Supporting Information
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Palladium-Catalyzed Carbonylative Cross-Coupling Reaction Between Aryl(Heteroaryl) Iodides and Tricyclopropylbismuth: Expedient Access to Aryl Cyclopropylketones

Supporting Information

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1. General information

Unless otherwise indicated, all reactions were run under argon in a flame dried glassware. Commercial reagents were used without further purification. Allylchloro[1,3-bis(2,6-di-i-propylphenyl)-4,5-dihydroimidazol-2-ylidene]palladium (II) ((SIPr)Pd(allyl)Cl)) was purchased from Strem Chemicals. 2-(4-Iodophenoxy)tetrahydro-2H-pyran 5f and 4-iodophenyl pivalate 5k were synthesized according to Dansereau, J.; Gautreau, S.; Gagnon, A. ChemistrySelect 2017, 2, 2593. (E)-(((3-iodoallyl)oxy)methyl)benzene 8 was synthesized according to Huang, Z.; Negishi, E.-i. Org. Lett. 2006, 8, 3675. Anhydrous solvents were obtained using an encapsulated solvent purification system and were further dried over 4 Å molecular sieves. The evolution of reactions was monitored by analytical thin-layer chromatography using silica gel 60 F254 precoated plates. Flash chromatography was performed employing 230-400 mesh silica using the indicated solvent system according to standard techniques. Melting points are uncorrected. Nuclear magnetic resonance spectra (1H, 13C) were recorded on a 300 MHz or 600 MHz spectrometer. Chemical shifts for 1H-NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.26 ppm; methanol, δ 3.31 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet, m = multiplet), coupling constant J in Hz and integration. Chemical shifts for 13C spectra are recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (δ 77.16 ppm) or the central peak of tetradeuteromethanol (δ 49.00 ppm) as the internal standard. IR spectra were recorded on a FT-IR from thin films and are reported in reciprocal centimeters (cm⁻¹). HRMS were performed on a TOF LCMS analyzer using the electrospray (ESI) mode.
2. Table S1: Optimization of reaction conditions: Palladium catalysts and ligands

![Diagram of optimized reaction conditions]

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<th>Entry</th>
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<th>(3) (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<sup>a</sup> Yields of isolated pure products.  <sup>b</sup> RSM = Recovered Starting Material.  <sup>c</sup> Pd(OAc)<sub>2</sub> (5 mol%), Phosphine (10 mol%).

3. Synthesis of tricyclopropybismuth (2a)

![Diagram of tricyclopropybismuth (2a)]

Bismuth chloride (3.23 g, 10.2 mmol) was dissolved in anhydrous THF under argon (70 mL) and cooled to −10 °C. Cyclopropylmagnesium bromide<sup>1</sup> (45 mL, 34 mmol, 0.75 M in THF, 3.3 equiv) was slowly added dropwise; a black precipitate was observed. The reaction mixture was stirred at room temperature for 1h, heated at 70 °C for 1h, and cooled to room

<sup>1</sup> Cyclopropylmagnesium bromide was titrated prior to use using the diphenyl ditelluride method as reported in: Aso, Y.; Yamashita, H.; Otsubo, T.; Ogura, F. J. Org. Chem. 1989, 54, 5627.
temperature. The solution was cannulated in a flask containing a stirred degassed biphasic solution of brine (100 mL) and diethyl ether (100 mL). The obtained biphasic solution was stirred for an additional 5 minutes. The stirring was stopped and the organic layer was cannulated under argon over a plug of celite and sodium sulfate in a flame dried round bottom flask. Tricyclopribylbimuth 2a was kept under argon as a THF/ether solution. Approximately 4 to 5 mL of this solution was transferred in a tared round bottom flask equipped with a septum. The solvents were removed with a stream of argon to generate a slight yellow oily residue. The mass of crude oily tricyclopribylbismuth 2a was calculated by weighing the flask with the septum. The crude residue was used directly in the carbonylative cross-coupling reaction (vide infra).

4. Synthesis of 1-(1-(benzyloxy)ethyl)-4-iodobenzene (5l)

![5l]

4-Iodobenzaldehyde (200 mg, 0.862 mmol) was dissolved in anhydrous THF (1.5 mL). The flask was cooled to −78 °C and methylmagnesium bromide (444 μL, 0.862 mmol, 1.94 M in diethyl ether, 1.0 equiv) was added dropwise. The reaction was warmed up to room temperature and was stirred for 1h. The reaction was quenched with aq. sat. NH₄Cl solution (50 mL) and was extracted with EtOAc (2 x 50 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to afford 202 mg of crude alcohol. The corresponding crude alcohol was taken directly into the next step without further purification. The residue was diluted in 1 mL of anhydrous DCM and was added dropwise to a solution of sodium hydride (39.0 mg, 0.997 mmol, 1.2 equiv) in anhydrous DCM (2 mL). The flask was cooled to 0 °C and benzyl bromide (106 μL, 0.895 mmol, 1.1 equiv) was added dropwise. The flask was warmed up to room temperature and was stirred overnight. The reaction mixture was transferred in a

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2 The flask was flame dried under argon, cooled down to r.t. and was tared with the septum.
separatory funnel containing 10 mL of an aq. sat. NaHCO₃ solution. The aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (2 x 10 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (1% to 10% EtOAc/Hex) to afford 1-iodo-4-(1-phenoxyethyl)benzene 5l (190 mg, 65%) as a pale yellow oil: Rf 0.43 (5% EtOAc/Hex); ¹H-NMR (300 MHz, CDCl₃) δ 7.70 (d, J = 8.4 Hz, 2H), 7.38-7.28 (m, 5H), 7.12 (d, J = 8.4 Hz, 2H), 4.46-4.27 (m, 3H), 1.45 (d, J = 6.6 Hz, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 143.6, 138.4, 137.7, 128.55, 128.49, 127.8, 127.7, 93.0, 76.8, 70.6, 24.2; IR (neat) 3084, 3063, 3029, 2974, 2924, 2865, 1722, 1702, 1685, 1584, 1480, 1453, 1391, 1268, 1086, 1057, 1005, 819, 696; HRMS (ESI) calcld for C₁₅H₁₅IO: 338.0168, found 451.0023 [M+TFA]+.

5. General procedure for the carbonylative cross-coupling

**Method A:** A sealed tube equipped with a magnetic stirring bar was charged with the aryl halide (1) or (5) (1.0 equiv), sodium carbonate (2.0 equiv), anhydrous lithium chloride (2.0 equiv) and (SIPr)Pd(allyl)Cl (0.05 equiv). Tricyclopropylbismuth (2a) (1.0 equiv), prepared as described above, was dissolved in anhydrous DMF (0.1 M) under argon and was added into the sealed tube. Carbon monoxide was bubbled in the reaction mixture for 45 seconds, then the tube was sealed and heated at 40 °C for 16 hours. The reaction mixture was cooled to room temperature, transferred in a separatory funnel containing 20 mL of an aq. sat. NaHCO₃ solution and was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography using the indicated solvent system to afford the desired aryl cyclopropyl ketone (3) or (6).

**Method B:** Same as method A except that 1.5 equivalents of tricyclopropylbismuth 2a instead of 1.0 equivalent and 0.1 equivalents of (SIPr)Pd(allyl)Cl instead of 0.05 equivalents were used and that the reaction was heated at 80 °C instead of 40 °C.
Method A was followed on 0.231 mmol scale starting from methyl 4-iodobenzoate 1a. The residue was purified on silica gel (10% EtOAc/Hex) to afford 3 and 4.

3: Pale yellow solid (46.2 mg, 98%); Rf 0.21 (10% EtOAc/Hex); m.p. 62.6 °C; 1H-NMR (300 MHz, CDCl₃) δ 8.12 (d, J = 8.7 Hz, 2H), 8.07 (d, J = 8.7 Hz, 2H), 3.94 (s, 3H), 2.71-2.62 (m, 1H), 1.29-1.24 (m, 2H), 1.11-1.05 (m, 2H); 13C-NMR (75 MHz, CDCl₃) δ 200.4, 166.4, 141.4, 133.6, 129.9, 128.0, 52.6, 17.8, 12.3; IR (neat) 2953, 2852, 1720, 1667, 1439, 1407, 1278, 1216, 1107, 1016, 993, 720; HRMS (ESI) calcd for C₁₂H₁₂O₃: 204.0786, found 205.0855 [M+H]+.

4: Colorless oil (1.0 mg, 2%); Rf 0.45 (10% EtOAc/Hex); 1H-NMR (300 MHz, CDCl₃) δ 7.91 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H), 1.97-1.88 (m, 1H), 1.07-1.01 (m, 2H), 0.79-0.75 (m, 2H); 13C-NMR (75 MHz, CDCl₃) δ 167.3, 150.1, 129.8, 127.4, 125.5, 52.1, 15.8, 10.4; IR (neat) 3085, 3004, 2951, 2840, 1716, 1609, 1434, 1274, 1180, 1102, 767; HRMS (ESI) calcd for C₁₁H₁₂O₂: 176.0837, found 177.0910 [M+H]+.

(4-(tert-butyl)phenyl)(cyclopropyl)methanone (6a)

Method B was followed on 0.173 mmol scale starting from 1-(tert-butyl)-4-iodobenzene 5a. The residue was purified on silica gel (4% EtOAc/Hex) to afford 6a: Pale yellow oil (23.0 mg, 66%); Rf 0.29 (4% EtOAc/Hex); 1H-NMR (300 MHz, CDCl₃) δ 7.97 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 2.72-2.63 (m, 1H), 1.35 (s, 9H), 1.26-1.20 (m, 2H), 1.05-0.98 (m, 2H); 13C-NMR (75 MHz, CDCl₃) δ 200.3, 156.5, 135.6, 128.1, 125.6, 35.2, 31.3, 17.1, 11.5; IR (neat)
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2966, 2942, 2869, 1658, 1603, 1411, 1380, 1360, 1230, 1201, 1110, 900, 705; HRMS (ESI) calcd for C_{14}H_{18}O: 202.1358, found 203.1432 [M+H]^+.

Cyclopropyl(3-(trifluoromethyl)phenyl)methanone (6b)

Method B was followed on 0.156 mmol scale starting from 1-iodo-3-(trifluoromethyl)benzene 5b. The residue was purified on silica gel (10% EtOAc/Hex) to afford 6b: Yellow oil (20.8 mg, 62%); R_f 0.42 (10% EtOAc/Hex); ^1H-NMR (300 MHz, CDCl_3) δ 8.26 (s, 1H), 8.19 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 2.71-2.63 (m, 1H), 1.31-1.26 (m, 2H), 1.14-1.08 (m, 2H); ^13C-NMR (75 MHz, CDCl_3) δ 199.4, 138.6, 131.3, 129.31, 129.26, 129.2, 125.044, 124.993, 17.5, 12.3; IR (neat) 3016, 2977, 2969, 2885, 1674, 1612, 1383, 1328, 1210, 1122, 1070, 1039, 999, 741, 694, 667; HRMS (ESI) calcd for C_{11}H_{9}F_{3}O: 214.0605, found 215.0684 [M+H]^+.

Cyclopropyl(o-tolyl)methanone (6c)

Method B was followed on 0.162 mmol scale starting from 1-iodo-2-methylbenzene 5c. The residue was purified on silica gel (4% EtOAc/Hex) to afford 6c: Colorless oil (23.0 mg, 89%); R_f 0.23 (4% EtOAc/Hex); ^1H-NMR (300 MHz, CDCl_3) δ 7.70 (dd, J = 7.5, 1.5 Hz, 1H), 7.36 (dt, J = 7.2, 1.5 Hz, 1H), 7.29-7.22 (m, 2H), 2.48 (s, 3H), 2.47-2.39 (m, 1H), 1.27-1.22 (m, 3H).
2H), 1.07-1.00 (m, 2H); $^{13}$C-NMR (75 MHz, CDCl$_3$) δ 205.2, 139.9, 137.0, 131.6, 130.9, 128.4, 125.7, 20.9, 20.8, 12.0. Spectral data are in agreement with those reported in the literature.3

Cyclopropyl(4-nitrophenyl)methanone (6d) and 1-cyclopropyl-4-nitrobenzene (7d)

Method B was followed on 0.183 mmol scale starting from 1-iodo-4-nitrobenzene 5d. The residue was purified on silica gel (10% EtOAc/Hex) to afford 6d and 7d.

6d: Yellow oil (15.4 mg, 44%); R$_f$ 0.22 (10% EtOAc/Hex); $^1$H-NMR (300 MHz, CDCl$_3$) δ 8.31 (d, $J = 9.0$ Hz, 2H), 8.14 (d, $J = 9.0$ Hz, 2H), 2.71-2.62 (m, 1H), 1.34-1.29 (m, 2H), 1.18-1.12 (m, 2H); $^{13}$C-NMR (75 MHz, CDCl$_3$) δ 199.3, 150.2, 142.6, 129.1, 123.9, 18.1, 12.8; IR (neat) 3106, 3076, 3007, 2855, 2161, 1663, 1601, 1520, 1410, 1384, 1344, 1321, 1213, 991, 853, 710; HRMS (ESI) calcd for C$_{10}$H$_9$NO$_3$: 191.0582, found 192.0667 [M+H]$^+$.  

7d: Brown oil (12.7 mg, 43%); R$_f$ 0.60 (10% EtOAc/Hex); $^1$H-NMR (300 MHz, CDCl$_3$) δ 8.10 (d, $J = 8.7$ Hz, 2H), 7.16 (d, $J = 8.7$ Hz, 2H), 2.04-1.94 (m, 1H), 1.15-1.10 (m, 2H), 0.85-0.79 (m, 2H); $^{13}$C-NMR (75 MHz, CDCl$_3$) δ 152.8, 126.1, 123.8, 16.0, 11.2; IR (neat) 3076, 3007, 2939, 2843, 2445, 1589, 1511, 1338, 1110, 1044, 749; HRMS (ESI) calcd for C$_9$H$_9$NO$_2$: 163.0633, found 164.0716 [M+H]$^+$.

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(4-(benzyloxy)phenyl)(cyclopropyl)methanone (6e)

Method B was followed on 0.182 mmol scale starting from 1-(benzyloxy)-4-iodobenzene 5e. The residue was purified on silica gel (10% EtOAc/Hex) to afford 6e: Yellow oil (24.6 mg, 54%); Rf 0.26 (10% EtOAc/Hex); 1H-NMR (300 MHz, CDCl3) δ 8.02 (d, J = 8.7 Hz, 2H), 7.46-7.32 (m, 5H), 7.03 (d, J = 9.0 Hz, 2H), 5.14 (s, 2H), 2.67-2.59 (m, 1H), 1.24-1.19 (m, 2H), 1.03-0.97 (m, 2H); 13C-NMR (75 MHz, CDCl3) δ 199.1, 162.5, 136.4, 131.4, 130.4, 128.8, 128.3, 127.6, 114.6, 70.2, 16.8, 11.4; IR (neat) 3118, 3094, 3058, 3007, 2945, 2876, 1651, 1599, 1570, 1383, 1225, 1172, 986, 838, 755, 700; HRMS (ESI) calcd for C17H16O2: 252.1150, found 253.1250 [M+H]+.

Cyclopropyl(4-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)methanone (6f)

Method B was followed on 0.154 mmol scale starting from 2-(4-iodophenoxy)tetrahydro-2H-pyran 5f. The residue was purified on silica gel (10% EtOAc/Hex with 2% of Et3N) to afford 6f: White solid (25.9 mg, 68%); Rf 0.39 (20% EtOAc/Hex); m.p. 68.3 °C; 1H-NMR (300 MHz, CDCl3) δ 8.02 (d, J = 9.0 Hz, 2H), 7.14 (d, J = 8.7, 2H), 5.56 (t, J = 3.3 Hz, 1H), 3.86-3.81 (m, 1H), 3.66-3.59 (m, 1H), 2.82-2.75 (m, 1H), 2.07-1.94 (m, 1H), 1.91-1.84 (m, 2H), 1.73-1.55 (m, 3H), 1.12-1.04 (m, 2H), 1.07-1.04 (m, 2H); 13C-NMR (75 MHz, CDCl3) δ 201.7, 162.6, 132.6, 131.2, 117.1, 97.5, 63.2, 31.2, 26.2, 19.7, 17.4, 11.9; IR (neat) 3121, 3094, 3058, 3007, 2945, 2876, 1651, 1599, 1570, 1383, 1225, 1172, 986, 838, 755, 700; HRMS (ESI) calcd for C15H18O3: 246.1256, found 247.1354 [M+H]+.
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**Benzo[d][1,3]dioxol-5-yl(cyclopropyl)methanone (6g) and 5-cyclopropylbenzo[d][1,3]dioxole (7g)**

Method B was followed on 0.171 mmol scale starting from 5-iodobenzo[d][1,3]dioxole 5g. The residue was purified on silica gel (10% EtOAc/Hex with 2% of Et₃N) to afford 6g and 7g.

**6g:** Colorless oil (18.7 mg, 57%); Rf 0.27 (10% EtOAc/Hex); ¹H-NMR (300 MHz, CDCl₃) δ 7.65 (dd, J = 8.1, 1.8 Hz, 1H), 7.47 (d, J = 1.5 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 6.04 (s, 2H), 2.61-2.53 (m, 1H), 1.22-1.17 (m, 2H), 1.02-0.96 (m, 2H); ¹³C-NMR (75 MHz, CDCl₃) δ 198.7, 151.6, 148.2, 133.0, 124.3, 108.1, 107.9, 101.9, 16.9, 11.5; IR (neat) 3007, 2900, 1660, 1602, 1504, 1488, 1442, 1377, 1244, 1136, 1113, 1032, 994, 745; HRMS (ESI) calcd for C₁₁H₁₀O₃: 190.0630, found 191.0709 [M+H]⁺.

**7g:** Colorless oil (8.1 mg, 29%); Rf 0.71 (10% EtOAc/Hex); ¹H-NMR (300 MHz, CDCl₃) δ 6.71 (d, J = 7.8 Hz, 1H), 6.59 (dd, J = 7.8, 1.8 Hz, 1H), 6.55 (d, J = 1.8 Hz, 1H), 5.90 (s, 2H), 1.89-1.80 (m, 1H), 0.92-0.86 (m, 2H), 0.63-0.58 (m, 2H); ¹³C-NMR (75 MHz, CDCl₃) δ 147.8, 138.0, 119.2, 108.2, 106.4, 100.9, 100.1, 15.4, 8.8. Spectral data are in agreement with those reported in the literature.⁴

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**Ethyl 3-(cyclopropanecarbonyl)benzoate (6h) and ethyl 3-cyclopropylbenzoate (7h)**

Method B was followed on 0.178 mmol scale starting from ethyl 3-iodobenzoate 5h. The residue was purified on silica gel (10% EtOAc/Hex) to afford 6h and 7h.

**6h:** Yellow oil (25.0 mg, 64%); R\(_f\) 0.30 (10% EtOAc/Hex); \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta \) 8.67 (t, \(J = 1.8 \) Hz, 1H), 8.23 (dt, \(J = 7.8, 1.2 \) Hz, 1H), 8.17 (dt, \(J = 7.5, 1.5 \) Hz, 1H), 7.55 (t, \(J = 7.5 \) Hz, 1H), 4.41 (q, \(J = 7.2 \) Hz, 2H), 2.74-2.69 (m, 1H), 1.41 (t, \(J = 7.2 \) Hz, 3H), 1.30-1.24 (m, 2H), 1.12-1.05 (m, 2H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta \) 200.0, 166.0, 138.3, 133.6, 132.1, 131.0, 129.3, 128.8, 61.5, 17.4, 14.4, 12.2; IR (neat) 3010, 2981, 2936, 2873, 1717, 1671, 1603, 1386, 1277, 1207, 1191, 1000, 721; HRMS (ESI) calcd for C\(_{13}\)H\(_{14}\)O\(_3\): 218.0943, found 219.1042 [M+H]+.

**7h:** Colorless oil (7.2 mg, 21%); R\(_f\) 0.57 (10% EtOAc/Hex); \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta \) 7.82 (dt, \(J = 7.5, 1.5 \) Hz, 1H), 7.74 (t, \(J = 2.1 \) Hz, 1H), 7.31 (t, \(J = 7.5 \) Hz, 1H), 7.27-7.24 (m, 1H), 4.37 (q, \(J = 7.2 \) Hz, 2H), 1.98-1.92 (m, 1H), 1.39 (t, \(J = 6.9 \) Hz, 3H), 1.01-0.98 (m, 2H), 0.77-0.73 (m, 2H); \(^{13}\)C-NMR (150 MHz, CDCl\(_3\)) \(\delta \) 166.9, 144.5, 130.4, 128.3, 126.7, 61.0, 15.4, 14.5, 9.5; IR (neat) 3085, 3004, 2981, 2903, 2864, 1715, 1606, 1586, 1463, 1440, 1391, 1367, 1275, 1259, 1215, 1173, 1106, 1083, 1020, 751, 690; HRMS (ESI) calcd for C\(_{12}\)H\(_{14}\)O\(_2\): 190.0994, found 191.1076 [M+H]+.
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1-(4-(cyclopropanecarbonyl)phenyl)ethanone (6i) and 1-(4-cyclopropylphenyl)ethanone (7i)

Method B was followed on 0.160 mmol scale starting from 1-(4-iodophenyl)ethanone 5i. The residue was purified on silica gel (from 10% to 20% EtOAc/Hex) to afford 6i and 7i.

6i: White solid (15.7 mg, 52%); Rf 0.24 (20% EtOAc/Hex); m.p. 73.0 °C; \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.08-8.01 (m, 4H), 2.71-2.63 (m, 1H), 2.64 (s, 3H), 1.29-1.24 (m, 2H), 1.12-1.06 (m, 2H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 200.3, 197.7, 141.3, 139.9, 128.5, 128.3, 27.0, 17.8, 12.3; IR (neat) 3121, 3091, 3046, 3007, 2977, 1683, 1661, 1409, 1387, 1358, 1315, 1261, 1228, 1035, 994, 956, 838, 755, 690; HRMS (ESI) calcd for C\(_{12}\)H\(_{12}\)O\(_2\): 188.0837, found 189.0906 [M+H]+.

7i: Colorless oil (5.8 mg, 23%); Rf 0.50 (20% EtOAc/Hex); \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 8.4\) Hz, 2H), 7.12 (d, \(J = 8.1\) Hz, 2H), 2.57 (s, 3H), 2.00-1.90 (m, 1H), 1.08-1.04 (m, 2H), 0.81-0.75 (m, 2H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 197.8, 150.5, 134.7, 128.6, 125.6, 26.7, 15.9, 10.5. Spectral data are in agreement with those reported in the literature.\(^4\)

4-(cyclopropanecarbonyl)benzaldehyde (6j) and 4-cyclopropylbenzaldehyde (7j)

Method B was followed on 0.170 mmol scale starting from 4-iodobenzaldehyde 5j. The residue was purified on silica gel (10% EtOAc/Hex) to afford 6j and 7j.

6j: Pale yellow oil (10.6 mg, 36%); Rf 0.16 (10% EtOAc/Hex); \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 10.10 (s, 1H), 8.14 (d, \(J = 8.4\) Hz, 2H), 7.98 (d, \(J = 8.1\) Hz, 2H), 2.72-2.64 (m, 1H), 1.31-1.26 (m, 2H), 1.13-1.08 (m, 2H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 200.3, 191.8, 142.5, 138.9, 129.9, 128.6,
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18.0, 12.5; IR (neat) 3115, 3079, 3004, 1698, 1664, 1601, 1572, 1521, 1500, 1384, 1220, 985, 834, 684; HRMS (ESI) calcd for C_{11}H_{10}O_{2}: 174.0681, found 175.0752 [M+H]^+.

7j: Yellow oil (7.1 mg, 29%); R_f 0.41 (10\% EtOAc/Hex); \(^1\)H-NMR (300 MHz, CDCl\(_3\)) δ 9.94 (s, 1H), 7.76 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.1 Hz, 2H), 2.01-1.92 (m, 1H), 1.13-1.06 (m, 2H), 0.84-0.78 (m, 2H); \(^1^3\)C-NMR (75 MHz, CDCl\(_3\)) δ 191.9, 152.3, 134.2, 130.0, 126.0, 16.1, 10.8; IR (neat) 3085, 3007, 2822, 2798, 2732, 2717, 2155, 1698, 1604, 1573, 1215, 1166, 1043, 1019, 989, 842, 717; HRMS (ESI) calcd for C_{10}H_{10}O: 146.0732, found 147.0800 [M+H]^+

4-(cyclopropanecarbonyl)phenyl pivalate 6k

\[
\text{6k}
\]

Method B was followed on 0.173 mmol scale starting from 4-iodophenyl pivalate 5k. The residue was purified on silica gel (10\% EtOAc/Hex) to afford 6k: Yellow oil (19.8 mg, 46%); R_f 0.30 (10\% EtOAc/Hex); \(^1\)H-NMR (300 MHz, CDCl\(_3\)) δ 8.07 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.7 Hz, 2H), 2.69-2.61 (m, 1H), 1.37 (s, 9H), 1.25-1.23 (m, 2H), 1.08-1.01 (m, 2H); \(^1^3\)C-NMR (75 MHz, CDCl\(_3\)) δ 199.5, 176.7, 154.8, 135.5, 129.7, 121.7, 39.4, 27.2, 17.2, 11.8; IR (neat) 2969, 2936, 2900, 2872, 1755, 1665, 1598, 1477, 1412, 1382, 1225, 1205, 1102, 992, 747, 633; HRMS (ESI) calcd for C_{15}H_{18}O_{3}: 246.1256, found 247.1416 [M+H]^+

(4-(1-(benzyloxy)ethyl)phenyl)(cyclopropyl)methanone (6l)

\[
\text{6l}
\]

Method B was followed on 0.143 mmol scale starting from 1-(1-(benzyloxy)ethyl)-4-iodobenzene 5l. The residue was purified on silica gel (10\% EtOAc/Hex) to afford 6l: Colorless oil (35.0 mg, 87%); R_f 0.34 (10\% EtOAc/Hex); \(^1\)H-NMR (300 MHz, CDCl\(_3\)) δ 8.04
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(d, J = 8.1 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.38-7.27 (m, 5H), 4.57 (q, J = 6.3 Hz, 1H), 4.47 (d, J = 12.0 Hz, 1H), 4.33 (d, J = 11.7 Hz, 1H), 2.72-2.65 (m, 1H), 1.50 (d, J = 6.6 Hz, 2H), 1.28-1.23 (m, 2H), 1.08-1.02 (m, 2H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 200.4, 149.0, 138.4, 137.5, 128.6, 128.5, 127.83, 127.76, 126.5, 77.0, 70.7, 24.2, 17.3, 11.7; IR (neat) 3091, 3070, 3031, 3007, 2968, 2927, 2867, 1665, 1608, 1572, 1452, 1415, 1383, 1224, 1095, 991, 735, 697; HRMS (ESI) calcd for C\(_{19}\)H\(_{20}\)O\(_2\): 280.1463, found 281.1553 [M+H]^+.

(3-bromophenyl)(cyclopropyl)methanone (6m)

![Structure of 6m](image.png)

Method A was followed on 0.255 mmol scale starting from 1-bromo-3-iodobenzene 5m. The residue was purified on silica gel (10% EtOAc/Hex) to afford 6m: Yellow oil (47.7 mg, 83%); RF 0.29 (10% EtOAc/Hex); \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.12 (t, J = 1.8 Hz, 1H), 7.92 (dt, J = 7.8, 1.2 Hz, 1H), 7.67 (ddd, J = 7.8, 2.1, 1.2 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 2.63-2.56 (m, 1H), 1.27-1.22 (m, 2H), 1.09-1.03 (m, 2H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 199.3, 139.8, 135.6, 131.2, 130.2, 126.6, 123.0, 17.4, 12.2; IR (neat) 3091, 3064, 3007, 2921, 2846, 1669, 1566, 1423, 1377, 1213, 995, 731, 680; HRMS (ESI) calcd for C\(_{10}\)H\(_9\)BrO: 223.9837, found 224.9883 [M+H]^+.

Cyclopropyl(thiophen-2-yl)methanone (6n)

![Structure of 6n](image.png)

Method A was followed on 0.250 mmol scale starting from 2-iodothiophene 5n. The residue was purified on silica gel (10% EtOAc/Hex) to afford 6n: Pale yellow oil (34.2 mg, 90%); RF 0.32 (10% EtOAc/Hex); \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, J = 1.8 Hz, 1H), 7.63 (d, J = 2.4 Hz, 1H), 7.15 (t, J = 2.4 Hz, 1H), 2.56-2.52 (m, 1H), 1.26-1.23 (m, 2H), 1.04-1.01 (m, 2H); \(^{13}\)C-
NMR (75 MHz, CDCl₃) δ 193.1, 145.1, 133.3, 131.6, 128.2, 18.2, 11.5; IR (neat) 3090, 3007, 1643, 1517, 1446, 1416, 1384, 1236, 1225, 1056, 953, 716; HRMS (ESI) calcd for C₈H₈OS: 152.0296, found 153.0362 [M+H]^+.

**(E)-4-(benzyloxy)-1-cyclopropylbut-2-en-1-one (9)**

![9](image)

Method A was followed on 0.176 mmol scale starting from *(E)-(((3-iodoallyloxy)methyl)benzene 8*. The residue was purified on silica gel (30% Et₂O/Hex) to afford 9: Colorless oil (23.4 mg, 61%); Rₚ 0.36 (30% Et₂O/Hex); ¹H-NMR (300 MHz, CDCl₃) δ 7.38-7.30 (m, 5H), 6.90 (dt, J = 15.9, 4.5 Hz, 1H), 6.51 (dt, J = 15.9, 1.9 Hz, 1H), 4.59 (s, 2H), 4.23 (dd, J = 4.4, 1.8 Hz, 2H), 2.18-2.10 (m, 1H), 1.13-1.08 (m, 2H), 0.96-0.89 (m, 2H); ¹³C-NMR (75 MHz, CDCl₃) δ 200.1, 141.6, 137.8, 129.7, 128.6, 128.0, 127.8, 73.0, 69.1, 19.4, 11.3; IR (neat) 3055, 3016, 2992, 2980, 2940, 2880, 2840, 2798, 1675, 1653, 1637, 1594, 1520, 1420, 1314, 1258, 1218, 1098, 1082, 882, 714, 682; HRMS (ESI) calcd for C₁₄H₁₆O₂: 216.1150, found 217.1213 [M+H]^+.

**6. ¹H-NMR and ¹³C-NMR Spectra**
The image contains a chemical structure and a graph, which appear to be related to an NMR spectrum. The chemical structure is labeled as '3' and includes a phenyl group connected to an oxygen atom, with another oxygen atom connected to a methyl group. The graph contains peaks at various ppm values, indicating the chemical shifts in the spectrum.
$\text{N} + \text{O}$

$\text{O}\text{, 7d}$
7g
6h
6k

[Chemical structure image]
6n