Supporting information for:

Catalytic Deallylation of Allyl- and Diallylmalonates

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1. General Methods. THF and toluene were distilled from sodium benzofenone ketyl. All other reagents were obtained from commercial sources. GC analyses were obtained on a Shimadzu GC-17A chromatograph equipped with a ZB-5 column (5% phenyl-95% dimethylpolysiloxane). Infrared spectra were recorded on a Bruker IFS 88 spectrometer and are reported in wave numbers (cm⁻¹). ¹H and ¹³C NMR spectra were recorded as CDCl₃ solution on a Varian UNITY 400 INOVA (¹H at 400 MHz, ¹³C at 100 MHz) by using Me₄Si as an internal standard. Melting points (uncorrected) were determined by using a Boëtius melting point apparatus. Mass spectra were obtained on a FINNIGAN MAT INCOS 50 instrument. All reactions were carried out under argon atmosphere in oven-dried Schlenk tubes. ¹H NMR yields were determined by using an internal standard (mesitylene).

2. Preparation of the Starting Material

Diethyl (but-1'-yl)(prop-2''-en-1''-yl)propandioate (1b). Alkylation of allylmalonate was carried out according to the previously reported procedure.¹ Sodium metal (0.58 g, 25 mmol) was added to absolute ethanol (25 mL). When the sodium had completely reacted, diethyl allylmalonate (4 g, 25 mmol) was slowly added. Butyl bromide (3.43 g, 25 mmol) was then added dropwise and the reaction mixture was refluxed for 60 min. The mixture was then acidified with glacial acetic acid, filtered and concentrated under reduced pressure. The residue was dissolved in water, extracted with ether and purified by distillation under reduced pressure. Yield 4.42 g (69 %) of a colourless liquid: ¹H NMR (CDCl₃, Me₄Si) δ 0.89 (t, *J* = 7.3 Hz, 3H), 1.12-1.21 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 6H), 1.28-1.36 (m, 2H), 1.83-1.89 (m, 2H), 2.64 (dm, *J* = 6.3 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 4H), 5.05-5.10 (m, 1H), 5.11-5.21 (m, 1H), 5.59-5.71 (m, 1H); ¹³C NMR (CDCl₃) δ 13.82, 14.07 (2C), 22.85, 25.94, 31.74, 36.77, 57.34, 61.02 (2C), 118.66, 132.59, 171.36 (2C); IR (CHCl₃) 859, 924, 1031, 1149, 1198, 1368, 1724, 2962 cm⁻¹; EI-MS *m/z* (%) 256 (M⁺, 1), 211 (30), 200 (100), 182 (85), 153 (70), 139 (66), 109 (85), 67 (95), 41 (95).

Diethyl phenyl(prop-2'-en-1'-yl)propandioate (1c). The preparation procedure was analogous to the preparation of **1b**. Diethyl phenylmalonate (1.12 g, 5 mmol), Na (0.115 g, 5 mmol), allyl bromide (0.61 g, 5 mmol) and ethanol (6 mL). Yield 1.1 g (78 %) of a colourless liquid: ¹H NMR (CDCl₃, Me₄Si) δ 1.24 (t, *J* = 7.2 Hz, 6H), 3.09 (d, *J* = 7.2 Hz, 2H), 4.14-4.28 (m, 4H), 5.02-5.11 (m, 2H), 5.71-5.82 (m, 1H), 7.25-7.44 (m, 5H); ¹³C NMR (CDCl₃) δ 13.95 (2C), 40.22, 61.51 (2C), 62.65, 118.74, 127.49, 128.02 (2C), 128.08 (2C), 133.00, 136.72, 170.25 (2C); IR (CHCl₃) 2983, 1728, 1447, 1237, 1185, 1025 cm⁻¹; EI-MS

m/z (%) 276 (M^+ , 6), 202 (65), 161 (30), 129 (100), 105 (25), 91 (29), 77 (20); HRMS calcd for $C_{16}H_{20}O_4$ 276.1362, found 276.1355.

Diethyl benzyl(prop-2'-en-1'-yl)propandioate (1d). The preparation procedure was analogous to the preparation of **1b**. Diethyl allylmalonate (1.5 g, 7.5 mmol), Na (0.19 g, 8.25 mmol), benzyl bromide (1.28 g, 7.5 mmol), and ethanol (12 mL). Yield 1.52 g (70 %) of a colourless liquid: 1H NMR ($CDCl_3$, Me_4Si) δ 1.24 (t, $J = 7.2$ Hz, 6H), 2.56 (d, $J = 7.6$ Hz, 2H), 3.24 (s, 2H), 4.11-4.24 (m, 4H), 5.12-5.15 (m, 1H), 5.17 (bs, 1H), 5.72-5.83 (m, 1H), 7.09-7.27 (m, 5H). The spectral characteristics of **1d** were in agreement with the previously published data.²

Diethyl (but-1'-yl)(but-2''-en-1''-yl)propandioate (1e). The preparation procedure was analogous to the preparation of **1b**. Diethyl butylmalonate (5.4 g, 25 mmol), Na (0.58 g, 25 mmol), crotyl chloride (2.26 g, 25 mmol) and ethanol (30 mL). Yield 3.84 g (57 %) of a colourless liquid: 1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, $J = 7.5$ Hz, 3H), 1.10-1.18 (m, 2H), 1.24 (t, $J = 7.2$ Hz, 6H), 1.27-1.35 (m, 2H), 1.64 (dm, $J = 6.4$ Hz, 3H), 1.81-1.90 (m, 2H), 2.57 (dm, $J = 7.4$ Hz, 2H), 4.14-4.21 (m, 4H), 5.19-5.32 (m, 1H), 5.45-5.56 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.86, 14.11 (2C), 17.97, 22.88, 25.94, 31.65, 35.64, 57.57, 60.94 (2C), 124.83, 129.30, 171.56 (2C); IR ($CHCl_3$) 968, 1033, 1131, 1194, 1466, 1724, 2961 cm^{-1} ; EI-MS m/z (%) 270 (M^+ , 3), 214 (32), 197 (100), 169 (31), 151 (43), 122 (50), 81 (40), 55 (41), 41 (38); HRMS calcd for $C_{15}H_{26}O_4$ 270.1831, found 270.1837.

Diethyl (but-1'-yl)(2''-methylprop-2''-en-1''-yl)propandioate (1f). The preparation procedure was analogous to the preparation of **1b**. Diethyl butylmalonate (5.4 g, 25 mmol), Na (0.58 g, 25 mmol), methallyl chloride (2.26 g, 25 mmol) and ethanol (30 mL). Yield 4.8 g (71 %) of a colourless liquid: 1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, $J = 7.3$ Hz, 3H), 1.11-1.19 (m, 2H), 1.25 (t, $J = 7.1$ Hz, 6H), 1.26-1.35 (m, 2H), 1.66 (bs, 3H), 1.84-1.91 (m, 2H), 2.67 (d, $J = 0.9$ Hz, 2H), 4.13-4.22 (m, 4H), 4.71-4.73 (m, 1H), 4.83-4.86 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.86, 14.01 (2C), 22.85, 23.18, 26.18, 31.75, 39.96, 56.95, 61.03 (2C), 115.29, 140.84, 171.76 (2C); IR ($CHCl_3$) 864, 902, 1189, 1725, 2962 cm^{-1} ; EI-MS m/z (%) 270 (M^+ , 14), 213 (67), 196 (100), 181 (41), 173 (40), 167 (50), 153 (42), 123 (34), 81 (38), 55 (60), 41 (38).

Diethyl (but-1'-yl)(3''-phenylprop-2''-en-1''-yl)propandioate (1g). The preparation procedure was analogous to the preparation of **1b**. Diethyl butylmalonate (1.08 g, 5 mmol), Na (0.12 mg, 5 mmol), cinnamyl bromide (0.98 g, 5 mmol) and ethanol (6 mL). Yield 1.1 g (67 %) of a yellowish liquid: 1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, $J = 7.3$ Hz, 3H), 1.16-1.28

(m, 2H), 1.23 (t, $J = 7.0$ Hz, 6H), 1.28-1.36 (m, 2H), 1.88-1.96 (m, 2H), 2.79 (dd, $J = 7.4, 1.2$ Hz, 2H), 4.19 (q, $J = 7.0$ Hz, 4H), 6.04 (dt, $J = 15.7, 7.5$ Hz, 1H), 6.43 (d, $J = 15.7$ Hz, 1H), 7.18-7.40 (m, 5H); ^{13}C NMR (CDCl_3) δ 13.88, 14.12 (2C), 22.88, 26.07, 32.15, 36.21, 57.77, 61.11 (2C), 124.33, 126.15 (2C), 127.28, 128.45 (2C), 133.55, 137.17, 171.39 (2C); IR (CHCl_3) 966, 1029, 1191, 1724, 2961 cm^{-1} ; EI-MS m/z (%) 332 (M^+ , 32), 275 (25), 258 (100), 229 (24), 185 (21), 169 (26), 141 (24), 129 (27), 117 (91), 91 (30); HRMS calcd for $\text{C}_{20}\text{H}_{28}\text{O}_4$ 332.1988, found 332.1983.

Diethyl methyl(1'-phenylprop-2'-en-1'-yl)propandioate (1h). Allylation of diethyl methylmalonate was carried out analogously the previously reported procedure.³ Cinnamyl acetate (71 mg, 4 mmol), triphenyl phosphite (99 mg, 0.32 mmol), and $[\text{Ir}(\text{cod})\text{Cl}]_2$ (54 mg, 0.08 mmol) were stirred in 10 mL of dry THF under Ar atmosphere. In a separate flask, diethyl methylmalonate (1.39 g, 8 mmol) was added to a suspension of hexane-washed sodium hydride (192 mg, 8 mmol) in 10 mL of dry THF. The resulting clear solution was added to the former by a syringe, and the combined mixture was stirred at room temperature for 3 h. The reaction mixture was partitioned between ether and water and the aqueous layer was extracted with ether. The combined organic layer was concentrated in vacuo and the product was separated by HPLC chromatography (97/3 hexan/EtOAc). Yield 0.73 g (63 %) of a yellowish liquid: ^1H NMR (CDCl_3 , Me_4Si) δ 1.17 (t, $J = 7.2$ Hz, 3H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.43 (s, 3H), 4.06 (q, $J = 7.2$ Hz, 2H), 4.14 (d, $J = 7.3$ Hz, 1H), 4.18 (q, $J = 7.2$ Hz, 2H), 5.09 (dm, $J = 16.9$ Hz, 1H), 5.13 (dm, $J = 10.2$ Hz, 1H), 6.33 (ddd, $J = 16.9, 10.2, 8.5$ Hz, 1H), 7.12-7.29 (m, 5H). The spectral characteristics of **1h** were in agreement with the previously published data.⁴

Diethyl di(prop-2'-en-1'-yl)propandioate (1i). The preparation procedure was analogous to the preparation of **1b**. Diethyl allylmalonate (4 g, 25 mmol), Na (0.58 g, 25 mmol), allyl bromide (3.2 g, 26.4 mmol) and ethanol (25 mL). Yield 4.69 g (78 %) of a colourless liquid: ^1H NMR (CDCl_3 , Me_4Si) δ 1.25 (t, $J = 7.0$ Hz, 6H), 2.64 (dt, $J = 7.1, 1.0$ Hz, 4H), 4.18 (q, $J = 7.0$ Hz, 4H), 5.07-5.15 (m, 4H), 5.60-5.72 (m, 2H). The spectral characteristics of **1i** were in agreement with the previously published data.¹

Diethyl (2'-methylprop-2'-en-1'-yl)(prop-2''-en-1''-yl)propandioate (1j). The preparation procedure was analogous to the preparation of **1b**. Diethyl allylmalonate (4 g, 20 mmol), Na (0.51 g, 22 mmol), methallyl chloride (2 g, 22 mmol) and ethanol (15 mL). Yield 3.9 g (76 %) of a colourless liquid: ^1H NMR (CDCl_3 , Me_4Si) δ 1.25 (t, $J = 7.2$ Hz, 6H), 1.67 (bs, 3H), 2.67 (dm, $J = 7.3$ Hz, 2H), 2.69-2.71 (m, 2H), 4.13-4.22 (m, 4H), 4.75-4.77 (m, 1H), 4.86-4.89 (m, 1H), 5.06-5.08 (m, 1H), 5.11 (dm, $J = 6.2$ Hz, 1H), 5.64-5.75 (m, 1H). The spectral characteristics of **1j** were in agreement with the previously published data.⁵

Diethyl (but-2'-en-1'-yl)(prop-2''-en-1''-yl)propandioate (1k). The preparation procedure was analogous to the preparation of **1b**. Diethyl allylmalonate (4 g, 20 mmol), Na (0.51 g, 22 mmol), crotyl chloride (2 g, 22 mmol) and ethanol (15 mL). Yield 3.54 g (70 %) of a colourless liquid: ^1H NMR (CDCl_3 , Me_4Si) δ 1.24 (t, $J = 6.8$ Hz, 6H), 1.64 (dm, $J = 6.4$ Hz, 3H), 2.57 (dm, $J = 7.2$ Hz, 2H), 2.62 (dm, $J = 7.6$ Hz, 2H), 4.17 (q, $J = 6.8$ Hz, 4H), 5.08-5.09 (m, 1H), 5.01 (dm, $J = 6.4$ Hz, 1H), 5.21-5.31 (m, 1H), 5.47-5.58 (m, 1H), 5.59-5.71 (m, 1H). The spectral characteristics of **1k** were in agreement with the previously published data.⁶

Diethyl (prop-2'-en-1'-yl)(3''-phenylprop-2''-en-1''-yl)propandioate (1l). The preparation procedure was analogous to the preparation of **1b**. Diethyl allylmalonate (1 g, 5 mmol), Na (115 mg, 5 mmol), cinnamyl bromide (0.99 g, 5 mmol) and ethanol (6 mL). Yield 1.15 g (73 %) of a yellowish liquid: ^1H NMR (CDCl_3 , Me_4Si) δ 1.25 (t, $J = 7.2$ Hz, 6H), 2.69 (dm, $J = 7.3$ Hz, 2H), 2.79 (dd, $J = 7.5$, 1.4 Hz, 2H), 4.17-4.23 (m, 4H), 5.11-5.17 (m, 2H), 5.64-5.76 (m, 1H), 6.00-6.08 (m, 1H), 6.44 (dm, $J = 13.7$ Hz, 1H), 7.21-7.33 (m, 5H). The spectral characteristics of **1l** were in agreement with the previously published data.⁷

Diethyl (3'-methylbut-2'-en-1'-yl)(prop-2''-en-1''-yl)propandioate (1m). The preparation procedure was analogous to the preparation of **1b**. Diethyl allylmalonate (0.44 g, 2.2 mmol), Na (60 mg, 2.4 mmol), 1-bromo-3-methylbut-2-en (0.33 g, 2.2 mmol) and ethanol (3 mL). Yield 0.5 g (85 %) of a yellowish liquid: ^1H NMR (CDCl_3 , Me_4Si) δ 1.23 (t, $J = 7.1$ Hz, 6H), 1.61 (s, 3H), 1.69 (s, 3H), 2.58-2.64 (m, 2H), 4.12-4.22 (m, 4H), 4.94-5.00 (m, 1H), 5.01 (s, 1H), 5.08-5.12 (m, 1H), 5.60-5.72 (m, 1H). The spectral characteristics of **1m** were in agreement with the previously published data.⁸

Diethyl 2-(4'-bromobutyl)(prop-2''-en-1''-yl)propandioate (1n). The preparation procedure was analogous to the preparation of **1a**. Diethyl allylmalonate (1.75 g, 8.75 mmol), K_2CO_3 (7.7 g, 55.8 mmol), Bu_4NHSO_4 (0.4 g, 1.2 mmol), 1,4-dibromobutane (2.28 g, 8.9 mmol) and CH_3CN (20 mL). Yield 710 mg (24 %) of a yellowish oil: ^1H NMR (CDCl_3 , Me_4Si) δ 1.25 (t, $J = 6.8$ Hz, 6H), 1.32-1.41 (m, 2H), 1.82-1.90 (m, 4H), 2.65 (d, $J = 7.6$ Hz, 2H), 3.41 (t, $J = 6.4$ Hz, 2H), 4.19 (q, $J = 7.0$ Hz, 4H), 5.08-5.15 (m, 2H), 5.58-5.69 (m, 1H); ^{13}C NMR (CDCl_3) δ 14.10 (2C), 22.34, 31.11, 32.68, 33.19, 36.82, 57.16, 61.23 (2C), 119.03, 132.32, 117.09 (2C). EI-MS m/z (%) 260 (35), 200 (100), 153 (60), 139 (50), 107 (47), 95

(20), 79 (28), 67 (75), 55 (45), 41 (97). Calcd for $C_{14}H_{23}BrO_4$: C 50.16, H 6.92, Br 23.84, O 19.09; found: C 50.11, H 7.08, Br 23.81, O 19.00.

3-Bis-(prop-2'-en-1'-yl)coumaran-2-one (1o). The preparation procedure was analogous to the preparation of **1a**. 2-Coumaranone (1 g, 7.46 mmol), K_2CO_3 (5.6 g, 40 mmol), Bu_4NHSO_4 (0.5 g, 1.5 mmol), allyl bromide (1.82 g, 15 mmol) and CH_3CN (15 mL). Yield 1.14 g (71 %) of a yellowish oil: 1H NMR ($CDCl_3$, Me_4Si) δ 2.57-2.67 (m, 4H), 5.00 (dm, J = 9.1 Hz, 2H), 5.05 (dm, J = 17.1 Hz, 2H), 5.40-5.51 (m, 2H), 7.06-7.32 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 41.67 (2C), 52.31, 110.61, 120.00 (2C), 123.61, 124.07, 128.73, 129.35, 131.12 (2C), 152.91, 178.52; IR ($CHCl_3$) 3083, 3030, 1801, 1463, 1228, 1054, 929, 881 cm^{-1} ; EI-MS m/z (%) 214 (M^+ , 35), 173 (83), 145 (30), 128 (100), 115 (30); HRMS calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.1000.

Ethyl bis(prop-2'-en-1'-yl)cyanoacetate (1p). The preparation procedure was analogous to the preparation of **1a**. Cyano ethylacetate (4.52 g, 40 mmol), K_2CO_3 (33 g, 240 mmol), Bu_4NHSO_4 (2 g, 8 mmol), allyl bromide (9.68 g, 80 mmol) and CH_3CN (80 mL). Yield 5.2 g (67 %) of a colourless liquid: 1H NMR ($CDCl_3$, Me_4Si) δ 1.31 (t, J = 7.0 Hz, 3H), 2.55 (dd, J = 13.8, 7.2 Hz, 2H), 2.65 (dd, J = 13.9, 7.4 Hz, 2H), 4.25 (q, J = 7.2 Hz, 2H), 5.21-5.24 (m, 2H), 5.22-5.28 (m, 2H), 5.76-5.87 (m, 2H). The spectral characteristics were in agreement with the previously published data.⁹

3. General Procedures for the Deallylation of Allylmalonates

General Procedure for Ruthenium-Catalyzed C-C Bond Cleavage of Substituted Malonates with Et_3Al . To a solution of a malonate (0.5 mmol) and $RuCl_2(PPh_3)_3$ (24 mg, 0.025 mmol) in dry toluene (3 mL) was added Et_3Al solution in toluene (0.5 mL, 1 mmol) under argon. The reaction mixture was stirred under argon at 20°C for 36 hours. After that it was quenched with a portion of water (1 mL) followed by 3M solution of HCl (3 mL). Organic layer was separated and dried (Na_2SO_4). The product was separated by column chromatography (silica gel, hexan/EtOAc).

General Procedure for Nickel-Catalyzed C-C Bond Cleavage of Substituted Malonates with Et_3Al . To a solution of a malonate (0.5 mmol) and $NiBr_2(PPh_3)_3$ (18.6 mg, 0.025 mmol) in dry toluene (3 mL) was added Et_3Al solution in toluene (0.5 mL, 1 mmol) under argon. The reaction mixture was stirred under argon at 20°C for 24 hours. After that it was quenched with a portion of water (1 mL) followed by 3M solution of HCl (3 mL). Organic layer was separated and dried (Na_2SO_4). The product was separated by column chromatography (silica gel, hexan/EtOAc).

4. Products of the C-C Bond Cleavage

Diethyl (but-1'-yl)propandioate (2b). Diethyl malonate derivative **1b** (128 mg, 0.5 mmol), $\text{NiBr}_2(\text{PPh}_3)_2$ (18.6 mg, 0.025 mmol), and 2M solution of Et_3Al in toluene (0.5 mL, 1 mmol). ^1H NMR yield 92 %. ^1H NMR (CDCl_3 , Me_4Si) δ 0.90 (t, $J = 7.2$ Hz, 3H), 1.27 (t, $J = 7.1$ Hz, 6H), 1.28-1.38 (m, 4H), 1.84-1.96 (m, 2H), 3.01 (t, $J = 7.5$ Hz, 1H), 4.14-4.25 (m, 4H). The spectral characteristics of **2b** were in agreement with the commercially available sample of the title compound (Aldrich).

Diethyl phenylpropandioate (2c). Diethyl malonate derivative **1c** (138 mg, 0.5 mmol), $\text{NiBr}_2(\text{PPh}_3)_2$ (18.6 mg, 0.025 mmol), and 2M solution of Et_3Al in toluene (0.5 mL, 1 mmol). ^1H NMR yield 98 %. ^1H NMR (CDCl_3 , Me_4Si) δ 1.26 (t, $J = 7.2$ Hz, 6H), 4.15-4.28 (m, 4H), 4.61 (s, 1H), 7.31-7.42 (m, 5H). The spectral characteristics of **2c** were in agreement with the previously published data.¹⁰

Diethyl benzylpropandioate (2d). Diethyl malonate derivative **1d** (145 mg, 0.5 mmol), $\text{NiBr}_2(\text{PPh}_3)_2$ (18.6 mg, 0.025 mmol), and 2M solution of Et_3Al in toluene (0.5 mL, 1 mmol). ^1H NMR yield 99 %. ^1H NMR (CDCl_3 , Me_4Si) δ 1.19 (t, $J = 7.2$ Hz, 6H), 3.22 (d, $J = 7.8$ Hz, 2H), 3.65 (t, $J = 7.8$ Hz, 1H), 4.08-4.22 (m, 4H), 7.16-7.34 (m, 5H). The spectral characteristics of **2d** were in agreement with the previously published data.¹¹

Diethyl methylpropandioate (2e). Diethyl malonate derivative **1h** (145 mg, 0.5 mmol), $\text{NiBr}_2(\text{PPh}_3)_2$ (18.6 mg, 0.025 mmol), and 2M solution of Et_3Al in toluene (0.5 mL, 1 mmol). ^1H NMR yield 96 %. ^1H NMR (CDCl_3 , Me_4Si) δ 1.27 (t, $J = 7.2$ Hz, 6H), 1.42 (d, $J = 7.3$ Hz, 3H), 3.42 (q, $J = 7.3$ Hz, 1H), 4.14-4.26 (m, 4H). The spectral characteristics of **2e** were in agreement with the commercially available sample of the title compound (Aldrich).

Diethyl (prop-2'-en-1'-yl)propandioate (2f). Diethyl malonate derivative **1i** (120 mg, 0.5 mmol), $\text{RuCl}_2(\text{PPh}_3)_3$ (24 mg, 0.025 mmol), and 2M solution of Et_3Al in toluene (0.5 mL, 1 mmol). ^1H NMR yield 91 %. ^1H NMR (CDCl_3 , Me_4Si) δ 1.27 (t, $J = 7.2$ Hz, 6H), 2.62-2.68 (m, 2H), 3.42 (t, $J = 7.1$ Hz, 1H), 4.14-4.24 (m, 4H), 5.04-5.16 (m, 2H), 5.72-5.84 (m, 1H). The spectral characteristics of **2f** were in agreement with the previously published data.¹

Diethyl (2'-methylprop-2'-en-1'-yl)propandioate (2g). Diethyl malonate derivative **1j** (127 mg, 0.5 mmol), NiBr₂(PPh₃)₂ (18.6 mg, 0.025 mmol), and 2M solution of Et₃Al in toluene (0.5 mL, 1 mmol). ¹H NMR yield 99 %. ¹H NMR (CDCl₃, Me₄Si) δ 1.26 (t, *J* = 7.3 Hz, 6H), 1.75 (bs, 3H), 2.62 (d, *J* = 7.9 Hz, 2H), 3.58 (t, *J* = 7.8 Hz, 1H), 4.16-4.23 (m, 4H), 4.72-4.75 (m, 1H), 4.77-4.81 (m, 1H). The spectral characteristics of **2g** were in agreement with the previously published data.³

Diethyl (but-2'-en-1'-yl)propandioate (2h). Diethyl malonate derivative **1k** (127 mg, 0.5 mmol), NiBr₂(PPh₃)₂ (18.6 mg, 0.025 mmol), and 2M solution of Et₃Al in toluene (0.5 mL, 1 mmol). ¹H NMR yield 98 %. ¹H NMR (CDCl₃, Me₄Si) δ 1.26 (t, *J* = 7.0 Hz, 6H), 1.63 (dm, *J* = 6.2 Hz, 3H), 2.54-2.62 (m, 2H), 3.36 (t, *J* = 7.6 Hz, 1H), 4.14-4.24 (m, 4H), 5.32-5.44 (m, 1H), 5.49-5.60 (m, 1H). The spectral characteristics of **2h** were in agreement with the previously published data.³

Diethyl (3'-phenylprop-2'-en-1'-yl)propandioate (2i). Diethyl malonate derivative **1l** (158 mg, 0.5 mmol), NiBr₂(PPh₃)₂ (18.6 mg, 0.025 mmol) and 2M solution of Et₃Al in toluene (0.5 mL, 1 mmol). ¹H NMR yield 85 %. ¹H NMR (CDCl₃, Me₄Si) δ 1.26 (t, *J* = 7.2 Hz, 6H), 2.80 (dd, *J* = 7.3, 7.3 Hz, 2H), 3.48 (t, *J* = 7.4 Hz, 1H), 4.14-4.26 (m, 4H), 6.16 (dt, *J* = 15.8, 7.1 Hz, 1H), 6.48 (d, *J* = 15.3 Hz, 1H), 7.18-7.36 (m, 5H). The spectral characteristics of **2i** were in agreement with the previously published data.³

Diethyl (3'-methylbut-2'-en-1'-yl)propandioate (2j). Diethyl malonate derivative **1m** (134 mg, 0.5 mmol), NiBr₂(PPh₃)₂ (18.6 mg, 0.025 mmol), and 2M solution of Et₃Al in toluene (0.5 mL, 1 mmol). ¹H NMR yield 99 %. ¹H NMR (CDCl₃, Me₄Si) δ 1.26 (t, *J* = 7.2 Hz, 6H), 1.63 (s, 3H), 1.68 (d, *J* = 0.9 Hz, 3H), 2.59 (dd, *J* = 7.6, 7.6 Hz, 2H), 3.57 (t, *J* = 7.8 Hz, 1H), 4.19 (q, *J* = 6.9 Hz, 4H), 5.02-5.11 (m, 1H). The spectral characteristics of **2j** were in agreement with the previously published data.³

Diethyl 2-(4-bromobutyl)propandioate (2k). Diethyl malonate derivative **1n** (167 mg, 0.5 mmol), NiBr₂(PPh₃)₂ (18.6 mg, 0.025 mmol), and 2M solution of Et₃Al in toluene (0.5 mL, 1 mmol). ¹H NMR yield 68 %. ¹H NMR (CDCl₃, Me₄Si) δ 1.26 (t, *J* = 6.8 Hz, 6H), 1.43-1.51 (m, 2H), 1.82-1.95 (m, 4H), 3.31 (t, *J* = 6.8 Hz, 1H), 3.38 (t, *J* = 6.5 Hz, 2H), 4.19 (q, *J* = 6.9 Hz, 4H). The spectral characteristics of **2k** were in agreement with the previously published data.¹²

3-(Prop-2'-en-1'-yl)coumaran-2-one (2l). Coumaranone derivative **1o** (107 mg, 0.5 mmol), $\text{NiBr}_2(\text{PPh}_3)_2$ (18.6 mg, 0.025 mmol), and 2M solution of Et_3Al in toluene (0.5 mL, 1 mmol). ^1H NMR yield 94 %. ^1H NMR (CDCl_3 , Me_4Si) δ 2.63 (ddd, $J = 14.2, 7.6, 7.6$ Hz, 1H), 2.83 (ddd, $J = 14.2, 5.6, 5.6$ Hz, 1H), 3.78 (app. t, $J = 6.2$ Hz, 1H), 5.09 (d, $J = 9.6$ Hz, 1H), 5.14 (dd, $J = 6.8, 1.1$ Hz, 1H), 5.67-5.79 (m, 1H), 7.06-7.31 (m, 2H), 7.42-7.68 (m, 2H); ^{13}C NMR (CDCl_3) δ 35.10, 43.09, 110.55, 119.00, 123.95, 124.37, 126.76, 128.78, 132.61, 135.59, 176.51; IR (CHCl_3) 1064, 1232, 1464, 1806, 3029 cm^{-1} ; EI-MS m/z (%) 174 (M^+ , 80), 145 (20), 133 (100), 105 (20), 77 (35), 51 (50); HRMS calcd for $\text{C}_{11}\text{H}_{10}\text{O}_2$ 174.0681, found 174.0687.

Ethyl (prop-2'-en-1'-yl)cyanoacetate (2m). Diallyl derivative **1p** (82 mg, 0.5 mmol), $\text{NiBr}_2(\text{PPh}_3)_2$ (18.6 mg, 0.025 mmol) and 2M solution of Et_3Al in toluene (0.5 mL, 1 mmol). ^1H NMR yield 59 %. ^1H NMR (CDCl_3 , Me_4Si) δ 1.29 (t, $J = 7.1$ Hz, 6H), 2.61-2.69 (m, 2H), 3.47 (dd, $J = 7.3, 6.2$ Hz, 1H), 4.21-4.28 (m, 2H), 5.19-5.28 (m, 2H) 5.72-5.88 (m, 1H). The spectral characteristics were in agreement with previously published data.¹³

E-1-Phenylprop-1-ene (3). ^1H NMR (CDCl_3 , Me_4Si) δ 1.88 (dd, $J = 6.1, 1.0$ Hz, 3H), 6.21 (dq, $J = 15.9, 6.1$ Hz, 1H), 6.39 (dm, $J = 15.9$ Hz, 1H), 7.16-7.37 (m, 5H). The spectral characteristics of **3** were in agreement with the previously published data.¹⁴

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