Supporting Information for

Rhodium-Catalyzed Deallylation of Allylmalonates and Related Compounds

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I. General

Rhodium-catalyzed reactions were performed under an atmosphere of dry argon using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods (THF, toluene-Na, benzophenone, dichloromethane-CaH₂) and distilled under nitrogen or argon before use. All reagents were obtained from commercial suppliers and were used without further purification unless otherwise mentioned.

GC analyses were performed on a Shimadzu GC-17A chromatograph equipped with a Zebron ZB-5 capillary column (5% phenyl/95% dimethylpolysiloxane). NMR spectra were recorded on a Varian UNITY 400 INOVA instrument at 400 MHz (¹H) and 100 MHz (¹³C) or a Bruker Avance spectrometre at 500 MHz (¹H) and 125.7 MHz (¹³C) as solutions in CDCl₃ or *d*₆-DMSO and are referenced to Me₄Si or to the central peak of the solvent. ¹⁹F NMR spectra are referenced to external standard CFC₃l₃. Infrared spectra were recorded on a Bruker IFS 88 instrument. Mass spectra were recorded on a FINNIGAN MAT INCOS 50 spectrometre. HR mass spectra were recorded on a ZAB-SEQ VG Analytical spectrometre. Yields were determined by GC or ¹H NMR analysis using mesitylene as an internal standard. HPLC separations were performed on a Gilson 321 H2 pumps with 25×250 mm preparative silica gel column (Labio, Czech Republic), filled with BIOSPHER PSI 100 sorbent (7μm mesh).

II. Preparation of starting materials.

Preparation of allylmalonates and related compounds. Preparation and spectral characteristics of diethyl allylbutylmalonate (**4a**), diethyl diallylmalonate (**4b**), diethyl allylbenzylmalonate (**4c**), diethyl allylphenylmalonate (**4d**), diethyl butylmethallylmalonate (**4e**), diethyl butylcrotylmalonate (**4f**), diethyl butylcinnamylmalonate (**4g**), diethyl butyl(1-phenyl-prop-2-en-1-yl)malonate (**4h**), diethyl allylmethallylmalonate (**4i**), diethyl allylcrotylmalonate (**4j**), diethyl allyl(2-methyl-but-2-en-4-yl)malonate (**4k**), diethyl allylcinnamylmalonate (**4l**), diethyl allyl(2-chloroallyl)malonate (**4m**), ethyl diallylcynoacetate (**4n**), and diallylcoumaranone (**4o**) was reported in our previous paper.¹ Rhodium complexes **1** and **2** were prepared by reported procedures.²

Diethyl (but-3-en-1-yl)butylpropandioate (**4p**).

To a dispersion of K_2CO_3 (2.40 g, 17 mmol) and Bu_4NI (0.25 g, 0.6 mmol) in acetonitrile (15 mL) was added diethyl butylmalonate (1.69 g, 7.8 mmol) and 3-butenyl bromide (1.21 g, 9 mmol). The mixture was refluxed until no further progress was observed (9h), then it was diluted with water and extracted consecutively with Et_2O (3×20 mL), brine (20 mL), collected extracts were dried over MgSO_4 , the solvent was evaporated under reduced pressure and the residue was distilled at a Kugelrohr apparatus. Column chromatography on silica gel (19/1 hexane/ EtOAc) afforded 0.96 g (45%) of a yellowish liquid: ^1H NMR (CDCl_3 , Me_4Si) δ 0.90 (t, $J = 7.5$ Hz, 3H), 1.08-1.18 (m, 2H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.28-1.38 (m, 2H), 1.85-1.92 (m, 2H), 1.93-2.02 (m, 4H), 4.18 (q, $J = 7.2$ Hz, 4H), 4.96 (d, $J = 11$ Hz, 1H), 5.04 (d, $J = 17.1$ Hz, 1H), 5.74-5.84 (m, 1H); ^{13}C NMR (CDCl_3) δ 13.8, 14.1 (2C), 22.9, 26.1, 28.3, 31.4, 31.9, 57.2, 61.0 (2C), 114.9, 137.7, 171.7 (2C); IR (neat) ν 3078, 2990, 1571, 1706, 1643, 1471, 1368, 1284, 1219, 1054, 918 cm^{-1} ; EI-MS m/z (%) 271 (M^+ , 2), 225 (12), 216(39), 173 (100), 142 (11), 127 (26), 81(10), 41 (14); HRMS calcd for $\text{C}_{15}\text{H}_{26}\text{O}_4$ 270.1831, found 270.1841.

Diethyl allyl(4-trifluoromethylbenzyl)propandioate (4q).

To a dispersion of K_2CO_3 (1.27 g, 9.2 mmol) and Bu_4NI (0.1 g, 0.25 mmol) in acetonitrile (10 mL) was added diethyl allylmalonate (0.38 g, 1.9 mmol) and 4-(trifluoromethyl)benzyl bromide (0.67 g, 2.8 mmol). The mixture was refluxed for 4h, then it was diluted with water and extracted consecutively with Et_2O (3×15 mL), saturated Na_2SO_3 (20 mL), brine (20 mL), collected extracts were dried over MgSO_4 and the solvent was evaporated under reduced pressure. Column chromatography on silica gel (19/1 hexane/ EtOAc) afforded 0.55 g (81%) of colourless liquid: ^1H NMR (CDCl_3 , Me_4Si) δ 1.23 (t, $J = 7.2$ Hz, 6H), 2.58 (d, $J = 7.3$ Hz, 2H), 3.28 (s, 2H), 4.10 - 4.25 (m, 4H), 5.12 - 5.20 (m, 2H), 5.74 (ddt, $J = 16.8, 10.4, 7.3$ Hz, 1H), 7.25 (d, $J = 7.9$ Hz, 2H), 7.50 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 13.97 (2C), 36.71, 37.88, 58.62, 61.43 (2C), 119.55, 125.13 (q, $J_{\text{C-F}} = 270.5$ Hz), 125.09 (q, $J_{\text{C-F}} = 3.4$ Hz), 129.23 (q, $J_{\text{C-F}} = 32.2$ Hz), 130.36 (2C), 132.23, 140.41, 170.43 (2C); ^{19}F NMR (CDCl_3) δ -63.03; IR (neat) 2984, 2940, 1739, 1619, 1331, 1210, 1167, 1129, 1068, 1020, 924, 856 cm^{-1} ; EI-MS m/z (%) 358.1 (M^+ , 11), 317.1 (52), 271.0 (100), 199.0 (32), 153.0 (52); HRMS calcd for $\text{C}_{18}\text{H}_{21}\text{O}_4\text{F}_3$ 358.1392, found 358.1387.

Diethyl allyl(4-methoxybenzyl)propandioate (4r).

To a dispersion of K_2CO_3 (1.91 g, 13.8 mmol) and Bu_4NI (0.2 g, 0.5 mmol) in acetonitrile (10 mL) was added diethyl allylmalonate (1.0 g, 5 mmol) and 4-methoxybenzyl bromide (1.12 g, 5.57 mmol). The mixture was refluxed for 4h, then it was diluted with water and extracted consecutively with Et_2O (3×15 mL), saturated Na_2SO_3 (20 mL), brine (20 mL), collected extracts were dried over MgSO_4 , the solvent was evaporated under reduced pressure. Column chromatography on silica gel (19/1 hexane/ EtOAc) afforded 0.89 g (55%) of colourless liquid: ^1H NMR (CDCl_3 , Me_4Si) δ 1.24 (t, $J = 7.1$ Hz, 6H), 2.55 (d, $J = 7.3$ Hz, 2H), 3.18 (s, 2H), 3.77 (s, 3H), 4.10 - 4.22 (m, 4H), 5.10 - 5.18 (m, 2H), 5.70 - 5.82 (m, 1H), 6.78 (dd, $J = 6.6, 2.1$ Hz, 2H), 7.02 (dd, $J = 6.6, 2.1$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 14.06 (2C), 36.35, 37.13, 55.14, 58.85, 61.19 (2C), 113.62 (2C), 119.13, 127.93, 130.95 (2C), 132.71, 158.50, 170.84 (2C); IR (neat) ν 2982, 1739, 1613, 1514, 1444, 1367, 1282, 1254, 1210, 1114, 1038, 923, 845 cm^{-1} ; EI-MS m/z (%) 320.2 (M^+ , 27), 279.1 (7), 233.1 (30), 173.1 (6), 121.1 (100); HRMS calcd for $\text{C}_{18}\text{H}_{24}\text{O}_5$ 320.1623, found 320.1617.

Diethyl allyl(4-methylbenzyl)propandioate (4s).

To a solution of 0.32 g of Na (13.9 mmol) in dry EtOH (25 mL) was added diethyl allylmalonate (2.07 g, 8.6 mmol). The mixture was stirred at room temperature for 20 min. Then 4-methylbenzyl bromide (2.54 g, 13.7 mmol) was added. The mixture was stirred at room temperature for 20 min, then it was diluted with water, acidified with 3M HCl and extracted consecutively with Et_2O (3×15 mL), saturated NaHCO_3 (20 mL), brine (20 mL), collected extracts were dried over MgSO_4 , the solvent was evaporated under reduced pressure. The residue was subjected to Kugelrohr distillation to distill off the rest of 4-methylbenzyl bromide. Yield 2.44 g (78 %) of the title compound as a colourless liquid: ^1H NMR (CDCl_3 , Me_4Si) δ 1.24 (t, $J = 7.2$ Hz, 6H), 2.20 (s, 3H), 2.47 (d, $J = 7.3$ Hz, 2H), 3.12 (s, 3H), 4.04 - 4.16 (m, 4H), 5.02 - 5.10 (m, 2H), 5.64 - 5.75 (m, 1H), 6.90 (d, $J = 8.1$, 2H), 6.98 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 14.00 (2C), 20.96, 36.25, 37.47, 58.76, 61.14 (2C), 119.09, 128.89 (2C), 129.77 (2C), 132.68, 132.79, 136.39, 170.77 (2C); IR (neat) ν 2981, 2937, 1737, 1514, 1444, 1278, 1206, 1183, 1045 cm^{-1} ; EI-MS m/z (%) 304.2 (M^+ , 17),

263.1 (34), 217.1 (98), 157.1 (30), 105.1 (100); HRMS calcd for $C_{18}H_{24}O_4$ 304.1675, found 304.1660.

III. Preparation of rhodium BIAP complexes.

Pyridine-2,6-dicarboxylic acid dichloride was prepared according to the literature procedure³ and racemic 2-amino-2-methylpropanamide, 2-amino-2,4-dimethylpentanamide, 2-amino-2,3,3-trimethylbutanamide and 2-amino-2-phenylpropanamide were synthesized by described methods.⁴

Pyridine-2,6-dicarboxylic acid bis-[(1-carbamoyl-1,2,2-trimethyl-propyl)-amide] (**17b**).

To a solution of 2-amino-2,3,3-trimethylbutanamide **15b** (2.88 g, 20 mmol) and triethylamine (4.2 mL, 30 mmol) in dry CH_2Cl_2 (40 mL) was added dropwise pyridine-2,6-dicarboxylic acid dichloride **16** (2.04 g, 10 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The reaction mixture was stirred at 20 °C for 24 h. The formed suspension was filtered off, washed with water (50 mL) and cold THF (50 mL) to give 3.5 g (83%) of the title compound: m.p. 292–303 °C; 1H NMR (DMSO- d_6 , 500 MHz) δ 1.08 (s, 18H), 1.65 (s, 6H), 7.18 (bs, 2H), 7.29 (bs, 2H), 8.22 (m, 3H), 8.53 (bs, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 16.7, 23.0, 36.8, 64.7, 124.1, 139.6, 149.2, 161.5, 173.1. Anal. Calcd for $C_{21}H_{33}N_5O_4$: C, 60.12; H, 7.93; N, 16.69. Found: C, 59.86; H, 7.70; N, 16.49.

Pyridine-2,6-dicarboxylic acid bis-[(1-carbamoyl-1-phenyl-ethyl)-amide] (**17c**).

To the solution of 2-amino-2-phenylpropanamide **15b** (1.64 g, 10 mmol) and triethylamine (2.1 mL, 15 mmol) in dry CH_2Cl_2 (40 mL) was added dropwise a solution of pyridine-2,6-dicarboxylic acid dichloride **16** (1.02 g, 10 mmol) in CH_2Cl_2 (25 mL) at 0 °C over 15 min. The reaction mixture was stirred at 20 °C for 2 hours and then evaporated to dryness. The residue was mixed with water and white crystalline solid was collected. Recrystallisation

from toluene furnished 1.95 g (85%) of the title compound as colourless crystals: m. p. 235–245 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ 2.10 (s, 6H), 7.32 (m, 4H), 7.44 (m, 6H), 7.62 (bs, 2H), 7.63 (bs, 2H), 8.19 (m, 3H), 9.70 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 22.0, 61.3, 124.4, 125.7, 127.3, 128.4, 139.9, 142.1, 149.4, 161.5, 174.0. Anal. Calcd for $\text{C}_{25}\text{H}_{25}\text{N}_5\text{O}_4$: C, 65.35; H, 5.48; N, 15.24. Found: C, 65.15; H, 5.69; N, 15.26.

Pyridine-2,6-dicarboxylic acid bis-[(1-carbamoyl-1-methyl-ethyl)-amide] (17d).

To a solution of 2-amino-2-methylpropanamide **15d** (2.4 g, 20 mmol) and triethylamine (4.2 ml, 30 mmol) in dry CH_2Cl_2 (25 mL) was added dropwise pyridine-2,6-dicarboxylic acid dichloride **16** (2.04 g, 10 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was then stirred 20 °C overnight. The formed suspension was filtered off and washed with water to give 1.94 g (58%) of the title compound as a white crystalline solid: 250–255 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ 1.58 (s, 12H), 7.16 (bs, 2H), 7.46 (bs, 2H), 8.18 (s, 3H), 9.00 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 24.5, 55.8, 123.8, 139.7, 148.7, 161.5, 175.9. Anal. Calcd for $\text{C}_{15}\text{H}_{21}\text{N}_5\text{O}_4$: C, 45.62; H, 6.31; N, 20.88. Found: C, 45.37; H, 6.58; N, 20.58.

Pyridine-2,6-dicarboxylic acid bis-[(1-carbamoyl-1,3-dimethyl-butyl)-amide] (17e).

A solution of pyridine-2,6-dicarboxylic acid dichloride **16** (2.04 g, 10 mmol) in dry acetone (30 mL) was added dropwise to a solution of 2-amino-2,4-dimethylpentanamide **15e** (2.88 g, 20 mmol) and triethylamine (4.2 ml, 30 mmol) in dry acetone (25 mL) at 0 °C over 20 min. The reaction mixture was stirred at 20 °C overnight. The formed suspension was filtered off and washed with acetone. The filtrate was evaporated to dryness, treated with water, white solid was collected, and crystallised (acetone/toluene) to give 3.85 g (92%) of the title compound as a colourless solid: m.p. 205–209 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ 0.89 (d, $J = 7.3$ Hz, 12H), 1.59–1.69 (m, 8H), 1.87 (m, 2H), 2.32 (m, 2H), 7.34 (bs, 2H), 7.59 (bs, 2H), 8.23 (s, 3H), 9.10 (bs, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 23.2, 23.6, 23.9, 24.5, 43.8,

59.0, 123.9, 139.8, 149.3, 161.4, 175.5. Anal. Calcd for $C_{21}H_{33}N_5O_4$: C, 60.12; H, 7.93; N, 16.69. Found: C, 60.08; H, 8.00; N, 16.49.

2,6-Bis(4-*t*-butyl-4-methyl-4,5-dihydro-1H-imidazol-5-on-2-yl)pyridine (18b).

A mixture of **17b** (2.9 g, 6.9 mmol) and 40 ml 1M CH_3ONa (40 mmol) was stirred at 20 °C for 3 days. Then the reaction mixture was neutralised with conc. HCl to pH ~ 7, the formed suspension was filtered off, and washed with water (75 mL) to give 2.4 g (91%) of the title compound as a white crystalline solid: m. p. 336–339 °C; 1H NMR (DMSO- d_6 , 500 MHz) δ 0.99 (s, 18H), 1.27 (s, 6H), 8.17 (t, J = 5.8 Hz, 1H), 8.34 (d, J = 5.8 Hz, 2H), 11.48 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 18.6, 24.6, 36.0, 76.9, 123.1, 139.1, 146.1, 157.7, 186.3. Anal. Calcd for $C_{21}H_{29}N_5O_2$: C, 65.77; H, 7.62; N, 18.26. Found: C, 65.90; H, 7.77; N, 18.26.

2,6-Bis(4-phenyl-4-methyl-4,5-dihydro-1H-imidazol-5-on-2-yl)pyridine (18c).

A mixture of **17c** (2.9 g, 4 mmol) and 1M CH_3ONa (100 mL, 100 mmol) was refluxed for 20 h. Then the mixture was neutralised with conc. HCl to pH ~ 7, the formed suspension was filtered off, and washed with water (25 mL) to give 1.51 g (89%) of the title compound as a colourless solid: m. p. 172–175 °C; 1H NMR (DMSO- d_6 , 500 MHz) δ 1.76 (s, 6H), 7.36 (m, 2H), 7.42 (m, 4H), 7.58 (m, 4H), 8.32 (t, J = 7.8 Hz, 1H), 8.55 (d, J = 7.8 Hz, 2H), 11.73 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 25.1, 74.1, 123.1, 125.7, 127.6, 128.5, 139.5, 139.8, 146.1, 185.0. Anal. Calcd for $C_{25}H_{25}N_5O_4$: C, 70.91; H, 5.00; N, 16.54. Found: C, 70.87; H, 5.06; N, 16.32.

2,6-Bis(4,4-dimethyl-4,5-dihydro-1H-imidazol-5-on-2-yl)pyridine (18d).

A mixture of **17d** (1.85 g, 5.5 mmol) and 1M CH_3ONa (40 mL, 40 mmol) was refluxed for 24 h. Then the reaction mixture was neutralised with conc. HCl to pH ~ 7, evaporated to

dryness, the residue was treated with water (20 mL), the formed suspension was filtered off and washed with hexane to give 1.4 g (85%) of the title compound as a colourless solid: m. p. 333–335 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ 1.32 (s, 12H), 8.17 (t, J = 5.8 Hz, 1H), 8.31 (d, J = 5.8 Hz, 2H), 11.55 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 23.8, 69.6, 123.8, 139.1, 146.2, 157.5, 187.0. Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{N}_5\text{O}_2$: C, 60.19; H, 5.72; N, 23.40. Found: C, 60.27; H, 5.97; N, 23.50.

2,6-Bis(4-isobutyl-4-methyl-4,5-dihydro-1H-imidazol-5-on-2-yl)pyridine (18e).

A mixture of **17e** (3.15 g, 7.5 mmol) and 1M CH_3ONa (60 mL, 60 mmol) was stirred at 20 °C for 4 days. Then the reaction mixture was neutralised with conc. HCl to pH $\sim$ 7, evaporated to dryness, the residue was treated with water (20 mL), and the formed suspension was filtered off and dried to give 2.5 g (87%) of the title compound as a white crystalline solid: m. p. 112–115 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ 0.85 (d, J = 6.7 Hz, 12H), 1.33 (s, 6H), 1.54 (m, 2H), 1.69 (m, 2H), 1.81 (m, 2H), 8.38 (d, J = 7.8 Hz, 2H), 11.61 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 23.4, 23.5, 24.3, 24.6, 46.2, 72.9, 123.4, 139.4, 146.3, 157.7, 187.0. Anal. Calcd for $\text{C}_{21}\text{H}_{29}\text{N}_5\text{O}_2$: C, 65.77; H, 7.62; N, 18.26. Found: C, 65.93; H, 7.65; N, 18.01.

2,6-Bis(1-benzyl-4-*t*-butyl-4-methyl-4,5-dihydro-1H-imidazol-5-on-2-yl)pyridine (19b).

A mixture of **18b** (1.92 g, 5 mmol), anhydrous K_2CO_3 (1.8 g, 13 mmol), KI (50 mg, 0.3 mmol), and benzyl bromide (1.57 mL, 13 mmol) was refluxed in DMF (20mL) for 48 h under argon atmosphere. Then the reaction mixture was filtered and the insoluble portion was washed with DMF (30 mL). The combined filtrates were evaporated in vacuo, the residue was treated with water (75 mL), the formed suspension was filtered off and recrystallised (*n*-heptane) to give 2.40 g (85%) of the title compound as a white crystalline solid: m. p. 170–171.5 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ 1.10 (s, 18H), 1.45 (s, 6H), 4.60 (d, J = 10.8 Hz, 2H), 4.68 (d, J = 10.8 Hz, 2H), 6.86 (m, 4H), 7.11 (m, 6H), 7.77 (t, J = 5.4 Hz, 1H), 7.90 (d, J = 5.4 Hz, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 19.3, 25.1, 36.7, 44.4, 75.7, 125.5, 127.0,

127.3, 128.4, 137.3, 138.1, 148.6, 158.3, 185.7. Anal. Calcd for $C_{35}H_{41}N_5O_2$: C, 74.52; H, 7.33; N, 12.42. Found: C, 74.37; H, 7.53; N, 12.55.

2,6-Bis(1-benzyl-4-phenyl-4-methyl-4,5-dihydro-1H-imidazol-5-on-2-yl)pyridine (19c).

A mixture of **18c** (2.12 g, 5 mmol), anhydrous K_2CO_3 (1.8 g, 13 mmol), KI (50 mg, 0.3 mmol), and benzyl bromide (1.57 mL, 13 mmol) was refluxed in DMF (20 mL) for 48 h under argon atmosphere. Then the reaction mixture was filtered, the insoluble portion was washed with DMF (30 mL). The combined filtrates were evaporated in vacuo, the residue was treated with water (75 mL), the formed suspension was filtered off and recrystallised (1:1 *n*-heptane/ $CHCl_3$) to give 1.80 g (60%) of the title compound as a colourless solid: m. p. 67–70 °C; 1H NMR (DMSO- d_6 , 500 MHz) δ 1.82 (s, 6H), 4.66 (s, 4H), 6.84 (d, J = 7.4 Hz, 4H), 7.11 (m, 6H), 7.40 (m, 2H), 7.48 (m, 4H), 7.63 (d, J = 7.4 Hz, 4H), 8.13 (m, 3H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 25.4, 44.3, 72.1, 124.6, 125.8, 126.1, 126.3, 127.2, 128.0, 128.5, 128.7, 137.4, 139.5, 147.7, 158.8, 184.1. Anal. Calcd for $C_{39}H_{33}N_5O_2$: C, 77.59; H, 5.51; N, 11.60. Found: C, 77.71; H, 5.68; N, 11.63.

2,6-Bis(1-benzyl-4,4-dimethyl-4,5-dihydro-1H-imidazol-5-on-2-yl)pyridine (19d).

A mixture of **18d** (1.03 g, 3.44 mmol), anhydrous K_2CO_3 (1.24 g, 9 mmol), KI (50 mg, 0.3 mmol) and benzyl bromide (1.2 mL, 10 mmol) was refluxed in DMF (15 mL) for 48 h under argon atmosphere. Then the reaction mixture was filtered, the insoluble portion was washed with DMF (20 mL). The combined filtrates were evaporated in vacuo, the residue was treated with water (75 mL), the formed suspension was filtered off and recrystallised (1:2 *n*-heptane/ $CHCl_3$) to give 0.65 g (39%) of the title compound as a white crystalline solid: m. p. 129–131.5 °C; 1H NMR (DMSO- d_6 , 500 MHz) δ 1.44 (s, 12H), 4.66 (s, 4H), 6.88 (d, J = 6.2 Hz, 4H), 7.19 (m, 6H), 7.95 (d, J = 8.2 Hz, 2H), 8.02 (t, J = 8.2 Hz, 1H); ^{13}C NMR (DMSO-

d_6 , 125 MHz) δ 24.0, 44.1, 67.6, 125.6, 126.2, 127.2, 128.6, 137.6, 139.1, 147.9, 157.6, 186.1. Anal. Calcd for $C_{29}H_{29}N_5O_2$: C, 72.63; H, 6.09; N, 14.60. Found: C, 72.79; H, 6.35; N, 14.41.

2,6-Bis(1-benzyl-4-isobutyl-4-methyl-4,5-dihydro-1H-imidazol-5-on-2-yl)pyridine (19e).

A mixture of **18e** (1.3 g, 4 mmol), anhydrous K_2CO_3 (1.4 g, 10 mmol), KI (50 mg, 0.3 mmol), and benzyl bromide (1.45 ml, 12 mmol) was refluxed in DMF (20 mL) for 48 h under argon atmosphere. Then the reaction mixture was filtered and the insoluble portion was washed with DMF (30 mL). The combined filtrates were evaporated in vacuo, the residue was washed with water (75 mL), dried, dissolved in ethyl acetate (150 mL), and filtered through a short pad of silica gel. The filtrate was evaporated to dryness to give 1.31 g (58%) of the title compound as a colourless oil: 1H NMR (DMSO- d_6 , 500 MHz) δ 0.84 (d, J = 6.6 Hz, 6H), 0.88 (d, J = 6.6 Hz, 6H), 1.40 (s, 6H), 1.56 (m, 2H), 1.76 (dd, J = 13.8, 6.5 Hz, 2H), 1.86 (dd, J = 13.8, 6.5 Hz, 2H), 4.63 (d, J = 15.9 Hz, 2H), 4.70 (, J = 15.9 Hz, 2H), 6.88 (m, 4H), 7.18 (m, 6H), 7.97 (m, 1H), 8.06 (m, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 23.7, 24.1, 24.2, 24.7, 39.9, 46.1, 70.9, 125.8, 126.5, 127.4, 128.5, 137.4, 139.0, 148.0, 157.8, 186.0. Anal. Calcd for $C_{35}H_{41}N_5O_2$: C, 74.52; H, 7.33; N, 12.42. Found: C, 74.32; H, 7.46; N, 12.60.

Complex of 2,6-bis(1-benzyl-4-isopropyl-4-methyl-4,5-dihydro-1H-imidazol-5-on-2-yl)pyridine with $RhCl_3$ (3a).

A mixture of ligand **19a**⁵ (107 mg, 0.2 mmol) and $RhCl_3 \cdot xH_2O$ (52.7 mg) was refluxed in 25 mL of methanol for 2 h. The formed orange solid was filtered off and washed with diethyl ether (30 mL) to give 121 mg (81%) of complex. Anal. Calcd for $C_{33}H_{37}N_5O_2RhCl_3$: C, 53.21; H, 5.01; N, 9.40. Found: C, 53.34; H, 4.78; N, 9.24. IR (neat) ν 2976, 1756, 1551, 1490, 1427, 1366, 1288, 735, 705 cm^{-1} .

Complex of 2,6-Bis(1-benzyl-4-*t*-butyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-on-2-yl)pyridine with RhCl₃ (3b).

A mixture of **19b** (114 mg, 0.2 mmol) and RhCl₃·xH₂O (52.7 mg) was refluxed in methanol (25 mL) for 3 h. The formed orange solid was filtered off and washed with diethyl ether (30 mL) to give 147 mg (95%) of the title complex. Anal. Calcd for C₃₅H₃₁N₅O₂RhCl₃: C, 54.38; H, 5.35; N, 9.06. Found: C, 54.64; H, 5.65; N, 8.91. IR (neat) ν 3630, 2972, 1757, 1544, 1496, 1433, 1373, 1153, 995, 737, 701 cm⁻¹.

Complex of 2,6-Bis(1-benzyl-4-phenyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-on-2-yl)pyridine with RhCl₃ (3c).

A mixture of **19c** (121 mg, 0.2 mmol) and RhCl₃·xH₂O (52.7 mg) was refluxed in methanol (25 mL) for 2 h. The formed orange solid was filtered off and washed with diethyl ether (30 mL) to give 110 mg (68%) of the title complex. Anal. Calcd for C₃₉H₃₃N₅O₂RhCl₃: C, 57.62; H, 4.09; N, 8.61. Found: C, 57.57; H, 3.97; N, 8.52. IR (neat) ν 3503, 3063, 1759, 1545, 1494, 1427, 1297, 995, 738, 695 cm⁻¹.

Complex of 2,6-Bis(1-benzyl-4,4-dimethyl-4,5-dihydro-1*H*-imidazol-5-on-2-yl)pyridine with RhCl₃ (3d).

A mixture of **19d** (96 mg, 0.2 mmol) and RhCl₃·xH₂O (52.7 mg) was refluxed in methanol (25 mL) for 2 h. The formed orange solid was filtered off and washed with diethyl ether (30 mL) to give 102 mg (74%) of the title complex. Anal. Calcd for C₂₉H₂₃N₅O₂RhCl₃: C, 50.57; H, 4.24; N, 10.17. Found: C, 50.79; H, 4.06; N, 9.85. IR (neat) ν 3640, 3498, 1759, 1496, 1434, 1325, 1220, 968, 939, 741, 677 cm⁻¹.

Complex of 2,6-Bis(1-benzyl-4-isobutyl-4-methyl-4,5-dihydro-1H-imidazol-5-on-2-yl)pyridine with RhCl₃ (3e).

A mixture of **19e** (114 mg, 0.2 mmol) and RhCl₃·xH₂O (52.7 mg) was refluxed in methanol (25 mL) for 3 h. The solution was concentrated to half of volume and diethylether (15 mL) was added. The formed orange solid was collected by filtration, washed with diethyl ether and dried to give 116 mg (75%) of the title complex. Anal. Calcd for C₃₅H₃₁N₅O₂RhCl₃: C, 54.38; H, 5.35; N, 9.06. Found: C, 54.34; H, 5.33; N, 8.99. IR (neat) ν 3641, 3501, 2962, 1759, 1552, 1493, 1429, 1358, 736 cm⁻¹.

IV. Conditions for Rh-catalyzed reactions of allylmalonates (Table 1).

Entry 1. Reaction of **4a** (19 mg, 0.07 mmol), [RhH(PPh₃)₄] (4 mg, 0.003 mmol) in dry toluene (3 mL) at 60 °C for 48h.

Entry 2. Reaction of **4a** (48 mg, 0.18 mmol), [RhH(PPh₃)₄] (212 mg, 0.18 mmol) in dry toluene (10 mL) at 20 °C for 24h, then at 60 °C for 48h. Yield 93 % of **6a** (GC), HPLC of resulting mixture (97/3 hexane/EtOAc) afforded 6 mg of **6a** (12 %) as a colourless liquid.

Entry 3. Reaction of **4a** (21 mg, 0.08 mmol), [RhH(PPh₃)₄] (4 mg, 0.003 mmol) and NaH (60 % dispersion in mineral oil, 6 mg, 0.15 mmol) in dry toluene (3 mL) at 20 °C for 3h, then at 60 °C for 5h.

Entry 4. Reaction of **4a** (13 mg, 0.05 mmol), [RhH(PPh₃)₄] (15 mg, 0.013 mmol) and (C₆F₅)₃B (17 mg, 0.03 mmol) in dry toluene (10 mL) at 60 °C for 5h.

Entry 5. Reaction of **4a** (20 mg, 0.07 mmol), [RhH(PPh₃)₄] (7 mg, 0.006 mmol) and AlCl₃ (8 mg, 0.06 mmol) in dry toluene (3 mL) at 60 °C for 10h.

Entry 6. Reaction of **4a** (16 mg, 0.06 mmol), [RhH(PPh₃)₄] (8 mg, 0.007 mmol) and ZnBr₂ (23 mg, 0.1 mmol) in dry toluene (3 mL) at 60 °C for 10h.

Entry 7. Reaction of **4a** (54 mg, 0.2 mmol), [RhH(PPh₃)₄] (14 mg, 0.012 mmol) in dry toluene (3 mL) and ZnEt₂ (1 M solution in hexane, 0.5 mL, 0.5 mmol) at 20 °C for 5h.

Entry 8. Reaction of **4a** (17 mg, 0.06 mmol), [RhH(PPh₃)₄] (8 mg, 0.006 mmol) and Et₃B (1 M solution in hexane, 0.1 mL, 0.1 mmol) in dry toluene (3 mL) at 20 °C for 5h. Yield 24 % (GC) of **6a**.

Entry 9. Reaction of **4a** (67 mg, 0.26 mmol), [RhH(PPh₃)₄] (13 mg, 0.011 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 19h. Yield 84 % (GC) of **5a** and 16 % (GC) of **7a**.

Entry 10. Reaction of **4b** (65 mg, 0.27 mmol), [RhH(PPh₃)₄] (12 mg, 0.01 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 19h. Yield 25 % (GC) of **5b** and 55 % (GC) of **6b**. HPLC (hexane/EtOAc 19/1) afforded 3 mg (4 %) of **6b** as a yellowish liquid.

V. Conditions for Rh-catalyzed reactions of allylmalonates (Table 2, Wilkinson's catalyst 2).

Entry 1. Reaction of **4a** (57 mg, 0.22 mmol), [Rh(PPh₃)₃Cl] (11 mg, 0.012 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 6h. Yield 65 % (GC) of **5a** and 35 % (GC) of **7a**. HPLC (hexane/EtOAc 19/1) afforded 5 mg (10%) of yellowish liquid **5a** and 2 mg (3%) of yellowish liquid **7a**.

Entry 2. Reaction of **4c** (80 mg, 0.27 mmol), [Rh(PPh₃)₃Cl] (12 mg, 0.012 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 77 % (GC) of **5c** and 23 % (GC) of **8a**. HPLC (95/5 hexane/EtOAc) afforded 8 mg (11 %) of **8a** as a colourless liquid.

Entry 3. Reaction of **4d** (67 mg, 0.24 mmol), [Rh(PPh₃)₃Cl] (12 mg, 0.012 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 73 % (GC) of **6d**. HPLC (96.5/3.5 hexane/EtOAc) afforded 21 mg (30 %) of **6d** as a yellowish oil.

Entry 4. Reaction of **4e** (68 mg, 0.25 mmol), [Rh(PPh₃)₃Cl] (12 mg, 0.012 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 28 % (GC) of **5a**.

Entry 5. Reaction of **4f** (66 mg, 0.24 mmol), [Rh(PPh₃)₃Cl] (12 mg, 0.012 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 6 % (GC) of **5a**.

Entry 8. Reaction of **4b** (71 mg, 0.29 mmol), [Rh(PPh₃)₃Cl] (12 mg, 0.012 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5b**.

Entry 9. Reaction of **4i** (60 mg, 0.22 mmol), [Rh(PPh₃)₃Cl] (12 mg, 0.012 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 82 % (GC) of **5i**.

Entry 10. Reaction of **4j** (62 mg, 0.23 mmol), [Rh(PPh₃)₃Cl] (12 mg, 0.012 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 93 % (GC) of **5j** and 7 % (GC) of **7a**.

Entry 11. Reaction of **4k** (77 mg, 0.27 mmol), [Rh(PPh₃)₃Cl] (12 mg, 0.012 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 78 % (GC) of **5k** and 22 % (GC) of **8b**. HPLC (97/3 hexane/EtOAc) afforded 6 mg (10 %) of **8b**.

Entry 12. Reaction of **4l** (128 mg, 0.4 mmol), [Rh(PPh₃)₃Cl] (14 mg, 0.015 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h.

Entry 13. Reaction of **4m** (70 mg, 0.25 mmol), [Rh(PPh₃)₃Cl] (12 mg, 0.012 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 23 % (GC) of **5m**.

Entry 14. Reaction of **4n** (50 mg, 0.26 mmol), [Rh(PPh₃)₃Cl] (12 mg, 0.012 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. A complex reaction mixture could not be separated into individual substances.

Entry 15. Reaction of **4o** (48 mg, 0.22 mmol), [Rh(PPh₃)₃Cl] (12 mg, 0.012 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. A complex reaction mixture could not be separated into individual substances.

Entry 16. Reaction of **4p** (62 mg, 0.23 mmol), [Rh(PPh₃)₃Cl] (12 mg, 0.012 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 31 % (GC) of **5p**. The rest of reaction mixture (69 %) could not be separated into individual substances.

VI. Conditions for Rh-catalyzed reactions of allylmalonates (Table 2, cat. **3a**).

Entry 1. Reaction of **4a** (58 mg, 0.22 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5a**.

Entry 2. Reaction of **4c** (112 mg, 0.39 mmol), **3a** (15.5 mg, 0.02 mmol) and Et₃Al (1.9 M solution in toluene, 0.5 mL, 0.95 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5c**.

Entry 3. Reaction of **4d** (64 mg, 0.23 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5d**.

Entry 4. Reaction of **4e** (82 mg, 0.3 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 39 % (GC) of **5a**.

Entry 5. Reaction of **4f** (69 mg, 0.26 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 77 % (GC) of **5a**.

Entry 6. Reaction of **4g** (56 mg, 0.18 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 29 % (GC) of **5a**.

Entry 7. Reaction of **4h** (73 mg, 0.27 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5a**.

Entry 8. Reaction of **4b** (59 mg, 0.25 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5b**.

Entry 9. Reaction of **4i** (60 mg, 0.24 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5i**.

Entry 10. Reaction of **4j** (59 mg, 0.22 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5j**.

Entry 11. Reaction of **4k** (75 mg, 0.28 mmol), **3a** (11 mg, 0.015 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5k**.

Entry 12. Reaction of **4l** (114 mg, 0.36 mmol), **3a** (14 mg, 0.018 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5l**.

Entry 13. Reaction of **4m** (77 mg, 0.28 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 45 % (GC) of diallylmalonate **4b** and 26% (GC) of allylmalonate **5b**.

Entry 14. Reaction of **4n** (51 mg, 0.26 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h.

Entry 15. Reaction of **4o** (50 mg, 0.23 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h.

Entry 16. Reaction of **4p** (61 mg, 0.23 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 30% (GC) of butylmalonate **5a**.

VII. Conditions for Rh-catalyzed reactions of allylmalonates (Table 3, cat. 2).

Entry 1. Reaction of **4q** (101 mg, 0.28 mmol), **2** (13 mg, 0.014 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 42 % (GC) of **5q** and 32 % (GC) of **6q**. HPLC (hexane/EtOAc 19/1) afforded 22 mg of **5q** (24 %) and 21 mg of **6q** (20 %).

Entry 2. Reaction of **4r** (78 mg, 0.24 mmol), **2** (12 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 88 % (GC) of **4r**. HPLC (hexane/EtOAc 19/1) afforded 23 mg of **4r** (34 %).

Entry 3. Reaction of **4s** (81 mg, 0.26 mmol), **2** (12 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 18h. Yield 66 % (GC) of **5s** and 25 % (GC) of **8c**. HPLC (hexane/EtOAc 19/1) afforded 31 mg (45 %) of **5s** and 11 mg (17%) of **8c**.

VIII. Conditions for Rh-catalyzed reactions of allylmalonates (Table 4).

Entry 1. Reaction of **4a** (58 mg, 0.22 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5a**.

Entry 2. Reaction of **4b** (59 mg, 0.24 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5b**.

Entry 3. Reaction of **4b** (59 mg, 0.24 mmol), **3a** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 70 % (GC) of **5b** and 20 % of **9** (GC).

Entry 4. Reaction of **4a** (63 mg, 0.24 mmol), **3b** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5a**.

Entry 5. Reaction of **4b** (57 mg, 0.24 mmol), **3b** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5b**.

Entry 6. Reaction of **4b** (57 mg, 0.24 mmol), **3b** (10 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 56 % (GC) of **5b** and 44 % of **9** (GC).

Entry 7. Reaction of **4a** (63 mg, 0.24 mmol), **3c** (11 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5a**.

Entry 8. Reaction of **4b** (57 mg, 0.24 mmol), **3c** (11.5 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5b**.

Entry 9. Reaction of **4b** (57 mg, 0.24 mmol), **3a** (11.5 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 35 % (GC) of **5a**, 11 % of **9** (GC).

Entry 10. Reaction of **4a** (69 mg, 0.27 mmol), **3d** (9 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5a**.

Entry 11. Reaction of **4b** (58 mg, 0.24 mmol), **3d** (9.5 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5b**.

Entry 12. Reaction of **4b** (58 mg, 0.24 mmol), **3d** (9.5 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 33 % (GC) of **5a**, 15 % of **9** (GC).

Entry 13. Reaction of **4a** (75 mg, 0.29 mmol), **3e** (11.5 mg, 0.015 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5a**.

Entry 14. Reaction of **4b** (58 mg, 0.24 mmol), **3e** (10.4 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 3h. Yield 100 % (GC) of **5b**.

Entry 15. Reaction of **4b** (58 mg, 0.24 mmol), **3e** (10.4 mg, 0.013 mmol) and Et₃Al (1.9 M solution in toluene, 0.3 mL, 0.57 mmol) in dry toluene (3 mL) at 20 °C for 24h. Yield 73 % (GC) of **5a**, 23 % of **9** (GC).

IX. Spectral data of selected reactions products.

Diethyl 4-(trifluoromethyl)benzylpropandioate (5q).

^1H NMR (CDCl_3 , Me_4Si) δ 1.21 (t, J = 6.9 Hz, 6H), 3.28 (d, J = 7.9 Hz, 2H), 3.65 (t, J = 7.6 Hz, 1H), 4.10 - 4.22 (m, 4H), 7.35 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 7.9 Hz, 2H); ^{13}C NMR (CDCl_3) δ 13.95 (2C), 34.35, 53.38, 61.64 (2C), 124.14 (q, $J_{\text{C-F}}$ = 270.1 Hz), 125.41 (q, $J_{\text{C-F}}$ = 3.8 Hz), 129.11 (q, $J_{\text{C-F}}$ = 32.2 Hz), 129.22 (2C), 142.02, 168.47 (2C); ^{19}F NMR (CDCl_3) δ -62.99; IR (neat) ν 2985, 2940, 1736, 1619, 1371, 1322, 1231, 1160, 1124, 1067, 1019, 857, 826 cm^{-1} ; EI-MS m/z (%) 318.0 (M^+ , 47), 244.0 (56), 227.0 (44), 216.0 (49), 199.0 (100), 159.0 (53); HRMS calcd for $\text{C}_{15}\text{H}_{17}\text{O}_4\text{F}_3$ 318.1079, found 318.1081.

Diethyl (4-methoxybenzyl)propandioate (5r).

^1H NMR (CDCl_3 , Me_4Si) δ 1.21 (t, J = 7.12 Hz, 6H), 3.15 (d, J = 7.8 Hz, 2H), 3.6 (t, J = 7.8 Hz, 1H), 3.77 (s, 3H), 4.10 - 4.20 (m, 4H), 6.78 - 6.83 (m, 2H), 7.10 - 7.14 (m, 2H); ^{13}C NMR (CDCl_3) δ 13.99 (2C), 33.83, 54.08, 55.18, 61.37 (2C), 113.84 (2C), 129.83, 129.86, 158.34, 168.89 (2C); IR (neat) 2982, 2937, 1751, 1612, 1514, 1370, 1300, 1253, 1179, 1152, 1110, 1036, 823 cm^{-1} ; EI-MS m/z (%) 280.1 (M^+ , 20), 206.0 (32), 161.0 (22), 121.0 (100); HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{O}_5$ 280.1311, found 280.1304.

Diethyl (4-methylbenzyl)propandioate (5s).

^1H NMR (CDCl_3 , Me_4Si) δ 1.22 (t, J = 7.1 Hz, 6H), 2.31 (s, 3H), 3.18 (d, J = 7.9 Hz, 2H), 3.62 (t, J = 7.8 Hz, 1H), 4.12 - 4.22 (m, 4H), 7.10 (s, 4H); ^{13}C NMR (CDCl_3) δ 13.97 (2C), 20.98, 34.22, 53.93, 61.37 (2C), 128.64 (2C), 129.12 (2C), 134.74, 136.17, 168.88 (2C); IR (neat) ν 2982, 2935, 1731, 1516, 1445, 1368, 1224, 1147, 1033 cm^{-1} ; EI-MS m/z (%) 264.0 (M^+ , 37), 190.0 (100), 173.0 (23), 145.0 (77), 105.0 (83); HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4$ 264.1351, found 264.1351.

Diethyl butyl(prop-1-en-1-yl)propandioate (6a).

^1H NMR (CDCl_3 , Me_4Si) δ 0.88 (t, $J = 7.3$ Hz, 3H), 1.12-1.22 (m, 2H), 1.24 (t, $J = 7.2$ Hz, 6H), 1.28-1.34 (m, 2H), 1.75 (dd, $J = 6.6, 1.7$ Hz, 3H), 1.96-2.04 (m, 2H), 4.12-4.24 (m, 4H), 5.57 (dq, $J = 15.9, 6.6$ Hz, 1H), 5.95 (dq, $J = 15.9, 1.6$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 13.9, 14.0 (2C), 18.3, 22.9, 26.3, 35.0, 59.3, 61.2 (2C), 127.3, 127.6, 171.0 (2C); IR (CHCl_3) ν 1201, 1208, 1220, 1236, 1725, 1787, 2932, 2964 cm^{-1} ; EI-MS m/z (%) 256 (M^+ , 7), 183 (100), 155 (33), 113 (16), 109 (47), 67 (32), 55 (25), 41 (20), 29 (43). HRMS calcd for $\text{C}_{14}\text{H}_{24}\text{O}_4$ 256.1675, found 256.1678.

Diethyl (prop-2-en-1-yl)(prop-1-en-1-yl)propandioate (6b).

^1H NMR (CDCl_3 , Me_4Si) δ 1.25 (t, $J = 7.2$ Hz, 6H), 1.75 (dd, $J = 1.7, 6.4$ Hz, 3H), 2.78 (d, $J = 7.2$ Hz, 2H), 4.12-4.24 (m, 4H), 5.02-5.12 (m, 2H), 5.56-5.74 (m, 2H), 5.78-5.84 (m, 1H); ^{13}C NMR (CDCl_3) δ 14.0 (2C), 18.3, 39.7, 59.2, 61.4 (2C), 118.6, 127.2, 127.9, 132.7, 170.4 (2C); IR (neat) ν 2982, 2930, 1739, 1445, 1228, 1196, 1043 cm^{-1} ; EI-MS m/z (%) 240 (M^+ , 4), 199 (97), 167 (100), 143 (30), 125 (62), 111 (24), 93 (100), 79 (27), 55 (17), 43 (32), 29 (58); HRMS calcd for $\text{C}_{13}\text{H}_{20}\text{O}_4$ 240.1361, found 240.1351.

Diethyl (prop-1-ene-1-yl)phenylpropandioate (6d).

^1H NMR (CDCl_3 , Me_4Si) δ 1.26 (t, $J = 7.1$ Hz, 6H), 1.79 (dd, $J = 1.7, 6.5$ Hz, 3H), 4.25 (q, $J = 7.1$ Hz, 4H), 5.42-5.52 (m, 1H), 6.18-6.26 (m, 1H), 7.25-7.42 (m, 5H); ^{13}C NMR (CDCl_3) δ 13.9 (2C), 18.3, 61.7 (2C), 65.4, 127.5, 127.9 (2C), 128.8 (2C), 129.1, 129.6, 137.6, 170.0 (2C); IR (neat) ν 3059, 3037, 2991, 2857, 1759, 1701, 1600, 1452, 1261, 1045, 777 cm^{-1} ; EI-MS m/z (%) 276 (M^+ , 2), 203 (100), 175 (20), 157 (25), 147 (18), 129 (95), 115 (15); HRMS calcd for $\text{C}_{16}\text{H}_{20}\text{O}_4$ 276.1361, found 276.1362.

Diethyl (4-trifluoromethylbenzyl)propenylpropandioate (6q).

^1H NMR (CDCl_3 , Me_4Si) δ 1.23 (t, $J = 7.2$ Hz, 6H), 1.75 (dd, $J = 6.4, 1.7$ Hz, 3H), 3.40 (s, 2H), 4.15 - 4.25 (m, 4H), 5.65 (dq, $J = 16.1, 6.5$ Hz, 1H), 5.83 (dq, $J = 16.0, 1.7$ Hz, 1H), 7.23 (d, $J = 8.1$ Hz, 2H), 7.50 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 13.93 (2C), 18.23, 41.84, 60.28, 61.61 (2C), 124.18 (q, $J_{\text{C-F}} = 270$ Hz), 124.88 (q, $J_{\text{C-F}} = 2.8$ Hz), 127.54, 128.17 (2C), 129.08 (q, $J_{\text{C-F}} = 32.7$ Hz), 130.47, 140.33, 170.10 (2C); ^{19}F NMR (CDCl_3) δ -62.99; IR (neat) ν 2983, 2940, 1736, 1619, 1446, 1323, 1266, 1220, 1165, 1126, 1068, 1020, 968, 857 cm^{-1} ; EI-MS m/z (%) 359.7 (M^+ , 52), 285.5 (63), 199.3 (100), 171.2 (27), 125.1 (35); HRMS calcd for $\text{C}_{18}\text{H}_{21}\text{O}_4\text{F}_3$ 358.1392, found 358.1383.

Ethyl 1-benzyl-2-oxo-cyclopentane-1-carboxylate (8a).

^1H NMR (CDCl_3 , Me_4Si) δ 1.26 (t, $J = 7.1$ Hz, 3H), 1.54-1.64 (m, 2H), 1.82-2.08 (m, 2H), 2.32-2.46 (m, 2H), 3.25 (d, $J = 13.7$ Hz, 1H), 3.20 (d, $J = 13.7$ Hz, 1H), 4.17 (q, $J = 7.1$ Hz, 5H), 7.10-7.30 (m, 5H); ^{13}C NMR (CDCl_3) δ 14.1, 19.5, 29.7, 31.7, 38.4, 38.9, 61.4, 61.6, 126.8, 128.3 (2C), 130.2 (2C), 136.6, 171.0, 215.0. The spectral characteristics agree with those previously reported.⁶

Ethyl 1-(3-methyl-but-2-en-1-yl)-2-oxocyclopentane-1-carboxylate (8b).

^1H NMR (CDCl_3 , Me_4Si) δ 1.25 (t, $J = 7.1$ Hz, 3H), 1.62 (s, 3H), 1.69 (s, 3H), 1.86-2.08 (m, 3H), 2.18-2.48 (m, 4H), 2.58-2.64 (m, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 4.96-5.04 (m, 1H); ^{13}C NMR (CDCl_3) δ 14.1, 17.9, 19.6, 25.9, 29.7, 32.0, 32.06, 38.2, 60.5, 61.3, 118.5, 135.6, 171.2, 215.2; EI-MS m/z (%) 224 (M^+ , 17), 195 (20), 156 (65), 135 (100), 110 (62), 69 (67), 41 (85). The spectral characteristics of **8b** are in agreement with previously published data.⁷

Ethyl 4-methylbenzyl-2-oxo-cyclopentanecarboxylate (8c).

^1H NMR (CDCl_3 , Me_4Si) δ 1.26 (t, $J = 7.1$ Hz, 3H), 1.52 - 1.62 (m, 2H), 1.80 - 2.00 (m, 2H), 2.30 (s, 3H), 2.32 - 5.42 (m, 2H), 3.12 (dd, $J = 15.9, 10.9$ Hz, 2H), 4.85 (q, $J = 7.2$ Hz, 2H), 7.05 (dd, $J = 18.4, 8.1$ Hz, 4H); ^{13}C NMR (CDCl_3) δ 14.07, 19.47, 20.99, 31.67, 38.40, 38.53, 61.45, 61.54, 129.03 (2C), 130.06 (2C), 133.43, 136.34, 171.07, 215.14; IR (neat) ν 2962, 2925, 1750, 1725, 1514, 1446, 1221, 1142, 1026 cm^{-1} ; EI-MS m/z (%) 260 (M^+ , 17), 242 (20), 187 (51), 171 (33), 105 (100); HRMS calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$ 260.1412, found 260.1418.

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