Nickel-Catalyzed Cycloaddition of Unsaturated Hydrocarbons and Carbonyl Compounds

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SUPPORTING INFORMATION

General Experimental

All reactions were conducted under an atmosphere of N₂ using standard Schlenk techniques or in a N₂ filled glove-box unless otherwise noted. Toluene was dried over neutral alumina under N₂ using a Grubbs-type solvent purification system. THF was freshly distilled from Na/benzophenone. Ni(COD)₂ was purchased from Strem and used without further purification. SIPr, IPr, IMes and ItBu ligands were prepared as previously reported.^{1,2,3} Diynes 2,2-di-but-2-ynyl-malonic acid dimethyl ester (**4a**) and 2,2-di-prop-2-ynyl-malonic acid dimethyl ester (**4b**) were synthesized by literature procedures or under slightly modified conditions.^{4,5} Sodium hydride was thoroughly washed with pentane and dried *in vacuo* prior to use. All other reagents were purchased and used without further purification unless otherwise noted.

¹H and ¹³C Nuclear Magnetic Resonance spectra of pure compounds were acquired at 300 and 75 MHz, respectively unless otherwise noted. All spectra are referenced to a singlet at 7.27 ppm for ¹H and to the center line of a triplet at 77.23 ppm for ¹³C. The abbreviations s, d, dd, dt, dq, t, td, tq, q, qt, quint, sept, septd, septt, m, brm, brd, brt, and brs stand for singlet, doublet, doublet of doublets, doublet of triplets, doublet of quartets, triplet, triplet of doublets, triplet of quartets, quartet, quartet of triplets, quintet, septet, septet of doublets, septet of triplets, multiplet, broad multiplet, broad doublet, broad triplet, and broad singlet, in that order. All ¹³C NMR spectra were proton decoupled. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. HRMS were performed at the mass spectrometry facility at The University of Utah.

Preparation of 2-but-2-ynyl-2,3,3-tris-ethoxycarbonyl-hept-5-ynoic acid ethyl ester (1a). To a stirred suspension of NaH (255.0 mg, 10.6 mmol) and dry THF (40 mL) in a 100 mL RBF was added tetraethyl 1,1,2,2-ethanetetracarboxylate (1.3000 g, 4.1 mmol) under N₂ counter-flow in two portions. The resulting solution was stirred at room temperature for 1 h after which time 1-bromo-2-butyne (1.409 g, 10.6 mmol) was added. The reaction mixture was then heated at reflux for 44 hrs at which time GC analysis showed no remaining starting ester or mono-alkylated ester. The solution was cooled to room temperature and quenched with 20 mL sat. NH₄Cl solution. The aqueous layer was extracted 3 x 10 mL Et₂O. The collected organics were washed with brine, dried with anhydrous Na₂SO₄, and concentrated *in vacuo*. The resulting crude yellow oil was purified by flash column chromatography (15% EtOAc/hexanes then 25% EtOAc/hexanes) to yield a pale yellow oil which was triturated with hexanes to afford **1a** (1.4848g, 86%) as a white solid. ¹H and ¹³C NMR were identical to those reported in literature.⁶

2-(1,1-bis-ethoxycarbonyl-hex-3-ynyl)-2-ethoxycarbonyl-hept-4-ynoic acid ethyl ester (1b).

Prepared analogously to **1a** with 351.6 mg NaH (14.7 mmol), 2.1197 g tetraethyl 1,1,2,2-ethanetetracarboxylate (6.7 mmol), and 2.1538 g 1-bromo-2-pentyne (6.7 mmol).

Purified by column chromatography eluting with 15% EtOAc/hexanes to yield **1b** (2.4211 g, 81%) as a yellow oil.

¹H NMR (300 MHz, CDCl₃): δ (ppm) 4.30-4.16 (m, 8H), 3.10 (t, *J* = 2.2 Hz, 4H), 2.12 (qt, *J* = 7.5, 2.2Hz, 4H), 1.29 (t, *J* = 7.1 Hz, 12H), 1.08 (t, *J* = 7.5 Hz, 6H). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ (ppm) 168.8, 84.0, 75.1, 62.0, 61.8, 22.8, 14.0, 13.9, 12.5. IR (neat): 2981, 1734, 1448, 1368, 1206, 1097, 1039 cm⁻¹. HRMS(EI): calcd for C₂₄H₃₅O₈ (MH⁺) 451.2332, obsd 451.2328.

Preparation of 2-allyl-2,3,3-tris-ethoxycarbonyl-hept-5-ynoic acid ethyl ester (9). To a stirred suspension of NaH (356.0 mg, 14.9 mmol) and dry THF (135 mL) in a 250 mL RBF was added tetraethyl 1,1,2,2-ethanetetracarboxylate (4.2970 g, 13.5 mmol) under N₂ counter-flow in two portions. The resulting solution was stirred at room temperature for 3 hrs after which time 1-bromo-2-butyne (1.9748 g, 14.9 mmol) was added. The

reaction mixture was then stirred at room temperature for 3 hrs then heated at reflux for 8 hrs at which time GC analysis showed no remaining starting ester. The solution was cooled to room temperature and quenched with 20 mL sat. NH_4Cl solution. The aqueous layer was extracted 3 x 10 mL Et_2O . The collected organics were washed with brine, dried with anhydrous Na_2SO_4 , and concentrated *in vacuo*. The resulting crude yellow oil was purified by flash column chromatography (15% EtOAc /hexanes then 25% EtOAc /hexanes) to yield 2,3,3-tris-ethoxycarbonyl-hept-5-ynoic acid ethyl ester (4.5511 g, 91%) as a pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 4.34 (s, 1H), 4.30-4.17 (m, 8H), 2.93 (q, $J = 2.6\text{ Hz}$, 2H), 1.78 (t, $J = 2.6\text{ Hz}$, 3H), 1.28 (t, $J = 7.2\text{ Hz}$, 12H). ^{13}C { ^1H } NMR (75 MHz, CDCl_3): δ (ppm) 168.7, 167.3, 79.4, 73.4, 62.0, 61.7, 57.7, 54.8, 24.6, 13.95, 13.91, 3.6. IR (neat): 2985, 1741, 1447, 1370, 1210, 1033, 863 cm^{-1} . HRMS(EI): calcd for $\text{C}_{18}\text{H}_{26}\text{O}_8$ (M^+) 370.1628, obsd 370.1627.

To a stirred suspension of NaH (77.8 mg, 3.2 mmol) and dry THF (40 mL) in a 100 mL RBF, 2,3,3-tris-ethoxycarbonyl-hept-5-ynoic acid ethyl ester (1 g, 2.7 mmol) was added in two portions under N_2 counter-flow. The resulting solution was stirred at room temperature for 1 h after which time 1-bromo-2-butyne (490 mg, 4.1 mmol) was added. The reaction mixture was then heated at reflux for 44 hrs. The solution was cooled to room temperature and quenched with 20 mL sat. NH_4Cl solution. The aqueous layer was extracted 3 x 10 mL Et_2O . The collected organics were washed with brine, dried with anhydrous Na_2SO_4 , and concentrated *in vacuo*. The crude product was purified by column chromatography eluting with 15% EtOAc /hexanes producing a yellow oil which was further purified by triturating with hexanes to yield **9** (982.3 mg, 89%) as a white solid. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 6.07-5.90 (m, 1H), 5.11 (d, $J = 17.0\text{ Hz}$, 1H), 5.05 (d, $J = 10.1\text{ Hz}$, 1H), 4.35-4.10 (m, 8H), 3.07 (q, $J = 2.4\text{ Hz}$, 2H), 2.86 (d, $J = 7.2\text{ Hz}$, 2H), 1.75 (t, 2.4 Hz, 3H), 1.28 (appt. q, 12H). ^{13}C { ^1H } NMR (75 MHz, CDCl_3): δ (ppm) 169.2, 161.1, 134.0, 119.1, 78.1, 74.8, 62.6, 62.3, 61.9, 61.7, 36.3, 22.8, 14.01, 13.99, 3.8. IR (neat): 2982, 1731, 1367, 1330, 1211, 1035 cm^{-1} . HRMS(CI): calcd for $\text{C}_{21}\text{H}_{31}\text{O}_8$ (MH^+) 411.2019, obsd 411.1999.

General [2+2+2] Cycloaddition Procedure with aldehydes. In a glove box, the diyne and aldehyde were added to an oven dried scintillation vial equipped with a magnetic stir bar and dissolved in toluene. To the stirring solution, a solution of $\text{Ni}(\text{COD})_2$ and SIPr (previously equilibrated for at least 6 h)⁷ was added. The reaction mixture was stirred at room temperature for 2 h (or until complete consumption of starting material was observed as

judged by GC or TLC) over which time the color changed from orange to brown. The mixture was concentrated *in vacuo* and purified by silica gel column chromatography.

4-Acetyl-5-(1-methyl-2-phenyl-vinyl)-cyclohex-4-ene-1,1,2,2-tetracarboxylic acid tetraethyl

ester (3a). The general procedure was used with 2-but-2-ynyl-2,3,3-tris-ethoxycarbonyl-hept-5-

ynoic acid ethyl ester (**1a**, 165.6 mg, 0.39 mmol), benzaldehyde (**2a**, 52.0 mg, 0.49 mmol),

Ni(COD)₂ (5.4 mg, 0.020 mmol), SIPr (15.3 mg, 0.039 mmol), and 3.9 mL of toluene. The

reaction mixture was purified by flash chromatography (12% EtOAc/hexanes then 15% EtOAc/hexanes) to yield dienone **3a** (166.3 mg, 80%) as a sticky pale yellow oil. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.36-7.29 (m, 2H), 7.25-7.19 (m, 3H), 6.24 (br s, 1H), 4.30-4.14 (brm, 8H), 3.12 (s, 2H), 3.07 (s, 2H), 2.20 (s, 3H), 2.10 (brs, 3H), 1.27 (t, *J* = 7.2 Hz, 12H). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ (ppm) 202.7, 169.72, 169.65, 145.9, 137.5, 137.0, 132.5, 130.4, 128.8, 128.4, 127.2, 62.0, 61.9, 57.3, 56.6, 35.2, 32.1, 30.3, 16.9, 14.0. IR (neat): 2983, 1723, 1672, 1264, 1200, 1098, 1056 cm⁻¹. HRMS(CI): calcd for C₂₉H₃₆O₉ (M⁺) 528.2359, obsd 528.2369. COSY summary; the following pertinent cross peaks were observed: H(3) and H(2) and H(4). NOE summary; the following pertinent enhancements were observed: irradiation of H(2) resulted in the enhancement of H(1) and H(4).

4-Acetyl-5-[2-(4-methoxy-phenyl)-1-methyl-vinyl]-cyclohex-4-ene-1,1,2,2-tetracarboxylic

acid tetraethyl ester (3b). The general procedure was used with 2-but-2-ynyl-2,3,3-tris-

ethoxycarbonyl-hept-5-ynoic acid ethyl ester (**1a**, 135.1 mg, 0.32 mmol), anisaldehyde (**2b**, 54.5

mg, 0.40 mmol) Ni(COD)₂ (4.4 mg, 0.016 mmol), SIPr (12.5 mg, 0.032 mmol), and 3.2 mL of

toluene. The reaction mixture was purified by flash chromatography (12% EtOAc/hexanes then 15% EtOAc/hexanes) to yield dienone **3b** (163.8 mg, 92%) as a sticky pale yellow oil. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.18 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.18 (brs, 1H), 4.31-4.15 (brm, 8H), 3.79 (s, 3H), 3.11 (s, 2H), 3.06 (s, 2H), 2.17 (s, 3H), 2.06 (brs, 3H), 1.26 (t, *J* = 6.8 Hz, 12H). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ (ppm) 203.0, 169.82, 169.75, 158.7, 146.7, 135.7, 132.5, 130.3, 130.2, 129.7, 113.9, 62.1, 62.0, 57.5, 56.7, 55.4, 35.2, 32.1, 30.4, 16.9, 14.0. IR (neat): 2983, 1738, 1670, 1607, 1260, 1036 cm⁻¹. HRMS(EI): calcd for C₃₀H₃₈O₁₀ (M⁺) 558.2465, obsd 558.2471. COSY summary; the following pertinent cross peaks were observed: H(3) and

H(2) and H(4). NOE summary; the following pertinent enhancements were observed: irradiation of H(2) resulted in the enhancement of H(1) and H(4).

4-Acetyl-5-[1-methyl-2-(4-trifluoromethyl-phenyl)-vinyl]-cyclohex-4-ene-1,1,2,2-

tetracarboxylic acid tetraethyl ester (3c). The general procedure was used with 2-but-2-ynyl-

2,3,3-tris-ethoxycarbonyl-hept-5-ynoic acid ethyl ester (**1a**, 134.3 mg, 0.32 mmol), α,α,α -

trifluoro-*p*-tolualdehyde (**2c**, 69.2 mg, 0.40 mmol), Ni(COD)₂ (8.8 mg, 0.032 mmol), SIPr (24.8

mg, 0.064 mmol), and 3.2 mL of toluene. The reaction mixture was purified by flash chromatography (12% EtOAc/hexanes then 15% EtOAc/hexanes) to yield dienone **3c** (127.1 mg, 67%) as a sticky yellow oil. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.60 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 6.27 (brs, 1H), 4.33-4.17 (brm, 8H), 3.12 (brs, 2H), 3.08 (brs, 2H), 2.21 (s, 3H), 2.07 (d, J = 1.2 Hz, 3H), 1.29 (t, J = 7.1 Hz, 12H). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ (ppm) 204.4, 169.8, 169.7, 145.2, 140.7, 140.2, 132.7, 129.1, 128.6, 125.46, 125.42, 62.2, 62.1, 57.4, 56.6, 35.4, 32.2, 30.3, 17.1, 14.1. IR (neat): 2985, 1734, 1617, 1416, 1230, 1124, 867 cm⁻¹. HRMS(EI): calcd for C₃₀H₃₅F₃O₉ (M⁺) 596.2233, obsd 596.2241. COSY summary; the following pertinent cross peaks were observed: H(3) and H(2) and H(4). NOE summary; the following pertinent enhancements were observed: irradiation of H(2) resulted in the enhancement of H(1) and H(4).

4-Acetyl-5-(1,3-dimethyl-but-1-enyl)-cyclohex-4-ene-1,1,2,2-tetracarboxylic acid tetraethyl

ester (3d). The general procedure was used with 2-but-2-ynyl-2,3,3-tris-ethoxycarbonyl-hept-5-

ynoic acid ethyl ester (**1a**, 140.0 mg, 0.33 mmol), isobutyraldehyde (**2d** 29.9 mg, 0.41 mmol)

Ni(COD)₂ (9.1 mg, 0.033 mmol), SIPr (12.9 mg, 0.033 mmol), and 3.3 mL of toluene. The reaction mixture was purified by flash chromatography (12% EtOAc/hexanes then 15% EtOAc/hexanes) collecting the fractions containing the spot with R_f 0.28 in 30% EtOAc/hexanes (purple with anisaldehyde stain). The remaining mixed fractions containing the dienolic ether and impurities were combined and allowed to re-equilibrate for 4 hrs. The re-equilibrated mixture was then re-chromatographed (12% EtOAc/hexanes then 15% EtOAc/hexanes). This process was repeated twice to yield dienone **3d** and a small amount of the dienolic ether (98.5 mg, 60%) as a sticky yellow oil. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 5.04 (dq, J = 9.1, 1.1 Hz, 1H), 4.32-4.12 (brm, 8H), 3.00 (s, 4H), 2.52 (septd, J = 6.6, 2.4 Hz, 1H), 2.16 (s, 3H), 1.82 (d, J = 1.1 Hz, 3H), 1.27 (appt td, J = 7.1, 1.7 Hz, 12H), 0.94

(d, $J = 6.7$ Hz, 6H). ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ (ppm) 203.4, 169.9, 169.8, 145.8, 138.8, 132.9, 131.8, 62.1, 61.9, 57.4, 56.7, 35.3, 32.0, 30.5, 27.5, 22.1, 15.1, 14.0. IR (neat): 2963, 1742, 1676, 1265, 1096, 1052 cm^{-1} . HRMS(CI): calcd for $\text{C}_{26}\text{H}_{38}\text{O}_9$ (M^+) 494.2516, obsd 494.2509. COSY summary; the following pertinent cross peaks were observed: H(3) and H(2) and H(4); H(4) and H(3) and H(5). NOE summary; the following pertinent enhancements were observed: irradiation of H(2) resulted in the enhancement of H(1) and H(4); irradiation of H(4) resulted in the enhancement of H(2).

4-Acetyl-5-(1-methyl-pent-1-enyl)-cyclohex-4-ene-1,1,2,2-tetracarboxylic acid tetraethyl ester (3e). The general procedure was used with 2-but-2-ynyl-2,3,3-tris-ethoxycarbonyl-hept-5-ynoic acid ethyl ester (**1a**, 96.7mg, 0.22 mmol), butyraldehyde (**2e**, 82.6 mg, 1.15 mmol), $\text{Ni}(\text{COD})_2$ (6.3 mg, 0.023 mmol), SIPr (9.0 mg, 0.023 mmol), and 2.2 mL of toluene. The

reaction mixture was purified by flash chromatography (12% EtOAc/hexanes then 15% EtOAc/hexanes) collecting the fractions containing the spot with R_f 0.28 in 30% EtOAc/hexanes (purple with anisaldehyde stain). The remaining mixed fractions containing the dienolic ether and impurities were combined and allowed to re-equilibrate for 4 hrs. The re-equilibrated mixture was then re-chromatographed (12% EtOAc/hexanes then 15% EtOAc/hexanes). This process was repeated twice to yield dienone **3e** and a small amount of the dienolic ether (88.9 mg, 73%) as a sticky pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 5.22 (tq, $J = 7.2, 1.4$ Hz, 1H), 4.29-4.09 (brm, 8H), 2.98 (s, 4H), 2.12 (s, 3H), 1.97 (q, $J = 7.3$ Hz, 2H), 1.79 (d, $J = 1.3$ Hz, 3H), 1.33 (quint, $J = 7.4$ Hz, 2H), 1.24 (appt td, $J = 7.1, 1.9$ Hz, 12H), 0.87 (t, $J = 7.4$ Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ (ppm) 203.5, 169.9, 146.0, 135.2, 132.1, 131.9, 62.0, 61.9, 57.5, 56.7, 35.4, 32.0, 30.6, 30.4, 22.1, 15.2, 14.2, 14.1, 14.0. IR (neat): 2982, 1738, 1674, 1445, 1367, 1265, 1051 cm^{-1} . HRMS(CI): calcd for $\text{C}_{26}\text{H}_{38}\text{O}_9$ (M^+) 494.2516, obsd 494.2495. COSY summary; the following pertinent cross peaks were observed: H(3) and H(2) and H(4); H(4) and H(3) and H(5). NOE summary; the following pertinent enhancements were observed: irradiation of H(2) resulted in the enhancement of H(1) and H(4); irradiation of H(4) resulted in the enhancement of H(2).

4-(1-Benzylidene-propyl)-5-propionyl-cyclohex-4-ene-1,1,2,2-tetracarboxylic acid tetraethyl ester (3f). The general procedure was used with 2-(1,1-bis-ethoxycarbonyl-hex-3-ynyl)-2-

ethoxycarbonyl-hept-4-ynoic acid ethyl ester (**1b**, 153.3 mg, 0.34 mmol), benzaldehyde (**2a**, 45.1 mg, 43 mmol) Ni(COD)₂ (13.3 mg, 0.017 mmol), SIPr (19.8 mg, 0.034 mmol), and 3.4 mL of toluene. The reaction mixture was purified by flash chromatography (12% EtOAc/hexanes then 15% EtOAc/hexanes) to yield dienone **3f** (158.4 mg, 84%) as a sticky pale yellow oil. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.37-7.15 (m, 5H), 6.26 (brs, 1H), 4.31-4.18 (brm, 8H), 3.09 (brs, 4H), 2.59 (q, *J* = 7.3 Hz, 2H), 2.48 (q, 7.6Hz, 2H), 1.29 (t, *J* = 7.2, 12H), 1.12 (t, *J* = 7.6 Hz, 3H), 1.00 (t, *J* = 7.3 Hz, 3H). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ (ppm) 207.8, 169.7, 143.4, 140.6, 137.0, 134.2, 130.0, 128.7, 128.3, 127.1, 62.0, 61.9, 57.3, 56.6, 36.2, 34.9, 33.1, 23.0, 14.0, 13.9, 12.7, 8.7. IR (neat): 2981, 2939, 1737, 1681, 1136, 1040 cm⁻¹. HRMS(EI): calcd for C₃₁H₄₀O₉ (M⁺) 556.2672, obsd 556.2681. COSY summary; the following pertinent cross peaks were observed: H(3) and H(2) and H(4); H(2) with H(5). NOE summary; the following pertinent enhancements were observed: irradiation of H(2) resulted in the enhancement of H(1) and H(4).

4-Methylene-3-(2-oxo-2-phenyl-ethyl)-cyclopent-2-ene-1,1-dicarboxylic acid dimethyl ester

(5a). The general procedure was used with 2,2-di-prop-2-ynyl-malonic acid dimethyl ester (**4a**, 118.4 mg, 0.57 mmol), benzaldehyde (**2a**, 63.4 mg, 0.60 mmol), Ni(COD)₂ (7.8 mg, 0.028 mmol), SIPr (21.8 mg, 0.056 mmol), and 5.7 mL of toluene. The reaction mixture was purified

by flash chromatography (5% EtOAc/hexanes) to yield ketone **5a** (36.1 mg, 20%) as an oily colorless solid. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.95 (d, *J* = 8.3, 2H), 7.57 (m, 1H), 7.46 (m, 2H) 6.07 (s, 1H), 4.99 (td, *J*₁ = *J*₂ = 1.9 Hz, 1H), 4.95 (t, *J* = 2.3 Hz, 1H), 3.85 (d, *J* = 1.5, 2H), 3.70 (s, 6H), 3.23 (t, *J* = 1.9 Hz, 2H). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ (ppm) 196.6, 170.8, 149.8, 141.8, 136.6, 134.2, 133.5, 128.8, 128.6, 104.6, 63.8, 53.1, 38.0, 37.4. IR (neat): 3065, 2955, 2846, 1733, 1687, 1434, 1256 cm⁻¹. HRMS(CI): calcd for C₁₈H₁₈O₅ (M⁺) 314.1154, obsd 315.1217.

3-Ethylidene-4-(1-methyl-2-oxo-2-phenyl-ethylidene)-cyclopentane-1,1-dicarboxylic acid dimethyl ester (5b).

The general procedure was used with 2,2-di-but-2-ynyl-malonic acid dimethyl ester (**4b**, 131.5 mg, 0.56 mmol), bezaldehyde (**2a**, 73.8 mg, 0.70 mmol), Ni(COD)₂

(7.7 mg, 0.028 mmol), SIPr (21.8 mg, 0.056 mmol), and 5.6 mL of toluene. The reaction mixture was purified by flash chromatography (10% EtOAc/hexanes then 12% EtOAc/hexanes) to yield dienone **5b** as the major isomer

(111.6 mg, 92%). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.82 (m, 2H), 7.58-7.43 (m, 3H), 6.01 (q, 6.9Hz, 1H) 3.65 (s, 6H), 3.04 (brs, 2H), 2.88 (brs, 2H), 2.10 (brs, 3H), 1.84 (d, 7.0 Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ (ppm) 200.4, 171.8, 138.6, 137.9, 136.7, 133.2, 129.6, 128.9, 126.1, 57.4, 53.0, 41.1, 37.9, 18.6, 16.0. IR (neat): 2955, 2856, 1737, 1662, 1443, 1269, 1067, 972 cm^{-1} . HRMS(EI): calcd for $\text{C}_{20}\text{H}_{22}\text{O}_5$ (M^+) 342.1467, obsd 342.1468. COSY summary; the following pertinent cross peaks were observed: H(3) and H(1) and H(2); H(4) with H(5). NOE summary; the following pertinent enhancements were observed: irradiation of H(1) resulted in the enhancement of H(2); irradiation of H(2) resulted in the enhancement of H(1); irradiation of H(3) results in the enhancement of H(5); irradiation of H(5) results in the enhancement of H(3).

4-Methyl-5-(1-methyl-2-oxo-2-phenyl-ethylidene)-cyclohexane-1,1,2,2-tetracarboxylic acid tetraethyl ester (10a) and 4-ethylidene-5-(2-oxo-2-phenyl-ethyl)-cyclohexane-1,1,2,2-tetracarboxylic acid tetraethyl ester (10b). The general procedure was used with 2-but-2-ynyl-2,3,3-tris-ethoxycarbonyl-hept-5-ynoic acid ethyl ester (**9**, 130.1 mg, 0.32 mmol), benzaldehyde (**2a**, 42.0 mg, 0.40 mmol), $\text{Ni}(\text{COD})_2$ (4.4 mg, 0.016 mmol), SIPr (12.5 mg, 0.032 mmol), and 3.2 mL of toluene. The reaction mixture was purified by flash chromatography (12% EtOAc/hexanes then 15% EtOAc/hexanes) to yield enone **10a** (46.3 mg, 28%) as a sticky pale yellow oil and ketone **10b** (82.7 mg, 51%) also as a sticky pale yellow oil.

4-Methyl-5-(1-methyl-2-oxo-2-phenyl-ethylidene)-cyclohexane-1,1,2,2-tetracarboxylic acid tetraethyl ester (10a). ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.11 (d, $J = 7.7$ Hz, 2H), 7.61-7.45

(m, 3H), 4.33-4.05 (m, 8H) 3.13 (d, $J = 15.7$, 1H), 2.84 (dd, $J = 15.7$, 0.9 Hz, 1H), 2.75 (dd, $J = 13.6$, 6.0 Hz, 1H), 2.69 (brt, $J = 6.1$ Hz, 1H), 2.27 (dd, $J = 13.7$, 2.6 Hz, 1H), 1.83 (brs, 3H), 1.35-1.23 (m, 12H), 0.96 (d, $J = 7.3$ Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ (ppm) 201.3, 170.8, 170.5, 170.4, 168.9, 136.7, 136.3, 133.4, 130.9, 129.8, 128.9, 62.1, 61.8, 61.7, 61.5, 58.7, 58.4, 36.0, 32.8, 29.1, 20.5, 16.1, 14.03, 13.99, 13.97, 13.92. IR (neat): 2982, 1735, 1666, 1596, 1450, 1266, 1058 cm^{-1} . HRMS(EI): calcd for $\text{C}_{28}\text{H}_{36}\text{O}_9$ (M^+)

516.2359, obsd 516.2341. COSY summary; the following pertinent cross peaks were observed: H(1) and H(2). NOE summary; the following pertinent enhancements were observed: irradiation of H(2) resulted in the enhancement of H(1); irradiation of H(1) resulted in the enhancement of H(2).

4-Ethylidene-5-(2-oxo-2-phenyl-ethyl)-cyclohexane-1,1,2,2-tetracarboxylic acid tetraethyl ester (10b). ^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.97 (d, $J = 7.3$ Hz, 2H), 7.62-7.42 (m, 3H),

5.20 (q, $J = 6.6$ Hz, 1H), 4.32-4.03 (m, 8H) 3.35 (dd, $J = 16.4, 6.2$ Hz, 1H), 3.27 (d, $J = 14.7$ Hz, 1H), 3.13 (brm, 1H), 2.84 (dd, $J = 16.3, 7.1$ Hz, 1H), 2.80 (d, $J = 15.4$ Hz, 1H), 2.40 (dd, $J = 13.5, 4.5$ Hz, 1H), 2.20 (dd, $J_1 = J_2 = 13.0$ Hz, 1H), 1.60 (d, $J = 6.6$ Hz, 3H), 1.30-1.18 (m, 12H). ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ (ppm) 198.8, 170.45, 170.37, 169.4, 168.9, 137.2, 134.9, 133.2, 128.7, 128.1, 117.9, 61.9, 61.62, 61.57, 59.5, 41.1, 36.3, 34.6, 31.9, 14.0, 13.92, 13.86, 13.2. IR (neat): 2984, 1735, 1688, 1448, 1261, 1100, 1040 cm^{-1} . HRMS(EI): calcd for $\text{C}_{28}\text{H}_{36}\text{O}_9$ (M^+) 516.2359, obsd 516.2364. COSY summary; the following pertinent cross peaks were observed: H(2) and H(1) and H(3); H(5) and H(6) and H(7). NOE summary; the following pertinent enhancements were observed: irradiation of H(2) resulted in the enhancement of H(1); irradiation of H(3) resulted in the enhancement of H(6).

Spiropyran (12). In a glove box, cyclohexanone (**11**, 43.6 mg, 0.44 mmol) was added to a scintillation vial equipped with a magnetic stir bar and dissolved in 2.2 mL toluene. The vial was sealed with a septum and placed under N_2 . To the stirring solution of cyclohexanone, a solution

of $\text{Ni}(\text{COD})_2$ (9.8 mg, 0.036 mmol) and SIPr (27.7 mg, 0.071 mmol) in 0.4 mL toluene (previously equilibrated for at least 6 h) was added. A solution of 2-but-2-ynyl-2,3,3-tris-ethoxycarbonyl-hept-5-ynoic acid ethyl ester (**1a**, 150.0 mg, 0.36 mmol) in 0.9 mL toluene was then added via syringe pump over 30 min. The resulting brownish orange solution was stirred at room temperature for an addition 1.5 hrs. The crude reaction mixture was concentrated *in vacuo* and purified by flash column chromatography on SiO_2 (12% EtOAc/hexanes then 15% EtOAc/hexanes). The fractions containing both the dienolic ether (upper red spot, anisaldehyde stain) and dienone (lower purple spot, anisaldehyde stain) were combined to yield dienolic ether **12** and a small amount dienone (144.8 mg, 83%) as a white solid. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 4.27-4.13 (m, 8H), 3.01 (s, 2H), 2.88 (s, 2H), 1.92 (brd, $J = 13.0$ Hz, 2H), 1.86 (s, 3H), 1.60 (s, 3H), 1.70-1.56 (brm, 3H), 1.51-1.40 (brm, 3H), 1.36-1.20

(m, 14H). ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ (ppm) 170.2, 170.1, 143.9, 124.0, 121.8, 104.9, 77.7, 61.8, 61.7, 58.7, 57.9, 31.7, 31.1, 30.3, 25.8, 21.4, 16.1, 14.0, 12.5. IR (neat): 2934, 2960, 1740, 1662, 1446, 1266, 1408 cm^{-1} . HRMS(EI): calcd for $\text{C}_{28}\text{H}_{40}\text{O}_9$ (M^+) 520.2672, obsd 520.2673.

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