Supplementary Material (ESI) for Organic & Biomolecular Chemistry

ELECTRONIC SUPPLEMENTARY INFORMATION

Easy access to *trans* 2,3-disubstituted cyclobutanones, 2,4,5 trisubstituted 3,6-dihydro 2H-pyrans and *cis*-substituted phenyl cyclopropyl sulfones by using the highly versatile 1-phenylsulfenyl- or 1-phenylsulfonyl-cyclopropyl ketones.

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Analytical data of 1b, 1c, 1e, 1f, 1j, 1k.

(Z)-4-methyl-1-phenyl-2-(phenylthio)pent-2-en-1-one 1b

Yellow oil. Yield 72%. IR (neat): 1670 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.13 (d, 6H, J = 6Hz), 3.21-3.29 (m, 1H), 6.53 (d, 1H, J = 9Hz), 7.10-7.71 (m, 10H). ^{13}C NMR δ: 21.96, 30.07, 126.61, 128.07, 128.88, 129.36, 129.89, 132.26, 132.28, 133.28, 134.35, 155.52, 193.98. MS m/z: 282 (M^+(80)), 267 (3), 239 (2), 211 (4), 172 (10), 145 (20), 121 (25), 105 (65), 77 (100). Anal. Calcd. for $C_{18}H_{18}OS$: C, 76.56; H, 6.42; S, 11.35. Found: C, 76.49; H, 6.38; S, 11.30.

(Z)-6-phenyl-3-(phenylthio)hex-3-en-2-one 1c

Yellow oil. Yield 79%. IR (neat): 1690 cm^{-1} . ^1H NMR ($CDCl_3$) δ: 2.24 (s, 3H), 2.71-2.88 (m, 4H), 7.03-7.31 (m, 11H). ^{13}C NMR δ: 27.48, 32.37, 34.52, 126.06, 126.25, 127.67, 128.28, 128.39, 128.50, 128.57, 129.17, 135.17, 150.26, 194.53. MS m/z: 282 (M^+(44)), 239 (3), 191 (17), 163 (11), 147 (17), 129 (26), 109 (15), 91 (100), 65 (35), 51 (20). Anal. Calcd. for $C_{18}H_{18}OS$: C, 76.56; H, 6.42; S , 11.35. Found: C, 76.52; H, 6.36; S, 11.28.

(Z)-1-phenyl-4-(phenylthio)non-3-en-5-one 1e

Yellow oil. Yield 50 %. IR (neat): 1680 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.79 (t,3H, , J = 7.2 Hz), 0.85-0.94 (m, 2H), 1.11-1.60 (m, 4H), 2.52-2.60 (m, 2H), 2.82-2.84 (m, 2H), 7.04-7.30 (m, 11H). ^{13}C NMR ($CDCl_3$) δ: 13.78, 22.12, 26.31, 32.25, 34.55, 39.09, 126.00, 126.21, 127.69, 128.41, 128.47, 129.12, 135.11, 135.64, 140.58, 149.26, 200.15. MS m/z: 324 (M^+(80)), 267 (5), 233 (45), 215 (3), 172 (16), 128 (46), 109 (18), 91 (100).Anal. Calcd. for $C_{21}H_{24}OS$: C,77.73; H, 7.46; S, 9.88. Found: C, 77.75; H, 7.58; S, 9.75.

(Z)-3-(Phenylthio)-oct-2-en-4-one 1f

The instability of this product precluded its purification by cromathography, but confirmation of the structure arises from GC MS, IR and ^1H NMR of the crude mixture. IR (neat): 1670 cm^{-1}, ^1H NMR ($CDCl_3$) δ: 0.87 (t, 3H, J = 5.7 Hz), 1.20-1.34 (m, 4H), 1.91 (d, 3H, J = 5.4 Hz), 2.58 (t, 2H, J = 5.7 Hz), 6,22 (m, 1H), 7.14-7.37 (m, 5H). MS m/z: 234 (M^+(72)), 219 (8), 192 (4), 177 (14), 149 (100), 134 (84), 115 (64),109 (55), 77 (32).

(Z)-3-(phenylthio)-4-(thiophen-2-yl)but-3-en-2-one 1j

Orange oil. Yield 90%. IR (neat): 1670 cm^{-1} . ^1H NMR ($CDCl_3$) δ: 2.38 (s, 3H), 7.10-7.79 (m, 8H), 8.35 (s, 1H). ^{13}C NMR δ: 27.53, 126.27, 126.69, 127.00, 127.25, 129.33, 133.20, 135.00, 136.94, 140.21, 182.93, 197.99. MS m/z: 260 (M^+(98)), 245 (2), 217 (44), 184 (100), 158 (4), 140 (35), 121 (12), 96 (32), 69 (25), 51 (41). Anal. Calcd. for $C_{14}H_{12}OS_2$: C, 64.58; H, 4.65; S ,24.63. Found: C, 64.52; H, 4.61; S, 24.58.

(Z)-4-(naphthalen-3-yl)-3-(phenylthio)but-3-en-2-one 1k

Orange oil. Yield 86%. IR (neat): 1680 cm^{-1} . ^1H NMR ($CDCl_3$) δ: 2.37 (s, 3H), 7.18-8.28 (m, 12H). ^{13}C NMR δ: 27.69, 126.43, 126.48, 127.13, 127.44, 127.61, 127.84, 127.92, 129.14, 129.41, 131.81, 132.02, 132.37, 132.91, 135.38, 144.38, 199.02. MS m/z: 304 (M^+(100)), 289 (2), 261 (48), 245 (8), 228 (54), 211 (19), 184 (40), 166 (8), 152 (76), 126 (15), 109 (10), 93 (6), 77 (30), 51 (37). Anal. Calcd. for $C_{20}H_{16}OS$: C, 78.91; H, 5.30; S , 10.53. Found: C, 78.86; H, 5.25; S, 10.50.

Analytical data of 2b, 2c, 2e, 2f, 2g, 2j, 2k.

(2-isopropyl-1-(phenylthio)cyclopropyl)(phenyl)methanone 2b
Yellow oil. Yield 71%. IR (neat): 1690 cm^{-1} . ^1H NMR ($CDCl_3$) δ: 0.92 (dd, 1H, *J* = 7.2 Hz, *J* = 4.5 Hz), 1.11 (d, 3H, *J* = 6.6Hz), 1.26 (d, 3H, *J* = 6.6Hz), 1.42-1.51 (m, 1H), 1.91-1.99 (m,1H), 2.30 (dd, 1H, *J* = 9.0 Hz, *J* = 4.5 Hz), 7.07-7.93 (10H). ^{13}C NMR δ: 21.96, 22.25, 22.61, 30.28, 38.52, 39.99, 125.70, 127.69, 127.76, 127.86, 128.76, 129.04, 132.10, 136.48. 199.80. MS m/z: 296 (M^+ (31)), 240 (6), 211 (7), 191 (10), 171 (7), 135 (21), 105 (100), 77 (98). Anal. Calcd. for $C_{19}H_{20}OS$: C, 76.99; H, 6.80; S, 10.82. Found: C, 76.78; H, 6.78; S, 10.79.

1-(2-phenethyl-1-(phenylthio)cyclopropyl)ethanone 2c
Yellow oil. Yield 73%. IR (neat): 1690 cm^{-1} . ^1H NMR ($CDCl_3$) δ: 0.94-0.97 (m,1H), 1.94-2.05 (m, 4H), 2.40 (s, 3H), 2.72 (t, 2H, *J* = 7.5 Hz), 7.11-7.29 (m, 10H). ^{13}C NMR δ: 27.29, 28.32, 31.56, 33.46, 35.54, 38.91, 125.28, 125.74, 125.96, 128.37, 128.43, 129.07, 137.07, 141.33, 208.47. MS m/z: 296 (M^+ (32)), 253 (3), 205 (3), 179 (4), 135 (24), 117 (16), 91 (100), 65 (28). Anal. Calcd. for $C_{19}H_{20}OS$: C, 76.99; H, 6.80; S, 10.82. Found: C, 76.84; H, 6.72; S, 10.75.

1-(2-phenyl ethyl-1-(phenylthio)cyclopropyl)pentan-1-one 2e Yellow oil. Yield 91 %. IR (neat): 1680 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.86 (t, 3H, *J* = 7.5 Hz), 0.89-0.94 (m, 1H), 1.19-1.31 (m, 2H), 1.44-1.56 (m,2H), 1.88-2.04 (m,4H), 2.70-2.79 (m, 2H), 2.81-2.86 (m, 2H), 7.10-7.30 (m, 10H). ^{13}C NMR ($CDCl_3$) δ: 13.84, 22.19, 26.40, 26.90, 31.58, 33.29, 35.56, 38.65, 39.75, 125.29, 125.69, 125.97, 128.38,128.39, 129.03, 137.29, 141.41, 208.47. MS m/z: 338 (M^+(74)), 305 (3), 253 (8), 161 (6), 143 (16), 143 (14), 117 (25), 109 (24), 91 (100), 77 (11). Anal. Calcd. for $C_{22}H_{26}OS$: C,78.06; H, 7.74; S, 9.47. Found: C, 78.02; H, 7.78; S, 9.45.

1-(2-methyl-1-(phenylthio)cyclopropyl)pentan-1-one 2f Colourless oil. Yield 90 %. IR (neat): 1680 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.83 (t, 3H, *J* = 7.2 Hz), 0.92 (dd, 1H, *J* = 7.5 Hz, *J* = 3.9 Hz), 1.16-1.26 (m, 2H), 1.30 (d, 3H, *J* = 6.3 Hz), 1.44-1.57 (m, 3H), 1.66 (dd, 1H, *J* = 1.5 Hz, *J* = 6.3 Hz), 1.89 (dd, 1H, *J* = 9.0 Hz, *J* = 3.9 Hz), 2.05-2.09 (m, 1H), 2.79-2,88 (m, 2H), 7.10-7.28 (m, 5H). ^{13}C NMR ($CDCl_3$) δ: 13.82, 14.34, 22.16, 26.38, 27.01, 28.21, 39.69, 39.83, 125.03, 125.40, 125.61, 128.97, 137.43, 209.09. MS m/z: 248 (M^+ (100)), 233 (4), 215 (18), 191 (12), 163 (98), 147 (28), 121 (98), 109 (68), 10531), 85 (90).77 (48). Anal. Calcd. for $C_{15}H_{20}OS$: C,72.54; H, 8.12; S, 12.91. Found: C, 72.74; H, 8.18; S, 12.85.

1-(2-furan-2-yl)-1-(phenylthio)cyclopropyl)ethanone 2g
Yellow oil. Yield 70%. IR (neat): 1680 cm^{-1} . ^1H NMR ($CDCl_3$) δ: 1.72 (dd, 1H, *J* = 7.5 Hz, *J* = 4.5 Hz), 2.35 (dd, 1H, *J* = 9.9 Hz, *J* = 4.5 Hz), 2.45 (s, 3H), 3.16 (dd, 1H, *J* = 9.0 Hz, *J* = 8.1 Hz), 6.15 (d, 1H, *J* = 3.3 Hz), 6.24-6.30 (m, 1H), 7.12 (d, *J* = 5.1 Hz), 7.20-7.43 (m, 5H). ^{13}C NMR δ: 24.89, 28.53, 30.25, 57.77, 108.95, 110.44, 126.29, 128.96, 129.36, 134.41, 142.07, 148.03, 177.86. MS m/z: 258 (M^+ (100)), 229 (28), 213 (14), 181 (8), 153 (6), 137 (21), 109 (18), 77 (26). Anal. Calcd. for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; S, 12.41. Found: C, 69.59; H, 5.58; S, 12.49.

1-(1-phenylthio)-2-(thiophen-2-yl)cyclopropyl)ethanone 2j
Yellow oil. Yield 76%. IR (neat): 1680 cm^{-1} . ^1H NMR ($CDCl_3$) δ: 1.67 (dd, 1H, *J* = 7.5 Hz, *J* = 4.5 Hz), 2.48 (s, 3H), 2.49 (dd, 1H, *J* = 9.0 Hz, *J* = 4.5 Hz), 3.29 (dd, 1H, *J* = 7.8 Hz, *J* = 9.3 Hz), 6.89-6.94 (m, 2H), 6.24-6.30 (m, 2H), 7.11-7.28 (m, 6H). ^{13}C NMR δ: 27.42, 28.58, 32.35, 42.21, 124.94, 125.55, 126.31, 126.65, 127.20, 129.01, 136.25, 139.32, 206.20. MS m/z: 274 (M^+ (100)), 256 (2), 231 (18), 216 (2), 197 (10), 153 (57), 137 (11), 121 (72), 109 (21), 77 (33). Anal. Calcd. for $C_{15}H_{14}OS_2$: C, 65.66; H, 5.14; S, 23.37. Found: C, 65.44; H, 5.37; S, 23.48.

1-(2-(naphthalene-3-yl)-1-(phenylthio)cyclopropyl)ethanone 2k
Yellow oil. Yield 80 %. IR (neat): 1680 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.91 (dd, 1H, *J* = 7.8 Hz, *J* = 4.5 Hz), 2.51 (s, 3H), 2.56 (dd, 1H, *J* = 9.0 Hz, *J* = 4.5 Hz), 3.29 (t, 1H, *J* = 8.7 Hz), 7.05-7.81 (m, 5H). ^{13}C NMR δ: 24.96, 28.45, 37.98, 41.68, 125.38, 125.90, 126.11, 127.24, 127.52, 127.63, 127.78, 128.14, 128.96, 132.68, 132.76, 132.97, 136.54, 234.78. MS m/z: 318 (M^+ (32)), 303 (4), 239 (6), 197 (25), 165 (100), 128 (28), 109 (34), 77 (45). Anal. Calcd. for $C_{21}H_{18}OS$: C, 79.21; H, 5.70; S, 10.67. Found: C, 79.34; H, 5.49; S, 10.82.

General method for reduction of ketones 2a-g.

To a solution of the ketone **2a-g** (6.23 mmol) in THF (30 mL) was added a solution of $LiAlH_4$ (2.0 M in THF, 4.67 mL, 9.35 mmol) and the mixture was stirred at -78 °C for 1 h. The resulting mixture was diluted with diethyl ether, treated with wet Na_2SO_4. The organic layer was filtered and washed with brine, dried (Na_2SO_4), and evaporated. The residue purified by column chromatography (silica gel; light petroleum-diethyl ether 10:1) give a *syn/anti* mixture of the **6a-g** products, the ratio of which was determined by ^1H NMR analysis and GC MS. The results are summarized in Tables 1.

1-(2-isopropyl-1-(phenylthio)cyclopropyl)ethanol 6a
Inseparable 85/15 *syn/anti* mixture**.** Colourless oil. Yield 96 %. IR (neat): 3400 cm^{-1}). ^1H NMR ($CDCl_3$) δ: 0.63-0.77 (m, 2H), 0.85-0.98 (m, 2H), 1.02 (d, 6H, *J* = 6.9 Hz), 1.06 (d, 6H, *J*= 6.6 Hz), 1.25 (d, 3H, *J* = 6.3 Hz),1.29 (d, 3H, *J* = 6.3 Hz), 1.24-1.31 (m, 1H), 1.33-1.38 (m, 1H), 1.57-1.67 (m, 2H), 1.94 (d, 2H, *J* = 8.1 Hz), 3.29 (dq, 1H, *J* = 8.1 Hz, *J* = 6.3 Hz), 3.65-3.70 (m, 1H), 7.15-7.53 (m, 10H). Major isomer: MS m/z: 236 (M^+ (24)), 218 (10), 193 (4), 180 (9), 164 (38), 151 (29), 135 (100), 123 (17), 110 (96), 91 (48), 77 (51), 65

(56), 43 (94). Minor isomer. MS m/z: 236 (M^+(17)), 218 (7), 203 (2), 180 (6), 164 (24), 145 (14), 135 (78), 109 (100), 91 (45), 65 (60), 43 (96).

1-(2-isopropyl-1-(phenylthio)cyclopropyl)(phenyl)methanol 6b Inseparable 94:6 mixture of two isomers. Colourless oil. Yield 92%. IR (neat): 3400 cm $^{-1}$). Major isomer: ^{1}H NMR ($CDCl_3$) δ: 0.74 (dd, 1H, *J* = 5.1 Hz, *J* = 6.6 Hz), 0.85-0.95 (m,1H), 0.93 (d, 3H, *J* = 4.8 Hz), 0.95 (d, 3H, *J* = 4.8 Hz), 1.05 (dd, 1H, *J* = 5.1 Hz, *J* = 8.7 Hz), 1.57-1.63 (m, 1H), 2.79 (d, 1H, *J* = 4.2 Hz), 4.67 (d, 1H, *J* = 4.2 Hz), 7.21-7.54 (m, 10H). ^{13}C NMR ($CDCl_3$) δ: 21.22, 22.09, 22.66, 29.94, 31.42, 39.35, 78.00, 126.19, 126.94, 127.83, 127.97, 128.89, 129.64, 136.11, 140.24. MS m/z: 248 (M^+(34)), 280 (12), 242 (10), 226 (21), 191 (13), 155 (16), 135 (54), 116 (76), 77 (100). Minor isomer: Spectral data worked out by reaction mixture: ^{1}H NMR ($CDCl_3$) δ: 0.64 (dd, 1H, *J* = 5.1 Hz, *J* = 6.9 Hz), 0.94 (d, 3H, *J* = 4.8 Hz), 0.95 (d, 3H, *J* = 4.8 Hz), 0.99 (dd, 1H, *J* = 6.9 Hz, *J* = 8.7 Hz), 1.46 (dd, 1H, *J* = 5.4 Hz, *J* = 9.0 Hz), 1.57-1.63 (m, 1H), 2.29 (d, 1H, *J* = 4.2 Hz), 4.64 (d, 1H, *J* = 4.2 Hz), 7.21-7.54 (m, 10H). MS m/z: 248 (M^+ (28)), 280 (10), 253 (80), 226 (16), 191 (14), 147 (36), 115 (68), 77 (100).

1-(2-phenylethyl-1-(phenylthio)cyclopropyl)ethanol 6c
Inseparable 70/30 *syn/anti* mixture**.** Colourless oil. Yield 85 %. IR (neat): 3400 cm $^{-1}$). ^{1}H NMR ($CDCl_3$) δ: 0-61-0.65 (m, 1H), 1.15-1.22 (m, 4H), 1.24 (d, 6H**,** *J* = 6.3 Hz), 1.57 (br s, 1H), 1.83 (d, 1H, *J* = 5.7 Hz), 1.91-2.02 (m, 5H), 2.67-2.75 (m, 4H), 3.39-3.44 (m, 1H), 3.60-3.64 (m, 1H), 7.11-7.48 (m, 10H). Major isomer: MS m/z: 298 (M^+(6)), 280 (3), 253 ((), 189 (5), 171 (13), 145 (10), 110 (26), 91 (100).Minor isomer: MS m/z: 298 (M^+ (6)), 280 (3), 253 (8), 189 (5), 171 (13), 145 (10), 110 (26), 91 (100).

1-(2-phenyl-1-(phenylthio)cyclopropyl)ethanol 6d
Inseparable 90:10 mixture of two isomers. Colourless oil. Yield 80 %. IR (neat): 3400 cm $^{-1}$). Major isomer: ^{1}H NMR ($CDCl_3$) δ: 1.34 (d, 3H, *J* = 6.3 Hz), 1.48 (dd, 1H, *J* = 6.3 Hz, *J* = 6.9 Hz), 1.93 (dd, 1H, *J* = 6.3 Hz, *J* =8.7 Hz), 2.09 (d, 1H, *J* = 6.9 Hz), 2.51 (dd, 1H, *J* = 7.2 Hz, *J* =9.0 Hz), 3.71 (m, 1H), 7.14-7.35 (m, 10H).
Minor isomer: Spectral data worked out by reaction mixture: ^{1}H NMR ($CDCl_3$) δ: 1.41 (d, 3H, *J* = 6.3 Hz), 1.50-1.54 (m, 1H), 1.72 (dd, 1H, *J* = 5.4 Hz, *J* = 9.3 Hz), 1.86 (d, 1H, *J* = 5.4 Hz), 2.56 (dd, 1H, *J* = 6.3 Hz, *J* =8.7 Hz), 3.90 (m, 1H), 7.14-7.35 (m, 10H). MS m/z, identical for the two isomers: 270 (M^+ (6)), 252 (5), 219 (4), 101 (4), 164 (72), 143 (62), 115 (100), 77(41), 91 (58), 65 (35).

1-(2-phenylethyl-1-(phenylthio)cyclopropyl)pentan-1-ol 6e Inseparable 60/40 *syn/anti* mixture. Yellow oil.Yield 86 %. IR (neat): 3380 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.58 (t, 3H, *J* = 5.7 Hz), 0.84-0.89 (m,4H), 0.91 (t, 3H, *J* = 6.6 Hz), 1.08-1.70 (m,14 H), 1.85-2.04 (m, 2H), 2.63-2.81 (m, 2H), 3.07 (t, 1H, *J* = 6.6 Hz), 3.32 (dd, 1H, *J* = 3.3 Hz, *J* = 9.3 Hz), 7.12 -7.50 (m, 10 H). MS m/z, identical for the two isomers: 340 (M^+ (4)), 322 (3), 279 (5), 253 (6), 231 (2), 175 (5), 145 (12), 129 (14), 110 (26), 91 (100).

1-(2-methyl-1-(phenylthio)cyclopropyl)pentan-1-ol 6f
Inseparable 60/40 *syn/anti* mixture. Yellow oil. Yield 70 %. IR (neat): 3380 cm^{-1}**.** ^{1}H NMR ($CDCl_3$) δ: 0.87 (t, 3H, *J* = 6.9 Hz), 0.89 (t, 3H, *J* = 6.9 Hz), 0.93-1.78 (m, 1H), 1.10-1.16 (m,1H), 1.19-157 (m, 16H), 1.29 (d, 6H), 1.60-1.78 (m, 2H), 3.11-3.18 (m, 1H), 3.31-3.38 (m, 1H),7.11-7.48 (m, 10H). MS m/z, identical for the two isomers: 250 (M^+(38)),232 (6), 217 (8), 189 (39), 163 (24), 135 (38), 110 (100), 93 (34), 77 (32).

1-(2-furan-2-yl)-1-(phenylthio)cyclopropyl)ethanol 6g
Inseparable 65:35 *syn/anti* mixture. Yellow oil. Yield 94 %. IR (neat): 3400 cm^{-1}**.** ^{1}H NMR ($CDCl_3$) δ:1.33 (d, 6H, *J* = 6.3 Hz), 1.35-1.38 (m, 1H), 1.42 (dd, 2H, *J* = 5.4 Hz, *J* = 6.9 Hz), 1.59 (dd, 1H, *J* = 5.4 Hz, *J* = 9.3 Hz),1.66 (dd, 1H, *J* = 5.4 Hz, *J* = 9.3 Hz), 2.00 (br s, 2H), 2.45-2.51 (m, 2H), 3.69 (q, 1H, *J* = 6.3 Hz), 3.84 (q, 1H, **,** *J* = 6.3 Hz), 6.06 (d, 1H, *J* = 3.0 Hz), 6.10 (d, 1H, *J* = 3.6 Hz), 6.30-6.34 (m,2H), 7.12-7.34 (m, 12H). MS m/z, identical for the two isomers: 260 (M^+(5)), 242 (3), 215 (5), 166 (12), 151 (24), 134 (9), 109 (100), 94 (24), 77 (88).

General method for the synthesis of 6h-j.

To a stirred solution of the ketone **2b** or **2c** (3.38 mmol) in THF methyl litium (1,6 M in diethyl ether, 2.54 mL, 4.05 mmol) or n-buthyl litium (1,6 M in hexane, 2.54 mL, 4.05 mmol) was added at -78 °C. The resulting mixture was stirred and warmed to room temperature over 16 h and then diluted with diethyl ether, quenched with saturated aqueous NH_4Cl. The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. Flash chromatography (light petroleum /diethyl ether, 5/1) provided **6h-j.**

1-(2-isopropyl-1-(phenyltio)cyclopropyl)-1-phenylethanol 6h Mixture 94:6 of two inseparable diastereoisomers. Yield 86 %. IR (neat): 3440 cm^{-1}. Major isomer. ^{1}H NMR ($CDCl_3$) δ: 0.44 (dd, 1H, *J* = 6.6 Hz, *J* = 5.7 Hz),1.05 (d, 3H, *J* = 6.6 Hz), 1.07 (d, 3H, *J* = 6.6 Hz), 1.30 (dd, 1H, *J* = 6.6 Hz, *J* = 9.6 Hz), 1.60 (dd,1H, *J* = 5.4 Hz, *J* = 9.3 Hz), 1.62-1.67 (m,1H), 1.63 (s, 3H),2.62 (br s, 1H), 7.05-7.60 (m, 10H). ^{13}C NMR ($CDCl_3$) δ: 17.85, 22.06, 22.51, 26.52, 30.46, 33.84, 43,98, 76.25, 125.69, 126.08, 126.93, 127.71, 128.31, 129.83, 136.94, 146.73**.** MS m/z: 312 (M^+ (12)), 294 (5), 256 (4), 240 (16), 192 (58),149 (100), 121 (84), 105 (29), 91 (42), 77 (52). Minor isomer: MS m/z: 312 (M^+ (22)), 296 (5), 256 (1), 240 (16), 210 (5), 192 (33),149 (62), 121 (78), 105 (42), 91 (65), 77 (100).

2-(2-phenethyl-1-(phenylthio)cyclopropyl)propan-2-ol 6i
Yellow oil. Yield 66 %. IR (neat): 3440cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.47 (t, 1H, *J* = 6.0 Hz), 1.21 (s, 3H), 1.24-1.30 (m, 1H), 1.34 (s, 3H), 1.43 (dd, *J* = 6.0 Hz, *J* = 9.3 Hz), 1.92-1.97 (m, 2H), 2.62-2.76 (m, 2H), 7.12-7.46 (m, 10H). ^{13}C NMR δ: 19.13, 24.45, 25.97, 28.71, 32.69, 35.82, 42.32, 73.34, 125.57, 125.74, 128.26, 128.34, 128.54, 129.07, 137.39, 142.10**.** MS m/z: 312 (M^+ (12)), 294 (6), 254 (7),

178 (12), 145 (13), 129 (11), 110 (37), 91 (100), 77 (18). Anal. Calcd. for $C_{20}H_{24}OS$: C,76.88; H, 7.74; S, 10.26. Found: C, 76.82; H, 7.72; S, 10.35.

1-(2-isopropyl-1-(phenylthio)cyclopropyl)-1-phenylpentan-1-ol 6j Colourless oil. Yield 92 %. IR (neat): 3440cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.30(dd, 1H, *J* = 5.7 Hz, *J* = 6.9 Hz), 0.83 (t, 3H, *J* = 6.9 Hz), 0.81-0.95 (m, 2H), 0.99 (d, 3H, *J* = 6.6 Hz), 1.01 (d, 3H, *J* = 6.6 Hz), 1.24-1.33 (m, 3H), 1.50-1.59 (m, 2H), 1.60-1.79 (m, 1H), 2.05-2.15 (m, 1H), 2. 46 (br s, 1H), 6.93-7.51 (m, 10H). ^{13}C NMR δ:14.01, 17.67, 22.04, 22.51, 23.14, 25.83, 30.52, 33.94, 37.31, 44.75, 78.39, 125.46, 126.73, 126.77, 127.68, 128.31, 129.33, 137.33. 144.59. MS m/z: 354 (M^+ (40)), 336 (4), 293 (7), 241 (9), 192 (91), 164 (98), 149 (100), 130 (38), 115 (24), 109 (30), 91 (52), 77 (45). Anal. Calcd. for $C_{23}H_{30}OS$: C,77.92; H, 8.53; S, 9.04. Found: C, 77.84; H, 8.62; S, 9.15.

Rearrangement of cyclopropyl carbinols 6a,c to ketones 10a,c.

To a solution of cyclopropylcarbinol **6a,c** (1.5 mmol) in 10 mL of methylene chloride was added anhydrous stannic chloride (391 mg 1.2 mmol). After stirring for 1h, water was added followed by ether (20 mL). The organic layer was washed with saturated sodium bicarbonate solution, dried (Na_2SO_4) and the solvents removed in vacuo. The residue was chromatographed on silica gel with diethyl ether-light petroleum 1:10 as eluent.

5-Chloro-6-methylheptan-2-one 10a
Yellow oil. Yield 65 %. IR (neat): 1760cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.97 (d, 3H, *J* = 6.6 Hz), 1.03 (d, 3H, *J* = 6.6 Hz), 1.05 (t, 3H, *J* = 7.5 Hz), 1.95-2.07 (m, 1H), 2.51 (q, 2H, *J* = 7.5 Hz), 2.65 (dd, 1H, *J* = 3.9Hz, *J* = 16.5 Hz) 2.91 (dd, 1H, *J* = 9.6 Hz, *J* = 16.5 Hz) 4,31-4.37 (m,1H). ^{13}C NMR δ:7.49, 17.24, 19.70, 34.05, 37.07, 47.89, 63.56, 208.67. MS m/z: 126 (M^+-36 (14)), 97 (18), 72 (48), 57 (100). Anal. Calcd. for $C_8H_{15}ClO$: C, 59.07; H, 9.29. Found: C, 59.14; H, 9.22.

5-chloro -7-phenyl-heptan-3-one 10c
Yellow oil. Yield 90 %. IR (neat): 1760cm^{-1}. ^{1}H NMR ($CDCl_3$) δ:1.05 (t, 3H, *J* = 6.3 Hz), 1.96-2.08 (m, 2H), 2.44 (q, 2H, *J* = 7.2 Hz), 2.69-2.79 (m, 2H), 2.88 (dd, 1H, *J* = 8.7 Hz, *J* = 5.1 Hz), 2.96 (dd, 1H, *J* = 8.1 Hz, *J* = 16.8 Hz), 4.31-4.35 (m, 1H), 7.18-7.30 (m, 5H). ^{13}C NMR δ: 7.43, 32.58, 36.87, 39.77, 50.58, 56.80, 126.12, 128.46, 128.49, 129.02, 140.68, 207.64. MS m/z: 224 (M^+ (1)), 189 (15), 159 (13), 117 (19), 91 (100), 77 (9), 57 (45). Anal. Calcd. for $C_{13}H_{17}ClO$: C, 69.48; H, 7.62. Found: C, 69.34; H, 7.52.

Rearrangement of cyclopropyl carbinols 6a,c to ketones 11c,f,g.

A stirred solution of cyclopropylcarbinol **6c,f,g** (1.2 mmol) and *p*-toluenesulfonic acid (20 mg, 1,2 mmol,) in dry benzene (10 mL) was refluxed for 1 h. After cooling to room temperature, the benzene solution was washed with 10 % $NaHCO_3$ and with brine, dried (Na_2SO_4) and evaporated to remove the solvent. The residue was chromatographed on silica gel with diethyl ether-light petroleum 1:10 as eluent.

7-phenyl-5-(phenylthio)heptan-3-one 11c
Yellow oil. Yield 65 %. IR (neat): 1760 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ:1.01 (t, 3H, *J* = 7.2 Hz), 1.81-1.98 (m, 2H), 2.36 (q, 2H, *J* = 7.2 Hz), 2.64-2.86 (m, 4H), 3.58-3.64 (m, 1H), 7.14-7.41 (m, 10H). ^{13}C NMR δ: 7.57, 33.08, 36.42, 36.65, 43.44, 47.85, 125.92, 127.18, 128.39, 128.94, 132.34, 134.25,141.39, 209.18. MS m/z: 298 (M^+ (37)), 207 (3), 188 (12), 159 (14), 131 (17), 109 (38), 91 (100), 77 (18). Anal. Calcd. for $C_{13}H_{22}OS$: C,76.47 ; H, 7.43.; S, 10.74. Found: C, 76.44; H, 7.52; S, 10.65.

2-(phenylthio)-nonan-4-one 11f
Yellow oil. Yield 70 %. IR (neat): 1760 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.88 (t, 3H, *J* = 6.9 Hz), 1.21-1.35 (m, 4H), 1.28 (d, 3H, *J* = 4.8 Hz), 1.49-1.61 (m, 2H), 2.36 (t, 2H, *J* = 6.9 Hz), 2.53 (dd, 1H, *J* = 8.7 Hz, *J* = 16.8 Hz), 2.72 (dd, 1H, *J* = 8.7 Hz, *J* = 5.4 Hz), 3.66-3.77 (m, 1H), 7.21-7.42 (m, 5H). ^{13}C NMR δ: 13.85, 21.01, 22.38, 23.29, 31.28, 38.23, 43.51, 49.36, 127.13, 128.89, 132.20, 134.35, 208.99. MS m/z: 250 (M^+ (70)), 194 (4), 179 (6), 152 259, 137 (52), 109 (62), 99 (100), 71 (58). Anal. Calcd. for $C_{15}H_{22}OS$: C,71.35 ; H, 8.86; S, 12.80. Found: C, 71.44; H, 8.73; S, 12.75.

1-furan-2-yl-1-phenylsulfenyl-pentan-3-one 11g.
Yellow oil. Yield 68 %. IR (neat): 1760 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.99 (t,3H, *J* = 7.2 Hz), 2.37 (q, 2H, *J* = 7.2 Hz), 2.93 (dd, 1H, *J* = 8.7 Hz, *J* = 17.1Hz), 3.06 (dd, 1H, *J* = 8.1 Hz, *J* = 16.8Hz), 5.92 (d, 1H, *J* = 3.3 Hz), 6.18-6.20 (m,1H), 7.08-7.48 (m, 6H). ^{13}C NMR δ: 7.54, 36.55, 41.37, 45.58, 107.24, 110.26, 128.01, 128.74, 128.99, 133.72, 141.88, 153.23, 207.68 MS m/z: 260 (M^+ (4)), 151(31), 135 (3),109 (34), 94 (18), 77 (6), 57 100).Anal. Calcd. for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19; S, 12.31. Found: C, 69.34; H, 6.23; S, 12.35.

General procedure for the synthesis of 3a-d,i.

To an ice-cooled solution containing **2a-d,i** (1 mmol) in 30 mL of CH_2Cl_2 was added m-chloroperbenzoic acid (344 mg, 2 mmol) in small portions. After the addition was complete, the solution was stirred at room temperature for 16 h and then it was diluted with CH_2Cl_2 and washed with a saturated $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure and the residue was chromatographed on silica gel using light petroleum-diethyl ether (1:1) as eluent to give **3a-d,i.**
Spectral data of the compounds **3a,d,i** has been previously reported.[1,2]

(2-isopropyl-1-(phenylsulfonyl)cyclopropyl)(phenyl)methanone 3b White solid, mp 106-108°C. Yield 96 %. IR (neat): 1150, 1310, 1660 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.12 (d, 3H, *J* = 6.9 Hz), 1.42 (d, 3H, *J* = 6.9 Hz), 1.47-1.52 (m, 1H), 1.85 (dd,1H, *J* = 5.1 Hz, *J* = 7.8 Hz), 2.43 (dt, 1H, *J* = 5.1 Hz, *J* = 9.6 Hz), 2.47-2.52 (m, 1H), 7.37-7.97 (m, 10H). ^{13}C NMR δ: 18.95, 22.90, 22.99, 27.61, 39.49, 56.49, 127.92, 128.28, 128.65, 130.24, 133.44, 133.54. MS m/z: 328 (M^+ (2)), 273 (18), 221 (3), 195 (10), 171 (18), 141 (5), 125 (7), 105 (86), 77 (100). Anal. Calcd. for $C_{19}H_{20}O_3S$: C, 69.49; H, 6.14; S, 9.76. Found: C, 69.54; H, 6.22; S, 9.66.

1-(2-phenethyl-1-(phenylsulfonyl)cyclopropyl)ethanone 3c
Yellow oil.Yield 98 %. IR (neat): 1150, 1310, 1690 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.59-1.69 (m,1H), 1.92 (dd, 1H, *J* = 5.1 Hz, *J* = 8.4 Hz), 2.02 (dd, 1H, *J* = 5.1 Hz, *J* = 9.3 Hz), 2.23 (s, 3H), 2.31-2.49 (m, 2H), 2.79-2.97 (m, 2H), 7.17-7.92 (m, 10H). ^{13}C NMR δ: 21.53, 28.39, 28.86, 34.04, 35.64, 56.98, 1.26, 127.74, 128.46, 128.56, 129.19, 133.65, 140.89, 141.10, 198.72. MS m/z: 328 (M^+ (2)), 287(13), 237 (2), 211 (41), 186 (15), 171 (3), 147 (2), 130 (14), 115 (18), 91 (100), 78 (60), 65 (27).Anal. Calcd. for $C_{19}H_{20}O_3S$: C, 69.49; H, 6.14; S, 9.76. Found: C, 69.34; H, 6.12; S, 9.85.

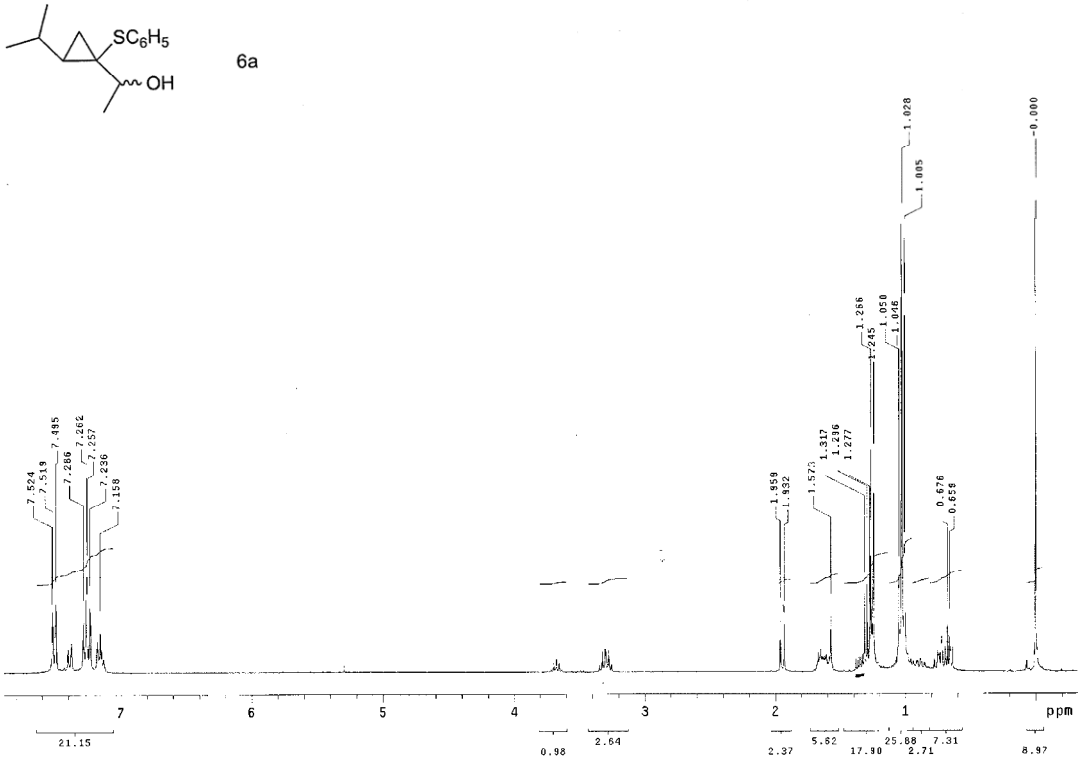
General method for reduction of the ketones 3a,b

To a stirred solution of the ketones **3a,b** (6.23 mmol) in dry THF (30 mL) cooled at -78°C, a solution of $LiAlH_4$ (2.0 M in THF, 4.67 mL, 9.35 mmol) was added dropwise. The mixture was stirred for 1h. The resulting mixture was treated with wet Na_2SO_4, diluted with diethyl ether and filtered. The organic layer was washed with brine, dried (Na_2SO_4) and evaporated. The residue was purified by column chromatography (silica gel; AcOEt/hexane 1:9) to give a *syn/anti* mixture of the products, the ratio of which was determined by ^1H NMR analysis and GC MS.

1-(*1R*,2S)-2-isopropyl-1-(phenylsulfonyl)cyclopropyl)ethanol 14a** Separable 70:30 mixture of two *sy:/anti* diastereoisomers. Colourless oil. Yield 82 %. IR (neat): 1140, 1290, 3500 cm^{-1}.
Minor isomer: ^1H NMR ($CDCl_3$) δ: 1.01 (d, 3H, *J* = 6.6 Hz), 1.06 (d, 3H, *J*= 6.6 Hz), 1.17 (d, 3H, *J* = 6.3 Hz), 1.21 (dd, 1H, *J* = 6.6 Hz, *J* = 3.3 Hz), 1.37 (dd, 1H *J* = 5.1 Hz, *J* = 9.3 Hz), 1.57 (dd, 1H, *J* = 8.1 Hz, *J* = 5.1 Hz), 1.94 (br s, 1H), 2.30-2.38 (m, 1H), 4.13 (q, 1H, *J* = 6.3 Hz), 7.54-7.92 (m, 5H). ^{13}C NMR δ: 17.11, 18.88, 23.02, 23.23, 26.46, 33.00, 50.92, 65.28, 128.36, 129.15, 133.52, 139.74. MS m/z: 268 (M^+ (1)), 253 (2), 213 (5), 195 (16), 143 (12), 125 (18), 108 (10), 93 (28), 77 (100). Anal. Calcd. for $C_{14}H_{20}O_3S$: C, 62.66; H, 7.51; S, 11.95. Found: C, 62.52; H, 7.48; S, 11.86.

Major isomer: ^1H NMR ($CDCl_3$) δ: 0.78 (d, 3H, *J* = 6.6 Hz), 1.10 (d, 3H, *J*= 6.6 Hz), 1.20 (dd, 1H, *J* = 9.0 Hz, *J* = 5.4 Hz), 1.21 (d, 3H, *J*= 6.6 Hz), 1.34 (dt, 1H, *J* = 10.2 Hz, *J* = 9.0 Hz), 1.58 (dd, 1H, *J* = 8.4 Hz, *J* = 5.4 Hz), 2.42-2.50 (m, 1H), 3.27 (br s, 1H), 4.12 (q, 1H, *J* = 6.6 Hz), 7.54-7.92 (m, 5H). ^{13}C NMR δ: 14.95, 20.87, 23.03, 23.43, 25.77, 34.65, 51.87, 65.02, 128.47, 129.11, 133.47, 140.18. MS m/z: 268 (M^+ (1)), 253 (2), 213 (10), 195 (26), 143 (32), 125 (34), 108 (12), 93 (38), 77 (100). Calcd. for $C_{14}H_{20}O_3S$: C, 62.66; H, 7.51; S, 11.95. Found: C, 62.48; H, 7.42; S, 11.88.

((*1R*,2S)-2-isopropyl-1-(phenylsulfonyl)cyclopropyl) (phenyl) methanol 14b**
Inseparable 70:30 mixture of two *syn/anti* diastereoisomers. Yellow oil. Yield 92 %. IR (neat): 1150, 1310, 1470, 3500 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.54 (dd, 1H, *J* = 5.1 Hz, *J* = 9.3 Hz), 0.57-0.61 (m, 1H), 0.97 (d, 3H, *J* = 6.6 Hz), 1.10-1.23 (m, 2H), 1.25 (d, 3H, *J* = 6.6 Hz), 1.52 (dd, 1H, *J* = 5.1 Hz, *J* = 8.4 Hz), 1.72 (dd, 1H, *J* = 3.9 Hz, *J* = 6.3Hz), 2.09-2.20 (m, 1H), 2.39-2.45 (m, 1H), 4.01 (d, 1H, *J* = 8.1Hz), 4.32 (d, 1H, *J* =10.6 Hz), 6.83-8.01 (m,10H).
MS (identical for the two *syn/anti* diastereoisomers) m/z: 330 (M^+(1)), 257 (3), 188 (4), 141 (16), 115 (25), 97 (8), 77 (100).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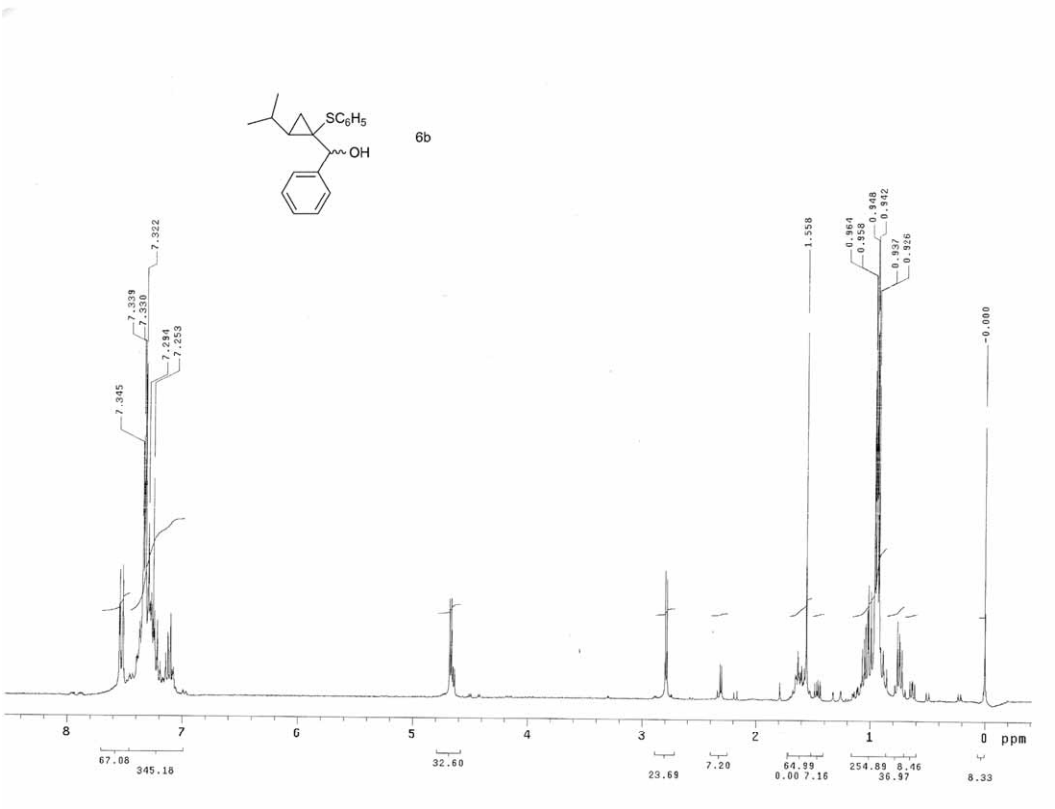

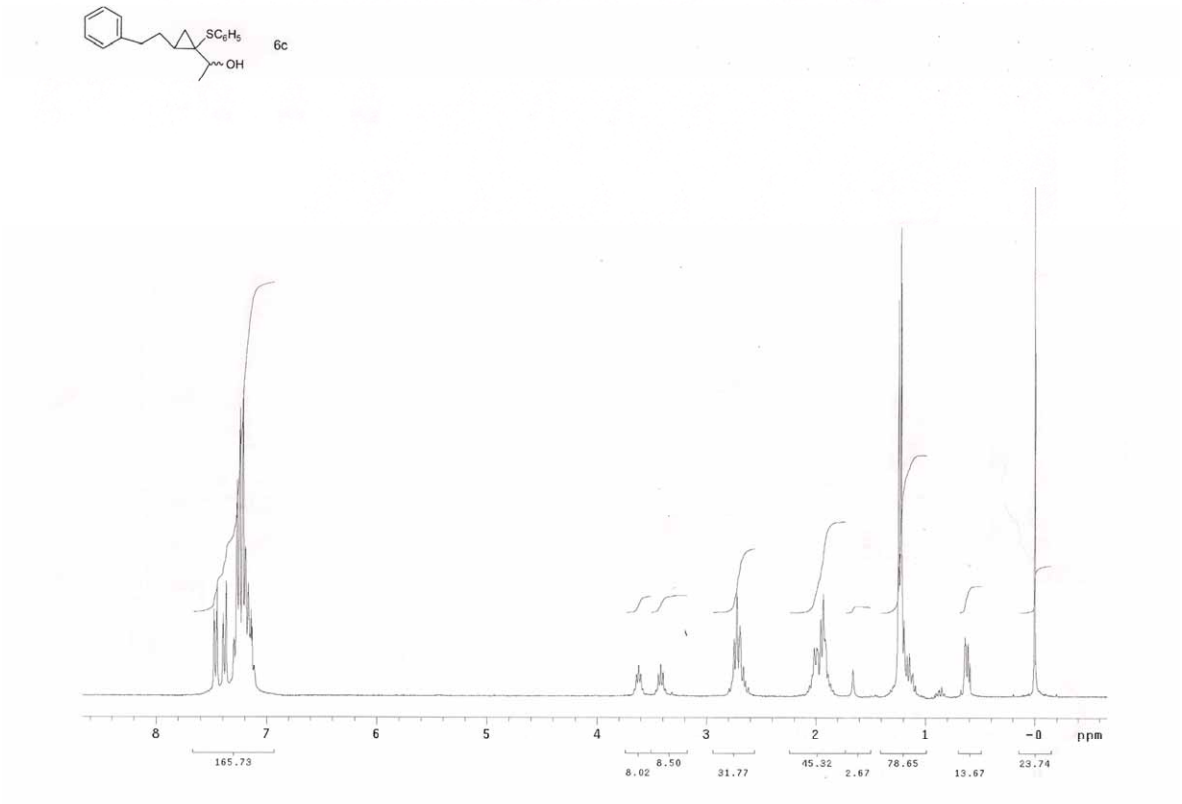

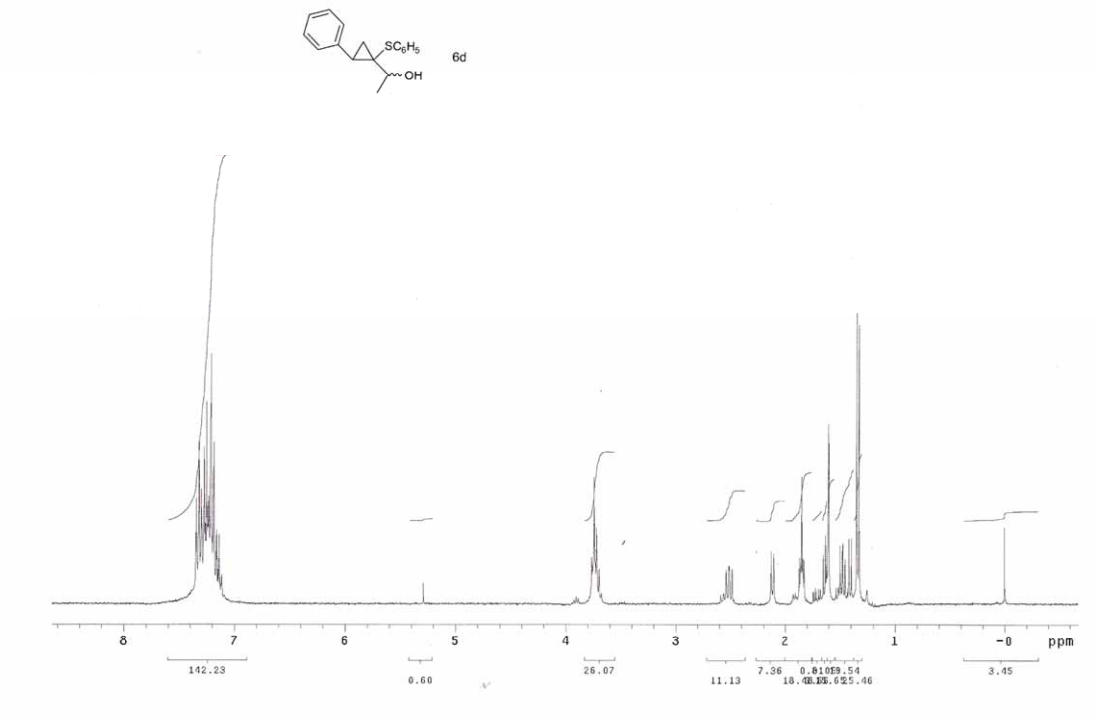

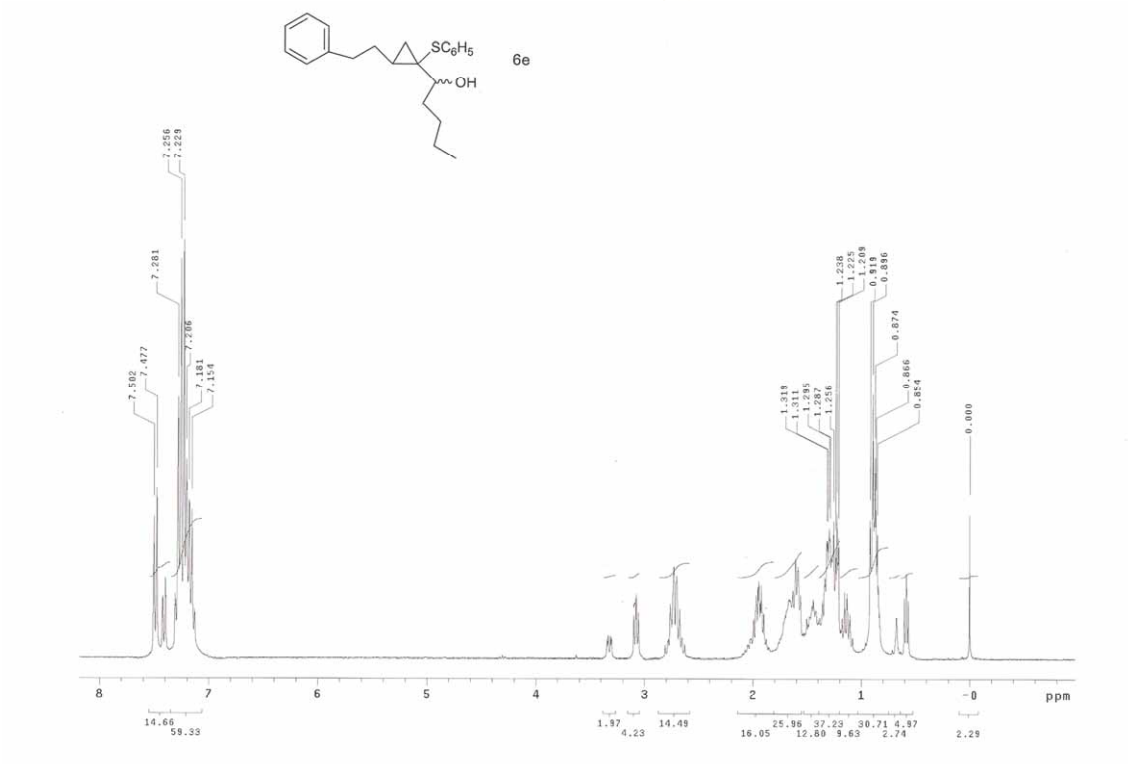

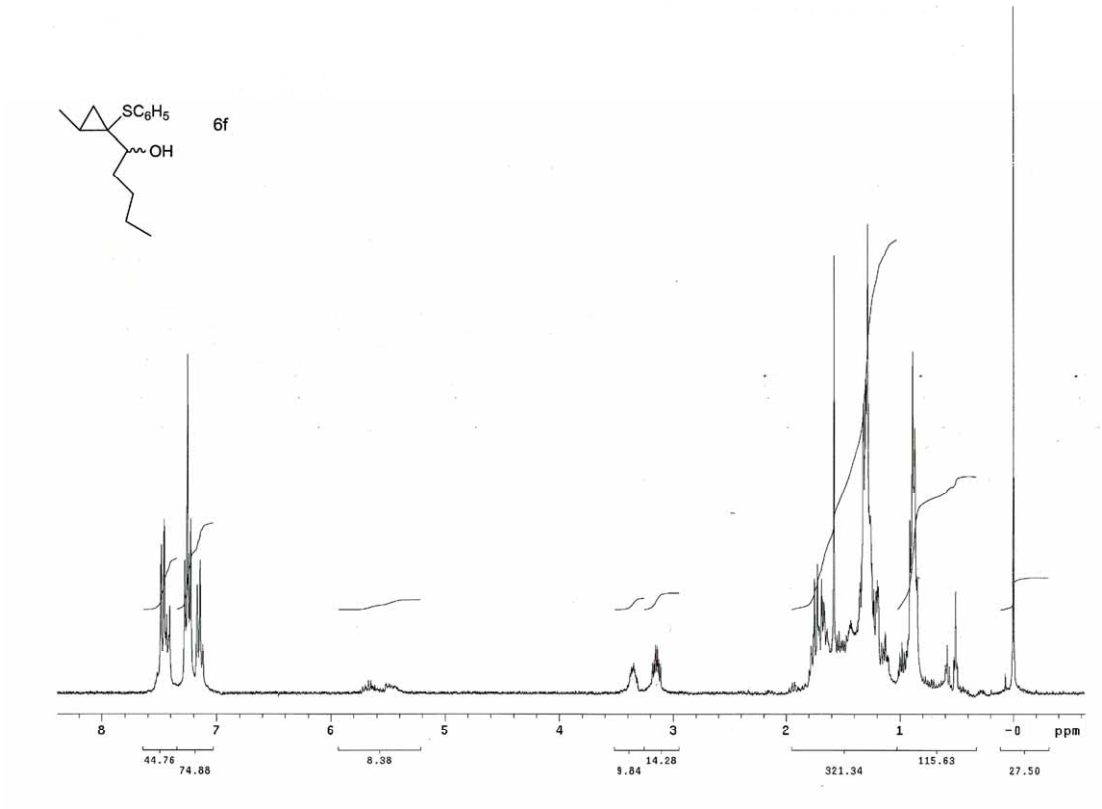

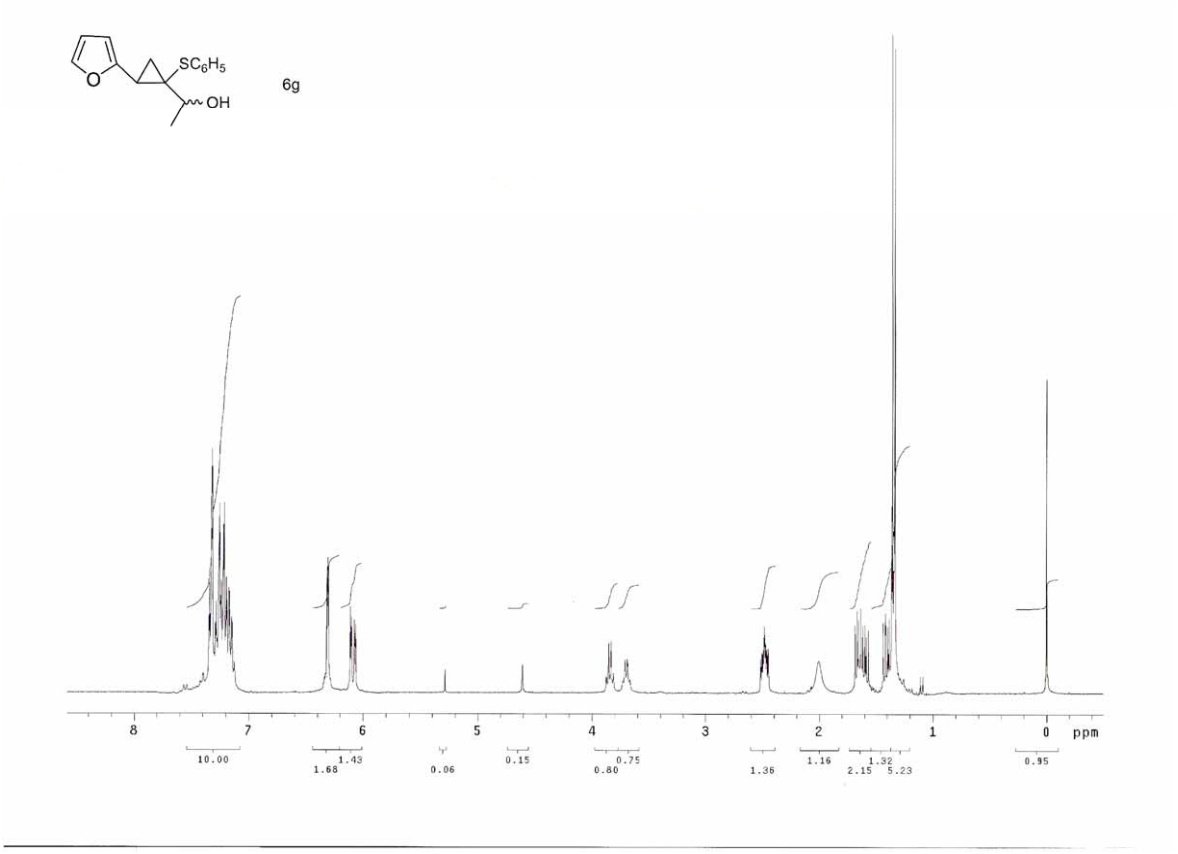
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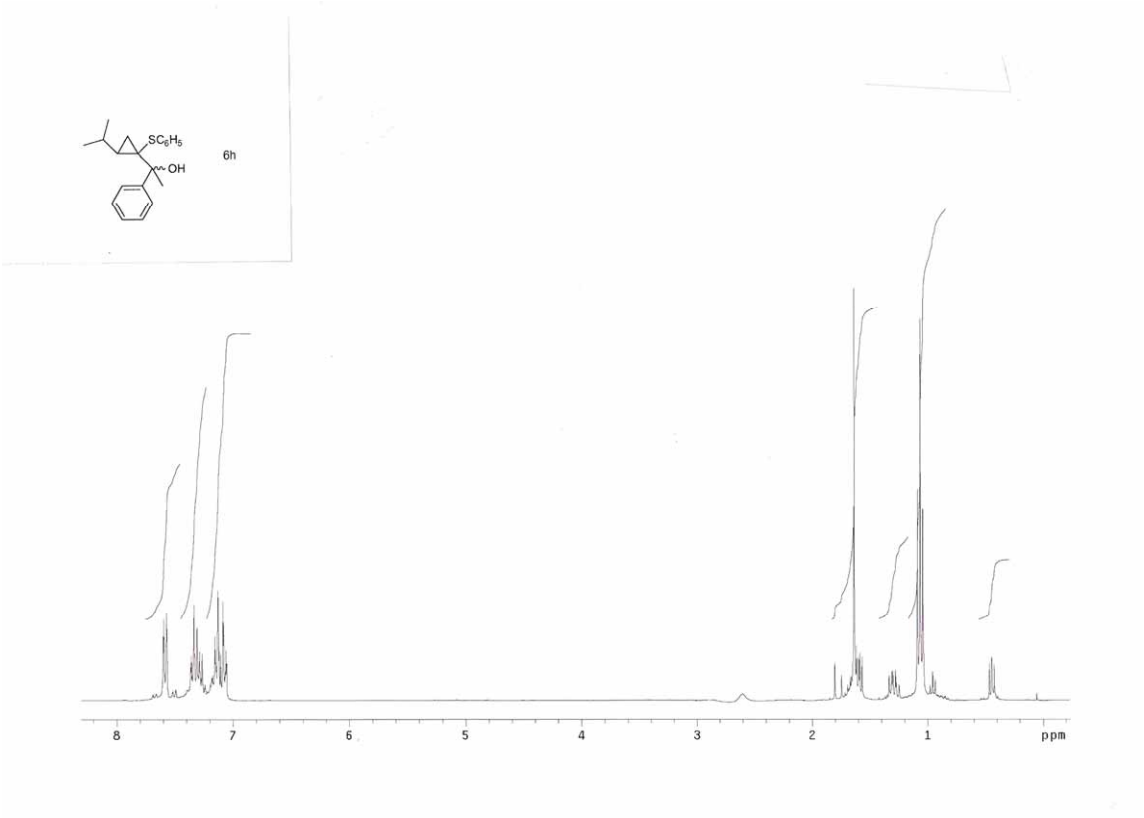

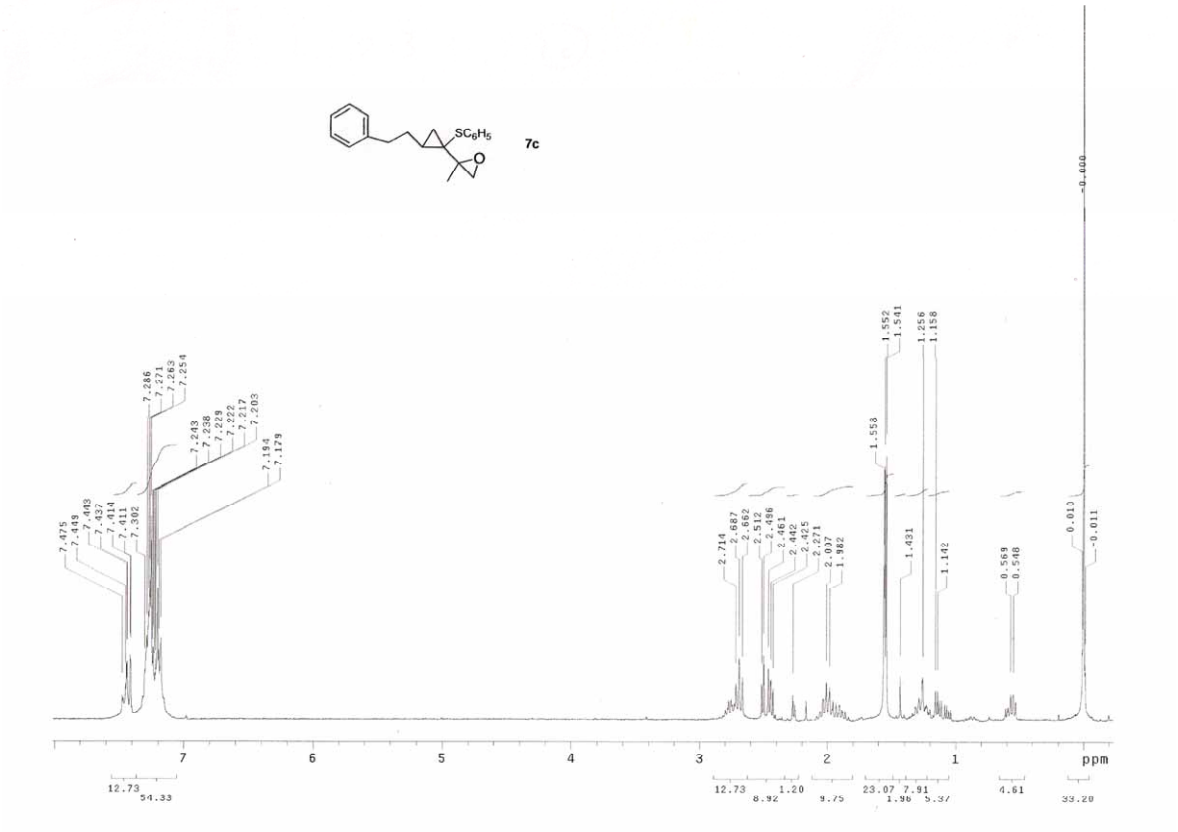
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