Supporting informations

Regioselective Synthesis of Trisubstituted 2,3-Dihydrofurans from Donor-Acceptor Cyclopropanes or from Reaction of the Corey Ylide with α -Sulfenyl-, α -Sulfinyl-, or α -Sulfonylenones.

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General method for the synthesis of the cyclopropanes 2a-i,n,o and the dihydrofurans 5e-m.

Trimethylsulfoxonium iodide (950 mg, 4.33 mmol) was rapidly added to a stirred suspension of pentane-washed NaH (173 mg, 4.33 mmol, 60 % in mineral oil) in DMSO (5 mL) under an argon atmosphere. After keeping the reaction mixture at room temperature for 2 h, a solution of the alkenes **1a-o** (3.94 mmol) was added and the reaction mixture was heated at 50 °C for 1 h. The mixture was diluted with diethyl ether, washed with brine and dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel (light petroleum-diethyl ether 10:1).

Cis geometry was assigned to compounds **2a-d**, **3a**, **3b**, by NOE experiments and to **2e**, **2f** by comparison with analogous compounds reported in the literature.¹

***cis*-1-[2-Isopropyl-1-(phenylsulfanyl)cyclopropyl]-1-ethanone. (2a)**

Yellow oil. Yield 87%. IR (neat): 1690 cm⁻¹. ¹H NMR (CDCl₃) δ: 0.92 (dd, 1H, *J* = 3.9 Hz, *J* = 7.8 Hz), 1.02 (d, 3H, *J* = 2.1 Hz), 1.05 (d, 3H, *J* = 2.1 Hz), 1.44-1.53 (m, 1H), 1.70-1.78 (m, 1H), 2.21 (dd, 1H, *J* = 3.9 Hz, *J* = 9.3 Hz), 2.43 (s, 3H), 7.07-7.29 (m, 5H). ¹³C NMR (CDCl₃) δ: 21.5, 22.3, 25.9, 27.7, 29.8, 39.1, 42.7, 124.9, 125.6, 128.6, 136.8, 207.4. MS *m/z*: 234 (M⁺ (38)), 43 (53). Anal. Calcd. for C₁₄H₁₈OS: C, 71.75; H, 7.74; S, 13.68. Found: C, 71.68; H, 7.56; S, 13.79.

***cis*-1-[2-Phenyl-1-(phenylsulfanyl)cyclopropyl]-1-ethanone. (2b)**

Red oil. Yield 68 %. IR (neat): 1680 cm⁻¹. ¹H NMR (CDCl₃) δ: 1.77 (dd, 1H, *J* = 4.8 Hz, *J* = 7.8 Hz), 2.46 (dd, 1H, *J* = 4.8 Hz, *J* = 9.3 Hz), 2.47 (s, 3H), 3.14 (t, 1H, *J* = 8.7 Hz), 7.06-7.82 (m, 10H). ¹³C NMR (CDCl₃) δ: 24.7, 28.4, 37.6, 41.4, 125.3, 126.1, 127.8, 127.9, 128.9, 129.2, 135.1, 136.5, 207.7. MS *m/z*: 268 (M⁺ (100)), 253 (8), 235 (7), 225 (13), 191 (21), 147 (94), 115 (96), 91 (53), 77 (16). Anal. Calcd. for C₁₇H₁₆OS: C, 80.08; H, 6.01; S, 11.95. Found: C, 78.18; H, 6.06; S, 11.89.

***cis*-1-[2-(4-Methylphenyl)-1-(phenylsulfanyl)cyclopropyl]ethanone. (2c)**

Yellow oil. Yield 85%. IR (neat): 1690 cm^{-1} . ^1H NMR (CDCl_3) δ : 1.74 (dd, 1H, $J = 3.9$ Hz, $J = 8.4$ Hz), 2.31 (s, 3H), 2.46 (s, 3H), 2.45-2.51 (m, 1H), 3.08 (t, 1H, $J = 8.4$ Hz), 7.07-7.22 (m, 9H). ^{13}C NMR (CDCl_3) δ : 21.1, 24.7, 28.3, 37.6, 41.4, 125.3, 126.0, 128.6, 128.9, 129.0, 132.0, 136.6, 137.1, 207.7. MS m/z : 282 ($\text{M}^+(100)$), 267 (3), 249 (4), 239 (6), 207 (85), 191 (10), 181 (3), 172 (5), 161 (28), 147 (11), 129 (60), 115 (24), 105 (20), 91 (18), 77 (21), 65 (8), 51 (12), 43 (92), 32 (23). Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{OS}$: C, 76.56; H, 6.42; S, 11.35. Found: C, 76.45; H, 6.34; S, 11.46.

***cis*-1-[2-(4-Methoxyphenyl)-1-(phenylsulfanyl)cyclopropyl]-1-ethanone.(2d)**

Yellow oil. Yield 81%. IR (neat): 1700 cm^{-1} . ^1H NMR (CDCl_3) δ : 1.72 (dd, 1H, $J = 4.5$ Hz, $J = 8.1$ Hz), 2.45-2.49 (m, 1H), 2.47 (s, 3H), 3.08 (t, 1H, $J = 8.1$ Hz), 3.79 (s, 3H), 6.79-7.34 (m, 9H). ^{13}C NMR (CDCl_3) δ : 25.0, 28.4, 37.5, 41.7, 55.2, 113.4, 125.3, 126.1, 128.9, 130.3, 132.9, 136.7, 158.9, 207.8. MS m/z : 298 ($\text{M}^+(100)$), 267 (3), 255 (4), 240 (4), 223 (12), 189 (14), 177 (27), 161 (5), 145 (45), 134 (27), 121 (36), 103 (9), 91 (16), 77 (12). Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_2\text{S}$: C, 72.45; H, 6.08; S, 10.74. Found: C, 72.38; H, 6.14; S, 10.89.

General method for the synthesis of 3a, b and 4c, d.

To an ice-cooled solution containing **2a-d** (1 mmol) in CH_2Cl_2 (30 mL), MCPBA (344 mg, 2 mmol) was added in small portions. 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 anhydrous Na_2SO_4 , concentrated under reduced pressure and the residue was chromatographed on silica gel using light petroleum-diethyl ether (1:1) as eluent to give **3a, b** (yield 80%, 84 %) and **4c, d** (yield 51%, 46 %).

***cis*-1-[2-Isopropyl-1-(phenylsulfonyl)cyclopropyl]-1-ethanone. (3a)**

Yellow oil. Yield 80 %. IR (neat): 1150, 1310, 1690 cm^{-1} . ^1H NMR (CDCl_3) δ : 1.08 (d, 3H, $J = 6.6$ Hz), 1.25 (d, 3H, $J = 6.6$ Hz), 1.30-1. (m, 1H), 1.91 (dd, 1H $J = 4.8$ Hz, $J = 8.4$ Hz), 2.01 (dd, 1H, $J = 4.8$ Hz, $J = 9.6$ Hz), 2.38-2.48 (m, 1H), 2.30 (s, 3H), 7.23-7.75 (m, 5H). ^{13}C NMR (CDCl_3) δ : 20.6, 22.7, 23.0, 26.9, 28.4, 43.4, 57.6, 127.6, 129.2, 133.6, 141.2, 198.6. MS m/z : 266 ($\text{M}^+(6)$), 251 (8), 211 (92), 173 (6), 159 (5), 143 (19), 125 (41), 109 (60), 91 (11), 77 (100), 55 (16). Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{S}$: C, 63.13; H, 6.81; S, 12.04. Found: C, 63.18; H, 6.76; S, 11.99.

***cis*-1-[2-Phenyl-1-(phenylsulfonyl)cyclopropyl]-1-ethanone. (3b)**

White crystals, m.p. 110-112 $^{\circ}\text{C}$. Yield 84%. IR (neat): 1150, 1310, 1680 cm^{-1} . ^1H NMR (CDCl_3) δ : 2.24 (dd, 1H, $J = 5.7$ Hz, $J = 10.5$ Hz), 2.50 (s, 3H), 2.69 (dd, 1H, $J = 5.7$ Hz, $J = 9.0$ Hz), 3.01(t, 1H, $J = 9.0$ Hz), 7.02-7.55 (m, 10H). ^{13}C NMR (CDCl_3) δ : 18.3, 29.0, 35.8, 58.4, 127.9, 128.1, 128.2, 128.7, 130.1, 131.6, 133.4, 139.9, 198.7. MS m/z : 300 ($\text{M}^+(8)$), 268 (8), 221 (7), 197 (6), 158 (60), 141 (15), 115 (63), 97 (33), 77(9), 43 (100). Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_3\text{S}$: C, 67.98; H, 5.37; S, 10.67 . Found: C, 68.05; H, 5.34; S, 10.56.

5-Methyl-2-(4-methylphenyl)-4-(phenylsulfonyl)-2,3-dihydrofuran. (4c)

Yellow oil. Yield 51 %. IR (neat): 1140, 1310 cm^{-1} . ^1H NMR (CDCl_3) δ : 2.32 (s, 3H), 2.33 (s, 3H), 2.85-2.91 (m, 1H), 3.20-3.27 (m, 1H), 5.52 (dd, 1H, $J = 6.3$ Hz, $J = 8.0$ Hz), 7.09-7.89 (m, 9H). ^{13}C NMR (CDCl_3) δ : 13.4, 21.1, 37.9, 83.15, 108.4, 125.8, 126.7, 129.1, 129.4, 132.8, 137.1, 138.5, 141.9, 165.7. MS m/z : 314 ($\text{M}^+(31)$), 295 (1), 248 (3), 221 (2), 205 (4), 191 (3), 172 (36), 155 (7), 129 (40), 115 (39), 91 (23), 77 (54), 63 (5), 43 (100). Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_3\text{S}$: C, 68.77; H, 5.77; S, 10.20 . Found: C, 68.65; H, 5.64; S, 10.26.

5-Methyl-2-(4-methoxyphenyl)-4-(phenylsulfonyl)-2,3-dihydrofuran.(4d)

Yellow oil. Yield 46%. IR (neat): 1150, 1310 cm^{-1} . ^1H NMR (CDCl_3) δ : 2.33 s, (3H), 2.85-2.93 (m, 1H), 3.17-3.26 (m, 1H), 3.79 (s, 3H), 5.51 (dd, 1H, $J = 10.2$ Hz, $J = 9.0$ Hz), 5.51 (dd, 1H, $J = 10.8$ Hz, $J = 9.0$ Hz), 6.83-7.90 (m, 9H). ^{13}C NMR (CDCl_3) δ : 13.3, 37.7, 55.3, 83.0, 108.3, 114.1, 126.7, 127.3, 128.3, 129.1, 132.7, 141.9, 159.8, 165.5. MS m/z : 330 (M^+ (100)), 299 (2), 265 (40), 223 (36), 189 (12), 158 (15), 145 (12), 115 (55), 105 (5), 91 (18), 77 (7), 65 (12). Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_4\text{S}$: C, 65.44; H, 5.49; S, 9.70. Found: C, 65.55; H, 5.54; S, 9.63.

***cis*-[2-(4-Methylphenyl)-1-(phenylsulfonyl)cyclopropyl](phenyl)methanone. (2e).**

Yellow oil. Yield 65 %. IR (neat): 1690 cm^{-1} . ^1H NMR (CDCl_3) δ : 1.73 (dd, 1H, $J = 7.8$ Hz, $J = 5.4$ Hz), 2.39 (s, 3H), 2.55 (dd, 1H, $J = 9.0$ Hz, $J = 5.4$ Hz), 2.90 (dd, 1H, $J = 7.8$ Hz, $J = 9.0$ Hz), 7.07-7.26 (m, 8H), 7.48-7.53 (m, 4H), 7.88-7.91 (m, 2H). ^{13}C NMR (CDCl_3) δ : 19.8, 21.2, 34.3, 40.7, 125.9, 128.1, 128.3, 128.8, 128.9, 129.0, 129.4, 131.7, 132.5, 135.5, 135.8, 137.2, 198.2. MS m/z : 237 (M^+ - 107 (14)), 225 (56), 210 (100), 192 (19), 181 (23), 165 (19), 147 (18), 115 (25), 105 (52), 91 (11), 77 (64), 65 (9), 51 (15). Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{OS}$: C, 80.20; H, 5.85; S, 9.31. Found: C, 80.18; H, 5.91; S, 9.28.

***cis*-(4-Chlorophenyl)-[2-(4-methylphenyl)-1-(phenylsulfonyl)cyclopropyl]**

methanone. (2f). Yellow oil. Yield 32 %. IR (neat): 1660 cm^{-1} . ^1H NMR (CDCl_3) δ : 1.75 (dd, 1H, $J = 6.0$ Hz, $J = 7.5$ Hz), 2.39 (s, 3H), 2.54 (dd, 1H, $J = 6.0$ Hz, $J = 9.3$ Hz), 2.88 (t, 1H, $J = 8.7$ Hz), 7.01-7.39 (m, 9H), 7.38 (d, 2H, $J = 8.4$ Hz), 7.84 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3) δ : 19.9, 21.2, 34.2, 40.6, 126.1, 128.2, 128.4, 128.8, 128.9, 129.0, 130.7, 131.4, 133.7, 135.4, 137.3, 138.8, 196.9. MS m/z : 380 (M^+ + 221), 378 (M^+ (50)), 343 (5), 269 (5), 239 (11), 207 (10), 161 (21), 139 (100), 129 (63), 105 (38), 77 (5). Anal. Calcd. for $\text{C}_{23}\text{H}_{19}\text{ClOS}$: C, 72.91; H, 5.05; S, 8.46. Found C, 72.88; H, 5.16; S, 8.59.

1-[2-Phenyl-1-(phenylsulfinyl)cyclopropyl]ethanone. (2g)

The geometry of **2g** was assigned on the basis of the ^1H NMR chemical shift of CH_3 protons of two geometric isomers. *Trans* geometry (COCH_3 and C_6H_5 *cis*) was assigned to the compounds having CH_3 chemical shift at higher fields, whereas the *cis* configuration was attributed to the other with the chemical shift of same protons at lower fields.² In addition, spectral data of *cis*-**2g** were identical with those of the same compounds obtained by oxidation of *cis*-**2b**. Red oil. Yield 45 %. Mixture 50:50 of two *trans* and two *cis* inseparable diastereoisomers. IR (neat): 1040, 1680 cm^{-1} .

First trans-diastereomer. ^1H NMR (CDCl_3) δ : 1.72 (s, 3H), 1.85 (dd, 1H, $J = 6.3$ Hz, $J = 9.6$ Hz), 1.99 (dd, 1H, $J = 6.3$ Hz, $J = 7.8$ Hz), 3.29 (dd, 1H, $J = 7.8$ Hz, $J = 9.6$ Hz), 7.22-7.62 (m, 10H).

Second trans-diastereomer. ^1H NMR (CDCl_3) δ : 1.60 (s, 3H), 2.09 (dd, 1H, $J = 6.3$ Hz, $J = 9.6$ Hz), 2.25 (dd, 1H, $J = 6.3$ Hz, $J = 8.4$ Hz), 3.13 (dd, 1H, $J = 8.4$ Hz, $J = 9.6$ Hz), 6.89-7.82 (m, 10H).

Third cis-diastereomer. ^1H NMR (CDCl_3) δ : 2.11 (dd, 1H, $J = 5.4$ Hz, $J = 7.8$ Hz), 2.32 (s, 3H), 2.41 (dd, 1H, $J = 5.4$ Hz, $J = 9.0$ Hz), 3.05 (t, 1H, $J = 8.4$ Hz), 7.22-7.62 (m, 10H).

Fourth cis-diastereomer. ^1H NMR (CDCl_3) δ : 1.94 (dd, 1H, $J = 6.3$ Hz, $J = 8.7$ Hz), 2.11 (s, 3H), 2.60 (dd, 1H, $J = 6.3$ Hz, $J = 8.4$ Hz), 3.47 (dd, 1H, $J = 8.4$ Hz, $J = 8.7$ Hz), 7.04-7.44 (m, 10H). MS m/z , the same for the four isomers: 284 (M^+ (2)), 267 (4), 249 (2), 236 (63), 221 (3), 193 (6), 178 (4), 158 (10), 135 (19), 115 (74), 97 (15), 77 (49), 63 (13), 43 (100).

2h, 2i: *trans* geometry was assigned by comparison with the corresponding isomer **3b, 3a**.

***trans*-1-[2-Phenyl-1-(phenylsulfonyl)cyclopropyl]-1-ethanone. (2h)**

Yellow oil. Yield 11 %. Spectral data worked out from the inseparable mixture of the cyclopropane **2h** and dihydrofuran **5h**. IR (neat): 1140, 1340, 1695 cm^{-1} .

^1H NMR (CDCl_3) δ : 2.06 (dd, 1H, $J = 6.0$ Hz, $J = 9.6$ Hz), 2.32 (dd, 1H, $J = 6.0$ Hz, $J = 7.5$ Hz), 2.39 (s, 3H), 3.58 (t, 1H, $J = 9.3$ Hz), 7.10-7.90 (m, 10H). MS m/z : 300 ($\text{M}^+(3)$), 158 (32), 141 (9), 115 (75), 91 (11), 77 (56), 63 (9), 43 (100).

***trans* - 1-[2-Isopropyl-1-(phenylsulfonyl)cyclopropyl]-1-ethanone. (2i)**

Red oil. Yield 27 %. Spectral data worked out from the inseparable mixture of the cyclopropane 2i and dihydrofuran 5i. IR (neat): 1150, 1310, 1690 cm^{-1} . ^1H NMR (CDCl_3) δ : 0.92 (d, 3H, $J = 6.3$ Hz), 1.03 (d, 3H, $J = 6.3$ Hz), 1.07-1.23 (m, 1H), 1.76 (dd, 1H, $J = 5.1$ Hz, $J = 8.4$ Hz), 1.86 (dd, 1H, $J = 5.1$ Hz, $J = 9.3$ Hz), 2.08-2.14 (m, 1H), 2.39 (s, 3H), 7.51-7.89 (m, 5H). ^{13}C NMR (CDCl_3) δ : 18.9, 21.9, 22.3, 26.8, 31.1, 38.2, 57.0, 127.9, 129.2, 133.7, 139.7, 197.9. MS m/z : 266 ($\text{M}^+(10)$), 223 (100), 207 (2), 141 (15), 125 (8), 97 (3), 77 (15), 51 (7).

***trans*-Methyl-2-(4-methylphenyl)-1-(phenylsulfinyl)cyclopropanecarboxylate.**

(2n). *Trans* geometry was assigned by oxidation to the corresponding sulfone *trans*-**2o**. Yellow oil. Yield 85%. Inseparable mixture (50/50) of two *trans* diastereoisomers. IR (neat): 1040, 1730 cm^{-1} . ^1H NMR (CDCl_3) δ : 1.91-1.96 (m, 2H), 2.12-2.17 (m, 2H), 2.23 (s, 3H), 2.29 (s, 3H), 2.85 (t, 1H, $J = 9.3$ Hz), 3.15 (t, 1H, $J = 9.3$ Hz), 3.38 (s, 3H), 3.43 (s, 3H), 6.59-7.89 (m, 18H). ^{13}C NMR (CDCl_3) δ : 17.7, 21.0, 21.1, 28.9, 30.4, 50.3, 51.9, 52.1, 125.8, 125.1, 128.3, 128.5, 128.6, 128.9, 128.9, 129.2, 131.2, 136.7, 136.9, 139.3, 143.2, 143.9, 166.6, 167.8. MS m/z : the same for the two diastereoisomers: 314 ($\text{M}^+(5)$), 297 (6), 266 (23), 207 (27), 187 (24), 159 (18), 129 (100), 115 (30), 105 (10), 91 (15), 77 (16), 59 (10).

Methyl-2-(4-methylphenyl)-1-(phenylsulfonyl)cyclopropane carboxylate. (2o).

The geometry of **2o** was assigned on the basis of the ^1H NMR chemical shift of COOCH_3 protons of two geometric isomers. *Trans* geometry (COOCH_3 and C_6H_5 *cis*) was assigned to the compounds having CH_3 chemical shift at higher fields, whereas the *cis* configuration was attributed to the other with the chemical shift of same protons at lower fields.² The pure *trans*-isomer was also obtained by MCPBA oxidation of *trans*-2n (vide infra).

Yellow oil. Yield 63 %. 50/50 Mixture of *trans/cis* diastereoisomers. IR (neat): 1140, 1300, 1710 cm^{-1} .

Trans-isomer: ^1H NMR (CDCl_3) δ : 2.26 (s, 3H), 2.34-2.44 (m, 2H), 3.29 (s, 3H), 3.41 (t, 1H, $J = 9.0$ Hz), 7.18-8.08 (m, 9H). ^{13}C NMR (CDCl_3) δ : 17.7, 21.1, 29.7, 32.9, 52.4, 128.4, 128.9, 129.0, 129.2, 129.8, 133.8, 137.5, 139.7, 170.5 MS m/z : 298 ($\text{M}^+ - 32$ (18)), 189 (22), 129 (100), 115 (38), 91 (42), 77 (10). Anal. Calcd. For $\text{C}_{18}\text{H}_{18}\text{O}_4\text{S}$: C, 65.44; H, 5.49; S, 9.70. Found: C, 65.36; H, 5.41; S, 9.82.

Cis-isomer. Spectral data worked out from the inseparable mixture of two geometric isomers. ^1H NMR (CDCl_3) δ : 2.34-2.44 (m, 1H), 2.37 (s, 3H), 2.78 (dd, 1H $J = 5.4$ Hz, $J = 9.3$ Hz), 3.14 (t, 1H $J = 9.3$ Hz), 3.72 (s, 3H), 6.91-8.04 (m, 9H). MS m/z : identical to the *trans*- isomer.

3-(4-Methylphenyl)-5-phenyl-4-(phenylsulfanyl)-2,3-dihydrofuran. (5e)

Colourless oil. Yield 21 %. IR (neat): 1710, 3020 cm^{-1} . ^1H NMR (CDCl_3) δ : 2.30 (s, 3H), 4.16 (dd, 1H, $J = 5.4$ Hz, $J = 10.2$ Hz), 4.52 (dd, 1H, $J = 5.4$ Hz, $J = 9.3$ Hz), 4.83 (t, 1H, $J = 9.3$ Hz), 6.99-8.01 (m, 14H). ^{13}C NMR (CDCl_3) δ : 21.1, 52.3, 76.3, 104.26, 125.6, 127.4, 127.6, 127.7, 128.1, 128.9, 129.3, 129.5, 130.0, 136.2, 136.7, 139.6, 159.1. MS m/z : 344 (M^+ (89)), 329 (4), 265 (3), 252 (3), 235 (15), 202 (16), 189 (10), 165 (16), 144 (6), 129 (24), 105 (100), 92 (4), 77 (37), 51 (8). Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{S}$: C, 80.20; H, 5.85; S, 9.31. Found: C, 80.26; H, 5.76; S, 9.42.

5-(4-Chlorophenyl)-3-(4-methylphenyl)-4-(phenylsulfanyl)-2,3-dihydrofuran. (5f)

Colourless oil. Yield 32 % . IR (neat): 1600 cm^{-1} . ^1H NMR (CDCl_3) δ : 2.31 (s, 3H), 4.15 (dd, 1H, $J = 5.4$ Hz, $J = 10.5$ Hz), 4.50 (dd, 1H, $J = 5.4$ Hz, $J = 9.3$ Hz), 4.81 (t, 1H, $J = 10.2$ Hz), 7.01-7.23 (m, 9H), 7.33 (d, 2H $J = 8.7$ Hz), 7.97 (d, 2H, $J = 8.7$ Hz). ^{13}C NMR (CDCl_3) δ : 21.1, 52.4, 76.3, 105.1, 125.8, 127.5, 127.6, 128.3, 128.4, 128.9, 129.0, 129.3, 135.3, 135.7, 136.7, 139.3, 157.7. MS m/z : 380 ($\text{M}^+ + 2$ (21)), 378 (M^+ (50)), 343 (5), 269 (5), 239 (11), 207 (10), 161 (21), 139 (100), 129 (63), 105 (38), 77(5).

Anal. Calcd. for $C_{23}H_{19}ClOS$: C, 72.91; H, 5.05; S, 8.46. Found: C, 72.96; H, 5.12; S, 8.42.

5-Methyl-3-phenyl-4-(phenylsulfinyl)-2,3-dihydrofuran. (5g)

Red oil. Yield 47%. Spectral data worked out from the inseparable reaction mixture containing **2g** and two diastereoisomers **5g** (50:50). IR (neat): 1040 cm^{-1} . *First diastereoisomer.* ^1H NMR (CDCl_3) δ : 2.32 (s, 3H), 3.67-3.73 (m, 1H), 4.22 (dd, 1H, $J = 6.6\text{ Hz}$, $J = 9.3\text{ Hz}$), 4.58 (dd, 1H, $J = 10.5\text{ Hz}$, $J = 9.3\text{ Hz}$), 7.04-7.44 (m, 10H). MS m/z : 284 ($M^+(2)$), 267 (5), 236 (100), 221 (5), 193 (33), 178 (5), 158 (23), 147 (41), 128 (32), 115 (46), 103 (15), 91 (21), 77 (54), 65 (14), 43 (64).

Second diastereoisomer. ^1H NMR (CDCl_3) δ : 2.33 (s, 3H), 4.31 (dd, 1H, $J = 4.8\text{ Hz}$, $J = 9.3\text{ Hz}$), 4.42-4.50 (m, 1H), 4.77 (dd, 1H, $J = 10.5\text{ Hz}$, $J = 9.3\text{ Hz}$), 7.04-7.44 (m, 10H). MS m/z : the same as the first isomer.

5-Methyl-3-phenyl-4-(phenylsulfonyl)-2,3-dihydrofuran. (5h)

Red oil. Yield 65 %. Spectral data worked out by reaction mixture containing **2h** and **5h**. IR (neat): 1150, 1310, 1630, 3030 cm^{-1} . ^1H NMR (CDCl_3) δ : 2.38 (s, 3H), 4.31 (dd, 1H, $J = 5.4\text{ Hz}$, $J = 9.3\text{ Hz}$), 4.41 (dd, 1H, $J = 5.4\text{ Hz}$, $J = 10.5\text{ Hz}$), 4.77 (dd, 1H, $J = 10.5\text{ Hz}$, $J = 9.3\text{ Hz}$), 6.99-7.34 (m, 10H). MS m/z : 300 ($M^+(54)$), 235 (43), 221 (15), 193 (27), 178 (5), 158 (57), 129 (39), 115 (60), 91 (23), 77 (100), 63 (10), 43 (74).

3-Isopropyl-5-methyl-4-(phenylsulfonyl)-2,3-dihydrofuran. (5i)

Yellow oil. Yield 63 %. IR (neat): 1150, 1310, 1630, 3030 cm^{-1} . ^1H NMR (CDCl_3) δ : 0.67 (d, 3H, $J = 7.2\text{ Hz}$), 0.84 (d, 3H, $J = 7.2\text{ Hz}$), 2.14-2.17 (m, 1H), 2.30 (s, 3H), 3.10-3.14 (m, 1H), 4.20-4.29 (m, 2H), 7.51-7.62 (m, 3H), 7.88-7.90 (m, 2H). ^{13}C NMR (CDCl_3) δ : 13.7, 14.6, 20.5, 28.1, 49.1, 70.9, 11.7, 126.7, 129.0, 132.6, 143.1, 168.0. MS m/z : 266 ($M^+(5)$), 251 (3), 211 (26), 141 (11), 125 (30), 109 (40), 91 (10), 77 (100). Anal. Calcd. for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81; S, 12.04. Found: C, 63.16; H, 6.76; S, 12.14.

3-(4-Methylphenyl)-5-phenyl-4-(phenylsulfonyl)-2,3-dihydrofuran. (5l)

Yellow oil. Yield 90 %. IR (neat): 1150, 1300, 1610, 3030 cm^{-1} .

^1H NMR (CDCl_3) δ : 2.30 (s, 3H), 4.43 (dd, 1H, $J = 4.2$ Hz, $J = 9.0$ Hz), 4.51 (dd, 1H, $J = 4.2$ Hz, $J = 9.6$ Hz), 4.85 (t, 1H, $J = 9.3$ Hz), 6.99-8.01 (m, 14H). ^{13}C NMR (CDCl_3) δ : 20.9, 50.0, 78.2, 116.1, 126.6, 127.1, 127.5, 127.9, 128.9, 129.1, 129.9, 130.6, 131.8, 132.5, 136.6, 138.1, 165.1. MS m/z : 376 (M^+ (73)), 311 (7), 234 (100), 205 (39), 189 (28), 165 (10), 105 (57), 77 (78). Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{O}_3\text{S}$: C, 73.38; H, 5.35; S, 8.52. Found: C, 73.28; H, 5.26; S, 8.64.

3,5-Phenyl-4-(phenylsulfinyl)-2,3-dihydrofuran. (5m)

60:40 Mixture of two diastereoisomers. Yellow oil. Yield 71 %. IR (neat): 1040 cm^{-1} .

^1H NMR (CDCl_3) δ : 3.79 (dd, 1H, $J = 6.0$ Hz, $J = 13.2$ Hz), 4.36 (dd, 1H, $J = 6.0$ Hz, $J = 9.0$ Hz), 4.70 (dd, 1H, $J = 9.3$ Hz, $J = 10.2$ Hz), 7.18-8.06 (m, 15H). ^{13}C NMR (CDCl_3) δ : 49.4, 79.1, 116.1, 124.7, 127.2, 127.7, 128.5, 128.6, 128.7, 129.0, 130.1, 131.2, 142.0, 142.9. Minor isomer (data worked out from the diastereoisomeric mixture) : ^1H NMR (CDCl_3) δ : 4.50 (dd, 1H, $J = 4.2$ Hz, $J = 9.0$ Hz), 4.65-4.69 (m, 1H), 4.93 (dd, 1H, $J = 9.0$ Hz, $J = 9.6$ Hz), 7.18-8.06 (m, 15H). MS m/z , the same for the two isomers: 330 ($\text{M}^+ - 16$ (70)), 251 (7), 221 (18), 191 (25), 178 (11), 165 (12), 121 (24), 105 (73), 77 (100). Anal. Calcd. For $\text{C}_{22}\text{H}_{18}\text{O}_2\text{S}$: C, 76.27; H, 5.24; O, 9.24; S, 9.25. Found: C, 76.29; H, 5.22; O, 9.23; S, 9.26.

(2S*, 4R*)-2,4-Diphenyltetrahydrofuran. (Calyxolane B). (6)³

A solution of **5m** (1.5 g, 4.3 mmol) in dry EtOH (20 mL) was added at 0 °C to a suspension of Ni-Raney in EtOH (50 mL) and under a hydrogen atmosphere (1 atm). After 72 h, the reaction mixture was filtered over celite and the solvent was evaporated. The residue was purified by flash chromatography (ethyl acetate/ light petroleum 1:10) to give **6** (0.82 g, 84 %). ^1H NMR (CDCl_3) δ : 2.02 (q, 1H, $J = 10.2$ Hz), 2.71-2.73 (m, 1H), 3.65 (m, 1H), 4.03 (t, 1H, $J = 8.4$ Hz), 4.37 (t, 1H, $J = 8.4$ Hz), 5.08 (dd, 1H, $J = 10.2$ Hz, $J = 5.7$ Hz), 7.20- 7.47 (m, 10H).

***trans*-[2-(4-Methylphenyl)-1-(phenylsulfonyl)cyclopropyl]methanol. (7)**

To a stirred solution of **2o** (5.3 g, 16 mmol) in dry THF (50 mL) at $-10\text{ }^{\circ}\text{C}$, a 1M solution of LiAlH_4 (16 mL, 16 mmol) in THF, was added dropwise. After 2 h at the same temperature, the mixture was treated with wet Na_2SO_4 , then filtered on celite, dried (Na_2SO_4) and the solvent evaporated under vacuum. The crude alcohol was chromatographed on silica gel using light petroleum-diethyl ether (1:1) as eluent to give 4g of **7**.

Yellow oil. Yield 82 %. IR (neat): 1150, 1310, 3510 cm^{-1} . ^1H NMR (CDCl_3) δ : 1.57 (dd, 1H, $J = 6.0\text{ Hz}$, $J = 7.2\text{ Hz}$), 2.00 (dd, 1H, $J = 6.0\text{ Hz}$, $J = 9.3\text{ Hz}$), 2.20 (s, 3H), 2.66 (br s, 1H), 3.16 (dd, 1H, $J = 7.2\text{ Hz}$, $J = 9.3\text{ Hz}$), 3.61 (d, 2H, $J = 13.5\text{ Hz}$), 6.83 (d, 2H, $J = 7.8\text{ Hz}$), 6.98 (d, 2H, $J = 7.8\text{ Hz}$), 7.53-7.65 (m, 3H), 7.93 (d, 2H, $J = 7.5\text{ Hz}$). ^{13}C NMR (CDCl_3) δ : 14.1, 20.7, 28.5, 48.2, 59.8, 128.2, 128.4, 129.0, 129.1, 130.3, 133.6, 136.9, 138.2. MS m/z : 302 (M^+ (6)), 284 (4), 161 (88), 143 (96), 131 (98), 115 (96), 91 (78), 77 (100).

Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_3\text{S}$: C, 67.52; H, 6.00; S, 10.60. Found: C, 67.48; H, 5.96; S, 10.52.

***trans*-[2-(4-Methylphenyl)-1-(phenylsulfonyl)cyclopropyl]carbaldehyde. (8)**

To a stirred solution of **7** (2.5 g, 8.3 mmol) in CH_2Cl_2 (50 mL) at room temperature, PCC (2.67g, 12.4 mmol) was added in one portion. The reaction mixture was stirred for 5 h, then filtered on silica gel and washed with a 2M NaOH solution and NH_4Cl solution. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give an oil which was purified by column chromatography on silica gel (light petroleum-diethyl ether 1:1 as eluent). Yellow oil. Yield 62%. IR (neat): 1140, 1310, 1710 cm^{-1} . ^1H NMR (CDCl_3) δ : 2.28 (s, 3H), 2.30-2.40 (m, 2H), 3.81 (t, 1H, $J = 9.0\text{ Hz}$), 7.00 (m, 4H), 7.57-7.69 (m, 3H), 7.98-8.01 (m, 2H), 9.29 (s, 1H). ^{13}C NMR (CDCl_3) δ : 18.2, 29.7, 36.3, 56.4, 127.3, 128.9, 129.3, 129.5, 133.1, 134.1, 136.6, 138.0, 190.8. MS m/z : 300 (M^+ (30)), 282 (3), 159 (37), 144 (15), 131 (100), 115 (45), 91 (36), 77 (27). Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_3\text{S}$: C, 67.98; H, 5.37; S, 10.67. Found: C, 67.88; H, 5.96; S, 10.52.

2-(4-Methylphenyl)-4-(phenylsulfonyl)-2,3-dihydrofuran. (9)

A solution of cyclopropane **8** (150 mg, 0.5 mmol) with PTSA (9.5 mg, 0.05 mmol) in 10 mL of benzene, was stirred for 16 h at room temperature. The reaction mixture was diluted with diethyl ether and washed with a saturated NaHCO₃ solution and brine. The organic phase was dried over Na₂SO₄ and evaporated. The residue, chromatographed on silica gel using light petroleum-diethyl ether (1:1) as eluent gave 120 mg of **9** as yellow oil. Yield 71 %. IR (neat): 1140, 1310 cm⁻¹. ¹H NMR (CDCl₃) δ: 2.33 (s, 3H), 2.81 (ddd, 1H, *J* = 1.8 Hz, *J* = 8.7 Hz, *J* = 14.1 Hz), 3.17 (ddd, 1H, *J* = 1.8 Hz, *J* = 10.8 Hz, *J* = 14.1 Hz), 5.75 (dd, 1H, *J* = 8.7 Hz, *J* = 10.8 Hz), 7.07-7.94 (m, 9H). ¹³C NMR (CDCl₃) δ: 21.2, 35.8, 87.6, 116.8, 125.7, 127.3, 129.2, 129.5, 133.1, 136.6, 138.8, 140.8, 155.7. MS *m/z*: 300 (M⁺ (41)), 282 (3), 159 (51), 144 (20), 131 (100), 115 (56), 105 (1), 91 (42), 77 (35). Anal. Calcd. for C₁₇H₁₆O₃S: C, 67.98; H, 5.37; S, 10.67. Found: C, 67.87; H, 5.42; S, 10.52.

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2a

2a

2d

3a

3a

3b

129.333
128.977
128.944
128.297
127.585
127.520

125.788

76.304

52.386

21.090

150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

5g + IV isomer: cis-2g

I isomer: trans-2g
and III isomer: cis-2g

II isomer: trans-2g

ppm

5i

2i

5i

5i

51

51

major diastereoisomer

major diastereoisomer

mixture of two diastereoisomers

7

8

9

8

9