Supplementary Information

Exploring a Unique Reactivity of N-Heterocyclic Carbenes (NHC) in Rhodium(III)-Catalyzed Intermolecular C–H Activation/Annulation

Debasish Ghorai, and Joyanta Choudhury*

Organometallics & Smart Materials Laboratory, Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhauri, Indore By-pass Road, Bhopal 462 066, INDIA.

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1. General methods and materials

$^1$H, $^{13}$C{$^1$H} and $^{19}$F NMR spectra were recorded on Bruker AVANCE III 400, 500 and 700 MHz NMR spectrometers at room temperature unless mentioned otherwise. Chemical shifts ($\delta$) are expressed in ppm using the residual proton resonance of the solvent as an internal standard (CHCl$_3$: $\delta$ = 7.26 ppm for $^1$H spectra, 77.2 ppm for $^{13}$C{$^1$H} spectra; CH$_3$CN: $\delta$ = 1.94 ppm for $^1$H spectra, 1.3 ppm for $^{13}$C{$^1$H} spectra). All coupling constants ($J$) are expressed in hertz (Hz) and only given for $^1$H-$^1$H couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), dt (doublet of triplets), ddd (doublet of doublet of doublets), m (multiplet). ESI mass spectroscopy was performed on a Bruker microTOF QII spectrometer. Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at different low temperatures for each crystal. Dry solvents and reagents were obtained from commercial suppliers and used without further purification. Deuterated solvents and RhCl$_3$.xH$_2$O were purchased from Aldrich. IrCl$_3$.xH$_2$O and RuCl$_3$.xH$_2$O were purchased from Johnson Matthey and used as received without further purification. [RhCp*Cl$_2$]$_2$, [IrCp*Cl$_2$]$_2$, [Ru(p-cym)Cl$_2$]$_2$, [RhCl(COD)]$_2$, N-substituted aryl imidazole$^5$, 1-nitro-4-(phenylethynyl)benzene$^6$, 1-methoxy-4-(phenylethynyl)benzene$^6$, 1,4-Diphenylbutadiyne$^7$ were synthesized according to reported procedures.
2. Stoichiometric silver-transmetalation method of the annulation reaction

In an oven dried Schlenk tube, a mixture of 1a (14.3 mg, 0.05 mmol) and Ag₂O (6.0 mg, 0.55 mmol) in dry and degassed CH₂Cl₂ (5 mL) was stirred under N₂ atmosphere at room temperature under dark condition. After 4 h, to that solution [RhCp*Cl₂]₂ (15.4 mg, 0.025 mmol) was added and the mixture was again stirred at room temperature for another 4 h. Then KPF₆ (18.4 mg, 0.1 mmol) and 2a (10.7 mg, 0.06 mmol) were added to this solution and stirred further for 16 h under the same condition. After that the whole reaction mixture was passed through a short celite pad which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated by silica gel column chromatography, eluted with a 7:1 (v/v) CHCl₃/MeOH solvent mixture affording 3a as a pale yellow solid (18 mg, 0.037 mmol, 75%).

3-methyl-4,5-diphenylimidazo[1,2-a]quinolinium hexafluorophosphate (3a):

1H NMR (400 MHz, CDCl₃, 300K): δ 8.63 (d, \( J = 1.9 \) Hz, 1H), 8.35 (d, \( J = 8.5 \) Hz, 1H), 7.97 (t, \( J = 7.2 \) Hz, 1H), 7.83 (d, \( J = 1.8 \) Hz, 1H), 7.67 – 7.63 (m, 1H), 7.60 (d, \( J = 8.1 \) Hz, 1H), 7.34 – 7.29 (m, 8H), 7.15 – 7.13 (m, 2H), 3.40 (s, 3H). HRMS (ESI, positive ion): \( M^+ = 335.1560 \) (calculated 335.1543 for \([C_{24}H_{19}N_2]^+\)).

**Figure S1.** Molecular structure of product 3a of hexafluorophosphate salt (30% probability level). Selected bond lengths (Å) and bond angles (°): C₁–N₁ = 1.342(4); C₁–N₂ = 1.364(4); C₁–C₁₂ = 1.429(4); C₅–N₂ = 1.394(4); C₅–C₆ = 1.400(5); C₆–C₁₁ = 1.445(4); C₁₁–C₁₂ = 1.363(4); N₁–C₁–N₂ = 106.9(3); N₂–C₁–C₁₂ = 121.2(3); N₁–C₁–C₁₂ = 131.8(3); C₁–N₂–C₅ = 122.6(3); N₂–C₅–C₆ = 116.9(3); C₅–C₆–C₁₁ = 120.5(3); C₁₂–C₁₁–C₆ = 121.1(3); C₁₁–C₁₂–C₁ = 117.3(3).
3. Optimization of the reaction conditions

To an oven dried Schlenk tube, 1a (0.1 mmol), Ag₂O / NaOAc (0.055 mmol/ 0.4 mmol), catalyst (0.005 mmol), AgOTf (0.3 mmol) and 2a (0.12 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with N₂ gas. To this mixture, dry and degassed CH₂Cl₂ (3.0 mL) was added under Schlenk technique and the reaction mixture was left with stirring at room temperature under dark. After a certain time, the whole reaction mixture was passed through a short celite pad and which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated by silica gel column chromatography, eluted with a 7:1 (v/v) CHCl₃/MeOH solvent mixture.

Table S1: Optimization studies

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Additives (equiv.)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[RhCp*Cl₂]₂</td>
<td>Ag₂O (0.55) + KPF₆ (2.5)</td>
<td>12</td>
<td>13&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>[RhCp*Cl₂]₂</td>
<td>NaOAc (4) + KPF₆ (2.5)</td>
<td>12</td>
<td>trace&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>[RhCp*Cl₂]₂</td>
<td>Ag₂O (0.55) + AgOTf (2)</td>
<td>12/24</td>
<td>55/66</td>
</tr>
<tr>
<td>4</td>
<td>[RhCp*Cl₂]₂</td>
<td>Ag₂O (2) + AgOTf (3)</td>
<td>24</td>
<td>49</td>
</tr>
<tr>
<td>5</td>
<td>[RhCp*Cl₂]₂</td>
<td>NaOAc (2.2) + AgOTf (2)</td>
<td>24</td>
<td>45</td>
</tr>
<tr>
<td>6</td>
<td>[RhCp*Cl₂]₂</td>
<td>NaOAc (4) + AgOTf (2)</td>
<td>12</td>
<td>56</td>
</tr>
<tr>
<td>7</td>
<td>[RhCp*Cl₂]₂</td>
<td>NaOAc (4) + AgOTf (2)</td>
<td>24</td>
<td>66</td>
</tr>
<tr>
<td>8</td>
<td>[RhCp*Cl₂]₂</td>
<td>NaOAc (4) + AgOTf (3)</td>
<td>24</td>
<td>81</td>
</tr>
<tr>
<td>9</td>
<td>[RhCp*Cl₂]₂</td>
<td>NaOAc (4) + AgOTf (3)</td>
<td>4</td>
<td>&lt;15&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>10</td>
<td>[RhCp*Cl₂]₂</td>
<td>NaOAc (4) + CuCl₂·2H₂O (3)</td>
<td>24</td>
<td>trace&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>11</td>
<td>[RhCp*Cl₂]₂</td>
<td>NaOAc (4) + Cu(OAc)₂·H₂O (3)</td>
<td>24</td>
<td>Not detected&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>12</td>
<td>[RhCp*Cl₂]₂</td>
<td>AgOTf (3)</td>
<td>24</td>
<td>Not detected&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>13</td>
<td>-----</td>
<td>NaOAc (4) + AgOTf (3)</td>
<td>24</td>
<td>Not detected&lt;sup&gt;c&lt;/sup&gt;</td>
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**Table S2**: Comparison of TON and TOF values of reported catalytic annulations methods with this work

<table>
<thead>
<tr>
<th>Entry</th>
<th>Directing group (DG)</th>
<th>Reaction Conditions</th>
<th>References</th>
<th>TON</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-substituted Pyridine</td>
<td>1 mol% Cp*Rh(H₂O)₃(OTf)₂, HOTf, MeOH, O₂ (1 atm), 120 °C, 22 h</td>
<td><em>J. Am. Chem. Soc.</em>, 2013, 135, 8850</td>
<td>99</td>
<td>4.5</td>
</tr>
<tr>
<td>2</td>
<td>2-substituted Pyridine</td>
<td>0.1 mol% Cp*Rh(H₂O)₃(OTf)₂, HOTf, MeOH, O₂ (1 atm), 120 °C, 8 days</td>
<td><em>J. Am. Chem. Soc.</em>, 2013, 135, 8850</td>
<td>740</td>
<td>3.85</td>
</tr>
<tr>
<td>3</td>
<td>2-substituted Pyridine</td>
<td>1 mol% [(RhCp*Cl₂)₂], 0.5 equiv. Cu(BF₄)₂·6H₂O, DME, O₂, 25 – 30 °C, 24 h</td>
<td><em>Chem. Eur. J.</em>, 2013, 19, 14181</td>
<td>47</td>
<td>1.95</td>
</tr>
<tr>
<td>4</td>
<td>N-substituted pyrazole</td>
<td>1 mol% [(RhCp*Cl₂)₂], 1 equiv. Cu(OAc)₂·H₂O, 1 equiv. Na₂CO₃, o-xylene, 150 °C, N₂, 2 h</td>
<td><em>J. Org. Chem.</em>, 2011, 76, 13</td>
<td>40.5</td>
<td>20.2</td>
</tr>
<tr>
<td>6</td>
<td>3-substituted thiophene</td>
<td>5 mol% [(RhCp*Cl₂)₂], 2 equiv. Cu(OAc)₂·H₂O, DCE, 83 °C, 16 h</td>
<td><em>Chem. Eur. J.</em>, 2014, 20, 385</td>
<td>8.6</td>
<td>0.86</td>
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<tr>
<td>7</td>
<td>Sulphonic acid</td>
<td>2 mol% [(RhCp*Cl₂)₂], 8 mol% AgSbF₆, 2 equiv. AgOAc, dioxane, 100 °C, 16 h, Ar</td>
<td><em>Chem. Commun.</em>, 2014, 50, 9776</td>
<td>21.5</td>
<td>1.34</td>
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<tr>
<td>8</td>
<td>Amide</td>
<td>2.5 mol% [(RhCp*Cl₂)₂], 30 mol% CsOAc, MeOH (0.2M), 60 °C, 16 h</td>
<td><em>J. Am. Chem. Soc.</em>, 2010, 132, 6908</td>
<td>18</td>
<td>1.12</td>
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<tr>
<td>9</td>
<td>Amide</td>
<td>4 mol% [(RhCp*Cl₂)₂], 1.1 equiv. Ag₂CO₃, CH₃CN, 120 °C, N₂, 6 h</td>
<td><em>J. Org. Chem.</em>, 2011, 76, 7583</td>
<td>5.6</td>
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<td></td>
<td>Substrate</td>
<td>Conditions</td>
<td>Journal</td>
<td>Year</td>
<td>Value</td>
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<td>----------------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>--------------------------------------------</td>
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<td>--------</td>
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<tr>
<td>10</td>
<td>Acetanilide</td>
<td>5 mol% [Cp*Rh(MeCN)]$_2$[SbF$_6$]$_2$, 20 mol% Cu(OAc)$_2$·H$_2$O/O$_2$ (1 atm), tAmOH (0.2 M), 60 °C, 16 h</td>
<td><em>J. Am. Chem. Soc.</em>, 2010, 132, 18326</td>
<td></td>
<td>1.12</td>
</tr>
<tr>
<td>11</td>
<td>Carboxylic acids</td>
<td>1 mol% [(RhCp*Cl)$_2$], 5 mol% Cu(OAc)$_2$·H$_2$O, DMF, 120 °C, 2 h</td>
<td><em>J. Org. Chem.</em>, 2007, 72, 5362</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>12</td>
<td>Azobenzene</td>
<td>1 mol% [(RHCp*Cl)$_2$], 0.5 Cu(BF$_4$)$_2$·6H$_2$O, tBuOH, 70 °C, 16 h, air</td>
<td><em>Chem. Eur. J.</em>, 2013, 19, 6198</td>
<td></td>
<td>2.84</td>
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<tr>
<td>13</td>
<td>N-substituted benzimidazole</td>
<td>5 mol% [(RhCp*Cl)$_2$], 1.2 equiv. Cu(OAc)$_2$·H$_2$O, toluene, 110 °C, 4 h</td>
<td><em>Chem. Eur. J.</em>, 2012, 18, 8896</td>
<td></td>
<td>2.45</td>
</tr>
<tr>
<td>14</td>
<td>2-substituted imidazole</td>
<td>5 mol% [(RhCp*Cl)$_2$], 1.2 equiv. Cu(OAc)$_2$·H$_2$O, toluene, 110 °C, 24h</td>
<td><em>Org. Lett.</em>, 2013, 15, 1878</td>
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<td>0.41</td>
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<tr>
<td>15</td>
<td>NHC</td>
<td>2 mol% [(RhCp*Cl)$_2$], 4 equiv. NaOAc, 3 equiv. AgOTf, DCE, Room Temp., 24 h, N$_2$</td>
<td>This work</td>
<td></td>
<td>0.79</td>
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<tr>
<td>16</td>
<td>NHC</td>
<td>0.5 mol% [(RhCp*Cl)$_2$], 4 equiv. NaOAc, 3 equiv. AgOTf, DCE, Reflux, 2 h, N$_2$</td>
<td>This work</td>
<td></td>
<td>43</td>
</tr>
</tbody>
</table>

4. General procedure for the synthesis of imidazolium salts

The syntheses of imidazolium salts were performed according to the reported procedure$^8$, by stirring a mixture of N-aryl imidazole or benzimidazole (5 mmol) and iodomethane (0.44 mL, 7 mmol) in dry THF (7 mL) for 24 h at room temperature. The resultant precipitate was collected by filtration and washed with hexane and then dried in vacuo.

**3-methyl-1-phenyl-1H-imidazol-3-ium iodide (1a):** $^1$H NMR (400 MHz, CD$_3$CN, 300K): δ 9.05 (s, 1H), 7.76 (s, 1H), 7.65 – 7.60 (m, 5H), 7.56 (s, 1H), 3.95 (s, 3H). HRMS (ESI, positive ion): M$^+$ = 159.0921 (calculated 159.0917 for [C$_{10}$H$_{11}$N$_2$]$^+$).

**3-methyl-1-(4-nitrophenyl)-1H-imidazol-3-ium iodide (1b):** $^1$H NMR (400 MHz, CD$_3$CN, 300K): δ 9.35 (s, 1H), 8.47 – 8.45 (m, 2H), 7.91 (d, J = 8.9 Hz, 2H), 7.88 (t, J = 1.7 Hz, 1H), 7.62 (s, 1H), 3.99 (s, 3H).

**1-(4-methoxyphenyl)-3-methyl-1H-imidazol-3-ium iodide (1c):** $^1$H NMR (400 MHz, CD$_3$CN, 300K): δ 9.05 (s, 1H), 7.69 – 7.68 (m, 1H), 7.58 – 7.54 (m, 3H), 7.14 – 7.12 (m, 2H), 3.95 (s, 3H), 3.86 (s, 3H).

**3-methyl-1-phenyl-1H-benzo[d]imidazol-3-ium iodide (1d):** $^1$H NMR (400 MHz, CDCl$_3$, 300K): δ 11.03 (s, 1H), 7.88 (dd, J = 8.1, 1.1 Hz, 2H), 7.82 (d, J = 8.1 Hz, 1H), 7.76 – 7.64 (m, 6H), 4.47 (s, 3H).
3-butyl-1-phenyl-1H-imidazol-3-ium iodide (1e): A mixture of N-phenyl imidazole (0.38 mL, 3 mmol) and iodobutane (0.375 mL, 3.3 mmol) in 1,4-dioxane (~10 mL) were refluxed at 100°C for 24h. After cooling, all volatiles were evaporated and the residue was washed several times with diethyl ether. Then resultant brown thick liquid was dried under reduced pressure which gives 1e (580 mg, 1.76 mmol, 59%). \(^1\)H NMR (400 MHz, CDCl\(_3\), 300K): \(\delta\) 10.40 (s, 1H), 7.81 (t, \(J = 1.8\) Hz, 1H), 7.78 – 7.77 (m, 1H), 7.77 – 7.74 (m, 2H), 7.52 – 7.43 (m, 3H), 4.51 (t, \(J = 7.4\) Hz, 2H), 1.97 – 1.92 (m, 2H), 1.41 – 1.35 (m, 2H), 0.91 (t, \(J = 7.4\) Hz, 3H).

3-benzyl-1-phenyl-1H-imidazol-3-ium bromide (1f): In an oven dried screw cap sealed tube, N-phenyl imidazole (253 µL, 2 mmol), CH\(_2\)Cl\(_2\) (2 mL) and benzyl bromide (476 µL, 4 mmol) were taken and flushed with N\(_2\). Then the mixture was stirred at 35°C in oil bath for 36 h. After cooling, all volatiles were evaporated and the residue was washed with hexane and diethyl ether. Final product 1f as pale yellow liquid was obtained after drying under reduced pressure (190 mg, 0.6 mmol, 30%). \(^1\)H NMR (400 MHz, CDCl\(_3\), 300K): \(\delta\) 10.68 (s, 1H), 7.77 (s, 1H), 7.69 (s, 1H), 7.61 (d, \(J = 7.6\) Hz, 2H), 7.52 (d, \(J = 3.0\) Hz, 2H), 7.34 – 7.25 (m, 3H), 7.19 – 7.17 (m, 3H), 5.66 (s, 2H).

5. General procedure for the annulation reactions

To an oven dried Schlenk tube, 1 (0.1 mmol), NaOAc (0.4 mmol), [RhCp*Cl\(_2\)]\(_2\) (0.005 mmol), AgOTf (0.3 mmol) and 2 (0.12 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with N\(_2\) gas. To this mixture, dry and degassed CH\(_2\)Cl\(_2\) (3.0 mL) was added under Schlenk technique and the reaction mixture was left with stirring at room temperature under dark. After 24 h stirring, the whole reaction mixture was passed through a short celite pad and which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated by silica gel column chromatography, eluted with a CHCl\(_3\)/MeOH solvent mixture.

6. Experimental characterization data for the products (3a-3p)

3-methyl-4,5-diphenylimidazo[1,2-a]quinolinium trifluoromethanesulfonate (3a): 39.2 mg, 81% yield. \(^1\)H NMR (400 MHz, CD\(_3\)CN, 300K): \(\delta\) 8.70 (d, \(J = 2.3\) Hz, 1H), 8.48 (d, \(J = 8.5\) Hz, 1H), 8.03 – 7.99 (m, 1H), 7.82 (d, \(J = 2.3\) Hz, 1H), 7.73 – 7.69 (m, 1H), 7.53 (dd, \(J = 8.3\), 0.9 Hz, 1H), 7.37 – 7.34 (m, 8H), 7.22 (dd, \(J = 6.6\), 3.0 Hz, 2H), 3.28 (s, 3H). \(^{13}\)C NMR (101 MHz, CD\(_3\)CN, 300K): \(\delta\) 147.20, 138.31, 135.62, 133.35, 133.03, 132.18, 131.73, 130.99, 130.18, 130.13, 129.34, 129.19, 129.13, 128.67, 125.44, 124.46, 123.72, 120.54, 117.32, 114.15, 38.69. \(^{19}\)F NMR (376 MHz, CDCl\(_3\), 300K): \(\delta\) -78.34 (s). HRMS (ESI, positive ion): M\(^+\) = 335.1549 (calculated 335.1543 for [C\(_{24}\)H\(_{19}\)N\(_2\)]\(^+\)).
Figure S2. Molecular structure of product 3a of trifluoromethanesulfonate sulfonate salt (30% probability level). Selected bond lengths (Å) and bond angles (°): C1-N1 = 1.396(9), C1-N2 = 1.315(8), C1-C12 = 1.428(8), C10-C11 = 1.482(9), C11-C12 = 1.352(9), N2-C1-N1 = 108.2(6), N2-C1-C12 = 131.9(7), N1-C1-C12 = 119.8(6).

3-butyl-4,5-diphenylimidazo[1,2-a]quinolinium trifluoromethanesulfonate (3b): 29 mg, 55% yield. $^1$H NMR (400 MHz, CDCl$_3$, 300K): δ 9.10 (d, $J$ = 2.3 Hz, 1H), 8.61 (d, $J$ = 8.5 Hz, 1H), 8.06 (d, $J$ = 2.3 Hz, 1H), 7.99 – 7.93 (m, 1H), 7.60 (t, $J$ = 7.7 Hz, 1H), 7.53 (dd, $J$ = 8.2, 1.0 Hz, 1H), 7.34 – 7.31 (m, 3H), 7.30 – 7.27 (m, 5H), 7.12 – 7.09 (m, 2H), 3.73 – 3.69 (m, 2H), 1.54 – 1.50 (m, 2H), 0.92 (dd, $J$ = 15.2, 7.5 Hz, 2H), 0.70 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, CD$_3$CN, 300K): δ 147.56, 137.95, 135.71, 133.48, 133.06, 131.82, 130.91, 130.20, 130.08, 129.48, 129.27, 129.09, 127.16, 125.44, 124.21, 117.29, 114.74, 50.42, 33.51, 20.16, 13.56. $^{19}$F NMR (376 MHz, CD$_3$CN, 300K): δ -79.29 (s). HRMS (ESI, positive ion): $M^+$ = 377.2018 (calculated 377.2012 for [C$_{27}$H$_{25}$N$_2$]$^+$).

3-benzyl-4,5-diphenylimidazo[1,2-a]quinolinium trifluoromethanesulfonate (3c): 36 mg, 64% yield. $^1$H NMR (400 MHz, CDCl$_3$, 300K): δ 9.09 (d, $J$ = 2.4 Hz, 1H), 8.61 (d, $J$ = 8.6 Hz, 1H), 7.92 (ddd, $J$ = 8.5, 7.1, 1.5 Hz, 1H), 7.70 (d, $J$ = 2.3 Hz, 1H), 7.69 – 7.54 (m, 2H), 7.27 – 7.22 (m, 7H), 7.17 – 7.15 (m, 4H), 7.10 (dd, $J$ = 6.5, 2.9 Hz, 2H), 6.79 – 6.77 (m, 2H), 4.97 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$, 300K): δ 147.62, 136.65, 134.26, 133.81, 132.71, 131.70, 130.99, 129.89, 129.32, 129.30, 129.15, 128.83, 128.64, 128.47, 128.27, 128.23, 127.09, 126.80, 124.41, 122.99, 122.47, 119.28, 117.09, 114.84, 53.40. HRMS (ESI, positive ion): $M^+$ = 411.1863 (calculated 411.1856 for [C$_{30}$H$_{23}$N$_2$]$^+$).
3-methyl-7-nitro-4,5-diphenylimidazo[1,2-a]quinolinium trifluoromethanesulfonate (3d):

48 mg, 90% yield. $^1$H NMR (400 MHz, CD$_3$CN, 300K): δ 8.83 (d, J = 2.4 Hz, 1H), 8.72 (t, J = 1.4 Hz, 2H), 8.27 (dd, J = 1.9, 0.9 Hz, 1H), 7.93 (d, J = 2.4 Hz, 1H), 7.42 – 7.38 (m, 8H), 7.27 (ddd, J = 5.4, 2.9, 1.5 Hz, 2H), 3.32 (s, 3H). $^{13}$C NMR (101 MHz, CD$_3$CN, 300K): δ 147.44, 146.81, 139.03, 134.66, 134.58, 132.69, 131.93, 131.08, 130.48, 129.92, 129.51, 129.46, 129.39, 126.66, 125.77, 125.63, 123.64, 120.45, 119.64, 115.23, 38.99. $^{19}$F NMR (376 MHz, CD$_3$CN, 300K): δ -79.28 (s). HRMS (ESI, positive ion): M$^+$ = 380.1404 (calculated 380.1394 for [C$_{24}$H$_{18}$N$_3$O$_2$]).

7-methoxy-3-methyl-4,5-diphenylimidazo[1,2-a]quinolinium trifluoromethanesulfonate (3e): 15 mg, 29% yield. $^1$H NMR (400 MHz, CD$_3$CN, 300K): δ 8.61 (d, J = 2.3 Hz, 1H), 8.40 (d, J = 9.3 Hz, 1H), 7.78 (d, J = 2.3 Hz, 1H), 7.62 (dd, J = 9.3, 2.8 Hz, 1H), 7.37 – 7.34 (m, 8H), 7.22 (ddd, J = 5.0, 3.3, 2.2 Hz, 2H), 6.83 (d, J = 2.8 Hz, 1H), 3.72 (s, 3H), 3.25 (s, 3H). $^{13}$C NMR (101 MHz, CD$_3$CN, 300K): δ 159.76, 146.50, 137.52, 135.61, 133.43, 132.12, 130.93, 130.14, 129.36, 129.30, 129.20, 128.52, 126.91, 126.36, 124.78, 122.16, 120.56, 118.96, 113.86, 110.80, 56.45, 38.58. $^{19}$F NMR (376 MHz, CD$_3$CN, 300K): δ -79.32 (s). HRMS (ESI, positive ion): M$^+$ = 365.1665 (calculated 365.1648 for [C$_{25}$H$_{21}$N$_2$O]).

7-methyl-5,6-diphenylbenzo[4,5]imidazo[1,2-a]quinolinium trifluoromethanesulfonate (3f): 44 mg, 82% yield. $^1$H NMR (400 MHz, CD$_3$CN, 300K): δ 9.15 (d, J = 8.7 Hz, 1H), 9.00 (dd, J = 6.7, 2.6 Hz, 1H), 8.16 (ddd, J = 8.7, 7.3, 1.4 Hz, 1H), 8.00 – 7.90 (m, 3H), 7.76 (t, J = 7.5 Hz, 1H), 7.65 (dd, J = 8.3, 1.2 Hz, 1H), 7.43 – 7.38 (m, 8H), 7.26 (dd, J = 6.6, 2.9 Hz, 2H), 3.44 (s, 3H). $^{13}$C NMR (101 MHz, CD$_3$CN, 300K): δ 152.19, 142.94, 135.66, 135.21, 134.39, 134.14, 133.78, 132.31, 130.83, 130.72, 130.29, 129.59, 129.55, 129.49, 129.13, 128.88, 128.65, 127.80, 125.76, 124.38, 123.69, 120.50, 117.82, 114.12, 34.94. $^{19}$F NMR (376 MHz, CD$_3$CN, 300K): δ -79.27 (s). HRMS (ESI, positive ion): M$^+$ = 385.1705 (calculated 385.1699 for [C$_{28}$H$_{21}$N$_2$]).
Figure S3. Molecular structure of product 3f of trifluoromethanesulfonate sulfonate salt (30% probability level). Selected bond lengths (Å) and bond angles (°): C1-N1 = 1.346(3), C1-N2 = 1.375(3), C1-C16 = 1.428(3), C15-C16 = 1.367(3), N1-C1-N2 = 109.07(19), N1-C1-C16 = 129.3(2), N2-C1-C16 = 121.6(2).

7-methyl-5,6-dipropylbenzo[4,5]imidazo[1,2-a]quinolinium trifluoromethanesulfonate (3g): 42 mg, 90% yield. $^1$H NMR (700 MHz, CD$_3$CN, 300K): δ 8.92 (d, $J$ = 8.6 Hz, 1H), 8.78 (d, $J$ = 8.6 Hz, 1H), 8.38 (dd, $J$ = 8.3, 1.1 Hz, 1H), 8.05 – 8.02 (m, 2H), 7.87 (ddd, $J$ = 8.3, 7.3, 0.8 Hz, 1H), 7.83 (ddd, $J$ = 8.1, 7.1, 0.9 Hz, 1H), 7.78 (ddd, $J$ = 8.4, 7.3, 1.1 Hz, 1H), 4.40 (s, 3H), 3.29 – 3.25 (m, 4H), 1.81 – 1.70 (m, 2H), 1.75 – 1.73 (m, 2H), 1.19 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR (176 MHz, CD$_3$CN, 300K): δ 151.79, 144.38, 135.19, 133.73, 133.04, 129.23, 128.68, 128.47, 128.04, 127.26, 124.62, 123.22, 121.19, 118.46, 117.63, 113.97, 35.33, 31.51, 30.15, 25.20, 25.06, 14.64, 13.96. $^{19}$F NMR (376 MHz, CDCl$_3$, 300K): δ -78.35 (s). HRMS (ESI, positive ion): M$^+$ = 317.2040 (calculated 317.2012 for [C$_{22}$H$_{25}$N$_2$]$^+$).

4,5-bis(methoxycarbonyl)-3-methylimidazo[1,2-a]quinolinium trifluoromethanesulfonate (3h): 22 mg, 49% yield. $^1$H NMR (400 MHz, CD$_3$CN, 300K): δ 8.75 (d, $J$ = 2.2 Hz, 1H), 8.47 (d, $J$ = 8.6 Hz, 1H), 8.24 (d, $J$ = 8.4 Hz, 1H), 8.17 – 8.13 (m, 1H), 8.04 (d, $J$ = 2.2 Hz, 1H), 7.91 (t, $J$ = 7.8 Hz, 1H), 4.08 (s, 3H), 4.07 (s, 3H), 4.02 (s, 3H). $^{13}$C NMR (101 MHz, CD$_3$CN, 300K): δ 165.60, 163.79, 138.28, 135.56, 133.03, 130.27, 129.93, 129.37, 126.74, 123.56, 120.38, 117.20, 116.46, 115.74, 55.37, 55.06, 38.70. $^{19}$F NMR (376 MHz, CDCl$_3$, 300K): δ -79.02 (s). HRMS (ESI, positive ion): M$^+$ = 299.1040 (calculated 299.1026 for [C$_{16}$H$_{15}$N$_2$O$_4$]$^+$).
3-butyl-4,5-bis(methoxycarbonylimidazo[1,2-a]quinolinium trifluoromethanesulfonate (3i): 19 mg, 39% yield. \(^1\)H NMR (400 MHz, CD\(_3\)CN, 300K): \(\delta 8.75\) (d, \(J = 2.4\) Hz, 1H), 8.46 (d, \(J = 8.6\) Hz, 1H), 8.24 (dd, \(J = 8.4, 0.9\) Hz, 1H), 8.15 (ddd, \(J = 8.6, 7.3, 1.3\) Hz, 1H), 8.08 (d, \(J = 2.4\) Hz, 1H), 7.91 (ddd, \(J = 8.3, 7.3, 1.0\) Hz, 1H), 4.41 – 4.37 (m, 2H), 4.09 (s, 3H), 4.07 (s, 3H), 1.85 – 1.81 (m, 2H), 1.42 – 1.34 (m, 2H), 0.96 (t, \(J = 7.4\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CD\(_3\)CN, 300K): \(\delta 165.65, 164.14, 138.54, 135.60, 134.52, 133.16, 130.26, 129.36, 128.69, 120.57, 120.40, 117.94, 116.45, 116.08, 55.55, 55.10, 51.52, 32.67, 20.30, 13.76. \(^{19}\)F NMR (376 MHz, CD\(_3\)CN, 300K): \(\delta -79.33\) (s). HRMS (ESI, positive ion): M\(^+\) = 341.1516 (calculated 341.1496 for [C\(_{19}\)H\(_{21}\)N\(_2\)O\(_4\)]\(^+\)).

3-methyl-4,5-dipropylimidazo[1,2-a]quinolinium trifluoromethanesulfonate (3j): 31 mg, 74% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\), 300K): \(\delta 8.75\) (d, \(J = 2.4\) Hz, 1H), 8.38 (d, \(J = 8.1\) Hz, 1H), 8.08 (dd, \(J = 10.4, 1.6\) Hz, 2H), 7.86 (ddd, \(J = 8.5, 7.2, 1.2\) Hz, 1H), 7.74 – 7.70 (m, 1H), 4.41 (s, 3H), 3.16 – 3.08 (m, 4H), 1.72 (ddd, \(J = 14.9, 7.5, 2.2\) Hz, 4H), 1.17 (td, \(J = 7.3, 1.6\) Hz, 6H). \(^{13}\)C NMR (176 MHz, CD\(_3\)CN, 300K): \(\delta 145.83, 139.51, 131.94, 131.19, 128.90, 128.61, 127.54, 124.37, 123.44, 117.47, 113.57, 39.34, 30.77, 29.50, 25.36, 24.96, 14.55, 13.96. \(^{19}\)F NMR (376 MHz, CDCl\(_3\), 300K): \(\delta -78.34\) (s). HRMS (ESI, positive ion): M\(^+\) = 267.1856 (calculated 267.1856 for [C\(_{18}\)H\(_{23}\)N\(_2\)]\(^+\)).

5-ethyl-3-methyl-4-phenylimidazo[1,2-a]quinolinium trifluoromethanesulfonate (3k): 34 mg, 78% yield. \(^1\)H NMR (700 MHz, CD\(_3\)CN, 300K): \(\delta 8.62\) (d, \(J = 2.3\) Hz, 1H), 8.43 (d, \(J = 8.4\) Hz, 1H), 8.34 (d, \(J = 8.3\) Hz, 1H), 8.00 (ddd, \(J = 8.5, 7.2, 1.2\) Hz, 1H), 7.87 – 7.85 (m, 1H), 7.74 (d, \(J = 2.3\) Hz, 1H), 7.65 – 7.62 (m, 3H), 7.50 – 7.49 (m, 2H), 3.22 (s, 3H), 2.90 (q, \(J = 7.6\) Hz, 2H), 1.16 (t, \(J = 7.6\) Hz, 3H). \(^{13}\)C NMR (176 MHz, CD\(_3\)CN, 300K): \(\delta 148.26, 138.19, 133.59, 132.75, 131.84, 131.47, 130.77, 130.13, 129.19, 128.16, 128.03, 127.53, 123.73, 123.62, 117.75, 113.65, 38.33, 23.43, 15.31. \(^{19}\)F NMR (376 MHz, CDCl\(_3\), 300K): \(\delta -78.35\) (s). HRMS (ESI, positive ion): M\(^+\) = 287.1568 (calculated 287.1543 for [C\(_{20}\)H\(_{19}\)N\(_2\)]\(^+\)).

3-butyl-5-methyl-4-phenylimidazo[1,2-a]quinolinium trifluoromethanesulfonate (3l): 32 mg, 69% yield. \(^1\)H NMR (400 MHz, CD\(_3\)CN, 300K): \(\delta 8.66\) (d, \(J = 2.4\) Hz, 1H), 8.42 (d, \(J = 8.2\) Hz, 1H), 8.32 (dd, \(J = 8.3, 1.0\) Hz, 1H), 8.01 (ddd, \(J = 8.5, 7.2, 1.3\) Hz, 1H), 7.87 – 7.85 (m, 1H), 7.83 (d, \(J = 2.3\) Hz, 1H), 7.66 – 7.64 (m, 3H), 7.50 – 7.48 (m, 2H), 3.57 – 3.53 (m, 2H), 2.44 (s, 3H), 1.53 – 1.49 (m, 2H), 0.91 (dt, \(J = 14.1, 7.0\) Hz, 2H), 0.74 (t, \(J = 7.3\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CD\(_3\)CN, 300K): \(\delta 143.35, 137.94, 134.19, 132.85, 131.50, 131.15, 130.79, 130.41, 129.10, 128.06, 126.57, 124.91, 123.75, 120.54, 117.50, 114.35, 50.17, 33.48, 20.19, 16.83, 13.59. \(^{19}\)F NMR (376 MHz, CD\(_3\)CN, 300K): \(\delta -79.24\) (s). HRMS (ESI, positive ion): M\(^+\) = 315.1877 (calculated 315.1856 for [C\(_{22}\)H\(_{23}\)N\(_2\)]\(^+\)).
5-ethyl-7-methyl-6-phenylbenzo[4,5]imidazo[1,2-a]quinolinium trifluoromethanesulfonate (3m): 45 mg, 93% yield. $^1$H NMR (400 MHz, CD$_3$CN, 300K): $\delta$ 9.09 (d, $J = 8.4$ Hz, 1H), 8.91 (dd, $J = 7.2$, 1.8 Hz, 1H), 8.49 (dd, $J = 8.3$, 1.3 Hz, 1H), 8.17 (ddd, $J = 8.7$, 7.2, 1.4 Hz, 1H), 7.95 – 7.84 (m, 4H), 7.71 – 7.69 (m, 3H), 7.58 – 7.56 (m, 2H), 3.38 (s, 3H), 3.01 (q, $J = 7.6$ Hz, 2H), 1.22 (t, $J = 7.6$ Hz, 3H), 1.19 (s, 3H). $^{13}$C NMR (101 MHz, CD$_3$CN, 300K): $\delta$ 154.01, 142.85, 135.07, 134.50, 134.03, 133.90, 131.64, 131.01, 130.44, 129.33, 128.79, 128.75, 128.62, 127.50, 124.01, 123.74, 123.58, 118.74, 117.71, 113.91, 34.59, 24.12, 15.32. $^{19}$F NMR (376 MHz, CDCl$_3$, 300K): $\delta$ -78.35 (s). HRMS (ESI, positive ion): M$^+$ = 337.1710 (calculated 337.1699 for [C$_{24}$H$_{21}$N$_2$]$^+$).

Figure S4. Molecular structure of product 3m of trifluoromethanesulfonate sulfonate salt (30% probability level). Selected bond lengths (Å) and bond angles (°): C$_1$-N$_1$ = 1.348(3), C$_1$-N$_2$ = 1.374(3), C$_1$-C$_{16}$ = 1.419(4), C$_{15}$-C$_{16}$ = 1.373(3), N$_1$-C$_1$-N$_2$ = 108.9(2), N$_1$-C$_1$-C$_{16}$ = 129.1(2), N$_2$-C$_1$-C$_{16}$ = 122.0(2).

3-methyl-5-(4-nitrophenyl)-4-phenylimidazo[1,2-a]quinolinium trifluoromethanesulfonate and 3-methyl-4-(4-nitrophenyl)-5-phenylimidazo[1,2-a]quinolinium trifluoromethanesulfonate (3n + 3n’ (2:1)): 35 mg, 66% yield. $^1$H NMR (400 MHz, CD$_3$CN, 300K): $\delta$ 8.78 (t, $J = 2.6$ Hz, 1H), 8.53 (dd, $J = 8.5$, 3.7 Hz, 1H), 8.17 – 8.14 (m, 2H), 8.04 (ddt, $J = 8.7$, 7.2, 1.5 Hz, 1H), 7.89 (t, $J = 2.7$ Hz, 1H), 7.72 – 7.70 (m, 1H), 7.64 – 7.54 (m, 2H), 7.49 – 7.47 (m, 1H), 7.38 – 7.35 (m, 4H), 7.23 – 7.21 (m, 1H), 3.32 (s, 1.94H), 3.32 (s, 0.98H). $^{13}$C NMR (101 MHz, CD$_3$CN, 300K): $\delta$ 149.23, 148.78, 147.43, 144.83, 142.56, 140.26, 137.93, 137.64, 135.02,
133.66, 133.49, 133.29, 132.70, 132.52, 132.03, 131.94, 131.77, 130.88, 130.46, 130.17, 129.60, 129.58, 129.55, 129.36, 128.93, 128.78, 125.14, 124.67, 124.62, 124.28, 124.19, 123.61, 122.52, 120.42, 117.56, 117.44, 114.48, 114.40, 39.07, 38.75. $^{19}$F NMR (376 MHz, CD$_3$CN, 300K): δ -79.27 (s), -79.27 (s). HRMS (ESI, positive ion): M$^+$ = 380.1422 (calculated 380.1394 for [C$_{24}$H$_{18}$N$_3$O$_2$]$^+$).

5-(4-methoxyphenyl)-3-methyl-4-phenylimidazo[1,2-a]quinolinium trifluoromethanesulfonate and 4-(4-methoxyphenyl)-3-methyl-5-phenylimidazo[1,2-a]quinolinium trifluoromethanesulfonate (3o + 3o' (1:1.2)): 18 mg, 35% yield. $^1$H NMR (400 MHz, CD$_3$CN, 300K): δ 8.69 (dd, $J$ = 6.6, 2.2 Hz, 1H), 8.47 (dd, $J$ = 8.6 Hz, 1H), 8.05 – 7.97 (m, 1H), 7.81 (dd, $J$ = 4.5, 2.3 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.56 (dd, $J$ = 30.9, 8.3 Hz, 1H), 7.40 – 7.35 (m, 4H), 7.25 – 7.20 (m, 2H), 7.14 – 7.11 (m, 1H), 6.90 – 6.87 (m, 2H), 3.76 (s, 3H), 3.31 (s, 1.3H). $^{13}$C NMR (101 MHz, CD$_3$CN, 300K): δ 161.14, 160.49, 147.49, 147.16, 135.81, 133.56, 133.39, 132.95, 132.91, 132.37, 132.18, 131.72, 131.65, 130.96, 130.20, 130.27, 130.08, 129.35, 129.29, 129.14, 129.12, 128.61, 127.52, 126.03, 125.75, 125.47, 125.12, 124.97, 124.66, 124.35, 117.28, 114.67, 114.47, 114.06, 56.06, 56.00, 38.78, 38.68. $^{19}$F NMR (376 MHz, CD$_3$CN, 300K): δ -79.32 (s), -79.33 (s). HRMS (ESI, positive ion): M$^+$ = 365.1670 (calculated 365.1648 for [C$_{25}$H$_{21}$N$_2$O]$^+$).

3-methyl-5-phenyl-4-(phenylethynyl)imidazo[1,2-a]quinolinium trifluoromethanesulfonate (3p): 20 mg, 40% yield. $^1$H NMR (400 MHz, CD$_3$CN, 300K): δ 8.66 (d, $J$ = 2.4 Hz, 1H), 8.42 (d, $J$ = 8.5 Hz, 1H), 8.01 (ddd, $J$ = 8.6, 6.7, 1.9 Hz, 1H), 7.95 (d, $J$ = 2.3 Hz, 1H), 7.73 – 7.67 (m, 5H), 7.54 – 7.52 (m, 2H), 7.42 – 7.41 (m, 1H), 7.38 – 7.34 (m, 2H), 7.23 – 7.20 (m, 2H), 4.53 (s, 3H). $^{13}$C NMR (101 MHz, CD$_3$CN, 300K): δ 151.79, 137.48, 135.48, 133.75, 132.07, 131.73, 131.07, 130.76, 130.49, 130.05, 129.80, 129.78, 129.47, 128.39, 126.07, 124.80, 123.73, 121.94, 118.33, 117.54, 114.51, 106.81, 102.85, 38.54. $^{19}$F NMR (376 MHz, CD$_3$CN, 300K): δ -79.30 (s). HRMS (ESI, positive ion): M$^+$ = 359.1572 (calculated 359.1543 for [C$_{26}$H$_{19}$N$_2$]$^+$).
Figure S5. Molecular structure of product 3p of trifluoromethanesulfonate sulfonate salt (30% probability level). Selected bond lengths (Å) and bond angles (°): C1-N1 = 1.358(6), C1-N2 = 1.365(6), C1-C12 = 1.418(6), C11-C12 = 1.375(6), N1-C1-N2 = 106.6(4), N1-C1-C12 = 131.6(4), N2-C1-C12 = 121.8(4).

7. Mechanistic studies

A. Synthesis of the cyclometalated Rh(III) intermediate complex 4:

A mixture of [RhCp*Cl2]2 (15.4 mg, 0.025 mmol) and NaOAc (32.8 mg, 0.4 mmol) was stirred in dry and degassed CH2Cl2 (5 mL) for 15 minute in dry Schlenk tube. 1a (14.3 mg, 0.05 mmol) was added to the reaction mixture and stirring continued for further 24 h at room temperature. The resulting solution was filtered through a Celite plug. Solvent was removed under reduced pressure and the solid formed was redissolved in minimum quantity of CH2Cl2. This solution was poured into hexane (~20 times) and kept in a refrigerator. Orange crystalline solid was formed and then decantation of liquid portion followed by washing with hexane produces the desired complex 4 (20 mg, 0.038 mmol, 76%) after drying under reduced pressure.
B. Single crystal X-ray structure of 4:

The structure of this complex was characterised by single crystal X-ray diffraction study, which was further confirmed by NMR, HRMS and elemental analysis.

Figure S6: Molecular structure of 4 (30% probability level) (left: shown without H atoms for clarification purpose; right: shown with all the H atoms). Selected bond lengths (Å) and bond angles (°): C1–Rh1 = 2.008(11); C6–Rh1 = 2.030(11); I1–Rh1 = 2.5972(15); C1–N1 = 1.362(15); C1–N2 = 1.364(15); N1–C1–N2 = 104.7(9); C1–Rh1–C6 = 77.0(4); C1–Rh1–I1 = 92.6(3), C6–Rh1–I1 = 96.2(3).

C. Characterization data of 4:

$^1$H NMR (400 MHz, CDCl$_3$, 300K): $\delta$ 7.74 (d, $J = 7.0$ Hz, 1H), 7.39 (d, $J = 1.7$ Hz, 1H), 7.14 – 7.05 (m, 1H), 7.03 – 6.93 (m, 3H), 3.90 (s, 3H), 1.85 (s, 15H). $^{13}$C NMR (176 MHz, CDCl$_3$, 300K): $\delta$ 182.62 (d, $J = 55.3$ Hz), 156.71 (d, $J = 34.5$ Hz), 145.61, 139.18, 125.00, 122.43, 122.20, 115.11, 110.88, 97.92 (d, $J = 4.7$ Hz), 38.01, 10.69. HRMS (ESI, positive ion): (M–I)$^+$ = 395.1008 (calculated 395.0989 for [C$_{20}$H$_{24}$N$_2$Rh]$^+$). Anal. Calcd for C$_{20}$H$_{24}$N$_2$IrRh(522.2)·1/4CH$_2$Cl$_2$: C, 44.75; H, 4.54; N, 5.15. Found: C, 45.11; H, 4.63; N, 5.10.
Figure S7. $^1$H NMR spectrum of 4 (400 MHz, CDCl$_3$, 300 K).

Figure S8. $^{13}$C{$^1$H} NMR spectrum of 4 (176 MHz, CDCl$_3$, 300 K).
Figure S9. ESI-HRMS of the Rh(III)-complex 4.

D. Stoichiometric reaction of the Rh(III) complex 4

A mixture of Complex 4 (26.1 mg, 0.05 mmol), AgOTf (38.5 mg, 0.15 mmol) and 2a (10.7 mg, 0.06 mmol) in dry and degassed CH$_2$Cl$_2$ (5.0 mL) were stirred in dry Schlenk tube at room temperature under dark. After 12 h stirring, the whole reaction mixture was passed through a short celite pad and which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated by silica gel column chromatography, eluted with a 7:1 (v/v) CHCl$_3$/MeOH solvent mixture 3a (18.3 mg, 0.0375 mmol, 75%).
E. Catalytic reaction with the Rh(III) complex 4

\[
\begin{align*}
\text{Me} & \quad \text{Ph} \\
\text{1a, 0.05 mmol} & \quad (1.2 \text{ eq}) \\
\text{Complex 4 (5 mol\%)} & \quad \text{AgOTf (3 equiv.)} \\
\text{NaOAc (4 equiv.)} & \quad \text{CH}_2\text{Cl}_2, \text{room temp.} \\
24 \text{ h} & \quad 3a, 83\%
\end{align*}
\]

To an oven dried Schlenk tube, \textit{1a} (14.3 mg, 0.05 mmol), NaOAc (16.4 mg, 0.2 mmol), complex 4 (0.0025 mmol), AgOTf (38.5 mg, 0.15 mmol) and \textit{2a} (10.7 mg, 0.06 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with N\textsubscript{2} gas. To this mixture, dry and degassed CH\textsubscript{2}Cl\textsubscript{2} (2.0 mL) was added under Schlenk technique and the reaction mixture was left with stirring at room temperature under dark. After 24 h, the whole reaction mixture was passed through a short celite pad and which was washed with dichloromethane (3×3 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated by silica gel column chromatography, eluted with a 7:1 (v/v) CHCl\textsubscript{3}/MeOH solvent mixture, afforded 3\textit{a} (20 mg, 0.041 mmol, 83\%).

F. Preliminary combined time dependent \textsuperscript{1}H NMR spectroscopic and ESI-MS study for the reaction of 4 with 2\textit{a}:

\[
\begin{align*}
\text{Me} & \quad \text{Ph} \\
\text{4, 0.02 mmol} & \quad (1.2 \text{ eq}) \\
\text{AgOTf (1 equiv.)} & \quad \text{CH}_2\text{Cl}_2, 0^\circ \text{C} \\
3\textit{a} & \quad \text{Me}
\end{align*}
\]

To an oven dried Schlenk tube, complex 4 (10.5 mg, 0.02 mmol), AgOTf (5.17 mg, 0.02 mmol) and \textit{2a} (3.92 mg, 0.022 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with N\textsubscript{2} gas. To this mixture, dry and degassed CH\textsubscript{2}Cl\textsubscript{2} (2.0 mL) was added under Schlenk technique and the reaction mixture was left with stirring at 0\textdegree C under dark. The progress of the reaction was monitored by withdrawing aliquots at different time intervals, removing the solvent under vacuum, adding 0.5 mL of CDCl\textsubscript{3}, and subjecting to \textsuperscript{1}H NMR spectroscopy as well as ESI-HRMS.
The $^1$H NMR spectral analysis established the gradual consumption of the cyclometalated intermediate 4 in the reaction with diphenylacetylene 2a as indicated by the decrease of the characteristic peaks at 1.85 ppm (Cp* protons) and 3.90 ppm (CH$_3$ protons), along with the evolution of the product 3a as indicated by the generation of the characteristic new peaks in the aromatic region and also at 3.43 ppm due to CH$_3$ protons (Figure S10, A). Most interestingly, a new peak due to Cp* protons at 1.61 ppm evolved which was speculated to be due to the Cp*Rh(I) intermediate 1” (Figure S10, A). An ESI-HRMS analysis of this sample provided evidence in favor of the formation of the postulated 3a-coordinated, 18-electron, Cp*Rh(I) complex 1” in this reaction (Figure S10, B). Further studies are underway to isolate and fully characterize the above-proposed intermediate.

Figure S10. (A) Time-dependent $^1$H NMR spectral profile for the reaction of the complex 4 (0.02 mmol) with diphenylacetylene 2a (0.022 mmol) in the presence of AgOTf (0.02 mmol) in CH$_2$Cl$_2$ at 0 °C: (a) only 4; (b) 4 + 2a, 10 min; (c) 4 + 2a, 60 min; (d) product 3a (for reference). (B) ESI-HRMS profile of the same reaction mixture as described in (c) above.
G. Preliminary reaction study of 4 with 2a in the absence of AgOTf

To an oven dried Schlenk tube, complex 4 (10.5 mg, 0.02 mmol) and 2a (3.92 mg, 0.022 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with N₂ gas. To this mixture, dry and degassed CH₂Cl₂:MeOH (1:4, v/v, 5 mL) solvent mixture was added under Schlenk technique and the reaction mixture was left with stirring at room temperature for 24 h.

The ^1H NMR and ^13C{^1H} NMR spectral analysis of the above mentioned reaction mixtures indicates that the major compound is 4 which is unaltered along with little formation of products but no intermediate was detected.

H. Determination of kinetic isotope effect (KIE)

Synthesis of N-Methyl-N-(pentadeuteriophenyl)imidazolium iodide (D₅-1a):

Synthesis of D₅-iodobenzene

The title compound was synthesized by following a similar procedure reported in the literature for the synthesis of iodobenzene₁², by stirring a mixture of D₆-benzene (0.23 mL, 2.5 mmol), AgOTf (642 mg, 2.5 mmol) and iodine (635 mg, 2.5 mmol) in dry CH₂Cl₂ (10 mL) for 15 min at room temperature in dark condition. Reaction mixture was passed through a short celite plug and washed with CH₂Cl₂. Then combined filtrate was washed with dilute NH₄OH solution, dilute Na₂SO₃ and water, followed by organic solution was dried over anhyd. Na₂SO₄, filtered and evaporated under reduced pressure. The resulting residue was utilized directly for further reaction purpose.
Synthesis of N-(pentadeuteriophenyl)imidazole

The title compound was synthesized by following a similar procedure reported in the literature for the synthesis of N-phenyl imidazole5. A mixture of CuI (28.5 mg, 0.15 mmol) and benzotriazole (38.5 mg, 0.3 mmol) in DMSO (~3 mL) was stirred at room temperature for 5 minutes. To that solution D₅-iodobenzene (627 mg, 3 mmol), imidazole (204 mg, 3 mmol) and KO'Bu (471 mg, 4.2 mmol) were added and heating the solution at 120°C for 12 h. After cooling, EtOAc (~30 mL) was added to that solution and washed with water (2x 30 mL). Then the whole organic solution was dried over Na₂SO₄ and filtrate was evaporated under reduced pressure. Final product (170 mg, 1.14 mmol, 38% yield) was separated by silica gel column chromatography using EtOAc and hexane (4:1, v/v) solvent mixture as an eluting solvent. ¹H NMR (500 MHz, CD₃CN, 300K): δ 7.97 (s, 1H), 7.47 (t, J = 1.3 Hz, 1H), 7.13 (s, 1H).

Synthesis of N-Methyl-N-(pentadeuteriophenyl)imidazolium iodide, D₅-1a

The title compound was synthesized by following a similar procedure reported in the literature for the synthesis of N-methyl-N-phenyl imidazolium iodide8, by stirring a mixture of N-(pentadeuteriophenyl) imidazole (300 mg, 2 mmol) and iodomethane (0.19 mL, 3 mmol) in dry THF (4 mL) for 24 h at room temperature. The resultant precipitate was collected by filtration and washed with hexane and then dried in vacuo (248 mg, 0.85 mmol, 42% yield). ¹H NMR (400 MHz, CD₃CN, 300K): δ 9.14 (br s, 1H), 7.77 (d, J = 1.8 Hz, 1H), 7.57 (s, 1H), 3.97 (d, J = 1.9 Hz, 3H). HRMS (ESI, positive ion): M⁺ = 164.1211 (calculated 164.1211 for [C₁₀H₆D₅N₂]⁺).

Determination of intermolecular kinetic isotope effect (KIE)

![Diagram]

To an oven dried Schlenk tube, 1a (14.3 mg, 0.05 mmol), D₅-1a (14.55 mg, 0.05 mmol), NaOAc (32.8 mg, 0.4 mmol), [RhCp*Cl₂]₂ (3.08 mg, 0.005 mmol), AgOTf (77.1 mg, 0.3 mmol)
and 4-Octyne (18 µL, 0.12 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with N₂ gas. To this mixture, dry and degassed CH₂Cl₂ (3.0 mL) was added under Schlenk technique and the reaction mixture was left with stirring at room temperature under dark. After different time intervals, the reaction mixture was passed through a short celite pad which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. To the crude residue, mesitylene (0.01 mmol) was added as internal standard and it was subjected to ¹H NMR spectroscopy. The ¹H NMR spectral analysis indicates the average value of $k_H/k_D = 0.87-0.94$ as shown in Figure S11.
Figure S11. $^1$H NMR spectra of $3j$ and crude reaction mixture using mesitylene as internal standard: (a) $3j$, (b) after 4 h (yield = 11%) and (c) after 11 h (yield = 27%) (d) second expt. after 4 h (yield = 10%).

I. Deuterium Exchange Experiment

To an oven dried Schlenk tube, $1a$ (28.6 mg, 0.1 mmol), NaOAc (32.8 mg, 0.4 mmol), $\text{[RhCp^*Cl}_2$ (3.08 mg, 0.005 mmol), AgOTf (77.1 mg, 0.3 mmol) and 4-Octyne (18 µL, 0.12 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube
was filled with N\textsubscript{2} gas. To this mixture, dry and degassed CH\textsubscript{2}Cl\textsubscript{2} (2 mL) and then D\textsubscript{2}O (1 mL) was added under Schlenk technique and the reaction mixture was left with stirring at room temperature under dark. After a certain time, the whole reaction mixture was passed through a short celite pad and which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. To the crude residue, mesitylene (0.01 mmol) was added as internal standard and it was subjected to \textsuperscript{1}H NMR spectroscopy.

\textbf{Figure S12.} \textsuperscript{1}H NMR spectra of pure \textbf{1a, 3j} and crude reaction mixture using mesitylene as internal standard.
The $^1$H NMR spectral analysis showed the incorporation of deuterium into the labeled protons of substrate, 1a as well as in annulated product, 3j as shown in Figure S12.

8. Importance of imidazo/benzimidazo-fused poly aromatic compounds

![Chemical structures](image1)

**Figure S13**: Examples of a few biologically active imidazo/benzimidazo-fused polyaromatic compounds.$^{13}$

Imidazo-fused poly aromatic cationic systems are found to be biologically important molecules. A few selected examples are shown in Figure S13. These types of molecules possess high affinity for DNA because of their planer geometry and charge characteristics which shows an effective antitumor or anticancer activity.$^{13}$ Additionally, these molecules display fluorescence property which might be useful in organic light-emitting diode (OLED) applications.$^{14}$ Fluorescence spectra of a few imidazo[1,2-a]quinolinium salts are shown in Figure S14 which have been synthesized by our protocol.

![Fluorescence spectra](image2)

**Figure S14**: Fluorescence spectra of selected imidazo[1,2-a]quinolinium salts at a concentration of $5 \times 10^{-8}$ M in acetonitrile.
9. $^1\text{H}$, $^{13}\text{C}$ & $^{19}\text{F}$ NMR and HRMS data

**Figure S15.** $^1\text{H}$ NMR spectrum of 1a (400 MHz, CD$_3$CN, 300 K).

**Figure S16.** ESI-HRMS (positive ion mode) spectrum of 1a.
Figure S17. $^1$H NMR spectrum of 1b (400 MHz, CD$_3$CN, 300 K).

Figure S18. $^1$H NMR spectrum of 1c (400 MHz, CD$_3$CN, 300 K).
Figure S19. $^1$H NMR spectrum of 1d (400 MHz, CDCl$_3$, 300 K).

Figure S20. $^1$H NMR spectrum of 1e (400 MHz, CDCl$_3$, 300 K).
Figure S21. $^1$H NMR spectrum of 1f (400 MHz, CDCl$_3$, 300 K).

Figure S22. $^1$H NMR spectrum of 3a (400 MHz, CDCl$_3$, 300 K).
**Figure S23.** ESI-HRMS (positive ion mode) spectrum of 3a.

**Figure S24.** $^1$H NMR spectrum of 3a (400 MHz, CD$_3$CN, 300 K).
Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 3a (101 MHz, CD$_3$CN, 300 K).

Figure S26. $^{19}\text{F}$ NMR spectrum of 3a (376 MHz, CDCl$_3$, 300 K).
Figure S27. $^1$H-$^1$H COSY NMR spectrum of 3a (400 MHz, CDCl$_3$, 300 K).

Figure S28. ESI-HRMS (positive ion mode) spectrum of 3a.
Figure S29. $^1$H NMR spectrum of 3b (400 MHz, CDCl$_3$, 300 K).

Figure S30. $^{13}$C{$^1$H} NMR spectrum of 3b (101 MHz, CD$_3$CN, 300 K).
Figure S31. $^{19}$F NMR spectrum of 3b (376 MHz, CD$_3$CN, 300 K).

Figure S32. ESI-MS (positive ion mode) spectrum of 3b.
Figure S33. $^1$H NMR spectrum of 3c (400 MHz, CDCl$_3$, 300 K).

Figure S34. $^{13}$C{$^1$H} NMR spectrum of 3c (101 MHz, CDCl$_3$, 300 K).
**Figure S35.** ESI-HRMS (positive ion mode) spectrum of 3c.

**Figure S36.** $^1$H NMR spectrum of 3d (400 MHz, CD$_3$CN, 300 K).
Figure S37. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 3d (101 MHz, CD$_3$CN, 300 K).

Figure S38. $^{19}\text{F}$ NMR spectrum of 3d (376 MHz, CD$_3$CN, 300 K).
**Figure S39.** ESI-HRMS (positive ion mode) spectrum of 3d.

**Figure S40.** $^1$H NMR spectrum of 3e (400 MHz, CD$_3$CN, 300 K).
Figure S41. $^{13}$C($^1$H) NMR spectrum of 3e (101 MHz, CD$_3$CN, 300 K).

Figure S42. $^{19}$F NMR spectrum of 3e (376 MHz, CD$_3$CN, 300 K).
Figure S43. ESI-HRMS (positive ion mode) spectrum of 3e.

Figure S44. $^1$H NMR spectrum of 3f (400 MHz, CD$_3$CN, 300 K).
**Figure S45.** $^{13}$C{$^1$H} NMR spectrum of 3f (101 MHz, CD$_3$CN, 300 K).

**Figure S46.** $^{19}$F NMR spectrum of 3f (376 MHz, CD$_3$CN, 300 K).
Figure S47. ESI-HRMS (positive ion mode) spectrum of 3f.

Figure S48. $^1$H NMR spectrum of 3g (700 MHz, CD$_3$CN, 300 K).
Figure S49. $^{13}$C\{$^1$H\} NMR spectrum of 3g (176 MHz, CD$_3$CN, 300 K).

Figure S50. $^{19}$F NMR spectrum of 3g (376 MHz, CDCl$_3$, 300 K).
Figure S51. ESI-HRMS (positive ion mode) spectrum of 3g.

Figure S52. $^1$H NMR spectrum of 3h (400 MHz, CD$_3$CN, 300 K).
**Figure S53.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 3h (101 MHz, CD$_3$CN, 300 K).

**Figure S54.** $^{19}\text{F}$ NMR spectrum of 3h (376 MHz, CDCl$_3$, 300 K).
Figure S55. ESI-HRMS (positive ion mode) spectrum of 3h.

Figure S56. $^1$H NMR spectrum of 3i (400 MHz, CD$_3$CN, 300 K).
Figure S57. $^{13}$C{$_1^1$H} NMR spectrum of 3i (101 MHz, CD$_3$CN, 300 K).

Figure S58. $^{19}$F NMR spectrum of 3i (376 MHz, CD$_3$CN, 300 K).
Figure S59. ESI-HRMS (positive ion mode) spectrum of 3i.

Figure S60. $^1$H NMR spectrum of 3j (400 MHz, CDCl$_3$, 300 K).
Figure S61. $^{13}$C{$^{1}$H} NMR spectrum of 3j (176 MHz, CD$_3$CN, 300 K).

Figure S62. $^{19}$F NMR spectrum of 3j (376 MHz, CDCl$_3$, 300 K).
Figure S63. ESI-HRMS (positive ion mode) spectrum of 3j.

Figure S64. $^1$H NMR spectrum of 3k (700 MHz, CD$_3$CN, 300 K).
Figure S65. $^{13}$C-$^1$H NMR spectrum of 3k (176 MHz, CD$_3$CN, 300 K).

Figure S66. $^{19}$F NMR spectrum of 3k (376 MHz, CDCl$_3$, 300 K).
Figure S67. ESI-HRMS (positive ion mode) spectrum of 3k.

Figure S68. $^1$H NMR spectrum of 3l (400 MHz, CD$_3$CN, 300 K).
Figure S69. $^{13}$C($^1$H) NMR spectrum of 3l (101 MHz, CD$_3$CN, 300 K).

Figure S70. $^{19}$F NMR spectrum of 3l (376 MHz, CD$_3$CN, 300 K).
Figure S71. ESI-HRMS (positive ion mode) spectrum of 3l.

Figure S72. $^1$H NMR spectrum of 3m (400 MHz, CD$_3$CN, 300 K).
Figure S73. $^{13}\text{C}\{^{1}\text{H}\}$ NMR spectrum of 3m (101 MHz, CD$_3$CN, 300 K).

Figure S74. $^{19}\text{F}$ NMR spectrum of 3m (376 MHz, CDCl$_3$, 300 K).
Figure S75. ESI-HRMS (positive ion mode) spectrum of 3m.

Figure S76. $^1$H NMR spectrum of 3n (400 MHz, CD$_3$CN, 300 K).
Figure S77. $^{13}$C{${}^1$H} NMR spectrum of 3n (101 MHz, CD$_3$CN, 300 K).

Figure S78. $^{19}$F NMR spectrum of 3n (376 MHz, CD$_3$CN, 300 K).
Figure S79. ESI-HRMS (positive ion mode) spectrum of 3n.

Figure S80. $^1$H NMR spectrum of 3o (400 MHz, CD$_3$CN, 300 K).
Figure S81. $^{13}$C($^1$H) NMR spectrum of 3o (101 MHz, CD$_3$CN, 300 K).

Figure S82. $^{19}$F NMR spectrum of 3o (376 MHz, CD$_3$CN, 300 K).
Figure S83. ESI-HRMS (positive ion mode) spectrum of 3o.

Figure S84. $^1$H NMR spectrum of 3p (400 MHz, CD$_3$CN, 300 K).
Figure S85. $^{13}$C($^1$H) NMR spectrum of 3p (101 MHz, CD$_3$CN, 300 K).

Figure S86. $^{19}$F NMR spectrum of 3p (376 MHz, CD$_3$CN, 300 K).
Figure S87. ESI-HRMS (positive ion mode) spectrum of 3p.
10. References