Supporting Information

An Unexpectedly Mild Thermal Alder-Ene type Cyclization of Enallenes

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S2-S6 Experimental and Spectral data
S7-S32 Copies of $^1$H and $^{13}$C NMR spectra
**Experimental**

**General.** Commercially available chemicals were used without further purification. The microwave heating was performed in a Smith Creator (Biotage AB, Uppsala, Sweden). Merck Silica gel 60 (240-400 mesh) was used for flash column chromatography. $^1$H-NMR (400 or 300 MHz) and $^{13}$C NMR (100 and 75 MHz) spectra were recorded with chloroform-$d_1$ (7.26 ppm $^1$H, 77 ppm $^{13}$C) as internal standard, unless otherwise stated. The preparative HPLC used was a Bischoff HPLC compact pump with a refractive index detector and column; Kromasil 100 SIL 5µm (250 x 20 mm).

Substrates 1a-d and 1g-j were prepared according to previously described procedure in reference 5.

Substrates 1e and f were prepared according to previously described procedure in reference 6.

**Compound 2b.** The reaction was carried out as in the general procedure, except that the reaction time was 36 h, to give regioisomers 2b and 2b’ (ratio 62:38), contaminated with byproduct 3b (2b:3b = 80:20) in a total yield of 87%. A sample of 2b, contaminated with a small amount of 3b, was obtained by preparative HPLC. $^1$H NMR (CDCl$_3$, 300 MHz) of 2b: $\delta$ 5.68 (s, 1H), 5.04 (br s, 1H), 5.03 (s, 1H), 3.72 (br s, 6H), 3.08 (td, $J = 6.8, 5.2, 1H$), 2.95 (m 1H), 2.27 (q, $J = 7.42, 2H$), 1.83 (m, 2H) 1.60 (m, 2H), 1.44 (m, 2H) 1.35-1.20 (m, 2H), 1.08 (t, $J = 7.47, 3H$); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 171.9, 171.2, 152.5, 144.6, 123.3, 112.8, 67.9, 52.8, 52.5, 44.1, 43. 0, 27.9, 27.2, 24.3, 23.6, 22.7, 13.0 ppm. A pure sample of 2b’ was contained by preparative HPLC. $^1$H NMR (CDCl$_3$, 300 MHz) of 2b’: $\delta$ 5.67 (q, $J = 6.8$ Hz, 1H), 5.55 (s, 1H), 3.71 (s, 6H), 3.07 (td, $J = 7.0, 4.2$ Hz, 1H), 2.90 (m, 1H), 1.90 (m, 2H), 1.80 (s, 3H), 1.72 (d, $J = 7.0$ Hz, 3H), 1.62 (m, 1H), 1.47 (m, 2H), 1.23 (m, 2H), 1.03 (m, 1H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 172.3, 171.5, 154.8, 130.8, 124.7, 121.1, 67.6, 52.7, 52.5, 43.8, 43.0, 28.6, 24.3, 23.9, 22.5, 14.1 (2C) ppm.
3b (distinguishable peaks in mixture with 2b): $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 5.51 (d, $J$ = 2.5 Hz, 1H), 3.29 (m, 1H), 3.15 (m, 1H) ppm.

**Compound 2c.** The reaction was carried out as in the general procedure, to give 2c in 88% total yield. $^1$H NMR (CDCl$_3$, 300 MHz) of 2c: $\delta$ 5.86 (t, $J$ = 4.0, 1H), 5.53 (s, 1H), 3.71 (s, 6H), 3.07 (td, $J$ = 7.0, 4.0, 1H), 2.88 (m, 1H) 2.16 (m, 4H), 1.95 (dq, $J$ = 14.4, 4.2, 1H), 1.84 (m, 1H), 1.73-1.40 (m, 7H), 1.22 (m, 2H), 1.03 (m, 1H) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 172.4, 171.6, 153.9, 132.0, 127.5, 120.3, 67.6, 52.7, 52.5, 43.8, 42.9, 28.8, 26.2, 25.9, 24.3, 23.9, 22.7, 22.5, 22.3 ppm.

**Compound 2d.** The reaction was carried out as in the general procedure, except that the reaction time was 108 days, to give 2d and 3d (ratio 95:5) in 86% total yield. A pure sample of 2d was obtained by preparative HPLC. $^1$H NMR (CDCl$_3$, 400 MHz) of 2d: $\delta$ 5.64 (s, 1H), 5.04 (s, 1H), 5.02 (s, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 2.97-3.15 (m, 2H) 1.92 (s, 3H), 1.79 (m, 1H), 1.78 (q, $J$ = 5.5, 1H) 1.57 (dd, $J$ = 18.8, 14.0, 1H), 1.3-0.93 (m, 3H), 0.92 (s, 3H), 0.82 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 172.1, 171.5, 153.4, 138.3, 123.7, 115.2, 68.3, 52.8, 52.6, 42.6, 41.4, 41.1, 35.5, 31.9, 29.6, 25.5, 21.0, 20.8 ppm.

3d (distinguishable peaks in mixture with 2d): $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 5.49 (d, $J$ = 2.6 Hz, 1H), 3.47 (m, 1H), 3.25 (m, 1H), 2.61 (dt, $J$ = 7.1, 2.3 Hz, 1H), 0.97 (s, 3H), 0.88 (s, 3H) ppm.

**Compound 2e.** The reaction was carried out as in the general procedure, to give 2e and 3e (ratio 90:10) in 82% total yield. A pure sample of 2e was obtained by preparative HPLC. $^1$H NMR (CDCl$_3$, 400 MHz) of 2e: $\delta$ 5.70 (s, 1H), 5.06 (s, 1H), 4.97 (s, 1H), 4.93 (tt, $J$ = 4.5, 3.7 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.18 (m, 2H), 2.05 (dt, $J$ = 14.4, 4.8 Hz, 1H), 1.93 (s, 3H), 1.90 (m, 1H), 1.76 (m, 1H), 1.67-1.40 (m, 3H), 1.21 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 178.0, 171.8, 171.0, 152.7, 138.1, 124.3, 115.4, 68.9, 68.1, 52.9, 52.7, 42.3, 40.0, 39.1, 31.8, 27.4 (3 C), 26.6, 21.0, 19.6 ppm.
**3e** (distinguishable peaks in mixture with **2e**): $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 5.47 (d, $J = 2.5$ Hz), 1.25 (s, 9H ppm).

**Compound 2f.** The reaction was carried out as in the general procedure above, to give **2f** and **3f** (ratio 81:19) in 72% total yield. A pure sample of **2f** was contained by preparative HPLC.

$^1$H NMR (CDCl$_3$, 400 MHz) of **2f**: $\delta$ 7.99 (d, $J = 7.9$ Hz, 2H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.44 (app. t, $J = 7.9$ Hz, 2H), 5.71 (s, 1H), 5.08 (s, 1H), 5.07 (s, 1H), 4.99 (tt, $J = 10.2$, 4.1 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.15 (m, 2H), 2.35-2.16 (m, 2H), 1.97-1.82 (m, 2H), 1.93 (s, 3H), 1.55 (m, 1H), 1.30 (m, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 171.8, 171.1, 166.2, 152.4, 137.8, 132.9, 130.8, 129.7 (2 C), 128.4 (2 C), 124.2, 115.8, 72.4, 67.7, 53.0, 52.8, 43.3, 42.0, 33.8, 28.2, 22.1, 20.9 ppm.

$^3$f (distinguishable peaks in mixture with **2f**): $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 5.58 (d, $J = 2.6$ Hz, 1H), 3.42 (m, 2H), 2.70 (m, 1H), 1.42 (s, 3H), 1.28 (s, 3H ppm).

**Compound 2g.** The reaction was carried out as in the general procedure above, except the reaction time was 72 h, to give stereoisomers *trans*-**2g** and *cis*-**2g'** (ratio 70:30), contaminated with small amounts of byproduct **3g** (**2g**: **3g** = 95:5) in a total yield of 81%. A pure sample of *trans*-**2g** was contained by preparative HPLC.

$^1$H NMR (CDCl$_3$, 300 MHz) of *trans*-**2g**: $\delta$ 5.67 (d, $J = 1.9$ Hz, 1H), 5.01 (t, $J = 1.5$ Hz, 1H), 4.94 (s, 1H), 3.77 (s, 3H), 3.68 (3H), 2.89 (ddddd, $J = 11.0$, 8.6, 3.9, 1.8 Hz, 1H), 2.66 (ddd, $J = 12.2$, 8.6, 4.0 Hz, 1H), 2.26 (dt, $J = 16.4$, 6.3, 4.1 Hz, 1H), 2.06 (m, 1H), 1.89 (s, 3H) 1.76-1.47 (m, 6H), 1.30 (m, 1H), 1.11 (m, 1H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 172.0, 171.2, 153.6, 139.1, 123.8, 114.3, 69.0, 52.6, 52.3, 51.1, 49.0, 32.7, 29.4, 28.4, 28.3, 25.8, 21.7 ppm. $^1$H NMR (CDCl$_3$, 300 MHz) of *cis*-**2g'**: $\delta$ 5.66 (s, 1H) 5.06 (t, $J = 1.3$ Hz, 1H), 4.99 (s, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 3.19 (ddd, $J = 12.5$, 8.8, 6.1 Hz, 1H), 3.01 (app. t, $J = 9.9$ Hz, 1H), 2.12 (ddd, $J = 13.5$, 9.5, 6.0 Hz, 1H), 1.92 (s, 3H), 1.91-1.72 (m, 7H), 1.47-1.13 (m, 2H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 152.7, 123.8, 115.2, 52.7, 52.4, 50.7, 48.7, 31.8, 31.3, 29.8, 29.0, 28.9, 27.1, 21.1 ppm.

$^3$g (distinguishable peaks in mixture with **2g**): $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 5.33 (d, $J = 2.5$ Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 1.49 (s, 3H), 1.25 (s, 3H ppm).
Compound 2h. The reaction was carried out as in the general procedure, to give 2h and 3h (ratio 65:35) in 77% total yield. Pure samples of 2h and 3h were obtained by preparative HPLC. $^1$H NMR (CDCl$_3$, 400 MHz) of 2h: $\delta$ 5.59 (s, 1H), 5.04 (s, 1H), 5.00 (s, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.46 (m, 1H), 3.41 (td, $J = 9.1, 7.8$ Hz, 1H), 2.00 (m, 1H), 1.92 (s, 3H), 1.74 (m, 1H), 1.65 (qd, $J = 5.4, 3.0$ Hz, 1H), 1.43 (m, 2H), 1.09 (m, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 171.2, 151.9, 138.5, 122.4, 116.0, 68.7, 52.9, 52.2, 49.6, 47.8, 32.2, 29.9, 27.2, 21.0 ppm.

$^1$H NMR (CDCl$_3$, 400 MHz) of 3h: $\delta$ 5.53 (d, $J = 1.3$ Hz, 1H), 3.77 (ddd, $J = 7.2, 5.4, 2.0$ Hz, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 3.23 (ddd, $J = 8.5, 5.1, 2.6$ Hz, 1H) ppm.

Compound 2i. The reaction was carried out as in the general procedure, except the reaction time was 72 h, to give 2i and 3i (ratio 85:15) in 35% total yield. $^1$H NMR (CDCl$_3$, 300 MHz) of 2i: $\delta$ 5.71 (s, 1H), 5.06 (t, $J = 1.2$ Hz, 1H), 5.03 (s, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.10 (m, 1H), 2.71 (dd, $J = 13.7, 8.6$ Hz, 1H), 2.24 (dd, $J = 13.7, 2.9$ Hz, 1H), 1.93 (s, 3H), 1.13 (d, $J = 7.0$ Hz, 3H) ppm.

$^1$H NMR (CDCl$_3$, 300 MHz) of 3i: $\delta$ 5.40 (d, $J = 2.4$ Hz, 1H), 3.25 (m, 1H), 2.9 (dd, $J = 13.0, 6.7$ Hz, 1H), 2.10 (dd, $J = 9.3, 8.2$ Hz, 1H), 2.02 (dd, $J = 13.0, 6.6$ Hz, 1H), 1.36 (dd, $J = 9.3, 7.3$ Hz, 1H), 1.28 (s, 3H), 1.21 (s, 3H) ppm.

Compound 4. Dimethyl (2-cyclohexenyl)malonate (100 mg, 0.47 mmol) was added to a suspension of sodium hydride (20 mg, 0.49 mmol) in THF (1 ml, degassed with argon) at room temperature. The reaction mixture was stirred at room temperature for 15 minutes, and then added to a solution of Pd(OAc)$_2$ (3 mg, 0.014 mmol), PPh$_3$ (11 mg, 0.04 mmol) and 1-chloro-3-methyl-2-butene (55 mg, 0.52 mmol) in THF (1.5 ml, degassed with argon). The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with 2 ml of Et$_2$O and sat. NaHCO$_3$-solution. The organic phase was collected and the aqueous phase was extracted with Et$_2$O (3 x 1 ml). The combined organic phases were washed with brine (1 x 1ml), and dried with MgSO$_4$. After evaporation of the solvent, 132 mg of 4 (99% yield) was obtained with no further purification needed. $^1$H NMR (CDCl$_3$, 300
MHz) of 4: δ 5.69 (m, 2H), 5.03 (t, $J = 7.5$ Hz, 1H), 3.69 (s, 3H), 3.67 (s, 3H), 2.89 (m, 1H), 2.65 (d, $J = 7.5$ Hz, 2H), 1.94 (m, 2H), 1.77 (m, 2H), 1.67 (s, 3H), 1.60 (s, 3H), 1.52 (m, 1H), 1.33 (m, 1H); $^{13}$C NMR (CDCl$_3$, 75 MHz): δ 171.6, 171.4, 135.0, 128.5, 128.2, 118.5, 61.7, 52.2, 52.0, 39.5, 31.6, 26.2, 25.1, 24.6, 22.6, 18.0 ppm.

**Compound 5.** A solution of 2a+3a in a ratio 90:10 (111 mg, containing 100 mg, 0.36 mmol of 2a), maleic anhydride (177 mg, 1.8 mmol) and one crystal of 2,6-di-tert-butyl-4-methylphenol (BHT) were dissolved in toluene (2.5 ml) and refluxed for 24 h. The solvent was removed under reduced pressure, followed by flash chromatography (pentane/Et$_2$O 2:1), which afforded 135 mg (93% yield) of 5. $^1$H NMR (CDCl$_3$, 400 MHz) of 5: δ 3.94 (dd, $J = 9.5, 4.9$ Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.45 (br. s, 1H), 3.39 (ddd, $J = 9.8, 9.8, 5.1$ Hz, 1H), 2.94 (td, $J = 6.9, 4.6$ Hz, 1H), 2.77 (m, 1H), 2.47 (d, $J = 7.1$ Hz, 2H), 1.97 (m, 1H), 1.75 (s, 3H), 1.59 (m, 2H), 1.42 (m, 2H), 1.22 (m, 2H), 1.01 (m, 1H). Compound 5 was characterized by an X-ray crystal structure (Figure 2).

![Figure 2. ORTEP drawing of 5. Thermal ellipsoids are drawn at 30% probability level.](image-url)
STANDARD PROTON

Pulse Sequence: zgpru
Solvent: CDCl3
Temp. 25.6 C / 298.1 K
Mercury-400B "n懦6"

Relax. delay 1.088 sec
Pulse 42.5 degrees
Acq. time 2.731 sec
Width 500.0 Hz
16 repetitions

OBSERVE: 399.9356489 MHz
DATA PROCESSING
Line Broadening 0.1 Hz
FT Size 8020
Total time 1 min, 2 sec
Pulse Sequence: si2pol
Solvent: CDCl3
Temp. 25.3 °C / 298.1 K
Mercury=38888 "nml3"
Relax. delay 1.000 sec
Pulse 67.0 degrees
Acq. time 1.815 sec
Width 15781.7 Hz
112 repetitions
OBSERVE Cl3, 75.4215775 MHz
DECOUPLE H1, 239.9473885 MHz
Power 35 dB
continuously on
WALTZ-15 modulated
DATA PROCESSING
Line broadening 1.3 Hz
FT size 1024
Total time 53 min, 4 sec
Pulse Sequence: z2pl
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
File: HF301hplo
INova-500 "nmrS"

Relax. delay 1.000 sec
Pulse 57.3 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE NL 299.9464283 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min. 49 sec

7  6  5  4  3  2  1
ppm

0.57  1.73  4.93  2.00  2.43  1.22  4.90  2.21  3.35  2.05
Pulse Sequence: s2pu 1
Solvent: CDCl3
Temp. 25.0°C / 288.1 K
Mercury-29080 "nucl.3"
Relax. delay 1.000 sec
Pulse 67.6 degrees
Acq. time 1.065 sec
Width 16761.7 Hz
576 repetitions
OBSERVE C13, 75.4215768 MHz
DECOUPLE Hz, 239.3475695 MHz
Power 36 dB
continuously on
VALTE-15 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 121372
Total line 50 min, 4 sec.
STANDARD PROTON

Pulse Sequence: 2DPN
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Mercury-4000B "narc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.731 sec
Width 5000.0 Hz
16 repetitions

OBSERVE H1, 396.935481 MHz
DATA PROCESSING
Line broadening 0.1 Hz
Pt size 65536
Total time 1 min, 2 sec

2h