Supporting Information

Ni-Catalyzed, ZnCl₂-Assisted Domino Coupling of Enones, Alkynes, and Alkenes

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General Comments. All reactions were carried out under dry N₂ atmosphere. ¹H and ¹³C NMR spectra were recorded in CDCl₃ with Me₄Si as an internal standard. MeCN was distilled from P₂O₅. THF and Et₂O were distilled from Na/benzophenone ketyl after treatment with LiAlH₄. DMF was distilled from BaO. Toluene and Et₃N were distilled from CaH₂. EtOH was distilled from Na. ZnCl₂ was dried under reduced pressure at 150 °C. Starting materials **2a–2c** and **2e** and the derived products **3** have been already reported in the preliminary communication.¹ Starting materials **2f**,² **2g**,³ **2h**,⁴ **2i**, and **2j** were prepared by allylation followed by propargylation of diethyl or dimethyl malonate. In geranyl and neryl-tethered enynes (*E*)- and (*Z*)-**2h**, the geranyl and neryl bromides as allylating reagents were prepared by bromination of the corresponding alcohols by the literature procedure.⁵ *N*-Tosyl amide **2k** was prepared by tosylation followed by allylation of propargyl amine. Other materials, except **2d** and **37**, were obtained from commercial suppliers and used without further purification.

Dimethyl 2-(3-methylbut-3-enyl)-2-(prop-2-ynyl)malonate (2d): The material was prepared by (1) conjugate addition of dimethyl malonate to methyl vinyl ketone, (2) Wittig reaction by CH₃PPh₃⁺Br[−]/BuLi in ether, and (3) propargylation. A colorless oil; *R*_f = 0.43 (hexane/AcOEt = 4:1); ¹H NMR (270 MHz, CDCl₃) δ 1.73 (s, 3 H, CH₃), 1.85-1.92 (m, 2 H, CH₂), 2.01 (t, *J* = 2.7 Hz, 1 H, CH), 2.17-2.23 (m, 2 H, CH₂), 2.84 (d, *J* = 2.7 Hz, 2 H, CH₂), 3.74 (s, 6 H, OCH₃), 4.68-4.75 (m, 2 H, =CH); IR (neat) 3290, 2955, 1738 (ν_{CO}), 1437, 1205 cm^{−1}; GC/MS (EI, 70 eV) *m/z* (rel int, %) 238 (M⁺, 0), 178 (M⁺ – HCO₂Me, 29), 170 (100). HRMS for C₁₁H₁₄O₂ (M⁺ – HCO₂Me): calcd 178.0994; found 178.0992.

Diethyl 2-(cyclopent-2-enyl)-2-(prop-2-ynyl)malonate (2i): a colorless oil; $R_f = 0.67$ (hexane/AcOEt = 4:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.24 (t, $J = 7.2$ Hz, 3 H, CH_3), 1.26 (t, $J = 7.1$ Hz, 3 H, CH_3), 1.71-1.81 (m, 1 H, one of CH_2), 2.00 (t, $J = 2.7$ Hz, 1 H, CH), 2.06-2.14 (m, 1 H, one of CH_2), 2.28-2.32 (m, 2 H, CH_2), 2.81 (d, $J = 2.7$ Hz, 2 H, CH_2), 3.62-3.67 (m, 1 H, CH), 4.15-4.25 (m, 4 H, OCH_2), 5.79-5.81 (m, 2 H, CH_2); IR (neat) 3290, 2990, 1735 (ν_{CH}), 1225, 1195, 1045 cm^{-1} ; DI/MS (EI, 70 eV) m/z (rel int, %) 264 (M^+ , 1), 198 (35), 179 (100), 67 (47). HRMS for $\text{C}_{12}\text{H}_{17}\text{O}_4$ ($\text{M}^+ - \text{C}_3\text{H}_3$): calcd, 225.1127; found, 225.1112.

Diethyl 2-(cyclohex-2-enyl)-2-(prop-2-ynyl)malonate (2j): a colorless oil; $R_f = 0.61$ (hexane/AcOEt = 4:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.24 (t, $J = 7.2$ Hz, 3 H, CH_3), 1.27 (t, $J = 7.1$ Hz, 3 H, CH_3), 1.32-1.42 (m, 1 H, one of CH_2), 1.51-1.62 (m, 1 H, one of CH_2), 1.75-2.05 (m, 5 H, CH_2 and CH), 2.80 (dd, $J = 17.1, 2.7$ Hz, 1 H, one of CH_2), 2.87 (dd, $J = 17.1, 2.7$ Hz, 1 H, one of CH_2), 3.10-3.18 (m, 1 H, CH), 4.15-4.25 (m, 4 H, OCH_2), 5.74 (s, 2 H, $=\text{CH}_2$); IR (neat) 3290, 2945, 1730 (ν_{CH}), 1225 cm^{-1} ; DI/MS (EI, 70 eV) m/z (rel int, %) 278 (M^+ , 1), 193 (100). HRMS for $\text{C}_{16}\text{H}_{22}\text{O}_4$ (M^+): calcd, 278.1518; found, 278.1540.

***N*-(Prop-2-ynyl)-*N*-tosylcyclohex-2-enamine (2k):** a colorless crystal; mp 61-62 $^{\circ}\text{C}$; $R_f = 0.49$ (hexane/AcOEt = 4:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.51-1.61 (m, 2 H, CH_2), 1.70-1.85 (m, 2 H, CH_2), 1.92-2.03 (m, 2 H, CH_2), 2.16 (t, $J = 2.4$ Hz, 1 H, CH), 2.42 (s, 3 H, CH_3), 3.91 (dd, $J = 18.5, 2.4$ Hz, 1 H, one of CH_2), 4.13 (dd, $J = 18.5, 2.4$ Hz, 1 H, one of CH_2), 4.46-4.50 (m, 1 H, CH), 5.30 (d, $J = 10.2$ Hz, 1 H, CH), 5.88 (ddt, $J = 10.2, 7.3, 2.0$ Hz, 1 H, CH), 7.28 (d, $J = 8.3$ Hz, 2 H, Ar), 7.81 (d, $J = 8.3$ Hz, 2 H, Ar); IR (disk) 3280, 2940, 1600, 1335, 1165, 1100, 1035, 815, 655 cm^{-1} ; DI/MS (EI, 70 eV) m/z (rel int, %) 289 (M^+ , 3), 134 (94), 133 (35), 106 (51), 91 (100); DI/MS (EI, 70 eV) m/z (rel int, %) 289 (M^+ , 3), 134 (94), 133 (35), 106 (51), 91 (100). HRMS for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{NS}$ (M^+): calcd, 289.1137; found, 289.1129.

Preparation of *cis*-4-acetoxycyclopent-2-enyl methyl carbonate (S1): To a solution of *cis*-4-hydroxycyclopent-2-enyl acetate (732 mg, 5.2 mmol) and pyridine (584 mg, 7.4 mmol) in CHCl₃ (6 mL) was added dropwise a solution of methyl chlorocarbonate (710 mg, 7.5 mmol) in CHCl₃ (2 mL) at 0 °C and the mixture was stirred at room temperature for 1 h. After the addition of aqueous HCl (5 %, 30 mL), the aqueous layer was extracted with CHCl₃ (20 mL x 3). The combined organic layer was washed with brine, dried over MgSO₄ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **S1** (929 mg, 90%). A colorless oil; *R*_f = 0.34 (hexane/AcOEt = 4:1); ¹H NMR (400 MHz, CDCl₃) δ 1.83 (dt, *J* = 15.1, 3.8 Hz, 1 H, one of CH₂), 2.06 (s, 3 H, CH₃), 2.90 (dt, *J* = 15.1, 7.6 Hz, 1 H, one of CH₂), 3.80 (s, 3 H, CH₃), 5.47-5.50 (m, 1 H, OCH), 5.53-5.55 (m, 1 H, OCH), 6.13 (s, 2 H, =CH); IR (neat) 2950, 1740 (ν_{CO}), 1440, 1360, 1260, 1240 cm⁻¹.

Preparation of dimethyl 2-(*cis*-4'-acetoxycyclopent-2'-enyl)-2-(3'-methylbut-2'-enyl)malonate (S4): To a suspension of NaH (60% in mineral oil, 445 mg, 11.1 mmol) in THF (10 mL) was added dimethyl prenylmalonate, which was prepared from the reaction of sodium dimethyl malonate with prenyl bromide, (2.24 g, 11.2 mmol) at room temperature and the mixture was stirred for 30 min. This reaction mixture was added dropwise to a solution of Pd(PPh₃)₄ (318 mg, 0.275 mmol) and **S1** (1.09 g, 5.44 mmol) in THF (10 mL) and then the mixture was stirred at room temperature for 3 h. After aqueous

HCl (5 %, 30 mL), the aqueous layer was extracted with Et₂O (20 mL x 4). The combined organic layer was washed with brine, dried over MgSO₄ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **S4** (1.25 g, 71%). A pale yellow oil; *R*_f = 0.40 (hexane/AcOEt = 4:1); ¹H NMR (400 MHz, CDCl₃) δ 1.61 (s, 3 H, CH₃), 1.63-1.67 (m, 1 H, one of CH₂), 1.69 (s, 3 H, CH₃) 2.02 (s, 3 H, CH₃), 2.52 (dt, *J* = 14.4, 8.2 Hz, 1 H, one of CH₂), 2.63 (d, *J* = 7.1 Hz, 2 H, CH₂), 3.29-3.34 (m, 1 H, CH), 3.68 (s, 3 H, OCH₃), 3.72 (s, 3 H, OCH₃), 4.95-4.99 (m, 1 H, =CH), 5.60-5.60 (m, 1 H, OCH), 5.77 (dt, *J* = 5.9, 2.2 Hz, 1 H, =CH), 6.10-6.11 (m, 1 H, =CH); IR (neat) 2950, 1730 (νCO), 1430, 1360, 1240, 1050 cm⁻¹.

Preparation of dimethyl 2-(*cis*-4'-acetoxycyclopent-2'-enyl)-2-propenylmalonate (S5**):**

The compound was prepared by the procedure employed for **S4**, starting NaH (60% in mineral oil, 371 mg, 9.28 mmol), dimethyl allylmalonate (1.61 g, 9.38 mmol), Pd(PPh₃)₄ (271 mg, 0.235 mmol), **S1** (922 mg, 4.61 mmol) and THF (30 mL). The crude product was purified by column chromatography on silica gel to give **S5** (968 mg, 71%). A colorless oil; *R*_f = 0.34 (hexane/AcOEt = 4:1); ¹H NMR (400 MHz, CDCl₃) δ 1.58-1.65 (m, 1 H, one of CH₂), 2.02 (s, 3 H, CH₃), 2.55 (dt, *J* = 14.4, 7.2 Hz, 1 H, one of CH₂), 2.65-2.69 (m, 2 H, CH₂), 3.30-3.35 (m, 1 H, CH), 3.69 (s, 3 H, OCH₃), 3.73 (s, 3 H, OCH₃), 5.09-5.14 (m, 2 H, =CH₂), 5.59-5.62 (m, 1 H, CH), 5.63-5.74 (m, 1 H, =CH), 5.79 (dt, *J* = 5.6, 2.2 Hz, 1 H, =CH), 6.11 (dt, *J* = 5.6, 1.7 Hz, 1 H, =CH); IR (neat) 2950, 1730 (νCO), 1240 cm⁻¹.

Preparation of *cis*-3-[1',1'-bis(methoxycarbonyl)methyl]-5-[1',1'-

bis(methoxycarbonyl)-3'-(4'-methylpentenyl)]cyclopentene (S6**):** To a suspension of NaH (60% in mineral oil, 324 mg, 8.10 mmol) in THF (20 mL) was added a solution of dimethylmalonate (1.09 g, 8.29 mmol) in THF (5 mL) at room temperature and the mixture was stirred for 30 min. This reaction mixture was added dropwise to a solution of Pd(PPh₃)₄ (250 mg, 0.216 mmol) and **S4** (1.24 g, 3.83 mmol) in THF (10 mL) and then the mixture was stirred at 70 °C for 20 h. After aqueous HCl (5 %, 30 mL), the aqueous layer was extracted with Et₂O (20 mL x 4). The combined organic layer was washed with brine, dried over MgSO₄ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **S6** (1.22 g, 81%). A

pale yellow oil; R_f = 0.34 (hexane/AcOEt = 6:1); ^1H NMR (400 MHz, CDCl_3) δ 1.35 (dt, J = 13.4, 8.7 Hz, 1 H, one of CH_2), 1.60 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 2.28 (dt, J = 13.4, 8.1 Hz, 1 H, one of CH_2), 2.56-2.67 (m, 2 H, CH_2), 3.19 (d, J = 9.5 Hz, 1 H, CH), 3.30-3.36 (m, 1 H, CH), 3.39-3.44 (m, 1 H, CH), 3.67 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 3.74 (s, 6H, OCH_3), 4.96-5.00 (m, 1 H, =CH), 5.63 (dt, J = 5.6, 2.1 Hz, 1 H, =CH), 5.87 (dt, J = 5.6, 2.1 Hz, 1 H, =CH); IR (neat) 2950, 1730 (ν_{CO}), 1430, 1220, 1060 cm^{-1} .

Preparation of *cis*-3-[1',1'-bis(methoxycarbonyl)methyl]-5-[1',1'-

bis(methoxycarbonyl)-3'-butenyl]cyclopentene (S7): The compound was prepared by the procedure employed for **S6**, starting NaH (60% in mineral oil, 247 mg, 6.18 mmol), dimethyl malonate (789 mg, 5.97 mmol), $\text{Pd}(\text{PPh}_3)_4$ (175 mg, 0.151 mmol), **S5** (968 mg, 3.27 mmol) and THF (25 mL). The crude product was purified by column chromatography on silica gel to give **S7** (1.03 g, 86%). A pale yellow oil; R_f = 0.29 (hexane/AcOEt = 4:1); ^1H NMR (400 MHz, CDCl_3) δ 1.35 (dt, J = 13.4, 8.7 Hz, 1 H, one of CH_2), 2.31 (dt, J = 13.4, 8.1 Hz, 1 H, one of CH_2), 2.64 (d, J = 7.6 Hz, 2 H, CH_2), 3.21 (d, J = 9.3 Hz, 1 H, CH), 3.31-3.42 (m, 2 H, CH_2), 3.68-3.74 (m, 12 H, OCH_3), 5.07-5.13 (m, 2 H, = CH_2), 5.65 (dt, J = 2.7, 7.3 Hz, 1 H, =CH), 5.63-5.73 (m, 1H, =CH), 5.87 (dt, J = 5.6, 2.1 Hz, 1H, =CH); IR (neat) 2950, 1730 (ν_{CO}), 1440, 1230, 1160, 1040 cm^{-1} .

Preparation of *cis*-3-[1',1'-bis(methoxycarbonyl)-3'-(4'-methylpentenyl)]-5-[1',1'-

bis(methoxycarbonyl)-3'-butynyl]cyclopentene (25a): To a suspension of NaH (60% in mineral oil, 201 mg, 5.03 mmol) in DMF (15 mL) was added drop wise **S6** (1.18 g, 2.98 mmol) in DMF (10 mL). To this reaction mixture was added dropwise a solution of propargyl bromide (795 mg, 6.68 mmol) in DMF (5 mL) and the mixture was stirred at room temperature for 2 h. After aqueous HCl (5 %, 30 mL), the aqueous layer was extracted with Et_2O (20 mL x 4). The combined organic layer was washed with brine, dried over MgSO_4 for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **25a** (1.10 g, 85%). A colorless solid; mp 89-91 $^\circ\text{C}$; R_f = 0.20 (hexane/AcOEt = 4:1); ^1H NMR (400 MHz, CDCl_3) δ 1.38 (dt, J = 12.7, 10.0 Hz, 1 H, one CH_2), 1.61 (s, 3 H, CH_3), 1.68 (s, 3H, CH_3), 2.00 (t, J = 2.7 Hz, 1 H, CH), 2.14 (dt, J = 12.7, 7.6 Hz, 1 H, one of CH_2), 2.58 (dd, J = 14.9, 7.8 Hz, 1 H, one of CH_2), 2.65 (dd, J = 14.9, 7.8 Hz, 1 H, one of CH_2), 2.80 (d, J = 2.7 Hz, 2 H, CH_2), 3.34-3.38 (m, 1 H, CH-), 3.56-3.61 (m, 1 H, CH), 3.67 (s, 3 H, OCH_3), 3.70 (s, 6

H, OCH₃), 3.75 (s, 3 H, OCH₃), 4.97-5.00 (m, 1 H, =CH), 5.82-5.87 (m, 2H, =CH); ¹³C NMR (500 MHz, CDCl₃) δ 17.84, 22.93, 26.03, 27.47, 31.88, 47.43, 47.45, 51.95, 52.15, 52.38, 52.64, 59.60, 60.70, 71.38, 79.11, 117.75, 132.02, 133.12, 135.57, 169.72, 170.20, 170.92, 171.40; IR (KBr) 3250, 2950, 1750 (νCO), 1730 (νCO), 1430, 1290, 1230, 1050 cm⁻¹; GC/MS (EI, 70 eV) *m/z* (rel int, %) 434 (M⁺, 10), 403 (20), 375 (45), 333 (67), 265 (60), 205 (85), 167 (100). Anal. Calcd for C₂₃H₃₀O₈: C, 63.58, H, 6.96. Found: C, 63.54, H, 6.97.

Preparation of *cis*-3-[1',1'-bis(methoxycarbonyl)-3'-butenyl]-5-[1',1'-

bis(methoxycarbonyl)-3'-butynyl]cyclopentene (25b):⁶ The compound was prepared by the procedure employed for **25a**, starting NaH (60% in mineral oil, 173 mg, 4.33 mmol), **S7** (1.03 g, 2.80 mmol), propargyl bromide (1.16 g, 9.78 mmol), and DMF (30 mL). The crude product was purified by column chromatography on silica gel to give **25b** (989 mg, 87%). A colorless solid; *R*_f = 0.33 (hexane/AcOEt = 4:1); ¹H NMR (400 MHz, CDCl₃) δ 1.38 (dt, *J* = 12.7, 10.0 Hz, 1 H, one of CH₂), 2.00 (t, *J* = 2.7 Hz, 1 H, CH), 2.16 (dt, *J* = 12.7, 7.6 Hz, 1 H, one of CH₂), 2.58-2.68 (m, 2 H, CH₂), 2.80 (d, *J* = 1.7 Hz, 2 H, CH₂), 3.34-3.49 (m, 1 H, CH), 3.57-3.65 (m, 1 H, C), 3.68 (s, 3 H, OCH₃), 3.70 (s, 3 H, OCH₃), 3.72 (s, 3 H, OCH₃), 3.76 (s, 3 H, OCH₃), 5.07-5.12 (m, 2 H, =CH₂), 5.63-5.74 (m, 1 H, =CH), 5.82-5.87 (m, 2H, CH=CH).

References

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General Procedure of Ni-catalyzed, ZnCl₂-Assisted Domino Coupling of 1 with 2 or 25.

In a 20-mL three-necked flask were placed ZnCl₂ (0.75–2.0 mmol), Ni catalyst

(0.025–0.05 mmol), Zn dust (0.75–2.0 mmol), Et₃N (1.5 mmol), and MeCN (3 mL), and the suspension was stirred at 25 °C for 10 min. To this suspension were added **1** (1.0 mmol) and **2** or **25** (0.5 mmol) at 25 °C, and the mixture was then stirred at the same temperature for 2~48 h (or at reflux for 1~24 h). After the addition of aqueous HCl (5 %, 30 mL), the aqueous layer was extracted with Et₂O (10 mL x 2). The combined organic layer was washed with brine, dried over MgSO₄ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel. An analytical sample was obtained by bulb-to-bulb distillation.

(5E)-Diethyl 4-methyl-5-(4-oxopentylidene)cyclohex-3-ene-1,1-dicarboxylate (3af):

colorless oil; bp 150 °C (2 mmHg); *R_f* = 0.20 (hexane/AcOEt = 2:1); ¹H NMR (500 MHz, CDCl₃) δ 1.23 (t, *J* = 7.0 Hz, 6 H, CH₃), 1.75 (d, *J* = 2.2 Hz, 3 H, CH₃), 2.16 (s, 3 H, CH₃), 2.43 (q, *J* = 7.3 Hz, 2 H, CH₂), 2.56 (t, *J* = 7.3 Hz, 2 H, CH₂), 2.64-2.67 (m, 2 H, CH₂), 2.84 (s, 2 H, CH₃), 4.16 (q, *J* = 7.0 Hz, 4 H, OCH₂), 5.45 (t, *J* = 7.3 Hz, 1 H, =CH), 5.50-5.54 (m, 1 H, =CH); The NOESY cross peaks were detected: 1.75 ppm vs. 5.45 and 5.50-5.54 ppm; ¹³C NMR (125 MHz, CDCl₃) δ 14.04, 19.51 (CH₃), 21.98 (CH₂), 29.93 (CH₃), 30.96, 31.31, 43.38 (CH₂), 54.03 (C), 61.40 (OCH₂), 122.43, 124.18 (=CH), 132.93, 133.08 (=C), 171.17, 208.26 (C=O); IR (neat) 2945, 1730 (ν_{CO}), 1445, 1370, 1310, 1250, 1185, 1100, 1065, 1040, 865 cm⁻¹; GC/MS (EI, 70 eV) *m/z* (rel int, %) 322 (M⁺, 5), 277 (9), 249 (61), 203 (100). Anal. Calcd for C₁₈H₂₆O₅: C, 67.06; H, 8.13. Found C, 67.04; H, 8.27.

(3E,4Z)-Diethyl 3-ethylidene-4-(4-oxopentylidene)cyclopentane-1,1-dicarboxylate ((E)-6af):

The product was obtained as a mixture with **14af** (*vide infra*) by the reaction with *E*-rich **2f**; colorless oil; *R_f* = 0.24 (hexane/AcOEt = 2:1); ¹H NMR of major (*E*, *Z*)-isomer

(500 MHz, CDCl₃) δ 1.23 (t, J = 7.1 Hz, 6 H, CH₃), 1.73 (d, J = 7.1 Hz, 3 H, CH₃), 2.14 (s, 3 H, CH₃), 2.42-2.56 (m, 4 H, CH₂), 2.92 (d, J = 1.8 Hz, 2 H, CH₂), 2.98 (s, 2 H, CH₂), 4.16 (q, J = 7.1 Hz, 4 H, OCH₂), 5.28 (t, J = 6.5 Hz, 1 H, =CH), 5.72-5.59 (m, 1 H, =CH); The NOESY cross peak was detected: 1.73 ppm vs. 2.98 ppm, 2.92 ppm vs. 5.28 ppm, and 2.42-2.56 ppm vs. 5.72-5.59 ppm; A few peaks of minor (*Z*)-**6af** was also detected: δ 1.63 (dt, J = 7.2, 1.8 Hz, CH₃), 5.18 (t, J = 6.6 Hz, =CH), 5.38 (q, J = 7.23 Hz, =CH); ¹³C NMR (125 MHz, CDCl₃) δ 14.04, 15.38 (CH₃), 23.40 (CH₂), 29.85 (CH₃), 38.32, 42.90, 43.74 (CH₂), 57.22 (C), 61.49 (OCH₂), 122.13, 122.27 (=CH), 136.97, 137.03 (=C), 171.52, 208.45 (C=O); IR (neat) 2990, 1730 (ν CO), 1445, 1365, 1250, 1195, 1165, 1065, 870 cm⁻¹; GC/MS (EI, 70 eV) m/z (rel int, %) 322 (M⁺, 19), 248 (26), 205 (100). HRMS for C₁₈H₂₆O₅: calcd 322.1781; found 322.1775.

(*Z*)-Diethyl 3-(4-Oxopentylidene)-4-vinylcyclopentane-1,1-dicarboxylate ester (14af**):**

The product was obtained as a mixture with **3af** by the reaction with (*Z*)-**2f**; colorless oil; R_f = 0.24 (hexane/AcOEt = 2:1); ¹H NMR (500 MHz, CDCl₃) δ 1.21-1.26 (m, 6 H, CH₃) 1.98 (dd, J = 13.3, 7.0 Hz, 1 H, one of CH₂), 2.11 (s, 3 H, CH₃), 2.24 (q, J = 7.2 Hz, 2 H, CH₂), 2.42 (t, J = 7.2 Hz, 2 H, CH₂), 2.66-2.72 (m, 1 H, one of CH₂), 2.77 (d, J = 15.6 Hz, 1 H, one of CH₂), 2.99 (dt, J = 15.6, 2.1 Hz, 1 H, one of CH₂), 3.34-3.42 (m, 1 H, CH), 4.11-4.47 (m, 4 H, OCH₂), 4.97 (d, J = 10.1 Hz, 1 H, =CH), 5.04 (dt, J = 15.9, 1.2 Hz, 1 H, =CH), 5.34 (t, J = 7.2 Hz, 1 H, =CH), 5.70 (ddd, J = 15.9, 10.1, 7.6 Hz, 1 H, =CH); The NOESY cross peak was detected: 2.77 ppm vs. 5.34 ppm; ¹³C NMR (125 MHz, CDCl₃) δ 14.02, 29.82, 29.93 (CH₃), 40.62, 41.73, 43.31, 43.38 (CH₂), 43.86 (CH), 59.05 (C), 61.42, 61.46 (OCH₂), 114.20 (=CH₂), 123.31, 140.07 (=CH), 140.83 (=C), 171.16, 171.44, 208.42 (C=O); IR (neat) 2990, 1730 (ν CO), 1445, 1365, 1250, 1190, 1065, 870 cm⁻¹; GC/MS (EI, 70 eV) m/z (rel int, %) 322 (M⁺, 1), 304 (8), 277 (M⁺ - OEt, 7), 264 (36), 248 (24), 231 (30), 190 (100). HRMS for C₁₈H₂₆O₅: calcd 322.1781; found 322.1772.

(Z)-Diethyl 3-(4-oxopentylidene)-4-(prop-1-en-2-yl)cyclopentane-1,1-dicarboxylate

(14ag): a colorless oil; bp 150 °C (2 mmHg); R_f = 0.24 (hexane/AcOEt = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 1.21-1.26 (m, 6 H, CH_3), 1.69 (s, 3 H, CH_3), 1.97 (dd, J = 13.1, 8.3 Hz, 1 H, one of CH_2), 2.10 (s, 3 H, CH_3), 2.12-2.19 (m, 2 H, CH_2), 2.40 (t, J = 7.3 Hz, 2 H, CH_2), 2.67-2.73 (m, 1 H, one of CH_2), 2.80 (d, J = 14.0 Hz, 1 H, one of CH_2), 2.96 (d x quin, J = 14.0, 2.5 Hz, one of CH_2), 3.37 (t, J = 8.3 Hz, 1 H, CH), 4.11-4.47 (m, 4 H, OCH_2), 4.71-4.73 (m, 1 H, =CH), 4.77-4.79 (m, 1 H, =CH), 5.36 (t, J = 7.3 Hz, 1 H, =CH); The NOESY cross peaks were detected: 2.80 ppm vs. 5.36 ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 13.98, 14.01, 19.45 (CH_3), 22.94, (CH_2), 29.75 (CH_3), 39.67, 42.62, 43.02 (CH_2), 47.14 (CH), 59.15 (C), 61.37, 61.39 (OCH_2), 111.09 ($=\text{CH}_2$), 123.44 ($=\text{CH}$), 140.64, 145.94 ($=\text{C}$), 171.32, 171.37, 208.46 ($\text{C}=\text{O}$); IR (neat) 2995, 1730 (ν_{CO}), 1445, 1365, 1290, 1260, 1240, 1190, 1165, 1095, 1075, 1020, 900, 865 cm^{-1} ; GC/MS (EI, 70 eV) m/z (rel int, %) 336 (M^+ , 17), 318 (8), 291 (15), 278 (18), 263 (22), 245 (24), 217 (66), 204 (100). Anal. Calcd for $\text{C}_{19}\text{H}_{28}\text{O}_5$: C, 67.83; H, 8.39. Found C, 67.66; H, 8.48.

Mixture of (4Z)-dimethyl 3-((E)-6-methylhepta-2,5-dien-2-yl)-4-(4-oxopentylidene)cyclopentane-1,1-dicarboxylate ((E)-20) and (Z)-dimethyl 3-(6-methylhepta-1,5-dien-2-yl)-4-(4-oxopentylidene)cyclopentane-1,1-dicarboxylate (21): a colorless oil; bp 185 °C (2 mmHg); R_f = 0.22 (hexane/AcOEt = 2:1); ^1H NMR of (E)-20 (500 MHz, CDCl_3) δ 1.57 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.96-3.03 (10 H, CH_2 and CH), 2.09 (s, 3 H, CH_3), 3.32 (t, J = 7.6 Hz, 1 H, CH), 3.70 (s, 3 H, OCH_3),

3.71(s, 3 H, OCH₃), 5.04 (t, *J* = 7.4 Hz, 1 H, =CH), 5.22 (t, *J* = 7.0 Hz, 1 H, =CH), 5.35 (t, *J* = 7.3 Hz, 1 H, =CH); The NOESY cross peaks were detected: 3.32 ppm vs. 5.22 ppm; ¹H NMR of **21** (500 MHz, CDCl₃) δ 1.61 (s, 3 H, CH₃), 1.68 (s, 3 H, CH₃), 1.96-3.03 (12 H, CH₂ and CH), 2.10 (s, 3 H, CH₃), 3.39 (t, *J* = 7.6 Hz, 1 H, CH), 3.70 (s, 3 H, OCH₃), 3.71 (s, 3 H, OCH₃), 4.75 (s, 1 H, =CH), 4.82 (s, 1 H, =CH), 5.11 (t, *J* = 7.4 Hz, 1 H, =CH), 5.35 (t, *J* = 7.3 Hz, 1 H, =CH); ¹³C NMR of mixture (125 MHz, CDCl₃) δ 13.38, 17.73, 22.85, 23.26, 25.67, 25.68, 26.23, 26.99, 29.72, 29.79, 33.49, 39.93, 40.43, 42.71, 42.99, 43.09, 46.20, 48.76, 52.64, 52.70, 52.74, 59.02, 59.13 (CH₃, CH₂, CH, and C), 109.28, 122.79, 123.47, 123.49, 124.04, 124.56, 131.60, 131.80, 135.06, 140.54, 140.66, 149.89 (=CH₂, =CH, and =C), 171.76, 171.88, 171.94, 208.38, 208.49 (C=O) IR (neat) 2945, 2925, 1735 (νCO), 1430, 1290, 1260, 1245, 1200, 1165, 1075, 890 cm⁻¹; GC/MS of (*E*)-**20** (EI, 70 eV) *m/z* (rel int, %) 376 (M⁺, 13), 189 (27), 109 (100); GC/MS of **21** (EI, 70 eV) *m/z* (rel int, %) 376 (M⁺, 19), 333 (29), 318 (32), 258 (39), 241 (49), 215 (49), 189 (73), 109 (87), 69 (100). HRMS of (*E*)-**20** for C₂₂H₃₂O₅: calcd 376.2250; found 376.2257. HRMS of **21** for C₂₂H₃₂O₅: calcd 376.2250; found 376.2255. Anal. Calcd for C₂₂H₃₂O₅: C, 70.18; H, 8.57. Found C, 70.45; H, 8.68.

(3Z,3aS*,6aR*)-Diethyl 3,3a,6,6a-tetrahydro-3-(4-oxopentylidene) pentalene-1,1(2H)-dicarboxylate (22ai): a colorless oil; *R*_f = 0.34 (hexane/AcOEt = 4/1); ¹H NMR (500 MHz, CDCl₃) δ 1.22 (t, *J* = 7.0 Hz, 3 H, CH₃), 1.25 (t, *J* = 7.0, 3 H, CH₃), 2.01-2.08 (m, 1 H, one of CH₂), 2.13 (s, 3 H, CH₃), 2.22-2.37 (m, 2 H, CH₂), 2.45-2.55 (m, 4 H, CH₂ and 2 x one of CH₂), 2.94 (ddd, *J* = 15.2, 2.17, 1.8 Hz, 1 H, one of CH₂), 3.53 (ddd, *J* = 8.5, 6.4, 2.1 Hz, 1 H, CH), 3.85 (d, *J* = 6.4 Hz, 1 H, CH), 4.14 (q, *J* = 7.0 Hz, 2 H, CH₂), 4.18 (q, *J* = 7.0 Hz, 2 H, CH₂), 5.14 (t, *J* = 7.3 Hz, 1 H, CH), 5.56-5.62 (m, 2 H, CH); ¹³C NMR (125 MHz, CDCl₃) δ 14.0, 14.1 (CH₃), 23.1 (CH₂), 29.9 (CH₃), 35.4, 39.0, 43.5, (CH₂), 45.6, 51.9 (CH), 61.1, 61.3 (CH₂), 63.0 (C), 102.3, 129.5, 130.9 (=CH), 141.5 (=C), 170.2, 171.5, 208.3 (C=O); IR (neat) 2990, 1730 (νCO), 1365, 1260, 1225, 1160, 1085 cm⁻¹; DI/MS (EI, 70 eV) *m/z* (rel int, %) 334 (M⁺, 19), 276 (75), 242 (56), 215 (63), 214 (88), 203 (64), 202 (100). Anal. Calcd for C₁₉H₂₆O₅: C, 68.24; H, 7.84. Found: C, 68.03; H, 7.84.

(3Z,3aS*,7aR*)-Diethyl 3,3a,7,7a-tetrahydro-3-(4-oxopentylidene)-2H-indene-1,1(6H)-dicarboxylate (22aj): colorless oil; bp 180 °C (2 mmHg); R_f = 0.22 (hexane/AcOEt = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 1.12-1.29 (m, 7 H, CH_3 and one of CH_2), 1.39-1.46 (m, 1 H, one of CH_2), 1.89-2.04 (m, 2 H, CH_2), 2.11 (s, 3 H, CH_3), 2.30 (q, J = 7.5 Hz, 2 H, CH_2), 2.45 (t, J = 7.5 Hz, 2 H, CH_2), 2.59 (d, J = 15.9 Hz, 1 H, one of CH_2), 2.88-2.96 (m, 1 H, CH), 3.19 (d x quin, J = 15.9, 2.5 Hz, one of CH_2), 3.33-3.38 (m, 1 H, CH), 4.04-4.47 (m, 4 H, OCH_2), 5.18-5.24 (m, 1 H, =CH), 5.74-5.79 (m, 1 H, =CH), 5.81-5.85 (m, 1 H, =CH); The NOESY cross peaks were detected: 2.30 ppm vs. 3.33-3.38 ppm; 2.59 ppm vs. 5.18-5.24 ppm; 2.88-2.96 ppm vs. 3.33-3.38 ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 14.05, 14.14 (CH_3), 22.35, 23.21, 23.53 (CH_2), 29.84 (CH_3), 39.14 (CH_2), 40.32, 42.33 (CH), 43.65 (CH_2), 61.24, 64.34 (OCH_2), 63.03 (C), 121.71, 126.95, 127.08 (=CH), 140.94 (=C), 169.71, 171.38, 208.25 (C=O); IR (neat) 2990, 2945, 1730 (ν_{CO}), 1445, 1365, 1295, 1255, 1235, 1200, 1165, 1100, 1070, 865, 695 cm^{-1} ; GC/MS (EI, 70 eV) m/z (rel int, %) 348 (M^+ , 0), 330 (6), 303 (6), 290 (18), 257 (25), 228 (64), 216 (63), 173 (100). Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{O}_5$: C, 68.94; H, 8.10. Found C, 68.91; H, 8.18.

(5E)-5-((3aR*,7aR*)-1,2,7,7a-tetrahydro-1-(toluene-4-sulfonyl)-3aH-indol-3(6H)-ylidene)pentan-2-one (22ak): a colorless oil; R_f = 0.14 (hexane/AcOEt = 4:1); ^1H NMR (400 MHz, CDCl_3) δ 1.62-1.70 (m, 1 H, one of CH_2), 1.88-1.99 (m, 1 H, one of CH_2), 2.08 (s, 3 H, CH_3), 2.21-2.42 (m, 6 H, CH_2), 2.43 (s, 3 H, CH_3), 3.24-3.30 (m, 1 H, CH), 3.59-3.62 (m, 1 H, CH), 3.72 (dd, J = 14.1, 1.3 Hz, 1 H, one of CH_2), 4.01 (dt, J = 14.1, 1.7 Hz, 1 H, one of CH_2), 5.09 (dt, J = 2.0, 4.3 Hz, 1 H, =CH), 5.35-5.40 (m, 1 H, =CH), 5.81-5.85 (m, 1 H, =CH), 7.31 (d, J = 8.2 Hz, 2 H, Ar), 7.69 (d, J = 8.2 Hz, 2 H, Ar); ^{13}C NMR (125 MHz, CDCl_3) δ 19.9 (CH_2), 21.5 (CH_3), 23.4, 25.5 (CH_2), 30.0 (CH_3), 41.4 (CH), 43.1, 53.1

(CH₂), 58.9 (CH), 120.9, 124.7, 127.3, 127.7, 128.7, 228.8, 129.6, 129.7, 129.8 (=CH), 133.8, 137.1, 143.4 (=C), 207.7 (C=O); IR (neat) 2925, 1715 (ν CO), 1345, 1165, 1095, 670 cm⁻¹; DI/MS (EI, 70 eV) m/z (rel int, %) 359 (M⁺, 6), 204 (98), 203 (41), 146 (50), 145 (50), 91 (100). HRMS for C₂₀H₂₅NO₃S (M⁺): calcd, 359.1556; found, 359.1548.

26: a colorless hard gum; R_f = 0.26 (hexane/AcOEt = 2:1); ¹H NMR (500 MHz, CDCl₃) δ 1.03 (q, J = 12.2 Hz, 1 H, one of CH₂), 1.44 (dt, J = 12.2, 6.3 Hz, 1 H, one of CH₂), 1.60 (s, 3 H, CH₃), 1.83 (dd, J = 14.8, 7.0 Hz, 1 H, one of CH₂), 1.91-2.00 (m, 1 H, one of CH₂), 2.03-2.14 (m, 1 H, one of CH₂), 2.08 (s, 3 H, CH₃), 2.34 (t, J = 7.0 Hz, 2 H, CH₂), 2.49 (dt, J = 10.1, 7.0 Hz, 1 H, CH), 2.58 (d, J = 15.0 Hz, 1 H, one of CH₂), 2.85-2.99 (m, 2 H, CH and one of CH₂), 3.03 (d, J = 15.0 Hz, 1 H, one of CH₂), 3.15 (dt, J = 12.2, 6.3 Hz, 1 H, CH), 3.28-3.40 (m, 2 H, CH and one of CH₂), 3.67 (s, 3H, CH₃), 3.67 (s, 3H, CH₃), 3.69 (s, 3H, CH₃), 3.70 (s, 3H, CH₃), 4.65 (s, 1 H, one of =CH₂), 4.68 (s, 1 H, one of =CH₂), 5.15 (t, J = 7.0 Hz, 1 H, =CH); ¹³C NMR (500 MHz, CDCl₃) δ 20.20 (CH₃), 24.09 (CH₂), 29.69 (CH₃), 30.20, 39.08, 41.73, 43.00 (CH₂), 45.82, 46.02, 50.11, 50.15 (CH), 52.32 (x 2), 52.40, 52.61, 52.64 (OCH₃ and CH), 60.55, 61.00 (C), 110.87 (=CH₂), 123.93 (=CH), 138.27, 146.06 (=C), 170.25, 170.62, 171.59, 172.75, 208.23 (O=C); IR (neat) 2950, 1730 (ν CO), 1040, 1160, 1230, 1440 cm⁻¹; GC/MS (EI, 70 eV) m/z (rel int, %) 504 (M⁺, 23), 486 (32), 444 (42), 412 (100), 386 (27), 354 (44). FT-ICRMS for C₂₇H₃₆O₉ + Na [(M + Na)⁺]: calcd, 527.2252; found, 527.2237.