Regiocontrolled functionalization of 2,3-dihalogenoimidazo[1,2-a]pyridines by Suzuki and Sonogashira cross-coupling reactions

P.-O. Delaye,a M. Pénichon,a H. Allouchi,a C. Enguehard-Gueiffierb and A. Gueiffierb

a) UMR INRA 1282 Infectiologie et Santé Publique, Recherche et Innovation en Chimie Médicinale, Université François Rabelais, 31 avenue Monge, 37200 Tours, France.

b) UMR INSERM 1069 Nutrition, Croissance et cancer, Université François Rabelais, 31 avenue Monge, 37200 Tours, France.

SUPPORTING INFORMATIONS

1) Generals considerations
2) Characterization data for products
3) Copies of NMR spectra for products
General considerations

All reagents were used directly as obtained commercially. Thin-layer chromatography (TLC) were performed using Merk® silica gel 60F254 plates. Column chromatography were preformed using Merck Geduran® Si 60 (40-63µm) silica. Melting points were determined on a capillary apparatus (Stuart, Staffordshire, United Kingdom) and are uncorrected. Microwave heating was performed using CEM® Explorer SP 12 S class apparatus (max power 300W). NMR experiments were performed at 300 mHz (1H) and 75 mHz (13C) on a Bruker-Avance 300 MHz spectrometer. Assignment of carbons noted C* may be interchanged. Mass spectra were determined on a Hewlett Packard 5988A spectrometer or on a Shimadzu QP 2010 spectrometer by direct inlet at 70 eV. NMR data for compounds 2a1, 2b2, 3a3, 3b4, 3d5, 3f6 and 6a6 were previously described in literature.

2,3-diodoimidazo[1,2-a]pyridine (1a)

To a stirred solution of 2-iodoimidazo[1,2-a]pyridine (1.22g, 5mmol, 1eq) in CH3CN (20mL) was added NIS (1.24g, 5.5mmol, 1.1eq) in one portion at room temperature. A white solid precipitated quickly. After 3h at room temperature the reaction was quenched with 30mL of water and extract thrice with 30mL of CH2Cl2. The combined organic phases were washed with 50mL of Na2SO4 aqueous saturated solution, dried on Na2SO4 and evaporated to dryness. The crude mixture was purified by column chromatography (silica, eluent: CH2Cl2). 1b was obtained as a gray solid (2.1g, 6.5mmol, yield: 90%). 1H NMR (CDCl3): 8.06 (dt, 1H, J = 6.9Hz, H-5), 7.56 (dt, 1H, J = 9.3Hz, 0.9Hz, H-8), 7.21 (ddd, 1H, J = 9.0Hz, 6.9Hz, 1.0Hz H-7), 6.91 (td, 1H, J = 9.0Hz, 0.6Hz, H-6). 13C NMR (CDCl3): δ: 149.4 (C-8a), 127.0 (C-5), 125.7 (C-7), 117.2 (C-8), 113.9 (C-6), 104.6 (C-2), 73.0 (C-3). m.p.: 114-118°C. HRMS (ESI): m/z calculated for C19H13N2+ [M+H]+: 370.85366, found: 370.85389.

2-iodo-3-bromomidazo[1,2-a]pyridine (1b)

To a stirred solution of 2-iodoimidazo[1,2-a]pyridine (1.75g, 7.2mmol, 1eq) in CH3CN (30mL) was added NBS (1.4g, 7.9mmol, 1.1eq) in one portion at room temperature. A white solid precipitated quickly. After 3h at room temperature the reaction was quenched with 30mL of water and extract thrice with 30mL of CH2Cl2. The combined organic phases were washed with 50mL of Na2SO4 aqueous saturated solution, dried on Na2SO4 and evaporated to dryness. The crude mixture was purified by column chromatography (silica, eluent: CH2Cl2). 1b was obtained as a gray solid (2.1g, 6.5mmol, yield: 90%). 1H NMR (CDCl3): 8.06 (dt, 1H, J = 6.9Hz, 0.9Hz, H-5), 7.56 (dt, 1H, J = 9.3Hz, 0.9Hz, H-8), 7.21 (ddd, 1H, J = 9.0Hz, 6.9Hz, 1.0Hz H-7), 6.91 (td, 1H, J = 9.0Hz, 0.9Hz, H-6). 13C NMR (CDCl3): δ: 147.4 (C-8a), 125.3 (C-7), 124.3 (C-5), 117.3 (C-8), 113.7 (C-6), 101.9 (C-2*), 95.9 (C-3*). m.p.: 114-118°C. HRMS (ESI): m/z calculated for C19H13BrN2+ [M+H]+: 322.86753, found: 322.86793.

General procedure for Suzuki coupling at C-2 position or C-3 position.

To a stirred solution of 2-iodoimidazo[1,2-a]pyridine (1.75g, 7.2mmol, 1eq) in CH3CN (20mL) was added NIS (1.24g, 5.5mmol, 1.1eq) in one portion at room temperature. A white solid precipitated quickly. After 3h at room temperature the reaction was quenched with 30mL of water and extract thrice with 30mL of CH2Cl2. The combined organic phases were washed with 50mL of Na2SO4 aqueous saturated solution, dried on Na2SO4 and evaporated to dryness. The crude mixture was purified by column chromatography (silica, eluent: CH2Cl2). 1b was obtained as a gray solid (2.1g, 6.5mmol, yield: 90%). 1H NMR (CDCl3): 8.06 (dt, 1H, J = 6.9Hz, 0.9Hz, H-5), 7.56 (dt, 1H, J = 9.3Hz, 0.9Hz, H-8), 7.21 (ddd, 1H, J = 9.0Hz, 6.9Hz, 1.0Hz H-7), 6.91 (td, 1H, J = 9.0Hz, 0.9Hz, H-6). 13C NMR (CDCl3): δ: 149.4 (C-8a), 127.0 (C-5), 125.7 (C-7), 117.2 (C-8), 113.9 (C-6), 104.6 (C-2), 73.0 (C-3). m.p.: 114-118°C. HRMS (ESI): m/z calculated for C19H13BrN2+ [M+H]+: 322.86753, found: 322.86793.

3-bromo-2-(thiophen-3-yl)imidazo[1,2-a]pyridine (2c)

then added. The reaction mixture was stirred for 30 minutes at room temperature. The reaction mixture was partitioned between CH$_2$Cl$_2$ (10mL) and water (10mL). The aqueous phase was extracted twice with CH$_2$Cl$_2$. The organic layers were combined, dried over MgSO$_4$, and evaporated to dryness. The crude mixture was purified by column chromatography (silica, eluent: CH$_2$Cl$_2$ / EtOAc 98/2). Yellow solid, yield: 80%. HRMS (ESI): m/z calculated for C$_{11}$H$_9$BrN$_2$ [M+H]$^+$: 278.95861, found: 278.95892.

3-bromo-2-methylimidazo[1,2-a]pyrididine (2d)


3-(furan-2-yl)-2-phenylimidazo[1,2-a]pyrididine (3c)

Eluent: CH$_2$Cl$_2$ / EtOAc 95/5. Brown solid, yield: 67%. HRMS (ESI): m/z calculated for C$_{17}$H$_{12}$N$_2$O [M+H]$^+$: 277.07945, found: 277.07940.

3-phenyl-2-(thiophen-3-yl)imidazo[1,2-a]pyridine (3e)

Eluent: CH$_2$Cl$_2$ / EtOAc 100/0 → 93/7. White solid, yield: 88%. HRMS (ESI): m/z calculated for C$_{20}$H$_{15}$N$_2$S [M+H]$^+$: 277.07940, found: 277.07945.

2-phenyl-3-(pyridin-4-yl)imidazo[1,2-a]pyridine (3f)

1b (200mg, 0.619mmol, 1eq), Pd(PPh$_3$)$_2$ (36mg, 0.031mmol, 5%) and phenylboronic acid (83mg, 0.681mmol, 1eq) were introduced into a screw-cap test tube. The tube was sealed with a rubber septum and then evacuated and refilled with argon thrice. DMF (2mL), Et$_3$N (278µL, 2mmol, 4eq) and alkyne (0.55mmol, 1.1eq) were then added. The reaction mixture was stirred for 30 minutes at room temperature. The reaction mixture was partitioned between CH$_2$Cl$_2$ (10mL) and brine (10mL). The aqueous phase was extracted twice with CH$_2$Cl$_2$ (10mL). Organic phases were combined, dried over MgSO$_4$ and evaporated to dryness. The crude mixture was purified by column chromatography (silica, eluent: mixture of petroleum ether and diethylether).

General procedure for Sonogashira coupling at C-2 position.

1b (161mg, 0.5mmol, 1eq), PdCl$_2$(PPh$_3$)$_2$ (35mg, 0.055mmol, 10%) and CuI (10mg, 0.055mmol, 10%) were introduced into a screw-cap test tube. The tube was sealed with a rubber septum and then evacuated and refilled with argon thrice. DMF (2mL), Et$_3$N (278µL, 2mmol, 4eq) and alkyne (0.55mmol, 1.1eq) were then added. The reaction mixture was stirred for 30 minutes at room temperature. The reaction mixture was partitioned between CH$_2$Cl$_2$ (10mL) and brine (10mL). The aqueous phase was extracted twice with CH$_2$Cl$_2$ (10mL). Organic phases were combined, dried over MgSO$_4$ and evaporated to dryness. The crude mixture was purified by column chromatography (silica, eluent: mixture of petroleum ether and diethylether).
3-bromo-2-(phenylethynyl)imidazo[1,2-a]pyridine (4a)

Eluent: PE/EtO 50/50. Orange solid, yield: 95%. 1H NMR (CDCl3) δ: 8.08 (dt, 1H, J = 6.9Hz, 0.9Hz, H-5), 7.64-7.61 (m, 3H, 2CH Ph, H-8), 7.38-7.36 (m, 3H, 3CH Ph), 7.31 (ddd, 1H, J = 9.0Hz, 6.9Hz, 1.2Hz, H-7), 6.98 (td, 1H, J= 6.9Hz, 1.2Hz, H-6). 13C NMR (CDCl3) δ: 145.1 (C-8a), 132.0 (2CH Ph), 129.0 (CH Ph), 128.5 (2CH Ph), 128.4 (C-2), 126.2 (C-7), 124.1 (C-5), 122.5 (Cq Ph), 117.7 (C-8), 114.1 (C-6), 99.4 (C-3), 94.6 (C=CH-Ph), 81.0 (C=CH-Ph). m.p.: 117-121°C. HRMS (ESI): m/z calculated for C15H8BrN2 [M+H]+: 297.00219, found: 297.00257.

3-bromo-2-(cyclopropylethynyl)imidazo[1,2-a]pyridine (4b)

Eluent: PE/EtO 50/50. Yellow solid, yield: 98%. 1H NMR (CDCl3) δ: 7.96 (dt, 1H, J = 6.9Hz, 0.9Hz, H-5), 7.47 (dt, 1H, J = 9.3Hz, 0.9Hz, H-8), 7.19 (ddd, 1H, J = 9.0Hz, 6.9Hz, 1.2Hz, H-7), 6.87 (td, 1H, J = 6.9Hz, 0.9Hz, H-6), 1.50 (quint, 1H, CH c-Pr), 0.88 (m, 4H, 2CH2 c-Pr). 13C NMR (CDCl3) δ: 144.9 (C-8a), 129.1 (C-2), 125.5 (C-7), 123.8 (C-5), 117.5 (C-8), 113.6 (C-6), 98.9 (C=CH-c-Pr), 98.4 (C-3), 67.6 (C=CH-c-Pr), 9.0 (2CH2 c-Pr), 0.4 (CH c-Pr). m.p.: 79-83°C. HRMS (ESI): m/z calculated for C12H13BrN2 [M+H]+: 261.00219, found: 261.00244.

General procedure for Sonogashira coupling at C-3 position.

4a-b (0.5mmol, 1eq), PdCl2(PPh3)2 (35mg, 0.05mmol, 10%) and CuI (10mg, 0.05mmol, 10%) were introduced into a screw-cap test tube. The tube was sealed with a rubber septum and then evacuated and refilled with argon thrice. DMF (2mL), Et3N (278μL, 2mmol, 4eq) and alkyne (0.55mmol, 1 eq) were then added. The reaction mixture was stirred for 1h30 at 80°C. After cooling, the reaction mixture was partitioned between CH2Cl2 (10mL) and brine (10mL). The aqeous phase was extracted twice with CH2Cl2 (10mL). Organic phases were combined, dried over MgSO4 and evaporated to dryness. The crude mixture was purified by column chromatography (silica, eluent: mixture of petroleum ether and diethylether).

2-(phenylethynyl)-3-(p-tolylethynyl)imidazo[1,2-a]pyridine (5a)

Eluent: PE/EtO 50/50. Orange solid, yield: 97%. 1H NMR (CDCl3) δ: 8.29 (d, 1H, J = 6.6Hz, H-5), 7.65-7.62 (m, 3H, Ph-2,6, H-8), 7.51 (d, 2H, J = 8.1Hz, tolyl-2,6), 7.39-7.35 (m, 3H, Ph-3,4,5), 7.32 (ddd, 1H, J = 9.0Hz, 6.9Hz, 1.2Hz, H-7), 7.21 (d, 2H, J = 7.8Hz, tolyl-3,5), 6.97 (td, 1H, J = 6.6Hz, 0.9Hz, H-6), 2.40 (s, 3H, CH3 tolyl). 13C NMR (CDCl3) δ: 144.7 (C-8a), 139.5 (tolyl-4), 132.0 (Ph-2,6), 131.9 (C-2), 131.5 (tolyl-2,6), 129.4 (tolyl-3,5), 128.9 (Ph-4), 128.5 (Ph-3,5), 127.1 (C-7), 125.3 (C-5), 122.7 (Ph-1), 119.3 (tolyl-1), 117.6 (C-8), 113.8 (C-6), 112.2 (C-3), 102.3 (C=CH-tolyl), 94.7 (C=C-Ph), 82.3 (C=C-Ph), 75.2 (C=C-tolyl), 21.7 (CH3 tolyl). m.p.: 113-117°C. HRMS (ESI): m/z calculated for C22H17N2 [M+H]+: 333.13917, found: 333.13888.

3-(cyclopropylethynyl)-2-(phenylethynyl)imidazo[1,2-a]pyridine (5b)

Eluent: PE/EtO 50/50→40/60. Brown solid, yield: 82%. 1H NMR (CDCl3) δ: 8.16 (dt, 1H, J = 6.9Hz, 0.9Hz, H-5), 7.63-7.59 (m, 2H, Ph-2,6), 7.54 (dt, 1H, J = 9.0Hz, 0.9Hz, H-8), 7.38-7.33 (m, 3H, Ph-3,4,5), 7.24 (ddd, 1H, J = 9.0Hz, 6.6Hz, 1.2Hz, H-7), 6.88 (td, 1H, J = 6.6Hz, 0.9Hz, H-6), 1.70-1.61 (m, 1H, CH c-Pr), 1.04-0.91 (m, 4H, 2CH2 c-Pr). 13C NMR (CDCl3) δ: 144.5 (C-8a), 132.0 (Ph-2,6), 131.9 (C-2), 128.7 (Ph-4), 128.4 (Ph-3,5), 126.3 (C-7), 125.1 (C-5), 123.0 (Ph-1), 117.6 (C-8), 113.3 (C-6), 112.5 (C-3), 106.8 (C=C-c-Pr), 93.7 (C=C-Ph), 82.8 (C=C-Ph), 62.4 (C=C-c-Pr), 9.6 (2CH2 c-Pr), 0.8 (CH c-Pr). m.p.: 105-109°C. HRMS (ESI): m/z calculated for C26H19N2 [M+H]+: 283.12298, found: 283.12315.

3-(3-methoxyprop-1-yn-1-yl)-2-(phenylethynyl)imidazo[1,2-a]pyridine (5c)

Eluent: PE/EtO 40/60. Brown oil, yield: 42%. 1H NMR (CDCl3) δ: 8.22 (dt, 1H, J = 6.9Hz, 0.9Hz, H-5), 7.62-7.57 (m, 3H, Ph-2,6, H-8), 7.38-7.34 (m, 3H, Ph-3,4,5), 7.30 (ddd, 1H, J = 9.0Hz, 6.9Hz, 1.2Hz, H-7), 6.94 (td, 1H, J = 6.9Hz, 0.9Hz, H-6), 4.53 (s, 2H, CH2OCH3), 3.52 (s, 3H, CH3OCH3). 13C NMR (CDCl3) δ: 145.1 (C-8a), 133.2 (C-2), 132.0 (Ph-2,6), 128.9 (Ph-4), 128.5 (Ph-3,5), 126.9 (C-7), 125.2 (C-5), 122.7 (Ph-1), 117.8 (C-8), 113.7 (C-6), 111.2 (C-3), 98.2 (C=C-CH2OCH3), 94.1 (C=C-Ph), 82.3 (C=C-Ph), 73.5 (C=C-CH2OCH3), 60.8 (CH2OCH3), 57.9 (CH3OCH3). HRMS (ESI): m/z calculated for C16H14N2O [M+H]+: 287.11789, found: 287.11822.
2-(cyclopropylethynyl)-3-(phenylethynyl)imidazo[1,2-α]pyridine (5d)

Eluent: PE/Et₂O 50/50. Brown oil, yield: 54%. ¹H NMR (CDCl₃) δ: 8.23 (dt, 1H, J = 6.9Hz, 0.9Hz, H-5), 7.60-7.54 (m, 3H, Ph-2,6, H-8), 7.47-7.37 (m, 3H, Ph-3,4,5), 7.27 (dd, 1H, J = 8.7Hz, 6.6Hz, 1.2Hz, H-7), 6.93 (td, 1H, J = 6.9Hz, 1.2Hz, H-6), 1.60-1.51 (m, 1H, CH c-Pr), 0.93-0.90 (m, 4H, 2CH₂ c-Pr). ¹³C NMR (CDCl₃) δ: 144.6 (C-8a), 132.9 (C-2), 131.5 (Ph-2,6), 128.9 (Ph-4), 128.6 (Ph-3,5), 126.8 (C-7), 125.1 (C-5), 122.5 (Ph-1), 117.5 (C-8), 113.6 (C-6), 113.3 (C-3), 101.5 (C=Ç-Ph), 99.5 (C=Ç-c-Pr), 76.1 (C=C-Ph), 68.5 (C=C-c-Pr), 9.1 (2CH₂ c-Pr), 0.6 (CH c-Pr). HRMS (ESI): m/z calculated for C₂₀H₁₄N₂ [M+H]⁺: 283.12298, found: 283.12319.

3-(4-methoxyphenylethynl)-2-(phenylethynyl)imidazo[1,2-α]pyridine (5e)

1b (200mg, 0.619mmol, 1eq), PdCl₂(PPh₃)₂ (43mg, 0.062mmol, 10%) and CuI (12mg, 0.062mmol, 10%) were introduced into a screw-cap test tube. The tube was sealed with a rubber septum and then evacuated and refilled with argon thrice. DMF (2.5mL), Et₃N (344μL, 2.48mmol, 4eq) and phenylacetylene (75μL, 0.68mmol, 1.1eq) were then added. The reaction mixture was stirred for 30 minutes at room temperature. 4-methoxyphenylacetylene (120μL, 0.929mmol, 1.5eq) was added, and the reaction heated at 80°C for 1h30. After cooling, the reaction mixture was partitioned between CH₂Cl₂ (12mL) and brine (12mL). The aqueous phase was extracted twice with CH₂Cl₂ (12mL). Organic phases were combined, dried over MgSO₄ and evaporate to dryness. The crude mixture was purified by column chromatography (silica, eluent: PE/EntO 40/60→20/80) to afford 5e as a dark yellow solid (140mg), yield: 65%. ¹H NMR (CDCl₃) δ: 8.25 (dt, 1H, J = 6.6Hz, 0.9Hz, H-5), 7.65-7.59 (m, 3H, Ph-2,6, H-8), 7.54 (d, 2H, J = 8.7Hz, 4-MeOPh-2,6), 7.37-7.34 (m, 3H, Ph-3,4,5), 7.29 (ddd, 1H, J = 9.0Hz, 6.9Hz, 1.5Hz, H-7), 6.96-6.89 (m, 3H, 4-MeOPh-3,5, H-6), 3.83 (s, 3H, OCH₃). ¹³C NMR (CDCl₃) δ: 160.3 (4-MeO-Ph4), 144.7 (C-8a), 133.4 (C-2*), 133.2 (4-MeO-Ph2,6), 132.0 (Ph-2,6), 131.7 (4-MeOPh1*), 128.8 (Ph-4), 128.4 (Ph-3,5), 126.9 (C-7), 125.2 (C-5), 122.7 (Ph-1), 117.6 (C-8), 114.3 (4-MeOPh3,5), 113.7 (C-6), 112.3 (C-3), 102.1 (C=Ç-4MeO-Ph), 94.5 (C=C-Ph), 82.4 (C=C-Ph*), 74.5 (C=C-4MeOPh*), 55.4 (OCH₃). m.p.: 54-58°C. HRMS (ESI): m/z calculated for C₂₅H₁₇N₂O [M+H]⁺: 349.13354, found: 349.13389.

2-methyl-3-(phenylethynyl)imidazo[1,2-α]pyridine (6b)

Eluent: PE/Et₂O 50/50→20/80. Orange oil, yield: 67%. ¹H NMR (CDCl₃) δ: 8.24 (dt, 1H, J = 6.9Hz, 0.9Hz, H-5), 7.57-7.53 (m, 3H, Ph-2,6, H-8), 7.40-7.33 (m, 3H, Ph-3,4,5), 7.21 (ddd, 1H, J = 9.0Hz, 6.9Hz, 1.2Hz, H-7), 6.87 (td, 1H, J = 6.9Hz, 1.2Hz, H-6), 2.58 (s, 3H, CH₃). ¹³C NMR (CDCl₃) δ: 148.5 (C-2), 144.9 (C-8a), 131.3 (Ph-2,6), 128.6 (Ph-3,4,5), 125.7 (C-7), 125.1 (C-5), 122.9 (Ph-1), 116.9 (C-8), 112.8 (C-6), 106.4 (C-3), 100.7 (C=Ç-Ph), 76.9 (C=C-Ph), 14.4 (CH₃). HRMS (ESI): m/z calculated for C₁₆H₁₂N₂ [M+H]⁺: 233.10732, found: 233.10744.

3-methyl-2-(phenylethynyl)imidazo[1,2-α]pyridine (6c)

Eluent: CH₂Cl₂/MeOH 99/1. Brown solid, yield: 70%. ¹H NMR (CDCl₃) δ: 7.82 (dt, 1H, J = 6.9Hz, 0.9Hz, H-5), 7.60-7.54 (m, 3H, Ph-2,6, H-8), 7.37-7.33 (m, 3H, Ph-3,4,5), 7.18 (ddd, 1H, J = 9.3Hz, 6.9Hz, 1.2Hz, H-7), 6.85 (td, 1H, J = 6.6Hz, 0.9Hz, H-6), 2.59 (s, 3H, CH₃). ¹³C NMR (CDCl₃) δ: 144.5 (C-8a), 131.7 (Ph-2,6), 128.4 (Ph-3,4,5), 126.5 (C-2), 124.4 (C-7), 123.8 (C-3*), 123.2 (Ph₁*), 122.9 (C-5), 117.7 (C-8), 112.8 (C-6), 92.7 (C=C-Ph), 83.1 (C=C-Ph), 9.2 (CH₃). m.p.: 119-123°C. HRMS (ESI): m/z calculated for C₁₃H₁₀N₂ [M+H]⁺: 233.10732, found: 233.10750.

2-(phenylethynyl)-3-(pyridin-4-yl)imidazo[1,2-α]pyridine (6d)

Eluent: CH₂Cl₂/MeOH 99/1. Off-white solid, yield: 89%. ¹H NMR (CDCl₃) δ: 8.81 (bd, 1H, J = 4.5Hz, Pyridyl-2,6), 8.37 (d, 1H, J = 7.2Hz, H-5), 7.76 (d, 1H, J = 5.7Hz, Pyridyl-3,5), 7.67 (d, 1H, J = 9.0Hz, H-8), 7.54-7.48 (m, 2H, Ph-2,6), 7.37-7.30 (m, 4H, Ph-3,4,5, H-7), 6.93 (td, 1H, J = 6.9Hz, 0.9Hz, H-6). ¹³C NMR (CDCl₃) δ: 150.1 (Pyridyl-2,6), 146.2 (C-8a), 136.9 (Pyridyl-1), 131.9 (Ph-2,6), 129.0 (Ph-4), 128.9 (C-2), 128.6 (Ph-3,5), 126.8 (C-7), 124.6 (Ph-1), 123.4 (C-5), 122.4 (Pyridyl-3,5), 118.5 (C-8), 114.2 (C-6), 93.4 (C=C-Ph), 82.7 (C=C-Ph), (C-3 is missing). m.p.: 87-91°C. HRMS (ESI): m/z calculated for C₂₀H₁₃N₃ [M+H]⁺: 296.11822, found: 296.11851.
2,3-diiodoimidazo[1,2-a]pyridine (1a) 

\( ^1\text{H} \) NMR (CDCl\(_3\))

\( ^{13}\text{C} \) NMR (CDCl\(_3\))
3-bromo-2-iodimidazo[1,2-a]pyridine (1b) ¹H NMR (CDCl₃)
3-bromo-2-iodoimidazo[1,2-a]pyridine (1b)

13C NMR (CDCl₃)
2-iodo-3-phenylimidazo[1,2-\alpha]pyridine (2a) $^1$H NMR (CDCl$_3$)
2-ido-3-phenylimidazo[1,2-a]pyridine (2a) $^{13}$C NMR (CDCl$_3$)
3-bromo-2-phenylimidazo[1,2-a]pyridine (2b) H NMR (CDCl₃)
3-bromo-2-phenylimidazo[1,2-a]pyridine (2b) $^{13}$C NMR (CDCl$_3$)
3-bromo-2-(thiophen-3-yl)imidazo[1,2-a]pyridine (2c) H NMR (CDCl₃)
3-bromo-2-(thiophen-3-yl)imidazo[1,2-a]pyridine (2c)

$^{13}$C NMR (CDCl$_3$)
3-bromo-2-methylimidazo[1,2-a]pyridine (2d)

$^1$H NMR (CDCl$_3$)
3-bromo-2-methylimidazo[1,2-a]pyridine (2d) $^{13}$C NMR (CDCl$_3$)
2-phenyl-3-(p-tolyl)imidazo[1,2-a]pyridine (3a)

$^1$H NMR (CDCl$_3$)
2-phenyl-3-(p-tolyl)imidazo[1,2-a]pyridine (3a)

$^{13}$C NMR (CDCl$_3$)
3-(4-methoxyphenyl)-2-phenylimidazo[1,2-a]pyridine (3b): H NMR (CDCl₃)
3-(4-methoxyphenyl)-2-phenylimidazo[1,2-a]pyridine (3b) $^{13}$C NMR (CDCl$_3$)
3-(furan-2-yl)-2-phenylimidazo[1,2-a]pyridine (3c)

H NMR (CDCl$_3$)
3-(furan-2-yl)-2-phenylimidazo[1,2-a]pyridine (3c) $^{13}$C NMR (CDCl$_3$)
3-methyl-2-phenylimidazo[1,2-a]pyridine (3d) H NMR (CDCl₃)
3-methyl-2-phenylimidazo[1,2-a]pyridine (3d) ¹³C NMR (CDCl₃)
3-phenyl-2-(thiophen-3-yl)imidazo[1,2-a]pyridine (3e) $^1$H NMR (CDCl$_3$)
3-phenyl-2-(thiophen-3-yl)imidazo[1,2-a]pyridine (3e) $^{13}$C NMR (CDCl$_3$)
2-phenyl-3-(pyridin-4-yl)-imidazo[1,2-a]pyridine (3f) H NMR (CDCl$_3$)
2-phenyl-3-(pyridin-4-yl)imidazo[1,2-a]pyridine (3f) 13C NMR (CDCl₃)
3-bromo-2-(phenylethynyl)imidazo[1,2-a]pyridine (4a)

$^1$H NMR (CDCl$_3$)
3-bromo-2-(phenylethynyl)imidazo[1,2-a]pyridine (4a) 

$\text{C NMR (CDCl}_3$)
3-bromo-2-(cyclopropylethynyl)imidazo[1,2-a]pyridine (4b) $^1$H NMR (CDCl$_3$)
3-bromo-2-(cyclopropylethynyl)imidazo[1,2-a]pyridine (4b) $^{13}$C NMR (CDCl$_3$)
2-(phenylethynyl)-3-(p-tolylethynyl)imidazo[1,2-a]pyridine (5a)

$^1$H NMR (CDCl$_3$)
2-(phenylethynyl)-3-(p-tolylethynyl)imidazo[1,2-a]pyridine (5a) - 1H-NMR (CDCl₃)
3-(cyclopropylethynyl)-2-(phenylethynyl)imidazo[1,2-a]pyridine (5b) \[^1H\] NMR (CDCl\(_3\))
3-(cyclopropylethynyl)-2-(phenylethynyl)imidazo[1,2-a]pyridine (5b) $^{13}$C NMR (CDCl$_3$)
3-(3-methoxyprop-1-yn-1-yl)-2-(phenylethynyl)imidazo[1,2-a]pyridine (5c) 

$^1$H NMR (CDCl$_3$)
3-(3-methoxyprop-1-yn-1-yl)-2-(phenylethynyl)imidazo[1,2-a]pyridine (5c) $^{13}$C NMR (CDCl$_3$)
2-(cyclopropylethynyl)-3-(phenylethynyl)imidazo[1,2-\(\alpha\)]pyridine (5d) \(^1\)H NMR (CDCl\(_3\))
2-(cyclopropylethynyl)-3-(phenylethynyl)imidazo[1,2-a]pyridine (5d) $^{13}$C NMR (CDCl$_3$)
3-(4-methoxyphenyl)ethynyl)-2-(phenylethynyl)imidazo[1,2-a]pyridine (5e)

$^1$H NMR (CDCl$_3$)
3-((4-methoxyphenyl)ethynyl)-2-(phenylethynyl)imidazo[1,2-a]pyridine (5e) $^{13}$C NMR (CDCl$_3$)
2-phenyl-3-(phenylethynyl)imidazo[1,2-a]pyridine (6a) $^1$H NMR (CDCl$_3$)
2-phenyl-3-(phenylethynyl)imidazo[1,2-a]pyridine (6a)

13C NMR (CDCl₃)
N

2-methyl-3-(phenylethynyl)imidazo[1,2-a]pyridine (6b)

$^1$H NMR (CDCl$_3$)
2-methyl-3-(phenylethynyl)imidazo[1,2-a]pyridine (6b) $^1$C NMR (CDCl$_3$)
3-methyl-2-(phenylethynyl)imidazo[1,2-a]pyridine (6c)

H NMR (CDCl₃)
3-methyl-2-(phenylethynyl)imidazo[1,2-a]pyridine (6c) 13C NMR (CDCl3)
2-(phenylethynyl)-3-(pyridin-4-yl)imidazo[1,2-a]pyridine (6d) $^1$H NMR (CDCl$_3$)
2-(phenylethynyl)-3-(pyridin-4-yl)imidazo[1,2-a]pyridine (6d)

$^{13}$C NMR (CDCl$_3$)