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Supporting Information

Electrochemically Driven Reductive Cyclization of *o*-Nitroanilines: Synthesis of 1,2-Fused Benzimidazole and Benzo[*d*]imidazole

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Table of Contents

1. General information	3
2. Cyclic voltammetry	4
3. Experimental procedures	6
4. Characterization data	9
5. ¹ H and ¹³ C NMR spectra	18

General information

¹H NMR spectra were recorded with a JEOL, Model JNM-ECZ-500R/S1, spectrometer (Solution-state NMR; 500 MHz) in CDCl₃ by using tetramethylsilane ($\delta = 0$ ppm) as an internal standard and dimethylsulfoxide-d₆ as solvents. ¹³C NMR spectra were recorded with a JEOL, Model JNM-ECZ- 500R/S1, spectrometer (Solution-state NMR; 126 MHz). High-resolution mass spectra (HRMS) were recorded with a Bruker micro TOF spectrometer in the ESI mode. Melting points were recorded with a Sanyo Gallenkamp apparatus. Reactions were monitored by thin-layer chromatography and visualized by UV. The structures of known compounds were corroborated by comparing their ¹H NMR and ¹³C NMR data with those in the literatures. All reagents and solvents were obtained from commercial sources and were used without further purification. Column chromatography was performed by using Merck silica gel 60 (Art 7734).

Cyclic voltammetry (CV) experiments were performed on PalmSens4 potentiostat (PalmSens BV), using a glassy carbon disc as working electrode, a Pt wire as counter electrode and Ag/AgCl as a pseudo-reference electrode. Cyclic voltammograms were recorded at 0.1 V s⁻¹ scan rate. Electrolysis reaction was conducted using a KORAD, KA3005D power supply (KORAD TECHNOLOGY CO., LTD). All electrodes for electrolyses, such as Pt plate (5 × 5 × 0.1 mm) and graphite rod (\emptyset 5 mm) were purchased from Minihua Store, China.

Cyclic voltammetry

Cyclic voltammetry experiments were conducted in a 4-neck flask that contained the analytes dissolved in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in acetonitrile. A glassy carbon disc (\emptyset 3 mm), a Pt wire (\emptyset 0.5 mm), and Ag/AgCl electrode were used as a working electrode, a counter electrode, and a pseudo-reference electrode, respectively. The voltage was measured by PalmSens4 potentiostat in the presence of ferrocene as an external standard, at a scan rate of 0.1 V s⁻¹.



Figure 1. Cyclic voltammograms of Blank and 1a

According to Figure 2, the redox potentials for <u>the oxidation</u> of **1a** (E = -1.59, -1.30 V vs. $[Fe(C_5H_5)_2]^{+/0}$) and the redox potentials for <u>the reduction</u> of **1a** (E = -0.80, -1.88, -2.66 V vs. $[Fe(C_5H_5)_2]^{0/+}$) were presented.

General Procedure for the Synthesis of 2.



A mixture of substrate 1 (0.5 mmol), formic acid (1.5 mmol, 3.0 equiv), TBAI (1.5 mmol, 3.0 equiv) in CH₃CN (10 mL) was added to an undivided electrochemical cell. The cell was equipped with a platinum plate anode ($5 \times 5 \times 0.1$ mm) and a platinum plate cathode ($5 \times 5 \times 0.1$ mm). The reaction mixture was stirred and electrolyzed at a constant current of 15 mA at room temperature (25–28 °C). The reaction was monitored by TLC until the substrate was totally consumed. Once the reaction was complete, the solvent was removed under reduced pressure using rotary evaporation. The residue was then treated with 20 mL of water and extracted with ethyl acetate (3×10 mL). The organic layer was combined and dried over anhydrous Na₂SO₄ and concentrated in vacuo. The resulting product was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent.



Figure 2. Electrolysis setup

General Procedure for the Gram-Scale Synthesis of 2.

A mixture of substrate 1 (5.0 mmol), formic acid (15.0 mmol, 3.0 equiv), TBAI (15.0 mmol, 3.0 equiv) in CH₃CN (100 mL) was added to an undivided electrochemical cell. The cell was equipped with a platinum plate anode ($10 \times 10 \times 0.1$ mm) and a platinum plate cathode ($10 \times 10 \times 0.1$ mm). The reaction mixture was stirred and electrolyzed at a constant current of 20 mA

at room temperature for 72 h. Once the reaction was complete, the solvent was removed under reduced pressure using rotary evaporation. The residue was then treated with 50 mL of water and extracted with ethyl acetate (3×20 mL). The organic layer was combined and dried over anhydrous Na₂SO₄ and concentrated in vacuo. The resulting product was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent.



Figure 3. Gram-scale electrolysis setup

General Procedure for the Synthesis of 1a-1n.¹¹



A mixture of 1-fluoro-2-nitrobenzene (1.41 g, 10 mmol) and 1,2,3,4-tetrahydroisoquinoline (11 mmol) in DMSO (40 mL) was treated with K_2CO_3 (2.07 g, 15 mmol) and stirred at 110 °C. The reaction was monitored by TLC until the 1-fluoro-2-nitrobenzene was completely consumed. Once the reaction was complete, the reaction was cooled to room temperature and was quenched with brine (50 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The resulting product was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent.

General Procedure for the Synthesis of 10–1u.



A mixture of *o*-nitroaniline (10 mmol) and benzyl bromide (20 mmol) in DMF (40 mL) was treated with K_2CO_3 (2.07 g, 15 mmol) and stirred at 110 °C. The reaction was monitored by TLC until the *o*-nitroaniline was completely consumed. Once the reaction was complete, the reaction was cooled to room temperature and was quenched with brine (50 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The resulting product was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent.

General Procedure for the Synthesis of 3.¹¹



A mixture of 1-fluoro-2-nitrobenzene (1.41 g, 10 mmol) and 1,2,3,4-tetrahydroisoquinoline (11 mmol) in DMSO (40 mL) was treated with K_2CO_3 (2.07 g, 15 mmol) and stirred at 110 °C. The reaction was monitored by TLC until the 1-fluoro-2-nitrobenzene was completely consumed. Once the reaction was complete, the reaction was cooled to room temperature and was quenched with brine (50 mL), and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layer was dried over Na₂SO₄, and concentrated under reduced pressure. The resulting residue was dissolved in a mixture of EtOH and H₂O (8:2 v/v, 40 mL), then treated with Fe powder (2.79 g, 50 mmol) and NH₄Cl (0.64 g, 12 mmol), and stirred at 90 °C for 4 h. After cooling to room temperature, the reaction mixture was filtered through celite and washed with ethyl acetate. The filtrate was then added with 30 mL of water and extracted with ethyl acetate (3 × 20 mL). The organic layer was combined and dried over anhydrous Na₂SO₄ and concentrated in vacuo. The resulting product was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent.

Characterization data

2-(2-Nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (*1a*).^{*18e*} Orange solid, mp = 81–82 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.81 (dd, *J* = 6.5, 1.3 Hz, 1H), 7.47 (ddd, *J* = 6.9, 5.8, 1.3 Hz, 1H), 7.23–7.16 (m, 4H), 7.12–7.08 (m, 1H), 7.00–6.95 (m, 1H), 4.32 (s, 2H), 3.40 (t, *J* = 4.6 Hz, 2H), 3.01 (t, *J* = 4.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 145.5, 141.5, 134.5, 133.5, 128.7, 126.6, 126.5, 126.3, 126.1, 120.2, 119.7, 52.4, 50.1, 28.8. HRMS (ESI): m/z calcd for C₁₅H₁₄N₂O₂ [M+H]⁺: 255.1134; found: 255.1147.

2-(4-Fluoro-2-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (*1b*). Red solid, mp = 70–72 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.57–7.54 (m, 1H), 7.23 (dd, *J* = 5.1, 1.5 Hz, 2H), 7.20–7.17 (m, 3H), 7.09–7.06 (m, 1H), 4.27 (s, 2H), 3.34 (t, *J* = 4.7 Hz, 2H), 3.00 (t, *J* = 4.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 156.5 (d, *J* = 244.9 Hz), 142.6, 134.4, 133.8, 129.0, 126.8, 126.4, 126.3, 122.4 (d, *J* = 7.6 Hz), 120.9 (d, *J* = 22.2 Hz), 113.2 (d, *J* = 26.8 Hz), 53.4, 50.9, 29.1. HRMS (ESI): m/z calcd for C₁₅H₁₃FN₂O₂ [M+H]⁺: 273.1039; found: 273.1032.

2-(4-Chloro-2-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (*Ic*). Orange solid, mp = 80–82 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 2.0 Hz, 1H), 7.42 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.21– 7.13 (m, 4H), 7.10–7.07 (m, 1H), 4.29 (s, 2H), 3.38 (t, *J* = 4.6 Hz, 2H), 3.00 (t, *J* = 4.6 Hz, 2H).¹³C NMR (126 MHz, CDCl₃) δ 144.1, 143.6, 141.2, 134.3, 133.4, 133.3, 128.7, 126.7, 126.2, 126.1, 124.9, 120.9, 52.4, 50.0, 28.7. HRMS (ESI): m/z calcd for C₁₅H₁₃ClN₂O₂: [M+H]⁺ 289.0744; found: 289.0732.

2-(4-Bromo-2-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (*Id*). Orange solid, mp = 79–80 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 1.9 Hz, 1H), 7.54 (dd, *J* = 7.1, 1.9 Hz, 1H), 7.19 (dt, *J* = 5.9, 2.6 Hz, 3H), 7.11–7.06 (m, 2H), 4.28 (s, 2H), 3.38 (t, *J* = 4.6 Hz, 2H), 3.00 (t, *J* = 4.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 144.4, 141.2, 136.2, 134.3, 133.2, 128.9, 128.6, 126.7, 1262, 121.1, 111.3, 60.3, 52.2, 49.8, 28.6. HRMS (ESI): m/z calcd for C₁₅H₁₃BrN₂O₂ [M+H]⁺: 333.0239; found: 333.0231.

2-(5-Fluoro-2-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (*1e*). Yellow solid, mp = 79–80 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.91 (dd, *J* = 7.3, 4.9 Hz, 1H), 7.20 (dd, *J* = 4.0, 2.1 Hz, 3H), 7.12–7.08 (m, 1H), 6.84 (dd, *J* = 9.0, 2.0 Hz, 1H), 6.62 (ddd, *J* = 7.4, 5.6, 2.1 Hz, 1H), 4.29 (s, 2H), 3.41 (t, *J* = 4.6 Hz, 2H), 3.03 (t, *J* = 4.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 165.6 (d, *J* = 254.7 Hz), 147.9 (d, *J* = 10.9 Hz), 136.9, 134.6, 133.3, 129.6 (d, *J* = 11.6 Hz), 128.8, 127.0, 126.5, 126.4, 106.8 (d, J = 24.1 Hz), 105.7 (d, J = 25.6 Hz), 52.3, 49.9, 28.8. HRMS (ESI): m/z calcd for C₁₅H₁₃FN₂O₂ [M+H]⁺: 273.1039; found: 273.1031.

2-(5-Chloro-2-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (*If*). Orange solid, mp = 70–80 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, *J* = 7.0 Hz, 1H), 7.19 (ddd, *J* = 7.3, 5.2, 2.5 Hz, 3H), 7.16 (d, *J* = 1.6 Hz, 1H), 7.13–7.08 (m, 1H), 6.90 (dd, *J* = 7.0, 1.5 Hz, 1H), 4.30 (s, 2H), 3.40 (t, *J* = 4.6 Hz, 2H), 3.03 (t, *J* = 4.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 146.3, 139.7, 138.8, 134.3, 133.1, 128.6, 128.2, 128.0, 126.8, 126.2, 119.5, 119.1, 52.1, 49.7, 28.6. HRMS (ESI): m/z calcd for C₁₅H₁₃ClN₂O₂ [M+H]⁺: 289.0744; found: 289.0744.

2-(4,5-Difluoro-2-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (*Ig*). Orange solid, mp = 76–78 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.81 (dd, *J* = 7.8, 6.7 Hz, 1H), 7.20 (dd, *J* = 4.7, 2.4 Hz, 3H), 7.11–7.08 (m, 1H), 7.01 (dd, *J* = 9.8, 5.5 Hz, 1H), 4.26 (s, 2H), 3.37 (t, *J* = 4.6 Hz, 2H), 3.03 (t, *J* = 4.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 154.4 (d, *J* = 43.5 Hz), 144.2 (d, *J* = 46.1 Hz), 143.8 (d, *J* = 27.7 Hz), 142.2 (d, *J* = 45.6 Hz), 135.8, 134.1, 134.29, 133.13, 128.88, 127.01, 126.42, 126.35, 116.13 (d, *J* = 20.0 Hz), 108.37 (d, *J* = 20.4 Hz), 52.7, 50.4, 28.6. HRMS (ESI): m/z calcd for C₁₅H₁₂F₂N₂O₂ [M+H]⁺: 291.0945; found: 291.0937.

6,7-Dimethoxy-2-(2-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (*1h*). Orange solid, mp = 144–146 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.83–7.78 (m, 1H), 7.46 (dd, *J* = 9.6, 3.9 Hz, 1H), 7.19 (d, *J* = 6.7 Hz, 1H), 6.96 (t, *J* = 6.1 Hz, 1H), 6.65 (s, 1H), 6.58 (s, 1H), 4.23 (s, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 3.40 (t, *J* = 4.6 Hz, 2H), 2.91 (t, *J* = 4.5 Hz, 2H). ¹³C NMR (400 MHz, CDCl₃) δ 147.7, 147.5, 145.5, 141.5, 133.4, 126.4, 126.3, 125.4, 120.1, 119.8, 111.4, 109.0, 55.9, 55.9, 52.2, 50.0, 28.2. HRMS (ESI): m/z calcd for C₁₇H₁₈N₂O₄ [M+H]⁺: 315.1345; found: 315.1335.

2-(4-Fluoro-2-nitrophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (*1i*). Orange solid, mp = 144-145 °C; NMR (500 MHz, CDCl₃) δ 7.54 (dd, *J* = 6.5, 2.0 Hz, 1H), 7.24–7.17 (m, 2H), 6.64 (s, 1H), 6.56 (s, 1H), 4.18 (s, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.32 (t, *J* = 4.6 Hz, 2H), 2.89 (t, *J* = 4.5 Hz, 2H). NMR (126 MHz, CDCl₃) δ 156.3 (d, *J* = 244.8 Hz), 147.9, 147.6, 142.5 (d, *J* = 2.7 Hz), 142.4 (d, *J* = 8.4 Hz), 126.2, 125.5, 122.4 (d, *J* = 7.7 Hz), 120.9 (d, *J* = 21.9 Hz), 113.1 (d, *J* = 26.9 Hz), 111.6, 109.1, 56.1, 56.0, 53.0, 50.8, 28.4. HRMS (ESI): m/z calcd for C₁₇H₁₇FN₂O₄ [M+H]⁺: 332.1172; found: 332.1116.

2-(4-Chloro-2-nitrophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (*Ij*). Orange solid, mp = 103–104 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 2.1 Hz, 1H), 7.40 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.12 (d, J = 7.1 Hz, 1H), 6.64 (s, 1H), 6.57 (s, 1H), 4.20 (s, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.38 (t, J = 4.6 Hz, 2H), 2.90 (t, J = 4.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 147.8, 147.5, 144.1, 141.1, 133.4, 126.1, 126.1, 125.0, 124.8, 120.9, 111.3, 108.9, 55.9, 55.9, 52.1, 49.95, 28.09. HRMS (ESI): m/z calcd for C₁₇H₁₇ClN₂O₄ [M+H]⁺: 349.0955; found: 349.0947.

2-(4-Bromo-2-nitrophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (*1k*). Orange solid, mp = 98–100 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 1.9 Hz, 1H), 7.53 (dd, *J* = 7.1, 1.9 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.64 (s, 1H), 6.57 (s, 1H), 4.20 (s, 2H), 3.86 (d, *J* = 6.1 Hz, 3H), 3.39 (t, *J* = 4.6 Hz, 3H), 2.90 (t, *J* = 4.5 Hz, 2H).¹³C NMR (126 MHz, CDCl₃) δ 147.8, 147.6, 144.5, 141.2, 136.2, 129.0, 126.1, 125.0, 121.1, 111.40, 108.9, 55.9, 55.9, 52.1, 49.8, 28.0. HRMS (ESI): m/z calcd for C₁₇H₁₇BrN₂O₄ [M+H]⁺: 393.0450; found: 393.0435.

2-(5-Fluoro-2-nitrophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (*II*). Yellow solid, mp = 141–142 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.90 (dd, *J* = 7.2, 4.9 Hz, 1H), 6.82 (dd, *J* = 9.1, 1.9 Hz, 1H), 6.66 (s, 1H), 6.63–6.60 (m, 1H), 6.59 (s, 1H), 4.22 (s, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 3.41 (t, *J* = 4.6 Hz, 2H), 2.93 (t, *J* = 4.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 165.6 (d, *J* = 254.7 Hz), 147.9 (d, *J* = 11.2 Hz), 147.9 (d, *J* = 31.4 Hz), 136.7, 129.6 (d, *J* = 11.5 Hz), 126.3, 125.0, 111.4, 109.1, 106.7 (d, *J* = 23.9 Hz), 105.7 (d, *J* = 25.7 Hz), 56.1, 56.1, 52.0, 49.8, 28.1. HRMS (ESI): m/z calcd for C₁₇H₁₇FN₂O₄ [M+H]⁺: 333.1251; found: 333.1243.

2-(5-Chloro-2-nitrophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (*1m*). Orange solid, mp = 154–155 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, *J* = 7.1 Hz, 1H), 7.13 (d, *J* = 1.5 Hz, 1H), 6.88 (dd, *J* = 7.0, 1.6 Hz, 1H), 6.65 (s, 1H), 6.59 (s, 1H), 4.22 (s, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 3.40 (t, *J* = 4.6 Hz, 2H), 2.93 (t, *J* = 4.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 147.8, 147.6, 146.3, 139.7, 138.7, 128.0, 126.1, 124.8, 119.4, 119.0, 111.3, 108.9, 55.9, 55.9, 51.8, 49.7, 28.0. HRMS (ESI): m/z calcd for C₁₇H₁₇ClN₂O₄ [M+H]⁺: 349.0955; found: 349.0950.

N-Benzyl-4-fluoro-2-nitroaniline (*In*). Orange solid, mp = 102–104 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.33 (s, 1H), 7.91 (dd, *J* = 7.3, 2.4 Hz, 1H), 7.40–7.29 (m, 6H), 7.19 (ddd, *J* = 7.9, 5.8, 2.4 Hz, 1H), 6.79 (dd, *J* = 7.6, 3.6 Hz, 1H), 4.55 (d, *J* = 4.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 152.8 (d, *J* = 238.5 Hz), 142.5, 137.3, 131.2, 129.2, 127.9, 127.1, 125.1 (d, *J* = 23.7 Hz), 115.67 (d, *J* = 7.1 Hz), 112.2 (d, *J* = 26.3 Hz), 47.5. HRMS (ESI): m/z calcd for C₁₃H₁₁FN₂O₂ [M+H]⁺: 247.0883; found: 247.0879.

N-Benzyl-4-chloro-2-nitroaniline (*1o*). Orange solid, mp = 58–60 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.41 (s, 1H), 8.20 (d, *J* = 2.0 Hz, 1H), 7.40 – 7.30 (m, 6H), 6.78 (d, *J* = 7.3 Hz, 1H),

4.55 (d, J = 4.5 Hz, 2H).¹³C NMR (126 MHz, CDCl₃) δ 143.8, 136.8, 136.3, 132.0, 129.0, 127.8, 126.9, 125.9, 120.5, 115.6, 47.1. HRMS (ESI): m/z calcd for C₁₃H₁₁ClN₂O₂ [M+H]⁺: 263.0587; found: 263.0586.

N-Benzyl-5-bromo-2-nitroaniline (*Ip*). Orange solid, mp = 92–94 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.42 (s, 1H), 8.34 (d, J = 1.9 Hz, 1H), 7.47 – 7.28 (m, 6H), 6.72 (d, J = 7.3 Hz, 1H), 4.54 (d, J = 4.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 144.1, 138.8, 136.7, 132.4, 128.9, 128.8, 127.8, 126.9, 115.9, 106.8, 47.1. HRMS (ESI): m/z calcd for C₁₃H₁₁BrN₂O₂ [M+H]⁺: 307.0082; found: 307.0080.

N-Benzyl-4-methyl-2-nitroaniline (*1q*). Orange solid, mp = 68–70 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.34 (s, 1H), 7.39–7.27 (m, 6H), 7.25–7.19 (m, 1H), 6.73 (d, *J* = 7.0 Hz, 1H), 4.54 (d, *J* = 4.5 Hz, 2H), 2.26 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 143.4, 137.7, 137.5, 131.8, 128.8, 128.4, 128.3, 127.5, 126.9, 126.0, 125.2, 114.1, 47.0, 19.9. HRMS (ESI): m/z calcd for C₁₄H₁₄N₂O₂ [M+H]⁺: 243.1134; found: 243.1129.

N-Benzyl-4-methoxy-2-nitroaniline (*Ir*). Red solid, mp = 84-85 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.36 (s, 1H), 7.65 (d, J = 2.4 Hz, 1H), 7.39 – 7.31 (m, 5H), 7.09 (dd, J = 7.4, 2.5 Hz, 1H), 6.78 (d, J = 7.5 Hz, 1H), 4.55 (d, J = 4.6 Hz, 2H), 3.79 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 149.8, 141.1, 137.6, 128.9, 128.6, 128.3, 127.6, 127.2, 126.9, 115.6, 107.1, 55.8, 47.2. HRMS (ESI): m/z calcd for C₁₄H₁₄N₂O₃ [M+H]⁺: 247.0883; found: 247.0848.

N,*N*-Dibenzyl-2-nitroaniline (*Is*).^{18e} Orange oil, ¹H NMR (500 MHz, CDCl₃) δ 7.74 (dd, *J* = 6.5, 1.3 Hz, 1H), 7.37 (ddd, *J* = 6.9, 6.3, 1.3 Hz, 2H), 7.33–7.28 (m, 4H), 7.26–7.22 (m, 5H), 7.09 (dd, *J* = 6.7, 0.7 Hz, 1H), 7.02–6.97 (m, 1H), 4.23 (s, 4H). ¹³C NMR HRMS (ESI): m/z calcd for: C₂₀H₁₈N₂O₂ [M+H]⁺: 319.1447 found: 319.1426.

N,*N*-Dibenzyl-5-fluoro-2-nitroaniline (*It*). Orange solid, mp = 82–84 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.88 (dd, *J* = 7.3, 4.7 Hz, 1H), 7.39 (d, *J* = 5.3 Hz, 1H), 7.34–7.27 (m, 6H), 7.22 (d, *J* = 5.8 Hz, 4H), 6.74 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.69–6.63 (m, 1H), 4.24 (s, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 165.11 (d, *J* = 255.0 Hz), 147.71 (d, *J* = 10.8 Hz), 136.55, 128.75, 128.33, 127.77, 109.16 (d, *J* = 24.9 Hz), 108.05 (d, *J* = 24.1 Hz), 56.56. HRMS(ESI): m/z calcd for C₂₀H₁₈FN₂O₂ [M+H]⁺: 337.1352; found: 337.1350.

N,*N*-Dibenzyl-5-chloro-2-nitroaniline (*1u*). Yellow oil, mp = 82–84 °C; Yellow oil, mp = 82–84 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, *J* = 7.0 Hz, 1H), 7.30 (dd, *J* = 12.2, 6.2 Hz, 6H),

7.20 (d, J = 5.7 Hz, 4H), 7.06 (d, J = 1.6 Hz, 1H), 6.93 (dd, J = 7.0, 1.7 Hz, 1H), 4.21 (s, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 146.0, 141.2, 139.1, 136.3, 128.5, 128.2, 127.6, 127.3, 122.7, 120.9, 56.3. HRMS (ESI): m/z calcd for C₂₀H₁₇ClN₂O₂ [M+H]⁺: 353.1057; found: 353.1055.

2-(3,4-Dihydroisoquinolin-2(1*H*)-yl) aniline (3).^{14b} Pale yellow solid, mp = 101–102 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.22 – 7.16 (m, 3H), 7.11 – 7.07 (m, 2H), 6.98 (t, J = 6.0 Hz, 1H), 6.81 – 6.77 (m, 2H), 4.10 (s, 2H), 3.25 (t, J = 4.6 Hz, 2H), 3.03 (t, J = 4.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 141.7, 139.2, 135.4, 134.3, 128.8, 126.4, 126.2, 125.6, 124.7, 120.1, 118.6, 115.1, 53.7, 49.2, 29.8. HRMS (ESI): m/z calcd for: C₁₅H₁₆N₂ [M+H]⁺: 225.1392 found: 225.1375.

5,6-Dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (*2a*).¹¹ Orange solid, 98.3 mg, 89% yield, mp = 101–102 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.32–8.28 (m,1H), 7.84–7.81 (m, 1H), 7.44– 7.36 (m, 3H), 7.34–7.27 (m, 3H), 4.34 (t, *J* = 5.5 Hz, 2H), 3.30 (t, *J* = 5.5 Hz, 2H). ¹³C NMR (500 MHz, CDCl₃) δ 149.0, 143.8, 134.6, 134.2, 130.1, 128.0, 127.7, 126.6, 125.6, 122.6, 122.4, 119.7, 109.0, 40.4, 28.2. HRMS (ESI): m/z calcd for C₁₅H₁₃N₂ [M+H]⁺: 221.1079; found: 221.1083.

10-Fluoro-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (*2b*).^{17b} White solid, mp = 162– 163 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.26 (dd, *J* = 5.0, 2.2 Hz, 1H), 7.48 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.41 (dd, *J* = 4.9, 2.1 Hz, 2H), 7.34–7.31 (m, 1H), 7.26 (dd, *J* = 7.0, 3.7 Hz, 1H), 7.07– 7.01 (m, 1H), 4.31 (t, *J* = 5.5 Hz, 2H), 3.29 (t, *J* = 5.5 Hz, 2H).¹³C NMR (126 MHz, CDCl₃) δ 159.6 (d, *J* = 237.3 Hz), 150.6, 144.5 (d, *J* = 12.9 Hz), 134.2, 131.4, 130.5, 128.2, 127.9, 126.50, 125.8, 111.0 (d, *J* = 26.2 Hz), 109.3 (d, *J* = 10.3 Hz), 105.6 (d, *J* = 24.0 Hz), 40.7, 28.2. ¹⁹F NMR (376 MHz, CDCl₃) δ –120.6 (td, *J* = 9.5, 4.6 Hz). HRMS (ESI): m/z calcd for C₁₅H₁₂FN₂ [M+H]⁺: 239.0985; found: 239.0964.

10-Chloro-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (2*c*).^{14a} White solid, mp = 166– 168 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.28 – 8.25 (m, 1H), 7.78 (d, *J* = 1.4 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.32 (dd, *J* = 3.7, 3.3 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.26 – 7.23 (m, 1H), 4.32 (t, *J* = 5.5 Hz, 2H), 3.30 (t, *J* = 5.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 150.2, 144.7, 134.1, 133.3, 130.5, 128.1, 127.9, 127.8, 126.2, 125.7, 123.0, 119.4, 109.7, 40.5, 28.1. HRMS (ESI): m/z calcd for C₁₅H₁₂ClN₂ [M+H]⁺: 255.0689; found: 255.0688.

10-Bromo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (*2d*). White solid, mp = 181–182 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.24 (dd, *J* = 4.1, 2.8 Hz, 1H), 7.94–7.92 (m, 1H), 7.43–

7.39 (m, 2H), 7.36 (ddd, J = 6.7, 4.1, 1.2 Hz, 1H), 7.31 (dd, J = 3.5, 2.9 Hz, 1H), 7.20 (dd, J = 6.6, 5.0 Hz, 1H), 4.28 (q, J = 5.2 Hz, 2H), 3.28 (dd, J = 9.4, 5.2 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 150.0, 145.1, 134.2, 133.5, 130.5, 128.0, 127.8, 126.1, 125.7, 125.5, 122.4, 115.3, 110.1, 40.5, 28.0. HRMS (ESI): m/z calcd for C₁₅H₁₂BrN₂ [M+H]⁺: 299.0184; found: 299.0161.

9-Fluoro-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (*2e*). Light brown solid, mp = 126–127 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.27–8.24 (m, 1H), 7.72 (dd, *J* = 6.9, 3.8 Hz, 1H), 7.41 (dd, *J* = 4.8, 2.1 Hz, 2H), 7.33–7.30 (m, 1H), 7.03 (dd, *J* = 6.8, 4.9 Hz, 2H), 4.29 (t, *J* = 5.5 Hz, 2H), 3.29 (t, *J* = 5.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 159.9 (d, *J* = 239.8 Hz), 150.1, 140.4, 134.9 (d, *J* = 13.1 Hz), 134.2, 130.4, 128.3, 128.0, 126.6, 125.6, 120.5 (d, *J* = 10.1 Hz), 110.9 (d, *J* = 25.1 Hz), 96.0 (d, *J* = 27.7 Hz), 40.8, 28.3. ¹⁹F NMR (376 MHz, CDCl₃) δ –118.65 (td, *J* = 9.2, 4.8 Hz). HRMS (ESI): m/z calcd for C₁₅H₁₂FN₂ [M+H]⁺: 239.0985; found: 239.0969.

9-Chloro-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (*2f*). White solid, mp = 155–156 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.26 (dd, *J* = 4.6, 2.7 Hz, 1H), 7.71 (d, *J* = 6.9 Hz, 1H), 7.43–7.41 (m, 2H), 7.36 (d, *J* = 1.5 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.24 (dd, *J* = 6.9, 1.5 Hz, 1H), 4.30 (t, *J* = 5.5 Hz, 2H), 3.30 (t, *J* = 5.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 149.9, 142.5, 135.2, 134.1, 130.4, 128.3, 128.1, 127.8, 126.3, 125.7, 123.1, 120.5, 109.2, 40.5, 28.1. HRMS (ESI): m/z calcd for C₁₅H₁₂ClN₂ [M+H]⁺: 255.0689; found: 255.0668.

9,10-Difluoro-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (2*g*). Light brown solid, mp = 160–162 °C; ¹H NMR (500 MHz,CDCl₃) δ 8.24 – 8.20 (m, 1H), 7.56 (dd, *J* = 8.5, 5.8 Hz, 1H), 7.41 (dd, *J* = 4.2, 2.9 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.13 (dd, *J* = 7.7, 5.5 Hz, 1H), 4.27 (t, J = 5.5 Hz, 2H), 3.29 (t, *J* = 5.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 150.8, 149.2 (dd, *J* = 32.6, 15.2 Hz), 149.1, 148.9, 147.4, 147.3 (dd, *J* = 30.2, 15.4 Hz), 147.1, 139.2 (d, *J* = 10.8 Hz), 133.9, 130.6, 130.2 (d, *J* = 10.7 Hz), 128.3, 128.0, 126.4, 125.6, 107.2 (d, *J* = 19.7 Hz), 97.2 (d, *J* = 22.6 Hz), 40.9, 28.2. ¹⁹F NMR (376 MHz, CDCl₃) δ –141.5 (dt, *J* = 20.7, 8.7 Hz), – 143.4 (ddd, *J* = 20.9, 10.6, 6.8 Hz). HRMS (ESI): m/z calcd for C₁₅H₁₂F₂N₂ [M+H]⁺: 257.0890; found: 257.0871.

2,3-Dimethoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (*2h*).¹¹ Pale yellow solid, mp = 180–182 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.81 – 7.77 (m, 2H), 7.35 – 7.32 (m, 1H), 7.26 (dd, *J* = 4.8, 2.5 Hz, 2H), 6.79 (s, 1H), 4.30 (t, *J* = 5.6 Hz, 2H), 4.01 (s, 3H), 3.95 (s, 3H), 3.23 (t, J = 5.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 150.7, 149.4, 148.6, 143.8, 134.7, 127.4, 122.3, 122.2, 119.3, 119.1, 110.7, 108.8, 107.9, 56.2, 56.0, 40.5, 27.8. HRMS (ESI): m/z calcd for C₁₇H₁₆N₂O₂ [M+H]⁺: 281.1290; found: 281.1285.

10-Fluoro-2,3-dimethoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (*2i*). Brown solid, mp = 194–196 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.73 (s, 1H), 7.45 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.22 (dd, *J* = 7.0, 3.6 Hz, 1H), 7.00 (td, *J* = 7.3, 1.9 Hz, 1H), 6.79 (s, 1H), 4.27 (t, *J* = 5.6 Hz, 2H), 4.00 (s, 3H), 3.94 (s, 3H), 3.22 (t, *J* = 5.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 159.6 (d, *J* = 236.7 Hz), 151.0, 150.9, 148.8, 144.4 (d, *J* = 12.9 Hz), 131.4, 127.4, 119.0, 110.8, 110.5 (d, *J* = 26.1 Hz), 109.0 (d, *J* = 10.3 Hz), 108.0, 105.3 (d, *J* = 24.5 Hz), 56.4, 56.2, 40.8, 27.9. ¹⁹F NMR (376 MHz, CDCl₃) δ –120.8 (td, *J* = 9.6, 4.6 Hz). HRMS (ESI): m/z calcd for C₁₇H₁₆FN₂O₂ [M+H] ⁺: 299.1196; found: 299.1192.

10-Chloro-2,3-dimethoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (*2j*). Brown solid, mp = 192–193 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.75 (s, 1H), 7.72 (s, 1H), 7.22 (d, *J* = 1.5 Hz, 2H), 6.79 (s, 1H), 4.27 (t, *J* = 5.6 Hz, 2H), 4.00 (s, 3H), 3.95 (s, 3H), 3.22 (t, *J* = 5.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 150.9, 150.5, 148.6, 144.6, 133.3, 127.7, 127.4, 122.6, 119.0, 118.7, 110.6, 109.4, 107.9, 56.2, 56.04, 40.6, 27.7. HRMS (ESI):m/z calcd for C₁₇H₁₆ClN₂O₂ [M+H]⁺: 315.0900; found: 315.0891.

10-Bromo-2,3-dimethoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (*2k*). Yellow solid, 61.0 mg, yield 34%; mp = 152–153 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, *J* = 1.4 Hz, 1H), 7.72 (s, 1H), 7.35 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.19 (d, *J* = 6.8 Hz, 1H), 6.79 (s, 1H), 4.27 (t, *J* = 5.6 Hz, 2H), 3.99 (s, 3H), 3.95 (s, 3H), 3.22 (t, *J* = 5.6 Hz, 2H). ¹³C NMR (500 MHz, CDCl₃) δ 151.0, 150.3, 148.6, 144.9, 133.6, 127.5, 125.3, 122.00, 118.5, 115.1, 110.6, 109.9, 108.0, 56.2, 56.0, 40.6, 27.7. HRMS (ESI): m/z calcd for C₁₇H₁₆BrN₂O₂ [M+H] ⁺: 359.0395; found: 359.0378.

9-Fluoro-2,3-dimethoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (*2I*). Yellow solid, mp = 192–194 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.74 (s, 1H), 7.70 (dd, *J* = 6.9, 3.8 Hz, 1H), 7.02 (dd, *J* = 6.1, 4.3 Hz, 2H), 6.80 (s, 1H), 4.26 (t, *J* = 5.5 Hz, 2H), 4.00 (s, 3H), 3.95 (s, 3H), 3.23 (t, *J* = 5.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 150.8, 150.2, 148.7, 127.2, 119.8 (d, *J* = 31.5 Hz), 110.4 (d, *J* = 78.9 Hz), 110.3, 107.7, 95.7 (d, *J* = 87.9 Hz), 56.3, 56.1, 40.7, 27.8. ¹⁹F NMR (376 MHz, CDCl₃) δ –119.2 (q, *J* = 8.0, 5.1 Hz). HRMS (ESI): m/z calcd for C₁₇H₁₆FN₂O₂ [M+H]⁺: 299.1196; found: 299.1189. 9-Chloro-2,3-dimethoxy-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (*2m*). Pale yellow solid, mp = 213–214 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.70 (s, 1H), 7.66 (d, *J* = 6.8 Hz, 1H), 7.29 (d, *J* = 1.4 Hz, 1H), 7.22–7.19 (m, 1H), 6.77 (s, 1H), 4.23 (t, *J* = 5.6 Hz, 2H), 3.98 (s, 3H), 3.93 (s, 3H), 3.20 (t, *J* = 5.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 150.9, 150.2, 148.6, 142.4, 135.3, 127.9, 127.4, 122.7, 119.9, 118.6, 110.6, 108.9, 107.8, 56.2, 56.0, 40.6, 27.6. HRMS (ESI): m/z calcd for C₁₇H₁₆ClN₂O₂ [M+H]⁺: 315.0900; found: 315.0892.

5-Fluoro-2-phenyl-1*H*-benzimidazole (*2n*). Pale yellow solid, mp = 224–226 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.03 (dd, *J* = 5.7, 1.5 Hz, 2H), 7.53–7.45 (m, 4H), 7.29 (s, 1H), 7.02 (ddd, *J* = 9.2, 6.3, 2.6 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 160.6, 158.7, 152.7, 130.4, 129.4, 129.1, 126.4, 111.2. HRMS (ESI): m/z calcd for C₁₃H₁₀FN₂ [M+H]⁺: 303.1298; found: 303.1292.

5-Chloro-2-phenyl-1*H*-benzimidazole (*2o*).^{9b} Yellow solid, mp = 179–180 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 8.16 (d, *J* = 5.9 Hz, 2H), 7.64–7.48 (m, 5H), 7.23 (d, *J* = 6.8 Hz, 1H). NMR (126 MHz, DMSO-d₆) δ 153.2, 130.8, 130.1, 129.6, 127.1, 122.9. HRMS (ESI): m/z calcd for C₁₃H₁₀ClN₂ [M+H]⁺: 229.0533; found: 229.0528.

5-Bromo-2-phenyl-1*H*-benzimidazole (*2p*). Yellow solid, mp = 190–192 °C; ¹H NMR (500 MHz, CDCl₃) δ 13.13 (d, *J* = 16.2 Hz, 1H), 8.16 (d, *J* = 5.9 Hz, 2H), 7.65–7.48 (m, 4H), 7.34 (dd, *J* = 11.2, 6.9 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 152.9 (d, *J* = 139.3 Hz), 145.7, 143.4, 136.7, 134.6, 130.8 (d, *J* = 19.6 Hz), 130.1 (d, *J* = 13.8 Hz), 129.5, 127.1, 125.5 (d, *J* = 199.8 Hz), 121.4 (d, *J* = 253.7 Hz), 115.26, 114.4 (d, *J* = 18.7 Hz), 113.6. HRMS (ESI): m/z calcd for C₁₃H₁₀BrN₂ [M+H]⁺: 273.0027; found: 273.0018.

5-Methyl-2-phenyl-1*H*-benzo[d]imidazole (2q)^{9b}. Orange solid, 107.6 mg, yield 91%; mp = 219–220 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, *J* = 5.9 Hz, 2H), 7.55 (d, *J* = 5.7 Hz, 1H), 7.52–7.39 (m, 4H), 7.10 (d, *J* = 6.6 Hz, 1H), 2.48 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 151.1, 130.0, 129.8, 129.7, 129.0, 126.3, 124.5, 119.2, 110.6, 21.7. HRMS(ESI): m/z calcd for: C₁₄H₁₃N₂ [M+H]⁺: 209.1079 found: 209.1079.

5-Methoxy-2-phenyl-1*H*-benzimidazole (*2r*). White oil, 94.8 mg, yield 84%; ¹H NMR (500 MHz, CDCl₃) δ 8.07–8.03 (m, 2H), 7.50 (d, *J* = 7.0 Hz, 1H), 7.45–7.40 (m, 3H), 7.05 (s, 1H), 6.88 (dd, *J* = 7.0, 1.9 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 156.6, 151.4, 142.1, 129.9, 129.0, 126.3, 125.94, 117.6, 112.5, 55.7, 29.2. HRMS (ESI): m/z calcd for C₁₄H₁₃N₂O [M+H]⁺: 225.1028; found: 225.1043.

1-Benzyl-2-phenyl-1*H*-benzimidazole (*2s*).¹¹ Pale yellow solid, 92.0 mg, yield 63%; ¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, *J* = 6.4 Hz, 1H), 7.69 (dd, *J* = 6.1, 1.3 Hz, 2H), 7.49–7.43 (m, 3H), 7.36–7.29 (m, 4H), 7.25–7.19 (m, 2H), 7.11 (d, *J* = 5.7 Hz, 2H), 5.46 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 154.1, 143.1, 136.3, 136.0, 130.0, 129.8, 129.2, 129.0, 128.7, 127.7, 125.9, 123.0, 122.6, 119.9, 110.5, 48.3. HRMS (ESI): m/z calcd for: C₂₀H₁₇N₂ [M+H]⁺: 285.1392 found: 285.1391.

1-Benzyl-6-fluoro-2-phenyl-1*H*-benzo[d]imidazole (*2t*). White solid, mp = 106–108 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.75–7.69 (m, 3H), 7.54–7.51 (m, 3H), 7.41 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.30–7.22 (m, 3H), 7.11 (td, *J* = 7.6, 2.0 Hz, 1H), 6.97 (d, *J* = 5.9 Hz, 2H), 5.57 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 159.0 (d, *J* = 237.0 Hz), 154.3, 139.3, 136.7, 136.3 (d, *J* = 13.7 Hz), 130.1, 130.0, 129.1, 128.9, 127.7, 126.3, 120.4 (d, *J* = 10.2 Hz), 110.5 (d, *J* = 25.1 Hz), 98.0 (d, *J* = 27.8 Hz), 47.6. ¹⁹F NMR (376 MHz, DMSO) δ –118.8 (td, *J* = 9.7, 5.0 Hz). HRMS (ESI): m/z calcd for C₂₀H₁₆FN₂ [M+H]⁺: 303.1298; found: 303.1292.

1-Benzyl-6-chloro-2-phenyl-1*H*-benzo[*d*]imidazole (2u)^{8f} Light brown solid, mp = 144–146 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, *J* = 6.8 Hz, 1H), 7.67 (dd, *J* = 5.9, 0.7 Hz, 2H), 7.50–7.43 (m, 3H), 7.37–7.31 (m, 3H), 7.30–7.27 (m, 1H), 7.20 (d, *J* = 1.5 Hz, 1H), 7.08 (d, *J* = 5.8 Hz, 2H), 5.42 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 154.9, 141.7, 136.6, 135.7, 130.1, 129.5, 129.1, 129.1, 128.8, 128.70, 127.9, 125.8, 123.4, 120.8, 110.5, 48.4. HRMS(ESI): m/z [M+H]⁺ calcd for C₂₀H₁₆FN₂: 319.1002; found: 319.0978.

Figure S1: ¹H and ¹³C NMR spectra of compound 1a



Figure S2: ¹H and ¹³C NMR spectra of compound 1b



18





Figure S4: ¹H and ¹³C NMR spectra of compound 1d





Figure S5: ¹H and ¹³C NMR spectrum of compound 1e



Figure S6: ¹H and ¹³C NMR spectra of compound 1f



Figure S7: ¹H and ¹³C NMR spectrum of compound 1g

Figure S8: ¹H and ¹³C NMR spectra of compound 1h



110 100 f1 (ppm) Figure S9: ¹H and ¹³C NMR spectra of compound 1i



Figure S10: ¹H and ¹³C NMR spectra of compound 1j



Figure S11: ¹H and ¹³C NMR spectra of compound 1k















Figure S15: ¹H and ¹³C NMR spectra of compound 10



Figure S16: ¹H and ¹³C NMR spectra of compound 1p



Figure S17: ¹H and ¹³C NMR spectra of compound 1q



Figure S18: ¹H and ¹³C NMR spectra of compound 1r





Figure S19: ¹H and ¹³C NMR spectra of compound 1s

Figure S20: ¹H and ¹³C NMR spectra of compound 1t





Figure S21: ¹H and ¹³C NMR spectra of compound 1u



Figure S22: ¹H and ¹³C NMR spectra of compound 3





Figure S24: ¹H and ¹³C NMR spectra of compound 2b











Figure S27: ¹H and ¹³C NMR spectra of compound 2e























Figure S33: ¹H and ¹³C NMR spectra of compound 2k









Figure S36: ¹H and ¹³C NMR spectra of compound 2n



Figure S37: ¹H and ¹³C NMR spectra of compound 20



Figure S38: ¹H and ¹³C NMR spectra of compound 2p



Figure S39: ¹H and ¹³C NMR spectra of compound 2q



Figure S40: ¹H and ¹³C NMR spectra of compound 2r





Figure S41: ¹H and ¹³C NMR spectra of compound 2s

Figure S42: ¹H and ¹³C NMR spectra of compound 2t



Figure S43: ¹H and ¹³C NMR spectra of compound 2u

