Electronic Supplementary Information

Pd-Catalyzed cascade cyclization of o-alkynylanilines via C-H/C-N bond cleavage leading to dibenzo[a,c]carbazoles

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1. General Information

$^1$H and $^{13}$C NMR spectra were recorded on Bruker Avance II-400 spectrometer (400 MHz for $^1$H, 100 MHz for $^{13}$C). $^1$H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CDCl$_3$ at 7.26 ppm or TMS, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broadened), and coupling constants (Hz). $^{13}$C NMR spectra were recorded on Bruker Avance II-400 (100.5 MHz) spectrometer with complete proton decoupling, and chemical shift reported in ppm (δ) relative to the central line for CDCl$_3$ at 77 ppm. High resolution mass spectra were recorded on a GC-TOF mass spectrometry. Column chromatography was carried out employing silica gel 60 N (spherical, neutral, 40~100 μm, KANTO Chemical Co.) and Silica gel 60 (Merck). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck).

All chemicals were purchased and used as received. The starting materials were prepared following the reported methods. The starting substrates and products were determined by $^1$H and $^{13}$C NMR spectroscopy, and high-resolution mass spectrometry. The structures of products were also determined by comparison with the reported authentic samples.

References

2. General Procedure for the Pd-catalyzed synthesis of dibenzo[a,c]carbazoles

To a mixture of 2-(biphenyl-2-ylethynyl)-N,N-dimethylaniline 1a (89.2 mg, 0.3 mmol), PaCl$_2$ (5.3 mg, 10 mol%), MnO$_2$ (78 mg, 3 equiv), PivOH (30.6 mg, 1.0 equiv) was added anhydrous dimethylacetamide (DMAc, 1.5 mL, 0.2 M) under N$_2$ atmosphere. The reaction mixture was stirred vigorously at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was passed through a short silica pad using CH$_2$Cl$_2$ as an eluent. After concentration, the residue was purified by silica gel chromatography, affording the product 2a as a brown solid (93%, 78.5 mg).

3. Representative synthetic method for biaryl-tethered o-alkynylanilines 1. The substrates 1 were prepared by Pd-catalyzed Sonogashira coupling of o-alkynylanilines with 2-halobiaryls. The o-alkynylanilines and 2-halobiaryls were prepared following the reported methods. 

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4. Characterization Data of 1-3

2-(Biphenyl-2-ylethynyl)-N,N-dimethylaniline (1a)

Brown oil (0.61 g, 93% yield). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.77-7.80 (m, 3H), 7.50-7.55 (m, 3H), 7.37-7.48 (m, 4H), 7.28 (t, $J$ = 8.0 Hz, 1H), 6.90-6.95 (m, 2H), 2.90 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.4, 143.3, 140.6, 134.2, 132.6, 129.4, 129.3, 129.0, 128.1, 127.8, 127.2, 126.9, 122.2, 120.1, 116.6, 115.0, 94.3, 91.6, 43.1; HRMS [m/z]: Calcd for C$_{22}$H$_{19}$N: 297.1517, Found: 297.1506.

2-(Biphenyl-2-ylethynyl)-N-methylaniline (1b)

Brown oil (0.48 g, 50% yield). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.74-7.78 (m, 3H), 7.51-7.60 (m, 3H), 7.40-7.50 (m, 4H), 7.29 (d, $J$ = 7.2 Hz, 1H), 6.72 (t, $J$ = 7.2 Hz, 1H), 6.58 (d, $J$ = 8.4 Hz, 1H), 4.22 (m, 1H), 2.74 (d, $J$ = 5.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.8, 143.2, 141.1, 132.3, 131.8, 129.9, 129.3, 129.1, 128.1, 128.0, 127.4, 127.1, 122.0, 115.8, 108.6, 107.1, 94.7, 89.4, 29.9.; HRMS [m/z]: Calcd for C$_{21}$H$_{17}$N: 283.1361, Found: 283.1374.

2-(Biphenyl-2-ylethynyl)-N,N-dihexylaniline (1c)
Brown oil (0.57 g, 62% yield). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.68 (d, $J = 8.0$ Hz, 2H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.41-7.46 (m, 3H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.14-7.21 (m, 2H), 6.87 (d, $J = 8.0$ Hz, 1H), 6.78 (t, $J = 8.0$ Hz, 1H), 3.20 (t, $J = 8.0$ Hz, 4H), 1.43-1.48 (m, 4H), 1.19-1.26 (m, 12H), 0.84 (t, $J = 8.0$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.6, 143.3, 140.8, 134.4, 132.7, 129.5, 129.4, 128.6, 128.0, 127.9, 127.3, 126.9, 122.5, 119.9, 119.6, 116.5, 93.5, 92.2, 52.4, 31.7, 27.3, 26.9, 22.7, 14.0; HRMS [m/z]: Calcd for C$_{32}$H$_{39}$N: 437.3083, Found: 437.3094.

1-(2-(Biphenyl-2-ylethynyl)phenyl)pyrrolidine (1d)

Yellow solid (0.54 g, 85% yield). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.65-7.67 (m, 2H), 7.60-7.62 (m, 1H), 7.31-7.47 (m, 6H), 7.25-7.27 (m, 1H), 7.13-7.17 (m, 1H), 6.60-6.66 (m, 2H), 3.38 (t, $J = 8.0$ Hz, 4H), 1.80-1.83 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.7, 143.1, 140.9, 135.3, 132.1, 129.5, 129.2, 127.9, 127.7, 127.2, 127.0, 122.7, 116.5, 113.6, 108.4, 93.7, 92.0, 50.1, 25.7; HRMS [m/z]: Calcd for C$_{24}$H$_{21}$N: 323.1674, Found: 323.1664.

2-(Biphenyl-2-ylethynyl)-N-benzyl-N-methylaniline (1e)

Brown oil (0.19 g, 12% yield). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.69-7.72 (m, 2H), 7.60-7.62 (m, 1H), 7.31-7.47 (m, 6H), 7.25-7.27 (m, 1H), 7.13-7.17 (m, 1H), 6.60-6.66 (m, 2H), 3.38 (t, $J = 8.0$ Hz, 4H), 1.80-1.83 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.5, 143.5, 140.7, 138.9, 134.4, 132.5, 129.4, 129.3, 129.1, 128.2, 128.04, 127.97, 127.8, 127.3, 126.8, 126.8, 122.1, 120.3, 117.7, 115.1, 94.6, 91.5, 59.6, 39.1; HRMS [m/z]: Calcd for C$_{28}$H$_{23}$N: 373.1830, Found: 373.1836.

2-(Biphenyl-2-ylethynyl)-N-methyl-N-phenylaniline (1f)

Brown oil (0.95 g, 87% yield). $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.54-7.56 (m, 2H), 7.31-7.35 (m, 3H), 7.25-7.30 (m, 5H), 7.22-7.23 (m, 1H), 7.17-7.21 (m, 3H), 7.09 (d, $J = 7.5$ Hz, 1H), 6.78 (t, $J = 7.0$ Hz, 1H), 6.69 (d, $J = 8.5$ Hz, 2H), 3.15 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 150.1,
149.0, 143.4, 140.4, 133.9, 132.2, 129.3, 128.7, 128.4, 127.8, 127.4, 127.3, 126.8, 124.9, 121.8, 121.6, 118.0, 115.0, 94.2, 90.0, 39.6; HRMS [m/z]: Calcd for C_{27}H_{21}N: 359.1674, Found: 359.1666.

2-(Biphenyl-2-ylethynyl)-N,N,4-trimethylaniline (1g)

Brown oil (0.27 g, 11% yield). \(^1^H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.68-7.70 (m, 3H), 7.32-7.47 (m, 6H), 7.09 (s, 1H), 7.03 (d, \(J = 8.0\) Hz, 1H), 6.79 (d, \(J = 8.0\) Hz, 1H), 2.78 (s, 6H), 2.25 (s, 3H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 152.3, 143.5, 140.8, 134.5, 132.7, 129.8, 129.7, 129.4, 128.1, 127.9, 127.2, 126.9, 122.3, 116.8, 115.4, 94.1, 91.6, 43.5, 20.2; HRMS [m/z]: Calcd for C_{23}H_{18}N: 311.1674, Found: 311.1680.

2-((Biphenyl-2-yl-2',3',4',5',6'-d\(_5\))ethynyl)-N,N,4-trimethylaniline (1g-\(d_5\))

Brown oil (0.61 g, 97% yield). \(^1^H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.68 (d, \(J = 8.0\) Hz, 1H), 7.39-7.44 (m, 2H), 7.32-7.37 (m, 1H), 7.08 (s, 1H), 7.02 (d, \(J = 8.0\) Hz, 1H), 6.79 (d, \(J = 8.4\) Hz, 1H), 2.78 (s, 6H), 2.24 (s, 3H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 152.3, 143.4, 140.6, 134.5, 132.7, 129.8, 129.7, 129.4, 128.1, 126.9, 122.3, 116.8, 115.4, 94.1, 91.6, 43.5, 20.2; HRMS [m/z]: Calcd for C_{23}H_{16}D_5N: 316.1988, Found: 316.1978.

2-(Biphenyl-2-ylethynyl)-N,N,5-trimethylaniline (1h)

Brown oil (0.12 g, 20% yield). \(^1^H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.66-7.70 (m, 3H), 7.45 (t, \(J = 8.0\) Hz, 2H), 7.31-7.42 (m, 4H), 7.16 (d, \(J = 8.0\) Hz, 1H), 6.67 (d, \(J = 12.0\) Hz, 2H), 2.82 (s, 6H), 2.33 (s, 3H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 154.2, 143.2, 140.7, 139.1, 134.0, 132.5, 129.32, 129.28, 127.9, 127.8, 127.1, 126.8, 122.3, 121.0, 117.3, 112.1, 93.7, 91.8, 43.0, 21.7; HRMS [m/z]: Calcd for C_{23}H_{12}N: 311.1674, Found: 311.1665.
2-(Biphenyl-2-yethynyl)-4-fluoro-N,N-dimethylaniline (1i)

Brown solid (0.25 g, 81% yield). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.53-7.55 (m, 3H), 7.25-7.34 (m, 5H), 7.19-7.22 (m, 1H), 6.83 (d, $J = 8.0$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 6.65-6.68 (m, 1H), 2.62 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.74 (d, $J = 238.0$ Hz), 151.1 (d, $J = 2.0$ Hz), 143.7, 140.6, 132.8, 129.5, 129.3, 128.5, 127.9, 127.4, 127.0, 121.7, 120.0 (d, $J = 23.0$ Hz), 118.0 (d, $J = 8.0$ Hz), 117.0 (d, $J = 10.0$ Hz), 115.7 (d, $J = 22.0$ Hz), 95.2, 90.2 (d, $J = 2.0$ Hz), 43.6; HRMS [m/z]: Calcd for C$_{22}$H$_{18}$FN: 315.1423, Found: 315.1429.

2-(Biphenyl-2-yethynyl)-N,N-dimethyl-4-(trifluoromethyl)aniline (1j)

Light yellow solid (0.73 g, 95% yield). $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.76-7.78 (m, 3H), 7.65 (s, 1H), 7.47-7.58 (m, 6H), 7.42-7.45 (m, 1H), 6.88 (d, $J = 10.0$ Hz, 1H), 2.96 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 155.9, 143.7, 140.6, 132.4, 131.7 (q, $J = 3.8$ Hz), 129.5, 128.6 (q, $J = 275.0$ Hz), 128.5, 127.9, 127.0, 125.7 (q, $J = 3.8$ Hz), 125.4, 123.3, 121.8, 121.0 (q, $J = 32.5$ Hz), 115.8, 113.0, 95.2, 90.8, 42.3; HRMS [m/z]: Calcd for C$_{23}$H$_{18}$F$_3$N: 365.1391, Found: 365.1396.

2-(Biphenyl-2-yethynyl)-5-fluoro-N,N-dimethylaniline (1k)

Brown oil (0.17 g, 57% yield). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.63-7.67 (m, 3H), 7.37-7.46 (m, 5H), 7.33 (d, $J = 6.0$ Hz, 1H), 7.19 (t, $J = 6.4$ Hz, 1H), 6.49-6.53 (m, 2H), 2.81 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.3 (d, $J = 247.0$ Hz), 156.11 (d, $J = 9.0$ Hz), 143.4, 140.7, 135.6 (d, $J = 10.0$ Hz), 132.4, 129.5, 129.4, 128.2, 127.9, 127.3, 127.0, 122.2, 110.3 (d, $J = 3.0$ Hz), 106.7 (d, $J = 22.0$ Hz), 103.9 (d, $J = 25.0$ Hz), 93.9 (d, $J = 1.0$ Hz), 90.9, 42.8; HRMS [m/z]: Calcd for C$_{22}$H$_{18}$FN: 315.1423, Found: 315.1428.

$N,N$-Dimethyl-2-((4'-methyl-biphenyl-2-yl)ethynyl)aniline (1l)
Brown oil (0.32 g, 90% yield). \( ^1 \text{H NMR (CDCl}_3, 400 \text{ MHz)} \delta 7.77 \text{ (d, } J = 8.0 \text{ Hz, 1H), 7.70 \text{ (d, } J = 8.0 \text{ Hz, 2H), 7.40-7.52 \text{ (m, 4H), 7.34-7.38 \text{ (m, 2H), 7.27-7.31 \text{ (m, 1H), 6.92-6.96 \text{ (m, 2H), 2.92 \text{ (s, 6H), 2.52 \text{ (s, 3H); 13C NMR (100 MHz, CDCl}_3) \delta 154.4, 143.3, 137.8, 136.8, 134.2, 132.6, 129.4, 129.2, 129.0, 128.5, 128.1, 126.7, 122.1, 120.1, 116.6, 115.2, 94.5, 91.5, 43.1, 21.1; HRMS [m/z]: Calcd for C}_{23}H_{21}N: 311.1674, Found: 311.1680.}

2-((4'-Chloro-biphenyl-2-yl)ethynyl)-N,N-dimethylaniline (1m)

Yellow solid (0.34 g, 97% yield). \( ^1 \text{H NMR (CDCl}_3, 400 \text{ MHz)} \delta 7.68 \text{ (d, } J = 8.0 \text{ Hz, 1H), 7.63 \text{ (d, } J = 8.0 \text{ Hz, 2H), 7.33-7.43 \text{ (m, 5H), 7.29-7.31 \text{ (m, 1H), 7.21-7.26 \text{ (m, 1H), 6.85-6.90 \text{ (m, 2H), 2.82 \text{ (s, 6H); 13C NMR (100 MHz, CDCl}_3) \delta 154.6, 142.1, 139.2, 134.2, 133.3, 132.8, 130.7, 129.3, 129.2, 128.2, 128.1, 127.3, 122.2, 120.3, 116.8, 115.0, 93.9, 92.1, 43.2; HRMS [m/z]: Calcd for C}_{22}H_{18}ClN: 331.1128, Found: 331.1129.}

10-(Biphenyl-2-ylethynyl)-N,N-dimethylphenanthren-9-amine (1n)

Yellow-green solid (0.23 g, 59% yield). \( ^1 \text{H NMR (CDCl}_3, 400 \text{ MHz)} \delta 8.62 \text{ (d, } J = 8.0 \text{ Hz, 1H), 8.57 \text{ (d, } J = 8.0 \text{ Hz, 1H), 8.42-8.44 \text{ (m, 1H), 7.86-7.91 \text{ (m, 2H), 7.69-7.71 \text{ (m, 2H), 7.59-7.65 \text{ (m, 2H), 7.53-7.56 \text{ (m, 1H), 7.38-7.51 \text{ (m, 7H), 3.09 \text{ (s, 6H); 13C NMR (100 MHz, CDCl}_3) \delta 151.5, 143.9, 141.1, 132.4, 132.2, 131.4, 131.2, 129.8, 129.4, 128.3, 128.2, 127.4, 127.3, 127.2, 126.9, 126.7, 126.3, 125.9, 125.4, 122.7, 122.6, 122.2, 114.5, 99.5, 89.8, 43.8; HRMS [m/z]: Calcd for C}_{30}H_{23}N: 397.1830, Found: 397.1829.}

2-((2-(Benzo[b]thiophen-3-yl)phenyl)ethynyl)-N,N-dimethylaniline (1o)
Brown oil (1.36 g, 96% yield). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.93-7.95 (m, 1H), 7.73-7.79 (m, 2H), 7.65 (s, 1H), 7.52-7.53 (m, 1H), 7.35-7.46 (m, 4H), 6.14-6.19 (m, 1H), 6.94-6.97 (m, 1H), 6.81 (d, $J = 8.0$ Hz, 1H), 6.73-6.78 (m, 1H), 2.73 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.3, 139.9, 138.5, 137.4, 136.3, 132.6, 130.1, 129.0, 127.9, 127.4, 125.4, 124.2, 124.1, 123.7, 123.5, 122.5, 120.1, 116.6, 114.9, 94.0, 92.3, 43.1; HRMS [m/z]: Calcd for C$_{24}$H$_{19}$NS: 353.1238, Found: 353.1229.

9-Methyl-9H-dibenzo[a,c]carbazole (2a)

Brown solid (78.5 mg, 95% yield). $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 8.86 (d, $J = 10.0$ Hz, 1H), 8.82-8.84 (m, 1H), 8.75 (d, $J = 10.0$ Hz, 1H), 8.62-8.64 (m, 1H), 8.61 (d, $J = 10.0$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.62-7.67 (m, 2H), 7.56-7.60 (m, 2H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.41 (d, $J = 8.0$ Hz, 1H), 4.31 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 140.8, 134.6, 130.9, 129.9, 127.3, 126.9, 126.1, 125.6, 124.0, 123.9, 123.64, 123.56, 123.5, 123.42, 123.41, 122.8, 121.8, 120.3, 113.4, 109.5, 34.5; HRMS [m/z]: Calcd for C$_{21}$H$_{15}$N: 281.1192, Found: 281.1205.

9-Hexyl-9H-dibenzo[a,c]carbazole (2c)

Brown solid (96.9 mg, 92% yield). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.95 (d, $J = 8.0$ Hz, 1H), 8.86-8.88 (m, 1H), 8.79 (d, $J = 8.0$ Hz, 1H), 8.69 (d, $J = 8.0$ Hz, 1H), 8.43-8.45 (m, 1H), 7.81 (t, $J = 8.0$ Hz, 1H), 7.67-7.69 (m, 2H), 7.58-7.64 (m, 2H), 7.54 (t, $J = 8.0$ Hz, 1H), 7.47 (t, $J = 8.0$ Hz, 1H), 4.63 (t, $J = 8.0$ Hz, 2H), 2.03-2.11 (m, 2H), 1.51-1.58 (m, 2H), 1.38-1.46 (m, 4H), 0.99 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.4, 133.6, 130.8, 130.0, 127.2, 126.8, 126.2, 125.4, 124.1, 123.6, 123.52, 123.50, 123.48, 123.39, 123.35, 122.4, 121.8, 120.2, 113.6, 109.6, 46.1, 31.4, 29.8, 26.6, 22.6, 14.0; HRMS [m/z]: Calcd for C$_{26}$H$_{23}$N: 351.2017, Found: 351.1984.
4-(9H-Dibenzo[a,c]carbazol-9-yl)butyl pivalate (2d)

Brown liquid (87.1 mg, 70% yield). ¹H NMR (CDCl₃, 400 MHz) δ 8.90 (d, J = 8.0 Hz, 1H), 8.83-8.87 (m, 1H), 8.76 (d, J = 8.0 Hz, 1H), 8.64 (d, J = 8.0 Hz, 1H), 8.40-8.42 (m, 1H), 7.77 (t, J = 8.0 Hz, 1H), 7.65-7.68 (m, 2H), 7.56-7.62 (m, 2H), 7.51 (t, J = 8.0 Hz, 1H), 4.72 (t, J = 8.0 Hz, 2H), 4.16 (t, J = 8.0 Hz, 2H), 2.11-2.19 (m, 2H), 1.78-1.85 (m, 2H), 1.20 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 178.4, 140.4, 133.5, 130.9, 129.9, 127.3, 126.9, 126.4, 125.5, 124.2, 123.7, 123.6, 123.4, 122.2, 121.9, 120.4, 113.8, 109.5, 63.5, 45.7, 38.7, 27.1, 26.6, 26.1; HRMS [m/z]: Calcd for C₂₉H₂₉NO₂: 423.2198, Found: 423.2208.

9-(4-Chlorobutyl)-9H-dibenzo[a,c]carbazole (2d’)

Yellow solid (11.0 mg, 10% yield). ¹H NMR (CDCl₃, 400 MHz) δ 8.85-8.90 (m, 2H), 8.77 (d, J = 8.0 Hz, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.44 (t, J = 8.0 Hz, 1H), 7.77 (t, J = 8.0 Hz, 1H), 7.65-7.68 (m, 2H), 7.56-7.61 (m, 2H), 7.50 (t, J = 8.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 4.74 (t, J = 8.0 Hz, 2H), 3.56 (t, J = 8.0 Hz, 2H), 2.19-2.27 (m, 2H), 1.89-1.96 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 140.5, 133.6, 130.9, 129.9, 127.3, 127.0, 126.5, 125.6, 124.3, 123.9, 123.8, 123.6, 123.5, 123.4, 122.3, 122.0, 120.5, 113.9, 109.6, 45.5, 44.3, 29.8, 27.4; HRMS [m/z]: Calcd for C₂₄H₂₃ClN: 357.1284, Found: 357.1293.

9-Phenyl-9H-dibenzo[a,c]carbazole (2f)

White solid (68.1 mg, 67% yield). ¹H NMR (CDCl₃, 400 MHz) δ 8.96 (d, J = 8.0 Hz, 1H), 8.82 (d, J = 8.0 Hz, 2H), 8.67 (d, J = 8.0 Hz, 1H), 7.81 (t, J = 8.0 Hz, 1H), 7.62-7.70 (m, 4H), 7.53-7.59 (m, 3H), 7.38-7.50 (m, 3H), 7.29 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H); ¹³C NMR
(100 MHz, CDCl₃) δ 142.1, 140.3, 134.5, 130.9, 130.2, 129.9, 129.1, 128.9, 127.4, 127.3, 125.9, 125.7, 124.00, 123.95, 123.82, 123.80, 123.5, 123.2, 121.7, 121.0, 114.2, 111.0; HRMS [m/z]: Calcd for C₂₆H₁₇N: 343.1361, Found: 343.1355.

9,12-Dimethyl-9H-dibenzo[a,c]carbazole (2g)

Light yellow solid (67.1 mg, 78% yield). ¹H NMR (CD₂Cl₂, 400 MHz) δ 8.77 (d, J = 8.0 Hz, 2H), 8.68 (d, J = 8.0 Hz, 1H), 8.59 (t, J = 8.0 Hz, 1H), 8.30 (s, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.58-7.60 (m, 2H), 7.51 (t, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 4.14 (s, 3H), 2.58 (s, 3H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 139.2, 134.7, 130.7, 130.0, 129.6, 127.2, 126.7, 126.2, 125.5, 125.2, 124.0, 123.5, 123.43, 123.41, 123.36, 123.0, 121.5, 112.7, 109.3, 34.5, 21.5; HRMS [m/z]: Calcd for C₂₂H₁₇N: 295.1361, Found: 295.1369.

9,12-Dimethyl-9H-dibenzo[a,c]carbazole-1,2,3,4-d₄ (2g-d₄)

Light yellow solid (67.5 mg, 76% yield). ¹H NMR (CD₂Cl₂, 400 MHz) δ 8.74-8.77 (m, 1H), 8.62-8.64 (m, 1H), 8.29 (s, 1H), 7.57-7.62 (m, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 4.26 (s, 3H), 2.54 (s, 3H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 139.3, 134.8, 130.7, 129.9, 129.7, 126.7, 126.2, 125.6, 125.2, 124.0, 123.4, 123.0, 121.5, 112.8, 109.3, 34.6, 21.5; HRMS [m/z]: Calcd for C₂₂H₁₃D₄N: 299.1612, Found: 299.1620.

9,11-Dimethyl-9H-dibenzo[a,c]carbazole (2h)

Gray-green solid (61.8 mg, 70% yield). ¹H NMR (CDCl₃, 400 MHz) δ 8.84-8.87 (m, 2H), 8.77 (d, J = 8.0 Hz, 1H), 8.68-8.70 (m, 1H), 8.48 (d, J = 8.0 Hz, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.65-7.68 (m, 2H), 7.58 (t, J = 8.0 Hz, 1H), 7.39 (s, 1H), 7.23 (d, J = 8.0 Hz, 1H), 4.37 (s, 3H), 2.63 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 141.1, 134.2, 133.6, 130.6, 129.8, 127.1, 126.8, 125.9, 125.2, 123.93, 123.88, 123.5, 123.4, 122.6, 121.8, 121.4, 121.2, 113.3, 109.6, 34.3, 22.1; HRMS [m/z]: Calcd for C₂₂H₁₇N: 295.1361, Found: 295.1367.
12-Fluoro-9-methyl-9H-dibenzo[a,c]carbazole (2i)

White solid (68.6 mg, 78% yield). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz) \(\delta\) 8.76-8.78 (m, 1H), 8.69 (d, \(J = 8.0\) Hz, 1H), 8.56-8.59, 8.13 (d, \(J = 10.4\) Hz, 1H), 7.71 (t, \(J = 8.0\) Hz, 1H), 7.61-7.67 (m, 2H), 7.55 (t, \(J = 8.0\) Hz, 1H), 7.42-7.45 (m, 1H), 7.20 (t, \(J = 8.8\) Hz, 1H), 4.21 (s, 3H); \(^{13}\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 157.9 (d, \(J = 233.0\) Hz), 137.1, 135.6, 130.9, 129.4, 127.3, 126.6, 126.2, 125.9, 123.9, 123.7, 123.6, 123.4, 123.1, 123.0, 122.9, 112.6 (d, \(J = 5.0\) Hz), 111.4 (d, \(J = 5.0\) Hz), 110.1 (d, \(J = 9.0\) Hz), 106.7 (d, \(J = 24.0\) Hz), 34.5; HRMS [m/z]: Calcd for C\(_{21}\)H\(_{14}\)FN: 299.1110, Found: 299.1105.

9-Methyl-12-(trifluoromethyl)-9H-dibenzo[a,c]carbazole (2j)

Brown solid (100.8 mg, 97% yield). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.65-8.69 (m, 2H), 8.60 (t, \(J = 8.0\) Hz, 2H), 8.40 (d, \(J = 8.0\) Hz, 1H), 7.71 (t, \(J = 8.0\) Hz, 1H), 7.53-7.64 (m, 4H), 7.43 (d, \(J = 8.0\) Hz, 1H), 4.09 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 141.7, 135.4, 131.0, 127.5, 126.9, 126.8, 126.0, 124.6 (q, \(J = 292.0\) Hz), 124.1, 124.0, 123.4, 123.2, 122.7, 122.6, 122.3, 122.0, 120.1 (q, \(J = 4.0\) Hz), 119.0 (q, \(J = 4.0\) Hz), 113.2, 109.4, 34.4.; HRMS [m/z]: Calcd for C\(_{22}\)H\(_{14}\)F\(_3\)N: 349.1078, Found: 349.1068.

11-Fluoro-9-methyl-9H-dibenzo[a,c]carbazole (2k)

White solid (76.3 mg, 85% yield). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.71 (d, \(J = 8.0\) Hz, 1H), 8.65 (d, \(J = 8.0\) Hz, 1H), 8.60 (d, \(J = 8.0\) Hz, 1H), 8.36 (d, \(J = 8.0\) Hz, 1H), 8.31 (d, \(J = 8.0\) Hz, 1H), 7.67 (t, \(J = 8.0\) Hz, 1H), 7.50-7.60 (m, 3H), 7.00-7.07 (m, 2H), 3.98 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.5 (d, \(J = 238.0\) Hz), 141.0 (d, \(J = 11.0\) Hz) 134.6, 130.3, 129.2, 127.1, 126.7, 125.9, 125.3, 123.8, 123.6, 123.34, 123.25, 123.1, 122.4, 122.3, 119.6, 112.9, 108.2 (d, \(J = 24.0\) Hz), 95.8 (d, \(J = 27\) Hz), 34.3; HRMS [m/z]: Calcd for C\(_{21}\)H\(_{14}\)FN: 299.1110, Found: 299.1105.
2,9-Dimethyl-9H-dibenzo[α,c]carbazole (2l)

White solid (71.5 mg, 81% yield). $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.71 (d, $J$ = 8.0 Hz, 1H), 8.57 (t, $J$ = 8.0 Hz, 1H), 7.60 (t, $J$ = 8.0 Hz, 1H), 7.54 (t, $J$ = 8.0 Hz, 1H), 7.42-7.49 (m, 3H), 7.38 (d, $J$ = 8.0 Hz, 1H), 4.08 (s, 3H), 2.72 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 140.5, 136.7, 134.5, 130.8, 129.9, 125.4, 125.2, 125.0, 124.5, 123.6, 123.3, 123.24, 123.23, 123.1, 122.6, 121.7, 119.9, 112.9, 109.3, 34.1, 22.0; HRMS [m/z]: Calcd for C$_{22}$H$_{17}$N: 295.1361, Found: 295.1365.

2-Chloro-9-methyl-9H-dibenzo[α,c]carbazole (2m)

Light yellow solid (81.6 mg, 87% yield). $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.24-8.44 (m, 5H), 7.29-7.49 (m, 6H), 3.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 140.1, 134.4, 132.7, 130.4, 129.9, 125.9, 125.4, 124.7, 124.5, 123.5, 123.3, 123.2, 122.63, 122.56, 122.4, 121.2, 120.2, 111.8, 109.2, 33.9; HRMS [m/z]: Calcd for C$_{21}$H$_{14}$ClN: 315.0843, Found: 315.0816.

9-Methyl-9H-tetrabenzo[α,c,g,i]carbazole (2n)

Off-white solid (100.0 mg, 87% yield). $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) δ 9.00-9.02 (m, 2H), 8.88 (d, $J$ = 8.0 Hz, 2H), 8.78-8.82 (m, 2H), 8.60 (d, $J$ = 8.0 Hz, 2H), 7.70-7.79 (m, 4H), 7.63-7.69 (m, 4H), 4.65 (s, 3H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 137.5, 130.7, 128.7, 128.1, 126.4, 125.7, 125.6, 125.36, 124.43, 124.0, 123.73, 123.65, 123.0, 117.0, 41.4; HRMS [m/z]: Calcd for C$_{29}$H$_{19}$N: 381.1517, Found: 381.1516.

Light brown solid (64.4 mg, 67% yield). $^1$H NMR (CD$_2$Cl$_2$, 500 MHz) $\delta$ 9.12 (d, $J$ = 10.0 Hz, 1H), 8.79 (d, $J$ = 10.0 Hz, 2H), 8.28 (d, $J$ = 10.0 Hz, 1H), 8.06 (d, $J$ = 10.0 Hz, 1H), 7.72 (t, $J$ = 10.0 Hz, 1H), 7.52-7.64 (m, 4H), 7.46 (t, $J$ = 10.0 Hz, 1H), 7.41 (t, $J$ = 10.0 Hz, 1H), 4.33 (s, 3H); $^{13}$C NMR (500 MHz, CD$_2$Cl$_2$) $\delta$ 141.2, 139.2, 137.0, 135.4, 134.4, 130.7, 126.1, 125.3, 125.1, 124.7, 124.5, 124.3, 124.0, 123.7, 123.6, 123.2, 122.32, 122.26, 121.2, 120.6, 113.5, 109.7, 34.7; HRMS [m/z]: Calcd for C$_{23}$H$_{15}$NS: 337.0925, Found: 337.0936.

2-(Biphenyl-2-yl)-1-methyl-1H-indole (3b)

White solid (49.9 mg, 60% yield). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.75 (d, $J$ = 8.0 Hz, 1H), 8.63-8.68 (m, 3H), 7.56 (d, $J$ = 8.0 Hz, 1H), 7.22-7.35 (m, 8H), 6.66 (s, 1H), 3.18 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.6, 140.9, 140.7, 137.2, 132.4, 131.1, 130.1, 129.0, 128.8, 128.2, 128.0, 127.3, 126.9, 121.1, 120.2, 119.5, 109.3, 102.5, 30.3; HRMS [m/z]: Calcd for C$_{21}$H$_{17}$N: 283.1361, Found: 283.1380.
5. $^1$H and $^{13}$C NMR Spectra