

Supporting Information

Silver(I)-Catalyzed C4-H Amination of 1-Naphthylamine Derivatives with Azodicarboxylates at Room Temperature

Yuxue Zhang, Mengxue Pei, Fan Yang,* and Yangjie Wu

College of Chemistry, Green Catalysis Center, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, China.

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1. General Information

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer with CDCl_3 as the solvent and TMS as an internal standard. Chemical shifts are expressed in parts per million (δ) and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplet), and coupling constants (J) were given in Hz. Chemical shifts as internal standard were referenced to CDCl_3 ($\delta = 7.26$ for ^1H and $\delta = 77.16$ for ^{13}C NMR as internal standard). Melting points were measured using a WC-1 microscopic apparatus. High resolution mass spectra were ensured on an Agilent Technologies 1290-6540 HPLC/Accurate-Mass Quadrupole Time-of-Flight LC/MS. All solvents and chemicals were obtained from commercial sources and used as-received without further purification unless otherwise noted.

2. Optimization of Reaction Conditions

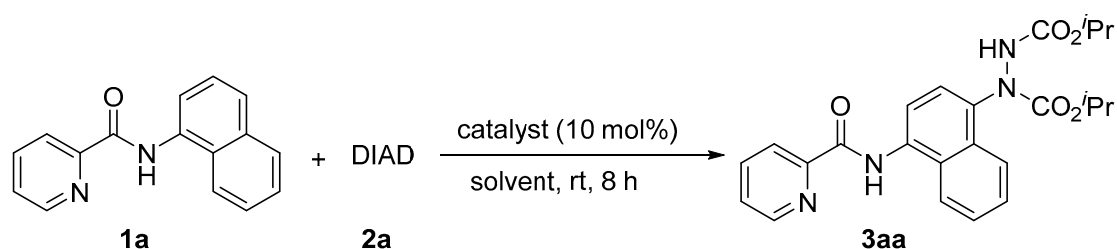


Table S1 Optimization of Catalyst and Solvent^a

Entry	Catalyst	Solvent	Yield (%) ^b
1	Ag_2O	DCE	80
2	Ag_2O	dioxane	90
3	Ag_2O	acetone	97
4	Ag_2O	THF	90
5	Ag_2O	DME	80
6	Ag_2O	DCM	<5
7	Ag_2O	methanol	<5
8	Ag_2O	DMF	<5
9	Ag_2O	DMSO	<5
10	Ag_2O	EtOAc	<5
11	Ag_2O	MeCN	<5
12	CuO	acetone	<5
13	Cu_2O	acetone	<5
14	Fe_2O_3	acetone	<5
15	AgOAc	acetone	<5
16	CuOAc	acetone	<5
17	$\text{NiCl}_2 \cdot \text{H}_2\text{O}$	acetone	<5
18	$\text{Co}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$	acetone	<5
19	-	acetone	<5

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (10 mol%) in solvent (1mL) at room temperature for 8 h. ^bIsolated yield based on **1a**. DCE (1,2-dichloroethane), THF

(tetrahydrofuran), DME (1,2-dimethoxyethane), DMF (N,N-dimethylformamide), DMSO (dimethyl sulfoxide), EtOAc (ethyl acetate).

Table S2 Optimization of Catalyst Loading^a

Entry	Ag ₂ O	Solvent	Yield (%) ^b
1	5 mol%	acetone	46
2	20 mol%	acetone	91
3	50 mol%	acetone	88

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (x mol%) in solvent (1 mL) at room temperature for 8 h. ^bIsolated yield based on **1a**.

Table S3 Optimization of Time^a

Entry	Ag ₂ O	Solvent	Time (h)	Yield (%) ^b
1	10 mol%	acetone	4	72
2	10 mol%	acetone	6	81
3	10 mol%	acetone	7	88

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (10 mol%) in solvent (1 mL) at room temperature for x h. ^bIsolated yield based on **1a**.

3 Experimental Section

3.1 Typical Procedure for the Synthesis of Substrate **1a**

A 100 mL round-bottom flask was equipped with a magnetic stir bar and charged with 1-naphthylamine (20 mmol, 2.86 g), picolinic acid (1.1 equiv, 2.70 g), N,N-dimethyl-4-aminopyridine (DMAP, 0.1 equiv, 0.244 g) dissolved in 30 mL anhydrous CH₂Cl₂ at 0 °C. After 1-ethyl-3-[3-(N,N-dimethylamino)propyl]carbodiimide hydrochloride (EDCI, 4.2 g, 1.1 equiv) in CH₂Cl₂ (20 mL) was added dropwise to the solution under a nitrogen atmosphere, the reaction was then warmed to room temperature, stirred for 12 h and quenched with water (30 mL). The reaction mixture was extracted with CH₂Cl₂ (3 × 20 mL) and the combined organic solvent was dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography (ethyl acetate/hexane = 1/5) to afford pure **1a** as a white solid (4.42 g, 89%).

All amides **1** as the substrates were prepared from the corresponding 1-naphthylamine derivatives and 2-picolinic acid according to the reported procedure.¹

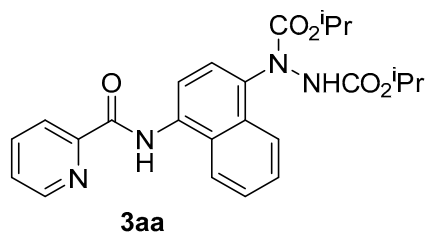
3.2 Typical Procedure for the C4-H Amination of 1-Naphthylamine Derivatives

A Schlenk tube was equipped with a magnetic stir bar and charged with N-(naphthalen-1-yl)picolinamide **1a** (0.1 mmol), **2a** (0.2 mmol, 2 equiv), Ag₂O (10 mol%) in acetone (1.0 mL). The resulting mixture was sealed and stirred for 8 h at room temperature. Upon completion, CH₂Cl₂ (10 mL) was added to the reaction system, and the resulting mixture was filtered through a pad of celite. The filtrate was extracted with H₂O (20 mL), and the aqueous layer was extracted with CH₂Cl₂ (2 × 10 mL). The collected organic layer was dried with anhydrous Na₂SO₄, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (200–300 mesh) using hexane-EtOAc as eluent (3:1, V/V) to afford the pure product **3aa**.

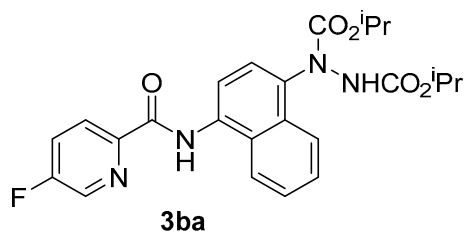
3.3 The Functionalization of the product 3

Mixture of **3** (0.1 mmol, 1.0 equiv), Pd(OAc)₂ (15 mol %), CH₃I or PhI (0.4mmol, 4.0 equiv), anhydrous KOAc (0.2 mmol, 2.0 equiv), and 1,4-dioxane or xylene (1 mL) was placed in a 25 mL Schlenk tube with a rubber plug under air. The tube was heated at 130 °C for 24 h or 12 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered through celite, and concentrated in vacuo. The residue was purified by silica gel column chromatography with petroleum ether-ethyl acetate (5:1, V/V) to afford the desired products.

4 Characterization Data of the Products

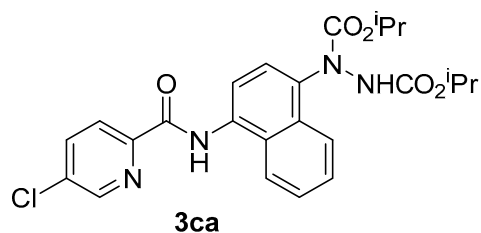


Diisopropyl 1-(4-(picolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3aa^[6d]): pale yellow solid (44.0 mg, 97%), R_f = 0.32 (25% EtOAc in hexane), mp 176.9-178.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 10.82 (s, 1H), 8.71 (d, J = 7.93 Hz, 1H), 8.36 (d, J = 7.93 Hz, 1H), 8.36 (d, J = 7.81 Hz, 1H), 8.12-8.10 (m, 2H), 7.94 (td, J_1 = 1.56 Hz, J_2 = 7.68 Hz, 1H), 7.75 (s, 1H), 7.63-7.56 (m, 2H), 7.54-7.51 (m, 1H), 7.28 (s, 1H), 5.02-5.01 (m, 2H), 1.25-1.05 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 162.2, 156.1, 149.8, 148.1, 137.8, 134.9, 132.7, 130.7, 126.9, 126.8, 126.7, 126.5, 126.0, 123.7, 122.5, 120.8, 118.1, 70.9, 70.0, 22.0, 21.8; HRMS (ESI⁺) m/z [M + H]⁺ calcd for C₂₄H₂₇N₄O₅: 451.1976, found: 451.1977.

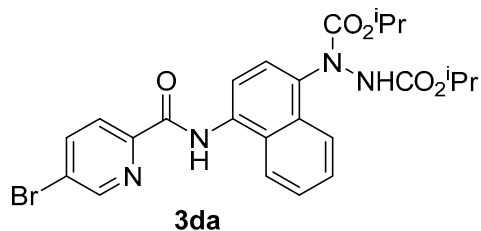


Diisopropyl 1-(4-(5-fluoropicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3ba): yellow solid (43.6 mg, 93%), R_f = 0.32 (25% EtOAc in hexane), mp 156.5-158.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 10.55 (s, 1H), 8.53 (d, J = 2.70 Hz, 1H), 8.40-8.37 (m, 2H), 8.09-8.05 (m, 2H), 7.77-7.75 (m, 1H), 7.64-7.54 (m, 3H), 7.36 (s, 1H), 5.05-5.01 (m, 2H), 1.44-1.09 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 161.4 (d, J = 263.43 Hz), 161.2, 156.1, 146.2 (d, J = 3.79 Hz), 136.8 (d, J = 25.40 Hz), 135.1, 132.5, 130.7, 126.8 (d, J = 11.09 Hz), 126.5, 125.9, 124.5, 124.4, 124.3 (d, J = 18.66 Hz), 123.8, 120.7, 118.3, 70.9, 70.0, 22.0; ¹⁹F NMR (376 MHz, CDCl₃): δ -121.18 (s,

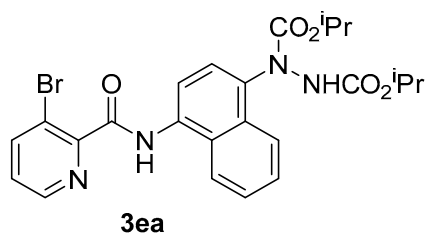
1F); HRMS (ESI⁺) *m/z* [M + H]⁺ calcd for C₂₄H₂₆FN₄O₅: 469.1882, found: 469.1881.



Diisopropyl 1-(4-(5-chloropicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3ca): yellow solid (45.0 mg, 93%), *R_f* = 0.32 (25% EtOAc in hexane), mp 170.9-172.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 10.57 (s, 1H), 8.64 (d, *J* = 2.07 Hz, 1H), 8.38 (d, *J* = 7.97 Hz, 1H), 8.30 (d, *J* = 8.36 Hz, 1H), 8.09-8.04 (m, 2H), 7.91 (dd, *J₁* = 2.31 Hz, *J₂* = 8.37 Hz, 1H), 7.76 (s, 1H), 7.62-7.56 (m, 2H), 7.32 (s, 1H), 5.02-5.01 (m, 2H), 1.43-1.09 (m, 12 H); ¹³C NMR (100 MHz, CDCl₃) δ 161.4, 156.1, 148.0, 147.2, 137.5, 135.5, 135.2, 132.4, 130.7, 126.9, 126.8, 126.2, 125.9, 123.8, 123.6, 120.6, 118.3, 70.9, 70.0, 22.0; HRMS (ESI⁺) *m/z* [M + H]⁺ calcd for C₂₄H₂₆ClN₄O₅: 485.1586, found: 485.1584.

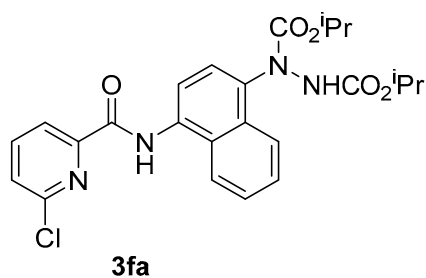


Diisopropyl 1-(4-(5-bromopicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3da): yellow solid (50.1 mg, 95%), *R_f* = 0.32 (25% EtOAc in hexane), mp 139.5-140.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 10.58 (s, 1H), 8.76 (d, *J* = 1.96 Hz, 1H), 8.38 (d, *J* = 7.95 Hz, 1H), 8.24 (d, *J* = 8.30 Hz, 1H), 8.08-8.04 (m, 3H), 7.75 (s, 1H), 7.62-7.56 (m, 2H), 7.29 (s, 1H), 5.02-5.01 (m, 2H), 1.25-1.09 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 161.5, 156.1, 149.4, 148.3, 140.5, 135.2, 132.4, 130.7, 126.8, 126.8, 126.6, 125.9, 124.5, 124.0, 123.8, 120.6, 118.3, 70.9, 70.0, 22.0; HRMS (ESI⁺) *m/z* [M + H]⁺ calcd for C₂₄H₂₆BrN₄O₅: 529.1081, found: 529.1077.

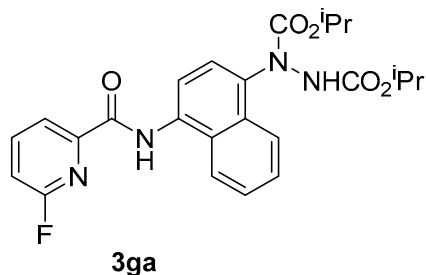


Diisopropyl 1-(4-(3-bromopicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3ea): yellow solid (50.3 mg, 95%), *R_f* = 0.32 (25% EtOAc in hexane),

mp 176.2-178.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.74 (s, 1H), 8.64 (dd, $J_1 = 1.00$ Hz, $J_2 = 4.40$ Hz, 1H), 8.40 (d, $J = 7.20$ Hz, 1H), 8.12-8.02 (m, 3H), 7.73 (s, 1H), 7.61-7.59 (m, 2H), 7.35 (dd, $J_1 = 4.53$ Hz, $J_2 = 8.08$ Hz, 1H), 7.23 (s, 1H), 5.02-5.00 (m, 2H), 1.25-1.09 (m, 12 H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.2, 156.0, 146.6, 146.3, 144.5, 135.0, 132.7, 130.7, 126.9, 126.7, 126.5, 125.9, 123.7, 120.7, 120.0, 118.3, 70.9, 70.0, 22.0; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{26}\text{BrN}_4\text{O}_5$: 529.1081, found: 529.1077.

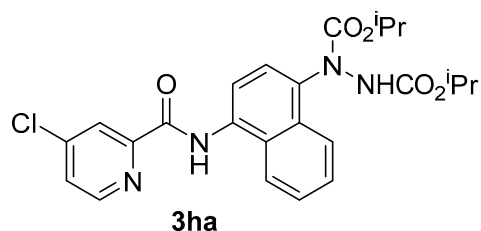


Diisopropyl 1-(4-(6-chloropicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3fa): yellow solid (40.2 mg, 83%), $R_f = 0.32$ (25% EtOAc in hexane), mp 218.0-219.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.40 (s, 1H), 8.33 (d, $J = 7.70$ Hz, 1H), 8.28 (d, $J = 7.48$ Hz, 1H), 8.06 (d, $J = 8.52$ Hz, 1H), 7.91 (t, $J = 7.76$ Hz, 1H), 7.76 (s, 1H), 7.65-7.55 (m, 3H), 7.24 (s, 1H), 5.02-4.99 (m, 2H), 1.26-1.10 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.9, 156.1, 150.3, 150.1, 140.4, 135.4, 132.3, 130.7, 127.5, 127.1, 126.8, 126.7, 125.8, 123.7, 121.3, 120.8, 118.8, 70.9, 70.0, 22.0; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{26}\text{ClN}_4\text{O}_5$: 485.1586, found: 485.1582.

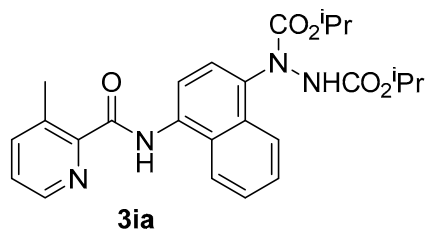


Diisopropyl 1-(4-(6-fluoropicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3ga): yellow solid (44.7 mg, 95%), $R_f = 0.32$ (25% EtOAc in hexane), mp 195.5-197.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.28 (s, 1H), 8.35 (d, $J = 7.92$ Hz, 1H), 8.25 (dd, $J_1 = 1.48$ Hz, $J_2 = 7.36$ Hz, 1H), 8.07-8.01 (m, 3H), 7.75 (s, 1H), 7.64-7.57 (m, 2H), 7.32 (s, 1H), 7.19 (dd, $J_1 = 1.96$ Hz, $J_2 = 8.16$ Hz, 1H), 5.02-4.99 (m, 2H), 1.25-1.10 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.0 (d, $J = 243.57$ Hz), 160.9, 156.1, 148.4 (d, $J = 10.63$ Hz), 143.0 (d, $J = 10.63$ Hz), 135.4, 132.2, 130.7, 127.0, 126.8, 126.7, 125.8, 123.8, 120.7, 120.3 (d, $J = 3.66$ Hz), 118.7, 113.2 (d, $J = 35.47$ Hz), 70.9, 70.0, 22.0; ^{19}F NMR (376 MHz, CDCl_3): δ -66.95 (s, 1F); HRMS (ESI^+) m/z $[\text{M}$

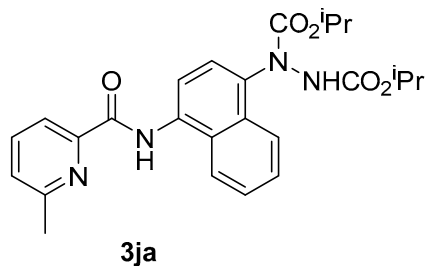
+ H]⁺ calcd for C₂₄H₂₆FN₄O₅: 469.1882, found: 469.1880.



Diisopropyl 1-(4-(4-chloropicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3ha): pale yellow solid (43.1 mg, 89%), *R*_f = 0.32 (25% EtOAc in hexane), mp 170.6-172.4 °C; ¹H NMR (400 MHz, CDCl₃) δ 10.67 (s, 1H), 8.59 (d, *J* = 5.24 Hz, 1H), 8.38 (d, *J* = 7.89 Hz, 1H), 8.35 (d, *J* = 1.80 Hz, 1H), 8.09-8.04 (m, 2H), 7.75 (s, 1H), 7.62-7.56 (m, 2H), 7.52 (dd, *J*₁ = 1.92 Hz, *J*₂ = 5.20 Hz, 1H), 7.35 (s, 1H), 5.02-5.01 (m, 2H), 1.25-1.10 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 161.0, 156.1, 151.3, 149.0, 146.4, 135.2, 132.3, 130.7, 126.8, 126.6, 125.9, 123.8, 123.2, 120.6, 118.3, 70.9, 70.0, 22.0, 21.9; HRMS (ESI⁺) *m/z* [M + H]⁺ calcd for C₂₄H₂₆ClN₄O₅: 485.1586, found: 485.1583.

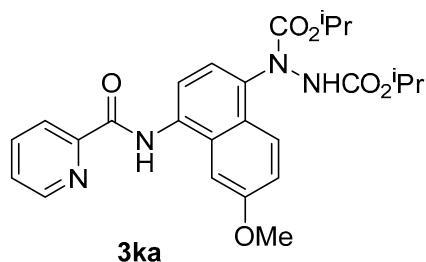


Diisopropyl 1-(4-(3-methylpicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3ia^[6d]): pale yellow solid (45.0 mg, 97%), *R*_f = 0.32 (25% EtOAc in hexane), mp 192.1-194.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.05 (s, 1H), 8.54 (d, *J* = 3.81 Hz, 1H), 8.37 (d, *J* = 7.24 Hz, 1H), 8.11-8.08 (m, 2H), 7.73 (s, 1H), 7.67 (d, *J* = 7.64 Hz, 1H), 7.61-7.55 (m, 2H), 7.40 (q, *J* = 7.74 Hz, 1H), 7.23 (s, 1H), 5.02-5.00 (m, 2H), 2.85 (s, 3H), 1.25-1.09 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 156.0, 146.7, 145.5, 141.4, 136.4, 134.6, 133.1, 130.7, 127.1, 126.6, 126.3, 126.2, 126.0, 123.6, 121.0, 118.0, 70.8, 69.9, 22.0, 20.8; HRMS (ESI⁺) *m/z* [M + K]⁺ calcd for C₂₅H₂₈N₄O₅K: 503.1691, found: 503.1691.

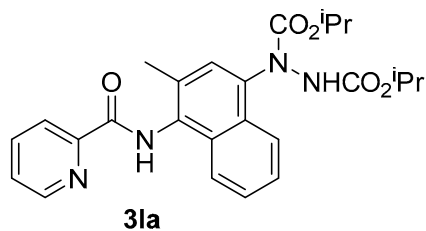


Diisopropyl 1-(4-(6-methylpicolinamido)naphthalen-1-yl)hydrazine-1,2-

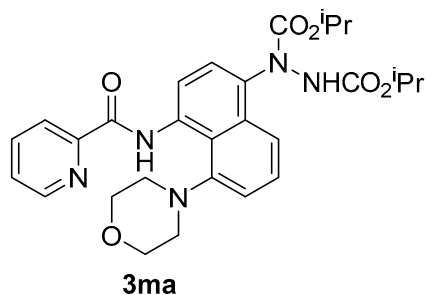
dicarboxylate (3ja): yellow solid (32.6 mg, 70%), $R_f = 0.32$ (25% EtOAc in hexane), mp 202.5-204.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.89 (s, 1H), 8.42 (d, $J = 7.57$ Hz, 1H), 8.17-8.08 (m, 3H), 7.83-7.73 (m, 2H), 7.64-7.56 (m, 2H), 7.37 (d, $J = 7.68$ Hz, 1H), 7.26 (s, 1H), 5.02-4.99 (m, 2H), 2.70 (s, 3H), 1.37-1.00 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.4, 157.2, 156.1, 149.1, 137.9, 134.8, 132.8, 130.8, 126.9, 126.7, 126.4, 126.4, 126.0, 123.7, 120.8, 119.6, 118.1, 70.8, 70.0, 24.4, 22.0; HRMS (ESI^+) m/z $[\text{M} + \text{K}]^+$ calcd for $\text{C}_{25}\text{H}_{28}\text{N}_4\text{O}_5\text{K}$: 503.1691, found: 503.1690.



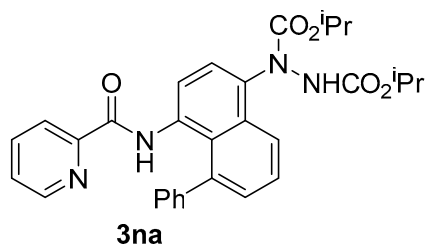
Diisopropyl 1-(6-methoxy-4-(picolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3ka): yellow solid (32.3 mg, 67%), $R_f = 0.32$ (25% EtOAc in hexane), mp 191.0-192.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.57 (s, 1H), 8.68 (d, $J = 4.20$ Hz, 1H), 8.36 (d, $J = 7.80$ Hz, 1H), 8.28 (d, $J = 8.00$ Hz, 1H), 8.05 (s, 1H), 7.94 (dt, $J_1 = 1.55$ Hz, $J_2 = 9.26$ Hz, 1H), 7.57-7.51 (m, 2H), 7.33 (d, $J = 2.88$ Hz, 1H), 7.26-7.23 (m, 2H), 5.02-4.99 (m, 2H), 3.96 (s, 3H), 1.29-1.09 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.3, 158.2, 156.0, 149.9, 148.2, 137.8, 135.3, 131.5, 128.6, 126.6, 126.2, 125.7, 123.2, 122.6, 119.6, 118.6, 100.4, 70.8, 69.9, 55.3, 22.0, 21.8; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{29}\text{N}_4\text{O}_6$: 481.2082, found: 481.2081.



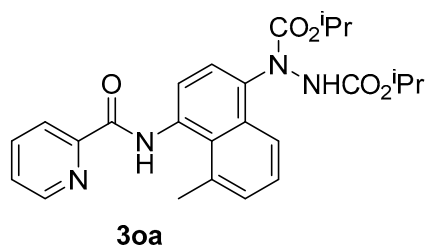
Diisopropyl 1-(3-methyl-4-(picolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3la): yellow solid (37.5 mg, 80%), $R_f = 0.32$ (25% EtOAc in hexane), mp 175.9-177.6 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.90 (s, 1H), 8.70 (d, $J = 4.20$ Hz, 1H), 8.33 (d, $J = 7.80$ Hz, 1H), 7.97-7.92 (m, 3H), 7.68 (s, 1H), 7.55-7.52 (m, 1H), 7.49-7.46 (m, 2H), 7.20 (s, 1H), 5.02-4.99 (m, 2H), 2.46 (s, 3H), 1.37-1.12 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.9, 155.9, 149.6, 148.3, 137.6, 137.2, 133.2, 131.3, 130.3, 129.3, 128.6, 126.7, 126.6, 126.0, 123.0, 122.7, 70.9, 70.0, 22.0, 18.9; HRMS (ESI^+) m/z $[\text{M} + \text{K}]^+$ calcd for $\text{C}_{25}\text{H}_{28}\text{N}_4\text{O}_5\text{K}$: 503.1691, found: 503.1690.



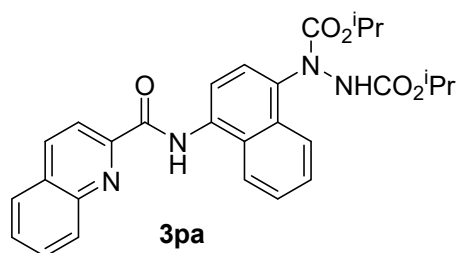
Diisopropyl 1-(5-morpholino-4-(picolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3ma): yellow solid (47.5 mg, 88%), $R_f = 0.32$ (25% EtOAc in hexane), mp 113.6-115.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 13.96 (s, 1H), 9.14 (d, $J = 8.50$ Hz, 1H), 8.73 (d, $J = 4.17$ Hz, 1H), 8.38 (d, $J = 7.84$ Hz, 1H), 7.95-7.72 (m, 3H), 7.54-7.47 (m, 2H), 7.41 (d, $J = 7.33$ Hz, 1H), 7.20 (s, 1H), 5.02-4.99 (m, 2H), 4.25 (s, 2H), 3.84 (s, 2H), 3.19-2.98 (m, 4H), 1.25-1.03 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.4, 156.0, 151.0, 149.5, 147.9, 137.6, 135.9, 134.0, 133.0, 126.5, 126.4, 123.5, 120.4, 120.3, 117.3, 116.5, 70.8, 70.0, 65.5, 55.1, 54.3, 53.8, 22.0; HRMS (ESI^+) m/z $[\text{M} + \text{K}]^+$ calcd for $\text{C}_{28}\text{H}_{33}\text{N}_5\text{O}_6\text{K}$: 574.2062, found: 574.2059.



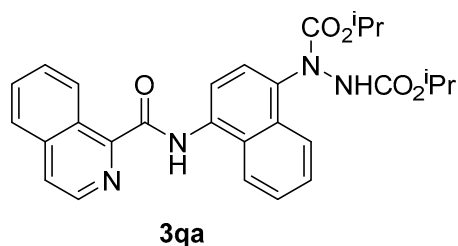
Diisopropyl 1-(5-phenyl-4-(picolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3na^[6d]): yellow solid (26.7 mg, 50%), $R_f = 0.32$ (25% EtOAc in hexane), mp 221.6-223.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.65 (s, 1H), 8.30 (d, $J = 7.88$ Hz, 1H), 8.16-8.07 (m, 3H), 7.80-7.73 (m, 2H), 7.56-7.52 (m, 1H), 7.42-7.28 (m, 5H), 7.19 (s, 2H), 7.01 (t, $J = 7.43$ Hz, 1H), 5.04-5.02 (m, 2H), 1.34-1.08 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.9, 155.9, 149.5, 147.3, 142.4, 138.1, 137.0, 135.7, 433.4, 132.1, 130.9, 129.2, 128.1, 126.9, 125.8, 125.7, 125.4, 123.1, 121.8, 70.9, 70.0, 29.7, 22.0; HRMS (ESI^+) m/z $[\text{M} + \text{K}]^+$ calcd for $\text{C}_{30}\text{H}_{30}\text{N}_4\text{O}_5\text{K}$: 565.1848, found: 565.1847.



Diisopropyl 1-(5-methyl-4-(picolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (30a^[6d]): yellow solid (41.0 mg, 80%), $R_f = 0.32$ (25% EtOAc in hexane), mp 181.1-183.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.67 (s, 1H), 8.65-8.64 (m, 1H), 8.36 (d, $J = 7.81$ Hz, 1H), 8.12 (d, $J = 7.33$ Hz, 1H), 7.94-7.90 (m, 2H), 7.75 (s, 1H), 7.51-7.48 (m, 1H), 7.39 (t, $J = 7.10$ Hz, 1H), 7.30 (d, $J = 6.88$ Hz, 1H), 5.01-4.99 (m, 2H), 2.99 (s, 3H), 1.25-1.03 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.2, 156.0, 149.9, 148.2, 137.7, 136.4, 133.7, 133.1, 132.4, 130.5, 128.6, 126.5, 126.3, 125.6, 122.7, 121.9, 70.8, 69.9, 25.1, 22.0; HRMS (ESI^+) m/z $[\text{M} + \text{K}]^+$ calcd for $\text{C}_{25}\text{H}_{28}\text{N}_4\text{O}_5\text{K}$: 503.1691, found: 503.1688.

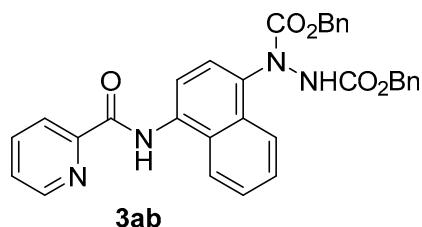


Diisopropyl 1-(4-(quinoline-2-carboxamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3pa^[6d]): yellow solid (34.1 mg, 68%), $R_f = 0.32$ (25% EtOAc in hexane), mp 185.4-187.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.02 (s, 1H), 8.47-8.37 (m, 3H), 8.26 (d, $J = 8.47$ Hz, 1H), 8.19 (d, $J = 8.33$ Hz, 1H), 8.11 (s, 1H), 7.92 (d, $J = 8.14$ Hz, 1H), 7.85-7.79 (m, 2H), 7.68-7.59 (m, 3H), 7.29 (s, 1H), 5.04-5.02 (m, 2H), 1.27-1.11 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.4, 156.1, 149.6, 146.3, 138.0, 135.0, 132.8, 130.8, 130.4, 129.8, 129.5, 128.3, 127.8, 127.0, 126.7, 126.5, 126.0, 123.8, 120.8, 118.8, 118.2, 70.9, 70.0, 22.0; HRMS (ESI^+) m/z $[\text{M} + \text{K}]^+$ calcd for $\text{C}_{28}\text{H}_{28}\text{N}_4\text{O}_5\text{K}$: 539.1691, found: 539.1690.

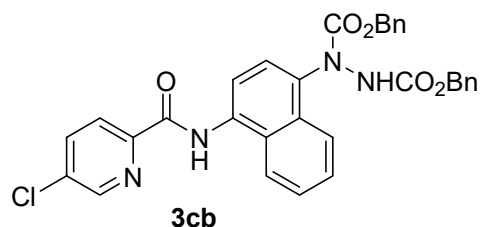


Diisopropyl 1-(4-(isoquinoline-1-carboxamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3qa): yellow solid (34.4 mg, 68%), $R_f = 0.32$ (25% EtOAc in hexane), mp 223.1-224.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.16 (s, 1H), 9.78 (d, $J = 7.92$ Hz, 1H), 8.62 (d, $J = 4.30$ Hz, 1H), 8.44 (d, $J = 7.26$ Hz, 1H), 8.16-8.07 (m, 2H), 7.90 (d, $J = 6.08$ Hz, 2H), 7.77-7.71 (m, 3H), 7.63-7.57 (m, 2H), 7.20 (s, 1H), 5.02 (s, 1H), 1.26-

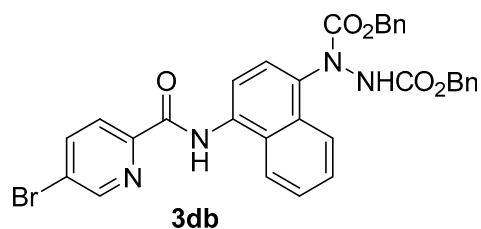
1.06 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.8, 156.1, 147.3, 140.0, 137.7, 134.9, 133.1, 130.8, 130.7, 129.0, 127.8, 127.4, 127.2, 126.9, 126.7, 126.4, 126.0, 125.1, 123.6, 121.0, 118.3, 70.9, 70.0, 22.0, 21.9; HRMS (ESI^+) m/z $[\text{M} + \text{K}]^+$ calcd for $\text{C}_{28}\text{H}_{28}\text{N}_4\text{O}_5\text{K}$: 539.1691, found: 539.1692.



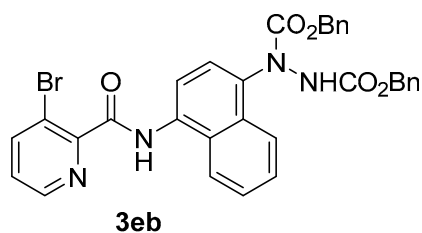
Dibenzyl 1-(4-(picolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3ab^[6d]): pale yellow solid (29.8 mg, 73%), R_f = 0.32 (25% EtOAc in hexane), mp 81.2-83.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.81 (s, 1H), 8.69-8.68 (m, 1H), 8.40 (d, J = 7.94 Hz, 1H), 8.34 (d, J = 7.81 Hz, 1H), 8.10-8.08 (m, 2H), 7.90 (dt, J_1 = 1.24 Hz, J_2 = 7.68 Hz, 1H), 7.78 (s, 1H), 7.58 (t, J = 6.99 Hz, 2H), 7.52-7.49 (m, 2H), 7.29-7.20 (m, 2H), 7.05 (s, 1H), 5.15 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.3, 156.1, 149.7, 148.1, 137.8, 135.7, 135.4, 134.4, 133.0, 130.6, 128.5, 128.2, 128.0, 127.6, 127.0, 126.8, 126.7, 126.6, 126.1, 123.6, 120.8, 118.0, 68.4, 67.8; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{27}\text{N}_4\text{O}_5$: 547.1976, found: 547.1973.



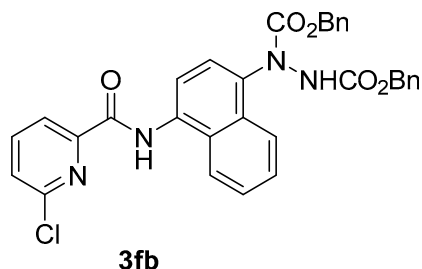
Dibenzyl 1-(4-(5-chloropicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3cb): yellow solid (48.4 mg, 83%), R_f = 0.32 (25% EtOAc in hexane), mp 68.9-70.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.55 (s, 1H), 8.61 (d, J = 2.12 Hz, 1H), 8.33 (d, J = 7.89 Hz, 1H), 8.26 (d, J = 8.33 Hz, 1H), 8.09-8.01 (m, 2H), 7.81-7.79 (m, 3H), 7.59-7.50 (m, 2H), 7.30-7.91 (m, 9H), 7.04 (s, 1H), 5.14 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.5, 156.2, 147.8, 147.2, 137.5, 135.7, 135.6, 135.5, 134.7, 132.7, 130.7, 128.5, 128.3, 128.2, 127.6, 127.0, 126.8, 126.7, 126.0, 123.8, 123.6, 120.7, 118.3, 68.4, 67.8; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{26}\text{ClN}_4\text{O}_5$: 581.1586, found: 581.1584.



Dibenzyl 1-(4-(5-bromopicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3db): pale yellow solid (58.6 mg, 94%), $R_f = 0.32$ (25% EtOAc in hexane), mp 69.4-71.6 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.55 (s, 1H), 8.71 (d, $J = 1.92$ Hz, 1H), 8.32 (d, $J = 7.93$ Hz, 1H), 8.19-8.10 (m, 2H), 8.01 (d, $J = 8.61$ Hz, 1H), 7.94 (d, $J = 7.72$ Hz, 1H), 7.83-7.75 (m, 2H), 7.58-7.49 (m, 2H), 7.26-7.18 (m, 9H), 7.03 (s, 1H), 5.13 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.6, 156.2, 149.4, 148.2, 140.5, 135.7, 135.5, 134.8, 132.6, 130.7, 128.5, 128.3, 128.2, 128.1, 127.6, 127.0, 126.8, 126.7, 126.0, 124.6, 124.0, 123.8, 120.6, 118.3, 68.4, 67.8; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{26}\text{BrN}_4\text{O}_5$: 625.1081, found: 625.1080.

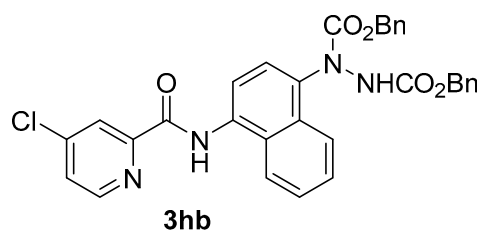


Dibenzyl 1-(4-(3-bromopicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3eb): white solid (41.8 mg, 67%), $R_f = 0.32$ (25% EtOAc in hexane), mp 74.1-75.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.74 (s, 1H), 8.63 (d, $J = 4.05$ Hz, 1H), 8.38 (d, $J = 7.87$ Hz, 1H), 8.10-8.01 (m, 3H), 7.76 (s, 1H), 7.58-7.50 (m, 3H), 7.34-7.72 (m, 10H), 7.05 (s, 1H), 5.15 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.1, 156.1, 146.5, 146.2, 144.5, 135.6, 135.4, 134.4, 132.9, 130.5, 128.5, 128.3, 128.1, 127.6, 126.9, 136.9, 126.6, 126.0, 123.5, 120.7, 120.0, 118.1, 68.4, 67.9; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{26}\text{BrN}_4\text{O}_5$: 625.1081, found: 625.1080.

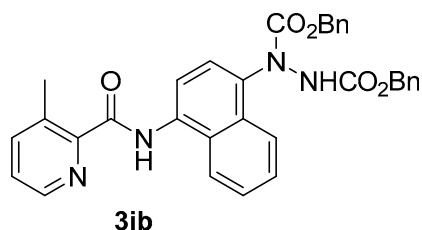


Dibenzyl 1-(4-(6-chloropicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3fb): pale yellow solid (41.9 mg, 72%), $R_f = 0.32$ (25% EtOAc in

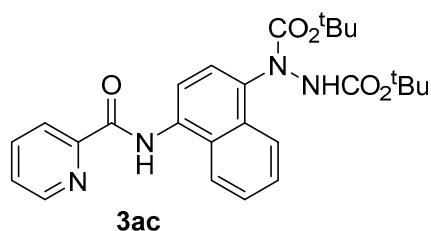
hexane), mp 75.9-77.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.37 (s, 1H), 8.29-8.23 (m, 2H), 8.03 (d, J = 8.56 Hz, 2H), 7.84-7.70 (m, 3H), 7.60 (t, J = 7.05 Hz, 1H), 7.51 (d, J = 7.88 Hz, 2H), 7.28-7.20 (m, 9H), 7.04 (s, 1H), 5.14 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.0, 156.2, 150.2, 150.1, 140.4, 135.6, 135.4, 135.0, 132.5, 130.6, 128.5, 128.3, 128.2, 127.6, 127.5, 127.1, 126.8, 126.0, 123.7, 121.3, 120.8, 118.7, 68.4, 67.8; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{26}\text{ClN}_4\text{O}_5$: 581.1586, found: 581.1585.



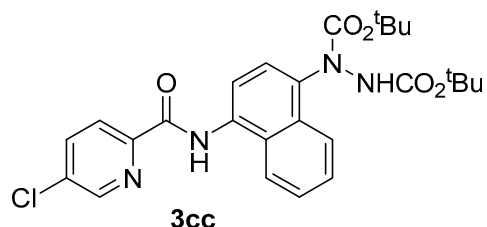
Dibenzyl 1-(4-(4-chloropicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3hb): pale yellow solid (46.7 mg, 80%), R_f = 0.32 (25% EtOAc in hexane), mp 70.5-71.1 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.65 (s, 1H), 8.57 (d, J = 5.24 Hz, 1H), 8.36-8.33 (m, 2H), 8.03 (d, J = 8.66 Hz, 2H), 7.77 (s, 1H), 7.59-7.55 (m, 2H), 7.50 (dd, J_1 = 1.96 Hz, J_2 = 5.16 Hz, 2H), 7.30-7.20 (m, 9H), 7.04 (s, 1H), 5.14 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.1, 156.1, 151.2, 149.0, 146.4, 135.6, 135.4, 134.7, 132.7, 130.6, 128.5, 128.3, 128.2, 127.7, 127.0, 126.9, 126.7, 126.1, 123.6, 123.2, 120.7, 118.1, 68.5, 67.9; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{26}\text{ClN}_4\text{O}_5$: 581.1586, found: 581.1586.



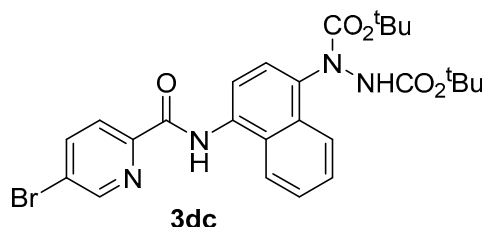
Dibenzyl 1-(4-(3-methylpicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3ib^[6d]): white solid (44.7 mg, 80%), R_f = 0.32 (25% EtOAc in hexane), mp 67.1-69.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.05 (s, 1H), 8.52 (d, J = 3.61 Hz, 1H), 8.35 (d, J = 7.92 Hz, 1H), 8.07 (d, J = 8.73 Hz, 2H), 7.75 (s, 1H), 7.65-7.49 (m, 4H), 7.38 (dd, J_1 = 4.46 Hz, J_2 = 7.72 Hz, 2H), 7.28-7.20 (m, 8H), 7.05 (s, 1H), 5.14 (s, 4H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.8, 156.1, 146.7, 145.5, 141.4, 136.4, 135.7, 135.5, 134.1, 133.5, 130.6, 128.5, 128.3, 128.2, 127.6, 127.1, 126.9, 126.5, 126.2, 123.5, 121.1, 117.8, 68.4, 67.8, 20.8; HRMS (ESI^+) m/z $[\text{M} + \text{K}]^+$ calcd for $\text{C}_{33}\text{H}_{28}\text{N}_4\text{O}_5\text{K}$: 599.1691, found: 599.1692.



Di-*tert*-butyl 1-(4-(picolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3ac^[6d]): pale yellow solid (45.8 mg, 95%), $R_f = 0.32$ (25% EtOAc in hexane), mp 215.5-216.8 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.80 (s, 1H), 8.69 (d, $J = 4.28$ Hz, 1H), 8.43 (d, $J = 7.29$ Hz, 1H), 8.34 (d, $J = 7.77$ Hz, 1H), 8.10-8.08 (m, 2H), 7.92 (t, $J = 7.26$ Hz, 1H), 7.73 (s, 1H), 7.59-7.57 (m, 2H), 7.51 (t, $J = 6.04$ Hz, 1H), 7.11 (s, 1H), 1.48-1.25 (m, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.2, 155.5, 149.9, 148.1, 137.8, 135.6, 132.4, 130.7, 126.6, 126.3, 123.9, 122.5, 120.7, 118.0, 82.0, 81.3, 28.2, 28.0; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{31}\text{N}_4\text{O}_5$: 479.2289, found: 479.2288.

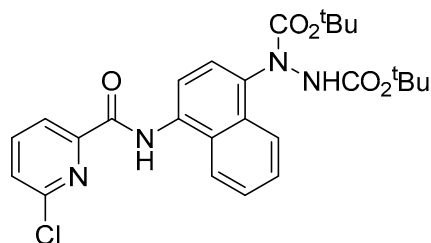


Di-*tert*-butyl 1-(4-(5-chloropicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3cc): white solid (25.8 mg, 50%), $R_f = 0.32$ (25% EtOAc in hexane), mp 170.1-172.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.56 (s, 1H), 8.65 (d, $J = 2.12$ Hz, 1H), 8.38 (d, $J = 7.54$ Hz, 1H), 8.31 (d, $J = 8.32$ Hz, 1H), 8.06-8.04 (m, 2H), 7.92 (dd, $J_1 = 2.17$ Hz, $J_2 = 8.33$ Hz, 1H), 7.22 (s, 1H), 7.62-7.57 (m, 2H), 7.00 (s, 1H), 1.49-1.30 (m, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.3, 155.4, 148.0, 147.2, 137.5, 135.7, 135.5, 132.0, 130.7, 126.7, 126.6, 126.4, 125.9, 125.5, 123.9, 123.6, 120.6, 118.2, 82.1, 81.4, 29.6, 28.2, 28.0; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{30}\text{ClN}_4\text{O}_5$: 513.1899, found: 513.1901.



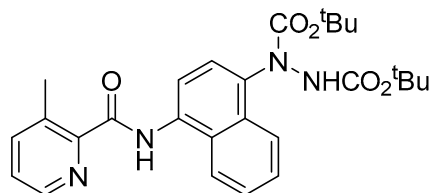
Di-*tert*-butyl 1-(4-(5-bromopicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3dc): pale yellow solid (29.4 mg, 53%), $R_f = 0.32$ (25% EtOAc in hexane), mp 182.7-184.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.57 (s, 1H), 8.77 (d, $J =$

1.95 Hz, 1H), 8.38 (d, $J = 7.58$ Hz, 1H), 8.24 (d, $J = 8.41$ Hz, 1H), 8.09-8.04 (m, 3H), 7.73 (s, 1H), 7.62-7.57 (m, 2H), 6.99 (s, 1H), 1.55-1.30 (m, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.5, 154.8, 149.4, 148.4, 140.5, 135.7, 132.0, 130.7, 126.7, 126.4, 125.4, 124.5, 123.9, 120.6, 118.2, 82.1, 81.4, 29.6, 28.2, 28.0; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{30}\text{BrN}_4\text{O}_5$: 557.1394, found: 557.1395.



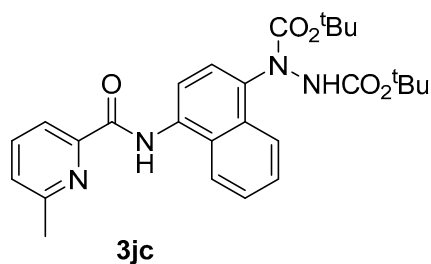
3fc

Di-*tert*-butyl 1-(4-(6-chloropicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3fc): pale yellow solid (34.8 mg, 68%), $R_f = 0.32$ (25% EtOAc in hexane), mp 207.8-209.6 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.39 (s, 1H), 8.33 (d, $J = 7.78$ Hz, 1H), 8.27 (d, $J = 7.35$ Hz, 1H), 8.05 (d, $J = 8.80$ Hz, 2H), 7.90 (t, $J = 7.79$ Hz, 1H), 7.73 (s, 1H), 7.64-7.57 (m, 2H), 7.55 (d, $J = 7.78$ Hz, 1H), 7.05 (s, 1H), 1.48-1.25 (m, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.9, 155.5, 154.7, 150.4, 150.1, 140.4, 136.0, 131.9, 130.7, 127.4, 127.0, 126.6, 125.3, 123.9, 121.2, 120.7, 118.8, 82.1, 82.5, 28.2, 28.0; HRMS (ESI^+) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{29}\text{ClN}_4\text{O}_5\text{Na}$: 535.1719, found: 535.1724.

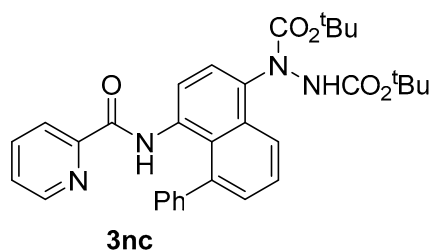


3ic

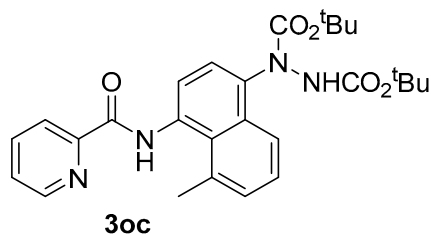
Di-*tert*-butyl 1-(4-(3-methylpicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3ic): yellow solid (39.5 mg, 80%), $R_f = 0.32$ (25% EtOAc in hexane), mp 197.0-198.1 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.04 (s, 1H), 8.54-8.53 (m, 1H), 8.37 (d, $J = 7.09$ Hz, 1H), 8.10-8.07 (m, 2H), 7.70-7.65 (m, 2H), 7.59-7.55 (m, 2H), 7.40 (dd, $J_1 = 4.58$ Hz, $J_2 = 7.70$ Hz, 1H), 7.03 (s, 1H), 2.85 (s, 3H), 1.48-1.25 (m, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 155.4, 146.8, 145.5, 141.4, 136.3, 135.2, 132.8, 130.7, 127.0, 126.4, 126.2, 126.2, 123.7, 121.0, 118.0, 82.0, 81.3, 28.2, 28.0, 20.8; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{33}\text{N}_4\text{O}_5$: 493.2445, found: 493.2446.



Di-*tert*-butyl 1-(4-(6-methylpicolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3jc): yellow solid (38.7 mg, 78%), $R_f = 0.32$ (25% EtOAc in hexane), mp 201.3-203.8 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.83 (s, 1H), 8.41 (d, $J = 7.48$ Hz, 1H), 8.15 (d, $J = 7.62$ Hz, 1H), 8.09-8.07 (m, 2H), 7.81 (t, $J = 7.68$ Hz, 1H), 7.73 (s, 1H), 7.37 (d, $J = 7.65$ Hz, 1H), 7.06 (s, 1H), 2.70 (s, 3H), 1.48-1.30 (m, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.4, 157.2, 155.4, 149.1, 137.9, 132.5, 130.8, 126.9, 126.4, 126.3, 123.9, 120.7, 119.6, 118.1, 82.0, 81.4, 28.2, 28.0, 24.4; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{32}\text{N}_4\text{O}_5$: 493.2445, found: 493.2448.



Di-*tert*-butyl 1-(5-phenyl-4-(picolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate (3nc): yellow solid (20.9 mg, 38%), $R_f = 0.32$ (25% EtOAc in hexane), mp 201.5-203.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.62 (s, 1H), 8.29 (d, $J = 6.17$ Hz, 1H), 8.16 (d, $J = 3.91$ Hz, 1H), 8.07 (d, $J = 7.73$ Hz, 2H), 7.77-7.73 (m, 2H), 7.54 (t, $J = 7.21$ Hz, 1H), 3.39-3.26 (m, 4H), 7.19 (s, 1H), 7.02-6.98 (m, 2H), 1.56-1.34 (m, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.9, 154.9, 149.6, 147.3, 142.4, 138.0, 137.0, 136.2, 133.0, 132.1, 130.8, 129.1, 128.1, 126.8, 125.7, 125.5, 123.2, 121.8, 82.1, 81.4, 29.6, 28.2, 28.1; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{35}\text{N}_4\text{O}_5$: 555.2602, found: 555.2603.



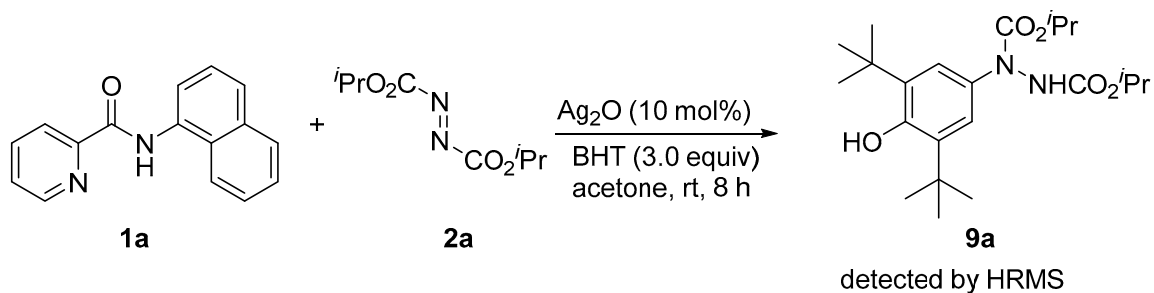
Di-*tert*-butyl 1-(5-methyl-4-(picolinamido)naphthalen-1-yl)hydrazine-1,2-

dicarboxylate (3oc): yellow solid (40.8 mg, 83%), $R_f = 0.32$ (25% EtOAc in hexane), mp 202.5-204.7 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.65 (s, 1H), 8.65 (d, $J = 4.43$ Hz, 1H), 8.35 (d, $J = 7.82$ Hz, 1H), 7.94-7.88 (m, 2H), 7.33-7.32 (m, 1H), 7.51-7.48 (m, 1H), 7.39 (t, $J = 7.15$ Hz, 1H), 7.29 (d, $J = 6.91$ Hz, 1H), 7.03 (s, 1H), 2.99 (s, 3H), 1.47-1.43 (m, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.2, 155.3, 154.9, 149.9, 148.1, 137.7, 137.0, 133.3, 133.0, 132.3, 130.3, 128.5, 126.5, 126.1, 125.2, 122.1, 82.0, 81.3, 28.2, 28.0, 25.1; HRMS (ESI^+) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{33}\text{N}_4\text{O}_5$: 493.2445, found: 493.2443.

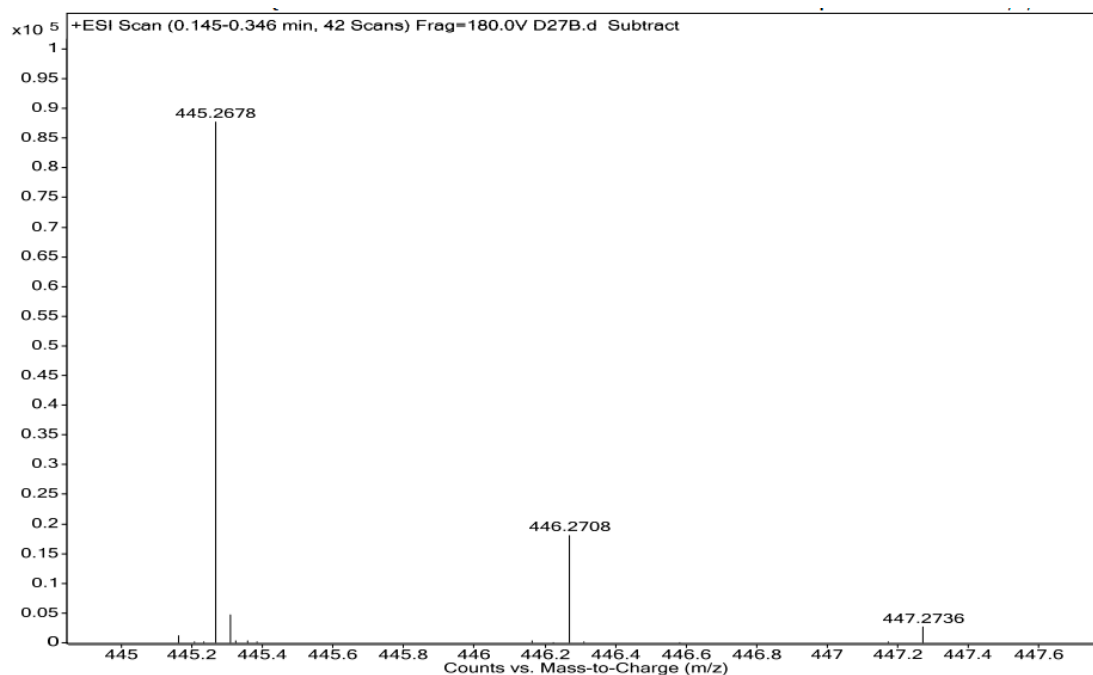
5 References

[1] R. Shang, L. Ilies, E. Nakamura, *J. Am. Chem. Soc.* **2015**, *137*, 7660-7663.

6 The Experiment of Trapping the Intermediate Radical



HRMS (ESI^+) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{38}\text{N}_2\text{O}_5$: 445.2673, found: 445.2678.



7. Copies of ^1H , ^{13}C NMR Spectra for the Products

