Modular synthesis of substituted-9,14-diaryl-9,14-dihydrodibenzo[a,c]phenazine via subsequent Buchwald-Hartwig amination and C-H amination strategy
Xiaobin Li†, Chengxi Zhang†, Chenchen Wang, Wenqiang Ye, Qian Zhang, Zhiyun Zhang, Jianhua Su, Yifeng Chen* and He Tian

Key Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, School of Chemistry and Molecular Engineering, East China University of Science & Technology, 130 Meilong Road, Shanghai, 200237, China.
E-mail: yifengchen@ecust.edu.cn
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1. General Experimental Protocols

All reactions were carried out under nitrogen atmosphere and anhydrous conditions unless otherwise indicated. Toluene was distilled from sodium/benzophenone. Dimethyl sulfone was purchased from Adamas [99.8%, SafeDry, with molecular sieves, Water ≤ 50 ppm (by K.F.), SafeSeal]. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.20 mm Huanghai silica gel plates (HSGF 254) using UV light as the visualizing agent. Chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (Huanghai, 300-400 mesh). All new compounds were characterized by means of $^1$H-NMR, $^{13}$C-NMR, $^{19}$F-NMR, and HR-MS. NMR spectra were recorded using a Bruker AVANCE III 400 MHz NMR spectrometer and can be found at the end of the paper. High-resolution mass spectra (HRMS) were recorded on a Waters GCT Premier mass spectrometer using EI-TOF, or JEOC AccuTOF LC-plus 4G using ESI, or Agilent Technologies 7250 GCQTOF using El. The UV/Vis spectra were recorded on a Nicolet CARY 100 spectrophotometer. The fluorescence spectra were recorded on Horiba Fluoromax 4. Single crystal X-ray diffraction data was collected at 193(2) K for 3f on a Bruker D8 Venture diffractometer. All $^1$H-NMR data are reported in δ units, parts per million (ppm), and were calibrated relative to the signals for residual chloroform (7.26 ppm) in deuterochloroform (CDCl$_3$). All $^{13}$C-NMR data are reported in ppm relative to CDCl$_3$ (77.16 ppm) and were obtained with $^1$H decoupling. The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet. $^{N9,N10}$-diphenylphenanthrene-9,10-diamine 1 was prepared followed by the reported procedure.$^1$

2. General procedure A for the Buchwald-Hartwig Amination

![Diagram]

To an oven-dried 10 mL Schlenk tube was added 1 (1.0 equiv), 4 (1.0 equiv), Pd$_2$dba$_3$ (1 mol%), P$^+$Bu$_3$•HBF$_4$ (4 mol%), and NaO$^+$Bu (2 equiv). The sealed tube was backfilled with N$_2$ (this process was repeated for three times) before toluene (4 mL) was added. The mixture was subsequently heated to 110 °C until 1 was consumed completely. After cooling to RT, the mixture was quenched with saturated NH$_4$Cl solution, diluted and extracted with EtOAc, washed with brine and the organic extracts were then combined and concentrated in vacuo. Purification by column chromatography to afford the desired product.
\(N^9-(4\text{-methoxyphenyl})-N^9,N^{10}\text{-diphenyIphenanthrene-9,10-diamine (2a)}\)

General procedure A was followed on 15 mmol scale with a reaction time of 17 hours and purification by flash column chromatography on silica gel (PE/DCM = 10/1-4/1) to afford 2a as a yellow-green solid (6.92 g, 99%). M.P. = 45–46 °C; \(R_f = 0.43\) (PE/DCM = 2/1). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.88 (t, \(J = 7.2\) Hz, 2H), 8.28 (ddd, \(J = 8.4, 2.4, 1.2\) Hz, 2H), 7.77 (td, \(J = 7.6, 0.8\) Hz, 1H), 7.70 (td, \(J = 7.6, 1.2\) Hz, 1H), 7.66–7.61 (m, 2H), 7.34–7.28 (m, 4H), 7.23–7.19 (m, 4H), 7.00 (t, \(J = 7.2\) Hz, 1H), 6.94–6.88 (m, 3H), 6.69 (d, \(J = 7.6\) Hz, 2H), 6.00 (bs, 1H), 3.80 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 155.2, 147.2, 146.1, 139.3, 135.4, 133.5, 131.4, 130.6, 130.4, 129.9, 129.4, 128.8, 127.4, 127.0, 126.7, 126.1, 126.1, 125.1, 123.4, 123.0, 122.9, 120.6, 119.4, 118.6 115.8, 114.8, 55.3; HRMS ESI: (m/z) [M+H]: calcd. for C\(_{33}H_{27}N_2O: 467.2118\); found: 467.2124.

\(N^9,N^9,N^{10}\text{-triphenyIphenanthrene-9,10-diamine (2b)}\)

General procedure A was followed on 0.5 mmol scale with a reaction time of 10 hours and purification by flash column chromatography on silica gel (PE to PE/DCM = 10/1) to afford 2b as a white solid (200.0 mg, 92%). M.P. = 211–212 °C; \(R_f = 0.54\) (PE/EtOAc = 50/1). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.78 (t, \(J = 8.4\) Hz, 2H), 8.06 (dd, \(J = 8.0, 0.8\) Hz, 1H), 8.02 (dd, \(J = 8.4, 0.8\) Hz, 1H), 7.70 (ddd, \(J = 8.4, 7.2, 1.2\) Hz, 1H), 7.62 (ddd, \(J = 8.4, 6.8, 1.2\) Hz, 1H), 7.52 (qd, \(J = 8.4, 1.2\) Hz, 2H), 7.19–7.12 (m, 8H), 7.05 (t, \(J = 7.6\) Hz, 2H), 6.90 (ddd, \(J = 8.4, 6.8, 1.6\) Hz, 2H), 6.76 (t, \(J = 7.2\) Hz, 1H), 6.50 (d, \(J = 8.0\) Hz, 2H), 5.86 (bs, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 146.5, 146.0, 135.7, 133.3, 131.4, 130.8, 130.4, 129.9, 129.5, 128.8, 127.5, 127.1, 126.8, 126.3, 126.2, 125.1, 123.0, 123.0, 121.9, 120.5, 119.6, 115.9; HRMS ESI: (m/z) [M+H]: calcd. for C\(_{32}H_{25}N_2: 437.0212\); found: 437.0214.

\(N^9-(3,4\text{-dimethoxyphenyl})-N^9,N^{10}\text{-diphenyIphenanthrene-9,10-diamine (2c)}\)

General procedure A was followed on 5 mmol scale with a reaction time of 11 hours and purification by flash column chromatography on silica gel (PE/DCM = 1/1) to afford 2c as a yellow solid (2.43 g, 98%). M.P. = 105–106 °C; \(R_f = 0.46\) (PE/DCM = 1/1). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.76 (t, \(J = 8.0\) Hz, 2H), 8.05 (d, \(J = 8.0\) Hz, 2H), 7.68 (t, \(J = 8.0\) Hz, 1H), 7.61 (t, \(J = 7.6\) Hz, 1H), 7.50 (q, \(J = 7.6\) Hz, 2H), 7.16 (t, \(J = 8.0\) Hz, 2H), 7.06–7.99 (m, 4H), 6.87 (t, \(J = 7.6\) Hz, 1H), 6.77–6.65 (m, 4H), 6.49 (d, \(J = 8.0\) Hz, 2H), 5.84 (bs, 1H), 3.79 (s, 3H), 3.57 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 149.6, 147.4, 146.3, 145.0, 139.8, 135.4, 133.7, 131.5, 130.7, 130.5, 130.1, 129.6, 128.9, 127.4, 127.1, 126.8, 126.2, 126.2, 125.2, 123.0, 120.8, 119.5, 118.9, 115.6, 114.5, 112.1, 106.8, 56.2, 56.0; HRMS ESI: (m/z) [M+H]: calcd. for C\(_{34}H_{29}N_2O_2: 497.2224\); found: 497.2216.

\(N^9-(4\text{-diphenyIamino)phenyl}-N^9,N^{10}\text{-diphenyIphenanthrene-9,10-diamine (2d)}\)
General procedure A was followed on 1 mmol scale with a reaction time of 22 hours and purification by flash column chromatography on silica gel (PE/DCM = 10/1–3/1) to afford 2d as a yellow solid (412.8 mg, 68%). M.P. = 168–170 °C; Rr = 0.61 (PE/DCM = 3/1). $^1$H NMR (400 MHz, CDCl3): $\delta$ 8.81 (t, J = 7.2 Hz, 2H), 8.08 (d, J = 7.6 Hz, 2H), 7.72 (t, J = 7.2 Hz, 1H), 7.66 (t, J = 7.2 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.28–7.21 (m, 6H), 7.15–7.10 (m, 6H), 7.03–7.01 (m, 6H), 6.93–6.86 (m, 4H), 6.56 (d, J = 8.0 Hz, 2H), 6.09 (bs, 1H); $^{13}$C NMR (100 MHz, CDCl3): $\delta$ 147.8, 146.6, 145.9, 142.3, 141.6, 135.8, 132.8, 131.3, 130.8, 130.3, 129.6, 129.5, 129.2, 128.8, 127.5, 127.1, 126.7, 126.2, 126.1, 125.0, 125.0, 123.5, 123.0, 123.0, 122.6, 122.3, 121.0, 119.7, 118.9, 116.2; HRMS ESI (m/z) [M]$^+$: calcd. for C$_{44}$H$_{33}$N$_3$: 603.2669; found: 603.2661.

$^{N^9}$-(anthracen-2-yl)-$^{N^9}$,N$^{10}$-diphenylphenanthrene-9,10-diamine (2e)

General procedure A was followed on 0.5 mmol scale with a reaction time of 3 hours and purification by flash column chromatography on Al$_2$O$_3$ (PE/DCM = 5/1) to afford 2e as a yellow solid (208.9 mg, 78%). M.P. = 276–277 °C; Rr = 0.50 (PE/EtOAc = 50/1). $^1$H NMR (400 MHz, CDCl3): $\delta$ 8.79 (t, J = 9.2 Hz, 2H), 8.25 (s, 1H), 8.04 (d, J = 8.4 Hz, 2H), 7.94 (s, 1H), 7.91–7.89 (m, 1H), 7.83 (d, J = 9.2 Hz, 1H), 7.80–7.78 (m, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.48–7.41 (m, 2H), 7.38–7.34 (m, 3H), 7.20–7.14 (m, 4H), 6.98–6.91 (m, 3H), 6.63 (t, J = 7.2 Hz, 1H), 6.46 (d, J = 8.0 Hz 2H); $^{13}$C NMR (100 MHz, CDCl3): $\delta$ 146.3, 146.1, 143.4, 135.8, 133.6, 132.8, 132.3, 131.3, 131.0, 130.8, 130.5, 130.1, 129.7, 129.6, 128.8, 128.7, 128.3, 127.8, 127.7, 127.3, 126.9, 126.4, 126.3, 126.1, 125.6, 125.1, 124.7, 124.4, 123.1, 123.1, 122.4, 122.2, 121.1, 119.6, 115.8, 115.1; HRMS ESI: (m/z) [M+H]$^+$: calcd. for C$_{40}$H$_{29}$N$_2$: 537.2325; found: 537.2340.

$^{N^9}$-(6-methoxynaphthalen-2-yl)-$^{N^9}$,N$^{10}$-diphenylphenanthrene-9,10-diamine (2f)

General procedure A was followed on 1 mmol scale with a reaction time of 23 hours and purification by flash column chromatography on silica gel (PE/DCM = 5/1–2/1) to afford 2f as a yellow solid (425.3 mg, 82%). M.P. = 87–88 °C; Rr = 0.39 (PE/DCM = 2/1). $^1$H NMR (400 MHz, CDCl3): $\delta$ 8.82 (t, J = 8.4 Hz, 2H), 8.14 (ddd, J = 8.0, 4.4, 0.4 Hz, 2H), 7.73 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.66–7.62 (m, 2H), 7.59–7.46 (m, 3H), 7.42–7.39 (m, 2H), 7.24–7.16 (m, 4H), 7.11–7.04 (m, 4H), 6.94 (tt, J = 7.2, 1.2 Hz, 1H), 6.76 (t, J = 7.2 Hz, 1H), 6.55 (d, J = 7.8 Hz, 2H), 5.90 (bs, 1H), 3.91 (s, 3H); $^{13}$C NMR (100 MHz, CDCl3): $\delta$ 156.8, 146.9, 146.1, 142.1, 135.7, 133.7, 131.4, 130.8, 130.7, 130.5, 130.1, 129.9, 129.5, 128.8, 128.4, 128.1, 127.5, 127.1, 126.8, 126.3, 126.2, 125.2, 125.0, 123.0, 122.3, 121.6, 120.1, 119.5, 119.1, 117.6, 115.7; HRMS ESI: (m/z) [M+H]$^+$: calcd. for C$_{27}$H$_{29}$N$_2$O: 517.2274; found: 517.2281.

$^{N^9}$-(benzo[b]thiophen-5-yl)-$^{N^9}$,N$^{10}$-diphenylphenanthrene-9,10-diamine (2g)
N⁰-(6-methoxypyridin-3-yl)-N⁰,N¹⁰-diphenylphenanthrene-9,10-diamine (2h)

General procedure A was followed on 7 mmol scale with a reaction time of 4 hours and purification by flash column chromatography on silica gel (PE/DCM = 3/1–DCM) to afford 2h as a yellow solid (3.44 g, 99%). M.P. = 74–75 °C; Rf = 0.69 (PE/acetone = 1/1). ¹H NMR (400 MHz, CDCl₃): δ 8.76 (t, J = 8.0 Hz, 2H), 8.03 (dd, J = 8.0, 0.8 Hz, 1H), 7.98–7.96 (m, 3H), 7.68 (dd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.62 (dd, J = 8.0, 0.8 Hz, 1H), 7.53–7.48 (m, 2H), 7.40 (dd, J = 8.8, 2.8 Hz, 1H), 7.20–7.16 (m, 2H), 7.05–6.97 (m, 4H), 6.89 (t, J = 7.6 Hz, 1H), 6.74 (t, J = 7.2 Hz, 1H), 6.49 (d, J = 8.8 Hz, 1H), 6.45 (d, J = 7.6 Hz, 2H), 5.81 (s, 1H), 3.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.8, 146.8, 145.9, 140.7, 136.8, 135.6, 133.5, 133.0, 131.0, 130.9, 130.5, 129.9, 129.8, 129.0, 127.6, 127.3, 126.9, 126.4, 126.2, 124.9, 123.2, 123.0, 121.2, 119.6, 118.2, 115.7, 111.1, 53.6; HRMS ESI: (m/z) [M+H]^+: calcd. for C₃₂H₂₅N₂O: 468.2070; found: 468.2067.

N⁰,N¹⁰-diphenyl-N⁰-(1-phenyl-1H-indol-6-yl)phenanthrene-9,10-diamine (2i)

General procedure A was followed on 0.5 mmol scale with a reaction time of 24 hours and purification by flash column chromatography on silica gel (PE/DCM = 10/1) to afford 2i as a yellow-green solid (221.4 mg, 80%). M.P. = 120–121 °C; Rf = 0.38 (PE/EtOAc = 60/1). ¹H NMR (400 MHz, CDCl₃): δ 8.76 (t, J = 8.8 Hz, 2H), 8.07 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.67 (dd, J = 8.4, 7.2, 1.6 Hz, 1H), 7.59 (dd, J = 8.0, 7.2, 1.2 Hz, 1H) 7.52–7.44 (m, 3H), 7.38–7.32 (m, 3H), 7.27–7.24 (m, 3H), 7.21 (d, J = 3.2 Hz, 1H), 7.15 (t, J = 7.2 Hz, 2H), 7.07 (td, J = 8.4, 1.6, 3H), 6.95 (t, J = 7.2 Hz, 2H), 6.86 (t, J = 7.2 Hz, 1H), 6.68 (t, J = 7.2 Hz, 1H), 6.58 (d, J = 3.2 Hz, 1H), 6.43 (d, J = 8.4 Hz, 2H), 5.85 (bs, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 147.7, 146.3, 142.1, 139.7, 136.5, 135.4, 134.0, 131.6, 130.8, 130.5, 130.2, 129.7, 129.5, 128.8, 127.9, 127.4, 126.9, 126.7, 126.3, 126.2, 126.1, 125.4, 125.3, 124.0, 123.0, 123.0, 121.9, 121.0, 119.5, 119.3, 116.5, 115.7, 104.1, 103.6; HRMS ESI: (m/z) [M+H]^+: calcd. for C₄₀H₃₀N₃: 552.2434; found: 552.2420.
N°,N°-diphenyl-N°-(pyridin-3-yl)phenanthrene-9,10-diamine (2j)

General procedure A was followed on 0.2 mmol scale with a reaction time of 2 hours and purification by flash column chromatography on silica gel (PE/EtOAc = 5/1) with 2% Et3N to afford 2j as a brown-yellow solid (76 mg, 87%). M.P. = 179–181 °C; Rf = 0.36 (PE/EtOAc = 2/1). 1H NMR (400 MHz, CDCl3): δ 8.77 (dd, J = 8.4, 4.4 Hz, 2H), 8.45 (d, J = 2.0 Hz, 1H), 8.07–8.03 (m, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.70 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.63 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.54–7.48 (m, 2H), 7.29–7.26 (m, 1H), 7.24–7.13 (m, 4H), 7.04–6.95 (m, 4H), 6.73 (t, J = 7.6 Hz, 1H), 6.46 (d, J = 8.4 Hz, 2H), 5.80 (s, 1H); 13C NMR (100 MHz, CDCl3): δ 145.7, 145.5, 143.0, 142.5, 142.1, 136.0, 132.4, 131.0, 130.7, 130.5, 129.9, 129.8, 129.0, 127.7, 127.5, 127.0, 126.7, 126.5, 126.3, 124.7, 123.8, 123.2, 123.1, 122.9, 120.5, 119.8, 115.7; HRMS ESI: (m/z) [M+H]+: calcd. for C31H25N3: 438.1965; found: 438.1966.

N°,N°-diphenyl-N°-(quinolin-3-yl)phenanthrene-9,10-diamine (2k)

General procedure A was followed on 0.5 mmol scale with a reaction time of 6 hours and purification by flash column chromatography on silica gel (PE/EtOAc = 10/1) to afford 2k as a brown-red solid (212.2 mg, 87%). M.P. = 113–115 °C; Rf = 0.47 (PE/EtOAc = 5/2). 1H NMR (400 MHz, CDCl3): δ 8.93 (d, J = 2.0 Hz, 1H), 8.80 (t, J = 7.6 Hz, 2H), 8.09 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.52–7.47 (m, 3H), 7.36 (d, J = 4.0 Hz, 2H), 7.25–7.16 (m, 4H), 7.03–6.95 (m, 3H), 6.65 (t, J = 7.2 Hz, 1H), 6.46 (d, J = 8.0 Hz, 2H), 5.80 (s, 1H); 13C NMR (100 MHz, CDCl3): δ 145.9, 145.8, 145.7, 143.6, 140.1, 136.0, 132.8, 131.0, 130.7, 130.7, 130.6, 130.0, 130.0, 128.9, 128.8, 127.8, 127.6, 127.4, 127.1, 127.1, 126.7, 126.6, 126.3, 124.7, 123.2, 123.1, 120.4, 119.7, 115.5; HRMS ESI: (m/z) [M+H]+: calcd. for C35H26N3: 488.2121; found: 488.2129.

3. General procedure B for the C-H Amination

To an 8 mL vial equipped with a stir bar was added 2 (1.0 equiv) and Cu(OAc)2 (2.0 equiv) dissolved in DMSO (using CaCl2 drying tube as a desiccator) under air. The mixture was subsequently heated to 120 °C and monitored by TLC until 2 was completely consumed. After cooling to RT, the mixture was quenched with water and filtered. The filtrate was diluted and extracted with EtOAc, washed with brine and the organic extracts were then combined and concentrated in vacuo. Purification by column chromatography yielded the desired product.
Characterization Data for products

11-methoxy-9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine (3a)

General procedure B was followed on 0.2 mmol scale with a reaction time of 12 hours and purification by flash column chromatography on silica gel (PE/DCM = 5/1–4/1) to afford 3a as a chartreuse solid (53.7 mg, 58%). M.P. = 219–220 °C; \( R_t = 0.53 \) (PE/DCM = 2/1). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \( \delta 8.76 \) (d, \( J = 8.4 \) Hz, 2H), 8.19 (dd, \( J = 14.4, 7.6 \) Hz, 2H), 7.69–7.64 (m, 3H), 7.61–7.55 (m, 2H), 7.37 (bs, 1H), 7.10–7.03 (m, 6H), 6.98–6.92 (m, 3H), 6.84–6.78 (m, 2H), 3.92 (s, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): \( \delta 157.5, 148.4, 147.5, 146.1, 138.7, 138.4, 137.9, 129.9, 129.7, 129.5, 128.8, 128.7, 128.1, 127.1, 127.0, 126.6, 126.6, 124.7, 124.7, 123.1, 123.1, 121.3, 120.7, 117.2, 116.3, 113.1, 110.6, 55.9; \) HRMS EI: calcd. for C\(_{33}\)H\(_{24}\)N\(_2\)O: 464.1883; found: 464.1886.

9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine (3b)

General procedure B was followed on 0.1 mmol scale with a reaction time of 13 hours and purification by flash column chromatography on silica gel (PE/DCM = 10/1) to afford 3b as a white solid (16.7 mg, 38%). \( R_t = 0.61 \) (PE/EtOAc = 30/1). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \( \delta 8.74 \) (d, \( J = 8.4 \) Hz, 2H), 8.14 (d, \( J = 8.0 \) Hz, 2H), 7.76 (dd, \( J = 5.6, 3.6 \) Hz, 2H), 7.65 (t, \( J = 7.2 \) Hz, 2H), 7.55 (t, \( J = 7.6 \) Hz, 2H), 7.35 (dd, \( J = 5.2, 3.6 \) Hz, 2H), 7.05–6.95 (m, 8H), 6.78 (t, \( J = 6.8 \) Hz, 2H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): \( \delta 147.8, 145.0, 138.3, 130.0, 129.6, 128.9, 127.5, 127.1, 126.6, 125.5, 124.7, 123.1, 121.1, 116.9. \) This product is matched with reported data.\(^2\)

11,12-dimethoxy-9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine (3c)

General procedure B was followed on 1.165 mmol scale with a reaction time of 12 hours and purification by flash column chromatography on silica gel (PE/DCM = 5/1–2/1) to afford 3c as a yellow solid (479.1 mg, 83%). M.P. = 174–175 °C; \( R_t = 0.46 \) (PE/EtOAc = 10/3). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \( \delta 8.76 \) (d, \( J = 8.0 \) Hz, 2H), 8.21 (d, \( J = 8.0 \) Hz, 2H), 7.67 (t, \( J = 7.2 \) Hz, 2H), 7.59 (t, \( J = 7.6 \) Hz, 2H), 7.32 (s, 2H), 7.05–6.95 (m, 8H), 6.78 (t, \( J = 7.2 \) Hz, 2H), 4.02 (s, 6H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): \( \delta 148.2, 146.8, 139.1, 138.0, 129.8, 129.7, 128.7, 127.1, 126.6, 124.7, 123.1, 120.8, 116.3, 111.0, 56.5; \) HRMS EI: calcd. for C\(_{34}\)H\(_{26}\)N\(_2\)O\(_2\): 494.1989; found: 494.1997.

N,N,9,14-tetraphenyl-9,14-dihydrodibenzo[a,c]phenazin-11-amine (3d)

General procedure B was followed on 0.5 mmol scale with a reaction time of 6 hours and purification by flash column chromatography on silica gel (PE/DCM = 20/1–2/1) to afford 3d as a yellow solid (93.3 mg, 31%). M.P. = 277–278 °C; \( R_t = 0.51 \) (PE/EtOAc = 35/1). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \( \delta 8.75 \) (d, \( J = 8.4 \) Hz, 2H), 8.13 (d, \( J = 8.0 \) Hz, 1H), 8.01 (d, \( J = 8.0 \) Hz, 1H), 7.68–7.48 (m, 6H),
7.34–7.30 (m, 4H), 7.23–7.21 (m, 4H), 7.10–7.00 (m, 9H), 6.89 (d, J = 8.0 Hz, 2H), 6.84–6.78 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 148.0, 147.8, 147.5, 145.7, 145.5, 139.7, 138.4, 137.9, 130.0, 130.0, 129.5, 129.5, 128.9, 128.8, 127.6, 127.1, 127.0, 126.6, 126.4, 123.1, 123.1, 123.0, 121.1, 121.0, 120.8, 117.0, 116.6; HRMS ESI: (m/z) [M]+: calcd. for C\(_{44}H_{31}N_3\): 601.2513; found: 603.2501.

5,14-diphenyl-5,14-dihydrodibenzo[a,c]naphtho[2,3-h]phenazine (3e)

General procedure B was followed on 0.056 mmol scale with a reaction time of 10 hours and purification by flash column chromatography on Al\(_2\)O\(_3\) (PE–EtOAc = 50/1) to afford 3e as a yellow-green solid (27.1 mg, 91%). M.P. = 199–201 °C; \(Rt = 0.37\) (PE/EtOAc = 50/1). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.97 (s, 1H), 8.75 (d, J = 8.0 Hz, 2H), 8.70 (d, J = 8.0 Hz, 1H), 8.51 (s, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 7.6 Hz, 1H), 8.05–7.96 (m, 3H), 7.79–7.70 (m, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.51–7.47 (m, 2H), 7.11 (d, J = 8.0 Hz, 2H), 7.06 (t, J = 7.2 Hz, 2H), 6.91 (t, J = 7.6 Hz, 2H), 6.85 (t, J = 7.2 Hz, 1H), 6.71 (t, J = 7.2 Hz, 1H), 6.66 (d, J = 8.4 Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 149.6, 147.1, 143.6, 139.9, 139.1, 138.8, 132.4, 131.6, 130.7, 130.3, 130.2, 130.0, 129.7, 129.5, 129.0, 128.7, 128.6, 128.3, 127.5, 127.2, 127.1, 126.9, 126.7, 126.1, 125.6, 125.0, 124.6, 123.2, 123.1, 122.1, 122.1, 120.0, 118.8, 115.6; HRMS ESI: (m/z) [M+H]+: calcd. for C\(_{40}H_{27}N_2\): 535.2169; found: 535.2167.

3-methoxy-7,16-diphenyl-7,16-dihydrotribenzo[a,c,h]phenazine (3f)

General procedure B was followed on 0.5 mmol scale with a reaction time of 14 hours and purification by flash column chromatography on silica gel (PE/DCM = 5/1–3/1) to afford 3f as a white solid (182.0 mg, 71%). M.P. = 273–274 °C; \(Rt = 0.55\) (PE/DCM = 5/1). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.73 (d, J = 8.4 Hz, 2H), 8.56 (dd, J = 6.4, 2.0 Hz, 2H), 8.41 (d, J = 8.8 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.73–7.69 (m, 2H), 7.65 (t, J = 8.0 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.35 (dd, J = 9.2, 2.4 Hz, 1H), 7.27 (d, J = 2.4 Hz, 1H), 7.11–7.03 (m, 4H), 6.96 (t, J = 7.6 Hz, 2H), 6.83 (t, J = 6.8 Hz, 1H), 6.73 (t, J = 7.2 Hz, 1H), 6.67 (d, J = 8.4 Hz, 2H), 3.98 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 157.8, 149.0, 147.4, 142.0, 140.1, 139.9, 139.3, 133.0, 130.6, 130.0, 129.6, 129.5, 128.8, 128.5, 127.4, 127.0, 126.9, 126.7, 126.6, 126.4, 125.2, 124.9, 124.5, 123.1, 123.1, 121.5, 119.9, 119.8, 117.7, 115.3, 106.2, 55.5; HRMS ESI: (m/z) [M+H]+: calcd. for C\(_{37}H_{27}N_2O\): 515.2118; found: 515.2108.

6,15-diphenyl-6,15-dihydrodibenzo[a,c]thieno[3,2-h]phenazine (3g)

General procedure B was followed on 0.2 mmol scale with a reaction time of 14 hours and purification by flash column chromatography on silica gel (PE/ EtOAc = 50/1) to afford 3g as a white solid (43.3 mg, 44%). M.P. = 131–132°C; \(Rt = 0.43\) (PE/EtOAc = 50/1). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.75 (d, J =
8.0 Hz, 2H), 8.37 (dd, J = 7.6, 1.2 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.71–7.63 (m, 4H), 7.58–7.54 (m, 2H), 7.01–7.00 (m, 4H), 6.95 (t, J = 8.0 Hz, 2H), 6.79–6.75 (m, 1H), 6.72–6.68 (m, 3H); **13C NMR** (100 MHz, CDCl3): δ 148.1, 147.7, 142.8, 139.9, 139.6, 139.1, 138.7, 137.6, 130.3, 130.1, 129.8, 129.7, 128.8, 128.7, 128.2, 127.3, 127.1, 126.8, 126.8, 124.9, 124.7, 124.3, 123.2, 123.2, 122.3, 121.2, 120.1, 120.0, 117.1, 115.0; **HRMS ESI**: (m/z) [M+H]+: calced. for C34H22N2S: 491.1577; found: 491.1583.

**11-methoxy-9,14-diphenyl-9,14-dihydrodibenzo[f,h]pyrido[2,3-b]quinoxaline (3h)**

General procedure B was followed on a 1.3 mmol scale with a reaction time of 8 hours and purification by flash column chromatography on silica gel (PE/DCM = 5/1) to afford 3h as a white solid (545.1 mg, 90%). M.P. = 234–236 °C; Rf = 0.66 (PE/acetonitrile = 10/1). **1H NMR** (400 MHz, CDCl3): δ 8.71 (d, J = 8.0 Hz, 2H), 8.14 (d, J = 8.0 Hz, 1H), 7.81 (t, J = 8.4 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.2 Hz, 2H), 7.10–7.02 (m, 3H), 6.93 (d, J = 8.0 Hz, 2H), 6.84 (t, J = 7.2 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 4.08 (s, 3H); **13C NMR** (100 MHz, CDCl3): δ 160.7, 154.6, 149.6, 145.7, 138.0, 136.0, 134.8, 130.8, 129.8, 129.3, 129.2, 129.0, 128.9, 128.1, 127.8, 127.3, 126.6, 126.4 125.2, 124.5, 124.0, 123.2, 123.1, 123.0, 121.3, 116.5, 150.2, 54.2; **HRMS ESI**: (m/z) [M+H]+: calced. for C32H24N2O: 466.1914; found: 466.1907.

**1,6,15-triphenyl-6,15-dihydro-1H-dibenzo[a,c]pyrrolo[2,3-h]phenazine (3i)**

General procedure B was followed on 0.2 mmol scale with a reaction time of 20 hours and purification by flash column chromatography on silica gel (PE/EtOAc = 100/1–50/1) to afford 3i as a yellow-green solid (77.2 mg, 70%). M.P. = 115–117 °C; Rf = 0.51 (PE/EtOAc = 50/1). **1H NMR** (400 MHz, CDCl3): δ 8.70 (t, J = 9.2 Hz, 2H), 8.19 (d, J = 8.0 Hz, 1H), 7.71–7.60 (m, 4H), 7.54 (t, J = 8.0 Hz, 1H), 7.49–7.43 (m, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.29–7.26 (m, 4H), 7.15 (d, J = 3.2 Hz, 1H), 6.90–6.85 (m, 5H), 6.79 (t, J = 8.0 Hz, 2H), 6.74 (d, J = 3.2 Hz, 1H), 6.71–6.66 (m, 1H), 6.58 (t, J = 7.2 Hz, 1H), 6.42 (d, J = 8.0 Hz, 2H); **13C NMR** (100 MHz, CDCl3): δ 149.4, 148.0, 142.3, 140.8, 140.8, 140.6, 133.6, 133.6, 132.3, 130.7, 130.4, 129.9, 129.8, 129.4, 128.9, 128.8, 128.5, 128.0, 127.8, 127.7, 127.0, 126.7, 126.6, 126.4, 125.9, 125.0, 123.1, 122.6, 120.7, 120.4, 119.9, 118.6, 117.0, 115.8, 103.6; **HRMS ESI**: (m/z) [M+H]+: calced. for C40H28N3: 550.2278; found: 550.2267.

**9,14-diphenyl-9,14-dihydrodibenzo[f,h]pyrido[2,3-b]quinoxaline (3j)**

General procedure B was followed on 0.2 mmol scale with a reaction time of 10 hours and purification by flash column chromatography on Al2O3 gel (PE–PE/EtOAc = 50/1) to afford 3j as a brown solid (25.9 mg, 30%). M.P. = 270–271 °C; Rf = 0.46 (PE/EtOAc = 50/1). **1H NMR** (400 MHz, CDCl3): δ 8.71 (dd, J = 8.4, 4.0 Hz, 2H), 8.37 (dd, J = 4.8, 1.6 Hz, 1H), 8.10 (d, J = 8.0, 1H), 7.94 (dd, J = 7.6, 1.6 Hz, 1H), 7.88 (d, J =
8.4, 1H), 7.73 (d, J = 8.0, 2H), 7.63 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.60–7.53 (m, 2H), 7.39 (ddd, J = 8.0, 6.8, 0.8 Hz, 1H), 7.23–7.18 (m, 3H), 7.14–7.10 (m, 2H), 7.06–7.00 (m, 3H), 6.90 (t, J = 7.2, 1H); 13C NMR (100 MHz, CDCl₃): δ 157.2, 148.3, 145.7, 144.4, 135.9, 135.7, 134.5, 134.5, 130.6, 130.0, 129.2, 129.0, 128.9, 128.2, 127.2, 126.8, 126.6, 125.3, 124.4, 123.7, 123.1, 123.1, 122.0, 122.0, 119.5, 117.2; HRMS ESI: (m/z) [M+H]+: calcd. for C₃₁H₂₂N₃: 436.1808; found: 436.1805.

7,16-diphenyl-7,16-dihydrodibenzo[f,h]quinolino[3,4-b]quinoxaline (3k)

General procedure B was followed on 0.2 mmol scale with a reaction time of 4 hours and purification by flash column chromatography on silica gel (PE/EtOAc = 50/1–10/1) to afford 3k as a brown solid (81.5 mg, 84%). M.P. = 160–161 °C; Rf = 0.44 (PE/EtOAc = 5/1). 1H NMR (400 MHz, CDCl₃): δ 9.49 (s, 1H), 8.76–8.73 (m, 2H), 8.49–8.46 (m, 1H), 8.41 (d, J = 8.4 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.75 (ddd, J = 8.0, 6.4, 0.8 Hz, 1H), 7.72–7.63 (m, 4H), 7.54 (t, J = 7.6 Hz, 1H), 7.13–7.05 (m, 4H), 6.96 (t, J = 8.0 Hz, 2H), 6.89 (t, J = 6.8 Hz, 1H), 6.76 (t, J = 7.2 Hz, 1H), 6.65 (d, J = 8.0 Hz, 2H); 13C NMR (100 MHz, CDCl₃): δ 149.4, 147.9, 147.4, 146.9, 146.5, 140.4, 139.3, 137.7, 130.3, 130.2, 129.9, 129.7, 129.3, 129.1, 128.8, 127.6, 127.6, 127.2, 127.1, 127.0, 126.7, 124.8, 124.4, 123.7, 123.2, 123.2, 123.0, 120.8, 119.2, 115.4; HRMS ESI: (m/z) [M+H]+: calcd. for C₃₅H₂₄N₃: 486.1965; found: 486.1964.

11-methoxy-9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine (5)

To a round-bottomed flask with 11-methoxy-9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine 3a (3.81 mmol, 1.77 g) in DCM (30 mL) was added BBr₃ (15.2 mmol, 1.45 mL) at -78 °C, the reaction mixture was allowed to slowly warm to 25 °C and then stirred for 3 h. The reaction mixture was quenched with water, the aqueous layer was extracted three times with DCM and separated organic layer was washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/DCM = 2/1 to 100% DCM) to afford the product S1 as a white solid (1.66 g, 97%).

To a round-bottomed flask with S1 (5.8 mmol, 2.55 g), DMAP (0.29 mmol, 35.4 mg) in DCM (25 mL) was added Et₃N (7.54 mmol, 1.10 mL) and Tf₂O (6.38 mmol, 1.073 mL) at 0 °C, the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with water, the aqueous layer was extracted three times with DCM and separated organic layer was washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/DCM = 10/1) to afford the product 5 as a white solid (3.05 g, 90%). M.P. = 169–171 °C. Rf = 0.62 (PE/EA = 50/1). 1H NMR (400 MHz,
room temperature and tube was evacuated and backfilled with N₂ (100 MHz, CDCl₃): δ 147.4, 147.2, 146.3, 146.1, 145.0, 137.4, 137.2, 130.2, 130.1, 129.2, 129.1, 129.1, 127.6, 127.2, 127.2, 126.8, 124.5, 123.2, 122.4, 122.3, 118.9 (q, J = 319.1 Hz), 118.2, 117.9, 117.7; ¹⁹F NMR (376 MHz, CDCl₃): δ -72.5; HRMS (EI): calcd. for C₃₃H₂₃F₃Na₂O₃S: 582.1225; found: 582.1224.

9,14-diphenyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,14-dihydrodibenzo[a,c]phenazine (6)

An oven-dried Schlenk tube containing a stirring bar was charged with 5 (0.2 mmol, 116.5 mg), B₂pin₂ (0.22 mmol, 55.9 mg), KOAc (0.3 mmol, 29.4 mg), Pd(dpff)Cl₂ (0.02 mmol, 14.6 mg), dpff (0.02 mmol, 11.1 mg). Then the Schlenk tube was evacuated and backfilled with N₂ (This process was repeated for three times). 4 mL 1,4-dioxane was then added and the tube was equipped with a balloon filled with N₂ at 100 °C for 12 h. The reaction mixture was quenched with water, the aqueous layer was extracted three times with EtOAc and separated organic layer was washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/DCM = 20/1–5/1) to afford the product 6 as a white solid (63.9 mg, 57%). M.P. = 165–166 °C; Rf = 0.50 (PE/EA = 20/1); ¹H NMR (400 MHz, CDCl₃): δ 8.73 (d, J = 7.6 Hz, 2H), 8.21 (s, 1H), 8.12 (dd, J = 14.4, 8.0 Hz, 2H), 7.80 (q, J = 7.2 Hz, 2H), 7.66–7.51 (m, 4H), 7.05–6.98 (m, 8H), 6.82–6.77 (m, 2H), 1.40 (s, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 148.0, 147.9, 144.2, 138.2, 138.0, 133.8, 132.2, 130.0, 130.0, 129.6, 129.5, 128.9, 128.8, 127.1, 127.0, 126.0, 126.0, 124.7, 123.1, 123.1, 121.4, 121.0, 117.2, 116.7, 84.1, 25.0; HRMS ESI: (m/z) [M+H]⁺: calcd. for C₃₈H₃₄BN₂O₂: 561.2708; found: 561.2711.

9,14-diphenyl-11-((trimethylsilyl)ethyl)-9,14-dihydrodibenzo[a,c]phenazine (7a) and 11-ethynyl-9,14-dihydrodibenzo[a,c]phenazine (7b)

An oven-dried Schlenk tube containing a stirring bar was charged with 5 (0.687 mmol, 400 mg), CuI (0.275 mmol, 53 mg), Pd(PPh₃)₄ (0.137 mmol, 159 mg). Then the sealed tube was evacuated and backfilled with N₂ (This process was repeated for three times). 10 mL MeCN and ethynyltrimethylsilane (2.061 mmol, 286 μL) were then added at room temperature and the reaction mixture was stirred at 110 °C for 12 h. The reaction
mixture was quenched with water, the aqueous layer was extracted three times with EtOAc and separated organic layer was washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/DCM = 10/1) to afford the product 7a as a yellow solid (287.1 mg, 79%). M.P. = 108–109 °C; Rf = 0.58 (PE/EA = 30/1).\(^1\)H NMR (400 MHz, CDCl₃): δ 8.73 (d, J = 8.4 Hz, 2H), 8.10 (ddd, J = 9.6, 8.4, 1.2 Hz, 2H), 7.86 (d, J = 1.6 Hz, 1H), 7.68–7.62 (m, 3H), 7.57–7.51 (m, 2H), 7.46 (dd, J = 8.4, 2.0 Hz, 1H), 7.07–7.03 (m, 4H), 6.99–6.97 (m, 4H), 6.85–6.80 (m, 2H), 0.30 (s, 9H); \(^1\)C NMR (100 MHz, CDCl₃): δ 147.7, 147.5, 145.5, 144.5, 137.8, 137.7, 137.0, 130.1, 130.0, 129.5, 129.4, 129.3, 129.0, 127.2, 127.1, 126.8, 126.7, 126.7, 124.7, 124.6, 123.2, 123.1, 121.5, 120.3, 117.5, 117.1, 104.6, 94.8, 0.1; HRMS ESI: (m/z) [M+H]+: calcd. for C₃₈H₂₄NiS₂: 531.2251; found: 531.2245.

To a round-bottomed flask with 7a (6 mmol, 3.18 g) in THF (70 ml) was added TBAF (6.3 mmol, 1 M in THF, 6.3 mL) at room temperature for 5 min. The reaction mixture was quenched with water, the aqueous layer was extracted three times with EtOAc and separated organic layer was washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/DCM = 10/1 to 8/1) to afford the product 7b as a white solid (2.31 g, 84%). M.P. = 202–203 °C; Rf = 0.58 (PE/EA = 30/1).\(^1\)H NMR (400 MHz, CDCl₃): δ 8.75 (d, J = 8.4 Hz, 2H), 8.16 (ddd, J = 8.8, 8.4, 1.2 Hz, 2H), 7.96 (d, J = 1.6 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.66 (ddt, J = 8.4, 7.6, 1.6 Hz, 2H), 7.60–7.55 (m, 2H), 7.53 (dd, J = 8.4, 1.6 Hz, 1H), 7.12–7.05 (m, 8H), 6.90–6.85 (m, 2H) 3.19 (s, 1H); \(^1\)C NMR (100 MHz, CDCl₃): δ 147.6, 147.4, 145.7, 144.6, 137.7, 137.6, 130.8, 130.1, 130.0, 129.5, 129.4, 129.3, 129.0, 127.2, 127.1, 126.9, 126.7, 126.7, 124.6, 124.6, 123.2, 123.1, 121.8, 121.6, 119.2, 117.6, 117.3, 83.2, 77.8; HRMS ESI: (m/z) [M+H]^+: calcd. for C₃₄H₂₅N₂: 459.1856; found: 459.1850.

**11-(naphthalen-2-yl)-9,14-diphenyl-9,14-dihydribenzo[a,c]phenazine (8a)**

An oven-dried Schlenk tube containing a stirring bar was charged with 5 (0.5 mmol, 291.3 mg), K₂CO₃ (1.0 mmol, 138.2 mg), naphthalen-1-ylboronic acid (0.75 mmol, 129.0 mg), Pd(PPh₃)₄ (0.002 mmol, 23.1 mg). Then the sealed tube was evacuated and backfilled with N₂ (This process was repeated for three times). 2.5 mL toluene and 2.5 ml H₂O were then added at room temperature and the reaction mixture was stirred at 110 °C for 12 h. The reaction mixture was quenched with sat. aq. NH₄Cl, the aqueous layer was extracted three times with EtOAc and separated organic layer was washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/DCM = 5/1) to afford the product 8a as a pale-yellow solid (250.0 mg, 89%). M.P. = 274–275 °C; Rf = 0.50 (PE/DCM = 3/1); \(^1\)H NMR (400 MHz, CDCl₃): 8.76 (d, J = 8.4 Hz, 2H), 8.19 (d, J =
7.6 Hz, 1H), 8.15 (d, J = 7.6 Hz, 1H), 8.11 (dd, J = 10.8, 2.0 Hz, 2H), 7.95 (t, J = 8.8 Hz, 2H), 7.92–7.79 (m, 3H), 7.75–7.62 (m, 3H), 7.62–7.47 (m, 4H), 7.13–6.98 (m, 8H), 6.88–6.75 (m, 2H). 13C NMR (100 MHz, CDCl3): δ 147.9, 147.8, 145.2, 144.4, 138.7, 138.3, 138.2, 137.8, 133.8, 132.8, 130.1, 129.7, 129.5, 129.0, 128.8, 128.4, 127.8, 127.5, 127.2, 127.1, 126.7, 126.6, 126.4, 126.2, 125.9, 125.6, 124.8, 124.7, 124.6, 123.2, 121.4, 121.3, 117.2, 116.9. HRMS ESI: (m/z) [M+H]⁺: calcd. for C₄₂H₂₉N₂: 561.2325; found: 561.2310.

11-(naphthalen-1-yl)-9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine (8b)

![Diagram](Diagram.png)

An oven-dried Schlenk tube containing a stirring bar was charged with 5 (0.5 mmol, 291.3 mg), K₂CO₃ (1.0 mmol, 138.2 mg), naphthalen-1-ylboronic acid (0.75 mmol, 129.0 mg), Pd(PPh₃)₄ (0.02 mmol, 23.1 mg). Then the sealed tube was evacuated and backfilled with N₂ (This process was repeated for three times). 2.5 mL toluene and 2.5 ml H₂O were then added at room temperature and the reaction mixture was stirred at 110 °C for 23 h. The reaction mixture was quenched with sat. aq. NH₄Cl, the aqueous layer was extracted three times with EtOAc and separated organic layer was washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/DCM = 5/1) to afford the product 8b as a pale-yellow solid (240.8 mg, 86%). M.P. = 297–298 °C; Rf = 0.50 (PE/DCM = 3/1); ¹H NMR (400 MHz, CDCl3): δ 8.76 (d, J = 8.4 Hz, 2H), 8.16 (dd, J = 8.0, 0.8 Hz, 1H), 8.10 (dd, J = 8.0, 0.8 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.96–7.85 (m, 4H), 7.66 (dd, J = 8.0, 6.8, 1.2 Hz, 2H), 7.59–7.44 (m, 7H), 7.12–7.02 (m, 8H), 6.88–6.78 (m, 2H). ¹³C NMR (100 MHz, CDCl3): δ 147.9, 147.9, 144.8, 144.0, 139.5, 138.2, 138.1, 134.0, 131.8, 130.1, 129.6, 129.5, 129.0, 128.8, 128.5, 128.1, 127.2, 127.2, 127.2, 126.9, 126.7, 126.4, 126.1, 126.1, 125.6, 124.7, 123.2, 123.2, 121.4, 121.4, 117.3, 117.3. HRMS ESI: (m/z) [M+H]⁺: calcd. for C₄₂H₂₀N₂: 561.2325; found: 561.2309.

4. X-ray Crystallography

Single crystals suitable for X-ray crystal analysis were obtained from EtOAc and DCM provided good quality crystals. Details of crystal data and structural refinements are given.

X-ray crystallographic data of compound (3f). (CCDC 1973195)
ORTEP of 3f showing thermal ellipsoids at the 30% probability level.

Single crystal X-ray diffraction data was collected at 193(2) K for 3f on a Bruker D8 Venture diffractometer.

Table 1. Crystal data and structure refinement of 3f.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>mo_d8v181051_0m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C37 H26 N2 O</td>
</tr>
<tr>
<td>Formula weight</td>
<td>514.60</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 7.9242(3) Å</td>
</tr>
<tr>
<td></td>
<td>b = 9.1825(4) Å</td>
</tr>
<tr>
<td></td>
<td>c = 18.6310(8) Å</td>
</tr>
<tr>
<td>Volume</td>
<td>1353.81(10) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.262 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.076 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>540</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.200 x 0.170 x 0.130 mm³</td>
</tr>
</tbody>
</table>
Theta range for data collection: 3.117 to 25.998°.

Index ranges:
-9 ≤ h ≤ 9,
-11 ≤ k ≤ 11,
-22 ≤ l ≤ 22

Reflections collected: 13446

Independent reflections: 4726 [R(int) = 0.0350]

Completeness to theta = 25.242°: 99.3%

Absorption correction: Semi-empirical from equivalents

Max. and min. transmission: 0.7456 and 0.6222

Refinement method: Full-matrix least-squares on F²

Data / restraints / parameters: 4726 / 2 / 363

Goodness-of-fit on F²: 1.086

Final R indices [I>2σ(I)]:
R1 = 0.0355, wR2 = 0.0827

R indices (all data):
R1 = 0.0422, wR2 = 0.0877

Absolute structure parameter: -0.6(9)

Extinction coefficient: 0.073(8)

Largest diff. peak and hole: 0.117 and -0.103 e.Å⁻³

5. Reference

6. NMR Data

1H NMR 400 M

13C NMR 100 M