**Carbon-Carbon Bond Formation in Palladium(II)-Catalyzed Allylic
Oxidation: A Novel Oxidative Carbocyclization of Allene Substituted
Olefines**

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Supporting Information

Scheme 1

a) $Pd(PPh_3)_4$, $NaBD_4$, CH_3CN , 3h, rt.

Scheme 2

a) NaH , **5**, THF, reflux.

Scheme 3

a) $Pd(PPh_3)_4$, $NaBH_4$, CH_3CN , 3h, rt; b) NaH , **5**, THF, reflux.

Experimental section 1H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were recorded using chloroform- d_1 (7.26 ppm 1H , 77 ppm ^{13}C) as internal standard. THF was dried over sodium and refluxed under argon atmosphere prior to use.

Bromoallenes 5 were prepared from the corresponding disubstituted propargylic alcohols according to a previously described procedure (Löfstedt, J.; Franzén J.; Bäckvall J. E. *J. Org. Chem. Soc.* **2001**, 66, 8015).

Allenes 1i and trifluoroacetate *cis-7* were prepared according to previously described methods (Franzén, J.; Löfstedt, J.; Dorange, I.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2002**, 124, 11246.). Trifluoroacetate *trans-8* was prepared from the corresponding pivalic ester according to the same method as that used for the preparation of *cis-7*.

General procedure for the preparation of malonates 4: Procedure for the preparation of dimethyl (2-cyclohexenyl)malonate (4a). To a solution of dimethyl malonate (0.49 mL, 4.3 mmol) in THF (15 mL) under argon was added NaH (60% in mineral oil, 0.17 g, 4.3 mmol) and the mixture was stirred for 10 min. To this mixture was added Pd(OAc)₂ (0.024 g, 0.11 mmol) and PPh₃ (0.093 g, 0.36 mmol) followed by **3a** (0.50 g, 3.6 mmol). The resulting mixture was refluxed for 14 h and partitioned between Et₂O (20 mL) and H₂O (20 mL). The aqueous phase was extracted with Et₂O (3 x 10 mL) and the combined organic phases were dried (Na₂SO₄). The solvent was removed in vacuo followed by flash chromatography (pentane:Et₂O, 80:20) to give 0.67 g (88% yield) of **4a**. ¹H NMR (CDCl₃, 400 MHz): 5.77 (br d, *J* = 10.5 Hz, 1H), 5.51 (br d, *J* = 10.5 Hz, 1H), 3.73 (s, 6H), 3.28 (d, *J* = 9.5 Hz, 1H), 2.90 (m, 1H), 1.99 (m, 2H), 1.75 (m, 2H), 1.57 (m, 1H), 1.36 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz): 169.1 (2C), 129.9, 127.6, 57.1, 52.6 (2C), 35.6, 26.9, 25.1, 21.1.

General procedure for the preparation of allenes 1. Preparation of dimethyl (2-cyclohexenyl)(3-methyl-1,2-butadienyl)malonate (1a). To a solution of **4a** (0.65 g, 3.1 mmol) in THF (20 mL) under argon was added NaH (60% in mineral oil, 0.13 g, 3.3 mmol) and the mixture was stirred for 10 min at r.t. Bromoallene **5** (0.90 g, 6.1 mmol) was added and the resulting mixture was refluxed for 14 h. Water was added and the aqueous phase was extracted with Et₂O (4 x 20 mL) and the combined organic phases were dried (Na₂SO₄). The solvent was removed in vacuo followed by flash chromatography (pentane:Et₂O, 85:15), which gave 0.65 g (76% yield) of **1a**. ¹H NMR (CDCl₃, 400 MHz): 5.73 (m, 1H), 5.63 (ddt, *J* = 12.5, 3.8, 1.9 Hz, 1H), 5.43 (septet, *J* = 2.9 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.01 (m, 1H), 1.95 (m, 2H), 1.75 (m, 2H), 1.66 (d, *J* = 2.9 Hz, 6H), 1.54 (m, 1H), 1.37 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz): 202.3, 170.7, 170.6, 128.8, 128.2, 99.1, 87.3, 62.5, 52.6, 52.5, 41.4, 25.2, 25.0, 22.5, 20.2, 20.0.

General procedure for the preparation of compounds 2: Procedure for the preparation of compound 2a. A solution of **1a** (0.28 g, 1.0 mmol) and Pd(O₂CCF₃)₂ (0.003 g, 0.01 mmol) in THF (5 mL) was refluxed for 4 h. The resulting mixture was dissolved in Et₂O (20 mL) and washed with 2M NaOH (3 x 10 mL). The aqueous phase was back-extracted with Et₂O (10 mL) and the combined

organic phases were dried (Na_2SO_4). The solvent was removed in vacuo followed by flash chromatography (pentane: Et_2O , 80:20) to give 0.26 g (94% yield) of **2a**. ^1H NMR (CDCl_3 , 400 MHz): 5.96 (dddd, $J = 10.3, 4.0, 2.4, 1.5$ Hz, 1H), 5.79 (ddt, $J = 10.3, 5.0, 2.5$ Hz, 1H), 5.70 (d, $J = 2.4$ Hz, 1H), 5.07 (m, 2H), 3.74 (s, 3H), 3.71 (s, 3H), 3.66 (m, 1H), 3.26 (ddd, $J = 10.6, 6.7, 5.1$ Hz, 1H), 2.04–1.87 (m, 5H), 1.48 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): 171.1, 170.6, 150.8, 138.9, 128.3, 126.3, 123.3, 115.1, 68.6, 52.9, 52.5, 44.4, 42.7, 23.4, 21.9, 21.8. – Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_4$: C, 69.54; H, 7.30. Found: C, 69.57; H, 7.47.

Procedure for the preparation of dimethyl (*trans*-4-deuterio-2-cyclohexenyl)malonate (*trans*-4a- d_1) and dimethyl (*trans*-2-deuterio-3-cyclohexenyl)malonate (*trans*-9a- d_1). To a solution of *cis*-**7** (0.15 g, 0.47 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.11 g, 0.09 mmol) in CH_3CN (3.5 ml) under argon was added NaBD_4 (0.04 g, 0.94 mmol). After 2 h was NH_4Cl (sat) added to the reaction mixture and the aqueous phase was extracted with Et_2O (4 x 20 ml) and the combined organic phases were dried (Na_2SO_4). The solvent was removed in vacuo followed by purification by preparative HPLC (SiO_2 pentane: Et_2O , 80:20), which gave 0.035 g (50% yield (based on recovered starting material, 70% conv.)) of a 1:1 mixture of *trans*-4a- d_1 and *trans*-9a- d_1 . Compounds *trans*-4a- d_1 and *trans*-9a- d_1 was separated by preparative HPLC (SiO_2 pentane: Et_2O , 95:5): *trans*-4a- d_1 : ^1H NMR (CDCl_3 , 400 MHz): 5.77 (dt, $J = 10.2, 2.7$ Hz, 1H), 5.51 (dtd, $J = 10.2, 2.7, 1.1$ Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.29 (d, $J = 9.5$ Hz, 1H), 2.90 (m, 1H), 1.97 (m, 1H), 1.77 (m, 1H), 1.70 (ddd, $J = 12.5, 7.0, 2.7$ Hz, 1H), 1.57 (m, 1H), 1.37 (dddd, $J = 12.5, 11.1, 8.5, 2.7$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): 169.1 (2C), 129.8, 127.6, 57.1, 52.6 (2C), 35.6, 26.8, 21.0.

trans-9a- d_1 : ^1H NMR (CDCl_3 , 400 MHz): 5.68 (m, 1H), 5.61 (ddd, $J = 9.9, 4.0, 2.2$ Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.29 (d, $J = 9.5$ Hz, 1H), 2.28 (ddd, $J = 14.1, 9.7, 2.8$ Hz, 1H), 2.08 (m, 2H), 1.83 (m, 1H), 1.76 (m, 1H), 1.35 (ddd, $J = 11.2, 9.1, 7.0$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): 169.3 (2C), 127.1, 125.4, 57.3, 52.6 (2C), 34.1, 26.7, 25.0.

Procedure for the preparation of dimethyl (*cis*-4-deuterio-2-cycloheptenyl)malonate (*cis*-4f- d_1) and dimethyl (*cis*-2-deuterio-3-cycloheptenyl)malonate (*cis*-9f- d_1). Compounds *cis*-4f- d_1 and

cis-9f-d₁ was prepared as a 1:1 mixture from *trans-7* in 23% yield as described for the preparation of *trans-4a-d₁* and *trans-9a-d₁* above. Compounds *cis-4f-d₁* and *cis-9f-d₁* was separated by preparative HPLC (SiO₂ pentane:Et₂O, 80:20): *cis-4f-d₁*: ¹H NMR (CDCl₃, 400 MHz): 5.83 (ddd, *J* = 11.0, 4.9, 2.2 Hz, 1H), 5.59 (dddd, *J* = 11.0, 4.9, 2.2, 0.7 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.47 (d, *J* = 8.4 Hz, 1H), 3.05 (m, 1H), 2.12 (m, 1H), 1.95 (m, 1H), 1.63 (m, 3H), 1.36 (m, 2H).

cis-9f-d₁: ¹H NMR (CDCl₃, 400 MHz): 5.85 (dt, *J* = 10.8, 5.9 Hz, 1H), 5.68 (ddt, *J* = 10.8, 7.4, 1.1 Hz, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.40 (d, *J* = 8.4 Hz, 1H), 2.33 (br. t, *J* = 9.7 Hz, 1H), 2.12 (m, 3H), 1.84 (m, 1H), 1.69 (m, 1H), 1.58 (m, 1H), 1.44 (m, 1H).

Procedure for the preparation of allene *trans-1a-d₁*. Compound *trans-1a-d₁* was prepared from *trans-4a-d₁* in 63% yield as described for **1a** above. ¹H NMR (CDCl₃, 400 MHz): 5.74 (dtd, *J* = 10.4, 2.5, 1.0 Hz, 1H), 5.64 (ddt, *J* = 10.4, 2.8, 1.7 Hz, 1H), 5.44 (septet, *J* = 2.9 Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.03 (m, 1H), 1.93 (m, 1H), 1.75 (m, 2H), 1.63 (d, *J* = 2.9 Hz, 6H), 1.54 (m, 1H), 1.37 (m, 1H).

Procedure for the preparation of allene *cis-1f-d₁*. Compound *cis-1f-d₁* was prepared from *cis-4f-d₁* in 56% yield as described for **1a** above. ¹H NMR (CDCl₃, 400 MHz): 5.79 (ddd, *J* = 10.8, 4.7, 2.1 Hz, 1H), 5.72 (dddd, *J* = 10.8, 4.4, 2.0, 0.9 Hz, 1H), 5.47 (septet, *J* = 2.8 Hz, 1H), 3.72 (s, 6H), 3.11 (m, 1H), 2.13 (m, 1H), 2.00 (m, 1H), 1.72 (m, 2H), 1.69 (d, *J* = 2.8 Hz, 3H), 1.68 (d, *J* = 2.8 Hz, 3H), 1.57 (m, 1H), 1.22 (m, 2H).

Procedure for the preparation of compound *cis-2a-d₁*. Compound *cis-2a-d₁* was prepared from *trans-1a-d₁* in 60% yield as described for **2a** above, employing 10 mol% Pd(O₂CCF₃)₂. ¹H NMR (CDCl₃, 400 MHz): 5.96 (m, 1 H), 5.70 (d, *J* = 2.6 Hz, 1 H), 5.07 (s, 2 H), 3.74 (s, 3 H), 3.71 (s, 3 H), 3.66 (m, 1 H), 3.26 (ddd, *J* = 10.6, 6.8, 5.1 Hz, 1 H), 1.97 (m, 2H), 1.93 (s, 3 H), 1.49 (m, 2 H).

Procedure for the preparation of compound *trans-2f-d₁*. Compound *trans-2f-d₁* was prepared from *cis-1f-d₁* in 56% yield as described for **2a** above, employing 10 mol% Pd(O₂CCF₃)₂. ¹H NMR (CDCl₃, 400 MHz): 5.95 (br. d, *J* = 4.4 Hz, 1H), 5.77 (d, *J* = 2.4 Hz, 1H), 5.07 (br s, 1H), 4.97 (br s, 1H), 3.78-3.70 (m, including s at 3.77 and 3.71 ppm, 7H), 2.51 (ddd, *J* = 12.0, 9.4, 2.6, Hz, 1H),

2.31 (m, 1H), 2.19 (m, 2H), 1.93 (m, including dd at 3.77 ppm, $J = 1.4, 0.9$ Hz, 4 H), 1.79 (m, 1H), 1.60 (dtd, $J = 13.1, 11.5, 3.6$ Hz, 1H).

Procedure for the preparation of allene 6. Compound **6** was prepared via NaBH_4 reduction of *cis*-**7**, as described for the preparation of compounds *trans*-**4a-d_l** and *trans*-**9a-d_l**, to give a 1:1 mixture of **4a** and **9a**. This 1:1 mixture of **4a** and **9a** was further reacted with bromoallene **5** as described for the preparation of **1a** to give a 1:1 mixture of compounds **1a** and **6**. Compound **6**: ^1H NMR (CDCl_3 , 400 MHz): 5.65 (m, 2 H), 5.47 (septet, $J = 2.9$ Hz, 1 H), 3.72 (s, 3 H), 3.71 (s, 3 H), 2.39 (dddd, $J = 12.4, 11.2, 5.0, 2.3$ Hz, 1 H), 2.12-1.97 (m, 4 H), 1.88 (br. d, $J = 12.4$ Hz, 1 H), 1.68 (d, $J = 2.9$ Hz, 6 H), 1.31 (dtd, $J = 12.4, 9.8, 7.2$ Hz, 1 H).

Characterization of allenes 1b-h and compounds 2b-i:

Allene **1b**: ^1H NMR (CDCl_3 , 400 MHz): 5.72 (m, 1H), 5.64 (ddt, $J = 10.4, 3.5, 1.7$ Hz, 1H), 5.45 (quintet, $J = 2.2$ Hz, 1 H), 3.71 (s, 3H), 3.70 (s, 3H), 3.02 (m, 1H), 2.08 (m, 4H), 1.95 (m, 2H), 1.75 (m, 2H), 1.65-1.45 (m, 7H), 1.35 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): 199.0, 170.7, 170.7, 128.8, 128.3, 106.2, 87.1, 62.5, 52.6, 52.5, 41.5, 31.2, 31.0, 27.5, 27.4, 26.2, 25.2, 25.1, 22.6

Allene **1c** (1:1 mixture of diastereoisomers): ^1H NMR (CDCl_3 , 400 MHz): 5.73 (m, 2H), 5.66 (ddt, $J = 10.2, 3.3, 1.6$ Hz, 2H), 5.55 (sextet, $J = 3.0$ Hz, 1 H), 5.53 (sextet, $J = 3.0$ Hz, 1 H), 3.71 (s, 3H), 3.70 (s, 3H), 3.69 (s, 3H), 3.69 (s, 3H), 3.00 (m, 2H), 1.94 (m, 8H), 1.77 (m, 4H), 1.66 (d, $J = 3.0$ Hz, 3H), 1.65 (d, $J = 3.0$ Hz, 3H), 1.58-1.32 (m, 4H), 0.97 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): 201.3 (2C), 170.7 (2C), 170.6 (2C), 128.8 (2C), 128.3 (2C), 105.5 (2C), 89.3 (2C), 62.5, 62.4, 52.6, 52.5, 52.4 (2C), 41.7, 41.4, 27.2, 27.0, 25.2 (2C), 25.1 (2C), 22.5 (2C), 18.8, 18.4, 12.2 (2C).

Allene **1d**: (1:1 mixture of diastereoisomers): ^1H NMR (CDCl_3 , 400 MHz): 5.72 (m, 2H), 5.68 (m, 2H), 5.56 (qd, $J = 2.9, 2.5$ Hz, 1 H), 5.53 (qd, $J = 2.9, 2.5$ Hz, 1 H), 3.71 (s, 6H), 3.70 (s, 6H), 2.99 (m, 2H), 2.11 (m, 2H), 1.96 (m, 4H), 1.78 (m, 4H), 1.67 (dd, $J = 2.9, 0.6$ Hz, 3H), 1.65 (dd, $J = 2.9, 0.6$ Hz, 3H), 1.53 (m, 2H), 1.32 (m, 2H), 1.00 (s, 6H), 0.98 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): 200.6, 200.5, 170.7, 170.6, 170.5 (2C), 128.9, 128.8, 128.4, 128.3, 109.9 (2C), 89.6 (2C),

62.5, 62.4, 52.5 (2C), 52.4 (2C), 41.8, 41.4, 32.3 (2C), 25.2 (2C), 25.1 (2C), 22.5 (2C), 21.5 (2C), 21.4, 21.3, 17.0, 16.6.

Allene **1e**: ^1H NMR (CDCl_3 , 400 MHz): 5.80 (dq, $J = 5.8, 2.2$ Hz, 1H), 5.63 (dq, $J = 5.8, 2.2$ Hz, 1H), 5.39 (septet, $J = 2.9$ Hz, 1H), 3.70 (s, 3H), 3.70 (s, 3H), 3.52 (m, 1H), 2.28 (m, 2H), 2.05 (m, 1H), 1.77 (m, 1H), 1.66 (d, $J = 2.9$ Hz, 3H), 1.66 (d, $J = 2.9$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 202.3, 171.0, 170.9, 133.1, 131.2, 99.1, 87.5, 62.4, 52.6 (2C), 51.3, 32.3, 25.7, 20.3, 20.2.

Allene **1f**: ^1H NMR (CDCl_3 , 400 MHz): 5.77 (dtd, $J = 11.2, 6.5, 2.2$ Hz, 1H), 5.71 (dd, $J = 11.2, 4.2$ Hz, 1H), 5.46 (septet, $J = 2.9$ Hz, 1H), 3.73 (s, 6H), 3.10 (br d, $J = 10.6$ Hz, 1H), 2.15 (br dd, $J = 11.7, 5.6$ Hz, 2H), 2.00 (m, 1H), 1.72 (m, 2H), 1.68 (d, $J = 2.9$ Hz, 3H), 1.67 (d, $J = 2.9$ Hz, 3H), 1.57 (m, 1H), 1.22 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): 202.6, 171.0, 170.9, 134.3, 131.0, 99.5, 88.2, 62.9, 52.7 (2C), 44.6, 31.7, 30.3, 28.4, 26.5, 20.2, 20.1.

Allene **1g**: ^1H NMR (CDCl_3 , 400 MHz): 5.69 (dddd, $J = 10.3, .3, 7.3, 1.3$ Hz, 1H), 5.48 (m, 2H), 3.71 (s, 3H), 3.70 (s, 3H), 3.33 (ddd, $J = 12.1, 9.3, 3.4$ Hz, 1H), 2.27 (m, 1H), 2.04 (ddd, $J = 13.5, 7.3, 4.0$ Hz, 1H), 1.76-1.61 (m, 8H), 1.51 (m, 2H), 1.30 (m, 4 H). ^{13}C NMR (CDCl_3 , 100 MHz): 202.4, 171.0, 170.9, 130.5, 129.7, 99.2, 88.1, 62.3, 52.6, 52.5, 41.5, 31.7, 29.7, 26.8, 26.4, 26.0, 20.2, 20.1.

Allene **1h**: ^1H NMR (CDCl_3 , 400 MHz): 5.69 (ddt, $J = 17.3, 10.2, 7.1$ Hz, 1H), 5.48 (septet, $J = 3.0$ Hz, 1H), 5.07 (br.d, $J = 17.3$ Hz, 1H), 5.05 (br.d, $J = 10.2$ Hz, 1H), 3.71 (s, 6H), 2.72 (dt, $J = 7.1, 1.4$ Hz, 2H), 1.69 (d, $J = 2.9$ Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): 201.9, 170.9 (2C), 133.1, 118.7, 100.2, 88.4, 58.5, 52.8 (2C), 39.0, 20.2 (2C).

Compound **2b**: ^1H NMR (CDCl_3 , 400 MHz): 5.96 (dddd, $J = 10.3, 4.0, 2.4, 1.5$ Hz, 1 H), 5.87 (m, 1 H), 5.77 (ddt, $J = 10.3, 5.1, 2.6$ Hz, 1 H), 5.62 (d, $J = 2.4$ Hz, 1 H), 3.73 (s, 3 H), 3.69 (s, 3 H), 3.65 (m, 1 H), 3.23 (ddd, $J = 10.3, 6.8, 5.2$ Hz, 1 H), 2.25 (m, 1 H), 2.14 (m, 3 H), 1.95 (m, 2 H), 1.69-1.43 (m, 6 H). ^{13}C NMR (CDCl_3 , 100 MHz): 171.4, 170.9, 151.3, 132.5, 128.1, 127.3, 126.8, 120.1, 68.5, 52.8, 52.4, 44.2, 42.5, 27.0, 25.8, 23.4, 22.8, 22.3, 21.9.

Compound **2c**: ^1H NMR (CDCl_3 , 400 MHz): 5.91 (dddd, $J = 10.2, 3.8, 2.4, 1.5$ Hz, 1 H), 5.79 (ddt, $J = 10.2, 5.0, 2.5$ Hz, 1 H), 5.68 (d, $J = 2.5$ Hz, 1 H), 5.05 (q, $J = 1.5$ Hz, 1 H), 5.03 (broad s, 1 H), 3.74 (s, 3 H), 3.70 (s, 3 H), 3.66 (m, 1 H), 3.24 (ddd, $J = 11.3, 6.6, 4.8$ Hz, 1 H), 2.26 (qtd, $J = 7.3, 1.5, 0.7$ Hz, 2 H), 1.96 (m, 2 H), 1.45 (m, 2 H), 1.05 (t, $J = 7.3$ Hz, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz): 171.0, 170.6, 150.5, 145.0, 128.3, 126.2, 122.6, 112.6, 68.7, 52.9, 52.5, 44.6, 42.7, 27.9, 23.5, 21.9, 12.8. – Anal. Calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_4$: C, 70.32; H, 7.64. Found: C, 70.51; H, 7.66.

Compound **E-2c'**: ^1H NMR (CDCl_3 , 400 MHz): 5.92 (dddd, $J = 10.2, 3.8, 2.4, 1.5$ Hz, 1 H), 5.78 (ddt, $J = 10.2, 4.9, 2.6$ Hz, 1 H), 5.67 (qq, $J = 6.9, 1.4$ Hz, 1 H), 5.58 (d, $J = 2.6$ Hz, 1 H), 3.73 (s, 3 H), 3.69 (s, 3 H), 3.66 (m, 1 H), 3.23 (ddd, $J = 12.3, 6.6, 5.0$ Hz, 1 H), 1.96 (m, 2 H), 1.81 (kvint, $J = 1.1$ Hz, 3 H), 1.72 (broad d, $J = 7.0$ Hz, 3 H), 1.46 (m, 2 H). ^{13}C NMR (CDCl_3 , 100 MHz): 171.3, 170.8, 152.4, 131.2, 128.2, 126.6, 124.5, 120.8, 68.5, 52.8, 52.4, 44.3, 42.6, 23.5, 21.9, 15.0, 14.1.

Compound **Z-2c'**: ^1H NMR (CDCl_3 , 400 MHz): 5.81 (m, 1 H), 5.66 (ddt, $J = 10.2, 4.0, 2.0$ Hz, 1 H), 5.46 (d, $J = 2.9$ Hz, 1 H), 5.42 (qq, $J = 6.8, 1.5$ Hz, 1 H), 3.75 (s, 3 H), 3.70 (s, 3 H), 3.60 (m, 1 H), 3.20 (ddd, $J = 13.2, 6.8, 4.2$ Hz, 1 H), 1.98 (m, 2 H), 1.76 (kvint, $J = 1.5$ Hz, 3 H), 1.61 (dq, $J = 6.8, 1.5$ Hz, 3 H), 1.42 (m, 1 H), 1.32 (m, 1 H). ^{13}C NMR (CDCl_3 , 100 MHz): 170.9 (2C), 150.5, 131.7, 128.6, 125.9, 123.6, 122.6, 69.2, 52.8, 52.4, 46.1, 43.1, 24.0, 23.3, 22.1, 14.8.

Compound **2d**: ^1H NMR (CDCl_3 , 400 MHz): 5.80 (m, 2 H), 5.65 (d, $J = 2.6$ Hz, 1 H), 5.01 (t, $J = 1.3$ Hz, 1 H), 4.96 (s, 1 H), 3.74 (s, 3 H), 3.70 (s, 3 H), 3.65 (m, 1 H), 3.23 (ddd, $J = 11.5, 6.8, 4.9$ Hz, 1 H), 2.54 (septet d, $J = 6.8, 1.1$ Hz, 1 H), 1.97 (m, 2 H), 1.50-1.35 (m, 2 H), 1.10 (d, $J = 6.8$ Hz, 3 H), 0.99 (d, $J = 6.8$ Hz, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz): 171.0, 170.7, 151.2, 150.2, 128.3, 126.1, 122.1, 110.5, 68.8, 52.7, 52.4, 45.2, 42.8, 32.1, 23.7, 22.8, 22.0, 21.2.

Compound **2d'**: ^1H NMR (CDCl_3 , 400 MHz): 5.79 (m, 1 H), 5.60 (ddt, $J = 10.1, 4.0, 2.0$ Hz, 1 H), 5.36 (dd, $J = 3.1, 0.7$ Hz, 1 H), 3.75 (s, 3 H), 3.69 (s, 3 H), 3.57 (m, 1 H), 3.18 (ddd, $J = 13.0, 6.3, 4.4$ Hz, 1 H), 1.98 (m, 2 H), 1.69 (m, 9 H), 1.41 (m, 1 H), 1.32 (m, 1 H). ^{13}C NMR (CDCl_3 , 100

MHz): 171.1, 170.9, 153.0, 129.3, 128.3, 126.2, 124.2, 121.8, 69.2, 52.7, 52.3, 46.4, 43.0, 24.1, 22.1, 21.9, 20.4, 18.1.

Compound **2e**: ^1H NMR (CDCl_3 , 400 MHz): 5.72 (dq, $J = 5.9, 2.5$ Hz, 1 H), 5.60 (d, $J = 1.8$ Hz, 1 H), 5.40 (dq, $J = 5.9, 2.3$ Hz, 1 H), 5.08 (s, 1 H), 5.00 (s, 1 H), 4.29 (ddq, $J = 7.8, 3.3, 2.3$ Hz, 1 H), 3.77-3.72 (m, including s at 3.73, 7 H), 2.63 (ddq, $J = 17.2, 9.2, 2.3$ Hz, 1 H), 2.43 (dddd, $J = 17.2, 5.5, 3.3, 2.3$ Hz, 1 H), 1.93 (s, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz): 171.3 (2C), 151.6, 138.3, 132.6, 128.7, 122.5, 116.1, 69.9, 54.7, 52.4 (2C), 47.4, 38.4, 21.0.

Compound **2e'**: ^1H NMR (CDCl_3 , 400 MHz): 5.88 (ddd, $J = 5.9, 4.4, 2.5$ Hz, 1 H), 5.68 (d, $J = 1.9$ Hz, 1 H), 5.63 (ddd, $J = 5.7, 4.3, 2.1$ Hz, 1 H), 5.13 (s, 1 H), 5.07 (s, 1 H), 4.10 (dt, $J = 7.5, 2.4$ Hz, 1 H), 3.77 (dt, $J = 9.9, 7.0$ Hz, 1 H), 3.74 (s, 3 H), 3.72 (s, 3 H), 2.55 (ddt, $J = 16.9, 9.9, 2.2$ Hz, 1 H), 2.04 (ddd, $J = 16.9, 5.1, 2.7$ Hz, 1 H), 1.92 (s, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz): 171.2, 171.0, 149.6, 138.7, 131.3, 130.5, 123.0, 115.9, 69.3, 57.1, 53.1, 52.5, 45.7, 35.6, 21.1.

Compound **2f**: ^1H NMR and ^{13}C NMR were in accordance with those previously reported (Franzén, J.; Löfstedt, J.; Dorange, I.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2002**, *124*, 11246.).

Compound **2g**: ^1H NMR (CDCl_3 , 400 MHz): 5.78 (d, $J = 2.2$ Hz, 1 H), 5.64 (ddd, $J = 10.3, 8.0, 1.1$ Hz, 1 H), 5.49 (tdd, $J = 10.3, 6.6, 1.5$ Hz, 1 H), 5.09 (s, 1 H), 5.02 (s, 1 H), 3.86 (ddt, $J = 9.9, 8.0, 1.9$ Hz, 1 H), 3.77 (s, 3 H), 3.69 (s, 3 H), 2.48 (dq, $J = 13.2, 9.9$ Hz, 1 H), 2.31 (ddd, $J = 11.0, 9.1, 2.2$ Hz, 1 H), 2.14 (ddd, $J = 13.2, 10.8, 2.2$ Hz, 1 H), 2.02 (m, 1 H), 1.90 (s, 3 H), 1.82 (ddt, $J = 14.3, 10.2, 3.9$ Hz, 1 H), 1.63 (m, 2 H), 1.36 (m, 2 H). ^{13}C NMR (CDCl_3 , 100 MHz): 171.7, 170.7, 151.5, 138.1, 134.3, 127.6, 125.4, 116.3, 68.2, 55.7, 52.7, 52.5, 48.1, 29.1, 27.7, 25.4, 24.3, 21.2.

Compound **2h**: ^1H NMR (CDCl_3 , 400 MHz): 6.05 (d, $J = 1.5$ Hz, 1 H), 5.19 (br.s, 1 H), 5.16 (br.s, 2 H), 5.04 (q, $J = 1.8$ Hz, 1 H), 3.74 (s, 6 H), 3.22 (t, $J = 1.8$ Hz, 2 H), 1.95 (dd, $J = 1.8, 0.9$ Hz, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz): 171.1 (2C), 148.9, 148.2, 137.6, 130.9, 116.8, 106.8, 63.3, 53.1 (2C), 39.5, 23.0.

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Compound **2i**: ^1H NMR (CDCl_3 , 400 MHz): 5.70 (d, $J = 2.4$ Hz, 1 H), 5.60 (dd, $J = 3.9, 2.0$ Hz, 1 H), 5.07 (s, 1 H), 5.00 (s, 1 H), 3.84 (m, 1 H), 3.74 (s, 3 H), 3.70 (s, 3 H), 3.28 (ddd, $J = 9.7, 6.9, 5.5$ Hz, 1 H), 2.24 (dddt, $J = 17.2, 8.6, 6.4, 2.4$ Hz, 1 H), 1.92 (s, 3 H), 1.89 (dt, $J = 17.2, 4.6$ Hz, 1 H), 1.66 (m, 2 H), 1.21 (s, 9 H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.0, 170.9, 170.5, 149.8, 149.6, 138.5, 123.7, 115.2, 112.9, 68.1, 53.0, 52.7, 43.9, 41.9, 39.0, 27.3 (3C), 25.2, 22.3, 21.7.