PtCl$_2$-Catalyzed Rearrangement of Methyleneacyclopropanes

Alois Fürstner* and Christophe Aïssa

Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany

e-mail: fuerstner@mpi-muelheim.mpg.de

General. All reactions were carried out in flame-dried glassware under Ar. The solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et$_2$O (Mg-anthracene), CH$_2$Cl$_2$ (P$_4$O$_{10}$), MeCN, Et$_3$N (CaH$_2$), MeOH (Mg), DMF, DMA (Desmodur®), dibutyltin dilaurate), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a Bruker DPX 300, AV 400, or DMX 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl$_3$: δ$_C$ ≈ 77.0 ppm; residual CHCl$_3$ in CDCl$_3$: δ$_H$ ≈ 7.24 ppm; CD$_2$Cl$_2$: δ$_C$ ≈ 53.8 ppm; residual CH$_2$Cl$_2$ in CD$_2$Cl$_2$: δ$_H$ ≈ 5.32 ppm). IR: Nicolet FT-7199 spectrometer, wavenumbers (ν) in cm$^{-1}$. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received.
Substrates

**5-(3-Bromo-propylsulfonyl)-1-tert-butyl-1H-tetrazole.** DEAD (1.73 mL, 11 mmol) was added to a solution of PPh₃ (2.89 g, 11 mmol) and 1-tert-butyl-1,4-dihydrotetrazole-5-thione (1.74 g, 11 mmol) in THF. The mixture was cooled to 0°C before 3-bromopropan-1-ol (0.9 mL, 10 mmol) was added via syringe. The resulting solution was stirred at ambient temperature for 30 min before all volatile materials were evaporated. The residue was purified by flash chromatography (hexanes/EtOAc gradient, 30/1→20/1→15/1→10/1) to give the title compound as a white solid (2.32 g, 83%). m.p.: 50-53°C. IR (film) 2982, 2938, 1507, 1473, 1431, 1409, 1375, 651, 544 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ = 3.54 (4H, q, J = 6.5 Hz), 2.42 (2H, quint., J = 6.7 Hz), 1.73 (9H, s). ¹³C NMR (CDCl₃, 75 MHz): δ = 152.2, 61.3, 32.2, 31.8, 31.7, 28.9 (3C). Anal. calcd for C₈H₁₅BrN₄S: C 34.42, H 5.42, N 20.07, found: C 34.74, H 5.52, N 20.14.

**1-tert-Butyl-5-cyclopropanesulfonyl-1H-tetrazole.** A solution of Mo₇O₂₄(NH₄)₆·xH₂O (2.1 g, 1.7 mmol) in H₂O₂ (30 % w/w, 21 mL) was added dropwise at 0°C within 5 minutes to a solution of 5-(3-bromo-propylsulfonyl)-1-tert-butyl-1H-tetrazole (5.54 g, 20.2 mmol) in EtOH (155 mL). After stirring for 90 min at room temperature, the solvent was evaporated. The crude material was dissolved in tert-butyl methyl ether, the organic phase was washed with water and brine, dried over Na₂SO₄ and concentrated.

A solution of the resulting colorless oil (5.77 g) in THF (45 mL) was slowly added via a dropping funnel within 9h to a solution of NaHMDS (3.74 g) in THF (900 mL) at –78°C. After the addition was complete, the reacton mixture was stirred for 1 h before it was quenched with sat. aq. NH₄Cl. The mixture was partitioned between water and tert-butyl methyl ether, the combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated. Purification of the residue by flash chromatography (hexanes/EtOAc, 10/1) furnished compound 2 as a white solid (3.76 g, 80%). m.p. 93-95 °C. IR (KBr): 3067, 3000, 1336, 1161, 1052, 877, 709, 615 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 3.33-3.23 (1H, m), 1.86 (9H, s), 1.55-1.46 (2H, m), 1.46-1.33 (2H, m). ¹³C NMR (75 MHz, CDCl₃): δ = 154.9, 65.5, 33.5, 29.9 (3C), 7.1 (2C). MS (EI) m/z (rel. intensity): 111 (13), 110 (30), 82 (6), 67 (5), 57 (100), 41 (66). HRMS (ESIpos): calcd for C₈H₁₄N₄NaO₂S: 253.072966, found
2-Allyloxy-3-methoxy-benzaldehyde. 2-Hydroxy-3-methoxy-benzaldehyde (760 mg, 5 mmol) was added as a solid to a stirred suspension of NaH (150 mg, 6.25 mmol) in DMF (5 mL) at 0°C. After stirring at room temperature for 2 h, allyliodide (0.9 mL, 10 mmol) was introduced and stirring was continued for 20 h. For work up, the mixture was diluted with tert-butyl methyl ether and washed with sat. aq. NH₄Cl and brine. Drying of the organic layer over Na₂SO₄, evaporation of the solvent, and purification of the residue by flash chromatography (hexanes/EtOAc, 15/1) gave the title compound as a pale yellow oil (737 mg, 68%). IR (neat): 3082, 3011, 2940, 2862, 2841, 2757, 1692, 1648, 1595, 1584, 1482, 1458, 1442, 1422, 1390, 1267, 1249, 1067, 983, 911, 786 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 10.46 (1H, s), 7.45-7.41 (1H, m), 7.16-7.14 (2H, m), 6.09 (1H, ddt, J = 17.2, 10.4, 5.8 Hz), 5.35 (1H, dq, J = 17.1, 1.6 Hz), 5.28 (1H, dq, J = 10.4, 1.2 Hz), 4.68 (2H), 3.92 (3H, s). ¹³C NMR (75 MHz, CDCl₃): δ = 190.7, 153.2, 151.4, 133.3, 130.3, 124.4, 119.2, 119.1, 118.2, 75.4, 56.2. MS (EI) m/z (rel. intensity): 192 (57), 151 (100), 136 (23), 131 (11), 122 (25), 108 (34), 93 (28), 65 (20), 52 (19), 41 (40). HRMS (EI): calcd for C₁₁H₁₂O₃: 192.078642, found 192.078848. Anal. calcd for C₁₁H₁₂O₃: C 53.55, H 4.87; found C 53.51, H 4.94.

Preparation of Alkylidenecyclopropanes by a Modified Julia-Kocienski Olefination

Representative procedure: 4-Cyclopropylidenemethyl-biphenyl (3). Cs₂CO₃ (1.95 g, 6 mmol) was added to a solution of 4-phenyl-benzaldehyde (364 mg, 2 mmol) and sulfone 2 (690 mg, 3 mmol) in THF (15 mL) and DMF (5 mL). The resulting suspension was stirred at 70°C for 40h. For work up, the mixture was poured into a saturated solution of NH₄Cl, the aqueous layer was extracted with tert-butyl methyl ether, the combined organic layers were washed with brine, dried over Na₂SO₄, filtered and evaporated. Purification of the residue by flash chromatography furnished product 3 as a white solid (313 mg, 76%). m.p. 66-68 °C. IR (KBr): 3086, 3033, 2971, 1747, 1596, 1580, 1558, 1521, 1488, 1450, 1427, 1408, 847, 757, 691 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.65-7.58 (6H, m), 7.46 (2H, t, J = 7.6 Hz), 7.38-7.33 (1H, m), 6.82-6.80 (1H, m), 1.51-1.46 (2H, m), 1.26-1.21 (2H, m). ¹³C NMR (75 MHz, CDCl₃): δ = 141.0, 139.6, 137.5, 128.9 (2C), 127.3 (2C), 127.2, 127.1 (2C), 127.0 (2C), 124.8, 118.0, 4.4, 0.9. MS (EI) m/z (rel. intensity): 206 (100), 191 (55), 165 (23), 152 (12), 128 (30), 101 (7), 91 (22). HRMS (EI): calcd for C₁₆H₁₄O: 206.109549, found 206.109351. The
deuterated compound 3-D was obtained analogously. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.68-7.56\) (6H, m), 7.46 (2H, \(t, J = 7.6\) Hz), 7.40-7.33 (1H, m), 1.48 (2H, dd, \(J = 10.1, 5.3\) Hz), 1.24 (2H, dd, \(J = 9.7, 5.7\) Hz). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 141.1, 139.6, 137.4, 128.9\) (2C), 127.3 (2C), 127.2, 127.1 (2C), 127.0 (2C), 124.7, 117.7 (1C, \(t, J = 24.0\) Hz), 4.4, 0.9. MS (EI) m/z (rel. intensity): 207 (100), 192 (41), 166 (13), 152 (12), 129 (21), 102 (4), 91 (15). HRMS (EI): calcd for C\(_{16}\)H\(_{13}\)D: 207.115829, found 207.115890.

1-Benzylx-3-cyclopropylidenemethyl-benzene (5). Prepared analogously as a white solid (156 mg, 66%). m.p. 72-74°C. IR (KBr): 3066, 3033, 2966, 2939, 2886, 1751, 1595, 1585, 1495, 1446, 1419, 1411, 1388, 1253, 1177, 1016, 993, 936, 1862, 808, 744, 696 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.52-7.32\) (5H, m), 7.31-7.24 (1H, m), 7.23-7.19 (1H, m), 7.14 (1H, \(d, J = 7.3\) Hz), 6.87 (1H, \(dd, J = 8.0, 2.6\) Hz), 6.74 (1H, quint, \(J = 1.8\) Hz), 5.12 (2H, s), 1.46-1.37 (2H, m), 1.24-1.15 (2H, m). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 159.1, 139.8, 137.3, 129.5, 128.7\) (2C), 128.0, 127.6 (2C), 124.9, 119.9, 118.2, 113.4, 112.9, 70.1, 18.62, 4.4, 0.7. MS (EI) m/z (rel. intensity): 236 (7), 145 (24), 91 (100). HRMS (EI): calcd for C\(_{17}\)H\(_{16}\)O: 236.120112, found 236.120433. Anal. calcd for C\(_{17}\)H\(_{16}\)O: C 86.41, H 6.82; found C 86.31, H 6.85.

4-Cyclopropylidenemethyl-benzoic acid methyl ester (7). Prepared analogously as a white solid (113 mg, 60%). m.p. 53-55 °C. IR (KBr): 3077, 3037, 2977, 2951, 2844, 1720, 1606, 1436, 1278, 1109, 866, 759, 697 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 8.00\) (2H, \(d, J = 8.4\) Hz), 7.58 (2H, \(d, J = 8.4\) Hz), 6.81 (1H, quint, \(J = 2.0\) Hz), 3.92 (3H, s), 1.52-1.44 (2H, m), 1.27-1.18 (2H, m). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 167.2, 143.0, 130.2\) (2C), 128.3, 126.6 (2C), 117.9, 52.2, 4.7, 0.9. MS (EI) m/z (rel. intensity): 188 (9), 157 (4), 129 (100). HRMS (EI): calcd for C\(_{12}\)H\(_{12}\)O\(_2\): 188.083732, found 188.083656. Anal. calcd for C\(_{12}\)H\(_{12}\)O\(_2\): C 76.57, H 6.43; found C 76.62, H 6.24.

1-Bromo-2-cyclopropylidenemethyl-4,5-dimethoxy-benzene (9). Prepared analogously as a white solid (319 mg, 59%). m.p. 102-105 °C. IR (KBr): 2960, 2835, 1778, 1597, 1505, 1461, 1450, 1381, 1257, 1208, 1163, 1026, 857. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.38\) (1H, s), 7.05 (1H, qt, \(J = 2.0\) Hz), 7.02 (1H, s), 3.89 (3H, s), 3.88 (3H, s), 1.45-1.39 (2H, m), 1.25-1.20 (2H, m). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 148.5, 148.3, 129.8, 124.9, 116.7, 115.2, 113.5, 109.4, 56.1, 55.8, 3.7, 0.7. MS (EI) m/z (rel. intensity): 270 (17), 268 (17), 239 (86), 237 (87), 189 (100), 145 (30). HRMS (ESIpos): calcd for C\(_{12}\)H\(_{13}\)BrO\(_2\)+Na 290.999126, found 290.998798. Anal. calcd for C\(_{12}\)H\(_{13}\)BrO\(_2\): C 77.75, H 7.46; found C 77.63, H 7.51.

2-Cyclopropylidenemethyl-1,4-dimethoxy-benzene (11). Prepared analogously as a white solid (75 mg, 64%). m.p. 68-70 °C. IR (KBr): 3114, 3085, 3045, 3008, 2961, 2934, 2836, 1721, 1636, 1586, 1500, 1645, 1453, 1417, 1180, 1045, 861, 816, 804 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.34\) (1H,
8.13 (1H, quint, J = 2.0 Hz), 8.05 (1H, d, J = 8.3 Hz), 6.98 (1H, d, J = 8.3 Hz), 6.78 (1H, quint, J = 2.0 Hz), 3.92 (3H, s), 3.90 (3H, s), 1.45-1.37 (2H, m), 1.21-1.14 (2H, m). 13C NMR (75 MHz, CDCl3): δ = 149.1, 148.2, 131.7, 122.2, 119.5, 118.0, 111.3, 109.4, 56.1, 55.9, 4.1, 0.7. MS (EI) m/z (rel. intensity): 190 (31), 175 (14), 159 (100). HRMS (EI): *calcd* for C12H14O2: 190.099338, *found* 190.099238. Anal. *calcd* for C12H14O2: C 75.76, H 7.42; *found* C 75.56, H 7.36.

2-Allyloxy-1-cyclopropylidenemethyl-3-methoxy-benzene (17). Prepared analogously as a colorless oil (173 mg, 80%). IR (neat): 3077, 3046, 3007, 2975, 2936, 2836, 1769, 1743, 1647, 1596, 1579, 1475, 1439, 1420, 1271, 1208, 1092, 989, 927, 812, 746 cm⁻¹. 1H NMR (400 MHz, CDCl3): δ = 7.42 (1H, dd, J = 7.9, 1.4 Hz), 7.14 (1H, quint, J = 2.0 Hz), 7.03 (1H, t, J = 8.0 Hz), 6.79 (1H, dd, J = 8.2, 1.4 Hz), 6.14 (1H, ddt, J = 17.2, 10.4, 5.8 Hz), 5.40 (1H, dq, J = 17.1, 1.6 Hz), 5.24 (1H, dq, J = 10.4, 1.2 Hz), 4.51 (2H, dt, J = 5.8, 1.3 Hz), 3.87 (3H, s), 1.44-1.38 (2H, m), 1.20-1.15 (2H, m). 13C NMR (100 MHz, CDCl3): δ = 153.2, 145.1, 134.5, 132.6, 125.4, 123.9, 118.5, 117.4, 112.5, 110.6, 74.4, 55.9, 4.2, 0.7. MS (EI) m/z (rel. intensity): 216 (7), 175 (100), 159 (12), 147 (7), 132 (18), 115 (15), 103 (10), 91 (10), 77 (9). HRMS (ESIpos): *calcd* for C14H16NaO2: 239.104248, *found* 239.104492. Anal. *calcd* for C14H16O2: C 68.74, H 6.29; *found* C 68.52, H 6.36.

4-Cyclopropylidenemethyl-1,2-dimethoxy-benzene (22). Prepared analogously as a white solid (73 mg, 62%), m.p. 78-81 °C. IR (KBr): 3084, 3044, 3008, 2963, 2925, 2840, 1781, 1600, 1585, 1516, 1471, 1455, 1419, 1229, 1158, 1141, 1027, 858, 827, 787, 776 cm⁻¹. 1H NMR (300 MHz, CDCl3): δ = 7.16 (1H, d, J = 1.8 Hz), 7.05 (1H, dd, J = 8.3, 1.9 Hz), 6.85 (1H, d, J = 8.3 Hz), 6.69 (1H, quint, J = 2.0 Hz), 3.92 (3H, s), 3.90 (3H, s), 1.45-1.37 (2H, m), 1.21-1.14 (2H, m). 13C NMR (75 MHz, CDCl3): δ = 149.1, 148.2, 131.7, 122.2, 119.5, 118.0, 111.3, 109.4, 56.1, 55.9, 4.1, 0.7. MS (EI) m/z (rel. intensity): 190 (31), 175 (14), 159 (100). HRMS (EI): *calcd* for C12H14O2: 190.099338, *found* 190.099238. Anal. *calcd* for C12H14O2: C 75.76, H 7.42; *found* C 75.56, H 7.36.
**1-Benzylxy-4-cyclopropylidenemethyl-benzene (25).** Prepared analogously as a white solid (145 mg, 56%). m.p. 72-74 °C. IR (KBr): 3060, 3037, 2968, 2942, 2922, 2865, 1764, 1606, 1573, 1510, 1452, 1414, 1381, 1249, 1012, 837, 741, 696 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.51-7.43 (3H, m), 7.42-7.38 (2H, m), 7.37-7.33 (1H, m), 6.96 (2H, d, J = 9.0 Hz), 6.70 (1H, quint, J = 2.0 Hz), 5.09 (2H, s), 1.42-1.36 (2H, m), 1.19-1.14 (2H, m). ¹³C NMR (75 MHz, CDCl₃): δ = 157.8, 137.2, 131.6, 128.7 (2C), 128.1, 127.8 (2C), 127.6 (2C), 122.0, 117.6, 115.0 (2C), 70.1, 4.1, 0.6. MS (EI) m/z (rel. intensity): 236 (6), 145 (52), 91 (100). HRMS (EI): calcd for C₁₇H₁₆O: 236.120118, found 236.120187. Anal. calcd for C₁₇H₁₆O: C 86.41, H 6.82; found C 86.35, H 6.84.

**Ph-PtCl₂ Catalyzed Rearrangement Reactions**

**Representative Procedure: 4-Cyclobuten-1-yl-biphenyl (4).** PtCl₂ (1 mg, 0.0038 mmol) was added to a solution of 4-cyclopropylidenemethyl-biphenyl 3 (90 mg, 0.437 mmol) in toluene (4.3 mL). CO was bubbled into the solution via a needle for ca. 30 seconds and the resulting mixture was then stirred at 80 °C under CO atmosphere (1 atm). For work up, the mixture was filtered under Argon through a short pad of silica and the filtrate was evaporated to give product 4 as a white, air sensitive solid (69 mg, 77%). IR (KBr): 3054, 3030, 2949, 2915, 1867, 2834, 1672, 1596, 1580, 1485, 1448, 1407, 840, 745, 689 cm⁻¹. ¹H NMR (300 MHz, CD₂CN): δ = 7.68-7.60 (4H, m), 7.50-7.42 (4H, m), 7.40-7.33 (1H, m), 6.82-6.80 (1H, t, J = 1.4 Hz), 2.87-2.83 (2H, m), 2.57-2.53 (2H, m). ¹³C NMR (75 MHz, CD₂CN): δ = 147.1, 141.4, 140.9, 135.1, 129.9 (2C), 128.6, 128.4, 127.9 (2C), 127.7 (2C), 125.7 (2C), 29.4, 27.0. MS (EI) m/z
All other cyclobutenes were prepared analogously. Their analytical and spectroscopic data are compiled below:

1-Benzylolxy-3-cyclobuten-1-yl-benzene (6). White, air sensitive solid (27 mg, 90%). IR (neat): 3041, 2948, 2918, 2838, 1591, 1576, 1485, 1464, 1455, 1433, 1383, 1324, 1286, 1241, 1220, 1205, 1183, 1160, 1012, 852, 803, 746, 696 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CD\(_3CN\)): \(\delta = 7.49-7.32 (5H, m)\), 7.25 (1H, t, \(J = 7.8\) Hz), 7.01-6.95 (2H, m), 6.92-6.86 (1H, m), 6.33 (1H, t, \(J = 1.4\) Hz), 5.11 (2H, s), 2.82-2.77 (2H, m), 2.55-2.48 (2H, m). 13C NMR (75 MHz, CD\(_3CN\)): \(\delta = 160.0, 147.4, 138.5, 137.5, 130.5, 129.5 (2C), 128.9, 128.8, 128.7 (2C), 117.8, 115.3, 111.5, 70.6, 29.5, 26.8. MS (EI) m/z (rel. intensity): 236 (16), 145 (3), 91 (100). HRMS (EI): \(\text{calcd for } C_{17}H_{16}O: 236.120119\), found 236.120340.

4-Cyclobuten-1-yl-benzoic acid methyl ester (8). White, air sensitive solid (25 mg, 80%). IR (neat): 2946, 2910, 2831, 1717, 1567, 1567, 1433, 1410, 1276, 1108, 1027, 735 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CD\(_3CN\)): \(\delta = 7.96 (2H, d, J = 8.4\) Hz), 7.47 (2H, d, \(J = 7.7\) Hz), 6.51 (1H, t, \(J = 1.4\) Hz), 3.86 (3H, s), 2.88-2.83 (2H, m), 2.58-2.53 (2H, m). 13C NMR (75 MHz, CD\(_3CN\)): \(\delta = 167.5, 146.6, 140.0, 131.9, 130.5 (2C), 130.0, 125.1 (2C), 52.6, 29.4, 27.2. MS (EI) m/z (rel. intensity): 188 (34), 157 (17), 129 (100), 59 (7). HRMS (EI): \(\text{calcd for } C_{12}H_{12}O_{2}: 188.083730\), found 188.083494.

1-Bromo-2-cyclobuten-1-yl-4,5-dimethoxy-benzene (10). White, air sensitive solid (18 mg, 61%). IR (KBr): 3084, 3001, 2919, 2834, 1690, 1593, 1565, 1508, 1458, 1432, 1338, 1259, 1211, 1170, 1027, 852, 785 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CD\(_2Cl_2\)): \(\delta = 6.99 (1H, s)\), 6.77 (1H, s), 6.56 (1H, s), 3.80 (6H, s), 2.92-2.89 (2H, m), 2.51-2.46 (2H, m). 13C NMR (75 MHz, CD\(_2Cl_2\)): \(\delta = 149.6, 149.1, 145.1, 132.5, 127.6, 117.3, 112.2, 111.3, 56.8, 56.7, 31.8, 27.0. MS (EI) m/z (rel. intensity): 270 (37), 268 (38), 242 (10), 240 (8), 189 (100), 158 (58). HRMS (EI): \(\text{calcd for } C_{12}H_{13}BrO_2: 268.009907\), found 268.010036.

2-Cyclobuten-1-yl-1,4-dimethoxy-benzene (12). Pale yellow, air sensitive solid (50 mg, 50%). IR (KBr): 3001, 2956, 2911, 2832, 1613, 1586, 1497, 1464, 1452, 1442, 1397, 1315, 1279, 1215, 1044, 854, 821, 814, 766, 739 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CD\(_3CN\)): \(\delta = 6.88 (1H, d, J = 8.8\) Hz), 6.79 (1H, dd, \(J = 8.8, 2.9\) Hz), 6.74 (1H, d, \(J = 3.3\) Hz), 6.34 (1H, t, \(J = 1.3\) Hz), 3.80 (3H, s), 3.74 (3H, s), 2.85-2.81 (2H, m), 2.56-2.51 (2H, m). 13C NMR (75 MHz, CD\(_3CN\)): \(\delta = 154.4, 153.6, 143.9, 133.4, 125.3, 114.0, 113.2, 112.8, 56.2 (2C), 30.6, 27.8. MS (EI) m/z (rel. intensity): 190 (100), 175 (51), 159 (75). HRMS (EI): \(\text{calcd for } C_{12}H_{14}O_2: 190.099384\), found 190.099162.
1-tert-Butyl-(4-cyclobuten-1-yl)-dimethyl-silane (14). Colorless, air sensitive oil (10 mg, 93%). IR (neat): 2928, 2857, 1631, 1472, 1254, 1099, 832, 773 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 5.69-5.67 (1H, m), 3.64 (2H, t, J = 6.6 Hz), 2.45-2.41 (2H, m), 2.36-2.32 (2H, m), 2.09-2.00 (2H, m), 1.66 (2H, quint, \(J = 6.7 Hz\)), 0.91 (9H, s), 0.06 (6H, s). \(^1\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 150.4, 126.9, 63.0, 31.3, 30.1, 27.5, 26.6, 26.1 (3C), 18.5, -5.1 (2C). MS (EI) \(m/z\) (rel. intensity): 169 (47), 141 (28), 75 (100). HRMS (CI): \textit{calcd} for C\(_{13}\)H\(_{17}\)OSi: 227.183121, \textit{found} 227.183220.

(3-Cyclobutenyl-propyl)-benzene (16). Colorless, air sensitive oil (30 mg, 95%). IR (neat): 3028, 2919, 2841, 1629, 1604, 1496, 1453, 1410, 853, 747, 696 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.32-7.27 (2H, m), 7.23-7.17 (3H, m), 5.71(1H, s), 2.79 (2H, dd, \(J = 8.2, 7.2 Hz\)), 2.46-2.43 (2H, m), 2.38-2.30 (4H, m). \(^1\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 150.0, 142.3, 128.4 (4C), 127.4, 125.9, 33.3, 33.0, 31.4, 26.7. MS (EI) \(m/z\) (rel. intensity): 158 (2), 143 (10), 130 (29), 91 (100). HRMS (EI): \textit{calcd} for C\(_{12}\)H\(_{14}\): 158.109551, \textit{found} 158.109352.

Compound 23. PtCl\(_2\) (2 mg, 0.0075 mmol) was added to a solution of compound 22 (30 mg, 0.158 mmol) in toluene (0.1 M) and the resulting mixture was stirred at 80°C under CO atmosphere for 4h. Purification of the crude mixture by flash chromatography (hexanes, then hexanes/EtOAc, 4/1) gave a first fraction of pure compound 23 (10 mg) and second fraction of a mixture of 23 and its regioisomer 24 (16 mg), both as colorless oils (combined yield 87%). IR (neat): 2931, 1831, 1498, 1642, 1234, 1235, 1173, 1139, 1109, 1027, 849, 759 cm\(^{-1}\). \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 6.94 (1H, s), 6.78 (1H, d, J = 8.3 Hz), 6.72 (1H, dd, \(J = 8.2, 2.1 Hz\)), 6.56 (1H, d, \(J = 2.1 Hz\)), 6.44 (1H, s), 3.93 (3H, s), 3.82 (3H, s), 3.76 (3H, s), 3.74 (3H, s), 3.10 (1H, t, \(J = 8.1 Hz\)), 2.69 (1H, dt, \(J = 11.1, 9.7 Hz\)), 2.39-2.33 (1H, m), 2.26-2.18 (4H, m), 2.08-1.94 (3H, m), 1.62-1.55 (1H, m). \(^1\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 149.2, 149.0, 148.8, 147.0, 142.2, 141.0, 140.8, 117.6, 111.0, 109.6, 106.9, 105.8, 57.5, 57.3, 56.1, 56.0, 55.9, 55.7, 53.4, 38.1, 29.6, 28.5, 19.5, 16.0. MS (EI) \(m/z\) (rel. intensity): 380 (42), 352 (74), 324 (100). HRMS (ESIpos): \textit{calcd} for C\(_{24}\)H\(_{28}\)O\(_4\)+Na: 403.187979, \textit{found} 403.188368.

Regioisomer 24: (resolved signals) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.00-6.95 (2H, m), 6.60 (1H, d, \(J = 2.0 Hz\)), 3.83 (3H, s), 3.82 (3H, s), 3.80 (3H, s), 3.68 (3H, s), 2.66-2.56 (4H, m), 2.55-2.48 (2H, m), 2.47-2.41 (2H, m). \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 148.9, 147.9, 147.2, 145.9, 117.9, 110.6, 110.0, 109.9, 55.8, 55.6, 33.8, 26.6, 26.3, 25.4, 16.7.

Compound 21. This compound was obtained analogously from substrate 11 as a white solid (16 mg, 53%). m.p. 160-163°C. IR (neat): 2942, 2831, 1587, 1487, 1463, 1436, 1416, 1281, 1253, 1221, 1204, 1178, 1081, 1057, 1032, 874, 796, 725 cm\(^{-1}\). \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 6.79 (1H, d, J = 2.9 Hz), 6.71 (1H, d, J =\)
8.6 Hz), 6.66 (1H, d, \(J = 8.8\) Hz), 6.63 (1H, dd, \(J = 8.8, 2.9\) Hz), 6.57 (1H, d, \(J = 8.6\) Hz), 3.86 (3H, s), 3.72 (3H, s), 3.51 (3H, s), 3.47 (3H, s), 3.21 (1H, dd, \(J = 9.1, 7.5\) Hz), 2.86 (1H, dt, \(J = 11.2, 9.9\) Hz), 2.83-2.77 (1H, m), 2.62-2.55 (1H, m), 2.21-2.09 (4H, m), 2.05 (1H, dddd, \(J = 11.9, 10.1, 9.1, 3.1\) ), 1.85-1.77 (1H, m), 1.63 (1H, ddt, \(J = 11.9, 9.5, 7.5\) Hz). 13C NMR (150 MHz, CDCl3): \(\delta = 152.9, 152.1, 151.9, 150.8, 139.9, 137.8, 135.5, 116.3, 111.8, 111.0, 110.2, 110.1, 57.6, 55.9, 55.8, 55.7, 55.6, 53.8, 28.4, 27.2, 20.2, 15.3\). MS (EI) \(m/z\) (rel. intensity): 380 (30), 352 (36), 324 (100). HRMS (ESIpos): calcd for C24H28O4+: Na: 403.187981, found 403.187676.

**Compound 26.** Obtained analogously from substrate 25 as a white solid (13 mg, 43%). m.p. 113-117°C. IR (neat): 3033, 2937, 2915, 2899, 2830, 1571, 1506, 1467, 1454, 1380, 1287, 1235, 1173, 1013, 835, 811, 745, 698 cm\(^{-1}\). 1H NMR (400 MHz, CDCl3): \(\delta = 7.49-7.31 (10H, m), 7.09 (2H, d, \(J = 8.8\) Hz), 6.97 (2H, d, \(J = 8.3\) Hz), 6.87 (2H, d, \(J = 8.8\) Hz), 5.07 (2H, s), 5.05 (2H, s), 2.68-2.63 (2H, m), 2.61-2.52 (4H, m), 2.51-2.42 (2H, m), 1.99-1.90 (2H, m). 13C NMR (100 MHz, CDCl3): \(\delta = 157.2, 156.6, 145.3, 139.4, 136.9, 136.7, 136.3, 128.7, 128.2 (4C), 127.6, 127.5 (2C), 127.2 (2C), 127.1 (2C), 126.8 (2C), 114.3 (2C), 114.0 (2C), 69.7, 69.6, 47.3, 33.6 (2C), 25.9, 25.1, 16.3\). MS (EI) \(m/z\) (rel. intensity): 472 (8), 444 (4), 381 (21), 91 (100). HRMS (EI): calcd for C34H32O2: 472.240592, found 472.240233.

**4-But-3-enyl-8-methoxy-2H-chromene (19).** PtCl2 (3.5 mg, 0.0132 mmol) was added to a solution of substrate 17 (33 mg, 0.139 mmol) in toluene (1.4 mL). The solution was stirred for 4.5 h at 80°C before it was transferred at room temperature into a flask containing a solution of the Grubbs catalyst Cl2(PCy3)2Ru=CHPh (5.7 mg, 0.00695 mmol) in CH2Cl2 (30 mL). The resulting mixture was refluxed for 30 min, the reaction was quenched with a few drops of ethyl vinyl ether, the solvent was evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 20/1) to give chromene 19 as a yellow oil (21 mg, 64%). IR (neat): 3075, 2997, 2934, 2836, 1641, 1603, 1576, 1477, 1440, 1270, 1220, 1199, 1176, 1152, 1091, 1050, 1007, 913 cm\(^{-1}\). 1H NMR (300 MHz, CDCl3): \(\delta = 6.95-6.79 (3H, m), 5.88 (1H, ddt, \(J = 17.0, 10.2, 6.5\) Hz), 5.65-5.60 (1H, m), 5.07 (1H, dq, \(J = 17.0, 1.7\) Hz), 5.01 (1H, dq, \(J = 10.1, 1.0\) Hz), 4.83-4.79 (2H, m), 3.88 (3H, s), 2.52-2.44 (2H, m), 2.35-2.26 (2H, m). 13C NMR (75 MHz, CDCl3): \(\delta = 148.2, 143.5, 138.1, 133.9, 124.4, 120.7, 117.9, 115.7, 115.1, 111.8, 65.7, 56.2, 32.2, 31.1\). MS (EI) \(m/z\) (rel. intensity): 216 (100), 201 (19), 175 (30). HRMS (EI): calcd for C14H16O2: 216.115032, found 216.115269.
Figure S-1. Overview over the spectral data recorded for compound 23 (DMX 600 spectrometer, CDCl₃). ¹H NMR shifts are given in red, ¹³C NMR shifts are shown in blue. The *signal assignments are unambiguous*, based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (*cosygs* and *cosydqtp*); HSQC (*invietgssi*) optimized for ¹J(C,H) = 145 Hz; HMBC (*inv4gslplrnd*) for correlations via ¹¹J(C,H); HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms.
Figure S-2. Selected NOESYs for compound 23.
Figure S-3. Selected long range couplings for compound 23.
Figure S-4. Overview over the spectral data recorded for compound 21 (DMX 600 spectrometer, CDCl₃). ¹H NMR shifts are given in red, ¹³C NMR shifts are shown in blue. The signal assignments are unambiguous, based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (cosygs and cosydqtp); HSQC (invietgssi) optimized for ¹J(C,H) = 145 Hz; HMBC (inv4gslplrdn) for correlations via ²J(C,H); HSQC-TOCSY (invietgsm1) using an MLEV17 mixing time of 120 ms.
Figure S-5. Selected NOESYs for compound 21.
Figure S-6. Selected long range couplings for compound 21.