

Pd-Sn Heterobimetallic Catalyst for Carbonylative Suzuki, Sonogashira and Aminocarbonylation Reactions using Chloroform as CO Surrogate

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(1) General Information

Pre-coated silica gel 60F₂₅₄ was used for thin layer chromatography and silica gel 60-120 mesh was used for column chromatography. PPh₃, DCM, DCE and other reagents were purified when necessary following standard laboratory protocol. PdCl₂, SnCl₂, 1,5-cyclooctadiene, all the aryl halides and the arylborons were purchased from common commercial sources and were used without further purification. Solvents were dried by conventional methods and distilled prior to use. The functionalised starting material alkynes have been prepared following the reported procedures and have been characterized and confirmed by ¹H NMR spectroscopy.

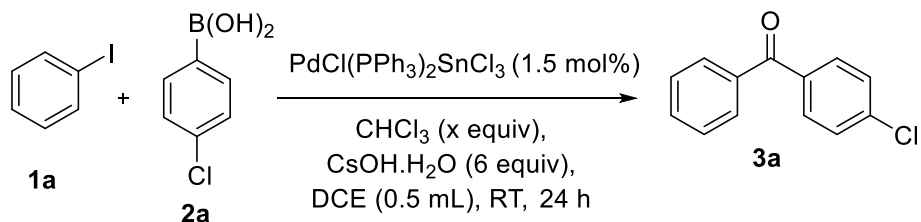
All inert reactions were carried out under aerobic condition. ¹H NMR spectra were acquired on a Bruker Avance III 400 spectrometer using CDCl₃ and DMSO-d₆ solvent. ¹H chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuteriochloroform: δ 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, dd = double doublet, m = multiplet), coupling constant (Hz). ¹³C chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl₃: δ 77.0 ppm). High-resolution mass spectra analysis (HRMS) was performed on a ThermoScientific Exactive Plus ORBITRAP mass spectrometer using methanol as a solvent with an electrospray ionization (ESI) positive method.

(2) General Procedure for Carbonylative Suzuki-Miyaura coupling using CHCl₃ as CO Source

With no precautions to exclude air or moisture, a 10-ml pressure tube equipped with a magnetic stir bar was charged with arylboronic acid (0.37 mmol), aryl halide (0.25 mmol), CsOH·H₂O (1.5 mmol, 251.0 mg), CHCl₃ (1 mmol, 80 μL), Pd(PPh₃)₂ClSnCl₃ (0.0037 mmol, 3.34 mg) and DCE (0.5 mL). The tube was capped tightly and stirred vigorously at room temperature for 24 h. After completion of the reaction, the combined organic layer was extracted with ethyl acetate, washed with water, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography through silica gel using petroleum ether: ethyl acetate (95:5) to afford the desire benzophenone product.

(3) Reaction Condition Optimization

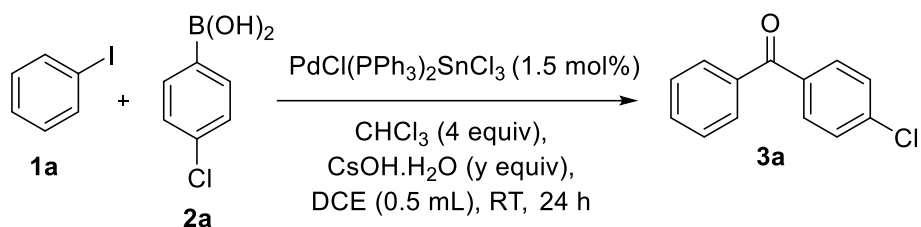
Table S1: Varying Chloroform Equivalencies



| Entry | Equiv. CHCl_3 | Yield (%) |
|-------|------------------------|-----------|
| 1 | 1 | trace |
| 2 | 2 | 30 |
| 3 | 3 | 60 |
| 4 | 4 | 80 |
| 5 | 5 | 55 |
| 6 | 6 | 50 |

Reaction Conditions: **1a** (0.25 mmol), **2a** (0.37 mmol), $\text{PdCl}(\text{PPh}_3)_2\text{SnCl}_3$ (1.5 mol%), DCE (0.5 mL) at RT for 24 h

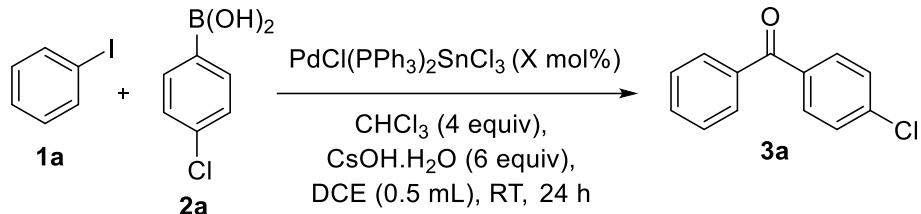
Table S2: Varying $\text{CsOH}\cdot\text{H}_2\text{O}$ Equivalencies



| Entry | Equiv. $\text{CsOH}\cdot\text{H}_2\text{O}$ | Yield (%) |
|-------|---|-----------|
| 1 | 1 | Trace |
| 2 | 2 | 15 |
| 3 | 3 | 27 |
| 4 | 4 | 40 |
| 5 | 5 | 62 |
| 6 | 6 | 80 |
| 7 | 7 | 80 |
| 8 | 10 | 80 |

Reaction Conditions: **1a** (0.25 mmol), **2a** (0.37 mmol), $\text{PdCl}(\text{PPh}_3)_2\text{SnCl}_3$ (1.5 mol%), DCE (0.5 mL) at RT for 24 h

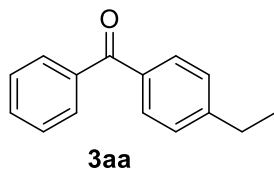
Table S3: Varying Catalyst Loading



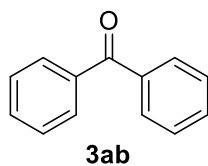
| Entry | Catalyst loading | Yield (%) |
|-------|------------------|-----------|
| 1 | 0.5 | 35 |
| 2 | 1 | 60 |
| 3 | 1.5 | 80 |
| 4 | 2 | 70 |

Reaction Conditions: **1a** (0.25 mmol), **2a** (0.37 mmol), $\text{PdCl}_2(\text{PPh}_3)_2\text{SnCl}_3$ (x mol%), DCE (0.5 mL) at RT for 24 h

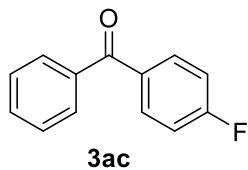
(4) Analytical data of Carbonylative Suzuki-Miyaura coupling product



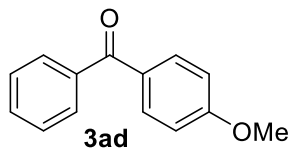
(4-Ethylphenyl) (phenyl) methanone¹: ^1H NMR (400 MHz, CDCl_3) δ 7.77 (dt, $J = 13.3, 6.1$ Hz, 3H), 7.58 (dd, $J = 10.5, 4.3$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 2.75 (q, $J = 7.6$ Hz, 2H), 1.29 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.58, 149.45, 137.98, 135.11, 132.18, 130.43, 130.32, 129.97, 128.22, 127.82, 127.74, 28.99, 15.28.



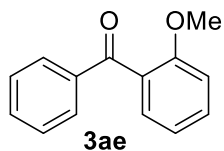
Benzophenone¹: ^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.78 (m, 4H), 7.60 (t, $J = 7.4$ Hz, 2H), 7.49 (t, $J = 7.6$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.30, 137.61, 132.44, 130.08, 128.29.



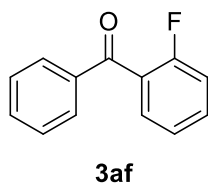
(4-Fluorophenyl) (phenyl)methanone²: ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.75 (m, 4H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 8.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 195.30, 166.66, 164.13, 137.50, 133.81, 133.78, 132.72, 132.63, 132.48, 129.89, 128.37, 115.57, 115.36.



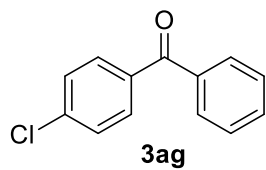
(4-methoxyphenyl) (phenyl)methanone²: ¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.52 (m, 3H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.02 – 6.96 (m, 1H), 3.87 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 195.32, 159.14, 140.83, 133.79, 128.73, 128.16, 127.74, 126.75, 126.67, 114.21, 114.17, 55.36.



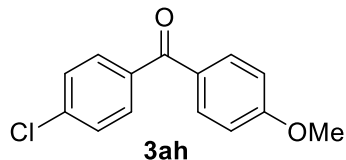
(2-methoxyphenyl) (phenyl)methanone³: ¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.80 (m, 2H), 7.58 – 7.53 (m, 1H), 7.50 – 7.41 (m, 3H), 7.37 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.04 (ddd, *J* = 22.6, 11.3, 4.6 Hz, 2H), 3.73 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 194.30, 162.41, 138.29, 136.58, 132.46, 131.16, 129.82, 128.54, 113.70, 55.54.



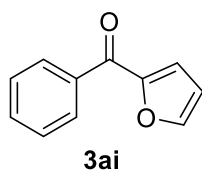
(2-fluorophenyl) (phenyl)methanone: ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.81 (m, 2H), 7.64 – 7.44 (m, 5H), 7.30 – 7.23 (m, 1H), 7.18 (dd, *J* = 13.6, 4.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 193.51, 161.36, 158.85, 137.41, 133.43, 133.12, 133.03, 130.78, 130.75, 130.40, 129.83, 129.82, 128.65, 128.48, 127.12, 126.98, 124.31, 124.28, 116.40, 116.18. HRMS(ESI) *m/z* calculated for C₁₃H₁₀FO [M + H]⁺: 201.07, found 201.07.



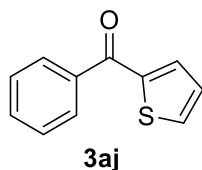
(4-chlorophenyl) (phenyl)methanone³: ¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.70 (m, 4H), 7.63 – 7.58 (m, 1H), 7.52 – 7.44 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 195.50, 138.91, 137.25, 135.88, 132.66, 131.48, 131.34, 129.94, 128.79, 128.65, 128.42.



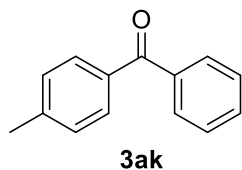
(4-chlorophenyl) (4-methoxyphenyl) methanone: ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.9 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 194.30, 163.41, 138.29, 136.58, 132.46, 131.16, 129.82, 128.54, 113.70, 55.54. HRMS(ESI) *m/z* calculated for C₁₄H₁₂ClO₂ [M + H]⁺: 247.05, found 247.05.



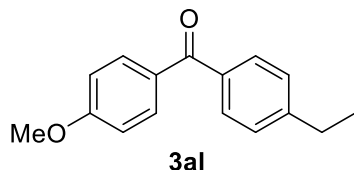
Furan-2-yl(phenyl)methanone⁵: ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.71 (s, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.24 (s, 1H), 6.60 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 182.6, 152.3, 147.1, 137.3, 132.6, 129.3, 128.4, 120.6, 112.2



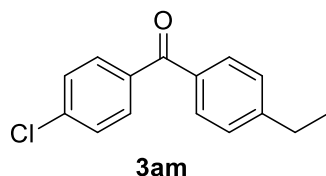
Phenyl(thiophen-2-yl) methanone¹: ¹H NMR (400 MHz, CDCl₃): δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.62-7.60 (m, 1H), 7.55-7.51 (m, 2H), 7.19 (t, *J* = 4.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 190.0, 141.3, 138.6, 133.9, 132.3, 129.3, 128.6, 128.4, 126.2.



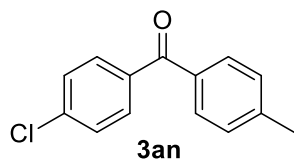
Phenyl(p-tolyl) methanone¹: ¹H NMR (400 MHz, CDCl₃) δ 7.81 – 7.70 (m, 4H), 7.60 – 7.55 (m, 1H), 7.48 (dd, *J* = 10.7, 4.3 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.53, 143.27, 137.97, 134.90, 132.19, 130.33, 130.21, 129.95, 129.01, 128.93, 128.24, 21.67.



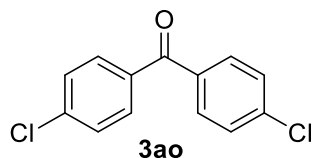
(4-ethylphenyl) (4-methoxyphenyl) methanone⁴: ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.9 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 195.56, 163.10, 148.89, 135.71, 132.50, 130.46, 130.13, 128.80, 127.73, 115.20, 113.52, 55.49, 28.95, 15.31.



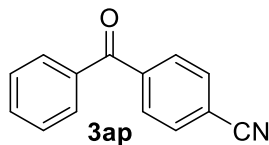
(4-chlorophenyl) (4-ethylphenyl) methanone: ¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.70 (m, 4H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 195.28, 149.73, 138.61, 136.25, 134.77, 131.38, 130.29, 128.57, 127.94, 28.99, 15.25. HRMS(ESI) *m/z* calculated for C₁₅H₁₄ClO [M + H]⁺: 245.07, found 245.07.



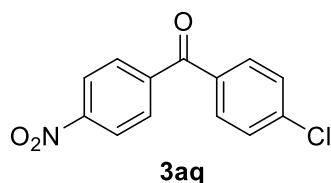
(4-chlorophenyl) (p-tolyl) methanone¹: ¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.67 (m, 4H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.34 – 7.25 (m, 1H), 2.45 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 195.29, 143.57, 138.62, 136.23, 134.54, 131.37, 130.20, 129.12, 128.92, 128.58, 21.69.



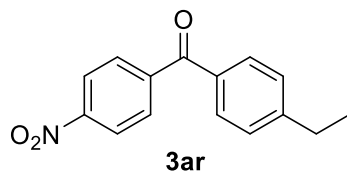
Bis(4-chlorophenyl) methanone³: ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.70 (m, 4H), 7.49 – 7.45 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 194.25, 139.18, 135.53, 131.33, 128.79.



4-benzoylbenzonitrile⁴: ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.84 (m, 2H), 7.80 (ddd, *J* = 6.1, 3.6, 1.7 Hz, 4H), 7.68 – 7.62 (m, 1H), 7.56 – 7.49 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 195.06, 141.24, 136.33, 133.75, 133.34, 132.17, 130.30, 130.24, 130.07, 128.77, 128.64, 122.94, 118.01, 115.68, 77.34, 77.02, 76.70, 29.70.



(4-Chlorophenyl) (4-nitrophenyl) methanone¹: ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 193.60, 149.96, 142.49, 140.16, 134.57, 131.47, 130.61, 129.40, 129.11, 128.65, 127.70, 124.24, 123.69.



(4-Ethylphenyl) (4-nitrophenyl) methanone¹: ¹H NMR (400 MHz, CDCl₃): δ 8.28 (d, *J* = 8, 2 H), 7.73 (d, *J* = 12 Hz, 2 H), 7.56 (d, *J* = 8, 2H), 7.34 (d, *J* = 8, 2 H), 2.76-2.70 (q, 2H), 1.30 ppm (t, *J* = 8, 3 H). ¹³C NMR (101 MHz, CDCl₃) δ 194.10, 149.73, 138.61, 136.25, 134.77, 131.38, 130.29, 128.57, 127.94, 28.99, 15.25.

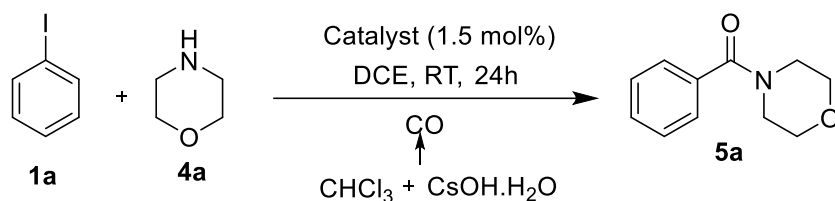
(5) General Procedure for Aminocarbonylation Reaction

A 10-ml pressure tube equipped with a magnetic stir bar was charged with amine (0.37 mmol), aryl halide (0.25 mmol), CsOH·H₂O (2 mmol, 336.0 mg), CHCl₃ (1 mmol, 80 μL), Pd(PPh₃)₂ClSnCl₃ (0.0037 mmol, 3.34 mg) and DCE (0.5 mL). The tube was capped tightly and stirred vigorously at room temperature for 24 h. After completion of the reaction, the combined

organic layer was extracted with ethyl acetate, washed with water, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography through silica gel using petroleum ether: ethyl (80:20 to 60:40) acetate to afford the desire amide product.

(6) Reaction Condition Optimization

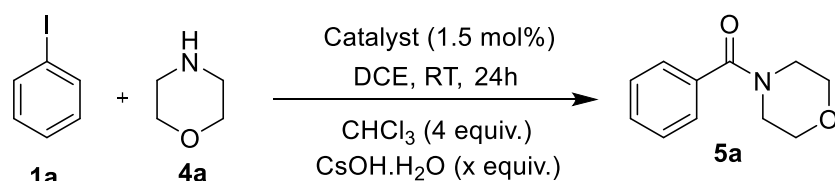
Table S4: Catalyst Screening of Aminocarbonylation Reaction



| Entry | Catalyst | Yield (%) |
|-------|--|-----------|
| 1 | Nil | 0 |
| 2 | PdCl ₂ (PPh ₃) ₂ | 32 |
| 3 | SnCl ₂ | 0 |
| 4 | PdCl(PPh ₃) ₂ SnCl ₃ | 75 |
| 5 | PdCl(COD)SnCl ₃ | 60 |
| 6 | PdCl(P-Toly) ₂ SnCl ₃ | 66 |
| 7 | PdCl(dppe)SnCl ₃ | 57 |

Reaction Conditions: **1a** (0.25 mmol), **4a** (0.37 mmol), Catalyst (1.5 mol %), CsOH.H₂O (8 equiv.) in DCE (0.5 mL) at RT for 24 h

Table S5: Varying CsOH.H₂O Equivalencies

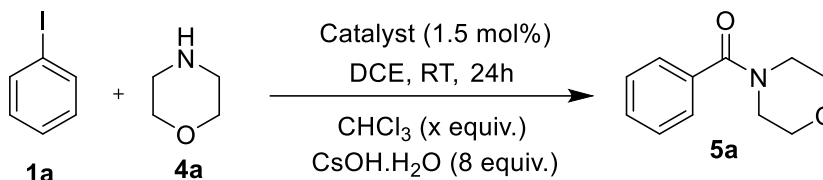


| Entry | Equiv.CsOH.H ₂ O | Yield (%) |
|-------|-----------------------------|-----------|
| 1 | 6 | 54 |

| | | |
|---|----|----|
| 2 | 8 | 75 |
| 3 | 10 | 75 |

Reaction Conditions: **1a** (0.25 mmol), **4a** (0.37 mmol), PdCl(PPh₃)₂SnCl₂ (1.5 mol %), CsOH.H₂O (x equiv.) in DCE (0.5 mL) at RT for 24 h

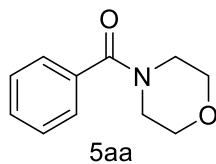
Table S6: Varying Chloroform Equivalencies



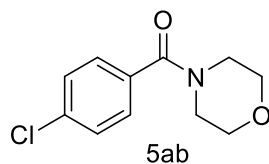
| Entry | Equiv.CHCl ₃ | Yield (%) |
|-------|-------------------------|-----------|
| 1 | 1 | trace |
| 2 | 2 | 10 |
| 3 | 3 | 25 |
| 4 | 4 | 40 |
| 5 | 6 | 50 |
| 6 | 8 | 75 |
| 7 | 10 | 70 |

Reaction Conditions: **1a** (0.25 mmol), **4a** (0.37 mmol), PdCl(PPh₃)₂SnCl₂ (1.5 mol %), CsOH.H₂O (8 equiv.) in CHCl₃ (y equiv.) DCE (0.5 mL) at RT for 24 h

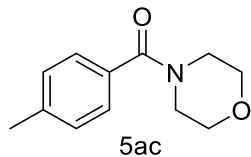
(7) Analytical data of Aminocarbonylation product



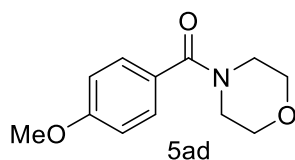
Morpholino(phenyl)methanone^{6,11}: ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.28 (m, 5H), 3.58 (d, *J* = 106.6 Hz, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 170.44, 135.33, 129.88, 128.57, 127.09, 66.90.



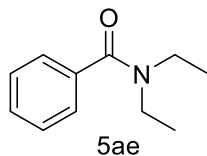
(4-chlorophenyl) (morpholino)methanone⁶: ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.22 (m, 4H), 3.51 (d, *J* = 94.0 Hz, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 169.29, 135.91, 133.57, 128.80, 128.65, 66.74.



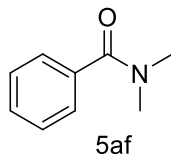
Morpholino(p-tolyl) methanone⁶: ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.23 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 3.65 (s, 8H), 2.33 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 170.68, 140.09, 129.13, 127.21, 66.86, 21.36.



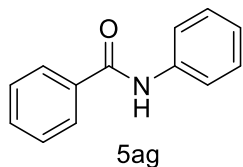
(4-methoxyphenyl) (morpholino)methanone^{6,11}: ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.23 (m, 2H), 6.84 (dd, *J* = 8.6, 1.8 Hz, 2H), 3.75 (s, 3H), 3.68 – 3.45 (m, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 170.36, 160.87, 129.16, 127.25, 113.75, 66.83, 55.31.



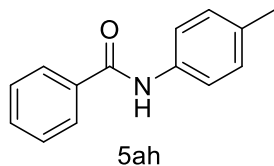
N,N-diethylbenzamide⁶: ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.24 (m, 5H), 3.38 (d, *J* = 117.7 Hz, 4H), 1.28 – 0.94 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 171.29, 137.27, 129.07, 128.37, 126.25, 43.27, 39.23, 14.19, 12.89.



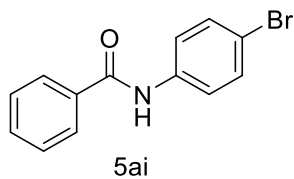
N,N-dimethylbenzamide⁶: ¹H NMR (400 MHz, CDCl₃) δ 7.40 (s, 5H), 3.04 (d, *J* = 54.8 Hz, 6H).



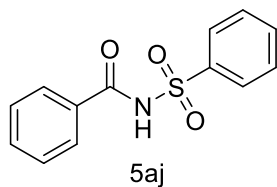
N-phenylbenzamide⁷: ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.84 (m, 2H), 7.69 – 7.62 (m, 2H), 7.59 – 7.46 (m, 3H), 7.42 – 7.34 (m, 2H), 7.20 – 7.13 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 165.77, 137.93, 135.03, 131.87, 129.13, 128.82, 127.03, 124.61, 120.22.



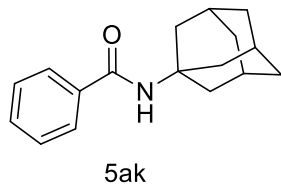
N-(p-tolyl) benzamide⁷: ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.83 (m, 2H), 7.57 – 7.44 (m, 5H), 7.18 (d, *J* = 8.2 Hz, 2H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.70, 135.37, 135.10, 134.27, 131.75, 129.60, 128.77, 127.02, 120.33, 77.36, 77.04, 76.73, 20.92.



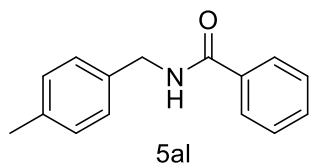
N-(4-bromophenyl) benzamide⁷: ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.84 (m, 2H), 7.58 – 7.54 (m, 3H), 7.49 (dd, *J* = 11.9, 5.0 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 165.69, 137.01, 134.64, 132.09, 128.89, 127.01, 121.73, 117.19.



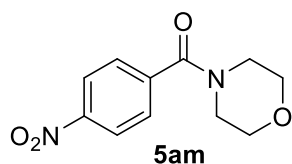
N-(phenylsulfonyl)benzamide¹⁰: ¹H NMR (400 MHz, CDCl₃) δ 8.14 (dd, *J* = 8.3, 1.3 Hz, 4H), 7.63 (ddd, *J* = 7.0, 4.1, 1.3 Hz, 2H), 7.53 – 7.46 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 172.33, 133.83, 130.24, 129.35, 128.51.



N-((3s,5s,7s)-adamantan-1-yl) benzamide: ^1H NMR (400 MHz, CDCl_3) δ 7.77 – 7.63 (m, 2H), 7.50 – 7.35 (m, 3H), 5.86 (s, 1H), 2.12 (s, 9H), 1.71 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.68, 136.02, 131.04, 128.45, 126.73, 52.28, 41.66, 36.39, 29.50. HRMS(ESI) m/z calculated for $\text{C}_{17}\text{H}_{22}\text{NO}$ $[\text{M} + \text{H}]^+$: 256.17, found 256.16.



N-(4-methylbenzyl) benzamide⁶: ^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.62 (m, 1H), 7.44 (dt, $J = 15.3, 7.4$ Hz, 1H), 7.27 – 7.09 (m, 1H), 6.74 (s, 1H), 4.57 (d, $J = 5.6$ Hz, 1H), 2.34 (s, 1H) ^{13}C NMR (101 MHz, CDCl_3) δ 167.45, 137.24, 135.26, 134.47, 131.48, 129.42, 128.54, 127.91, 127.05, 43.87, 21.13.

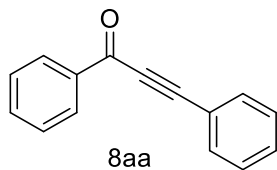


Morpholino(4-nitrophenyl) methanone: ^1H NMR (400 MHz, CDCl_3) δ 8.39 – 8.14 (m, 2H), 7.63 – 7.46 (m, 2H), 3.93 – 3.26 (m, 8H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.67, 141.73, 139.85, 133.50, 131.77, 130.79, 130.27, 129.97, 129.76, 128.26, 127.62, 64.54, 41.19. HRMS(ESI) m/z calculated for $\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_4$ $[\text{M} + \text{H}]^+$: 237.09, found 237.08.

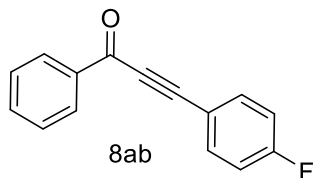
(8) General Procedure for Carbonylative Sonogashira Coupling

A 10-ml pressured tube equipped with a magnetic stir bar was charged with alkyne (0.37 mmol), aryl halide (0.25 mmol), $\text{CsOH}\cdot\text{H}_2\text{O}$ (1.5 mmol, 251.0 mg), CHCl_3 (1 mmol, 80 μL), $\text{Pd}(\text{PPh}_3)_2\text{ClSnCl}_3$ (0.0037 mmol, 3.34 mg) and DCE (0.5 mL). The tube was capped tightly and stirred vigorously at room temperature for 24 h. After completion of the reaction, the combined organic layer was extracted with ethyl acetate, washed with water, dried over sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography through silica gel using petroleum ether: ethyl acetate (90:10 to 95:5) to afford the desired alkyne product.

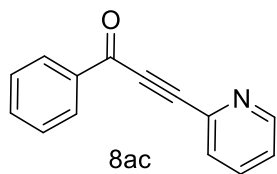
(9) Analytical data of Carbonylative Sonogashira product



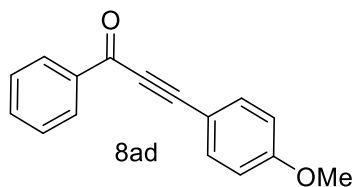
1,3-diphenylprop-2-yn-1-one⁸: ¹H NMR (400 MHz, CDCl₃) δ 8.30 – 8.16 (m, 2H), 7.73 – 7.61 (m, 3H), 7.57 – 7.41 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 178.07, 136.92, 134.15, 133.10, 130.82, 129.61, 128.72, 128.65, 120.17, 93.15, 86.91.



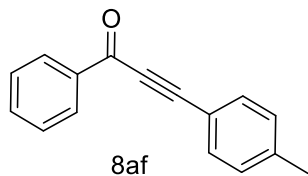
3-(4-fluorophenyl)-1-phenylprop-2-yn-1-one⁸: ¹H NMR (400 MHz, CDCl₃) δ 8.25-8.29 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.43- 7.54 (m, 3H), 7.21 (t, *J* = 8.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 177.9, 163.6 (d, *J*_{C-F} = 252.2 Hz), 136.4 and 133.4 (d, *J*_{C-F} = 8.9 Hz), 133.82, 129.50, 128.31, 116.31 (d, *J*_{C-F} = 22.2 Hz), 92.0, 86.8



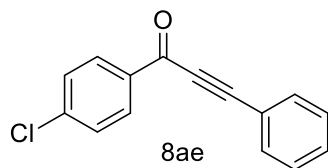
1-phenyl-3-(pyridin-2-yl) prop-2-yn-1-one⁹: ¹H NMR (400 MHz, CDCl₃) δ 8.65 – 8.60 (m, 1H), 7.69 (td, *J* = 7.7, 1.8 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.54 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.26 – 7.22 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 169.0, 150.07, 143.49, 136.20, 132.07, 128.99, 128.40, 127.18, 122.76, 122.27, 89.28, 88.59.



3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one⁸: ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.0 Hz, 2H), 7.62-7.69 (m, 3H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 177.0, 161.7, 135.0, 135.1, 133.9, 129.5, 128.5, 114.2, 111.8, 94.3, 86.3, 55.4.



1-phenyl-3-(p-tolyl) prop-2-yn-1-one⁸: ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.2 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 7.6 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 178.0, 141.6, 136.9, 134.0, 133.1, 129.6, 129.5, 128.6, 117.0, 93.8, 86.8, 21.8.



1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one⁸: ¹H NMR (400 MHz, CDCl₃) δ 8.18 (dt, J = 8.4, 2.4 Hz, 2H), 7.71 (dt, J = 7.2, 1.6 Hz, 2H), 7.51-7.55 (m, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 176.6, 140.7, 135.3, 133.1, 131.0, 130.8, 129.0, 128.7, 119.8, 93.6, 86.6

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