Conjugate Reduction and Reductive Aldol Cyclization of α, β-Unsaturated Thioesters Catalyzed by (BDP)CuH

Ninglin Li,[a] Jun Ou,[a] Michel Miesch,[b] Pauline Chiu*,[a]

[a]Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China
[b]Université de Strasbourg, Institut de Chimie, UMR 7177, Laboratoire de Chimie Organique Synthétique, 1 rue Blaise Pascal, BP 296/R8, 67008 Strasbourg, France

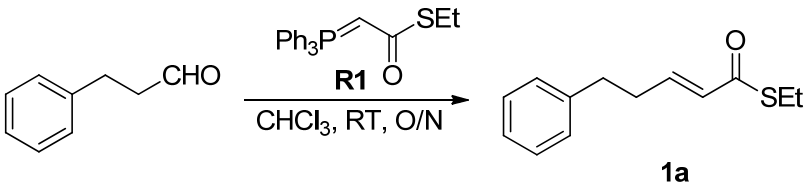
Table of Contents

General Experimental

Preparative: All reactions were performed in oven-dried round-bottomed flasks under a positive pressure of dry argon. Reactions were monitored by thin layer chromatography (TLC) using E. Merck silica gel plates, Kieselgel 60 F_{254} with 0.2 mm thickness. Components were visualized by illumination with short-wavelength ultra-violet light and/or staining. Flash column chromatography was performed with E. Merck silica gel 60 (230-400 mesh ASTM). Solvents and chemicals were purified according to standard procedures. Dichloromethane (DCM), tetrahydrofuran (THF) and toluene were distilled from CaH_2 under argon.

Analytical: All ^1H and ^{13}C NMR spectra were recorded in deuteriochloroform ($CDCl_3$) unless otherwise specified, with tetramethylsilane (TMS) as an internal standard at ambient temperature on a Bruker DPX 300, 400, 500 or 600 MHz Fourier Transform Spectrometer operating at 300 MHz, 400 MHz, 500 MHz or 600 MHz for ^1H and at 75 MHz, 100 MHz, 125 MHz or 150 MHz respectively for ^{13}C. All the spectra were calibrated at δ 7.26 ppm for ^1H and δ 77.03 ppm for ^{13}C. Spectral features were designated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = mutiplet and br = broad. IR absorption spectra were recorded as a solution in CH_2Cl_2 or CCl_4 on a BioRad Fourier Transform 165 Spectrophotometer from 4000 cm^{-1} to 400 cm^{-1}. Mass Spectra were recorded on a Finnigan MAT 95 mass spectrometer or API QSTAR PULSAR LC/MS/TOF System for both low resolution and high resolution, with accurate mass reported for the molecular ion (M^+) or next largest fragment thereof. Melting points were measured on Zeiss Asiolab Microscope using Linkam TC92 temperature controller.

Typical procedure A for the synthesis of unsaturated thioesters



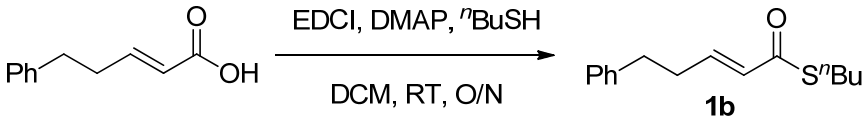
1a

S-ethyl 2-(triphenylphosphoranylidene)ethanethioate (**R1**) was synthesized according to the literature procedure.[1]

To a solution of 3-phenylpropanal (0.1459 g, 1.087 mmol) in HPLC grade $CHCl_3$ (9 mL) was added **R1** (8.1222 g, 2.3315 mmol). The reaction mixture was stirred at room temperature overnight. The reaction mixture was concentrated in vacuo and the residue was purified by flash chromatography (5% EtOAc in hexane) to afford **1a** (0.2186 g, 98%) as a pale yellow oil. **1a**: R_f

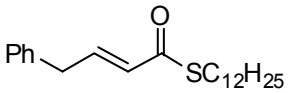
(5% EtOAc in hexane): 0.35; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.25 (m, 2H), 7.19-7.14 (m, 3H), 6.90 (dt, *J* = 15.5, 6.8 Hz, 1H), 6.10 (dt, *J* = 15.5, 1.5 Hz, 1H), 2.91 (q, *J* = 7.4 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.49-2.45 (m, 2H), 1.25 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 143.8, 140.5, 129.0, 128.4 (2C), 128.2 (2C), 126.1, 34.2, 33.7, 22.9, 14.7 ppm. The characterization corresponded to that of **1a** documented in the literature.[2]

Typical procedure B for synthesis of unsaturated thioesters



1b

EDCI (1.6318 g, 8.5122 mmol) and DMAP (69.5 mg, 0.568 mmol) were added to a solution of (*E*)-5-phenylpent-2-enoic acid (0.9997 g, 5.673 mmol) in DCM (60 mL) at 0 °C. Butanethiol (0.795 mL, 7.38 mmol) was added after 15 minutes. The resulting mixture was allowed to slowly warm to room temperature overnight. The mixture was washed with a saturated aqueous solution of $NaHCO_3$, then H_2O. The organics were dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography (5% EtOAc in hexane) to afford **1b** (1.1332 g, 80%) as a pale yellow oil. **1b**: R_f (5% EtOAc in hexane): 0.36; IR (CH_2Cl_2): 3065, 3028, 2960, 2932, 1668 (C=O), 1454 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.26 (m, 2H), 7.23-7.16 (m, 3H), 6.92 (dt, *J* = 15.5, 6.8 Hz, 1H), 6.13 (dt, *J* = 15.5, 1.5 Hz, 1H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.81-2.75 (m, 2H), 2.55-2.48 (m, 2H), 1.63-1.53 (m, 2H), 1.46-1.36 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.2, 143.9, 140.7, 129.2, 128.5 (2C), 128.4 (2C), 126.2, 34.4, 33.9, 31.7, 28.4, 22.0, 13.6 ppm; LRMS (EI, 20 eV): m/z 248 (M^+, 1), 159 (100), 91 (76), 77 (24); HRMS (EI, 20 eV): calcd for $C_{15}H_{20}OS$ (M^+), 248.1229 found 248.1230.

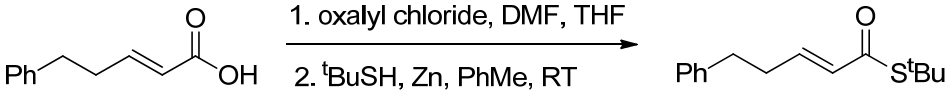


1c

According to the typical procedure B, EDCI (0.83 g, 4.3 mmol) and DMAP (40 mg, 0.33 mmol) were treated with (*E*)-5-phenylpent-2-enoic acid (0.50 g, 2.8 mmol) in DCM (10.0 mL) and dodecanethiol (0.87 g, 4.3 mmol). After workup, the residue was purified by flash chromatography (5% EtOAc in hexane) to afford **1c** (1.0 g, 97%) as a pale yellow oil. **1c:** R_f (5% EtOAc in hexane): 0.69; IR (CH_2Cl_2): 2928, 2856, 1666 (C=O), 1632, 1455, 1035 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.28 (m, 2H), 7.22-7.18 (m, 3H), 6.94 (dt, *J* = 15.4, 6.9 Hz, 1H), 6.14 (td, *J* = 15.5, 1.5 Hz, 1H), 2.95 (t, *J* = 7.3 Hz, 2H), 2.80 (t, *J* = 7.4 Hz, 1H), 2.54-2.52 (m, 2H), 1.63-1.59 (m, 3H), 1.40-1.29 (m, 18H), 0.92-0.87 (t, *J* = 6.4 Hz，3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 143.8, 140.7, 129.2, 128.5, 128.44, 128.4,

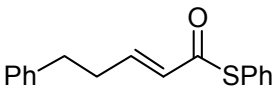
128.3, 126.2, 34.3, 33.9, 31.9, 29.6, 29.6, 29.5, 29.4, 29.1, 28.9, 28.7, 22.7, 14.1 ppm. LRMS (EI, 20 eV): m/z 360.2 (M^+, 1.29), 90.1 (39), 159.1 (100); LRMS (EI, 20 eV): m/z 360.2 (M+, 1.29), 90.1 (39), 159.1 (100); HRMS (EI, 20 eV): calcd for $C_{23}H_{36}OS$ (M^+) 360.2481, found 360.2478.

Typical procedure C for synthesis of unsaturated thioesters



1d

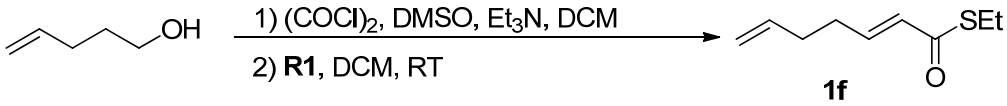
Oxalyl chloride (2.2 mL, 26 mmol) in 10 mL THF and six drops of DMF was added to a solution of (*E*)-5-phenylpent-2-enoic acid (2.9981 g, 17.014 mmol) in 120 mL THF. The resulting mixture was stirred for 1 hour and then concentrated under reduced pressure. The residue was dissolved in 150 mL PhMe. Then ^{t}BuSH (2.0 mL, 17 mmol) and zinc dust (1.13 mg, 17.0 mmol) were added. After stirring for 1 hour, the mixture was washed with saturated aqueous solution of $NaHCO_3$, and the aqueous layer was extracted by 50% EtOAc in hexane. The extracts were dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography (3% EtOAc in hexane) to afford **1d** (2.9921 g, 71%) as a pale yellow oil. **1d**: R_f (5% EtOAc in hexane): 0.44; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.26 (m, 2H), 7.23-7.17 (m, 3H), 6.86 (dt, *J* = 6.8, 15.5 Hz, 1H), 6.05 (dt, *J* = 15.5, 1.5 Hz, 1H), 2.79-2.75 (m, 2H), 2.52-2.46 (m, 2H), 1.51 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 142.8, 140.8, 129.8, 128.5 (2C), 128.3 (2C), 126.2, 47.9, 34.4, 33.8, 30.0 ppm; LRMS (EI, 20 eV): m/z 248 (M^+, 1), 191 (9), 159 (100), 131 (11); HRMS (EI, 20 eV): calcd for $C_{15}H_{20}OS$ (M^+) 248.1235, found 248.1232 ppm. The characterization corresponded to that of **1d** documented in the literature. [3]



1e

According to Typical procedure C, oxalyl chloride (360 μL, 4.26 mmol) in 2 mL THF and two drops of DMF was added to a solution of (*E*)-5-phenylpent-2-enoic acid (492.0 mg, 2.792 mmol) in 18 mL THF. The resulting mixture was stirred for 1 hour and then concentrated under reduced pressure. Then PhSH (290 μL, 2.84 mmol) and zinc (185.9 mg, 2.843 mmol) was added and stirred for 1 hour. After workup, the residue was purified by flash chromatography (3% EtOAc in hexane) to afford **1e** (566.7 mg, 76%) as a pale yellow oil. **1e:** R_f (5% EtOAc in hexane): 0.41; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.38 (m, 5H), 7.32-7.27 (m, 2H), 7.23-7.16 (m, 3H), 7.01 (dt, *J* = 15.5, 6.8 Hz, 1H), 6.19 (dt, *J* = 15.5, 1.4 Hz, 1H), 2.82-2.76 (m, 2H), 2.57-2.50 (m, 2H) ppm; ^{13}C NMR (100 MHz,

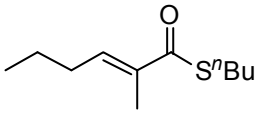
$CDCl_3$): δ 187.9, 145.5, 140.6, 134.6 (2C), 129.36, 129.2 (2C), 128.6 (2C), 128.4 (2C), 128.3, 127.6, 126.3, 34.3, 34.0 ppm. The characterization corresponded to that of **1e** documented in the literature.[4]



1f

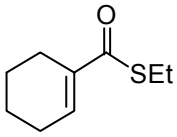
DMSO (1.0 mL, 14 mmol) in 10 mL DCM was added to a solution of oxalyl chloride (600 µL, 7.09 mmol) in 10 mL DCM at – 78 °C. After stirring for 15 minutes, 4-penten-1-ol (498.0 mg, 5.782 mmol) was added over in 9 mL DCM. NEt_3 was added after 15 minutes. The resulting mixture was allowed to slowly warm to room temperature after 1 hour and stirred at room temperature for another 1 hour.

Wittig reagent **R1** (1.715 g, 4.706 mmol) was then added and the mixture was allowed to stir overnight. The mixture was quenched with water, and extracted with 50% EtOAc/ hexane. The extracts were dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography (2% EtOAc in hexane) to afford **1f** (0.6120 g, 77%). **1f**: R_f (3% EtOAc in hexane): 0.31; IR (CH_2Cl_2): 3051, 2974, 2931, 2874, 1668 (C=O), 1450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.88 (dt, J = 15.5, 6.5, 1H), 6.11 (dt, J = 15.5, 1.5 Hz, 1H), 5.84-5.74 (m, 1H), 5.08-5.00 (m, 2H), 2.94 (q, J = 7.4 Hz, 2H), 2.32-2.15 (m, 4H), 1.27 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 144.2, 137.0, 129.1, 115.7, 32.0, 31.4, 23.1, 14.8 ppm; LRMS (ESI): m/z 171 ($[M^+ + H]^+$, 23), 155 (21), 129 (100); HRMS (ESI): calcd for $C_9H_{14}OS$ ($[M^+ + H]^+$), 171.0843, found 171.0846.



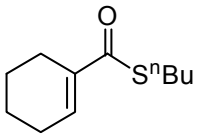
1g

According to the typical procedure B, EDCI (7.1931 g, 37.450 mmol) and DMAP (452.0 mg, 3.121 mmol) were treated with (*E*)-2-methylhex-2-enoic acid (3.9931 g, 31.155 mmol) in DCM (310 mL) and butanethiol (4.0 mL, 37 mmol). After workup, the residue was purified by flash chromatography (3% EtOAc in hexane) to afford **1g** (4.8693 g, 78%) as a pale yellow oil. R_f (5% EtOAc in hexane): 0.39; IR (CH_2Cl_2): 3035, 2963, 2933, 2874, 1650 (C=O), 1621, 1465, 1382, 1205 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.74-6.70 (m, 1H), 2.89 (t, J = 7.4 Hz, 2H), 2.19-2.14 (m, 2H), 1.86 (d, J = 0.5 Hz, 3H), 1.60-1.52 (m, 2H), 1.51-1.44 (m, 2H), 1.44-1.35 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.0, 140.6, 136.2, 31.7, 30.7, 28.6, 22.1, 21.8, 13.9, 13.6, 12.4 ppm; LRMS (EI, 20 eV): m/z 200 (M^+, 3), 136 (46), 111 (100); HRMS (EI, 20 eV): calcd for $C_{11}H_{20}OS$ (M^+), 200.1229 found 200.1228.



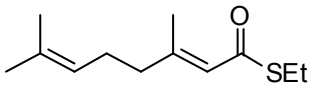
1h

According to the typical procedure B, EDCI (4.6155 g, 24.077 mmol) and DMAP (0.2110 mg, 1.727 mmol) were treated with cyclohex-1-enecarboxylic acid (1.9983 g, 15.839 mmol) in DCM (150 mL) and ethanethiol (1.4 mL, 19 mmol). After workup, the residue was purified by flash chromatography (5% EtOAc in hexane) to afford **1h** (2.3117 g, 86%) as a pale yellow oil. **1h**: R*f* (5% EtOAc in hexane): 0.78; IR (CH_2Cl_2): 3057, 2933, 2862, 1654 (C=O), 1641 (C=C), 1450, 1258 cm-1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98-6.95 (m, 1H), 2.91 (q, *J* = 7.4 Hz, 2H), 2.32-2.28 (m, 2H), 2.24-2.19 (m, 2H), 1.68-1.60 (m, 4H), 1.26 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.2, 138.6, 138.0, 25.8, 24.1, 22.9, 22.0, 21.6, 14.9 ppm; LRMS (EI, 20 eV): m/z 170 (M^+, 2), 109 (100), 81 (36), 89 (8); HRMS (EI, 20 eV): calcd for $C_9H_{14}OS$ (M^+) 170.0760, found 170.0758.



1i

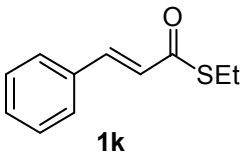
According to the typical procedure B, EDCI (5.5698 g, 23.779 mmol) and DMAP (0.1986 mg, 1.585 mmol) were treated with cyclohex-1-enecarboxylic acid (1.9996 g, 15.850 mmol) in DCM (160 mL) and butanethiol (2.0 mL, 19 mmol). After workup, the residue was purified by flash chromatography (2% EtOAc in hexane) to afford **1i** (2.6289 g, 84%) as a pale yellow oil. **1i:** R_f (5% EtOAc in hexane): 0.78; IR (CH_2Cl_2): 3064, 2984, 2933, 1733 (C=O), 1447, 1374, 1247cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99-6.96 (m, 1H), 2.90 (t, *J* = 7.4 Hz, 2H), 2.32-2.29 (m, 2H), 2.23-2.19 (m, 2H), 1.66-1.55 (m, 6H), 1.43-1.37 (m, 2 H), 0.92 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.2, 138.6, 138.0, 31.8, 28.2, 25.8, 24.1, 22.1, 22.0, 21.6, 13.7 ppm; LRMS (EI, 20 eV): m/z 198 (M+, 5), 109 (100), 89 (40), 81 (36); HRMS (EI, 20 eV): calcd for $C_{11}H_{18}OS$ (M^+), 198.1073 found 198.1079.



1j

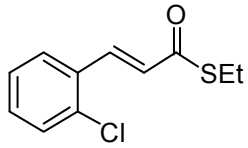
According to the typical procedure B, EDCI (5.4882 g, 28.629 mmol) and DMAP (0.3120 mg, 2.554 mmol) were treated with (*E*)-3,7-dimethylocta-2,6-dienoic acid (4.001 g, 23.78 mmol) in DCM (230 mL) and ethanethiol (2.1 mL, 29 mmol). After workup, the residue was purified by flash chromatography (3% EtOAc in hexane) to afford **1j** (4.025 g, 80%) as a pale yellow oil. **1j**: R_f (5% EtOAc in hexane): 0.41; IR (CH_2Cl_2): 3025, 2992, 2922, 2851, 1668 (C=O), 1623 (C=C), 1447, 1378, 1258 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 (s, 1H), 5.15-5.11 (m, 1H), 2.89 (q, *J* = 7.4 Hz, 2H), 2.62-2.58 (m, 2H), 2.18-2.12 (m, 2H), 1.86 (s, 3H), 1.67 (s, 3H), 1.61 (s, 3H), 1.26 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.9, 157.2, 132.3, 123.6, 123.5, 34.4, 26.8, 25.7, 25.2, 23.2, 17.7, 15.0 ppm; LRMS (EI, 20 eV): m/z 212 (M^+, 9), 151 (100), 123(90), 109 (94);

HRMS (EI, 20 eV): calcd for $C_{12}H_{20}OS$ (M^+) 212.1229, found 212.1217.



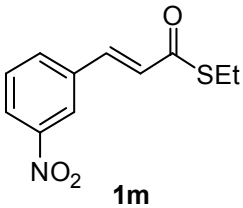
1k

According to the typical procedure B, EDCI (1.0579 g, 5.518 mmol) and DMAP (70 mg, 0.57 mmol) were treated with cinnamic acid (0.7482 g, 5.050 mmol) in DCM (25 mL) and ethanethiol (450 μL, 6.08 mmol). After workup, the residue was purified by flash chromatography (5% EtOAc in hexane) to afford **1k** (0.8532 g, 88%) as a pale yellow oil. **1k:** R_f (5% EtOAc in hexane): 0.38; ^{1}H NMR (400 MHz, CDCl3): δ 7.60 (d, J = 15.8 Hz, 1H), 7.55-7.51 (m, 2H), 7.40-7.37 (m, 3H), 6.71 (d, J = 15.8 Hz, 1H), 3.02 (q, J = 7.4 Hz, 2H), 1.32 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 140.1, 134.1, 130.4, 128.8 (2C), 128.3 (2C), 125.1, 23.3, 14.8 ppm. The characterization corresponded to that of **1k** documented in the literature.[3]



1l

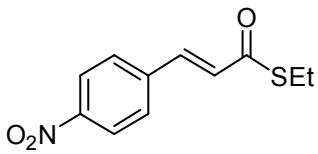
According to the typical procedure B, EDCI (5.4862 g, 28.476 mmol) and DMAP (285.6 mg, 2.190 mmol) were treated with (*E*)-3-(2-chlorophenyl)acrylic acid (4.0001 g, 21.905 mmol) in DCM (210 mL) and ethanethiol (2.0 mL, 26 mmol). After workup, the residue was purified by flash chromatography (3% EtOAc in hexane) to afford **1l** (4.1467 g, 84%) as a pale yellow oil. **1l**: R_f (10% EtOAc in hexane): 0.39; IR (CH_2Cl_2): 3055, 2992, 2911, 1733 (C=O), 1664 (C=C), 1616, 1464, 1371, 1247 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 15.8 Hz, 1H), 7.64-7.61 (m, 1H), 7.43-7.41 (m, 1H), 7.34-7.27 (m, 2H), 6.69 (d, J = 15.8 Hz, 1H), 3.03 (q, J = 7.4 Hz, 2H), 1.33 (t, J = 7.4 Hz, 3H) PPM; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 136.2, 135.5, 132.6, 131.2, 130.3, 127.7, 127.6, 127.1, 23.5, 14.8; LRMS (EI, 20 eV): m/z 226 (M^+, 18),191 (14), 165 (100), 76 (15); HRMS (EI, 20 eV): calcd for $C_{11}H_{11}OClS$ (M^+) 226.0214, found 226.0206.



1m

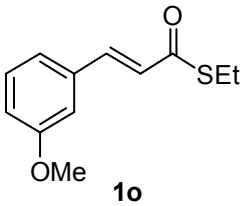
According to the typical procedure B, EDCI (5.2507 g, 27.390 mmol) and DMAP (296.5 mg, 2.427 mmol) were treated with (*E*)-3-(3-nitrophenyl)acrylic acid (4.0003 g, 20.709 mmol) in DCM (200 mL) and ethanethiol (2 mL, 25 mmol). After workup, the residue was purified by flash chromatography (EtOAc: DCM: hexane= 5: 1: 94) to afford **1m** (3.7841 g, 77%) as a pale yellow solid. **1m**: R_f (10% EtOAc in hexane): 0.39; mp: 77-79 ^{o}C; IR (CH_2Cl_2): 3046, 2986, 2938, 2878, 1661 (unsaturated C=O), 1621, 1523, 1348 cm^{-1}; 1H NMR (400 MHz, $CDCl_3$): δ 8.38-8.37 (m, 1H), 8.24-8.21 (m, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 15.8 Hz, 1H), 7.60-7.56 (m, 1H), 6.79 (d, J = 15.8 Hz, 1H), 3.03 (q, J = 7.4 Hz, 2H), 1.32 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR

(100 MHz, $CDCl_3$): δ 189.4, 148.8, 137.1, 136.1, 133.9, 130.0, 127.8, 124.7, 122.6, 23.7, 14.7 ppm; LRMS (EI, 20 eV): m/z 237 (M^+, 4), 176 (100), 130 (14); HRMS (EI, 20 eV): calcd for $C_{11}H_{11}O_3NS$ (M^+) 237.0454, found 237.0453.



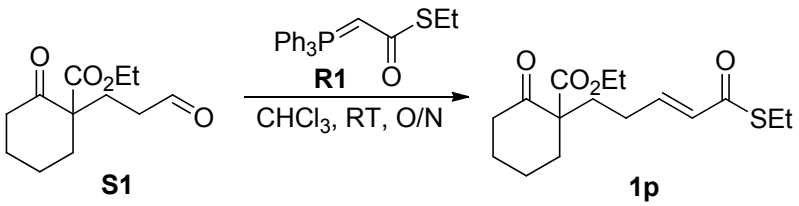
1n

According to the typical procedure B, EDCI (5.1917 g, 26.921 mmol) and DMAP (286.5 mg, 2.071 mmol) were treated with (*E*)-3-(4-nitrophenyl)acrylic acid (3.9993 g, 20.704 mmol) in DCM (200 mL) and ethanethiol (2 mL, 25 mmol). After workup, the residue was purified by flash chromatography (6% EtOAc in hexane) to afford **1n** (4.182 g, 85%) as a pale yellow solid. **1n**: R_f (10% EtOAc in hexane): 0.38; mp: 106-108; IR (CH_2Cl_2): 3080, 2974, 2993, 2934, 1662 (unsaturated C=O), 1622, 1523, 1457, 1347 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.26-8.23 (m, 2H), 7.70-7.67 (m, 2H), 7.61 (d, *J* = 15.8 Hz, 1H), 6.79 (d, *J* = 15.8 Hz, 1H), 3.05 (q, *J* = 7.4 Hz, 2H), 1.34 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.4, 148.6, 140.5, 137.0, 128.9 (2C), 128.8 (2C), 124.2, 23.7, 14.7 ppm; LRMS (EI, 20 eV): m/z 237 (M^+, 2), 176 (86), 130 (39), 77 (100); HRMS (EI, 20 eV): calcd for $C_{11}H_{11}O_3NS$ (M^+) 237.0454, found 237.0453.

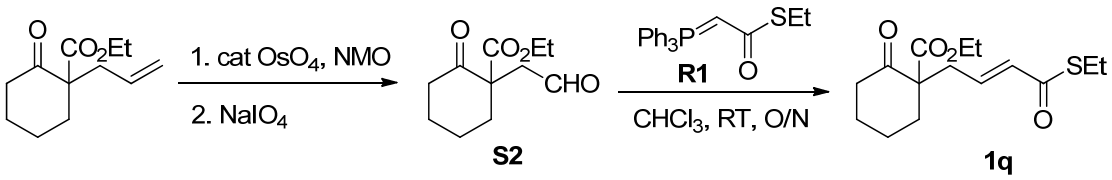


1o

According to the typical procedure B, EDCI (2.5933 g, 13.470 mmol) and DMAP (162.3 mg, 1.122 mmol) were treated with (*E*)-3-(3-methoxyphenyl)-acrylic acid (1.9996 g, 11.222 mmol) in DCM (25 mL) and ethanethiol (970 μL, 13.4 mmol). After workup, the residue was purified by flash chromatography (3% EtOAc in hexane) to afford **1o** (1.8644 g, 75%) as a pale yellow oil. **1o**: R_f (5% EtOAc in hexane): 0.41; IR (CH_2Cl_2): 3056, 2970, 2934, 2839, 1664 (C=O), 1612, 1581, 1486, 1455, 1292, 1244 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 15.8 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 2.2 Hz, 1H), 6.94 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.69 (d, *J* = 15.8 Hz, 1H), 3.83 (s, 3H), 3.04 (d, *J* = 7.4 Hz, 1H), 3.00 (d, *J* = 7.4 Hz, 1H), 1.25 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 159.8, 141.8, 129.5, 120.7, 114.1, 111.7, 55.2, 45.5, 31.5, 23.4, 14.8 ppm; LRMS (EI, 20 eV): m/z 222 (M^+, 15), 161 (100), 133 (43), 77 (13); HRMS (EI, 20 eV): calcd for $C_{12}H_{14}O_2S$ (M^+) 222.0709, found 222.0712.



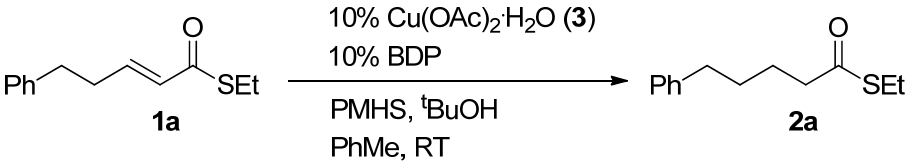
Thioester **1p** was prepared according to typical procedure for the preparation of **1a**, using aldehyde **S1**[5] (2.7243 g, 12.040 mmol), **R1** (6.582 g, 18.06 mmol) in HPLC grade $CHCl_3$ (20 mL) to afford **1p** (3.1051 g, 83%) as a pale yellow oil. **1p**: R*f* (20% EtOAc in hexane): 0.53; IR (CH_2Cl_2): 3054, 2945, 2870, 1711 (saturated C=O), 1668 (unsaturated C=O), 1631 (C=C), 1452, 1311, 1253, 1191 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.57 (dt, *J* = 15.5, 6.5 Hz, 1H), 5.83 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.96-3.91 (m, 2H), 2.65 (q, *J* = 7.4 Hz, 2H), 2.26-2.16 (m, 3H), 1.96-1.94 (m, 1H), 1.84-1.69 (m, 3H), 1.49-1.34 (m, 4H),1.45-1.36 (m, 1H), 1.00-0.97 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 189.8, 171.5, 143.9, 128.8, 61.3, 60.2, 40.9, 36.3, 32.8, 27.4, 27.0, 22.9, 22.5, 14.7, 14.0 ppm; LRMS (EI, 20 eV): m/z 312 (M^+, 3), 251 (77), 205 (100), 170 (79); HRMS (EI, 20 eV): calcd for $C_{16}H_{24}O_4S$ (M^+) 312.1395, found 312.1399.



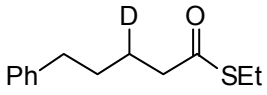
To a solution of ethyl 1-allyl-2-oxocyclohexanecarboxylate[6] (3.16 g, 15 mmol) in THF (22 mL) and H_2O (4.5 mL) was added OsO_4 (0.038 g, 0.15 mmol) in ^{t}BuOH (0.5 mL). When the solution turned black, NMO (4.02 g, 30.1 mmol) was added in portions to the reaction mixture. The black color faded and stirring was continued overnight at RT. The crude mixture was filtered through celite. The filtrate was extracted with Et_2O (3 x 30 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*.

The residue was dissolved in DCM (15 mL). To this was added H_2O (6 mL) and $NaIO_4$ (7.07 g, 33.1 mmol). The reaction mixture was stirred overnight at room tempearture. The mixture was filtered through celite. The filtrate was extracted with DCM (3 x 3 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (20% EtOAc in hexane) to afford **S2** (2.6 g, 82%) as a pale yellow oil. **S2**: R_f (20% EtOAc in hexane): 0.29; IR (CCl_4): 2942, 2869, 1805, 1736, 1718, 1447, 1370,. 1315, 1205, 1161, 1131, 1094, 1031, 956 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.66 (t, *J* = 1.6 Hz, 1H), 4.21-4.12 (m, 2H), 2.78-2.59 (m, 3H), 2.45-2.36 (m, 2H), 2.14-1.96 (m, 1H), 1.78-1.51 (m, 4H), 1.22 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.0, 199.1, 171.3, 61.9, 59.1, 47.8, 40.5, 36.8, 27.0, 22.0, 14.0 ppm; HRMS (EI, 20 eV): calcd for $C_{11}H_{16}O_4$ (M^+) 212.1049, found: 212.1049.

Typical procedure for 1, 4- reduction of unsaturated thioesters using (BDP)CuH

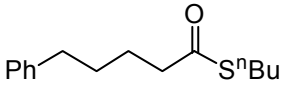


A solution of **3** (39.4 mg, 0.200 mmol) and BDP (89.1 mg, 0.199 mmol) in 1.0 mL PhMe was stirred at room temperature for 5 minutes. PMHS (360 µL, 6.01 mmol) was added and the reaction mixture became greenish-yellow. Thioester **1a** (440.5 mg, 1.999 mmol) in 1.0 mL PhMe and ^{t}BuOH (380 µL, 3.97 mmol) were added sequentially. The reaction was monitored by TLC and quenched by the addition of saturated aqueous NH_4Cl solution. The reaction mixture was filtered through a pad of silica gel. The filtrate was extracted with EtOAc (3 x 10 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by flash chromatography using 1.5% EtOAc in hexane to afford **2a** (403.8 mg, 91%) as a pale yellow oil. **2a**: R_f(5% EtOAc in hexane): 0.56; IR (CH_2Cl_2): 3035, 2938, 2857, 1684 (C=O), 1449, 1264 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.29 (m, 2H), 7.16-7.20 (m, 3H), 2.87 (q, *J* = 7.4 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.56 (m, 2H), 1.63-1.73 (m, 4H), 1.24 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl3): δ 199.6, 142.1, 128.42, 128.37, 125.8, 43.9, 35.6, 30.7, 25.3, 23.3, 14.8 ppm; LRMS (ESI): m/z 245 ([M$^+$+Na]$^+$, 32), 161 (100), 162 (13); HRMS (ESI): calcd for $C_{13}H_{18}OS$ ([M$^+$+Na]$^+$), 245.0976, found 245.0983.



2a-d$_1$

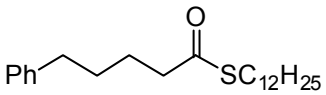
According to the typical procedure for 1,4-reduction using (BDP)CuH, **3** (20.0 mg, 0.10 mmol), BDP (45.0 mg, 0.10 mmol), Ph_2SiD_2 (0.28 g, 1.50 mmol) were stirred at in 0.5 mL PhMe. Then **1a** (0.22 g, 1.0 mmol) and ^{t}BuOH (0.44 g, 2.0 mmol) in 0.5 mL toluene were added. After workup, the residue was purified by flash chromatography using 2% EtOAc in hexane to afford **2a-d$_1$** (129 mg, 58% yield) as pale yellow oil. R*f* (5% EtOAc in hexane): 0.56; IR (CH_2Cl_2): 3030, 2933, 2860, 1683 (C=O), 1454 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.29 (m, 2H), 7.16-7.20 (m, 3H), 2.87 (q, *J* = 7.4 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.56 (m, 2H), 1.63-1.73 (m, 3H), 1.24 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.5, 142.0, 128.4, 128.4, 125.8, 43.8, 35.6, 30.6, 24.9 (t, *J* = 19.5 Hz), 23.2, 14.8 ppm; LRMS (ESI): m/z 246 ([M+Na$^+$]$^+$, 246(45), 162 (89), 118 (100); HRMS (ESI): calcd for $C_{13}H_{17}ODS$ ([M+Na$^+$]$^+$), 246.1033, found 246.1039.



2b

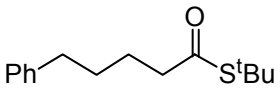
According to the typical procedure for 1, 4-reduction using (BDP)CuH, **3** (39.4mg, 0.200 mmol) and BDP (89.1mg, 0.199 mmol) were stirred in 1.0

mL PhMe. PMHS (360 μL, 6.01 mmol), thioester **1b** (496.4 mg, 1.999 mmol) in 1.0 mL PhMe and ^{t}BuOH (380 μL, 3.97 mmol) were added. After workup, the residue was purified by flash chromatography using 2% EtOAc in hexane to afford **2b** (449.8 mg, 90%) as a pale yellow oil. **2b:** R*f* (5% EtOAc in hexane): 0.44; IR (CH_2Cl_2): 3084, 3026, 2926, 2862, 1670 (C=O), 1602, 1494, 1454 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (m, 2H), 7.19-7.15 (m, 3H), 2.87 (t, *J* = 7.3 Hz, 2H), 2.64-2.60 (m, 2H), 2.58-2.55 (m, 2H), 1.73-1.63 (m, 4H), 1.56-1.51 (m, 2H), 1.41-1.35 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 142.2, 128.5 (2C), 128.4 (2C), 125.9, 44.0, 35.7, 31.8, 30.8, 28.7, 25.4, 22.1, 13.7 ppm; LRMS (EI. 20 eV): m/z 161 (M^{+}-C_4H_9S, 96), 117 (84), 91 (100); HRMS (EI, 20 eV): calcd for $C_{11}H_{13}O$ (M^{+}-C_4H_9S) 161.0961, found 161.0954.



2c

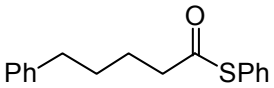
According to the typical procedure for 1, 4-reduction using (BDP)CuH, **3** (39.4 mg, 0.200 mmol) and BDP (89.1mg, 0.199 mmol) were stirred in 1.0 mL PhMe. PMHS (360 μL, 6.01 mmol), thioester **1b** (721.2 mg, 1.999 mmol) in 1.0 mL PhMe and ^{t}BuOH (380 μL, 3.97 mmol) were added. After workup, the residue was purified by flash chromatography using 3% EtOAc in hexane to afford **2c** (435.1 mg, 60%) as a pale yellow oil, along with recoverd **1c** (129.8 mg, 18%) **2c:** R*f* (5% EtOAc in hexane): 0.49; IR (CH_2Cl_2): 3063, 3042, 2927, 2854, 1686 (C=O), 1455, 1267 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.27 (m, 2H), 7.21-7.16 (m, 3H), 2.87 (t, 2H, *J* = 7.27), 2.66-2.55 (m, 3H), 1.72-1.68 (m, 3H), 1.66-1.54 (m, 3H), 1.25-1.27 (m, 19H), 0.92-0.87 (t, 3H, *J* = 6.4 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.5, 142.0, 128.4, 126.1, 43.9, 41.7, 35.6, 31.9, 30.7, 29.6, 29.6, 29.5, 29.4, 29.2, 29.1, 28.9, 28.8, 25.3, 22.7, 14.1 ppm; LRMS (EI, 20 eV): m/z 161.1 (M+-$C_{12}H_{25}$, 100), 160.1 (90); HRMS (EI, 20 eV): calcd for $C_{23}H_{38}OS$, 362.2638, found 362.2538.



2d

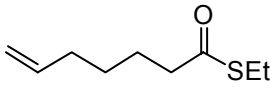
According to the typical procedure for 1, 4-reduction using (BDP)CuH, **3** (39.2 mg, 0.199 mmol) and BDP (89.5 mg, 0.200 mmol) were dissolved in 1.0 mL PhMe. PMHS (600 μL, 10.0 mmol), thioester **2d** (496.3 mg, 1.998 mmol) in 1.0 mL PhMe and ^{t}BuOH (380 μL, 3.97 mmol) were added. After workup, the residue was purified by flash chromatography using 3% EtOAc in hexane to afford **2d** (260.0 mg, 51%) as a pale yellow oil, along with recovered **1d** (170.0 mg, 34%).**2d:** R*f* (5% EtOAc in hexane): 0.49; IR (CH_2Cl_2): 3066, 3029, 2966, 2829, 2863, 1679 (C=O), 1455, 1365 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.24 (m, 2H), 7.19-7.15 (m, 3H), 2.64-2.59 (m, 2H), 2.49-2.40 (m, 2H), 1.72-1.58 (m, 4H), 1.45 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 142.1, 128.4 (2C), 128.3 (2C), 125.8,

47.8, 44.4, 35.6, 30.7, 29.9 (3C), 25.2 ppm; LRMS (ESI): m/z 273 ($[M^+ + Na^+]^+$, 38), 161 (100), 117 (27); HRMS (ESI): calcd for $C_{15}H_{22}ONaS$ ($[M^+ + Na^+]^+$) 273.1289, found 273.1294.



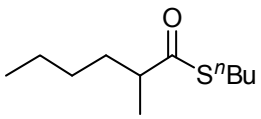
2e

According to the typical procedure for 1,4-reduction using (BDP)CuH, **3** (78.6 mg, 0.400 mmol) and BDP (89.2 mg, 0.200 mmol) were dissolved in 1.0 mL PhMe. PMHS (600 μL, 10.0 mmol), thioester **1e** (536.1 mg, 1.998 mmol) in 1.0 mL PhMe and ^{t}BuOH (380 μL, 3.97 mmol) were added. After workup, the residue was purified by flash chromatography using 3% EtOAc in hexane to afford **2e** (44.4 mg, 8%) as a pale yellow oil, along with recovered **1e** (440.7 mg, 82%). **2e:** R*f* (5% EtOAc in hexane): 0.46; IR (CH_2Cl_2): 3065, 3028, 2937, 2860, 1703 (C=O), 1477, 1440 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (s, 5H), 7.35-7.32 (m, 2H), 7.26-7.22 (m, 3H), 2.74-2.67 (m, 4H), 1.85-1.75 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 141.9, 134.4 (2C), 129.3, 129.1 (2C), 128.4 (2C), 128.3 (2C), 127.9, 125.8, 43.5, 35.5, 30.7, 25.2 ppm; LRMS (EI, 20 eV): m/z 191 (M^+- C_6H_5S, 84), 117 (46), 91 (100); HRMS (EI, 20 eV): calcd for $C_{11}H_{13}O$ (M^+-C_6H_5S) 161.0961, found 161.0964.



2f

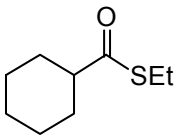
According to the typical procedure for 1,4-reduction using (BDP)CuH, **3** (39.5 mg, 0.201 mmol) and BDP (89.3 mg, 0.200 mmol) were dissolved in 1.0 mL PhMe. PMHS (360 μL, 6.01 mmol), thioester **1f** (340.0 mg, 1.997 mmol) in 1.0 mL PhMe and ^{t}BuOH (380 μL, 3.97 mmol) were added. After workup, the residue was purified by flash chromatography using 3% EtOAc in hexane to afford **4.3a** (300.5 mg, 87%) as a pale yellow oil. **2f:** R*f* (5% EtOAc in hexane): 0.55; IR (CH_2Cl_2): 3078, 2974, 2934, 2862, 1686 (C=O), 1455 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82-5.75 (m, 1H), 5.08-4.94 (m, 2H), 2.87 (q, *J* = 7.4 Hz, 2H), 2.56-2.52 (m, 2H), 2.09-2.03 (m, 2H), 1.71-1.64 (m, 2H), 1.46-1.34 (m, 2H), 1.24 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 138.3, 114.8, 44.0, 33.4, 28.2, 25.1, 23.2, 14.8 ppm; LRMS (EI, 20 eV): m/z 111 (M^+-C_2H_5, 100), 83 (78), 69 (31); HRMS (EI, 20 eV): calcd for $C_7H_{11}O$ (M^+-C_2H_5), 111.0804, found 111.0789.



2g

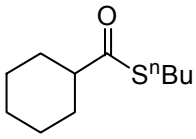
According to the typical procedure for 1,4-reduction using (BDP)CuH, **3** (78.7 mg, 0.400 mmol) and BDP (89.6 mg, 0.201 mmol) were dissolved in 1.0 mL PhMe. PMHS (600 μL, 10.0 mmol), thioester **1g** (400.1 mg, 1.999 mmol) in 1.0 mL PhMe and ^{t}BuOH (380 μL, 3.97 mmol) were added. After workup, the residue was purified by flash chromatography using 2% EtOAc in hexane to afford **2g** (391.8 mg, 97%) as a pale yellow oil. **2g**: R*f* (5% EtOAc in hexane): 0.64; IR (CH_2Cl_2): 3101, 2974, 2858, 2733, 1668 (C=O), 1458,

1379 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.86 (t, *J* = 7.3 Hz, 2H), 2.65-2.56 (m, 1H), 1.75-1.68 (m, 1H), 1.58-1.51 (m, 2H), 1.43-1.22 (m, 7H), 1.15 (d, *J* = 6.9 Hz, 3H), 0.93-0.86 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.2, 48.7, 33.9, 31.8, 29.4, 28.3, 22.7, 22.0, 17.8, 14.0, 13.6 ppm; LRMS (EI, 20 eV): m/z 145 (M^+-C_4H_9, 9), 113 (33), 85 (100); HRMS (EI, 20 eV): calcd for $C_7H_{13}OS$ (M^+-C_4H_9) 145.0682, found 145.0077.



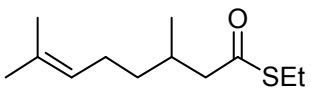
2h

According to the typical procedure for 1,4-reduction using (BDP)CuH, **3** (39.4 mg, 0.200 mmol) and BDP (89.2 mg, 0.200 mmol) were dissolved in 1.0 mL PhMe. PMHS (600 μL, 10.0 mmol), thioester **1h** (340.5 mg, 1.998 mmol) in 1.0 mL PhMe and ^{t}BuOH (380 μL, 3.97 mmol) were added. After workup, the residue was purified by flash chromatography using 3% EtOAc in hexane to afford **2h** (87.5 mg, 25%) as a pale yellow oil along with recovered **1h** (233.6 mg, 69%). **2h:** R*f* (5% EtOAc in hexane): 0.50; IR (CH_2Cl_2): 2924, 2856, 1674 (C=O), 1450 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): δ 2.82 (q, *J* = 7.4 Hz, 2H), 2.76-2.42 (m, 1H), 1.96-1.93 (m, 2H), 1.63-1.58 (m, 4H), 1.48-1.46 (m, 1H), 1.14 (t, *J* = 7.4 Hz, 3H), 1.12-1.04 (m, 3H) ppm; ^{13}C NMR (125 MHz, C_6D_6): δ 202.0, 53.2, 30.2 (2C), 26.2, 26.0 (2C), 23.4, 15.4 ppm; LRMS (EI, 20 eV): m/z 171 (M^+-H, 4), 111 (56), 83 (100); HRMS (EI, 20 eV): calcd for $C_9H_{15}OS$ (M^+-H), 171.0838, found 171.0839.



2i

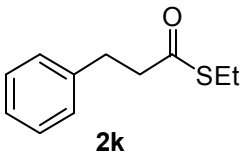
According to the typical procedure for 1,4-reduction using (BDP)CuH, **3** (39.5 mg, 0.201 mmol) and BDP (89.2 mg, 0.200 mmol) were dissolved in 1.0 mL PhMe. PMHS (600 μL, 10.0 mmol), thioester **1i** (396.1 mg, 1.994 mmol) in 1.0 mL PhMe and ^{t}BuOH (380 μL, 3.97 mmol) were added. After workup, the residue was purified by flash chromatography using 3% EtOAc in hexane to afford **2i** (89.4 mg, 22%) as a pale yellow oil and recovered **1i** (268.3 mg, 68%). **2i:** R_f (5% EtOAc in hexane): 0.51; ^1H NMR (500 MHz, C_6D_6): δ 2.82 (t, *J* = 7.3 Hz, 2H), 2.41-2.35 (m, 1H), 1.88-1.86 (m, 2H), 1.55-1.48 (m, 4H), 1.46-1.40 (m, 2H), 1.38-1.37 (m, 1H), 1.25-1.19 (m, 2H), 1.18-0.95 (m, 3H), 0.75 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (125 MHz, C_6D_6): δ 202.0, 53.3, 32.6, 30.2 (2C), 28.7, 26.2, 26.0 (2C), 22.5, 14.0 ppm. The characterization corresponded to that of **2i** documented in the literature.[7]



2j

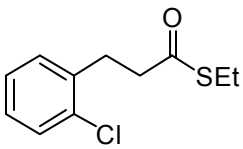
According to the typical procedure for 1,4-reduction using (BDP)CuH, **3** (78.5 mg, 0.400 mmol) and BDP (89.4 mg, 0.200 mmol) were dissolved in 1.0 mL PhMe. PMHS (600 μL, 10.0 mmol), thioester **1j** (424.5 mg, 1.999 mmol) in 1.0 mL PhMe and ^{t}BuOH (380 μL, 3.97 mmol) were added. After workup, the

residue was purified by flash chromatography using 3% EtOAc in hexane to afford **2j** (375.4 mg, 88%) as a pale yellow oil, along with recovered **2j** (14.9 mg, 4%). **2j**: R*f* (5% EtOAc in hexane): 0.55; IR (CH_2Cl_2): 3057, 2966, 2930, 2854, 1682 (C=O), 1456 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.10-5.06 (m, 1H), 2.87 (q, *J* = 7.4 Hz, 2H), 2.54 (dd, *J* = 14.4, 5.9 Hz, 1H), 2.34 (dd, *J* = 14.4, 8.2 Hz, 1H), 2.06-1.94 (m, 3H), 1.68 (d, *J* = 1.0 Hz, 3H), 1.60 (s, 3H), 1.39-1.31 (m, 1H), 1.26-1.20 (m, 1H),1.24 (t, *J* = 7.4 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 131.6, 124.2, 51.4, 36.7, 30.8, 25.7, 25.4, 23.3, 19.5, 17.7, 14.8 ppm; LRMS (EI, 20 eV): m/z 213 (M^+-H, 10), 153 (23), 111 (48), 109 (100); HRMS (EI, 20 eV): calcd for $C_{12}H_{22}OS$ (M^+-H) 213.1308, found 213.1306.



2k

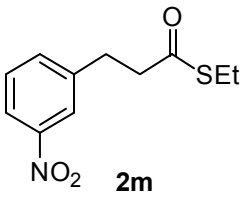
According to the typical procedure for 1,4-reduction using (BDP)CuH, **3** (78.5 mg, 0.400 mmol) and BDP (89.1 mg, 0.199 mmol) were dissolved in 1.0 mL PhMe. PMHS (600 µL, 10.0 mmol), thioester **1k** (384.0 mg, 1.997 mmol) in 1.0 mL PhMe and ^{t}BuOH (380 µL, 3.97 mmol) were added. After workup, the residue was purified by flash chromatography using 3% EtOAc in hexane to afford **2k** (348.8 mg, 90%) as a pale yellow oil. **2k:** R*f* (5% EtOAc in hexane): 0.45; IR (CH_2Cl_2): 3067, 3031, 2972, 2933, 2876, 1685 (C=O), 1497, 1454 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.34 (m, 2H), 7.31-7.23 (m, 3H), 3.07-3.00 (m, 2H), 2.95-2.88 (m, 4H), 1.30 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 140.2, 128.5 (2C), 128.3 (2C), 126.3, 45.5, 31.5, 23.3, 14.8 ppm; LRMS (EI, 20 eV): m/z 194 (M^+, 30), 133 (39), 105 (100), 77 (67); HRMS (EI, 20 eV): calcd for $C_{11}H_{14}OS$ (M^+) 194.0706, found 194.0759.



2l

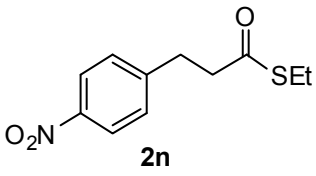
According to the typical procedure for 1,4-reduction using (BDP)CuH, **3** (78.6 mg, 0.400 mmol) and BDP (89.4 mg, 0.200 mmol) were dissolved in 1.0 mL PhMe. PMHS (600 µL, 10.0 mmol), thioester **2l** (453.1 mg, 1.998 mmol) in 1.0 mL PhMe and ^{t}BuOH (380 µL, 3.97 mmol) were added. After workup, the residue was purified by flash chromatography using 3% EtOAc in hexane to afford **2l** (394.5 mg, 86 %) as a pale yellow oil and recovered **1l** (15.4 mg, 3%).

2l: R*f* (5% EtOAc in hexane): 0.48; IR (CH_2Cl_2): 3070, 2974, 2934, 2876, 1690 (C=O), 1475, 1446 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.32 (m, 1H), 7.24-7.13 (m, 3H), 3.11-3.07 (m, 2H), 2.91-2.85 (m, 4H), 1.24 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 137.7, 134.0, 130.6, 129.6, 127.9, 126.9, 43.5, 29.5, 23.4, 14.8 ppm; LRMS (EI, 20 eV): m/z 193 (M^+-Cl, 45), 139 (100), 125 (58), 77 (25); HRMS (EI, 20 eV): calcd for $C_{11}H_{13}OS$ (M^+-Cl) 193.0682, found 193.0690.



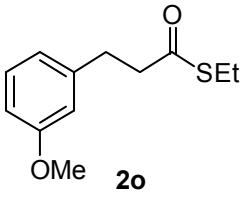
2m

According to the typical procedure for 1,4-reduction using (BDP)CuH, **3** (19.6 mg, 0.100 mmol) and BDP (44.7 mg, 0.100 mmol) were dissolved in 1.0 mL PhMe. PMHS (180 μL, 3.00 mmol), thioester **1m** (237.1 mg, 0.9993 mmol) in 2.0 mL PhMe and ^{t}BuOH (380 μL, 3.97 mmol) were added. After workup, the residue was purified by flash chromatography using 6% EtOAc in hexane to afford **2m** (194.6 mg, 81%) as a pale yellow oil and recovered **1m** (8.3 mg, 4%). **2m:** R*f* (10% EtOAc in hexane): 0.42; IR (CH_2Cl_2): 3063, 3045, 2972, 2931, 2874, 1682 (C=O), 1529, 1352 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (t, *J* = 2.2, 2H), 7.51 (d, *J* = 7.6, 1H), 7.47-7.43 (m, 1H), 3.07 (q, *J* = 7.3 Hz, 2H), 2.91-2.82 (m, 4H), 1.23 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 148.4, 142.1, 134.8, 129.4, 123.3, 121.6, 44.6, 30.9, 23.5, 14.7 ppm; LRMS (EI, 20 eV): m/z 239 (M^+, 2), 150 (100), 136 (44), 77 (19); HRMS (EI, 20 eV): calcd for $C_{11}H_{13}O_3NS$ (M^+) 239.0611, found 239.0610.



2n

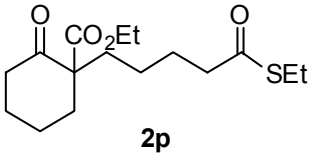
According to the typical procedure for 1,4-reduction using (BDP)CuH, **3** (39.1 mg, 0.199 mmol) and BDP (89.4 mg, 0.200 mmol) were dissolved in 2.0 mL PhMe. PMHS (600 μL, 10.0 mmol), thioester **1n** (474.0 mg, 1.998 mmol) in 2.0 mL PhMe and ^{t}BuOH (380 μL, 3.97 mmol) were added. After workup, the residue was purified by flash chromatography using 6% EtOAc in hexane to afford **2n** (430.1 mg, 90%) as a pale yellow oil. **2n:** R*f* (10% EtOAc in hexane): 0.44; IR (CH_2Cl_2): 3078, 3047, 2972, 2934, 1682 (C=O), 1522, 1348 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16-8.12 (m, 2H), 7.36-7.26 (m, 2H), 3.11-3.06 (m, 2H), 2.92-2.84 (m, 4H), 1.23 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 147.9, 146.8, 129.3 (2C), 123.8 (2C), 44.4, 31.1, 23.5, 14.7 ppm; LRMS (EI, 20 eV): m/z 239 (M^+, 14), 150 (100), 136 (41), 77 (92); HRMS (EI, 20 eV): calcd for $C_{11}H_{13}O_3NS$ (M^+) 239.0611, found 239.0615.



2o

According to the typical procedure for 1, 4-reduction using (BDP)CuH**, 3** (39.1 mg, 0.199 mmol) and BDP (89.4 mg, 0.200 mmol) were dissolved in 1.0 mL PhMe. PMHS (600 μL, 10.0 mmol), thioester **1o** (444.0 mg, 1.999 mmol) in 1.0 mL PhMe and ^{t}BuOH (380 μL, 3.97 mmol) were added. After workup, the residue was purified by flash chromatography using 2% EtOAc in hexane to afford **2o** (385.9 mg, 86%) as a pale yellow oil and recovered **1o** (15.3 mg, 3%). R*f* (5% EtOAc in hexane): 0.42; IR (CH_2Cl_2): 3071, 2974, 2934, 2876, 1685 (C=O), 1531, 1353 cm^{-1}; ^{1}H NMR (400

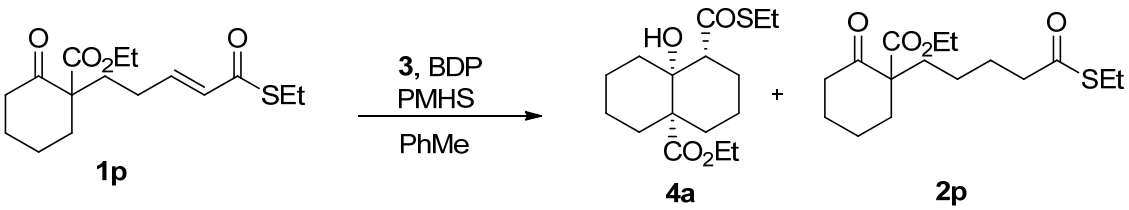
MHz, $CDCl_3$): δ 7.22-7.17 (m, 1H), 6.79-6.74 (m, 3H), 3.79 (s, 3H), 2.96-2.83 (m, 6H), 1.25 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 159.8, 141.8, 129.5, 120.7, 114.1, 111.7, 55.2, 45.5, 31.5, 23.4, 14.8 ppm; LRMS (EI, 20 eV): m/z 224 (M^+, 92), 163 (87), 121 (100), 91 (52); HRMS (EI, 20 eV): calcd for $C_{12}H_{16}O_2S$ (M^+) 224.0871, found 224.0867.



2p

According to the typical procedure for 1,4-reduction using (BDP)CuH, **3** (11.5 mg, 0.0585 mmol) and BDP (13.6 mg, 0.0305 mmol) were dissolved in 2.0 mL PhMe. PMHS (90 μL, 1.5 mmol), thioester **2.6c** (93.4 mg, 0.299 mmol) in 1.0 mL PhMe and ^tBuOH (60 μL, 0.63 mmol) were added. After workup, the residue was purified by flash chromatography using 3% EtOAc in hexane to afford **2p** (81.2 mg, 86%) as a pale yellow oil. **2p:** R*f* (10% EA in hexane): 0.51; IR (CH_2Cl_2): 2939, 2868, 1786 (ketone C=O), 1709 (thioester C=O), 1683 (ester C=O), 1452, 1273 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 4.20 (d, *J* = 7.6 Hz, 1H), 4.17 (d, *J* = 7.6 Hz, 1H), 2.85 (q, *J* = 7.4 Hz, 2H), 2.54-2.40 (m, 5H), 2.01-1.97 (m, 1H), 1.88-1.82 (m, 1H), 1.76-1.51 (m, 8H), 1.45-1.39 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.9, 199.4, 172.0, 61.2, 60.8, 43.8, 41.1, 36.1, 34.3, 27.6, 25.9, 23.7, 23.2, 22.6, 14.8, 14.2 ppm; LRMS (EI, 20 eV): m/z 314 (M^+, 1), 253 (4), 179 (40), 133 (100); HRMS (EI, 20 eV): calcd for $C_{16}H_{26}O_4S$ (M^+) 314.1552, found 314.1557.

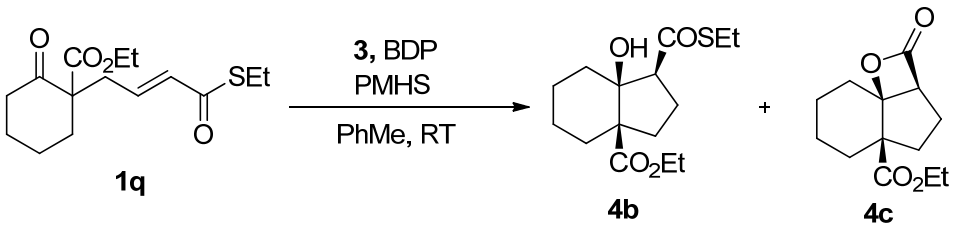
Typical procedure for reductive aldol reactions



1p **4a** **2p**

A solution of **3** (23.4 mg, 0.119 mmol) and BDP (26.6 mg, 0.0596 mmol) in 2.0 mL PhMe was stirred for 5 minutes. PMHS (90 μL, 1.5 mmol) was added and the reaction mixture turned greenish yellow. Thioester **1p** (93.1 mg, 0.298 mmol) in 1.0 mL PhMe was added. The reaction was monitored by TLC and quenched by the addition of saturated aqueous NH_4Cl solution. The reaction mixture was filtered through a pad of silica gel. The filtrate was extracted with EtOAc (3 x 10 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by flash chromatography using 10% EtOAc in hexane to afford **4a** (53.9 mg, 57 %) as a pale yellow oil and **2p** (21.5 mg, 23%). **4a**: R*f* (10% EtOAc in hexane): 0.53; IR (CH_2Cl_2): 3468, 2937, 2870, 1695 (thioester C=O), 1655 (ester C=O), 1456, 1236 cm^{-1}; ^1H NMR (500 MHz, toluene-d_8, 80 ^oC): δ 4.33

(s, 1H), 3.96-3.86 (m, 2H), 2.95 (dd, J = 11.9, 3.8 Hz, 1H), 2.70 (qd, J = 7.4, 0.7 Hz, 2H), 2.32-2.08 (m, 2H), 1.98-1.92 (m, 2H), 1.71-1.67 (m, 1H), 1.60-1.53 (m, 4H), 1.52-1.32 (m, 4H), 1.31-1.22 (m, 1H), 1.06 (t, J = 7.4 Hz, 3H), 0.98 (m, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (125 MHz, toluene-d_8, 80 ^{o}C): δ 200.7, 177.1, 73.3, 60.5, 55.4, 51.8, 35.7, 31.6, 31.0, 26.1, 23.7, 23.5, 23.2, 20.9, 14.8, 14.2 ppm; LRMS (EI, 20 eV):m/z 253 (M^+-C_2H_4, 11), 179 (54), 135 (100); HRMS (EI, 20 eV): calcd for $C_{14}H_{21}O_4$ (M^+-SC_2H_5), 253.1440, found 253.1441.



According to typical procedure for reductive aldol reaction of **1p**, **3** (11.9 mg, 0.0605 mmol) and BDP (13.5 mg, 0.0302 mmol) were dissolved in 2.0 mL PhMe. PMHS (90 μL, 1.5 mmol), thioester **1q** (89.1 mg, 0.298 mmol) in 1.0 mL PhMe were added. The reaction was monitored by TLC. After the reaction was complete and worked up, the residue was purified by flash chromatography using 10% EtOAc in hexane to afford **4b** (53.1 mg, 60%) as a pale yellow oil and **4c** (10.3 mg, 14%) as a pale yellow oil. **4b:** R*f* (10% EA in hexane): 0.55; IR (CH_2Cl_2): 3452, 2982, 2941, 2866, 1647 (thioester C=O), 1636 (ester C=O), 1452 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.17 (q, J = 7.1 Hz, 2H), 3.93 (d, J = 1.1 Hz, 1H), 3.35-3.31 (m, 1H), 2.92 (q, J = 7.4 Hz, 2H), 2.46-2.36 (m, 2H), 2.26-2.23 (m, 1H), 2.02-1.85 (m, 3H), 1.80-1.76 (m, 1H), 1.67-1.62 (m, 1H), 1.48-1.29 (m, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.4, 175.9, 82.5, 60.7, 57.0, 56.0, 33.8, 33.3, 32.8, 23.6, 23.3 (2C), 22.4, 14.5, 14.1 ppm; LRMS (EI, 20 eV): m/z 300 (M^+, 2), 239 (69), 193 (100), 165 (96); HRMS (EI, 20 eV): calcd for $C_{15}H_{24}O_4S$ (M^+) 300.1390, found 300.1388. **4c**: R_f (10% EtOAc in hexane): 0.59; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.22-4.16 (m, 2H), 3.46 (m, 1H), 2.54-2.38 (m, 2H), 2.07-1.87 (m, 6H), 1.58-1.52 (m, 2H), 1.38-1.30 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.25-1.20 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.7, 170.9, 88.0, 60.9, 58.6, 53.0, 33.3, 32.8, 29.5, 24.0, 22.6, 21.1, 14.2 ppm. The characterization corresponded to that of **4c** documented in the literature.[8]

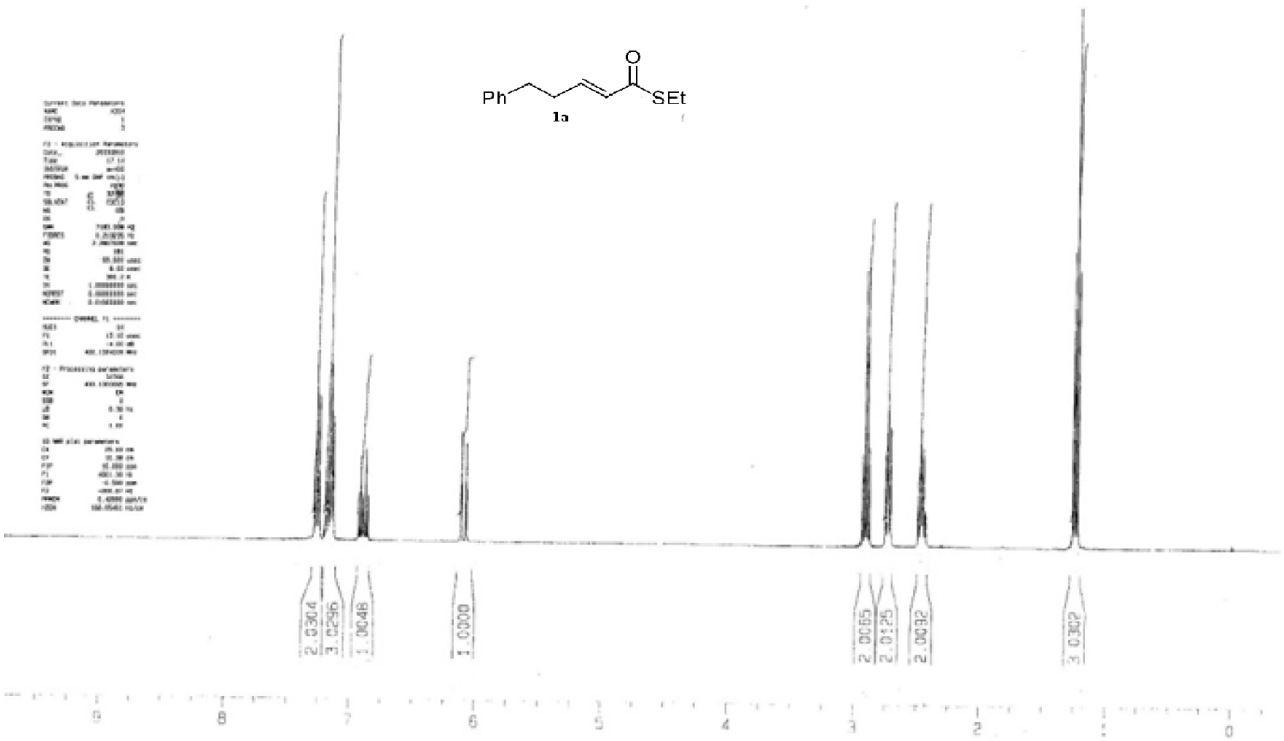
According to typical procedure for reductive aldol reaction of **1p**, **3** (29.7 mg, 0.151 mmol) and BDP (67.2 mg, 0.150 mmol) were dissolved in 2.0 mL PhMe. PMHS (90 μL, 1.5 mmol), thioester **1q** (89.1 mg, 0.298 mmol) in 1 mL PhMe were added. The reaction was monitored by TLC. After

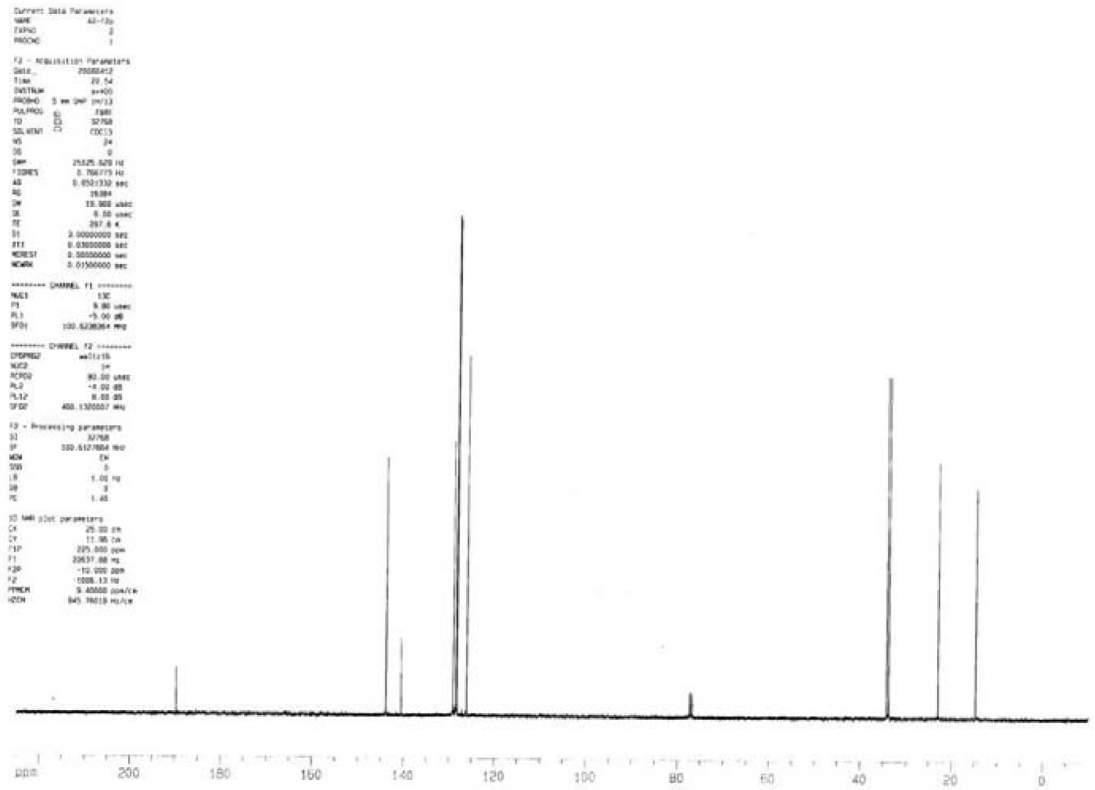
the reaction was complete and worked up, the residue was purified by flash chromatography using 10% EtOAc in hexane to afford **4b** (72.2 mg, 81%) as a pale yellow oil.

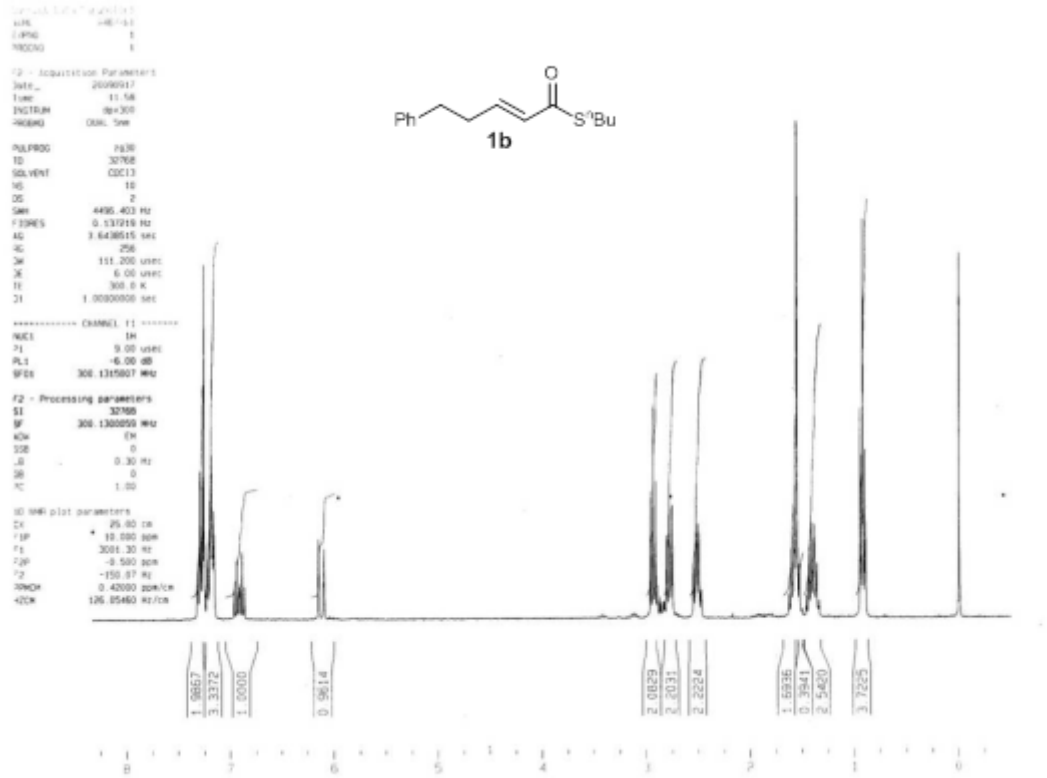
References

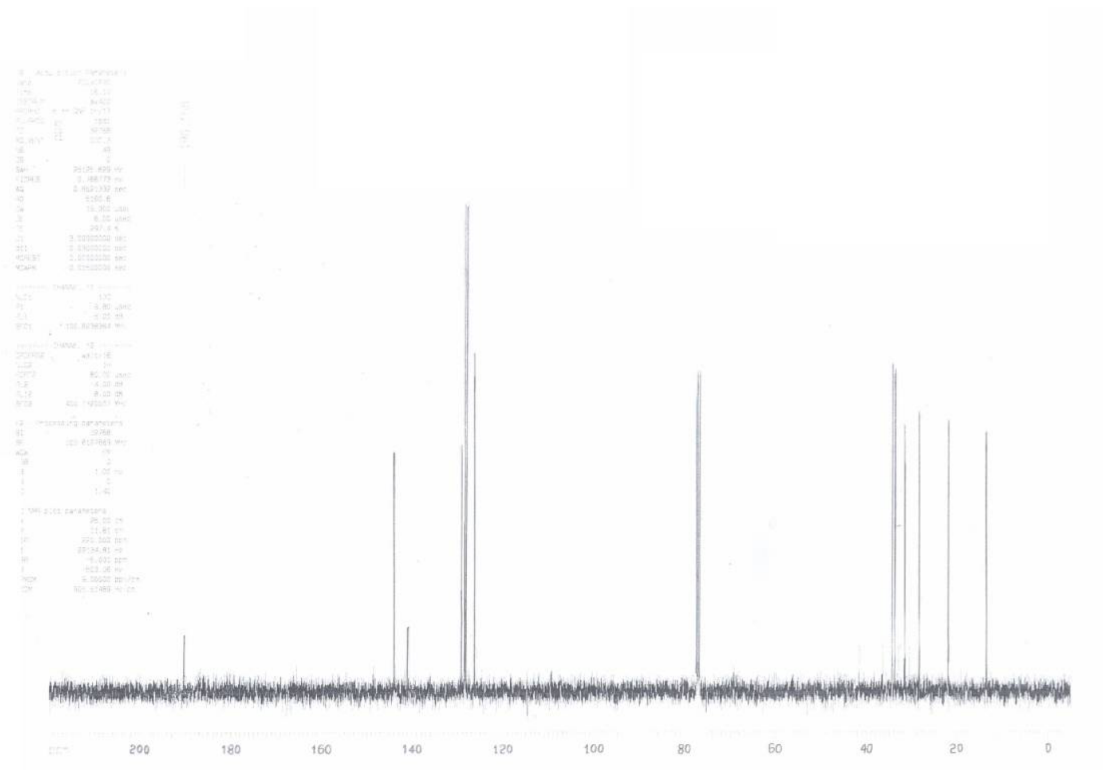
1. G. E. Keck, E. P. Bonen and S. A. Mabury, *J. Org. Chem.* 1985, **50**, 709.
2. H. Kakei, R.Tsuji, T. Ohshima and M. Shibasaki, *J. Am. Chem. Soc.* 2005, **127**, 8962.
3. A. W. van Zijl, A. J. Minnaard and B. L. Feringa, *J. Org. Chem.* 2008**, 73**, 5651.
4. M. Yoshimatsu, M. Naito, M. Kawahigashi, H. Shimizu and T. Kataoka, *J. Org. Chem.* 1995**, 60**, 4798.
5. H. C. Aspinall, N. Greeves and C. Valla, *Org. Lett.* 2005 , **7,** 1919.
6. P. S. Aburel, C. Roemming, K. Ma and K. Undheim, *J. Chem. Soc. Perkin Trans. 1,* 2001, 1458.
7. T. Inoue, T. Takeda, N. Kambe, A. Ogawa, I. Ryu and N. Sonoda, *J. Org. Chem.* 1994**, 59**, 5824.
8. H. Henry-Riyad, C. Lee, V. C. Purohit and D. Romo, *Org. Lett.* 2006**, 8**, 4363.

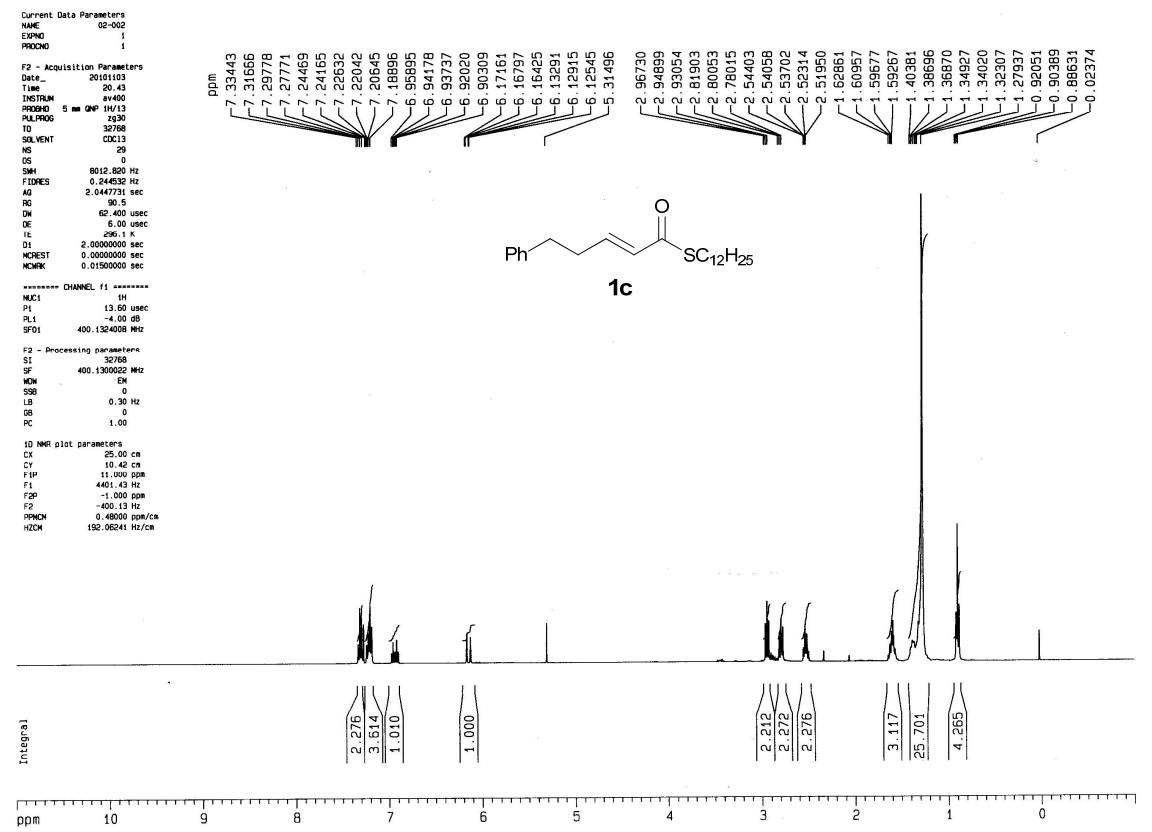
^{1}H and ^{13}C NMR Spectra of New Compounds







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Time 20.43
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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 29
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 90.5
DW 62.400 usec
DE 6.00 usec
TE 296.1 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -4.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300022 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 10.42 cm
F1P 11.000 ppm
F1 4401.43 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.48000 ppm/cm
HZCM 192.06241 Hz/cm
ppm
7.33443
7.31666
7.29778
7.27771
7.24469
7.24165
7.22632
7.22042
7.20645
7.18896
6.95895
6.94178
6.93737
6.92020
6.90309
6.17161
6.16797
6.16425
6.13291
6.12915
6.12545
5.31496
2.96730
2.94899
2.93054
2.81903
2.80053
2.78015
2.54403
2.54058
2.53702
2.52314
2.51950
1.62861
1.60957
1.59677
1.59267
1.40381
1.38696
1.36870
1.34927
1.34020
1.32307
1.27937
0.92051
0.90389
0.88631
0.02374
O
Ph
SC12H25
1c
Integral
2.276
3.614
1.010
1.000
2.212
2.272
2.276
3.117
25.701
4.265
ppm
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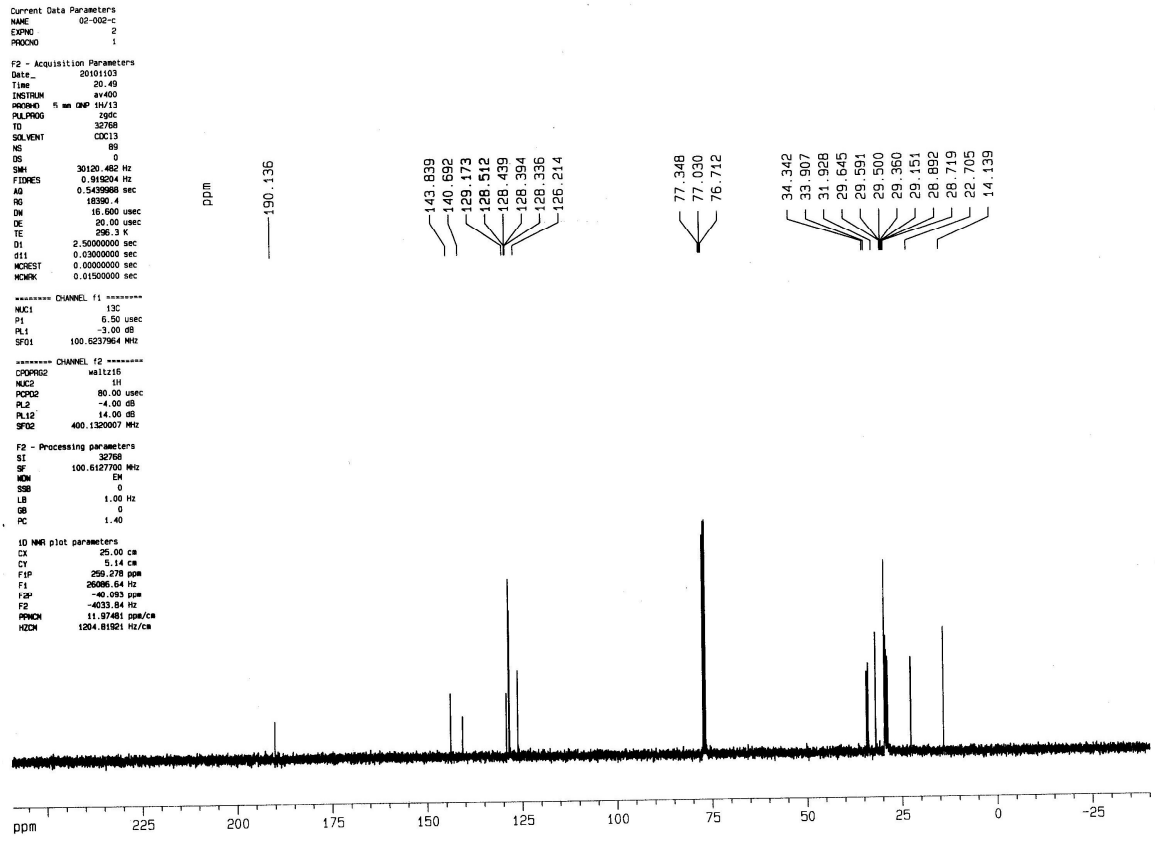
9
8
7
6
5
4
3
2
1
0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PROCNO 1
F2 - Acquisition Parameters
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Time 20.49
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PULPROG zgpc
TD 32768
SOLVENT CDCl3
NS 89
DS 0
SWH 30120.482 Hz
FIDRES 0.919204 Hz
AQ 0.5439988 sec
RG 16390.4
DW 16.600 usec
DE 20.00 usec
TE 296.3 K
D1 2.50000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 6.50 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.00 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 5.14 cm
F1P 259.278 ppm
F1 26086.64 Hz
F2P -40.093 ppm
F2 -4033.84 Hz
PPMCM 11.97481 ppm/cm
HZCM 1204.81921 Hz/cm
ppm
190.136
143.839
140.692
129.173
128.512
128.439
128.394
128.336
126.214
77.348
77.030
76.712
34.342
33.907
31.928
29.645
29.591
29.500
29.360
29.151
28.892
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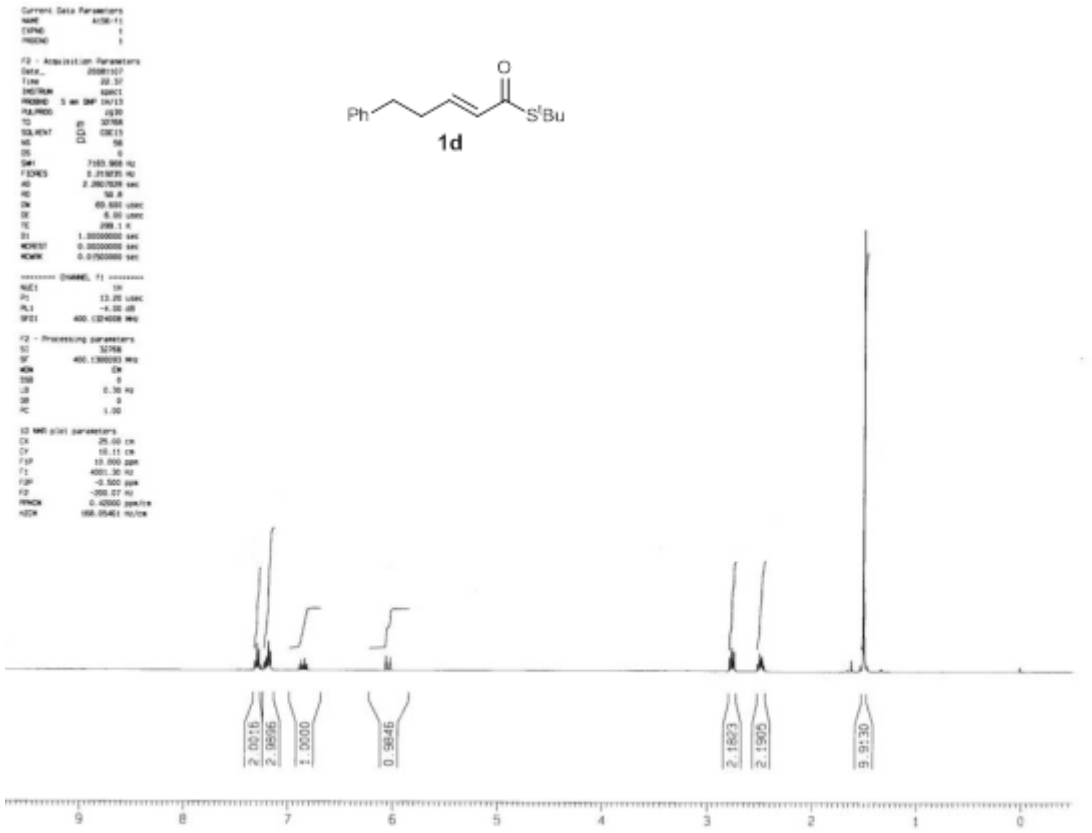
22.705
14.139
ppm
225
200
175
150
125
100
75
50
25
0
-25


Ph
O
S^{t}Bu
1d
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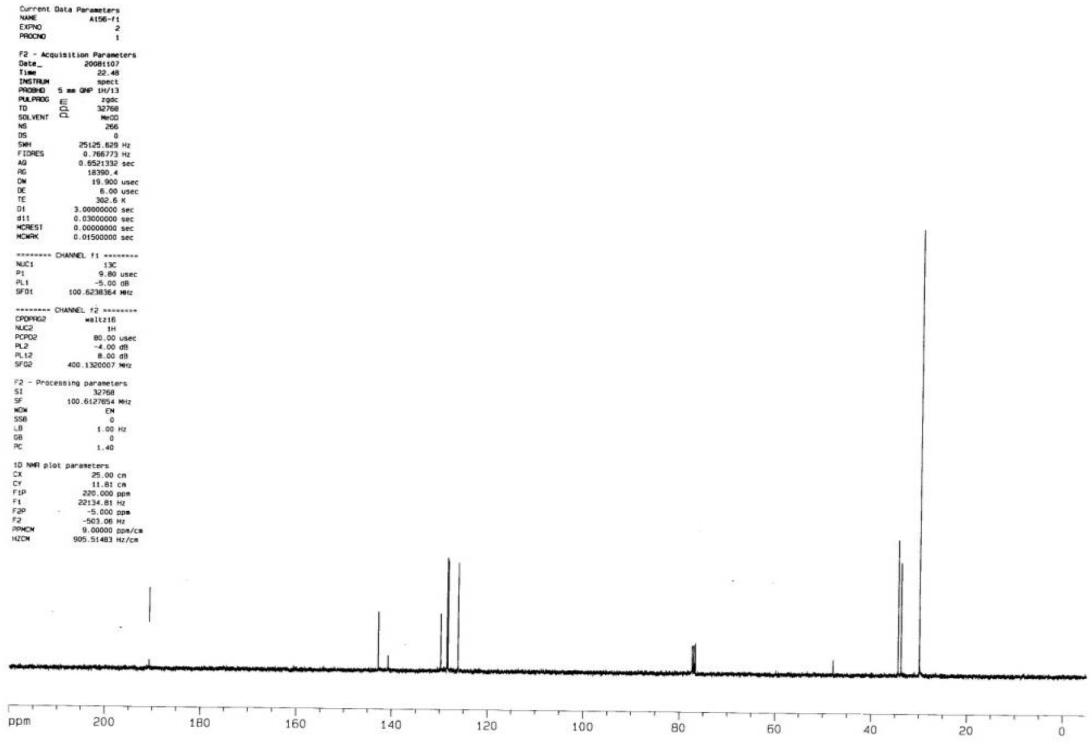
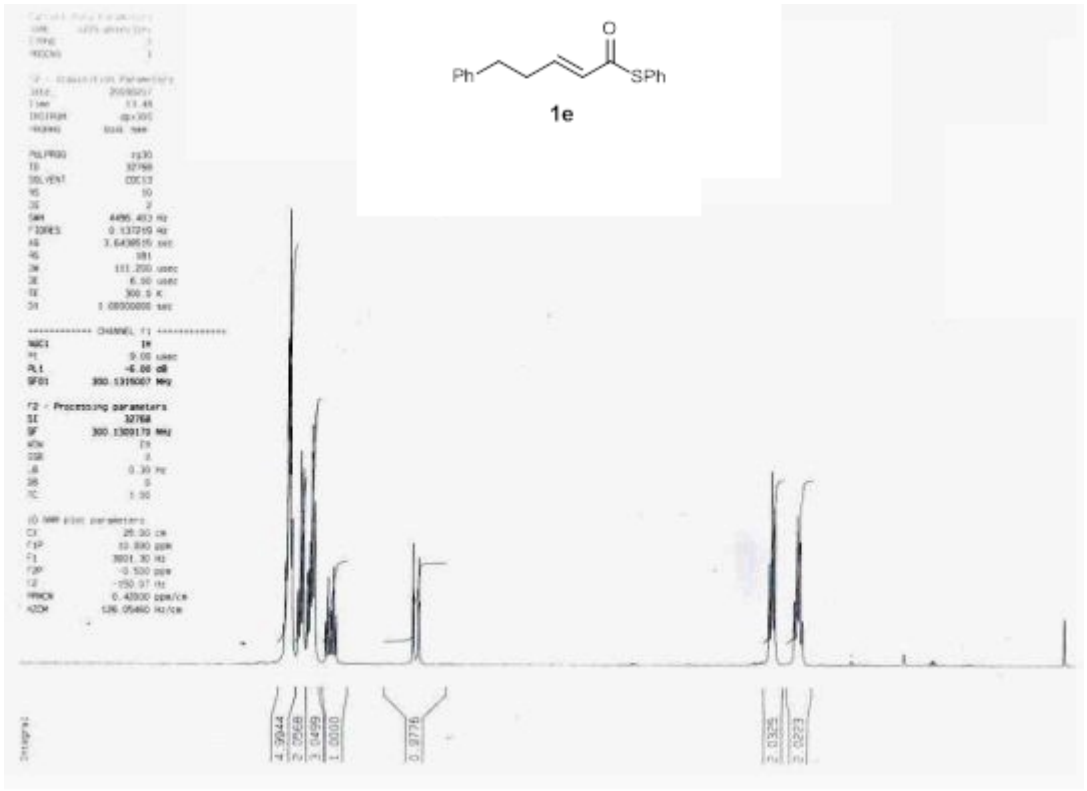
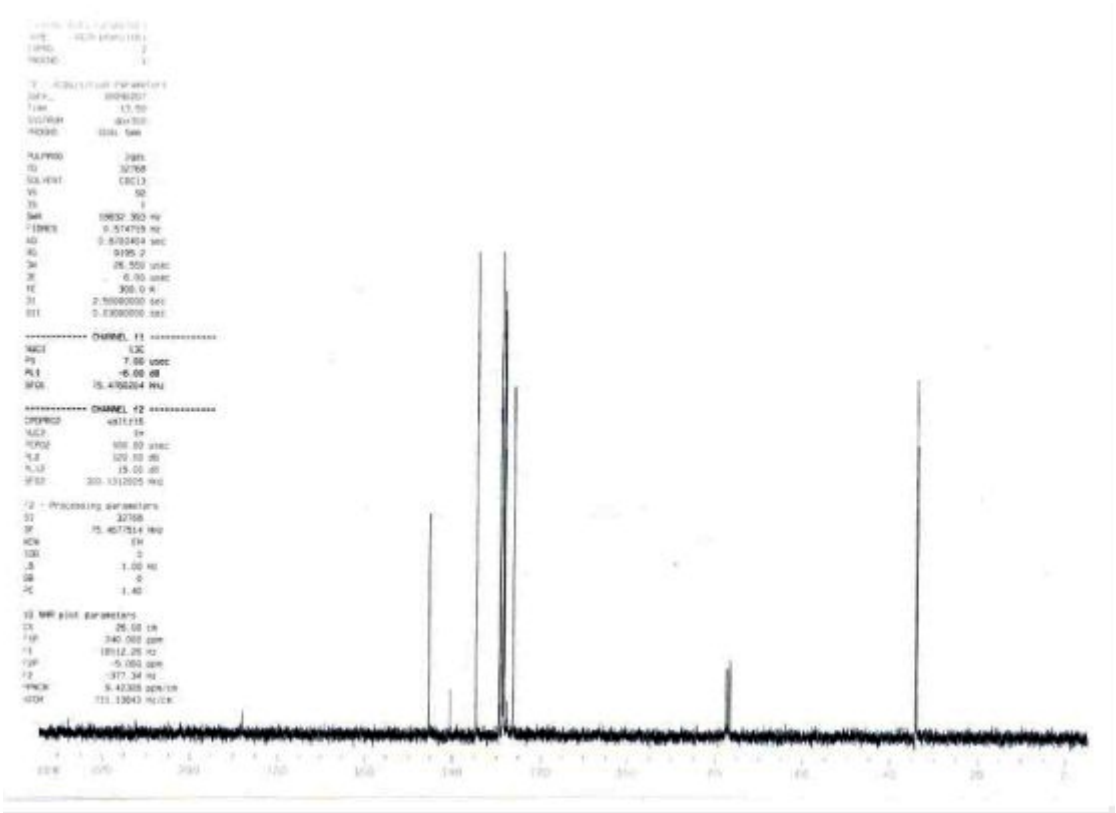
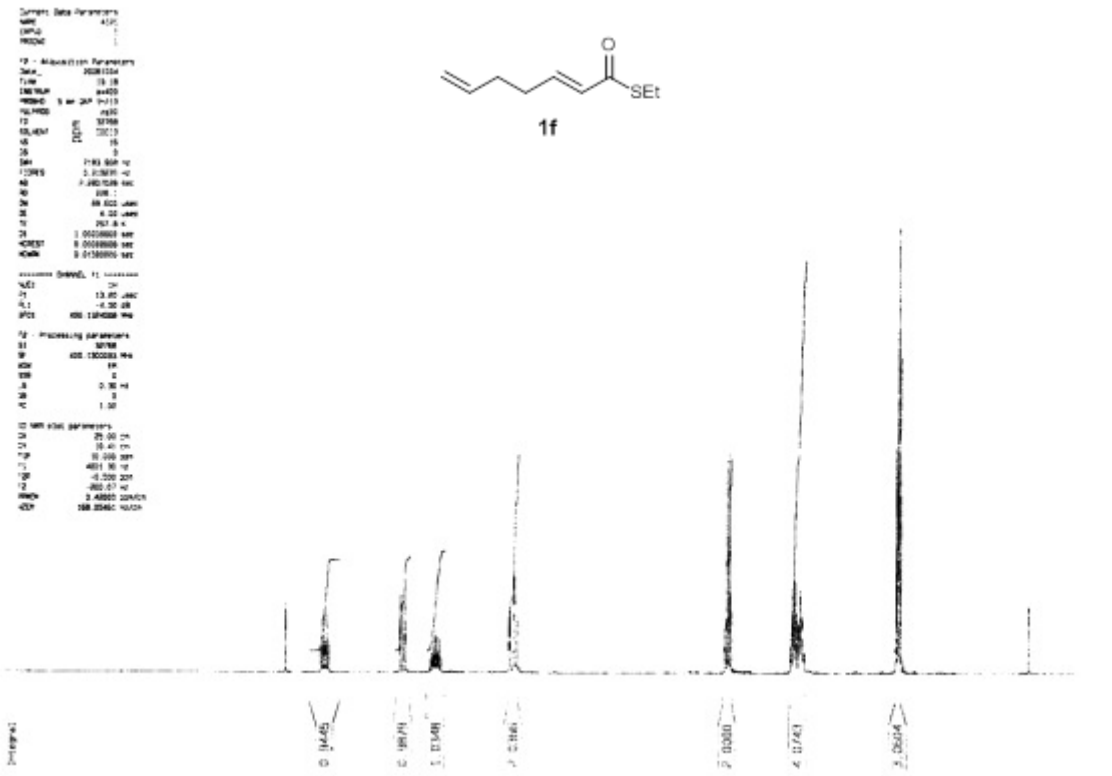
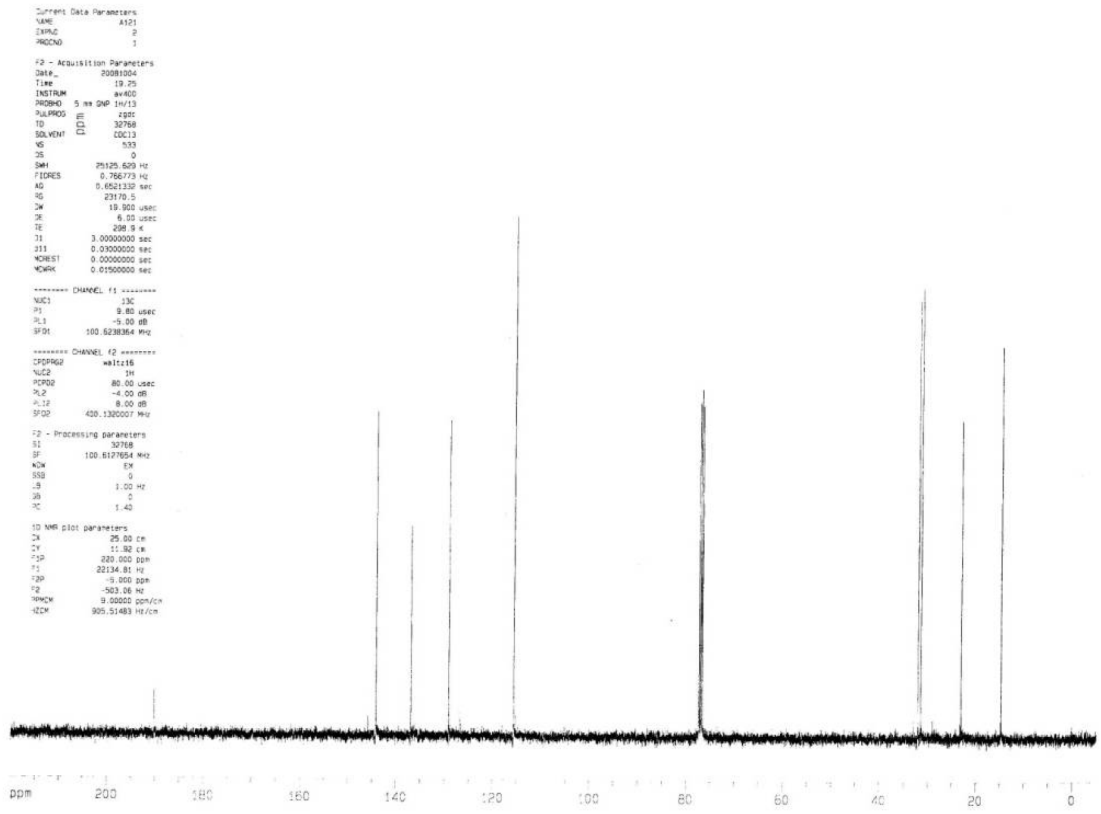
2.0096
1.0000
0.9846
2.1803
2.1905
9.1130
9
8
7
6
5
4
3
2
1
0

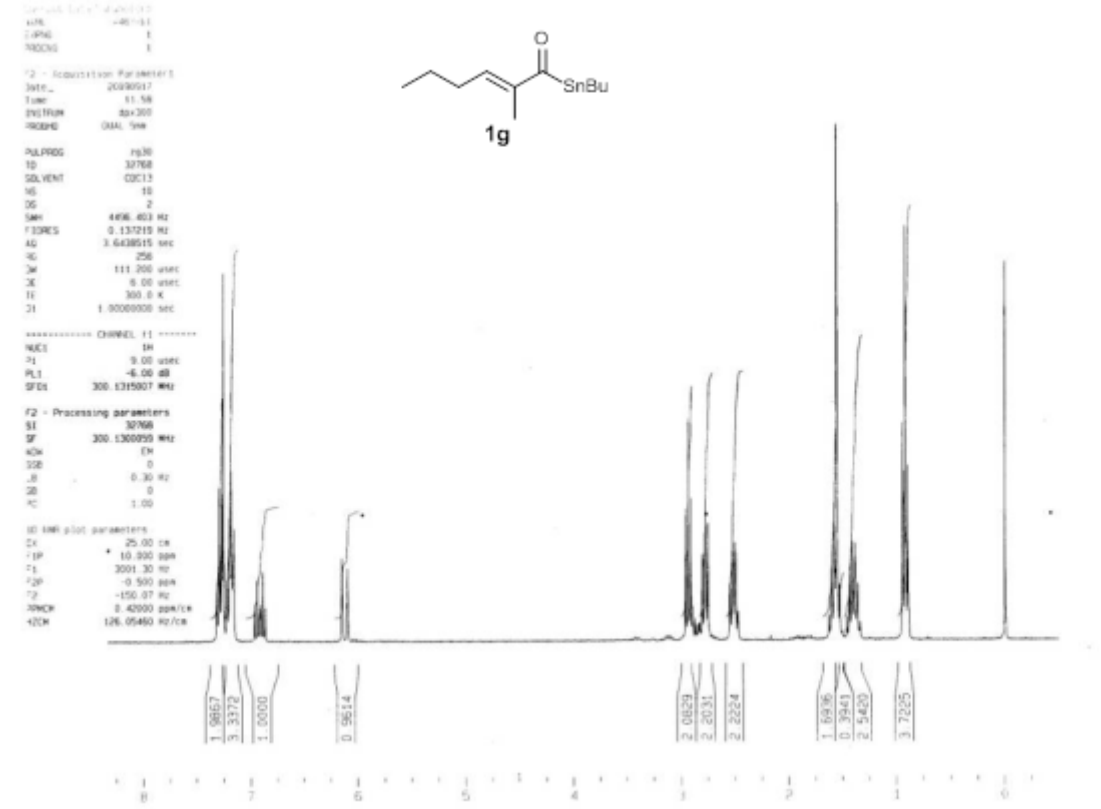

ppm
200
180
160
140
120
100
80
60
40
20
0

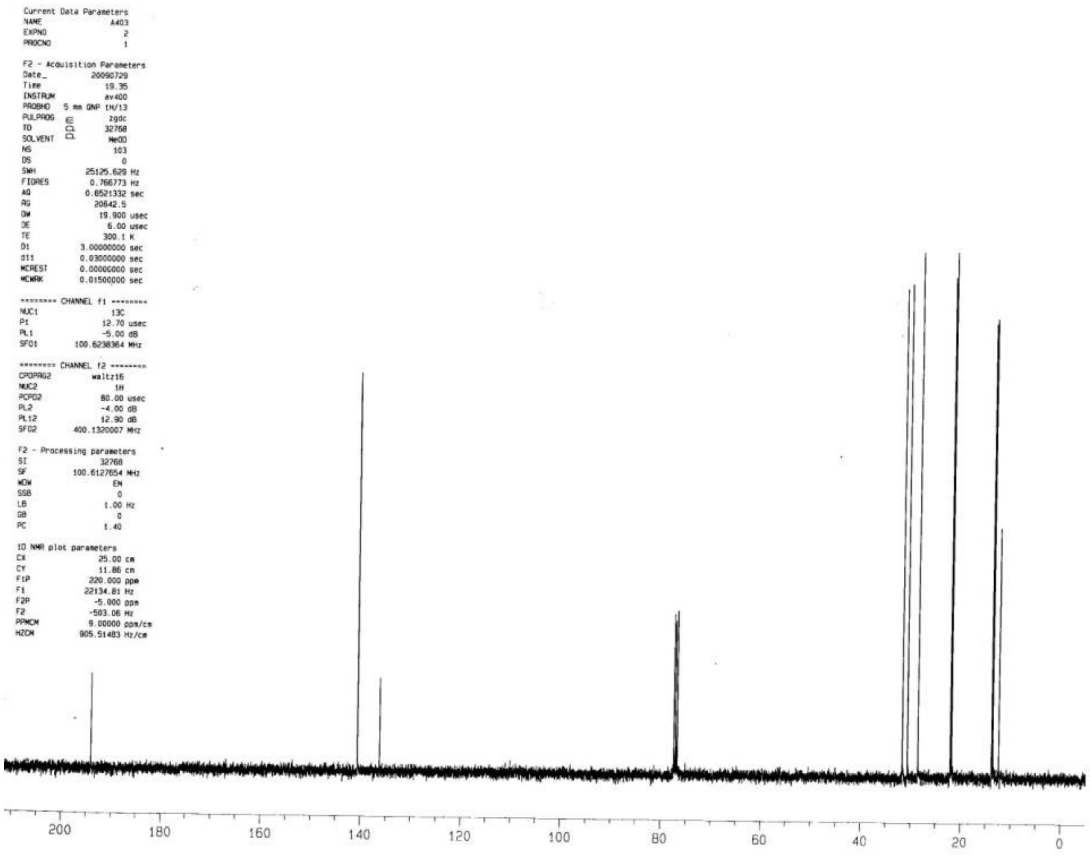

Ph
O
SPh
1e




SEt
1f


ppm
200
180
160
140
120
100
80
60
40
20
0


O
SnBu
1g
1.9857
3.3372
1.0000
0.9514
2.0829
2.2031
2.2224
1.6496
0.3941
2.5420
3.7225
8
7
6
5
4
3
2
1
0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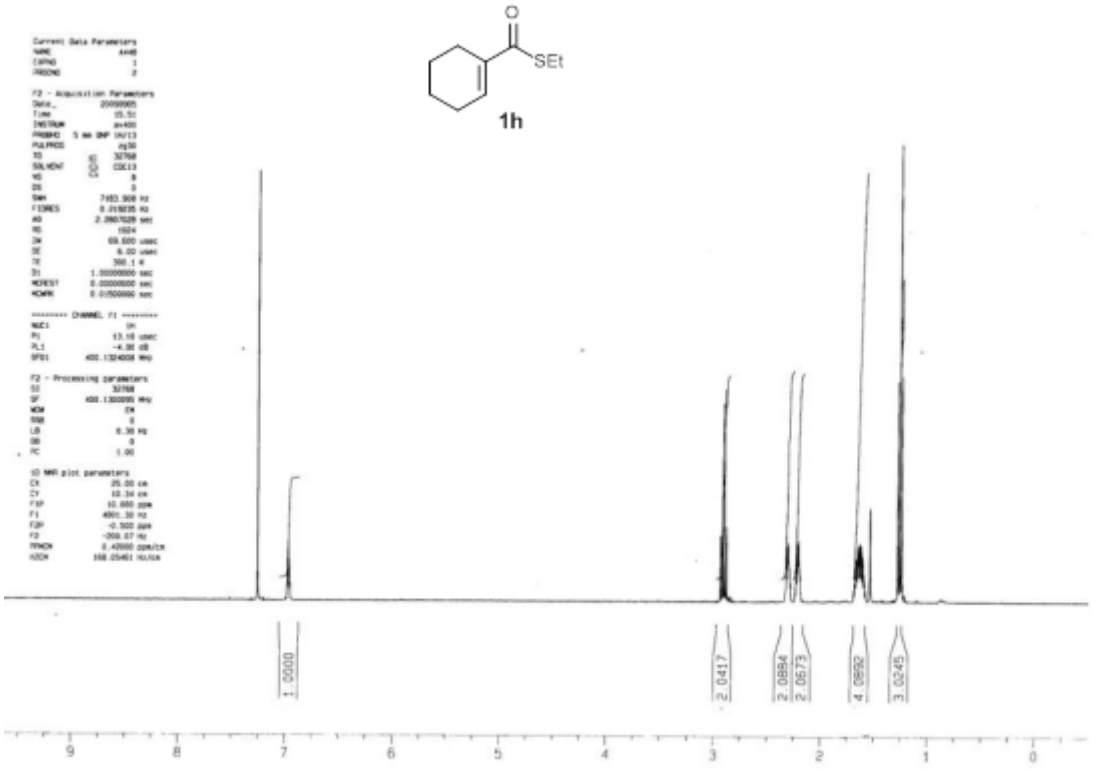
PULPROG zgdc
TD 32768
SOLVENT MeOD
NS 103
DS 0
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 20642.5
DW 19.900 usec
DE 6.00 usec
TE 300.1 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
-------- CHANNEL f1 --------
NUC1 13C
P1 12.70 usec
PL1 -5.00 dB
SFO1 100.6238364 MHz
-------- CHANNEL f2 --------
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.90 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127654 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 11.86 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 9.00000 ppm/cm
HZCM 905.51483 Hz/cm
ppm
200
180
160
140
120
100
80
60
40
20
0


O
SEt
1h
1.0000
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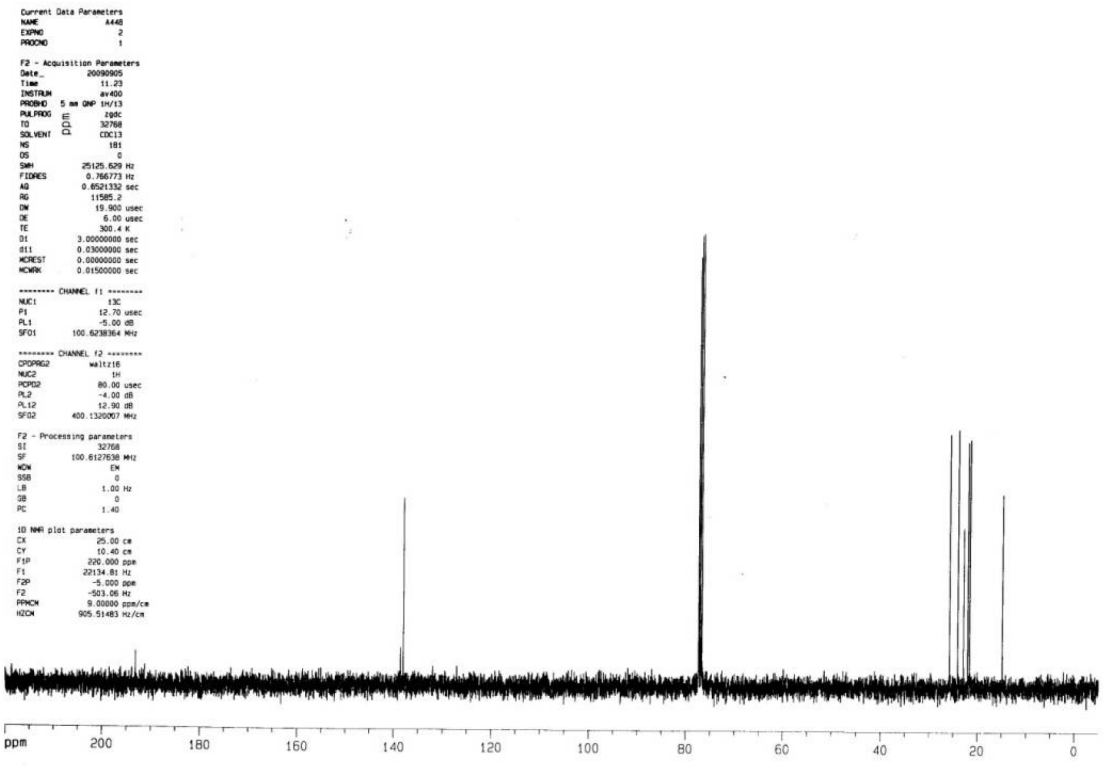
2.0894
2.0673
4.0692
3.0245
9
8
7
6
5
4
3
2
1
0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EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
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Time 11.23
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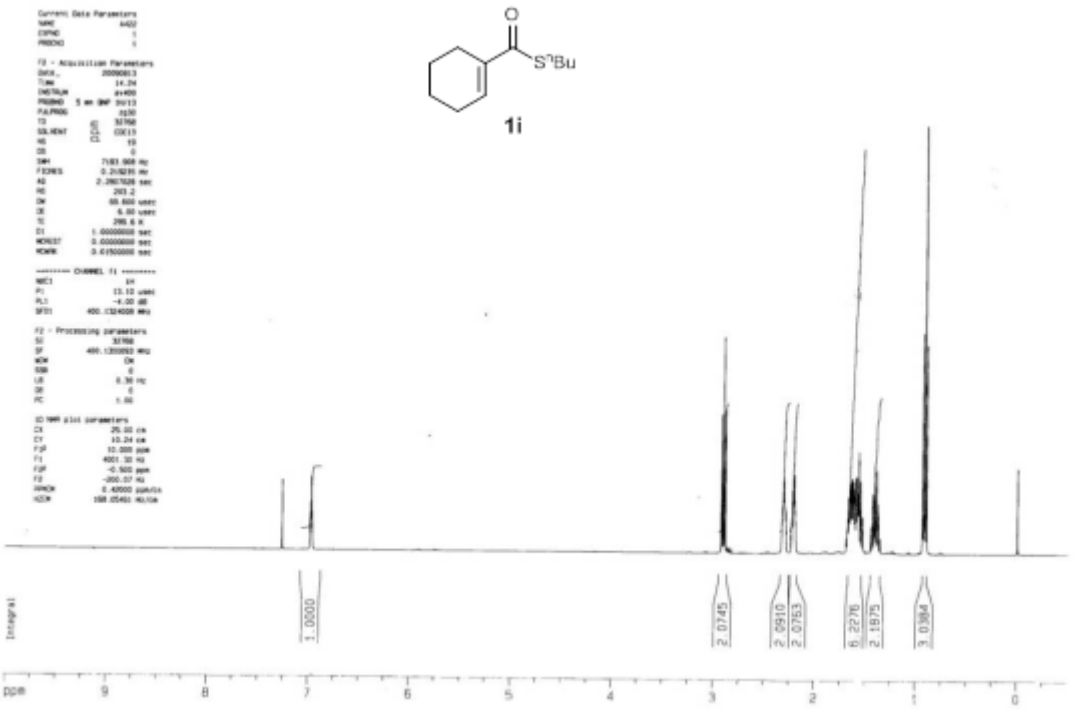
PROBHD 5 mm BNP 1H/13
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 181
DS 0
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 11585.2
DW 19.900 usec
DE 6.00 usec
TE 300.4 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
-------- CHANNEL f1 --------
NUC1 13C
P1 12.70 usec
PL1 -5.00 dB
SFO1 100.6238364 MHz
-------- CHANNEL f2 --------
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.90 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127638 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 10.40 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 9.00000 ppm/cm
HZCM 905.51483 Hz/cm
ppm
200
180
160
140
120
100
80
60
40
20
0


O
S^{t}Bu
1i
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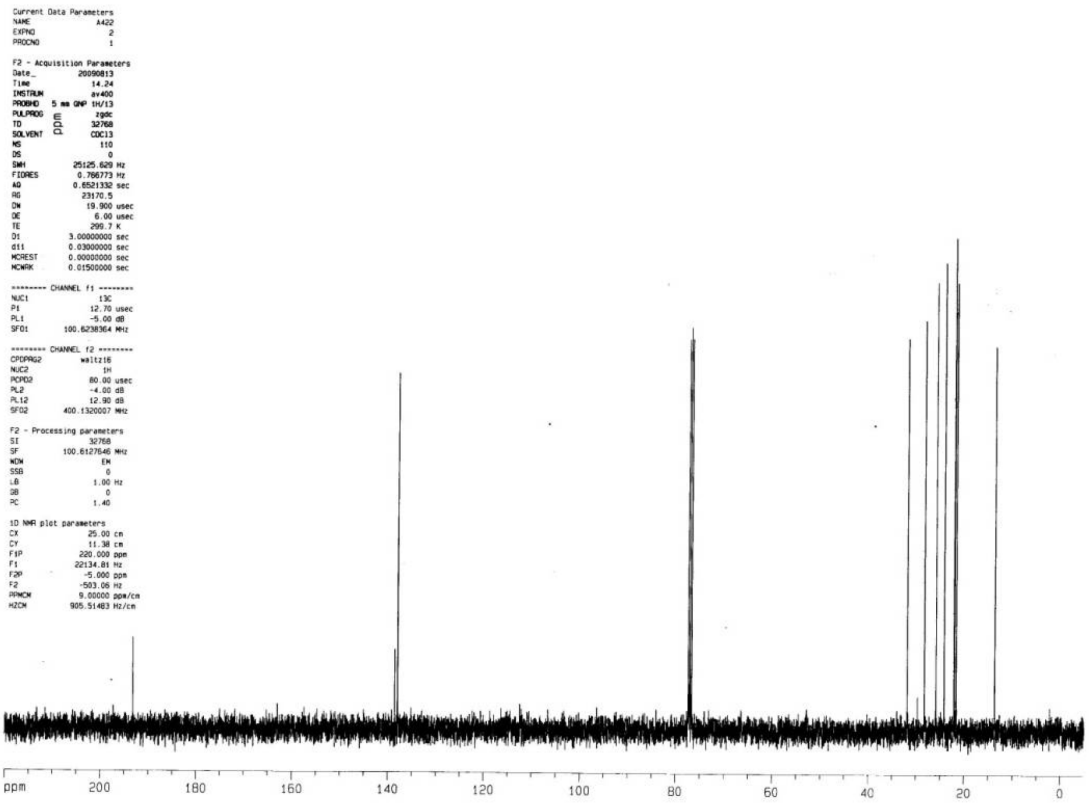
2.0745
2.0910
2.0763
6.2276
2.1875
3.0964
ppm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PROCNO 1
F2 - Acquisition Parameters
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Time 14.24
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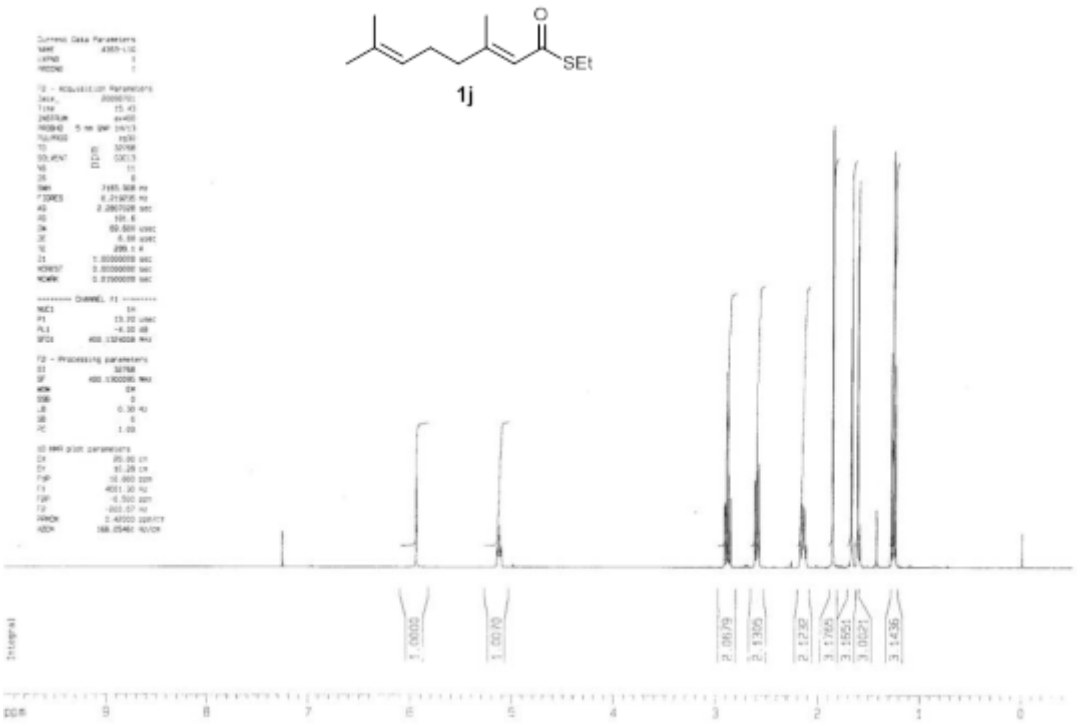
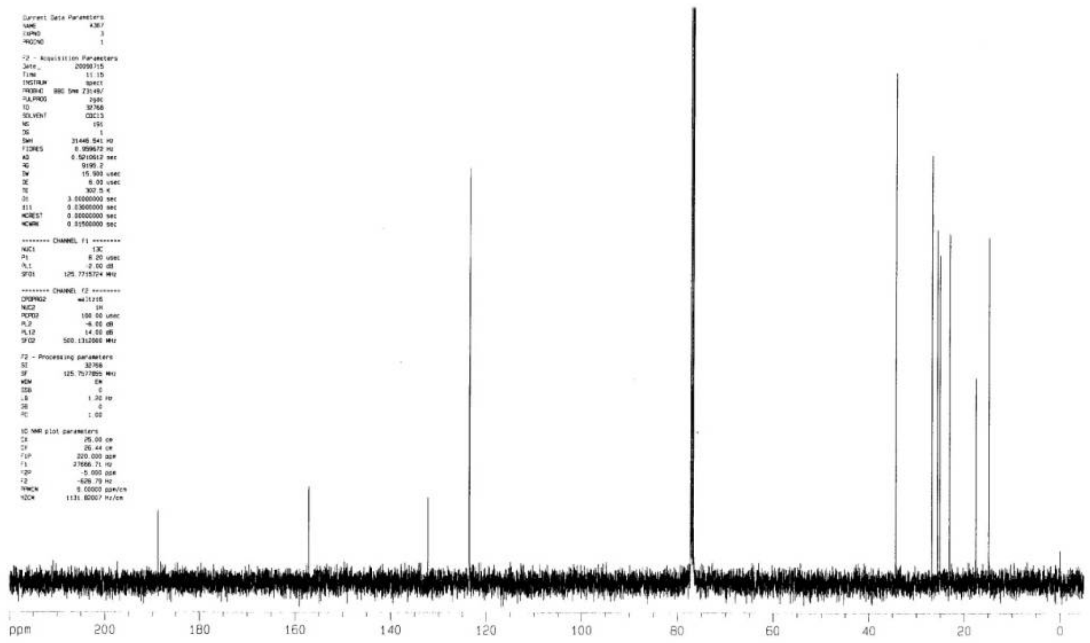
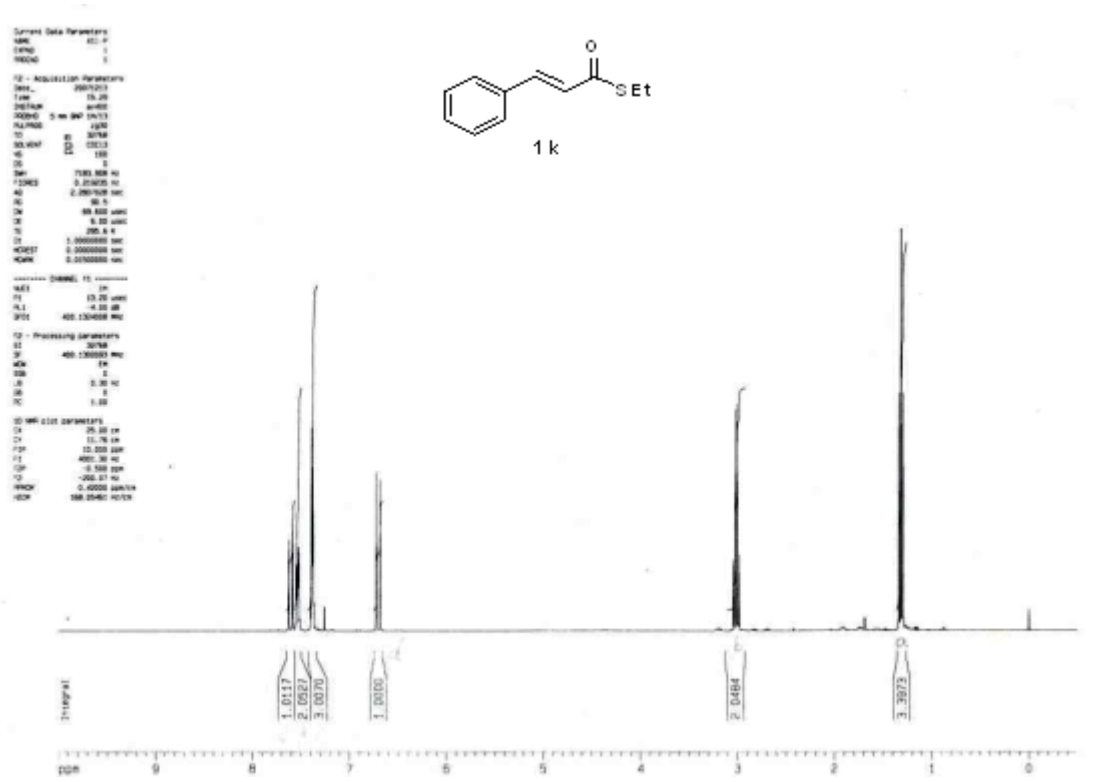
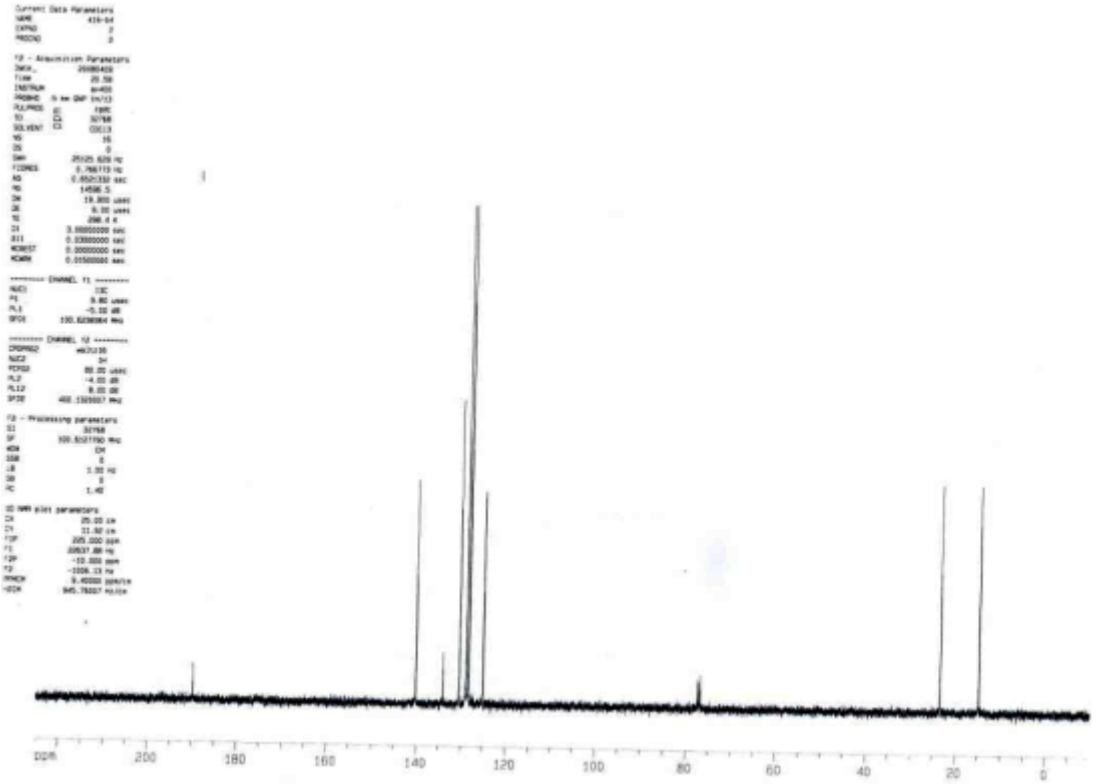
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 110
DS 0
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 23170.5
DW 19.900 usec
DE 6.00 usec
TE 299.7 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
-------- CHANNEL f1 --------
NUC1 13C
P1 12.70 usec
PL1 -5.00 dB
SF01 100.6238364 MHz
-------- CHANNEL f2 --------
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.90 dB
SF02 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127646 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 11.38 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 9.00000 ppm/cm
HZCM 905.51483 Hz/cm
ppm

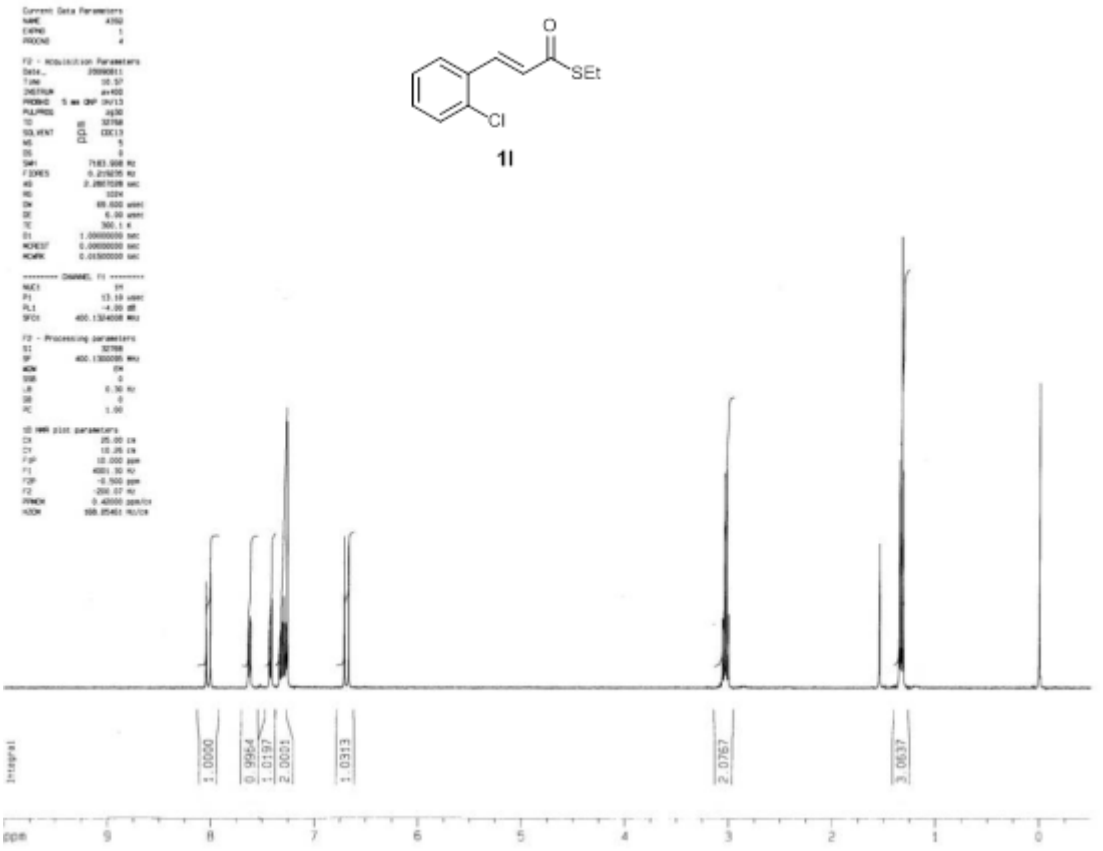


1j





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SEt
Cl
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Integral
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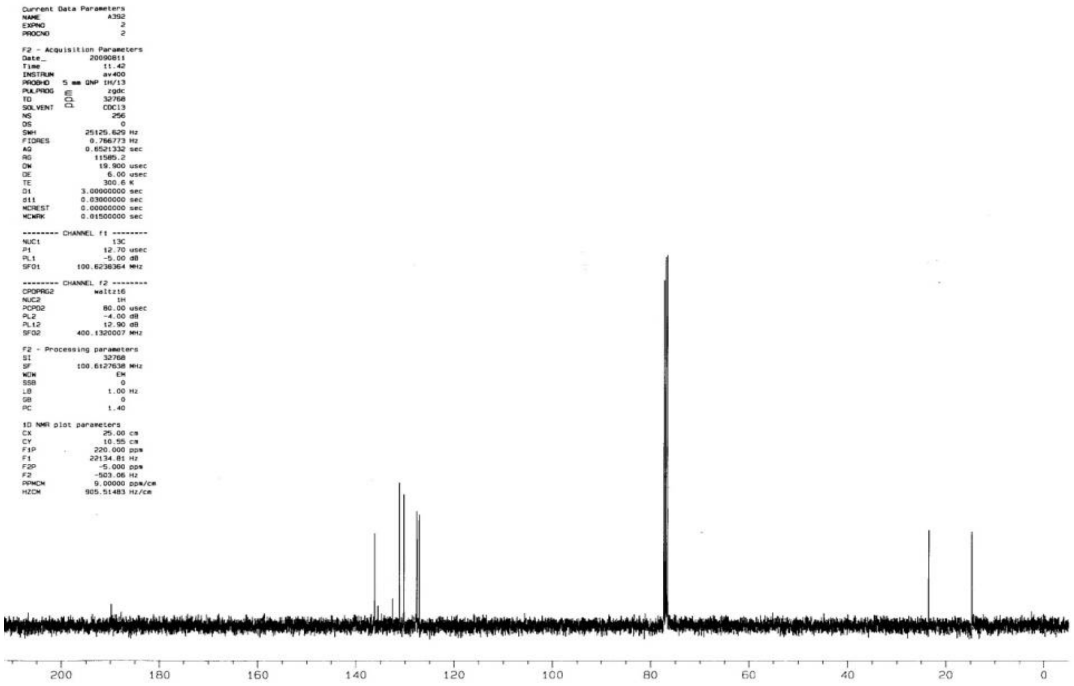
2.0001
1.0313
2.0767
3.0637
ppm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PROCNO 2
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Time 11.42
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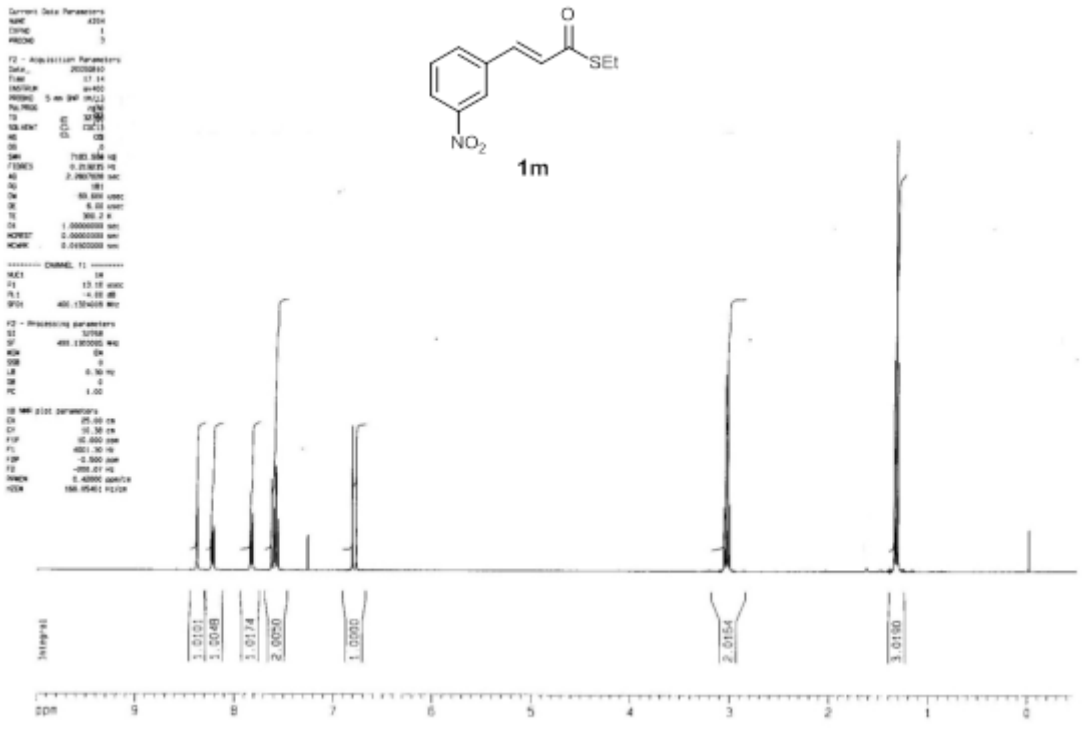
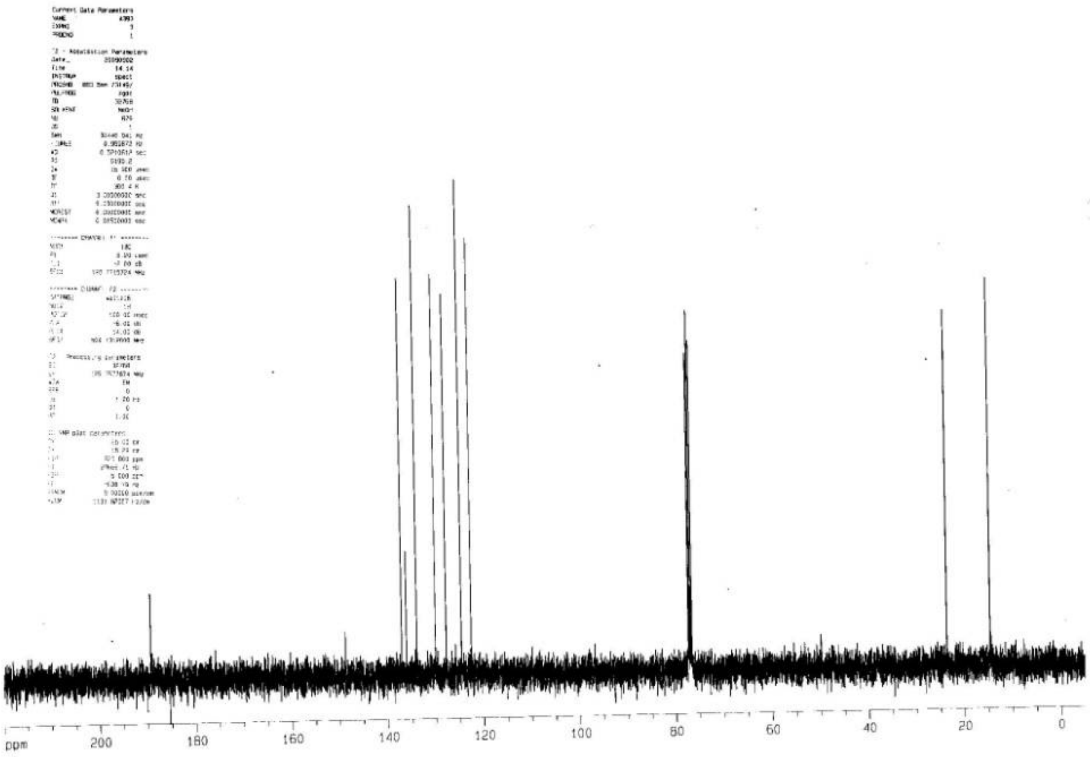
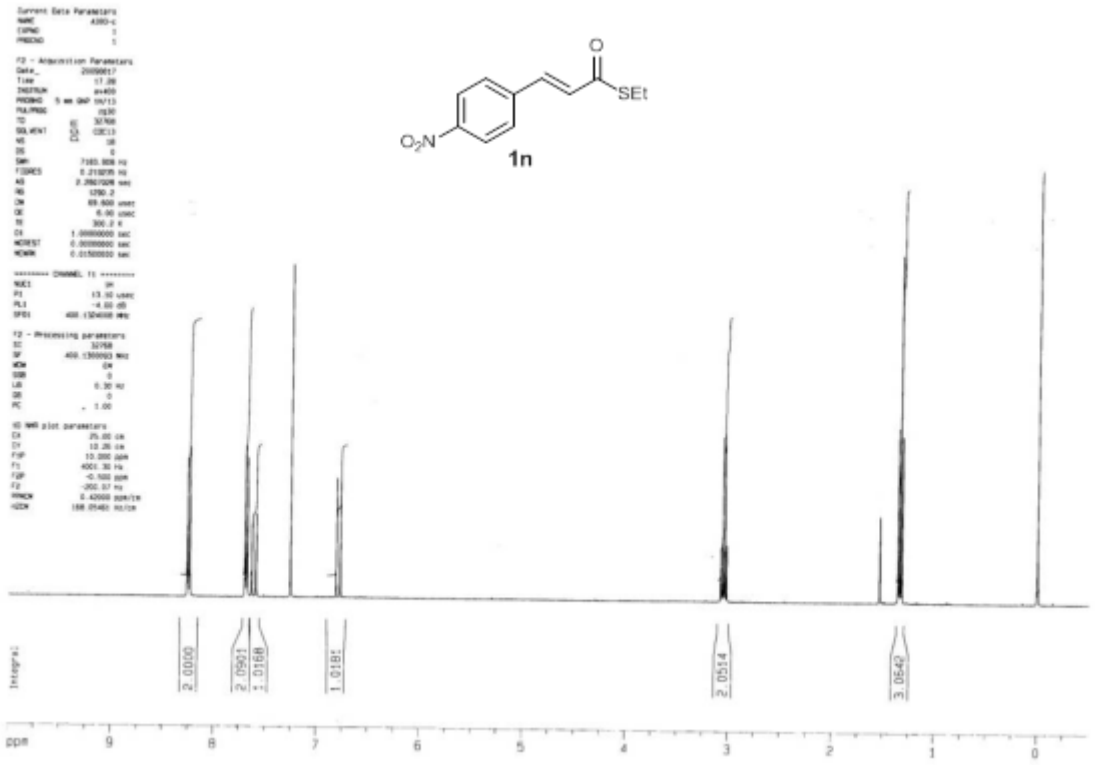
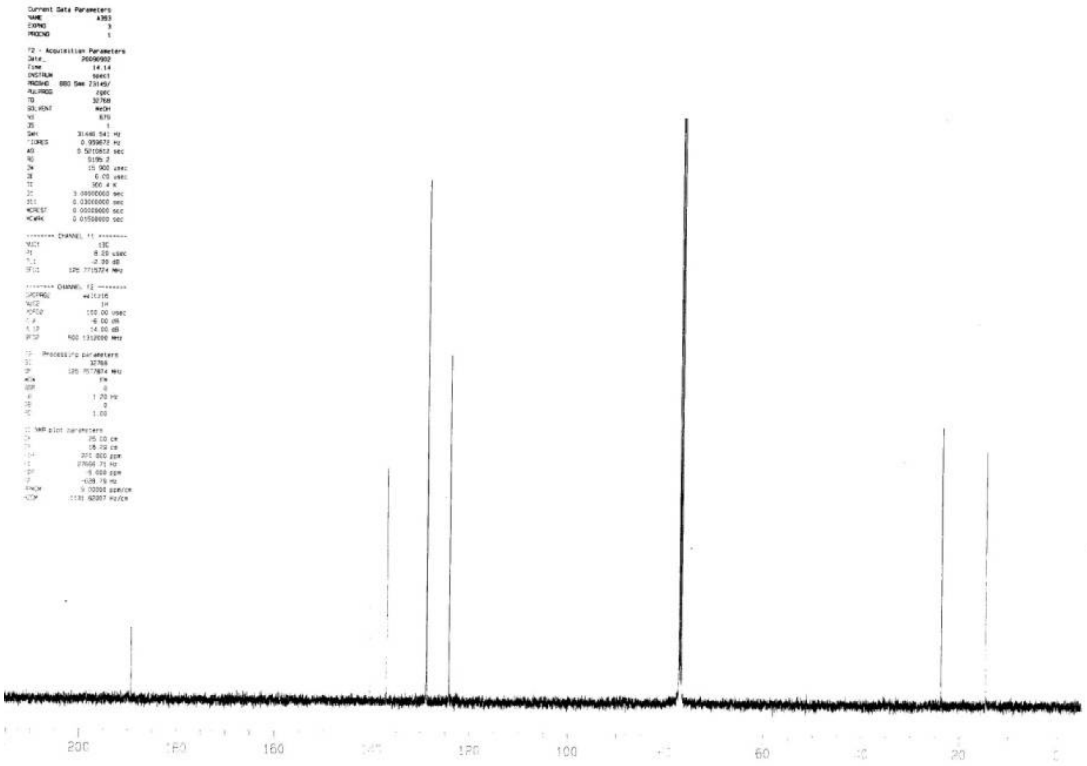
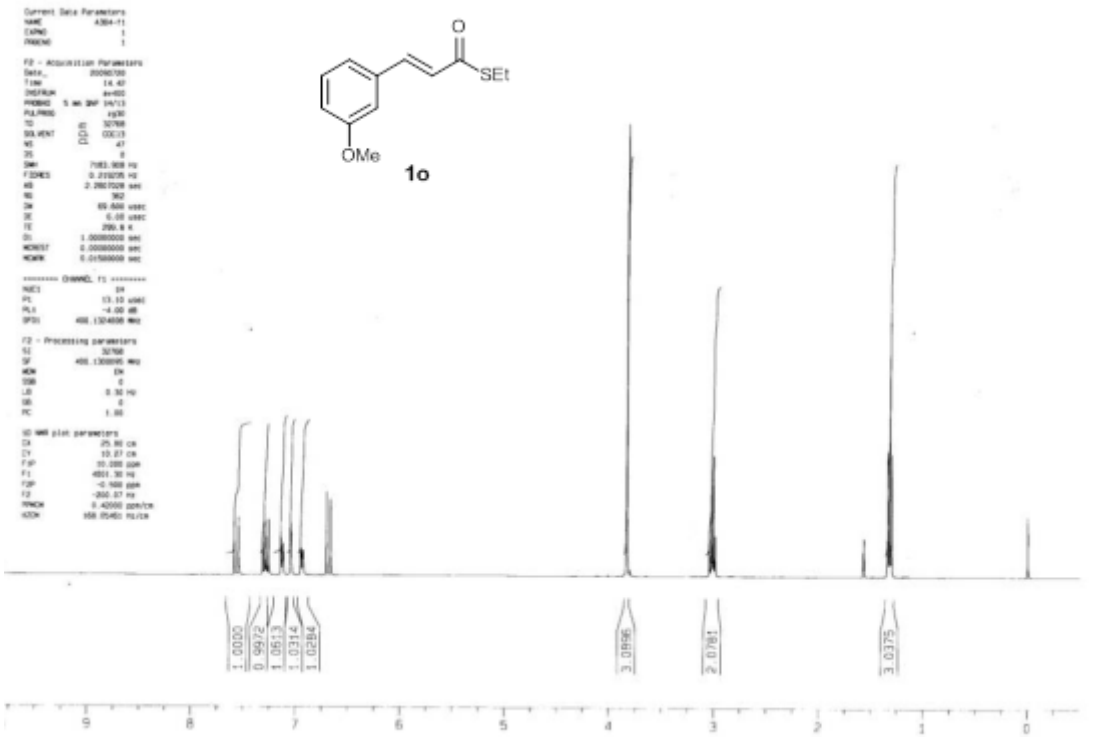
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 256
DS 0
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 11585.2
DW 19.900 usec
DE 6.00 usec
TE 300.6 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
-------- CHANNEL f1 --------
NUC1 13C
P1 12.70 usec
PL1 -5.00 dB
SFO1 100.6238364 MHz
-------- CHANNEL f2 --------
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.90 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127638 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 10.55 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 9.00000 ppm/cm
HZCM 905.51483 Hz/cm
200
180
160
140
120
100
80
60
40
20
0

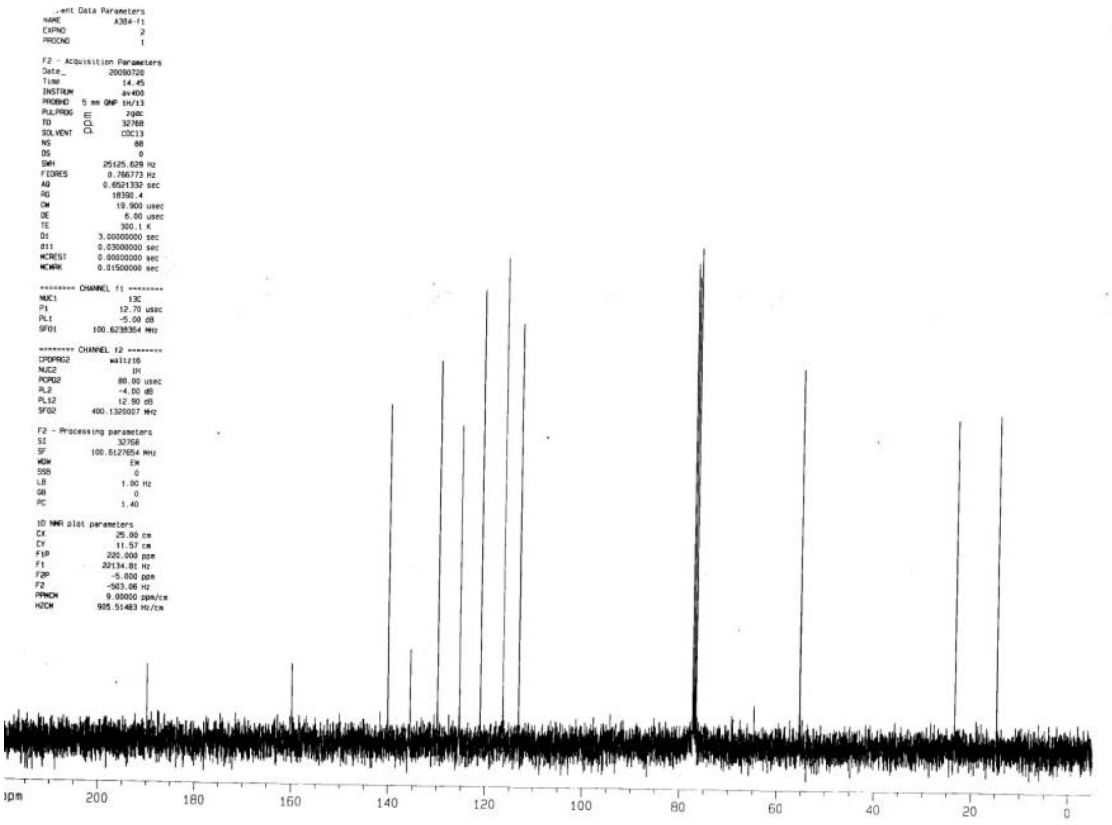

O
SEt
NO2
1m
Integral
1.0101
1.0048
1.0174
2.0050
1.0000
2.0154
3.0190
ppm
9
8
7
6
5
4
3
2
1
0


ppm
200
180
160
140
120
100
80
60
40
20
0






O
SEt
OMe
1o
1.0000
0.9972
1.0613
1.0314
1.0284
3.0896
2.0781
3.0375
9
8
7
6
5
4
3
2
1
0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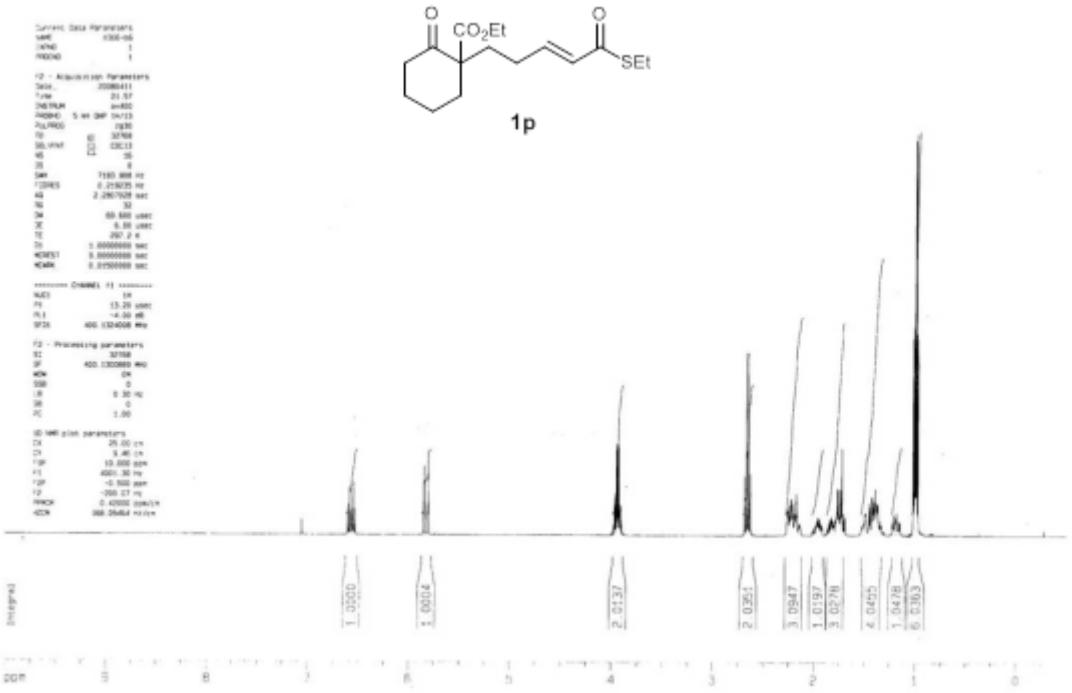
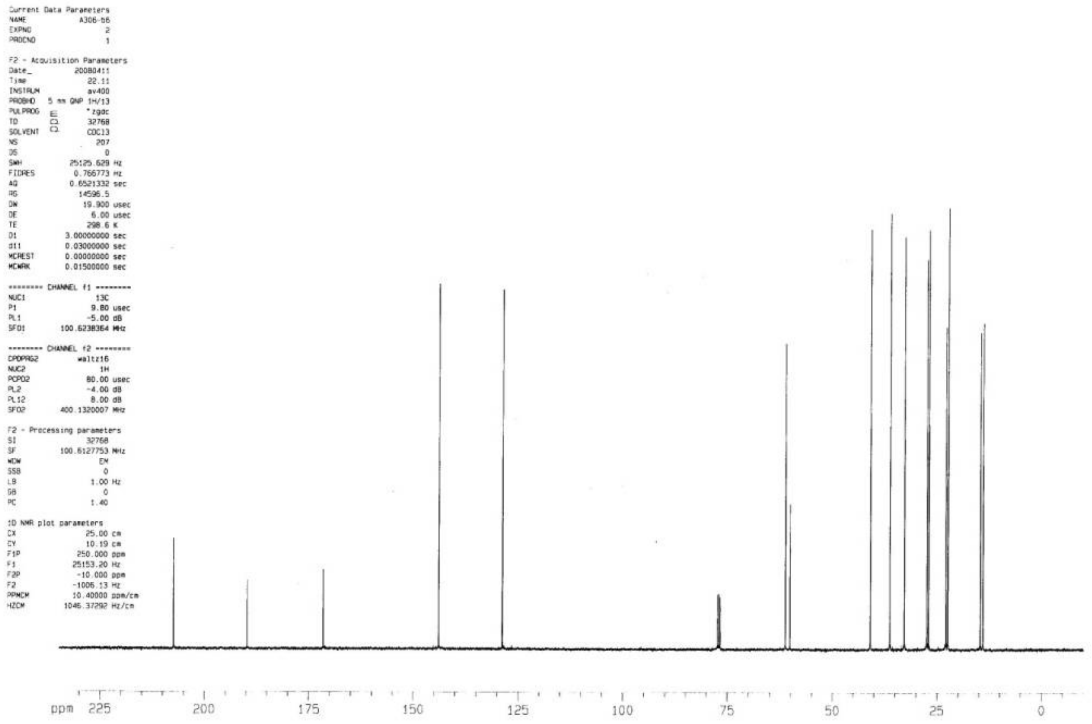
200
180
160
140
120
100
80
60
40
20
0


CO2Et
SEt
1p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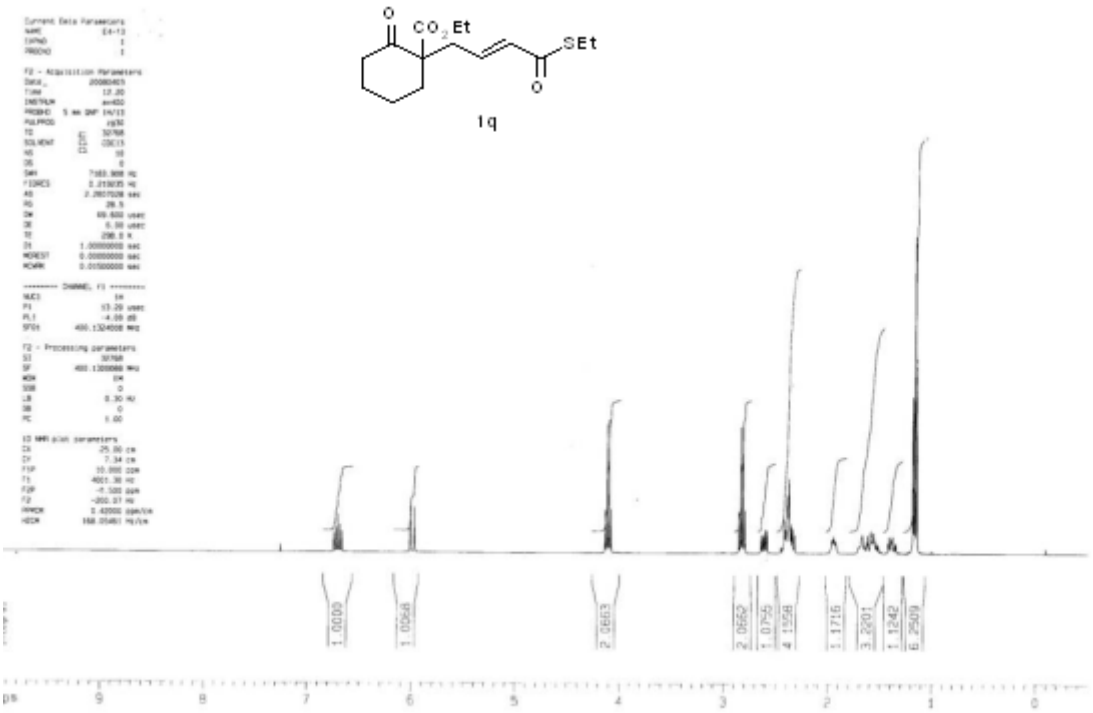
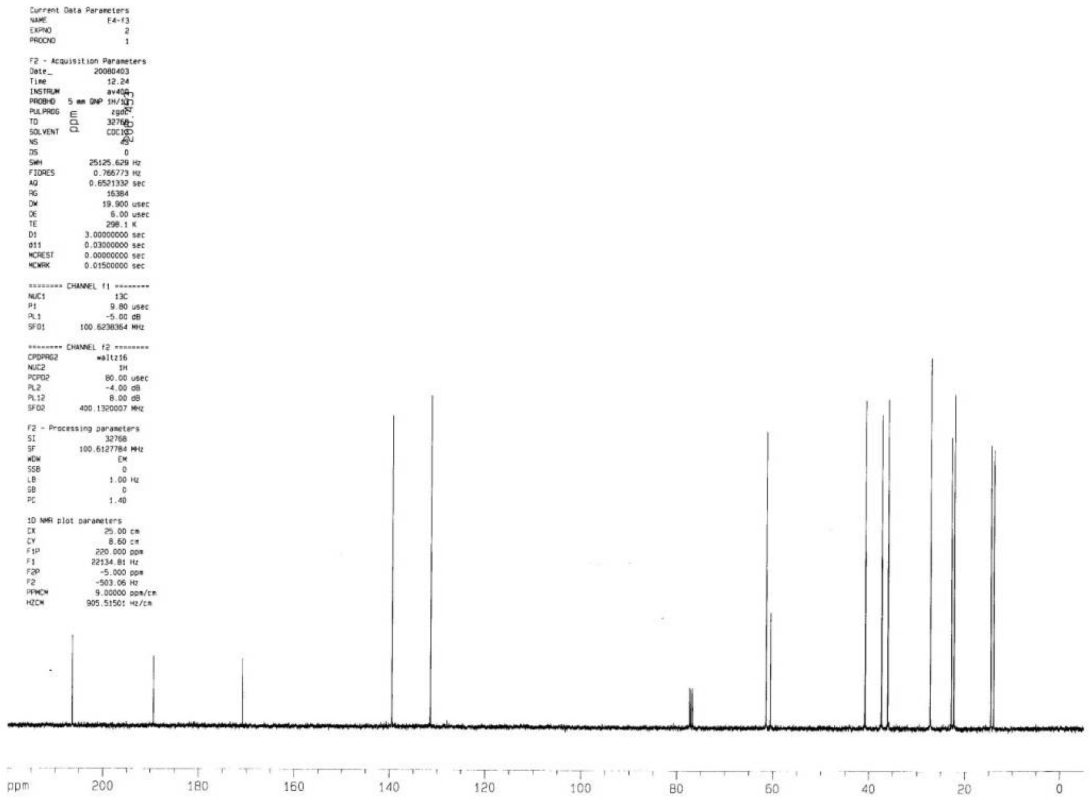
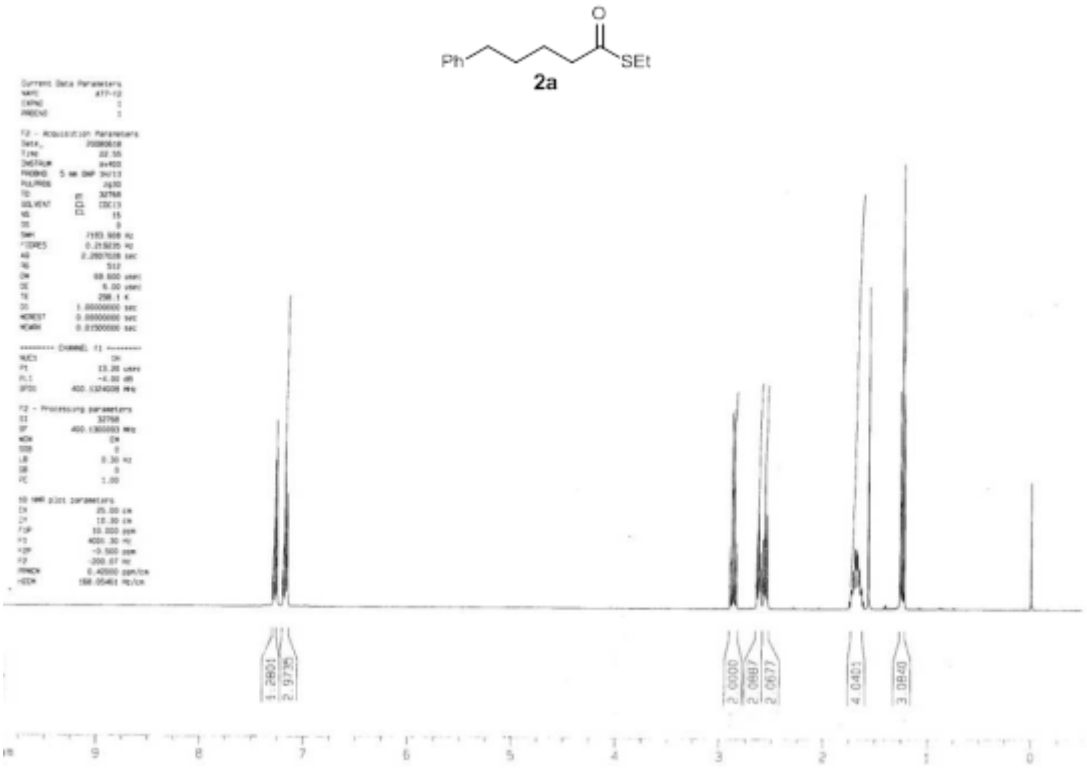
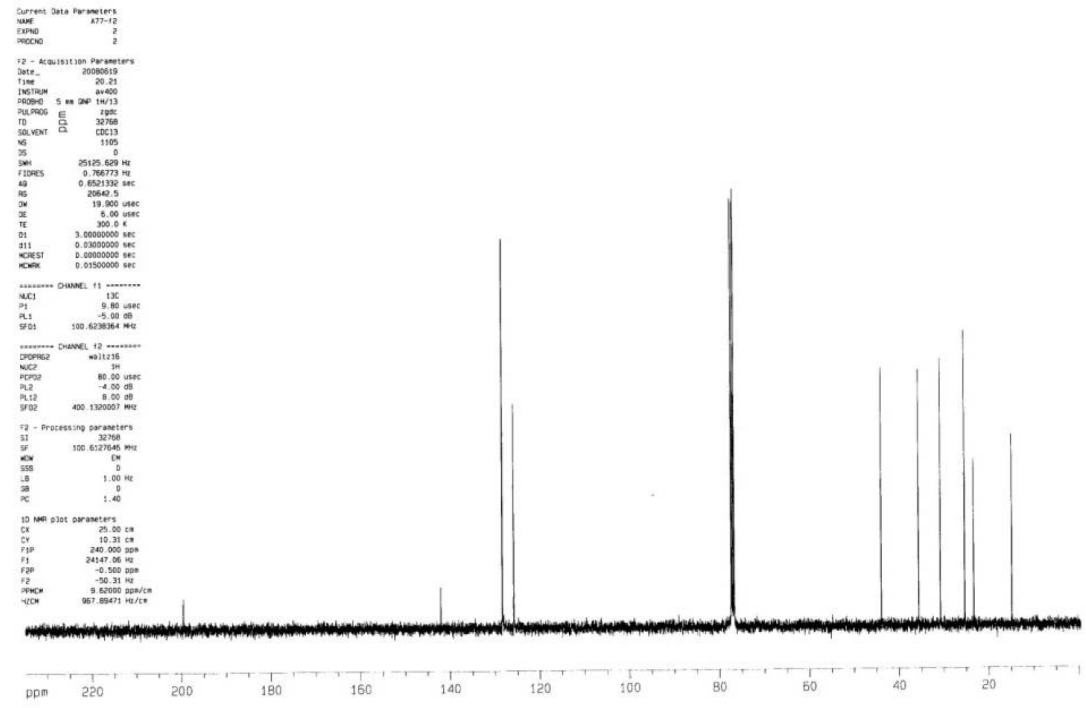
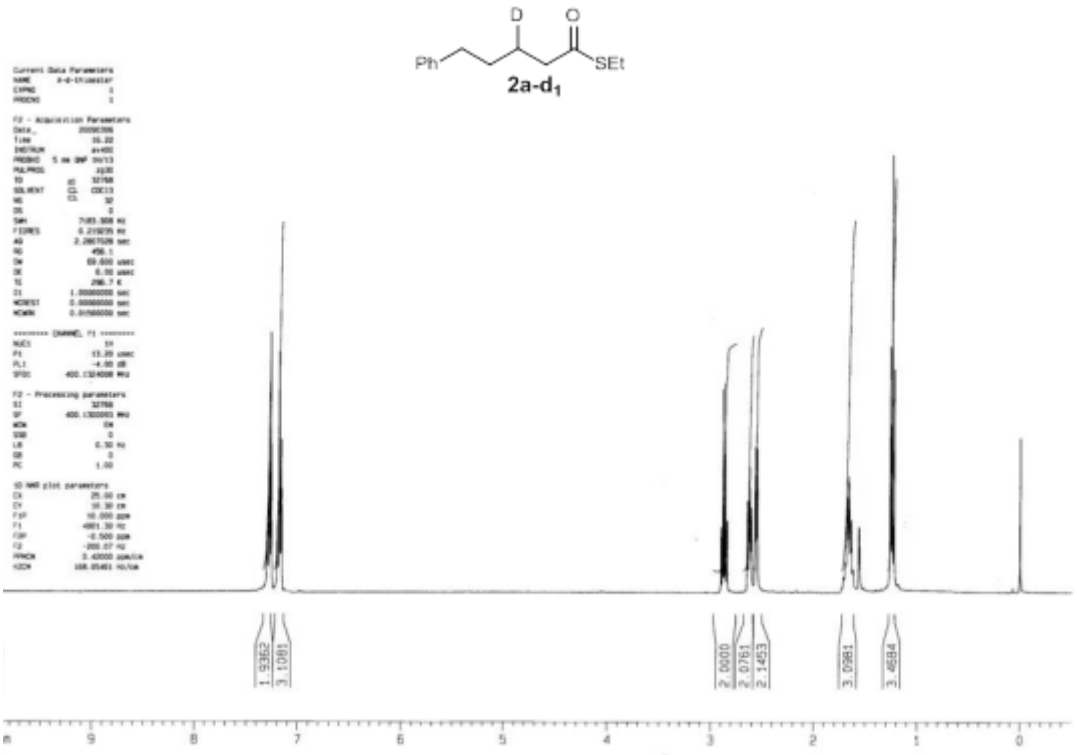
200
175
150
125
100
75
50
25
0

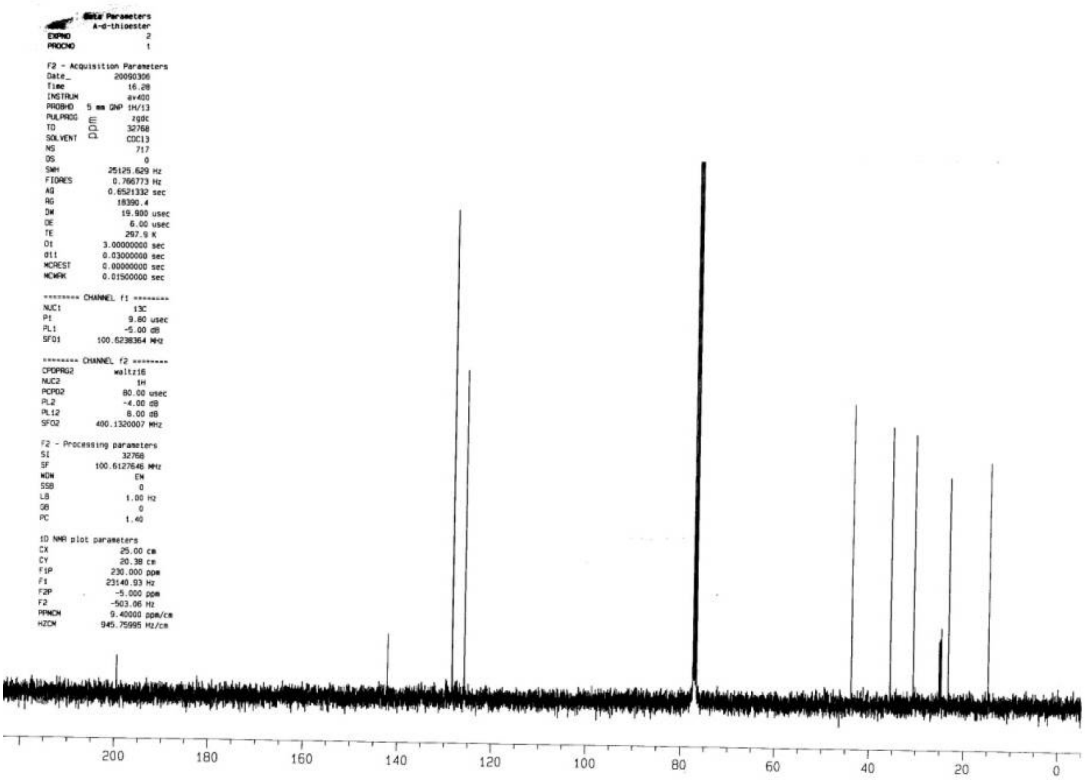

O
CO2Et
SEt
O
1q
1.0000
1.0068
2.2663
2.0662
1.0755
4.1958
1.1716
3.2201
1.1242
6.2949
ppm

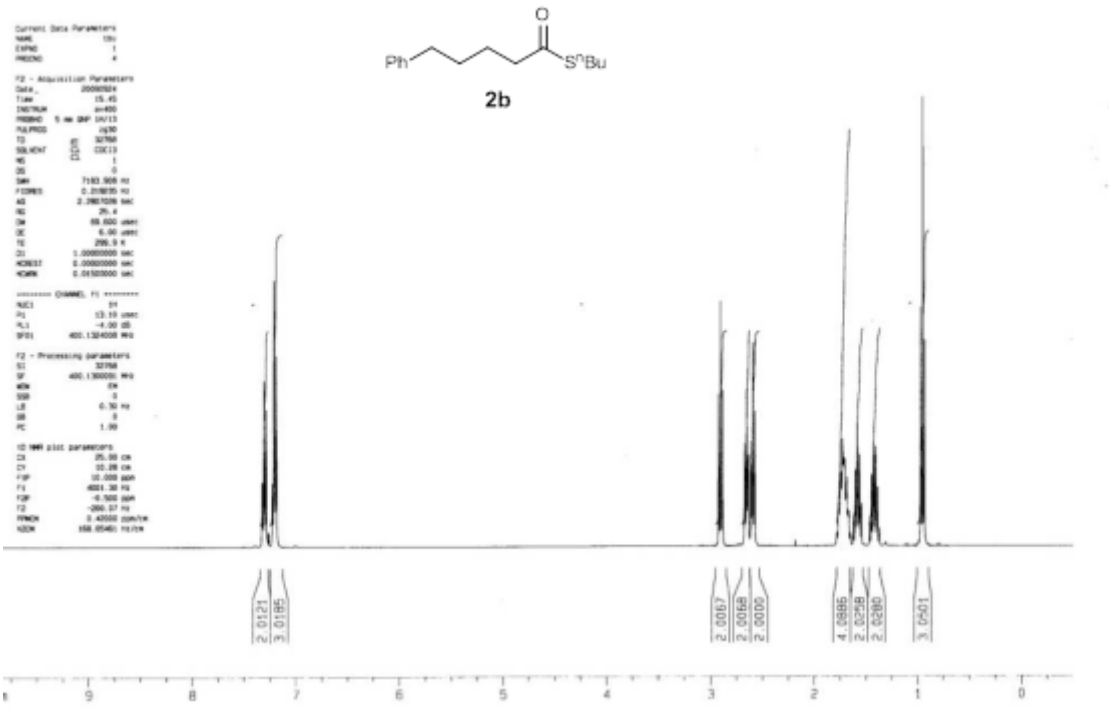

Current Data Parameters
NAME E4-f3
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080403
Time 12.24
INSTRUM av400
PROBHD 5 mm BNP 1H/13
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 256
DS 0
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.1 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.80 usec
PL1 -5.00 dB
SFO1 100.6238364 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 8.00 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127784 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 8.60 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 9.00000 ppm/cm
HZCM 905.5150t Hz/cm
ppm
200
180
160
140
120
100
80
60
40
20
0

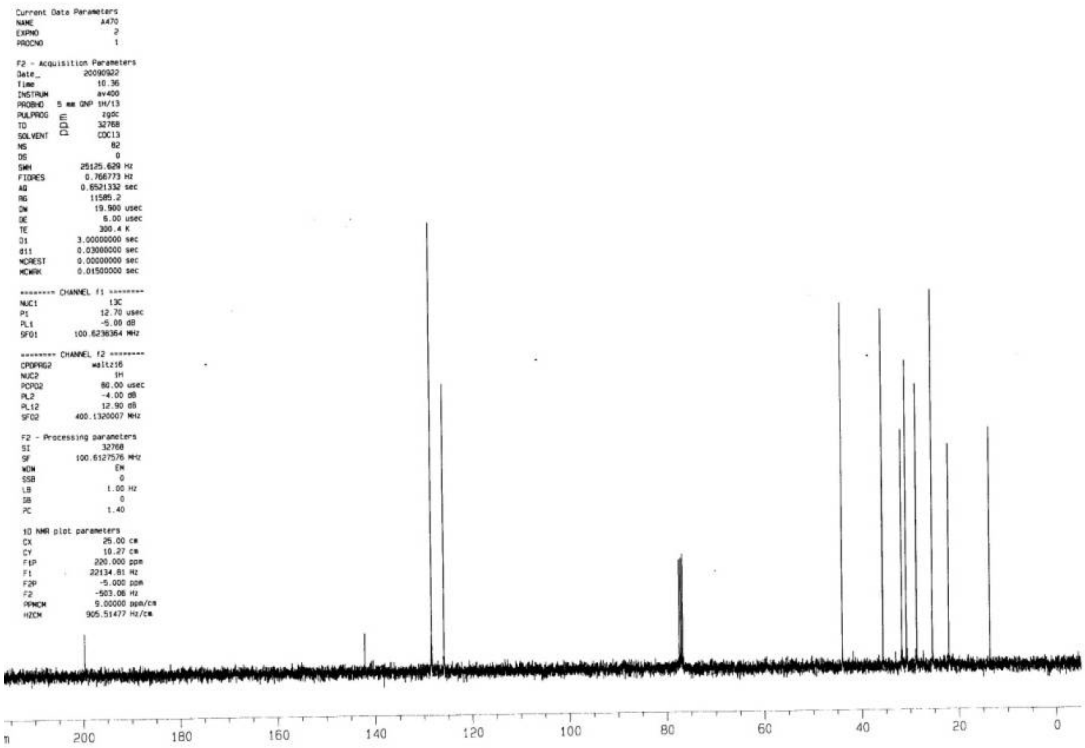

Ph
SEt
O
2a
1.2861
2.9735
2.0000
2.0987
2.0677
4.0461
3.0840

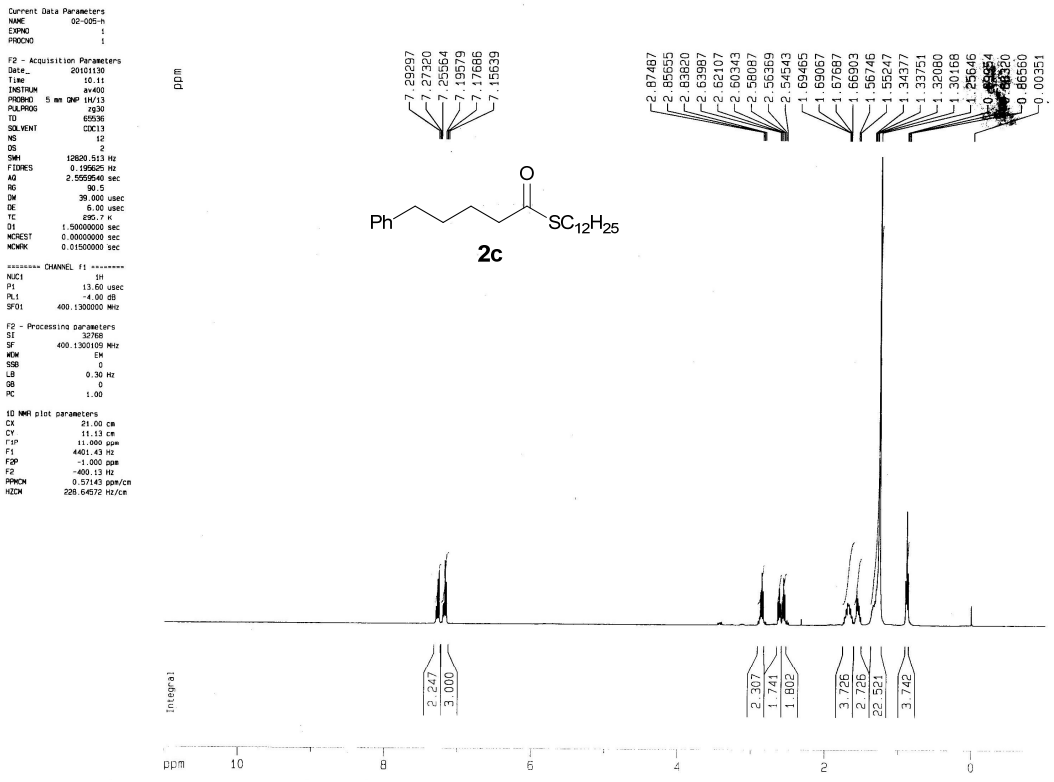

Current Data Parameters
NAME A77-f2
EXPNO 2
PROCNO 2
F2 - Acquisition Parameters
Date_ 20080619
Time 20.21
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpc
TD 32768
SOLVENT CDCl3
NS 1105
DS 0
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 20642.5
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
-------- CHANNEL f1 --------
NUC1 13C
P1 9.80 usec
PL1 -5.00 dB
SFO1 100.6238364 MHz
-------- CHANNEL f2 --------
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 8.00 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127646 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 10.31 cm
F1P 240.000 ppm
F1 24147.06 Hz
F2P -0.500 ppm
F2 -50.31 Hz
PPMCM 9.62000 ppm/cm
HZCM 967.89471 Hz/cm
ppm
220
200
180
160
140
120
100
80
60
40
20

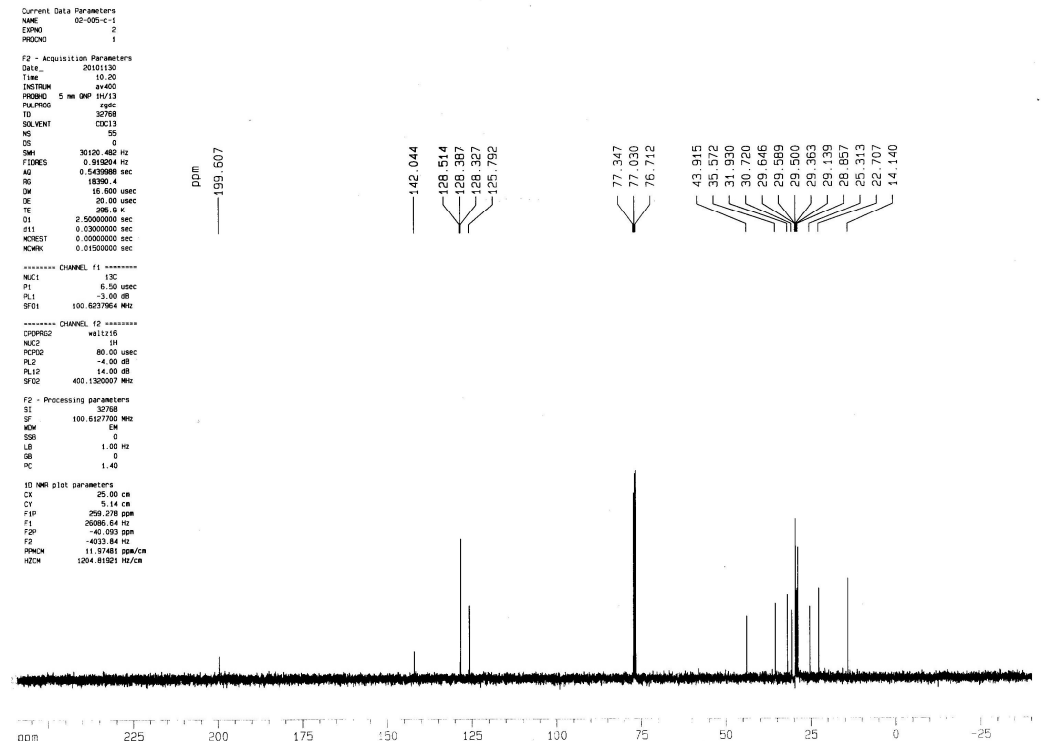

D
O
Ph
SEt
2a-d1
1.9362
3.1081
2.0000
2.0761
2.1453
3.0981
3.4684

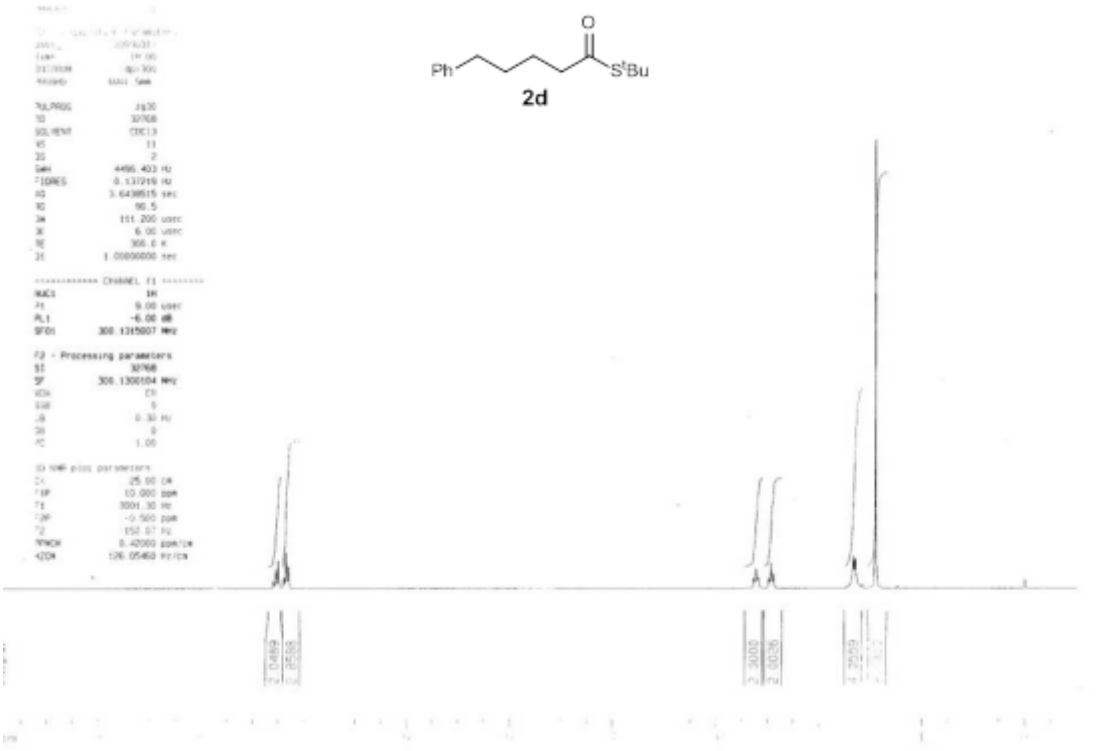

Data Parameters
A-d-thioester
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090306
Time 16.28
INSTRUM av400
PROBHD 5 mm DNP 1H/13
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 717
DS 0
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 18390.4
DW 19.900 usec
DE 6.00 usec
TE 297.9 K
D1 3.00000000 sec
D11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 9.80 usec
PL1 -5.00 dB
SFO1 100.5238364 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 8.00 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127646 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 20.38 cm
F1P 230.000 ppm
F1 23140.93 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 9.40000 ppm/cm
HZCM 945.75995 Hz/cm
ppm

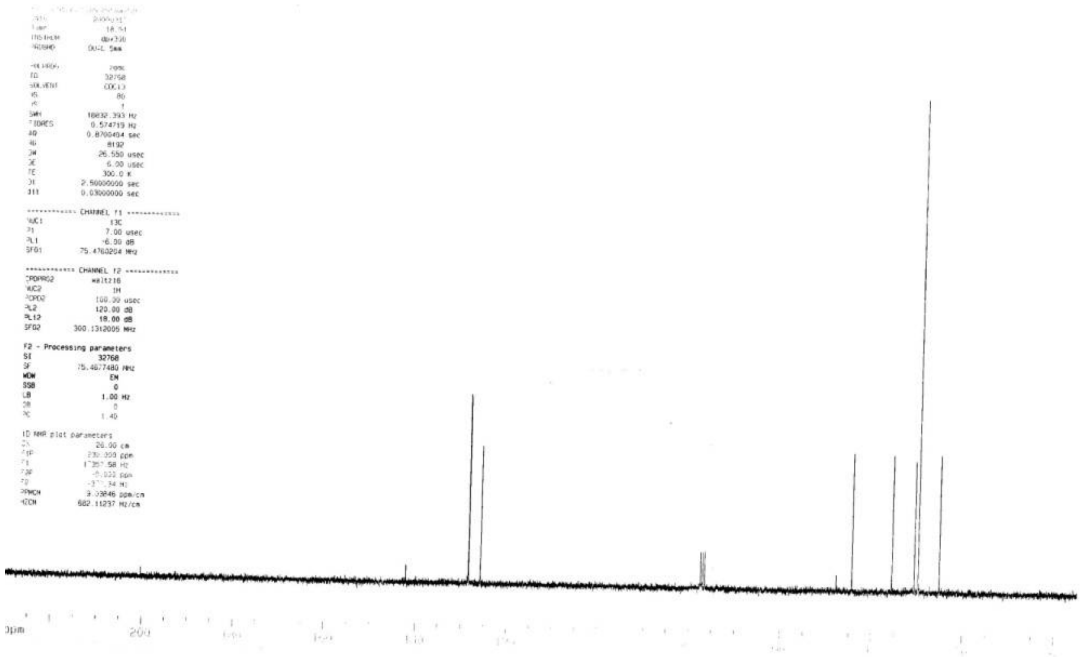

Ph
S^nBu
2b
2.0121
3.0185
2.0067
2.0068
2.0000
4.0886
2.0258
2.0200
3.0401

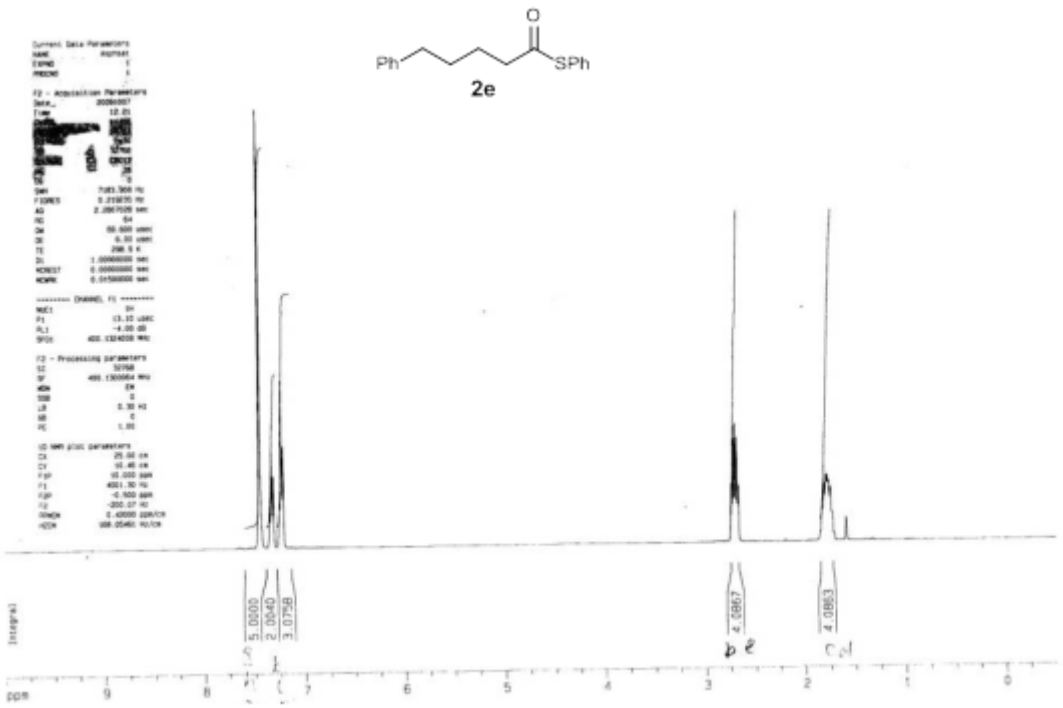

Current Data Parameters
NAME x470
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090922
Time 10.36
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 82
DS 0
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 11585.2
DW 19.900 usec
DE 6.00 usec
TE 300.4 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 12.70 usec
PL1 -5.00 dB
SF01 100.6236364 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.90 dB
SF02 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127576 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 10.27 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 9.00000 ppm/cm
HZCM 905.51477 Hz/cm

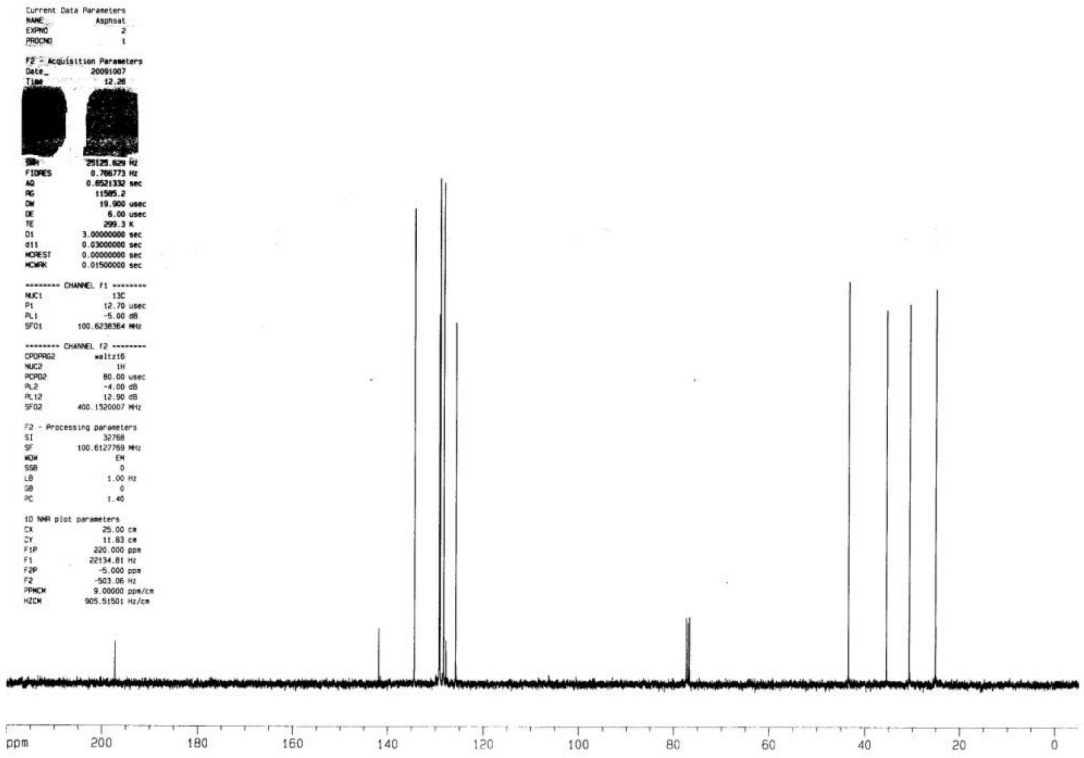

Current Data Parameters
NAME 02-005-h
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101130
Time 10.11
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 12
DS 2
SWH 12820.513 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 90.5
DW 39.000 usec
DE 6.00 usec
TE 295.7 K
D1 1.50000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -4.00 dB
SFO1 400.1300000 MHz
F2 - Processing parameters
SI 32768
SF 400.1300109 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 21.00 cm
CY 11.13 cm
F1P 11.000 ppm
F1 4401.43 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.57143 ppm/cm
HZCM 228.64572 Hz/cm
ppm
7.29297
7.27320
7.25564
7.19579
7.17686
7.15639
2.87487
2.85655
2.83820
2.63987
2.62107
2.60343
2.58087
2.56369
2.54543
1.69465
1.69067
1.67687
1.66903
1.56746
1.55247
1.34377
1.33751
1.32080
1.30168
1.25646
0.88320
0.86560
0.00351
O
Ph
SC12H25
2c
Integral
2.247
3.000
2.307
1.741
1.802
3.726
2.726
22.521
3.742
ppm
10
8
6
4
2
0

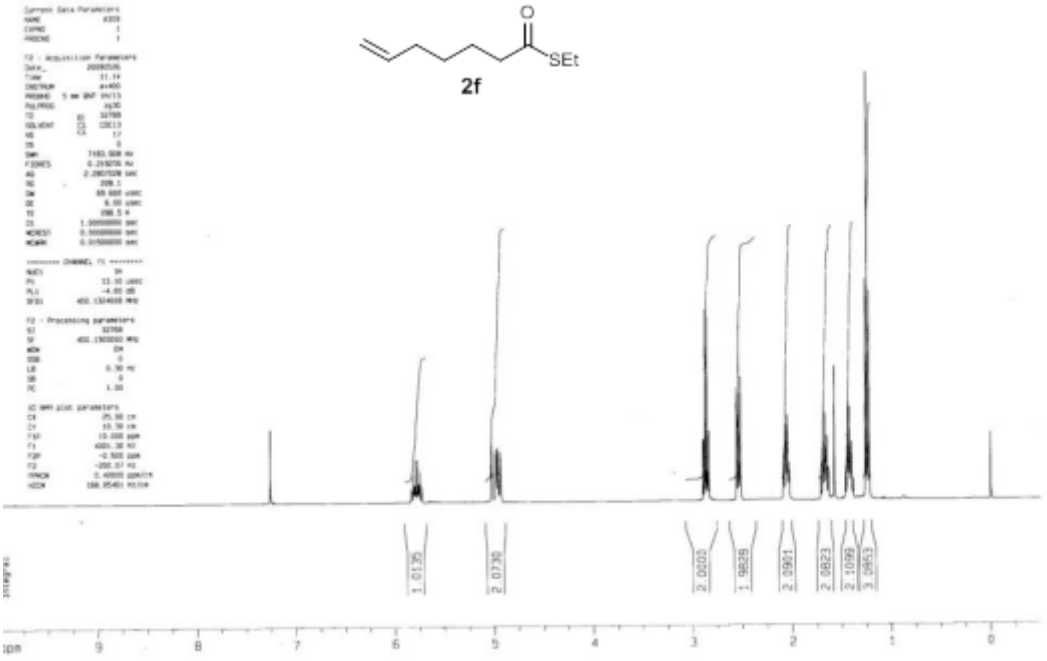

Current Data Parameters
NAME 02-005-c-1
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101130
Time 10.20
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 55
DS 0
SWH 30120.482 Hz
FIDRES 0.919204 Hz
AQ 0.5439988 sec
RG 18390.4
DW 16.600 usec
DE 20.00 usec
TE 295.6 K
D1 2.50000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 6.50 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.00 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 5.14 cm
F1P 259.278 ppm
F1 26086.64 Hz
F2P -40.093 ppm
F2 -4033.84 Hz
PPMCM 11.97481 ppm/cm
HZCM 1204.81921 Hz/cm
ppm
199.607
142.044
128.514
128.387
128.327
125.792
77.347
77.030
76.712
43.915
35.572
31.930
30.720
29.646
29.589
29.500
29.363
29.139
28.857
25.313
22.707
14.140
ppm
225
200
175
150
125
100
75
50
25
0
-25






Ph
SPh
O
2e
5.0000
2.0040
3.0758
4.0867
4.0863
ppm


Current Data Parameters
NAME Asphsat
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091007
Time 12.26
SW 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 11585.2
DW 19.900 usec
DE 6.00 usec
TE 299.3 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 12.70 usec
PL1 -5.00 dB
SFO1 100.6238364 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.90 dB
SFO2 400.1520007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127769 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 11.83 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 9.00000 ppm/cm
HZCM 905.51501 Hz/cm
ppm


O
SEt
2f
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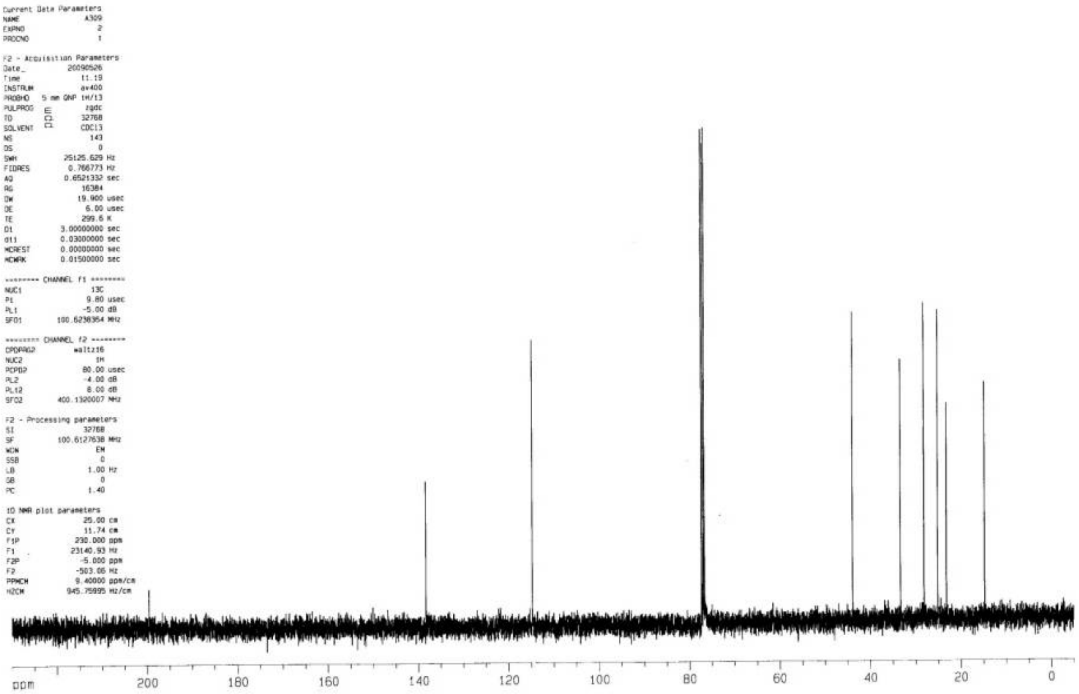
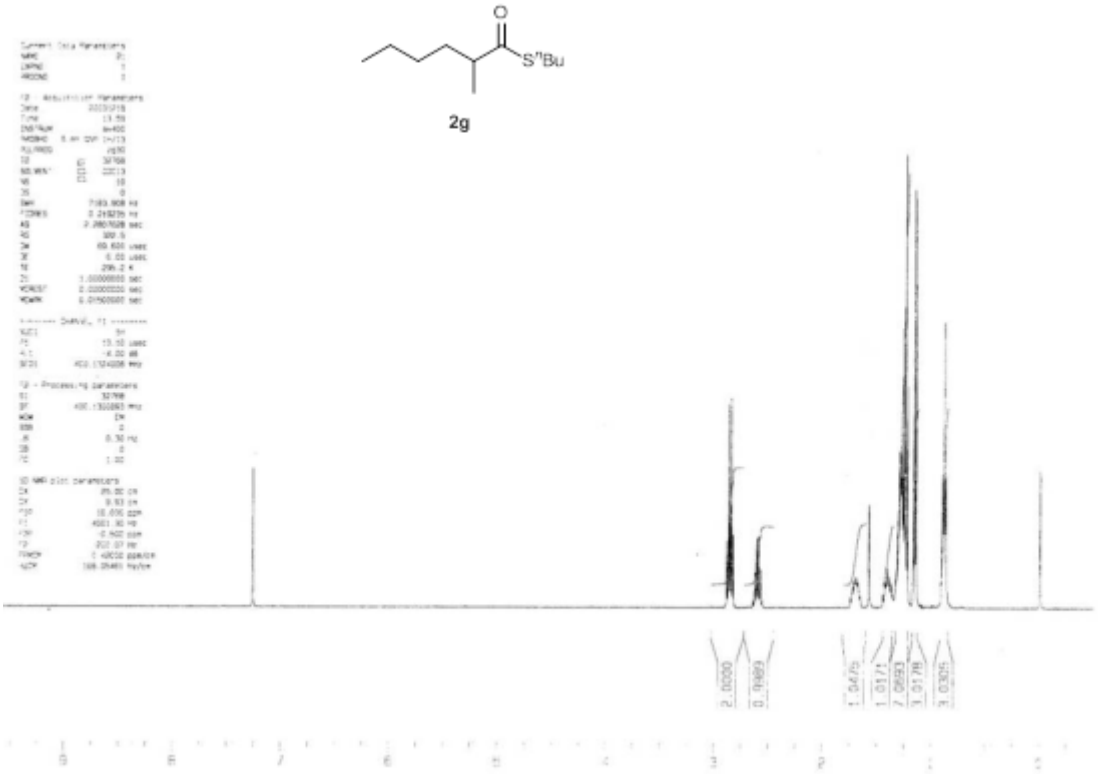
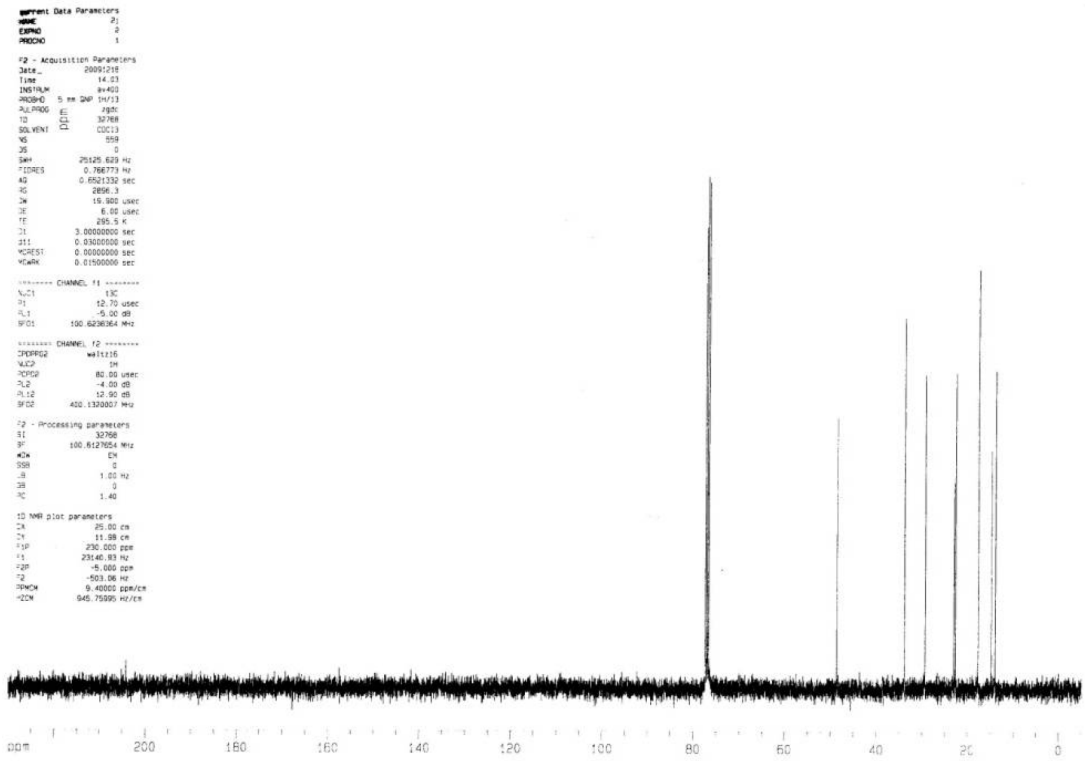
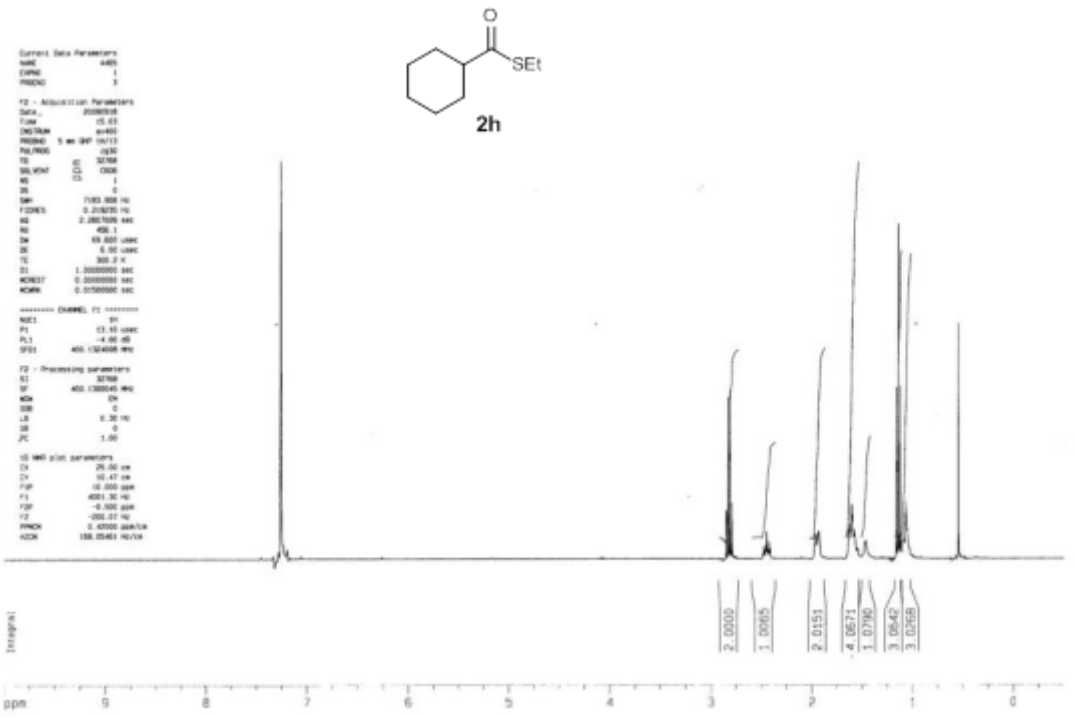
2.0730
2.0000
1.9828
2.0961
2.0823
2.1099
3.0853
ppm

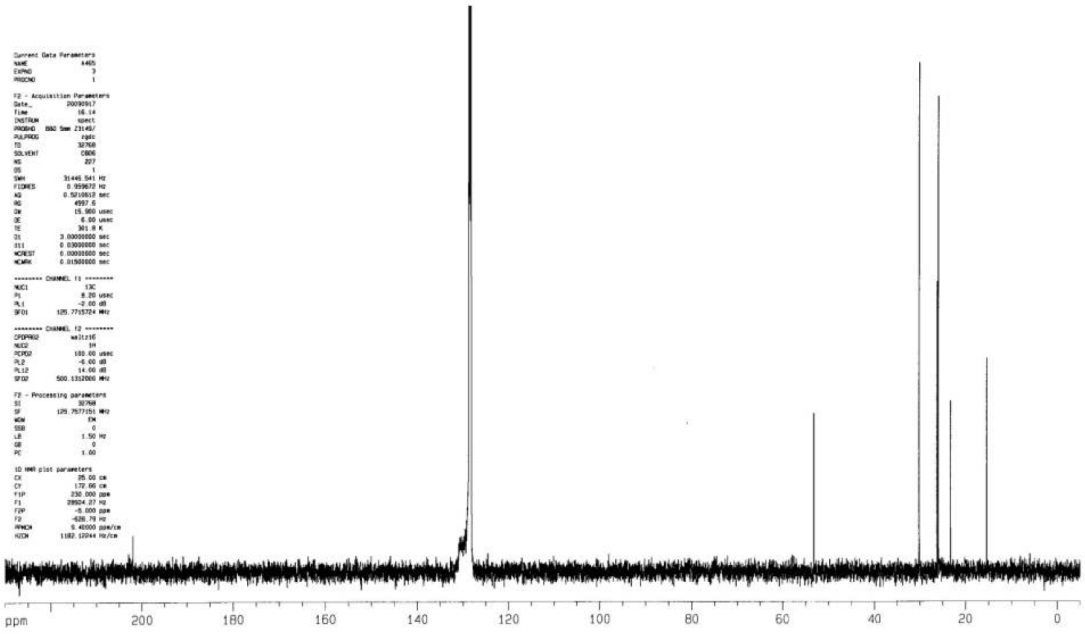

ppm
200
180
160
140
120
100
80
60
40
20
0

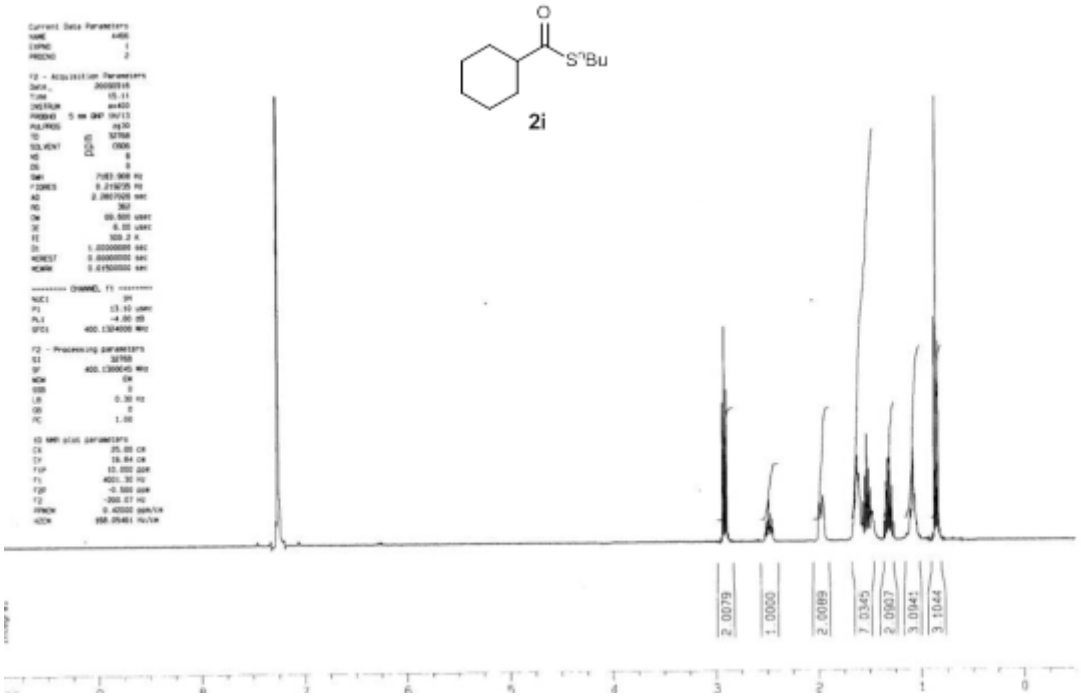


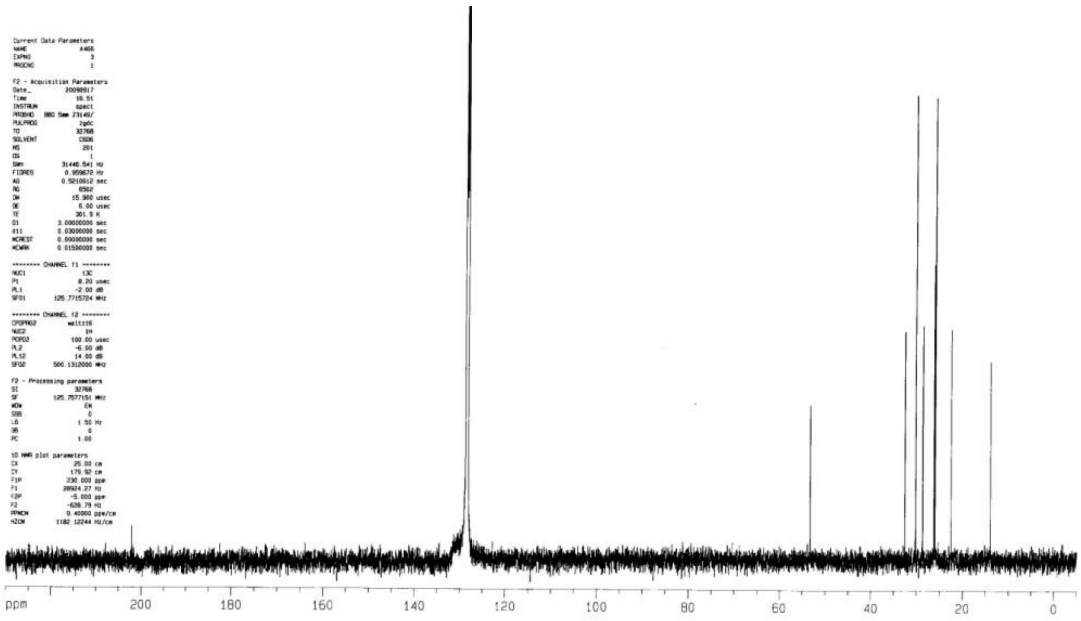
2g

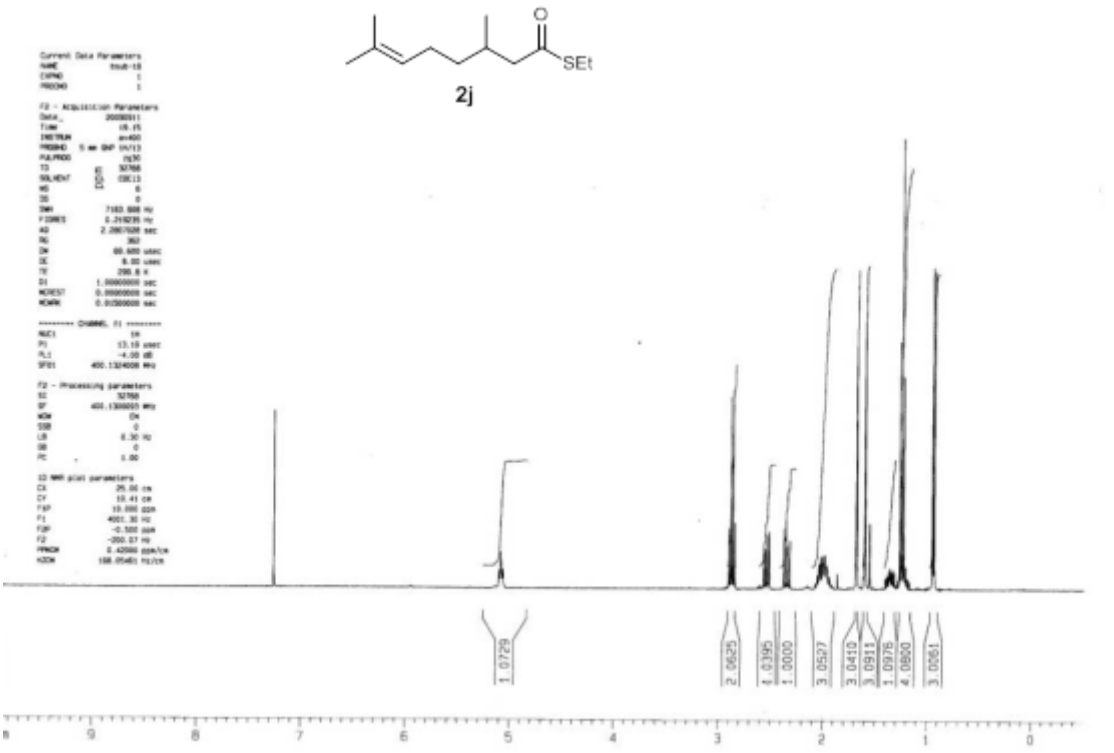


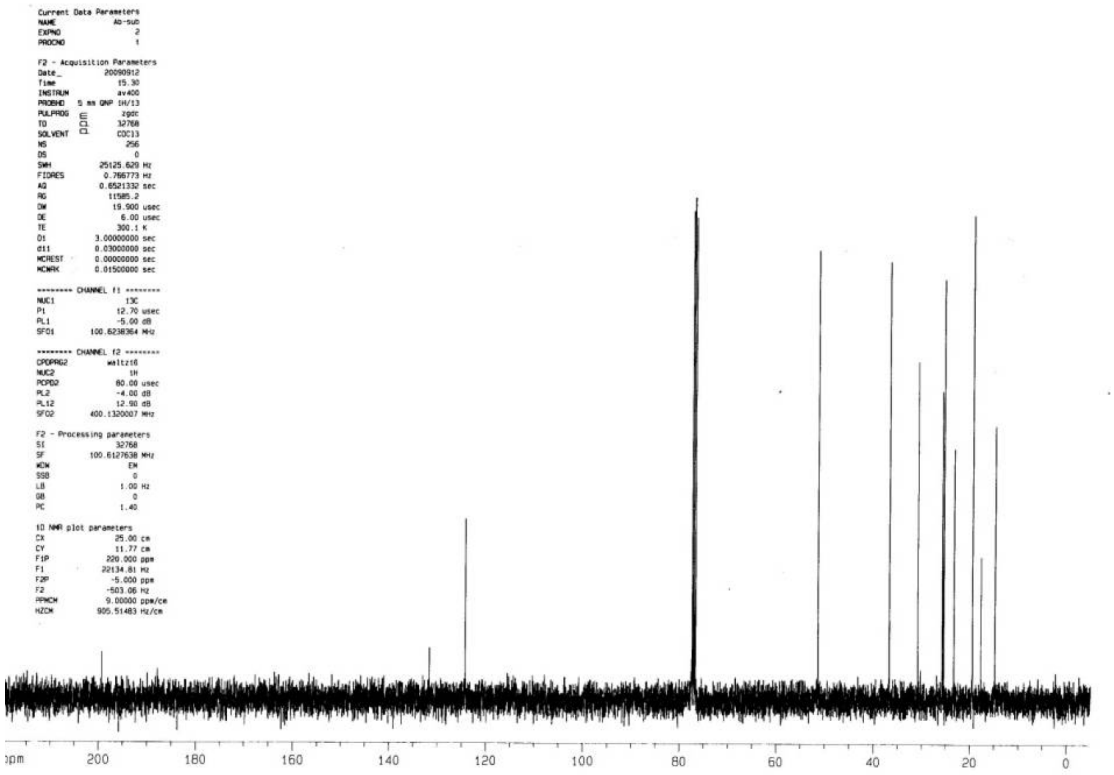

O
SEt
2h
2.0000
1.0065
2.0151
4.0671
1.0796
3.0642
3.0268
ppm

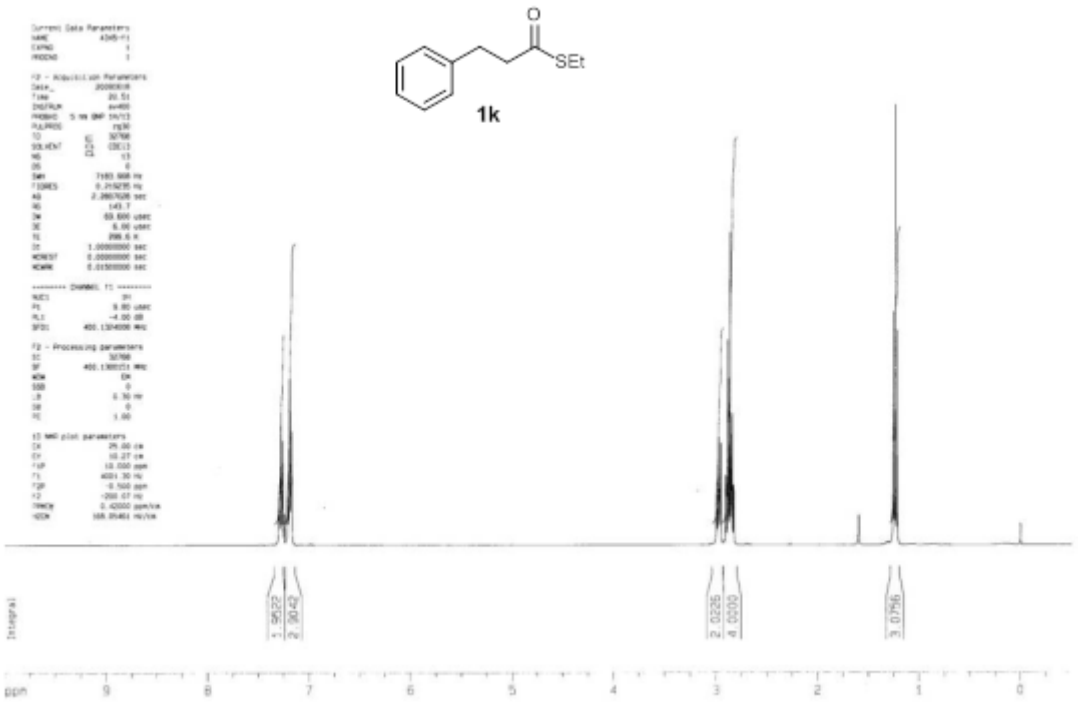

ppm
200
180
160
140
120
100
80
60
40
20
0

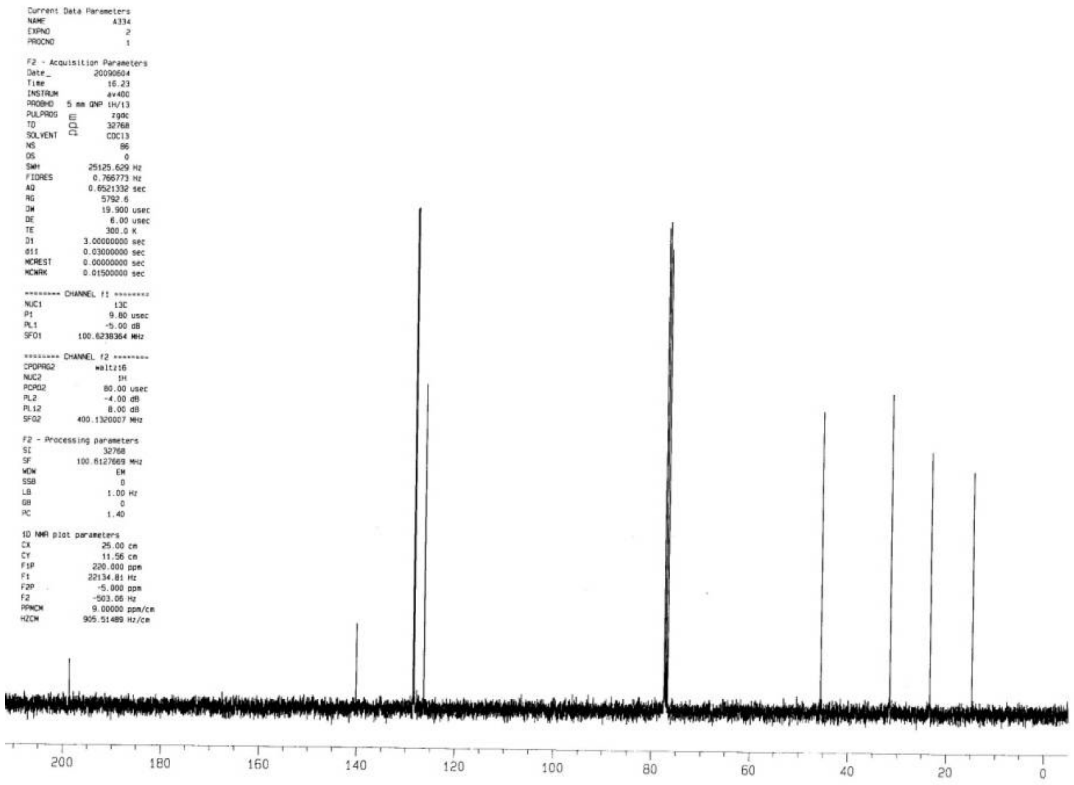

O
S^{n}Bu
2i
2.0079
1.0000
2.0089
7.0345
2.0907
3.0941
3.1044

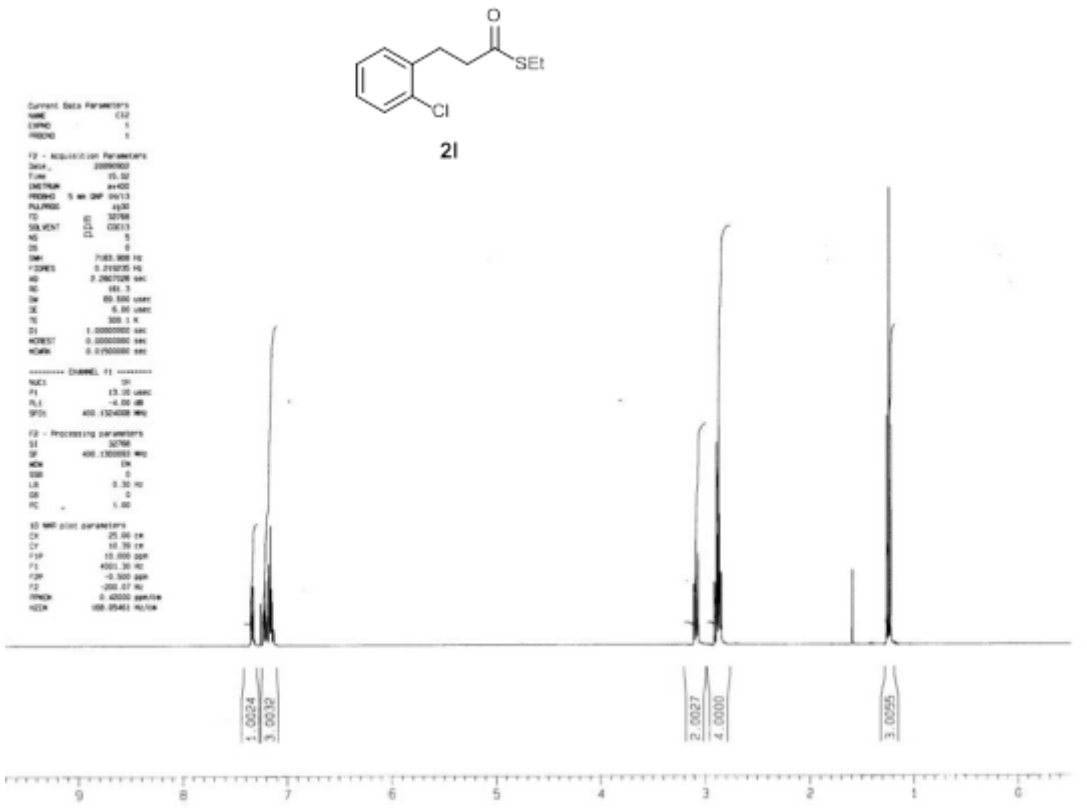

ppm
200
180
160
140
120
100
80
60
40
20
0

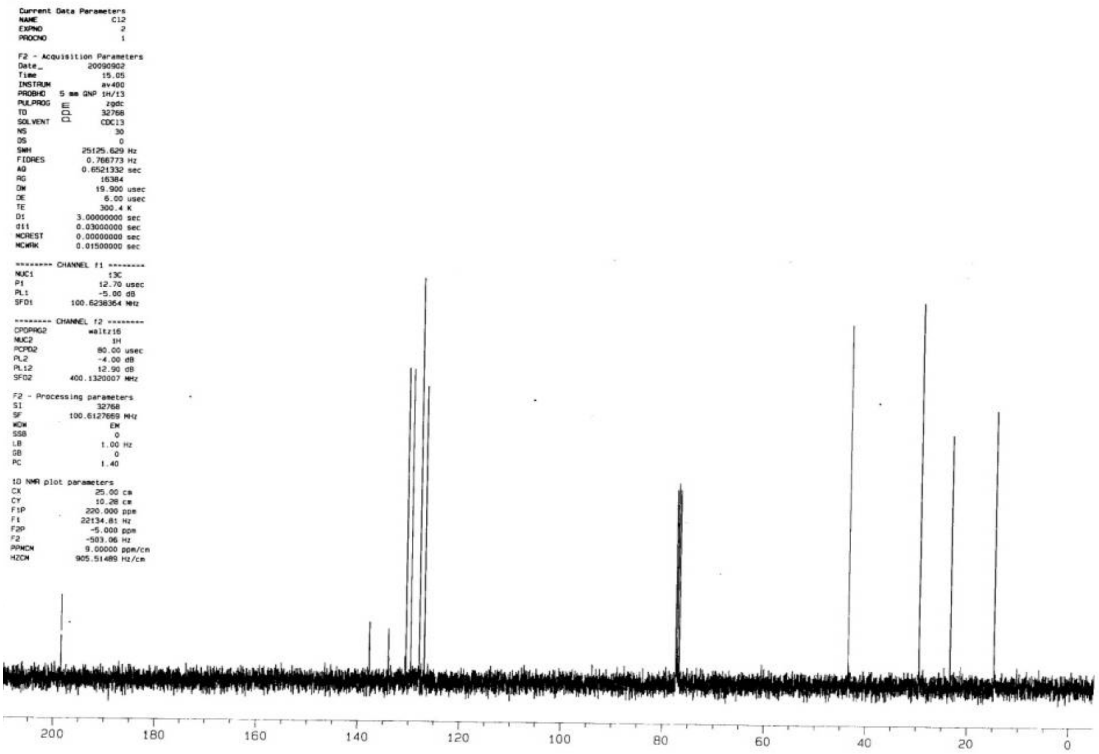

O
SEt
2j
1.0729
2.0625
1.0395
1.0000
3.0527
3.0410
3.0911
1.0976
4.0800
3.0061

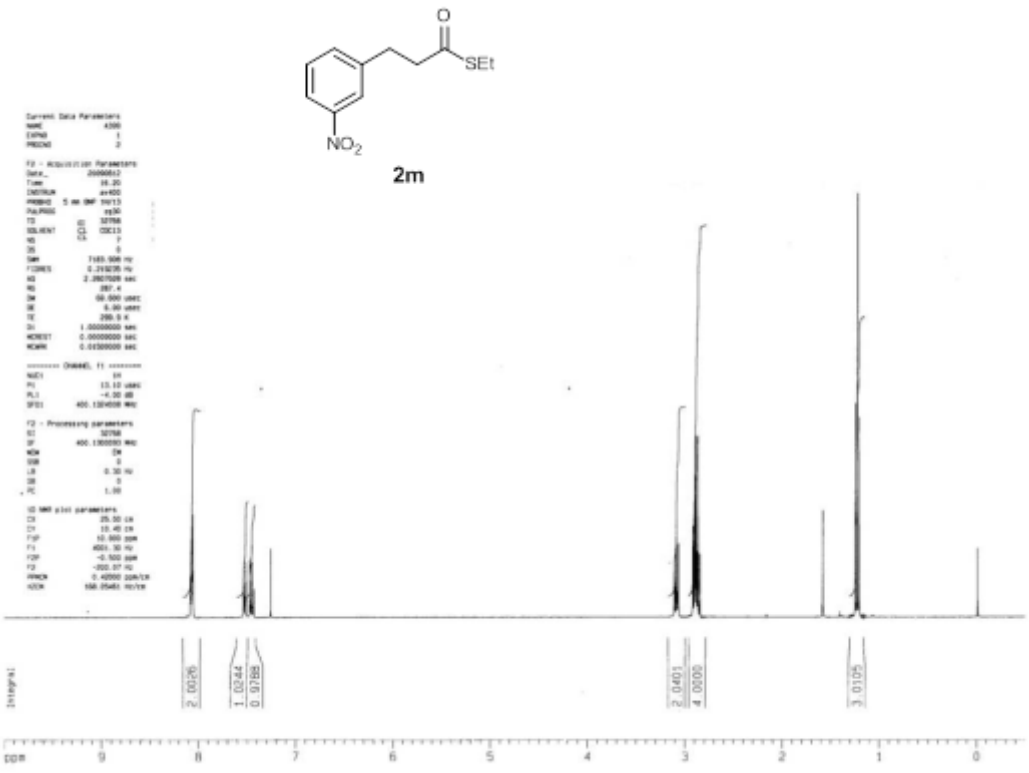

Current Data Parameters
NAME Ab-sub
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090912
Time 15.30
INSTRUM av400
PROBHD 5 mm BNP 1H/13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 256
DS 0
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 11585.2
DW 19.900 usec
DE 6.00 usec
TE 300.1 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 12.70 usec
PL1 -5.00 dB
SFO1 100.6238364 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.90 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127638 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 11.77 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 9.00000 ppm/cm
HZCM 905.51483 Hz/cm
ppm
200
180
160
140
120
100
80
60
40
20
0

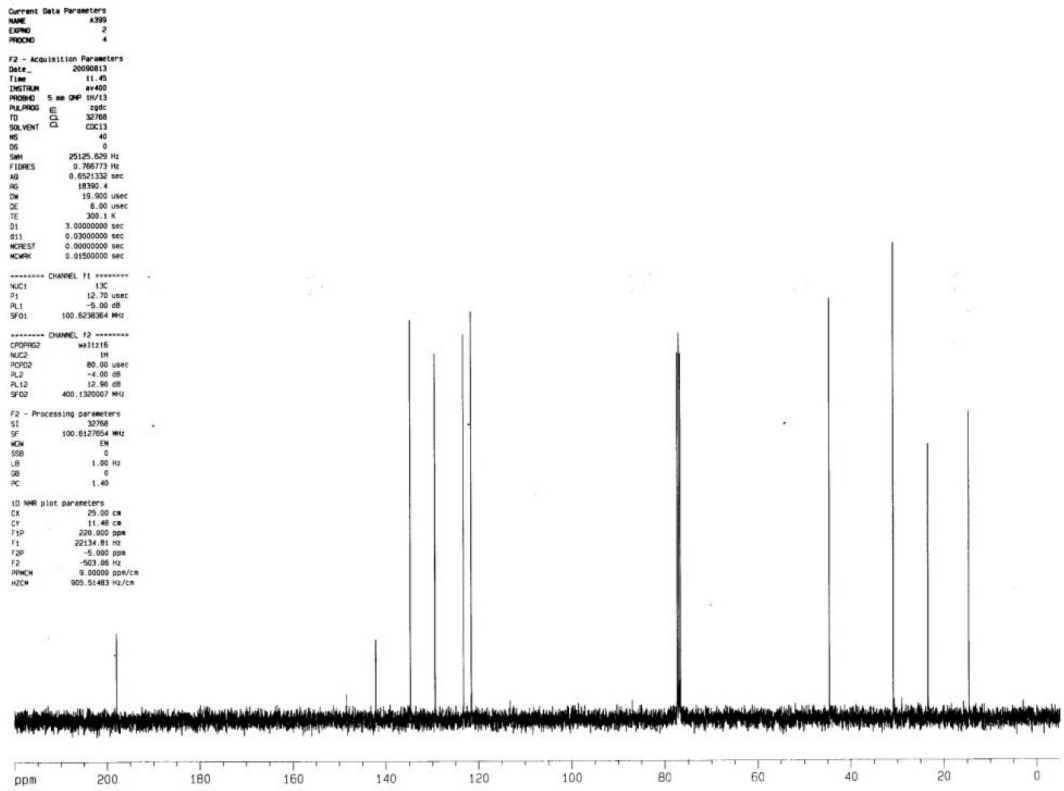

O
SEt
1k
Integral
1.9625
2.3042
2.0226
4.0000
3.0796
ppm
9
8
7
6
5
4
3
2
1
0

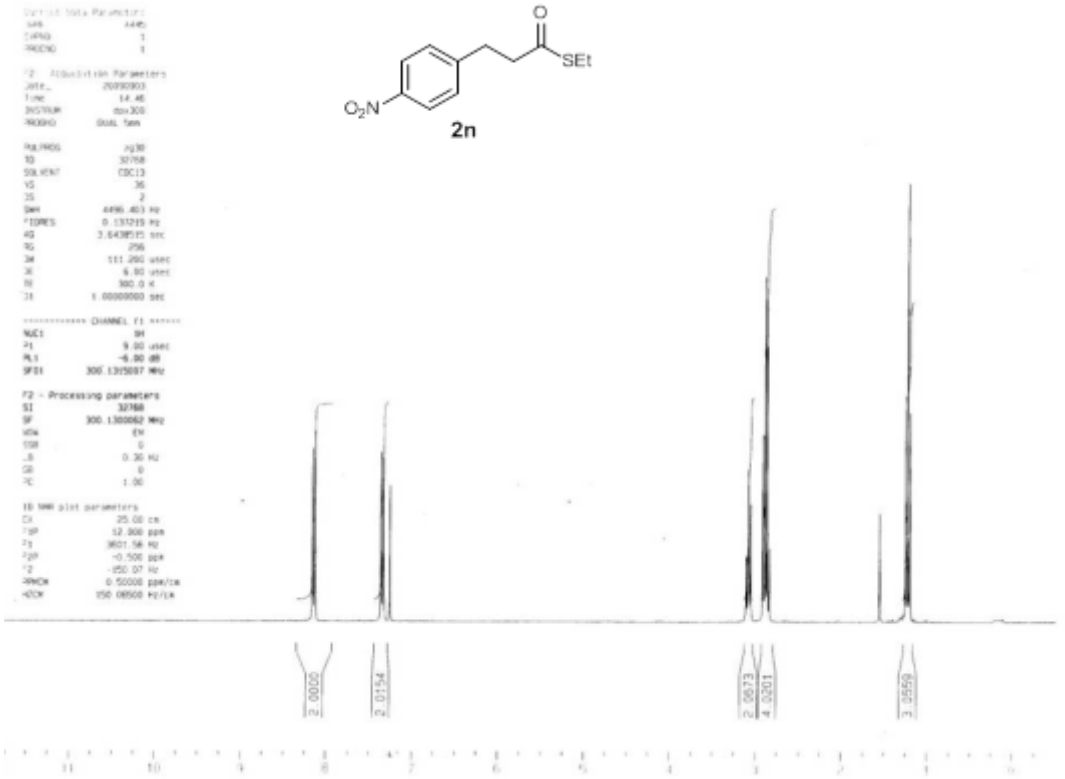

Current Data Parameters
NAME A334
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090604
Time 16.23
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 86
DS 0
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 5792.6
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 9.80 usec
PL1 -5.00 dB
SFO1 100.6238364 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 8.00 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127689 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 11.56 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 9.00000 ppm/cm
HZCM 905.51489 Hz/cm
ppm
200
180
160
140
120
100
80
60
40
20
0

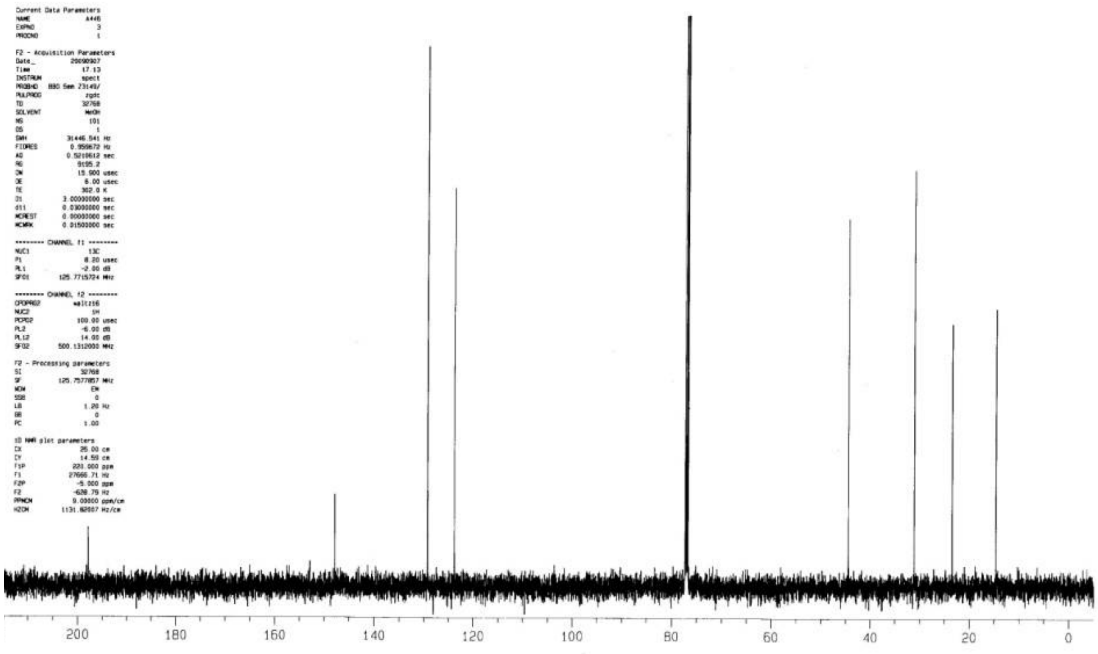

O
SEt
Cl
2l
1.0024
3.0632
2.0027
4.0000
3.0095
9
8
7
6
5
4
3
2
1
0

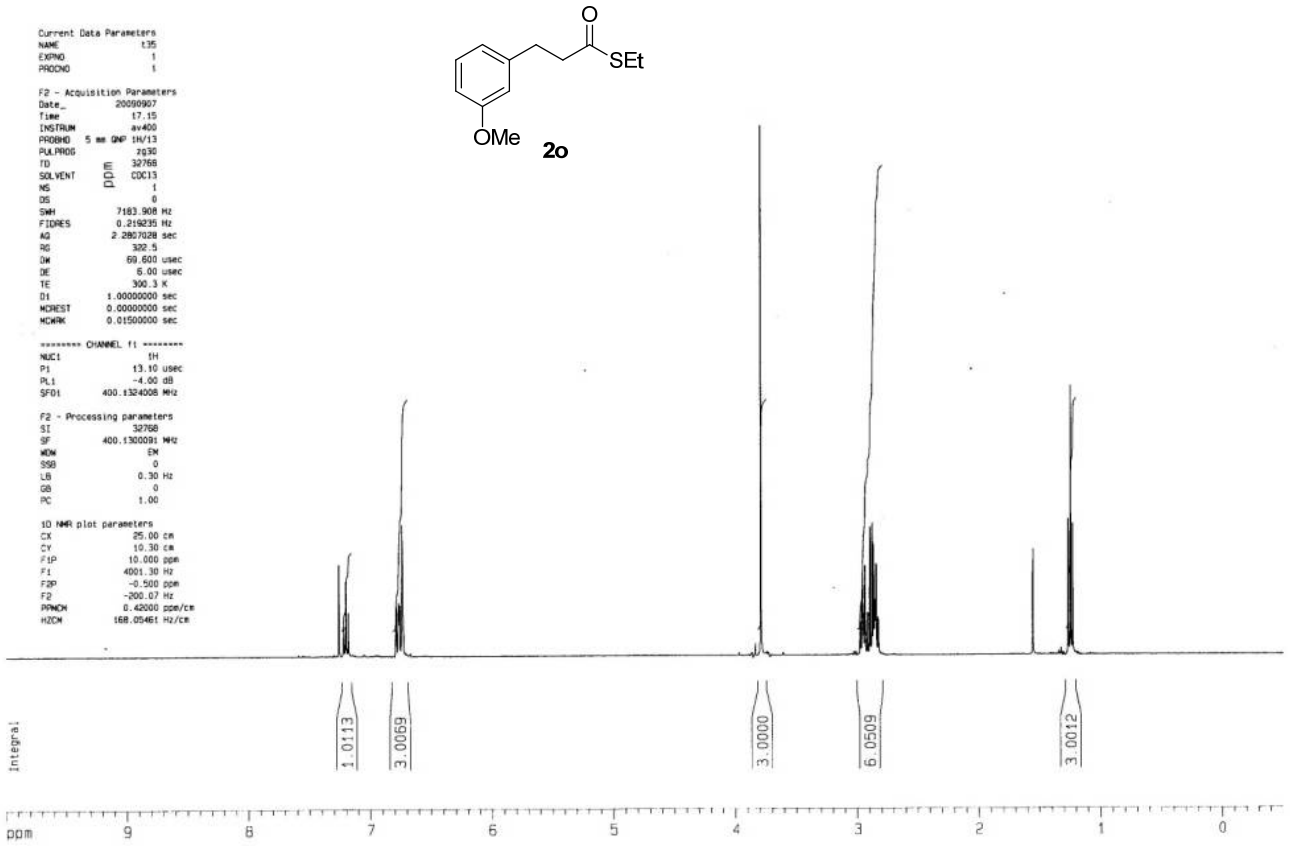

Current Data Parameters
NAME C12
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090902
Time 15.05
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 30
DS 0
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 300.4 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
-------- CHANNEL f1 --------
NUC1 13C
P1 12.70 usec
PL1 -5.00 dB
SFO1 100.6238364 MHz
-------- CHANNEL f2 --------
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.90 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127669 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 10.26 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 9.00000 ppm/cm
HZCM 905.51489 Hz/cm
200
180
160
140
120
100
80
60
40
20
0

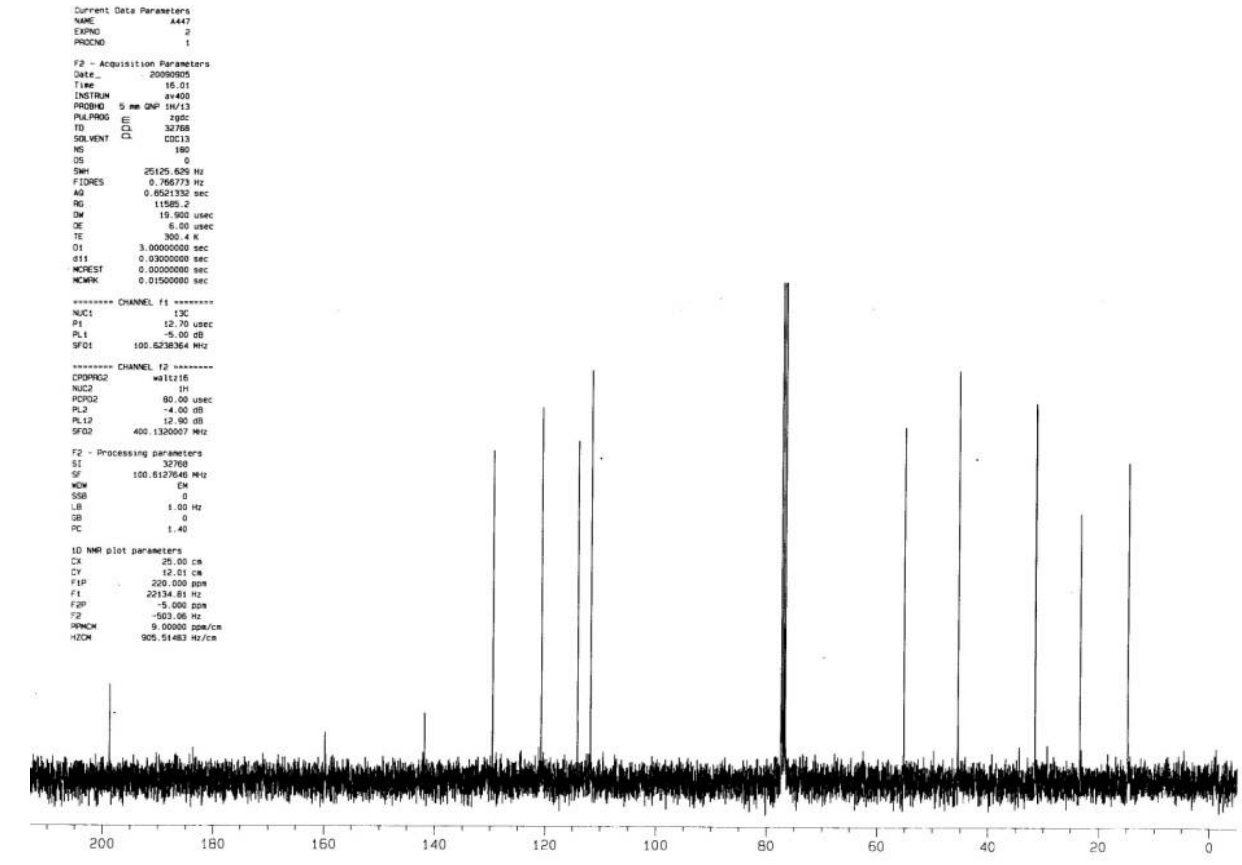

O
SEt
NO2
2m
Integral
2.0026
1.0044
0.9788
2.0401
4.0000
3.0105
ppm

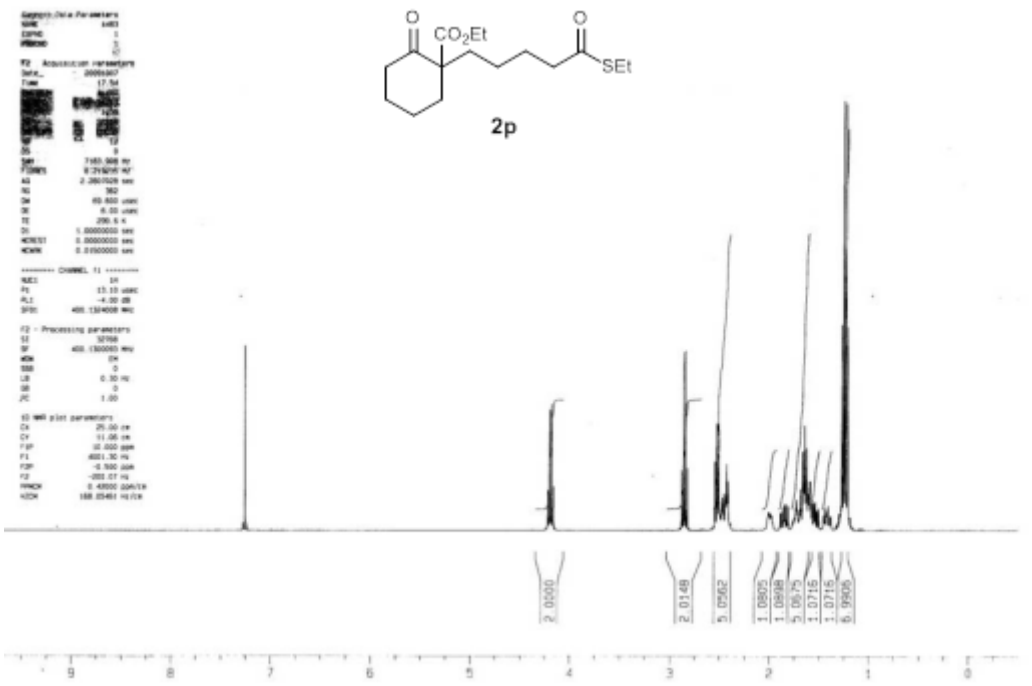

Current Data Parameters
NAME A399
EXPNO 2
PROCNO 4
F2 - Acquisition Parameters
Date_ 20090813
Time 11.45
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpc
TD 32768
SOLVENT CDCl3
NS 40
DS 0
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 18390.4
DW 19.900 usec
DE 6.00 usec
TE 300.1 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
-------- CHANNEL f1 --------
NUC1 13C
P1 12.70 usec
PL1 -5.00 dB
SF01 100.6238364 MHz
-------- CHANNEL f2 --------
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.90 dB
SF02 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127654 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 11.48 cm
F1P 226.000 ppm
F1 22134.81 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 9.00000 ppm/cm
HZCM 905.51483 Hz/cm
ppm
200
180
160
140
120
100
80
60
40
20
0

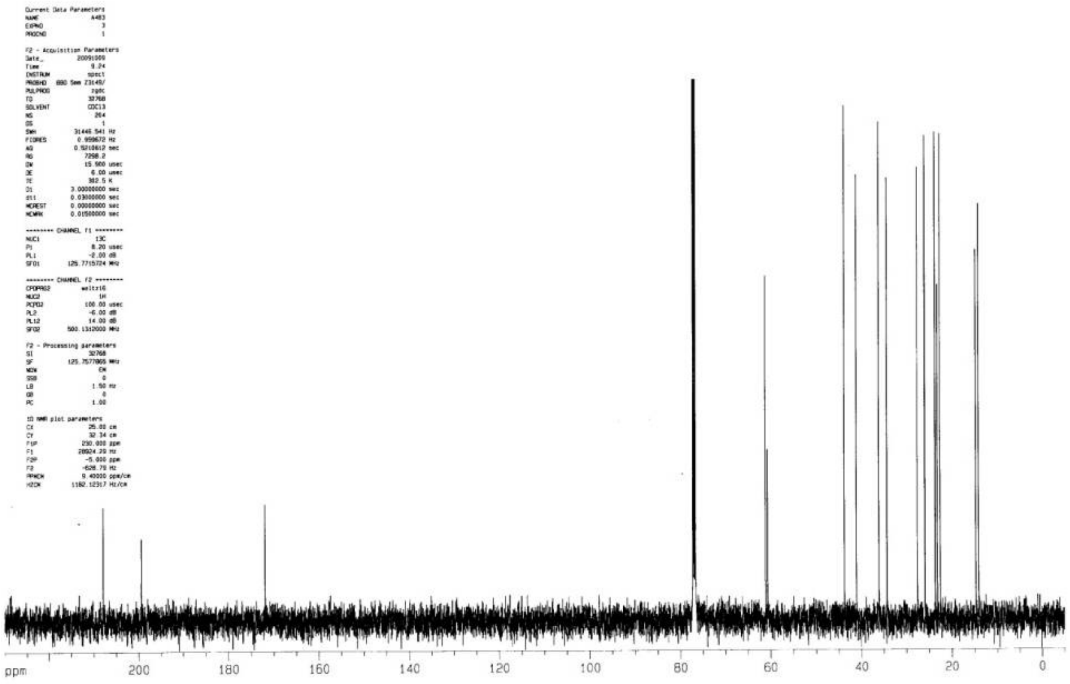

O
SEt
O_2N
2n
2.0000
2.0154
2.0673
4.0301
3.0569

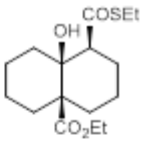

200
180
160
140
120
100
80
60
40
20
0


Current Data Parameters
NAME t35
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090907
Time 17.15
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 1
DS 0
SWH 7183.908 Hz
FIDRES 0.219235 Hz
AQ 2.2807028 sec
RG 322.5
DW 69.600 usec
DE 6.00 usec
TE 300.3 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.10 usec
PL1 -4.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 10.30 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.42000 ppm/cm
HZCM 168.05461 Hz/cm
O
SEt
OMe
2o
Integral
1.0113
3.0069
3.0000
6.0509
3.0012
ppm
9
8
7
6
5
4
3
2
1
0


Current Data Parameters
NAME A447
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090905
Time 16.01
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 180
DS 0
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 11585.2
DW 19.900 usec
DE 6.00 usec
TE 300.4 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 12.70 usec
PL1 -5.00 dB
SFO1 100.6238364 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.90 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127646 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 12.01 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 9.00000 ppm/cm
HZCM 905.51483 Hz/cm
200
180
160
140
120
100
80
60
40
20
0

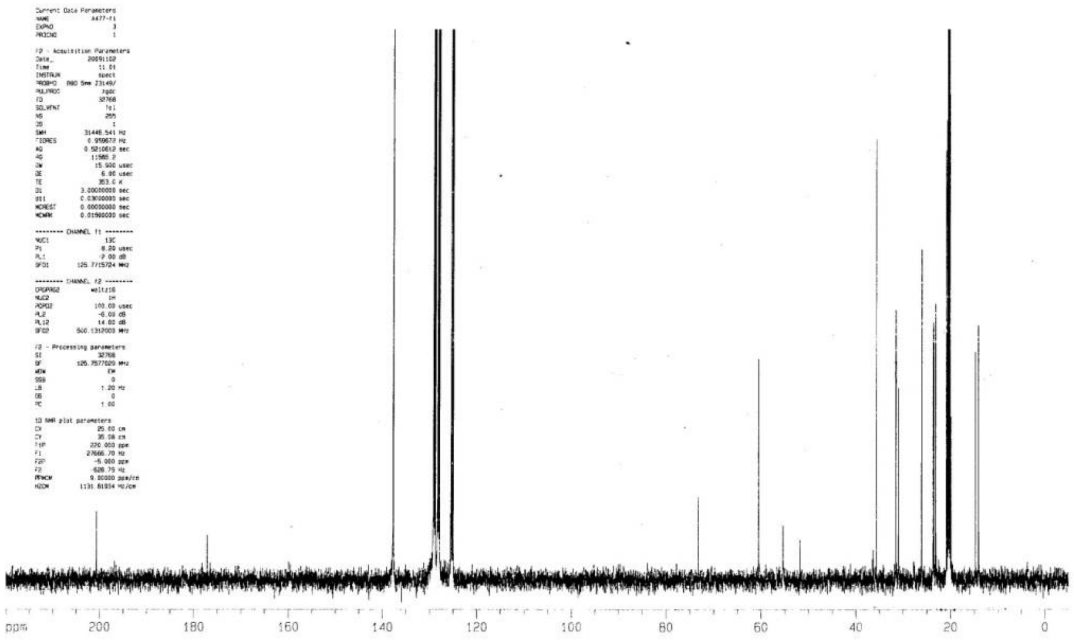

CO2Et
SEt
2p
2.0000
2.0148
5.0562
1.0805
1.0898
5.0675
1.0715
1.0715
6.9906


ppm
200
180
160
140
120
100
80
60
40
20
0

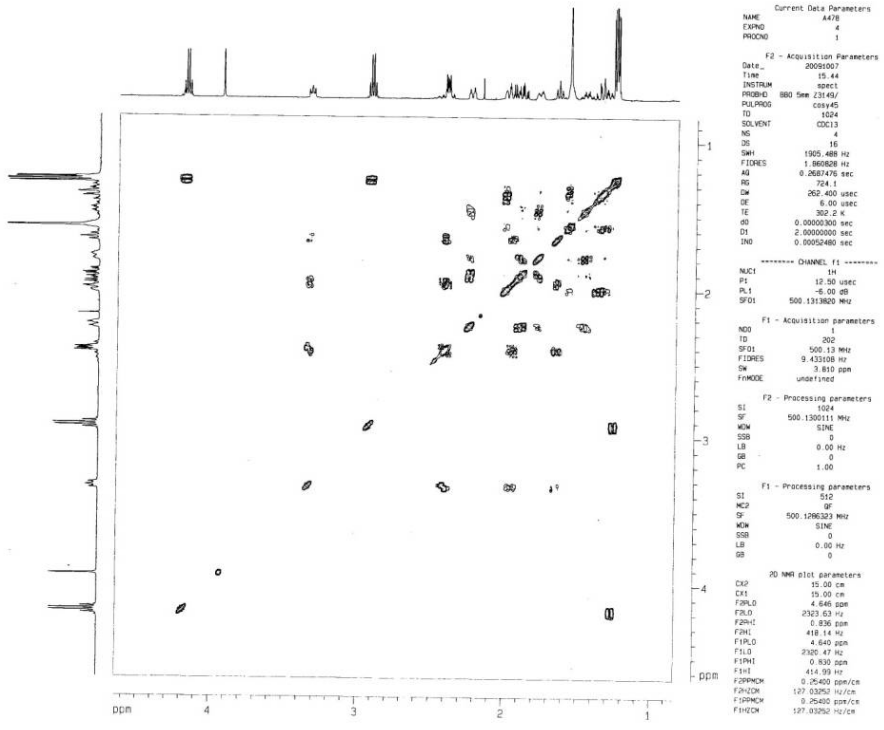

COSEt
OH
CO2Et

4a

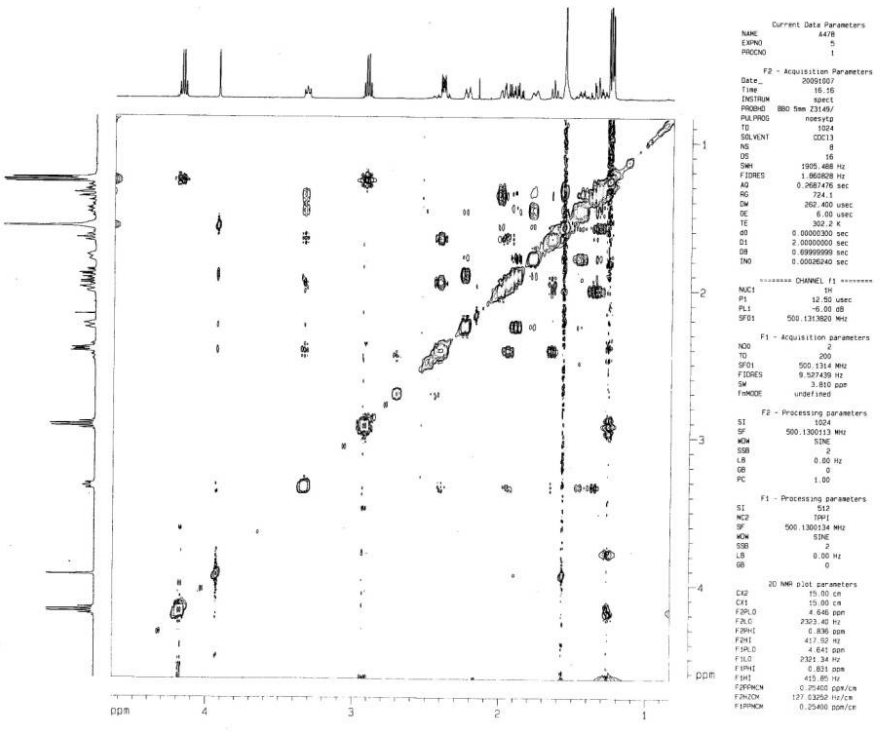
0.9194
1.9273
1.0095
2.0000
2.1185
1.7486
1.1490
4.1538
5.1456
1.5119
3.0976
3.0460
0.5024
ppm
10
9
8
7
6
5
4
3
2
1
0

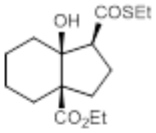

ppm
200
180
160
140
120
100
80
60
40
20
0

H-H COSY of **4a**

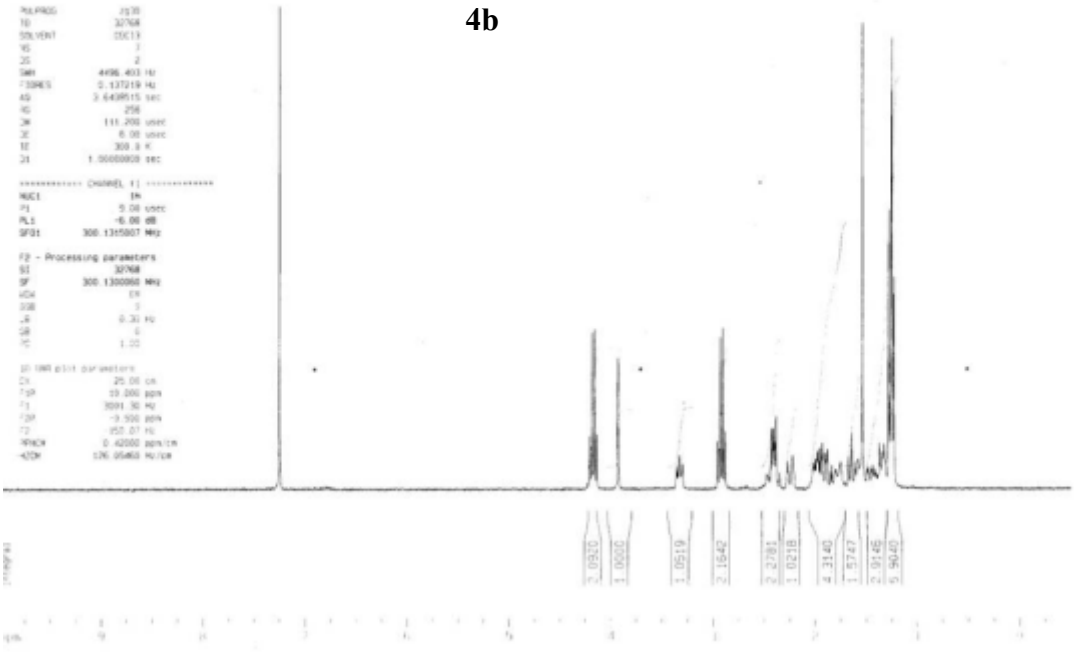


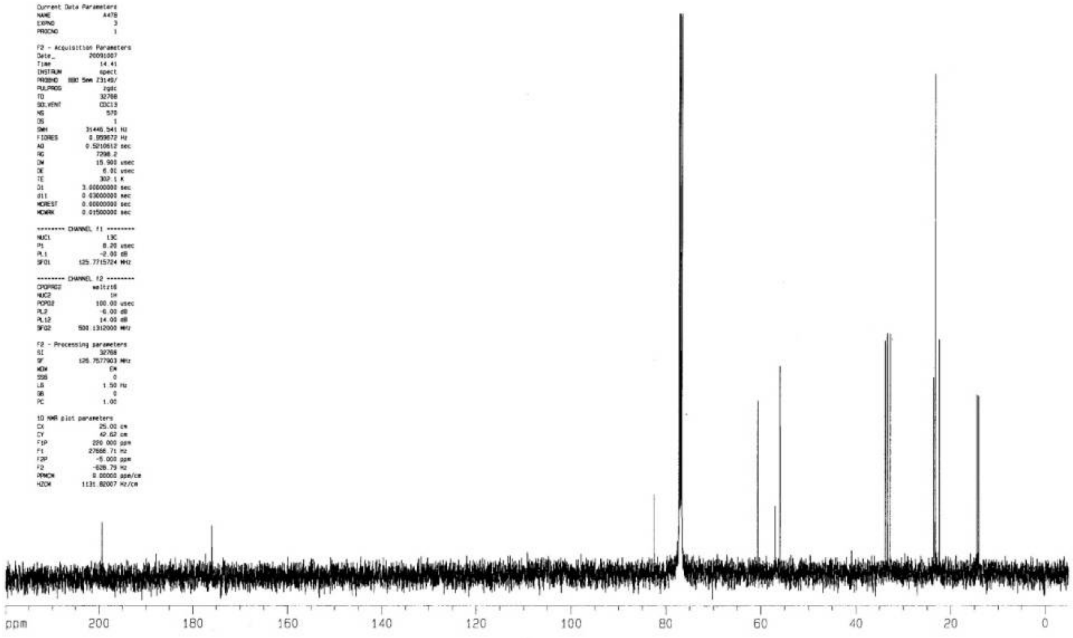
NOESY of **4a**



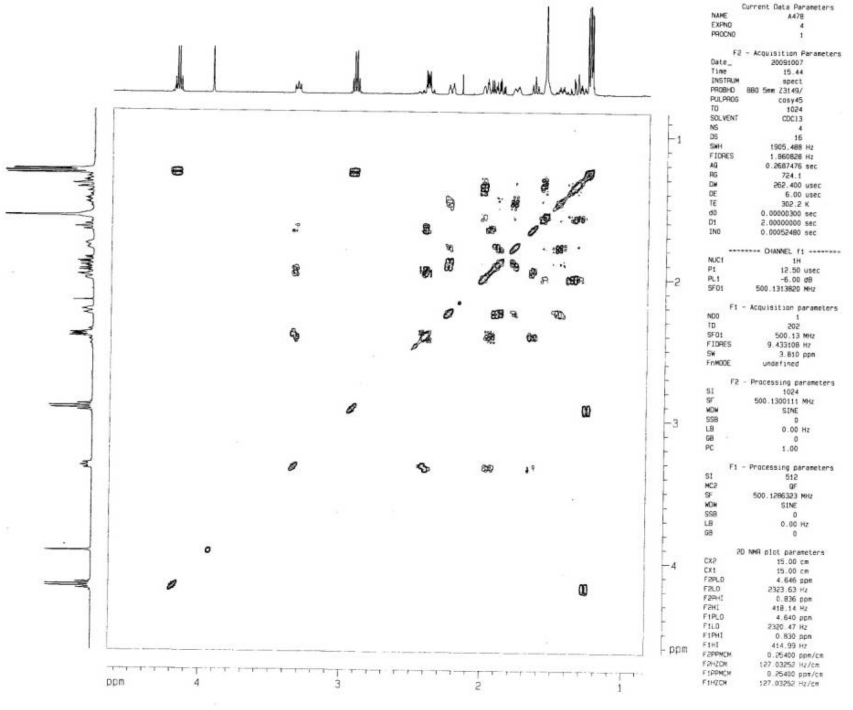


4b





H-H COSY of **4b**



NOESY of **4b**