Supporting information

Direct synthesis of aryl-annulated [c]carbazoles by gold(I)-catalysed cascade reaction of azide-diynes and arenes

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Table of Contents

Reaction Optimisation Using N-Boc-pyrrole ................................................................. S2
Experimental Section ...................................................................................................... S3
1. General Methods ....................................................................................................... S3
2. Preparation of the Cyclisation Precursors ................................................................. S3
3. Gold-Catalysed Cascade Cyclisation ......................................................................... S11
4. Preparation of the Catalyst ...................................................................................... S29
5. References ............................................................................................................... S29
NMR Spectra ................................................................................................................. S30
**Table S1. Reaction Optimisation Using N-Boc-pyrrole**

![Reaction Scheme](image.png)

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⁴ Reaction conditions: 9F (5 equiv.), gold catalyst (5 mol %). ⁵ Combined isolated yields. ⁶ Determined by ¹H NMR spectroscopy. ⁷ Contained small amounts of impurities.
**Experimental Section**

1. General Methods

IR spectra were determined on a JASCO FT/IR-4100 spectrometer. Exact mass (HRMS) spectra were recorded on JMS-HX/HX 110A mass spectrometer or Shimadzu LC-ESI-IT-TOF-MS equipment. $^1$H NMR spectra were recorded using a JEOL AL-400 or JEOL AL-500 spectrometer at 500 MHz frequency. Chemical shifts are reported in $\delta$ (ppm) relative to Me$_4$Si (in CDCl$_3$) as internal standard. $^{13}$C NMR spectra were recorded using a JEOL AL-500 and referenced to the residual solvent signal. Melting points were measured by a hot stage melting points apparatus (uncorrected). For column chromatography, silica gel (Wakogel C-200: Wako Pure Chemical Industries, Ltd), and amine silica gel (CHROMATOREX NH-DM1020: Fuji Silysia Chemical Ltd) were employed.

2. Preparation of the Cyclisation Precursors

**2-Ethynylaniline (S1)**$^{1,2}$

\[
\begin{align*}
\text{NH}_2 & \quad \text{TMS} \\
\text{Pd(PPh}_3\text{)}_2\text{Cl}_2 & \quad \text{CuI} \\
\text{Et}_3\text{N} & \quad \text{THF} \\
\text{rt} & \quad 96\% \\
\text{NH}_2 & \quad \text{TMS} \\
\text{K}_2\text{CO}_3 & \quad \text{MeOH} \\
\text{rt} & \quad 90\%
\end{align*}
\]

A mixture of 2-iodoaniline (4.38 g, 20.0 mmol), TMS acetylene (3.39 mL, 24.0 mmol), PdCl$_2$(PPh$_3$)$_2$ (337 mg, 0.48 mmol), CuI (91.4 mg, 0.48 mmol), and Et$_3$N (13.9 mL, 100 mmol) in THF (20 mL) was stirred at room temperature under Ar for 3 h. The mixture was filtered through a pad of Celite and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20/1) to give 2-[(trimethylsilyl)ethynyl]-aniline$^2$ (3.65 g, 96%) as an orange oil. To a solution of this oil (1.70 g, 9.00 mmol) in MeOH (30 mL) was added K$_2$CO$_3$ (410 mg, 2.97 mmol). The reaction mixture was stirred at room temperature for 2 h and concentrated in vacuo. The residue was diluted with H$_2$O. The organic layer was washed with H$_2$O and brine, dried over MgSO$_4$, filtered, and concentrated in vacuo to give S1 (951 mg, 90%) as a brown oil. The spectral data were in good agreement with those previously reported.$^2$

**(Bromoethynyl)benzene (S2)**$^{1,3}$

\[
\begin{align*}
\text{H} & \quad \text{NBS} \\
\text{AgNO}_3 & \quad \text{acetone} \\
\text{rt} & \quad 89\%
\end{align*}
\]

To a solution of ethynylbenzene (1.27 mL, 10.0 mmol) in acetone (50 mL) were added NBS (1.96 g, 11.0 mmol) and AgNO$_3$ (170 mg, 1.00 mmol). The mixture was stirred at room temperature for 7 h. The mixture was diluted with $n$-hexane and filtered through a pad of silica gel. The filtrate was concentrated in vacuo to give S2 (1.74 g, 89%) as a brown oil. The spectral data were in good agreement with those previously reported.$^3$
2-(Phenylbuta-1,3-diyln-1-yl)aniline (S3)\textsuperscript{1,4a}

![Chemical structure of S1, S2, and S3 with reaction scheme]

To a mixture of S1 (1.06 g, 9.09 mmol), CuCl (45.0 mg, 0.455 mmol), NH\textsubscript{2}OH·HCl (253 mg, 3.64 mmol), and n-BuNH\textsubscript{2} (2.26 mL, 22.8 mmol) in dry EtOH (22.8 mL) was added a solution of S2 (2.14 g, 11.8 mmol) in dry EtOH (4.55 mL) via dropping funnel at 0 °C under Ar.\textsuperscript{4b} The mixture was stirred at room temperature for 1.5 h and concentrated in vacuo. The residue was diluted with Et\textsubscript{2}O. The organic layer was washed with saturated aqueous NH\textsubscript{4}Cl, H\textsubscript{2}O, and brine, dried over Na\textsubscript{2}SO\textsubscript{4}, filtered, and concentrated in vacuo. The filtrate was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to give S3 (1.80 g, 92%) as a light yellow powder. The spectral data were in good agreement with those previously reported\textsuperscript{4a}: \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ: 4.32 (s, 2H), 6.69-6.70 (m, 2H), 7.16 (dd, \textit{J} = 7.5, 1.5 Hz, 1H), 7.32-7.39 (m, 4H), 7.52-7.54 (m, 2H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) δ: 73.9, 78.7, 78.9, 82.6, 105.7, 114.2, 117.7, 121.5, 128.3 (2C), 129.0, 130.5, 132.2 (2C), 132.8, 149.5.

1-Azido-2-(phenylbuta-1,3-diyln-1-yl)benzene (1a)\textsuperscript{1,5}

![Chemical structure of S3 and 1a with reaction scheme]

A solution of S3 (1.09 g, 5.00 mmol) in THF/H\textsubscript{2}O/conc. HCl (1/1/1, 10.0 mL) was cooled to 0 °C. To the solution was added NaNO\textsubscript{2} (690 mg, 10.0 mmol) in H\textsubscript{2}O (10.0 mL) via dropping funnel at 0 °C. After the mixture was stirred at 0 °C for 15 min, NaN\textsubscript{3} (650 mg, 10.0 mmol) in H\textsubscript{2}O (10.0 mL) was slowly added to the mixture at 0 °C,\textsuperscript{6} and the mixture was stirred for 3 h. The reaction mixture was quenched with H\textsubscript{2}O. The resulting mixture was extracted with Et\textsubscript{O}Ac twice. The combined organic layer was washed with brine, dried over MgSO\textsubscript{4}, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20/1) to give 1a (1.09 g, 90%) as an light yellow powder: mp 93–96 °C; IR (neat) 2130, 2100; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ: 7.11 (t, \textit{J} = 7.0 Hz, 1H), 7.15 (d, \textit{J} = 8.5 Hz, 1H), 7.33-7.41 (m, 4H), 7.50-7.54 (m, 3H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) δ: 73.6, 77.0, 79.3, 83.3, 113.8, 118.5, 121.6, 124.6, 128.4 (2C), 129.3, 130.4 132.5 (2C), 134.4, 142.6; HRMS (ESI) calcd for C\textsubscript{16}H\textsubscript{10}N\textsubscript{3} [M+H]\textsuperscript{+}: 244.0869, found 244.0867.
2-(o-Tolylbuta-1,3-diy-1-yl)aniline (S5)

\[
\begin{align*}
\text{S1} & \quad \text{Br} \\
\text{S4} & \quad \text{CuCl} \\
\text{NH2OH\cdotHCl} & \quad \text{EtOH} \\
0^\circ \text{C} & \quad 75\% \\
\text{S5} & 
\end{align*}
\]

By a procedure identical with that described for the preparation of S3, S1 (451 mg, 3.85 mmol) was converted to S5 (671 mg, 75%) by the reaction with S4 (983 mg, 5.04 mmol): yellow powder; mp 100–101.5 °C; IR (neat) 3479, 3392, 2211, 2137; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 2.49 (s, 3H), 4.32 (s, 2H), 6.67-6.71 (m, 2H), 7.14-7.18 (m, 2H), 7.21-7.28 (m, 2H) 7.35 (d, \(J = 8.0\) Hz, 1H), 7.49 (d, \(J = 7.6\) Hz, 1H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 20.7, 77.4, 79.1 (2C), 81.7, 106.2, 114.4, 117.9, 121.6, 125.7, 129.1, 129.6, 130.6, 132.8, 133.1, 141.6, 149.5; HRMS (ESI) calcd for C\(_{17}\)H\(_{14}\)N \([\text{M+H]}^+\): 232.1126, found 232.1114.

1-Azido-2-(o-tolylbuta-1,3-diy-1-yl)benzene (1b)

\[
\begin{align*}
\text{S5} & \quad 1) \text{NaN_3, THF, conc. HCl, H_2O} \\
& \quad 2) \text{Na_2S, H_2O} \\
0^\circ \text{C} & \quad 87\% \\
\text{1b} & 
\end{align*}
\]

By a procedure identical with that described for the preparation of 1a, S5 (550 mg, 2.38 mmol) was converted to 1b (530 mg, 87%): light yellow powder: mp 61–63 °C; IR (neat) 2127, 2094; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 2.49 (s, 3H), 7.09-7.17 (m, 3H), 7.20-7.28 (m, 2H), 7.38 (ddd, \(J = 7.9, 7.9, 1.5\) Hz, 1H), 7.49-7.52 (m, 2H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 20.7, 77.1, 77.5, 79.4, 82.4, 113.9, 118.5, 121.4, 124.6, 125.6, 129.3, 129.6 (2C), 130.3, 134.4, 141.8, 142.5; HRMS (FAB) calcd for C\(_{17}\)H\(_{12}\)N\(_3\) \([\text{M+H]}^+\): 258.1031, found 258.1026.

2-(m-Tolylbuta-1,3-diy-1-yl)aniline (S7)

\[
\begin{align*}
\text{S1} & \quad \text{Br} \\
\text{S6} & \quad \text{CuCl} \\
\text{NH2OH\cdotHCl} & \quad \text{EtOH} \\
0^\circ \text{C} & \quad 77\% \\
\text{S7} & 
\end{align*}
\]

By a procedure identical with that described for the preparation of S3, S1 (421 mg, 3.59 mmol) was converted to S7 (637 mg, 77%) by the reaction with S6 (912 mg, 4.67 mmol: yellow powder; mp 67–69 °C; IR (neat) 3476, 3378, 2207, 2136; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 2.34 (s, 3H), 4.32 (s, 2H), 6.66-6.70 (m, 2H), 7.13-7.26 (m, 3H),
7.32-7.35 (m, 3H); 13C NMR (125 MHz, CDCl3) δ: 21.2, 73.5, 78.4, 79.1, 82.9, 106.2, 114.4, 117.9, 121.6, 128.3, 129.5, 130.1, 130.6, 133.0, 133.1, 138.2, 149.5; HRMS (ESI) calcd for C17H14N [M+H]+: 232.1126, found 232.1127

1-Azido-2-(m-tolylnbuta-1,3-diyn-1-yl)benzene (1c)

By a procedure identical with that described for the preparation of \textit{1a}, \textbf{S7} (500 mg, 2.16 mmol) was converted to \textbf{1c} (180 mg, 32%): beige powder; mp 70–71 ºC; IR (neat) 2126, 2094; 1H-NMR (CDCl3) δ: 2.34 (s, 3H), 7.09-7.12 (m, 1H), 7.15 (d, \textit{J} = 7.5 Hz, 1H), 7.19 (d, \textit{J} = 8.0 Hz, 1H), 7.21 (dd, \textit{J} = 8.0, 8.0 Hz, 1H), 7.33-7.35 (m, 2H), 7.38 (ddd, \textit{J} = 8.0, 8.0, 1.5 Hz, 1H), 7.50 (dd, \textit{J} = 8.0, 1.5 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ: 21.7, 73.0, 76.6, 79.5, 83.6, 114.0, 118.5 (2C), 124.7, 129.2 (2C), 130.3, 132.4 (2C), 134.4, 139.8, 142.5; HRMS (FAB) calcd for C17H12N3 [M+H]+: 258.1031, found 258.1037.

2-(p-Tolylbuta-1,3-diyn-1-yl)aniline (S9)

By a procedure identical with that described for the preparation of \textit{S3}, \textbf{S1} (805 mg, 6.87 mmol) was converted to \textbf{S9} (966 mg, 61%) by the reaction with \textbf{S8} (2.14 g, 11.8 mmol): yellow powder. The spectral data were in good agreement with those previously reported.\textsuperscript{4a}

1-Azido-2-(p-tolylbuta-1,3-diyn-1-yl)benzene (1d)

By a procedure identical with that described for the preparation of \textit{1a}, \textbf{S9} (966 mg, 4.18 mmol) was converted to \textbf{1d} (570 mg, 53%): yellow powder; mp 100–102 ºC; IR (neat) 2116, 2092; 1H NMR (500 MHz, CDCl3) δ: 2.37 (s,
3H), 7.08-7.15 (m, 1H), 7.13-7.15 (m, 3H), 7.36-7.39 (m, 1H), 7.42-7.44 (m, 2H), 7.50 (dd, $J = 7.7, 1.4$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 21.6, 73.0, 76.6, 79.5, 83.6, 114.0, 118.5 (2C), 124.6, 129.2 (3C), 130.2, 134.4 (2C), 139.8, 142.5; HRMS (FAB) calcd for C$_{17}$H$_{12}$N$_3$ [M+H]$^+$: 258.1031, found 258.1026.

2-[(4-Chlorophenyl)buta-1,3-diynyl]aniline (S11)

By a procedure identical with that described for the preparation of S3, S1 (389 mg, 3.32 mmol) was converted to S11 (617 mg, 74%) by the reaction with S10 (932 mg, 4.32 mmol): yellow powder; mp 134-136 °C; IR (neat) 3477, 3378, 2206, 2139; $^1$H NMR (400 MHz, CDCl$_3$) δ: 4.31 (s, 2H), 6.67-6.71 (m, 2H), 7.17 (dd, $J = 8.8, 8.0$ Hz, 1H), 7.31-7.35 (m, 3H), 7.45 (dd, $J = 6.7, 2.0$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 74.9, 78.8, 79.2, 81.4, 105.9, 114.4, 118.0, 120.4, 128.9 (2C), 130.8, 133.1 (2C), 133.5, 135.3, 149.6; HRMS (ESI) calcd for C$_{16}$H$_{11}$ClN [M+H]$^+$: 252.0580, found 252.0575.

1-Azido-2-[(4-chlorophenyl)buta-1,3-diynyl]benzene (1e)

By a procedure identical with that described for the preparation of 1a, S11 (500 mg, 1.99 mmol) was converted to 1e (351 mg, 63%): white powder; mp 144-145 °C; IR (neat) 2129, 2097; $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.09-7.16 (m, 2H), 7.31 (d, $J = 8.6$ Hz, 2H), 7.37-7.41 (m, 1H), 7.45 (d, $J = 8.6$ Hz, 2H), 7.50 (dd, $J = 8.0, 1.1$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 74.6, 77.5, 79.0, 82.0, 113.6, 118.5, 120.1, 124.7, 128.8 (2C), 130.5, 133.7 (2C), 134.4, 135.5, 142.7; HRMS (FAB) calcd for C$_{16}$H$_{9}$ClN$_3$ [M+H]$^+$: 278.0485, found 278.0481.
2-[(4-Nitrophenyl)buta-1,3-diyn-1-yl]aniline (S13)

By a procedure identical with that described for the preparation of S3, S1 (562 mg, 4.80 mmol) was converted to S13 (653 mg, 52%) by the reaction with S12 (1.42 g, 6.24 mmol): orange powder; mp 215–217 ºC; IR (neat) 3499, 3397, 2127, 2097, 1591; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 4.34 (s, 2H), 6.69-6.72 (m, 2H), 7.21 (ddd, \(J = 7.8, 7.8, 1.0\) Hz, 1H), 7.36 (d, \(J = 6.9\) Hz, 1H), 7.66 (d, \(J = 8.5\) Hz, 2H), 8.23 (d, \(J = 8.5\) Hz, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 78.4, 79.0, 80.4, 91.2, 105.3, 114.5 (2C), 118.1, 123.7, 128.9, 131.3, 133.0 (2C), 133.2, 133.4, 149.9; HRMS (FAB) calcd for C\(_{16}\)H\(_{11}\)N\(_2\)O\(_2\) [M+H]\(^+\): 263.0821, found 263.0825.

1-Azido-2-[(4-nitrophenyl)buta-1,3-diyn-1-yl]benzene (1f)

By a procedure identical with that described for the preparation of 1a, S13 (550 mg, 2.10 mmol) was converted to 1f (108 mg, 18%): yellow powder; mp 168–171 ºC; IR (neat) 2131, 2100, 1518; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.14 (dd, \(J = 7.6, 7.6\) Hz, 1H), 7.18 (d, \(J = 7.6\) Hz, 1H), 7.41-7.45 (m, 1H), 7.53 (ddd, \(J = 7.6, 1.2\) Hz, 1H), 7.66-7.71 (m, 2H), 8.20-8.25 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 78.4, 78.6, 79.9, 80.7, 113.1, 118.6, 123.7 (2C), 124.7, 128.6, 131.0, 133.2, 134.5 (2C), 143.0, 147.5; HRMS (FAB) calcd for C\(_{16}\)H\(_{9}\)N\(_4\)O\(_2\) [M+H]\(^+\): 289.0726, found 289.0722.

2-[(4-Methoxyphenyl)buta-1,3-diyn-1-yl]aniline (S15)

2-[(4-Methoxyphenyl)buta-1,3-diyn-1-yl]aniline (S15)\(^{1a}\)
By a procedure identical with that described for the preparation of \( S_3, S_1 \) (972 mg, 8.30 mmol) was converted to \( S_{15} \) (1.31 g, 64%) by the reaction with \( S_{14} \) (2.61 g, 12.4 mmol). The spectral data were in good agreement with those previously reported.\(^{4a}\)

1-Azido-2-[(4-methoxyphenyl)buta-1,3-diyn-1-yl]benzene (1g)

![1-Azido-2-[(4-methoxyphenyl)buta-1,3-diyn-1-yl]benzene (1g)](image)

By a procedure identical with that described for the preparation of \( 1a, S_{15} \) (495 mg, 2.00 mmol) was converted to \( 1g \) (188 mg, 34%): orange solid: mp 89–90 ºC; IR (neat) 2127, 2096; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 3.83 (s, 3H), 6.86 (d, \( J = 7.6 \) Hz, 2H), 7.08-7.15 (m, 2H), 7.37 (ddd, \( J = 7.9, 7.9, 1.7 \) Hz, 1H), 7.46-7.51 (m, 3H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \): 55.3, 72.5, 76.4, 77.2, 79.6, 83.6, 113.5, 114.1, 118.5 (2C), 124.6, 130.2, 134.2, 134.3 (2C), 142.5, 160.4; HRMS (FAB) calcd for C\(_{17}\)H\(_{12}\)N\(_3\)O \( [M+H]^+ \): 274.0980, found 274.0981.

4-Amino-3-(phenylbuta-1,3-diyn-1-yl)benzonitrile (S17)

![4-Amino-3-(phenylbuta-1,3-diyn-1-yl)benzonitrile (S17)](image)

By a procedure identical with that described for the preparation of \( S_3, S_{16} \) (325 mg, 2.29 mmol) was converted to \( S_{17} \) (463 mg, 84%) by the reaction with \( S_2 \) (538 mg, 2.97 mmol): white solid: mp 181–182 ºC; IR (neat) 3473, 3355, 2216, 2127, 2097; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 4.83 (br s, 2H), 6.70 (d, \( J = 8.6 \) Hz, 1H), 7.34-7.41 (m, 4H), 7.54 (dd, \( J = 8.6, 1.7 \) Hz, 2H), 7.62 (d, \( J = 1.7 \) Hz, 1H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \): 73.2, 75.6, 80.5, 83.8, 100.4, 114.1, 119.0, 121.3, 128.5 (3C), 129.6, 132.5 (2C), 133.9, 137.4, 152.4; HRMS (FAB\(^+\)) calcd for C\(_{17}\)H\(_{11}\)N\(_2\) \( [M+H]^+ \): 243.0922, found 243.0919.
4-Azido-3-(phenylbuta-1,3-diyn-1-yl)benzonitrile (1h)

By a procedure identical with that described for the preparation of \(1\text{a}, \text{S17}\) (242 mg, 1.00 mmol) was converted to \(1\text{h}\) (56.4 mg, 21%): orange powder; mp 138–140 °C; IR (neat) 2226, 2122, 2084; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.23 (d, \(J = 8.6\) Hz, 1H), 7.35-7.43 (m, 3H), 7.54-7.56 (m, 2H), 7.63 (dd, \(J = 8.3, 1.7\) Hz, 1H), 7.77 (d, \(J = 1.7\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 73.0, 74.3, 81.6, 84.7, 108.5, 115.3, 117.4, 119.4, 121.1, 128.5 (2C), 129.8, 132.6 (2C), 133.2, 137.9, 146.9; HRMS (FAB) calcd for C\(_{17}\)H\(_9\)N\(_4\) [M+H]\(^+\): 269.0827, found 269.0826.

4-Methoxy-2-(phenylbuta-1,3-diyn-1-yl)aniline (S19)

By a procedure identical with that described for the preparation of \(\text{S3, S18}\), \(\text{S19}\) (452 mg, 3.07 mmol) was converted to \(\text{S19}\) (680 mg, 90%) by the reaction with \(\text{S2}\) (723 mg, 3.99 mmol): yellow crystals; mp 85–87 °C; IR (neat) 3 456, 3367, 2209, 2125; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 3.73 (s, 3H), 4.05 (s, 2H), 6.65 (d, \(J = 8.7\) Hz, 1H), 6.80 (dd, \(J = 8.7, 2.9\) Hz, 1H), 6.87 (d, \(J = 2.9\) Hz, 1H), 7.32-7.39 (m, 3H), 7.52 (dd, \(J = 7.9, 2.4\) Hz, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 55.8, 73.8, 78.6, 79.0, 82.8, 106.6, 116.1, 118.8, 121.8, 128.4 (3C), 129.2, 132.4 (2C), 144.0, 151.7; HRMS (ESI) calcd for C\(_{17}\)H\(_{14}\)NO [M+H]\(^+\): 248.1075, found 248.1088.

1-Azido-4-methoxy-2-(phenylbuta-1,3-diyn-1-yl)benzene (1i)

By a procedure identical with that described for the preparation of \(\text{1a, S19}\) (495 mg, 2.00 mmol) was converted to \(1\text{i}\) (454 mg, 83%): pale yellow solid; mp 75–77 °C; IR (neat) 2121, 2088; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 3.79 (s, 3H), 6.95 (dd, \(J = 8.6, 2.9\) Hz, 1H), 7.01 (d, \(J = 2.9\) Hz, 1H), 7.05 (d, \(J = 8.6\) Hz, 1H), 7.32-7.40 (m, 3H), 7.52-7.55
(m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 55.7, 73.5, 76.9, 79.1, 83.4, 114.4, 117.6, 118.1, 119.7, 121.5, 128.4 (2C), 129.4, 132.5 (2C), 135.3, 156.3; HRMS (FAB) calcd for C$_{17}$H$_{12}$N$_3$ [M+H]$^+$: 274.0980, found 274.0981.

**Diethyl 1H-Indole-1,5-dicarboxylate (10F)**

$$
\begin{array}{c}
\text{EtO}_2\text{C} \quad \text{NaH, EtOCOCl} \\
\text{THF} \\
0 \degree \text{C to rt} \\
\text{EtO}_2\text{C} \quad 10\text{F}
\end{array}
$$

To a suspension of NaH (60% dispersion in paraffin liquid; 160 mg, 4.00 mmol) in THF (2.0 mL) at 0 °C was added S20 (378 mg, 2.00 mmol), and the mixture was stirred at 0 °C for 10 min under Ar. To the reaction mixture was added dropwise ClCO$_2$Et (0.286 mL, 3.00 mmol). After being stirred at room temperature for 2 h, the reaction mixture was diluted with H$_2$O and extracted with EtOAc. The combined organic layer was dried over Na$_2$SO$_4$ and filtered and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 30/1) to give 10F (453 mg, 87%) as a white solid: mp 73–74 °C; IR (neat) 1742, 1710; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.42 (t, $J = 7.2$ Hz, 3H), 1.48 (t, $J = 7.2$ Hz, 3H), 4.40 (q, $J = 7.2$ Hz, 2H), 4.51 (q, $J = 7.2$ Hz, 2H), 6.67 (d, $J = 3.5$ Hz, 1H), 7.67 (d, $J = 3.5$ Hz, 1H), 8.04 (dd, $J = 8.7$, 1.7 Hz, 1H), 8.21 (d, $J = 9.3$ Hz, 1H), 8.30-8.31 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 14.3 (2C), 60.8, 63.5, 108.3, 114.7, 123.1, 125.2, 125.7, 126.7, 130.2, 137.8, 150.7, 166.9; HRMS (ESI) calcd for C$_{14}$H$_{16}$NO$_4$ [M+H]$^+$: 262.1079, found 262.1066.

3. **Gold-Catalysed Cascade Cyclisation**


$$
\begin{array}{c}
\text{PhN}_3 \\
1\text{a} \\
\text{OMe} \\
\text{8A} \\
\text{3aA}
\end{array}
$$

**Condition A (Table 1, Entry 10):** To a solution of 1a (48.6 mg, 0.200 mmol) and 8A (216 mg, 2.00 mmol) in DCE (1.00 mL) was added [JohnPhosAu(MeCN)SbF$_6$] (7.70 mg, 10.0 $\mu$mol) at 80 °C. The mixture was stirred at 80 °C in pre-heated bath for 1 h. After disappearance of 1a on TLC, the reaction mixture was allowed to warm to 140 °C and stirred at this temperature for 16 h. The mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20/1) to give 3aA (48.3 mg, 75%).

**Condition B (Table 1, Entry 12):** To a solution of 1a (48.6 mg, 0.200 mmol) in anisole (8A) (1.00 mL) was added [BrettPhosAu(MeCN)SbF$_6$] (10.1 mg, 10.0 $\mu$mol) at 140 °C. The mixture was stirred at 140 °C in pre-heated bath for 19.5 h and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20/1) to give 3aA (55.6 mg, 86%) as a white solid. Recrystallization from EtOAc–hexane gave pure 3aA.

Compound 3aA: colorless crystals; mp 168–172 °C; IR (neat): 3404; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.80 (s, 3H), 7.37-7.42 (m, 3H), 7.44-7.47 (m, 2H), 7.51-7.60 (m, 6H), 8.39 (s, 1H), 8.55 (d, $J = 8.0$ Hz, 1H), 8.78 (d, $J = 9.7$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 55.3, 107.6, 111.1, 114.0, 115.3, 117.8, 120.1, 121.9, 123.6, 124.3, 124.9,
125.3, 127.3, 128.3 (2C), 128.9, 130.1 (2C), 135.5, 138.6, 138.7, 141.4, 155.4; HRMS (ESI) caleld for C_{23}H_{18}NO [M+H]^+ 324.1383, found 324.1379.

3-(4-Methoxyphenyl)-2-(phenylethynyl)-1H-indole (2aA) (Table 1, Entry 4).

To a solution of 1a (48.6 mg, 0.200 mmol) and anisole (8A) (216 mg, 2.00 mmol) in 1,2-DCE (1.00 mL) was
added [BrettPhosAu(MeCN)SbF_6] (10.1 mg, 10.0 \mu mol) at 80 °C. The mixture was stirred at 80 °C in pre-heated bath for 30 h and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20/1) to give 2aA as brown solid (42.1 mg, 65%). Recrystallization from EtOAc–hexane gave pure 2aA: colorless crystals; mp 97–107 °C; IR (neat): 3409, 2205; 1H NMR (500 MHz, CDCl3) δ: 3.89 (s, 3H), 7.06 (d, J = 8.6 Hz, 2H), 7.17 (dd, J = 7.4, 7.4 Hz, 1H), 7.28 (dd, J = 7.4, 7.4 Hz, 1H), 7.34-7.37 (m, 4H), 7.47-7.49 (m, 2H), 7.80 (d, J = 8.6 Hz, 2H), 7.82 (d, J = 8.0 Hz, 1H), 8.26 (s, 1H); 13C NMR (125 MHz, CDCl3) δ: 55.3, 82.3, 94.3, 110.9, 114.0 (2C), 115.5, 120.1, 120.6, 122.4, 122.7, 123.9, 126.1, 126.7, 128.4 (3C), 130.0 (2C), 131.3 (2C), 136.0, 158.4; HRMS (ESI) caleld for C_{23}H_{18}NO [M+H]^+ 324.1383, found 324.1378.

2,3-Dimethoxy-5-phenyl-7H-benzo[c]carbazole (3aB).

According to the general procedure described for the preparation of 3aA, 1a (48.6 mg, 0.200 mmol) was converted into 3aB (49.9 mg, 70%) (condition A; 80 °C, 2 h then 140 °C, 15 h). The reaction of 1a (48.6 mg, 0.200 mmol) and 2B (1.00 mL) under condition B (140 °C, 27 h) gave 3aB (70 mg, quant) as a white solid. Recrystallization from EtOAc–hexane gave pure 3aB: colorless crystals; mp 245–257 °C; IR (neat): 3332; 1H NMR (500 MHz, CDCl3) δ: 3.82 (s, 3H), 4.20 (s, 3H), 7.38-7.40 (m 3H), 7.44 (dd, J = 7.4 Hz, 2H), 7.50-7.57 (m, 5H), 8.13 (s, 1H), 8.34 (s, 1H), 8.46 (d, J = 8.0 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ: 55.7, 55.9, 103.3, 107.3, 111.1, 111.5, 114.7, 120.0, 121.4, 122.6, 123.6, 124.2, 125.7, 127.2, 128.3 (2C), 130.1 (2C), 136.2, 138.4, 138.8, 141.7, 146.7, 149.9; HRMS (ESI) caleld for C_{24}H_{20}NO_2 [M+H]^+ 354.1489, found 354.1489.

1,3-Dimethoxy-5-phenyl-7H-benzo[c]carbazole (3aC).
According to the general procedure (condition A; 80 °C, 2 h then 140 °C, 15 h) described for the preparation of 3aA, 1a (48.6 mg, 0.200 mmol) was converted into 3aC (28.3 mg, 40%). The reaction of 1a (48.6 mg, 0.200 mmol) and 8C (1.00 mL) under the condition B (140 °C, 26 h) gave 3aC (67.3 mg, 95%) as a brown solid. Recrystallization from EtOAc–hexane gave pure 3aC: colorless crystals; mp 205–210 °C; IR (neat): 3396; 1H NMR (400 MHz, CDCl3) δ: 3.73 (s, 3H), 4.14 (s, 3H), 6.77 (d, J = 2.3 Hz, 1H), 6.94 (d, J = 2.3 Hz, 1H), 7.25-7.29 (dd, 1H), 7.36-7.51 (m, 8H), 8.29 (s, 1H), 8.87 (d, J = 8.1 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ: 55.1, 55.2, 98.4, 99.5, 110.5, 114.4, 114.7, 118.0, 119.3, 124.3, 126.7, 127.2, 128.2 (2C), 130.0 (2C), 130.2, 136.0, 139.1, 141.9, 155.6, 156.9; HRMS (ESI) calcd for C24H20NO2 [M+H]+ 354.1489, found 354.1490.

5-Phenyl-7H-[1,3]dioxolo[4',5':4,5]benzo[1,2-c]carbazole (3aD).

According to the general procedure (condition B; 140 °C, 18 h) described for the preparation of 3aA, 1a (48.6 mg, 0.200 mmol) was converted into 3aD (51.1 mg, 76%) as a white solid. Recrystallization from EtOAc–hexane gave pure 3aD: colorless crystals; mp 192–198 °C; IR (neat): 3411; 1H NMR (500 MHz, CDCl3) δ: 6.07 (s, 2H), 7.31 (s, 1H), 7.37 (dd, J = 7.7, 7.7 Hz, 1H), 7.41 (s, 1H), 7.43-7.46 (m, 2H), 7.48-7.55 (m, 5H), 8.18 (s, 1H), 8.30 (s, 1H), 8.47 (d, J = 8.0 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ: 100.9, 101.1, 104.6, 111.0, 111.5, 115.4, 120.1, 121.6, 123.7, 123.9, 124.3, 126.8, 127.2, 128.3 (2C), 130.1 (2C), 136.2, 138.8, 139.0, 141.6, 145.2, 148.1; HRMS (ESI) calcd for C23H16NO2 [M+H]+ 338.1176, found 338.1173.

2,3-Dimethyl-5-phenyl-7H-benzo[c]carbazole (3aE).

According to the general procedure (condition B; 140 °C, 1 h) described for the preparation of 3aA, 1a (48.6 mg, 0.200 mmol) was converted into 3aE (26.7 mg, 42%) as a white solid. In the case, the reaction was conducted using 20 mol % BrettPhosAu(MeCN)SbF6 (40.4 mg, 0.04 mmol). Recrystallization from EtOAc–hexane gave pure 3aE: colorless crystals; mp 232–242 °C; IR (neat): 3422; 1H NMR (500 MHz, CDCl3) δ: 2.38 (s, 3H), 2.58 (s, 3H), 7.37-7.40 (m, 1H), 7.42-7.47 (m, 3H), 7.50-7.58 (m, 5H), 7.73 (s, 1H), 8.29 (s, 1H), 8.60 (d, J = 7.4 Hz, 2H); 13C NMR (125 MHz, CDCl3) δ: 19.2, 20.7, 110.0, 112.7, 114.5, 120.0, 122.0, 123.5, 124.0, 124.1, 126.5, 127.1 (2C), 128.2 (2C), 128.9, 130.3 (2C), 132.3, 136.3, 136.4, 138.6, 139.0, 141.6; HRMS (ESI) calcd for C24H20N [M+H]+ 322.1590, found 322.1589.
3-Methoxy-5-(o-tolyl)-7H-benzo[c]carbazole (3bA)

According to the general procedure (condition B; 140 °C, 20 h) described for the preparation of 3aA, 1d (51.4 mg, 0.200 mmol) was converted into 3bA (60.3 mg, 89%) as a colorless oil: IR (neat): 3407; 1H NMR (500 MHz, CDCl3) δ: 2.05 (s, 3H), 3.73 (s, 3H), 6.93 (d, J = 2.9 Hz, 1H), 7.31-7.32 (m, 2H), 7.36-7.39 (m, 4H), 7.41 (s, 1H), 7.42-7.45 (m, 1H), 7.53 (d, J = 8.0 Hz, 1H), 8.28 (s, 1H), 8.54 (d, J = 7.4 Hz, 1H), 8.76 (d, J = 9.2 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ: 20.1, 55.2, 107.4, 111.1, 113.7, 115.2, 117.7, 120.1, 121.8, 123.7, 124.3, 124.8, 125.0, 125.7, 127.7, 129.2, 129.9, 130.4, 135.5, 137.0, 138.2, 138.6, 140.7, 155.5; HRMS (ESI) calecd for C24H20NO [M+H]+ 338.1539, found 338.1538.

3-Methoxy-5-(m-tolyl)-7H-benzo[c]carbazole (3cA)

According to the general procedure (condition B; 140 °C, 20 h) described for the preparation of 3aA, 1c (51.4 mg, 0.200 mmol) was converted into 3cA (63.6 mg, 94%) as a colorless oil: IR (neat): 3411; 1H NMR (500 MHz, CDCl3) δ: 2.46 (s, 3H), 3.80 (s, 3H), 7.27 (d, J = 7.4 Hz, 1H), 7.36-7.39 (m, 4H), 7.41-7.42 (m, 2H), 7.44 (dd, J = 7.4, 7.4 Hz, 1H), 7.53 (s, 1H), 7.55 (d, J = 8.0 Hz, 1H), 8.33 (s, 1H), 8.54 (d, J = 7.4 Hz, 1H), 8.77 (d, J = 9.2 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ: 21.5, 55.3, 107.7, 111.1, 113.9, 115.2, 117.8, 120.1, 121.9, 123.7, 124.3, 124.8, 125.3, 127.2, 128.0, 128.2, 128.9, 130.8, 135.5, 138.0, 138.7, 138.8, 141.4, 155.4; HRMS (ESI) calecd for C24H20NO [M+H]+ 338.1539, found 338.1538.

3-Methoxy-5-(p-tolyl)-7H-benzo[c]carbazole (3dA)

According to the general procedure (condition B; 140 °C, 20 h) described for the preparation of 3aA, 1b (51.4 mg, 0.200 mmol) was converted into 3dA (47.0 mg, 70%). Recrystallization from EtOAc–hexane gave pure 3dA: colorless crystals; mp 162–170 °C; IR (neat): 3407; 1H NMR (500 MHz, CDCl3) δ: 2.47 (s, 3H), 3.79 (s, 3H), 7.30
(d, J = 8.0 Hz, 2H), 7.34-7.40 (m, 2H), 7.41-7.46 (m, 5H), 7.48 (d, J = 8.0 Hz, 1H), 8.22 (s, 1H) 8.52 (d, J = 8.0 Hz, 1H), 8.75 (d, J = 9.2 Hz, 1H); ^13C NMR (125 MHz, CDCl3) δ: 21.3, 55.3, 107.6, 111.1, 114.0, 117.8, 120.0, 121.9, 123.6, 124.3, 124.8, 125.2, 128.9, 129.0 (2C), 130.0 (2C), 130.1, 135.5, 136.9, 138.4, 138.6, 138.7, 155.4; HRMS (ESI) calcd for C24H20NO [M+H]^+ 338.1539, found 338.1539.

5-(4-chlorophenyl)-3-methoxy-7H-benzo[c]carbazole (3eA)

According to the general procedure (condition B; 140 °C, 22.5 h) described for the preparation of 3aA, 1e (55.5 mg, 0.200 mmol) was converted into 3eA (53.5 mg, 74%). Recrystallization from EtOAc–hexane gave pure 3eA: colorless crystals; mp 170–177 °C; IR (neat): 3406; ^1H NMR (500 MHz, CDCl3) δ: 3.11 (s, 3H), 7.30 (d, J = 2.9 Hz, 1H), 7.36-7.40 (m, 3H), 7.43-7.51 (m, 6H), 8.23 (s, 1H), 8.52 (d, J = 7.4 Hz, 1H), 8.76 (d, J = 9.2 Hz, 1H); ^13C NMR (125 MHz, CDCl3) δ: 55.3, 107.1, 111.1, 114.0, 115.5, 118.0, 120.2, 121.9, 123.5, 124.5, 124.9, 125.2, 128.5 (2C), 128.6, 131.4 (2C), 133.2, 135.3, 137.1, 138.7, 139.8, 155.5; HRMS (ESI) calcd for C23H17ClNO [M–H]– 367.1088, found 367.1088.

3-Methoxy-5-(4-nitrophenyl)-7H-benzo[c]carbazole (3fA)

According to the general procedure (condition B; 140 °C, 23 h) described for the preparation of 3aA, 1f (57.6 mg, 0.200 mmol) was converted into 3fA (32.0 mg, 43%). Recrystallization from EtOAc–hexane gave pure 3fA: colorless crystals; mp 244–248 °C; IR (neat): 3343, 1498, 1344; ^1H NMR (600 MHz, CDCl3) δ: 3.82 (s, 3H), 7.39-7.45 (m, 3H), 7.49 (dd, J = 7.4 Hz, 1H), 7.57 (s, 1H), 7.60 (d, J = 7.7 Hz, 1H), 7.77 (d, J = 8.8 Hz, 2H), 8.40 (d, J = 8.8 Hz, 2H), 8.43 (s, 1H), 8.56 (d, J = 7.7 Hz, 1H), 8.81 (d, J = 8.8 Hz, 1H); ^13C NMR (125 MHz, CDCl3) δ: 55.4, 106.8, 111.3, 114.3, 116.5, 118.3, 120.4, 122.2, 123.4, 123.7 (2C), 125.0, 125.2, 125.4, 128.1, 131.0 (2C), 135.2, 135.8, 139.0, 147.2, 148.6, 155.9; HRMS (ESI) calcd for C23H17N2O3 ([M–H]–) 367.1088, found 367.1088.

3-Methoxy-5-(4-methoxyphenyl)-7H-benzo[c]carbazole (3gA)
According to the general procedure (condition B; 140 °C, 12 h) described for the preparation of 3aA, 1g (54.6 mg, 0.200 mmol) was converted into 3gA (42.8 mg, 61%) as a brown solid: mp 175–185 °C; IR (neat): 3406; 1H NMR (500 MHz, CDCl3) δ: 3.78 (s, 3H), 3.88 (s, 3H), 7.00 (d, J = 8.6 Hz, 2H), 7.33-7.45 (m, 8H), 8.19 (s, 1H), 8.51 (d, J = 8.0 Hz, 1H), 8.74 (d, J = 8.6 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ: 55.3, 55.3, 107.5, 111.1, 113.7 (2C), 114.0, 115.0, 117.8, 120.0, 121.8, 123.6, 124.2, 124.8, 125.2, 129.0, 131.1 (2C), 133.7, 135.5, 138.2, 138.7, 155.4, 158.8; HRMS (ESI) calcd for C24H20NO2 [M+H]+ 354.1489, found 354.1489.

4-Phenyl-3,6-dihydropyrrolo[2,3-c]carbazole (6aA) and Its [3,2-c]-Isomer (7aA) (Table 3, Entry 1)

![Chemical Structure](image)

To a solution of 1a (24.3 mg, 0.100 mmol) and 9A (0.0347 mL, 0.5 mmol) in DCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF6] (5.05 mg, 5.00 μmol) at 80 ºC. The mixture was stirred at 80 ºC in pre-heated bath for 8 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 5/1) to give a mixture of 6aA and 7aA containing a small amount of impurities (17.6 mg, <62%; 6aA:7aA = 25:75). These isomers were separated by column chromatography on amine silica gel (hexane/CHCl3 = 2/1) to give, in the order of elution, 6aA and 7aA.

**Compound 6aA**: brown viscous oil; IR (neat) 3406; 1H NMR (500 MHz, CDCl3) δ: 7.15 (dd, J = 2.5, 1.5 Hz, 1H), 7.24 (s, 1H), 7.28–7.32 (m, 1H), 7.35 (dd, J = 3.0, 3.0 Hz, 1H), 7.38–7.45 (m, 3H), 7.52 (dd, J = 8.0, 8.0 Hz, 2H), 7.66–7.69 (m, 2H), 8.04 (s, 1H), 8.28 (d, J = 7.0 Hz, 1H), 8.54 (s, 1H); 13C NMR (125 MHz, CDCl3) δ: 101.4, 106.2, 110.5, 113.7, 119.2, 121.1, 121.3, 123.6, 124.18, 124.23, 125.0, 127.4, 128.5 (2C), 128.9, 129.2 (2C), 134.9, 139.1, 139.7; HRMS (ESI) calcd for C20H15N2 [M+H]+: 283.1230, found 283.1231.

**Compound 7aA**: white solid; mp 231–234 ºC; IR (neat) 3395; 1H NMR (500 MHz, CDCl3) δ: 6.87 (dd, J = 3.5, 2.5 Hz, 1H), 7.31–7.34 (m, 3H), 7.39–7.44 (m, 2H), 7.51–7.54 (m, 3H), 7.78–7.79 (m, 2H), 8.08 (d, J = 6.5 Hz, 1H), 8.27 (s, 1H), 8.79 (s, 1H); 13C NMR (125 MHz, CDCl3) δ: 103.4, 104.6, 106.8, 110.7, 119.5, 120.2, 120.3, 121.7 (2C), 124.3, 127.0, 128.5 (2C), 129.1 (2C), 130.2, 133.7, 137.1, 138.7, 141.6; HRMS (ESI) calcd for C20H15N2 [M+H]+: 283.1230, found 283.1231.

3-Benzyl-4-phenyl-3,6-dihydropyrrolo[2,3-c]carbazole (6aB) and Its [3,2-c]-Isomer (7aB) (Table 3, Entry 2)
To a solution of 1a (24.3 mg, 0.100 mmol) and 9B (78.6 mg, 0.500 mmol) in DCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF₆] (5.05 mg, 5.00 µmol) at 80 °C. The mixture was stirred at 80 °C in pre-heated bath for 10 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 10/1) to give a 6aB (4.20 mg, 11%) and 7aB (19.0 mg, 51%) in the order of elution, 6aB and 7aB; (6aB:7aB = 18:82).

Compound 6aB: yellow solid; mp 163–168 °C; IR (neat) 3728; ¹H NMR (500 MHz, CDCl₃) δ: 5.00 (s, 2H), 6.47 (m, 2H), 7.05 (s, 1H), 7.06-7.13 (m, 3H), 7.20 (d, J = 3.0 Hz, 1H), 7.22-7.28 (m, 5H), 7.30-7.35 (m, 2H), 7.41 (dt, J = 8.0, 1.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 8.06 (s, 1H), 8.30 (d, J = 8.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 52.2, 100.2, 108.7, 110.5, 113.8, 119.2, 121.2, 123.4, 123.7, 124.2, 125.8 (2C), 126.6, 126.9, 127.1, 127.6 (2C), 128.2 (2C), 128.7, 129.9 (2C), 130.8, 134.0, 138.8, 139.2, 140.6; HRMS (ESI) calcld for C₂₇H₂₁N₂ [M+H]⁺: 373.1699, found 373.1700.

Compound 7aB: white solid; mp 173–178 °C; IR (neat) 3728; ¹H NMR (500 MHz, CDCl₃) δ: 6.02 (s, 2H), 6.84 (d, J = 3.0 Hz, 1H), 7.00-7.04 (m, 2H), 7.24-7.33 (m, 7H), 7.39-7.42 (m, 2H), 7.50 (t, J = 8.0 Hz, 2H), 7.75 (d, J = 7.5 Hz, 2H), 8.01 (d, J = 8.5 Hz, 1H), 8.23 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 53.2, 103.6, 104.8, 106.9, 110.6, 119.3, 121.0, 121.7, 122.6, 123.9, 126.5 (2C), 126.6, 127.0, 127.5, 128.4 (2C), 128.9 (2C), 129.2 (2C), 132.6, 134.1, 138.0, 138.7 (2C), 141.3; HRMS (ESI) calcld for C₂₇H₂₁N₂ [M+H]⁺: 373.1699, found 373.1702.

4-Phenyl-3-tosyl-3,6-dihydropyrrolo[2,3-c]carbazole (6aC) and Its [3,2-c]-Isomer (7aC) (Table 3, Entry 3)

To a solution of 1a (24.3 mg, 0.100 mmol) and 9C (111 mg, 0.500 mmol) in TCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF₆] (10.1 mg, 10.0 µmol) at 140 °C. The mixture was stirred at 140 °C in pre-heated bath for 30 min and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 5/1) to give a mixture of 6aC and 7aC (14.7 mg, 34%; 6aC:7aC = 58:42). These isomers were separated by column chromatography on silica gel (toluene) to give, in the order of elution, 6aC and 7aC.

Compound 6aC: brown viscous oil; IR (neat) 3736; ¹H NMR (500 MHz, CDCl₃) δ: 2.24 (s, 3H), 6.98 (d, J = 8.5 Hz, 2H), 7.18-7.21 (m, 3H), 7.27-7.31 (m, 2H), 7.37-7.47 (m, 7H), 7.80 (d, J = 4.0 Hz, 1H), 8.13-8.14 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ: 21.5, 110.0, 110.8, 111.6, 114.1, 119.8, 121.1, 122.8, 125.4, 126.5 (2C), 127.0, 127.4, 127.7 (2C), 128.9, 129.1 (2C), 129.3 (2C), 130.2, 132.0, 134.4, 136.6, 139.6, 141.8, 144.0; HRMS (ESI) calcld for C₂₇H₂₁N₂O₂S [M+H]⁺: 437.1318, found 437.1318.

Compound 7aC: white viscous oil; IR (neat) 3390; ¹H NMR (500 MHz, CDCl₃) δ: 2.24 (s, 3H), 6.98 (d, J = 8.6 Hz, 2H), 7.19 (t, J = 7.2 Hz, 3H), 7.29 (dt, J = 12.4, 3.3 Hz, 2H), 7.37-7.39 (m, 3H), 7.42 (t, J = 7.4 Hz, 1H), 7.45-7.47 (m, 3H), 7.80 (d, J = 4.0 Hz, 1H), 8.14 (d, J = 7.4 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ: 21.5, 109.3, 110.0, 112.6, 114.2, 119.2, 121.7, 125.5, 125.7, 125.9, 126.8 (2C), 127.3, 128.3, 128.6 (2C), 128.9 (2C), 129.0 (2C), 132.4, 133.1, 133.6, 139.6, 139.7, 140.1, 144.3; HRMS (ESI) calcld for C₂₇H₂₁N₂O₂S [M+H]⁺: 437.1318, found 437.1317.
Methyl 4-Phenylpyrrolo[2,3-c]carbazole-3(6H)-carboxylate (6aD) and Its [3,2-c]-Isomer (7aD) (Table 3, Entry 4)

To a solution of 1a (24.3 mg, 0.100 mmol) and 9D (62.3 mg, 0.500 mmol) in DCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF$_6$] (5.05 mg, 5.00 µmol) at 80 ºC. The mixture was stirred at 80 ºC in pre-heated bath for 1.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 5/1) to give a mixture of 6aD and 7aD (21.2 mg, 62%; 6aD:7aD = 81:19). These isomers were separated by column chromatography on amine silica gel (hexane/CHCl$_3$ = 1/2) to give, in the order of elution, 6aD and 7aD.

**Compound 6aD:** white powder; mp 173–175 ºC; IR (neat) 3380, 1751; 1H NMR (500 MHz, CDCl$_3$) δ: 3.25 (s, 3H), 7.28 (d, $J = 3.5$ Hz, 1H), 7.31-7.37 (m, 3H), 7.42-7.53 (m, 6H), 7.80 (d, $J = 3.4$ Hz, 1H), 8.21 (s, 1H), 8.25 (d, $J = 8.0$ Hz, 1H); 13C NMR (125 MHz, CDCl$_3$) δ: 53.2, 106.2, 110.2, 110.7, 114.1, 119.6, 121.3, 123.1, 125.1, 125.8, 126.6, 127.2, 127.4, 128.5 (2C), 128.7 (2C), 136.4, 139.6, 139.6, 143.1, 152.0; HRMS (ESI) calcd for C$_{22}$H$_{17}$N$_2$O$_2$ [M+H$^+$$^\cdot$]: 341.1290, found 341.1284.

**Compound 7aD:** orange viscous oil; IR (neat) 3398, 1734; 1H NMR (500 MHz, CDCl$_3$) δ: 4.12 (s, 3H), 6.88 (d, $J = 4.6$ Hz, 1H), 7.27-7.30 (m, 1H), 7.41-7.47 (m, 3H), 7.49-7.53 (m, 3H), 7.63 (d, $J = 3.5$ Hz, 1H), 7.66 (d, $J = 8.0$ Hz, 2H), 7.94 (d, $J = 8.0$ Hz, 1H), 8.36 (s, 1H); 13C NMR (125 MHz, CDCl$_3$) δ: 54.2, 107.8, 109.0, 110.2, 110.4, 119.2, 122.0, 123.3, 124.9, 125.3, 125.5, 127.2, 128.6 (2C), 129.2 (2C), 129.9, 133.4, 139.3, 139.5, 140.6, 152.2; HRMS (ESI) calcd for C$_{22}$H$_{17}$N$_2$O$_2$ [M+H$^+$$^\cdot$]: 341.1290, found 341.1284.

2,2-Dimethyl-1-(4-phenylpyrrolo[2,3-c]carbazol-3(6H)-yl)propan-1-one (6aE) (Table 3, Entry 5)

To a solution of 1a (24.3 mg, 0.100 mmol) and 9E (75.6 mg, 0.500 mmol) in DCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF$_6$] (5.05 mg, 5.00 µmol) at 80 ºC. The mixture was stirred at 80 ºC in pre-heated bath for 1.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 5/1) to give an inseparable mixture of 6aE and minor isomer (21.9 mg, 60%; 6aE: minor isomer = 82:18); orange viscous oil; IR (neat) 3393, 1695; 1H NMR (500 MHz, CDCl$_3$) δ: 1.37 (s, 9H), 7.23 (d, $J = 3.4$ Hz, 1H), 7.25 (s, 1H), 7.32 (dd, $J = 7.2$, 5.4 Hz, 2H), 7.42-7.49 (m, 6H), 7.74 (d, $J = 4.0$ Hz, 1H), 8.23 (d, $J = 9.7$ Hz, 2H); 13C NMR (125 MHz, CDCl$_3$; including amide rotamers) δ: 28.8 and 29.3 (totally 3C), 41.6, 105.6, 107.9, 108.3, 109.9, 110.1, 119.1, 122.0, 122.5,
123.5, 124.6, 124.9, 125.7, 126.6, 127.1, 127.4, 128.5 \, (2C), 129.3 \, (2C), 131.3, 139.2, 140.8, 177.9; HRMS (ESI) calcd for C_{25}H_{23}N_{2}O \, [M+H]^+: 367.1810, found 367.1801.

dert-Butyl 4-Phenylpyrrolo[2,3-c]carbazole-3(6H)-carboxylate (6aF) and Its [3,2-c]-Isomer (7aF) (Table 3, Entry 6)

![Chemical structure of tert-Butyl 4-Phenylpyrrolo[2,3-c]carbazole-3(6H)-carboxylate (6aF) and Its [3,2-c]-Isomer (7aF)]

To a solution of 1a (24.3 mg, 0.100 mmol) and 9F (83.6 mg, 0.500 mmol) in DCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF_{6}] (5.05 mg, 5.00 \mu mol) at 80 °C. The mixture was stirred at 80 °C in pre-heated bath for 1.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 10/1) to give a mixture of 6aF and 7aF (23.1 mg, 60%; 6aF:7aF = 92:8). These isomers were separated by reverse-column chromatography on silica gel (MeCN/0.1% TFA aq.) to give, in the order of elution, 6aF and 7aF.

Compound 6aF: pale yellow solid; mp 173–178 °C; IR (neat) 3397, 1742; \(^1H\) NMR (500 MHz, CDCl_{3}) δ: 1.30 (s, 9H), 7.21 (d, \(J = 3.5\) Hz, 1H), 7.29 (s, 1H), 7.32 (t, \(J = 8.0\) Hz, 2H), 7.40-7.46 (m, 4H), 7.57 (d, \(J = 8.0\) Hz, 2H), 7.73 (d, \(J = 4.0\) Hz, 1H), 8.16 (s, 1H), 8.24 (d, \(J = 8.0\) Hz, 1H); \(^13C\) NMR (125 MHz, CDCl_{3}) δ: 27.6 (3C), 83.5, 105.5, 110.1, 110.7, 113.8, 119.5, 121.2, 123.2, 124.9, 125.9, 126.6, 127.4 (2C), 127.5, 128.5 (2C), 128.8, 129.1, 136.4, 139.5, 140.8, 177.9; HRMS (ESI) calcd for C_{25}H_{23}N_{2}O_{2} \, [M+H]^+: 383.1754, found 383.1755.

Compound 7aF: white viscous oil; IR (neat) 3592, 1747; \(^1H\) NMR (500 MHz, CDCl_{3}) δ: 1.72 (s, 9H), 6.84 (d, \(J = 3.5\) Hz, 1H), 7.28 (d, \(J = 8.0\) Hz, 6.5, 1.5 Hz, 1H), 7.38-7.44 (m, 4H), 7.50 (t, \(J = 7.0\) Hz, 2H), 7.56 (d, \(J = 4.0\) Hz, 1H), 7.65 (d, \(J = 7.0\) Hz, 2H), 7.78 (d, \(J = 8.5\) Hz, 1H), 8.27 (s, 1H); \(^13C\) NMR (125 MHz, CDCl_{3}) δ: 27.6 (3C), 83.6, 107.6, 108.1, 110.0, 110.4, 119.0, 122.1, 123.2, 124.7, 125.4, 125.9, 127.1, 128.5 (2C), 129.2 (2C), 129.9, 133.3, 139.2, 139.5, 140.8, 150.0; HRMS (ESI) calcd for C_{25}H_{23}N_{2}O_{2} \, [M+H]^+: 383.1754, found 383.1755.

tert-Butyl 4-(o-Tolyl)pyrrolo[2,3-c]carbazole-3(6H)-carboxylate (6bF) and Its [3,2-c]-Isomer (7bF) (Table 5)

![Chemical structure of tert-Butyl 4-(o-Tolyl)pyrrolo[2,3-c]carbazole-3(6H)-carboxylate (6bF) and Its [3,2-c]-Isomer (7bF)]

To a solution of 1b (25.7 mg, 0.100 mmol) and 9F (83.6 mg, 0.500 mmol) in TCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF_{6}] (5.05 mg, 5.00 \mu mol) at 110 °C. The mixture was stirred at 110 °C in pre-heated bath for 0.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 10/1) to give a mixture of 6bF and 7bF (22.8 mg, 58%; 6bF:7bF = 95:5). These isomers were separated by column chromatography on amine silica gel (toluene) to give, in the order of elution, 6bF and 7bF.
Compound 6bF: pale yellow solid; mp 154–156 ºC; IR (neat) 3734, 1730; ¹H NMR (500 MHz, CDCl₃) δ: 1.32 (s, 9H), 2.17 (s, 3H), 7.20 (d, J = 3.4 Hz, 1H), 7.21 (s, 1H), 7.23-7.26 (m, 3H), 7.30 (dd, J = 7.5, 7.5 Hz, 1H), 7.34-7.37 (m, 1H), 7.42 (dd, J = 7.5, 7.5 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 3.4 Hz, 1H), 8.13 (br s, 1H), 8.25 (d, J = 7.4 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 20.2, 27.6 (3C), 83.1, 104.9, 110.5, 110.7, 113.8, 119.5, 121.2, 123.3, 124.9, 125.2, 125.6, 126.7, 128.0, 128.1, 128.4, 129.0, 129.9, 135.5, 135.9, 139.5, 142.1, 149.1; HRMS (FAB) calcd for C₂₆H₂₅N₂O₂ [M+H]+: 397.1911, found 397.1921.

Compound 7bF: white solid; mp 96–98 ºC; IR (neat) 3707, 1732; ¹H NMR (500 MHz, CDCl₃) δ: 1.73 (s, 9H), 2.17 (s, 3H), 6.36 (d, J = 4.0 Hz, 1H), 7.23 (s, 1H), 7.28 (m, 2H), 7.32-7.34 (m, 3H), 7.40 (ddd, J = 7.4, 7.4, 1.1 Hz, 1H), 7.44 (d, J = 7.4 Hz, 1H), 7.49 (d, J = 4.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 8.26 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 20.3, 28.2 (3C), 83.5, 108.1, 108.3, 110.0, 110.2, 119.0, 121.1, 124.1, 124.6, 125.1, 125.5, 126.0, 127.5, 129.4, 130.1, 130.3, 133.1, 136.4, 139.4, 140.2, 150.1; HRMS (FAB) calcd for C₂₆H₂₅N₂O₂ [M+H]+: 397.1911, found 397.1912.

**tert-Butyl 4-(m-Tolyl)pyrrolo[2,3-c]carbazole-3(6H)-carboxylate (6cF) and Its [3,2-c]-Isomer (7cF) (Table 5)**

![Chemical Structure](image)

To a solution of 1c (25.7 mg, 0.100 mmol) and 9F (83.6 mg, 0.500 mmol) in TCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF₆] (5.05 mg, 5.00 µmol) at 110 ºC. The mixture was stirred at 110 ºC in pre-heated bath for 0.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 10/1) to give a mixture of 6cF and 7cF (21.7 mg, 55%; 6cF:7cF = 95:5). These isomers were separated by column chromatography on amine silica gel (hexane/toluene = 1/5) to give, in the order of elution, 6cF and 7cF.

Compound 6cF: pale yellow solid; mp 185–186 ºC; IR (neat) 3413, 1732; ¹H NMR (500 MHz, CDCl₃) δ: 1.30 (s, 9H), 2.37 (s, 3H), 7.13 (d, J = 7.4 Hz, 1H), 7.20 (d, J = 3.4 Hz, 1H), 7.26-7.32 (m, 3H), 8.13 (br s, 1H), 8.25 (d, J = 8.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 21.5, 27.5 (3C), 83.5, 105.4, 110.1, 110.7, 113.7, 119.5, 121.2, 123.2, 124.5, 124.9, 125.8, 127.4, 127.5, 128.1, 128.6, 128.9, 129.1, 136.4, 137.9, 139.5, 142.6, 149.7; HRMS (FAB) calcd for C₂₆H₂₅N₂O₂ [M+H]+: 397.1911, found 397.1920.

Compound 7cF: pale yellow viscous oil; IR (neat) 3394, 1743; ¹H NMR (500 MHz, CDCl₃) δ: 1.72 (s, 9H), 2.46 (s, 3H), 6.84 (d, J = 4.0 Hz, 1H), 7.23 (d, J = 7.4 Hz, 1H), 7.25-7.29 (m, 1H), 7.37 (s, 1H), 7.38-7.47 (m, 5H), 7.55 (d, J = 3.4 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 8.25 (br s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 21.6, 28.2 (3C), 83.6, 107.5, 108.2, 110.0, 110.3, 119.0, 122.1, 123.2, 124.7, 125.3, 125.9, 126.3, 127.9, 128.4, 129.9, 133.4, 138.1, 139.2, 139.5, 140.7, 150.0; HRMS (FAB) calcd for C₂₆H₂₅N₂O₂ [M+H]+: 397.1911, found 397.1909.
**t**-

Butyl 4-(p-Tolyl)pyrrolo[2,3-c]carbazole-3(6H)-carboxylate (6dF) and Its [3,2-c]-Isomer (7dF) (Table 5)

![Reaction Scheme](image)

To a solution of 1d (24.3 mg, 0.100 mmol) and 9F (83.6 mg, 0.500 mmol) in TCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF6] (5.05 mg, 5.00 µmol) at 110 ºC. The mixture was stirred at 110 ºC in pre-heated bath for 0.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 10/1) to give a mixture of 6dF and 7dF (22.6 mg, 57%; 6dF:7dF = 95:5). These isomers were separated by column chromatography on amine silica gel (toluene) to give, in the order of elution, 6dF and 7dF.

Compound 6dF: pale yellow solid; mp 170–172 ºC; IR (neat) 3402, 1736; 1H NMR (500 MHz, CDCl3) δ: 1.31 (s, 9H), 2.41 (s, 3H), 7.21 (d, J = 3.4 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.29-7.32 (m, 2H), 7.40-7.43 (m, 1H), 7.46-7.49 (m, 3H), 7.72 (d, J = 4.0 Hz, 1H), 8.16 (s, 1H), 8.23 (d, J = 7.4 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ: 21.2, 27.6 (3C), 83.4, 105.4, 109.9, 110.6, 113.7, 119.5, 121.2, 123.3, 124.8, 125.8, 127.3 (2C), 127.7, 128.8, 129.1, 129.2 (2C), 136.2, 136.5, 139.5, 139.8, 149.6; HRMS (FAB) calcd for C26H25N2O2 [M+H]+: 397.1911, found 397.1912.

Compound 7dF: white solid; mp 164–166 ºC; IR (neat) 3415, 1742; 1H NMR (500 MHz, CDCl3) δ: 1.72 (s, 9H), 2.45 (s, 3H), 6.84 (d, J = 3.4 Hz, 1H), 7.27 (ddt, J = 7.4, 7.4, 1.7 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.36 (s, 1H), 7.38-7.43 (m, 2H), 7.55 (t, J = 3.7 Hz, 3H), 7.98 (d, J = 8.0 Hz, 1H), 8.25 (s, 1H); 13C NMR (125 MHz, CDCl3) δ: 21.2, 28.2 (3C), 83.5, 107.4, 108.2, 110.0, 110.2, 119.0, 122.1, 123.2, 124.6, 125.3, 125.9, 129.1 (2C), 129.3 (2C), 129.9, 133.3, 136.9, 137.9, 139.3, 139.5, 150.0; HRMS (FAB) calcd for C26H25N2O2 [M+H]+: 397.1911, found 397.1923.

**t**-

Butyl 4-(4-Chlorophenyl)pyrrolo[2,3-c]carbazole-3(6H)-carboxylate (6eF) and Its [3,2-c]-Isomer (7eF) (Table 5)

![Reaction Scheme](image)

To a solution of 1e (27.8 mg, 0.100 mmol) and 9F (83.6 mg, 0.500 mmol) in TCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF6] (5.05 mg, 5.00 µmol) at 110 ºC. The mixture was stirred at 110 ºC in pre-heated bath for 1.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 10/1) to give a mixture of 6eF and 7eF (27.2 mg, 65%; 6eF:7eF = 95:5). These isomers were separated by column chromatography on amine silica gel (toluene) to give, in the order of elution, 6eF and 7eF.
Compound 6eF: pale yellow solid; mp 185–187 ºC; IR (neat) 3395, 1740; 1H NMR (500 MHz, CDCl3) δ: 1.37 (s, 9H), 7.21 (d, J = 3.4 Hz, 1H), 7.26 (s, 1H), 7.32 (dd, J = 7.3, 1.0 Hz, 1H), 7.39 (dd, J = 6.3, 1.7 Hz, 2H), 7.43 (ddd, J = 6.5, 6.5, 1.0 Hz, 1H), 7.48 (m, 3H), 7.72 (d, J = 4.0 Hz, 1H), 8.18 (s, 1H), 8.24 (d, J = 7.4 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ: 27.7 (3C), 83.6, 105.6, 110.0, 110.8, 114.1, 119.6, 121.3, 123.1, 125.1, 125.9, 127.4, 128.5 (2C), 128.7 (2C), 129.1, 132.3, 136.4, 139.6, 141.3, 149.3; HRMS (FAB) calcd for C25H22ClN2O2 [M+H]+: 417.1364, found 417.1373.

Compound 7eF: white solid; mp 103–105 ºC; IR (neat) 3394, 1747; 1H NMR (500 MHz, CDCl3) δ: 1.72 (s, 9H), 6.77 (d, J = 3.4 Hz, 1H), 7.25-7.31 (m, 1H), 7.31 (s, 1H), 7.41 (d, J = 3.4 Hz, 2H), 7.45-7.47 (m, 2H), 7.55-7.57 (m, 3H), 7.98 (d, J = 8.0 Hz, 1H), 8.25 (s, 1H); 13C NMR (125 MHz, CDCl3) δ: 28.2 (3C), 83.7, 107.4, 107.7, 110.1, 110.6, 119.1, 122.0, 123.0, 124.9, 125.6, 126.0, 128.7 (2C), 123.0, 130.4 (2C), 131.9, 133.1, 139.1, 139.3, 139.5, 150.0; HRMS (FAB) calcd for C25H22ClN2O2 [M+H]+: 417.1364, found 417.1367.

tert-Butyl 4-(4-Nitrophenyl)pyrrolo[2,3-c]carbazole-3(6H)-carboxylate (6fF) and Its [3,2-c]-Isomer (7fF) (Table 5)

To a solution of 1f (28.8 mg, 0.100 mmol) and 9F (83.6 mg, 0.500 mmol) in TCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF6] (5.05 mg, 5.00 μmol) at 110 ºC. The mixture was stirred at 110 ºC in pre-heated bath for 1.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 5/1) to give a mixture of 6fF and 7fF (27.4 mg, 64%; 6fF: 7fF = 91:9). These isomers were separated by column chromatography on amine silica gel (hexane/toluene = 1/5) to give, in the order of elution, 6fF and 7fF.

Compound 6fF: yellow solid; mp 186–188 ºC; IR (neat) 3396, 1738, 1514; 1H NMR (500 MHz, CDCl3) δ: 1.40 (s, 9H), 7.24 (d, J = 3.4 Hz, 1H), 7.31 (s, 1H), 7.34 (dd, J = 7.3, 1.5 Hz, 1H), 7.46-7.51 (m, 2H), 7.66-7.68 (m, 2H), 7.73 (d, J = 3.4 Hz, 1H), 8.26-8.29 (m, 4H); 13C NMR (125 MHz, CDCl3) δ: 27.8 (3C), 83.8, 105.9, 110.2, 110.9, 115.0, 119.9, 121.5, 122.9, 123.6 (2C), 125.6, 126.1, 126.1, 127.1, 128.1 (2C), 129.0, 136.2, 139.8, 146.2, 149.1, 149.8; HRMS (FAB) calcd for C25H22N3O4 [M+H]+: 428.1605, found 428.1614.

Compound 7fF: orange solid; mp 189–191 ºC; IR (neat) 3415, 1744, 1508; 1H NMR (500 MHz, CDCl3) δ: 1.74 (s, 9H), 6.77 (d, J = 4.0 Hz, 1H), 7.29-7.32 (m, 1H), 7.40 (s, 1H), 7.44-7.46 (m, 2H), 7.61 (d, J = 4.0 Hz, 1H), 7.80 (dd, J = 6.6, 2.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 1H), 8.35-8.37 (m, 3H); 13C NMR (125 MHz, CDCl3) δ: 28.1 (3C), 84.0, 107.2, 107.8, 110.2, 111.4, 119.3, 121.8, 122.8, 123.9 (2C), 125.3, 126.1, 126.2, 129.8 (2C), 130.1, 130.4, 139.0, 139.7, 146.8, 147.6, 149.8; HRMS (FAB) calcd for C25H22N3O4 [M+H]+: 428.1605, found 428.1606.
tert-Butyl 4-(4-Methoxyphenyl)pyrrolo[2,3-c]carbazole-3(6H)-carboxylate (6gF) and Its [3,2-c]-Isomer (7gF) (Table 5)

To a solution of 1g (27.3 mg, 0.100 mmol) and 9F (83.6 mg, 0.500 mmol) in TCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF6] (5.05 mg, 5.00 μmol) at 110 ºC. The mixture was stirred at 110 ºC in pre-heated bath for 0.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 5/1) to give a mixture of 6gF and 7gF (27.8 mg, 67%; 6gF:7gF = 95:5). These isomers were separated by column chromatography on amine silica gel (toluene) to give, in the order of elution, 6gF and 7gF.

Compound 6gF: white solid; mp 118–120 ºC; IR (neat) 3397, 1743; 1H NMR (500 MHz, CDCl3) δ: 1.34 (s, 9H), 3.82 (s, 3H), 6.93 (dd, J = 6.6, 2.0 Hz, 2H), 7.20 (d, J = 4.0 Hz, 1H), 7.24 (s, 1H), 7.30 (dd, J = 7.3, 7.3, 1.3 Hz, 1H), 7.39-7.44 (m, 2H), 7.47 (dd, J = 6.3, 2.3 Hz, 2H), 7.71 (d, J = 3.4 Hz, 1H), 8.17 (s, 1H), 8.23 (d, J = 7.4 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ: 27.7 (3C), 55.4, 83.4, 105.5, 109.8, 110.7, 113.5, 114.0 (2C), 119.4, 121.1, 123.2, 124.8, 125.9, 127.7, 128.4 (2C), 128.5, 129.1, 135.3, 136.6, 139.5, 149.6, 158.5; HRMS (FAB) calcd for C26H25N2O3 [M+H]+: 413.1860, found 413.1861.

Compound 7gF: white solid; mp 102–105 ºC; IR (neat) 3398, 1728; 1H NMR (500 MHz, CDCl3) δ: 1.72 (s, 9H), 3.89 (s, 3H), 6.83 (d, J = 3.4 Hz, 1H), 7.04 (dd, J = 6.3, 2.3 Hz, 2H), 7.26-7.29 (m, 1H), 7.35 (s, 1H), 7.40 (dd, J = 7.4, 7.4, 1.1 Hz, 1H), 7.44 (d, J = 7.4 Hz, 1H), 7.55 (d, J = 4.0 Hz, 1H), 7.58 (dd, J = 6.6, 2.0 Hz, 2H), 7.97 (d, J = 7.4 Hz, 1H), 8.26 (s, 1H); 13C NMR (125 MHz, CDCl3) δ: 28.2 (3C), 55.4, 83.6, 107.3, 108.1, 110.0, 110.1, 114.0 (2C), 118.9, 122.1, 123.2, 124.6, 125.2, 125.8, 129.9, 130.2 (2C), 133.0, 133.3, 139.3, 139.5, 150.0, 158.9; HRMS (FAB) calcd for C26H25N2O3 [M+H]+: 413.1860, found 413.1860.

tert-Butyl 9-Cyano-4-phenylpyrrolo[2,3-c]carbazole-3(6H)-carboxylate (6hF) and Its [3,2-c]-Isomer (7hF) (Table 5)

To a solution of 1h (26.8 mg, 0.100 mmol) and 9F (83.6 mg, 0.500 mmol) in TCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF6] (5.05 mg, 5.00 μmol) at 110 ºC. The mixture was stirred at 110 ºC in pre-heated bath for 1 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 3/1) to give an inseparable mixture of 6hF and 7hF (24.9 mg, 61%; 6hF:7hF = 81:19): brown solid; IR (neat) 3332, 2218, 1730;
1H NMR (500 MHz, CDCl₃; mixture of isomers) δ: 1.33 (s, 9H), 6.84 (d, $J = 4.0$ Hz, 0.2H), 7.15 (d, $J = 4.0$ Hz, 0.8H), 7.27 (s, 0.8H), 7.32-7.36 (m, 1.2H), 7.39-7.53 (m, 4.2H), 7.59-7.62 (m, 1H), 7.65 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.76 (d, $J = 3.4$ Hz, 0.8H), 8.32 (s, 0.2H), 8.51 (d, $J = 1.1$ Hz, 0.8H), 8.57 (s, 0.8H), 8.69 (s, 0.2H); 13C NMR (125 MHz, CDCl₃; mixture of isomers) δ: 27.6, 28.4, 84.5, 105.0, 107.7, 108.2, 110.7, 111.3, 120.7, 121.0, 125.8, 126.1, 127.0, 127.4, 127.5, 127.6, 128.7, 129.2, 129.7, 131.5, 135.0, 139.5, 140.2, 141.2, 150.1; HRMS (ESI) calcd for C₂₆H₂₂N₃O₂ [M+H]+: 408.1712, found 408.1709.

tert-Butyl 9-Methoxy-4-phenylpyrrolo[2,3-c]carbazole-3(6H)-carboxylate (6iF) and Its [3,2-c]-Isomer (7iF) (Table 5)

To a solution of 1i (27.3 mg, 0.100 mmol) and 9F (83.6 mg, 0.500 mmol) in TCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF₆] (5.05 mg, 5.00 μmol) at 110 ºC. The mixture was stirred at 110 ºC in pre-heated bath for 0.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 5/1) to give a mixture of 6iF and 7iF (21.5 mg, 52%; 6iF:7iF = 91:9). These isomers were separated by column chromatography on amine silica gel (toluene/Et₂O = 6/1) to give, in the order of elution, 6iF and 7iF.

Compound 6iF: light brown solid; mp 189–190 ºC; IR (neat) 3413, 1747; 1H NMR (500 MHz, CDCl₃) δ: 1.30 (s, 9H), 3.98 (s, 3H), 7.07 (dd, $J = 8.9, 2.6$ Hz, 1H), 7.18 (d, $J = 4.0$ Hz, 1H), 7.28 (s, 1H), 7.32 (dd, $J = 7.4, 7.4$ Hz, 1H), 7.36 (d, $J = 9.2$ Hz, 1H), 7.42 (dd, $J = 7.7, 7.7$ Hz, 2H), 7.57 (d, $J = 7.4$ Hz, 2H), 7.70 (d, $J = 2.3$ Hz, 1H), 7.72 (d, $J = 4.0$ Hz, 1H), 8.03 (s, 1H); 13C NMR (125 MHz, CDCl₃) δ: 27.6 (3C), 56.2, 83.5, 104.4, 105.3, 110.3, 111.3, 113.8, 113.9, 123.7, 125.8, 126.6, 127.3, 127.4 (2C), 128.5 (2C), 128.8, 129.0, 134.6, 137.3, 142.7, 149.6, 153.9; HRMS (FAB) calcd for C₂₆H₂₅N₂O₃ [M+H]+: 413.1860, found 413.1869.

Compound 7iF: white solid; mp 145–146 ºC; IR (neat) 3589, 1734; 1H NMR (500 MHz, CDCl₃) δ: 1.74 (s, 9H), 3.95 (s, 3H), 6.83 (d, $J = 4.0$ Hz, 1H), 7.08 (dd, $J = 8.6, 2.9$ Hz, 1H), 7.36 (d, $J = 6.6$ Hz, 1H), 7.40 (s, 1H), 7.41-7.43 (m, 1H), 7.49-7.52 (m, 2H), 7.55-7.56 (m, 2H), 7.64-7.67 (m, 2H), 8.19 (s, 1H); 13C NMR (125 MHz, CDCl₃) δ: 28.2 (3C), 55.9, 83.4, 107.8, 108.3, 108.9, 110.5, 110.6, 114.5, 122.6, 123.0, 125.2, 127.1, 128.5 (2C), 129.2 (2C), 129.9, 133.2, 134.6, 140.1, 140.8, 150.1, 153.3; HRMS (FAB) calcd for C₂₆H₂₅N₂O₃ [M+H]+: 413.1860, found 413.1869.

tert-Butyl 6-Phenylindolo[2,3-c]carbazole-5(8H)-carboxylate (11A) (Table 6)

To a solution of 1a (27.3 mg, 0.100 mmol) and 10A (83.6 mg, 0.500 mmol) in TCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF₆] (5.05 mg, 5.00 μmol) at 110 ºC. The mixture was stirred at 110 ºC in pre-heated bath for 0.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 5/1) to give a mixture of 11A.

Compound 11A: light brown solid; mp 189–190 ºC; IR (neat) 3413, 1747; 1H NMR (500 MHz, CDCl₃) δ: 1.33 (s, 9H), 6.84 (d, $J = 4.0$ Hz, 0.2H), 7.15 (d, $J = 4.0$ Hz, 0.8H), 7.27 (s, 0.8H), 7.32-7.36 (m, 1.2H), 7.39-7.53 (m, 4.2H), 7.59-7.62 (m, 1H), 7.65 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.76 (d, $J = 3.4$ Hz, 0.8H), 8.32 (s, 0.2H), 8.51 (d, $J = 1.1$ Hz, 0.8H), 8.57 (s, 0.8H), 8.69 (s, 0.2H); 13C NMR (125 MHz, CDCl₃; mixture of isomers) δ: 27.6, 28.4, 84.5, 105.0, 107.7, 108.2, 110.7, 111.3, 120.7, 121.0, 125.8, 126.1, 127.0, 127.4, 127.5, 127.6, 128.7, 129.2, 129.7, 131.5, 135.0, 139.5, 140.2, 141.2, 150.1; HRMS (ESI) calcd for C₂₆H₂₂N₃O₂ [M+H]+: 408.1712, found 408.1709.
To a solution of 1a (24.3 mg, 0.100 mmol) and 10A (109 mg, 0.500 mmol) in TCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF6] (5.05 mg, 5.00 μmol) at 110 °C. The mixture was stirred at 110 °C in pre-heated bath for 3 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/toluene = 1/1) to give 11A (15.1 mg, 35%): white powder; mp 194–195 °C; IR (neat) 3412, 1750; 1H NMR (500 MHz, CDCl3) δ: 1.23 (s, 9H), 7.33 (dd, J = 7.4, 7.4 Hz, 1H), 7.36-7.39 (m, 1H), 7.44-7.46 (m, 5H), 7.51-7.57 (m, 2H), 7.67-7.68 (m, 2H), 8.25 (dd, J = 7.2, 2.0 Hz, 1H), 8.35 (s, 1H), 8.78 (d, J = 8.0 Hz, 1H), 8.82-8.83 (m, 1H); 13C NMR (125 MHz, CDCl3) δ: 27.5 (3C), 83.6, 110.9, 112.1, 114.6, 115.6, 119.4, 122.4, 122.6, 122.7, 122.9, 123.4, 125.4, 126.2, 126.5, 126.9, 127.2 (2C), 129.1 (2C), 129.4, 131.6, 137.4, 140.0, 140.5, 142.2, 151.1; HRMS (ESI) calcd for C29H25N2O2 [M+H]+: 433.1916, found 433.1912.

2,2-Dimethyl-1-[6-phenylindolo[2,3-c]carbazol-5(8H)-yl]propan-1-one (11B) (Table 6)

To a solution of 1a (24.3 mg, 0.100 mmol) and 10B (101 mg, 0.500 mmol) in TCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF6] (5.05 mg, 5.00 μmol) at 110 °C. The mixture was stirred at 110 °C in pre-heated bath for 6.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/toluene = 1/1) to give 11B (4.90 mg, 12%): yellow solid; mp 227–230 °C; IR (neat) 3412, 1692; 1H NMR (500 MHz, CDCl3) δ: 0.63 (s, 9H), 7.40-7.43 (m, 2H), 7.49-7.51 (m, 6H), 7.58 (dd, J = 8.0, 8.0 Hz, 2H), 7.74-7.75 (m, 2H), 8.38 (s, 1H), 8.86 (d, J = 8.6 Hz, 1H), 8.89-8.90 (m, 1H); 13C NMR (125 MHz, CDCl3) δ: 27.7 (3C), 46.4, 110.9, 111.4, 111.6, 116.1, 119.52, 119.55, 121.1, 122.9, 123.1, 123.6 (2C), 125.5, 126.1, 127.4, 128.0, 129.1 (2C), 130.5 (2C), 132.7, 136.4, 138.8, 139.5, 140.0, 186.7; HRMS (ESI) calcd for C29H25N2O [M+H]+: 417.1967, found 417.1977

Ethyl 6-Phenylindolo[2,3-c]carbazole-5(8H)-carboxylate (11C) (Table 6)

To a solution of 1a (24.3 mg, 0.100 mmol) and 10C (94.6 mg, 0.500 mmol) in TCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF6] (5.05 mg, 5.00 μmol) at 110 °C. The mixture was stirred at 110 °C in pre-heated bath for 6.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/toluene = 1/2) to give 11C (17.9 mg, 44%): white powder; mp 226–228 °C; IR (neat) 3410, 1725; 1H NMR (500 MHz, CDCl3) δ: 0.94 (t, J = 7.2 Hz, 3H), 3.59 (q, J = 7.3 Hz, 2H), 7.32-7.35 (m, 1H), 7.36-7.40 (m, 1H), 7.45-7.47 (m, 5H), 7.52-7.59 (m, 2H), 7.63 (dd, J = 8.0, 1.1 Hz, 2H), 8.32-8.34 (m, 2H), 8.78 (d, J = 7.4 Hz, 1H), 8.82-8.83 (m, 1H); 13C NMR (125 MHz,
CDCl₃ δ: 13.9, 62.9, 110.9, 112.0, 114.6, 115.7, 119.5, 122.3, 122.6, 122.9 (2C), 123.5, 125.6, 125.9, 126.7, 126.9 (3C), 129.0 (3C), 131.1, 137.4, 140.05, 140.11, 142.3, 152.5; HRMS (ESI) calcd for C_{27}H_{21}N_{2}O_{2} [M+H]^+: 405.1603, found 405.1594.

**Ethyl 2-Bromo-6-phenylindolo[2,3-c]carbazole-5(8H)-carboxylate (11D) (Table 6)**

![Chemical Structure](image1)

To a solution of 1a (24.3 mg, 0.100 mmol) and 10D (134 mg, 0.500 mmol) in DCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF₆] (5.05 mg, 5.00 μmol) at 80 °C. The mixture was stirred at 80 °C in pre-heated bath for 4.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 5/1) to give 11D (24.0 mg, 50%): white powder; mp 246–248 °C; IR (neat) 3420, 1729; ¹H NMR (500 MHz, CDCl₃) δ: 0.95 (t, J = 7.2 Hz, 3H), 3.59 (q, J = 7.3 Hz, 2H), 7.37 (dd, J = 7.4, 7.4 Hz, 1H), 7.42-7.45 (m, 1H), 7.49-7.54 (m, 4H), 7.55 (s, 1H), 7.64-7.66 (m, 3H), 8.19 (d, J = 8.6 Hz, 1H), 8.39 (s, 1H), 8.66 (d, J = 8.0 Hz, 1H), 8.90 (d, J = 1.7 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 13.9, 63.1, 111.0, 112.8, 115.7, 115.8, 116.0, 119.9, 121.2, 122.4, 123.3, 125.4, 125.9, 126.9 (2C), 127.1, 127.7, 129.0, 129.1 (2C), 129.4, 131.6, 137.3, 138.8, 140.0, 142.0, 152.1; HRMS (ESI) calcd for C_{27}H_{20}BrN_{2}O_{2} [M+H]^+: 483.0708, found 483.0695.

**Ethyl 2-Chloro-6-phenylindolo[2,3-c]carbazole-5(8H)-carboxylate (11E) (Table 6)**

![Chemical Structure](image2)

To a solution of 1a (24.3 mg, 0.100 mmol) and 10E (112 mg, 0.500 mmol) in DCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF₆] (5.05 mg, 5.00 μmol) at 80 °C. The mixture was stirred at 80 °C in pre-heated bath for 4.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 5/1) to give 11E (23.0 mg, 52%): white powder; mp 241–243 °C; IR (neat) 3420, 1728; ¹H NMR (500 MHz, CDCl₃) δ: 0.95 (t, J = 7.2 Hz, 3H), 3.59 (q, J = 7.1 Hz, 2H), 7.36-7.39 (m, 1H), 7.42-7.45 (m, 1H), 7.51-7.53 (m, 5H), 7.56 (s, 1H), 7.65 (dd, J = 6.6, 1.4 Hz, 2H), 8.24 (d, J = 9.2 Hz, 1H), 8.40 (s, 1H), 8.69 (d, J = 8.0 Hz, 1H), 8.76 (d, J = 2.3 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 13.9, 63.1, 111.0, 112.8, 115.6, 115.7, 119.9, 121.7, 122.4, 122.5, 123.4, 125.9, 126.9 (2C), 127.1, 128.3, 129.0, 129.1 (3C), 131.7, 137.3, 138.5, 140.1, 142.1, 152.2; HRMS (ESI) calcd for C_{27}H_{20}ClN_{2}O_{2} [M+H]^+: 439.1213, found 439.1195.
**Diethyl 6-Phenylindolo[2,3,c]carbazole-2,5(8H)-dicarboxylate (11F) (Table 6)**

![Chemical structure of 11F]

To a solution of 1a (24.3 mg, 0.100 mmol) and 10F (131 mg, 0.500 mmol) in DCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF₆] (5.05 mg, 5.00 μmol) at 80 °C. The mixture was stirred at 80 °C in pre-heated bath for 7.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 5/1) to give 11F (31.8 mg, <67%): white powder; mp 292–294 °C; IR (neat) 3342, 1698; ¹H NMR (500 MHz, CDCl₃) δ: 0.97 (t, J = 7.2 Hz, 3H), 1.54 (t, J = 7.2 Hz, 3H), 3.60 (q, J = 7.3 Hz, 2H), 4.53 (q, J = 7.1 Hz, 2H), 7.39 (dd, J = 7.4, 7.4 Hz, 1H), 7.46 (dd, J = 7.4, 7.4 Hz, 1H), 7.51-7.60 (m, 4H), 7.61 (s, 1H), 7.68 (d, J = 7.4 Hz, 2H), 8.27 (dd, J = 8.6, 1.1 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 9.61 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 13.9, 14.5, 61.1, 63.3, 111.0, 112.6, 114.0, 115.9, 120.0, 121.9, 122.5, 123.6, 125.0 (2C), 125.7, 126.0, 127.0 (3C), 127.2, 128.0, 128.9, 129.1 (2C), 131.6, 137.5, 140.2, 142.0, 152.1, 167.0; HRMS (ESI) calcd for C₃₀H₂₅N₂O₄ [M+H]⁺: 477.1814, found 477.1824.

**tert-Butyl 3-[2-(Phenylethynyl)-1H-indol-3-yl]-1H-pyrrole-1-carboxylate (4aF) and Its 2-Indolyl Isomer (5aF) (Scheme 5)**

![Chemical structure of 4aF and 5aF]

To a solution of 1a (24.3 mg, 0.100 mmol) and 9F (83.6 mg, 0.500 mmol) in DCE (0.5 mL) was added [BrettPhosAu(MeCN)SbF₆] (5.05 mg, 5.00 μmol) at 60 °C. The mixture was stirred at 60 °C in pre-heated bath for 1.5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 10/1) to give a mixture of 4aF and 5aF (9.40 mg, 25%; 4aF:5aF = 69:31). These isomers were separated by column chromatography on silica gel (hexane/toluene = 1/2) to give, in the order of elution, 4aF and 5aF.

**Compound 4aF:** brown viscous oil; IR (neat) 3404, 2978, 1738; ¹H NMR (500 MHz, CDCl₃) δ: 1.63 (s, 9H), 6.96 (dd, J = 3.2, 1.4 Hz, 1H), 7.20 (dd, J = 4.0, 4.0, 1.5 Hz, 1H), 7.29 (dd, J = 3.5, 3.5, 1.0 Hz, 1H), 7.34-7.40 (m, 5H), 7.55-7.57 (m, 2H), 7.80 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 8.21 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 28.0 (3C), 82.4, 83.6, 95.7, 110.9, 112.1, 115.4, 116.2, 116.9, 120.2, 120.3, 120.4, 120.6, 122.8, 123.9, 125.9, 128.5, 128.5 (2C), 131.3 (2C), 136.2, 148.9; HRMS (FAB) calcd for C₂₅H₂₂N₂O₂ [M⁺]: 382.1681, found 382.1677.

**Compound 5aF:** brown viscous oil; IR (neat) 3370, 2979, 1734; ¹H NMR (500 MHz, CDCl₃) δ: 1.19 (s, 9H), 6.34 (dd, J = 3.2, 3.2 Hz, 1H), 6.44 (dd, J = 3.4, 1.7 Hz, 1H), 7.13 (dd, J = 7.4, 7.4 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.31-7.34 (m, 4H), 7.44-7.46 (m, 2H), 7.48-7.50 (m, 2H), 8.22 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 27.3 (3C), 102.8, 103.8, 111.6, 114.9, 117.8, 118.0, 118.2, 118.8, 119.8, 120.2, 120.3, 120.4, 120.6, 122.8, 123.9, 125.9, 128.5, 128.5 (2C), 131.3 (2C), 136.2, 148.9; HRMS (FAB) calcd for C₂₅H₂₂N₂O₂ [M⁺]: 382.1681, found 382.1677.

S27
81.7, 83.2, 94.8, 110.7, 110.8, 115.5, 117.3, 120.4, 120.5, 122.6, 123.7, 126.2, 127.8, 128.3 (2C), 128.4, 131.4 (2C), 135.4, 149.5; HRMS (FAB) calcd for C_{25}H_{22}N_{2}O_{2} [M⁺]: 382.1681, found 382.1678.

3,6-Dimethyl-4-phenyl-3,6-dihydropyrrolo[2,3-c]carbazole (6aF-Me₂) and Its [3,2-c]-Isomer (7aF-Me₂)

6aF 7aF

1) HCl/dioxane 80 °C
2) NaH, MeI, DMF 0 °C to rt

To a solution of 6aF and 7aF (50.0 mg, 0.130 mmol; 6aF: 7aF = 16:84) in 4 M HCl/dioxane (5.7 mL) was stirred at 80 °C for 16 min. The solvent was removed under vacuum. The crude was then poured into aqueous NaHCO₃, extracted with EtOAc, dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by amine silica gel (hexane/CHCl₃ = 2/3) to give an isomeric mixture of 6aA and 7aA (22.0 mg, 60%). To a solution of this mixture (obtained by repeated reactions; 75.1 mg, 0.266 mmol) in DMF (0.912 mL) was added NaH (60% dispersion in paraffin liquid; 84.8 mg, 2.12 mmol) at 0 °C under Ar. The reaction mixture was stirred at room temperature for 30 min. MeI (0.132 ml, 2.12 mmol) was added to the reaction mixture. After being stirred for 14 h, the mixture was quenched with H₂O, extracted with CHCl₃, washed with brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 30/1) to give 6aF-Me₂ and 7aF-Me₂ (52.8 mg, 64%; 6aF-Me₂: 7aF-Me₂ = 12:88). These isomers were separated by careful column chromatography on silica gel (hexane/EtOAc = 30/1) to give, in the order of elution, 6aF-Me₂ and 7aF-Me₂.

Compound 6aF-Me₂: white powder; mp 140–142 °C; ¹H NMR (500 MHz, CDCl₃) δ: 3.39 (s, 3H), 3.91 (s, 3H), 7.09-7.15 (m, 3H), 7.26-7.31 (m, 1H), 7.44-7.46 (m, 5H), 7.56 (d, J = 6.9 Hz, 2H), 8.30 (d, J = 7.4 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 29.4, 37.2, 99.1, 106.3, 112.9, 118.4, 121.2, 122.9, 123.0, 123.9, 126.0, 127.2, 127.3, 127.6 (2C), 129.3, 130.3 (2C), 131.1, 135.5, 140.4, 141.2; HRMS (ESI) calcd for C_{22}H_{19}N_{2} [M+H⁺]: 311.1548, found 311.1556.

Compound 7aF-Me₂: white powder; mp 111–113 °C; ¹H NMR (500 MHz, CDCl₃) δ: 3.96 (s, 3H), 4.55 (s, 3H), 6.74 (d, J = 2.9 Hz, 1H), 7.03 (d, J = 3.4 Hz, 1H), 7.23 (ddd, J = 7.6, 1.3 Hz, 1H), 7.27 (s, 1H), 7.40-7.53 (m, 5H), 7.77-7.78 (m, 2H), 8.56 (d, J = 8.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 29.5, 39.0, 102.0, 102.7, 106.7, 108.6, 118.6, 120.7, 121.8, 122.3, 123.7, 126.9, 127.0, 127.5, 128.4 (2C), 129.1 (2C), 132.3, 133.8, 139.2, 141.7; HRMS (ESI) calcd for C_{22}H_{19}N_{2} [M+H⁺]: 311.1548, found 311.1545.

5,8-Dimethyl-6-phenyl-5,8-dihydroindololo[2,3-c]carbazole (11A-Me₂)

11A NaOMe MeOH/THF 60 °C

To a solution of 11A (121 mg, 0.280 mmol) in THF (2.8 mL) was added NaOMe (5 M in MeOH) (1.68 mL, 8.39 mmol) at 60 °C. The mixture was stirred at 60 °C for 60 h. The mixture was quenched with sat. NaHCO₃ and the whole was extracted with Et₂O, dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 5/1) to give S21 (52.2 mg, 56%) as a solid. To a solution of this solid (52.2 mg, 0.157 mmol) in DMF (0.502 mL) was added NaH (60% dispersion in paraffin liquid; 50.2 mg, 1.26 mmol)
at 0 °C under Ar. After being stirred at room temperature for 10 min, MeI (0.0391 ml, 0.628 mmol) was added to the mixture. After being stirred for 40 h, the mixture was quenched with H2O, extracted with CHCl3, washed with brine, dried over Na2SO4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 30/1) to give 11A-Me2 (36.1 mg, 64%): yellow viscous oil; 1H NMR (500 MHz, CD2Cl2) δ: 3.46 (s, 3H), 3.97 (s, 3H), 7.40-7.44 (m, 3H), 7.47-7.57 (m, 7H), 7.62 (dd, J = 8.3, 1.4 Hz, 2H), 8.93 (d, J = 8.0 Hz, 1H), 8.96 (d, J = 8.0 Hz, 1H); 13C NMR (125 MHz, CD2Cl2) δ: 29.4, 33.7, 108.5, 109.0, 110.1, 115.5, 117.9, 118.4, 118.6, 122.3, 122.5, 123.4, 123.5, 124.8, 125.0, 125.1, 127.3, 127.9 (2C), 130.1 (2C), 134.1, 135.9, 141.1, 141.4, 142.3; HRMS (ESI) calcd for C26H21N2 [M+H]+: 361.1705, found 361.1690.

4. Preparation of the Catalyst

\[ \text{[BrettPhosAu\textsubscript{MeCN}]SbF\textsubscript{6}} \]

This catalyst was prepared according to the literature procedure for the synthesis of [LAu-MeCN]SbF\textsubscript{6} (L = \{2-[2,4,6-(i-Pr)\textsubscript{3}C\textsubscript{6}H\textsubscript{2}]C\textsubscript{6}H\textsubscript{4}\}P(t-Bu)\textsubscript{2}). AgSbF\textsubscript{6} (0.6 M solution in CH\textsubscript{2}Cl\textsubscript{2}; 1.98 mL, 1.19 mmol) was added to a stirred solution of chloro[2-(dicyclohexylphosphino)-3,6-dimethoxy-2',4',6'-triisopropyl-1,1'-biphenyl]gold(I) (Brett-PhosAuCl) (897 mg, 1.17 mmol) in MeCN (7.5 mL) and CH\textsubscript{2}Cl\textsubscript{2} (7.5 mL), and the mixture was stirred at room temperature in the dark (using aluminium foil) for 8 h. The mixture was filtered through a pad of Celite and the solvent was removed in vacuo to afford a white powder (1.29 g, quant): 1H NMR (500 MHz, CDCl\textsubscript{3}) δ: 0.90 (d, J = 6.3 Hz, 6H), 1.07-1.09 (m, 2H), 1.17-1.24 (m, 4H), 1.27 (d, J = 6.9 Hz, 6H), 1.33 (d, J = 6.9 Hz, 6H), 1.37-1.40 (m, 4H), 1.49-1.50 (m, 2H), 1.67-1.98 (m, 8H), 2.25-2.30 (m, 2H), 2.37 (s, 3H), 2.55-2.59 (m, 2H), 2.92-2.98 (m, 1H), 3.56 (s, 3H), 3.94 (s, 3H), 6.95-7.12 (m, 4H); 13C NMR (125 MHz, CDCl\textsubscript{3}) δ: 2.52, 24.1 (d, J = 19.2 Hz, 4C), 24.8 (2C), 25.6 (2C), 26.5 (d, J = 16.8 Hz, 2C), 27.0 (d, J = 13.2 Hz, 2C), 30.0 (2C), 30.6 (2C), 33.7, 34.6, 34.7, 38.1 (d, J = 36.0 Hz, 2C), 54.9, 56.0, 110.8 (d, J = 7.2 Hz), 114.2, 114.7, 115.1, 118.9, 121.6 (2C), 131.5 (d, J = 8.4 Hz), 136.7 (d, J = 13.2 Hz), 147.3, 149.2, 153.1 (d, J = 10.8 Hz), 154.8; HRMS (FAB) calcd for C\textsubscript{35}H\textsubscript{53}AuO\textsubscript{2}P+ [M–MeCN–SbF\textsubscript{6}]\textsuperscript{+}: 733.3443, found 733.3444.

5. References

S33
DFILE A-138 H-2.als
COMNT single_pulse
DATIM 2016-02-12 16:31:11
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 kHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PMI 6.82 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 46

\[ \text{N}_3 \]

1d
DFILE A137.als
COMNT single_pulse
DATIM 2018-04-25 19:54:36
OBNUC 1H
EXMOD single_pulse_dec
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7567.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 7.15 ussec
IRNUC 1H
CTEMP 21.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 52

NH₂
S13
NO₂

DFILE A137.als
COMNT single_pulse
DATIM 2018-04-26 08:01:47
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 16384
FREQU 25163.56 Hz
SCANS 2200
ACQTM 0.6511 sec
PD 1.0000 sec
PW1 3.67 ussec
IRNUC 1H
CTEMP 22.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 70

NH₂
S13
NO₂
**dfile A143.als**

**Comment:** single_pulse

**Date:** 2018-04-26 16:32:13

**OBNUC:** 13C

**EXMOD:** single_pulse_dec

**OBFRQ:** 125.77 MHz

**OBSET:** 7.29 Hz

**OBFIN:** 4.21 Hz

**POINT:** 13107

**FREQU:** 7621.95 Hz

**SCANS:** 8

**ACQTM:** 1.7197 sec

**PD:** 5.0000 sec

**PW1:** 3.15 usec

**IRNUC:** 1H

**CTEMP:** 21.7 c

**SLVNT:** CDCl3

**EXREF:** 0.00 ppm

**BF:** 0.12 Hz

**RGAIN:** 70

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**dfile A143.als**

**Comment:** proton.jxp

**Date:** 2018-04-26 16:32:13

**OBNUC:** 1H

**EXMOD:** proton.jxp

**OBFRQ:** 399.78 MHz

**OBSET:** 4.19 KHz

**OBFIN:** 7.29 Hz

**POINT:** 13107

**FREQU:** 7621.95 Hz

**SCANS:** 8

**ACQTM:** 1.7197 sec

**PD:** 5.0000 sec

**PW1:** 3.15 usec

**IRNUC:** 1H

**CTEMP:** 20.1 c

**SLVNT:** CDCl3

**EXREF:** 0.00 ppm

**BF:** 0.12 Hz

**RGAIN:** 44
**DFILE** 7aB H-1.als
**COMNT** single_pulse
**DATIM** 2017-02-22 17:49:26
**OBNUC** 1H
**EXMOD** single_pulse.ex2
**OBFRQ** 500.16 MHz
**OBSET** 2.41 KHz
**OBFIN** 6.01 Hz
**POINT** 13107
**FREQU** 7507.39 Hz
**SCANS** 8
**ACQTM** 1.7459 sec
**PD** 5.0000 sec
**PMI** 7.15 usec
**CTEMP** 19.8 c
**SLVNT** CDCL3
**EXREF** 0.00 ppm
**BF** 0.12 Hz
**RGAIN** 44

**DFILE** 7aB H-1.als
**COMNT** single_pulse
**DATIM** 2017-02-24 05:49:26
**OBNUC** 13C
**EXMOD** single_pulse_dec
**OBFRQ** 125.77 MHz
**OBSET** 7.87 KHz
**OBFIN** 4.21 Hz
**POINT** 13107
**FREQU** 7507.39 Hz
**SCANS** 8
**ACQTM** 1.7459 sec
**PD** 5.0000 sec
**PMI** 7.15 usec
**CTEMP** 20.2 c
**SLVNT** CDCL3
**EXREF** 77.00 ppm
**BF** 1.30 Hz
**RGAIN** 60

**DFILE** 7aB C-1.als
**COMNT** single_pulse
**DATIM** 2017-02-24 05:49:26
**OBNUC** 13C
**EXMOD** single_pulse_dec
**OBFRQ** 125.77 MHz
**OBSET** 7.87 KHz
**OBFIN** 4.21 Hz
**POINT** 13107
**FREQU** 7507.39 Hz
**SCANS** 8
**ACQTM** 1.7459 sec
**PD** 5.0000 sec
**PMI** 7.15 usec
**CTEMP** 20.2 c
**SLVNT** CDCL3
**EXREF** 77.00 ppm
**BF** 1.30 Hz
**RGAIN** 60

**DFILE** 7aB C-1.als
**COMNT** single_pulse
**DATIM** 2017-02-24 05:49:26
**OBNUC** 13C
**EXMOD** single_pulse_dec
**OBFRQ** 125.77 MHz
**OBSET** 7.87 KHz
**OBFIN** 4.21 Hz
**POINT** 13107
**FREQU** 7507.39 Hz
**SCANS** 8
**ACQTM** 1.7459 sec
**PD** 5.0000 sec
**PMI** 7.15 usec
**CTEMP** 20.2 c
**SLVNT** CDCL3
**EXREF** 77.00 ppm
**BF** 1.30 Hz
**RGAIN** 60
DFILE C-42 u H.als
COMNT single_pulse
DATIM 2017-01-27 21:23:46
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 7.15 usec
IRNUC 1H
CTEMP 19.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
Rgain 44

\[ \text{MeO} \]
\[ \text{NH} \]
\[ \text{6iF} \]

DFILE C-42 u C.als
COMNT single_pulse_dec
DATIM 2017-01-28 08:11:48
OBNUC 13C
EXMOD single_pulse_dec
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OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1024
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.67 usec
IRNUC 1H
CTEMP 19.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
Rgain 60

\[ \text{MeO} \]
\[ \text{NH} \]
\[ \text{6iF} \]
FILE C-24 H-1.als
COMNT single_pulse
DATIM 2018-03-06 18:32:48
OBNUC 1H
EDMOD single_pulse
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQ 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 7.15 usec
IRNUC 1H
CTEMP 19.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 48

FILE C-24 C-1.als
COMNT single_pulse_dec
DATIM 2018-03-08 04:06:05
OBNUC 13C
EDMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 13107
FREQ 25252.14 Hz
SCANS 2048
ACQTM 0.5190 sec
PD 1.0000 sec
PW1 3.67 usec
IRNUC 1H
CTEMP 19.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60

Cl
EnO

Cl

11E

Cl
EnO

11E
**S93**

**DFILE** B58 up C.als
**COMNT** single_pulse_dec
**DATIM** 2018-04-29 16:54:31
**OBNUC** 1H
**EXMOD** single_pulse_dec
**OBFRQ** 125.77 MHz
**OBSET** 7.87 KHz
**OBFIN** 4.21 Hz
**POINT** 13107
**FREQU** 25252.14 Hz
**SCANS** 4218
**ACQTM** 0.5190 sec
**PD** 1.0000 sec
**PW1** 3.67 usec
**IRNUC** 1H
**CTEMP** 21.5 c
**SLVNT** CDCL3
**EXREF** 77.00 ppm
**BF** 0.12 Hz
**RGAIN** 60

![NMe](image1)

**DFILE** B-58 u H.als
**COMNT** single_pulse
**DATIM** 2016-04-27 14:43:56
**OBNUC** 1H
**EXMOD** single_pulse, ex2
**OBFRQ** 500.16 MHz
**OBSET** 2.41 KHz
**OBFIN** 6.01 Hz
**POINT** 13107
**FREQU** 7507.39 Hz
**SCANS** 8
**ACQTM** 1.7459 sec
**PD** 5.0000 sec
**PW1** 6.82 usec
**IRNUC** 1H
**CTEMP** 21.7 c
**SLVNT** CDCL3
**EXREF** 0.00 ppm
**BF** 0.12 Hz
**RGAIN** 56

![NMe](image2)