Supporting Information

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Iridium-Catalyzed Arylative Cyclization of Alkynones by 1,4-Iridium Migration**

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1. General Information

All air-sensitive reactions were carried out under a nitrogen atmosphere using oven-dried apparatus. Anhydrous toluene and MeCN were dried and purified by passage through activated alumina columns using a solvent purification system. Xylenes were degassed by freeze-pump-thaw and stored in a Young’s flask under nitrogen prior to use. All commercially available reagents were used as received unless otherwise stated. Arylboronic acids were used as received unless the sample contained >10% boroxine as determined by \(^1\)H NMR analysis. In this case, the boronic acid was stirred in a mixture of Et\(_2\)O and water for 30 minutes. The organic phase was separated, dried (Na\(_2\)SO\(_4\)), filtered, and concentrated in vacuo to give the corresponding boronic acid which was used without further purification. All petroleum ether used was 40-60 °C petroleum ether.

Thin layer chromatography (TLC) was performed on Merck DF-Alufoilien 60F\(_{254}\) 0.2 mm precoated plates. Compounds were visualized by exposure to UV light or by dipping the plates into solutions of potassium permanganate or vanillin followed by heating. Flash column chromatography was carried out using silica gel (Fisher Scientific 60Å particle size 35-70 micron). Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. The solvent of recrystallization is reported in parentheses. Infra-red spectra were recorded on either a Shimadzu IRAffinity-1 or a Nicolet Avatar 360 FT instrument on the neat compound. NMR spectra were acquired on either a Bruker AVA500 or a Bruker AVA400 spectrometer. \(^1\)H and \(^13\)C NMR spectra were referenced to external tetramethylsilane via the residual protonated solvent (\(^1\)H) or the solvent itself (\(^13\)C). All chemical shifts are reported in parts per million (ppm). For CDCl\(_3\), the shifts are referenced to 7.27 ppm for \(^1\)H NMR spectroscopy and 77.0 ppm for \(^13\)C NMR spectroscopy. For D\(_6\)-DMSO, the shifts are referenced to 2.50 ppm for \(^1\)H NMR spectroscopy and 39.52 ppm for \(^13\)C NMR spectroscopy. High-resolution mass spectra were recorded using electrospray ionization (ESI) or electron impact (EI) techniques at the EPSRC National Mass Spectrometry Facility, at the School of Chemistry, University of Edinburgh, or at the School of Chemistry, University of Nottingham. X-ray diffraction data were collected at 120 K on either an Agilent SuperNova diffractometer using Mo K\(\alpha\) radiation at 0.71 Å or on an Agilent GV1000 using CuK\(\alpha\) radiation, and refined in SHELXTL. Optical rotations were performed on a Bellingham and Stanley ADP 400 polarimeter. Chiral HPLC analysis was performed on an Agilent Technologies 1260 Infinity instrument using a CHIRALPAK® IA-3 column (4.6 × 250 mm).
2. Synthesis of Substrates

2-Methyl-2-(3-phenylprop-2-yn-1-yl)cyclopentane-1,3-dione (1a)

2-Methyl-2-propargyl-1,3-cyclopentanedione (1g)\(^1\) (1.50 g, 10.0 mmol) was added to a solution of Pd(PPh\(_3\))\(_2\)Cl\(_2\) (140 mg, 0.199 mmol), CuI (106 mg, 0.557 mmol), and Et\(_3\)N (2.4 mL, 17.2 mmol) in anhydrous DMSO (20 mL). Bromobenzene (1.08 mL, 10.3 mmol) was added and the mixture was stirred at 90 °C for 2 h. The reaction was cooled to room temperature, water (50 mL) was added, and the mixture was extracted with Et\(_2\)O (50 mL). The combined organic phases were washed with 10% aqueous HCl (3 × 20 mL), dried (Na\(_2\)SO\(_4\)), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (10% EtOAc/hexane) to give alkynone 1a (1.90 g, 84%) as a pale yellow solid. \(R_f = 0.35\) (30% EtOAc/hexane); m.p. 64–65 °C (Et\(_2\)O/hexane); IR \(2970, 1721\) (C=O), 1412, 1065, 760 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.37–7.27\) (5H, m, ArH), 2.90–2.80 (4H, m, CH\(_2\)CH\(_2\)), 2.70 (2H, s, CH\(_2\)C≡C), 1.19 (3H, s, CH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 215.6, 131.6, 128.3, 122.5, 83.9, 82.9, 55.5\) (C), 36.0 (2 × CH\(_2\)), 25.9 (CH\(_2\)), 18.9 (CH\(_3\)); HRMS (ESI) Exact mass calcd for C\(_{15}\)H\(_{18}\)NO\(_2\) [M+NH\(_4\)]\(^+\): 244.1338, found: 244.1332.

Preparted according to: P. T. Lansbury, A. K. Serelis, J. E. Hengeveld, D. G. Hangauer Jr, Tetrahedron 1980, 36, 2701-2710.

2-Methyl-2-propargyl-1,3-cyclopentanedione (1g)\(^1\) (1.50 g, 10.0 mmol) was added to a solution of Pd(PPh\(_3\))\(_2\)Cl\(_2\) (140 mg, 0.199 mmol), CuI (106 mg, 0.557 mmol), and Et\(_3\)N (2.4 mL, 17.2 mmol) in anhydrous DMSO (20 mL). 4-Bromoanisole (1.72 mL, 13.7 mmol) was added and the mixture was stirred at 90 °C for 2 h. The reaction was cooled to room temperature, water (50 mL) was added, and the mixture was extracted with Et\(_2\)O (50 mL). The organic layer was washed with 10% aqueous HCl (3 × 20 mL), dried (Na\(_2\)SO\(_4\)), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (10% EtOAc/hexane) to give alkynone 1b (1.82 g, 71%) as a brown solid. \(R_f = 0.33\) (30% EtOAc/hexane); m.p. 80-85 °C (hexane); IR 2965, 1722 (C=O), 1508, 1242, 1032,
Supporting Information

833 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.26 (2H, d, \(J = 8.9\) Hz, ArH), 6.80 (2H, d, \(J = 8.9\) Hz, ArH), 3.80 (3H, s, OCH\(_3\)); \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 215.8 (2 × C), 159.6 (C), 133.0 (2 × CH), 114.6 (C), 113.9 (2 × CH), 82.7 (C), 82.4 (C), 55.5 (C), 55.3 (CH\(_3\)), 36.0 (2 × CH\(_2\)), 26.2 (CH\(_3\)), 18.8 (CH\(_3\)); HRMS (ESI) Exact mass calcd for C\(_{16}\)H\(_{17}\)O\(_3\) [M+H]\(^+\): 257.1178, found: 257.1173.

2-[3-(4-Chlorophenyl)-2-propynyl]-2-methylcyclopentane-1,3-dione (1c)

Et\(_3\)N (21 mL) was added to a flask containing 2-methyl-2-propargyl-1,3-cyclopentanedione (1g)\(^1\) (594 mg, 3.96 mmol), 1-bromo-4-chlorobenzene (1.14 g, 5.94 mmol), PPh\(_3\) (41.7 mg, 0.159 mmol), Pd(OAc)_2 (17.8 mg, 0.080 mmol), and CuI (30.2 mg, 0.159 mmol) and the mixture was stirred at 50 °C for 21 h. The reaction was cooled to room temperature, water (20 mL) and saturated aqueous NH\(_4\)Cl (5 ml) were added, and the mixture was extracted with EtOAc (3 × 25 mL). The combined organic phases were washed with brine (40 mL), dried (MgSO\(_4\)), filtered, and concentrated \textit{in vacuo}. The mixture was purified by column chromatography (30% EtOAc/hexane) to give alkyne 1c (382 mg, 37%) as a pale yellow solid. \(R_f = 0.39\) (30% EtOAc/hexane); m.p. 85-90 °C (hexane); IR 2968, 1719 (C=O), 1491, 1412, 1094, 835 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.25 (4H, s, ArH), 2.90-2.77 (4H, m, CH\(_2\)CH\(_2\)), 2.69 (2H, s, CH\(_3\)C=), 1.19 (3H, s, CH\(_3\)); \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 215.3 (2 × C), 134.4 (C), 132.8 (2 × CH), 128.6 (2 × CH), 121.0 (C), 85.1 (C), 81.8 (C), 55.4 (C), 35.9 (2 × CH\(_2\)), 25.6 (CH\(_2\)), 19.1 (CH\(_3\)); HRMS (ESI) Exact mass calcd for C\(_{15}\)H\(_{14}\)ClO\(_2\) [M+H]\(^+\): 261.0676, found: 261.0677.

2-Methyl-2-[3-(4-nitrophenyl)prop-2-yn-1-yl]cyclopentane-1,3-dione (1d)

Prepared according to a previously reported procedure.\(^2\)

2. J. D. Dooley, S. Reddy Chidipudi, H. W. Lam, \textit{J. Am. Chem. Soc.} \textbf{2013}, \textit{135}, 10829-10836.
2-Methyl-2-[3-(methylphenyl)prop-2-yn-1-yl]cyclopentane-1,3-dione (1e)

2-Methyl-2-propargyl-1,3-cyclopentanedione (1g)\(^1\) (1.50 g, 10.0 mmol) was added to a solution of \(\text{Pd(OAc)}_2\) (56 mg, 0.25 mmol), \(\text{PPh}_3\) (262 mg, 1.00 mmol), CuI (106 mg, 0.557 mmol), and Et\(_3\)N (2.4 mL, 17.2 mmol) in anhydrous DMSO (20 mL). A solution of 3-bromotoluene (1.33 mL, 11.0 mmol) in anhydrous DMSO (10 mL) was added and the mixture was stirred at 90 °C for 2 h. The reaction was cooled to room temperature, water (50 mL) was added, and the mixture was extracted with Et\(_2\)O (50 mL). The organic phase was washed with 10% aqueous HCl (3 × 20 mL), dried (Na\(_2\)SO\(_4\)), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (10% EtOAc/hexane) to give alkynone 1e (2.10 g, 88%) as a brown oil. \(R_f = 0.48\) (30% EtOAc/hexane); IR 2924, 1724 (C=O), 1485, 1263, 1069, 758 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.14-7.09\) (4H, m, ArH), 2.92-2.77 (4H, m, CH\(_2\)CH\(_2\)), 2.69 (2H, s, CH\(_2\)C=C), 2.31 (3H, s, ArCH\(_3\)), 1.18 (3H, s, O=CCCH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 215.6\) (2 × C), 138.0 (C), 132.1 (CH), 129.2 (CH), 128.6 (CH), 128.1 (CH), 122.3 (C), 83.5 (C), 83.0 (C), 55.4 (C), 35.9 (2 × CH\(_2\)), 26.0 (CH\(_2\)), 21.1 (CH\(_3\)), 18.8 (CH\(_3\)); HRMS (ESI) Exact mass calc for C\(_{16}\)H\(_{17}\)O\(_2\) [M+H]: 241.1229; found: 241.1224.

2-[3-(1-Methyl-2,5-dioxo-3-cyclopenten-1-yl)-1-propynyl]benzonitrile (1f)

Et\(_3\)N (26 mL) was added to a flask containing 2-methyl-2-propargyl-1,3-cyclopentanedione (1g)\(^1\) (790 mg, 5.28 mmol), 2-iodobenzonitrile (1.33 g, 5.81 mmol), Pd(PPh\(_3\))\(_2\)Cl\(_2\) (74.4 mg, 0.106 mmol), and CuI (20.1 mg, 0.106 mmol) and the mixture was stirred at 60 °C for 5 h. The reaction was cooled to room temperature, water (20 mL) and saturated aqueous NH\(_4\)Cl (5 ml) were added, and the mixture was extracted with EtOAc (3 × 25 mL). The combined organic phases were washed with brine (40 mL), dried (MgSO\(_4\)), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (30% → 40% EtOAc, 70% → 60% hexane) to give alkynone 1f (970 mg, 73%) as a pale yellow solid. \(R_f = 0.23\) (30% EtOAc/hexane); m.p. 100-105 °C (hexane); IR 2974, 2224 (C=N), 1717 (C=O), 1485, 1263, 1069, 758 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.62-7.57\) (1H, m, ArH), 7.50 (1H, td, \(J = 7.7, 1.3\) Hz, ArH), 7.47-7.43 (1H, m, ArH), 7.37 (1H, td, \(J = 7.6, 1.3\) Hz, ArH), 3.07-2.83 (4H, m, CH\(_2\)CH\(_2\)), 2.81 (2H, s, CH\(_2\)C=C), 1.22 (3H, s, CH\(_3\)); \(^{13}\)C NMR
(126 MHz, CDCl₃) δ 215.1 (2 × C), 132.5 (CH), 132.5 (CH), 132.3 (CH), 128.3 (CH), 126.6 (C), 117.4 (C), 115.0 (C), 91.5 (C), 78.8 (C), 55.6 (C), 35.7 (2 × CH₂), 24.5 (CH₂), 20.2 (CH₃); HRMS (ESI) Exact mass calcd for C₁₁₆H₁₄NO₂ [M+H⁺]: 252.1019, found: 252.1007.

2-Methyl-2-(2-propynyl)-1,3-indandione (S1)

Dimethyl phthalate (4.9 mL, 30 mmol) was added to a two-necked flask under nitrogen containing NaH (60% in mineral oil, 1.56 g, 39.0 mmol) in anhydrous toluene (90 mL). Methyl propionate (3.7 mL, 39 mmol) was added and the mixture was heated at reflux for 2 h. The mixture was cooled to room temperature, NaH (60% in mineral oil, 1.56 g, 39.0 mmol) was added, and the mixture was heated at reflux at 4 days. The mixture was cooled to room temperature and H₂O (10 ml) was added carefully under nitrogen. The mixture was diluted with H₂O (200 mL), and the aqueous layer was separated and washed with hexanes (100 mL). The aqueous layer was acidified (pH 2) with conc. HCl. The mixture was extracted with CH₂Cl₂ (3 × 75 mL) and the combined organic phases were dried (MgSO₄), filtered, and concentrated in vacuo to a volume of ~100 mL. The mixture was cooled to 0 °C, and Et₃N (10.8 mL, 78.0 mmol) and propargyl bromide (80% solution in toluene, 8.2 mL, 78 mmol) were added. The mixture was stirred at room temperature for 20 h. Water (50 mL) and 2 M aqueous HCl (40 ml) were added, and the mixture was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic phases were dried (MgSO₄), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (20% EtOAc/hexane) followed by recrystallization from hexane to give alkyne S1 as a pale yellow solid (948 mg, 16%). Rᵢ = 0.18 (20% EtOAc/hexane); m.p. 87-88 °C (hexane); IR 3256 (C≡C-H), 2972, 1705 (C=O), 1595, 1258, 694 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.05-8.00 (2H, m, Ar-H), 7.91-7.86 (2H, m, Ar-H), 2.69 (2H, d, J = 2.7 Hz, CH₂), 1.76 (1H, t, J = 2.7 Hz, =CH), 1.32 (3H, s, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 202.5 (2 × C), 141.4 (2 × C), 135.9 (2 × CH), 123.5 (2 × CH), 78.6 (C), 71.1 (CH), 52.7 (C), 23.9 (CH₂), 19.1 (CH₃); HRMS (ESI) Exact mass calcd for C₁₃H₁₂O₂ [M+H⁺]: 199.0754, found: 199.0743.
2-Methyl-2-(3-phenyl-2-propynyl)-1,3-indandione (1i)

Et₃N (10 mL) was added to a flask containing alkyne S1 (401 mg, 2.02 mmol), iodobenzene (0.27 mL, 2.4 mmol), Pd(PPh₃)₂Cl₂ (28.4 mg, 0.0405 mmol), and CuI (7.7 mg, 0.040 mmol) and the mixture was stirred at 60 °C for 6 h. The reaction was cooled to room temperature, water (20 mL) and saturated aqueous NH₄Cl (5 ml) were added, and the mixture was extracted with EtOAc (3 × 25 mL). The combined organic phases were washed with brine (40 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (20% EtOAc/hexane) to give alkyne 1i (402 mg, 72%) as an orange solid. R_f = 0.22 (20% EtOAc/hexane); m.p. 76-78 °C (Et₂O/petroleum ether); IR 2907, 1711 (C=O), 1593, 1275, 922, 766, 694 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.07-8.01 (2H, m, ArH), 7.91-7.85 (2H, m, ArH), 7.19-7.15 (1H, m, ArH), 7.14-7.09 (2H, m, ArH), 6.92-6.88 (2H, m, ArH), 2.90 (2H, s, CH₂), 1.37 (3H, s, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 202.9 (2 × C), 141.7 (2 × C), 135.8 (2 × CH), 131.3 (2 × CH), 127.9 (2 × CH), 127.8 (CH), 123.4 (2 × CH), 122.7 (C), 84.3 (C), 83.7 (C), 53.2 (C), 25.6 (CH₂), 18.6 (CH₃); HRMS (ESI) Exact mass calcd for C₁₉H₁₅O₂ [M+H]+: 275.1067, found: 275.1059.

2-Phenyl-2-(2-propynyl)-1,3-indandione (S2)

2 M aqueous NaOH (1.1 mL, 2.2 mmol) was added to a slurry of 2-phenyl-1,3-indandione (500 mg, 2.25 mmol) in water (5 mL). When all of the solid had dissolved, forming a bright red solution, propargyl bromide (80% solution in toluene, 0.40 mL, 3.6 mmol) was added. The mixture was stirred at 80 °C for 60 h. The mixture was cooled to room temperature, EtOAc (10 mL) was added, and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were dried (MgSO₄), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (20% EtOAc/petroleum ether) to give alkyne S2 (543 mg, 93%) as a white solid. R_f = 0.33 (20% EtOAc/petroleum ether); m.p. 136-138 °C (MeOH); IR 3289 (C≡CH), 1706 (C=O), 1592, 1252, 783 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.10-8.05 (2H, m, ArH), 7.92-7.86 (2H, m, ArH), 7.43-7.38 (2H, m, ArH), 7.35-7.25 (3H, m, ArH), 3.15 (2H, d, J = 2.6 Hz, CH₂), 1.77 (1H, t, J = 2.6 Hz, ≡CH); ¹³C NMR (101 MHz, CDCl₃) δ 199.8 (C), 142.2 (C), 136.0 (2 × CH), 135.4 (C), 129.0 (2 × CH), 128.2 (CH), 126.7 (2 × CH), 123.7 (2 × CH), 78.8 (C), 70.9 (CH), 60.9 (C), 24.6 (CH₂);
HRMS (ESI) Exact mass calcd for C\textsubscript{18}H\textsubscript{12}NaO\textsubscript{2} [M+Na]\textsuperscript{+}: 283.0730, found: 283.0730.

2-Phenyl-2-(3-phenyl-2-propynyl)-1,3-indandione (1j)

![Chemical Structure](image)

Et\textsubscript{3}N (5 mL) was added to a flask containing (MeCN)\textsubscript{2}PdCl\textsubscript{2} (6.0 mg, 0.023 mmol), PPh\textsubscript{3} (12.1 mg, 0.0461 mmol), and CuI (4.4 mg, 0.023 mmol). The mixture was stirred at room temperature for 5 min, alkyne S\textsubscript{2} (300 mg, 1.15 mmol) and iodobenzene (0.15 mL, 1.3 mmol) were added, and the mixture was stirred at 60 °C for 3 h. The reaction was cooled to room temperature, water (10 mL) and saturated aqueous NH\textsubscript{4}Cl (5 mL) were added, and the mixture was extracted with EtOAc (3 × 15 mL). The combined organic phases were washed with brine (20 mL), dried (MgSO\textsubscript{4}), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (20% EtOAc/hexane) to give alkynone 1j (232 mg, 60%) as an orange solid. \(R_f = 0.36\) (20% EtOAc/petroleum ether); m.p. 110-112 °C (MeOH); IR 1710 (C=O), 1593, 1489, 1440, 1264 cm\textsuperscript{-1}; \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) 8.12-8.06 (2H, m, ArH), 7.91-7.85 (2H, m, ArH), 7.49-7.45 (2H, m, ArH), 7.38-7.27 (3H, m, ArH), 7.20-7.09 (3H, m, ArH), 7.17-7.12 (2H, m, ArH), 3.38 (2H, s, CH\textsubscript{2}); \(^13\)C NMR (101 MHz, CDCl\textsubscript{3}) 200.3 (2 × C), 142.3 (2 × C), 136.0 (2 × CH), 135.5 (C), 131.3 (2 × CH), 128.9 (2 × CH), 128.1 (CH), 127.9 (2 × CH), 127.9 (CH), 126.8 (2 × CH), 123.6 (2 × CH), 122.6 (C), 84.4 (C), 83.5 (C), 61.0 (C), 25.9 (CH\textsubscript{2}); HRMS (ESI) Exact mass calcd for C\textsubscript{24}H\textsubscript{16}NaO\textsubscript{2} [M+Na]\textsuperscript{+}: 359.1043, found: 359.1041.

2-Methyl-2-(3-phenylprop-2-yn-1-yl)cyclohexane-1,3-dione (1k)

![Chemical Structure](image)

2-Methyl-2-(1-propyn-3-yl)cyclohexane-1,3-dione (S\textsubscript{3})\textsuperscript{3} (1.48 g, 9.01 mmol) was added to a solution of Pd(OAc)\textsubscript{2} (40.4 mg, 0.180 mmol), PPh\textsubscript{3} (189 mg, 0.721 mmol), CuI (68.6 mg, 0.360 mmol), and Et\textsubscript{3}N (1.38 mL, 9.90 mmol) in anhydrous DMSO (20 mL). A solution of 3-bromobenzene (1.41 mL, 13.5 mmol) in anhydrous DMSO (10 mL) was added and the mixture was stirred at 90 °C for 2 h. The reaction was cooled to room temperature, water (50 mL) was added, and the mixture was extracted with Et\textsubscript{2}O (50 mL). The organic phase was washed with 10% aqueous HCl (3 × 20 mL), dried (Na\textsubscript{2}SO\textsubscript{4}), filtered, and concentrated in vacuo. The mixture was

\textsuperscript{3} Prepared according to: K. Kato, C. Matsuba, T. Kusakabe, H. Takayama, S. Yamamura, T. Mochida, H. Akita, T. y. A. Peganova, N. V. Vologdin, O. V. Gusev, \textit{Tetrahedron} 2006, 62, 9988-9999.
purified by column chromatography (10% EtOAc/hexane) to give alkynone 1k (1.63 g, 75%) as a pale yellow solid. \( R_f = 0.33 \) (30% EtOAc/hexane); m.p. 60-65 °C (hexane); IR 2967, 1694 (C=O), 1410, 1315, 1022, 766 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.35-7.33 (2H, m, ArH), 7.28-7.26 (3H, m, ArH), 2.87 (2H, s, CH\(_2\)C=C), 2.73 (4H, td, \( J = 7.2, 2.1 \) Hz, CH\(_2\)CH\(_2\)CH\(_2\)), 2.01 (2H, qd, \( J = 7.2, 2.1 \) Hz, CH\(_2\)CH\(_2\)CH\(_2\)), 1.36 (3H, s, CH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 209.3 (2 \times C), 131.6 (2 \times CH), 128.2 (2 \times CH), 128.0 (CH), 123.1 (C), 85.6 (C), 83.0 (C), 64.0 (C), 38.5 (2 \times CH\(_2\)), 26.4 (CH\(_3\)), 17.3 (CH\(_3\)); HRMS (ESI) Exact mass calcd for C\(_{16}\)H\(_{17}\)O\(_2\) [M+H]\(^+\): 241.1223, found: 241.1211.

2-[3-(4-Methoxyphenyl)prop-2-yn-1-yl]-2-methylcyclopentene-1,3-dione (II)

\[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{S3} \\
\text{Me} \\
\end{array}
\xrightarrow{\text{Pd(OAc)\(_2\)} (2.5 mol%), CuI (5.6 mol%), PPh\(_3\) (10 mol%) \text{DMSO, 50 °C, 21 h}}
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{O} \\
\text{11} \\
\end{array}
\]

2-Methyl-2-(1-propyn-3-yl)cyclohexane-1,3-dione (S3)\(^3\) (1.64 g, 10.0 mmol) was added to a solution of Pd(OAc)\(_2\) (56 mg, 0.25 mmol), PPh\(_3\) (262 mg, 1.00 mmol), CuI (106 mg, 0.557 mmol), and Et\(_3\)N (2.4 mL, 17.2 mmol) in anhydrous DMSO (20 mL). A solution of 4-bromoanisole (1.72 mL, 13.7 mmol) in anhydrous DMSO (10 mL) was added and the mixture was stirred at 90 °C for 2 h. The reaction was cooled to room temperature, water (50 mL) was added, and the mixture was extracted with Et\(_2\)O (50 mL). The organic phase was washed with 10% aqueous HCl (3 \times 20 mL), dried (Na\(_2\)SO\(_4\)), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (10% EtOAc/hexane) to give alkynone II (2.21 g, 82%) as a pale yellow solid. \( R_f = 0.28 \) (30% EtOAc/hexane); m.p. 70-75 °C (hexane); IR 2965, 1721 (C=O), 1508, 1244, 1032, 841 cm\(^{-1}\); 7.30-7.24 (2H, m, ArH), 6.82-6.76 (2H, m, ArH), 3.79 (3H, s, OCH\(_3\)), 2.84 (2H, s, CH\(_2\)C=C), 2.73 (4H, t, \( J = 3.8 \) Hz, CH\(_2\)CH\(_2\)CH\(_2\)), 2.08-1.92 (2H, m, CH\(_2\)CH\(_2\)CH\(_2\)), 1.34 (3H, s, CCH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 209.4 (2 \times C), 159.4 (C), 133.0 (2 \times CH), 115.2 (C), 113.8 (2 \times CH), 83.9 (C), 82.9 (C), 64.0 (C), 55.3 (CH\(_3\)), 38.6 (2 \times CH\(_2\)), 26.8 (CH\(_2\)), 21.5 (CH\(_3\)), 17.3 (CH\(_3\)); HRMS (ESI) Exact mass calcd for C\(_{17}\)H\(_{19}\)O\(_3\) [M+H]\(^+\): 271.1334, found: 271.1329.

2-[3-(4-Chlorophenyl)prop-2-yn-1-yl]-2-methylcyclopentene-1,3-dione (1m)

\[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{S3} \\
\text{Me} \\
\end{array}
\xrightarrow{\text{Pd(OAc)\(_2\)} (2 mol%), CuI (4 mol%), PPh\(_3\) (10 mol%) \text{DMSO, 50 °C, 21 h}}
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{Cl} \\
\text{1m} \\
\end{array}
\]

Et\(_3\)N (21 mL) was added to a flask containing 2-methyl-2-(1-propyn-3-yl)cyclohexane-1,3-dione (S3)\(^3\) (650 mg, 3.96 mmol), 4-bromochlorobenzene (1.14 g, 5.94 mmol), PPh\(_3\) (41.7 mg, 0.159),
Pd(OAc)$_2$ (17.8 mg, 0.0793 mmol), and CuI (30.2 mg, 0.159 mmol), and the mixture was stirred at 50 °C for 21 h. The reaction was cooled to room temperature, water (20 mL) and saturated aqueous NH$_4$Cl (5 ml) were added, and the mixture was extracted with EtOAc (3 × 25 mL). The combined organic phases were washed with brine (40 mL), dried (MgSO$_4$), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (25% EtOAc/hexane) to give alkyne 1m (512 mg, 63%) as a pale yellow solid. $R_f = 0.36$ (30% EtOAc/hexane); m.p. 80-85 °C (hexane); IR 2965, 1690 (C=O), 1489, 1317, 1088, 1022, 839 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.27-7.23 (4H, m, ArH), 2.86 (2H, s, CH$_2$C≡C), 2.79-2.67 (4H, m, CH$_2$CH$_2$CH$_2$), 2.05-1.97 (2H, m, CH$_2$CH$_2$CH$_2$), 1.37 (3H, s, CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 209.0 (2 × C), 134.0 (C), 132.8 (2 × CH), 128.5 (2 × CH), 121.6 (C), 86.8 (C), 81.7 (C), 64.1 (C), 38.3 (2 × CH$_2$), 25.9 (CH$_2$), 22.0 (CH$_3$), 17.3 (CH$_2$); HRMS (ESI) Exact mass calcd for C$_{16}$H$_{16}$ClO$_2$ [M+H]$^+$: 275.0839, found: 275.0836.

1-Methyl-3-methyl-3-(2-propynyl)-1,3-dihydroquinoline-2,4-dione (S5)

Propargyl bromide (80% solution in toluene, 858 µL, 7.70 mmol) was added to a solution of 1,3-dimethyl-1,2,3,4-tetrahydroquinoline-2,4-dione (S4)$^4$ (1.04 g, 5.50 mmol) and t-BuOK (678 mg, 6.04 mmol) in DMSO (50 mL). The mixture was stirred at room temperature for 16 h, diluted with water (50 mL), and extracted with EtOAc (3 × 25 mL). The combined organic phases were dried (Na$_2$SO$_4$), filtered and concentrated in vacuo. The mixture was purified by column chromatography (20% EtOAc/hexane) to give alkyne S5 (650 mg, 52%) as a yellow oil. $R_f = 0.33$ (25% EtOAc/petroleum ether); IR 3272 (C≡C-H), 1698 (C=O), 1656 (C=O), 1375, 1102, 758 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.06-8.03 (1H, m, ArH), 7.68-7.63 (1H, m, ArH), 7.27-7.18 (2H, m, ArH), 3.51 (3H, s, NCH$_3$), 2.90 (2H, d, $J = 2.6$ Hz, CH$_2$), 1.84 (1H, t, $J = 2.6$ Hz, ≡CH), 1.47 (3H, s, CCH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 195.8 (C), 172.4 (C), 143.2 (CH), 136.2 (CH), 128.3 (CH), 123.2 (CH), 120.0 (C), 114.8 (CH), 80.0 (C), 70.3 (CH), 56.8 (C), 29.9 (CH$_3$), 26.2 (CH$_2$), 24.4 (CH$_3$); HRMS (ESI) Exact mass calcd for C$_{14}$H$_{14}$NO$_2$ [M+H]$^+$: 228.1025, found: 228.1026.

4. Prepared according to: Dittmer, D. C.; Li, Q.; Avilov, D. V. J. Org. Chem. 2005, 70, 4682–4686.
3-[3-(4-Chlorophenyl)-2-propynyl]-1-methyl-3-methyl-1,3-dihydroquinoline-2,4-dione (1n)

Alkyne S5 (1.02 g, 4.49 mmol) was added to a solution of Pd(PPh₃)₂Cl₂ (63.2 mg, 0.0900 mmol), CuI (34.3 mg, 0.180 mmol), and Et₃N (691 µL, 4.96 mmol) in anhydrous MeCN (15 mL) in a sealed tube. A solution of 4-chlorobromobenzene (1.29 g, 5.41 mmol) in anhydrous MeCN (5 mL) was added, the tube was sealed, and the mixture was stirred at 110 °C for 16 h. The reaction was cooled to room temperature, water (50 mL) was added, and the mixture was extracted with EtOAc (50 mL). The organic phase was washed with aqueous 10% HCl (3 × 20 mL), dried (Na₂SO₄), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (10% EtOAc/hexane) to give alkynone 1n (0.95 g, 63%) as a yellow solid. Rᶠ = 0.46 (25% EtOAc/petroleum ether); m.p. 96-98 °C (MeOH/hexane); IR 2943, 1687 (C=O), 1651 (C=O), 1472, 1375, 1088, 758 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.08 (1H, dd, J = 7.7, 1.5 Hz, ArH), 7.67-7.62 (1H, m, ArH), 7.23-7.18 (2H, m, ArH), 7.16-7.12 (2H, m, ArH), 7.00-6.96 (2H, m, ArH), 3.50 (3H, s, NCH₃), 3.08 (1H, d, J = 16.2 Hz, CH₂), 3.02 (1H, d, J = 16.2 Hz, CH₂), 1.55 (3H, s, CCH₃); ¹³C NMR (126 MHz, CDCl₃) δ 196.1 (C), 172.6 (C), 143.4 (C), 136.2 (CH), 133.8 (C), 132.7 (2 × CH), 128.3 (2 × CH), 128.2 (CH), 123.2 (CH), 121.5 (C), 120.4 (C), 114.8 (CH), 86.1 (C), 81.8 (C), 56.6 (C), 29.9 (CH₃), 29.0 (CH₂), 23.3 (CH₃); HRMS (ESI) Exact mass calcd for C₂₀H₁₇³⁵ClNO₂ [M+H]+: 338.0948, found: 338.0940.

Ethyl 2-oxo-1-(3-phenyl-2-propynyl)cyclopentanecarboxylate (8)

Et₃N (40 mL) was added to a flask containing (MeCN)₂PdCl₂ (41.5 mg, 0.160 mmol), PPh₃ (83.9 mg, 0.320 mmol), and CuI (30.5 mg, 0.160 mmol). The mixture was stirred at room temperature for 5 min, ethyl 2-oxo-1-(2-propynyl)cyclopentanecarboxylate (S6)⁵ (1.56 g, 8.03 mmol) and iodobenzene (1.1 mL, 9.8 mmol) were added, and the mixture was stirred at 60 °C for 8 h. The reaction was cooled to room temperature, water (50 mL) and saturated aqueous NH₄Cl (25 ml) were added, and the mixture was extracted with EtOAc (3 × 50 mL). The combined organic phases were washed with brine (75 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (20% EtOAc/hexane) to give alkynone 8 (1.74 g, 52% yield).

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⁵ Prepared according to: F. Barabé, G. v. Béthournay, G. Bellavance, L. Barriault, Org. Lett. 2009, 11, 4236-4238.
80%) as a yellow oil. $R_f = 0.23$ (10% EtOAc/petroleum ether); IR 2978, 1751 (C=O), 1726 (C=O), 1227, 1148, 1028 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.38-7.34 (2H, m, ArH), 7.31-7.27 (3H, m, ArH), 4.20 (2H, q, $J = 7.1$ Hz, OCH$_2$), 3.00-2.91 (2H, m, CH$_2$C≡C), 2.60-2.47 (2H, m, CH$_2$C=O and CH$_2$CH$_2$CH$_2$C=O), 2.43-2.28 (2H, m, CH$_2$C=O and CH$_2$CH$_2$CH$_2$C=O), 2.18-2.04 (2H, m, CH$_2$CH$_2$C=O), 1.27 (3H, t, $J = 7.1$ Hz, CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 213.9 (C), 170.5 (C), 131.6 (2 × CH), 128.2 (2 × CH), 128.0 (CH), 123.2 (C), 85.3 (C), 82.8 (C), 61.7 (CH$_2$), 59.1 (C), 38.4 (CH$_3$), 32.8 (CH$_2$), 24.2 (CH$_2$), 19.9 (CH$_2$), 14.1 (CH$_3$); HRMS (ESI) Exact mass calcd for C$_{17}$H$_{19}$O$_3$ [M+H]$^+$: 271.1329, found: 271.1321.
3. Rhodium-Catalyzed Arylative Cyclization of 1a

(±)-(3aR,9bR)-5-[(E)-Benzylidene]-9b-hydroxy-3a-methyl-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one (2a), 2-[(E)-2,3-diphenylprop-2-en-1-yl]-2-methylcyclopentane-1,3-dione (5), and (±)-5-(diphenylmethylidene)-7-methylcycloheptane-1,4-dione (6)

Alkynone 1a (90.5 mg, 0.400 mmol), phenylboronic acid (73.2 mg, 0.600 mmol), [Rh(cod)Cl]₂ (3.0 mg, 0.006 mmol), and KF (34.8 mg, 0.600 mmol) were added to an oven-dried microwave vial. The vial was sealed with a septum-lined cap and purged with nitrogen for 1 h. Anhydrous toluene (4.0 mL) and t-BuOH (57 µL, 0.60 mmol) were added, and the mixture was stirred at 65 °C for 16 h. The reaction was cooled to room temperature, water (5 mL) and saturated aqueous NH₄Cl (5 mL) were added, and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (20 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The mixture was subjected to column chromatography (10% EtOAc/petroleum ether) leading to isolation of ketone 6 (20.5 mg, 17%) as a white solid, ketone 5 (22.0 mg, 18%) as a pale yellow solid, and alcohol 2a (49.5 mg, 41%) as a white solid.

(±)-(3aR,9bR)-5-[(E)-Benzylidene]-9b-hydroxy-3a-methyl-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one (2a). R_f = 0.42 (40% EtOAc/hexane); m.p. 144-145 °C (hexane); IR 3468 (OH), 2936, 1717 (C=O), 1207, 1076, 758, 694 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.72 (1H, dd, J = 7.7, 1.2 Hz, ArH), 7.68 (1H, dd, J = 7.9, 1.2 Hz, ArH), 7.43-7.32 (4H, m, ArH), 7.30-7.25 (3H, m, ArH), 7.24 (1H, d, J = 1.4 Hz, C=CH), 2.79 (1H, d, J = 14.1 Hz, CH₂C=C), 2.68-2.58 (2H, m, CH₂C=C and CH₂C=O), 2.53-2.29 (3H, m, CH₂C=O and CH₂COH), 1.83 (1H, d, J = 1.6 Hz, OH), 1.01 (3H, s, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 219.9 (C), 140.1 (C), 137.1 (C), 134.3 (C), 132.1 (C), 129.1 (2 × CH), 128.8 (CH), 128.4 (2 × CH), 128.2 (CH), 127.9 (CH), 127.1 (CH), 126.5 (CH), 124.2 (CH), 80.1 (C), 54.1 (C), 35.9 (CH₂), 35.2 (CH₂), 34.3 (CH₂), 13.9 (CH₃); HRMS (ESI) Exact mass calcd for C₂₃H₂₃O₂ [M+H]^+: 305.1542, found: 305.1538.
2-[(E)-2,3-Diphenylprop-2-en-1-yl]-2-methylcyclopentane-1,3-dione (5). R_f = 0.53 (40% EtOAc/hexane); m.p. 85-90 °C (CH_2Cl_2/hexane) IR 1742 (C=O), 1210, 929, 730, 702 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl_3) \(\delta\) 7.54-7.52 (2H, m, ArH), 7.47-7.43 (2H, m, ArH), 7.37-7.33 (3H, m, ArH), 7.32-7.27 (3H, m, ArH), 6.67 (1H, s, C=C=H), 3.26 (2H, s, CH_2C=C), 2.48-2.41 (2H, m, CH_2CH_2), 1.86-1.80 (2H, m, CH_2CH_2), 1.10 (3H, s, CH_3); \(^{13}\)C NMR (126 MHz, CDCl_3) \(\delta\) 216.7 (2 \times C), 141.5 (C), 138.3 (C), 137.4 (C), 132.5 (CH), 128.9 (2 \times CH), 128.6 (2 \times CH), 128.3 (CH), 128.2 (2 \times CH), 128.0 (CH), 127.0 (CH), 55.5 (C), 36.7 (CH_2), 34.9 (2 \times CH), 22.1 (CH_3); HRMS (ESI) Exact mass calcd for C_{21}H_{20}NaO_2 [M+Na]^+: 327.1356, found: 327.1354.

(±)-5-(Diphenylmethylidene)-7-methylcycloheptane-1,4-dione (6). R_f = 0.62 (40% EtOAc/hexane); m.p. 110-120 °C (CH_2Cl_2/hexane); IR 1708 (C=O), 1215, 760, 702, 699 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl_3) \(\delta\) 7.39-7.23 (6H, m, ArH), 7.20-7.17 (2H, m, ArH), 7.11-7.08 (2H, m, ArH), 2.85-2.64 (6H, m, CH_2CH_2 and CH_3CH), 2.29-2.20 (1H, m, CHCH_3), 0.99 (3H, d, \(J = 6.4\) Hz, CHCH_3); \(^{13}\)C NMR (126 MHz, CDCl_3) \(\delta\) 211.5 (C), 207.5 (C), 144.6 (C), 140.8 (C), 139.2 (C), 138.3 (C), 128.9 (2 \times CH), 128.6 (2 \times CH), 128.5 (2 \times CH), 128.3 (2 \times CH), 127.8 (CH), 127.8 (CH), 45.2 (CH), 38.9 (CH_2), 37.6 (CH_2), 34.4 (CH_2), 15.6 (CH_3); HRMS (ESI) Exact mass calcd for C_{21}H_{24}O_2 [M+H]^+: 305.1536, found: 305.1527.
4. Racemic Iridium Catalyzed Arylative Cyclizations

General Procedure

The appropriate alkynone (0.40 mmol), the appropriate arylboronic acid (0.60 mmol), [Ir(cod)Cl]₂ (4.0 mg, 0.0060 mmol), and KF (34.8 mg, 0.600 mmol) were added to an oven-dried microwave vial. The vial was sealed with a septum-lined cap and purged with nitrogen for 1 h. Anhydrous toluene (4.0 mL) and t-BuOH (57 µL, 0.60 mmol) were added and the mixture was stirred at 65 °C for 16 h. The reaction was cooled to room temperature, water (5 mL) and saturated aqueous NH₄Cl (5 mL) were added, and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (20 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The mixture was purified by column chromatography to give the arylative cyclization product.

(±)-(3aR,9bR)-5-[(E)-Benzyldiene]-9b-hydroxy-3a-methyl-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one (2a) and (±)-2-[(E)-3-[(3aS,9bS)-5-[(E)-benzyldiene]-9b-hydroxy-3a-methyl-3-oxo-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[a]naphthalen-6-yl]-3-phenylallyl]-2-methylcyclopentane-1,3-dione (7)

Alkynone 1a (90.5 mg, 0.400 mmol), phenylboronic acid (73.2 mg, 0.600 mmol), [Ir(cod)Cl]₂ (4.0 mg, 0.0060 mmol), and KF (34.8 mg, 0.600 mmol) were added to an oven-dried microwave vial. The vial was sealed with a septum-lined cap and purged with nitrogen for 1 h. Anhydrous toluene (4.0 mL) and t-BuOH (57 µL, 0.60 mmol) were added, and the mixture was stirred at 65 °C for 16 h. The reaction was cooled to room temperature, water (5 mL) and saturated aqueous NH₄Cl (5 mL) were added, and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (20 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The mixture was subjected to column chromatography (40% EtOAc/petroleum ether) leading to the isolation of arylative cyclization product 2a (88.0 mg, 72%) as a white solid and 2:1 adduct 7 (28.4 mg, 27%) as a white solid.
Supporting Information

(±)-(3aR,9bR)-5-[(E)-Benzyldiene]-9b-hydroxy-3a-methyl-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one (2a). Data as described above.

(±)-2-[(E)-3-[(3aS,9bS)-5-[(E)-Benzyldiene]-9b-hydroxy-3a-methyl-3-oxo-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[a]naphthalen-6-yl]-3-phenylallyl]-2-methylcyclopentane-1,3-dione (7). Rf = 0.13 (40% EtOAc/hexane); m.p. 206-208 °C (CH2Cl2/Et2O); IR 3438 (OH), 2926, 1736 (C=O), 1721, 1070 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.68 (1H, dd, J = 7.6, 1.3 Hz, ArH), 7.47 (1H, dd, J = 7.5, 1.4 Hz, ArH), 7.41 (1H, t, J = 7.6 Hz, ArH), 7.30-7.13 (7H, m, ArH), 6.94 (1H, s, C=CHPh), 6.78-6.84 (4H, m, ArH), 5.86 (1H, t, J = 7.5 Hz, CH₂CH=CHPh), 2.72-2.42 (7H, m, O=CC₆H₄C=O and CH₂CH=CH₂COH), 2.33-1.99 (5H, m, CH₂COOH and CH₂COH and CH₂C=CH), 1.82 (1H, d, J = 1.4 Hz, OH), 1.14 (3H, s, CH₃C(C=O)₂), 0.83 (3H, s, CH₃COOH); ¹³C NMR (101 MHz, CDCl₃) δ 219.7 (C), 215.1 (2 × C), 147.8 (C), 142.4 (C), 142.1 (C), 139.4 (C), 136.9 (C), 134.8 (C), 133.9 (CH), 132.3 (CH), 132.1 (C), 129.7 (2 × CH), 129.1 (2 × CH), 128.1 (2 × CH), 127.8 (CH), 127.6 (2 × CH), 127.0 (CH), 126.9 (CH), 125.2 (CH), 123.1 (CH), 80.7 (C), 57.1 (C), 54.6 (C), 35.8 (CH₂), 35.1 (CH₂), 34.9 (CH₂), 34.8 (CH₂), 34.73 (CH₂), 34.69 (CH₂), 16.7 (CH₃), 15.1 (CH₃); HRMS (ESI) Exact mass calcd for C₃₆H₃₄NaO₄ [M+Na⁺]: 554.2349, found: 553.2325.

Slow diffusion of Et₂O into a solution of 7 in CH₂Cl₂ provided crystals that were suitable for X-ray diffraction:
(±)-(3aR,9bR)-9b-Hydroxy-5-[(E)-4-methoxybenzylidene]-3a-methyl-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one (2b). According to the general procedure, reaction of alkyne 1b (102 mg, 0.400 mmol) and phenylboronic acid (73.2 mg, 0.600 mmol) gave, after purification by column chromatography (40% EtOAc/petroleum ether), alcohol 2b (82.4 mg, 62%) as a white solid. $R_f = 0.31$ (30% EtOAc/hexane); m.p. 130-140 °C (i-PrOH); IR 3289 (OH), 2931, 1719 (C=O), 1508, 1250, 1022, 756 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.71 (1H, dd, $J = 7.7, 1.5$ Hz, ArH), 7.66 (1H, dd, $J = 7.8, 1.4$ Hz, ArH), 7.38 (1H, ddd, $J = 7.7, 7.5, 1.4$ Hz, ArH) 7.33 (1H, ddd, $J = 7.8, 7.5, 1.5$ Hz, ArH), 7.24-7.19 (2H, m, ArH), 7.17 (1H, d, $J = 1.6$ Hz, C=CH), 6.93-6.88 (2H, m, ArH), 3.85 (3H, s, OCH₃), 2.80 (1H, d, $J = 14.1$ Hz, CH₂C=C), 2.66-2.58 (2H, m, CH₃C=C and CH₂C=O), 2.52-2.29 (3H, m, CH₂C=O and CH₂COH), 1.83 (1H, d, $J = 2.1$ Hz, OH), 1.01 (3H, s, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 220.0 (C), 158.7 (C), 139.9 (C), 134.5 (C), 130.7 (C), 130.4 (2 × CH), 129.7 (C), 128.5 (CH), 128.1 (CH), 127.6 (CH), 126.5 (CH), 124.1 (CH), 113.9 (2 × CH), 80.1 (C), 55.3 (CH₃), 54.1 (C), 35.9 (CH₂), 35.2 (CH₂), 34.3 (CH₂), 13.9 (CH₃); HRMS (ESI) Exact mass calcd for C₂₂H₂₆NO₃ [M+Na]⁺: 352.1913, found: 352.1907.

(±)-(3aR,9bR)-9b-Hydroxy-5-[(E)-4-chlorobenzylidene]-3a-methyl-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one (2c). According to the general procedure, reaction of alkyne 1c (104 mg, 0.400 mmol) and phenylboronic acid (73.2 mg, 0.600 mmol) gave, after purification by column chromatography (30% EtOAc/petroleum ether), alcohol 2c (96.2 mg, 71%) as a pale yellow solid. $R_f = 0.31$ (30% EtOAc/hexane); m.p. 187-188 °C (Et₂O/hexane); IR 3451 (OH), 2957, 1717 (C=O), 1231, 1082, 858, 770 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.73 (1H, dd, $J = 7.8, 1.3$ Hz, ArH), 7.66 (1H, dd, $J = 7.9, 1.2$ Hz, ArH), 7.41 (1H, ddd, $J = 7.9, 7.4, 1.3$ Hz, ArH), 7.37-7.32 (3H, m, ArH), 7.23-7.19 (2H, m, ArH), 7.15 (1H, d, $J = 1.1$ Hz, C=CH), 2.70 (1H, d, $J = 14.1$ Hz, CH₂C=C), 2.67-2.57 (2H, m, CH₂C=C and CH₂C=O), 2.50-2.39 (2H, m, CH₂C=O and CH₂COH), 2.33 (1H, dt, $J = 13.6, 9.7$ Hz, CH₂COH), 1.84 (1H, s, OH), 1.01 (3H, s, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 219.6 (C), 140.2 (C), 135.5 (C), 134.0 (C), 133.0 (C), 132.9 (C), 130.4 (2 × CH), 129.0 (CH), 128.6 (2 × CH), 128.2 (CH), 126.7 (CH), 126.5 (CH), 124.2 (CH), 80.0 (C), 54.1 (C), 35.9 (CH₂), 35.2 (CH₂), 34.2 (CH₂), 14.1 (CH₃); HRMS (ESI) Exact mass calcd for C₂₂H₁₉ClNaO₂ [M+Na]⁺: 361.0966, found: 361.0957.
(±)-(3aR,9bR)-9b-Hydroxy-5-[(E)-4-nitrobenzylidene]-3a-methyl-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one (2d). According to the general procedure, reaction of 2-methyl-2-[3-(4-nitrophenyl)prop-2-yn-1-yl]cyclopentane-1,3-dione (1d)² (108 mg, 0.400 mmol) and phenylboronic acid (73.2 mg, 0.600 mmol) gave, after purification by column chromatography (40% EtOAc/petroleum ether), alcohol 2d (128 mg, 92%) as a yellow solid. \( R_f = 0.31 \) (40% EtOAc/hexane); m.p. 186-187 °C (EtOAc/hexane); IR 3563 (OH), 2984, 1732 (C=O), 1591, 1508, 1339, 758 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.28-8.22 (2H, m, ArH), 7.75 (1H, dd, \( J = 7.8, 1.3 \) Hz, ArH), 7.67 (1H, dd, \( J = 8.0, 1.1 \) Hz, ArH), 7.49-7.41 (3H, m, ArH), 7.40-7.35 (1H, m, ArH), 7.21 (1H, s, C=C\( _2 \)H), 2.71 (1H, dd, \( J = 14.0, 1.9 \) Hz, CH\( _2 \)=C), 2.68-2.58 (2H, m, CH\( _2 \)C=CH and CH\( _2 \)=C=O), 2.47-2.31 (3H, m, CH\( _3 \)=C=O and CH\( _2 \)COH), 1.87 (1H, d, \( J = 1.9 \) Hz, OH), 1.02 (3H, s, CH\( _3 \)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 219.1 (C), 146.5 (C), 143.9 (C), 140.6 (C), 136.0 (C), 133.6 (C), 129.9 (2 × CH), 129.8 (CH), 128.4 (CH), 126.9 (CH), 125.4 (CH), 124.4 (CH), 123.8 (2 × CH), 79.7 (C), 54.2 (C), 35.9 (CH\( _2 \)), 35.3 (CH\( _2 \)), 34.3 (CH\( _2 \)), 14.5 (CH\( _3 \)); HRMS (ESI) Exact mass calcd for C\(_{21}\)H\(_{19}\)N\(_2\)O\(_4\) \([\text{M+Na}]^+\): 372.1212, found: 372.1202.

Cooling a solution of 2d in EtOAc/hexane in a freezer provided crystals that were suitable for X-ray diffraction:

(±)-(3aR,9bR)-9b-Hydroxy-5-[(E)-3-methylbenzylidene]-3a-methyl-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one (2e). According to the general procedure, reaction of alkynone 1e (96.0 mg, 0.400 mmol) and phenylboronic acid (73.2 mg, 0.600 mmol) gave, after purification by column
Supporting Information

chromatography (10% EtOAc/hexane), alcohol 2e (91.1 mg, 72%) as a white solid. \( R_f = 0.29 \) (30% EtOAc/hexane); m.p. 110-120 °C (i-PrOH); IR 3468 (OH), 2953, 1717 (C=O), 1450, 1076, 959, 694 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta 7.74 \) (1H, d, \( J = 1.5 \) Hz, ArH), 7.69 (1H, dd, \( J = 7.9, 1.2 \) Hz, ArH), 7.41 (1H, ddd, \( J = 7.7, 7.4, 1.3 \) Hz, ArH), 7.36 (1H, ddd, \( J = 7.9, 7.4, 1.5 \) Hz, ArH), 7.29-7.24 (1H, m, ArH), 7.22 (1H, d, \( J = 1.4 \) Hz, C=CH), 7.13-7.07 (3H, m, ArH), 2.81 (1H, d, \( J = 14.1 \) Hz, CH\(_2\)C=C), 2.69-2.59 (2H, m, CH\(_2\)C=C and CH\(_2\)C=O), 2.51 (1H, ddd, \( J = 19.0, 9.0, 2.4 \) Hz, CH\(_2\)C=O), 2.43 (1H, ddd, \( J = 13.6, 9.2, 2.4 \) Hz, CH\(_2\)COH), 2.40-2.26 (1H, m, CH\(_2\)COH), 2.37 (3H, s, ArCH\(_3\)), 1.86 (1H, s, OH), 1.03 (3H, s, CCH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta 220.0 \) (C), 140.1 (C), 137.9 (C), 137.0 (C), 134.3 (C), 131.9 (C), 129.8 (CH), 128.7 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 126.5 (CH), 126.2 (CH), 124.1 (CH), 80.1 (C), 54.2 (C), 35.9 (CH\(_2\)), 35.2 (CH\(_2\)), 34.4 (CH\(_2\)), 21.5 (CH\(_3\)), 13.8 (CH\(_3\)) HRMS (ESI) Exact mass calcd for C\(_{22}\)H\(_{26}\)NO\(_2\) [M+NH\(_4\)]\(^+\): 336.1964, found: 336.1958.

![Chemical Structure](image)

(±)-2-[(E)-{(3aR,9bR)-9b-Hydroxy-3a-methyl-3-oxo-1,2,3,3a,4,9b-hexahydro-5H-cyclopenta[a]naphthalene-5-ylidene)methyl]benzonitrile (2f).

In a modification of the general procedure, reaction of alkynone 1f (101 mg, 0.400 mmol), phenylboronic acid (73.2 mg, 0.600 mmol), and [Ir(cod)Cl]\(_2\) (6.7 mg, 0.010 mmol) gave, after purification by column chromatography (10% EtOAc/CH\(_2\)Cl\(_2\)), alcohol 2f (114 mg, 86%) as a pale yellow solid. \( R_f = 0.38 \) (10% EtOAc/CH\(_2\)Cl\(_2\)); m.p. 138-139 °C (MeOH); IR 3420 (OH), 2938, 2228 (C≡N), 1717 (C=O), 1086, 966, 760 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta 7.74 \) (1H, dd, \( J = 7.8, 1.1 \) Hz, ArH), 7.72-7.68 (2H, m, ArH), 7.60 (1H, td, \( J = 7.7, 1.2 \) Hz, ArH), 7.45 (1H, ddd, \( J = 7.8, 7.6, 1.3 \) Hz, ArH), 7.43-7.35 (3H, m, ArH), 7.28 (1H, d, \( J = 1.5 \) Hz, C=CH), 2.69-2.58 (2H, m, CH\(_2\)C=C and CH\(_2\)C=O), 2.52-2.40 (3H, m, CH\(_2\)C=C and CH\(_2\)C=O and CH\(_2\)COH), 2.39-2.30 (1H, m, CH\(_2\)COH), 1.89 (1H, d, \( J = 2.1 \) Hz, OH), 1.03 (3H, s, CH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta 219.7 \) (C), 140.9 (C), 140.6 (C), 136.8 (C), 133.3 (C), 133.0 (CH), 132.7 (CH), 129.9 (CH), 129.8 (CH), 128.4 (CH), 127.6 (CH), 126.7 (CH), 124.7 (CH), 123.6 (CH), 118.0 (C), 112.7 (C), 80.0 (C), 54.3 (C), 35.9 (CH\(_2\)), 35.4 (CH\(_2\)), 34.7 (CH\(_2\)), 14.2 (CH\(_3\)); HRMS (ESI) Exact mass calcd for C\(_{23}\)H\(_{19}\)NNaO\(_2\) [M+Na\(^+\)]: 352.1308, found: 352.1306.

![Chemical Structure](image)

(±)-(6aR,11bS)-5-[(E)-Benzyldiene]-11b-hydroxy-6a-methyl-5,6,6a,11b-tetrahydro-7H-benzo[c]fluoren-7-one (2i). According to the general procedure, reaction of alkynone 1i (110 mg, 0.400 mmol) and phenylboronic acid (73.2 mg, 0.600 mmol) gave, after purification by column chromatography (30% EtOAc/hexane), alcohol 2i
(97.5 mg, 67%) as a pale yellow solid. \(R_f = 0.31\) (30% EtOAc/hexane); m.p. 70-71 °C (hexane); IR 3422 (OH), 2924, 1701 (C=O), 1600, 1449, 1294, 1034, 756, 698 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.13 (1H, dd, \(J = 7.9, 1.2\) Hz, ArH), 7.85-7.82 (1H, m, ArH), 7.73-7.69 (1H, m, ArH), 7.63 (1H, td, \(J = 7.6, 1.2\) Hz, ArH), 7.55 (1H, dd, \(J = 7.9, 1.2\) Hz, ArH), 7.49-7.27 (8H, m, ArH), 6.98 (1H, s, C=CH), 3.20 (1H, d, \(J = 13.7, 0.9\) Hz, CH\(_2\)), 2.60 (1H, dd, \(J = 13.7, 1.4\) Hz, CH\(_2\)), 2.46 (1H, s, OH), 1.30 (3H, s, CH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 206.9 (C), 156.0 (C), 139.0 (C), 137.3 (C), 136.6 (C), 135.2 (CH), 133.5 (C), 133.2 (C), 129.3 (CH), 129.1 (2 × CH), 128.5 (CH), 128.3 (2 × CH), 128.2 (CH), 127.7 (CH), 127.3 (CH), 127.0 (CH), 125.10 (CH), 125.05 (CH), 123.9 (CH), 78.4 (C), 56.4 (C), 34.8 (CH\(_2\)), 19.0 (CH\(_3\)); HRMS (ESI) Exact mass calcd for C\(_{28}\)H\(_{28}\)O\(_2\) [M+H]: 353.1536, found: 353.1516.

(±)-(6aS,11bS)-5-[\(E\)-Benzyldiene]-11b-hydroxy-6a-phenyl-5,6,6a,11b-tetrahydro-\(7\)H-benzo[c]fluoren-7-one (2j). In a modification of the general procedure, reaction of alkynone 1j (134 mg, 0.400 mmol), phenylboronic acid (73.2 mg, 0.600 mmol), and \([\text{Ir(cod)}\text{Cl}]_2\) (6.7 mg, 0.010 mmol) gave, after purification by column chromatography (25% EtOAc/petroleum ether), alcohol 2j (104 mg, 63%) as a pale yellow solid. \(R_f = 0.24\) (25% EtOAc/petroleum ether); m.p. 86-88 °C (MeOH); IR 3475 (OH) 1717 (C=O), 1601, 1495, 1288, 1042 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.12 (1H, dd, \(J = 7.9, 0.9\) Hz, ArH), 7.79 (1H, d, \(J = 7.6\) Hz, ArH), 7.71 (1H, d, \(J = 7.8\) Hz, ArH), 7.65-7.60 (1H, m, ArH), 7.54 (1H, dd, \(J = 7.8, 0.8\) Hz, ArH), 7.47-7.41 (2H, m, ArH), 7.40-7.21 (11 H, m, ArH), 6.93 (1H, s, C=CH), 3.81 (1H, d, \(J = 13.7\) Hz, CH\(_2\)), 3.16 (1H, dd, \(J = 13.7, 1.7\) Hz, CH\(_2\)), 2.08 (1H, s, OH); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 205.1 (C), 157.4 (C), 139.6 (C), 139.1 (C), 137.1 (C), 136.9 (C), 135.8 (CH), 134.6 (C), 133.7 (C), 129.3 (CH), 129.0 (2 × CH), 128.7 (2 × CH), 128.5 (CH) 128.5 (2 × CH), 128.3 (2 × CH), 128.1 (CH), 127.7 (CH), 127.4 (CH), 127.0 (2 × CH), 125.5 (CH), 125.3 (CH), 123.4 (CH), 78.4 (C), 64.5 (C), 34.2 (CH\(_2\)); HRMS (ESI) Exact mass calcd for C\(_{36}\)H\(_{24}\)NaO\(_2\) [M+Na]: 437.1512, found: 437.1513.

(±)-(4aR,10aR)-9-[\(E\)-Benzyldiene]-4a-hydroxy-10a-methyl-3,4,4a,9,10,10a-hexahydrophenanthren-1(2H)-one (2k). According to the general procedure, reaction of alkynone 1k (96.0 mg, 0.400 mmol) and phenylboronic acid (73.2 mg, 0.600 mmol) gave, after purification by column chromatography (10% EtOAc/hexane), alcohol 2k (90.4 mg, 71%) as a white solid. \(R_f = 0.29\) (30% EtOAc/hexane); m.p. 170-171 °C (MeOH); IR 3503 (OH), 2934, 1686 (C=O), 1167, 982, 754, 696 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.74 (1H, dd, \(J = 7.7, 1.5\) Hz, ArH), 7.64 (1H, dd, \(J = 7.6, 1.5\) Hz, ArH), 7.40-
7.25 (6H, m, ArH), 7.24 (1H, d, \( J = 1.4 \) Hz, C=CH), 3.20 (1H, dd, \( J = 15.0, 2.0 \) Hz, CH\(_2\)C=C), 2.81 (1H, dd, \( J = 15.0, 0.9 \) Hz, CH\(_2\)C=C), 2.70 (1H, ddd, \( J = 14.9, 13.0, 6.6 \) Hz, CH\(_2\)C=O), 2.46-2.37 (1H, m, CH\(_2\)C=O), 2.34-2.13 (2H, m, CH\(_2\)COH), 2.02-1.94 (2H, m, CH\(_2\)CH\(_2\)COH and OH), 1.93-1.85 (1H, m, CH\(_2\)CH\(_2\)OH), 1.02 (3H, s, CH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 213.7 (C), 142.1 (C), 137.2 (C), 133.9 (C), 129.2 (2 \( \times \) CH), 128.5 (CH), 128.4 (2 \( \times \) CH), 127.8 (CH), 127.08 (CH), 127.06 (CH), 125.3 (CH), 123.7 (CH), 78.4 (C), 53.3 (C), 36.9 (CH\(_2\)), 36.8 (CH\(_2\)), 36.7 (CH\(_2\)), 20.9 (CH\(_2\)), 15.9 (CH\(_3\)); HRMS (ESI) Exact mass calcd for C\(_{22}\)H\(_{23}\)O\(_2\) [M+H]+: 319.1698, found: 319.1696.

\((\pm)-(4aR,10aR)-4a\)-Hydroxy-9-[(E)-4-methoxybenzylidene]-10a-methyl-3,4,4a,9,10,10a-hexahydrophenanthren-1(2H)-one (2l). According to the general procedure, reaction of alkynone 1l (108 mg, 0.400 mmol) and phenylboronic acid (73.2 mg, 0.600 mmol) gave, after purification by column chromatography (10% EtOAc/hexane), alcohol 2l (80.7 mg, 58%) as a white solid. \( R_f = 0.25 \) (30% EtOAc/hexane); m.p. 133-134 °C (Et\(_2\)O/hexane); IR 3466 (O\( H \)), 2936, 1717 (C=O), 1452, 1238, 1034, 758, 694 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.73-7.70 (1H, m, ArH), 7.64-7.61 (1H, m, ArH), 7.36-7.29 (2H, m, ArH), 7.29-7.24 (2H, m, ArH), 7.17 (1H, d, \( J = 1.3 \) Hz, C=CH), 6.93-6.88 (2H, m, ArH), 3.84 (3H, s, OCH\(_3\)), 3.19 (1H, dd, \( J = 15.1, 1.9 \) Hz, CH\(_2\)C=C), 2.80 (1H, dd, \( J = 15.1, 1.2 \) Hz, CH\(_2\)C=C), 2.76-2.66 (1H, m, CH\(_2\)C=O), 2.46-2.40 (1H, m, CH\(_2\)C=O), 2.33-2.14 (2H, m, CH\(_2\)COH), 1.99-1.86 (3H, m, CH\(_2\)CH\(_2\)CH\(_2\) and OH), 1.01 (3H, s, CCH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 213.8 (C), 158.6 (C), 141.9 (C), 134.3 (C), 130.6 (2 \( \times \) CH), 130.5 (C), 129.8 (C), 128.2 (CH), 127.7 (CH), 126.8 (CH), 125.1 (CH), 123.6 (CH), 113.9 (2 \( \times \) CH), 78.4 (C), 55.3 (CH\(_3\)), 53.3 (C), 36.9 (CH\(_2\)), 36.8 (CH\(_2\)), 36.6 (CH\(_2\)), 20.9 (CH\(_2\)), 15.9 (CH\(_3\)); HRMS (ESI) Exact mass calcd for C\(_{23}\)H\(_{23}\)O\(_3\) [M+H]+: 366.2069, found: 366.2066.

Slow evaporation of a solution of 2l in EtOAc/hexane provided crystals that were suitable for X-ray diffraction:
(±)-(4aR,10aR)-4a-Hydroxy-9-[(E)-4-chlorobenzylidene]-10a-methyl-3,4,4a,9,10,10a-hexahydrophenanthren-1(2H)-one (2m). According to the general procedure, reaction of alkyne 1m (110 mg, 0.400 mmol) and phenylboronic acid (73.2 mg, 0.600 mmol) gave, after purification by column chromatography (10% EtOAc/cyclohexane), alcohol 2m (112.6 mg, 80%) as a white solid. Rf = 0.36 (30% EtOAc/hexane); m.p. 166-167 °C (MeOH); IR 3497 (OH), 2953, 1682 (C=O), 1489, 1190, 870, 756 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.72 (1H, dd, J = 7.8, 1.3 Hz, ArH), 7.64 (1H, dd, J = 7.7, 1.4 Hz, ArH), 7.39-7.30 (4H, m, ArH), 7.26-7.20 (2H, m, ArH), 7.17 (1H, s, C=CH), 3.17 (1H, dd, J = 15.0, 2.0 Hz, CH₂C=C), 2.73 (1H, dd, J = 15.0, 0.8 Hz, CH₂C=C), 2.67 (1H, ddd, J = 15.0, 12.7, 6.6 Hz, CH₂C=O), 2.46-2.40 (1H, m, CH₂C=O), 2.32-2.14 (2H, m, CH₂COH), 2.02-1.96 (1H, m, CH₂CH₂CH₂), 1.94 (1H, d, J = 2.0 Hz, OH), 1.92-1.84 (1H, m, CH₂CH₂CH₂), 1.02 (3H, s, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 213.4 (C), 142.1 (C), 142.1 (C), 135.7 (C), 133.7 (C), 132.9 (C), 130.5 (2 × CH), 128.7 (CH), 128.6 (2 × CH), 127.9 (CH), 125.7 (CH), 125.4 (CH), 123.8 (CH), 78.3 (C), 53.4 (C), 36.9 (CH₂), 36.7 (CH₂), 36.6 (CH₂), 20.8 (CH₂), 16.1 (CH₃); HRMS (ES) Exact mass calcd for C₂₂H₂₁³⁵ClNaO₂ [M+Na]⁺: 375.1128, found: 375.1113.
(±)-(6aR,12bS)-8-[(E)-4-Chlorobenzylidene]-12b-hydroxy-5,6a-dimethyl-6a,7,8,12b-tetrahydrobenzo[k]phenanthridin-6(5H)-one (2n). According to the general procedure, reaction of alkynone 1n (135 mg, 0.400 mmol) and phenylboronic acid (73.2 mg, 0.600 mmol) gave, after purification by column chromatography (10% EtOAc/hexane), alcohol 2n (120 mg, 72%) as a white solid. $R_f = 0.38$ (30% EtOAc/petroleum ether); m.p. 174-176 °C (MeOH/hexane); IR 3293 (OH), 2936, 1638 (C=O), 1377, 1018, 752 cm$^{-1}$; $^1$H NMR (400 MHz, D$_6$-DMSO, 85 °C) δ 7.88-7.84 (1H, m, ArH), 7.57-7.47 (3H, br m, ArH), 7.46-7.42 (2H, m, ArH), 7.36 (1H, ddd, $J = 8.1, 7.5, 1.6$ Hz, ArH), 7.32-7.26 (1H, m, ArH), 7.20-7.13 (3H, m, ArH and C=CH), 7.08 (1H, dd, $J = 8.1, 1.0$ Hz, ArH), 7.00 (1H, br s, ArH), 5.71 (1H, s, OH), 3.22 (1H, br d, $J = 16.1$ Hz, CH$_2$), 3.09 (3H, s, NCH$_3$), 2.82 (1H, dd, $J = 16.1, 2.4$ Hz, CH$_2$), 1.00 (3H, s, CCH$_3$); $^{13}$C NMR (101 MHz, D$_6$-DMSO, 85 °C) δ 171.7 (C), 138.3 (C), 137.5 (C), 136.2 (C), 134.5 (C), 133.6 (C), 130.8 (C), 130.5 (2 × CH), 130.4 (C), 128.0 (CH), 127.8 (2 × CH), 127.5 (CH), 126.9 (CH), 126.8 (CH), 126.5 (CH), 123.3 (CH), 123.1 (CH), 121.9 (CH), 113.9 (CH), 72.2 (C), 45.8 (C), 32.3 (CH$_2$), 28.9 (CH$_3$), 18.0 (CH$_3$); HRMS (ESI) Exact mass calcd for C$_{26}$H$_{25}^{35}$ClNO$_3$ [M+H]$^+$: 416.1417, found: 416.1413.

(±)-Ethyl (3aS,9bR)-5-[(E)-benzylidene]-9b-hydroxy-1,2,3,4,5,9b-hexahydro-3aH-cyclopenta[a]naphthalene-3a-carboxylate (9)

Alkynone 8 (108 mg, 0.400 mmol), phenylboronic acid (146 mg, 1.21 mmol), [Ir(cod)Cl]$\_2$ (6.7 mg, 0.010 mmol), and KF (69.7 mg, 1.20 mmol) were added to an oven-dried microwave vial. The vial was sealed with a septum-lined cap and purged with nitrogen for 1 h. Anhydrous toluene (4.0 mL) and i-PrOH (126 µL, 1.32 mmol) were added and the mixture was stirred at 65 °C for 4 h. A solution of [Ir(cod)Cl]$\_2$ (6.7 mg, 0.010 mmol) in anhydrous toluene (1.0 mL) was added, and the mixture was stirred at 65 °C for 14 h. The reaction was cooled to room temperature, water (5 mL) and saturated aqueous NH$_4$Cl (5 mL) were added, and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (20 mL), dried (MgSO$_4$), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (10% hexane/toluene) to give alcohol 9 (100 mg, 72%) as a white solid. $R_f = 0.30$ (10% EtOAc/hexane); m.p. 100-105 °C (CH$_2$Cl$_2$/hexane); IR 3482 (OH), 2969, 1693 (C=O), 1313, 1201, 1020 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.72 (1H, dd, $J = 7.7, 1.2$ Hz, ArH), 7.56 (1H, dd, $J = 7.9, 1.3$ Hz, ArH), 7.40-7.23 (6H, m, ArH), 7.07 (1H, d, $J = 1.7$ Hz, C=CH), 4.38 (1H, d, $J = 2.2$ Hz, OH), 3.93
(±)-(3aR,9bR)-5-[(E)-Benzyldiene]-9b-hydroxy-8-methoxy-3a-methyl-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one (10a). According to the general procedure, reaction of alkyne 1a (90.5 mg, 0.400 mmol) and 4-methoxyphenylboronic acid (91.2 mg, 0.600 mmol) gave, after purification by column chromatography (40% EtOAc/hexane), alcohol 10a (91.9 mg, 69%) as a white solid. Rf = 0.35 (40% EtOAc/hexane); m.p. 189-190 °C (MeOH); IR 3478 (OH), 2961, 1736 (C=O), 1491, 1207, 866, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.64 (1H, d, J = 8.8 Hz, ArH), 7.40-7.34 (2H, m, ArH), 7.28-7.24 (4H, m, ArH), 7.13 (1H, d, J = 1.5 Hz, C=CH), 6.92 (1H, dd, J = 8.8, 2.8 Hz, ArH), 3.90 (3H, s, OCH₃), 2.79 (1H, d, J = 14.2 Hz, CH₂C=C), 2.68-2.59 (2H, m, CH₂C=O and CH₂C=C), 2.51 (1H, ddd, J = 19.0, 9.0, 2.4 Hz, CH₂C=O), 2.42 (1H, ddd, J = 13.6, 9.2, 2.4 Hz, CH₂COH), 2.35 (1H, dddd, J = 13.5, 10.9, 9.1, 2.2 Hz, CH₂COH), 1.84 (1H, d, J = 2.2 Hz, OH), 1.02 (3H, s, CCH₃); ¹³C NMR (126 MHz, CDCl₃) δ 219.8 (C), 160.2 (C), 141.5 (C), 137.3 (C), 131.6 (C), 129.1 (2 × CH), 128.4 (2 × CH), 126.9 (C), 126.8 (CH), 126.0 (CH), 125.7 (CH), 114.8 (CH), 110.6 (CH), 80.3 (C), 55.4 (CH₃), 54.2 (C), 35.8 (CH₂), 35.1 (CH₂), 34.4 (CH₂), 13.7 (CH₃); HRMS (ESI) Exact mass calcd for C₂₂H₂₄NaO₃ [M+Na⁺]: 357.1618, found: 357.1622.

(±)-(3aR,9bR)-5-[(E)-Benzyldiene]-8-chloro-9b-hydroxy-3a-methyl-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one (10b). In a modification of the general procedure, reaction of alkyne 1a (90.5 mg, 0.400 mmol), 4-chlorophenylboronic acid (93.8 mg, 0.600 mmol), and [Ir(cod)Cl]₂ (6.7 mg, 0.01 mmol) gave, after purification by column chromatography (30% EtOAc/hexane), alcohol 10b (83.6 mg, 62%) as a pale yellow solid. Rf = 0.54 (40% EtOAc/hexane); m.p. 178-179 °C (Et₂O/hexane); IR 3468 (OH), 2962, 1724 (C=O), 1192, 1076, 947, 810, 694 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.71 (1H, d, J = 2.3 Hz, ArH), 7.61 (1H, d, J = 8.6 Hz, ArH), 7.40-7.34 (2H, m, ArH), 7.33-7.23 (4H, m, ArH), 7.20 (1H, d, J = 1.4 Hz, C=CH), 2.78 (1H, d, J = 14.3 Hz, CH₂C=C), 2.69-2.56 (2H, m, CH₂C=C and CH₂C=O), 2.55-2.25 (3H, m, CH₂C=O and CH₂COH),
1.82 (1H, d, J = 2.2 Hz, OH), 0.99 (3H, s, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 219.2 (C), 141.8 (C), 136.8 (C), 134.5 (C), 132.7 (C), 131.1 (C), 129.1 (2 × CH), 128.5 (2 × CH), 128.40 (CH), 128.39 (CH), 127.3 (CH), 126.7 (CH), 125.7 (CH), 79.9 (C), 53.9 (C), 35.8 (CH₂), 35.0 (CH₂), 34.2 (CH₂), 13.7 (CH₃); HRMS (ESI) C₂₁H₁₉³⁵ClNaO₃ [M+Na]⁺: 361.0966, found: 361.0959.

(±)-Ethyl (3aR,9bR)-5-[(E)-benzylidene]-9b-hydroxy-3a-methyl-3-oxo-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[a]naphthalene-8-carboxylate (10c). In a modification of the general procedure, reaction of alkynone 1a (90.5 mg, 0.400 mmol), 4-(ethoxycarbonyl)phenylboronic acid (232 mg, 1.20 mmol), [Ir(cod)Cl]₂ (6.7 mg, 0.010 mmol), KF (69.7 mg, 1.20 mmol), and t-BuOH (0.11 mL, 1.2 mmol) at 90 °C for 16 h gave, after purification by column chromatography (10% Et₂O/CH₂Cl₂), alcohol 10c (52.8 mg, 35%) as a white solid. Rf = 0.30 (10% Et₂O/CH₂Cl₂); m.p. 174-175 °C (EtOH); IR 3449 (OH), 2976, 1738 (C=O), 1678 (C=O), 1292, 1256, 1030, 770, 698 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.40 (1H, d, J = 1.7 Hz, ArH), 7.99 (1H, dd, J = 8.3, 1.9 Hz, ArH), 7.74 (1H, d, J = 8.3 Hz, ArH), 7.41-7.36 (2H, m, ArH), 7.34-7.27 (4H, m, ArH and C=CH), 4.42 (2H, qd, J = 7.1, 0.8 Hz, OCH₂), 2.81 (1H, d, J = 14.3 Hz, CH₂=C=C), 2.70-2.60 (2H, m, CH₃=C=C and CH₂=C=O), 2.54-2.43 (2H, m, CH₂=C=O and CH₂=COH), 2.38-2.28 (1H, m, CH₂=COH), 1.90 (1H, d, J = 2.1 Hz, OH), 1.44 (1H, t, J = 7.1 Hz, CH₂CH₃), 1.01 (3H, s, O=CCCH₃); ¹³C NMR (126 MHz, CDCl₃) δ 219.3 (C), 166.2 (C), 140.2 (C), 138.6 (C), 136.6 (C), 131.5 (C), 130.6 (C), 130.2 (CH), 129.1 (2 × CH), 129.0 (CH), 128.5 (2 × CH), 128.1 (CH), 127.5 (CH), 124.3 (CH), 79.9 (C), 61.2 (CH₂), 54.0 (C), 36.0 (CH₂), 35.0 (CH₂), 34.2 (CH₂), 14.4 (CH₃), 13.8 (CH₃); HRMS (ESI) Exact mass calcd for C₂₁H₂₁NaO₄ [M+Na]⁺: 399.1572, found: 399.1556.

(±)-(3aR,9bR)-5-[(E)-Benzylidene]-9b-hydroxy-3a,7-dimethyl-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one (10d). According to the general procedure, reaction of alkyfone 1a (90.5 mg, 0.400 mmol) and 3-methylphenylboronic acid (81.6 mg, 0.600 mmol) gave, after purification by column chromatography (40% EtOAc/hexane), alcohol 10d (87.0 mg, 68%) as a white solid. Rf = 0.44 (40% EtOAc/hexane); m.p. 154-155 °C (MeOH); IR 3445 (OH), 2928, 1715 (C=O), 1443, 1206, 1067, 835, 702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.61 (1H, d, J = 7.9 Hz, ArH), 7.49 (1H, s, ArH), 7.40-7.34 (2H, m, ArH), 7.30-7.19 (5H, m, ArH and C=CH), 2.77 (1H, d, J = 14.1 Hz, CH₂=C=C), 2.67-2.55 (2H, m, CH₂=C=C and CH₂=C=O), 2.52-2.25 (3H, m, CH₂=C=O and CH₂=COH), 2.41 (3H, s, ArCH₃), 1.77 (1H, d, J = 2.1 Hz, OH), 1.00 (3H, s, O=CCCH₃); ¹³C NMR (126 MHz, CDCl₃) δ 220.0 (C), 137.8 (C), 137.4 (C), 137.2 (C), 134.1 (C), 132.2 (C), 129.8 (CH), 129.1 (2 ×
CH), 128.4 (2 × CH), 127.7 (CH), 127.0 (CH), 126.5 (CH), 124.5 (CH), 80.0 (C), 54.2 (C), 35.9 (CH₂), 35.2 (CH₂), 34.3 (CH₂), 21.3 (CH₃), 13.9 (CH₃); HRMS (ESI) Exact mass calcd for C₂₅H₂₂NaO₂ [M+Na]+: 341.1517, found: 341.1507.

(±)-(3aR,9bR)-5-[(E)-Benzyldiene]-7-bromo-9b-hydroxy-3a-methyl-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one (10e). According to the general procedure, reaction of alkynone 1a (90.5 mg, 0.400 mmol) and 3-bromophenylboronic acid (90.5 mg, 0.400 mmol) in toluene (8 mL) at 90 °C for 16 h gave, after purification by column chromatography (30% EtOAc/hexane), alcohol 10e (83.8 mg, 59%) as a white solid. R_f = 0.31 (30% EtOAc/hexane); m.p. 146-147 °C (EtOAc/hexane); IR 3426 (OH), 3172, 2961, 2918, 2893, 2795, 2169, 1740, 1600, 1500, 1400, 1300, 1200, 1100, 1000, 900, 800, 700, 600, 500 cm⁻¹; 1H NMR (400 MHz, CDCl₃) δ 8.21 (1H, s, ArH), 7.84 (1H, s, ArH), 8.15 (1H, s, ArH), 7.91-7.84 (2H, m, ArH), 7.53-7.46 (2H, m, ArH), 7.42-7.36 (3H, m, ArH and C=CH), 7.34-7.27 (3H, m, ArH), 2.88 (1H, d, J = 14.2 Hz, CH₂C=C), 2.75-2.62 (2H, m, CH₂C=C and CH₂C=O), 1.97 (1H, d, J = 2.3 Hz, OH), 1.04 (3H, s, CH₃); 13C NMR (126 MHz, CDCl₃) δ 219.8 (C), 138.9 (C), 137.1 (C), 133.5 (C), 133.1 (C), 133.0 (C), 132.3 (C), 129.2 (2 × CH), 128.6 (CH), 128.5 (2 × CH), 128.0 (CH), 127.6 (CH), 127.2 (CH), 126.5 (CH), 126.4 (CH), 125.5 (CH), 123.2 (CH), 80.5 (C), 54.4 (C), 36.5 (CH₂), 35.0 (CH₂), 34.6 (CH₂), 13.6 (CH₃); HRMS (ESI) Exact mass calcd for C₂₅H₂₂NaO₂ [M+Na]+: 377.1517, found: 377.1507.
(±)-(3aR,9bR,E)-9b-hydroxy-3a-methyl-5-(phenylmethylene-d)-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one-6,7,8,9-d4 ([D₃]-2a). According to the general procedure, reaction of alkyne 1a (22.8 mg, 0.101 mmol), d₅-phenylboronic acid (19.0 mg, 0.150 mmol), [Ir(COD)Cl]₂ (1.0 mg, 0.0015 mmol), KF (8.7 mg, 0.15 mmol), and t-BuOH (14.5 μL) in toluene (1 mL) gave, after purification by column chromatography (10% Et₂O/CH₂Cl₂), alcohol [D₅]-2a (17.6 mg, 56%) as a white solid. Rₐ = 0.34 (10% Et₂O/CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 7.41-7.33 (2H, m, ArH), 7.31-7.27 (3H, m, ArH), 2.80 (1H, d, J = 14.1 Hz, CH₂C=C), 2.69-2.58 (2H, m, C=CH₂ and CH₂C=O), 2.53-2.28 (3H, m, CH₂C=O and CH₂COH), 1.85 (1H, d, J = 2.1 Hz, OH), 1.01 (3H, s, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 219.9 (C), 140.0 (C), 137.0 (C), 134.2 (C), 132.0 (C), 129.1 (2 × CH), 128.5 (2 × CH), 128.3 (t, Jₖ= 23.6 Hz, CD), 127.7 (t, Jₖ= 24.5 Hz, CD), 127.6 (t, Jₖ= 23.2 Hz, CD), 127.1 (CH), 126.1 (t, Jₖ= 23.6 Hz, CD), 123.8 (t, Jₖ= 23.8 Hz, CD), 80.1 (C), 54.1 (C), 35.9 (CH₂), 35.2 (CH₂), 34.3 (CH₂), 13.9 (CH₃). HRMS (ESI) Exact mass calcd for C₃₁H₁₆D₅O₂ [M+H]⁺: 310.1850, found: 310.1842.

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5. Enantioselective Iridium-Catalyzed Arylative Cyclizations

(3aR,9bR)-9b-Hydroxy-5-[(E)-4-chlorobenzylidene]-3a-methyl-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one (2c)

[Ir(coe)₂Cl]₂ (9.0 mg, 0.010 mmol) and (R)-Difluorphos (L1) (13.7 mg, 0.0201 mmol) were added to an oven-dried microwave vial, a septum was fitted, and the vial was purged with nitrogen for 1 h. Degassed xylenes (1 mL) were added and the mixture was stirred at room temperature for 30 min under nitrogen. In a separate microwave vial, alkynone 1c (52.1 mg, 0.200 mmol), phenylboronic acid (36.3 mg, 0.300 mmol), and KF (34.8 mg, 0.300 mmol) were added. This vial was sealed with a septum-lined cap and purged with nitrogen for 1 h. The solution of catalyst was added to the vial containing the alkynone under nitrogen. ²Amyl alcohol (33 µL, 0.30 mmol) was added and the mixture was stirred at 110 °C for 20 h. The reaction was cooled to room temperature, water (5 mL) and saturated aqueous NH₄Cl (5 mL) were added, and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (20 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (5% Et₂O/CH₂Cl₂) to give alcohol 2c (21.6 mg, 32%) as a white solid. Alkynone 1c (29.0 mg, 56%) was recovered as a brown solid. The NMR data of 2c matched those of the racemic product above. [α]D²¹⁴ +170 (c 2.21, CHCl₃). Enantiomeric excess was determined by HPLC with a Chiralpak IA-3 column (80:20 hexane/i-PrOH, 1.0 mL/min, 230 nm, room temperature): tᵣ (major) = 7.3 min, tᵣ (minor) = 10.4 min; 90% ee.
Slow diffusion petroleum ether of into a solution of 2c in Et\textsubscript{2}O provided crystals that were suitable for X-ray diffraction, thus allowing confirmation of the absolute stereochemistry.

\[(6aR,11bS)-5-[(E)-Benzyldene]-11b-hydroxy-6a-methyl-5,6,6a,11b-tetrahydro-7H-benzo[c]fluoren-7-one (2i)\]
Supporting Information

acid (36.3 mg, 0.300 mmol), and KF (34.8 mg, 0.300 mmol) were added. This vial was sealed with a septum-lined cap and purged with nitrogen for 1 h. The solution of catalyst was added to the vial containing the alkynone under nitrogen. t-Amyl alcohol (33 µL, 0.30 mmol) was added and the mixture was stirred at 110 °C for 20 h. The reaction was cooled to room temperature, water (5 mL) and saturated aqueous NH₄Cl (5 mL) were added, and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (20 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (5% Et₂O/CH₂Cl₂) to give alcohol 2o (43.6 mg, 62%) as an orange solid. Alkynone 1i (35.0 mg, 35%) was recovered as a brown solid in >90% purity by ¹H NMR spectroscopy. The NMR data of 2i matched those of the racemic product above. [α]D²⁴₂ −24.2 (c 0.83, MeOH). Enantiomeric excess was determined by HPLC with a Chiralpak IA-3 column (90:10 hexane:i-PrOH, 0.8 mL/min, 230 nm, room temperature); tᵣ (major) = 13.6 min, tᵣ (minor) = 15.8 min; 91% ee
6. Semi-Quantitative ICP-MS Analysis

Samples were analyzed by ICP-MS using an Agilent 7500ce (with octopole reaction system), employing an rf forward power of 1540 W and reflected power of 1 W, with argon gas flows of 0.70 L min\(^{-1}\) and 0.15 L min\(^{-1}\) for carrier and makeup flows (1.5mm ID torch), respectively. Sample solutions were taken up into the Micro mist nebulizer by peripump at a rate of approximately 1.0 mL min\(^{-1}\). Skimmer and sample cones were made of nickel.

The instrument was operated in spectrum acquisition mode. Each mass was analyzed in semi quant mode (three points per unit mass). A 1000 fold and 100 fold dilution of the Merck Multielement standard VI were used to calculate a response curve across the mass range from 6-238 amu. Separate cross check standards were analyzed to confirm accuracy of the response curve calibration.

**Sample preparation:** Ketone X (22.8 mg, 0.101 mmol), phenylboronic acid (18.3 mg, 0.150 mmol), [Ir(cod)Cl]\(_2\) (1.0 mg, 0.0015 mmol), and KF (8.7 mg, 0.15 mmol), anhydrous toluene (1.0 mL) and \(t\)-BuOH (14.5 µL, 0.150 mmol) were added to an oven-dried microwave vial. The mixture was stirred and the volatiles were removed with a stream of nitrogen. The residue was dissolved in conc. HNO\(_3\) (1.5 mL) and the solution was diluted to a volume of 10 mL using deionized water. The organic precipitate was filtered and the filtrate was submitted to ICP-MS analysis.

| Element | Concentration (ppb) |
|---------|---------------------|
| Fe      | 130.0               |
| Co      | 4.5                 |
| Ni      | 29.0                |
| Cu      | 19.0                |
| Ru      | 0.2                 |
| Rh      | 3.0                 |
| Pd      | 62.0                |
| Ag      | 5.6                 |
| Ir      | 43000.0             |
| Pt      | 0.1                 |
| Au      | 0.2                 |

Table 1: ICP-MS analysis data (semi-quantitative).
7. **NMR Spectra**
Supporting Information
