SUPPORTING INFORMATION

Ruthenium Carbene Complexes with N,N'-Bis(mesityl)imidazol-2-ylidene Ligands: RCM Catalysts of Extended Scope

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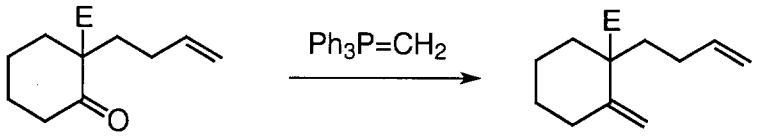
Experimental Section

General. All reactions were carried out under Ar in pre-dried glassware using Schlenk techniques. The solvents were dried by distillation over the drying agents indicated and were stored and transferred under Ar: CH_2Cl_2 (P_4O_{10}), toluene (Na/K), THF (magnesium/anthracene), pyridine (KOH), EtOH (Mg), MeOH (Mg). Flash chromatography: Merck silica gel (230-400 mesh) using hexane/EtOAc in various proportions as eluent. Mp: Gallenkamp apparatus (uncorrected). NMR: Spectra were recorded on a Bruker DPX 300 spectrometer in the solvent indicated. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. IR: Nicolet FT-7199, wavenumbers in cm^{-1}. MS: Finnigan MAT 8200 (70 eV); HRMS: Finnigan MAT SSQ 7000 (70 eV). Elemental analyses: Dornis & Kolbe, Mülheim. Commercially available reagents (Aldrich, Fluka) were used as received.

Substrates

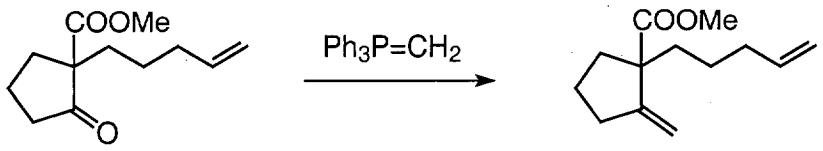
Table 1. The following substrates required for the preparation of the products displayed in Table 1 have been previously described and have been prepared according to literature procedures: ref.[20] (entry 1), ref.[3] (entries 3, 4, 7), ref.[21] (entry 8), ref.[22] (entry 9), ref.[11b] (entries 11-13). The remaining dienes have been obtained as described below:

1-But-3-enyl-2-methylene-cyclohexanecarboxylic acid ethyl ester



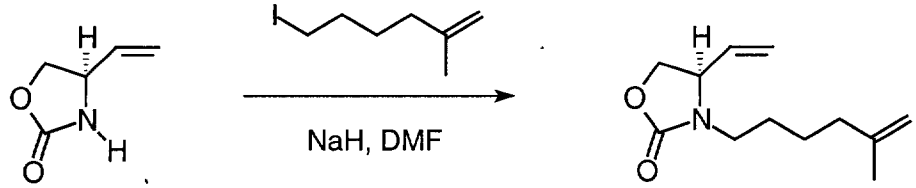
To a solution of methylene triphenylphosphorane (3.70 g, 13.4 mmol) in THF (250 mL) was added dropwise 1-but-3-enyl-2-oxo-cyclohexanecarboxylic acid ethyl ester (2.31 g, 10.3 mmol)[23] at -15 °C. The solution was allowed to warm up to room temperature and stirred for 20 h. After the reaction was quenched with aqueous saturated NaCl (50 mL) the product was extracted with tert-butyl methylether (3 x 50 mL). The organic phase was dried over Na_2SO_4, concentrated and the residue was purified by flash chromatography (hexane/ethyl acetate, 50:1 → 30:1) to yield the title compound as a colorless oil (1.65 g; 72%). ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 5.82 (1 H, ddt, *J* = 17.2, 10.2, 6.6 Hz), 5.00 (1 H, dq, *J* = 17.2, 1.6 Hz), 4.95 (1 H, dq, *J* = 10.2, 1.2 Hz), 4.86 (1H, s), 4.74 (1H, s), 4.13 (2H, q, *J* = 7.1 Hz), 2.32 - 2.20 (2H, m), 2.17 - 1.85 (4H, m), 1.72 - 1.30 (6H, m), 1.22 (3H, t, *J* = 7.1 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 174.9, 150.9, 139.0, 114.5, 108.3, 60.7, 52.9, 36.1, 35.7, 35.4, 29.1, 28.7, 23.5, 14.4; IR (film): 3080, 2978, 2936, 2858, 1728, 1642, 1447, 1366, 1298, 1264, 1229, 1199, 1137, 1116, 1030, 994, 908, 894, 673 cm^{-1}; MS (EI) *m/z* (rel. intensity) 222 ([M$^+$], 1), 207 (4), 193 (4), 176 (8), 168 (41), 149 (82), 139 (47), 134 (64), 121 (67), 107 (75), 93 (100), 79 (87), 67 (82), 55 (50), 41 (63), 29 (62); $C_{14}H_{22}O_2$ (222.33) *calcd.* C 75.63, H 9.97, *found* C 75.57, H 9.85.

2-Methylene-1-pent-4-enyl-cyclopentanecarboxylic acid methyl ester



To a solution of methylene triphenylphosphorane (1.10 g, 4.0 mmol) in THF (75 mL) was added dropwise 2-oxo-1-pent-4-enyl-cyclopentanecarboxylic acid methyl ester (0.65 g, 3.1 mmol)[23] at -15 °C. The solution was allowed to warm up to room temperature and stirred for 20 h. After the reaction was quenched with aqueous saturated NaCl (50 mL) the product was extracted with tert-butyl methylether (3 x 50 mL). The organic phase was dried over Na_2SO_4, concentrated and the residue purified by flash chromatography (hexane/ethyl acetate, 50:1 → 30:1) to yield **6a** (0.41 g; 64%) as a colorless oil. ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 5.81 (1 H, ddt, *J* = 17.0, 10.2, 6.6 Hz), 5.06 - 4. 91 (4 H, m), 3.63 (3H, s), 2.42 - 2.28 (3H, m), 2.09 - 1.88 (3H, m), 1.82 - 1.17 (6H, m); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 175.9, 155.8, 139.1, 114.6, 107.4, 56.8, 52.1, 38.9, 35.5, 34.4, 34.1, 25.3, 24.4; IR (film): 3078, 2951, 1730, 1642, 1458, 1433, 1324, 1292, 1261, 1234, 1195, 1149, 998, 911, 893, 855, 833, 790, 754 cm^{-1}; MS (EI) *m/z* (rel. intensity) 208 ([M^+], 1), 193 (1), 180 (2), 176 (7), 165 (2), 149 (77), 140 (40), 121 (27), 107 (50), 95 (57), 81 (100), 67 (62), 55 (26), 41 (44), 29 (13); $C_{13}H_{20}O_2$ (208.30) *calcd.* C 74.96, H 9.68, *found* C 74.79, H 9.66.

(*R*)-3-(5-Methyl-5-hexenyl)-4-vinyloxazolidin-2-one.



To a solution of (*R*)-4-vinyloxazolidin-2-one (300 mg, 2.7 mmol) in DMF (30 mL) is added NaH (76 mg, 3.2 mmol) at 0°C. After the evolution of gas has ceased, 5-iodo-2-methylhex-1-ene (3.7 mmol) is introduced and the reaction is stirred at ambient temperature for 1 h. Standard extractive work up followed by flash chromatography of the crude product (hexane/ethyl acetate, 4/1→2/1) affords the title compound as a colorless syrup (488 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.72 - 5.61 (1H, m), 5.36 - 5.30 (2H, m), 4.66 - 4.62 (2H, m), 4.38 (1H, t, *J* = 8.5 Hz), 4.26 - 4.18 (1H, m), 3.93 - 3.87 (1H, m), 3.37 - 3.28 (1H, m), 3.03 - 2.95 (1H, m), 2.01 - 1.96 (2H, m), 1.66 (3H, s), 1.51 - 1.36 (4H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 157.8, 145.2, 134.8, 120.9, 110.1, 66.8, 59.1, 41.7, 37.1, 26.6, 24.4, 22.1; MS (EI): *m/z* (rel. intensity) 209 ([M^+], 9), 164 (10), 152 (21), 126 (33), 96 (30), 82 (12), 81 (34), 68 (14), 56 (11), 55 (100), 54 (32), 53 (12), 42 (10), 41 (37), 39 (21), 29 (23), 27 (14); IR (film): 3487, 3074, 2933, 2864, 1751, 1648, 1412, 1319, 1253, 1152, 1103, 1063, 992, 937, 886, 762; $C_{12}H_{19}NO_2$ (209.29) *calcd.* C 68.87, H 9.15, N 6.69, *found* C 68.74, H 9.08, N 6.74.

Table 2.

Representative Procedure (A): Acrylic acid 1-methyl-but-3-enyl ester (23). 4-Penten-2-ol (1.55 mL, 10 mmol) and triethylamine (4.20 mL, 30 mmol) are dissolved in CH_2Cl_2 (50 mL). Acrylic acid chloride (0.89 mL, 11 mmol) is added slowly at 0 °C and the resulting mixture is stirred for 14 h at room temperature. The organic phase is washed with 1 N HCl (3 x 25 mL) and brine (25 mL) followed by drying over Na_2SO_4. Evaporation of the solvents and flash chromatography of the crude product (hexane/ethyl acetate 40:1) affords **23** as a colourless syrup (543 mg, 39 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.34 (1 H, dd, *J* = 17.3, 1.5 Hz), 6.05 (1 H, dd, *J* = 17.3, 10.4 Hz), 5.80 - 5.65 (2H, m), 5.10 - 4.94 (3H, m), 2.40 - 2.22 (2H, m), 1.22 (3H, d, *J* = 6.3 Hz) ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 165.7, 133.5, 130.2, 128.9, 117.7, 70.2, 40.2, 19.3; IR (film): 3080, 2980, 2935, 1723, 1640, 1620, 1406, 1382, 1296, 1272, 1198, 1126, 1058, 1048, 986, 966, 919 cm^{-1}; MS (EI) *m/z* (rel. intensity) 140 ([M^+], < 1), 99 (25), 68 (8), 55 (100), 41 (12), 27 (14); HR-MS (CI) ($C_8H_{12}O_2$ + H^+) *calcd.* 141.0916 *found* 141.0913; $C_8H_{12}O_2$ (140.18) *calcd.* C 68.55, H 8.63, *found* C 68.63, H 8.71.

The following compounds have been analogeously prepared:

Acrylic acid 3-methyl-but-3-enyl ester (27). Colorless syrup. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.36 (1 H, dd, *J* = 17.3, 1.5 Hz), 6.08 (1 H, dd, *J* = 17.3, 10.5 Hz), 5.79 (1 H, dd, *J* = 10.5, 1.5 Hz), 4.79 (1H, s), 4.73 (1H, t, *J* = 0.9 Hz), 4.25 (2H, t, *J* = 6.8), 2.36 (2H, t, *J* = 6.8), 1.74 (3H, s); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 166.2, 141.6, 130.6, 128.5, 112.3, 62.8, 36.6, 22.5; IR (film): 3078, 2970, 2939, 2918, 1727, 1652, 1636, 1621, 1456, 1408, 1297, 1270, 1188, 1059, 985, 893, 811 cm^{-1}; MS (GC-EI) *m/z* (rel. intensity) 140 ([M^+], < 1), 95 (1), 85 (1), 73 (2), 68 (86), 55 (100), 41 (14), 39 (12), 27 (23); HR-MS (CI) ($C_8H_{12}O_2$ + H^+) *calcd.* 141.0916 *found* 141.0912; $C_8H_{12}O_2$ (140.18) *calcd.* C 68.55, H 8.63, *found* C 68.46, H 8.70.

Acrylic acid 1-vinyl-hexyl ester (31). Colorless syrup. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.38 (1 H, dd, *J* = 17.3, 1.5 Hz), 6.08 (1 H, dt, *J* = 17.3, 10.3 Hz), 5.81 -5.75 (2H, m), 5.26 (1 H, dd, *J* = 17.3, 10.5 Hz), 5.21 (1 H, dt, *J* = 17.3, 1.3 Hz), 5.13 (1 H, dt, *J* = 10.5, 1.1 Hz), 1.68 - 1.53 (2H, m), 1.37 - 1.21 (6H, m), 0.85 (3H, t, *J* = 6.7 Hz); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 165.5, 136.5, 130.5, 128.8, 116.6, 75.0, 34.1, 31.5, 24.7, 22.5, 13.9; IR (film): 3087, 3030, 2957, 2933, 2861, 1727, 1637, 1619, 1467, 1405, 1295, 1268, 1192, 1124, 1094, 1045, 986, 965, 931, 809 cm^{-1}; MS (EI) *m/z* (rel. intensity) 182 ([M^+], < 1), 127 (2), 111 (14), 95 (3), 81 (8), 68 (11), 55 (100), 41 (13), 27 (15); HR-MS (CI) ($C_{11}H_{18}O_2$ + H^+) *calcd.* 183.1385 *found* 183.1385; $C_{11}H_{18}O_2$ (182.26) *calcd.* C 72.49, H 9.95, *found* C 72.29, H 9.99.

Acrylic acid 1-ethyl-2-methyl-allyl ester (35). Colorless syrup. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.38 (1H, dd, *J* = 17.3, 1.7 Hz), 6.11 (1 H, dd, 17.3, 10.3 Hz), 5.79 (1H, dd, *J* = 10.3, 1.7 Hz), 5.16 (1H, t, *J* = 6.7 Hz), 4.94 (1 H, q, *J* = 1.7 Hz), 4.90 - 4.87 (1 H, m), 1.73 -1.63 (5H, m), 0.87 (3H, t, *J* = 7.4 Hz); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 165.5, 142.8, 130.4, 128.8, 112.8, 78.7, 25.6, 18.1, 9.6; IR (film): 3081, 3036, 2973, 2939, 2880, 1727, 1653, 1636, 1619, 1456, 1405, 1378, 1294, 1269, 1192, 1091, 1045, 984, 966, 900, 809 cm^{-1}; MS (EI) *m/z* (rel. intensity) 154 ([M^+], < 1), 125 (3), 111 (1), 99 (3), 82 (35), 67 (28), 55 (100), 41 (11), 27 (20); HR-MS (CI) ($C_9H_{14}O_2$ + H^+) *calcd.* 155.1072 *found* 155.1072; $C_9H_{14}O_2$ (154.21) *calcd.* C 70.10, H 9.15, *found* C 70.26, H 9.13.

N-Allyl-N-phenyl-acrylamide (39). Pale yellow syrup. The analytical data are in accordance with those reported previously.[24]

Acrylic acid 2-allyl-phenyl ester (43). Colorless syrup. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.37 - 7.21 (3H, m), 7.16 - 7.11 (1H, m), 6.66 (1H, dd, *J* = 17.3, 1.3 Hz), 6.38 (1H, dd, *J* = 17.3, 10.4 Hz), 6.07 (1 H, dd, *J* = 10.4, 1.3 Hz), 6.02 - 5.85 (1H, m), 5.12 (1H, dd *J* = 1.4, 1.1 Hz), 5.09 - 5.05 (1H, m), 3.35 (2H, d, *J* = 6.6 Hz); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 164.4, 148.8, 135.8, 132.5, 131.9, 130.3, 127.8, 127.4, 126.2, 122.3, 116.2, 34.6; IR (film): 3079, 3036, 3008, 2980, 2915, 2850, 1743, 1635, 1624, 1583, 1489, 1454, 1403, 1294, 1251, 1216, 1152, 1119, 1020, 985, 915, 802, 754, 676, 645, 557 cm^{-1}; MS (EI) *m/z* (rel. intensity) 188 ([M^{+}], 13), 170 (1), 160 (3), 144 (5), 133 (27), 118 (7), 105 (3), 91 (2), 77 (5), 63 (2), 55 (100), 39 (3), 27 (13); HR-MS (EI) ($C_{12}H_{12}O_2$) *calcd.* 188.0837 *found* 188.0835; $C_{12}H_{12}O_2$ (188.23) *calcd.* C 76.57, H 6.43, *found* C 76.39, H 6.52.

Acrylic acid pent-4-enyl ester (45). Colorless syrup. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.34 (1 H, d, *J* = 17.3 Hz) 6.07 (1H, dd, *J* = 17.3, 10.4 Hz), 5.83 - 5.67 (2H, m), 5.00 (1H, d, *J* = 17.3 Hz), 4.93 (1H, d, *J* = 10.4 Hz), 4.12 (2H, t, *J* = 6.6 Hz), 2.09 (2H, tt, *J* = 7.2, 6.6 Hz), 1.73 (2H, dt, *J* = 10.4, 7.2 Hz); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 166.1, 137.3, 130.4, 128.5, 115.2, 63.8, 29.9, 27.7; IR (film): 3079, 2957, 2851, 1727, 1639, 1620, 1408, 1296, 1271, 1190, 1060, 987, 9696, 915, 811 cm^{-1}; MS (EI) *m/z* (rel. intensity) 140 ([M^{+}], < 1), 99 (1), 84 (2), 73 (3), 68 (68), 55 (100), 41 (21), 27 (29); $C_8H_{12}O_2$ (140.18) *calcd.* C 68.55, H 8.63, *found* C 68.40, H 8.56.

Acrylic acid undecenyl-10-enyl ester (47). Colorless syrup. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.37 (1 H, dd, *J* = 17.3, 1.4 Hz), 6.09 (1H, dd, *J* = 17.3, 10.4 Hz), 5.84 - 5.74 (2H, m), 5.00 - 4.88 (2H, m), 4.12 (2H, t, *J* = 6.7 Hz), 2.01 (2H, tt, *J* = 6.9, 6.7 Hz), 1.64 (2H, dt, *J* = 10.4, 6.9 Hz), 1.40 - 1.21 (12H, m); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 166.3, 134.2, 130.4, 128.7, 114.1, 64.7, 33.8, 29.4, 29.3, 29.2, 29.1, 28.9, 28.6, 25.9; IR (film): 3076, 2975, 2927, 2855, 1728, 1639, 1620, 1467, 1408, 1295, 1271, 1191, 1060, 986, 966, 910, 810 cm^{-1}; MS (EI) *m/z* (rel. intensity) 224 ([M^{+}], 1), 152 (7), 137 (1), 123 (5), 110 (11), 96 (18), 82 (27), 67 (27), 55

(100), 41 (50), 27 (26). HR-MS (EI) ($C_{14}H_{24}O_2$) *calcd.* 224.1776 *found* 224.1775; $C_8H_{12}O_2$ (224.34) *calcd.* C 74.95, H 10.78, *found* C 74.82, H 10.69.

Representative Procedure (B): 2-Methyl-acrylic acid 1-methyl-but-3-enyl ester (25). 4-Penten-2-ol (1.03 mL, 10 mmol), dicyclohexylcarbodiimide (2.26 g, 11 mmol) and *N,N'*-dimethylaminopyridine (122 mg, 1 mmol) are dissolved in CH_2Cl_2 (50 mL). Methacrylic acid (0.85 mL, 10 mmol) is added slowly and the mixture is stirred for 14 h at room temperature. The suspension is filtered through a short pad of silica, the insoluble residues are washed with CH_2Cl_2, the combined filtrates are concentrated to ca. 50 mL, the organic phase is washed with 1 N HCl (2 x 25 mL) and brine (25 mL) and dried Na_2SO_4. Evaporation of the solvents and flash chromatography of the crude product (hexane/ethyl acetate 20:1) delivers the title compound as a colorless oil (843 mg, 55 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.02 (1H, s), 5.77 - 5.68 (1H, m), 5.47 (1H, s), 5.07 - 4.94 (3H, m) 2.36 - 2.21 (3H, m), 1.88 (3H, s), 1.21 (3H, d, J = 6.3 Hz) ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 166.8, 136.7, 133.6, 124.9, 117.6, 70.2, 40.2, 19.3, 18.1; IR (film): 3080, 2980, 2931, 1718, 1639, 1452, 1379, 1318, 1296, 1172, 1125, 1060, 1010, 994, 939, 918, 814 cm^{-1}; MS (EI) *m/z* (rel. intensity) 154 ([M^+], < 1), 113 (26), 82 (2), 69 (100), 41 (53), 39 (15); HR-MS (CI) ($C_9H_{14}O_2 + H^+$) *calcd.* 155.1072; *found* 155.1071; $C_9H_{14}O_2$ (154.21) *calcd.* C 70.10, H 9.15, *found* C 70.15, H 8.98.

The following compounds have been obtained analogeously:

2-Methyl-acrylic acid 3-methyl-but-3-enyl ester (29). Colorless syrup. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.07 (1 H, dt, J = 1.5, 1.2 Hz), 5.51 (1 H, dt, J = 1.5, 1.2 Hz), 4.78 (1H, s), 4.73 (1H, s), 4.23 (2 H, t, J = 6.8 Hz), 2.36 (2 H, t, J = 6.8 Hz), 1.91 (3H, dd, J = 1.2, 1.2 Hz), 1.75 (1H, s); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 167.4, 141.7, 136.4, 125.3, 112.3, 62.9, 36.7, 22.5, 18.2; IR (KBr): 3078, 2960, 2930, 2855, 1721, 1652, 1638, 1628, 1453, 1322, 1298, 1165, 1034, 1013, 941, 893, 815 cm^{-1}; MS (EI) *m/z* (rel. intensity) 154 ([M^+], < 1), 109 (3), 108 (3), 87 (2), 84 81), 81 (2), 68 (100), 53 (8), 41 (76). HR-MS (CI) ($C_9H_{14}O_2 + H^+$) *calcd.* 155.1072, *found* 155.1071; $C_9H_{14}O_2$ (154.21) *calcd.* C 70.10, H 9.15, *found* C 69.94, H 8.99.

2-Methyl-acrylic acid 1-vinyl-hexyl ester (33). Colorless syrup. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.09 (1 H, q, *J* = 1.1 Hz), 5.78 (1 H, ddd, *J* = 17.0, 10.5, 6.2 Hz), 5.52 (1 H, q, *J* = 1.3 Hz), 5.27 - 5.11 (3H, m), 1.92 (3 H, dd, *J* = 1.3, 1.1 Hz), 1.66 - 1.57 (2H, m), 1.37 - 1.21 (6H, m), 0.86 (3H, t, *J* = 6.7 Hz); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 166.7, 136.7, 136.6, 125.1, 116.3, 75.0, 34.2, 31.5, 24.6, 22.5, 18.3, 13.9; IR (film): 3088, 3016, 2957, 2931, 2861, 1721, 1639, 1453, 1403, 1379, 1314, 1294, 1165, 1010, 988, 935, 813 cm^{-1}; MS (EI) *m/z* (rel. intensity) 196 ([M^+], < 1), 167 (1), 153 (1), 140 (1), 125 (7), 110 (5), 95 (3), 81 (7), 69 (100), 54 (12), 41 (36), 29 (6); HR-MS (CI) ($C_8H_{12}O_2$ + H^+) *calcd.* 197.1542, *found* 197.1548; $C_{12}H_{20}O_2$ (196.29) *calcd.* C 73.43, H 10.27, *found* C 73.51, H 10.33.

2-Methyl-acrylic acid 1-ethyl-2-methyl-allyl ester (37). Colorless syrup. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.10 (1 H, q, 1.0 Hz), 5.53 - 5.51 (1H, m), 5.13 (1H, t, *J* = 6.7 Hz), 4.93 - 4.92 (1H, m), 4.87 (1 H, q, 1.5 Hz), 1.92 (3H, t, 1.5 Hz), 1.73 - 1.63 (5H, m), 0.86 (3H, t, *J* = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 166.7, 143.0, 136.7, 125.1, 112.6, 78.7, 25.6, 18.3, 18.1, 9.6; IR (film): 3080, 2972, 2938, 2880, 1720, 1653, 1639, 1454, 1401, 1379, 1322, 1309, 1292, 1165, 1091, 1009, 969, 937, 902, 813 cm^{-1}; MS (EI) *m/z* (rel. intensity) 168 ([M^+], < 1), 140 (1), 99 (2), 87 (2), 82 (40), 69 (100), 55 (19), 41 (54), 39 (17), 29 (7); $C_{10}H_{16}O_2$ (168.24) *calcd.* C 71.39, H 9.59, *found* C 71.26, H 9.65.

***N*-Allyl-2-methyl-acrylamide (41)**. Colorless syrup. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.98 (1H, s, br), 5.81 (1 H, ddt, *J* = 17.3, 10.1, 5.7 Hz), 5.66 (1 H, q, *J* = 0.8 Hz), 5.29 (1 H, q, *J* = 1.4 Hz), 5.15 (1 H, dt, *J* = 17.3, 1.6 Hz), 5.09 (1 H, dt, *J* = 10.1, 1.5 Hz), 3.91 (1 H, ddd, *J* = 5.7, 1.6, 1.5 Hz), 3.88 (1 H, ddd, *J* = 5.7, 1.6, 1.5 Hz), 1.93 (3H, dd, *J* = 1.4, 0.8 Hz); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 168.2, 139.9, 134.1, 119.4, 116.4, 42.0, 18.6; IR (film): 3322, 3084, 2982, 2955, 2924, 2857, 1658, 1619, 1534, 1455, 1421, 1375, 1310, 1259, 1218, 1145, 988, 922, 808, 655 cm^{-1}; MS (EI) *m/z* (rel. intensity) 125 ([M^+], 5), 110 (12), 97 (8), 82 (27), 69 (60), 56 (10), 41 (100), 27 (5); HR-MS (EI) ($C_7H_{11}NO$) *calcd.* 125.0841, *found* 125.0838; $C_7H_{11}NO$ (125.17) *calcd.* C 67.17, H 8.86, N 11.19, *found* C 67.28, H 8.73, N 11.08.

Products

Representative Procedure for RCM: Complex **3a** (8.4 mg, 0.01 mmol) is added to a solution of diene **33** (196 mg, 1.0 mmol) in toluene (25 mL). The reaction mixture is stirred at 80 °C for 2 hours. Evaporation of the solvent and flash chromatography (hexane/ethyl acetate 10:1) gives butenolide **34** as a colorless syrup (133 mg, 79 %). The analytical data of the material thus obtained are in full agreement with those reported in ref.[25]

The following compounds have been obtained analogously:

2,3,4,5,6,7-Hexahydro-indene-3a-carboxylic acid ethyl ester (16). Colorless syrup. ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 5.42 (1 H, d, *J* = 2.2 Hz), 4.11 (2 H, q, *J* = 7.1 Hz), 2.48 - 2.17 (5H, m), 2.11 - 1.91 (1H, m), 1.80 - 1.59 (4H, m), 1.45 - 1.13 (2H, m), 1.19 (3H, t, *J* = 7.1 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 176.6, 144.8, 124.1, 60.6, 57.9, 38.6, 37.9, 30.6, 28.1, 27.7, 24.4, 14.4; IR (film): 3044, 2973, 2933, 2855, 1726, 1663, 1457, 1446, 1387, 1365, 1299, 1252, 1230, 1214, 1174, 1131, 1096, 1031, 998, 947, 863, 823, 804 cm^{-1}; MS (EI) *m/z* (rel. intensity) 194 ([M$^+$], 8), 148 (1), 121 (100), 105 (2), 93 (22), 79 (28), 67 (10), 55 (5), 41 (6), 29 (5); $C_{12}H_{18}O_2$ (194.27) *calcd.* C 74.19, H 9.34, *found* C 74.04, H 9.26.

1,2,3,4,5,6-Hexahydro-indene-3a-carboxylic acid methyl ester (17). Colorless syrup. ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 5.50 (1 H, t, *J* = 1.6 Hz), 3.62 (3H, s), 2.57 - 2.42 (1H, m), 2.37 (1H, dt, *J* = 12.5, 3.2 Hz), 2.32 - 2.13 (2H, m), 2.07 - 1.96 (2H, m), 1.73 - 1.52 (3H, m), 1.47 - 1.32 (2H, m), 1.15 (1H, ddd, *J* = 14.0, 12.5, 3.2 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 177.2, 142.7, 120.2, 110.6, 52.0, 39.0, 33.2, 31.0, 25.3, 21.9, 20.4; IR (film): 3078, 2949, 2872, 2837, 1729, 1684, 1449, 1433, 1340, 1300, 1280, 1236, 1218, 1192, 1161, 1079, 992, 920, 888, 826, 792, 760 cm^{-1}; MS (EI) *m/z* (rel. intensity) 180 ([M$^+$], 10), 121 (100), 105 (3), 93 (23), 79 (32), 67 (13), 55 (5), 41 (7); $C_{11}H_{16}O_2$ (180.25) *calcd.* C 73.30, H 8.95, *found* C 73.18, H 9.04.

4,5-Dimethyl-cyclohept-4-ene-1,1-dicarboxylic acid diethyl ester (18). Colorless syrup. ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ 4.13 (4 H, q, *J* = 7.1 Hz), 2.15 - 2.03 (8H, m), 1.21 (6H, t, *J* = 7.1 Hz); ^{13}C-NMR (CD_2Cl_2, 75.5 MHz) δ 172.4, 130.6, 61.4, 58.4, 31.3, 31.2, 21.1, 14.2;

IR (film): 2981, 2935, 2857, 1730, 1651, 1447, 1385, 1367, 1300, 1235, 1178, 1154, 1091, 1077, 1031, 940, 859 cm^{-1}; MS (EI) *m/z* (rel. intensity) 268 ([M^+], 10), 223 (7), 194 (5), 173 (100), 145 (8), 127 (41), 121 (16), 93 (8), 79 (5), 67 (5), 41 (6), 29 (10); $C_{15}H_{24}O_4$ (268.35) *calcd.* C 67.14, H 9.01, *found* C 67.20, H 9.11.

(*R*)-6-Methyl-1-aza-10-oxa-bicyclo[6.3.0]undec-6-en-11-one (20b). ^1H NMR (300 MHz, $CDCl_3$): δ 5.18 - 5.16 (1H, m), 4.49 - 4.39 (2H, m), 3.99 - 3.90 (1H, m), 3.54 - 3.46 (1H, m), 3.23 - 3.15 (1H, m), 2.33 - 2.25 (1H, m), 2.21 - 2.14 (1H, m), 1.91 - 1.71 (2H, m), 1.78 (3H, d, *J* = 1.3 Hz), 1.63 - 1.40 (2H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 157.5, 144.6, 120.8, 68.1, 53.4, 47.7, 31.4, 27.0, 26.8, 24.4; MS (EI): *m/z* (rel. intensity) 181 ([M^+], 47), 180 (11), 166 (85), 153 (18), 152 (16), 140 (28), 139 (116), 138 (78), 136 (14), 126 (13), 125 (37), 122 (42), 109 (10), 108 (31), 105 (11), 96 (18), 95 (39), 94 (100), 93 (21), 91 (16), 82 (26), 81 (55), 80 (34), 79 (44), 77 (20), 69 (21), 68 (28), 67 (51), 65 (14), 56 (19), 55 (50), 54 (26), 53 (36), 42 (22), 41 (93), 39 (51), 30 (12), 29 (20), 28 (30), 27 (28); IR (film): 3568, 3479, 2929, 2869, 1748, 1668, 1416, 1300, 1242, 1184, 1051, 832, 762; $C_{10}H_{15}NO_2$ (181.23) *calcd.* C 66.27, H 8.34, N 7.73, *found* C 66.18, H 8.26, N 7.81.

2-Methyl-*N*-propenyl-acrylamide (42). Colorless syrup (mixture of isomers). **(*Z*)-Isomer**: ^1H-NMR ($CDCl_3$, 300 MHz) δ 7.31 (1H, s, br), 6.82 - 6.72 (1H, m), 5.73 (1H, s), 5.40 (1H, s), 4.85 (1H, dq, *J* = 7.2, 7.1 Hz), 1.98 (3H, dd, *J* = 1.3, 0.8 Hz), 1.64 (3H, dd, *J* = 7.1, 1.8 Hz); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 165.1, 146.7, 122.0, 120.1, 105.8, 18.0, 10.8. **(*E*)-Isomer**: ^1H-NMR ($CDCl_3$, 300 MHz) δ 7.31 (1H, s, br), 6.82 - 6.72 (1H, m), 5.69 (1H, s), 5.36 (1H, s), 5.20 (1H, dq, *J* = 13.5, 6.7 Hz), 1.95 (3H, dd, *J* = 1.3, 0.8 Hz), 1.67 (3H, dd, *J* = 6.7, 1.6 Hz); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 165.0, 139.5, 123.3, 120.2, 108.6, 18.5, 14.8; IR (KBr) 3298, 3199, 3072, 2960, 2920, 2658, 1678, 1656, 1618, 1507, 1451, 1436, 1373, 1317, 1269, 1221, 1153, 958, 932, 870, 804, 731, 700, 649; MS (EI) *m/z* (rel. intensity) 125 ([M^+], 35), 110 (7), 97 (8), 82 (18), 69 (80), 56 (8), 41 (100), 39 (19), 28 (7); HR-MS (EI) ($C_7H_{11}NO$) *calcd.* 125.0841, *found* 125.0838; $C_7H_{11}NO$ (125.17) *calcd.* C 67.17, H 8.86, N 11.19, *found* C 67.24, H 8.93, N 11.03.

5*H*-Benzo[*b*]oxepin-2-one (44). Colorless syrup. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.27 - 7.11 (4H, m), 6.91 (1H, dt, *J* = 11.0, 6.6 Hz), 5.90 (1H, d, *J* = 11.0 Hz), 3.48 (2 H, d, *J* = 6.6 Hz); ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 163.8, 151.7, 147.7, 132.5, 129.2, 128.6, 125.9, 122.0, 121.4, 31.4; IR (KBr): 3408, 3063, 3047, 3027, 2973, 2928, 1715, 1606, 1582, 1486, 1449, 1392, 1253, 1229, 1194, 1157, 1100, 986, 920, 836, 721, 786, 755, 733, 671, 615, 565, 542 cm^{-1}; MS (EI) *m/z* (rel. intensity) 160 ([M^+], 100), 131 (98), 115 (6), 103 (17), 89 (3), 77 (15), 63 (7), 51 (19), 39 (10), 27 (3); HR-MS (EI) ($C_{10}H_8O_2$) *calcd.* 160.0524, *found* 160.0522.

Compounds **5**,[3] **7**,[11b] **14**,[20] **15**,[3] **19**,[21] **20a**,[22] **21**,[11b] **22**,[11b] **24**,[26] **26**,[27] **28**,[28] **30**,[29] **32**,[30] **36**,[31] **38**,[32] **40**,[33] **46**,[34] and **48**[34] have been previously described. Their analytical and spectroscopic data are in full agreement with those reported in the literature.

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