Supporting Information

Nickel-Catalyzed Addition of Arylboronic Acids to Alkyl Nitriles for Synthesis of Arylketones in Fluorinated Solvent

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1. General information

Fluorinated reagents such as HFC-245fa, HCFC-244bb, HCFO-1233xf and HFO-1234yf (the purity are more than 99%) were prepared and separated by ourselves. Besides these, the other reagents and solvents (Analytical Grade) were purchased from commercial sources and used as received. The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. The yields were determined by GC (equipped with a BD-35 separation capillary column (Agilent technologies co., LTD., 30 m × 0.32 mm) and FID detector) using bromobenzene as internal reference.

The crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate as eluents). $^1$H NMR (500 MHz) and $^{13}$C NMR (125 MHz) spectra were recorded using CDCl$_3$ as solvent. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard. $^{19}$F NMR (470 MHz) chemical shifts were determined relative to CFCl$_3$ at δ 0.0. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet).

2. Experimental procedures

General procedure for the synthesis of arylketones 3a-y:

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. NiBr$_2$·diglyme (5 mol%), 1,10-phen (10 mol%) and a magnetic stir bar were placed in the tube. Then, arylboronic acid (1.0 mmol), NaHCO$_3$ (2.0 equiv), H$_2$O (2.0 mmol) and alkyl nitrile (1.0 mL) were added to the tube. After that the autoclave was capped with a stopper. The autoclave was cool down by liquid nitrogen, then created vacuum at this temperature and added HCFC-244bb (2.0 mL, 2.6 g) by self-suction. Finally the autoclave was wormed in an oil bath at 100 °C for 5 h. After the reaction, the autoclave was cooled to room temperature and vented the excess HCFC-244bb carefully. Water (30 mL) was added to the mixture, and the mixture was extracted with dichloromethane (3 x 15 mL). The organic layers were washed with brine, dried over Na$_2$SO$_4$, and evaporated the organic solvent by rotatory evaporator. The crude product was then purified by column chromatography.
3. Characterization data for products

1-(4-methoxyphenyl)ethan-1-one (3a). Light yellow solid, mp 36-37 °C. \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.90 (d, \(J = 9.0\) Hz, 2H), 6.90 (d, \(J = 9.0\) Hz, 2H), 3.83 (s, 3H), 2.52 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 196.8, 163.5, 130.6, 130.4, 113.7, 55.5, 26.3.

1-p-tolylethanone (3c). Colorless oil. \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.88 (d, \(J = 8.0\) Hz, 2H), 7.28 (d, \(J = 8.0\) Hz, 2H), 2.60 (s, 3H), 2.43 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 197.9, 143.9, 134.8, 129.3, 128.5, 26.6, 21.7.

1-(4-ethylphenyl)ethanone (3d) Colorless oil. \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.89 (d, \(J = 8.5\) Hz, 2H), 7.28 (t, \(J = 8.5\) Hz, 2H), 2.71 (q, \(J = 7.5\) Hz, 2H), 2.58 (s, 3H), 1.26 (t, \(J = 8.0\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 197.9, 150.1, 135.0, 128.6, 128.1, 29.0, 26.6, 15.5.

1-((1,1'-biphenyl]-4-yl)ethan-1-one (3e). Light yellow solid, mp 116-117 °C. \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.12 (d, \(J = 9.0\) Hz, 2H), 7.78 (d, \(J = 8.5\) Hz, 2H), 7.72 (d,
J = 7.5 Hz, 2H), 7.56 (t, J = 7.5 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 2.73 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 197.8, 145.9, 140.0, 135.9, 129.0, 129.0, 128.3, 127.4, 127.3, 26.7.

1-(4-fluorophenyl)ethan-1-one (3f). Light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.08-8.05 (m, 2H), 7.21 (t, J = 8.5 Hz, 2H), 2.67 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 196.6, 165.9 (d, J_CF = 253.0 Hz), 133.7 (d, J_CF = 3.0 Hz), 131.0 (d, J_CF = 9.3 Hz), 115.8 (d, J_CF = 21.9 Hz), 26.6; ¹⁹F NMR (470 MHz, CDCl₃) δ -105.3 (s, 1F).

1-(4-chlorophenyl)ethan-1-one (3g). Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 9.0 Hz, 2H), 2.53 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 196.9, 139.7, 135.6, 129.9, 129.0, 26.7.

1-(4-nitrophenyl)ethan-1-one (3h). Light yellow solid, mp 76-78 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.30 (d, J = 8.5 Hz, 2H), 8.12 (d, J = 9.0 Hz, 2H), 2.69 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 196.2, 150.2, 141.2, 129.2, 123.7, 26.8.

1-(4-(trifluoromethyl)phenyl)ethan-1-one (3i). Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 8.09 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 2.68 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 197.1, 139.8, 134.5 (q, J_CF = 32.5 Hz), 128.7, 125.8 (q, J_CF = 3.8 Hz), 123.7 (q, J_CF = 271.1 Hz), 26.9; ¹⁹F NMR (470 MHz, CDCl₃) δ -63.1 (s, 3F).
1-(3-methoxyphenyl)ethan-1-one (3j). Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$
7.54 (d, $J = 7.5$ Hz, 1H), 7.48 (d, $J = 4.0$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 1H), 7.11-7.09
(m, 1H), 3.84 (s, 3H), 2.58 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 198.0, 159.9,
138.6, 129.6, 121.2, 119.6, 112.4, 55.5, 26.8.

1-(3-fluorophenyl)ethan-1-one (3k). Light yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$
7.75-7.73 (m, 1H), 7.66-7.63 (m, 1H), 7.48-7.43 (m, 1H), 7.29-7.25 (m, 1H), 2.61 (s,
3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 196.8 (d, $J_{\text{CF}} = 2.0$ Hz), 162.9 (d, $J_{\text{CF}} = 246.5$
Hz), 139.2 (d, $J_{\text{CF}} = 6.1$ Hz), 130.3 (d, $J_{\text{CF}} = 7.5$ Hz), 124.1 (d, $J_{\text{CF}} = 3.0$ Hz), 120.1 (d,
$J_{\text{CF}} = 21.4$ Hz), 115.0 (d, $J_{\text{CF}} = 22.1$ Hz), 26.7; $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -112.0
(s, 1F).

1-(3-chlorophenyl)ethanone (3l). Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$
7.93 (s, 1H), 7.83 (d, $J = 7.5$ Hz, 1H), 7.55-7.52 (m, 1H), 7.41 (t, $J = 7.5$ Hz, 1H), 2.60 (s,
3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 196.7, 138.7, 135.0, 133.1, 130.0, 128.5, 126.5,
26.7.

1-(3-(trifluoromethyl)phenyl)ethan-1-one (3m). Colorless oil. $^1$H NMR (500 MHz,
CDCl$_3$) $\delta$ 8.21 (s, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.63 (t, $J =
7.5$ Hz, 1H), 2.66 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 197.2, 138.2, 132.0, 131.9
(q, $J_{\text{CF}} = 32.8$ Hz), 130.1 (q, $J_{\text{CF}} = 3.5$ Hz), 129.9, 125.7 (q, $J_{\text{CF}} = 3.8$ Hz), 124.3 (q,
$J_{\text{CF}} = 270.8$ Hz), 27.2; $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -62.8 (s, 3F).
1-(3-nitrophenyl)ethan-1-one (3n). Light yellow solid, mp 76-79 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.78 (s, 1H), 8.45-8.43 (m, 1H), 8.30 (d, $J = 7.5$ Hz, 1H), 7.70 (t, $J = 8.0$ Hz, 1H), 2.70 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 195.7, 148.5, 138.3, 133.8, 129.9, 127.5, 123.3, 26.8.

1-(2-methoxyphenyl)ethan-1-one (3o). Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.73 (dd, $J = 1.5$, 7.5 Hz, 1H), 7.48-7.45 (m, 1H), 7.01-6.96 (m, 2H), 3.92 (s, 3H), 2.62 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 199.9, 158.9, 133.7, 130.4, 128.3, 120.6, 111.6, 55.5, 31.8.

1-(2-fluorophenyl)ethan-1-one (3p). Light yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.90-7.86 (m, 1H), 7.55-7.50 (m, 1H), 7.24-7.21 (m, 1H), 7.16-7.12 (m, 1H), 2.65 (d, $J = 5.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 196.0 (d, $J_{CF} = 3.3$ Hz), 162.3 (d, $J_{CF}$ = 253.3 Hz), 134.7 (d, $J_{CF}$ = 9.0 Hz), 130.6 (d, $J_{CF}$ = 2.4 Hz), 125.8 (d, $J_{CF}$ = 12.6 Hz), 124.4 (d, $J_{CF}$ = 3.5 Hz), 116.7 (d, $J_{CF}$ = 23.6 Hz), 31.5 (d, $J_{CF}$ = 7.4 Hz); $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -109.4 (s, 1F).

1-(2-chlorophenyl)ethan-1-one (3q). Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.56-7.54 (m, 1H), 7.43-7.37 (m, 2H), 7.34-7.31 (m, 1H), 2.65 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 200.5, 139.2, 132.0, 131.3, 130.7, 129.4, 126.9, 30.7.
1-(naphthalen-2-yl)ethan-1-one (3r). White solid, mp 53-56 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.38 (s, 1H), 7.97-7.95 (m, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.81-7.79 (m, 2H), 7.54-7.47 (m, 2H), 2.65 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 198.5, 136.0, 134.9, 132.9, 130.6, 130.0, 128.9, 128.8, 128.2, 127.2, 124.3, 27.1.

Propiophenone (3s). Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 7.0$ Hz, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 2H), 3.01 (q, $J = 7.0$ Hz, 2H), 1.23 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 200.9, 137.0, 132.9, 128.6, 128.0, 31.8, 8.3.

1-(p-tolyl)propan-1-one (3t). Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 2.97 (q, $J = 7.0$ Hz, 2H), 2.40 (s, 3H), 1.22 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 200.6, 143.6, 134.5, 129.2, 128.1, 31.7, 21.6, 8.3.

1-(4-chlorophenyl)propan-1-one (3u). White solid, mp 33-34 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.90 (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 9.0$ Hz, 2H), 2.98 (q, $J = 7.0$ Hz, 2H), 1.22 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 199.6, 139.3, 135.2, 129.4, 128.9, 31.8, 8.2.
1-(3-chlorophenyl)propan-1-one (3v). White solid, mp 45-46 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.93 (s, 1H), 7.84 (d, $J = 7.5$ Hz, 1H), 7.54-7.52 (m, 1H), 7.41 (t, $J = 8.0$ Hz, 1H), 2.98 (q, $J = 7.0$ Hz, 2H), 1.23 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 199.5, 138.5, 135.0, 132.8, 129.9, 128.2, 126.1, 32.0, 8.1.

![1-(3-chlorophenyl)propan-1-one (3v)](image)

1-phenylbutan-1-one (3w). Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 7.5$ Hz, 2H), 7.55 (t, $J = 7.0$ Hz, 1H), 7.45 (t, $J = 7.5$ Hz, 2H), 2.95 (t, $J = 7.5$ Hz, 2H), 1.81-1.74 (m, 2H), 1.01 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 200.5, 137.1, 132.9, 128.6, 128.0, 40.5, 17.8, 13.9.

![1-phenylbutan-1-one (3w)](image)

1-phenylpentan-1-one (3x). Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 7.0$ Hz, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 2H), 2.97 (t, $J = 8.0$ Hz, 2H), 1.76-1.70 (m, 2H), 1.45-1.38 (m, 2H), 0.96 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 200.6, 137.1, 132.9, 128.6, 128.1, 38.3, 26.5, 22.5, 13.9.

![1-phenylpentan-1-one (3x)](image)

1-(4-hydroxyphenyl)heptan-1-one (3y). White solid, mp 62-63 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.91 (d, $J = 8.5$ Hz, 2H), 6.91 (d, $J = 9.0$ Hz, 2H), 6.67 (s, 1H), 2.92 (t, $J = 8.0$ Hz, 2H), 1.75-1.69 (m, 2H), 1.40-1.35 (m, 2H), 1.32-1.30 (m, 4H), 0.88 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 200.3, 160.5, 130.8, 129.9, 115.4, 38.4, 31.7, 29.1, 24.8, 22.5, 14.0.

![1-(4-hydroxyphenyl)heptan-1-one (3y)](image)
4. References

Table S1. References for products.

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5. Copies of $^1$H, $^{13}$C and $^{19}$F NMR Spectra of the Products
3e

Chemical structure diagram.
3h

3i
$\text{Cl}$

$\text{O}$

$\text{3i}$

$\text{F}_3\text{C}$

$\text{O}$

$\text{3m}$