Highly Regioselective Synthesis of 2,3-Disubstituted Indenes via a Novel Palladium-catalyzed Cyclization Reaction of Propargylic Carbonates with Carbon Nucleophiles

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General Remarks:

Column chromatography was carried out on silica gel. ^1H NMR spectra were recorded on 300 MHz or 400 MHz in CDCl_3 and ^{13}C NMR spectra were recorded on 75 MHz or 100 MHz in CDCl_3 using TMS as internal standard. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1} . Melting points were determined on a microscopic apparatus and were uncorrected. All new compounds were further characterized by element analysis; copies of their ^1H NMR and ^{13}C NMR spectra are provided. Unless otherwise stated, all nucleophiles were purchased from commercial suppliers and used without further purification.

Starting Materials:

Diethyl (2-iodophenyl)malonate, ethyl (2-iodophenyl)(phenylsulfonyl)acetate were prepared according to the literature.¹

References

(1) Zhang, D.; Yum, E. K.; Liu, Z.; Larock, R. C. *Org. Lett.* **2005**, 7, 4963.

Typical procedure for the preparation of propargylic alcohols

To a solution of diethyl (2-iodophenyl)malonate (0.72 g, 2.0 mmol) and prop-2-yn-1-ol (0.13 g, 2.4 mmol) in Et_3N (8.0 mL) was added $\text{PdCl}_2(\text{PPh}_3)_2$ (70 mg, 5 mol %). The mixture was stirred for 5 min and CuI (38 mg, 10 mol %) was added. The resulting mixture was then stirring under an argon atmosphere at room temperature for 12 h. The ammonium salt was removed by filtration. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford diethyl 2-(2-(3-hydroxyprop-1-ynyl)phenyl)malonate 0.41 g (70 %) as an oil; ^1H NMR (300 MHz, CDCl_3) δ 7.47-7.44 (m, 2H), 7.38-7.24 (m, 2H), 5.25 (s, 1H), 4.48 (s, 2H), 4.27-4.18 (m, 4H), 2.75 (s, 1H), 1.28-1.22 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.0, 134.8, 132.1, 128.7, 128.6, 127.8, 123.0, 92.7, 82.9, 61.9, 55.9, 51.3, 13.9; IR (neat, cm^{-1}) 3452, 2984, 1733, 1486, 1306, 1219, 1151, 1031.

Diethyl 2-(2-(3-hydroxybut-1-ynyl)phenyl)malonate: The alcohol was prepared by the same method. But employing diethyl (2-iodophenyl)malonate (0.72 g, 2.0 mmol) and but-3-yn-2-ol (0.17 g, 2.4 mmol) for 12 h afforded alcohol 0.41 g (67 %) as an oil: ^1H NMR (300 MHz, CDCl_3) δ 7.45-7.42 (m, 2H), 7.36-7.23 (m, 2H), 5.23 (s, 1H), 4.77-4.73 (m, 1H), 4.27-4.18 (m, 4H), 2.88-2.87 (d, $J = 5.1$ Hz, 1H), 1.55-1.53 (d, $J = 6.6$ Hz, 3H) 1.28-1.23 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.0, 134.8, 131.9, 128.6, 128.5, 127.8, 123.0, 96.5, 81.3, 61.8, 58.5, 56.0, 24.1, 13.9; IR (neat, cm^{-1}) 3438, 2983, 1732, 1485, 1308, 1151, 1031.

Diethyl 2-(2-(3-hydroxy-3-phenylprop-1-ynyl)phenyl)malonate: The alcohol was prepared by the same method. But employing diethyl (2-iodophenyl)malonate (0.72 g, 2.0 mmol) and 1-phenylprop-2-yn-1-ol (0.32 mg, 2.4 mmol) for 12 h afforded alcohol 0.63 g (86 %) as an oil: ^1H NMR (300 MHz, CDCl_3) δ 7.59-7.56 (m, 2H), 7.47-7.43 (m, 2H), 7.38-7.21 (m, 5H), 5.66-5.62 (m, 1H), 5.26 (s, 1H), 4.22-4.10 (m, 4H), 3.39-3.35 (m, 1H), 1.22-1.15 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 167.9, 140.5, 134.8, 132.1,

128.7, 128.6, 128.4, 128.1, 127.8, 126.5, 122.8, 94.3, 83.7, 64.7, 61.8, 55.8, 13.8; IR (neat, cm^{-1}) 3483, 2984, 1734, 1450, 1305, 1151, 1030.

Diethyl 2-(2-(3-(4-chlorophenyl)-3-hydroxyprop-1-ynyl)phenyl)malonate: The alcohol was prepared by the same method. But employing diethyl (2-iodophenyl)malonate (0.72 g, 2.0 mmol) and 1-(4-chlorophenyl)prop-2-yn-1-ol (0.40 mg, 2.4 mmol) for 12 h afforded alcohol 0.66g (82 %) as an oil: ^1H NMR (300 MHz, CDCl_3) δ 7.55-7.45 (m, 4H), 7.39-7.26 (m, 4H), 5.66-5.65 (d, J = 5.1 Hz, 1H), 5.20 (s, 1H), 4.25-4.08 (m, 4H), 3.12-3.10 (d, J = 6.0 Hz, 1H), 1.25-1.21 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.0, 139.0, 135.0, 134.1, 132.1, 129.0, 128.8, 128.7, 128.0, 127.9, 122.6, 93.7, 84.3, 64.2, 62.0, 56.0, 13.9; IR (neat, cm^{-1}) 3440, 2983, 1734, 1488, 1303, 1151, 1030.

Diethyl 2-(2-(3-hydroxy-3-methylbut-1-ynyl)phenyl)malonate: The alcohol was prepared by the same method. But employing diethyl (2-iodophenyl)malonate (0.72 g, 2.0 mmol) and 2-methylbut-3-yn-2-ol (0.20 g, 2.4 mmol) for 12 h afforded alcohol 0.59 g (93%) as an oil: ^1H NMR (300 MHz, CDCl_3) δ 7.44-7.39 (m, 2H), 7.36-7.24 (m, 2H), 5.21 (s, 1H), 4.29-4.19 (m, 4H), 2.80 (s, 1H), 1.61 (s, 6H), 1.29-1.24 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.1, 134.9, 131.8, 128.5, 127.8, 123.1, 99.4, 79.6, 65.4, 61.9, 56.1, 31.2, 13.9; IR (neat, cm^{-1}) 3420, 2983, 1735, 1448, 1369, 1166, 1031.

Typical procedure for the preparation of propargylic carbonates 1a-e. To a solution of propargylic alcohol (2.0 mmol), pyridine (0.63 g, 8.0 mmol), and DMAP (44.8 mg, 0.4 mmol) in CH_2Cl_2 (10 mL) was added at 0 °C methyl chloroformate (0.75 g, 8.0 mmol). After stirring for 2 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 . The CH_2Cl_2 solution was washed with a saturated aqueous copper sulfate solution, water, dried over anhydrous sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel to afford the corresponding propargylic carbonates.

3-(2-(Di(ethoxycarbonyl)methyl)phenyl)prop-2-ynyl methyl carbonate (1a): The **1a** was prepared by the above method, But employing diethyl 2-(2-(3-hydroxyprop-1-ynyl)phenyl)malonate (0.58 g, 2.0 mmol) and methyl chloroformate afforded **1a** 0.61 g (87 %) as a solid: mp 59-61 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.50-7.48 (d, J = 7.5 Hz, 2H), 7.41-7.35 (m, 1H), 7.32-7.26 (m, 1H), 5.24 (s, 1H), 4.99 (s, 2H), 4.29-4.18 (m, 4H), 3.84 (s, 3H), 1.30-1.25 (t, J = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 167.9, 155.1, 135.1, 132.5, 129.2, 128.6, 127.9, 122.4, 87.2, 84.6, 61.8, 56.0, 55.5, 55.1, 13.9; IR (KBr, cm^{-1}) 3478, 2987, 1753, 1445, 1267, 1027; Anal.Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_7$: C 62.06; H 5.79. Found: C 61.82; H 6.01.

3-(2-((Ethoxycarbonyl)(phenylsulfonyl)methyl)phenyl)prop-2-ynyl methyl carbonate (1b): The **1b** was prepared by the same method, But employing ethyl 2-(2-(3-hydroxyprop-1-ynyl)phenyl)-2-(phenylsulfonyl)acetate (0.72 g, 2.0 mmol) and methyl chloroformate afforded **1b** 0.69 g (80 %) as a solid: mp 84-86 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.98-7.96 (d, J = 7.5 Hz, 1H), 7.70-7.68 (m, 2H), 7.63-7.58 (m,

1H), 7.47-7.28 (m, 5H), 5.85 (s, 1H), 4.87 (s, 2H), 4.30-4.17 (m, 2H), 3.87 (s, 3H), 1.27-1.22 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.1, 155.1, 137.4, 134.0, 132.3, 130.0, 129.7, 129.4, 129.2, 129.1, 128.6, 123.7, 87.3, 83.8, 71.1, 62.6, 55.7, 55.2, 13.8; IR (KBr, cm^{-1}) 3466, 2959, 1746, 1446, 1264, 1151, 1084, 1022; Anal.Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_7\text{S}$: C 60.57; H 4.84. Found: C 60.55; H 4.69.

4-(2-(Di(ethoxycarbonyl)methyl)phenyl)but-3-yn-2-yl methyl carbonate (1c): The **1c** was prepared by the above method, But employing diethyl 2-(2-(3-hydroxybut-1-ynyl)phenyl)malonate (0.61 g, 2.0 mmol) afforded **1c** 0.58 g (80 %) as an oil: ^1H NMR (300 MHz, CDCl_3) δ 7.49-7.45 (m, 2H), 7.39-7.33 (m, 1H), 7.30-7.25 (m, 1H), 5.59-5.53 (q, $J = 6.6$ Hz, 1H), 5.23 (s, 1H), 4.29-4.19 (m, 4H), 3.83 (s, 3H), 1.66-1.64 (d, $J = 6.6$ Hz, 3H), 1.29-1.23 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 167.9, 154.7, 135.2, 132.3, 129.1, 128.6, 127.8, 122.5, 91.7, 82.9, 64.7, 61.8, 55.6, 54.9, 21.3, 14.0; IR (neat, cm^{-1}) 3444, 2984, 1751, 1448, 1262, 1148, 1027; Anal.Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_7$: C 62.97; H 6.12. Found: C 62.82; H 6.18.

3-(2-(Di(ethoxycarbonyl)methyl)phenyl)-1-phenylprop-2-ynyl methyl carbonate (1d): The **1d** was prepared by the above method, But employing diethyl 2-(2-(3-hydroxy-3-phenylprop-1-ynyl)phenyl)malonate (0.73 g, 2.0 mmol) afforded **1d** 0.70 g (82 %) as an oil: ^1H NMR (300 MHz, CDCl_3) δ 7.63-7.60 (m, 2H), 7.52-7.48 (m, 2H), 7.44-7.35 (m, 4H), 7.31-7.25 (m, 1H), 6.54 (s, 1H), 5.25 (s, 1H), 4.26-4.13 (m, 4H), 3.82 (s, 3H), 1.26-1.21 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 167.9, 154.8, 136.2, 135.2, 132.5, 129.3, 128.7, 127.9, 127.8, 122.4, 89.8, 85.5, 70.1, 61.8, 55.5, 55.0, 13.9; IR (neat, cm^{-1}) 3477, 2984, 1753, 1444, 1262, 1031; Anal.Calcd for $\text{C}_{24}\text{H}_{24}\text{O}_7$: C 67.91; H 5.70. Found: C 67.87; H 5.87.

3-(2-(Di(ethoxycarbonyl)methyl)phenyl)-1-(4-chlorophenyl)prop-2-ynyl methyl carbonate (1e): The **1e** was prepared by the above method, But employing diethyl 2-(2-(3-(4-chlorophenyl)-3-hydroxyprop-1-ynyl)phenyl)malonate (0.80 g, 2.0 mmol) afforded **1e** 0.78 g (85 %) as an oil: ^1H NMR (300 MHz, CDCl_3) δ 7.58-7.49 (m, 4H), 7.41-7.36 (m, 3H), 7.31-7.26 (m, 1H), 6.50 (s, 1H), 5.21 (s, 1H), 4.27-4.13 (m, 4H), 3.82 (s, 3H), 1.27-1.21 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 167.8, 154.7, 135.2, 134.8, 132.5, 129.4, 129.2, 128.9, 128.8, 127.9, 122.1, 89.3, 85.8, 69.2, 61.8, 55.5, 55.1, 13.9; IR (neat, cm^{-1}) 3437, 2983, 1752, 1443, 1261, 1031; Anal.Calcd for $\text{C}_{24}\text{H}_{23}\text{ClO}_7$: C 62.82; H 5.05. Found: C 62.88; H 5.13.

Typical procedure for the preparation of propargylic carbonates **1f**.

A 80 mg (2.0 mmol) amount of sodium hydride (60% suspension in mineral oil) was placed in a flask under a argon atmosphere, and washed with dry petroleum ether. A solution of diethyl 2-(2-(3-hydroxy-3-methylbut-1-ynyl)phenyl)malonate (0.63 g, 2.0 mmol) in dry THF (4.0 mL) was added. After stirring for 6 h at 0°C , methyl cholroformate (0.28 g, 3.0 mmol) was added to the mixture, and it was stirred again at 0°C for another 2 h. The reaction mixture was then filtered and concentrated. The residue was purified by column chromatography on silica gel to afford the corresponding propargylic carbonates **1f** 0.69 g (92 %) as an oil: ^1H NMR (300 MHz, CDCl_3) δ 7.48-7.45 (m, 2H), 7.37-7.24 (m, 2H), 5.34 (s, 1H), 4.29-4.18 (m, 4H), 3.78 (s, 3H), 1.80 (s, 6H), 1.29-1.25 (t, $J = 7.5$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.1, 153.4, 135.3, 132.1, 128.8, 128.5, 127.7, 122.8, 94.4, 82.1, 74.4, 61.7, 55.4, 54.3, 28.7,

13.9; IR (neat, cm^{-1}) 3479, 2987, 1752, 1443, 1270, 1032; Anal.Cald for $\text{C}_{20}\text{H}_{24}\text{O}_7$: C 63.82; H 6.43. Found: C 63.76; H 6.19.

General procedure for the preparation of substituted indenenes.

To a solution of 3-(2-(di(ethoxycarbonyl)methyl)phenyl)prop-2-ynyl methyl carbonate **1a** (69.6 mg, 0.20 mmol) in NMP (2.0 mL) was added K_2CO_3 (55.2 mg, 0.40 mmol). The mixture was stirred for 10 min and $\text{Pd}(\text{PPh}_3)_4$ (11.5 mg, 0.01 mmol, 5 mol %), nucleophiles (0.24 mmol) was added. The resulting mixture was then heated under an argon atmosphere at 100 °C. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was allowed to cool to room temperature and quenched with a saturated aqueous solution of ammonium chloride, and the mixture was extracted with EtOAc. The combined organic extracts were washed with water and saturated brine. The organic layers were dried over Na_2SO_4 , filtered. Solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford corresponding 2,3-disubstituted indenenes.

3aa: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 64.4 mg (83%) of the indicated compound as a solid: mp: 59-61 °C; ^1H NMR (400 MHz, CDCl_3) δ 13.07 (s, 1H), 7.57-7.54 (dd, $J = 7.2, 3.6$ Hz, 1H), 7.25-7.18 (m, 1H), 7.15-7.11 (m, 1H), 6.93-6.91 (dd, $J = 7.2, 3.6$ Hz, 1H), 4.21-4.06 (m, 4H), 3.60 (s, 3H), 1.94 (s, 3H), 1.80 (s, 3H), 1.22-1.19 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.5, 172.6, 168.3, 167.8, 145.5, 140.9, 139.6, 136.7, 128.5, 125.4, 124.7, 119.6, 94.5, 71.4, 61.9, 61.8, 51.7, 19.2, 14.0, 13.0; IR (KBr, cm^{-1}) 3367, 2918, 1729, 1442, 1246, 1058; Anal.Cald for $\text{C}_{21}\text{H}_{24}\text{O}_7$: C 64.94; H 6.23. Found: C 65.00; H 5.94.

3ab: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 57.9 mg (72%) of the indicated compound as an oil: ^1H NMR (300 MHz, CDCl_3) δ 13.21 (s, 1H), 7.64-7.61 (m, 1H), 7.32-7.27 (m, 1H), 7.23-7.20 (m, 1H), 7.01-6.99 (d, $J = 7.2$ Hz, 1H), 4.27-4.12 (m, 6H), 2.01 (s, 3H), 1.87 (s, 3H), 1.30-1.20 (m, 6H), 1.16-1.11 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 175.3, 172.1, 168.4, 167.9, 145.6, 140.7, 139.6, 136.8, 128.3, 125.3, 124.6, 119.6, 94.8, 71.4, 61.8, 61.7, 60.5, 19.2, 14.0, 13.0; IR (neat, cm^{-1}) 2982, 2923, 1732, 1465, 1247, 1060; Anal.Cald for $\text{C}_{22}\text{H}_{26}\text{O}_7$: C 65.66; H 6.51. Found: C 65.47; H 6.62.

3ac: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 52.0 mg (56%) of the indicated compound as an oil: ^1H NMR (400 MHz, CDCl_3) δ 13.77 (s, 1H), 7.58-7.57 (d, J = 6.8 Hz, 1H), 7.46-7.44 (m, 2H), 7.25-7.12 (m, 5H), 7.01-6.99 (d, J = 8.0 Hz, 1H), 4.24-4.16 (m, 4H), 4.12-4.07 (m, 2H), 1.76 (s, 3H), 1.29-1.10 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.0, 172.7, 167.9, 167.5, 145.7, 140.1, 139.7, 136.9, 134.5, 130.1, 128.2, 128.0, 127.7, 125.3, 124.6, 119.9, 94.8, 71.4, 61.8, 61.6, 60.9, 54.2, 14.0, 13.9, 13.1; IR (neat, cm^{-1}) 2982, 1732, 1640, 1258, 1053; Anal.Calcd for $\text{C}_{27}\text{H}_{28}\text{O}_7$: C 69.81; H 6.08. Found: C 70.02; H 6.17.

3ad: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 55.8 mg (75%) of the indicated compound as a solid: mp: 94-96 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 16.76 (s, 1H), 7.67-7.65 (d, J = 6.8 Hz, 1H), 7.37-7.33 (m, 1H), 7.28-7.24 (m, 1H), 7.06-7.04 (d, J = 7.6 Hz, 1H), 4.29-4.18 (m, 4H), 2.05 (s, 3H), 1.94 (s, 6H), 1.27-1.23 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.6, 167.8, 145.1, 141.8, 140.0, 138.4, 128.8, 126.0, 124.9, 119.4, 105.0, 71.5, 61.9, 23.2, 14.0, 12.8; IR (KBr, cm^{-1}) 3458, 2981, 1729, 1466, 1204, 1025; Anal.Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_6$: C 67.73; H 6.50. Found: C 67.62; H 6.38.

3ae: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 61.6 mg (71%) of the indicated compound as an oil: ^1H NMR (400 MHz, CDCl_3) δ 17.53 (s, 1H), 7.63-7.61 (d, J = 6.8 Hz, 1H), 7.49-7.47 (d, J = 7.6 Hz, 2H), 7.33-7.24 (m, 3H), 7.17-7.13 (m, 2H), 7.09-7.07 (d, J = 6.8 Hz, 1H), 4.23-4.10 (m, 4H), 2.05 (s, 3H), 1.83 (s, 3H), 1.26-1.14 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.4, 183.8, 168.0, 167.2, 145.4, 141.2, 140.0, 138.8, 135.6, 130.8, 128.8, 127.9, 127.8, 126.0, 124.9, 119.7, 104.2, 71.5, 61.9, 61.8, 24.8, 14.0, 12.9; IR (neat, cm^{-1}) 3435, 2982, 1731, 1465, 1241, 1055; Anal.Calcd for $\text{C}_{26}\text{H}_{26}\text{O}_6$: C 71.87; H 6.03. Found: C 72.02; H 5.96.

3af: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 33.7 mg (34%) of the indicated compound as a solid: mp: 119-121 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 18.13 (s, 1H), 7.51-7.48 (m, 5H), 7.28-7.23 (m, 2H), 7.16-7.08 (m, 6H), 6.82-6.80 (d, J = 7.8 Hz, 1H), 4.15-4.08 (q, J = 7.8 Hz, 4H), 1.70 (s, 3H), 1.20-1.15 (t, J = 7.8 Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 189.6, 167.2, 145.0, 140.4,

139.6, 139.1, 136.7, 130.8, 128.3, 127.8, 127.7, 125.6, 124.7, 120.0, 103.7, 71.3, 61.8, 13.9, 13.4; IR (KBr, cm^{-1}) 2983, 1725, 1438, 1239, 1042; Anal.Calcd for $\text{C}_{31}\text{H}_{28}\text{O}_6$: C 74.98; H 5.68. Found: C 74.96; H 5.46.

3ag: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 61.4 mg (80%) of the indicated compound as a solid: mp: 188-190 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.61-7.60 (d, J = 6.8 Hz, 1H), 7.30-7.26 (m, 1H), 7.22-7.19 (m, 1H), 6.98-6.96 (d, J = 6.8 Hz, 1H), 4.31-4.18 (m, 4H), 2.65-2.55 (m, 4H), 2.17-2.11 (m, 2H), 2.01 (s, 3H), 1.30-1.23 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.6, 172.9, 169.3, 166.8, 144.1, 142.7, 139.4, 134.9, 128.7, 125.9, 124.9, 120.8, 110.2, 71.7, 62.9, 61.9, 37.0, 28.0, 20.8, 14.0, 13.9, 13.4; IR (KBr, cm^{-1}) 3200, 2981, 1732, 1368, 1246, 1056; Anal.Calcd for $\text{C}_{22}\text{H}_{24}\text{O}_6$: C 68.74; H 6.29. Found: C 68.82; H 6.16.

3ah: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 62.6 mg (76%) of the indicated compound as a solid: mp: 148-150 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.61-7.59 (m, 1H), 7.27-7.25 (m, 1H), 7.22-7.19 (m, 1H), 6.97-6.95 (d, J = 7.6 Hz, 1H), 4.24-4.20 (m, 4H), 2.49-2.44 (m, 4H), 2.01 (s, 3H), 1.27-1.20 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.3, 171.2, 169.2, 166.7, 144.2, 142.6, 139.4, 134.9, 128.7, 125.8, 124.8, 120.7, 109.1, 71.7, 62.8, 61.9, 50.8, 41.8, 32.1, 28.4, 28.3, 13.9, 13.4; IR (KBr, cm^{-1}) 3069, 2960, 1731, 1369, 1248, 1038; Anal.Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_6$: C 69.88; H 6.84. Found: C 69.73; H 6.86.

3ca: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 52.3 mg (65%) of the indicated compound as an oil: ^1H NMR (400 MHz, CDCl_3) δ 13.09 (s, 1H), 7.61-7.59 (m, 1H), 7.32-7.26 (m, 1H), 7.23-7.19 (m, 1H), 7.00-6.99 (d, J = 7.6 Hz, 1H), 4.29-4.12 (m, 4H), 3.67 (s, 3H), 2.53-2.46 (m, 2H), 1.89 (s, 3H), 1.29-1.19 (m, 6H), 1.04-1.00 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.0, 172.6, 168.6, 168.1, 146.5, 145.8, 139.7, 136.8, 128.5, 125.6, 124.5, 119.3, 94.7, 71.2, 61.8, 61.7, 51.7, 21.1, 19.2, 13.9, 12.7; IR (neat, cm^{-1}) 3444, 2981, 1731, 1443, 1246, 1064; Anal.Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_7$: C 65.66; H 6.51. Found: C 65.37; H 6.62.

3da: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 52.0 mg (56%) of the indicated compound as a solid: mp 102-104 °C; ^1H NMR (300 MHz, CDCl_3) δ 12.89 (s, 1H), 7.64-7.62 (d, $J = 7.8$ Hz, 1H), 7.34-7.09 (m, 7H), 7.02-7.00 (d, $J = 7.5$ Hz, 1H), 4.16-4.09 (m, 2H), 4.03-3.94 (m, 1H), 3.89-3.88 (m, 2H), 3.78-3.67 (m, 1H), 3.60 (s, 3H), 1.86 (s, 3H), 1.22-1.17 (t, $J = 7.2$ Hz, 3H), 1.12-1.08 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 175.0, 172.1, 168.4, 167.8, 145.5, 142.8, 139.7, 139.1, 128.6, 128.4, 128.0, 126.0, 125.9, 124.8, 119.8, 94.8, 71.4, 61.9, 61.7, 51.5, 33.9, 19.2, 13.9, 13.7; IR (KBr, cm^{-1}) 3740, 2922, 1733, 1458, 1229, 1052; Anal.Calcd for $\text{C}_{27}\text{H}_{28}\text{O}_7$: C 69.81; H 6.08. Found: C 69.65; H 5.89.

3ea: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 31.9 mg (32%) of the indicated compound as an oil: ^1H NMR (300 MHz, CDCl_3) δ 12.92 (s, 1H), 7.64-7.61 (d, $J = 7.8$ Hz, 1H), 7.34-7.22 (m, 2H), 7.17-7.13 (m, 2H), 7.06-7.00 (m, 3H), 4.17-4.09 (m, 2H), 4.04-3.96 (m, 1H), 3.90-3.82 (m, 2H), 3.79-3.74 (m, 1H), 3.59 (s, 3H), 1.85 (s, 3H), 1.26-1.18 (m, 3H), 1.14-1.06 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 175.1, 172.0, 168.3, 167.7, 145.2, 142.2, 139.6, 139.5, 137.6, 131.6, 129.8, 128.7, 128.0, 126.2, 124.9, 119.9, 94.7, 71.3, 62.1, 61.9, 51.6, 33.2, 19.2, 13.9, 13.8; IR (neat, cm^{-1}) 3409, 2923, 1727, 1650, 1442, 1244, 1043; Anal.Calcd for $\text{C}_{27}\text{H}_{27}\text{ClO}_7$: C 64.99; H 5.45. Found: C 65.23; H 5.37.

3fa: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 43.8 mg (73%) of the indicated compound as a solid: mp 96-98 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.58-7.55 (d, $J = 7.5$ Hz, 1H), 7.32-7.29 (m, 2H), 7.23-7.17 (m, 1H), 6.90 (s, 1H), 5.25 (d, $J = 0.6$ Hz, 1H), 5.15 (d, $J = 0.6$ Hz, 1H), 4.22-4.07 (m, 4H), 2.09 (s, 3H), 1.18-1.13 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.3, 146.8, 143.6, 142.6, 136.4, 131.8, 128.6, 126.3, 123.7, 121.6, 116.2, 69.8, 61.7, 21.8, 13.8; IR (KBr, cm^{-1}) 3419, 2982, 1734, 1231, 1055; Anal.Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_4$: C 71.98; H 6.71. Found: C 72.13; H 6.76.

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