**Supplementary Information**

**Rhodium-Catalyzed Arylative Cyclization of Alkynyl Malonates by 1,4-Rhodium(I) Migration**

Luke O’Bien,†‡ Somnath Narayan Karad,†‡ William Lewis,‡ and Hon Wai Lam*,†‡

†The GlaxoSmithKline Carbon Neutral Laboratories for Sustainable Chemistry, University of Nottingham, Jubilee Campus, Triumph Road, Nottingham, NG7 2TU, United Kingdom

‡School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom

**Supplementary Information**

1. General Information 2
2. Preparation of Substrates 3
3. Rhodium-Catalyzed Arylative Cyclization of Alkynyl Malonates 14
4. Enantioselective Cyclizations 31
5. Possible Catalytic Cycle 33
6. NMR Spectra 34
7. HPLC Traces 80
8. References 81
1. **General Information**

All air-sensitive reactions were carried out under an inert atmosphere using oven-dried apparatus. 1,4-Dioxane was purchased from Acros Organics and degassed before use using a stream of argon (30 min). All commercially available reagents were used as received unless otherwise stated. Petroleum ether refers to Sigma-Aldrich product 24587 (petroleum ether boiling point 40-60 °C). Thin layer chromatography (TLC) was performed on Merck DF-Alufoilien 60F254 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 gentle heating. Flash column chromatography was carried out using silica gel (Fisher Scientific 60 Å particle size 35-70 micron or Fluorochem 60 Å particle size 40-63 micron). Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. The solvent of recrystallization is reported in parentheses. Infrared (IR) spectra were recorded on Bruker platinum ALPHA FTIR spectrometer on the neat compound using the attenuated total refraction technique. NMR spectra were acquired on Bruker Ascend 400 or Ascend 500 spectrometers. $^1$H and $^{13}$C NMR spectra were referenced to external tetramethylsilane via the residual protonated solvent ($^1$H) or the solvent itself ($^{13}$C). $^{19}$F NMR spectra were referenced through the solvent lock ($^2$H) signal according to the IUPAC-recommended secondary referencing method following Bruker protocols. All chemical shifts are reported in parts per million (ppm). For CDCl$_3$, the shifts are referenced to 7.26 ppm for $^1$H NMR spectroscopy and 77.16 ppm for $^{13}$C NMR spectroscopy. $^{13}$C NMR assignments were made using the DEPT sequence with secondary pulses at 90° and 135°. Coupling constants ($J$) are quoted to the nearest 0.1 Hz. High-resolution mass spectra were recorded using electrospray ionization (ESI) techniques. X-ray diffraction data were collected at 120 K on an Agilent SuperNova díffractometer using CuKα radiation.
2. Preparation of Substrates

Known procedures were used for the preparation of S1, S2, S3, S4, S5, S6, and S7. Substrates 1a, 1b, 1f, 1h, 1p, 1q were prepared by known methods.
Preparation of Substrate 1c

**Bis(2,2,2-trifluoroethyl) 2-(2-thienylmethyl)malonate (S1c).** To a solution of *ortho*-phenylenediamine (1.88 g, 17.4 mmol) in EtOH (300 mL) at 25 °C were added 2-thienylcarboxaldehyde (3.24 mL, 34.7 mmol), Meldrum’s acid (2.51 g, 17.4 mmol), and L-proline (399 mg, 3.47 mmol). The resulting mixture was vigorously stirred for 24 h and concentrated *in vacuo* to leave a residue, which was dissolved in CH$_2$Cl$_2$ (200 mL) and washed with 1 M aqueous HCl solution (150 mL). The aqueous layer was extracted with CH$_2$Cl$_2$ (2 × 100 mL). The combined organic layers were washed with H$_2$O, dried (MgSO$_4$), filtered, and concentrated in *vacuo* to leave a residue (4.80 g), which was used directly in the next step without further purification. In a sealed vessel containing a stirrer bar, a solution of this crude compound (4.80 g) and concentrated H$_2$SO$_4$ (433 µL, 8.1 mmol) in TFE (45 mL) were stirred at 100 °C for 2 h. The reaction was cooled to room temperature, diluted with Et$_2$O (200 mL), and washed with saturated aqueous NaHCO$_3$ solution (3 × 100 mL), H$_2$O (100 mL), and brine (100 mL). The organic layer was dried (MgSO$_4$), filtered, and concentrated in *vacuo*. The residue was passed through a plug of silica gel using 2% EtOAc/petroleum ether as the eluent to give S1c (674 mg) as a yellow oil which was not pure, but which was used directly in the next step. $R_f = 0.30$ (10% EtOAc/petroleum ether).

**Bis(2,2,2-trifluoroethyl) 2-(3-phenylprop-2-yn-1-yl)-2-(2-thienylmethyl)malonate (1c).** A flask was charged with NaH (60% dispersion in mineral oil, 85.6 mg, 2.14 mmol), purged with argon for 30 min, and then suspended in THF (5 mL) at 0 °C. A proportion of impure malonate S1c (650 mg out of the 674 mg prepared as above) in THF (2 mL) was added to the ice-cooled suspension. The resulting solution was warmed to room temperature and stirred for 45 min. Alkynyl bromide S6 (80 wt. % in toluene, 868 µL, 3.56 mmol) was added dropwise and the resulting solution was stirred at room temperature for 3 h. The reaction was quenched with H$_2$O (25 mL), extracted with Et$_2$O (3 × 25 mL), and the combined organic layers were washed with brine (25 mL), dried (MgSO$_4$), filtered, and concentrated
in vacuo. The residue was purified by column chromatography (0% to 2% EtOAc/petroleum ether) to give the title compound 1c (950 mg, 12% over two steps) as an orange oil. Rf = 0.30 (10% EtOAc/petroleum ether); IR 1758 (C=O), 1411, 1279, 1157, 1067, 972, 906, 756, 690, 531 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.43 (2H, dd, J = 6.7, 3.0 Hz, ArH), 7.34-7.30 (3H, m, ArH), 7.21 (1H, dd, J = 5.0, 1.2 Hz, ArH), 7.00-6.92 (2H, m, ArH), 4.63-4.46 (4H, m, 2 × CH₂CF₃), 3.76 (2H, s, CH₃CS), 3.08 (2H, s, CH₂C≡C); ¹³C NMR (101 MHz, CDCl₃) δ 167.4 (2 × C), 135.5 (C), 131.9 (2 × CH), 128.5 (CH), 128.3 (2 × CH), 127.4 (CH), 125.6 (CH), 122.8 (C), 122.6 (q, JcF = 277.4 Hz, 2 × C), 85.3 (C), 82.7 (C), 61.6 (q, JcF = 37.4 Hz, 2 × CH₂), 58.6 (C), 32.1 (CH₂), 23.6 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ −73.8 (t, J = 8.2 Hz, 6 × F); HRMS (ESI) Exact mass calculated for [C₂₁H₁₆F₆NaO₄S]⁺ [M+Na]⁺: 501.0568, found 501.0566.

**Preparation of Substrate 1d**

Bis(2,2,2-trifluoroethyl) 2-(3-phenylprop-2-yln-1-yl)malonate (S₁d). A flask was charged with NaH (60% dispersion in mineral oil, 251 mg, 6.28 mmol), purged with argon for 30 min, and then suspended in THF (25 mL) at 0 °C. A solution of bis(2,2,2-trifluoroethyl) malonate (3.00 g, 11.2 mmol) in THF (5 mL) was added to the ice-cooled suspension. The resulting solution was stirred at 0 °C for 45 min. Alkynyl bromide S₆ (80 wt. % solution in toluene, 1.82 mL, 7.47 mmol) was added dropwise and the resulting solution was stirred at room temperature for 3 d. The reaction was quenched with H₂O (30 mL), extracted with Et₂O (3 × 30 mL), and the combined organic layers were washed with brine (50 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0% to 1% EtOAc/petroleum ether) to give the title compound S₁d (978 mg, 41%) as a yellow oil. Rf = 0.26 (10% EtOAc/petroleum ether); IR 1756 (C=O), 1492, 1280, 1158, 1067, 965, 757, 691, 659, 535 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.34 (2H, m, ArH), 7.32-7.27 (3H, m, ArH), 4.58 (4H, q, J = 8.2 Hz, 2 × CH₂CF₃), 3.91 (1H, t, J = 7.6 Hz, CH₂CH), 3.09 (2H, d, J = 7.6 Hz, CH₂C≡C); ¹³C NMR (101 MHz, CDCl₃) δ 165.9 (2 × C), 131.8 (2 × CH), 128.4 (CH), 128.4 (2 × CH), 122.8 (C), 122.6 (q, JcF = 277.4 Hz, 2 × C), 83.7 (C), 83.5 (C), 61.5 (q, JcF = 37.4 Hz, 2 × CH₂), 50.7 (CH), 19.5 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ −73.5 (t, J = 8.3 Hz, 6 × F); HRMS (ESI) Exact mass calculated for [C₁₆H₁₂F₆NaO₄S]⁺ [M+Na]⁺: 405.0537, found 405.0535.
**Bis(2,2,2-trifluoroethyl) 2-(2-oxo-2-phenylethyl)-2-(3-phenylprop-2-yn-1-yl)malonate (1d).** A flask was charged with NaH (60% dispersion in mineral oil, 66 mg, 1.65 mmol), purged with argon for 30 min, and then suspended in THF (15 mL) at 0 °C. A solution of malonate S1d (500 mg, 1.31 mmol) in THF (3 mL) was added to the ice-cooled suspension. The resulting solution was stirred at 0 °C for 45 min. A solution of 2-bromoacetoephone (521 mg, 2.62 mmol) in THF (3 mL) was added dropwise and the resulting solution was stirred at room temperature for 24 h. The reaction was quenched with H2O (20 mL), extracted with Et2O (3 × 20 mL), and the combined organic layers were washed with brine (25 mL), dried (MgSO4), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0% to 5% EtOAc/petroleum ether) to give the title compound 1d (385 mg, 59%) as a white solid. Rf = 0.31 (20% EtOAc/petroleum ether); m.p. 91-92 °C (Et2O); IR 2921, 1754 (C=O), 1593 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 8.05-7.97 (2H, m, ArH), 7.65-7.57 (1H, m, ArH), 7.53-7.46 (2H, m, ArH), 7.33-7.26 (5H, m, ArH), 4.68-4.49 (4H, m, 2 × CH2CF3), 4.02 (2H, s, CH2C=O), 3.38 (2H, s, CH2C≡C); 13C NMR (101 MHz, CDCl3) δ 196.4 (C), 167.5 (2 × C), 136.3 (C), 134.0 (CH), 131.8 (2 × CH), 129.0 (2 × CH), 128.5 (CH), 128.4 (2 × CH), 128.3 (2 × CH), 122.7 (C), 122.7 (q, JCF = 277.4 Hz, 2 × C), 84.9 (C), 83.0 (C), 61.7 (q, JCF = 37.4 Hz, 2 × CH2), 55.2 (C), 41.4 (CH2), 24.6 (CH2); 19F NMR (376 MHz, CDCl3) δ -73.8 (t, J = 8.2 Hz, 6 × F); HRMS (ESI) Exact mass calculated for [C2dH18F6NaO3]+ [M+Na]+: 523.0951, found 523.0951.

**1-Phenyl 2,2-bis(2,2,2-trifluoroethyl) 5-phenylpent-4-ynyl-1,2,2-tricarboxylate (1e).**

A flask was charged with NaH (60% dispersion in mineral oil, 53 mg, 1.26 mmol), purged with argon for 30 min, and then suspended in THF (15 mL) at 0 °C. A solution of malonate S1d (400 mg, 1.05 mmol) in THF (3 mL) was added to the ice-cooled suspension. The resulting solution was stirred at 0 °C for 45 min. A solution of phenyl bromoacetate (452 mg, 2.10 mmol) in THF (3 mL) was added dropwise and the resulting solution was stirred at room temperature for 16 h. The reaction was quenched with H2O (30 mL), extracted with Et2O (3 × 20 mL), and the combined organic layers were washed with brine (25 mL), dried (MgSO4), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0% to 4% EtOAc/petroleum ether) to give the title compound 1e (481 mg, 89%) as a pale yellow oil. Rf = 0.28 (20% EtOAc/petroleum ether); IR 1755 (C=O), 1593...
Supplementary Information

(C=O), 1411, 1281, 1160, 1065, 973, 756, 689, 496 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.35 (4H, m, ArH), 7.34-7.28 (3H, m, ArH), 7.25-7.21 (1H, m, ArH), 7.11-7.05 (2H, m, ArH), 4.65-4.51 (4H, m, 2 × CH₂CF₃), 3.56 (2H, s, CH₂C=O), 3.35 (2H, s, CH₂C≡C); ¹³C NMR (101 MHz, CDCl₃) δ 168.8 (C), 167.0 (2 × C), 150.3 (C), 131.9 (2 × CH), 129.7 (2 × CH), 128.7 (CH), 128.5 (2 × CH), 126.4 (CH), 122.6 (q, J<sub>C-F</sub> = 277.4 Hz, 2 × C), 122.6 (C), 121.5 (2 × CH), 85.2 (C), 82.2 (C), 61.9 (q, J<sub>C-F</sub> = 37.2 Hz, 2 × CH₂), 55.5 (C), 37.4 (CH₂), 25.0 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ -73.8 (t, J = 8.2 Hz, 6 × F); HRMS (ESI) Exact mass calculated for [C₂₃H₁₄F₆NaO₆]⁺ [M+Na]⁺: 539.0905, found 539.0906.

Preparation of Substrate 1g

Bis(2,2,2-trifluoroethyl) 2-(2-methoxyphenyl)malonate (S1g). To a stirred solution of diethyl 2-(2-methoxyphenyl)malonate (S3, 4.65 g, 17.5 mmol) in Et₂O (32 mL) at 0 °C was added a solution of NaOH (2.79 g, 69.9 mmol) in H₂O (60 mL) and the resulting mixture was stirred vigorously at room temperature for 24 h. The aqueous layer was separated and washed with Et₂O (2 × 50 mL), acidified to pH 2 with 6 M aqueous HCl solution, and extracted with EtOAc (5 × 50 mL). The combined organic extracts were washed with brine (50 mL), dried (MgSO₄), filtered, and concentrated in vacuo to leave the malonic acid as an off-white solid (3.31 g) that was used in the next step without further purification. A microwave vial fitted with a stirrer bar was charged with this malonic acid (3.31 g, 15.8 mmol), TFE (20 mL), benzene (20 mL) and concentrated H₂SO₄ (335 µL, 6.30 mmol). The vial was then capped with a crimp capped PTFE seal and concentrated in vacuo to leave the malonic acid as a white solid (2.20 g, 34% over two steps) as a brown oil. R<sub>f</sub> = 0.33 (10% EtOAc/petroleum ether); IR 1771 (C=O), 1747, 1416, 1254, 1135, 955, 865, 749, 654, 543 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.34 (1H, m, ArH), 7.28 (1H, dd, J = 7.7, 1.7 Hz, ArH), 6.99 (1H, td, J = 7.6, 1.1 Hz, ArH), 6.93 (1H, dd, J = 8.3, 1.1 Hz, ArH), 5.28 (1H, s, ArCH), 4.59-4.52 (4H, m, 2 × CH₂CF₃), 3.83 (3H, s, OCH₃); ¹³C NMR (101 MHz, CDCl₃) δ 166.5 (2 × C), 157.0 (C), 130.4 (CH), 129.5 (CH), 122.7 (q, J<sub>C-F</sub> = 277.3 Hz, 2 × C), 121.0 (CH), 120.0 (C), 111.0
(CH), 61.3 (q, J_{C,F} = 37.3 Hz, 2 × CH₂), 55.7 (CH), 50.8 (CH₃); ¹⁹F NMR (376 MHz, CDCl₃) δ –73.9 (t, J = 8.3 Hz, 6 × F); HRMS (ESI) Exact mass calculated for [C₁₄H₁₂F₆OsNa]⁺ [M+Na]⁺: 397.0481, found 397.0483.

**Bis(2,2,2-trifluoroethyl) 2-(2-methoxyphenyl)-2-(3-phenylprop-2-yn-1-yl)malonate (1g)**. A solution of malonate S₁g (1.00 g, 2.67 mmol) in DMF (3 mL) was added to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 128.2 mg, 3.21 mmol) in DMF (7 mL). The resulting solution was warmed to room temperature and stirred for 30 min. Alkynyl bromide S₆⁶ (80 wt. % in toluene, 1.30 mL, 5.34 mmol) was added dropwise and the resulting solution was warmed to 60 °C and stirred for 2 h. The reaction was cooled to room temperature and quenched with saturated aqueous NH₄Cl solution (50 mL). This solution was extracted with EtOAc (3 × 50 mL), and the combined organic layers were dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0% to 2% EtOAc/petroleum ether) to give title compound 1g (951 mg, 73%) as a yellow oil. R₇ = 0.27 (10% EtOAc/petroleum ether); IR 2973, 1756 (C=O), 1493, 1282, 1155, 972, 753, 692, 651, 556 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.47–7.31 (2H, m, ArH); 7.25–7.23 (5H, m, ArH), 7.01 (1H, td, J = 8.3, 1.2 Hz, ArH), 6.92 (1H, dd, J = 8.2, 1.2 Hz, ArH), 4.63–4.50 (4H, m, 2 × CH₂CF₃), 3.78 (3H, s, OCH₃), 3.47 (2H, s, CH₂C=C); ¹³C NMR (101 MHz, CDCl₃) δ 167.8 (2 × C), 156.6 (C), 131.7 (2 × CH), 130.1 (CH), 128.6 (CH), 128.3 (2 × CH), 128.1 (CH), 124.7 (C), 123.3 (C), 122.8 (q, J_{C,F} = 277.5 Hz, 2 × C), 120.8 (CH), 111.3 (CH), 84.9 (C), 83.7 (C), 61.5 (q, J_{C,F} = 37.1 Hz, 2 × CH₂), 60.8 (C), 55.6 (CH₃), 26.5 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ –73.6 (t, J = 8.3 Hz, 6 × F); HRMS (ESI) Exact mass calculated for [C₂₃H₂₂F₆NO₅]+ [M+NH₄]⁺: 506.1398, found 506.1397.

**Bis(2,2,2-trifluoroethyl) 2-(3-phenylprop-2-yn-1-yl)-2-(3-thienyl)malonate (1i)**

A sealed tube was charged with the 3-thienylmalonic acid (2.50 g, 13.4 mmol), concentrated H₂SO₄ (163 µL, 2.69 mmol), TFE (30 mL), and a stirrer bar. The mixture was then stirred at 100 °C for 1.5 h. The reaction was cooled to room temperature and diluted with Et₂O (200 mL). The solution was then washed with saturated aqueous NaHCO₃ solution (3 × 100 mL), H₂O (100 mL), and brine (100 mL). The organic layer was dried (MgSO₄) and concentrated in vacuo. The residual solvent was removed under high vacuum to leave the crude malonate ester S₁i (2.52 g), which was used in the next step without further purification. A solution of this malonate ester in THF (5 mL) was added to
an ice-cooled suspension of NaH (60% dispersion in mineral oil, 864 mg, 21.6 mmol) in THF (20 mL). The resulting solution was warmed to room temperature and stirred for 30 min. Alkynyl bromide S6 (80 wt. % in toluene, 5.27 mL, 21.6 mmol) was added dropwise and the resulting solution was warmed to 60 °C and stirred for 18 h. The reaction was cooled to room temperature and quenched with saturated aqueous NH₄Cl solution (50 mL). This solution was extracted with EtOAc (3 × 50 mL), and the combined organic layers were dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0% to 2% EtOAc/petroleum ether) to give title compound 1i (908 mg, 14% over two steps) as a pale brown solid. RF = 0.25 (7% EtOAc/petroleum ether); IR 1757 (C=O), 1415, 1241, 1157, 1085, 1009, 974, 762, 696, 625 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.58 (1H, dd, J = 3.0, 1.4 Hz, ArH), 7.37-7.23 (7H, m, ArH), 4.66-4.55 (4H, m, 2 × CH₂CF₃), 3.49 (2H, s, CH₂C≡C); ¹³C NMR (101 MHz, CDCl₃) δ 167.1 (2 × C), 133.8 (C), 131.8 (2 × CH), 128.43 (CH), 128.36 (2 × CH), 127.4 (CH), 126.8 (CH), 124.7 (CH), 122.8 (C), 122.6 (q, JCF = 277.3 Hz, 2 × C), 84.8 (C), 83.2 (C), 61.6 (q, JCF = 37.4 Hz, 2 × CH₂), 59.7 (C), 27.5 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ −73.7 (t, J = 8.1 Hz, 6 × F); HRMS (ESI) Exact mass calculated for [C₂₀H₁₄F₆O₄SNa]⁺ [M+Na]⁺: 487.0409, found 487.0414.

**Preparation of Substrate 1j**

**Bis(2,2,2-trifluoroethyl) 2-benzyl-2-(prop-2-yn-1-yl)malonate (S1j).** A flask was charged with NaH (60% dispersion in mineral oil, 844 mg, 21.1 mmol), purged with argon for 30 min, and then suspended in THF (200 mL) at 0 °C. A solution malonate S2 (6.00 g, 16.7 mmol) in THF (20 mL) was added to the ice-cooled suspension. The resulting solution was stirred at 0 °C for 45 min. Propargyl bromide (80 wt. % in toluene, 3.58 mL, 24.1 mmol) was added dropwise and the resulting solution was stirred at room temperature for 16 h. The reaction was quenched with H₂O (150 mL), extracted with Et₂O (3 × 120 mL), and the combined organic layers were washed with brine (150 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0% to 1% EtOAc/petroleum ether) to give the title compound S1j (2.01 g, 30%) as a pale yellow oil. RF = 0.33 (10% EtOAc/petroleum ether); IR 1756 (C=O), 1412, 1281, 1155, 1086, 994, 908, 742, 702, 648 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.27 (3H, m, ArH), 7.20-7.10 (2H, m, ArH), 4.61-4.43 (4H, m, 2 × CH₂CF₃), 3.47 (2H, s, CH₂Ph), 2.76 (2H, d, J = 2.7 Hz, CH₂C≡C), 2.21 (1H, t, J = 2.6 Hz,
Bis(2,2,2-trifluoroethyl) 2-benzyl-2-[3-(4-methoxyphenyl)prop-2-yn-1-yl]malonate (1j). A flask was charged with CuI (24.0 mg, 0.13 mmol), Pd(PPh₃)₂Cl₂ (44.2 mg, 0.06 mmol), 4-iodoanisole (591 mg, 2.52 mmol) and purged with argon for 20 min. Freshly degassed (purging with argon for 30 min) THF (25 mL), and Et₃N (1.05 mL, 6.30 mmol) were added and the mixture was degassed with a stream of argon for 15 min. Malonate S1j (500 mg, 1.26 mmol) was added and the mixture was stirred at room temperature for 18 h. The reaction was quenched with saturated aqueous NH₄Cl solution (10 mL), extracted with EtOAc (3 × 20 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0% to 3% EtOAc/petroleum ether) to give the title compound 1j (345 mg, 54%) as a yellow oil. Rf = 0.29 (10% EtOAc/petroleum ether); IR 2969, 1757 (C=O), 1510, 1443, 1284, 973, 742, 535 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.35 (2H, m, ArH), 7.33-7.27 (3H, m, ArH), 7.20 (2H, dd, J = 7.5, 1.9 Hz, ArH), 6.98 (1H, dd, J = 5.2, 3.6 Hz, ArH), 6.88-6.83 (2H, m, ArH), 4.60-4.51 (4H, m, 2 × CH₂CF₃), 3.82 (3H, s, OCH₃), 3.51 (2H, s, CH₂Ph), 2.96 (2H, s, CH₂C≡C); ¹³C NMR (101 MHz, CDCl₃) δ 167.8 (2 × C), 159.8 (C), 134.5 (C), 133.3 (2 × CH), 130.0 (2 × CH), 128.9 (2 × CH), 127.8 (CH), 122.6 (q, Jₐ-C = 277.4 Hz, 2 × C), 115.0 (C), 114.1 (2 × CH), 85.2 (C), 81.5 (C), 61.4 (q, Jₐ-C = 37.3 Hz, 2 × CH₂), 58.8 (C), 55.5 (CH₃), 37.6 (CH₂), 23.4 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ -73.7 (t, J = 8.2 Hz, 6 × F); HRMS (ESI) Exact mass calculated for [C₂H₂O₆NaO₅]+ [M+Na]+: 525.1108, found 525.1107.

Bis(2,2,2-trifluoroethyl) 2-benzyl-2-(3-(3-methylphenyl)prop-2-yn-1-yl)malonate (1k)

A flask was charged with NaH (60% dispersion in mineral oil, 141 mg, 3.53 mmol), purged with argon for 30 min, and then suspended in THF (15 mL) at 0 °C. A solution of malonate S2² (1.00 g, 2.79 mmol) in THF (3 mL) was added to the ice-cooled suspension. The resulting solution was stirred at 0 °C for 45 min. Alkynyl bromide S7 (72 wt. % in toluene, 1.48 mL, 5.58 mmol) was added dropwise and the resulting solution was stirred at 50 °C for 18 h. The reaction was quenched with
H₂O (20 mL), extracted with Et₂O (3 × 20 mL), and the combined organic layers were washed with brine (25 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0% to 1% EtOAc/petroleum ether) to give the title compound 1k (870 mg, 64%) as a pale yellow oil. Rf = 0.36 (10% EtOAc/petroleum ether); IR 1757 (C=O), 1486, 1282, 1155, 1085, 974, 784, 742, 702, 651 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.27 (3H, m, ArH), 7.25-7.18 (5H, m, ArH), 7.15 (1H, d, J = 7.4 Hz, ArH), 4.58-4.50 (4H, m, 2 × CH₂CF₃), 3.53 (2H, s, CH₂Ph), 2.98 (2H, s, CH₂C≡C), (3H, s, CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 167.7 (2 × C), 138.2 (C), 134.4 (C), 132.4 (CH), 130.0 (2 × CH), 129.4 (CH), 129.0 (CH), 128.9 (2 × CH), 128.4 (CH), 127.8 (CH), 122.7 (C), 122.7 (q, JCF = 277.2 Hz, 2 × C), 85.5 (C), 82.56 (C), 61.4 (q, JCF = 37.4 Hz, 2 × CH₂), 58.8 (C), 37.6 (CH₂), 23.4 (CH₂), 21.4 (CH₃); ¹⁹F NMR (376 MHz, CDCl₃) δ −73.7 (t, J = 8.2 Hz, 6 × F); HRMS (ESI) Exact mass calculated for [C₂₄H₂₈F₆NaO₄]+ [M+Na]+: 509.1158, found 509.1158.

**Bis(2,2,2-trifluoroethyl) 2-benzyl-2-(3-(naphthalen-1-yl)prop-2-yn-1-yl)malonate (1l)**

A flask was charged with CuI (24.0 mg, 0.13 mmol) and Pd(PPh₃)₂Cl₂ (44.2 mg, 0.06 mmol), and was then purged with argon for 20 min. Freshly degassed (purging with argon for 30 min) THF (25 mL), and Et₃N (1.05 mL, 6.30 mmol) were added and the mixture was degassed with a stream of argon for 15 min. Malonate S1j (500 mg, 1.26 mmol) and 1-iodonaphthalene (0.37 mL, 2.52 mmol) were added and the mixture was stirred at room temperature for 40 h. The reaction was quenched with saturated aqueous NH₄Cl solution (10 mL), extracted with EtOAc (3 × 20 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0% to 5% EtOAc/petroleum ether) to give the title compound 1l (426 mg, 65%) as a yellow oil. Rf = 0.39 (10% EtOAc/petroleum ether); IR 1755 (C=O), 1218, 1148, 1085, 968, 841, 800, 701, 652, 523 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.32-8.29 (1H, m, ArH), 7.88-7.83 (2H, m, ArH), 7.69 (1H, dd, J = 7.2, 1.2 Hz, ArH), 7.60 (1H, ddd, J = 8.3, 6.9, 1.4 Hz, ArH), 7.53 (1H, ddd, J = 8.2, 6.8, 1.4 Hz, ArH), 7.44 (1H, dd, J = 8.3, 7.1 Hz, ArH), 7.35-7.29 (3H, m, ArH), 7.26-7.23 (2H, m, ArH), 4.63-4.50 (4H, m, 2 × CH₂CF₃), 3.62 (2H, s, CH₂Ph), 3.16 (2H, s, CH₂C≡C); ¹³C NMR (101 MHz, CDCl₃) δ 167.8 (2 × C), 134.4 (C), 133.5 (C), 133.3 (C), 130.9 (CH), 130.0 (2 × CH), 129.0 (CH), 128.9 (2 × CH), 128.5 (CH), 127.9 (CH), 127.0 (CH), 126.6 (CH), 126.1 (CH), 125.3 (CH), 122.7 (q, JCF = 277.3 Hz, 2 × C), 120.5 (C), 87.9 (C), 83.4 (C), 61.5 (q, JCF = 37.4 Hz, 2 × CH₂), 58.8 (C), 37.8 (CH₂), 23.8
Bis(2,2,2-trifluoroethyl) 2-benzyl-2-(3-(2-thienyl)prop-2-yn-1-yl)malonate (1m)

A flask was charged with CuI (24.0 mg, 0.13 mmol) and Pd(PPh₃)₂Cl₂ (44.2 mg, 0.06 mmol), and was then purged with argon for 20 min. Freshly degassed (purging with argon for 30 min) THF (25 mL), and Et₃N (1.05 mL, 6.30 mmol) were added and the mixture was degassed with a stream of argon for 15 min. Malonate S1j (500 mg, 1.26 mmol) and 2-iodothiophene (0.28 mL, 2.52 mmol) were added and the mixture was stirred at room temperature for 18 h. The reaction was quenched with saturated aqueous NH₄Cl solution (10 mL), extracted with EtOAc (3 × 20 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0% to 1% EtOAc/petroleum ether) to give the title compound 1m (591 mg, 98%) as an orange oil. R_f = 0.35 (10% EtOAc/petroleum ether); IR 1754 (C=O), 1443, 1279, 1159, 1073, 972, 883, 700, 528 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.28 (3H, m, ArH), 7.26-7.24 (1H, m, ArH), 7.22-7.17 (3H, m, ArH), 6.98 (1H, dd, J = 5.2, 3.6 Hz, ArH), 4.59-4.50 (4H, m, 2 × CH₂CF₃), 3.50 (2H, s, CH₂Ph), 3.00 (2H, s, CH₂C≡C); ¹³C NMR (101 MHz, CDCl₃) δ 167.6 (2 × C), 134.3 (C), 132.3 (CH), 130.0 (2 × CH), 128.9 (2 × CH), 127.9 (CH), 127.2 (CH), 127.1 (CH), 122.7 (C), 122.6 (q, J_C-F = 277.4 Hz, 2 × C), 87.1 (C), 78.4 (C), 61.5 (q, J_C-F = 37.4 Hz, 2 × CH₂), 58.7 (C), 37.7 (CH₂), 23.7 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ –73.6 (t, J = 8.3 Hz, 6 × F); HRMS (ESI) Exact mass calculated for [C₇H₁₅F₆NO₄]⁺ [M+Na]⁺: 501.0565, found 501.0566.

2,2-Dimethyl 1-phenyl 5-phenylpent-4-yne-1,2,2-tricarboxylate (1n)

A solution of malonate S4⁴ (2.00 g, 8.12 mmol) in THF (10 mL) was added over 10 min to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 389.7 mg, 9.75 mmol) in THF (40 mL). The resulting solution was warmed to room temperature, stirred for 45 min and recooled to 0 °C. A solution of phenyl 2-bromoacetate (2.62 g, 12.2 mmol) in THF (10 mL) was added dropwise and the resulting solution was stirred at 0 °C for 2.5 h. The reaction was quenched with saturated aqueous
NH$_4$Cl solution (50 mL). This mixture was extracted with EtOAc (3 × 50 mL), and the combined organic layers were washed with H$_2$O (50 mL), brine (50 mL), dried (MgSO$_4$), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0% to 5% EtOAc/petroleum ether) to give the title compound In (2.34 g, 76%) as a colorless oil. R$_f$ = 0.26 (10% EtOAc/petroleum ether); IR 2953, 1750 (C=O), 1727 (C=O), 1491, 1431, 1275, 1192, 1080, 756, 690 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42-7.35 (4H, m, ArH), 7.32-7.21 (4H, m, ArH), 7.12-7.08 (2H, m, ArH), 3.81 (6H, s, 2 × OCH$_3$), 3.51 (2H, s, CH$_2$C=O), 3.31 (2H, s, CH$_2$C=O); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.5 (2 × C), 169.2 (C), 150.5 (C), 138.8 (2 × CH), 129.6 (2 × CH), 128.4 (2 × CH), 128.3 (CH), 126.1 (CH), 123.0 (C), 121.6 (2 × CH), 84.4 (C), 83.9 (C), 55.5 (C), 53.4 (2 × CH$_3$), 37.5 (CH$_2$), 24.9 (CH$_2$); HRMS (ESI) Exact mass calculated for [C$_{22}$H$_{20}$NaO$_6$]$^+$ [M+Na]$^+$: 403.1152, found 403.1155.

**Diphenyl 2-methyl-2-(3-phenylprop-2-yn-1-yl)malonate (1o)**

![Chemical Structure]

A flask was charged with NaH (60% dispersion in mineral oil, 177 mg, 4.43 mmol), purged with argon for 30 min, and then suspended in THF (14 mL) at 0 °C. A solution of diphenyl 2-methylmalonate S5 (1.00 g, 3.70 mmol) in THF (4 mL) was added to the ice-cooled suspension. The resulting solution was stirred at 0 °C for 45 min. Alkynyl bromide S6 (80 wt. % in toluene, 978 µL, 4.01 mmol) was added dropwise and the resulting solution was stirred at room temperature for 3 h. The reaction was quenched with H$_2$O (25 mL), extracted with Et$_2$O (3 × 25 mL), and the combined organic layers were washed with brine (25 mL), dried (MgSO$_4$), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0% to 2% EtOAc/petroleum ether) to give the title compound 1o (950 mg, 67%) as a white solid. R$_f$ = 0.27 (10% EtOAc/petroleum ether); m.p. 81-82 °C (Et$_2$O); IR 3060, 1749 (C=O), 1590, 1488, 1193, 1158, 1085, 915, 743, 687 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44-7.38 (6H, m, ArH), 7.33-7.25 (5H, m, ArH), 7.18-7.14 (4H, m, ArH), 3.30 (2H, s, CH$_2$C≡C), 1.91 (3H, s, CH$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.5 (2 × C), 150.7 (2 × C), 131.9 (2 × CH), 129.8 (4 × CH), 128.4 (2 × CH), 128.3 (CH), 126.4 (2 × CH), 123.1 (C), 121.4 (4 × CH), 84.2 (C), 84.1 (C), 54.2 (C), 27.2 (CH$_2$), 20.3 (CH$_3$); HRMS (ESI) Exact mass calculated for [C$_{25}$H$_{20}$NaO$_4$]$^+$ [M+Na]$^+$: 407.1254, found 407.1263.
Supplementary Information

Bis(2,2,2-trifluoroethyl) 2-benzyl-2-(but-2-yn-1-yl)malonate (1r)

A flask was charged with NaH (60% dispersion in mineral oil, 83.6 mg, 2.09 mmol), purged with argon for 30 min, and then suspended in THF (12 mL) at 0 °C. A solution of malonate S2 (500 mg, 1.40 mmol) in THF (3 mL) was added to the ice-cooled suspension. The resulting solution was stirred at 0 °C for 45 min. 1-Bromo-2-butyne (183 μL, 2.09 mmol) was added dropwise and the resulting solution was stirred at 50 °C for 16 h. The reaction was quenched with H2O (25 mL), extracted with Et2O (3 × 25 mL), and the combined organic layers were washed with brine (25 mL), dried (MgSO4), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0% to 1% EtOAc/petroleum ether) to give the title compound 1r (444 mg, 77%) as a pale yellow oil. Rf = 0.49 (10% EtOAc/petroleum ether); IR 1756 (C=O), 1497, 1412, 1282, 1158, 1085, 965, 743, 702, 651 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 7.31-7.25 (3H, m, ArH), 7.16-7.14 (2H, m, ArH), 4.58-4.43 (4H, m, 2 × CH2CF3), 3.43 (2H, s, CH2Ph), 2.70 (2H, q, J = 2.4 Hz, CH2C≡C), 1.84 (3H, t, J = 2.5 Hz, CH3); 13C NMR (101 MHz, CDCl3) δ 167.9 (2 × C), 134.6 (C), 129.9 (2 × CH), 128.8 (2 × CH), 127.7 (CH), 122.7 (q, J_{C:F} = 277.3 Hz, 2 × C), 80.8 (C), 72.5 (C), 61.4 (q, J_{C:F} = 37.3 Hz, 2 × CH2), 58.8 (C), 37.4 (CH2), 22.8 (CH2), 3.6 (CH3); 19F NMR (376 MHz, CDCl3) δ −73.7 (t, J = 8.1 Hz, 6 × F); HRMS (ESI) Exact mass calculated for [C18H20F6NO4]+ [M+NH4]+: 428.1291, found 428.1289.

3. Rhodium-Catalyzed Arylative Cyclization of Alkynyl Malonates

General Procedure A

An oven-dried microwave vial fitted with a stirrer bar was charged with the appropriate substrate 1 (0.30 mmol), the appropriate arylboronic acid (0.45 mmol), KF (26.1 mg, 0.45 mmol) and [Rh(cod)Cl]2 (7.4 mg, 0.015 mmol). The vial was sealed with a septum-lined cap and purged with argon for 30 min. 1,4-Dioxane (2.7 mL) and H2O (0.3 mL), both of which were freshly degassed separately (purging with argon for 30 min) were added. The mixture was stirred at 70 °C for 20 h. The reaction was cooled to room temperature, H2O (15 mL) was added, and the mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (20 mL), dried
Supplementary Information

(E)-2-benzyl-4-benzyldiene-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2aa), bis(2,2,2-trifluoroethyl) (E)-2-benzyl-2-(2,3-diphenylallyl)malonate (3aa), and bis(2,2,2-trifluoroethyl) 2-benzyl-2-(3,3-diphenylallyl)malonate (3ab)

General Procedure A was followed using malonate ester 1a (236 mg, 0.50 mmol) and phenylboronic acid (91.4 mg, 0.75 mmol). Purification by column chromatography (0% to 1% EtOAc/n-pentane) gave a 1:1.25 mixture of inseparable alkyne hydroarylation products 3aa and 3ab, respectively (53.4 mg, 19%) as a yellow oil followed by arylative cyclization product 2aa (152 mg, 67%) as a yellow oil.

Data for 2aa: Rf = 0.32 (10% EtOAc/petroleum ether); IR 2922, 1742 (C=O), 1685 (C=O), 1454, 1273, 1156, 925, 848, 760, 656 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.13 (1H, dd, J = 7.9, 1.4 Hz, ArH), 7.77 (1H, dd, J = 8.1, 1.1 Hz, ArH), 7.60 (1H, ddd, J = 8.3, 7.2, 1.5 Hz, ArH), 7.45-7.40 (4H, m, ArH), 7.36-7.33 (3H, m, ArH and =CHPh), 7.17-7.09 (5H, m, ArH), 4.48 (1H, dq, J = 12.7, 8.4 Hz, CH₂H₂CF₃), 4.26 (1H, dq, J = 12.7, 8.4 Hz, CH₂H₂CF₃), 3.66 (1H, dd, J = 14.6, 1.4 Hz, =CCH₃H₃), 3.40 (1H, d, J = 13.7 Hz, CH₂H₂Ph), 3.25 (1H, d, J = 13.7 Hz, CH₂H₂Ph), 3.04 (1H, dd, J = 14.6, 1.6 Hz, =CCH₃H₃); ¹³C NMR (101 MHz, CDCl₃) δ 193.6 (C), 169.9 (C), 141.1 (C), 136.7 (C), 135.4 (C), 134.3 (CH), 131.0 (C), 130.8 (2 × CH), 130.3 (C), 129.8 (CH), 129.2 (2 × CH), 128.6 (2 × CH), 128.6 (CH), 128.4 (CH), 128.2 (2 × CH), 127.8 (CH), 127.0 (CH), 124.5 (CH), 122.7 (q, J_C,F = 277.6 Hz, C), 61.0 (q, J_C,F = 36.9 Hz, CH₂), 60.3 (C), 38.8 (CH₂), 34.1 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ −73.5 (t, J = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C₂₇H₂₁F₃NaO₃]⁺ [M+Na]⁺: 473.1332, found 473.1335.

Data for 1:1.25 mixture of 3aa and 3ab, respectively: Rf = 0.38 (10% EtOAc/petroleum ether); IR 3029, 1751 (C=O), 1413, 1280, 1155, 1086, 961, 767, 699, 649 cm⁻¹; ¹⁹F NMR (376 MHz, CDCl₃) δ −73.5 (−73.6) (m, 6 × F for each of 3aa and 3ab); HRMS (ESI) Exact mass calculated for [C₂₉H₂₃F₆NO₄]⁺ [M+NH₄]⁺: 568.1917, found 568.1921.

Characteristic signals for minor regioisomer 3aa: ¹H NMR (400 MHz, CDCl₃) δ 6.82 (1H, s, =CH), 6.76-6.73 (2H, m, ArH), 3.94-3.85 (2H, m, CH₂CF₃), 3.80-3.72 (2H, m, CH₂CF₃), 3.68 (2H, s, CH₃Ph), 3.05 (2H, s, CH₂C=CH), [9 × ArH concealed within the multiplet 7.43-7.28 and 4 × ArH concealed within the multiplet 7.35-7.14].

(MgSO₄), filtered, and concentrated in vacuo. The residue was purified by column chromatography using EtOAc/n-pentane to give the arylative cyclization product 2.
concealed within the multiplet at 7.23-7.01 ppm; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 168.5 (2 \(\times\) C), 142.7 (C), 137.5 (C), 137.2 (C), 135.4 (CH), 135.3 (C), 130.0 (2 \(\times\) CH), 129.2 (2 \(\times\) CH), 128.9 (2 \(\times\) CH), 128.3 (2 \(\times\) CH), 128.2 (2 \(\times\) CH), 128.0 (2 \(\times\) CH), 127.8 (2 \(\times\) CH), 127.4 (CH), 127.2 (CH), 122.6 (q, \(J_{C,F} = 276.3\) Hz, 2 \(\times\) C), 61.1 (q, \(J_{C,F} = 37.1\) Hz, 2 \(\times\) CH\(_2\)), 59.1 (C), 38.7 (CH\(_2\)), 34.0 (CH\(_2\)).

Data for major regioisomer 3ab: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.93-6.91 (2H, m, ArH), 5.95 (1H, t, \(J = 7.2\) Hz, \(\text{HC} = \text{C}\)), 4.52-4.34 (4H, m, 2 \(\times\) CH\(_2\)CF\(_3\)), 3.33 (2H, s, CH\(_3\)CH\(_2\)CH), 2.84 (2H, d, \(J = 7.2\) Hz, CCH\(_2\)CH), [6 \(\times\) ArH concealed within the multiplet 7.43-7.28 and 7 \(\times\) ArH concealed within the multiplet at 7.23-7.01 ppm]; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 168.6 (2 \(\times\) C), 146.5 (C), 142.6 (C), 139.2 (C), 134.5 (C), 130.0 (2 \(\times\) CH), 129.9 (2 \(\times\) CH), 128.6 (2 \(\times\) CH), 128.5 (2 \(\times\) CH), 128.4 (2 \(\times\) CH), 127.8 (4 \(\times\) CH), 127.5 (CH), 122.7 (q, \(J_{C,F} = 276.3\) Hz, 2 \(\times\) C), 121.3 (CH), 61.3 (q, \(J_{C,F} = 37.3\) Hz, 2 \(\times\) CH\(_2\)), 59.3 (C), 38.2 (CH\(_2\)), 32.0 (CH\(_2\)).

Note: Assignment of the NMR data for 3aa and 3ab was made simpler by the isolation of 3ab in a purer form from the enantioselective reaction described on page 28.

![Image of 2,2,2-Trifluoroethyl (E)-4-benzylidene-2-methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ba).](image)

The title compound was prepared according to General Procedure A, using malonate ester 1b (119 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/n-pentane) to give a pale yellow oil (65.5 mg, 58%). \(R_f = 0.30\) (10% EtOAc/petroleum ether); IR 2956, 1744 (C=O), 1684 (C=O), 1452, 1270, 1109, 873 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.09 (1H, dd, \(J = 7.9, 1.5\) Hz, ArH), 7.74 (1H, dd, \(J = 8.1, 1.1\) Hz, ArH), 7.62 (1H, ddd, \(J = 8.0, 7.3, 1.5\) Hz, ArH), 7.46-7.31 (7H, m, ArH and =CHPh), 4.55 (1H, dq, \(J = 12.6, 8.4\) Hz, CH\(_3\)H\(_6\)CF\(_3\)), 4.30 (1H, dq, \(J = 12.6, 8.4\) Hz, CH\(_3\)H\(_6\)CF\(_3\)), 3.59 (1H, dd, \(J = 14.1, 1.5\) Hz, =CCH\(_3\)H\(_6\)), 3.07 (1H, dd, \(J = 14.1, 1.2\) Hz, =CCH\(_3\)H\(_6\)) 1.46 (3H, s, CH\(_3\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 195.1 (C), 171.0 (C), 141.5 (C), 136.7 (C), 134.4 (CH), 131.3 (C), 130.2 (CH), 129.6 (C), 129.1 (2 \(\times\) CH), 128.7 (2 \(\times\) CH), 128.7 (CH), 128.3 (CH), 127.8 (CH), 124.7 (CH), 122.7 (q, \(J_{C,F} = 277.5\) Hz, C), 60.9 (q, \(J_{C,F} = 36.9\) Hz, CH\(_2\)), 55.4 (C), 37.4 (CH\(_2\)), 19.8 (CH\(_3\)); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -73.8 (t, \(J = 8.3\) Hz, 3 \(\times\) F); HRMS (ESI) Exact mass calculated for [C\(_{21}\)H\(_{18}\)F\(_3\)O\(_3\)]\(^+\) [M+H]\(^+\): 375.1203, found 375.1202.

![Image of 2,2,2-Trifluoroethyl (E)-4-benzylidene-1-oxo-2-(2-thienylmethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ca).](image)

The title compound was prepared according to General Procedure A, using malonate ester 1c (144 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/n-pentane) to give a yellow oil (68.8 mg, 50%). \(R_f = 0.29\).
**Supplementary Information**

0.46 (10% EtOAc/petroleum ether); IR 2925, 1751 (C=O), 1684 (C=O), 1595, 1278, 1155, 1070, 972, 758, 697, 510 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.12 (1H, dd, \(J = 7.9, 1.4\) Hz, ArH), 7.75 (1H, dd, \(J = 8.1, 1.1\) Hz, ArH), 7.60 (1H, ddd, \(J = 8.2, 7.3, 1.5\) Hz, ArH), 7.45-7.29 (7H, m, ArH and =CHPh), 7.05 (1H, dd, \(J = 5.1, 1.3\) Hz, ArH), 6.73-6.69 (2H, m, ArH), 4.53 (1H, dq, \(J = 12.7, 8.4\) Hz, CH\(_2\)H\(_3\)CF\(_3\)), 4.25 (1H, dq, \(J = 12.7, 8.4\) Hz, CH\(_2\)H\(_3\)CF\(_3\)), 3.65-3.59 (2H, m, =CCH\(_2\)H\(_3\) and CH\(_2\)H\(_3\)CS), 3.43 (1H, d, \(J = 14.7\) Hz, CH\(_2\)H\(_3\)CS), 3.06 (1H, dd, \(J = 14.5, 1.6\) Hz, =CCH\(_2\)H\(_3\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 193.4 (C), 169.8 (C), 141.4 (C), 136.9 (C), 136.6 (C), 134.4 (CH), 130.8 (C), 130.2 (CH), 130.1 (C), 129.2 (2 × CH), 128.8 (CH), 128.6 (3 × CH), 128.4 (CH), 127.8 (CH), 126.6 (CH), 125.3 (CH), 124.6 (CH), 122.6 (q, \(J_{C-F} = 277.6\) Hz, C), 61.1 (q, \(J_{C-F} = 37.0\) Hz, CH\(_2\)), 60.3 (C), 34.1 (CH\(_2\)), 33.5 (CH\(_2\)); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) –73.5 (t, \(J = 8.3\) Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C\(_{25}\)H\(_{19}\)F\(_3\)NaO\(_3\)]\(^+\) [M+Na\(^+\)]: 479.0899, found 479.0900.

![2,2,2-Trifluoroethyl \((E)-4-benzylidene-1-oxo-2-(2-oxo-2-phenylethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2da)\)](image)

The title compound was prepared according to a slight modification of General Procedure A (in that the reaction was left for 24 h), using malonate ester 1d (150 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 4% EtOAc/n-pentane) to give a pale yellow oil (52.3 mg, 36%). \(R_f = 0.26\) (10% EtOAc/petroleum ether); IR 1751 (C=O), 1682 (C=O), 1598, 1452, 1156, 1079, 909, 727, 694, 657 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.10 (1H, dd, \(J = 7.9, 1.5\) Hz, ArH), 7.81-7.79 (2H, m, ArH), 7.73 (1H, dd, \(J = 8.0, 1.1\) Hz, ArH), 7.64-7.60 (1H, m, ArH), 7.58-7.54 (1H, m, ArH), 7.47-7.40 (3H, m, ArH), 7.34-7.27 (4H, m, ArH and =CH), 7.20-7.17 (2H, m, ArH), 4.55 (1H, dq, \(J = 12.6, 8.4\) Hz, CH\(_2\)H\(_3\)CF\(_3\)), 4.29 (1H, dq, \(J = 12.6, 8.4\) Hz, CH\(_2\)H\(_3\)CF\(_3\)), 3.66-3.54 (4H, m, =CCH\(_2\) and CH\(_2\)C=O); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 195.8 (C), 193.8 (C), 169.9 (C), 141.8 (C), 136.4 (2 × C), 134.4 (CH), 133.5 (CH), 131.6 (C), 130.4 (CH), 130.3 (C), 129.0 (2 × CH), 128.7 (3 × CH), 128.6 (2 × CH), 128.3 (CH), 128.1 (2 × CH), 127.7 (CH), 124.7 (CH), 122.7 (q, \(J_{C-F} = 277.4\) Hz, C), 61.1 (q, \(J_{C-F} = 36.9\) Hz, CH\(_2\)), 57.0 (C), 41.8 (CH\(_2\)), 35.0 (CH\(_2\)); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) –73.7 (t, \(J = 8.4\) Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C\(_{25}\)H\(_{23}\)NF\(_3\)O\(_4\)]\(^+\) [M+H\(^+\)]: 496.1730, found 496.1738.

![2,2,2-Trifluoroethyl \((E)-4-benzylidene-1-oxo-2-(2-oxo-2-phenoxyethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ea)\)](image)

The title compound was prepared according to General Procedure A, using malonate ester 1e (155 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 3% EtOAc/n-pentane) to give a white solid (81.6 mg, 55%). \(R_f = 0.31\) (20% EtOAc/petroleum ether); m.p. 138-140 °C (Et\(_2\)O); IR 3062, 1754 (C=O), 1687 (C=O),
1594, 1278, 1145, 958, 758, 698, 496 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.12 (1H, dd, J = 7.9, 1.5 Hz, ArH), 7.75 (1H, dd, J = 8.0, 1.1 Hz, ArH), 7.65-7.61 (1H, m, ArH), 7.47-7.40 (9H, m, ArH and =CHPh), 7.22-7.17 (1H, m, ArH), 6.94-6.90 (2H, m, ArH), 4.53 (1H, dq, J = 12.6, 8.3 Hz, CH₃H₅CF₃), 4.22 (1H, dq, J = 12.6, 8.3 Hz, CH₃H₅CF₃), 3.71 (1H, dd, J = 14.2, 1.0 Hz, =CH₃H₅), 3.46 (1H, dd, J = 14.2, 1.6 Hz, =CH₃H₅), 3.18-3.09 (2H, m, CH₂C=O); ¹³C NMR (101 MHz, CDCl₃) δ 193.2 (C), 169.3 (C), 168.8 (C), 150.4 (C), 141.6 (C), 136.4 (C), 134.6 (CH), 130.7 (C and CH), 130.0 (C), 129.4 (2 × CH), 129.1 (2 × CH), 128.8 (2 × CH), 128.8 (CH), 128.3 (CH), 127.9 (CH), 126.0 (CH), 124.7 (CH), 122.6 (q, J_C-F = 277.4 Hz, C), 121.5 (2 × CH), 61.2 (q, J_C-F = 36.9 Hz, CH₂), 57.1 (C), 38.1 (CH₂), 35.7 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ −73.7 (t, J = 8.4 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C₂₈H₂₁F₃NaO₅]⁺ [M+Na]⁺: 517.1233, found 517.1233.

Slow evaporation of a solution of 2ea in CH₂Cl₂/petroleum ether gave crystals that were suitable for X-ray crystallography.

2,2,2-Trifluoroethyl (E)-4-benzylidene-1-oxo-2-phenyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2fa). The title compound was prepared according to General Procedure A, using malonate ester 1f (137 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/n-pentane) to give a yellow oil (81.0 mg, 62%). Rᵣ = 0.42 (10% EtOAc/petroleum ether); IR 2919, 1749 (C=O), 1682 (C=O), 1596, 1447, 1280, 1158, 972, 732, 696 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.15 (1H, dd, J = 7.9, 1.4 Hz, ArH), 7.65 (1H, dd, J = 8.0, 1.1 Hz, ArH), 7.58-7.53 (1H, m, ArH), 7.48-7.29 (6H, m, ArH and =CHPh), 7.24-7.15 (4H,
Supplementary Information

m, ArH), 6.96-6.93 (2H, m, ArH), 4.54 (1H, dq, J = 12.7, 8.4 Hz, CH$_2$H$_6$CF$_3$), 4.39 (1H, dq, J = 12.7, 8.4 Hz, CH$_2$H$_6$CF$_3$), 3.92 (1H, dd, J = 14.5, 0.8 Hz, =CCH$_3$), 3.82 (1H, dd, J = 14.5, 1.9 Hz, =CCH$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 193.5 (C), 169.9 (C), 141.1 (C), 136.9 (C), 134.4 (CH), 134.0 (C), 131.1 (C), 130.3 (CH), 130.2 (C), 129.1 (2 × CH), 128.8 (2 × CH), 128.7 (CH), 128.5 (CH), 128.3 (2 × CH), 128.2 (CH), 128.0 (CH), 127.9 (2 × CH), 124.6 (CH), 122.7 (q, J$_{C-F}$ = 277.5 Hz, C), 64.3 (C), 61.2 (q, J$_{C-F}$ = 36.9 Hz, CH$_2$), 35.2 (CH$_2$); $^{19}$F NMR (376 MHz, CDCl$_3$) δ −73.7 (t, J = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C$_{26}$H$_{26}$F$_3$O$_3$]$^+$ [M+H]$^+$: 437.1359, found 437.1343.

2,2,2-Trifluoroethyl (E)-4-benzylidene-2-((2-methoxyphenyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ga). The title compound was prepared according to General Procedure A, using malonate ester 1g (147 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/n-pentane) to give a pale yellow oil (75.1 mg, 54%). R$_f$ = 0.29 (10% EtOAc/petroleum ether); IR 2923, 1751 (C=O), 1682 (C=O), 1596, 1494, 1157, 1029, 973, 774, 698 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.19 (1H, dt, J = 7.8, 1.1 Hz, ArH), 7.61-7.57 (2H, m, ArH), 7.49-7.43 (1H, m, ArH), 7.34-7.29 (2H, m, ArH), 7.26-7.22 (1H, m, ArH), 7.17 (1H, ddd, J = 8.2, 6.9, 2.2 Hz, ArH), 7.04-6.99 (3H, m, ArH and =CHPh), 6.70-6.63 (2H, m, ArH), 6.58-6.56 (1H, m, ArH), 4.66 (1H, dq, J = 12.7, 8.4 Hz, CH$_2$H$_6$CF$_3$), 4.36 (1H, dq, J = 12.7 8.4 Hz, CH$_2$H$_6$CF$_3$), 4.27 (1H, d, J = 13.8 Hz, =CCH$_3$), 3.52 (1H, dd, J = 13.8, 1.8 Hz, =CCH$_3$), 3.15 (3H, s, OCH$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 194.9 (C), 170.2 (C), 156.9 (C), 142.5 (C), 137.0 (C), 134.4 (CH), 132.9 (C), 131.0 (C), 130.1 (CH), 129.1 (CH), 129.0 (2 × CH), 128.6 (CH), 128.3 (2 × CH), 128.1 (CH), 128.0 (CH), 127.3 (CH), 124.9 (C), 124.8 (CH), 122.9 (q, J$_{C-F}$ = 277.7 Hz, C), 120.0 (CH), 110.4 (CH), 63.2 (C), 60.8 (q, J$_{C-F}$ = 36.7 Hz, CH$_2$), 54.3 (CH$_3$), 34.8 (CH$_2$); $^{19}$F NMR (376 MHz, CDCl$_3$) δ −73.7 (t, J = 8.5 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C$_{27}$H$_{22}$F$_3$O$_4$]$^+$ [M+H]$^+$: 467.1465, found 467.1464.

2,2,2-Trifluoroethyl (E)-4-benzylidene-1-oxo-3,4-dihydro-[2,2'-binaphthalene]-2(1H)-carboxylate (2ha). The title compound was prepared according to a slightly modification of General Procedure A (in that 2.0 equivalents of the boronic acid and 10 mol% catalyst loading was used), using malonate ester 1h (153 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (0% to 1% EtOAc/n-pentane) to give a yellow oil (82.3 mg, 56%). R$_f$ = 0.41 (10% EtOAc/petroleum ether); IR 2924, 1745 (C=O), 1682 (C=O), 1596, 1278, 1157, 1081, 967, 777, 699 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.25 (1H, dt, J = 7.8, 1.2 Hz,
Supplementary Information

ArH), 7.77-7.70 (2H, m, ArH), 7.64-7.59 (2H, m, ArH), 7.50 (1H, ddd, J = 8.3, 5.9, 2.6 Hz, ArH), 7.31-7.27 (2H, m, ArH), 7.17 (1H, dd, J = 8.2, 7.3 Hz, ArH), 7.09-6.93 (6H, m, ArH and =CHPh), 6.57-6.54 (2H, m, ArH), 4.60-4.43 (2H, m, CH₂CF₃), 4.27 (1H, d, J = 14.0 Hz, =CCH₃H₆), 3.74 (1H, dd, J = 14.0, 1.7 Hz, =CCH₃H₆); ¹³C NMR (101 MHz, CDCl₃) δ 194.8 (C), 170.9 (C), 141.7 (C), 136.3 (C), 134.6 (CH), 134.2 (C), 132.4 (C), 131.6 (C), 131.0 (C), 130.9 (C), 130.5 (CH), 129.2 (CH), 129.2 (CH), 128.8 (CH), 128.3 (CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.0 (CH), 126.2 (CH), 125.9 (CH), 125.5 (CH), 124.8 (CH), 124.5 (CH), 123.7 (CH), 122.6 (q, JCF = 277.8 Hz, C), 65.2 (C), 61.2 (q, JCF = 36.9 Hz, CH₂), 36.6 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ –73.3 (t, J = 8.4 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C₂₀H₁₅F₃O₃S]⁺ [M+H]+: 504.1781, found 504.1783.

2,2,2-Trifluoroethyl (E)-4-benzylidene-1-oxo-2-(3-thienyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ia). The title compound was prepared according to General Procedure A, using malonate ester 1i (139 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 2% EtOAc/n-pentane) to give a yellow oil (75.7 mg, 57%). Rf = 0.25 (10% EtOAc/petroleum ether); IR 2924, 1749 (C=O), 1682 (C=O), 1596, 1445, 1280, 1156, 908, 731, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.15 (1H, ddd, J = 7.9, 1.5, 0.5 Hz, ArH), 7.69 (1H, dd, J = 8.1, 1.2 Hz, ArH), 7.58 (1H, ddd, J = 8.0, 7.2, 1.5 Hz, ArH), 7.48-7.33 (6H, m, ArH), 7.30 (1H, s, =CHPh), 7.16 (1H, dd, J = 5.1, 3.0 Hz, ArH), 6.89 (1H, dd, J = 3.0, 1.4 Hz, ArH), 6.76 (1H, dd, J = 5.1, 1.4 Hz, ArH), 4.57 (1H, dq, J = 12.6, 8.3 Hz, CH₃H₆CF₃), 4.40 (1H, dq, J = 12.6, 8.3 Hz, CH₃H₆CF₃), 3.89-3.80 (2H, m, =CCH₂); ¹³C NMR (101 MHz, CDCl₃) δ 192.4 (C), 169.5 (C), 141.1 (C), 136.7 (C), 134.5 (CH), 134.4 (C), 131.0 (C), 130.4 (CH), 129.7 (C), 129.2 (2 × CH), 128.9 (2 × CH), 128.7 (CH), 128.6 (CH), 128.0 (CH), 127.6 (CH), 125.4 (CH), 124.7 (CH), 123.9 (CH), 122.7 (q, JCF = 277.5 Hz, C), 61.5 (C), 61.3 (q, JCF = 36.8 Hz, CH₂), 35.6 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ –73.3 (t, J = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C₂₀H₁₈F₃O₃S]⁺ [M+H]+: 443.0923, found 443.0923.

2,2,2-Trifluoroethyl (E)-2-benzyl-4-(4-methoxybenzylidene)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ja). The title compound was prepared according to General Procedure A, using malonate ester 1j (151 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 2% EtOAc/n-pentane) to give a yellow oil (91.8 mg, 64%). Rf = 0.31 (10% EtOAc/petroleum ether); IR 2964, 1750 (C=O), 1686 (C=O), 1605, 1510, 1279, 1249, 1157, 1031, 701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.10 (1H, ddd, J = 7.9, 1.5 Hz, ArH), 7.73 (1H, dd, J = 8.1, 1.1 Hz, ArH), 7.60-7.55 (1H, m, ArH), 7.39 (1H, ddd, J = 8.1, 7.2, 1.1
2,2,2-Trifluoroethyl (E)-2-benzyl-4-(3-methylbenzylidene)-1-oxo-1,2,3,4-
tetrahydronaphthalene-2-carboxylate (2ka). The title compound was
prepared according to General Procedure A, using malonate ester 1k (146 mg,
0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by
column chromatography (0% to 1.5% EtOAc/pentane) to give a yellow oil (103 mg, 74%). Rf =
0.31 (10% EtOAc/petroleum ether); IR 1752 (C=O), 1695 (C=O), 1602, 1455, 1281, 1153, 1060, 913,
729, 698 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.11 (1H, dd, \(J = 7.9, 1.4\) Hz, ArH), 7.76 (1H, dd, \(J =
8.1, 1.1\) Hz, ArH), 7.59 (1H, ddd, \(J = 8.3, 7.2, 1.5\) Hz, ArH), 7.42 (1H, ddd, \(J = 8.2, 7.3, 1.1\) Hz,
ArH), 7.37 (1H, s, =CHAr), 7.31-7.27 (1H, m, ArH), 7.13-7.10 (8H, m, ArH), 4.47 (1H, dq, \(J = 12.6,
8.4\) Hz, CH\(_2\)H\(_6\)CF\(_3\)), 4.31-4.20 (1H, m, CH\(_2\)H\(_6\)CF\(_3\)), 3.65 (1H, dd, \(J = 14.7, 1.4\) Hz, =CHCHCF\(_3\)),
3.38 (1H, d, \(J = 13.8\) Hz, CH\(_2\)H\(_6\)Ph), 3.26 (1H, d, \(J = 13.8\) Hz, CH\(_2\)H\(_6\)Ph), 3.01 (1H, dd, \(J = 14.7, 1.7\) Hz,
=CHCHCF\(_3\)), 2.39 (3H, s, CH\(_3\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 193.7 (C), 169.9 (C), 141.1 (C),
138.2 (C), 136.6 (C), 135.4 (C), 134.3 (CH), 130.8 (2 \(\times\) CH), 130.7 (C), 130.3 (C), 130.0 (CH), 129.9 (CH),
128.6 (CH), 128.5 (CH), 128.4 (CH), 128.2 (2 \(\times\) CH), 127.0 (CH), 126.3 (CH), 124.4 (CH), 122.7 (q, \(J_{CF} = 97.7\)
Hz, C), 61.0 (q, \(J_{CF} = 36.9\) Hz, CH\(_2\)), 60.2 (C), 38.9 (CH\(_2\)), 34.2 (CH\(_2\)),
21.6 (CH\(_3\)); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) –73.5 (t, \(J = 8.4\) Hz, 3 \(\times\) F); HRMS (ESI) Exact mass calculated for [C\(_{28}\)H\(_{24}\)F\(_{3}\)O\(_3\)]\(^+\) [M+H]\(^+\): 481.1621, found 481.1616.

2,2,2-Trifluoroethyl (E)-2-benzyl-4-(naphthalen-1-ylmethylene)-1-oxo-
1,2,3,4-tetrahydronaphthalene-2-carboxylate (2la). The title compound was
prepared according to General Procedure A, using malonate ester 1l (157 mg,
0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by
column chromatography (0% to 1.5% EtOAc/pentane) to give a yellow oil
(102 mg, 68%). Rf = 0.38 (10% EtOAc/petroleum ether); IR 3061, 1757 (C=O), 1683 (C=O), 1282,
1152, 974, 908, 778, 752, 663 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.14 (1H, dd, \(J = 7.9, 1.4\) Hz,
Supplementary Information

2,2,2-Trifluoroethyl (E)-2-benzyl-1-oxo-4-(2-thienylmethylene)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ma). The title compound was prepared according to General Procedure A, using malonate ester 1m (144 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/n-pentane) to give a yellow oil (91.7 mg, 66%). Rf = 0.29 (10% EtOAc/petroleum ether); IR 2930, 1759 (C=O), 1681 (C=O), 1283, 1148, 974, 920 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.08 (1H, dd, J = 7.9, 1.5 Hz, ArH), 7.73 (1H, dd, J = 8.1, 1.0 Hz, ArH), 7.57 (1H, ddd, J = 8.3, 7.2, 1.5 Hz, ArH), 7.45 (1H, s, =CHAr), 7.41-7.35 (2H, m, ArH), 7.22-7.14 (6H, m, ArH), 7.06 (1H, dd, J = 5.1, 3.6 Hz, ArH), 4.45 (1H, dq, J = 12.6, 8.3 Hz, CH₃H₅CF₃), 4.29 (1H, dq, J = 12.6, 8.3 Hz, CH₃H₅CF₃), 3.80 (1H, dd, J = 14.8, 1.3 Hz, =CCH₃H₅), 3.43-3.36 (2H, m, CH₂Ph), 3.02 (1H, dd, J = 14.8, 1.7 Hz, =CCH₃H₅); ¹³C NMR (101 MHz, CDCl₃) δ 193.5 (C), 170.0 (C), 140.9 (C), 135.3 (C), 134.4 (CH), 133.8 (C), 133.6 (C), 132.6 (C), 132.2 (C), 130.8 (2 × CH), 130.4 (C), 128.9 (CH), 128.8 (CH), 128.6 (CH), 128.5 (CH), 128.0 (2 × CH), 127.8 (CH), 126.9 (2 × CH), 126.5 (CH), 126.2 (CH), 125.5 (CH), 124.6 (2 × CH), 122.6 (q, JCF = 277.5 Hz, C), 60.9 (q, JCF = 36.9 Hz, CH₂), 60.5 (C), 38.6 (CH₂), 34.7 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ −73.7 (t, J = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C₃H₄F₃Na₄O₃S]⁺ [M+H⁺]: 501.1672, found 501.1667.

Methyl (E)-4-benzylidene-1-oxo-2-(2-oxo-2-phenoxethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2na). The title compound was prepared according to General Procedure A, using malonate ester 1n (114 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 7.5% EtOAc/n-pentane) to give a white solid (91.2 mg, 71%). Rf = 0.38 (20% EtOAc/petroleum ether); m.p. 136-137 °C (Et₂O); IR 2938, 1756 (C=O), 1685 (C=O), 1593, 1280,
Phenyl (E)-4-benzylidene-2-methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2oa). The title compound was prepared according to General Procedure A, using malonate ester 1o (115 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/n-pentane) to give a white solid (60.5 mg, 55%). Rf = 0.32 (10% EtOAc/petroleum ether); m.p. 95-96 °C (Et2O); IR 2968, 1758 (C=O), 1682 (C=O), 1514, 1412, 1282, 1156, 974, 808, 758 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.15 (1H, dd, J = 7.9, 1.4 Hz, ArH), 7.78 (1H, dd, J = 8.0, 1.3 Hz, ArH), 7.62 (1H, ddd, J = 8.0, 7.2, 1.5 Hz, ArH), 7.47-7.28 (9H, m, ArH and =CHPh), 7.20-7.16 (1H, m, ArH), 6.97-6.94 (2H, m, ArH), 3.77 (1H, dd, J = 14.0, 1.5 Hz, =CCH₂H₅), 3.15 (1H, dd, J = 14.0, 1.3 Hz, =CCH₂H₅), 1.57 (3H, s, CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 195.7 (C), 171.2 (C), 150.7 (C), 141.6 (C), 136.8 (C), 134.3 (CH), 131.8 (C), 130.0 (C), 129.9 (CH), 129.4 (2 × CH), 129.3 (2 × CH), 128.7 (2 × CH), 128.6 (CH), 128.3 (CH), 127.8 (CH), 126.0 (CH), 124.7 (CH), 121.5 (2 × CH), 55.4 (C), 37.7 (CH₂), 20.1 (CH₃); HRMS (ESI) Exact mass calculated for [C₂₇H₂₃O₅]⁺ [M+H]⁺: 427.1540, found 427.1541.

2,2,2-Trifluoroethyl (E)-4-benzylidene-2-ethoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2pa). The title compound was prepared according to a slight modification of General Procedure A (in that 2.0 equivalents of the boronic acid and 10 mol% catalyst loading was used), using malonate ester 1p (128 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (0% to 1.5% EtOAc/n-pentane) to give a yellow oil (43.5 mg, 36%). Rf = 0.27 (10% EtOAc/petroleum ether); IR 2979, 1768 (C=O), 1688 (C=O), 1596, 1282, 1226, 1162, 1041, 755, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.08 (1H, dd, J = 7.8, 1.5 Hz, ArH), 7.79 (1H, d, J = 8.0 Hz, ArH), 7.63 (1H, ddd, J = 8.1, 7.2, 1.5 Hz, ArH), 7.46-7.30 (7H, m, ArH and =CHPh), 4.62 (1H, dq, J = 12.6, 8.3 Hz, CH₂H₅CF₃), 4.43 (1H, dq, J = 12.6, 8.3 Hz, CH₂H₅CF₃), 3.65-3.56
(2H, m, OCH₂H₂ and =CCH₂H₂), 3.50-3.41 (2H, m, OCH₂H₂ and =CCH₂H₂), 1.10 (3H, t, J = 7.0 Hz, CH₂CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 191.5 (C), 169.0 (C), 141.5 (C), 136.6 (C), 134.6 (CH), 130.5 (CH), 130.0 (C), 129.3 (C), 129.2 (2 × CH), 128.7 (2 × CH), 128.6 (CH), 128.4 (CH), 127.9 (CH), 124.5 (CH), 122.7 (q, Jₐₓ-F = 277.3 Hz, C), 84.0 (CH₂), 63.2 (C), 61.0 (q, Jₓ-F = 37.0 Hz, CH₂), 36.3 (CH₂), 15.5 (CH₃); ¹⁹F NMR (376 MHz, CDCl₃) δ -73.7 (t, J = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C₂₂H₂₀F₃O₃]⁺ [M+H]⁺: 405.1308, found 405.1311.

**2,2,2-Trifluoroethyl (E)-4-benzyldiene-1-oxo-2-(3-thienylmethoxy)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2qa).** The title compound was prepared according to a slight modification of General Procedure A (in that 2.0 equivalents of the boronic acid and 10 mol% catalyst loading was used), using malonate ester 1q (148 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (0% to 2% EtOAc/n-pentane) to give a pale yellow oil (47.4 mg, 33%). Rf = 0.28 (10% EtOAc/petroleum ether); IR 2926, 1750 (C=O), 1686 (C=O), 1597, 1410, 1282, 1158, 1084, 194, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.04 (1H, dd, J = 7.9, 1.5 Hz, ArH), 7.78 (1H, d, J = 8.1 Hz, ArH), 7.65-7.61 (1H, m, ArH), 7.44-7.30 (7H, m, ArH and =CHPh), 7.15 (1H, dd, J = 5.0, 3.0 Hz, ArH), 7.06 (1H, m, ArH), 6.93 (1H, dd, J = 4.9, 1.2 Hz, ArH), 4.71 (1H, d, J = 11.2 Hz, CH₂Ar), 4.64 (1H, dq, J = 12.5, 8.3 Hz, CH₂CF₃), 4.55 (1H, d, J = 11.2 Hz, CH₂Ar), 4.46 (1H, dq, J = 12.5, 8.3 Hz, CH₂CF₃), 3.67 (1H, dd, J = 14.7, 0.8 Hz, =CCH₂H₂), 3.51 (1H, dd, J = 14.7, 0.8 Hz, =CCH₂H₂); ¹³C NMR (101 MHz, CDCl₃) δ 191.3 (C), 168.8 (C), 141.5 (C), 138.5 (C), 136.5 (C), 134.7 (CH), 130.7 (CH), 129.9 (C), 129.3 (C), 129.2 (2 × CH), 128.8 (2 × CH), 128.7 (CH), 128.4 (CH), 127.9 (CH), 127.3 (CH), 125.6 (CH), 124.5 (CH), 122.9 (CH), 122.7 (q, Jₓ-F = 277.3 Hz, C), 83.8 (CH₂), 65.0 (C), 61.1 (q, Jₓ-F = 37.0 Hz, CH₂), 36.6 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ -73.5 (t, J = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C₂₂H₂₀F₃NSO₃]⁺ [M+NH₄]⁺: 490.1294, found 490.1295.

**2,2,2-Trifluoroethyl (E)-2-benzyl-4-ethylidene-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ra).** The title compound was prepared according to General Procedure A, using malonate ester 1r (123 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/n-pentane) to give a brown oil that contained unidentified inseparable impurities (30.0 mg, <26%). The exact yield was not determined. Rf = 0.39 (10% EtOAc/petroleum ether); IR 2926, 1750 (C=O), 1686 (C=O), 1597, 1410, 1282, 1158, 1084, 914, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (1H, dd, J = 7.9, 1.4 Hz, ArH), 7.57 (1H, d, J = 7.8 Hz, ArH), 7.50 (1H, ddd, J = 8.1, 7.6, 1.4 Hz, ArH), 7.35-7.31 (1H, m, ArH), 7.25-7.19 (5H, m,
ArH), 6.40 (1H, q, J = 7.0 Hz, =CHCH3), 4.53-4.43 (1H, m, CH2H5CF3), 4.34 (1H, dq, J = 12.7, 8.4 Hz, CH2H5CF3), 3.42 (1H, d, J = 13.8, CH2H5Ph), 3.36-3.28 (2H, m, =CCH2H5 and CH2H5Ph), 2.61 (1H, d, J = 14.5 Hz, =CCH2H5), 1.77 (3H, d, J = 7.0 Hz, =CHCH3); 13C NMR (101 MHz, CDCl3) δ 193.9 (C), 170.3 (C), 141.4 (C), 135.9 (C), 134.1 (CH), 130.8 (2 × CH), 129.8 (C), 129.6 (C), 128.4 (2 × CH), 128.3 (CH), 127.7 (CH), 127.1 (CH), 125.4 (CH), 123.7 (CH), 122.7 (q, Jc-F = 277.6 Hz, C), 61.0 (q, Jc-F = 36.9 Hz, CH2), 59.9 (C), 39.2 (CH2), 32.7 (CH2), 14.3 (CH3); 19F NMR (376 MHz, CDCl3) δ −73.5 (t, J = 8.4 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C22H19F3NaO3]+ [M+Na]+: 411.1178, found 411.1181.

2,2,2-Trifluoroethyl (E)-2-benzyl-4-benzylidene-7-methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ab). The title compound was prepared according to General Procedure A, using malonate ester 1a (142 mg, 0.30 mmol) and 4-methylphenylboronic acid (61.2 mg, 0.45 mmol), and purified by column chromatography (0% to 1% EtOAc/n-pentane) to give a yellow oil (110 mg, 79%). Rf = 0.32 (10% EtOAc/petroleum ether); IR 2924, 1751 (C=O), 1686 (C=O), 1495, 1280, 1158, 963, 732, 698, 513 cm−1; 1H NMR (400 MHz, CDCl3) δ 7.92 (1H, dd, J = 2.0, 0.9 Hz, ArH), 7.66 (1H, d, J = 8.1 Hz, ArH), 7.42-7.38 (3H, m, ArH), 7.35-7.28 (4H, m, ArH and =CHPh), 7.14-7.07 (5H, m, ArH), 4.46 (1H, dq, J = 12.6, 8.4 Hz, CH2H5CF3), 4.27 (1H, dq, J = 12.6, 8.4 Hz, CH2H5CF3), 3.62 (1H, dd, J = 14.6, 1.4 Hz, =CCH2H5), 3.37 (1H, d, J = 13.7 Hz, CH2H5Ph), 3.23 (1H, d, J = 13.7 Hz, CH2H5Ph), 3.01 (1H, dd, J = 14.6, 1.6 Hz, =CCH2H5), 2.42 (3H, s, CH3); 13C NMR (101 MHz, CDCl3) δ 193.9 (C), 170.0 (C), 138.7 (C), 138.5 (C), 136.8 (C), 135.4 (C), 135.4 (CH), 131.0 (C), 130.8 (2 × CH), 130.0 (C), 129.2 (2 × CH), 128.9 (CH), 128.6 (2 × CH), 128.4 (CH), 128.2 (2 × CH), 127.6 (CH), 127.0 (CH), 124.4 (CH), 122.7 (q, Jc-F = 277.5 Hz, C), 61.0 (q, Jc-F = 37.0 Hz, CH2), 60.3 (C), 38.8 (CH2), 34.1 (CH2), 21.2 (CH3); 19F NMR (376 MHz, CDCl3) δ −73.5 (t, J = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C28H20F3O3]+ [M+H]+: 465.1675, found 465.1672.

2,2,2-Trifluoroethyl (E)-2-benzyl-4-benzylidene-7-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ac). The title compound was prepared according to General Procedure A, using malonate ester 1a (142 mg, 0.30 mmol) and 4-fluorophenylboronic acid (63.0 mg, 0.45 mmol), and purified by column chromatography (0% to 1% EtOAc/n-pentane) to give a yellow solid (95.1 mg, 68%). Rf = 0.31 (10% EtOAc/petroleum ether); m.p. 135-136 °C (Et2O); IR 3022, 1743 (C=O), 1686 (C=O), 1493, 1270, 1156, 971, 824, 767, 700 cm−1; 1H NMR (400 MHz, CDCl3) δ 7.78-7.72 (2H, m, ArH), 7.43-7.39 (2H, m, ArH), 7.35-7.29 (5H, m, ArH and =CHPh), 7.15-7.10 (5H, m, ArH), 4.48


2,2,2-Trifluoroethyl (E)-2-benzyl-4-benzyldiene-1-oxo-1,2,3,4-tetrahydroanthracene-2-carboxylate (2ad). The title compound was prepared according to General Procedure A, using malonate ester 1a (142 mg, 0.30 mmol) and 2-naphthylboronic acid (77.4 mg, 0.45 mmol), and purified by column chromatography (0% to 1% EtOAc/n-pentane) to give a yellow oil (84.5 mg, 56%). Rf = 0.33 (10% EtOAc/petroleum ether); IR 2924, 1749 (C=O), 1687 (C=O), 1586, 1443, 1281, 1156, 972, 734, 698 cm⁻¹; 1H NMR (400 MHz, CDCl₃) δ 8.70 (1H, s, ArH), 8.16 (1H, s, ArH), 7.98 (1H, dd, J = 8.3, 1.2 Hz, ArH), 7.89 (1H, dd, J = 8.3, 1.1 Hz, ArH), 7.60 (1H, ddd, J = 8.2, 6.8, 1.3 Hz, ArH), 7.54-7.50 (2H, m, ArH and =CHPh), 7.45-7.41 (2H, m, ArH), 7.39-7.33 (3H, m, ArH), 7.17-7.11 (5H, m, ArH), 4.49 (1H, dq, J = 12.6, 8.4 Hz, CH₃CH₂CF₃), 4.23 (1H, ddd, J = 12.6, 8.4 Hz, CH₃CH₂CF₃), 3.70 (1H, dd, J = 14.4, 1.3 Hz, =CHCH₂Ph), 3.49 (1H, d, J = 13.8 Hz, CH₂CH₂Ph), 3.26 (1H, d, J = 13.8 Hz, CH₂CH₂Ph), 3.09 (1H, dd, J = 14.4, 1.6 Hz, =CHCH₂Ph); 13C NMR (101 MHz, CDCl₃) δ 194.0 (C), 170.1 (C), 136.9 (2 × C), 136.3 (C), 135.5 (C), 132.6 (C), 131.4 (C), 130.9 (2 × CH), 130.3 (CH), 130.0 (CH), 129.3 (2 × CH), 129.3 (CH), 129.2 (CH), 128.7 (2 × CH), 128.5 (C), 128.2 (2 × CH), 128.1 (CH), 127.7 (CH), 127.0 (2 × CH), 123.6 (CH), 122.7 (q, J₃₁₋₂ = 277.4 Hz, C), 61.0 (q, J₃₋₂ = 37.1 Hz, CH₂), 60.7 (C), 38.9 (CH₂), 34.2 (CH₂); 19F NMR (376 MHz, CDCl₃) δ −73.5 (t, J = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C₂₇H₂₄F₄NO₃]⁺ [M+H]⁺: 501.1672, found 501.1670.

2,2,2-Trifluoroethyl (E)-4-benzyldiene-6,7-dimethoxy-1-oxo-2-(3-thienyl)-1,2,3,4-tetrahydroanthalene-2-carboxylate (2ie). The title compound was prepared according to General Procedure A, using malonate ester 1i (139 mg, 0.30 mmol) and 3,4-dimethoxyphenylboronic acid (81.9 mg, 0.45 mmol), and purified by column chromatography (0% to 10% EtOAc/n-pentane) to give a yellow oil (74.6 mg, 50%). Rf = 0.29 (10% EtOAc/petroleum ether); IR 2941, 1737 (C=O),
1668 (C=O), 1594, 1509, 1241, 1209, 1154, 763, 729 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.58 (1H, s, ArH), 7.48-7.43 (2H, m, ArH), 7.38-7.32 (3H, m, ArH and =CHPh), 1H, T=1.14 Hz, ArH), 7.06 (1H, s, ArH), 6.87 (1H, dd, J = 2.9, 1.4 Hz, ArH), 6.77 (1H, dd, J = 5.1, 1.4 Hz, ArH), 4.58 (1H, dq, J = 12.7, 8.4 Hz, CH₃H₅CF₃), 4.39 (1H, dq, J = 12.7, 8.4 Hz, CH₃H₅CF₃), 3.98 (3H, s, OCH₃), 3.96 (3H, s, CH₃), 3.82-3.8 (2H, m, =CCH₂); ¹³C NMR (101 MHz, CDCl₃) δ 191.3 (C), 169.8 (C), 154.5 (C), 150.8 (C), 136.8 (C), 136.2 (C), 134.8 (C), 131.3 (C), 129.1 (2 × CH), 129.0 (CH), 128.9 (2 × CH), 127.9 (CH), 127.6 (CH), 125.2 (CH), 123.7 (CH), 123.2 (CH), 122.8 (q, J₇F = 277.4 Hz, C), 109.2 (CH), 106.1 (CH), 61.3 (q, J₇F = 36.8 Hz, CH₂), 61.2 (C), 56.3 (2 × CH₃), 36.1 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ −73.6 (t, J = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C₂₅H₂₂F₃O₅S]⁺ [M+H]⁺: 503.1135, found 503.1135.

![2,2,2-Trifluoroethyl](image)

2,2,2-Trifluoroethyl (E)-2-benzyl-6,7-dichloro-1-oxo-4-(2-thienylmethylene)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2mf). The title compound was prepared according to General Procedure A, using malonate ester 1m (144 mg, 0.30 mmol) and 3,4-dichlorophenylboronic acid (96.5 mg, 0.45 mmol), and purified by column chromatography (0% to 1% EtOAc/n-pentane) followed by a preparative TLC (8% EtOAc/n-pentane) to give a yellow oil (80.4 mg, 51%). R₇ = 0.32 (10% EtOAc/petroleum ether); IR 2927, 1749 (C=O), 1691 (C=O), 1579, 1455, 1282, 1160, 907, 732, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.13 (1H, s, ArH), 7.79 (1H, s, ArH), 7.40 (1H, dd, J = 5.1, 1.2 Hz, ArH), 7.37 (1H, s, =CHAr), 7.21-7.17 (6H, m, ArH), 7.08 (1H, dd, J = 5.1, 3.6 Hz, ArH), 4.43 (1H, dq, J = 12.6, 8.4 Hz, CH₃H₅CF₃), 4.28 (1H, dq, J = 12.6, 8.4 Hz, CH₃H₅CF₃), 3.81 (1H, dd, J = 15.0, 1.2 Hz, =CCH₃), 3.43 (1H, d, J = 13.8 Hz, CH₃H₅Ph), 3.35 (1H, d, J = 13.8 Hz, CH₃H₅Ph), 2.94 (1H, dd, J = 15.0, 1.7 Hz, =CCH₃); ¹³C NMR (101 MHz, CDCl₃) δ 191.6 (C), 169.3 (C), 140.4 (C), 139.0 (C), 139.0 (C), 135.0 (C), 132.9 (C), 130.9 (CH), 130.8 (2 × CH), 130.2 (CH), 129.5 (C), 128.5 (2 × CH), 127.7 (CH), 127.5 (CH), 127.4 (CH), 126.4 (C), 125.9 (CH), 123.6 (CH), 122.5 (q, J₇F = 277.4 Hz, C), 61.1 (q, J₇F = 37.1 Hz, CH₂), 59.7 (C), 39.2 (CH₂), 34.2 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ −73.6 (t, J = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C₂₅H₂₂Cl₂F₃NO₅S]⁺ [M+NH₄]⁺: 542.0566, found 542.0557.

![6-Ethyl 2-(2,2,2-trifluoroethyl)](image)

6-Ethyl 2-(2,2,2-trifluoroethyl) (E)-2-benzyl-1-oxo-4-(2-thienylmethylene)-1,2,3,4-tetrahydronaphthalene-2,7-dicarboxylate (2mg). The title compound was prepared according to General Procedure A, using malonate ester 1m (144 mg, 0.30 mmol) and 3-ethoxycarbonylphenylboronic acid (87.3 mg, 0.45 mmol), and purified by column chromatography (0% to 2.5% EtOAc/n-pentane) to give a yellow solid (88.9 mg, 56%). R₇ = 0.24 (10%
Methyl (E)-4-benzylidene-7-methoxy-1-oxo-2-(2-oxo-2-phenoxyethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2nh). The title compound was prepared according to General Procedure A, using malonate ester 1n (114 mg, 0.30 mmol) and 4-methoxyphenylboronic acid (68.4 mg, 0.45 mmol), and purified by column chromatography (0% to 5% EtOAc/n-pentane) to give a pale yellow oil (69.8 mg, 51%). Rf = 0.28 (15% EtOAc/petroleum ether); IR 2952, 1736 (C=O), 1684 (C=O), 1603, 1492, 1282, 1142, 909, 727, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.76 (1H, d, J = 8.7 Hz, ArH), 7.57 (1H, d, J = 2.8 Hz, ArH), 7.42-7.28 (7H, m, ArH), 7.24 (1H, s, =CHPh), 7.21-7.16 (2H, m, ArH), 6.99-6.96 (2H, m, ArH), 3.89 (3H, s, OCH₃) 3.66 (1H, dd, J = 13.9, 0.9 Hz, =CCH₂H), 3.60 (3H, s, OCH₃), 3.33 (1H, dd, J = 13.9, 1.7 Hz, =CCH₂H), 3.18 (1H, d, J = 16.6 Hz, CH₂H₃C=O), 3.04 (1H, d, J = 16.6 Hz, CH₂H₃C=O); ¹³C NMR (101 MHz, CDCl₃) δ 194.1 (C), 171.1 (C), 169.1 (C), 160.0 (C), 156.9 (C), 134.9 (C), 131.4 (C), 131.2 (2 × C), 129.4 (2 × CH), 129.1 (2 × CH), 128.7 (2 × CH), 128.4 (CH), 127.5 (CH), 126.3 (CH), 125.9 (CH), 122.9 (CH), 109.7 (2 × CH), 57.1 (C), 55.8 (CH₃), 52.9 (CH₃), 38.7 (CH₂), 36.1 (CH₂); HRMS (ESI) Exact mass calculated for [C₂₈H₂₈N₂O₇]⁺ [M+NH₄]⁺: 546.1557, found 546.1546.

Methyl (E)-4-benzylidene-7-chloro-1-oxo-2-(2-oxo-2-phenoxyethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ni). The title compound was prepared according to General Procedure A, using malonate ester 1n (114 mg, 0.30 mmol) and 4-chlorophenylboronic acid (70.4 mg, 0.45 mmol), and purified by column chromatography (0% to 5% EtOAc/n-pentane) to give a pale yellow oil (62.4 mg, 45%). Rf = 0.21 (10% EtOAc/petroleum ether); IR 2927, 1737 (C=O), 1692 (C=O), 1591, 1492,
1192, 1144, 907, 730, 700 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 (1H, d, J = 2.3 Hz, ArH), 7.67 (1H, d, J = 8.5 Hz, ArH), 7.54 (1H, dd, J = 8.5, 2.4 Hz, ArH), 7.44-7.39 (2H, m, ArH), 7.35-7.29 (6H, m, ArH and =CHPh), 7.21-7.17 (1H, m, ArH), 7.00-6.96 (2H, m, ArH), 3.67 (1H, dd, J = 14.0, 0.8 Hz, =CH$_2$H$_6$), 3.58 (3H, s, OCH$_3$), 3.33 (1H, dd, J = 14.0, 1.8 Hz, =CH$_2$H$_6$), 3.22 (1H, d, J = 16.7 Hz, CH$_2$H$_6$C=O), 3.03 (1H, d, J = 16.7 Hz, CH$_2$H$_6$C=O); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 193.0 (C), 170.8 (C), 169.1 (C), 150.5 (C), 134.9 (C), 134.9 (C), 134.2 (C), 131.6 (C), 130.7 (C), 130.6 (CH), 129.5 (2 × CH), 129.1 (2 × CH), 128.8 (2 × CH), 128.0 (CH), 127.9 (CH), 126.4 (CH), 126.0 (CH), 121.6 (2 × CH), 57.0 (C), 53.0 (CH$_3$), 38.6 (CH$_2$), 35.9 (CH$_2$); HRMS (ESI) Exact mass calculated for [C$_{27}$H$_{25}$ClNO$_5$]+ [M+NH$_4$]+: 478.1416, found 478.1418.

2,2,2-Trifluoroethyl (E)-5-benzyl-7-benzylidene-4-oxo-4,5,6,7-tetrahydrobenzo[c]thiophene-5-carboxylate (2aj) and 2,2,2-trifluoroethyl (E)-6-benzyl-4-benzylidene-7-oxo-4,5,6,7-tetrahydrobenzo[b]thiophene-6-carboxylate (2aj′)

General Procedure A was followed using malonate ester 1a (142 mg, 0.30 mmol) and 3-thienylboronic acid (57.6 mg, 0.45 mmol). Purification by column chromatography (0% to 2% EtOAc/n-pentane) gave arylation cyclization product 2aj (29.0 mg, 21%) as a brown oil followed by arylation cyclization product 2aj′ (57.5 mg, 42%) as a brown oil.

Data for 2aj: R$_f$ = 0.26 (10% EtOAc/petroleum ether); IR 2927, 1730 (C=O), 1686 (C=O), 1518, 1433, 1283, 1163, 1083, 972, 700 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.25 (1H, d, J = 3.1 Hz, ArH), 7.47 (1H, d, J = 3.1 Hz, ArH), 7.40-7.30 (5H, m, ArH), 7.23 (1H, s, =CHPh), 7.12-7.08 (5H, m, ArH), 4.48 (1H, dq, J = 12.6, 8.4 Hz, CH$_2$H$_6$CF$_3$), 4.32 (1H, dq, J = 12.6, 8.4 Hz, CH$_2$H$_6$CF$_3$), 3.56 (1H, dd, J = 15.0, 1.4 Hz, =CH$_2$H$_6$), 3.33 (1H, d, J = 13.7 Hz, CH$_2$H$_6$Ph), 3.24 (1H, d, J = 13.7 Hz, CH$_2$H$_6$Ph), 2.98 (1H, dd, J = 15.0, 1.4 Hz, =CH$_2$H$_6$); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 189.0 (C), 169.8 (C), 141.8 (C), 136.4 (C), 135.3 (C), 135.3 (C), 132.9 (CH), 130.9 (2 × CH), 129.2 (2 × CH), 128.6 (2 × CH), 128.2 (2 × CH), 127.9 (CH), 127.7 (C), 127.6 (CH), 127.0 (CH), 122.7 (q, J$_{CF}$ = 277.6 Hz, C), 119.1 (CH), 61.3 (C), 61.1 (q, J$_{CF}$ = 37.0 Hz, CH$_2$), 38.7 (CH$_2$), 34.3 (CH$_2$); $^{19}$F NMR (376 MHz, CDCl$_3$) δ −73.5 (t, J = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C$_{25}$H$_{20}$F$_3$OS]$^+ [M+H]^+$: 457.1080, found 457.1087.
Data for 2aj: \( R_f = 0.24 \) (10% EtOAc/petroleum ether); IR 2927, 1749 (C=O), 1664 (C=O), 1494, 1430, 1283, 1162, 972, 757, 700 cm\(^{-1}\); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.69 (1H, d, \( J = 5.2 \) Hz, Ar\( H \)), 7.41-7.30 (6H, m, Ar\( H \)), 7.24 (1H, s, =CHPh), 7.15-7.06 (5H, m, Ar\( H \)), 4.49 (1H, dq, \( J = 12.7, 8.4 \) Hz, CH\( aH_bH CF_3 \)), 4.37 (1H, dq, \( J = 12.7, 8.4 \) Hz, CH\( aH_bH CF_3 \)), 3.63 (1H, dd, \( J = 15.2, 1.4 \) Hz, =CCH\( aH_bH \)), 3.35 (1H, d, \( J = 13.7 \) Hz, CH\( aH_bH Ph \)), 3.28 (1H, d, \( J = 13.7 \) Hz, CH\( aH_bH Ph \)), 3.04 (1H, dd, \( J = 15.2, 1.4 \) Hz, =CCH\( aH_bH \)); \(^1^C\) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 187.1 (C), 169.7 (C), 150.1 (C), 136.1 (C), 135.5 (CH), 135.3 (C), 134.6 (C), 130.8 (2 x CH), 130.7 (CH), 129.2 (2 x CH), 128.7 (2 x CH), 128.6 (C), 128.2 (2 x CH), 128.0 (CH), 127.1 (CH), 124.4 (CH), 122.7 (q, \( J_{CF} = 277.5 \) Hz, C), 61.1 (q, \( J_{CF} = 36.9 \) Hz, CH\(_2\)), 60.7 (C), 39.4 (CH\(_2\)), 34.7 (CH\(_2\)); \(^1^9^F\) NMR (376 MHz, CDCl\(_3\)) \( \delta \) –73.5 (t, \( J = 8.4 \) Hz, 3 x F); HRMS (ESI) Exact mass calculated for \([C_{25}H_{20}F_3O_5S]^+ [M+H]^+\): 457.1080, found 457.1085.
4. Enantioselective Cyclizations

Evaluation of Chiral Ligands

The reaction of substrate $1b$ with PhB(OH)$_2$ to give $2ba$ was conducted in the presence of $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ (5 mol%, 10 mol% Rh) and various chiral ligands (10 mol%) as shown in the Table below:

Reactions were conducted using 0.05 mmol of $1b$. Yields determined by $^1$H NMR spectroscopy using 1,4-dimethoxybenzene as an internal standard.

From these studies, ($R$)-MeO-BIPHEP (L1) emerged as a promising ligand, which was then employed in the reaction of substrate $1a$ with PhB(OH)$_2$ as described below:
2,2,2-Trifluoroethyl (E)-2-benzyl-4-benzylidene-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate [(+)-2aa]

An oven-dried microwave vial was fitted with a stirrer bar and charged with [Rh(C₂H₄)₂Cl]₂ (5.8 mg, 0.015 mmol) and (R)-MeO-BIPHEP (L₁, 17.5 mg, 0.03 mmol). The vial was sealed with a septum-lined cap and purged with argon for 30 min. 1,4-Dioxane (1.8 mL) and H₂O (0.2 mL), both of which were freshly degassed separately (purging with argon for 30 min) were added. The mixture was stirred at room temperature for 30 min. Meanwhile, a separate oven-dried microwave vial was fitted with a stirrer bar and charged with malonic ester 1a (142 mg, 0.30 mmol), phenylboronic acid (54.9 mg, 0.45 mmol), and KF (26.1 mg, 0.45 mmol). The vial was sealed with a septum-lined cap and purged with argon for 30 min. Degassed 1,4-dioxane (0.9 mL), degassed H₂O (0.1 mL) and the solution of catalyst (see above) were added. The mixture was stirred at 70 °C for 20 h. The reaction was cooled to room temperature, H₂O (15 mL) was added, and the mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (20 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0% to 1% EtOAc/n-pentane) to give a 1:20 inseparable mixture of alkyne hydroarylation products 3aa and 3ab, respectively (20.9 mg, 13%) as a yellow oil followed by arylative cyclization product 2aa (115 mg, 85%) as a yellow oil and.

Data for (+)-2aa: See above (page 15) and [α]²⁵D +36.0 (c 1.00, CHCl₃); Enantiomeric excess was determined by HPLC using a Chiralpak AD-H column (95:5 iso-hexane:i-PrOH, 1.0 mL/min, 254 nm, 25 °C) tᵣ (major) = 8.9 min, tᵣ (minor) = 16.3 min, 76% ee.

Data for 1:20 mixture of 3aa and 3ab, respectively, Rᵣ = 0.38 (10% EtOAc/petroleum ether); IR 3030, 1752 (C=O), 1411, 1281, 1159, 1084, 975, 759, 699, 650 cm⁻¹; ¹⁹F NMR (376 MHz, CDCl₃) δ –73.6 (t, J = 8.2 Hz, 6 × F); HRMS (ESI) Exact mass calculated for [C₂₉H₂₈F₆NO₄][M+NH₄]⁺: 568.1917, found 568.1919.

Data for major regioisomer: ¹H NMR (400 MHz, CDCl₃) 7.41-7.28 (6H, m, ArH), 7.24-7.13 (7H, m, ArH), 6.94-6.91 (2H, m, ArH), 5.95 (1H, t, J = 7.2 Hz, =CHCH₂), 4.56-4.34 (4H, m, 2 × CH₂CF₃), 3.33 (2H, s, CH₂Ph), 2.84 (2H, d, J = 7.2 Hz, =CHCH₂); ¹³C NMR (101 MHz, CDCl₃) δ 168.6 (2 ×
Characteristics signals for minor regioisomer: $^1$H NMR (400 MHz, CDCl$_3$) 6.82 (1H, s, =CHPh), 6.76-6.73 (2H, m, ArH), 3.93-3.84 (2H, m, CH$_2$CF$_3$), 3.80-3.73 (2H, m, CH$_2$CF$_3$), 3.69 (2H, s, CH$_3$Ph), 3.05 (2H, s, CH$_3$C=CH).

5. Possible Catalytic Cycle

A possible catalytic cycle for these reactions is depicted below, using substrate 1a and PhB(OH)$_2$ as example reaction partners. Heating a mixture of [Rh(cod)Cl]$_2$, KF, and H$_2$O may generate rhodium hydroxide 4 (R = H), which can undergo transmetalation with PhB(OH)$_2$ to give arylrhodium species 5. Phenylrhodation of the alkyne of 1a gives alkenylrhodium species 6, which then undergoes alkenyl-to-aryl 1,4-Rh(I) migration to give arylrhodium species 7. Cyclization of 7 by 1,2-addition onto one of the esters produces rhodium alkoxide 8, which collapses to release the product 2aa and regenerate the active rhodium complex 4 (which could have a either a trifluoroethoxide or hydroxide counterion).
6. NMR Spectra

![NMR Spectra](image-url)
Supplementary Information
Supplementary Information
Supplementary Information

(-)-2aa
(from enantioselective reaction)
7. **HPLC Traces**

![HPLC Traces](image)

### Table 1: HPLC Data

<table>
<thead>
<tr>
<th>RT [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area</th>
<th>Height</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.845</td>
<td>BB</td>
<td>0.2352</td>
<td>1907.724</td>
<td>120.1835</td>
<td>50.13</td>
</tr>
<tr>
<td>16.142</td>
<td>BB</td>
<td>0.4457</td>
<td>1808.094</td>
<td>62.9667</td>
<td>49.87</td>
</tr>
</tbody>
</table>

### Table 2: HPLC Data

<table>
<thead>
<tr>
<th>RT [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area</th>
<th>Height</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.876</td>
<td>BV</td>
<td>0.2419</td>
<td>22006.997</td>
<td>1411.1356</td>
<td>88.24</td>
</tr>
<tr>
<td>16.269</td>
<td>BB</td>
<td>0.4523</td>
<td>3060.150</td>
<td>100.7775</td>
<td>11.76</td>
</tr>
</tbody>
</table>
8. References