Supporting Information

on

Silicon-Assisted Ring Opening of Donor-Acceptor Substituted Cyclopropanes. An Expedient Entry to Substituted Dihydrofurans

by

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4a: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.62 (4H, m), 7.44-7.35 (6H, m), 4.07-3.99 (1H, m), 3.64 (3H, s), 3.51 (3H, s), 2.17-2.01 (2H, m), 2.05-2.00 (1H, dd, *J* = 15.1 and 6.1 Hz), 1.84-1.77 (1H, dd, *J* = 15.1 and 8.3 Hz), 1.03 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 168.8, 136.2, 136.1, 133.4, 133.0, 129.5, 129.4, 127.71, 127.69, 59.6, 52.4, 49.7, 39.9, 27.7, 23.1, 18.2.

4b: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.62 (4H, m), 7.44-7.34 (6H, m), 4.72-4.64 (1H, m), 2.56-2.50 (1H, ddd, *J* = 14.2, 9.8 and 1.4 Hz), 2.28-2.22 (1H, ddd, *J* = 15.6, 7.8 and 1.5 Hz), 2.06 (3H, s), 1.97 (1H, s), 1.90-1.85 (1H, dd, *J* = 14.5 and 5.5 Hz), 1.61-1.55 (1H, dd, *J* = 14.4 and 9.0 Hz), 1.06 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.7, 167.3, 136.1, 136.0, 134.0, 133.7, 129.4, 129.3, 127.72, 127.69, 111.7, 81.3, 38.2, 29.2, 27.7, 19.3, 18.1, 14.9.

4c: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.61 (4H, m), 7.43-7.34 (6H, m), 4.70-4.61 (1H, m), 4.08 (2H, q, *J* = 7.1 Hz), 2.56-2.50 (1H, dd, *J* = 14.4 and 9.8 Hz), 2.27-2.22 (1H, dd, *J* = 14.5 and 7.7 Hz), 2.03 (3H, s), 1.89-1.84 (1H, dd, *J* = 14.4 and 5.8 Hz), 1.60-1.54 (1H, dd, *J* = 14.5 and 8.7 Hz), 1.20 (3H, t, *J* = 7.2 Hz), 1.05 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 166.3, 136.1, 136.0, 134.0, 133.9, 129.3, 129.2, 127.64, 127.59, 101.6, 81.0, 59.2, 37.6, 27.7, 19.4, 18.0, 14.4, 14.1.

3-hydroxy-4-t-butyldiphenylsilylbutyl phenyl ketone: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.87 (2H, m), 7.68-7.62 (4H, m), 7.52 (1H, t, *J* = 7.3 Hz), 7.43-7.35 (8H, m), 3.90-3.82 (1H, m), 3.06-2.87 (2H, m), 1.91-1.77 (2H, m), 1.59-1.49 (2H, m), 1.04 (9H, s). ^{13}C NMR (100 MHz,

$CDCl_3$): δ 200.8, 136.1, 136.0, 134.3, 134.2, 129.44, 129.36, 128.5, 128.1, 127.9, 127.8, 127.6, 68.9, 35.1, 34.8, 27.8, 20.6, 18.1.

7: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.60 (4H, m), 7.43-7.34 (6H, m), 4.86-4.78 (1H, m), 2.55-2.49 (1H, dd, *J* = 14.5 and 9.6 Hz), 2.28-2.20 (5H, m), 1.97-1.89 (3H, m), 1.67-1.61 (1H, dd, *J* = 14.4 and 9.0 Hz), 1.05 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 177.0, 135.99, 135.97, 133.7, 133.5, 129.5, 129.4, 127.8, 127.7, 113.0, 85.0, 36.3, 33.9, 27.7, 23.9, 21.6, 19.4, 18.1.

3-carbomethoxy-5-*t*-butyldipheylsilylmethyl-γ-lactone (1:1.8 mixture of diastereomers): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.58 (m), 7.43-7.34 (m), 4.82-4.74 (m), 4.51-4.44 (m), 3.72 (s), 3.65 (s), 3.44-3.40 (dd, *J* = 9.6 and 4.6 Hz), 3.39-3.33 (dd, *J* = 11.4 and 8.9 Hz), 2.09-1.95 (m), 1.88-1.81 (m), 1.71-1.64 (m), 1.64-1.58 (dd, *J* = 14.6 and 10.2 Hz), 1.52-1.45 (dd, *J* = 14.4 and 10.5 Hz), 1.05 (s), 1.04 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 168.2, 168.0, 135.9, 135.8, 133.6, 133.4, 132.6, 129.6, 127.9, 127.8, 79.6, 78.8, 52.84, 52.81, 47.9, 47.3, 34.5, 34.1, 27.6, 27.5, 18.5, 18.1, 18.0.

Characteristic peaks for the major isomer in the ^{1}H NMR: δ 4.51-4.44 (1H, m), 3.72 (3H, s), 3.39-3.33 (1H, dd, *J* = 11.4 and 8.9 Hz), 1.64-1.58 (1H, dd, *J* = 14.6 and 10.2 Hz), 1.04 (9H, s).

Characteristic peaks for the minor isomer in the ^{1}H NMR: δ 4.82-4.72 (1H, m), 3.65 (3H, s), 3.44-3.40 (1H, dd, *J* = 9.6 and 4.6 Hz), 1.52-1.45 (1H, dd, *J* = 14.4 and 10.5 Hz), 1.05 (9H, s).

3-phenylsulfonyl-5-*t*-butyldipheylsilylmethyl-γ-lactone (1:1.3 mixture of diastereomers): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.37 (m), 4.78-4.70 (m), 4.51-4.44 (m), 3.96 (t, *J* = 9.7 Hz), 3.85-3.82 (dd, *J* = 10.0 and 2.4 Hz), 2.36-2.30 (ddd, *J* = 14.8, 6.1 and 2.7 Hz), 2.22-2.14 (ddd, *J* = 14.2, 9.5 and 8.0 Hz), 2.11-2.01 (m), 1.89-1.81 (m), 1.66-1.60 (m), 1.49-1.43 (dd, *J* = 14.4 and 10.8 Hz), 1.05 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 166.9, 137.0, 136.7, 136.0, 135.91, 135.87, 134.6, 134.5, 133.5, 133.2, 132.5, 132.4, 129.8, 129.7, 129.5, 129.2, 129.1, 128.1, 128.0, 79.7, 77.8, 65.9, 64.7, 32.4, 31.2, 27.6, 27.5, 19.0, 18.4, 18.1.

Characteristic ^{1}H signals for the major isomer. δ 4.78-4.70 (1H, m), 3.85-3.82 (1H, dd, *J* = 10.0 and 2.4 Hz), 2.36-2.30 (1H, ddd, *J* = 14.8, 6.1 and 2.7 Hz), 1.49-1.43 (1H, dd, *J* = 14.4 and 10.8 Hz).

Characteristic ^{1}H signals for the minor isomer. δ 4.51-4.44 (1H, m), 3.96 (1H, t, *J* = 9.7 Hz), 2.22-2.14 (1H, ddd, *J* = 14.2, 9.5 and 8.0 Hz), 1.66-1.60 (1H, m).

5-*t*-butyldipheylsilylmethyl-γ-lactone: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.71 (4H, m), 7.45-7.35 (6H, m), 4.60-4.53 (1H, m),2.40-2.23 (2H, m), 2.06-2.01 (1H, dd, *J* = 14.4 and 3.9 Hz), 1.69-1.41 (3H, m),1.05 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.9, 136.0, 135.9, 133.9, 132.9, 129.62, 129.58, 127.9, 127.8, 80.1, 30.6, 29.6, 27.6, 18.5, 18.1.

Procedure for the scheme 2: To a solution of allyl-*t*-butyldiphenylsilane (0.816 g, 2.9 mmol) and 2-diazo-1,3-cyclohexanedione in anhydrous hexanes (2 mL), rhodium(II)acetate dimer (14 mg, 2 mol%) was added. After refluxing for 5h, the reaction mixture was concentrated on a rotovap under reduced pressure and the residue, thus obtained, was chromatographed over silica gel (EtOAc/hexanes) to furnish pure **7** (91 mg, 15% overall; 95% based on the reacted allylsilane).

$HClO_4$-assisted hydrolysis of 4a: A solution of **4a** (80 mg, 0.2 mmol) in 10% $HClO_4$ in THF (2mL) was refluxed for 5 h. The reaction mixture was cooled and then taken in ether (15 mL). It was washed with water (2 x 10 mL) and brine (1 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated on a rotovap under reduced pressure. Column chromatography of the crude material over silica gel (EtOAc/hexanes) furnished pure 3-carbomethoxy-5-*t*-butyldiphenylsilylmethyl-γ-lactone (65 mg, 84.3%).

$HClO_4$-assisted hydrolysis of **4d**: The procedure used for the hydrolysis of **4a** above was followed to obtain 3-phenylsulfonyl-5-*t*-butyldiphenylsilylmethyl-γ-lactone in 85% yield.

Dealkyldecarboxylation of 3-carbomethoxy-5-*t*-butyldiphenylsilylmethyl-γ-lactone: To a solution of 3-carbomethoxy-5-*t*-butyldiphenylsilylmethyl-γ-lactone (22 mg, 0.056 mmol) in DMSO (0.5 mL), NaCl (7 mg, 0.112 mmol) and a droplet of water were added. After refluxing for 4 h (oil bath temperature 160-180 °C), the mixture was cooled to 25 °C and taken in ether (10 mL). This was washed with water (2 x 5 mL) and brine (1 x 5 mL). Solvent removal and purification of the residue through silica gel column chromatography (EtOAc/hexanes) furnished pure 5-*t*-butyldiphenylsilylmethyl-γ-lactone (16 mg, 85%).

Desulfonation of 3-phenylsulfonyl-5-*t*-butyldiphenylsilylmethyl-γ-lactone: To a solution of 3-phenylsulfonyl-5-*t*-butyldiphenylsilylmethyl-γ-lactone (42 mg, 0.09 mmol) and anhydrous disodium hydrogen phosphate (50 mg, 0.35 mmol) in methanol (1 mL) was added pulverized 5% sodium amalgum (262 mg). The reaction mixture was stirred for 4 h and then poured into water (10 mL). The product was extracted into ether and the ether solution was washed with brine, dried over Na_2SO_4, and the solvent evaporated. Purification of the residue by silica gel column chromatography (EtOAc/hexanes) furnished pure 5-*t*-butyldiphenylsilylmethyl-γ-lactone (22 mg, 74%).