Supporting Information for:

Palladium-Catalyzed Dearomative Arylalkynylation of Indoles

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1. General information

Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware heated with heating gun prior to use. 1H and 13C NMR spectra were recorded on Bruker AVANCE III 500MHz with TMS as internal standard. Anhydrous THF and toluene were freshly distilled over Na and benzophenone. Anhydrous DMF, DMA, and CH3CN were freshly distilled over calcium hydride. Melting points were measured on a Büchi Melting Point B-545 apparatus and uncorrected. Commercial reagents were used as received without further purification unless otherwise noticed. HRMS were recorded on Agilent 6210 LCT (EI source) or Waters Xevo Q-Tof Mass Spectrometer (ESI source). Column chromatography was carried out using silica gel (200-300 mesh). Substrates 1 were synthesized according to the literature procedure and were known compounds.1

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2. Palladium-catalyzed dearomative arylalkynylation of indole

To a dried Schlenk tube were added Pd(CH$_3$CN)$_2$Cl$_2$ (2.6 mg, 0.01 mmol), P'Bu$_3$-HBF$_4$ (5.8 mg, 0.02 mmol), and iPr$_2$NH (0.4 mmol) under N$_2$, after which 2.0 mL DMF was introduced via a syringe and the resulting mixture was stirred at room temperature for 0.5 h. To the above mixture were subsequently added 1 (0.2 mmol), 2 (0.3 mmol), and CuI (0.002 mmol) under N$_2$. The Schlenk tube was then sealed by Teflon cap and the mixture was stirred at 60 °C for 12 h. The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl/petroleum ether 1:10 (v/v) to afford the products 3.

10b-Methyl-11-(phenylethynyl)-10b,11-dihydro-6H-isindo[2,1-a]indol-6-one (3aa)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 55.6 mg, 82% yield, m.p. 147–150 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.93 (d, $J$ = 7.5 Hz, 1H), 7.76 (d, $J$ = 8.0 Hz, 1H), 7.67 (td, $J$ = 7.5, 1.0 Hz, 1H), 7.61 (d, $J$ = 7.5 Hz, 1H), 7.54 (td, $J$ = 7.5, 1.0 Hz, 1H), 7.48 (d, $J$ = 7.5 Hz, 1H), 7.41 (td, $J$ = 7.5, 1.0 Hz, 1H), 7.20 (td, $J$ = 7.5, 1.0 Hz, 1H), 7.14–7.17 (m, 1H), 7.08–7.11 (m, 2H), 6.78–6.80 (m, 2H), 4.25 (s, 1H), 1.72 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.6, 149.1, 138.7, 135.7, 132.8, 132.5, 131.1, 129.1, 128.8, 127.89,
127.87, 126.0, 125.0, 124.6, 123.1, 122.4, 117.6, 87.0, 86.6, 75.3, 43.1, 26.7. HRMS

m/z (ESI+): Calculated for C_{24}H_{18}NO ([M+H]^+): 336.1383, Found 336.1414.
8-Chloro-10b-methyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3ba)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 53.5 mg, 72% yield, m.p. 108–111 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.89 (d, \(J = 1.5\) Hz, 1H), 7.74 (d, \(J = 8.0\) Hz, 1H), 7.63 (dd, \(J = 8.0, 2.0\) Hz, 1H), 7.54 (d, \(J = 8.0\) Hz, 1H), 7.48 (d, \(J = 7.5\) Hz, 1H), 7.41 (td, \(J = 7.5, 1.0\) Hz, 1H), 7.17–7.23 (m, 2H), 7.12–7.15 (m, 2H), 6.84–6.86 (m, 2H), 4.24 (s, 1H), 1.71 (s, 3H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 167.0, 147.2, 138.4, 135.6, 135.1, 134.7, 132.6, 131.2, 129.2, 128.1, 128.0, 126.1, 125.3, 124.6, 124.4, 122.2, 117.7, 87.3, 86.3, 75.1, 43.1, 26.6. HRMS m/z (ESI+): Calculated for \(\text{C}_{24}\text{H}_{17}\text{ClNO} ([M+H]^+)\): 370.0993, Found 370.0980.
9-Chloro-10b-methyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3ca)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 51.0 mg, 69% yield, m.p. 162–165 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.62 (d, $J = 1.5$ Hz, 1H), 7.52 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.48 (d, $J = 7.5$ Hz, 1H), 7.41 (td, $J = 7.5$, 1.0 Hz, 1H), 7.17–7.23 (m, 2H), 7.12–7.15 (m, 2H), 6.87–6.89 (m, 2H), 4.24 (s, 1H), 1.72 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 167.5, 150.6, 138.9, 138.5, 135.3, 131.3, 131.2, 129.4, 129.2, 128.1, 128.0, 126.1, 125.8, 125.2, 123.7, 122.2, 117.6, 87.4, 86.2, 74.9, 43.1,
26.6. HRMS *m/z* (ESI+): Calculated for C_{24}H_{17}ClNO ([M+H]^+): 370.0993, Found 370.0977.
9,10b-Dimethyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3da)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 59.0 mg, 84% yield, m.p. 165–167 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.80 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.47 (d, $J = 7.5$ Hz, 1H), 7.38–7.41 (m, 2H), 7.35 (d, $J = 8.0$ Hz, 1H), 7.15–7.20 (m, 2H), 7.11 (t, $J = 7.5$ Hz, 2H), 6.80–6.82 (m, 2H), 4.23 (s, 1H), 2.51 (s, 3H), 1.71 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 168.8, 149.5, 143.3, 138.9, 135.5, 131.1, 130.2, 129.7, 129.0, 127.9, 126.0, 124.8, 124.4, 123.6, 122.6, 117.6, 86.9, 86.8, 75.0, 43.1, 26.8, 22.0. HRMS $m/z$ (ESI+): Calculated for C$_{25}$H$_{20}$NO ([M+H]$^+$): 350.1539, Found 350.1566.
8,10b-Dimethyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3ea)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 58.3 mg, 83% yield, m.p. 161–164 °C; $^1$H NMR (500 MHz, CDCl$_3$): \(\delta\) 7.80 (d, \(J = 7.5\) Hz, 1H), 7.74 (d, \(J = 7.5\) Hz, 1H), 7.47 (d, \(J = 7.5\) Hz, 1H), 7.38–7.41 (m, 2H), 7.35 (d, \(J = 8.0\) Hz, 1H), 7.15–7.20 (m, 2H), 7.09–7.12 (m, 2H), 6.80–6.82 (m, 2H), 4.23 (s, 1H), 2.51 (s, 3H), 1.71 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): \(\delta\) 168.8, 149.5, 143.3, 138.9, 135.6, 131.2, 130.3, 129.8, 129.0, 127.87, 127.86, 126.0, 124.8, 124.5, 123.6, 122.6, 117.6, 86.9, 86.8, 75.0, 43.2, 26.8, 22.0. HRMS \(m/z\) (ESI+): Calculated for C$_{25}$H$_{20}$NO ([M+H]$^+$): 350.1539, Found 350.1549.
10,10b-Dimethyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3fa)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 58.0 mg, 82% yield, m.p. 134–138 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.76–7.77 (m, 2H), 7.46–7.49 (m, 1H), 7.39–7.45 (m, 3H), 7.15–7.21 (m, 2H), 7.10 (t, $J = 7.5$ Hz, 2H), 6.79–6.81 (m, 2H), 4.32 (s, 1H), 2.61 (s, 3H), 1.75 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 167.9, 147.0, 138.1, 135.5, 134.3, 133.4, 133.2, 131.2, 129.1, 129.0, 127.9, 126.0, 124.9, 122.5, 122.3, 117.3, 86.2, 86.1, 75.6, 42.3, 24.8, 18.8. HRMS m/z (ESI+): Calculated for C$_{25}$H$_{20}$NO ([M+H]$^+$): 350.1539, Found 350.1524.
8-Methoxy-10b-methyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-alindol-6-one (3ga)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 57.0 mg, 78% yield, m.p. 101–104 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.74 (d, $J = 8.0$ Hz, 1H), 7.46–7.50 (m, 2H), 7.38–7.42 (m, 2H), 7.10–7.23 (m, 5H), 6.86 (d, $J = 7.5$ Hz, 2H), 4.22 (s, 1H), 3.89 (s, 3H), 1.69 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.5, 160.5, 141.5, 138.7, 135.9, 134.2, 131.2, 129.0, 127.9, 126.0, 124.9, 124.0, 122.5, 120.8, 117.6, 107.1, 86.9, 86.7, 74.9, 55.7, 43.2, 26.8. HRMS m/z (ESI+): Calculated for C$_{25}$H$_{20}$NO$_2$ ([M+H]$^+$): 366.1489, Found 366.1461.
3b-Methyl-4-(phenylethynyl)-3b,4-dihydro-10H-thieno[3′,2′:3,4]pyrrolo[1,2-a]indol-10-one (3ha)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 31.5 mg, 47% yield, m.p. 148–150 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.78 (d, $J = 4.5$ Hz, 1H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.44 (d, $J = 7.5$ Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 1H), 7.14–7.20 (m, 5H), 6.95 (d, $J = 7.0$ Hz, 2H), 4.20 (s, 1H), 1.71 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 164.8, 160.1, 139.2, 136.8, 135.3, 135.2, 131.3 129.1, 128.0, 127.98, 126.0, 124.8, 122.5, 121.1, 117.4, 86.7, 86.6, 74.2, 42.8, 26.0. HRMS $m/z$ (ESI+): Calculated for C$_{22}$H$_{16}$NO$_{2}$ ([M+H]$^+$): 342.0947, Found 342.0958.
11-(Phenylethynyl)-10b-(m-tolyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3ia)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 60.0 mg, 73% yield, m.p. 147–150 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.90 (dd, $J = 14.5$, 8.0 Hz, 2H), 7.75 (d, $J = 7.5$ Hz, 1H), 7.60 (td, $J = 7.5$, 1.0 Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.38–7.42 (m, 2H), 7.44–7.36 (m, 2H), 7.25 (t, $J = 7.5$ Hz, 1H), 7.08–7.20 (m, 5H), 6.85–6.86 (m, 2H), 4.90 (s, 1H), 2.34 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 169.2, 148.7, 142.1, 139.3, 138.7, 135.6, 132.6, 132.1, 131.2, 129.1, 129.0, 128.8, 128.7, 128.0, 127.9, 125.7, 125.6, 125.2, 124.6, 124.1, 122.4, 122.2, 117.5, 87.7, 86.7, 80.4, 45.2, 21.6. HRMS $m/z$ (ESI+): Calculated for C$_{30}$H$_{22}$NO ([M+H]$^+$): 412.1696, Found 412.1662.
10b-(4-Methoxyphenyl)-11-(phenylethynyl)-10b,11-dihydro-6H-isooindolo[2,1-a]indol-6-one (3ja)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 51.2 mg, 60% yield, m.p. 112–115 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.91 (d, $J$ = 7.5 Hz, 1H), 7.85 (d, $J$ = 7.5 Hz, 1H), 7.71 (d, $J$ = 8.0 Hz, 1H), 7.58–7.62 (m, 3H), 7.49 (td, $J$ = 7.5, 1.5 Hz, 1H), 7.38–7.41 (m, 2H), 7.10–7.19 (m, 4H), 6.82–6.88 (m, 4H), 4.83 (s, 1H), 3.75 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.1, 159.4, 148.9, 139.2, 135.7, 134.0, 132.6, 132.1, 131.2, 129.1, 128.6, 128.0, 127.9, 126.3, 125.7, 125.3, 124.6, 124.0, 122.4, 117.6, 114.2, 87.8, 86.7, 80.2, 55.3, 45.2. HRMS m/z (ESI+): Calculated for C$_{30}$H$_{22}$NO$_2$ ([M+H]$^+$): 428.1645, Found 428.1611.
11-(Phe ny lethynyl)-10b-(4-(trifluoromethyl)phenyl)-10b,11-dihydro-6H-
isoindolo[2,1-a]indol-6-one (3ka)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether
1:10 (v/v); white solid, 71.6 mg, 77\% yield, m.p. 86–90 °C; 1H NMR (500 MHz,
CDCl₃): δ 7.94 (d, J = 7.5 Hz, 1H), 7.85–7.89 (m, 3H), 7.74 (d, J = 8.0 Hz, 1H), 7.61
–7.65 (m, 3H), 7.53 (td, J = 7.5, 1.0 Hz, 1H), 7.39–7.44 (m, 2H), 7.12–7.21 (m, 4H),
6.84–6.86 (m, 2H), 4.85 (s, 1H). 13C NMR (125 MHz, CDCl₃): δ 169.0, 147.6, 146.3,
139.1, 135.0, 132.9, 132.2, 131.2, 130.5 (q, J = 32.5 Hz), 129.4, 129.2, 128.2, 128.0,
126.0 (q, J = 3.8 Hz), 125.7, 125.59, 125.58, 124.9, 124.0, 122.7, 122.2, 117.6, 88.2,
86.0, 80.2, 45.3. HRMS m/z (ESI+): Calculated for C₃₀H₁₉F₃NO ([M+H]+): 466.1413,
Found 466.1432.
10b-(Naphthalen-2-yl)-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3la)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 65.2 mg, 73% yield, m.p. 177–180 °C; \(^1\)H NMR (500 MHz, CDCl₃): \(\delta\) 8.12 (s, 1H), 7.94 (d, \(J = 8.0\) Hz, 2H), 7.86–7.90 (m, 2H), 7.78–7.83 (m, 3H), 7.60 (t, \(J = 7.5\) Hz, 1H), 7.44–7.51 (m, 3H), 7.39–7.43 (m, 2H), 7.13–7.22 (m, 4H), 6.88 (d, \(J = 7.0\) Hz, 2H), 5.03 (s, 1H). \(^{13}\)C NMR (125 MHz, CDCl₃): \(\delta\) 169.2, 148.5, 139.3, 139.2, 135.5, 133.0, 132.9, 132.7, 132.2, 131.2, 129.2, 129.1, 128.8, 128.2, 128.1, 128.0, 127.5, 126.6, 126.5, 125.7, 125.5, 124.7, 124.1, 123.8, 123.1, 122.4, 117.6, 87.8, 86.6, 80.6, 45.0. HRMS \(m/z\) (ESI+): Calculated for C\(_{33}\)H\(_{22}\)NO ([M+H]\(^+\)): 448.1696, Found 448.1692.
10b-(Furan-2-yl)-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3ma)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 59.0 mg, 76% yield, m.p. 131–134 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.94 (d, $J$ = 7.5 Hz, 1H), 7.81 (t, $J$ = 8.0 Hz, 2H), 7.67 (td, $J$ = 7.5, 1.0 Hz, 1H), 7.56 (t, $J$ = 7.5 Hz, 1H), 7.39–7.46 (m, 3H), 7.16–7.21 (m, 2H), 7.12 (t, $J$ = 7.5 Hz, 2H), 6.83–6.85 (m, 2H), 6.25–6.26 (m, 2H), 4.91 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.1, 153.2, 146.0, 143.2, 139.4, 135.5, 132.7, 132.4, 131.2, 129.2, 129.1, 128.0, 127.9, 125.8, 125.3, 124.6, 122.3, 117.5, 110.3, 106.7, 87.7, 85.9, 76.3, 42.2. HRMS m/z (ESI+): Calculated for C$_{27}$H$_{18}$NO$_2$ ([M+H]$^+$): 388.1332, Found 388.1331.
2-Isopropyl-10b-phenyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3na)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 47.5 mg, 54% yield, m.p. 178–180 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.90 (d, $J = 7.5$ Hz, 1H), 7.72–7.78 (m, 4H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 2H), 7.23–7.29 (m, 3H), 7.19 (t, $J = 7.5$ Hz, 1H), 7.13 (t, $J = 8.0$ Hz, 2H), 6.86 (d, $J = 7.5$ Hz, 2H), 4.85 (s, 1H), 2.86–2.94 (m, 1H), 1.24 (d, $J = 7.0$ Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.2, 148.6, 146.3, 142.4, 137.2, 135.4, 132.5, 132.3, 131.2, 128.9, 128.7, 128.1, 128.0, 127.9, 127.2, 125.1, 124.5, 124.1, 123.8, 122.5, 117.2, 87.7, 86.9, 80.7, 45.3, 33.9, 24.2, 24.0. HRMS $m/z$ (ESI+): Calculated for C$_{32}$H$_{26}$NO ([M+H]$^+$): 440.2009, Found 440.1992.
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 71.4 mg, 82% yield, m.p. 74–76 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.91 (d, $J = 7.5$ Hz, 1H), 7.70–7.76 (m, 3H), 7.60 (t, $J = 7.0$ Hz, 1H), 7.46–7.51 (m, 2H), 7.35 (t, $J = 7.5$ Hz, 2H), 7.25–7.29 (m, 2H), 7.11–7.20 (m, 3H), 6.85 (d, $J = 7.0$ Hz, 2H), 6.69 (dd, $J = 8.5$, 2.5 Hz, 1H), 4.81 (s, 1H), 3.90 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 169.0, 160.7, 148.6, 142.3, 140.4, 132.7, 132.2, 131.2, 128.9, 128.8, 128.2, 128.0, 127.9, 127.1, 126.0, 125.0, 124.6, 124.1, 122.5, 111.5, 103.2, 87.5, 87.0, 81.2, 55.7, 44.7. HRMS m/z (ESI+): Calculated for C$_{30}$H$_{22}$NO$_2$ ([M+H]$^+$): 428.1645, Found 428.1637.
2-Methyl-10b-phenyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3pa)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 51.8 mg, 63% yield, m.p. 192–195 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.91 (d, \(J = 7.5\) Hz, 1H), 7.71–7.76 (m, 4H), 7.59 (t, \(J = 7.5\), 1H), 7.49 (t, \(J = 7.5\) Hz, 1H), 7.35 (t, \(J = 8.0\) Hz, 2H), 7.26–7.29 (m, 1H), 7.17–7.21 (m, 3H), 7.13 (t, \(J = 7.5\) Hz, 2H), 6.85–6.86 (m, 2H), 4.83 (s, 1H), 2.34 (s, 3H). \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 169.1, 148.5, 142.2, 136.9, 135.6, 135.1, 132.5, 132.3, 131.2, 129.7, 128.9, 128.7, 128.1, 128.0, 127.9, 126.3, 125.1, 124.5, 124.0, 122.4, 117.2, 87.7, 86.7, 80.7, 45.3, 21.2. HRMS \(m/z\) (ESI+): Calculated for C\(_{30}\)H\(_{23}\)NO ([M+H]+): 412.1696, Found 412.1692.
10b-Methyl-11-(p-tolylethynyl)-10b,11-dihydro-6H-isouindolo[2,1-a]indol-6-one (3ab)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 55.0 mg, 82% yield, m.p. 118–120 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.91 (d, $J$ = 7.5 Hz, 1H), 7.75 (d, $J$ = 8.0 Hz, 1H), 7.64–7.67 (m, 1H), 7.60 (d, $J$ = 7.5 Hz, 1H), 7.52–7.55 (m, 1H), 7.47 (d, $J$ = 7.5 Hz, 1H), 7.40 (t, $J$ = 7.5 Hz, 1H), 7.19 (td, $J$ = 7.5, 0.5 Hz, 1H), 6.90 (d, $J$ = 7.5 Hz, 2H), 6.69 (d, $J$ = 8.0 Hz, 2H), 4.24 (s, 1H), 2.23 (s, 3H), 1.72 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.6, 149.1, 138.7, 138.0, 135.8, 132.8, 132.4, 131.0, 129.0, 128.7, 128.6, 126.0, 124.9, 124.5, 123.1, 119.4, 117.6, 87.1, 85.9, 75.3, 43.2, 26.7, 21.3. HRMS $m/z$ (ESI+): Calculated for C$_{25}$H$_{20}$NO ([$\text{M+H}^+$]): 350.1539, Found 350.1558.
10b-Methyl-11-((4-(pentyloxy)phenyl)ethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3ac)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 71.6 mg, 85% yield, m.p. 114–115 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.91 (d, $J = 7.5$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.66 (td, $J = 7.5, 1.0$ Hz, 1H), 7.60 (d, $J = 7.5$ Hz, 1H), 7.53 (td, $J = 7.5, 1.0$ Hz, 1H), 7.46 (d, $J = 7.5$ Hz, 1H), 7.40 (td, $J = 7.5, 1.0$ Hz, 1H), 7.19 (td, $J = 7.5, 1.0$ Hz, 1H), 6.70–6.73 (m, 2H), 6.60 −6.62 (m, 2H), 4.22 (s, 1H), 3.85 (t, $J = 6.5$ Hz, 2H), 1.72–1.75 (m, 2H), 1.71 (s, 3H), 1.32–1.41 (m, 4H), 0.91 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.6, 158.9, 149.2, 138.7, 136.0, 132.8, 132.5, 132.0, 129.0, 128.9, 126.0, 124.9, 124.5, 123.2, 117.6, 114.3, 114.1, 87.0, 85.1, 75.3, 67.9, 43.2, 28.8, 28.1, 26.7, 22.4, 13.9. HRMS m/z (ESI+): Calculated for C$_{29}$H$_{28}$NO$_2$ ([M+H]$^+$): 422.2115, Found 422.2092.
10b-Methyl-11-(o-tolylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3ad)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 61.3 mg, 87% yield, m.p. 115–117 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.91 (d, $J = 6.5$ Hz, 1H), 7.76 (d, $J = 6.5$ Hz, 1H), 7.41–7.65 (m, 5H), 6.87–7.20 (m, 5H), 4.30 (s, 1H), 1.74 (s, 3H), 1.72 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.3, 149.0, 139.8, 138.5, 136.2, 133.0, 132.6, 131.6, 129.04, 129.02, 128.8, 127.9, 125.9, 125.1, 125.0, 124.7, 123.2, 122.2, 117.6, 90.3, 85.9, 75.1, 43.3, 26.8, 19.9. HRMS m/z (ESI+): Calculated for C$_{25}$H$_{20}$NO ([M+H]$^+$): 350.1539, Found 350.1550.
11-((4-Chlorophenyl)ethynyl)-10b-methyl-10b,11-dihydro-6H isoindolo[2,1-a]indol-6-one (3ae)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 56.0 mg, 76% yield, m.p. 126–128 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.92 (d, $J = 7.5$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.66 (td, $J = 7.5$, 1.0 Hz, 1H), 7.59 (d, $J = 7.5$ Hz, 1H), 7.54 (td, $J = 7.5$, 0.5 Hz, 1H), 7.46 (d, $J = 7.5$ Hz, 1H), 7.41 (td, $J = 7.5$, 1.0 Hz, 1H), 7.20 (td, $J = 7.5$, 1.0 Hz, 1H), 7.05–7.08 (m, 2H), 6.68–6.71 (m, 2H), 4.22 (s, 1H), 1.72 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.6, 149.0, 138.7, 135.4, 134.0, 132.8, 132.5, 132.4, 129.2, 128.8, 128.3, 126.0, 125.0, 124.6, 123.1, 120.9, 117.7, 87.6, 85.9, 75.3, 43.1, 26.6. HRMS $m/z$ (ESI+): Calculated for C$_{24}$H$_{17}$ClNO ([M+H]$^+$): 370.0993, Found 370.0988.
11-((3-Chlorophenyl)ethynyl)-10b-methyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3af)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 55.0 mg, 75% yield, m.p. 115–118 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.93 (d, $J$ = 7.0 Hz, 1H), 7.67–7.76 (m, 2H), 7.57–7.61 (m, 2H), 7.41–7.46 (m, 2H), 7.02–7.21 (m, 3H), 6.64–6.74 (m, 2H), 4.23 (s, 1H), 1.73 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.5, 148.9, 138.8, 135.3, 133.7, 132.8, 132.5, 131.1, 129.24, 129.23, 129.1, 128.9, 128.2, 126.0, 125.1, 124.7, 124.1, 123.1, 117.8, 88.0, 85.7, 75.3, 43.1, 26.6. HRMS $m/z$ (ESI+): Calculated for C$_{24}$H$_{17}$ClNO ([M+H]$^+$): 370.0993, Found 370.0983.
10b-Methyl-11-((trimethylsilyl)ethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3ag)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 41.4 mg, 62% yield, m.p. 138–140 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.88 (d, \(J = 7.5\) Hz, 1H), 7.72 (d, \(J = 8.0\) Hz, 1H), 7.64 (td, \(J = 7.5, 1.0\) Hz, 1H), 7.50–7.55 (m, 2H), 7.37–7.41 (m, 2H), 7.17 (td, \(J = 7.5, 1.0\) Hz, 1H), 4.03 (s, 1H), 1.65 (s, 3H), -0.24 (s, 9H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 168.6, 149.1, 138.7, 135.6, 132.8, 132.3, 129.0, 128.6, 126.0, 124.9, 124.4, 123.2, 117.6, 102.8, 91.5, 75.2, 43.5, 26.6, -0.6. HRMS \(m/z\) (ESI+): Calculated for C\(_{21}\)H\(_{22}\)NOSi ([M+H]+): 332.1465, Found 332.1493.
11-(Hept-1-yn-1-yl)-10b-methyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3ah)²

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20 (v/v); brown oil, 34.7 mg, 52% yield; ¹H NMR (500 MHz, CDCl₃): δ 7.87 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.63 (td, J = 7.5, 0.9 Hz, 1H), 7.48–7.55 (m, 2H), 7.34–7.41 (m, 2H), 7.15 (td, J = 7.5, 0.8 Hz, 1H), 3.98 (s, 1H), 1.68–1.78 (m, 2H), 1.63 (s, 3H), 1.06 (dd, J = 14.6, 7.3 Hz, 2H), 0.90–0.94 (m, 2H), 0.82–0.87 (m, 2H), 0.77 (t, J = 7.3 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 168.5, 149.2, 138.4, 136.8, 132.9, 132.3, 128.7, 128.5, 125.8, 124.8, 124.4, 123.1, 117.5, 76.8, 75.2, 42.7, 30.4, 27.8, 26.5, 21.9, 18.3, 13.8.
11-(Cyclopropylethynyl)-10b-methyl-10b,11-dihydro-6H isoindolo[2,1-a]indol-6-one (3ai)

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20 (v/v); brown solid, 37.7 mg, 60% yield; m.p. 142-144 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.88 (d, $J = 7.6$ Hz, 1H), 7.68–7.74 (m, 1H), 7.64 (td, $J = 7.5$, 1.0 Hz, 1H), 7.49–7.55 (m, 2H), 7.37 (t, $J = 6.9$ Hz, 2H), 7.16 (td, $J = 7.5$, 1.0 Hz, 1H), 3.94 (s, 1H), 1.23–1.31 (m, 3H), 0.74–0.83 (m, 1H), 0.34–0.45 (m, 2H), 0.01 (s, 1H), -0.17--0.10 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.6, 149.2, 138.5, 136.5, 132.8, 132.2, 128.8, 128.5, 125.8, 124.9, 124.3, 123.1, 117.6, 90.7, 76.7, 75.3, 72.4, 42.7, 26.3, 7.8, -0.9.

3. Synthetic transformations of products

10b-Methyl-11-phenethyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (4)

The mixture of Pd/C (5.0 mg, 0.0050 mmol, 10 mol%) and compound 3aa (47.0 mg, 0.14 mmol, 1.0 eq) in EtOH (10.0 mL) was stirred with a hydrogen balloon at room temperature for 24 h. The resulting mixture was then filtered and washed with EtOH. After the solvent EtOH was removed under vacuum, the residue was purified by flash column chromatography on silica gel, eluting with ethyl acetate/petroleum
ether 1:10 (v/v) to give compound 4 (40.4 mg, 85%) as a white solid, m.p. 128–130 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.92 (d, \(J = 7.5\) Hz, 1H), 7.78 (d, \(J = 8.0\) Hz, 1H), 7.64 (t, \(J = 7.5\) Hz, 1H), 7.52 (dd, \(J = 15.0\), 7.5 Hz, 2H), 7.38–7.42 (m, 2H), 7.17–7.21 (m, 3H), 7.13 (t, \(J = 7.5\) Hz, 1H), 6.91 (d, \(J = 7.5\) Hz, 2H), 3.19 (dd, \(J = 9.5\), 4.0 Hz, 1H), 2.37–2.41 (m, 2H), 1.58 (s, 3H), 1.52–1.56 (m, 1H), 1.03–1.11 (m, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 167.3, 148.2, 141.3, 139.0, 138.0, 133.7, 132.3, 128.7, 128.4, 128.3, 128.2, 126.3, 125.8, 124.9, 124.2, 123.1, 117.5, 75.2, 49.6, 34.9, 32.0, 27.4. HRMS \textit{m/z} (ESI+): Calculated for C\(_{24}\)H\(_{22}\)NO ([M+H]\(^+\)): 340.1696, Found 340.1693.
To a solution of compound 3ag (33.2 mg, 0.10 mmol, 1.0 equiv) in THF (2 mL) was added tetrabutyl ammonium fluoride trihydrate (31.6 mg, 0.10 mmol, 1.0 equiv). The resulting mixture was then stirred at 0 °C for 3 h. After which, the mixture was concentrated and the residue was purified by flash column chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v) to give compound 5 (23.8 mg, 92%) as a white solid, m.p. 147–149 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.86–7.87 (m, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.63 (td, $J = 7.5$, 1.0 Hz, 1H), 7.57–7.58 (m, 1H), 7.50 (td, $J = 7.5$, 1.0 Hz, 1H), 7.32–7.36 (m, 1H), 7.28 (d, $J = 8.0$ Hz, 1H), 7.15
(td, $J = 7.5, 1.0$ Hz, 1H), 5.49 (d, $J = 12.0$ Hz, 1H), 5.42 (d, $J = 12.0$ Hz, 1H), 1.82 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 201.8, 170.2, 150.5, 139.8, 133.3, 131.7, 130.7, 129.2, 128.8, 125.08, 125.06, 123.4, 122.0, 117.4, 107.8, 83.9, 72.1, 29.4. HRMS $m/z$ (ESI+): Calculated for C$_{18}$H$_{14}$NO ([M+H]$^+$): 260.1070, Found 260.1067.
4. X-ray structural analysis of compound 3aa
Bond precision: C-C = 0.0041 Å  Wavelength = 0.71073 Å

Cell: a = 15.3015(18) Å  b = 12.1976(10) Å  c = 9.6252(8) Å
  α = 90°  β = 90°  γ = 90°

Temperature: 293 K

Calculated  Reported

Volume  1796.5(3) Å³  1796.5(3) Å³
Space group  P n a 21  P n a 21
Hall group  P 2c -2n  P 2c -2n
Molely formula  C24 H17 N O  C24 H17 N O
Sum formula  C24 H17 N O  C24 H17 N O
Mr  335.39  335.39
Dx, g cm⁻³  1.240  1.240
Z  4  4
M (mm⁻¹)  0.075  0.075
F₀₀₀  704.0  704.0
F₀₀₀'  704.28
h,k,lmax  18,14,11  18,14,11
Nref  3291 [1752]  1750
Tmin, Tmax  0.964, 0.976  0.986, 1.000
Tmin'  0.964

Correction method: # Reported T Limits: Tmin = 0.986 Tmax = 1.000
AbsCorr = MULTI-SCAN

Data completeness = 1.00/0.53  θ(max) = 25.330°
R(reflections) = 0.0376 (1347)  wR²(reflections) = 0.0824 (1750)
S = 1.048  Npar = 236