Supporting Information

Rhodium(III)-Catalyzed Indole Synthesis at Room Temperature

Using the Transient Oxidizing Directing Group Strategy

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General Information. All reactions were carried out in dried glass wares under a dry nitrogen atmosphere using Schlenk technique. The air and moisture sensitive reagents were stored in a dry and nitrogen-filled glove box. All commercially available reagents were purchased from Sigma-Aldrichi, Acros, Alfa Aesar, TCI, Adamas-beta, Sinocompound and other commercial suppliers and used directly without further purification. All solvents used in the reactions were freshly distilled according to the stored under a nitrogen atmosphere. Especially, standard methods and Dichloromethane (CH₂Cl₂) and dichloroethane (DCE) were distilled over CaH₂ and stored under a nitrogen atmosphere. ¹H NMR (400 MHz), ¹³C NMR (100 MHz) and ¹⁹F NMR (377 MHz) spectra were recorded in CDCl₃ solutions using a Bruker AVANCE 400 spectrometer at 298 K. The chemical shifts (δ) were calibrated using TMS (0 ppm for ¹H) and residual undeuterated solvent CHCl₃ (77.0 ppm for 13 C). HRMS (High-Resolution Mass Spectra) were performed by the Shanghai Mass Spectrometry Center in Shanghai Institute of Organic Chemistry, Chinese Academic of Sciences (Instrument: Thermo Fisher Scientific LTQ FT Ultra, Operation Mode: DART Positive). Reactions were monitored by TLC and detected the target compound by the UV light (254 nm or 365 nm). The desired products were purified by flash chromatography using silica gel (300-400 mesh).

Preparation and data of substrates

3-Substituted *N*-Methyl Anilines and 1-(benzyloxy)-4-(prop-1-yn-1-yl)benzene are known compounds, but prepared by following the recently reported precedures.^{1,2}

Synthesis of 3-substituted N-Methyl Anilines¹



General Procedure : In a nitrogen-filled glovebox, a 100 mL Schlenk tube equipped whit a magic stir bar was charged with aniline **1'** (5.0 mmol), [RuCp*Cl₂]₂ (0.0077 g, 0.025 mmol, 0.5 mol%), dpePhos (0.0323 g, 0.06 mmol, 1.2 mol%), LiO⁷Bu (0.0200 g, 0.25 mmol, 5 mol%). Then, the tube was fitted with a rubber septum and moved out of the glovebox. The methanol (5.0 mL) was added into the Schlenk tube through the rubber septum using syrings, and then the septum was replaced with a Telfon screwcap under nitrogen flow. Finally, the reaction mixture was stirred at 100 °C for 24 hour. When finished, the reaction mixture was cooled to room temperature and filtered through a pad of silica gel, washed with 60 mL of ethyl acetate. The organic layer was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to provide the corresponding product in 70–90 % yields.

Synthesis of 3-(methoxymethyl)-*N*-methylaniline (1aa)



This substrate was synthesized following the *general procedure*. The Schlenk tube was charged with 3-(methoxymethyl)aniline (0.6859 g, 5.0 mmol), $[RuCp*Cl_2]_2$ (0.0077 g, 0.025 mmol, 0.5 mol%), dpePhos (0.0323 g, 0.06 mmol, 1.2 mol%) and LiO'Bu (0.0200 g, 0.25 mmol, 5 mol%) in methanol (5.0 mL) and the reaction mixture was stirred at 100 °C for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100 : 4), the product **1aa** was obtained.

Physical state : colorless oil;

¹**H NMR** (400 MHz, CDCl₃): δ 7.15 (t, *J* = 7.7 Hz, 1H), 6.66 (d, *J* = 7.4 Hz, 1H), 6.59 (s, 1H), 6.53 (d, *J* = 8.0, 1.9 Hz, 1H), 4.39 (s, 2H), 3.72 (s, 1H), 3.37 (s, 3H), 2.81 (s, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 149.5, 139.2, 129.1, 116.5, 111.7, 111.4, 74.9, 57.9, 30.6.

Synthesis of 3-fluoro-*N*-methylaniline (1ab)



This substrate was synthesized following the *general procedure*. The Schlenk tube was charged with 3-fluoroaniline (0.5556 g, 5.0 mmol), $[RuCp*Cl_2]_2$ (0.0077 g, 0.025 mmol, 0.5 mol%), dpePhos (0.0323 g, 0.06 mmol, 1.2 mol%) and LiO'Bu (0.0200 g, 0.25 mmol, 5 mol%) in methanol (5.0 mL) and the reaction mixture was stirred at 100 °C for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100 : 2), the product **1ab** was obtained.

Physical state: colorless oil;

¹**H NMR** (400 MHz, CDCl₃): δ 7.1 (q, *J* = 8.0 Hz, 1H), 6.4 (ddd, *J* = 10.7, 8.3, 2.0 Hz, 2H), 6.3 (dt, *J* = 11.7, 2.1 Hz, 1H), 3.8 (s, 1H), 2.8 (s, 3H);

¹⁹**F NMR** (377MHz, CDCl₃): δ -113.07;

¹³**C NMR** (100 MHz, CDCl₃): δ 164.2 (d, *J* = 242.5 Hz), 151.1 (d, *J* = 10.8 Hz), 130.2 (d, *J* = 10.3 Hz), 108.3 (d, *J* = 2.2 Hz), 103.5 (d, *J* = 21.6 Hz), 98.9 (d, *J* = 25.3 Hz), 30.6.

Synthesis of 3-iodo-N-methylaniline (1ae)



This substrate was synthesized following the *general procedure*. The Schlenk tube was charged with 3-iodoaniline (1.0951 g, 5.0 mmol), $[RuCp*Cl_2]_2$ (0.0077 g, 0.025 mmol, 0.5 mol%), dpePhos (0.0323 g, 0.06 mmol, 1.2 mol%) and LiO^{*t*}Bu (0.0200 g, 0.25 mmol, 5 mol%) in methanol (5.0 mL) and the reaction mixture was stirred at 100 °C for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100 : 2), the product **1ae** was obtained.

Physical state: colorless oil;

¹**H NMR** (400 MHz, CDCl₃): δ 7.00 (d, J = 7.7 Hz, 1H), 6.90 - 6.84 (m, 2H), 6.51 (d, J = 10.2 Hz, 1H), 3.68 (s, 1H), 2.76 (s, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 150.4, 130.5, 125.9, 120.7, 111.7, 95.2, 30.4.

Synthesis of 3'-N-methylaminoacetophenone (1ah)



This substrate was synthesized following the *general procedure*. The Schlenk tube was charged with 3'-aminoacetophenone (0.6758 g, 5.0 mmol), $[RuCp*Cl_2]_2$ (0.0077 g, 0.025 mmol, 0.5 mol%), dpePhos (0.0323 g, 0.06 mmol, 1.2 mol%) and LiO'Bu (0.0200 g, 0.25 mmol, 5 mol%) in methanol (5.0 mL) and the reaction mixture was stirred at 100 °C for 48 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100 : 4), the product **1ah** was obtained.

Physical state: colorless oil;

¹**H NMR** (400 MHz, CDCl₃): δ 7.28-7.25 (m, 2H), 7.18-7.17 (m, 1H), 6.80-6.77 (m, 1H), 3.93 (s, 1H), 2.86 (s, 3H), 2.56 (s, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 198.7, 149.4, 138.0, 129.2, 117.5, 117.2, 110.8, 30.5, 26.7.

Synthesis of 4-(benzyloxy)-N-(4-(2-chloroethoxy)benzyl)aniline (1ai)³



1ai was prepared using the reported procedure ^[3] 4-benzyloxyaniline (1 g, 5 mmol), 4-(2-chloroethoxy)benzaldehyde (0.923 g, 5 mmol). The product **1ai** was obtained as white solid in 72% yield (1.320 g).

Physical state: white solid;

¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, J = 6.8 Hz, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.30 (m, 3H), 6.88 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.9 Hz, 2H), 6.61 (d, J = 8.9 Hz, 2H), 4.98 (s, 2H), 4.22 (t, J = 5.9 Hz, 2H), 4.21(s, 2H), 3.81 (t, J = 5.9 Hz, 2H);
¹³C NMR (100 MHz, CDCl₃):δ 157.6, 151.8, 142.1, 137.6, 132.1, 129.2, 128.6, 127.9, 127.6, 116.2, 114.9, 114.6, 70.9, 68.2, 49.0, 42.0;



Synthesis of 4-(ethylamino)phenyl acetate (1aj)

A 50 mL Schlenk flask equipped whit a magic stir bar was charged with 4-iodophenol (2.20 g, 10 mmol), ethyl amine (1.1 mL, 2equiv.), CuI (0.19 g, 10 mol%), L-proline (0.2302g, 20 mol%), K₂CO₃ (2.76g, 2 equiv.) and DMSO (6 mL). the reaction mixture was stirred at 60 °C for 12 hours. After cooling down, the reaction mixture was diluted with 25 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the same solvent (25 mL). The collected filtrate was washed with water (3×25mL), and the organic phase was dried over Na₂SO₄, filtered, concentrated under reduced pressure. The residue was then purified by chromatography on silica gel with pentane/ ethyl acetate (4:1) as eluent to afford *p*-ethylaminophenol as white solid (0.49g, 36% yield). This newly obtained p-ethylaminophenol (274.4 mg, 2 mmol) was treated with t-butyl dicarbonate (048 mL, lequiv.) in THF (8 mL) at room temperature for 12 hours. Then, the solvent was revomed under reduced pressure. The obtained residue was washed with hexane (10 mL x 3) and then dissolved in toluene (10 mL). To the resulting toluene solution, acetic anhydride (02 mL, 1equiv.), sodium acetate (0.16 g, 1equiv.) was added, and the reaction mixture was stirred at 110 °C for 12 hours. After cooling down, the reaction mixture was filtered through a pad of silica gel with several washings, and concentrated. The residue was dissolved in CH2Cl2 (6 mL) and then stirred with CF₃COOH (0.5 mL) at room temperature for 3 hours. Then the reaction mixture was neutralized with K₂CO₃ aqueous solution (0.5 M, 15 mL), extracted with ethyl estate (10 mL x 3). The organic phase was dried over Na₂SO₄ and concentrated under reduced pressure to give the product 1aj (215 mg, 60% yield).

Physical state: white solid;

¹H NMR (400 MHz, CDCl₃): δ 6.91 – 6.85 (m, 2H), 6.56 (d, J = 8.8 Hz, 2H), 3.11 (q, J = 7.1 Hz, 3H), 2.25 (s, 3H), 1.23 (t, J = 7.2 Hz, 4H);
¹³C NMR (100 MHz, CDCl₃): δ 170.4, 146.4, 141.9, 122.1, 113.1, 38.8, 21.1, 14.8;

HRMS (ESI): Calcd for $C_{10}H_{14}NO_2$ ([M + H]⁺) : 180.1019, found: 180.1018.

Synthesis of 1-(benzyloxy)-4-(prop-1-yn-1-yl)benzene (2t)^{2a}



In a nitrogen-filled glovebox, a 150 mL Schlenk flask equipped whit a magic stir bar was charged with 1-(benzyloxy)-4-iodobenzene(3.1013 g, 10.0 mmol), $PdCl_2(PPh_3)_2$ (0.1404 g, 0.2 mmol, 2 mol%), CuI (0.0381 g, 0.2 mmol, 2 mol%), "Bu₄NF· 3H₂O (3.1551 g, 1.0 equiv.). Then, the tube was fitted with a rubber septum and moved out of the glovebox. The trimethyl(prop-1-yn-1-yl)silane (2.2448 g, 2.0 equiv.), THF (60.0 mL), and Et₃N (6.0 mL) were added into the Schlenk tube through the rubber septum using syrings, and then the septum was replaced with a Telfon screwcap under nitrogen flow. Finally, the reaction mixture was stirred at room temperature for 24 hours. When finished, the reaction mixture was cooled to room temperature and filtered through a pad of silica gel, washed with 60 mL of ethyl acetate. The organic layer was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to provide product **2t**.

Physical state: slight yellow solid;

¹**H NMR** (400 MHz, CDCl₃): δ 7.39-7.26 (m, 7H), 6.86-6.82 (m, 2H), 4.97 (s, 2H), 1.98 (s, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 158.1, 136.6, 132.7, 128.5, 127.9, 127.4, 116.4, 114.6, 84.2, 79.4, 69.8, 4.2.

Synthesis of 4-(prop-1-yn-1-yl)phenyl acetate (2u)^{2b}



Under nitrogen flow, a 100 mL Schlenk flask equipped with a magic stir bar was charged with 4-iodophenol (2.20 g, 10 mmol), 1M solution of 1-propyne in THF (15 mL, 1.5 equiv.), Pd(PPh₃)2Cl₂ (0.142 g, 4 mol%), CuI (0.181g, 1 mol%), THF (10 mL) and triethyl amine (TFA) (25 mL). After the reaction mixture was stirred at room temperature for 3 hours, the solvent was removed under reduced pressure. The resultant residue was extracted with ethyl acetate (15 mL), and filtered through a pad of silica gel with washings. The filtrate is concentrated under reduced pressure to dark oil. The obtained dark oil was treated with acetic anhydride (1 mL) and sodium acetate (0.82 g) in toluene (15 mL) at 110 °C for 12 hours. The reaction mixture was filtered through a pad of silica gel with washings, concentrated. The the residue was purified by flash chromatography on silica gel with pentane/ ethyl acetate (4 :1) as eluent to provide the corresponding product **2u** (1.22 g, 70% yield).

Physical state: slight cyan solid;

¹**H NMR** (400 MHz, CDCl₃): δ 7.39 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.2 Hz, 2H), 2.24 (s, 3H), 2.01 (s, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 169.2, 149.9, 132.6, 121.7, 121.5, 86.0, 79.0, 21.0, 4.2.

Screening of the Reaction Conditions

 Table S1. Optimization of the reaction conditions.^a

		[Cp*RhCl ₂] ₂ (2.5 mol%) Ag salt (10 mol%), additive		
	$\begin{array}{c} & & \\ & & \\ & H \\ & H \end{array} + P H = H \\ H \end{array}$	Isoamyl nitrite (1.5 equiv), so room temperature, 24 h	Ivent Ph	= Ph
	1a :	2a		3a
entry	solvent	additive	Ag salt (10	Yield(%) ^b
	(1.0 mL)		mol%)	
1	DCM	-	AgSbF ₆	40
2	DCE	-	AgSbF ₆	31
3	1,4-dioxane	-	AgSbF ₆	trace
4	chlorobenzene	-	AgSbF ₆	trace
5	CH ₃ CN	-	AgSbF ₆	0
6	DMF	-	AgSbF ₆	0
7	tert-amyl	-	AgSbF ₆	0
	alcohol			
8 ^c	DCM	-	-	24
9	DCM	-	AgBF ₄	0
10	DCM	-	AgOAc	42
11	DCM	-	Ag ₃ PO ₄	14
12	DCM	-	Ag ₂ CO ₃	25
13	DCM	-	Ag ₂ O	0
14	DCM	LiOAc (1.0 equiv)	AgSbF ₆	34
15	DCM	NaOAc (1.0 equiv)	AgSbF ₆	7
16	DCM	KOAc (1.0 equiv)	AgSbF ₆	0
17	DCM	CsOAc (1.0 equiv)	AgSbF ₆	0
18	DCM	HOAc (1.0 equiv)	AgSbF ₆	65
19	DCM	PivOH (1.0 equiv)	AgSbF ₆	70
20	DCM	PivOH (0.5 equiv)	AgSbF ₆	68
21	DCM	benzoic acid (0.5 equiv)	AgSbF ₆	57

22	DCM	2,4,6-trimenthylbenzoic	AgSbF ₆	40	
		acid (50 mol%)			
23	DCM	1-Adamantanecarboxylic	AgSbF ₆	41	
		acid (50 mol%)			
24	DCM	<i>p-</i> ^{<i>t</i>} BuPhCOOH (50	AgSbF6	83	
mol%)					
25	DCM	m-NO ₂ -PhCOOH (50	AgSbF ₆	38	
		mol%)			
26	DCM	p-OMe-PhCOOH (50	AgSbF ₆	31	
		mol%)			
27^d	DCM	<i>p</i> - <i>t</i> BuPhCOOH (50 mol%)	AgSbF ₆	40	

^{*a*}Reaction Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $[Cp*RhCl_2]_2$ (0.005 mmol, 2.5 mol%), Ag Salt (0.02 mmol, 10 mol%), additive (0.5 - 1.0 equiv.), *iso*-amyl nitrite (0.3 mmol), N₂ and solvent (1.0 mL) at room temperature for 24 h. ^{*b*}Yield of isolated product. ^{*c*}Cp*Rh(CH₃CN)₃[SbF₆]₂(0.01mmol, 5 mol) was used. ^{*d*}*t*-butyl nitrite (0.3 mmol) was used as oxidant.

Experimental Procedures

In a nitrogen-filled glovebox, a 25 mL Schlenk tube equipped with a stir bar was charged [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) or PivOH (0.0204 g, 1.0 equiv.), disubstituted alkynes (0.3 mmol) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The tube was fitted with a rubber septum and moved out of the glove box. Then *N*-alkyl anilines (0.2 mmol) and dichloromethane (1.0 mL) were added to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at room temperature for 24 h. when the reaction finished, the reaction mixture was diluted with 10 mL of ethyl acetate and filtered through a pad of silica gel. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel to provide the corresponding product.

Product Characterization



1,2-Diphenyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinolone (3a)

3a (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3a** was obtained in 83% yield (51.5 mg, slight yellow solid). ¹H NMR (400MHz, CDCl₃): δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.23 (m, 7H), 7.18 (t, *J* = 7.1 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.0 Hz, 1H), 3.99 – 3.97 (m, 2H), 2.95 (t, *J* = 6.1 Hz, 2H), 2.13 (p, *J* = 6.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) : δ 136.0, 135.6, 134.3, 131.8, 130.7, 129.7, 128.4, 128.2, 127.8, 125.3, 125.0, 122.0, 120.2, 119.1, 117.0, 114.4, 43.2, 25.1, 23.0. *This compound has been known.* ^[4a] *Its NMR spectra are identical withthe authorized ones.*



1-Methyl-2,3-diphenyl-1*H*-indole (3b)

3b (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with *N*-methylaniline (0.0214 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), $[Cp*RhCl_2]_2$ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3b** was obtained in 65% yield

(37.0 mg, white solid). ¹**H NMR** (400MHz, CDCl₃): δ 7.80 (d, J = 7.9 Hz, 1H), 7.41 – 7.14 (m, 13H), 3.65 (s, 3H). *This compound has been known*. ^[4a] Its NMR spectra are *identical withthe authorized ones*.



1-Ethyl-2,3-diphenyl-1*H*-indole (3c)

3c (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with *N*-ethylaniline (0.0242 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3c** was obtained in 84% yield (50.0 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.81 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.12 (m, 12H), 4.12 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). *This compound has been known.* ^[4b] *Its NMR spectra are identical withthe authorized ones.*



1-Isopropyl-2,3-diphenyl-1*H*-indole (3d)

3d (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with *N*-isopropylaniline (0.0242 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), $[Cp*RhCl_2]_2$ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3d** was obtained in 88% yield

(55.3 mg, white solid). ¹**H** NMR (400MHz, CDCl₃): δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.35 – 7.10 (m, 12H), 4.56 – 4.51 (m, 1H), 1.60 (s, 3H), 1.59 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) : δ 137.5, 135.2, 134.6, 132.8, 131.1, 129.9, 128.3, 128.1, 128.0, 128.0, 125.3, 121.5, 119.9, 119.7, 115.1, 112.2, 47.8, 21.5. *This compound has been known*. ^[4b] Its NMR spectra are identical with the authorized ones.



1-Cyclohexyl-2,3-diphenyl-1*H*-indole (3e)

3e (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with *N*-cyclohexylaniline (0.0351g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3e** was obtained in 70% yield (49.3 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.34 (m, 3H), 7.29 – 7.20 (m, 7H), 7.15 – 7.11 (m, 2H), 4.11 – 4.05 (m, 1H), 2.38 (q, *J* = 12.1, 11.0 Hz, 2H), 1.94 – 1.84 (m, 4H), 1.33 – 1.17 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 137.7, 135.3, 135.0, 132.8, 131.1, 129.9, 128.3, 128.0, 127.9, 125.3, 121.3, 119.8, 119.6, 115.1, 112.6, 56.4, 31.5, 26.2, 25.5; HRMS (ESI) Calcd for C₂₆H₂₆N ([M + H]⁺) : 352.2060, found : 352.2057.



1,2,3-Triphenyl-1*H*-indole (3f)

3f (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with diphenylamine (0.0338g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%),

4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3f** was obtained in 73% yield (50.7 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.72 (d, *J* = 5.4 Hz, 1H), 7.32 – 7.20 (m, 8H), 7.15 – 7.12 (m, 5H), 7.08 – 7.00 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ 138.1, 137.9, 137.0, 134.9, 131.6, 131.2, 130.2, 129.0, 128.2, 127.9, 127.5, 127.3, 127.1, 125.9, 122.7, 120.9, 119.6, 116.7, 110.6. *This compound has been known*. ^[5] *Its NMR spectra are identical withthe authorized ones*.



1-Benzyl-2,3-diphenyl-1*H*-indole (3g)

3g (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with *N*-benzylaniline (0.0367g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3g** was obtained in 83% yield (59.5 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.83 (d, *J* = 8.9 Hz, 1H), 7.34 (d, *J* = 7.1 Hz, 2H), 7.27 – 7.13 (m, 14H), 6.98 (d, *J* = 6.8 Hz, 2H), 5.25 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 138.0, 137.8, 136.9, 135.1, 131.7, 131.0, 129.9, 128.6, 128.3, 128.2, 128.1, 127.3, 127.1, 126.0, 125.5, 122.3, 120.4, 119.7, 115.6, 110.5, 47.5. *This compound has been known.* ^[5] *Its NMR spectra are identical withthe authorized ones.*



1-Allyl-2,3-diphenyl-1*H*-indole (3h)

3h (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with *N*-allylaniline (0.0266g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3h** was obtained in 72% yield (44.6 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.16 (m, 13H), 5.99 - 5.89 (m, 1H), 5.17 (d, *J* = 10.4 Hz, 1H), 4.99 (d, *J* = 17.1 Hz, 1H), 4.65 (d, *J* = 4.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 137.6, 136.8, 135.1, 133.7, 131.8, 131.0, 129.8, 128.3, 128.1, 127.2, 125.5, 122.2, 120.3, 119.7, 116.6, 115.4, 110.3 46.5; HRMS (ESI) Calcd for C₂₃H₂₀N ([M + H]⁺) : 310.1590, found : 310.1588.



3-(2,3-Diphenyl-1*H*-indol-1-yl)propanenitrile (3i)

3i (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 3-(phenylamino)-propanenitrile (0.0292g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:2), the product **3i** was obtained in 55% yield (35.2 mg, white solid). ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, J = 7.9 Hz, 1H), 7.40 – 7.37 (m, 4H), 7.33 – 7.14 (m, 9H), 4.40 – 4.36 (m, 2H), 2.55 – 2.51 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 136.6, 135.8, 134.3, 130.9, 129.7, 128.8, 128.7, 128.2, 127.6, 125.8, 122.8, 121.0, 120.2, 116.9, 116.8, 109.2, 39.3, 18.0; HRMS (ESI)

Calcd for $C_{23}H_{19}N_2([M + H]^+)$: 323.1543, found: 323.1543.



4,4,6,9-Tetramethyl-1,2-diphenyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinoline (3j)

3j (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 1,2,3,4-tetrahydro-2,2,4,7-tetramethylquinoline (0.0379g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:2), the product **3j** was obtained in 71% yield (52.0 mg, pale yellow oil). ¹H NMR (400MHz, CDCl₃): δ 7.33 – 7.10 (m, 7H), 7.01 – 6.93 (m, 4H), 6.79 – 6.76 (m, 1H), 3.20 – 3.19 (m, 1H), 2.04 (s, 3H), 1.89 – 1.76 (m, 2H), 1.45 (s, 3H), 1.40 (s, 3H), 1.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 137.0, 136.8, 134.8, 133.0, 132.2, 132.1, 131.6, 128.0, 127.8, 127.5, 127.2, 126.8, 125.7, 124.6, 123.8, 121.1, 118.2, 116.7, 56.4, 49.1, 30.2, 28.9, 26.7, 20.1, 18.6; HRMS (ESI) Calcd for C₂₇H₂₈N ([M + H]⁺) : 366.2216, found : 366.2214.

Ph N Ph

1,2-Diphenyl-6,7-dihydrobenzo[6,7]azepino[3,2,1-hi]indole (3k)

3k (0.2 mmol scale) was synthesized following the *general procedurewith slight modifications*. The reaction was carried out with 5,6,11,11 a-tetrahydro-4aH-benzo[b][1]benzazepine(0.0395g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g,

0.3 mmol). The reaction mixture was stirred at 80 °C in DCE (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3k** was obtained in 75% yield (55.7 mg, white solid). *This compound has been known*. ^[4b] Its NMR spectra are identical with the authorized ones.



9-Methyl-1,2-diphenyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (31)

31 (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 7-methyl-1,2,3,4-tetrahydroquinoline (0.0294 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **31** was obtained in 70% yield (45.7 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.32 – 7.17 (m, 10H), 7.10 – 7.06 (m, 1H), 6.76 (s, 1H), 3.97 (t, *J* = 5.6 Hz, 2H), 2.92 (t, *J* = 5.6 Hz, 2H), 2.37 (s, 3H), 2.15 – 2.11 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 135.9, 135.8, 132.8, 131.9, 130.6, 129.6, 129.6, 128.3, 128.1, 127.6, 125.2, 125.1, 121.6, 120.8, 116.4, 113.9, 43.0, 24.9, 23.1, 21.8; HRMS (ESI) Calcd for C₂₄H₂₂N ([M + H]⁺) : 324.1747, found : 324.1744.



8-Fluoro-4-methyl-1,2-diphenyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (3m)
3m (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 6-fluoro-1,2,3,4-tetrahydro-2-methylquinoline (0.0330 g, 0.2)

mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3m** was obtained in 76% yield (52.0 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.38 – 7.20 (m, 10H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 9.6 Hz, 1H), 4.60 -4.57 (m, 1H), 3.12 – 3.03 (m, 1H), 2.95 - 2.89 (m, 1H), 2.33 – 2.23 (m, 1H), 2.08 – 2.03 (m, 1H), 1.03 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 158.8 (d, *J* = 234.1 Hz), 137.1, 135.1, 131.8, 130.7, 129.9, 129.2, 128.5, 128.2, 125.3, 125.0 (d, *J* = 10.3 Hz), 122.4 (d, *J* = 9.6 Hz), 115.1 (d, *J* = 5.0 Hz), 107.8 (d, *J* = 26.5 Hz), 101.7 (d, *J* = 24.7 Hz), 46.8, 28.2, 20.7 (d, *J* = 1.5 Hz), 20.2; HRMS (ESI) Calcd for C₂₄H₂₁FN ([M + H]⁺):342.1653, found : 342.1650.



8-Bromo-1,2-diphenyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinoline (3n)

3n (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 6-bromo-1,2,3,4-tetrahydroquinoline (0.0424 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3n** was obtained in 71% yield (55.1 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.73 (d, *J* = 1.4 Hz, 1H), 7.37 – 7.23 (m, 9H), 7.18 – 7.13 (m, 1H), 7.07 (s, 1H), 4.01 (t, *J* = 4.0 Hz, 2H), 2.96 (t, *J* = 6.1 Hz, 2H), 2.15 (p, *J* = 6.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 136.8, 134.9, 132.9, 131.1, 130.6, 129.5, 128.4, 128.3, 128.0, 126.4, 125.6, 123.7, 122.0, 119.4, 114.0, 113.5, 43.1, 24.8, 22.7; HRMS (ESI) Calcd for C₂₃H₁₉BrN ([M +

H]⁺) : 388.0695, found : 388.0693.



5-Chloro-2,3-bis(4-isopropylphenyl)-1-methyl-1*H*-indole (30)

30 (0.2 mmol scale) was synthesized following the general procedure. The reaction out with 4-chloro-N-methylaniline (0.0283 was carried g, 0.2 mmol), 1,2-bis(4-isopropylphenyl)acetylene (0.0787 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **30** was obtained in 76% yield (61.0 mg, pale yellow oil). ¹H NMR (400MHz, CDCl₃): δ 7.74 (d, J = 1.9 Hz, 1H), 7.28 – 7.12 (m, 10H), 3.62 (s, 3H), 2.97 – 2.84 (m, 2H), 1.28 (d, J = 6.9 Hz, 6H), 1.25 (d, J = 6.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 148.8, 146.1, 138.9, 135.6, 131.9, 130.9, 129.5, 128.8, 128.2, 126.4, 126.3, 125.7, 122.0, 119.1, 114.5, 110.4, 33.9, 33.7, 31.1, 23.9, 23.9; HRMS (ESI) Calcd for C₂₇H₂₉ClN $([M + H]^+)$: 402.1983, found : 402.1981.



1,5-Dimethyl-2,3-diphenyl-1*H*-indole (3p)

3p (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with *N*-methyl-*p*-toluidine (0.0242 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), $[Cp*RhCl_2]_2$ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel

(petroleum ether/diethyl ether = 100:1), the product **3p** was obtained in 78% yield (46.5 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.57 (s, 1H), 7.37 – 7.23 (m, 10H), 7.18 – 7.10 (m, 2H), 3.62 (s, 3H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 137.8, 135.8, 135.4, 132.0, 131.1, 129.9, 129.4, 128.3, 128.1, 127.9, 127.1, 125.4, 123.7, 119.1, 114.6, 109.3, 30.9, 21.5. *This compound has been known*. ^[4a] Its NMR spectra are identical withthe authorized ones.



7-Chloro-1-methyl-2,3-diphenyl-1*H*-indole (3q)

3q (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 2-chloro-*N*-methylaniline (0.0283 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3q** was obtained in 76% yield (48.2 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.14 (m, 11H), 7.02 (t, *J* = 7.8 Hz, 1H), 3.97 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 139.9, 134.5, 133.0, 131.4, 131.3, 130.2, 130.0, 128.4, 128.2, 128.2, 125.8, 123.9, 120.7, 118.3, 117.2, 115.9, 34.2; HRMS (ESI) Calcd for C₂₁H₁₇ClN ([M + H]⁺) : 318.1044, found : 318.1042.



7-Methoxy-1-methyl-2,3-diphenyl-1*H*-indole (3r)

3r (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 2-methoxy-*N*-methylaniline (0.0274 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆

(0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:2), the product **3r** was obtained in 66% yield (41.5 mg, white solid). Its NMR spectra are identical withthe authorized ones.¹H NMR (400MHz, CDCl₃): δ 7.37 – 7.22 (m, 10H), 7.15 (t, *J* = 6.6 Hz, 1H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 3.96 (s, 3H), 3.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.8, 138.6, 135.4, 132.0, 131.3, 129.9, 129.1, 128.3, 128.0, 127.9, 127.1, 125.4, 120.4, 115.5, 112.4, 103.2, 55.6, 34.2. *This compound has been known.* ^[5] Its NMR spectra are identical withthe authorized ones.



5-Methoxy-1-methyl-2,3-diphenyl-1*H*-indole (3s)

3s (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 4-methoxy-*N*-methylaniline (0.0274 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:2), the product **3s** was obtained in 72% yield (45.0 mg, white solid). Its NMR spectra are identical withthe authorized ones. ¹H NMR (400MHz, CDCl₃): δ 7.37 - 7.33 (m, 3H), 7.29 - 7.24 (m, 8H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 3.83 (s, 3H), 3.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 154.8, 138.3, 135.3, 132.7, 131.9, 131.0, 129.7, 128.3, 128.2, 127.9, 127.2, 125.4, 114.8, 112.4, 110.3, 101.2, 56.0, 31.0. *This compound has been known*. ^[4b] Its NMR spectra are identical withthe authorized ones.



Methyl 1-methyl-2,3-diphenyl-1*H*-indole-7-carboxylate (3t)

3t (0.2 mmol scale) was synthesized following the *general procedure with slight modifications*. The reaction was carried out with dimethyl anthranilate (0.0330 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 50 °C in DCE (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product **3t** was obtained in 71% yield (48.5 mg, white solid). ¹**H NMR** (400MHz, CDCl₃): δ 7.89 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.37 – 7.25 (m, 9H), 7.21 – 7.16 (m, 2H), 3.99 (s, 3H), 3.63 (s, 3H); ¹³**C NMR** (100 MHz, CDCl₃): δ 168.3, 140.5, 135.4, 134.6, 131.5, 131.2, 130.0, 129.6, 128.3, 128.2, 128.1, 125.9, 125.3, 123.8, 119.3, 116.3, 116.0, 52.2, 35.2; HRMS (ESI) Calcd for C₂₃H₂₀NO₂ ([M + H]⁺) : 342.1489, found : 342.1486.



methyl 1-methyl-2,3-diphenyl-1*H*-indole-5-carboxylate (3u)

3u (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with methyl 4-(methylamino)benzoate (0.0330 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product **3u** was obtained in 85% yield (58.3 mg, white solid). ¹H NMR (400 MHz, CDCl₃): δ 8.52 (s, 1H), 8.00 (d *J* = 8.6 Hz, 1H), 7.40 - 7.26 (m, 10H), 7.22-7.19 (m, 1H), 3.91 (s, 3H), 3.66 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 168.1, 139.6, 138.9, 134.3, 131.2, 131.0, 129.8, 128.4, 128.3, 126.6, 125.9, 123.5, 122.6, 122.1, 116.4, 109.2, 51.8, 31.1. *This compound has been known.* ^[4a] Its NMR spectra are identical withthe authorized ones.



1-Methyl-5-nitro-2,3-diphenyl-1*H*-indole (3v)

3v (0.2 mmol scale) was synthesized following the *general procedure with slight modifications*. The reaction was carried out with *N*-methyl-4-nitroaniline (0.0304 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), $[Cp*RhCl_2]_2$ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 50 °C in DCE (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:2), the product **3v** was obtained in 71% yield (46.6 mg, yellow solid). ¹H NMR (400MHz, CDCl₃): δ 8.67 (d, *J* = 2.1 Hz, 1H), 8.16 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.42 – 7.38 (m, 4H), 7.34 – 7.23 (m, 7H), 3.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 142.0, 140.6, 139.9, 133.4, 130.9, 130.5, 129.7, 128.8, 128.6, 128.5, 126.4, 126.4, 117.6, 117.4, 116.9, 109.5, 31.4; HRMS (ESI) Calcd for C₂₁H₁₇N₂O₂ ([M + H]⁺) : 329.1284, found : 329.1285.



1-Methyl-7-nitro-2,3-diphenyl-1*H*-indole (3w)

3w (0.2 mmol scale) was synthesized following the *general procedurewith slight modifications*. The reaction was carried out with *N*-methyl-2-nitroaniline (0.0304 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), $[Cp*RhCl_2]_2$ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 50 °C in DCE (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:2), the product **3w** was obtained in 76% yield (50.0 mg, yellow solid). ¹H NMR (400MHz, CDCl₃): δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.16 (m, 11H), 3.57 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 141.8, 136.7, 133.7, 132.0, 131.1, 130.5, 130.0, 129.2, 128.6, 128.5, 128.4, 126.4, 125.5, 119.9, 119.2, 116.6, 35.1; HRMS (ESI) Calcd for C₂₁H₁₇N₂O₂ ([M + H]⁺) : 329.1285, found : 329.1282.



1-Methyl-2,3-diphenyl-1*H*-indole-5-carbonitrile (3x)

3x (0.2 mmol scale) was synthesized following the *general procedurewith slight modifications*. The reaction was carried out with 4-(methylamino)benzonitrile (0.0264 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 50 °C in DCE (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3x** was obtained in 77% yield (47.5 mg, yellow solid). ¹H NMR (400MHz, CDCl₃): δ 8.09 (s, 1H), 7.50 – 7.22 (m, 12H), 3.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 139.7, 138.6, 133.6, 130.9, 130.6, 129.6, 128.6, 128.5, 128.4, 126.8, 126.2, 125.2, 124.9, 120.8, 115.8, 110.4, 102.9, 31.1. *This compound has been known*. ^[4a] Its NMR spectra are identical with the authorized ones.



1-Methyl-2,3-diphenyl-5-(trifluoromethyl)-1*H*-indole (3y)

3y (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 4-(methylamino)benzonitrile (0.0264 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3y** was obtained in 78% yield (54.9 mg, yellow solid). ¹H NMR (400MHz, CDCl₃): δ 8.05 (s, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.39 – 7.38 (m, 3H), 7.32 – 7.28 (m, 6H), 7.24 – 7.20 (m, 1H), 3.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 139.4, 138.5,

134.2, 131.1, 131.0, 129.8, 128.5, 128.4, 128.4, 126.4, 126.1, 125.4 (q, J = 124.1 Hz), 122.5 (q, J = 31.7 Hz), 118.8 (q, J = 3.3 Hz), 117.3 (t, J = 4.3 Hz), 116.0, 109.8, 31.1. *This compound has been known.* ^[4a] Its NMR spectra are identical with the authorized ones.

1,6-Dimethyl-2,3-diphenyl-1*H*-indole (3z)

3z (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with *N*,3-dimethylaniline (0.0242 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3z** was obtained in 75% yield (44.6 mg, yellow solid). ¹H NMR (400MHz, CDCl₃): δ 7.68 (t, *J* = 5.6 Hz, 1H), 7.33 – 7.13 (m, 11H), 7.02 (t, *J* = 6.1 Hz, 1H), 3.60 (s, 3H), 2.53 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 137.7, 137.1, 135.4, 132.1, 132.0, 131.1, 129.8, 128.3, 128.1, 127.8, 125.4, 124.9, 121.9, 119.3, 114.9, 109.5, 30.8, 21.9. *This compound has been known*. ^[4a] Its NMR spectra are identical withthe authorized ones.



6-(Methoxymethyl)-1-methyl-2,3-diphenyl-1*H*-indole (3aa)

3aa (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 3-(methoxymethyl)-*N*-methylaniline (0.0302 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), $[Cp*RhCl_2]_2$ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography

on silica gel (petroleum ether/diethyl ether = 100:3), the product **3aa** was obtained in 73% yield (47.9 mg, colorless oil). ¹H NMR (400MHz, CDCl₃): δ 7.76 (d, *J* = 8.2 Hz, 1H), 7.41 (s, 1H), 7.35 – 7.14 (m, 12H), 4.64 (s, 2H), 3.66 (s, 3H), 3.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 138.0, 137.4, 135.1, 132.3, 131.8, 131.1, 129.8, 128.3, 128.1, 128.0, 126.6, 125.5, 120.5, 119.5, 115.0, 109.0, 75.4, 57.8, 30.9; HRMS (ESI) Calcd for C₂₃H₂₂NO ([M + H]⁺) : 328.1696, found : 328.1694.



4-Fluoro-1-methyl-2,3-diphenyl-1*H*-indole (3ab)

3ab (0.2 mmol scale) was synthesized following the *general procedure with slight modifications*. The reaction was carried out with 3-fluoro-*N*-methylaniline (0.0250 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3ab** was obtained in 96% yield (57.6 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.35 – 7.34 (m, 3H), 7.29 – 7.25 (m, 4H), 7.23 – 7.21 (m, 2H), 7.20 – 7.15 (m, 3H), 6.85 – 6.80 (m, 1H), 3.65 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 156.9 (d, *J* = 248.9 Hz), 139.8 (d, *J* = 11.0 Hz), 138.2 (d, *J* = 1.5 Hz), 134.8, 131.3, 131.2, 130.8 (d, *J* = 2.6 Hz), 128.3, 128.1, 127.4, 125.8, 122.2 (d, *J* = 8.1 Hz), 115.5 (d, *J* = 18.1 Hz), 113.5, 105.6, 105.5 (d, *J* = 24.6 Hz), 31.4; ¹⁹F NMR (377MHz, CDCl₃): δ – 117.83; HRMS (ESI) Calcd for C₂₁H₁₇NF ([M + H]⁺) :302.1340, found : 302.1340.



6-Chloro-1-methyl-2,3-diphenyl-1*H*-indole (3ac)

3ac (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 3-chloro-*N*-methylaniline (0.0283 g, 0.2 mmol),

diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3ac** was obtained in 80% yield (50.9 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.58 (d, *J* = 8.5 Hz, 1H), 7.30 – 7.27 (m, 4H), 7.23 – 7.21 (m, 2H), 7.18 – 7.16 (m, 4H), 7.11 – 7.03 (m, 2H), 3.53 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 138.2, 137.7, 134.6, 131.4, 131.0, 129.7, 128.4, 128.3, 128.2, 127.9, 125.8, 125.6, 120.7, 120.5, 115.2, 109.6, 31.0. *This compound has been known*. ^[4a] Its NMR spectra are identical withthe authorized ones.



6-Bromo-1-methyl-2,3-diphenyl-1*H*-indole (3ad)

3ad (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 3-bromo-*N*-methylaniline (0.0372 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3ad** was obtained in 75% yield (54.4 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.62 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 1.4 Hz, 1H), 7.39 – 7.36 (m, 3H), 7.31 – 7.23 (m, 7H), 7.19 – 7.15 (m, 1H), 3.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 138.2, 138.1, 134.6, 131.3, 131.0, 129.7, 128.4, 128.2, 125.9, 125.8, 123.3, 120.9, 115.5, 115.2, 112.6, 31.0. *This compound has been known*. ^[4a] Its NMR spectra are identical withthe authorized ones.



6-Iodo-1-methyl-2,3-diphenyl-1*H*-indole (3ae)

3ae (0.2 mmol scale) was synthesized following the *general procedure with slight modifications*. The reaction was carried out with 3-iodo-*N*-methylaniline (0.0466 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), $[Cp*RhCl_2]_2$ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3ae** was obtained in 65% yield (53.2 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.75 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.38 – 7.35 (m, 3H), 7.29 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.26 – 7.22 (m, 4H), 7.19 – 7.15 (m, 1H), 3.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 138.6, 137.9, 134.5, 131.2, 131.0, 129.7, 128.8, 128.4, 128.2, 126.3, 125.8, 121.2, 118.7, 115.2, 85.7, 77.2, 31.0; HRMS (ESI) Calcd for C₂₁H₁₇NI ([M + H]⁺) : 410.0400, found : 410.0400.



1-Methyl-2,3-diphenyl-6-(trifluoromethyl)-1*H*-indole (3af)

3af (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with *N*-methyl-3-(trifluoromethyl)aniline (0.0350 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3af** was obtained in 76% yield (53.4 mg, colorless oil). ¹H NMR (400MHz, CDCl₃): δ 7.84 (d, *J* = 8.4 Hz, 1H), 7.69 (s, 1H), 7.42 – 7.38 (m, 4H), 7.32 (dd, *J* = 6.8, 3.0 Hz, 2H), 7.28 – 7.27 (m, 4H), 7.22 – 7.18 (m, 1H), 3.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 140.3, 136.2, 134.4, 131.1, 131.0, 129.8, 129.2, 128.5, 128.5, 128.3, 126.0, 125.3 (d, *J* = 275.7 Hz), 124.1 (d, *J* = 27.6 Hz), 119.9, 116.7 (q, *J* = 3.6 Hz), 115.5, 107.2 (q, *J* = 4.3 Hz), 31.1; HRMS (ESI) Calcd for C₂₂H₁₇F₃N ([M + H]⁺) : 352.1308, found : 352.1306.



1-Methyl-6-nitro-2,3-diphenyl-1*H*-indole (3ag)

3ag (0.2 mmol scale) was synthesized following the *general procedure with slight modifications*. The reaction was carried out with *N*-methyl-3-nitroaniline (0.0304 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), $[Cp*RhCl_2]_2$ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:2), the product **3ag** was obtained in 61% yield (40.1 mg, yellow solid). ¹H NMR (400MHz, CDCl₃): δ 8.38 (d, *J* = 2.1 Hz, 1H), 8.04 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.43 – 7.41 (m, 3H), 7.34 – 7.23 (m, 7H), 3.76 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 143.5, 142.9, 135.8, 133.6, 131.5, 130.7, 130.4, 129.7, 128.9, 128.6, 128.4, 126.3, 119.4, 116.2, 115.6, 106.7, 31.3; HRMS (ESI) Calcd for C₂₁H₁₇O₂N₂ ([M + H]⁺) : 329.1285, found : 329.1284.



1-(1-Methyl-2,3-diphenyl-1*H*-indol-6-yl)ethanone (3ah)

3ah (0.2 mmol scale) was synthesized following the *general procedure with slight modifications*. The reaction was carried out with 1-(3-(methylamino)phenyl)ethanone(0.0298 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 80 °C in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product **3ah** was obtained in 68% yield (44.2 mg, yellow solid). ¹H NMR (400 MHz, CDCl₃): δ 8.10 (s, 1H), 7.79 (d, J = 1.1 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.34 - 7.30 (m, 2H), 7.27 (d, J = 4.8 Hz, 4H), 7.21 - 7.15 (m, 1H), 3.73 (s, 3H), 2.70 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 198.3, 141.6, 136.9, 134.4, 131.4, 131.2, 131.0, 130.7, 129.8, 128.6, 128.6, 128.4, 126.0, 120.8, 119.2, 115.6, 110.6, 31.2, 27.0; HRMS (ESI) Calcd for C₂₃H₂₀NO ([M + H]⁺) : 326.1539, found : 326.1540.



5-(benzyloxy)-2-(4-(benzyloxy)phenyl)-1-(4-(2-chloroethoxy)benzyl)-3-methyl-1H -indole (3ai)

3ai was synthesized following the general procedure with slight modifications. The reaction was carried out with 4-(benzyloxy)-N-(4-(2-chloroethoxy)benzyl)aniline 1ai (0.0736g, 0.2 mmol), 1-((benzyloxy)methyl)-4-(prop-1-yn-1-yl)benzene (0.0709 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0102 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 80C° in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), the product **3ai** was obtained in 47% yield (55.2 mg, white solid). ¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, J = 7.2 Hz, 2H), 7.46 (d, J = 6.6 Hz, 2H), 7.44 – 7.32 (m, 6H), 7.24 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 2.4 Hz, 1H), 7.07 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 8.6 Hz, 2H), 6.93 - 6.84 (m, 3H), 6.77 (d, J = 8.7 Hz, 2H), 5.14 (s, 2H), 5.13 (s, 2H), 5.10(s, 2H), 4.17 (t, J = 5.9 Hz, 2H), 3.78 (t, J = 5.9 Hz, 2H), 2.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 158.7, 157.3, 153.4, 138.5, 137.9, 136.9, 132.2, 131.8, 131.6, 129.2, 128.8, 128.7, 128.2, 127.9, 127.8, 127.7, 127.5, 124.7, 114.9, 114.8, 112.4, 111.0, 108.6, 102.5, 71.1, 70.2, 68.1, 47.2, 42.1, 9.7; HRMS (ESI) Calcd for C₃₈H₃₅ClNO₃ $([M + H]^+)$: 588.2300, found: 588.2301.



1-(4-(2-(azepan-1-yl)ethoxy)benzyl)-5-(benzyloxy)-2-(4-(benzyloxy)phenyl)-3-met hyl-1H-indole (3ai-2)

A solution of **3ai** (50 mg, 0.085 mmol), azepane (100 µL, 0.86 mmol) in acetonitrile (2 mL) was stirred at 90° over night. The reaction mixture was neutralized with Na₂CO₃ aqueous and extracted with EtOAc. The crude product was purified by silica gel column chromatography using gradient eluent of EtOAc/hexane to EtOAc, the product **3ai-2** was obtained in 92% yield (50.9 mg, white solid). ¹H NMR (400 MHz, CDCl₃): δ 7.48-7.46 (m, 4H), 7.45 – 7.37 (m, 4H), 7.37 – 7.32 (m, 2H), 7.30 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.8 Hz, 1H), 7.13 (m, 3H), 6.81 (dd, J = 8.8, 2.4 Hz, 1H), 6.74 (s, 4H), 5.16 (s, 2H), 5.15 (s, 2H), 5.12 (s, 2H), 3.91 (t, J = 6.1 Hz, 2H), 2.77 (t, J = 6.0 Hz, 2H), 2.63 (m, 4H), 2.16 (s, 3H), 1.58 – 1.46 (m, 8H); ¹³C NMR (100 MHz, CDCl₃): δ 158.1, 156.6, 152.6, 137.8, 136.9, 131.5, 131.3, 128.8, 128.5, 128.4, 128.0, 127.9, 127.7, 127.6, 127.4, 123.8, 111.9, 111.2, 107.6, 102.1, 69.8, 69.4, 55.1, 54.4, 46.1, 3.10, 9.5; HRMS (ESI) Calcd for C₄₄H₄₇N₂O₃ ([M + H]⁺) : 651.3581, found: 651.3582.



Zindoxifene (3aj)

3aj (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 4-(ethylamino)phenyl acetate (0.0358g, 0.2 mmol), 4-(prop-1-yn-1-yl)phenyl acetate (0.0523 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF6 (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 40 °C in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **3aj** was obtained in 67% yield (47.2 mg, white solid). ¹H NMR (400 MHz, CDCl3): δ 7.36 (d, J = 8.6 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.20 (d, J = 8.6 Hz, 2H), 6.94 (dd, J = 8.7, 2.3 Hz, 1H), 4.02 (q, J = 7.1 Hz, 2H), 2.31 (s, 6H), 2.18 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl3): δ 170.6, 169.4, 150.5, 144.1, 137.5, 134.0, 131.5, 129.8, 128.9, 121.7,

115.7, 111.1, 110.0, 109.4, 38.9, 21.3, 15.5, 9.3. This compound has been known.^[6] Its NMR spectra are identical with the authorized ones.



1-Methyl-2,3-di-p-tolyl-1*H*-indole (4a)

4a (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with *N*-methylaniline (0.0214 g, 0.2 mmol), 1,2-di-*p*-tolylethyne (0.0619 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **4a** was obtained in 79% yield (49.2 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.79 (t, *J* = 7.9 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.29 – 7.13 (m, 8H), 7.09 – 7.05 (m, 2H), 3.59 (s, 3H), 2.34 (s, 3H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 137.7, 137.6, 137.3, 134.8, 132.3, 130.9, 129.7, 129.1, 129.0, 128.9, 127.1, 121.9, 120.0, 119.6, 114.7, 109.4, 30.8, 21.3, 21.1. *This compound has been known.* ^[4a] *Its NMR spectra are identical withthe authorized ones.*



2,3-Bis(4-ethylphenyl)-1-methyl-1*H*-indole (4b)

4b (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with *N*-methylaniline (0.0214 g, 0.2 mmol), 1,2-bis(4-ethylphenyl)ethyne (0.0703 g, 0.3 mmol), $[Cp*RhCl_2]_2$ (0.0031g, 2.5 mol%), AgSbF₆(0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room

temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **4b** was obtained in 86% yield (58.5 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.33 (m, 1H), 7.27 – 7.13 (m, 8H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.60 (s, 3H), 2.68 – 2.58 (m, 4H), 1.26 – 1.20 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 143.9, 141.1, 137.6, 137.2, 132.5, 131.0, 129.7, 129.2, 127.8, 127.6, 127.1, 121.9, 119.9, 119.6, 114.7, 109.4, 30.8, 28.6, 28.5, 15.3, 15.3. *This compound has been known*. ^[7]Its NMR spectra are identical withthe authorized ones.



2,3-Bis(4-isopropylphenyl)-1-methyl-1*H*-indole (4c)

4c (0.2 mmol scale) was synthesized following the general procedure. The reaction carried *N*-methylaniline 0.2 was out with (0.0214)g, mmol), 1,2-bis(4-isopropylphenyl)ethyne (0.0787 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 4c was obtained in 80% yield (58.8 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.80 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.28 – 7.10 (m, 10H), 3.61 (s, 3H), 2.95 - 2.83 (m, 2H), 1.28 - 1.23 (m, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 148.5, 145.6, 137.6, 137.2, 132.6, 131.0, 129.6, 129.3, 127.1, 126.3, 126.1, 121.9, 119.9, 119.7, 114.7, 109.4, 33.8, 33.7, 30.9, 24.0, 23.9; HRMS (ESI) Calcd for C₂₇H₃₀N ([M + H]⁺) : 368.2373, found : 368.2370.



1-Ethyl-2,3-bis(3-fluorophenyl)-1*H*-indole (4d)

4d (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with *N*-ethylaniline (0.0242)0.2 mmol), g, 1,2-bis(3-fluorophenyl)ethyne (0.0643 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 4d was obtained in 68% yield (45.4 mg, brown oil). ¹H NMR (400MHz, CDCl₃): δ 7.70 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.31 - 7.21 (m, 2H), 7.15 - 7.10 (m,7.04 - 6.88 (m, 5H), 6.81 - 6.76 (m, 1H), 4.05 (q, J = 7.2 Hz, 2H), 1.20 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 162.8 (d, J = 244.5 Hz), 162.6 (d, J = 247.3Hz), 161.5 (d, J = 19.9 Hz), 137.2 (d, J = 8.4 Hz), 136.1, 136.0 (d, J = 2.2 Hz), 134.0 (d, J = 8.1 Hz), 130.2 (d, J = 8.5 Hz), 129.6 (d, J = 8.8 Hz), 126.9, 126.8 (d, J = 3.0Hz), 125.4 (d, J = 2.7 Hz), 122.6, 120.5, 119.6, 117.8 (d, J = 21.6 Hz), 116.3 (d, J = 21.5 Hz), 115.5 (d, J = 21.0 Hz), 114.7 (d, J = 2.5 Hz), 112.5 (d, J = 21.1 Hz), 109.9, 38.7, 15.3; HRMS (ESI) Calcd for C₂₂H₁₈F₂N ([M + H]⁺) 334.1402, found : 334.1399.



1-Ethyl-2,3-di-m-tolyl-1*H*-indole (4e)

4e (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with *N*-ethylaniline (0.0242 g, 0.2 mmol), 1,2-di-*m*-tolylethyne (0.0619 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **4e** was obtained in 75% yield (48.8 mg, pale yellow oil). ¹H NMR (400MHz, CDCl₃): δ 7.72 (d, *J* = 7.9 Hz, 1H),

7.29 (d, J = 8.2 Hz, 1H), 7.17 – 6.94 (m, 9H), 6.84 (d, J = 7.3 Hz, 1H), 3.98 (q, J = 7.1 Hz, 2H), 2.21 (s, 3H), 2.16 (s, 3H), 1.14 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 137.8, 137.4, 137.4, 136.0, 135.2, 132.2, 131.5, 130.4, 128.8, 128.2, 128.2, 127.9, 127.3, 126.9, 126.1, 121.8, 119.9, 119.8, 109.7, 38.6, 21.5, 21.4, 15.3; HRMS (ESI) Calcd for C₂₄H₂₄N ([M + H]⁺) : 326.1903, found : 326.1901.



1-Ethyl-2,3-bis(4-methoxyphenyl)-1H-indole (4f)

4f (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with *N*-ethylaniline (0.0242)g, 0.2 mmol). 1,2-bis(4-methoxyphenyl)ethyne (0.0715 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product 4f was obtained in 84% yield (60.1 mg, colorless solid). ¹H NMR (400MHz, CDCl₃): δ 7.76 (d, J = 7.9 Hz, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.25 – 7.08 (m, 6H), 6.86 (d, J =8.7 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 4.06 (q, J = 7.1 Hz, 2H), 3.74 (s, 3H), 3.71 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.3, 157.4, 136.6, 135.9, 132.1, 130.7, 127.7, 127.3, 124.4, 121.7, 119.8, 119.5, 114.6, 113.8, 113.6, 109.6, 55.1, 55.0, 38.4, 15.3. This compound has been known. ^[8] Its NMR spectra are identical with the authorized ones.



1-Ethyl-2,3-bis(3-(trifluoromethoxy)phenyl)-1*H*-indole (4g)

4g (0.2 mmol scale) was synthesized following the general procedure. The reaction

was carried with *N*-ethylaniline (0.0242)0.2 mmol). out g, 1,2-bis(3-(trifluoromethoxy)phenyl)ethyne (0.1039 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product 4g was obtained in 78% yield (72.6 mg, colorless solid). ¹H NMR $(400 \text{ MHz}, \text{ CDCl}_3)$: δ 7.68 (d, J = 8.0 Hz, 1H), 7.35 (dd, J = 13.9, 8.0 Hz, 2H), 7.24 – 7.11 (m, 7H), 6.97 (s, 1H), 6.93 (d, J = 7.9 Hz, 1H), 4.05 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 149.3 (q, J = 1.9 Hz), 136.8, 136.3, 135.8, 133.7, 130.1, 129.5, 129.3, 127.9, 126.8, 123.5, 122.8, 122.0, 120.9, 120.7, 120.4 (q, J = 256.7 Hz), 119.5, 118.2, 114.7, 110.1, 38.8, 15.3; HRMS (ESI) Calcd for $C_{24}H_{18}F_6NO_2$ ([M + H]⁺) : 466.1236, found : 466.1233.



1,2-Bis(4-(tert-butyl)phenyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (4h)

4h (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), 1,2-bis(4-(tert-butyl)phenyl)ethyne (0.0872 g, 0.3 mmol), $[Cp*RhCl_2]_2$ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product **4h** was obtained in 85% yield (71.7 mg, white solid). ¹**H NMR** (400MHz, CDCl₃): δ 7.54 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.17 (m, 6H), 6.98 – 6.95 (m, 1H), 6.86 (d, *J* = 6.8 Hz, 1H), 3.95 – 3.92 (m, 2H), 2.91 (t, *J* = 5.9 Hz, 2H), 2.10 – 2.05 (m,
2H), 1.25 (s, 9H), 1.23 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 150.6, 147.7, 135.9, 134.3, 132.7, 130.3, 129.1, 128.9, 125.2, 125.0, 121.8, 120.0, 118.9, 117.2, 43.2, 34.6, 34.4, 31.4, 31.3, 25.1, 23.0; HRMS (ESI) Calcd for C₃₁H₃₆N ([M + H]⁺) : 422.2842, found : 422.2839.



1,2-Bis(3-methoxyphenyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinoline (4i)

4i (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), 1,2-bis(3-methoxyphenyl)ethyne (0.0715 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product 4i was obtained in 75% yield (55.4 mg, brown oil). ¹H NMR (400MHz, CDCl₃): δ 7.54 (d, J = 8.0 Hz, 1H), 7.20 - 7.15 (m, 1H), 7.08 (t, J = 7.9 Hz, 1H), 7.01 - 6.97 (m, 1H),6.89 - 6.76 (m, 6H), 6.62 (dd, J = 7.9, 2.2 Hz, 1H), 3.98 - 3.95 (m, 2H), 3.60 (s, 3H), 3.56 (s, 3H), 2.92 (t, J = 6.0 Hz, 2H), 2.10 (p, J = 6.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 159.4, 159.4, 136.9, 135.9, 134.3, 133.0, 129.4, 129.1, 124.9, 123.1, 122.1, 122.0, 120.3, 119.2, 117.1, 116.2, 114.7, 114.4, 113.5, 111.4, 55.2, 55.0, 43.2, 25.0, 22.9; HRMS (ESI) Calcd for C₂₅H₂₄NO₂ ([M + H]⁺) : 370.1802, found : 370.1803.



1,1'-((5,6-Dihydro-4H-pyrrolo[3,2,1-ij]quinoline-1,2-diyl)bis(3,1-phenylene))dieth

anone (4j)

4j (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), 1,1'-(ethyne-1,2-diylbis(3,1-phenylene))diethanone (0.0787)0.3 mmol), g, [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:10), the product 4j was obtained in 70% yield (55.1 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.98 – 7.93 (m, 3H), 7.77 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.34 (t, J = 7.7 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 7.0 Hz, 1H), 4.09 (t, J = 5.7 Hz, 2H), 3.05 (t, J = 6.1 Hz, 2H), 2.52 (s, 3H), 2.45 (s, 3H), 2.26 – 2.21 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 198.1, 197.5, 137.2, 137.1, 135.7, 135.1, 135.0, 134.4, 134.1, 131.9, 130.2, 129.6, 128.9, 128.6, 127.7, 125.2, 124.6, 122.2, 120.7, 119.6, 116.6, 114.0, 43.1, 26.5, 26.4, 24.9, 22.8; HRMS (ESI) Calcd for $C_{27}H_{24}NO_2$ ($[M + H]^+$) : 394.1802, found : 394.1798.



1-(4-Ethylphenyl)-2-(p-tolyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinoline (4k) 2-(4-Ethylphenyl)-1-(p-tolyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinoline (4k')

4k and **4k'**(0.2 mmol scale) were synthesized following the *general procedure*. The reaction was carried out with 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), 1-ethyl-4-(p-tolylethynyl)benzene (0.0661 g, 0.3 mmol), $[Cp*RhCl_2]_2$ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash

chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the inseparable products (**4k** and **4k**^{*}) were obtained in 73% yield (1 : 1 determined by ¹H NMR, 51.3 mg, viscous liquid). ¹H NMR (400MHz, CDCl₃): δ 7.53 (dd, *J* = 7.5, 5.9 Hz, 2H), 7.20 – 7.15 (m, 8H), 7.11 (t, *J* = 8.2 Hz, 4H), 7.04 – 6.97 (m, 6H), 6.89 (d, *J* = 6.6 Hz, 2H), 3.99 (q, *J* = 5.2 Hz, 4H), 2.96 (t, *J* = 6.1 Hz, 4H), 2.64 – 2.59 (m, 2H), 2.58 – 2.53 (m, 2H), 2.31 (s, 3H), 2.26 (s, 3H), 2.14 (p, *J* = 6.0 Hz, 4H), 1.21 – 1.19 (m, 3H), 1.18 – 1.15 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 143.7, 140.9, 137.5, 135.9, 135.8, 134.6, 134.2, 132.9, 132.7, 130.6, 130.5, 129.5, 129.1, 128.9, 127.8, 127.6, 125.1, 121.9, 121.8, 120.0, 118.9, 117.1, 117.0, 114.1, 114.0, 43.1, 43.0, 28.6, 28.5, 25.1, 23.0, 21.3, 21.1, 15.3, 15.2; HRMS (ESI) Calcd for C₂₆H₂₆N([M + H]⁺) : 352.2060, found 352.2057.



1-(4-Bromophenyl)-2-phenyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinoline (4l) 2-(4-Bromophenyl)-1-phenyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinoline (4l')

41 and **41'**(0.2 mmol scale) were synthesized following the *general procedure*. The reaction was carried out with 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), 1-bromo-4-(phenylethynyl)benzene (0.0771 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the inseparable products (**41** and **41'**) were obtained in 77% yield (1 : 1 determined by ¹H NMR, 59.8 mg, colorless oil). ¹H NMR (400MHz, CDCl₃): δ 7.52 – 7.47 (m, 2H), 7.38 (d, *J* = 7.1 Hz, 2H), 7.29 – 7.18 (m, 11H), 7.11 – 7.09 (m, 5H), 7.03 – 6.98 (m, 2H), 6.90 (d, *J* = 7.0 Hz, 2H), 3.96 – 3.94 (m, 4H), 2.94 (t, *J* = 5.9 Hz, 4H), 2.11 (p, *J* = 6.1, 5.6 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 136.2, 135.2, 134.6, 134.5, 134.4, 134.3, 132.2, 131.6, 131.4, 131.3, 131.1, 130.7, 130.6, 129.7, 128.5, 128.3, 128.0, 125.6, 124.9,

124.6, 122.11, 122.07, 122.01, 120.5, 120.4, 119.4, 119.3, 119.0, 117.1, 116.7, 114.9, 113.2, 43.2, 43.1, 25.0, 25.0, 22.9, 22.9; HRMS (ESI) Calcd for $C_{23}H_{19}BrN([M + H]^+)$: 388.0695, found 388.0694.



1-Methyl-2-phenyl-3-(4-(trimethylsilyl)phenyl)-1H-indole (4m)

1-Methyl-3-phenyl-2-(4-(trimethylsilyl)phenyl)-1H-indole (4m')

4m and 4m'(0.2 mmol scale) were synthesized following the general procedure. The reaction was carried out with N-methylaniline (0.0214 g, 0.2 mmol), trimethyl(4-(phenylethynyl)phenyl)silane (0.0751 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the inseparable products (4m and 4m') were obtained in 70% yield (1.2 : 1 determined by ¹H NMR, 49.8 mg, colorless oil). ¹H NMR (400MHz, CDCl₃): δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1X1.2 H), 7.51 (d, *J* = 7.8 Hz, 1+ 1X1.2 H), 7.42 – 7.26 (m, 9 + 9X1.2 H), 7.19 – 7.15 (m, 2 + 2X1.2 H), 3.65 (s, 3X1.2 H), 3.63 (s, 3H), 0.28 (s, 9X1.2 H), 0.25 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 140.2, 137.8, 137.7, 137.4, 137.3, 135.6, 135.2, 133.2, 133.19, 132.1, 132.0, 131.2, 130.3, 129.9, 129.0, 128.4, 128.2, 128.0, 127.0, 126.9, 125.5, 122.1, 120.2, 119.8, 119.6, 115.1, 115.0, 109.5, 31.0, 30.9, -1.0, -1.1; HRMS (ESI) Calcd for $C_{24}H_{26}NSi([M + H]^+)$: 356.1829, found 356.1827.



1-Isopropyl-2-phenyl-3-(4-(trimethylsilyl)phenyl)-1H-indole (4n) 1-Isopropyl-3-phenyl-2-(4-(trimethylsilyl)phenyl)-1H-indole (4n')

4n and 4n'(0.2 mmol scale) were synthesized following the general procedure. The reaction was carried out with N-isopropylaniline (0.0242 g, 0.2 mmol), trimethyl(4-(phenylethynyl)phenyl)silane (0.0751 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the inseparable products (4n and 4n') were obtained in 74% yield (1.5 : 1 determined by ¹H NMR, 56.8 mg, pale yellow oil). ¹H NMR (400MHz, CDCl₃): δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1X1.5 H), 7.63 (d, *J* = 8.3 Hz, 1 + 1X1.5 H), 7.50 (d, J = 7.8 Hz, 1 + 1X1.5 H), 7.40 - 7.24 (m, 8 + 8X1.5 H), 7.15 - 7.10 (m, 3) + 3X1.5 H), 4.59 - 4.48 (m, 1 + 1X1.5 H), 1.61 - 1.58 (m, 6 + 6X1.5 H), 0.28 (s, 9X1.5 H), 0.24 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 140.2, 137.6, 137.5, 136.6, 135.7, 135.3, 134.6, 133.2, 133.1, 133.0, 132.9, 131.2, 131.1, 130.3, 130.0, 129.9, 129.1, 128.4, 128.2, 128.1, 128.0, 127.9, 125.4, 125.3, 121.4, 120.1, 119.9, 119.7, 115.1, 115.0, 112.3, 112.2, 47.8, 21.5, 21.4, -1.0, -1.1; HRMS (ESI) Calcd for $C_{26}H_{30}NSi ([M + H]^+) : 384.2142$, found 384.2140.



Methyl 1,3-dimethyl-2-phenyl-1H-indole-5-carboxylate (40)

40 (0.2 mmol scale) was synthesized following the general procedure with slight

modifications. The reaction was carried out with methyl 4-(methylamino)benzoate (0.0330 g, 0.2 mmol), 1-phenyl-1-propyne (0.0348 g, 0.3 mmol), $[Cp*RhCl_2]_2$ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 80 °C in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product **40** was obtained in 52% yield (29.1 mg, white solid). ¹H NMR (400 MHz, CDCl₃): δ 8.38 (d, *J* = 1.2 Hz, 1H), 7.96 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.45 – 7.38 (m, 3H), 7.31 (d, *J* = 8.6 Hz, 1H), 3.95 (s, 3H), 3.62 (s, 3H), 2.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 168.4, 139.6, 138.9, 131.4, 130.5, 128.4, 128.1, 128.0, 123.1, 121.8, 120.9, 110.1, 108.8, 51.8, 31.1, 9.3; HRMS (ESI) Calcd for C₁₈H₁₈O₂N ([M + H]⁺) : 280.1332, found : 280.1332.



Methyl 3-ethyl-1-methyl-2-phenyl-1H-indole-5-carboxylate (4p)

4p (0.2 mmol scale) was synthesized following the *general procedure with slight modifications*. The reaction was carried out with methyl 4-(methylamino)benzoate (0.0330 g, 0.2 mmol), 1-phenyl-1-butyne (0.0391 g, 0.3 mmol), $[Cp*RhCl_2]_2$ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 80 °C in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product **4p** was obtained in 70% yield (41.1 mg, white solid). ¹H NMR (400 MHz, CDCl₃): δ 8.42 (d, *J* = 1.4 Hz, 1H), 7.95 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.39 – 7.37 (m, 2H), 7.32 (d, *J* = 8.6 Hz, 1H), 3.95 (s, 3H), 3.59 (s, 3H), 2.73 (q, *J* = 7.5 Hz, 2H), 1.23 (d, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 168.4, 139.6, 138.5, 131.6, 130.5, 128.4, 128.2, 127.0, 123.0, 122.0, 120.9, 116.9, 108.9, 51.8, 31.0, 17.7, 16.1; HRMS (ESI) Calcd for C₁₉H₂₀O₂N ([M + H]⁺) : 294.1489., found : 294.1488.



Methyl 2,3-dibutyl-1-methyl-1H-indole-5-carboxylate (4q)

4q (0.2 mmol scale) was synthesized following the *general procedure with slight modifications*. The reaction was carried out with methyl 4-(methylamino)benzoate (0.0330 g, 0.2 mmol), 5-decyne (0.0415 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 80 °C in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product **4q** was obtained in 73% yield (44.0 mg, colorless oil). ¹**H** NMR (400 MHz, CDCl₃): δ 8.28 (d, *J* = 1.3 Hz, 1H), 7.85 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 1H), 3.93 (s, 3H), 3.68 (s, 3H), 2.75 – 2.70 (m, 4H), 1.64 – 1.52 (m, 4H), 1.48 – 1.36 (m, 4H), 0.95 (q, *J* = 7.4 Hz, 6H); ¹³**C** NMR (100 MHz, CDCl₃): δ 168.5, 139.2, 138.4, 127.4, 122.0, 121.2, 120.4, 113.3, 108.1, 51.7, 33.7, 32.3, 29.8, 24.3, 24.2, 22.9, 22.7, 14.0, 13.9; HRMS (ESI) Calcd for C₁₉H₂₈O₂N ([M + H]⁺) : 302.2115, found :302.2115.



Methyl 2-acetyl-1-methyl-3-phenyl-1H-indole-5-carboxylate (4r)

4r (0.2 mmol scale) was synthesized following the *general procedure with slight modifications*. The reaction was carried out with methyl 4-(methylamino)benzoate (0.0330 g, 0.2 mmol), 4-phenyl-3-butyn-2-one (0.0433 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 60 °C in DCM (1.0 mL) for 48 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:6), the product **4r** was obtained in 43% yield (26.4 mg, sight yellow solid). ¹**H NMR** (400 MHz, CDCl₃): δ 9.18 (d, *J* = 1.3 Hz, 1H), 8.05 (dd, J = 8.6, 1.7 Hz, 1H), 7.59 – 7.56 (m, 3H), 7.45 – 7.42 (m, 2H), 7.37 (d, J = 8.6 Hz, 1H), 3.96 (s, 3H), 3.53 (s, 3H), 1.98 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 194.4, 168.0, 147.5, 139.0, 131.6, 130.2, 129.9, 128.9, 126.1, 125.4, 124.9, 124.7, 116.7, 109.3, 51.9, 31.0, 30.2; HRMS (ESI) Calcd for C₁₉H₁₈O₃N ([M + H]⁺) : 308.1281., found : 308.1281.



Dimethyl 1-methyl-3-phenyl-1H-indole-2,5-dicarboxylate (4s)

4s (0.2 mmol scale) was synthesized following the *general procedure with slight modifications*. The reaction was carried out with methyl 4-(methylamino)benzoate (0.0330 g, 0.2 mmol), methyl phenylpropiolate (0.0481 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 60 °C in DCM (1.0 mL) for 48 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:6), the product **4s** was obtained in 58% yield (37.5 mg, sight yellow solid). ¹H NMR (400 MHz, CDCl₃): δ 8.93 (s, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.53 – 7.50 (m, 3H), 7.45 – 7.38 (m, 3H), 3.96 (s, 3H), 3.79 (s, 3H), 3.58 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 167.9, 165.0, 148.3, 139.2, 130.8, 130.2, 129.2, 128.2, 125.9, 124.7, 124.2, 124.0, 109.5, 106.1, 51.9, 50.9, 31.1; HRMS (ESI) Calcd for C₁₉H₁₈O₄N ([M + H]⁺) : 324.123., found : 324.1230.

Mechanistic Studies

Experiment to Probe the Intermediate.

In a nitrogen-filled glovebox, a 25 mL Schlenk tube equipped with a stir bar was charged 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), 4-tert-butylbenzoic acid (0.0356 g, 0.2 mmol) and iso-amyl nitrite (0.0351g, 0.3 mmol) and dichloromethane (1.0 mL). The reaction mixture was stirred at room temperature for 24 h. when the reaction finished, the reaction mixture was diluted with 10 mL of ethyl acetate and filtered through a pad of silica gel. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel to provide the isolated product 5a (100% yield).



Experiments to Identify the Role of Benzoic Acid

(1) In a nitrogen-filled glovebox, a 25 mL Schlenk tube equipped with a stir bar was charged 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and *iso*-amyl nitrite (0.0351g, 0.3 mmol). The tube was fitted with a rubber septum and moved out of the glove box. Then dichloromethane (1.0 mL) was added to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at room temperature for 6 h. when the reaction finished, the reaction mixture was diluted with 10 mL of ethyl acetate and filtered through a pad of silica gel. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel. The product **3a** was obtained in 43% yield.

(2) In a nitrogen-filled glovebox, a 25 mL Schlenk tube equipped with a stir bar was charged 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%). The

tube was fitted with a rubber septum and moved out of the glove box. Then dichloromethane (1.0 mL) was added to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at room temperature for 24 h. when the reaction finished, the reaction mixture was diluted with 10 mL of ethyl acetate and filtered through a pad of silica gel. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel, the product **3a** was obtained in 15% yield.



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