Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

An aqueous and recyclable copper(I)-catalyzed route to α-sulfenylated carbonyl compounds from propargylic alcohols and aryl thiols

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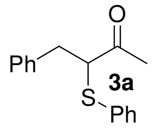
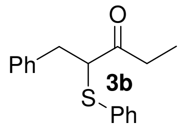
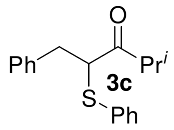
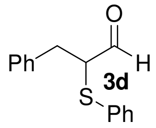
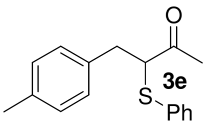
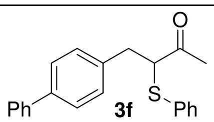
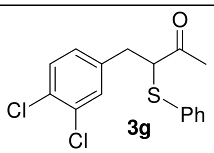
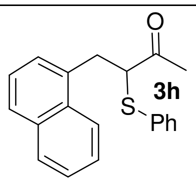
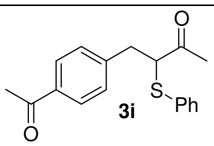
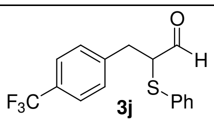
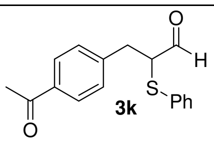
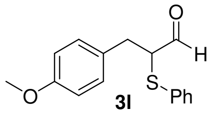
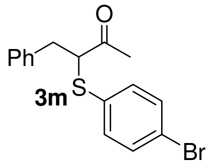
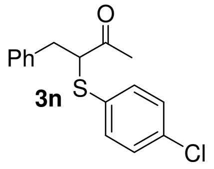
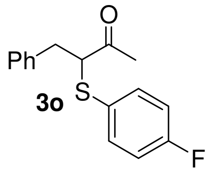
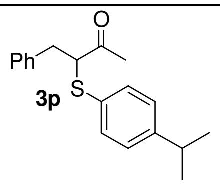
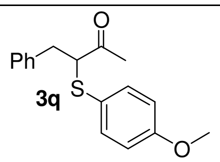
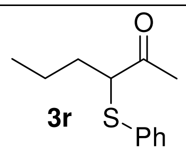
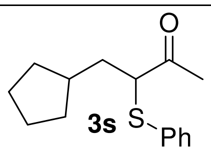
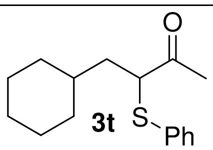
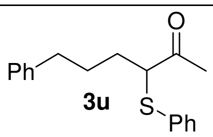
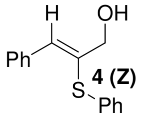
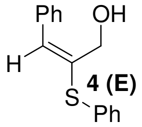
A. Checklist of characterization data of all compounds.

Sr. No.	*Compounds*	*Known / Unknown*	*IR*	*^{1}H NMR*	*^{13}C NMR*	*HRMS*
1	 3a	Known	–	√	√	–
2	 3b	Unknown	√	√	√	√
3	 3c	Known	√	√	√	√
4	 3d	Known	–	√	√	–
5	 3e	Unknown	√	√	√	√
6	 3f	Unknown	√	√	√	√
7	 3g	Unknown	√	√	√	√
8	 3h	Unknown	√	√	√	√
9	 3i	Unknown	√	√	√	√
10	 3j	Unknown	√	√	√	√
11	 3k	Unknown	√	√	√	√

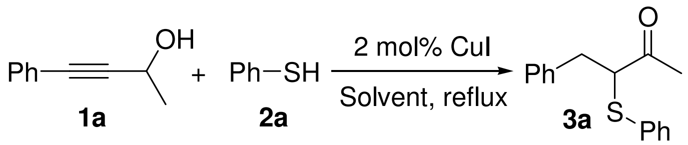
12	 3l	Unknown	√	√	√	√
13	 3m	Known	-	√	√	-
14	 3n	Unknown	√	√	√	√
15	 3o	Unknown	√	√	√	√
16	 3p	Unknown	√	√	√	√
17	 3q	Known	√	√	√	-
18	 3r	Known	–	√	√	–
19	 3s	Known	–	√	√	–
20	 3t	Unknown	√	√	√	√
21	 3u	Unknown	√	√	√	√

22	 4 (Z)	Known	–	√	√	–
23	 4 (E)	Known	–	√	√	–

B. General considerations.

^{1}H and ^{2}H NMR spectra were recorded with a Varian 300 (300 MHz), Varian 400 (400 MHz) and Varian 500 (500 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CHCl_3$ (δ = 7.26 ppm) as an internal standard. All coupling constants are absolute values and are expressed in Hz. The description of the signals include: s = singlet, d = doublet, t = triplet, m = multiplet and dd = doublet of doublets, at = apparent triplet. ^{13}C NMR spectra were recorded with a Varian 300 (75 MHz) and Varian 400 (100 MHz) spectrometer as solutions in $CDCl_3$ with complete proton decoupling. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CDCl_3$ (δ = 77.0 ppm) as an internal standard. IR spectra were recorded by a Perkin Elmer FT-IR Spectrometer. High-Resolution Mass Spectra (HRMS) were performed with a micrOTOF (Bruker) spectrometer by Na-formate. The molecular fragments are quoted as the relation between mass and charge (*m*/*z*). The routine monitoring of reactions was performed with silica gel pre-coated Al plate, which was analyzed with iodine and/or uv light respectively. Solvents, reagents and chemicals were purchased from Aldrich. All reactions were executed with oven-dried glassware under nitrogen atmosphere. Solvent 1,2-Dichloroethane was dried by distilling over anhydrous phosphorus pentoxide prior to use. $NaBD_4$ 98 atom % D 90% (CP) purchased from Aldrich was used for reduction of aldehyde or ketone to prepare alcohols having deuterium at the hydriodic position.

C. Table of solvent selection and optimization of reaction time.[a]

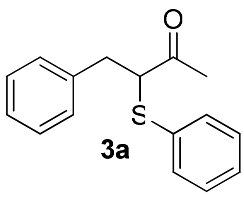


Entry	Solvent	Time (h)	Yield (%)[b]
1	Water	48	97
2	Acetonitrile	48	15
3	Toluene	48	40
4	Nitromethane	48	60
5	1,2-Dichloroethane	48	90
6	Water	60	97
7	Water	36	82

[a] Reaction conditions: **1a** (1 mmol), **2a** (1.5 mmol) and CuI (2 mol%), at reflux in 2.0 mL solvent. [b] Conversion based on ^{1}H NMR analysis.

D. Experimental procedures for the synthesis of all compounds including their spectroscopic data are provided below.

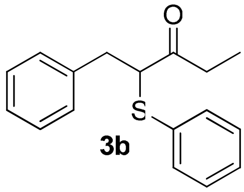
4-Phenyl-3-(phenylthio)butan-2-one (3a):[1]



At first, the catalyst CuI (4 mg, 2 mol%) was weighed and transferred to a 5 mL vial containing a magnet under nitrogen atmosphere. The cap of the vial was closed tightly. 2.0 mL of degassed water followed by alcohol **1a** (145 µL, 1 mmol) and benzenethiol **2a** (154 µL, 1.5 mmol) were added to the vial by syringe and was stirred using a magnetic stirrer at reflux for 24 h. After allowing the mixture to cool to room temperature, the reaction mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic phase was washed with water and brine, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica-gel (100–200 mess) column chromatography using 3% (*v/v*) ethyl acetate / pentane solution to afford the desired product **3a** (240 mg, 0.94 mmol, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3 H, H-1), 3.00 (dd, J = 6.9 Hz, 14.4 Hz, 1 H, H-4), 3.19 (dd, J = 8.4 Hz, 14.1 Hz, 1 H, H-4), 3.90 (dd, J = 6.9 Hz, 8.4 Hz, 1 H, H-3), 7.18–7.37

(m, 10 H, H-arom) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.1, 36.9, 59.0, 127.1, 128.5, 128.8, 129.4, 133.0, 133.3, 138.3, 204.5 ppm.

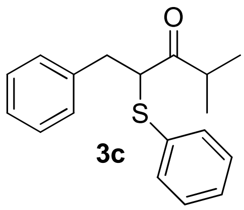
1-Phenyl-2-(phenylthio)pentan-3-one (3b):



3b

Alcohol **1b** (120 µL, 1 mmol), benzenethiol **2a** (154 µL, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3b** as a yellowish oil (248 mg, 0.92 mmol, 92%). IR (Neat): ῦ = 2962, 1705, 1439, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t, J = 7.2 Hz, 3 H, H-1), 2.31–2.41 (m, 1 H, H-2), 2.60–2.68 (m, 1 H, H-2), 3.04 (dd, J = 6.4 Hz, 13.6 Hz, 1 H, H-5), 3.23 (dd, J = 8.8, 14 Hz, 1 H, H-5), 3.92- 3.96 (m, 1 H, H-4), 7.20–7.40 (m, 10 H, H-arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.8, 34.1, 36.9, 57.8, 126.7, 127.5, 128.2, 128.5, 129.1, 132.8, 133.1, 138.2, 207.0 ppm. HRMS: calcd. for $C_{17}H_{18}NaOS$ 293.0976; found 293.0971.

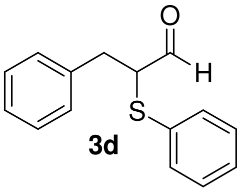
4-Methyl-1-phenyl-2-(phenylthio)pentan-3-one (3c):[1]



3c

Alcohol **1c** (128 µL, 1 mmol), benzenethiol **2a** (154 µL, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3c** as a yellowish oil (244 mg, 0.86 mmol, 86%). IR (Neat): ῦ = 2969, 1707, 1439, 699 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.76 (d, J = 6.9 Hz, 3 H, H-5), 1.04 (d, J = 6.7 Hz, 3 H, CH_3), 2.70–2.79 (m, 1 H, H-4), 3.00 (dd, J = 5.7 Hz, 13.8 Hz, 1 H, H-1), 3.22 (dd, J = 9.6 Hz, 13.8 Hz, 1 H, H-1), 3.97 22 (dd, J = 5.7 Hz, 9.6 Hz, 1 H, H-2), 7.42–7.38 (m, 2 H, H-arom), 7.14–7.35 (m, 8 H, H-arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.8, 18.3, 37.3, 39.3, 56.5, 126.5, 128.3, 129.0, 129.2, 132.8, 133.6, 138.5, 208.7 ppm. HRMS: calcd. for $C_{18}H_{20}OSNa$ 307.1133; found 307.1115.

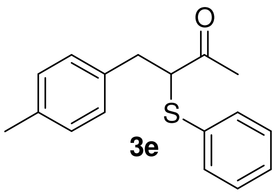
3-Phenyl-2-(phenylthio)propanal (3d):[1]



3d

Alcohol **1d** (125 μL, 1 mmol), benzenethiol **2a** (154 μL, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3d** as a reddish brown oil (232 mg, 0.96 mmol, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.00 (dd, J = 6.9 Hz, 14.4 Hz, 1 H, H-3), 3.22 (dd, J = 8.1 Hz, 14.4 Hz, 1 H, H-3), 3.81–3.87 (m, 1 H, H-2), 7.23–7.41 (m, 10 H, H-arom), 9.50 (d, J = 3.6 Hz, 1 H, H-1) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 34.4, 58.1, 127.1, 128.6, 128.8, 129.3, 129.3, 131.6, 133.4, 137.3, 194.2 ppm.

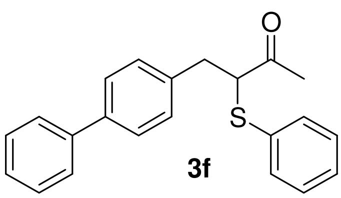
3-(Phenylthio)-4-(p-tolyl)butan-2-one (3e):



3e

Alcohol **1e** (160 mg, 1 mmol), benzenethiol **2a** (154 μL, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3e** as a yellowish oil (224 mg, 0.83 mmol, 83%). IR (Neat): ῦ = 2919, 1708, 1438, 805, 689 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 3 H, H-1), 2.34 (s, 3 H, H-methyl), 2.30 (dd, J = 6.8 Hz, 14.4 Hz, 1 H, H-4), 3.17 (dd, J = 8.8 Hz, 14.1 Hz, 1 H, H-4), 3.92 (t, J = 6.9 Hz, 1 H, H-3), 7.11–7.34 (m, 9 H, H-arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 27.7, 36.2, 58.8, 128.1, 128.9, 129.1, 129.2, 132.8, 132.8, 134.8, 136.3, 204.4 ppm. HRMS: calcd. for $C_{17}H_{18}NaOS$ 293.0976; found 293.0971.

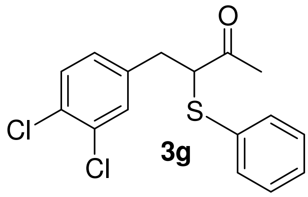
4-([1,1'-Biphenyl]-4-yl)-3-(phenylthio)butan-2-one (3f):



3f

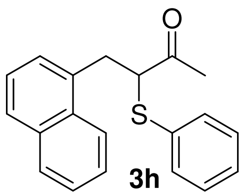
Alcohol **1f** (222 mg, 1 mmol), benzenethiol **2a** (154 μL, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3f** as a reddish brown oil (299 mg, 0.90 mmol, 90%). IR (Neat): ῦ = 3053, 3031, 1707, 1486, 754, 687 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, H-1), 3.09 (dd, J = 6.8 Hz, 14.4 Hz, 1 H, H-4), 3.27 (dd, J = 8.0 Hz, 16 Hz, 1 H, H-4), 3.97–4.00 (m, 1 H, H-3), 7.28–7.62 (m, 14 H, H-arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8, 36.2, 58.6, 126.1, 127.2, 127.1, 128.2, 128.7, 129.5, 132.6, 133, 137.0, 139.6, 140.7, 204.1ppm. HRMS: calcd. for $C_{22}H_{20}NaOS$ 355.1133; found 355.1127.

4-(3, 4-Dichlorophenyl)-3-(phenylthio)butan-2-one (3g):



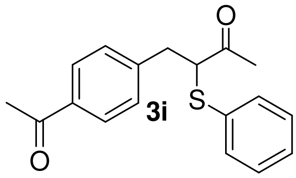
Alcohol **1g** (215mg, 1 mmol), benzenethiol **2a** (154 µL, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3g** as a reddish brown oil (295 mg, 0.91 mmol, 91%). IR (Neat): ṽ = 3059, 1705, 1471, 1132, 739, 689cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, H-1), 2.92 (dd, J = 8 Hz, 16 Hz, 1 H, H-4), 3.14 (dd, J = 8.0 Hz, 16 Hz, 1 H, H-4), 3.82 (t, J = 7.2, 1 H, H-3), 7.28–7.37 (m, 8 H, H-arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28, 35.4, 58.1, 128.6, 128.6, 129.2, 130.3, 130.7, 131.0, 131.8, 132.3, 133.4, 138.4, 203.3 ppm. HRMS: calcd. for $C_{16}H_{14}Cl_2NaOS$ 347.0040; found 347.0035.

4-(Naphthalen-1-yl)-3-(phenylthio)butan-2-one (3h):



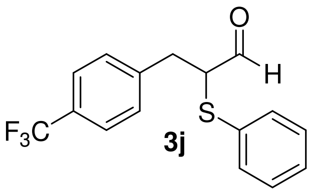
Alcohol **1h** (196 mg, 1 mmol), benzenethiol **2a** (154 µL, 1.5 mmol) and the catalyst AuCl (5 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3**h as a reddish brown oil (287 mg, 0.95 mmol, 95%). IR (Neat): ṽ = 3055, 1705, 1438, 1352, 775, 741cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21 (s, 3 H, H-1), 3.51 (dd, J = 5.6 Hz, 14.4 Hz, 1 H, H-4), 3.67 (dd, J = 8.8 Hz, 14.8 Hz, 1 H, H-4), 4.10–4.13 (m, 1 H, H-3), 7.28–7.55 (m, 9 H, H-arom), 7.77 (d, 1 H, H-arom), 7.88–7.95 (m, 2 H, H-arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.1, 33.7, 57.7, 123.1, 125.3, 125.6, 126.2, 126.6, 127.6, 128.3, 128.7, 129.1, 131.6, 132.6, 133.2, 133.9, 204.2 ppm. HRMS: calcd. for $C_{20}H_{18}NaOS$ 329.0976; found 329.0971.

4-(4-Acetylphenyl)-3-(phenylthio)butan-2-one (3i):



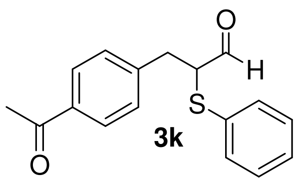
Alcohol **1i** (188 mg, 1 mmol), benzenethiol **2a** (154 µL, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3i** as a yellowish oil (253 mg, 0.85 mmol, 85%). IR (Neat): ῦ = 2927, 1679, 1266, 820, 729 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3 H, H-1), 2.58 (s, 3 H, H-COC$\underline{H}_3$), 3.03 (dd, J = 6.9 Hz, 14.1 Hz, 1 H, H-4), 3.24 (dd, J = 8.1 Hz, 14.1 Hz, 1 H, H-4), 3.90 (dd, J = 6.9 Hz, 8.1 Hz, 1 H, H-3), 7.28–7.37 (m, 7 H, H-arom), 7.87–7.91 (m, 2 H, H-arom) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.5, 27.9, 36.3, 58.0, 128.5, 128.5, 129.1, 129.3, 132.0, 133.3, 135.7, 143.7, 197.6, 203.5 ppm. HRMS: calcd. for $C_{18}H_{18}NaO_2S$ 321.0925; found 321.0920.

2-(Phenylthio)-3-(4-(trifluoromethyl)phenyl)propanal (3j):



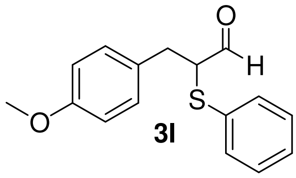
Alcohol **1j** (200 mg, 1 mmol), benzenethiol **2a** (154 µL, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3j** as a reddish brown oil (218 mg, 0.90 mmol, 90%). IR (Neat): ῦ = 2988, 2901, 1717, 1323, 775, 1066 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.01 (dd, J = 67.6 Hz, 14.4 Hz, 1 H, H-3), 3.27 (dd, J = 7.6 Hz, 14.4 Hz, 1 H, H-3), 3.80–3.84 (m, 1 H, H-2), 7.28–7.50 (m, 7 H, H-arom), 7.53-7.60 (m, 2 H, H –arom) 9.55 (d, J = 2.8 Hz, 1 H, H-1) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.8, 57.7, 125.4, 125.5, 125.5, 128.8, 129.3, 129.5, 130.7, 133.7, 141.4, 193.5 ppm. HRMS: calcd. for $C_{16}H_{13}F_3NaOS$ 333.0537; found 333.0531.

3-(4-Acetylphenyl)-2-(phenylthio)propanel (3k):



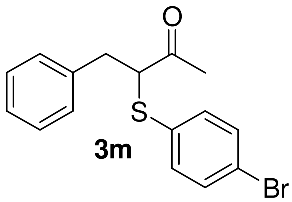
Alcohol **1k** (174 mg, 1 mmol), benzenethiol **2a** (154 µL, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3k** as a yellowish oil (207 mg, 0.73 mmol, 73%). IR (Neat): ῡ = 2959, 2929, 1720, 1683, 1267, 1073, 745 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.60 (s, 3 H, H-COC$\underline{H}_3$), 3.01 (dd, J = 7.2 Hz, 14.4 Hz, 1 H, H-3), 3.26 (dd, J = 7.5 Hz, 14.4 Hz, 1 H, H-3), 3.80–3.86 (m, 1 H, H-2), 7.26–7.40 (m, 7 H, H-arom), 7.91–7.93 (m, 2 H, H-arom), 9.54 (d, J = 3.0 Hz, 1 H, H-1) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.6, 34.0, 57.6, 128.7, 128.7, 128.8, 129.0, 129.3, 129.4, 133.6, 135.9, 142.9, 193.6, 197.6 ppm. HRMS: calcd. for $C_{17}H_{16}NaO_2S$ 307.0769; found 307.0753.

3-(4-Methoxyphenyl)-2-(phenylthio)propanal (3l):



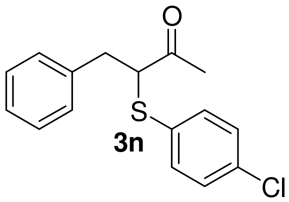
Alcohol **1l** (162 mg, 1 mmol), benzenethiol **2a** (154 µL, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3l** as a light brown oil (174 mg, 0.64 mmol, 64%). IR (Neat): ῡ = 2835, 1715, 1511, 1246, 1032, 690 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.95 (dd, J = 6.6 Hz, 14.4 Hz, 1 H, H-3), 3.15 (dd, J = 8.4 Hz, 14.7 Hz, 1 H, H-3), 3.77–3.83 (m, 4 H, H-2 and H-OC$\underline{H}_3$), 6.87 (dd, J = 1.8 Hz, 6.6 Hz, 2 H, H-arom), 7.16 (dd, J = 1.8 Hz, 6.9 Hz, 2 H, H-arom), 7.28–7.32 (m, 3 H, H-arom), 7.38–7.41 (m, 2 H, H-arom), 9.48 (d, J = 3.9 Hz, 1 H, H-1) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.4, 55.2, 58.1, 114.0, 128.3, 129.0, 129.1, 130.1, 131.5, 133.1, 158.5, 194.3 ppm. HRMS: calcd. for $C_{16}H_{16}NaO_2S$ 295.0769; found 295.0770.

3-((4-Bromophenyl)thio)-4-phenylbutan-2-one (3m):[2]



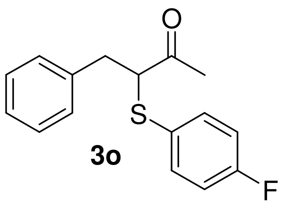
Alcohol **1a** (145 µL, 1 mmol), 4-bromobenzenethiol **2b** (284 mg, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3m** as a yellowish oil (248 mg, 0.74 mmol, 74%). IR (Neat): ῡ = 3027, 2912, 1705, 1472, 813, 697 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 2.23 (s, 3 H, H-1), δ = 3.00 (dd, J = 6.8 Hz, 14.4 Hz, 1 H, H-4), 3.19 (dd, J = 8.0 Hz, 14 Hz, 1 H, H-4), 3.90 (t, J = 6.8, 1 H, H-3), 7.19–7.33 (m, 7 H, H-arom), 7.42–7.44 (m, 2 H, H-arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.6, 36.5, 58.5, 122.6, 126.9, 128.5, 129.0, 131.6, 132.2, 134.5 137.7, 203.8 ppm.

3-((4-Chlorophenyl)thio)-4-phenylbutan-2-one (3n):



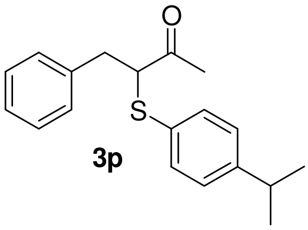
Alcohol **1a** (145 µL, 1 mmol), 4-chlorobenzenethiol **2c** (217 mg, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3n** as a yellowish oil (223 mg, 0.77 mmol, 77%). IR (Neat): ṽ = 3415, 3028, 1706, 1475, 1093, 716 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.26 (s, 3 H, H-1), 3.02 (dd, J = 7 Hz, 14 Hz, 1 H, H-4), 3.20 (dd, J = 9.0 Hz, 14.5 Hz, 1 H, H-4), 3.92 (t, J = 6.5, 1 H, H-3), 7.23–7.36 (m, 9 H, H-arom) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.7, 36.4, 58.6, 126.8, 128.6, 129.0, 129.3, 130.9, 134.4, 134.6, 137.7, 203.8 ppm. HRMS: calcd. for $C_{16}H_{15}ClNaOS$ 313.0430; found 313.0424.

3-((4-Fluorophenyl)thio)-4-phenylbutan-2-one (3o):



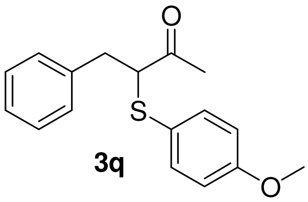
Alcohol **1a** (145 µL, 1 mmol), 4-fluorobenzenethiol **2d** (160 µL, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3o** as a yellowish oil (248 mg, 0.90 mmol, 90%). IR (Neat): ṽ = 3030, 1706, 1488, 1222, 829 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 3 H, H-1), 3.00 (dd, J = 6.4 Hz, 14 Hz, 1 H, H-4), 3.17 (dd, J = 8.4 Hz, 14 Hz, 1 H, H-4), 3.85 (t, J = 6.4, 1 H, H-3), 7.02 (m, 2 H, H-arom), 7.20-7.38 (m, 7 H, H-arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8, 36.4, 58.09, 116.1, 116.4, 126.8, 127.2, 128.5, 129.0, 136.0, 136.1, 137.9, 161.8, 164.3, 203.7 ppm. HRMS: calcd. for $C_{16}H_{15}FNaOS$ 297.0725; found 297.0720.

3-((4-Isopropylphenyl)thio)-4-phenylbutan-2-one (3p):



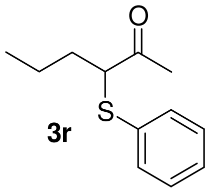
Alcohol **1a** (145 μL, 1 mmol), 4-isopropylbenzenethiol **2e** (233 μL, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3p** as reddish yellow oil (217 mg, 0.73 mmol, 73%). IR (Neat): ῡ = 2961, 2924, 1705, 1350, 833, 709 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22–1.30 (m, 6 H, H-methyl), 2.25 (s, 3 H, H-1), 2.89–3.00 (m, 1 H, C<u>*H*</u>(CH_3)$_2$), 3.04 (dd, *J* = 8.4 Hz, 14.4 Hz, 1 H, H-4), 3.21 (dd, *J* = 8.4 Hz, 14.4 Hz, 1 H, H-4), 3.90 (t, *J* = 7.2, 1 H, H-3), 7.09–7.34 (m, 9 H, H-arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.1 24.2, 28.1, 34.1, 36.9, 59.2, 127, 127.5, 127.6, 128.8, 129.4, 129.5, 133.9, 138.5, 149.7, 204.5 ppm. HRMS: calcd. for $C_{19}H_{22}NaOS$ 321.1289; found 321.1284.

3-((4-Methoxyphenyl)thio)-4-phenylbutan-2-one (3q):[2]



Alcohol **1a** (145 μL, 1 mmol), 4-methoxybenzenethiol **2f** (184 μL, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3q** as a reddish yellow oil (182 mg, 0.64 mmol, 64%). IR (Neat): ῡ = 2988, 2901, 1705, 1492, 1245, 827, 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (d, *J* = 2 Hz, 3 H, H-1), 2.97 (dd, *J* = 6.8, 16 Hz, 1 H, H-4), 3.13 (dd, *J* = 8.8 Hz, 14.4 Hz, 1 H, H-4), 3.78–3.80 (m, 1 H, H-3), 3.81 (s, 3 H, H-methoxy), 6.84–6.88 (m, 2 H, H-arom), 7.20–7.34 (m, 7 H, H-arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.1, 36.2, 55.2, 59, 114.6, 122.1, 126.6, 128.4, 129.0, 136.3, 138.2, 160.3, 203.8 ppm.

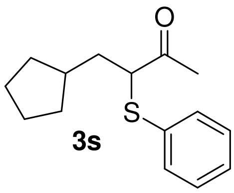
3-(Phenylthio)hexan-2-one (3r):[1]



3r

Alcohol **1m** (324 μL, 3 mmol), benzenethiol **2a** (103 μL, 1 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3r** as a yellowish oil (139 mg, 0.67 mmol, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96 (t, J = 7.2 Hz, 3 H, H-6), 1.38–1.60 (m, 2 H, H-5), 1.64–1.86 (m, 2 H, H-4), 2.26 (s, 3 H, H-1), 3.65 (t, J = 7.5 Hz, 1 H, H-3), 7.24–7.44 (m, 5 H, H-arom) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 20.8, 26.6, 32.7, 57.8, 128.1, 129.3, 132.4, 133.4, 205.8 ppm.

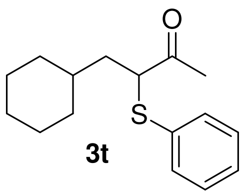
4-Cyclopentyl-3-(phenylthio)butan-2-one (3s):[1]



3s

Alcohol **1n** (138 mg, 1 mmol), benzenethiol **2a** (308 μL, 3 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3s** as a yellowish oil (178 mg, 0.73 mmol, 73%). IR (Neat): ῦ = 2947, 1705, 1353, 1209, 1025, 739, 690 cm-1. ^{1}H NMR (400 MHz, CDCl3): δ = 1.08–1.18 (m, 2 H, H-aliphatic), 1.50–1.68 (m, 4 H, H-aliphatic), 1.71–1.90 (m, 4 H, H-aliphatic), 1.93–2.26 (m, 1 H, H-aliphatic), 2.26 (s, 3 H, H-1), 3.69 (t, J = 7.6 Hz, 1 H, H-3), 7.23–7.35 (m, 3 H, H-arom), 7.36–7.39 (m, 2 H, H-arom) ppm. ^{13}C NMR (125 MHz, CDCl3): δ = 24.9, 25.0, 26.2, 36.5, 37.7, 57.0, 127.7, 129.0, 132.1, 133.2, 205.6 ppm. HRMS: calcd. for $C_{15}H_{20}NaOS$ 271.1133; found 271.1131.

4-Cyclohexyl-3-(phenylthio)butan-2-one (3t):

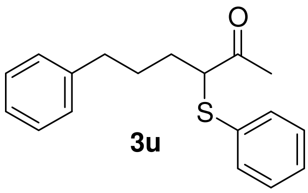


3t

Alcohol **1o** (138 mg, 1 mmol), benzenethiol **2a** (308 μL, 3 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** to obtain **3t** as a yellowish oil (196 mg, 0.75 mmol, 75%). IR (Neat): ῦ = 2920, 1703, 1439, 1209, 1025, 739, 689 cm-1. ^{1}H

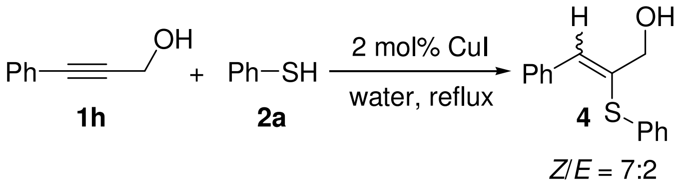
NMR (400 MHz, $CDCl_3$): δ = 0.90–0.96 (m, 2 H, H-aliphatic), 1.17–1.26 (m, 3 H), 1.40–1.70 (m, 8 H, H-aliphatic), 2.25 (s, 3 H, H-1), 3.76 (t, J = 7.6 Hz, 1 H, H-3), 7.25–7.36 (m, 5 H, H-arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.0, 26.1, 26.2, 26.4, 33.1, 35.3, 37.8, 55.3, 127.7, 129.0, 132.0, 133.0, 133.2, 205.5 ppm. HRMS: calcd. for $C_{16}H_{22}NaOS$ 285.1289; found 285.1284.

6-Phenyl-3-(phenylthio)hexan-2-one (3u):

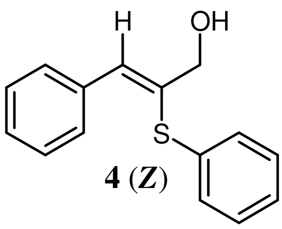


Alcohol **1p** (174 mg, 1 mmol), benzenethiol **2a** (308 µL, 3 mmol) and the catalyst CuI (4 mg, 2 mol%) in water (2.5 mL) were treated as described for **3a** for 72 h to obtain **3u** as a yellowish oil (229 mg, 0.81 mmol, 81%). IR (Neat): ṽ = 2988, 2937, 1703, 1354,740, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.73–1.78 (m, 2 H, H-5), 1.85–1.90 (m, 2 H, H-4), 2.24 (s, 3 H, H-1), 2.67 (t, J = 6.8, 2 H, H-6), 3.63 (t, J = 6.4 Hz, 1 H, H-3), 7.18–7.38 (m, 10 H, H-arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.5, 28.9, 29.7, 35.4, 57.6, 125.9, 127.9, 128.3, 129, 132.4, 132.9, 141.5, 205 ppm. HRMS: calcd. for $C_{18}H_{20}NaOS$ 307.1133; found 307.1127.

E. Isolation and characterization of intermediate 4.



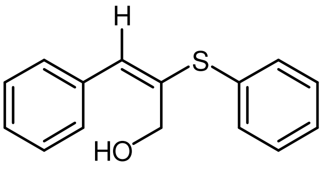
(Z)-3-Phenyl-2-(phenylthio)prop-2-en-1-ol (4-Z):[1]



4 (**Z**)

Alcohol **1h** (125 µL, 1 mmol), benzenethiol **2a** (154 µL, 1.5 mmol) and the catalyst CuI (4 mg, 2 mol%) were treated in water as described for **3f** for 18 h. Column chromatographic purification afforded the *E*- and *Z*- isomers of **4** (100 mg., 0.41 mmol, 41%) as a colorless oil (*Z* : *E* = 7 : 2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (bs, 1 H, H-alcohol), 4.23 (s, 2 H, H-1), 7.20 (s, 1 H, H-3), 7.26–7.43 (m, 8 H, H-aromatic), 7.68–7.70 (m, 2 H, H-arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 66.3, 126.9, 127.8, 128.1, 129.1, 129.2, 129.3, 130.3, 133.2, 133.3, 133.4, ppm.

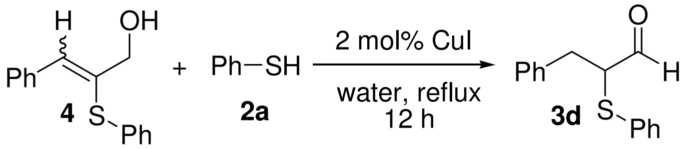
(E)-3-Phenyl-2-(phenylthio)prop-2-en-1-ol (4-E):[1]



4 (***E***)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.09 (brs, 1 H, H-alcohol), 4.37 (s, 2 H, H-1), 6.96 (s, 1 H, H-3), 7.28–7.39 (m, 8 H, H-arom), 7.49–7.51 (m, 2 H, H-arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 60.3, 127.6, 127.7, 128.1, 128.5, 128.7, 128.8, 129.1, 129.3 129.4, 131.5, 135.5, 135.9, 136.7 ppm.

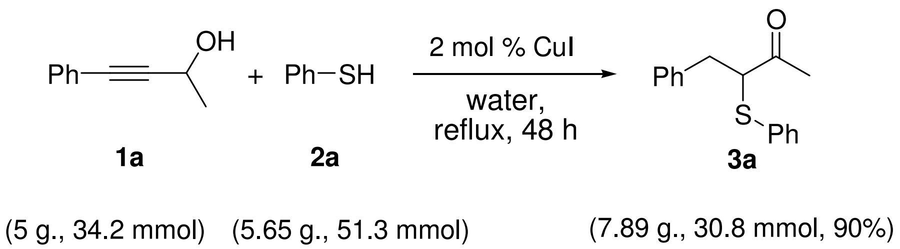
F. Cu-catalyzed conversion of intermediate 4 to product 3d in presence of 2a.[a]



Entry	Amount of **2a**	Yield[b]
1	0 mol%	N.R.
2	10 mol%	>95%

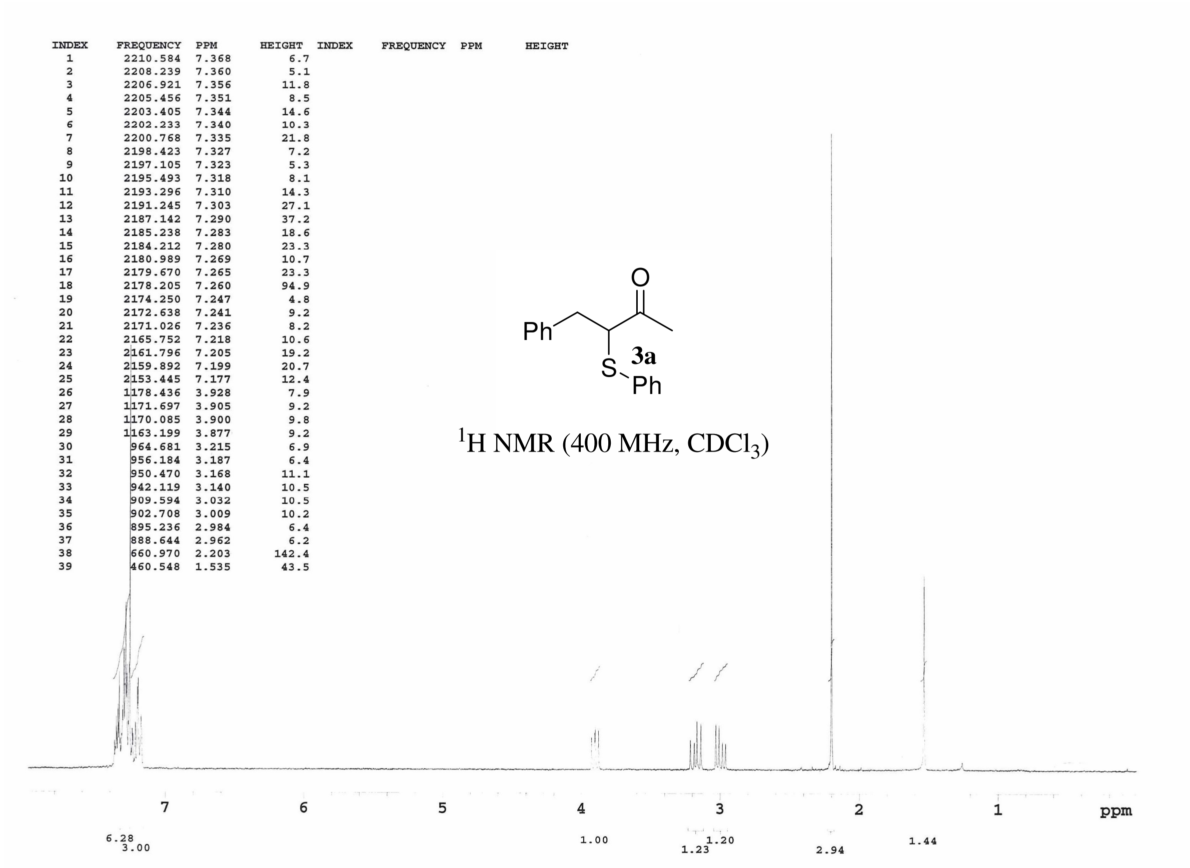
[a] Reaction conditions: **4** (0.5 mmol), **2a** (x mmol) and CuI (2 mol%), water (2.0 mL) for 12 h at reflux. [b] Conversion based on ^{1}H NMR analysis of the crude reaction mixture.

G. Large scale experiment.



CuI (130 mg, 0.68 mmol, 2 mol%) was weighed and transferred to a 25 mL vial containing a magnet under nitrogen atmosphere. The cap of the vial was closed tightly. 10 mL of degassed water followed by alcohol **1a** (5 g, 4.98 mL, 34.2 mmol) and benzenethiol **2a** (5.65 g, 5.27 mL, 51.3 mmol) were added to the vial by syringe and was stirred using a magnetic stirrer at reflux for 24 h. After allowing the mixture to cool to room temperature, the reaction mixture was extracted with ethyl acetate (3 × 60 mL). The combined organic phase was washed with water and brine, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica-gel (100–200 mess) column chromatography using 3% (*v/v*) ethyl acetate / pentane solution to afford the desired product **3a** (7.89 g, 30.8 mmol, 90%).

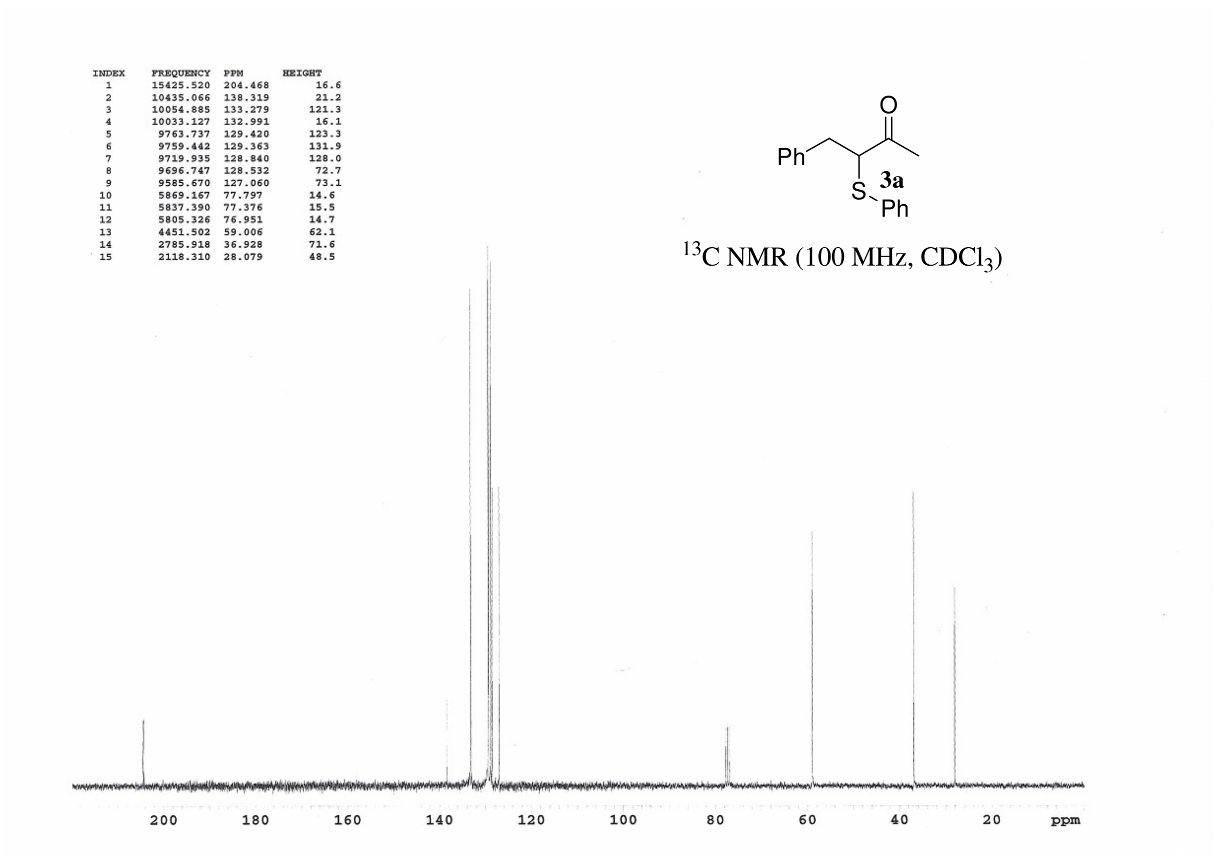
H. Copies of ^{1}H and ^{13}C NMR Spectra of all products.



INDEX	FREQUENCY	PPM	HEIGHT
1	2210.584	7.368	6.7
2	2208.239	7.360	5.1
3	2206.921	7.356	11.8
4	2205.456	7.351	8.5
5	2203.405	7.344	14.6
6	2202.233	7.340	10.3
7	2200.768	7.335	21.8
8	2198.423	7.327	7.2
9	2197.105	7.323	5.3
10	2195.493	7.318	8.1
11	2193.296	7.310	14.3
12	2191.245	7.303	27.1
13	2187.142	7.290	37.2
14	2185.238	7.283	18.6
15	2184.212	7.280	23.3
16	2180.989	7.269	10.7
17	2179.670	7.265	23.3
18	2178.205	7.260	94.9
19	2174.250	7.247	4.8
20	2172.638	7.241	9.2
21	2171.026	7.236	8.2
22	2165.752	7.218	10.6
23	2161.796	7.205	19.2
24	2159.892	7.199	20.7
25	2153.445	7.177	12.4
26	1178.436	3.928	7.9
27	1171.697	3.905	9.2
28	1170.085	3.900	9.8
29	1163.199	3.877	9.2
30	964.681	3.215	6.9
31	956.184	3.187	6.4
32	950.470	3.168	11.1
33	942.119	3.140	10.5
34	909.594	3.032	10.5
35	902.708	3.009	10.2
36	895.236	2.984	6.4
37	888.644	2.962	6.2
38	660.970	2.203	142.4
39	460.548	1.535	43.5

3a

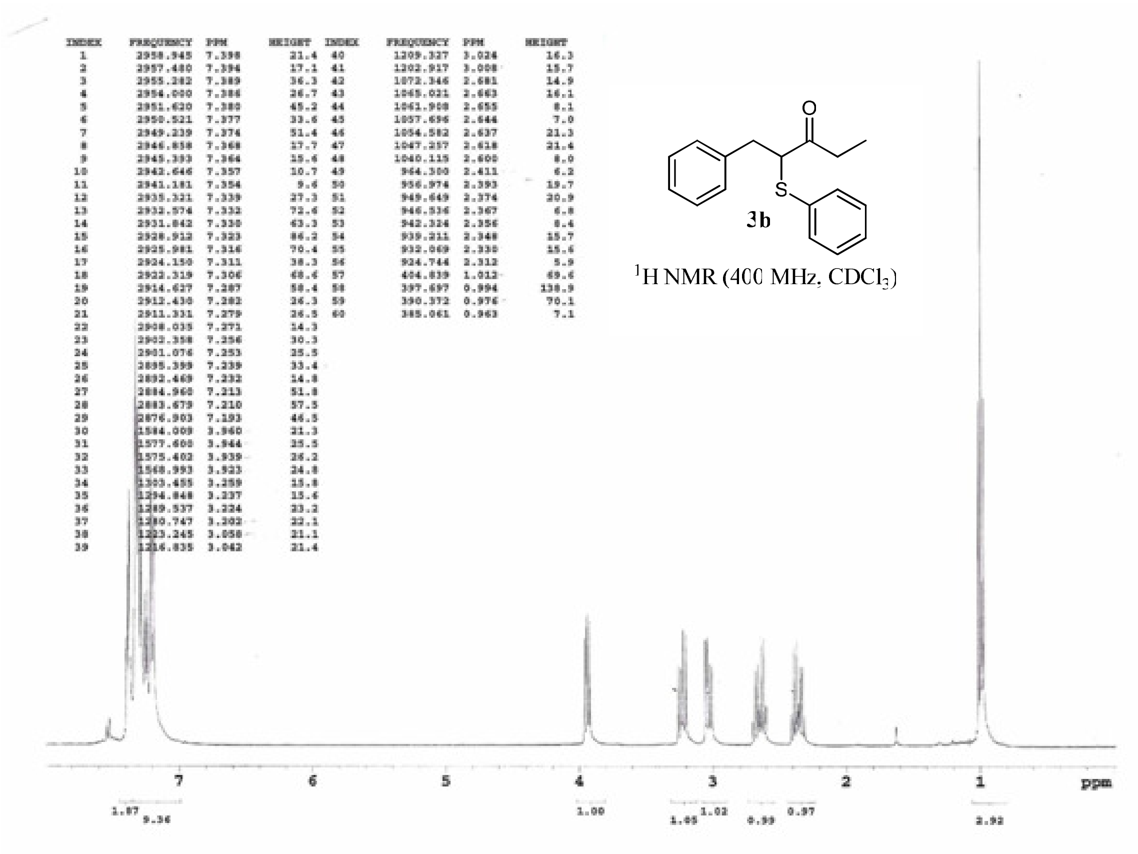
^{1}H NMR (400 MHz, $CDCl_3$)

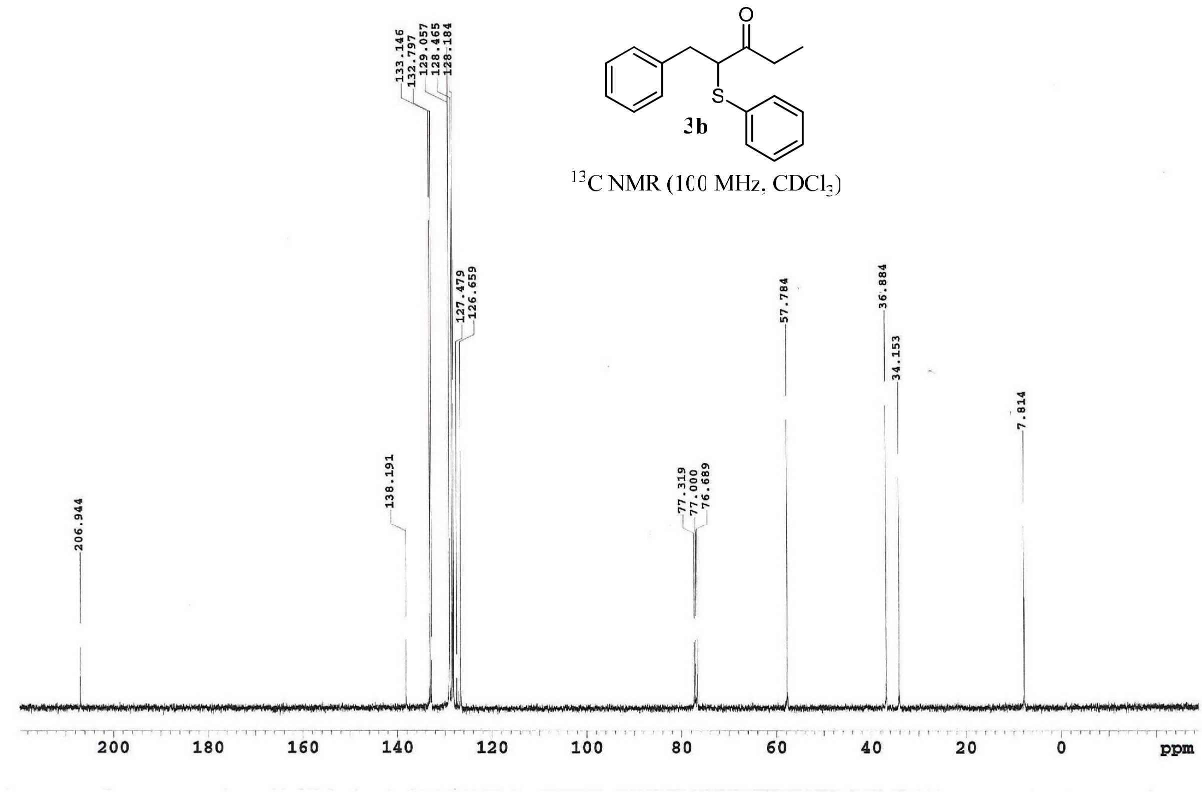


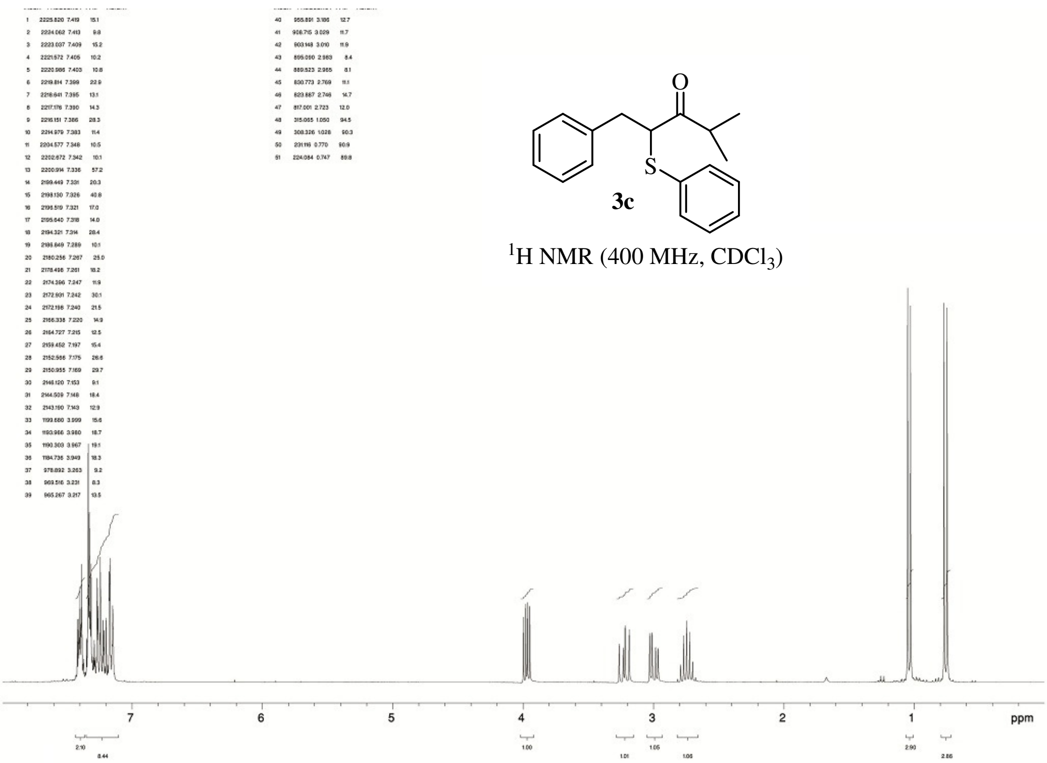
INDEX	FREQUENCY	PPM	HEIGHT
1	15425.520	204.468	16.6
2	10435.066	138.319	21.2
3	10054.885	133.279	121.3
4	10033.127	132.991	16.1
5	9763.737	129.420	123.3
6	9759.442	129.363	131.9
7	9719.935	128.840	128.0
8	9696.747	128.532	72.7
9	9585.670	127.060	73.1
10	5869.167	77.797	14.6
11	5837.390	77.376	15.5
12	5805.326	76.951	14.7
13	4451.502	59.006	62.1
14	2785.918	36.928	71.6
15	2118.310	28.079	48.5

3a

^{13}C NMR (100 MHz, $CDCl_3$)

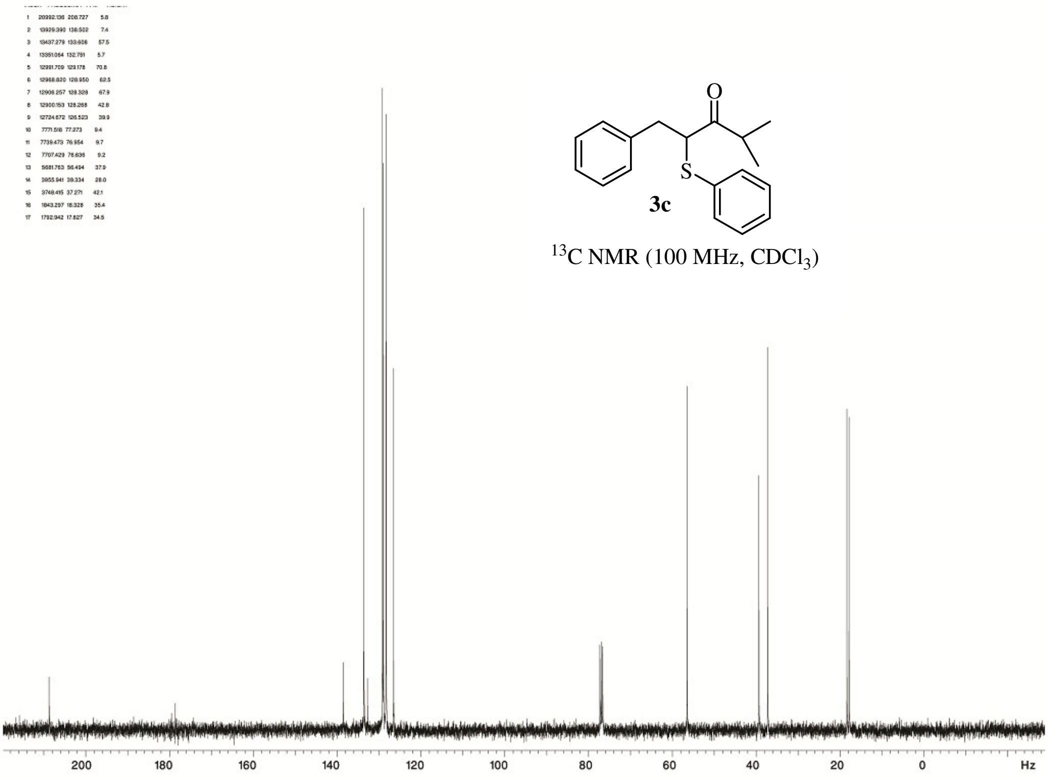

3b
1H NMR (400 MHz, CDCl3)
7
6
5
4
3
2
1
ppm
1.87
9.36
1.00
1.05
1.02
0.99
0.97
2.92


3b
13C NMR (100 MHz, CDCl3)
206.944
138.191
133.146
132.797
129.057
128.465
128.184
127.479
126.659
77.319
77.000
76.689
57.784
36.884
34.153
7.814
200
180
160
140
120
100
80
60
40
20
0
ppm



3c

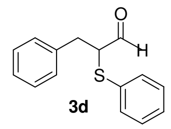
^{1}H NMR (400 MHz, $CDCl_3$)



3c

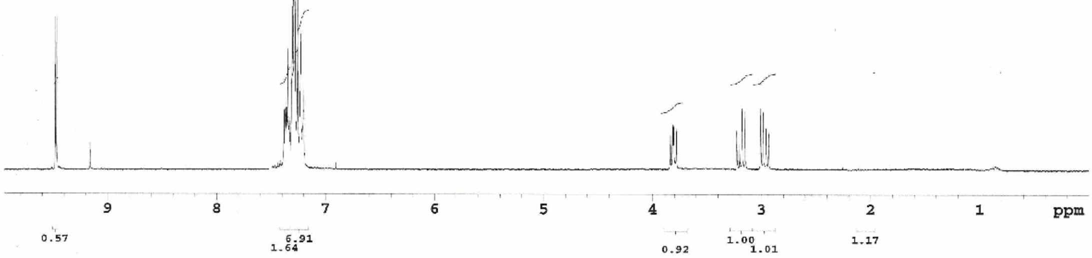
^{13}C NMR (100 MHz, $CDCl_3$)

INDEX	FREQUENCY	PPM	HEIGHT
1	2845.255	9.483	35.4
2	2841.593	9.471	35.3
3	2215.272	7.384	14.2
4	2213.660	7.378	9.5
5	2212.928	7.376	9.7
6	2212.049	7.373	14.4
7	2211.170	7.370	12.8
8	2209.704	7.365	17.0
9	2208.532	7.361	22.6
10	2206.774	7.355	14.7
11	2205.602	7.351	28.1
12	2204.284	7.347	11.7
13	2201.354	7.337	11.0
14	2200.328	7.334	12.3
15	2195.786	7.319	11.6
16	2194.028	7.313	46.3
17	2192.124	7.306	37.8
18	2190.658	7.302	49.7
19	2189.340	7.297	27.4
20	2187.435	7.291	48.0
21	2186.556	7.288	46.6
22	2184.066	7.280	40.7
23	2178.205	7.260	301.9
24	2172.198	7.240	18.3
25	2170.294	7.234	31.6
26	2168.682	7.228	33.2
27	2166.338	7.220	9.8
28	2162.089	7.206	18.7
29	1247.734	4.159	8.1
30	1240.555	4.135	23.7
31	1233.376	4.111	23.8
32	1226.344	4.087	8.7
33	1152.944	3.843	8.6
34	1149.281	3.831	8.5
35	1146.058	3.820	10.4
36	1144.886	3.816	10.9
37	1142.395	3.808	10.5
38	1141.369	3.804	10.7
39	1138.000	3.793	10.2
40	1134.484	3.781	10.2
41	968.637	3.228	9.9
42	960.579	3.202	9.1
43	954.133	3.180	14.7
44	946.221	3.154	14.0
45	902.708	3.009	14.6
46	895.822	2.986	14.0
47	888.204	2.960	10.1
48	881.465	2.938	9.4
49	613.648	2.045	108.1
50	385.096	1.284	30.2
51	378.064	1.260	60.3
52	370.885	1.236	28.5

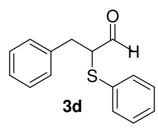


3d

[1]H NMR (400 MHz, $CDCl_3$)

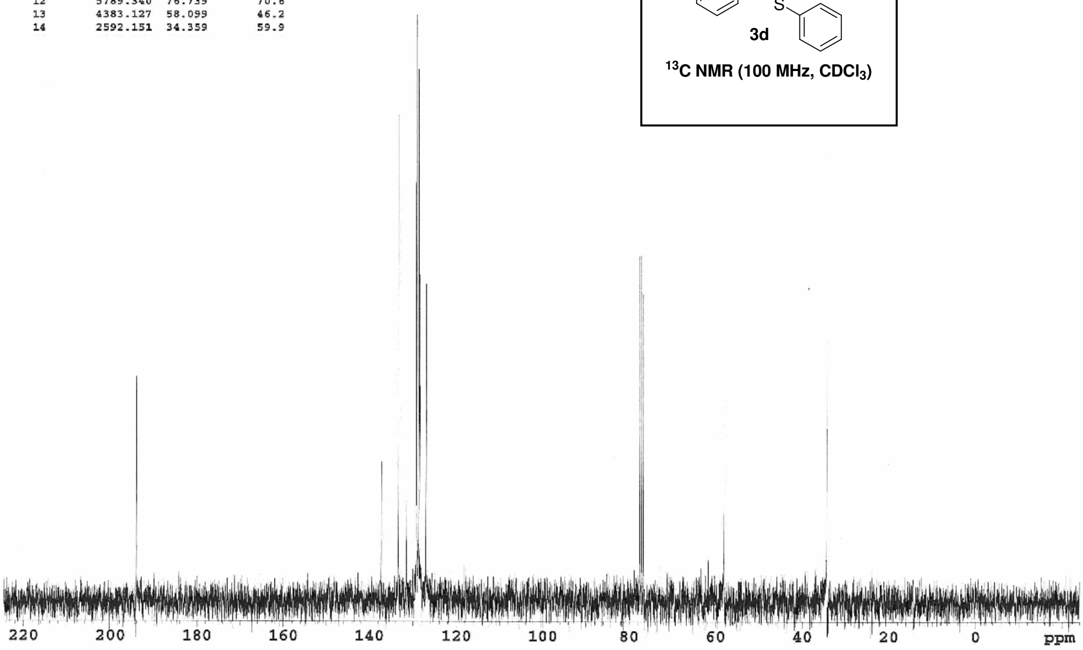


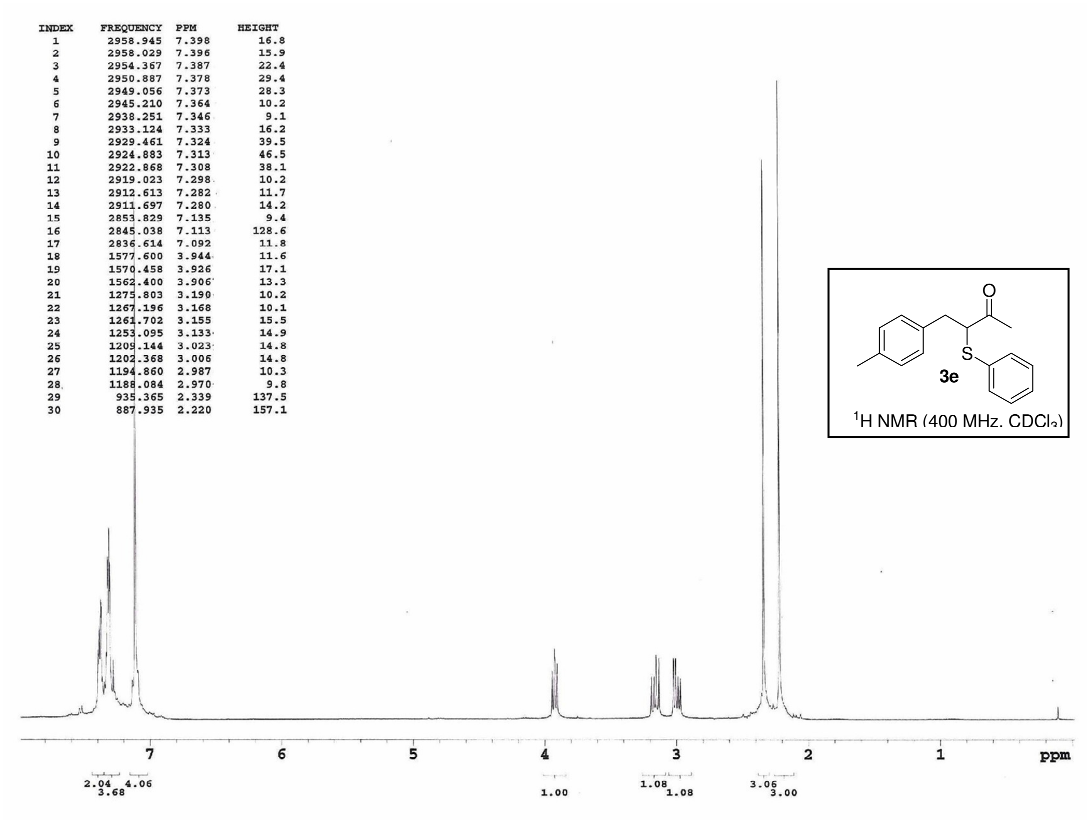
INDEX	FREQUENCY	PPM	HEIGHT
1	14649.171	194.178	51.5
2	10358.388	137.302	31.8
3	10063.805	133.398	112.1
4	9924.959	131.557	22.7
5	9756.339	129.322	129.8
6	9749.754	129.235	135.0
7	9715.114	128.776	122.6
8	9697.079	128.537	75.0
9	9587.719	127.087	73.0
10	5853.467	77.589	79.3
11	5821.404	77.164	79.4
12	5789.340	76.739	70.6
13	4383.127	58.099	46.2
14	2592.151	34.359	59.9



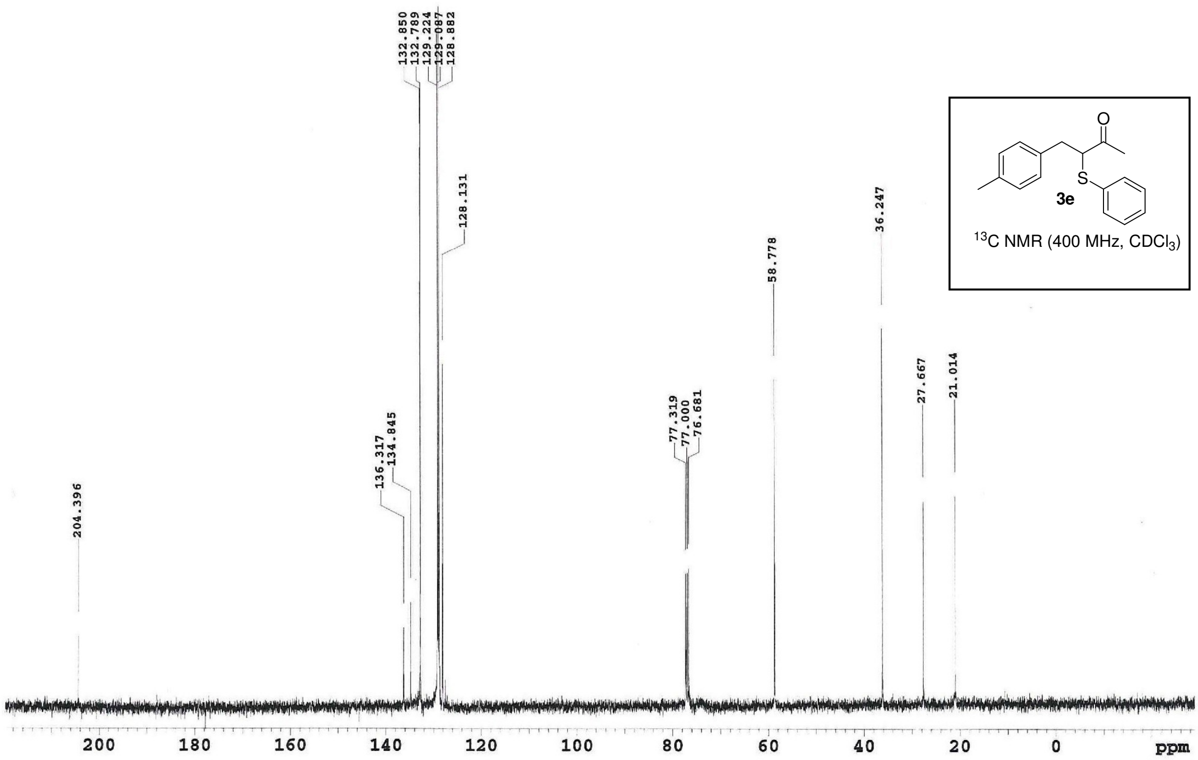
3d

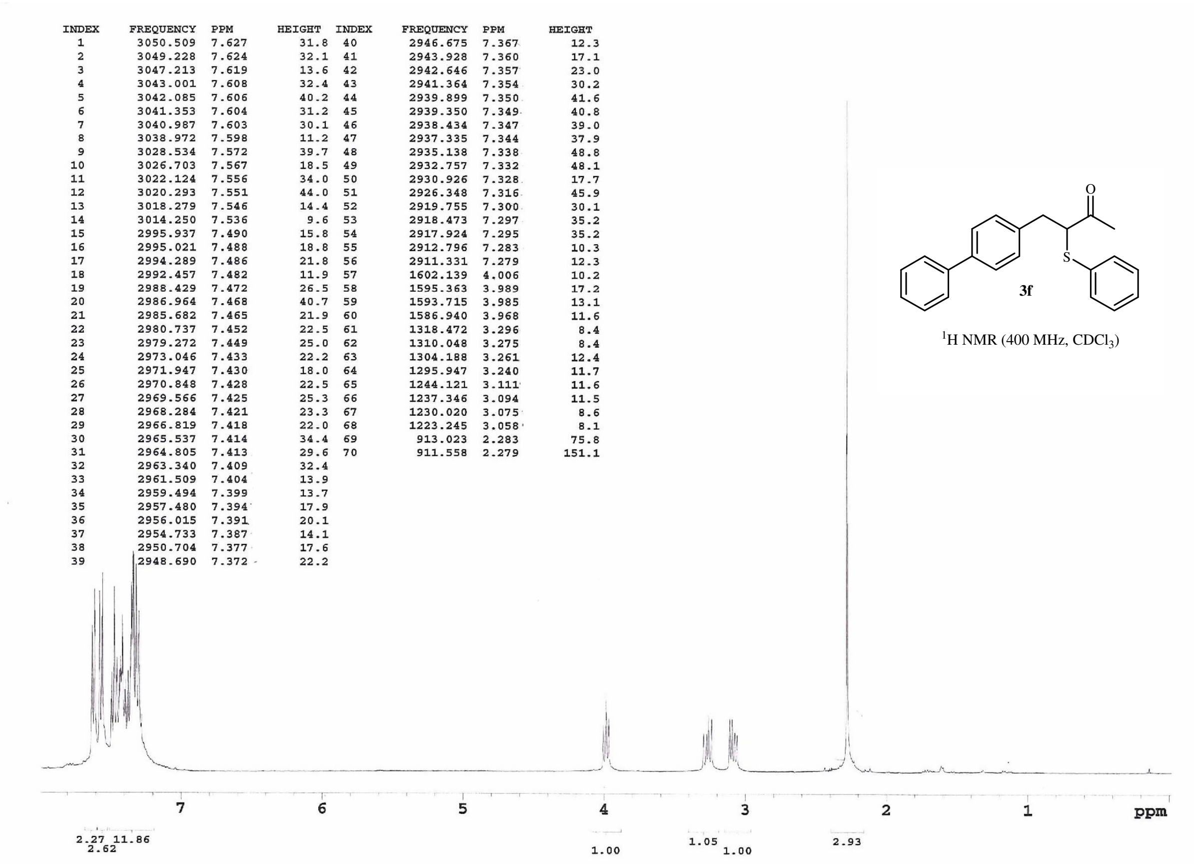
[13]C NMR (100 MHz, $CDCl_3$)





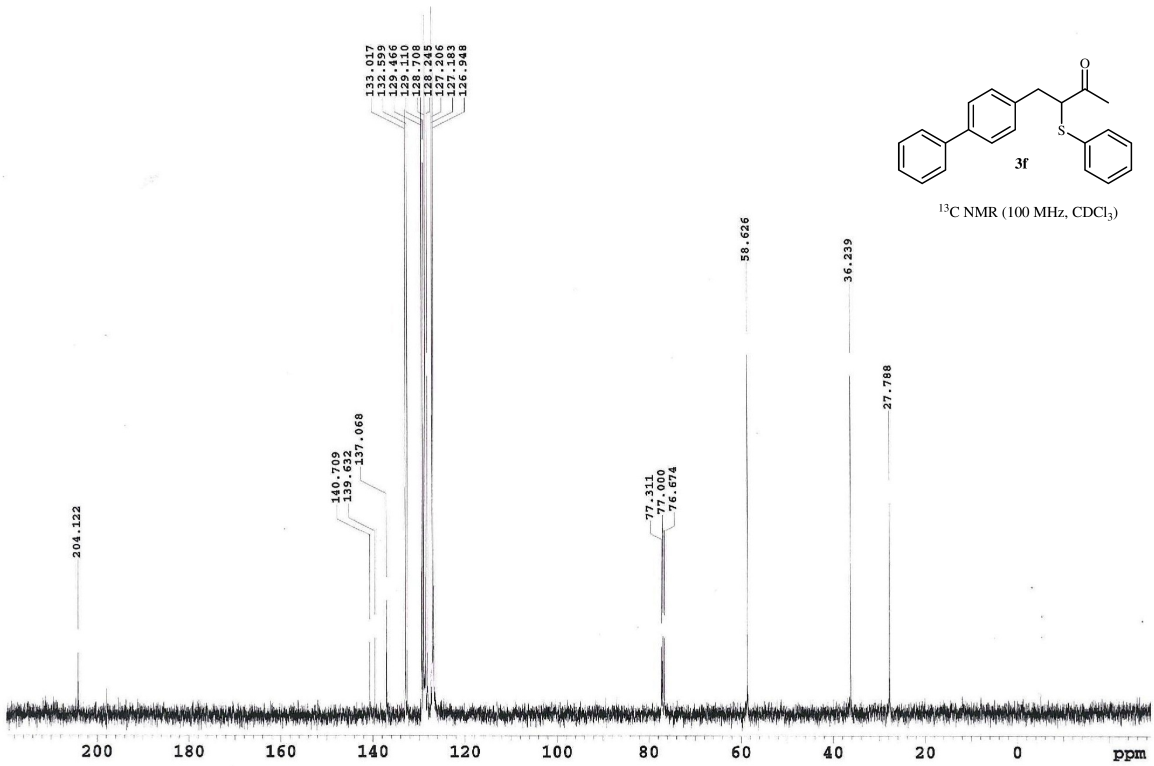
INDEX	FREQUENCY	PPM	HEIGHT
1	2958.945	7.398	16.8
2	2958.029	7.396	15.9
3	2954.367	7.387	22.4
4	2950.887	7.378	29.4
5	2949.056	7.373	28.3
6	2945.210	7.364	10.2
7	2938.251	7.346	9.1
8	2933.124	7.333	16.2
9	2929.461	7.324	39.5
10	2924.883	7.313	46.5
11	2922.868	7.308	38.1
12	2919.023	7.298	10.2
13	2912.613	7.282	11.7
14	2911.697	7.280	14.2
15	2853.829	7.135	9.4
16	2845.038	7.113	128.6
17	2836.614	7.092	11.8
18	1577.600	3.944	11.6
19	1570.458	3.926	17.1
20	1562.400	3.906	13.3
21	1275.803	3.190	10.2
22	1267.196	3.168	10.1
23	1261.702	3.155	15.5
24	1253.095	3.133	14.9
25	1209.144	3.023	14.8
26	1202.368	3.006	14.8
27	1194.860	2.987	10.3
28	1188.084	2.970	9.8
29	935.365	2.339	137.5
30	887.935	2.220	157.1



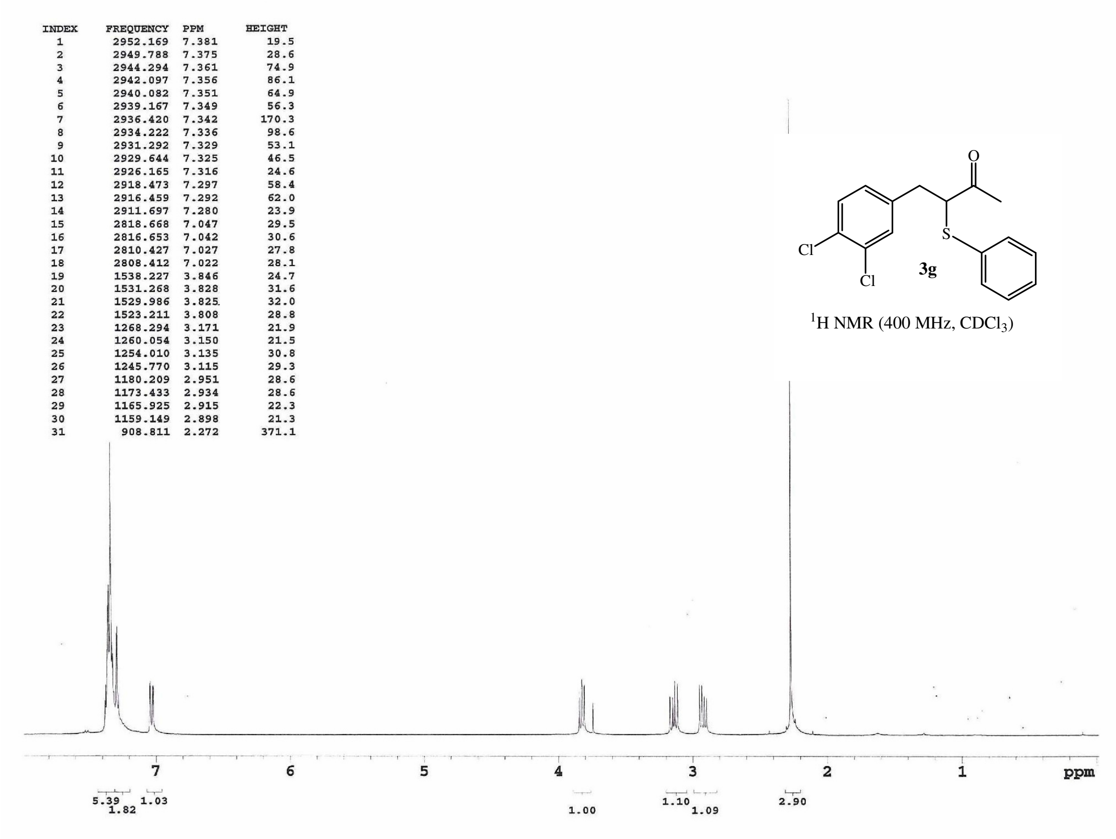


INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3050.509	7.627	31.8	40	2946.675	7.367	12.3
2	3049.228	7.624	32.1	41	2943.928	7.360	17.1
3	3047.213	7.619	13.6	42	2942.646	7.357	23.0
4	3043.001	7.608	32.4	43	2941.364	7.354	30.2
5	3042.085	7.606	40.2	44	2939.899	7.350	41.6
6	3041.353	7.604	31.2	45	2939.350	7.349	40.8
7	3040.987	7.603	30.1	46	2938.434	7.347	39.0
8	3038.972	7.598	11.2	47	2937.335	7.344	37.9
9	3028.534	7.572	39.7	48	2935.138	7.338	48.8
10	3026.703	7.567	18.5	49	2932.757	7.332	48.1
11	3022.124	7.556	34.0	50	2930.926	7.328	17.7
12	3020.293	7.551	44.0	51	2926.348	7.316	45.9
13	3018.279	7.546	14.4	52	2919.755	7.300	30.1
14	3014.250	7.536	9.6	53	2918.473	7.297	35.2
15	2995.937	7.490	15.8	54	2917.924	7.295	35.2
16	2995.021	7.488	18.8	55	2912.796	7.283	10.3
17	2994.289	7.486	21.8	56	2911.331	7.279	12.3
18	2992.457	7.482	11.9	57	1602.139	4.006	10.2
19	2988.429	7.472	26.5	58	1595.363	3.989	17.2
20	2986.964	7.468	40.7	59	1593.715	3.985	13.1
21	2985.682	7.465	21.9	60	1586.940	3.968	11.6
22	2980.737	7.452	22.5	61	1318.472	3.296	8.4
23	2979.272	7.449	25.0	62	1310.048	3.275	8.4
24	2973.046	7.433	22.2	63	1304.188	3.261	12.4
25	2971.947	7.430	18.0	64	1295.947	3.240	11.7
26	2970.848	7.428	22.5	65	1244.121	3.111	11.6
27	2969.566	7.425	25.3	66	1237.346	3.094	11.5
28	2968.284	7.421	23.3	67	1230.020	3.075	8.6
29	2966.819	7.418	22.0	68	1223.245	3.058	8.1
30	2965.537	7.414	34.4	69	913.023	2.283	75.8
31	2964.805	7.413	29.6	70	911.558	2.279	151.1
32	2963.340	7.409	32.4				
33	2961.509	7.404	13.9				
34	2959.494	7.399	13.7				
35	2957.480	7.394	17.9				
36	2956.015	7.391	20.1				
37	2954.733	7.387	14.1				
38	2950.704	7.377	17.6				
39	2948.690	7.372	22.2				

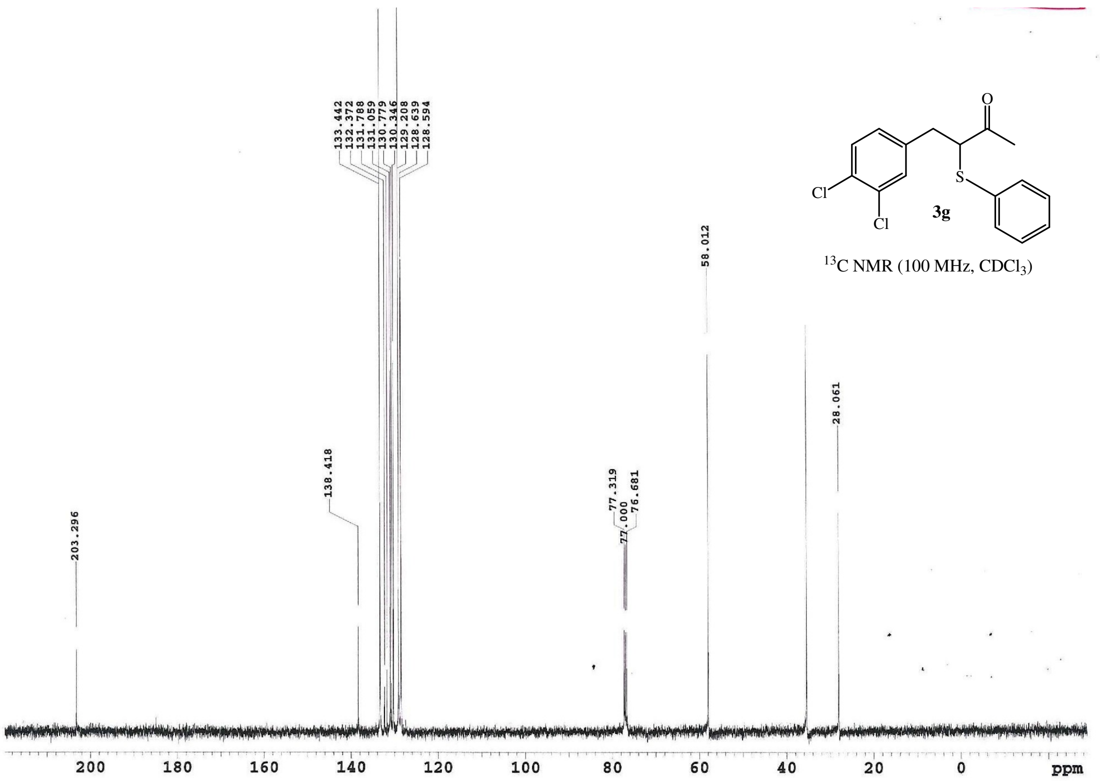
[1]H NMR (400 MHz, $CDCl_3$)

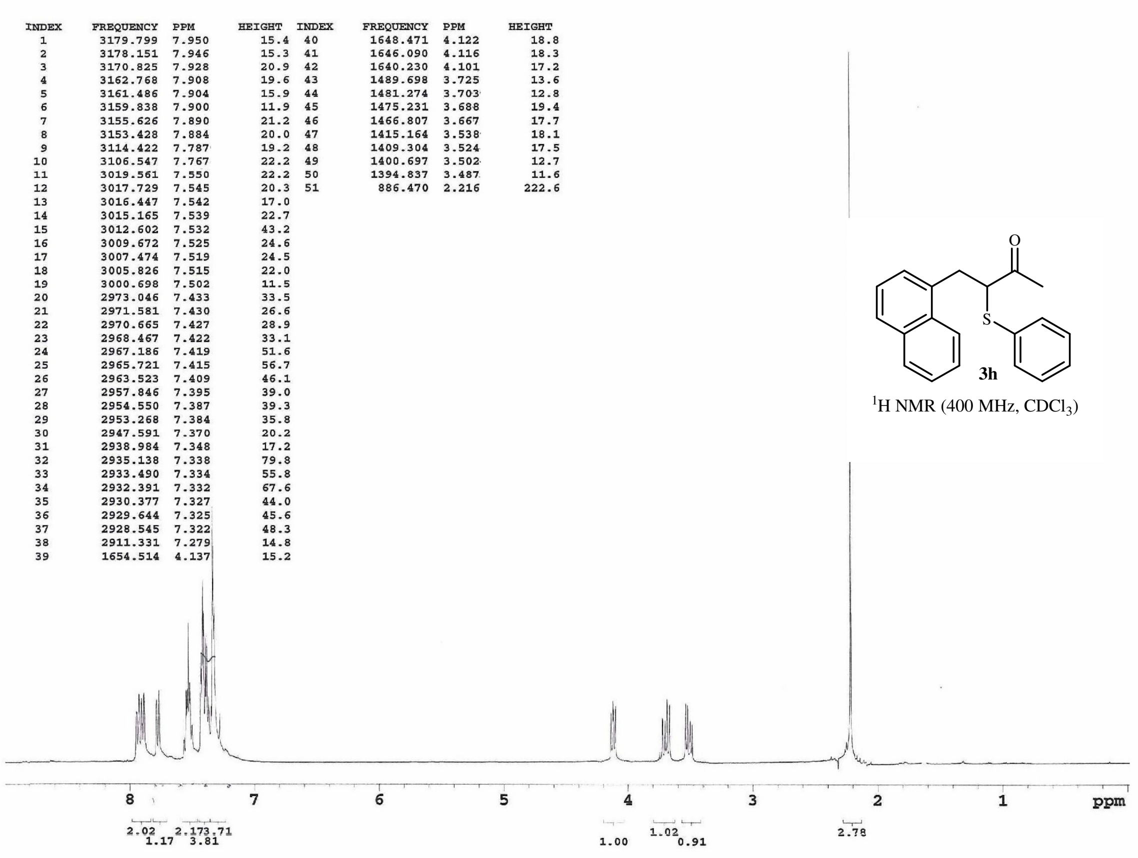


[13]C NMR (100 MHz, $CDCl_3$)



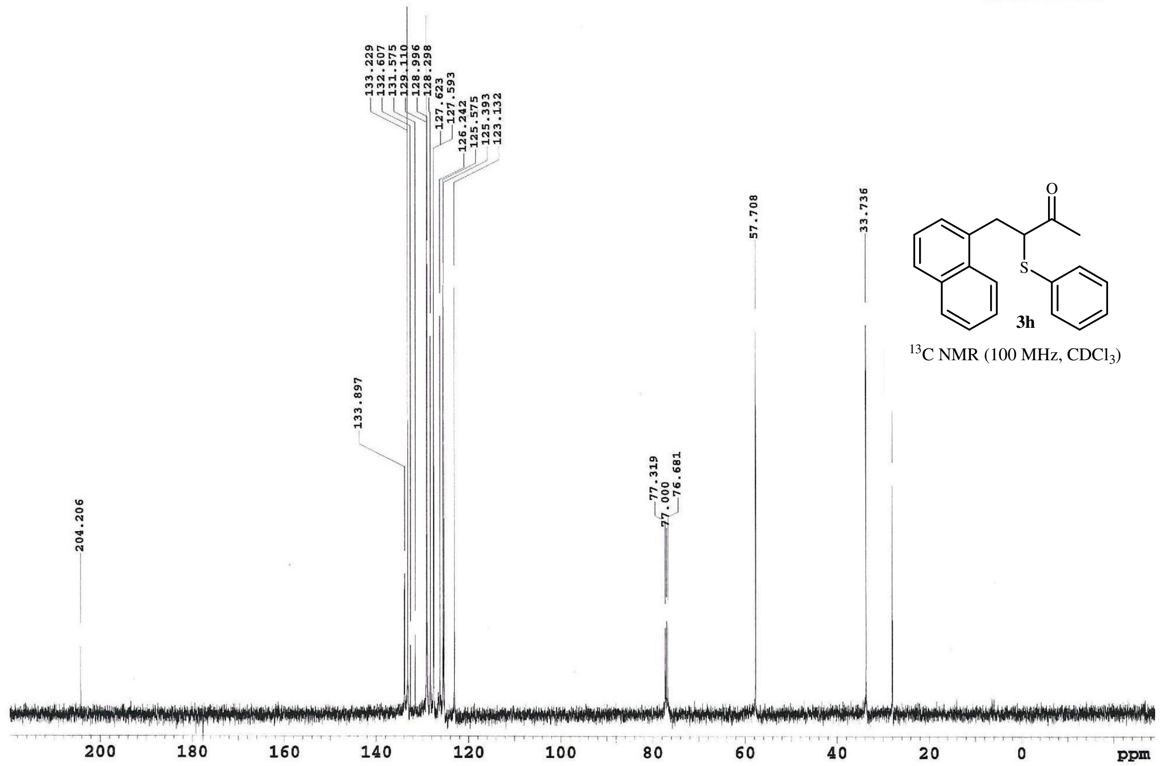
INDEX	FREQUENCY	PPM	HEIGHT
1	2952.169	7.381	19.5
2	2949.788	7.375	28.6
3	2944.294	7.361	74.9
4	2942.097	7.356	86.1
5	2940.082	7.351	64.9
6	2939.167	7.349	56.3
7	2936.420	7.342	170.3
8	2934.222	7.336	98.6
9	2931.292	7.329	53.1
10	2929.644	7.325	46.5
11	2926.165	7.316	24.6
12	2918.473	7.297	58.4
13	2916.459	7.292	62.0
14	2911.697	7.280	23.9
15	2818.668	7.047	29.5
16	2816.653	7.042	30.6
17	2810.427	7.027	27.8
18	2808.412	7.022	28.1
19	1538.227	3.846	24.7
20	1531.268	3.828	31.6
21	1529.986	3.825	32.0
22	1523.211	3.808	28.8
23	1268.294	3.171	21.9
24	1260.054	3.150	21.5
25	1254.010	3.135	30.8
26	1245.770	3.115	29.3
27	1180.209	2.951	28.6
28	1173.433	2.934	28.6
29	1165.925	2.915	22.3
30	1159.149	2.898	21.3
31	908.811	2.272	371.1



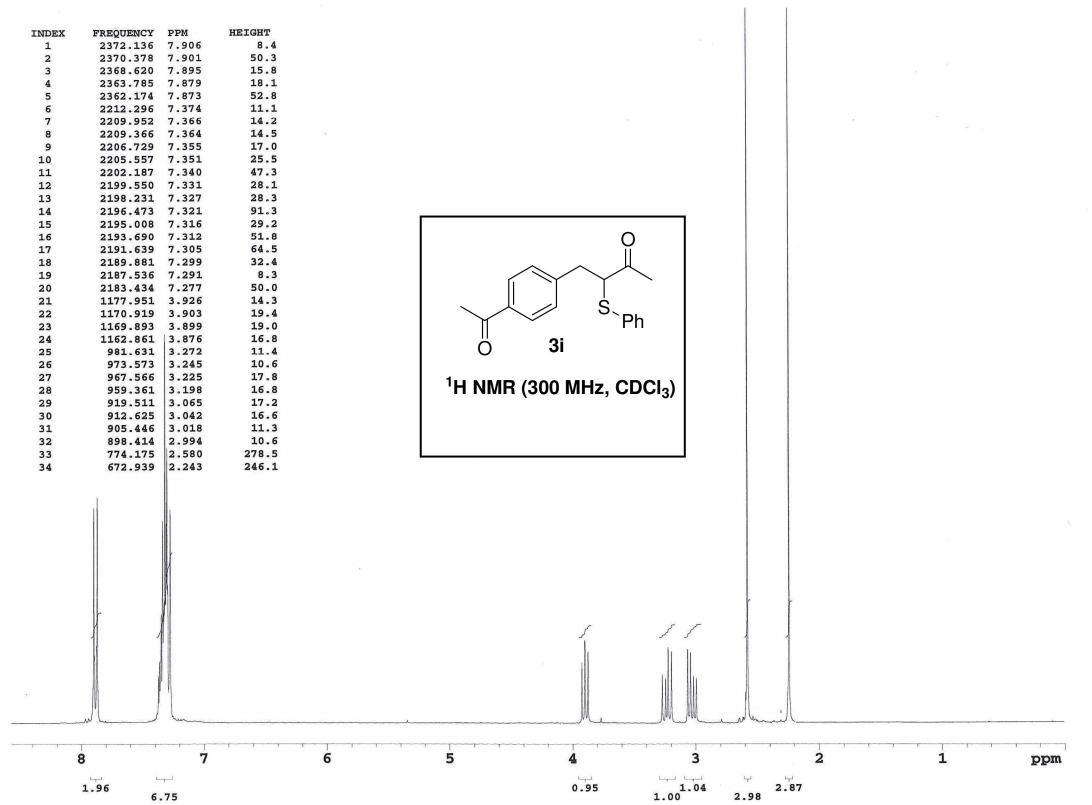


INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3179.799	7.950	15.4	40	1648.471	4.122	18.8
2	3178.151	7.946	15.3	41	1646.090	4.116	18.3
3	3170.825	7.928	20.9	42	1640.230	4.101	17.2
4	3162.768	7.908	19.6	43	1489.698	3.725	13.6
5	3161.486	7.904	15.9	44	1481.274	3.703	12.8
6	3159.838	7.900	11.9	45	1475.231	3.688	19.4
7	3155.626	7.890	21.2	46	1466.807	3.667	17.7
8	3153.428	7.884	20.0	47	1415.164	3.538	18.1
9	3114.422	7.787	19.2	48	1409.304	3.524	17.5
10	3106.547	7.767	22.2	49	1400.697	3.502	12.7
11	3019.561	7.550	22.2	50	1394.837	3.487	11.6
12	3017.729	7.545	20.3	51	886.470	2.216	222.6
13	3016.447	7.542	17.0				
14	3015.165	7.539	22.7				
15	3012.602	7.532	43.2				
16	3009.672	7.525	24.6				
17	3007.474	7.519	24.5				
18	3005.826	7.515	22.0				
19	3000.698	7.502	11.5				
20	2973.046	7.433	33.5				
21	2971.581	7.430	26.6				
22	2970.665	7.427	28.9				
23	2968.467	7.422	33.1				
24	2967.186	7.419	51.6				
25	2965.721	7.415	56.7				
26	2963.523	7.409	46.1				
27	2957.846	7.395	39.0				
28	2954.550	7.387	39.3				
29	2953.268	7.384	35.8				
30	2947.591	7.370	20.2				
31	2938.984	7.348	17.2				
32	2935.138	7.338	79.8				
33	2933.490	7.334	55.8				
34	2932.391	7.332	67.6				
35	2930.377	7.327	44.0				
36	2929.644	7.325	45.6				
37	2928.545	7.322	48.3				
38	2911.331	7.279	14.8				
39	1654.514	4.137	15.2				

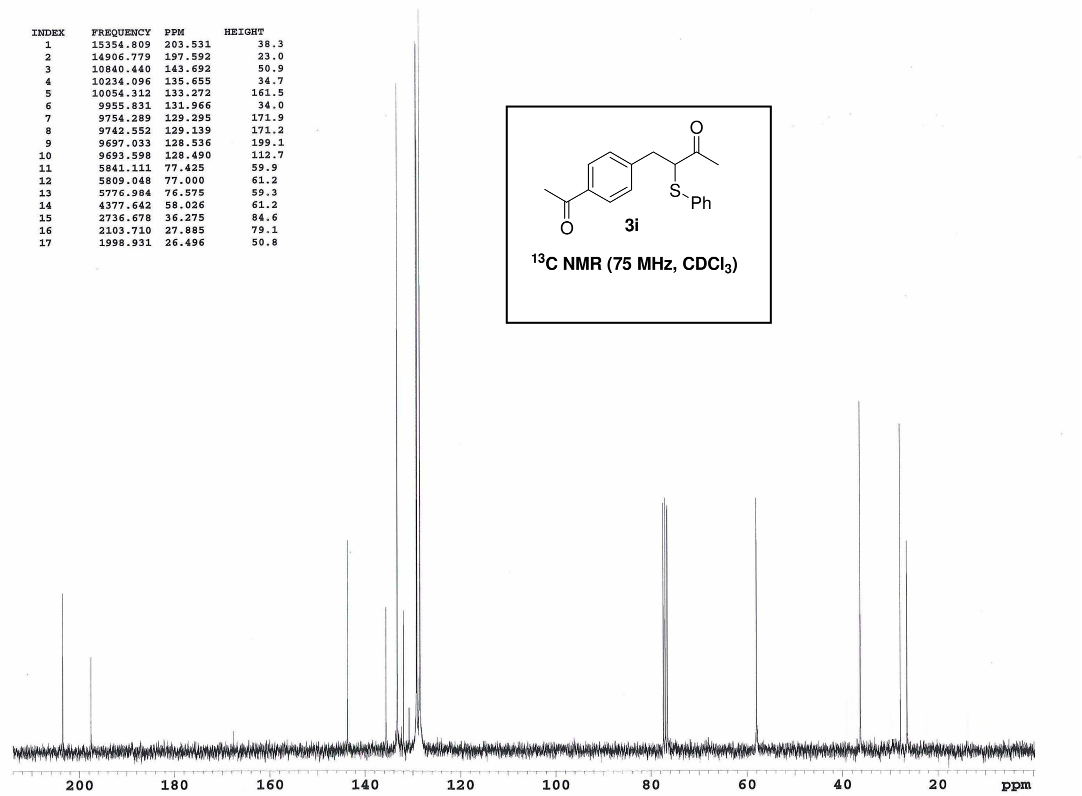
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

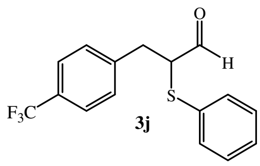


INDEX	FREQUENCY	PPM	HEIGHT
1	2372.136	7.906	8.4
2	2370.378	7.901	50.3
3	2368.620	7.895	15.8
4	2363.785	7.879	18.1
5	2362.174	7.873	52.8
6	2212.296	7.374	11.1
7	2209.952	7.366	14.2
8	2209.366	7.364	14.5
9	2206.729	7.355	17.0
10	2205.557	7.351	25.5
11	2202.187	7.340	47.3
12	2199.550	7.331	28.1
13	2198.231	7.327	28.3
14	2196.473	7.321	91.3
15	2195.008	7.316	29.2
16	2193.690	7.312	51.8
17	2191.639	7.305	64.5
18	2189.881	7.299	32.4
19	2187.536	7.291	8.3
20	2183.434	7.277	50.0
21	1177.951	3.926	14.3
22	1170.919	3.903	19.4
23	1169.893	3.899	19.0
24	1162.861	3.876	16.8
25	981.631	3.272	11.4
26	973.573	3.245	10.6
27	967.566	3.225	17.8
28	959.361	3.198	16.8
29	919.511	3.065	17.2
30	912.625	3.042	16.6
31	905.446	3.018	11.3
32	898.414	2.994	10.6
33	774.175	2.580	278.5
34	672.939	2.243	246.1



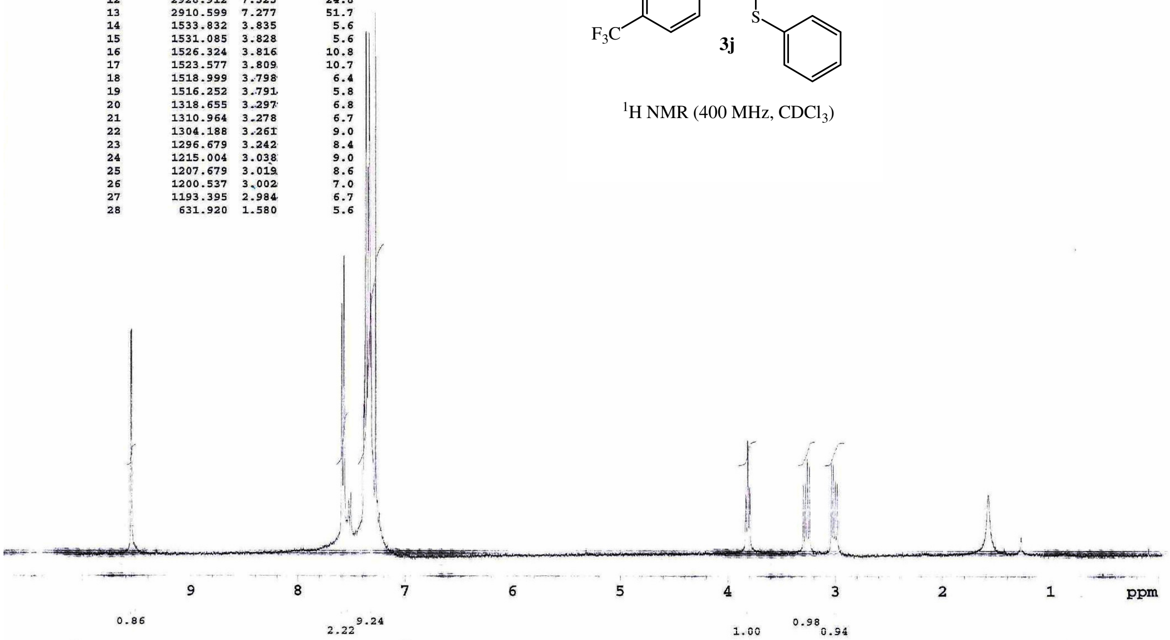
INDEX	FREQUENCY	PPM	HEIGHT
1	15354.809	203.531	38.3
2	14906.779	197.592	23.0
3	10840.440	143.692	50.9
4	10234.096	135.655	34.7
5	10054.312	133.272	161.5
6	9955.831	131.966	34.0
7	9754.289	129.295	171.9
8	9742.552	129.139	171.2
9	9697.033	128.536	199.1
10	9693.598	128.490	112.7
11	5841.111	77.425	59.9
12	5809.048	77.000	61.2
13	5776.984	76.575	59.3
14	4377.642	58.026	61.2
15	2736.678	36.275	84.6
16	2103.710	27.885	79.1
17	1998.931	26.496	50.8

INDEX	FREQUENCY	PPM	HEIGHT
1	3821.850	9.555	21.3
2	3818.920	9.548	21.4
3	3036.225	7.591	23.7
4	3028.168	7.571	28.3
5	3009.672	7.525	5.2
6	3002.530	7.507	5.8
7	2954.550	7.387	14.2
8	2952.718	7.382	17.0
9	2945.759	7.365	49.9
10	2938.251	7.346	36.9
11	2934.222	7.336	49.7
12	2928.912	7.323	24.8
13	2910.599	7.277	51.7
14	1533.832	3.835	5.6
15	1531.085	3.828	5.6
16	1526.324	3.816	10.8
17	1523.577	3.809	10.7
18	1518.999	3.798	6.4
19	1516.252	3.791	5.8
20	1318.655	3.297	6.8
21	1310.964	3.278	6.7
22	1304.188	3.261	9.0
23	1296.679	3.242	8.4
24	1215.004	3.038	9.0
25	1207.679	3.019	8.6
26	1200.537	3.002	7.0
27	1193.395	2.984	6.7
28	631.920	1.580	5.6

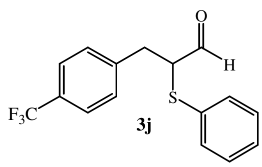


3j

^1H NMR (400 MHz, $CDCl_3$)

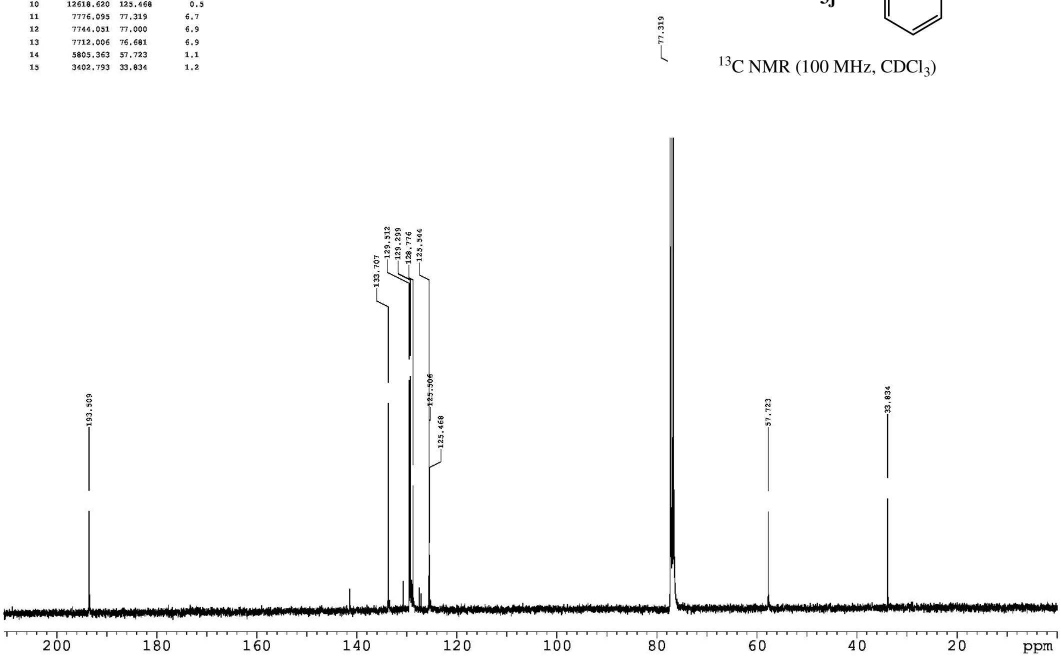


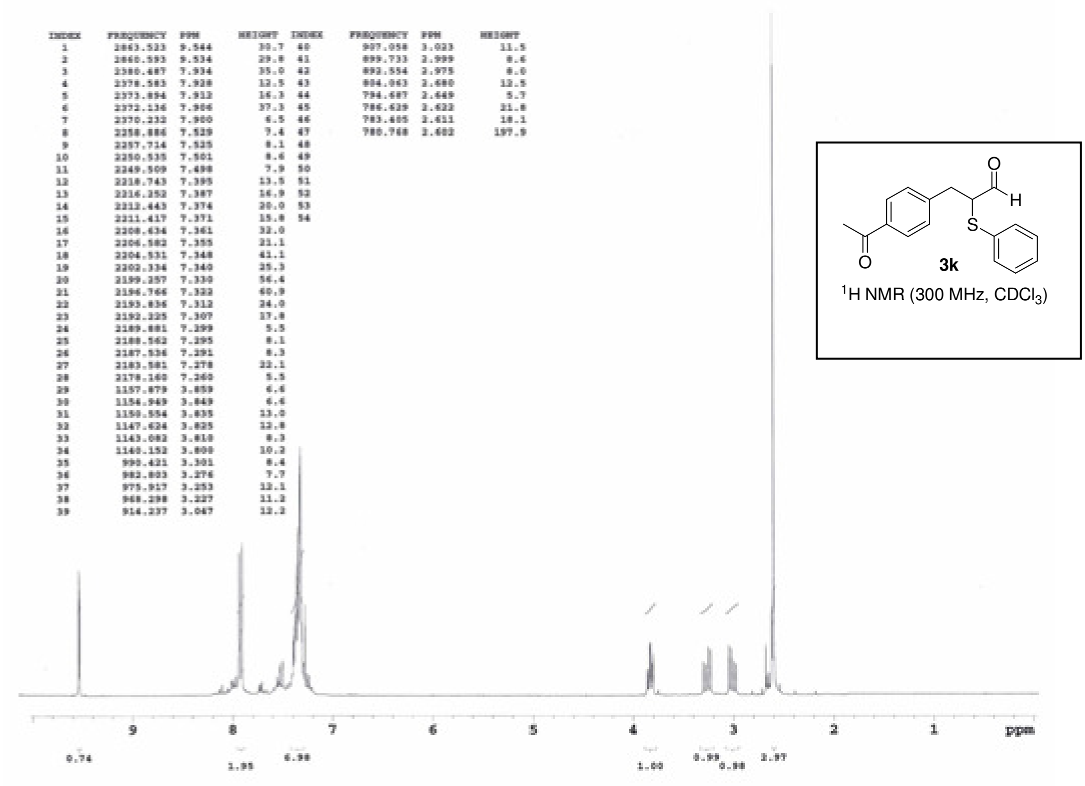
1	19461.633	193.509	1.1
2	13447.197	133.707	2.2
3	13145.827	130.710	0.3
4	13025.279	129.512	2.5
5	13003.916	129.299	2.5
6	12977.975	129.042	0.3
7	12951.272	128.776	1.4
8	12626.249	125.544	1.0
9	12622.435	125.506	1.0
10	12618.620	125.468	0.5
11	7776.095	77.319	6.7
12	7744.051	77.000	6.9
13	7712.006	76.681	6.9
14	5805.363	57.723	1.1
15	3402.793	33.834	1.2

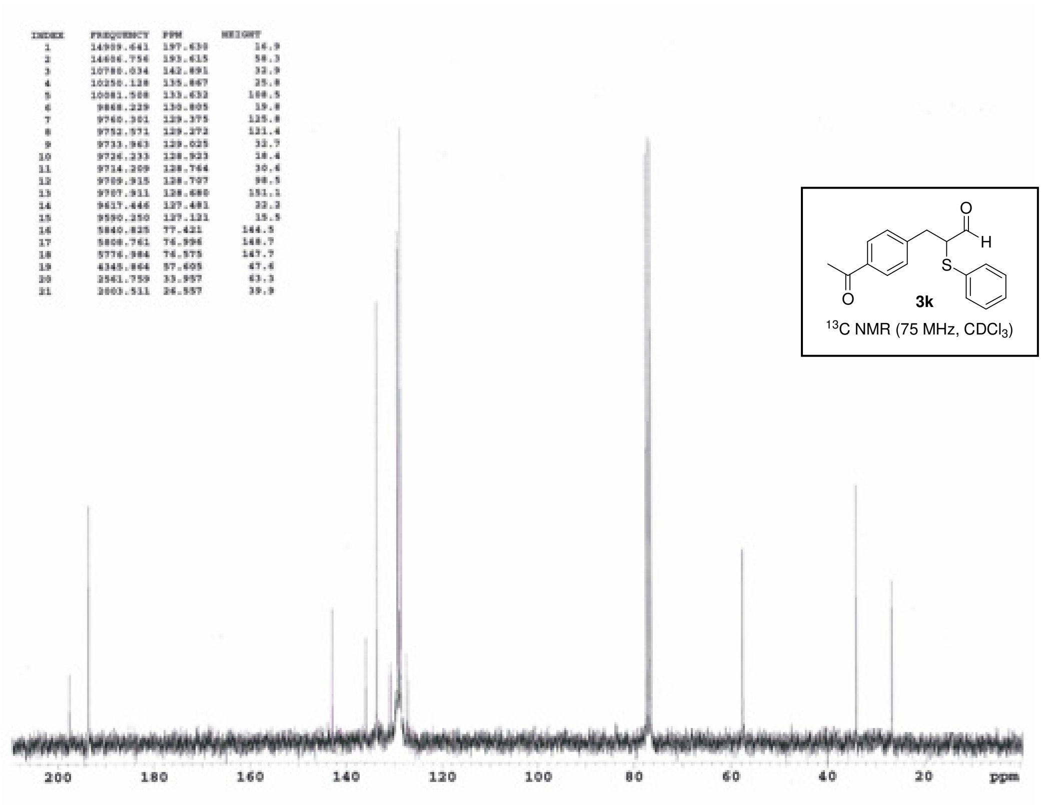


3j

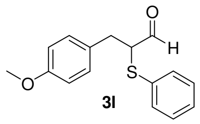
^{13}C NMR (100 MHz, $CDCl_3$)




3k
1H NMR (300 MHz, CDCl3)
ppm

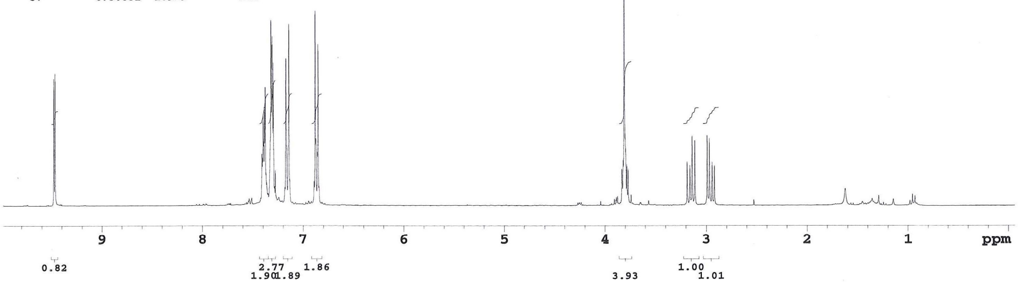

3k
13C NMR (75 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
ppm

INDEX	FREQUENCY	PPM	HEIGHT
1	2844.770	9.482	31.1
2	2840.961	9.469	32.3
3	2223.724	7.412	12.4
4	2223.138	7.410	12.6
5	2222.405	7.407	9.9
6	2221.526	7.404	11.6
7	2219.768	7.399	21.6
8	2218.596	7.395	16.2
9	2216.398	7.387	24.1
10	2213.761	7.379	28.9
11	2196.473	7.321	45.4
12	2193.250	7.310	41.4
13	2190.320	7.300	34.8
14	2184.020	7.279	8.6
15	2152.081	7.173	35.9
16	2150.323	7.167	14.5
17	2145.342	7.150	14.1
18	2143.584	7.145	44.5
19	2064.616	6.881	47.6
20	2062.712	6.875	16.4
21	2058.023	6.859	13.1
22	2056.119	6.853	39.5
23	1149.529	3.831	8.9
24	1145.866	3.819	11.1
25	1142.643	3.808	215.2
26	1139.566	3.798	17.4
27	1138.247	3.794	13.8
28	1135.171	3.784	10.1
29	1131.362	3.771	9.0
30	956.138	3.187	10.7
31	947.934	3.159	9.8
32	941.634	3.138	17.1
33	933.576	3.112	15.9
34	897.096	2.990	17.2
35	890.356	2.968	16.5
36	882.738	2.942	10.6
37	875.852	2.919	9.8

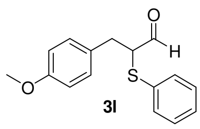


3l

^{1}H NMR (300 MHz, $CDCl_3$)

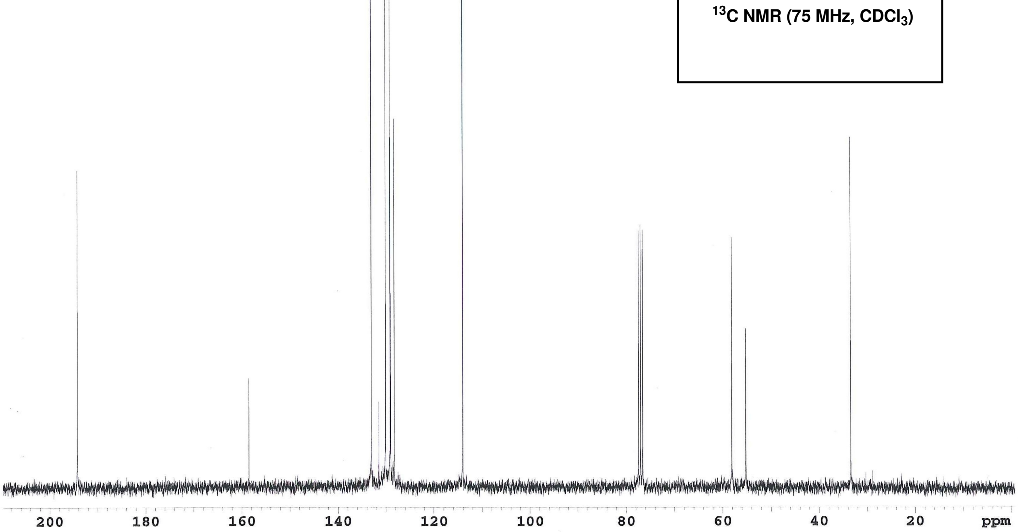


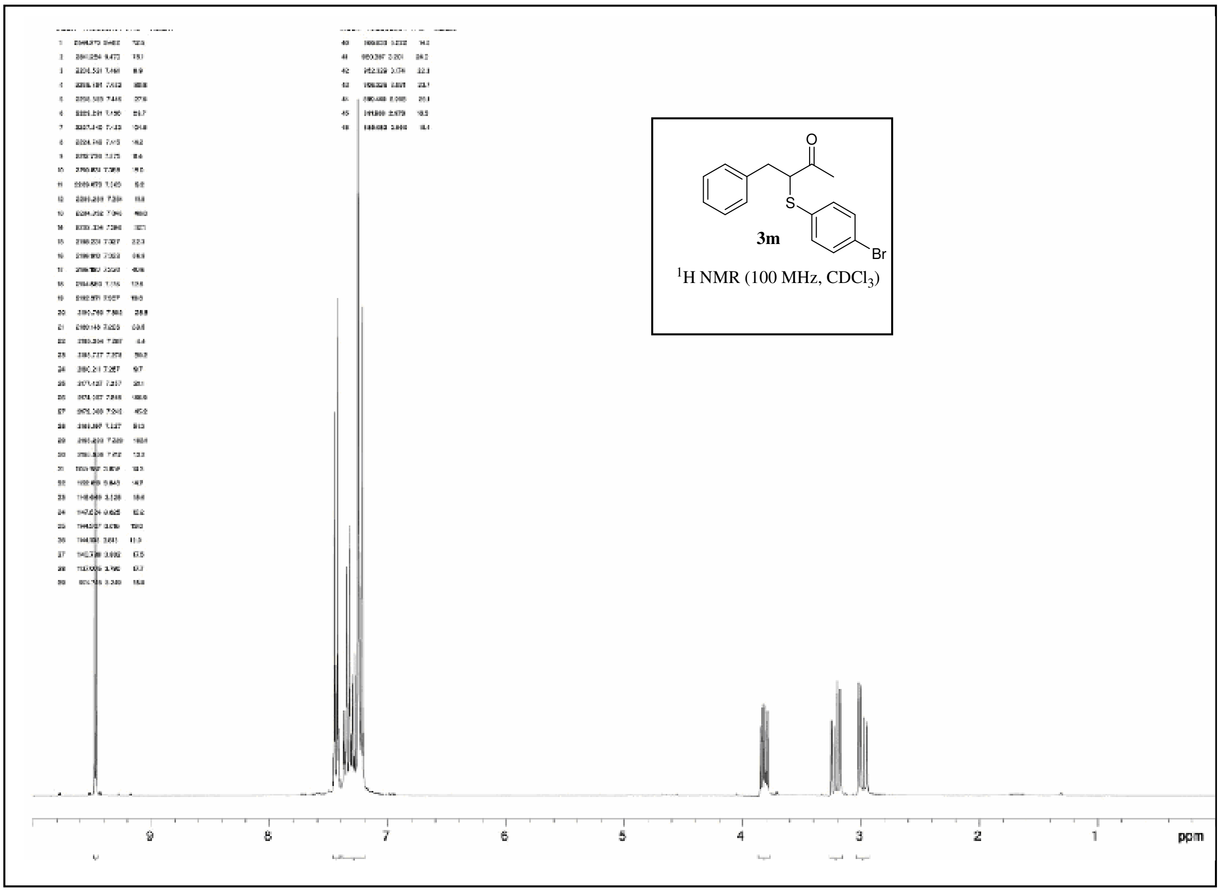
INDEX	FREQUENCY	PPM	HEIGHT
1	14658.286	194.298	77.8
2	11959.513	158.526	26.8
3	10041.143	133.097	146.5
4	9921.763	131.515	21.1
5	9813.835	130.084	183.4
6	9743.124	129.147	150.6
7	9734.249	129.029	47.5
8	9678.424	128.289	90.3
9	8602.007	114.021	200.0
10	5841.111	77.425	62.8
11	5809.047	77.000	64.3
12	5776.984	76.575	63.1
13	4382.508	58.091	61.1
14	4164.934	55.207	38.9
15	2520.821	33.414	85.7

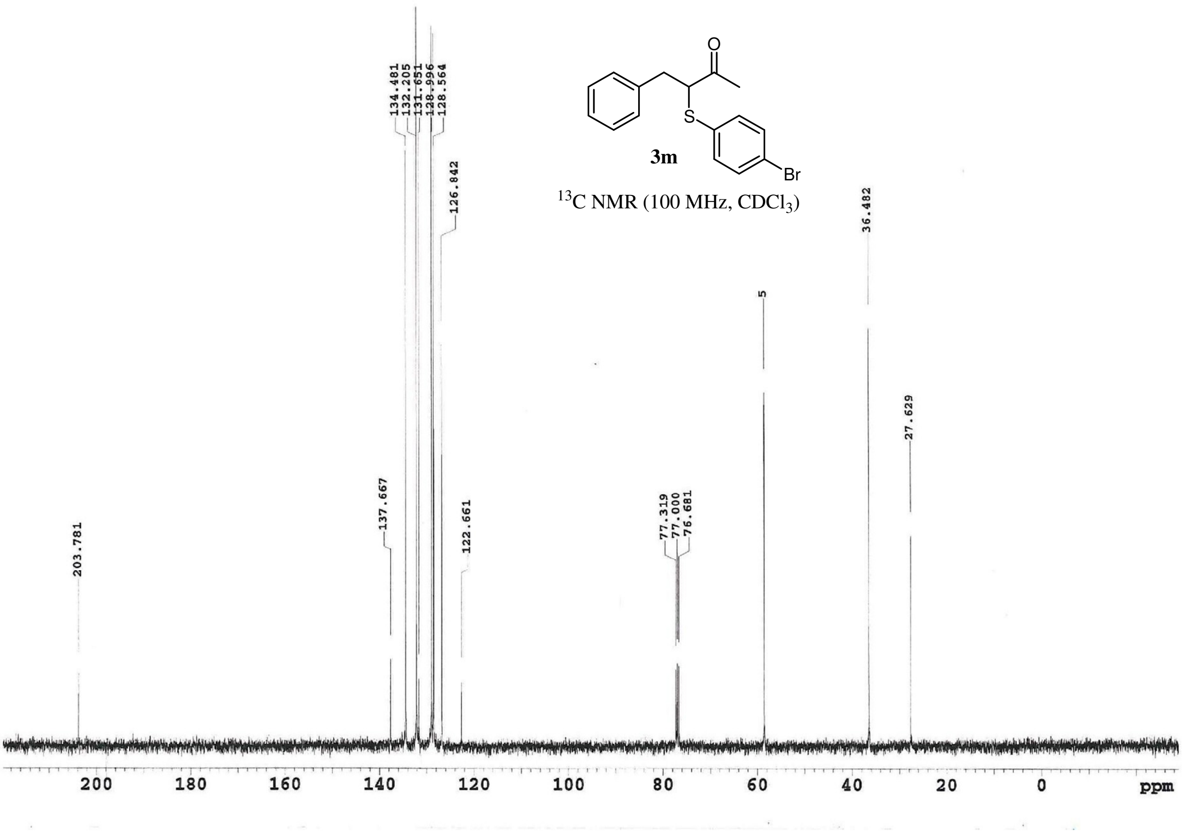


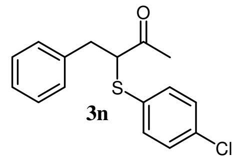
3l

^{13}C NMR (75 MHz, $CDCl_3$)



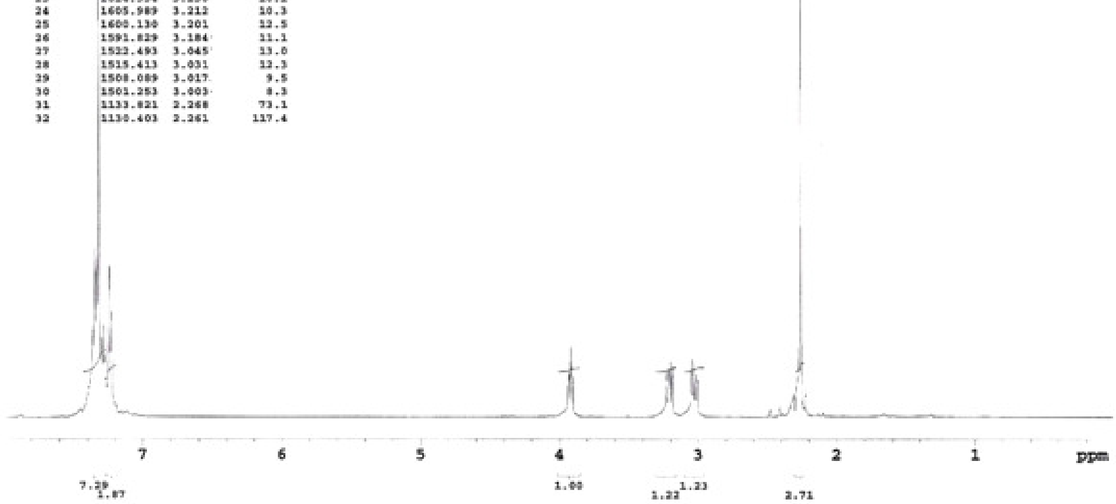

O
S
3m
Br
¹H NMR (100 MHz, CDCl₃)
9
8
7
6
5
4
3
2
1
ppm


134.481
132.205
131.651
128.996
128.564
126.842
O
S
3m
Br
¹³C NMR (100 MHz, CDCl₃)
36.482
27.629
137.667
122.661
203.781
77.319
77.000
76.681
200
180
160
140
120
100
80
60
40
20
0
ppm

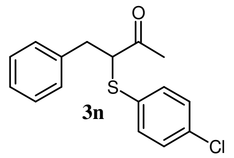


3n

^{1}H NMR (500 MHz, $CDCl_3$)

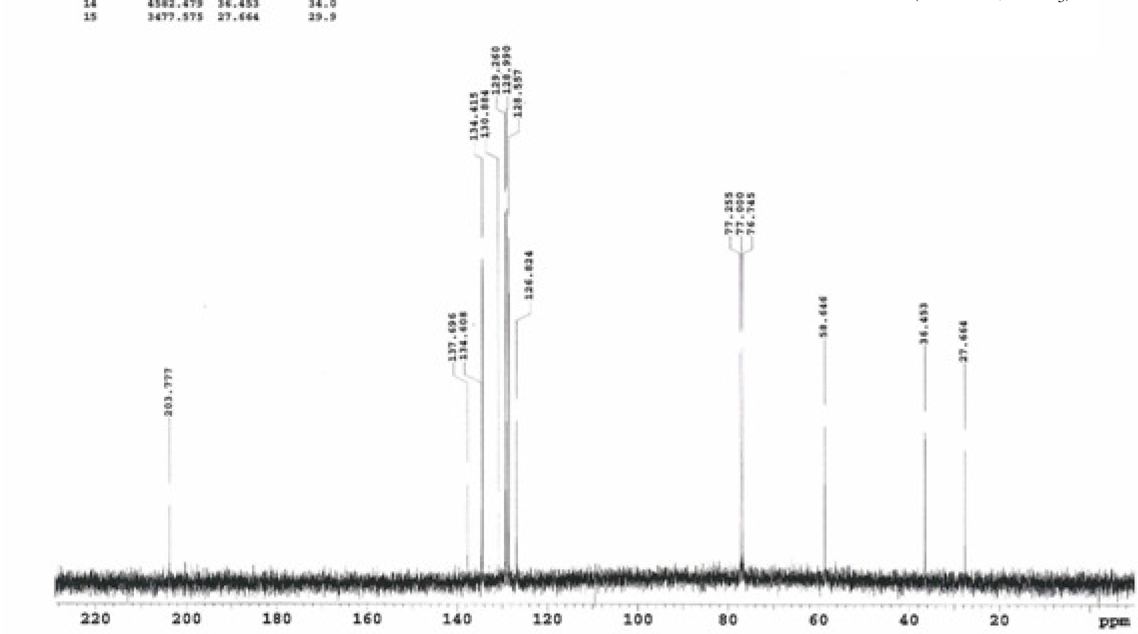


INDEX	FREQUENCY	PPM	HEIGHT
1	3679.231	7.359	20.3
2	3677.522	7.356	19.1
3	3675.569	7.352	16.4
4	3671.907	7.345	33.6
5	3670.442	7.342	37.4
6	3664.094	7.329	33.6
7	3662.874	7.327	35.5
8	3658.967	7.319	92.1
9	3655.305	7.312	154.1
10	3647.493	7.296	17.5
11	3646.272	7.294	17.3
12	3644.807	7.291	13.6
13	3639.436	7.280	20.4
14	3636.262	7.274	13.0
15	3635.774	7.273	13.9
16	3632.844	7.267	8.8
17	3631.624	7.264	8.3
18	3619.905	7.241	33.4
19	3612.825	7.227	23.5
20	1965.364	3.931	9.9
21	1958.528	3.918	15.5
22	1950.227	3.901	8.9
23	1614.534	3.230	10.1
24	1605.989	3.212	10.3
25	1600.130	3.201	12.5
26	1591.829	3.184	11.1
27	1522.493	3.045	13.0
28	1515.413	3.031	12.3
29	1508.089	3.017	9.5
30	1501.253	3.003	8.3
31	1133.821	2.268	73.1
32	1130.403	2.261	117.4



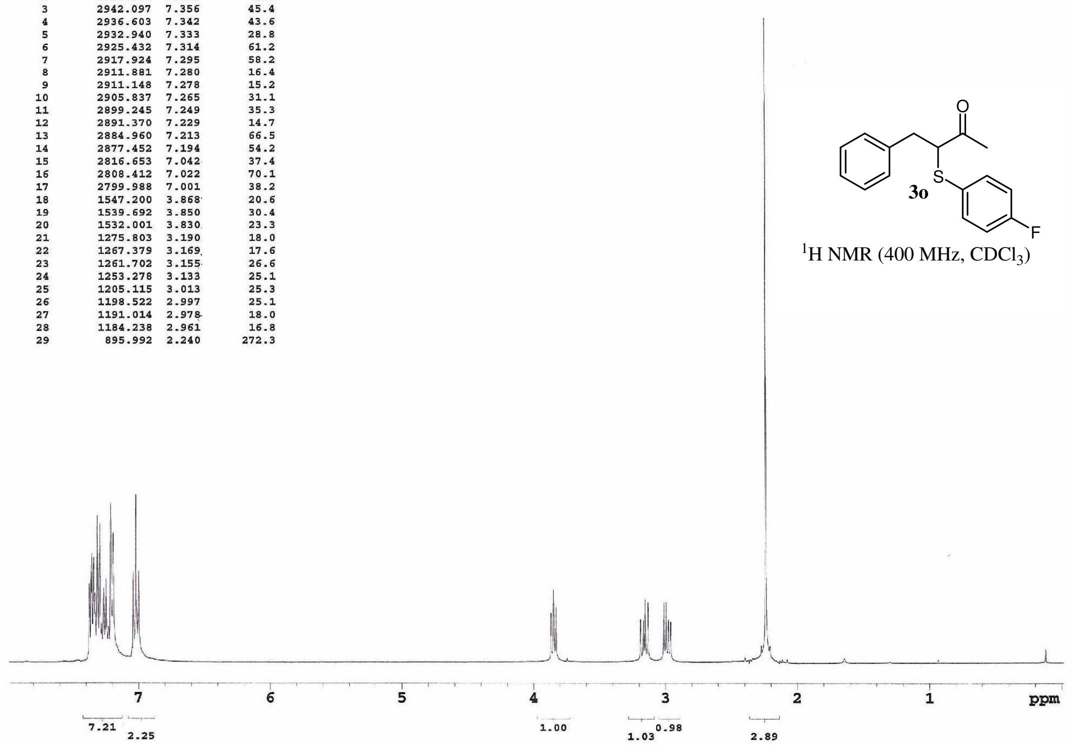
3n

^{13}C NMR (125 MHz, $CDCl_3$)

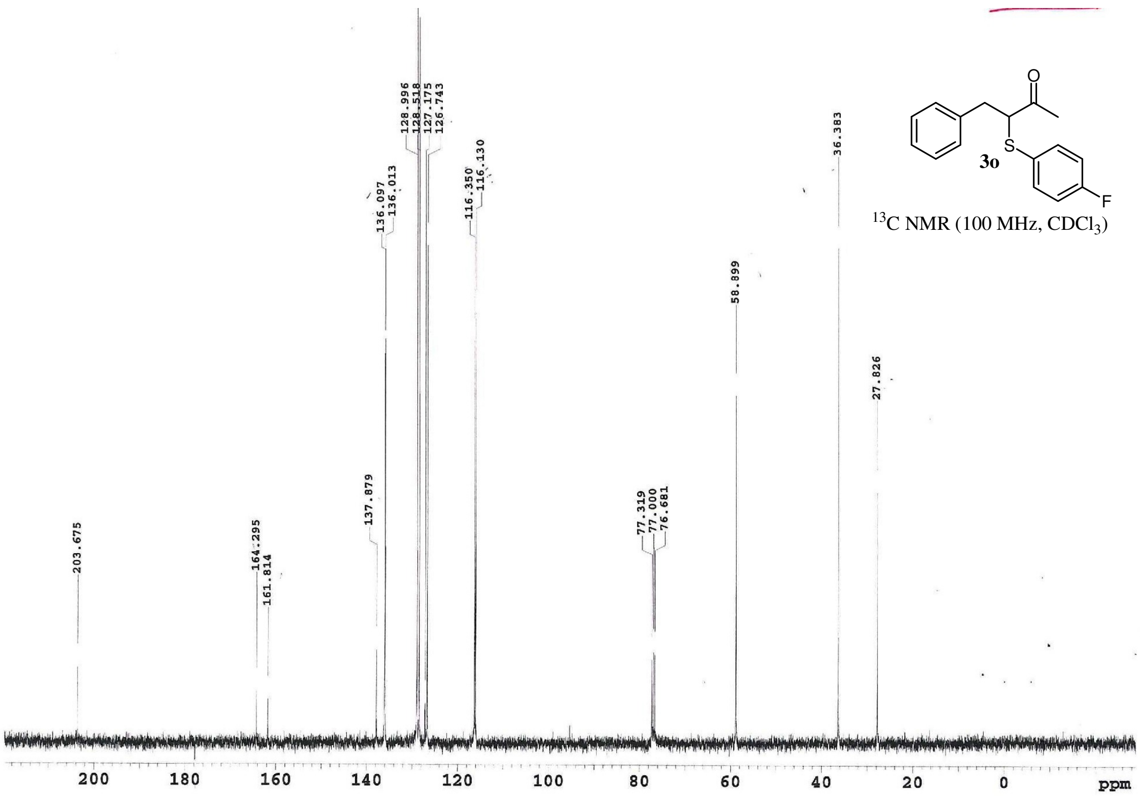


INDEX	FREQUENCY	PPM	HEIGHT
1	25616.379	203.777	17.2
2	17309.464	137.696	22.2
3	16921.329	134.608	16.3
4	16897.071	134.415	73.6
5	16453.096	130.884	15.5
6	16248.959	129.260	84.0
7	16215.088	128.990	84.9
8	16160.621	128.557	78.5
9	15942.753	126.824	36.6
10	9711.537	77.255	52.0
11	9679.498	77.000	53.1
12	9647.458	76.745	51.9
13	7372.200	58.646	35.4
14	4582.479	36.453	34.0
15	3477.575	27.664	29.9

INDEX	FREQUENCY	PPM	HEIGHT
1	2950.155	7.376	32.7
2	2944.844	7.363	40.3
3	2942.097	7.356	45.4
4	2936.603	7.342	43.6
5	2932.940	7.333	28.8
6	2925.432	7.314	61.2
7	2917.924	7.295	58.2
8	2911.881	7.280	16.4
9	2911.148	7.278	15.2
10	2905.837	7.265	31.1
11	2899.245	7.249	35.3
12	2891.370	7.229	14.7
13	2884.960	7.213	66.5
14	2877.452	7.194	54.2
15	2816.653	7.042	37.4
16	2808.412	7.022	70.1
17	2799.988	7.001	38.2
18	1547.200	3.868	20.6
19	1539.692	3.850	30.4
20	1532.001	3.830	23.3
21	1275.803	3.190	18.0
22	1267.379	3.169	17.6
23	1261.702	3.155	26.6
24	1253.278	3.133	25.1
25	1205.115	3.013	25.3
26	1198.522	2.997	25.1
27	1191.014	2.978	18.0
28	1184.238	2.961	16.8
29	895.992	2.240	272.3

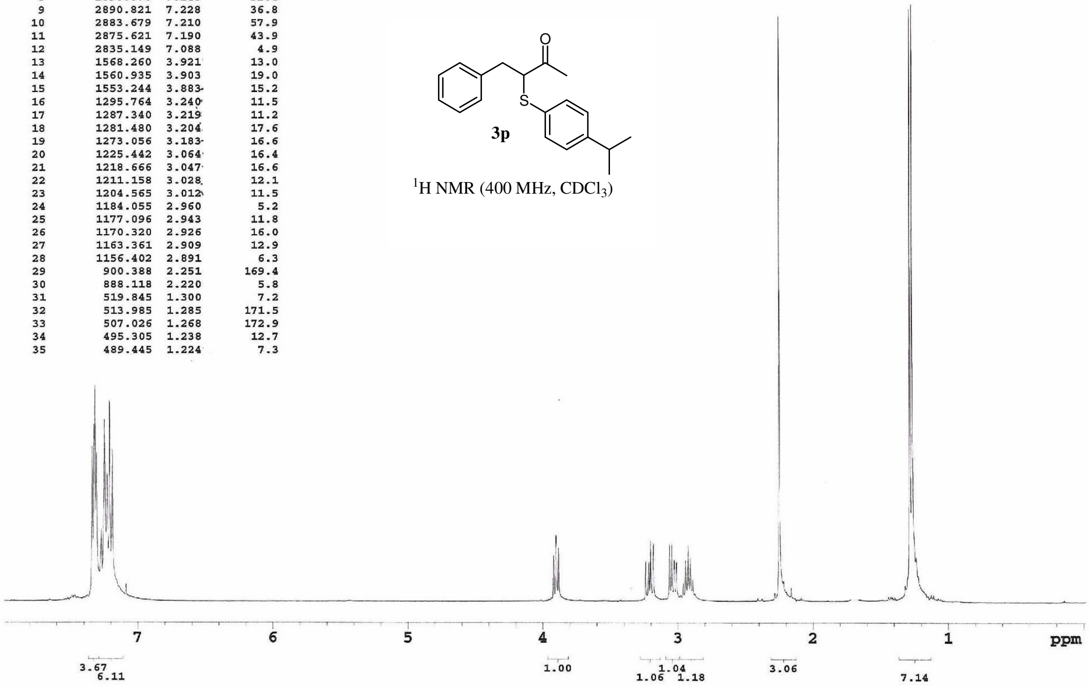


^{1}H NMR (400 MHz, $CDCl_3$)

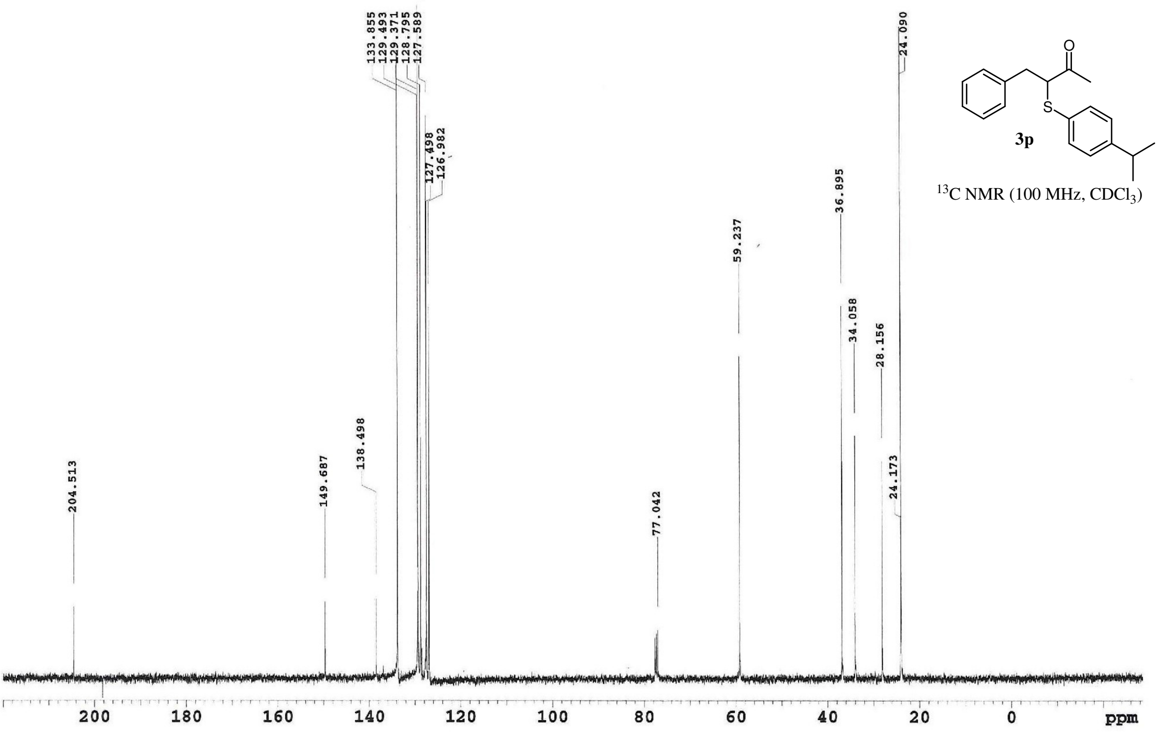


^{13}C NMR (100 MHz, $CDCl_3$)

INDEX	FREQUENCY	PPM	HEIGHT
1	2934.772	7.338	44.5
2	2932.757	7.332	21.6
3	2929.278	7.324	51.0
4	2926.714	7.317	62.2
5	2921.953	7.305	42.7
6	2910.965	7.278	12.6
7	2908.401	7.272	20.9
8	2898.878	7.248	52.4
9	2890.821	7.228	36.8
10	2883.679	7.210	57.9
11	2875.621	7.190	43.9
12	2835.149	7.088	4.9
13	1568.260	3.921	13.0
14	1560.935	3.903	19.0
15	1553.244	3.883	15.2
16	1295.764	3.240	11.5
17	1287.340	3.219	11.2
18	1281.480	3.204	17.6
19	1273.056	3.183	16.6
20	1225.442	3.064	16.4
21	1218.666	3.047	16.6
22	1211.158	3.028	12.1
23	1204.565	3.012	11.5
24	1184.055	2.960	5.2
25	1177.096	2.943	11.8
26	1170.320	2.926	16.0
27	1163.361	2.909	12.9
28	1156.402	2.891	6.3
29	900.388	2.251	169.4
30	888.118	2.220	5.8
31	519.845	1.300	7.2
32	513.985	1.285	171.5
33	507.026	1.268	172.9
34	495.305	1.238	12.7
35	489.445	1.224	7.3



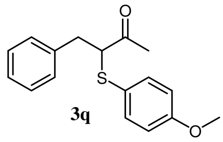
[1]H NMR (400 MHz, $CDCl_3$)



[13]C NMR (100 MHz, $CDCl_3$)

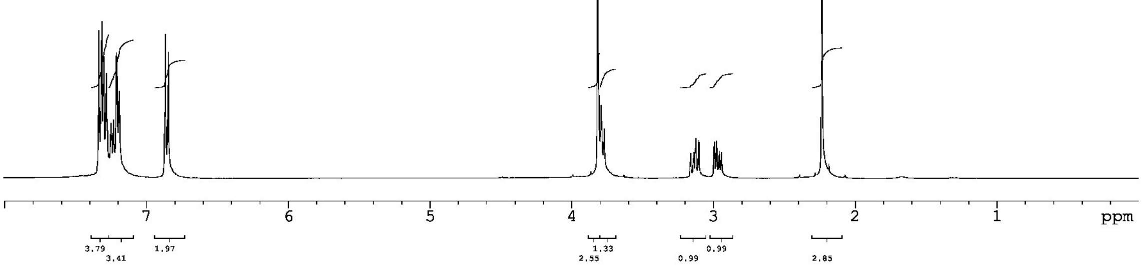
1	2935.687	7.340	31.3
2	2933.856	7.335	72.7
3	2931.658	7.330	29.3
4	2927.080	7.318	67.9
5	2924.883	7.313	77.4
6	2921.953	7.305	46.3
7	2920.304	7.301	60.0
8	2918.839	7.298	36.9
9	2914.261	7.286	41.7
10	2912.796	7.283	51.7
11	2910.049	7.276	26.6
12	2905.288	7.264	10.8
13	2900.893	7.253	22.1
14	2899.611	7.250	27.2
15	2898.146	7.246	20.2
16	2894.483	7.237	22.1
17	2892.286	7.231	28.9
18	2889.722	7.225	14.4
19	2884.594	7.212	61.9
20	2882.946	7.208	53.8
21	2880.749	7.202	23.4
22	2876.353	7.191	43.0
23	2748.712	6.872	31.6
24	2746.698	6.867	70.9
25	2744.683	6.862	25.4
26	2739.922	6.850	45.9
27	2737.908	6.845	62.1
28	2734.794	6.838	13.2
29	1527.422	3.819	124.8
30	1525.591	3.814	274.6
31	1523.394	3.809	43.8
32	1518.266	3.796	23.1
33	1516.435	3.791	35.9
34	1514.603	3.787	28.2
35	1509.659	3.774	17.8
36	1508.011	3.770	24.4
37	1505.996	3.765	12.6
38	1263.899	3.160	12.6
39	1255.292	3.138	12.7

40	1249.615	3.124	19.7
41	1241.191	3.103	18.7
42	1197.423	2.994	18.1
43	1190.831	2.977	18.4
44	1183.139	2.958	13.3
45	1176.730	2.942	12.7
46	895.077	2.238	116.3
47	893.245	2.233	237.5

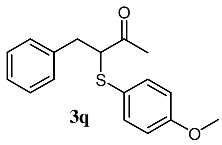


3q

^{1}H NMR (400 MHz, $CDCl_3$)

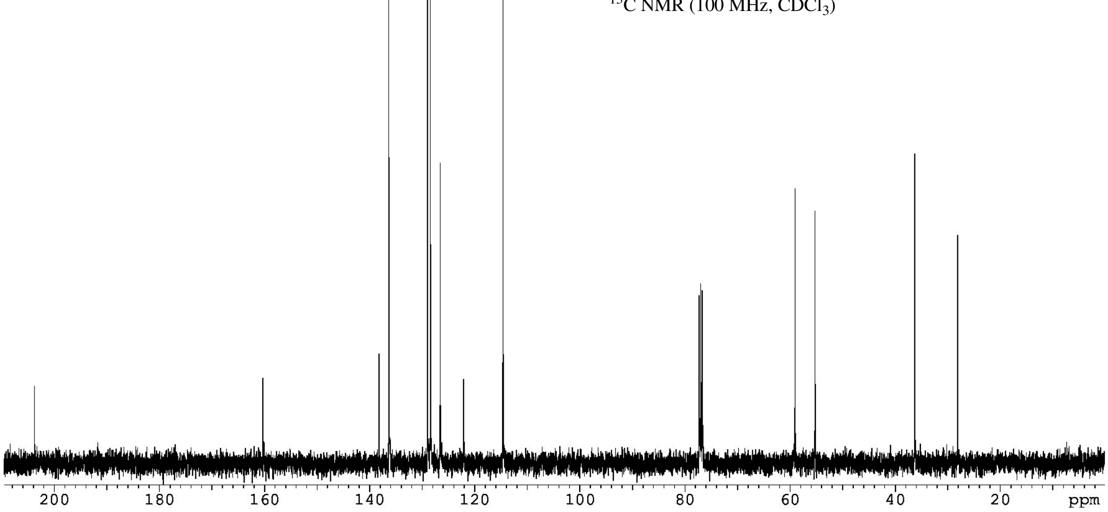


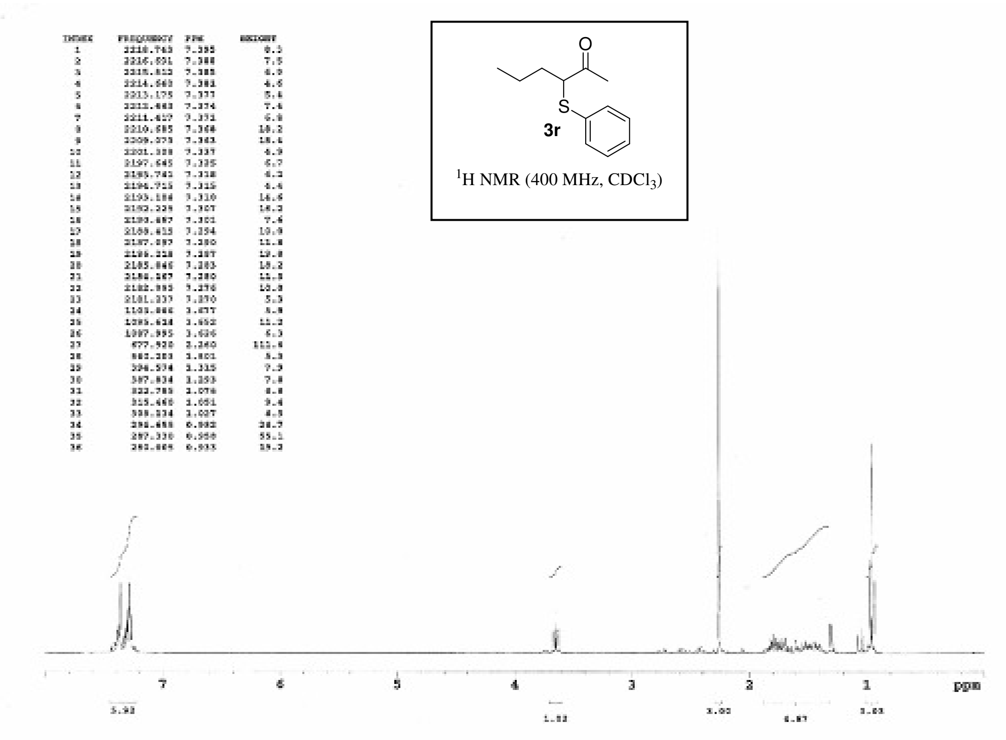
1	20496.211	203.796	4.1
2	16119.856	160.282	4.5
3	13903.450	138.244	5.8
4	13711.946	136.339	29.7
5	12974.161	129.004	25.6
6	12916.939	128.435	27.3
7	12729.250	126.568	16.0
8	12279.102	122.093	4.5
9	11526.821	114.613	31.8
10	7775.333	77.311	9.0
11	7744.051	77.000	9.6
12	7712.007	76.681	9.2
13	5938.119	59.043	14.7
14	5555.874	55.243	13.5
15	3646.942	36.262	16.5
16	2827.520	28.114	12.2

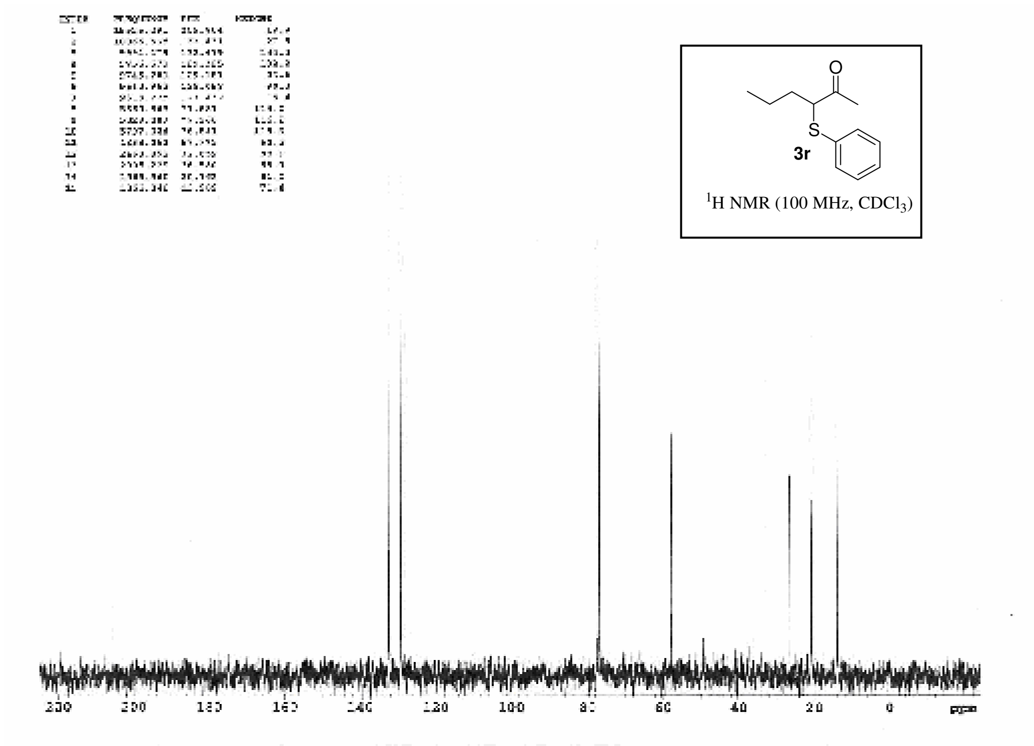


3q

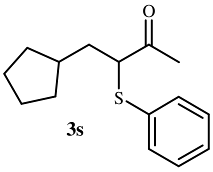
^{13}C NMR (100 MHz, $CDCl_3$)




O
S
3r
^{1}H NMR (400 MHz, CDCl$_3$)

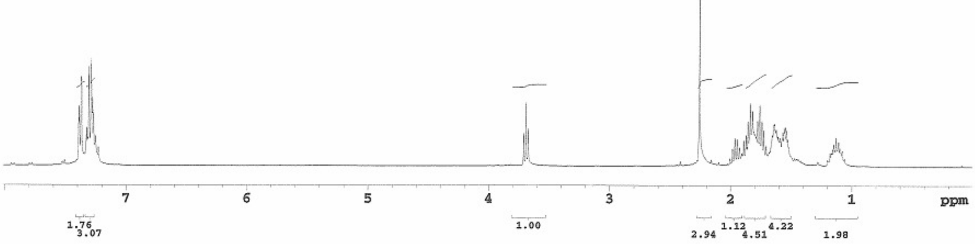

O
S
3r
^{1}H NMR (100 MHz, CDCl$_3$)

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2957.113	7.393	15.1	40	760.660	1.902	3.4	79	464.173	1.161	5.3
2	2955.465	7.389	18.8	41	757.180	1.893	8.1	80	460.145	1.150	7.0
3	2949.605	7.375	27.8	42	749.489	1.874	9.8	81	456.848	1.142	5.1
4	2948.873	7.373	28.4	43	746.742	1.867	6.1	82	452.087	1.130	9.0
5	2948.140	7.371	27.9	44	743.079	1.858	14.1	83	447.692	1.119	5.0
6	2945.393	7.364	7.6	45	735.754	1.840	20.1	84	443.846	1.110	7.7
7	2938.617	7.347	4.1	46	728.246	1.821	17.6	85	440.000	1.100	5.7
8	2932.025	7.331	9.7	47	723.668	1.809	10.9	86	435.971	1.090	4.5
9	2929.827	7.325	12.2	48	721.104	1.803	10.2	87	431.943	1.080	4.8
10	2927.447	7.319	9.1	49	715.976	1.790	9.5				
11	2926.714	7.317	8.6	50	711.581	1.779	14.4				
12	2925.981	7.316	8.6	51	704.439	1.761	19.5				
13	2923.784	7.310	31.3	52	697.480	1.744	14.3				
14	2916.276	7.291	34.0	53	690.521	1.726	11.4				
15	2913.529	7.284	17.0	54	683.196	1.708	6.6				
16	2912.796	7.283	16.9	55	673.490	1.684	4.4				
17	2911.881	7.280	21.7	56	670.743	1.677	4.7				
18	2908.401	7.272	17.8	57	665.799	1.665	7.5				
19	2903.640	7.260	7.2	58	662.869	1.657	9.8				
20	2901.076	7.253	9.5	59	658.107	1.645	13.2				
21	2896.498	7.242	4.2	60	655.544	1.639	13.4				
22	2892.469	7.232	6.0	61	653.346	1.633	11.3				
23	2882.763	7.207	5.1	62	650.782	1.627	11.5				
24	2875.255	7.189	7.0	63	648.951	1.623	11.5				
25	2873.423	7.184	4.8	64	644.922	1.612	9.5				
26	2867.563	7.169	5.4	65	642.541	1.606	9.2				
27	1484.204	3.711	10.4	66	639.794	1.600	8.0				
28	1476.696	3.692	20.1	67	637.963	1.595	8.9				
29	1469.004	3.673	11.9	68	635.216	1.588	7.9				
30	1075.825	2.690	7.2	69	629.356	1.574	8.9				
31	1075.276	2.688	7.0	70	627.158	1.568	10.7				
32	920.165	2.301	22.5	71	622.947	1.557	12.1				
33	919.799	2.300	21.9	72	619.101	1.548	12.4				
34	904.783	2.262	147.9	73	615.255	1.538	11.4				
35	794.356	1.986	5.5	74	611.593	1.529	8.5				
36	786.664	1.967	8.8	75	608.113	1.520	6.0				
37	779.156	1.948	8.6	76	601.154	1.503	3.2				
38	771.098	1.928	5.9	77	472.231	1.181	4.2				
39	763.590	1.909	4.1	78	468.019	1.170	4.1				

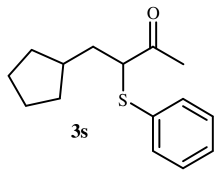


3s

^{1}H NMR (400 MHz, $CDCl_3$)

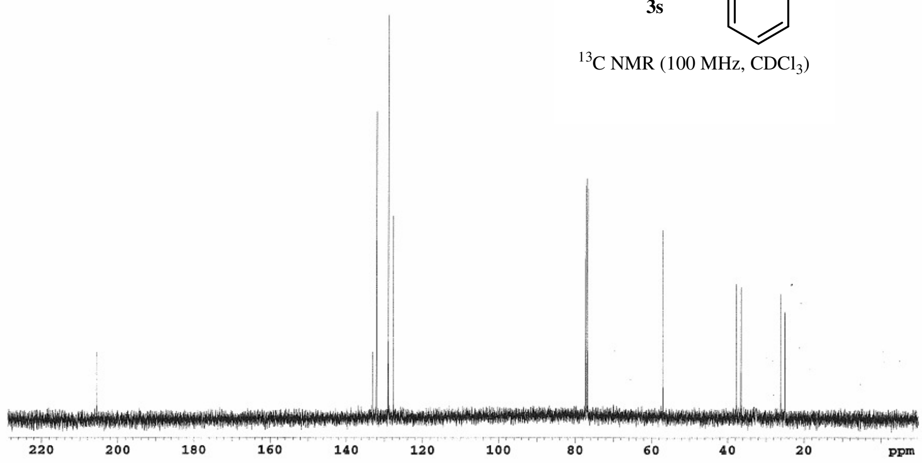


INDEX	FREQUENCY	PPM	HEIGHT
1	25842.486	205.576	18.1
2	16738.247	133.152	18.2
3	16608.716	132.122	82.9
4	16219.665	129.027	109.0
5	16057.637	127.738	54.7
6	9711.537	77.255	62.9
7	9679.498	77.000	64.8
8	9647.458	76.745	62.0
9	7164.401	56.993	50.8
10	4743.591	37.735	36.4
11	4587.971	36.497	35.5
12	3289.458	26.167	33.7
13	3142.076	24.995	28.8
14	3136.126	24.948	28.7

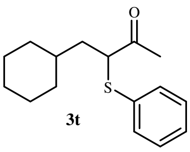


3s

^{13}C NMR (100 MHz, $CDCl_3$)

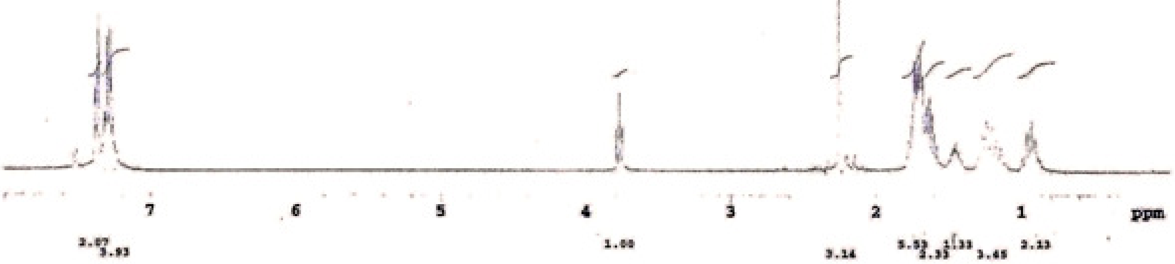


INDEX	FREQUENCY	PPM	HEIGHT
1	2954.183	7.386	27.9
2	2952.535	7.382	28.9
3	2950.338	7.376	15.6
4	2946.858	7.368	39.8
5	2945.943	7.365	53.2
6	2944.661	7.362	41.9
7	2930.010	7.326	17.8
8	2927.447	7.319	20.9
9	2925.615	7.315	19.3
10	2924.150	7.311	17.3
11	2922.136	7.306	45.8
12	2921.220	7.304	43.4
13	2919.572	7.300	25.2
14	2918.290	7.296	18.8
15	2914.444	7.287	49.1
16	2912.613	7.282	37.8
17	2910.782	7.278	31.3
18	2910.232	7.276	31.7
19	2906.570	7.267	21.9
20	2905.654	7.265	17.7
21	2902.175	7.256	10.0
22	1514.787	3.787	14.5
23	1507.278	3.768	26.9
24	1499.404	3.749	15.8
25	902.036	2.255	218.2
26	708.468	1.771	10.2
27	701.875	1.755	15.8
28	694.916	1.737	37.8
29	687.857	1.720	36.5
30	680.815	1.702	42.9
31	672.941	1.682	32.7
32	660.488	1.651	22.6
33	653.529	1.634	25.4
34	646.387	1.616	19.7
35	639.428	1.599	13.1
36	583.207	1.458	9.7
37	507.392	1.269	13.0
38	495.672	1.239	17.2
39	492.743	1.232	15.6
40	479.739	1.199	15.7
41	468.752	1.172	10.9
42	385.061	0.963	13.3
43	373.158	0.933	17.4
44	363.452	0.909	11.2

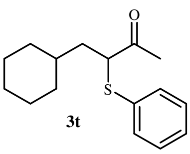


3t

^{1}H NMR (400 MHz, $CDCl_3$)

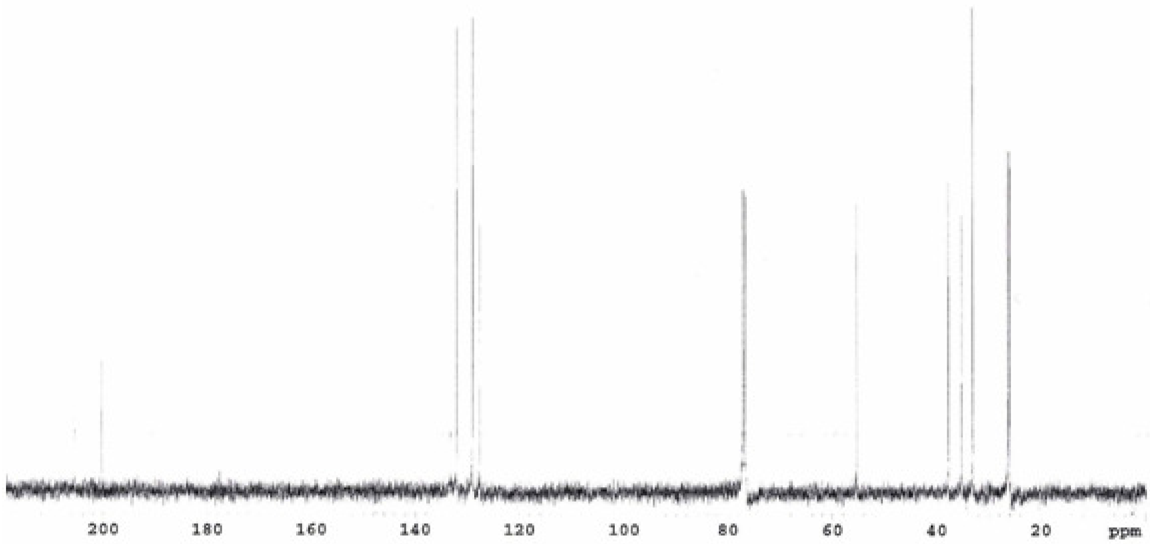


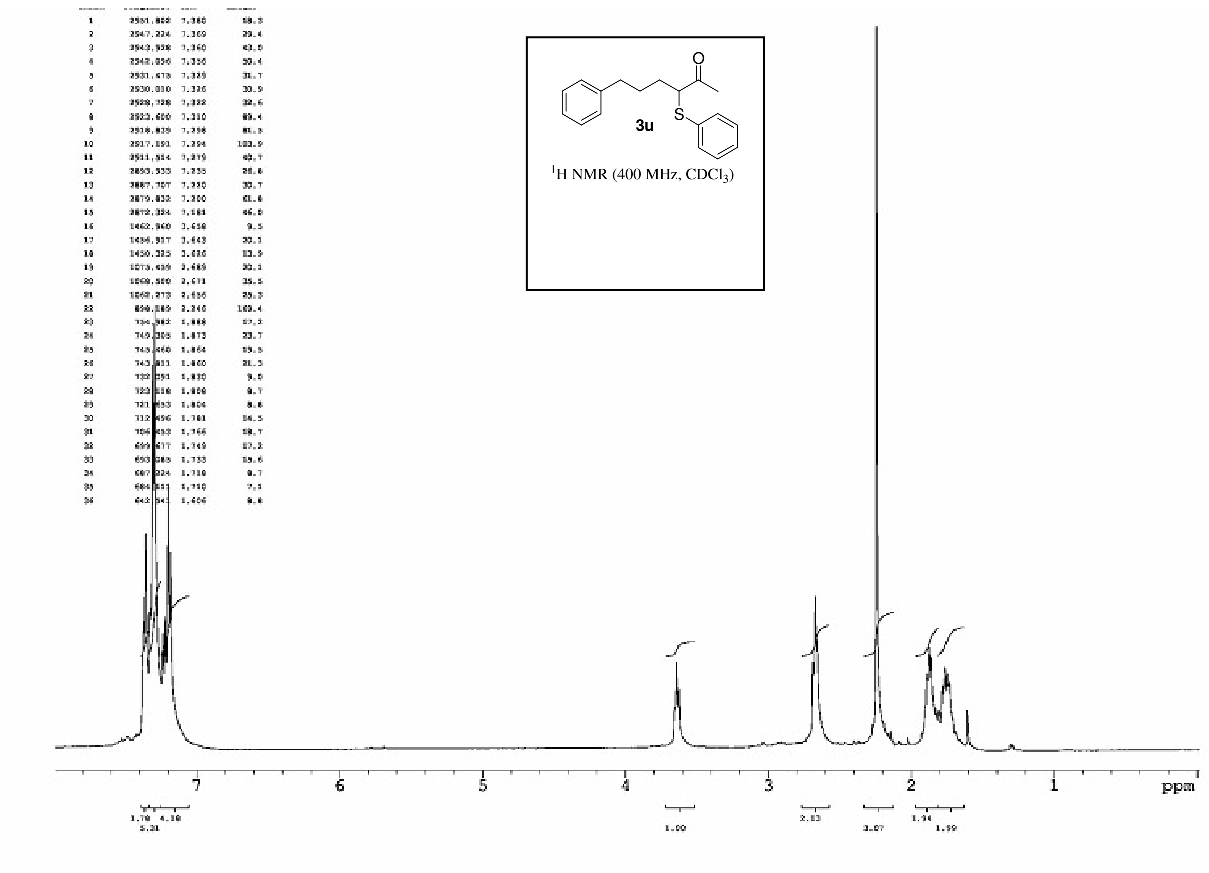
INDEX	FREQUENCY	PPM	HEIGHT
1	20669.403	205.518	1.4
2	13400.657	133.244	1.6
3	13283.923	132.084	9.1
4	12977.212	129.034	9.3
5	12845.983	127.729	5.2
6	7776.095	77.319	5.9
7	7744.051	77.000	5.9
8	7712.006	76.681	5.8
9	5567.318	55.356	5.6
10	3801.822	37.802	6.0
11	3550.045	35.299	5.4
12	3331.074	33.121	9.5
13	2653.564	26.385	6.6
14	2629.149	26.142	4.6
15	2623.808	26.089	6.6
16	2619.993	26.051	6.3

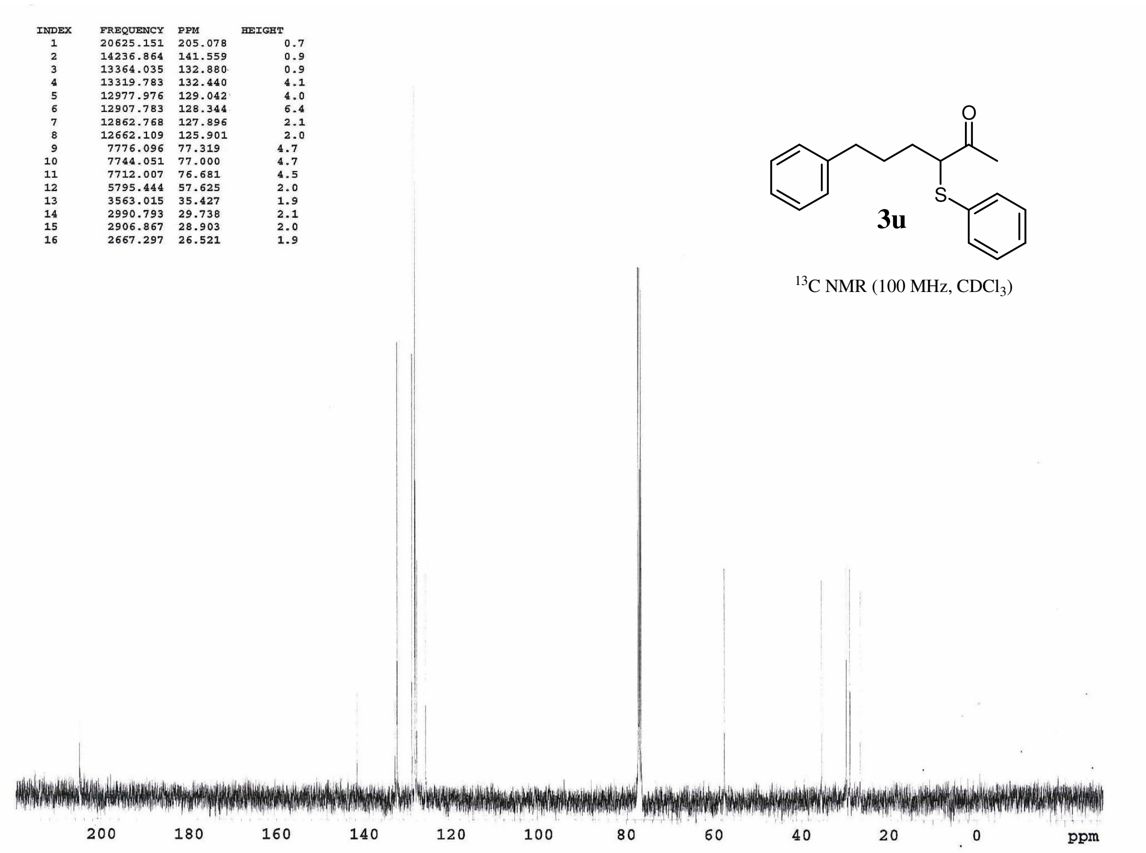


3t

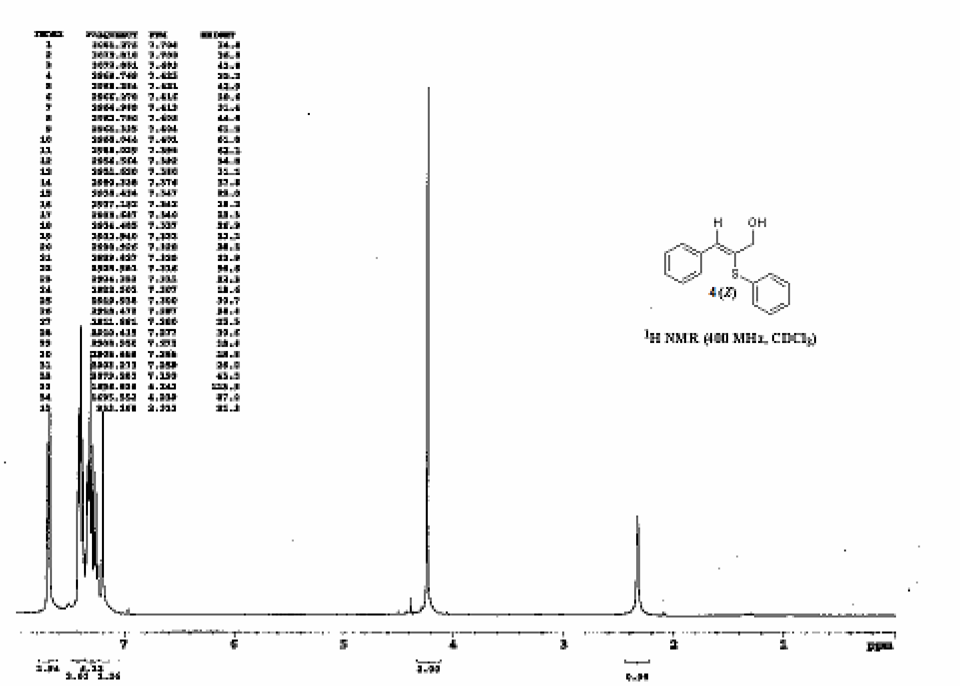
^{13}C NMR (100 MHz, $CDCl_3$)

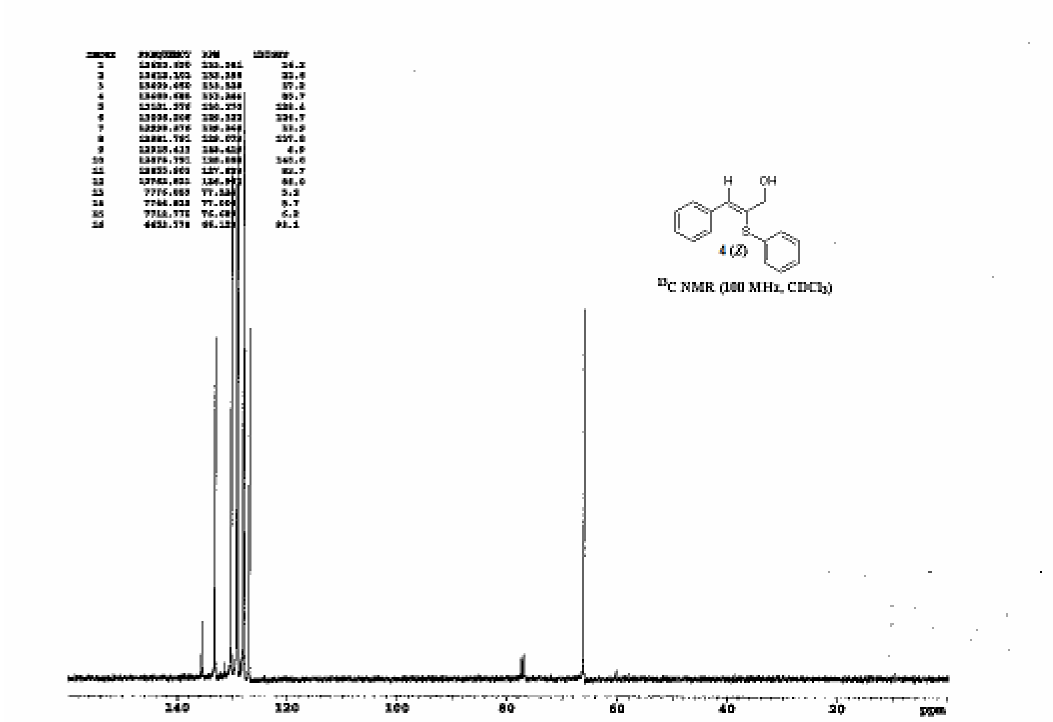


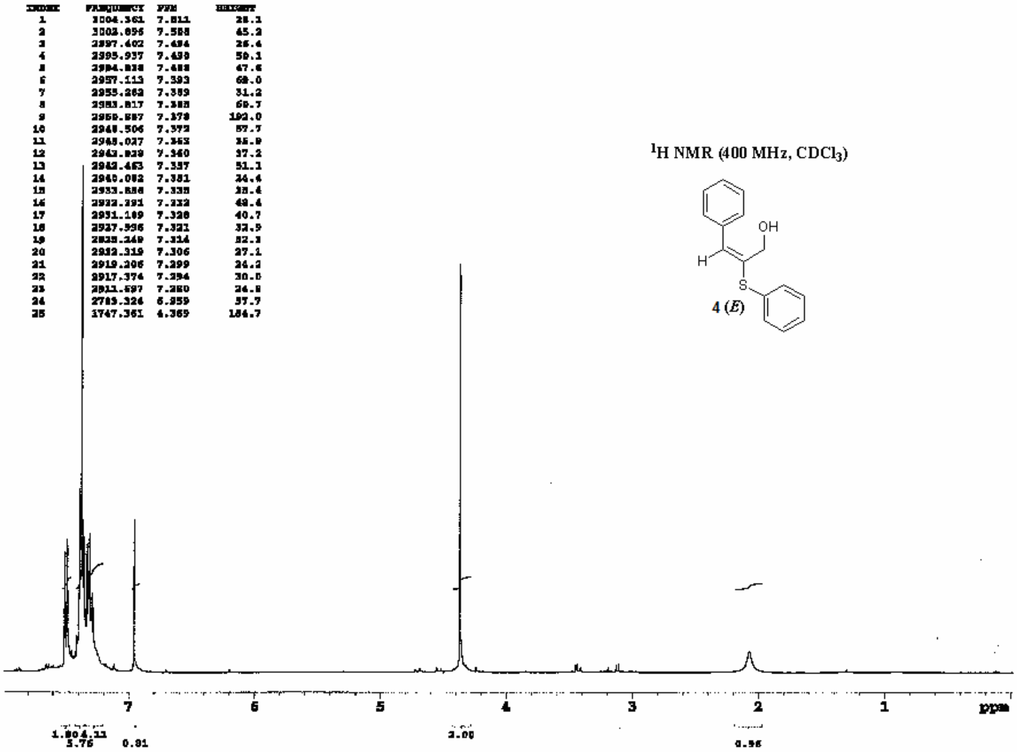

3u
^{1}H NMR (400 MHz, $CDCl_3$)
ppm
7
6
5
4
3
2
1
1.00
2.03
3.07
1.99

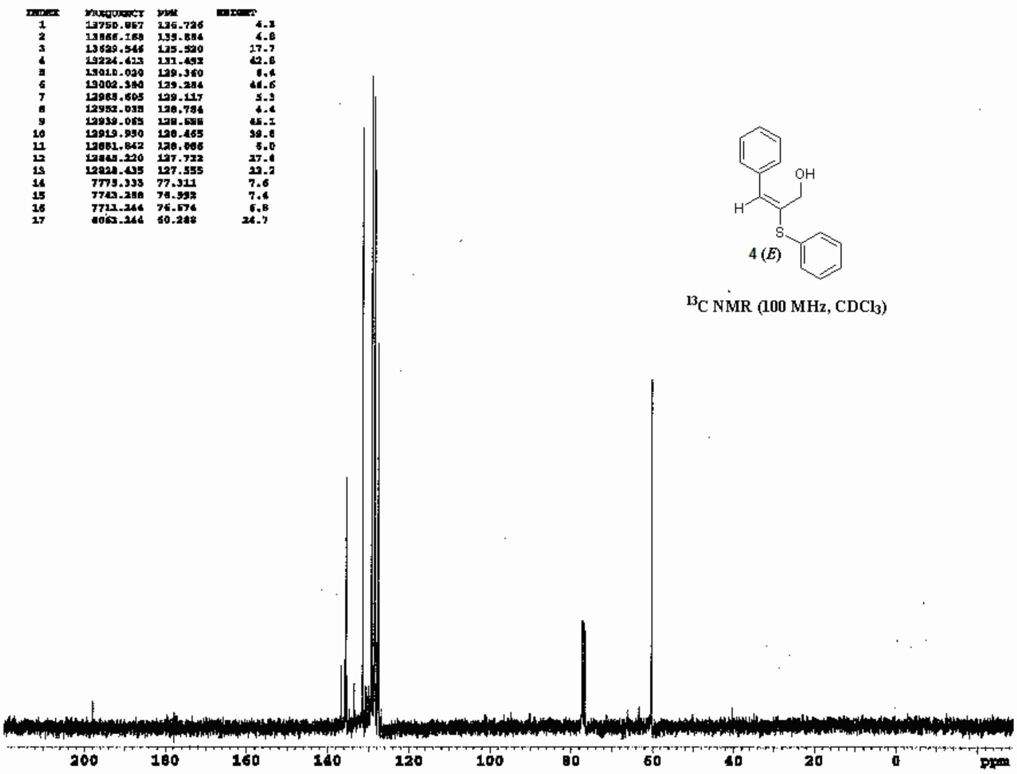

INDEX FREQUENCY PPM HEIGHT
1 20625.151 205.078 0.7
2 14236.864 141.559 0.9
3 13364.035 132.880 0.9
4 13319.783 132.440 4.1
5 12977.976 129.042 4.0
6 12907.783 128.344 6.4
7 12862.768 127.896 2.1
8 12662.109 125.901 2.0
9 7776.096 77.319 4.7
10 7744.051 77.000 4.7
11 7712.007 76.681 4.5
12 5795.444 57.625 2.0
13 3563.015 35.427 1.9
14 2990.793 29.738 2.1
15 2906.867 28.903 2.0
16 2667.297 26.521 1.9
3u
^{13}C NMR (100 MHz, $CDCl_3$)
200
180
160
140
120
100
80
60
40
20
0
ppm

I. Copies of NMR spectra of isolated intermediate 4.






INDEX FREQUENCY PPM HEIGHT
1 3004.361 7.511 28.1
2 3002.896 7.508 45.2
3 2997.402 7.494 26.4
4 2995.937 7.490 50.1
5 2994.838 7.488 47.6
6 2957.113 7.393 68.0
7 2955.282 7.389 31.2
8 2953.817 7.385 60.7
9 2950.887 7.378 192.0
10 2948.506 7.372 57.7
11 2945.027 7.363 35.9
12 2943.928 7.360 37.2
13 2942.463 7.357 51.1
14 2940.082 7.351 34.4
15 2933.858 7.335 38.4
16 2932.391 7.332 48.4
17 2931.109 7.328 40.7
18 2927.996 7.321 32.9
19 2925.249 7.314 82.1
20 2922.319 7.306 27.1
21 2919.206 7.299 24.2
22 2917.374 7.294 30.0
23 2911.697 7.280 24.8
24 2783.324 6.959 57.7
25 1747.361 4.369 184.7
1H NMR (400 MHz, CDCl3)
OH
H
S
4 (E)
7
6
5
4
3
2
1
ppm
1.80 4.11
3.76
0.81
2.00
0.95


INDEX FREQUENCY PPM HEIGHT
1 13750.867 136.726 4.1
2 13666.168 135.884 4.8
3 13629.546 135.520 17.7
4 13224.413 131.492 42.8
5 13010.020 129.360 6.4
6 13002.380 129.284 46.6
7 12985.605 129.117 5.3
8 12952.035 128.784 4.4
9 12939.065 128.656 45.1
10 12913.950 128.405 39.8
11 12881.842 128.086 5.0
12 12848.220 127.722 27.4
13 12828.435 127.555 33.2
14 7775.333 77.311 7.6
15 7743.288 76.993 7.4
16 7711.244 76.674 6.8
17 6063.244 60.288 24.7
OH
H
S
4 (E)
13C NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

J. References.

1 S. Biswas and J. S. M. Samec, *Chem. Commun.*, 2012, **48**, 6586.

2 T. Aoyama, T. Takido and M. Kodomari, *Synlett*, 2005, 2739.