

Supporting Information

Iron(III)-Promoted Oxidative Coupling of Naphthylamines: Synthetic and Mechanistic Investigations

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1. General information.

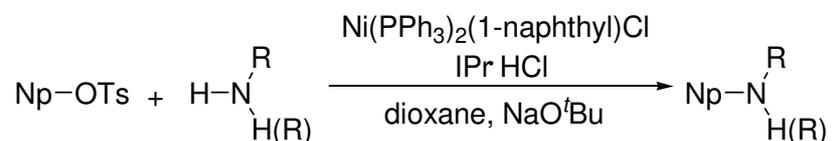
^1H and ^{13}C NMR spectra were recorded on a BRUKER AVANCE 400 spectrometer. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), and coupling constant (Hz). Mass spectra were obtained on a Bruker Daltonics Inc. APEXII FT-ICR. Melting points were measured with a X-4 micro melting-point apparatus and uncorrected.

All reactions were carried out with oven-dried glassware in air unless stated otherwise. Start materials (naphthylamines) were synthesized according to the previously published procedure.¹ Other reagents and solvents were purchased commercially and used without further purification. All yields refer to isolated yields (average of two run) of compounds estimated to be > 95% pure as determined by ^1H NMR. The known compounds were partly characterized by melting points, MS, ^1H NMR and compared to authentic samples or the literature data. New compounds were characterized by ^1H NMR, ^{13}C NMR, and HRMS.

2. Experimental procedures

2.1 General procedure for the synthesis of naphthylamines¹

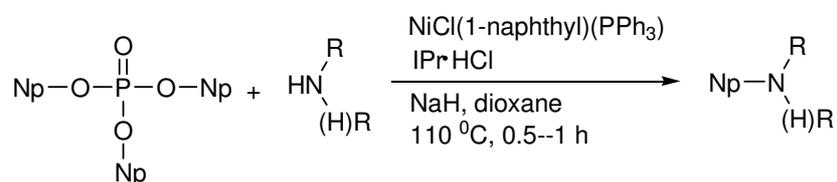
Method A:^{1a}



An oven-dried 100-mL three-necked flask was charged with NaO^tBu (1.6 mmol, 154 mg), Ni(PPh₃)₂(1-naphthyl)Cl (5 mol% relative to the tosylate, 37 mg), and IPr·HCl (10 mol% relative to the tosylate, 42 mg). The 1- or 2-naphthyl tosylate (1 mmol) and the amine (1.5 mmol) were added at this time if solid. The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. The

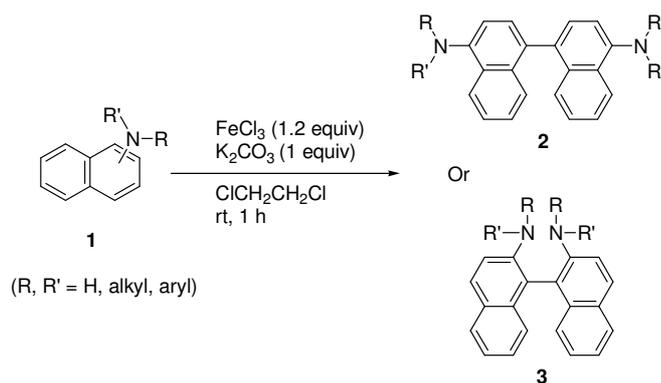
amine (1.5 mmol) was added at this time via syringe if liquid. Then dried dioxane (5 mL) was added via syringe. The reaction mixture was heated at an oil bath of 110 °C for 30 min. The reaction mixture is allowed to cool to room temperature and filtered through a pad of silica gel that was washed with ethyl acetate (20 mL × 3). Then the combined organic phases were evaporated under reduced pressure and the residue purified by column chromatography.

Method B:^{1b}



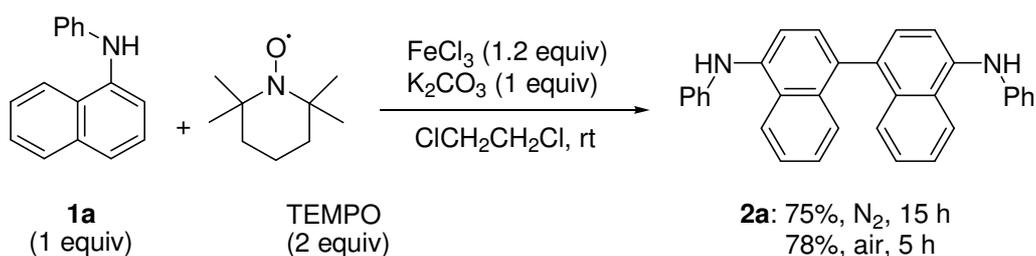
An oven-dried 50-mL three-necked flask was charged with NaH (2 mmol), NiCl(1-naphthyl)(PPh₃)₂ (5 mol% for amine), and IPr·HCl (10 mol% for amine). The aryl phosphate (1 mmol) and the amine (1 mmol, if solid) were added at this time. The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. The amine (1 mmol, if liquid) was added via syringe at this time, followed by dried dioxane (10 mL). The reaction mixture was heated at 110 °C for 30–60 min and then allowed to cool to room temperature, and filtered through a silica-gel pad that was washed with ethyl acetate (10 mL × 3). The combined organic phases were evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give the desired product.

2.2 General procedure for the FeCl₃-mediated oxidative coupling of 1- and 2-naphthylamines



An oven-dried 50 mL three necked flask was charged with K_2CO_3 (1 mmol, 0.14 g, finely ground), naphthylamine **1** (1 mmol). Then 1,2-dichloroethane (6 mL) was added via syringe, the mixture was stirred for 5 min at room temperature, and then $FeCl_3$ (1.2 mmol, 0.19 g) was added for one time. The reaction mixture continued to be stirred for 1 h at room temperature. After the start material were consumed completely (monitored by TLC), 1 mL of Et_3N was added, the reaction mixture is allowed to stirred for another 5 min and filtered through a pad of silica gel that was washed with ethyl acetate (20 mL \times 3). Then the combined organic phases were evaporated under reduced pressure and the residue purified by column chromatography.

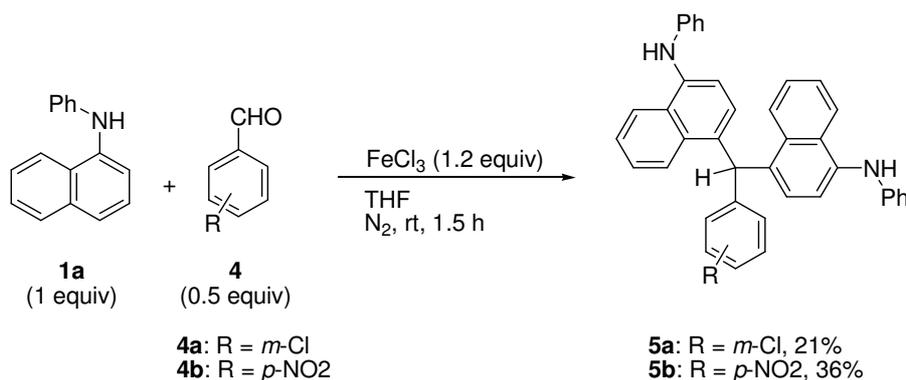
2.3 The effect of radical inhibitors on $FeCl_3$ -mediated oxidative couplings



An oven-dried 100-mL three-necked flask was charged with *N*-phenyl-1-naphthylamine **1a** (1 mmol, 220 mg), K_2CO_3 (1 mmol, 0.14g), TEMPO (2 mmol, 0.32 g), $FeCl_3$ (1.2 mmol, 0.19g), and then 1,2-dichloroethane (6 mL) was added via syringe. The mixture was stirred at room temperature for 5 hours and then filtered through a pad of silica gel that was washed with ethyl acetate (20 mL \times 3). Then the

combined organic phases were evaporated under reduced pressure and the residue purified by column chromatography on silicagel with petroleum/ethyl acetate to give the desired product **2a** (0.17 g (78%) in air and 0.16 g (75%) under N₂ atmosphere, respectively).

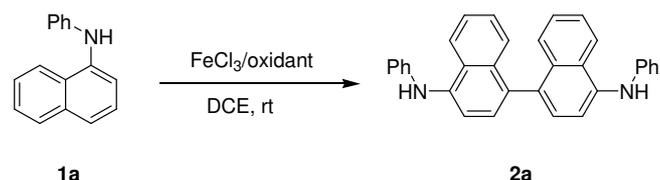
2.4 The *N*-phenyl-1-naphthylamine/iron(III) chloride system reacts with aromatic aldehydes



An oven-dried 100-mL three-necked flask was charged with *N*-phenyl-1-naphthylamine **1a** (2 mmol, 440 mg), FeCl₃ (2.4 mmol, 400mg), and 3-chlorobenzaldehyde **4a** (1 mmol, 140 mg) or 4-nitrobenzaldehyde **4b** (1 mmol, 151 mg). The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice, followed by the addition of dried THF (10 mL). The reaction mixture was stirred at room temperature for 4 h, and filtered through a pad of silica gel that was washed with ethyl acetate (20 mL × 3). Then the combined organic phases were evaporated under reduced pressure and the residue purified by column chromatography on silica gel with petroleum/ethyl acetate to give the desired product (**5a**, 117 mg, 21% and **5b**, 205mg, 36%, respectively).

2.5 FeCl₃-catalyzed oxidative couplings of 1- and 2-naphthylamines

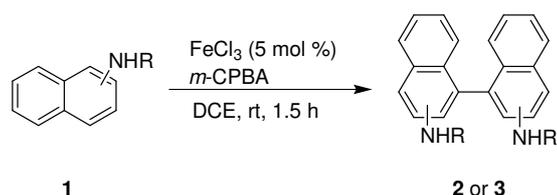
2.5.1 Screening of conditions

Table S1. Screening of conditions for catalytic oxidative couplings using FeCl₃ as catalyst^a

run	FeCl ₃ (equiv)	oxidant (equiv)	time (h)	isolated yield
1	FeCl ₃ (0.3)	none	24	25%
2	FeCl ₃ (0.3)	BPO ^b (2)	24	18%
3	FeCl ₃ (0.3)	O ₂	24	20%
4	FeCl ₃ (0.3)	DDQ ^c (2)	24	13%
5	FeCl ₃ (0.3)	DTBP ^d (2)	24	19%
6	FeCl ₃ (0.3)	<i>m</i> -CPBA ^e (2)	0.5	76%
7	FeCl ₃ (0.1)	<i>m</i> -CPBA (2)	1	75%
8	FeCl ₃ (0.1)	<i>m</i> -CPBA (1)	1	74%
9	FeCl ₃ (0.05)	<i>m</i> -CPBA (1)	1.5	75%
10	FeCl ₃ (0.05)	<i>m</i> -CPBA (0.5)	15	45%
11	none	<i>m</i> -CPBA (1)	15	NR ^f

^a Reagents: **1a** (1 mmol), DCE (6 mL). ^b BPO: benzoyl peroxide. ^c DDQ: 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. ^d DTBP: di-*tert*-butyl peroxide. ^e *m*-CPBA: 3-chloroperbenzoic acid. ^f no reaction occurred.

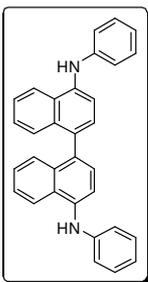
2.5.2 General procedure for the FeCl₃-catalyzed oxidative coupling of 1- and 2-naphthylamines



An oven-dried 50-mL three necked flask was charged with the starting material **1** (1 mmol), FeCl₃ (5 mol % relative to compound **1**, 8.5 mg), and 1,2-dichloroethane (6 mL). The resulting mixture was stirred at room temperature, to which a solution of *m*-CPBA (1 mmol, 0.17 g) in 1,2-dichloroethane (5 mL) was added dropwise. The reaction mixture was stirred for another 1 h, and filtered through a pad of silica gel that was washed with ethyl acetate (20 mL × 3). Then the combined organic phases were evaporated under reduced pressure and the residue purified by column chromatography.

3. Characterization data for compounds

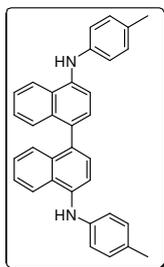
***N,N'*-Diphenyl-(1,1'-binaphthyl)-4,4'-diamine (2a)** (CAS Registry No. 51927-78-7).



Colorless solid: mp 181–182 °C (lit.² mp 183–184 °C). ¹H NMR (400 MHz, CDCl₃): δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.54–7.40 (m, 8H), 7.35–7.28 (m, 6H), 7.12 (d, *J* = 8.0 Hz, 4H), 6.97 (t, *J* = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 144.66, 138.54, 134.28, 133.54, 129.56, 128.39, 127.70, 127.51, 126.29, 125.74, 122.01, 120.92, 117.86, 115.39. MS

(EI): *m/z* 436 (M⁺).

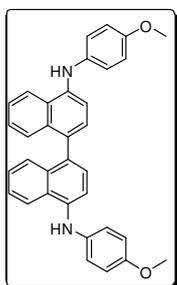
***N,N'*-Bis(*p*-tolyl)-(1,1'-binaphthyl)-4,4'-diamine (2b)** (CAS Registry No. 174081-58-4).



Colorless solid: mp 170–171 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.55–7.35 (m, 8H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.22–7.02 (m, 8H), 2.35 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 140.82, 138.51, 138.42, 133.67, 130.61, 129.50, 127.82, 126.93, 126.39,

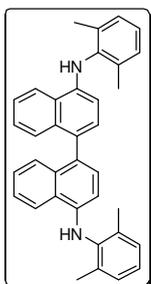
125.62, 125.03, 121.15, 118.53, 113.41, 20.25. MS (EI): *m/z* 464 (M⁺).

***N,N'*-Bis(*p*-anisyl)-(1,1'-binaphthyl)-4,4'-diamine (2c)** (CAS Registry No. 879505-49-4).



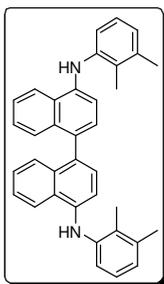
Colorless solid: mp 203–204 °C (lit.³ mp 193 °C). ¹H NMR (400 MHz, CDCl₃): δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.61–7.40 (m, 4H), 7.40–7.25 (m, 4H), 7.25–7.03 (m, 4H), 6.92 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 6H). MS (EI): *m/z* 496 (M⁺).

***N,N'*-Bis(2,6-dimethylphenyl)-(1,1'-binaphthyl)-4,4'-diamine (2d)** (CAS Registry No. 879505-47-2).



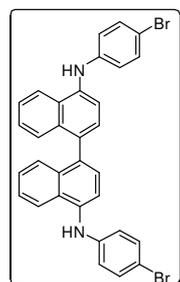
Colorless solid: mp 303–305 °C (lit.³ mp 274 °C). ¹H NMR (400 MHz, CDCl₃): δ 8.24–8.14 (m, 2H), 7.58–7.45 (m, 4H), 7.37–7.29 (m, 2H), 7.26–7.06 (m, 8H), 6.33 (br. s, 2H), 2.30 (s, 12H). MS (EI): *m/z* 492 (M⁺).

***N,N'*-Bis(2,3-dimethylphenyl)-(1,1'-binaphthyl)-4,4'-diamine (2e)** (CAS Registry No. 879505-48-3).



Colorless solid: mp 174–175 °C (lit.³ mp 279 °C). ¹H NMR (400 MHz, CDCl₃): δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.57–7.42 (m, 4H), 7.38–7.28 (m, 4H), 7.09 (t, *J* = 7.5 Hz, 2H), 7.05–6.96 (m, 4H), 6.95 (d, *J* = 7.2 Hz, 2H), 5.90 (br. s, 2H), 2.40 (s, 6H), 2.30 (s, 6H). MS (EI): *m/z* 492 (M⁺).

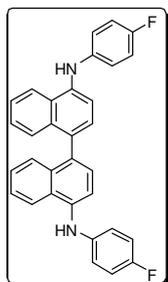
***N,N'*-Bis(4-bromophenyl)-(1,1'-binaphthyl)-4,4'-diamine (2f)**.



Colorless solid: mp 85–87 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.10 (d, *J* = 8.7 Hz, 2H), 7.53–7.45 (m, 6H), 7.45–7.30 (m, 8H), 6.95 (d, *J* = 8.5 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 143.29, 137.21,

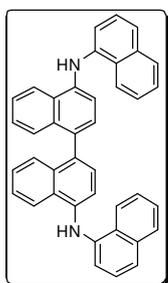
133.65, 131.80, 127.68, 127.37, 126.89, 125.90, 125.45, 121.51, 118.54, 115.9, 112.22. HRMS: calcd. for $C_{32}H_{22}N_2Br_2$: 592.0150 [M^+]; found: 592.0146.

***N,N'*-Bis(4-fluorophenyl)-(1,1'-binaphthyl)-4,4'-diamine (2g)** (CAS Registry No. 879505-50-7).



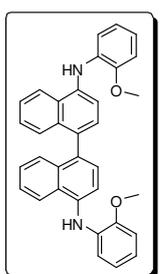
Colorless solid: mp 155–156 °C (lit.³ oil). 1H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, $J = 8.6$ Hz, 2H), 7.54–7.45 (m, 4H), 7.41–7.30 (m, 6H), 7.16–7.08 (m, 4H), 7.03 (t, $J = 8.4$ Hz, 4H). MS (EI): m/z 472 (M^+).

***N,N'*-Di(1-naphthyl)-(1,1'-binaphthyl)-4,4'-diamine (2h).**



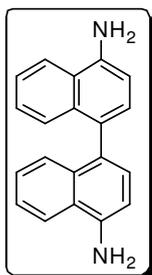
Colorless solid: mp 220–222 °C. 1H NMR (400 MHz, $CDCl_3$): δ 8.19 (t, $J = 9.9$, 4H), 7.92 (d, $J = 7.7$ Hz, 2H), 7.61–7.45 (m, 10H), 7.45–7.35 (m, 6H), 7.17 (dd, $J = 13.2, 7.6$ Hz, 4H). HRMS: calcd. for $C_{40}H_{28}N_2$: 536.2252 [M^+]; found: 536.2261.

***N,N'*-Bis(o-anisyl)-(1,1'-binaphthyl)-4,4'-diamine (2i).**



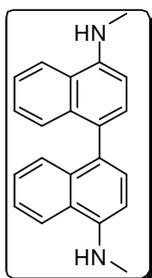
Yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 7.5$ Hz, 2H), 7.52 (t, $J = 8.3$ Hz, 4H), 7.46 (d, $J = 7.9$ Hz, 2H), 7.34 (t, $J = 7.6$ Hz, 2H), 7.25–7.22 (m, 2H), 7.03–6.96 (m, 2H), 6.94–6.87 (m, 4H), 4.01 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.95, 137.46, 133.73, 133.48, 133.12, 127.74, 127.55, 126.87, 125.63, 125.11, 121.62, 120.52, 119.64, 115.14, 110.14, 55.30. HRMS: calcd. for $C_{44}H_{48}N_2$: 496.2151 [M^+]; found: 496.2157.

4,4'-Diamino-1,1'-binaphthalene (2j) (CAS Registry No. 481-91-4).



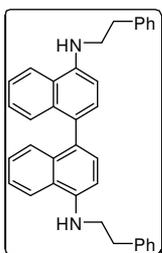
Brown solid: mp 203–204 °C (lit.⁴ mp 202 °C). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.32 (t, *J* = 7.0 Hz, 2H), 7.23–7.14 (m, 4H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.78 (d, *J* = 7.6 Hz, 2H), 5.86 (br. s, 4H). MS (EI): 284 m/z (M⁺)

***N,N'*-Dimethyl-(1,1'-binaphthyl)-4,4'-diamine (2k)** (CAS Registry No. 36101-09-4).⁵



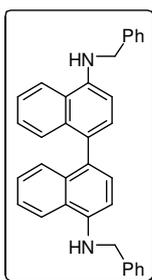
Colorless solid: mp 127–128 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.51–7.36 (m, 6H), 7.27 (t, *J* = 7.5 Hz, 2H), 6.75 (d, *J* = 7.7 Hz, 2H), 4.63 (br. s, 2H), 3.11 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 141.68, 133.46, 129.68, 128.24, 127.14, 125.43, 124.68, 123.31, 119.66, 106.01, 31.86. MS (EI): m/z 312(M⁺).

***N,N'*-Bis(phenylethyl)-(1,1'-binaphthyl)-4,4'-diamine (2l)**.



Colorless solid: mp 197–198 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.17–7.91 (m, 2H), 7.56–7.43 (m, 4H), 7.43–7.20 (m, 16H), 3.73 (t, *J* = 7.3 Hz, 4H), 3.27 (t, *J* = 7.3, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 142.41, 139.39, 134.22, 128.99, 128.88, 127.77, 126.73, 125.76, 124.76, 123.70, 120.01, 104.95, 45.73, 35.53. MS (EI): m/z 492 (M⁺). HRMS: calcd. for C₃₆H₃₂N₂: 492.2565 [M⁺]; found: 492.2572.

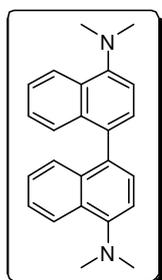
***N,N'*-Dibenzyl-(1,1'-binaphthyl)-4,4'-diamine (2m)**.



Colorless solid: mp 171–172 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 4H), 7.44–7.37 (m, 8H), 7.37–7.28 (m, 4H), 7.26–7.24 (m, 2H), 6.78 (d, *J* = 6.4 Hz, 2H), 4.57 (s, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 142.50, 139.10, 134.17, 129.02, 128.90,

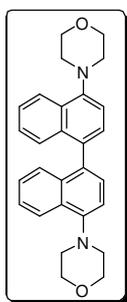
128.10, 127.82, 127.65, 125.80, 124.80, 123.60, 120.14, 105.08, 49.11. HRMS: calcd. for $C_{34}H_{28}N_2$: 464.2252 [M^+]; found: 464.2259.

***N,N,N',N'*-Tetramethyl-1,1'-naphthidine (2n)** (CAS Registry No. 34614-42-1).



Colorless solid: mp 127–128 °C (lit.⁶ mp124–126). 1H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, $J = 8.2$ Hz, 2H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.44–7.38 (m, 4H), 7.30–7.24 (m, 2H), 7.19 (d, $J = 7.3$ Hz, 2H), 3.00 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.83, 133.63, 127.57, 126.78, 125.41, 124.88, 123.58, 113.36, 45.04. MS (EI): m/z 340 (M^+).

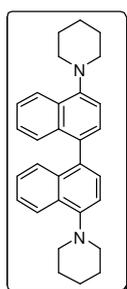
4,4'-dimorpholino-1,1'-binaphthyl (2o).



Colorless solid: mp 236–237 °C. 1H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, $J = 8.5$ Hz, 2H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.41 (d, $J = 7.8$ Hz, 4H), 7.28 (t, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 7.5$ Hz, 2H), 4.10–4.05 (m, 8H), 3.28–3.20 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.23, 134.44, 134.38, 128.88, 128.12, 127.46, 126.02, 125.46, 123.67, 114.47, 67.67, 53.77.

HRMS: calcd. for $C_{28}H_{28}N_2O_2$: 424.2151 [M^+]; found: 424.2155.

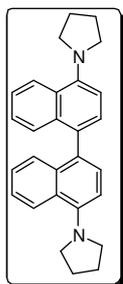
4,4'-di(piperidin-1-yl)-1,1'-binaphthyl (2p) (CAS Registry No. 1027919-53-4).



Colorless solid: mp174–175 °C. 1H NMR (400 MHz, $CDCl_3$): δ 8.35–8.25 (m, 2H), 7.50–7.30 (m, 6H), 7.30–7.20 (m 2H), 7.20–7.07 (m, 2H), 3.45–3.01 (m, 8H), 1.98–1.80 (m, 8H), 1.80–1.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.68, 134.35, 133.61, 129.09, 128.06, 127.27, 125.60, 124.96, 123.93, 114.16, 54.81, 26.79, 24.73. HRMS: calcd. For

$C_{30}H_{32}N_2$:420.2565 [M^+]; found: 420.2571.

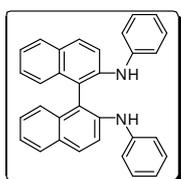
4,4'-di(pyrrolidin-1-yl)-1,1'-binaphthyl (2q) (CAS Registry No. 879505-44-9).



Colorless solid: mp190–191 °C (lit.³ mp 177 °C). ¹H NMR (400 MHz, CDCl₃): δ 8.32 (d, *J* = 8.5 Hz, 2H), 7.46–7.38 (m, 4H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.28–7.23 (m, 2H), 7.10 (d, *J* = 7.2 Hz, 2H), 3.55–3.40 (m, 8H), 2.15–2.0 (m, 8H). MS (EI): *m/z* 392 (M⁺).

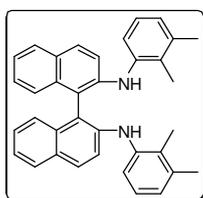
***N,N'*-Diphenyl-(1,1'-binaphthyl)-2,2'-diamine (3a)** (CAS Registry No.

17704-02-8).



Colorless solid: mp164–165 °C (lit.⁶ mp162.5–164 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, *J* = 9.0 Hz, 2H), 7.85 (d, *J* = 8.1 Hz), 7.68 (d, *J* = 9.0 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.25–7.13 (m, 8H), 7.00–6.88 (m, 6H), 5.8 (br. s, 2H). MS (EI): *m/z* 436 (M⁺).

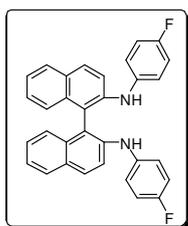
***N,N'*-Bis(2,3-dimethylphenyl)-1,1'-binaphthyl-2,2'-diamine (3b)**.



Colorless solid: mp186–188 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.84–7.77 (m, 4H), 7.31–7.22 (m, 8H), 7.07–6.97 (m, 4H), 6.93–6.87 (m, 2H), 2.24 (d, *J* = 2.5 Hz, 6H), 1.90 (d, *J* = 2.6 Hz, 6H); ¹³C

NMR (100 MHz, CDCl₃): δ 142.11, 140.06, 137.92, 133.97, 130.84, 129.33, 128.68, 128.22, 126.96, 125.90, 125.70, 124.11, 122.77, 121.03, 116.53, 113.99, 20.56, 13.63. HRMS: calcd. for C₃₆H₃₂N₂: 492.2565 [M⁺]; found: 492.2571.

***N,N'*-Bis(4-fluorophenyl)-(1,1'-binaphthyl)-2,2'-diamine (3c)**.

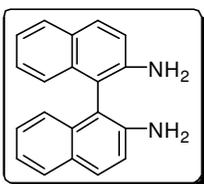


Yellow solid: mp 228–230 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.86 (t, *J* = 9.9 Hz, 4H), 7.51 (d, *J* = 9.0 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.29–7.22 (m, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.98–6.86 (m, 8H); ¹³C

NMR (100 MHz, CDCl₃): δ 160.20, 157.79, 141.28, 138.61, 134.07, 129.76, 129.44, 128.43, 127.31, 124.43, 123.60, 122.99 (d, *J* = 7.9 Hz), 117.37, 116.17, 115.95, 115.69. HRMS: calcd. for C₃₂H₂₂N₂F₂: 472.1751 [M⁺]; found:

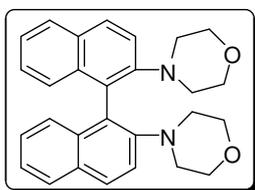
472.1757.

1,1'-binaphthyl-2,2'-diamine (3e) (CAS Registry No. 4488-22-6).



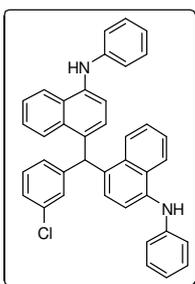
Colorless solid: mp 189–190 °C (lit.⁷ mp 187.5–189). ¹H NMR (400 MHz, CDCl₃): δ 7.83–7.78 (m, 4H), 7.27–7.18 (m, 4H), 7.16 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 3.42 (br.s, 4H). MS (EI): *m/z* 284 (M⁺).

2,2'-dimorpholino-1,1'-binaphthyl (3g).



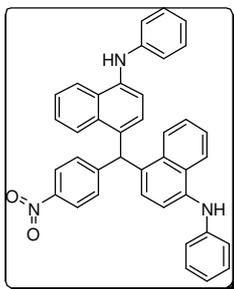
Colorless solid: mp 78–89 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.29 (d, *J* = 8.6 Hz, 2H), 7.78 (t, *J* = 9.4 Hz, 4H), 7.56 (t, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 3.98–3.93 (m, 8H), 3.22–3.17 (m, 8H); ¹³C NMR (100 MHz, CDCl₃): δ 145.72, 131.,55, 130.61, 127.40,127.29,126.76,124.61, 123.82, 123.55, 119.10, 66.80, 51.34. HRMS: calcd. for C₂₈H₂₈N₂O₂: 424.2151 [M⁺]; found: 424.2157.

(3-Chlorophenyl)bis[1-(4-phenylaminonaphthyl)]methane (5a).



Colorless solid: mp 243–245 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.48–7.38 (m, 4H), 7.30–7.18 (m, 9H), 7.10–6.95 (m, 5H), 6.95–6.87 (m, 2H), 6.87–6.79 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 146.16, 144.69, 138.33, 134.60, 133.91, 132.81, 130.02, 129.88, 129.48, 128.36, 128.17, 126.96, 126.78, 125.59, 124.78, 122.61, 120.72, 117.70, 115.18, 48.96. HRMS: calcd. for C₃₉H₂₉N₂Cl: 560.2019 [M⁺]; found:560.2026.

(4-nitrophenyl)bis[1-(4-phenylaminonaphthyl)]methane (5b).



Yellow solid: mp 163–165 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.16 (d, $J = 8.6$ Hz, 2 H), 8.13 (d, $J = 8.6$ Hz, 2H), 7.92 (d, $J = 8.4$ Hz, 2H), 7.48 (t, $J = 8.4$ Hz, 2H), 7.43 (t, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.28–7.20 (m, 8H), 7.01 (d, $J = 7.6$ Hz, 4H), 6.97–6.88 (m, 3H), 6.18 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 151.44, 146.23, 143.75, 138.19, 132.18, 132.09, 130.13, 128.88, 127.63, 127.57, 126.34, 125.11, 123.91, 123.30, 122.01, 120.38, 117.35, 113.93, 48.43. MS (EI): m/z 571 (M^+). HRMS: calcd. for $\text{C}_{39}\text{H}_{29}\text{N}_3\text{O}_2$: 571.2260 [M^+]; found: 571.2266.

4. References

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5. Copies of ^1H and ^{13}C NMR spectra for compounds

