Supporting Information

Nickel-catalyzed direct cross-coupling of heterocyclic

phosphonium salt with aryl bromide

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General Information

Commercially available aryl halides were used without further purification. Starting materials **1a-l** were prepared according to reported methods.^[1-5] Analytical thin layer chromatography (TLC) was performed using silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm). Flash chromatography was performed using Merck silica gel (200-300 mesh) for column chromatography with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ¹H, ¹⁹F, and ¹³C NMR spectra were recorded in CDCl₃ on Jeol 400 MHz spectrometers. Tetramethylsilane (TMS) served as internal standard for ¹H and ¹³C NMR analysis.

Optimization of Reaction Conditions

PPh ₃ N 1a	Br Ni(PPh ₃) ₂ Cl ₂ (5 mol%) <u>Mg (3 equiv.)</u> LiCl (4 equiv.) N ₂ , solvent, r.t., 12 h 2a	N 3a
Entry	Solvent	Yield ^b
1	THF	50%
2	DME	38%
3	1,4-dioxane	<5%
4	2-MeTHF	<5%
5	СрОМе	<5%
6	^t BuOMe	<5%
7	THP	<5%
8	DMF	<5%

Table S1. Optimization of reaction conditions by using different solvents^{*a*}

^{*a*} Unless otherwise noted, the reactions were performed at room temperature for 12 h under nitrogen atmosphere by using **1a** (0.5 mmol), **2a** (1.5 mmol), Ni(PPh₃)₂Cl₂ (5 mol%, 0.025 mmol), magnesium turnings (1.5 mmol), and LiCl (2 mmol) in solvent (2 mL). ^{*b*} Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard.

	⊕ PPh ₃ OTf	+ Br	Ni(PPh ₃) ₂ Cl ₂ (x mol%) <u>Mg (3 equiv.)</u> LiCl (4 equiv.) N ₂ , THF, temp., 12 h			
	1a	2a		3a		
Entry	Ni(PPł (x me	n ₃) ₂ Cl ₂ pl%)	Temp.		Yield ^b	
1	5		0 °C		16%	
2	5	i	r.t.		50%	
3	5		60 °C		48%	
4	1	0	r.t.		55%	
5	2	0	r.t.		63%	
6	2	0	r.t.		55% ^c	

Table S2. Optimization of reaction conditions by using different catalyst loadings at different temperatures^a

^{*a*} Unless otherwise noted, the reactions were performed at different temperatures for 12 h under nitrogen atmosphere by using **1a** (0.5 mmol), **2a** (1.5 mmol), Ni(PPh₃)₂Cl₂ (x mol%), magnesium turnings (1.5 mmol), and LiCl (2 mmol) in THF (2 mL). ^{*b*} Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard. ^{*c*} Using 2 equiv. of LiCl.

Table S3. Optimization of reaction conditions by using different ligands^{*a,b*}



^{*a*} Unless otherwise noted, the reactions were performed at room temperature for 12 h under nitrogen atmosphere by using **1a** (0.5 mmol), **2a** (1.5 mmol), Ni(PPh₃)₂Cl₂ (20 mol%, 0.1 mmol), ligand (20 mol%, 0.1 mmol), magnesium turnings (1.5 mmol), and LiCl (2 mmol) in THF (2 mL). ^{*b*} Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard.

Table S4. Optimization of reaction conditions by using NiCl₂·glyme and different ligands^{*a,b*}



^{*a*} Unless otherwise noted, the reactions were performed at room temperature for 12 h under nitrogen atmosphere by using **1a** (0.5 mmol), **2a** (1.5 mmol), NiCl₂·glyme (20 mol%, 0.1 mmol), ligand (20 mol%, 0.1 mmol), magnesium turnings (1.5 mmol), and LiCl (2 mmol) in THF (2 mL). ^{*b*} Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard.

Experimental Procedure

Typical procedures for the cross-coupling reaction of phosphonium salts with aryl bromides (Tables 2-3)



To an oven-dried seal tube equipped with a magnetic stir bar was added magnesium turnings (36.5 mg, 1.5 mmol) and LiCl (84.7 mg, 2 mmol). Then the mixture was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling to room temperature, dry THF (2 mL) was added and the seal tube was backfilled with nitrogen (x 3). Then phosphonium salt (1, 0.5 mmol), Ni(PPh₃)₂Cl₂ (65.4 mg, 0.1 mmol), and 1,10-phenanthroline-5,6-dione (L10, 21.0 mg, 0.1 mmol) were weighed into the seal tube, followed by the addition of aryl bromide (2, 1.5 mmol) by syringe. The reaction mixture was stirred at room temperature for 12 h followed by quenching with saturated NH₄Cl solution (10 mL) and extracting with EtOAc (20 mL x 3). The combined

organic layers were washed with brine, dried over Na_2SO_4 , and concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3-4** as a white solid.

Control Experiments

3 mmol scale reaction

To an oven-dried seal tube equipped with a magnetic stir bar was added magnesium turnings (0.219 g, 9 mmol) and LiCl (0.508 g, 12 mmol). Then the mixture was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling to room temperature, dry THF (12 mL) was added and the seal tube was backfilled with nitrogen (x 3). Then phosphonium salt (1a, 1.468 g, 3 mmol), Ni(PPh₃)₂Cl₂ (0.392 g, 0.6 mmol), and 1,10-phenanthroline-5,6-dione (L10, 0.126 g, 0.6 mmol) were weighed into the seal tube, followed by the addition of bromobenzene (2a, 1.413 g, 9 mmol) by syringe. The reaction mixture was stirred at room temperature for 12 h followed by quenching with saturated NH₄Cl solution (30 mL) and extracting with EtOAc (70 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3a** as a white solid (0.297 g, 64%).

Direct cross-coupling of phosphonium salt 1a with phenylmagnesium bromide 5

To an oven-dried seal tube equipped with a magnetic stir bar was added LiCl (84.7 mg, 2 mmol), then it was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling to room temperature, the seal tube was backfilled with nitrogen (x 3). Then phosphonium salt (1a, 244.7 mg, 0.5 mmol), Ni(PPh₃)₂Cl₂ (65.4 mg, 0.1 mmol), and 1,10-phenanthroline-5,6-dione (L10, 21.0 mg, 0.1 mmol) were weighed into the seal tube, followed by the addition of Grignard Reagent (5, 1.5 mL, 1.5 mmol, 1 M in THF) by syringe. The reaction mixture was stirred at room temperature for 12 h followed by quenching with saturated NH₄Cl solution (10 mL) and extracting with EtOAc (20 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure to afford the crude product, which was further purified

through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3a** as a white solid (0.0321 g, 41% yield).

Treatment of phosphonium salt 1a with magnesium followed by quenching with iodine

To an oven-dried seal tube equipped with a magnetic stir bar was added magnesium turnings (36.5 mg, 1.5 mmol) and LiCl (84.7 mg, 2 mmol). Then the mixture was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling to room temperature, dry THF (2 mL) was added and the seal tube was backfilled with nitrogen (x 3). Then phosphonium salt (**1a**, 244.7 mg, 0.5 mmol), Ni(PPh₃)₂Cl₂ (65.4 mg, 0.1 mmol), and 1,10-phenanthroline-5,6-dione (**L10**, 21.0 mg, 0.1 mmol) were weighed into the seal tube. The reaction mixture was stirred at room temperature for 12 h followed by the addition of I₂ (0.3807 g, 1.5 mmol) and further stirring at room temperature for 2 h before quenching with saturated Na₂S₂O₅ solution (10 mL) and extracting with EtOAc (20 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. TLC analysis against authentic sample showed that no any iodinated product **6** was obtained.

Preparation of arylnickel compound 7 and its cross-coupling with phosphonium salt 1a

The reaction was performed in an argon-filled glove box.⁶ To a flame-dried round-bottomed flask was added bpy (156 mg, 1.0 mmol), Ni(cod)₂ (275 mg, 1.0 mmol) and THF (10 mL). After the reaction mixture was stirred at room temperature for overnight, 1-bromo-2-methylbenzene (205 mg, 1.2 mmol) was added and the color changed from dark purple to red. After stirring at room temperature for 4 h, the mixture solution was concentrated under reduced pressure. The solid was washed with dry *n*-pentane for several times and then dried under vacuum for 2 h to give arylnickel compound 7 as a red solid.

To an oven-dried seal tube equipped with a magnetic stir bar was added magnesium turnings (21.9 mg, 0.9 mmol) and LiCl (50.8 mg, 1.2 mmol). Then the mixture was dried under reduced pressure by a heat gun (320 $^{\circ}$ C) for 3 min. After cooling down to room temperature, dry THF (1.5 mL) was added and the seal tube was backfilled with nitrogen (x 3). Then phosphonium salt (1a, 0.3 mmol)

was added, followed by the addition of arylnickel compound 7 (23.2 mg, 0.6 mmol). The reaction mixture was stirred at room temperature for 12 h before quenching with saturated NH_4Cl solution (10 mL) and extracting with EtOAc (20 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated under reduced pressure. Crude NMR and TLC analysis showed that no desired product **8** was formed.

Characterization data of products

4-Phenylpyridine (3a): 57.4 mg. Yield = 74%. ¹**H NMR (400 MHz, CDCl₃):** δ 8.66 (d, J = 5.6 Hz, 2H), 7.74-7.58 (m, 2H), 7.57-7.41 (m, 5H) ppm. ¹³**C NMR (100 MHz, CDCl₃):** δ 150.1, 148.4, 138.0, 129.1, 129.1, 127.0, 121.6 ppm. **HRMS (ESI, m/z):** [M+H]⁺, calcd. for C₁₁H₁₀N⁺: 156.0808, found: 156.0809. **FTIR (KBr, neat):** v 3058, 2923, 1588, 1483, 1410, 830, 761, 730, 688, 608 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-(4-(Trifluoromethoxy)phenyl)pyridine (3b): 50.2 mg. Yield = 42%. ¹H NMR (400 MHz, CDCl₃): δ 8.67 (dd, J = 4.5, 1.6 Hz, 2H), 7.68-7.62 (m, 2H), 7.47 (dt, J = 4.5, 1.5 Hz, 2H), 7.36-7.29 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.4, 149.9, 146.9, 136.8, 128.5, 121.5, 121.5, 120.4 (q, J = 257.0 Hz) ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ -57.86 (s, 3F) ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₂H₉F₃NO⁺: 240.0631, found: 240.0636. FTIR (KBr, neat): v 3420, 1599, 1489, 1265, 1212, 1167, 807 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-(4-Fluorophenyl)pyridine (3c): 46.6 mg. Yield = 54%. ¹H NMR (400 MHz, CDCl₃): δ 8.64 (dt, J = 4.5, 1.5 Hz, 2H), 7.63-7.56 (m, 2H), 7.46-7.42 (m, 2H), 7.19-7.12 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 163.4 (d, J = 247.3 Hz), 150.2, 147.2, 134.1, 128.7 (d, J = 8.3 Hz), 121.4, 116.1 (d, J = 21.7 Hz) ppm. ¹⁹F

NMR (376 MHz, CDCl₃): δ -112.45 (s, 1F) ppm. **HRMS (ESI, m/z):** [M+H]⁺, calcd. for C₁₁H₉FN⁺: 174.0714, found:174.0719. **FTIR (KBr, neat):** *v* 3039, 1607, 1516, 1488, 1220, 1162, 812, 555 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-(3-Fluoro-4-methoxyphenyl)pyridine (3d): 57.7 mg. Yield = 57%. ¹H NMR (400 MHz, CDCl₃): δ 8.64 (d, J = 6.1 Hz, 2H), 7.50-7.46 (m, 2H), 7.41-7.39 (m, 2H), 7.05 (t, J = 8.7 Hz, 1H), 3.93 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 152.5 (d, J = 245.0 Hz), 149.9, 148.6 (d, J = 10.7 Hz), 147.1 (d, J = 2.3 Hz), 130.4 (d, J = 6.3 Hz), 122.8 (d, J = 3.6 Hz), 121.1, 114.5 (d, J = 19.2 Hz), 113.6 (d, J = 2.5 Hz), 56.2 ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ -134.02 (s, 1F) ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₂H₁₁FNO⁺: 204.0819, found: 204.0825. FTIR (KBr, neat): v 3031, 2948, 2848, 1546, 1528, 1495, 1300, 1276, 1138, 805 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-([1,1'-Biphenyl]-4-yl)pyridine (3e): 72.8 mg. Yield = 63%. ¹H NMR (400 MHz, CDCl₃): δ 8.68 (d, J = 4.5 Hz, 2H), 7.72 (s, 4H), 7.65 (dd, J = 8.3, 1.2 Hz, 2H), 7.56 (d, J = 5.9 Hz, 2H), 7.48 (t, J = 7.7 Hz, 2H), 7.42-7.36 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.2, 147.8, 141.9, 140.2, 136.8, 128.9, 127.8, 127.7, 127.3, 127.0, 121.4 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₇H₁₄N⁺: 232.1121, found: 232.1126. FTIR (KBr, neat): v 3024, 2924, 2853, 1603, 1588, 1481, 1404, 816, 765, 700, 690 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-(4-(*tert***-Butyl)phenyl)pyridine (3f):** 69.7 mg. Yield = 66%. ¹H NMR (400 MHz, CDCl₃): δ 8.66-8.61 (m, 2H), 7.61-7.57 (m, 2H), 7.54-7.48 (m, 4H), 1.37 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 152.3, 150.1, 148.0, 135.1, 126.6, 126.0, 121.4, 34.6, 31.2 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₅H₁₈N⁺: 212.1434, found:

212.1439. FTIR (KBr, neat): v 3037, 2968, 2869, 1594, 1536, 1475, 1397, 1118, 1032, 811 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-(*p***-Tolyl)pyridine (3g):** 43.4 mg. Yield = 51%. ¹H NMR (400 MHz, CDCl₃): δ 8.67-8.60 (m, 2H), 7.54 (d, J = 7.7 Hz, 2H), 7.51-7.46 (m, 2H), 7.29 (d, J = 7.7 Hz, 2H), 2.41 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.1, 148.2, 139.2, 135.1, 129.8, 126.8, 121.3, 21.2 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₂H₁₂N⁺: 170.0964, found: 170.0966. FTIR (KBr, neat): v 3030, 1597, 1541, 1488, 1404, 1235, 1213, 1029, 801, 710 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-(3,5-Dimethylphenyl)pyridine (3h): 48.4 mg. Yield = 53%. ¹H NMR (400 MHz, **CDCl₃):** δ 8.63 (dd, J = 4.7, 1.4 Hz, 2H), 7.50-7.45 (m, 2H), 7.24 (s, 2H), 7.08 (s, 1H), 2.39 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.0, 148.5, 138.6, 138.0, 130.6, 124.8, 121.6, 21.3 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₃H₁₄N⁺: 184.1121, found: 184.1122. FTIR (KBr, neat): v 3025, 2914, 1617, 1595, 1548, 1402, 1221, 1028, 822, 697, 646 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-(4-Methoxy-3-methylphenyl)pyridine (3i): 44.0 mg. Yield = 44%. ¹H NMR (400 MHz, CDCl₃): δ 8.61-8.58 (m, 2H), 7.48-7.44 (m, 4H), 6.91 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 2.29 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 158.7, 150.0, 148.0, 129.8, 129.1, 127.4, 125.4, 121.0, 110.2, 55.4, 16.4 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₃H₁₄NO⁺: 200.1070, found: 200.1071. FTIR (KBr, neat): *v* 2966, 2840, 1596, 1488, 1293, 1255, 1226, 1143, 1021, 806 cm⁻¹. The residue obtained was purified by

silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

MeO

4-(4-Methoxyphenyl)pyridine (3j): 47.7 mg. Yield = 52%. ¹H NMR (400 MHz, CDCl₃): δ 8.60 (d, J = 5.2 Hz, 2H), 7.62-7.54 (m, 2H), 7.49-7.42 (m, 2H), 7.03-6.95 (m, 2H), 3.85 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 160.5, 150.1, 147.7, 130.3, 128.1, 121.0, 114.5, 55.4 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₂H₁₂NO⁺: 186.0913, found: 186.0916. FTIR (KBr, neat): v 2967, 2938, 2842, 1607, 1488, 1287, 1257, 1228, 1035, 809 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-(3-Methoxyphenyl)pyridine (3k): 54.8 mg. Yield = 59%. ¹H NMR (400 MHz, **CDCl₃):** δ 8.67-8.62 (m, 2H), 7.50-7.47 (m, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.21 (ddd, *J* = 7.7, 1.6, 0.9 Hz, 1H), 7.17-7.13 (m, 1H), 6.97 (ddd, *J* = 8.3, 2.6, 0.8 Hz, 1H), 3.87 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 160.1, 150.1, 148.2, 139.5, 130.1, 121.7, 119.3, 114.3, 112.7, 55.3 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₂H₁₂NO⁺: 186.0913, found: 186.0917. FTIR (KBr, neat): *v* 2959, 2935, 2837, 1596, 1583, 1546, 1477, 1302, 1216, 1032, 796 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-(2-Methoxyphenyl)pyridine (3l): 57.0 mg. Yield = 61%. ¹H NMR (400 MHz, **CDCl₃):** δ 8.63-8.60 (m, 2H), 7.48-7.45 (m, 2H), 7.39 (ddd, J = 8.3, 7.5, 1.8 Hz, 1H), 7.33 (dd, J = 7.6, 1.7 Hz, 1H), 7.05 (td, J = 7.5, 1.0 Hz, 1H), 7.00 (d, J = 8.3 Hz, 1H), 3.83 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 156.4, 149.4, 146.2, 130.4, 130.1, 127.5, 124.2, 121.0, 111.3, 55.4 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₂H₁₂NO⁺: 186.0913, found: 186.0917. FTIR (KBr, neat): v 3015, 2965, 2836, 1590, 1483, 1270, 1233, 1024, 760, 609 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-(2,5-Dimethoxyphenyl)pyridine (3m): 53.8 mg. Yield = 50%. ¹H NMR (400 MHz, CDCl₃): δ 8.62 (d, J = 4.0 Hz, 2H), 7.50-7.42 (m, 2H), 6.93-6.89 (m, 3H), 3.80 (s, 3H), 3.76 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 153.8, 150.7, 149.4, 146.1, 128.4, 124.2, 116.2, 114.5, 112.7, 56.1, 55.8 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₃H₁₄NO₂⁺: 216.1019, found: 216.1023. FTIR (KBr, neat): v 3010, 2948, 2831, 1596, 1488, 1405, 1232, 1022, 827, 711 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-(Benzo[*d*][1,3]dioxol-5-yl)pyridine (3n): 49.7 mg. Yield = 50%. ¹H NMR (400 MHz, CDCl₃): δ 8.60 (d, *J* = 4.9 Hz, 2H), 7.41 (dt, *J* = 4.5, 1.2 Hz, 2H), 7.15-7.12 (m, 1H), 7.12-7.09 (m, 1H), 6.93-6.89 (m, 1H), 6.02 (d, *J* = 1.1 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.1, 148.5, 148.5, 147.9, 132.2, 121.2, 120.9, 108.8, 107.2, 101.4 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₂H₁₀NO₂⁺: 200.0706, found: 200.0709. FTIR (KBr, neat): *v* 3034, 2891, 1599, 1514, 1418, 1415, 1239, 1015, 924, 802 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

N,N-Diphenyl-4-(pyridin-4-yl)aniline (30): 99.2 mg. Yield = 62%. ¹H NMR (400 MHz, CDCl₃): δ 8.76-8.59 (m, 2H), 7.56-7.48 (m, 4H), 7.32-7.28 (m, 4H), 7.18-7.12 (m, 6H), 7.11-7.06 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): 149.7, 149.2, 148.5, 147.0, 130.1, 129.4, 127.7, 125.0, 123.7, 122.5, 121.1 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₂₃H₁₉N₂⁺: 323.1543, found: 323.1548. FTIR (KBr, neat): *v* 3033, 2923, 2853, 1590, 1485, 1331, 1279, 809, 753, 696 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

N,N-Dimethyl-3-(pyridin-4-yl)aniline (3p): 57.3 mg. Yield = 58%. ¹H NMR (400 MHz, CDCl₃): δ 8.65 (d, J = 5.2 Hz, 2H), 7.52 (d, J = 5.2 Hz, 2H), 7.34 (t, J = 7.9 Hz, 1H), 7.00-6.94 (m, 1H), 6.94-6.90 (m, 1H), 6.84-6.79 (m, 1H), 3.01 (s, 3H), 3.01 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.9, 149.9, 149.6, 138.9, 129.7, 121.9, 115.1, 113.1, 110.7, 40.5 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₃H₁₅N₂⁺: 199.1230, found: 199.1235. FTIR (KBr, neat): v 3024, 2892, 2809, 1594, 1546, 1400, 1235, 989, 776, 698 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

2-(4-(Pyridin-4-yl)phenyl)pyridine (3q): 81.5 mg. Yield = 70%. ¹H NMR (400 MHz, CDCl₃): δ 8.65 (d, J = 4.8 Hz, 1H), 8.63-8.58 (m, 2H), 8.11-7.99 (m, 2H), 7.77-7.63 (m, 4H), 7.54-7.43 (m, 2H), 7.20 (q, J = 4.3 Hz, 1H) ppm.¹³C NMR (100 MHz, CDCl₃): δ 156.4, 150.3, 149.8, 147.7, 140.0, 138.4, 136.8, 127.6, 127.3, 122.5, 121.5, 120.6 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₆H₁₃N₂⁺: 233.1073, found: 233.1078. FTIR (KBr, neat): v 3036, 1591, 1563, 1540, 1464, 1434, 1405, 819, 719, 713 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-(Thiophen-2-yl)pyridine (3r): 51.0 mg. Yield = 64%. ¹H NMR (400 MHz, **CDCl₃):** δ 8.57 (d, J = 5.0 Hz, 2H), 7.53-7.42 (m, 3H), 7.42-7.36 (m, 1H), 7.11 (ddd, J = 5.0, 3.7, 0.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.3, 141.3, 141.0, 128.4, 127.1, 125.3, 119.8 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₉H₈NS⁺: 162.0372, found: 162.0373. FTIR (KBr, neat): v 3050, 1597, 1546, 1422, 1221, 990, 812, 729, 710, 695 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-(Benzo[b]thiophen-4-yl)pyridine (3s): 55.6 mg. Yield = 53%. ¹H NMR (400 MHz, CDCl₃): δ 8.83 (d, J = 6.1 Hz, 2H), 8.00 (dt, J = 7.9, 1.0 Hz, 1H), 7.80-7.76 (m, 2H), 7.59 (d, J = 5.8 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.43 (dd, J = 4.9, 1.0 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 149.8, 148.7, 140.7, 137.2, 134.7, 129.1, 127.4, 126.9, 124.6, 124.3, 123.8, 122.9, 122.3 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₃H₁₀NS⁺: 212.0528, found: 212.0534. FTIR (KBr, neat): v 3446, 1597, 1541, 1400, 1204, 824, 786, 760, 699, 647 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

1-Methyl-4-(pyridin-4-yl)-1*H***-indole (3t):** 35.1 mg. Yield = 36%. ¹H NMR (400 MHz, CDCl₃): 8.65-8.59 (m, 2H), 7.94 (d, J = 1.4 Hz, 1H), 7.65-7.60 (m, 2H), 7.53 (dd, J = 8.6, 1.8 Hz, 1H), 7.42 (d, J = 8.6 Hz, 1H), 7.13 (d, J = 3.1 Hz, 1H), 6.58 (dd, J = 3.1, 0.8 Hz, 1H), 3.84 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.5, 149.0, 137.2, 130.1, 129.0, 128.9, 121.8, 120.6, 119.8, 109.9, 101.7, 33.0 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₄H₁₃N₂⁺: 209.1073, found: 209.1069. FTIR (KBr, neat): v 3551, 3415, 1636, 1615, 1593, 1250, 1024, 796, 618 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

MeO

4-(6-Methoxynaphthalen-2-yl)pyridine (3u): 75.8 mg. Yield = 64%. ¹H NMR (400 MHz, CDCl₃): δ 8.68 (d, J = 4.9 Hz, 2H), 8.06 (s, 1H), 7.84 (t, J = 9.4 Hz, 2H), 7.72 (dd, J = 8.5, 1.8 Hz, 1H), 7.62 (d, J = 5.9 Hz, 2H), 7.24-7.16 (m, 2H), 3.95 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 158.4, 150.2, 148.3, 134.7, 133.0, 130.0, 128.9, 127.7, 126.2, 125.0, 121.6, 119.6, 105.5, 55.4 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₆H₁₄NO⁺: 236.1070, found: 236.1073. FTIR (KBr, neat): v 2924, 2853, 1625, 1590, 1495, 1257, 1208, 1023, 834, 801 cm⁻¹. The residue obtained was

purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

3-Methoxy-4-phenylpyridine (4b): 62.5 mg. Yield = 67%. ¹H NMR (400 MHz, CDCl₃): δ 8.37 (s, 1H), 8.31 (d, J = 4.8 Hz, 1H), 7.57 (dd, J = 8.2, 1.3 Hz, 2H), 7.48-7.36 (m, 3H), 7.25 (d, J = 4.8 Hz, 1H), 3.90 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 152.5, 142.9, 137.5, 135.6, 134.3, 129.1, 128.2, 128.2, 124.4, 56.2 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₂H₁₂NO⁺: 186.0913, found: 186.0916. FTIR (KBr, neat): v 3058, 2925, 2841, 1505, 1479, 1410, 1280, 1015, 747, 698 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 20:1).

3-Methyl-4-phenylpyridine (4c): 32.6 mg. Yield = 39%. ¹H NMR (400 MHz, CDCl₃): δ 8.55 (s, 1H), 8.51 (d, J = 5.1 Hz, 1H), 7.48-7.39 (m, 3H), 7.35-7.29 (m, 2H), 7.21 (d, J = 5.1 Hz, 1H), 2.29 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.9, 149.7, 147.1, 138.8, 130.0, 128.5, 128.4, 128.1, 124.2, 17.2 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₂H₁₂N⁺: 170.0964, found: 170.0968. FTIR (KBr, neat): v 3398, 3028, 2925, 1591, 1478, 1443, 1404, 743, 770, 702 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

2,4-Diphenylpyridine (4d): 82.0 mg. Yield = 71%. ¹H NMR (400 MHz, CDCl₃): δ 8.80-8.72 (m, 1H), 8.13-8.04 (m, 2H), 7.98-7.91 (m, 1H), 7.74-7.66 (m, 2H), 7.57-7.41 (m, 7H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 158.0, 150.0, 149.2, 139.4, 138.4, 129.0, 129.0, 128.7, 127.0, 127.0, 120.2, 118.7 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₇H₁₄N⁺: 232.1121, found: 232.1126. FTIR (KBr, neat): *v* 3056,

1593, 1578, 1541, 1470, 1443, 1387, 762, 733, 694 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

3,4-Diphenylpyridine (4e): 95.6 mg. Yield = 83%. ¹H NMR (400 MHz, CDCl₃): δ 8.65-8.63 (m, 1H), 8.61 (d, J = 5.1 Hz, 1H), 7.32 (dd, J = 5.1, 0.6 Hz, 1H), 7.27-7.21 (m, 6H), 7.17-7.11 (m, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.9, 148.6, 147.6, 138.5, 137.6, 135.6, 129.7, 129.2, 128.1, 127.7, 127.2, 124.5 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₇H₁₄N⁺: 232.1121, found: 232.1126. FTIR (KBr, neat): v 3056, 3021, 1584, 1472, 1443, 1399, 832, 762, 749, 700 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-Phenyl-2-(*p*-tolyl)pyridine (4f): 77.8 mg. Yield = 63%. ¹H NMR (400 MHz, CDCl₃): δ 8.73 (d, J = 5.2 Hz, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.93-7.90 (m, 1H), 7.72-7.67 (m, 2H), 7.54-7.40 (m, 4H), 7.32 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 158.0, 149.9, 149.1, 139.0, 138.6, 136.6, 129.4, 129.4, 129.0, 127.0, 126.8, 119.9, 118.4, 21.2 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₈H₁₆N⁺: 246.1277, found: 246.1283. FTIR (KBr, neat): v 3028, 2920, 1594, 1541, 1468, 1384, 1183, 820, 760, 695 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-Phenyl-5,6,7,8-tetrahydroquinoline (4g): 84.3 mg. Yield = 81%. ¹H NMR (400 MHz, CDCl₃): δ 8.39 (d, *J* = 4.9 Hz, 1H), 7.47-7.34 (m, 3H), 7.28 (dt, *J* = 6.9, 1.2 Hz,

2H), 6.96 (d, J = 4.9 Hz, 1H), 3.01 (t, J = 6.5 Hz, 2H), 2.63 (t, J = 6.3 Hz, 2H), 1.94-1.87 (m, 2H), 1.75-1.69 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 157.5, 149.5, 146.4, 139.3, 129.8, 128.4, 128.2, 127.7, 121.9, 32.9, 27.3, 22.9, 22.9 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₅H₁₆N⁺: 210.1277, found: 210.1283. FTIR (KBr, neat): v 3054, 2929, 2854, 1579, 1546, 1437, 1402, 865, 764, 702 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

4-Methyl-2-phenylquinoline (4h): 92.7 mg. Yield = 84%. ¹H NMR (400 MHz, CDCl₃): δ 8.25-8.21 (m, 1H), 8.20-8.16 (m, 2H), 7.97 (dd, J = 8.3, 1.1 Hz, 1H), 7.73 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.71-7.69 (m, 1H), 7.57-7.52 (m, 3H), 7.50-7.45 (m, 1H), 2.73 (d, J = 0.8 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 156.9, 148.0, 144.7, 139.7, 130.2, 129.2, 129.1, 128.7, 127.4, 127.1, 125.9, 123.5, 119.6, 18.9 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₆H₁₄N⁺: 220.1121, found: 220.1126. FTIR (KBr, neat): v 3059, 2920, 1597, 1550, 1495, 1450, 1348, 769, 755, 693 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 20:1).

4-Phenylquinoline (4i): 58.6 mg. Yield = 57%. ¹**H NMR (400 MHz, CDCl₃):** δ 8.94 (d, J = 4.4 Hz, 1H), 8.21-8.17 (m, 1H), 7.92 (dd, J = 8.5, 1.2 Hz, 1H), 7.72 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.57-7.45 (m, 6H), 7.32 (d, J = 4.4 Hz, 1H) ppm. ¹³**C NMR (100 MHz, CDCl₃):** δ 149.9, 148.6, 148.4, 137.9, 129.8, 129.5, 129.2, 128.5, 128.3, 126.7, 126.5, 125.8, 121.3 ppm. **HRMS (ESI, m/z):** [M+H]⁺, calcd. for C₁₅H₁₂N⁺: 206.0964, found: 206.0964. **FTIR (KBr, neat):** v 3058, 2923, 1583, 1574, 1507, 1490, 1444, 1390, 769, 695 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

2-Phenylpyrazine (4j): 33.2 mg. Yield = 43%. ¹H NMR (400 MHz, CDCl₃): δ 9.03 (d, J = 1.4 Hz, 1H), 8.67-8.58 (m, 1H), 8.50 (d, J = 2.5 Hz, 1H), 8.06-7.97 (m, 2H), 7.56-7.42 (m, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 152.8, 144.1, 142.9, 142.2, 136.3, 129.9, 129.0, 126.9 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₀H₉N₂⁺: 157.0760, found: 157.0766. FTIR (KBr, neat): v 3050, 1474, 1447, 1405, 1148, 1082, 1019, 772, 744, 692 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 5:1).

2,3-Dimethyl-5-phenylpyrazine (4k): 73.2 mg. Yield = 79%. ¹H NMR (400 MHz, CDCl₃): δ 8.69 (s, 1H), 7.97 (d, J = 7.5 Hz, 2H), 7.51-7.37 (m, 3H), 2.59 (s, 3H), 2.55 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 151.6, 150.4, 149.3, 138.1, 136.7, 129.1, 128.8, 126.5, 22.2, 21.7 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₂H₁₃N₂⁺: 185.1073, found:185.1079. FTIR (KBr, neat): v 3050, 2982, 1462, 1446, 1386, 1178, 1167, 776, 743, 689 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 10:1).

2-Phenylquinoxaline (4I): 48.0 mg. Yield = 47%. ¹H NMR (400 MHz, CDCl₃): δ 9.33 (s, 1H), 8.23-8.09 (m, 4H), 7.82-7.71 (m, 2H), 7.61-7.48 (m, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 151.8, 143.3, 142.3, 141.5, 136.7, 130.3, 130.2, 129.6, 129.5, 129.1, 129.1, 127.5 ppm. HRMS (ESI, m/z): [M+H]⁺, calcd. for C₁₄H₁₁N₂⁺: 207.0917, found: 207.0922. FTIR (KBr, neat): v 3059, 2923, 2853, 1548, 1488, 1316, 957, 772, 761, 689 cm⁻¹. The residue obtained was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent (petroleum ether/EtOAc = 10:1).

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¹H, ¹⁹F, and ¹³C NMR spectra of products

¹³C NMR spectrum of 3a (100 MHz, CDCl₃)

¹³C NMR spectrum of 3b (100 MHz, CDCl₃)

¹³C NMR spectrum of 3c (100 MHz, CDCl₃)

S26

S36

S39

S40

¹H NMR spectrum of 4b (400 MHz, CDCl₃)

¹³C NMR spectrum of 4d (100 MHz, CDCl₃)

¹H NMR spectrum of 4f (400 MHz, CDCl₃)

¹³C NMR spectrum of 4h (100 MHz, CDCl₃)

¹³C NMR spectrum of 4i (100 MHz, CDCl₃)

¹H NMR spectrum of 4j (400 MHz, CDCl₃)

S52

¹³C NMR spectrum of 4l (100 MHz, CDCl₃)

