

Supporting Information

Synthesis and Utility of 2,2-Dimethyl-2*H*-pyrans: Dienes for Sequential Diels-Alder/retro-Diels-Alder Reactions.

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General remarks. ¹H NMR and ¹³C NMR spectra of CDCl₃ solutions were recorded either at 400 and 100 MHz or at 500 and 125 MHz (Bruker Ac 200 and AMX2-500), respectively. Microwave reactions were conducted in sealed glass vessels (capacity 10 mL) using a CEM Discover microwave reactor. FT-IR spectra were measured in chloroform solutions using a Perkin Elmer FT-IR Spectrum BX spectrophotometer. Mass spectra (low resolution) (EI/CI) were obtained with a Hewlett-Packard 5995 gas chromatograph/mass spectrometer. High-resolution mass spectra were recorded with a Micromass Autospec mass spectrometer. Microanalyses were performed with a Fisons Instruments EA 1108 carbon, hydrogen, and nitrogen analyzer. Analytical thin-layer chromatography plates used were E. Merck Brinkman UV-active silica gel (Kieselgel 60 F254) on aluminum. Flash column chromatography was carried out with E. Merck silica gel 60 (particle size less than 0.020 mm) using appropriate mixtures of ethyl acetate and hexanes, or hexanes and dichloromethane as eluents. All reactions were performed in oven-dried glassware. All materials were obtained from commercial suppliers and used as received.

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Experimental Section

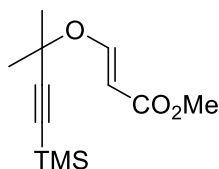
When necessary, the propargyl alcohols were prepared by addition of the lithium acetylides onto acetone following the standard procedures (see below for a general procedure).

The propargyl vinyl ethers were prepared according to our previous experimental procedure (see below for a general procedure).¹ Products **14b**², **14c**³, **14d**⁴, **14n**⁵ have been previously described. Products **3c**, **3e** and **3f** exist as a mixture of tautomers. Nevertheless, they react with benzynes as 2*H*-pyrans. Aryl trifluoromethanesulfonates **13a**, **13c** and **13d** are commercially available. **13b**,⁶ **13e**⁷ and **13f**⁶ were prepared using literature procedures.

General procedure for the synthesis of propargyl alcohols: A terminal alkyne (13 mmol) was dissolved in 25 mL of dry THF in a round-bottom flask. After the mixture was cooled to -78 °C, a 1.6M solution of BuLi in hexanes (13 mmol) was added dropwise. The temperature was maintained between -78 °C and -40 °C for 1 h with stirring of the solution. Acetone (10 mmol) was then added slowly and the stirring was continued overnight allowing the reaction mixture to warm up to room temperature slowly without additional cooling. After completion, the reaction was quenched with saturated NH₄Cl solution and extracted with CH₂Cl₂. This was followed by isolation of the corresponding product by flash column chromatography (silica gel, appropriate mixtures of *n*-hexane/EtOAc) for high boiling alkynes. If the alkyne used had a relatively low boiling point (< 120 °C), evaporation of the solvent and excess reaction led to a crude alcohol which did not need chromatographic purification.

Representative procedure for the synthesis of Propargyl Vinyl Ethers (2) from tertiary alcohols:¹ Methyl propiolate (7.5 mmol) was added dropwise (time of addition 10 minutes. More if needed, until completion) to a solution of 2-methyl-4-(trimethylsilyl)but-3-yn-2-ol (5.0 mmol) and DABCO (0.50 mmol) in a 1:10 mixture of dry CH₂Cl₂ and hexane (10 mL). The reaction mixture was stirred for 5 min (TLC control). The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel; *n*-hexane/EtOAc, 90:10) to give **2a** (90%).

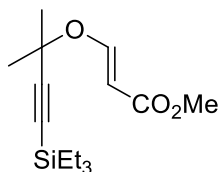
(*E*)-Methyl 3-(2-methyl-4-(trimethylsilyl)but-3-yn-2-yloxy)acrylate (2a). Colorless oil: ¹H



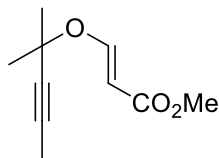
NMR (CDCl₃, 500 MHz): δ = 0.18 (s, 9H), 1.54 (s, 6H), 3.68 (s, 3H), 5.35 (d, 1H, ³*J*(H,H) = 12.1 Hz), 7.90 (d, 1H, ³*J*(H,H) = 12.1 Hz). ¹³C NMR (CDCl₃, 125 MHz): δ = -0.3 (3C), 29.3 (2C), 50.9, 75.6, 92.1, 99.2, 105.0, 158.7, 168.3 ppm. HRMS (ESI⁺): *m/z* [M+Na]⁺ calculated for C₁₂H₂₀O₃Si

263.1079, found 263.1082.

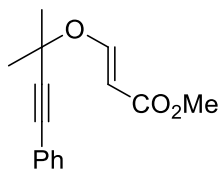
(E)-Methyl 3-(2-methyl-4-(triethylsilyl)but-3-yn-2-yloxy)acrylate (2b). Colorless oil: ^1H NMR (CDCl_3 , 400 MHz): δ = 0.56 (q, 6H, $^3J(\text{H,H})$ = 7.9 Hz), 0.94 (t, 9H, $^3J(\text{H,H})$ = 7.9 Hz), 1.51 (s, 6H), 3.62 (s, 3H), 5.29 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz), 7.90 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 4.1 (3C), 7.2 (3C), 29.3 (2C), 50.7, 75.5, 89.4, 99.0, 106.3, 158.6, 167.9 ppm.



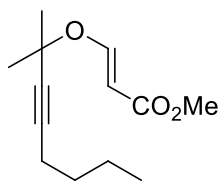
(E)-Methyl 3-(2-methylpent-3-yn-2-yloxy)acrylate (2c). Colorless oil: ^1H NMR (CDCl_3 , 500 MHz): δ = 1.52 (s, 6H), 1.85 (s, 3H), 3.68 (s, 3H), 5.34 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz), 7.89 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz). ^{13}C NMR (CDCl_3 , 125 MHz): δ = 3.5, 29.6 (2C), 50.9, 75.7, 79.3, 83.3, 98.8, 159.0, 168.5 ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{10}\text{H}_{14}\text{O}_3$ 205.0841, found 205.0841.



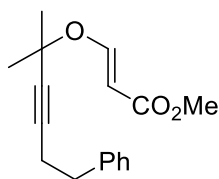
(E)-Methyl 3-(2-methyl-4-phenylbut-3-yn-2-yloxy)acrylate (2d). Colorless oil: ^1H NMR (CDCl_3 , 500 MHz): δ = 1.66 (s, 6H), 3.69 (s, 3H), 5.41 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz), 7.29-7.34 (m, 3H), 7.43-7.45 (m, 2H), 7.97 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz). ^{13}C NMR (CDCl_3 , 125 MHz): δ = 29.4 (2C), 51.0, 75.7, 86.8, 88.7, 99.4, 121.8, 128.3 (2C), 128.9, 131.8 (2C), 158.7, 168.3 ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_{16}\text{O}_3$ 267.0997, found 267.0997.



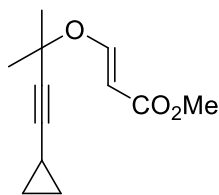
(E)-methyl 3-(2-methyloct-3-yn-2-yloxy)acrylate (2e). Colorless oil: ^1H NMR (CDCl_3 , 400 MHz): δ = 0.90 (t, 3H, $^3J(\text{H,H})$ = 7.2 Hz), 1.35-1.44 (m, 2H), 1.46-1.51 (m, 2H), 1.51 (s, 6H), 2.22 (t, 2H, $^3J(\text{H,H})$ = 6.8 Hz), 3.68 (s, 3H), 5.34 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz), 7.91 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 13.5, 18.2, 21.8, 29.6 (2C), 30.4, 50.9, 75.8, 80.1, 87.9, 98.7, 159.0, 168.4 ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{13}\text{H}_{20}\text{O}_3$ 247.1310, found 247.1311.



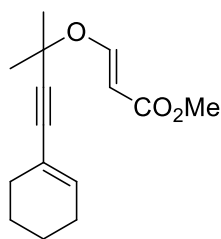
(E)-methyl 3-(2-methyl-6-phenylhex-3-yn-2-yloxy)acrylate (2f). Colorless oil: ^1H NMR (CDCl_3 , 500 MHz): δ = 1.50 (s, 6H), 2.51 (t, 2H, $^3J(\text{H,H})$ = 7.4 Hz), 2.82 (t, 2H, $^3J(\text{H,H})$ = 7.4 Hz), 3.70 (s, 3H), 5.35 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz), 7.19-7.22 (m, 3H), 7.27-7.31 (m, 2H), 7.88 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz). ^{13}C NMR (CDCl_3 , 125 MHz): δ = 20.9, 29.4 (2C), 34.8, 50.9, 75.6, 81.1, 86.9, 98.9, 126.3, 128.3 (2C), 128.5 (2C), 140.3, 158.9, 168.4 ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{20}\text{O}_3$ 295.1310, found 295.1316.



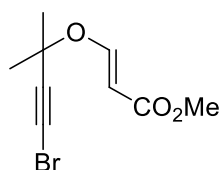
(E)-Methyl 3-(4-cyclopropyl-2-methylbut-3-yn-2-yloxy)acrylate (2g). Colorless oil: ^1H NMR (CDCl_3 , 400 MHz): δ = 0.66-0.70 (m, 2H), 0.76-0.81 (m, 2H), 1.21-1.28 (m, 1H), 1.50 (s, 6H), 3.68 (s, 3H), 5.32 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz), 7.87 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ = -0.7, 8.5 (2C), 29.6 (2C), 50.9, 75.2, 75.8, 91.1, 98.7, 158.9, 168.4 ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{12}\text{H}_{16}\text{O}_3$ 231.0997, found 231.0991.



(E)-methyl 3-(4-cyclohexenyl-2-methylbut-3-yn-2-yloxy)acrylate (2h). Colorless oil: ^1H NMR (CDCl_3 , 400 MHz): δ = 1.56 (s, 6H), 1.56-1.64 (m, 4H), 2.05-2.11 (m, 4H), 3.68 (s, 3H), 5.35 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz), 6.12-6.14 (m, 1H), 7.91 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 21.3, 22.1, 25.6, 28.9, 29.5 (2C), 51.0, 75.9, 86.0, 88.7, 98.9, 119.5, 136.4, 158.9, 168.4 ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_{20}\text{O}_3$ 271.1310, found 271.1303.

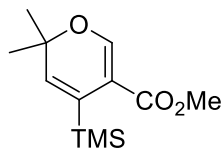


(E)-Methyl 3-(4-bromo-2-methylbut-3-yn-2-yloxy)acrylate (2i). Colorless oil: ^1H NMR (CDCl_3 , 400 MHz): δ = 1.57 (s, 6H), 3.69 (s, 3H), 5.37 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz), 7.79 (d, 1H, $^3J(\text{H,H})$ = 12.1 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 29.1 (2C), 47.9, 51.0, 75.9, 80.0, 99.9, 158.1, 168.1 ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_9\text{H}_{11}\text{BrO}_3\text{Si}$ 268.9789, found 268.9787.

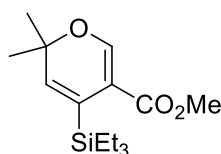


Representative procedure for the synthesis of 2H-pyrans (3). Propargyl vinyl ether **2a** (1.0 mmol) and imidazole (0.1 mmol) in dry Toluene (5 mL) were placed in a round bottom flask and the solution was heated for 48 hours under reflux (TLC control). After removing the solvent at reduced pressure the products were purified by flash column chromatography (silica gel, n-hexane/EtOAc 95/5) to yield 250.7 mg of 2H-pyran **3a** (92%).

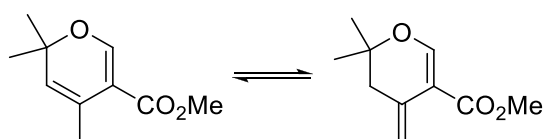
Methyl 2,2-dimethyl-4-(trimethylsilyl)-2H-pyran-5-carboxylate (3a). Product **2a** refluxed in toluene for 2 days. Yield: 250.7 mg, 92%. Colorless oil: ^1H NMR (CDCl_3 , 500 MHz): δ = 0.14 (s, 9H), 1.35 (s, 6H), 3.70 (s, 3H), 5.43 (s, 1H), 7.46 (s, 1H). ^{13}C NMR (CDCl_3 , 125 MHz): δ = -0.2 (3C), 27.2 (2C), 50.9, 77.2, 109.7, 129.7, 133.3, 154.6, 167.2 ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{12}\text{H}_{20}\text{O}_3\text{Si}$ 263.1079, found 263.1080.



Methyl 2,2-dimethyl-4-(triethylsilyl)-2H-pyran-5-carboxylate (3b). Product **2b** refluxed in toluene for 4 days. Yield: 178.0 mg, 82%. Colorless oil: ^1H NMR (CDCl_3 , 400 MHz): δ = 0.65 (q, 6H, $^3J(\text{H,H})$ = 7.9 Hz), 0.88 (t, 9H, $^3J(\text{H,H})$ = 7.9 Hz), 1.35 (s, 6H), 3.70 (s, 3H), 5.42 (d, 1H, $^3J(\text{H,H})$ = 1.3 Hz), 7.45 (d, 1H, $^3J(\text{H,H})$ = 1.3 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 3.7 (3C), 7.6 (3C), 27.1 (2C), 50.9, 77.1, 110.1, 126.1, 135.1, 154.4, 167.2 ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_{26}\text{O}_3\text{Si}$ 305.1549, found 305.1550.

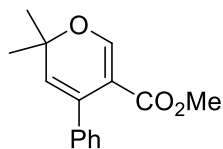


Methyl 2,2,4-trimethyl-2H-pyran-5-carboxylate (3c). Product **2c** refluxed in toluene for 12 hours. Yield: 500 mg, 77%. Colorless oil: ^1H NMR (CDCl_3 , 500 MHz): nearly 1:1 mixture of tautomers δ = 1.27 (s, 6H), 1.34 (s, 6H), 1.98 (d, 1H, $^3J(\text{H,H})$ = 1.4 Hz), 2.28 (s, 2H), 3.69 (s, 3H), 3.72 (s, 3H), 4.84 (s, 1H), 4.87 (s, 1H), 5.78 (s, 1H), 7.46 (s, 1H), 7.52 (s, 1H). ^{13}C NMR (CDCl_3 ,



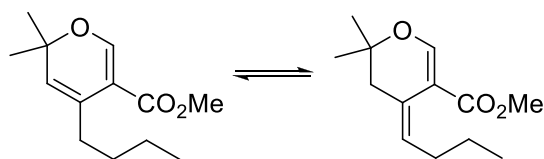
125 MHz): δ = 20.3, 26.1 (2C), 27.8 (2C), 43.0, 50.8, 51.0, 78.6, 79.1, 106.4, 108.0, 112.1, 120.6, 127.1, 131.5, 155.8, 155.9, 166.5, 166.7 ppm. HRMS (ESI⁺): m/z [M+Na]⁺ calculated for C₁₀H₁₄O₃Si 205.0841, found 205.0838.

Methyl 2,2-dimethyl-4-phenyl-2H-pyran-5-carboxylate (3d). Product **2d** refluxed in toluene



for 4 hours. Yield: 837.9 mg, 86%. Colorless oil: ¹H NMR (CDCl₃, 500 MHz): δ = 1.48 (s, 6H), 3.56 (s, 3H), 5.17 (s, 1H), 7.16-7.18 (m, 2H), 7.25-7.31 (m, 3H), 7.59 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ = 27.3 (2C), 51.0, 79.3, 108.6, 123.0, 127.0 (2C), 127.2 127.7 (2C), 132.7, 139.4, 156.2, 165.9 ppm. HRMS (ESI⁺): m/z [M+Na]⁺ calculated for C₁₅H₁₆O₃ 267.0997, found 267.0994.

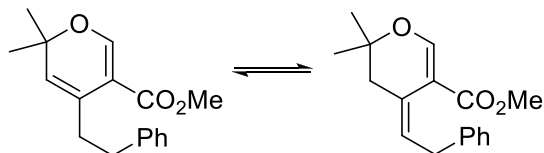
Methyl 4-butyl-2,2-dimethyl-2H-pyran-5-carboxylate (3e). Product **2e** refluxed in toluene for



1 day. Yield: 170.7 mg, 83%. Colorless oil: ¹H NMR (CDCl₃, 400 MHz): nearly 1:2 mixture of tautomers δ = 0.89 (t, 3H, ³J(H,H) = 7.6 Hz), 1.31-1.35 (m, 4H), 1.35 (s, 6H), 2.39 (t,

2H, ³J(H,H) = 7.1 Hz), 3.69 (s, 3H), 4.91 (s, 1H), 7.47 (s, 1H), and 0.91 (t, 3H, ³J(H,H) = 7.6 Hz), 1.26 (s, 6H), 1.39-1.44 (m, 2H), 2.05-2.11 (m, 2H), 2.30 (s, 2H), 3.71 (s, 3H), 6.34 (t, 3H, ³J(H,H) = 7.2 Hz), 7.42 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ = 13.9, 23.1, 26.4 (2C), 29.5, 35.8, 51.0, 77.8, 107.1, 123.3, 127.3, 153.7, 167.1. HRMS (ESI⁺): m/z [M+Na]⁺ calculated for C₁₃H₂₀O₃ 247.1310, found 247.1307.

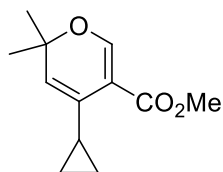
Methyl 2,2-dimethyl-4-phenethyl-2H-pyran-5-carboxylate (3f). Product **2f** refluxed in toluene



for 1 day. Yield: 449.5 mg, 89%. Colorless oil: ¹H NMR (CDCl₃, 400 MHz): nearly 2:1 mixture of tautomers δ = 1.31 (s, 6H), 2.70 (bs, 4H), 3.73 (s, 3H), 4.80 (s, 1H), 7.14-7.29

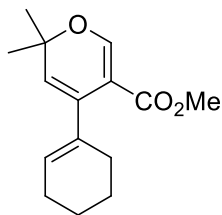
(m, 5H), 7.53 (s, 1H). 1.29 (s, 6H), 2.41 (s, 2H), 3.49 (d, 2H, ³J(H,H) = 7.6 Hz), 3.70 (s, 3H), 6.59 (t, 1H, ³J(H,H) = 7.6 Hz), 7.14-7.29 (m, 5H), 7.48 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 26.4 (2C), 33.5, 35.9, 51.0, 77.9, 107.0, 124.3, 125.2, 125.9, 128.38 (2C), 128.42 (2C), 141.0, 154.3, 166.9, 27.7 (2C), 35.1, 35.6, 51.0, 78.9, 121.0, 125.7, 128.1 (2C), 128.2, 128.7, (2C), 130.2, 142.0, 156.6, 166.2 ppm. HRMS (ESI⁺): m/z [M+Na]⁺ calculated for C₁₇H₂₀O₃ 295.1310, found 295.1305.

Methyl 4-cyclopropyl-2,2-dimethyl-2H-pyran-5-carboxylate (3g). Product **2g** refluxed in

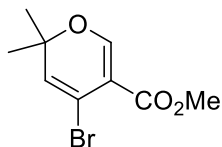


toluene for 1 day. Yield: 325.5 mg, 91%. Colorless oil: ¹H NMR (CDCl₃, 400 MHz): δ = 0.35-0.39 (m, 2H), 0.64-0.69 (m, 2H), 1.32 (s, 6H), 1.92-2.00 (m, 1H), 3.70 (s, 3H), 4.79 (s, 1H), 7.44 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 6.3 (2C), 13.0, 27.7 (2C), 50.9, 79.0, 108.3, 117.4, 132.9, 155.6, 166.3 ppm. HRMS (ESI⁺): m/z [M+Na]⁺ calculated for C₁₂H₁₆O₃ 231.0997, found 231.0995.

Methyl 4-cyclohexenyl-2,2-dimethyl-2H-pyran-5-carboxylate (3h). Product **2h** refluxed in toluene for 4 hours. Yield: 148.9 mg, 88%. Colorless oil: ¹H NMR (CDCl₃, 400 MHz): δ = 1.36 (s, 6H), 1.55-1.65 (m, 4H), 1.91-1.93 (m, 2H), 2.05-2.08 (m, 2H), 3.67 (s, 3H), 4.97 (s, 1H), 5.52-5.54 (m, 1H), 7.43 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 22.2, 22.8, 25.4, 27.4 (2C), 28.4, 51.0, 78.9, 108.2, 120.0, 123.2, 134.8, 137.9, 155.9, 166.1 ppm. HRMS (ESI⁺): m/z [M+Na]⁺ calculated for C₁₅H₂₀O₃ 271.1310, found 271.1306.



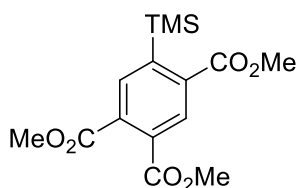
Methyl 4-bromo-2,2-dimethyl-2H-pyran-5-carboxylate (3i). Product **2i** refluxed in toluene for 2 hours. Yield: 500 mg, 76%. Colorless oil: ¹H NMR (CDCl₃, 400 MHz): δ = 1.41 (s, 6H), 3.74 (s, 3H), 5.58 (s, 1H), 7.48 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 27.2 (2C), 51.3, 81.9, 107.1, 110.9, 126.0, 156.5, 164.1 ppm. HRMS (ESI⁺): m/z [M+Na]⁺ calculated for C₉H₁₁BrO₃Si 268.9789, found 268.9787.



Diels-Alder reaction of 2H-pyran 3a with DMAD. 2H-pyran **3a** (100.0 mg, 0.42 mmol) and dimethyl acetylenedicarboxylate (2.0 eq.) in dry Toluene (5 mL) were placed in a round bottom flask and the solution was heated for 5 hours under reflux. After removing the solvent at reduced pressure the products were purified by flash column chromatography (silica gel, n-hexane/EtOAc 85/15) to yield **6** (93%).

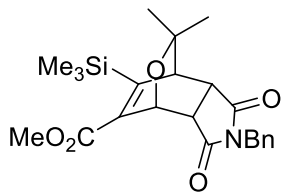
Domino Reaction of PVE 2a with DMAD: Diels-Alder reaction of 2H-pyran 3a intermediate with DMAD. PVE **2a** (1.0 mmol) and dimethyl acetylenedicarboxylate (2.0 mmol) in dry Toluene (2 mL) were placed in a microwave-special closed vial and the solution was irradiated for 1 hour in a single-mode microwave oven (200 Watt, 150 °C). After removing the solvent at reduced pressure the products were purified by flash column chromatography (silica gel, n-hexane/EtOAc 85/15) to yield **6** (80%).

Trimethyl 5-(trimethylsilyl)benzene-1,2,4-tricarboxylate (6). Yield: 150.3 mg, 93%. White solid. Melting point = 64.5-66.5 °C: ¹H NMR (CDCl₃, 400 MHz): δ = 0.33 (s, 9H), 3.91 (s, 3H), 3.92 (s, 6H), 7.91 (s, 1H), 8.37 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 0.1 (3C), 52.4, 52.7, 52.8, 130.3, 131.2, 134.5, 135.3, 137.8, 147.5, 166.8, 167.1, 168.3 ppm. HRMS (ESI⁺): m/z [M+Na]⁺ calculated for C₁₅H₂₀O₆Si 347.0927, found 347.0929.



Diels-Alder reaction of 2H-pyran 3a with N-benzylmaleimide. 2H-pyran **3a** (177.7 mg, 0.739 mmol) and N-benzylmaleimide (207.5 mg, 1.5 eq.) in dry Toluene (5 mL) were placed in a round bottom flask and the solution was heated for 16 hours under reflux. After removing the solvent at reduced pressure the products were purified by flash column chromatography (silica gel, n-hexane/EtOAc 70/30) to yield **8** (270.8 mg; 86%).

Methyl (4R,7R,7aR)-2-benzyl-8,8-dimethyl-1,3-dioxo-6-(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1H-4,7-(epoxymethano)isoindole-5-carboxylate (8).

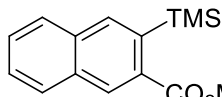


Yield: 270.8 mg, 86%. Colorless liquid: ^1H NMR (CDCl_3 , 400 MHz): δ = 0.07 (s, 9H), 0.93 (s, 3H), 1.29 (s, 3H), 3.25 (dd, 1H, $^3J(\text{H,H})$ = 8.0 and 3.8 Hz), 3.33 (dd, 1H, $^3J(\text{H,H})$ = 7.8 and 3.9 Hz), 3.43 (d, 1H, $^3J(\text{H,H})$ = 3.9 Hz), 3.73 (s, 3H), 4.39 (d, 1H, $^3J(\text{H,H})$ = 14.0 Hz), 4.49 (d, 1H, $^3J(\text{H,H})$ = 14.0 Hz), 5.28 (d, 1H, $^3J(\text{H,H})$ = 4.0 Hz), 7.23 (bs, 5H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = -1.8 (3C), 27.2, 28.2, 37.7, 42.3, 43.2, 45.4, 51.8, 67.2, 72.9, 127.9, 128.6 (2C), 128.8 (2C), 135.5, 140.6, 163.1, 163.6, 174.9, 177.4 ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{23}\text{H}_{29}\text{NO}_5\text{Si}$ 450.1713, found 450.1711.

Representative procedure for the synthesis of 2-naphthoates 14. 2H-pyran **3g** (104.1.0 mg, 0.50 mmol), CsF (190 mg, 2.5 eq) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.152 mL, 1.25 eq.) in acetonitrile (8 mL) were placed in a round bottom flask and the solution was stirred for 24 hours at room temperature (TLC control). The reaction was quenched with water and extracted using CH_2Cl_2 . After removing the solvent at reduced pressure the products were purified by flash column chromatography (silica gel, n-hexane/EtOAc 95/5) to yield **14g** (111.4 mg, 98%).

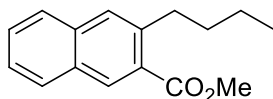
NOTE: Method A: room temperature. Method B: 60 °C

Methyl 3-(trimethylsilyl)-2-naphthoate (14a). Method B. Yield: 146.8 mg, 91%. White solid.



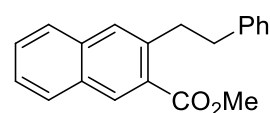
Melting point = 72-73 °C: ^1H NMR (CDCl_3 , 400 MHz): δ = 0.40 (s, 9H), 3.96 (s, 3H), 7.53 (t, 1H, $^3J(\text{H,H})$ = 7.1 Hz), 7.58 (t, 1H, $^3J(\text{H,H})$ = 7.1 Hz), 7.87 (d, 1H, $^3J(\text{H,H})$ = 8.0 Hz), 7.90 (d, 1H, $^3J(\text{H,H})$ = 8.0 Hz), 8.13 (s, 1H), 8.57 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 0.5 (3C), 52.0, 127.1, 128.0, 128.2, 128.7, 131.1, 132.0, 132.6, 134.4, 136.5, 137.7, 168.8 ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_{18}\text{O}_2\text{Si}$ 281.0974, found 281.0973.

Methyl 3-butyl-2-naphthoate (14e). Method A. Yield: 131.9 mg, 92%. Colorless oil: ^1H NMR



(CDCl_3 , 400 MHz): δ = 0.98 (t, 3H, $^3J(\text{H,H})$ = 7.2 Hz), 1.40-1.50 (m, 2H), 1.62-1.70 (m, 2H), 3.10-3.12 (m, 2H), 3.96 (s, 3H), 7.45 (t, 1H, $^3J(\text{H,H})$ = 7.2 Hz), 7.53 (t, 1H, $^3J(\text{H,H})$ = 7.2 Hz), 7.67 (s, 1H), 7.77 (d, 1H, $^3J(\text{H,H})$ = 8.2 Hz), 7.86 (d, 1H, $^3J(\text{H,H})$ = 8.2 Hz), 8.44 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 14.0, 22.7, 33.9, 34.2, 51.9, 125.8, 127.0, 127.9, 128.1, 128.6, 128.9, 130.9, 131.8, 134.9, 140.1, 168.2 ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{18}\text{O}_2$ 265.1204, found 265.1200.

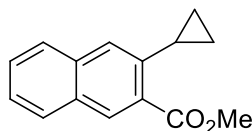
Methyl 3-phenethyl-2-naphthoate (14f). Method A. Yield: 104.4 mg, 93%. Colorless oil: ^1H NMR



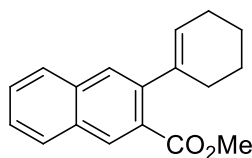
(CDCl_3 , 400 MHz): δ = 2.96-3.00 (m, 2H), 3.40-3.44 (m, 2H), 3.98 (s, 3H), 7.19-7.23 (m, 1H), 7.25-7.32 (m, 4H), 7.46-7.50 (m, 1H), 7.53-7.57 (m, 1H), 7.65 (s, 1H), 7.77 (d, 1H, $^3J(\text{H,H})$ = 8.1 Hz), 7.89

(d, 1H, $^3J(\text{H,H}) = 8.1$ Hz), 8.50 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 36.9, 38.3, 52.1, 125.8, 126.0, 127.1, 127.9, 128.1, 128.3$ (2C), 128.6 (2C), $128.7, 129.4, 131.1, 132.1, 135.0, 139.0, 142.0, 168.0$ ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{20}\text{H}_{18}\text{O}_2$ 313.1204, found 313.1210.

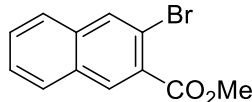
Methyl 3-cyclopropyl-2-naphthoate (14g). Method A. Yield: 111.4 mg, 98%. Colorless oil: ^1H NMR (CDCl_3 , 400 MHz): $\delta = 0.74\text{--}0.78$ (m, 2H), $1.00\text{--}1.04$ (m, 2H), $2.64\text{--}2.71$ (m, 1H), 3.97 (s, 3H), $7.42\text{--}7.46$ (m, 1H), $7.49\text{--}7.53$ (m, 1H), 7.51 (s, 1H), 7.74 (d, 1H, $^3J(\text{H,H}) = 8.2$ Hz), 7.84 (d, 1H, $^3J(\text{H,H}) = 8.2$ Hz), 8.36 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 8.1$ (2C), $14.3, 52.1, 125.1, 125.9, 127.2, 127.9, 128.5, 129.9, 130.8, 131.1, 134.8, 140.2, 168.5$ ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_{14}\text{O}_2$ 249.0891, found 249.0894.



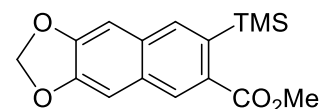
Methyl 3-cyclohexenyl-2-naphthoate (14h). Method A. Yield: 60.1 mg, 52%. Colorless oil: ^1H NMR (CDCl_3 , 400 MHz): $\delta = 1.68\text{--}1.74$ (m, 2H), $1.77\text{--}1.83$ (m, 2H), $2.18\text{--}2.23$ (m, 2H), $2.27\text{--}2.31$ (m, 2H), 3.90 (s, 3H), $5.65\text{--}5.68$ (m, 1H), $7.45\text{--}7.49$ (m, 1H), $7.51\text{--}7.55$ (m, 1H), 7.64 (s, 1H), 7.80 (d, 1H, $^3J(\text{H,H}) = 8.1$ Hz), 7.87 (d, 1H, $^3J(\text{H,H}) = 8.1$ Hz), 8.33 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 22.1, 23.2, 25.7, 30.5, 52.1, 125.1, 126.2, 127.5, 127.9, 128.0, 128.5, 128.6, 130.9, 131.4, 134.7, 139.5, 141.9, 168.8$ ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{18}\text{O}_2$ 289.1204, found 289.1203.



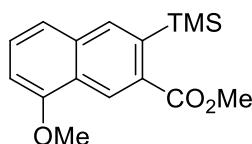
Methyl 3-bromo-2-naphthoate (14i). Method A. Yield: 72.8 mg, 53%. White solid: ^1H NMR (CDCl_3 , 400 MHz): $\delta = 3.98$ (s, 3H), $7.50\text{--}7.59$ (m, 2H), 7.74 (d, 1H, $^3J(\text{H,H}) = 8.0$ Hz), 7.84 (d, 1H, $^3J(\text{H,H}) = 8.0$ Hz), 8.12 (s, 1H), 8.32 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 52.5, 117.0, 126.7, 127.1, 128.6, 128.8, 129.1, 131.1, 132.2, 133.0, 135.2, 166.6$ ppm. Although product **14i** had been previously prepared,⁸ its NMR spectra had not been described.



Methyl 7-(trimethylsilyl)naphtho[2,3-d][1,3]dioxole-6-carboxylate (14j). Method A. Yield: 116.3 mg, 78%. White solid. Melting point = $108\text{--}109$ °C: ^1H NMR (CDCl_3 , 400 MHz): $\delta = 0.37$ (s, 9H), 3.93 (s, 3H), 6.06 (s, 2H), 7.13 (s, 1H), 7.14 (s, 1H), 7.91 (s, 1H), 8.38 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 0.5$ (3C), $51.9, 101.4, 104.1, 104.4, 129.8, 130.1, 130.7, 132.2, 135.2, 136.1, 148.5, 149.4, 168.8$ ppm. HRMS (ESI^+): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Si}$ 302.0974, found 302.0982.

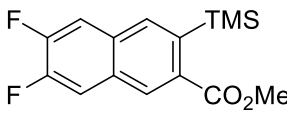


Methyl 8-methoxy-3-(trimethylsilyl)-2-naphthoate (14k). Method A. 96:4 ratio of isomers. Yield: 118.8 mg, 83%. White solid. Melting point = $118\text{--}119$ °C: ^1H NMR (CDCl_3 , 400 MHz): $\delta = 0.39$ (s, 9H), 3.96 (s, 3H), 4.01 (s, 3H), 6.85 (d, 1H, $^3J(\text{H,H}) = 7.3$ Hz), 7.43 (d, 1H, $^3J(\text{H,H}) = 8.1$ Hz), $7.46\text{--}7.50$ (m, 1H), 8.08 (s, 1H), 8.97 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 0.5$ (3C),

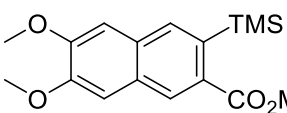


52.0, 55.6, 104.9, 120.1, 124.7, 125.4, 128.4, 131.3, 135.4, 136.0, 138.3, 156.1, 168.9 ppm. HRMS (ESI⁺): m/z [M+Na]⁺ calculated for C₁₆H₂₀O₃Si 311.1079, found 311.1077. Characteristic ¹H NMR signals for minor isomer: 8.50 (s, 1H), 8.59 (s, 1H).

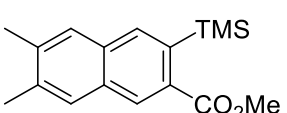
Methyl 6,7-difluoro-3-(trimethylsilyl)-2-naphthoate (14l). Method A. Yield: 150.3 mg, 98%.

 White solid. Melting point = 101-102 °C: ¹H NMR (CDCl₃, 400 MHz): δ = 0.38 (s, 9H), 3.95 (s, 3H), 7.55-7.61 (m, 2H), 8.02 (s, 1H), 8.45 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 0.4 (3C), 52.1, 113.9 (d, J(C,F) = 16.2 Hz), 114.3 (d, J(C,F) = 16.2 Hz), 129.3 (dd, J(C,F) = 7.6 and 1.4 Hz), 130.0 (dd, J(C,F) = 4.5 and 2.1 Hz), 131.4 (dd, J(C,F) = 7.6 and 1.4 Hz), 132.6 (d, J(C,F) = 2.6 Hz), 135.6 (dd, J(C,F) = 4.9 and 1.4 Hz), 138.4 (d, J(C,F) = 2.1 Hz), 150.8 (dd, J(C,F) = 253 and 16.2 Hz), 151.3 (dd, J(C,F) = 253 and 16.2 Hz), 168.3 ppm. HRMS (ESI⁺): m/z [M+Na]⁺ calculated for C₁₅H₁₆F₂O₂Si 317.0785, found 317.0786.

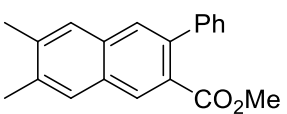
Methyl 6,7-dimethoxy-3-(trimethylsilyl)-2-naphthoate (14m). Method B. Yield: 166.7 mg, 93%.

 White solid. Melting point = 109-110 °C: ¹H NMR (CDCl₃, 400 MHz): δ = 0.37 (s, 9H), 3.93 (s, 3H), 4.00 (s, 3H), 4.02 (s, 3H), 7.15 (s, 1H), 7.16 (s, 1H), 7.96 (s, 1H), 8.44 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 0.5 (3C), 50.6, 55.91, 55.92, 106.7, 107.2, 128.6, 129.5, 130.7, 130.9, 134.6, 135.9, 150.8, 151.6, 168.8 ppm. HRMS (ESI⁺): m/z [M+Na]⁺ calculated for C₁₇H₂₂O₂Si 318.1287, found 318.1298.

Methyl 6,7-dimethyl-3-(trimethylsilyl)-2-naphthoate (14o). Method B. Yield: 129.0 mg, 82%.

 White solid. Melting point = 94-95 °C: ¹H NMR (CDCl₃, 400 MHz): δ = 0.41 (s, 9H), 2.43 (s, 3H), 2.44 (s, 3H), 3.96 (s, 3H), 7.62 (s, 1H), 7.63 (s, 1H), 8.03 (s, 1H), 8.48 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 0.6 (3C), 20.1, 20.2, 51.9, 127.5, 128.1, 130.3, 131.1, 131.5, 133.4, 135.4, 136.5, 136.9, 138.2, 168.9 ppm. HRMS (ESI⁺): m/z [M+Na]⁺ calculated for C₁₇H₂₂O₂Si 309.1287, found 309.1289.

Methyl 6,7-dimethyl-3-phenyl-2-naphthoate (14p). Method A. Yield: 169.2 mg, 83%.

 White solid. Melting point = 101-102 °C: ¹H NMR (CDCl₃, 400 MHz): δ = 2.45 (s, 6H), 3.70 (s, 3H), 7.35-7.45 (m, 5H), 7.61 (s, 1H), 7.68 (s, 1H), 7.70 (s, 1H), 8.31 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 20.1, 20.3, 51.8, 126.8, 127.2, 127.9 (3C), 128.0, 128.5 (2C), 128.7, 130.1, 130.5, 133.4, 136.6, 138.0, 138.4, 141.8, 169.1 ppm. HRMS (ESI⁺): m/z [M+Na]⁺ calculated for C₂₀H₁₈O₂Si 313.1204, found 313.1201.

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