

Supporting Information

Ready synthesis of free *N-H* 2-arylindoles via copper-catalyzed amination of 2-bromo-arylacetylenes with aqueous ammonia and sequential intramolecular cyclization

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I General information

All reagents unless otherwise noted were obtained from commercial source (>99%) and used without further purification. The reactions were carried out under argon atmosphere and the products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90°C) and ethyl acetate as eluate. Compounds described in the literature were characterized by comparison of their ¹H NMR and ¹³C NMR spectra to the reported data. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded in CDCl₃ or DMSO-*d*₆ and chemical shifts were reported in parts per million relative to TMS. MS data were performed on HP1100. High resolution mass spectrometric data (HRMS) were performed on HPLC-Q-ToF MS. HPLC analyses were tested on Waters 2695-2996.

II Experimental procedures for all compounds

The 2-bromo-anilines were obtained from commercial source or can conveniently be prepared by NBS bromination of anilines along with a catalytic amount of ammonium acetate (NH₄OAc) in CH₃CN as described in the literature.¹

The 2-bromo-iodides were prepared based the Sandmeyer reaction as described in the literature.²

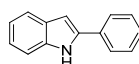
The 2-arylhaloarenes were prepared based the Sonogashira coupling as described in the literature.³

General Procedure for the synthesis of 2-arylindoles

Amination: A flame-dried test tube with a magnetic stirring bar was charged with 2-arylhaloarenes (0.4 mmol), Cu(OTf)₂ (0.04 mmol), picolinaldehyde oxime (0.08 mmol), K₂CO₃ (0.5 mmol), NH₃-H₂O (1.0 mL) in DMSO (1.5 mL) and stirred at 100 °C under argon. The mixture reacted at the indicated temperature for 18 h and cooled to room temperature. The resulting mixture was extracted with ethyl acetate (3×25 mL). The combined organic layers were dried over Na₂SO₄ and then concentrated under vacuum.

Cyclization: The residue was direct treated with ZnBr₂ (0.2 mmol) and toluene (4 mL) and reflux under 110 °C for 6 h or 15 h. After cyclization completion detected by HPLC, the toluene was removed under vacuum and then purified by column chromatography on silica gel with an eluent of petroleum ether and ethyl acetate. All the physical data of the known compounds were in agreement with those reported in the literatures.

2-phenyl-1H-indole (3a)⁴



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5) giving a white solid. Yield: 67 mg, 87%.

¹H NMR (400 MHz, CDCl₃): δ= 8.34 (br, 1H), 7.67 (d, J = 7.2 Hz, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.40 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 1.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ= 137.9, 136.8, 132.4, 129.2, 129.0, 127.7, 125.2, 122.3, 120.6, 120.3, 110.9, 100.0. MS (API, m/z): 194.1 [M+H]⁺. M.p.: 186-187

¹ B. Das, K. Venkateswarlu, A. Majhi, V. Siddaiah and K. R. Reddy, *J Mol Catal a-Chem*, 2007, **267**, 30-33.

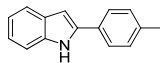
² T. Jensen, H. Pedersen, B. Bang-Andersen, R. Madsen and M. Jorgensen, *Angew. Chem. Int. Ed.*, 2008, **47**, 888-890.

³ T. Kashiki, S. Shinamura, M. Kohara, E. Miyazaki, K. Takimiya, M. Ikeda and H. Kuwabara, *Org. Lett.*, 2009, **11**, 2473-2475.

⁴ L. Ackermann, S. Barfusser and H. K. Potukuchi, *Adv. Synth. Catal.*, 2009, **351**, 1064-1072.

°C.

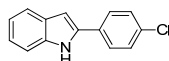
2-(p-tolyl)-1H-indole (3b)⁴



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5) giving a white solid. Yield: 70 mg, 85%.

¹H NMR (400 MHz, CDCl₃): δ= 8.28 (br, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.78 (s, 1H), 2.39 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ=138.0, 137.6, 136.6, 129.7, 129.5, 129.3, 125.0, 122.1, 120.5, 120.2, 110.8, 99.4, 21.2. MS (API, m/z): 208.1 [M+H]⁺. M.p.: 212-213 °C.

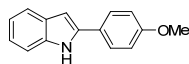
2-(4-chlorophenyl)-1H-indole (3c)⁴



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5) giving a pale orange solid. Yield: 76 mg, 84%.

¹H NMR (400 MHz, CDCl₃): δ= 8.27 (br, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.42-7.38 (m, 3H), 7.20 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.80 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ=136.9, 136.7, 133.5, 130.9, 129.23, 129.20, 126.3, 122.7, 120.8, 120.5, 110.9, 100.5. MS (API, m/z): 228.1 [M+H]⁺. M.p.: 196-197 °C.

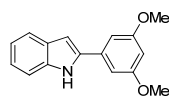
2-(4-methoxyphenyl)-1H-indole (3d)⁴



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5-1/2) giving a white solid. Yield: 77 mg, 87%.

¹H NMR (400 MHz, CDCl₃): δ= 8.26 (br, 1H), 7.61-7.58 (m, 3H), 7.38 (d, J = 8.0 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1H), 7.10 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 6.71 (s, 1H), 3.86 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ=159.4, 138.0, 136.6, 129.4, 126.5, 125.2, 121.9, 120.3, 120.2, 114.5, 110.7, 98.8, 55.4. MS (API, m/z): 224.1 [M+H]⁺. M.p.: 227-228 °C.

2-(3,5-dimethoxyphenyl)-1H-indole (3e)

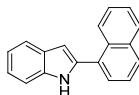


Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5-1/1) giving a pale orange solid. Yield: 83 mg, 83%.

¹H NMR (400 MHz, CDCl₃): δ= 8.36 (br, 1H), 7.62 (d, J = 7.6, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H), 6.81-6.80 (m, 3H), 6.4 (s, 1H), 3.86 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ=161.2, 137.8, 136.7, 134.3, 129.1, 122.4, 120.7, 120.3, 110.9, 103.6, 100.4, 99.7, 55.5.

HR-ESI-MS: $[M-H]^-$ m/z calcd for $C_{16}H_{14}NO_2$ 252.1025, found: 252.1023. GC-MS (EI) m/z : 253 (M^+ , 100%). M.p.: 127-128 °C.

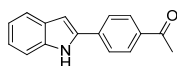
2-(naphthalen-1-yl)-1H-indole (3f)⁵



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5) giving a white solid. Yield: 81 mg, 83%.

1H NMR (400 MHz, $CDCl_3$): δ =8.32-8.31 (m, 2H), 7.91-7.87 (m, 2H), 7.70 (d, J = 7.6, 1H), 7.63 (d, J = 7.2 Hz, 1H), 7.55-7.49 (m, 3H), 7.44 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 8.4 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H), 6.80 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =136.7, 136.3, 133.9, 131.5, 131.1, 128.8, 128.6, 128.5, 127.2, 126.7, 126.2, 125.7, 125.3, 122.2, 120.6, 120.2, 110.8, 103.7. MS (API, m/z): 244.1 $[M+H]^+$. M.p.: 102-103 °C.

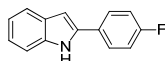
1-(4-(1H-indol-2-yl)phenyl)ethanone (3g)⁴



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5-1/1) giving an orange solid. Yield: 64 mg, 68%.

1H NMR (400 MHz, $CDCl_3$) δ =8.48 (br, 1H), 8.03 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 6.97 (s, 1H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =197.4, 137.3, 136.6, 136.3, 135.8, 129.2, 129.1, 124.8, 123.3, 121.1, 120.6, 111.1, 102.0, 26.6. MS (API, m/z): 236.1 $[M+H]^+$. M.p.: 212-213 °C.

2-(4-fluorophenyl)-1H-indole (3h)³

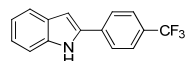


Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5) giving a white solid. Yield: 74 mg, 88%.

1H NMR (400 MHz, $CDCl_3$) δ =8.22 (br, 1H), 7.63-7.59 (m, 3H), 7.38 (d, J = 8.0 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 7.15-7.11 (m, 3H), 6.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =163.64 (d, J = 246 Hz, 1C), 137.01, 136.81, 129.24, 128.72 (d, J = 3.0 Hz, 1C), 126.88 (d, J = 8.0 Hz, 1C), 122.42, 120.64, 120.39, 116.15 (d, J = 21 Hz, 1C), 110.88, 99.94. ^{19}F NMR (400 MHz, $CDCl_3$) δ =-113.9 Hz. MS (API, m/z): 212.1 $[M+H]^+$. M.p.: 185-186 °C.

2-(4-(trifluoromethyl)phenyl)-1H-indole (3i)⁴

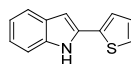
⁵ G. A. Kraus and H. T. Guo, *Org. Lett.*, 2008, **10**, 3061-3063.



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5) giving a white solid. Yield: 87 mg, 83%.

^1H NMR (400 MHz, CDCl_3) δ =8.37 (br, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 8.0 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 6.92 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ =137.15, 136.11, 135.71, 129.03, 126.03 (q, J = 32 Hz, 1C), 125.45, 125.12, 123.21, 121.05, 120.66, 111.09, 101.73. ^{19}F NMR (400 MHz, CDCl_3) δ =-63.0 Hz. MS (API, m/z): 262.1 $[\text{M}+\text{H}]^+$. M.p.: 251-252 $^\circ\text{C}$.

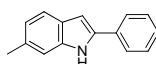
2-(thiophen-2-yl)-1H-indole (3j)⁶



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5) giving a white solid. Yield: 45 mg, 57%.

^1H NMR (400 MHz, CDCl_3) δ =8.21 (br, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.29-7.25 (m, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.13-7.08 (m, 2H), 6.73 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ =136.5, 135.6, 132.3, 129.1, 127.9, 124.6, 122.9, 122.6, 120.5, 110.8, 100.4. MS (API, m/z): 200.1 $[\text{M}+\text{H}]^+$. M.p.: 186-187 $^\circ\text{C}$.

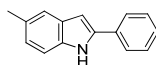
6-methyl-2-phenyl-1H-indole (4a)⁶



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5) giving a pale orange solid. Yield: 66 mg, 80%.

^1H NMR (400 MHz, CDCl_3) δ =8.20 (br, 1H), 7.64 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 8.0 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.18 (s, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.77 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ =137.3, 137.2, 132.5, 132.2, 129.0, 127.4, 127.1, 125.0, 122.0, 120.3, 110.9, 99.8, 21.8. MS (API, m/z): 208.1 $[\text{M}+\text{H}]^+$. M.p.: 189-190 $^\circ\text{C}$.

5-methyl-2-phenyl-1H-indole (4b)⁷



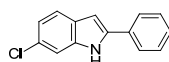
⁶ T. Kashiki, S. Shinamura, M. Kohara, E. Miyazaki, K. Takimiya, M. Ikeda and H. Kuwabara, *Org. Lett.*, 2009, **11**, 2473-2475.

⁷ A. Carpita and A. Ribecai, *Tetrahedron Lett.*, 2009, **50**, 6877-6881.

Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5) giving a pale orange solid. Yield: 74 mg, 90%.

^1H NMR (400 MHz, CDCl_3) δ =8.22 (br, 1H), 7.64 (d, J = 7.6 Hz, 2H), 7.45-7.41 (m, 3H), 7.33-7.27 (m, 2H), 7.02 (d, J = 8.4 Hz, 1H), 6.75 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ =137.9, 135.2, 132.5, 129.54, 129.48, 129.0, 127.6, 125.1, 124.0, 120.3, 110.5, 99.6, 21.5. MS (API, m/z): 208.1 $[\text{M}+\text{H}]^+$. M.p.: 220-221 °C.

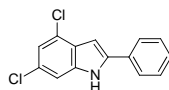
6-chloro-2-phenyl-1H-indole (4c)⁸



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5) giving a pale orange solid. Yield: 74 mg, 82%.

^1H NMR (400 MHz, CDCl_3) δ =8.30 (br, 1H), 7.64 (d, J = 7.6 Hz, 2H), 7.51 (d, J = 8.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.38 (s, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 8.4 Hz, 1H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ =138.6, 137.1, 131.9, 129.1, 128.0, 127.8, 125.1, 121.5, 121.0, 110.8, 99.9. MS (API, m/z): 228.1 $[\text{M}+\text{H}]^+$. M.p.: 182-183 °C.

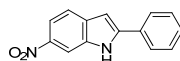
4,6-dichloro-2-phenyl-1H-indole (4d)⁹



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5) giving a white solid. Yield: 84 mg, 80%.

^1H NMR (400 MHz, CDCl_3) δ =8.34 (br, 1H), 7.59 (d, J = 7.6 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.21 (s, 1H), 7.11 (s, 1H), 6.83 (d, J = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ =139.1, 137.1, 131.2, 129.2, 128.4, 127.7, 126.9, 126.2, 125.2, 120.5, 109.6, 98.4. MS (API, m/z): 262.0 $[\text{M}+\text{H}]^+$. M.p.: 109-110 °C.

6-nitro-2-phenyl-1H-indole (4e)¹⁰



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5-1/1) giving a red solid. Yield: 66 mg, 69%.

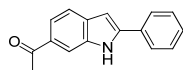
⁸ L. Joucla, N. Batail and L. Djakovitch, *Adv. Synth. Catal.*, 2010, **352**, 2929-2936.

⁹ R. B. Carlin and E. E. Fisher, *J. Am. Chem. Soc.*, 1948, **70**, 3421-3424.

¹⁰ R. Sanz, V. Guilarte and A. Perez, *Tetrahedron Lett.*, 2009, **50**, 4423-4426.

^1H NMR (400 MHz, DMSO- d_6) δ =12.36 (s, 1H), 8.30 (s, 1H), 7.96-7.91 (m, 3H), 7.73 (d, J = 8.8 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.16 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ =144.2, 141.9, 135.4, 133.7, 130.8, 129.1, 128.9, 125.7, 120.1, 114.8, 107.7, 99.8. MS (EI, m/z): 238 $[\text{M}]^+$, 165, 208, 192. M.p.: 219-220 $^\circ\text{C}$.

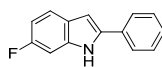
1-(2-phenyl-1H-indol-6-yl)ethanone (4f)



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5-1/1) giving an orange solid. Yield: 65 mg, 69%.

^1H NMR (400 MHz, CDCl_3) δ =8.84 (br, 1H), 8.14 (s, 1H), 7.76-7.72 (m, 3H), 7.65 (d, J = 8.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H), 6.87 (s, 1H), 2.68 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ =198.3, 141.8, 136.3, 133.2, 131.6, 131.5, 129.2, 128.6, 125.5, 120.8, 120.2, 111.9, 100.2, 26.84. HR-ESI-MS: $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{16}\text{H}_{14}\text{NO}_2$ 258.0895, found: 258.0897. GC-MS (EI) m/z : 220 (100%), 235 (M^+ , 70%). M.p.: 212-213 $^\circ\text{C}$.

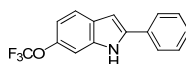
6-fluoro-2-phenyl-1H-indole (4g)¹¹



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5) giving a white solid. Yield: 68 mg, 80%.

^1H NMR (400 MHz, DMSO- d_6) δ =11.66 (br, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.76-7.72 (m, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.15 (d, J = 6.0 Hz, 1H), 6.92-6.85 (m, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ =159.62 (d, J = 234 Hz, 1C), 139.04 (d, J = 4 Hz, 1C), 137.65 (d, J = 13 Hz, 1C), 132.62, 129.56, 128.08, 126.07, 125.49, 121.70 (d, J = 11 Hz, 1C), 108.50 (d, J = 24 Hz, 1C), 108.38, 99.34 (d, J = 3.0 Hz, 1C), 97.87 (d, J = 25 Hz, 1C). ^{19}F NMR (400 MHz, DMSO- d_6) δ =-121.5. MS (API, m/z): 212.1 $[\text{M}+\text{H}]^+$. M.p.: 171-172 $^\circ\text{C}$.

2-phenyl-6-(trifluoromethoxy)-1H-indole (4h)



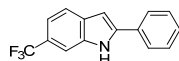
Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/3) giving a white solid. Yield: 85 mg, 77%.

^1H NMR (400 MHz, CDCl_3) δ =8.36 (br, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.44 (t,

¹¹ Y. Q. Fang and M. Lautens, *J. Org. Chem.*, 2008, **73**, 538-549.

$J = 8.0$ Hz, 2H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.26 (s, 1H), 7.00 (dd, $J_1=8.0$ Hz, $J_2=1.0$ Hz, 1H), 6.80 (d, $J = 1.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) $\delta=145.15, 139.43, 136.36, 131.88, 129.14, 128.12, 127.97, 125.19, 124.62, 121.88$ (q, $J = 255$ Hz, 1C), 114.39, 103.96, 99.87. ^{19}F NMR (400 MHz, CDCl_3) $\delta=-57.9$. MS (API, m/z): 278.0 $[\text{M}+\text{H}]^+$. HR-ESI-MS: $[\text{M}+\text{Na}]^+$ m/z calcd for $\text{C}_{16}\text{H}_{14}\text{NO}_2$ 258.0895, found: 258.0897. M.p.: 167-168 °C.

2-phenyl-6-(trifluoromethyl)-1H-indole (4i)¹²



Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/5) giving a white solid. Yield: 73 mg, 70%.

^1H NMR (400 MHz, CDCl_3) $\delta=8.51$ (br, 1H), 7.70-7.67 (m, 4H), 7.47 (t, $J = 8.4$ Hz, 2H), 7.40-7.35 (m, 2H), 6.87 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3) $\delta=140.58, 135.60, 131.61, 129.21, 128.49, 125.16$ (q, $J = 269$ Hz, 1C), 125.43, 124.23 (q, $J = 32$ Hz, 1C), 120.92, 117.04 (q, $J = 4$ Hz, 1C), 117.00, 108.39 (q, $J = 4$ Hz, 1C), 100.07; ^{19}F NMR (400 MHz, CDCl_3) $\delta=-60.6$. MS (API, m/z): 262.1 $[\text{M}+\text{H}]^+$. M.p.: 181-182 °C.

¹² J. L. Rutherford, M. P. Rainka and S. L. Buchwald, *J. Am. Chem. Soc.*, 2002, **124**, 15168-15169.

III Copys for ^1H NMR and ^{13}C NMR.

