Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Metal-free synthesis of γ-ketosulfones through Brønsted acid-promoted conjugate addition of sulfinamides

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Table of contents

1. General information

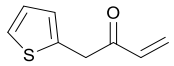
Reagents were purchased as reagent grade and were used without further purification other than those above-mentioned. CH_2Cl_2 was purified by passage through a drying column and THF was distilled from sodium/benzophenone immediately prior to use. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AC300 spectrometer at 300 MHz in $CDCl_3$ at 25°C. Chemical shifts values are given in ppm downfield from tetramethylsilane (TMS) with the chloroform resonance as the internal standard. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintuplet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, br = broad. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. Infrared (IR) spectra were recorded as neat films on Bruker Vector22 spectrophotometer. Mass spectra and high resolution mass spectra were obtained on a Thermoquest TLM LCQ Deca ion-trap spectrometer with a Q-TOF micro spectrometer using ESI. Melting points are uncorrected and were recorded on a micromelting point apparatus. Analytical thin layer chromatography was performed on Merck 60F-254 precoated silica (0.2 mm) on glass and was revealed by UV light or by spraying with a potassium permanganate solution, followed by charring at 150 °C. Flash chromatography separations were carried out on on Merck Kieselgel (40-63µm).

Vinylketones **1h**, **1i** and **1j**,[1] **1k**,[2] **1m**[3] and sulfinamide **1b**[4] were synthesised according to the literature procedures.

2. Experimental procedures

2.1. Preparation of Starting Materials

1-(Thien-2-yl)but-3-en-2-one (1e)

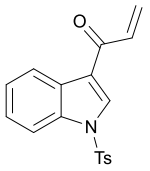


To a solution of *N*-methoxy-*N*-methyl-2-(thien-2-yl)acetamide[5] (300 mg, 1.62 mmol) in dry THF (30 mL) was added dropwise vinylmagnesium bromide solution 1.0 M in THF (3.24 mL, 3.24 mmol) at 0 °C. The mixture was then stirred 12 hours at room temperature before quenching by an aqueous saturated solution of NH_4Cl (10 mL). The aqueous layer was then extracted with AcOEt (2 × 20 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated. Flash chromatography (cyclohexane/ethyl acetate: 9/1) afforded the compound **1e** as a yellow oil (113 mg, 46 %).

IR (neat) ν_{max}/cm^{-1} 3107, 1694, 1674, 1533, 920; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 5.2 Hz, 1.1 Hz, 1H), 6.98 (*br* t, *J* = 3.5 Hz, 1H), 6.90 (m, 1H), 6.45 (dd, *J* = 17.5, 10.1 Hz, 1H), 6.33 (dd, *J* = 17.5, 1.4 Hz, 1H), 5.86 (dd, *J* = 10.0 Hz, 1.4 Hz, 1H), 4.06 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1, 135.1, 134.3, 129.5, 127.2, 127.0, 125.3, 41.0; HRMS (TOF-ESI) *m/z*: no satisfying analysis was obtained due to the low stability of the product.

[1] J. Barluenga, H. Fanlo, S. López and J. Flórez, *Angew. Chem. Int. Ed.*, 2007, **46**, 4136-4140.
[2] M. Radi, M. Pagano, L. Franchi, D. Castagnolo, S. Schenone, G. Casaluce, C. Zamperini, E. Dreassi, G. Maga, A. Samuele, E. Gonzalo, B. Clotet, J. A. Esté and M. Botta, *ChemMedChem*, 2012, **7**, 883-896.
[3] H. Pessoa-Mahana, G. Recabarren-Gajardo, J. Fiedler Temer, G. Zapata-Torres, C. D. Pessoa-Mahana, C. Saitz Barría and R. Araya-Maturana, *Molecules*, 2012, **17**, 1388-1407.
[4] J. L. García Ruano, A. Parra, F. Yuste and V. M. Mastranzo, *Synthesis*, 2008, 311-312.
[5] T. Kambe, T. Maruyama, M. Nakano, Y. Yamaura, T. Shono, A. Seki, K. Sakata, T. Maruyama, H. Nakai and M. Toda, *Chem. Pharm. Bull.*, 2011, **59**, 1523-1534.

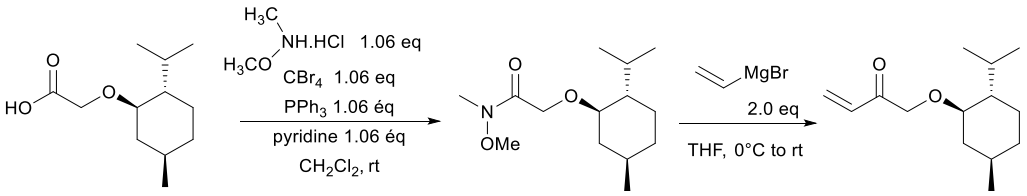
1-(1-Tosyl-1*H*-indol-3-yl)vinylketone (1n)



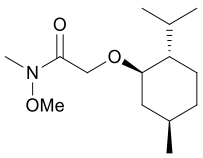
A solution of 1-(1-tosyl-1*H*-indol-3-yl)prop-2-en-1-ol[6] (150 mg, 0.46 mmol) and MnO_2 (240 mg, 2.75 mmol) in dry CH_2Cl_2 (5 mL) was stirred at room temperature for 4 hours. Three new portions of MnO_2 (3x240 mg, 3x2.75 mmol) were successively added each 12 hours to the reaction mixture. The solution was then filtered through Celite® and washed with CH_2Cl_2. After evaporation of the solvent, flash chromatography (cyclohexane/ethyl acetate: 75/25 to 7/3) afforded the compound **1n** as a brown foam (92 mg, 61 %).

IR (neat) ν_{max}/cm^{-1} 3104, 1651, 1604, 1535, 1379, 1175, 993; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (dd, J = 6.7, 2.6 Hz, 1H), 8.25 (s, 1H), 7.93 (dd, J = 6.5 Hz, 2.1 Hz, 1H), 7.82 (d, J = 8.3 Hz, 2H), 7.39-7.34 (m, 2H), 7.27 (d, J = 8.2 Hz, 2H), 7.04 (dd, J = 16.7 ,10.4 Hz, 1H), 6.47 (dd, J = 16.9, 1.1 Hz, 1H), 5.88 (dd, J = 10.1, 1.1 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.6, 146.1, 135.1, 134.6, 133.2, 132.2, 130.4 (2C), 128.7, 128.0, 127.3, 126.1, 125.0, 123.4, 121.5, 113.2, 21.7; HRMS (TOF-ESI) *m/z*: Calcd for $C_{18}H_{16}NO_3S$ [M + H]$^+$ 326.0845, found 326.0855.

The **1-{[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohex-1-yl]oxy}but-3-en-2-one 1o** was synthesized by a sequence of procedures shown below:



2-{[(1*R*,2*S*,5*R*)-2-*iso*Propyl-5-methylcyclohex-1-yl]oxy}-*N*-methoxy-*N*-methylacetamide (8)[7]



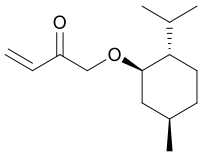
To a solution of (-)-menthoxy acetic acid (320 mg, 1.50 mmol) in dry CH_2Cl_2 (20 mL) was added *N*,*O*-dimethyl hydroxylamine hydrochloride (156 mg, 1.59 mmol), CBr_4 (540 mg, 1.59 mmol) and pyridine (128 µL, 1.59 mmol). PPh_3 (420 mg, 1.59 mmol) was then added portion-wise, and the solution was stirred at room temperature for 14 hours. After evaporation of the solvent, flash chromatography (cyclohexane/ethyl acetate: 7/3) afforded compound **8** as a colourless oil (280 mg, 73 %).

IR (neat) ν_{max}/cm^{-1} 2954, 2920, 2869, 1693, 1453, 1136, 1086, 996; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.30 (d, J = 15.2 Hz, 1H), 4.20 (d, J = 15.2 Hz, 1H), 3.68 (s, 3H), 3.18 (s, 3H), 2.30 (m, 1H), 2.10 (br d, J = 11.4 Hz, 1H), 1.61 (m, 2H), 1.34-1.26 (m, 2H), 1.03-0.93 (m, 2H), 0.90 (d, J = 6.9 Hz, 3H), 0.88 (d, J = 6.9 Hz, 3H), 0.78 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0, 80.1, 66.1, 61.5, 48.4, 40.2, 34.6, 31.7, 25.5, 23.4, 22.4, 21.1 (2C), 16.3; HRMS (TOF-ESI) *m/z*: Calcd for $C_{14}H_{27}NO_3Na$ [M + Na]$^+$ 280.1883, found 280.1880.

[6] S. Breitler and E. M. Carreira, *J. Am. Chem. Soc.*, 2015, **137**, 5296-5299.

[7] The title product was synthesized according to the following procedure: H.A. Duong, R. E. Gilligan, M. L. Cooke, R. J. Phipps and M. J. Gaunt, *Angew. Chem. Int. Ed.*, 2011, **50**, 463-466.

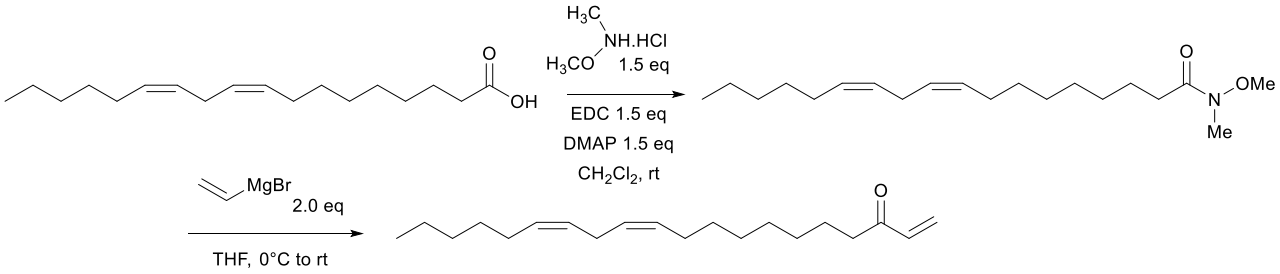
1-{[(1*R*,2*S*,5*R*)-2-*iso*Propyl-5-methylcyclohex-1-yl]oxy}but-3-en-2-one (1o)



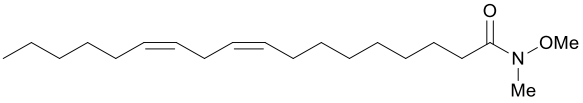
To a solution of the previous menthol-derived Weinreb amide **8** (100 mg, 0.39 mmol) in dry THF (10 mL) was added dropwise vinylmagnesium bromide solution 1.0 M in THF (780 µL, 0.78 mmol) at 0 °C. The mixture was then stirred 2 hours at room temperature before quenching by an aqueous saturated solution of NH_4Cl (4 mL). The aqueous layer was then extracted with AcOEt (10 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated. Flash chromatography (cyclohexane/ethyl acetate: 95/5) afforded the compound **1o** as a colourless oil (61 mg, 70 %).

IR (neat) ν_{max}/cm^{-1} 2955, 2920, 2870, 1702, 1453, 1411, 1111; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.60 (dd, J = 17.6, 10.6 Hz, 1H), 6.32 (dd, J = 17.6, 1.4 Hz, 1H), 5.78 (dd, J = 10.6, 1.4 Hz, 1H), 4.30 (d, J = 16.5 Hz, 1H), 4.14 (d, J = 16.5 Hz, 1H), 3.12 (td, J = 10.5, 4.1 Hz, 1H), 2.24 (qtd, J = 7.0, 2.6 Hz, 1H), 2.04 (br d, J = 11.9 Hz, 1H), 1.64-1.60 (m, 2H), 1.34-1.26 (m, 2H), 0.94-0.81 (m, 2H), 0.92 (d, J = 6.9 Hz, 3H), 0.88 (d, J = 6.9 Hz, 3H), 0.76 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.0, 132.7, 129.0, 80.4, 73.1, 48.3, 40.1, 34.1, 31.7, 25.7, 23.4, 22.4, 21.1, 16.3; HRMS (TOF-ESI) *m/z*: Calcd for $C_{14}H_{24}O_2Na$ [M + Na]$^+$ 247.1669, found 247.1674.

The **(11*Z*,14*Z*)-icosa-1,11,14-trien-3-one** was synthesized by a sequence of procedures shown below:



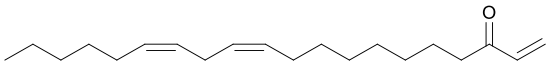
(9*Z*,12*Z*)-*N*-Methoxy-*N*-methyloctadeca-9,12-dienamide (9)



To a solution of linoleic acid (460 µL, 1.50 mmol) in dry CH_2Cl_2 (1 mL) was added *N*,*O*-dimethyl hydroxylamine (215 mg, 2.25 mmol), *N*-(3-dimethylaminopropyl)-*N*'-ethyl carbodiimide hydrochloride (430 mg, 2.25 mmol) and DMAP (275 mg, 2.25 mmol). The mixture was stirred at room temperature for 48 hours before quenching by addition of a saturated solution of NH_4Cl (1 mL). The aqueous layer was then extracted with CH_2Cl_2 (2×10 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated. Flash chromatography (cyclohexane/ethyl acetate: 9/1) afforded compound **9** as a colourless oil (259 mg, 53 %).

IR (neat) ν_{max}/cm^{-1} 2926, 2854, 1670, 1464, 1382, 1177, 989, 722; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.41-5.27 (m, 4H, =CH), 3.67 (s, 3H), 3.17 (s, 3H), 2.76 (t, J = 5.8 Hz, 2H), 2.40 (t, J = 7.4 Hz, 2H), 2.03 (m, 4H), 1.62 (m, 2H), 1.30 (m, 14H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 130.3, 130.2, 128.1, 128.1, 61.3, 32.4, 32.1, 31.7, 29.8, 29.6, 29.5 (2C), 29.3, 27.3 (2C), 25.8 , 24.8, 22.7, 14.2; HRMS (TOF-ESI) *m/z*: Calcd for $C_{20}H_{37}O_2NNa$ [M + Na]$^+$ 346.2717, found 346.2731.

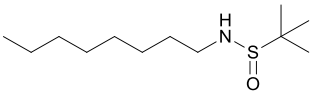
(11*Z*,14*Z*)-Icosa-1,11,14-trien-3-one (1p)



To a solution of the previous linoleic Weinreb amide **9** (230 mg, 0.71 mmol) in dry THF (4.5 mL) was added dropwise vinylmagnesium bromide solution 1.0 M in THF (1.78 mL, 1.78 mmol) at 0 °C. The mixture was then stirred 4 hours at room temperature before quenching by a saturated solution of NH_4Cl (2 mL). The aqueous layer was then extracted with AcOEt (2×10 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated. Flash chromatography (cyclohexane/ethyl acetate: 95/5) afforded the compound **1p** as a colourless oil (173 mg, 84 %).

IR (neat) ν_{max}/cm^{-1} 2926, 2854, 1684, 1466, 1399, 954, 724; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.35 (dd, J = 17.7, 10.3 Hz, 1H), 6.20 (dd, J = 17.7, 1.2 Hz, 1H), 5.80 (dd, J = 10.3, 1.2 Hz, 1H), 5.40-5.28 (m, 4H), 2.77 (t, J = 5.7 Hz, 2H), 2.57 (t, J = 7.4 Hz, 2H), 2.03 (m, 4H), 1.61 (m, 2H), 1.30 (m, 14H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.2, 136.7, 130.3, 130.2, 128.2, 128.0, 127.9, 39.8, 31.7, 29.7, 29.5 (2C), 29.4, 29.3, 27.3 (2C), 25.8, 24.1, 22.7, 14.2; HRMS (TOF-ESI) *m/z*: Calcd for $C_{20}H_{34}ONa$ $[M + Na]^+$ 313.2502, found 313.2502.

***N*-Octyl-*tert*-butylsulfinamide (2d)**



A solution of *tert*-butylsulfinamide (300 mg, 2.48 mmol), octanal (778 µL, 4.96 mmol) and anhydrous $CuSO_4$ (790 mg, 4.96 mmol) in dry CH_2Cl_2 (2 mL) was stirred at room temperature overnight. The resulting mixture was then filtrated through Celite®, washed with CH_2Cl_2 and evaporated. The residue was dissolved in MeOH (10 mL) and cooled to 0 °C before adding $NaBH_4$ (470 mg, 14.4 mmol). The mixture was then stirred 4 hours more before quenching by addition of acetone (2 mL). After evaporation of the solvent and addition of water (2 mL), the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was then purified by flash chromatography (cyclohexane/ethyl acetate: 4/6 to 3/7) to yield the desired product **2d** as a colourless oil (512 mg, 88%).

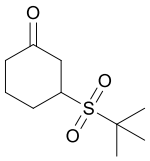
IR (neat) ν_{max}/cm^{-1} 2924, 2854, 1469, 1055; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.62 (t, J = 6.5 Hz, 1H), 3.22-3.01 (m, 2H), 1.54 (m, 2H), 1.40-1.21 (m, 10H), 1.20 (s, 9H), 0.87 (t, J = 6.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 63.2, 55.6, 45.9, 33.0, 31.9, 31.2, 29.3, 26.9, 22.7 (3C), 14.2; HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_{27}NONaS$ $[M + Na]^+$ 256.1706, found 256.1711.

2.2. Preparation of ketosulfones 3 or alkoxysulfones 4

General procedure for the synthesis of ketosulfones 3

To a solution of alkene **1** (0.20 mmol) in CH_3CN (c = 0.4 mol.L^{-1}) were successively added sulfinamide **2** (0.40 mmol) and aqueous HBF_4 48% wt. (0.20 mmol). The resulting mixture was stirred at room temperature until disappearance of the starting material (4 to 48 hours) before quenching by addition of water (2 mL). The solution was then extracted with CH_2Cl_2 (3×10 mL). The organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated. Crude product was purified by flash chromatography with cyclohexane/ethyl acetate to yield the desired ketosulfone **3**.

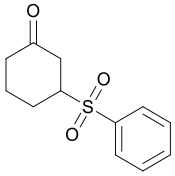
3-(*tert*-Butylsulfonyl)cyclohexanone (3aa)



3aa was prepared following the general procedure by reacting **1a** (19.4 μL, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 24 hours. Flash chromatography (cyclohexane/ethyl acetate: 4/6) afforded the title compound **3aa** as a white solid (32 mg, 73%).

M.p.: 108-109 °C; IR (neat) ν_{max}/cm^{-1} 2968, 1705, 1270, 1110, 664; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57-3.47 (m, 1H), 2.75 (d, J = 9.1 Hz, 2H), 2.40-2.21 (m, 4H), 2.08-1.97 (m, 1H), 1.75-1.63 (m, 1H), 1.42 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.4, 61.4, 55.8, 42.4, 40.5, 25.3, 24.2 (3C), 23.8; HRMS (TOF-ESI) *m/z*: Calcd for $C_{10}H_{18}O_3NaS$ $[M + Na]^+$ 241.0869, found 241.0875.

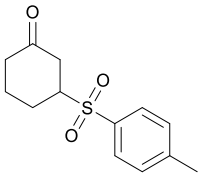
3-(Benzenesulfonyl)cyclohexanone (3ab)



3ab was prepared following the general procedure by reacting **1a** (19.4 μL, 0.20 mmol), benzenesulfinamide **2b** (56 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 24 hours. Flash chromatography (cyclohexane/ethyl acetate: 7/3 to 6/4) afforded the title compound **3ab** as a white solid (44 mg, 92%).

M.p.: 87-88 °C; IR (neat) ν_{max}/cm^{-1} 2965, 1706, 1260, 1137, 1084, 1019, 798; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (br d, J = 7.2 Hz, 2H,), 7.68 (br t, J = 7.7 Hz, 1H), 7.57 (br t, J = 7.2 Hz, 2H), 3.33-3.23 (m, 1H), 2.57 (m, 2H), 2.41-2.17 (m, 4H), 1.91 (qd, J = 12.7, 3.1 Hz, 1H), 1.71-1.57 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.6, 136.8, 134.4, 129.6 (2C), 129.1 (2C), 62.4, 40.6, 40.5, 23.8, 23.6; HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_{14}O_3NaS$ $[M + Na]^+$ 261.0556, found 261.0562. The data presented above is in agreement with that detailed in the literature. [8]

3-Tosylcyclohexanone (3ac)



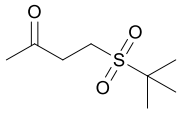
3ac was prepared following the general procedure by reacting **1a** (19.4 μL, 0.20 mmol), *p*-toluenesulfinamide **2c** (62 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 24 hours. Flash chromatography (cyclohexane/ethyl acetate: 7/3 to 6/4) afforded the title compound **3ac** as a yellow solid (38 mg, 75%).

M.p.: 82-83 °C; IR (neat) ν_{max}/cm^{-1} 2952, 1713, 1283, 1086, 1018, 664; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 3.30-3.20 (m, 1H), 2.53 (m, 2H), 2.44 (s, 3H), 2.41-2.18 (m, 4H), 1.95-1.73 (m, 1H), 1.67-1.58 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.7, 145.4, 133.6, 130.1 (2C), 129.0 (2C), 62.4, 40.6 (2C), 23.8, 23.6, 21.7; HRMS (TOF-ESI) *m/z*:

[8] N. K. Jana and J. G. Verkade, *Org. Lett.*, 2003, **5**, 3787-3790.

Calcd for $C_{13}H_{16}O_3NaS$ $[M + Na]^+$ 275.0712, found 275.0721. The data presented above are in agreement with that detailed in the literature.[9]

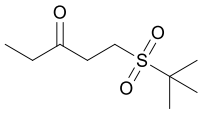
4-(*tert*-Butylsulfonyl)butan-2-one (3ca)



3ca was prepared following the general procedure by reacting **1c** (16.7 μL, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 7 hours. Flash chromatography (cyclohexane/ethyl acetate: 3/7) afforded the title compound **3ca** as a white solid (26 mg, 68%).

M.p.: 56-57 °C; IR (neat) ν_{max}/cm^{-1} 2978, 1714, 1475, 1300, 1160, 1108 (CH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.20 (t, J = 6.9 Hz, 2H), 3.02 (t, J = 7.7 Hz, 2H), 2.24 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.7, 59.2, 40.2, 34.1, 30.1, 23.4 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_8H_{16}O_3NaS$ $[M + Na]^+$ 215.0712, found 215.0719. The data presented above are in agreement with that detailed in the literature.[10]

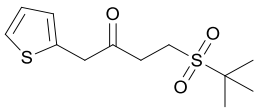
1-(*tert*-Butylsulfonyl)pentan-3-one (3da)



3da was prepared following the general procedure by reacting **1d** (19.9 μL, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 7 hours. Flash chromatography (cyclohexane/ethyl acetate: 5/5 to 4/6) afforded the title compound **3da** as a white solid (39 mg, 95%).

M.p.: 55-56 °C; IR (neat) ν_{max}/cm^{-1} 2978, 1714, 1414, 1265, 1114, 976; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.21 (t, J = 6.9 Hz, 2H), 2.98 (t, J = 7.6 Hz, 2H), 2.51 (q, J = 7.3 Hz, 2H), 1.40 (s, 9H), 1.07 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.6, 59.1, 40.1, 36.2, 32.7, 23.4 (3C), 7.9; HRMS (TOF-ESI) *m/z*: Calcd for $C_9H_{18}O_3NaS$ $[M + Na]^+$ 229.0869, found 229.0865.

4-(*tert*-Butylsulfonyl)-1-(thien-2-yl)butan-2-one (3ea)

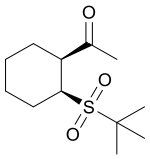


3ea was prepared following the general procedure by reacting **1e** (30 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 10 hours. Flash chromatography (cyclohexane/ethyl acetate: 75/25) afforded the title compound **3ea** as a white solid (35 mg, 64%).

M.p.: 84-85 °C; IR (neat) ν_{max}/cm^{-1} 2962, 1717, 1473, 1265, 1108, 1007, 669; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (dd, J = 5.1, 1.1 Hz, 1H), 6.98 (dd, J = 5.0, 3.6 Hz, 1H), 6.91 (m, 1H), 3.99 (s, 2H), 3.21 (t, J = 6.6 Hz, 2H), 3.08 (t, J = 6.8 Hz, 2H), 1.71 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.5, 134.4, 127.5, 127.4, 125.7, 59.3, 43.9, 40.4, 32.5, 23.6 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_{18}O_3NaS_2$ $[M + Na]^+$ 297.0590, found 297.0592.

[9] N. K. Jana and J. G. Verkade, *Org. Lett.*, 2003, **5**, 3787-3790.
[10] M. J. Tilby, D. F. Dewez, L. R. E. Pantaine, A. Hall, C. Martínez-Lamenca and M. C. Willis, *ACS Catal.* 2022, **12**, 6060-6067.

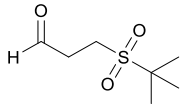
1-Acetyl-*2*-*tert*-butylsulfonyl cyclohexane (3fa)



3fa was prepared following the general procedure by reacting **1f** (25.7 μL, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 48 hours. Flash chromatography (cyclohexane/ethyl acetate: 5/5) afforded the title compound **3fa** as a brown foam (33 mg, 67%).

IR (neat) ν_{max}/cm^{-1} 2944, 1711, 1271, 1110, 681; ^1H NMR (300 MHz, $CDCl_3$) δ 3.59 (m, 1H), 2.90 (m, 1H), 2.62-2.51 (m, 1H), 2.23 (s, 3H), 2.02 (m, 2H), 1.81-1.74 (m, 2H), 1.47-1.41 (m, 3H), 1.36 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.9, 61.1, 57.1, 48.3, 29.1, 27.6, 26.2, 24.6, 23.5 (3C), 21.9; HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_{22}O_3SNa$ $[M + Na]^+$ 269.1182, found 269.1180.

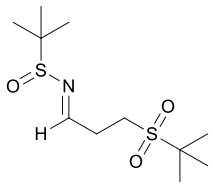
3-(*tert*-Butylsulfonyl)propanal (3ga)



3ga was prepared following the general procedure by reacting **1g** (13.4 μL, 0.20 mmol), *tert*-butylsulfinamide **2a** (24 mg, 0.20 mmol), HBF_4 (26 μL, 0.20 mmol) for 4 hours. Flash chromatography (cyclohexane/ethyl acetate: 3/7) afforded the title compound **3ga** as a colourlesss oil (14 mg, 39%).

IR (neat) ν_{max}/cm^{-1} 2988, 1723, 1297, 1110; ^1H NMR (300 MHz, $CDCl_3$) δ 9.87 (s, 1H), 3.25 (t, J = 7.4 Hz, 2H), 3.10 (t, J = 7.0 Hz, 2H), 1.44 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8, 59.4, 38.7, 34.8, 23.5 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_7H_{14}O_3NaS$ $[M + Na]^+$ 201.0556, found 201.0564.

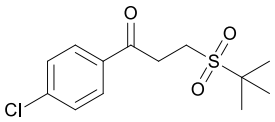
(*E*)-*N*-[3-(*tert*-Butylsulfonyl)propyliden-1-yl]- *tert*-butylsulfinamide (5ga)



5ga was prepared following the general procedure by reacting **1g** (13.4 μL, 0.20 mmol), *tert*-butylsulfinamide **2a** (73 mg, 0.60 mmol), HBF_4 (26 μL, 0.20 mmol) for 24 hours. Flash chromatography (cyclohexane/ethyl acetate: 3/7) afforded the title compound **5ga** as a white solid (14,5 mg, 26%).

M.p.: 101-102 °C; IR (neat) ν_{max}/cm^{-1} 2985, 1651, 1300, 1263, 1117, 1078; ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (t, J = 3.1 Hz, 1H,), 3.34-3.28 (m, 2H), 3.15-3.09 (m, 2H), 1.45 (s, 9H), 1.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 59.4, 57.2, 41.2, 27.5, 23.6 (3C), 22.5 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_{11}H_{24}NO_3S_2$ $[M + H]^+$ 282.1192, found 282.1205.

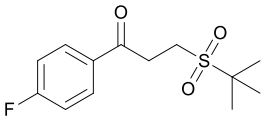
3-(*tert*-Butylsulfonyl)-1-(4-chlorophenyl)propan-1-one (3ha)



3ha was prepared following the general procedure by reacting **1h** (33 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 5 hours. Flash chromatography (cyclohexane/ethyl acetate: 7/3) afforded the title compound **3ha** as a white solid (16 mg, 28%).

M.p.: 146-147 °C; IR (neat) ν_{max}/cm^{-1} 2982, 1674 , 1588, 1301, 1265, 1116; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 3.55 (dd, J = 8.5, 6.4 Hz, 2H), 3.38 (dd, J = 8.5, 6.5 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.3, 140.5, 134.4, 129.7 (2C), 129.3 (2C), 59.3, 40.5, 29.8, 23.5 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_{13}H_{17}O_3NaSCl$ $[M + Na]^+$ 311.0479, found 311.0476.

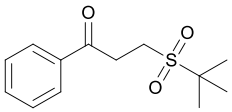
3-(*tert*-Butylsulfonyl)-1-(4-fluorophenyl)propan-1-one (3ia)



3ia was prepared following the general procedure by reacting **1i** (30 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 5 hours. Flash chromatography (cyclohexane/ethyl acetate: 7/3 to 6/4) afforded the title compound **3ia** as a white solid (16 mg, 29%).

M.p.: 103-104 °C; IR (neat) ν_{max}/cm^{-1} 2925, 1684, 1596, 1267, 1108, 979, 736; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (m, 2H), 7.16 (br t, J = 8.7 Hz, 2H), 3.56 (dd, J = 8.4, 6.3 Hz, 1H), 3.38 (dd, J = 8.5, 6.4 Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9, 166.3 (d, J = 254.4 Hz), 131.0 (d, J = 9.3 Hz, 2C), 116.1 (d, J = 21.9 Hz, 2C), 59.4, 40.7, 29.8, 23.6 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_{13}H_{17}O_3NaSF$ $[M + Na]^+$ 295.0775, found 295.0779.

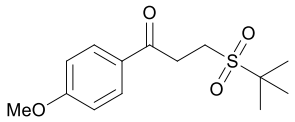
3-(*tert*-Butylsulfonyl)-1-phenylpropan-1-one (3ja)



3ja was prepared following the general procedure by reacting **1h** (26.4 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 5 hours. Flash chromatography (cyclohexane/ethyl acetate: 7/3 to 6/4) afforded the title compound **3ja** as a white solid (31 mg, 61%).

M.p.: 120-121 °C; IR (neat) ν_{max}/cm^{-1} 2935, 2920, 1687, 1262, 1108, 1002, 740, 688; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (br d, J = 7.3 Hz, 2H), 7.60 (br t, J = 7.6 Hz, 1H), 7.49 (br t, J = 7.7 Hz, 2H), 3.60 (dd, J = 8.5, 6.6 Hz, 1H), 3.39 (dd, J = 8.6, 6.7 Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 136.1, 133.9, 128.9, 128.3, 59.3, 40.6, 29.8 , 23.6 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_{13}H_{18}O_3NaS$ $[M + Na]^+$ 277.0869, found 277.0887.

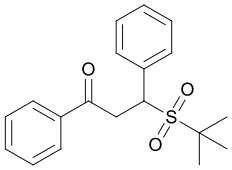
3-(*tert*-Butylsulfonyl)-1-(4-methoxyphenyl)propan-1-one (3ka)



3ka was prepared following the general procedure by reacting **1k** (32 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 4 hours. Flash chromatography (cyclohexane/ethyl acetate: 5/5) afforded the title compound **3ka** as a white solid (33 mg, 58%).

M.p.: 75-76 °C; IR (neat) ν_{max}/cm^{-1} 2926, 1674, 1601, 1573, 1251, 1112, 977 ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 3.54 (dd, J = 8.5, 6.8 Hz, 2H), 3.37 (dd, J = 8.5, 6.6 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9, 164.1, 130.6 (2C), 129.2, 114.1 (2C), 59.3, 55.7, 40.7, 29.3, 23.5 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_{14}H_{20}O_4NaS$ $[M + Na]^+$ 307.0975, found 307.0982.

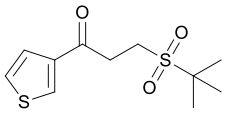
3-(*tert*-Butylsulfonyl)-1,3-diphenylpropan-1-one (3la)



3la was prepared following the general procedure by reacting **1l** (42 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 48 hours. Flash chromatography (cyclohexane/ethyl acetate: 9/1 to 8/2) afforded the title compound **3la** as a white solid (38 mg, 57%).

M.p.: 136-137 °C; IR (neat) ν_{max}/cm^{-1} 2926, 1687, 1281, 1177, 1108; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 7.3 Hz, 2H), 7.62 (d, J = 7.9 Hz, 2H), 7.55 (t, J = 7.1 Hz, 1H), 7.43 (m, 2H), 7.40-7.29 (m, 3H), 5.19 (dd, J = 9.2 Hz, J = 3.5 Hz, 1H), 4.15 (dd, J = 17.9 Hz, J = 3.5 Hz, 1H), 3.72 (dd, J = 17.9 Hz, J = 9.2 Hz, 1H), 1.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4 , 136.4, 135.0, 133.7, 129.9 (2C), 129.0 (3C), 128.8 (2C), 128.3 (2C), 62.4, 60.1, 39.6, 24.4 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_{19}H_{22}O_3NaS$ $[M + Na]^+$ 353.1182, found 353.1189.

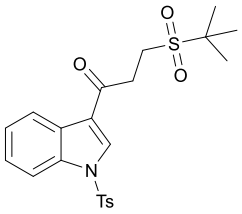
3-(*tert*-Butylsulfonyl)-1-(thien-3-yl)propan-1-one (3ma)



3ma was prepared following the general procedure by reacting **1m** (28 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 6 hours. Flash chromatography (cyclohexane/ethyl acetate: 6/4) afforded the title compound **3ma** as a white solid (29 mg, 55%).

M.p.: 133-134 °C; IR (neat) ν_{max}/cm^{-1} 2952, 1669, 1416, 1264, 1106, 771 ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J = 3.4 Hz, 1H), 7.67 (d, J = 4.9 Hz, 1H), 7.15 (t, J = 4.6 Hz, 1H), 3.52 (dd, J = 8.3, 6.2 Hz, 1H), 3.37 (dd, J = 8.5, 6.6 Hz, 1H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.1, 143.0, 134.6, 132.8, 128.5, 59.3, 40.5, 30.2, 23.5 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_{11}H_{16}O_3S_2Na$ $[M + Na]^+$ 283.0433, found 283.0435.

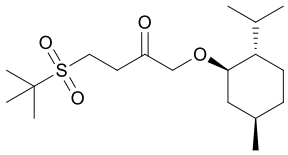
3-(*tert*-Butylsulfonyl)-1-(1-tosyl-1*H*-indol-3-yl)propan-1-one (3na)



3na was prepared following the general procedure by reacting **1n** (65 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 24 hours. Flash chromatography (cyclohexane/ethyl acetate: 7/3 to 6/4) afforded the title compound **3na** as a brown solid (45 mg, 50%).

M.p.: 143-144 °C; IR (neat) ν_{max}/cm^{-1} 2971, 1666, 1539, 1266, 1116, 978; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.25 (dd, J = 7.3, 2.2 Hz, 1H), 7.96 (dd, J = 6.9, 1.3 Hz, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.40-7.26 (m, 4H), 3.54-3.50 (m, 2H), 3.44-3.38 (m, 2H), 2.36 (s, 3H, CH_3-Ar), 1.47 (s, 9H, *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 146.2, 135.0, 134.5, 133.2, 132.5, 130.4 (2C), 127.4 (2C), 126.0, 125.1, 122.9, 120.4, 113.3, 59.4, 40.3, 30.7, 23.5 (3C), 21.8; HRMS (TOF-ESI) *m/z*: Calcd for $C_{22}H_{25}NO_5NaS_2$ [M + Na]$^+$ 470.1066, found 470.1073.

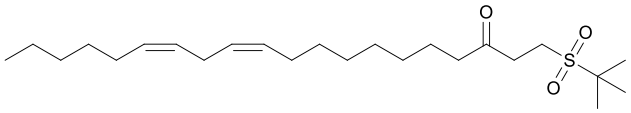
4-(*tert*-Butylsulfonyl)- 1-{[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohex-1-yl]oxy}but-3-en-2-one (3oa)



3oa was prepared following the general procedure by reacting **1o** (44 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) in a mixture of CH_2Cl_2/CH_3CN (8/2, 1 mL) for 17 hours. Flash chromatography (cyclohexane/ethyl acetate: 7/3) afforded the title compound **3oa** as a yellow oil (41 mg, 59%).

IR (neat) ν_{max}/cm^{-1} 2955, 2920, 1722, 1301, 1116; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.20 (d, J = 16.8 Hz, 1H), 4.00 (d, J = 16.8 Hz, 1H), 3.26-6.09 (m, 4H), 2.22 (m, 1H), 2.03 (br d, J = 11.3 Hz, 1H), 1.64 (m, 2H), 1.43 (s, 9H), 1.35-1.18 (m, 4H), 0.91 (m, 8H), 0.78 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.6, 80.6, 73.9, 59.3, 48.2, 40.0, 39.9, 34.5, 31.6, 30.5, 25.8, 23.5 (3C), 23.4, 22.4, 21.1, 16.4; HRMS (TOF-ESI) *m/z*: Calcd for $C_{18}H_{34}O_4NaS$ [M + Na]$^+$ 369.2070, found 369.2080.

(11*Z*,14*Z*)-1-(*tert*-Butylsulfonyl)icosa-11,14-dien-3-one (3pa)



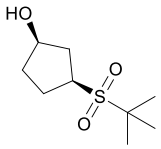
3pa was prepared following the general procedure by reacting **1p** (58 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 6 hours. Flash chromatography (cyclohexane/ethyl acetate: 7/3) afforded the title compound **3pa** as a yellow foam (42 mg, 51%).

IR (neat) ν_{max}/cm^{-1} 2982, 1712, 1268, 1102; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.35-5.27 (m, 4H), 3.21 (t, J = 7.8 Hz, 2H), 2.99 (t, J = 7.2 Hz, 2H), 2.76 (t, J = 5.8 Hz, 2H), 2.49 (t, J = 7.4 Hz, 2H), 2.03 (m, 4H), 1.60 (m, 2H), 1.42 (s, 9H), 1.30 (m, 14H), 0.88 (t, J = 7.0 Hz, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.3, 130.3, 130.2, 128.2, 128.0, 59.2, 43.1, 40.2, 33.1, 31.7 , 29.7, 29.5, 29.4, 29.2, 28.2, 27.3, 25.8, 24.9, 23.9, 23.5 (3C), 22.7, 14.2; HRMS (TOF-ESI) *m/z*: Calcd for $C_{24}H_{44}O_3NaS$ [M + Na]$^+$ 435.2903, found 435.2915.

General procedure for the synthesis of hydroxysulfones 4

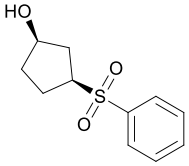
The ketosulfone **3** (0.20 mmol) was dissolved in MeOH (c = 0.1 mol.L^{-1}) at 0 °C and $NaBH_4$ (0.24 mmol) was then added. After stirring at room temperature for 2 hours, the reaction mixture was quenched by the addition of acetone (2 mL) before evaporation of the solvent. Water (2 mL) was then added, the aqueous layer was extracted with AcOEt (3×10 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography with cyclohexane/ethyl acetate to yield the desired hydroxysulfone **4**.

3-(*tert*-Butylsulfonyl)cyclopentanol (4ba)



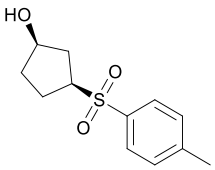
4ba was prepared following the general procedure by reacting **1b** (32.8 µL, 0.40 mmol), *tert*-butylsulfinamide **2a** (96 mg, 0.80 mmol), HBF_4 (52 µL, 0.40 mmol) for 24 hours. $NaBH_4$ (18 mg, 0.48 mmol) was next added. Flash chromatography (cyclohexane/ethyl acetate: 1/9) afforded the title compound **4ba** as a white solid (73 mg, 88%, *cis*/*trans* = 10/1).
M.p.: 79-80 °C; IR (neat) ν_{max}/cm^{-1} 3499, 2993, 1282, 1143, 688; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.31 (br s, 1H), 3.72-3.62 (m, 1H), 2.47-2.20 (m, 4H), 2.13-2.06 (m, 1H), 2.02-1.91 (m, 1H), 1.79-1.72 (m, 1H), 1.44 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 72.4, 60.3, 55.7, 37.4, 35.6, 25.8, 24.3 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_9H_{18}O_3NaS$ [M+ Na]$^+$ 229.0869, found 229.0868.

3-(Benzenesulfonyl)cyclopentanol (4bb)



4bb was prepared following the general procedure by reacting **1b** (16.8 µL, 0.20 mmol), benzenesulfinamide **2b** (56 mg, 0.40 mmol), HBF_4 (26 µL, 0.20 mmol) for 24 hours. $NaBH_4$ (9.1 mg, 0.24 mmol) was next added. Flash chromatography (cyclohexane/ethyl acetate: 3/7 to 2/8) afforded the title compound **4bb** as a colourless oil (30 mg, 66%, *cis*/*trans* = 21/1).
IR (neat) ν_{max}/cm^{-1} 3480, 1446, 1284, 1142, 1085; 690; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (br d, *J* = 7.4 Hz, 2H), 7.67 (br t, *J* = 7.8 Hz, 1H), 7.57 (br t, *J* = 6.9 Hz, 2H), 4.32 (br s, 1H), 3.61 (qt, *J* = 8.5 Hz, 1H), 2.35-2.10 (m, 4H), 1.96-1.85 (m, 2H), 1.83-1.73 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 134.0, 129.5 (2C), 128.7 (2C), 72.7, 63.2, 36.3, 35.6, 24.8; HRMS (TOF-ESI) *m/z*: Calcd for $C_{11}H_{14}O_3NaS$ [M + Na]$^+$ 249.0556, found 249.0560.

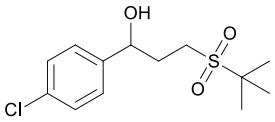
3-(*p*-Toluensulfonyl)-cyclopentan1-ol (4bc)



4bc was prepared following the general procedure by reacting **1b** (16.8 µL, 0.20 mmol), *p*-toluenesulfinamide **2c** (62 mg, 0.40 mmol), HBF_4 (26 µL, 0.20 mmol) for 24 hours. $NaBH_4$ (9.1 mg, 0.24 mmol) was next added. Flash chromatography (cyclohexane/ethyl acetate: 4/6) afforded the title compound **4bc** as a colourless oil (58 mg, 75%, *cis*/*trans* = 17/1).

IR (neat) ν_{max}/cm^{-1} 3492, 1478, 1284, 1185; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 4.31 (br s, 1H), 3.58 (qt, J = 6.7 Hz, 1H), 2.45 (s, 3H), 2.28-2.13 (m, 4H), 1.95-1.84 (m, 2H), 1.79-1.74 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 135.0, 130.0 (2C), 128.6 (2C), 72.6, 63.2, 36.2, 35.5, 24.6, 21.6; HRMS (TOF-ESI) *m/z*: Calcd for $C_{12}H_{16}O_3NaS$ [M + Na]$^+$ 263.0712, found 263.0710. The data presented above are in agreement with that detailed in the literature. [11]

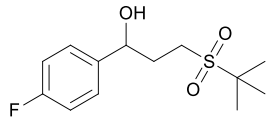
3-(*tert*-Butylsulfonyl)-1-(4-chlorophenyl)propan-1-ol (4ha)



4ha was prepared following the general procedure by reacting **1h** (33 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 5 hours. $NaBH_4$ (9.1 mg, 0.24 mmol) was next added. Flash chromatography (cyclohexane/ethyl acetate: 4/6) afforded the title compound **4ha** as a colourless oil (11 mg, 18%).

IR (neat) ν_{max}/cm^{-1} 3469, 2924, 1282, 1110, 748; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (m, 4H), 4.95 (dd, J = 8.5, 4.5 Hz, 1H), 3.07 (t, J = 7.3 Hz, 2H), 2.33-2.21 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 133.8, 129.0 (2C), 127.2 (2C), 71.8, 59.3, 42.1, 30.2, 23.6 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_{13}H_{19}O_3NaSCl$ [M + Na]$^+$ 313.0636, found 313.0638.

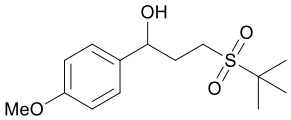
3-(*tert*-Butylsulfonyl)-1-(4-fluorophenyl)propan-1-ol (4ia)



4ia was prepared following the general procedure by reacting **1i** (30 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 5 hours. $NaBH_4$ (9.1 mg, 0.24 mmol) was next added. Flash chromatography (cyclohexane/ethyl acetate: 4/6 to 3/7) afforded the title compound **4ia** as a white solid (17 mg, 31%).

M.p.: 61-62 °C; IR (neat) ν_{max}/cm^{-1} 3479, 2990, 1509, 1260, 1109; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.7 Hz, J = 5.4 Hz, 2H), 7.04 (t, J = 8.6 Hz, 2H), 4.91 (dd, J = 8.0, 4.6 Hz, 1H), 3.07 (t, J = 7.5 Hz, 2H), 2.52 (br s, 1H), 2.31-2.22 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5 (d, J = 245 Hz), 139.3, 127.5 (d, J = 8.0 Hz, 2C), 115.6 (d, J = 21.3 Hz, 2C), 71.9, 59.3, 42.2, 30.2, 23.6 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_{13}H_{19}O_3FNaS$ [M + Na]$^+$ 297.0931, found 297.0937.

3-(*tert*-Butylsulfonyl)-1-(4-methoxyphenyl)propan-1-ol (4ka)

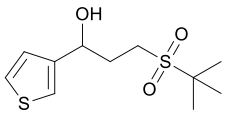


4ka was prepared following the general procedure by reacting **1k** (32 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 4 hours. $NaBH_4$ (9.1 mg, 0.24 mmol) was next added. Flash chromatography (cyclohexane/ethyl acetate: 4/6) afforded the title compound **4ka** as a yellow oil (28 mg, 49%).

IR (neat) ν_{max}/cm^{-1} 3490, 2938, 1672, 1512, 1244, 1109, 1030; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 4.84 (t, J = 6.5 Hz, 2H), 3.80 (s, 3H), 3.11-2.98 (m, 2H), 2.27 (q, J = 7.5 Hz, 2H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 135.6, 127.1 (2C), 114.2 (2C), 72.3, 59.2, 55.4, 42.5, 30.0, 23.6 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_{14}H_{22}O_4NaS$ [M + Na]$^+$ 309.1131, found 309.1143.

[11] M. Fernández, U. Uria, L. Orbe, J. L. Vicario, E. Reyes and L. Carrillo, *J. Org. Chem.*, 2014, **79**, 441-445.

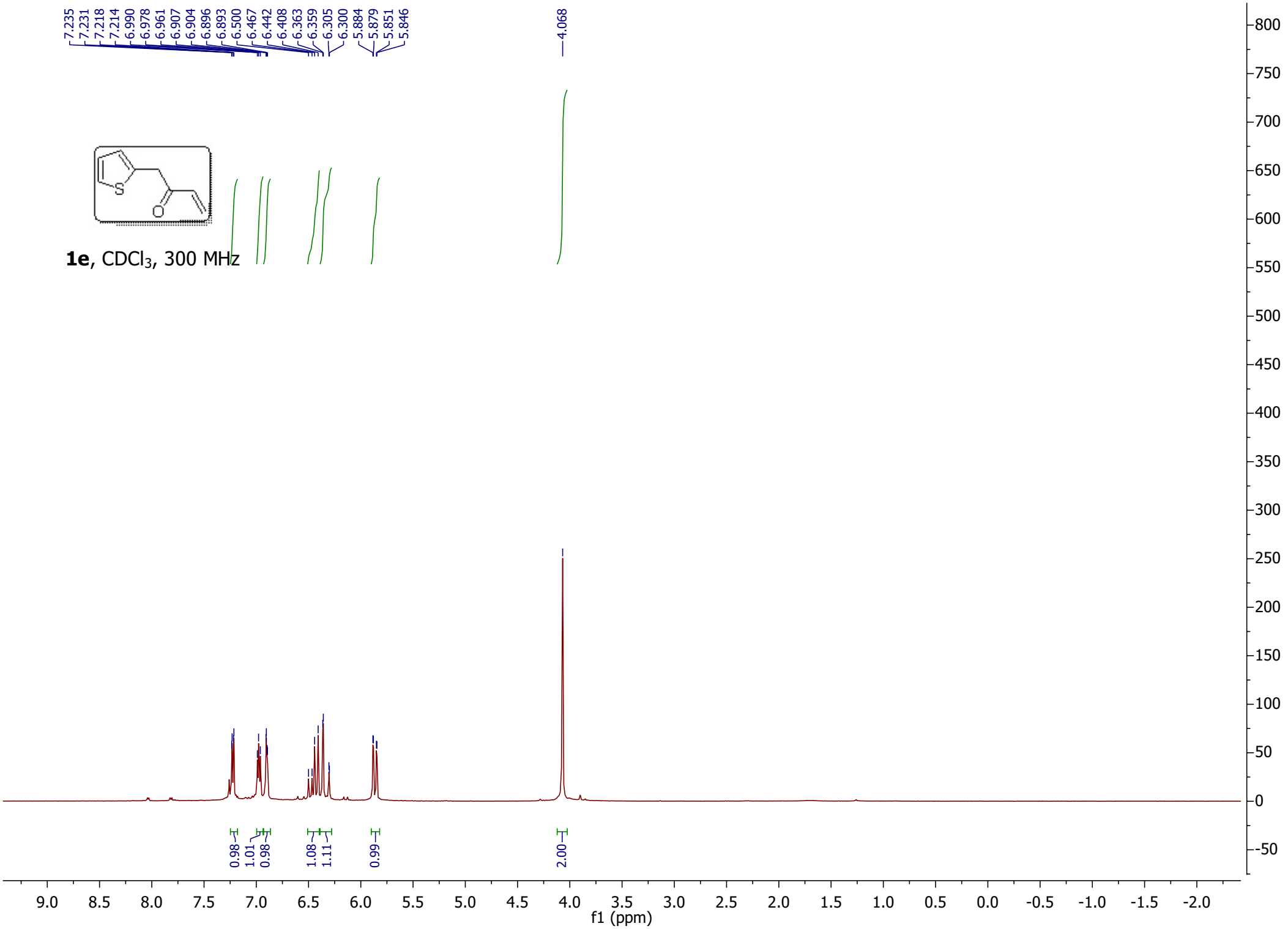
3-(*tert*-Butylsulfonyl)-1-(thien-3-yl)propan-1-ol (4ma)



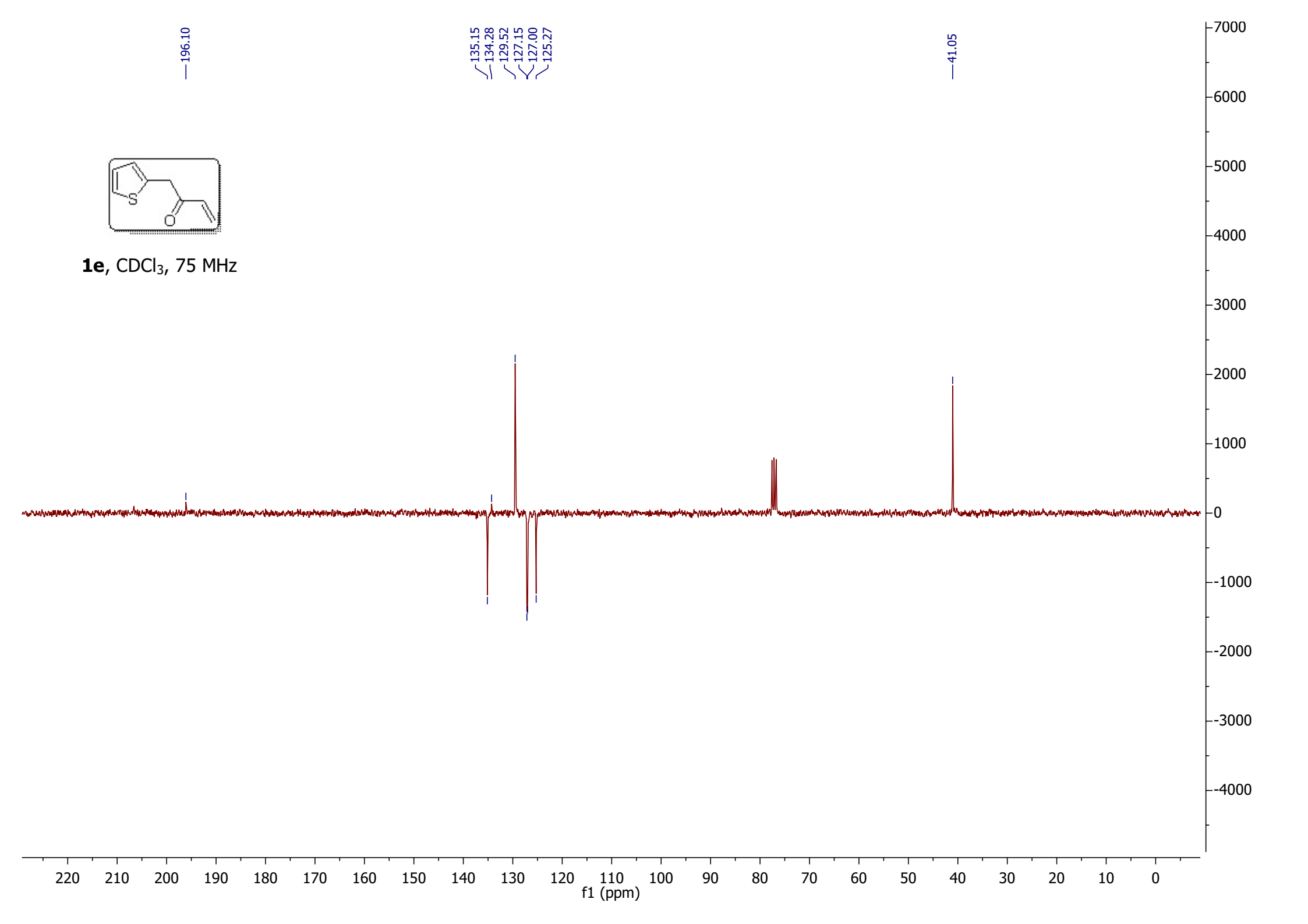
4ma was prepared following the general procedure by reacting **1m** (28 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 6 hours. $NaBH_4$ (9.1 mg, 0.24 mmol) was next added. Flash chromatography (cyclohexane/ethyl acetate: 4/6) afforded the title compound **4ma** as a white solid (24 mg, 47%).

M.p.: 82-83 °C; IR (neat) ν_{max}/cm^{-1} 3473, 297, 1255, 1086, 777; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 4.7 Hz, 1H), 7.00-6.96 (m, 2H), 5.17 (dd, J = 7.3, 5.3 Hz, 1H), 3.11 (t, J = 7.4 Hz, 2H), 2.71 (br s, 1H), 2.45-2.35 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2, 127.0, 125.0, 124.1, 68.6, 59.3, 42.2, 30.3, 25.6 (3C); HRMS (TOF-ESI) *m/z*: Calcd for $C_{11}H_{18}O_2NaS_2$ $[M + Na]^+$ 285.0590, found 285.0601.

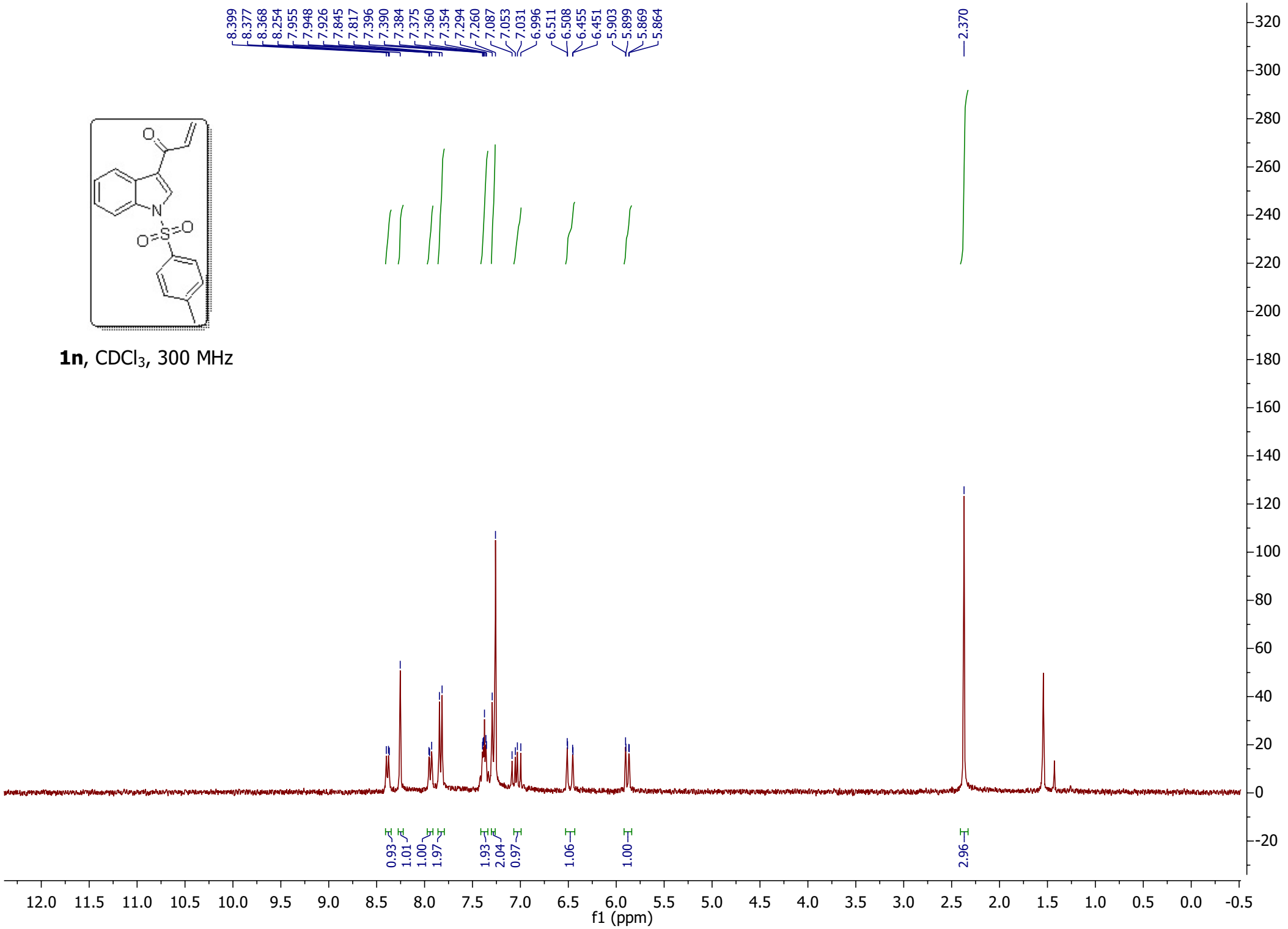
3. Copies of ^{1}H and ^{13}C spectra



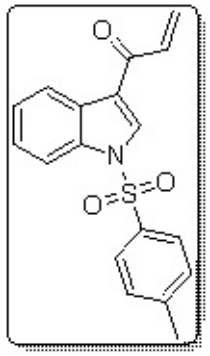
1e, $CDCl_3$, 300 MHz



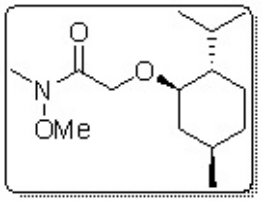
1e, $CDCl_3$, 75 MHz



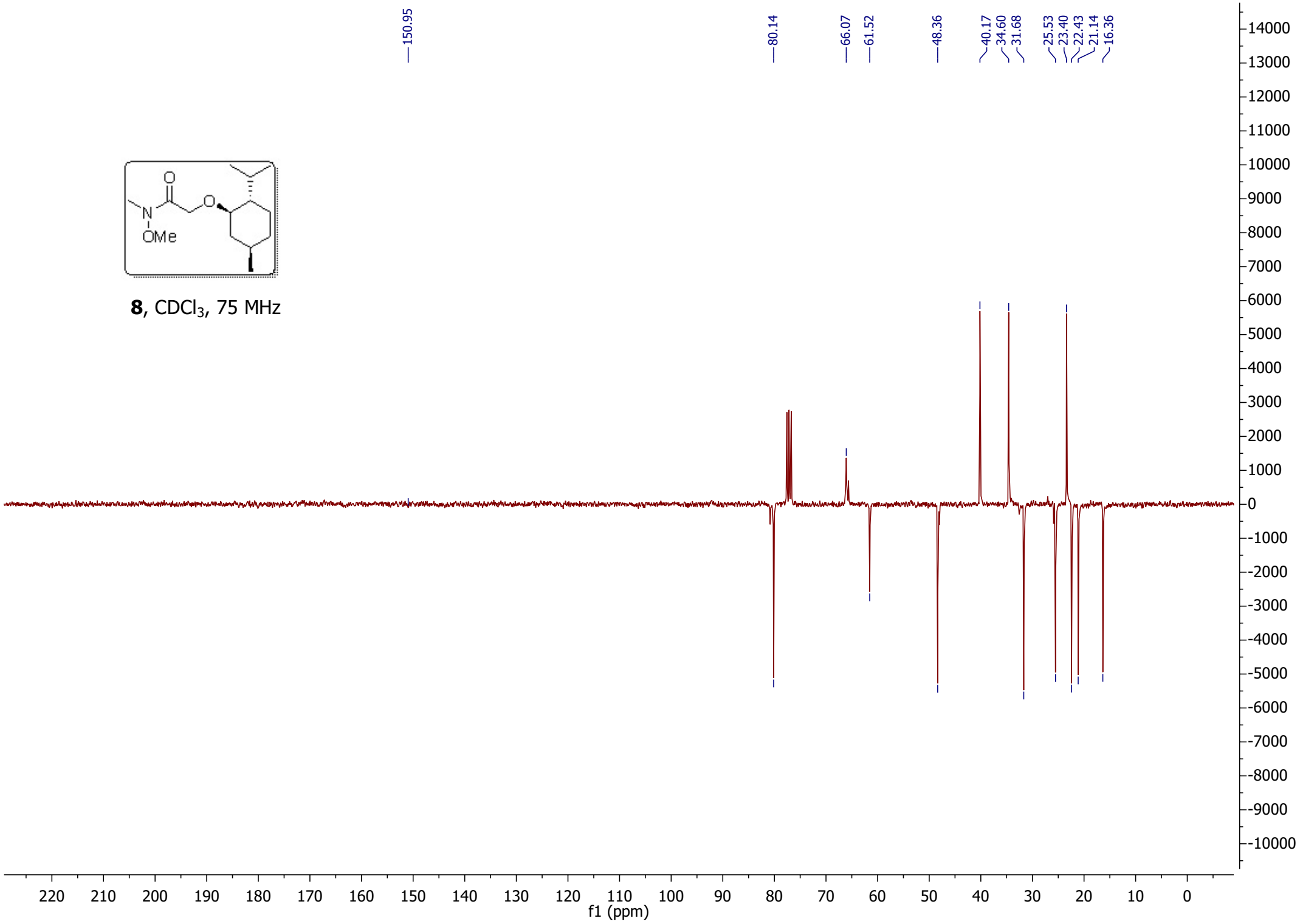
1n, $CDCl_3$, 300 MHz

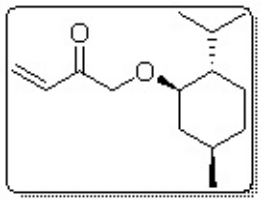


1n, $CDCl_3$, 75 MHz

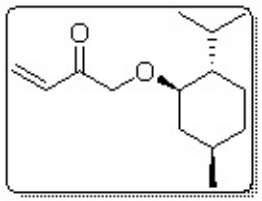


8, $CDCl_3$, 300 MHz

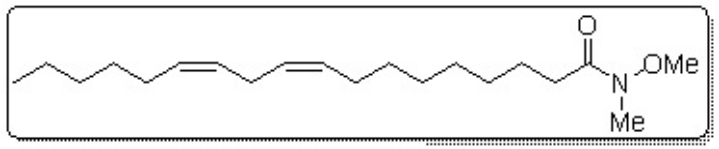

150.95
80.14
66.07
61.52
48.36
40.17
34.60
31.68
25.53
23.40
22.43
21.14
16.36
O
N
OMe
O
8, $CDCl_3$, 75 MHz
f1 (ppm)



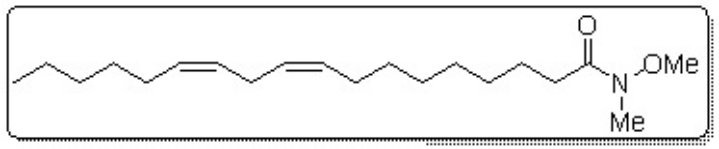
1o, $CDCl_3$, 300 MHz



1o, $CDCl_3$, 75 MHz

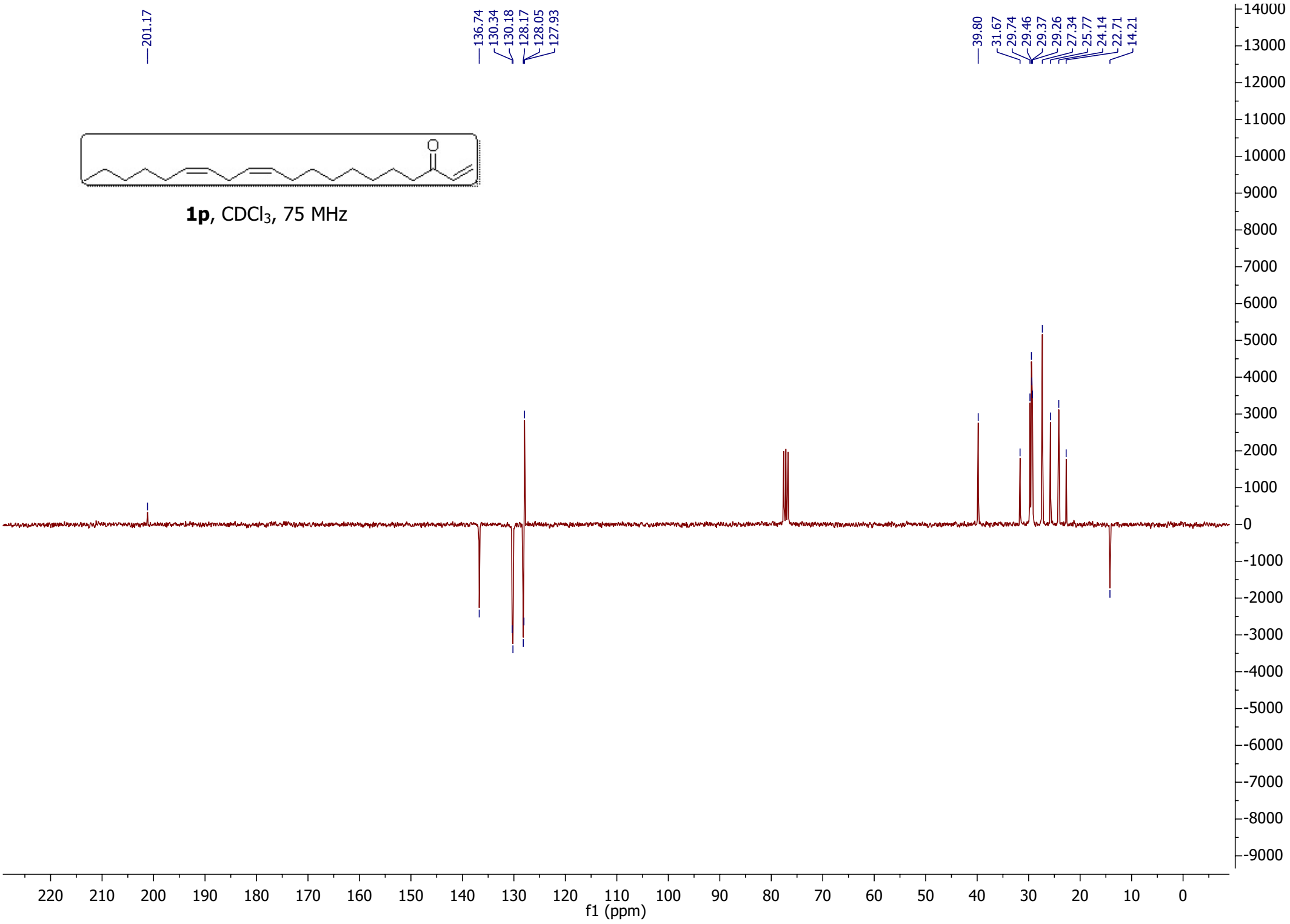


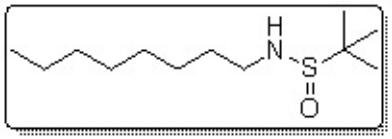
9, $CDCl_3$, 300 MHz



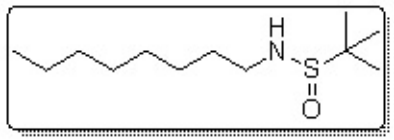
9, $CDCl_3$, 75 MHz

1p, $CDCl_3$, 300 MHz

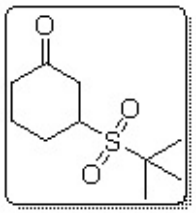

201.17
136.74
130.34
130.18
128.17
128.05
127.93
39.80
31.67
29.74
29.46
29.37
29.26
27.34
25.77
24.14
22.71
14.21
O
1p, $CDCl_3$, 75 MHz
f1 (ppm)



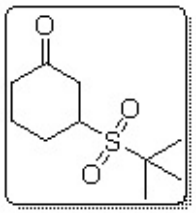
2d, $CDCl_3$, 300 MHz



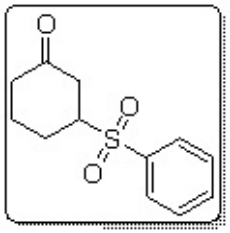
2d, $CDCl_3$, 75 MHz



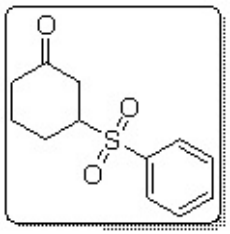
3aa, $CDCl_3$, 300 MHz



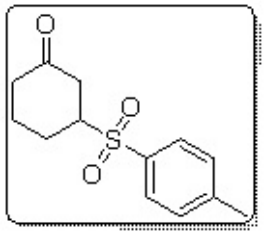
3aa, $CDCl_3$, 75 MHz



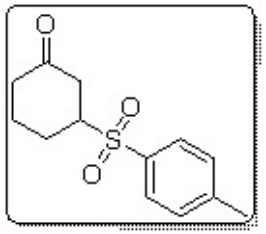
3ab, $CDCl_3$, 300 MHz



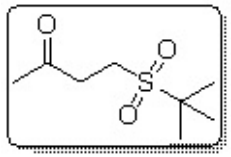
3ab, $CDCl_3$, 75 MHz



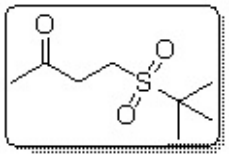
3ac, $CDCl_3$, 300 MHz



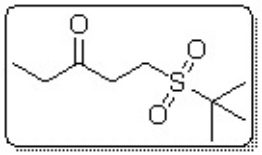
3ac, $CDCl_3$, 75 MHz



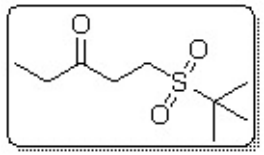
3ca, $CDCl_3$, 300 MHz



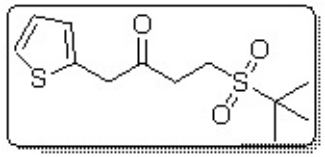
3ca, $CDCl_3$, 75 MHz



3da, $CDCl_3$, 300 MHz



3da, $CDCl_3$, 75 MHz

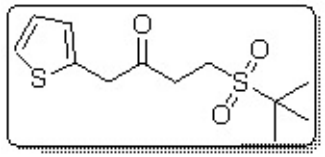


3ea, $CDCl_3$, 300 MHz

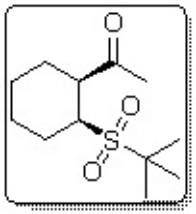
7.242
7.238
7.225
7.221
6.993
6.981
6.976
6.964
6.920
6.911
6.909
3.990
3.240
3.218
3.195
3.103
3.080
3.058
1.412

0.97
1.01
1.00
2.00
2.01
1.96
9.35

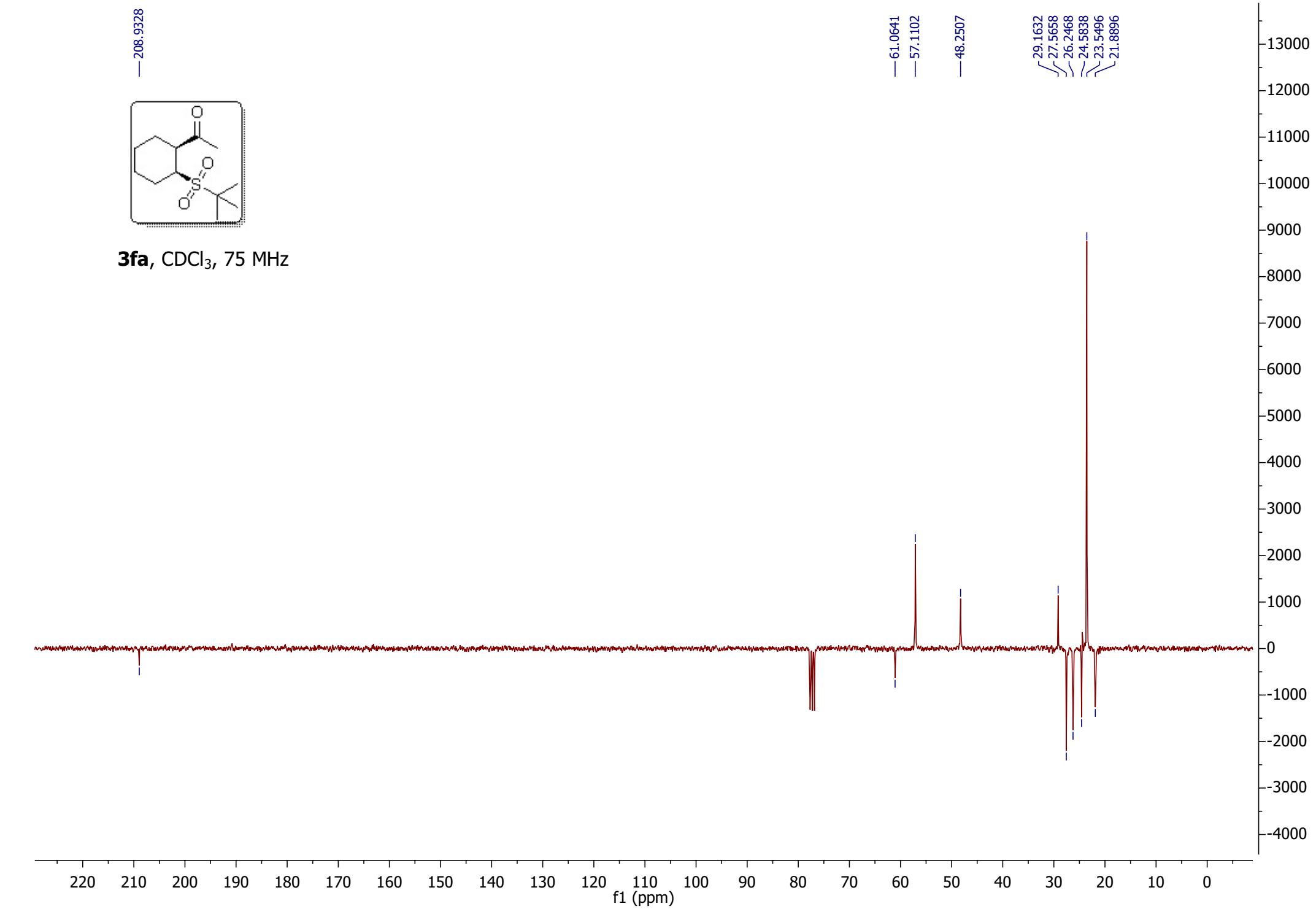
f1 (ppm)

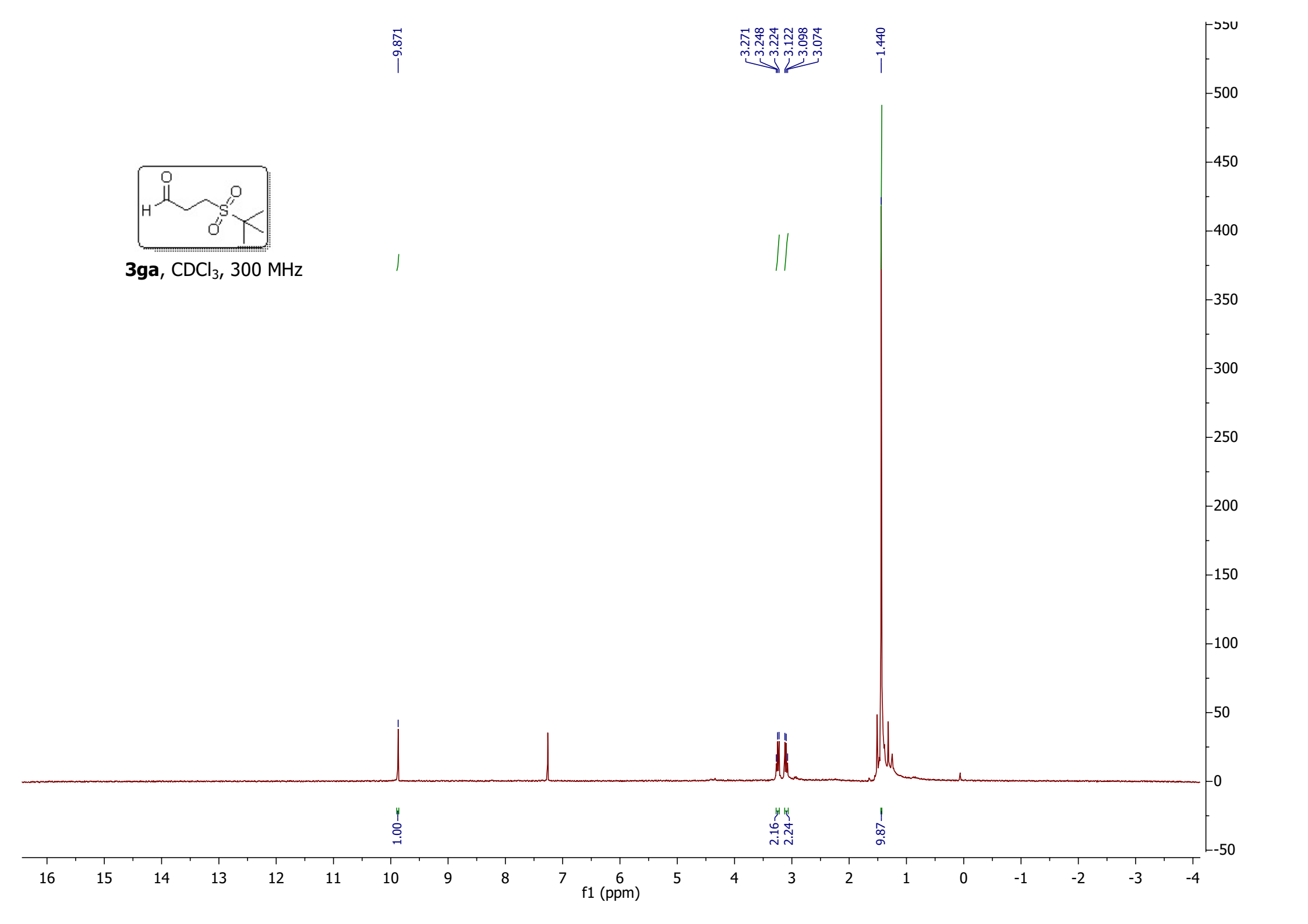


3ea, $CDCl_3$, 75 MHz

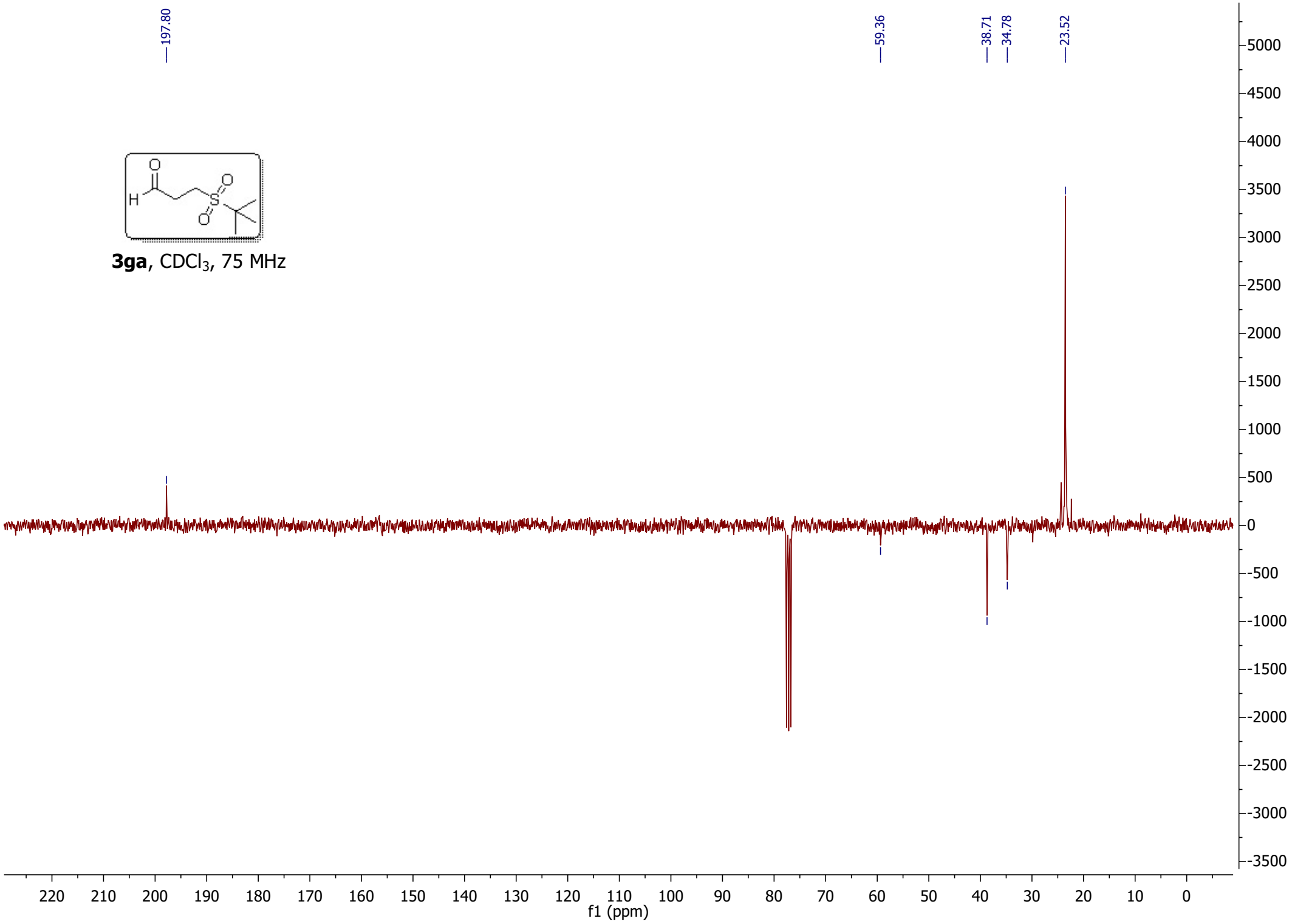


3fa, $CDCl_3$, 300 MHz

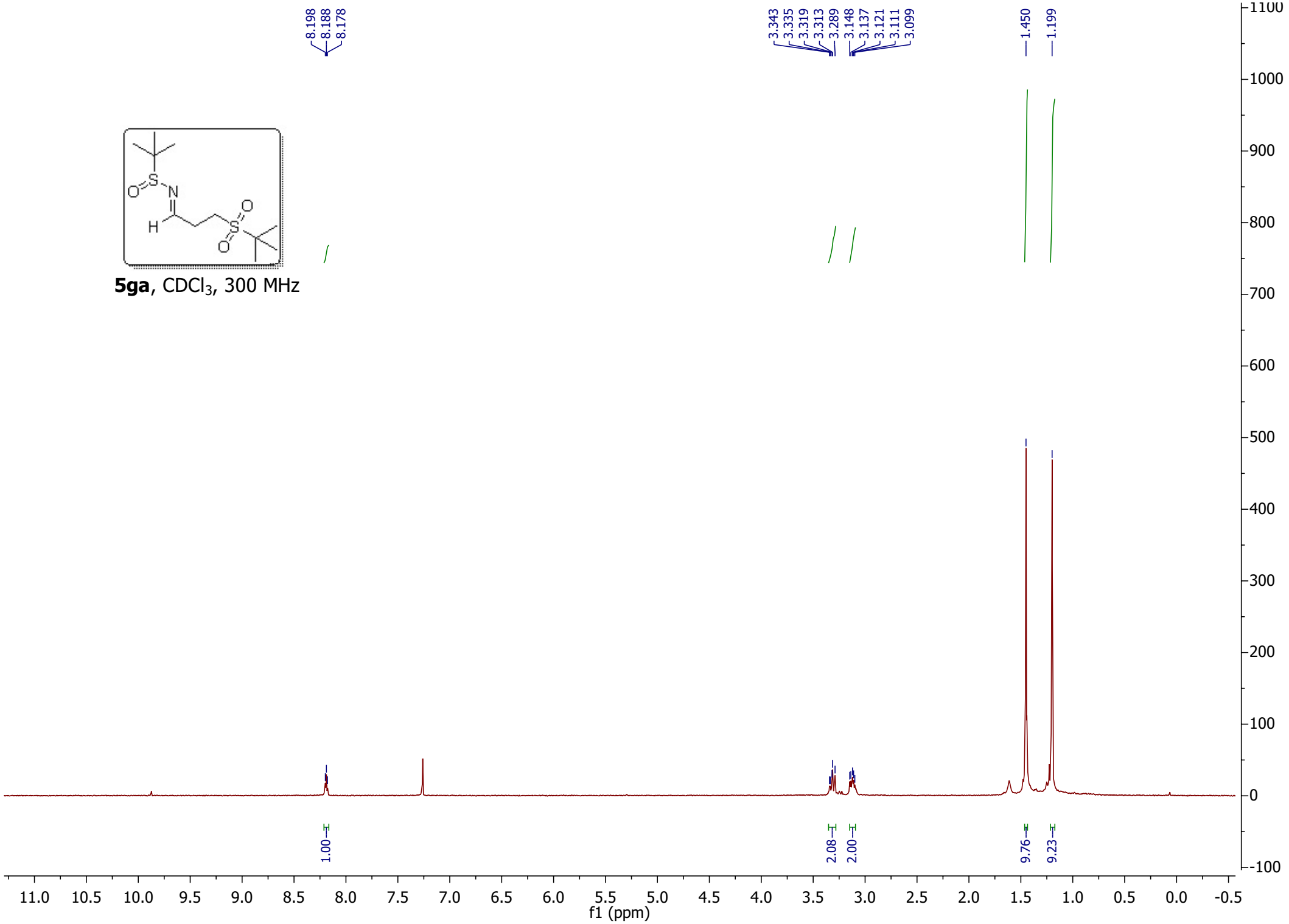

208.9328
61.0641
57.1102
48.2507
29.1632
27.5658
26.2468
24.5838
23.5496
21.8896
O
O
S
O
O
3fa, CDCl3, 75 MHz
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



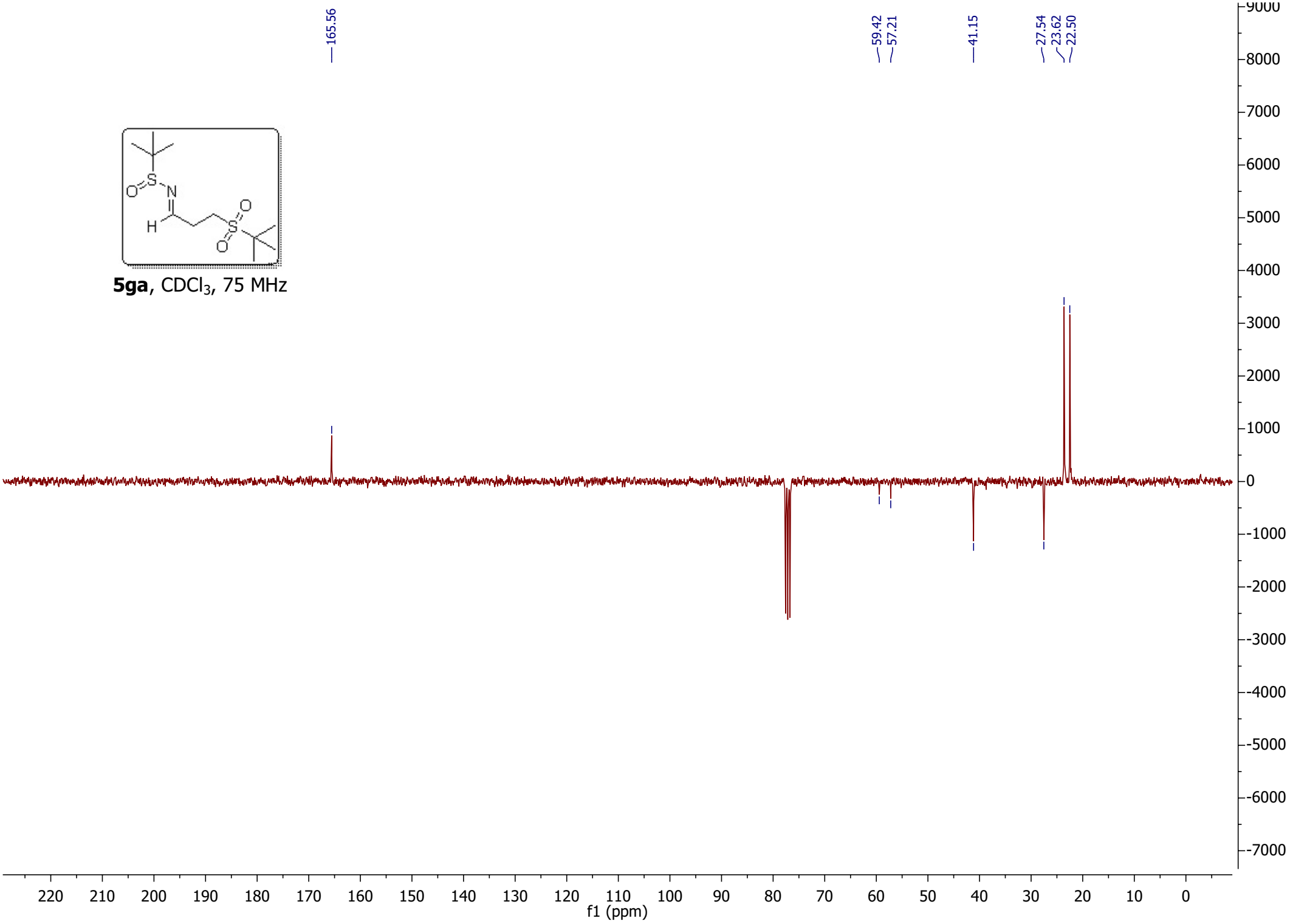
3ga, $CDCl_3$, 300 MHz

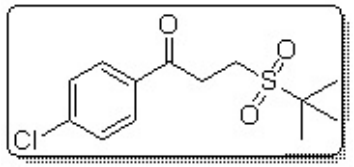


3ga, $CDCl_3$, 75 MHz

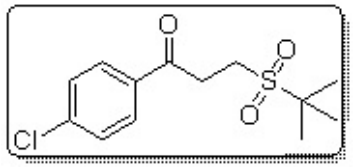


5ga, $CDCl_3$, 300 MHz

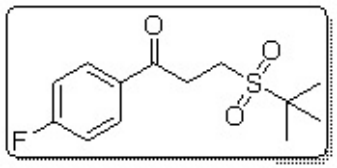

165.56
59.42
57.21
41.15
27.54
23.62
22.50
O
S
N
H
O
S
O
O
5ga, $CDCl_3$, 75 MHz
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
-6000
-7000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



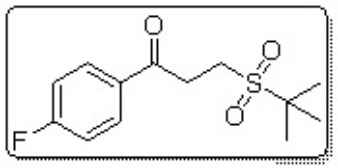
3ha, $CDCl_3$, 300 MHz



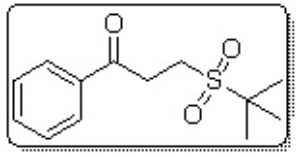
3ha, $CDCl_3$, 75 MHz



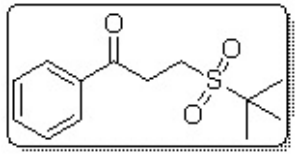
3ia, $CDCl_3$, 300 MHz



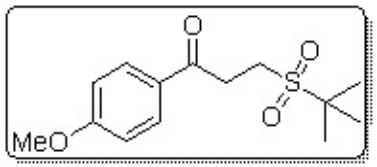
3ia, $CDCl_3$, 75 MHz



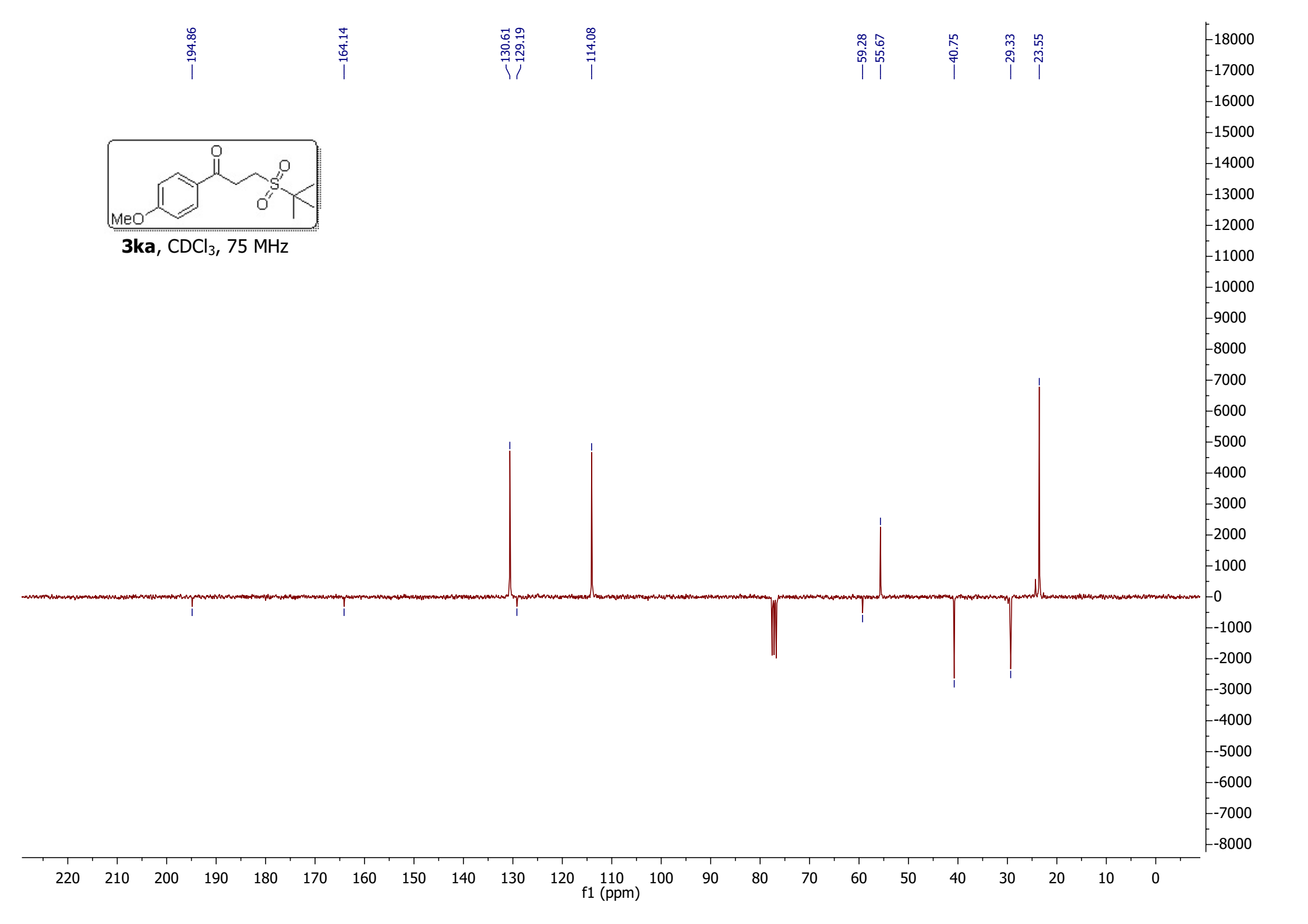
3ja, $CDCl_3$, 300 MHz



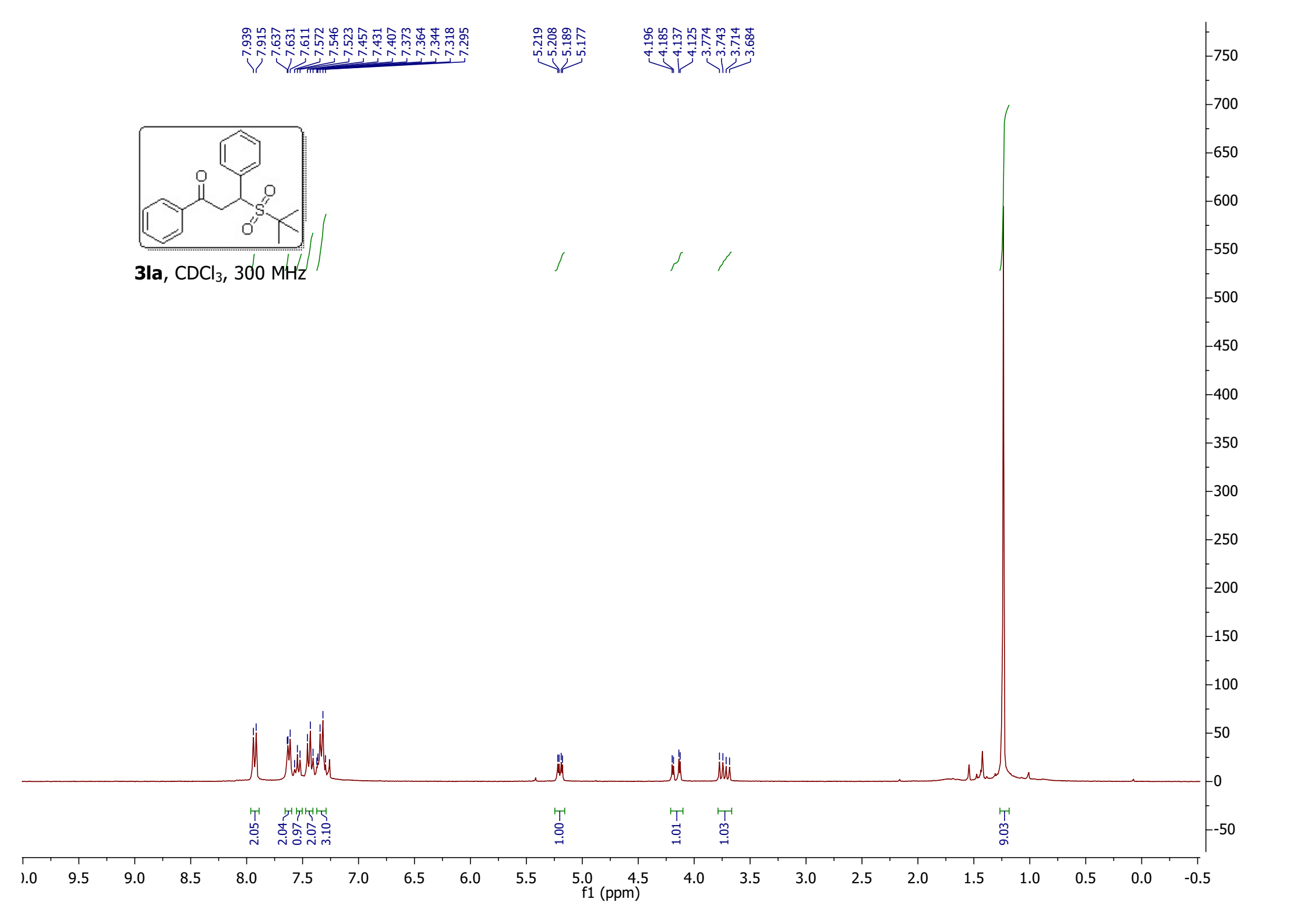
3ja, $CDCl_3$, 75 MHz

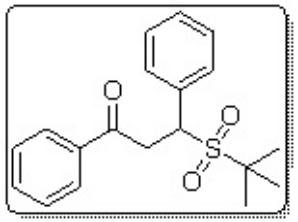


3ka, $CDCl_3$, 300 MHz

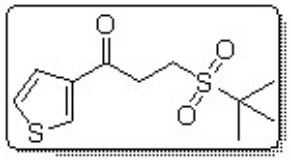


3ka, $CDCl_3$, 75 MHz

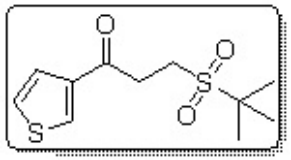

7.939
7.915
7.637
7.631
7.611
7.572
7.546
7.523
7.457
7.431
7.407
7.373
7.364
7.344
7.318
7.295
5.219
5.208
5.189
5.177
4.196
4.185
4.137
4.125
3.774
3.743
3.714
3.684
3la, CDCl3, 300 MHz
2.05
2.04
0.97
2.07
3.10
1.00
1.01
1.03
9.03
f1 (ppm)



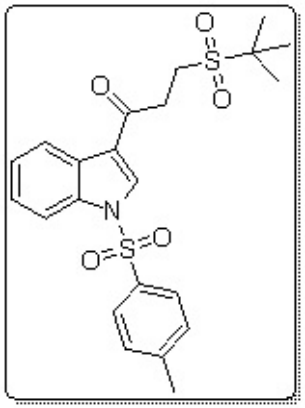
3la, $CDCl_3$, 75 MHz



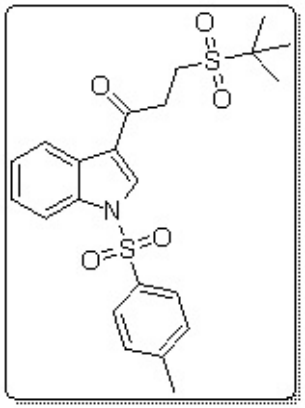
3ma, $CDCl_3$, 300 MHz



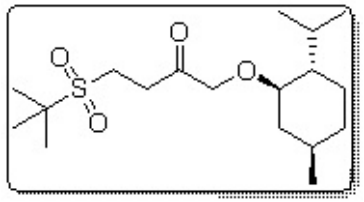
3ma, $CDCl_3$, 75 MHz



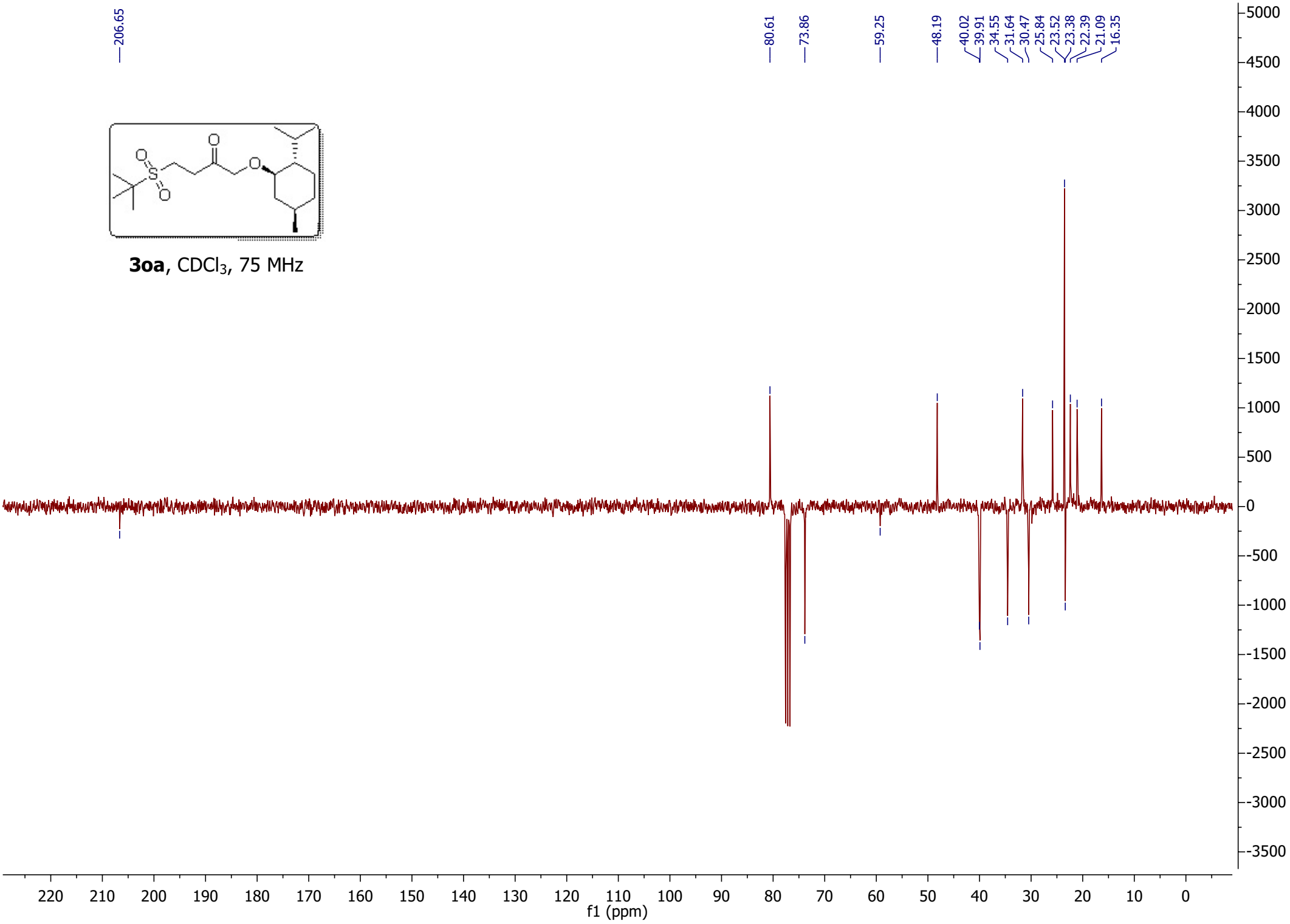
3na, $CDCl_3$, 300 MHz



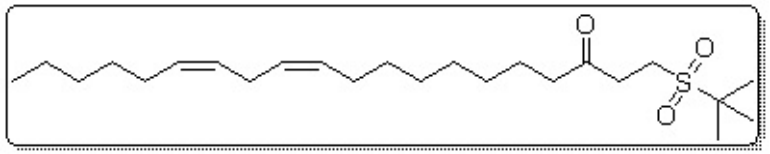
3na, $CDCl_3$, 75 MHz



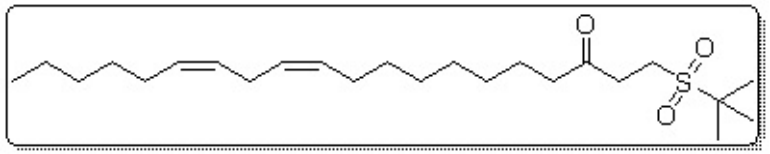
3oa, $CDCl_3$, 300 MHz



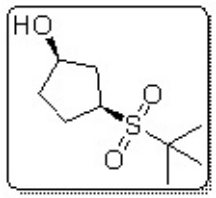
3oa, $CDCl_3$, 75 MHz



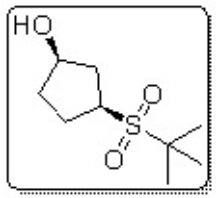
3pa, $CDCl_3$, 300 MHz



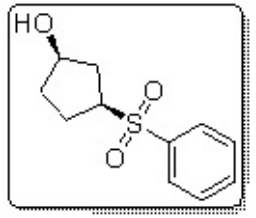
3pa, $CDCl_3$, 75 MHz



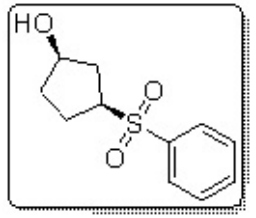
4ba, $CDCl_3$, 300 MHz



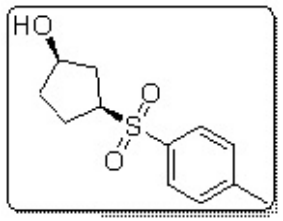
4ba, $CDCl_3$, 75 MHz



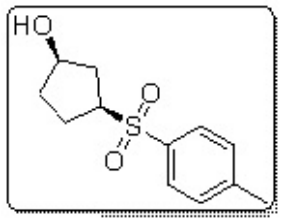
4bb, $CDCl_3$, 300 MHz



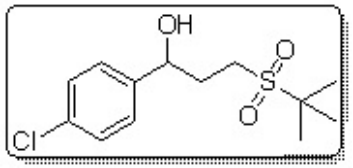
4bb, $CDCl_3$, 75 MHz



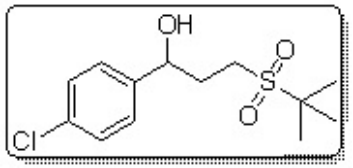
4bc, $CDCl_3$, 300 MHz



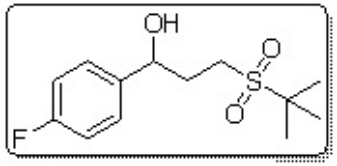
4bc, $CDCl_3$, 75 MHz



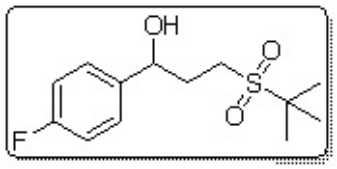
4ha, $CDCl_3$, 300 MHz



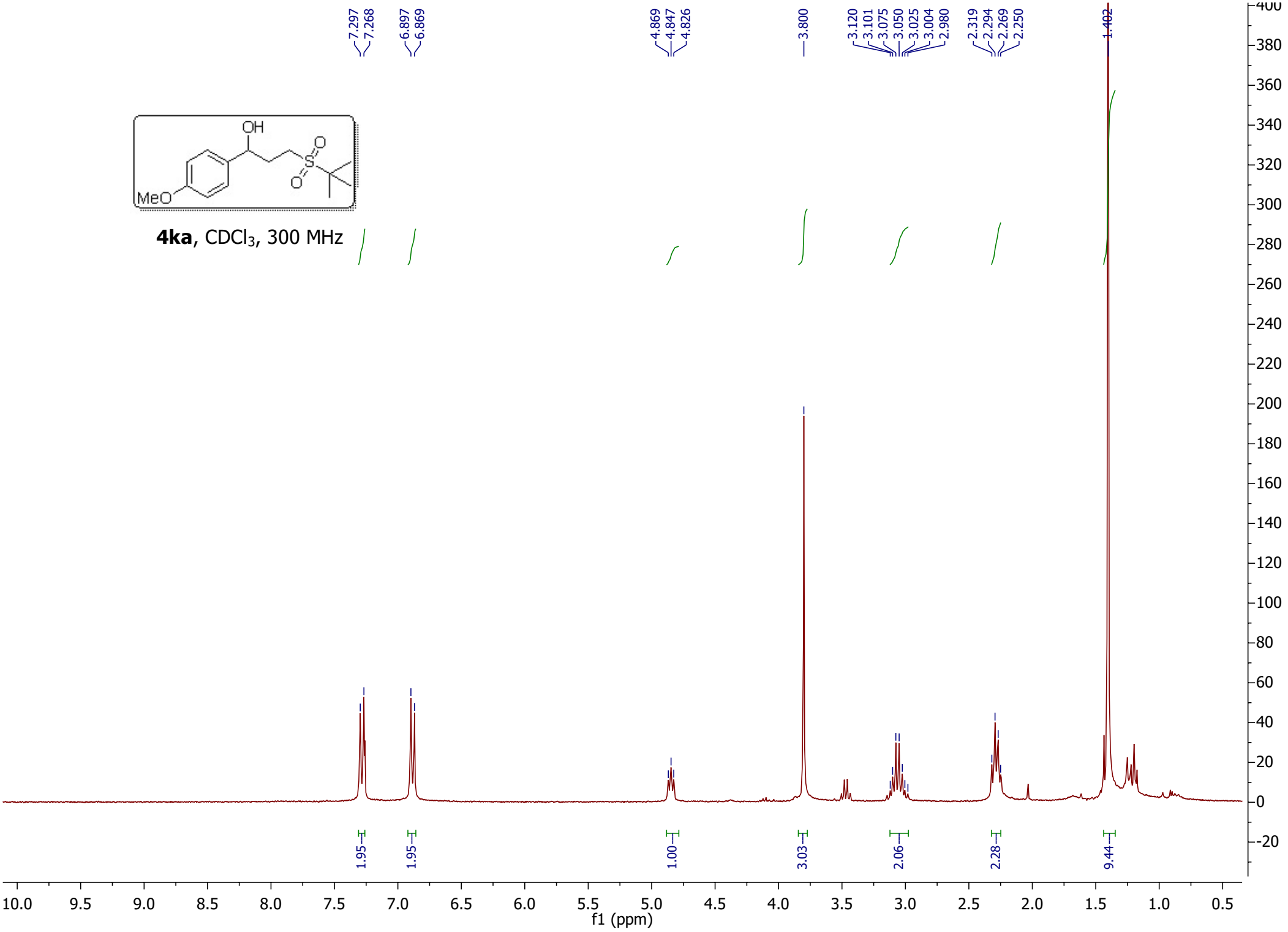
4ha, $CDCl_3$, 75 MHz

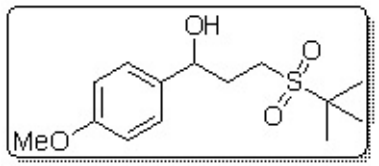


4ia, $CDCl_3$, 300 MHz

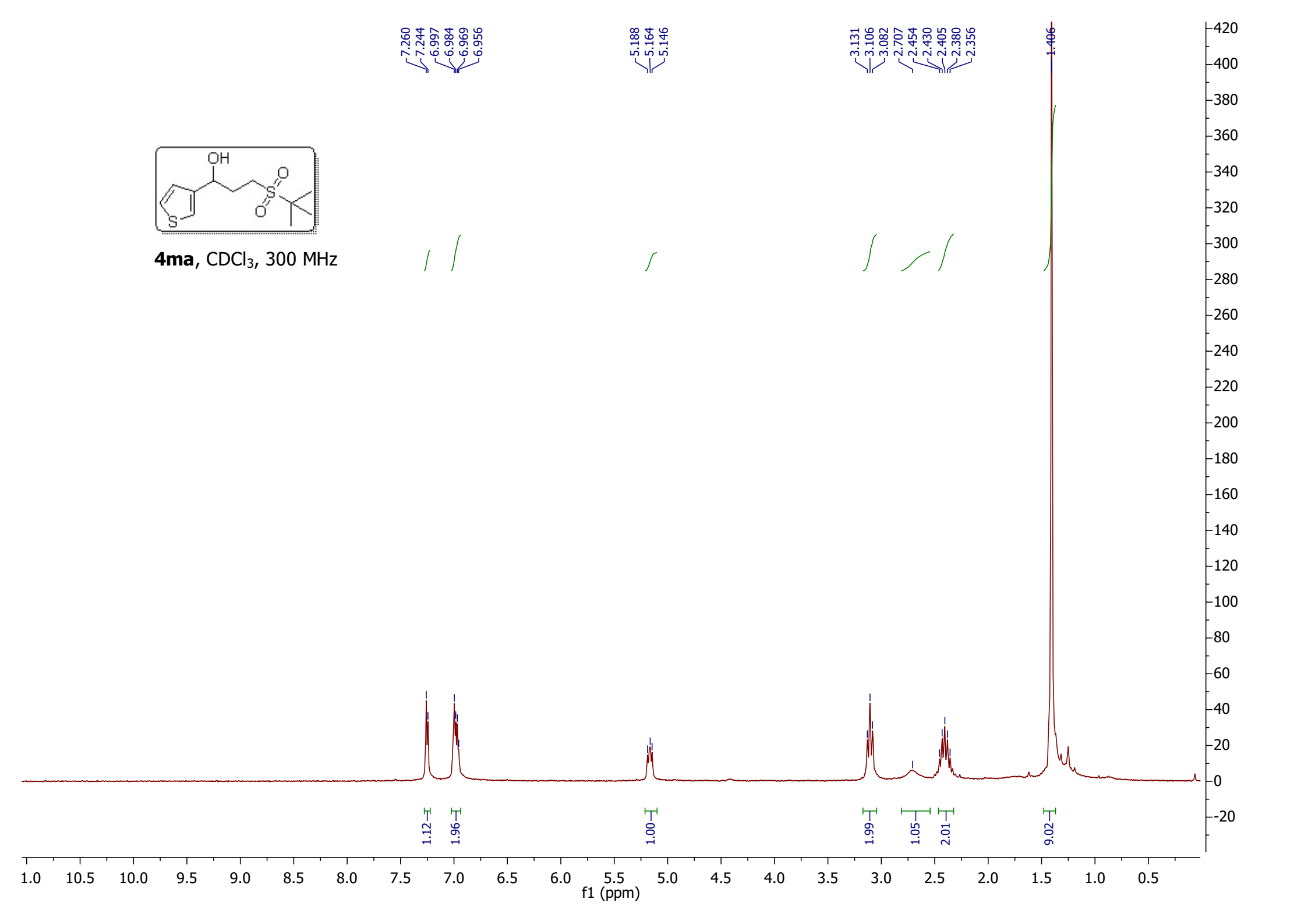


4ia, $CDCl_3$, 75 MHz

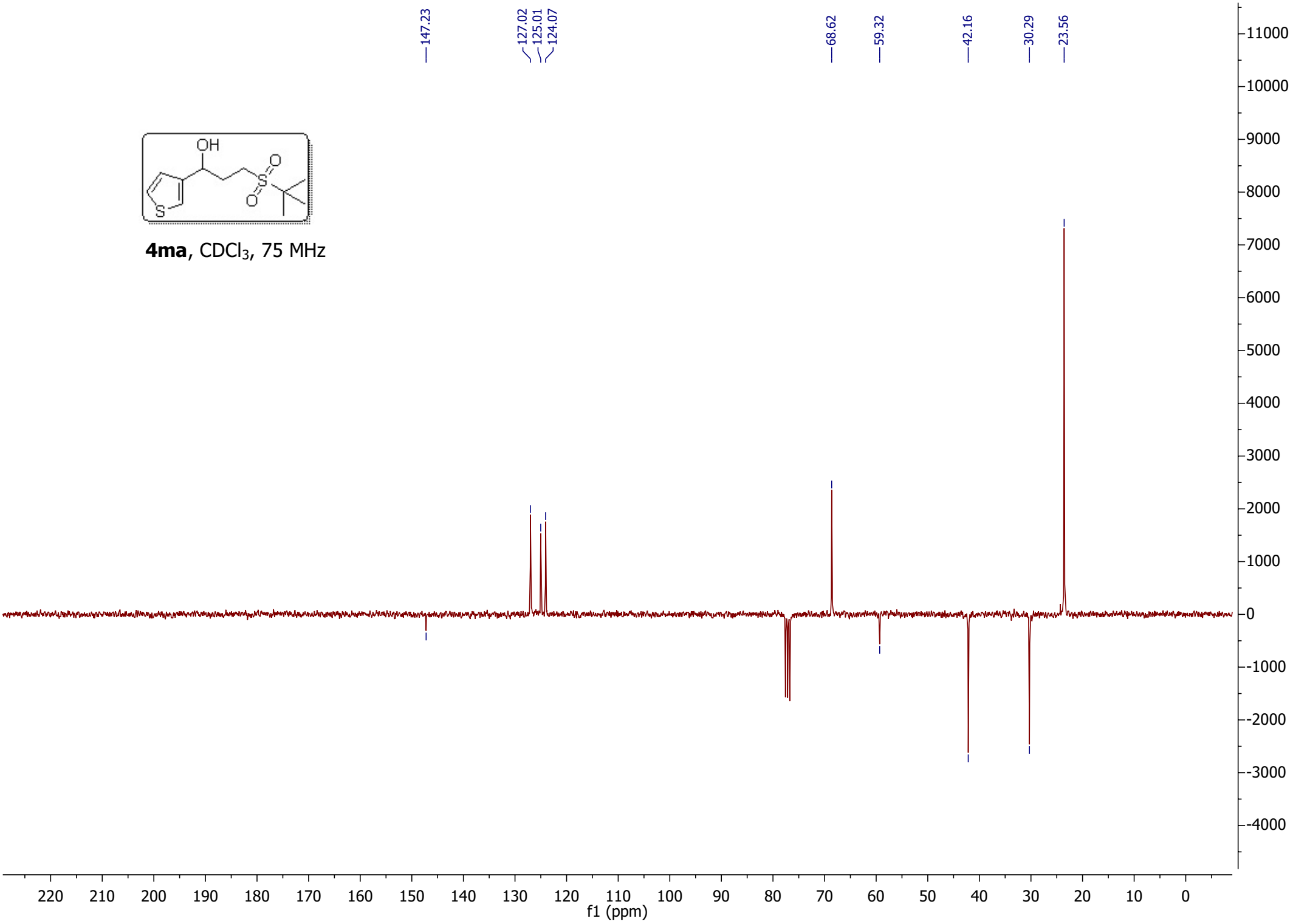

7.297
7.268
6.897
6.869
4.869
4.847
4.826
3.800
3.120
3.101
3.075
3.050
3.025
3.004
2.980
2.319
2.294
2.269
2.250
1.402
OH
MeO
O
O
S
4ka, CDCl3, 300 MHz
1.95
1.95
1.00
3.03
2.06
2.28
9.44
f1 (ppm)



4ka, $CDCl_3$, 75 MHz



4ma, $CDCl_3$, 300 MHz


147.23
127.02
125.01
124.07
68.62
59.32
42.16
30.29
23.56
OH
O
S
O
S
4ma, CDCl3, 75 MHz
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)