Supporting Information

Alkene Promoted NHC Ligand Substitution in Orthometalated Ru-NHC Complexes *via* σ-bond metathesis: A Mechanistic Insight

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1. General Considerations

All manipulations were performed under argon/N_2 atmosphere using either standard Schlenk line or Glove box techniques. All the glassware were dried at 140 °C in an oven overnight before use. The solvents used for the synthesis were dried, distilled, and degassed by standard methods and stored over 4 Å molecular sieves. NMR measurements were performed on Bruker 400 and 500 MHz FT-NMR spectrometers. The NMR chemical shifts were referenced to the residual proton and carbon signals of the deuterated solvents ($CDCl_3$, ^1H 7.26 ppm and $^{13}C\{^1H\}$ 77.16 ppm) and the ^1H NMR signals are reported relative to tetramethylsilane. ^{19}F NMR spectra were referenced externally to α,α,α-trifluorotoluene (0.05% in $CDCl_3$; δ = –63.73 ppm). Coupling constants are expressed in Hz. ESI-MS spectra were recorded with an Agilent 6545A Q-TOF Mass spectrometer. The substituted imidazole/ benzimidazole[1], orthometalated Ru^{II}-NHC complexes (**I-V**)[2] were prepared according to the literature procedures. All other chemicals were purchased from the commercial sources and used as received without further purification.

2. General procedure for the synthesis of various azolium salts[3]

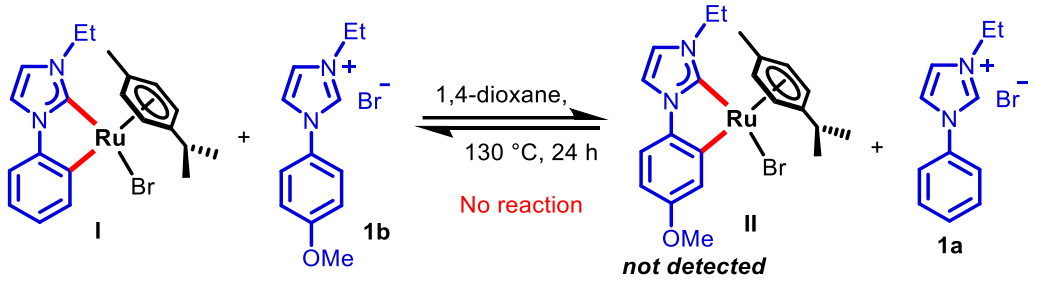
Substituted imidazole/benzimidazole, excess alkyl halide, and CH_3CN were taken in a pressure tube and the resulting suspension was heated at 90 °C for 12 h. After cooling to ambient temperature, the reaction mixture was concentrated in vacuo and diethyl ether was added to it to yield an off-white precipitate. The obtained residue was washed with diethyl ether and dried in vacuo, providing the desired azolium salts **1a-1l** as off-white hygroscopic solids.

3. General procedure for the synthesis of orthometalated Ru^{II} -NHC complexes[2]

To a 25 mL pressure tube equipped with a magnetic stirring bar, imidazolium salt **1** (0.394 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (121.0 mg, 0.197 mmol) and Cs_2CO_3 (141.0 mg, 0.433 mmol) were added. Solvent THF (6 mL) was then added and stirred at 70 °C for 12 h. After that, the reaction mixture was cooled and volatiles were removed in vacuo. The resulted residue was extracted with dichloromethane and filtered through an alumina pad to obtain a clear orange-red solution. Concentration followed by the addition of hexane resulted in the precipitation of a solid, which was washed with hexane and dried in vacuum to obtain orange-red powder.

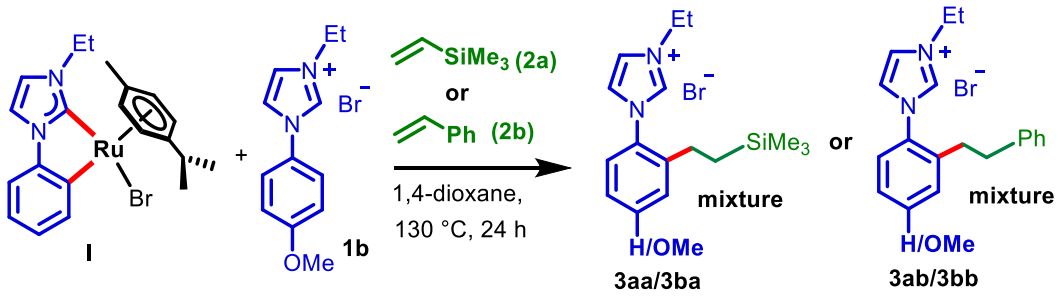
4. Experiments to establish the σ-bond metathesis pathway

a)



In a pressure tube, imidazolium salt **1b** (28 mg, 0.098 mmol) and orthometalated Ru-NHC complex **I** (48 mg, 0.098 mmol) were taken and stirred in 1,4-dioxane at 130 °C (oil bath temperature) for 24 h. After 24 h, only starting materials (**I** and **1b**) were recovered.

b)



In a pressure tube (25 mL), imidazolium salt **1b** (28 mg, 0.098 mmol), orthometalated Ru-NHC complex **I** (48 mg, 0.098 mmol), and trimethylvinylsilane **2a** (43 µL, 0.294 mmol, 3 equiv.) were stirred in 1,4-dioxane (1.0 mL) at 130 °C (oil bath temperature) for 24 h. After completion, the reaction mixture was cooled and volatiles were removed in vacuo. The obtained residue was extracted with dichloromethane and after drying, the crude NMR was recorded in $CDCl_3$ that confirmed the formation of a mixture of products (**3aa** and **3ba**). Afterwards, the mixture was purified by column chromatography to provide the desired products **3aa** and **3ba** separately. A similar reaction mixture was also obtained for the reaction with styrene **2b** instead of trimethylvinylsilane **2a**. MS (ESI, positive ions), **3aa**: *m/z* 273.1759 (calculated for $[M - Br]^+$ 273.1787), **3ba**: *m/z* 303.1868 (calculated for $[M - Br]^+$ 303.1893).

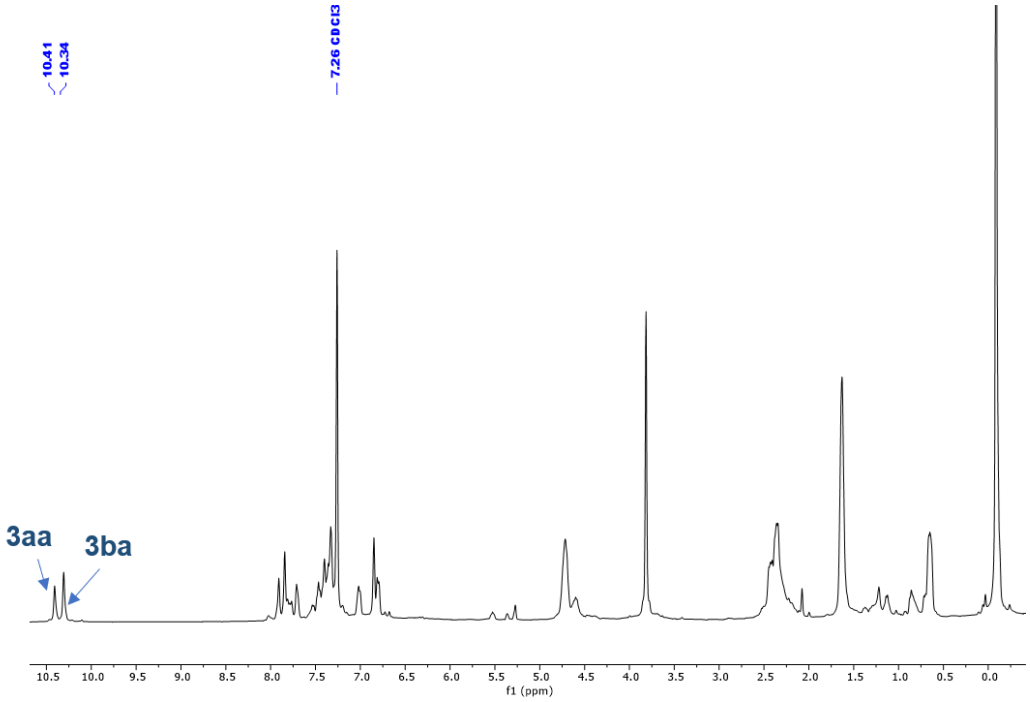


Figure S1. ^{1}H NMR spectrum ($CDCl_3$) of the reaction mixture of the above reaction with **2a** showing the formation of a mixture of **3aa** and **3ba**.

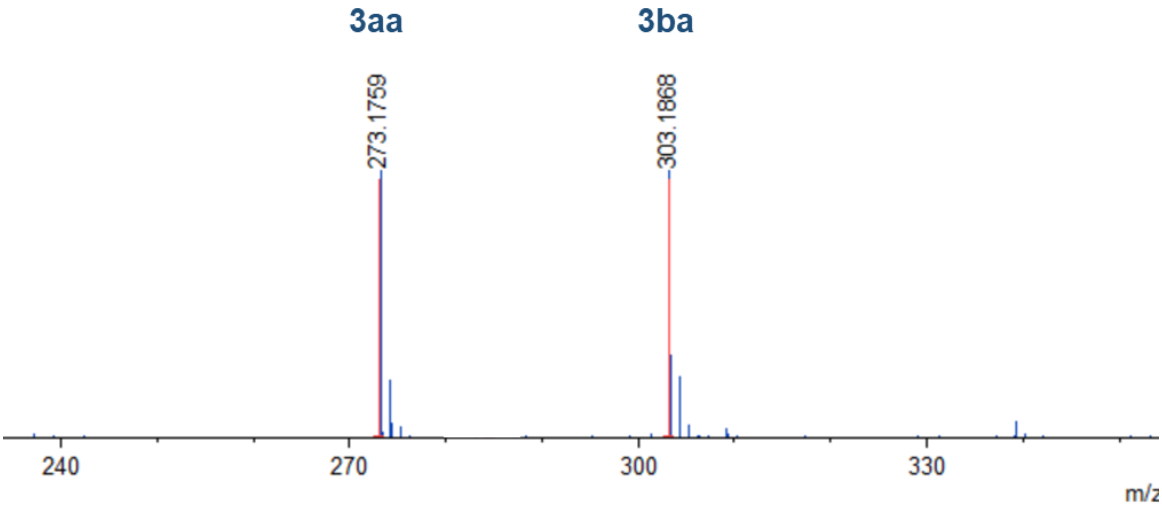
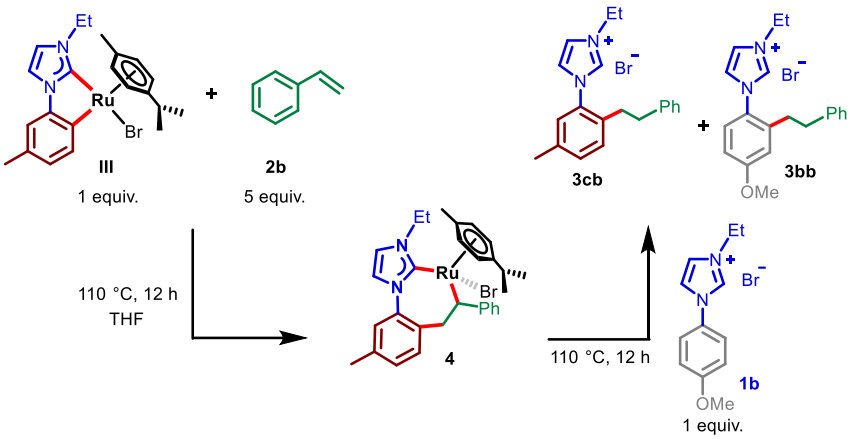


Figure S2. ESI-MS spectrum of the above reaction mixture showing the formation of the compounds **3aa** and **3ba**.

c) Detection of key intermediates

1)



In a pressure tube, orthometalated Ru-NHC complex **III** (30 mg, 0.060 mmol), and styrene **2b** (34 µL, 0.294 mmol, 5 equiv.) were stirred in THF at 110 °C (oil bath temperature) for 12 h. After completion, the reaction mixture was cooled. An aliquot of this reaction was analyzed by NMR and ESI-MS (Figure S3) that showed the formation of the alkene-inserted complex **4**, by the appearance of a new set of peaks with a characteristics ABX type ^{1}H NMR splitting pattern (Figure S5). The reaction mixture was further stirred at 110 °C after adding the imidazolium salt **1b** (17 mg, 0.060 mmol, 1 equiv.) for 12 h. ^{1}H NMR and ESI-MS analysis shows that along with the starting materials **III** and **1b**, products **3cb** (corresponding to complex **III**) and **3bb** (corresponding to imidazolium salt **1b**) were formed. MS (ESI, positive ions): **3cb**: *m/z* 291.1857 (calculated for $[M - Br]^+$ 291.1861), **3bb**: *m/z* 307.1809 (calculated for $[M - Br]^+$ 307.1810).

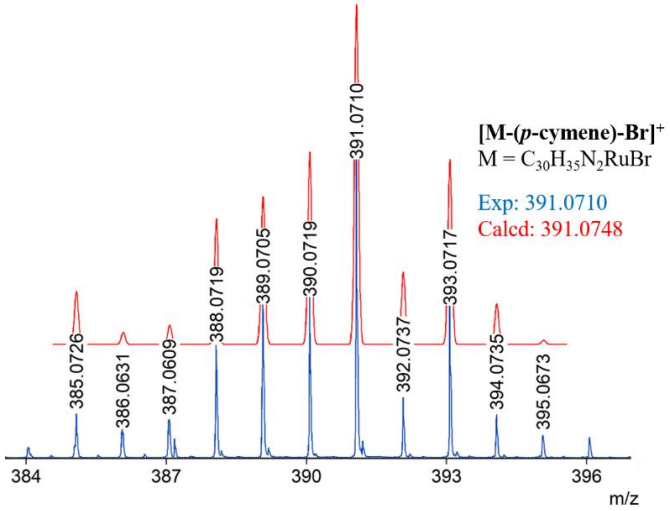


Figure S3. ESI-MS data of complex **4**.

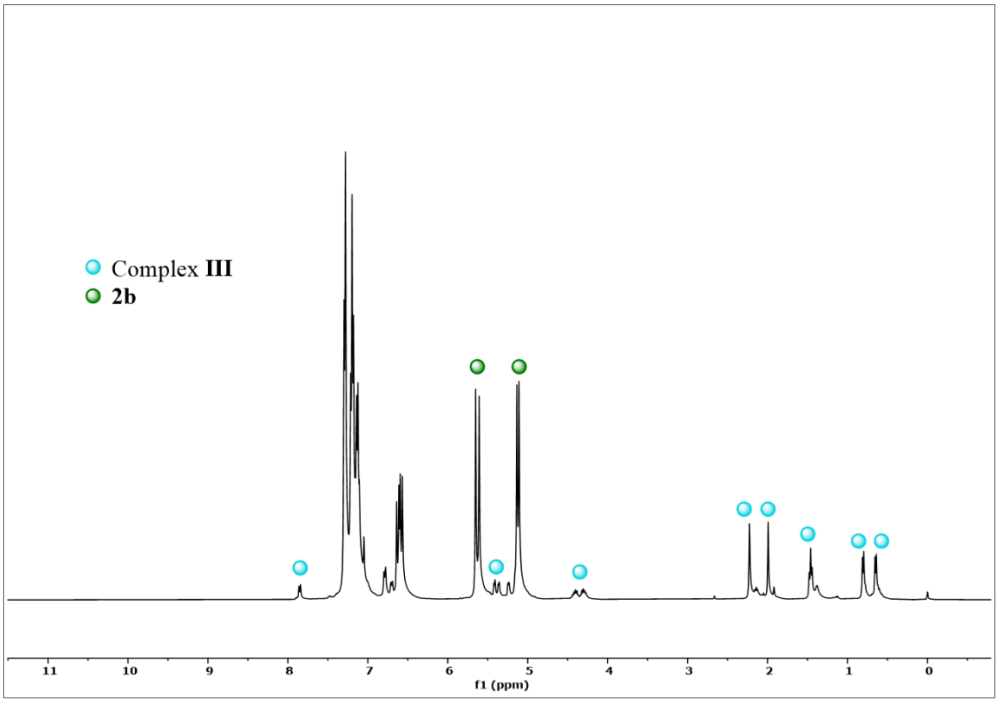


Figure S4. ^{1}H NMR spectrum of a mixture of starting materials, complex **III** and **2b**, (before heating at 110 °C) in $CDCl_3$.

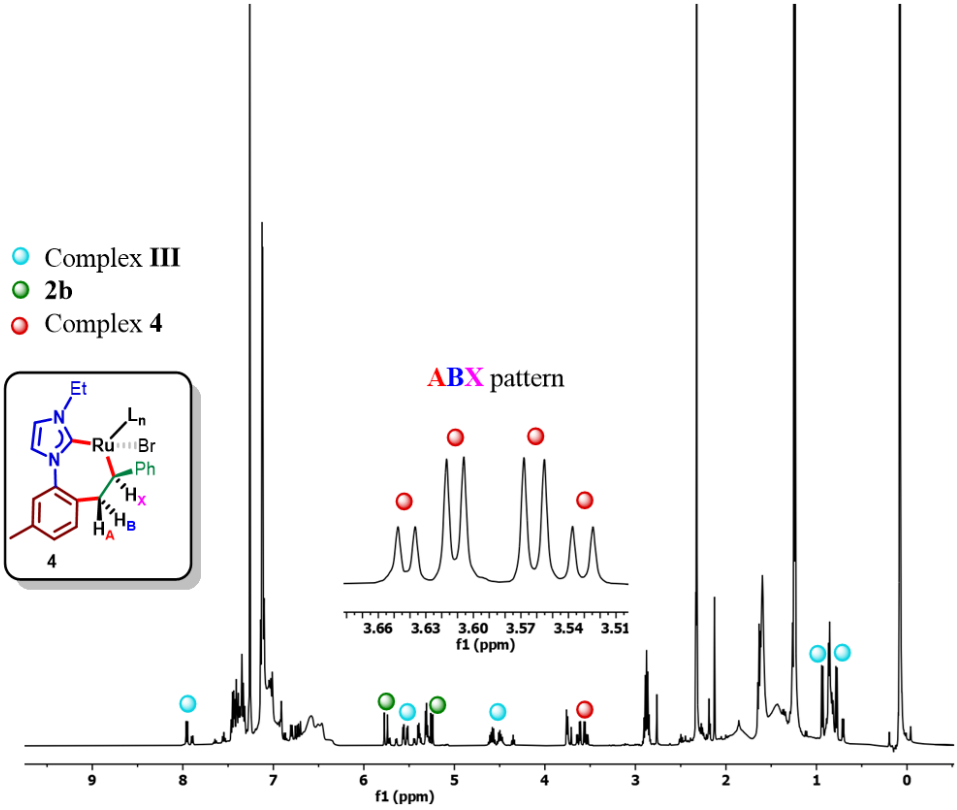


Figure S5. ^{1}H NMR spectrum of reaction mixture in $CDCl_3$.

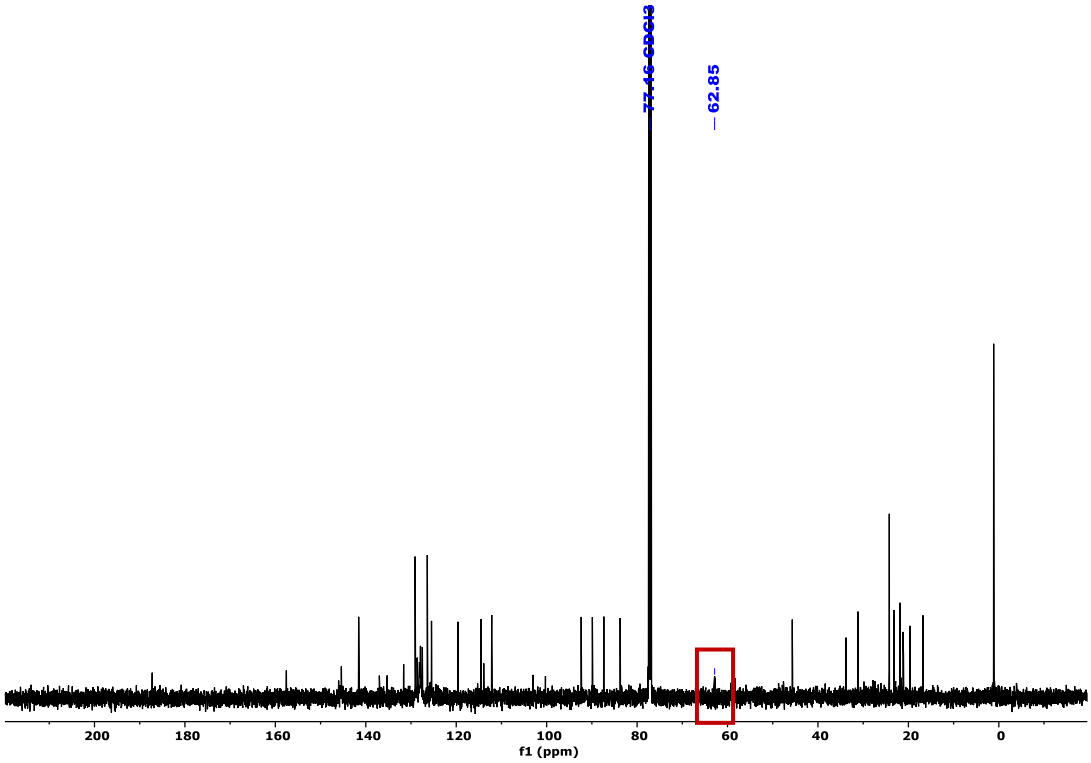


Figure S6. $^{13}C\{^{1}H\}$ NMR of reaction mixture in $CDCl_3$.

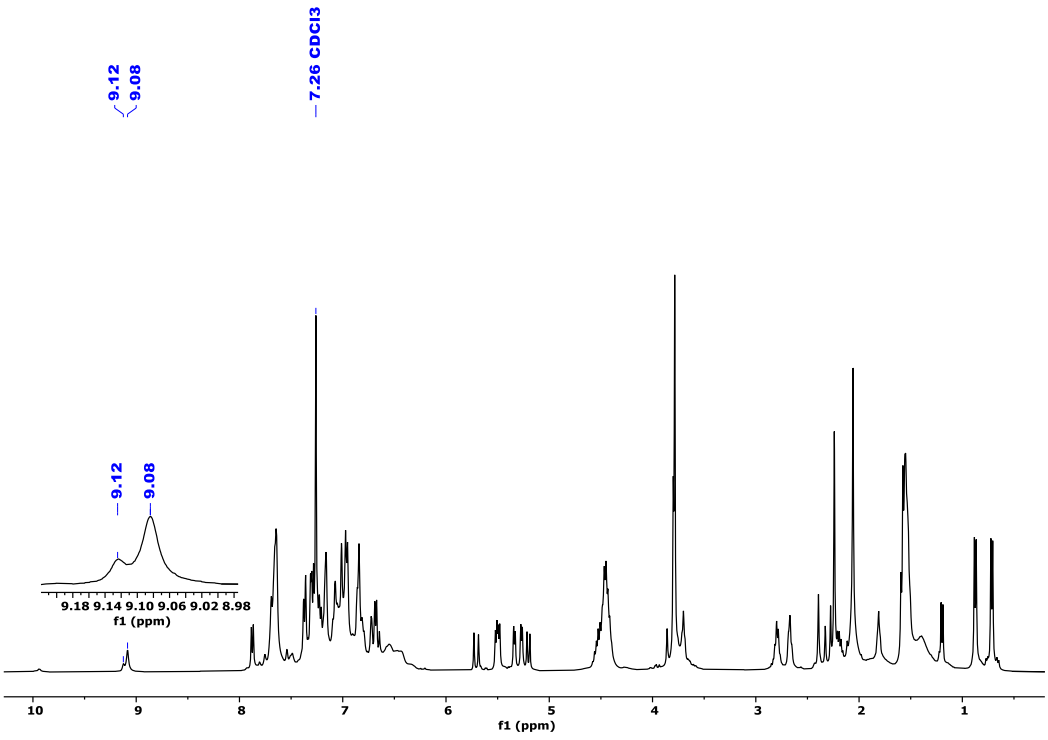
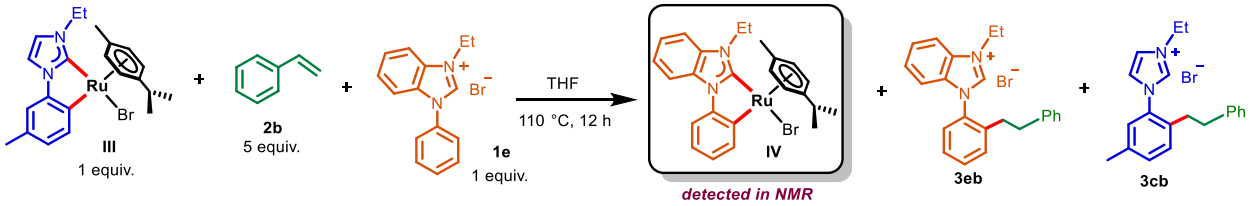


Figure S7. ^{1}H NMR spectrum of reaction mixture in $CDCl_3$, after the addition of **1b**.

2)

(a)



In a pressure tube, orthometalated Ru-NHC complex **III** (30 mg, 0.060 mmol), styrene **2b** (34 µL, 0.294 mmol) and **1e** were stirred in THF at 110 °C (oil bath temperature) for 12 h. The reaction mixture was then filtered through an alumina pad and the cyclometalated complex **IV**, derived from **1e**, was detected along with the starting complex **III** in ^{1}H NMR (Figure S8) and ESI-MS analysis. Product **3eb** corresponding to imidazolium salt **1e** and **3cb** corresponding to **III** were also detected in ESI-MS analysis of the crude reaction mixture. MS (ESI, positive ions): **3eb**: *m/z* 327.1809 (calculated for $[M - Br]^+$ 327.1861); **3cb**: *m/z* 291.1815 (calculated for $[M - Br]^+$ 291.1861); complex **IV**: *m/z* 537.0417 (calculated for $[M - Br]^+$ 537.0479).

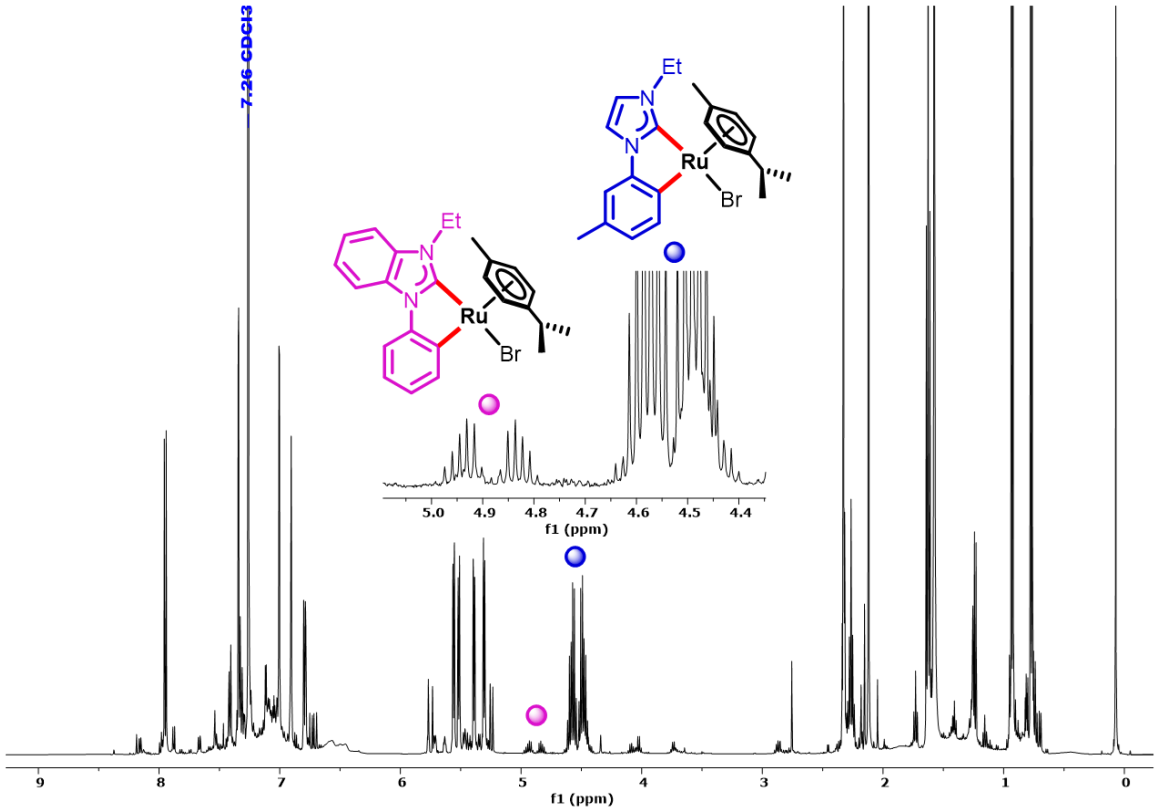
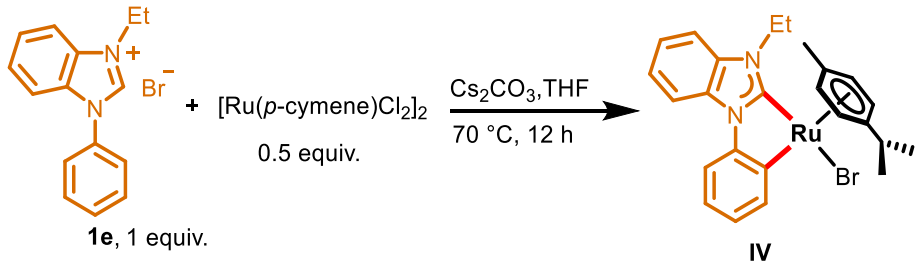


Figure S8. ^{1}H NMR spectrum of reaction mixture in $CDCl_3$, after alumina filtration.

(b)



1e, 1 equiv. **IV**

To a pressure tube equipped with a magnetic stirring bar, imidazolium salt **1e** (50 mg, 0.165 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (51.0 mg, 0.0824 mmol) and Cs_2CO_3 (108.0 mg, 0.330 mmol) were added. THF (6 mL) was then added and stirred at 70 °C for 12 h. After that, the reaction mixture was cooled and all the volatiles were removed in vacuo. The resulted residue was extracted with dichloromethane and filtered through an alumina pad. Concentration followed by the addition of hexane resulted in the precipitation of a solid, which was washed with hexane and dried in vacuum to obtain an orange-red powder in 71% yield (63 mg, 0.117 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 7.3, 1.6 Hz, 1H), 7.98 – 7.96 (m, 1H), 7.67 (dd, J = 7.8, 1.5 Hz, 1H), 7.44 – 7.42 (m, 1H), 7.31 – 7.28 (m, 2H), 7.08 – 6.98 (m, 2H), 5.77 (dd, J = 6.3, 1.4 Hz, 1H), 5.71 (dd, J = 5.9, 1.4 Hz, 1H), 5.47 (dd, J = 6.1, 1.4 Hz, 1H), 5.35 (dd, J = 5.9, 1.3 Hz, 1H), 4.98 – 4.89 (m, 1H), 4.87 – 4.78 (m, 1H), 2.29 (s, J = 7.0 Hz, 1H), 2.15 (s, 3H), 1.72 (t, J = 7.3 Hz, 3H), 0.95 (d, J = 7.0 Hz, 3H), 0.75 (d, J = 7.0 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.5, 162.6, 147.0, 142.0, 141.5, 135.3, 132.0, 124.0, 123.0, 122.4, 112.6, 111.5, 110.1, 104.5, 101.8, 94.9, 92.2, 88.8, 84.1, 43.8, 31.2, 23.0, 21.9, 19.6, 15.7 ppm. MS (ESI, positive ions): *m/z* 537.0414 (calculated for $[M + H]^+$ 537.0479).

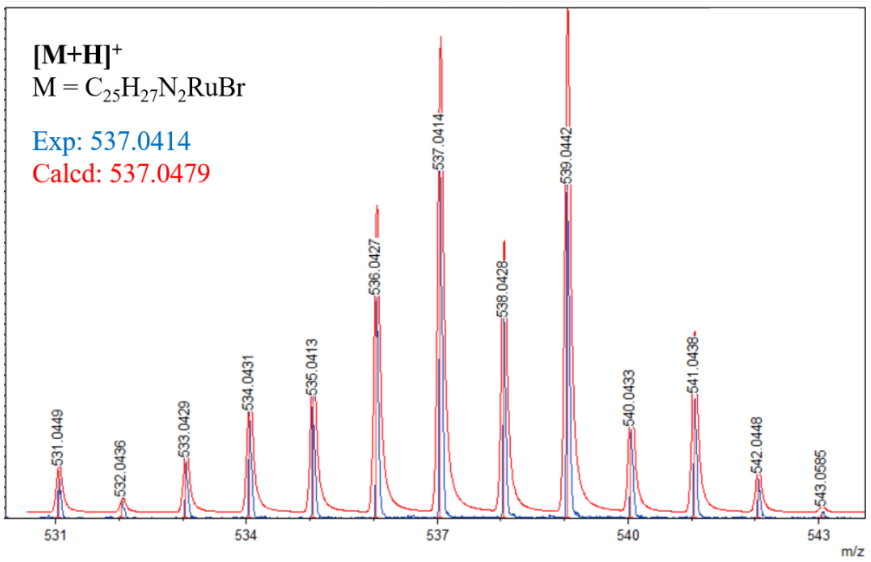


Figure S9. ESI-MS data of complex **IV**.

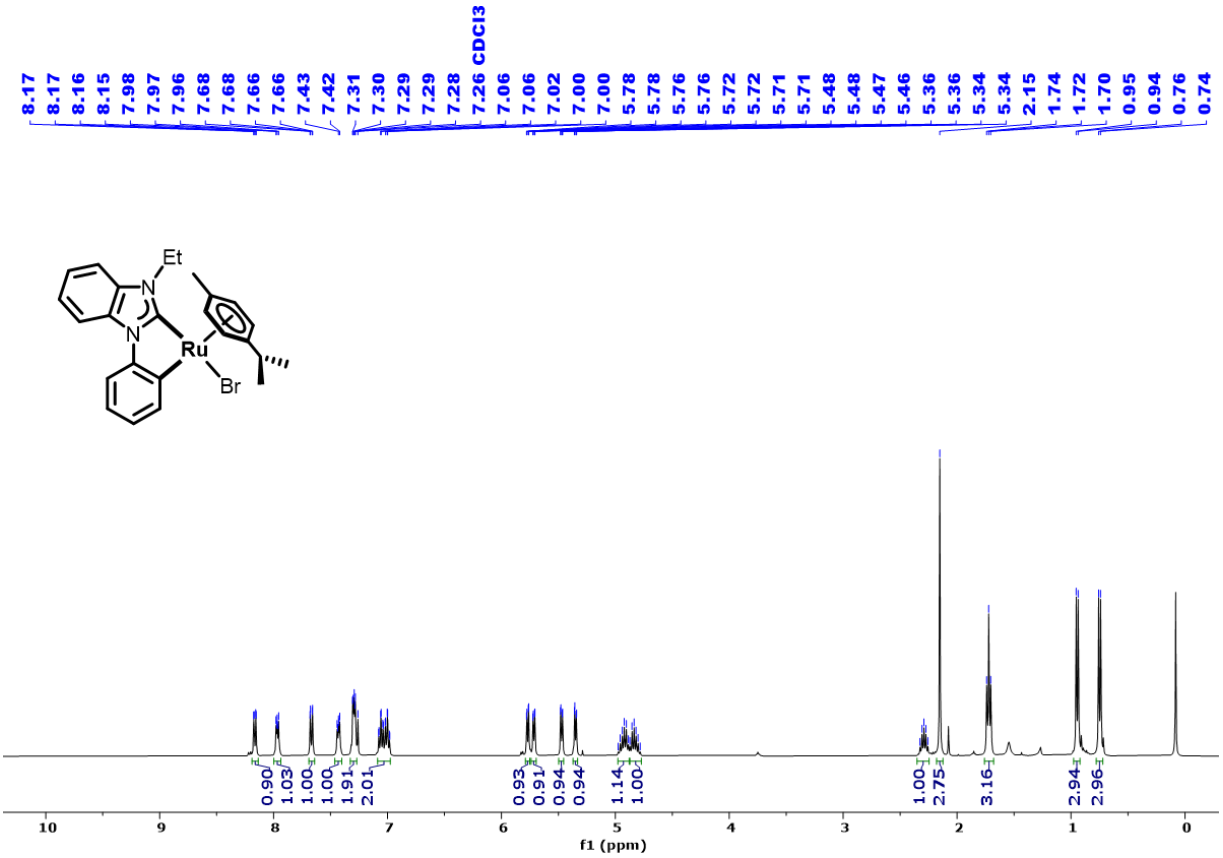


Figure S10. ^{1}H NMR spectrum of complex **IV** in $CDCl_3$.

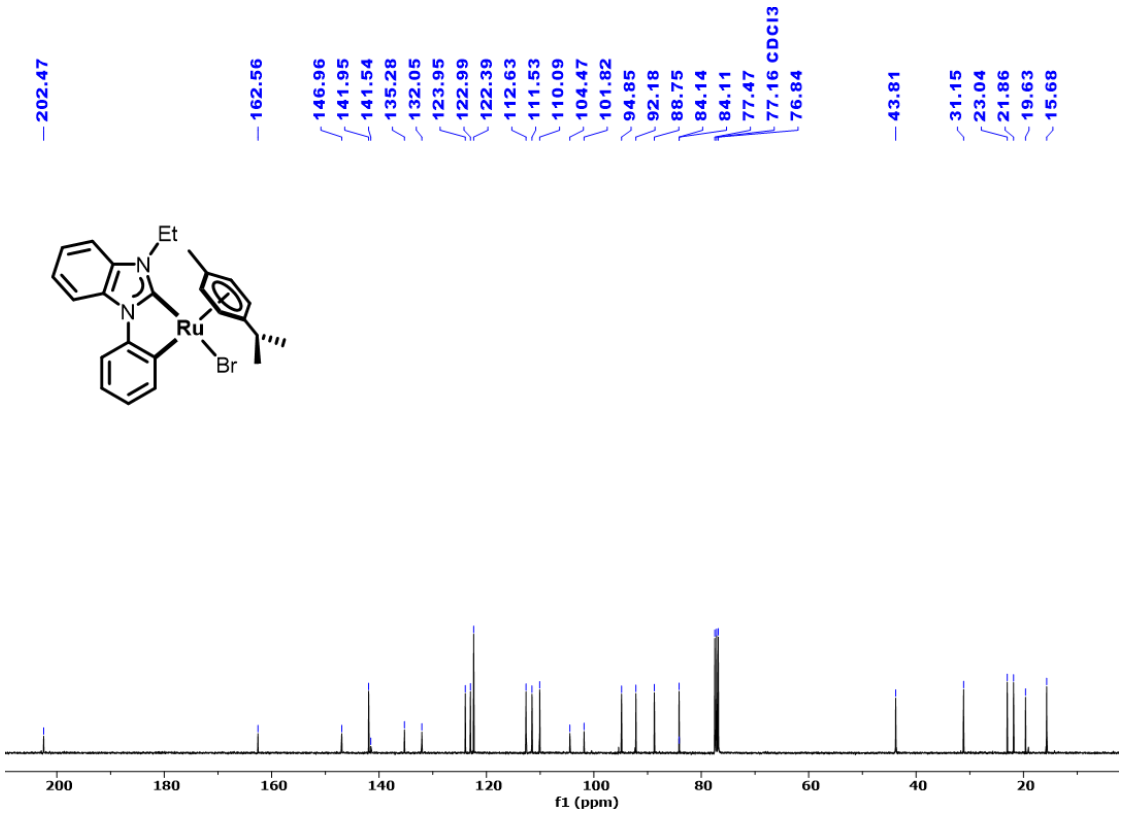


Figure S11. $^{13}C\{^{1}H\}$ NMR of complex **IV** in $CDCl_3$.

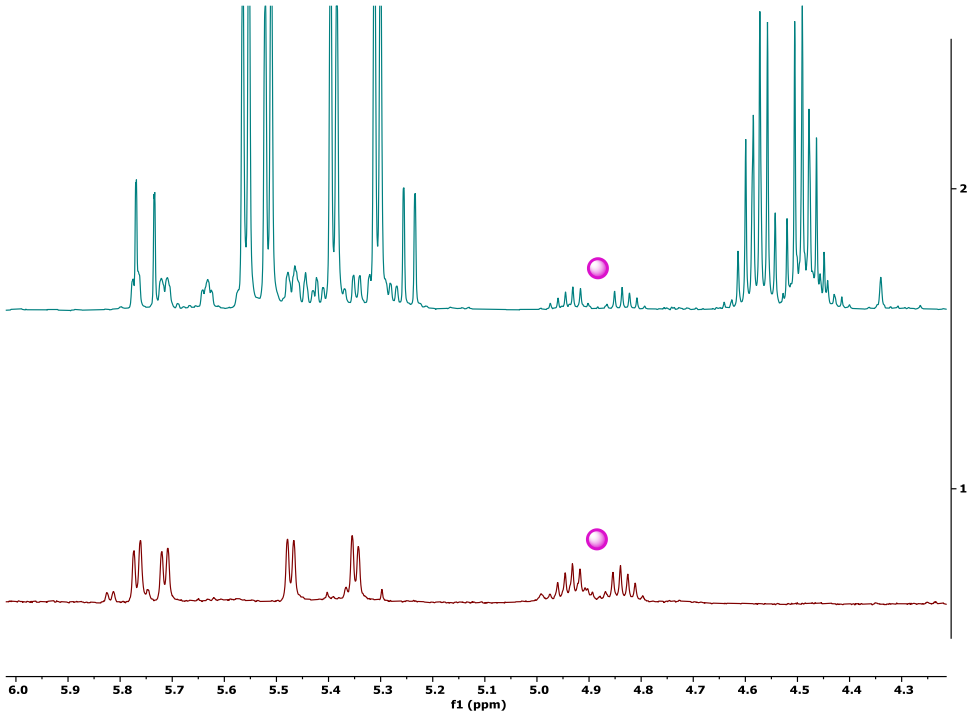
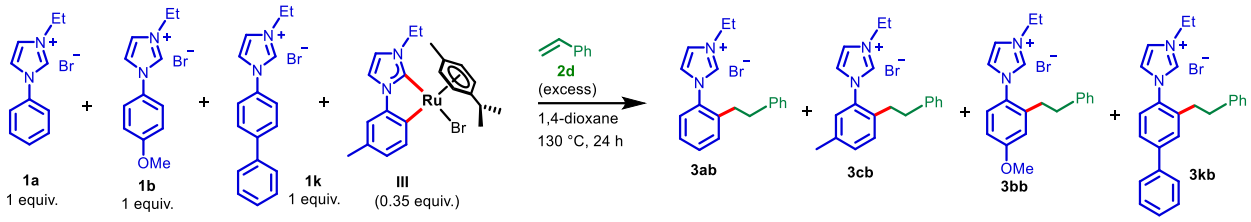


Figure S12. Comparison of the ^{1}H NMR spectra of the reaction mixture and isolate complex **IV** in $CDCl_3$.

5. Relay race of NHC ligands



In a pressure tube (25 mL), a mixture of imidazolium salts [**1a** (30 mg, 0.118 mmol), **1b** (33 mg, 0.118 mmol), and **1k** (39 mg, 0.118 mmol)], orthometalated Ru-NHC complex **III** (21 mg, 0.0413 mmol), and styrene **2b** (135 µL, 1.18 mmol) were stirred in 1,4-dioxane at 130 °C (oil bath temperature) for 24 h. After completion, the reaction mixture was cooled and volatiles were removed in vacuo. The obtained residue was extracted with dichloromethane and after drying, NMR was recorded in $CDCl_3$. Formation of the desired products **3ab**, **3bb**, **3cb**, and **3kb** was confirmed by ^{1}H NMR and ESI-MS analysis.

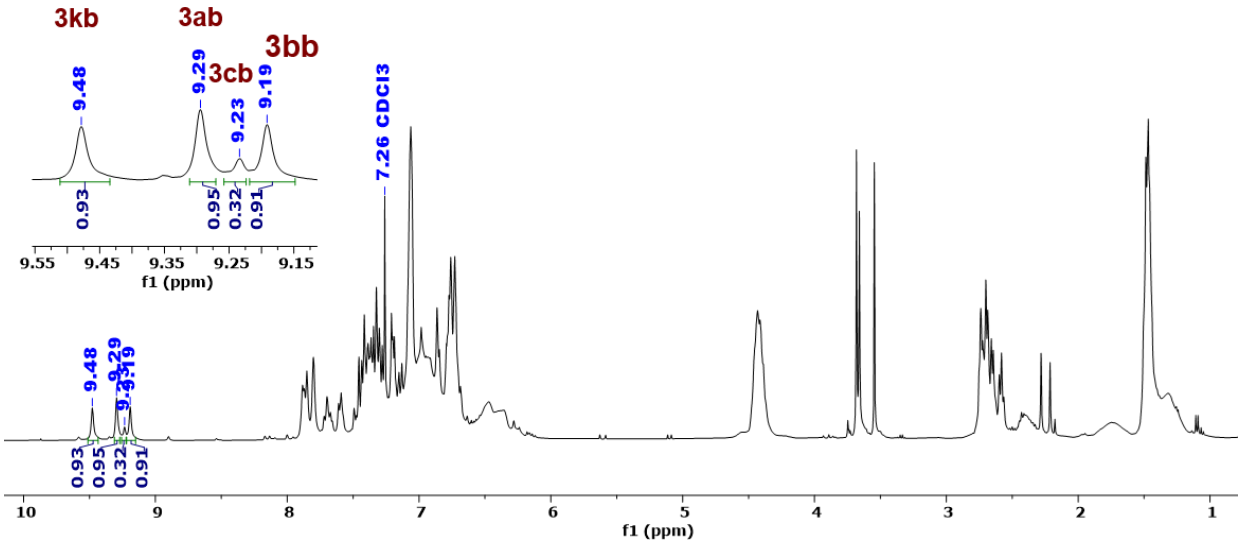


Figure S13. ^{1}H NMR spectrum of the reaction mixture in $CDCl_3$.

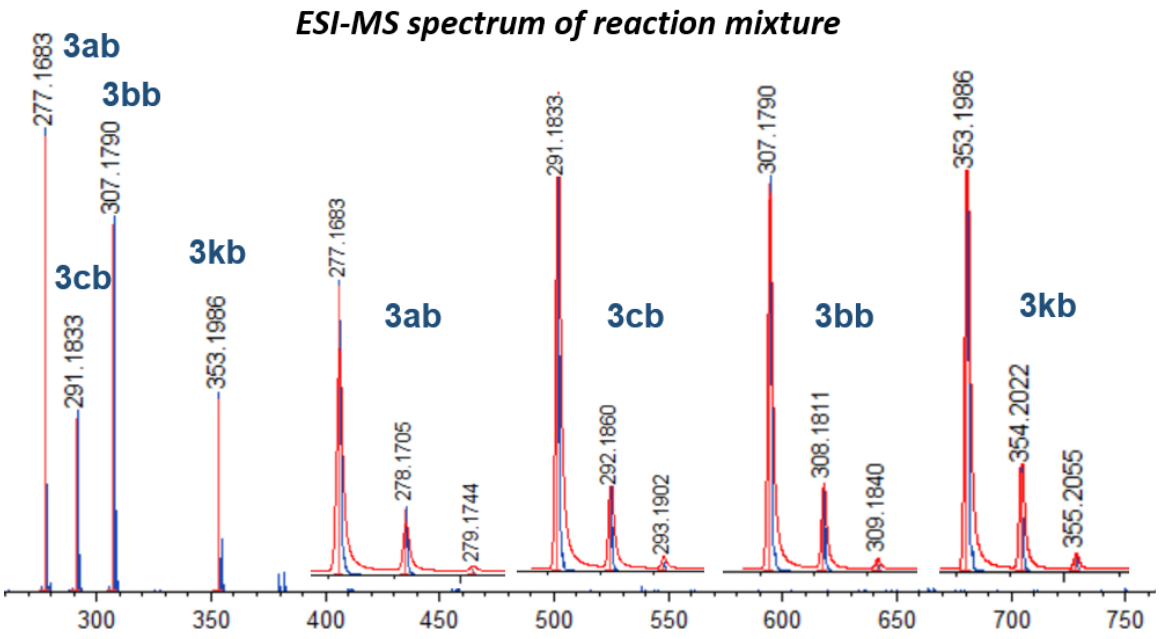
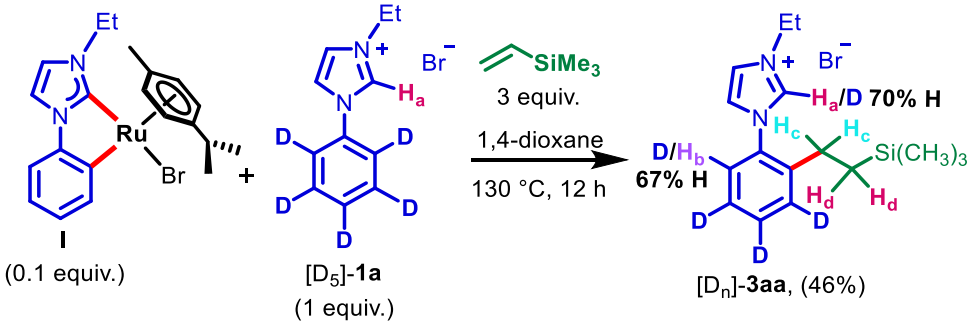


Figure S14. ESI-MS data of the above reaction mixture.

6. Deuterium labelling experiments for proving a metathesis pathway

a)



In a pressure tube (25 mL), N-D_5-phenyl imidazolium salt, [D_5]-**1a** (51 mg, 0.197 mmol), trimethylvinylsilane **2a** (87 µL, 0.591 mmol, 3 equiv.) and complex **I** (10.0 mg, 0.0197 mmol, 10 mol%) were stirred in 1,4-dioxane (1.0 mL) at 130 °C (oil bath temperature) for 12 h (standard reaction time is 24 h). After completion, the reaction mixture was cooled and volatiles were removed in vacuo. The obtained residue was extracted with dichloromethane and after drying, the crude NMR was recorded in $CDCl_3$. ^{1}H NMR analysis reveals 44% deuterium incorporation at the C2-position of [D_n]-**3aa** (Figure S15). Thereafter, the mixture was purified by column chromatography eluting with methanol and DCM (1:10) to provide the desired product [D_n]-**3aa**

in ~ 46% yield. However, the deuterium incorporation at the C2-position of the isolated compound [D_n]-**3aa** was decreased to 30% (Figure S16), due to H-exchange of the acidic C2-H during silica gel column chromatography.

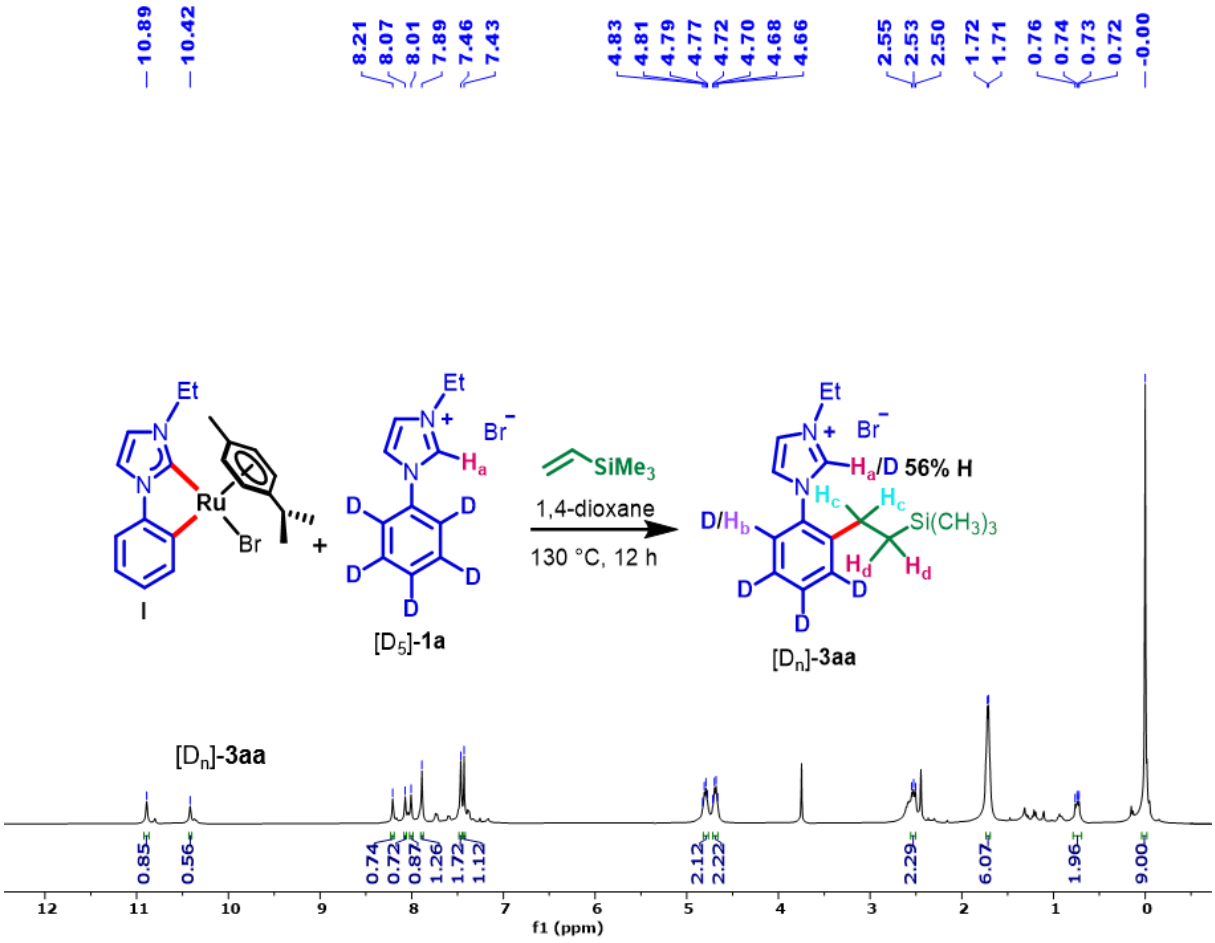


Figure S15. ^{1}H NMR spectrum of reaction mixture in $CDCl_3$.

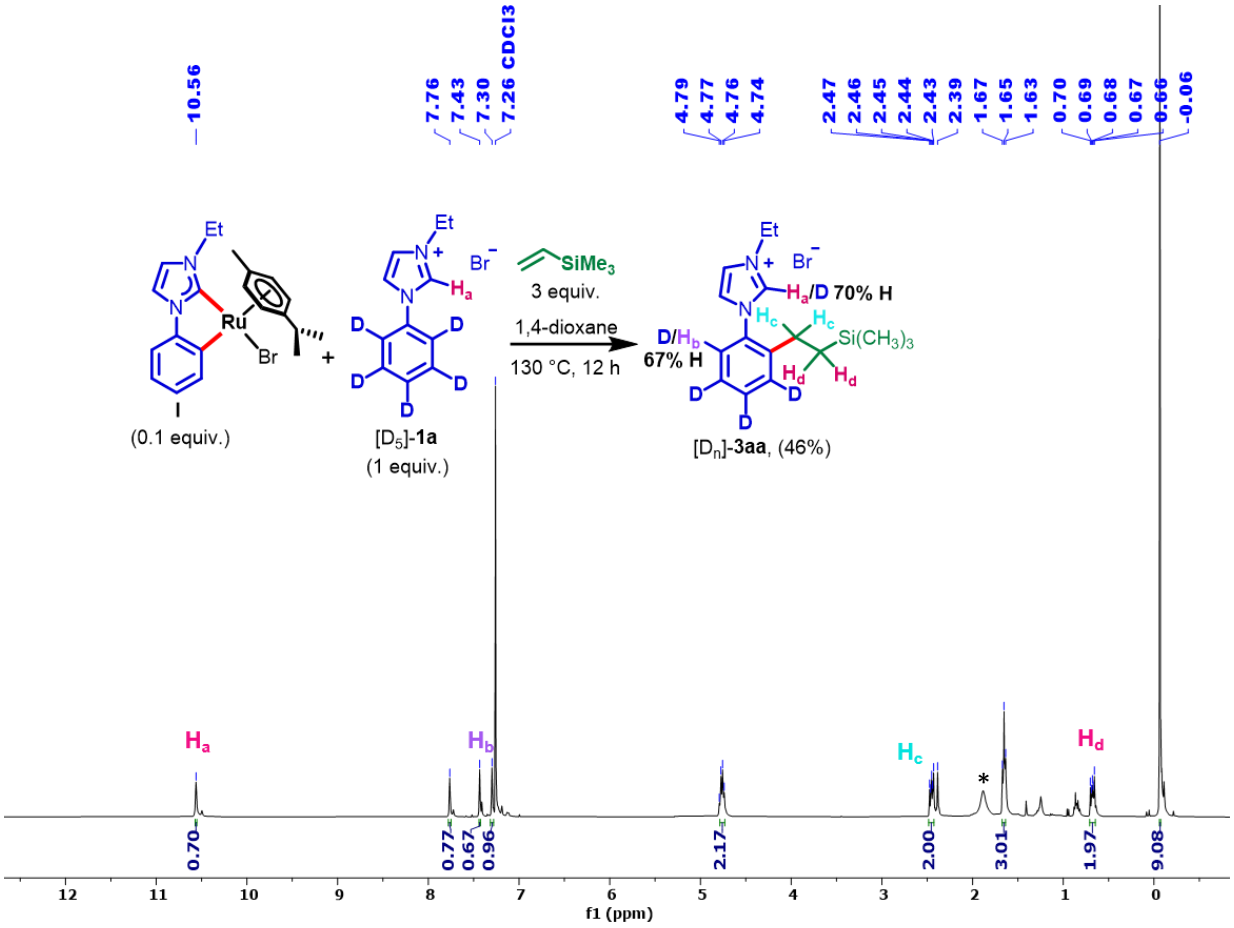
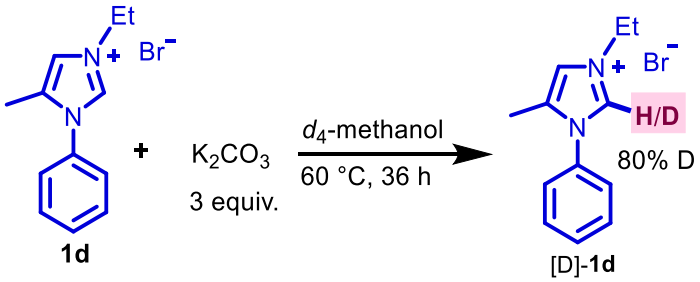


Figure S16. ^{1}H NMR spectrum of isolated [D_n]-**3aa** in $CDCl_3$. * indicates water in $CDCl_3$.

b)

1)



In a pressure tube, imidazolium salt **1d** (65 mg, 0.243 mmol) and K_2CO_3 (100 mg, 0.868 mmol) were stirred in d_4-methanol (0.6 mL) at 60 °C (oil bath temperature) for 36 h. After completion, the reaction mixture was cooled and volatiles were removed in vacuo. The obtained residue was

extracted with DCM and filtered through a short celite pad. After drying, the ^{1}H NMR was recorded in $CDCl_3$.

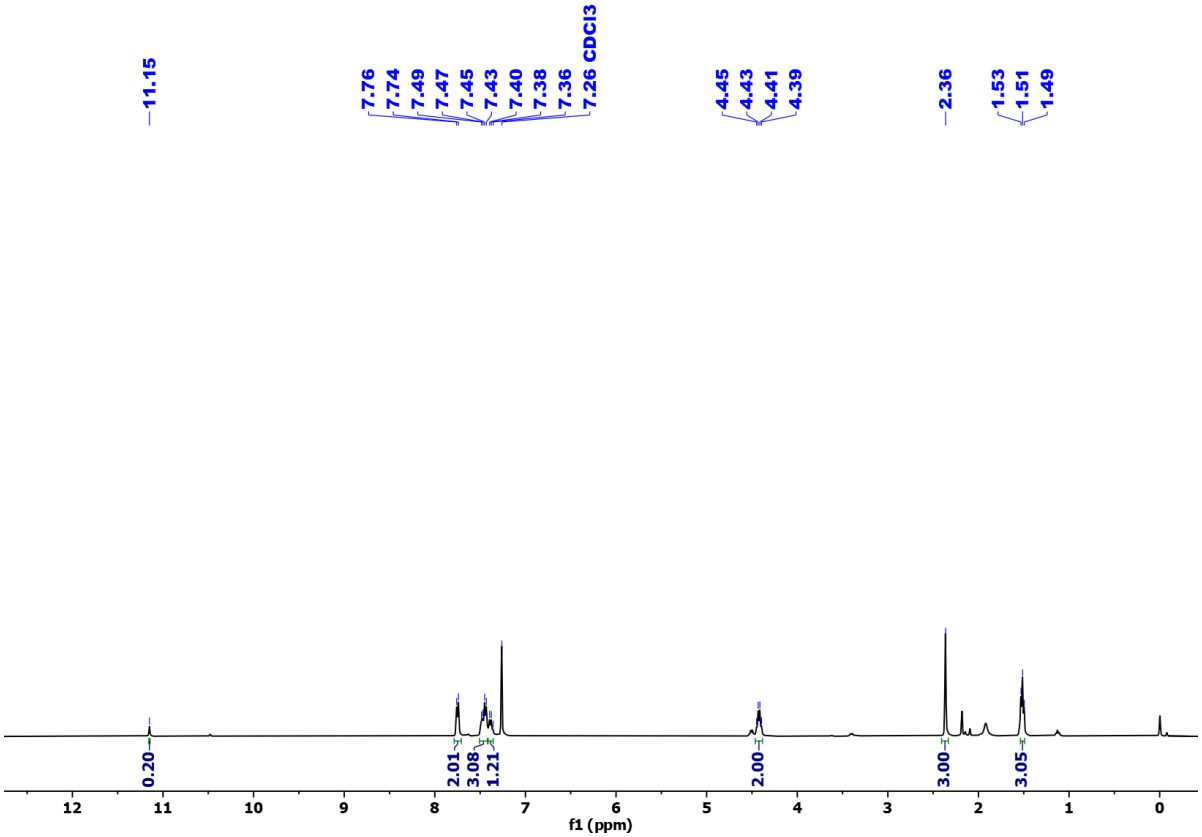
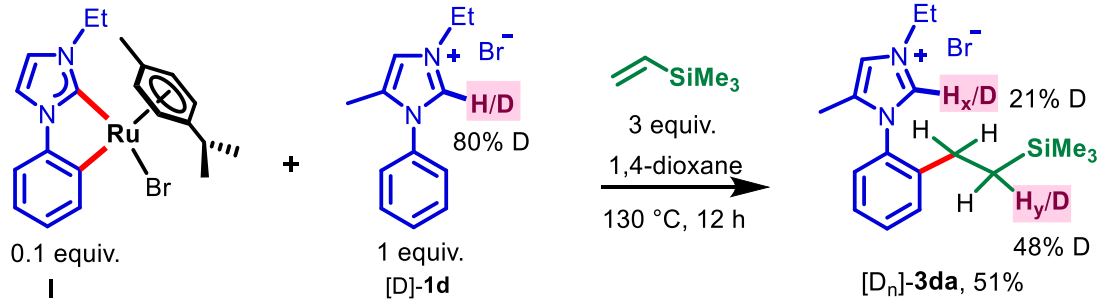


Figure S17. ^{1}H NMR spectrum of [D]-**1d** in $CDCl_3$.

2)



In a pressure tube, imidazolium salt, [D]-**1d** (53 mg, 0.197 mmol), trimethylvinylsilane **2a** (87 µL, 0.591 mmol, 3 equiv.), and complex **I** (10.0 mg, 0.0197 mmol, 10 mol%) were stirred in 1,4-dioxane (1.0 mL) at 130 °C (oil bath temperature) for 12 h. After completion, the reaction mixture was cooled and all the volatiles were removed in vacuo. The obtained residue was then extracted

with dichloromethane and after drying, the NMR was recorded in $CDCl_3$ that showed 63% hydrogen incorporation at the imidazolium C2 position. Thereafter, the mixture was purified by column chromatography eluting with methanol and DCM (1:10) to provide the desired product [D_n]-**3da** in ~ 51% yield, however the hydrogen content at C2-position was increased to 79% during silica gel coloumn chromatography.

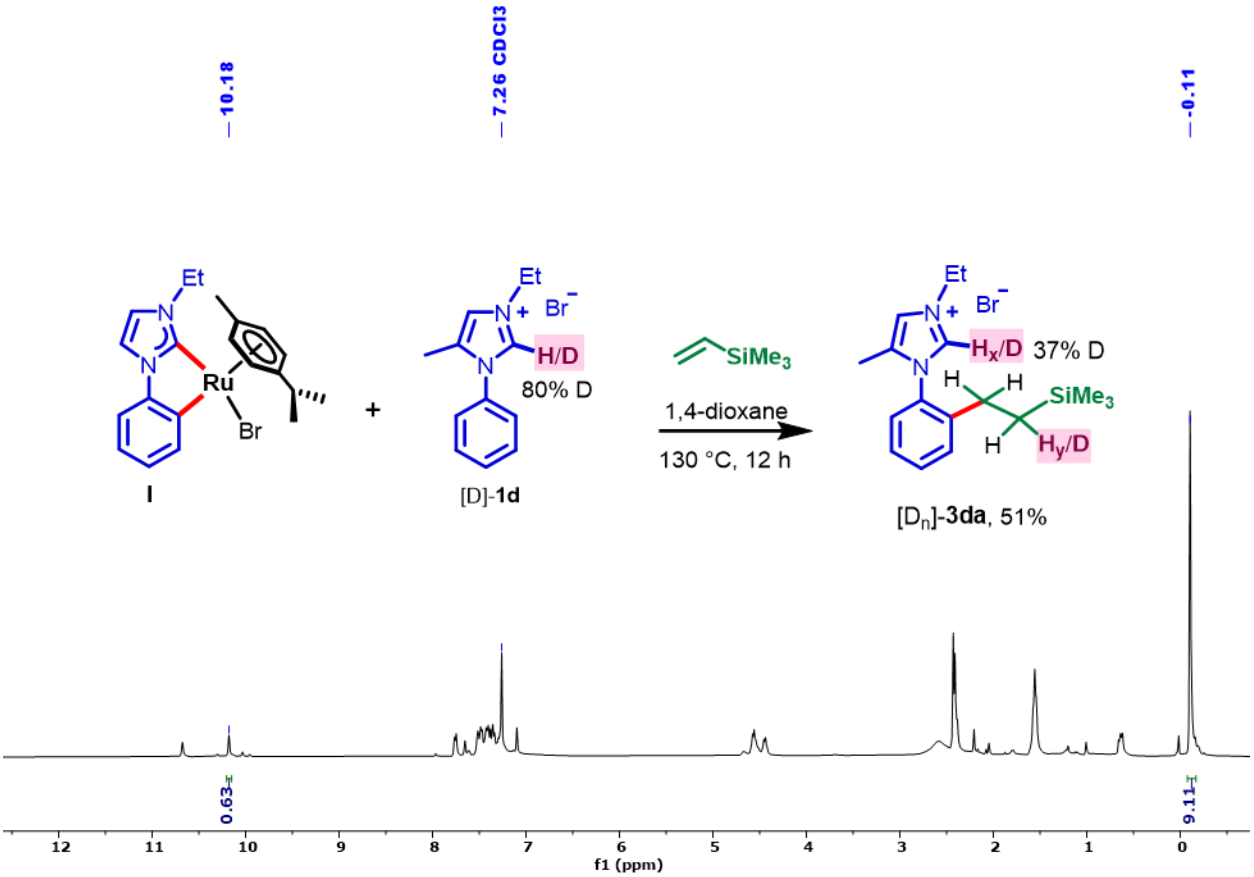


Figure S18. ^1H NMR spectrum of reaction mixture in $CDCl_3$.

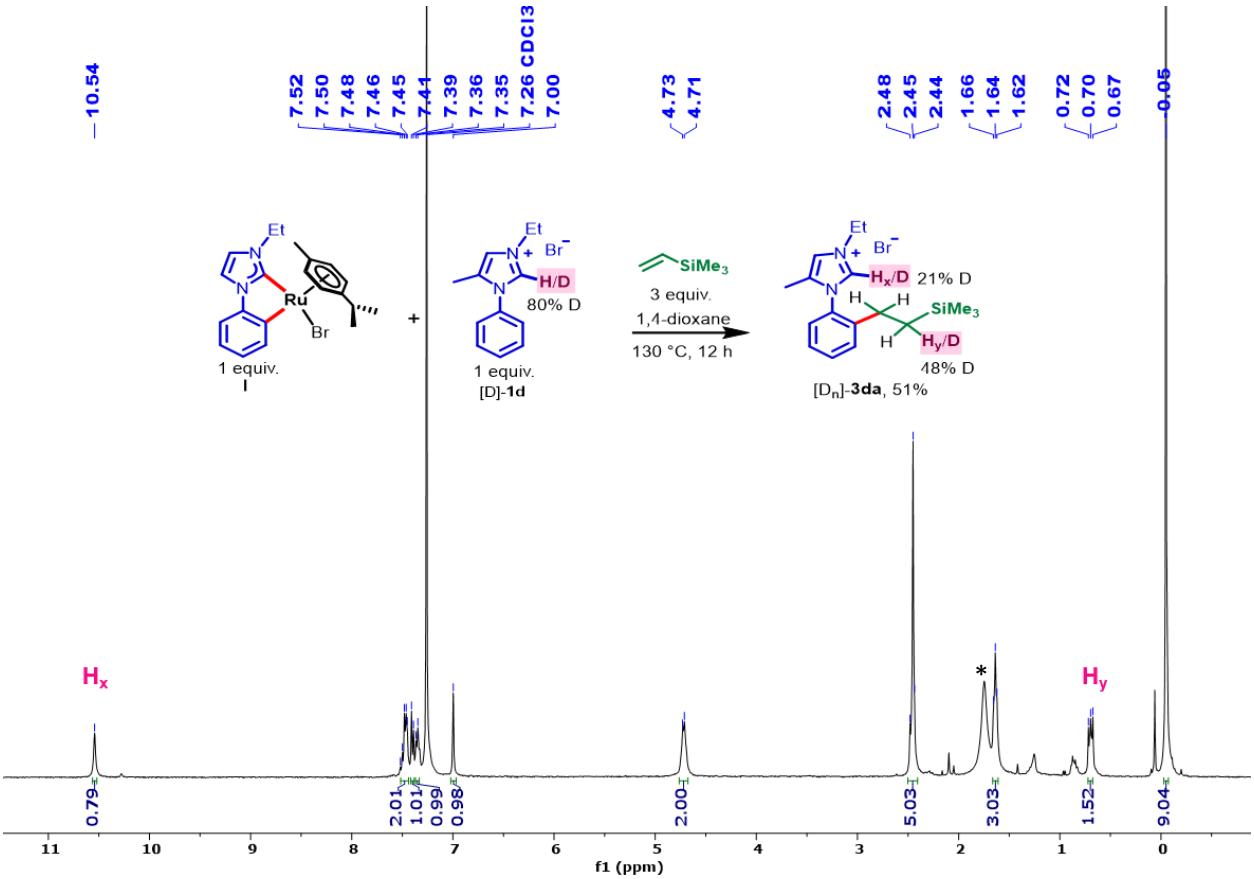
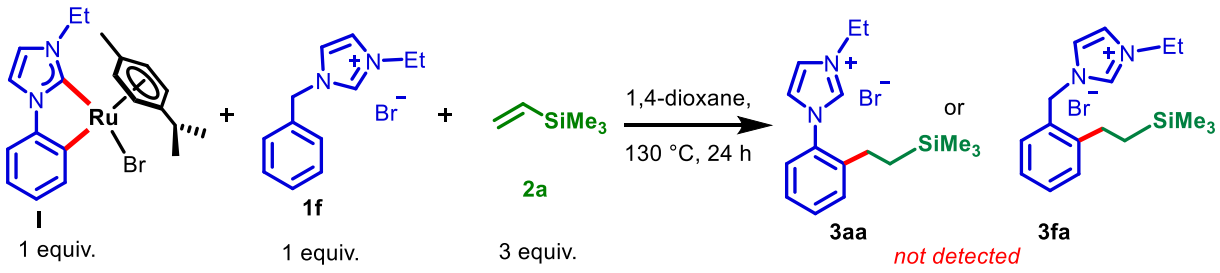


Figure S19. ^{1}H NMR spectrum of the isolated compound [D_n]-**3da** in $CDCl_3$. * indicates water in $CDCl_3$.

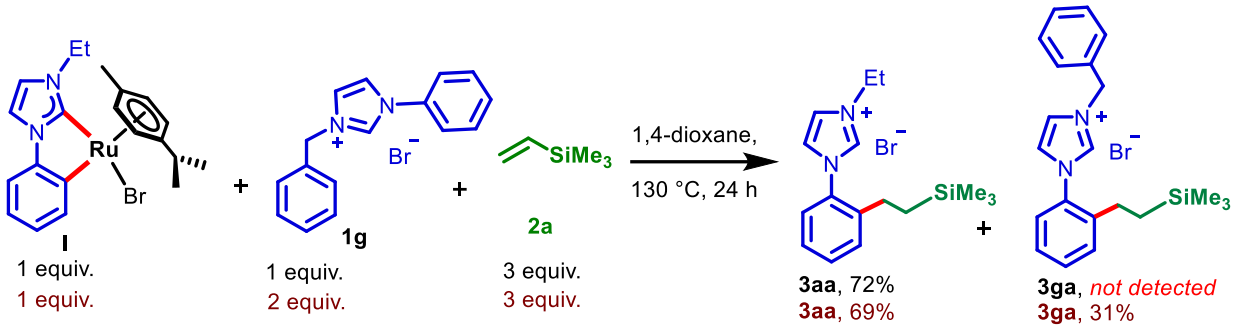
7. Control experiments

a)



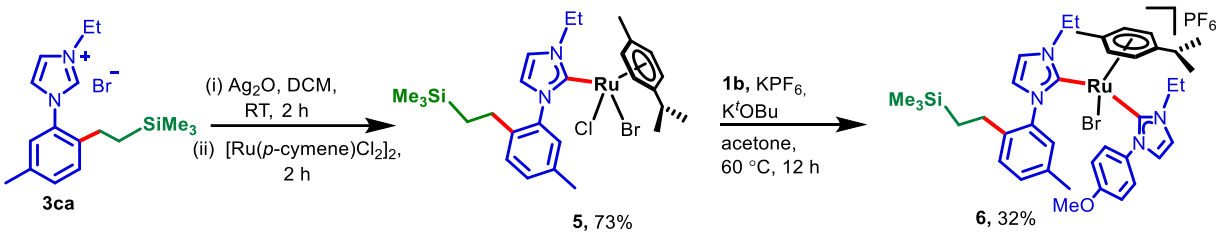
In a pressure tube, imidazolium salt **1f** (28 mg, 0.103 mmol), Ru-NHC complex **I** (50 mg, 0.103 mmol), and trimethylvinylsilane **2a** (45 µL, 0.309 mmol) were stirred in 1,4-dioxane at 130 °C (oil bath temperature) for 24 h. After 24 h, only starting material could be recovered.

b)



In a pressure tube, imidazolium salt **1g** (33 mg, 0.103 mmol), Ru-NHC complex **I** (50 mg, 0.103 mmol), and trimethylvinylsilane **2a** (45 µL, 0.309 mmol, 3 equiv.) were stirred in 1,4-dioxane at 130 °C (oil bath temperature) for 24 h. After completion, the reaction mixture was purified by column chromatography eluting with methanol and DCM (1:10) and only the product **3aa** was obtained in 72% (26 mg, 0.074 mmol) yield. When the same reaction was performed with 2 equiv. of **1g** (66 mg, 0.206 mmol), product **3aa** was obtained in 69% yield (25 mg, 0.071 mmol) along with **3ga** (13 mg, 0.0319 mmol, 31%).

c)



In a pressure tube, imidazolium salt **3ca** (100 mg, 0.295 mmol) and Ag_2O (34 mg, 0.148 mmol, 0.5 equiv.) were stirred in DCM at RT for 2 h. After that, [Ru(*p*-cymene)Cl_2]$_2$ (91 mg, 0.148 mmol) was added to the reaction mixture and again stirred for 2 h at RT. After completion, the reaction mixture was filtered through an alumina pad to obtain a clear yellow solution. Concentration followed by addition of hexane resulted in the precipitation of a solid, which was washed with hexane and dried in vacuum to obtain a bright yellow air stable powder **5** in 73% (136 mg, 0.215 mmol) yield. Complex **5** (30 mg, 0.051) was then stirred with imidazolium salt **1b** (14 mg, 0.051 mmol), KPF_6 (9 mg, 0.051 mmol), and KO^{t}Bu (6 mg, 0.051 mmol) in acetone (5 mL) at 60 °C for 12 h. The reaction mixture was then filtered through a celite pad and the obtained filtrate was dried in vacuum followed by washing with water to remove inorganic salts. Finally, the residue was

extracted with DCM to obtain the complex **6** in 32% yield (15 mg, 0.0163 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.55 (s, 1H), 7.06 (d, J = 11.6 Hz, 5H), 6.89 (d, J = 8.4 Hz, 1H), 6.81 (d, J = 7.0 Hz, 2H), 6.65 (d, J = 7.8 Hz, 1H), 5.67 (d, J = 5.7 Hz, 1H), 5.64 (d, J = 6.1 Hz, 1H), 5.39 (d, J = 5.9 Hz, 1H), 5.20 (d, J = 6.0 Hz, 1H), 4.62 – 4.60 (m, 2H), 3.81 (s, 3H), 3.75 (s, 2H), 2.76 (s, 2H), 2.63 (s, 3H), 2.04 (s, 2H), 1.88 – 1.86 (m, 1H), 1.25 (s, 6H), 0.80 (d, J = 6.8 Hz, 3H), 0.69 (d, J = 6.8 Hz, 3H), 0.05 (s, 9H) ppm. ^{19}F NMR (471 MHz, C_6D_6) δ -70.81 (d, J = 711.8 Hz) ppm. ^{31}P NMR (202 MHz, C_6D_6) δ -143.16 (hept, J = 711.7 Hz) ppm.

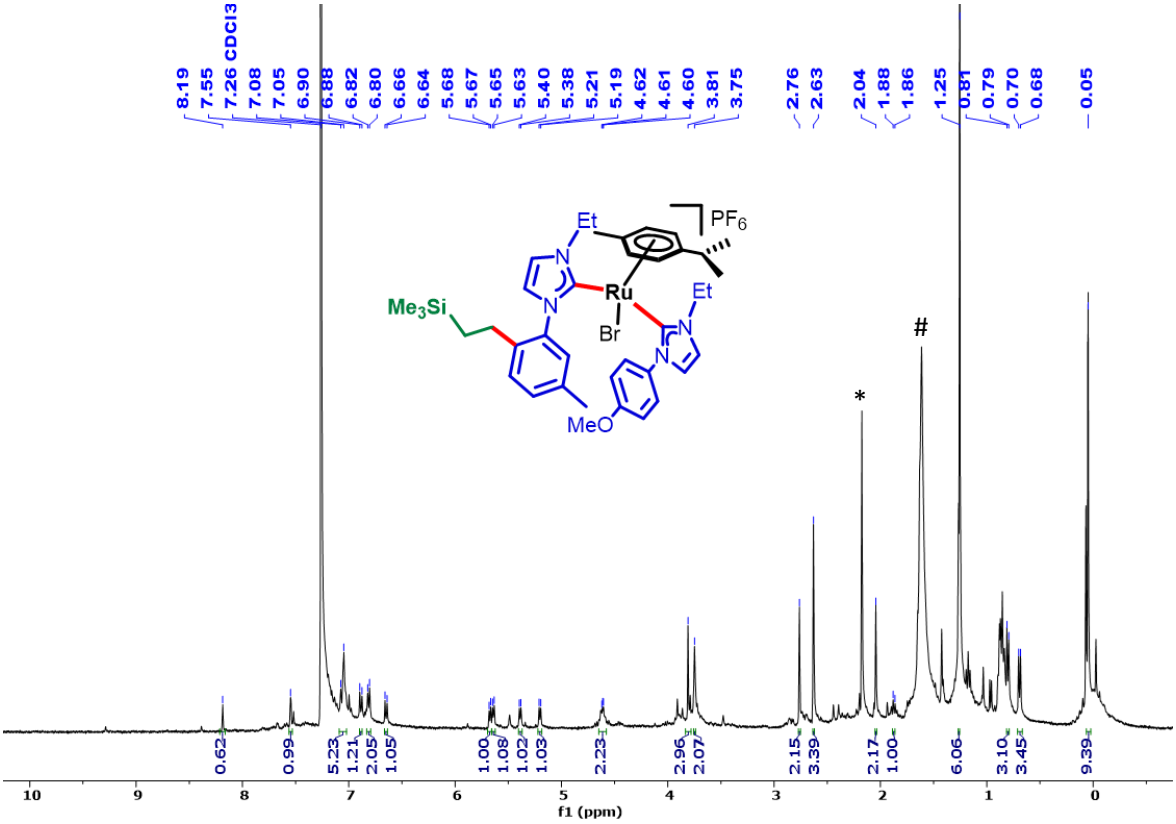


Figure S20. ^{1}H NMR spectrum of **6** in $CDCl_3$. * and # indicate acetone and water impurities in $CDCl_3$.

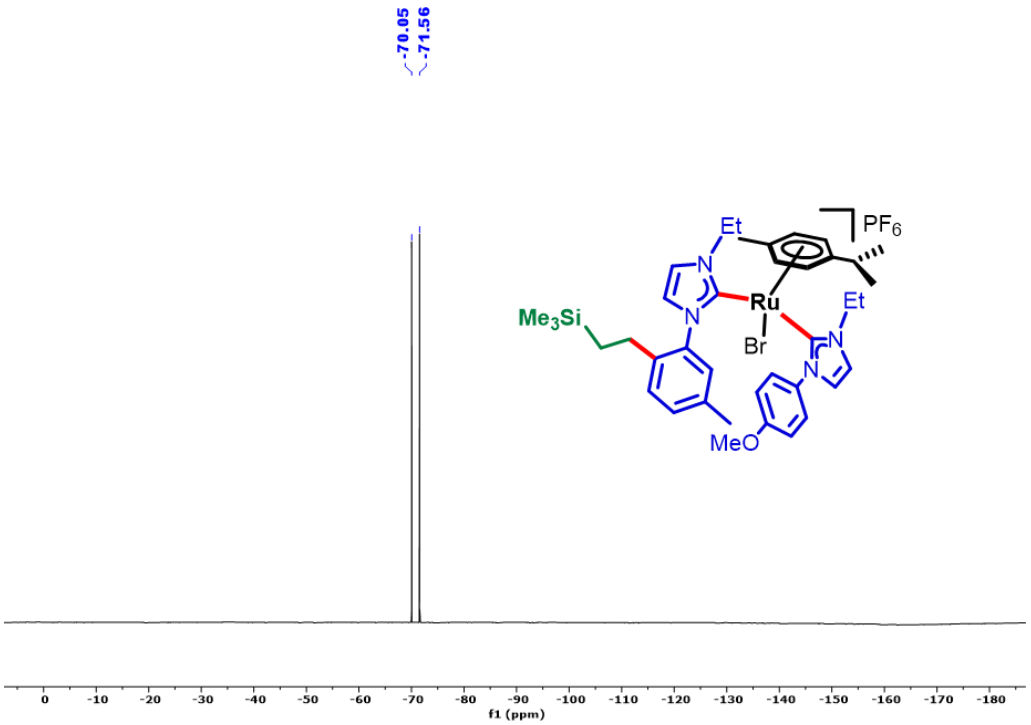


Figure S21. ^{19}F NMR spectrum of **6** in $CDCl_3$.

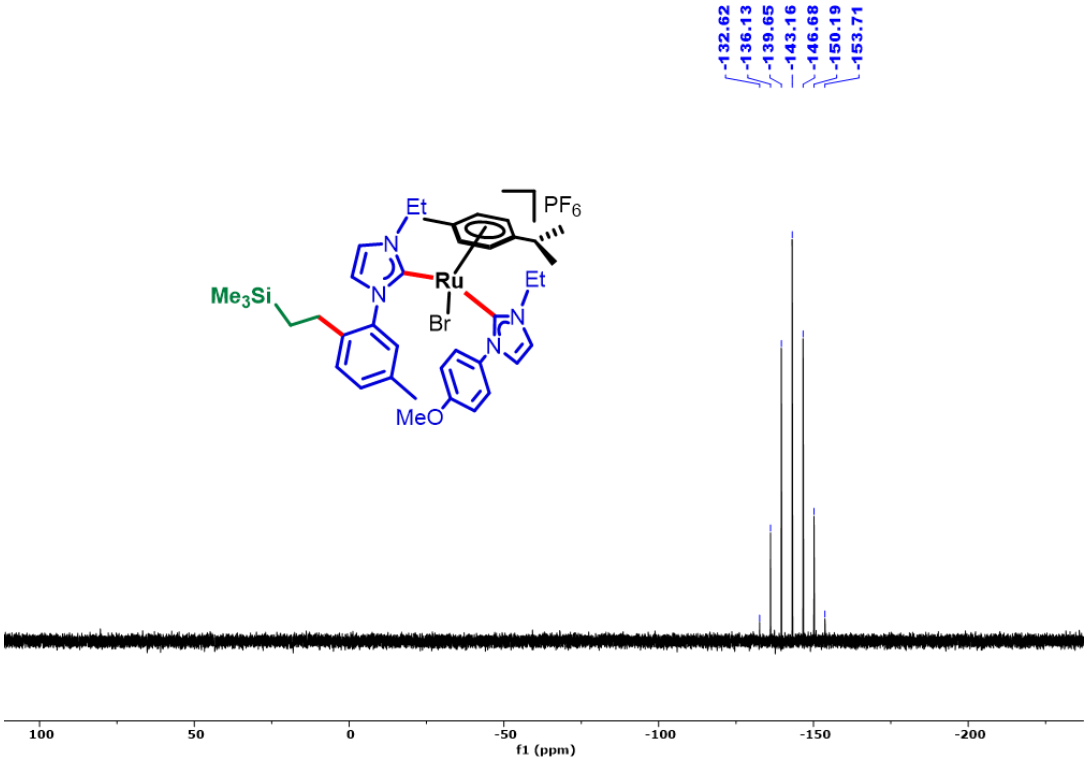


Figure S22. ^{31}P NMR spectrum of **6** in $CDCl_3$.

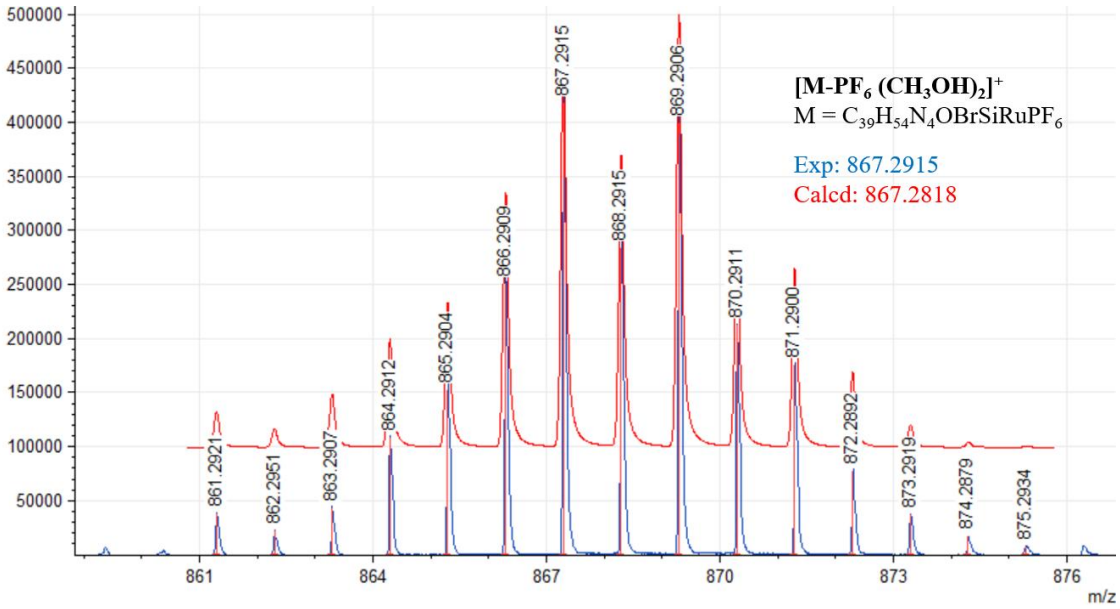
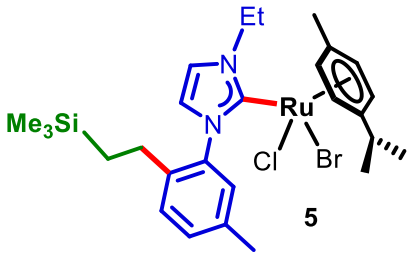


Figure S23. ESI-MS data of complex **6**.



5

Dark red solid. Isolated yield: 136 mg (0.215 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.21 (s, 1H), 7.04 (s, 1H), 6.82 (d, J = 7.6 Hz, 1H), 6.65 (d, J = 7.5 Hz, 1H), 5.68 – 5.60 (m, 2H), 5.39 (d, J = 5.8 Hz, 1H), 5.20 (d, J = 6.7 Hz, 1H), 4.61 (q, J = 6.9 Hz, 2H), 2.86 – 2.84 (m, 1H), 2.76 – 2.66 (m, 4H), 2.04 (s, 3H), 1.94 – 1.88 (m, 1H), 1.63 (s, 3H), 0.88 –0.80 (m, 5H), 0.69 (d, J = 6.7 Hz, 3H), 0.05 (s, 9H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 191.0, 144.7, 143.7, 126.8, 124.8, 124.7, 119.1, 118.4, 92.6, 90.5, 88.5, 84.3, 45.6, 30.8, 28.0, 27.0, 22.8, 21.9, 18.8, 17.8, 16.9, -1.5 ppm. MS (ESI, positive ions): *m/z* 557.1649 (calculated for $[M - Br]^+$ 557.1693).

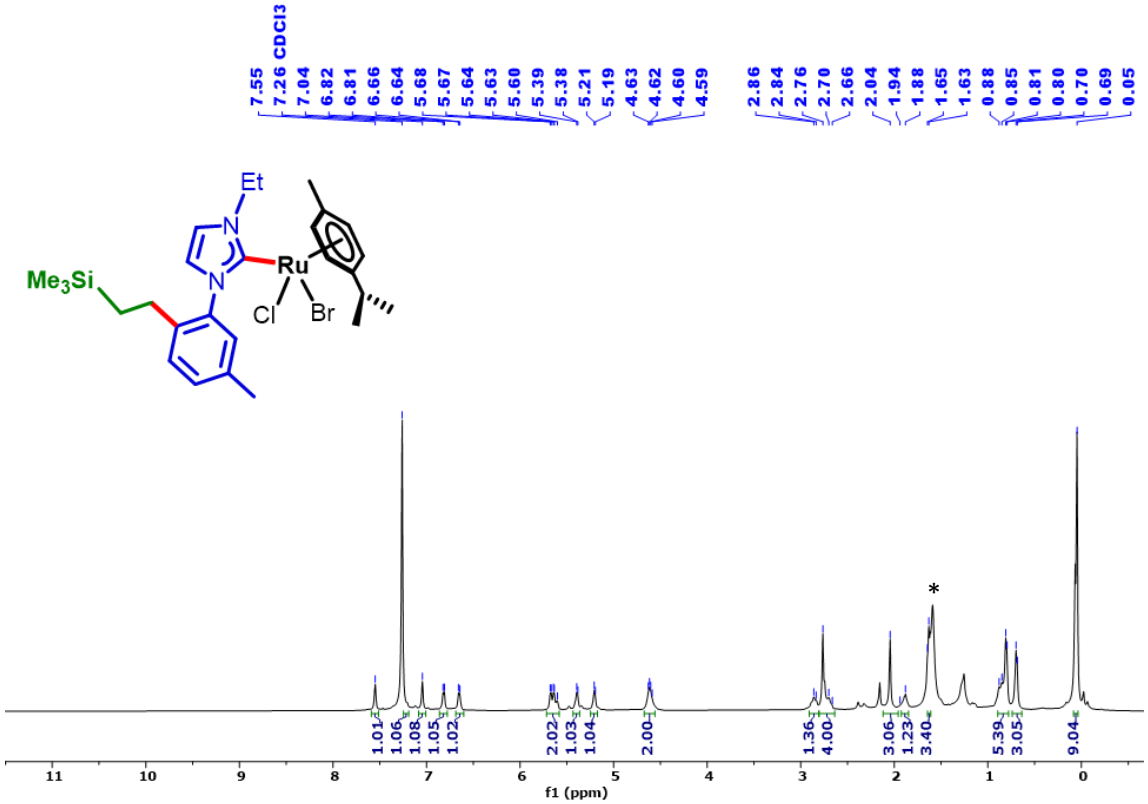


Figure S24. ^{1}H NMR spectrum of **5** in $CDCl_3$. * indicates water in $CDCl_3$.

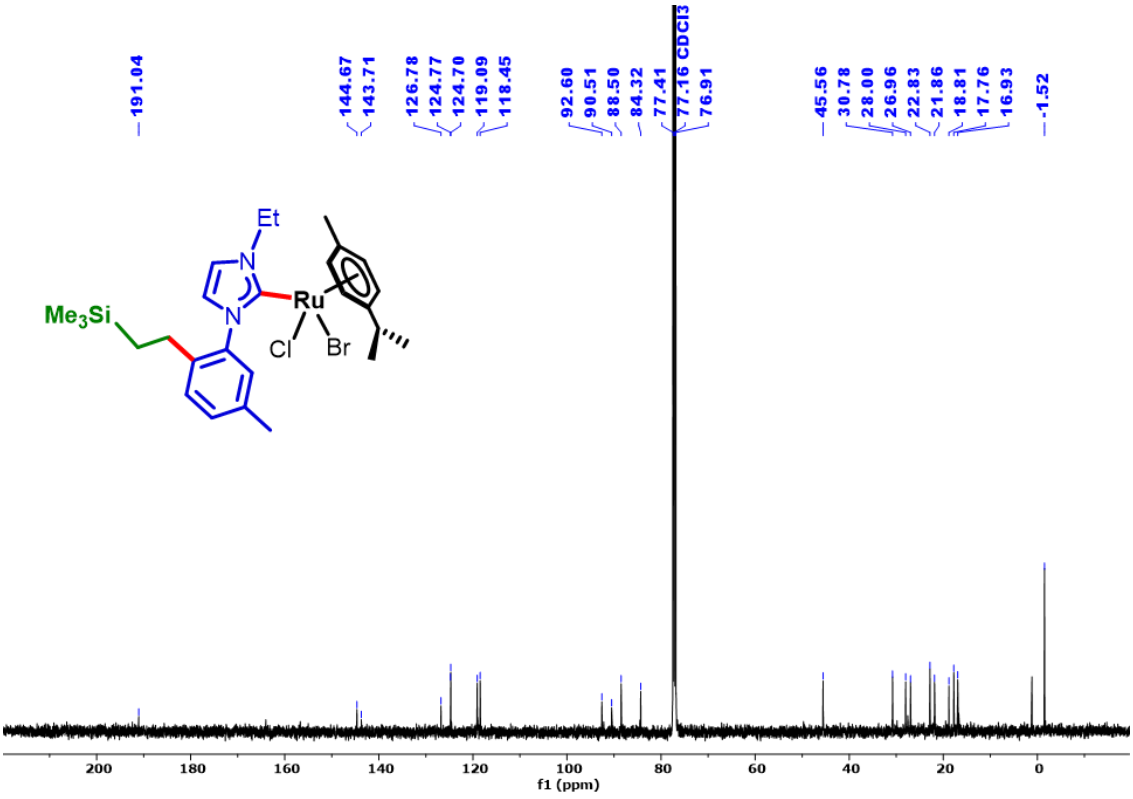


Figure S25. $^{13}C\{^{1}H\}$ NMR of **5** in $CDCl_3$.

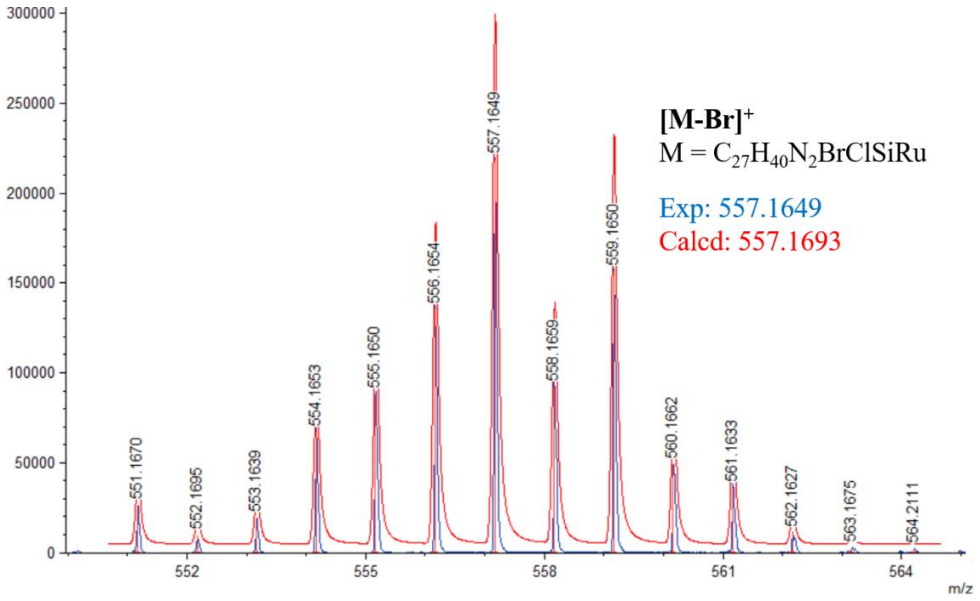
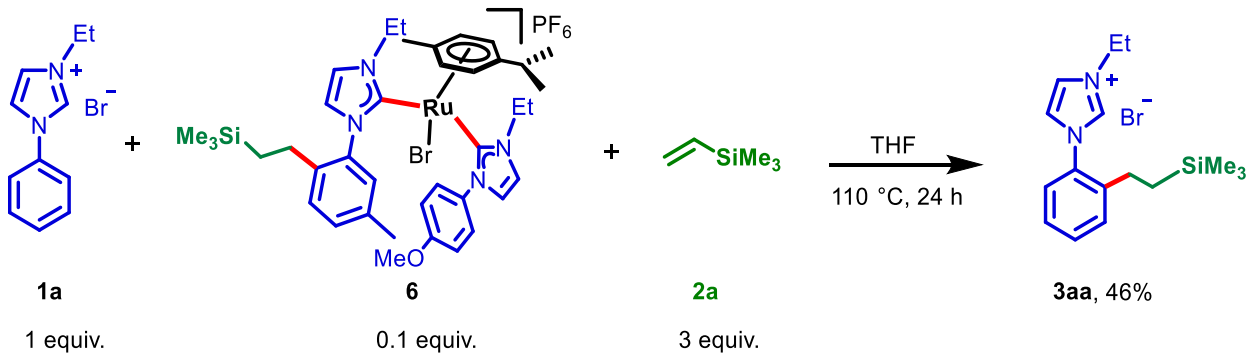


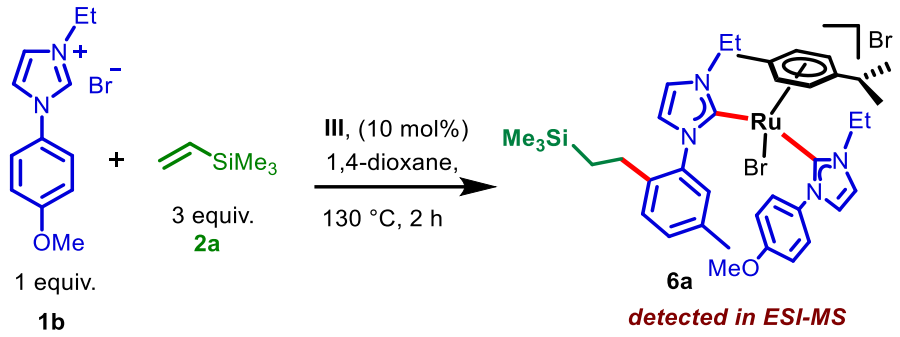
Figure S26. ESI-MS data of complex **5**.

d)



In a pressure tube, imidazolium salt **1a** (30 mg, 0.1183 mmol), alkene **2a** (52 µL, 0.355 mmol, 3 equiv.) and complex **6** (11.0 mg, 0.0118 mmol, 10 mol%) were stirred in THF at 110 °C (oil bath temperature) for 24 h. After completion, the reaction mixture was purified by column chromatography eluting with methanol and DCM (1:10) to provide the desired product **3aa** (19 mg, 0.054 mmol, 46%).

e)



In a pressure tube, imidazolium salt **1b** (56 mg, 0.197 mmol), alkene **2a** (87 µL, 0.591 mmol, 3 equiv.), and complex **III** (10.0 mg, 0.0197 mmol, 10 mol%) were stirred in 1,4-dioxane (1.0 mL) at 130 °C (oil bath temperature) for 2 h. After completion, the reaction mixture was submitted for ESI-MS analysis (Figure S20) and detected the presence of complex **6a**.

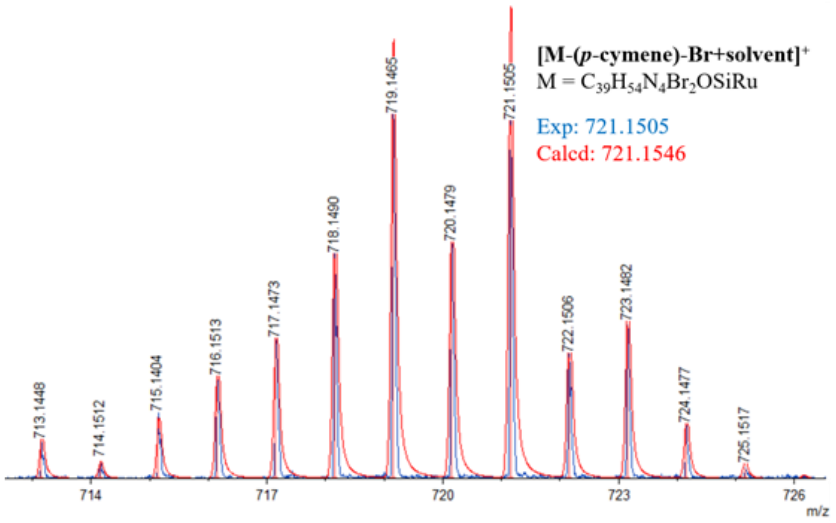
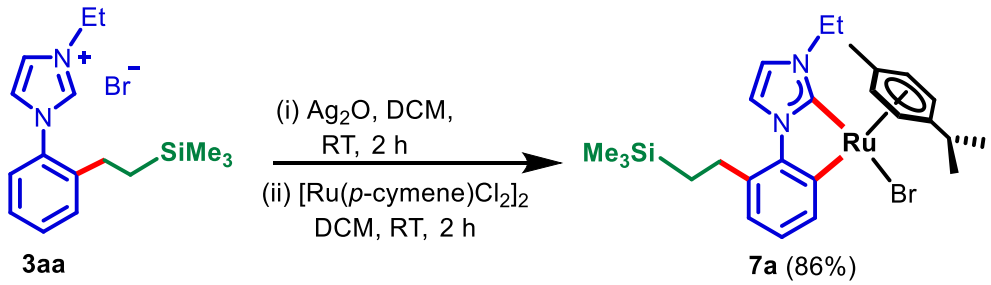
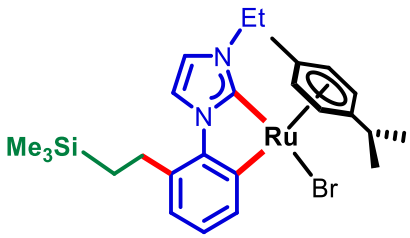


Figure S27. ESI-MS data of complex **6a**.

f)



In a pressure tube, the functionalized imidazolium salt **3aa** (50 mg, 0.142 mmol) and Ag_2O (16 mg, 0.071 mmol, 0.5 equiv.) were stirred in DCM at ambient temperature for 2 h. After that, [Ru(*p*-cymene)Cl_2]$_2$ (22 mg, 0.071 mmol) was added to the reaction mixture and again stirred for 2 h. After completion, the reaction mixture was filtered through an alumina pad to obtain a yellow solution. Concentration followed by the addition of hexane resulted in the precipitation of a solid, which was washed with hexane and dried in vacuum to obtain a bright yellow air stable powder **7a** in 86% yield (73 mg, 0.122 mmol).



7a

Dark red solid. Isolated yield: 73 mg (0.122 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.8 Hz, 1H), 7.57 (s, 1H), 7.05 (s, 1H), 6.84 (t, J = 7.5 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 5.51 (d, J = 6.4 Hz, 2H), 5.43 (d, J = 6.6 Hz, 1H), 5.30 (d, J = 6.3 Hz, 1H), 4.63 – 4.51 (m, 2H), 2.92 – 2.86 (m, 1H), 2.78 – 2.71 (m, 1H), 2.20 – 2.14 (m, 4H), 1.63 (t, J = 7.5 Hz, 3H), 0.89 – 0.87 (m, 5H), 0.74 (d, J = 7.2 Hz, 3H), 0.04 (s, 9H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 189.6, 164.2, 143.7, 140.0, 129.4, 124.6, 124.0, 119.0, 118.3, 104.5, 99.4, 93.5, 90.6, 88.3, 84.2, 45.9, 31.1, 28.3, 23.1, 21.8, 19.7, 17.4, 16.7, -1.5 ppm. MS (ESI, positive ions): *m/z* 589.0983 (calculated for [M + H]$^+$ 589.1011).

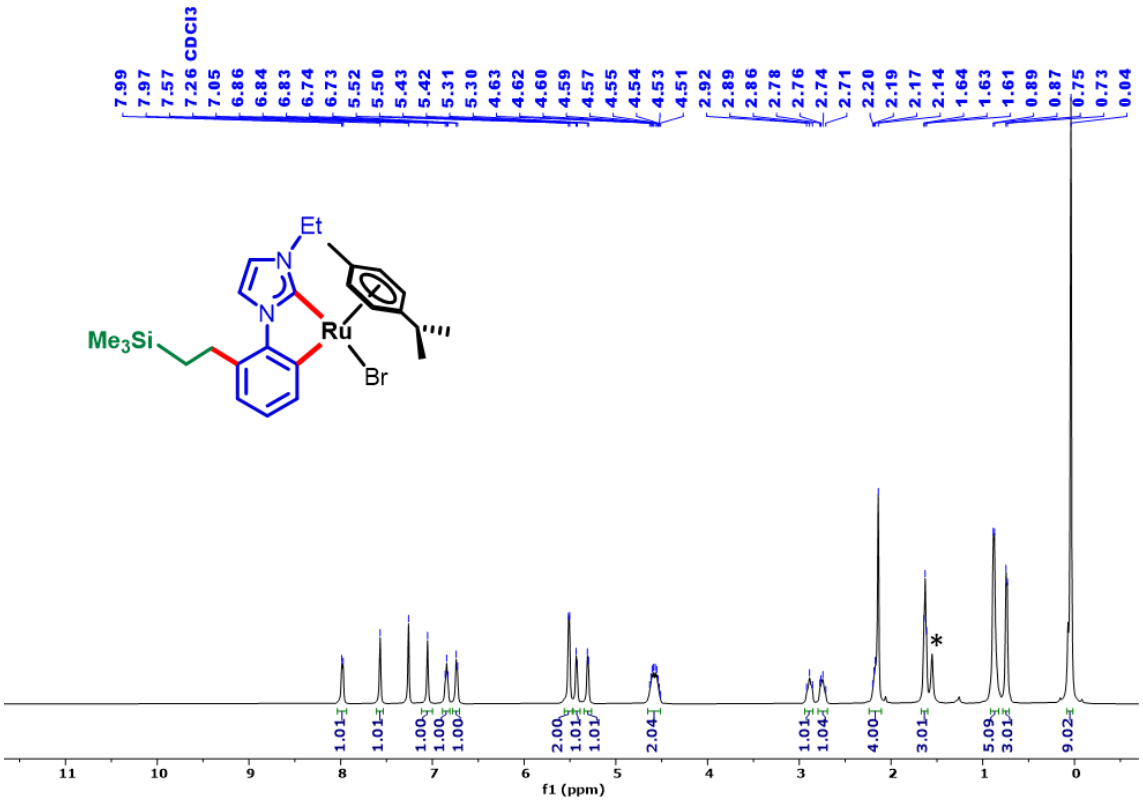


Figure S28. ^{1}H NMR spectrum of **7a** in $CDCl_3$. * indicates water in $CDCl_3$.

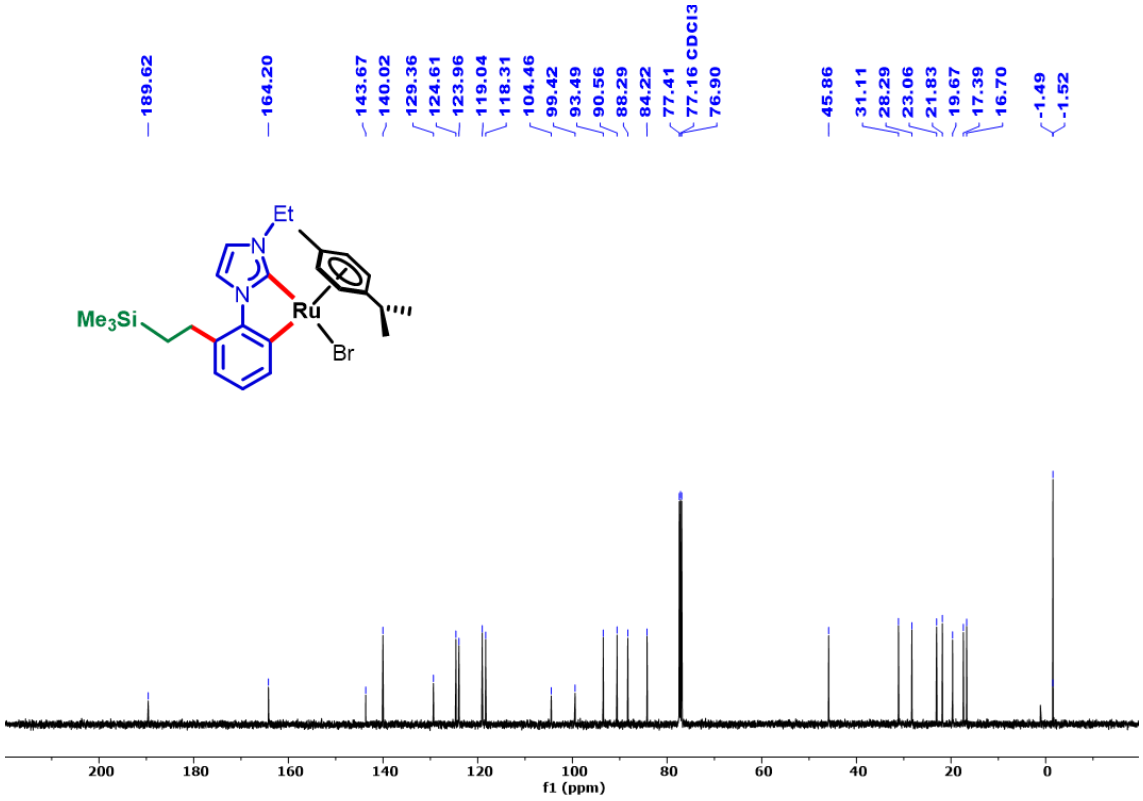


Figure S29. $^{13}C\{^{1}H\}$ NMR of **7a** in $CDCl_3$.

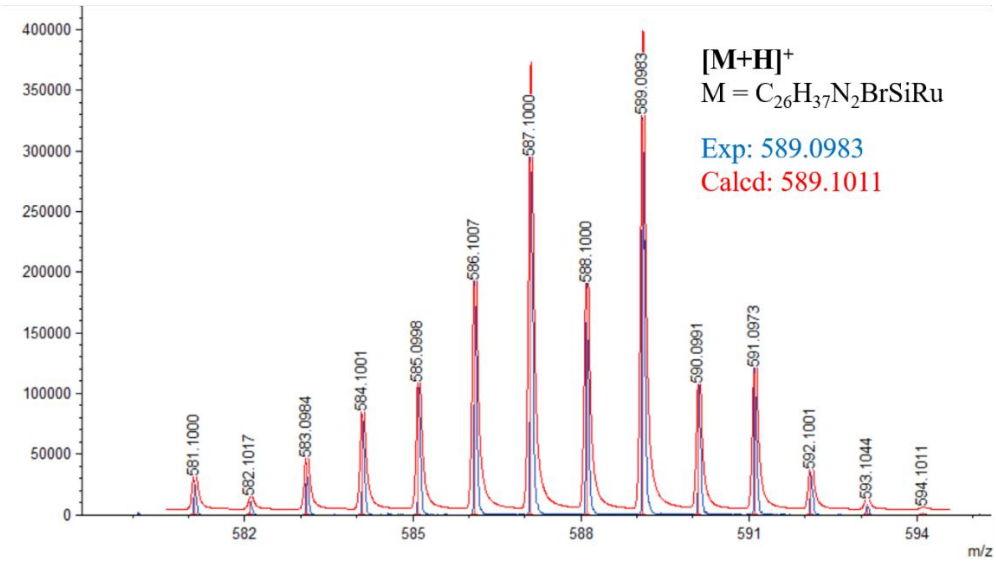
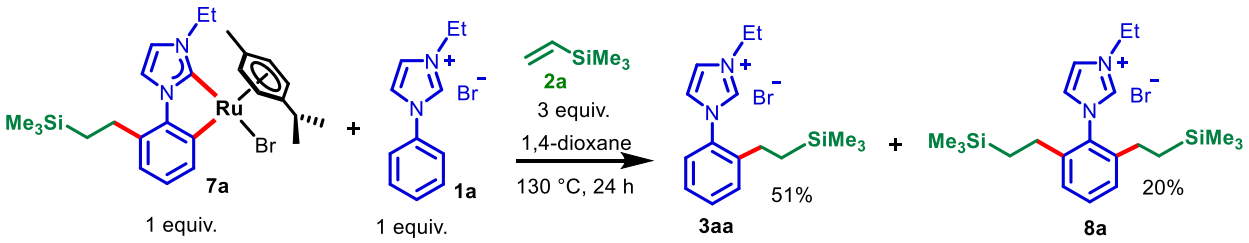


Figure S30. ESI-MS data of complex **7a**.

g)



In a pressure tube, imidazolium salt **1a** (30 mg, 0.118 mmol), alkene **2a** (56 µL, 0.355 mmol, 3 equiv.), and complex **7a** (71 mg, 0.118 mmol) were stirred in 1,4-dioxane at 130 °C (oil bath temperature) for 24 h. After completion, the reaction mixture was purified by column chromatography eluting with methanol and DCM (1:10) to provide the desired product **8a** (11 mg, 0.024 mmol, 20%) along with **3aa** (19 mg, 0.054 mmol, 46%).

Hygroscopic, off-white solid (**8a**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 7.93 (s, 1H), 7.40 (t, J = 7.7 Hz, 1H), 7.22 (s, 1H), 7.21 – 7.18 (m, 2H), 4.82 (q, J = 7.2 Hz, 2H), 2.31 – 2.25 (m, 2H), 2.24 – 2.17 (m, 1H), 1.64 (t, J = 7.3 Hz, 3H), 0.74 (ddd, J = 14.5, 12.7, 5.1 Hz, 2H), 0.61 (ddd, J = 14.5, 12.8, 5.1 Hz, 2H), -0.09 (s, 18H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.1, 138.7, 131.6, 131.4, 127.6, 124.1, 122.3, 45.9, 25.8, 19.0, 16.5, -1.9 ppm. MS (ESI, positive ions): *m/z* 373.2556 (calculated for $[M - Br]^+$ 373.2495).

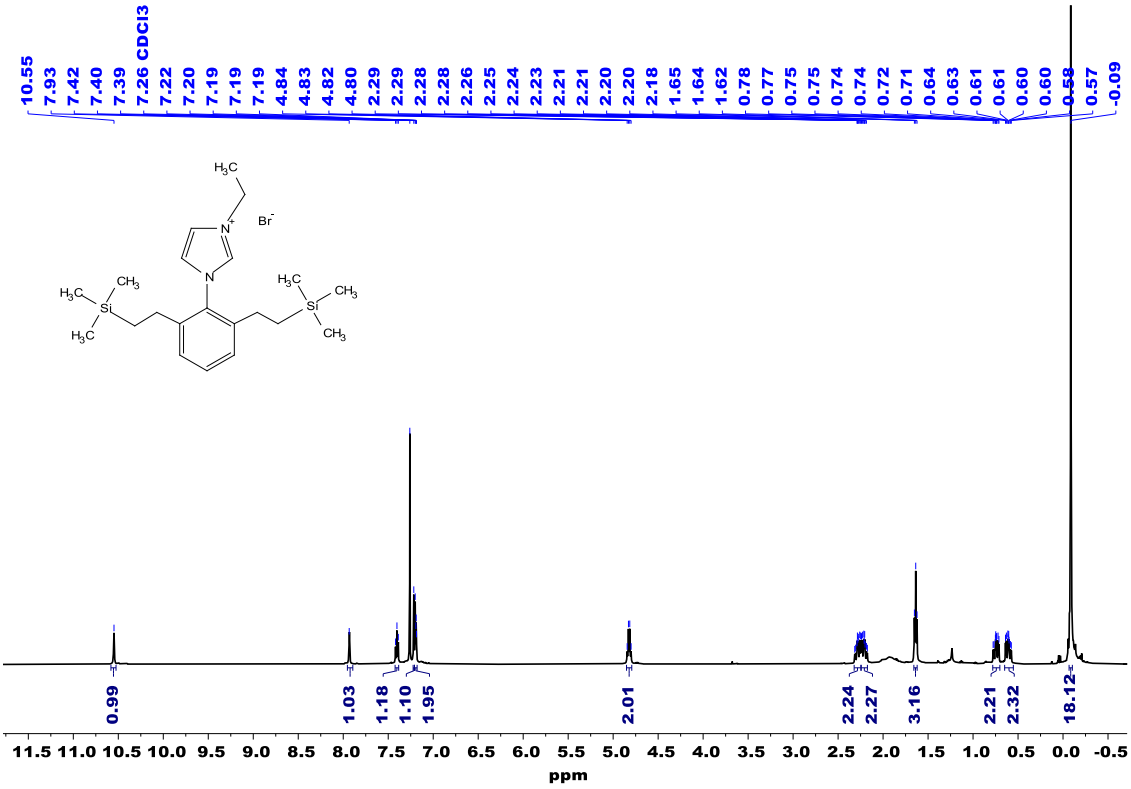


Figure S31. ^{1}H NMR of **8a** in $CDCl_3$.

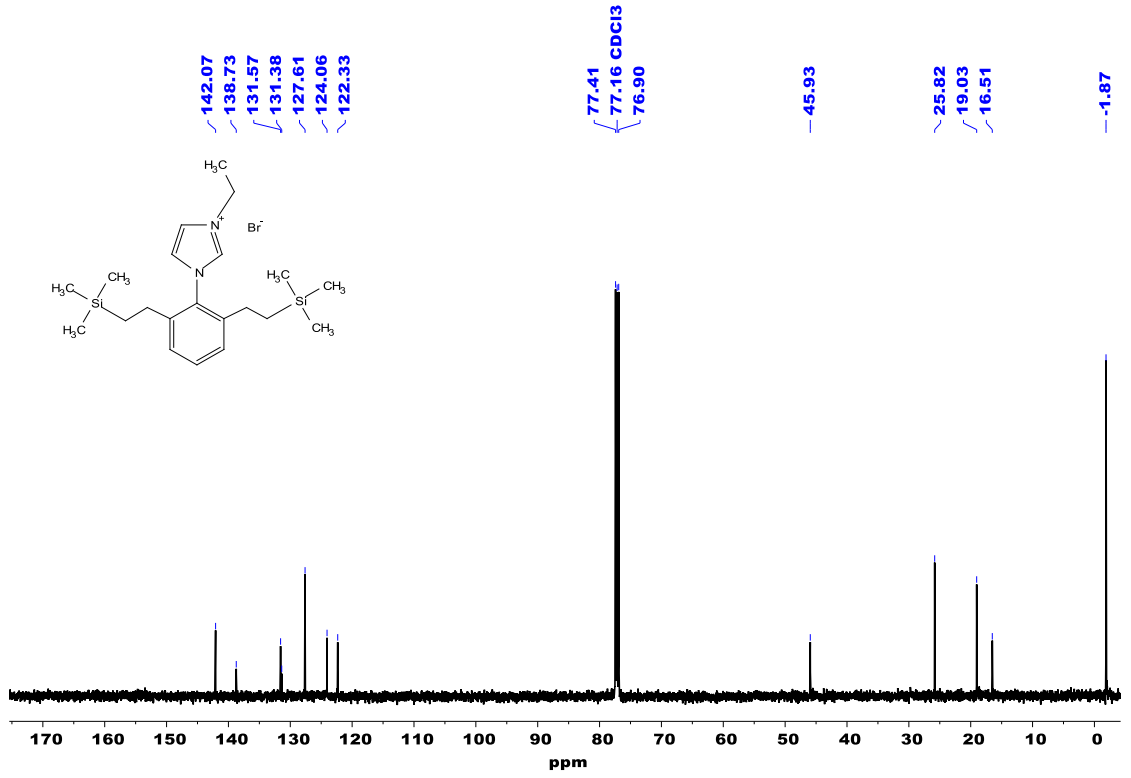
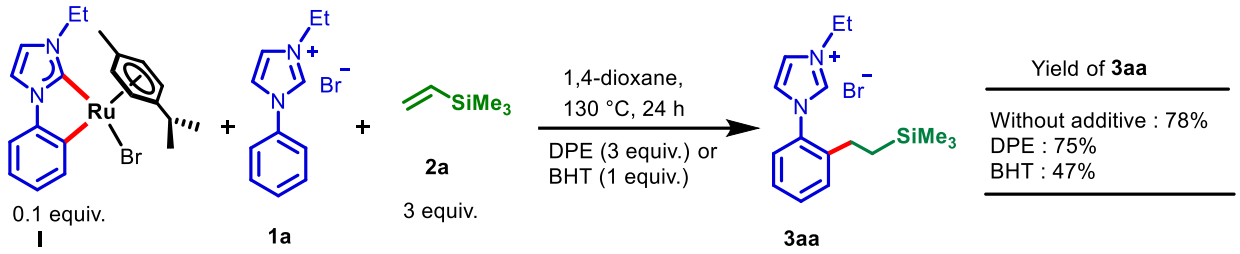


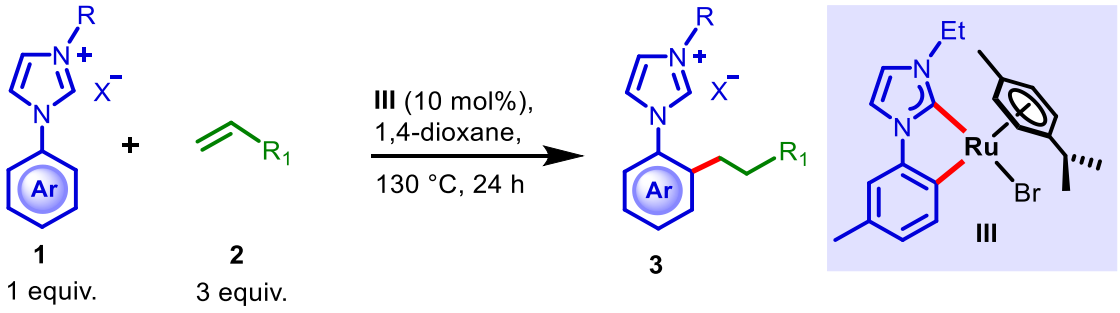
Figure S32. $^{13}C\{^{1}H\}$ NMR of **8a** in $CDCl_3$.

h) Radical scavenger experiments



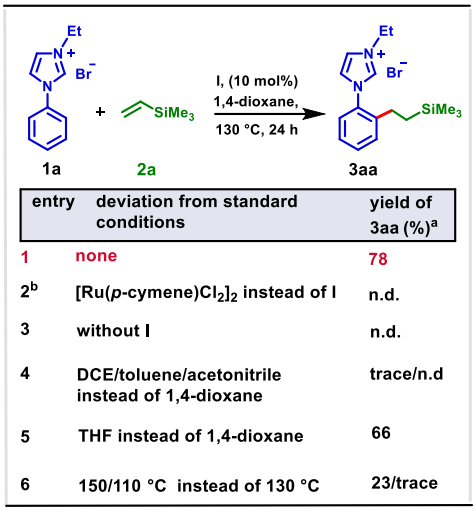
In a pressure tube, imidazolium salt **1a** (50 mg, 0.197 mmol), trimethylvinylsilane **2a** (87 µL, 0.591 mmol, 3 equiv.), complex **I** (10 mg, 0.0197 mmol) and BHT (43 mg, 0.197 mmol) or DPE (106 mg, 0.591 mmol) were stirred in 1,4-dioxane (1 mL) at 130 °C (oil bath temperature) for 24 h. After completion, the reaction mixture was purified by column chromatography eluting with methanol and DCM (1:10) to provide the desired product **3aa**.

8. General procedure for the synthesis of *ortho*-alkylated azolium salts

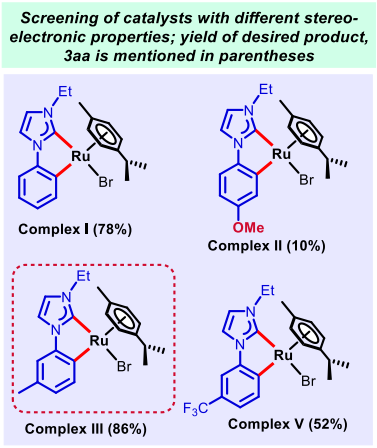


In a pressure tube, imidazolium salt **1** (0.197 mmol), alkene **2** (87 µL, 0.591 mmol, 3 equiv.) and complex **III** (10.0 mg, 0.0197 mmol, 10 mol%) were stirred in 1,4-dioxane at 130 °C (oil bath temperature) for 24 h. After completion, the reaction mixture was purified by column chromatography eluting with methanol and DCM (1:10) to provide the desired product **3**.

9. Table S1. Optimization of reaction conditions



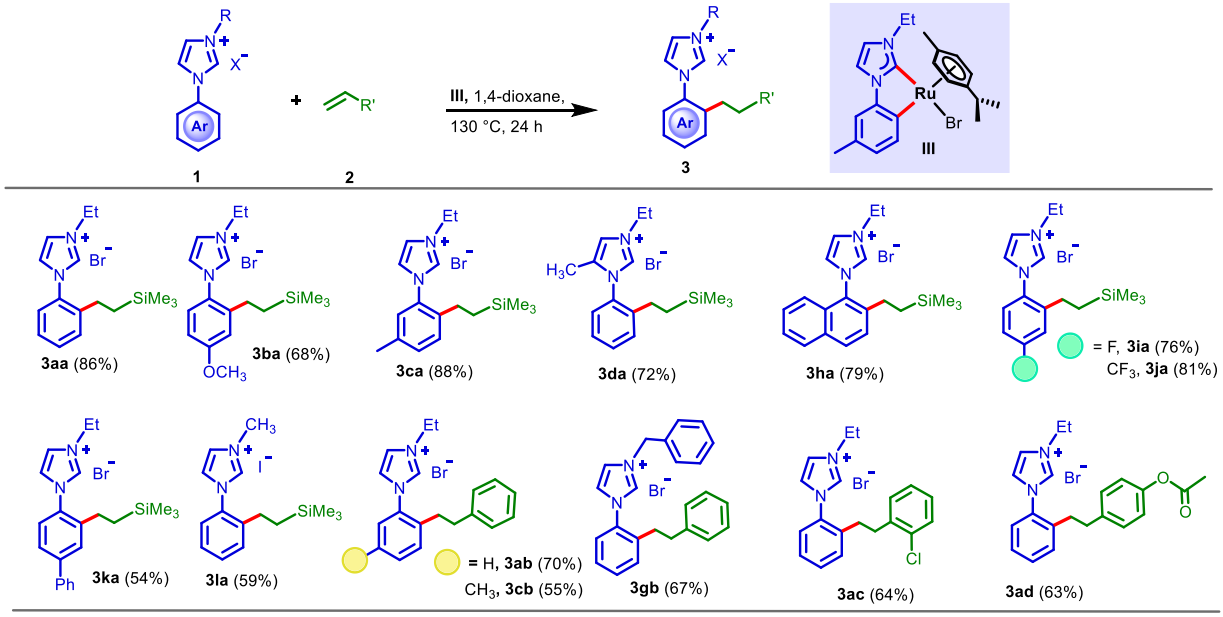
entry	deviation from standard conditions	yield of 3aa (%)[a]
1	none	78
2[b]	$[Ru(p\text{-cymene})Cl_2]_2$ instead of I	n.d.
3	without I	n.d.
4	DCE/toluene/acetonitrile instead of 1,4-dioxane	trace/n.d
5	THF instead of 1,4-dioxane	66
6	150/110 °C instead of 130 °C	23/trace



[a]Reaction conditions: **1a** (0.197 mmol), **2a** (0.591 mmol), and Ru-NHC complex (10 mol%) in 1,4-dioxane at 130 °C for 24 h, all are isolated yields. [b]5 mol% [Ru].

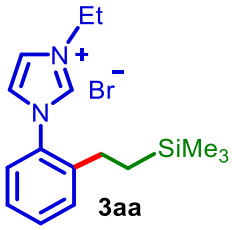
10. Table S2. Substrate scope

We examined the scope and limitation of the present methodology towards various azolium salts and alkenes under the optimized reaction conditions and to our delight, a wide range of substrates are compatible to afford the corresponding products, demonstrating the utility of this methodology.



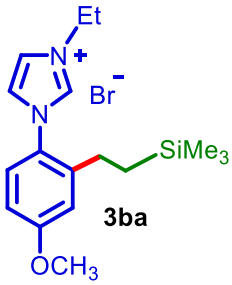
[a]Reaction conditions: **1** (0.197 mmol), **2** (0.591 mmol), and complex **III** (10 mol%), in 1,4-dioxane at 130 °C for 24 h, all are isolated yields. Molecular structure of the compound **3la** at 50% probability level, counterion and hydrogen atoms are omitted for clarity.

11. Analytical data of the isolated products



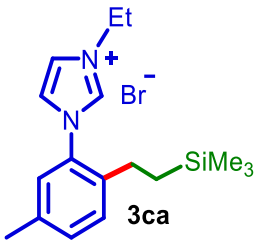
3aa

Hygroscopic off-white solid. Isolated yield: 60 mg (0.169 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.88 (s, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.33 (d, J = 10.4 Hz, 2H), 4.73 (q, J = 7.8 Hz, 2H), 2.45 – 2.42 (m, 2H), 1.63 (t, J = 7.2 Hz, 3H), 0.69 – 0.64 (m, 2H), -0.08 (s, 9H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.6, 137.6, 132.9, 131.5, 130.5, 127.7, 126.9, 123.6, 122.4, 45.9, 25.5, 18.6, 16.1, -1.9 ppm. MS (ESI, positive ions): *m/z* 273.1790 (calculated for $[M - Br]^+$ 273.1787).



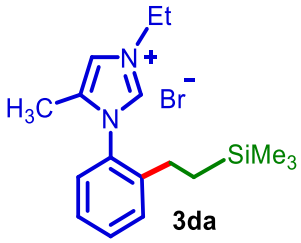
3ba

Hygroscopic off-white solid. Isolated yield: 51 mg (0.134 mmol, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.78 (s, 1H), 7.36 (d, J = 8.7 Hz, 1H), 6.87 (s, 1H), 6.82 (d, J = 8.7 Hz, 1H), 4.72 (q, J = 7.3 Hz, 2H), 3.83 (s, 3H), 2.42 – 2.32 (m, 2H), 1.64 (t, J = 7.3 Hz, 3H), 0.68 – 0.64 (m, 2H), -0.07 (s, 9H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.5, 142.2, 137.9, 128.2, 125.8, 123.9, 122.0, 115.6, 112.5, 55.8, 45.8, 25.8, 18.5, 16.1, -1.8 ppm. MS (ESI, positive ions): *m/z* 303.1892 (calculated for $[M - Br]^+$ 303.1893).



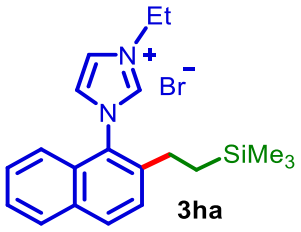
3ca

Hygroscopic off-white solid. Isolated yield: 64 mg (0.173 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.88 (s, 1H), 7.33 – 7.32 (m, 4H), 4.82 (q, J = 7.9 Hz, 2H), 2.46 – 2.41 (m, 5H), 1.70 (t, J = 7.9, 6.4 Hz, 3H), 0.72, – 0.68 (m, 2H), -0.02 (s, 9H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.9, 137.6, 137.4, 132.7, 132.3, 130.3, 127.2, 123.6, 122.2, 45.9, 25.1, 20.8, 18.7, 16.2, -1.8 ppm. MS (ESI, positive ions): *m/z* 291.1857 (calculated for $[M - Br]^+$ 291.1861).



3da

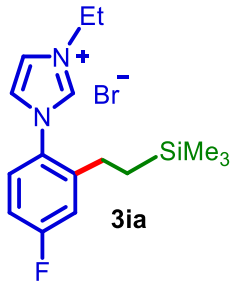
Hygroscopic off-white solid. Isolated yield: 52 mg (0.142 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.47 – 7.45 (m, 2H), 7.39 (dd, J = 7.7, 1.6 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.03 (s, 1H), 4.68 (q, J = 7.3 Hz, 2H), 2.47 – 2.44 (m, 5H), 1.61 (t, J = 7.3 Hz, 3H), 0.71 – 0.67 (m, 2H), -0.06 (s, 9H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.5, 137.9, 133.1, 131.4, 131.0, 130.5, 127.8, 127.0, 120.4, 43.2, 25.6, 18.8, 16.1, 9.3, -1.9 ppm. MS (ESI, positive ions): *m/z* 287.1938 (calculated for $[M - Br]^+$ 287.1943).



3ha

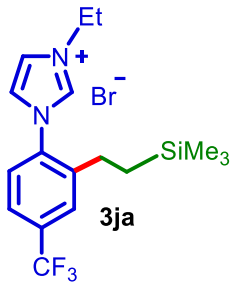
Hygroscopic off-white solid. Isolated yield: 63 mg (0.155 mmol, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 8.05 (s, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.92 – 7.89 (m, 1H), 7.54 – 7.51 (m, 2H), 7.47 (dd, J = 8.6, 1.9 Hz, 1H), 7.29 (s, 1H), 7.09 – 7.06 (m, 1H), 4.99 – 4.78 (m, 2H), 2.43 (dt, J = 12.1, 5.5 Hz, 2H), 1.67 (t, J = 7.3 Hz, 3H), 0.87 – 0.84 (m, 1H), 0.72 – 0.63 (m, 1H),

-0.05 (s, J = 2.6 Hz, 9H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 140.8, 138.8, 132.5, 131.8, 129.4, 129.0, 128.5, 127.4, 127.0, 127.0, 124.6, 122.9, 120.7, 46.1, 26.2, 19.6, 16.4, -1.9 ppm. MS (ESI, positive ions): *m/z* 323.1951 (calculated for $[M - Br]^+$ 323.1944).



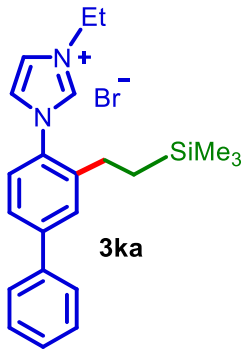
3ia

Hygroscopic off-white solid. Isolated yield: 56 mg (0.149 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.96 (d, J = 1.8 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.34 (s, 1H), 7.07 (dd, J = 9.7, 2.5 Hz, 1H), 7.01 – 6.97 (m, 1H), 4.67 (q, J = 7.9 Hz, 2H), 2.41 – 2.37 (m, 2H), 1.61 (t, J = 7.9 Hz, 3H), 0.68 – 0.63 (m, 2H), -0.10 (d, J = 1.2 Hz, 9H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 164.8, 162.8, 143.7, 143.7, 137.7, 129.2, 129.1, 129.0, 123.8, 122.8, 117.1, 116.9, 114.7, 114.6, 45.8, 25.6, 18.1, 16.0, -1.9 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.15 ppm. MS (ESI, positive ions): *m/z* 291.1697 (calculated for $[M - Br]^+$ 291.1693).



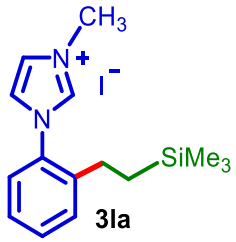
3ja

Hygroscopic off-white solid. Isolated yield: 67 mg (0.159 mmol, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 7.93 – 7.86 (m, 1H), 7.75 (7, J = 8.2 Hz, 1H), 7.68 (t, J = 2.7 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.41 – 7.38 (m, 1H), 4.74 – 4.68 (m, 2H), 2.55 – 2.51 (m, 2H), 1.66 (td, J = 6.7, 2.4 Hz, 3H), 0.74 – 0.70 (m, 2H), -0.05 (d, J = 3.1 Hz, 9H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 142.0, 138.1, 138.0, 135.8, 128.1, 127.6, 127.6, 127.5, 127.5, 124.8, 124.8, 124.8, 123.4, 123.3, 122.8, 122.7, 46.1, 25.8, 18.4, 15.9, -1.9 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.03 ppm. MS (ESI, positive ions): *m/z* 341.1658 (calculated for $[M - Br]^+$ 341.1661).



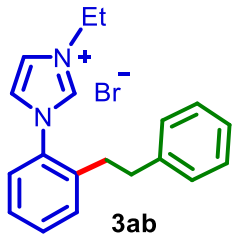
3ka

Hygroscopic off-white solid. Isolated yield: 65 mg (0.152 mmol, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.54 (s, 1H), 8.09 (s, 1H), 7.61 (d, J = 9.8 Hz, 3H), 7.55 – 7.44 (m, 7H), 7.35 (d, J = 3.2 Hz, 1H), 4.81 (q, J = 7.4 Hz, 2H), 2.58 – 2.54 (m, 2H), 1.72 (t, J = 7.3 Hz, 3H), 0.80 – 0.75 (m, 2H), 0.00 (s, 9H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.4, 140.8, 139.4, 137.5, 132.0, 129.1, 129.1, 129.0, 128.3, 127.2, 127.2, 126.2, 123.6, 122.7, 45.8, 25.7, 18.6, 16.1, -1.9 ppm. MS (ESI, positive ions): *m/z* 349.2099 (calculated for $[M - Br]^+$ 349.2100).



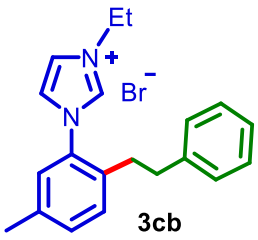
3la

Hygroscopic off-white solid. Isolated yield: 45 mg (0.116 mmol, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.71 (s, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 7.9 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 7.30 (s, 1H), 4.33 (s, 3H), 2.48 – 2.43 (m, 2H), 0.73 – 0.68 (m, 2H), -0.04 (s, 9H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.6, 137.7, 132.8, 131.7, 130.5, 127.8, 127.1, 124.1, 123.5, 38.1, 25.5, 18.8, -1.8 ppm. MS (ESI, positive ions): *m/z* 259.1627 (calculated for $[M - Br]^+$ 259.1631).



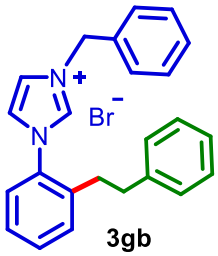
3ab

Hygroscopic off-white solid. Isolated yield: 49.26 mg (0.138 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.72 (s, 1H), 7.53 (t, J = 7.0 Hz, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.18 (d, J = 2.8 Hz, 3H), 6.82 (d, J = 6.4 Hz, 2H), 6.73 (s, 1H), 4.54 (q, J = 7.5 Hz, 2H), 2.84 (t, J = 7.1 Hz, 2H), 2.76 (t, J = 7.0 Hz, 2H), 1.57 (t, J = 7.2 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.3, 137.0, 136.8, 133.7, 131.5, 131.1, 128.8, 128.7, 128.1, 127.0, 126.6, 123.4, 122.2, 45.8, 37.3, 32.7, 15.7 ppm. MS (ESI, positive ions): *m/z* 277.1697 (calculated for $[M - Br]^+$ 277.1705).



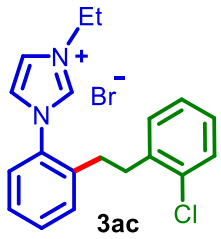
3cb

Hygroscopic off-white solid. Isolated yield: 40 mg (0.108 mmol, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.72 (s, 1H), 7.36 (s, 2H), 7.22 – 7.20 (m, 3H), 7.15 (s, 1H), 6.86 – 6.84 (m, 2H), 6.70 (s, 1H), 4.59 (q, J = 7.4 Hz, 2H), 2.85 (t, J = 7.0 Hz, 2H), 2.73 (t, J = 7.0 Hz, 2H), 2.38 (s, 3H), 1.60 (t, J = 7.1 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.5, 138.4, 136.7, 133.7, 133.4, 132.4, 130.9, 128.8, 128.7, 127.2, 126.5, 123.4, 122.1, 45.8, 37.3, 32.3, 20.8, 15.8 ppm. MS (ESI, positive ions): *m/z* 291.1857 (calculated for $[M - Br]^+$ 291.1861).



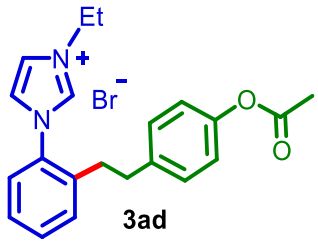
3gb

Hygroscopic off-white solid. Isolated yield: 55 mg (0.132 mmol, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.56 – 7.54 (m, 3H), 7.49 (d, J = 7.5 Hz, 1H), 7.42 – 7.41 (m, 3H), 7.38 – 7.37 (m, 2H), 7.16 – 7.11 (m, 4H), 6.80 (dd, J = 7.9, 1.6 Hz, 2H), 6.53 (t, J = 1.8 Hz, 1H), 5.80 (s, 2H), 2.86 – 2.80 (m, 4H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.3, 138.1, 137.1, 133.8, 133.2, 131.6, 131.3, 129.7, 129.6, 129.4, 128.7, 128.2, 127.0, 126.6, 123.2, 121.6, 54.0, 37.3, 32.8 ppm. MS (ESI, positive ions): *m/z* 339.1860 (calculated for $[M - Br]^+$ 339.1861).



3ac

Hygroscopic off-white solid. Isolated yield: 49 mg (0.126 mmol, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.63 (s, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.37 (t, J = 7.5 Hz, 1H), 7.18 – 7.08 (m, 3H), 6.93 – 6.88 (m, 2H), 4.63 (q, J = 7.4 Hz, 2H), 2.93 (t, J = 7.1 Hz, 2H), 2.82 (t, J = 7.5 Hz, 2H), 1.63 (t, J = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.6, 137.6, 136.8, 133.8, 133.7, 131.6, 131.3, 131.1, 129.6, 128.4, 127.3, 127.2, 123.5, 122.0, 45.9, 35.4, 30.6, 15.7 ppm. MS (ESI, positive ions): *m/z* 449.1538 (calculated for $[M - Br]^+$ 449.1551).



3ad

Hygroscopic off-white solid. Isolated yield: 51 mg (0.124 mmol, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 7.74 (s, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.9 Hz, 1H), 6.81 – 6.78 (m, 2H), 6.73 – 6.70 (m, 3H), 4.48 (q, J = 7.3 Hz, 2H), 2.83 – 2.80 (m, 2H), 2.76 – 2.73 (m, 2H), 2.24 (s, 3H), 1.52 (t, J = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.5, 149.1, 138.0, 137.0, 135.9, 133.8, 131.4, 131.2, 129.8, 128.0, 126.6, 123.9, 122.5, 121.8, 45.5, 36.8, 32.6, 21.1, 15.9 ppm. MS (ESI, positive ions): *m/z* 335.1752 (calculated for $[M - Br]^+$ 335.1760).

12. NMR spectra of the isolated products

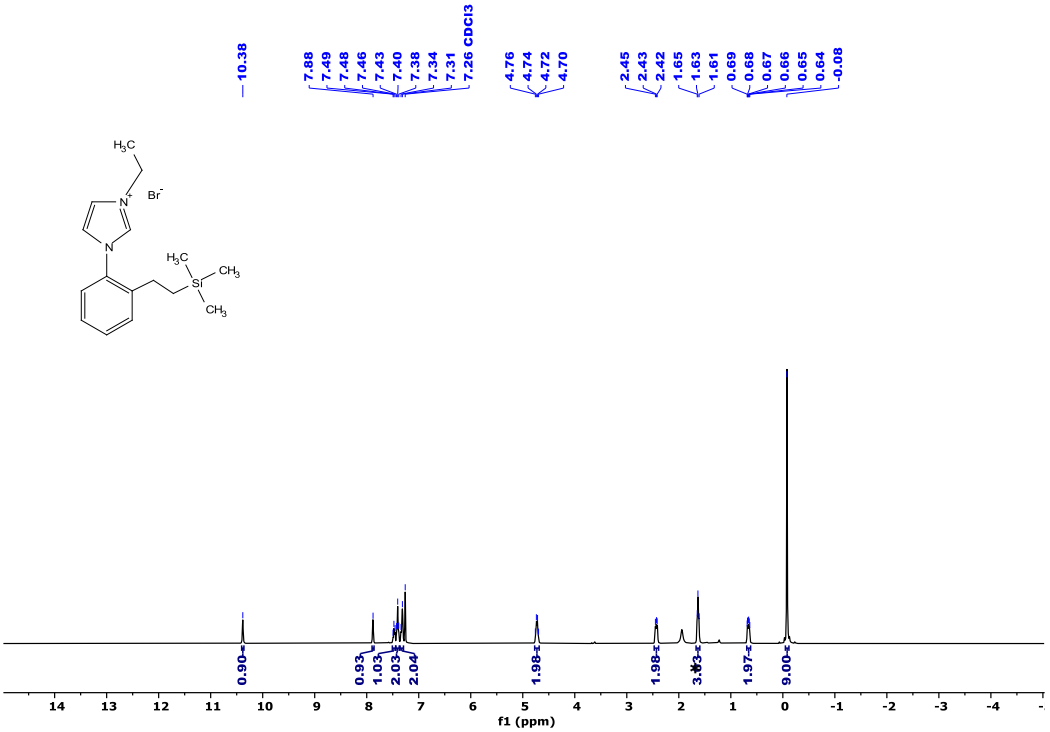


Figure S33. ^{1}H NMR of **3aa** in $CDCl_3$. * indicates H_2O in $CDCl_3$.

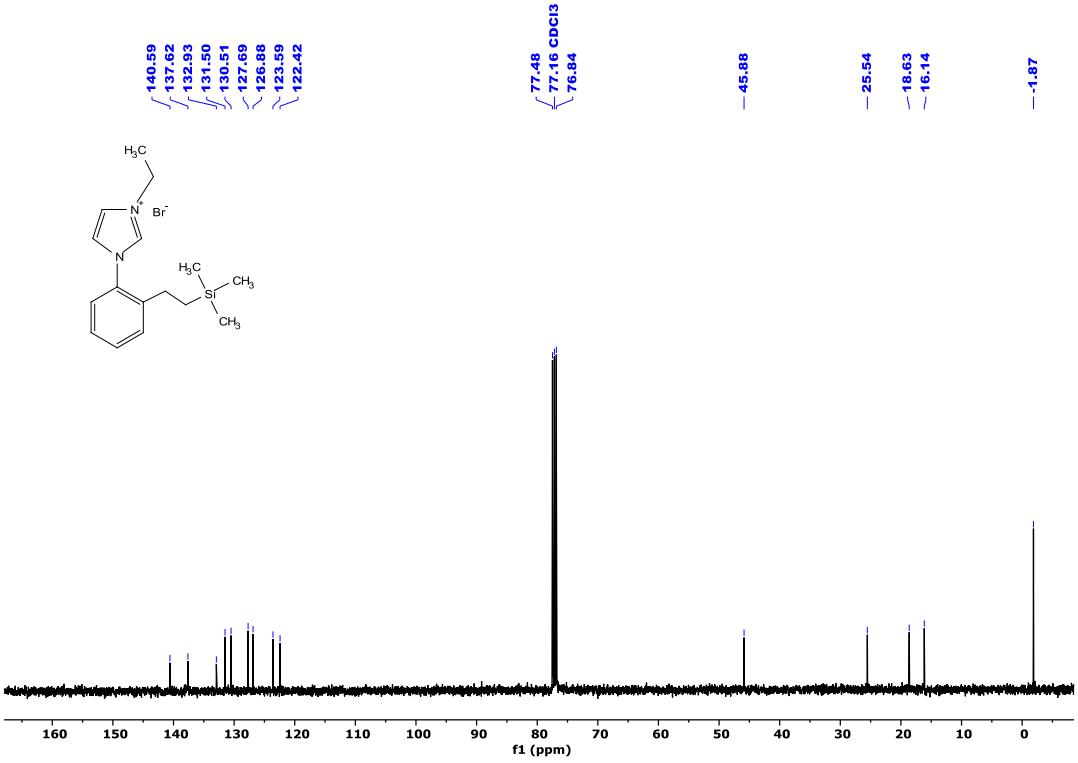


Figure S34. $^{13}C\{^{1}H\}$ NMR of **3aa** in $CDCl_3$.

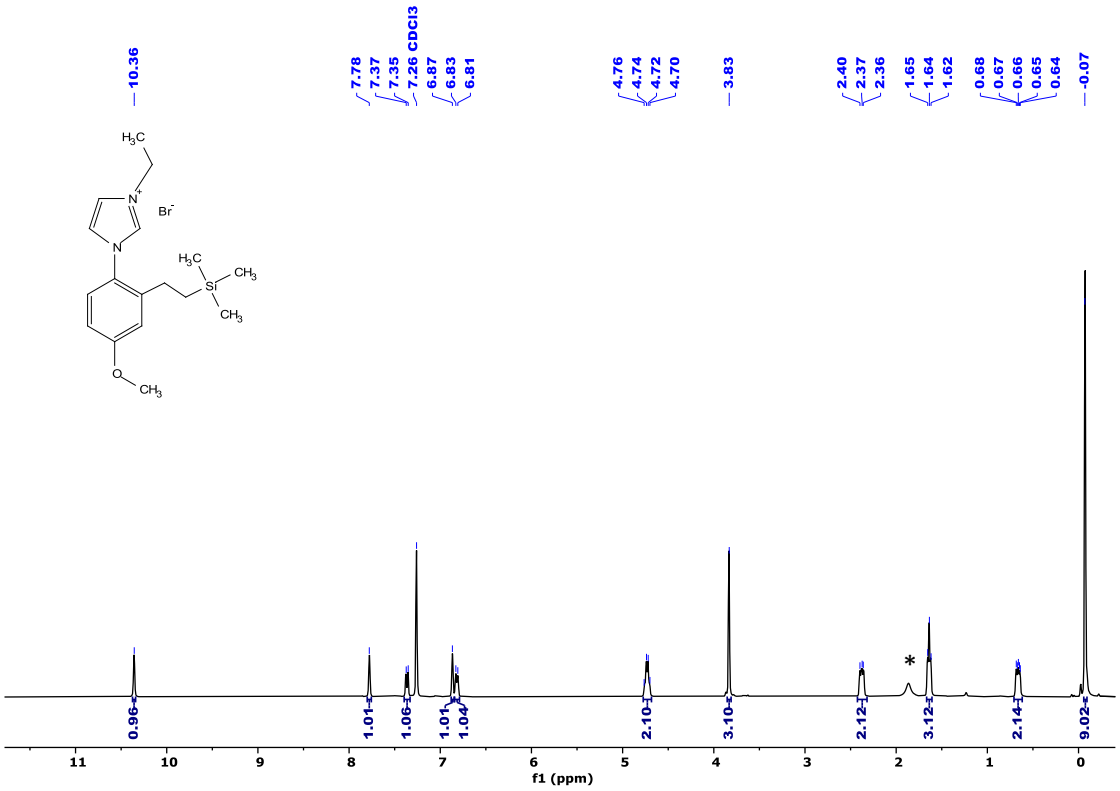


Figure S35. ^{1}H NMR of **3ba** in $CDCl_3$. * indicates H_2O in $CDCl_3$.

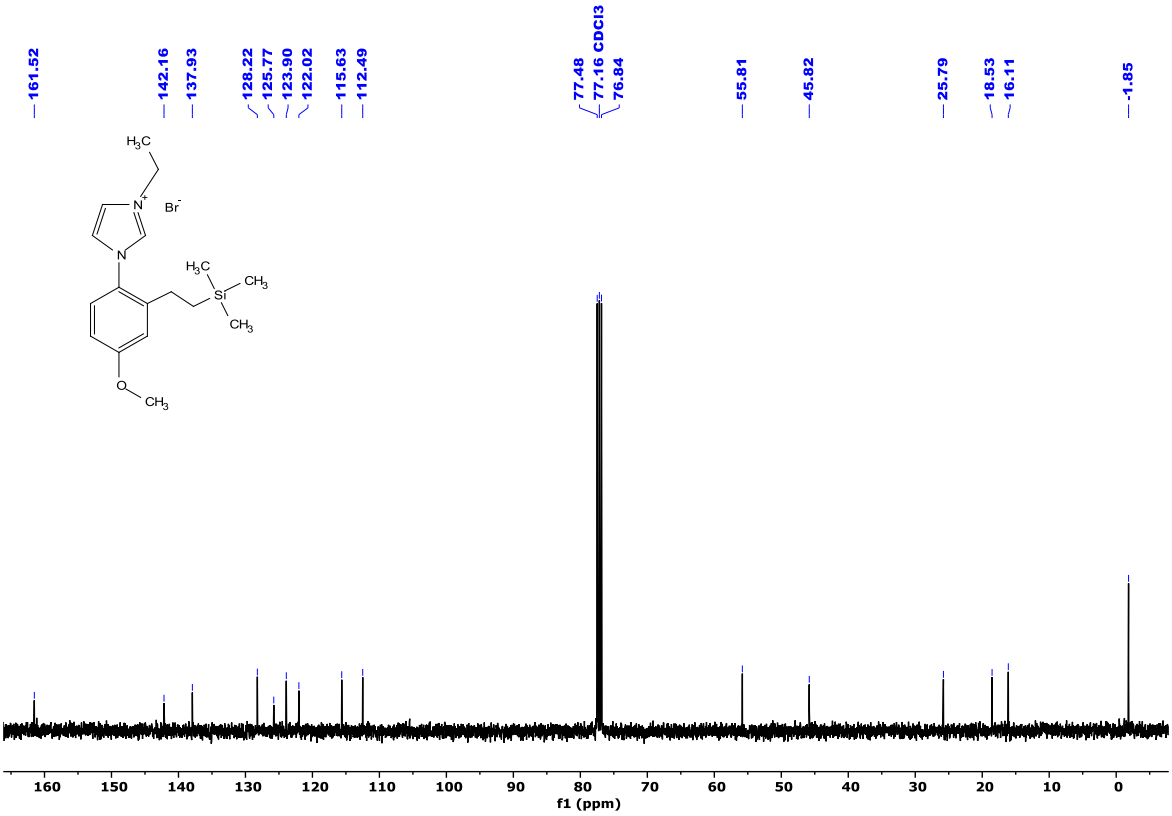


Figure S36. $^{13}C\{^{1}H\}$ NMR of **3ba** in $CDCl_3$.

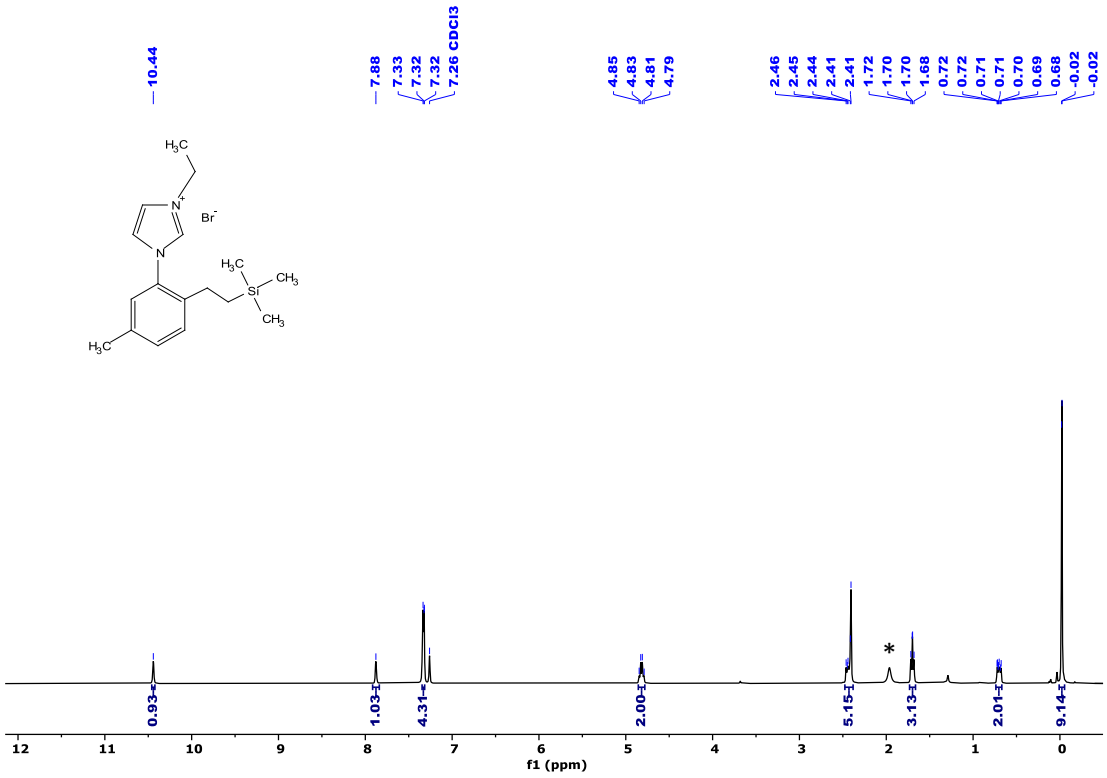


Figure S37. ^{1}H NMR of **3ca** in $CDCl_3$. * indicates H_2O in $CDCl_3$.

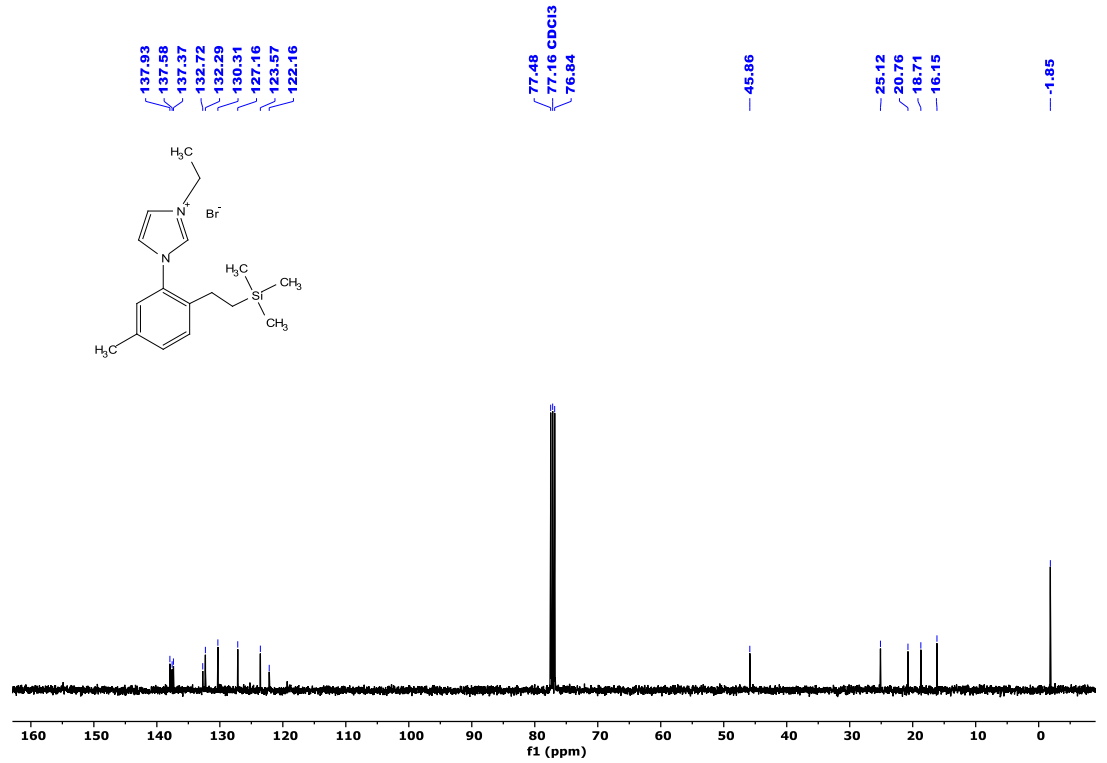


Figure S38. $^{13}C\{^{1}H\}$ NMR of **3ca** in $CDCl_3$.

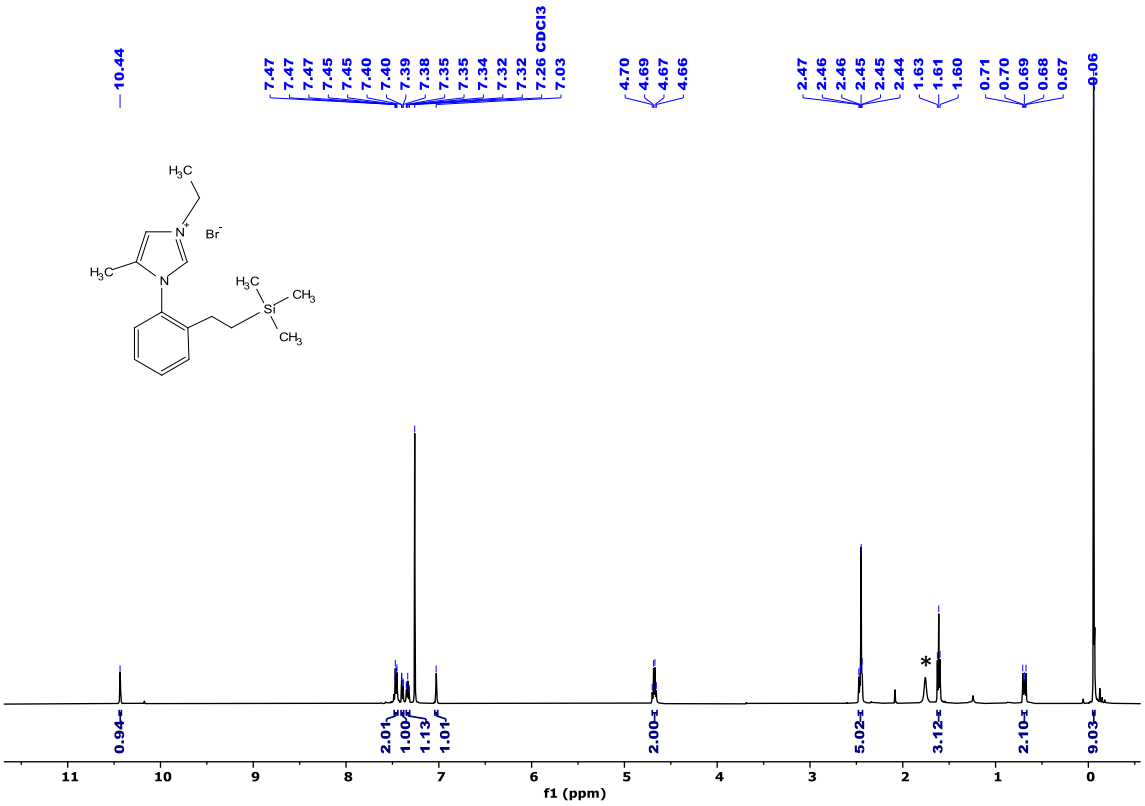


Figure S39. ^{1}H NMR of **3da** in $CDCl_3$. * indicates H_2O in $CDCl_3$.

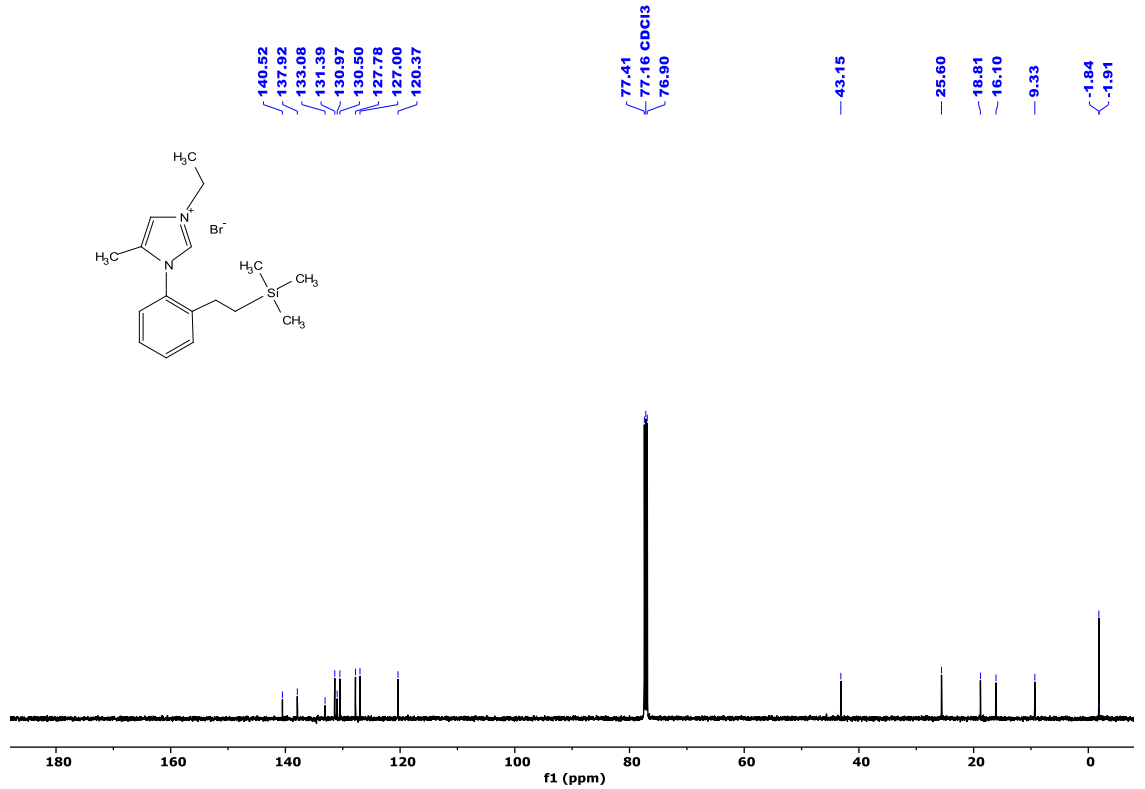


Figure S40. $^{13}C\{^{1}H\}$ NMR of **3da** in $CDCl_3$.

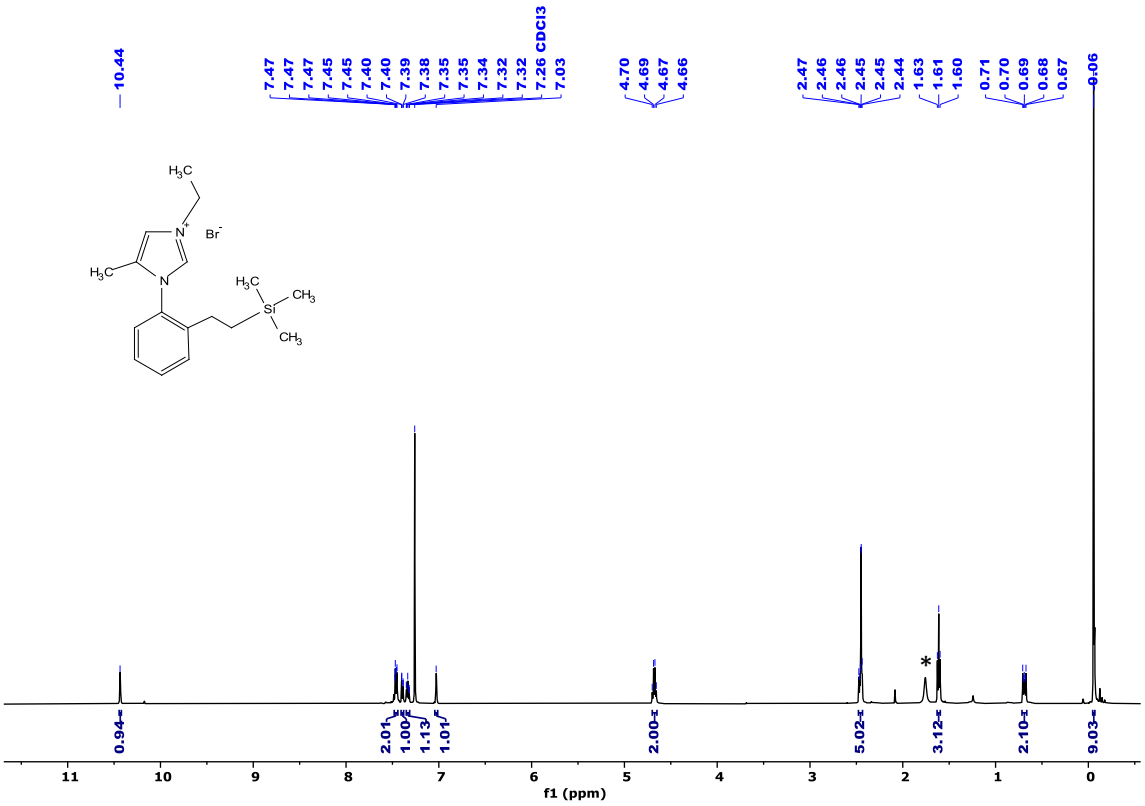


Figure S41. ^{1}H NMR of **3da** in $CDCl_3$. * indicates H_2O in $CDCl_3$.

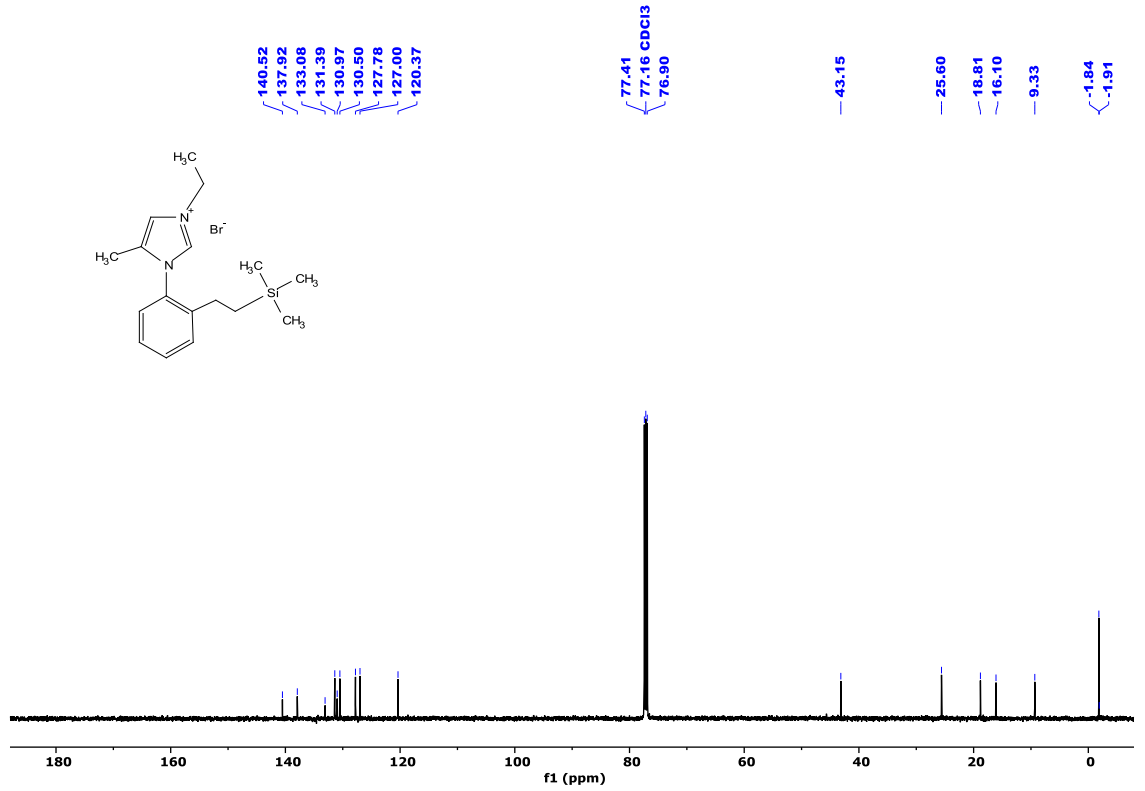


Figure S42. $^{13}C\{^{1}H\}$ NMR of **3da** in $CDCl_3$.

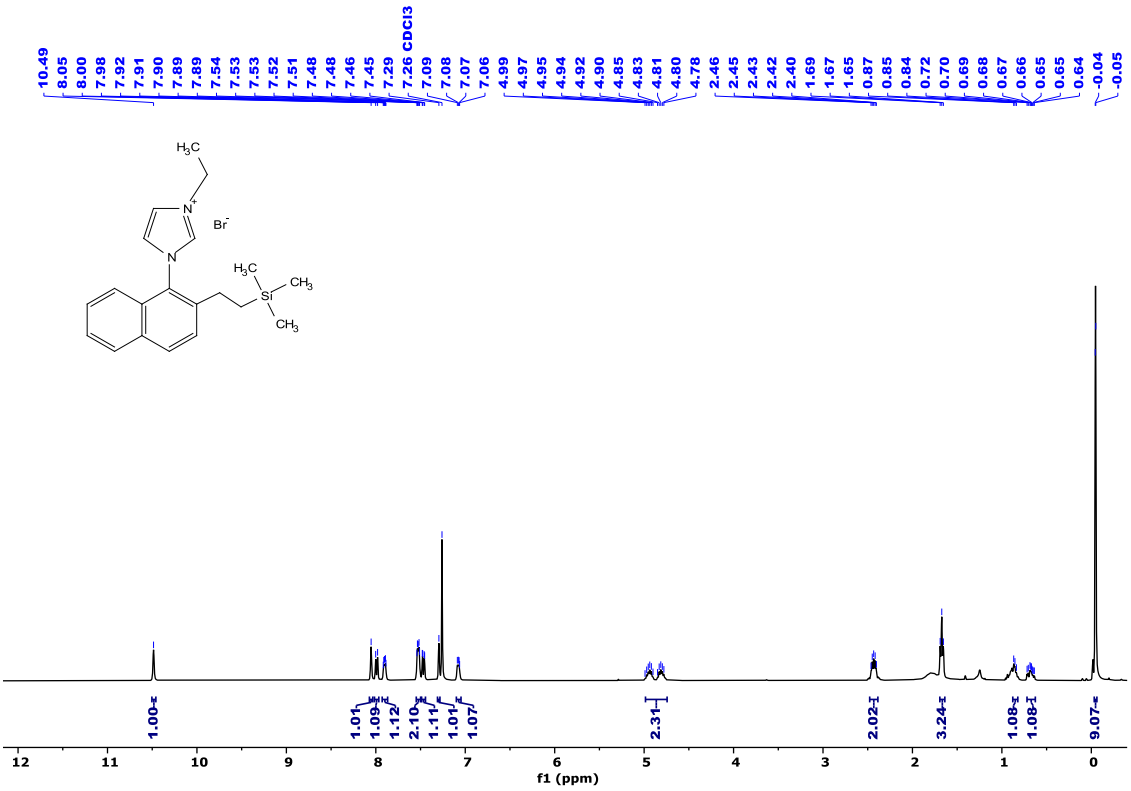


Figure S43. ^{1}H NMR of **3ha** in $CDCl_3$.

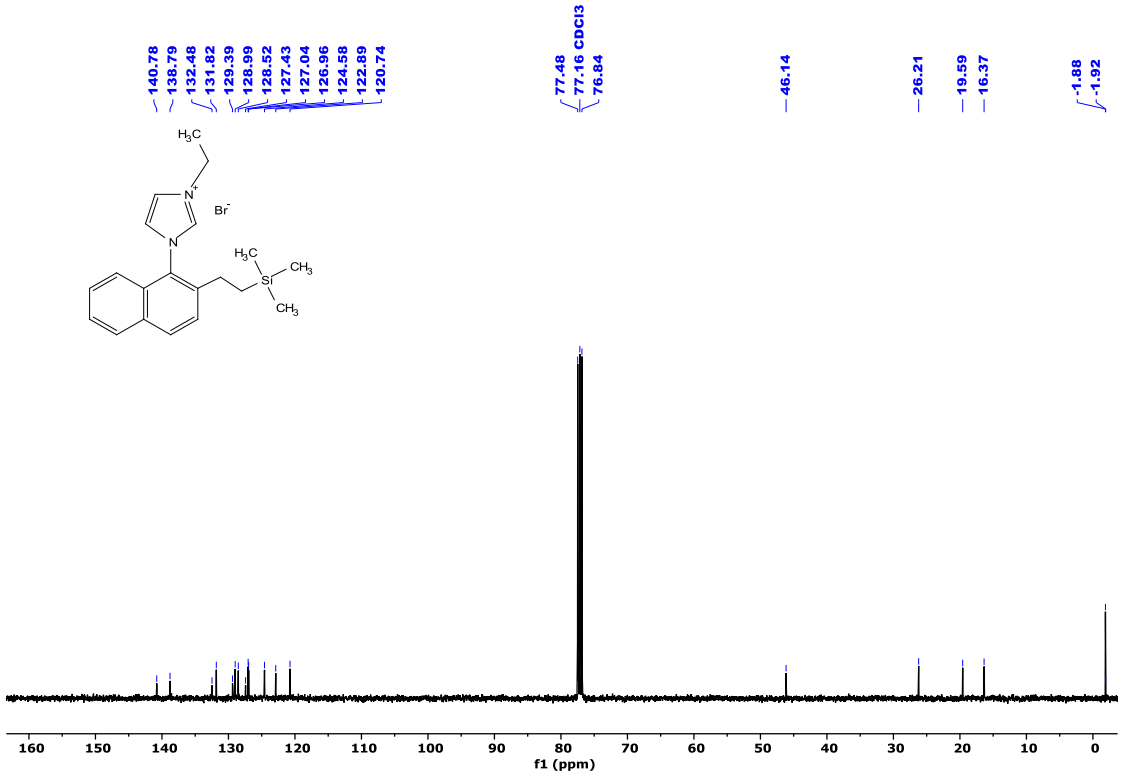


Figure S44. $^{13}C\{^{1}H\}$ NMR of **3ha** in $CDCl_3$.

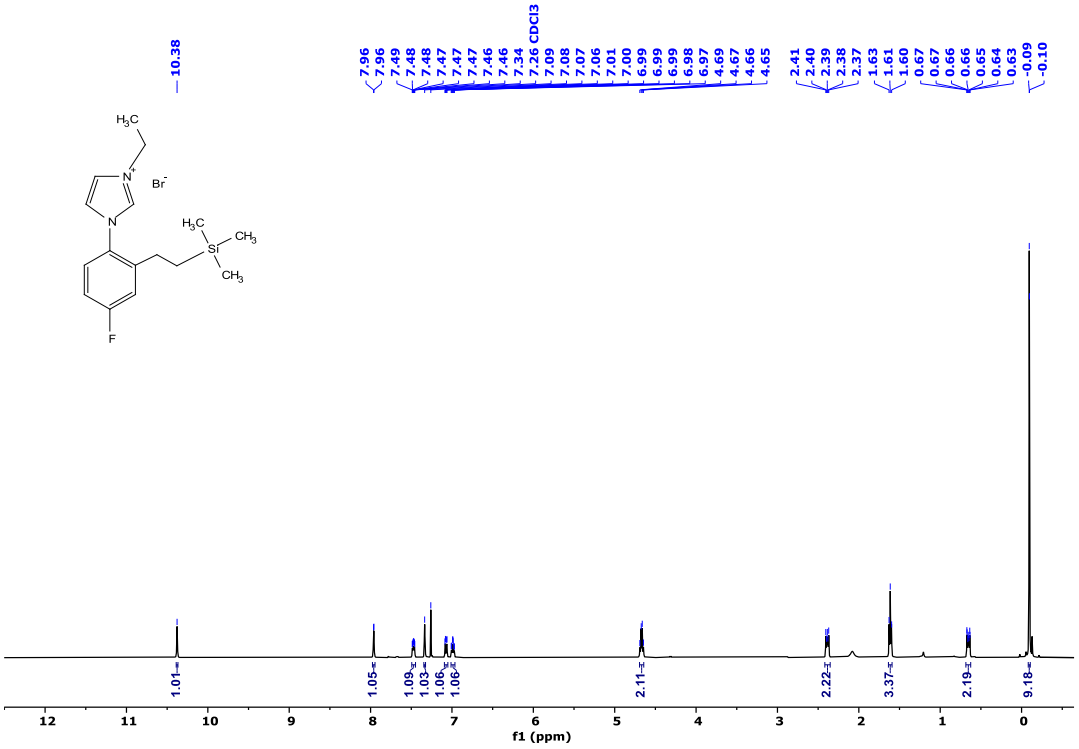


Figure S45. ^{1}H NMR of **3ia** in $CDCl_3$.

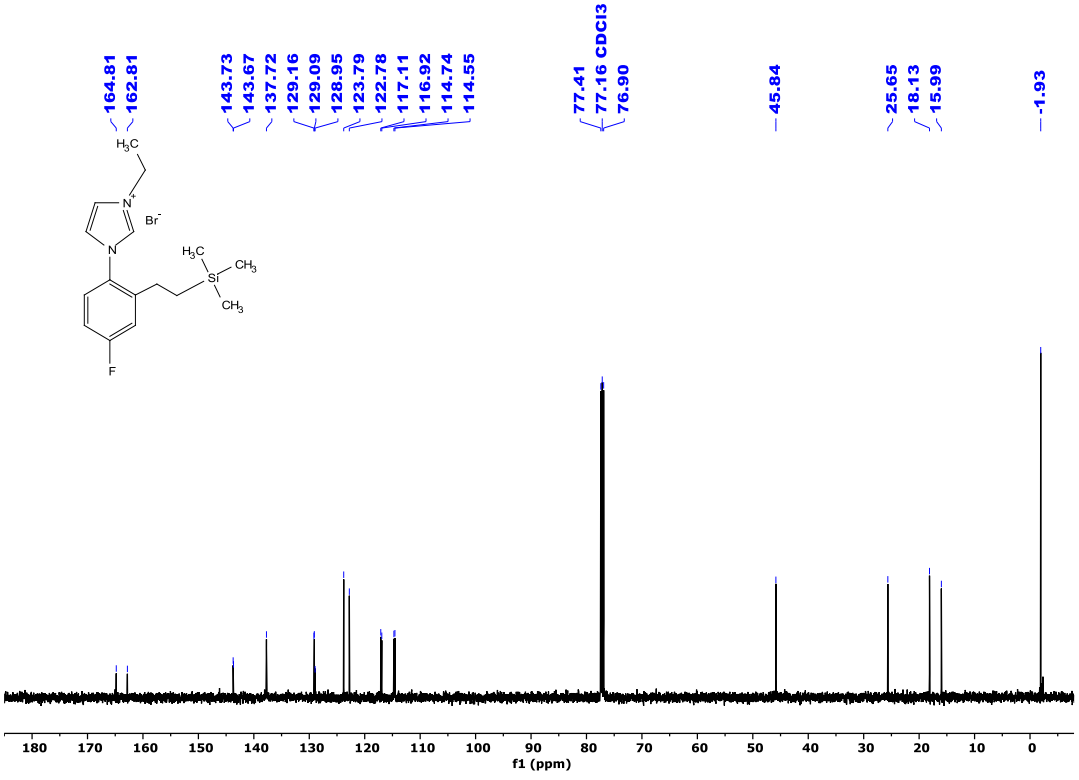


Figure S46. $^{13}C\{^{1}H\}$ NMR of **3ia** in $CDCl_3$.

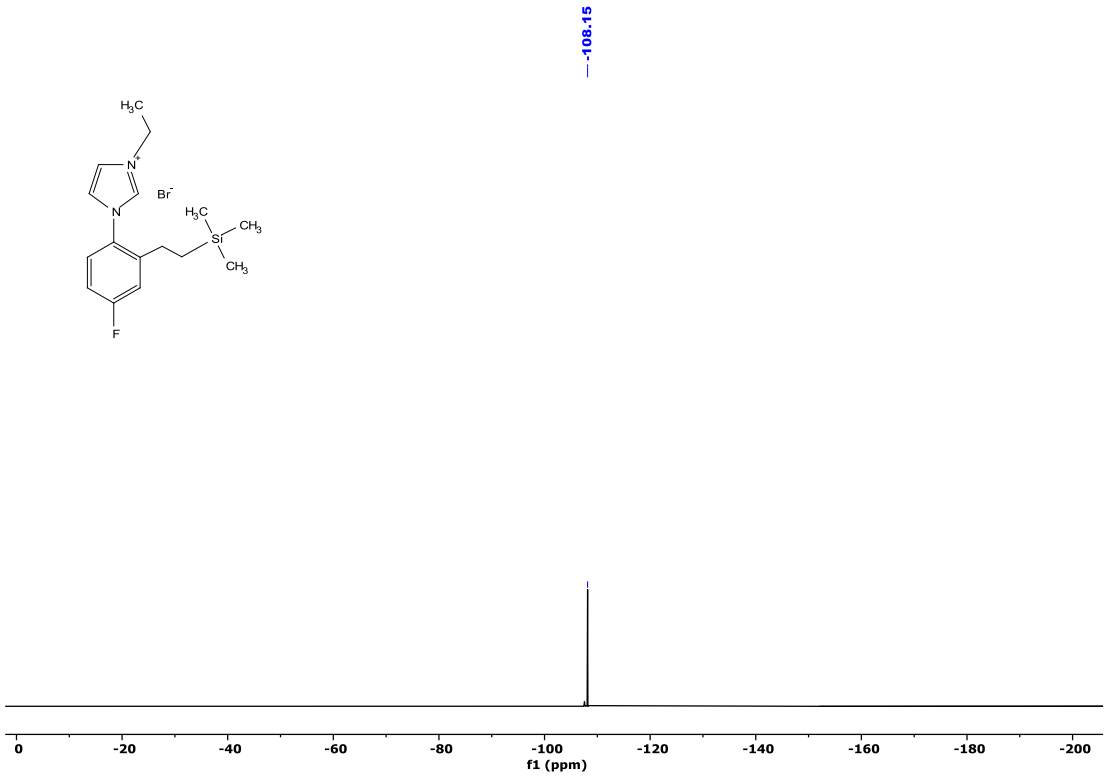


Figure S47. ^{19}F NMR of **3ia** in $CDCl_3$.

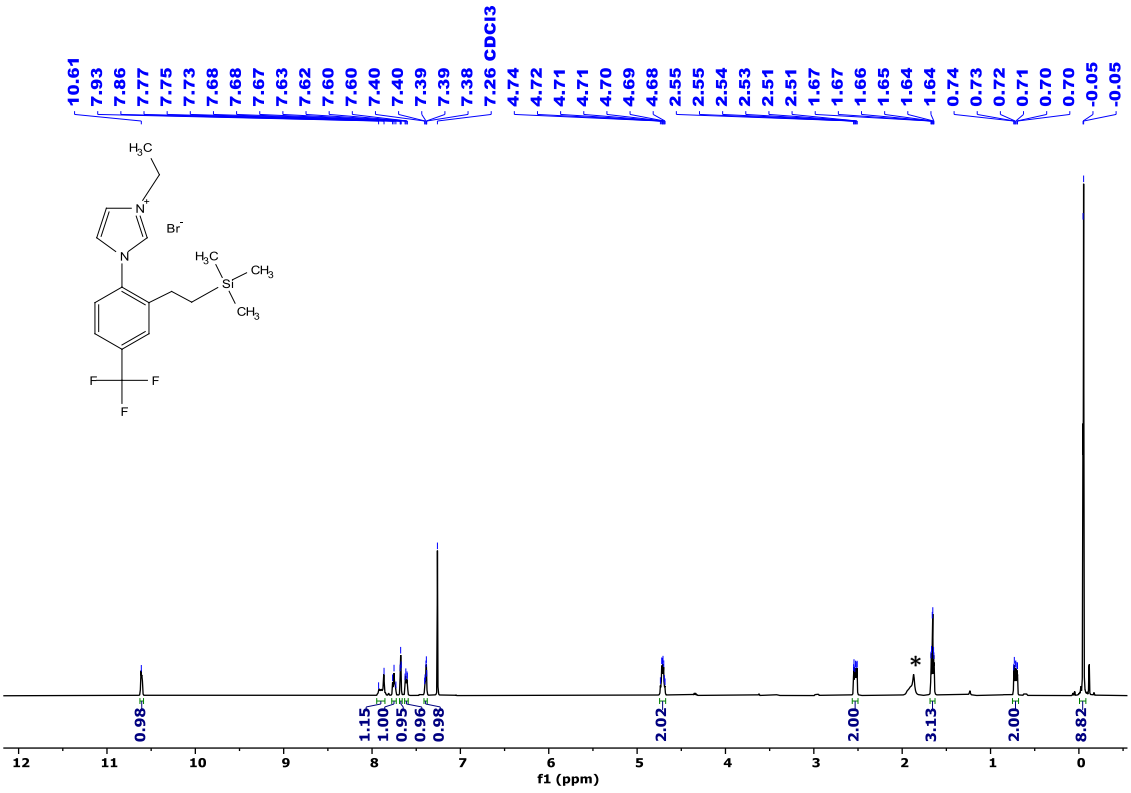


Figure S48. ^{1}H NMR of **3ja** in $CDCl_3$. * indicates H_2O in $CDCl_3$.

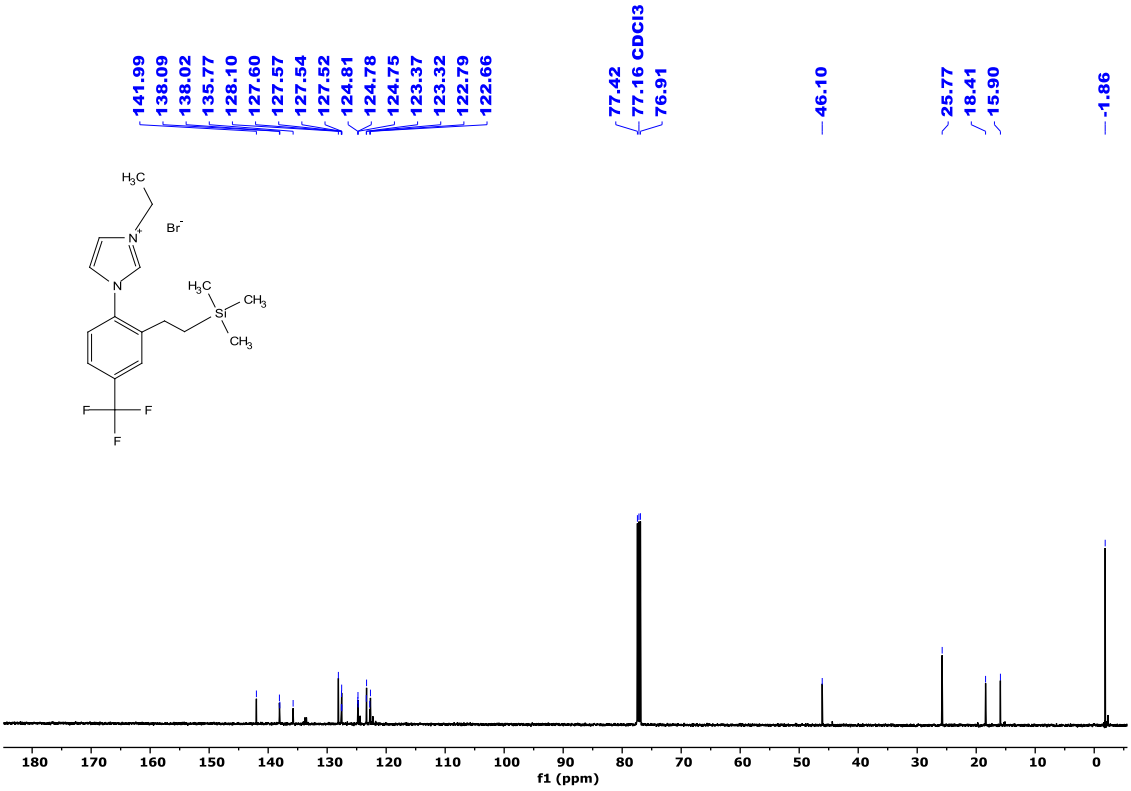


Figure S49. $^{13}C\{^{1}H\}$ NMR of **3ja** in $CDCl_3$.

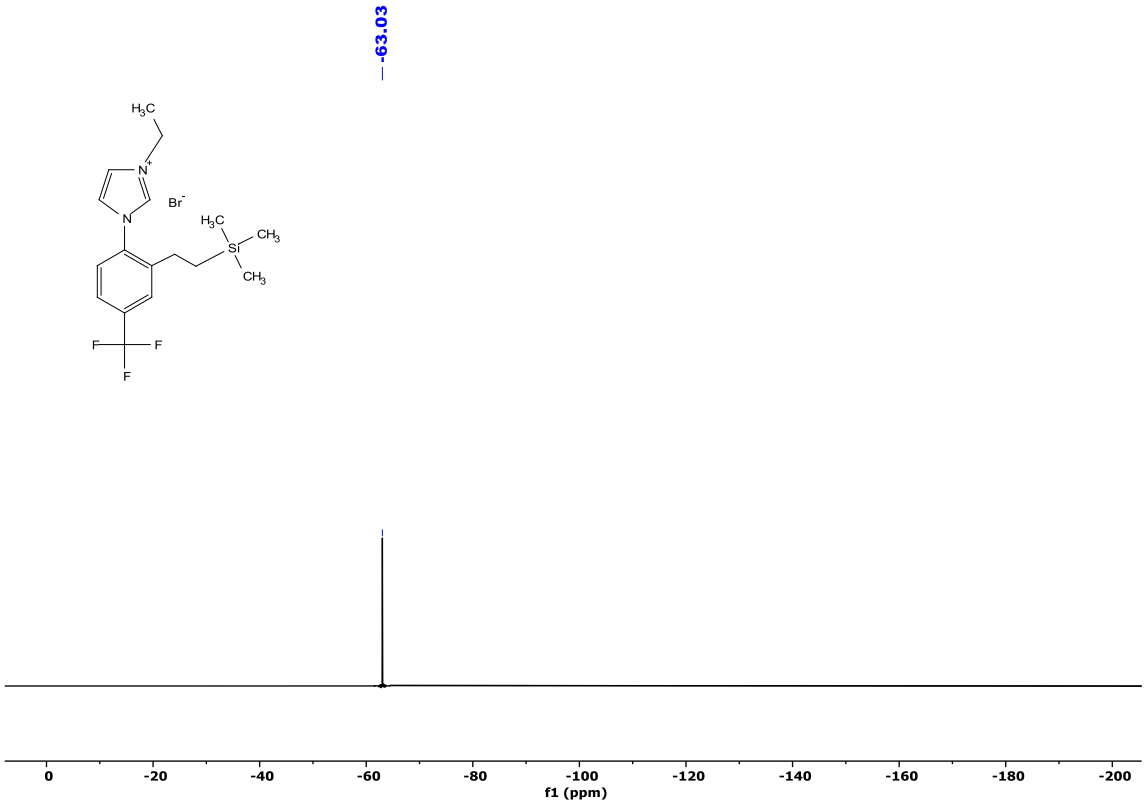


Figure S50. ^{19}F NMR of **3ja** in $CDCl_3$.

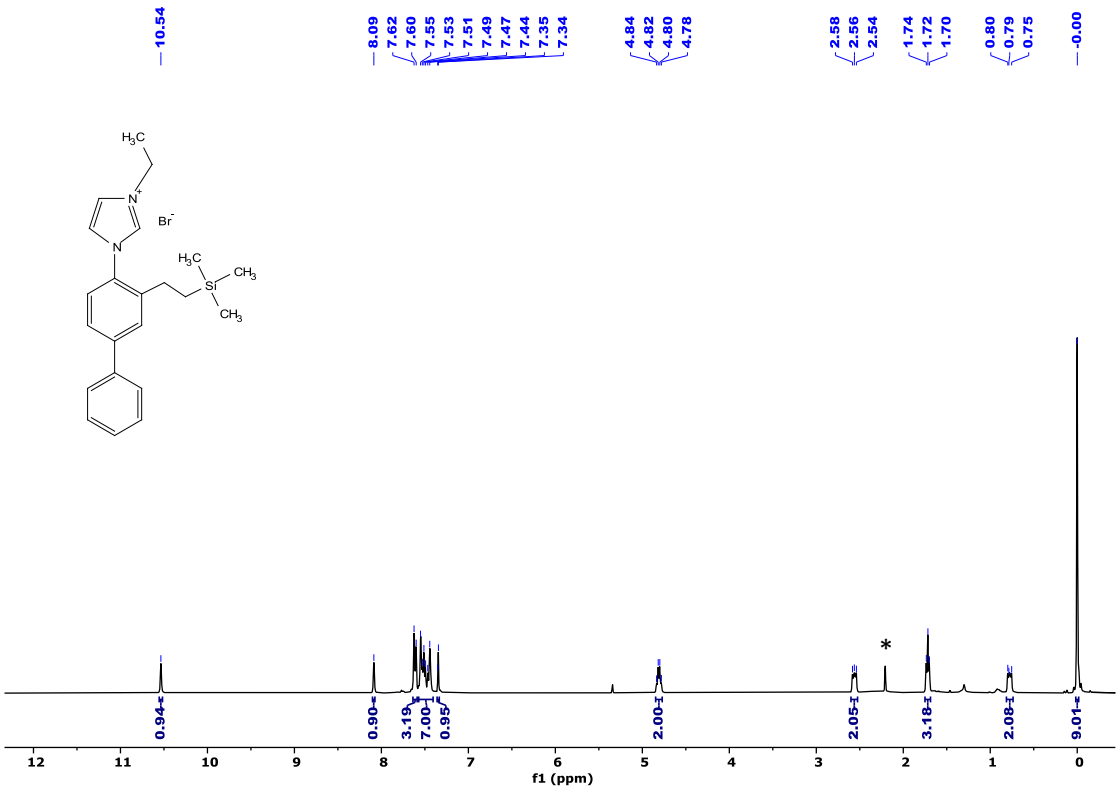


Figure S51. ^{1}H NMR of **3ka** in $CDCl_3$. * indicates H_2O in $CDCl_3$.

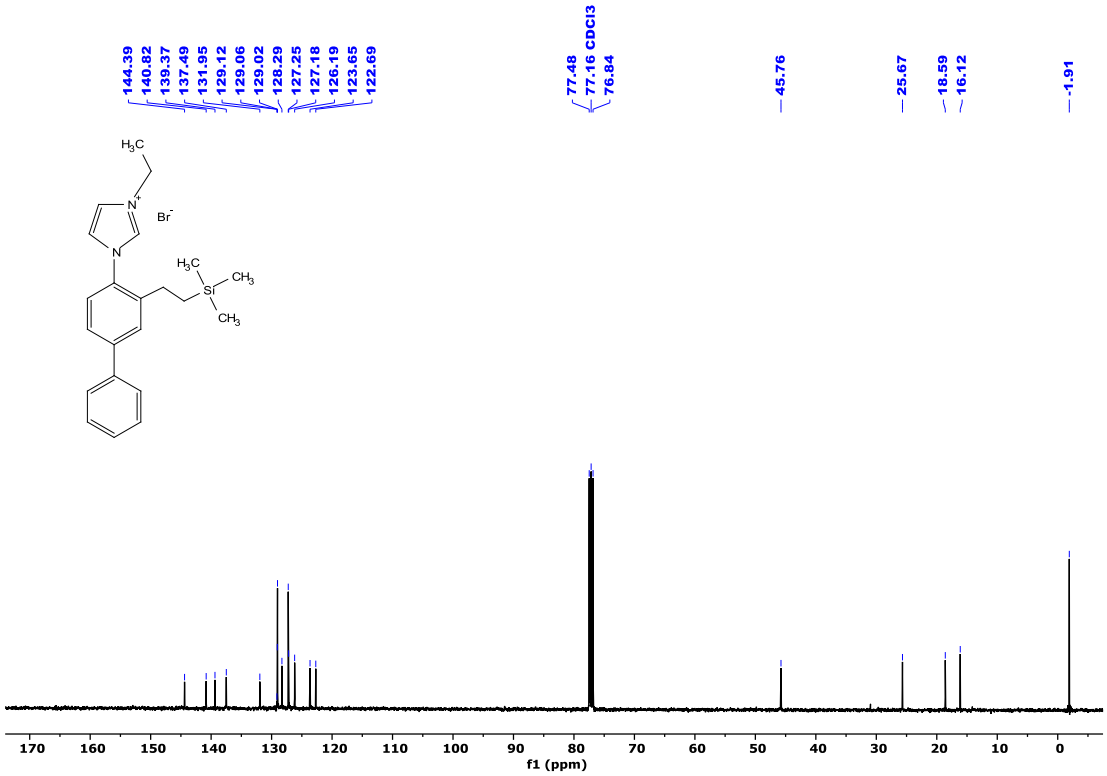


Figure S52. $^{13}C\{^{1}H\}$ NMR of **3ka** in $CDCl_3$.

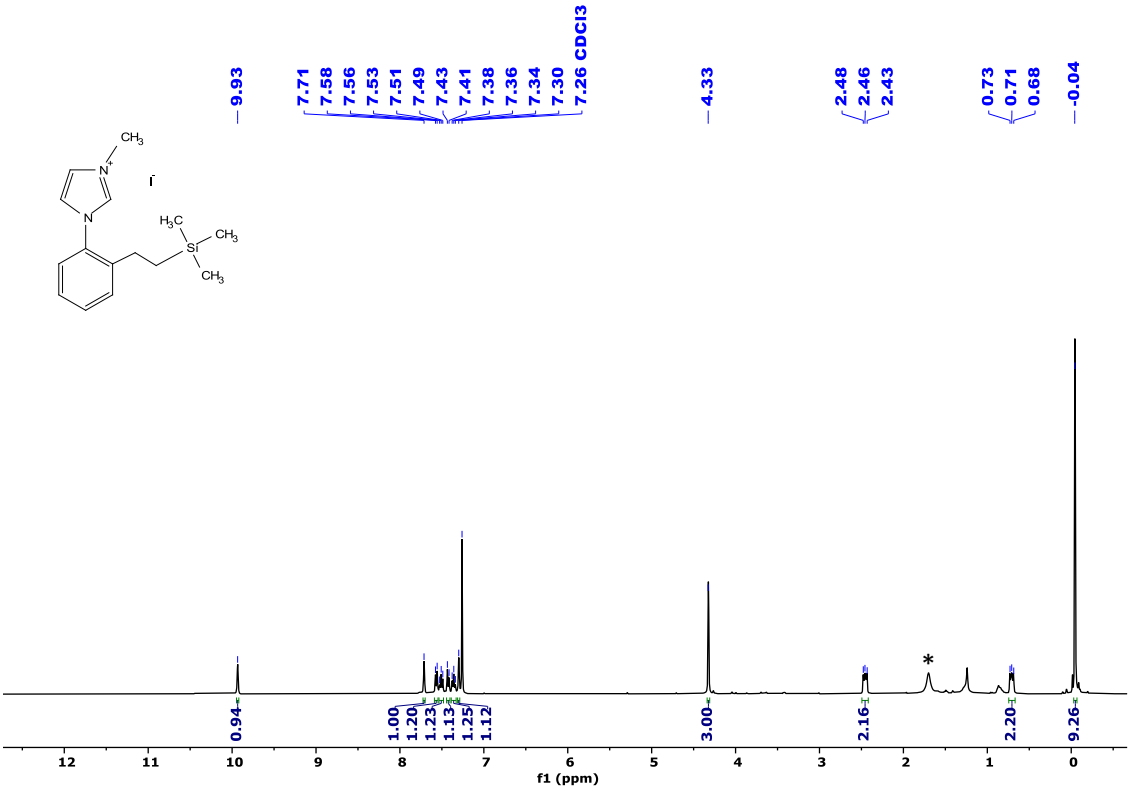


Figure S53. ^{1}H NMR of **3la** in $CDCl_3$. * indicates H_2O in $CDCl_3$.

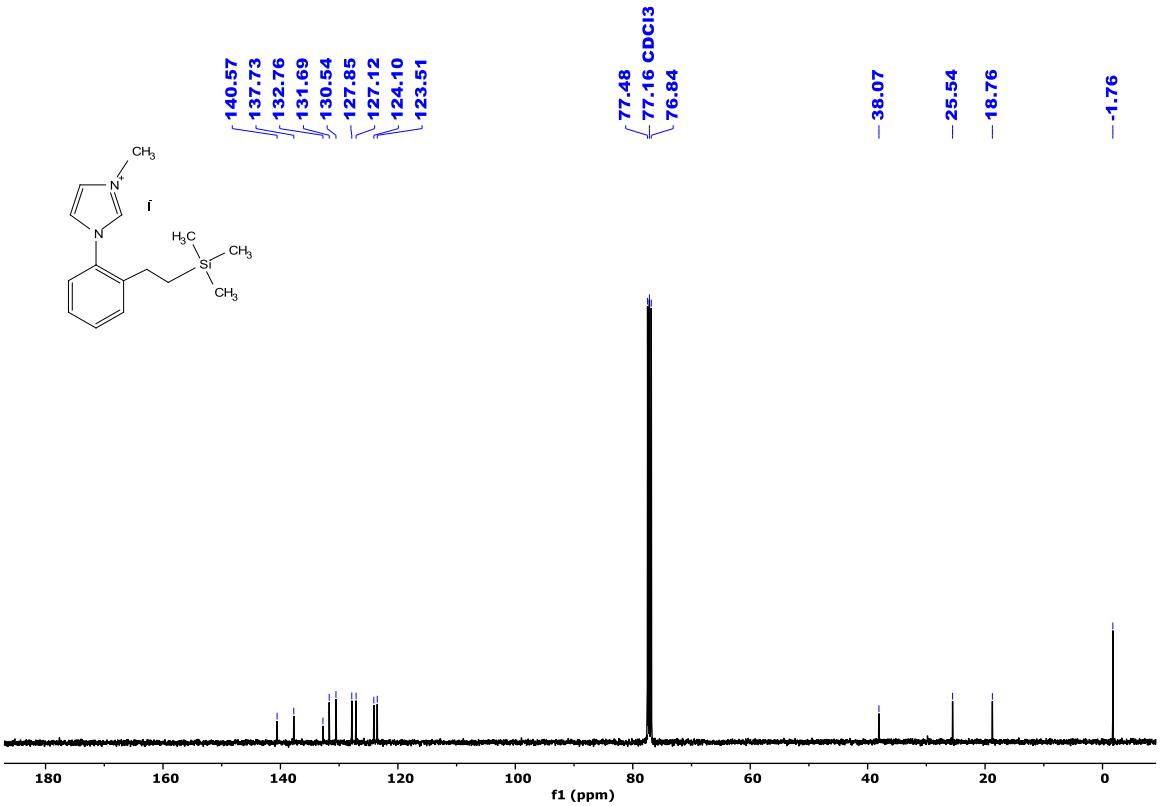


Figure S54. $^{13}C\{^{1}H\}$ NMR of **3la** in $CDCl_3$.

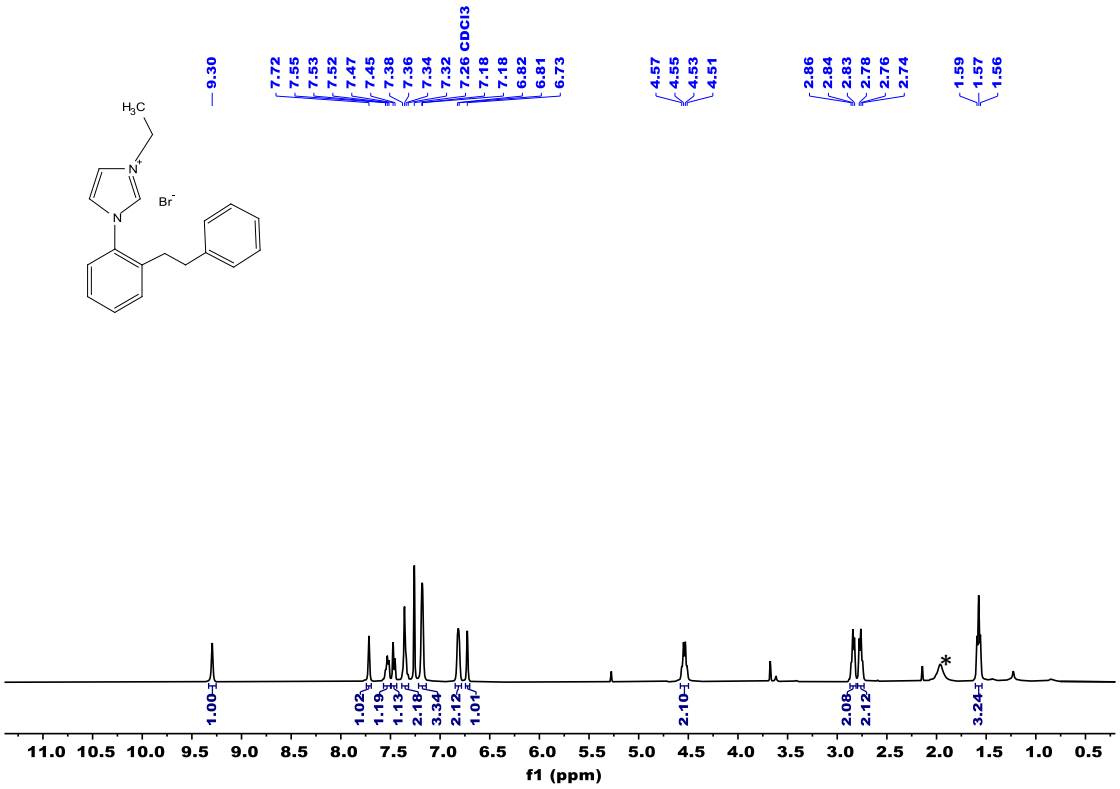


Figure S55. ^{1}H NMR of **3ab** in $CDCl_3$. * indicates H_2O in $CDCl_3$.

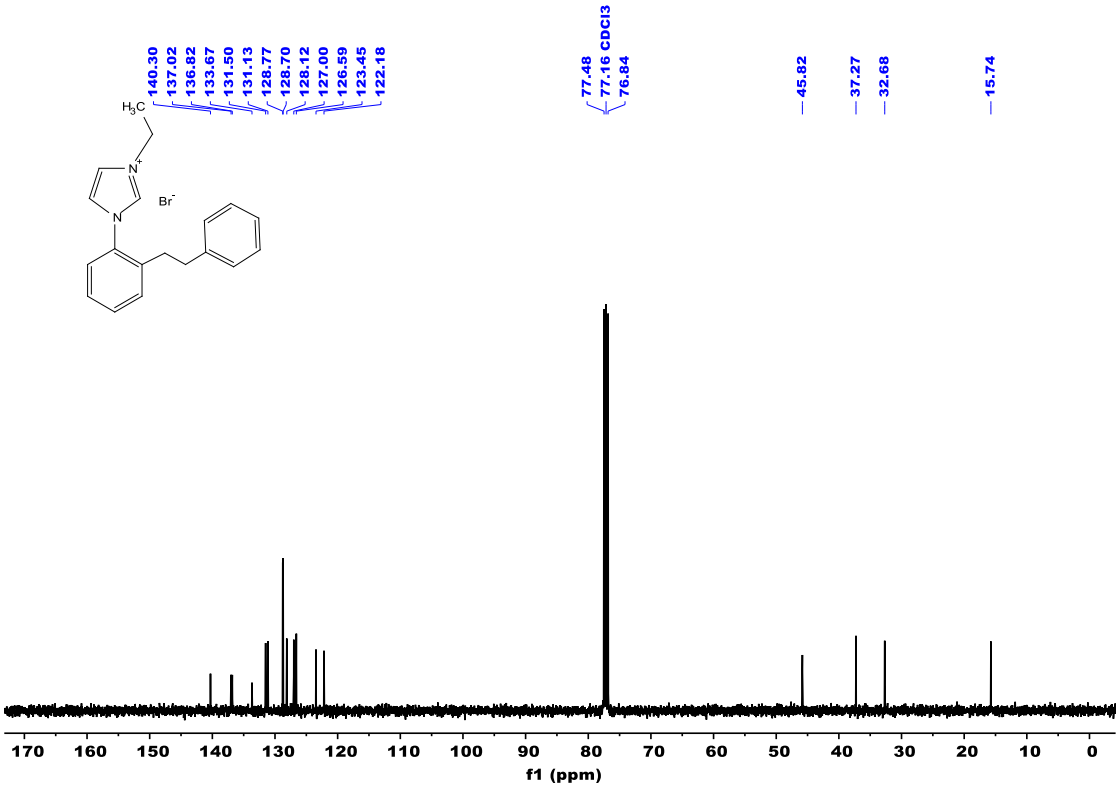


Figure S56. $^{13}C\{^{1}H\}$ NMR of **3ab** in $CDCl_3$.

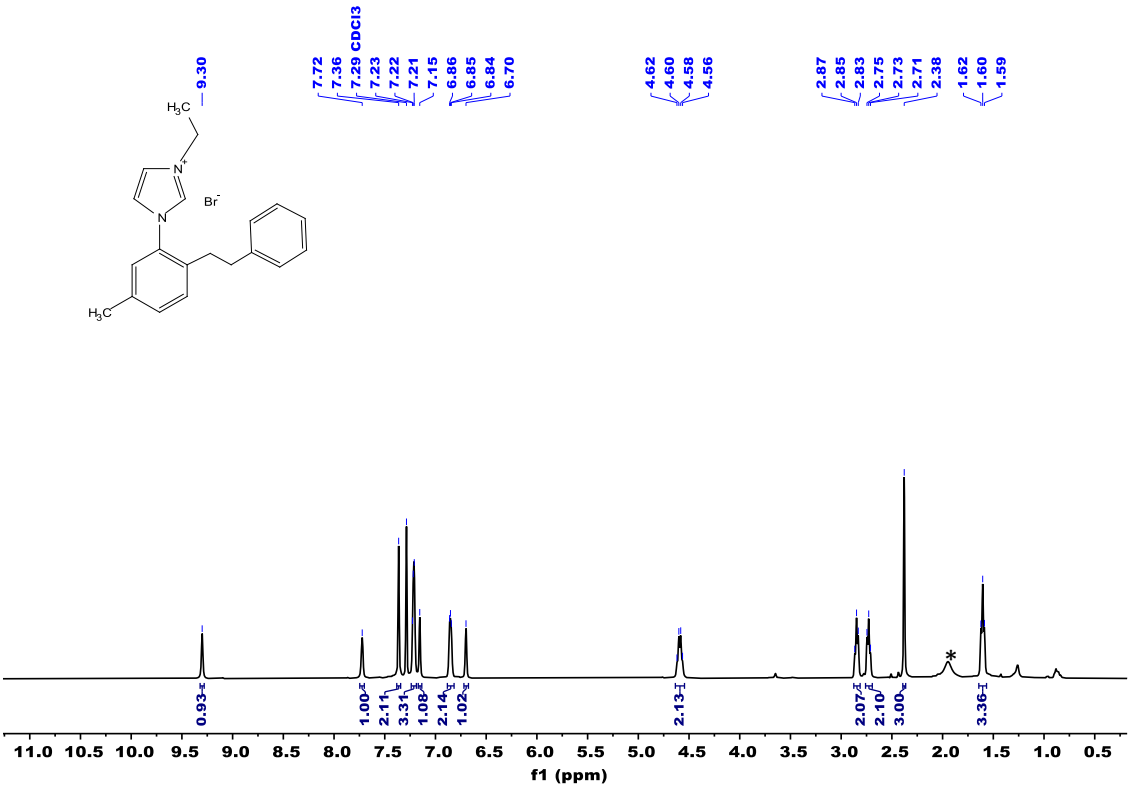


Figure S57. ^{1}H NMR of **3cb** in $CDCl_3$. * indicates H_2O in $CDCl_3$.

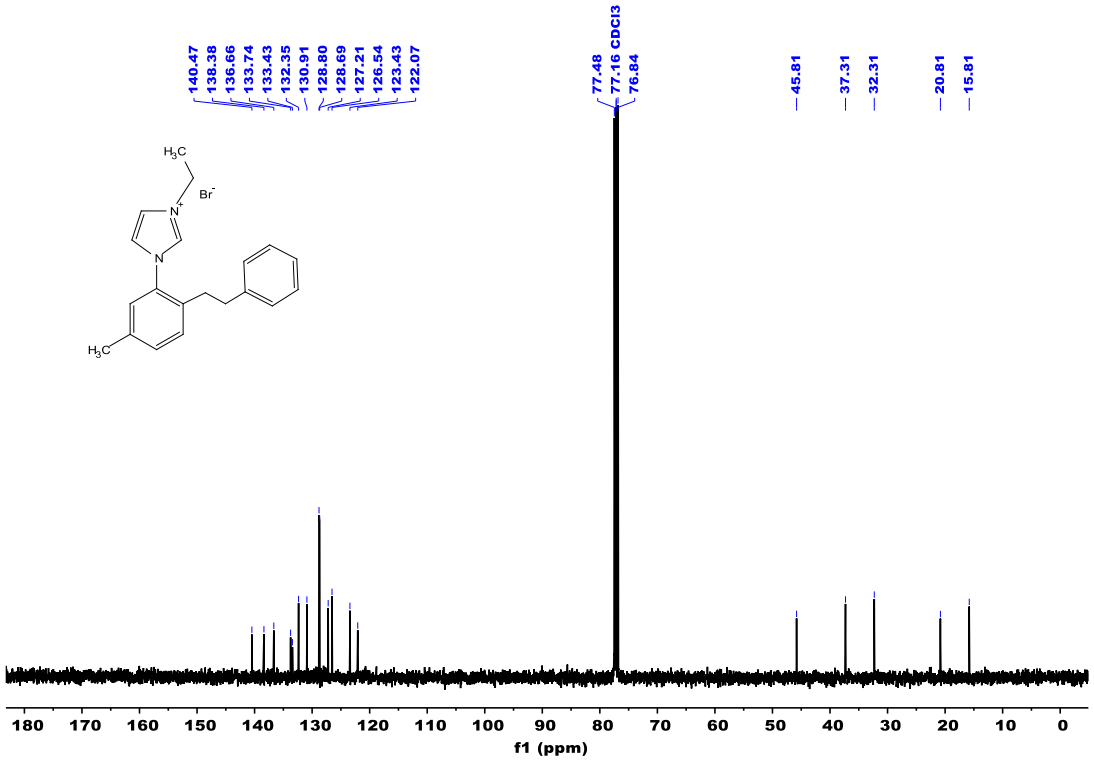


Figure S58. $^{13}C\{^{1}H\}$ NMR of **3cb** in $CDCl_3$.

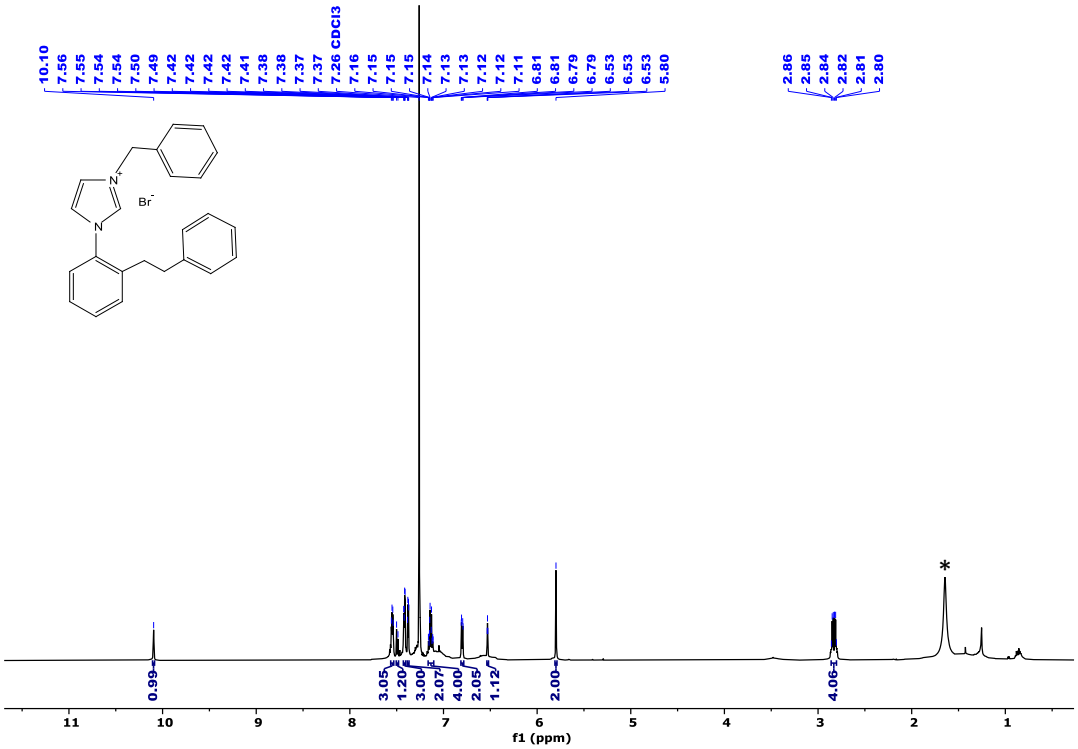


Figure S59. ^{1}H NMR of **3gb** in $CDCl_3$. * indicates H_2O in $CDCl_3$.

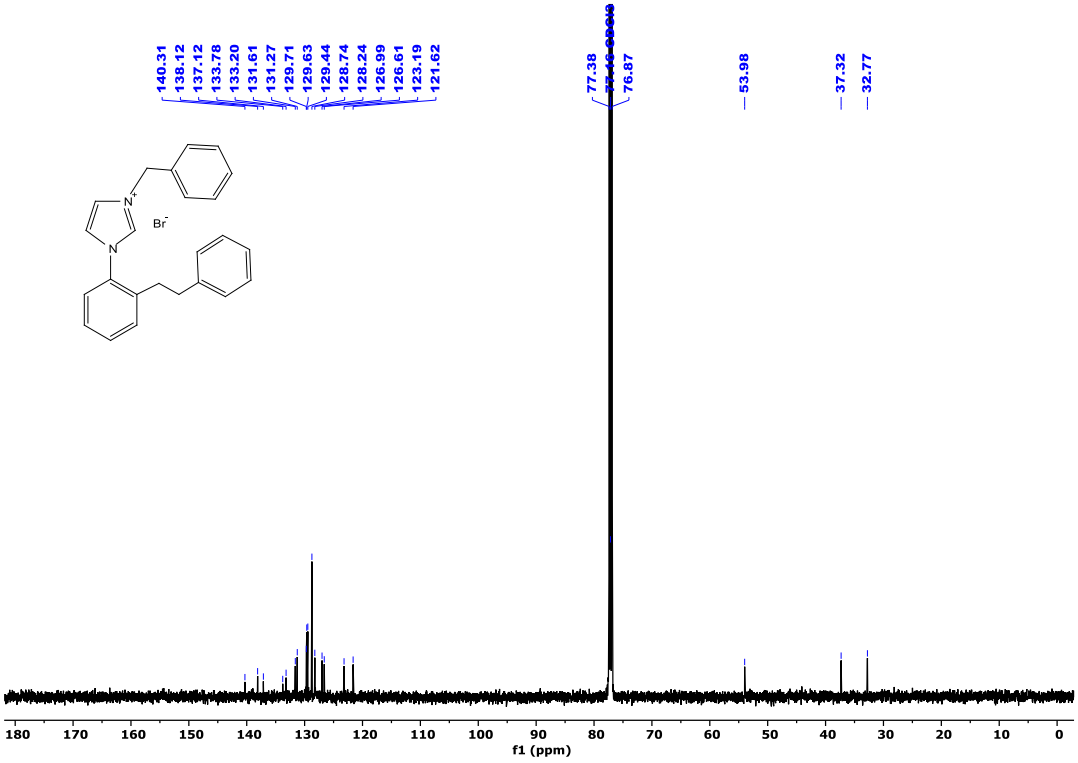


Figure S60. $^{13}C\{^{1}H\}$ NMR of **3gb** in $CDCl_3$.

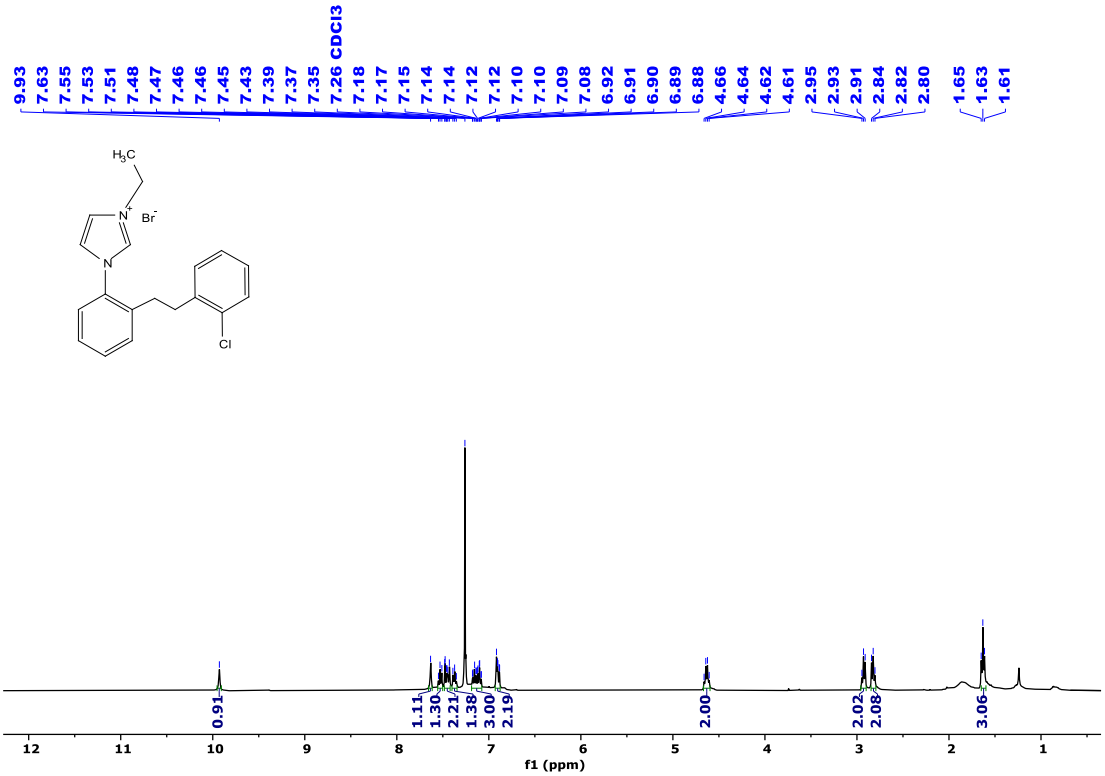


Figure S61. ^{1}H NMR of **3ac** in $CDCl_3$.

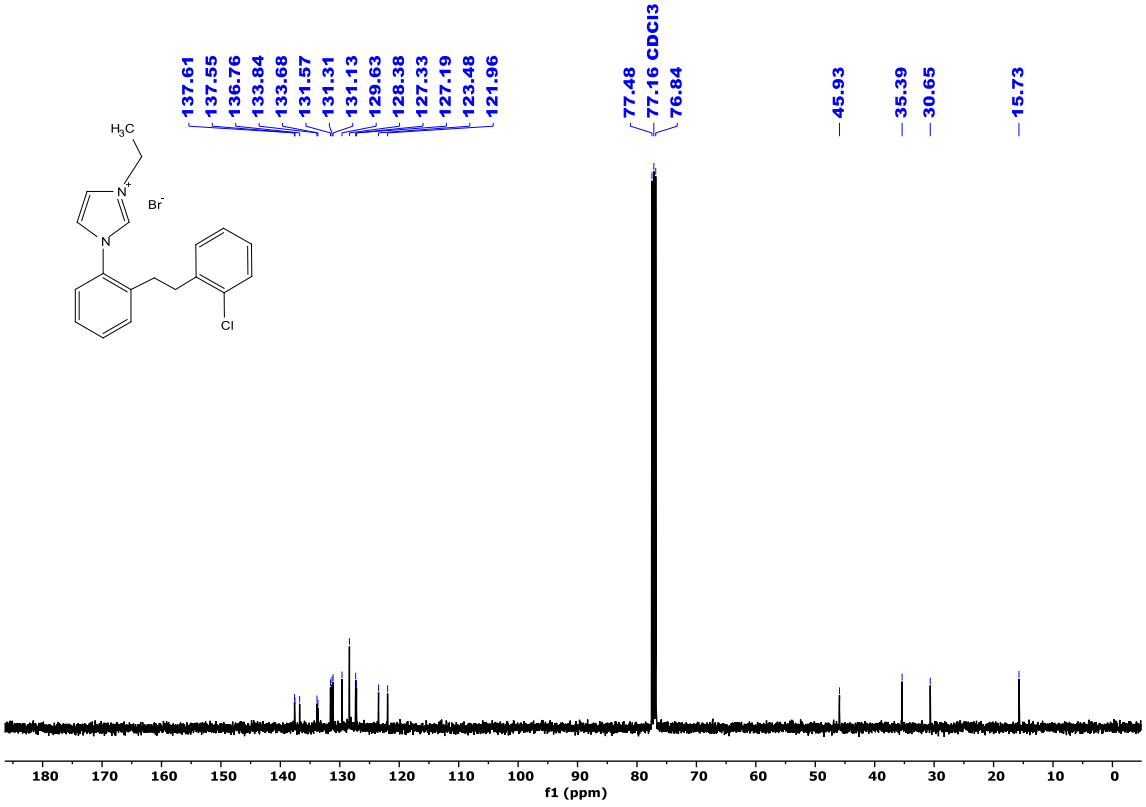


Figure S62. $^{13}C\{^{1}H\}$ NMR of **3ac** in $CDCl_3$.

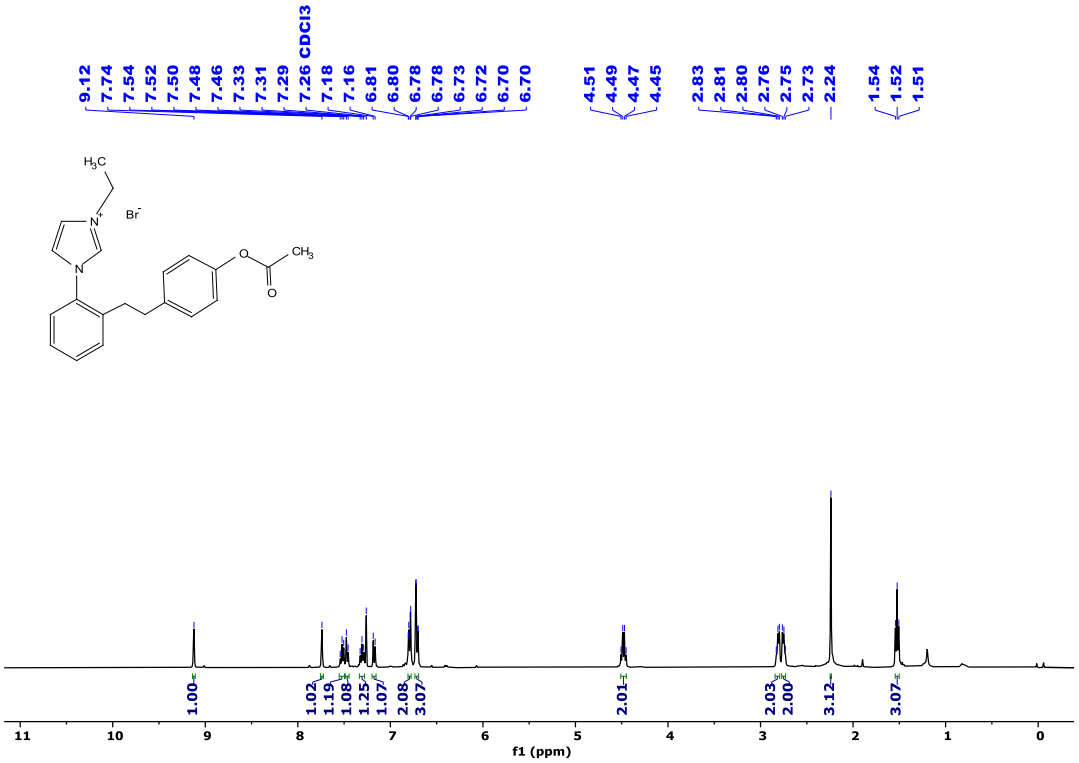


Figure S63. ^{1}H NMR of **3ad** in $CDCl_3$.

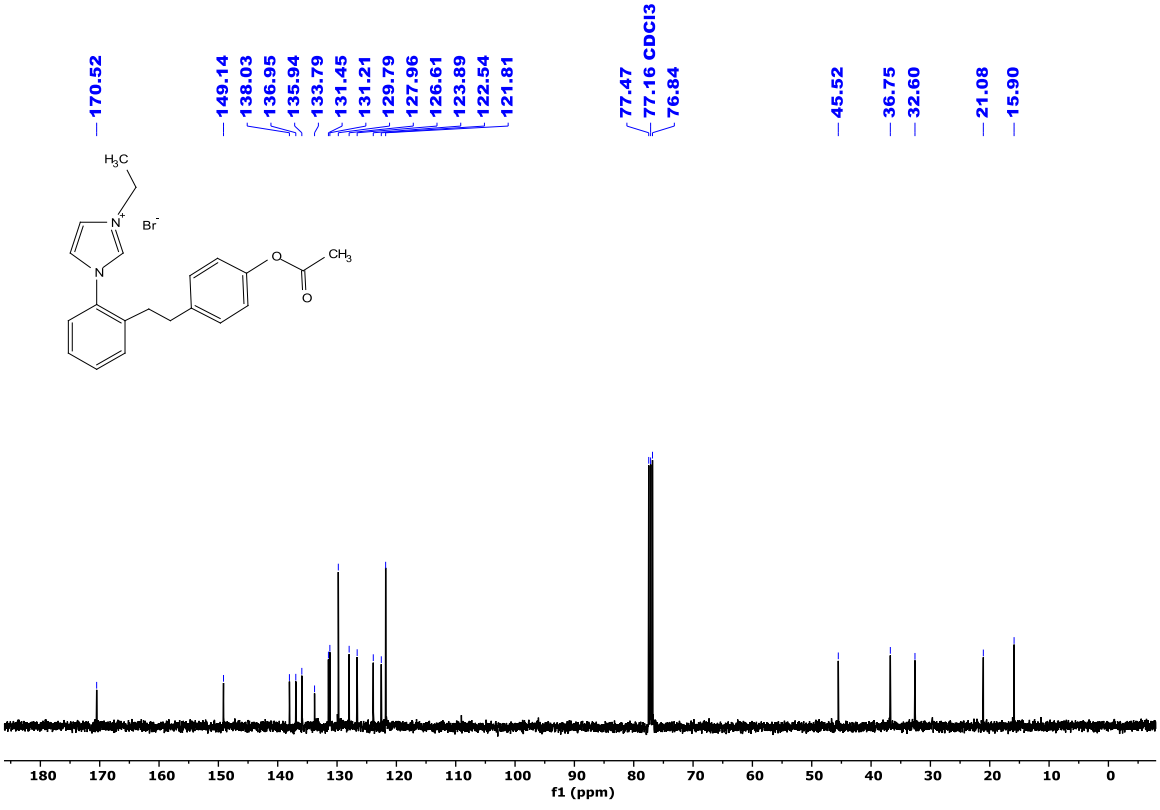


Figure S64. $^{13}C\{^{1}H\}$ NMR of **3ad** in $CDCl_3$.

13. Crystallographic data

Single crystal X-ray Crystallography: X-ray data were collected on a Bruker AXS Kappa APEX2 CCD diffractometer equipped with a PHOTON-II detector. The compound was measured by using MoKα radiation (λ = 0.71073 Å).[4a] Crystals was either frozen in paratone oil inside a cryo-loop under a cold stream of N_2 or placed inside a cryo-loop using paratone oil and after mounting on the goniometer head, it was optically centered. Bruker APEX2 and Bruker SAINT/APEX2-SAINT programme were used for the data collection and unit cell determination, respectively. Processing of the raw frame data was performed using Bruker SAINT or SAINT/XPREP.[4b-c] The structure was solved by SHELXS-97 or SHELXT-2018/2 methods[4d] and refined against F^2 using all reflections with SHELXL-2014/7 (WinGX) or SHELXL-2019/2 program.[4e-f] The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed at calculated positions. The graphical representations were performed using the program Mercury.[4g]

Table S3. Crystal data of the compound 7a.

Empirical formula	$C_{26}H_{37}BrN_2RuSi$
Formula weight	586.64
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 13.9782(8) Å α = 90°.
	b = 12.5557(6) Å β = 110.614(2)°.
	c = 16.6745(8) Å γ = 90°.
Volume	2739.1(2) $Å^3$
Z, Calculated density	4, 1.423 Mg/m^3
Absorption coefficient	2.090 mm^{-1}
F(000)	1200
Crystal size	0.290 x 0.250 x 0.200 mm
Theta range for data collection	2.082 to 24.999°.
Limiting indices	-12<=h<=16, -14<=k<=14, -19<=l<=19
Reflections collected / unique	19156 / 4824 [R(int) = 0.0256]
Completeness to theta = 24.999	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4824 / 0 / 287
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0255, wR2 = 0.0594
R indices (all data)	R1 = 0.0358, wR2 = 0.0631
Extinction coefficient	n/a
Largest diff. peak and hole	0.318 and -0.473 $e.Å^{-3}$

14. Computational studies

Gaussian 16 software, revision B.01 program. was used to carry out all the theoretical studies.[5] DFT calculations were performed with B3LYP[6] exchange-correlation functional by using 6-31G(d',p')[7] basis set for H, C, O, N, Br, and Si atoms where as LanL2DZ basis set was used for Ru.[8] Solvation effect of 1,4-dioxane was considered during the calculation using the SMD solvation model.

Computed energies (au) and cartesian coordinates (Å) of the optimized structures

Species are numbered in accordance with the text of the manuscript.

Complex I

Charge = 0 Multiplicity = 1

C	-0.88811	-0.35391	-0.73014
H	-1.62302	-0.34665	0.08005
C	-0.54627	-1.64639	-1.3262
H	-0.97413	-2.57542	-0.94045
C	0.45865	-1.67746	-2.32671
C	1.04449	-0.44761	-2.80705
H	1.84591	-0.47003	-3.54869
C	0.55846	0.80962	-2.29075
H	1.00031	1.73309	-2.67709
C	-0.53199	0.91253	-1.355
C	-1.10541	2.28919	-0.9641
H	-0.28726	3.02602	-1.07256
C	-1.61293	2.34121	0.5062
H	-0.80145	2.07772	1.20026
H	-1.96088	3.35745	0.745
H	-2.44727	1.64316	0.66442
C	-2.23949	2.68021	-1.96755
H	-1.84903	2.70389	-2.99631
H	-3.06241	1.95171	-1.92684
H	-2.6396	3.67617	-1.72259
C	1.06596	-3.01363	-2.76852
H	1.3407	-2.98475	-3.83354
H	1.97932	-3.18003	-2.16385
H	0.36267	-3.84039	-2.59241
C	2.27164	1.33474	-0.18989
C	3.1266	2.05067	-1.07446
H	3.23093	1.71926	-2.1157
C	3.86396	3.17759	-0.66001

H	4.50889	3.69796	-1.38086
C	3.78745	3.6489	0.66653
H	4.36181	4.53045	0.97778
C	2.97933	2.97142	1.59633
H	2.91198	3.29997	2.64109
C	2.26568	1.84781	1.14493
C	1.2339	0.93571	3.40669
H	1.5925	1.70892	4.09163
C	0.53949	-0.2214	3.63252
H	0.16813	-0.66423	4.56133
C	0.89339	-0.10293	1.32039
C	-0.17001	-2.26928	2.23497
H	-0.67653	-2.35056	1.25805
H	-0.90812	-2.44756	3.03895
C	1.02066	-3.2648	2.31494
H	0.65078	-4.28952	2.15872
H	1.7581	-3.00875	1.52941
H	1.50324	-3.20577	3.30167
N	1.44078	1.01019	1.99941
N	0.30737	-0.849	2.36899
Br	2.98486	-1.83327	-0.2188
Ru	1.09278	-0.24508	-0.6001

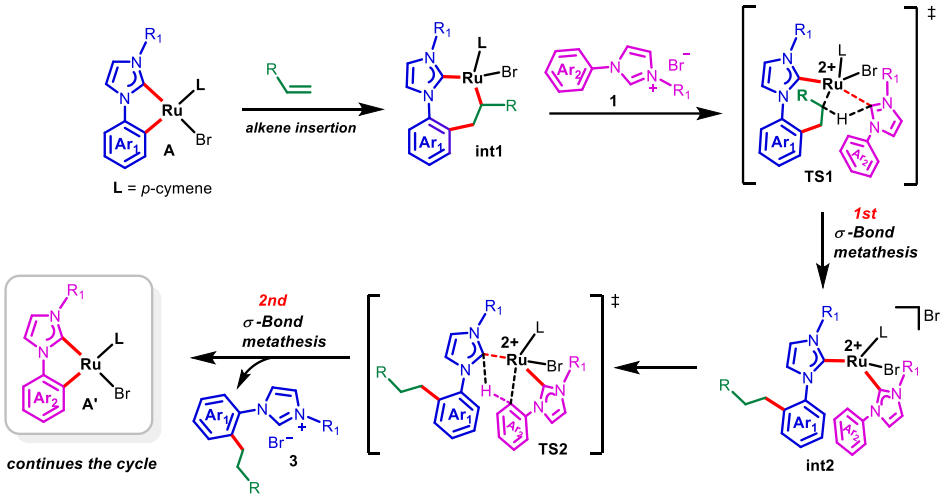
Int1

C	-0.25411	-1.59834	-2.08894
H	-0.65028	-2.61763	-2.07137
C	1.17715	-1.35345	-2.10509
H	1.84072	-2.22341	-2.13066
C	1.70426	-0.09695	-2.72665
C	0.89287	1.00858	-2.61742
H	1.20535	1.99785	-2.97749
C	-0.40516	0.84414	-1.90157
H	-1.03415	1.73519	-1.82333
C	-1.10776	-0.45102	-1.97344
C	-2.65439	-0.52067	-2.0452
H	-3.05992	0.2888	-1.41196
C	-3.24088	-1.8773	-1.54556
H	-2.88121	-2.11445	-0.5333
H	-4.34003	-1.82012	-1.51862
H	-2.96023	-2.70136	-2.21865
C	-3.11141	-0.24737	-3.51935
H	-2.74727	0.7326	-3.86408
H	-2.7217	-1.02155	-4.19828
H	-4.21106	-0.25133	-3.58177

C	3.10835	-0.08325	-3.33523
H	3.38046	0.92562	-3.67989
H	3.84999	-0.418	-2.58991
H	3.15765	-0.77706	-4.19249
C	-2.08011	-1.41757	2.71318
H	-2.85397	-1.13501	3.43168
C	-1.31507	-2.53653	2.62565
H	-1.29123	-3.43691	3.24605
C	-0.61551	-1.10926	0.86291
C	0.41936	-3.52578	1.04372
H	0.90962	-3.19424	0.11177
H	-0.25274	-4.37974	0.8223
C	1.49439	-3.92173	2.09354
H	2.05071	-4.79806	1.72604
H	2.19141	-3.07806	2.219
H	1.03504	-4.17508	3.06071
N	-1.68351	-0.53292	1.65589
N	-0.4398	-2.37825	1.51105
Br	2.56653	-0.9738	0.61123
Ru	0.40245	-0.33424	-0.50305
C	-2.60327	0.54991	1.24186
C	-2.18029	1.84084	0.82354
C	-3.98994	0.22564	1.28544
C	-3.19735	2.76103	0.44511
C	-4.96392	1.16462	0.9234
H	-4.28948	-0.78321	1.59541
C	-4.5624	2.44498	0.49205
H	-5.31186	3.19115	0.19553
H	-6.02754	0.89489	0.96356
H	-2.88763	3.76348	0.11913
C	-0.72881	2.38305	0.81344
C	0.45798	0.99023	0.5405
H	-0.66221	3.04716	-0.06546
H	-0.67149	3.05847	1.69263
H	0.43349	0.56787	1.55756
Si	2.06837	2.04544	0.61443
C	1.68484	3.89516	0.71805
H	2.62131	4.46566	0.78737
H	1.14912	4.26629	-0.1653
H	1.08594	4.15558	1.60017
C	2.99008	1.6327	2.2056
H	3.28168	0.5748	2.21979
H	3.90149	2.2366	2.31125
H	2.36762	1.81919	3.09109

C	3.29629	1.92023	-0.80816
H	3.61605	0.88544	-0.97573
H	2.88639	2.31187	-1.74691
H	4.19285	2.5113	-0.57556

15. A plausible reaction pathway



Scheme S1. A plausible reaction pathway.

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