13677800	-1.97417200	0.10426600
C	-0.31205500	-2.11878900	-1.19126600
C	-0.25214900	-2.05721900	1.36483000
C	-2.09151600	-3.17835800	0.15291800
C	-1.19371000	3.25853200	0.21835200
H	-0.88278000	-2.08666100	2.26680900
H	0.34872000	-2.97975900	1.34305200
H	0.43495600	-1.21048500	1.46895700
H	0.41493200	-1.31276100	-1.33266800
H	0.23852600	-3.07222300	-1.17930900
H	-0.97942800	-2.12617700	-2.06706300
H	-2.71563200	-3.18009300	1.05942400
H	-2.75156500	-3.22150200	-0.72717900
H	-1.49961500	-4.10533500	0.16254700
C	-0.48281200	3.49023800	-1.12848500

C	-2.16026400	4.43275700	0.43538500
C	-0.18103000	3.28250600	1.37948700
H	0.05449100	4.45235300	-1.11234300
H	0.23450400	2.69100300	-1.34786500
H	-1.21195200	3.52842800	-1.95229700
H	0.33735900	4.25441200	1.40543800
H	-0.69177200	3.14937500	2.34576500
H	0.56445800	2.48661000	1.27436700
H	-1.58651200	5.37039600	0.47461800
H	-2.88683900	4.53208200	-0.38535600
H	-2.71120700	4.34446000	1.38437600

**B**

**E = -577.051181**

C	0.22910400	-1.09539600	0.01165400
C	-0.19908000	0.24165800	0.00076100
C	0.76964700	1.24842400	-0.00888100
C	2.12804600	0.95058000	-0.00770300
C	2.53941700	-0.38838800	0.00315400
C	1.57795100	-1.40945100	0.01268900
H	-0.49592700	-1.91058700	0.01955200
H	0.43177700	2.28557900	-0.01750500
H	2.85285200	1.76365500	-0.01534800
H	1.92124100	-2.44433800	0.02110100
O	3.82729500	-0.79637600	0.00540000
C	4.84019200	0.18716200	-0.00373900
H	4.78857100	0.83111200	0.89053900
H	5.79115900	-0.35787400	-0.00012300
H	4.78679900	0.81631500	-0.90837400
C	-1.63954400	0.64341800	-0.00195700
C	-2.69573000	-0.44842400	0.00840700
C	-4.12229700	0.09094700	0.02244700
H	-2.53541400	-1.09123700	-0.87554300
H	-2.52002800	-1.09841500	0.88308000
H	-4.26206400	0.74193500	0.90198500

H	-4.24795800	0.77497500	-0.84143100
O	-1.95645500	1.81798200	-0.01338400
C	-5.15293400	-0.98164200	-0.00445300
H	-6.18859000	-0.75969600	0.26016700
H	-4.93776800	-1.95759800	-0.44850400

**C**

**E = -890.883787**

C	0.63106900	-1.60556000	-0.08600300
C	-0.57030400	-0.83304800	-0.12777200
C	-0.45897400	0.58913100	-0.15940800
C	0.75263200	1.22877600	-0.08478800
C	1.91645500	0.39312400	0.03843000
C	1.87740000	-1.03936500	0.01671200
H	0.53133000	-2.68994900	-0.10326800
H	-1.36369400	1.17116900	-0.30804400
C	0.85798900	2.76712300	-0.15597400
C	3.15760400	-1.89157400	0.09867700
C	-1.78160600	-1.51429400	-0.16845100
C	4.07928500	-1.57738300	-1.09743500
C	3.88278400	-1.62921000	1.43428900
C	2.81955200	-3.38932200	0.04098600
C	1.68855800	3.19632000	-1.38671000
C	-0.53121500	3.40584500	-0.31379200
C	1.45519000	3.33246200	1.15397800
O	3.11940500	0.93045200	0.15100100
H	3.06627000	1.89545700	0.16955800
H	0.85343300	3.02165700	2.02080700
H	2.49445800	3.03591700	1.36911000
H	1.45307000	4.43141000	1.11385200
H	1.72516500	4.29403800	-1.44285400
H	2.73140200	2.84385000	-1.38812000
H	1.22577900	2.82356900	-2.31237200
H	-1.03138700	3.08580900	-1.24003600
H	-1.18799000	3.18431900	0.54122400

H	-0.42118400	4.49796400	-0.36457400
H	4.43430700	-0.54016400	-1.09430600
H	4.96207900	-2.23279100	-1.05800000
H	3.56245500	-1.76846900	-2.05071000
H	2.32294900	-3.66955400	-0.90116700
H	3.75250200	-3.96711000	0.09800300
H	2.18960500	-3.70863900	0.88587900
H	3.22679000	-1.86033000	2.28789800
H	4.76496500	-2.28300400	1.50339700
H	4.22747500	-0.59276800	1.52919900
C	-3.12419400	-1.02788900	-0.00772800
C	-3.45488400	0.12828300	0.73636100
C	-4.16499100	-1.77991500	-0.59872000
C	-4.77493700	0.53945400	0.83469900
H	-2.68282700	0.66119000	1.29147300
C	-5.47977900	-1.34679200	-0.51960700
H	-3.92480300	-2.69451000	-1.14482800
C	-5.78410200	-0.18538300	0.19373100
H	-5.02802500	1.41852700	1.42800100
H	-6.27356300	-1.91989600	-0.99910400
H	-6.82095100	0.14519600	0.27320300
H	-1.70603400	-2.59119600	-0.36106800

**Mes-Acr•**

**E = -1368.326551**

N	-1.42695700	0.76246500	0.10579700
C	1.80962900	2.56438200	-0.08005500
C	0.89122400	1.48779000	-0.02824100
C	1.38454400	3.88185400	-0.15306400
C	0.01662400	4.16209000	-0.18813900
C	-0.91636500	3.12923200	-0.12557600
C	-0.50673300	1.79020700	-0.01835500
C	-2.01543200	-1.57992100	-0.19979800
C	-1.05014300	-0.57112600	-0.05334200
C	-1.62184700	-2.90962300	-0.29719800

C	-0.26847900	-3.26269700	-0.26280100
C	0.69335200	-2.27294500	-0.15420400
C	0.33536300	-0.90666600	-0.06207200
C	1.31366100	0.12990800	0.00673800
C	-2.82959000	1.07487900	0.36425700
C	2.76523500	-0.20408900	0.03895700
C	3.41544200	-0.38653200	1.27227600
C	4.77593400	-0.70085900	1.28866600
C	5.51025800	-0.83817600	0.10898100
C	4.84737500	-0.65780400	-1.10569400
C	3.48693700	-0.34276100	-1.15925700
C	2.63937100	-0.24680300	2.55624200
C	6.98619000	-1.14606900	0.15113500
C	2.78994600	-0.15717500	-2.48220600
H	2.87583500	2.33045400	-0.06672200
H	2.11676600	4.69076400	-0.19327300
H	-0.33463500	5.19247800	-0.27067900
H	-1.97637600	3.36861600	-0.17841000
H	-3.07697500	-1.33861000	-0.25630300
H	-2.39220400	-3.67470300	-0.40578100
H	0.03209000	-4.31025500	-0.33254200
H	1.75416500	-2.53099000	-0.14411100
H	-3.30400400	0.25385000	0.91012600
H	-3.40618800	1.22510000	-0.55882700
H	-2.89219000	1.97047200	0.99280400
H	5.27589800	-0.84513500	2.25147900
H	5.40361500	-0.76817100	-2.04163500
H	3.28153300	-0.41702100	3.43234400
H	1.80472900	-0.96421400	2.58976300
H	2.19485600	0.75723600	2.63859000
H	7.57771400	-0.22821200	0.30671200
H	7.22933100	-1.83508700	0.97416700
H	7.32866600	-1.60377400	-0.78868700
H	3.48327500	-0.30359300	-3.32286300
H	2.35630300	0.85214200	-2.55944000



H	1.95594300	-0.86819500	-2.58910700
B	-5.72981500	-0.45133200	0.05682900
F	-4.99378600	-0.60926600	-1.15451200
F	-7.00579200	-1.01202100	-0.07361000
F	-5.00555300	-1.11239400	1.09527200
F	-5.81324200	0.92742400	0.36442500

**Mes-Acr<sup>+</sup>**

**E = -1368.236617**

N	-2.00112000	0.02608000	-1.27235300
C	0.64678500	-2.46301000	-0.53189600
C	-0.00449200	-1.20185200	-0.69558200
C	-0.04343600	-3.63086100	-0.67674800
C	-1.43161000	-3.58725000	-0.96455000
C	-2.09078100	-2.40118600	-1.14507400
C	-1.38529100	-1.17220900	-1.04566400
C	-2.08265400	2.44043000	-1.03677500
C	-1.37864800	1.20845700	-0.98669600
C	-1.42602800	3.61463500	-0.78219400
C	-0.04405100	3.64005800	-0.46573100
C	0.64538100	2.46568200	-0.37636700
C	-0.00154400	1.21694600	-0.62503200
C	0.68653400	0.00154200	-0.48855500
C	-3.39003600	0.05660400	-1.74965900
C	2.11832400	-0.01017000	-0.07552800
C	3.12847500	0.08165400	-1.04781800
C	4.45806700	0.07574500	-0.62858900
C	4.79988600	-0.01435600	0.72409600
C	3.77289900	-0.10797800	1.66342300
C	2.42516200	-0.11095700	1.29154300
C	2.77778100	0.18264200	-2.51076600
C	6.24534800	0.00963800	1.14918700
C	1.33563100	-0.24348400	2.32312800
H	1.70618300	-2.46267100	-0.27518800
H	0.45593200	-4.59067300	-0.54352500
H	-1.99865800	-4.51776600	-1.01691500

H	-3.16715200	-2.40633600	-1.27508400
H	-3.15582800	2.45343200	-1.19101000
H	-1.99082400	4.54787000	-0.79658800
H	0.45201300	4.59027500	-0.26727300
H	1.69949200	2.45161700	-0.09982700
H	-3.50792900	0.90433300	-2.43113100
H	-4.06004100	0.14002400	-0.88556700
H	-3.59379700	-0.85127100	-2.32026200
H	5.25031500	0.14409500	-1.37913700
H	4.02294200	-0.18363200	2.72489200
H	3.68153600	0.21514900	-3.13365100
H	2.18926400	1.09038200	-2.71885500
H	2.17050700	-0.67657100	-2.83684700
H	6.36426800	-0.31790600	2.19119100
H	6.85921500	-0.64404700	0.51183700
H	6.65884200	1.02779900	1.06902100
H	1.73898300	-0.12327500	3.33717200
H	0.85642000	-1.23356500	2.26344100
H	0.52042500	0.47849200	2.17657200
B	-3.12552400	-0.01420700	1.69018100
F	-1.69674800	0.01509800	1.60699900
F	-3.54060300	-0.06312100	3.00768100
F	-3.63045700	1.14809800	1.03093400
F	-3.58628700	-1.15025300	0.95920800

**D**

**E = -891.096005**

C	0.68992700	-1.58910300	-0.10984100
C	-0.51410100	-0.85396600	-0.19866400
C	-0.39992000	0.54411200	-0.21379100
C	0.81796000	1.21964400	-0.09671000
C	1.98337000	0.43204500	0.03290400
C	1.93239000	-0.99143000	0.01226300
H	0.61305500	-2.67526400	-0.12362900
H	-1.30528500	1.12759200	-0.37031800

O	3.22799100	0.96822500	0.17112600
H	3.16563700	1.92569600	0.19867000
C	3.21400500	-1.84242900	0.12405500
C	0.72887800	2.76895800	-0.16038200
C	4.16434300	-1.53181300	-1.04992100
C	3.91435100	-1.57715200	1.47189800
C	2.90237700	-3.34653600	0.06547300
C	2.04518900	3.54232600	0.04840700
C	0.19351900	3.17312300	-1.54845400
C	-0.23915800	3.26189100	0.93457900
C	-1.75804800	-1.55955700	-0.32075100
H	4.48111500	-0.48260700	-1.05318800
H	5.06402400	-2.16448500	-0.98030600
H	3.67122300	-1.74943400	-2.01064400
H	3.24300900	-1.82686300	2.30878800
H	4.81241600	-2.21016700	1.55776500
H	4.22048500	-0.52975800	1.57410900
H	2.42369800	-3.63462000	-0.88317800
H	3.84387900	-3.91106700	0.14371100
H	2.25527000	-3.66958800	0.89538500
H	0.10028900	4.26898400	-1.61981300
H	0.87525900	2.83263800	-2.34319400
H	-0.79599300	2.73887200	-1.74879200
H	2.49484700	3.35278900	1.03751700
H	2.78017000	3.35128100	-0.75092400
H	1.83753300	4.62177900	0.01195100
H	-1.25219200	2.85537700	0.80818100
H	0.11921000	2.96864400	1.93355300
H	-0.31936900	4.36044300	0.90591300
C	-3.09287000	-1.07857500	-0.08550500
C	-3.39836500	0.04954300	0.71488700
C	-4.18450500	-1.79294200	-0.63757000
C	-4.71276600	0.45550100	0.91041600
H	-2.59493900	0.58031200	1.22635600
C	-5.49439300	-1.37955300	-0.44266000

H	-3.98069000	-2.68047000	-1.24148300
C	-5.76973400	-0.24539400	0.32625000
H	-4.91778900	1.32341300	1.54063700
H	-6.31234400	-1.94601800	-0.89231900
H	-6.79989700	0.07941700	0.48140900
H	-1.68124500	-2.60485200	-0.63645500

**3aa**

**E = -1468.243456**

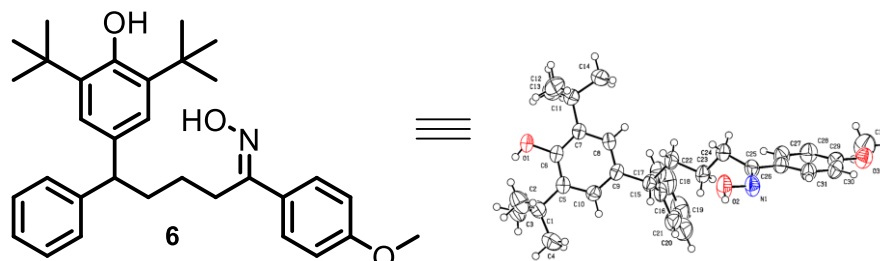
C	3.09390200	0.21783100	1.01670000
C	1.95386100	0.51130600	0.26930200
C	1.56557100	-0.39513300	-0.70933900
C	2.26664700	-1.58003100	-0.96009000
C	3.41500900	-1.82990900	-0.18137500
C	3.85173200	-0.93511900	0.82146800
H	3.39700200	0.93620300	1.77778800
H	0.67747800	-0.17697500	-1.29747600
C	1.22363900	1.82200200	0.52113000
C	2.61577100	5.33306600	-0.06502400
C	3.14703100	5.22870200	-1.34912800
C	3.07457700	4.01045200	-2.02360400
C	2.47677100	2.90646300	-1.41936900
C	1.93576200	3.00022500	-0.13298300
C	2.01549900	4.22676800	0.53396500
H	2.67240600	6.27951300	0.47648100
H	3.62116200	6.09155100	-1.82047700
H	3.49381300	3.91625100	-3.02744300
H	2.44211200	1.95136200	-1.94790000
H	1.60168400	4.31545000	1.54224700
C	-0.25988500	1.82102600	0.11269400
C	-1.11599000	0.80924800	0.87010700
H	-0.34313600	1.65689300	-0.97688100
H	-0.65471100	2.83706900	0.28242800
C	-2.56935700	0.83799100	0.41761600
H	-0.71853600	-0.20876100	0.74477100

H	-1.06571900	1.01287400	1.95201100
C	-3.44487300	-0.18245500	1.12574700
H	-3.00783500	1.84010700	0.57039900
H	-2.63892200	0.65064600	-0.66941200
O	-2.97541400	-0.94172500	1.95177200
C	-4.89974300	-0.23842800	0.78213500
C	-5.49772400	0.59954400	-0.16087300
C	-5.70443600	-1.18298400	1.44126600
C	-6.85904900	0.51128800	-0.45011000
H	-4.90611600	1.34547800	-0.69366800
C	-7.05472900	-1.28332000	1.16687200
H	-5.23334300	-1.83581500	2.17713000
C	-7.64509800	-0.43445400	0.21637400
H	-7.28993700	1.18226700	-1.19185600
H	-7.68788500	-2.01253600	1.67355900
O	-8.97018700	-0.60862700	0.01836900
C	-9.61966200	0.21807100	-0.92315700
H	-10.67201100	-0.08851800	-0.92094900
H	-9.55224000	1.28306800	-0.64278800
H	-9.20523000	0.08226100	-1.93666500
O	4.16862300	-2.95982100	-0.35517000
H	3.77621000	-3.49992200	-1.04490200
C	5.10854400	-1.21699400	1.66696500
C	1.77601000	-2.56422400	-2.04362800
C	5.37210400	-0.09509400	2.68367300
C	6.34908900	-1.30702600	0.75578200
C	4.92977900	-2.52415900	2.46465400
C	2.83685400	-2.72319400	-3.15602200
C	1.41230300	-3.92750600	-1.41251200
C	0.49869000	-2.06167400	-2.73696600
H	4.54466800	0.01704600	3.40118800
H	6.27731600	-0.33847100	3.26058700
H	5.54353400	0.87618800	2.19464600
H	6.49155100	-0.36256000	0.20705900
H	7.25002900	-1.48448400	1.36535900

H	6.26102200	-2.12105600	0.02670100
H	4.78519100	-3.38760600	1.80480600
H	5.82089800	-2.70892900	3.08640000
H	4.05850100	-2.44936300	3.13442900
H	1.05529300	-4.62317700	-2.18831000
H	2.24074400	-4.42427100	-0.88560600
H	0.60862400	-3.79586500	-0.67251100
H	3.02394100	-1.75177700	-3.63827900
H	3.81391500	-3.08923600	-2.80673500
H	2.48022400	-3.42579000	-3.92578200
H	-0.33432600	-1.94439300	-2.02779500
H	0.65897200	-1.10136400	-3.24943100
H	0.18624400	-2.79414200	-3.49664200
H	1.25164200	1.99850800	1.61012300

## 7. X-Ray Structure of Product 6

X-ray crystallography of **6**



**Figure S6.** ORTEP diagram (50% probability) of **6**

A single crystal of **6** was obtained *via* evaporation of its hexanes/dichloromethane solvent mixture. A suitable crystal of **6** was selected and analyzed by an Agilent Gemini X-ray Single Crystal Diffractometer. Using Olex2<sup>14</sup>, the structure was solved with the ShelXT<sup>15</sup> structure solution program using Direct Methods and refined with the ShelXL<sup>16</sup> refinement package using Least Squares minimization. Details of the crystal, data collection, and structure refinement parameters for crystallographic analysis of **6** are summarized in **Table S1**. Crystallographic data (CCDC 2304202) for **6** can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S1.** Parameters for crystallographic analysis of **6**

Identification code	1_a
Empirical formula	C32 H41 N O3

Formula weight	3487.66
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 <sub>1/c</sub>
Unit cell dimensions	a = 12.962(3) Å    α = 90°. b = 9.7854(17) Å    β = 98.354(5)° c = 23.918(5) Å    γ = 90°.
Volume	3001.6(10) Å <sup>3</sup>
Z	4
Density (calculated)	1.079 Mg/m <sup>3</sup>
Absorption coefficient	0.068 mm <sup>-1</sup>
F(000)	1056
Crystal size	0.120 x 0.200 x 0.200 mm <sup>3</sup>
Theta range for data collection	2.506 to 24.099°.
Index ranges	-15 ≤ h ≤ 14, -11 ≤ k ≤ 11, -28 ≤ l ≤ 28
Reflections collected	65016
Independent reflections	5325 [R(int) = 0.0806]
Completeness to theta = 24.996°	99.5 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5325 / 0 / 330
Goodness-of-fit on F <sup>2</sup>	1.018
Final R indices [I > 2σ(I)]	R1 = 0.0635, wR2 = 0.1342
R indices (all data)	R1 = 0.1248, wR2 = 0.1642
Extinction coefficient	n/a
Largest diff. peak and hole	0.326 and -0.229 e.Å <sup>-3</sup>

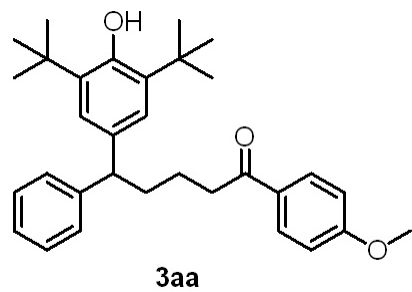
## 8. References

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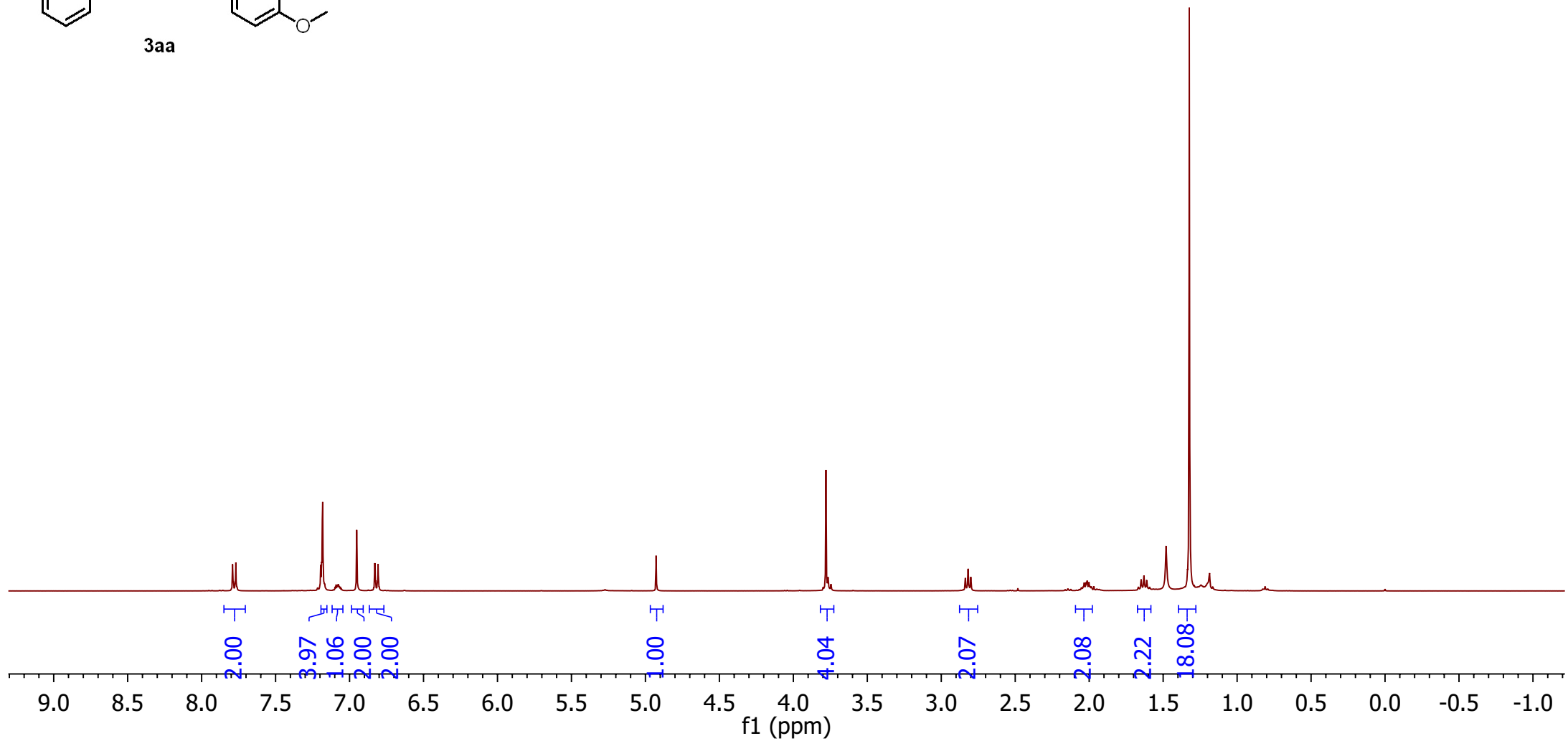
**<sup>1</sup>H(CDCl<sub>3</sub>, 400 MHz)**



7.79  
7.77  
7.20  
7.19  
7.18  
7.18  
7.10  
7.09  
7.08  
7.08  
7.07  
7.07  
7.06  
7.05  
6.95  
6.83  
6.81  
4.93

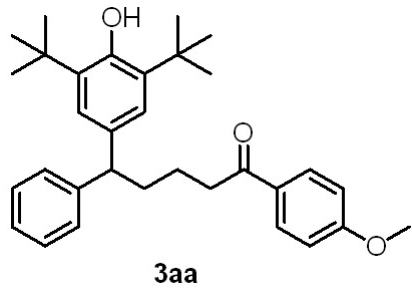
3.80  
3.79  
3.78  
3.77  
3.75

2.84  
2.82  
2.80  
2.05  
2.05  
2.04  
2.03  
2.02  
2.01  
2.00  
1.99  
1.98  
1.67  
1.65  
1.64  
1.63  
1.61  
1.59  
1.32  
1.32



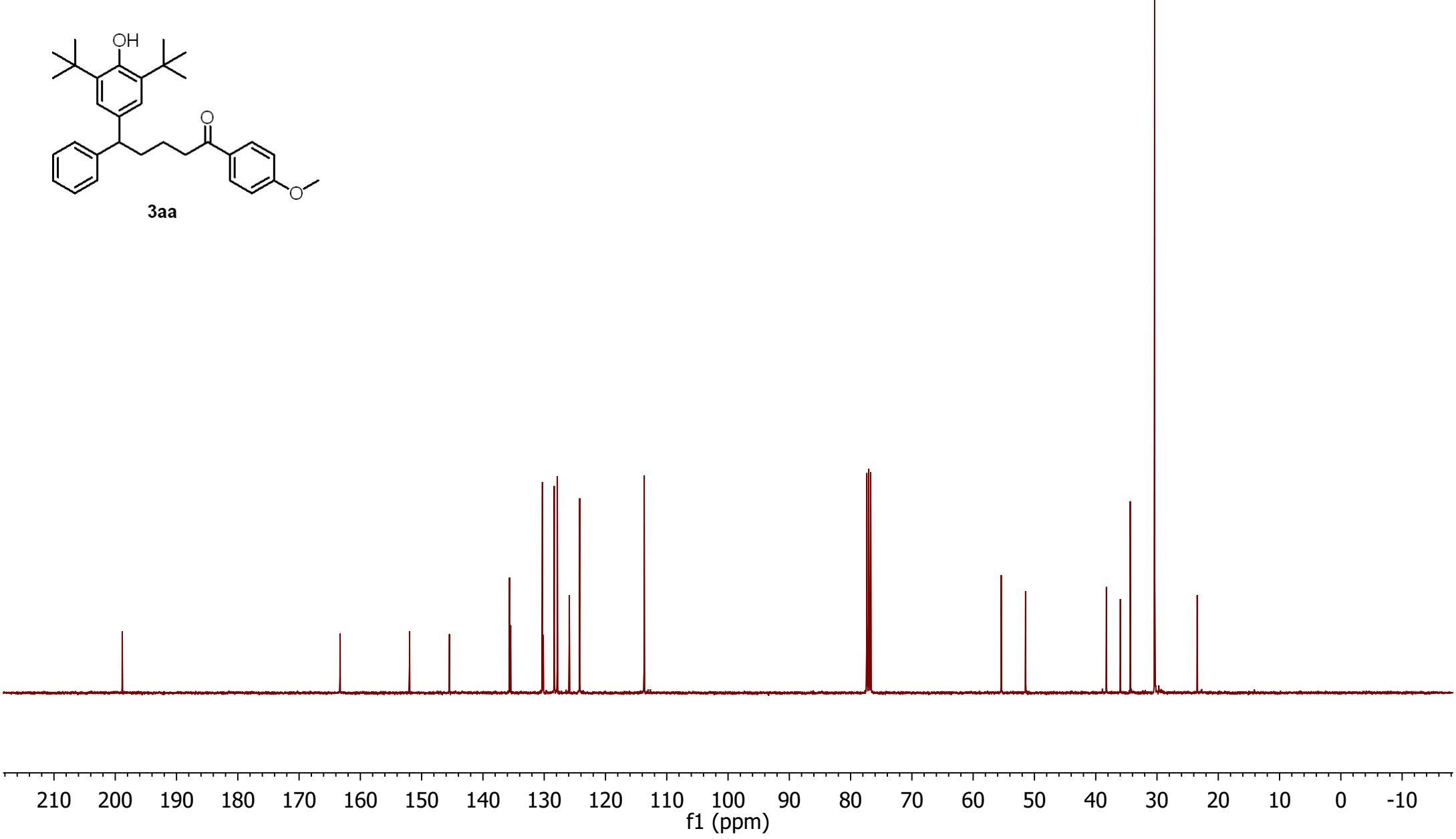
<sup>1</sup>H NMR Spectrum of **3aa**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



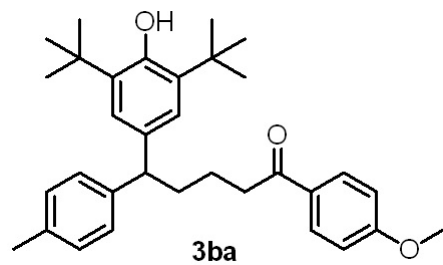
—198.9  
—163.3  
152.0  
145.5  
135.7  
135.5  
130.3  
130.1  
128.4  
127.9  
125.9  
124.2  
—113.7

—55.4  
—51.4  
~38.3  
~36.0  
~34.4  
~30.4  
~23.4



<sup>13</sup>C NMR Spectrum of **3aa**

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



7.78  
7.78  
7.76  
7.08  
7.07  
7.06  
7.06  
7.05  
7.00  
6.98  
6.82  
6.82  
6.80  
6.80  
6.79

4.91

3.77  
3.74  
3.74  
3.72  
3.70

2.82  
2.81  
2.80  
2.79

2.21  
2.21

2.04

2.03

2.02

2.02

2.01

2.00

1.99

1.98

1.97

1.96

1.66

1.64

1.63

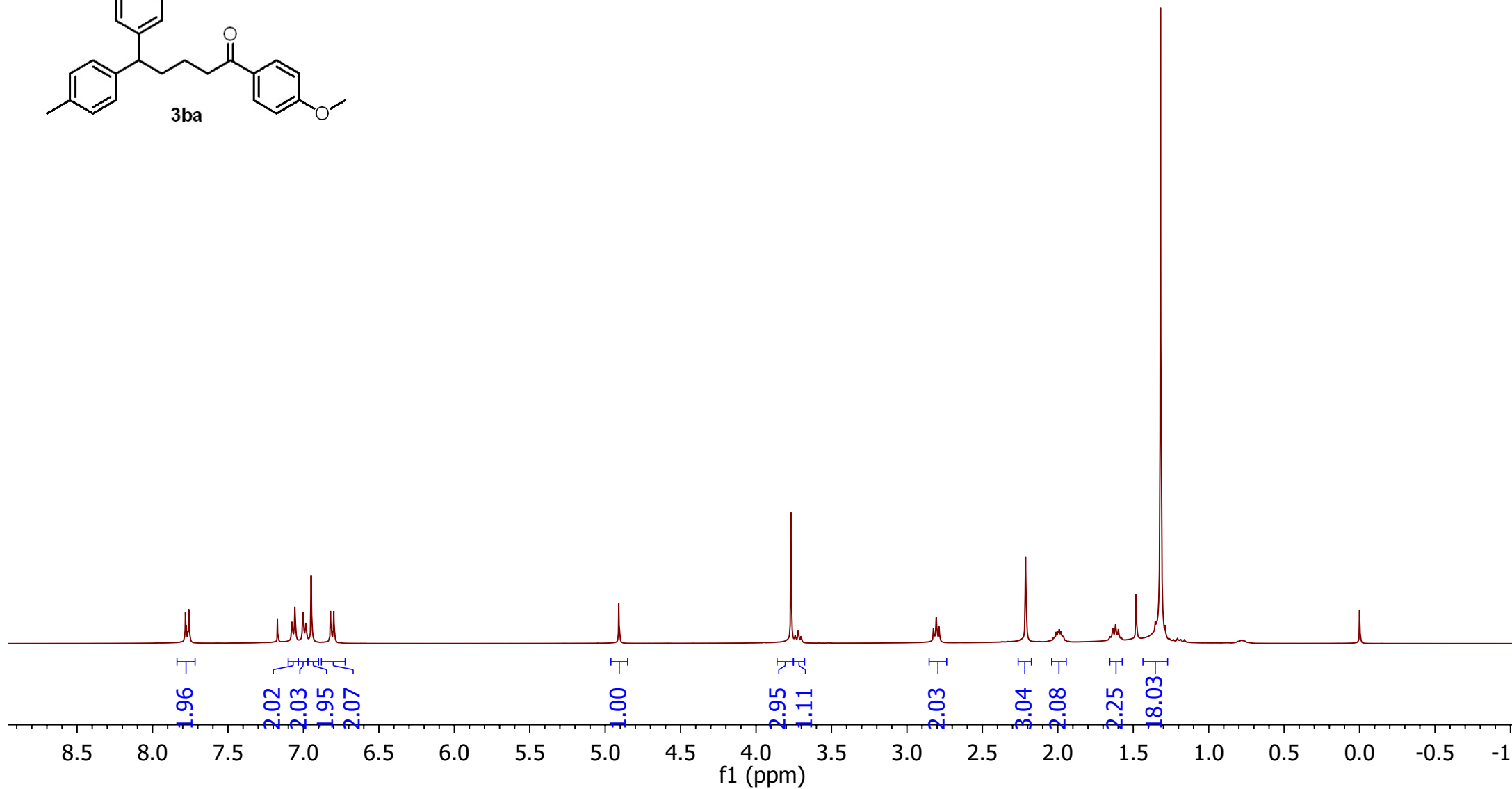
1.62

1.60

1.59

1.58

1.37



<sup>1</sup>H NMR Spectrum of **3ba**



**<sup>1</sup>H(CDCI<sub>3</sub>, 400 MHz)**

7.79  
7.77  
7.10  
7.08  
6.93  
6.83  
6.80  
6.75  
6.73

4.91

3.77  
3.73  
3.72  
3.69  
3.68

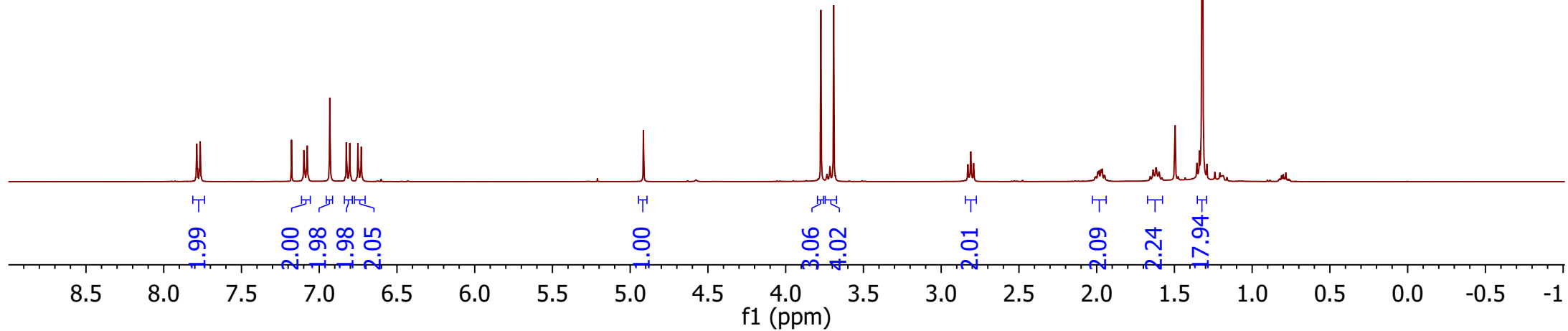
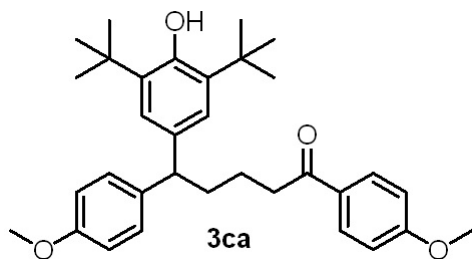
2.83  
2.81  
2.79

2.01  
2.00  
1.99  
1.98

1.97  
1.97  
1.96  
1.95

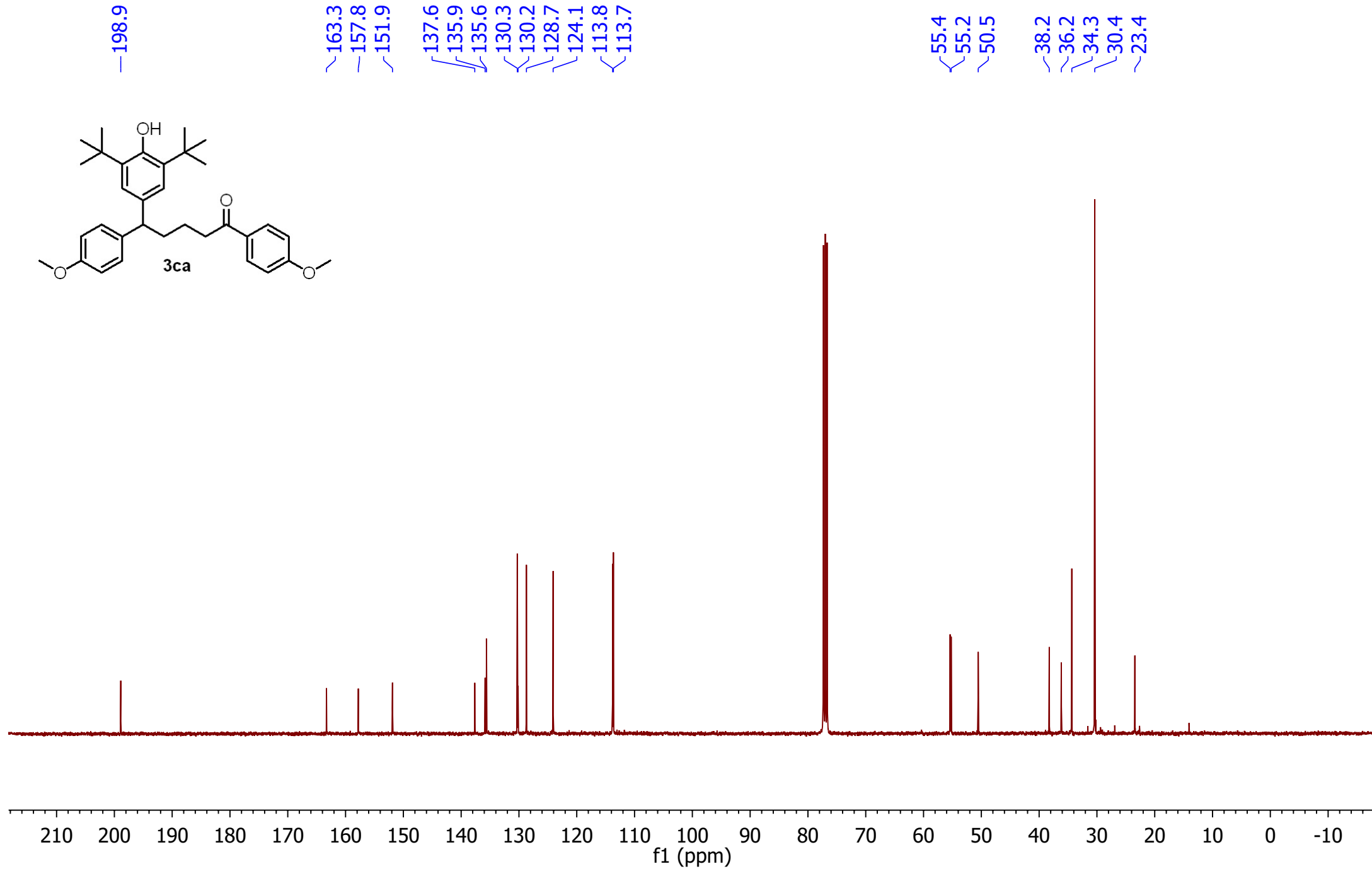
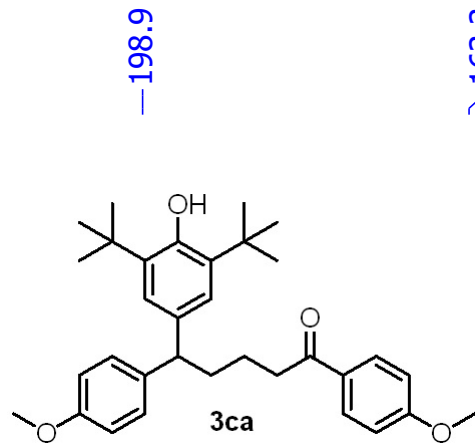
1.95  
1.66  
1.64  
1.64  
1.62  
1.62

1.60  
1.58  
1.32



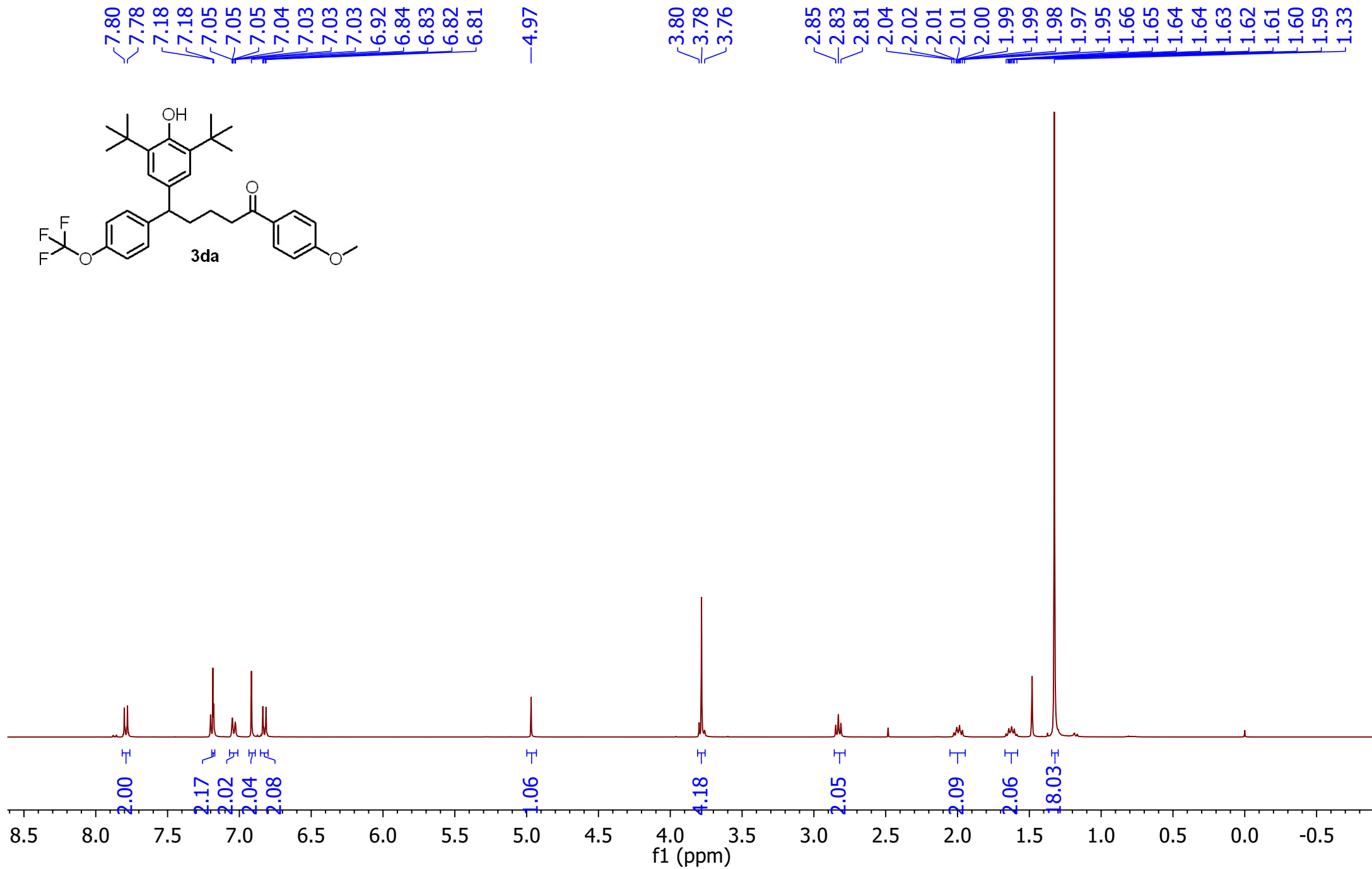
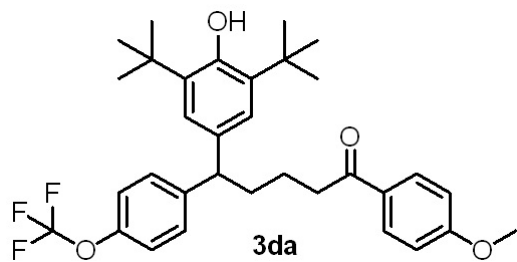
<sup>1</sup>H NMR Spectrum of **3ca**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



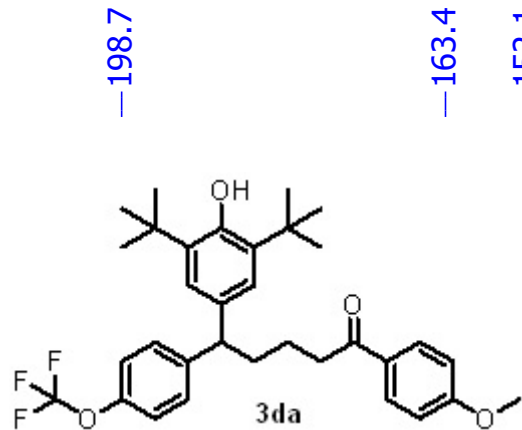
<sup>13</sup>C NMR Spectrum of **3ca**

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



<sup>1</sup>H NMR Spectrum of **3da**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



—198.7

—163.4

—152.1

—147.4

—144.2

—135.8

—134.8

—130.3

—130.1

—129.0

—124.1

—120.8

—113.7

—55.4

—50.8

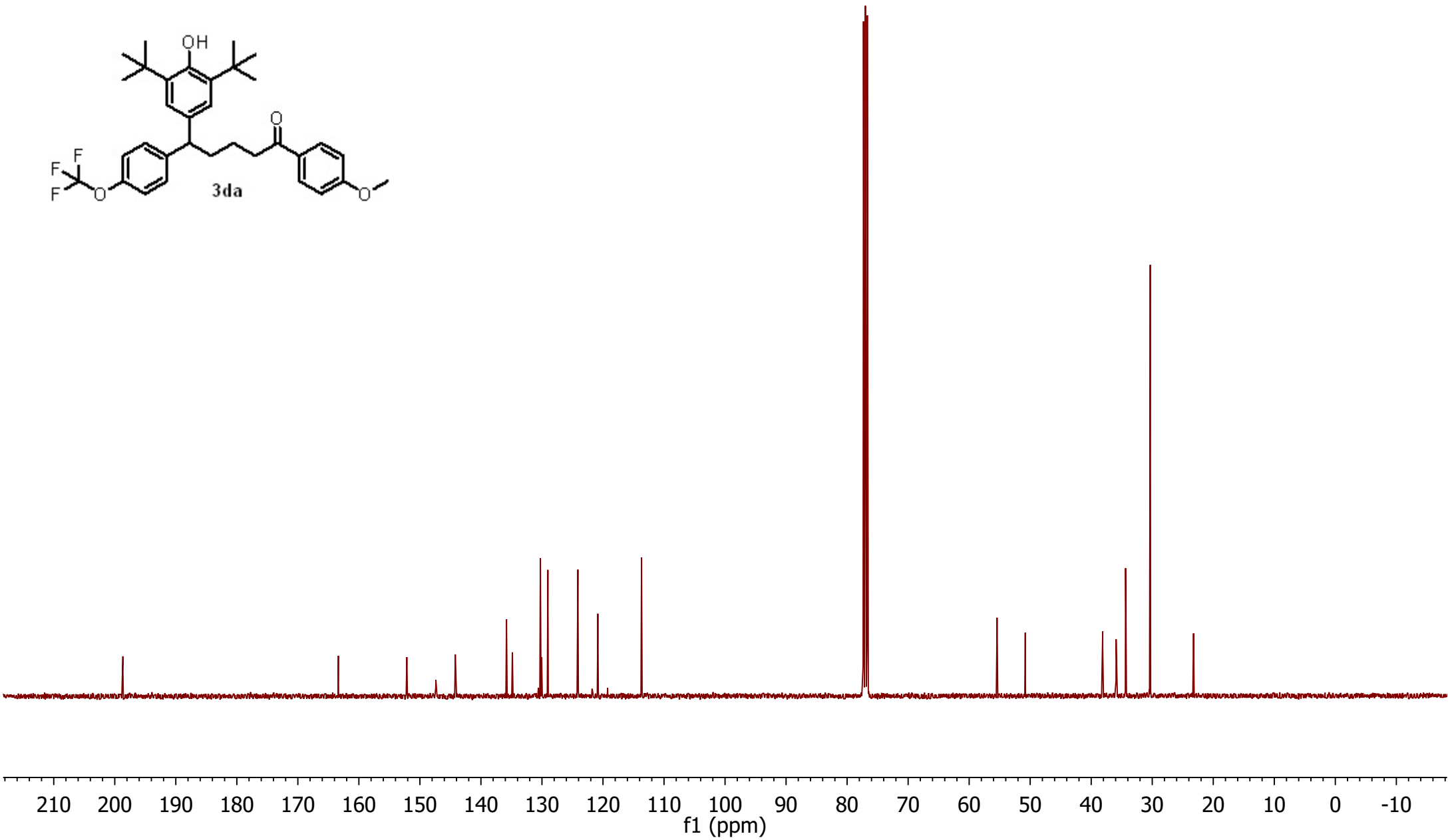
—38.1

—35.9

—34.4

—30.3

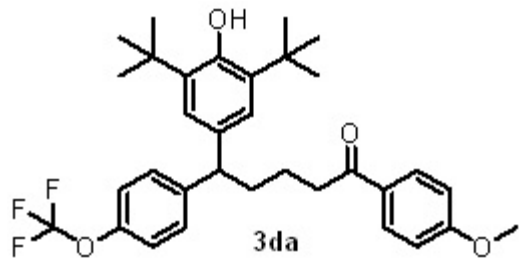
—23.2



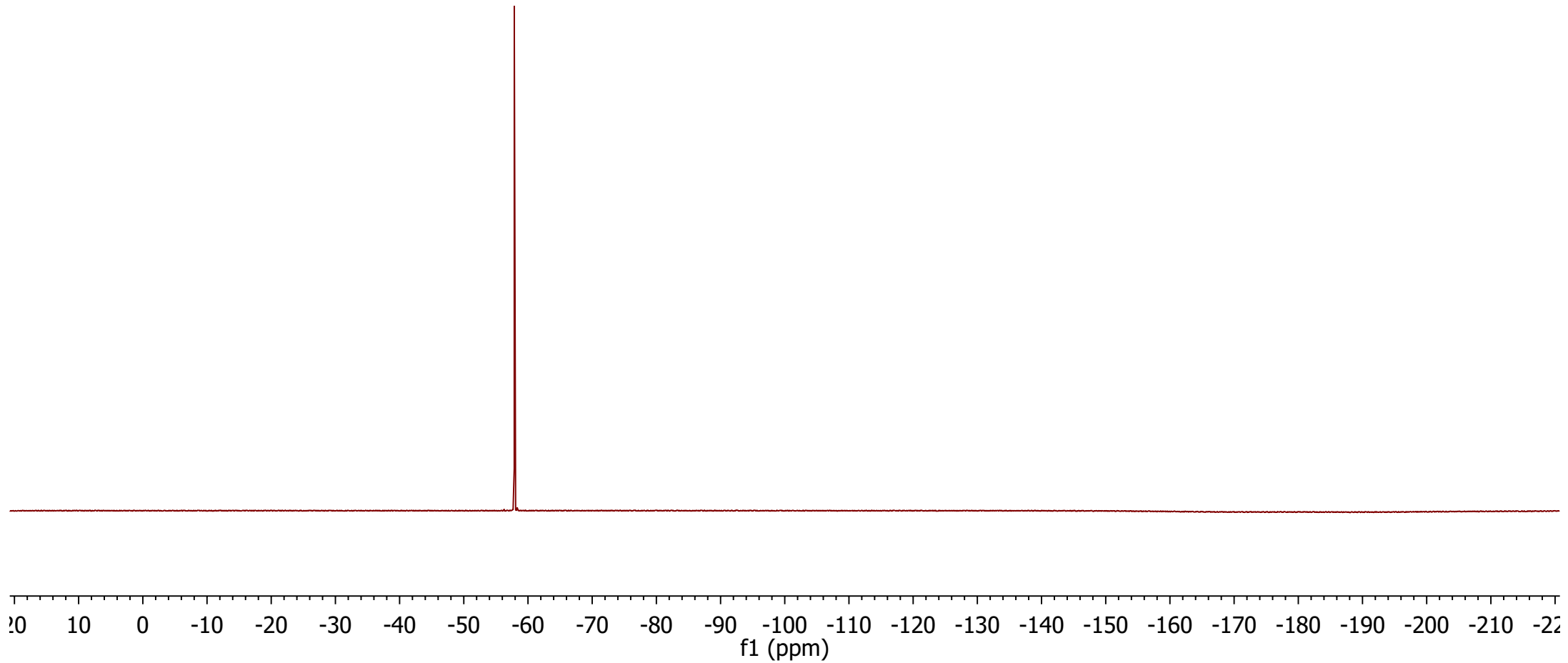
<sup>13</sup>C NMR Spectrum of **3da**



**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

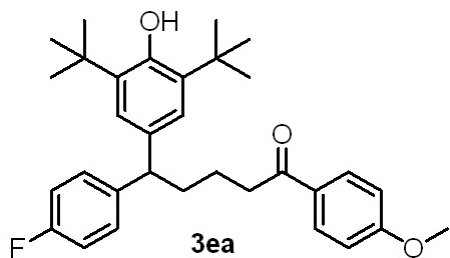


---57.86



<sup>19</sup>F NMR Spectrum of **3da**

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

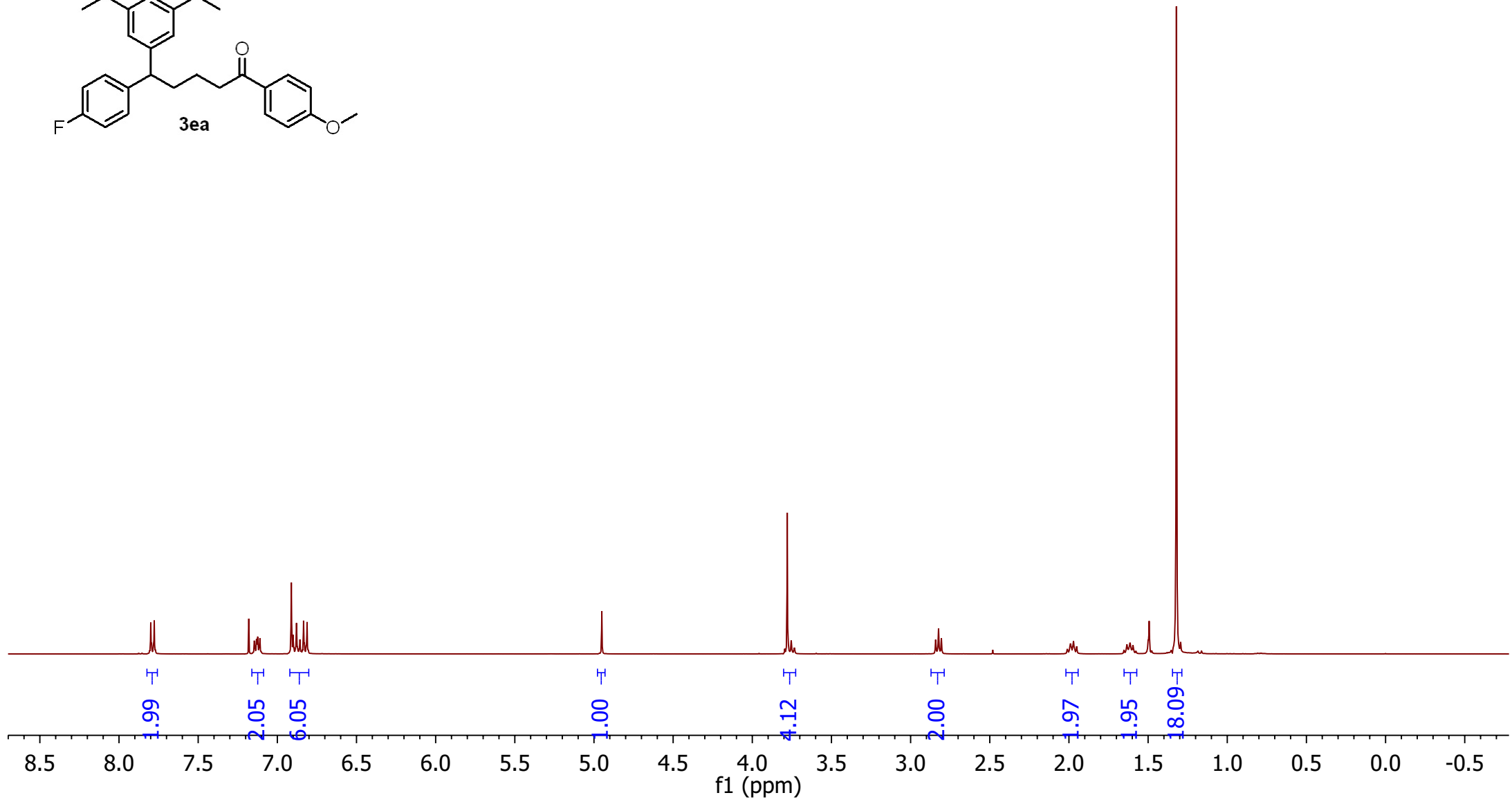


7.80  
7.78  
7.15  
7.13  
7.12  
7.11  
6.91  
6.90  
6.88  
6.86  
6.83  
6.81

4.95

3.78

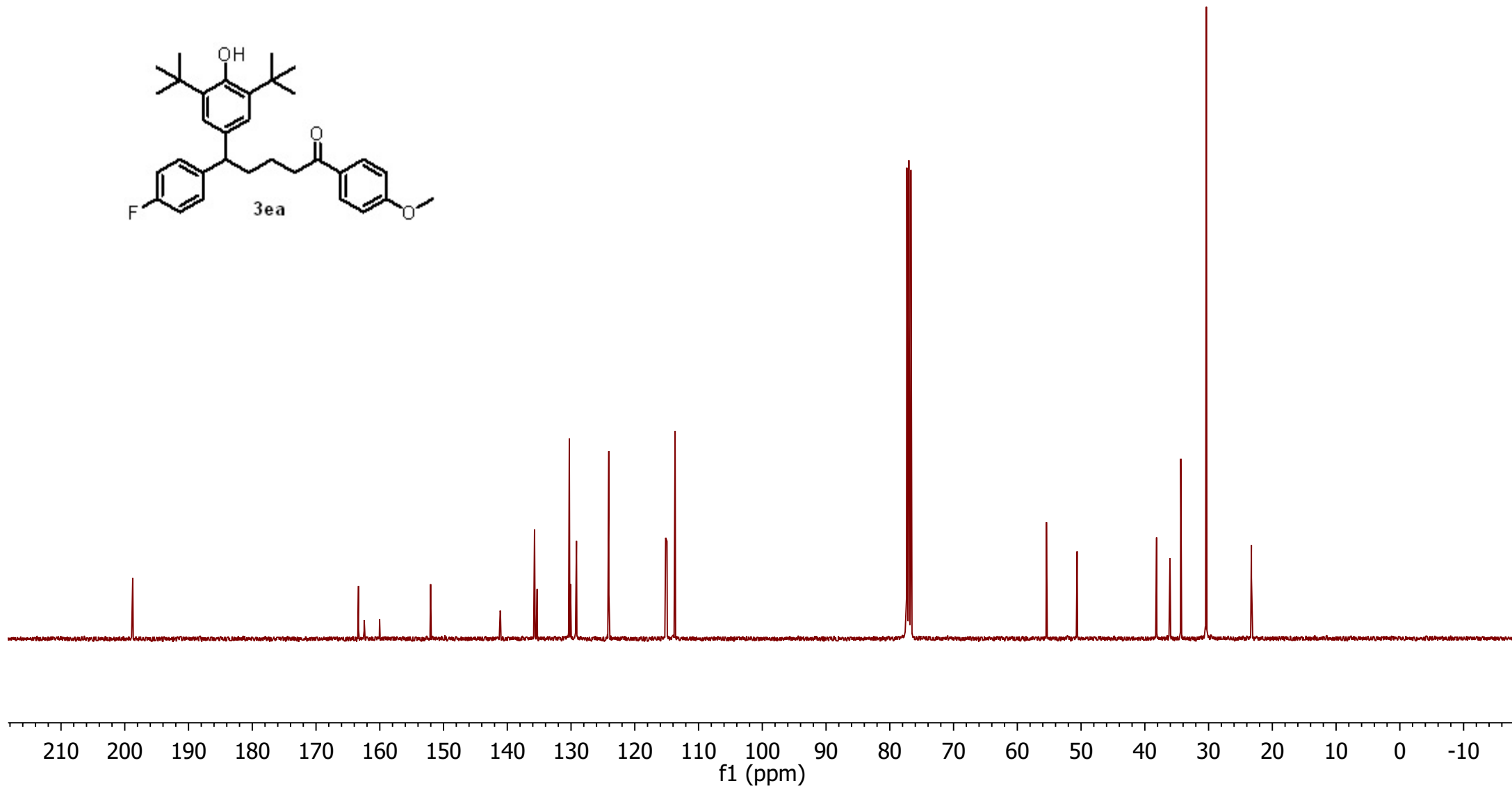
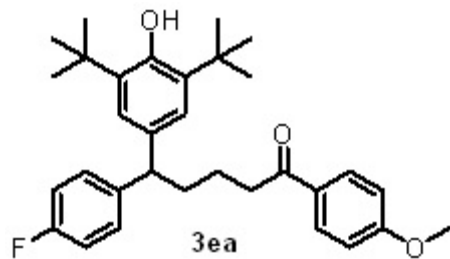
2.84  
2.82  
2.81  
2.01  
2.01  
1.99  
1.99  
1.98  
1.98  
1.97  
1.96  
1.95  
1.65  
1.64  
1.63  
1.63  
1.62  
1.61  
1.61  
1.60  
1.60  
1.58  
1.32



<sup>1</sup>H NMR Spectrum of **3ea**

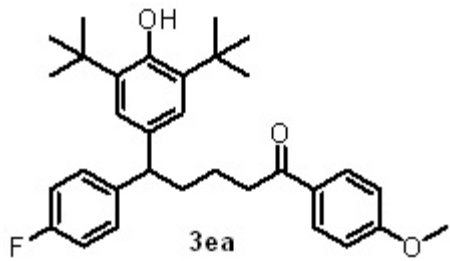
**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**

—198.7  
163.3  
162.4  
160.0  
152.0  
141.1  
141.1  
135.7  
135.3  
130.3  
130.1  
129.2  
129.1  
124.1  
115.2  
115.0  
113.7  
—55.4  
—50.6  
38.2  
36.1  
34.4  
30.3  
23.3

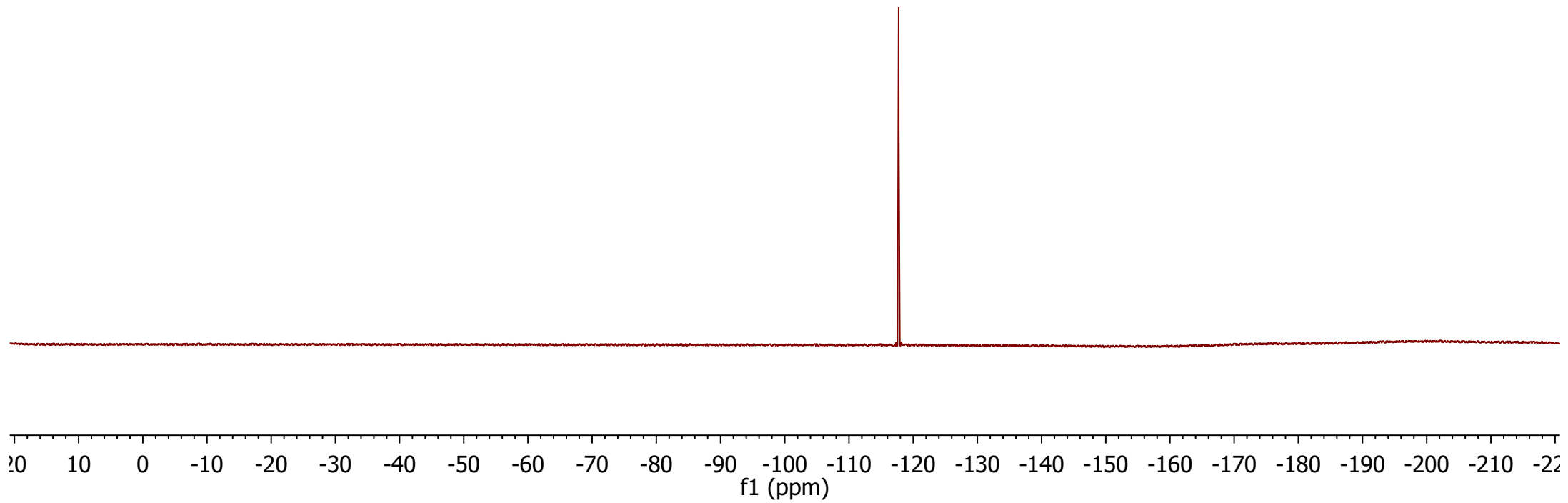


<sup>13</sup>C NMR Spectrum of 3ea

19F (CDCl3, 376 MHz)

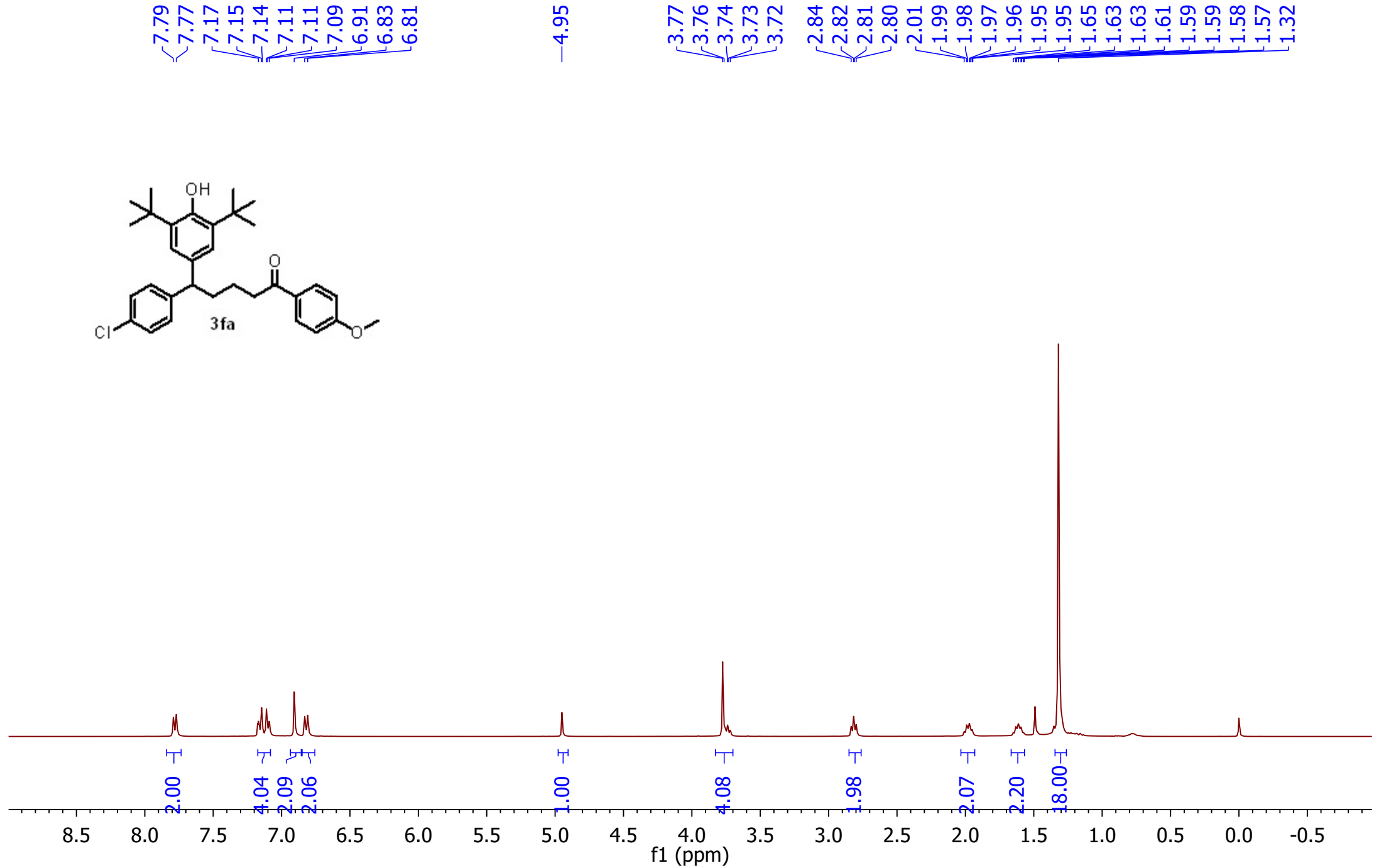
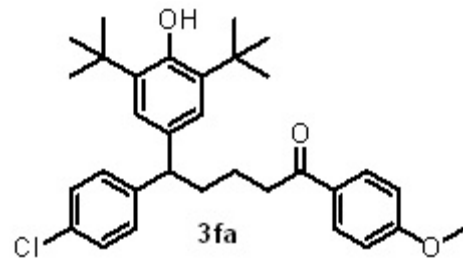


--117.73



19F NMR Spectrum of 3ea

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



<sup>1</sup>H NMR Spectrum of **3fa**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**

—197.7

—162.3

151.1

143.0

134.8

133.9

130.5

129.2

129.0

128.2

127.4

123.0

—112.7

—54.4

—49.8

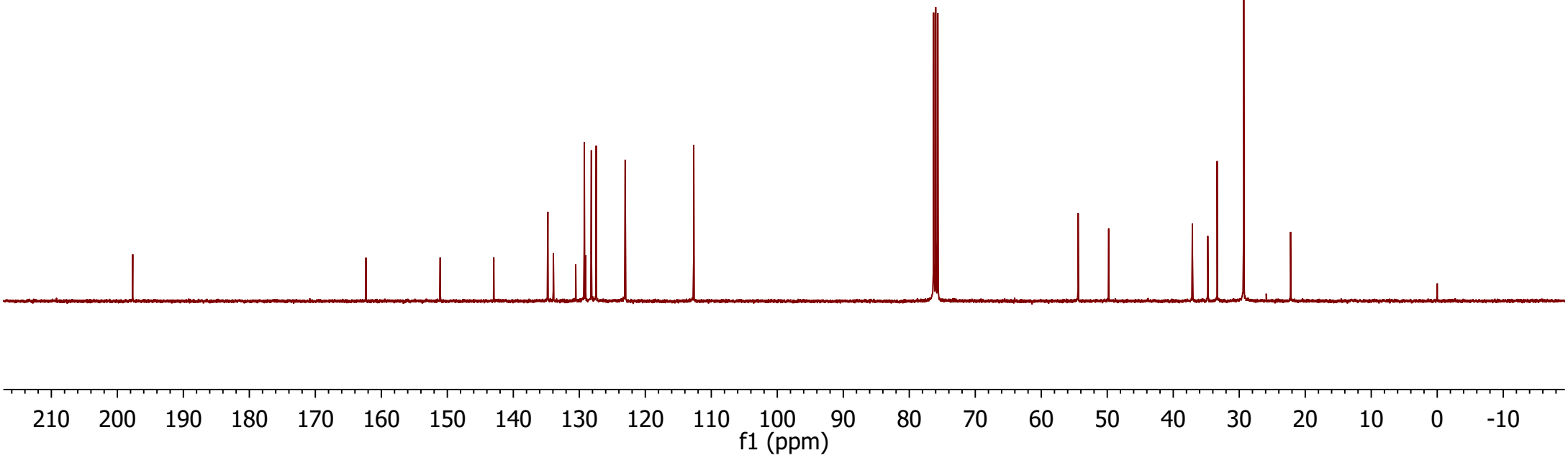
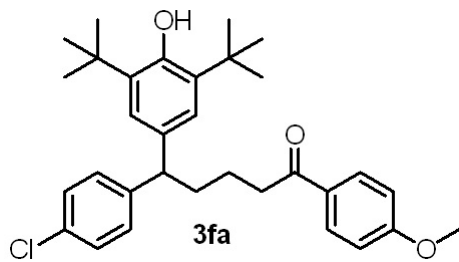
~37.1

~34.8

~33.3

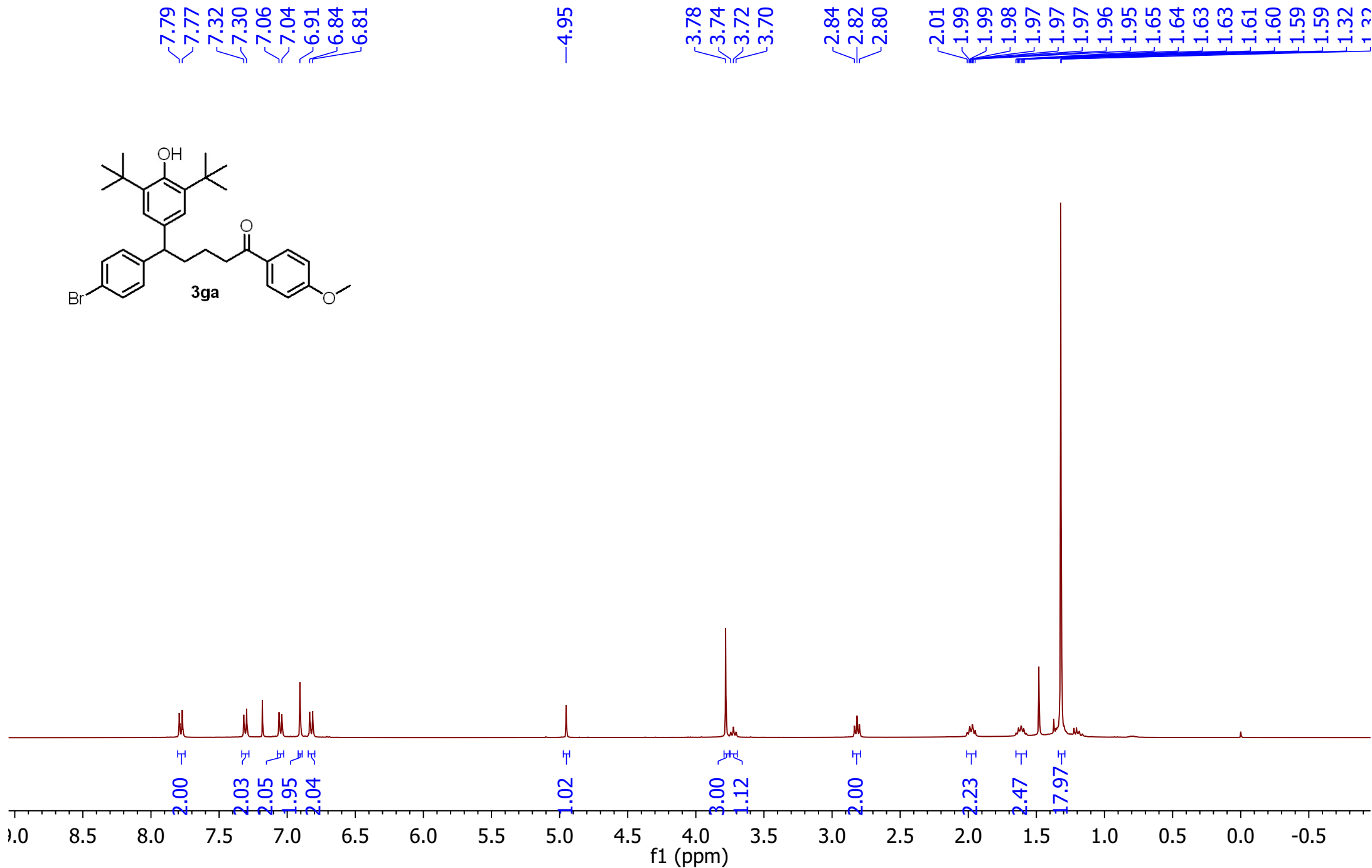
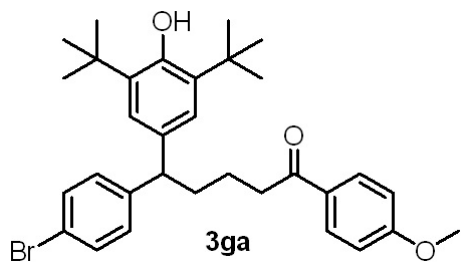
~29.3

~22.2



<sup>13</sup>C NMR Spectrum of **3fa**

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



<sup>1</sup>H NMR Spectrum of **3ga**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**

—198.7

—163.3

—152.1

—144.5

—135.8

—134.8

—131.4

—130.3

—130.1

—129.6

—124.0

—119.6

—113.7

—55.4

—50.9

—38.1

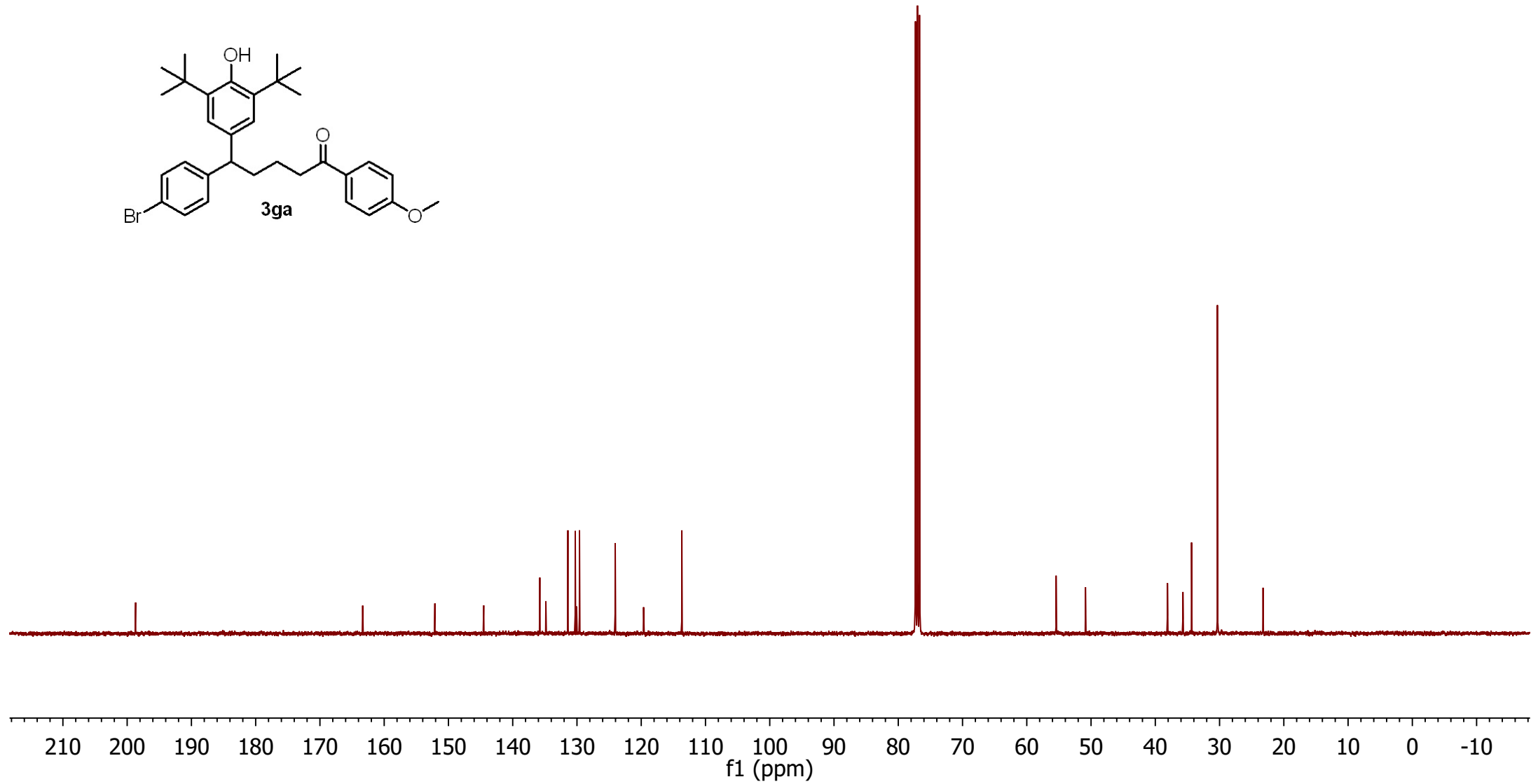
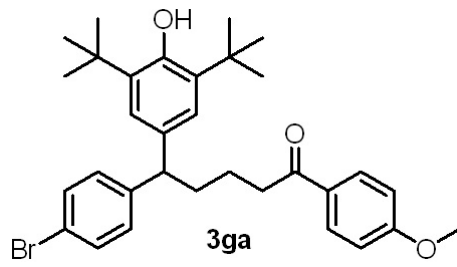
—35.7

—34.4

—30.3

—30.3

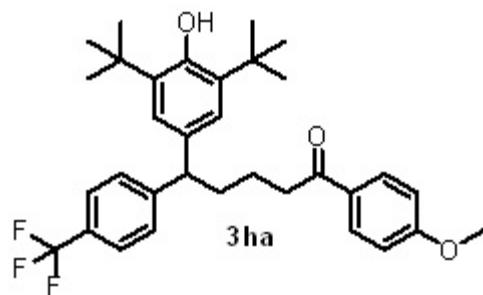
—23.2



<sup>13</sup>C NMR Spectrum of **3ga**



**<sup>1</sup>H(CDCI<sub>3</sub>, 400 MHz)**

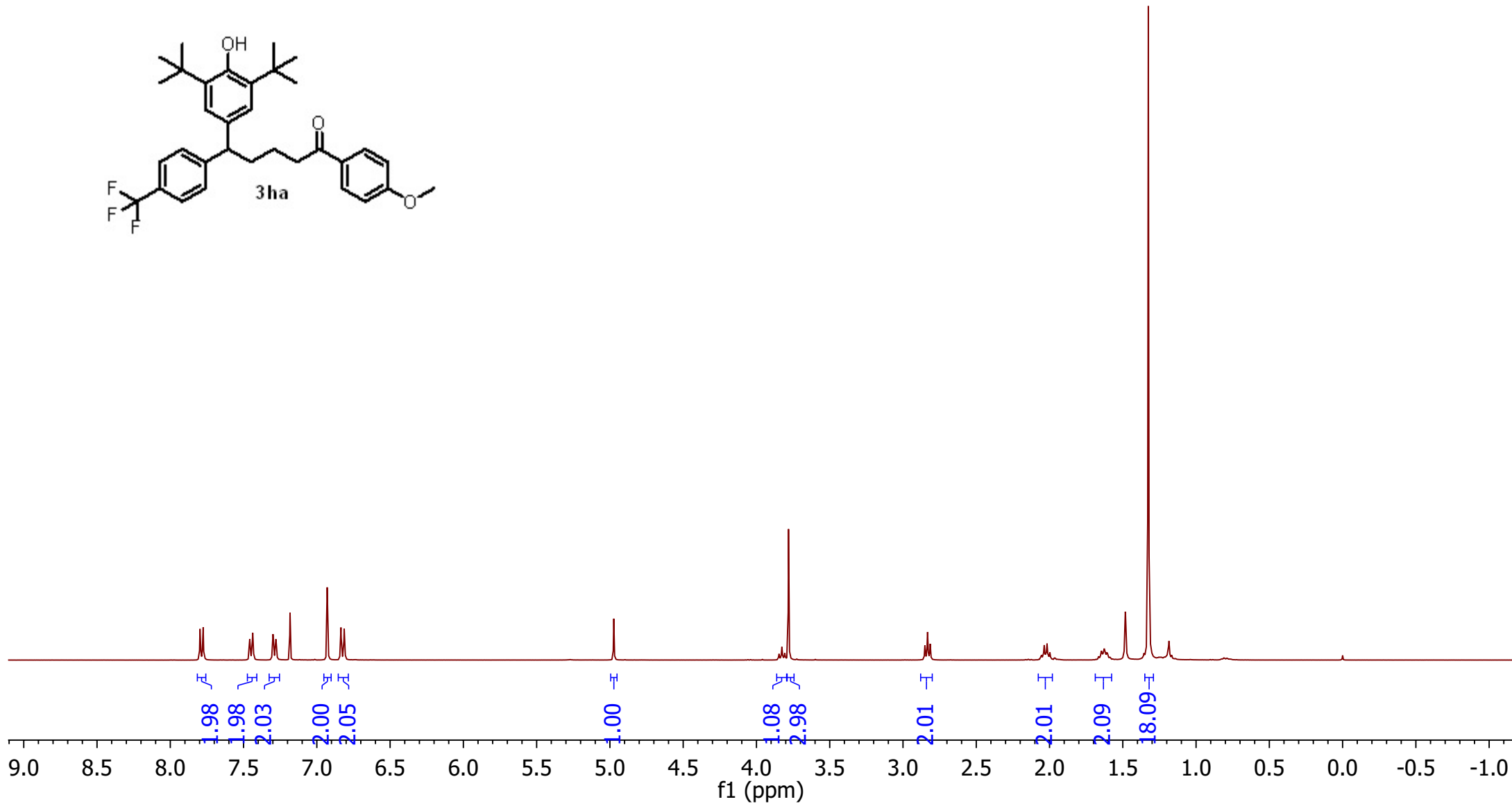


7.80  
7.78  
7.46  
7.44  
7.30  
7.28  
6.93  
6.84  
6.81

4.97

3.85  
3.83  
3.81  
3.78

2.85  
2.83  
2.81  
2.06  
2.05  
2.04  
2.03  
2.02  
2.01  
2.00  
1.67  
1.66  
1.65  
1.65  
1.63  
1.63  
1.61  
1.61  
1.59  
1.59  
1.33



<sup>1</sup>H NMR Spectrum of **3ha**

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**

—198.6

—163.4

152.3

149.6

149.6

136.2

135.9

134.4

130.3

130.0

129.7

128.7

128.4

128.1

128.0

126.6

125.7

125.4

125.4

125.3

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123.6

123.0

113.7

113.0

112.6

55.4

51.4

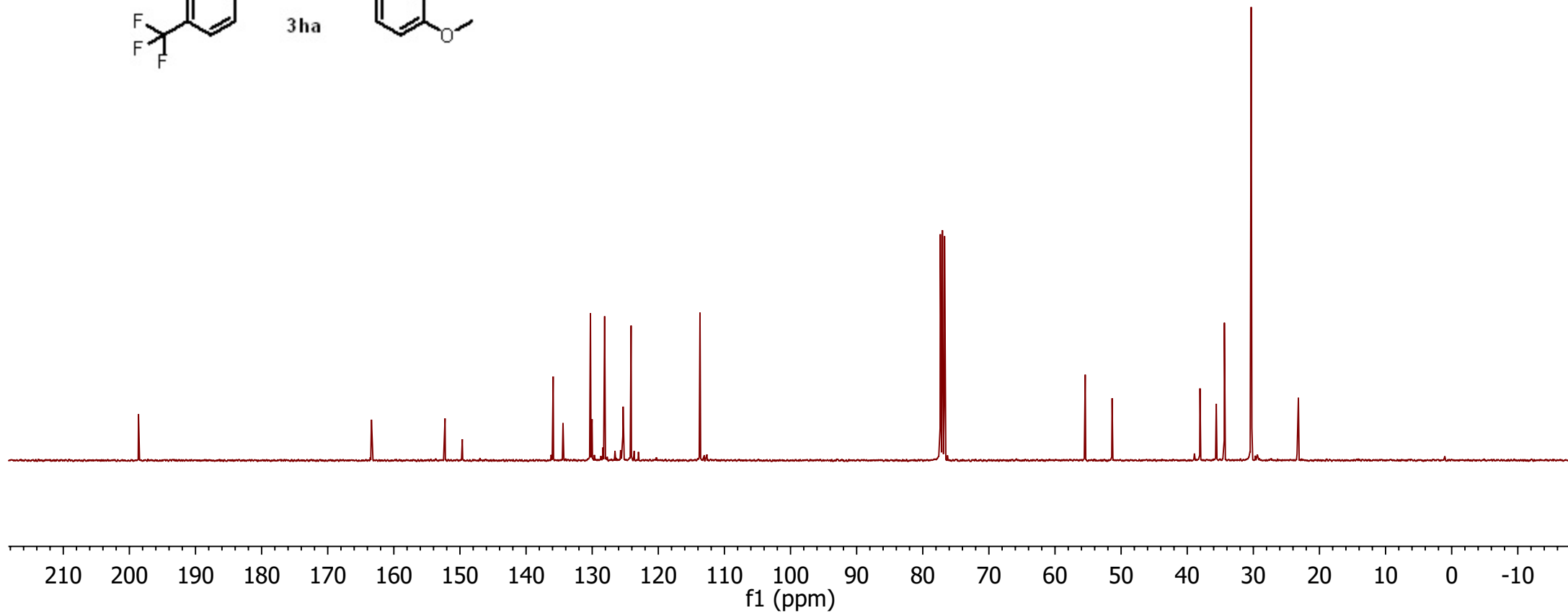
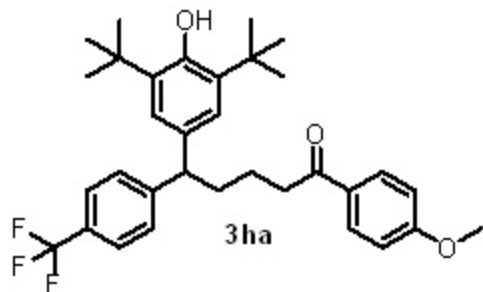
38.1

35.6

34.4

30.3

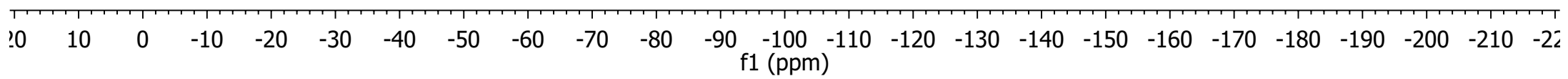
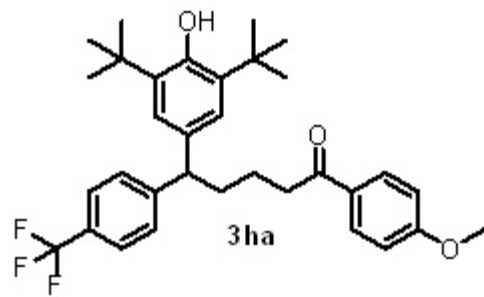
23.2



<sup>13</sup>C NMR Spectrum of **3ha**

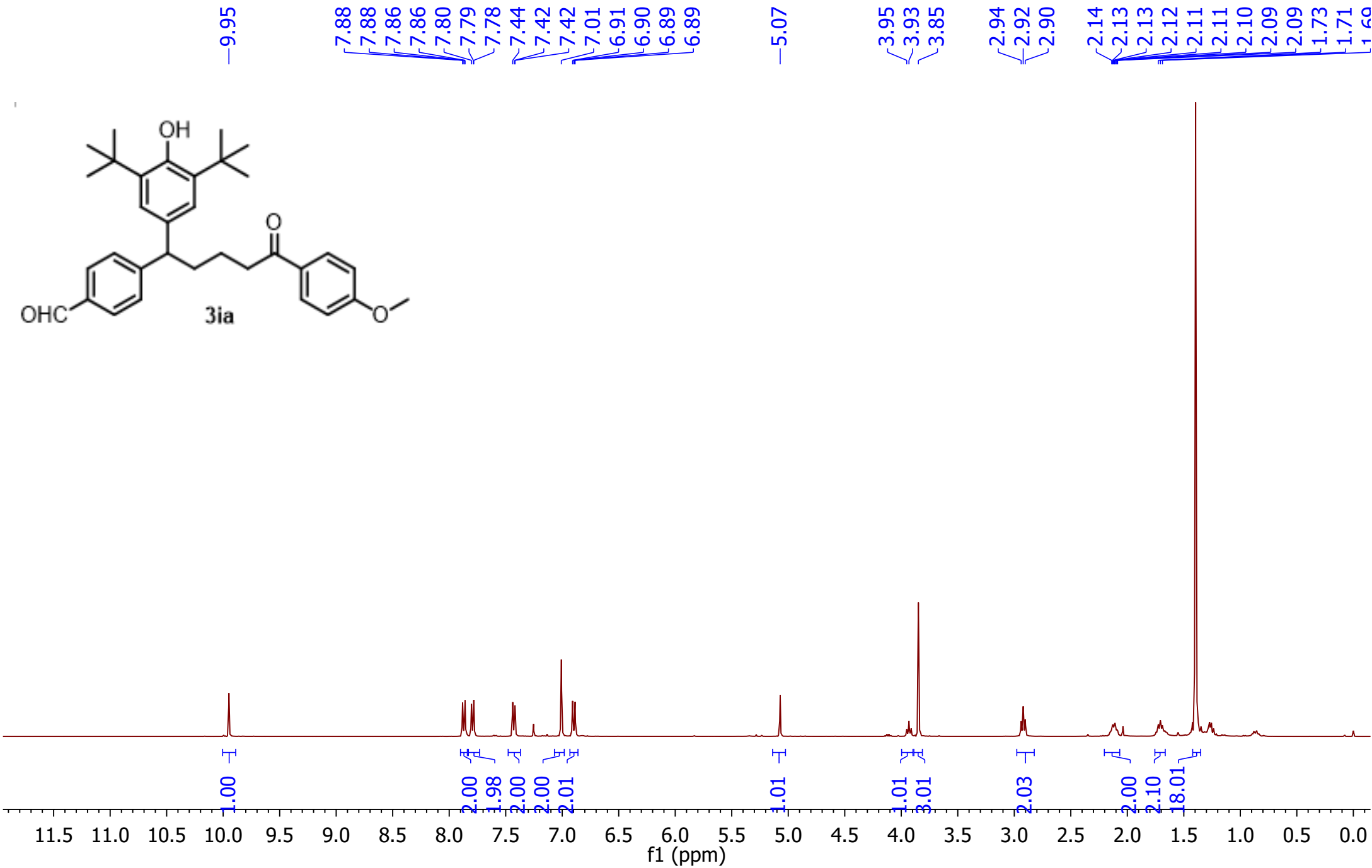
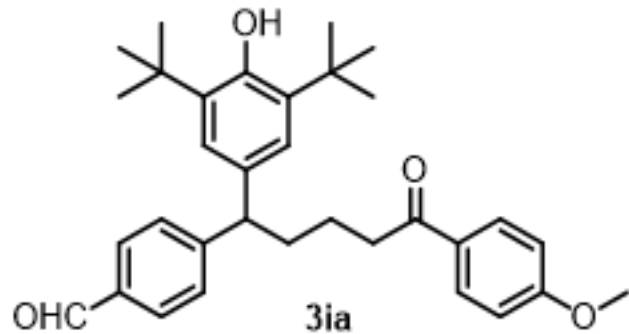
**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

---62.33



<sup>19</sup>F NMR Spectrum of **3ha**

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



<sup>1</sup>H NMR Spectrum of **3ia**

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**

—198.6

—192.0

—163.4

—152.9

—152.3

—135.9

—134.6

—134.3

—130.3

—130.1

—130.0

—128.5

—124.2

—113.7

—55.5

—51.7

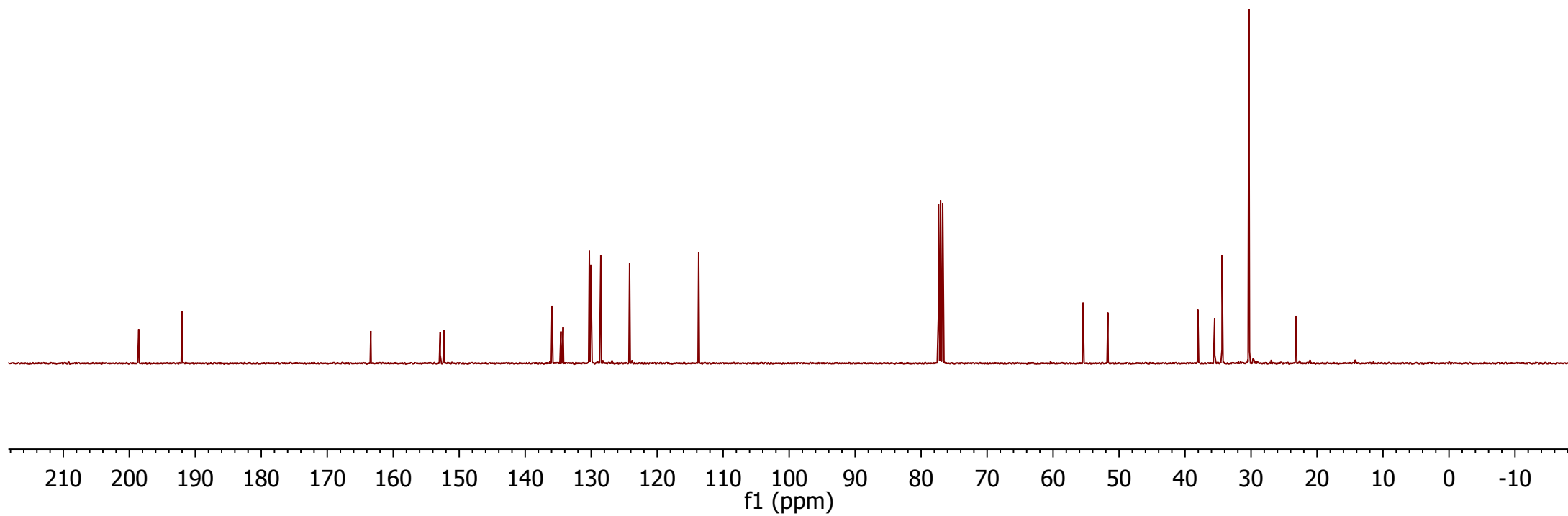
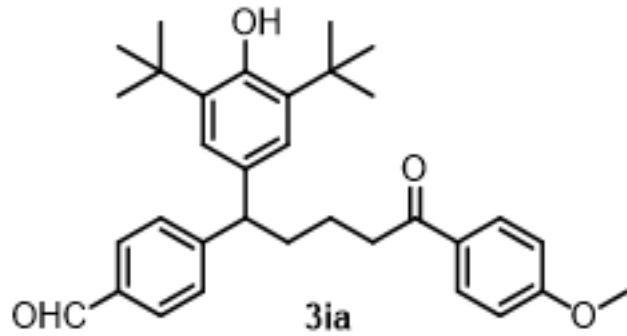
—38.1

—35.5

—34.4

—30.3

—23.2



<sup>13</sup>C NMR Spectrum of **3ia**

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

8.14  
8.13  
8.12  
8.11  
7.89  
7.88  
7.87  
7.86  
7.42  
7.42  
7.41  
7.40  
6.99  
6.91  
6.90  
6.89  
6.88

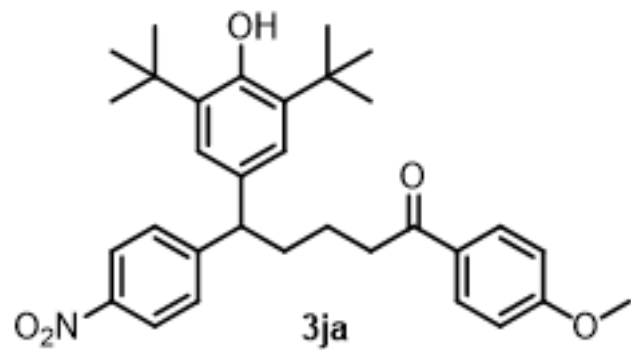
-5.10

3.98  
3.96  
3.94  
3.85  
3.80

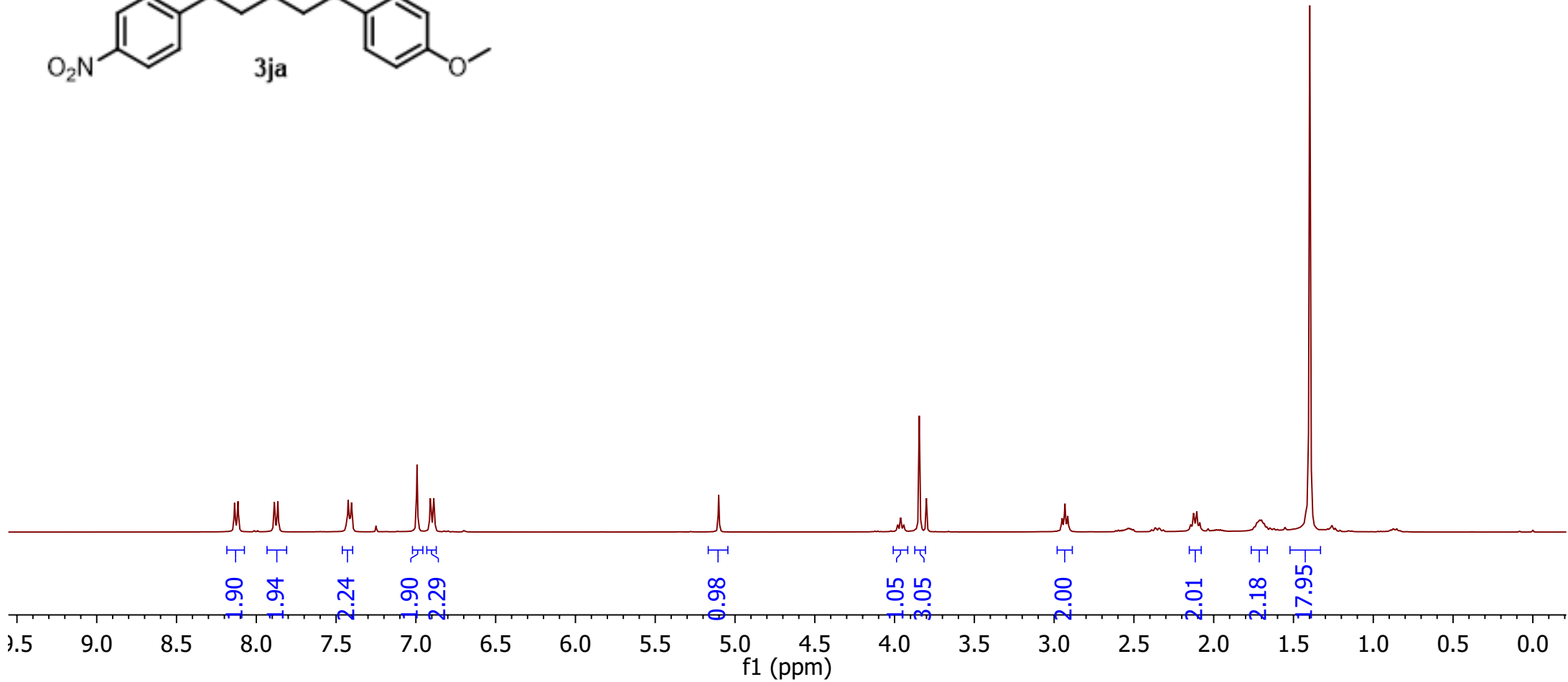
2.95  
2.93  
2.91

2.15  
2.13  
2.11  
2.09

1.75  
1.74  
1.73  
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1.71  
1.71  
1.70  
1.69  
1.68  
1.67  
1.65  
1.40

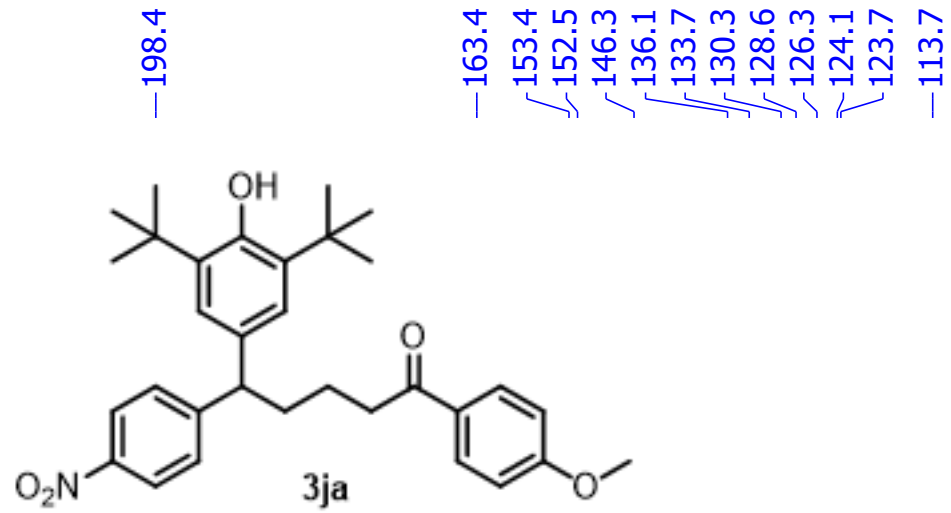


**3ja**



<sup>1</sup>H NMR Spectrum of 3ja

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



—198.4

—163.4

—153.4

—152.5

—146.3

—136.1

—133.7

—130.3

—128.6

—126.3

—124.1

—123.7

—113.7

—55.5

—51.4

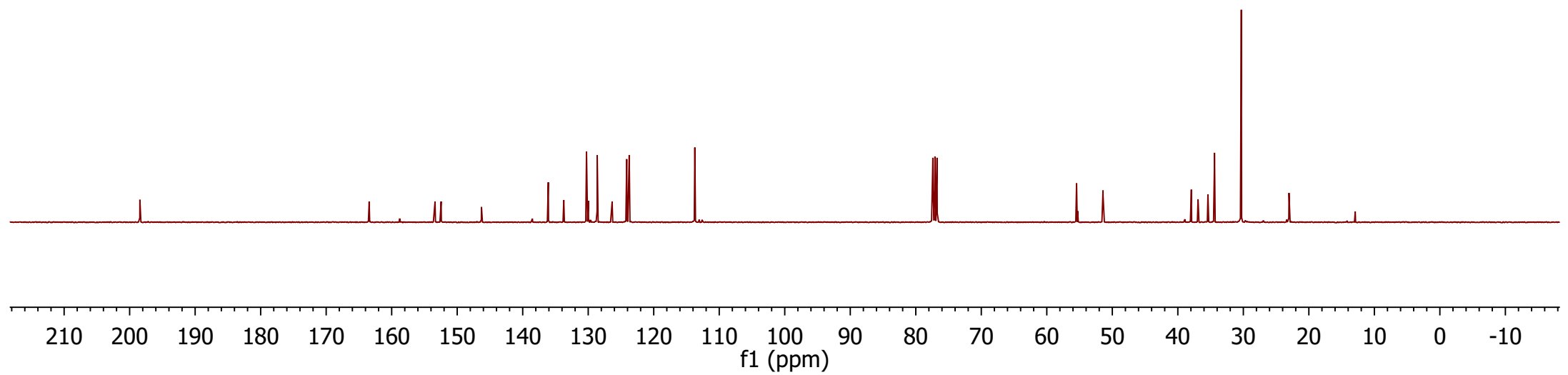
—37.9

—35.4

—34.4

—30.3

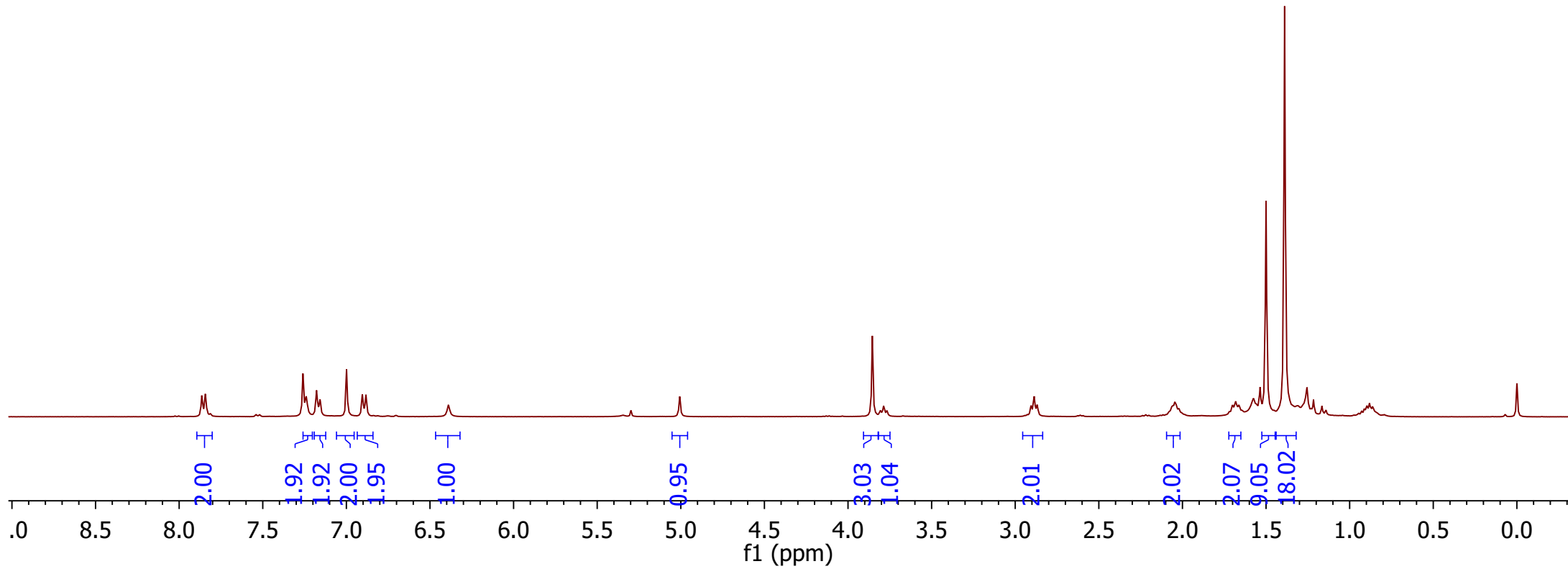
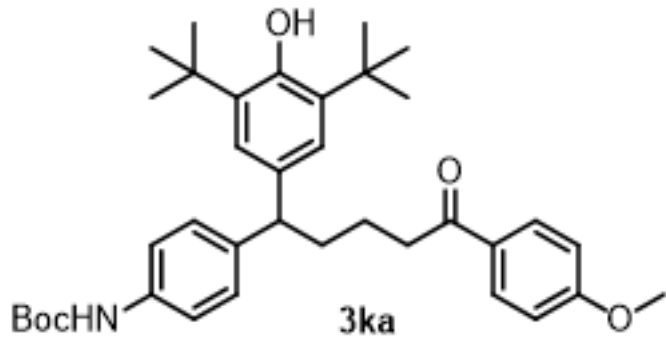
—23.0



<sup>13</sup>C NMR Spectrum of **3ja**

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

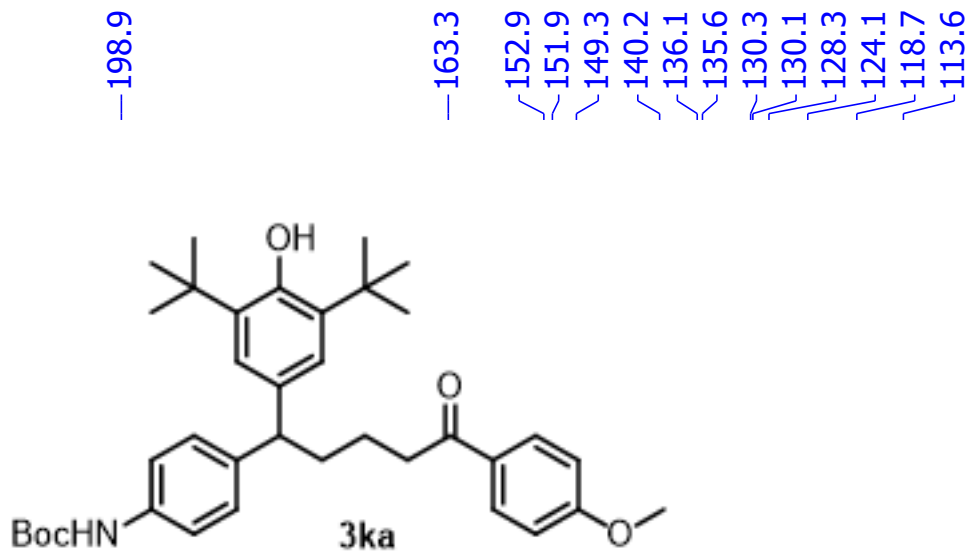
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7.26  
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7.18  
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3.85  
3.81  
3.79  
3.77  
2.91  
2.89  
2.87  
2.07  
2.06  
2.05  
2.04  
2.02  
1.72  
1.70  
1.68  
1.66  
1.64  
1.50  
1.39



<sup>1</sup>H NMR Spectrum of **3ka**



**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



—198.9

—163.3

—152.9

—151.9

—149.3

—140.2

—136.1

—135.6

—130.3

—130.1

—128.3

—124.1

—118.7

—113.6

—55.4

—50.7

—38.2

—35.9

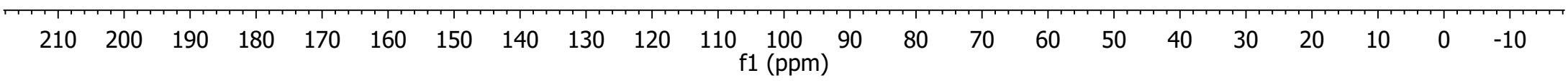
—34.3

—30.3

—28.4

—28.3

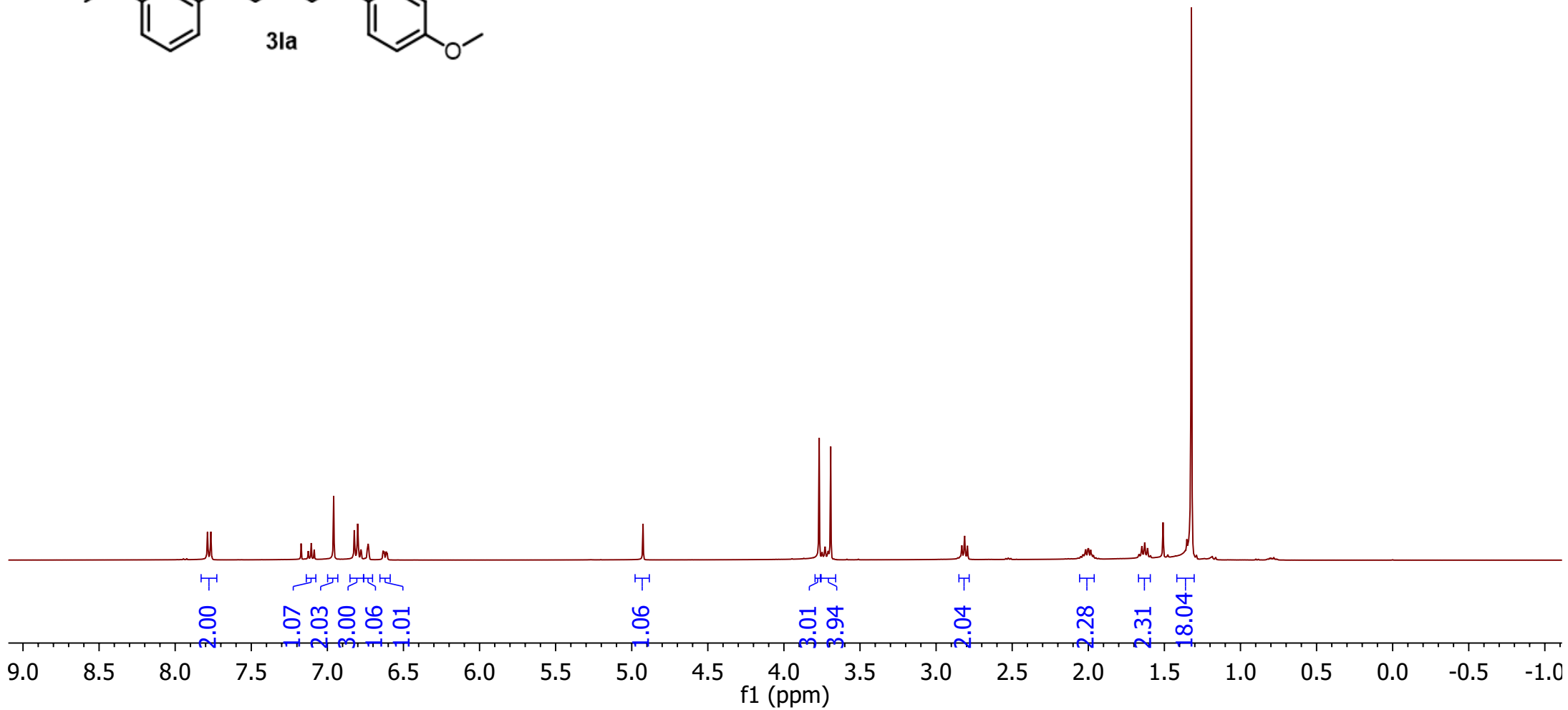
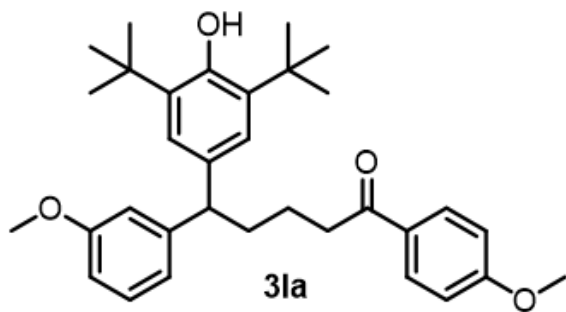
—23.4



<sup>13</sup>C NMR Spectrum of **3ka**

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

7.79  
7.78  
7.77  
7.77  
7.13  
7.11  
7.09  
6.96  
6.83  
6.82  
6.82  
6.81  
6.80  
6.80  
6.78  
6.78  
6.78  
6.74  
6.73  
6.73  
6.63  
6.63  
6.61  
6.61  
4.93  
3.77  
3.75  
3.73  
3.71  
3.69  
2.83  
2.81  
2.79  
2.05  
2.04  
2.03  
2.02  
2.02  
2.00  
2.00  
1.98  
1.98  
1.97  
1.96  
1.95  
1.67  
1.65  
1.63  
1.61  
1.59  
1.32



<sup>1</sup>H NMR Spectrum of **3la**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**

—198.8

163.3

159.6

152.0

147.2

135.7

135.3

130.3

130.2

129.2

124.2

120.3

113.9

113.7

111.0

55.4

55.1

51.5

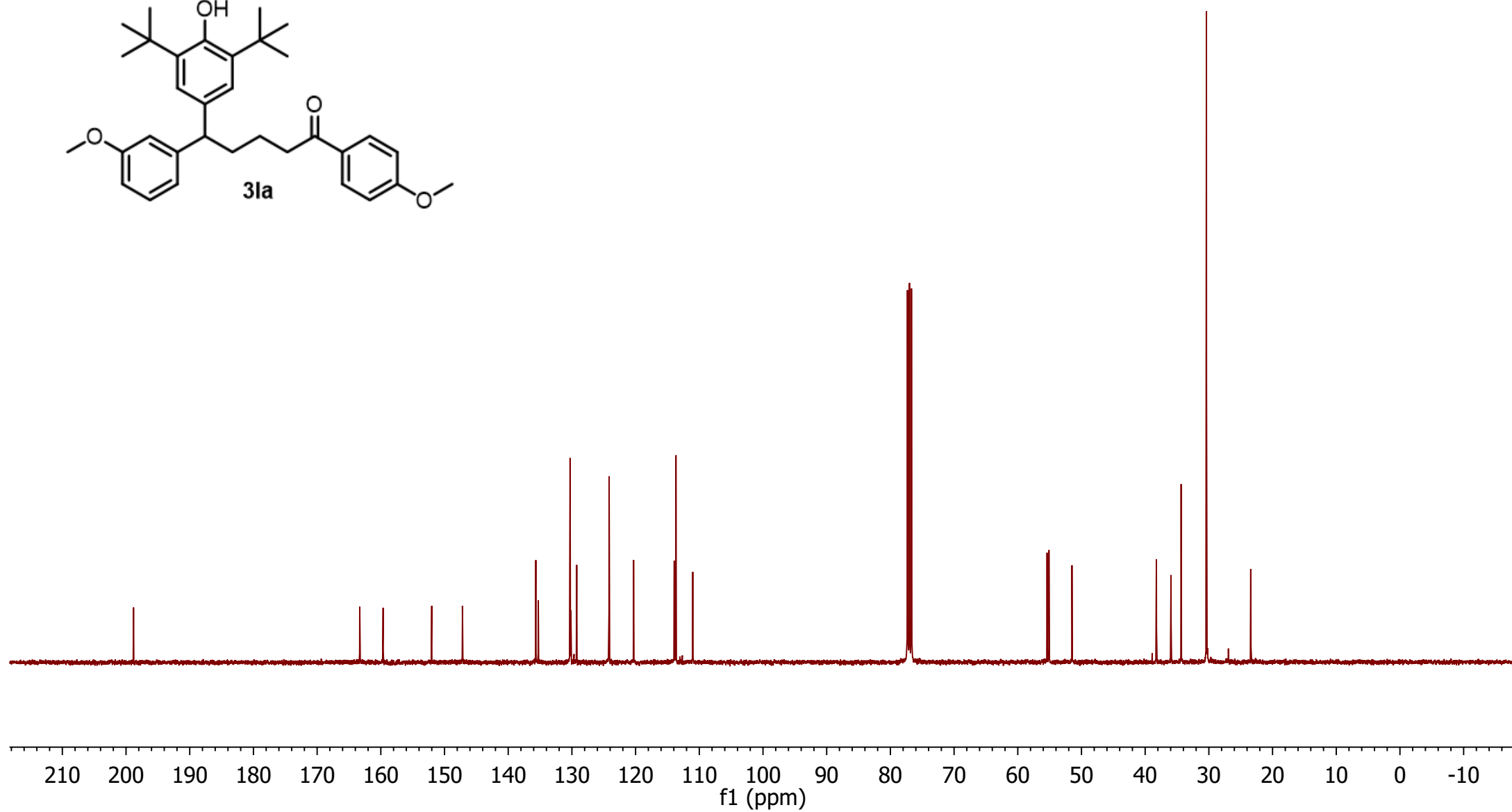
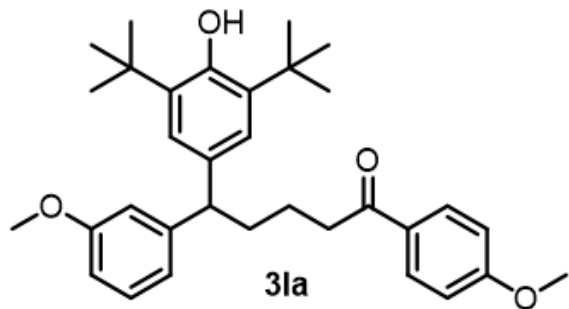
38.2

35.9

34.4

30.4

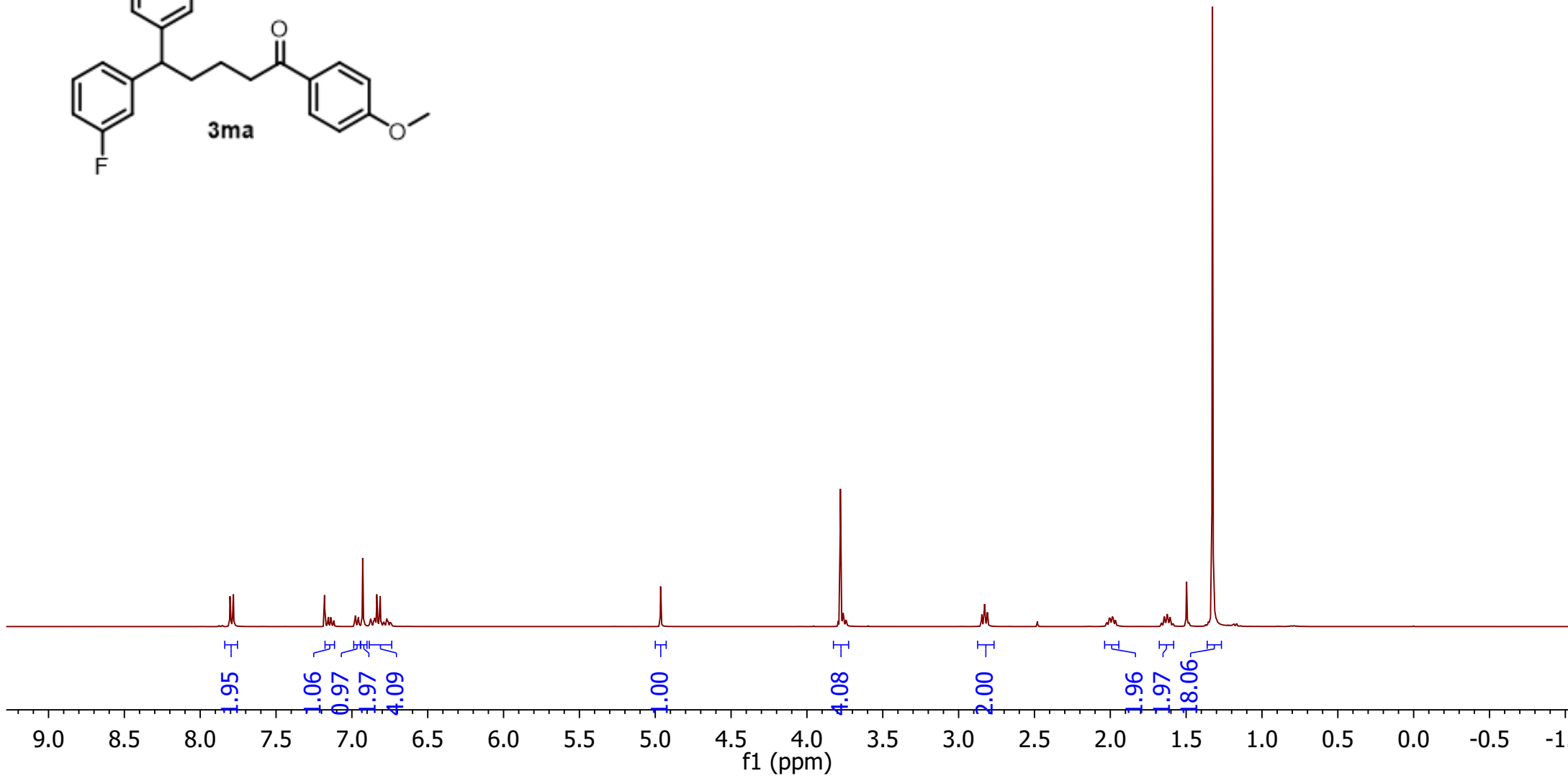
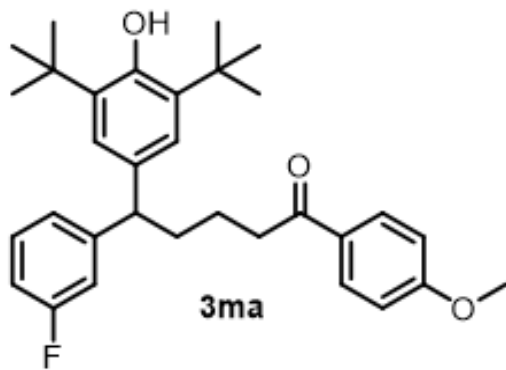
23.4



<sup>13</sup>C NMR Spectrum of **3la**

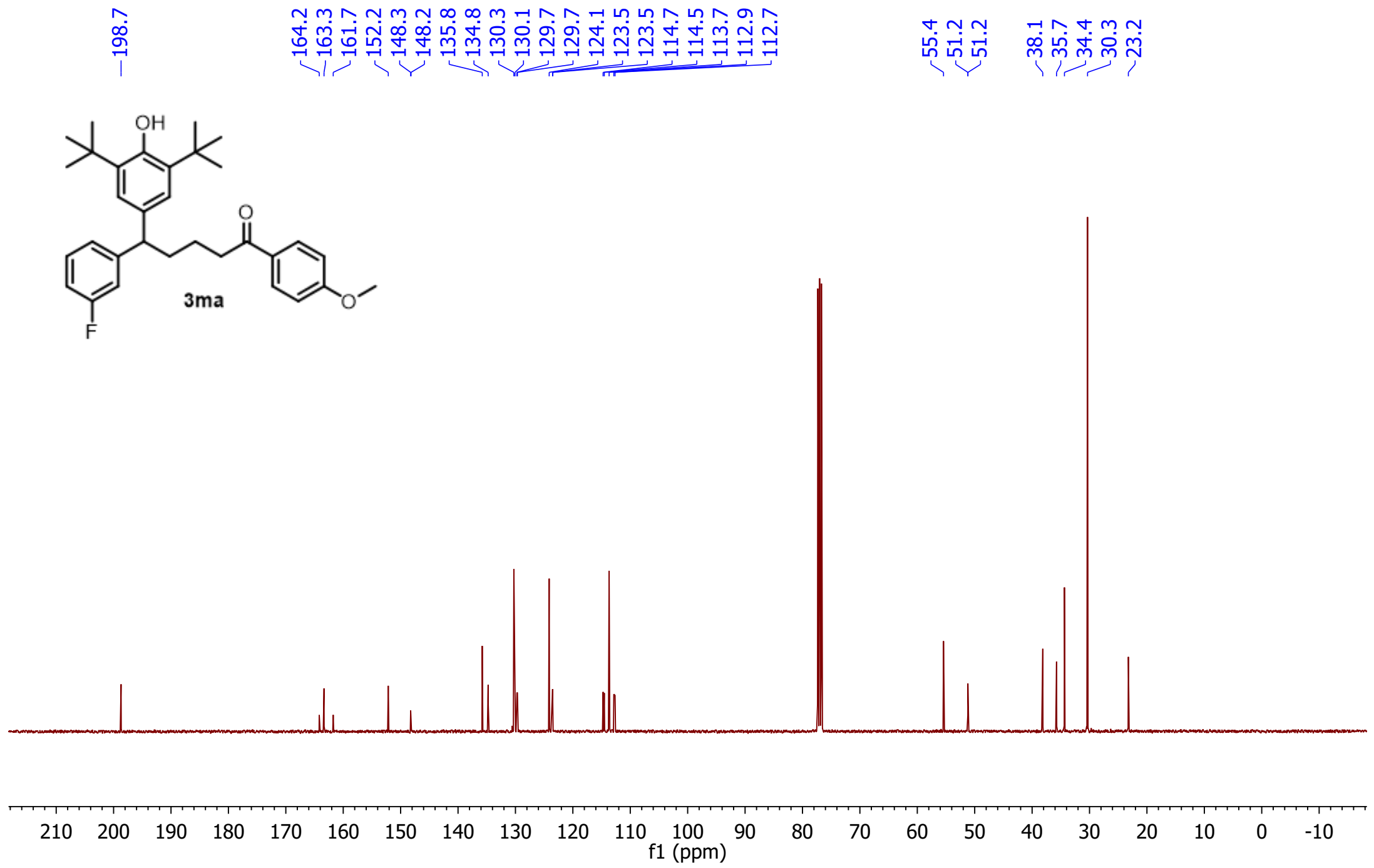
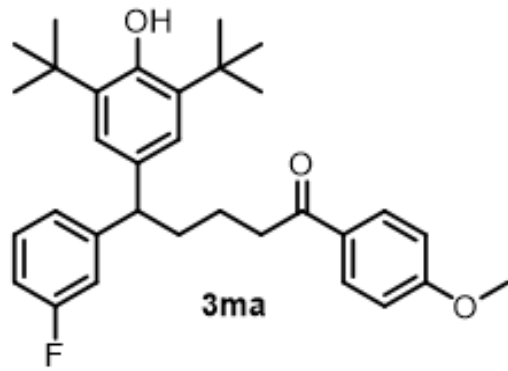
**<sup>1</sup>H(CDCl<sub>3</sub>, 400 MHz)**

7.80  
7.78  
7.18  
7.16  
7.15  
7.14  
7.13  
7.12  
6.98  
6.98  
6.97  
6.96  
6.96  
6.95  
6.93  
6.88  
6.88  
6.87  
6.86  
6.85  
6.85  
6.84  
6.84  
6.83  
6.82  
6.81  
6.81  
6.79  
6.79  
6.79  
6.77  
6.77  
6.76  
6.76  
6.75  
6.75  
4.96  
3.78  
2.85  
2.83  
2.81  
2.01  
2.00  
2.00  
1.99  
1.98  
1.98  
1.97  
1.96  
1.64  
1.63  
1.62  
1.61  
1.33



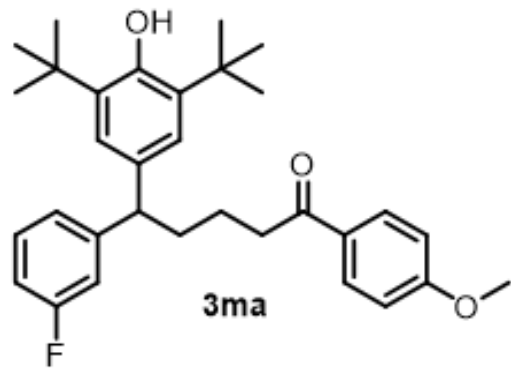
<sup>1</sup>H NMR Spectrum of 3ma

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



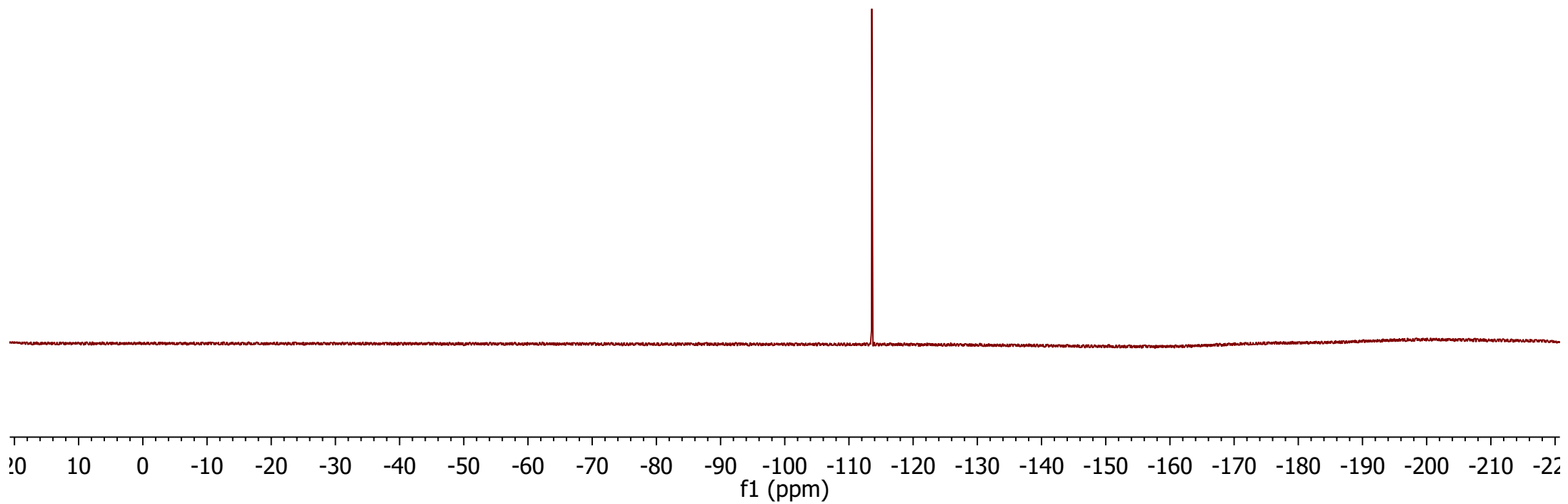
<sup>13</sup>C NMR Spectrum of **3ma**

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**



**3ma**

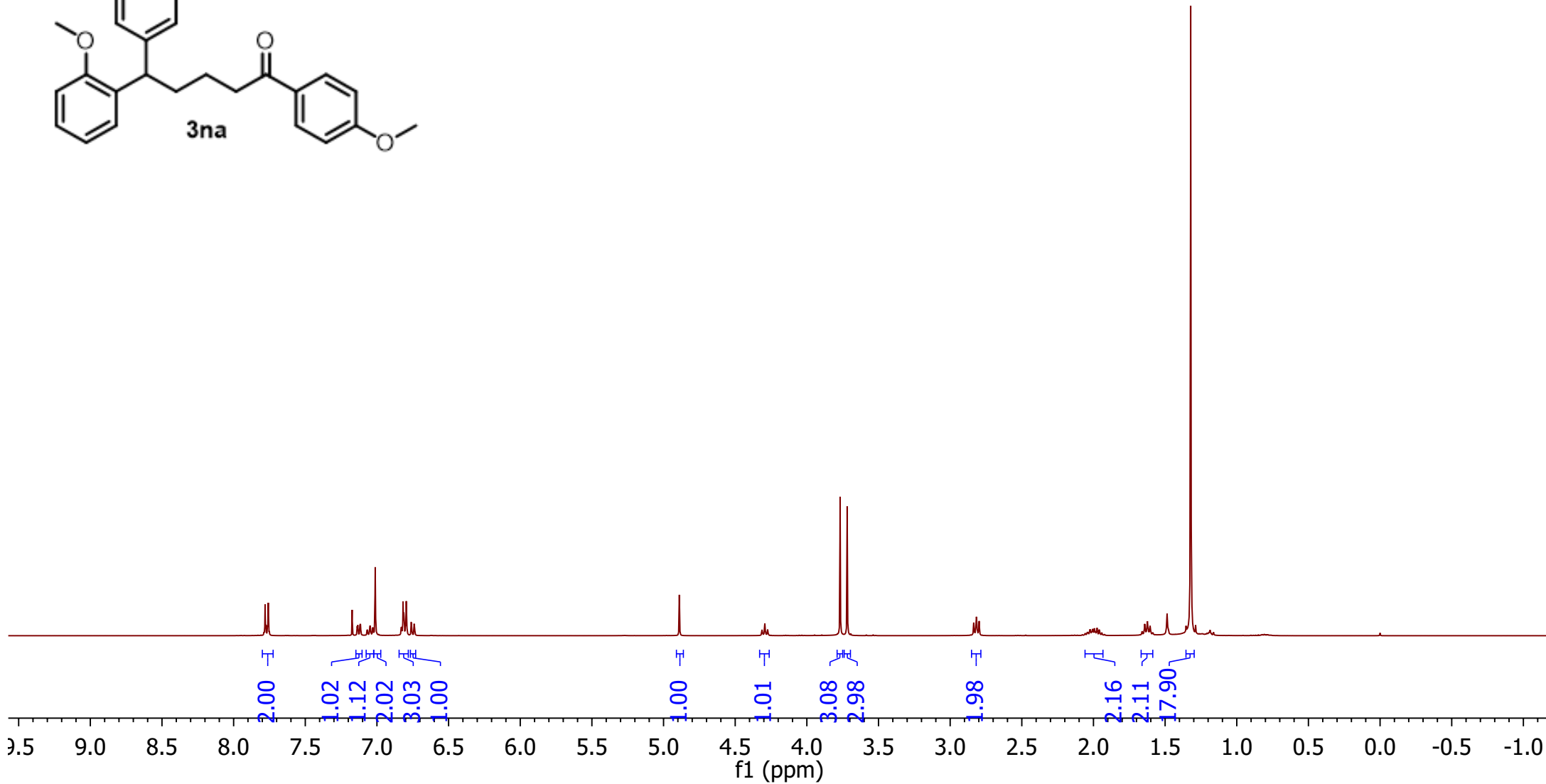
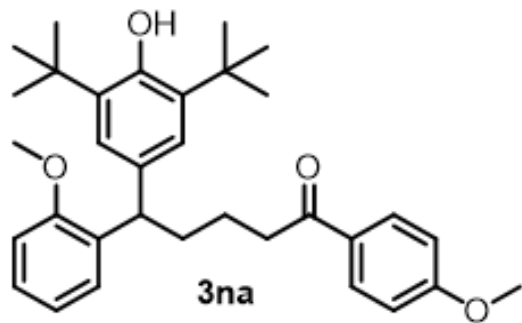
---113.56



<sup>19</sup>F NMR Spectrum of **3ma**

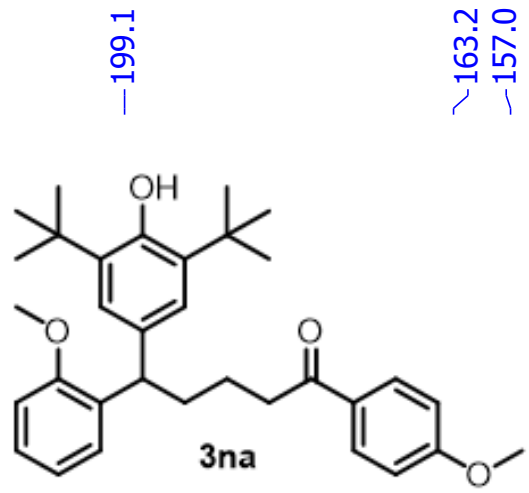
**<sup>1</sup>H(CDCl<sub>3</sub>, 400 MHz)**

7.79  
7.78  
7.78  
7.76  
7.76  
7.75  
7.14  
7.13  
7.12  
7.11  
7.07  
7.07  
7.05  
7.05  
7.05  
7.04  
7.03  
7.03  
7.01  
6.83  
6.83  
6.82  
6.81  
6.81  
6.80  
6.80  
6.79  
6.76  
6.76  
6.74  
6.74  
4.89  
4.31  
4.29  
4.27  
3.77  
3.72  
2.84  
2.82  
2.81  
2.80  
2.03  
2.02  
2.01  
2.01  
2.00  
1.99  
1.99  
1.97  
1.96  
1.96  
1.66  
1.64  
1.62  
1.60  
1.32



<sup>1</sup>H NMR Spectrum of **3na**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



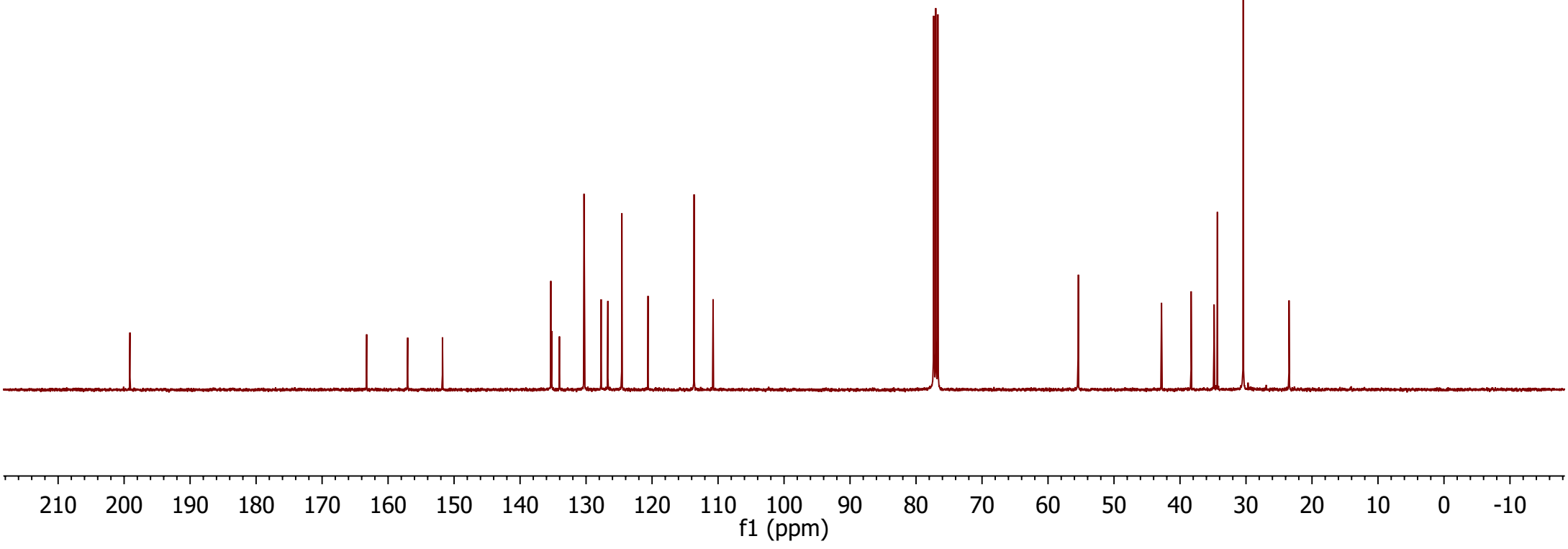
199.1

163.2  
157.0  
151.8

135.3  
135.2  
134.0  
130.3  
130.2  
127.7  
126.7  
124.6  
120.6  
113.6  
110.8

55.4  
55.4

42.8  
38.3  
34.8  
34.3  
30.4  
23.5

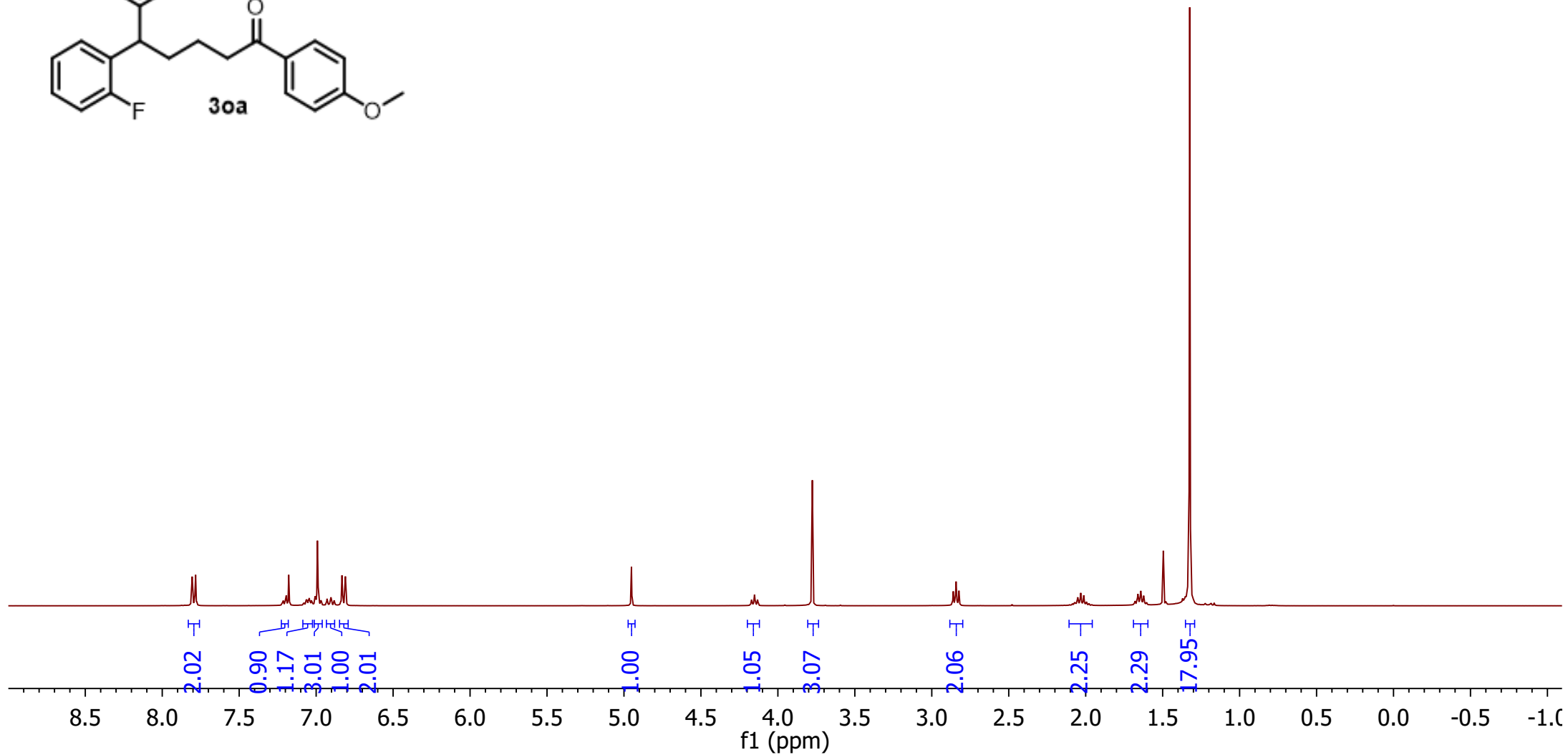
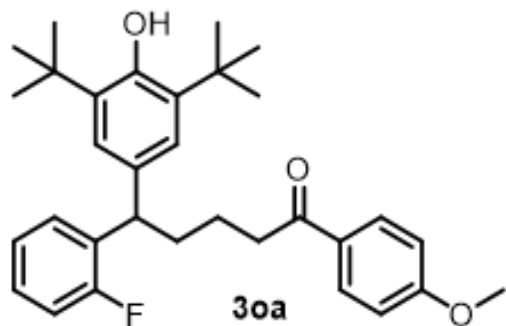


<sup>13</sup>C NMR Spectrum of **3na**



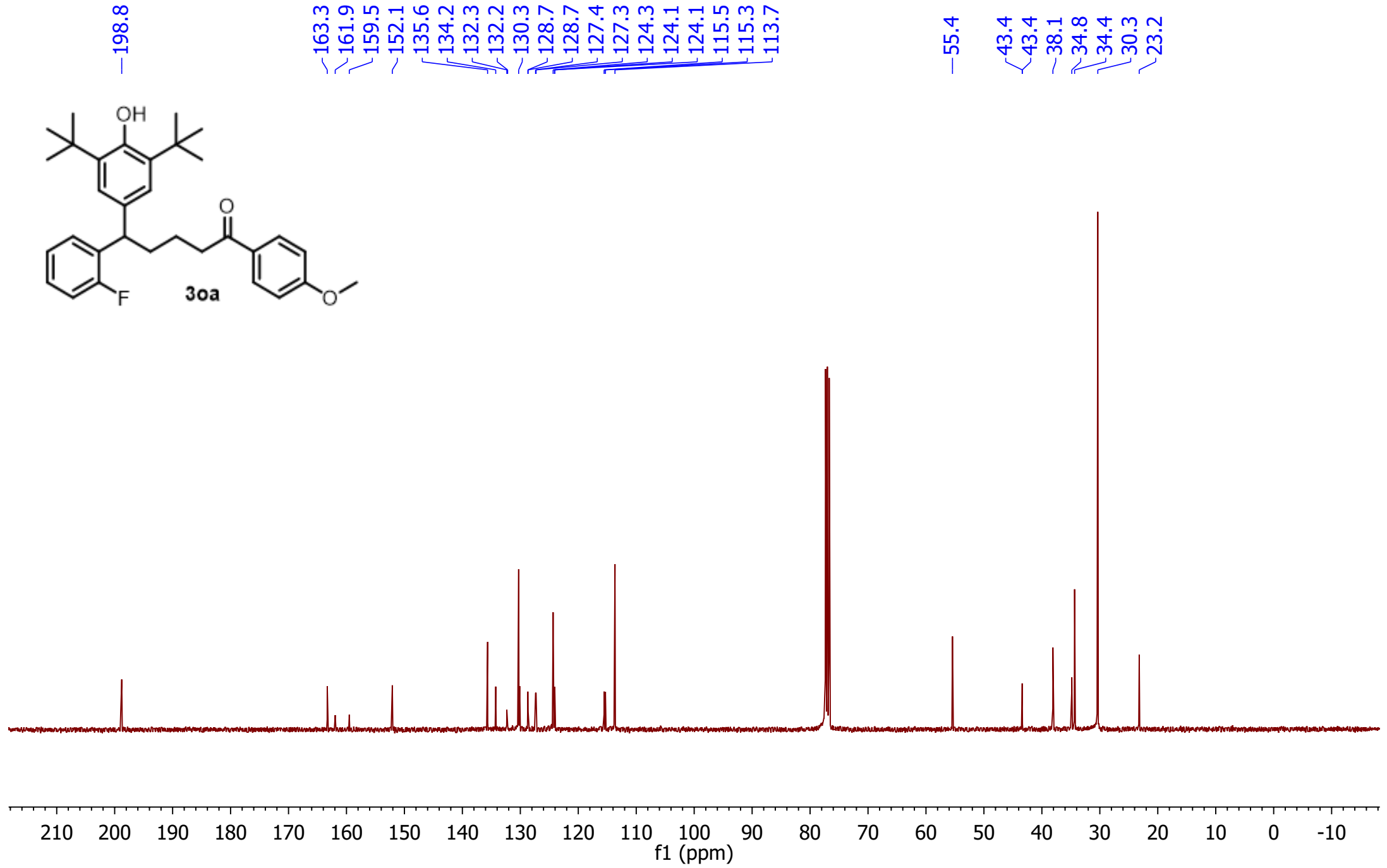
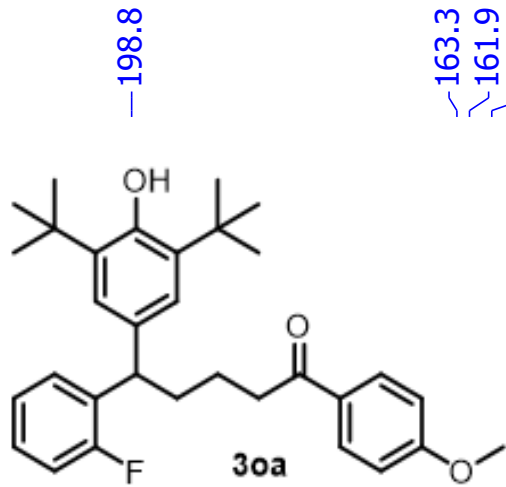
**<sup>1</sup>H(CDCl<sub>3</sub>, 400 MHz)**

7.81  
7.78  
7.22  
7.21  
7.20  
7.19  
7.18  
7.08  
7.07  
7.06  
7.06  
7.05  
7.05  
7.04  
7.04  
7.03  
7.03  
7.01  
7.00  
6.99  
6.99  
6.97  
6.97  
6.93  
6.93  
6.91  
6.91  
6.90  
6.90  
6.88  
6.88  
6.83  
6.81  
4.95  
4.17  
4.15  
4.13  
3.78  
2.86  
2.84  
2.82  
2.07  
2.07  
2.05  
2.03  
2.01  
2.00  
1.99  
1.68  
1.66  
1.64  
1.62  
1.60  
1.32



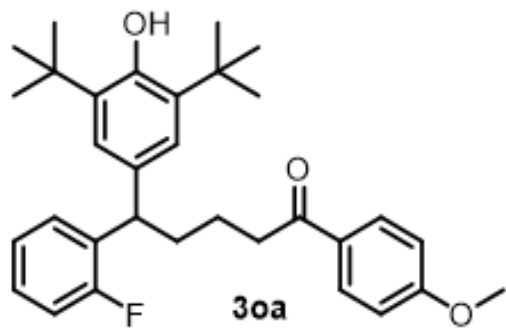
<sup>1</sup>H NMR Spectrum of **3oa**

**$^{13}\text{C}$ ( $\text{CDCl}_3$ , 101 MHz)**

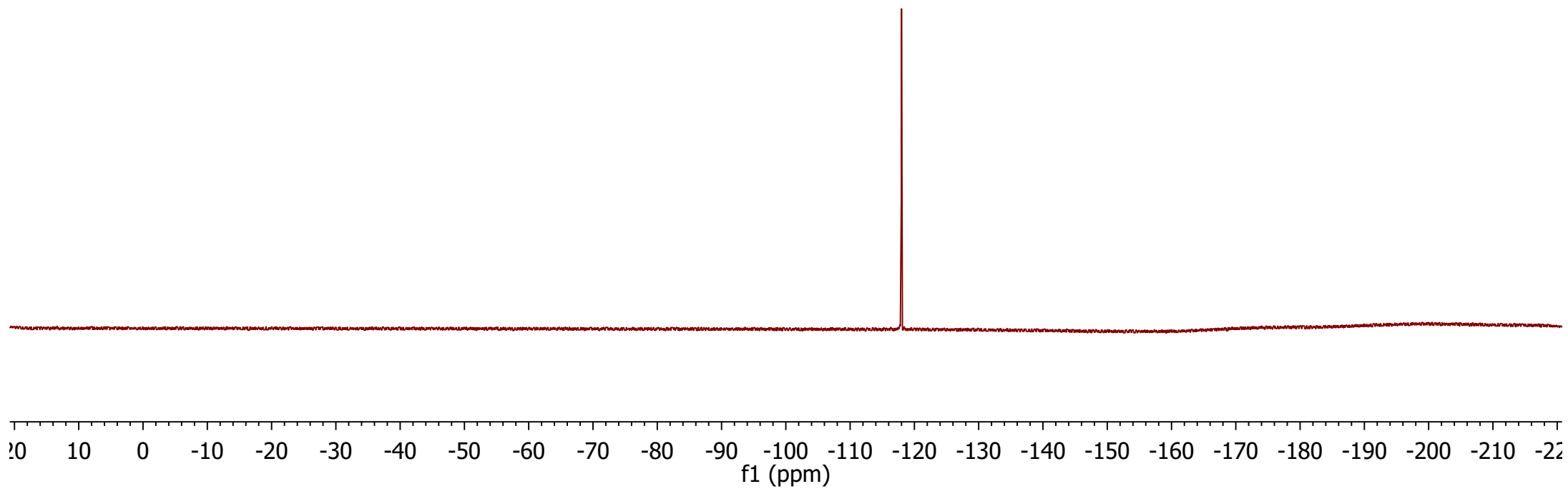


$^{13}\text{C}$  NMR Spectrum of **3oa**

**<sup>19</sup>F (CDCl<sub>3</sub>, 376 MHz)**

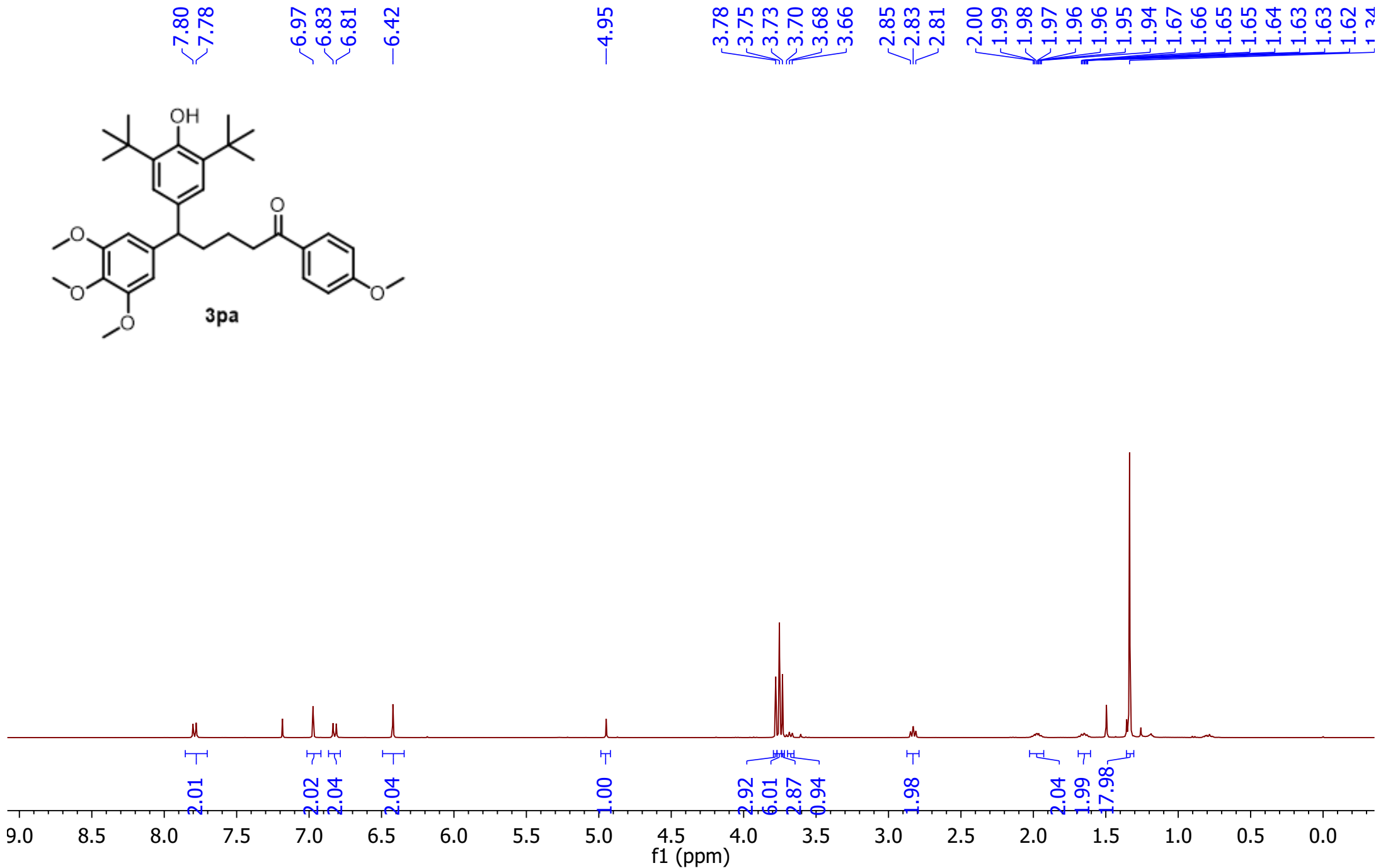
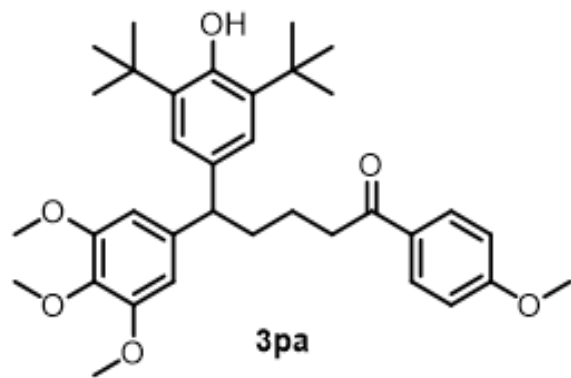


--118.00



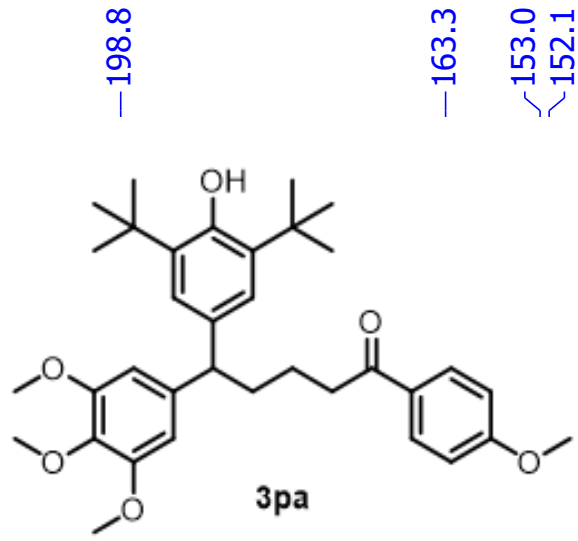
<sup>19</sup>F NMR Spectrum of **30a**

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



<sup>1</sup>H NMR Spectrum of **3pa**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



—198.8

—163.3

153.0

152.1

141.1

136.4

135.7

135.2

130.3

130.1

124.1

—113.7

—105.1

60.8

56.1

55.4

51.8

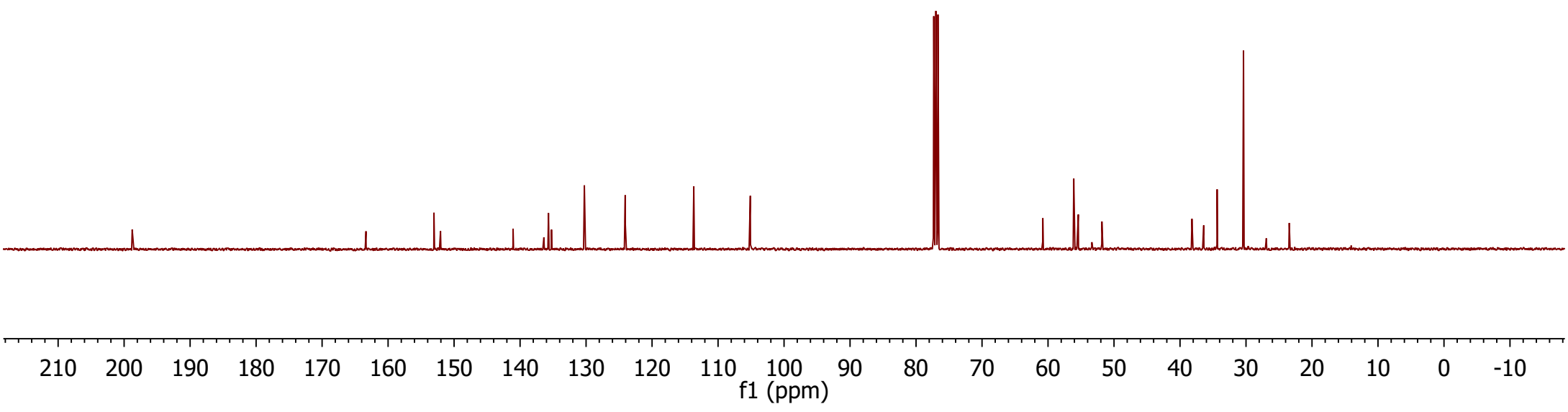
38.2

36.4

34.4

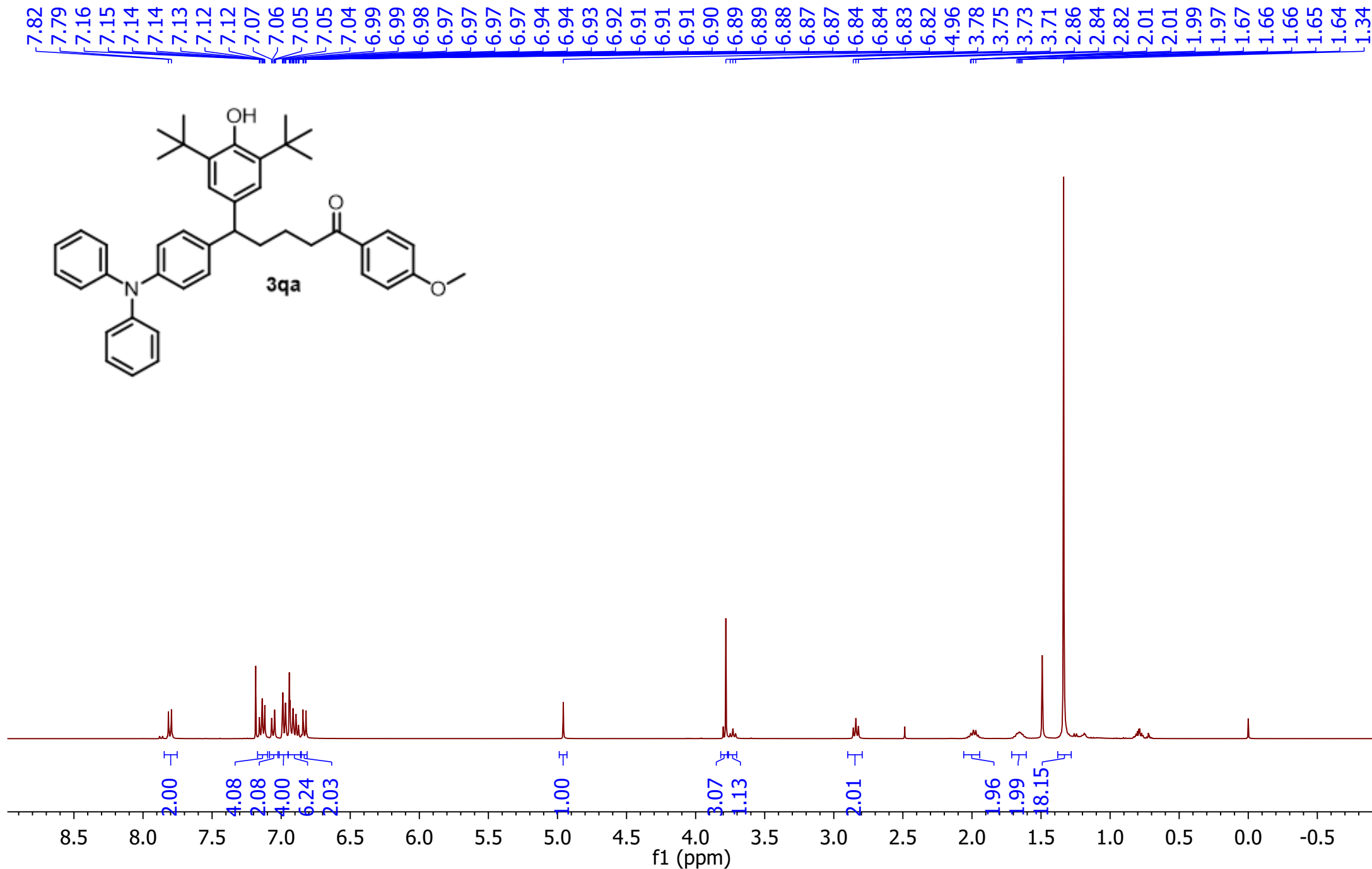
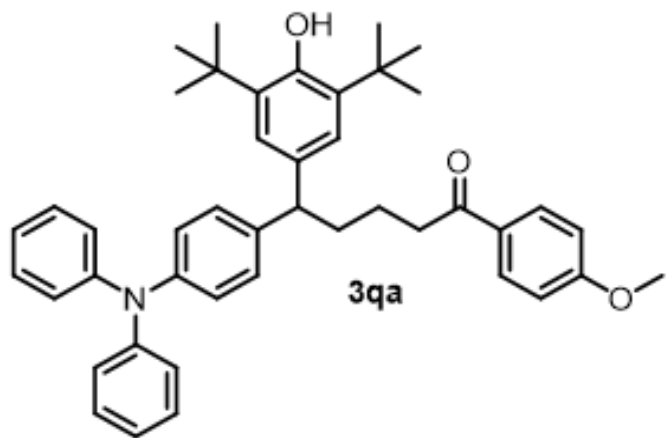
30.4

23.4



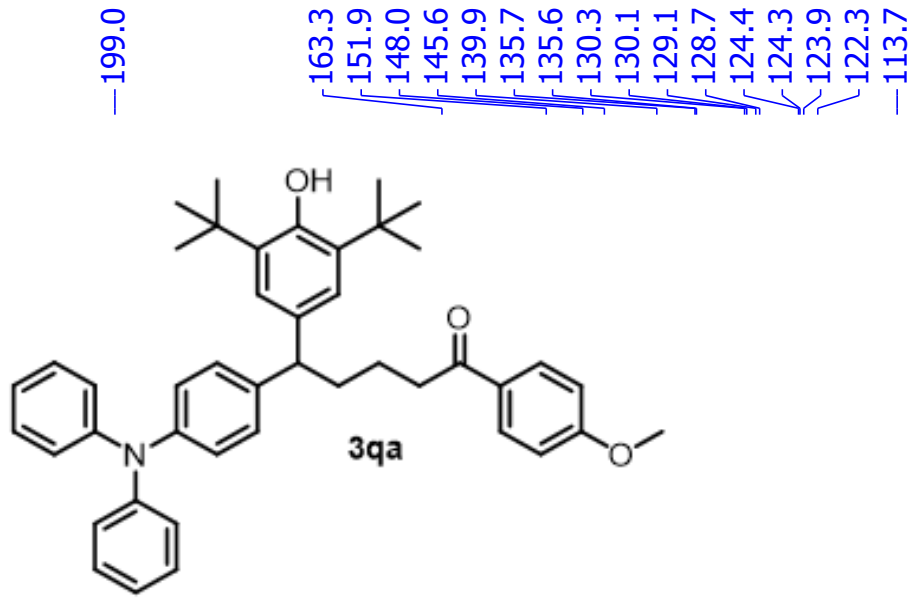
<sup>13</sup>C NMR Spectrum of **3pa**

**<sup>1</sup>H(CDCI<sub>3</sub>, 400 MHz)**



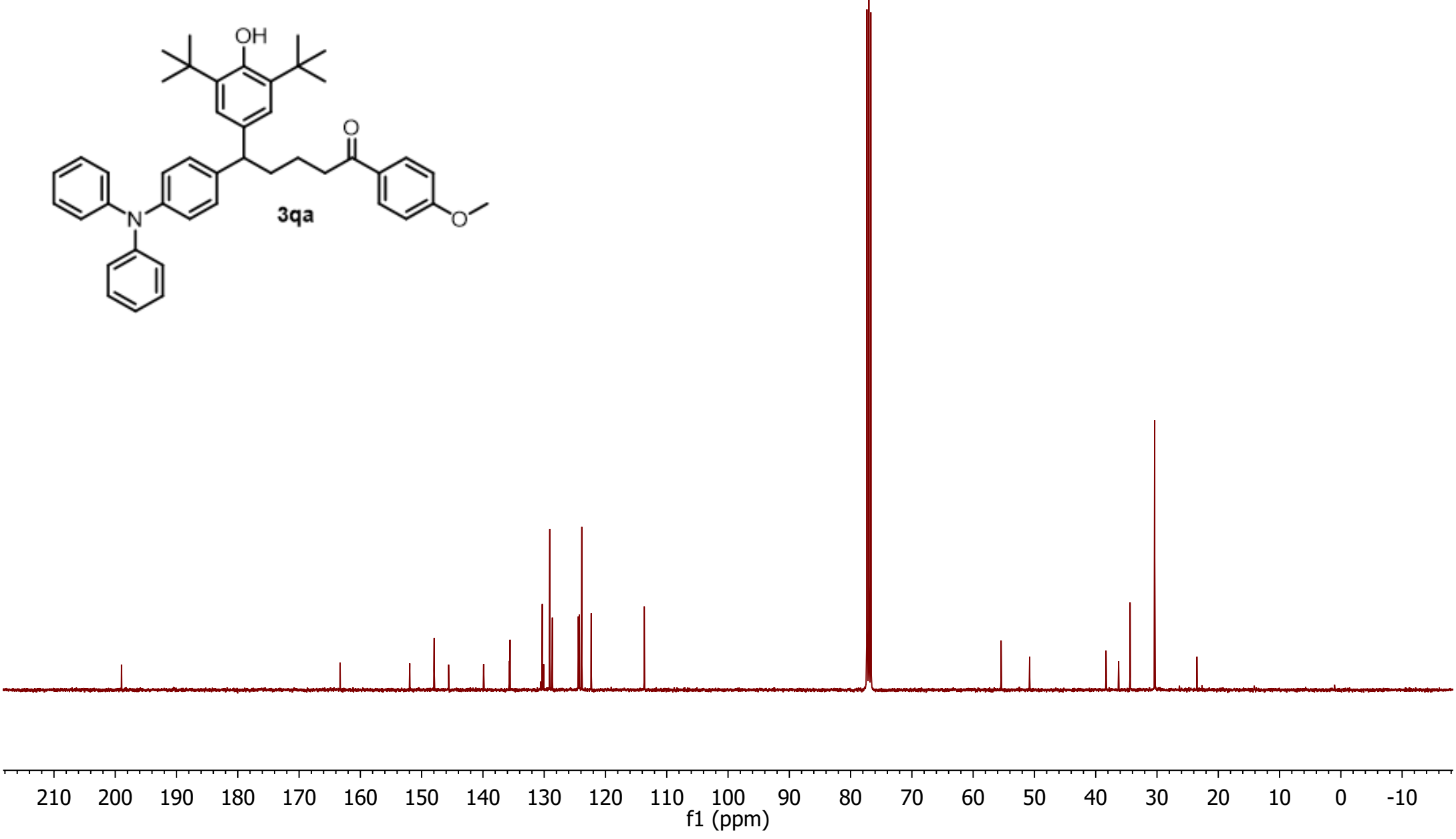
<sup>1</sup>H NMR Spectrum of **3qa**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



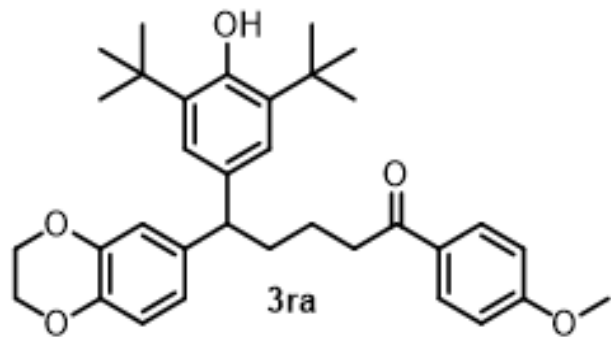
- 199.0
- 163.3
- 151.9
- 148.0
- 145.6
- 139.9
- 135.7
- 135.6
- 130.3
- 130.1
- 129.1
- 128.7
- 124.4
- 124.3
- 123.9
- 122.3
- 113.7

- 55.4
- 50.8
- ~ 38.3
- ~ 36.3
- ~ 34.4
- ~ 30.4
- ~ 23.5



<sup>13</sup>C NMR Spectrum of 3qa

**<sup>1</sup>H(CDCI<sub>3</sub>, 400 MHz)**

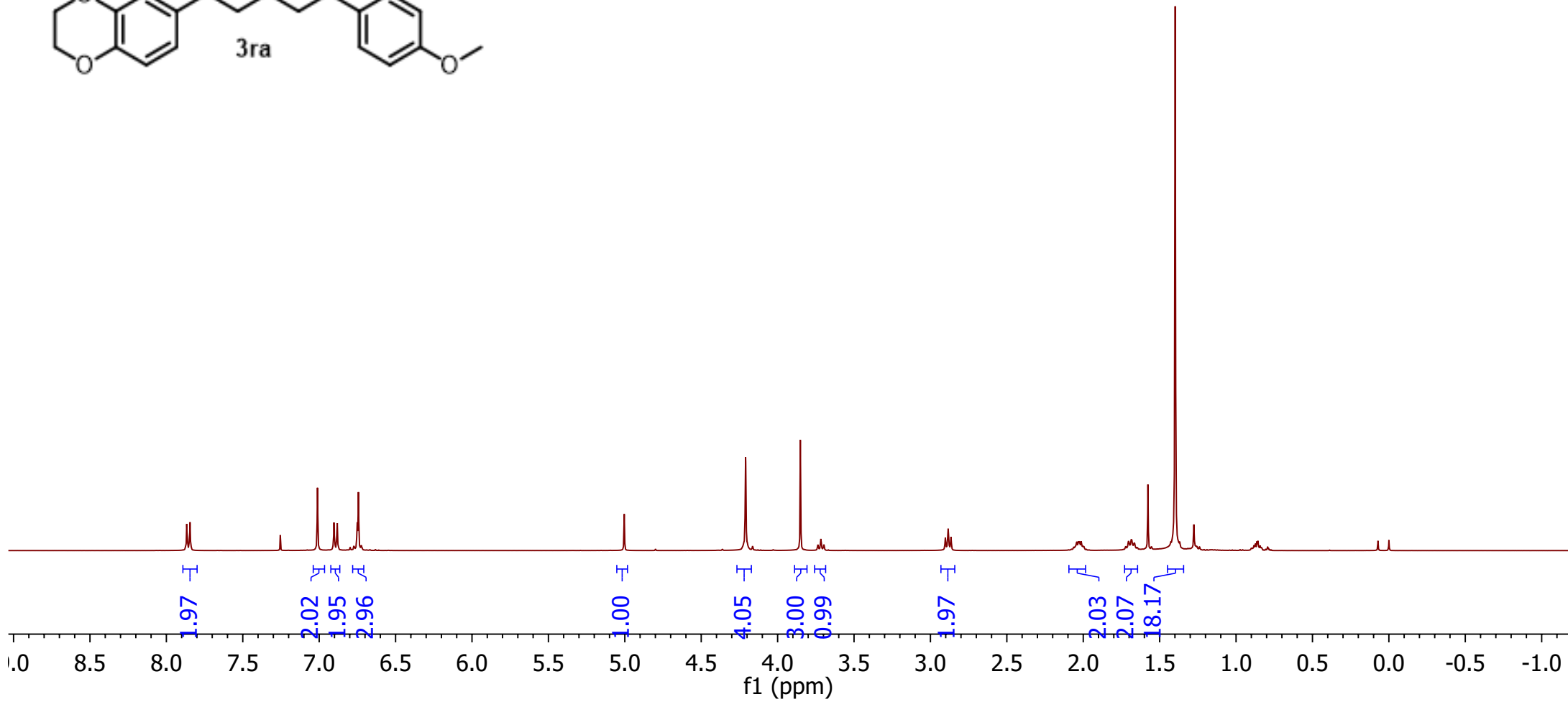


7.87  
7.86  
7.85  
7.85  
7.01  
6.90  
6.88  
6.77  
6.77  
6.76  
6.75  
6.74  
6.72  
6.72

— 5.00

4.21  
3.85  
3.74  
3.72  
3.70

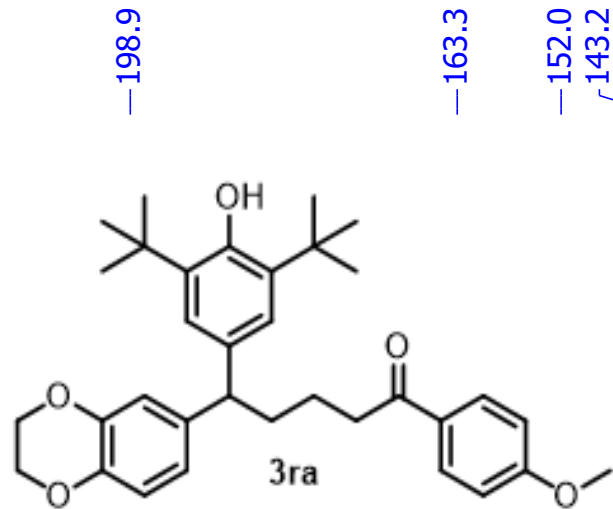
2.90  
2.88  
2.87  
2.06  
2.05  
2.04  
2.04  
2.03  
2.02  
2.01  
2.00  
2.00  
1.72  
1.70  
1.69  
1.68  
1.68  
1.67  
1.65  
1.64  
1.40



<sup>1</sup>H NMR Spectrum of 3ra



**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



—198.9

—163.3

—152.0

—143.2

—141.7

—139.0

—135.6

—135.6

—130.3

—130.1

—124.0

—120.7

—117.0

—113.6

—64.4

—64.3

—55.4

—50.7

—38.3

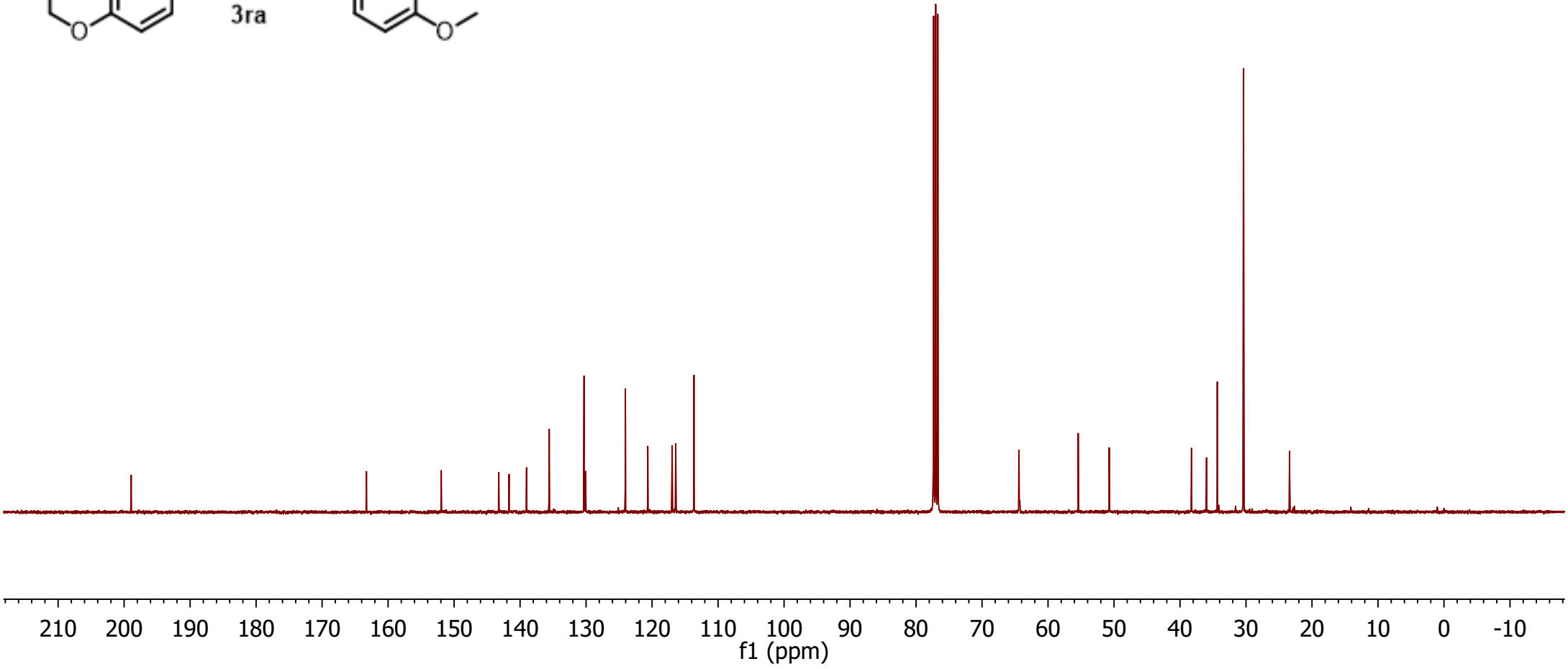
—36.0

—34.4

—30.4

—30.3

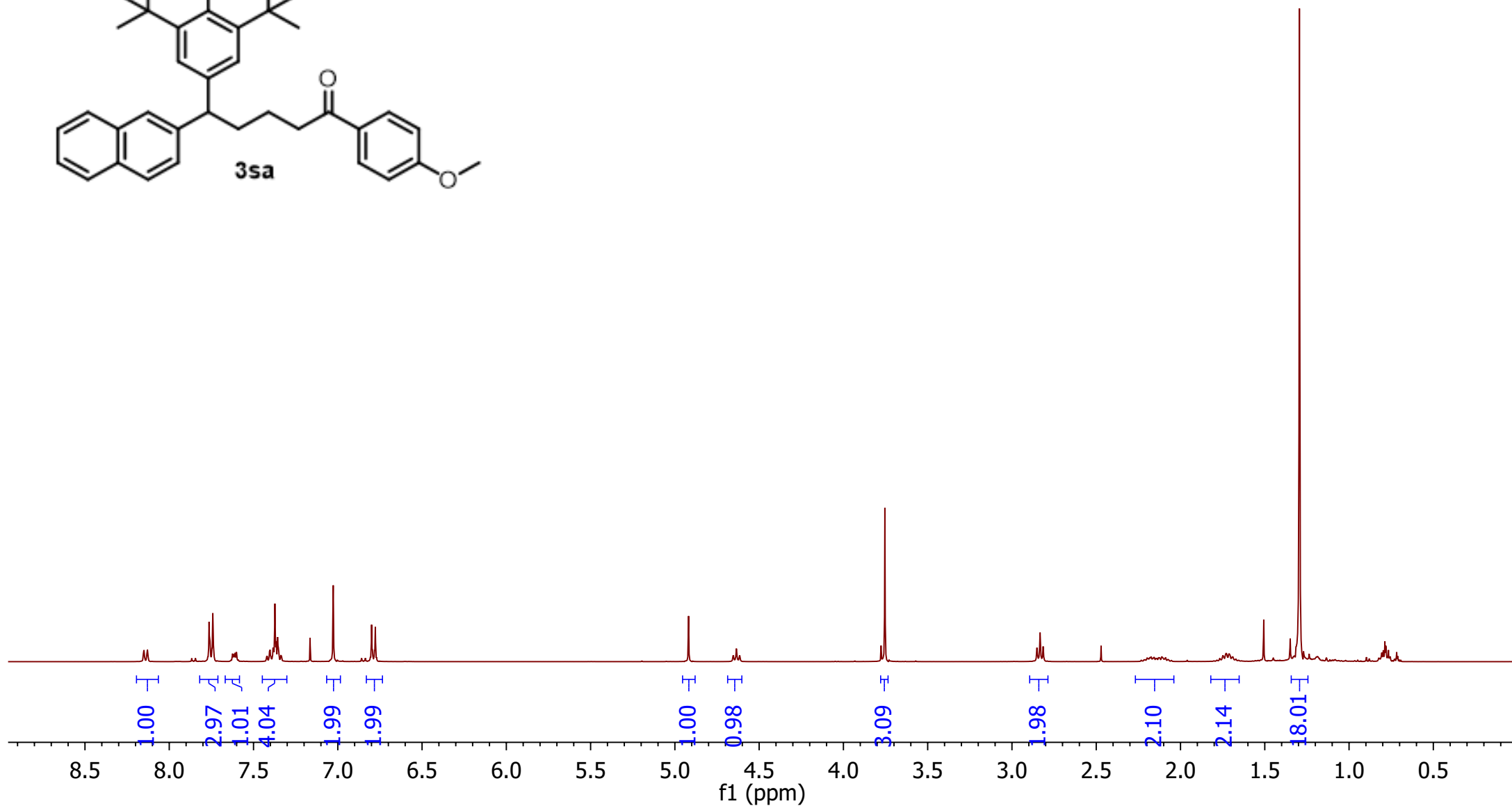
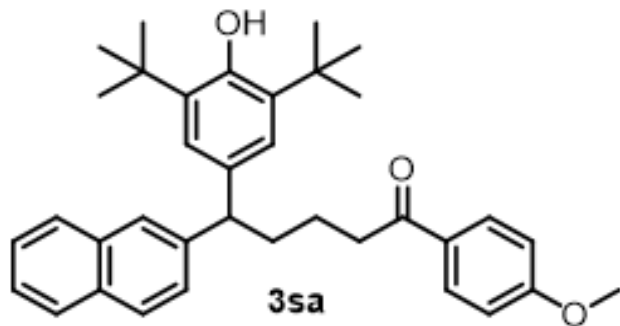
—23.4



<sup>13</sup>C NMR Spectrum of **3ra**

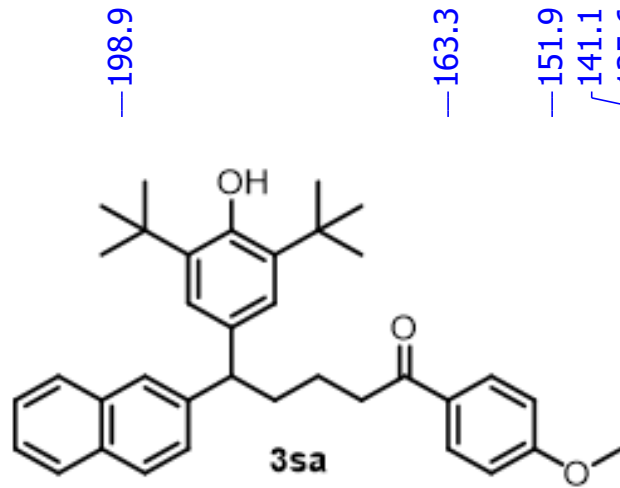
**<sup>1</sup>H(CDCI<sub>3</sub>, 400 MHz)**

8.15  
8.13  
8.13  
7.76  
7.76  
7.74  
7.74  
7.62  
7.62  
7.61  
7.60  
7.42  
7.42  
7.41  
7.40  
7.40  
7.38  
7.38  
7.37  
7.37  
7.36  
7.35  
7.35  
7.34  
7.34  
7.33  
7.03  
6.80  
6.79  
6.78  
6.78  
4.92  
4.65  
4.63  
4.62  
3.75  
2.85  
2.83  
2.81  
2.17  
2.16  
2.16  
2.11  
2.11  
2.09  
1.75  
1.74  
1.73  
1.73  
1.73  
1.71  
1.71  
1.71  
1.70  
1.69  
1.29



<sup>1</sup>H NMR Spectrum of **3sa**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



—198.9

—163.3

—151.9

—141.1

—135.6

—134.9

—134.1

—132.0

—130.3

—130.1

—128.8

—126.6

—125.8

—125.5

—125.2

—124.5

—124.2

—123.7

—113.7

—55.4

—45.9

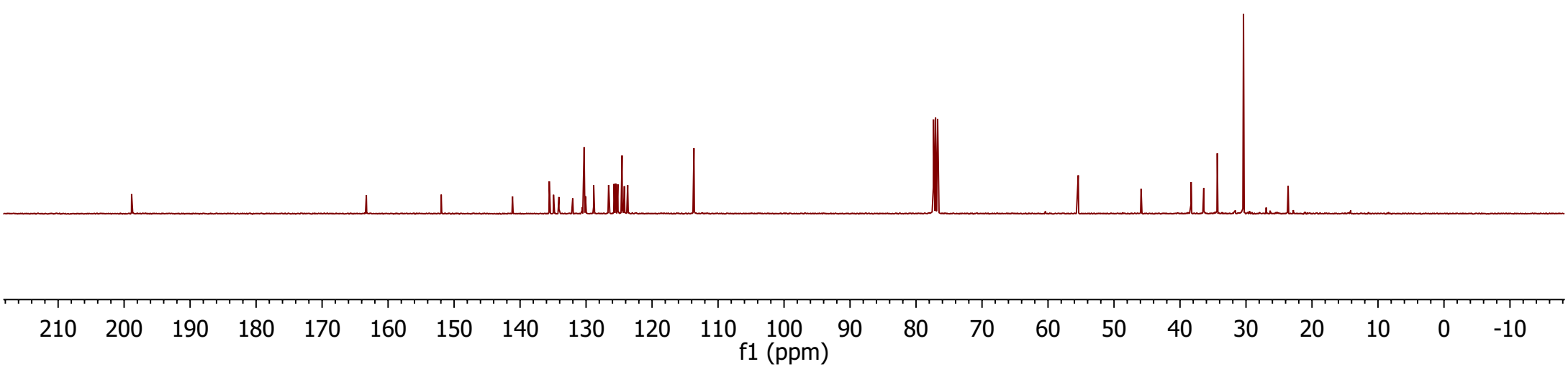
—38.3

—36.4

—34.4

—30.4

—23.6



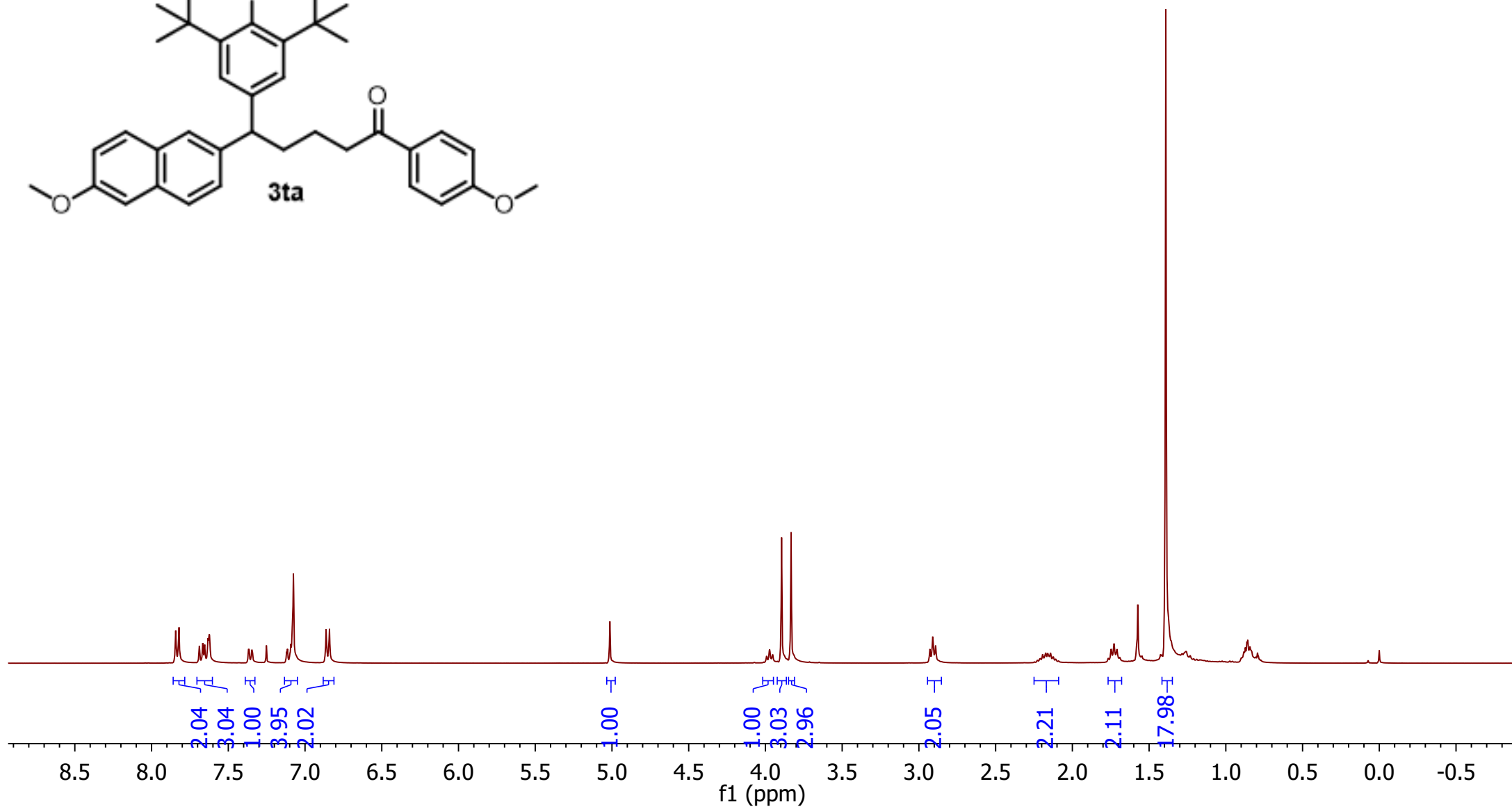
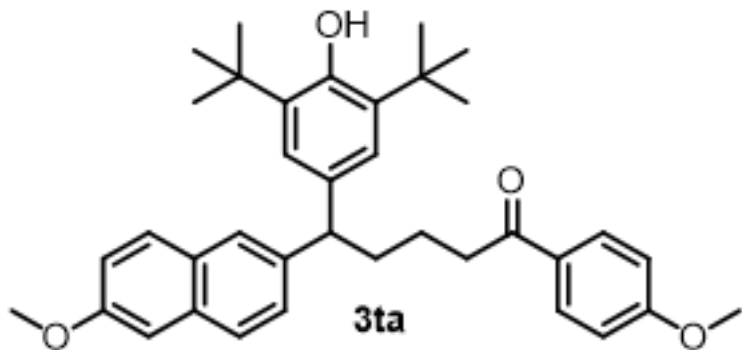
<sup>13</sup>C NMR Spectrum of **3sa**

**<sup>1</sup>H(CDCI<sub>3</sub>, 400 MHz)**

7.84  
7.83  
7.82  
7.69  
7.67  
7.65  
7.63  
7.63  
7.62  
7.37  
7.36  
7.35  
7.34  
7.12  
7.11  
7.10  
7.09  
7.08  
7.08  
7.06  
6.86  
6.84  
—5.01

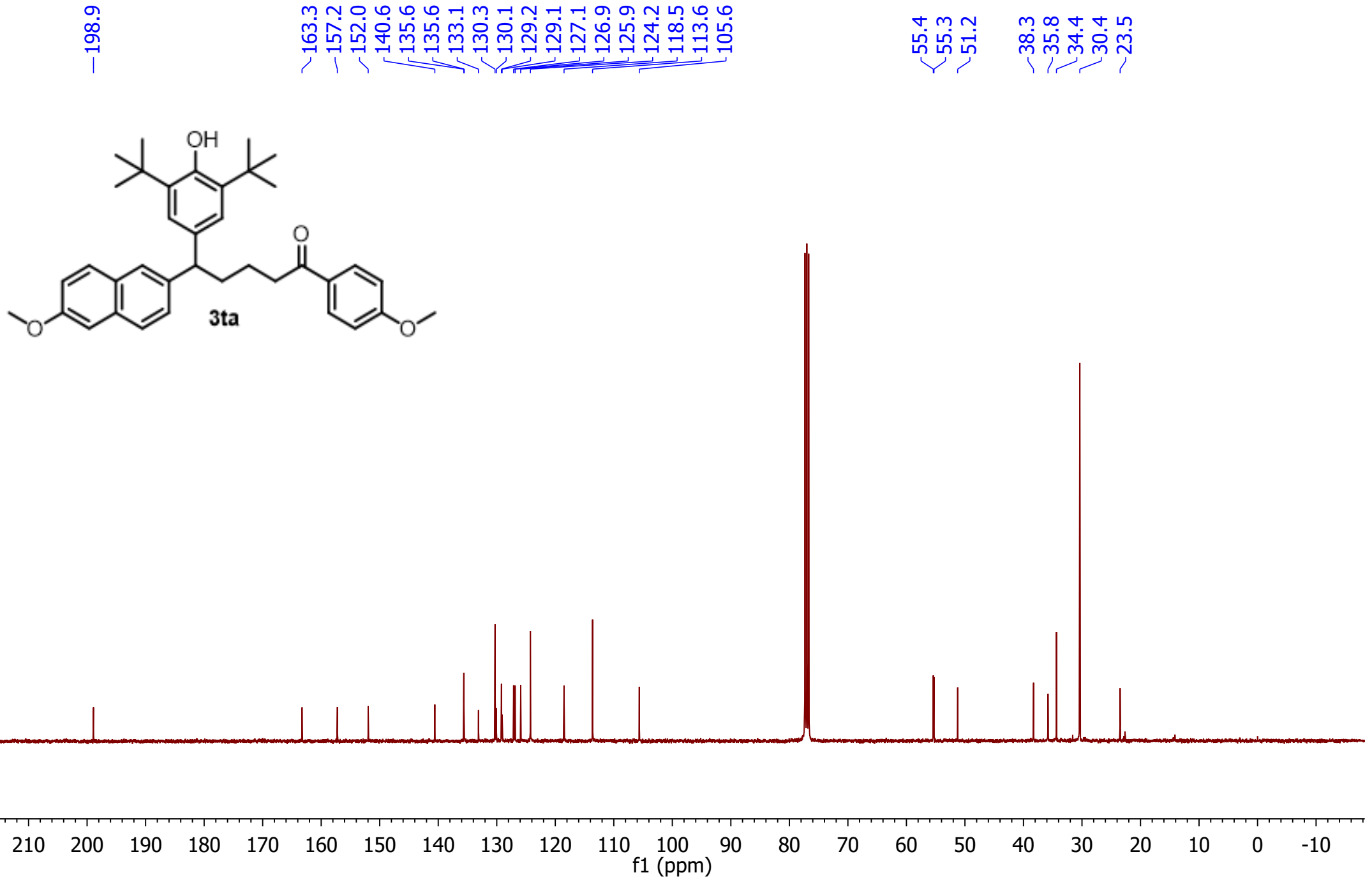
3.99  
3.97  
3.95  
3.89  
3.83

2.93  
2.91  
2.91  
2.89  
2.25  
2.23  
2.21  
2.21  
2.19  
2.18  
2.17  
2.16  
2.15  
2.14  
2.13  
2.12  
2.11  
2.09  
1.75  
1.73  
1.71  
1.39



<sup>1</sup>H NMR Spectrum of 3ta

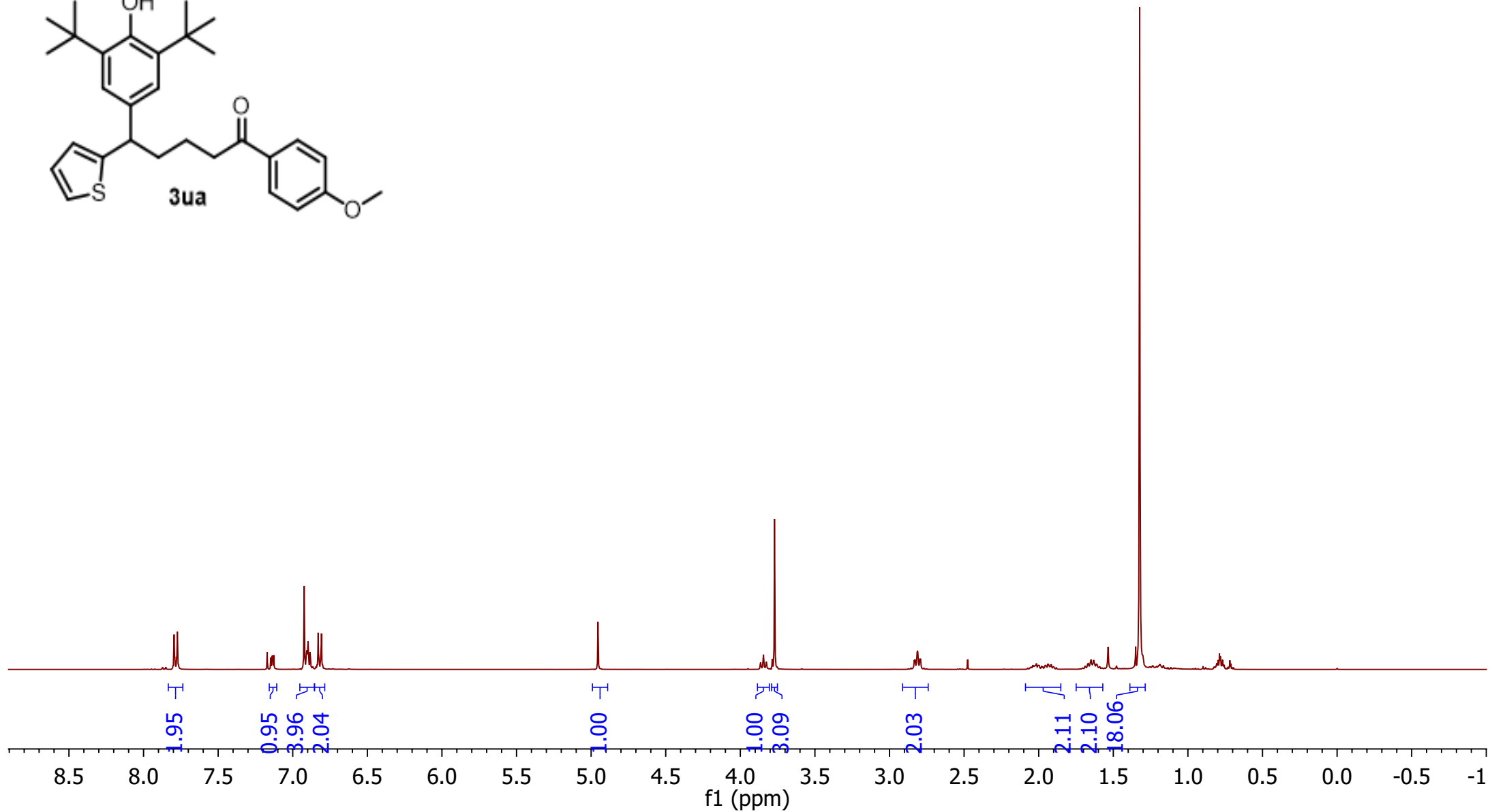
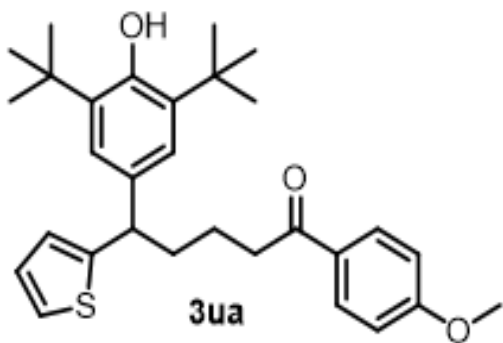
**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



<sup>13</sup>C NMR Spectrum of **3ta**

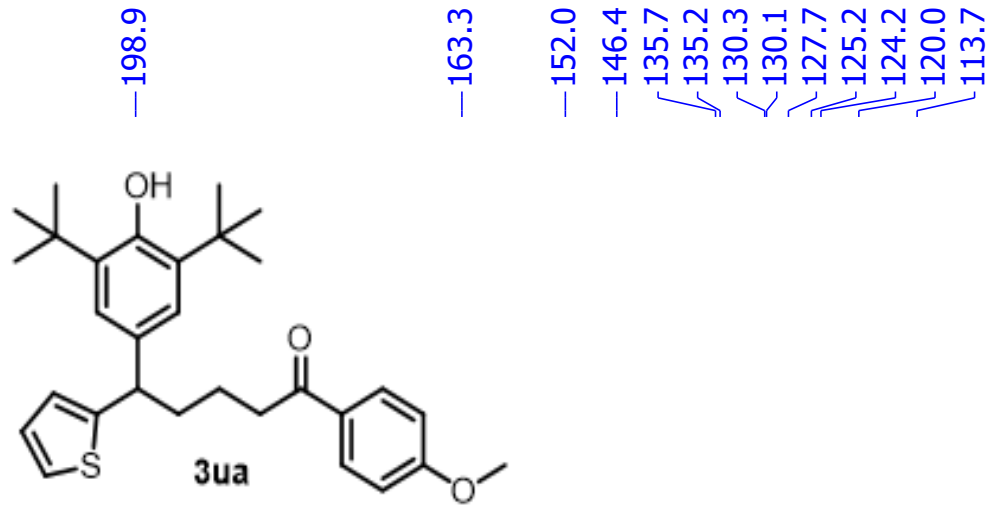
**<sup>1</sup>H(CDCl<sub>3</sub>, 400 MHz)**

7.80  
7.79  
7.78  
7.77  
7.77  
7.15  
7.14  
7.13  
7.13  
6.92  
6.91  
6.91  
6.90  
6.89  
6.88  
6.88  
6.84  
6.83  
6.82  
6.81  
6.81  
6.80  
4.95  
3.86  
3.85  
3.83  
3.77  
2.83  
2.83  
2.82  
2.81  
2.81  
2.80  
2.79  
2.04  
2.02  
2.01  
2.00  
2.00  
1.96  
1.94  
1.93  
1.93  
1.92  
1.67  
1.67  
1.66  
1.65  
1.65  
1.64  
1.63  
1.63  
1.61  
1.61  
1.61  
1.32



<sup>1</sup>H NMR Spectrum of **3ua**

**<sup>13</sup>C(CDCl<sub>3</sub>, 01 MHz)**



—198.9

—163.3

—152.0

—146.4

135.7

135.2

130.3

130.1

127.7

125.2

124.2

120.0

113.7

—55.4

—46.9

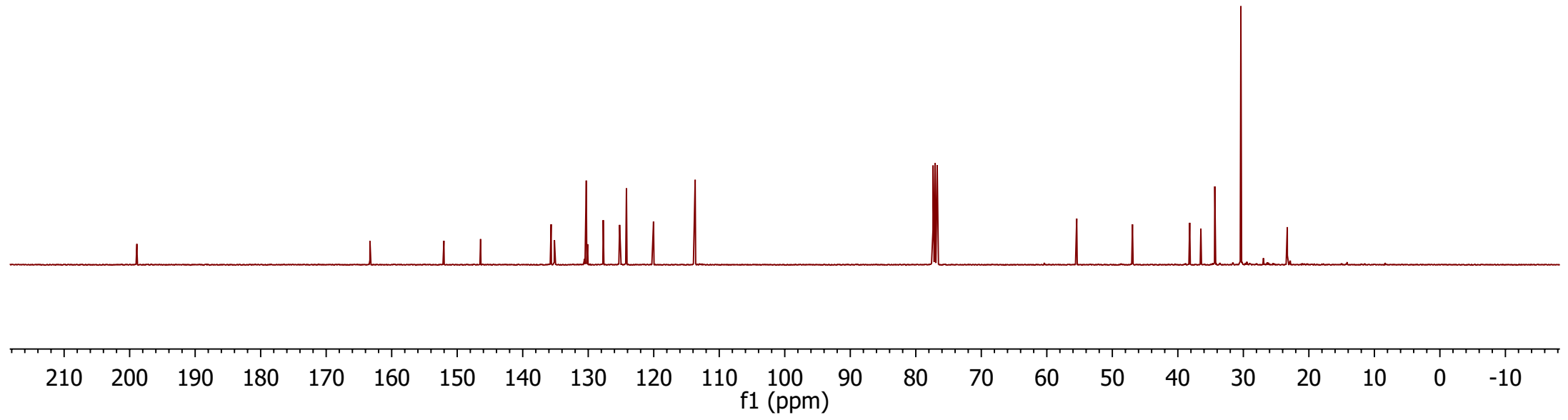
38.2

36.5

34.4

30.4

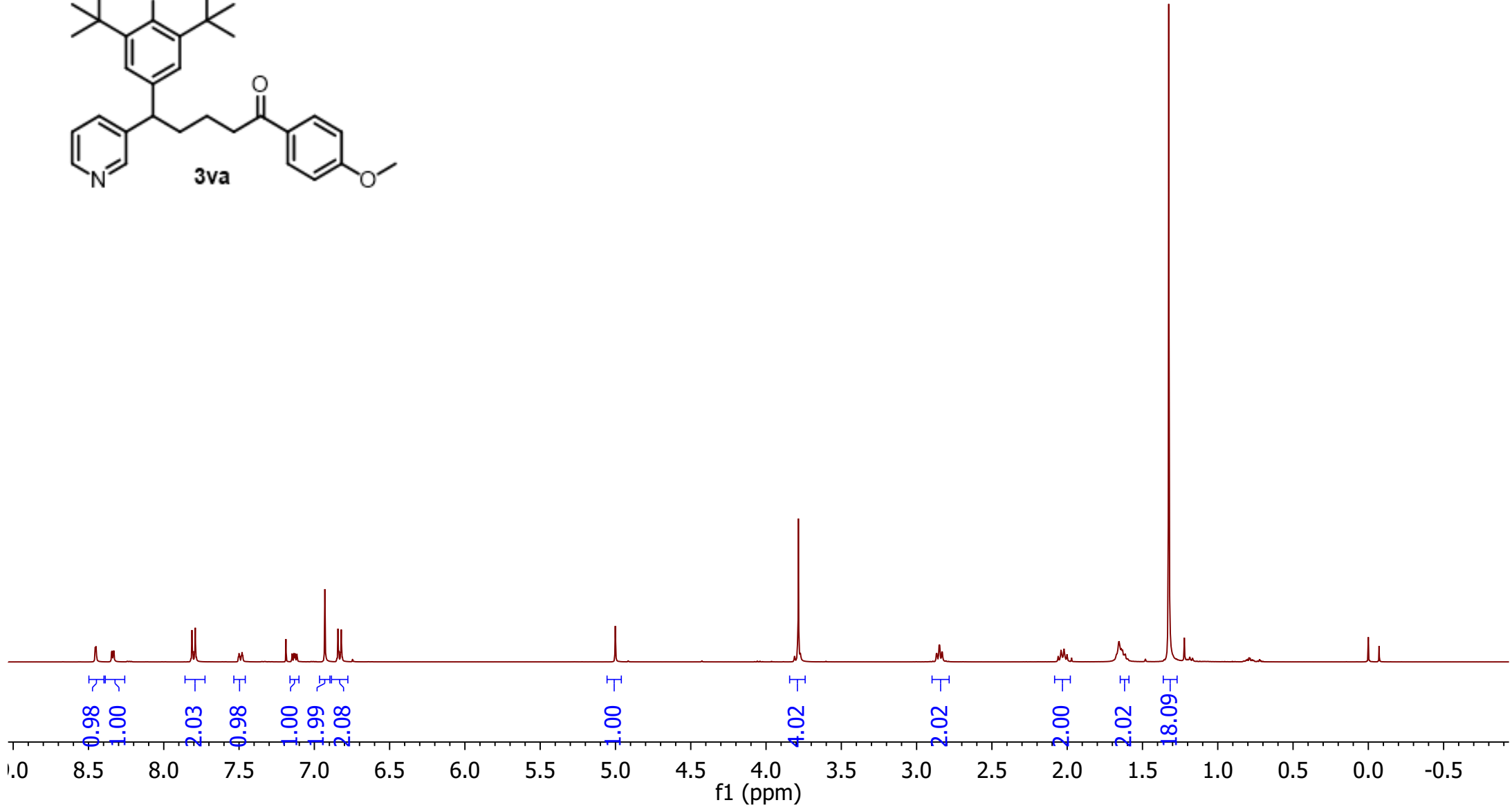
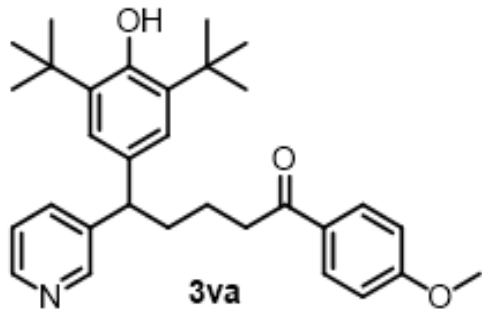
23.3



<sup>13</sup>C NMR Spectrum of **3ua**

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

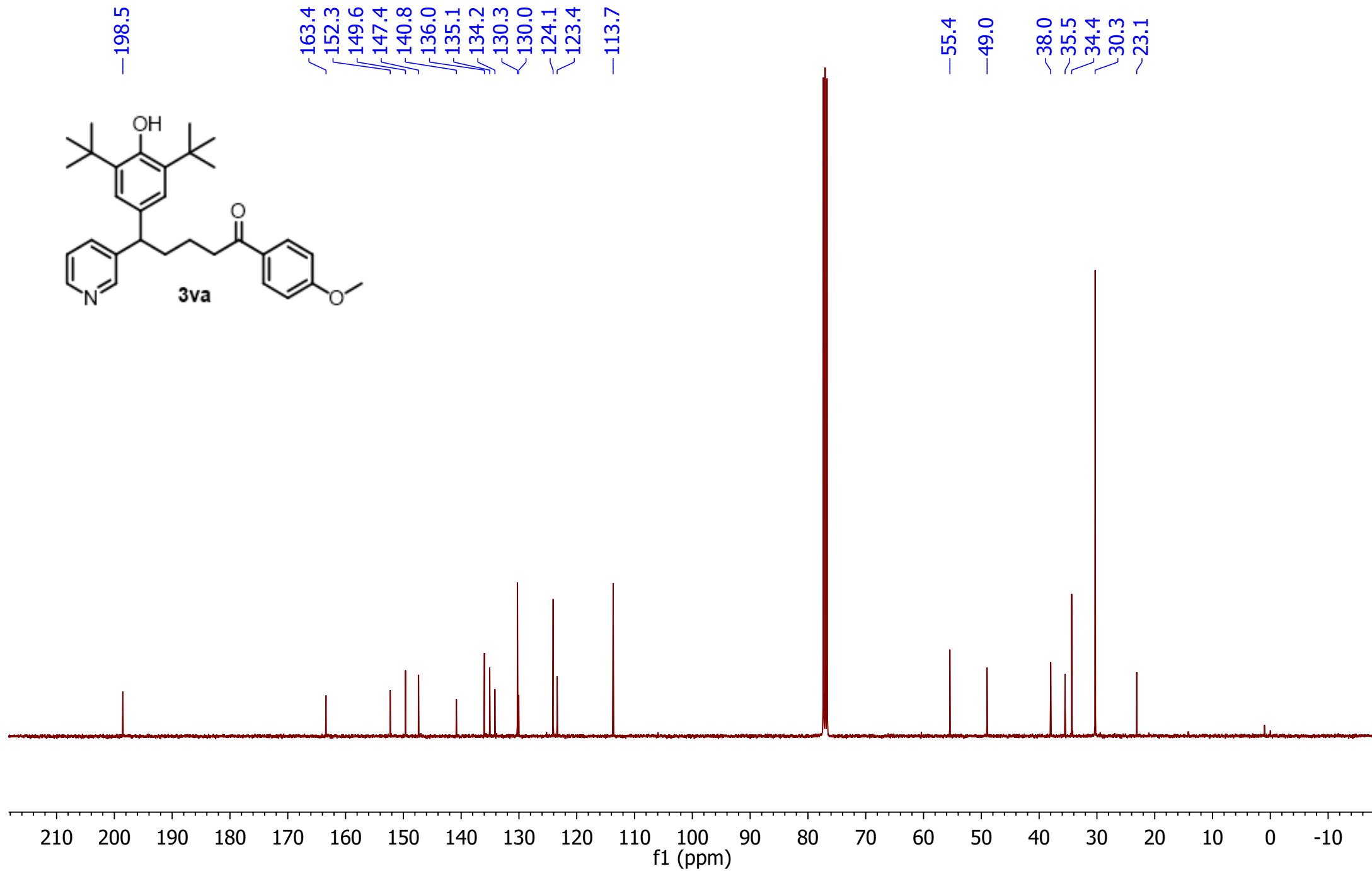
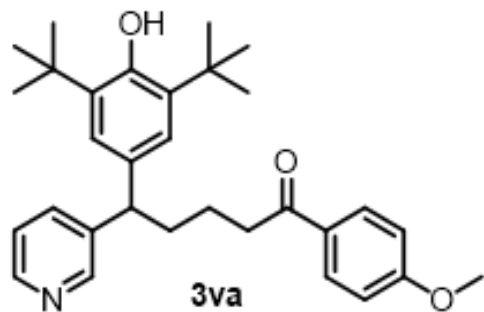
8.46  
8.45  
8.35  
8.34  
8.33  
8.33  
7.81  
7.81  
7.80  
7.79  
7.78  
7.50  
7.50  
7.49  
7.49  
7.48  
7.47  
7.15  
7.15  
7.14  
7.13  
7.13  
7.13  
7.12  
7.11  
6.93  
6.84  
6.84  
6.83  
6.82  
6.81  
5.00  
3.81  
3.79  
3.78  
3.77  
2.87  
2.86  
2.85  
2.85  
2.83  
2.83  
2.06  
2.04  
2.02  
2.00  
1.67  
1.66  
1.65  
1.64  
1.63  
1.63  
1.62  
1.62  
1.61  
1.33



<sup>1</sup>H NMR Spectrum of **3va**



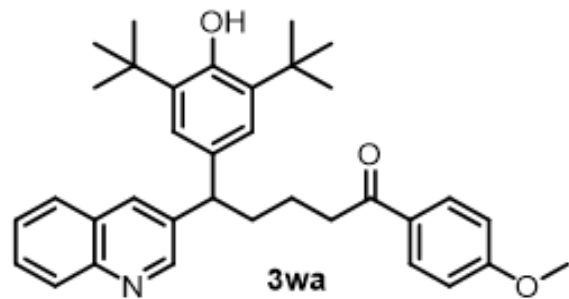
**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



<sup>13</sup>C NMR Spectrum of **3va**



**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



—198.5

—163.4

~152.4

~151.7

~146.6

~138.2

~136.1

~134.0

~133.5

~130.3

~130.0

~128.9

~128.8

~128.2

~127.6

~126.6

~124.2

~113.7

—55.4

—49.2

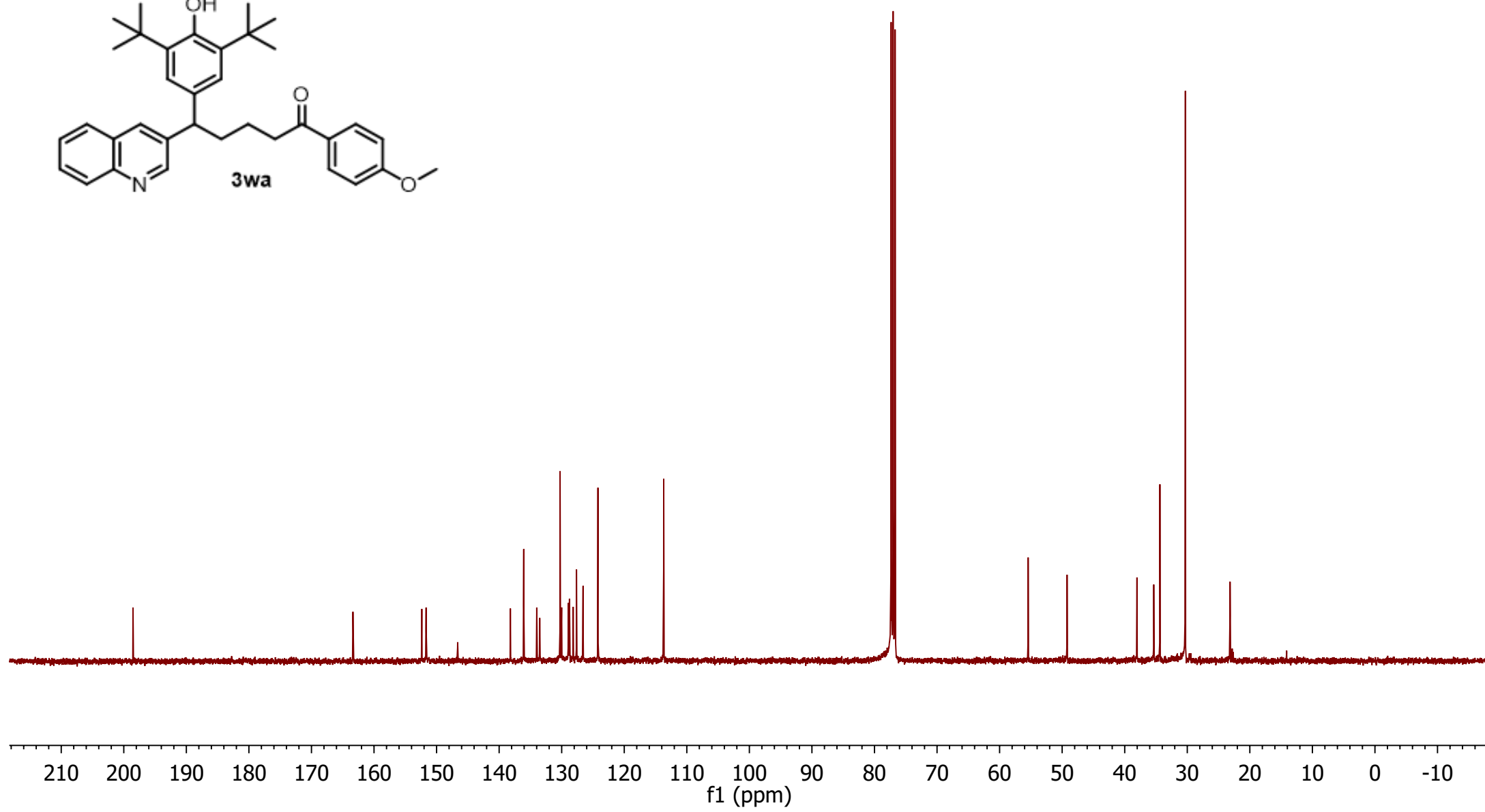
~38.0

~35.4

~34.4

~30.3

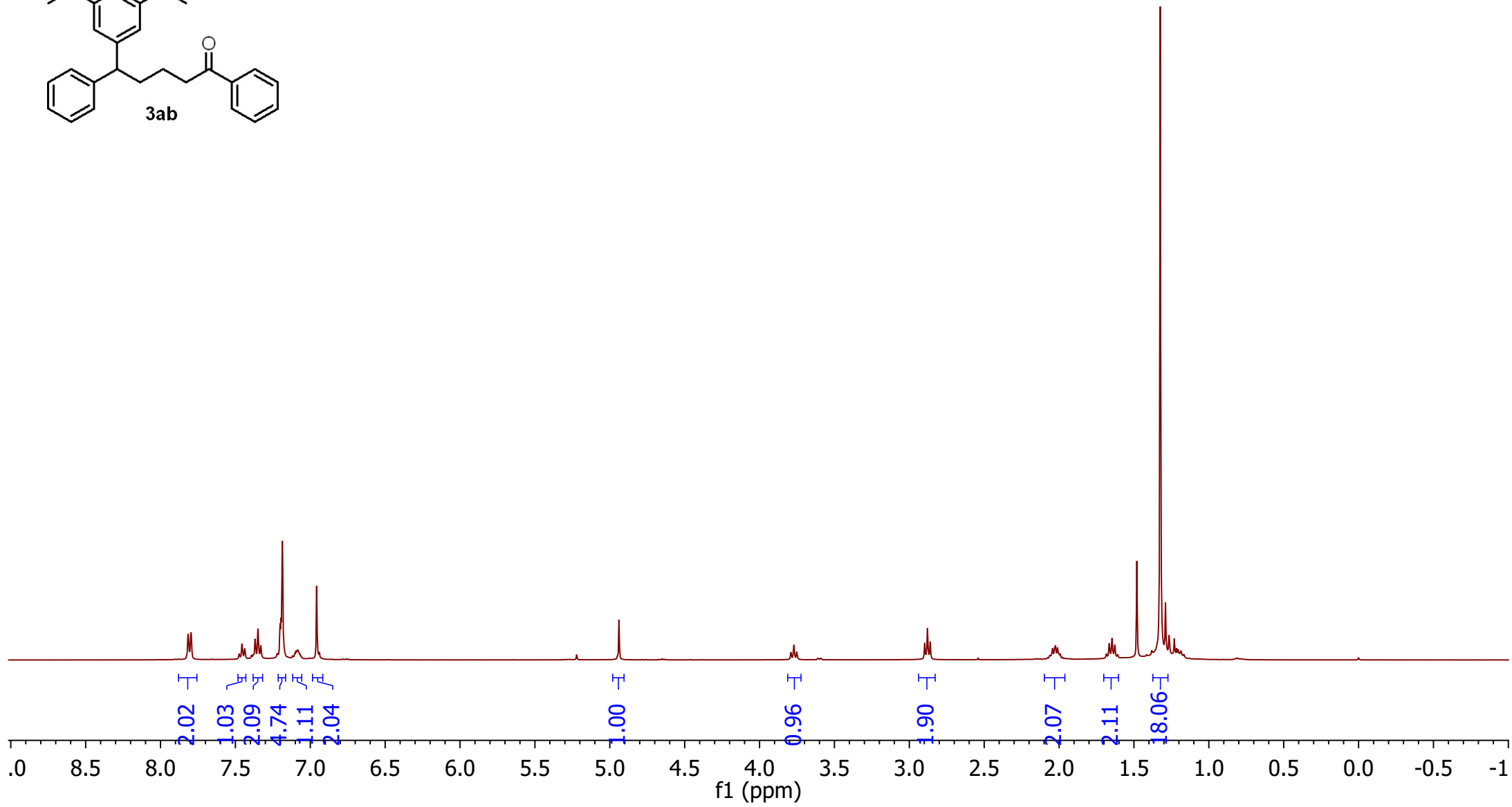
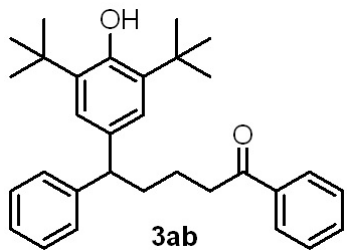
~23.2



<sup>13</sup>C NMR Spectrum of **3wa**

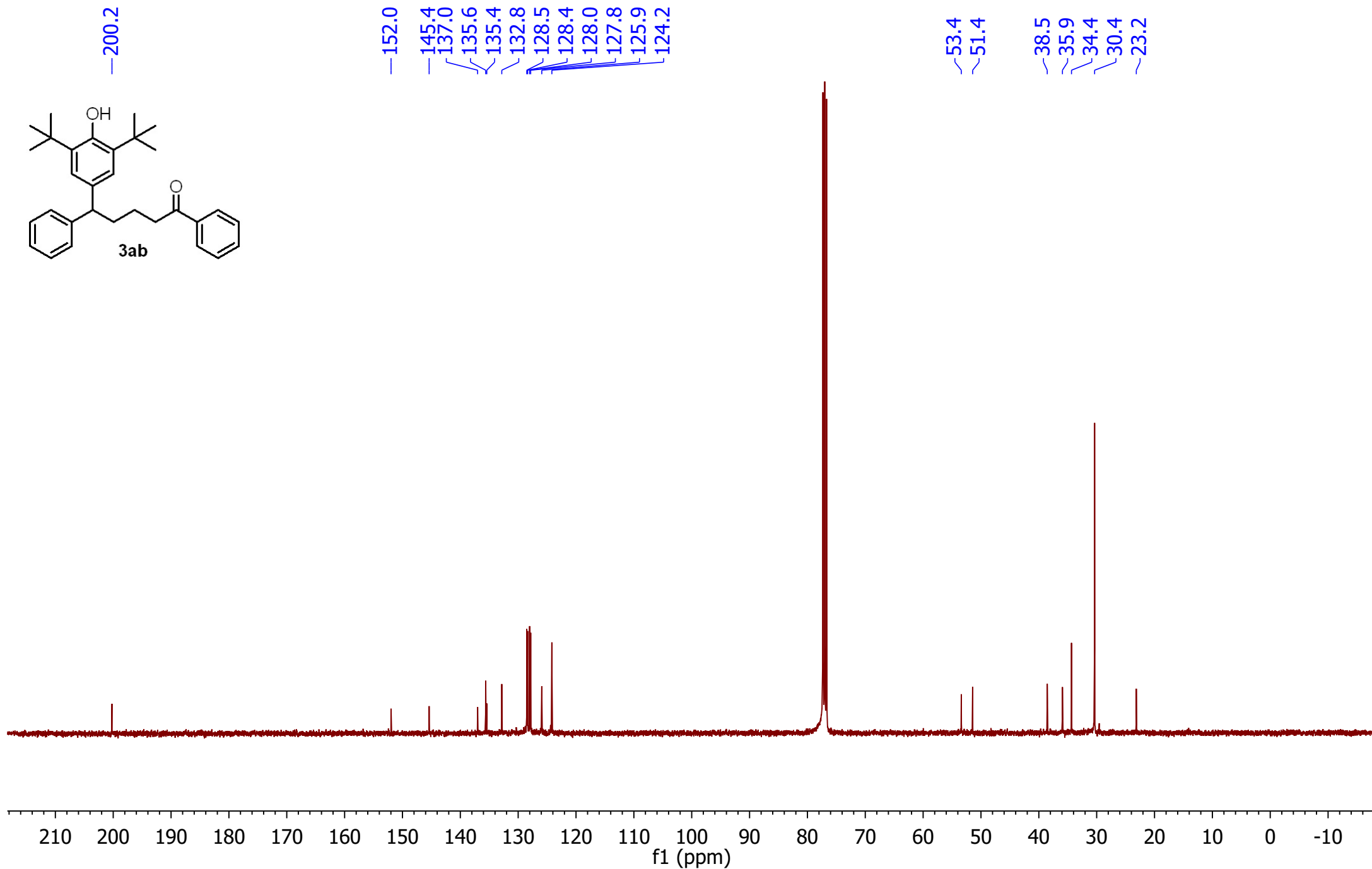
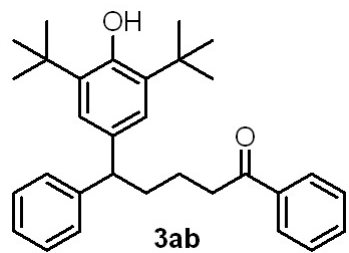
**<sup>1</sup>H(CDCI<sub>3</sub>, 400 MHz)**

7.82  
7.81  
7.81  
7.80  
7.79  
7.47  
7.47  
7.46  
7.44  
7.43  
7.37  
7.36  
7.35  
7.33  
7.22  
7.22  
7.20  
7.20  
7.19  
7.18  
7.17  
7.12  
7.10  
7.10  
7.09  
7.08  
7.08  
7.07  
6.96  
6.94  
4.94  
3.79  
3.77  
2.90  
2.88  
2.86  
2.08  
2.06  
2.06  
2.05  
2.04  
2.03  
2.02  
2.01  
2.00  
1.99  
1.98  
1.68  
1.67  
1.65  
1.63  
1.61  
1.32



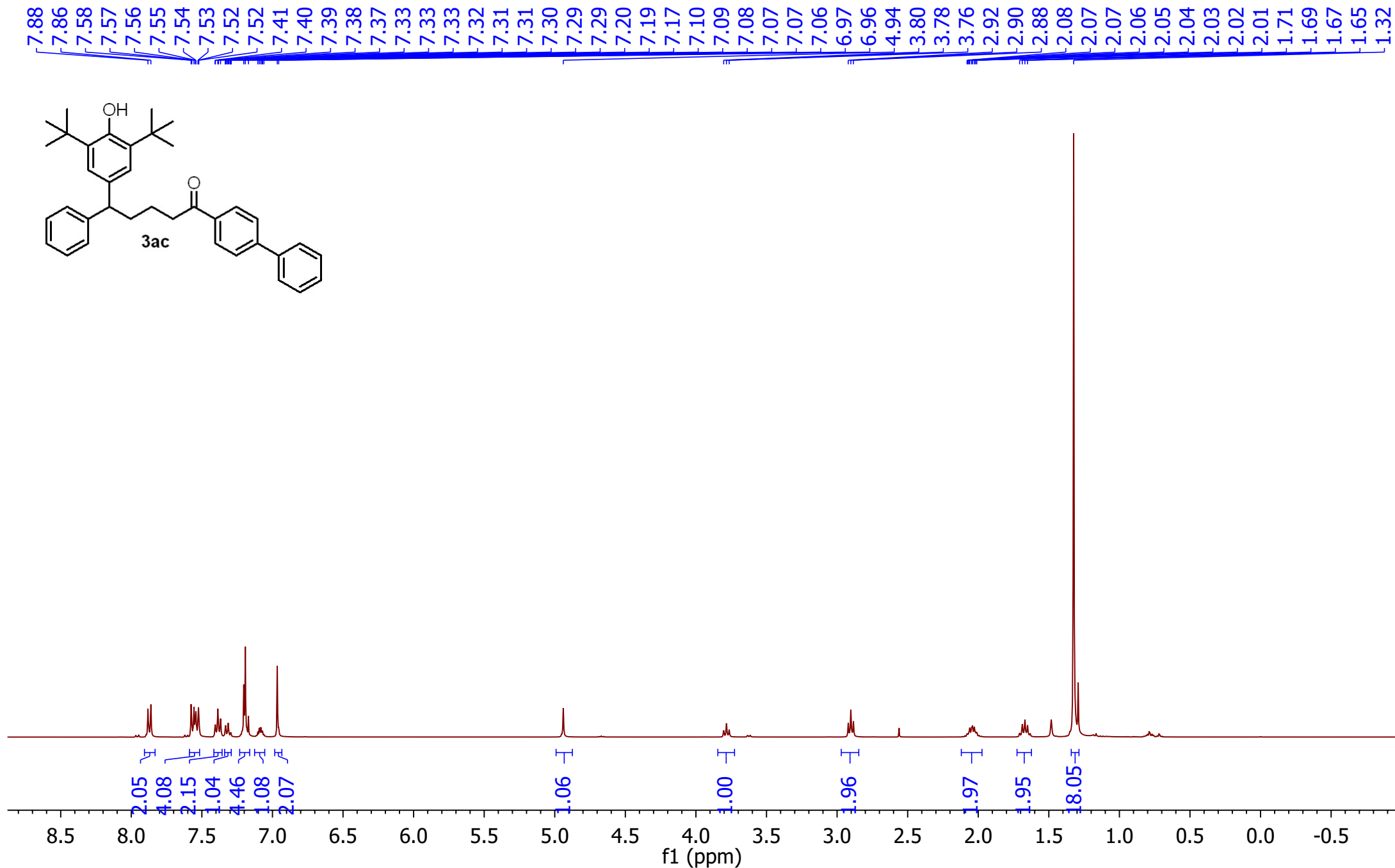
<sup>1</sup>H NMR Spectrum of **3ab**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



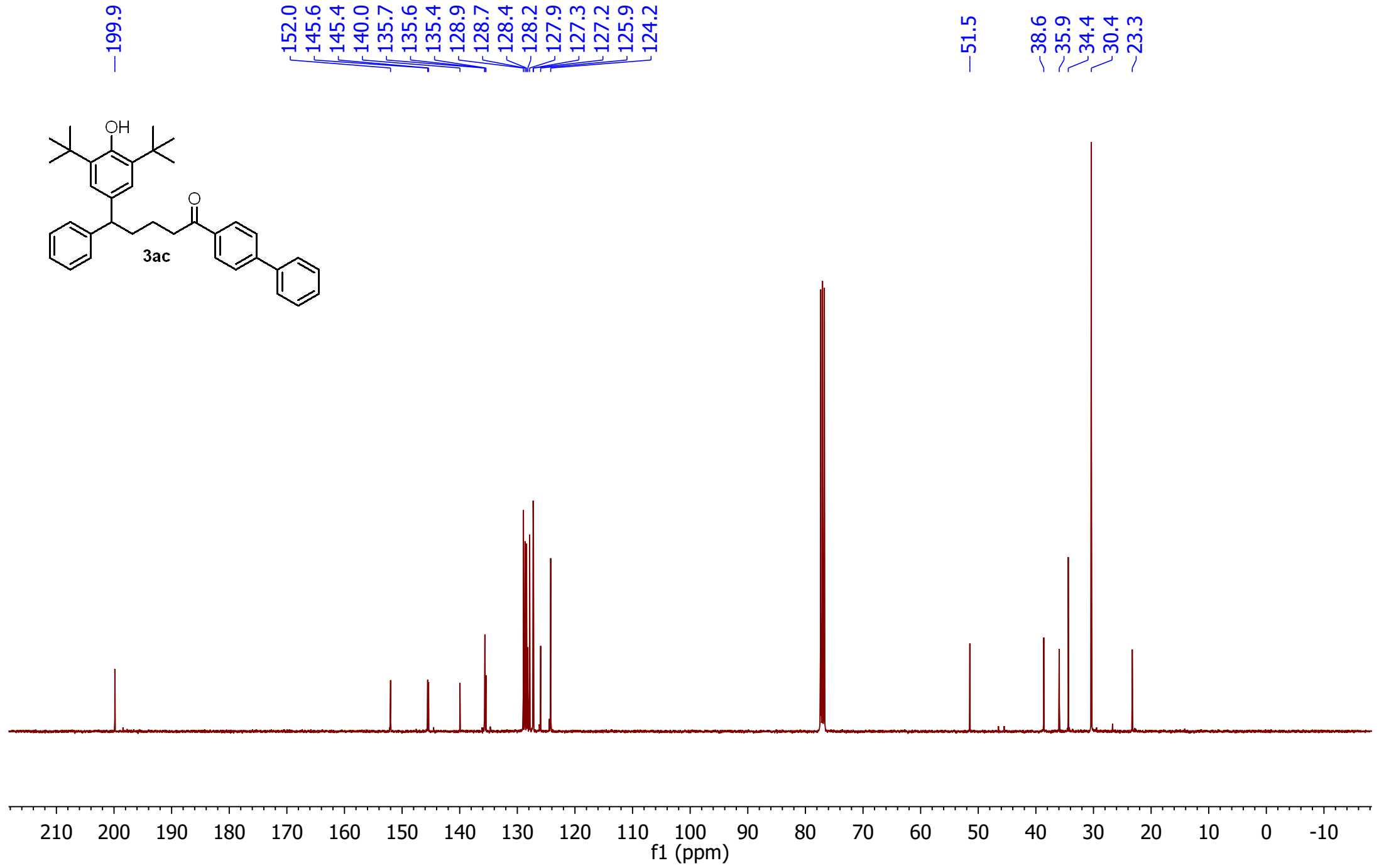
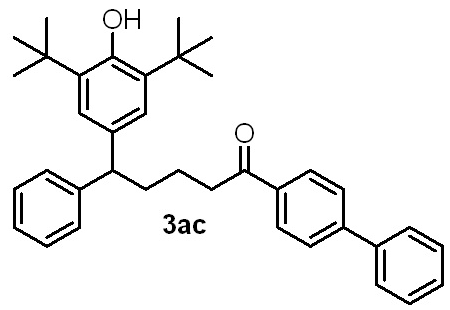
<sup>13</sup>C NMR Spectrum of **3ab**

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



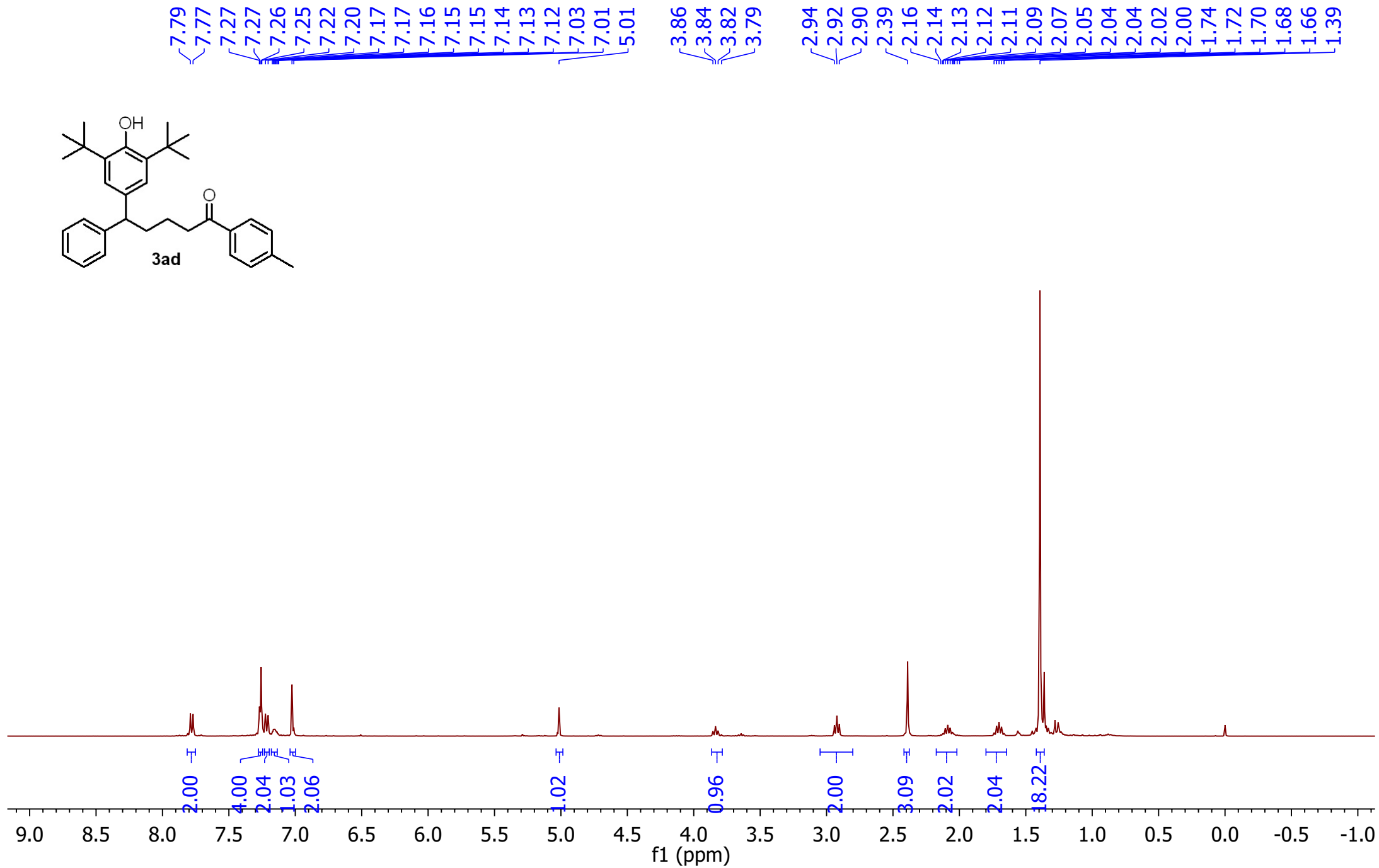
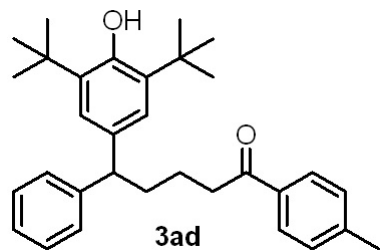
<sup>1</sup>H NMR Spectrum of **3ac**

**$^{13}\text{C}$ ( $\text{CDCl}_3$ , 101 MHz)**



$^{13}\text{C}$  NMR Spectrum of **3ac**

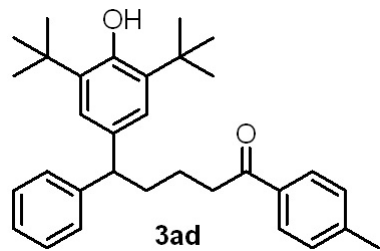
**<sup>1</sup>H (CDCl<sub>3</sub>, 400 MHz)**



<sup>1</sup>H NMR Spectrum of **3ad**

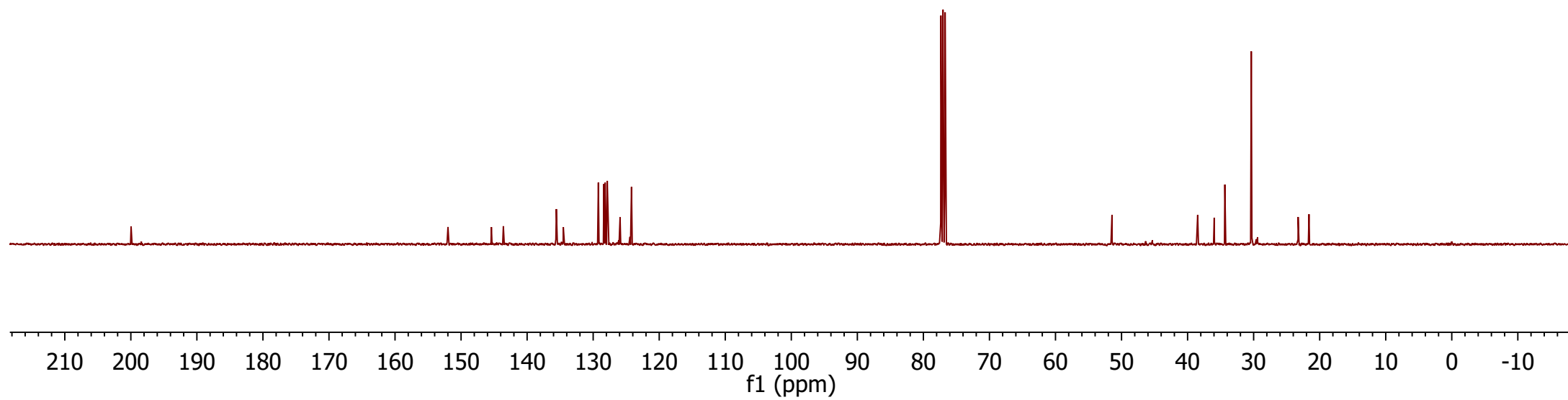


**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



152.0  
145.4  
143.6  
135.6  
135.5  
134.5  
129.2  
128.4  
128.2  
127.9  
125.9  
124.2

51.4  
38.5  
36.0  
34.4  
30.4  
23.3  
21.6



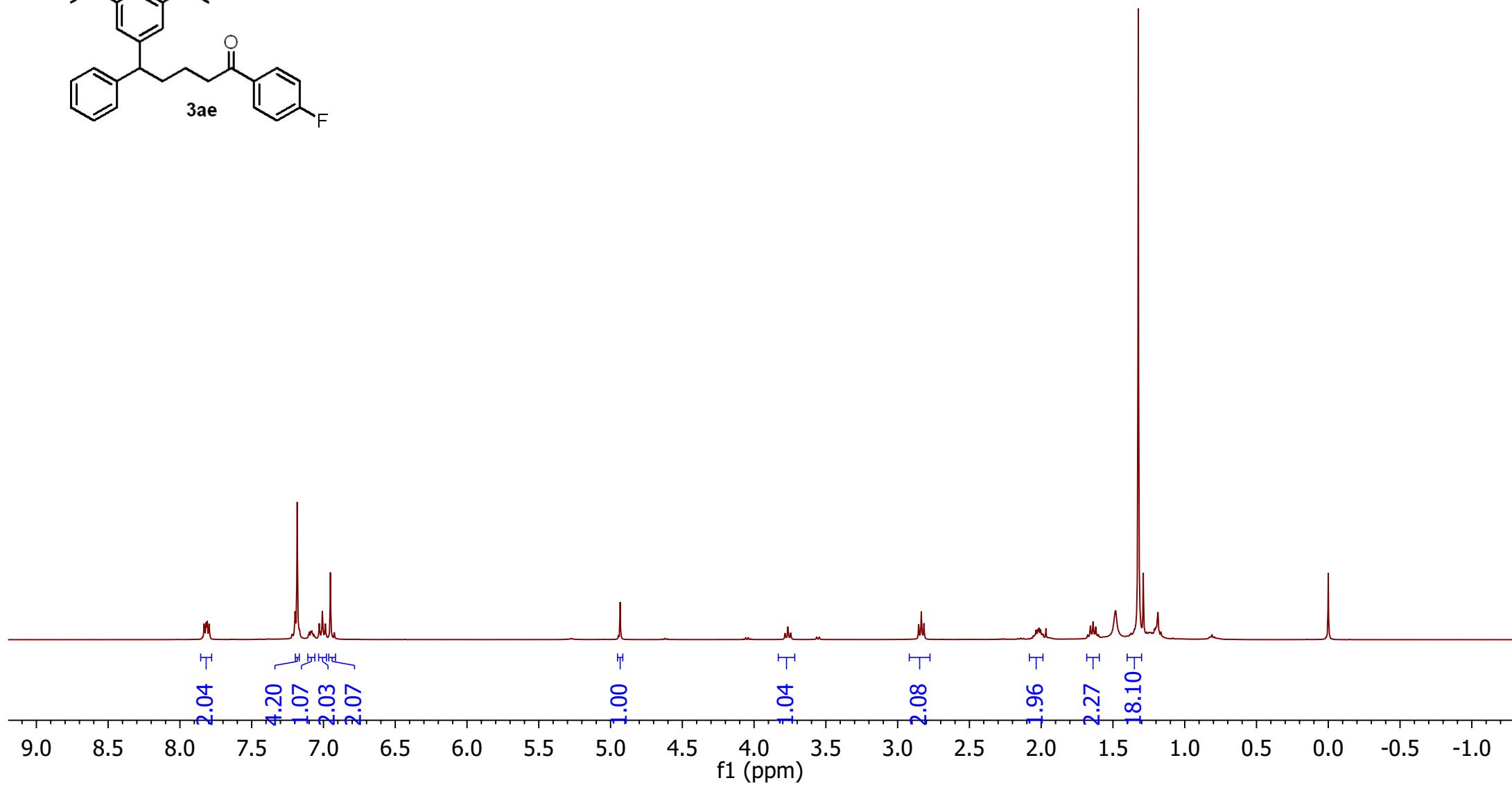
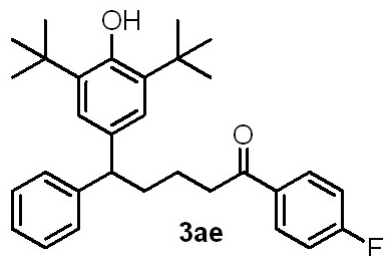
<sup>13</sup>C NMR Spectrum of **3ad**

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

7.83  
7.83  
7.82  
7.81  
7.81  
7.80  
7.80  
7.18  
7.10  
7.10  
7.09  
7.08  
7.08  
7.07  
7.07  
7.06  
7.03  
7.01  
7.00  
6.99  
6.95  
6.94  
6.92  
4.93

3.78  
3.76  
3.75

2.85  
2.84  
2.82  
2.05  
2.05  
2.04  
2.04  
2.02  
2.02  
2.00  
1.99  
1.99  
1.68  
1.66  
1.64  
1.62  
1.60  
1.32



<sup>1</sup>H NMR Spectrum of **3ae**

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

—197.6

~165.9

~163.3

—151.0

—144.3

—134.7

—134.4

—129.7

—129.6

—127.4

—126.8

—124.9

—123.2

—114.7

—114.5

—50.4

~37.5

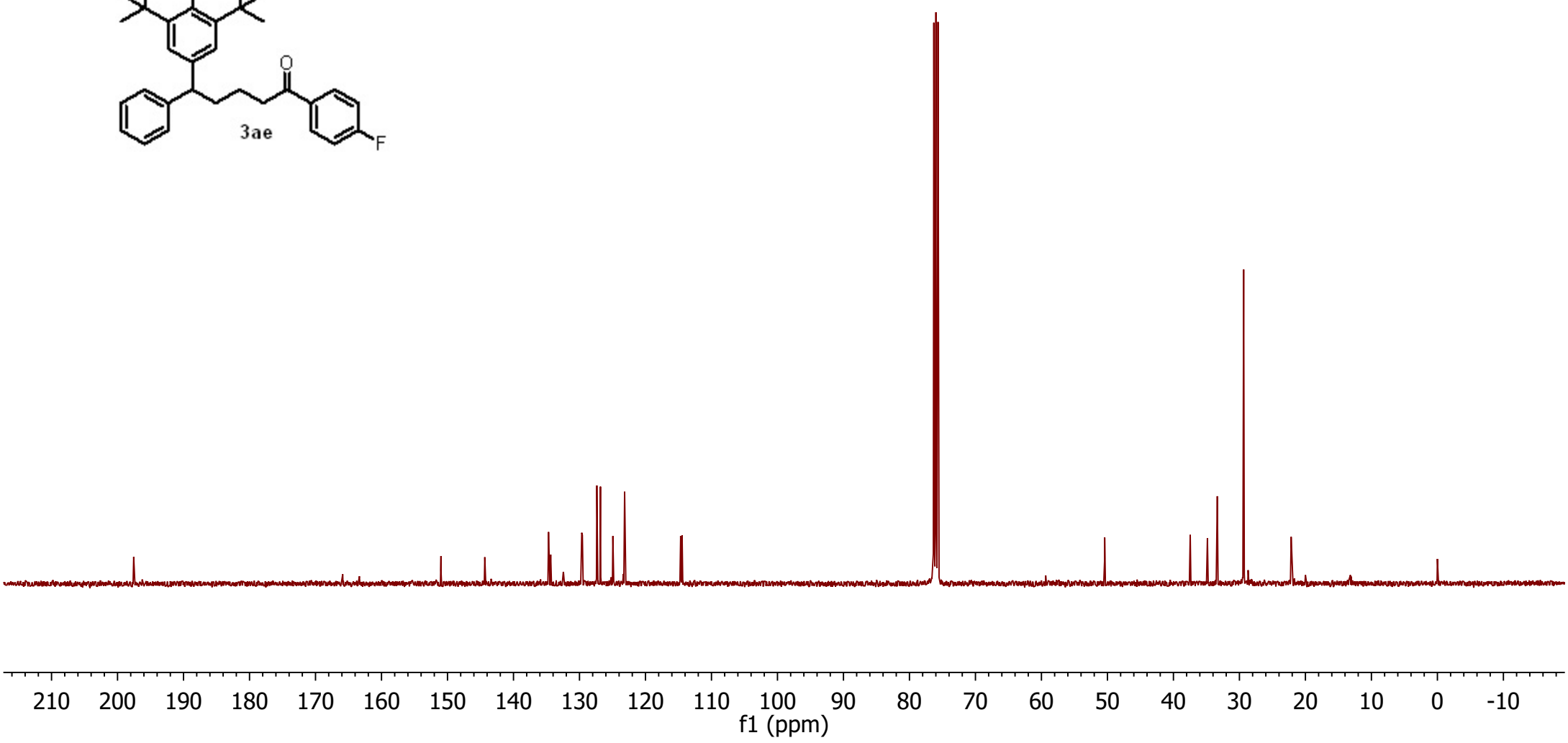
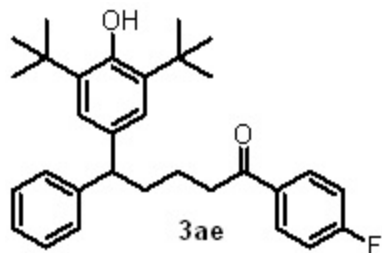
~34.9

~33.4

~29.4

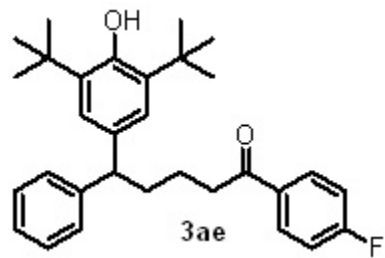
~29.3

~22.2

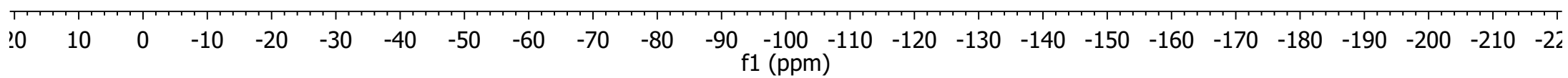


<sup>13</sup>C NMR Spectrum of 3ae

**<sup>19</sup>F(CDCl<sub>3</sub>, 376 MHz)**



--105.80

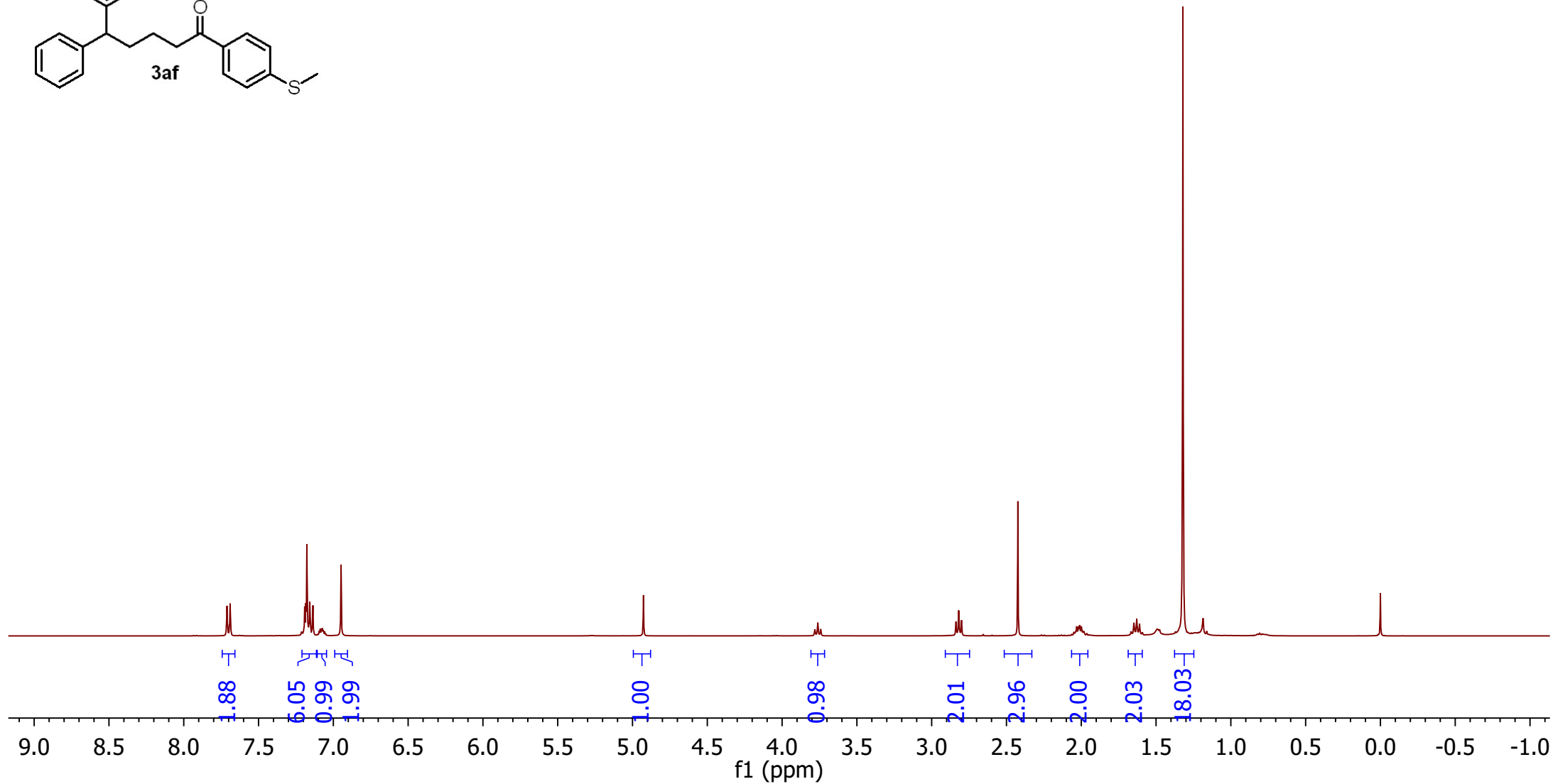
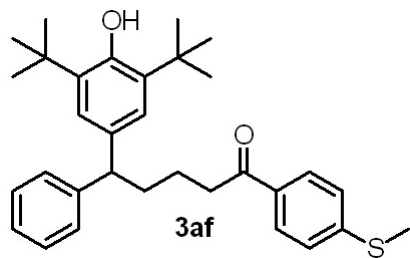


<sup>19</sup>F NMR Spectrum of **3ae**

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

7.71 7.71 7.69 7.69 7.19 7.18 7.18 7.17 7.16 7.16 7.15 7.14 7.14 7.09 7.09 7.08 7.07 7.07 7.07 7.06 7.05 6.95 4.93 3.78 3.76 3.74

2.84 2.82 2.80 2.42 2.05 2.04 2.04 2.03 2.02 2.01 2.00 1.99 1.98 1.96 1.67 1.66 1.65 1.63 1.61 1.59 1.32



<sup>1</sup>H NMR Spectrum of **3af**

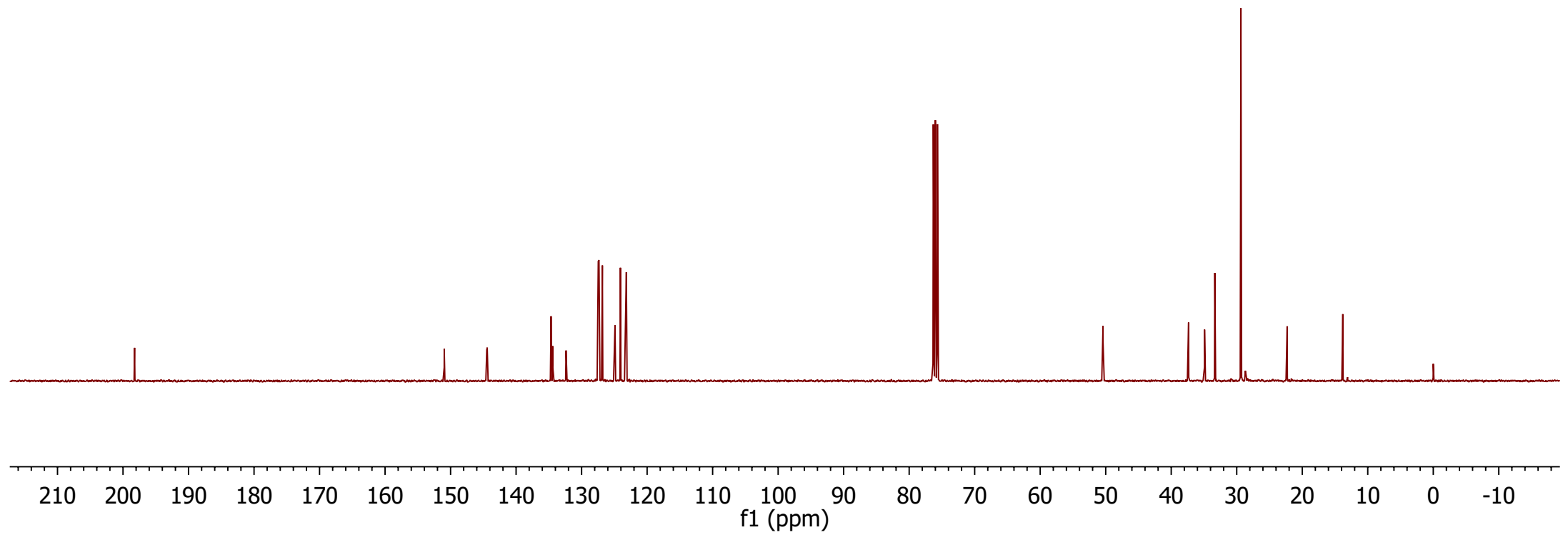
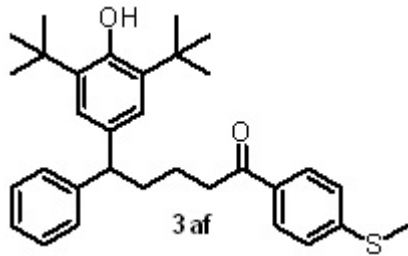
<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)

—198.2

151.0  
144.5  
144.4  
134.7  
134.4  
132.4  
127.5  
127.3  
126.8  
124.9  
124.1  
123.2

—50.4

37.3  
34.9  
33.3  
29.4  
22.3  
13.8



<sup>13</sup>C NMR Spectrum of 3af

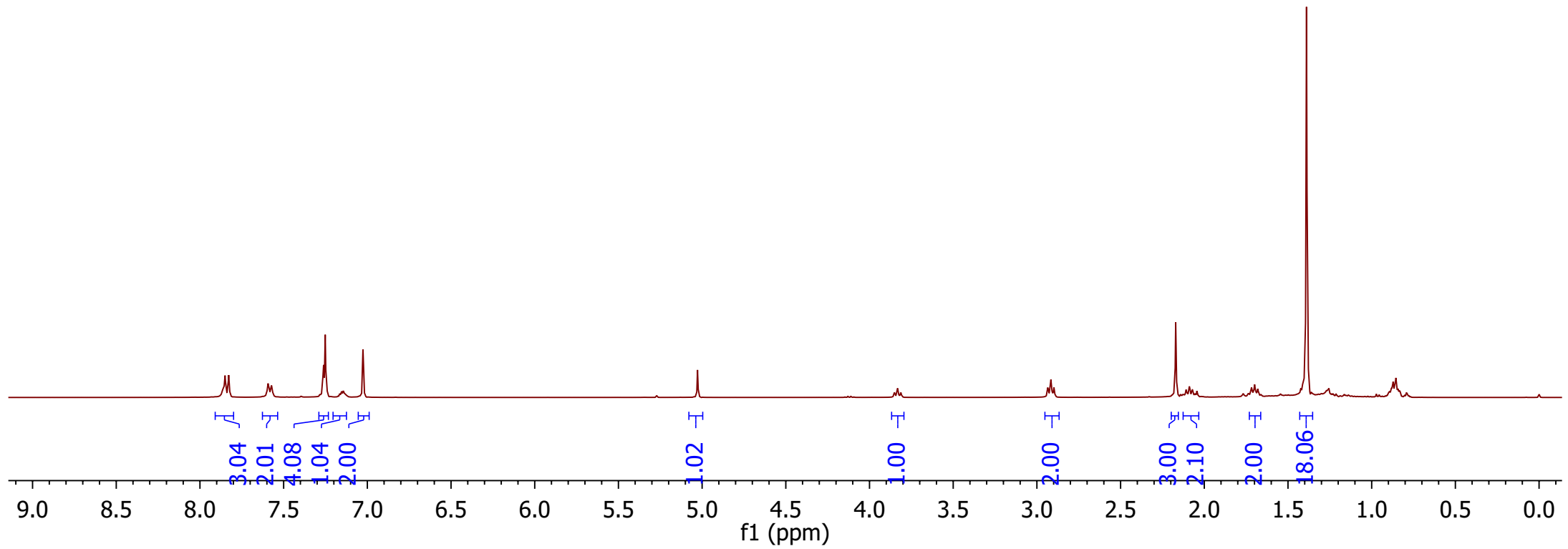
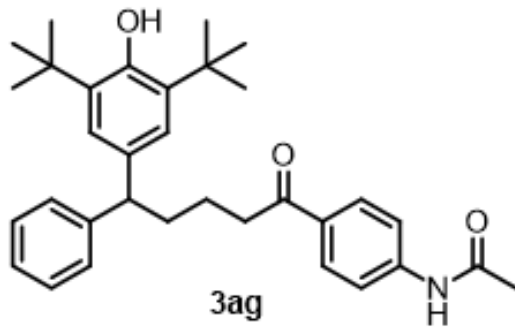
**<sup>1</sup>H (CDCl<sub>3</sub>, 400 MHz)**

7.86  
7.86  
7.85  
7.85  
7.83  
7.59  
7.57  
7.26  
7.26  
7.25  
7.24  
7.24  
7.16  
7.15  
7.14  
7.03

—5.03

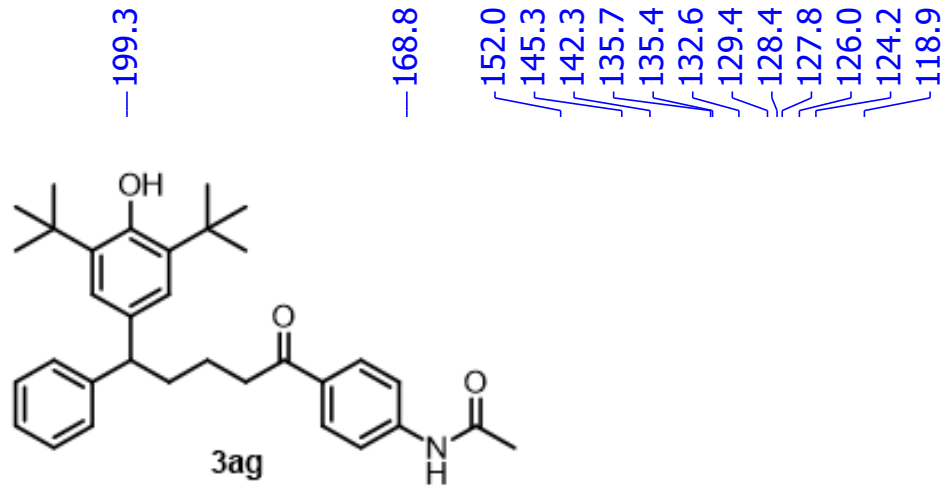
3.85  
3.83  
3.81

2.93  
2.92  
2.90  
2.17  
2.14  
2.13  
2.12  
2.11  
2.09  
2.07  
2.05  
2.04  
1.72  
1.70  
1.68  
1.39



<sup>1</sup>H NMR Spectrum of **3ag**

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



—199.3

—168.8

152.0

145.3

142.3

135.7

135.4

132.6

129.4

128.4

127.8

126.0

124.2

118.9

—51.4

38.4

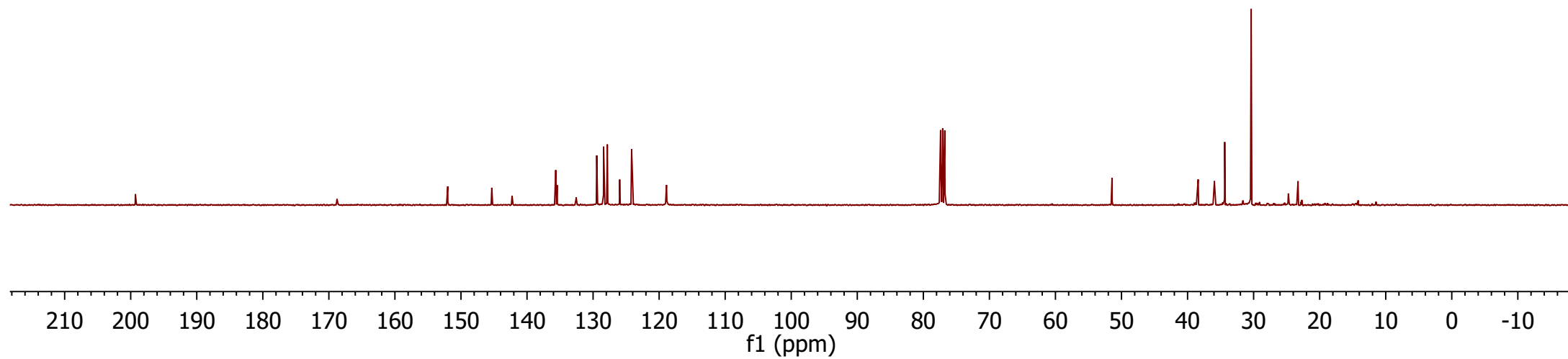
35.9

34.4

30.4

24.7

23.3



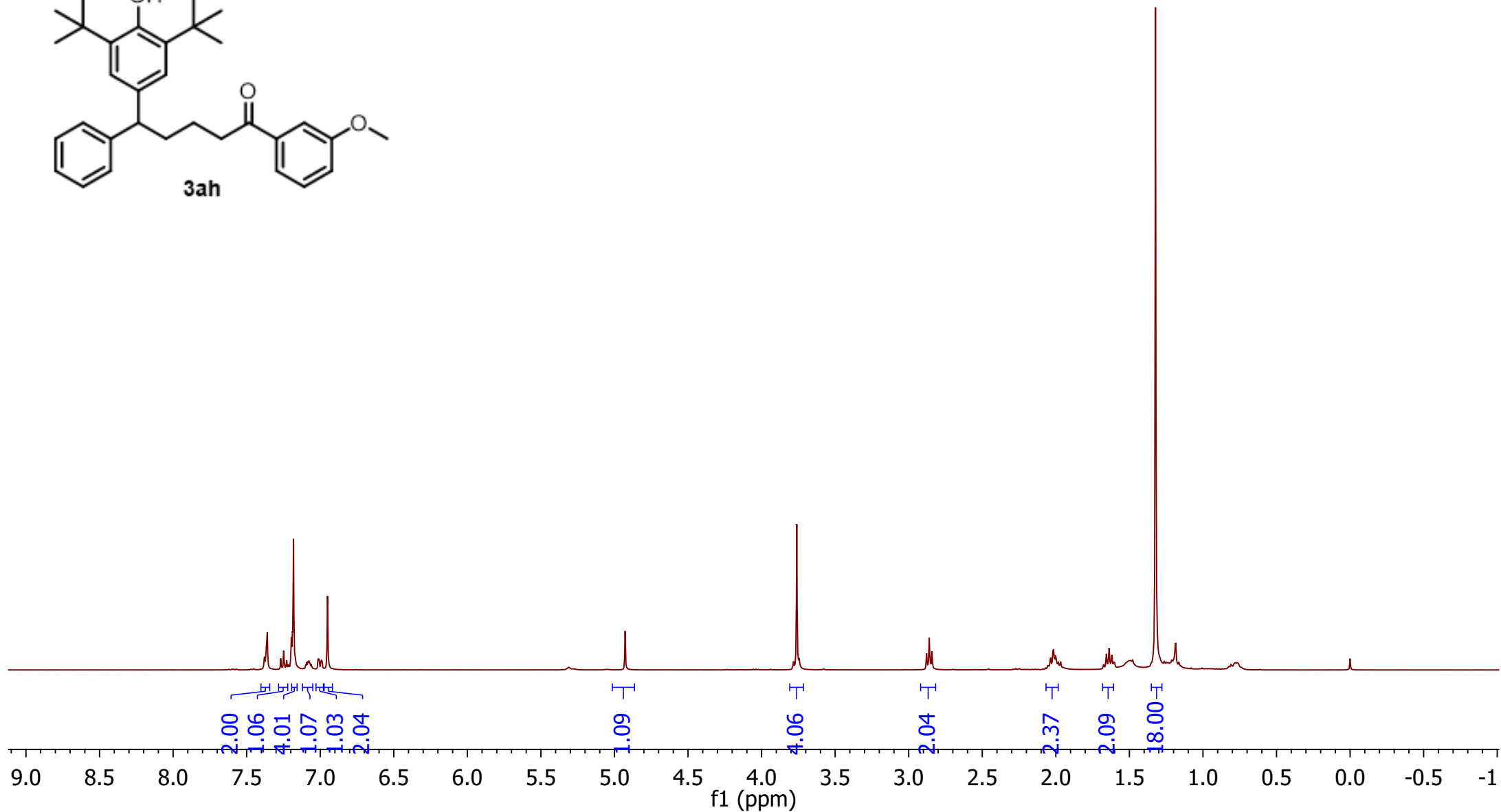
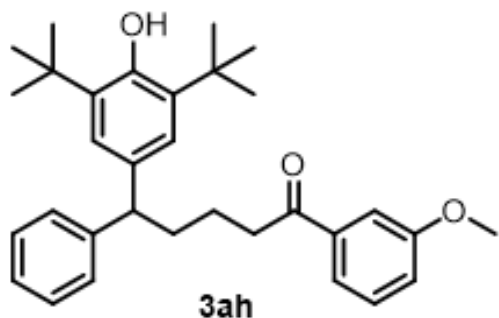
<sup>13</sup>C NMR Spectrum of **3ag**



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

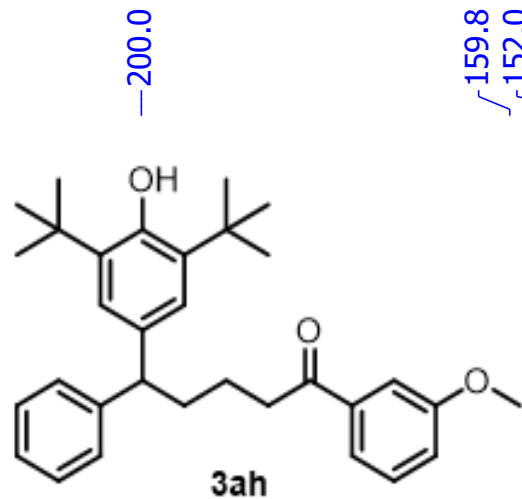
7.38  
7.38  
7.37  
7.37  
7.36  
7.36  
7.27  
7.25  
7.23  
7.20  
7.19  
7.18  
7.11  
7.10  
7.09  
7.08  
7.08  
7.07  
7.06  
7.06  
7.01  
7.01  
7.00  
6.99  
6.99  
6.95  
4.93  
3.76

2.88  
2.86  
2.84  
2.05  
2.05  
2.04  
2.02  
2.02  
2.00  
1.99  
1.98  
1.68  
1.66  
1.64  
1.62  
1.60  
1.32



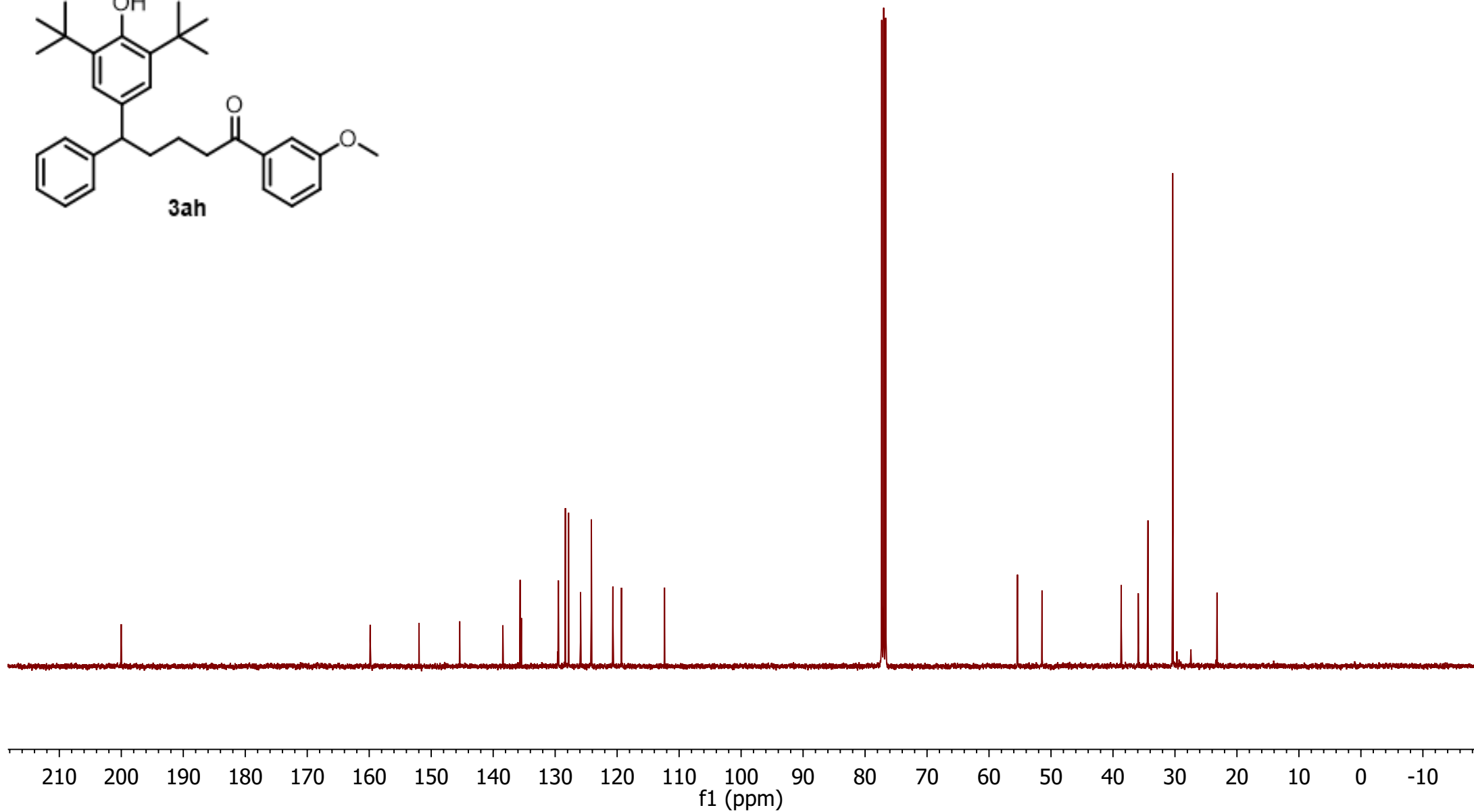
<sup>1</sup>H NMR Spectrum of **3ah**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



159.8  
152.0  
145.4  
138.4  
135.7  
135.4  
129.5  
128.4  
127.8  
125.9  
124.2  
120.7  
119.3  
112.4

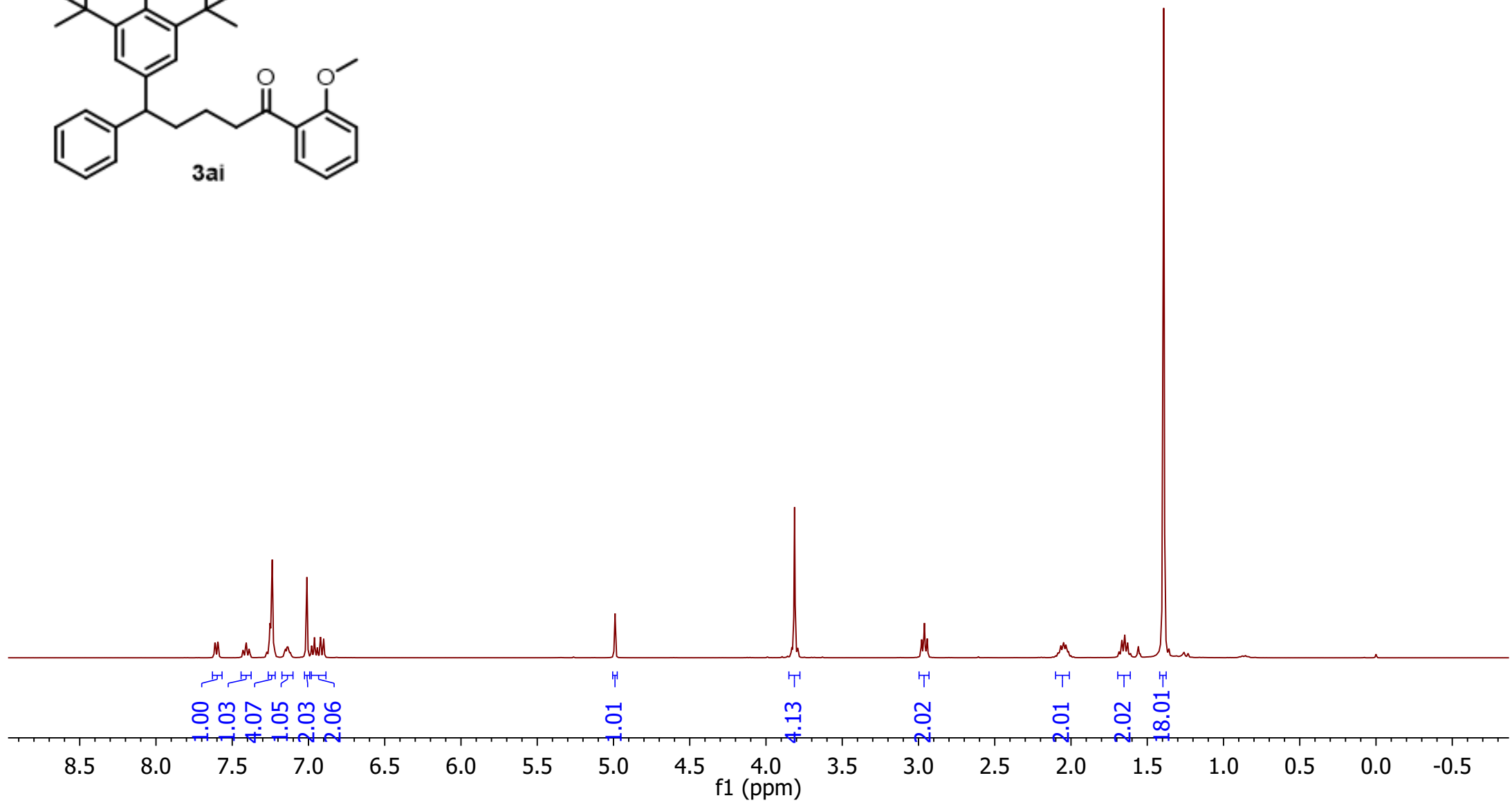
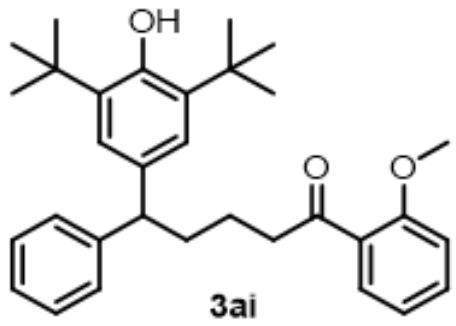
55.4  
51.4  
38.7  
35.9  
34.4  
30.4  
23.2



<sup>13</sup>C NMR Spectrum of **3ah**

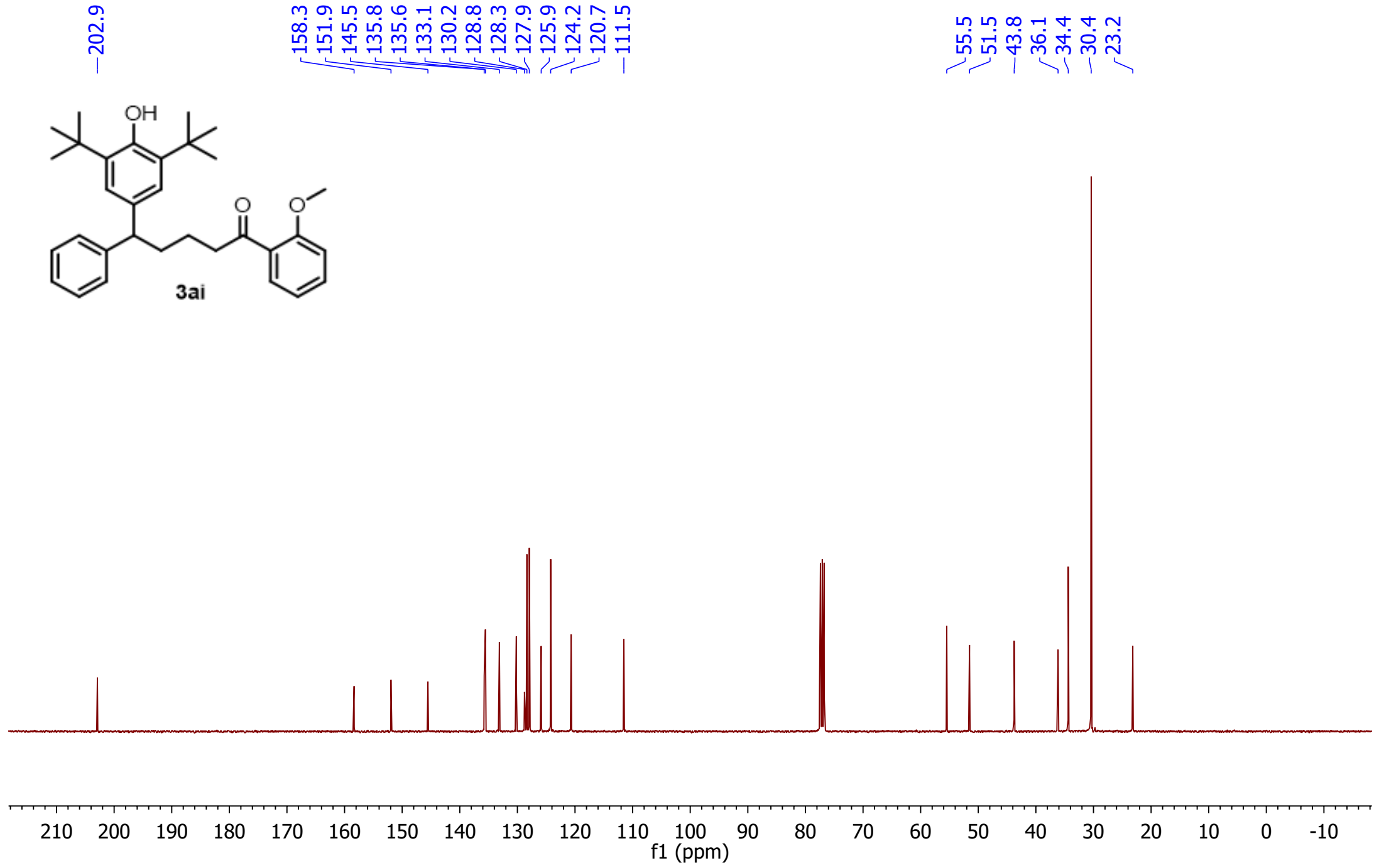
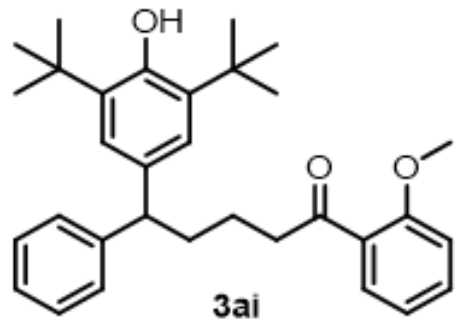
**<sup>1</sup>H (CDCl<sub>3</sub>, 400 MHz)**

7.61 7.61 7.59 7.59 7.43 7.42 7.41 7.41 7.39 7.39 7.25 7.24 7.24 7.16 7.15 7.14 7.13 7.13 7.12 7.01 6.98 6.96 6.94 6.92 6.90 4.99 3.81 2.98 2.96 2.94 2.10 2.09 2.08 2.07 2.07 2.05 2.05 2.03 2.02 2.02 1.69 1.67 1.65 1.63 1.61 1.39



<sup>1</sup>H NMR Spectrum of **3ai**

**<sup>13</sup>C (CDCl<sub>3</sub>, 101 MHz)**



<sup>13</sup>C NMR Spectrum of **3ai**



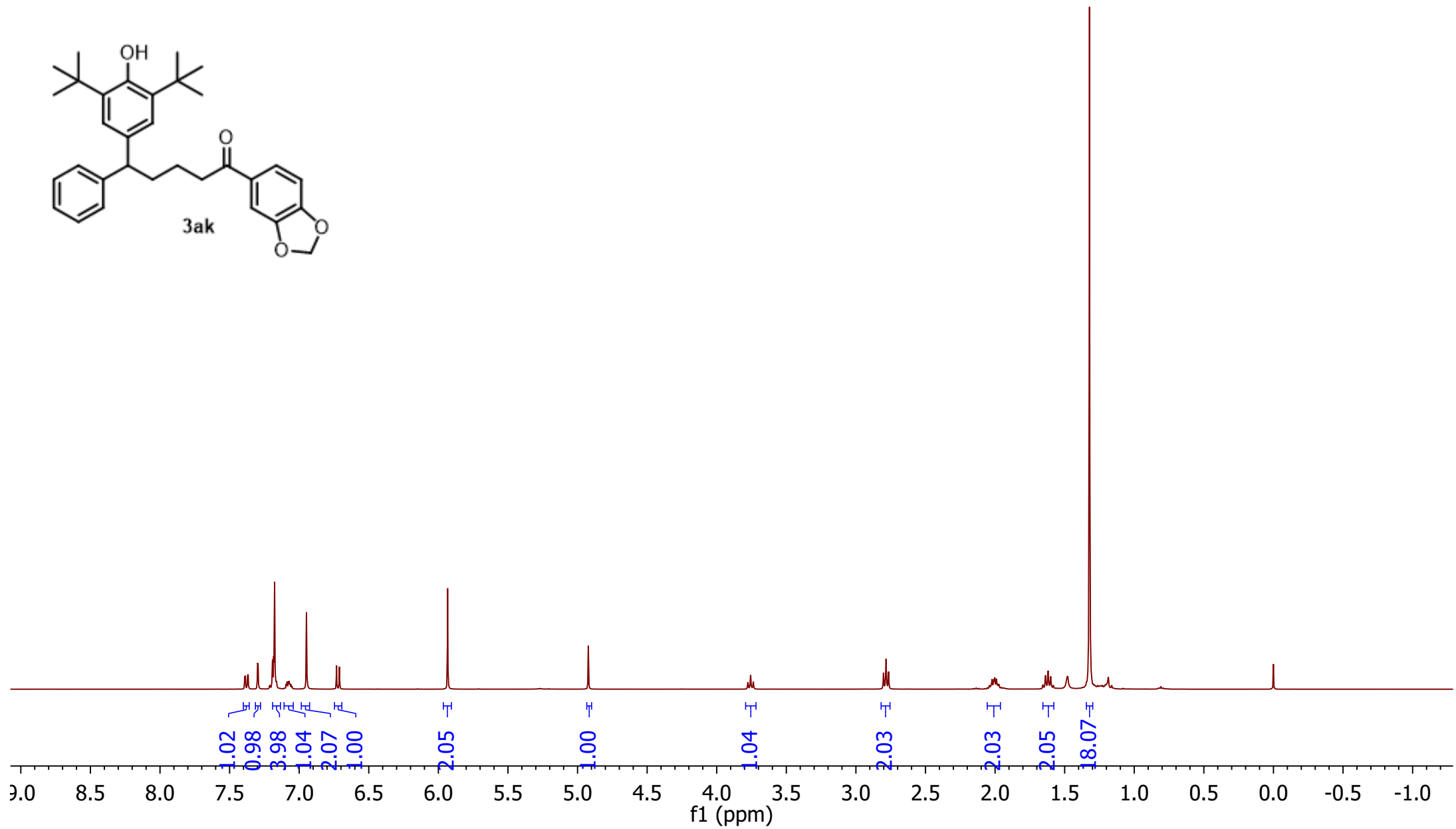
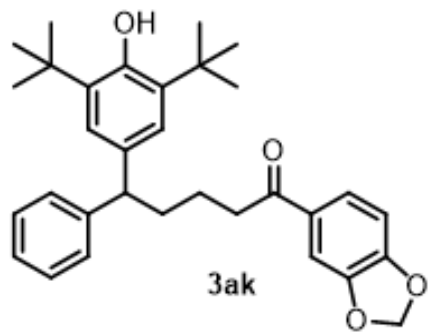


**<sup>1</sup>H(CDCI<sub>3</sub>, 400 MHz)**

7.39  
7.39  
7.37  
7.37  
7.30  
7.29  
7.18  
7.18  
7.17  
7.16  
7.09  
7.09  
7.08  
7.07  
7.07  
7.06  
7.06  
7.05  
6.95  
6.73  
6.71  
5.93  
4.92

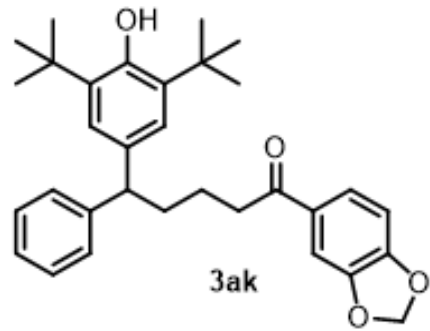
3.78  
3.76  
3.74

2.80  
2.78  
2.77  
2.06  
2.04  
2.04  
2.03  
2.02  
2.01  
2.00  
1.99  
1.98  
1.97  
1.96  
1.66  
1.64  
1.62  
1.60  
1.58  
1.32



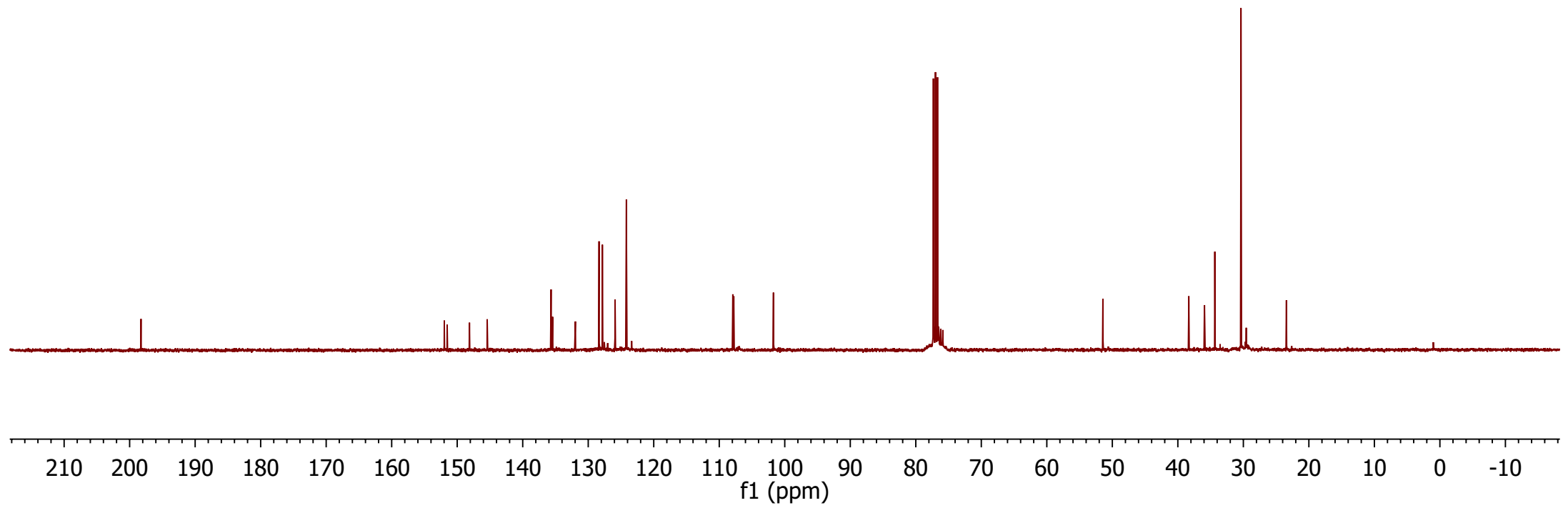
<sup>1</sup>H NMR Spectrum of **3ak**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



152.0  
151.5  
148.1  
145.4  
135.7  
135.4  
132.0  
128.3  
127.8  
125.9  
124.2  
107.9  
107.8  
101.7

51.4  
38.3  
35.9  
34.4  
30.4  
29.6  
23.4

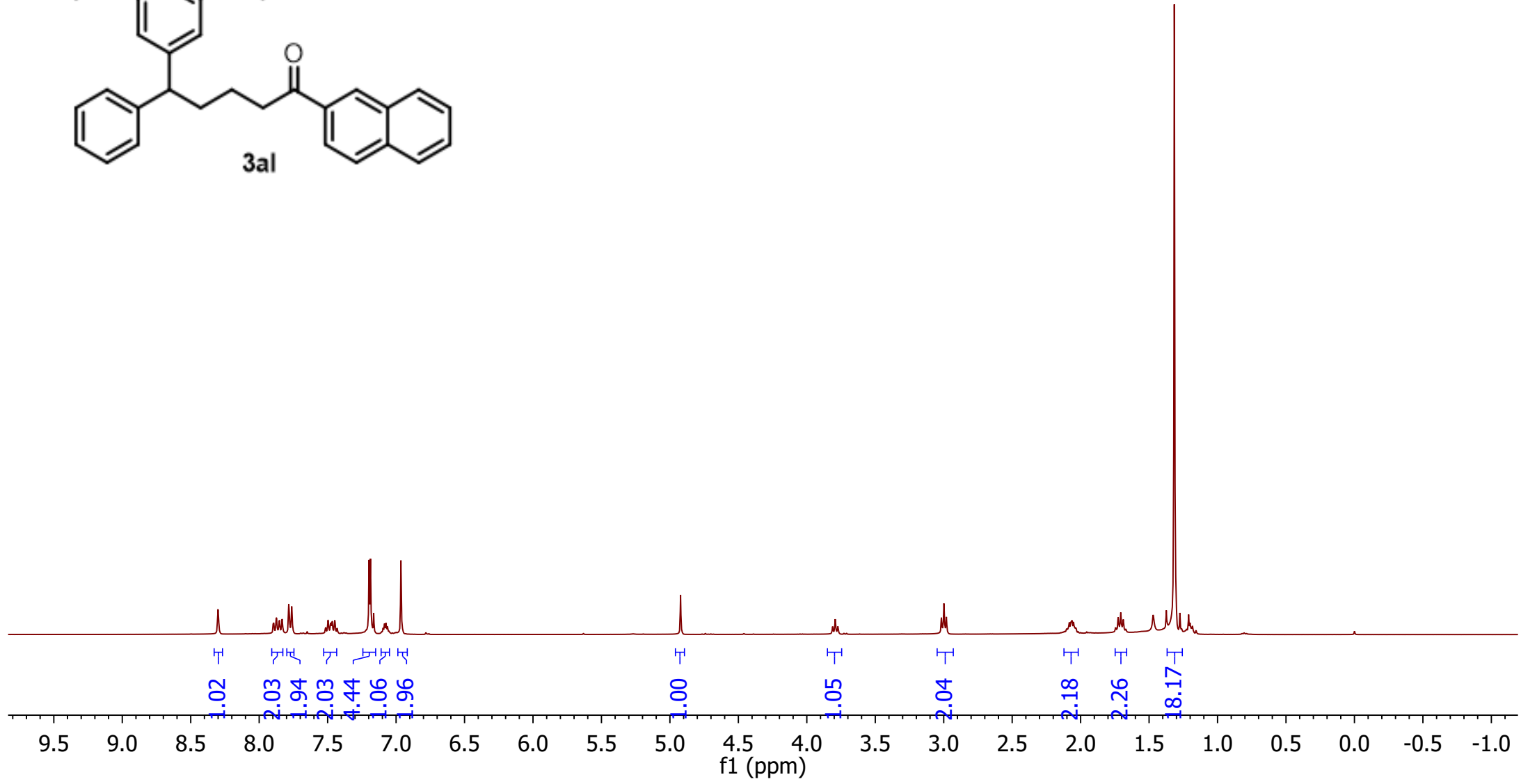
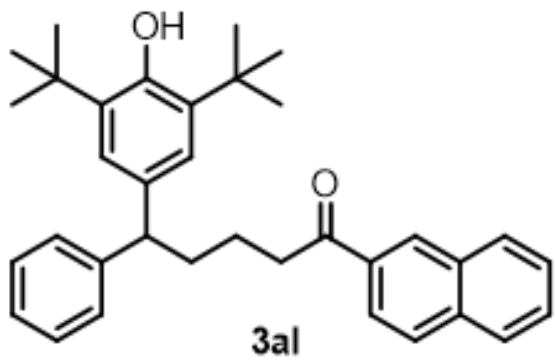


<sup>13</sup>C NMR Spectrum of **3ak**



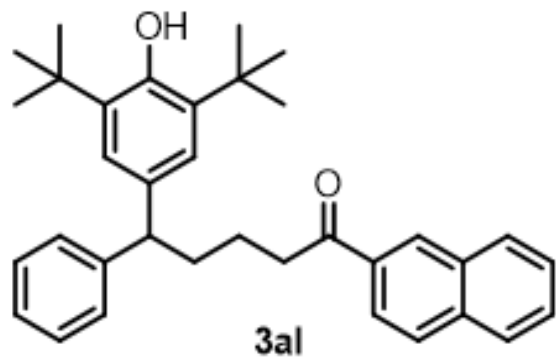
**<sup>1</sup>H(CDCl<sub>3</sub>, 400 MHz)**

8.30 8.30 7.90 7.89 7.88 7.87 7.85 7.83 7.78 7.76 7.52 7.51 7.50 7.50 7.48 7.48 7.47 7.47 7.45 7.43 7.20 7.19 7.11 7.10 7.08 7.07 6.96 4.92 3.81 3.79 3.77 3.02 3.00 2.98 2.10 2.10 2.09 2.08 2.07 2.06 2.05 2.04 2.03 1.74 1.73 1.71 1.69 1.67 1.32



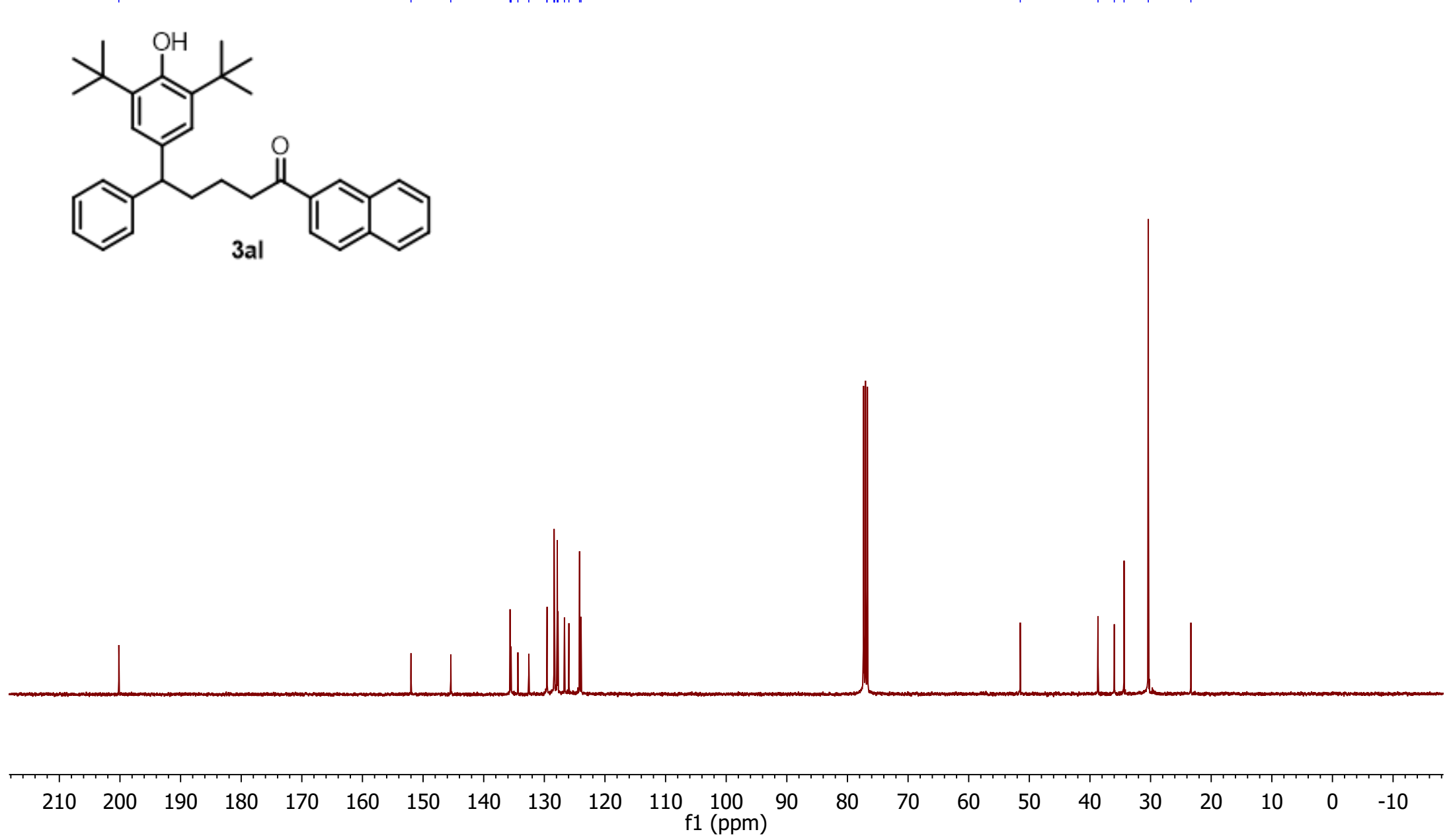
<sup>1</sup>H NMR Spectrum of **3al**

**<sup>13</sup>H(CDCI<sub>3</sub>, 101 MHz)**



— 200.2  
— 152.0  
— 145.4  
— 135.7  
— 135.5  
— 135.5  
— 134.4  
— 132.6  
— 129.6  
— 129.5  
— 128.4  
— 128.4  
— 128.3  
— 127.9  
— 127.7  
— 126.7  
— 125.9  
— 124.2  
— 124.0

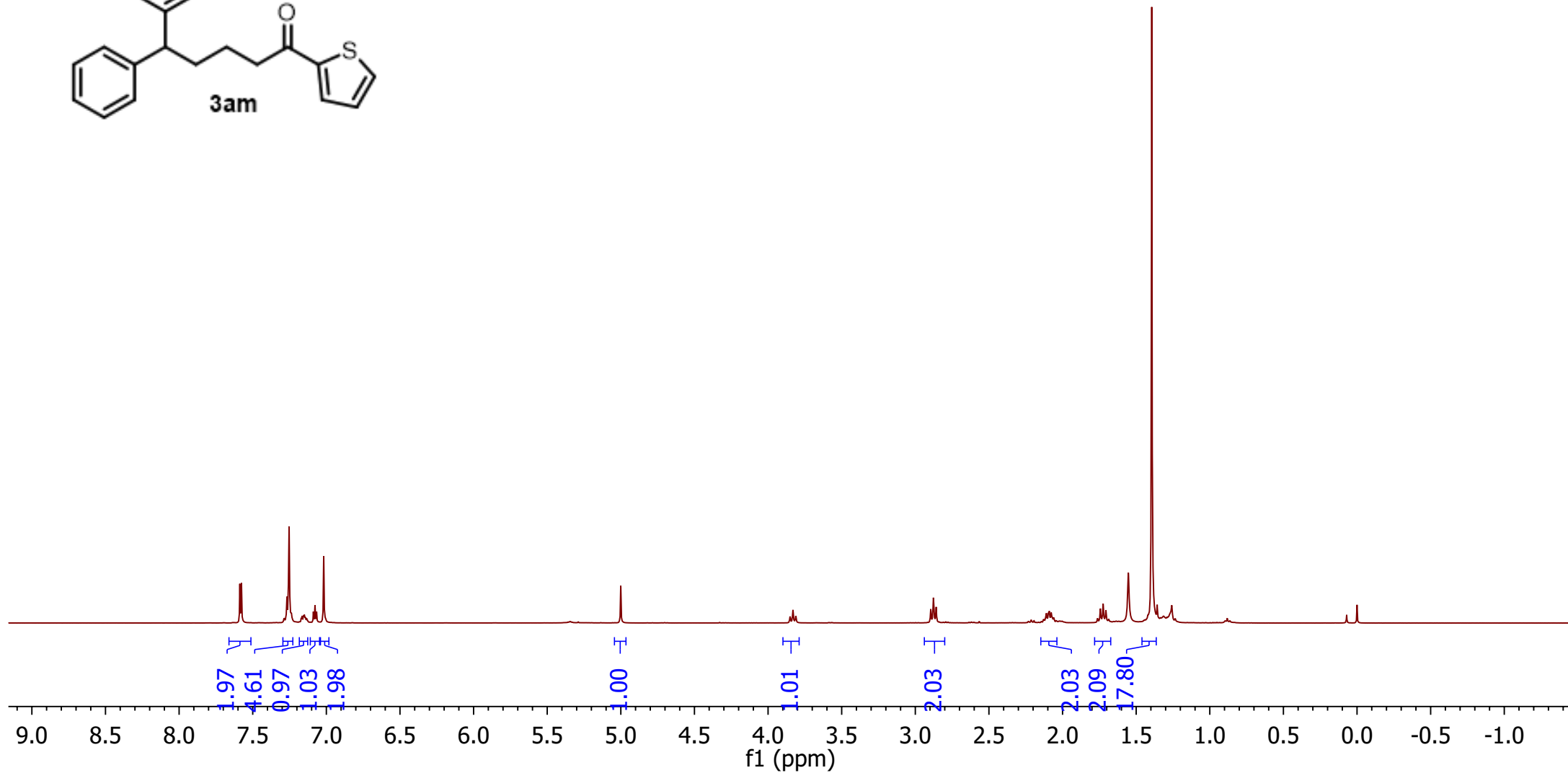
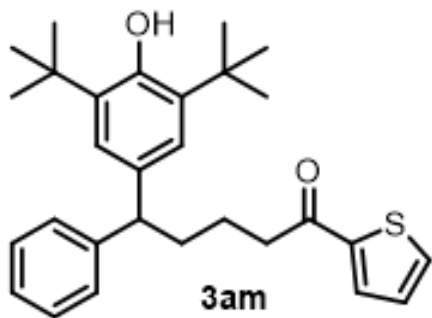
— 51.5  
— 38.7  
— 36.0  
— 34.4  
— 30.4  
— 23.3



<sup>13</sup>C NMR Spectrum of 3al

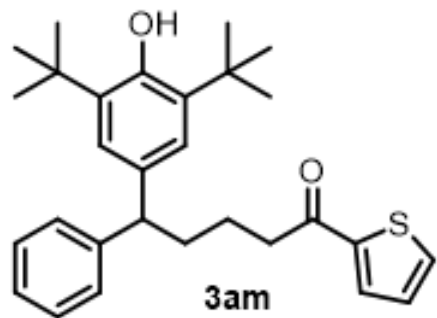
**<sup>1</sup>H(CDCl<sub>3</sub>, 400 MHz)**

7.59 7.58 7.29 7.28 7.28 7.27 7.27 7.26 7.25 7.25 7.24 7.24 7.23 7.17 7.16 7.16 7.15 7.14 7.14 7.13 7.13 7.09 7.08 7.07 7.02 5.00 3.85 3.83 3.81 2.90 2.88 2.86 2.14 2.13 2.12 2.12 2.11 2.10 2.09 2.08 2.07 2.06 2.04 2.04 1.76 1.74 1.72 1.71 1.69 1.39



<sup>1</sup>H NMR Spectrum of **3am**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**

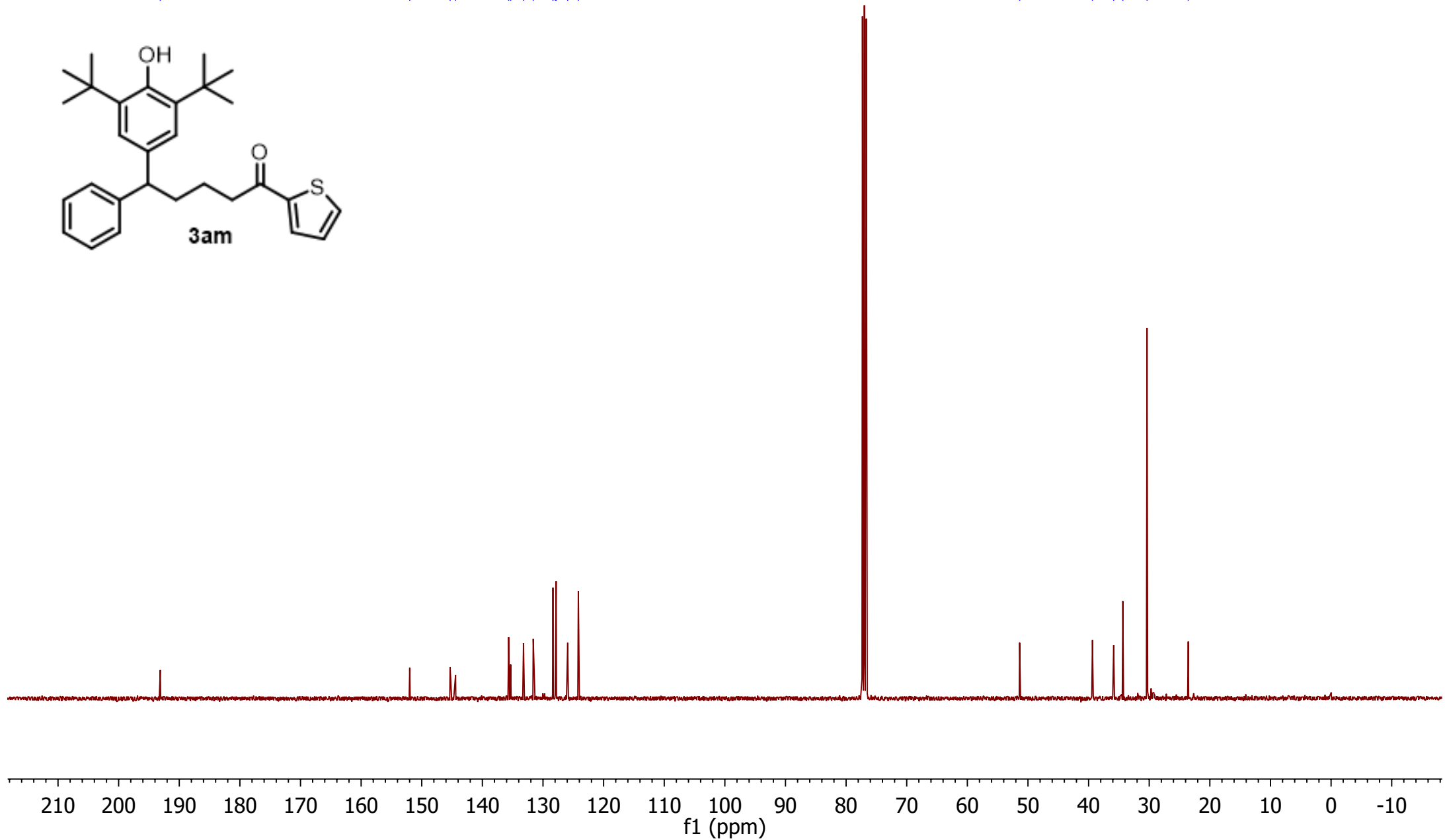


— 193.1

~ 152.0  
~ 145.3  
~ 144.4  
~ 135.7  
~ 135.3  
~ 133.2  
~ 131.6  
~ 128.4  
~ 128.0  
~ 127.8  
~ 125.9  
~ 124.2

— 51.4

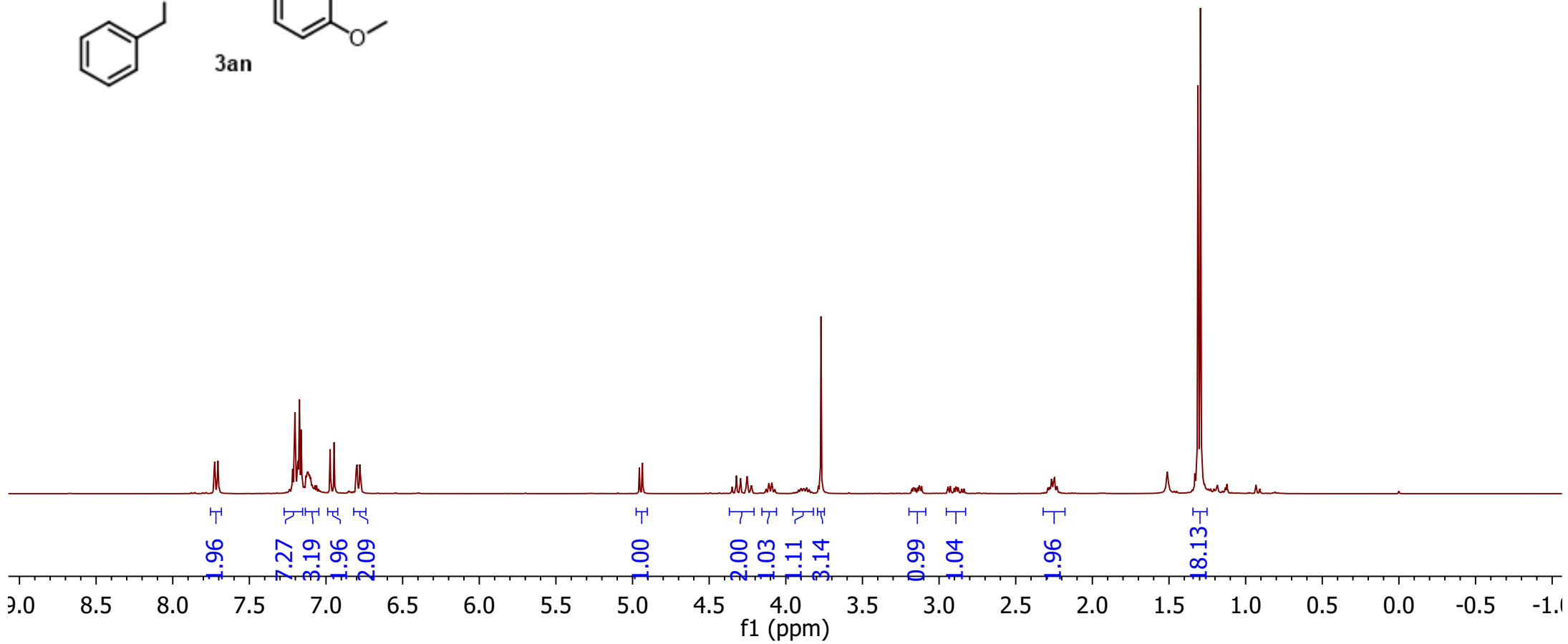
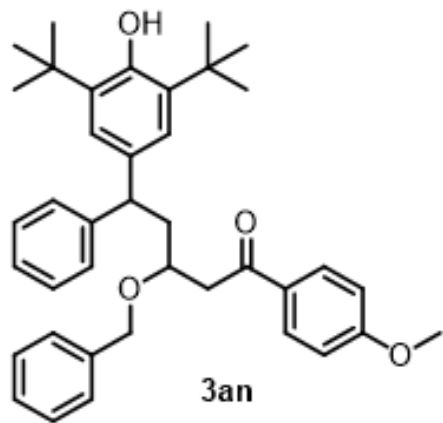
~ 39.4  
~ 35.9  
~ 34.3  
~ 30.4  
~ 23.6



<sup>13</sup>C NMR Spectrum of **3am**

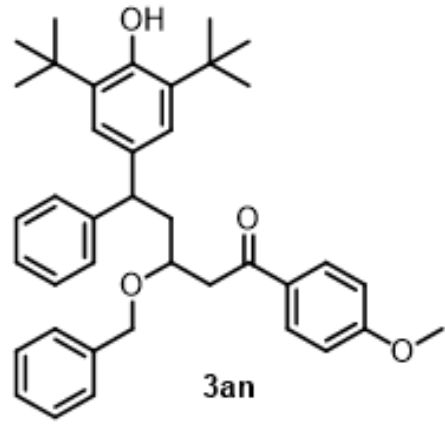
**<sup>1</sup>H(CDCI<sub>3</sub>, 400 MHz)**

7.73 7.73 7.71 7.70 7.22 7.21 7.20 7.20 7.19 7.19 7.18 7.17 7.16 7.16 7.13 7.13 7.12 7.12 7.11 7.11 7.10 7.10 7.10 7.09 7.08 7.07 7.06 6.97 6.95 6.80 6.80 6.78 6.78 4.96 4.94 4.32 4.30 4.26 4.25 4.23 4.22 4.11 4.11 4.09 3.77 3.13 3.11 2.94 2.93 2.27 2.26 2.25 2.25 1.31 1.29



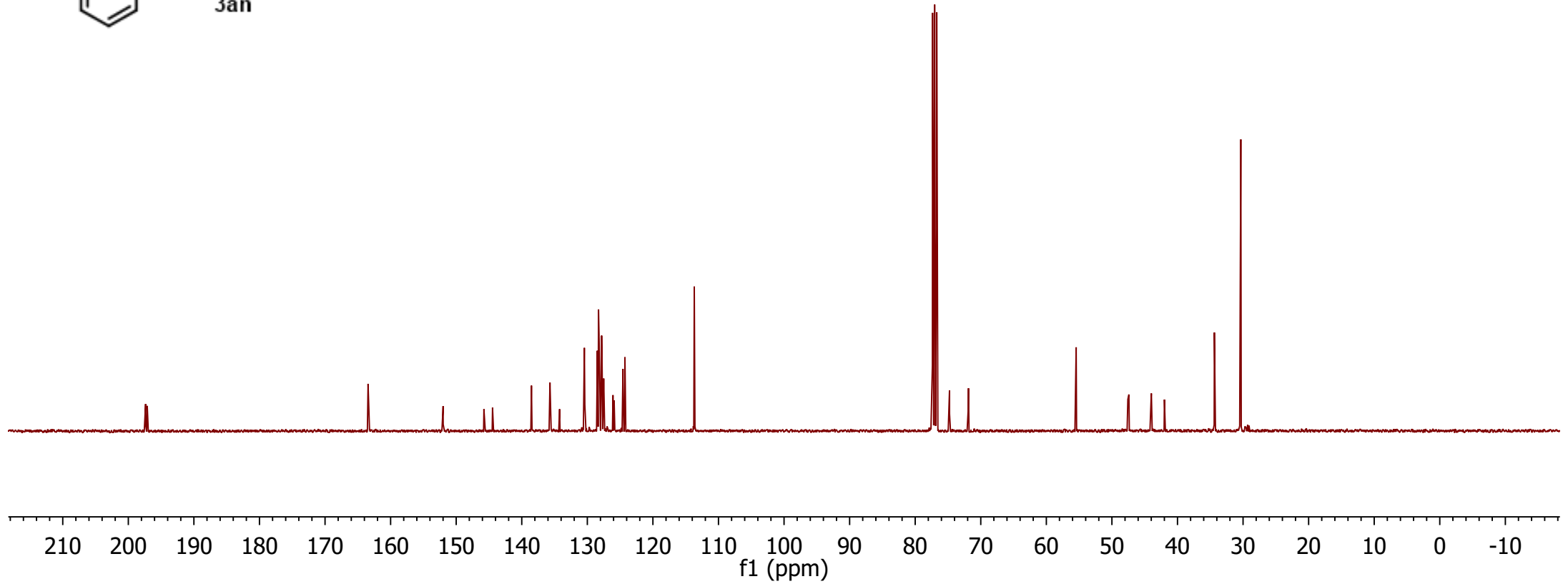
<sup>1</sup>H NMR Spectrum of **3an**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



197.4  
197.1

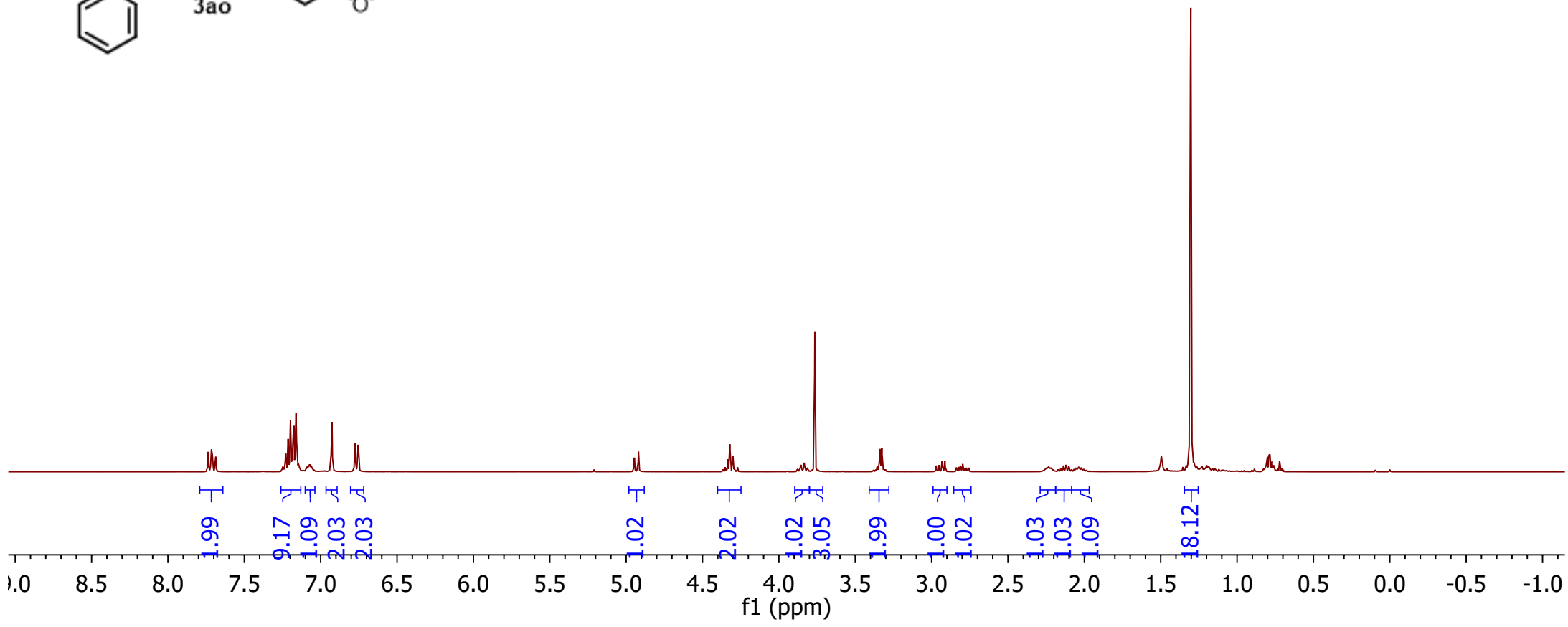
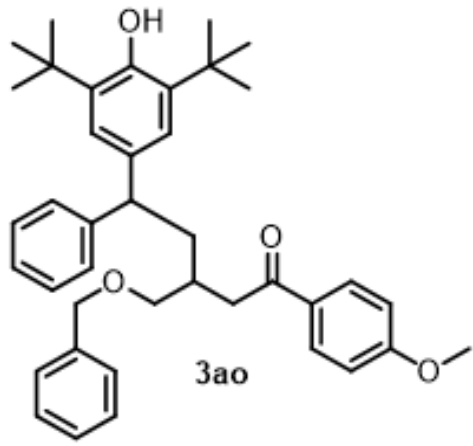
163.4  
152.1  
152.0  
145.8  
144.5  
138.5  
135.8  
135.7  
135.7  
134.2  
130.5  
130.5  
130.4  
130.3  
128.5  
128.4  
128.3  
128.2  
127.8  
127.8  
127.7  
127.5  
127.5  
126.1  
125.9  
124.6  
124.3  
113.7  
74.8  
74.8  
71.9  
71.9  
55.5  
47.6  
47.4  
44.0  
44.0  
42.0  
41.9  
34.4  
30.4  
30.3



<sup>13</sup>C NMR Spectrum of **3an**

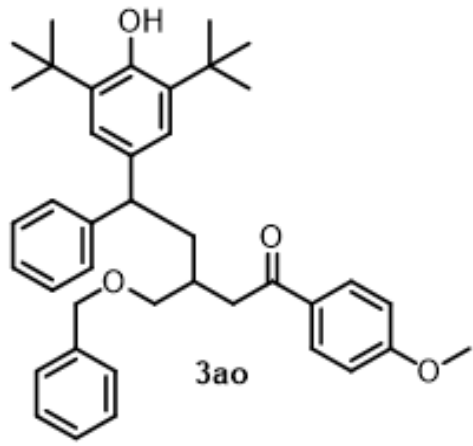
**<sup>1</sup>H(CDCl<sub>3</sub>, 400 MHz)**

7.74  
7.73  
7.72  
7.72  
7.71  
7.70  
7.69  
7.23  
7.23  
7.22  
7.21  
7.20  
7.19  
7.18  
7.18  
7.17  
7.16  
7.16  
7.16  
7.15  
7.14  
7.09  
7.08  
7.07  
7.07  
7.06  
6.93  
6.93  
6.78  
6.75  
4.95  
4.92  
4.33  
4.32  
4.30  
3.85  
3.83  
3.76  
3.36  
3.34  
3.34  
3.33  
2.97  
2.95  
2.93  
2.91  
2.81  
2.80  
2.14  
2.12  
2.12  
2.10  
1.31  
1.30

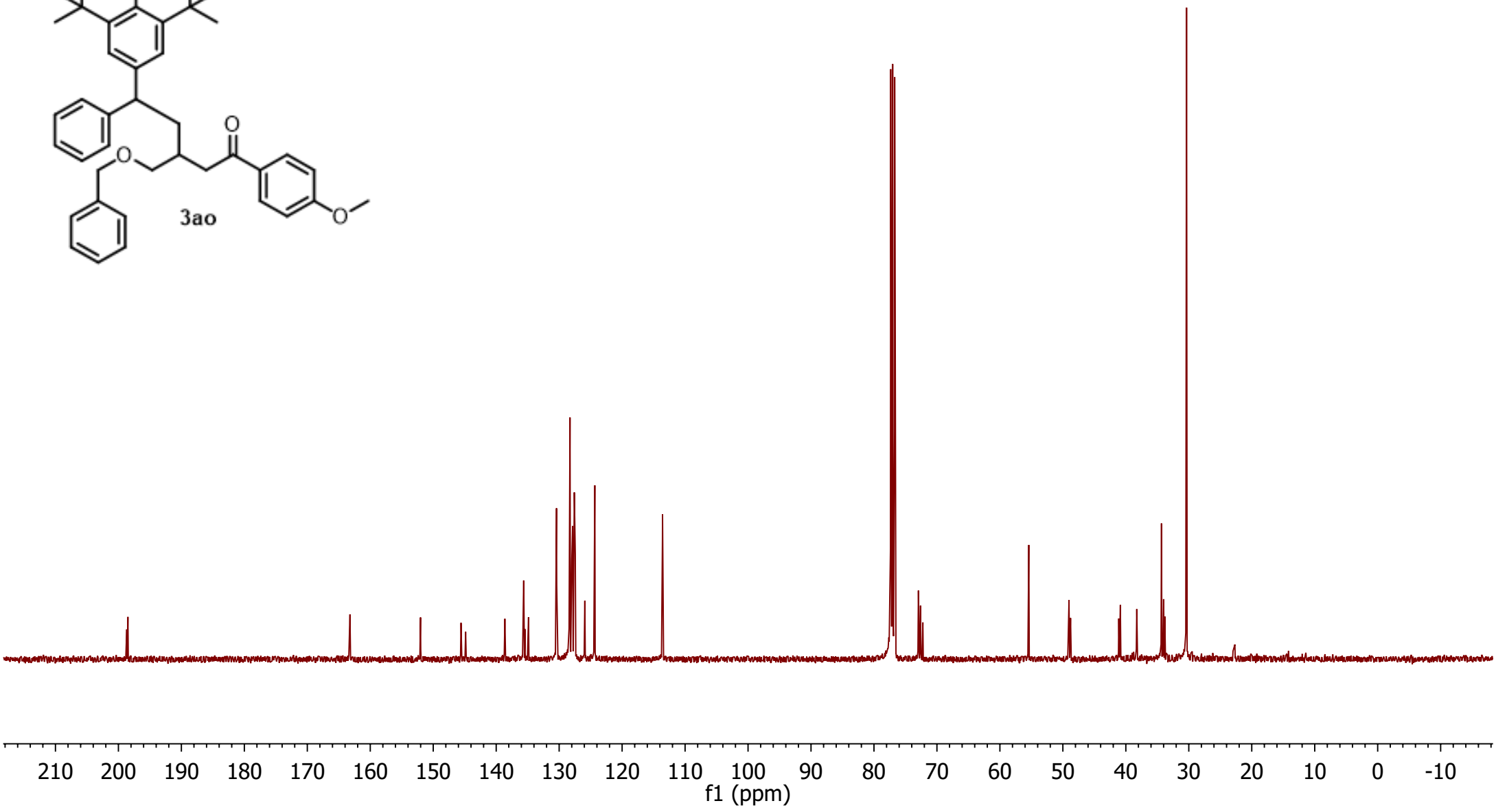


<sup>1</sup>H NMR Spectrum of **3ao**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



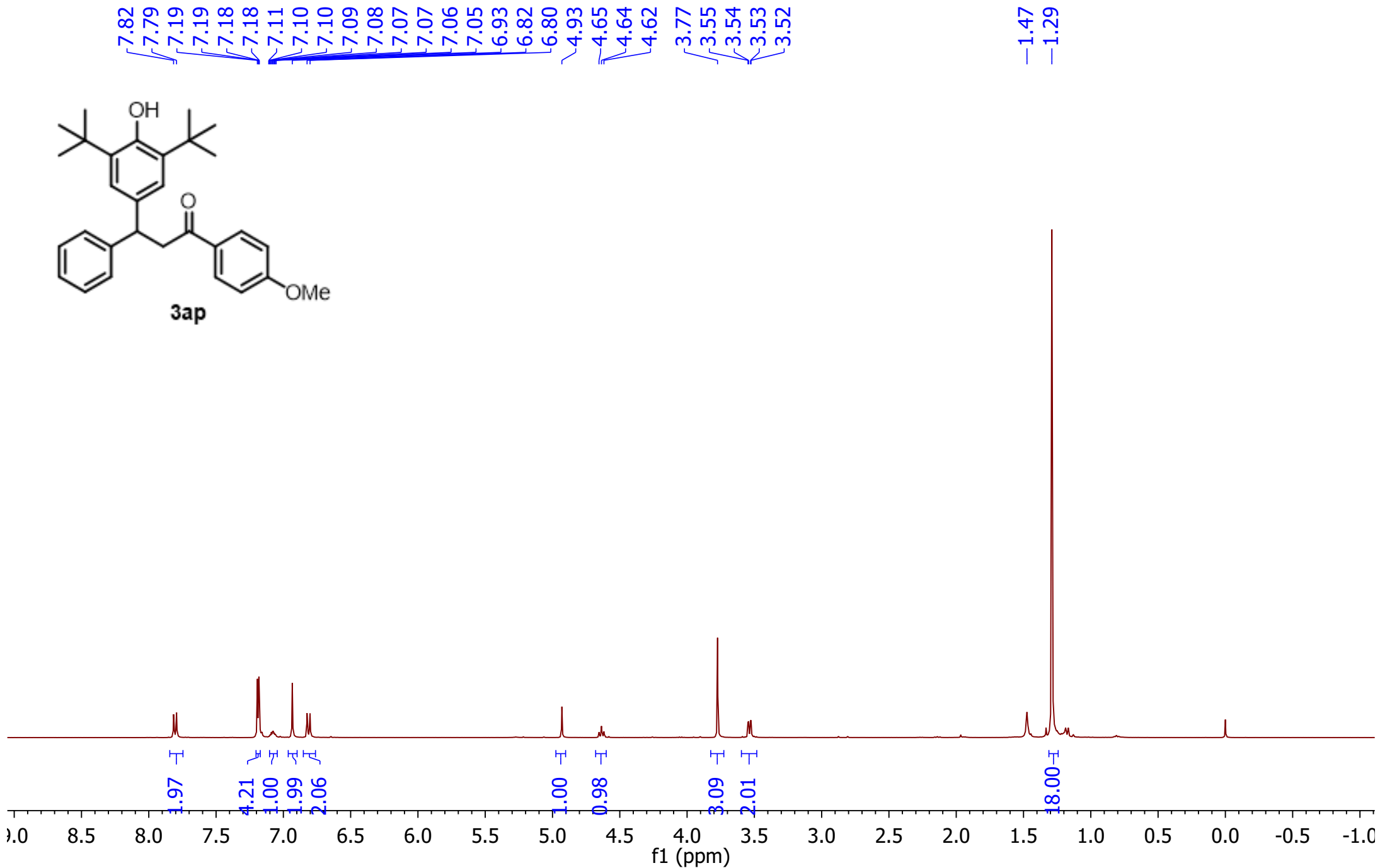
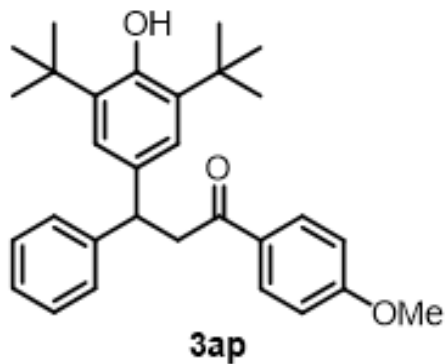
- 198.7
- 198.5
- 163.2
- 152.0
- 152.0
- 145.6
- 144.9
- 138.6
- 138.6
- 135.7
- 135.6
- 135.4
- 134.9
- 130.4
- 130.4
- 128.4
- 128.4
- 128.3
- 128.0
- 127.9
- 127.6
- 127.6
- 127.4
- 126.0
- 125.9
- 124.3
- 113.6
- 113.6
- 73.0
- 72.9
- 72.6
- 72.2
- 55.4
- 49.0
- 48.8
- 41.1
- 40.9
- 38.3
- 38.3
- 34.4
- 34.3
- 34.0
- 33.8
- 30.4



<sup>13</sup>C NMR Spectrum of **3ao**

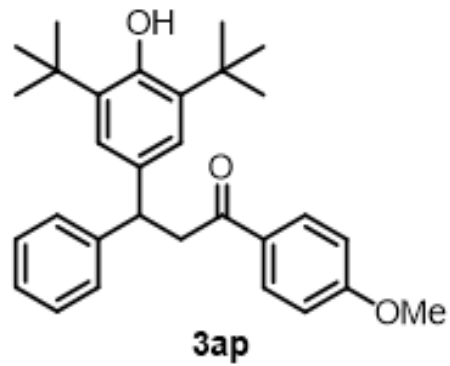


**<sup>1</sup>H(CDCI<sub>3</sub>, 400 MHz)**



<sup>1</sup>H NMR Spectrum of **3ap**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



—197.3

—163.3

152.1

144.7

135.7

134.8

130.5

130.3

128.4

127.9

126.1

124.4

—113.6

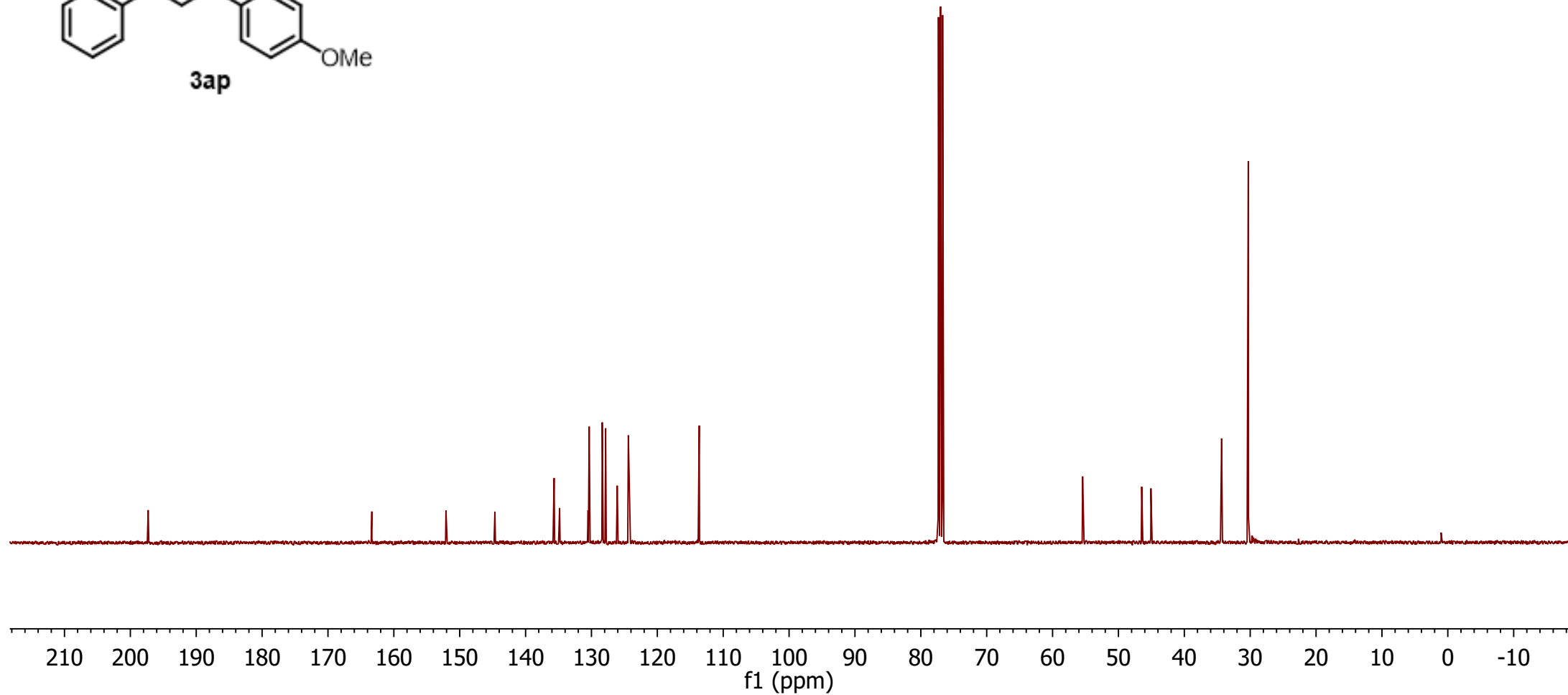
—55.4

46.5

45.1

—34.3

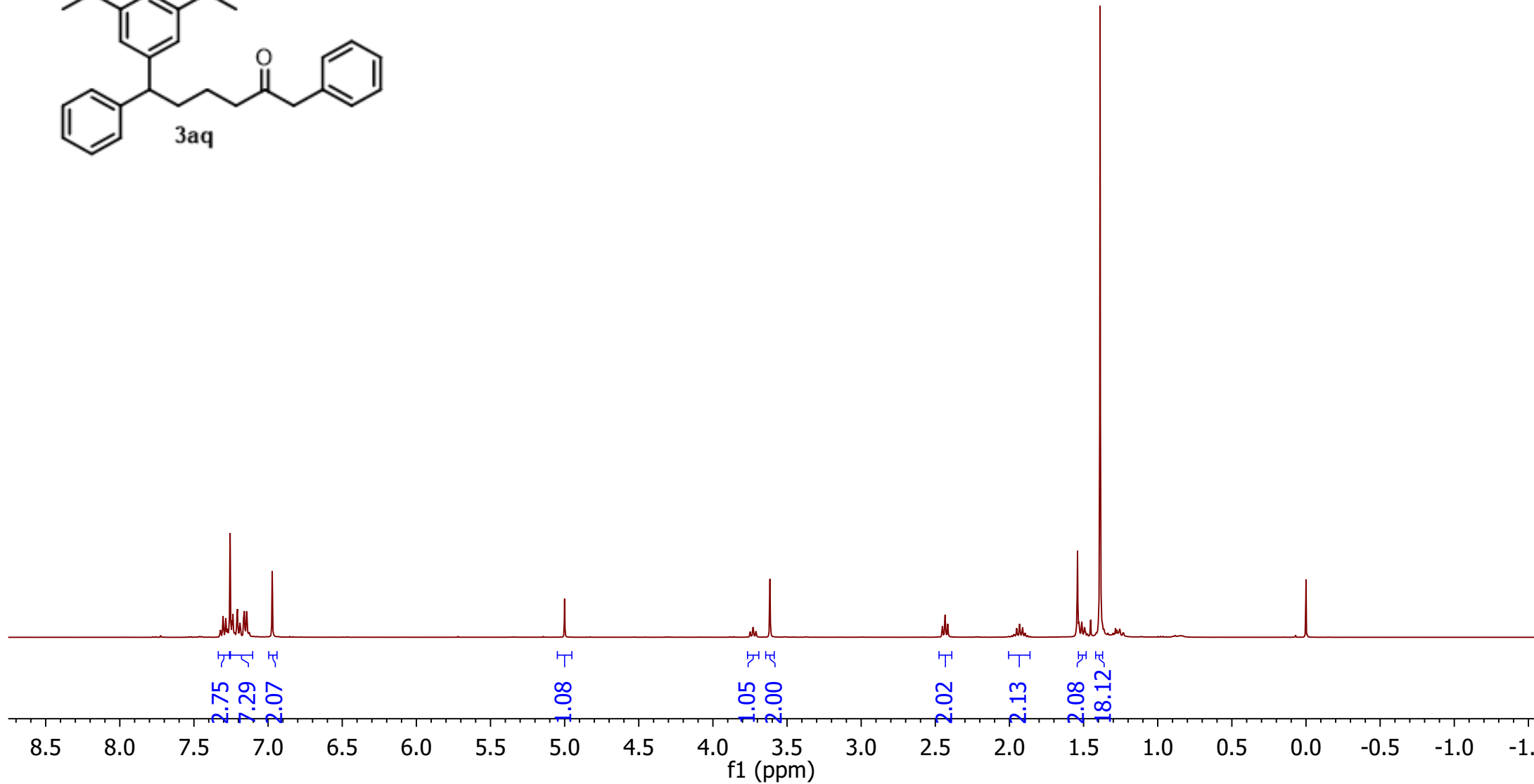
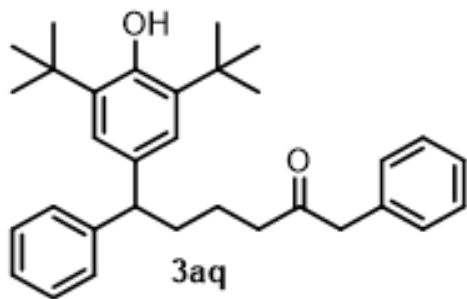
—30.3



<sup>13</sup>C NMR Spectrum of **3ap**

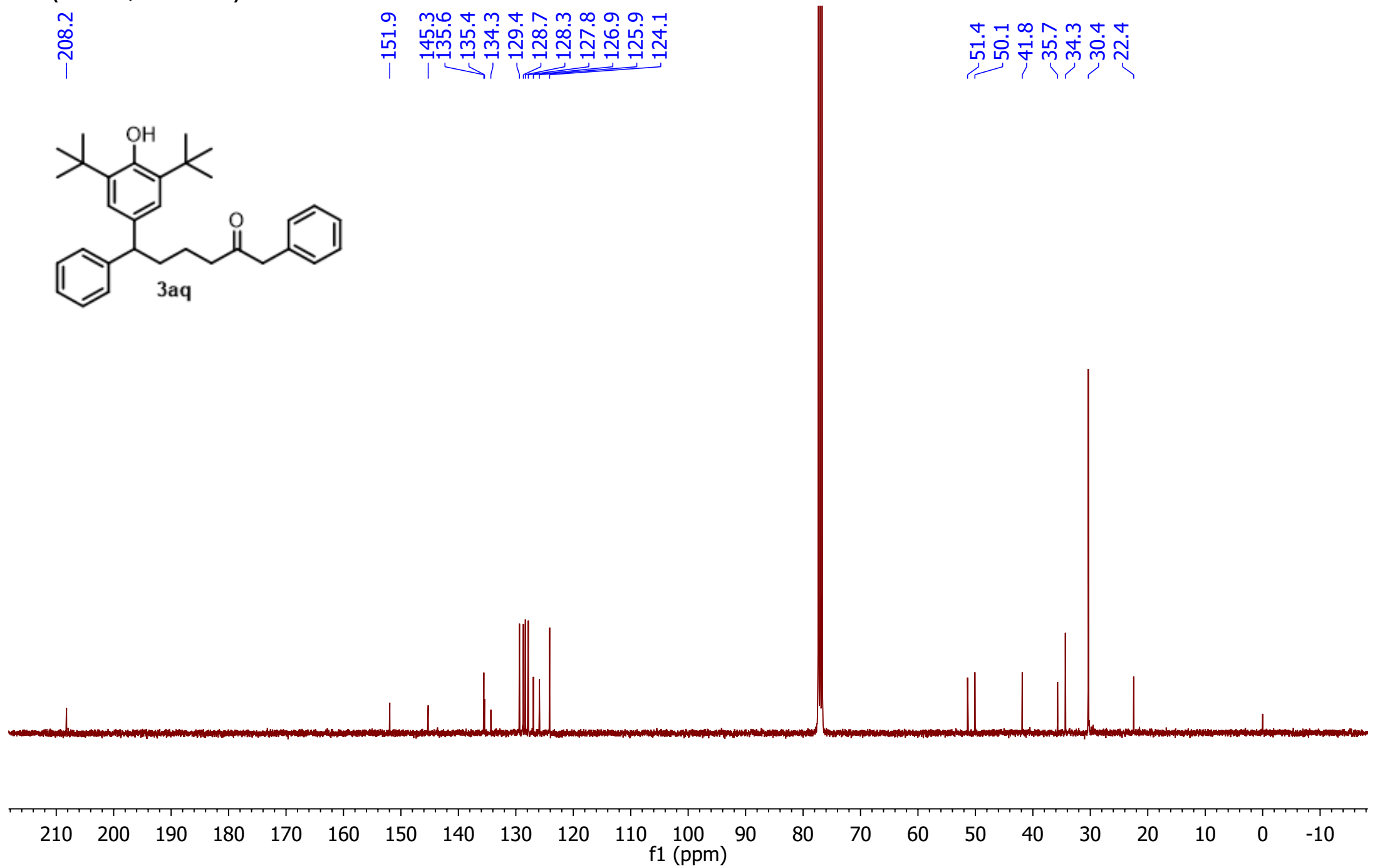
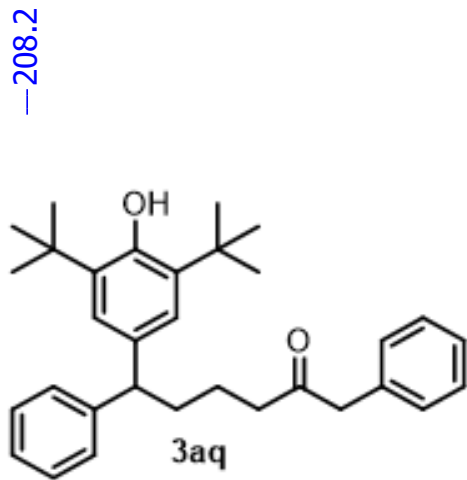
**<sup>1</sup>H(CDCl<sub>3</sub>, 400 MHz)**

7.32  
7.30  
7.30  
7.29  
7.29  
7.28  
7.27  
7.24  
7.24  
7.23  
7.22  
7.22  
7.21  
7.21  
7.20  
7.19  
7.19  
7.19  
7.18  
7.16  
7.16  
7.14  
7.14  
7.13  
7.13  
7.12  
7.10  
6.97  
5.00  
3.75  
3.73  
3.71  
3.62  
2.45  
2.43  
2.42  
2.00  
1.99  
1.98  
1.97  
1.97  
1.95  
1.94  
1.93  
1.91  
1.90  
1.89  
1.88  
1.86  
1.53  
1.51  
1.49  
1.49  
1.48  
1.47  
1.39



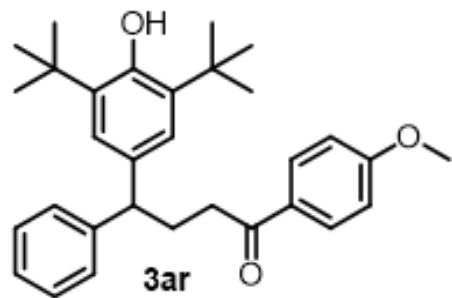
<sup>1</sup>H NMR Spectrum of **3aq**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**

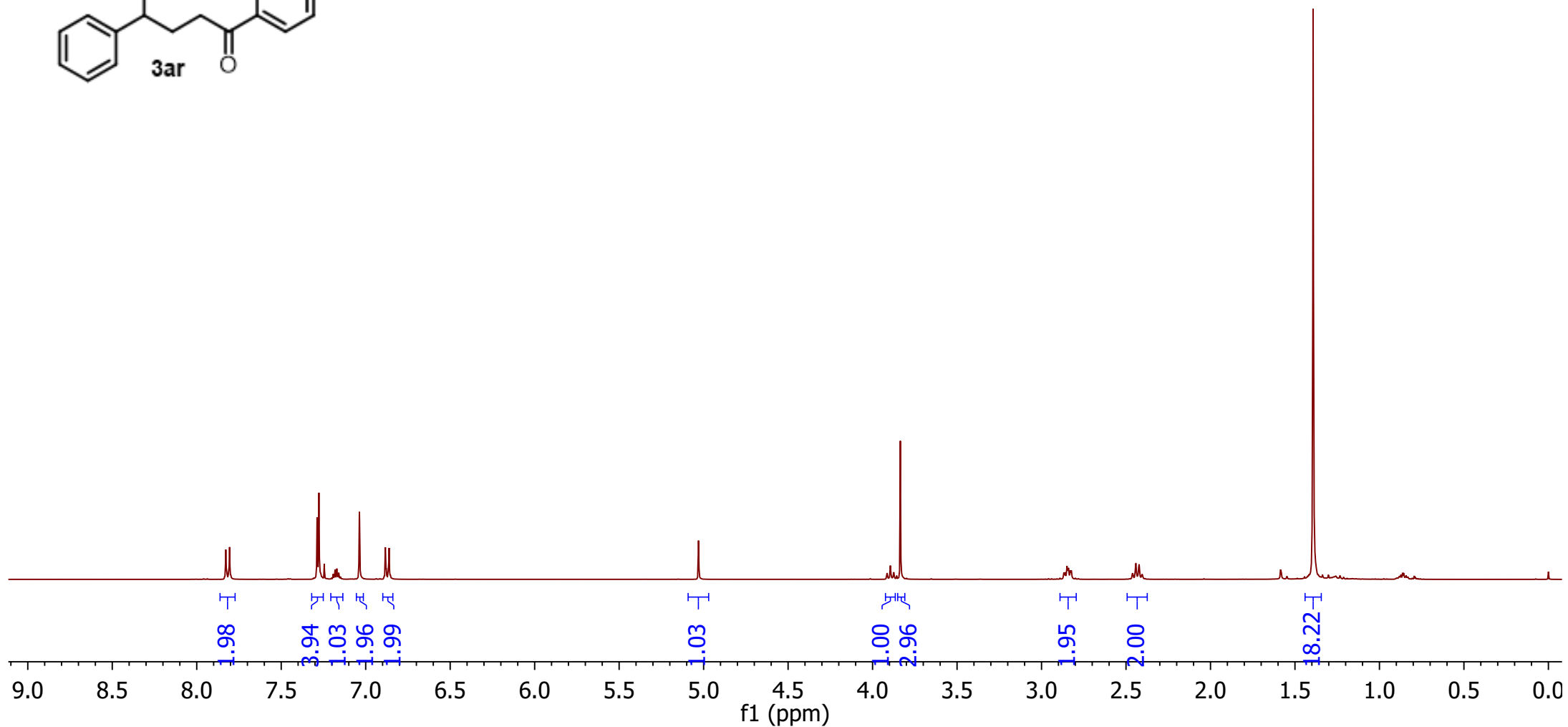


<sup>13</sup>C NMR Spectrum of **3aq**

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

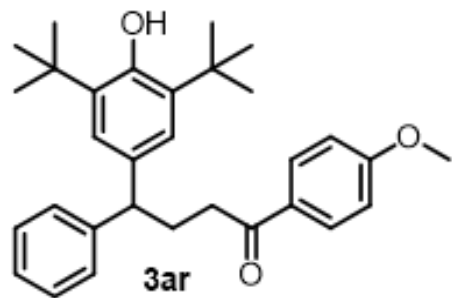


7.83  
7.81  
7.29  
7.28  
7.19  
7.18  
7.17  
7.16  
7.16  
7.15  
7.04  
6.90  
6.89  
6.88  
6.88  
6.87  
6.86  
6.85  
6.85  
6.84  
6.83  
5.03  
3.91  
3.89  
3.87  
3.84  
2.87  
2.86  
2.85  
2.84  
2.84  
2.83  
2.82  
2.46  
2.46  
2.44  
2.42  
2.42  
2.41  
2.40  
-1.39



<sup>1</sup>H NMR Spectrum of **3ar**

**$^{13}\text{C}$ ( $\text{CDCl}_3$ , 101 MHz)**



—198.9

—163.3

—152.1

—145.0

—135.7

—135.1

—130.3

—130.2

—128.4

—127.9

—126.1

—124.3

—113.6

—55.4

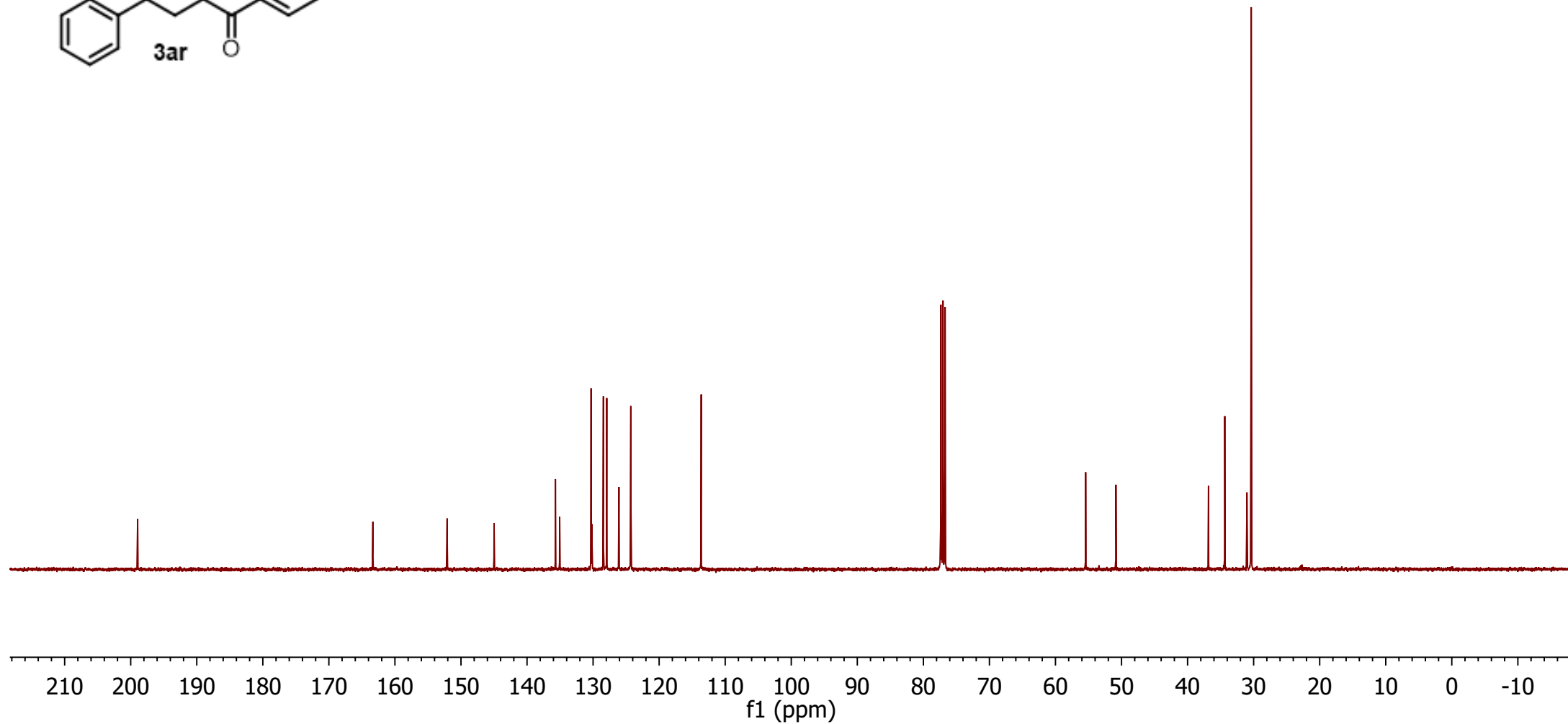
—50.8

—36.8

—34.4

—31.0

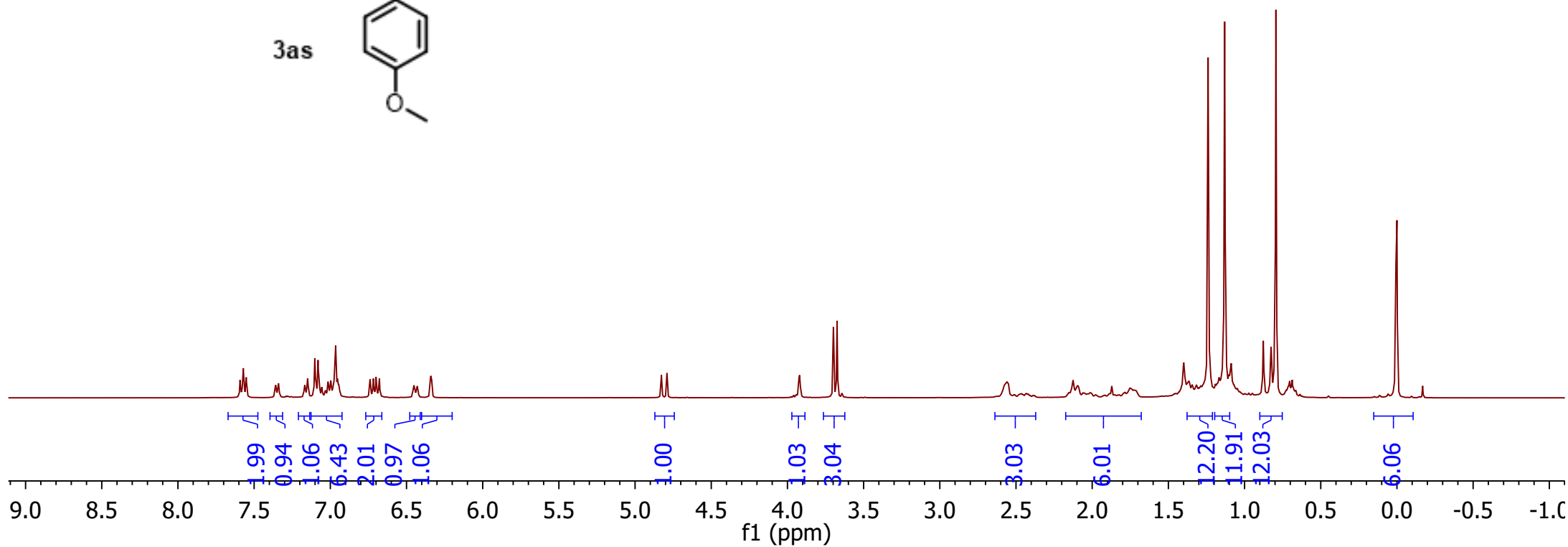
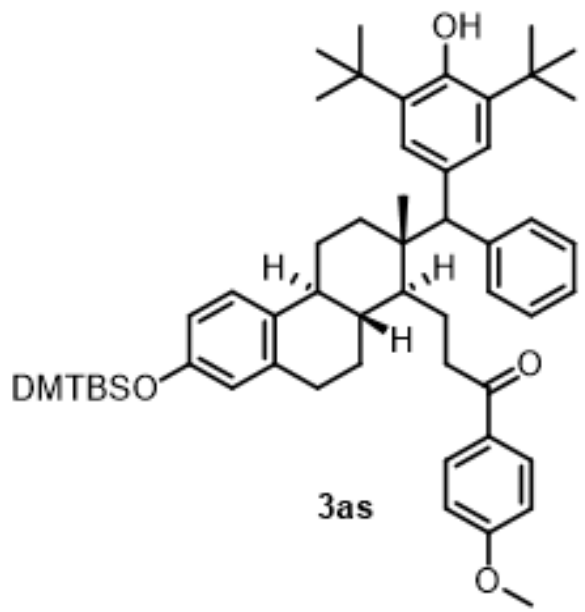
—30.4



$^{13}\text{C}$  NMR Spectrum of **3ar**

**<sup>1</sup>H(CDCI<sub>3</sub>, 400 MHz)**

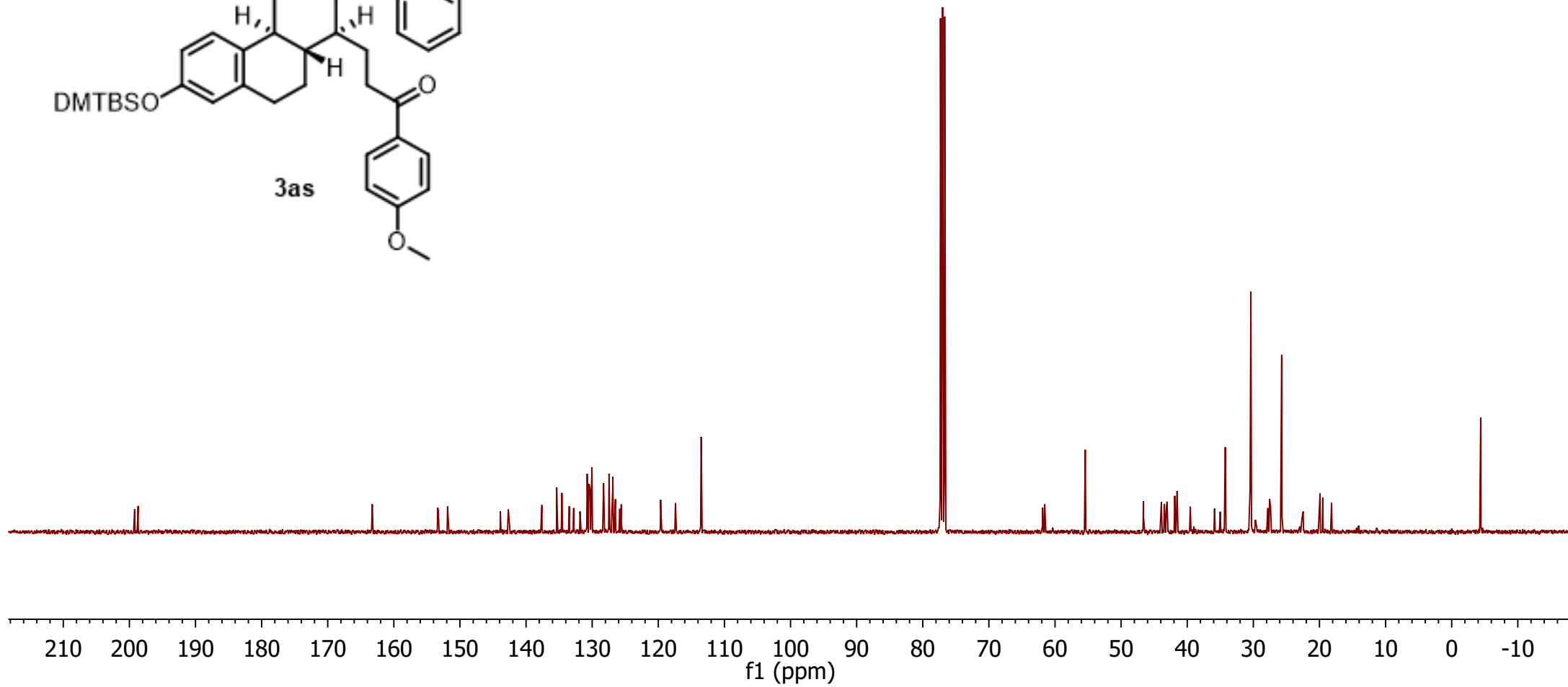
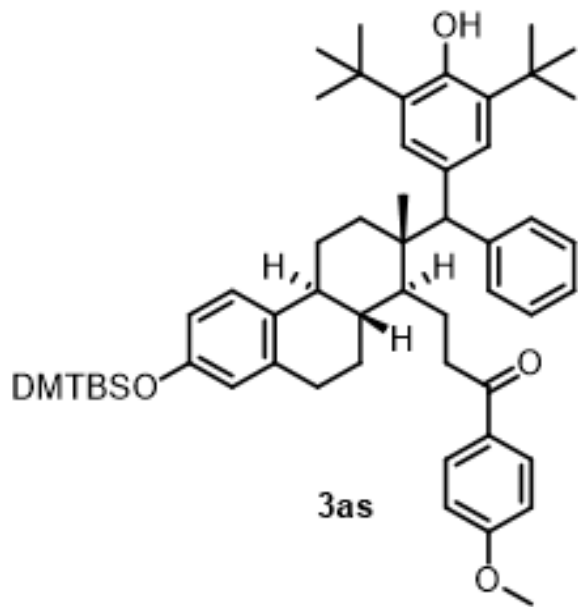
7.59  
7.57  
7.57  
7.55  
7.34  
7.15  
7.10  
7.09  
7.08  
7.07  
7.01  
7.00  
7.00  
6.97  
6.96  
6.95  
6.74  
6.72  
6.70  
6.68  
6.34  
6.34  
6.34  
4.83  
4.79  
3.92  
3.92  
3.70  
3.67  
2.56  
2.55  
2.13  
1.40  
1.38  
1.38  
1.36  
1.26  
1.26  
1.24  
1.22  
1.18  
1.17  
1.15  
1.15  
1.13  
1.10  
1.10  
1.09  
0.88  
0.83  
0.81  
0.79  
0.01  
-0.00



<sup>1</sup>H NMR Spectrum of **3as**

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**

198.7  
163.3  
153.4  
151.9  
137.7  
137.6  
135.4  
134.6  
133.5  
132.8  
130.8  
130.5  
130.3  
130.1  
130.0  
128.3  
127.5  
127.4  
126.9  
126.5  
126.5  
125.6  
119.6  
119.5  
117.4  
117.4  
113.5  
61.9  
61.6  
55.4  
46.8  
46.6  
43.9  
43.5  
43.1  
43.0  
41.9  
41.5  
39.5  
35.9  
34.3  
34.2  
30.5  
30.4  
27.8  
27.5  
27.4  
25.7  
25.7  
19.9  
19.5  
18.2  
18.2  
-4.4

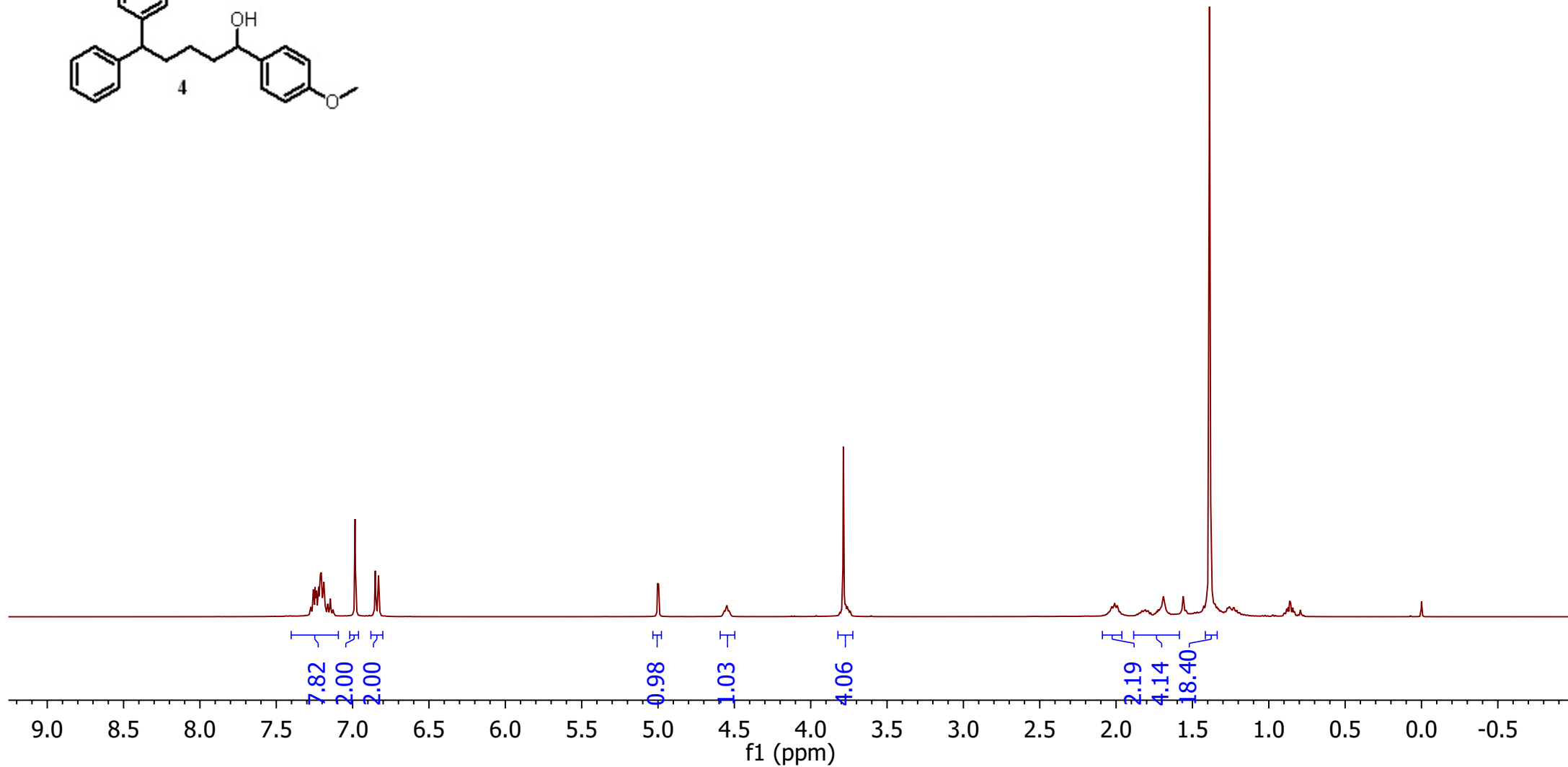
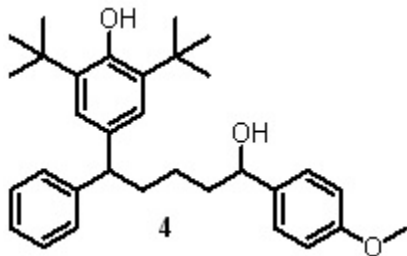


<sup>13</sup>C NMR Spectrum of 3as



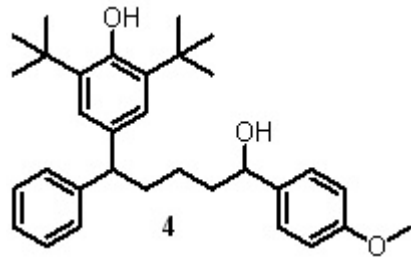
**<sup>1</sup>H(CDCI<sub>3</sub>, 400 MHz)**

7.28  
7.27  
7.26  
7.25  
7.25  
7.24  
7.24  
7.23  
7.22  
7.22  
7.21  
7.21  
7.20  
7.19  
7.19  
7.18  
7.18  
7.17  
7.16  
7.16  
7.15  
7.15  
7.13  
6.98  
6.85  
6.85  
6.84  
6.83  
5.00  
5.00  
4.55  
4.55  
3.80  
3.79  
3.77  
3.76  
3.75  
2.04  
2.03  
2.02  
2.01  
2.00  
1.99  
1.99  
1.81  
1.72  
1.71  
1.71  
1.70  
1.69  
1.69  
1.68  
1.39  
1.39



<sup>1</sup>H NMR Spectrum of 4

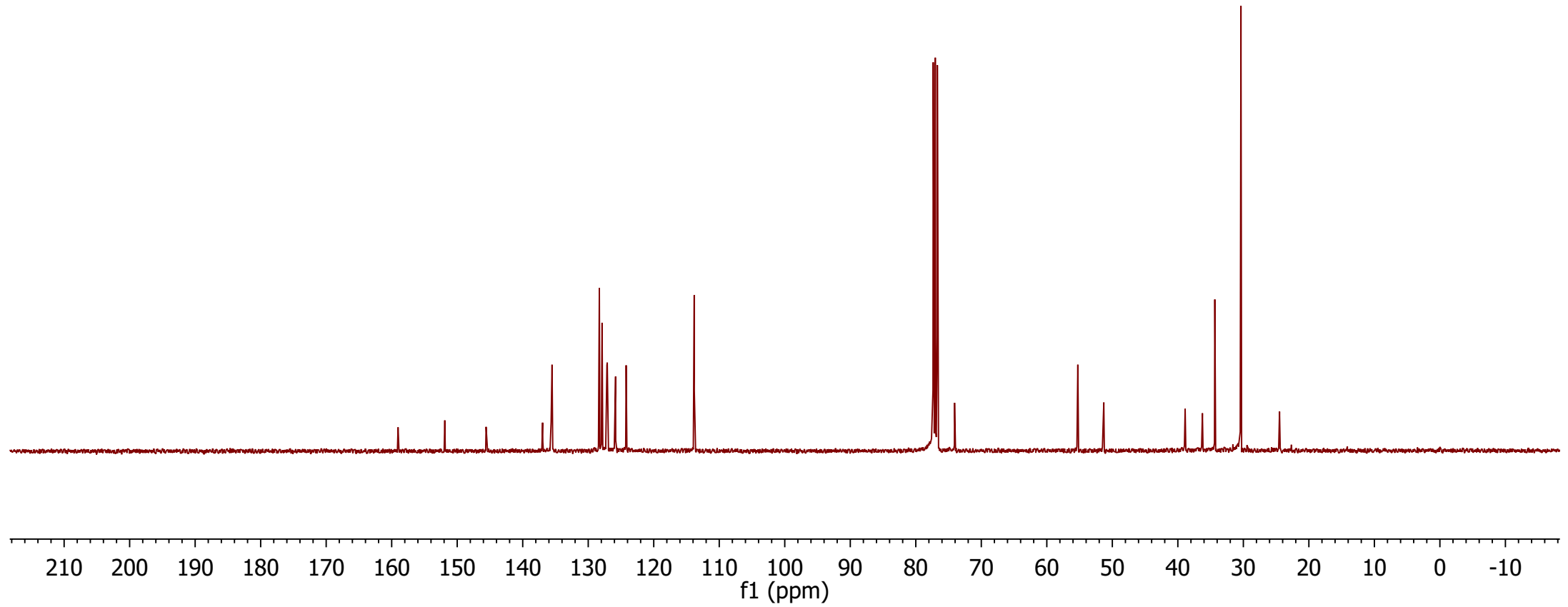
**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**



159.0  
159.0  
151.9  
145.6  
145.5  
137.0  
136.9  
135.7  
135.7  
135.5  
128.3  
127.9  
127.1  
127.1  
125.8  
124.2  
124.2

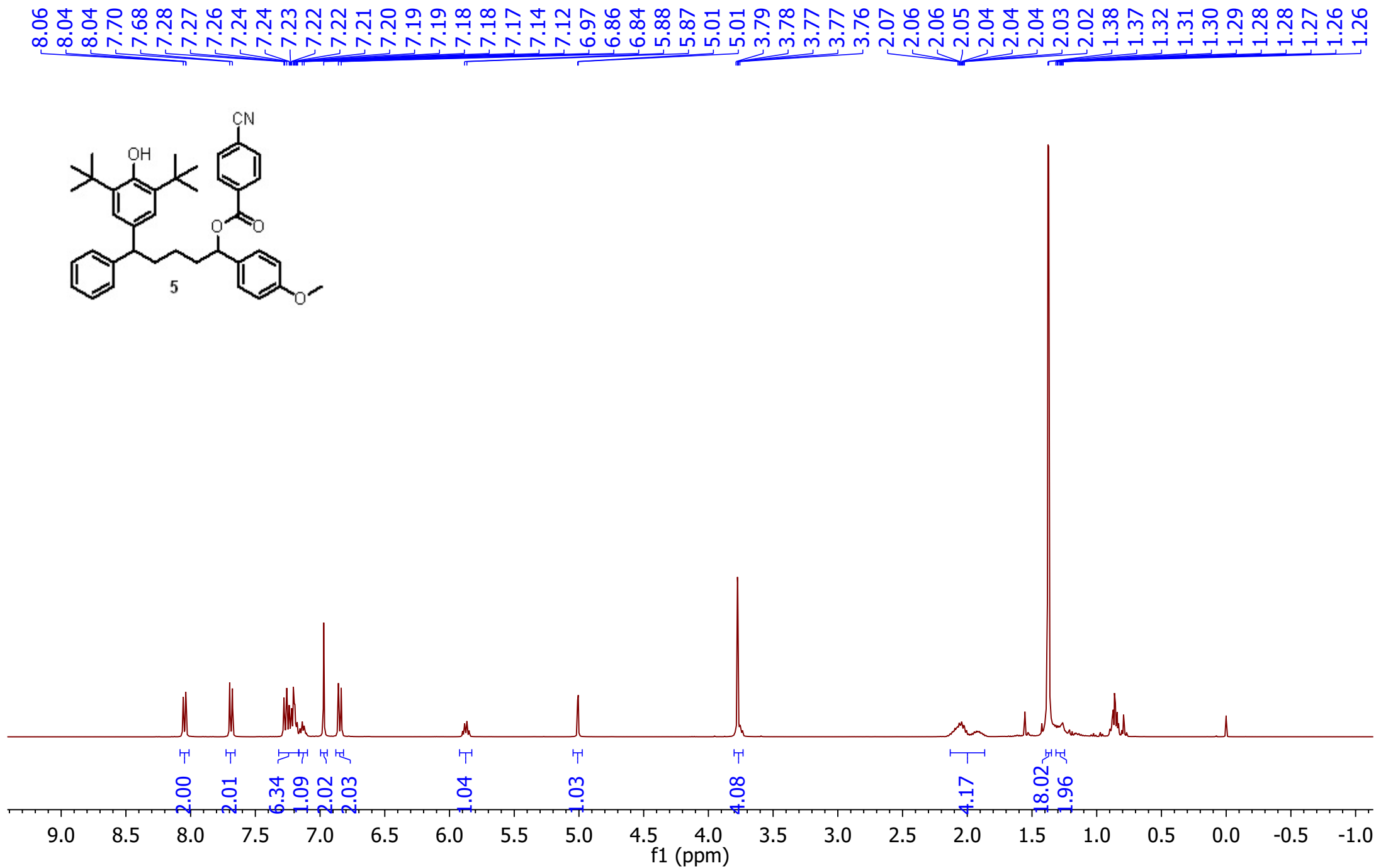
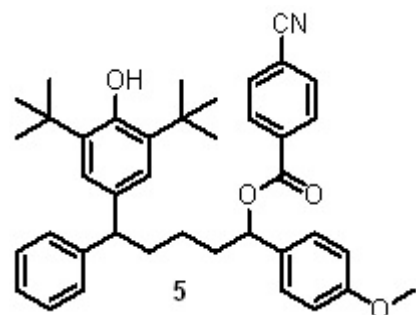
74.1  
74.0

55.3  
51.3  
51.3  
38.9  
38.8  
36.3  
36.2  
34.4  
30.4  
24.5  
24.4



<sup>13</sup>C NMR Spectrum of 4

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



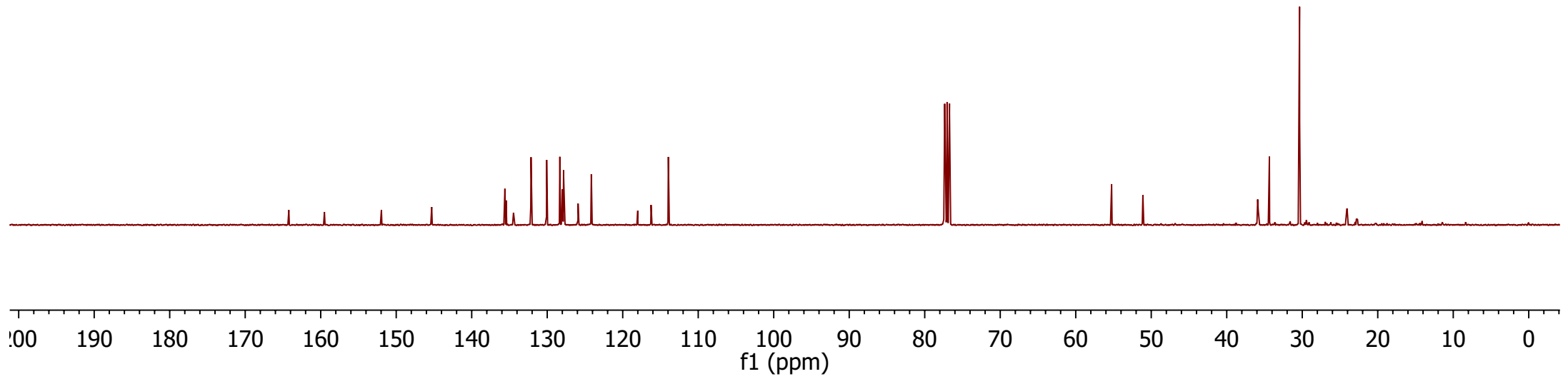
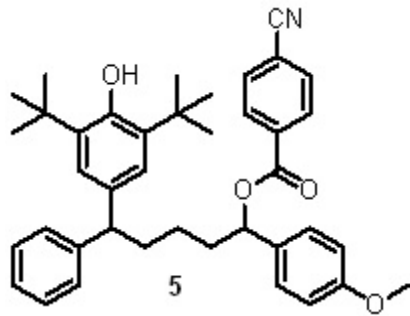
<sup>1</sup>H NMR Spectrum of 5

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**

164.2  
159.5  
159.5  
152.0  
151.9  
145.3  
135.6  
135.4  
134.5  
134.4  
132.2  
132.1  
132.0  
130.1  
128.3  
128.0  
128.0  
127.9  
127.8  
125.9  
125.9  
124.2  
118.0  
116.2  
114.0

55.2  
51.1

35.9  
35.9  
35.8  
34.3  
30.4  
24.1  
24.1

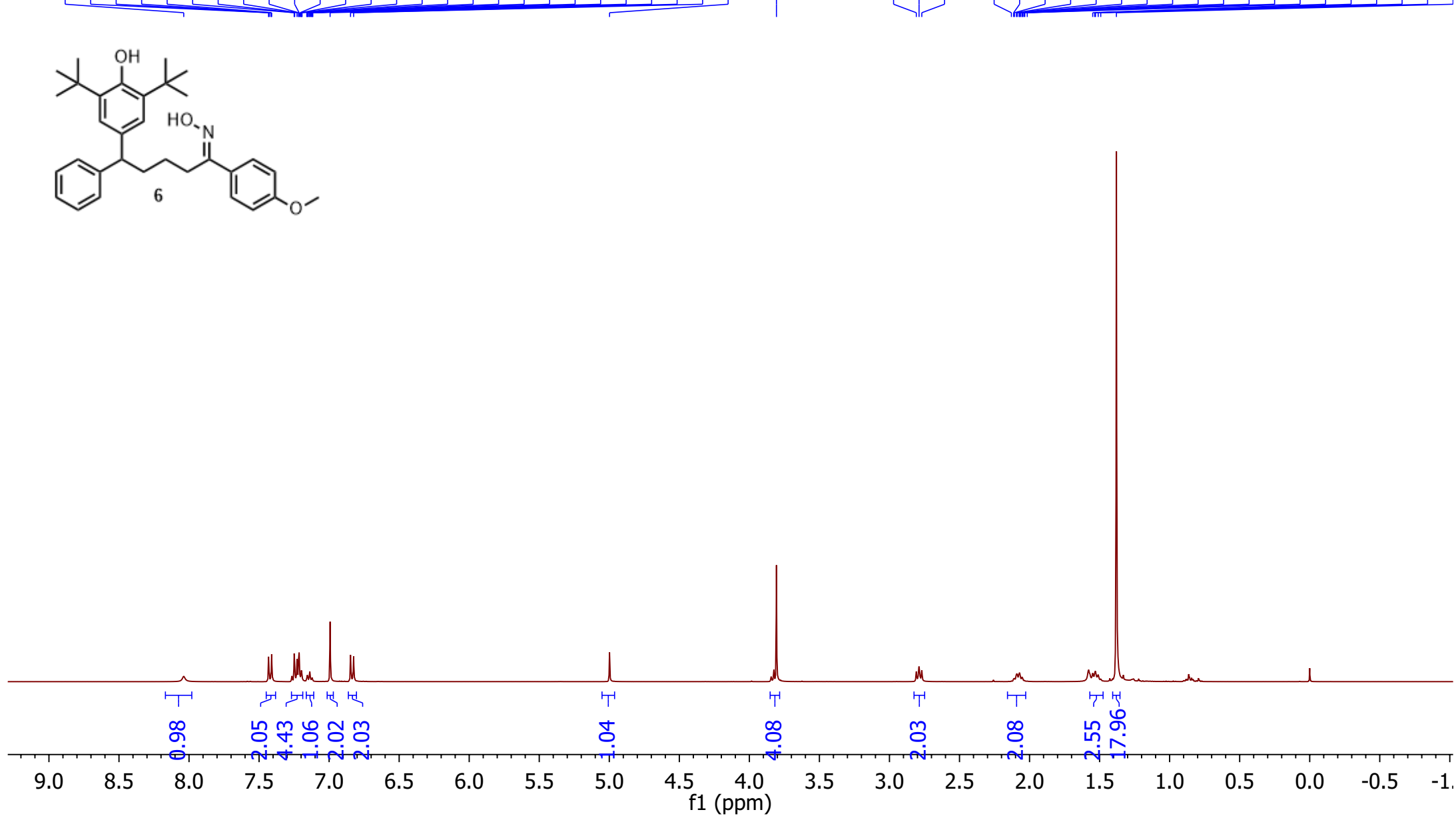
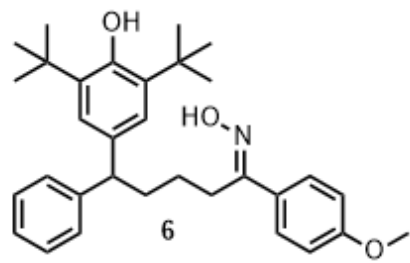


<sup>13</sup>C NMR Spectrum of 5

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

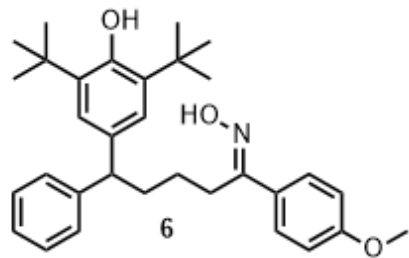
8.04  
7.43  
7.43  
7.42  
7.41  
7.25  
7.25  
7.23  
7.22  
7.21  
7.21  
7.20  
7.20  
7.19  
7.16  
7.16  
7.15  
7.14  
7.14  
7.13  
7.13  
7.12  
7.12  
6.99  
6.85  
6.83  
5.00  
— 3.81

2.81  
2.79  
2.77  
2.13  
2.11  
2.11  
2.09  
2.09  
2.07  
2.07  
2.06  
2.05  
2.05  
2.04  
2.03  
2.02  
1.55  
1.53  
1.53  
1.51  
1.49  
1.38



<sup>1</sup>H NMR Spectrum of 6

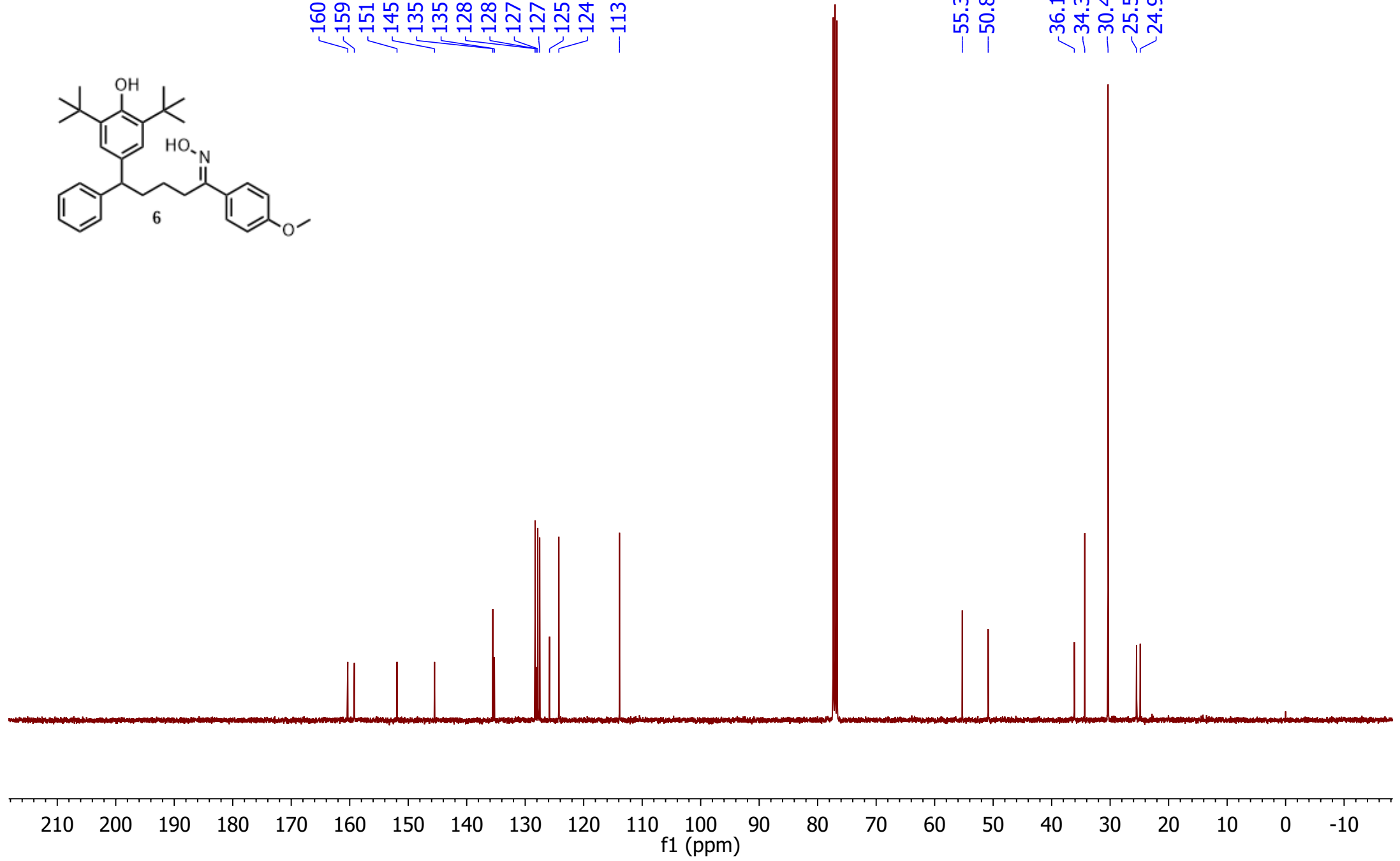
**<sup>13</sup>C(CDCl<sub>3</sub>, 101Hz)**



160.3  
159.2  
151.9  
145.5  
135.5  
135.3  
128.3  
128.1  
127.9  
127.5  
125.8  
124.2  
-113.9

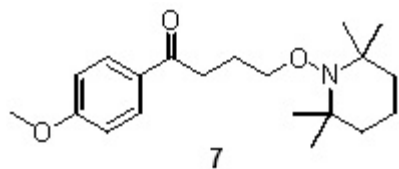
-55.3  
-50.8

36.1  
34.3  
30.4  
25.5  
24.9



<sup>13</sup>C NMR Spectrum of 6

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



8.00  
7.97

6.97  
6.97  
6.95

3.89  
3.86  
3.84  
3.83

3.08  
3.06  
3.04

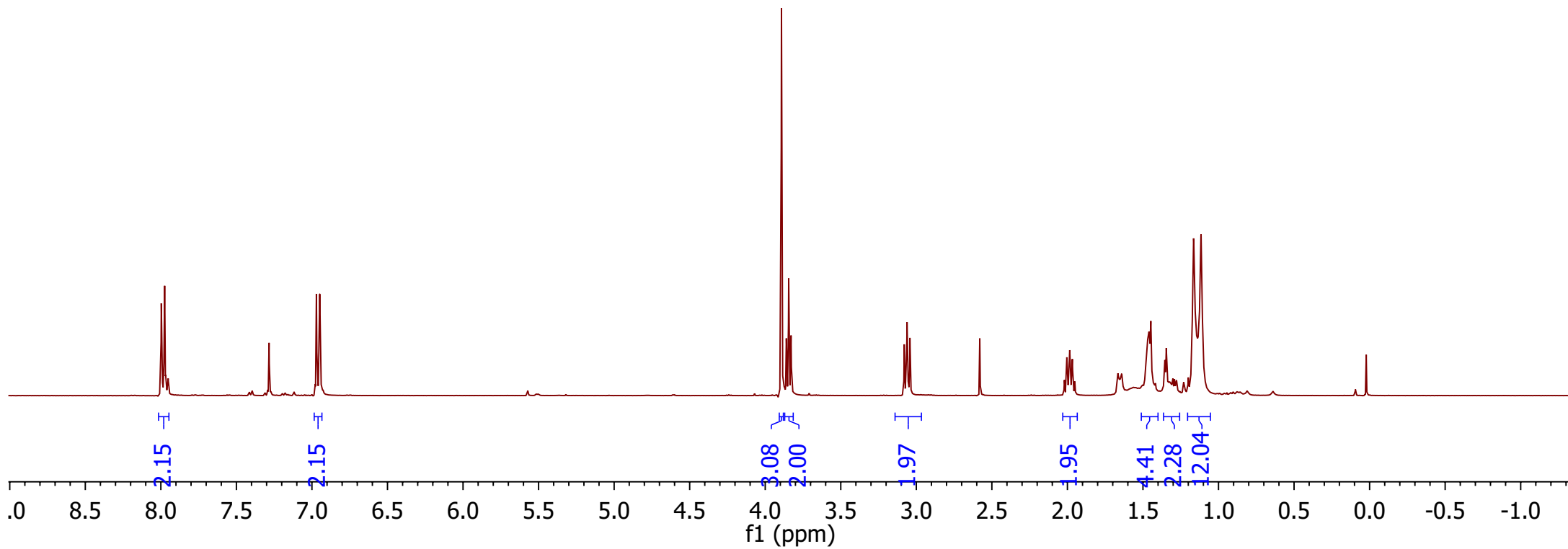
2.02  
2.00  
2.00

1.99  
1.99  
1.98

1.98  
1.97  
1.97

1.95  
1.48  
1.47

1.46  
1.45



<sup>1</sup>H NMR Spectrum of 7

**<sup>13</sup>C(CDCl<sub>3</sub>, 101 MHz)**

—198.8

—163.3

130.3  
130.2

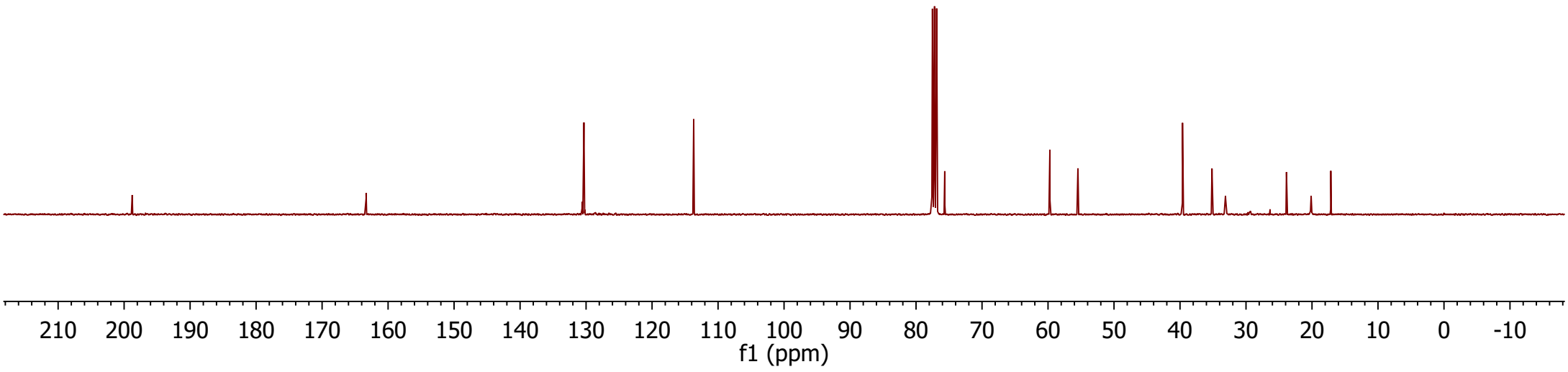
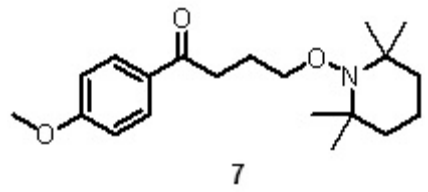
—113.7

—75.6

—59.7  
—55.5

~39.6  
~35.2  
~33.1

~23.9  
~20.1  
~17.1



<sup>13</sup>C NMR Spectrum of 7