

Supporting Information 1

N-Heterocyclic Carbene-Catalyzed Nucleophilic Aroylation of Fluorobenzenes

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General procedure. Under an atmosphere of argon, 60% sodium hydride in oil (60 mg, 1.5 mmol) was added to a mixture of imidazolium salt **3a** – **f** (0.005 – 0.3 mmol), fluorobenzenes (1 mmol), and **7a** – **e** (1 mmol) in DMF (10 ml). After the reaction, the mixture was poured into ice-water. The product was extracted with ethyl acetate, washed with water and brine, and dried over Na₂SO₄. The combined organic layers were concentrated, and the residue was purified by silica gel column chromatography (hexane-ethyl acetate) to give ketones.

4-Chloro-4'-nitrobenzophenone 4b: yellow needles (recrystallized from *n*-hexane-acetone); Mp. 102 – 103 °C (lit.¹ 98 °C); IR (KBr) 1343, 1514 (NO₂), 1664 (CO) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.51 (2H, d, *J* = 8.5 Hz), 7.76 (2H, d, *J* = 8.5 Hz), 7.92 (2H, d, *J* = 9.1 Hz), 8.36 (2H, d, *J* = 9.1 Hz).

4-Methoxyl-4'-nitrobenzophenone 4c: yellow needles (recrystallized from *n*-hexane-acetone); Mp. 126 – 127 °C (lit.² 126 – 127 °C); IR (KBr) 1315, 1509 (NO₂), 1638 (CO) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.91 (3H, s), 6.99 (2H, d, *J* = 7.9 Hz), 7.81 (2H, d, *J* = 7.9 Hz), 7.88 (2H, d, *J* = 9.1 Hz), 8.33 (2H, d, *J* = 9.1 Hz).

3-Methoxyl-4'-nitrobenzophenone 4d: yellow needles (recrystallized from *n*-hexane-acetone); Mp. 80.5 – 81.5 °C; IR (ATR) 1352, 1516 (NO₂), 1649 (CO) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.88 (3H, s, OCH₃), 7.18 – 7.20 (1H, m), 7.31 (1H, d, *J*=7.6 Hz), 7.36 – 7.37 (1H, m), 7.42 (1H, t, *J*=7.6 Hz), 7.94 (2H, d, *J*=8.0 Hz), 8.34 (2H, d, *J*=8.0 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 55.6, 114.3, 119.9, 122.9, 123.5, 129.6, 130.7, 137.6, 142.9, 149.8, 159.9, 194.6; HRMS (FAB) *m/z* Calcd for C₁₄H₁₁NO₄ (M+1): 258.0766, Found: 258.0768.

4-Benzoylbenzophenone 8: colorless prisms (recrystallized from *n*-hexane-acetone); Mp. 160–161 °C (lit.³ 160–161 °C); IR (KBr) 1638 (CO) cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.52 (4H, t, *J* = 7.5 Hz), 7.64 (2H, tt, *J* = 7.5 Hz, 2 Hz), 7.85 (4H, dd, *J* = 7.5 Hz, 2 Hz), 7.90 (4H, s).

5'-Benzyoxy-2,5-difluoro-4-nitrobenzophenone 11e: yellowish needles (recrystallized from hexane-acetone); Mp 132–133 °C; IR (KBr): 1670 (CO) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.12 (2H, s, OCH₂Ph), 7.35 (1H, t, *J*=7.5 Hz, H-3), 7.45–7.26 (9H, m), 7.89 (1H, dd, *J*=8.0 Hz, 5.5 Hz, H-3); ¹³C NMR (126 MHz, CDCl₃) δ 29.8, 70.5, 114.4 (dd, *J*_{FC}=28.8 Hz, 2.4 Hz), 115.0, 120.0 (dd, *J*_{FC}=24.0 Hz, 3.6 Hz), 122.0, 123.0, 127.6, 128.4, 128.8, 130.2, 133.8 (dd, *J*_{FC}=25.2 Hz, 6.6 Hz), 136.2, 136.9, 138.5 (t, *J*_{FC}=8.4 Hz), 151.6 (dd, *J*_{FC}=265.1 Hz, 2.4 Hz), 154.4 (dd, *J*_{FC}=253.1 Hz, 3.6 Hz), 159.3, 189.5; HRMS (FAB) *m/z* Calcd for C₂₀H₁₃F₂NO₄ (M+1): 370.0891, Found: 370.0885.

4-Nitro-2,2',5-trifluorobenzophenone 11f: yellow prisms (recrystallized from *n*-hexane-dichloromethane); Mp 91 °C; IR (KBr): 1666 (CO) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.09 (1H, ddd, *J*=11.0 Hz, 8.5 Hz, 1.0 Hz, H-3), 7.27 (1H, ddd, *J*=9.0 Hz, 7.5 Hz, 1.0 Hz, H-5), 7.53 (1H, dd, *J*=10.0 Hz, 5.5 Hz, H-6), 7.58 (1H, m, H-4), 7.76 (1H, ddd, *J*=9.0 Hz, 7.5 Hz, 2.0 Hz, H-6), 7.79 (1H, dd, *J*=8.5 Hz, 6.0 Hz, H-3); ¹³C NMR (126 MHz, CDCl₃) δ 114.3 (d, *J*_{FC}=28.8 Hz), 116.6 (d, *J*_{FC}=28.8 Hz), 120.1 (d, *J*_{FC}=24.0 Hz), 124.0 (d, *J*_{FC}=3.6 Hz), 125.0 (d, *J*_{FC}=10.8 Hz), 131.2, 134.2 (dd, *J*_{FC}=16.2 Hz, 6.6 Hz), 136.1 (d, *J*_{FC}=9.8 Hz), 139.0 (dd, *J*_{FC}=18.2 Hz, 7.2 Hz), 151.7 (d, *J*_{FC}=263.9 Hz), 155.0 (dd, *J*_{FC}=255.5 Hz), 161.7 (d, *J*_{FC}=256.7 Hz), 186.4; HRMS (FAB) *m/z* Calcd for C₁₃H₇F₃NO₃ (M+1): 282.0378, Found: 282.0356.

4-Nitro-2,2',5,5'-tetrafluorobenzophenone 11g: yellow prisms (recrystallized from *n*-hexane-dichloromethane); Mp. 88 – 89 °C; IR (KBr): 1265, 1425 (NO₂), 1670 (CO) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.14 (1H, td, *J*=9.5 Hz, 4.0 Hz, H-3□), 7.31 – 7.36 (1H, m, H-4□), 7.49 – 7.53 (1H, m, H-6□), 7.61 (1H, dd, *J*=10.0 Hz, 5.5 Hz, H-6), 7.86 (1H, dd, *J*=9.0 Hz, 5.5 Hz, H-3); ¹³C NMR (126 MHz, CDCl₃) δ 114.4 (dd, *J*_{FC}=30.0 Hz, 2.4 Hz), 117.1 (d, *J*_{FC}=25.2 Hz), 118.2 (dd, *J*_{FC}=25.2 Hz, 8.0 Hz), 120.2 (dd, *J*_{FC}=28.8 Hz, 2.4 Hz), 122.7 (dd, *J*_{FC}=24.0 Hz, 9.6 Hz), 126.4 (dd, *J*_{FC}=14.4 Hz, 6.5 Hz), 133.4 (dd, *J*_{FC}=16.8 Hz, 6.0 Hz), 139.2, 151.6 (dd, *J*_{FC}=265 Hz, 3.6 Hz), 155.1 (d, *J*_{FC}=256 Hz), 157.5 (d, *J*_{FC}=252 Hz), 158.7 (dd, *J*_{FC}=250 Hz, 7.2 Hz), 185.1; HRMS (FAB) *m/z* Calcd for C₁₃H₆F₄NO₃ (M+1): 300.0284, Found: 300.0280.

5'-Methoxy-4-nitro-2,2',5-trifluorobenzophenone 11h: yellow prisms (recrystallized from hexane-dichloromethane); Mp 98 – 99 °C; IR (KBr): 1535 (NO₂), 1668 (CO) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.87 (3H, s, OCH₃), 7.07 (1H, t, *J*=9.5 Hz, H-3□), 7.15 – 7.18 (1H, m, H-4□), 7.29 (1H, dd, *J*=5.5 Hz, 3.5 Hz, H-6□), 7.57 (1H, dd, *J*=10.0 Hz, 5.5 Hz, H-6), 7.86 (1H, dd, *J*=8.5 Hz, 5.5 Hz, H-3); ¹³C NMR (126 MHz, CDCl₃) δ 55.9, 113.3, 114.1 (dd, *J*_{FC}=30.0 Hz, 2.5 Hz), 117.4 (d, *J*_{FC}=24.0 Hz), 119.8 (d, *J*_{FC}=24.0 Hz), 122.6 (d, *J*_{FC}=9.6 Hz), 125.2 (d, *J*_{FC}=13.2 Hz), 133.9 (dd, *J*_{FC}=15.6 Hz, 6.0 Hz), 138.7 (dd, *J*_{FC}=16.8 Hz, 8.4 Hz), 151.5 (dd, *J*_{FC}=263.9 Hz, 3.6 Hz), 154.9 (d, *J*_{FC}=254.3 Hz), 155.9, 156.1 (d, *J*_{FC}=249.5 Hz), 186.1; HRMS (FAB) *m/z* Calcd for C₁₄H₉F₃NO₄ (M+1): 312.0484, Found: 312.0504.

5'-Methoxy-4-nitro-2,2',6-trifluorobenzophenone 12: yellow prisms (recrystallized from hexane-acetone), Mp 70 – 72 °C, IR (ATR): 1283, 1537 (NO₂), 1676 (CO) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.86 (3H, s, OCH₃), 7.04 (1H, dd, *J*=10.3 Hz, 9.2 Hz, H-3□), 7.19 (1H, dt, *J*=9.2 Hz, 3.4 Hz H-4□), 7.42 (1H, dd, *J*=5.7 Hz, 3.4 Hz, H-6□), 7.86 – 7.90(2H, m, *J*=6.9 Hz, H-3, 5), ¹³C NMR (126 MHz, CDCl₃) δ 56.0, 108.1 (dd, *J*_{FC}=31.2, 8.4Hz), 112.7, 117.9, (d, *J*_{FC}=25.2 Hz z) 123.9, (d, *J*_{FC} =8.4 Hz), 124.6 (d, *J*_{FC}=10.8 Hz), 124.7, (t, *J*_{FC}=22.1 Hz), 149.2, (t, *J*_{FC} =10.8 Hz), 156.1, 157.1, (d, *J*_{FC}=250.7 Hz), 159.3, (dd, *J*_{FC}=256.7 Hz, 8.4 Hz), 182.8, HRMS (FAB) *m/z* Calc for C₁₄H₉F₃NO₄ (M+1): 312.0484, Found 312.0483.

REFERENCES (Word Style “TF_References_Section”).

- (1) Morley, J. O. *Synthesis*, **1977**, 54.
- (2) Sugiyama, N.; Baba, S. *J. Chem. Soc. Jpn.* **1963**, 84, 936.
- (3) Murray, R. W.; Trozzolo, A. M. *Org. Chem.* **1961**, 26, 3109.