Supporting Information

Palladium-Catalyzed Double Coupling Reaction of Terminal Alkynes with Isonitriles: A Direct Approach to Symmetrical N-Aryl Dialkynylimines

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Table of Contents

Experimental...........................................................................................................................................S2
General methods and materials.............................................................................................................S2
General procedure for the synthesis of N-aryl dialkynylimines 3....................................................S2
X-ray data for compound 3g..................................................................................................................S3
X-ray data for compound 5....................................................................................................................S4
X-ray data for compound 6c..................................................................................................................S5
Spectral data of all compounds..........................................................................................................S6-S15
Copies of 1H NMR and 13C NMR spectra of all compounds..........................................................S16-S42
Experimental

General methods and materials. Proton nuclear magnetic resonance spectra ($^1$H NMR) and carbon nuclear magnetic resonance spectra ($^{13}$C NMR) were recorded at 400 MHz and 100 MHz or 500 MHz and 125 MHz, respectively, using CDCl$_3$ as reference standard ($\delta$ 7.26 ppm) for $^1$H NMR and ($\delta$ 77.04 ppm) for $^{13}$C NMR. HRMS were recorded using ESI. Melting points were uncorrected. Precoated silica gel plates GF-254 were used for thin-layer analytical chromatography. Column chromatography was performed on silica gel (300-400 mesh). Unless otherwise noted, all reactions were carried out under the atmosphere of nitrogen. Solvents if necessary were dried and distilled according to standard methods prior to use. All reagents were purchased from commercial sources (Aladdin, Macklin, Adamas, and Guoyao) and used as received without further purification.

General procedure for the synthesis of N-aryl dialkynylimines 3.

A mixture of terminal alkynes 1 (0.2 mmol), isonitriles 2 (0.2 mmol), Pd(dppf)Cl$_2$ (0.01 mmol, 5 mol%), Cu(OAc)$_2$ (0.2 mmol, 1.0 eq) and 3.0 mL CH$_3$CN was stirred at rt for 1-2 h under the atmosphere of nitrogen. The progress of the reaction was monitored by thin-layer chromatography. Upon completion, the mixture was evaporated under reduced pressure, and the residue was separated by column chromatography (ethyl acetate/petroleum ether = 1:50 to 1:10) to give the pure products 3.
### Figure S1 X-ray data for compound 3g (CCDC 1960026)

![Figure S1](image)

**Table S1. Crystal data and structure refinement for 3g**

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<th>Compound</th>
<th>3g</th>
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<tr>
<td>Empirical formula</td>
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<td>Space group</td>
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<td>c/Å</td>
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Figure S2 X-ray data for compound 5 (CCDC 2032367)

![X-ray structure of compound 5](image)

**Table S2. Crystal data and structure refinement for 5**

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Figure S3 X-ray data for compound 6c (CCDC 1960024)

Table S3. Crystal data and structure refinement for 6c

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<td>b/Å</td>
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55
Spectral data of all compounds

*N-(naphthalen-2-yl)-1,5-diphenylpenta-1,4-diyn-3-imine (3a):* brown oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.85 (dd, $J = 11.1$, 8.3 Hz, 3H), 7.74 (s, 1H), 7.67 (dd, $J = 7.6$, 1.6 Hz, 2H), 7.52–7.28 (m, 9H), 7.27–7.20 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.6, 133.9, 133.6, 132.7, 132.5, 132.0, 130.2, 128.6, 128.6, 128.4, 128.2, 127.8, 126.4, 125.8, 121.9, 121.3, 120.8, 118.9, 95.2, 90.4, 88.7, 84.5 ppm; HRMS (ESI) m/z: [M+H]$^+$ Calcd for C$_{27}$H$_{18}$N 356.1434; Found 356.1423.

*N-(1,5-bis(4-tert-butylphenyl)penta-1,4-diyn-3-ylidene)naphthalen-2-amine (3b):* pale brown solid, m.p. 99.0–102.2 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (t, $J = 7.9$ Hz, 3H), 7.79 (s, 1H), 7.67 (d, $J = 8.3$ Hz, 2H), 7.55–7.45 (m, 5H), 7.31 (q, $J = 9.0$ Hz, 4H), 1.38 (s, 9H), 1.31 (s, 9H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.8, 153.4, 147.7, 134.3, 133.7, 132.5, 132.3, 131.9, 128.3, 128.2, 127.8, 126.3, 125.6, 125.5, 122.0, 118.8, 118.3, 117.8, 95.6, 90.8, 88.4, 84.3, 35.0, 35.0, 31.2, 31.1 ppm; HRMS (ESI) m/z: [M+H]$^+$ Calcd for C$_{35}$H$_{34}$N 468.2686; Found 468.2676.

*N-(1,5-bis(4-(pentyloxy)phenyl)penta-1,4-diyn-3-ylidene)naphthalen-2-amine (3c):* pale brown oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.85 (t, $J = 8.2$ Hz, 3H), 7.72 (s, 1H), 7.61 (d, $J = 8.7$ Hz, 2H), 7.50–7.41 (m, 3H), 7.28–7.20 (m, 3H), 6.90 (d, $J = 8.7$ Hz, 2H), 6.76 (d, $J = 8.7$ Hz, 2H), 3.98 (t, $J = 6.6$ Hz, 2H), 3.91 (t, $J = 6.6$ Hz, 2H), 1.78–1.73 (m, 4H), 1.47–1.31 (m, 9H), 0.95–0.87 (m, 6H) ppm; $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ 160.7, 160.5, 147.8, 134.4, 134.4, 134.3, 133.7, 131.8, 128.2, 128.1, 127.8, 126.3, 125.4, 122.2, 118.7, 114.7,
$N$-(1,5-$bis$(3-methoxyphenyl)penta-1,4-diyn-3-ylidene)naphthalen-2-amine (3d): pale brown oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.84–7.74 (m, 3H), 7.65 (d, $J = 1.6$ Hz, 1H), 7.44–7.35 (m, 3H), 7.27–7.19 (m, 2H), 7.15–7.07 (m, 2H), 6.95–6.90 (m, 1H), 6.88–6.80 (m, 2H), 6.65 (d, $J = 1.3$ Hz, 1H), 3.77 (s, 3H), 3.56 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.4, 159.3, 147.7, 134.0, 133.6, 131.9, 129.6, 129.6, 128.3, 128.1, 127.8, 126.4, 125.7, 125.2, 124.9, 122.2, 121.9, 121.6, 118.6, 117.3, 117.1, 116.9, 116.7, 95.2, 90.3, 88.1, 84.2, 55.4, 55.2 ppm; HRMS (ESI) m/z: [M+H]$^+$ Calcd for C$_{29}$H$_{22}$O$_2$N 416.1645; Found 416.1636.

$N$-(1,5-$bis$(2-methoxyphenyl)penta-1,4-diyn-3-ylidene)naphthalen-2-amine (3e): reddish brown oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.89–7.80 (m, 4H), 7.65 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.55 (dd, $J = 8.7, 2.0$ Hz, 1H), 7.52–7.38 (m, 3H), 7.37–7.29 (m, 2H), 7.05–6.91 (m, 2H), 6.86 (t, $J = 7.5$ Hz, 1H), 6.79 (d, $J = 8.6$ Hz, 1H), 3.98 (s, 3H), 3.55 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.2, 161.1, 147.7, 134.5, 134.4, 134.2, 133.7, 131.9, 131.8, 131.4, 128.3, 128.1, 127.7, 126.0, 125.4, 122.3, 120.5, 120.4, 118.7, 110.9, 110.8, 110.7, 110.2, 92.7, 92.3, 88.6, 87.1, 55.9, 55.5 ppm; HRMS (ESI) m/z: [M+H]$^+$ Calcd for C$_{29}$H$_{22}$O$_2$N 416.1645; Found 416.1635.

113.0, 112.4, 96.0, 90.9, 88.1, 84.2, 68.2, 68.2, 28.9, 28.8, 28.2, 28.1, 22.5, 22.4, 14.1, 14.0 ppm; HRMS (ESI) m/z: [M+H]$^+$ Calcd for C$_{37}$H$_{38}$O$_2$N 528.2897; Found 528.2883.
\(N-(1,5\text{-bis}(4\text{-dimethylamino})\text{phenyl})\text{penta-1,4-diyn-3-ylidene})\text{naphthalen-2-amine (3f)}\): black solid, m.p. 85.7-88.4 °C; \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) 7.85 (dd, \(J = 8.5, 3.6\) Hz, 3H), 7.56 (d, \(J = 8.9\) Hz, 2H), 7.52–7.40 (m, 4H), 7.20–7.14 (m, 2H), 6.67 (d, \(J = 9.0\) Hz, 2H), 6.52 (d, \(J = 9.0\) Hz, 2H), 3.02 (s, 6H), 2.96 (s, 6H) ppm; \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) 151.1, 151.0, 148.2, 134.9, 134.1, 134.1, 133.7, 131.6, 128.0, 128.0, 127.7, 126.0, 125.1, 122.6, 118.7, 111.6, 111.5, 107.7, 107.0, 98.0, 92.6, 88.5, 84.8, 40.1, 40.0 ppm; \text{HRMS (ESI)} m/z: \([\text{M+H}]^+\) Calcd for C\(_{31}\)H\(_{28}\)N\(_3\) 442.2278; Found 442.2267.

\(N-(1,5\text{-bis}(4\text{-fluorophenyl})\text{penta-1,4-diyn-3-ylidene})\text{naphthalen-2-amine (3g)}\): pale brown solid, m.p. 129.1-132.1 °C; \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) 7.86–7.71 (m, 3H), 7.69–7.53 (m, 3H), 7.45–7.33 (m, 3H), 7.26–7.17 (m, 2H), 7.02 (t, \(J = 8.7\) Hz, 2H), 6.89 (t, \(J = 8.7\) Hz, 2H) ppm; \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) 163.6 (d, \(^1\text{J}_{\text{CF}} = 252\) Hz), 163.5 (d, \(^1\text{J}_{\text{CF}} = 251\) Hz), 147.5, 134.7 (d, \(^3\text{J}_{\text{CF}} = 8.0\) Hz), 134.6 (d, \(^3\text{J}_{\text{CF}} = 8.0\) Hz), 133.6, 133.57, 132.0, 128.4, 128.1, 127.8, 126.5, 125.8, 121.7, 118.7, 117.3 (d, \(^4\text{J}_{\text{CF}} = 3.0\) Hz), 116.8 (d, \(^4\text{J}_{\text{CF}} = 3.0\) Hz), 116.0 (d, \(^2\text{J}_{\text{CF}} = 22.0\) Hz), 115.9 (d, \(^2\text{J}_{\text{CF}} = 22.0\) Hz), 94.1, 89.3, 88.2, 84.2 ppm; \text{HRMS (ESI)} m/z: \([\text{M+H}]^+\) Calcd for C\(_{27}\)H\(_{16}\)NF\(_2\) 392.1245; Found 392.1238.

\(N-(1,5\text{-bis}(4\text{-chlorophenyl})\text{penta-1,4-diyn-3-ylidene})\text{naphthalen-2-amine (3h)}\): pale brown solid, m.p. 129.8-131.4 °C; \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) 7.91–7.81 (m, 3H), 7.71 (d, \(J = 1.7\) Hz, 1H), 7.64–7.57 (m, 2H), 7.52–7.43 (m, 3H), 7.41–7.36 (m, 2H), 7.27–7.22 (m, 4H) ppm; \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) 147.3, 136.6, 136.2, 133.8, 133.7, 133.5, 133.3, 132.0, 129.0, 128.9, 128.4, 128.1, 127.8, 126.5, 125.9, 125.8, 124.0, 121.7, 118.7, 117.3 (d, \(^4\text{J}_{\text{CF}} = 3.0\) Hz), 116.8 (d, \(^4\text{J}_{\text{CF}} = 3.0\) Hz), 116.0 (d, \(^2\text{J}_{\text{CF}} = 22.0\) Hz), 115.9 (d, \(^2\text{J}_{\text{CF}} = 22.0\) Hz), 94.1, 89.3, 88.2, 84.2 ppm; \text{HRMS (ESI)} m/z: \([\text{M+H}]^+\) Calcd for C\(_{27}\)H\(_{16}\)NF\(_2\) 392.1245; Found 392.1238.
121.7, 119.7, 119.1, 118.8, 93.9, 89.2, 89.1, 85.0 ppm; HRMS (ESI) m/z: [M+H]^+ Calcd for C_{27}H_{16}NCl$_2$ 424.0654; Found 424.0644.

*N-(1,5-bis(2-chlorophenyl)penta-1,4-diyn-3-ylidene)naphthalen-2-amine* (3i): pale brown solid, m.p. 89.2-91.6 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.88–7.79 (m, 4H), 7.69 (dd, J = 7.6, 1.6 Hz, 1H), 7.56–7.41 (m, 4H), 7.39–7.23 (m, 5H), 7.16 (td, J = 7.5, 1.2 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 147.3, 137.2, 134.5, 134.3, 133.6, 133.1, 132.2, 131.1, 130.9, 129.6, 129.5, 128.5, 128.3, 127.8, 126.7, 126.6, 126.4, 125.8, 121.9, 121.5, 121.1, 118.8, 92.9, 91.7, 88.5, 87.2 ppm; HRMS (ESI) m/z: [M+H]^+ Calcd for C_{27}H_{16}NCl$_2$ 424.0654; Found 424.0646.

*N-(1,5-bis(4-(trifluoromethyl)phenyl)penta-1,4-diyn-3-ylidene)naphthalen-2-amine* (3j): pale brown oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.87 (ddd, J = 8.6, 7.3, 6.2 Hz, 3H), 7.79 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 1.8 Hz, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.57–7.40 (m, 7H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 147.2, 133.5, 132.8, 132.7, 132.2, 131.9, 131.8, 131.6, 131.4, 128.5, 128.2, 127.8, 126.6, 126.1, 125.50 (q), 124.9 (q), 124.4, 122.4, 122.2, 121.5, 118.9, 93.1, 89.8, 88.6, 85.6 ppm; HRMS (ESI) m/z: [M+H]^+ Calcd for C$_{29}$H$_{16}$NF$_6$ 492.1181; Found 492.1169.

*N-(1,5-bis(4-bromophenyl)penta-1,4-diyn-3-ylidene)naphthalen-2-amine* (3k): pale brown solid, m.p. 95.8-98.5 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.86–7.72 (m, 3H), 7.64 (d, J = 1.8 Hz, 1H), 7.53–7.44 (m, 4H), 7.43–7.38 (m, 2H), 7.37–7.32 (m, 2H), 7.19 (s, 1H), 7.16–7.03 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 147.3, 133.9, 133.8, 133.5, 133.3, 132.1, 131.9, 131.9, 128.4, 128.1, 127.8, 126.5, 125.9,
1,5-Di[(1,1'-biphenyl)-4-yl]-N-(naphthalen-2-yl) penta-1,4-diyn-3-imine (3l): pale brown oil; ^1H NMR (400 MHz, CDCl₃): δ 7.85–7.77 (m, 3H), 7.69 (d, J = 8.3 Hz, 3H), 7.60–7.53 (m, 4H), 7.49–7.30 (m, 14H), 7.18 (s, 1H) ppm; ^13C NMR (100 MHz, CDCl₃): δ 147.6, 142.9, 142.7, 140.1, 139.9, 133.9, 133.6, 133.1, 133.0, 132.0, 129.0, 129.0, 128.3, 128.2, 128.1, 128.0, 127.8, 127.2, 127.2, 127.1, 126.4, 125.7, 121.9, 120.1, 119.5, 118.9, 95.2, 90.4, 89.3, 85.2 ppm; HRMS (ESI) m/z: [M+H]^+ Calcd for C_{27}H_{16}NBr_{2} 513.9629; Found 513.9613.

N-(1,5-di(naphthalen-2-yl)penta-1,4-diyn-3-ylidene)naphthalen-2-amine (3m): pale brown solid, m.p. 129.6-131.6 °C; ^1H NMR (400 MHz, CDCl₃): δ 8.27 (s, 1H), 7.97–7.66 (m, 12H), 7.60–7.45 (m, 7H), 7.35 (dd, J = 8.5, 1.5 Hz, 1H) ppm; ^13C NMR (100 MHz, CDCl₃): δ 147.7, 133.9, 133.7, 133.6, 133.6, 133.5, 132.9, 132.7, 132.1, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 127.7, 127.6, 126.9, 126.9, 126.4, 125.7, 122.0, 118.9, 118.6, 117.9, 95.8, 90.9, 88.9, 84.9 ppm; HRMS (ESI) m/z: [M+H]^+ Calcd for C_{39}H_{26}N 508.2060; Found 508.2047.

N-(1,5-di(thiophen-3-yl)penta-1,4-diyn-3-ylidene)napht halen-2-amine (3n): brown solid, m.p. 131.8-133.6 °C; ^1H NMR (400 MHz, CDCl₃): δ 7.88–7.84 (m, 3H), 7.77 (dd, J = 2.8, 1.2 Hz, 1H), 7.73 (d, J = 1.9 Hz, 1H), 7.52–7.43 (m, 4H), 7.36–7.32 (m, 2H), 7.23 (dd, J = 5.0, 3.0 Hz, 1H), 6.98 (dd, J = 5.0, 1.0 Hz, 1H) ppm; ^13C NMR (100 MHz, CDCl₃): δ 147.5, 133.8, 133.6, 132.4, 132.1, 131.9, 130.2, 129.8, 128.3, 128.1, 127.8, 127.8, 126.4,
125.9, 125.8, 125.7, 121.9, 120.5, 119.9, 118.7, 90.6, 88.3, 85.7, 84.4 ppm; HRMS (ESI) m/z: [M+H]^+ Calcd for C_{23}H_{14}NS_2 368.0562; Found 368.0562.

![Diagram of N-(1,5-di(thiophen-2-yl)penta-1,4-diyn-3-ylidene)naphthalen-2-amine (3o)]

N-(1,5-di(thiophen-2-yl)penta-1,4-diyn-3-ylidene)naphthalen-2-amine (3o): brown solid, m.p. 66.1-68.9 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.87–7.73 (m, 3H), 7.67 (d, J = 1.6 Hz, 1H), 7.46–7.36 (m, 4H), 7.31 (dd, J = 5.1, 1.0 Hz, 1H), 7.19 (s, 1H), 7.14 (dd, J = 3.7, 1.0 Hz, 1H), 7.01 (dd, J = 5.1, 3.7 Hz, 1H), 6.90 (dd, J = 5.1, 3.7 Hz, 1H) ppm; ^13C NMR (100 MHz, CDCl_3): δ 147.3, 135.1, 135.1, 133.6, 132.9, 132.1, 130.7, 130.0, 128.4, 128.2, 127.8, 127.5, 127.5, 126.4, 125.8, 122.0, 121.2, 120.6, 118.9, 92.2, 89.2, 88.6, 84.3 ppm; HRMS (ESI) m/z: [M+H]^+ Calcd for C_{23}H_{14}NS_2 368.0562; Found 368.0562.

![Diagram of N-(1,5-dicyclopentylpenta-1,4-diyn-3-ylidene)naphthalen-2-amine (3p)]

N-(1,5-dicyclopentylpenta-1,4-diyn-3-ylidene)naphthalen-2-amine (3p): pale brown solid, m.p. 86.4-89.1 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.81 (dt, J = 7.8, 5.6 Hz, 3H), 7.56–7.39 (m, 3H), 7.30 (dd, J = 8.5, 1.8 Hz, 1H), 1.61–1.42 (m, 1H), 1.25 (ddd, J = 9.8, 6.6, 4.1 Hz, 1H), 1.01–0.88 (m, 4H), 0.83–0.73 (m, 2H), 0.65–0.54 (m, 2H) ppm; ^13C NMR (100 MHz, CDCl_3): δ 147.6, 134.4, 133.4, 131.4, 127.9, 127.7, 127.6, 126.1, 125.1, 121.6, 117.9, 101.3, 95.6, 76.1, 72.0, 9.2, 9.1, 0.1, 0.0 ppm; HRMS (ESI) m/z: [M+H]^+ Calcd for C_{21}H_{18}N 284.1434; Found 284.1424.

![Diagram of N-(pentadeca-6,9-diyn-8-ylidene)naphthalen-2-amine (3q)]

N-(pentadeca-6,9-diyn-8-ylidene)naphthalen-2-amine (3q): yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.79 (t, J = 7.5 Hz, 3H), 7.51 (d, J = 1.7 Hz, 1H), 7.43 (pd, J = 6.9, 1.4 Hz, 2H), 7.29 (dd, J = 8.7, 2.0 Hz, 1H), 2.45 (t, J = 7.2 Hz, 2H), 2.20 (t, J = 7.0 Hz, 2H), 1.71 – 1.61 (m, 2H), 1.50–1.30 (m, 6H), 1.07 (td, J = 7.6, 5.0 Hz, 4H), 0.93 (t, J = 7.2 Hz, 3H), 0.71 (dd, J = 9.2, 4.7 Hz, 3H) ppm; ^13C NMR (100
MHz, CDCl$_3$): $\delta$ 147.8, 134.9, 133.6, 131.6, 128.2, 127.9, 127.7, 126.1, 125.2, 121.6, 117.8, 97.9, 92.4, 80.8, 77.4, 31.2, 30.7, 27.8, 27.3, 22.2, 22.0, 19.4, 19.3, 13.9, 13.7 ppm; HRMS (ESI) m/z: [M+H]$^+$ Calcd for C$_{25}$H$_{30}$N 344.2373; Found 344.2367.

**N-((1,5-dicyclohexylpenta-1,4-diyn-3-ylidene)naphthale n-2-amine (3r):** yellow oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79 (dd, $J$ = 10.3, 7.8 Hz, 3H), 7.53 (d, $J$ = 1.7 Hz, 1H), 7.46–7.39 (m, 2H), 7.30 (dd, $J$ = 8.6, 2.0 Hz, 1H), 2.75–2.54 (m, 1H), 2.44 (tt, $J$ = 7.7, 3.7 Hz, 1H), 1.92 (dd, $J$ = 9.6, 3.6 Hz, 2H), 1.77 (dt, $J$ = 9.7, 4.8 Hz, 2H), 1.65–1.54 (m, 5H), 1.47–1.28 (m, 8H), 1.21–1.08 (m, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.9, 135.2, 133.6, 131.6, 128.1, 127.9, 127.7, 126.1, 125.1, 121.7, 117.9, 101.3, 96.0, 80.9, 77.4, 32.0, 31.4, 29.7, 29.2, 25.8, 25.6, 24.9, 24.1 ppm; HRMS (ESI) m/z: [M+H]$^+$ Calcd for C$_{27}$H$_{30}$N 368.2373; Found 368.2363.

**N-((1,5-dicyclopropylpenta-1,4-diyn-3-ylidene)-2,6-dimethylbenzenamine (3s):** yellow solid, m.p. 68.3–71.3 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.97 (d, $J$ = 7.5 Hz, 2H), 6.91–6.85 (m, 1H), 2.02 (s, 6H), 1.52–1.40 (m, 1H), 1.15–1.05 (m, 1H), 0.97–0.88 (m, 4H), 0.70 (tt, $J$ = 4.0, 2.7 Hz, 2H), 0.42–0.29 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.2, 136.5, 127.4, 126.1, 123.5, 101.3, 94.8, 75.0, 71.4, 17.7, 9.4, 8.9, -0.0, -0.3 ppm; HRMS (ESI) m/z: [M+H]$^+$ Calcd for C$_{19}$H$_{20}$N 262.1590; Found 262.1584.

**2-Chloro-N-((1,5-diphenylpenta-1,4-diyn-3-ylidene)-6-methylbenzenamine (3t):** yellow oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75–7.63 (m, 2H), 7.45–7.23 (m, 7H), 7.19–7.11 (m, 3H), 7.01 (t, $J$ = 7.8 Hz, 1H), 2.19 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.4, 138.4, 132.8, 132.6, 130.3, 130.1, 129.4, 128.6, 128.6, 128.5, 127.1, 125.0, 123.6, 121.0, 120.5,
N-(1,5-diphenylpenta-1,4-diyn-3-ylidene)-4-fluorobenzene (3u): yellow oil; {\textsuperscript{1}H} NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.66 (dd, \( J = 7.9, 1.5 \) Hz, 2H), 7.44–7.25 (m, 10H), 7.16–7.06 (m, 2H) ppm; {\textsuperscript{13}C} NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 161.1 (d, \( ^1{J}_{\text{CF}} = 244 \) Hz), 145.9 (d, \( ^4{J}_{\text{CF}} = 3.0 \) Hz), 133.9, 133.9, 132.6, 132.5, 130.3, 129.9, 128.6 (d, \( ^3{J}_{\text{CF}} = 8.0 \) Hz), 123.3 (d, \( ^3{J}_{\text{CF}} = 8.0 \) Hz), 121.2, 120.7, 115.4 (d, \( ^2{J}_{\text{CF}} = 23.0 \) Hz), 95.3, 90.4, 88.3, 84.1 ppm; HRMS (ESI) m/z: [M+H]{\textsuperscript{+}} Calcd for C\textsubscript{24}H\textsubscript{17}NCl 354.1044; Found 354.1036.

N-(4-methoxyphenyl)-1,5-diphenylpenta-1,4-diyn-3-imine (3v): yellow solid, m.p. 176.9-179.2 °C; {\textsuperscript{1}H} NMR (500 MHz, CDCl\textsubscript{3}): \( \delta \) 7.65 (d, \( J = 6.5 \) Hz, 2H), 7.47–7.34 (m, 10H), 6.95 (d, \( J = 8.9 \) Hz, 2H), 3.85 (s, 3H) ppm; {\textsuperscript{13}C} NMR (125 MHz, CDCl\textsubscript{3}): \( \delta \) 158.5, 142.8, 132.5, 132.4, 131.3, 130.0, 129.7, 128.6, 128.5, 124.0, 121.5, 121.1, 113.8, 94.6, 89.6, 88.9, 84.8, 55.5 ppm; HRMS (ESI) m/z: [M+H]{\textsuperscript{+}} Calcd for C\textsubscript{24}H\textsubscript{18}NO 336.1383; Found 336.1385.

(E)-1-(tert-butyl)-5-(tert-butylimino)-4-(4-(pentyloxy)phenyl)-1,5-dihydro-2\textit{H}-pyrrol-2-one (4): yellow oil; {\textsuperscript{1}H} NMR (500 MHz, CDCl\textsubscript{3}): \( \delta \) 7.12 (d, \( J = 8.5 \) Hz, 2H), 6.89 (d, \( J = 8.5 \) Hz, 2H), 6.18 (s, 1H), 3.97 (t, \( J = 6.5 \) Hz, 2H), 1.83–1.78 (m, 2H), 1.66 (s, 9H), 1.46–1.37 (m, 4H), 1.07 (s, 9H), 0.94 (t, \( J = 7.0 \) Hz, 3H) ppm; {\textsuperscript{13}C} NMR (125 MHz, CDCl\textsubscript{3}): \( \delta \) 169.9, 159.4, 147.7, 142.8, 133.3, 129.9, 127.3, 114.0, 68.1, 57.3, 56.0, 32.1, 29.8, 28.9, 28.2, 22.5, 14.1 ppm; {\textsuperscript{13}C} NMR (125 MHz, CDCl\textsubscript{3}) \( \delta \) 169.9, 159.4, 147.7, 142.8, 133.3, 129.9,
(Z)-4-cyclopropyl-1-(2,4,4-trimethylpentan-2-yl)-5-((2,4,4-trimethylpentan-2-yl)imino)-1,5-dihydro-2H-pyrrol-2-one (5): yellow oil; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta 5.78\ (d, J = 0.8\) Hz, 1H), 1.99 (s, 2H), 1.94 (s, 2H), 1.92–1.84 (m, 1H), 1.70 (s, 6H), 1.58 (s, 6H), 1.10–1.04 (m, 2H), 1.01 (s, 9H), 0.92 (s, 9H), 0.77–0.70 (m, 2H) ppm; \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta 171.3\), 149.3, 146.1, 126.0, 60.9, 59.2, 55.1, 50.4, 33.1, 32.1, 31.9, 31.7, 31.6, 31.2, 12.1, 12.0 ppm; HRMS (ESI) m/z: \([M+H]^+\) Calcd for C\(_{23}\)H\(_{35}\)N\(_2\)O\(_2\) 371.2693; Found 371.2699.

2-Iodo-1-phenyl-3-(2-phenylethynyl)benzo[f]quinoline (6a): yellow solid, m.p. 84.5-85.3 °C; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta 8.08\ (m, 2H), 7.89\ (t, J = 9.2\) Hz, 1H), 7.78 (d, J = 3.1 Hz, 1H), 7.71–7.56 (m, 4H), 7.56–7.37 (m, 5H), 7.34–7.29 (m, 2H), 7.18 (d, J = 7.3 Hz, 1H) ppm; \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta 162.3, 154.2, 153.2, 148.7, 146.0, 133.1, 132.3, 129.9, 129.5, 129.0, 128.9, 128.7, 128.5, 128.4, 128.3, 127.4, 126.5, 124.5, 122.0, 105.7, 101.0, 91.9 ppm; HRMS (ESI) m/z: \([M+H]^+\) Calcd for C\(_{27}\)H\(_{17}\)IN 482.0400; Found 482.0402.

1-(4-Tert-butylphenyl)-3-(2-(4-tert-butylphenyl)ethynyl)-2-iodobenzo[f]quinoline (6b): yellow oil; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta 8.15–7.98\ (m, 2H), 7.90–7.83\ (m, 1H), 7.79–7.59\ (m, 3H), 7.52 (dd, J = 33.4, 10.2 Hz, 4H), 7.29–7.05\ (m, 4H), 1.50 (s, 9H), 1.38 (s, 9H) ppm; \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta 162.5, 148.9, 143.1, 142.8, 142.5, 133.5, 132.6, 132.1, 129.2, 128.9, 128.6, 128.5, 128.3, 128.2, 127.1, 126.6,
126.2, 125.5, 125.3, 119.1, 105.9, 101.4, 91.7, 34.9, 34.8, 31.5, 31.3 ppm; HRMS (ESI) m/z: [M+H]^+ Calcd for C_{35}H_{33}IN 594.1652; Found 594.1655.

2-Iodo-1-(4-(pentyloxy)phenyl)-3-(2-(4-(pentyloxy)phenyl)ethynyl)benzo[f]quinoline (6c): yellow solid, m.p. 88.2-90.3 °C; \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96 (dt, \(J = 14.8, 8.9\) Hz, 2H), 7.78 (t, \(J = 7.0\) Hz, 1H), 7.60 (d, \(J = 8.7\) Hz, 1H), 7.55–7.30 (m, 3H), 7.21–7.03 (m, 5H), 6.92–6.74 (m, 2H), 4.03 (t, \(J = 6.5\) Hz, 2H), 3.92 (m, 2H), 1.87–1.78 (m, 2H), 1.72 (m, 2H), 1.50–1.30 (m, 8H), 0.88 (m, 6H) ppm; \( ^{13}\)C NMR (100MHz, CDCl\(_3\)) \(\delta\) 160.4, 159.6, 153.7, 138.0, 134.0, 133.2, 132.6, 130.7, 130.1, 129.8, 129.0, 128.5, 128.2, 127.3, 126.6, 124.7, 115.8, 114.7, 114.2, 113.6, 106.9, 102.2, 91.3, 68.3, 68.2, 29.0, 28.9, 28.3, 28.2, 22.6, 22.5, 14.1, 14.0 ppm; HRMS (ESI) m/z: [M+H]^+ Calcd for C_{37}H_{37}INO\(_2\) 654.1863; Found 654.1858.
Copies of $^1$H and $^{13}$C NMR spectra of all compounds

3a

$^1$H 400 MHz, CDCl$_3$

$^{13}$C 100 MHz, CDCl$_3$
$3n$

$^1H$ 400 MHz, CDCl$_3$

$^{13}$C 100 MHz, CDCl$_3$
$^1$H 400 MHz, CDCl$_3$

$^1$C 100 MHz, CDCl$_3$
$^1$H 400 MHz, CDCl$_3$

$^{13}$C 100 MHz, CDCl$_3$
$^1$H 400 MHz, CDCl$_3$

$^{13}$C 100 MHz, CDCl$_3$
$^1\text{H} 400 \text{ MHz CDCl}_3$

$^{13}\text{C} 100 \text{ MHz CDCl}_3$
$^{1}H$ 400 MHz CDCl₃

$^{13}C$ 100 MHz CDCl₃

6c