

Supplementary Information

Rhodium-catalysed cyclisation reaction of allenynes with arylboronic acids

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General. All reactions were carried out with standard Schlenk techniques under an argon atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 (^1H at 300.07 MHz and ^{13}C at 75.46 MHz) spectrometer, unless otherwise noted. All NMR data were obtained in CDCl_3 . Proton chemical shifts were referenced to the residual proton signal of the solvent at 7.26 ppm. Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.0 ppm. High-resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrometer. Column chromatography was performed with silica gel 60 N (Kanto Chemical Co). Preparative thin-layer chromatography was performed with silica 60 PF254 (Merck).

Materials. Unless otherwise noted, all chemicals and anhydrous solvents were obtained from commercial suppliers and used without further purification. 1,4-Dioxane was distilled over sodium–benzophenone ketyl. *n*-Dibutyl ether was distilled over calcium hydride. $[\text{RhCl}(\text{nbd})]_2$ ¹ and $[\text{Rh}(\text{OH})(\text{cod})]_2$ ² were prepared according to the reported procedure. Allenynes **1a–1d** were prepared from dimethyl (4-methylpenta-2,3-dienyl)malonate³ and the corresponding alkynyl bromides in the presence of NaH in a THF solution. Allenynes **1e** and **1f** were prepared from the corresponding dimethyl (alka-2,3-dienyl)malonates⁴ and 1-bromobut-2-yne in the presence of NaH in a THF solution. Allenynes **5a** and **5b** were prepared from the corresponding dimethyl (alka-3,4-dienyl)malonates and 1-bromopent-2-yne in the presence of NaH in a THF solution. Alkenyne **9** was prepared from dimethyl 2-(4-methylpenta-2,3-dienyl)malonate³ and 1-tosyloxyhex-3-yne⁵ in the presence of NaH in a DMF solution.

1a: IR (neat): 2955, 1970, 1738, 1437, 1291, 1210 cm^{-1} ; ^1H NMR: δ = 1.64 (d, J = 2.7 Hz, 6H), 1.74 (t, J = 2.4 Hz, 3H), 2.69 (d, J = 7.5 Hz, 2H), 2.80 (q, J = 2.5 Hz, 2H), 3.72 (s, 6H), 4.72–4.83 (m, 1H); ^{13}C NMR: δ = 3.5, 20.5, 22.9, 32.5, 52.6, 57.4, 73.2, 78.6, 82.3, 95.1, 170.3, 203.5; HRMS (CI^+): Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4$, M^+ 264.1362. Found m/z 264.1365.

1b: IR (neat): 2979, 1970, 1740, 1437, 1289, 1208 cm^{-1} ; ^1H NMR: δ = 1.07 (t, J = 7.4 Hz, 3H), 1.64 (d, J = 3.3 Hz, 6H), 2.10 (qt, J = 7.4, 2.4 Hz, 2H), 2.69 (d, J = 7.5 Hz, 2H), 2.80 (t, J = 2.3 Hz, 2H), 3.71 (s, 6H), 4.71–4.82 (m, 1H); ^{13}C NMR: δ = 12.4, 14.2, 20.5, 22.9, 32.6, 52.6, 57.5, 73.6, 82.4, 84.8, 95.1, 170.3, 203.6; HRMS (FAB^+): Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_4$, M^+ 278.1518. Found m/z 278.1521.

1c: IR (neat): 2953, 1970, 1738, 1437, 1291, 1210 cm^{-1} ; ^1H NMR: δ = 1.65 (d, J = 2.7 Hz, 6H), 2.71 (d, J = 7.8 Hz, 2H), 2.92 (t, J = 2.1 Hz, 2H), 3.34 (s, 3H), 3.73 (s, 6H), 4.05 (t, J = 2.1 Hz, 2H), 4.74–4.82 (m, 1H); ^{13}C NMR: δ = 20.2, 22.6, 32.4, 52.4, 56.9, 57.0, 59.6, 78.6, 81.0, 82.0, 95.1, 169.8, 203.4; HRMS (EI^+): Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_5$, M^+ 294.1467. Found m/z 294.1461.

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1d: IR (neat): 2970, 1970, 1740, 1437, 1289, 1208 cm^{-1} ; ^1H NMR: δ = 1.10 (d, J = 7.2 Hz, 6H), 1.65 (d, J = 2.7 Hz, 6H), 2.43–2.55 (m, 1H), 2.70 (d, J = 7.8 Hz, 2H), 2.81 (d, J = 2.1 Hz, 2H), 3.72 (s, 6H), 4.71–4.83 (m, 1H); ^{13}C NMR (100 MHz): δ = 20.315, 20.323, 22.6, 23.1, 32.4, 52.4, 57.5, 73.4, 82.3, 89.1, 94.9, 170.3, 203.8; HRMS (EI^+): Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$, M^+ 292.1675. Found m/z 292.1670.

1e: IR (neat): 2926, 1968, 1740, 1437, 1289, 1210 cm^{-1} ; ^1H NMR: δ = 1.44–1.62 (m, 6H), 1.75 (t, J = 2.7 Hz, 3H), 2.03–2.10 (m, 4H), 2.71 (d, J = 7.8 Hz, 2H), 2.81 (q, J = 2.4 Hz, 2H), 3.72 (s, 6H), 4.72–4.81 (m, 1H); ^{13}C NMR: δ = 3.5, 22.8, 26.0, 27.2, 31.4, 32.8, 52.5, 57.5, 73.3, 78.6, 82.1, 102.3, 170.4, 200.5; HRMS (EI^+): Calcd for $\text{C}_{18}\text{H}_{24}\text{O}_4$, M^+ 304.1675. Found m/z 304.1667.

1f: IR (neat): 2953, 1952, 1738, 1437, 1293, 1210 cm^{-1} ; ^1H NMR: δ = 1.72 (t, J = 2.7 Hz, 3H), 2.07 (d, J = 3.0 Hz, 3H), 2.84–2.90 (m, 4H), 3.69 (s, 3H), 3.70 (s, 3H), 5.25–5.34 (m, 1H), 7.16–7.23 (m, 1H), 7.27–7.34 (m, 2H), 7.35–7.40 (m, 2H); ^{13}C NMR: δ = 3.2, 16.8, 22.9, 32.1, 52.4, 57.0, 72.9, 78.7, 86.5, 100.5, 125.4, 126.3, 127.9, 136.4, 169.8, 169.9, 205.4; HRMS (EI^+): Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_4$, M^+ 326.1518. Found m/z 326.1516.

1g: IR (neat): 2955, 1968, 1740, 1439, 1294, 1210 cm^{-1} ; ^1H NMR: δ = 1.62 (dd, J = 7.1, 3.2 Hz, 3H), 1.75 (t, J = 2.6 Hz, 3H), 2.72 (dd, J = 7.8, 2.4 Hz, 2H), 2.80 (q, J = 2.6 Hz, 2H), 3.73 (s, 6H), 4.83–4.95 (m, 1H), 4.98–5.11 (m, 1H); ^{13}C NMR: δ = 3.0, 13.9, 22.6, 31.9, 52.1, 57.1, 72.9, 78.3, 83.6, 85.1, 169.7, 206.1; HRMS (EI^+): Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$, M^+ 250.1205. Found m/z 250.1206.

1h: IR (neat): 2988, 2242, 1972, 1640, 1437, 1321 cm^{-1} ; ^1H NMR: δ = 1.16 (t, J = 7.5 Hz, 3H), 1.76 (d, J = 3.3 Hz, 6H), 2.23 (qt, J = 7.4, 2.3 Hz, 2H), 2.68 (d, J = 6.6 Hz, 2H), 2.90 (t, J = 2.4 Hz, 2H), 5.01–5.09 (m, 1H); ^{13}C NMR: δ = 12.4, 13.6, 20.2, 28.4, 36.8, 37.3, 69.9, 80.6, 88.9, 98.7, 114.8, 204.5; HRMS (EI^+): Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2$, M^+ 212.1313. Found m/z 212.1310.

1i: IR (neat): 2979, 1968, 1701, 1437, 1358, 1175 cm^{-1} ; ^1H NMR: δ = 1.07 (t, J = 7.5 Hz, 3H), 1.63 (d, J = 2.7 Hz, 6H), 2.05–2.16 (m, 2H), 2.13 (s, 6H), 2.74 (d, J = 7.2 Hz, 2H), 2.79 (t, J = 2.3 Hz, 2H), 4.70–4.80 (m, 1H); ^{13}C NMR: δ = 12.4, 14.1, 20.4, 21.0, 26.8, 30.9, 70.8, 74.2, 82.6, 85.3, 96.0, 203.2, 204.9; HRMS (CI^+): Calcd for $\text{C}_{16}\text{H}_{23}\text{O}_2$, $\text{M}+\text{H}^+$ 247.1698. Found m/z 247.1700.

5a: IR (neat): 2979, 1968, 1734, 1437, 1202 cm^{-1} ; ^1H NMR: δ = 1.08 (t, J = 7.5 Hz, 3H), 1.67 (d, J = 3.0 Hz, 6H), 1.81–1.91 (m, 2H), 2.07–2.17 (m, 4H), 2.79 (t, J = 2.4 Hz, 2H), 3.73 (s, 6H), 4.88–4.97 (m, 1H); ^{13}C NMR: δ = 12.3, 14.1, 20.6, 23.2, 24.1, 31.6, 52.5, 56.9, 73.5, 84.8, 87.7, 95.6, 170.7, 201.3; HRMS (EI^+): Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$, M^+ 292.1675. Found m/z 292.1677.

5b: IR (neat): 2926, 1966, 1740, 1437, 1202 cm^{-1} ; ^1H NMR: δ = 1.08 (t, J = 7.5 Hz, 3H), 1.46–1.64 (m, 6H), 1.80–1.90 (m, 2H), 2.05–2.18 (m, 8H), 2.79 (t, J = 2.4 Hz, 2H), 3.73 (s, 6H), 4.90–4.99 (m, 1H); ^{13}C NMR: δ = 12.2, 14.0, 23.2, 24.0, 26.1, 27.4, 31.6, 52.4, 56.9, 73.5, 84.7, 87.6, 103.3, 170.8, 198.1; HRMS (EI^+): Calcd for $\text{C}_{20}\text{H}_{28}\text{O}_4$, M^+ 332.1988. Found m/z 332.1986.

9: IR (neat): 2979, 1970, 1738, 1447, 1202 cm^{-1} ; ^1H NMR: δ = 1.09 (t, J = 7.4 Hz, 3H), 1.66 (d, J = 3.0 Hz, 6H), 2.07–2.22 (m, 6H), 2.57 (d, J = 7.5 Hz, 2H), 3.71 (s, 6H), 4.70–4.80 (m, 1H); ^{13}C NMR: δ = 12.4, 14.0, 14.2, 20.5, 31.6, 32.8, 52.4, 57.1, 78.0, 82.1, 82.4, 95.3, 171.1, 203.5; HRMS (EI^+): Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$, M^+ 292.1675. Found m/z 292.1677.

General procedure for the rhodium-catalysed reaction of allenynes with arylboronic acid: To an oven-dried, Ar-purged flask was added [RhCl(nbd)]₂ (1.4 mg, 3.0 μmol, 5 mol % Rh), KOH (3.0 mg, 53 μmol), **2a** (20.4 mg, 0.17 mmol) and a solution of **1a** (28.3 mg, 0.11 mmol) in dry THF (1.5 mL). The reaction mixture was stirred at 50 °C for 12 h, and then quench with addition of water (2.0 mL). The resulting aqueous solution was extracted with ethyl acetate (4 x 10 mL). The combined extracts were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 5/1) to give the purified product **3aa** (52.2 mg, 0.081 mmol, 76% yield).

3aa: IR (KBr): 3052, 1740, 1701, 1636, 1441 cm⁻¹; ¹H NMR (400 MHz): δ = 1.27 (s, 3H), 1.92 (t, *J* = 1.3 Hz, 3H), 2.00–2.05 (m, 1H), 2.07 (s, 3H), 2.09–2.14 (m, 1H), 2.52–2.59 (m, 1H), 2.76–2.83 (m, 1H), 3.80 (s, 3H), 3.83 (s, 1H), 7.15–7.19 (m, 2H), 7.21–7.26 (m, 1H), 7.29–7.35 (m, 2H); ¹³C NMR (100 MHz): δ = 20.6, 20.8, 23.2, 34.3, 41.4, 44.7, 52.1, 64.3, 126.5, 127.6, 128.0, 128.1, 133.0, 135.6, 143.5, 145.6, 170.9, 200.0; Anal. Calcd for C₂₀H₂₂O₃: C 77.39, H 7.14. Found: C 77.49, H 7.13.

3ab: IR (KBr): 2950, 1744, 1713, 1644, 1437 cm⁻¹; ¹H NMR: δ = 1.34 (s, 3H), 1.89 (t, *J* = 1.2 Hz, 3H), 1.99–2.05 (m, 1H), 2.09 (s, 3H), 2.10–2.16 (m, 1H), 2.50–2.58 (m, 1H), 2.74–2.82 (m, 1H), 3.79 (s, 1H), 3.81 (s, 3H), 7.03–7.09 (m, 2H), 7.43–7.49 (m, 2H); ¹³C NMR: δ = 20.7, 20.8, 23.5, 34.5, 41.5, 44.9, 52.2, 64.2, 120.3, 126.4, 129.7, 131.2, 132.7, 136.4, 142.3, 145.8, 170.7, 199.5; HRMS (EI⁺): Calcd for C₂₀H₂₁BrO₃, M⁺ 388.0674. Found m/z 388.0671.

3ac: IR (KBr): 2996, 1736, 1717, 1644, 1559, 1437 cm⁻¹; ¹H NMR: δ = 1.38 (s, 3H), 1.90 (t, *J* = 1.4 Hz, 3H), 1.98–2.04 (m, 1H), 2.10 (s, 3H), 2.10–2.16 (m, 1H), 2.50–2.59 (m, 1H), 2.74–2.83 (m, 1H), 3.76 (s, 1H), 3.81 (s, 3H), 7.11 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 1.7 Hz, 1H), 7.39 (ddd, *J* = 7.8, 2.1, 1.2 Hz, 1H); ¹³C NMR: δ = 20.6, 20.8, 23.4, 34.4, 41.6, 44.9, 52.2, 64.2, 122.2, 126.3, 126.7, 129.6, 129.8, 131.0, 132.7, 136.8, 145.7, 145.9, 170.7, 199.7; HRMS (EI⁺): Calcd for C₂₀H₂₁BrO₃, M⁺ 388.0674. Found m/z 388.0670.

3ad: IR (KBr): 2969, 1736, 1713, 1643, 1644 cm⁻¹; ¹H NMR: δ = 1.37 (s, 3H), 1.90 (t, *J* = 1.2 Hz, 3H), 1.99–2.05 (m, 1H), 2.09–2.16 (m, 1H), 2.10 (s, 3H), 2.50–2.58 (m, 1H), 2.79 (d, *J* = 16.8 Hz, 1H), 3.77 (s, 1H), 3.81 (s, 3H), 7.06 (dt, *J* = 7.2, 1.7 Hz, 1H), 7.16 (t, *J* = 1.7 Hz, 1H), 7.20–7.31 (m, 2H); ¹³C NMR: δ = 20.7, 20.8, 23.4, 34.4, 41.6, 44.9, 52.2, 64.2, 126.2, 126.3, 126.6, 128.1, 129.4, 132.6, 133.8, 136.6, 145.2, 145.8, 170.6, 199.6; HRMS (EI⁺): Calcd for C₂₀H₂₁ClO₃, M⁺ 344.1179. Found m/z 344.1180.

3ae: IR (neat): 2960, 1736, 1713, 1642, 1325 cm⁻¹; ¹H NMR: δ = 1.32 (s, 3H), 1.91 (s, 3H), 1.98–2.04 (m, 1H), 2.06–2.14 (m, 1H), 2.08 (s, 3H), 2.50–2.59 (m, 1H), 2.74–2.83 (m, 1H), 3.80 (s, 3H), 3.81 (s, 3H), 3.85 (s, 1H), 6.69–6.82 (m, 3H), 7.25 (t, *J* = 8.0 Hz, 1H); ¹³C NMR: δ = 20.6, 20.8, 23.4, 34.3, 41.5, 44.8, 52.1, 55.2, 64.3, 111.4, 114.0, 120.5, 127.3, 129.1, 132.8, 135.5, 144.9, 145.7, 159.2, 170.8, 199.8; HRMS (EI⁺): Calcd for C₂₁H₂₄O₄, M⁺ 340.1675. Found m/z 340.1674.

3af: IR (KBr): 2953, 1738, 1723, 1705, 1646 cm⁻¹; ¹H NMR: δ = 1.25 (s, 3H), 1.94 (s, 3H), 2.01–2.07 (m, 1H), 2.08 (s, 3H), 2.10–2.16 (m, 1H), 2.52–2.61 (m, 1H), 2.76–2.85 (m, 1H), 3.76 (s, 1H), 3.81 (s, 3H), 3.93 (s, 3H), 7.35–7.45 (m, 2H), 7.85–7.88 (m, 1H), 7.93 (dt, *J* = 7.2, 1.7 Hz, 1H); ¹³C NMR (150 MHz): δ = 20.6, 20.8, 23.3, 34.4, 41.5, 44.8, 52.16, 52.20, 64.2, 126.7, 127.8, 128.3, 129.2, 130.1, 132.72, 132.73, 136.6, 143.9, 146.0, 167.0, 170.8, 199.8; HRMS (EI⁺): Calcd for C₂₂H₂₄O₅, M⁺ 368.1624. Found m/z 368.1627.

3ag: A mixture of atropisomers (56:44); IR (KBr): 2955, 1744, 1713, 1644, 1437 cm^{-1} ; ^1H NMR: δ = 1.23 (s, 1.32H), 1.30 (s, 1.68 H), 1.82–1.86 (m, 3H), 1.91–2.24 (m, 8H), 2.53–2.63 (m, 1H), 2.77–2.88 (m, 1H), 3.29 (s, 0.56H), 3.52 (s, 0.44H), 3.80 (s, 1.68H), 3.81 (s, 1.32H), 6.94–7.24 (m, 4H); ^{13}C NMR: δ = 19.4, 19.5, 19.8, 20.4, 20.6, 20.7, 23.0, 23.6, 33.7, 33.9, 41.60, 41.64, 44.9, 45.4, 52.2, 64.36, 64.41, 125.5, 125.6, 126.3, 126.7, 126.8, 127.7, 128.5, 128.6, 129.7, 129.9, 132.5, 132.6, 134.6, 135.29, 135.32, 135.5, 142.8, 143.0, 145.0, 145.5, 170.8, 199.8, 200.1; HRMS (EI^+): Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_3$, M^+ 324.1725. Found m/z 324.1729.

3ah: IR (KBr): 2954, 1744, 1698, 1638, 1435 cm^{-1} ; ^1H NMR: δ = 1.36 (s, 3H), 1.90 (t, J = 1.4 Hz, 3H), 2.00–2.05 (m, 1H), 2.08 (s, 3H), 2.12–2.17 (m, 1H), 2.49–2.58 (m, 1H), 2.73–2.81 (m, 1H), 3.81 (s, 3H), 4.01 (s, 1H), 6.98–7.04 (m, 2H), 7.26–7.31 (m, 1H); ^{13}C NMR: δ = 20.7, 20.8, 23.1, 34.5, 41.3, 44.9, 52.2, 64.2, 121.0, 122.3, 125.0, 127.9, 132.8, 136.2, 143.6, 145.9, 170.8, 199.7; HRMS (EI^+): Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_3\text{S}$, M^+ 316.1133. Found m/z 316.1133.

3ba: IR (neat): 2965, 1748, 1715, 1646, 1437 cm^{-1} ; ^1H NMR: δ = 0.86 (t, J = 7.5 Hz, 3H), 1.27 (s, 3H), 1.98–2.04 (m, 1H), 2.08 (s, 3H), 2.07–2.13 (m, 1H), 2.19–2.39 (m, 2H), 2.54–2.64 (m, 1H), 2.81 (d, J = 16.2 Hz, 1H), 3.71 (s, 1H), 3.81 (s, 3H), 7.10–7.15 (m, 2H), 7.21–7.28 (m, 1H), 7.29–7.36 (m, 2H); ^{13}C NMR: δ = 12.2, 20.6, 23.3, 27.8, 33.6, 41.4, 44.8, 52.1, 64.2, 126.5, 128.0, 128.7, 133.0, 134.1, 134.7, 141.9, 145.5, 170.9, 199.9; HRMS (EI^+): Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_3$, M^+ 324.1725. Found m/z 324.1728.

3ca: IR (KBr): 2928, 1744, 1715, 1642, 1437 cm^{-1} ; ^1H NMR: δ = 1.26 (s, 3H), 2.00–2.18 (m, 2H), 2.08 (s, 3H), 2.65–2.73 (m, 1H), 2.94 (d, J = 16.8 Hz, 1H), 3.28 (s, 3H), 3.81 (s, 3H), 3.88 (s, 1H), 4.09 (d, J = 11.1 Hz, 1H), 4.17 (d, J = 10.8 Hz, 1H), 7.20–7.38 (m, 5H); ^{13}C NMR: δ = 20.7, 23.4, 33.7, 40.9, 45.0, 52.2, 58.1, 64.1, 73.5, 126.9, 128.2, 128.6, 129.0, 132.3, 140.5, 141.0, 146.9, 170.6, 199.3; HRMS (EI^+): Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_4$, M^+ 340.1675. Found m/z 340.1674.

3da: IR (neat): 2961, 1748, 1715, 1646, 1437 cm^{-1} ; ^1H NMR: δ = 0.87 (d, J = 6.9 Hz, 3H), 0.95 (d, J = 6.6 Hz, 3H), 1.30 (s, 3H), 1.92–1.98 (m, 1H), 2.02–2.07 (m, 1H), 2.10 (s, 3H), 2.59 (dd, J = 16.4, 2.3 Hz, 1H), 2.66–2.78 (m, 1H), 2.84 (d, J = 16.2 Hz, 1H), 3.39 (s, 1H), 3.80 (s, 3H), 6.99–7.04 (m, 2H), 7.26–7.35 (m, 3H); ^{13}C NMR: δ = 20.6, 20.8, 21.1, 23.6, 31.7, 33.2, 41.5, 45.1, 52.1, 64.1, 126.4, 127.5, 129.9, 132.8, 134.4, 137.8, 139.5, 145.2, 170.9, 200.1; HRMS (EI^+): Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_3$, M^+ 338.1882. Found m/z 339.1885.

3ea: IR (KBr): 2926, 1744, 1703, 1628, 1439 cm^{-1} ; ^1H NMR: δ = 1.23–1.68 (m, 8H), 1.93 (t, J = 1.4 Hz, 3H), 1.99–2.06 (m, 1H), 2.08–2.15 (m, 1H), 2.52–2.67 (m, 2H), 2.75–2.83 (m, 1H), 2.86–2.98 (m, 1H), 3.81 (s, 3H), 3.84 (s, 1H), 7.13–7.36 (m, 5H); ^{13}C NMR: δ = 20.9, 26.2, 27.9, 28.5, 29.4, 33.0, 34.4, 41.5, 44.4, 52.2, 64.6, 126.4, 127.4, 127.8, 128.0, 130.1, 135.7, 143.4, 153.4, 170.8, 200.6; HRMS (EI^+): Calcd for $\text{C}_{23}\text{H}_{26}\text{O}_3$, M^+ 350.1882. Found m/z 350.1877.

3fa: IR (KBr): 2950, 1738, 1711, 1613, 1335 cm^{-1} ; ^1H NMR (400 MHz): δ = 1.96 (s, 3H), 2.05 (dd, J = 7.2, 1.6 Hz, 1H), 2.23–2.27 (m, 1H), 2.47 (s, 3H), 2.63–2.69 (m, 1H), 2.87 (d, J = 12.7 Hz, 1H), 3.84 (s, 3H), 3.98 (s, 1H), 6.89–6.93 (m, 2H), 6.95–7.02 (m, 4H), 7.07–7.17 (m, 4H); ^{13}C NMR: δ = 20.7, 21.0, 35.0, 42.3, 45.5, 52.3, 64.3, 126.4, 127.2, 127.7, 128.0, 128.1, 128.2, 134.0, 134.7, 141.6, 142.5, 146.6, 170.8, 201.1; HRMS (EI^+): Calcd for $\text{C}_{25}\text{H}_{24}\text{O}_3$, M^+ 372.1725. Found m/z 372.1722.

3ha: IR (KBr): 2967, 2245, 1719, 1642, 1435 cm^{-1} ; ^1H NMR: δ = 0.87 (t, J = 7.5 Hz, 3H), 1.27 (s, 3H), 2.06–2.12 (m, 1H), 2.10 (s, 3H), 2.15–2.21 (m, 1H), 2.27 (q, J = 7.5 Hz, 2H), 2.70 (dd, J = 16.0, 2.3 Hz, 1H), 2.89 (d, J = 16.0 Hz, 1H), 3.74 (s, 1H), 7.07–7.14 (m, 2H), 7.23–7.37 (m, 3H); ^{13}C NMR: δ = 12.1, 20.9, 23.4, 28.0, 35.9, 42.7, 44.4, 50.3, 118.0, 126.9, 128.2, 128.6, 131.1, 132.2, 135.5, 141.4, 148.3, 195.0; HRMS (EI^+): Calcd for $\text{C}_{20}\text{H}_{21}\text{NO}$, M^+ 291.1623. Found m/z 291.1627.

3ia: IR (KBr): 3432, 2963, 1688, 1443, 1362 cm^{-1} ; ^1H NMR (600 MHz): δ = 0.83 (t, J = 7.6 Hz, 3H), 0.96 (s, 3H), 1.35 (s, 3H), 1.74 (s, 3H), 1.76 (dd, J = 10.0, 1.7 Hz, 1H), 1.79–1.83 (m, 1H), 2.20–2.36 (m, 3H), 2.28 (s, 3H), 2.43 (s, 1H), 2.98–3.03 (m, 1H), 3.47 (s, 1H), 7.10–7.13 (m, 2H), 7.19–7.23 (m, 1H), 7.27–7.31 (m, 2H); ^{13}C NMR: δ = 12.2, 20.1, 21.7, 24.2, 27.6, 28.9, 32.8, 38.1, 45.4, 66.4, 79.3, 126.0, 126.2, 127.8, 129.0, 131.5, 136.7, 139.2, 142.2, 212.4; HRMS (EI^+): Calcd for $\text{C}_{22}\text{H}_{28}\text{O}_2$, M^+ 324.2089. Found m/z 324.2085.

6a: IR (KBr): 2954, 1740, 1686, 1615, 1252 cm^{-1} ; ^1H NMR: δ = 0.86 (t, J = 7.5 Hz, 3H), 1.51 (s, 3H), 1.58–1.82 (m, 2H), 1.85–1.97 (m, 1H), 2.18 (s, 3H), 2.25–2.37 (m, 3H), 2.64 (d, J = 17.4 Hz, 1H), 3.08 (dd, J = 17.3, 2.9 Hz, 1H), 3.48 (t, J = 2.9 Hz, 1H), 3.81 (s, 3H), 7.04–7.09 (m, 2H), 7.21–7.28 (m, 1H), 7.21–7.37 (m, 2H); ^{13}C NMR (100 MHz): δ = 11.9, 23.08, 23.09, 25.6, 25.8, 26.7, 33.2, 38.1, 52.1, 57.6, 126.4, 128.0, 128.7, 131.0, 131.8, 135.6, 142.2, 147.9, 172.5, 199.4; HRMS (EI^+): Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_3$, M^+ 338.1882. Found m/z 338.1888.

6b: IR (neat): 2930, 1740, 1686, 1605, 1449, 1250 cm^{-1} ; ^1H NMR: δ = 0.86 (t, J = 7.5 Hz, 3H), 1.43–1.96 (m, 14H), 2.26–2.38 (m, 3H), 2.63 (d, J = 17.4 Hz, 1H), 2.73–2.84 (m, 1H), 2.96–3.14 (m, 2H), 3.55 (t, J = 3.0 Hz, 1H), 3.81 (s, 3H), 7.03–7.07 (m, 2H), 7.21–7.35 (m, 3H); ^{13}C NMR: δ = 12.0, 25.8, 26.1, 26.3, 26.7, 28.4, 28.8, 31.1, 32.1, 33.3, 37.6, 52.1, 58.0, 126.4, 127.9, 128.7, 129.1, 131.2, 135.6, 142.2, 155.7, 172.5, 200.5; HRMS (EI^+): Calcd for $\text{C}_{25}\text{H}_{30}\text{O}_3$, M^+ 378.2195. Found m/z 378.2191.

10: IR (KBr): 2963, 1736, 1705, 1632, 1266 cm^{-1} ; ^1H NMR: δ = 0.89 (t, J = 7.5 Hz, 3H), 1.49 (s, 3H), 1.79–1.91 (m, 2H), 2.06–2.23 (m, 2H), 2.16 (s, 3H), 2.32–2.53 (m, 3H), 2.68 (dd, J = 15.2, 6.5 Hz, 1H), 3.53 (d, J = 5.7 Hz, 1H), 3.74 (s, 3H), 7.08–7.15 (m, 2H), 7.22–7.38 (m, 3H); ^{13}C NMR (100 MHz): δ = 13.3, 20.8, 23.1, 24.2, 27.1, 31.8, 40.0, 41.8, 52.1, 59.9, 126.4, 128.1, 128.8, 133.8, 134.1, 134.9, 142.7, 149.6, 172.3, 202.4; HRMS (EI^+): Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_3$, M^+ 338.1882. Found m/z 338.1878.