**One-pot Assembly of Tricyclo[6.2.1.0^{1,6}]undecan-4-one and Related Polycyclic
Compounds by Tandem Electroreductive Cyclization**

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Compound 4: To a stirred solution of LDA, prepared from diisopropylamine (5.08 mL, 36.25 mmol) and butyllithium (2.4 M solution in hexane, 15.09 mL, 36.22 mmol), in THF (40 mL) was added dropwise a THF solution (10 mL) of ethyl 4-pentenoate (**3**) (4.18 g, 32.66 mmol) at $-78\text{ }^{\circ}\text{C}$. The resulting mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 20 min, $0\text{ }^{\circ}\text{C}$ for 20 min and then recooled to $-78\text{ }^{\circ}\text{C}$ with stirring. A THF solution (10 mL) of 2,3-dibromopropene (3.80 mL, 36.77 mmol) was added dropwise at $-78\text{ }^{\circ}\text{C}$, and then the mixture was allowed to warm to room temperature over 3 h. After addition of saturated aqueous NH_4Cl (100 mL) at $0\text{ }^{\circ}\text{C}$, the resulting mixture was extracted with Et_2O . The ethereal layer was washed with brine, dried, and evaporated. The residue was purified by column chromatography on silica gel using 20:1 hexane/EtOAc to afford compound **4** (6.04 g, 75%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 5.80–5.70 (1H, m), 5.63 (1H, br s), 5.46 (1H, br s), 5.10–5.04 (2H, m), 4.14 (2H, q, $J=7.1\text{ Hz}$), 2.86–2.77 (2H, m), 2.58–2.56 (1H, m), 2.40–2.25 (1H, m), 1.25 (3H, t, $J=7.1\text{ Hz}$). ^{13}C NMR (100 MHz, CDCl_3) δ 173.9, 134.3, 131.0, 118.8, 117.5, 60.5, 43.4, 42.8, 35.5, 14.3. Anal. Calcd. for $\text{C}_{10}\text{H}_{15}\text{O}_2\text{Br}$: C, 48.77; H 6.14. Found: C, 48.46; H, 6.03.

(E)-Olefin 5 and (Z)-Olefin 6: To a stirred solution of ester **4** (2.45 g, 9.92 mmol) in dichloromethane (20 mL) was added dropwise DIBAL-H (0.95 M solution in hexane, 10.5 mL, 9.98 mmol) at $-78\text{ }^{\circ}\text{C}$. After 1 h of stirring at $-78\text{ }^{\circ}\text{C}$, water (11.5 mL) was slowly added at $-78\text{ }^{\circ}\text{C}$.

The resulting mixture was diluted with Et₂O (50 mL), and then allowed to warm to room temperature over 1 h. After stirring at room temperature over night, a heavy white precipitate began to form. MgSO₄ (3 g) was added to the mixture with stirring, and the resulting mixture was filtered through Celite and washed with Et₂O. Evaporation of the combined filtrate and washings gave the aldehyde, which was immediately used without purification.

To a solution of triethyl phosphonoacetate (2.17 mL, 10.94 mmol) in THF (20 mL) was slowly added butyllithium (2.4 M solution in hexane, 4.45 mL, 10.92 mmol) at -78 °C. After 10 min of stirring at -78 °C, the mixture was allowed to warm to 0 °C, and then the mixture was recooled to -78 °C. A solution of the above aldehyde in THF (10 mL) was added dropwise, and the resulting mixture was stirred at -78 °C for 1 h, and allowed to warm to room temperature over 1 h. After addition of water (30 mL) at 0 °C, the mixture was separated. The organic layer was washed with brine, dried and evaporated. The residue was purified by column chromatography on silica gel using 97:3 hexane/EtOAc to give rise to (*Z*)-olefin **6** (354 mg, 13%) as a colorless oil and (*E*)-olefin **5** (1.69 g, 63%) as a colorless oil.

(*E*)-Olefin 5: ¹H NMR (400 MHz, CDCl₃) δ 6.74 (1H, dd, *J*=15.6, 8.5 Hz), 5.84 (1H, d, *J*=15.4 Hz), 5.78–5.40 (1H, m), 5.57 (1H, br s), 5.45 (1H, br s), 5.10–5.02 (2H, m), 4.18 (2H, q, *J*=7.1 Hz), 2.77–2.66 (1H, m), 2.60–2.52 (1H, m), 2.47–2.39 (1H, m), 2.30–2.12 (2H, m), 1.29 (3H, t, *J*=7.1 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 149.6, 134.7, 131.4, 122.0, 118.7, 117.4, 60.2, 45.2, 39.8, 37.5, 14.2. IR (neat, cm⁻¹) 1721. Anal. Calcd. for C₁₂H₁₇BrO₂: C, 52.76; H, 6.27. Found: C, 53.14; H, 6.16.

(*Z*)-Olefin 6: ¹H NMR (400 MHz) δ 5.92 (1H, dd, *J*=10.0, 10.0 Hz), 5.81 (1H, dd, *J*=10.0, 1.0 Hz), 5.80–5.70 (1H, m), 5.58 (1H, br s), 5.43 (1H, br s), 5.07–5.00 (2H, m), 4.19 (2H, q, *J*=7.1 Hz), 3.99–3.89 (1H, m), 2.59–2.52 (1H, m), 2.45–2.38 (1H, m), 2.31–2.23 (1H, m), 2.14–2.06 (1H, m), 1.30 (3H, t, *J*=7.1 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 151.1, 135.3, 131.8, 120.8, 118.1, 116.9, 60.1, 46.0, 38.4, 36.1, 14.3. IR (neat, cm⁻¹) 1719. Anal. Calcd. for C₁₂H₁₇BrO₂: C, 52.76; H, 6.27. Found: C, 52.55; H, 6.20.

Compound 8: To a stirred solution of LDA, prepared from diisopropylamine (2.22 mL, 15.83 mmol) and butyllithium (2.4 M solution in hexane, 6.31 mL, 15.14 mmol), in THF (25 mL) was added dropwise a THF solution (10 mL) of compound **7** (3.0 g, 14.42 mmol) at $-78\text{ }^{\circ}\text{C}$. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min, at $0\text{ }^{\circ}\text{C}$ for 30 min, and then recooled to $-78\text{ }^{\circ}\text{C}$ with stirring. A THF solution (5 mL) of 2,3,-dibromopropene (1.64 mL, 15.87 mmol) was slowly added at $-78\text{ }^{\circ}\text{C}$. The resulting mixture was allowed to warm to $0\text{ }^{\circ}\text{C}$, and then continued to stir at $0\text{ }^{\circ}\text{C}$ for 1 h. After addition of saturated aqueous NH_4Cl (50 mL) at $0\text{ }^{\circ}\text{C}$, the mixture was separated. The organic layer was washed with brine, dried and evaporated. The residue was purified by column chromatography on silica gel using 4:1 hexane/EtOAc to furnish compound **8** (3.43 g, 73%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 5.78–5.66, 5.61 (1H, br s), 5.55 (1H, br s), 5.31 (1H, br s), 5.13–5.04 (2H, m), 3.59 (2H, d, $J=6.6$ Hz), 3.10 (1H, d, $J=14.0$ Hz), 2.57–2.40 (4H, m), 2.24–1.90 (4H, m), 0.98 (6H, d, $J=6.6$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 200.6, 175.9, 133.4, 128.9, 121.2, 118.5, 117.8, 101.7, 74.7, 47.2, 45.2, 39.9, 39.7, 27.9, 27.6, 25.8, 19.0. IR (neat, cm^{-1}) 1608.5. HRMS calcd for $\text{C}_{16}\text{H}_{13}\text{O}_2\text{Br}$ (M^+): 326.0857 Found 326.0881.

Compound 9: To a stirred solution of compound **8** (1.05 g, 3.22 mmol) in diethyl ether (15 mL) was added dropwise DIBAL-H (0.95 M solution in hexane, 3.55 mL, 3.37 mmol) at $-78\text{ }^{\circ}\text{C}$. After stirring at $-78\text{ }^{\circ}\text{C}$ for 1 h, water (4.6 mL) was slowly added at $-78\text{ }^{\circ}\text{C}$. The resulting mixture was diluted with Et_2O (30 mL), and then allowed to warm to room temperature over 1 h. After stirring at room temperature over night, a heavy white precipitate began to form. MgSO_4 (1.5 g) was added to the mixture with stirring, and the resulting mixture was filtered through Celite and washed with Et_2O . Evaporation of the combined filtrate and washings gave an oil, which was dissolved in THF (10 mL). To the mixture was added 5% aqueous HClO_4 (5 mL) at $0\text{ }^{\circ}\text{C}$. After 10 min of stirring at $0\text{ }^{\circ}\text{C}$, the resulting mixture was neutralized with aqueous NaHCO_3 at $0\text{ }^{\circ}\text{C}$. After addition of Et_2O (20 mL), the mixture was separated. Evaporation of the solvent, the residue was purified by column chromatography on silica gel using 4:1 hexane/ EtOAc to furnish enone **9** (533 mg, 65%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 6.86 (1H, d, $J=10.2$ Hz), 5.98 (1H, d, $J=10.2$ Hz), 5.84–5.72 (1H, m), 5.64 (1H, br s), 5.62 (1H, d, $J=1.7$ Hz), 5.20–5.10 (2H, m), 2.71 (2H, br s), 2.50 (2H, ddd, $J=7.6, 6.1, 1.2$ Hz), 2.35 (br d, $J=7.7$ Hz), 2.14–2.06 (2H, m), 1.96–1.88 (2H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 156.3, 132.8, 128.4, 128.1, 121.8, 119.3, 49.3, 43.0, 39.3, 33.9, 30.9. IR (neat, cm^{-1}) 1681.8. HRMS calcd for $\text{C}_{12}\text{H}_{15}\text{OBr}$ (M^+): 254.0306 Found 254.0280.

Compound 10: To a stirred solution of LDA, prepared from diisopropylamine (2.45 mL, 17.48 mmol) and butyllithium (2.4 M solution in hexane, 7.20 mL, 17.28 mmol), in THF (30 mL) was added dropwise a THF solution (10 mL) of compound **7** (3.0 g, 14.42 mmol) at $-78\text{ }^{\circ}\text{C}$. After

addition of HMPA (4.90 mL, 28.16 mmol) at $-78\text{ }^{\circ}\text{C}$, the resulting mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min, at $0\text{ }^{\circ}\text{C}$ for 1 h, and then re-cooled to $-78\text{ }^{\circ}\text{C}$. A THF solution (10 mL) of 1,3-diiodopropane (2.15 mL, 18.72 mmol) was added dropwise at $-78\text{ }^{\circ}\text{C}$, and then the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 4 h, and allowed to warm to room temperature over 1 h. The mixture was continued to stir at room temperature for 12 h. After addition of saturated aqueous NH_4Cl (100 mL) at $0\text{ }^{\circ}\text{C}$, the resulting mixture was extracted with Et_2O . The ethereal layer was washed with brine, dried, and evaporated. The residue was purified by column chromatography on silica gel using 4:1 hexane/EtOAc to afford compound **10** (2.49 g, 46%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 5.80–5.70 (1H, m), 5.25 (1H, br s), 5.20–5.00 (2H, m), 3.58 (2H, d, $J=6.6\text{ Hz}$), 3.14 (2H, t, $J=6.8\text{ Hz}$), 2.45 (2H, t, $J=6.3\text{ Hz}$), 2.38–2.32 (1H, m), 2.25–2.15 (1H, m), 2.15–1.95 (1H, m), 1.95–1.50 (6H, m), 0.98 (6H, d, $J=6.8\text{ Hz}$). ^{13}C NMR (100 MHz, CDCl_3) δ 201.8, 176.0, 133.9, 118.1, 102.0, 74.9, 45.9, 39.8, 35.9, 29.3, 28.0, 25.7, 19.2. IR (neat, cm^{-1}) 1651.0. HRMS calcd for $\text{C}_{16}\text{H}_{25}\text{O}_2$ (M^+-127): 249.1854 Found 249.1824.

Compound 11: To a stirred solution of compound **10** (1.00 g, 2.66 mmol) in diethyl ether (10 mL) was added dropwise DIBAL-H (0.95 M solution in hexane, 4.20 mL, 3.99 mmol) at $-78\text{ }^{\circ}\text{C}$. After 30 min of stirring at $-78\text{ }^{\circ}\text{C}$, the mixture was allowed to warm to room temperature over 1 h, and then the mixture was continued to stir at room temperature for 6 h. To the mixture was added 10% aqueous HCl (1 mL) at $0\text{ }^{\circ}\text{C}$, and the resulting mixture was stirred at room temperature for 1 h. After addition of saturated aqueous NaHCO_3 (30 mL) at $0\text{ }^{\circ}\text{C}$, the mixture was extracted with diethyl ether (30 mL). The ethereal layer was washed with brine, dried, and evaporated. The residue

was purified by column chromatography on silica gel using 4:1 hexane/EtOAc to afford compound **11** (560 mg, 69%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 6.68 (1H, d, $J=10.3$ Hz), 5.94 (1H, d, $J=10.3$ Hz), 5.83–5.70 (1H, m), 5.18–5.10 (2H, m), 3.23–3.15 (2H, m), 2.53–2.35 (2H, m), 2.24 (2H, d, $J=7.3$ Hz), 1.95–1.75 (4H, m), 1.65–1.50 (2H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 198.7, 156.7, 133.0, 128.3, 118.9, 42.3, 38.8, 38.1, 33.9, 30.8, 28.2. IR (neat, cm^{-1}) 1681.8. HRMS calcd for $\text{C}_{12}\text{H}_{17}\text{OI}$ (M^+): 304.0324 Found 304.0281.

12

Compound 12: To a stirred solution of compound **8** (800 mg, 2.45 mmol) in diethyl ether (10 mL) was added dropwise MeLi (1.2 M solution in diethyl ether, 2.04 mL, 2.45 mmol) at -78 °C. After 30 min of stirring at -78 °C, the mixture was allowed to warm to room temperature, and then continued to stir at room temperature for 2 h. The mixture was poured into water, and the resulting mixture was acidified with 10% aqueous HClO_4 at 0 °C. After 1 h of stirring at room temperature, the mixture was extracted with diethyl ether (20 mL). The ethereal layer was washed with aqueous NaHCO_3 , brine, dried and evaporated. The residue was purified by column chromatography on silica gel using 4:1 hexane/EtOAc to afford compound **12** (278 mg, 85% based on recovered starting material), a colorless oil, together with unchanged **8** (400 mg).

^1H NMR (400 MHz, CDCl_3) δ 5.92 (1H, br s), 5.75–5.50 (3H, m), 5.20–5.05 (2H, m), 2.82 (1H, d, $J=15.4$ Hz), 2.66 (1H, d, $J=15.4$ Hz), 2.60–2.35 (3H, m), 2.35–2.25 (1H, m), 2.20–2.08 (1H, m), 2.07–1.90 (1H, m), 1.99 (3H, s). ^{13}C NMR (100 MHz, CDCl_3) δ 198.6, 165.2, 133.1, 129.1, 128.4, 121.1, 119.3, 47.3, 42.0, 34.1, 29.7, 20.6. IR (neat, cm^{-1}) 1670.2. HRMS calcd for $\text{C}_{13}\text{H}_{17}\text{OBr}$ (M^+):

268.0462 Found 268.0436.

14

Compound 14: To a stirred solution of LDA, prepared from diisopropylamine (0.56 mL, 4.00 mmol) and butyllithium (2.4 M solution in hexane, 1.60 mL, 3.84 mmol), in THF (10 mL) was added dropwise a THF solution (5 mL) of compound **13** (810 mg, 3.65 mmol) and HMPA (1.27 mL, 7.30 mmol) at $-78\text{ }^{\circ}\text{C}$. After 1 h of stirring at $-78\text{ }^{\circ}\text{C}$, 2,3-dibromopropene (0.45 mL, 4.35 mmol) was added at $-78\text{ }^{\circ}\text{C}$, and then the resulting mixture was allowed to warm to room temperature. The mixture was continued to stir overnight, and then saturated aqueous NH_4Cl (30 mL) was added at $0\text{ }^{\circ}\text{C}$. The mixture was extracted with diethyl ether (15 mL). The ethereal layer was washed with brine, dried, and evaporated. The residue was purified by column chromatography on silica gel using 4:1 hexane/EtOAc to afford compound **14** (950 mg, 82% based on recovered starting material), a colorless oil, together with unchanged **13** (60 mg).

^1H NMR (400 MHz, CDCl_3) δ 5.80–5.62 (1H, m), 5.59 (1H, br s), 5.53 (1H, br s), 5.37 (1H, br s), 5.10–5.02 (2H, m), 3.55–3.45 (2H, m), 3.08 (1H, d, $J=14.6\text{ Hz}$), 2.61 (1H, d, $J=14.6\text{ Hz}$), 2.30–2.20 (1H, m), 2.10–1.95 (2H, m), 1.94–1.72 (3H, m), 0.96 (6H, d, $J=6.6\text{ Hz}$). ^{13}C NMR (100 MHz, CDCl_3) δ 205.2, 172.6, 134.7, 130.6, 122.2, 119.6, 106.9, 75.3, 55.8, 49.2, 44.4, 36.9, 32.2, 28.6, 20.3, 20.0. IR (neat, cm^{-1}) 1612.4. HRMS calcd for $\text{C}_{17}\text{H}_{25}\text{O}_2$ (M^+-79): 261.1855 Found 261.1817.

Compound 15: To a stirred solution of compound **14** (500 mg, 1.47 mmol) in diethyl ether (10 mL) was added dropwise DIBAL-H (0.95 M solution in hexane, 3.40 mL, 3.23 mmol) at $-78\text{ }^{\circ}\text{C}$. After 30 min of stirring at $-78\text{ }^{\circ}\text{C}$, the mixture was allowed to warm to room temperature over 1 h, and then the mixture was continued to stir at room temperature for 30 min. To the mixture was added 10% aqueous HCl (1 mL) at $0\text{ }^{\circ}\text{C}$, and the resulting mixture was stirred at room temperature for 30 min. After addition of saturated aqueous NaHCO_3 (30 mL) at $0\text{ }^{\circ}\text{C}$, the mixture was extracted with diethyl ether (30 mL). The ethereal layer was washed with brine, dried, and evaporated. The residue was purified by column chromatography on silica gel using 4:1 hexane/EtOAc to afford compound **15** (280 mg, 71%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 6.18 (1H, d, $J=12.9$ Hz), 5.93 (1H, d, $J=12.9$ Hz), 5.82–5.68 (1H, m), 5.62 (1H, br s), 5.61 (1H, br s), 5.17–5.05 (2H, m), 2.72–2.57 (4H, m), 2.35–2.20 (2H, m), 2.00–1.92 (1H, m), 1.90–1.75 (3H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 204.2, 150.2, 133.1, 129.8, 128.6, 121.7, 119.4, 50.8, 45.8, 44.7, 44.7, 35.1, 17.7. IR (neat, cm^{-1}) 1656.7. HRMS calcd for $\text{C}_{13}\text{H}_{17}\text{OBr}$ (M^+): 268.0463 Found 268.0433.

Compound 16: ^1H NMR (600 MHz, CDCl_3) δ 4.78 (1H, br s), 4.56 (1H, br s), 4.09 (2H, q, $J=7.2$ Hz), 2.62 (1H, br d, $J=4.8$ Hz), 2.35–2.28 (4H, m), 2.18 (1H, dq, $J=16.8, 2.4$ Hz), 2.06–2.00 (1H,

m), 2.00–1.94 (1H, m), 1.47–1.42 (2H, m), 1.22 (3H, t, $J=7.2$ Hz), 0.84 (1H, ddd, $J=12.6, 4.8, 1.8$ Hz). ^{13}C NMR (150 MHz, CDCl_3) δ 173.4, 155.0, 101.7, 60.1, 46.2, 40.6, 40.4, 37.6, 37.0, 35.5, 31.9, 14.2. IR (neat, cm^{-1}) 1737.7. HRMS calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2$ (M^+): 194.1307 Found 194.1304.

17

Compound 17: ^1H NMR (600 MHz, CDCl_3) δ 4.81 (1H, br s), 4.58 (1H, br s), 4.09 (1H, d, $J=7.2$ Hz), 2.64 (1H, br d, $J=3.6$ Hz), 2.29 (1H, dd, $J=15.6, 8.4$ Hz), 2.16 (1H, dd, $J=15.0, 7.8$ Hz), 2.15 (1H, ddd, $J=16.2, 4.2, 3.0$ Hz), 2.10 (1H, br s, d, $J=4.2$ Hz), 1.97 (1H, br ddd, $J=16.2, 8.4, 8.4$ Hz), 1.91 (1H, ddd, $J=15.6, 4.2, 1.8$ Hz), 1.60 (1H, br ddd, $J=11.4, 9.0, 2.4$ Hz), 1.39–1.35 (1H, m), 1.31–1.27 (1H, m), 1.22 (3H, d, $J=7.2$ Hz), 1.21–1.17 (1H, m). ^{13}C NMR (150 MHz, CDCl_3) δ 172.9, 154.3, 102.5, 60.1, 46.0, 41.7, 41.2, 38.4, 37.6, 36.0, 14.2. IR (neat, cm^{-1}) 1735.8. HRMS calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2$ (M^+): 194.1307 Found 194.1307.

18

Compound 18: ^1H NMR (600 MHz, CDCl_3) δ 4.80 (1H, br s), 4.56 (br s), 2.74 (1H, br d, $J=4.2$ Hz), 2.46–2.37 (2H, m), 2.26 (1H, dddd, $J=14.4, 6.6, 4.8, 1.8$ Hz), 2.13 (1H, br ddd, $J=16.2, 2.4, 2.4$ Hz), 2.11–2.03 (2H, m), 1.97–1.82 (4H, m), 1.76 (1H, ddd, $J=12.0, 7.8, 1.8$ Hz), 1.39 (1H, br dt, $J=12.0, 4.2$ Hz), 1.27 (1H, dq, $J=10.2, 1.8$ Hz). ^{13}C NMR (150 MHz, CDCl_3) δ 212.7, 154.2, 102.3, 47.3, 46.7, 46.4, 44.4, 42.2, 40.2, 39.3, 38.7, 30.0. IR (neat, cm^{-1}) 1716.5. HRMS calcd for $\text{C}_{12}\text{H}_{16}\text{O}$ (M^+): 176.1201 Found 176.1162.

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Compound 19: ^1H NMR (400 MHz, CDCl_3) δ 6.84 (1H, d, $J=10.0$ Hz), 5.86 (1H, d, $J=10.0$ Hz), 4.95 (1H, br q, $J=2.4$ Hz), 4.87 (1H, br q, $J=2.4$ Hz), 2.74–2.63 (1H, m), 2.50–2.44 (4H, m), 2.10 (1H, br dd, $J=12.8, 8.0$ Hz), 2.02–1.89 (2H, m), 1.40 (1H, dd, $J=12.8, 10.0$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 199.3, 157.8, 154.7, 126.9, 106.2, 106.1, 106.0, 46.9, 45.6, 42.4, 36.7, 35.6, 35.4. IR (neat, cm^{-1}) 1679.9. HRMS calcd for $\text{C}_{12}\text{H}_{16}\text{O}$ (M^+): 176.1201 Found 176.1161.

20

Compound 20: ^1H NMR (400 MHz, CDCl_3) δ 6.79 (1H, d, $J=10.4$ Hz), 5.89 (1H, d, $J=10.4$ Hz), 4.80 (1H, br s), 4.67 (1H, br s), 2.44 (1H, dd, $J=6.0, 1.6$ Hz), 2.42 (1H, d, $J=6.8$ Hz), 2.24–2.11 (2H, m), 1.96–1.88 (1H, m), 1.86–1.78 (1H, m), 1.75–1.52 (6H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 199.6, 157.7, 144.8, 127.5, 110.3, 44.7, 37.6, 36.0, 34.5, 33.8, 32.8, 23.0. IR (neat, cm^{-1}) 1681.8. HRMS calcd for $\text{C}_{12}\text{H}_{16}\text{O}$ (M^+): 176.1201 Found 176.1167.

21

Compound 21: ^1H NMR (400 MHz, CDCl_3) δ 5.84 (0.88H, br s), 5.78 (0.12H, br s), 4.94 (0.88H, br s), 4.93 (0.12H, br s), 4.86 (0.88H, br s), 4.56 (0.12H, br s), 1.15 (2.64H, d, $J=6.4$ Hz), 1.14 (0.36H, d, $J=6.4$ Hz). IR (neat, cm^{-1}) 1672.2. HRMS calcd for $\text{C}_{13}\text{H}_{18}\text{O}$ (M^+): 190.1357 Found 190.1334.

22

Compound 22: ^1H NMR (400 MHz, CDCl_3) δ 5.81 (1H, br s), 4.78 (1H, br q, $J=2.0$ Hz), 4.67 (1H, br q, $J=2.0$ Hz), 2.39–2.31 (4H, m), 2.11 (1H, br d, $J=14.0$ Hz), 2.05–1.90 (2H, m), 1.96 (3H, d, $J=1.6$ Hz), 1.87–1.71 (3H, m), 1.65–1.51 (2H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 199.0, 168.2, 145.1, 127.3, 67.4, 41.9, 40.4, 34.2, 33.4, 32.7, 30.8, 22.9, 20.0. IR (neat, cm^{-1}) 1672.2.

HRMS calcd for $\text{C}_{13}\text{H}_{18}\text{O}$ (M^+): 190.1357 Found 190.1326.

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Compound 23: ^1H NMR (400 MHz, CDCl_3) δ 4.80 (1H, br s), 4.57 (1H, br s), 2.63 (1H, d, $J=4.8$ Hz), 2.60 (1H, t, $J=12.4$ Hz), 2.50–2.40 (2H, m), 2.16 (1H, dd, $J=12.4$, 3.2 Hz), 2.03–1.56 (9H, m), 1.29 (1H, ddd, $J=12.0$, 4.0, 4.0 Hz), 1.22–1.15. ^{13}C NMR (100 MHz, CDCl_3) δ 212.8, 154.3, 102.3, 50.3, 48.2, 46.2, 45.3, 44.3, 40.6, 40.3, 40.2, 32.9, 19.7. IR (neat, cm^{-1}) 1705.0. HRMS calcd for $\text{C}_{13}\text{H}_{18}\text{O}$ (M^+): 190.1357 Found 190.1328.

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Compound 24: ^1H NMR (600 MHz, CDCl_3) δ 6.23 (0.9H, d, $J=12.6$ Hz), 6.17 (0.1H, d, $J=12.6$ Hz), 5.80 (0.1H, d, $J=12.6$ Hz), 5.79 (0.9H, d, $J=12.6$ Hz), 4.90 (1H, br q, $J=2.4$ Hz), 4.83 (1H, qd,

$J=2.4, 1.2$ Hz), 2.70–2.55 (3H, m), 2.47 (1H, dq, $J=16.8, 1.8$ Hz), 2.33 (1H, dq, $J=16.2, 2.4$ Hz), 2.08 (1H, ddd, $J=13.2, 7.2, 1.0$ Hz), 1.85–1.75 (4H, m), 1.29 (1H, dd, $J=13.2, 10.2$ Hz), 1.11 (3H, d, $J=7.2$ Hz). ^{13}C NMR (150 MHz, CDCl_3) δ 207.0, 204.4, 155.3, 152.0, 128.0, 106.0, 48.8, 48.6, 47.7, 44.6, 39.7, 36.6, 30.9, 19.7, 19.6.

Compound 25: ^1H NMR (400 MHz, CDCl_3) δ 5.90–5.77 (1H, m), 5.15–5.05 (2H, m), 2.45 (1H, dd, $J=15.1, 6.1$ Hz), 2.37–2.10 (5H, m), 2.08–1.98 (1H, m), 1.91–1.46 (7H, m), 1.35–1.22 (1H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 129.9, 117.8, 44.6, 43.6, 42.5, 42.4, 36.1, 32.5, 30.7, 22.5. IR (neat, cm^{-1}) 1714.6. HRMS calcd for $\text{C}_9\text{H}_{13}\text{O}$ (M^+-41): 137.0967 Found 137.0943.