Supplemental materials for:

The Direct Acyl-Alkylation of Arynes

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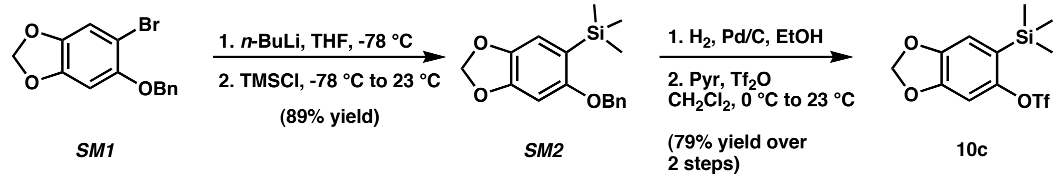
Materials and Methods. Unless stated otherwise, reactions were performed in flame-dried glassware sealed with rubber septa under a nitrogen atmosphere using dry, deoxygenated solvents. Commercially obtained reagents were used as received. Cesium fluoride was purchased from the Sigma-Aldrich Chemical Company, Milwaukee, WI. Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized using a combination of UV, anisaldehyde, ceric ammonium molybdate, and potassium permanganate staining. ICN silica gel (particle size 0.032 - 0.063 mm) was used for flash chromatography. ^{1}H NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz) or a Varian Inova 500 (at 500 MHz) and are reported relative to Me_4Si (δ 0.0). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on a Varian Mercury 300 (at 75 MHz), or a Varian Inova 500 (at 125 MHz) and are reported relative to Me_4Si (δ 0.0). Data for ^{13}C NMR spectra are reported in terms of chemical shift. ^{19}F NMR spectra were recorded on a

Varian Mercury 300 (at 300 MHz) and are reported relative to CF_3COOH (δ -76.54). Data for ^{19}F NMR spectra are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Spectrum BXII spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectra were obtained from the California Institute of Technology Mass Spectral Facility.

Synthesis of Aryne Precursors

Aryne precursor 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1**) was purchased from the Sigma-Aldrich Chemical Company, Milwaukee, WI. Aryne precursors 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**10a**)[1] and 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**10b**)[2] were prepared according to literature procedures.



SM2. A flame-dried reaction flask equipped with a magnetic stir bar was charged with benzyl protected sesamol ***SM1***[3] (325 mg, 1.06 mmol, 1.0 equiv) in THF (3.5 mL, 0.3 M), and the mixture was cooled to –78 °C in a dry ice/acetone bath. A 2.5 M solution of *n*-BuLi in hexanes (634 μL, 1.59 mmol, 1.5 equiv) was added slowly at –78 °C. After 15 minutes, TMSCl (200 μL, 1.59 mmol, 1.5 equiv) was added slowly at -78 °C. After 5 minutes, the cold bath was removed and the reaction mixture was allowed to warm to 23 °C. After 15 minutes, the mixture was quenched with saturated aqueous NH_4Cl (5 mL). The aqueous layer was extracted with Et_2O (3 x 5 mL). The organics were combined and dried over Na_2SO_4. After filtration, the residue was concentrated under reduced pressure. Purification by flash chromatography (10:1 hexanes/EtOAc eluent) provided aryl intermediate ***SM2*** (282 mg, 89% yield) as a clear oil: R_F 0.57 (3:1 hexanes/EtOAc); ^1H NMR (300 MHz, $CDCl_3$) δ 7.45-7.29 (m, 5H), 6.85 (s, 1H), 6.53 (s, 1H), 5.91 (s, 2H), 5.01 (s, 2H), 0.23 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 149.6, 141.5, 137.3, 128.7, 128.0, 127.5, 119.3, 113.7, 101.3, 95.2, 71.0, -0.5; IR (film) 2953, 2894, 1606, 1502, 1473, 1410, 1386, 1243, 1177, 1042 cm^{-1}; HRMS (EI^+) calc'd for $[C_{17}H_{20}O_3Si]^+$: *m/z* 300.1182, found 300.1187.

Aryne Precursor 10c. A reaction flask equipped with a magnetic stir bar was charged with aryl intermediate ***SM2*** (1.24 g, 4.13 mmol, 1 equiv) in absolute EtOH (17 mL, 0.25 M). To this mixture was added 10% Pd/C (440 mg, 0.413 mmol, 0.1 equiv), and the reaction vessel was stirred at room temperature under a balloon of H_2 (1 atm). After 14 hours the mixture was filtered through a short plug of celite (Et_2O eluent), and the solvent was evaporated under reduced pressure to afford a colorless oil, which was used immediately without further purification.

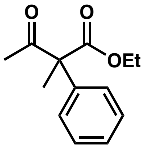
A flame-dried reaction flask equipped with a magnetic stir bar was charged with the *ortho*-silyl phenol in CH_2Cl_2 (20 mL, 0.2 equiv), and the mixture was cooled to 0 °C. Pyridine (1.05 mL, 13 mmol, 3 equiv) and Tf_2O (1.46 mL, 8.67 mmol, 2 equiv) were sequentially added, and the reaction mixture was allowed to warm to room temperature. After 5.5 hours the mixture was extracted with H_2O (20 mL). The aqueous layer was back-extracted with CH_2Cl_2 (3 x 10 mL). The organics were combined and dried over Na_2SO_4. After filtration, the residue was concentrated under reduced pressure. Purification by flash chromatography (10:1 hexanes/CH_2Cl_2 eluent) provided aryne precursor **10c** (1.116 g, 79% yield) as a clear oil: R_F 0.54 (3:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) _ 6.88 (s, 1H), 6.84 (s, 1H), 6.03 (s, 2H), 0.33 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) _ 149.7, 148.8, 147.1, 125.1, 113.4, 113.4, 102.6, 102.5, -0.5; ^{19}F NMR (300 MHz, $CDCl_3$) _ -74.63; IR (film) 2960, 2903, 1479, 1422, 1247, 1216, 1141, 984, 843 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{11}H_{13}O_5F_3SiS]^+$: *m/z* 342.0205, found 342.0211.

Synthesis of β-Ketoester Substrates

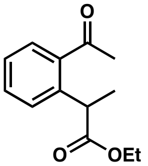
Methyl acetoacetate (**8a**), ethyl 2-methyl-3-oxobutanoate (**2**), ethyl 2-oxocyclopentanecarboxylate (**12b**), and methyl 2-oxocycloheptanecarboxylate (**12f**) were purchased from the Sigma-Aldrich Chemical Company, Milwaukee, WI. Substrates **8b,**[4] **8c,**[5] **8d,**[6] **8e,**[7] **8f,**[8] **8g,**[9] **8h,**[10] **12b,**[11] **12c,**[12] and **12d**[13] were prepared according to literature procedures.

Representative procedure for the acyl-alkylation of arynes (Tables 1, 2, and 3): A flame-dried long reaction tube equipped with a magnetic stir bar was charged with acetonitrile (2 mL). Methyl acetoacetate (**8a**) (43.2 μL, 0.4 mmol, 1.0 equiv), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1**) (121.4 μL, 0.5 mmol, 1.25 equiv) , and cesium fluoride (152 mg, 1.0 mmol, 2.5 equiv) were sequentially added to the flask. A septum was placed on the reaction vessel, and the mixture was then heated at 80 °C for 45-60 minutes. When benzyne precursor **1** was consumed by TLC analysis, the mixture was extracted with brine (4 mL). The aqueous layer was back-extracted with Et_2O (3 x 4 mL). The organics were combined and dried over Na_2SO_4. After filtration, the residue was concentrated under reduced pressure and purified by flash chromatography.

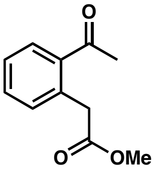
Spectral Data



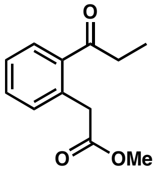
6. Purification by flash chromatography (20:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (37.1 mg, 42% yield) as a clear oil: R_F 0.36 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) _ 7.40-7.27 (m, 5H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.10 (s, 3H), 1.77 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) _ 205.1, 172.1, 138.8, 128.8, 127.9, 127.5, 64.9, 61.8, 27.4, 21.6, 14.2; IR (film) 2986, 1715, 1251 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{13}H_{16}O_3]^+$: *m/z* 220.1100, found 220.1089.



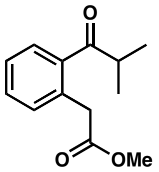
7. Purification by flash chromatography (20:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (46.4 mg, 53% yield) as a clear oil: R_F 0.42 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) _ 7.68 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.49-7.29 (m, 3H), 4.41 (q, *J* = 7.0 Hz, 1H), 4.17-4.05 (m, 2H), 2.59 (s, 3H), 1.50 (d, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) _ 202.4, 174.8, 140.4, 137.8, 132.0, 129.3, 128.8, 126.9, 60.8, 41.7, 29.9, 18.4, 14.3; IR (film) 2982, 1731, 1687, 1201 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{13}H_{16}O_3]^+$: *m/z* 220.1100, found 220.1091.



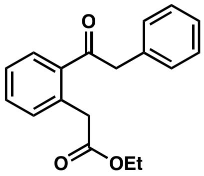
9a. Purification by flash chromatography (10:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (69 mg, 90% yield) as a clear oil: R_F 0.46 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.47-7.33 (m, 2H), 7.24-7.20 (m, 1H), 3.91 (s, 2H), 3.66 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) _ 201.3, 172.0, 137.1, 134.4, 132.8, 132.1, 130.1, 127.5, 51.9, 40.2, 28.8; IR (film) 3001, 2952, 1739, 1683 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{11}H_{12}O_3]^+$: *m/z* 192.0787, found 192.0787.



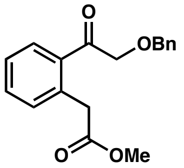
9b. Purification by flash chromatography (15:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (64.7 mg, 78% yield) as a clear oil: R_F 0.32 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) _ 7.77 (dd, J = 7.6, 1.5 Hz, 1H), 7.48-7.31 (m, 2H), 7.26-7.22 (m, 1H), 3.92 (s, 2H), 3.68 (s, 3H), 2.97 (q, J = 7.3 Hz, 2H), 1.18 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) _ 204.4, 172.2, 137.7, 134.2, 132.7, 131.8, 129.1, 127.5, 52.0, 40.1, 34.0, 8.4; IR (film) 2979, 2951, 1739, 1685, 1225, 1165 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{12}H_{14}O_3]^+$: *m/z* 206.0943, found 206.0933.



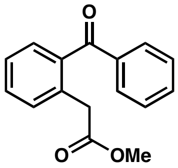
9c. Purification by flash chromatography (15:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (71.9 mg, 84% yield) as a clear oil: R_F 0.35 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) _ 7.78 (d, J = 7.4 Hz, 1H), 7.53-7.25 (m, 3H), 3.91 (s, 2H), 3.72 (s, 3H), 3.56-3.44 (m, 1H), 1.21 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) _ 207.9, 172.2, 137.2, 134.7, 132.9, 131.7, 128.9, 127.5, 52.0, 40.0, 37.7, 19.0; IR (film) 2973, 1741, 1683, 1229, 1165 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{13}H_{16}O_3]^+$: *m/z* 220.1100, found 220.1094.



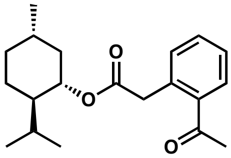
9d. Purification by flash chromatography (20:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (95.5 mg, 85% yield) as a clear oil: R_F 0.35 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) _ 7.86 (dd, J = 7.6, 1.5 Hz, 1H), 7.49-7.24 (m, 8H), 4.28 (s, 2H), 4.14 (q, J = 7.2 Hz, 2H), 3.92 (s, 2H), 1.25 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) _ 201.1, 171.7, 137.6, 134.7, 132.8, 131.9, 129.8, 129.4, 128.8, 128.7, 127.5, 127.0, 60.9, 47.8, 40.1, 14.4; IR (film) 3362, 2982, 1732, 1690, 1216, 1175 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{18}H_{18}O_3]^+$: *m/z* 282.1256, found 282.1266.



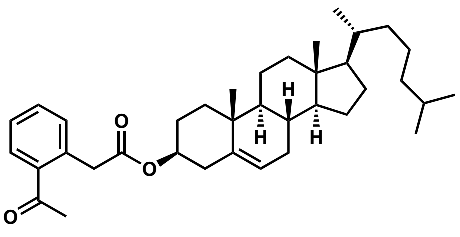
9e. Purification by flash chromatography (15:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (66.2 mg, 53% yield) as a clear oil: R$_F$ 0.28 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, CDCl$_3$) _ 7.66 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.48 (app. dt, *J* = 7.6, 1.4 Hz, 1H), 7.41-7.27 (m, 7H), 4.68 (s, 2H), 4.67 (s, 2H), 3.97 (s, 2H), 3.69 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) _ 200.1, 172.1, 137.5, 135.3, 134.7, 132.9, 132.4, 129.0, 128.7, 128.3, 128.2, 127.5, 73.6, 73.4, 52.2, 39.7; IR (film) 3030, 2950, 1736, 1700, 1230, 1213, 1167, 1110 cm^{-1}; HRMS (EI$^+$) calc'd for (M-H) [C$_{18}$H$_{17}$O$_4$]$^+$: *m/z* 297.1127, found 297.1136.



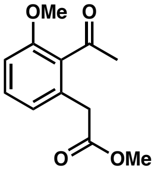
9f. Purification by flash chromatography (10:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (101 mg, 99% yield) as a clear oil: R$_F$ 0.38 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, CDCl$_3$) _ 7.84-7.79 (m, 1H), 7.61-7.54 (m, 1H), 7.50-7.30 (m, 7H), 3.90 (s, 2H), 3.55 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) _ 198.2, 171.8, 138.4, 137.9, 134.1, 133.1, 131.9, 131.0, 130.5, 130.2, 128.4, 126.7, 52.0, 38.8; IR (film) 2951, 1739, 1662, 1270 cm^{-1}; HRMS (EI$^+$) calc'd for [C$_{16}$H$_{14}$O$_3$]$^+$: *m/z* 254.0943, found 254.0952.



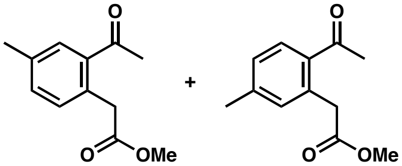
9g. Purification by flash chromatography (15:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (90.7 mg, 72% yield) as a clear oil: R$_F$ 0.50 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, CDCl$_3$) _ 7.81 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.51-7.34 (m, 2H), 7.28 (dd, *J* = 7.4, 1.1 Hz, 1H), 4.76-4.66 (m, 1H), 3.97 (s, 2H), 2.62 (s, 3H), 2.11-2.02 (m, 1H), 1.98-1.86 (m, 1H), 1.75-1.64 (m, 2H), 1.58-1.33 (m, 3H), 1.11-1.00 (m, 2H), 0.93 (d, *J* = 4.3 Hz, 3H), 0.91 (d, *J* = 5.1 Hz, 3H), 0.77 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) _ 201.4, 171.3, 137.7, 134.6, 132.7, 131.9, 129.8, 127.4, 74.8, 47.2, 41.0, 40.6, 34.4, 31.6, 29.0, 26.3, 23.6, 22.2, 20.9, 16.5; IR (film) 2955, 2929, 2870, 1732 1687, 1258, 1172 cm^{-1}; HRMS (EI$^+$) calc'd for [C$_{20}$H$_{28}$O$_3$]$^+$: *m/z* 316.2039, found 316.2034.



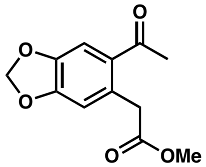
9h. Purification by flash chromatography (15:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (163.5 mg, 75% yield) as a clear oil: R_F 0.50 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) _ 7.79 (dd, J = 7.6, 1.5 Hz, 1H), 7.48-7.33 (m, 2H), 7.24 (dd, J = 7.6, 1.0 Hz, 1H), 5.36 (d, J = 5.1 Hz, 1H), 4.72-4.55 (m, 1H), 3.91 (d, J = 1.6 Hz, 2H), 2.59 (s, 3H), 2.35 (d, J = 7.7 Hz, 2H), 2.05-1.76 (m, 5H), 1.70-1.05 (m, 21H), 1.02 (s, 3H), 0.91 (d, J = 6.4 Hz, 3H), 0.86 (dd, J = 6.5, 1.2 Hz, 6H), 0.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) _ 201.3, 171.2, 139.9, 137.5, 134.7, 132.8, 132.1, 130.0, 127.5, 122.7, 74.6, 56.9, 56.3, 50.2, 42.5, 40.7, 39.9, 39.7, 38.2, 37.2, 36.8, 36.4, 36.0, 32.1, 32.0, 29.0, 28.4, 28.2, 27.9, 24.5, 24.0, 23.0, 22.8, 21.2, 19.5, 18.9, 12.0; IR (film) 3451, 2946, 2868, 1732, 1686, 1258, 1170 cm^{-1}; HRMS (EI^{+}) calc'd for $[C_{37}H_{54}O_3]^+$: *m/z* 546.4073, found 546.4080.



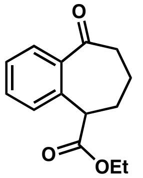
11a. Purification by flash chromatography (15:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (84.6 mg, 95% yield) as a clear oil: R_F 0.29 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) _ 7.30 (d, J = 8.2 Hz, 1H), 6.90-6.81 (m, 2H), 3.84 (s, 3H), 3.68 (s, 2H), 3.66 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) _ 205.3, 171.9, 157.3, 132.7, 131.2, 130.8, 123.6, 110.4, 55.8, 52.2, 38.3, 32.3; IR (film) 3005, 2952, 2842, 1738, 1691, 1598, 1583, 1471, 1438, 1351, 1267 cm^{-1}; HRMS (EI^{+}) calc'd for $[C_{12}H_{14}O_4]^+$: *m/z* 222.0892, found 222.0892.



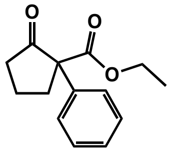
11b. Purification by flash chromatography (15:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation products as a mixture of inseparable isomers (67.9 mg, 82% yield) as a clear oil: R_F 0.26 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) _ 7.74 (d, J = 8.0 Hz, 1H), 7.61 (s, 1H), 7.27 (d, J = 7.5 Hz, 1H), 7.19 (d, J = 7.9 Hz, 1H), 7.13 (d, J = 7.7 Hz, 1H), 7.05 (s, 1H), 3.90 (s, 2H), 3.89 (s, 2H), 3.69 (s, 3H), 3.68 (s, 3H), 2.58 (s, 3H), 2.56 (s, 3H), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) _ 201.5, 200.7, 172.4, 172.3, 143.0, 137.3, 137.1, 134.9, 134.3, 133.9, 132.9, 132.7, 131.5, 130.9, 130.8, 129.6, 128.2, 52.0, 40.6, 39.9, 28.9, 28.8, 21.6, 21.2; IR (film) 2952, 1740, 1680 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{12}H_{14}O_3]^+$: *m/z* 206.0943, found 206.0945.



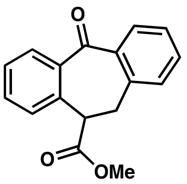
11c. Purification by flash chromatography (7:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (70.7 mg, 75% yield) as a clear oil: R_F 0.18 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) _ 7.29 (s, 1H), 6.70 (s, 1H), 6.03 (s, 2H), 3.84 (s, 2H), 3.69 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) _ 199.0, 172.2, 150.6, 146.9, 131.2, 130.7, 113.0, 110.5, 102.2, 52.0, 40.7, 28.9; IR (film) 1738, 1678, 1613, 1507, 1491, 1375, 1274, 1245 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{12}H_{12}O_5]^+$: *m/z* 236.0685, found 236.0692.



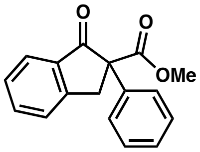
13a. Purification by flash chromatography (15:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (46.9 mg, 51% yield) as a clear oil: R_F 0.32 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) _ 7.67 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.51-7.40 (m, 1H), 7.42-7.35 (m, 1H), 7.22-7.18 (m, 1H), 4.25-4.16 (m, 2H), 4.02 (dd, *J* = 7.4, 5.6 Hz, 1H), 2.84-2.73 (m, 1H), 2.70-2.57 (m, 1H), 2.47-2.33 (m, 1H), 2.16-2.03 (m, 1H), 1.92-1.76 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) _ 206.2, 173.4, 139.7, 136.8, 132.1, 128.8, 128.7, 127.8, 61.4, 49.0, 41.0, 28.5, 20.4, 14.2; IR (film) 2939, 1730, 1681, 1254, 1188 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{14}H_{16}O_3]^+$: *m/z* 232.1100, found 232.1095.



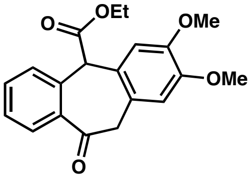
SM3. Purification by flash chromatography (25:1 hexanes/EtOAc eluent) provided the α-arylated product (30.3 mg, 33% yield) as a clear oil: R_F 0.42 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.28 (m, 5H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.94-2.82 (m, 1H), 2.59-2.44 (m, 2H), 2.42-2.27 (m, 1H), 2.10-1.86 (m, 2H), 1.21 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.2, 170.9, 136.4, 128.7, 127.8, 127.6, 65.2, 62.1, 38.0, 35.1, 19.5, 14.2; IR (film) 2976, 1747, 1712, 1445, 1212 cm^{-1}.



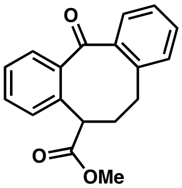
13b. Purification by flash chromatography (25:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (63.9 mg, 61% yield) as a clear oil: R_F 0.31 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, CDCl$_3$) _ 8.10 (dd, *J* = 7.7, 1.6 Hz, 1H), 8.01 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.53-7.30 (m, 4H), 7.24-7.18 (m, 2H), 4.26 (t, *J* = 4.8 Hz, 1H), 3.56 (d, *J* = 5.1 Hz, 2H), 3.50 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) _ 194.4, 172.5, 138.8, 138.6, 138.4, 137.5, 132.7, 131.5, 130.6, 130.3, 129.6, 128.9, 128.0, 127.4, 52.4, 50.6, 37.8; IR (film) 2951, 1737, 1649, 1599, 1292, 1240, 1170 cm^{-1}; HRMS (EI$^+$) calc'd for [C$_{17}$H$_{14}$O$_3$]$^+$: *m/z* 266.0943, found 266.0941.



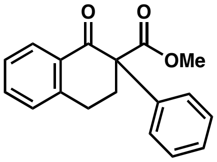
SM4. Purification by flash chromatography (25:1 hexanes/EtOAc eluent) provided the α-arylated product (42 mg, 39% yield) as a clear oil: R_F 0.35 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, CDCl$_3$) _ 7.74 (d, *J* = 7.4 Hz, 1H), 7.54 (app. dt, *J* = 7.4, 1.2 Hz, 1H), 7.42-7.14 (m, 7H), 4.13 (d, *J* = 17.3 Hz, 1H), 3.6 (s, 3H), 3.47 (d, *J* = 17.3 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) _ 200.4, 171.2, 138.9, 135.9, 135.2, 128.9, 128.5, 128.2, 127.8, 127.5, 126.4, 125.3, 65.6, 53.5, 41.0; IR (film) 2952, 1745, 1716, 1606, 1211 cm^{-1}; HRMS (EI$^+$) calc'd for [C$_{17}$H$_{14}$O$_3$]$^+$: *m/z* 266.0943, found 266.0934.



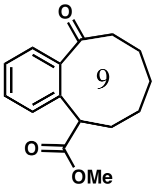
13c. Purification by flash chromatography (1:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (75.7 mg, 65% yield) as a clear oil: R_F 0.12 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, CDCl$_3$) _ 8.10 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.52-7.30 (m, 3H), 6.87 (s, 1H), 6.76 (s, 1H), 4.88 (s, 1H), 4.43 (d, *J* = 14.8 Hz, 1H), 4.24-4.13 (m, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 3.72 (d, *J* = 15.4 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) _ 194.8, 171.4, 148.8, 148.0, 139.9, 134.8, 133.1, 131.3, 131.0, 129.8, 128.3, 124.7, 114.0, 113.8, 62.1, 59.4, 56.3, 56.2, 49.5, 14.4; IR (film) 2978, 2937, 1728, 1673, 1598, 1518, 1262, 1230, 1201, 1112, 1025 cm^{-1}; HRMS (EI$^+$) calc'd for [C$_{20}$H$_{20}$O$_5$]$^+$: *m/z* 340.1311, found 340.1326.



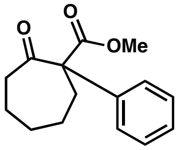
13d. Purification by flash chromatography (15:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (50 mg, 45% yield) as a clear oil: R_F 0.39 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, CDCl$_3$) _ 8.19 (dd, J = 7.8, 1.5 Hz, 1H), 7.94 (dd, J = 7.7, 1.6 Hz, 1H), 7.57-7.49 (m, 2H), 7.47-7.30 (m, 2H), 7.24-7.16 (m, 2H), 3.88 (dd, J = 11.6, 4.9 Hz, 1H), 3.62 (s, 3H), 2.71-2.53 (m, 2H), 2.20-1.95 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) _ 194.3, 173.7, 141.3, 140.7, 139.2, 136.7, 133.9, 133.0, 131.3, 131.1, 130.8, 127.7, 127.2, 126.3, 52.3, 45.3, 35.6, 30.6; IR (film) 2951, 1736, 1638, 1595, 1292, 1254, 1219 cm^{-1}; HRMS (EI$^+$) calc'd for [C$_{18}$H$_{16}$O$_3$]$^+$: *m/z* 280.1100, found 280.1108.



SM5. Purification by flash chromatography (15:1 hexanes/EtOAc eluent) provided the α-arylated product (61.5 mg, 55% yield) as a clear oil: R_F 0.31 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, CDCl$_3$) _ 8.15 (dd, J = 8.0, 1.3 Hz, 1H), 7.50-7.42 (m, 1H), 7.38-7.28 (m, 4H), 7.25-7.14 (m, 3H), 3.75 (s, 3H), 3.08-2.91 (m, 2H), 2.88-2.70 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) _ 194.7, 172.3, 143.2, 136.4, 133.9, 132.3, 128.9, 128.7, 128.5, 127.9, 127.9, 127.1, 63.7, 53.0, 32.6, 26.0; IR (film) 2951, 1732, 1682, 1600, 1253 cm^{-1}; HRMS (EI$^+$) calc'd for [C$_{18}$H$_{16}$O$_3$]$^+$: *m/z* 280.1100, found 280.1107.



13e. Purification by flash chromatography (20:1 hexanes/EtOAc eluent) provided the desired acyl-alkylation product (67.6 mg, 69% yield) as a clear oil: R_F 0.29 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, CDCl$_3$) _ 7.40-7.17 (m, 4H), 3.95 (dd, J = 11.7, 4.8 Hz, 1H), 3.66 (s, 3H), 2.96-2.85 (m, 1H), 2.84-2.72 (m, 1H), 2.07-1.80 (m, 4H), 1.77-1.45 (m, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) _ 211.4, 174.5, 143.3, 134.9, 130.1, 127.9, 127.2, 124.9, 52.3, 46.0, 43.5, 32.3, 26.0, 25.4, 23.8; IR (film) 2936, 2860, 1732, 1693, 1435, 1249, 1201 cm^{-1}; HRMS (EI$^+$) calc'd for [C$_{15}$H$_{18}$O$_3$]$^+$: *m/z* 246.1256, found 246.1255.



SM6. Purification by flash chromatography (15:1 hexanes/EtOAc eluent) provided the α-arylated product (29.9 mg, 30% yield) as a clear oil: R_F 0.39 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.28 (m, 3H), 7.22-7.18 (m, 2H), 3.69 (s, 3H), 2.83-2.72 (m, 2H), 2.61-2.54 (m, 2H), 2.24-2.13 (m, 2H), 2.00-1.56 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.89, 172.8, 139.1, 128.7, 127.8, 127.7, 68.5, 52.8, 42.2, 34.0, 30.7, 26.7, 25.8; IR (film) 2928.79, 1729, 1703, 1490, 1446, 1228, 1155 cm^{-1}.

Independent Chemical Correlation / Structural Proof

Acyl-alkylation product **9a** was independently prepared according to a literature procedure.[14] The product obtained through our methodology was identical by all spectroscopic data to the compound prepared by this alternative method. Spectroscopic data for acyl-alkylation product **9f** was identical to all the reported data in the literature.[15]

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