# Rh(III)-catalysed synthesis of cinnolinium and fluoranthenium salts by using C-H activation/annulation reactions: Organelle specific mitochondrial staining application

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# Electronic

# **Supporting Information**

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# 1. Parallel competitive reaction



### Scheme S1

A solution of 2-phenyl-2H-indazole **1a** (58 mg, 0.3 mmol), 1,2-di-p-tolylethyne **2b** (62 mg, 0.3 mmol), AgBF<sub>4</sub> (58 mg 0.3 mmol), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (9.0 mg, 5.0 mol %), and Cu(OAc)<sub>2</sub> (54 mg 0.3 mmol) in 1,2-DCE (3 mL). The tube was sealed with a Teflon-coated screw cap and the reaction solution was heated at 110 °C for 3 hours. At the same time, another solution of 2-phenyl-2H-indazole **1a** (58 mg, 0.3 mmol), 1,2-bis(4-chlorophenyl)ethyne **2d** (74 mg, 0.3 mmol), AgBF<sub>4</sub> (58 mg 0.3 mmol), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (9.0 mg, 5.0 mol %), and Cu(OAc)<sub>2</sub> (54 0.3 mmol) in 1,2-DCE (3 mL). The tube was sealed with a Teflon-coated screw cap and the reaction solution was heated at 110 °C for 3 hours. At the same time, another solution of 2-phenyl-2H-indazole **1a** (58 mg, 0.3 mmol), 1,2-bis(4-chlorophenyl)ethyne **2d** (74 mg, 0.3 mmol), AgBF<sub>4</sub> (58 mg 0.3 mmol), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (9.0 mg, 5.0 mol %), and Cu(OAc)<sub>2</sub> (54 0.3 mmol) in 1,2-DCE (3 mL). The tube was sealed with a Teflon-coated screw cap and the reaction solution was heated at 110 °C for 3 hours. After cooling ambient temperature, the solvent was removed from both the reaction mixtures under reduced pressure and the residues of the reaction mixtures were separately purified by silica gel (100-200 mesh) column chromatography using Methanol/DCM as the eluant to afford **3e** 32% and **3g** 24% (3e:3g =  $\sim$ 1.3:1).



#### Scheme S2

A solution of 5,6-diphenylindazolo[2,3-a]quinoline **1a** (111 mg, 0.3 mmol), 1,2-di-ptolylethyne **2c** (61 mg, 0.3 mmol), AgBF<sub>4</sub> 58 mg (0.3 mmol), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (9 mg, 5.0 mol %), and Cu(OAc)<sub>2</sub> (0.3 mmol) in 1,2-DCE 3.0 mL. The tube was sealed with a Teflon-coated screw cap and the reaction solution was heated at 110 °C for 3 hours. At the same time, another solution of 2-phenyl-2H-indazole **1a** (111 mg, 0.3 mmol), 1,2-bis(4- chlorophenyl)ethyne **2d** (74 mg, 0.3 mmol), AgBF<sub>4</sub> 58 mg (0.3 mmol), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (9 mg, 5.0 mol %), and Cu(OAc)<sub>2</sub> (0.3 mmol) in 1,2-DCE 3 ml. The tube was sealed with a Teflon-coated screw cap and the reaction solution was heated at 110 °C for 3 hours. After cooling ambient temperature, the solvent was removed from both the reaction mixtures under reduced pressure and the residues of the reaction mixtures were separately purified by silica gel (100-200 mesh) column chromatography using Methanol/DCM as the eluant to afford **5b** 30% and **5d** 47% (**5b:5d** = ~1.7:1.0)

## 2. H to D exchange experiments



Scheme S3

To an oven-dried 20 mL reaction tube with septum containing were added 2-phenyl-2Hindazole **1a** 58.2 mg (0.3 mmol, 1.0 equiv), [RhCp\*Cl<sub>2</sub>]2 (9.18 mg, 0.015 mmol, 0.05 equiv), Cu(OAc)<sub>2</sub> 55.6 mg, (0.3 mmol, 1.0 equiv), Acetic acid- $d_4$  0.38 ml (20.0 equiv) and 1,2-DCE 3.0 ml. The reaction mixture was heated at 110 °C for 12 h. After the reaction mixture was cooled to room temperature diluted with CH<sub>2</sub>Cl<sub>2</sub>, filtered through celite and the filtrate was concentrated under reduced pressure. After that, purification was performed by column chromatography on silica gel using hexane and ethyl acetate (90:10) as eluent. Desired product colourless solid **1a**- $d_3$  52 mg was obtained in 90% of yield. The H/D exchange was found to be 76% at the protons attached to C-2 and C-5 in the recovered 2-phenyl-2H-indazole **1a**- $d_3$ . Also found H/D exchange 25% at the indazole *2-H* position. These results also clearly reveal that the C-H bond activation as a key intermediate in the reaction as well as it is the reversible process.

0.00



Figure SI1: Preliminary mechanistic study



### Scheme S4

To an oven-dried 20 mL reaction tube with septum containing were added 2-phenyl-2Hindazole **1a** 58 mg (0.3 mmol, 1.0 equiv), diphenylacetylene **2a** 52 mg (0.3 mmol), AgBF<sub>4</sub> 58 mg (0.3 mmol%), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (9 mg, 0.015 mmol, 0.05 equiv), Cu(OAc)<sub>2</sub> 56 mg, (0.3 mmol, 1.0 equiv), acetic acid- $d_4$  0.38 ml (20.0 equiv) and 1,2-DCE 3.0 ml. The reaction mixture was heated at 110 °C for 12 h. After the reaction mixture was cooled to room temperature diluted with CH<sub>2</sub>Cl<sub>2</sub>, filtered through celite and the filtrate was concentrated under reduced pressure. After that, purification was performed by column chromatography on silica gel using DCM and Methanol (95:5) as eluent. Desired product colourless solid **3a** was obtained in 78% of yield.

# 3. Photoluminescence spectrum



Figure SI2: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 3a



Figure SI3: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 3b



Figure SI4: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 3c



Figure SI5: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 3d



Figure SI6: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 3f



Figure SI7: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 4g



Figure SI8: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 3h



Figure SI9: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 5a



Figure SI10: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 5b



Figure SI11: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 5c



Figure SI12: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 5d



Figure SI13: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 5e



Figure SI14: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 5f



Figure SI15: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 5g



Figure SI16: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 5h



Figure SI17: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 5i



Figure SI18: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 5j



Figure SI19: Normalized absorption (black), Fluorescence in DCM (red) spectra of compound 5k

# 4. Copy of <sup>1</sup>H, <sup>13</sup>C and HRMS spectra



Figure S21: <sup>13</sup>C NMR spectrum of compound 3a in CDCl<sub>3</sub>



Figure S23: <sup>19</sup>F spectrum of compound 3a



Figure S25: <sup>1</sup>H NMR spectrum of compound 3b in CDCl<sub>3</sub>



Figure S27: DEPT-135 NMR spectrum of compound 3b in CDCl<sub>3</sub>





-10.37 -10.37



Figure S29: <sup>1</sup>H NMR spectrum of compound 3c in CDCl<sub>3</sub>



Figure S31: DEPT-135 NMR spectrum of compound 3c in CDCl<sub>3</sub>



Figure S32: HRMS spectrum of compound 3c



Figure S33: <sup>1</sup>H NMR spectrum of compound 3d in CDCl<sub>3</sub>



Figure S34: <sup>13</sup>C NMR spectrum of compound 3d in CDCl<sub>3</sub>



Figure S35: HRMS spectrum of compound 3d





Figure S36: <sup>1</sup>H NMR spectrum of compound 3e in CDCl<sub>3</sub>



Figure S37: <sup>13</sup>C NMR spectrum of compound 3e in CDCl<sub>3</sub>



Figure S38: DEPT-135 NMR spectrum of compound 3e in CDCl<sub>3</sub>



Figure S39: HRMS spectrum of compound 3e





Figure S41: <sup>13</sup>C NMR spectrum of compound 3f in CDCl<sub>3</sub>



Figure S42: DEPT-135 NMR spectrum of compound 3f in CDCl<sub>3</sub>



Figure S43: HRMS spectrum of compound 3f





Figure S45: <sup>13</sup>C NMR spectrum of compound 3g in DMSO-d<sub>6</sub>



Figure S46: DEPT-135 NMR spectrum of compound 3g in DMSO-d<sub>6</sub>



Figure S47: HRMS spectrum of compound 3g

-10.89





Figure S48: <sup>1</sup>H NMR spectrum of compound 3h in DMSO-d<sub>6</sub>



Figure S49: <sup>13</sup>C NMR spectrum of compound 3h in DMSO-d<sub>6</sub>



Figure S50: DEPT-135 NMR spectrum of compound 3h in DMSO-d<sub>6</sub>



Figure S51: HRMS spectrum of compound 3h

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Figure S54: DEPT-135 NMR spectrum of compound 5a in CDCl<sub>3</sub>

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Figure S55: HRMS spectrum of compound 5a



Figure S57: <sup>11</sup>B spectrum of compound 5a





Figure S59: <sup>13</sup>C NMR spectrum of compound 5b in CDCl<sub>3</sub>



Figure S60: DEPT-135 NMR spectrum of compound 5b in CDCl<sub>3</sub>



Figure S61: HRMS spectrum of compound 5b





Figure S63: <sup>13</sup>C NMR spectrum of compound 5c in CDCl<sub>3</sub>





Figure S64: DEPT-135 NMR spectrum of compound 5c in CDCl<sub>3</sub>



Figure S65: HRMS spectrum of compound 5c



Figure S67: <sup>13</sup>C NMR spectrum of compound 5d in CDCl<sub>3</sub>



Figure S68: DEPT-135 NMR spectrum of compound 5d in CDCl<sub>3</sub>

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Figure S69: HRMS spectrum of compound 5d



Figure S71: <sup>13</sup>C NMR spectrum of compound 5e in CDCl<sub>3</sub>







Figure S73: HRMS spectrum of compound 5e



Figure S74: <sup>13</sup>C NMR spectrum of compound 5f in CDCl<sub>3</sub>



Figure S75: DEPT-135 NMR spectrum of compound 5f in CDCl<sub>3</sub>

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	575.2739 575.2236	-24.9 -43.3 25.4 44.2	28.5 C45 H35 30.5 C41 H27	624.3 N4 618.1	6.581 0.328	0.14 72.03	45 35 41 27	4								-
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Figure S76: HRMS spectrum of compound 5f



Figure S78: <sup>13</sup>C NMR spectrum of compound 5g in CDCl<sub>3</sub>



Figure S79: DEPT-135 NMR spectrum of compound 5g in CDCl<sub>3</sub>



Figure S80: HRMS spectrum of compound 5g



Figure S81: <sup>1</sup>H NMR spectrum of compound 5h in CDCl<sub>3</sub>



Figure S82: <sup>13</sup>C NMR spectrum of compound 5h in CDCl<sub>3</sub>



Figure S83: DEPT-135 NMR spectrum of compound 5h in CDCl<sub>3</sub>

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Figure S84: HRMS spectrum of compound 5h



Figure S86: <sup>13</sup>C NMR spectrum of compound 5i in CDCl<sub>3</sub>



Figure S87: DEPT-135 NMR spectrum of compound 5i in CDCl<sub>3</sub>

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Figure S88: HRMS spectrum of compound 5i



Figure S90: <sup>13</sup>C NMR spectrum of compound 5j in CDCl<sub>3</sub>



Figure S91: DEPT-135 NMR spectrum of compound 5j in CDCl<sub>3</sub>



Figure S92: HRMS spectrum of compound 5j



Figure S93: <sup>1</sup>H NMR spectrum of compound 5k in CDCl<sub>3</sub>

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Figure S94: <sup>13</sup>C NMR spectrum of compound 5k in CDCl<sub>3</sub>



Figure S95: HRMS spectrum of compound 5k+5k'

#### 7.02



Figure S96: <sup>1</sup>H NMR spectrum of compound 5l in CDCl<sub>3</sub>







Figure S98: HRMS spectrum of compound 51+51'

# 5. DFT Calculations

# **Table 2. Data of DFT studies**<sup>1</sup>

Method	]	B3LYP/6-311G*	
Compound	LUMO (eV)	HOMO (eV)	Gap (eV)
<b>3</b> a	-5.6346	-9.2603	3.6257
<b>3</b> b	-5.6934	-9.1038	3.4104
3c	-5.6850	-9.0847	3.3997
3d	-5.7168	-9.3781	3.6613
<b>3</b> e	-5.7206	-9.0012	3.2806
3f	-5.8308	-9.1160	3.2852
3g	-5.7962	-9.3231	3.5269
3h	-5.7775	-9.1544	3.3769
5a	-5.1511	-8.5408	3.3897
5b	-5.1040	-8.4167	3.3127
5c	-5.0251	-8.1794	3.1543
5d	-5.3217	-8.6695	3.3478
5e	-5.3013	-8.6377	3.3364
5f	-5.0958	-8.4758	3.38
5g	-5.0039	-8.3479	3.344
5h	-5.0814	-8.1149	3.0335
5i	-4.605	-7.466	2.86
5j	-5.31873	-8.6741	3.3553
5k	-5.0436	-8.3190	3.2754
5k'	-5.12689	-8.48288	3.3559
51	-5.2531	-8.5745	3.3214
51'	-5.2466	-8.5773	3.3307



Figure S99: HOMO-LUMO of the compound 3a



Figure S100: HOMO-LUMO of the compound 3b



Figure S101: HOMO-LUMO of the compound 3c



Figure S102: HOMO-LUMO of the compound 3d



Figure S103: HOMO-LUMO of the compound 3e



Figure S104: HOMO-LUMO of the compound 3f



Figure S105: HOMO-LUMO of the compound 3g



Figure S106: HOMO-LUMO of the compound 3h



Figure S107: HOMO-LUMO of the compound 5a



Figure S108: HOMO-LUMO of the compound 5b



Figure S109: HOMO-LUMO of the compound 5c



Figure S110: HOMO-LUMO of the compound 5d



Figure S111: HOMO-LUMO of the compound 5e



Figure S112: HOMO-LUMO of the compound 5f



Figure S113: HOMO-LUMO of the compound 5g



Figure S114: HOMO-LUMO of the compound 5h



Figure S115: HOMO-LUMO of the compound 5i



Figure S116: HOMO-LUMO of the compound 5j



Figure S117: HOMO-LUMO of the compound 5k



Figure S118: HOMO-LUMO of the compound 51

## 6. Reference

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