

Distinctive Reactivity of *N*-benzylidene-[1,1'-biphenyl]-2-amines in Photoredox Catalysis

Shrikant D. Tambe, Kwan Hong Min, Naeem Iqbal, Eun Jin Cho*

Department of Chemistry, Chung-Ang University, 84 Heukseok-ro, Dongjak-gu

Seoul 06974, Republic of Korea

E-mail: ejcho@cau.ac.kr

Supporting Information

| | |
|---|------|
| General Considerations | S-2 |
| Analytic Data for Synthesized Compounds | S-3 |
| NMR Spectra (¹H NMR and ¹³C NMR) | S-16 |

General Considerations

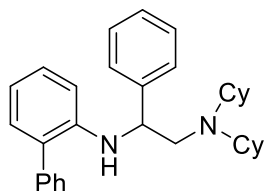
General information

All other reagents required for the syntheses of diamines **2** and **3** were purchased from Sigma-Aldrich, Alfa Aesar, TCI, or Acros Organics. Flash column chromatography was performed using Zeochem silica gel 60 (60–200 mesh). EvoluChem LEDs (blue and 455 nm).

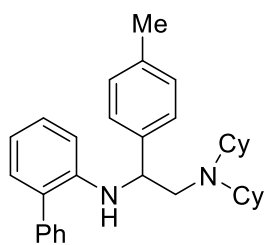
General analytical information

The synthesized diamines **2** and **3** were characterized using ^1H NMR, ^{13}C NMR, and FT-IR spectroscopies. NMR spectra were recorded on a Varian 600 MHz instrument (600 MHz for ^1H NMR and 151 MHz for ^{13}C NMR). Copies of ^1H and ^{13}C NMR spectra are included at the end of the Supporting Information. ^1H NMR chemical shifts are reported in parts per million (ppm) relative to residual chloroform (7.26 ppm) in the deuterated solvent. $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra are reported in ppm relative to deuteriochloroform (77.23 ppm). Coupling constants were reported in Hz. FT-IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer (ThermoFisher). Mass spectral data of all unknown compounds were acquired at the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high-resolution mass spectrometer. A quadrupole mass analyzer was used for HRMS measurements. Melting points were recorded on a Stuart SMP30 apparatus.

Analytic Data for Synthesized Compounds

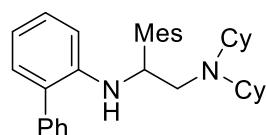


N1-([1,1'-biphenyl]-2-yl)-N2,N2-dicyclohexyl-1-phenylethane-1,2-diamine **2a**: white solid (72%); mp 132-137 °C; **¹H NMR (600 MHz, CDCl₃)** δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.48 – 7.44 (m, 4H), 7.40 – 7.34 (m, 3H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.02 (dd, *J* = 8.2, 7.4 Hz, 1H), 6.73 (dd, *J* = 7.4, 7.3 Hz, 1H), 6.31 (d, *J* = 8.2 Hz, 1H), 5.38 (s, 1H), 4.11 (dd, *J* = 10.9, 4.3 Hz, 1H), 2.91 (dd, *J* = 13.7, 4.3 Hz, 1H), 2.38 (dd, *J* = 13.7, 10.9 Hz, 1H), 2.35 – 2.29 (m, 2H), 1.69 – 1.63 (m, 4H), 1.60 – 1.53 (m, 4H), 1.14 – 1.06 (m, 8H), 1.02 – 0.94 (m, 4H).; **¹³C NMR (151 MHz, CDCl₃)** δ 145.79, 144.24, 140.33, 130.06, 130.04, 129.06, 128.83, 128.75, 128.38, 127.06, 126.45, 116.85, 112.75, 57.80, 57.19, 54.01, 32.70, 31.03, 26.68, 26.65, 26.28.; **IR (neat)**: ν_{\max} = 3305, 3026, 2927, 2851, 1603, 1505, 1488, 749, 700 cm⁻¹; **HRMS** *m/z* (FAB) calc. for C₃₂H₄₁N₂ [M+H] = 453.3270, Found 453.3267; **R_f** 0.61 (hex/EtOAc, 9/1)

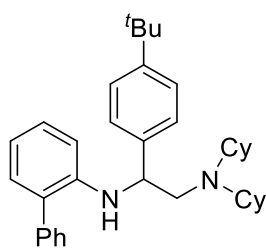


N1-([1,1'-biphenyl]-2-yl)-N2,N2-dicyclohexyl-1-(p-tolyl)ethane-1,2-diamine **2b**: white solid (84%); mp 140-145 °C; **¹H NMR (600 MHz, CDCl₃)** δ 7.55 (d, *J* = 7.7 Hz, 2H), 7.45 (dd, *J* = 7.3, 6.7 Hz, 2H), 7.36 – 7.32 (m, 3H), 7.18 (d, *J* = 7.3 Hz, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 7.02 (dd, *J* = 8.2, 7.3 Hz, 1H), 6.71 (dd, *J* = 7.4, 7.3 Hz, 1H), 6.32 (d, *J* = 8.2 Hz, 1H), 5.36 (s, 1H), 4.07 (dd, *J* = 10.7, 3.1 Hz, 2H), 2.88 (dd, *J* = 13.7, 3.1 Hz, 1H), 2.38 (s, 3H), 2.34 (dd, *J* = 13.7, 10.7 Hz, 1H), 2.33 – 2.28 (m, 2H), 1.69 – 1.62 (m, 4H), 1.59 – 1.52 (m, 4H),

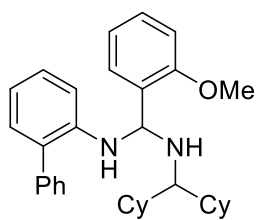
1.14 – 1.05 (m, 8H), 1.01 – 0.93 (m, 4H).; ¹³C NMR (151 MHz, CDCl₃) δ 145.91, 141.21, 140.36, 136.57, 130.05, 130.03, 129.55, 129.03, 128.73, 128.38, 127.03, 126.35, 116.78, 112.76, 57.78, 56.90, 54.10, 32.72, 30.99, 26.69, 26.65, 26.29, 21.36.; IR (neat): ν_{max} = 3303, 3018, 2927, 2851, 1603, 1507, 1488, 735, 701 cm⁻¹; HRMS m/z (FAB) calc. for C₃₃H₄₃N₂ [M+H] = 467.3426, Found 467.3425; R_f 0.63 (hex/EtOAc, 9/1)



N-(3-([1,1'-biphenyl]-2-yl)-2-mesitylpropyl)-N-cyclohexylcyclohexanamine **2c**: white solid (93%); mp 147-152 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.45 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.42 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.06 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.00 (ddd, *J* = 8.2, 7.3, 1.6 Hz, 1H), 6.90 (s, 1H), 6.79 (s, 1H), 6.67 (ddd, *J* = 7.3, 7.3, 1.4 Hz, 1H), 6.20 (d, *J* = 8.2 Hz, 1H), 5.23 (s, 1H), 4.54 (dd, *J* = 11.6, 4.5 Hz, 1H), 2.76 (dd, *J* = 13.7, 4.5 Hz, 1H), 2.65 (dd, *J* = 13.7, 11.6 Hz, 1H), 2.49 (s, 3H), 2.46 (s, 3H), 2.35 – 2.30 (m, 2H), 2.28 (s, 3H), 1.69 – 1.60 (m, 6H), 1.57 – 1.53 (m, 2H), 1.15 – 1.05 (m, 6H), 1.02 – 0.94 (m, 6H).; ¹³C NMR (151 MHz, CDCl₃) δ 146.29, 140.35, 137.12, 136.02, 135.38, 135.20, 131.94, 130.10, 130.03, 129.85, 128.74, 128.63, 127.02, 116.20, 110.97, 57.38, 53.01, 48.26, 33.23, 30.80, 26.78, 26.70, 26.37, 21.62, 21.07, 20.96.; IR (neat): ν_{max} = 3309, 2987, 2925, 2852, 1604, 1506, 1489, 733, 701 cm⁻¹; R_f 0.62 (hex/EtOAc, 9/1)

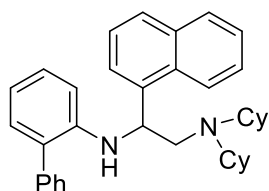


N1-([1,1'-biphenyl]-2-yl)-1-(4-(tert-butyl)phenyl)-N2,N2-dicyclohexylethane-1,2-diamine **2d**: white solid (96%); mp 157-162 °C; **¹H NMR (600 MHz, CDCl₃)** δ 7.55 (d, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.32 (m, 5H), 7.08 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.02 (ddd, *J* = 7.9, 7.5 1.3 Hz, 1H), 6.71 (dd, *J* = 7.5, 7.3 Hz, 1H), 6.33 (d, *J* = 7.9 Hz, 1H), 5.35 (s, 1H), 4.08 (dd, *J* = 10.7, 4.4 Hz, 1H), 2.89 (dd, *J* = 13.6, 4.4 Hz, 1H), 2.38 (dd, *J* = 13.6, 10.7 Hz, 1H), 2.33 – 2.28 (m, 2H), 1.68 – 1.62 (m, 4H), 1.57 – 1.51 (m, 4H), 1.35 (s, 8H), 1.13 – 1.05 (m, 8H), 1.01 – 0.93 (m, 4H).; **¹³C NMR (151 MHz, CDCl₃)** δ 149.75, 145.93, 141.05, 140.39, 130.04, 130.01, 129.00, 128.73, 128.37, 127.02, 126.05, 125.67, 116.72, 112.71, 57.77, 56.76, 53.99, 34.66, 32.69, 31.67, 31.06, 26.69, 26.66, 26.29.; **IR (neat)**: ν_{max} = 3307, 3018, 2928, 2852, 1604, 1506, 1488, 746, 701 cm⁻¹; **HRMS** *m/z* (FAB) calc. for C₃₆H₄₉N₂ [M+H] = 509.3896, Found 509.3893; **R_f** 0.66 (hex/EtOAc, 9/1)

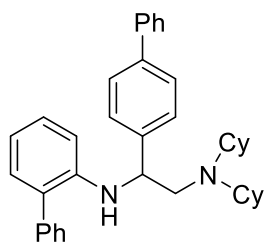


N1-([1,1'-biphenyl]-2-yl)-N2,N2-dicyclohexyl-1-(2-methoxyphenyl)ethane-1,2-diamine **2e**: white solid (80%); mp 155-160 °C; **¹H NMR (600 MHz, CDCl₃)** δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.44 (dd, *J* = 7.6, 7.3 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.29 (dd, *J* = 8.1, 7.5 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 7.03 – 7.00 (m, 2H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.72 (dd, *J* = 7.4, 7.3 Hz, 1H), 6.33 (d, *J* = 8.2 Hz, 1H), 5.35 (s, 1H), 4.06 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.84 (s, 3H), 2.90 (dd, *J* = 12.8, 4.5 Hz, 1H), 2.37 (dd, *J* = 12.8, 11.5 Hz, 1H), 2.33 – 2.27 (m, 2H), 1.68 – 1.62 (m, 4H), 1.57 – 1.51 (m, 4H), 1.13 – 1.04 (m, 8H), 1.00 – 0.93 (m, 4H).; **¹³C NMR (151 MHz, CDCl₃)** δ 159.95, 146.06, 145.60, 140.10, 129.82, 129.80, 129.62, 128.84,

128.52, 128.18, 126.84, 118.66, 116.68, 112.55, 112.29, 111.60, 57.58, 57.05, 55.18, 53.67, 32.48, 30.79, 26.46, 26.42, 26.05.; **IR (neat)**: ν_{\max} = 3301, 3056, 2926, 2851, 1597, 1505, 1487, 1270, 1047, 738, 700 cm^{-1} ; **HRMS** m/z (FAB) calc. for $\text{C}_{33}\text{H}_{43}\text{N}_2\text{O}$ $[\text{M}+\text{H}] = 483.3375$, Found 483.3373; **R_f** 0.54 (hex/EtOAc, 9/1)

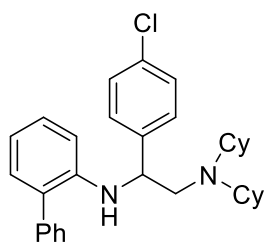


N-([1,1'-biphenyl]-2-yl)-N',N'-dicyclohexyl-1-(naphthalen-1-yl)methanamine **2f**: white solid (48%); mp 153-158 °C; **¹H NMR (600 MHz, CDCl₃)** δ 7.91 – 7.84 (m, 4H), 7.62 – 7.57 (m, 3H), 7.51 – 7.45 (m, 4H), 7.37 (td, $J = 7.32, 1.16$ Hz, 1H), 7.11 (d, $J = 7.5$ Hz, 1H), 6.95 (t, $J = 8.3, 7.3$ Hz, 1H), 6.71 (t, $J = 7.5, 7.3$ Hz, 1H), 6.36 (d, $J = 8.3$ Hz, 1H), 5.48 (s, 1H), 4.27 (dd, $J = 10.6, 4.2$ Hz, 1H), 2.97 (dd, $J = 13.3, 4.2$ Hz, 1H), 2.44 (dd, $J = 13.3, 10.6$ Hz, 1H), 2.38 – 2.32 (m, 2H), 1.69 – 1.63 (m, 4H), 1.60 – 1.51 (m, 4H), 1.15 – 1.06 (m, 8H), 1.01 – 0.93 (m, 4H).; **¹³C NMR (151 MHz, CDCl₃)** δ 145.90, 142.01, 140.34, 133.93, 133.15, 130.09, 129.13, 129.11, 128.79, 128.65, 128.43, 127.97, 127.95, 127.12, 126.12, 125.57, 124.99, 124.87, 116.97, 112.94, 57.86, 57.51, 53.97, 32.75, 31.01, 26.70, 26.66, 26.29.; **IR (neat)**: ν_{\max} = 3296, 3055, 2928, 2852, 1602, 1506, 1488, 744, 701 cm^{-1} ; **HRMS** m/z (FAB) calc. for $\text{C}_{36}\text{H}_{43}\text{N}_2$ $[\text{M}+\text{H}] = 503.3426$, Found 503.3422; **R_f** 0.61 (hex/EtOAc, 9/1)



N1-([1,1'-biphenyl]-2-yl)-1-([1,1'-biphenyl]-4-yl)-N2,N2-dicyclohexylethane-1,2-diamine **2g**: white solid (85%); mp 142-147 °C; **¹H NMR (600 MHz, CDCl₃)** δ 7.60 (d, $J = 6.9$ Hz, 2H), 7.58 (d, $J = 8.2$ Hz, 2H), 7.54 (d, $J = 6.7$ Hz, 2H), 7.49 (d, $J = 8.2$ Hz, 2H), 7.46 – 7.42 (m, 4H),

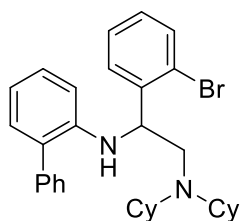
7.33 (t, $J = 7.4$ Hz, 2H), 7.08 (dd, $J = 7.4, 1.7$ Hz, 1H), 7.02 (ddd, $J = 8.2, 7.3, 1.7$ Hz, 1H), 6.71 (ddd, $J = 7.4, 7.3, 1.1$ Hz, 1H), 6.33 (dd, $J = 8.2, 1.1$ Hz, 1H), 5.38 (s, 1H), 4.12 (dd, $J = 11.0, 4.5$ Hz, 1H), 2.92 (dd, $J = 13.6, 4.5$ Hz, 1H), 2.39 (dd, $J = 13.6, 11.0$ Hz, 1H), 2.34 – 2.28 (m, 2H), 1.67 – 1.62 (m, 4H), 1.57 – 1.52 (m, 4H), 1.00 – 0.93 (m, 8H), 1.00 – 0.93 (m, 4H).; **^{13}C NMR (151 MHz, CDCl_3)** δ 145.82, 143.40, 141.33, 140.33, 140.03, 130.12, 130.07, 129.13, 128.93, 128.79, 128.43, 127.62, 127.28, 127.11, 126.90, 124.01, 116.96, 112.81, 57.85, 56.98, 54.00, 32.72, 31.06, 26.69, 26.66, 26.28.; **IR (neat):** $\nu_{\text{max}} = 3297, 2987, 2927, 2853, 1602, 1505, 749, 699 \text{ cm}^{-1}$; **HRMS** m/z (FAB) calc. for $\text{C}_{38}\text{H}_{45}\text{N}_2$ $[\text{M}+\text{H}] = 529.3583$, Found 529.3586; **R_f** 0.52 (hex/EtOAc, 9/1)



N1-([1,1'-biphenyl]-2-yl)-1-(4-chlorophenyl)-N2,N2-dicyclohexylethane-1,2-diamine **2i**: white solid (76%); mp 80-85 °C; **^1H NMR (600**

MHz, CDCl_3) δ 7.55 (d, $J = 7.6$ Hz, 2H), 7.46 (dd, $J = 7.6, 7.4$ Hz, 2H), 7.39 (d, $J = 8.1$ Hz, 2H), 7.38 – 7.33 (m, 3H), 7.11 (d, $J = 7.4$

Hz, 1H), 7.04 (dd, $J = 8.2, 7.4$ Hz, 1H), 6.75 (dd, $J = 7.4, 7.4$ Hz, 1H), 6.27 (d, $J = 8.2$ Hz, 1H), 5.38 (s, 1H), 4.09 (dd, $J = 10.9, 4.4$ Hz, 1H), 2.88 (dd, $J = 13.6, 4.4$ Hz, 1H), 2.35 (d, $J = 13.6, 10.9$ Hz, 1H), 2.34 – 2.29 (m, 2H), 1.70 – 1.64 (m, 4H), 1.59 – 1.54 (m, 4H), 1.14 – 1.06 (m, 8H), 1.01 – 0.94 (m, 4H).; **^{13}C NMR (151 MHz, CDCl_3)** δ 145.49, 142.79, 140.16, 132.59, 130.16, 130.00, 129.20, 129.01, 128.77, 128.38, 127.82, 127.14, 117.17, 112.68, 57.82, 56.71, 53.88, 32.67, 31.00, 26.64, 26.61, 26.24.; **IR (neat):** $\nu_{\text{max}} = 3301, 3020, 2927, 2852, 1604, 1505, 1485, 747, 739, 701 \text{ cm}^{-1}$; **HRMS** m/z (FAB) calc. for $\text{C}_{32}\text{H}_{40}\text{ClN}_2$ $[\text{M}+\text{H}] = 487.2880$, Found 487.2881; **R_f** 0.66 (hex/EtOAc, 9/1)



N1-([1,1'-biphenyl]-2-yl)-1-(2-bromophenyl)-N2,N2-dicyclohexylethane-

e-1,2-diamine **2k**: white solid (36%); mp 142-147 °C; **¹H NMR (600**

MHz, CDCl₃) δ 7.53 (d, *J* = 7.2 Hz, 2H), 7.47 – 7.42 (m, 5H), 7.37 –

7.33 (m, 3H), 7.27 – 7.24 (m, 1H), 7.07 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.99

(ddd, *J* = 7.9, 7.4, 1.6 Hz, 1H), 6.70 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 1H), 6.28 (d, *J* = 7.9 Hz,

1H), 5.35 (s, 1H), 4.08 (dd, *J* = 10.8, 4.4 Hz, 1H), 2.88 (dd, *J* = 13.6, 4.4 Hz, 1H), 2.35

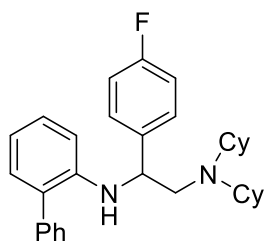
(dd, *J* = 13.6, 10.8 Hz, 1H), 2.32 – 2.27 (m, 2H), 1.66 – 1.61 (m, 4H), 1.56 – 1.50 (m, 4H),

1.11 – 1.04 (m, 8H), 0.99 – 0.92 (m, 4H).; **¹³C NMR (151 MHz, CDCl₃)** δ 145.80, 144.25,

140.33, 130.07, 130.05, 129.07, 128.84, 128.75, 128.38, 127.07, 126.46, 116.85, 112.75,

57.80, 57.19, 54.01, 32.70, 31.03, 26.68, 26.65, 26.28.; **IR (neat):** *v*_{max} = 3309, 3060,

2928, 2852, 1603, 1505, 1488, 747, 700, 661 cm⁻¹; **R_f** 0.63 (hex/EtOAc, 9/1)



N1-([1,1'-biphenyl]-2-yl)-N2,N2-dicyclohexyl-1-(4-fluorophenyl)ethane-

ne-1,2-diamine **2l**: white solid (96%); mp 145-150 °C; **¹H NMR (600**

MHz, CDCl₃) δ 7.53 (d, *J* = 7.5 Hz, 2H), 7.45 (dd, *J* = 7.5, 7.2 Hz,

2H), 7.40 (dd, *J* = 8.5, ⁴*J*_{H-F} = 5.3 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H),

7.10 (d, *J* = 7.4 Hz, 1H), 7.05 (dd, *J*_{H-F} = 8.9 Hz, *J* = 8.5 Hz, 2H), 7.02 (dd, *J* = 7.9, 6.8 Hz,

1H), 6.73 (dd, *J* = 7.4, 6.8 Hz, 1H), 6.27 (d, *J* = 7.9 Hz, 1H), 5.36 (s, 1H), 4.08 (dd, *J* =

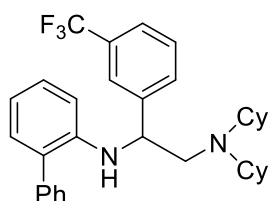
10.8, 4.7 Hz, 2H), 2.87 (dd, *J* = 13.5, 4.5 Hz, 1H), 2.34 (dd, 1H), 2.32 – 2.27 (m, 4H), 1.68

– 1.63 (m, 7H), 1.57 – 1.52 (m, 7H), 1.13 – 1.04 (m, 13H), 1.00 – 0.93 (m, 5H).; **¹³C NMR**

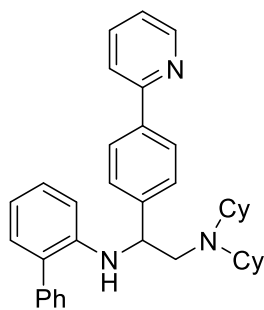
(151 MHz, CDCl₃) δ 162.07 (d, ¹*J*_{C-F} = 244.5 Hz), 145.61, 140.22, 139.77 (d, ⁴*J*_{C-F} = 2.9

Hz), 130.14, 130.01, 129.18, 128.77, 128.37, 127.86 (d, ³*J*_{C-F} = 7.9 Hz), 127.12, 117.07,

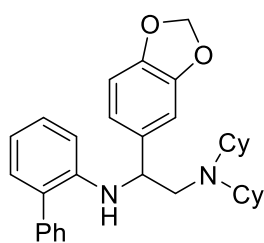
115.65 (d, $^2J_{C-F} = 21.2$ Hz), 112.68, 57.82, 56.58, 54.05, 32.68, 31.03, 26.66, 26.63, 26.25.; **IR (neat)**: $\nu_{\max} = 3299, 3032, 2926, 2851, 1603, 1505, 1488, 1220, 737, 701$ cm^{-1} ; **HRMS** m/z (FAB) calc. for $\text{C}_{32}\text{H}_{40}\text{FN}_2$ $[\text{M}+\text{H}] = 471.3176$, Found 471.3174; **R_f** 0.64 (hex/EtOAc, 9/1)



N1-([1,1'-biphenyl]-2-yl)-N2,N2-dicyclohexyl-1-(3-(trifluoromethyl)phenyl)ethane-1,2-diamine **2m**: white solid (91%); mp 152-157 °C; **¹H NMR (600 MHz, CDCl₃)** δ 7.69 (s, 1H), 7.67 (d, $J = 7.8$ Hz, 1H), 7.57 – 7.55 (m, 3H), 7.51 – 7.47 (m, 3H), 7.37 (t, $J = 7.4$ Hz, 1H), 7.13 (dd, $J = 7.4, 1.7$ Hz, 1H), 7.04 (ddd, $J = 8.2, 7.4, 1.7$ Hz, 1H), 6.77 (ddd, $J = 7.4, 7.4, 1.1$ Hz, 1H), 6.24 (dd, $J = 8.2, 1.1$ Hz, 1H), 5.41 (s, 1H), 4.17 (dd, $J = 10.7, 4.6$ Hz, 1H), 2.92 (dd, $J = 13.6, 4.6$ Hz, 1H), 2.38 (dd, $J = 13.6, 10.7$ Hz, 1H), 2.35 – 2.30 (m, 2H), 1.70 – 1.66 (m, 4H), 1.59 – 1.54 (m, 4H), 1.15 – 1.08 (m, 8H), 1.02 – 0.96 (m, 4H).; **¹³C NMR (151 MHz, CDCl₃)** δ 145.52, 145.45, 140.12, 131.12 (q, $^2J_{C-F} = 32.0$ Hz), 130.24, 130.03, 129.87, 129.41, 129.33, 128.82, 128.46, 127.21, 124.53 (q, $^1J_{C-F} = 272.3$ Hz), 124.11 (q, $^3J_{C-F} = 3.8$ Hz), 123.23 (q, $^3J_{C-F} = 3.8$ Hz), 117.38, 112.66, 57.87, 57.24, 53.91, 32.63, 31.08, 26.64, 26.61, 26.22.; **IR (neat)**: $\nu_{\max} = 3297, 3017, 2927, 2852, 1604, 1506, 1488, 1327, 1124, 738, 703$ cm^{-1} ; **HRMS** m/z (FAB) calc. for $\text{C}_{33}\text{H}_{40}\text{F}_3\text{N}_2$ $[\text{M}+\text{H}] = 521.3144$, Found 521.3142; **R_f** 0.63 (hex/EtOAc, 9/1)

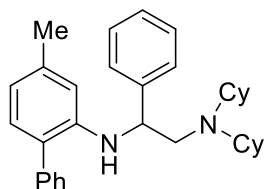


N1-([1,1'-biphenyl]-2-yl)-N2,N2-dicyclohexyl-1-(4-(pyridin-2-yl)phenyl)ethane-1,2-diamine **2o**: white solid (52%); mp 175-180 °C; **¹H NMR (600 MHz, CDCl₃)** δ 8.71 (d, *J* = 4.8 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.76 – 7.73 (m, 2H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.47 (dd, *J* = 7.8, 7.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.22 (ddd, *J* = 5.3, 2.8 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.01 (dd, *J* = 8.1, 7.5 Hz, 1H), 6.73 (dd, *J* = 7.5, 7.2 Hz, 1H), 6.35 (d, *J* = 8.1 Hz, 1H), 5.43 (s, 1H), 4.17 (dd, *J* = 10.8, 4.4 Hz, 1H), 2.95 (dd, *J* = 13.6, 4.4 Hz, 1H), 2.42 (dd, *J* = 13.6, 10.8 Hz, 1H), 2.37 – 2.32 (m, 2H), 1.70 – 1.65 (m, 4H), 1.61 – 1.53 (m, 4H), 1.15 – 1.08 (m, 8H), 1.02 – 0.95 (m, 4H).; **¹³C NMR (151 MHz, CDCl₃)** δ 157.68, 149.83, 145.70, 145.31, 140.29, 138.41, 136.83, 130.07, 130.03, 129.07, 128.74, 128.40, 127.48, 127.07, 126.87, 122.06, 120.57, 116.97, 112.89, 57.79, 57.08, 53.84, 32.69, 30.98, 26.66, 26.62, 26.25.; **IR (neat)**: ν_{\max} = 3306, 2987, 2972, 2927, 2854, 1586, 1505, 1488, 1435, 750, 701 cm⁻¹; **HRMS** *m/z* (FAB) calc. for C₃₇H₄₄N₃ [M+H] = 530.3535, Found 530.3532; **R_f** 0.25 (hex/EtOAc, 9/1)



N1-([1,1'-biphenyl]-2-yl)-1-(benzo[d][1,3]dioxol-5-yl)-N2,N2-dicyclohexylethane-1,2-diamine **2p**: pale yellow solid (36%); mp 80-85 °C; **¹H NMR (600 MHz, CDCl₃)** δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.46 (dd, *J* = 7.6, 7.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.11 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.06 (ddd, *J* = 8.2, 7.2, 1.7 Hz, 1H), 6.98 (s, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.75 (dd, *J* = 7.3, 7.2 Hz, 1H), 6.39 (d, *J* = 8.2 Hz, 1H), 5.97 (d, *J* = 1.6 Hz, 1H), 5.95 (d, *J* = 1.6 Hz, 1H), 5.36 (s, 1H), 4.04 (dd, *J* = 10.7, 4.4 Hz, 1H), 2.87 (dd, *J* =

13.6, 4.4 Hz, 1H), 2.36 (dd, $J = 13.6, 10.7$ Hz, 1H), 2.33 – 2.26 (m, 2H), 1.70 – 1.63 (m, 4H), 1.60 – 1.53 (m, 4H), 1.15 – 1.04 (m, 8H), 1.02 – 0.94 (m, 4H).; ^{13}C NMR (151 MHz, CDCl_3) δ 153.53, 150.31, 145.06, 139.97, 131.06, 130.27, 129.94, 129.26, 128.99, 128.80, 128.39, 127.21, 121.73, 117.47, 112.50, 57.83, 56.56, 53.22, 32.59, 31.02, 26.58, 26.55, 26.16.; IR (neat): $\nu_{\text{max}} = 3300, 3013, 2925, 2851, 1603, 1504, 1485, 1242, 1039, 737, 701$ cm^{-1} ; HRMS m/z (FAB) calc. for $\text{C}_{33}\text{H}_{41}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}] = 497.3168$; R_f 0.55 (hex/EtOAc, 9/1)



N2,N2-dicyclohexyl-N1-(4-methyl-[1,1'-biphenyl]-2-yl)-1-phenyletha-

ne-1,2-diamine **2q**: white solid (78%); mp 144-146 °C; ^1H NMR (600

MHz, CDCl_3) δ 7.51 (d, $J = 7.5$ Hz, 2H), 7.44 – 7.40 (m, 4H), 7.35

(dd, $J = 7.5, 7.5$ Hz, 2H), 7.31 (t, $J = 7.5$ Hz, 1H), 7.25 (t, $J = 7.4$ Hz, 1H), 6.97 (d, $J = 7.5$

Hz, 1H), 6.52 (d, $J = 7.5$ Hz, 1H), 6.10 (s, 1H), 5.31 (s, 1H), 4.08 (dd, $J = 10.7, 4.4$ Hz,

1H), 2.87 (dd, $J = 13.6, 4.4$ Hz, 1H), 2.35 (dd, $J = 13.6, 10.7$ Hz, 1H), 2.32 – 2.27 (m, 2H),

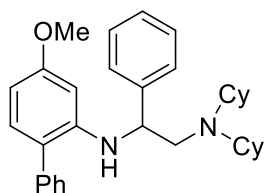
2.12 (s, 3H), 1.63 (t, $J = 13.1$ Hz, 4H), 1.55 – 1.50 (m, 4H), 1.11 – 1.03 (m, 8H), 0.98 –

0.91 (m, 4H).; ^{13}C NMR (151 MHz, CDCl_3) δ 145.67, 144.37, 140.36, 138.06, 130.17,

129.96, 128.81, 128.72, 127.01, 126.90, 126.47, 126.45, 117.64, 113.53, 57.75, 57.09,

54.02, 32.70, 31.01, 26.69, 26.65, 26.29, 21.84.; IR (neat): $\nu_{\text{max}} = 3306, 3024, 2927, 2852,$

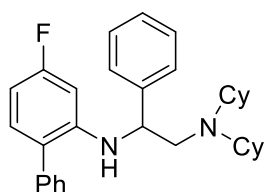
1615, 1516, 1489, 766, 700 cm^{-1} ; R_f 0.56 (hex/EtOAc, 9/1)



N2,N2-dicyclohexyl-N1-(4-methoxy-[1,1'-biphenyl]-2-yl)-1-phenylethane-1,2-diamine **2r**: white solid (85%); mp 153-158 °C; **¹H NMR (600**

MHz, CDCl₃) δ 7.50 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.44 – 7.40 (m, 4H),

7.35 (dd, *J* = 8.0, 7.2 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.26 (dd, *J* = 8.2, 2.4 Hz, 1H), 5.88 (d, *J* = 2.4 Hz, 1H), 5.41 (s, 1H), 4.08 (dd, *J* = 10.9, 4.4 Hz, 1H), 3.57 (s, 3H), 2.88 (dd, *J* = 13.6, 4.4 Hz, 1H), 2.37 (dd, *J* = 13.6, 10.9 Hz, 1H), 2.32 – 2.28 (m, 2H), 1.66 – 1.61 (m, 4H), 1.56 – 1.51 (m, 4H), 1.11 – 1.05 (m, 8H), 0.99 – 0.92 (m, 4H).; **¹³C NMR (151 MHz, CDCl₃)** δ 160.05, 147.06, 144.09, 140.10, 130.62, 130.26, 128.89, 128.72, 127.16, 126.80, 126.49, 122.30, 101.35, 99.52, 57.83, 57.33, 55.01, 53.92, 32.69, 31.03, 26.68, 26.65, 26.28.; **IR (neat):** *v*_{max} = 3303, 3024, 2927, 2851, 1613, 1515, 1488, 1305, 1212, 1171, 765, 701 cm⁻¹; **R_f** 0.46 (hex/EtOAc, 9/1)

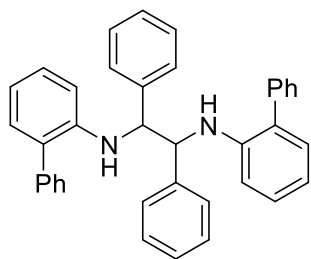


N2,N2-dicyclohexyl-N1-(4-fluoro-[1,1'-biphenyl]-2-yl)-1-phenylethane-1,2-diamine **2s**: pale yellow solid (83%); mp 140-147 °C; **¹H NMR**

(600 MHz, CDCl₃) δ 7.47 (d, *J* = 7.3 Hz, 2H), 7.43 (dd, *J* = 7.5, 7.3

Hz, 2H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.36 (dd, *J* = 7.3, 7.2 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.98 (dd, *J* = 8.3 Hz, ⁴*J*_{H-F} = 6.7 Hz, 1H), 6.36 (ddd, ³*J*_{H-F} = 8.3 Hz, *J* = 8.3, 2.5 Hz, 1H), 5.98 (dd, ³*J*_{H-F} = 12.1 Hz, *J* = 2.5 Hz, 1H), 5.46 (s, 1H), 4.03 (dd, *J* = 10.8, 4.5 Hz, 1H), 2.88 (dd, *J* = 13.6, 4.5 Hz, 1H), 2.34 (dd, *J* = 13.6, 10.8 Hz, 1H), 2.30 – 2.25 (m, 2H), 1.66 – 1.61 (m, 4H), 1.54 – 1.51 (m, 4H), 1.11 – 1.02 (m, 8H), 0.97 – 0.91 (m, 4H).; **¹³C NMR (151 MHz, CDCl₃)** δ 163.47 (d, ¹*J*_{C-F} = 242.2 Hz), 147.57 (d,

$^3J_{C-F} = 11.0$ Hz), 143.42, 139.52, 130.80 (d, $^3J_{C-F} = 9.8$ Hz), 130.16, 128.99, 128.87, 127.36, 127.23, 126.40, 124.97, 102.94 (d, $^2J_{C-F} = 21.5$ Hz), 99.92 (d, $^2J_{C-F} = 26.1$ Hz), 57.91, 57.23, 53.85, 32.66, 31.08, 26.66, 26.62, 26.25.; **IR (neat)**: $\nu_{\max} = 3287, 2987, 2901, 1615, 1513, 1488, 1066, 751, 700$ cm^{-1} ; **R_f** 0.58 (hex/EtOAc, 9/1)

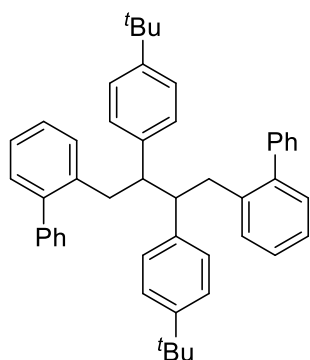


N1,N2-di([1,1'-biphenyl]-2-yl)-1,2-diphenylethane-1,2-diamine **3a**:

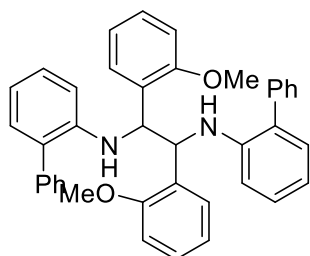
white solid (75%); mp 154-162 °C; **$^1\text{H NMR}$ (600 MHz, CDCl_3)** δ

7.50 (dd, $J = 7.5$ Hz, 2H), 7.45 – 7.36 (m, 4H), 7.28 (d, $J = 7.5$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 2H), 7.20 – 7.16 (m, 3H), 7.13 (t, $J = 7.3$

Hz, 1H), 7.07 – 6.99 (m, 7H), 6.93 (t, $J = 7.8$ Hz, 1H), 6.70 (t, $J = 7.4$ Hz, 1H), 6.68 – 6.65 (m, 3H), 6.34 (d, $J = 8.2$ Hz, 1H), 6.09 (d, $J = 8.2$ Hz, 1H), 4.81 (d, $J = 6.9$ Hz, 1H), 4.68 (d, $J = 6.9$ Hz, 1H), 4.61 (s, 1H), 4.49 (s, 1H).; **$^{13}\text{C NMR}$ (151 MHz, CDCl_3)** δ 143.96, 143.47, 139.83, 139.44, 139.16, 138.40, 130.05, 129.81, 129.51, 129.13, 128.97, 128.87, 128.63, 128.62, 128.48, 128.35, 128.33, 127.64, 127.58, 127.51, 127.39, 126.75, 117.45, 117.39, 111.90, 111.75, 64.11, 62.47.; **IR (neat)**: $\nu_{\max} = 3412, 3060, 3027, 2923, 1602, 1507, 1489, 1437, 744, 702$ cm^{-1} ; **R_f** 0.41 (hex/EtOAc, 9/1)



N1,N2-di([1,1'-biphenyl]-2-yl)-1,2-di(naphthalen-1-yl)ethane-1,2-diamine **3b**: white solid (85%); mp 160-167 °C; **¹H NMR (600 MHz, CDCl₃)** δ 7.49 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.39 (m, 4H), 7.25 – 7.21 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.01 – 6.93 (m, 6H), 6.68 – 6.64 (m, 4H), 6.35 (d, *J* = 8.2 Hz, 1H), 6.09 (d, *J* = 8.2 Hz, 1H), 4.61 – 4.59 (m, 2H), 4.54 (s, 1H), 4.43 (s, 1H), 1.29 (s, 9H), 1.27 (s, 9H).; **¹³C NMR (151 MHz, CDCl₃)** δ 150.24, 144.30, 143.82, 139.51, 139.24, 136.60, 135.84, 129.98, 129.88, 129.68, 129.59, 129.05, 128.90, 128.60, 128.57, 128.47, 128.33, 127.52, 127.41, 126.98, 126.22, 125.80, 125.27, 117.14, 117.12, 111.93, 111.72, 63.68, 62.49, 34.61, 34.58, 31.55, 31.54.; **IR (neat)**: ν_{\max} = 3407, 3057, 2962, 2904, 1605, 1507, 1489, 746, 703 cm⁻¹; **R_f** 0.51 (hex/EtOAc, 9/1)



N1,N2-di([1,1'-biphenyl]-2-yl)-1,2-bis(2-methoxyphenyl)ethane-1,2-diamine **3c**: white solid (81%); mp 158-165 °C; **¹H NMR (600 MHz, CDCl₃)** δ 7.47 (dd, *J* = 7.5 Hz, 2H), 7.42 – 7.33 (m, 5H), 7.27 (d, *J* = 7.0 Hz, 2H), 7.24 – 7.22 (m, 2H), 7.09 – 6.89 (m, 7H), 6.73 – 6.64 (m, 5H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 8.2 Hz, 1H), 6.34 (d, *J* = 7.6 Hz, 1H), 6.20 (t, *J* = 2.1 Hz, 1H), 6.16 (d, *J* = 8.3 Hz, 1H), 4.75 (s, 1H), 4.47 (s, 1H), 3.67 (s, 3H), 3.56 (s, 3H).; **¹³C NMR (151 MHz, CDCl₃)** δ 160.05, 159.51, 143.42, 140.26, 139.40, 139.20, 130.10, 129.91, 129.87, 129.70, 129.44, 129.43, 129.11, 128.97, 128.65, 128.52, 128.38, 127.55, 127.51, 119.51, 119.12, 117.52, 113.41, 113.08, 113.00, 112.66, 111.89, 64.05, 62.56, 55.27, 55.14.; **IR (neat)**: ν_{\max} = 3396, 2987, 2901, 1600, 1505, 1488, 1257,

1050, 749, 704 cm^{-1} ; R_f 0.21 (hex/EtOAc, 9/1)

