

Supporting Information for:

Bi(OTf)₃-Catalyzed Cycloisomerization of Aryl-Allenenes

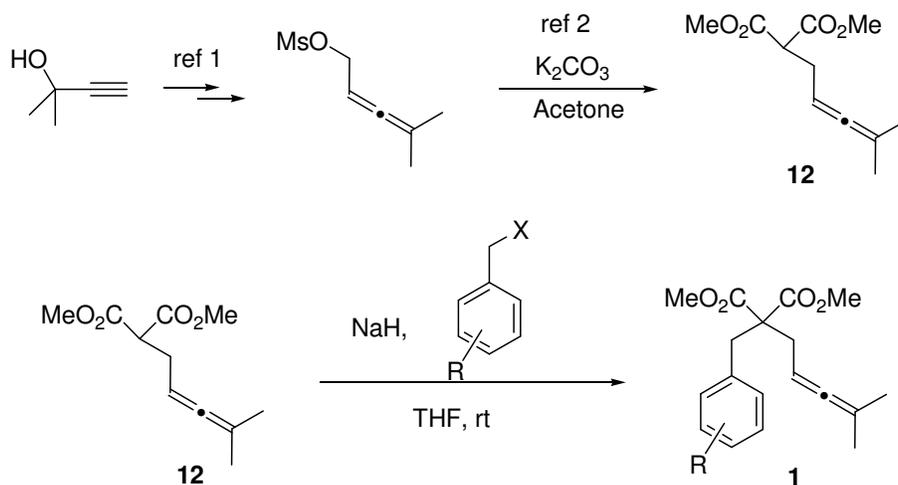
*Gilles Lemière, Bastien Cacciuttolo, Emilie Belhassen and Elisabet Duñach**

General remarks:

Reactions were carried out under an anhydrous atmosphere of Nitrogen. Glassware was oven-dried prior to use. Anhydrous THF and Et₂O were obtained by distillation over sodium/benzophenone under nitrogen and used freshly distilled. Et₃N was distilled from KOH, CH₂Cl₂ from CaH₂. Anhydrous MeNO₂ was obtained by drying over CaCl₂. Other commercially available reagents were used as received unless stated otherwise. Column chromatography was carried out on silica gel (spherical, neutral, 63-200 μm, Geduran Si 60, Merck KGaA). GC/MS analyses were performed with a Shimadzu QP2010S-MS chromatograph (EI, 70 eV) equipped with a SLB-5ms capillary column (thickness: 0.25 mm, length: 30 m, inside diameter: 0.25 mm). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck). NMR spectra (¹H, ¹³C, DEPT, COSY ¹H-¹H and ¹H-¹³C, nOe) were recorded on a BRUKER AC 200 spectrometer. ¹H NMR spectra are referenced at 7.26 ppm for CDCl₃. ¹³C NMR spectra are referenced at 77.00 ppm for CDCl₃. Chemical shifts are given in ppm.

Preparation of Starting Materials

General Scheme for the Synthesis of Allenic Substrate of type 1^{1,2}

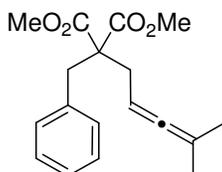


¹ M. Murakami, S. Kadowaki, T. Matsuda *Org. Lett.* **2005**, *7*, 3953-3956.

² C. Kammerer, G. Prestat, T. Gaillard, D. Madec, G. Poli *Org. Lett.* **2008**, *10*, 405-408.

General Procedure 1: To a suspension of sodium hydride (1.2 equiv.) in THF was added dropwise the malonate derivative **12** (1 equiv.) at 0°C. The mixture was allowed to stir for 30 min prior to introduce the benzyl halide (1.2 equiv.) dropwise. After being stirred for 1 h at room temperature, the mixture was quenched at 0°C with a saturated aqueous solution of NH₄Cl. The organic layer was extracted twice with Et₂O, washed with a saturated aqueous solution of NaCl, dried over MgSO₄ and concentrated under reduced pressure. Purification by chromatography on silica gel (pentane/EtOAc: 95/5) afforded the allenic substrate **1**.

Dimethyl 2-benzyl-2-(4-methylpenta-2.3-dienyl)malonate 1a



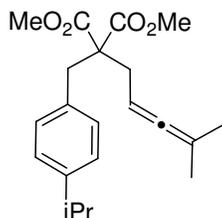
Allenic substrate **1a** was obtained as a colorless oil (1.42 g, 86%) following the general procedure 1 from malonate **12** (1.0 g, 4.71 mmol) and benzyl bromide (616 μL, 5.18 mmol).

¹H NMR (200 MHz, CDCl₃) δ 7.35-7.22 (m, 3H), 7.19-7.07 (m, 2H), 5.03-4.79 (m, 1H), 3.74 (s, 6H), 3.32 (s, *J* = 11.6 Hz, 2H), 2.52 (d, *J* = 7.4 Hz, 2H), 1.74 (d, *J* = 2.9 Hz, 6H).

¹³C NMR (50 MHz, CDCl₃) δ 203.9, 171.1, 136.1, 129.9, 128.2, 126.9, 95.5, 83.0, 59.1, 52.3, 37.6, 31.7, 20.5.

HRMS (ESI⁺) Calcd for [C₁₈H₂₃O₄]⁺: 303.15909; Found: 303.15994.

Dimethyl 2-(4-isopropylbenzyl)-2-(4-methylpenta-2.3-dienyl)malonate 1b



Allenic substrate **1b** was obtained as a colorless oil (738 mg, 91%) following the general procedure 1 from malonate **12** (500 mg, 2.36 mmol) and 1-(bromomethyl)-4-isopropylbenzene (603 mg, 2.83mmol).

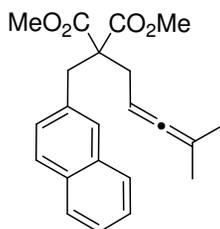
¹H NMR (200 MHz, CDCl₃) δ 7.11 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 5.11-4.65 (m, 1H), 3.71 (s, 6H), 3.25 (s, 2H), 2.85 (sept, *J* = 6.9 Hz, 1H), 2.48 (d, *J* = 7.4 Hz, 2H), 1.71 (d, *J* = 2.9 Hz, 6H), 1.22 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (50 MHz, CDCl₃) δ 203.8, 171.1, 147.3, 133.2, 129.8, 126.2, 95.4, 83.0, 59.1, 52.2, 37.1, 33.6, 31.7, 23.9, 20.5.

MS (EI, 70 eV) : 344 (1). 284 (4). 247 (5). 212 (3). 157 (13). 133 (29). 105 (19). 82 (100). 67 (23). 53 (9). 41 (33).

HRMS (ESI⁺) Calcd for [C₂₁H₂₈O₄Na]⁺: 367.1880; Found: 381.1888.

Dimethyl 2-(4-methylpenta-2.3-dienyl)-2-(naphthalen-2-ylmethyl)malonate **1c**



Allenic substrate **1c** was obtained as a colorless oil (589 mg, 66%) following the General Procedure 1 from malonate **12** (500 mg, 2.36 mmol) and 2-(bromomethyl)naphthalene (625.7, 2.83 mmol).

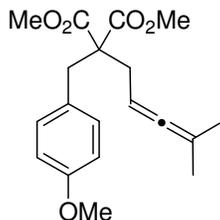
¹H NMR (200 MHz, CDCl₃) δ 7.84 – 7.69 (m, 3H), 7.59 (bs, 1H), 7.51 – 7.37 (m, 2H), 7.21 (dd, *J* = 8.4, 1.7 Hz, 1H), 4.99 – 4.84 (m, 1H), 3.72 (s, 6H), 3.45 (s, 2H), 2.53 (d, *J* = 7.4 Hz, 2H), 1.76 (d, *J* = 2.9 Hz, 6H).

¹³C NMR (50 MHz, CDCl₃) δ 204.0, 171.2, 133.7, 133.3, 132.4, 128.9, 128.0, 127.8, 127.6, 127.6, 126.0, 125.7, 95.6, 83.1, 59.3, 52.4 (2C), 37.7, 31.8, 20.6.

MS (EI, 70 eV) : 352 (11). 270 (15) . 210 (35) . 141 (100). 115 (37) . 82 (22). 67 (22). 59 (22). 41 (50).

HRMS (ESI⁺) Calcd for [C₂₂H₂₄O₄Na]⁺: 375.1567; Found: 355.1567.

Dimethyl 2-(4-methoxybenzyl)-2-(4-methylpenta-2.3-dienyl)malonate **1d**



Allenic substrate **1c** was obtained as colorless oil (669 mg, 85%) following the General Procedure 1 from malonate **12** (500 mg, 2.36 mmol) and 1-(bromomethyl)-4-methoxybenzene (568 mg, 2.830 mmol).

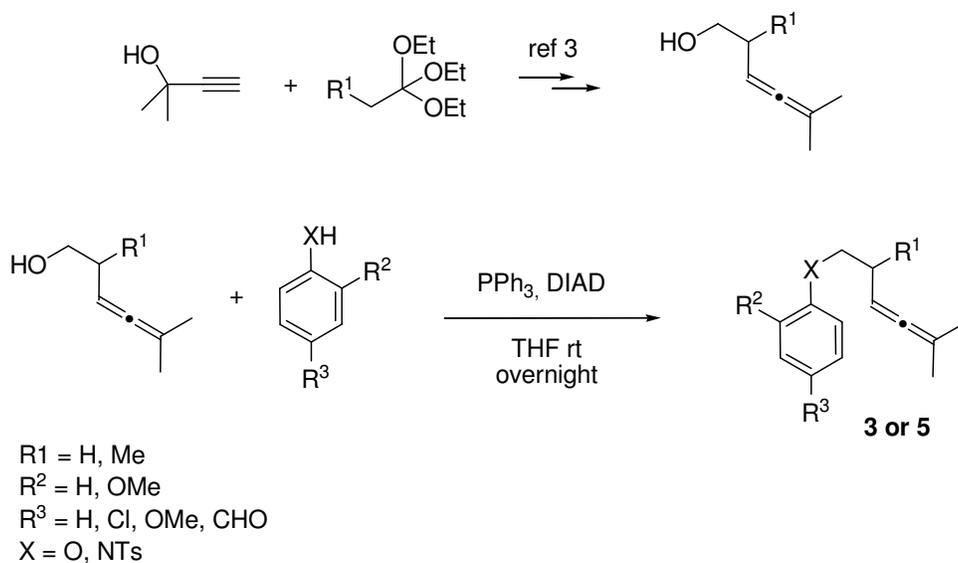
¹H NMR (200 MHz, CDCl₃) δ 7.02 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 4.93-4.78 (m, 1H), 3.77 (s, 3H), 3.70 (s, 6H), 3.22 (s, 2H), 2.47 (d, *J* = 7.4 Hz, 2H), 1.70 (d, *J* = 2.9 Hz, 6H).

¹³C NMR (50 MHz, CDCl₃) δ 203.9, 171.2, 158.5, 130.9, 128.0, 113.7, 95.5, 83.1, 59.2, 55.1, 52.3, 36.8, 31.8, 20.5.

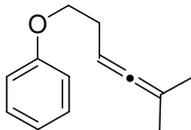
MS (EI, 70 eV) : 332 (2). 250 (31). 190 (15). 121 (100). 77 (23). 67 (9). 59 (8). 41 (15).

HRMS (ESI⁺) Calcd for [C₁₉H₂₄O₅Na]⁺: 355.1516; Found: 355.1517.

General Scheme for the Synthesis of Allenic substrate of type 3 and 5³



(5-methylhexa-3,4-dienyloxy)benzene 3a



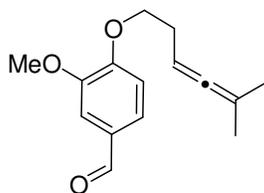
To a solution of 5-methylhexa-3,4-dien-1-ol (300 mg, 2.68 mmol) in THF (12 mL) was added triphenylphosphine (878 mg, 3.35 mmol) and phenol (503 mg, 5.36 mmol). Diisopropyl azodicarboxylate (660 μ L, 3.35 mmol) was subsequently added dropwise over 1 hour at 0°C. The mixture was allowed to stir overnight at room temperature and was concentrated under reduced pressure. Purification by chromatography on silica gel (pentane/Et₂O: 95/5) afforded the allenic substrate **3a** as a colorless oil (714 mg, 72%).

¹H NMR (200 MHz, CDCl₃) δ 7.34 – 7.22 (m, 8H), 6.98 – 6.86 (m, 9H), 5.14 – 4.94 (m, 3H), 4.01 (t, *J* = 6.8 Hz, 6H), 2.43 (q, *J* = 6.7 Hz, 6H), 1.68 (d, *J* = 2.9 Hz, 18H).

¹³C NMR (50 MHz, CDCl₃) δ 202.5, 159.0, 129.4, 120.5, 114.5, 95.7, 84.7, 67.3, 29.2, 20.6.

3-methoxy-4-(5-methylhexa-3,4-dienyloxy)benzaldehyde 3b

³ D. Xu, Z. Lu, Z. Li, S. Ma *Tetrahedron* **2004**, *60*, 11879-11887.



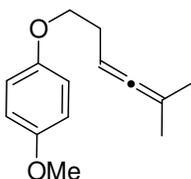
To a solution of 5-methylhexa-3,4-dien-1-ol (320 mg, 2.85 mmol) in THF (12 mL) was added triphenylphosphine (878 mg, 3.35 mmol) and vanillin (814 mg, 5.36 mmol). Diisopropyl azodicarboxylate (660 μ L, 3.35 mmol) was subsequently added dropwise over 1 hour at 0°C. The mixture was allowed to stir overnight at room temperature and was concentrated under reduced pressure. Purification by chromatography on silica gel (pentane/AcOEt: 90/10) afforded the allenic substrate **3b** as a colorless oil (710 mg, 100%).

$^1\text{H NMR}$ (200 MHz, CDCl_3) δ 9.83 (s, 1H), 7.42 (dd, $J = 9.8, 1.7$ Hz, 2H), 6.95 (d, $J = 8.0$ Hz, 1H), 5.13-4.90 (m, $J = 6.0, 2.9$ Hz, 1H), 4.13 (t, $J = 6.9$ Hz, 2H), 3.90 (s, 3H), 2.50 (q, $J = 6.8$ Hz, 2H), 1.65 (d, $J = 2.8$ Hz, 6H).

$^{13}\text{C NMR}$ (50 MHz, CDCl_3) δ 202.6, 190.9, 154.0, 149.8, 129.9, 126.7, 111.3, 109.2, 96.1, 84.2, 68.3, 55.9, 28.8, 20.5.

HRMS (ESI⁺) Calcd for $[\text{C}_{15}\text{H}_{19}\text{O}_3]^+$: 247.1329; Found: 247.1328.

1-methoxy-4-(5-methylhexa-3,4-dienyloxy)benzene 3c

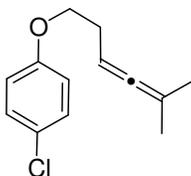


To a solution of 5-methylhexa-3,4-dien-1-ol (300 mg, 2.68 mmol) in THF (12 mL) was added triphenylphosphine (878 mg, 3.35 mmol) and 4-methoxyphenol (664 mg, 5.36 mmol). Diisopropyl azodicarboxylate (660 μ L, 3.35 mmol) was subsequently added dropwise over 1 hour at 0°C. The mixture was allowed to stir overnight at room temperature and was concentrated under reduced pressure. Purification by chromatography on silica gel (pentane/Et₂O: 95/5) afforded the allenic substrate **3c** as a colorless oil (647 mg, 100%).

$^1\text{H NMR}$ (200 MHz, CDCl_3) δ 6.83 (s, 4H), 5.17-4.88 (m, 1H), 3.96 (t, $J = 6.8$ Hz, 2H), 3.77 (s, 3H), 2.40 (q, $J = 6.7$ Hz, 2H), 1.68 (d, $J = 2.9$ Hz, 6H).

$^{13}\text{C NMR}$ (50 MHz, CDCl_3) δ 202.5, 153.7, 153.1, 115.5, 114.6, 95.4, 84.8, 68.2, 55.7, 29.3, 20.6.

1-chloro-4-(5-methylhexa-3,4-dienyloxy)benzene 3d



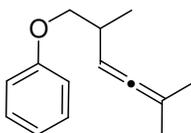
To a solution of 5-methylhexa-3,4-dien-1-ol (300 mg, 2.68 mmol) in THF (12 mL) was added triphenylphosphine (878 mg, 3.35 mmol) and 4-chlorophenol (689 mg, 5.36 mmol).

Diisopropyl azodicarboxylate (660 μ L, 3.35 mmol) was subsequently added dropwise over 1 hour at 0°C. The mixture was allowed to stir overnight at room temperature and was concentrated under reduced pressure. Purification by chromatography on silica gel (pentane/Et₂O: 95/5) afforded the allenic substrate **3d** as a colorless oil (637 mg, 100%).

¹H NMR (200 MHz, CDCl₃) δ 7.33-7.13 (m, 2H), 6.91-6.73 (m, 2H), 5.13-4.89 (m, 1H), 3.97 (t, J = 6.7 Hz, 2H), 2.41 (q, J = 6.6 Hz, 2H), 1.67 (d, J = 2.9 Hz, 6H).

¹³C NMR (50 MHz, CDCl₃) δ 202.5, 157.6, 129.2, 125.3, 115.8, 95.9, 84.6, 67.7, 29.1, 20.6.

(2,5-dimethylhexa-3,4-dienyloxy)benzene **3e**

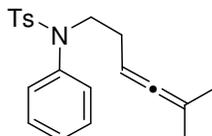


To a solution of 2,5-dimethylhexa-3,4-dien-1-ol (500 mg, 4.0 mmol) in THF (20 mL) was added triphenylphosphine (1.25 g, 4.8 mmol) and phenol (800 mg, 8.0 mmol). Diisopropyl azodicarboxylate (945 μ L, 4.8 mmol) was subsequently added dropwise over 1 hour at 0°C. The mixture was allowed to stir overnight at room temperature and was concentrated under reduced pressure. Purification by chromatography on silica gel (pentane/Et₂O: 95/5) afforded the allenic substrate **3e** as a colorless oil (781 mg, 97%).

¹H NMR (200 MHz, CDCl₃) δ 7.38-7.14 (m, 2H), 7.00-6.79 (m, 3H), 5.15-4.87 (m, 1H), 3.87 (dd, J = 9.0, 6.3 Hz, 1H), 3.73 (dd, J = 8.9, 7.1 Hz, 1H), 2.76-2.42 (m, 1H), 1.74-1.60 (m, 6H), 1.10 (d, J = 6.8 Hz, 3H).

¹³C NMR (50 MHz, CDCl₃) δ 201.3, 159.1, 129.4, 120.5, 114.5, 96.7, 91.2, 72.7, 33.6, 20.7, 20.7, 17.1.

4-methyl-N-(5-methylhexa-3,4-dienyl)-N-phenylbenzenesulfonamide **5**



To a solution of 5-methylhexa-3,4-dien-1-ol (544 mg, 4.85 mmol) in THF (12 mL) was added triphenylphosphine (1.27 g, 4.85 mmol) and *N*-tosylaniline (1 g, 4.05 mmol). Diisopropyl azodicarboxylate (954 μ L, 4.85 mmol) was subsequently added dropwise over 1 hour at 0°C. The mixture was allowed to stir overnight at room temperature and was concentrated under reduced pressure. Purification by chromatography on silica gel (pentane/AcOEt: 95/5) afforded the allenic substrate **5** as a yellowish oil (1.16, 84%).

¹H NMR (200 MHz, CDCl₃) δ 7.39 (d, J = 8.3 Hz, 2H), 7.28-7.09 (m, 5H), 7.03-6.89 (m, 2H), 4.91-4.64 (m, J = 5.9, 2.9 Hz, 1H), 3.50 (t, J = 7.4 Hz, 2H), 2.34 (s, 3H), 1.99 (dt, J = 7.8, 6.8 Hz, 2H), 1.57 (d, J = 2.9 Hz, 6H).

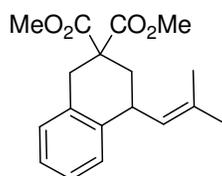
¹³C NMR (50 MHz, CDCl₃) δ 202.3, 143.2, 139.0, 135.3, 129.3, 128.9, 127.8, 127.6, 95.6, 85.0, 50.3, 28.3, 21.5, 20.5.

HRMS (ESI⁺) Calcd for [C₂₀H₂₄NO₂S]⁺: 342.1522; Found: 355.1523.

Cyclized Compounds

General Procedure 2 for Bi(OTf)₃-Catalyzed Cycloisomerization of Allenes : To a solution of allenic substrate (1 equiv.) in nitromethane (0.2 M) at the indicated temperature (rt or reflux according to the tables) was added Bi(OTf)₃ (0.05 equiv. or 0.01 equiv.) under inert atmosphere. After complete consumption of the substrate (TLC monitoring), the reaction mixture was quenched with a saturated aqueous solution of NaHCO₃, extracted thrice with diethyl ether, washed with a saturated aqueous solution of NaCl, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford the cyclized compound.

Dimethyl 4-(2-methylprop-1-enyl)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate 2a



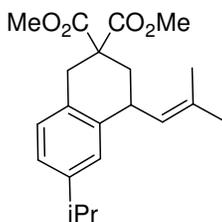
Cyclized product **2a** was obtained as a colorless oil (74.7 mg, 99%) following the General Procedure 2 with allenic substrate **1a** (75.0 mg, 0.25 mmol) and Bi(OTf)₃ (8.0 mg, 0.012 mmol).

¹H NMR (200 MHz, CDCl₃) δ 7.25-7.02 (m, 4H), 5.13 (bd, *J* = 9.2 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.45 (dd, *J* = 16.4, 1.9 Hz, 1H), 3.18 (d, *J* = 17.1 Hz, 1H), 2.53 (ddd, *J* = 13.5, 5.8, 2.2 Hz, 1H), 1.89 (dd, *J* = 13.4, 11.8 Hz, 1H), 1.79 (d, *J* = 0.9 Hz, 3H), 1.75 (d, *J* = 1.1 Hz, 3H).

¹³C NMR (50 MHz, CDCl₃) δ 172.2, 171.3, 138.0, 133.2, 133.1, 128.6, 128.1, 127.7, 126.2, 126.1, 53.6, 52.8, 52.6, 35.2, 35.1, 34.9, 25.7, 17.8.

HRMS (ESI⁺) Calcd for [C₁₈H₂₃O₄]⁺: 303.15909; Found: 303.15964.

dimethyl 6-isopropyl-4-(2-methylprop-1-enyl)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate 2b



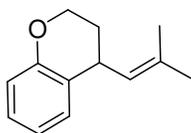
Cyclized product **2b** was obtained as a colorless oil (97 mg, 97%) following the General Procedure 2 with allenic substrate **1b** (100 mg, 0.29 mmol) and Bi(OTf)₃ (9.5 mg, 0.015 mmol).

¹H NMR (200 MHz, CDCl₃) δ 7.12-6.83 (m, 3H), 5.14 (d, *J* = 9.0 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 3.70-3.38 (m, 1H), 3.42 (A of AB, *J* = 17.0 Hz, 1H), 3.14 (B of AB, *J* = 16.4 Hz, 1H), 2.81 (sept, *J* = 7.0 Hz, 1H), 2.50 (ddd, *J* = 13.3, 5.5, 2.0 Hz, 1H), 1.93-1.76 (m, 1H), 1.80 (s, 3H), 1.76 (s, 3H), 1.20 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (50 MHz, CDCl₃) δ 172.3, 171.4, 146.7, 137.7, 133.1, 130.4, 128.5, 127.9, 126.1, 124.1, 53.7, 52.7, 52.6, 35.3, 35.2, 34.6, 33.7, 25.7, 24.1, 23.9, 17.9.

HRMS (ESI⁺) Calcd for [C₂₁H₂₈O₄Na]⁺: 367.1880; Found: 381.1882.

4-(2-methylprop-1-enyl)chroman 4a



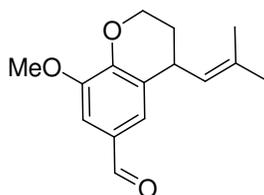
Cyclized product **4a** was obtained as a colorless oil (70 mg, 93%) following the General Procedure 2 from allenic substrate **3a** (75 mg, 0.4 mmol) and Bi(OTf)₃ (2.5 mg, 0.004 mmol).

¹H NMR (200 MHz, CDCl₃) δ 7.16-6.99 (m, 2H), 6.90-6.77 (m, 2H), 5.19 (d, *J* = 5.9 Hz, 1H), 4.31 (ddd, *J* = 10.9, 5.2, 3.7 Hz, 1H), 4.17 (ddd, *J* = 10.9, 9.4, 2.8 Hz, 1H), 3.81-3.69 (m, 1H), 2.12-1.96 (m, 1H), 1.93-1.84 (m, 1H), 1.80 (s, 3H), 1.80 (s, 3H).

¹³C NMR (50 MHz, CDCl₃) δ 154.5, 132.5, 129.5, 127.84 (s), 127.41 (s), 125.72 (s), 120.14 (s), 116.52 (d, *J* = 8.2 Hz), 65.09 (s), 33.95 (s), 29.43 (s), 25.79 (s), 17.99 (s).

MS (EI, 70 eV): 188(50), 173(75), 145(100), 131(65), 115(30), 105(23), 91(36), 77(55), 65(21).

8-methoxy-4-(2-methylprop-1-enyl)chroman-6-carbaldehyde 4b



Cyclized product **4b** was obtained as a colorless oil (67 mg, 67%) following the General Procedure 2 from allenic substrate **3b** (100 mg, 0.4 mmol) and Bi(OTf)₃ (13 mg, 0.020 mmol).

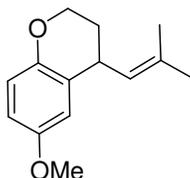
¹H NMR (200 MHz, CDCl₃) δ 9.78 (s, 1H), 7.25 (d, *J* = 1.7 Hz, 1H), 7.22-7.15 (m, 1H), 5.14 (d, *J* = 9.4 Hz, 1H), 4.48 (ddd, *J* = 11.0, 5.3, 3.6 Hz, 1H), 4.30 (ddd, *J* = 11.1, 9.4, 2.9 Hz,

1H), 3.92 (s, $J = 5.6$ Hz, 3H), 3.76 (td, $J = 9.0, 5.8$ Hz, 1H), 2.15-1.98 (m, 1H), 1.94-1.82 (m, 1H), 1.80 (s, 6H).

^{13}C NMR (50 MHz, CDCl_3) δ 191.2, 149.7, 149.0, 133.8, 128.9, 127.2, 126.6, 126.3, 107.1, 66.2, 56.0, 33.7, 28.7, 25.8, 18.1.

HRMS (ESI⁺) Calcd for $[\text{C}_{15}\text{H}_{19}\text{O}_3]^+$: 247.1329; Found: 247.1329.

6-methoxy-4-(2-methylprop-1-enyl)chroman 4c



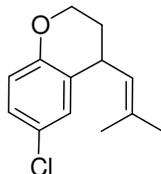
Cyclized product **4c** was obtained as a colorless oil (69 mg, 92%) following the General Procedure 2 from allenic substrate **3c** (75.0 mg, 0.344 mmol) and $\text{Bi}(\text{OTf})_3$ (13 mg, 0.0034 mmol,).

^1H NMR (200 MHz, CDCl_3) δ 6.78-6.53 (m, 3H), 5.16 (bd, $J = 9.4$ Hz, 1H), 4.25 (ddd, $J = 10.8, 5.1, 3.6$ Hz, 1H), 4.10 (ddd, $J = 10.8, 9.5, 2.7$ Hz, 1H), 3.74 (s, 3H), 2.13-1.93 (m, 1H), 1.90-1.79 (m, 1H), 1.78 (s, 3H), 1.78 (s, 3H).

^{13}C NMR (50 MHz, CDCl_3) δ 153.2, 148.5, 132.7, 127.8, 126.5, 117.0, 114.5, 112.9, 65.0, 55.7, 34.3, 29.5, 25.8, 18.0.

MS (EI, 70 eV) : 218(90), 203(63), 175(100), 160(33), 132(27), 115(29), 91(58), 77(56), 55(52), 41(68).

6-chloro-4-(2-methylprop-1-enyl)chroman 3d



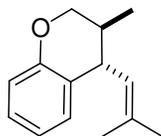
Cyclized product **4d** was obtained as a colorless oil (95 mg, 95%) following the General Procedure 2 from allenic substrate **3d** (100 mg, 0.45 mmol) and $\text{Bi}(\text{OTf})_3$ (15 mg, 0.022 mmol).

^1H NMR (200 MHz, CDCl_3) δ 7.09-6.91 (m, 2H), 6.78-6.62 (m, 1H), 5.22-5.03 (m, 1H), 4.28 (ddd, $J = 10.9, 5.0, 3.7$ Hz, 1H), 4.13 (ddd, $J = 12.2, 9.0, 2.7$ Hz, 1H), 3.67 (td, $J = 9.2, 6.0$ Hz, 1H), 2.08-1.91 (m, 1H), 1.90-1.68 (m, 7H).

^{13}C NMR (50 MHz, CDCl_3) δ 153.1, 133.4, 128.99, 127.4 (2C), 127.0, 124.8, 117.9, 65.3, 34.0, 29.1, 25.8, 18.0.

MS (EI, 70 eV) : 222(75), 207(58), 187(100), 179(61), 165(40), 131(32), 115(48), 103(35), 77(48), 55(52).

trans-3-methyl-4-(2-methylprop-1-enyl)chroman 4e



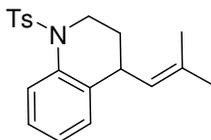
Cyclized product **4e** was obtained as a colorless oil (96 mg, 91%) following the General Procedure 2 from allenic substrate **3e** (106 mg, 0.52 mmol) and Bi(OTf)₃ (16 mg, 0.025 mmol).

¹H NMR (200 MHz, CDCl₃) δ 7.19-6.95 (m, 2H), 6.92-6.74 (m, 2H), 5.09-4.90 (m, 1H), 4.22 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.77 (t, *J* = 10.5 Hz, 1H), 3.30 (t, *J* = 9.7 Hz, 1H), 1.98-1.80 (m, 1H), 1.84 (d, *J* = 1.2 Hz, 3H), 1.78 (d, *J* = 1.2 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H).

¹³C NMR (50 MHz, CDCl₃) δ 154.3, 134.1, 129.6, 127.3, 126.9, 125.2, 120.2, 116.3, 71.1, 42.0, 33.3, 25.9, 18.3, 15.5.

MS (EI, 70 eV) : 202(25), 187(11), 145(100), 115(12), 91(15), 77(10), 69(15)

4-(2-methylprop-1-enyl)-1-tosyl-1,2,3,4-tetrahydroquinoline **6**



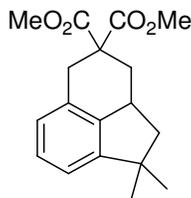
Cyclized product **6** was obtained as a colorless oil (84 mg, 82%) following the General Procedure 2 from allenic substrate **5** (102 mg, 0.29 mmol) and Bi(OTf)₃ (4 mg, 0.006 mmol).

¹H NMR (200 MHz, CDCl₃) δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.34-7.15 (m, 3H), 7.14-6.95 (m, 2H), 4.61 (d, *J* = 9.4 Hz, 1H), 3.97 (dt, *J* = 13.5, 5.0 Hz, 1H), 3.72-3.56 (m, 1H), 3.17 (dt, *J* = 9.1, 6.2 Hz, 1H), 2.38 (s, 3H), 1.82-1.67 (m, 1H), 1.66 (s, 3H), 1.55 (s, 3H), 1.44-1.29 (m, 1H).

¹³C NMR (50 MHz, CDCl₃) δ 143.5, 136.51, 136.3, 134.3, 132.7, 129.5, 128.4, 127.2, 126.6, 125.3, 125.1, 45.4, 35.4, 28.7, 25.6, 21.4, 17.7.

HRMS (ESI⁺) Calcd for [C₂₀H₂₄NO₂S]⁺: 342.1522; Found: 355.1523.

Dimethyl 1.1-dimethyl-1.2.2a.3-tetrahydroacenaphthylene-4.4(5H)-dicarboxylate **9a**



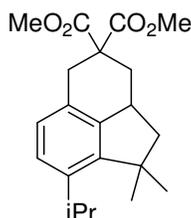
Cyclized product **9a** was obtained as a colorless oil (73.5 mg, 98%) following the General Procedure 2 from allenic substrate **1a** (75 mg, 0.248 mmol) and Bi(OTf)₃ (8.0 mg, 0.0124 mmol).

¹H NMR (200 MHz, CDCl₃) δ 7.20-7.06 (m, 1H), 6.96 (d, *J* = 7.5 Hz, 2H), 3.76 (s, 3H), 3.76 (s, 3H), 3.67 (d, *J* = 17.4 Hz, 1H), 3.01-2.79 (m, 2H), 2.72 (dd, *J* = 12.2, 4.9 Hz, 1H), 2.15 (dd, *J* = 11.6, 6.3 Hz, 1H), 1.73 (t, *J* = 12.4 Hz, 1H), 1.56 (t, *J* = 11.2 Hz, 1H), 1.33 (s, 3H), 1.21 (s, 3H).

¹³C NMR (50 MHz, CDCl₃) δ 172.5, 171.9, 150.9, 141.0, 130.6, 127.4, 124.9, 119.3, 55.2, 52.8, 52.8, 50.2, 43.79, 34.9, 34.4, 32.5, 28.1, 27.5.

HRMS (ESI⁺) Calcd for [C₁₈H₂₃O₄]⁺: 303.15909; Found: 303.15945.

Dimethyl 8-isopropyl-1.1-dimethyl-1.2.2a.3-tetrahydroacenaphthylene-4.4(5H)-dicarboxylate **9b**



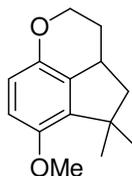
Cyclized product **9b** was obtained as a colorless oil (65 mg, 87%) following the General Procedure 2 from allenic substrate **1b** (75 mg, 0.22 mmol) and Bi(OTf)₃ (7.2 mg, 0.011 mmol).

¹H NMR (200 MHz, CDCl₃) δ 7.08 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 3.76 (s, 6H), 3.61 (d, *J* = 17.1 Hz, 1H), 3.27 (sept, *J* = 6.9 Hz, 1H), 2.93 (d, *J* = 17.2 Hz, 1H), 2.87-2.64 (m, 2H), 2.07 (dd, *J* = 11.7, 6.5 Hz, 1H), 1.76 (t, *J* = 12.2 Hz, 1H), 1.60 (t, *J* = 11.3 Hz, 1H), 1.48 (s, 3H), 1.31 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (50 MHz, CDCl₃) δ 172.5, 172.0, 145.6, 142.8, 140.9, 127.6, 125.6, 125.0, 55.1, 52.8, 52.7, 51.1, 45.0, 34.5, 34.4, 32.4, 29.7, 28.3, 26.2, 24.8, 24.1.

HRMS (ESI⁺) Calcd for [C₂₁H₂₉O₄]⁺: 345.2060; Found: 345.2063.

6-methoxy-5,5-dimethyl-3,3a,4,5-tetrahydro-2H-cyclopenta[de]chromene **10c**



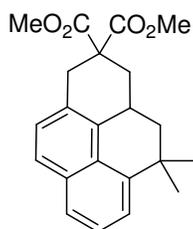
Cyclized product **10c** was obtained as a colorless oil (48 mg, 69%) following the General Procedure 2 from allenic substrate **3c** (70 mg, 0.32 mmol), Bi(OTf)₃ (10 mg, 0.016 mmol) in MeNO₂ (8 mL, 0.02M).

¹H NMR (200 MHz, CDCl₃) δ 6.62 (d, *J* = 8.7 Hz, 1H), 6.53 (d, *J* = 8.6 Hz, 1H), 4.42 (ddd, *J* = 11.1, 3.9, 2.1 Hz, 1H), 4.09 (ddd, *J* = 12.6, 11.2, 2.3 Hz, 1H), 3.76 (s, 3H), 3.16 (dq, *J* = 16.8, 5.6 Hz, 1H), 2.17-2.00 (m, 2H), 1.69-1.50 (m, 2H), 1.45 (s, *J* = 4.7 Hz, 3H), 1.32 (s, 3H).

¹³C NMR (50 MHz, CDCl₃) δ 150.6, 146.9, 138.7, 130.3, 112.9, 112.3, 67.9, 56.6, 51.5, 46.0, 36.2, 29.5, 28.4, 26.2.

MS (EI, 70 eV) : 218(52), 203(100), 175(24), 115(32), 91(30), 77(30).

Dimethyl 5.5-dimethyl-3.3a.4.5-tetrahydropyrene-2.2(1H)-dicarboxylate 11c



Cyclized product **11c** was obtained as a colorless solid (68 mg, 97%) following the General Procedure 2 from allenic substrate **1c** (70 mg, 0.20 mmol), Bi(OTf)₃ (7 mg, 0.010 mmol).

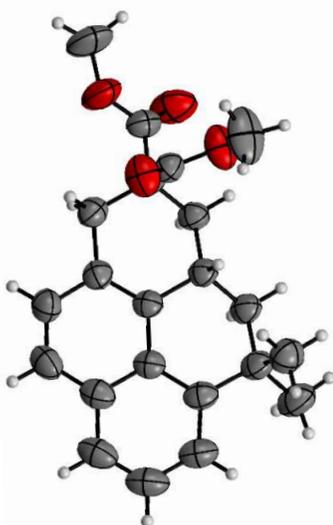
¹H NMR (200 MHz,) δ 7.62-7.48 (m, 2H), 7.45-7.24 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 3.71 (s, 3H), 3.63 (d, *J* = 17.5 Hz, 1H), 3.63 (s, 3H), 3.17 (dd, *J* = 17.1, 2.0 Hz, 1H), 3.01 – 2.79 (m, *J* = 29.1 Hz, 1H), 2.56 (ddd, *J* = 13.0, 4.4, 1.6 Hz, 1H), 1.90 (t, *J* = 12.7 Hz, 1H), 1.78 (dd, *J* = 12.6, 4.2 Hz, 1H), 1.61 (t, *J* = 12.5 Hz, 1H), 1.40 (s, 3H), 1.23 (s, 3H).

¹³C NMR (50 MHz,) δ 172.4, 171.7, 144.2, 132.4, 132.0, 128.6, 128.0, 126.5, 126.5, 125.9, 125.1, 122.0, 53.8, 52.8, 52.8, 44.7, 35.3, 34.9, 34.5, 31.1, 30.9, 29.1.

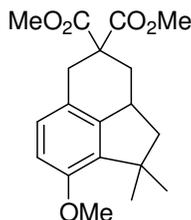
Masse : 352 (14). 292 (16). 277 (20). 233 (100). 217 (16). 203 (32). 191 (16). 178 (10). 101 (5). 59 (34). 44 (7).

HRMS (ESI⁺) Calcd for [C₂₂H₂₅O₄]⁺: 353.1747; Found: 355.1748.

Crystallographic structure of 11c (CCDC 880361)



Dimethyl 8-methoxy-1,1-dimethyl-1,2,2a,3-tetrahydroacenaphthylene-4,4(5H)-dicarboxylate 9d



Cyclized product **9d** was obtained as a colorless oil (72 mg, 96%) following the General Procedure 2 from allenic substrate **1d** (75 mg, 0.23 mmol) and Bi(OTf)₃ (7.4 mg, 0.011 mmol).

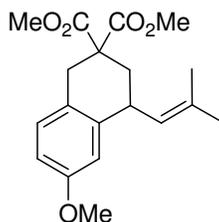
¹H NMR (200 MHz, CDCl₃) δ 6.93 (d, *J* = 8.2 Hz, 2H), 6.66 (d, *J* = 8.3 Hz, 2H), 3.77 (s, 3H), 3.74 (s, 6H), 3.57 (d, *J* = 16.4 Hz, 1H), 2.94-2.74 (m, 1H), 2.85 (d, *J* = 16.4 Hz, 1H), 2.68 (dd, *J* = 12.2, 4.8 Hz, 1H), 2.06 (dd, *J* = 11.7, 6.5 Hz, 1H), 1.74 (t, *J* = 12.5 Hz, 1H), 1.58 (t, 1H), 1.43 (s, 3H), 1.25 (s, 3H).

¹³C NMR (50 MHz, CDCl₃) δ 172.6, 172.0, 154.7, 142.7, 136.0, 126.2, 122.7, 110.4, 55.5, 55.3, 52.8, 52.8, 50.4, 44.7, 35.5, 34.4, 32.0, 28.1, 25.1.

Masse : 332 (23). 317 (14). 285 (6). 273 (44). 213 (100). 197 (52). 181 (16). 165 (25). 154 (14). 129 (30). 115 (31). 99 (11). 77 (15). 59 (50). 44 (57).

HRMS (ESI⁺) Calcd for [C₁₉H₂₄O₅Na]⁺: 355.1516; Found: 355.1518.

dimethyl 6-methoxy-4-(2-methylprop-1-enyl)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate 2f

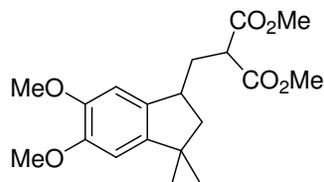


Cyclized product **2d** was obtained as a colorless oil (73 mg, 97%) following the General Procedure 2 from allenic substrate **1d** (75 mg, 0.23 mmol) and TfOH (1 μL, 0.0115 mmol).

¹H NMR (200 MHz, CDCl₃) δ 7.04 (d, *J* = 8.3 Hz, 1H), 6.76-6.58 (m, 2H), 5.12 (d, *J* = 9.2 Hz, 1H), 3.81-3.56 (m, 10H), 3.38 (d, *J* = 16.1 Hz, 1H), 3.10 (d, *J* = 16.0 Hz, 1H), 2.50 (ddd, *J* = 13.4, 5.7, 2.1 Hz, 1H), 1.86 (dd, *J* = 13.9, 12.3 Hz, 1H), 1.76 (dd, *J* = 8.0, 1.0 Hz, 6H).

¹³C NMR (50 MHz, CDCl₃) δ 172.3, 171.3, 158.2, 139.3, 133.4, 129.5, 127.6, 125.3, 113.4, 111.9, 55.1, 53.8, 52.8, 52.6, 35.5, 35.0, 34.2, 25.7, 17.8.

Dimethyl 2-((5,6-dimethoxy-3,3-dimethyl-2,3-dihydro-1H-inden-1-yl)methyl)malonate 13



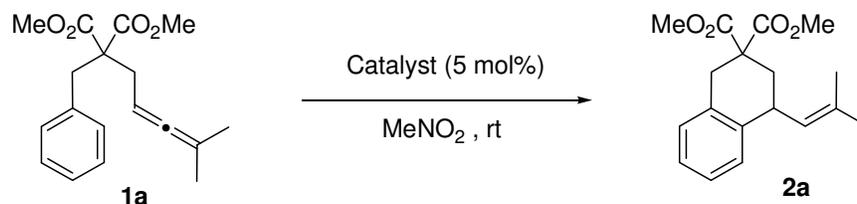
To a solution of veratrol (138 mg, 1.0 mmol) and Bi(OTf)₃ (16 mg, 0.025 mmol) in nitromethane (1 mL) was added over 1 hour at room temperature allene **12** (106 mg, 0.5 mmol) diluted in nitromethane (1 mL). After consumption of the allenic substrate (1 hour by TLC monitoring), the reaction mixture was quenched with a saturated aqueous solution of NaHCO₃, extracted thrice with diethyl ether, washed with a saturated aqueous solution of NaCl, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (pentane/AcOEt: 9/1) to afford the indane **13** (164 mg, 94%) as a colorless oil.

¹H NMR (200 MHz, CDCl₃) δ 6.72 (s, 1H), 6.64 (s, 1H), 3.87 (s, 6H), 3.79 (s, 3H), 3.74 (s, 3H), 3.53 (dd, *J* = 9.9, 5.3 Hz, 1H), 3.17-2.96 (m, 1H), 2.63 (ddd, *J* = 13.9, 10.0, 4.1 Hz, 1H), 2.14 (dd, *J* = 12.2, 7.3 Hz, 1H), 1.88 (ddd, *J* = 13.7, 10.7, 5.3 Hz, 1H), 1.51 (dd, *J* = 12.2, 8.8 Hz, 1H), 1.33 (s, 3H), 1.13 (s, 3H).

¹³C NMR (50 MHz, CDCl₃) δ 170.0, 169.8, 148.6, 148.2, 144.0, 135.8, 106.6, 105.3, 56.1, 52.6, 50.2, 48.1, 43.0, 39.8, 34.7, 29.5, 29.3.

HRMS (ESI⁺) Calcd for [C₁₉H₂₇O₆]⁺: 351.1802; Found: 355.1803.

Screening of Catalysts



Entry ^[a]	Catalyst	Time(h)	Conversion ^[c]	Yield of 2a
1	Bi(OTf)₃	0.5	100%	99%
2	AgOTf	12	16%	13%
3	Cu(OTf) ₂	12	20%	12%
4	Fe(OTf) ₂	12	72%	67%
5	In(OTf) ₃	12	100%	91%
6	Sn(OTf) ₂	12	100%	82%
7	Al(OTf) ₃	12	100%	97%
8	TfOH	0.5	100%	96%

Recycling of the Catalyst

To a solution of allenic substrate **3a** (75 mg, 0.4 mmol) in nitromethane (2 mL) at room temperature was added Bi(OTf)₃ (13 mg, 0.02 mmol) under inert atmosphere. After 10 min, distilled water (2 mL) and diethyl ether (5 mL) were added and the two layers were separated. The organic layer was concentrated under reduced pressure and the residue was purified by column chromatography to afford the cyclized compound **4a** (70 mg, 93% yield). The aqueous layer was evaporated under reduced pressure and the catalyst was quantitatively recovered as a white solid.

A second run, using the recovered Bi(OTf)₃, under the same reaction conditions (rt, 10 min) afforded the cyclized compound **4a** (71 mg, 95% yield) after purification.