SUPPORTING INFORMATION

for the
communication
entitled

Synthesis of Amino-Substituted α- and δ-Carbolines via Metal-Free [2 + 2 + 2] Cycloaddition of Functionalized Alkyne-Nitriles with Ynamides

authored by

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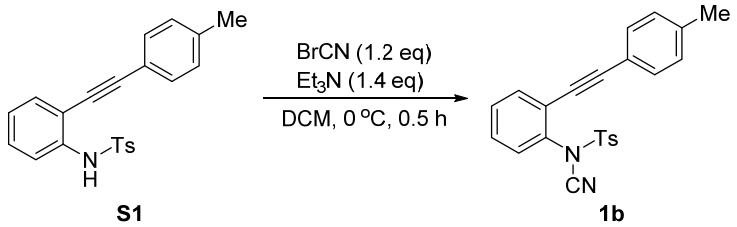
GENERAL EXPERIMENTAL INFORMATION

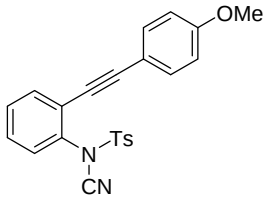
All reactions were performed in oven-dried glassware under nitrogen atmosphere. Solvents were distilled prior to use. Chromatographic separations were performed using 200~300 mesh silica gel. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker's Ascend^{TM} 400 NMR spectrometer using $CDCl_3$ as solvent with TMS or residual solvent as standard unless otherwise noted. ^{13}C NMR (100 MHz) spectra were reported in ppm with the internal chloroform signal at 77.2 ppm as a standard. Infrared spectra was obtained on a PerkinElmer FT/IR spectrophotometer and relative intensities are expressed qualitatively as s (strong), m (medium), and w (weak). TLC analysis was performed using 254 nm polyester-backed plates and visualized using UV and $KMnO_4$ stain. High-resolution mass spectra (HRMS) were performed on a Bruker MicrOTOF-Q II mass spectrometer. All spectral data obtained for new compounds are reported here.

General Procedure for Synthesis of Alkyne-Cyanamides 1b-1h and 1j.[1]



To a solution of **S1** (722.9 mg, 2.0 mmol) in DCM (10.0 mL) was added BrCN (254.2 mg, 2.4 mmol) at 0 ^{o}C, then Et_3N (0.4 mL, 2.8 mmol) was added dropwise. After stirring at 0 ^{o}C for 0.5 h, the resulting mixture was diluted by ether and filtered through a celite pad. The filtrate was washed with saturated K_2CO_3 solution and dried over anhydrous Na_2SO_4. The solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [gradient eluent: 6:1 petroleum ether/EtOAc] to afford the desired product **1b** (765.2 mg, 1.98 mmol) in 99% yield.

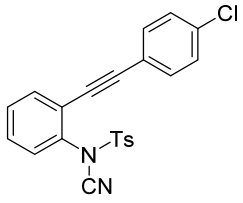
1b: R_f = 0.35 [4:1 petroleum ether/EtOAc]; white solid; mp = 152–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.38 (s, 3H), 7.06-7.08 (m, 2H), 7.12-7.14 (m, 2H), 7.28-7.31 (m, 2H), 7.39-7.51 (m, 4H), 7.62-7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 82.7, 97.2, 107.7, 119.3, 123.0, 128.6, 129.1, 129.3, 130.30, 130.33, 130.5, 131.8, 133.3, 133.4, 134.1, 139.4, 146.5, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2227w, 1511w, 1381s, 1191s, 1172s, 1086m; HRMS (ESI): m/z calcd for $C_{23}H_{19}N_2O_2S$ $[M+H]^+$: 387.1162; found 387.1166.



1c

Alkyne-cyanamide **1c** (796.9 mg, 1.98 mmol) was prepared from the corresponding **S1** (754.9 mg, 2.0 mmol) and BrCN (254.2 mg, 2.4 mmol) in 99% yield after stirring at 0 ^{o}C for 0.5 h.

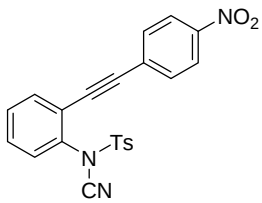
1c: R_f = 0.22 [4:1 petroleum ether/EtOAc]; white solid; mp = 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 3.85 (s, 3H), 6.83-6.87 (m, 2H), 7.08 (d, 2H, J = 8.3 Hz), 7.33-7.49 (m, 6H), 7.62-7.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 55.5, 82.2, 97.2, 107.7, 114.0, 114.5, 123.1, 128.5, 129.1, 130.2, 130.3, 130.5, 133.1, 133.4, 134.0, 146.5, 160.3, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2229w, 1596w, 1509m, 1377s, 1245s, 1171s; HRMS (ESI): m/z calcd for $C_{23}H_{18}N_2O_3SNa$ $[M+Na]^+$: 425.0930; found 425.0927.



1d

Alkyne-cyanamide **1d** (651.0 mg, 1.60 mmol) was prepared from the corresponding **S1** (763.7 mg, 2.0 mmol) and BrCN (254.2 mg, 2.4 mmol) in 80% yield after stirring at 0 ^{o}C for 0.5 h.

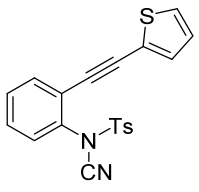
1d: R_f = 0.35 [4:1 petroleum ether/EtOAc]; white solid; mp = 143–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 3H), 7.09-7.11 (m, 2H), 7.29-7.37 (m, 4H), 7.43-7.51 (m, 4H), 7.62-7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 84.2, 95.6, 107.7, 120.8, 122.4, 128.6, 128.7, 129.8, 130.3, 130.4, 130.6, 133.1, 133.3, 133.4, 134.3, 135.3, 146.6; IR (neat) (cm^{-1}) 2227w, 1493w, 1382s, 1170m, 1088m, 1013w; HRMS (ESI): m/z calcd for $C_{22}H_{16}ClN_2O_2S$ $[M+H]^+$: 407.0616; found 407.0616.



1e

Alkyne-cyanamide **1e** (651.2 mg, 1.56 mmol) was prepared from the corresponding **S1** (784.9 mg, 2.0 mmol) and BrCN (254.2 mg, 2.4 mmol) in 78% yield after stirring at 0 ^{o}C for 0.5 h.

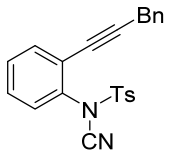
1e: R_f = 0.23 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 145–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 7.15 (d, 2H, J = 8.1 Hz), 7.45-7.53 (m, 3H), 7.55-7.67 (m, 5H), 8.20-8.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 88.1, 94.4, 107.7, 121.8, 123.6, 128.6, 129.1, 130.2, 130.4, 130.7, 130.8, 132.6, 133.4, 133.7, 134.7, 146.7, 147.6; IR (neat) (cm^{-1}) 1513s, 1385s, 1338s, 1192s, 1173s, 1013w; HRMS (ESI): m/z calcd for $C_{22}H_{15}N_3O_4SNa$ $[M+Na]^+$: 440.0675; found 440.0681.



1f

Alkyne-cyanamide **1f** (749.4 mg, 1.98 mmol) was prepared from the corresponding **S1** (706.9 mg, 2.0 mmol) and BrCN (254.2 mg, 2.4 mmol) in 99% yield after stirring at 0 ^{o}C for 0.5 h.

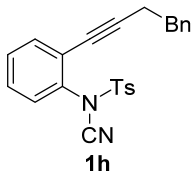
1f: R_f = 0.29 [4:1 petroleum ether/EtOAc]; white solid; mp = 118–119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 6.99-7.02 (m, 1H), 7.14 (d, 2H, J = 8.1 Hz), 7.23-7.25 (m, 1H), 7.32-7.34 (m, 1H), 7.42-7.51 (m, 4H), 7.63-7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 86.9, 90.4, 107.5, 122.1, 122.4, 127.3, 128.5, 129.6, 130.31, 130.33, 130.6, 133.0, 133.2, 133.5, 133.9, 146.7, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2224w, 1384s, 1189m, 1176s, 1090m, 1033w; HRMS (ESI): m/z calcd for $C_{20}H_{14}N_2O_2S_2Na$ $[M+Na]^+$: 401.0389; found 401.0386.



1g

Alkyne-cyanamide **1g** (765.2 mg, 1.98 mmol) was prepared from the corresponding **S1** (722.9 mg, 2.0 mmol) and BrCN (254.2 mg, 2.4 mmol) in 99% yield after stirring at 0 ^{o}C for 0.5 h.

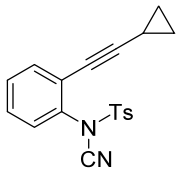
1g: R_f = 0.32 [4:1 petroleum ether/EtOAc]; colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.62 (s, 2H), 7.19 (d, 2H, J = 8.1 Hz), 7.27-7.46 (m, 9H), 7.62-7.64 (m, 2H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 21.6, 25.9, 77.0, 96.5, 108.0, 123.8, 127.5, 128.9, 129.25, 129.30, 130.3, 130.7, 131.2, 131.6, 134.1, 134.5, 135.0, 136.7, 147.9; IR (neat) (cm^{-1}) 2231m, 1486m, 1385s, 1190s, 1172s, 1037w; HRMS (ESI): m/z calcd for $C_{23}H_{18}N_2O_2SNa$ $[M+Na]^+$: 409.0981; found 409.0979.



1h

Alkyne-cyanamide **1h** (761.0 mg, 1.90 mmol) was prepared from the corresponding **S1** (751.0 mg, 2.0 mmol) and BrCN (254.2 mg, 2.4 mmol) in 95% yield after stirring at 0 ^{o}C for 0.5 h.

1h: R_f = 0.48 [4:1 petroleum ether/EtOAc]; white solid; mp = 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44-2.48 (m, 5H), 2.80 (t, 2H, J = 7.7 Hz), 7.21-7.25 (m, 3H), 7.30-7.37 (m, 8H), 7.67-7.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 22.0, 34.8, 75.4, 98.0, 107.5, 123.6, 126.6, 128.5, 128.6, 128.8, 128.9, 129.7, 130.2, 130.5, 133.7, 133.8, 134.3, 140.6, 146.5; IR (neat) (cm^{-1}) 2229w, 1593w, 1484w, 1382s, 1275w, 1171s; HRMS (ESI): m/z calcd for $C_{24}H_{20}N_2O_2SNa$ $[M+Na]^+$: 423.1138; found 423.1136.

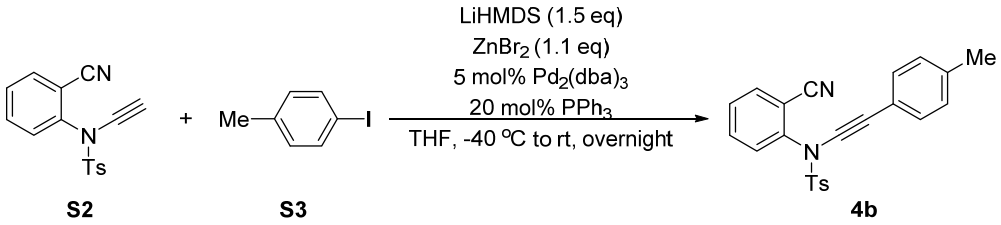


1j

Alkyne-cyanamide **1j** (666.1 mg, 1.98 mmol) was prepared from the corresponding **S1** (622.8 mg, 2.0 mmol) and BrCN (254.2 mg, 2.4 mmol) in 99% yield after stirring at 0 ^{o}C for 0.5 h.

1j: R_f = 0.48 [4:1 petroleum ether/EtOAc]; white solid; mp = 65–66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.72-0.84 (m, 4H), 1.18-1.25 (m, 1H), 2.49 (s, 3H), 7.30-7.37 (m, 6H), 7.67-7.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.4, 9.0, 22.0, 69.9, 102.2, 107.4, 123.7, 128.6, 128.7, 129.6, 130.3, 130.4, 133.5, 133.7, 134.3, 146.5; IR (neat) (cm^{-1}) 2227w, 1488w, 1386s, 1173m, 1082m, 1032w; HRMS (ESI): m/z calcd for $C_{19}H_{16}N_2O_2SNa$ $[M+Na]^+$: 359.0825; found 359.0823.

General Procedure for Synthesis of Ynamide-Nitriles 4b, 4e-4g and 4m.[1]

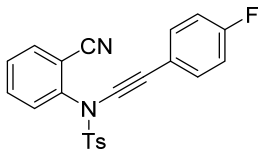


S2 **S3** **4b**

To a solution of **S2** (592.7 mg, 2.0 mmol) in THF (8.0 mL) was added LiHMDS (3.0 mL, 3.0 mmol, 1.0 M in THF) at -40 ^{o}C. After stirring at -40 ^{o}C for 40.0 min, $ZnBr_2$ (495.5 mg, 2.2 mmol) in THF (2.0 mL) was added and stirred for another 20.0 min. Then the mixture of $Pd_2(dba)_3$ (91.6 mg, 0.1 mmol), PPh_3 (104.9 mg, 0.4 mmol) and 1-iodo-4-methylbenzene **S3** (0.4 mL, 3.0 mmol) in THF (1.0 mL) was added dropwise. The reaction mixture was warmed up to room temperature slowly and stirred overnight. When the reaction was judged to be completed by TLC, the mixture was added brine to quench the reaction. The resulting mixture was filtered through a celite pad, extracted with EtOAc and dried over anhydrous Na_2SO_4. The organic layer was filtered and the solvent was

concentrated under the reduced pressure, then the residue was purified by flash silica gel column chromatrography [gradient eluent: 4:1~2:1 petroleum ether/EtOAc] to afford the desired product **4b** (649.3 mg, 1.68 mmol) in 84% yield.

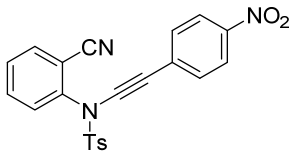
4b: R_f = 0.39 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 127–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.47 (s, 3H), 7.10 (d, 2H, J = 7.8 Hz), 7.30-7.32 (m, 2H), 7.36 (d, 2H, J = 8.1 Hz), 7.46-7.50 (m, 2H), 7.61-7.65 (m, 1H), 7.68 (dd, 1H, J = 8.1, 1.7 Hz), 7.74-7.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 22.0, 71.5, 81.0, 112.9, 115.4, 119.0, 128.9, 129.2, 129.4, 129.8, 130.0, 132.2, 132.9, 133.7, 134.3, 138.9, 140.8, 145.9; IR (neat) (cm^{-1}) 2237w, 1596w, 1488w, 1375s, 1176s, 1109w; HRMS (ESI): m/z calcd for $C_{23}H_{18}N_2O_2SNa$ $[M+Na]^+$: 409.0981; found 409.0984.



4e

Ynamide-nitrile **4e** (718.4 mg, 1.84 mmol) was prepared from **S2** (592.7 mg, 2.0 mmol) and 1-fluoro-4-iodobenzene (0.4 mL, 3.0 mmol) in 92% yield after stirring at rt overnight.

4e: R_f = 0.38 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 135–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 6.96-7.02 (m, 2H), 7.36-7.43 (m, 4H), 7.47-7.51 (m, 2H), 7.63-7.70 (m, 2H), 7.73-7.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 70.5, 81.3, 112.7, 115.3, 115.8 (d, J = 21.9 Hz), 118.2, 128.8, 129.5, 129.9, 130.1, 132.9, 133.8, 134.3, 134.4, 140.6, 146.1, 162.9 (d, J = 248.4 Hz); IR (neat) (cm^{-1}) 2237w, 1506w, 1489w, 1374m, 1230w, 1178s; HRMS (ESI): m/z calcd for $C_{22}H_{15}FN_2O_2SNa$ $[M+Na]^+$: 413.0730; found 413.0741.

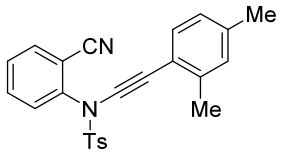


4f

Ynamide-nitrile **4f** (743.0 mg, 1.78 mmol) was prepared from **S2** (592.7 mg, 2.0 mmol) and 1-iodo-4-nitrobenzene (747.0 mg, 3.0 mmol) in 89% yield after stirring at rt overnight.

4f: R_f = 0.27 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 124–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 7.39 (d, 2H, J = 8.1 Hz), 7.49-7.57 (m, 4H), 7.67-7.76 (m, 4H), 8.14-8.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 70.7, 86.8, 112.6, 115.0, 123.8, 128.7, 129.6, 129.95, 130.04, 130.3, 131.9, 132.7, 134.0, 134.5, 139.8, 146.5, 146.9; IR (neat) (cm^{-1}) 2233s, 1594s, 1485m,

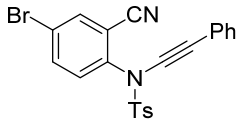
1339s, 1220w, 1172s; HRMS (ESI): m/z calcd for $C_{22}H_{15}N_3O_4SNa$ $[M+Na]^+$: 440.0675; found 440.0671.



4g

Ynamide-nitrile **4g** (680.9 mg, 1.70 mmol) was prepared from **S2** (592.7 mg, 2.0 mmol) and 1-iodo-2,4-dimethylbenzene (0.4 mL, 3.0 mmol) in 85% yield after stirring at rt overnight.

4g: R_f = 0.41 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 126–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.33 (s, 3H), 2.47 (s, 3H), 6.91 (d, 1H, J = 7.8 Hz), 6.99 (s, 1H), 7.25 (d, 1H, J = 7.3 Hz), 7.35 (d, 2H, J = 8.1 Hz), 7.46-7.51 (m, 2H), 7.61-7.65 (m, 1H), 7.70 (dd, 1H, J = 8.1, 1.6 Hz), 7.76-7.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.6, 22.0, 70.3, 84.5, 113.1, 115.5, 118.9, 126.5, 128.9, 129.5, 129.7, 130.0, 130.4, 132.5, 133.0, 133.7, 134.3, 138.8, 140.7, 140.9, 145.9; IR (neat) (cm^{-1}) 2234w, 1596w, 1483w, 1370s, 1294w, 1175s; HRMS (ESI): m/z calcd for $C_{24}H_{20}N_2O_2SNa$ $[M+Na]^+$: 423.1138; found 423.1139.

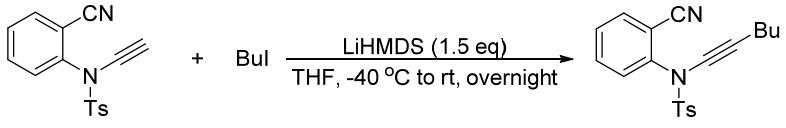


4m

Ynamide-nitrile **4m** (126.4 mg, 0.28 mmol) was prepared from the corresponding **S2** (750.5 mg, 2.0 mmol) and iodobenzene (0.3 mL, 3.0 mmol) in 14% yield after stirring at rt overnight.

4m: R_f = 0.53 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 104–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 7.26-7.42 (m, 8H), 7.73-7.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 71.8, 81.2, 114.0, 114.4, 121.9, 123.1, 128.5, 128.77, 128.80, 130.2, 131.1, 132.2, 132.5, 136.8, 137.0, 139.8, 146.3; IR (neat) (cm^{-1}) 2237w, 1594w, 1480m, 1374s, 1169s, 1023w; HRMS (ESI): m/z calcd for $C_{22}H_{15}BrN_2O_2SNa$ $[M+Na]^+$: 472.9930; found 472.9951.

General Procedure for Synthesis of Ynamide-Nitrile 4j.[1]



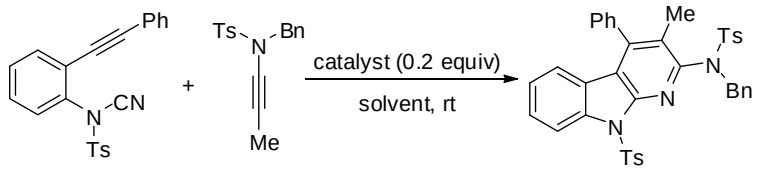
S2 **S4** **4j**

To a solution of **S2** (592.7 mg, 2.0 mmol) in THF (10.0 mL) was added LiHMDS (3.0 mL, 3.0 mmol, 1.0 *M* in THF) at -40 °C. After stirring for 1.0 h, 1-iodobutane **S4** (0.9 mL, 8.0 mmol) in THF (2.0 mL) was added. Then the reaction mixture was warmed up to room temperature slowly and stirred overnight. When the reaction was judged to be completed by TLC, the mixture was added

brine to quench the reaction. The resulting mixture was extracted with EtOAc and dried over anhydrous Na_2SO_4. The organic layer was filtered and the solvent was concentrated under the reduced pressure, then the residue was purified by flash silica gel column chromatrography [gradient eluent: 5:1 petroleum ether/EtOAc] to afford the desired product **4j** (282.0 mg, 0.80 mmol) in 40% yield.

4j: R_f = 0.48 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 86–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 7.2 Hz), 1.30-1.39 (m, 2H), 1.43-1.50 (m, 2H), 2.27 (t, 2H, J = 6.9 Hz), 2.47 (s, 3H), 7.34-7.40 (m, 3H), 7.46 (t, 1H, J = 7.6 Hz), 7.58-7.62 (m, 1H), 7.66-7.73 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 18.2, 21.9, 22.0, 30.8, 71.6, 72.8, 113.0, 115.5, 128.8, 129.2, 129.5, 129.9, 133.0, 133.6, 134.2, 141.2, 145.6; IR (neat) (cm^{-1}) 2231w, 1595w, 1485w, 1370s, 1176s, 1089m; HRMS (ESI): m/z calcd for $C_{20}H_{20}N_2O_2SNa$ $[M+Na]^+$: 375.1138; found 375.1137.

General Procedure for Condition Optimization of the Cycloaddition.

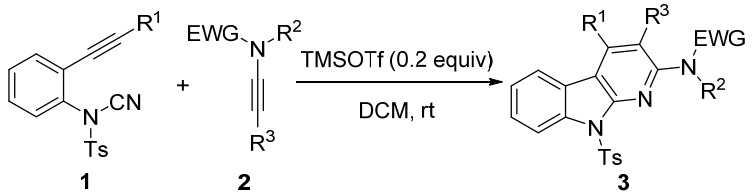


entry[a]	catalyst	solvent	time (h)	yield (%)[b]
1	BF_3•Et_2O	DCM	2.0	86
2	$AlCl_3$	DCM	1.0	88
3	ZnI_2	DCM	24.0	0
4	Tf_2O	DCM	1.0	61
5	TfOMe	DCM	24.0	77
6	TMSOTf	DCM	0.2	99
7	TfOH	DCM	0.2	81
8	TFA	DCM	24.0	0
9	CSA	DCM	24.0	0
10	TMSOTf	DCE	0.2	99
11	TMSOTf	toluene	0.2	38
12	TMSOTf	THF	24.0	0
13	TMSOTf	Et_2O	24.0	12
14[c]	TMSOTf	DCM	0.2	99

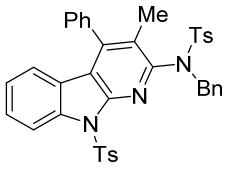
[a]Unless otherwise specified, reactions were carried out using **1a** (0.20 mmol) and **2a** (0.22 mmol) with catalyst (0.04 mmol) in solvent (1.0 mL) at rt. [b]Isolated yields. [c]**1a** ((1.00 mmol) and **2a** (1.10 mmol) were used.

Entry 14: To an oven-dried sealed tube was added alkyne-cyanamide **1a**[1] (372.4 mg, 1.0 mmol), ynamide **2a**[2] (329.3 mg, 1.1 mmol), DCM (5.0 mL, alkyne-cyanamide *concn* = 0.20 *M*) and TMSOTf (36.1 μL, 0.2 mmol) at rt. When the reaction was judged to be completed by TLC after stirring at rt for 10 min, the mixture was purified by flash silica gel column chromatrography [gradient eluent: 10:1~4:1 petroleum ether/EtOAc] to afford 2-amino-α-carboline **3a** (665.1 mg, 1.0 mmol) in 99% yield.

General Procedure for Synthesis of 2-Amino-α-Carbolines.

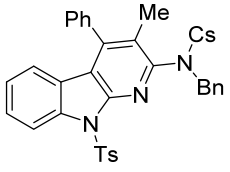


To an oven-dried sealed tube was added alkyne-cyanamide **1a**[1] (74.5 mg, 0.20 mmol), ynamide **2a**[2] (65.9 mg, 0.22 mmol), DCM (1.0 mL, alkyne-cyanamide *concn* = 0.20 *M*) and TMSOTf (7.2 μL, 0.04 mmol) at rt. When the reaction was judged to be completed by TLC after stirring at rt for 0.5 h, the mixture was purified by flash silica gel column chromatrography [gradient eluent: 10:1~4:1 petroleum ether/EtOAc] to afford 2-amino-α-carboline **3a** (133.0 mg, 0.20 mmol) in 99% yield.



3a

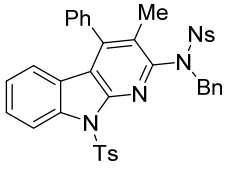
3a: R_f = 0.62 [4:1 petroleum ether/EtOAc]; white solid; mp = 210–211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.93 (s, 3H), 2.29 (s, 3H), 2.54 (s, 3H), 4.17 (d, 1H, J = 12.8 Hz), 4.75 (d, 1H, J = 12.9 Hz), 6.63-6.66 (m, 3H), 6.86 (d, 1H, J = 7.0 Hz), 6.98-7.12 (m, 4H), 7.17 (d, 2H, J = 8.1 Hz), 7.32 (d, 1H, J = 7.4 Hz), 7.41-7.55 (m, 6H), 7.75-7.78 (m, 2H), 8.10-8.13 (m, 2H), 8.47 (d, 1H, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 21.7, 21.9, 54.2, 114.6, 116.8, 122.45, 122.48, 123.4, 127.8, 127.9, 128.1, 128.3, 128.6, 129.05, 129.13, 129.2, 129.4, 129.6, 129.8, 130.1, 135.2, 136.2, 136.8, 137.0, 138.9, 143.9, 145.2, 146.8, 147.3, 148.5; IR (neat) (cm^{-1}) 2923w, 1568w, 1454w, 1358m, 1277w, 1163s; HRMS (ESI): m/z calcd for $C_{39}H_{34}N_3O_4S_2$ $[M+H]^+$: 672.1985; found 672.1981.



3b

2-Amino-α-carboline **3b** (132.9 mg, 0.19 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2b**[3] (70.4 mg, 0.22 mmol) in 96% yield after stirring at rt for 10 min.

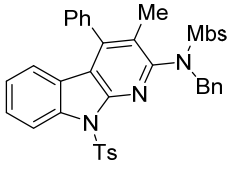
3b: R_f = 0.50 [4:1 petroleum ether/EtOAc]; white solid; mp = 268–269 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.89 (s, 3H), 2.31 (s, 3H), 4.17 (d, 1H, J = 12.8 Hz), 4.75 (d, 1H, J = 12.8 Hz), 6.63-6.67 (m, 3H), 6.86 (d, 1H, J = 7.2 Hz), 6.99-7.07 (m, 3H), 7.10-7.14 (m, 1H), 7.19 (d, 2H, J = 8.1 Hz), 7.31 (d, 1H, J = 7.4 Hz), 7.42-7.55 (m, 4H), 7.69-7.73 (m, 2H), 7.75-7.79 (m, 2H), 8.19-8.22 (m, 2H), 8.47 (dt, 1H, J = 8.5, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.5, 21.8, 54.3, 114.7, 117.1, 122.4, 122.6, 123.6, 128.0, 128.1, 128.2, 128.5, 128.7, 129.2, 129.3, 129.5, 129.7, 129.8, 129.9, 130.6, 134.8, 136.8, 136.9, 137.8, 139.0, 139.7, 145.4, 147.1, 147.4, 148.1; IR (neat) (cm^{-1}) 2921w, 1347s, 1278w, 1165s, 1149w, 1090m; HRMS (ESI): m/z calcd for $C_{38}H_{31}ClN_3O_4S_2$ $[M+H]^+$: 692.1439; found 692.1439.



3c

2-Amino-α-carboline **3c** (139.2 mg, 0.20 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2c**[3] (72.7 mg, 0.22 mmol) in 99% yield after stirring at rt for 10 min.

3c: R_f = 0.32 [4:1 petroleum ether/EtOAc]; white solid; mp = 231–232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (s, 3H), 2.29 (s, 3H), 4.26 (d, 1H, J = 12.8 Hz), 4.85 (d, 1H, J = 12.8 Hz), 6.64-6.69 (m, 3H), 6.88 (d, 1H, J = 7.4 Hz), 7.01-7.08 (m, 3H), 7.13-7.20 (m, 3H), 7.32 (d, 1H, J = 6.6 Hz), 7.44-7.57 (m, 4H), 7.73 (d, 2H, J = 8.2 Hz), 8.45-8.47 (m, 3H), 8.52-8.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 21.7, 54.6, 114.7, 117.4, 122.3, 122.6, 123.7, 124.7, 127.7, 128.2, 128.3, 128.7, 128.8, 129.26, 129.34, 129.5, 129.8, 129.9, 130.3, 134.3, 136.6, 136.7, 139.0, 145.0, 145.5, 147.3, 147.4, 147.6, 150.5; IR (neat) (cm^{-1}) 1533w, 1350s, 1212w, 1167s, 1092s, 1002w; HRMS (ESI): m/z calcd for $C_{38}H_{31}N_4O_6S_2$ $[M+H]^+$: 703.1680; found 703.1677.

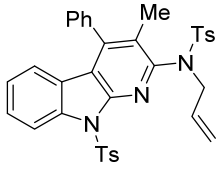


3d

2-Amino-α-carboline **3d** (114.2 mg, 0.17 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2d**[3] (69.4 mg, 0.22 mmol) in 83% yield after stirring at rt for 10.0 min.

3d: R_f = 0.32 [4:1 petroleum ether/EtOAc]; white solid; mp = 225–226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.93 (s, 3H), 2.30 (s, 3H), 3.96 (s, 3H), 4.17 (d, 1H, J = 13.0 Hz), 4.74 (d, 1H, J = 12.9 Hz), 6.62-6.66 (m, 3H), 6.86 (d, 1H, J = 7.3 Hz), 6.98-7.12 (m, 4H), 7.18-7.23 (m, 4H), 7.32 (d, 1H, J = 7.5 Hz), 7.42-7.55 (m, 4H), 7.77-7.79 (m, 2H), 8.13-8.17 (m, 2H), 8.47 (d, 1H, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 21.7, 54.1, 56.0, 114.7, 116.8, 122.5, 123.5, 127.80, 127.84, 128.2,

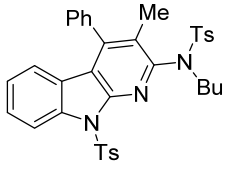
128.27, 128.29, 128.4, 128.6, 129.1, 129.2, 129.4, 129.7, 129.9, 130.8, 131.2, 135.3, 136.8, 137.1, 138.9, 145.3, 146.9, 147.3, 148.7, 163.4; IR (neat) (cm^{-1}) 1596w, 1368m, 1342m, 1262m, 1172s, 1093s; HRMS (ESI): m/z calcd for $C_{39}H_{34}N_3O_5S_2$ $[M+H]^+$: 688.1934; found 688.1931.



3e

2-Amino-α-carboline **3e** (118.1 mg, 0.19 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2e**[3] (54.9 mg, 0.22 mmol) in 95% yield after stirring at rt for 10 min.

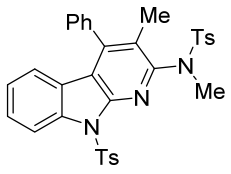
3e: R_f = 0.46 [4:1 petroleum ether/EtOAc]; white solid; mp = 194–195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.32 (s, 3H), 2.51 (s, 3H), 3.76 (s, 1H), 4.18 (s, 1H), 4.43 (dq, 1H, J = 17.0, 1.4 Hz), 4.74 (dq, 1H, J = 10.1, 1.2 Hz), 5.53-5.64 (m, 1H), 6.69 (d, 1H, J = 7.4 Hz), 7.02-7.07 (m, 1H), 7.12 (d, 2H, J = 8.0 Hz), 7.35-7.62 (m, 8H), 7.69-7.72 (m, 2H), 8.04-8.07 (m, 2H), 8.45 (dt, 1H, J = 8.5, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0, 21.7, 21.9, 53.1, 114.7, 116.9, 119.1, 122.5, 123.5, 128.2, 128.3, 128.7, 129.1, 129.4, 129.5, 130.0, 132.3, 136.1, 136.7, 137.2, 138.9, 143.9, 145.0, 147.0, 147.4, 148.8, three carbons missing due to overlap; IR (neat) (cm^{-1}) 2925w, 1448w, 1344m, 1162s, 1090m, 1056w; HRMS (ESI): m/z calcd for $C_{35}H_{32}N_3O_4S_2$ $[M+H]^+$: 622.1829; found 622.1826.



3f

2-Amino-α-carboline **3f** (119.9 mg, 0.19 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2f**[4] (58.4 mg, 0.22 mmol) in 94% yield after stirring at rt for 10 min.

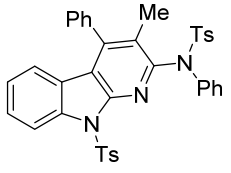
3f: R_f = 0.41 [4:1 petroleum ether/EtOAc]; white solid; mp = 235–236 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (t, 3H, J = 7.3 Hz), 0.89-1.23 (m, 4H), 2.31 (s, 3H), 2.34 (s, 3H), 2.50 (s, 3H), 3.21-3.28 (m, 1H), 3.45-3.52 (m, 1H), 6.70 (d, 1H, J = 7.5 Hz), 7.03-7.07 (m, 1H), 7.10 (d, 2H, J = 8.1 Hz), 7.40-7.61 (m, 8H), 7.72-7.75 (m, 2H), 8.03-8.05 (m, 2H), 8.46 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 16.1, 20.1, 21.7, 21.8, 30.2, 50.2, 114.7, 116.8, 122.5, 123.5, 127.9, 128.1, 128.2, 128.6, 128.7, 129.0, 129.2, 129.5, 129.6, 129.9, 136.2, 136.6, 137.2, 138.8, 143.7, 144.9, 147.0, 147.5, 149.0; IR (neat) (cm^{-1}) 1598w, 1454w, 1363s, 1349s, 1164s, 1090m; HRMS (ESI): m/z calcd for $C_{36}H_{36}N_3O_4S_2$ $[M+H]^+$: 638.2142; found 638.2139.



3g

2-Amino-α-carboline **3g** (103.7 mg, 0.17 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2g**[5] (49.1 mg, 0.22 mmol) in 87% yield after stirring at rt for 10 min.

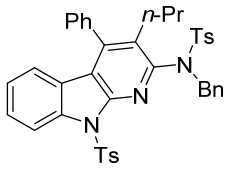
3g: R_f = 0.40 [4:1 petroleum ether/EtOAc]; white solid; mp = 192–193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.33 (s, 3H), 2.50 (s, 3H), 3.03 (s, 3H), 6.68 (d, 1H, J = 8.0 Hz), 7.02-7.06 (m, 1H), 7.10 (d, 2H, J = 8.4 Hz), 7.31-7.59 (m, 8H), 7.74-7.77 (m, 2H), 8.09-8.12 (m, 2H), 8.44-8.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8, 21.76, 21.85, 37.2, 114.7, 117.0, 122.5, 122.6, 123.5, 127.9, 128.1, 128.2, 128.8, 129.1, 129.4, 129.5, 129.9, 135.3, 136.3, 137.1, 138.7, 143.8, 145.1, 147.3, 147.5, 150.5, one carbon missing due to overlap; IR (neat) (cm^{-1}) 1597w, 1448w, 1356s, 1210w, 1168s, 1089w; HRMS (ESI): m/z calcd for $C_{33}H_{30}N_3O_4S_2$ $[M+H]^+$: 596.1672; found 596.1669.



3h

2-Amino-α-carboline **3h** (106.6 mg, 0.16 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2h**[4] (62.8 mg, 0.22 mmol) in 81% yield after stirring at rt for 0.5 h.

3h: R_f = 0.37 [4:1 petroleum ether/EtOAc]; white solid; mp = 199–200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 2.31 (s, 3H), 2.43 (s, 3H), 6.65 (d, 1H, J = 7.9 Hz), 7.01-7.06 (m, 3H), 7.15-7.53 (m, 13H), 7.76 (d, 2H, J = 8.1 Hz), 8.18 (d, 2H, J = 8.0 Hz), 8.48 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 21.77, 21.80, 114.8, 117.5, 122.5, 122.6, 123.6, 126.9, 127.2, 127.8, 128.1, 128.2, 128.3, 128.8, 129.0, 129.35, 129.39, 129.6, 129.7, 136.2, 136.7, 136.9, 138.7, 139.6, 143.7, 144.9, 147.6, 147.8, 149.7; IR (neat) (cm^{-1}) 1596w, 1453w, 1354s, 1175m, 1165s, 1090w; HRMS (ESI): m/z calcd for $C_{38}H_{32}N_3O_4S_2$ $[M+H]^+$: 658.1829; found 658.1825.

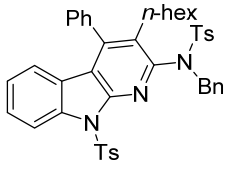


3i

2-Amino-α-carboline **3i** (126.0 mg, 0.18 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2i**[4] (72.0 mg, 0.22 mmol) in 90% yield after stirring at rt for 10 min.

2-Amino-α-carboline **3i** (133.0 mg, 0.19 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2i** (72.0 mg, 0.22 mmol) in 95% yield after stirring at 100 ^{o}C for 1.5 h.

3i: R_f = 0.49 [4:1 petroleum ether/EtOAc]; white solid; mp = 208–209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.21-0.32 (m, 1H), 0.47 (t, 3H, J = 7.2 Hz), 0.93-1.04 (m, 1H), 2.27 (s, 3H), 2.35 (td, 1H, J = 12.1 Hz, 5.0 Hz), 2.49-2.56 (m, 1H), 2.54 (s, 3H), 4.22 (d, 1H, J = 12.9 Hz), 4.70 (d, 1H, J = 12.8 Hz), 6.54 (d, 1H, J = 7.9 Hz), 6.61-6.63 (m, 2H), 6.95-7.05 (m, 4H), 7.08-7.12 (m, 1H), 7.17 (d, 2H, J = 8.2 Hz), 7.35 (d, 1H, J = 7.3 Hz), 7.40-7.54 (m, 6H), 7.76-7.79 (m, 2H), 8.09-8.11 (m, 2H), 8.48 (d, 1H, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 21.7, 21.9, 23.1, 30.7, 54.4, 114.7, 117.2, 122.56, 122.58, 123.4, 127.9, 128.2, 128.26, 128.28, 128.5, 128.6, 128.8, 129.2, 129.3, 129.6, 129.7, 130.1, 134.4, 135.4, 136.1, 136.8, 139.0, 143.9, 145.3, 147.1, 147.2, 148.2; IR (neat) (cm^{-1}) 3392w, 1568w, 1362m, 1348s, 1164s, 1090m; HRMS (ESI): m/z calcd for $C_{41}H_{38}N_3O_4S_2$ $[M+H]^+$: 700.2298; found 700.2294.

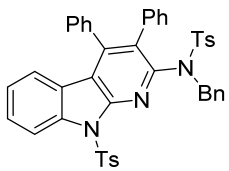


3j

2-Amino-α-carboline **3j** (121.7 mg, 0.16 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2j**[6] (81.3 mg, 0.22 mmol) in 82% yield after stirring at rt for 10 min.

2-Amino-α-carboline **3j** (132.1 mg, 0.18 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2j** (81.3 mg, 0.22 mmol) in 89% yield after stirring at 100 ^{o}C for 4.0 h.

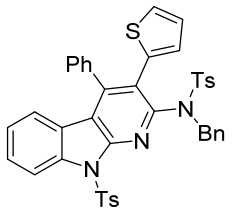
3j: R_f = 0.52 [4:1 petroleum ether/EtOAc]; white solid; mp = 205–206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.71-1.05 (m, 11H), 2.25 (s, 3H), 2.33-2.40 (m, 1H), 2.53 (s, 3H), 2.55-2.58 (m, 1H), 4.23 (d, 1H, J = 12.9 Hz), 4.69 (d, 1H, J = 12.9 Hz), 6.56 (d, 1H, J = 7.9 Hz), 6.62-6.64 (m, 2H), 6.97-7.04 (m, 4H), 7.09-7.17 (m, 3H), 7.35 (d, 1H, J = 7.1 Hz), 7.40-7.53 (m, 6H), 7.77-7.79 (m, 2H), 8.08-8.10 (m, 2H), 8.48 (d, 1H, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.7, 21.9, 22.4, 28.5, 29.4, 29.7, 31.0, 54.3, 114.6, 117.2, 122.6, 123.4, 127.9, 128.21, 128.25, 128.3, 128.5, 128.8, 129.2, 129.3, 129.6, 129.7, 130.0, 134.5, 135.4, 136.0, 136.7, 136.8, 139.0, 143.9, 145.2, 147.1, 147.2, 148.2, one carbon missing due to overlap; IR (neat) (cm^{-1}) 3369w, 1455w, 1345m, 1210w, 1175m, 1158s; HRMS (ESI): m/z calcd for $C_{44}H_{44}N_3O_4S_2$ $[M+H]^+$: 742.2768; found 742.2764.



3k

2-Amino-α-carboline **3k** (142.4 mg, 0.19 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2k**[2] (79.5 mg, 0.22 mmol) in 97% yield after stirring at rt for 10 min.

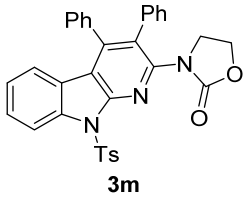
3k: R_f = 0.43 [4:1 petroleum ether/EtOAc]; white solid; mp = 255–256 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.43 (s, 3H), 4.37 (s, 1H), 4.74 (s, 1H), 6.61-6.63 (m, 2H), 6.74 (d, 1H, J = 7.8 Hz), 6.93-7.34 (m, 18H), 7.43-7.47 (m, 1H), 7.66 (d, 2H, J = 8.0 Hz), 8.14 (d, 2H, J = 8.4 Hz), 8.54 (d, 1H, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.80, 21.83, 53.9, 114.6, 116.7, 122.6, 122.7, 123.5, 126.7, 127.0, 127.9, 128.0, 128.2, 128.36, 128.41, 128.44, 129.0, 129.2, 129.7, 130.0, 130.2, 134.2, 134.9, 135.3, 136.2, 136.36, 136.44, 138.9, 143.9, 145.5, 146.9, 147.1, 148.3, one carbon missing due to overlap; IR (neat) (cm^{-1}) 3026w, 1598w, 1443w, 1377m, 1349s, 1161s; HRMS (ESI): m/z calcd for $C_{44}H_{36}N_3O_4S_2$ $[M+H]^+$: 734.2142; found 734.2138.



3l

2-Amino-α-carboline **3l** (137.6 mg, 0.19 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2l**[2] (80.8 mg, 0.22 mmol) in 93% yield after stirring at rt for 10 min.

3l: R_f = 0.36 [4:1 petroleum ether/EtOAc]; white solid; mp = 266–267 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.47 (s, 3H), 4.50 (s, 2H), 6.39 (dd, 1H, J = 3.5, 1.2 Hz), 6.61-6.64 (m, 2H), 6.72-6.78 (m, 2H), 6.98-7.15 (m, 7H), 7.22-7.31 (m, 5H), 7.39 (d, 2H, J = 8.0 Hz), 7.46-7.50 (m, 1H), 7.88-7.90 (m, 2H), 8.01-8.03 (m, 2H), 8.52 (d, 1H, J = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.79, 21.81, 54.0, 114.7, 116.8, 122.3, 122.7, 123.6, 125.9, 126.8, 127.3, 127.8, 128.1, 128.29, 128.35, 128.4, 128.6, 128.8, 129.3, 129.77, 129.78, 129.9, 130.7, 134.8, 135.3, 136.2, 136.4, 136.5, 138.9, 143.8, 145.5, 148.1, 148.4, 148.6; IR (neat) (cm^{-1}) 1597w, 1442w, 1379s, 1350s, 1160s, 1090m; HRMS (ESI): m/z calcd for $C_{42}H_{34}N_3O_4S_3$ $[M+H]^+$: 740.1706; found 740.1709.



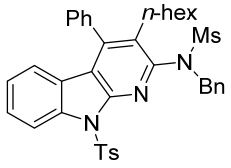
3m

2-Amino-α-carboline **3m** (73.9 mg, 0.13 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2m**[7] (41.2 mg, 0.22 mmol) in 66% yield after stirring at rt for 17.0 h.

2-Amino-α-carboline **3m** (98.5 mg, 0.18 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2m**[11] (41.2 mg, 0.22 mmol) in 88% yield after stirring at 100 ^{o}C for 5.0 h.

3m: R_f = 0.37 [2:1 petroleum ether/EtOAc]; white solid; mp = 281–282 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 3.92 (t, 2H, J = 7.9 Hz), 4.32 (t, 2H, J = 7.8 Hz), 6.75 (d, 1H, J = 7.7 Hz), 7.02-7.11 (m, 5H), 7.15-7.20 (m, 3H), 7.27-7.32 (m, 5H), 7.44-7.48 (m, 1H), 8.17-8.20 (m, 2H), 8.48 (d, 1H, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 46.8, 62.8, 114.5, 116.7, 122.5, 122.6,

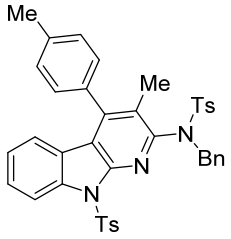
123.6, 127.4, 127.9, 128.2, 128.32, 128.33, 128.6, 129.0, 129.9, 130.0, 130.5, 135.3, 135.7, 136.2, 138.5, 145.6, 146.1, 146.9, 148.7, 156.5; IR (neat) (cm^{-1}) 1757m, 1571w, 1372m, 1190w, 1178s, 1086m; HRMS (ESI): m/z calcd for $C_{33}H_{26}N_3O_4S$ $[M+H]^+$: 560.1639; found 560.1648.



3n

2-Amino-α-carboline **3n** (131.8 mg, 0.20 mmol) was prepared from alkyne-cyanamide **1a** (74.5 mg, 0.20 mmol) and ynamide **2n**[8] (64.6 mg, 0.22 mmol) in 99% yield after stirring at rt for 10 min.

3n: R_f = 0.41 [4:1 petroleum ether/EtOAc]; white solid; mp = 165–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.73 (t, 3H, J = 7.3 Hz), 0.82-1.05 (m, 8H), 2.32 (s, 2H), 2.35 (s, 3H), 3.27 (s, 3H), 4.82 (s, 2H), 6.56 (d, 1H, J = 7.8 Hz), 6.90-6.93 (m, 2H), 7.02-7.06 (m, 1H), 7.10-7.22 (m, 5H), 7.30 (d, 2H, J = 8.1 Hz), 7.44-7.49 (m, 4H), 8.03-8.05 (m, 2H), 8.46 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.8, 22.4, 27.9, 29.4, 29.6, 31.0, 37.1, 55.4, 114.5, 117.6, 122.60, 122.63, 123.7, 127.5, 128.2, 128.3, 128.4, 128.6, 129.0, 129.9, 130.0, 133.9, 135.2, 136.5, 136.8, 138.8, 145.5, 147.3, 147.5, 148.5, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2928w, 1454w, 1347s, 1173m, 1155s, 1091w; HRMS (ESI): m/z calcd for $C_{38}H_{40}N_3O_4S_2$ $[M+H]^+$: 666.2455; found 666.2452.

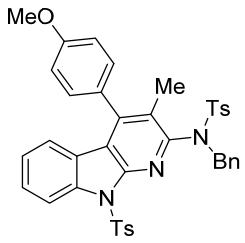


3o

2-Amino-α-carboline **3o** (134.4 mg, 0.20 mmol) was prepared from alkyne-cyanamide **1b** (77.3 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 98% yield after stirring at rt for 10.0 min.

3o: R_f = 0.31 [4:1 petroleum ether/EtOAc]; white solid; mp = 244–245 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.93 (s, 3H), 2.29 (s, 3H), 2.45 (s, 3H), 2.53 (s, 3H), 4.16 (d, 1H, J = 12.9 Hz), 4.75 (d, 1H, J = 12.9 Hz), 6.64-6.66 (m, 2H), 6.71-6.76 (m, 2H), 6.97-7.11 (m, 4H), 7.16-7.24 (m, 4H), 7.33 (d, 1H, J = 7.6 Hz), 7.42-7.47 (m, 1H), 7.53 (d, 2H, J = 8.1 Hz), 7.74-7.77 (m, 2H), 8.10-8.12 (m, 2H), 8.47 (d, 1H, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 21.6, 21.7, 21.9, 54.1, 114.6, 116.9, 122.5, 122.6, 123.4, 127.6, 127.8, 128.1, 128.19, 128.25, 129.0, 129.2, 129.6, 129.8, 130.02, 130.05, 134.0, 135.2, 136.3, 136.8, 138.4, 138.9, 143.9, 145.2, 147.0, 147.3, 148.4; IR (neat) (cm^{-1}) 1596w,

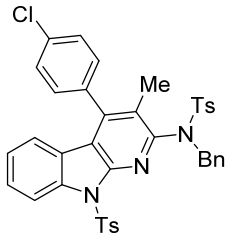
1456w, 1360s, 1351s, 1163s, 1090m; HRMS (ESI): m/z calcd for $C_{40}H_{36}N_3O_4S_2$ $[M+H]^+$: 686.2142; found 686.2141.



3p

2-Amino-α-carboline **3p** (139.0 mg, 0.20 mmol) was prepared from alkyne-cyanamide **1c** (80.5 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 99% yield after stirring at rt for 10.0 min.

3p: R_f = 0.25 [4:1 petroleum ether/EtOAc]; white solid; mp = 256–257 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.93 (s, 3H), 2.29 (s, 3H), 2.54 (s, 3H), 3.89 (s, 3H), 4.16 (d, 1H, J = 12.9 Hz), 4.74 (d, 1H, J = 12.9 Hz), 6.63-6.66 (m, 2H), 6.76-6.80 (m, 2H), 6.95-7.01 (m, 3H), 7.04-7.11 (m, 3H), 7.17 (d, 2H, J = 8.1 Hz), 7.23-7.26 (m, 1H), 7.44-7.48 (m, 1H), 7.53 (d, 2H, J = 8.1 Hz), 7.74-7.76 (m, 2H), 8.10-8.12 (m, 2H), 8.47 (d, 1H, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 21.8, 21.9, 54.2, 55.5, 114.5, 114.7, 114.8, 117.2, 122.57, 122.65, 123.4, 127.8, 128.15, 128.23, 128.3, 129.08, 129.15, 129.3, 129.6, 130.1, 130.3, 135.2, 136.3, 136.8, 138.9, 143.9, 145.2, 146.8, 147.3, 148.5, 159.7; IR (neat) (cm^{-1}) 1597w, 1514w, 1369m, 1346s, 1246m, 1172s; HRMS (ESI): m/z calcd for $C_{40}H_{36}N_3O_5S_2$ $[M+H]^+$: 702.2091; found 702.2091.

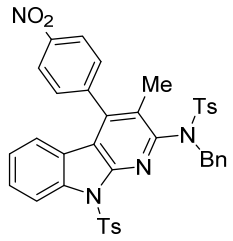


3q

2-Amino-α-carboline **3q** (110.2 mg, 0.16 mmol) was prepared from alkyne-cyanamide **1d** (81.4 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 78% yield after stirring at rt for 10.0 min.

3q: R_f = 0.31 [4:1 petroleum ether/EtOAc]; white solid; mp = 276–277 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (s, 3H), 2.30 (s, 3H), 2.54 (s, 3H), 4.16 (d, 1H, J = 12.9 Hz), 4.74 (d, 1H, J = 12.9 Hz), 6.64 (d, 2H, J = 7.4 Hz), 6.71 (d, 1H, J = 7.9 Hz), 6.82 (d, 1H, J = 7.7 Hz), 7.00 (t, 2H, J = 7.5 Hz), 7.07-7.12 (m, 2H), 7.18 (d, 2H, J = 8.1 Hz), 7.28 (d, 1H, J = 8.5 Hz), 7.42-7.55 (m, 5H), 7.75 (d, 2H, J = 8.1 Hz), 8.09 (d, 2H, J = 8.0 Hz), 8.49 (d, 1H, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 21.8, 21.9, 54.1, 114.8, 116.6, 122.2, 122.3, 123.6, 127.9, 128.2, 128.3, 128.5, 129.1, 129.2, 129.5, 129.6, 129.8, 129.9, 130.1, 134.7, 135.1, 135.4, 136.1, 136.7, 139.0, 144.0, 145.3, 145.4, 147.3,

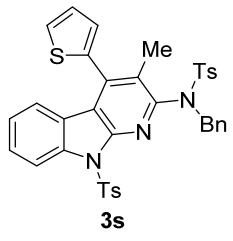
148.6; IR (neat) (cm^{-1}) 1347w, 1276m,1162m, 1089m, 990w, 750s; HRMS (ESI): m/z calcd for $C_{39}H_{33}ClN_3O_4S_2$ $[M+H]^+$: 706.1596; found 706.1597.



3r

2-Amino-α-carboline **3r** (50.2 mg, 0.07 mmol) was prepared from alkyne-cyanamide **1e** (83.5 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 35% yield after stirring at rt for 10.0 min.

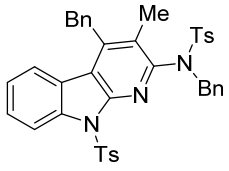
3r: R_f = 0.21 [4:1 petroleum ether/EtOAc]; white solid; mp = 256–257 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (s, 3H), 2.31 (s, 3H), 2.55 (s, 3H), 4.18 (d, 1H, J = 12.9 Hz), 4.76 (d, 1H, J = 12.8 Hz), 6.58 (d, 1H, J = 7.9 Hz), 6.64-6.67 (m, 2H), 6.99-7.13 (m, 5H), 7.20 (d, 2H, J = 8.1 Hz), 7.48-7.58 (m, 4H), 7.76-7.78 (m, 2H), 8.07-8.09 (m, 2H), 8.33 (dd, 1H, J = 8.4, 2.4 Hz), 8.43 (dd, 1H, J = 8.4, 2.4 Hz), 8.51 (d, 1H, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 21.8, 21.9, 54.1, 115.0, 116.0, 121.7, 122.0, 123.7, 124.5, 124.8, 128.0, 128.2, 128.3, 128.8, 129.0, 129.1, 129.2, 129.7, 130.2, 135.1, 136.0, 136.6, 139.1, 143.9, 144.0, 144.1, 145.5, 147.4, 148.2, 148.8; IR (neat) (cm^{-1}) 1521w, 1370m, 1347s, 1214w, 1163s, 1091w; HRMS (ESI): m/z calcd for $C_{39}H_{33}N_4O_6S_2$ $[M+H]^+$: 717.1836; found 717.1836.



3s

2-Amino-α-carboline **3s** (134.2 mg, 0.20 mmol) was prepared from alkyne-cyanamide **1f** (75.7 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 99% yield after stirring at rt for 10.0 min.

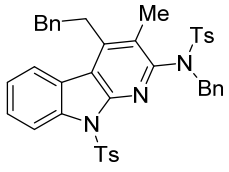
3s: R_f = 0.29 [4:1 petroleum ether/EtOAc]; white solid; mp = 242–243 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3H), 2.29 (s, 3H), 2.53 (s, 3H), 4.17 (d, 1H, J = 13.0 Hz), 4.75 (d, 1H, J = 13.0 Hz), 6.66-6.68 (m, 2H), 6.79 (d, 1H, J = 7.8 Hz), 6.99-7.03 (m, 2H), 7.08-7.25 (m, 6H), 7.46-7.54 (m, 4H), 7.74-7.77 (m, 2H), 8.07-8.10 (m, 2H), 8.47 (d, 1H, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 21.7, 21.9, 54.2, 114.7, 118.3, 122.2, 122.5, 123.7, 127.2, 127.9, 128.21, 128.25, 128.6, 129.0, 129.2, 129.6, 130.1, 131.9, 135.1, 136.2, 136.5, 136.7, 139.0, 139.6, 144.0, 145.3, 147.1, 148.4, two carbons missing due to overlap; IR (neat) (cm^{-1}) 1569w, 1446w, 1378m, 1340s, 1292w, 1088m; HRMS (ESI): m/z calcd for $C_{37}H_{32}N_3O_4S_3$ $[M+H]^+$: 678.1549; found 678.1548.



3t

2-Amino-α-carboline **3t** (100.1 mg, 0.15 mmol) was prepared from alkyne-cyanamide **1g** (77.3 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 73% yield after stirring at rt for 10.0 min.

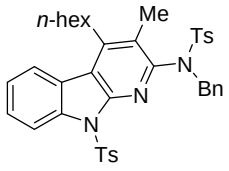
3t: R_f = 0.35 [4:1 petroleum ether/EtOAc]; white solid; mp = 233–234 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 3H), 2.29 (s, 3H), 2.54 (s, 3H), 4.08 (d, 1H, J = 12.5 Hz), 4.36 (d, 1H, J = 16.2 Hz), 4.48 (d, 1H, J = 16.2 Hz), 4.76 (d, 1H, J = 12.4 Hz), 6.52-6.54 (m, 2H), 6.64-6.67 (m, 2H), 6.91-6.94 (m, 2H), 7.04-7.08 (m, 1H), 7.10-7.17 (m, 5H), 7.22-7.26 (m, 1H), 7.48-7.55 (m, 3H), 7.70-7.77 (m, 3H), 8.09-8.11 (m, 2H), 8.52 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 21.7, 21.9, 35.8, 54.2, 114.8, 117.5, 122.4, 122.9, 123.8, 126.6, 127.7, 127.8, 128.1, 128.2, 128.4, 128.9, 129.1, 129.3, 129.6, 130.1, 131.0, 134.9, 136.16, 136.24, 136.8, 138.9, 143.9, 144.6, 145.3, 147.7, 148.3; IR (neat) (cm^{-1}) 1450w, 1366s, 1343s, 1175m, 1092s, 1071w; HRMS (ESI): m/z calcd for $C_{40}H_{36}N_3O_4S_2$ $[M+H]^+$: 686.2142; found 686.2142.



3u

2-Amino-α-carboline **3u** (130.2 mg, 0.19 mmol) was prepared from alkyne-cyanamide **1h** (80.1 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 93% yield after stirring at rt for 10 min.

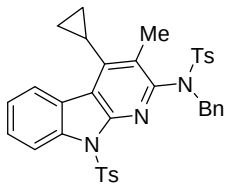
3u: R_f = 0.36 [4:1 petroleum ether/EtOAc]; white solid; mp = 102–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 3H), 2.28 (s, 3H), 2.53 (s, 3H), 2.65-2.73 (m, 1H), 2.79-2.87 (m, 1H), 3.29-3.34 (m, 2H), 4.15 (d, 1H, J = 13.2 Hz), 4.73 (d, 1H, J = 13.0 Hz), 6.65 (d, 2H, J = 7.7 Hz), 6.99 (t, 2H, J = 7.6 Hz), 7.08 (t, 1H, J = 7.3 Hz), 7.16 (t, 4H, J = 6.9 Hz), 7.21-7.24 (m, 1H), 7.28 (d, 2H, J = 7.6 Hz), 7.42 (t, 1H, J = 7.7 Hz), 7.51 (d, 2H, J = 7.9 Hz), 7.56-7.60 (m, 1H), 7.73 (d, 2H, J = 8.0 Hz), 8.02-8.07 (m, 3H), 8.58 (d, 1H, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.7, 21.9, 32.4, 34.0, 54.0, 115.1, 116.6, 122.6, 123.9, 126.6, 127.8, 128.1, 128.16, 128.23, 128.24, 128.9, 129.0, 129.2, 129.60, 129.64, 130.0, 135.3, 136.2, 136.9, 138.9, 140.7, 143.9, 145.2, 147.0, 147.7, 148.4, one carbon missing due to overlap; IR (neat) (cm^{-1}) 1597w, 1456w, 1349s, 1209w, 1165s, 1090s; HRMS (ESI): m/z calcd for $C_{41}H_{38}N_3O_4S_2$ $[M+H]^+$: 700.2298; found 700.2309.



3v

2-Amino-α-carboline **3v** (125.1 mg, 0.18 mmol) was prepared from alkyne-cyanamide **1i**[9] (76.1 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 92% yield after stirring at rt for 10 min.

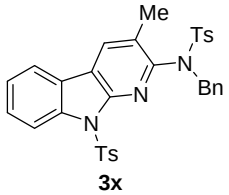
3v: R_f = 0.42 [4:1 petroleum ether/EtOAc]; white solid; mp = 178–179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, 3H, J = 6.9 Hz), 1.27-1.54 (m, 8H), 2.18 (s, 3H), 2.26 (s, 3H), 2.51 (s, 3H), 2.92-3.04 (m, 2H), 4.11 (d, 1H, J = 13.0 Hz), 4.72 (d, 1H, J = 13.0 Hz), 6.61-6.63 (m, 2H), 6.94-6.98 (m, 2H), 7.03-7.08 (m, 1H), 7.13 (d, 2H, J = 8.1 Hz), 7.38-7.42 (m, 1H), 7.49-7.57 (m, 3H), 7.70-7.72 (m, 2H), 7.92 (d, 1H, J = 7.9 Hz), 8.05-8.07 (m, 2H), 8.55 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 14.3, 21.7, 21.8, 22.7, 28.1, 29.7, 30.6, 31.7, 54.0, 115.0, 116.5, 122.67, 122.74, 123.8, 127.7, 127.9, 128.1, 128.2, 129.0, 129.2, 129.50, 129.53, 130.0, 135.3, 136.3, 136.9, 138.8, 143.8, 145.1, 147.6, 148.2, 148.4; IR (neat) (cm^{-1}) 1580w, 1368s, 1347s, 1213w, 1162s, 1090m; HRMS (ESI): m/z calcd for $C_{39}H_{42}N_3O_4S_2$ $[M+H]^+$: 680.2611; found 680.2612.



3w

2-Amino-α-carboline **3w** (125.9 mg, 0.20 mmol) was prepared from alkyne-cyanamide **1j** (67.3 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 99% yield after stirring at rt for 10 min.

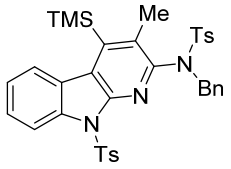
3w: R_f = 0.34 [4:1 petroleum ether/EtOAc]; white solid; mp = 212–213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.39-0.43 (m, 1H), 0.61-0.66 (m, 1H), 1.19-1.21 (m, 2H), 1.93-2.00 (m, 1H), 2.25 (s, 3H), 2.29 (s, 3H), 2.50 (s, 3H), 4.12 (d, 1H, J = 12.9 Hz), 4.70 (d, 1H, J = 12.9 Hz), 6.61-6.63 (m, 2H), 6.94-6.98 (m, 2H), 7.03-7.08 (m, 1H), 7.13 (d, 2H, J = 8.1 Hz), 7.36-7.40 (m, 1H), 7.49-7.56 (m, 3H), 7.71-7.73 (m, 2H), 8.06-8.08 (m, 2H), 8.31 (d, 1H, J = 7.8 Hz), 8.53 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.7, 9.8, 12.4, 15.9, 21.6, 21.8, 54.0, 114.5, 118.6, 122.6, 123.3, 124.6, 127.7, 127.9, 128.06, 128.14, 128.9, 129.2, 129.5, 130.0, 132.5, 135.2, 136.3, 136.8, 138.7, 143.8, 145.1, 147.4, 147.6, 148.3; IR (neat) (cm^{-1}) 1574w, 1364s, 1346s, 1174s, 1162s, 1021m; HRMS (ESI): m/z calcd for $C_{36}H_{34}N_3O_4S_2$ $[M+H]^+$: 636.1985; found 636.1983.



3x

2-Amino-α-carboline **3x** (100.1 mg, 0.17 mmol) was prepared from alkyne-cyanamide **1k**[9] (59.3 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 84% yield after stirring at rt for 10 min.

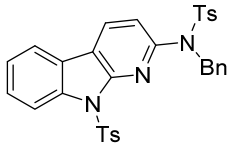
3x: R_f = 0.43 [4:1 petroleum ether/EtOAc]; white solid; mp = 189–190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.28 (s, 3H), 2.53 (s, 3H), 4.18 (s, 1H), 4.72 (s, 1H), 6.66-6.69 (m, 2H), 6.96-7.00 (m, 2H), 7.05-7.10 (m, 1H), 7.15 (d, 2H, J = 8.1 Hz), 7.36-7.40 (m, 1H), 7.50 (d, 2H, J = 8.0 Hz), 7.54-7.58 (m, 1H), 7.71-7.74 (m, 2H), 7.86 (d, 1H, J = 7.7 Hz), 7.92 (s, 1H), 8.02-8.04 (m, 2H), 8.47 (d, 1H, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6, 21.7, 21.9, 54.0, 115.2, 118.6, 121.0, 122.3, 123.9, 127.8, 128.2, 128.7, 129.0, 129.2, 129.6, 130.1, 131.1, 131.3, 135.4, 136.1, 136.7, 139.0, 143.9, 145.2, 147.9, 148.6, one carbon missing due to overlap; IR (neat) (cm^{-1}) 1597w, 1496w, 1346m, 1163s, 1155w, 1091m; HRMS (ESI): m/z calcd for $C_{33}H_{30}N_3O_4S_2$ $[M+H]^+$: 596.1672; found 596.1670.



3y

2-Amino-α-carboline **3y** (73.5 mg, 0.11 mmol) was prepared from alkyne-cyanamide **1l**[9] (73.7 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 55% yield after stirring at rt for 0.5 h.

3y: R_f = 0.52 [4:1 petroleum ether/EtOAc]; white solid; mp = 195–196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.46 (s, 9H), 2.27 (s, 3H), 2.31 (s, 3H), 2.52 (s, 3H), 4.12 (d, 1H, J = 13.1 Hz), 4.68 (d, 1H, J = 13.2 Hz), 6.63 (d, 2H, J = 7.4 Hz), 6.98 (t, 2H, J = 7.5 Hz), 7.05-7.10 (m, 1H), 7.14 (d, 2H, J = 8.1 Hz), 7.35 (t, 1H, J = 7.7 Hz), 7.49-7.57 (m, 3H), 7.71 (d, 2H, J = 8.3 Hz), 8.00-8.06 (m, 3H), 8.56 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.5, 20.5, 21.7, 21.9, 54.0, 114.7, 122.7, 123.1, 123.2, 125.6, 127.8, 127.9, 128.15, 128.19, 129.0, 129.2, 129.6, 130.1, 135.3, 136.0, 136.4, 137.0, 139.0, 143.8, 145.1, 147.2, 147.48, 147.52; IR (neat) (cm^{-1}) 1598w, 1453m, 1353s, 1254m, 1168s, 1092s; HRMS (ESI): m/z calcd for $C_{36}H_{38}N_3O_4S_2Si$ $[M+H]^+$: 668.2068; found 668.2077.



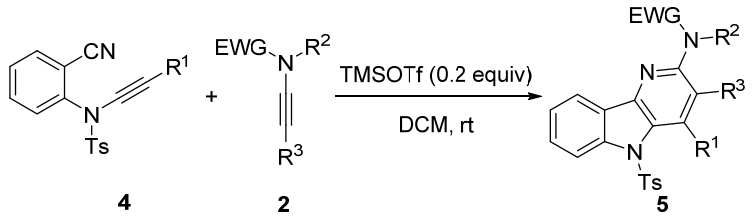
3z

2-Amino-α-carboline **3z** (60.5 mg, 0.10 mmol) was prepared from alkyne-cyanamide **1k** (59.3 mg, 0.20 mmol) and ynamide **2o**[4] (74.2 mg, 0.26 mmol) in 52% yield after stirring at rt for 10.0 min.

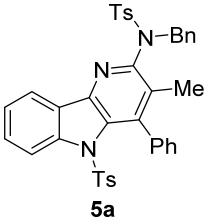
2-Amino-α-carboline **3z** (71.0 mg, 0.12 mmol) was prepared from alkyne-cyanamide **1k** (59.3 mg, 0.20 mmol) and ynamide **2o** (74.2 mg, 0.26 mmol) in 61% yield after stirring at 100 ^{o}C for 10.0 min.

3z: R_f = 0.54 [4:1 petroleum ether/EtOAc]; white solid; mp = 182–183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.43 (s, 3H), 5.14 (s, 2H), 7.02 (d, 2H, J = 8.1 Hz), 7.12-7.20 (m, 3H), 7.24-7.37 (m, 5H), 7.48-7.52 (m, 1H), 7.56 (d, 1H, J = 8.3 Hz), 7.67-7.72 (m, 4H), 7.83 (d, 1H, J = 7.7 Hz), 8.07 (d, 1H, J = 8.3 Hz), 8.38 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.77, 21.82, 51.6, 115.1, 116.6, 117.7, 120.6, 122.6, 124.0, 127.5, 127.6, 127.8, 128.2, 128.4, 128.5, 129.7, 129.9, 130.0, 136.27, 136.31, 136.9, 138.0, 143.9, 145.0, 149.2, 149.7; IR (neat) (cm^{-1}) 1585w, 1447m, 1391s, 1351s, 1187s, 1006w; HRMS (ESI): m/z calcd for $C_{32}H_{28}N_3O_4S_2$ $[M+H]^+$: 582.1516; found 582.1517.

General Procedure for Synthesis of 3-Amino-δ-Carbolines.

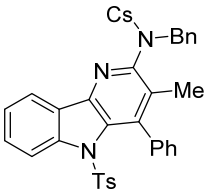


To an oven-dried sealed tube was added ynamide-nitrile **4a**[1] (74.5 mg, 0.20 mmol), ynamide **2a** (65.9 mg, 0.22 mmol), DCM (1.0 mL, ynamide-nitrile *concn* = 0.20 *M*) and TMSOTf (7.2 μL, 0.04 mmol) at rt. When the reaction was judged to be completed by TLC after stirring at rt for 0.5 h, the mixture was purified by flash silica gel column chromatrography [gradient eluent: 10:1~4:1 petroleum ether/EtOAc] to afford 3-amino-δ-carboline **5a** (131.7 mg, 0.20 mmol) in 98% yield.



5a

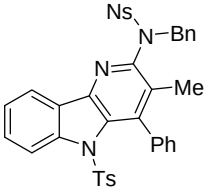
5a: R_f = 0.54 [4:1 petroleum ether/EtOAc]; white solid; mp = 252–253 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H), 2.24 (s, 3H), 2.46 (s, 3H), 4.46 (s, 1H), 4.92 (s, 1H), 6.96 (d, 2H, J = 8.1 Hz), 7.03 (d, 2H, J = 8.1 Hz), 7.14-7.23 (m, 9H), 7.36-7.39 (m, 4H), 7.50-7.53 (m, 3H), 7.65 (d, 1H, J = 7.6 Hz), 8.19 (d, 1H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2, 21.6, 21.8, 54.4, 119.4, 120.1, 125.8, 126.8, 128.0, 128.06, 128.12, 128.3, 128.98, 129.01, 129.05, 129.1, 129.6, 129.7, 132.8, 133.0, 133.1, 135.3, 137.2, 142.6, 142.8, 143.6, 144.4, 145.6, 150.3, two carbons missing due to overlap; IR (neat) (cm^{-1}) 2924w, 1340s, 1173m, 1160s, 1091m, 1025w; HRMS (ESI): m/z calcd for $C_{39}H_{34}N_3O_4S_2$ $[M+H]^+$: 672.1985; found 672.1981.



5b

3-Amino-δ-carboline **5b** (137.1 mg, 0.20 mmol) was prepared from ynamide-nitrile **4a** (74.5 mg, 0.20 mmol) and ynamide **2b** (70.4 mg, 0.22 mmol) in 99% yield after stirring at rt for 1.5 h.

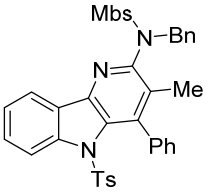
5b: R_f = 0.57 [4:1 petroleum ether/EtOAc]; white solid; mp = 260–261 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 3H), 2.25 (s, 3H), 4.44 (s, 1H), 4.94 (s, 1H), 6.96 (d, 2H, J = 8.2 Hz), 7.02-7.04 (m, 2H), 7.10-7.22 (m, 6H), 7.34-7.43 (m, 7H), 7.52-7.58 (m, 3H), 7.64 (d, 1H, J = 7.6 Hz), 8.20 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.1, 21.7, 54.7, 119.4, 120.1, 125.9, 126.8, 127.9, 128.1, 128.16, 128.19, 128.4, 128.7, 129.1, 129.3, 129.7, 130.4, 133.0, 133.1, 133.3, 134.9, 136.8, 137.1, 139.4, 142.76, 142.83, 144.5, 145.7, 150.0, one carbon missing due to overlap; IR (neat) (cm^{-1}) 1575w, 1358s, 1276w, 1173m, 1091m, 1026w; HRMS (ESI): m/z calcd for $C_{38}H_{31}ClN_3O_4S_2$ $[M+H]^+$: 692.1439; found 692.1436.



5c

3-Amino-δ-carboline **5c** (139.2 mg, 0.20 mmol) was prepared from ynamide-nitrile **4a** (74.5 mg, 0.20 mmol) and ynamide **2c** (72.7 mg, 0.22 mmol) in 99% yield after stirring at rt for 1.5 h.

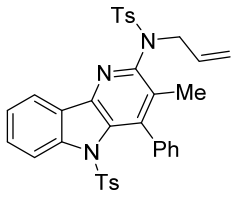
5c: R_f = 0.44 [4:1 petroleum ether/EtOAc]; white solid; mp = 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99 (s, 3H), 2.28 (s, 3H), 4.47 (s, 1H), 5.00 (s, 1H), 6.98-7.25 (m, 11H), 7.37-7.42 (m, 4H), 7.54-7.58 (m, 2H), 7.81 (d, 2H, J = 8.6 Hz), 8.21 (d, 3H, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.0, 21.7, 55.0, 119.5, 120.0, 123.6, 126.1, 126.8, 127.5, 128.2, 128.3, 128.4, 128.5, 129.1, 129.5, 129.7, 129.8, 130.2, 133.0, 133.1, 133.4, 134.4, 136.9, 142.9, 143.0, 144.2, 144.6, 145.8, 149.4, 150.2; IR (neat) (cm^{-1}) 1529w, 1349s, 1167s, 1107w, 1089w, 1026w; HRMS (ESI): m/z calcd for $C_{38}H_{31}N_4O_6S_2$ $[M+H]^+$: 703.1680; found 703.1676.



5d

3-Amino-δ-carboline **5d** (126.6 mg, 0.18 mmol) was prepared from ynamide-nitrile **4a** (74.5 mg, 0.20 mmol) and ynamide **2d** (69.4 mg, 0.22 mmol) in 92% yield after stirring at rt for 1.0 h.

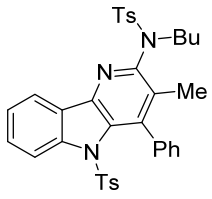
5d: R_f = 0.30 [4:1 petroleum ether/EtOAc]; white solid; mp = 235–236 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06 (s, 3H), 2.24 (s, 3H), 3.86 (s, 3H), 4.45 (s, 1H), 4.92 (s, 1H), 6.82-6.85 (m, 2H), 6.96 (d, 2H, J = 8.2 Hz), 7.02-7.04 (m, 2H), 7.13-7.20 (m, 6H), 7.33-7.40 (m, 5H), 7.50-7.56 (m, 3H), 7.67 (d, 1H, J = 7.6 Hz), 8.19 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2, 21.7, 54.4, 55.7, 113.6, 119.4, 120.2, 125.8, 126.8, 128.0, 128.1, 128.16, 128.19, 128.3, 129.0, 129.1, 129.7, 129.8, 129.9, 131.1, 132.8, 133.07, 133.15, 135.4, 137.2, 142.6, 142.8, 144.4, 145.5, 150.5, 163.2; IR (neat) (cm^{-1}) 2924w, 1497w, 1380m, 1341s, 1174s, 1020m; HRMS (ESI): m/z calcd for $C_{39}H_{34}N_3O_5S_2$ $[M+H]^+$: 688.1934; found 688.1931.



5e

3-Amino-δ-carboline **5e** (123.1 mg, 0.20 mmol) was prepared from ynamide-nitrile **4a** (74.5 mg, 0.20 mmol) and ynamide **2e** (54.9 mg, 0.22 mmol) in 99% yield after stirring at rt for 0.5 h.

5e: R_f = 039 [4:1 petroleum ether/EtOAc]; white solid; mp = 200–201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.42 (s, 3H), 2.44 (s, 3H), 3.89-4.44 (m, 2H), 4.90-4.95 (m, 2H), 5.70-5.80 (m, 1H), 6.95 (d, 2H, J = 8.2 Hz), 7.03-7.05 (m, 2H), 7.15 (d, 2H, J = 8.0 Hz), 7.34-7.60 (m, 10H), 8.20 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5, 21.7, 21.8, 53.4, 119.5, 119.8, 120.2, 125.7, 125.8， 126.8, 128.19, 128.20, 129.01, 129.03, 129.037, 129.043, 130.0, 132.2, 132.7, 132.9, 133.2, 135.2, 137.3, 142.7, 142.9, 143.6, 144.4, 145.6, 150.6; IR (neat) (cm^{-1}) 1595w, 1375m, 1351s, 1187m, 1166s, 1089m; HRMS (ESI): m/z calcd for $C_{35}H_{32}N_3O_4S_2$ $[M+H]^+$: 622.1829; found 622.1826.

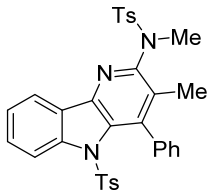


5f

3-Amino-δ-carboline **5f** (122.5 mg, 0.19 mmol) was prepared from ynamide-nitrile **4a** (74.5 mg, 0.20 mmol) and ynamide **2f** (58.4 mg, 0.22 mmol) in 96% yield after stirring at rt for 0.5 h.

5f: R_f = 0.48 [4:1 petroleum ether/EtOAc]; white solid; mp = 164–165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, 3H, J = 7.1 Hz), 1.26-1.50 (m, 4H), 2.24 (s, 3H), 2.43 (s, 3H), 2.45 (s, 3H), 3.48 (s, 1H), 3.62 (s, 1H), 6.96 (d, 2H, J = 8.1 Hz), 7.05-7.08 (m, 2H), 7.12 (d, 2H, J = 8.0 Hz), 7.34-7.54 (m, 9H), 7.60 (d, 1H, J = 7.7 Hz), 8.20 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 17.7, 20.3, 21.7, 21.8, 30.2, 50.2, 119.5, 120.2, 125.7, 126.8, 128.19, 128.22, 128.23, 128.9, 129.0, 129.1,

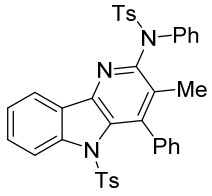
132.8, 132.9, 133.2, 135.2, 137.4, 142.7, 142.9, 143.4, 144.4, 145.7, 150.8, two carbons missing due to overlap; IR (neat) (cm^{-1}) 2925w, 1574w, 1372s, 1188m, 1164s, 1088m; HRMS (ESI): m/z calcd for $C_{36}H_{36}N_3O_4S_2$ $[M+H]^+$: 638.2142; found 638.2139.



5g

3-Amino-δ-carboline **5g** (107.2 mg, 0.18 mmol) was prepared from ynamide-nitrile **4a** (74.5 mg, 0.20 mmol) and ynamide **2g** (49.1 mg, 0.22 mmol) in 90% yield after stirring at rt for 0.5 h.

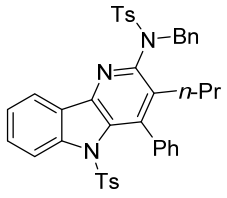
5g: R_f = 0.31 [4:1 petroleum ether/EtOAc]; white solid; mp = 170–171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.43 (s, 3H), 2.45 (s, 3H), 3.15 (s, 3H), 6.98 (d, 2H, J = 8.1 Hz), 7.06-7.09 (m, 2H), 7.16 (d, 2H, J = 8.0 Hz), 7.33-7.54 (m, 9H), 7.61-7.63 (m, 1H), 8.19 (dt, 1H, J = 8.4, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5, 21.7, 21.8, 37.5, 119.3, 120.2, 125.7, 126.8, 128.0, 128.2, 129.0, 129.07, 129.11, 129.14, 129.9, 131.2, 132.9, 133.4, 134.4, 137.4, 142.8, 142.9, 143.6, 144.4, 145.5, 152.2, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2922w, 1353s, 1191w, 1178s, 1168s, 1089w; HRMS (ESI): m/z calcd for $C_{33}H_{30}N_3O_4S_2$ $[M+H]^+$: 596.1672; found 596.1671.



5h

3-Amino-δ-carboline **5h** (107.9 mg, 0.16 mmol) was prepared from ynamide-nitrile **4a** (74.5 mg, 0.20 mmol) and ynamide **2h** (62.8 mg, 0.22 mmol) in 82% yield after stirring at rt for 2.0 h.

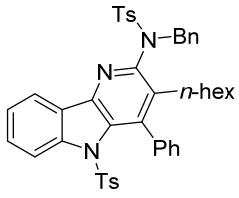
5h: R_f = 0.41 [4:1 petroleum ether/EtOAc]; white solid; mp = 230–231 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.30 (s, 3H), 2.47 (s, 3H), 6.92 (d, 2H, J = 8.2 Hz), 7.02-7.04 (m, 2H), 7.24-7.31 (m, 7H), 7.35-7.44 (m, 6H), 7.52-7.56 (m, 1H), 7.63-7.65 (m, 2H), 7.79 (d, 1H, J = 7.5 Hz), 8.18 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6, 21.7, 21.9, 119.1, 120.5, 125.6, 126.6, 127.6, 128.0, 128.1, 128.2, 128.4, 128.8, 129.1, 129.15, 129.17, 129.5, 129.9, 130.7, 132.9, 133.7, 136.8, 137.1, 139.6, 142.8, 143.2, 143.6, 144.4, 145.4, 151.7; IR (neat) (cm^{-1}) 2923w, 1452w, 1371m, 1357s, 1187w, 1166s; HRMS (ESI): m/z calcd for $C_{38}H_{32}N_3O_4S_2$ $[M+H]^+$: 658.1829; found 658.1825.



5i

3-Amino-δ-carboline **5i** (135.8 mg, 0.19 mmol) was prepared from ynamide-nitrile **4a** (74.5 mg, 0.20 mmol) and ynamide **2i** (72.0 mg, 0.22 mmol) in 97% yield after stirring at rt for 1.0 h.

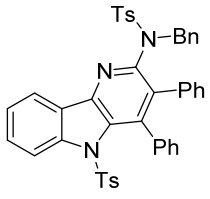
5i: R_f = 0.40 [4:1 petroleum ether/EtOAc]; white solid; mp = 185–186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.40 (t, 3H, J = 7.2 Hz), 0.58-0.77 (m, 2H), 2.24 (s, 3H), 2.44 (s, 3H), 2.56-2.85 (m, 2H), 4.49 (d, 1H, J = 12.9 Hz), 4.91 (d, 1H, J = 12.7 Hz), 6.97-6.99 (m, 2H), 7.04-7.07 (m, 2H), 7.11-7.18 (m, 8H), 7.36-7.44 (m, 7H), 7.51-7.55 (m, 1H), 7.63-7.65 (m, 1H), 8.20 (dt, 1H, J = 8.3, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 21.7, 21.8, 22.2, 31.1, 54.4, 119.6, 120.1, 125.8, 126.8, 127.99, 128.02, 128.05, 128.2, 128.4, 128.98, 129.03, 129.1, 129.2, 129.7, 130.0, 133.0, 133.3, 135.0, 135.6, 136.9, 137.4, 142.8, 143.0, 143.6, 144.4, 145.6, 150.1; IR (neat) (cm^{-1}) 2923w, 1456w, 1351m, 1276w, 1175s, 1090w; HRMS (ESI): m/z calcd for $C_{41}H_{38}N_3O_4S_2$ $[M+H]^+$: 700.2298; found 700.2295.



5j

3-Amino-δ-carboline **5j** (146.9 mg, 0.20 mmol) was prepared from ynamide-nitrile **4a** (74.5 mg, 0.20 mmol) and ynamide **2j** (81.3 mg, 0.22 mmol) in 99% yield after stirring at rt for 1.0 h.

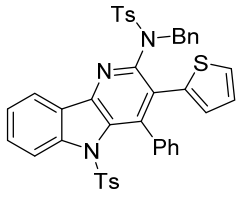
5j: R_f = 0.43 [4:1 petroleum ether/EtOAc]; white solid; mp = 140–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.60-1.00 (m, 11H), 2.24 (s, 3H), 2.44 (s, 3H), 2.60-2.89 (m, 2H), 4.50 (d, 1H, J = 13.0 Hz), 4.90 (d, 1H, J = 12.8 Hz), 6.97-7.19 (m, 12H), 7.34-7.55 (m, 8H), 7.64 (d, 1H, J = 7.6 Hz), 8.20 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.7, 21.8, 22.4, 28.6, 29.1, 29.6, 31.0, 54.4, 119.6, 120.1, 125.8, 126.9, 127.99, 128.03, 128.3, 128.4, 128.98, 129.03, 129.1, 129.2, 129.8, 130.0, 133.1, 133.3, 135.0, 135.7, 136.9, 137.6, 142.8, 143.0, 143.6, 144.4, 145.5, 150.1, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2928w, 1573w, 1372s, 1186m, 1164s, 1089m; HRMS (ESI): m/z calcd for $C_{44}H_{44}N_3O_4S_2$ $[M+H]^+$: 742.2768; found 742.2764.



5k

3-Amino-δ-carboline **5k** (145.3 mg, 0.20 mmol) was prepared from ynamide-nitrile **4a** (74.5 mg, 0.20 mmol) and ynamide **2k** (79.5 mg, 0.22 mmol) in 99% yield after stirring at rt for 1.0 h.

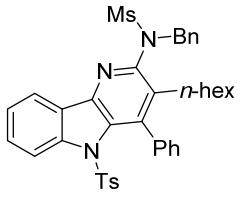
5k: R_f = 0.41 [4:1 petroleum ether/EtOAc]; white solid; mp = 105–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.46 (s, 3H), 4.46 (s, 2H), 6.66 (d, 2H, J = 7.3 Hz), 6.96-7.17 (m, 19H), 7.40-7.46 (m, 3H), 7.56-7.61 (m, 1H), 7.76 (d, 1H, J = 7.6 Hz), 8.23 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 21.8, 54.9, 119.7, 120.6, 126.0, 126.7, 126.8, 127.0, 127.4, 127.5, 127.7, 128.17, 128.20, 128.9, 129.1, 129.4, 129.5, 129.8, 130.4, 131.6, 132.7, 133.2, 134.7, 135.2, 135.9, 136.9, 137.2, 143.0, 143.4, 143.6, 144.6, 147.6, 149.8; IR (neat) (cm^{-1}) 1597w, 1376w, 1350m, 1175m, 1161s, 1087m; HRMS (ESI): m/z calcd for $C_{44}H_{36}N_3O_4S_2$ $[M+H]^+$: 734.2142; found 734.2138.



5l

3-Amino-δ-carboline **5l** (146.5 mg, 0.20 mmol) was prepared from ynamide-nitrile **4a** (74.5 mg, 0.20 mmol) and ynamide **2l** (80.8 mg, 0.22 mmol) in 99% yield after stirring at rt for 1.0 h.

5l: R_f = 0.45 [4:1 petroleum ether/EtOAc]; white solid; mp = 208–209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 2.47 (s, 3H), 4.51 (s, 2H), 6.44 (d, 1H, J = 2.8 Hz), 6.74-6.77 (m, 3H), 6.95-7.07 (m, 7H), 7.13-7.23 (m, 8H), 7.39-7.45 (m, 3H), 7.57-7.62 (m, 1H), 7.68 (d, 1H, J = 7.6 Hz), 8.23 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 21.8, 54.7, 119.9, 120.6, 125.9, 126.1, 126.9, 127.2, 127.5, 127.6, 127.9, 128.10, 128.12, 128.9, 129.1, 129.4, 129.8, 130.0, 130.5, 131.3, 132.5, 133.2, 134.8, 135.5, 135.6, 137.1, 143.61, 143.63, 143.9, 144.7, 147.8, 150.7, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2925w, 1596w, 1456w, 1353s, 1238w, 1162s; HRMS (ESI): m/z calcd for $C_{42}H_{34}N_3O_4S_3$ $[M+H]^+$: 740.1706; found 740.1706.

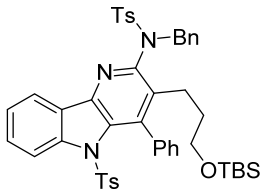


5m

3-Amino-δ-carboline **5m** (131.8 mg, 0.20 mmol) was prepared from ynamide-nitrile **4a** (74.5 mg, 0.20 mmol) and ynamide **2n** (64.6 mg, 0.22 mmol) in 99% yield after stirring at rt for 1.0 h.

5m: R_f = 0.36 [4:1 petroleum ether/EtOAc]; white solid; mp = 140–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.73 (t, 3H, J = 7.3 Hz), 0.78-0.81 (m, 4H), 0.95-1.03 (m, 2H), 2.27 (s, 3H), 2.41-2.58 (m, 2H), 3.10 (s, 3H), 4.89 (s, 1H), 4.95 (s, 1H), 6.96 (d, 2H, J = 8.2 Hz), 7.04-7.06 (m, 2H), 7.16-7.25

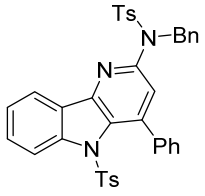
(m, 7H), 7.29-7.32 (m, 3H), 7.41-7.45 (m, 1H), 7.53-7.57 (m, 1H), 7.99 (d, 1H, *J* = 7.2 Hz), 8.17 (d, 1H, *J* = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.7, 22.4, 28.8, 28.9, 29.6, 31.0, 37.7, 55.5, 119.3, 120.3, 125.7, 126.5, 127.8, 127.9, 128.1, 128.3, 128.5, 129.1, 129.3, 129.8, 130.1, 133.5, 133.7, 135.4, 136.6, 137.2, 142.99, 143.01, 144.4, 145.7, 150.2; IR (neat) (cm^{-1}) 2923w, 1371s, 1342s, 1179s, 1152s, 1025w; HRMS (ESI): m/z calcd for $C_{38}H_{40}N_3O_4S_2$ $[M+H]^+$: 666.2455; found 666.2451.



5n

3-Amino-δ-carboline **5n** (106.3 mg, 0.13 mmol) was prepared from ynamide-nitrile **4a** (74.5 mg, 0.20 mmol) and ynamide **2p**[10] (100.7 mg, 0.22 mmol) in 64% yield after stirring at rt for 21.0 h.

5n: R_f = 0.47 [4:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.09 (s, 6H), 0.82 (s, 9H), 0.91-0.98 (m, 2H), 2.25 (s, 3H), 2.46 (s, 3H), 2.64-2.83 (m, 2H), 3.12 (t, 2H, *J* = 6.3 Hz), 4.44 (d, 1H, *J* = 12.7 Hz), 4.91 (d, 1H, *J* = 12.7 Hz), 6.98 (d, 2H, *J* = 8.2 Hz), 7.04-7.06 (m, 2H), 7.10-7.20 (m, 9H), 7.35-7.40 (m, 4H), 7.45-7.48 (m, 2H), 7.51-7.55 (m, 1H), 7.62 (d, 1H, *J* = 7.6 Hz), 8.20 (d, 1H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.2, 18.4, 21.7, 21.8, 25.9, 26.2, 31.8, 54.6, 63.3, 119.7, 120.2, 125.8, 126.9, 128.1, 128.16, 128.19, 128.23, 128.4, 129.0, 129.05, 129.13, 129.3, 129.7, 130.1, 133.2, 133.3, 135.2, 135.4, 136.7, 137.2, 142.9, 143.0, 143.6, 144.4, 145.7, 150.2; IR (neat) (cm^{-1}) 2924w, 1453w, 1350m, 1176m, 1089s, 1006w; HRMS (ESI): m/z calcd for $C_{47}H_{52}N_3O_5S_2Si$ $[M+H]^+$: 830.3112; found 830.3108.

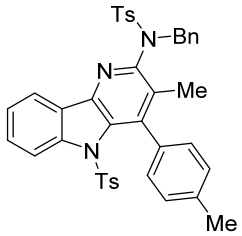


5o

3-Amino-δ-carboline **5o** (72.4 mg, 0.11 mmol) was prepared from ynamide-nitrile **4a** (74.5 mg, 0.20 mmol) and ynamide **2o** (62.8 mg, 0.22 mmol) in 55% yield after stirring at rt for 0.5 h.

5o: R_f = 0.32 [4:1 petroleum ether/EtOAc]; white solid; mp = 160–161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.41 (s, 3H), 5.05 (s, 2H), 6.80-6.83 (m, 2H), 6.90-6.93 (m, 2H), 7.15-7.21 (m, 5H), 7.32-7.38 (m, 3H), 7.44-7.55 (m, 7H), 7.72-7.77 (m, 3H), 8.20 (dt, 1H, *J* = 8.3, 0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 21.8, 51.6, 119.5, 120.7, 122.2, 126.0, 127.0, 127.6, 128.0, 128.43, 128.45, 128.6, 128.68, 128.70, 128.85, 128.89, 129.4, 129.5, 130.8, 131.9, 136.0, 136.7, 138.8, 142.8,

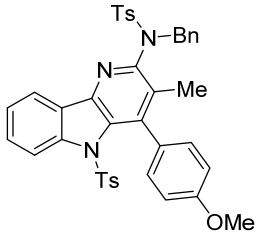
143.1, 143.8, 144.5, 148.4, 150.7; IR (neat) (cm^{-1}) 1590w, 1373m, 1354s, 1174m, 1164s, 1090w; HRMS (ESI): m/z calcd for $C_{38}H_{32}N_3O_4S_2$ $[M+H]^+$: 658.1829; found 658.1841.



5p

3-Amino-δ-carboline **5p** (135.8 mg, 0.20 mmol) was prepared from ynamide-nitrile **4b** (77.3 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 99% yield after stirring at rt for 0.5 h.

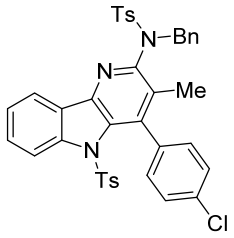
5p: R_f = 0.36 [4:1 petroleum ether/EtOAc]; white solid; mp = 160–161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3H), 2.25 (s, 3H), 2.39 (s, 3H), 2.46 (s, 3H), 4.45 (s, 1H), 4.92 (s, 1H), 6.95-6.97 (m, 2H), 7.03-7.06 (m, 2H), 7.12-7.20 (m, 11H), 7.37 (td, 1H, J = 7.5, 0.9 Hz), 7.50-7.54 (m, 3H), 7.65 (dq, 1H, J = 7.7, 0.7 Hz), 8.19 (dt, 1H, J = 8.4, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2, 21.6, 21.7, 21.8, 54.4, 119.4, 120.1, 125.7, 126.7, 128.0, 128.2, 128.3, 128.7, 128.9, 128.98, 129.00, 129.1, 129.7, 133.0, 133.2, 133.4, 134.2, 135.38, 135.40, 137.7, 142.7, 142.8, 143.6, 144.3, 145.5, 150.3, one carbon missing due to overlap; IR (neat) (cm^{-1}) 1596w, 1449w, 1376m,1187w, 1177s, 1022w; HRMS (ESI): m/z calcd for $C_{40}H_{36}N_3O_4S_2$ $[M+H]^+$: 686.2142; found 686.2159.



5q

3-Amino-δ-carboline **5q** (139.0 mg, 0.20 mmol) was prepared from ynamide-nitrile **4c**[1] (80.5 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 99% yield after stirring at rt for 10.0 min.

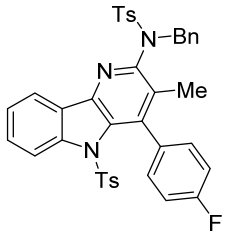
5q: R_f = 0.68 [2:1 petroleum ether/EtOAc]; white solid; mp = 171–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H), 2.25 (s, 3H), 2.46 (s, 3H), 3.83 (s, 3H), 4.45 (s, 1H), 4.93 (s, 1H), 6.87 (d, 2H, J = 8.6 Hz), 6.97 (d, 2H, J = 8.2 Hz), 7.04-7.06 (m, 2H), 7.12-7.20 (m, 9H), 7.38 (t, 1H, J = 7.5 Hz), 7.50-7.54 (m, 3H), 7.65 (d, 1H, J = 7.6 Hz), 8.18 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.1, 21.7, 21.8, 54.4, 55.3, 113.4, 119.4, 120.1, 125.7, 126.7, 128.0, 128.2, 128.3, 129.0, 129.1, 129.5, 129.7, 131.0, 133.2, 133.36, 133.43, 135.39, 135.42, 142.4, 142.8, 143.6, 144.3, 145.5, 150.3, 159.3, two carbons missing due to overlap; IR (neat) (cm^{-1}) 1610w, 1513w, 1350m, 1249m, 1164s, 1089w; HRMS (ESI): m/z calcd for $C_{40}H_{36}N_3O_5S_2$ $[M+H]^+$: 702.2091; found 702.2092.



5r

3-Amino-δ-carboline **5r** (134.2 mg, 0.19 mmol) was prepared from ynamide-nitrile **4d**[1] (81.4 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 95% yield after stirring at rt for 0.5 h.

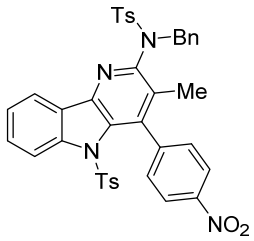
5r: R_f = 0.43 [4:1 petroleum ether/EtOAc]; white solid; mp = 168–169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.02 (s, 3H), 2.28 (s, 3H), 2.46 (s, 3H), 4.46 (s, 1H), 4.93 (s, 1H), 6.99-7.27 (m, 15H), 7.39 (t, 1H, J = 7.4 Hz), 7.51-7.56 (m, 3H), 7.69 (d, 1H, J = 7.5 Hz), 8.17 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.1, 21.7, 21.8, 54.4, 119.1, 120.2, 125.7, 126.4, 127.8, 128.0, 128.27, 128.29, 129.0, 129.1, 129.2, 129.6, 131.1, 132.6, 132.9, 133.7, 134.1, 135.3, 135.4, 141.0, 142.7, 143.7, 144.5, 145.4, 150.2, two carbons missing due to overlap; IR (neat) (cm^{-1}) 1596w, 1493w, 1347m, 1235w, 1176m, 1088m; HRMS (ESI): m/z calcd for $C_{39}H_{33}ClN_3O_4S_2$ $[M+H]^+$: 706.1596; found 706.1592.



5s

3-Amino-δ-carboline **5s** (129.7 mg, 0.19 mmol) was prepared from ynamide-nitrile **4e** (78.1 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 94% yield after stirring at rt for 0.5 h.

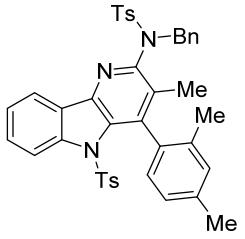
5s: R_f = 0.40 [4:1 petroleum ether/EtOAc]; white solid; mp = 258–259 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3H), 2.27 (s, 3H), 2.47 (s, 3H), 4.45 (s, 1H), 4.92 (s, 1H), 6.97-7.06 (m, 6H), 7.12-7.21 (m, 9H), 7.37-7.41 (m, 1H), 7.51-7.56 (m, 3H), 7.65-7.68 (m, 1H), 8.18 (d, 1H, J = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.1, 21.7, 21.8, 54.4, 115.2 (d, J = 21.4 Hz), 119.3, 120.2, 125.8, 126.6, 128.00, 128.01, 128.3, 129.0, 129.08, 129.15, 129.7, 131.6 (d, J = 8.3 Hz), 132.9, 133.0, 133.06, 133.08, 133.4, 135.32, 135.34, 141.5, 142.8, 143.7, 144.6, 145.6, 150.4, 162.5 (d, J = 246.1 Hz); IR (neat) (cm^{-1}) 2924w, 1598w, 1458w, 1360s, 1232w, 1168m; HRMS (ESI): m/z calcd for $C_{39}H_{33}FN_3O_4S_2$ $[M+H]^+$: 690.1891; found 690.1892.



5t

3-Amino-δ-carboline **5t** (131.9 mg, 0.18 mmol) was prepared from ynamide-nitrile **4f** (83.5 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 92% yield after stirring at rt for 0.5 h.

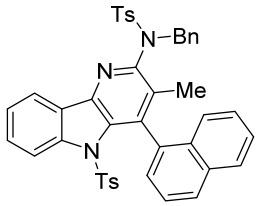
5t: R_f = 0.27 [4:1 petroleum ether/EtOAc]; white solid; mp = 80–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3H), 2.28 (s, 3H), 2.48 (s, 3H), 4.46 (s, 1H), 4.94 (s, 1H), 6.97-7.05 (m, 4H), 7.12-7.34 (m, 9H), 7.40-7.44 (m, 1H), 7.53-7.58 (m, 3H), 7.69 (d, 1H, J = 7.6 Hz), 8.17-8.21 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2, 21.7, 21.8, 54.4, 119.2, 120.4, 123.4, 126.0, 126.6, 127.7, 128.1, 128.4, 129.0, 129.19, 129.23, 129.5, 129.7, 130.9, 132.16, 132.21, 133.2, 135.1, 135.2, 139.9, 142.6, 143.8, 143.9, 145.0, 145.8, 147.5, 150.6; IR (neat) (cm^{-1}) 1518w, 1344s, 1234w, 1162m, 1089w, 1026w; HRMS (ESI): m/z calcd for $C_{39}H_{33}N_4O_6S_2$ $[M+H]^+$: 717.1836; found 717.1832.



5u

3-Amino-δ-carboline **5u** (138.6 mg, 0.20 mmol) was prepared from ynamide-nitrile **4g** (80.1 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 99% yield after stirring at rt for 10.0 min.

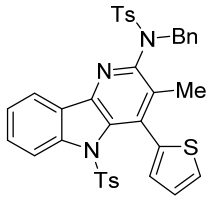
5u: R_f = 0.45 [4:1 petroleum ether/EtOAc]; white solid; mp = 205–206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42-1.57 (m, 2H), 1.80 (s, 3H), 2.08 (s, 1H), 2.31 (s, 3H), 2.32 (s, 3H), 2.50 (s, 3H), 4.38-4.99 (m, 2H), 6.55-7.14 (m, 12H), 7.25-7.29 (m, 2H), 7.40 (t, 1H, J = 7.5 Hz), 7.51-7.76 (m, 4H), 8.18 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6, 21.5, 21.7, 21.8, 118.5, 120.3, 125.2, 126.0, 126.2, 127.3, 127.9, 128.3, 128.9, 129.1, 129.2, 129.9, 130.5, 133.0, 134.0, 135.2, 135.6, 137.8, 142.5, 143.6, 144.1, 144.4, 149.6, eight carbons missing due to overlap and steric hindrance. IR (neat) (cm^{-1}) 2923w, 1614w, 1458w, 1358m, 1342m, 1158m; HRMS (ESI): m/z calcd for $C_{41}H_{38}N_3O_4S_2$ $[M+H]^+$: 700.2298; found 700.2292.



5v

3-Amino-δ-carboline **5v** (142.9 mg, 0.20 mmol) was prepared from ynamide-nitrile **4h**[1] (84.5 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 99% yield after stirring at rt for 10.0 min.

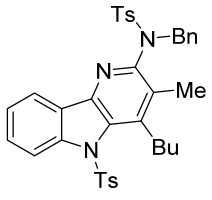
5v: R_f = 0.29 [4:1 petroleum ether/EtOAc]; white solid; mp = 89–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72-1.81 (m, 3H), 2.24 (s, 3H), 2.53 (s, 3H), 4.34-5.04 (m, 2H), 6.85-7.59 (m, 19H), 7.75-7.84 (m, 4H), 8.18 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 21.9, 125.3, 126.0, 128.0, 128.4, 128.6, 128.8, 129.0, 129.1, 129.3, 130.1, 142.6, 143.7, 149.7, twelve carbons missing due to overlap and steric hindrance. IR (neat) (cm^{-1}) 2925w, 1597w, 1456w, 1373m, 1350m, 1162s; HRMS (ESI): m/z calcd for $C_{43}H_{36}N_3O_4S_2$ $[M+H]^+$: 722.2142; found 722.2143.



5w

3-Amino-δ-carboline **5w** (123.4 mg, 0.18 mmol) was prepared from ynamide-nitrile **4i**[1] (75.7 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 91% yield after stirring at rt for 10.0 min.

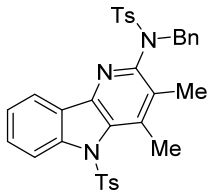
5w: R_f = 0.33 [4:1 petroleum ether/EtOAc]; white solid; mp = 257–258 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 2.25 (s, 3H), 2.45 (s, 3H), 4.44 (s, 1H), 4.92 (s, 1H), 6.95 (d, 2H, J = 8.2 Hz), 7.03-7.05 (m, 2H), 7.12-7.19 (m, 9H), 7.37 (t, 1H, J = 7.4 Hz), 7.45-7.55 (m, 4H), 7.60 (d, 1H, J = 7.6 Hz), 8.21 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5, 21.7, 21.8, 54.3, 119.8, 120.2, 126.0, 127.0, 127.4, 128.0, 128.3, 128.4, 128.9, 129.0, 129.1, 129.2, 129.6, 129.7, 132.5, 133.6, 133.7, 135.2, 135.3, 136.1, 137.4, 142.9, 143.7, 144.6, 146.0, 150.6, one carbon missing due to overlap; IR (neat) (cm^{-1}) 1598w, 1457w, 1360m, 1339w, 1174w, 1091w; HRMS (ESI): m/z calcd for $C_{37}H_{32}N_3O_4S_3$ $[M+H]^+$: 678.1549; found 678.1546.



5x

3-Amino-δ-carboline **5x** (108.2 mg, 0.17 mmol) was prepared from ynamide-nitrile **4j** (70.5 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 83% yield after stirring at rt for 0.5 h.

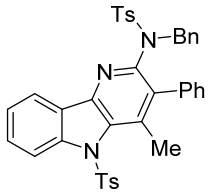
5x: R_f = 0.46 [4:1 petroleum ether/EtOAc]; white solid; mp = 144–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 (t, 3H, J = 7.3 Hz), 1.05-1.16 (m, 2H), 1.24-1.31 (m, 2H), 2.13 (s, 6H), 2.37 (s, 3H), 3.11 (s, 1H), 3.34 (s, 1H), 4.23 (d, 1H, J = 12.7 Hz), 4.83 (d, 1H, J = 12.6 Hz), 6.84 (q, 4H, J = 7.9 Hz), 6.98-7.10 (m, 7H), 7.24 (t, 1H, J = 7.4 Hz), 7.35-7.43 (m, 4H), 8.11 (d, 1H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 15.4, 21.6, 21.8, 22.8, 30.68, 30.74, 54.5, 120.1, 120.4, 126.3, 127.4, 128.0, 128.3, 128.78, 128.83, 128.9, 129.1, 129.5, 129.7, 131.3, 133.7, 134.8, 135.3, 135.4, 143.3, 143.5, 144.6, 146.1, 146.4, 150.5; IR (neat) (cm^{-1}) 2923w, 1458w, 1369m, 1344m, 1164s, 1088m; HRMS (ESI): m/z calcd for $C_{37}H_{38}N_3O_4S_2$ $[M+H]^+$: 652.2298; found 652.2305.



5y

3-Amino-δ-carboline **5y** (108.5 mg, 0.18 mmol) was prepared from ynamide-nitrile **4k**[1] (62.1 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 89% yield after stirring at rt for 1.0 h.

5y: R_f = 0.50 [4:1 petroleum ether/EtOAc]; white solid; mp = 212–213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.23 (s, 3H), 2.44 (s, 3H), 2.64 (s, 3H), 4.35 (d, 1H, J = 13.0 Hz), 4.92 (d, 1H, J = 12.8 Hz), 6.89 (d, 2H, J = 8.2 Hz), 6.94-6.96 (m, 2H), 7.11-7.22 (m, 7H), 7.29-7.33 (m, 1H), 7.45-7.51 (m, 4H), 8.18 (d, 1H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 19.3, 21.7, 21.8, 54.4, 120.0, 120.2, 126.2, 127.3, 128.0, 128.3, 128.8, 128.9, 129.0, 129.1, 129.2, 129.5, 131.6, 134.0, 135.1, 135.4, 135.5, 141.3, 143.1, 143.6, 144.7, 146.1, 149.6; IR (neat) (cm^{-1}) 2924w, 1596w, 1338m, 1287w, 1176s, 1089w; HRMS (ESI): m/z calcd for $C_{34}H_{32}N_3O_4S_2$ $[M+H]^+$: 610.1829; found 610.1832.

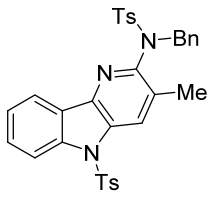


5z

3-Amino-δ-carboline **5z** (112.7 mg, 0.17 mmol) was prepared from ynamide-nitrile **4k** (62.1 mg, 0.20 mmol) and ynamide **2k** (79.5 mg, 0.22 mmol) in 84% yield after stirring at rt for 1.0 h.

5z: R_f = 0.59 [4:1 petroleum ether/EtOAc]; white solid; mp = 253–254 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 3H), 2.40 (s, 3H), 2.45 (s, 3H), 4.44 (s, 2H), 6.73 (d, 2H, J = 7.4 Hz), 6.95 (d, 2H, J = 8.1 Hz), 7.05-7.10 (m, 4H), 7.16-7.56 (m, 12H), 7.71 (d, 1H, J = 7.6 Hz), 8.23 (d, 1H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.7, 21.8, 54.1, 119.9, 120.7, 126.3, 127.2, 127.5, 127.8, 128.0,

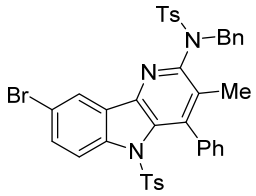
128.2, 128.9, 128.96, 129.04, 129.3, 129.4, 130.0, 130.6, 131.8, 135.0, 135.3, 135.9, 136.2, 138.2, 141.6, 143.4, 143.5, 144.9, 147.3, 148.8; IR (neat) (cm^{-1}) 1597w, 1348m, 1173m, 1158s, 1088w, 1027w; HRMS (ESI): m/z calcd for $C_{39}H_{34}N_3O_4S_2$ $[M+H]^+$: 672.1985; found 672.1982.



5aa

3-Amino-δ-carboline **5aa** (47.7 mg, 0.08 mmol) was prepared from ynamide-nitrile **4l**[1] (59.3 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 40% yield after stirring at rt for 24.0 h.

5aa: R_f = 0.32 [4:1 petroleum ether/EtOAc]; white solid; mp = 154–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.34 (s, 3H), 2.47 (s, 3H), 4.67 (s, 2H), 7.09-7.20 (m, 7H), 7.27-7.29 (m, 2H), 7.38-7.41 (m, 1H), 7.55-7.59 (m, 1H), 7.66-7.73 (m, 4H), 7.85 (dq, 1H, J = 7.7, 0.7 Hz), 8.25-8.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 21.77, 21.80, 54.7, 115.0, 120.5, 124.4, 124.8, 125.4, 126.8, 127.9, 128.3, 129.08, 129.13, 129.3, 129.6, 130.2, 132.0, 134.2, 134.9, 135.5, 135.6, 139.4, 141.6, 143.7, 145.6, 148.7; IR (neat) (cm^{-1}) 2922w, 1596w, 1455w, 1344s, 1204w, 1159s; HRMS (ESI): m/z calcd for $C_{33}H_{30}N_3O_4S_2$ $[M+H]^+$: 596.1672; found 596.1678.

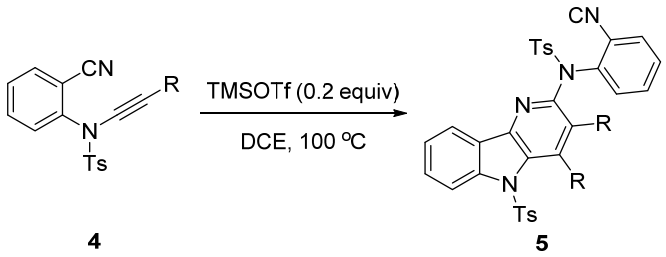


5bb

3-Amino-δ-carboline **5bb** (141.1 mg, 0.19 mmol) was prepared from ynamide-nitrile **4m** (90.3 mg, 0.20 mmol) and ynamide **2a** (65.9 mg, 0.22 mmol) in 94% yield after stirring at rt for 0.5 h.

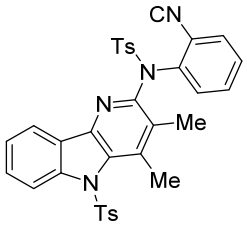
5bb: R_f = 0.43 [4:1 petroleum ether/EtOAc]; white solid; mp = 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3H), 2.28 (s, 3H), 2.51 (s, 3H), 4.40 (s, 1H), 4.97 (s, 1H), 6.98-7.04 (m, 4H), 7.10-7.29 (m, 9H), 7.37-7.40 (m, 3H), 7.48-7.50 (m, 2H), 7.62 (dd, 1H, J = 8.8, 2.2 Hz), 7.70 (d, 1H, J = 2.1 Hz), 8.08 (d, 1H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.3, 21.7, 21.9, 54.7, 119.4, 120.9, 123.1, 126.8, 128.1, 128.2, 128.3, 128.4, 129.0, 129.2, 129.3, 129.7, 129.8, 131.8, 133.1, 133.2, 134.0, 135.2, 135.3, 137.0, 141.5, 142.8, 143.9, 144.1, 144.8, 150.7, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2925w, 1597w, 1350m, 1163s, 1090m, 1013m; HRMS (ESI): m/z calcd for $C_{39}H_{32}BrN_3O_4S_2$ $[M+Na]^+$: 772.0910; found 772.0947.

General Procedure for Synthesis of 3-Amino-δ-Carbolines 5cc and 5dd.



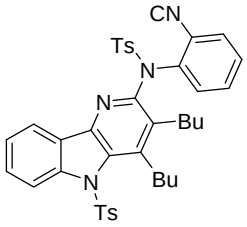
4 **5**

To an oven-dried sealed tube was added ynamide-nitrile **4k** (62.1 mg, 0.20 mmol), DCE (1.0 mL, ynamide-nitrile *concn* = 0.20 *M*) and TMSOTf (7.2 μL, 0.04 mmol) at rt. When the reaction was judged to be completed by TLC after stirring at 100 ^{o}C for 15.0 min, the mixture was purified by flash silica gel column chromatrography [gradient eluent: 4:1~2:1 petroleum ether/EtOAc] to afford 3-amino-δ-carboline **5cc** (38.5 mg, 0.06 mmol) in 62% yield.



5cc

5cc: R_f = 0.25 [2:1 petroleum ether/EtOAc]; white solid; mp = 203–204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 3H), 2.45 (s, 3H), 2.77 (s, 3H), 2.80 (s, 3H), 6.92 (d, 2H, *J* = 8.2 Hz), 7.02-7.04 (m, 2H), 7.10 (d, 2H, *J* = 8.1 Hz), 7.23-7.26 (m, 2H), 7.31-7.35 (m, 1H), 7.40-7.45 (m, 3H), 7.48-7.52 (m, 1H), 7.61-7.65 (m, 1H), 7.75-7.79 (m, 1H), 8.18 (d, 1H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0, 19.7, 21.7, 21.9, 116.1, 117.7, 119.9, 120.2, 126.1, 127.3, 128.75, 128.82, 129.0, 129.2, 129.9, 131.2, 131.8, 132.8, 133.1, 134.3, 134.9, 135.6, 141.9, 142.1, 143.2, 144.2, 144.8, 145.7, 150.0, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2234w, 1595w, 1450w, 1354s, 1289w, 1169s; HRMS (ESI): m/z calcd for $C_{34}H_{29}N_4O_4S_2$ $[M+H]^+$: 621.1625; found 621.1627.



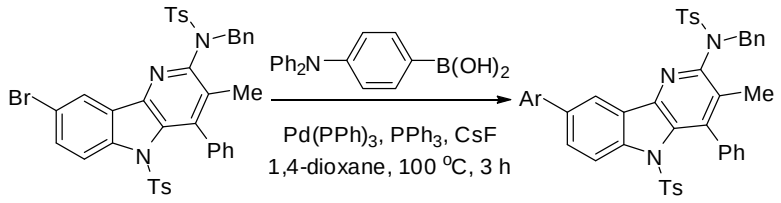
5dd

3-Amino-δ-carboline **5dd** (39.5 mg, 0.06 mmol) was prepared from ynamide-nitrile **4j** (70.5 mg, 0.20 mmol) in 56% yield after stirring at 100 ^{o}C for 10.0 min.

5dd: R_f = 0.26 [4:1 petroleum ether/EtOAc]; white solid; mp = 122–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 3H, *J* = 7.3 Hz), 1.03 (t, 3H, *J* = 6.8 Hz), 1.30-1.39 (m, 2H), 1.48-1.56 (m, 2H), 1.59-1.69 (m, 4H), 2.23 (s, 3H), 2.46 (s, 3H), 3.11 (t, 2H, *J* = 7.9 Hz), 3.46 (s, 2H), 6.94 (s, 4H), 7.08

(d, 2H, J = 8.2 Hz), 7.14-7.16 (m, 2H), 7.32-7.44 (m, 4H), 7.50-7.58 (m, 2H), 7.81 (dd, 1H, J = 7.5, 1.9 Hz), 8.20 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.3, 21.7, 21.9, 23.3, 28.3, 30.0, 32.0, 33.7, 115.8, 117.4, 120.2, 120.6, 126.3, 127.3, 128.5, 128.6, 129.0, 129.19, 129.22, 130.1, 131.1, 132.8, 134.5, 135.2, 135.5, 136.4, 142.3, 143.7, 143.9, 144.9, 146.4, 147.0, 150.9, two carbons missing due to overlap; IR (neat) (cm^{-1}) 2922w, 1595w, 1446w, 1361s, 1165s, 1086m; HRMS (ESI): m/z calcd for $C_{40}H_{41}N_4O_4S_2$ $[M+H]^+$: 705.2564; found 705.2567.

General Procedure for Synthesis of 3-Amino-δ-Carboline 6.[3]

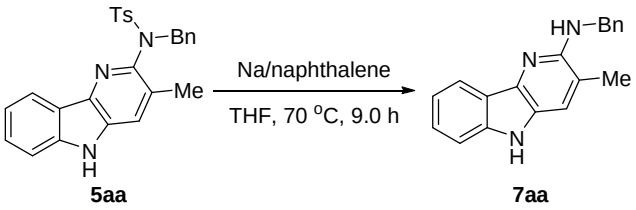


5bb **6:** 99%

To an oven-dried sealed tube was added 3-amino-δ-carboline **5bb** (75.1 mg, 0.10 mmol), (4-benzhydrylphenyl)boronic acid (69.4 mg, 0.24 mmol), Pd $(PPh_3)_4$ (11.6 mg, 0.01 mmol), PPh_3 (5.2 mg, 0.02 mmol), CsF (48.6 mg, 0.32 mmol) and 1,4-dioxane (1.25 mL) in sequence. The solution was heated to 100 °C and monitored by TLC analysis. When the reaction was judged to be completed after 3.0 h, the reaction mixture was cooled to rt, filtered through a celite pad, concentrated in vacuo, and purified by flash silica gel column chromatrography [gradient eluent: 10:1~4:1 petroleum ether/EtOAc] to afford 3-amino-δ-carboline **6** (90.6 mg, 0.10 mmol) in 99% yield.

6: R_f = 0.38 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 3H), 2.26 (s, 3H), 2.40 (s, 3H), 4.43 (s, 1H), 4.97 (s, 1H), 6.97 (d, 2H, J = 8.1 Hz), 7.05-7.09 (m, 3H), 7.11-7.23 (m, 13H), 7.28-7.32 (m, 4H), 7.36-7.40 (m, 5H), 7.52-7.56 (m, 4H), 7.68-7.79 (m, 3H), 8.22 (d, 1H, J = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2, 21.7, 21.8, 54.7, 117.8, 119.7, 123.4, 124.1, 124.6, 126.9, 127.7, 128.0, 128.09, 128.15, 128.3, 128.7, 129.12, 129.13, 129.2, 129.5, 129.8, 133.19, 133.23, 133.3, 134.2, 135.3, 135.5, 137.2, 138.4, 141.7, 142.7, 143.6, 144.5, 145.6, 147.7, 147.8, 150.5, two carbons missing due to overlap; IR (neat) (cm^{-1}) 2924w, 1589m, 1471m, 1348s, 1274m, 1089m; HRMS (ESI): m/z calcd for $C_{57}H_{47}N_4O_4S_2$ $[M+H]^+$: 915.3033; found 915.3021.

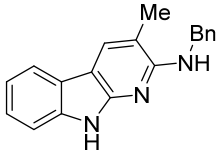
General Procedure for Synthesis of Carbolines 7aa, 9x and 9z.[11]



5aa **7aa**

To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol) and THF (1.6 mL) at rt. Then a solution of naphthalene (160.2 mg, 1.25 mmol) in THF (0.4 mL) was added and stirred until the intense green color was observed. To this solution was added a solution of 3-amino-δ-carboline **5aa** (59.6 mg, 0.10 mmol) in THF (0.4 mL). The reaction mixture was heated to 70 ^{o}C and stirred for 9.0 h. After completion of the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [gradient eluent: 4:1~1:1 petroleum ether/EtOAc] to afford the desired product **7aa** (28.2 mg, 0.10 mmol) in 98% yield.

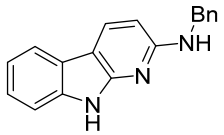
7aa: R_f = 0.58 [2:1 petroleum ether/EtOAc]; yellow solid; mp = 210–211 °C; ^{1}H NMR (400 MHz, DMSO) δ 2.27 (s, 3H), 4.70 (d, 2H, J = 5.8 Hz), 6.16 (t, 1H, J = 6.0 Hz), 7.04-7.08 (m, 1H), 7.14-7.18 (m, 1H), 7.25-7.30 (m, 3H), 7.38-7.40 (m, 1H), 7.46-7.50 (m, 3H), 7.92 (d, 1H, J = 7.8 Hz), 10.74 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 18.3, 44.9, 111.6, 116.7, 118.3, 119.5, 121.0, 121.8, 125.3, 126.5, 127.0, 127.9, 128.2, 136.1, 139.5, 142.1, 152.3; IR (neat) (cm^{-1}) 3308m, 1585m, 1479s, 1379w, 1254m, 1006s; HRMS (ESI): m/z calcd for $C_{19}H_{18}N_3$ $[M+H]^+$: 288.1495; found 288.1496.



9x

2-Amino-α-carboline **9x** (24.1 mg, 0.08 mmol) was prepared from 2-amino-α-carboline **3x** (59.6 mg, 0.10 mmol) in 84% yield after stirring at 70 ^{o}C for 9.0 h.

9x: R_f = 0.42 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 90–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 3H), 4.60 (t, 1H, J = 5.5 Hz), 4.78 (d, 2H, J = 5.2 Hz), 7.17 (t, 1H, J = 7.4 Hz), 7.24-7.37 (m, 5H), 7.41-7.43 (m, 2H), 7.82 (d, 1H, J = 7.6 Hz), 7.89 (s, 1H), 8.45 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6, 46.3, 106.3, 109.4, 110.7, 118.9, 119.7, 122.6, 123.6, 127.4, 128.1, 128.8, 130.1, 136.8, 140.0, 150.7, 155.6; IR (neat) (cm^{-1}) 3401m, 1608s, 1484s, 1349m, 1239s, 1147w; HRMS (ESI): m/z calcd for $C_{19}H_{18}N_3$ $[M+H]^+$: 288.1495; found 288.1498.

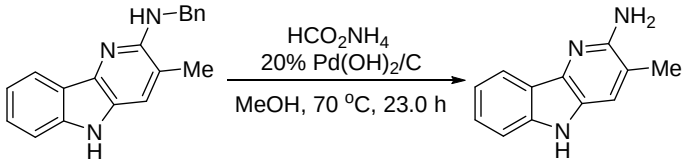


9z

2-Amino-α-carboline **9z** (25.7 mg, 0.09 mmol) was prepared from 2-amino-α-carboline **3z** (58.2 mg, 0.10 mmol) in 94% yield after stirring at 70 ^{o}C for 9.0 h.

9z: R_f = 0.22 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 150–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61 (d, 2H, J = 5.4 Hz), 5.06 (t, 1H, J = 5.6 Hz), 6.31 (d, 1H, J = 8.4 Hz), 7.15-7.19 (m, 1H), 7.23-7.40 (m, 7H), 7.82 (d, 1H, J = 7.7 Hz), 8.02 (d, 1H, J = 8.4 Hz), 9.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.8, 100.4, 107.3, 110.7, 119.1, 120.0, 122.6, 124.1, 127.5, 127.7, 128.8, 130.7, 137.1, 139.4, 152.1, 157.6; IR (neat) (cm^{-1}) 3056w, 1615s, 1524m, 1416s, 1327m, 1233s; HRMS (ESI): m/z calcd for $C_{18}H_{16}N_3$ $[M+H]^+$: 274.1339; found 274.1340.

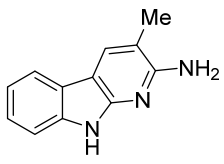
General Procedure for Synthesis of Carbolines 8aa, 10x and 10z.[12]



7aa **8aa**

To an oven-dried sealed tube was added 3-amino-δ-carboline **7aa** (28.7 mg, 0.1 mmol), 20% $Pd(OH)_2$/C (28.7 mg), HCO_2NH_4 (31.5 mg, 5.0 mmol) and MeOH (1.0 mL) at rt. Then the reaction mixture was heated to 70 ^{o}C and stirred for 23.0 h. After completion of the reaction, the mixture was filtered over a celite pad. Then the solvent was concentrated to afford the desired product **8aa** (19.5 mg, 0.10 mmol) in 99% yield.

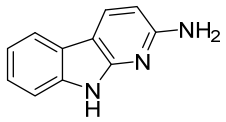
8aa: R_f = 0.24 [1:2 petroleum ether/EtOAc]; white solid; mp = 209–210 °C; ^{1}H NMR (400 MHz, DMSO) δ 2.23 (s, 3H), 5.49 (s, 2H), 7.08 (t, 1H, J = 7.4 Hz), 7.31 (t, 1H, J = 7.4 Hz), 7.41 (d, 1H, J = 8.1 Hz), 7.49 (s, 1H), 7.92 (d, 1H, J = 7.8 Hz), 10.81 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 18.2, 111.4, 115.9, 118.1, 119.2, 120.8, 121.2, 125.1, 127.4, 136.1, 139.5, 153.1; IR (neat) (cm^{-1}) 3402w, 1632w, 1560w, 1421s, 1254m, 1005m; HRMS (ESI): m/z calcd for $C_{12}H_{12}N_3$ $[M+H]^+$: 198.1026; found 198.1025.



10x

2-Amino-α-carboline **10x** (19.5 mg, 0.10 mmol) was prepared from 2-amino-α-carboline **9x** (28.7 mg, 0.10 mmol) in 99% yield after stirring at 70 ^{o}C for 23.0 h.

10x: R_f = 0.31 [1:2 petroleum ether/EtOAc]; white solid; mp = 187–188 °C; ^{1}H NMR (400 MHz, DMSO) δ 2.17 (s, 3H), 5.85 (s, 2H), 7.04 (t, 1H, *J* = 7.4 Hz), 7.17 (t, 1H, *J* = 7.6 Hz), 7.31 (d, 1H, *J* = 8.0 Hz), 7.78 (d, 1H, *J* = 7.7 Hz), 7.90 (s, 1H), 11.01 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 17.5, 105.3, 108.3, 110.4, 118.3, 118.6, 121.8, 122.8, 129.7, 137.0, 150.6, 157.0; IR (neat) (cm^{-1}) 3321w, 1629s, 1574m, 1416s, 1311s, 1227s; HRMS (ESI): m/z calcd for $C_{12}H_{12}N_3$ $[M+H]^+$: 198.1026; found 198.1025.

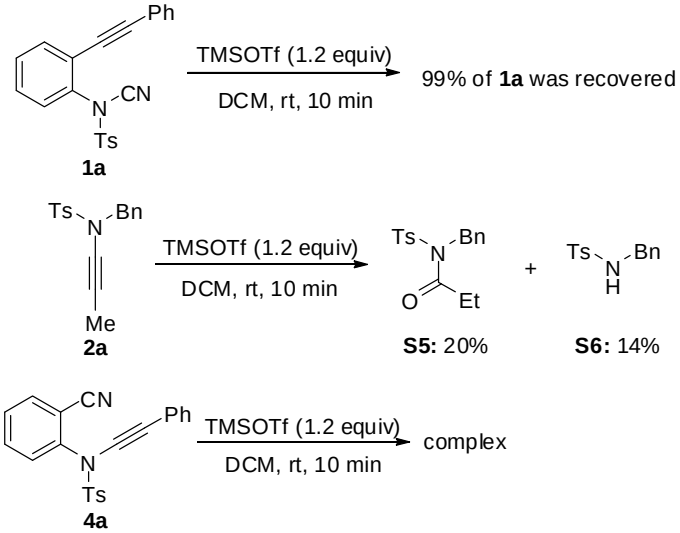


10z

2-Amino-α-carboline **10z** (18.1 mg, 0.10 mmol) was prepared from 2-amino-α-carboline **9z** (27.3 mg, 0.10 mmol) in 99% yield after stirring at 70 ^{o}C for 23.0 h.

10z: R_f = 0.31 [1:2 petroleum ether/EtOAc]; white solid; mp = 171–172 °C; ^{1}H NMR (400 MHz, DMSO) δ 6.08 (s, 2H), 6.31-6.34 (m, 1H), 7.06 (t, 1H, *J* = 7.4 Hz), 7.18 (t, 1H, *J* = 7.5 Hz), 7.31-7.33 (m, 1H), 7.79 (d, 1H, *J* = 7.7 Hz), 8.02 (d, 1H, *J* = 8.2 Hz), 11.11 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 101.1, 104.8, 110.5, 118.3, 118.8, 122.0, 122.9, 129.9, 137.0, 152.0, 158.7; IR (neat) (cm^{-1}) 3152w, 1607s, 1571s, 1458s, 1354s, 1127m; HRMS (ESI): m/z calcd for $C_{11}H_{10}N_3$ $[M+H]^+$: 184.0869; found 184.0870.

Further Investigation of the Mechanisms.



Above reactions were carried out to further investigate the mechanisms. Considering most of the cycloadditions of alkyne-cyanamide **1** with ynamide **2** in the present of 0.2 equiv TMSOTf could be completed within 10min, we used the starting materials **1a**, **2a** and **4a** to react with excess TMSOTf

within 10 min, respectively. From the experiments, we can see that there was no reaction occured for **1a**, and 99% of the starting material was recovered. But for the reaction of **2a**, the starting material **2a** was depleted with products **S5** and **S6** afforded. So we proposed that the catalyst TMSOTf should coordinate to ynamide **2** forming an intermediate to initiate the cycloaddition of alkyne-cyanamide **1** with ynamide **2**. For the reaction of **4a**, the reaction was complex. Considering that the ynamide-nitrile **4a** is a kind of ynamide, we thought that TMSOTf should also coordinate to the alkynyl group not nitrile group, and the previous work also referred to this.[13] Because ynamide **2** is more active than ynamide-nitrile **4**, so the cycloaddition of ynamide-nitrile **4** with ynamide **2** would also be initiated via the coordination to ynamide **2** by TMSOTf.

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