Supporting Information

Reactions were run in dried glassware under a nitrogen atmosphere. THF was distilled from sodium benzophenone ketyl prior to use. Flash column chromatgraphy was carried out on silica gel 60 (Cica-MERCK). The α-methylene-β-acetoxy ketones were prepared from the reaction of the corresponding aldehyde with methyl vinyl ketone in the presence of DABCO in THF followed by acetylation of the hydroxy group. ^{1}H-NMR, ^{13}C-NMR and NOESY spectra were acquired on a 500 MHz or 90 MHz spectrometer using $CDCl_3$ or acetone-d_6 as a solvent. Chemical shifts are reported in δ from TMS as an internal standard. Mass spectra and HRMS were obtained by EI at 70eV or FAB. Melting points are uncorrected.

Cyclic oxosulfonium hexafluorophosphate.

(a) A mixture of tetrahydrothiophene (4.06 g, 46.05 mmol), diphenyliodonium hexafluorophosphate (19.62 g, 46.05 mmol), and cupper benzoate (0.34 g, 0.025 equiv) was heated at 80 °C for 18h. After being cooled to room temperature, the solidified mixture was dissolved in a small amount of acetone. The acetone solution was then poured into an excess of ether. The precipitated solid was filtered and purified by recrystallization from ethanol. The colorless sulfonium salt was obtained as a white solid in 32% yield. mp 147-148°C

(b) To a solution of NaOH (0.27 g, 9 equiv) in water (28 mL) was added 70% *m*-chloroperoxybenzoic acid (1.14 g, 6 equiv), and the mixture was stirred at room temperature for 30 min. A sulfonium salt (0.24 g, 0.77 mmol) was then added to the mixture, and the resulting mixture was stirred at 40°C for 18h. After 10% aqueous hydrochloric acid was added dropwise at room temperature, the mixture was washed with ether several times. The aqueous layer was then concentrated under reduced pressure, and the residue was purified by recrystallization from ethanol to give oxosulfonium salt **2** in

67% yield as a white solid. mp 196-197°C; ^{1}H-NMR (90 MHz, acetone-d_6) δ 2.76-2.93 (m, 4H), 4.38-4.63 (m, 4H), 7.92-8.35 (m, 5H); IR (KBr) 1040 (S=O), 850 (P-F) cm^{-1}; MS (70eV) m/z 180 (M^+-146(-HPF_6)); Anal. Calcd. for $C_{10}H_{13}OSPF_6$: C, 36.82; H, 4.02. Found: C, 36.46; H, 4.00.

Reaction of oxosulfonium ylide 2 with 4-hexen-3-one.

To a solution of five-membered oxosulfonium salt (0.10 g, 0.31 mmol) in dry THF (2 mL) was added dropwise a solution of lithium bis(trimethylsilyl)amide (in THF 1M sol. 0.32 mL, 0.32mmol), and the mixture was stirred at room temperature for 10 min. A solution of 4-hexen-3-one (0.03 g, 0.31 mmol) in dry THF (2 mL) was then added dropwise to the mixture, and the resulting solution was stirred for 14 h. The mixture was quenched with water and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using AcOEt-$CHCl_3$ (1/1) as an eluent to give **3** in 98% yield as colorless liquid. ; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 0.94-2.76 (m, 17H), 7.44-7.55 (m, 5H); ^{13}C-NMR (22.49 MHz, $CDCl_3$) δ 8.07, 18.01, 22.40, 23.51, 25.06, 33.53, 33.86, 37.95, 56.91, 123.98, 129.18, 130.89, 144.19, 209.36; IR (KBr) 1695 (C=O), 1050 (S=O) cm^{-1}; MS (70eV) m/z 278 (M^+); HRMS (70eV) calcd. for $C_{16}H_{22}O_2S$ (M^+) 278.1341, found (M^+) 278.1368.

General Procedure for the Reaction of Cyclic Oxosulfonium Ylide 2 with α-methylene-β-acetoxy ketones 5a-e. To a solution of five-membered oxosulfonium salt (0.10 g, 0.31 mmol) in dry THF (2 mL) was added dropwise a solution of lithium bis(trimethylsilyl)amide or lithium *tert*-butoxide (2.05 equiv), and the mixture was stirred at room temperature for 10 min. A solution of **5a-e** (0.31 mmol) in dry THF (2 mL) was then added dropwise to the mixture, and the resulting solution was stirred for 1-19 h. The mixture was quenched with water and extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated

under reduced pressure. The residue was purified by flash column chromatography on silica gel using AcOEt as an eluent.

6a: 23%; viscous solid; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 1.26-2.67 (m, 10H), 2.93-3.03 (brt, 1H), 5.15 (s, 1H), 5.27 (s, 1H), 7.45-7.65 (m, 5H); ^{13}C-NMR (22.49 MHz, $CDCl_3$) δ 22.51, 24.00, 26.79, 30.74, 61.54, 62.03, 65.25, 117.59, 125.12, 129.18, 131.18, 142.94, 145.38; IR (KBr) 1650 (C=C), 1090 (oxirane), 1030 (S=O) cm^{-1}; MS (Fab) m/z 263 (M^++1); HRMS (Fab) calcd. for $C_{15}H_{19}O_2S$ (M^++1) 263.1106, found (M^++1) 263.1131.

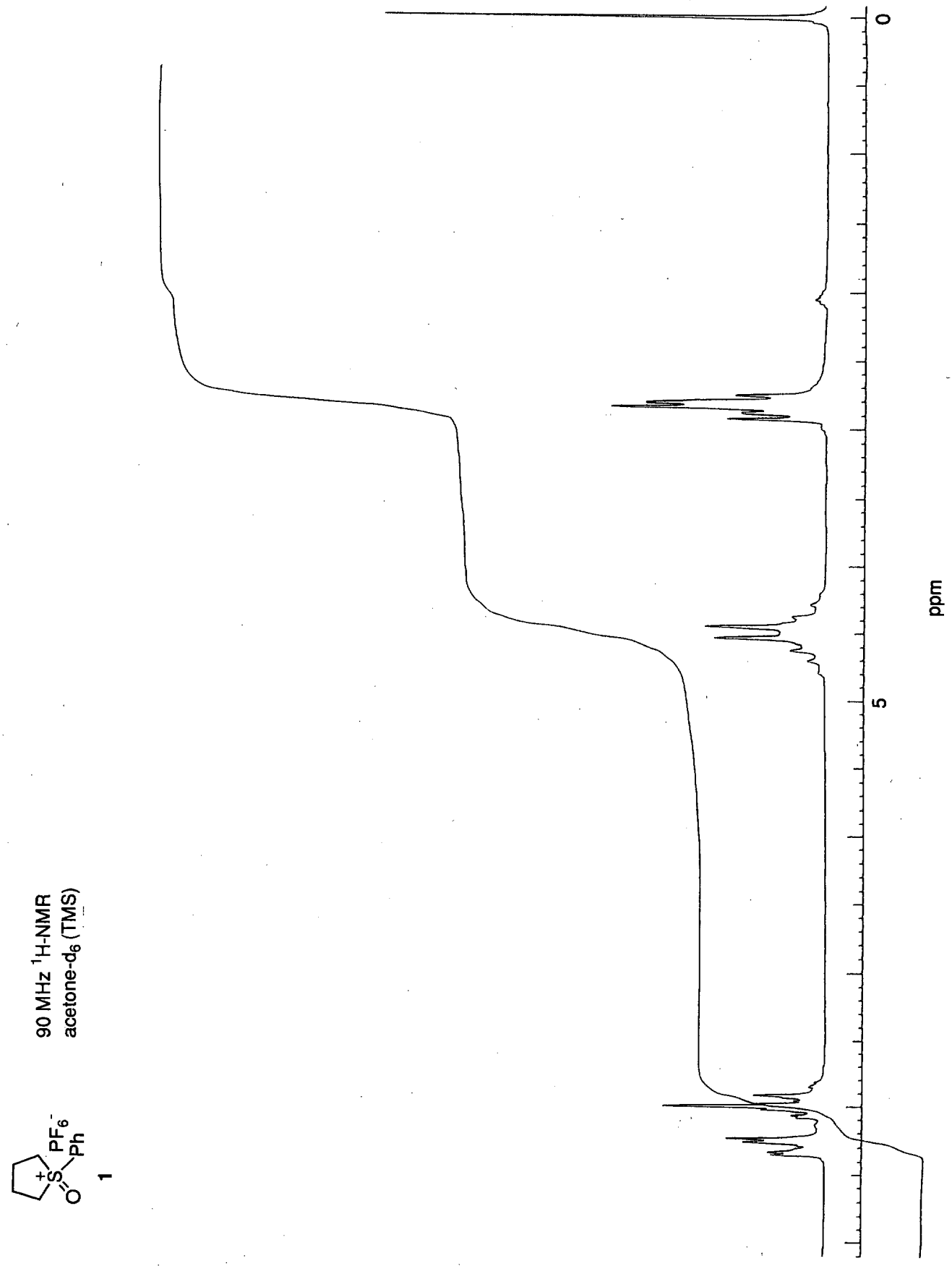
6b: 56%; white solid, mp 92-95°C ; ^{1}H-NMR (90 MHz, acetone-d_6) δ 1.10-2.92 (m, 14H), 5.56 (q, *J*=6.8 Hz, 1H), 7.54-7.72 (m, 5H); ^{13}C-NMR (22.49 MHz, acetone-d_6) δ 12.35, 22.59, 24.73, 25.79, 28.93, 60.97, 62.71, 64.63, 124.71, 125.36, 129.80, 131.51, 137.58, 144.19; IR (KBr) 1095 (oxirane), 1040 (S=O), 860 (C=C) cm^{-1}; HRMS (70eV) calcd. for $C_{16}H_{20}O_2S$ (M^+) 276.1184, found (M^+) 276.1207.

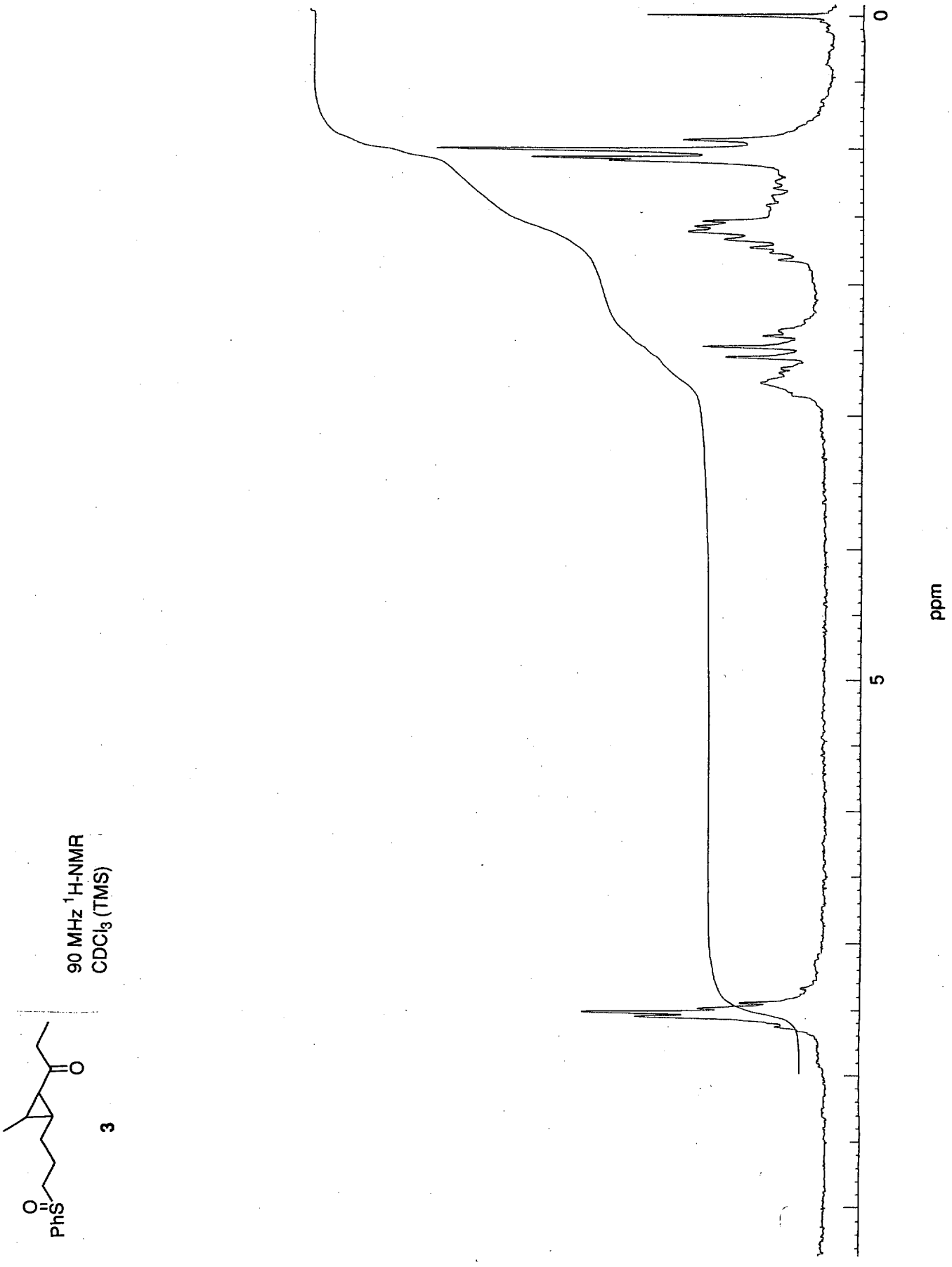
6c: 66%; white solid, mp 92-94°C ; ^{1}H-NMR (500.13 MHz, acetone-d_6) δ 0.78 (t, *J*=7.5 Hz, 3H), 1.21-1.28 (m, 1H), 1.29 (s, 3H), 1.55-1.62 (m, 2H), 1.66-1.74 (m, 1H), 2.05-2.12 (m, 2H), 2.30-2.34 (m, 1H), 2.36-2.39 (m, 1H), 2.50-2.55 (m, 1H), 2.84-2.87 (m, 1H), 5.46 (t, *J*=7.4 Hz, 1H), 7.57-7.70 (m, 5H); ^{13}C-NMR (125.76 MHz, acetone-d_6) δ 14.13, 20.73, 22.71, 24.97, 25.98, 29.08, 60.97, 62.69, 65.38, 125.35, 129.83, 131.53, 132.23, 136.33, 144.33; IR (KBr) 1090 (oxirane), 1030 (S=O), 860 (C=C) cm^{-1}; HRMS (70eV) calcd. for $C_{17}H_{22}O_2S$ (M^+) 290.1340, found (M^+) 290.1334.

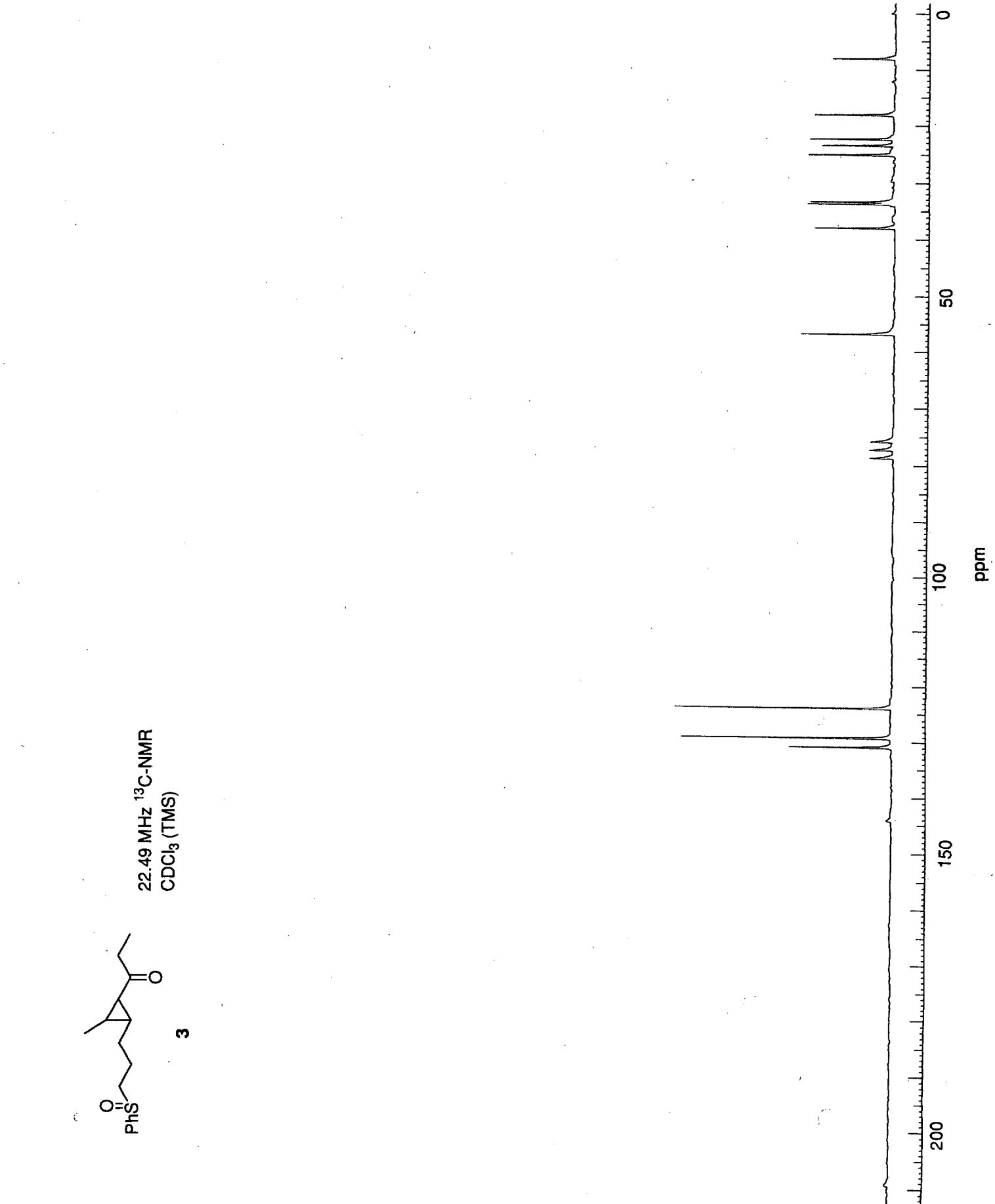
6d: 74%; colorless syrup ; ^{1}H-NMR (90 MHz, acetone-d_6) δ 0.73 (d, *J*=5.7 Hz, 3H), 0.80 (d, *J*=5.7 Hz, 3H), 1.21-2.92 (m, 12H), 5.28 (d, *J*=10.0 Hz, 1H), 7.55-7.73 (m, 5H); ^{13}C-NMR (22.49 MHz, acetone-d_6) δ 22.75, 22.86, 23.05, 25.19, 25.95, 26.95, 28.90, 60.95, 62.54, 65.82, 125.28, 129.72, 131.45, 134.52, 137.93, 144.29; IR

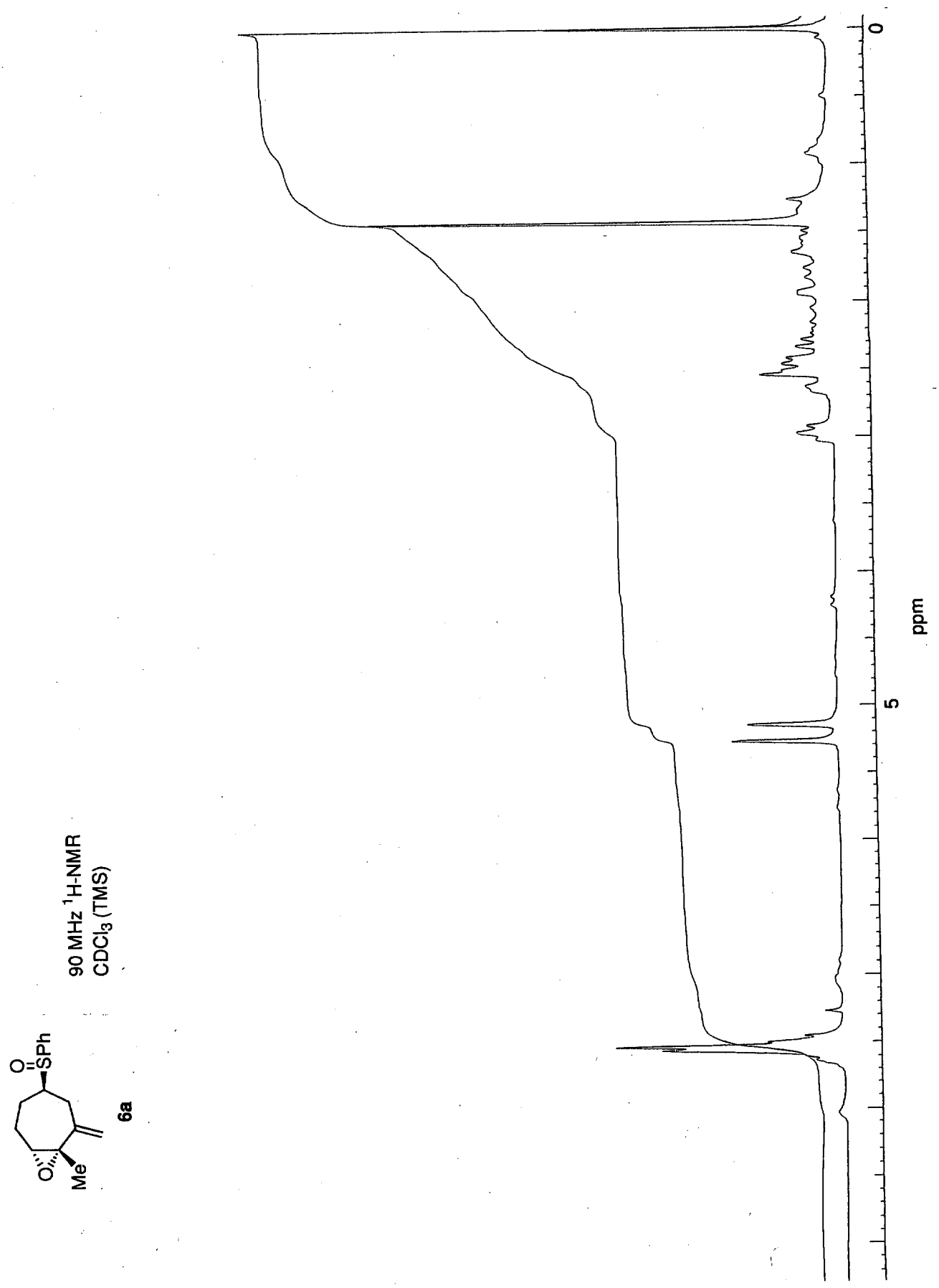
(neat) 1380 (*i*-Pr) 1090 (oxirane), 1040 (S=O), 870 (C=C) cm^{-1}; HRMS (70eV) calcd. for $C_{18}H_{24}O_2S$ (M^+) 304.1497, found (M^+) 304.1497.

6e: 67%; white solid, mp 118-122°C ; ^{1}H-NMR (90 MHz, acetone-d_6) δ 1.20-3.05 (m, 11H), 6.54 (s, 1H), 6.85-7.74 (m, 10H); ^{13}C-NMR (22.49 MHz, acetone-d_6) δ 22.56, 25.19, 26.27, 29.06, 61.43, 63.49, 63.84, 125.28, 127.47, 128.66, 129.15, 129.96, 130.80, 131.64, 137.09, 139.36, 143.56; IR (KBr) 1445 (Ph), 1090 (oxirane), 1040 (S=O), 890 (C=C) cm^{-1}; HRMS (70eV) calcd. for $C_{21}H_{22}O_2S$ (M^+) 338.1340, found (M^+) 338.1331.








90 MHz ^{1}H-NMR
$CDCl_3$ (TMS)
O
SPh
O
Me
6a
0
5
ppm