Supporting Information

Annulation Cascade of Arylnitriles with Alkynes to Stable Delocalized PAH Carbocations via Intramolecular Rhodium Migration

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I. General remarks

NMR spectra were recorded on a Varian Inova 400 spectrometer. The ¹H NMR (400 MHz) chemical shifts were recorded relative to CDCl₃ or CD₃CN as the internal reference (CDCl₃: $\delta_{\rm H} = 7.26$ ppm; CD₃CN: $\delta_{\rm H} = 1.94$ ppm). The ¹³C NMR (100 MHz) chemical shifts were given using CDCl₃ or CD₃CN as the internal standard (CDCl₃: $\delta_{\rm C} = 77.16$ ppm; CD₃CN: $\delta_{\rm C} = 118.26$ ppm). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI) or a Waters-Q-TOF-Premier (ESI). X-Ray single-crystal diffraction data were collected on an Oxford Xcalibur E single crystal diffractometer. UV/Vis spectra experiments were conducted on a HITACHI U-2910. Absolute quantum yields and fluorescence spectra were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system. The HepG2 (human hepatoma cell line) was purchased from Shanghai Institute of Biochemistry and Cell Biology, Chinese Academy of Sciences. The confocal imaging measurements were conducted on a LSM 780 (Zeiss) confocal fluorescent microscope.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $[Cp*RhCl_2]_2^1$ were prepared according to the literature procedures. The solvents were purified and dried using an Innovative Technology PS-MD-5 Solvent Purification System. RhCl₃ xH₂O were purchased from Shanxi Kaida Chemical Engineering (China) CO., Ltd. AgSbF₆ was purchased from Alfa Aesar.

II. Optimization of the oxidative annulation of arylnitriles with alkynes

A Schlenk tube with a magnetic stir bar was charged with metal complex (5.0 μ mol, 5.0 mol %), AgSbF₆ (20 μ mol, 20 mol %, if required), oxidant, additives, benzonitrile (30.9 mg, 0.3 mmol), diphenylacetylene (53.5 mg, 0.3 mmol), and solvent (0.5 mL) under an N₂ atmosphere. The resulting solution was stirred at room temperature for 10 min and then at the indicated temperature for 12 h. Subsequently, it was diluted with 10 mL of dichloromethane. The mixture was evaporated under reduced pressure and

the residue was absorbed into small amounts of silica gel. Purification was performed by column chromatography on silica gel (dichloromethane/ethyl acetate = 20:1, v/v, then dichloromethane/methanol = 20:1, v/v) to provide **3aa**.

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Entry	Metal complex	Oxidant	Additive	Additive 2	Solvent	Yield ^[b]
Lindy	ineur compren	(equiv)	1	(equiv)	(mL)	(%)
		(•••••••)	(equiv)	(•4)	(1112)	(,,,,,
1	[Cp*RhCl ₂] ₂	AgOAc	-	CH ₃ COOH	DCE (0.5)	7
	L 1 232	(3.0)		(6.0)		
2	[Cp*RhCl ₂] ₂	AgOAc	NaSbF ₆	CH ₃ COOH	DCE (0.5)	39
		(3.0)	(2.0)	(6.0)		
3	[Cp*RhCl ₂] ₂	AgOAc	NaSbF ₆	CH ₃ COOH	DCE (0.5)	21
		(3.0)	(2.0)	(8.0)		
4	[Cp*RhCl ₂] ₂	AgOAc	NaSbF ₆	CH ₃ COOH/H ₂ O	DCE (0.5)	45
		(3.0)	(2.0)	(6.0/8.0)		
5	[Cn*DhCl]	$\Lambda \sim 0 \Lambda \sim$	Nashe		DCE(0.5)	12
3		(2 0)	(2.0)	(60/100)	DCE (0.3)	43
		(3.0)	(2.0)	(0.0/10.0)		
6	[Cp*RhCl ₂] ₂	AgOAc	$NaSbF_6$	CH ₃ COOH/H ₂ O	toluene	25
		(3.0)	(2.0)	(6.0/8.0)	(0.5)	
7	[Cn*RhCl_]	AgOAc	NaSbF	CH ₂ COOH/H ₂ O	1.4-dioxane	trace
·	(-F2)2	(3.0)	(2.0)	(6.0/8.0)	(0.5)	
		(2.2)	()	(010) 010)	(0.0)	
8	[Cp*RhCl ₂] ₂	AgOAc	NaSbF ₆	CH ₃ COOH/H ₂ O	THF (0.5)	-
		(3.0)	(2.0)	(6.0/8.0)		
9	[Cp*RhCl ₂] ₂	Cu(OAc) ₂	NaSbF ₆	CH ₃ COOH/H ₂ O	DCE (0.5)	32
		(3.0)	(2.0)	(6.0/8.0)		
10	[Cn*DhCl]	ΔαΟ	NaShE		DCE(0.5)	70
10	$[Cp^*KiiCi_2]_2$	Ag_2O	(2.0)	(6.0/8.0.)	DCE (0.3)	19
		(3.0)	(2.0)	(0.0/8.0)		
11 ^[c]	$[Cp*RhCl_2]_2$	Ag ₂ O	$NaSbF_6$	CH ₃ COOH/H ₂ O	DCE (0.5)	88
		(3.0)	(2.0)	(6.0/8.0)		

Table S1. Optimization for the synthesis of delocalized carbocation^[a]

12 ^[c]	[Cp*RhCl ₂] ₂	Ag ₂ O	NaSbF ₆	CH ₃ COOH/H ₂ O	DCE (0.5)	86
		(3.0)	(1.5)	(6.0/8.0)		
13	[Cp*RhCl ₂] ₂	Ag ₂ O	NaSbF ₆	CH ₃ COOH/H ₂ O	DCE (0.5)	80
		(2.5)	(1.5)	(6.0/8.0)		
14 ^[d]	[Cp*RhCl ₂] ₂	Ag ₂ O	NaSbF ₆	CH ₃ COOH/H ₂ O	DCE (0.5)	83
		(3.0)	(1.5)	(6.0/8.0)		
15	[Cp*IrCl ₂] ₂	Ag ₂ O	NaSbF ₆	CH ₃ COOH/H ₂ O	DCE (0.5)	ND
		(3.0)	(1.5)	(6.0/8.0)		
16	$[{RuCl_2(p-cymene)}_2]$	Ag ₂ O	NaSbF ₆	CH ₃ COOH/H ₂ O	DCE (0.5)	ND
		(3.0)	(1.5)	(6.0/8.0)		

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), AgSbF₆ (20 mol %), oxidant (x equiv), additives (x equiv), and solvent at 120 °C under N₂ for 12 h. [b] Isolated yield. [c] Benzonitrile was used with 0.2 mmol. [d] The reaction was carried out for 18 h.

III. General procedure for the synthesis of delocalized carbocation



A Schlenk tube with a magnetic stir bar was charged with $AgSbF_6$ (6.9 mg, 20 µmol), $NaSbF_6$ (38.9 mg, 0.15 mmol), $[Cp*RhCl_2]_2$ (3.1 mg, 5.0 µmol), Ag_2O (69.5 mg, 0.30 mmol), CH_3COOH (36 µL, 0.6 mmol), H_2O (14.4 µL, 0.8 mmol), arylnitrile (0.20 mmol), alkyne (0.30 mmol), and DCE (0.5 mL) under an N₂ atmosphere. The resulting mixture was stirred at room temperature for 10 min and then at the indicated temperature for appropriate time. Subsequently, it was diluted with 10 mL of dichloromethane. The mixture was evaporated under reduced pressure and the residue was absorbed into small amounts of silica gel. The purification was performed by column chromatography on silica gel to provide the desired product **3**.

IV. General procedure for the preparation of aryl nitriles



Aryl nitriles **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1r**, **1s**, **1t** were purchased from the commercial suppliers and used without any further purification. The preparation of aryl nitriles **1n**, **1o**, **1p** and **1q** was conducted as the following procedure.²

A Schlenk tube with a magnetic stir bar was charged with $Pd_2(dba)_3$ (9.6 mg, 0.01 mmol), $P^tBu_3BF_4$ (12.2 mg, 0.04 mmol), Na_2CO_3 (1.0 mol/L in water, 1.8 mL), 4-bromobenzonitrile (127.4 mg, 0.7 mmol), arylboronic acid (1.4 mmol), and dry toluene (2.0 mL) under an N_2 atmosphere. The resulting mixture was stirred at 100 °C for 12 h. Purification was conducted by column chromatography on silica gel to provide the desired products **1n**, **1o**, **1p** and **1q**.

V. General procedure for the preparation of alkynes



Alkynes 2a and 2g were purchases from the commercial suppliers directly and were used without any further purification. Alkynes 2b, 2c, 2d, 2e and 2f were synthesized by following the literature procedures.³

VI. Preparation and characterization of the described substances



2,3,7,12,13-Pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin-1-ium hexafluoroantimonate (3aa)

Following the general procedure. Benzonitrile (20.6 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3aa** as an orange solid (76.2 mg, 86% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.00 (t, J = 7.6 Hz, 1H), 7.66-7.63 (m, 6H), 7.45 (d, J = 8.0 Hz, 1H), 7.38-7.27 (m, 9H), 7.22-7.20 (m, 5H), 7.13-7.08 (m, 3H), 6.97 (d, J = 6.4 Hz, 2H), 6.85 (d, J = 7.2 Hz, 2H), 6.72-6.70 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 155.9, 152.2, 138.4, 137.8, 136.0, 135.6, 135.3, 134.3, 134.1, 133.2, 131.51, 131.48, 131.1, 130.85, 130.79, 130.6, 130.5, 130.02, 130.00, 129.9, 129.6, 129.4, 129.1, 128.8, 128.6, 128.5, 128.4, 128.2, 128.0, 127.8, 127.5,

127.4, 126.0, 124.2, 122.4, 122.2, 115.0. HRMS (ESI⁺): calcd for $C_{49}H_{32}NO^+$, 650.2478; found 650.2470.



5-Methyl-2,3,7,12,13-pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin-1 -ium hexafluoroantimonate (3ba)

Following the general procedure. 4-Methylbenzonitrile (23.4 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3ba** as a brown solid (52.7 mg, 59% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.71-7.64 (m, 5H), 7.41-7.37 (m, 6H), 7.33-7.27 (m, 4H), 7.21-7.19 (m, 5H), 7.12-7.07 (m, 4H), 6.96 (d, J = 7.2 Hz, 2H), 6.81 (d, J = 7.6 Hz, 2H), 6.76-6.70 (m, 3H), 2.50 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 155.6, 152.3, 151.4, 137.9, 136.0, 135.6, 135.1, 134.3, 134.2, 133.8, 133.2, 131.6, 131.5, 131.2, 130.8, 130.74, 130.66, 130.5, 130.0, 129.8, 129.7, 129.5, 129.4, 129.1, 128.8, 128.52, 128.47, 128.44, 128.1, 128.0, 127.7, 127.3, 126.8, 126.1, 124.3, 123.8, 121.9, 113.5, 23.8. HRMS (ESI⁺): calcd for C₅₀H₃₄NO⁺, 664.2635; found 664.2632.



5-Methoxy-2,3,7,12,13-pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin -1-ium hexafluoroantimonate (3ca) Following the general procedure. 4-Methoxybenzonitrile (26.6 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3ca** as a brown solid (43.0 mg, 47% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.69-7.64 (m, 5H), 7.40-7.35 (m, 5H), 7.32-7.29 (m, 2H), 7.28-7.26 (m, 2H), 7.21-7.19 (m, 4H), 7.11-7.06 (m, 4H), 6.98-6.96 (m, 3H), 6.82-6.73 (m, 6H), 3.80 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 168.2, 154.6, 152.3, 140.7, 137.6, 136.1, 136.0, 134.3, 134.2, 133.3, 133.0, 131.7, 131.4, 131.0, 130.9, 130.8, 130.7, 130.4, 130.0, 129.72, 129.65, 129.5, 129.4, 129.1, 128.8, 128.4, 128.1, 128.0, 127.7, 127.2, 126.1, 125.893, 125.889, 121.5, 111.6, 110.4, 110.1, 107.1, 56.4. HRMS (ESI⁺): calcd for C₅₀H₃₄NO₂⁺, 680.2584; found 680.2580.



5-Phenoxy-2,3,7,12,13-pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin-1-ium hexafluoroantimonate (3da)

Following the general procedure. 4-Phenoxybenzonitrile (39.0 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3da** as a yellow solid (85.6 mg, 87% yield). ¹H NMR (CD₃CN, 400 MHz): δ (ppm) 7.63-7.60 (m, 5H), 7.47-7.42 (m, 4H), 7.40-7.38 (m, 3H), 7.34-7.31 (m, 4H), 7.29-7.26 (m, 4H), 7.21-7.19 (m, 2H), 7.18-7.14 (m, 3H), 7.12-7.10 (m, 4H), 6.90 (d, J = 2.0 Hz, 1H), 6.86-6.84 (m, 2H), 6.81 (d, J = 2.0 Hz, 1H), 6.79-6.77 (m, 1H), 6.73-6.69 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 167.5, 155.5, 154.4, 153.1, 141.1, 139.2, 137.4, 136.8, 135.6, 135.0, 134.4, 133.8, 132.9, 132.3, 131.9, 131.7, 131.5, 131.4, 131.3, 131.09, 131.07,

130.63, 130.59, 130.4, 130.2, 130.1, 130.0, 129.20, 129.18, 129.0, 128.9, 128.6, 128.5, 127.8, 127.0, 126.9, 126.6, 122.0, 121.5, 112.6, 111.7, 109.9. HRMS (ESI⁺): calcd for $C_{55}H_{36}NO_2^+$, 742.2741; found 742.2742.



5-Fluoro-2,3,7,12,13-pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin-1 -ium hexafluoroantimonate (3ea)

Following the general procedure. 4-Fluorobenzonitrile (24.2 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3ea** as an orange solid (82.0 mg, 91% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.69-7.66 (m, 5H), 7.46 (d, J = 8.4 Hz, 1H), 7.41-7.33 (m, 5H), 7.29-7.27 (m, 3H), 7.24-7.21 (m, 6H), 7.14-7.07 (m, 3H), 6.97-6.95 (m, 3H), 6.85 (d, J = 7.6 Hz, 2H), 6.74-6.68 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 168.9 (d, J_{C-F} = 260.3 Hz), 155.2, 153.2, 141.2, 141.1, 139.5, 139.3, 136.6, 135.9, 134.2, 134.1, 134.0, 133.2, 131.7, 131.1 (d, J_{C-F} = 1.9 Hz), 130.95, 130.94, 130.6, 130.4, 130.2 (d, J_{C-F} = 8.5 Hz), 129.9, 129.62, 129.56, 129.3 (d, J_{C-F} = 7.8 Hz), 128.8, 128.6, 128.44 (d, J_{C-F} = 2.0 Hz), 128.4, 128.1, 128.0, 127.8, 127.3, 126.7 (d, J_{C-F} = 5.0 Hz), 125.64, 121.76, 121.73, 112.47, 111.1 (d, J_{C-F} = 27.0 Hz), 110.1 (d, J_{C-F} = 25.6 Hz). ¹⁹F NMR (CDCl₃, 400 MHz): δ (ppm) -89.99–90.05 (m), -107.76– -107.83 (m), -154.28, -154.33. HRMS (ESI⁺): calcd for C₄₉H₃₁FNO⁺, 668.2384; found 668.2381.



5-Chloro-2,3,7,12,13-pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin-1 -ium hexafluoroantimonate (3fa)

Following the general procedure. 4-Chlorobenzonitrile (27.5 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3fa** as an orange solid (87.6 mg, 95% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.67-7.65 (m, 5H), 7.51 (s, 1H), 7.44-7.35 (m, 9H), 7.20-7.19 (m, 6H), 7.12-7.06 (m, 3H), 6.95 (d, *J* = 6.0 Hz, 2H), 6.83 (d, *J* = 6.8 Hz, 2H), 6.71-6.69 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 155.4, 153.3, 146.1, 138.9, 137.0, 136.8, 135.6, 134.3, 134.1, 134.0, 133.2, 131.6, 131.1, 131.0, 130.9, 130.6, 130.4, 130.2, 130.1, 129.8, 129.5, 129.4, 129.2, 128.8, 128.6, 128.5, 128.4, 128.1, 128.0, 127.7, 127.3, 126.4, 125.7, 123.3, 122.3, 121.3, 113.4. HRMS (ESI⁺): calcd for C₄₉H₃₁ClNO⁺, 684.2089; found 684.2093.



5-Bromo-2,3,7,12,13-pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin-1 -ium hexafluoroantimonate (3ga)

Following the general procedure. 4-Bromobenzonitrile (36.4 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then

dichloromethane/methanol = 20:1, v/v) afforded **3ga** as an orange solid (90.4 mg, 94% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.68-7.65 (m, 6H), 7.43-7.34 (m, 7H), 7.26-7.19 (m, 8H), 7.12-7.06 (m, 3H), 6.95 (d, J = 6.4 Hz, 2H), 6.83 (d, J = 7.2 Hz, 2H), 6.71-6.69 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 155.5, 153.3, 138.7, 136.9, 136.7, 135.6, 135.3, 134.4, 134.1, 134.0, 133.2, 131.7, 131.1, 131.02, 130.96, 130.94, 130.6, 130.4, 130.2, 129.9, 129.6, 129.4, 129.3, 128.8, 128.6, 128.5, 128.4, 128.2, 128.0, 127.7, 127.3, 126.4, 126.2, 125.8, 125.1, 121.1, 113.7. HRMS (ESI⁺): calcd for C₄₉H₃₁BrNO⁺, 728.1584; found 728.1576.



2,3,7,12,13-Pentaphenyl-5-(trifluoromethyl)isoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]iso quinolin-1-ium hexafluoroantimonate (3ha)

Following the general procedure. 4-(Trifluoromethyl)benzonitrile (34.2 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3ha** as a red solid (88.6 mg, 93% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.93 (d, J = 8.0 Hz, 1H), 7.80 (s, 1H), 7.69-7.67 (m, 6H), 7.49 (d, J = 8.4 Hz, 1H), 7.44-7.37 (m, 6H), 7.27-7.21 (m, 6H), 7.16-7.08 (m, 3H), 6.96 (d, J = 6.8 Hz, 2H), 6.88 (d, J = 7.2 Hz, 2H), 6.75-6.68 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 168.0, 155.5, 153.5, 138.6 (q, J = 33.0 Hz), 138.1, 137.08, 136.8, 136.7, 135.5, 135.2, 134.0, 133.9, 133.2, 131.6, 131.3, 131.0, 130.98, 130.8, 130.5, 130.4, 130.3, 129.9, 129.7, 129.4, 129.3, 128.8, 128.6, 128.4, 128.3, 128.1, 128.0, 127. 8, 127.4, 125.7 (q, J = 3.7 Hz), 122.8 (q, J = 272.9 Hz), 121.90, 120.4 (q, J = 4.5 Hz), 117.5 (q, J = 3.4 Hz), 116.0. ¹⁹F NMR (CDCl₃, 400 MHz): δ (ppm) -63.00, -63.42, -154.14, -154.19. HRMS (ESI⁺): calcd for C₅₀H₃₁F₃NO⁺, 718.2352; found 718.2355.



5-(Methoxycarbonyl)-2,3,7,12,13-pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]i soquinolin-1-ium hexafluoroantimonate (3ia)

Following the general procedure. Methyl 4-cyanobenzoate (32.2 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3ia** as a red solid (90.5 mg, 96% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.24 (s, 1H), 7.82 (s, 1H), 7.67 (m, 5H), 7.44-7.20 (m, 14H), 7.13-7.05 (m, 3H), 6.95 (d, *J* = 6.8 Hz, 2H), 6.83 (d, *J* = 7.2 Hz, 2H), 6.73-6.66 (m, 3H), 3.85 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 165.3, 155.6, 152.9, 138.2, 137.9, 136.4, 135.9, 135.7, 134.9, 134.1, 133.9, 133.2, 131.5, 131.12, 131.07, 130.9, 130.6, 130.5, 130.2, 130.1, 129.9, 129.6, 129.51, 129.48, 129.2, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.7, 127.3, 125.9, 125.1, 122.3, 121.7, 116.4, 53.3. HRMS (ESI⁺): calcd for C₅₁H₃₄NO₃⁺, 708.2533; found 708.2530.



5-Acetyl-2,3,7,12,13-pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin-1ium hexafluoroantimonate (3ja)

Following the general procedure. 4-Acetylbenzonitrile (29.0 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then

dichloromethane/methanol = 20:1, v/v) afforded **3ja** as a red solid (57.0 mg, 61% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.06 (s, 1H), 7.70-7.69 (m, 6H), 7.47 (d, J = 8.4 Hz, 1H), 7.43-7.36 (m, 6H), 7.29-7.28 (m, 2H), 7.23-7.20 (m, 5H), 7.14 (t, J = 7.8 Hz, 1H), 7.09 (t, J = 7.8 Hz, 2H), 6.97 (d, J = 6.8 Hz, 2H), 6.84 (d, J = 8.0 Hz, 2H), 6.74-6.69 (m, 3H), 2.49 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 197.4, 155.6, 152.7, 144.1, 138.3, 136.2, 136.1, 135.7, 134.9, 134.1, 133.9, 133.4, 131.5, 131.2, 131.1, 130.9, 130.6, 130.5, 130.3, 130.1, 129.9, 129.53, 129.51, 129.3, 128.8, 128.7, 128.6, 128.5, 128.45, 128.2, 128.1, 127.7, 127.4, 125.9, 123.7, 122.5, 120.3, 116.3, 27.2. HRMS (ESI⁺): calcd for C₅₁H₃₄NO₂⁺, 692.2584; found 692.2584.



5-Cyano-2,3,7,12,13-pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin-1ium hexafluoroantimonate (3ka)

Following the general procedure. Terephthalonitrile (25.6 mg, 0.2 mmol), diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3ka** as a red solid (80.0 mg, 88% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.79 (s, 1H), 7.70-7.63 (m, 5H), 7.50 (d, J = 8.8 Hz, 1H), 7.44-7.33 (m, 6H), 7.29-7.28 (m, 3H), 7.23-7.13 (m, 6H), 7.09 (t, J = 7.6 Hz, 2H), 6.95 (d, J = 7.2 Hz, 2H), 6.86 (d, J = 7.6 Hz, 2H), 6.76-6.67 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 155.3, 153.7, 137.8, 137.3, 136.6, 135.37. 135.35, 134.0, 133.7, 133.3, 131.6, 131.5, 131.1, 130.9, 130.6, 130.5, 130.43, 130.36, 130.34, 129.9, 129.7, 129.4, 129.2, 128.9, 128.8, 128.6, 128.5, 128.3, 128.1, 127.8, 127.47, 127.46, 125.6, 122.7, 121.5, 120.7, 117.5, 115.8, 110.1. HRMS (ESI⁺): calcd for C₅₀H₃₁N₂O⁺, 675.2431; found 675.2430.



5-Formyl-2,3,7,12,13-pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin-1 -ium hexafluoroantimonate (3la)

Following the general procedure. 4-Formylbenzonitrile (26.2 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3la** as a red solid (58.9 mg, 64% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 10.04 (s, 1H), 8.03 (s, 1H), 7.71-7.66 (m, 5H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.45-7.37 (m, 6H), 7.32-7.29 (m, 3H), 7.22-7.08 (m, 8H), 6.97 (d, *J* = 6.8 Hz, 2H), 6.86 (d, *J* = 7.2 Hz, 2H), 6.78-6.71 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 191.1, 155.7, 153.1, 142.0, 138.6, 136.7, 136.6, 135.7, 135.2, 134.1, 134.0, 133.4, 131.6, 131.3, 131.1, 131.0, 130.6, 130.5, 130.4, 130.3, 130.2, 129.9, 129.7, 129.6, 129.5, 129.3, 128.9, 128.8, 128.60, 128.55, 128.47, 128.3, 128.1, 127.8, 127.4, 126.1, 125.9, 122.5, 120.1, 117.1. HRMS (ESI⁺): calcd for C₅₀H₃₂NO₂⁺, 678.2428; found 678.2429.



5-Nitro-2,3,7,12,13-pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin-1-i um hexafluoroantimonate (3ma)

Following the general procedure. 4-Nitrobenzonitrile (29.6 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column

chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3ma** as a red solid (40.5 mg, 43% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.33 (s, 1H), 7.88 (s, 1H), 7.69-7.67 (m, 5H), 7.51 (d, J = 8.4 Hz, 1H), 7.44-7.36 (m, 6H), 7.27-7.13 (m, 8H), 7.09 (t, J = 7.2 Hz, 2H), 6.95 (d, J = 7.2 Hz, 2H), 6.86 (d, J = 7.6 Hz, 2H), 6.74-6.68 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 155.4, 153.9, 153.1, 138.9, 138.0, 137.5, 135.6, 135.4, 134.0, 133.7, 133.4, 131.7, 131.5, 131.1, 131.0, 130.7, 130.52, 130.49, 130.40, 130.36, 129.9, 129.8, 129.7, 129.5, 129.2, 128.9, 128.80, 128.76, 128.7, 128.5, 128.3, 128.1, 127.8, 127.4, 125.6, 122.3, 118.5, 116.7, 115.0. HRMS (ESI⁺): calcd for C₄₉H₃₁N₂O₃⁺, 695.2329; found 695.2326.



2,3,5,7,12,13-Hexaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin-1-ium

hexafluoroantimonate (3na)

Following the general procedure. [1,1'-Biphenyl]-4-carbonitrile (35.8 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3na** as a yellow solid (53.8 mg, 56% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.77 (s, 1H), 7.691-7.688 (m, 5H), 7.48-7.35 (m, 12H), 7.27-7.21 (m, 8H), 7.11-7.07 (m, 3H), 7.00 (d, J = 5.2 Hz, 2H), 6.84 (d, J = 7.2 Hz, 2H), 6.74-6.72 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 155.5, 152.5, 151.6, 139.2, 138.2, 135.99, 135.94, 135.8, 134.2, 134.1, 134.0, 133.3, 131.6, 131.4, 131.1, 130.9, 130.6, 130.5, 130.1, 130.0, 129.8, 129.7, 129.6, 129.5, 129.43, 129.39, 129.1, 128.8, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.7, 127.4, 127.3, 126.0, 122.4, 122.1, 121.4, 113.9. HRMS (ESI⁺): calcd for C₅₅H₃₆NO⁺, 726.2791; found 726.2797.



5-([1,1'-Biphenyl]-4-yl)-2,3,7,12,13-pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin-1-ium hexafluoroantimonate (30a)

Following the general procedure. [1,1':4',1"-Terphenyl]-4-carbonitrile (51.1 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **30a** as a yellow solid (73.9 mg, 71% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.813-7.810 (m, 1H), 7.72-7.71 (m, 4H), 7.66-7.64 (m, 2H), 7.59-7.57 (m, 2H), 7.54-7.53 (m, 3H), 7.47-7.41 (m, 4H), 7.39-7.33 (m, 6H), 7.30-7.27 (m, 5H), 7.24-7.21 (m, 3H), 7.15-7.08 (m, 3H), 7.03-7.00 (m, 2H), 6.87-6.85 (m, 2H), 6.77-6.71 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 155.5, 152.6, 151.1, 142.7, 140.1, 138.3, 138.1, 136.2, 136.0, 135.9, 134.4, 134.2, 134.0, 133.3, 131.7, 131.6, 131.2, 130.9, 130.8, 130.7, 130.6, 130.1, 130.0, 129.9, 129.7, 129.54, 129.52, 129.2, 129.1, 128.9, 128.64, 128.57, 128.4, 128.12, 128.10, 128.0, 127.8, 127.4, 127.3, 127.2, 126.1, 122.21, 122.20, 121.2, 114.1. HRMS (ESI⁺): calcd for C₆₁H₄₀NO⁺, 802.3104; found 802.3098.



2,3,7,12,13-Pentaphenyl-5-(thiophen-2-yl)isoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoqu inolin-1-ium hexafluoroantimonate (3pa)

Following the general procedure A. 4-(Thiophen-2-yl)benzonitrile (37.1 mg, 0.2

mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3pa** as a yellow solid (75.2 mg, 78% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.74-7.66 (m, 5H), 7.46-7.37 (m, 7H), 7.35-7.28 (m, 5H), 7.25-7.21 (m, 5H), 7.14-7.07 (m, 5H), 6.99 (d, J = 6.8 Hz, 2H), 6.84 (d, J = 7.2 Hz, 2H), 6.76-6.70 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 155.0, 152.6, 144.1, 142.0, 138.5, 136.2, 136.0, 135.9, 134.3, 134.2, 133.9, 133.2, 131.7, 131.4, 131.2, 130.9, 130.8, 130.7, 130.5, 130.12, 130.06, 129.8, 129.7, 129.6, 129.5, 129.23, 129.20, 128.8, 128.6, 128.5, 128.4, 128.1, 128.0, 127.8, 127.3, 127.0, 125.9, 121.8, 120.0, 119.2, 113.7. HRMS (ESI⁺): calcd for C₅₃H₃₄NOS⁺, 732.2356; found 732.2358.



5-(Naphthalen-2-yl)-2,3,7,12,13-pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]is oquinolin-1-ium hexafluoroantimonate (3qa)

Following the general procedure. 4-(Naphthalen-2-yl)benzonitrile (45.9 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3qa** as a yellow solid (62.1 mg, 61% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.91-7.82 (m, 5H), 7.74-7.66 (m, 4H), 7.6-7.597 (m, 1H), 7.55-7.50 (m, 3H), 7.45 (d, J = 8.4 Hz, 1H), 7.41-7.34 (m, 5H), 7.30-7.27 (m, 5H), 7.24-7.21 (m, 3H), 7.15-7.09 (m, 4H), 7.03-7.01 (m, 2H), 6.87 (d, J = 7.6 Hz, 2H), 6.77-6.71 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 155.6, 152.6, 151.6, 138.3, 136.6, 136.1, 136.0, 135.8, 134.3, 134.2, 134.0, 133.6, 133.4, 133.3, 131.7, 131.5, 131.2, 130.9, 130.7, 130.6, 130.1, 130.0, 129.9, 129.7, 129.5, 129.3, 129.2, 128.9, 128.8, 128.6, 128.5, 128.4, 128.1, 128.08, 128.05, 127.8, 127.77,

127.5, 127.4, 127.3, 127.0, 126.1, 125.3, 122.7, 122.2, 121.6, 114.0. HRMS (ESI⁺): calcd for $C_{59}H_{38}NO^+$, 776.2948; found 776.2941.



4-Methyl-2,3,7,12,13-pentaphenylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin-1 -ium hexafluoroantimonate (3ra-1) and its isomer (3ra-2)

Following the general procedure. 3-Methylbenzonitrile (23.4 mg, 0.2 mmol) and diphenylacetylene (53.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3ra-1** and its isomer **3ra-2** (8.3: 1 from ¹H NMR spectrum) as a yellow solid (40.6 mg, 45% yield). HRMS (ESI⁺): calcd for $C_{50}H_{34}NO^+$, 664.2635; found 664.2636.





Following the general procedure. Benzonitrile (20.6 mg, 0.2 mmol) and 1,2-di-p-tolylethyne (61.9 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3ab** as an orange solid (38.6 mg, 40% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.97 (t, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.4

Hz, 1H), 7.48 (m, 3H), 7.37 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.18 (d, J = 7.6 Hz, 2H), 7.12-7.08 (m, 7H), 6.98-6.92 (m, 4H), 6.79 (d, J = 7.6 Hz, 2H), 6.71 (d, J = 8.0 Hz, 2H), 6.50 (d, J = 7.6 Hz, 2H), 2.55 (s, 3H), 2.35-2.33 (m, 6H), 2.29-2.27 (m, 6H), 1.94 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 155.6, 152.4, 141.6, 140.2, 140.1, 139.0, 138.4, 138.2, 137.9, 137.8, 135.9, 135.4, 134.1, 133.4, 133.1, 131.8, 131.5, 131.4, 131.3, 130.9, 130.5, 130.3, 130.2, 129.9, 129.6, 129.2, 129.1, 128.8, 128.6, 128.4, 127.4, 127.1, 126.6, 123.9, 123.7, 122.0, 121.6, 114.5, 21.70, 21.68, 21.49, 21.48, 21.44, 21.3. HRMS (ESI⁺): calcd for C₅₅H₄₄NO⁺, 734.3417; found 734.3418.



10-Methoxy-2,3,7,12,13-pentakis(4-methoxyphenyl)isoquinolino[2,1-*b*]pyrano[4,3 ,2-*ij*]isoquinolin-1-ium hexafluoroantimonate (3ac)

Following the general procedure. Benzonitrile (20.6 mg, 0.2 mmol) and 1,2-bis(4-methoxyphenyl)ethyne (71.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3ac** as a red solid (50.7 mg, 48% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.96 (t, J = 8.0 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 9.6 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.20 (d, J = 8.4 Hz, 2H), 7.14-7.11 (m, 3H), 6.92-6.81 (m, 9H), 6.74-6.71 (m, 2H), 6.66 (d, J = 8.4 Hz, 2H), 6.26 (d, J = 8.8 Hz, 2H), 3.96 (s, 3H), 3.81-3.78 (m, 9H), 3.70 (s, 3H), 3.47 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 161.1, 160.8, 160.7, 159.9, 159.3, 159.2, 155.5, 152.3, 138.1, 138.0, 136.2, 135.6, 134.2, 134.0, 133.6, 132.4, 131.7, 131.3, 131.0, 130.1, 128.0, 126.38, 126.36, 125.1, 123.6, 123.4, 122.3, 121.5, 120.7, 119.2, 116.2, 115.7, 115.0, 114.04, 113.99, 113.5, 113.3, 111.0, 110.1,

55.7, 55.6, 55.5, 55.44, 55.35, 55.0. HRMS (ESI⁺): calcd for C₅₅H₄₄NO₇⁺, 830.3112; found 830.3112.



10-Fluoro-2,3,7,12,13-pentakis(4-fluorophenyl)isoquinolino[2,1-*b*]pyrano[4,3,2-*ij*] isoquinolin-1-ium hexafluoroantimonate (3ad)

Benzonitrile (20.6 mg, 0.2 mmol) and 1, Following the general procedure. 2-bis(4-fluorophenyl)ethyne (64.3 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3ad** as a yellow solid (80.2 mg, 81%) yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.02 (t, J = 8.0 Hz, 1H), 7.64-7.59 (m, 3H), 7.46-7.42 (m, 1H), 7.37 (t, J = 8.4 Hz, 2H), 7.30 (d, J = 7.6 Hz, 1H), 7.22-7.16 (m, 4H), 7.06 (t, J = 8.4 Hz, 2H), 7.02-6.93 (m, 7H), 6.90-6.85 (m, 3H), 6.42 (t, J = 8.2 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 163.7 (d, J = 250.2 Hz), 163.6 (d, J = 251.4 Hz), 163.3 (d, J = 254.0 Hz), 163.0 (d, J = 248.5 Hz), 162.5 (d, J = 247.7Hz), 162.2 (d, J = 249.3 Hz), 155.6, 151.4, 138.6, 137.96, 135.3, 135.1, 134.2 (d, J = 8.8 Hz), 133.8, 133.1 (d, J = 8.1 Hz), 132.9 (d, J = 2.6 Hz), 132.4 (d, J = 7.8 Hz), 132.3 (d, J = 7.8 Hz), 132.1 (d, J = 10.0 Hz), 132.0 (d, J = 8.9 Hz), 131.7 (d, J = 3.6 Hz), 131.0 (d, J = 8.4 Hz), 130.0 (d, J = 3.5 Hz), 129.5 (d, J = 3.5 Hz), 127.0 (d, J = 3.5 Hz), 126.1, 125.7 (d, J = 3.4 Hz), 124.0, 122.3, 122.26, 121.6, 118.2 (d, J = 21.5 Hz), 116.80 (d, J = 21.5 Hz), 116.78 (d, J = 22.0 Hz), 116.0 (d, J = 21.6 Hz), 115.4 (d, J = 21.9 Hz), 115.3 (d, J = 21.9 Hz), 114.8, 113.2 (d, J = 23.7 Hz). ¹⁹F NMR (CDCl₃, 400 MHz): δ (ppm) -105.48, -108.20, -109.70, -110.59, -111.01, -111.98, -154.22, -154.28. HRMS (ESI⁺): calcd for $C_{49}H_{26}F_6NO^+$, 758.1913; found 758.1915.





Following the general procedure. Benzonitrile (20.6 mg, 0.2 mmol) and 1, 2-bis(4-chlorophenyl)ethyne (74.1 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3ae** as a yellow solid (49.2 mg, 45% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.01 (t, J = 7.8 Hz, 1H), 7.65-7.55 (m, 5H), 7.39-7.28 (m, 6H), 7.19-7.11 (m, 8H), 6.91 (d, J = 7.6 Hz, 2H), 6.85 (d, J = 7.6 Hz, 2H), 6.69 (d, J = 7.6 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 155.6, 151.3, 138.8, 137.8, 137.7, 136.8, 136.5, 135.6, 135.04, 135.00, 134.94, 134.86, 134.1, 133.5, 132.7, 132.6, 132.5, 132.3, 131.8, 131.7, 131.3, 131.0, 130.8, 130.2, 130.0, 129.3, 129.24, 129.22, 128.7, 128.6, 127.8, 126.63, 126.60, 124.3, 124.2, 122.564, 122.556, 121.9, 115.0. HRMS (ESI⁺): calcd for C₄₉H₂₆Cl₆NO⁺, 854.0140; found 854.0141.



9-Methyl-2,3,7,12,13-penta-m-tolylisoquinolino[2,1-*b*]pyrano[4,3,2-*ij*]isoquinolin-1-ium hexafluoroantimonate (3af)

Following the general procedure. Benzonitrile (20.6 mg, 0.2 mmol) and 1, 2-di-*m*-tolylethyne (61.9 mg, 0.3 mmol) were used. Purification via column

chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3af** as an orange solid (73.0 mg, 75% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.01 (t, J = 7.8 Hz, 1H), 7.68-7.59 (m, 2H), 7.50-7.43 (m, 3H), 7.30 (d, J = 7.6 Hz, 1H), 7.24-7.15 (m, 6H), 7.08-6.95 (m, 7H), 6.78-6.72 (m, 4H), 6.61-6.56 (m, 2H), 2.49 (s, 3H), 2.30-2.21 (m, 9H), 2.05 (s, 3H), 1.73 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 155.7, 152.3, 138.8, 138.2, 137.8, 137.6, 137.4, 136.1, 135.5, 135.2, 134.4, 134.3, 134.2, 132.4, 132.0, 131.5, 130.80, 130.75, 130.6, 130.4, 130.39, 130.38, 130.36, 130.1, 129.9, 129.83, 129.80, 129.4, 129.3, 129.0, 128.73, 128.71, 128.016, 128.005, 127.98, 127.6, 127.4, 127.3, 126.7, 125.8, 124.60, 124.58, 124.57, 124.55, 124.2, 122.3, 122.1, 114.8, 110.1, 21.8, 21.7, 21.5, 21.44, 21.36, 20.9. HRMS (ESI⁺): calcd for C₅₅H₄₄NO⁺, 734.3417; found 734.3418.



10-Methoxy-2,3,7,12,13-pentakis(4-methoxyphenyl)-5-nitroisoquinolino[2,1-*b*]py rano[4,3,2-*ij*]isoquinolin-1-ium hexafluoroantimonate (3mc)

Following the general procedure. 4-Nitrobenzonitrile (29.6 mg, 0.2 mmol) and 1, 2-bis(4-methoxyphenyl)ethyne (71.5 mg, 0.3 mmol) were used. Purification via column chromatography on silica gel (dichloromethane/ethyl acetate = 10:1, v/v, then dichloromethane/methanol = 20:1, v/v) afforded **3mc** as a deep red solid (55.7 mg, 50% yield). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.32 (s, 1H), 7.84 (s, 1H), 7.54-7.48 (m, 3H), 7.23-7.20 (m, 2H), 7.15-7.11 (m, 4H), 6.92-6.84 (m, 9H), 6.78-6.76 (m, 1H), 6.65 (d, J = 8.4 Hz, 2H), 6.25 (d, J = 8.4 Hz, 2H), 3.98 (s, 3H), 3.82 (s, 3H), 3.79-3.77 (m, 6H), 3.71 (s, 3H), 3.46 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 161.7,

161.076, 161.071, 160.2, 159.4, 159.3, 155.0, 154.1, 153.1, 139.0, 138.43, 138.37, 135.0, 134.6, 134.2, 132.3, 131.7, 131.5, 131.4, 130.1, 127.5, 126.6, 126.2, 123.0, 122.0, 120.9, 118.9, 117.7, 116.6, 116.2, 115.5, 115.3, 114.1, 113.8, 113.6, 113.4, 110.9, 55.7, 55.6, 55.5, 55.44, 55.36, 55.0. HRMS (ESI⁺): calcd for $C_{55}H_{43}N_2O_9^+$, 875.2963; found 875.2962.

VII. Representative experiments on a 1.0 mmol scale



A Schlenk tube with a magnetic stir bar was charged with AgSbF₆ (69 mg, 200 μ mol), NaSbF₆ (388.1 mg, 1.5 mmol), [Cp*RhCl₂]₂ (30.9 mg, 50 μ mol), Ag₂O (695.2 mg, 3.0 mmol), CH₃COOH (360.4 mg, 6.0 mmol), H₂O (144.2 μ L, 8.0 mmol), benzonitrile or methyl 4-cyanobenzoate (2.0 mmol), diphenylacetylene (534.7 mg, 3.0 mmol), and DCE (5.0 mL) under an N₂ atmosphere. The resulting mixture was stirred at room temperature for 10 min and then at 120 °C for 12 h. Subsequently, it was diluted with 30 mL of dichloromethane. The mixture was evaporated under reduced pressure and the residue was absorbed to small amounts of silica gel. Purification was performed by column chromatography on silica gel to provide the desired product **3aa** (623.4 mg, 70% yield) or **3ia** (813.2 mg, 86%).

VIII. Mechanistic study

1. Control experiments



A Schlenk tube with a magnetic stir bar was charged with AgSbF₆ (6.9 mg, 20 μ mol), [Cp*RhCl₂]₂ (3.1 mg, 5.0 μ mol), Ag₂O (69.5 mg, 0.30 mmol), CH₃COOH (36 μ L, 0.6 mmol), H₂O (14.4 μ L, 0.8 mmol), methyl 4-cyanobenzoate (32.2 mg, 0.2 mmol), diphenylacetylene (53.5 mg, 0.3 mmol), and DCE (0.5 mL) under an N₂ atmosphere. The resulting mixture was stirred at room temperature for 10 min and then at 120 °C for 12 h. The mixture was diluted with 10 mL of dichloromethane when it cooled down. The mixture was evaporated under reduced pressure and the residue was absorbed into small amounts of silica gel. Purification was performed by column chromatography on silica gel to provide **2a** (42.8 mg, 79% yield), **1i** (24.6 mg, 76% yield), **3ia** (13.5 mg, 14% yield). The proposed three compounds were not detected.



A Schlenk tube with a magnetic stir bar was charged with $AgSbF_6$ (6.9 mg, 20 μ mol), $NaSbF_6$ (38.9 mg, 0.15 mmol), $[Cp*RhCl_2]_2$ (3.1 mg, 5.0 μ mol), Ag_2O (69.5 mg, 0.30 mmol), CH₃COOH (36.0 μ L, 0.6 mmol), H₂O (14.4 μ L, 0.8 mmol), methyl 4-cyanobenzoate (32.2 mg, 0.2 mmol), and DCE (0.5 mL) under an N₂ atmosphere. The resulting mixture was stirred at room temperature for 10 min and then at 120 °C for 12 h. The mixture was diluted with 10 mL of dichloromethane when it cooled down. The mixture was evaporated under reduced pressure and the residue was absorbed into small amounts of silica gel. Purification was performed by column

chromatography on silica gel to provide compound **1i** (27.7 mg, 86% yield recovered). The proposed amide was not detected.



2. The reaction of *ortho*-substituted arylnitriles with alkynes

For **1s**: A Schlenk tube with a magnetic stir bar was charged with AgSbF₆ (6.9 mg, 20 μ mol), NaSbF₆ (38.9 mg, 0.15 mmol), [Cp*RhCl₂]₂ (3.1 mg, 5.0 μ mol), Ag₂O (69.5 mg, 0.30 mmol), CH₃COOH (36.0 μ L, 0.6 mmol), H₂O (14.4 μ L, 0.8 mmol), 2-methylbenzonitrile (23.4 mg, 0.2 mmol), diphenylacetylene (53.5 mg, 0.3 mmol) and DCE (0.5 mL) under an N₂ atmosphere. The resulting mixture was stirred at room temperature for 10 min and then at 120 °C for 12 h. The mixture was diluted with 10 mL of dichloromethane when it cooled down. The mixture was evaporated under reduced pressure and the residue was absorbed into small amounts of silica gel. The purification was performed by column chromatography on silica gel to provide compound **1s** (35.4 mg, 66% yield recovered). The proposed annulation intermediate was not detected.

For **1t**: A Schlenk tube with a magnetic stir bar was charged with AgSbF₆ (6.9 mg, 20 μ mol), NaSbF₆ (38.9 mg, 0.15 mmol), [Cp*RhCl₂]₂ (3.1 mg, 5.0 μ mol), Ag₂O (69.5 mg, 0.30 mmol), CH₃COOH (36.0 μ L, 0.6 mmol), H₂O (14.4 μ L, 0.8 mmol), 1-naphthonitrile (30.6 mg, 0.2 mmol), diphenylacetylene (53.5 mg, 0.3 mmol) and DCE (0.5 mL) under an N₂ atmosphere. The resulting mixture was stirred at room temperature for 10 min and then at 120 °C for 12 h. The mixture was diluted with 10 mL of dichloromethane when it cooled down. The mixture was evaporated under reduced pressure and the residue was absorbed into small amounts of silica gel.

Purification was performed by column chromatography on silica gel to provide compound **1s** (37.4 mg, 70% yield recovered). The proposed annulation intermediate was not detected.

3. Intermolecular competition experiment



A Schlenk tube with a magnetic stir bar was charged with AgSbF₆ (6.9 mg, 20 µmol), NaSbF₆ (38.9 mg, 0.15 mmol), [Cp*RhCl₂]₂ (3.1 mg, 5.0 µmol), Ag₂O (69.5 mg, 0.30 mmol), CH₃COOH (36 µL, 0.6 mmol), H₂O (14.4 µL, 0.8 mmol), 4-methoxybenzonitrile (26.6 mg, 0.2 mmol), 4-bromobenzonitrile (36.4 mg, 0.2 mmol), diphenylacetylene (53.5 mg, 0.3 mmol) and DCE (0.5 mL) under an N₂ atmosphere. The resulting mixture was stirred at room temperature for 10 min and then at 120 °C for 12 h. The mixture was diluted with 10 mL of dichloromethane when it cooled down. The mixture was evaporated under reduced pressure and the residue was absorbed into small amounts of silica gel. Purification was performed by column chromatography on silica gel to provide a mixture containing **3ca** and **3ga** 57.6 mg (**3ca: 3ga** \approx 1: 3.3 according to the ¹H NMR spectrum).



Figure S1. ¹H NMR spectrum of the mixture obtained from the intermolecular competition experiment.

4. Spectra of MAIDL-TOF-MS

General procedure for the preparation of the sample: A Schlenk tube with a magnetic stir bar was charged with $AgSbF_6$ (6.9 mg, 20 µmol), $NaSbF_6$ (38.9 mg, 0.15 mmol), $[Cp*RhCl_2]_2$ (3.1 mg, 5.0 µmol), Ag_2O (69.5 mg, 0.30 mmol), CH₃COOH (36.0 µL, 0.6 mmol), H₂O (14.4 µL, 0.8 mmol), arylnitrile (0.20 mmol), diphenylacetylene (53.5 mg, 0.3 mmol) and DCE (0.5 mL) under an N₂ atmosphere. The resulting mixture was stirred at room temperature for 10 min and then at 120 °C for 1 h. The reaction mixture was used as the sample for the MAIDL-TOF-MS detection.



Figure S2. MAIDL-TOF-MS spectrum of the intermediate E.



Figure S3. MAIDL-TOF-MS spectra of the intermediates C and D.



Figure S4. MAIDL-TOF-MS spectrum for the detection of the 1:1 and 1:2 annulation products.

IX. Photophysical properties of the representative products

Compound	λ_{abs}/nm	λ_{ex}/nm	λ_{em}/nm	Stokes shift	$arPhi_{ m F}$
				(cm^{-1})	
3aa	501	502	575	2569	0.11
3ca	468	472	549	3153	0.23
3da	476	478	561	3183	0.08
3ha	518	518	592	2413	0.14
3ia	534	535	599	2032	0.21
3la	548	548	608	1801	0.27
3ma	559	563	622	1812	0.23
3ac	492	492	604	3769	0.10
3ae	503	504	576	2520	0.11

Table S2. Photophysical data of the representative products^[a]

	3mc	587	595	674	2199	< 0.01
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[a] Emission maximum in CH_2Cl_2 at 10.0 μ M.











Figure S5. The absorption and emission spectra of the representative products.

X. Cytotoxicity assay and cell imaging experiment

1. Cell culture

The used HepG2 cells were incubated in DMEM (Dublecco's Minimum Eagle's Medium) in which 10% (v/v) FBS (fetal bovine serum), penicillin (100 units/mL) and streptomycin (100 mg/mL) was supplemented at 37 $^{\circ}$ C in a 5% CO₂ containing

humidified atmosphere.

2. Cytotoxicity assay

The cytotoxicity experiments of **3da** and **3ia** were investigated by CellTiler 96®AQueous One Solution Cell Proliferation Assay. HepG2 cells were seeded at 1×104 cells/well in 96-well culture plates for a stationary culture. After being incubated for 24 h, the medium was replaced with fresh complete medium, and the sample was then added to achieve final concentrations at 0, 0.625, 1.25, 2.5, 5.0, 10.0 and 20.0 μ M. After 24 hours of incubation, 20 μ L of CellTiler 96®AQueous One Solution in PBS was added to each well and the plates were incubated for additional one hour. Afterwards, the absorbance of each sample was recorded on the ELISA plate reader (model 680, BioRad) at a wavelength of 490 nm. The cell viability was calculated by the following formula: (mean optical density (OD) in treated wells/mean OD in control wells) $\times 100\%$.



Figure S6. Cell viability values (%) estimated by CellTiler 96®AQueous One Solution Cell Proliferation Assay employing HepG2 cells, stained with 0−20 µM of 3ia, at 37 °C for 24 h.



Figure S7. Cell viability values (%) estimated by CellTiler 96®AQueous One Solution Cell Proliferation Assay employing HepG2 cells, stained with 0–20 μM of 3da, at 37 °C for 24 h.

3. Confocal imaging experiment

For subcellular localization experiments, HepG2 cells were incubated with 1 μ M **3da** or **3ia** in PBS (phosphate buffered solution) containing 1‰ DMSO for 15 min at 37 \mathbb{C} . After incubation HepG2 cells were washed twice with PBS and 1.0 μ M LysoTrackers were then added to incubate for 30 min, respectively. Finally, the cells were washed twice with PBS before imaging. The cells were observed with a LSM 780 (Zeiss) confocal laser scanning microscope.



Figure S8. Co-staining of HepG2 cells with 3ia (1.0 μ M) and LTG (LysoTracker® Green DND-26) (1.0 μ M): a) fluorescent image of HepG2cells stained with LTG for 30 min (λ_{ex} = 488 nm, λ_{em} = 460–560 nm); b) fluorescent image of HepG2 cells stained with 3ia for 15 min

 $(\lambda_{ex} = 552 \text{ nm}, \lambda_{em} = 550-650 \text{ nm}); \text{ c})$ bright-field image; and d) merged images of (a), (b) and (c).



Figure S9. Co-staining of HepG2 cells with 3da (1.0 μ M) and LTR (LysoTrackerTM Red DND-99) (1.0 μ M): a) fluorescent image of HepG2cells stained with LTR for 30 min (λ_{ex} = 546 nm, λ_{em} = 550–650 nm); b) fluorescent image of HepG2 cells stained with 3da for 15 min (λ_{ex} = 488 nm, λ_{em} = 500–600 nm); c) bright-field image; and d) merged images of (a), (b) and (c).

XI. Single crystal X-ray structures of 3ea and 3ia

Identification code	3ea
Empirical formula	$C_{50}H_{33}Cl_2F_7NOSb$
Formula weight	989.42
Temperature/K	293.15
Crystal system	trigonal
Space group	R-3
a/Å	28.6364(8)
b/Å	28.6364(8)
c/Å	29.7717(8)
α/\circ	90
β/°	90
$\gamma/^{\circ}$	120
Volume/Å ³	21143.1(14)
Z	18
$\rho_{calc}g/cm^3$	1.399
μ/mm^{-1}	0.765
F(000)	8928.0
Crystal size/mm ³	$0.4 \times 0.35 \times 0.3$
Radiation	MoKa ($\lambda = 0.71073$)
2Θ range for data collection/	°6.08 to 52.744
Index ranges	$\text{-}35 \leq h \leq 21, \text{-}19 \leq k \leq 35, \text{-}23 \leq l \leq 37$
Reflections collected	19566
Independent reflections	9597 [$R_{int} = 0.0228$, $R_{sigma} = 0.0499$]
Data/restraints/parameters	9597/0/559
Goodness-of-fit on F ²	1.044
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0613, wR_2 = 0.1712$
Final R indexes [all data]	$R_1 = 0.1073, wR_2 = 0.1921$
Largest diff. peak/hole / e $Å^{-3}$	0.75/-0.71

Table S3. Crystal data and structure refinement for 3ea





Table S4. Crystal data and structure refinement for 3ia.

Identification code	3ia
Empirical formula	$C_{51.5}H_{35}ClF_6NO_3Sb$
Formula weight	987.00
Temperature/K	296.7(8)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.14367(15)
b/Å	44.3544(8)
c/Å	12.23171(19)
α/°	90
β/°	109.9481(17)
$\gamma/^{\circ}$	90
Volume/Å ³	4663.08(14)
Z	4
$\rho_{calc}g/cm^3$	1.406
μ/mm^{-1}	5.787
F(000)	1988.0
Crystal size/mm ³	$0.7 \times 0.45 \times 0.35$
Radiation	$CuK\alpha$ ($\lambda = 1.54184$)
2Θ range for data collection/c	9.744 to 145.286
Index ranges	$-9 \le h \le 11, -54 \le k \le 53, -15 \le l \le 10$
Reflections collected	25902
Independent reflections	9073 [$R_{int} = 0.0435$, $R_{sigma} = 0.0397$]
Data/restraints/parameters	9073/0/587
Goodness-of-fit on F ²	1.069
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0801, wR_2 = 0.2260$
Final R indexes [all data]	$R_1 = 0.0896, wR_2 = 0.2355$
Largest diff. peak/hole / e Å $^{-3}$	2.19/-1.40





XII. DFT calculation^{4, 5}

1. Complete Reference for Gaussian 09

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.

2. Computational Methods

The DFT calculations were carried out with the GAUSSIAN 09 series of programs. Density functional theory $B3LYP^1$ with a standard 6-31+G(d) basis set was used for geometry optimizations. Harmonic frequency calculations were performed for stationary point to confirm them as a local minima.

3. B3LYP Geometries for the Optimized Compounds and Transition State (3ia)

0	-0.27815800	-1.44429700	-0.55475400
С	-1.53074800	-2.06582900	-0.55306200
С	-0.13796500	-0.14729700	-0.31263000
0	-4.32345100	4.43851000	0.91510400
С	-4.61852400	3.14229000	0.72798500
С	-5.43928000	5.30403300	1.22750600
Ν	1.13859200	0.32054600	-0.22474500
С	1.36812200	1.71535900	-0.41357600
С	2.21787300	-0.56048500	0.14918400
С	0.32037900	2.59799500	-0.16923300

С	2.70089700	2.03122300	-0.94763600
С	-1.23710600	0.68844400	-0.13882600
С	-1.01006100	2.08442600	0.04790100
С	-2.54054300	0.10062400	-0.09598300
С	1.87102200	-1.68549600	1.06608900
С	3.48876800	-0.19944500	-0.17084000
С	-2.13026500	2.88177100	0.35846500
С	0.51445600	4.07816000	-0.10502600
С	1.25150800	-1.38765500	2.29307200
С	2.19670400	-3.01708800	0.77422500
С	-2.66015200	-1.33324800	-0.33069900
С	-1.37948300	-3.50254900	-0.84725100
С	-3.61787600	0.94435800	0.16684200
С	3.73636300	1.05788300	-0.86932300
С	2.96824500	3.23858500	-1.62870800
С	-0.10172500	4.93372800	-1.03445200
С	1.28971100	4.63670200	0.92364700
С	4.65482000	-1.03701600	0.25705300
С	-4.01773100	-1.95688400	-0.37963500
0	-5.73883400	2.67835500	0.80327700
С	-2.11319700	-4.47612700	-0.14760200
С	-0.46855000	-3.91287300	-1.83923800
Н	-2.01188800	3.94088500	0.54234300
С	-3.40261800	2.31316900	0.41149200
С	-4.55972600	-2.37654700	-1.60366500
С	-4.77802900	-2.10177400	0.79215100
С	5.00359000	1.34672300	-1.41320100
С	5.23343000	-1.95752700	-0.63002000
С	5.20746500	-0.88050600	1.53621200
Н	-4.63143800	0.56411800	0.20204100
Н	2.19148200	3.97851500	-1.75031100
С	4.21662900	3.49038300	-2.18372600
Н	1.01048300	-0.35650400	2.54368300
С	0.97175700	-2.40151600	3.21101700
Н	-0.70593700	4.51501400	-1.83569500
С	0.07509100	6.31652000	-0.94993800
С	5.24581800	2.54807800	-2.06541000
Н	6.22649600	2.74904000	-2.48687700
Н	2.66526700	-3.26223700	-0.17287000
С	1.91612500	-4.02973300	1.69325100
Н	4.81744300	-2.07976100	-1.62765500
С	6.33972700	-2.71692500	-0.23947800
Н	5.79522200	0.61176200	-1.32345300
Н	4.38518700	4.42309400	-2.71406300

Η	1.76149200	3.98517300	1.65478500
С	1.45796800	6.02048100	1.01271900
Н	-2.80590600	-4.17879700	0.63163900
С	-1.94356500	-5.82898400	-0.44195100
Н	-3.98113400	-2.26212500	-2.51667600
С	-5.83630500	-2.94183700	-1.65339700
Н	0.10355600	-3.17063800	-2.38805900
С	-0.31190800	-5.26592100	-2.13714600
Н	4.77001100	-0.16543400	2.22832600
С	6.31176400	-1.64232000	1.92677200
Н	-4.36943400	-1.77633400	1.74614200
С	-6.05304900	-2.66990500	0.74066800
Н	2.17219000	-5.05766200	1.45247000
С	1.30433400	-3.72661600	2.91275300
Н	-2.51162400	-6.57194400	0.11075300
С	-1.04804300	-6.22824500	-1.43868900
Н	0.50719900	-2.15446900	4.16181100
Н	-6.24549700	-3.26324700	-2.60719500
С	-6.58410800	-3.09181600	-0.48217100
Н	-6.16724800	5.28389100	0.41317100
Н	-5.00656500	6.29750600	1.34003200
Н	-5.91701700	4.97833600	2.15443100
Н	6.72749500	-1.51577900	2.92268700
С	6.87961600	-2.56232200	1.04077600
Н	1.09052400	-4.51647100	3.62744200
Н	-6.63096500	-2.77965000	1.65418200
Н	6.77788100	-3.42786700	-0.93486700
Н	-0.92481400	-7.28262400	-1.67012000
Н	7.73917800	-3.15314800	1.34489000
Н	-0.39775400	6.96533800	-1.68217500
С	0.85599800	6.86332200	0.07367600
Н	0.38162900	-5.56872700	-2.91682100
Н	-7.57726600	-3.53038700	-0.52198000
Н	2.05863000	6.43888800	1.81564800
Н	0.99077700	7.93923700	0.14086500

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XIV. Copies of NMR spectra

¹H NMR spectra of **3aa** (CDCl₃)



¹³C NMR spectra of **3aa** (CDCl₃)



¹H NMR spectra of **3ba** (CDCl₃)



¹³C NMR spectra of **3ba** (CDCl₃)



¹H NMR spectra of **3ca** (CDCl₃)



¹³C NMR spectra of **3ca** (CDCl₃)



¹H NMR spectra of **3da** (CD₃CN)



¹³C NMR spectra of **3da** (CD₃CN)



¹H NMR spectra of **3ea** (CDCl₃)



¹³C NMR spectra of **3ea** (CDCl₃)



¹⁹F NMR spectra of **3ea** (CDCl₃)



¹H NMR spectra of **3fa** (CDCl₃)



¹³C NMR spectra of **3fa** (CDCl₃)



¹H NMR spectra of **3ga** (CDCl₃)



¹³C NMR spectra of **3ga** (CDCl₃)



¹H NMR spectra of **3ha** (CDCl₃)



¹³C NMR spectra of **3ha** (CDCl₃)



¹⁹F NMR spectra of **3ha** (CDCl₃)



^{30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190} fl (ppm)

¹H NMR spectra of **3ia** (CDCl₃)



¹³C NMR spectra of **3ia** (CDCl₃)



¹H NMR spectra of **3ja** (CDCl₃)



¹³C NMR spectra of **3ja** (CDCl₃)



¹H NMR spectra of **3ka** (CDCl₃)



¹³C NMR spectra of **3ka** (CDCl₃)



¹H NMR spectra of **3la** (CDCl₃)



¹³C NMR spectra of **3la** (CDCl₃)



¹H NMR spectra of **3ma** (CDCl₃)



¹³C NMR spectra of **3ma** (CDCl₃)



¹H NMR spectra of **3na** (CDCl₃)



¹³C NMR spectra of **3na** (CDCl₃)



¹H NMR spectra of **3oa** (CDCl₃)



¹³C NMR spectra of **30a** (CDCl₃)



¹H NMR spectra of **3pa** (CDCl₃)



¹³C NMR spectra of **3pa** (CDCl₃)



¹H NMR spectra of **3qa** (CDCl₃)



¹³C NMR spectra of **3qa** (CDCl₃)





¹H NMR spectra of **3ra** and its isomer (CDCl₃)

¹H NMR spectra of **3ab** (CDCl₃)



¹³C NMR spectra of **3ab** (CDCl₃)



¹H NMR spectra of **3ac** (CDCl₃)



¹³C NMR spectra of **3ac** (CDCl₃)



¹H NMR spectra of **3ad** (CDCl₃)







¹⁹F NMR spectra of **3ad** (CDCl₃)

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¹H NMR spectra of **3ae** (CDCl₃)



¹³C NMR spectra of **3ae** (CDCl₃)



¹H NMR spectra of **3af** (CDCl₃)



¹³C NMR spectra of **3af** (CDCl₃)



¹H NMR spectra of **3mc** (CDCl₃)



¹³C NMR spectra of **3mc** (CDCl₃)

