Supporting Information

Iridium Complex-Catalyzed [2+2+2] Cycloaddition of α,ω -Diyne with Monoynes and Monoenes

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Experimental Section

General. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker AVANCE-400 spectrometer or JEOL JNM-ECP 500A spectrometer using Me_4Si as an internal standard. Samples were dissolved in CDCl_3 . GC analyses were performed on a Shimadzu GC-14B using 3.2 mm x 2 m glass columns packed with 5% OV-17 on 60/80 mesh Chromosorb WAW-DMCS. The products were purified by column chromatography on 70-230 mesh silica gel (Merck; Silica Gel 60N). Recycling preparative HPLC was performed on an LC-918R (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL-1HF and 2HF columns using CHCl_3 as an eluent. Elemental analyses were carried out on a Yanaco MT-5 CHN analyzer. High-resolution mass spectra were obtained with a JEOL Mstation JMS-700.

Materials. All reagents and solvents were dried and purified before use by the usual procedures. Diyne **1a** was prepared by reaction of the sodium salt of dimethyl malonate with propargyl bromide. Dienes **1b**, **1c**, **1d** and **9** were prepared according to the published methods. Diyne **1e** was prepared by reaction of the sodium salt of 2,2-di(2-propynyl)-1,3-propanediol with methyl iodide. Diyne **1f** was prepared by the acetylation of 2,2-di(2-propynyl)-1,3-propanediol. 2,2-Di(2-propynyl)-1,3-propanediol was prepared according to the published methods. Dienes **1g** and **7** were purchased. Diyne **5** was prepared by reaction of the sodium salt of dimethyl malonate with 1-bromo-2-butyne. Diyne **9b** was prepared by reaction of the sodium salt of tetraethyl 1,1,2,2-ethanetetracarboxylate with 1-bromo-2-butyne. Diyne **11a** was prepared by reaction of the sodium salt of dimethyl propargylmalonate with 1-bromo-2-butyne. Diyne **11b** was prepared by reaction of the sodium salt of dimethyl propargylmalonate with 1-bromo-2-heptyne. Tetraethyl 1,1,2,2-ethanetetracarboxylate and dimethyl propargylmalonate were purchased. Monoynes **2a-n** and monoenes **14**, **17**, and **19** were purchased. Monoynes **2o** was prepared by reaction of the sodium salt of 2-butyne-1,4-diol with iodomethane. Ligands were purchased. $[\text{Ir}(\text{cod})\text{Cl}]_2$ ¹, $[\text{Ir}(\text{cod})\text{OMe}]_2$ ², $[\text{Ir}(\text{cod})_2]\text{BF}_4$ ³, and $[\text{Ir}(\text{cot})_2\text{Cl}]_2$ ⁴ were prepared according to the published methods. $\text{Ir}(\text{cod})(\text{acac})$ was purchased.

3a⁵: ^1H NMR (400 MHz, CDCl_3) δ 0.91 (t, $J = 7.6$ Hz, 3H), 1.34 (sextet, $J = 7.6$ Hz, 2H), 1.56 (quintet, $J = 7.6$ Hz, 2H), 2.55 (t, $J = 7.6$ Hz, 2H), 3.555 (s, 2H), 3.563 (s, 2H), 3.73 (s, 6H), 6.97 (d, $J = 7.7$ Hz, 1H), 7.00 (s, 1H), 7.07 (d, $J = 7.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.8, 22.3, 33.8, 35.4, 40.2, 40.5, 52.8 (2C), 60.4, 123.8, 124.1, 127.1, 136.9, 139.8, 141.7, 172.1 (2C).

3b: ^1H NMR (400 MHz, CDCl_3) δ 0.88 (t, $J = 7.0$ Hz, 3H), 1.27-1.30 (m, 10H), 1.54-1.59 (m, 2H), 2.54 (t, $J = 7.6$ Hz, 2H), 3.556 (s, 2H), 3.564 (s, 2H), 3.73 (s, 6H), 6.97 (d, $J = 7.7$ Hz, 1H), 7.00 (s, 1H), 7.07 (d, $J = 7.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 22.6, 29.2, 29.3, 29.4, 31.7, 31.8, 35.8, 40.2, 40.5, 52.8 (2C), 60.4, 123.8, 124.1, 127.1, 137.0, 139.9, 141.8, 172.1 (2C). Anal.

Calcd for C₂₁H₃₀O₄: C, 72.80; H, 8.73. Found: C, 72.87; H, 9.00.

3c: ¹H NMR (400 MHz, CDCl₃) δ 1.92 (quintet, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 3.56 (s, 4H), 3.73 (s, 6H), 6.97 (d, *J* = 7.7 Hz, 1H), 7.00 (s, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.14-7.28 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 33.1, 35.2, 35.4, 40.2, 40.5, 52.8 (2C), 60.4, 123.9, 124.2, 125.7, 127.2, 128.2 (2C), 128.4 (2C), 137.2, 140.0, 141.2, 142.2, 172.1 (2C). Anal.

Calcd for C₂₂H₂₄O₄: C, 74.98; H, 6.86. Found: C, 74.75; H, 6.86.

3d: ¹H NMR (400 MHz, CDCl₃) δ 2.05 (quintet, *J* = 6.5 Hz, 2H), 2.72 (t, *J* = 7.2 Hz, 2H), 3.51 (t, *J* = 6.5 Hz, 2H), 3.57 (s, 4H), 3.74 (s, 6H), 6.99 (d, *J* = 7.7 Hz, 1H), 7.02 (s, 1H), 7.10 (d, *J* = 7.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 32.5, 34.1, 40.2, 40.5, 44.2, 52.9 (2C), 60.4, 124.1, 124.3, 127.3, 137.6, 139.5, 140.2, 172.1 (2C). Anal. Calcd for C₁₆H₁₉ClO₄: C, 61.84; H, 6.16; Cl, 11.41. Found: C, 61.57; H, 6.05; Cl, 11.69.

3e⁵: ¹H NMR (400 MHz, CDCl₃) δ 3.63 (s, 2H), 3.65 (s, 2H), 3.76 (s, 6H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.38-7.42 (m, 4H), 7.53-7.55 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 40.3, 40.6, 52.9 (2C), 60.5, 123.0, 124.2, 126.2, 127.0, 127.1 (2C), 128.6 (2C), 139.0, 140.4, 140.5, 141.2, 172.0 (2C).

3f: ¹H NMR (400 MHz, CDCl₃) δ 1.61-1.79 (m, 4H), 2.17-2.18 (m, 2H), 2.35-2.37 (m, 2H), 3.57 (s, 4H), 3.73 (s, 6H), 6.05 (m, 1H), 7.09-7.19 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 22.1, 23.0, 25.8, 27.6, 40.2, 40.5, 52.8 (2C), 60.5, 120.7, 123.8, 123.9, 124.3, 136.5, 138.0, 139.8, 141.9, 172.1 (2C). Exact mass calcd for C₁₉H₂₂O₄: 314.1518. Found: 314.1509. Anal. Calcd for C₁₉H₂₂O₄: C, 72.59; H, 7.05. Found: C, 72.24; H, 7.03.

3g: ¹H NMR (400 MHz, CDCl₃) δ 3.37 (s, 3H), 3.58 (s, 2H), 3.59 (s, 2H), 3.74 (s, 6H), 4.40 (s, 2H), 7.11-7.17 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 40.3, 40.4, 52.9 (2C), 58.0, 60.4, 74.6, 123.6, 124.0, 126.7, 137.1, 139.4, 140.1, 172.0 (2C). Anal. Calcd for C₁₅H₁₈O₅: C, 64.74; H, 6.52. Found: C, 64.65; H, 6.24.

3h: ¹H NMR (400 MHz, CDCl₃) δ 1.99 (br, 1H), 3.57 (s, 4H), 3.73 (s, 6H), 4.61 (s, 2H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.19 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 40.2, 40.4, 52.9 (2C), 60.4, 65.1, 122.9, 124.2, 125.9, 139.2, 139.9, 140.2, 172.0 (2C). Anal. Calcd for C₁₄H₁₆O₅: C, 63.63; H, 6.10. Found: C, 63.38; H, 6.12.

3i: ¹H NMR (400 MHz, CDCl₃) δ 1.55 (s, 6H), 1.94 (br, 1H), 3.57 (s, 2H), 3.59 (s, 2H), 3.74 (s, 6H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.33 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 31.8 (2C), 40.2, 40.6, 52.9 (2C), 60.4, 72.4, 120.3, 123.3, 123.8, 138.1, 139.8, 148.2, 172.1 (2C). Anal. Calcd for C₁₆H₂₀O₅: C, 65.74; H, 6.90. Found: C, 65.50; H, 6.84.

3j: ¹H NMR (400 MHz, CDCl₃) δ 1.85 (br, 1H), 2.80 (t, *J* = 6.6 Hz, 2H), 3.56 (s, 2H), 3.57 (s, 2H), 3.73 (s, 6H), 3.80 (t, *J* = 6.6 Hz, 2H), 7.02 (d, *J* = 7.7 Hz, 1H), 7.05 (s, 1H), 7.12 (d, *J* = 7.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 38.9, 40.2, 40.4, 52.8 (2C), 60.3, 63.6, 124.1, 124.7, 127.7, 137.4, 137.9, 140.2, 171.1, 172.0. Anal. Calcd for C₁₅H₁₈O₅: C, 64.74; H, 6.52. Found: C, 64.34;

H, 6.52.

3l⁵: ¹H NMR (400 MHz, CDCl₃) δ 2.22 (s, 6H), 3.36 (s, 2H), 3.58 (s, 4H), 3.74 (s, 6H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.15 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 40.2, 40.4, 45.3 (2C), 52.8 (2C), 60.4, 64.2, 123.8, 124.8, 127.9, 137.8, 138.6, 140.0, 172.0 (2C). HRMS: Calcd for C₁₆H₂₁NO₄ (M⁺), 291.1471. Found: *m/z* 291.1475.

3m: ¹H NMR (400 MHz, CDCl₃) δ 1.94 (quintet, *J* = 7.3 Hz, 2H), 2.30 (t, *J* = 7.1 Hz, 2H), 2.72 (t, *J* = 7.3 Hz, 2H), 3.56 (s, 4H), 3.74 (s, 6H), 6.98 (d, *J* = 7.5 Hz, 1H), 7.02 (s, 1H), 7.12 (d, *J* = 7.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 16.2, 26.8, 34.0, 40.0, 40.3, 52.8 (2C), 60.2, 119.4, 124.1, 124.2, 127.1, 137.9, 138.5, 140.2, 171.9 (2C). Anal. Calcd for C₁₇H₁₉NO₄: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.64; H, 6.43; N, 4.58.

3o: ¹H NMR (400 MHz, CDCl₃) δ 1.19 (t, *J* = 7.6 Hz, 6H), 2.60 (q, *J* = 7.6 Hz, 4H), 3.55 (s, 4H), 3.73 (s, 6H), 6.99 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 15.3 (2C), 25.4 (2C), 40.4 (2C), 52.8 (2C), 60.4, 123.9 (2C), 137.3 (2C), 140.5 (2C), 172.2 (2C). Anal. Calcd for C₁₇H₂₂O₄: C, 70.32; H, 7.64. Found: C, 69.91; H, 7.62.

3p: ¹H NMR (400 MHz, CDCl₃) δ 0.93 (t, *J* = 7.3 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H), 1.37 (sextet, *J* = 7.5 Hz, 2H), 1.46-1.62 (m, 6H), 2.42 (t, *J* = 6.8 Hz, 2H), 2.70 (t, *J* = 7.7 Hz, 2H), 3.51 (s, 2H), 3.54 (s, 2H), 3.73 (s, 6H), 6.99 (s, 1H), 7.19 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.5, 13.9, 19.2, 21.9, 22.6, 30.9, 32.9, 34.3, 40.0, 40.5, 52.9 (2C), 60.4, 79.4, 93.1, 122.1, 124.3, 127.6, 137.0, 139.5, 143.7, 172.0 (2C). Anal. Calcd for C₂₃H₃₀O₄: C, 74.56; H, 8.16. Found: C, 74.43; H, 8.19.

3q: ¹H NMR (400 MHz, CDCl₃) δ 0.91 (t, *J* = 7.3 Hz, 3H), 1.29-1.36 (m, 2H), 1.52-1.58 (m, 2H), 2.16 (s, 6H), 2.55 (t, *J* = 7.7 Hz, 2H), 3.46 (s, 4H), 6.97 (d, *J* = 7.7 Hz, 1H), 7.00 (s, 1H), 7.08 (d, *J* = 7.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 22.3, 26.5 (2C), 33.8, 35.4, 37.3, 37.6, 74.8, 124.1, 124.3, 127.3, 136.8, 139.7, 141.9, 204.9 (2C). Anal. Calcd for C₁₇H₂₂O₂: C, 79.03; H, 8.58. Found: C, 79.05; H, 8.72.

3r: ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, *J* = 7.4 Hz, 3H), 1.35 (sextet, *J* = 7.6 Hz, 2H), 1.58 (quintet, *J* = 7.6 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 3.29 (d, *J* = 15.5 Hz, 2H), 3.56 (s, 3H), 3.93 (dd, *J* = 15.5, 4.9 Hz, 2H), 6.96 (d, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.19-7.23 (m, 1H), 7.27-7.31 (m, 2H), 7.37-7.39 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 22.4, 33.8, 35.5, 42.4, 42.7, 52.5, 59.7, 123.8, 124.2, 126.6 (2C), 126.9 (2C), 128.4 (2C), 138.2, 141.1, 141.5, 142.9, 175.9. Anal. Calcd for C₂₁H₂₄O₂: C, 81.78; H, 7.84. Found: C, 81.52; H, 7.77.

3s: ¹H NMR (400 MHz, CDCl₃) δ 2.02 (br, 1H), 3.30 (d, *J* = 15.5 Hz, 2H), 3.56 (s, 3H), 3.94 (d, *J* = 15.5 Hz, 2H), 4.60 (s, 2H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.20-7.40 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 42.3, 42.5, 52.6, 59.6, 65.3, 123.1, 124.2, 125.7, 126.6 (2C), 127.0, 128.5 (2C), 139.5, 140.6, 141.5, 142.4, 175.8. Anal. Calcd for C₁₈H₁₈O₃: C, 76.57; H, 6.43. Found: C, 76.27; H, 6.47.

3t: ¹H NMR (500 MHz, CDCl₃) δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.26-1.45 (m, 2H), 1.47-1.63 (m, 2H), 2.57 (t, *J* = 7.8 Hz, 2H), 3.06 (s, 3H), 3.69-3.78 (m, 6H), 3.81 (s, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 7.03

(s, 1H), 7.11 (d, $J = 7.3$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.9, 22.3, 33.7, 35.4, 37.5, 37.6, 38.1, 53.9, 77.2, 123.9, 124.2, 127.7, 135.4, 138.3, 142.5, 169.5. HRMS: Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_4\text{S}$ (M^+), 310.1239. Found: m/z 310.1240

3u: ^1H NMR (400 MHz, CDCl_3) δ 0.92 (t, $J = 7.4$ Hz, 3H), 1.35 (sextet, $J = 7.4$ Hz, 2H), 1.53-1.61 (m, 2H), 2.55 (t, $J = 7.6$ Hz, 2H), 2.78 (s, 2H), 2.79 (s, 2H), 3.34-3.36 (m, 10H), 6.93 (d, $J = 7.6$ Hz, 1H), 6.97 (s, 1H), 7.05 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 22.4, 34.0, 35.5, 38.6, 38.9, 48.1, 59.2 (2C), 76.1 (2C), 124.5, 124.8, 126.4, 139.2, 141.0, 142.1. Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_2$: C, 77.82; H, 9.99. Found: C, 77.64; H, 10.17.

3v: ^1H NMR (400 MHz, CDCl_3) δ 2.10 (br, 1H), 2.80 (s, 2H), 2.81 (s, 2H), 3.33 (s, 6H), 3.35 (s, 4H), 4.60 (s, 2H), 7.10 (d, $J = 7.8$ Hz, 1H), 7.13 (d, $J = 7.8$ Hz, 1H), 7.16 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 38.6, 38.7, 48.2, 59.1 (2C), 65.3, 76.0 (2C), 123.7, 124.8, 125.3, 139.1, 141.6, 142.5. Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3$: C, 71.16; H, 8.53. Found: C, 71.43; H, 8.56.

3w: ^1H NMR (500 MHz, CDCl_3) δ 0.92 (t, $J = 7.3$ Hz, 3H), 1.31-1.39 (m, 2H), 1.53-1.61 (m, 2H), 2.06 (s, 6H), 2.56 (t, $J = 7.8$ Hz, 2H), 2.84 (s, 2H), 2.85 (s, 2H), 4.10 (s, 4H), 6.97 (d, $J = 7.3$ Hz, 1H), 6.99 (s, 1H), 7.07 (d, $J = 7.3$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.9, 20.8 (2C), 22.3, 33.9, 35.5, 38.4, 38.7, 46.5, 66.8 (2C), 124.5, 124.8, 126.9, 138.0, 140.9, 141.6, 171.0 (2C). HRMS: Calcd for $\text{C}_{19}\text{H}_{26}\text{O}_4$ (M^+), 318.1831. Found: m/z 318.1786.

3x⁶: ^1H NMR (400 MHz, CDCl_3) δ 0.92 (t, $J = 7.5$ Hz, 3H), 1.36 (sextet, $J = 7.5$ Hz, 2H), 1.58 (quintet, $J = 7.5$ Hz, 2H), 2.05 (quintet, $J = 7.4$ Hz, 2H), 2.57 (t, $J = 7.7$ Hz, 2H), 2.84-2.89 (m, 4H), 6.94 (d, $J = 7.5$ Hz, 1H), 7.04 (s, 1H), 7.11 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 22.4, 25.5, 32.5, 32.8, 34.1, 35.5, 124.0, 124.4, 126.2, 140.8, 141.3, 144.2.

4a⁷: ^1H NMR (500 MHz, CDCl_3) δ 2.14 (s, 1H), 2.67 (d, $J = 2.7$ Hz, 2H), 3.35 (s, 2H), 3.55 (s, 4H), 3.74 (s, 12H), 6.94 (d, $J = 7.3$ Hz, 1H), 6.97 (s, 1H), 7.09 (d, $J = 7.3$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 22.2, 37.3, 40.3, 40.5, 52.7 (2C), 52.9 (2C), 58.3, 60.3, 72.1, 79.2, 124.1, 125.5, 128.5, 134.2, 138.8, 140.2, 170.0 (2C), 172.0 (2C).

4b⁷: ^1H NMR (500 MHz, CDCl_3) δ 3.16 (s, 4H), 3.56 (s, 8H), 3.62 (s, 6H), 3.74 (s, 12H), 6.94 (d, $J = 7.3$ Hz, 1H), 6.95 (s, 1H), 7.09 (d, $J = 7.3$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 39.2 (2C), 40.3 (2C), 40.5 (2C), 52.1 (2C), 52.9 (4C), 60.4 (2C), 60.5, 123.9 (2C), 125.8 (2C), 128.8 (2C), 134.9 (2C), 138.5 (2C), 139.9 (2C), 171.3 (2C), 172.0 (42C).

6a: ^1H NMR (400 MHz, CDCl_3) δ 0.93 (t, $J = 7.2$ Hz, 3H), 1.38 (sextet, $J = 7.2$ Hz, 2H), 1.50 (quintet, $J = 7.2$ Hz, 2H), 2.15 (s, 3H), 2.19 (s, 3H), 2.53 (t, $J = 7.2$ Hz, 2H), 3.52 (s, 2H), 3.55 (s, 2H), 3.74 (s, 6H), 6.78 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 15.0, 18.5, 22.7, 32.8, 33.0, 39.5, 40.2, 52.8 (2C), 59.5, 128.5, 129.0, 130.3, 135.7, 138.8, 139.9, 172.4 (2C). Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{O}_4$: C, 71.67; H, 8.23. Found: C, 71.33; H, 8.15.

6e: ^1H NMR (400 MHz, CDCl_3) δ 2.12 (s, 3H), 2.25 (s, 3H), 3.60 (s, 4H), 3.78 (s, 6H), 6.90 (s, 1H), 7.25-7.32 (m, 3H), 7.36-7.40 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 16.6, 18.6, 39.7, 40.3, 53.0

(2C), 59.5, 126.5, 127.9 (2C), 128.2, 129.4 (2C), 130.0, 130.5, 137.5, 139.2, 141.1, 141.9, 172.4 (2C). Anal. Calcd for C₂₁H₂₂O₄: C, 74.54; H, 6.55. Found: C, 74.51; H, 6.65.

6g: ¹H NMR (400 MHz, CDCl₃) δ 2.20 (s, 3H), 2.21 (s, 3H), 3.37 (s, 3H), 3.53 (s, 2H), 3.56 (s, 2H), 3.75 (s, 6H), 4.38 (s, 2H), 6.95 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.7, 18.5, 39.6, 39.9, 52.9 (2C), 58.0, 59.5, 73.0, 129.2, 129.6, 130.4, 134.8, 138.1, 139.1, 172.3 (2C). Anal. Calcd for C₁₇H₂₂O₅: C, 66.65; H, 7.24. Found: C, 66.24; H, 7.24.

6o: ¹H NMR (400 MHz, CDCl₃) δ 1.11 (t, *J* = 7.5 Hz, 6H), 2.19 (s, 6H), 2.64 (q, *J* = 7.5 Hz, 4H), 3.56 (s, 4H), 3.74 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 14.8 (2C), 15.7 (2C), 22.3 (2C), 40.5 (2C), 52.8 (2C), 59.0, 128.9 (2C), 136.3 (2C), 139.1 (2C), 172.5 (2C). Anal. Calcd for C₁₉H₂₆O₄: C, 71.67; H, 8.23. Found: C, 71.57; H, 8.46.

6p: ¹H NMR (500 MHz, CDCl₃) δ 0.947 (t, *J* = 7.3 Hz, 3H), 0.952 (t, *J* = 7.3 Hz, 3H), 1.34-1.56 (m, 6H), 1.56-1.64 (m, 2H), 2.17 (s, 3H), 2.30 (s, 3H), 2.48 (t, *J* = 6.9 Hz, 2H), 2.78 (t, *J* = 7.3 Hz, 2H), 3.52 (s, 2H), 3.55 (s, 2H), 3.75 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 13.5, 13.9, 15.6, 17.6, 19.3, 21.9, 23.2, 31.1, 31.5, 32.0, 40.0, 40.5, 52.9 (2C), 59.2, 78.6, 97.0, 122.6, 128.4, 132.7, 135.5, 138.0, 142.2, 172.3 (2C). HRMS: Calcd for C₂₅H₃₄O₄ (M⁺), 398.2457. Found: *m/z* 398.2459.

6q: ¹H NMR (400 MHz, CDCl₃) δ 2.26 (s, 6H), 3.41 (s, 6H), 3.56 (s, 4H), 3.74 (s, 6H), 4.49 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 15.6 (2C), 40.3 (2C), 52.9 (2C), 58.3 (2C), 59.2, 68.4 (2C), 131.1 (2C), 134.4 (2C), 139.1 (2C), 172.2 (2C). Anal. Calcd for C₁₉H₂₆O₆: C, 65.13; H, 7.48. Found: C, 65.03; H, 7.35.

8a⁵: ¹H NMR (400 MHz, CDCl₃) δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.35 (sextet, *J* = 7.7 Hz, 2H), 1.59 (quintet, *J* = 7.6 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 5.07 (s, 4H), 7.04 (s, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 22.3, 33.8, 35.4, 73.38, 73.43, 120.6, 120.8, 127.5, 136.3, 139.2, 142.2.

8o: ¹H NMR (400 MHz, CDCl₃) δ 1.22 (t, *J* = 7.6 Hz, 6H), 2.66 (q, *J* = 7.6 Hz, 4H), 5.07 (s, 4H), 7.04 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 15.4 (2C), 25.5 (2C), 73.5 (2C), 120.6 (2C), 136.8 (2C), 140.9 (2C). Anal. Calcd for C₁₂H₁₆O: C, 81.77; H, 9.15; O, 9.06. Found: C, 81.77; H, 9.34.

10a: ¹H NMR (400 MHz, CDCl₃) δ 0.91 (t, *J* = 7.3 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 12H), 1.27-1.35 (m, 2H), 1.55 (quintet, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 7.6 Hz, 2H), 3.48 (s, 2H), 3.50 (s, 2H), 4.12-4.25 (m, 8H), 6.88 (s, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.7 (4C), 13.9, 22.3, 33.4, 34.4, 34.7, 35.1, 57.47, 57.52, 61.6 (4C), 126.3, 128.0 (2C), 129.7, 132.4, 140.5, 169.9 (4C). Anal. Calcd for C₂₆H₃₆O₈: C, 65.53; H, 7.61. Found: C, 65.23; H, 7.57.

10b: ¹H NMR (500 MHz, CDCl₃) δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.207 (t, *J* = 7.3 Hz, 6H), 1.212 (t, *J* = 7.3 Hz, 6H), 1.36 (sextet, *J* = 7.8 Hz, 2H), 1.43-1.53 (m, 2H), 2.14 (s, 3H), 2.18 (s, 3H), 2.54 (t, *J* = 7.8 Hz, 2H), 3.34 (s, 2H), 3.40 (s, 2H), 4.12-4.25 (m, 8H), 6.80 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.7 (4C), 13.9, 14.4, 19.4, 22.7, 32.5, 32.9, 33.2, 33.6, 56.9, 57.5, 61.58 (2C), 61.59 (2C), 128.4, 128.8, 130.6, 131.1, 132.3, 138.1, 170.15 (2C), 170.16 (2C). HRMS: Calcd for C₂₈H₄₀O₈

(M⁺), 504.2723. Found: *m/z* 504.2711. Anal. Calcd for C₂₈H₄₀O₈: C, 66.65; H, 7.99. Found: C, 66.65; H, 8.01.

10c: ¹H NMR (400 MHz, CDCl₃) δ 1.10 (t, *J* = 7.5 Hz, 6H), 1.21 (t, *J* = 7.1 Hz, 12H), 2.17 (s, 6H), 2.66 (q, *J* = 7.5 Hz, 4H), 3.38 (s, 4H), 4.14-4.23 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 13.7 (4C), 14.7 (2C), 14.9 (2C), 22.8 (2C), 33.3 (2C), 57.2 (2C), 61.5 (4C), 128.7 (2C), 130.6 (2C), 137.6 (2C), 170.2 (4C). Anal. Calcd for C₂₈H₄₀O₈: C, 66.65; H, 7.99. Found: C, 66.44.; H, 7.94.

10d: ¹H NMR (500 Hz, CDCl₃) δ 0.95 (t, *J* = 7.3 Hz, 6H), 1.20 (t, *J* = 7.3 Hz, 6H), 1.21 (t, *J* = 7.3 Hz, 6H), 1.36-1.56 (m, 6H), 1.61 (quintet, *J* = 7.3 Hz, 2H), 2.15 (s, 3H), 2.35 (s, 3H), 2.48 (t, *J* = 6.9 Hz, 2H), 2.83 (t, *J* = 7.3 Hz, 6H), 3.34 (s, 2H), 3.39 (s, 2H), 4.10-4.26 (m, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 13.6, 13.7 (4C), 14.0, 15.0, 17.5, 19.3, 22.0, 23.2, 31.1, 32.0, 32.1, 33.1, 33.5, 57.0, 57.4, 61.7 (4C), 79.2, 96.7, 121.8, 128.4, 130.5, 130.8, 134.8, 140.5, 170.09 (2C), 170.13 (2C). HRMS: Calcd for C₃₄H₄₈O₈ (M⁺), 584.3349. Found: *m/z* 584.3342.

12a⁵: ¹H NMR (500 MHz, CDCl₃) δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.37 (sextet, *J* = 7.3 Hz, 2H), 1.58 (quintet, *J* = 7.7 Hz, 2H), 2.18 (s, 3H), 2.56 (t, *J* = 7.8 Hz, 2H), 3.54 (s, 2H), 3.58 (s, 2H), 3.74 (s, 6H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 14.0, 15.3, 22.7, 32.87, 32.88, 40.0, 40.6, 52.8 (2C), 59.8, 121.1, 128.1, 131.5, 139.1, 139.5, 139.6, 172.3 (2C). Anal. Calcd for C₁₈H₂₄O₄: C, 71.03; H, 7.95. Found: C, 70.81; H, 7.95.

12b: ¹H NMR (500 MHz, CDCl₃) δ 0.88 (t, *J* = 7.3 Hz, 3H), 1.18-1.40 (m, 10H), 1.51 (quintet, *J* = 7.8 Hz, 2H), 2.19 (s, 3H), 2.55 (t, *J* = 7.8 Hz, 2H), 3.55 (s, 2H), 3.58 (s, 2H), 3.74 (s, 6H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 14.1, 15.3, 22.6, 29.2, 29.5, 29.7, 30.7, 31.8, 33.2, 40.0, 40.6, 52.9 (2C), 59.8, 121.1, 128.1, 131.5, 136.8, 139.1, 139.6, 172.3 (2C). Anal. Calcd for C₂₂H₃₂O₄: C, 73.30; H, 8.95. Found: C, 73.11; H, 9.00.

12c: ¹H NMR (500 MHz, CDCl₃) δ 1.54-1.80 (m, 4H), 2.07-2.21 (m, 4H), 2.16 (s, 3H), 3.54 (s, 2H), 3.60 (s, 2H), 3.75 (s, 6H), 5.48-5.52 (m, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 16.3, 22.2, 23.1, 25.3, 30.4, 40.0, 40.7, 52.9 (2C), 59.8, 120.9, 125.7, 127.4, 130.8, 137.5, 138.6, 139.1, 143.4, 172.3 (2C). Anal. Calcd for C₂₀H₂₄O₄: C, 73.15; H, 7.37. Found: C, 73.50; H, 7.38.

12d: ¹H NMR (500 Hz, CDCl₃) δ 1.56 (br, 1H), 1.79 (tt, *J* = 7.8, 6.4 Hz, 2H), 2.20 (s, 3H), 2.66 (t, *J* = 7.8 Hz, 2H), 3.54 (s, 2H), 3.58 (s, 2H), 3.67 (t, *J* = 6.4 Hz, 2H), 3.74 (s, 6H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 15.3, 29.2, 33.3, 39.9, 40.6, 52.9 (2C), 59.8, 62.3, 121.2, 128.1, 131.6, 137.1, 138.5, 139.2, 172.2 (2C). Anal. Calcd for C₁₇H₂₂O₅: C, 66.65; H, 7.24. Found: C, 66.83; H, 7.19.

12e: ¹H NMR (500 MHz, CDCl₃) δ 0.30 (s, 9H), 2.35 (s, 3H), 3.55 (s, 2H), 3.62 (s, 2H), 3.74 (s, 6H), 7.02 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 0.07 (3C), 19.5, 39.8, 40.8, 52.9 (2C), 59.4, 120.9, 133.5, 136.6, 138.9, 139.2, 140.8, 172.2 (2C). Anal. Calcd for C₁₇H₂₄O₄Si: C, 63.72; H, 7.55. Found: C, 63.55; H, 7.52.

12f: ^1H NMR (500 MHz, CDCl_3) δ 0.88-1.00 (m, 6H), 1.22-1.61 (m, 8H), 2.48-2.61 (m, 4H), 3.55 (s, 2H), 3.57 (s, 2H), 3.74 (s, 6H), 6.94 (d, $J = 7.3$ Hz, 1H), 6.98 (d, $J = 7.3$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.91, 13.94, 22.8, 23.1, 29.7, 32.0, 32.3, 34.0, 39.5, 40.5, 52.8 (2C), 60.2, 121.3, 128.4, 136.5, 137.1, 138.8, 139.1, 172.2 (2C). Anal. Calcd for $\text{C}_{21}\text{H}_{30}\text{O}_4$: 72.80; H, 8.73. Found: C, 73.00; H, 8.77.

13a⁵: ^1H NMR (500 MHz, CDCl_3) δ 0.92 (t, $J = 7.3$ Hz, 3H), 1.35 (sextet, $J = 7.3$ Hz, 2H), 1.55 (quintet, $J = 7.8$ Hz, 2H), 2.23 (s, 3H), 2.52 (t, $J = 7.8$ Hz, 2H), 3.48 (s, 2H), 3.58 (s, 2H), 3.72 (s, 6H), 6.8 (s, 1H), 6.84 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.9, 18.9, 22.4, 33.9, 35.4, 39.1, 40.6, 52.9 (2C), 59.9, 121.4, 128.1, 133.3, 135.9, 139.6, 142.1, 172.1 (2C). Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{O}_4$: C, 71.03; H, 7.95. Found: C, 70.83; H, 7.92.

13b: ^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.18-1.39 (m, 10H), 1.56 (quintet, $J = 7.8$ Hz, 2H), 2.22 (s, 3H), 2.51 (t, $J = 7.8$ Hz, 2H), 3.49 (s, 2H), 3.58 (s, 2H), 3.74 (s, 6H), 6.80 (s, 1H), 6.84 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.1, 18.9, 22.6, 29.2, 29.4, 29.5, 31.7, 31.9, 35.8, 39.1, 40.7, 52.9 (2C), 59.9, 121.4, 128.1, 133.3, 135.9, 139.6, 142.2, 172.3 (2C). Anal. Calcd for $\text{C}_{22}\text{H}_{32}\text{O}_4$: C, 73.30; H, 8.95. Found: C, 73.38; H, 8.94.

13c: ^1H NMR (500 MHz, CDCl_3) δ 1.60-1.79 (m, 4H), 2.10-2.21 (m, 2H), 2.24 (s, 3H), 2.32-2.39 (m, 2H), 3.51 (s, 2H), 3.59 (s, 2H), 3.74 (s, 6H), 6.00-6.06 (m, 1H), 7.00 (s, 1H), 7.03 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 19.0, 22.1, 23.0, 25.8, 27.6, 39.2, 40.7, 52.9 (2C), 59.9, 118.1, 124.2, 124.9, 133.2, 136.6, 137.0, 139.4, 142.3, 172.2 (2C). Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_4$: C, 73.15; H, 7.37. Found: C, 73.50; H, 7.38.

13d: ^1H NMR (500 Hz, CDCl_3) δ 1.64 (br, 1H), 1.77 (tt, $J = 7.8, 6.4$ Hz, 2H), 2.15 (s, 3H), 2.55 (t, $J = 7.8$ Hz, 2H), 3.42 (s, 2H), 3.50 (s, 2H), 3.58 (t, $J = 6.4$ Hz, 2H), 3.67 (s, 6H), 6.75 (s, 1H), 6.79 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 18.9, 31.8, 34.3, 39.1, 40.6, 52.9 (2C), 59.8, 62.1, 121.4, 128.1, 133.5, 136.2, 139.7, 141.0, 172.3 (2C). Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{O}_5$: C, 66.65; H, 7.24. Found: C, 66.30; H, 7.28.

13e: ^1H NMR (500 MHz, CDCl_3) δ 0.23 (s, 9H), 2.26 (s, 3H), 3.54 (s, 2H), 3.62 (s, 2H), 3.75 (s, 6H), 7.12 (s, 1H), 7.18 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ -1.01 (3C), 18.9, 39.5, 40.7, 52.9 (2C), 59.6, 126.3, 132.8, 133.0, 139.0, 139.2, 139.6, 172.2 (2C). Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4\text{Si}$: C, 63.72; H, 7.55. Found: C, 64.04; H, 7.58.

13f: ^1H NMR (500 MHz, CDCl_3) δ 0.92 (t, $J = 7.3$ Hz, 3H), 0.93 (t, $J = 7.3$ Hz, 3H), 1.26-1.43 (m, 4H), 1.48-1.62 (m, 4H), 2.52 (t, $J = 7.8$ Hz, 2H), 2.53 (t, $J = 7.8$ Hz, 2H), 3.51 (s, 2H), 3.57 (s, 2H), 3.74 (s, 6H), 6.79 (s, 1H), 6.84 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.89, 13.91, 22.4, 22.6, 32.3, 33.1, 33.8, 35.5, 38.9, 40.6, 52.8 (2C), 60.1, 121.5, 127.2, 135.4, 138.2, 139.7, 142.0, 172.2 (2C). Anal. Calcd for $\text{C}_{21}\text{H}_{30}\text{O}_4$: C, 72.80; H, 8.73; O, 18.47. Found: C, 73.12; H, 8.78.

15: ^1H NMR (400 MHz, CDCl_3) δ 1.68 (s, 6H), 2.84-2.85 (m, 2H), 2.90 (d, 2H, $J = 16.4$ Hz), 3.04 (d, 2H, $J = 16.4$ Hz), 3.42-3.46 (m, 2H), 3.73 (s, 6H), 4.23-4.27 (m, 2H); ^{13}C NMR (100 MHz,

CDCl₃) δ 18.1 (2C), 37.5 (2C), 44.6 (2C), 52.8 (2C), 58.4, 75.4 (2C), 122.0 (2C), 129.1 (2C), 172.1 (2C). Anal. Calcd for C₁₇H₂₂O₅: C, 66.65; H, 7.24. Found: C, 66.69; H, 7.26.

16a: ¹H NMR (500 MHz, CDCl₃) δ 1.78 (t, J = 2.8 Hz, 3H), 2.12 (s, 3H), 2.18 (s, 3H), 2.20 (s, 3H), 2.70 (d, J = 2.8 Hz, 2H), 3.51 (s, 2H), 3.55 (s, 2H), 3.57 (s, 6H), 3.60 (s, 2H), 3.74 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 3.5, 16.8, 17.0, 17.1, 25.0, 31.4, 40.4, 40.6, 52.3 (2C), 52.8 (2C), 58.9, 59.1, 74.5, 78.8, 129.6, 131.1, 132.4, 135.7, 136.1, 137.0, 171.1 (2C), 172.4 (2C). HRMS: Calcd for C₂₆H₃₂O₈ (M⁺), 472.2097. Found: m/z 472.2104.

18: ¹H NMR (400 MHz, CDCl₃) δ 2.18 (s, 3H), 2.19 (s, 3H), 2.22 (br, 1H), 2.82 (t, J = 7.1 Hz, 2H), 3.51 (s, 2H), 3.55 (s, 2H), 3.73 (t, J = 7.1 Hz, 2H), 3.75 (s, 6H), 6.82 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 15.0, 18.4, 36.0, 39.4, 40.0, 52.8 (2C), 59.3, 62.6, 129.1, 129.7, 130.4, 135.1, 136.4, 139.0, 172.2 (2C). Anal. Calcd for C₁₇H₂₂O₅: C, 66.65; H, 7.24. Found: C, 66.48; H, 7.24.

20: ¹H NMR (400 MHz, CDCl₃) δ 2.21 (s, 6H), 3.54 (s, 4H), 3.75 (s, 6H), 6.89 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 18.6 (2C), 39.7 (2C), 52.9 (2C), 59.4, 128.0 (2C), 130.8 (2C), 138.3 (2C), 172.3 (2C). Anal. Calcd for C₁₅H₁₈O₄: C, 68.68; H, 6.92. Found: C, 68.71; H, 7.03.

21: ¹H NMR (500 MHz, CDCl₃) δ 0.96 (t, J = 7.3 Hz, 3H), 1.48 (sextet, J = 7.3 Hz, 2H), 1.74 (tt, J = 7.3, 6.4 Hz, 2H), 2.08 (s, 3H), 2.19 (s, 3H), 3.46 (s, 2H), 3.52 (s, 2H), 3.74 (s, 6H), 3.89 (t, J = 6.4 Hz, 2H), 6.49 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 12.0, 13.8, 19.0, 19.3, 31.5, 39.0, 39.8, 52.8 (2C), 59.7, 68.2, 111.6, 119.5, 129.9, 130.8, 139.7, 156.5, 172.4 (2C). Anal. Calcd for C₁₉H₂₆O₅: C, 68.24; H, 7.84. Found: C, 68.25; H, 7.90.

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3a

3e

3l

3t

3w

3x

4a

4b

6p

8a

10b

10d

S21

16a