Electronic Supporting Information

Cationic and Neutral Ruthenium (II) Complexes bearing Silyl-Phosphines; Synthesis, Structures, and Catalytic Studies in Selective Hydroboration of Carbonyl Compounds

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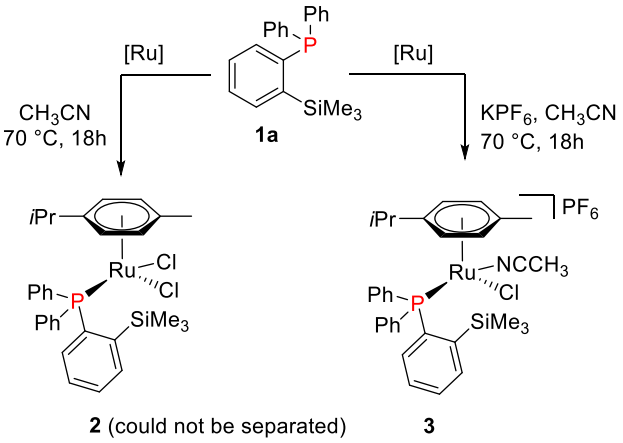
General experimental procedures

All reagents were obtained from commercial sources (Loba Chemie, Spectrochem, Sigma-Aldrich, TCI, and Avra). The silylated phosphines **1a-1c** were synthesised using a significantly modified synthetic technique previously described. [1] The starting material $[Ru(p\text{-cymene})Cl_2]_2$ was prepared according to the reported procedure.[2] Dichloromethane (DCM) was dried in an Argon/Nitrogen environment using a distillation system over calcium hydride. THF and n-hexane were dried in an environment of nitrogen and argon using a distillation apparatus over sodium metal and benzophenone. The ligands and metal complexes were synthesised in N_2 and Ar atmospheres using Tensil Schlenk tubes and Schlenk flasks. All catalytic reactions were performed in a borosil-sealed tube and Tensil Schlenk tubes under N_2 conditions. For column chromatography, Spectrochem chemical company's 100-200 mesh silica gel was employed. Gradient elution was performed using distilled hexane and ethyl acetate. UV light was used to identify TLC plates at 254 nm. The NMR spectra were measured using a "Bruker AVANCE NEO Ascend 400 and 700" 400 and 700 MHz FT-NMR. Chemical shifts are expressed in parts per million (ppm) relative to tetramethylsilane (TMS), with the residual solvent serving as an internal standard ($CDCl_3$, ^1H; 7.26 ppm, and ^{13}C; 77.16 ppm, and DMSO-d6, ^1H; 2.5 ppm, and ^{13}C; 39.52 ppm). Coupling constants are expressed in Hertz units. Individual peaks are reported as multiplicities (integration and coupling constants in Hz), where s = singlet, d = doublet, t = triplet, q = quartet, and dd = doublet of doublet, br = broad. ESI-MS/HR-MS spectra were measured using the "Xevo G2-XS QT of Quadrupole Time of Flight Mass Spectrometer Waters." "Elementar, UNICUBE" was used to do elemental analysis measurements. The Rigaku Smart Lab X-ray diffractometer was used for the XRD analysis.

Supporting Spectral Data of Compounds



Scheme S1. Reactivity of phosphine **1a** with $[Ru(p\text{-cymene})Cl_2]_2$].

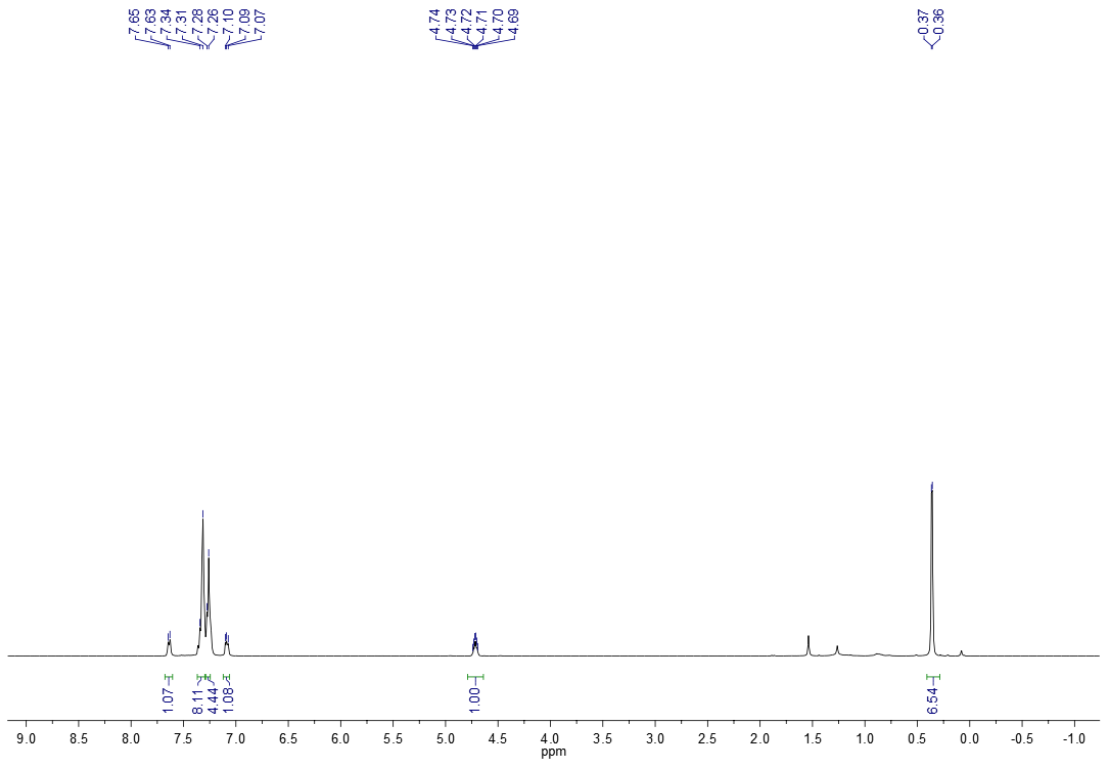


Figure S1. ^{1}H NMR spectrum of compound **1b** measured in $CDCl_3$.

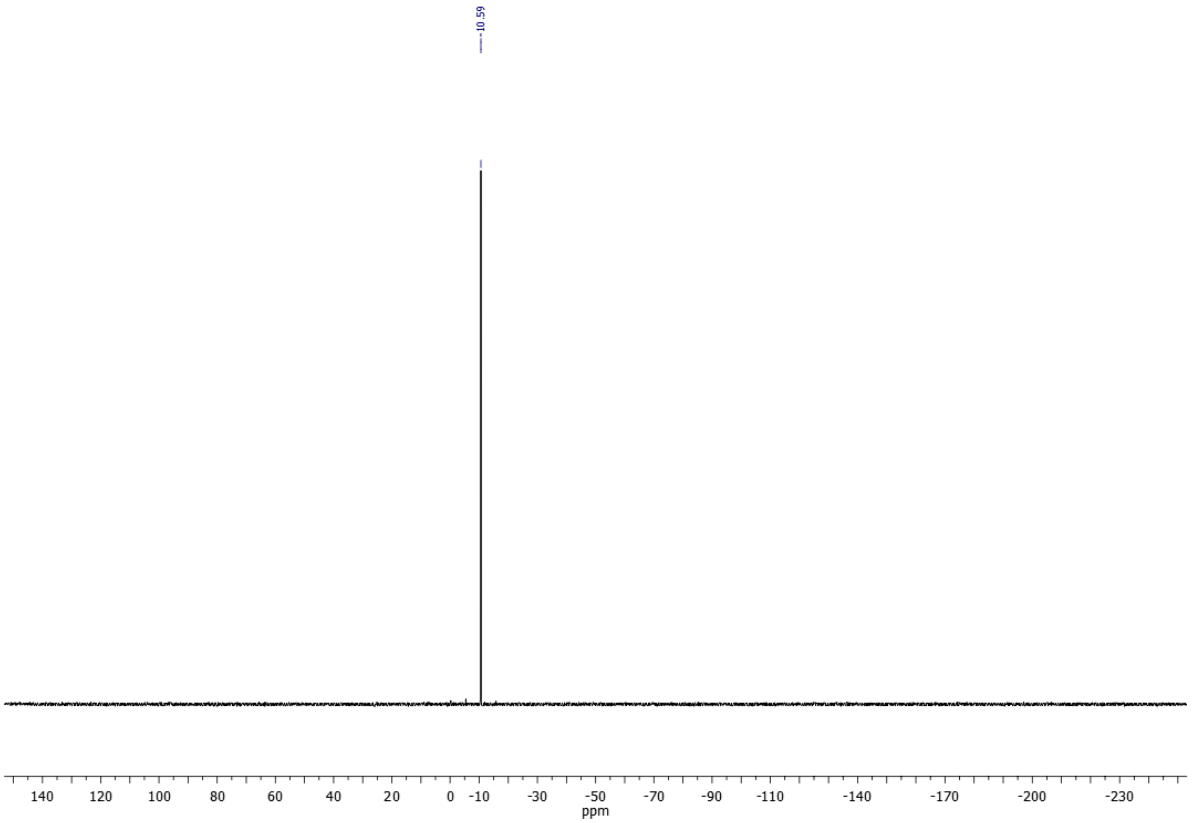


Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of compound **1b** measured in $CDCl_3$.

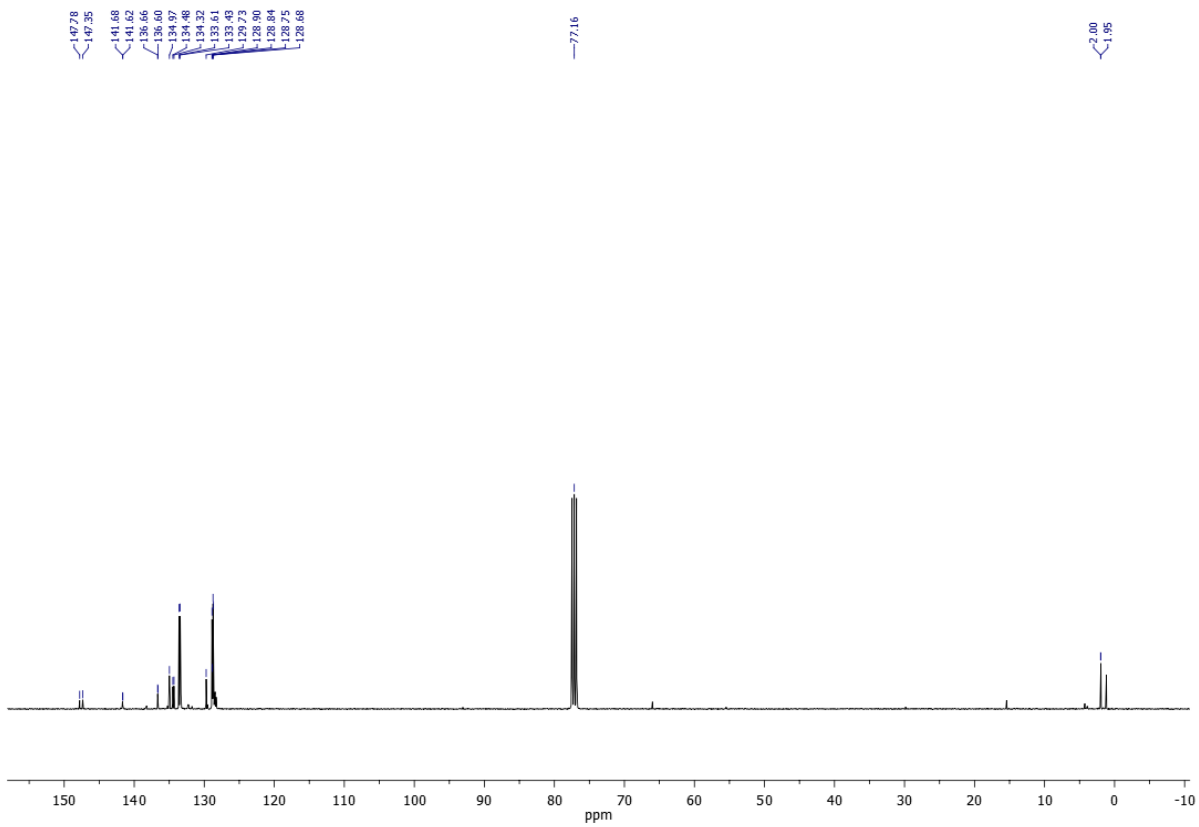


Figure S3. ^{13}C NMR spectrum of compound **1b** measured in $CDCl_3$.

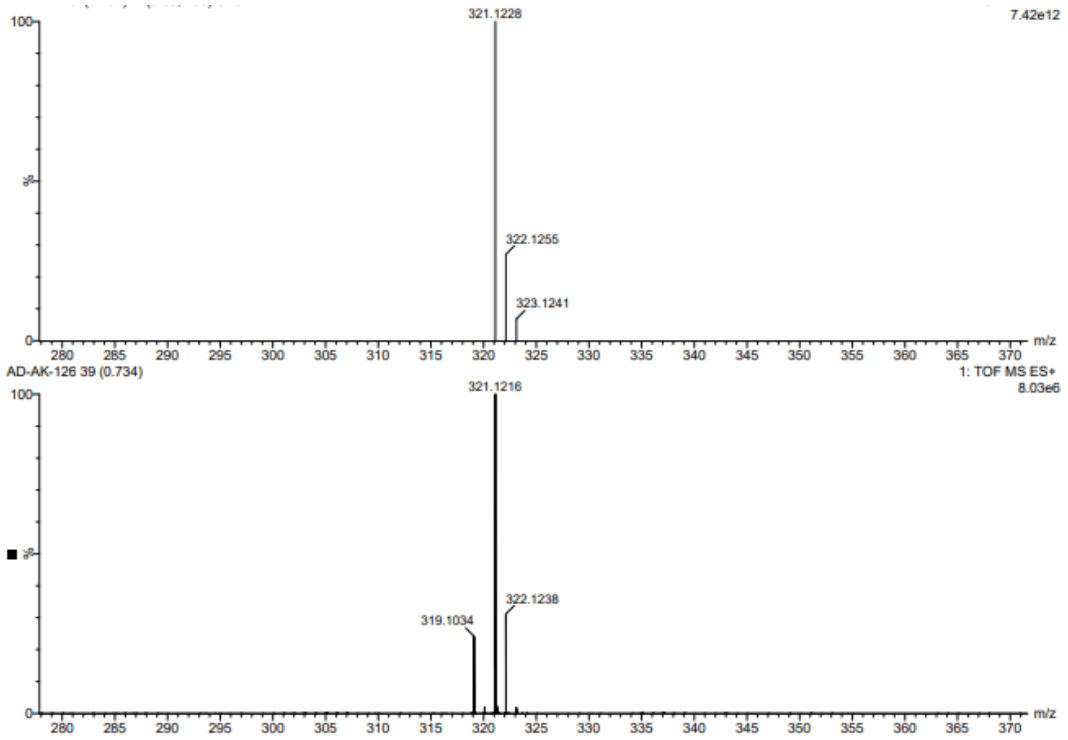


Figure S4. ESI-HRMS spectrum of compound **1b** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

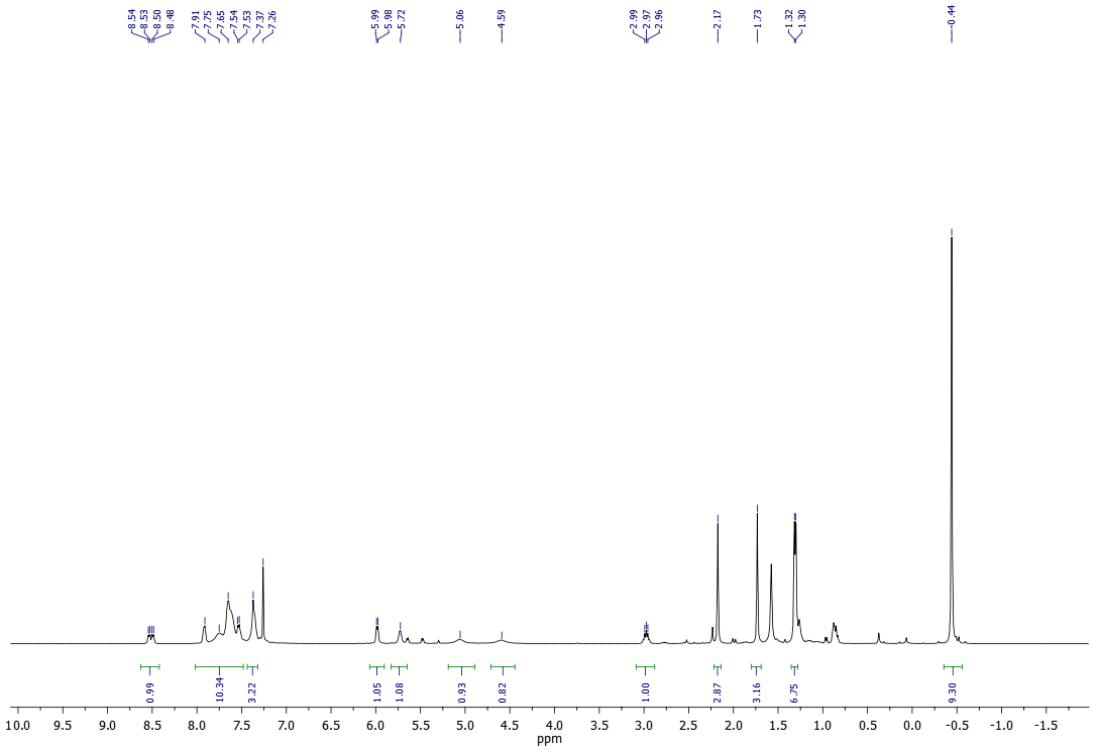


Figure S5. ^{1}H NMR spectrum of compound **3** measured in $CDCl_3$.

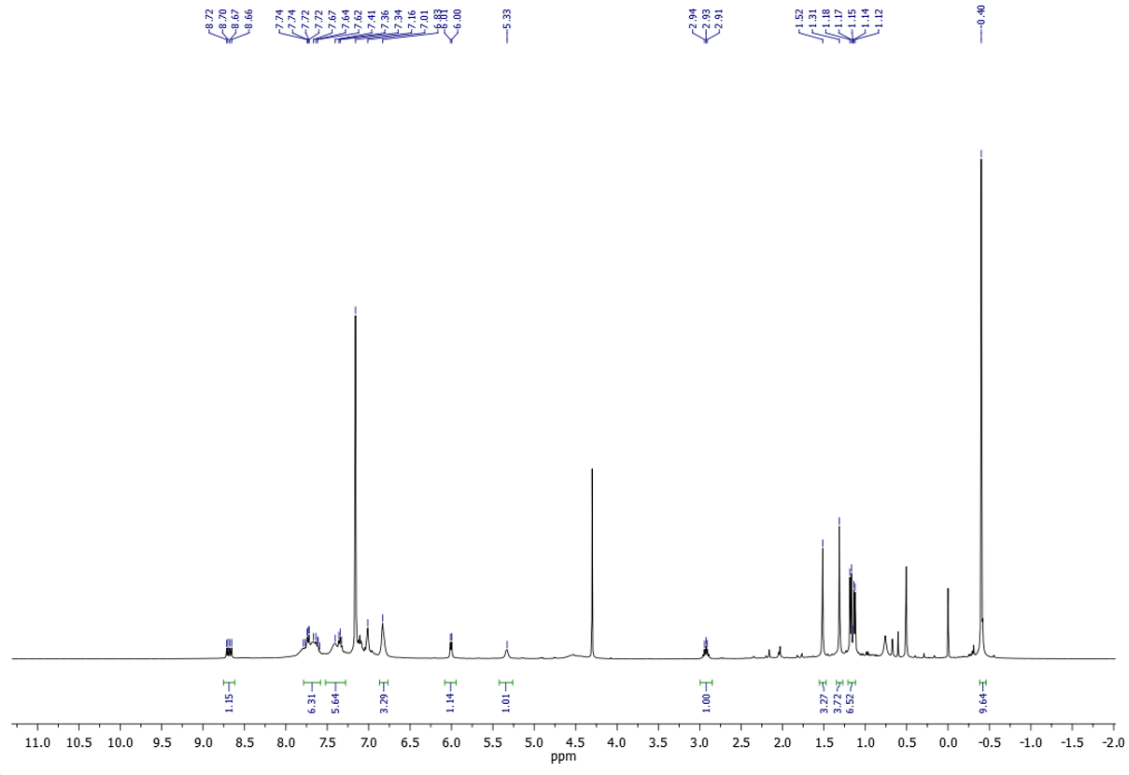


Figure S6. ^{1}H NMR spectrum of compound **3** measured in C_6D_6.

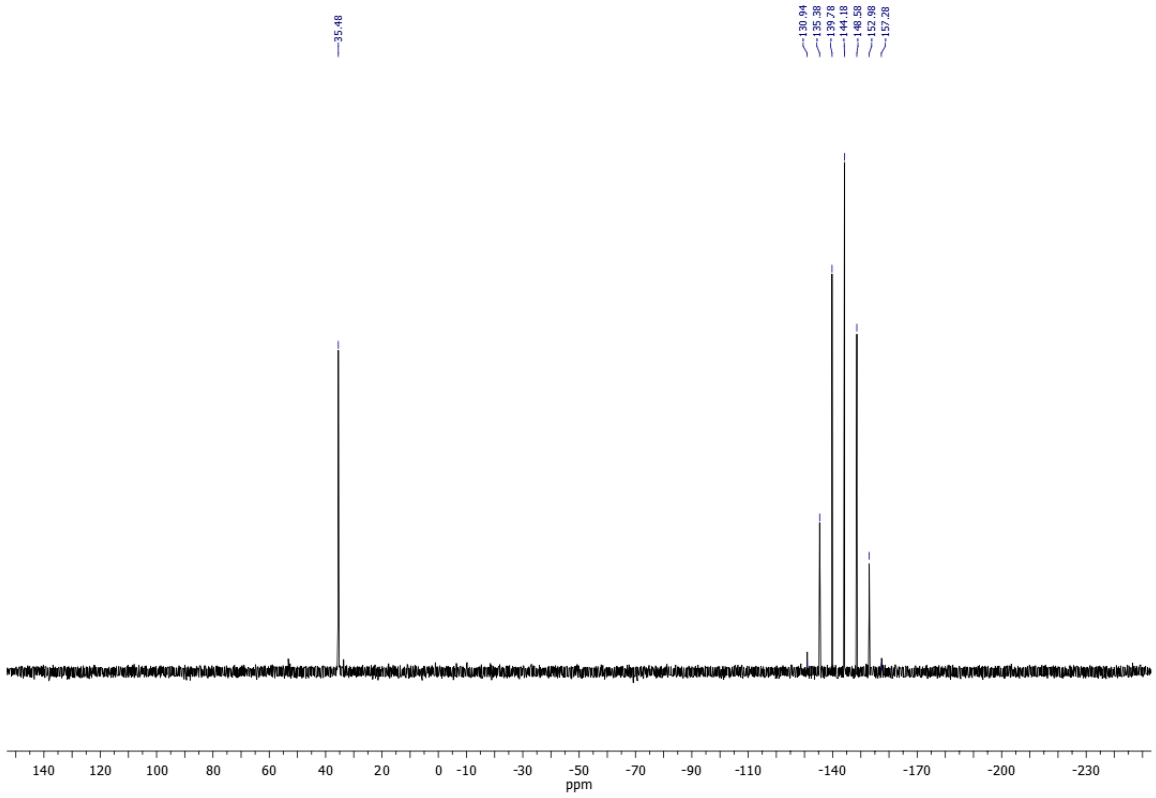


Figure S7. ^{31}P NMR spectrum of compound **3** measured in $CDCl_3$.

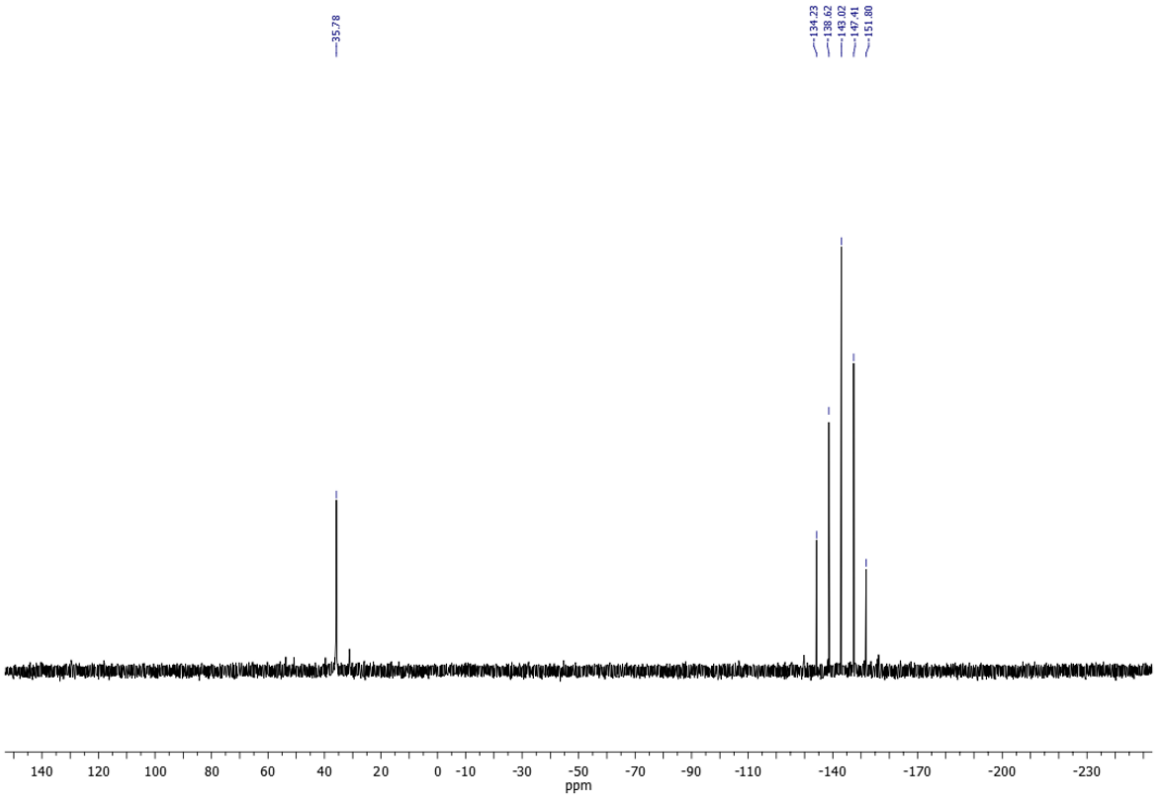


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of compound **3** measured in C_6D_6.

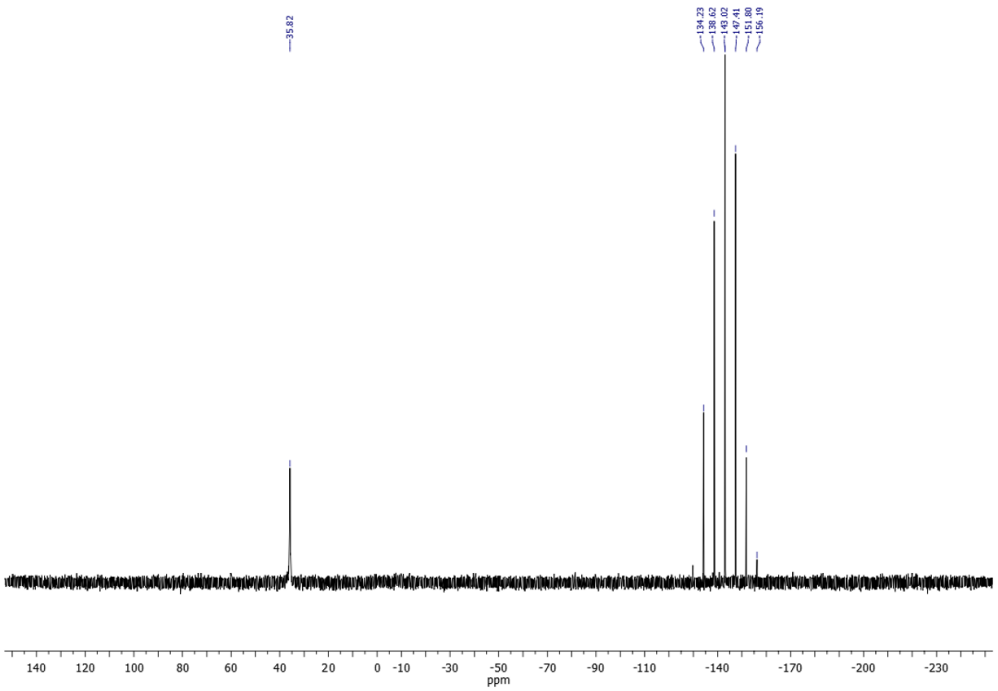


Figure S9. ^{31}P NMR spectrum of compound **3** measured in C_6D_6.

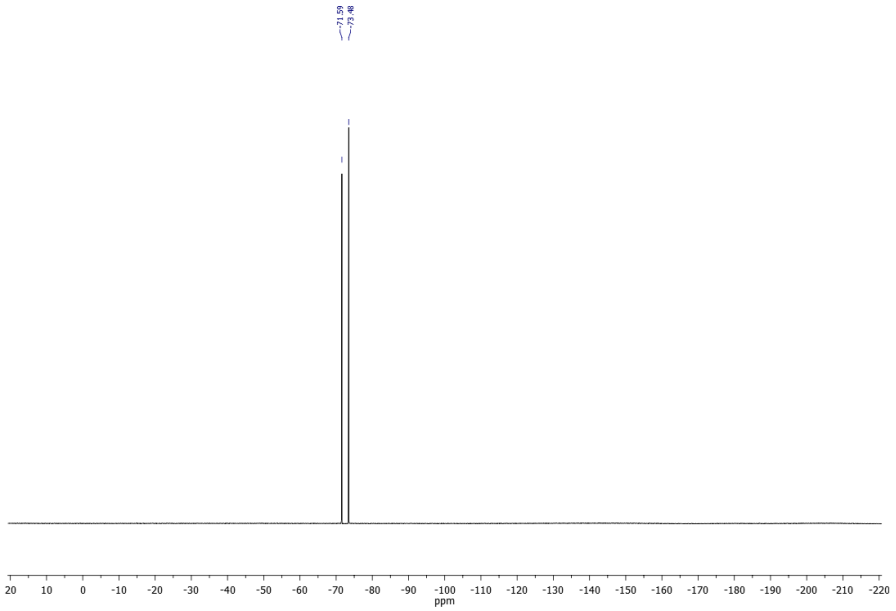


Figure S10. ^{19}F NMR spectrum of compound **3** measured in $CDCl_3$.

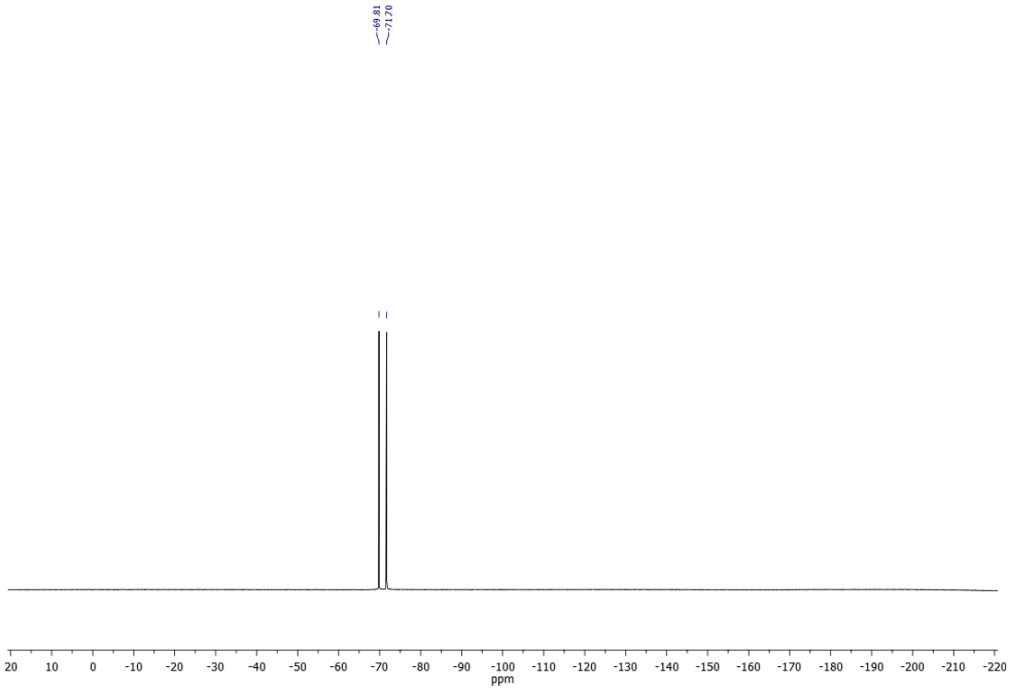


Figure S11. ^{19}F NMR spectrum of compound **3** measured in C_6D_6.

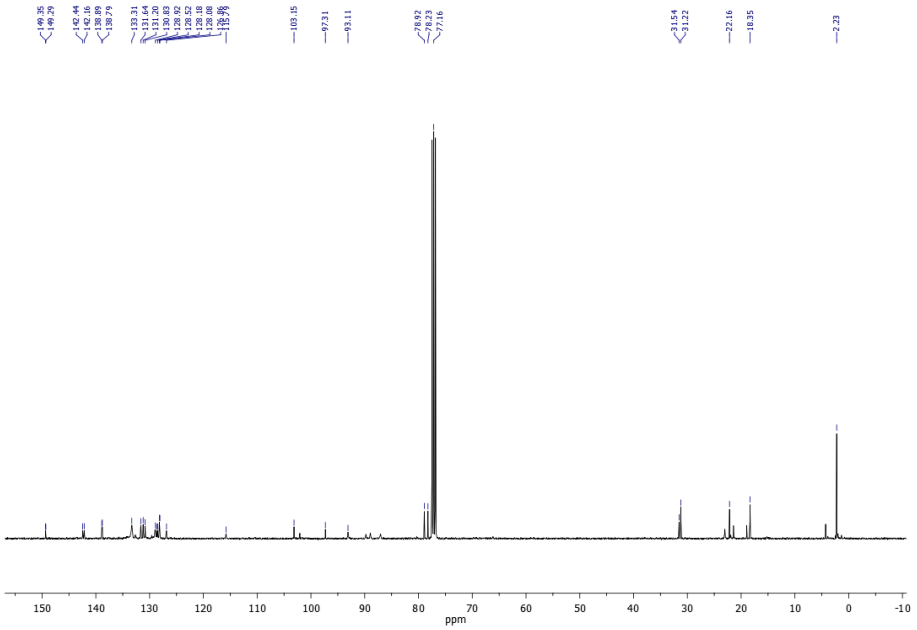


Figure S12. ^{13}C NMR spectrum of compound **3** measured in $CDCl_3$.

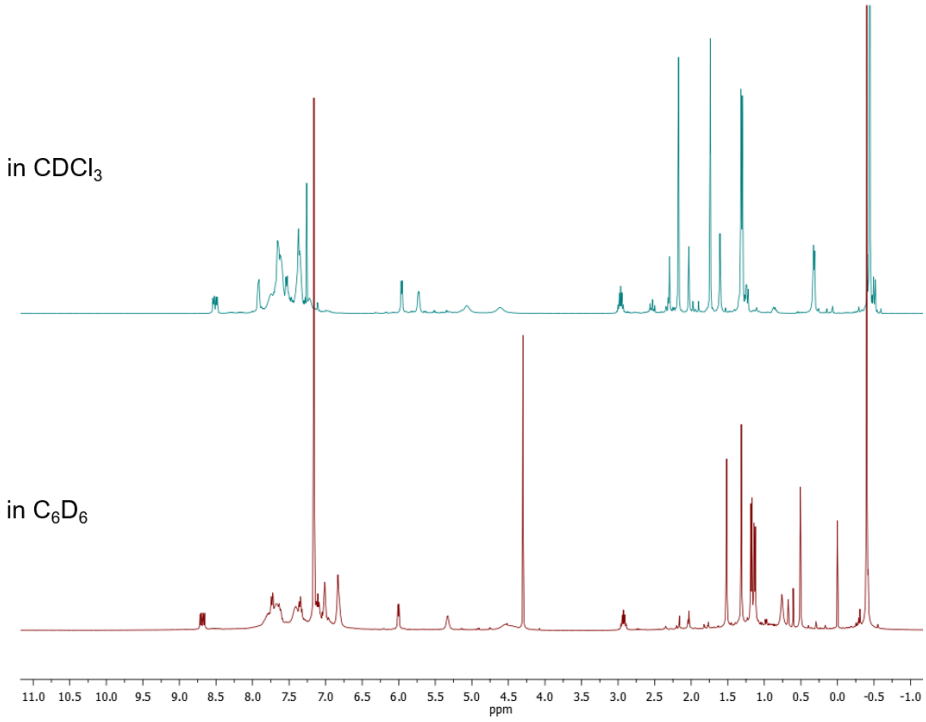


Figure S13. ^{1}H NMR stacking spectrum of compound **3** measured in $CDCl_3$ and C_6D_6.

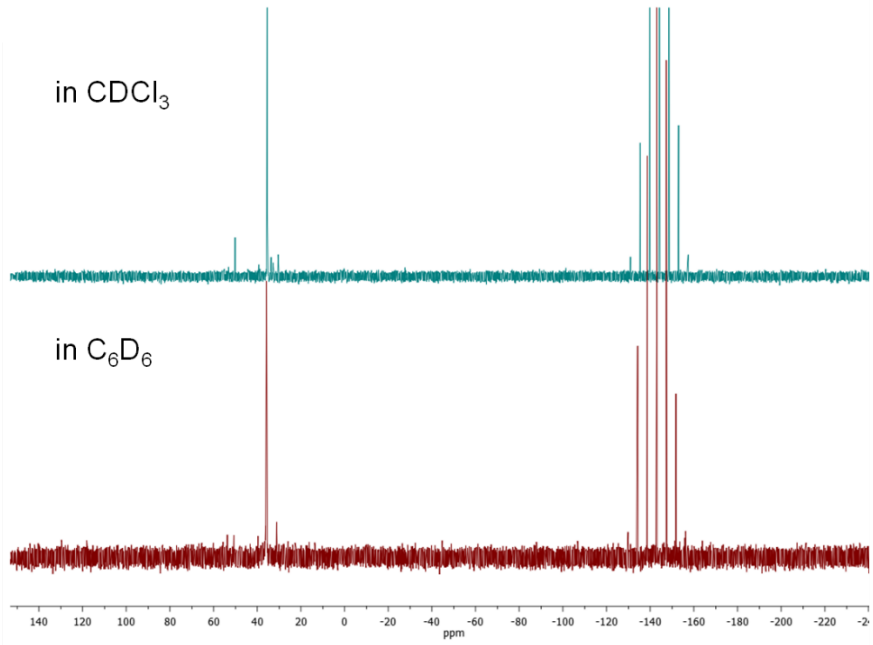


Figure S14. ^{31}P NMR stacking spectrum of compound **3** measured in $CDCl_3$ and C_6D_6.

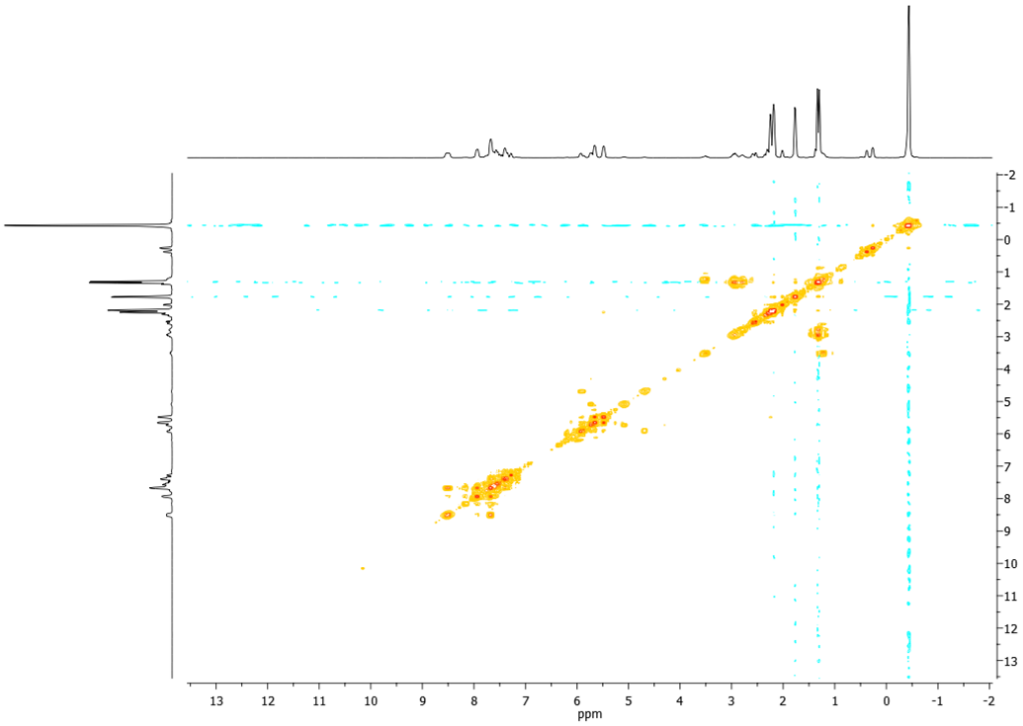


Figure S15. ^{1}H-^{1}H COSY NMR spectrum of compound **3** measured in $CDCl_3$.

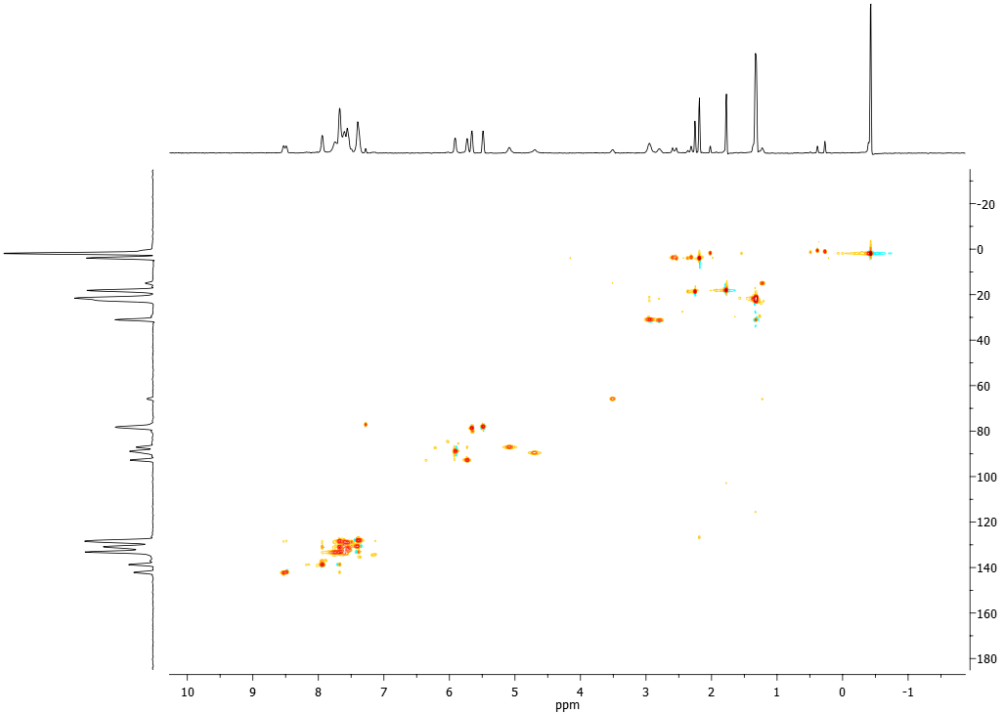


Figure S16. The HSQC spectrum of compound **3** measured in $CDCl_3$.

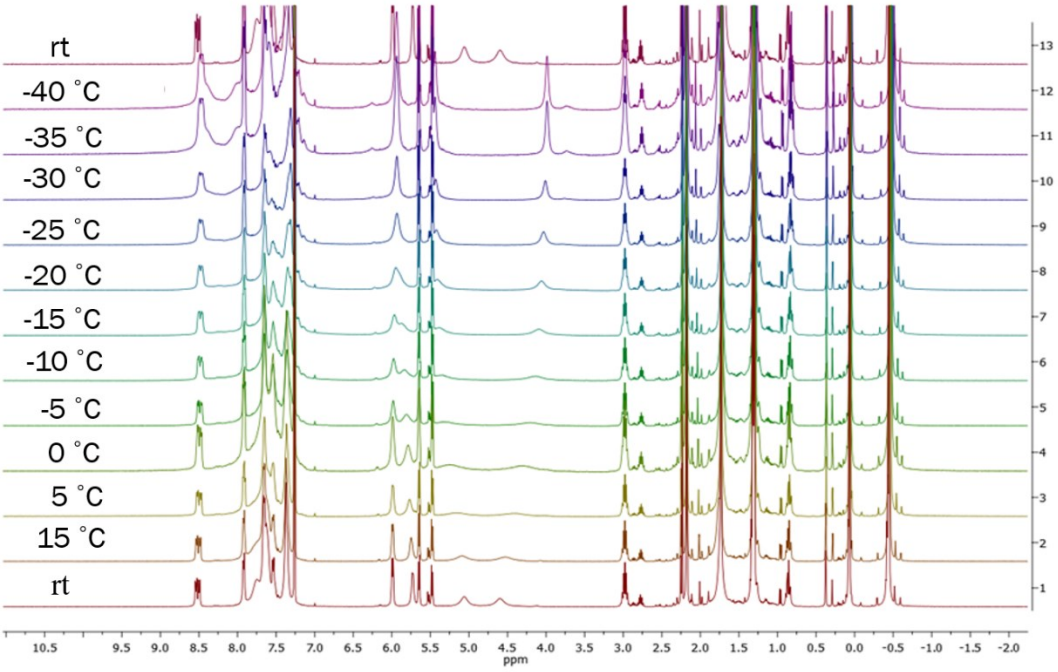


Figure S17. VT {^{1}H} NMR spectra of compound **3** measured in $CDCl_3$.

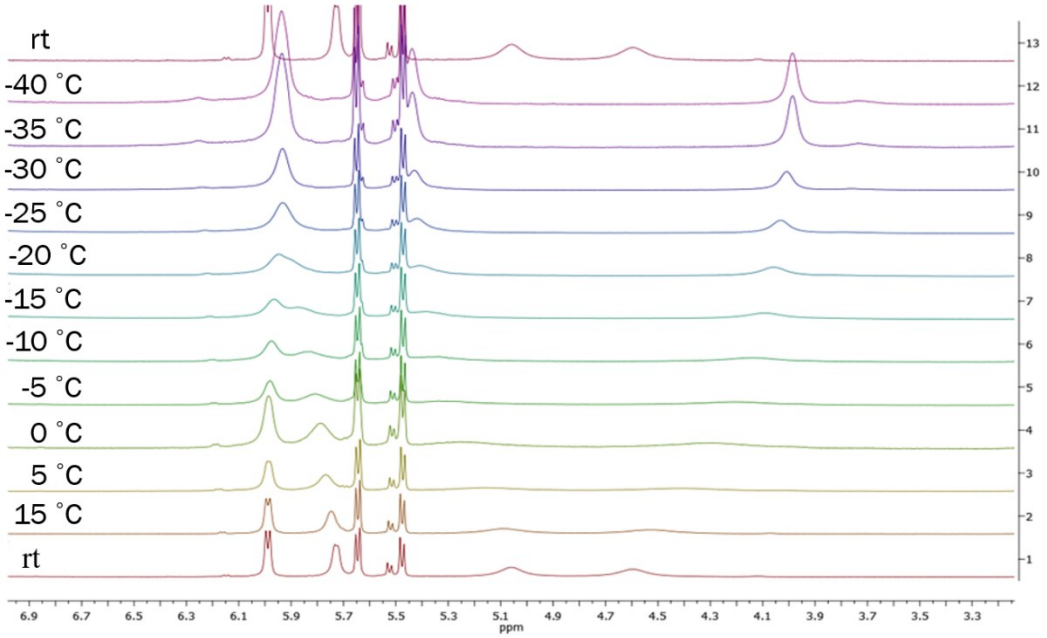


Figure S18. VT {^{1}H} NMR spectra of compound **3** measured in $CDCl_3$ (*p*-cymene proton region).

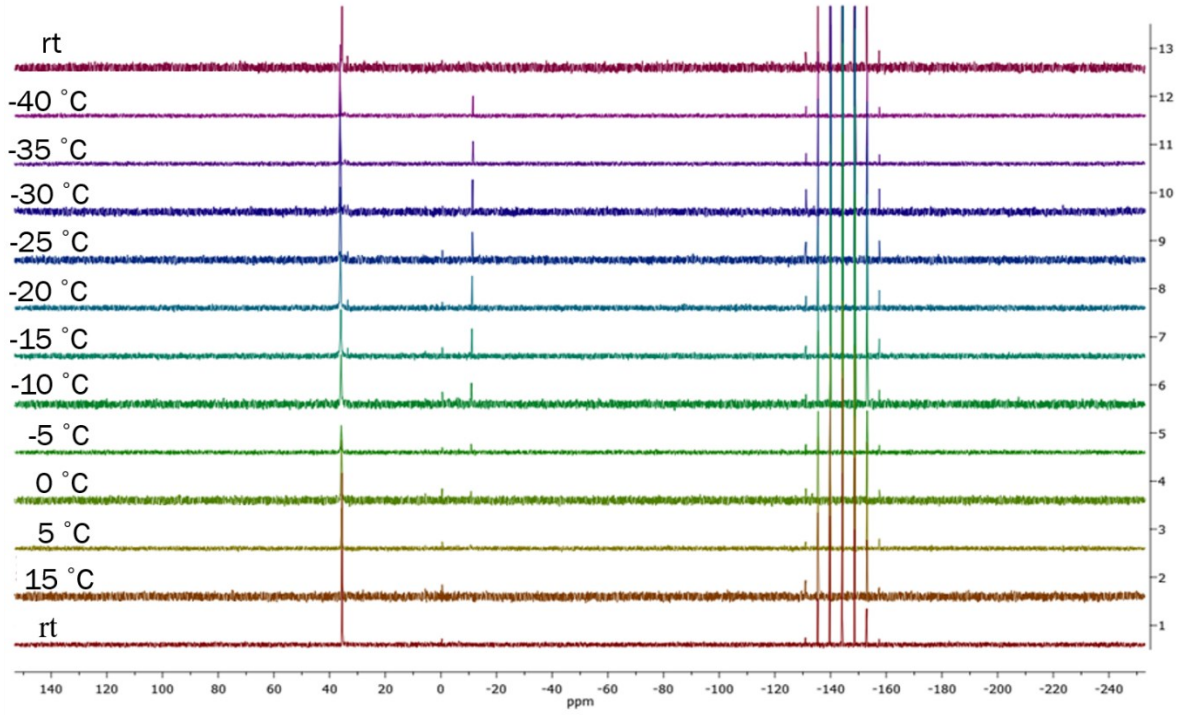


Figure S19. VT $\{^{31}P\}$ NMR spectra of compound **3** measured in $CDCl_3$.

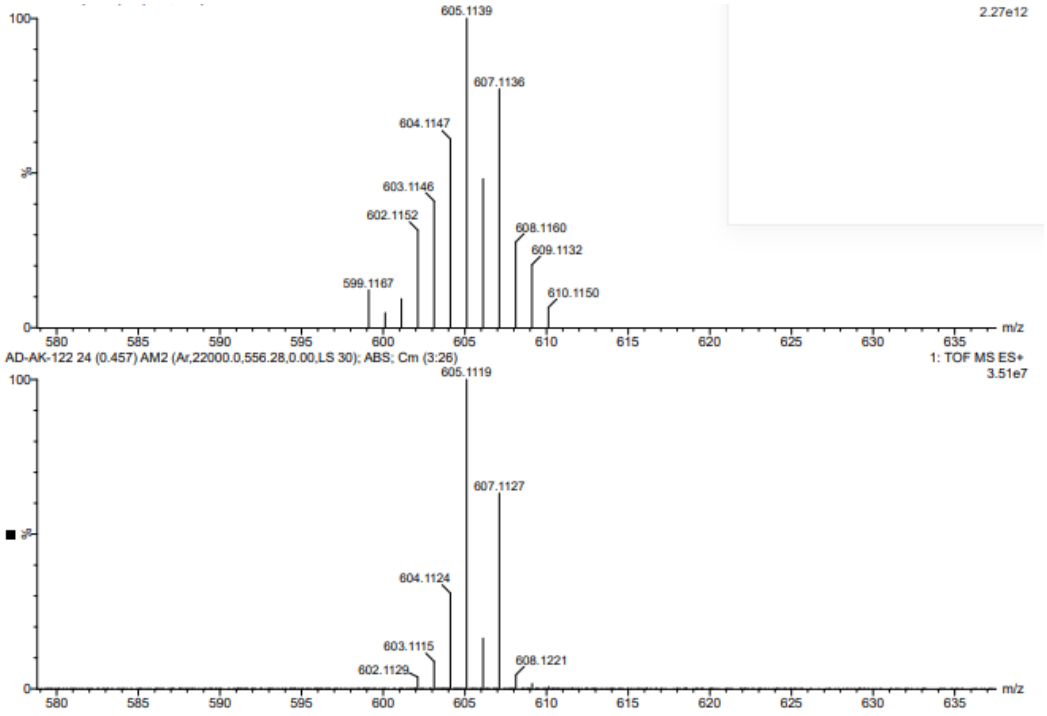


Figure S20. ESI-HRMS spectrum of compound **3** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

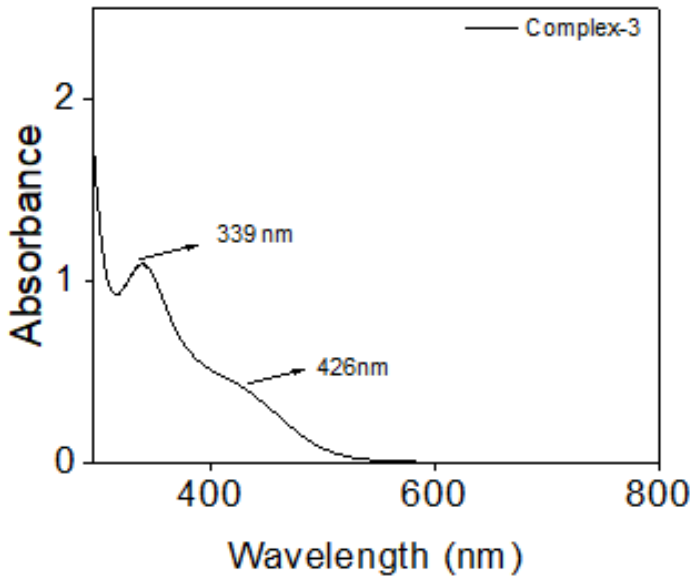


Figure S21. UV-Vis spectrum of the complex **3** in CH_2Cl_2 medium.

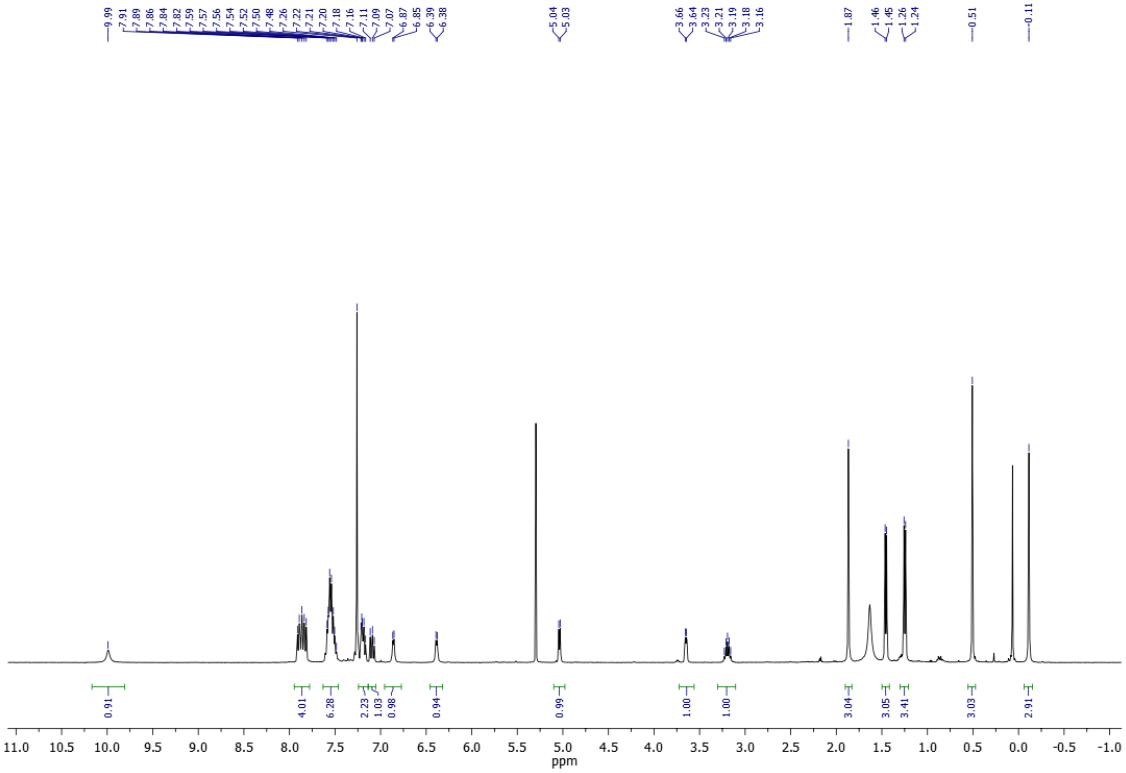


Figure S22. ^{1}H NMR spectrum of compound **5** measured in $CDCl_3$.

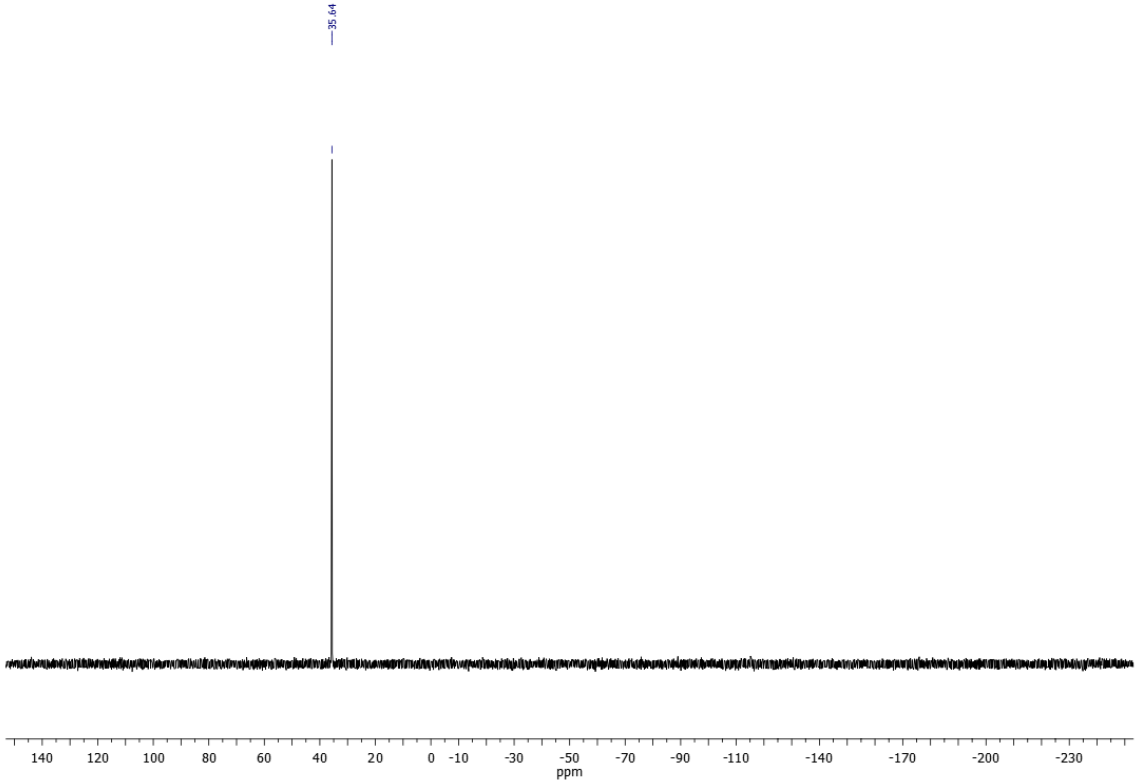


Figure S23. $^{31}P\{^{1}H\}$ NMR spectrum of compound **5** measured in $CDCl_3$.

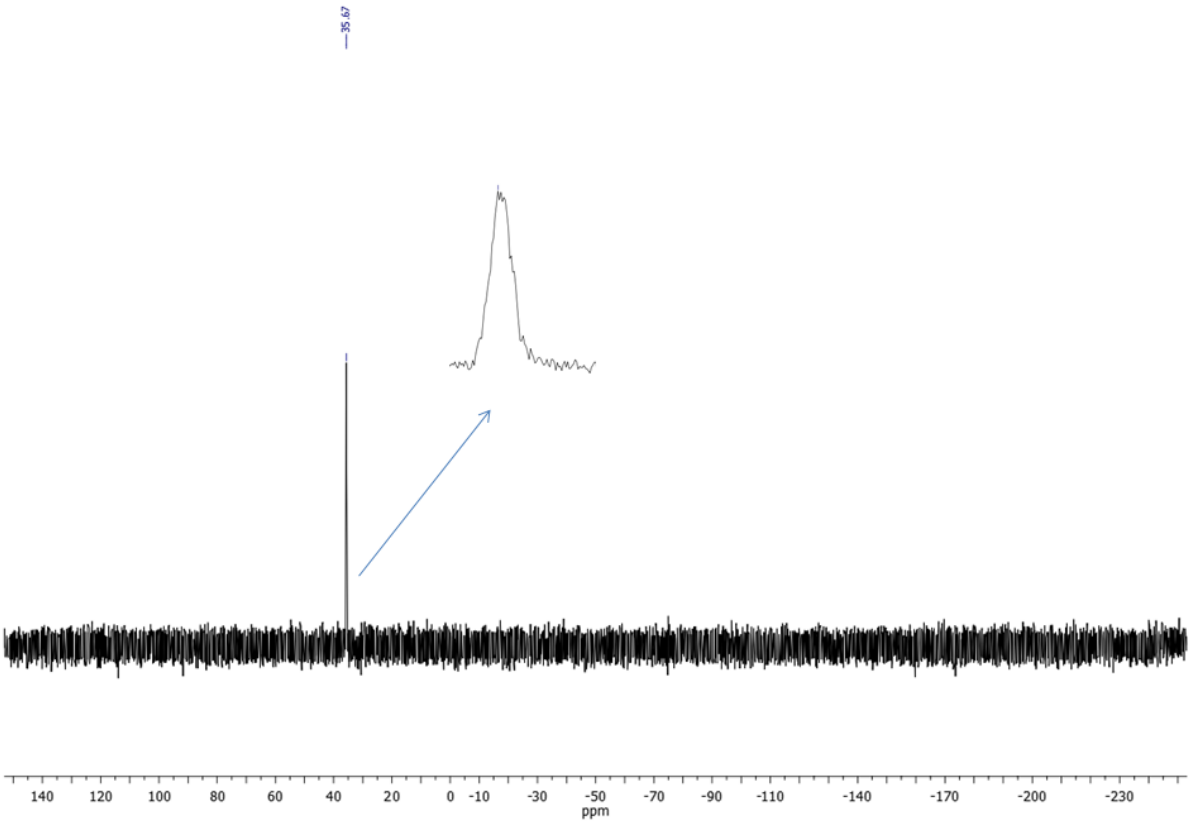


Figure S24. ^{31}P NMR spectrum of compound **5** measured in $CDCl_3$.

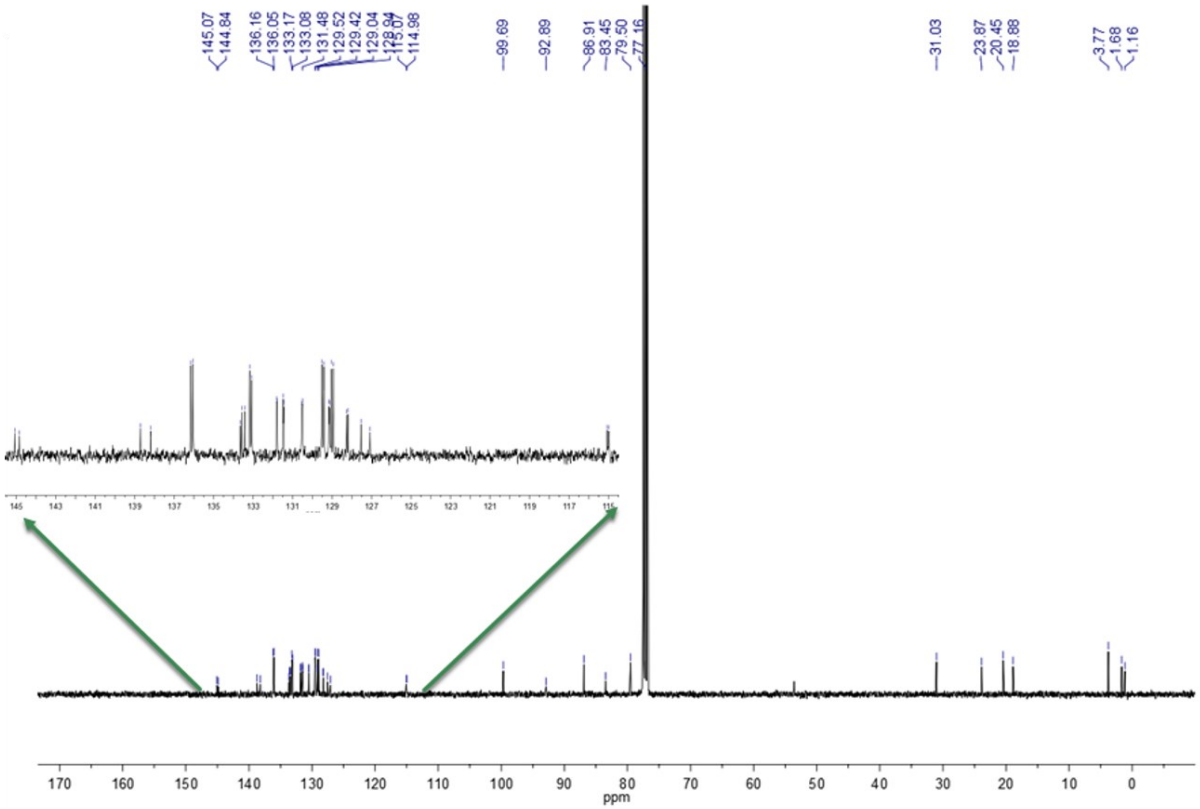


Figure S25. ^{13}C NMR spectrum of compound **5** measured in $CDCl_3$.

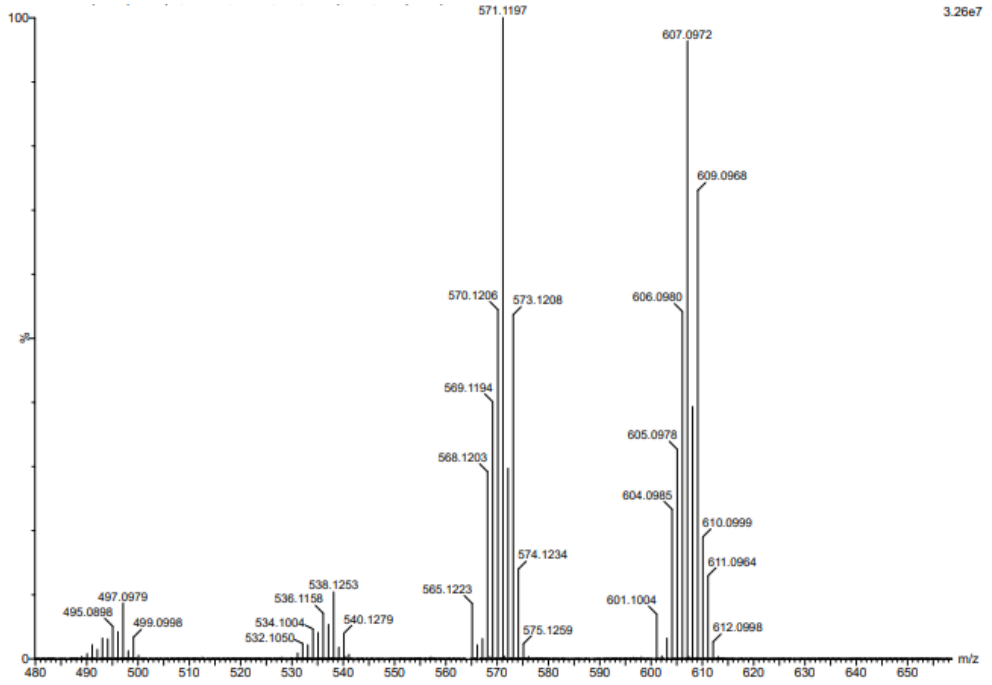


Figure S26. ESI-HRMS spectrum of compound **5** measured in acetonitrile.

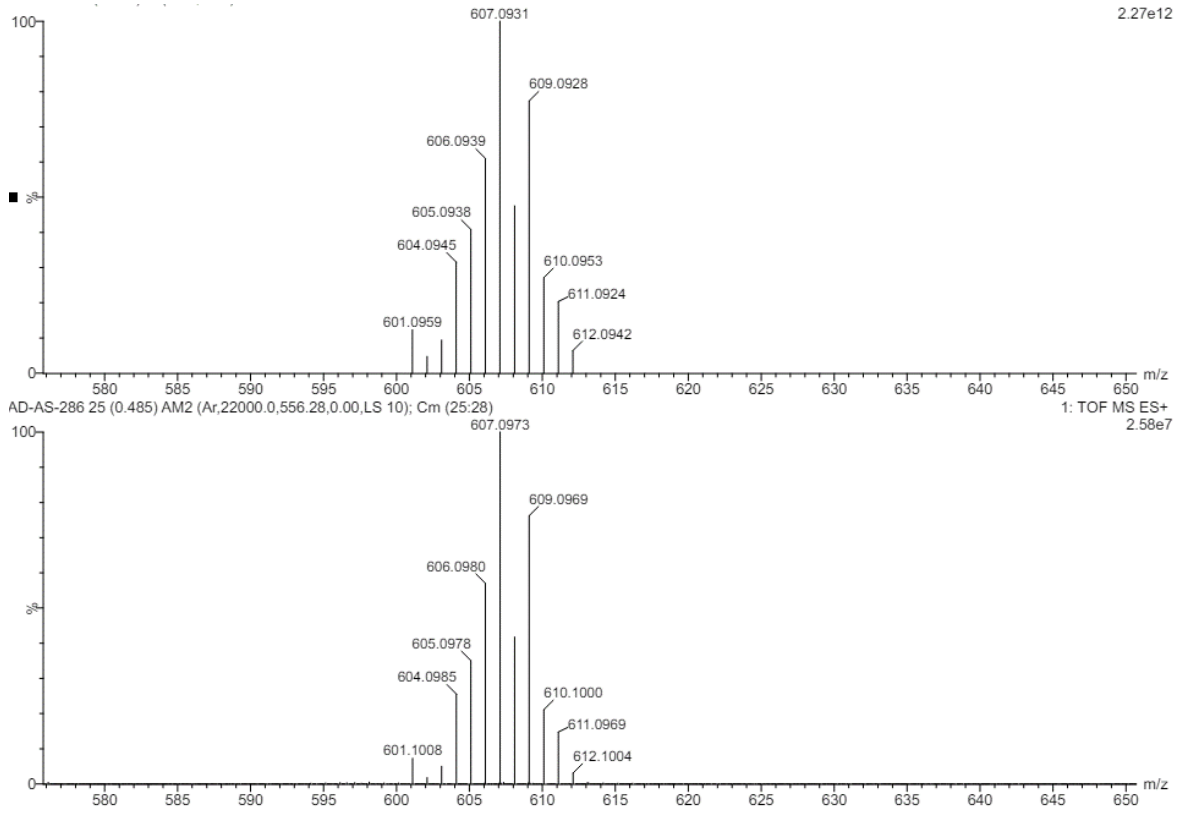


Figure S27. ESI-HRMS spectrum of compound **5** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

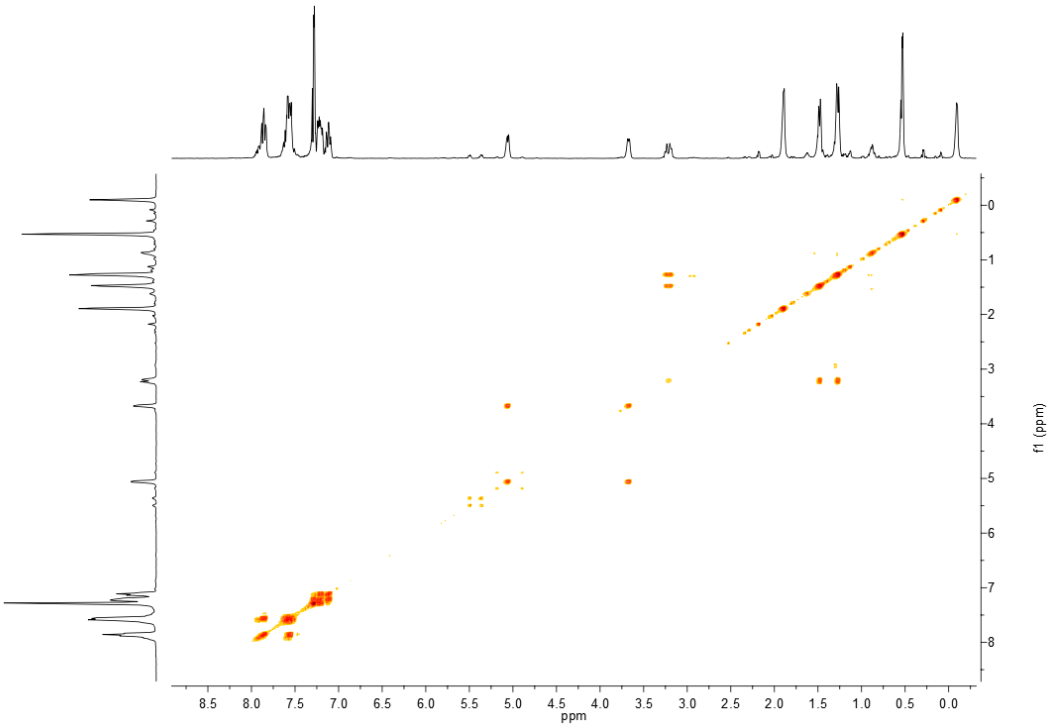


Figure S28. ^{1}H-^{1}H COSY NMR spectrum of compound **5** measured in $CDCl_3$

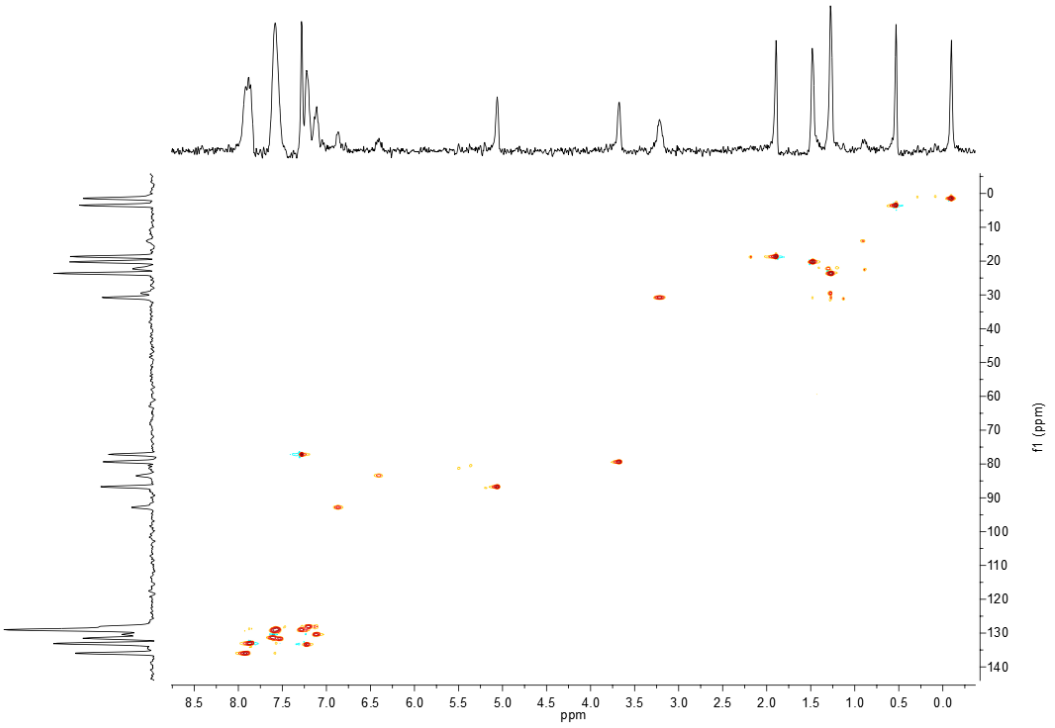


Figure S29. HSQC spectrum of compound **5** measured in $CDCl_3$

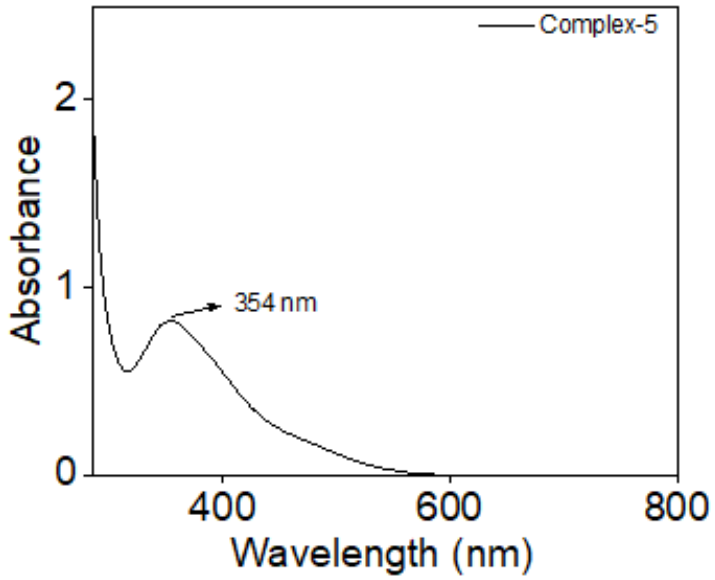


Figure S30. UV-Vis spectrum of the complex **5** in CH_2Cl_2 medium.

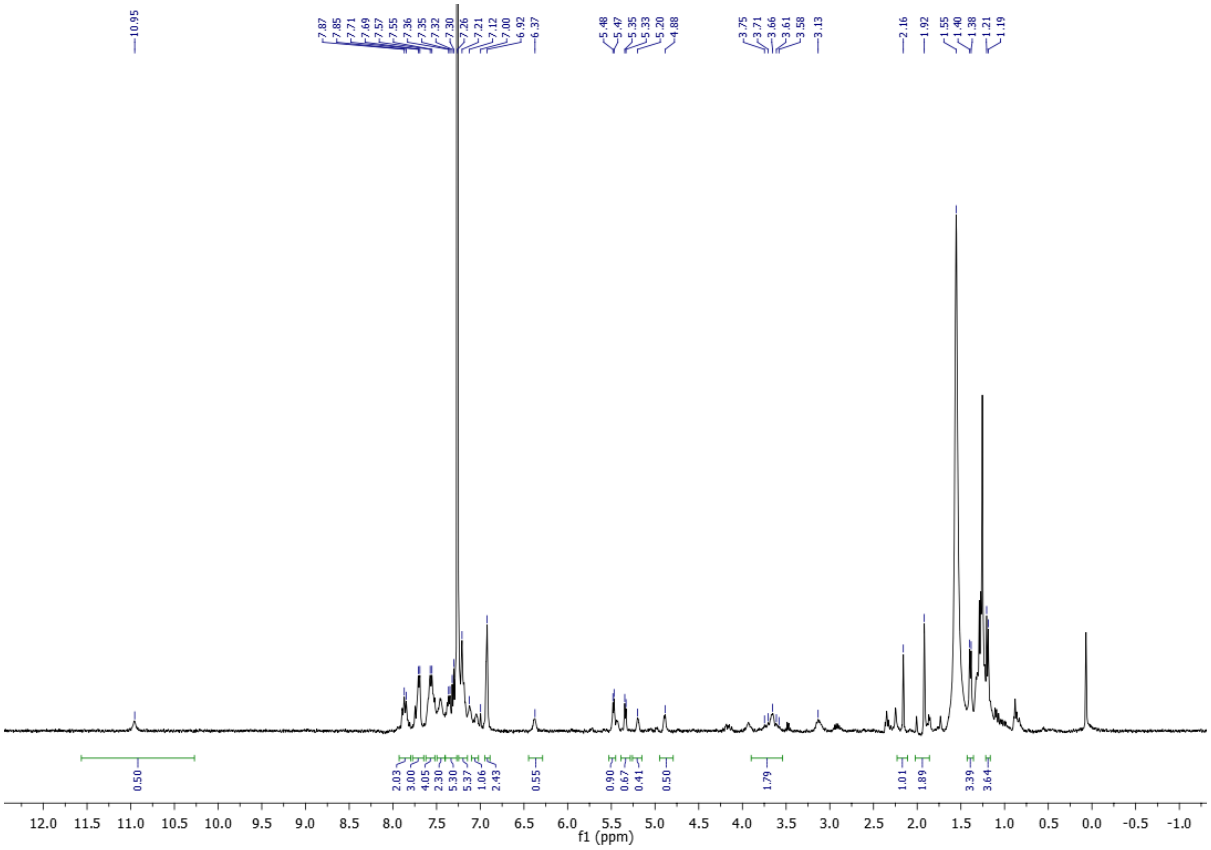


Figure S31. ^{1}H NMR spectrum of compound **6** measured in $CDCl_3$.

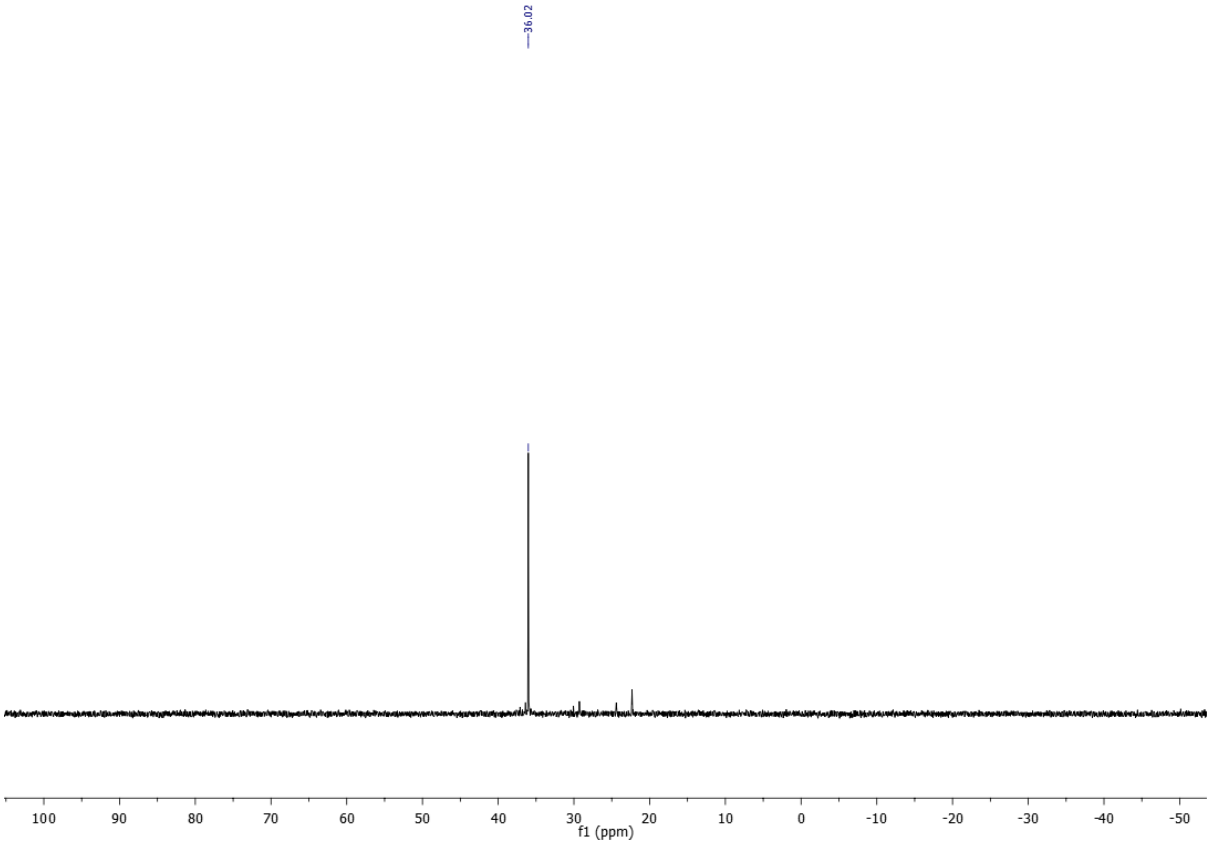


Figure S32. $^{31}P(^{1}H)$ NMR spectrum of compound **6** measured in $CDCl_3$.

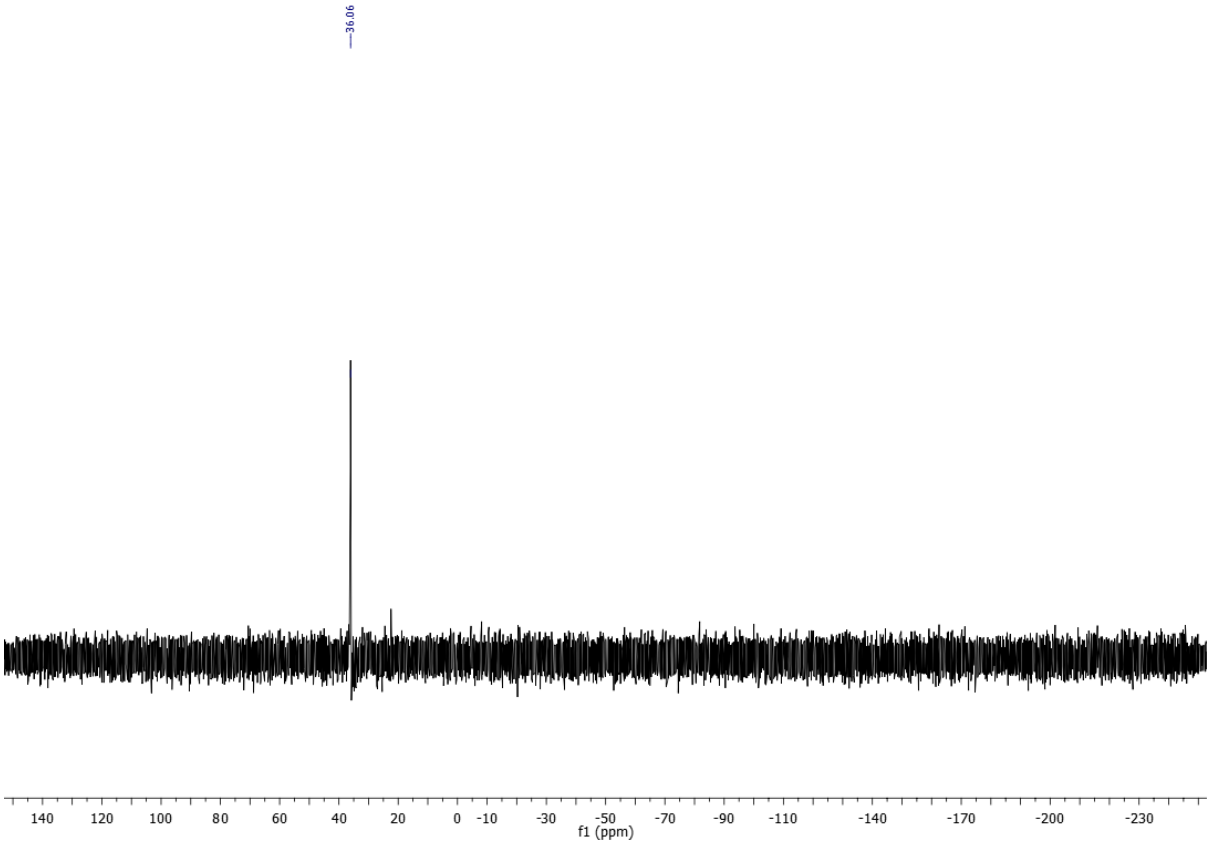


Figure S33. ^{31}P NMR spectrum of compound **6** measured in $CDCl_3$.

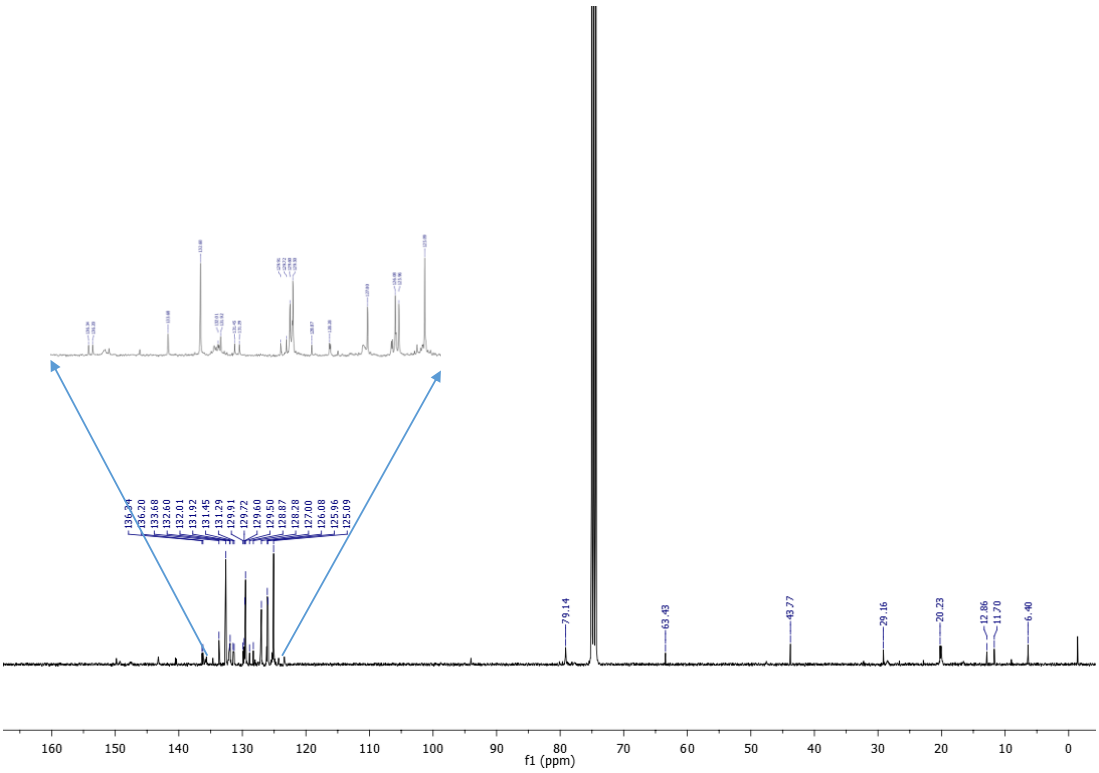


Figure S34. ^{13}C NMR spectrum of compound **6** measured in $CDCl_3$.

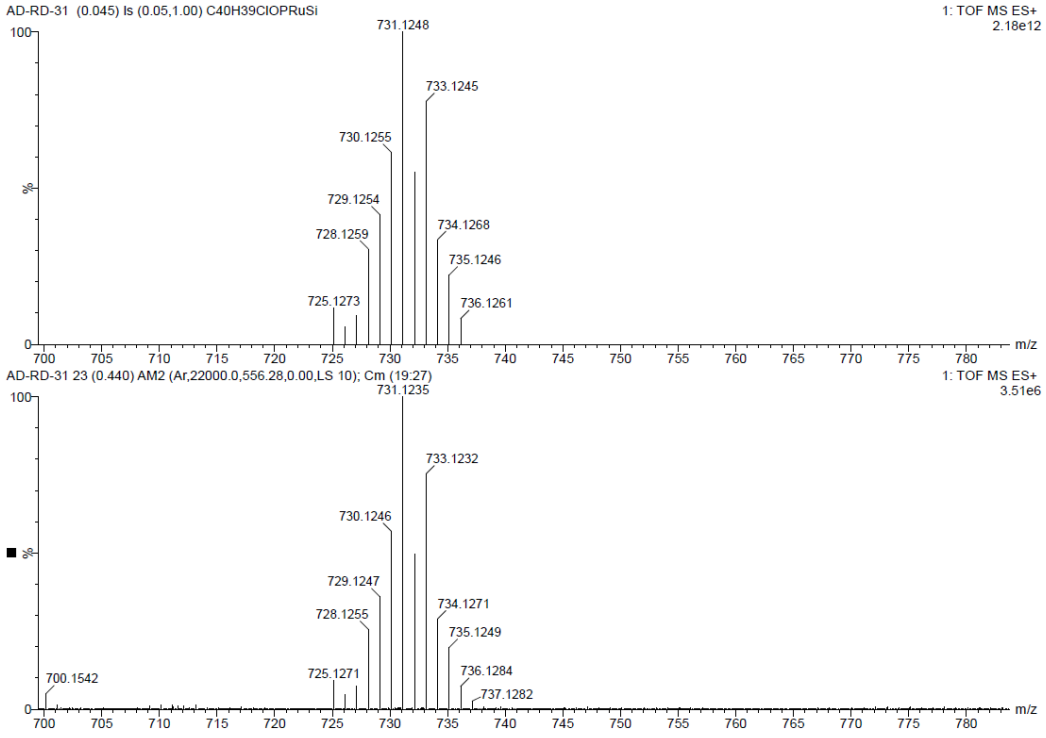


Figure 35. ESI-HRMS spectrum of compound **6** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

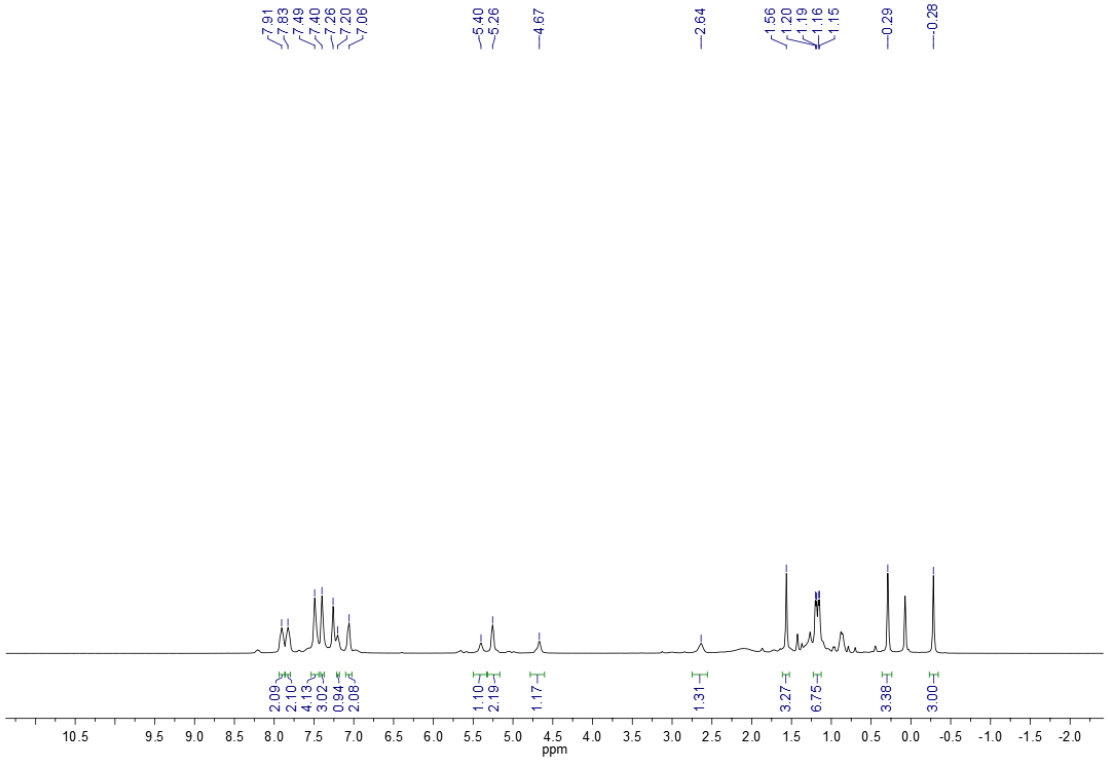


Figure S36. ^{1}H NMR spectrum of compound **5'** measured in $CDCl_3$.

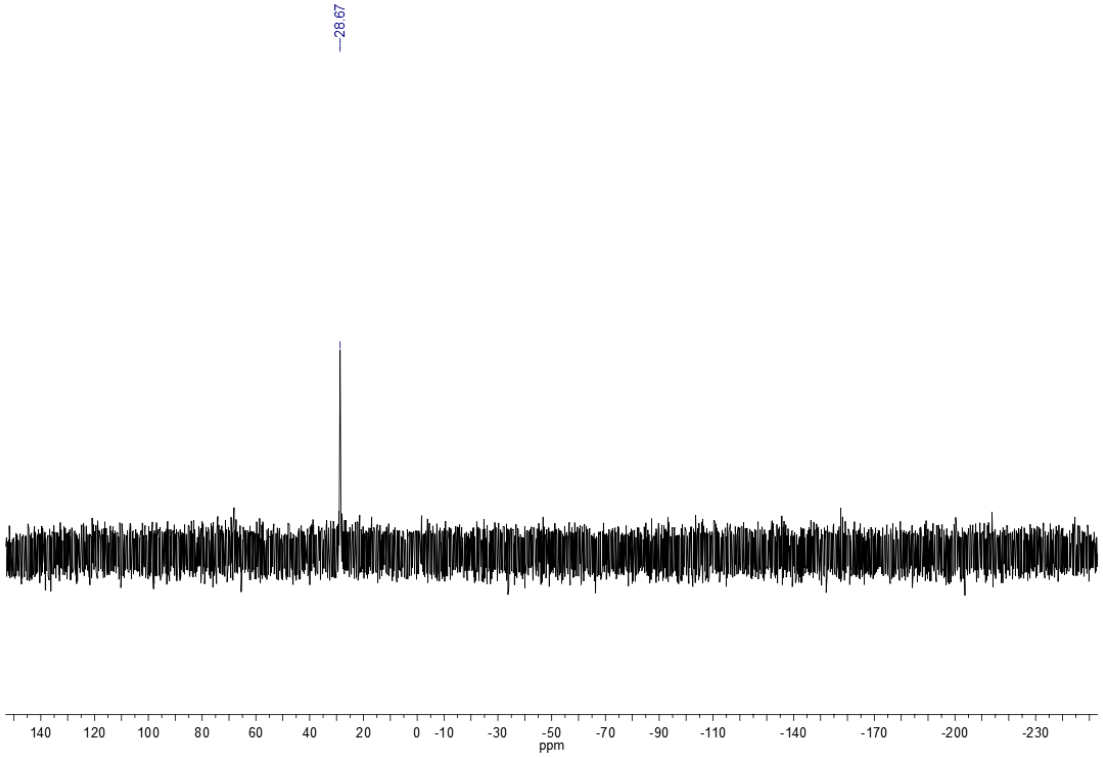


Figure S37. ^{31}P NMR spectrum of compound **5'** measured in $CDCl_3$.

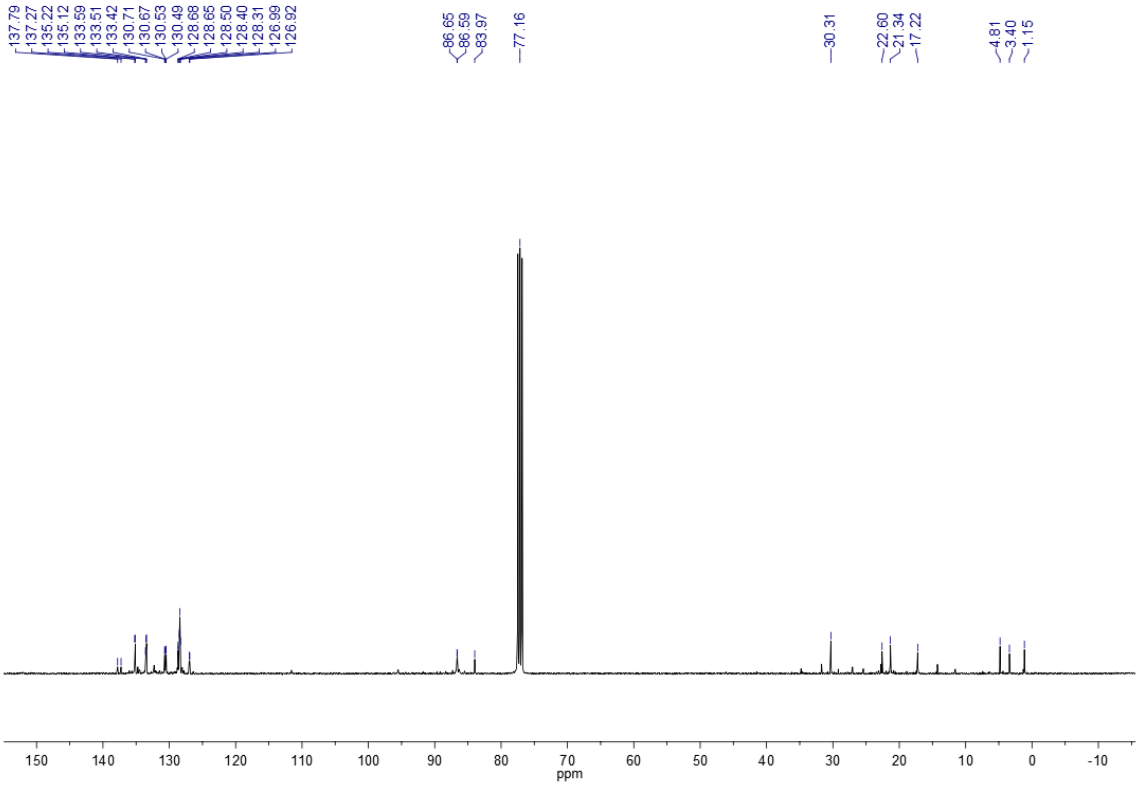


Figure S38. ^{13}C NMR spectrum of compound **5'** measured in $CDCl_3$.

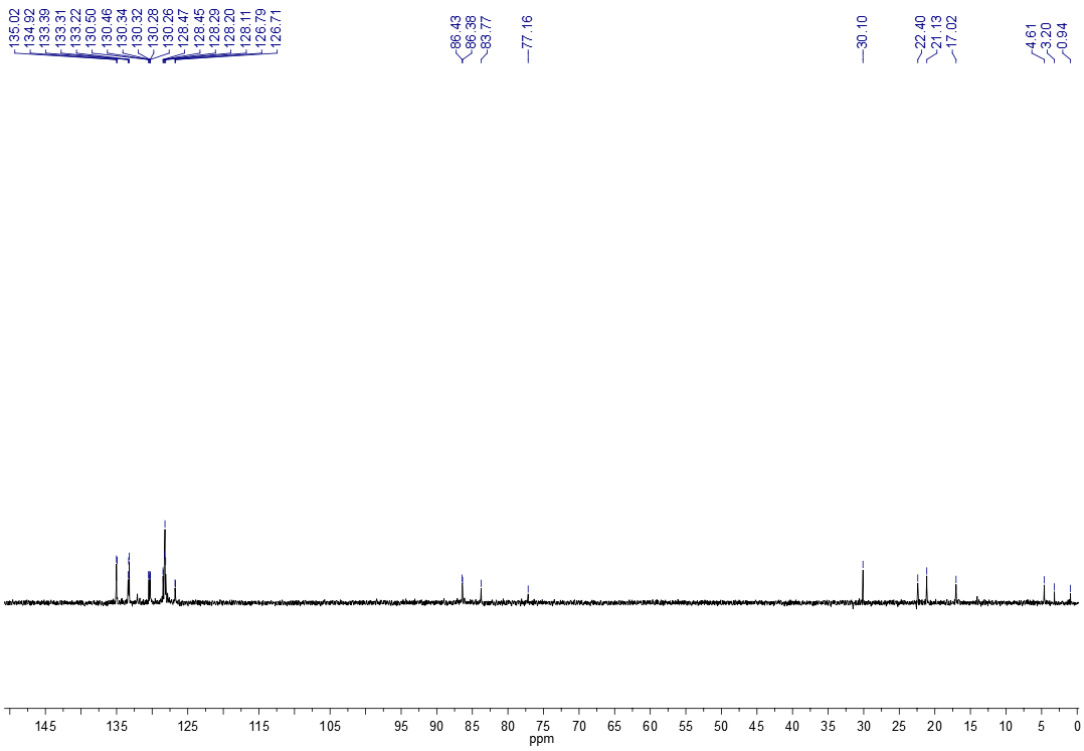


Figure S39. DEPT-135{^{13}C} NMR spectrum of compound **5'** measured in $CDCl_3$.

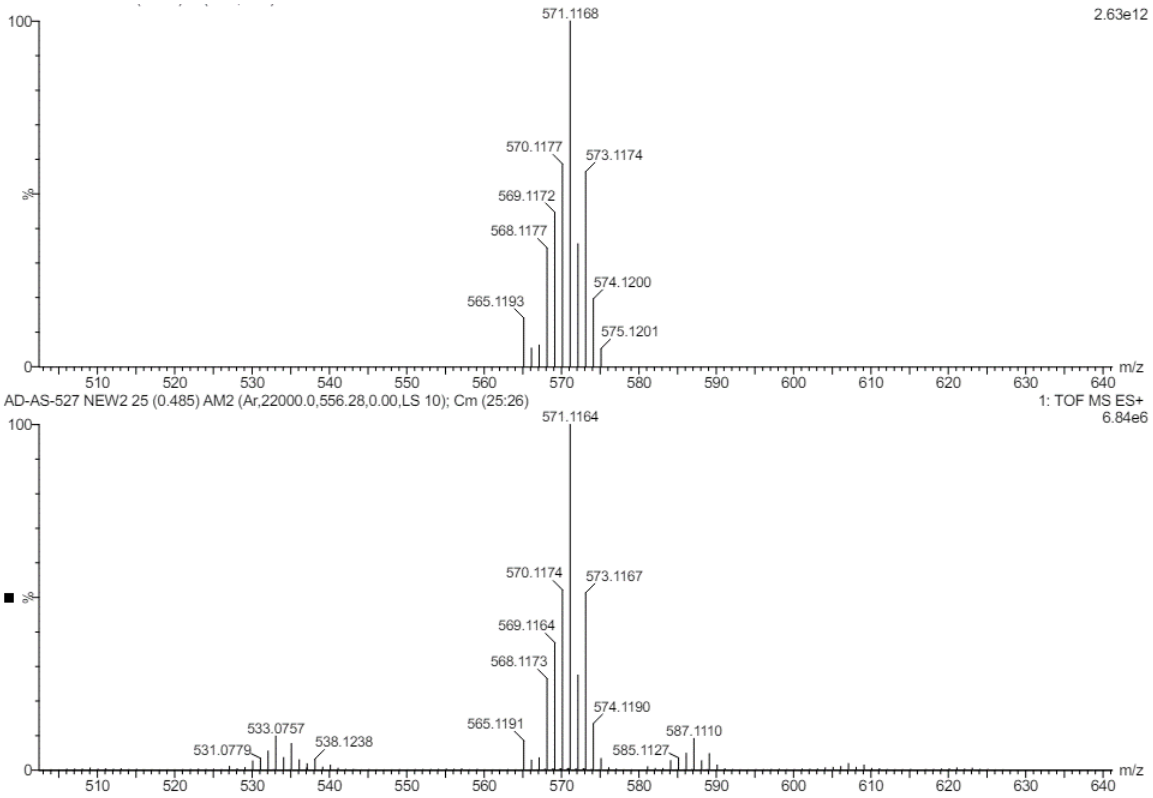


Figure 40. ESI-HRMS spectrum of compound **5'** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

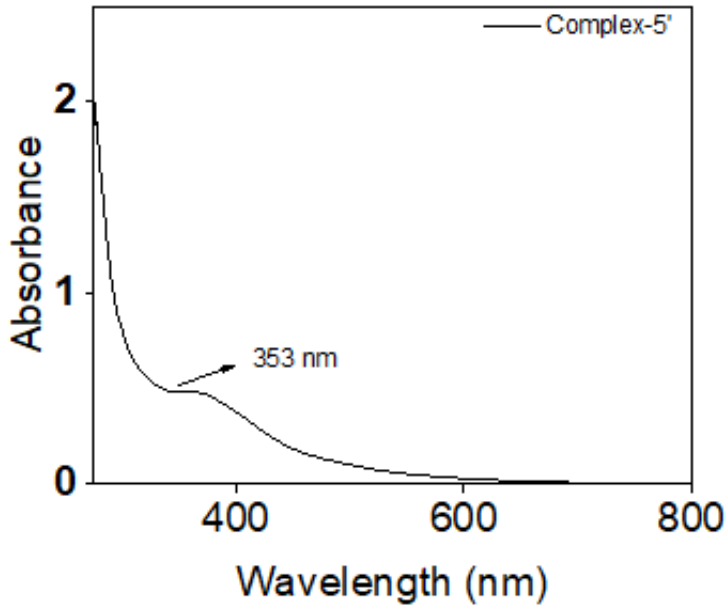


Figure S41. UV-Vis spectrum of the complex **5'** in CH_2Cl_2 medium.

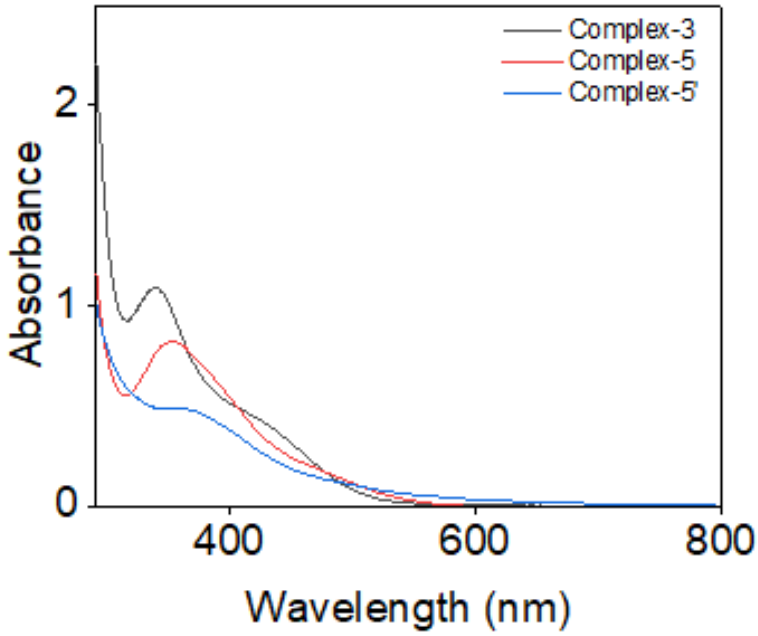
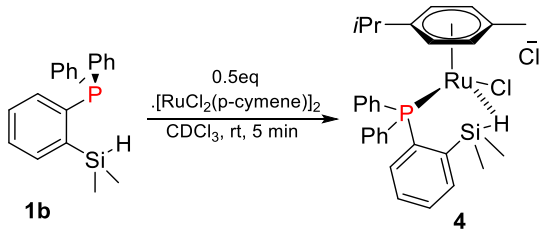


Figure S42. Stacking UV-Vis spectrum of the complexes **3**, **5**, **5'** in CH_2Cl_2 medium.

Plausible mechanism for the formation of compound 4 through NMR experiment studies



Scheme S2. NMR experiment determination of complex **4**.

Synthetic procedure for NMR experiments-1

A solution comprising 12 mg of silylated phosphine **1b** in 0.4 ml of $CDCl_3$ was prepared in an Eppendorf vial. Similarly, another Eppendorf vial containing 9 mg of (p-Cymene) ruthenium (II) chloride dimer was added to 0.4 ml of $CDCl_3$. Subsequently, both solutions were transferred to NMR tube under an argon atmosphere. The transition in color of the reaction mixture to a vivid blood red was observed. Subsequent proton and phosphorus NMR spectroscopy analyses were conducted at regular intervals. The spectra revealed the presence of intermediate **A** and **4** in the reaction mixture. Notably, a characteristic doublet in the proton NMR spectrum at -7.24 ppm suggested a potential Si-H-Ru interaction, corroborating the presence of intermediate **4**. Furthermore, the phosphorus NMR spectrum displayed a singlet at 28.4 ppm indicative of intermediate **A** and the peak at 55.3 ppm for **4**.

Supporting spectral data

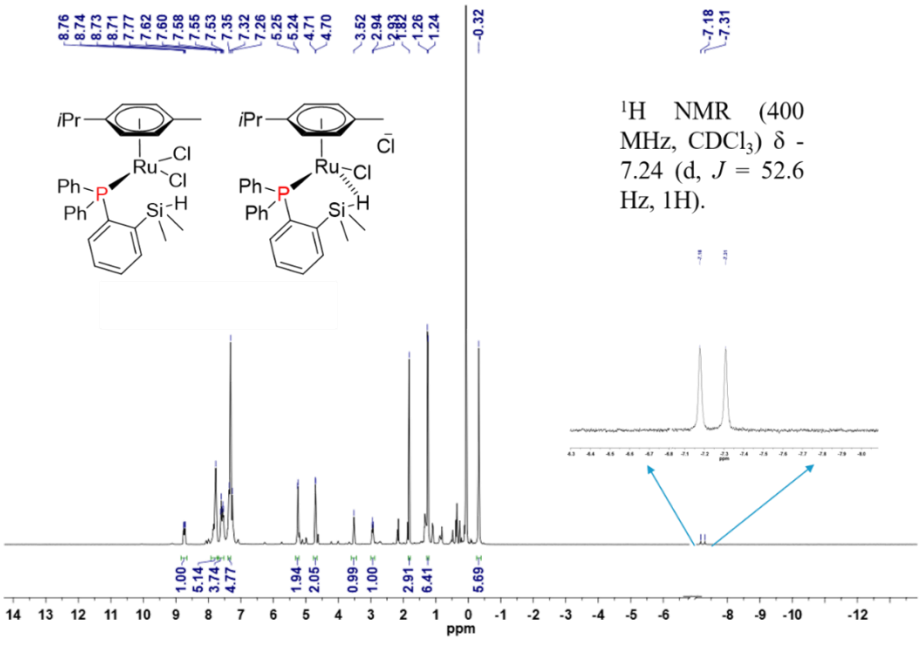


Figure S43. ^{1}H NMR of reaction mixture after 5 min showing the presence of intermediate **A** and **4** measured in $CDCl_3$.

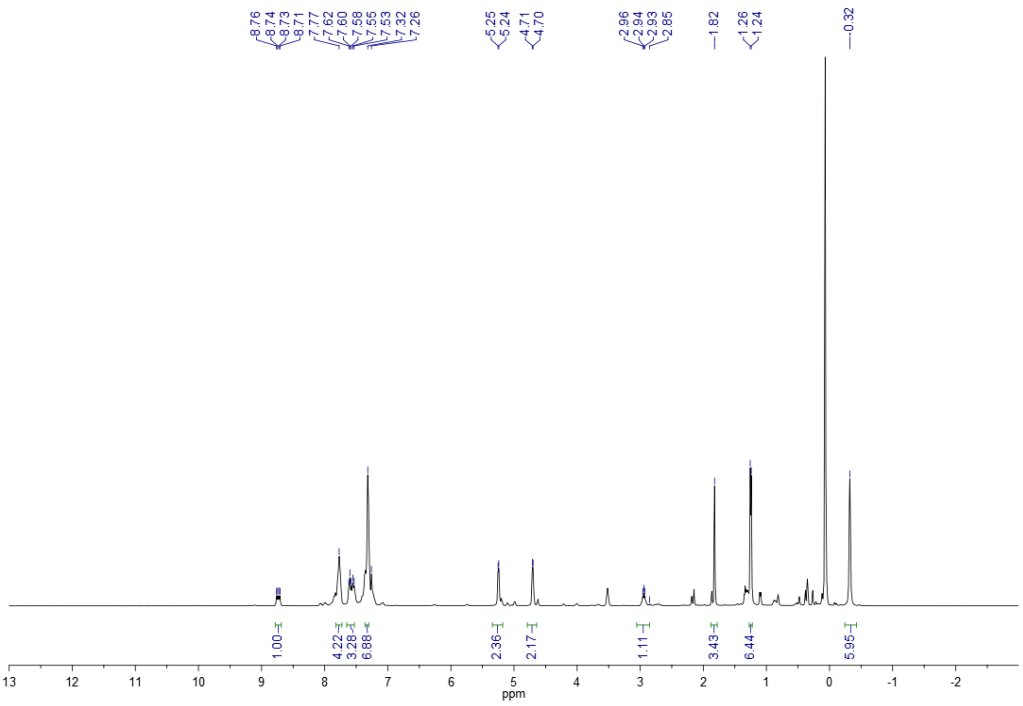


Figure S44. ^{1}H NMR of reaction mixture after 5 min showing the presence of intermediate **A** and **4** measured in $CDCl_3$.

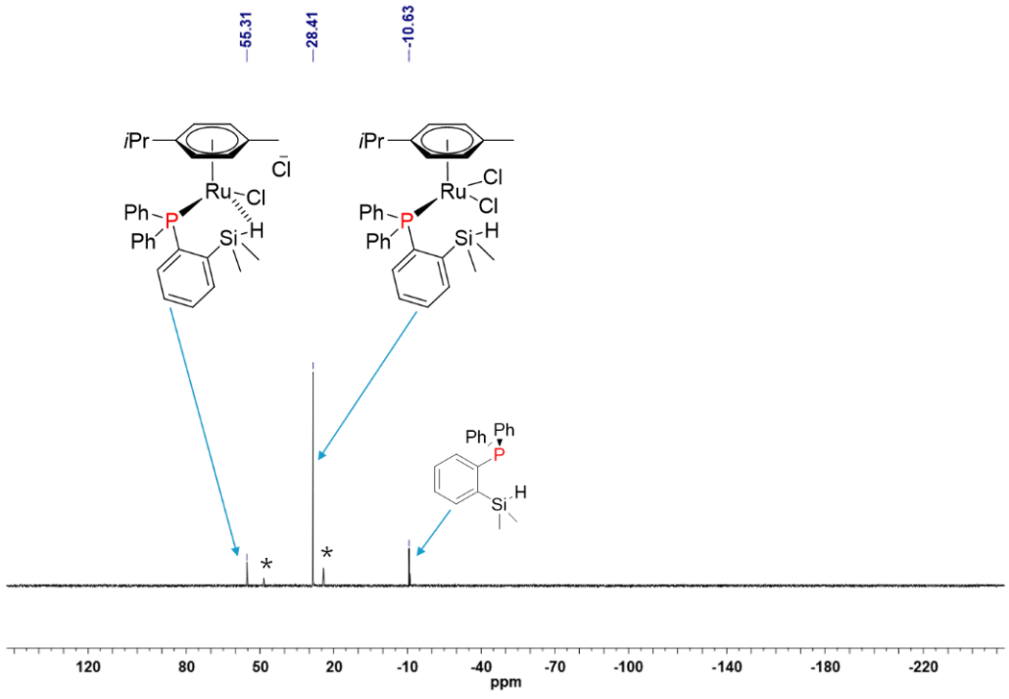


Figure S45. ^{31}P NMR of reaction mixture after 5 min showing the presence of intermediate **A** and **4** measured in $CDCl_3$. (* = Unidentified impurities).

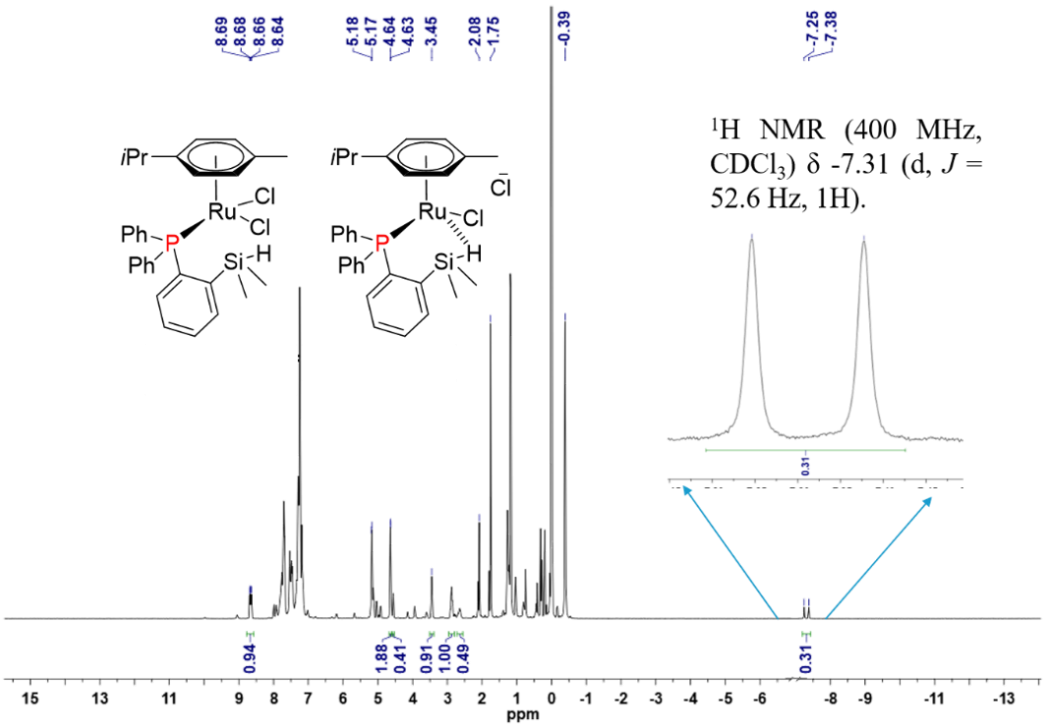


Figure S46. ^{1}H NMR of reaction mixture after 10 min showing the presence of intermediate **A** and **4** measured in $CDCl_3$.

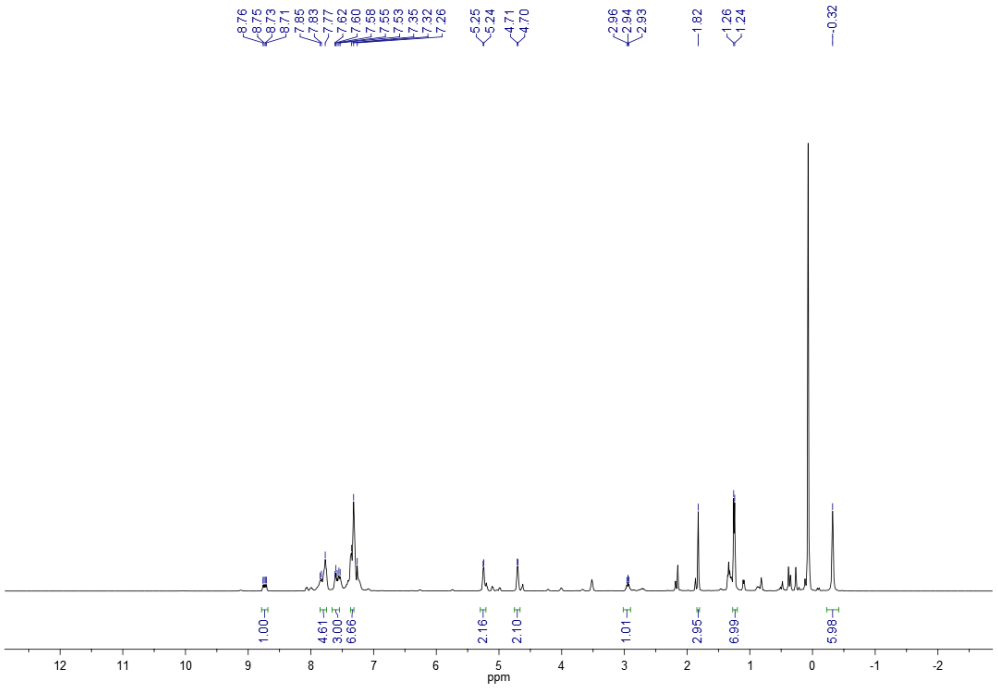


Figure S47. ^{1}H NMR of reaction mixture after 10 min showing the presence of intermediate **A** and **4** measured in $CDCl_3$.

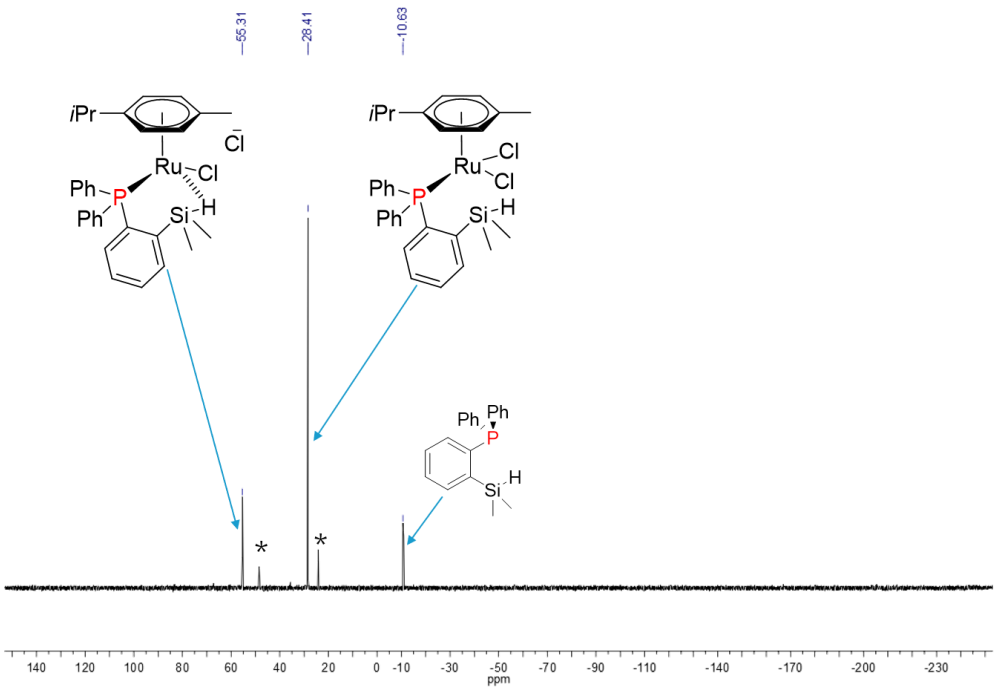


Figure S48. ^{31}P NMR of reaction mixture after 10 min showing the presence of intermediate **A** and **4** measured in $CDCl_3$. (* = Unidentified impurities).

Synthetic procedure for NMR experiments-2

A solution comprising 24 mg of silylated phosphine **1b** in 0.4 mL of C_6D_6 was prepared in an Eppendorf vial. Similarly, another Eppendorf vial containing 19 mg of (p-cymene) ruthenium (II) chloride dimer was added to 0.4 mL of C_6D_6. Subsequently, both solutions were transferred to NMR tube under an argon atmosphere. The transition in color of the reaction mixture to a vivid blood red was observed. Subsequent proton and phosphorus NMR spectroscopy analyses were conducted at regular intervals. The spectra revealed the presence of intermediate **A** and **4** in the reaction mixture. Notably, a characteristic doublet in the proton NMR spectrum at -6.89 ppm suggested a potential Si-H-Ru interaction, corroborating the presence of intermediate **4**. Furthermore, the phosphorus NMR spectrum displayed a singlet at 55.26 ppm indicative of intermediate **4**.

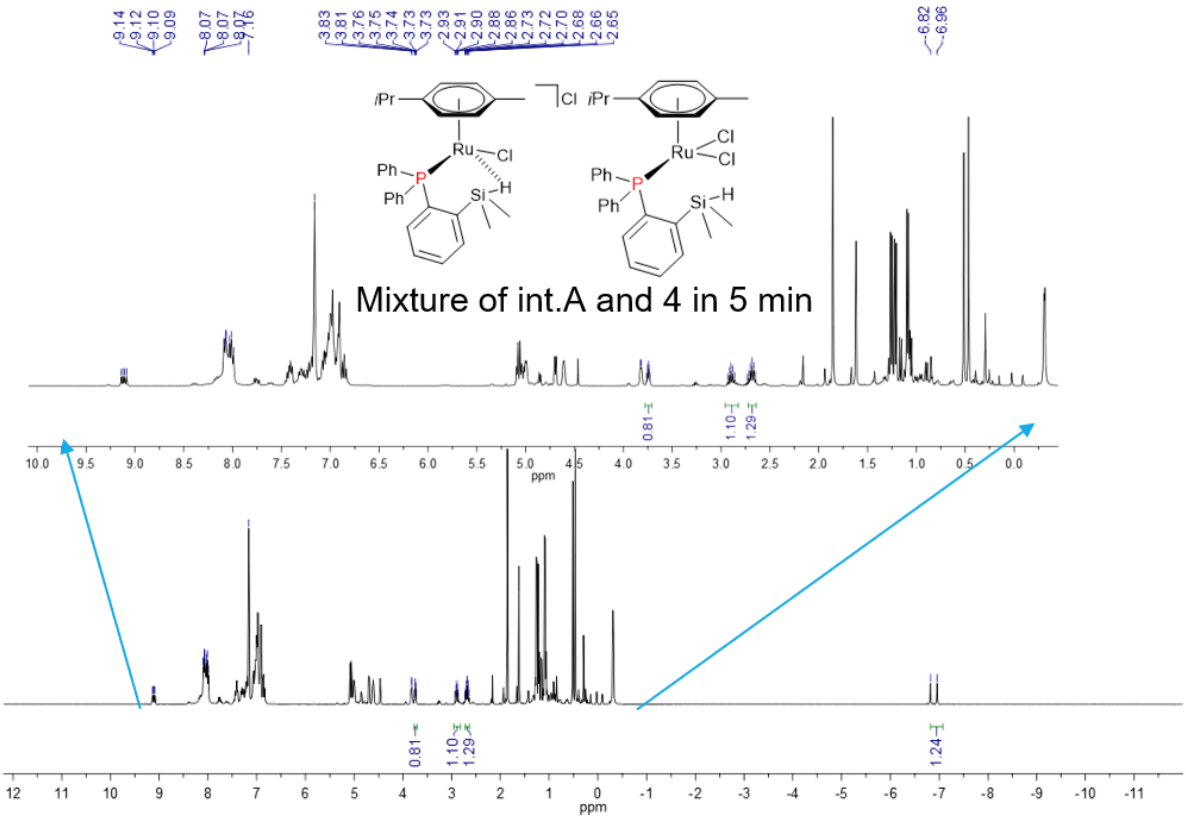


Figure S49. ^{1}H NMR of reaction mixture after 5 min, showing the presence of both intermediate **int. A** and **4**.

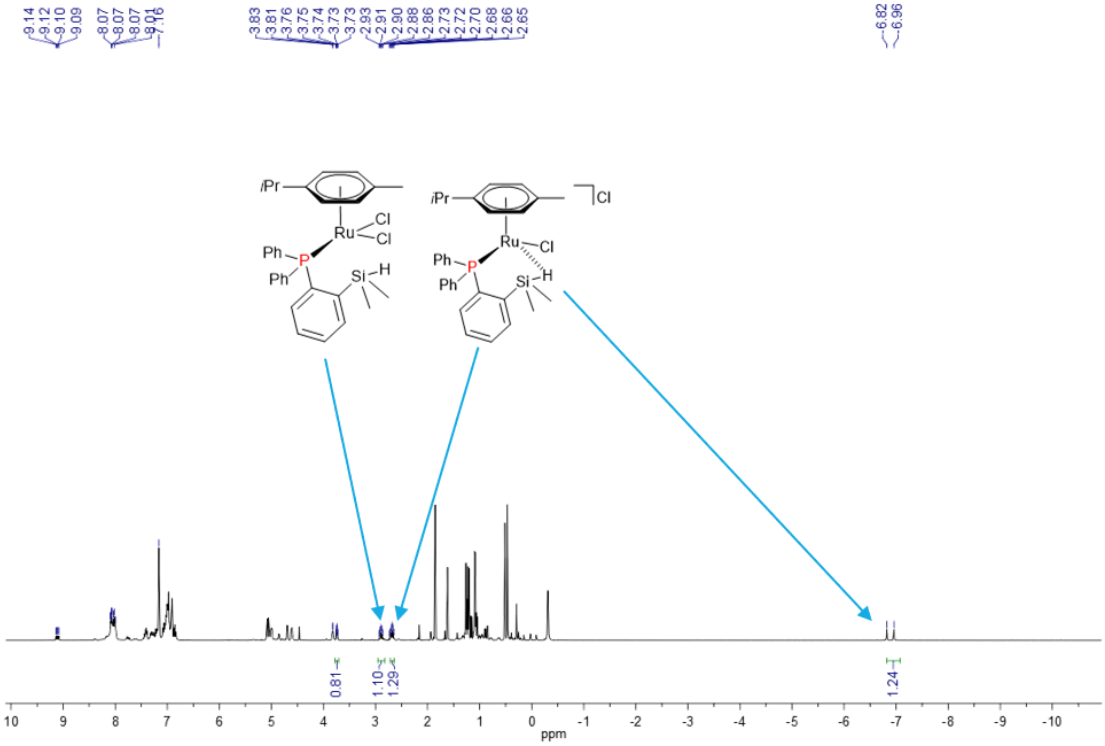


Figure S50. ^{1}H NMR of reaction mixture after 5 min, showing the presence of both intermediate **int. A** and **4**.

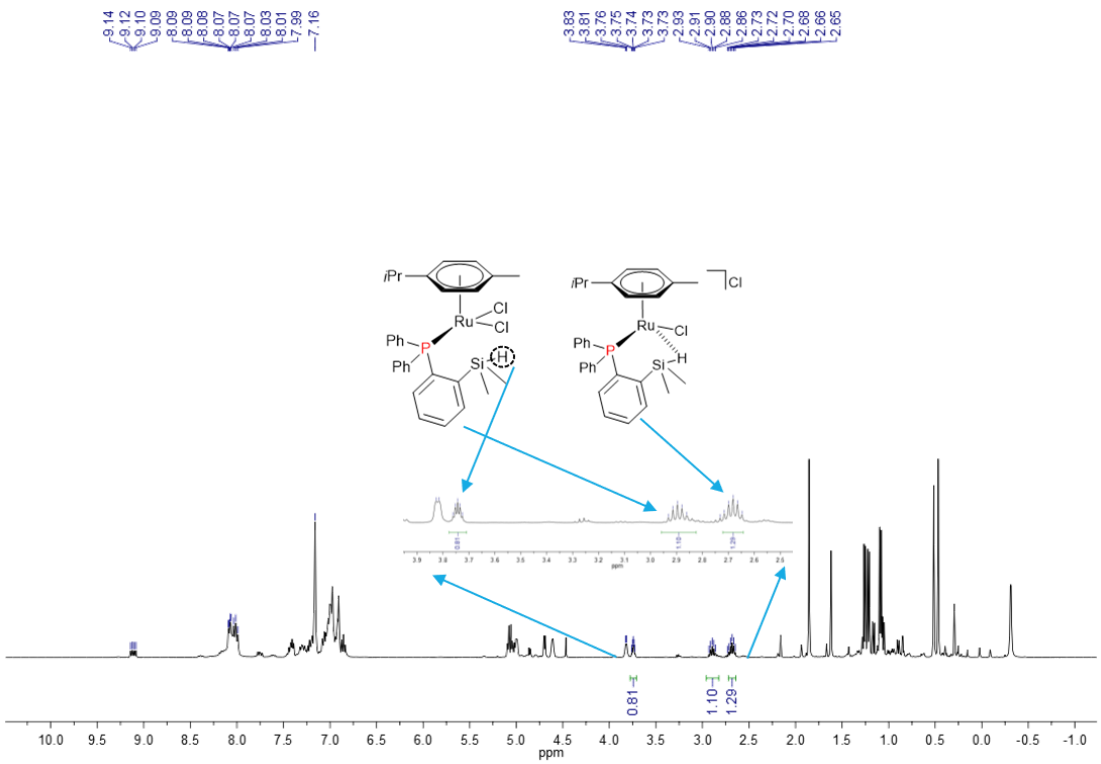


Figure S51. ^{1}H NMR of reaction mixture after 5 min, showing the presence of both intermediate **int. A** and **4**.

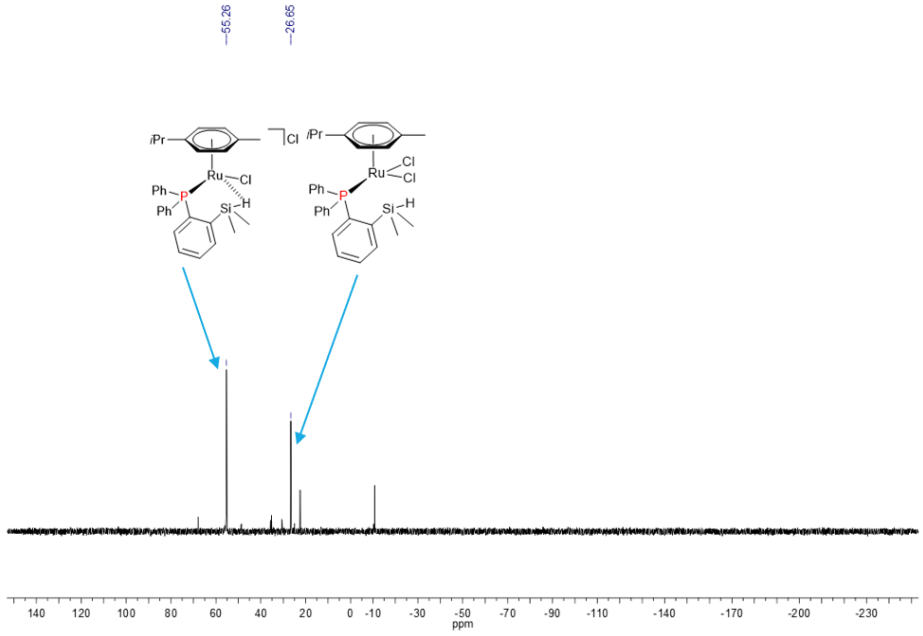


Figure S52. ^{31}P NMR of reaction mixture after 5 min, showing the presence of both intermediate **int. A** and **4**

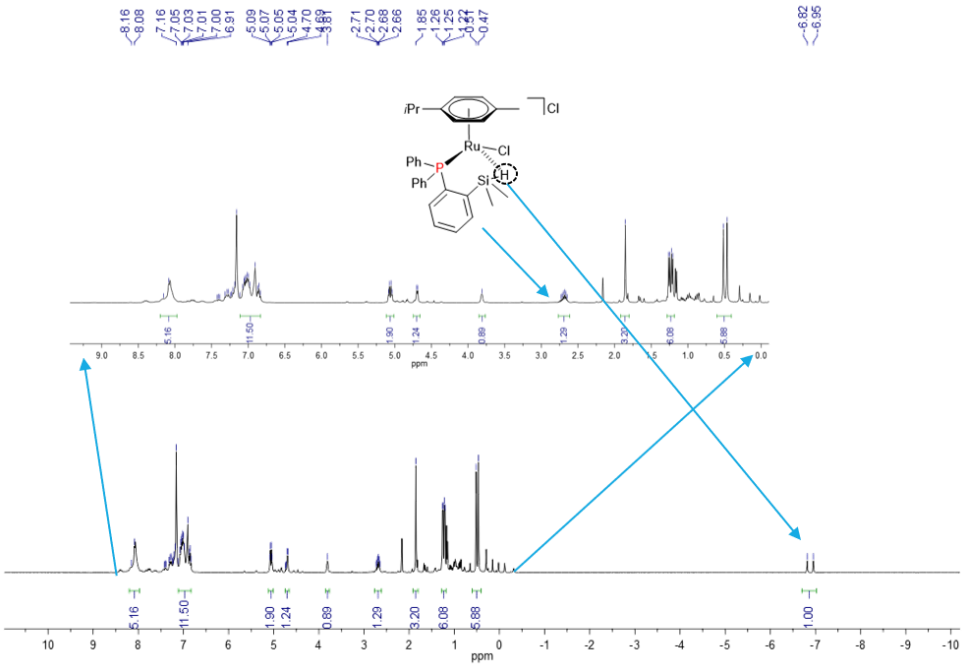


Figure S53. ^{1}H NMR of reaction mixture after 10 min, showing the presence of **4**

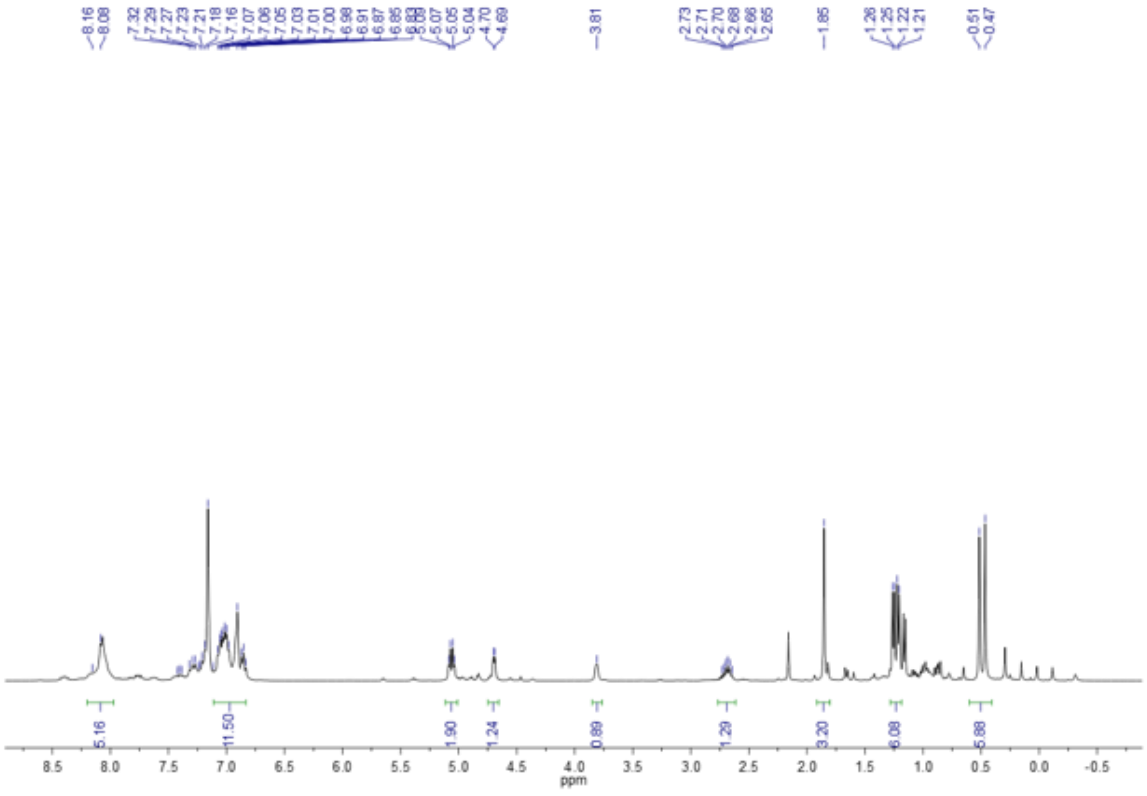


Figure S54. ^{1}H NMR of reaction mixture after 10 min, showing the presence of **4.**

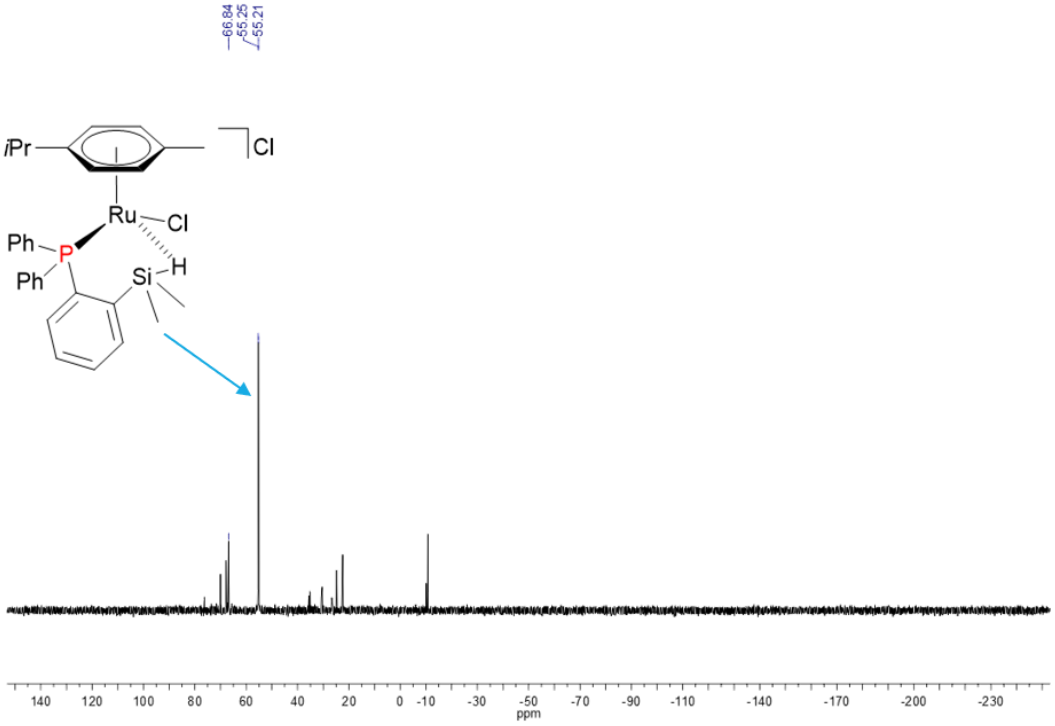
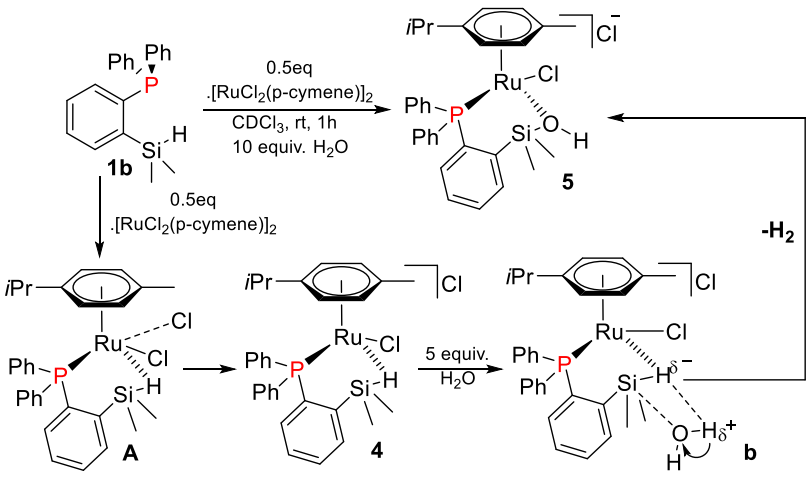


Figure S55. ^{31}P NMR of reaction mixture after 10 min, showing the presence of **4.**

Synthetic procedure for NMR tube experiment with addition of H_2O for compound 5

Scheme S3



A solution comprising 12 mg of silylated phosphine **1b** dissolved in 0.4 ml of $CDCl_3$ was prepared within an Eppendorf vial. Concurrently, an equivalent volume of $CDCl_3$ was introduced into another Eppendorf vial containing 9 mg of (*p*-Cymene) ruthenium (II) chloride dimer. Subsequently, both solutions were transferred to a NMR tube under

an inert argon atmosphere. The transition of the reaction mixture's color to a vivid blood-red hue was visually observed. Following a 10-minute interval, 5 µL of H_2O (5 equiv.) was added to the reaction mixture within the NMR tube. The mixture was then manually agitated for 10 minutes. Proton and phosphorus NMR measurements were performed at regular intervals thereafter. The NMR analysis revealed that upon the addition of water to the reaction mixture containing intermediate **4**, the formation of compound **5** was observed after 10 minutes. Furthermore, after 20 minutes, the ratio of intermediates to compound **5** remained nearly unchanged. Subsequently, it was observed that after 45 minutes, complete conversion had occurred. The NMR tube was then removed, and the solvent was evaporated from the reaction mixture. The residue was washed with *n*-hexane (1 × 3 mL) to yield a faint-orange solid, which was subsequently dried under vacuum to afford compound **5** as a faint-orange solid.

Supporting spectral data

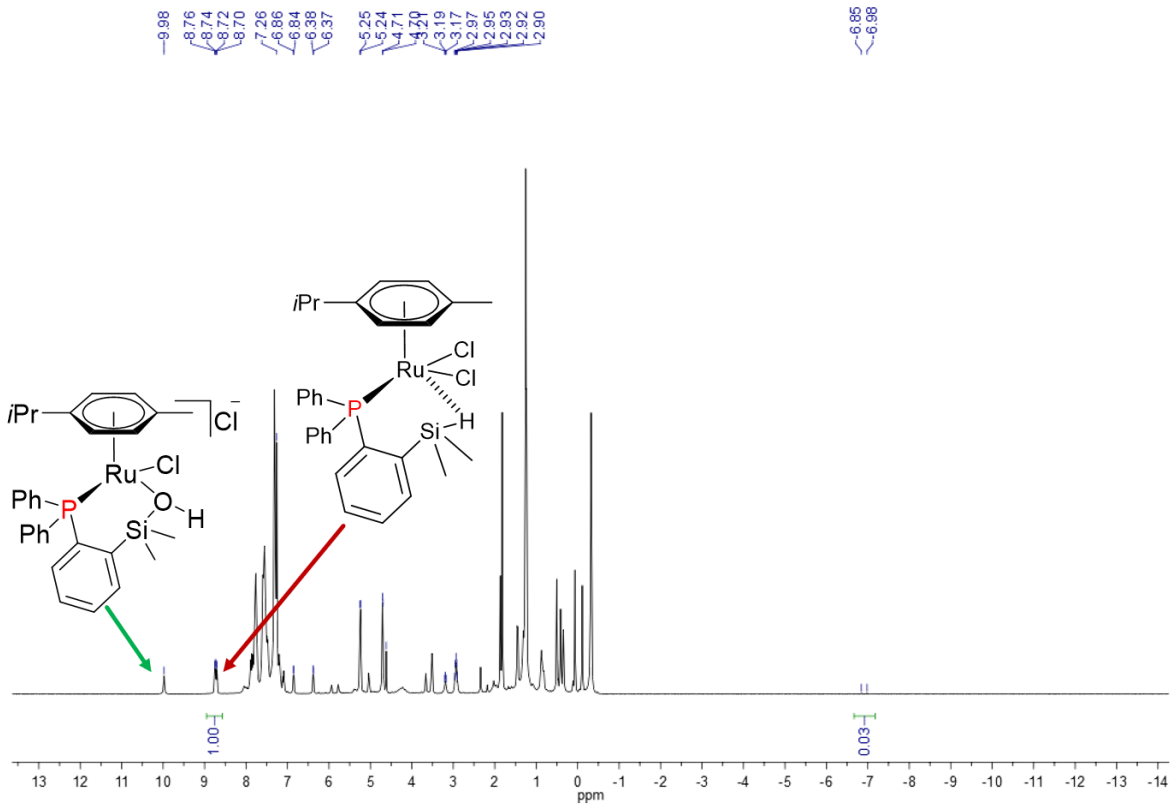


Figure S56. ^1H NMR of reaction mixture, 10 min after addition of H_2O showing the presence of both intermediate **4** and **5** measured in $CDCl_3$.

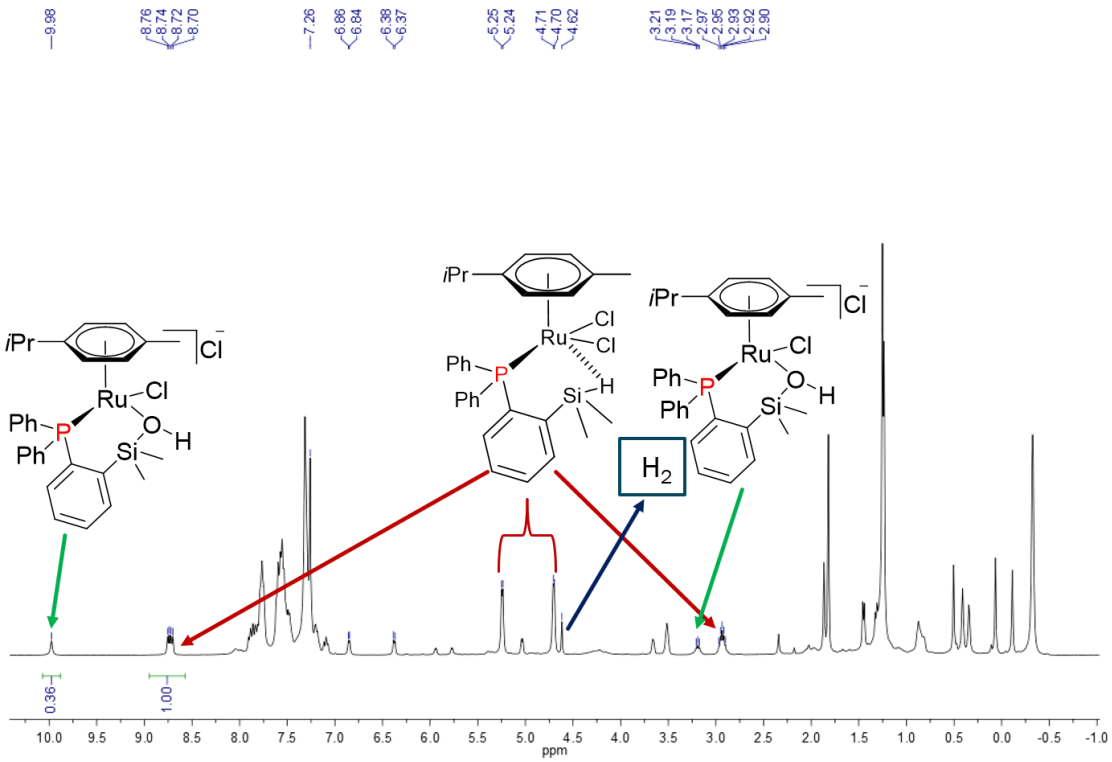


Figure S57. ^{1}H NMR of reaction mixture, 10 min after addition of H_2O showing the presence of both intermediate **4** and **5** and release of **H_2**

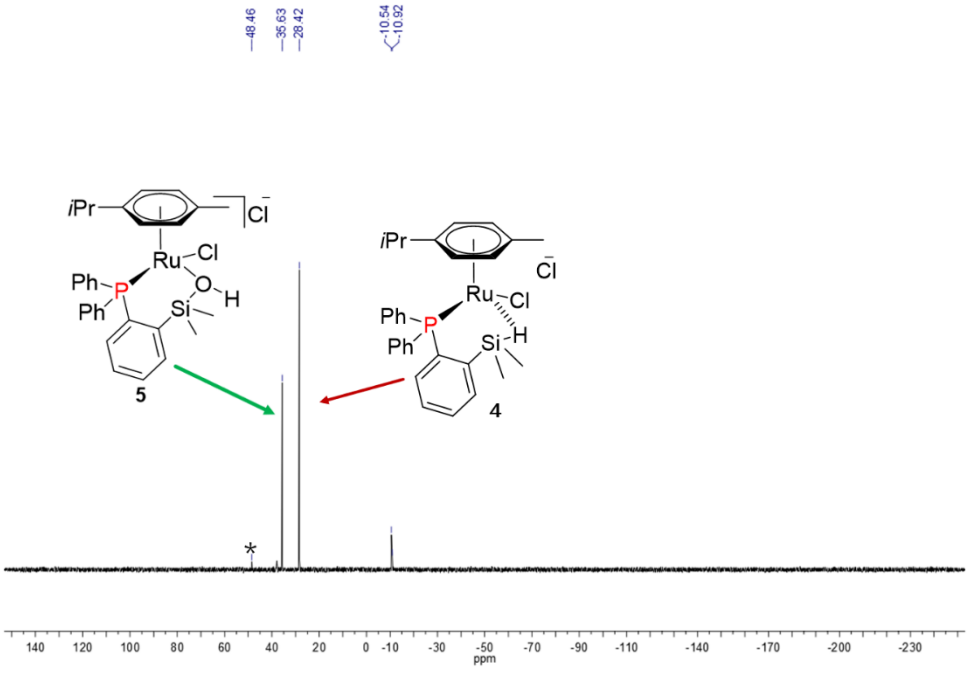


Figure S58. ^{31}P NMR of reaction mixture, 10 min after addition of H_2O showing the presence of both intermediate **4** and complex **5** (* = Unidentified impurities).

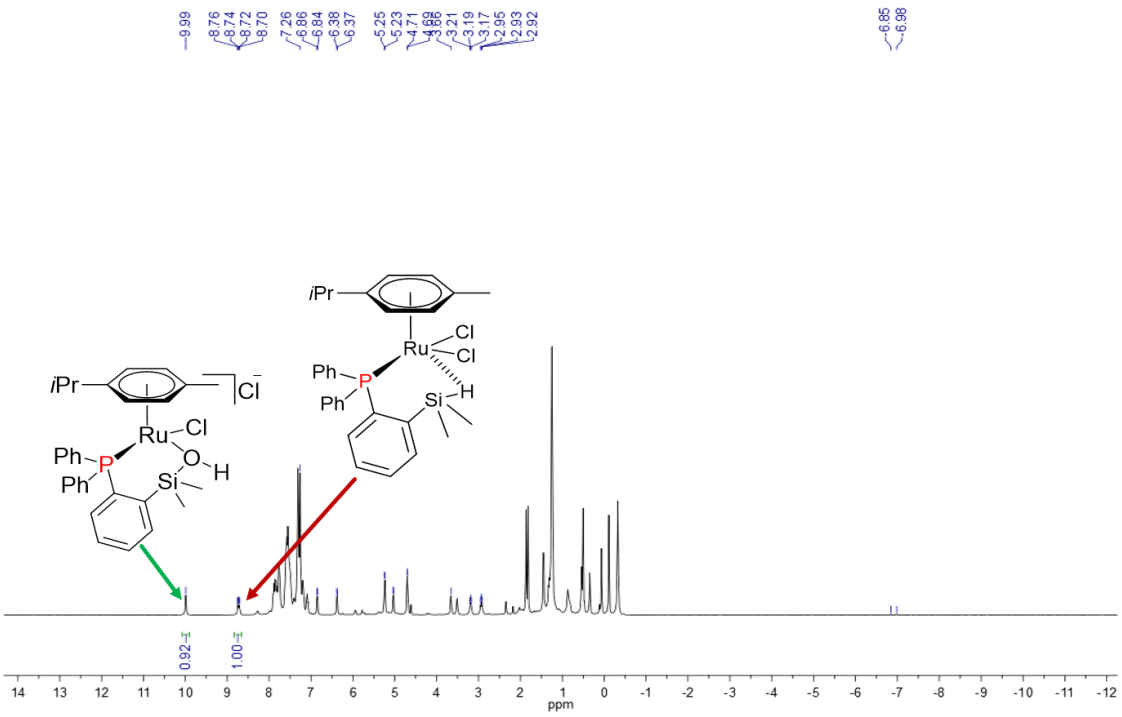


Figure S59. ^{1}H NMR of reaction mixture, 20 min after addition of H_2O showing the presence of both intermediate **4** and **5.**

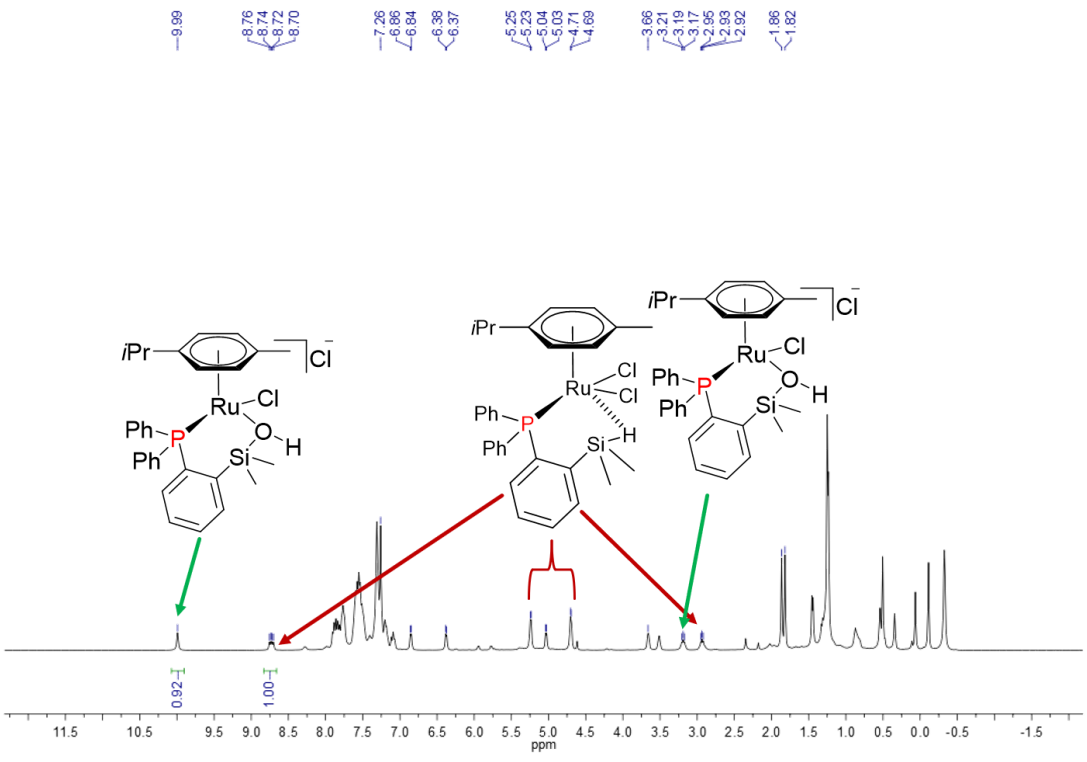


Figure S60. ^{1}H NMR of reaction mixture, 20 min after addition of H_2O showing the presence of both intermediate **4** and **5.**

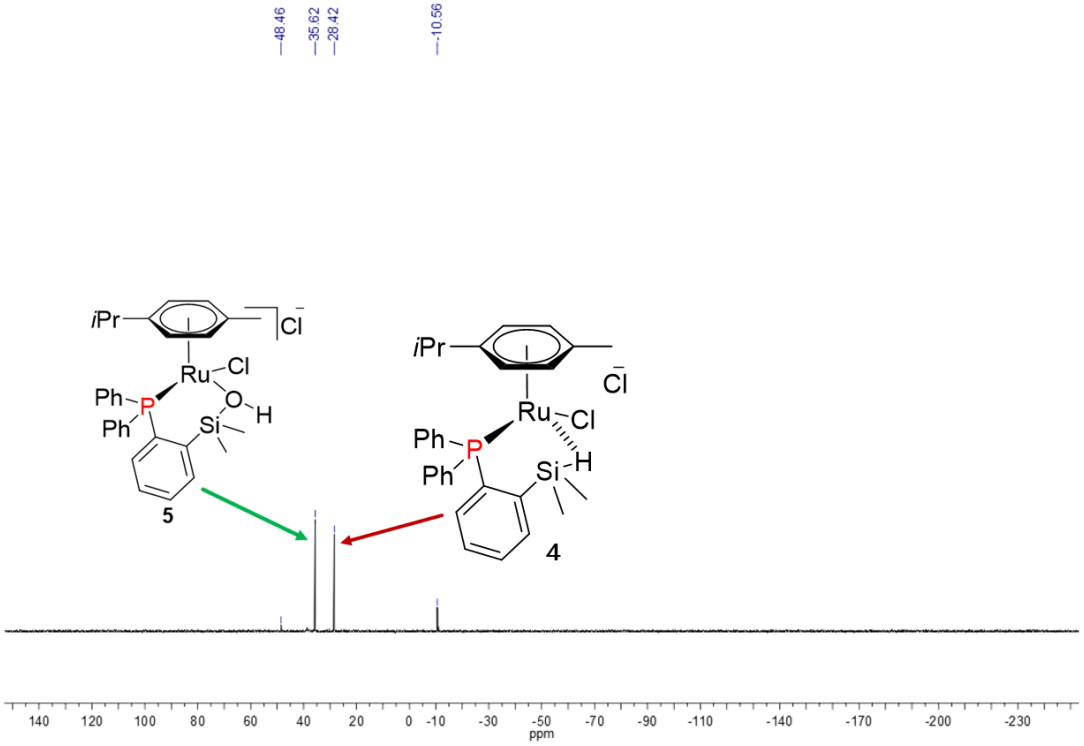


Figure S61. ^{31}P NMR of reaction mixture, 20 min after addition of H_2O showing the presence of both intermediate **4** and **5**.

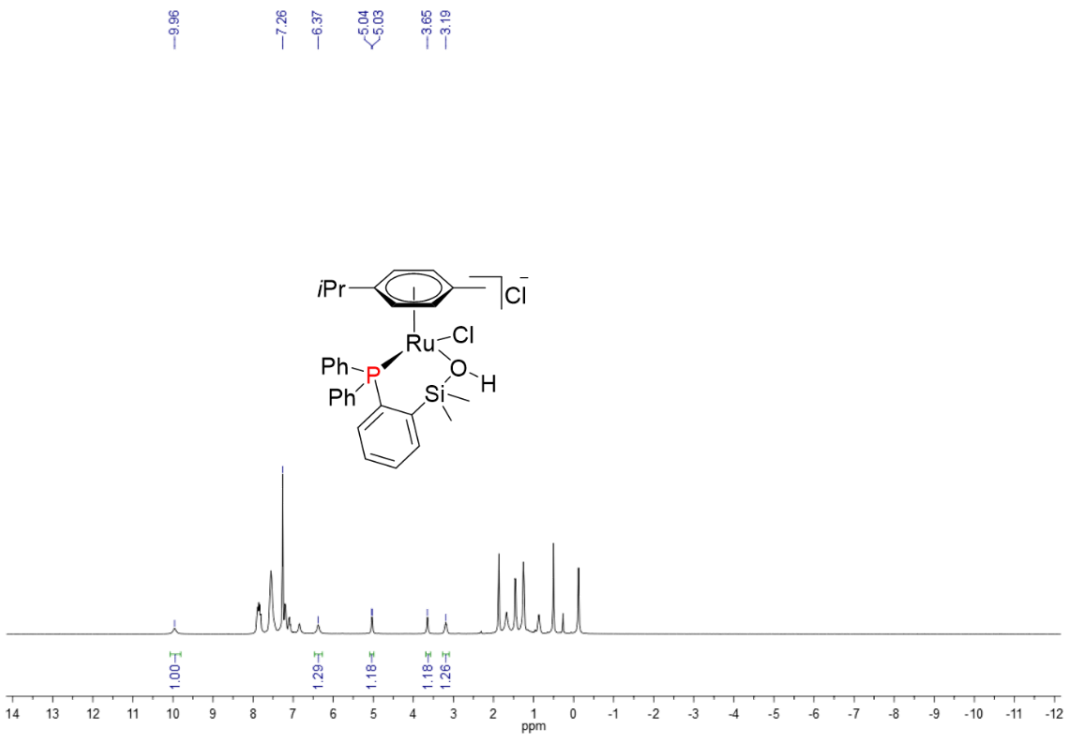


Figure S62. ^{1}H NMR of reaction mixture, 45 min after addition of H_2O showing the presence of **5**.

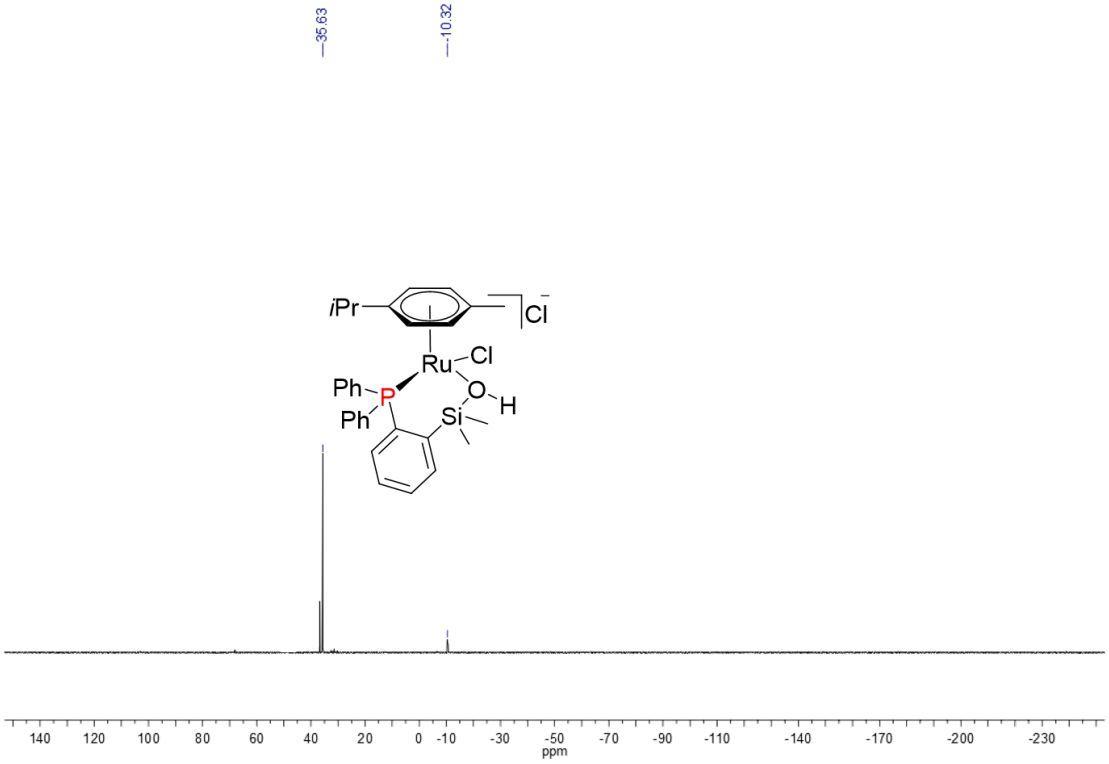


Figure S63. ^{31}P NMR of reaction mixture, 45 min after addition of H_2O showing the presence of **5**.

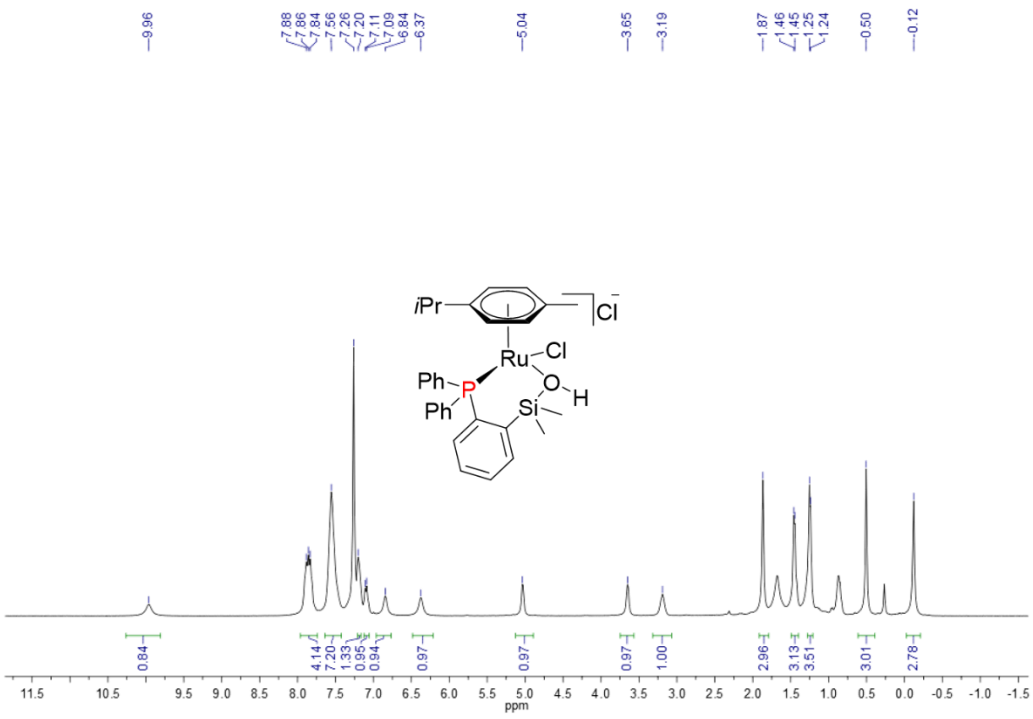


Figure S64. ^{1}H NMR of reaction mixture, 1h after addition of H_2O and after washing with hexane.

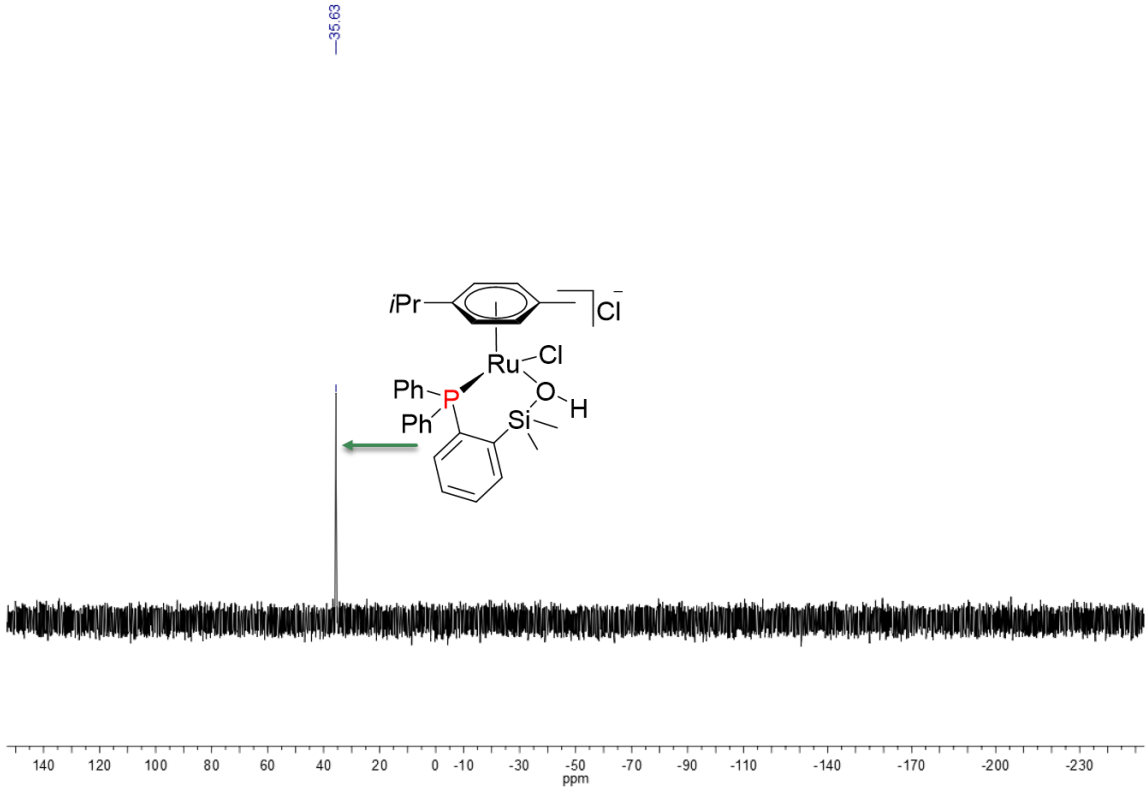
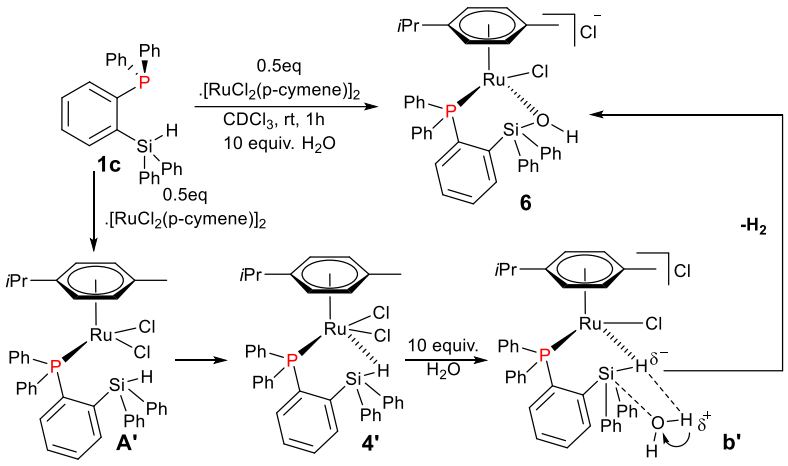


Figure S65. ^{31}P NMR of reaction mixture, 1h after addition of H_2O and after washing with hexane.

Synthetic procedure for NMR tube experiment for compound 4' which upon addition of H_2O formed compound 6



A solution comprising 12 mg of silylated phosphine **1c** dissolved in 0.4 ml of dry $CDCl_3$ was prepared within an Eppendorf vial. Concurrently, an equivalent volume of dry $CDCl_3$ was introduced into another Eppendorf vial containing 6.6 mg of (*p*-Cymene) ruthenium (II) chloride dimer. Subsequently, both solutions were transferred to a NMR

tube under an inert argon atmosphere. The transition of the reaction mixture's color to a vivid blood-red hue was visually observed. Following a 1-hour interval, 4.8 µL of H_2O (10 equiv.) was added to the reaction mixture within the NMR tube. The mixture was then manually agitated for 10 minutes. Proton and phosphorus NMR measurements were performed at regular intervals thereafter. The NMR analysis revealed that due to the presence of atmospheric moisture reaction mixture contained intermediates **4'** and **b** in 50% ratio. Furthermore, after 1 hour, we added 5 equiv. of H_2O due to which compound **6** was formed solely. The NMR tube was then removed, and the solvent was evaporated from the reaction mixture. The residue was washed with *n*-hexane (1 × 3 mL) to yield a faint-orange solid, which was subsequently dried under vacuum to afford compound **6** as a faint-orange solid.

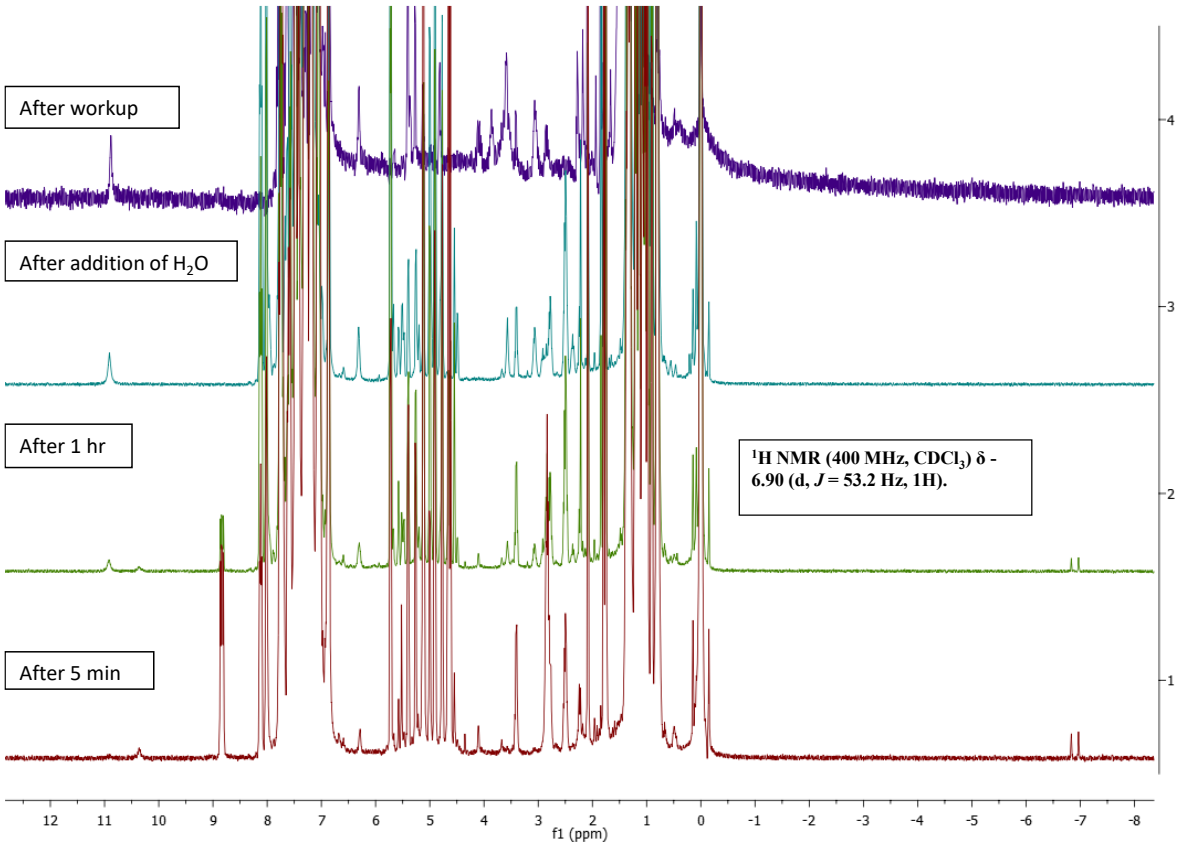


Figure S66. ^{1}H NMR stacking spectrum of compound **4'** changing to **6** measured in $CDCl_3$.

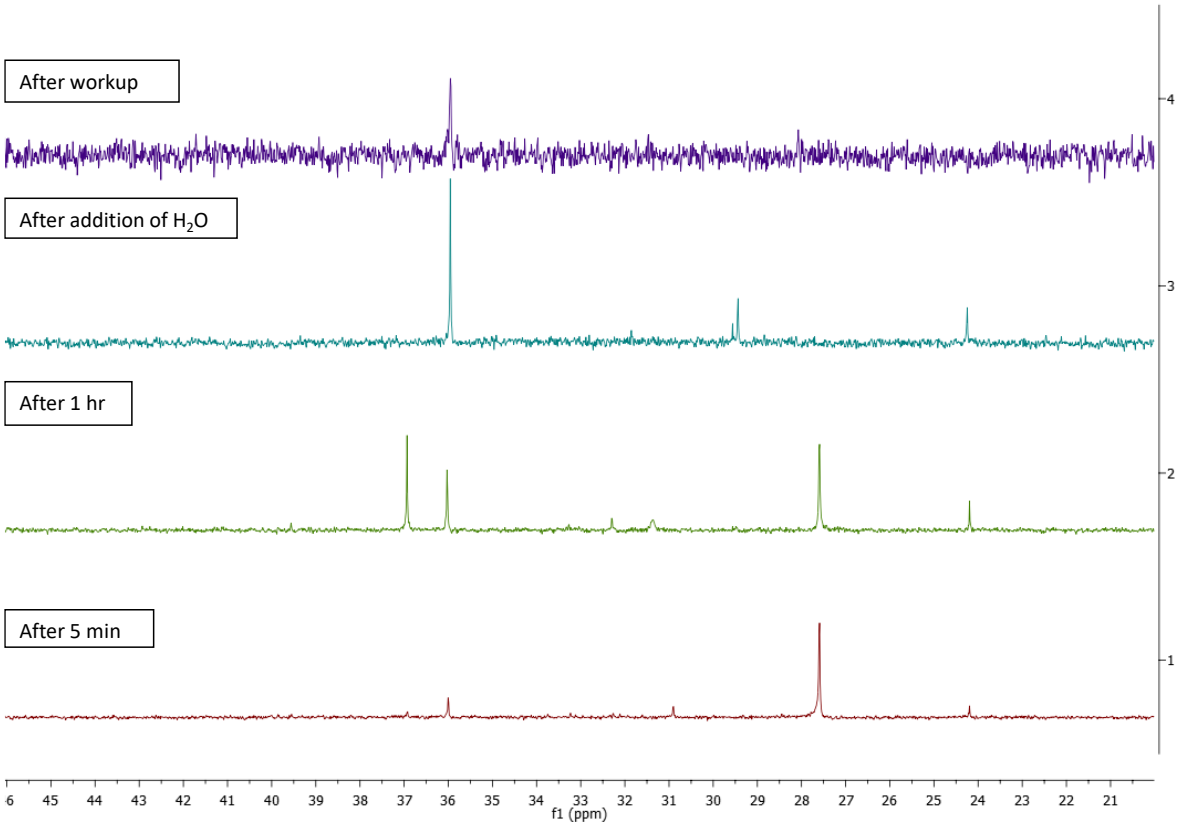
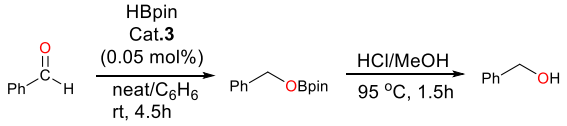


Figure S67. ^{31}P NMR stacking spectrum of compound **4'** changing to **6** measured in $CDCl_3$.



entry	deviation from the standard conditions	yield of product (%)[b]
1	**none**	93.7
2	0.1 mol% cat. **3**	93.5
3	5 mol% cat. **3**	93
4	1 mol% cat. **3**	93.2
5	0.5 mol% cat.**3**	93
6	1 mol% cat.**5**	92
7	2 mol% cat.**3**	93.5
8	0.025 mol% cat. **3**	90
9	12h instead of 6h	93.6
10	4h instead of 6h	85.5
11	8h instead of 6h	93

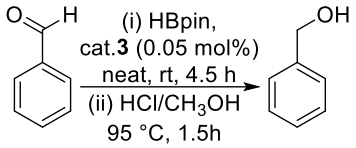
[a]Reaction conditions: **Aldehyde** (1 equiv.), **HBpin** (1 equiv.), cat.**3** (0.05 mol%), neat condition, RT, 6 h. [b]Isolated yields.

Table S1. Optimisation table for the synthesis of primary alcohol from aldehyde.

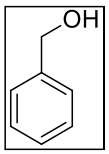
General Procedure for Aldehydes to Alcohol conversion (8a-8r)

In a nitrogen atmosphere, a 25 mL schlenk tube was charged with 1 equiv. of aldehyde, 1 equiv. of pinacolborane, and 0.05 mol% of Cat.**3** [benzene, 1-2 ml, for solid substrates]. For the duration of 4.5 hours, the reaction mixture was stirred at room temperature. After the reaction was complete, the resulting boronate ester residue was treated with 1.5 h of refluxing methanol and 1 M aqueous HCl. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohols (8a-r) were obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent.

Preparation of primary alcohol (8a)[3,4]

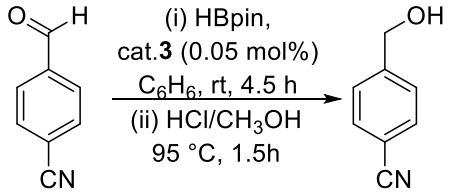


8a was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8a**) was obtained

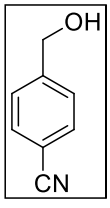


by drying, evaporating, and washing with n-hexane (2×2 mL). (86 mg, 93.7%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.30 – 7.16 (m, 5H, Ph*H*), 4.56 (s, 2H, Ph-CH_2), 2.34 (s, 1H, O*H*). ^{13}C NMR (101 MHz, $CDCl_3$); δ = 140.9 (Ph*C*), 128.6 (Ph*C*), 127.6 (Ph*C*), 127.1 (Ph*C*), and 65.2 (Ph-*C*H_2) ppm.

Preparation of primary alcohol (8b)[3]

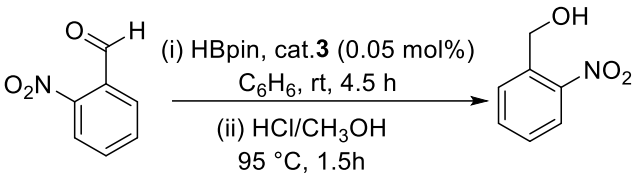


8b was prepared according to the general procedure. The aliquot is then dichloromethane

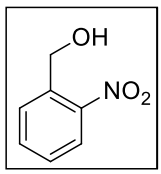


extracted after being evaporated under vacuum. The pure primary alcohol (**8b**) was obtained by drying, evaporating, and washing with n-hexane (2 × 2 mL). (30 mg, 98.5%) ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.62 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.46 (d, *J* = 8.1 Hz, 2H, Ar*H*), 4.76 (s, 2H, Ar-CH_2), 2.33 (s, 1H, O*H*). ^{13}C NMR (101 MHz, $CDCl_3$); δ = 146.4 (Ar*C*), 132.4 (Ar*C*), 127.1 (Ar*C*), 118.9 (Ar*C*N), 111.2 (Ar*C*), and 64.2 (Ar-*C*H_2) ppm.

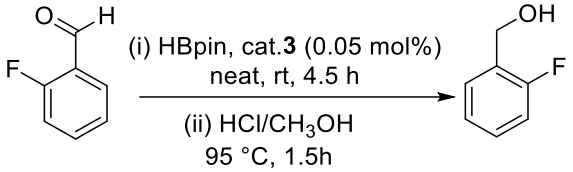
Preparation of alcohol (8c)[5]



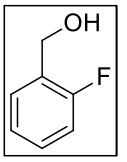
8c was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8c**) was obtained by drying, evaporating, and washing with *n*-hexane (2 × 2 mL). (27.5 mg, 91 %) ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.10 (dd, *J* = 8.2, 1.0 Hz, 1H, Ar*H*), 7.75 (d, *J* = 7.3 Hz, 1H, Ar*H*), 7.67 (td, *J* = 7.6, 1.1 Hz, 1H, Ar*H*), 7.50 – 7.44 (m, 1H, Ar*H*), 4.97 (s, 2H, Ar-CH_2), 2.71 (s, 1H, O*H*). ^{13}C NMR (101 MHz, $CDCl_3$); δ = 147.8 (Ar*C*), 136.9 (Ar*C*), 134.3 (Ar*C*), 130.1 (Ar*C*), 128.6 (Ar*C*), 125.1 (Ar*C*), and 62.6 (Ar-*C*H_2) ppm.



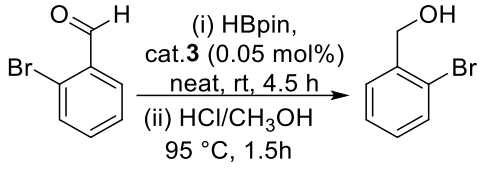
Preparation of alcohol (8d)[3,4,6]



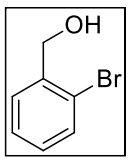
8d was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8d**) was obtained by drying, evaporating, and washing with *n*-hexane (2 × 2 mL). (55 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (td, *J* = 7.5, 1.5 Hz, 1H, Ar*H*), 7.32 – 7.26 (m, 1H, Ar*H*), 7.15 (td, *J* = 7.5, 0.9 Hz, 1H, Ar*H*), 7.08 – 6.99 (m, 1H, Ar*H*), 4.77 (s, 2H, Ar-CH_2), 1.79 (s, 1H, O*H*) ppm. ^{19}F NMR (377 MHz, $CDCl_3$) δ = -119.83 (s) ppm.



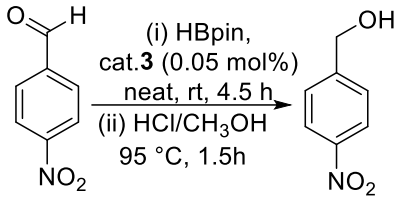
Preparation of alcohol (8e)[3]



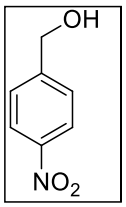
8e was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8e**) was obtained by drying, evaporating, and washing with *n*-hexane (2 × 2 mL). (28 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.55 (dd, *J* = 7.9, 0.7 Hz, 1H, Ar*H*), 7.49 (dd, *J* = 7.6, 1.0 Hz, 1H, Ar*H*), 7.34 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.17 (td, *J* = 7.7, 1.5 Hz, 1H, Ar*H*), 4.76 (s, 2H, Ar-CH_2), 2.00 (s, 1H, O*H*).^{13}C NMR (101 MHz, $CDCl_3$); δ = 139.9 (Ar*C*), 132.7 (Ar*C*), 129.3 (Ar*C*), 129.1 (Ar*C*), 127.8 (Ar*C*), 122.7 (Ar*C*), and 65.3 (Ar-*C*H_2) ppm.



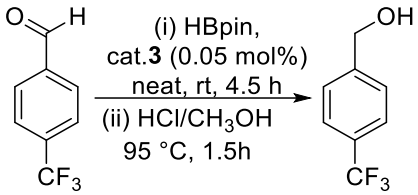
Preparation of alcohol (8f)[3,4]



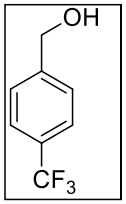
8f was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8f**) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent. (28 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.20 (d, *J* = 8.6 Hz, 2H, Ar*H*), 7.52 (d, *J* = 8.6 Hz, 2H, Ar*H*), 4.83 (s, 2H, Ar-CH_2), 2.33 (s, 1H, O*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 148.3 (Ar*C*), 147.4 (Ar*C*), 127.1 (Ar*C*), 123.8 (Ar*C*), and 64.1(Ar-*C*H_2) ppm.



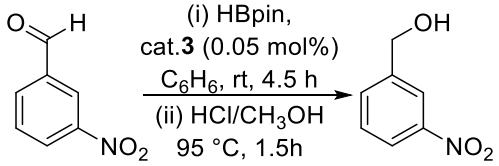
Preparation of alcohol (8g)[3,7]



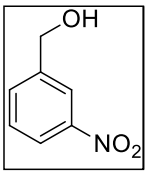
8g was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8g**) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent. (38 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.54 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.39 (d, *J* = 8.0 Hz, 2H, Ar*H*), 4.68 (s, 2H, Ar-CH_2), 2.02 (s, 1H, O*H*). ^{19}F NMR (377 MHz, $CDCl_3$); δ = -62.49 (s). ^{13}C NMR (101 MHz, $CDCl_3$); δ = 144.9 (Ar*C*), 129.9 (d, *J* = 32.3 Hz, Ar*C*), 126.9 (Ar*C*), 125.6 (q, *J* = 7.7, 3.8 Hz, Ar-*C*F_3), 122.9 (Ar*C*), and 64.5 (Ar-*C*H_2) ppm.



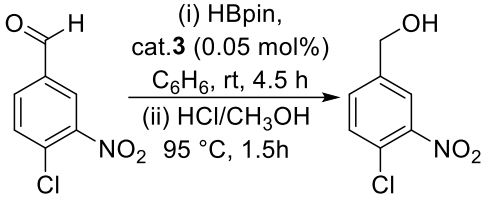
Preparation of alcohol (8h)[8]



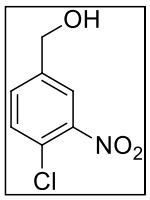
8h was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8h**) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent. (29 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.25 (s, 1H, Ar*H*), 8.14 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.70 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.53 (t, *J* = 7.9 Hz, 1H, Ar*H*), 4.83 (s, 2H, Ar-CH_2), 1.98 (s, 1H, O*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 148.6 (Ar*C*), 143.0 (Ar*C*), 132.7 (Ar*C*), 129.6 (Ar*C*), 122.6 (Ar*C*), 121.6 (Ar*C*), and 64.1(Ar-*C*H_2) ppm.



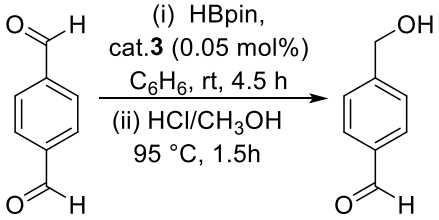
Preparation of alcohol (8i)[9]



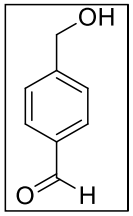
8i was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8i**) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent (37 mg, 91.5%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.87 (s, 1H, Ar*H*), 7.50 (s, 2H, Ar*H*), 4.75 (s, 2H, Ar-CH_2), 2.22 (s, 1H, O*H*) ppm ^{13}C NMR (101 MHz, $CDCl_3$); δ = 140.4 (Ar*C*), 131.9 (Ar*C*), 130.8 (Ar*C*), 130.1 (Ar*C*), 124.6 (Ar*C*), 122.4 (Ar*C*), and 62.2 (Ar-*C*H_2) ppm.



Preparation of alcohol (8j)[10]

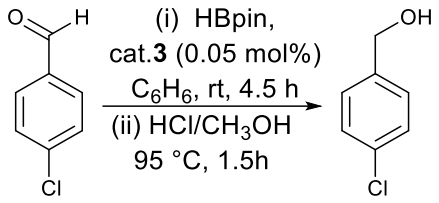


8j was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8j**) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent. (30 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 10.00 (s, 1H, ArCO*H*), 7.87 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.53 (d, *J* = 8.0 Hz, 2H,

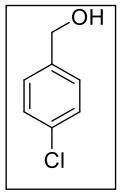


Ar*H*), 4.80 (s, 2H, Ar-CH_2), 2.34 (t, *J* = 7.5 Hz, 1H, O*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 192.2 (Ar*C*OH), 147.9 (Ar*C*), 135.8 (Ar*C*), 130.2 (Ar*C*), 127.1 (Ar*C*), and 64.7 (Ar-*C*H_2) ppm.

Preparation of alcohol (8k)[11]

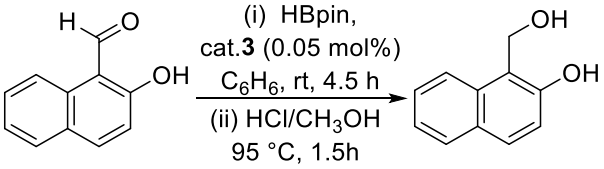


8k was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8k**) was obtained

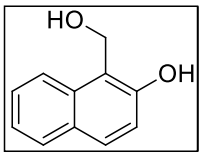


by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent. (28 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.35 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.30 (d, *J* = 8.5 Hz, 2H, Ar*H*), 4.67 (s, 2H, Ar-CH_2), 2.00 (s, 1H, O*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 139.3 (Ar*C*), 133.5 (Ar*C*), 128.8 (Ar*C*), 128.4 (Ar*C*), and 64.6 (Ar-*C*H_2) ppm.

Preparation of alcohol (8l)[12]

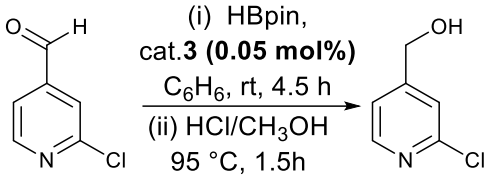


8l was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8l**) was obtained by

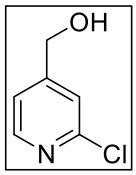


drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent. (51 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.22 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.77 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.64 (d, *J* = 8.3 Hz, 1H, Ar*H*), 7.44 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.32 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.06 (d, *J* = 8.0 Hz, 1H, Ar*H*), 4.81 (s, 2H, Ar-CH_2), 2.58 (s, 2H, O*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 151.8 (Ar*C*), 133.6 (Ar*C*), 129.8 (Ar*C*), 129.0 (Ar*C*), 126.9 (Ar*C*), 123.4 (Ar*C*), 123.3 (Ar*C*), 118.2 (Ar*C*), 117.4 (Ar*C*), and 56.1 (Ar-*C*H_2) ppm.

Preparation of alcohol (8m)[13]

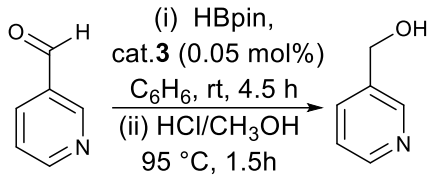


8m was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8m**) was obtained

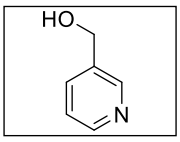


by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent (38 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.35 (d, *J* = 1.5 Hz, 1H, Py*H*), 7.69 (dd, *J* = 8.2, 2.2 Hz, 1H, Py*H*), 7.32 (d, *J* = 8.2 Hz, 1H, Py*H*), 4.72 (s, 2H, Py-CH_2), 1.89 (brs, 1H, O*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 150.7 (Py*C*), 148.3 (Py*C*), 137.8 (Py*C*), 135.3 (Py*C*), 124.3 (Py*C*), and 61.9 (Py-*C*H_2) ppm.

Preparation of alcohol (8n)[13]

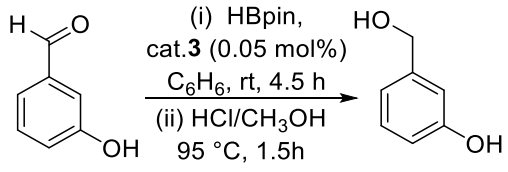


8n was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8n**) was obtained

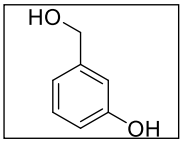


by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent. (36 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.50 (s, 1H, Py*H*), 7.40 (d, *J* = 7.6 Hz, 1H, Py*H*), 7.22 (dt, *J* = 15.2, 7.8 Hz, 2H, Py*H*), 4.62 (s, 2H, Py-CH_2), 2.43 (s, 1H, O*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 143.2 (Py*C*), 130.7 (Py*C*), 130.2 (Py*C*), 129.9 (Py*C*), 125.4 (Py*C*), 122.7 (Py*C*), and 64.4 (Py-*C*H_2) ppm.

Preparation of alcohol (8o)[14]



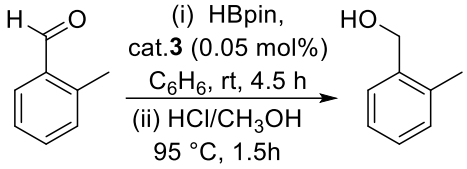
8o was prepared according to the general procedure. The aliquot is then dichloromethane



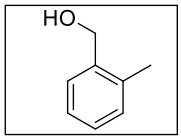
extracted after being evaporated under vacuum. The pure primary alcohol (8o) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl

acetate/hexane mixture as eluent. (29 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.22 (d, *J* = 7.8 Hz, 1H, Ar*H*), 6.92 (d, *J* = 7.4 Hz, 1H, Ar*H*), 6.87 (s, 1H, Ar*H*), 6.76 (d, *J* = 8.5 Hz, 1H, Ar*H*), 4.94 (s, 1H, O*H*), 4.66 (s, 2H, Ar-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$); δ = 143.1 (Ar*C*), 130.0 (Ar*C*), 119.3 (Ar*C*), 114.7 (Ar*C*), 113.9 (Ar*C*), and 65.2 (Ar-*C*H_2) ppm.

Preparation of alcohol (8p)[15]

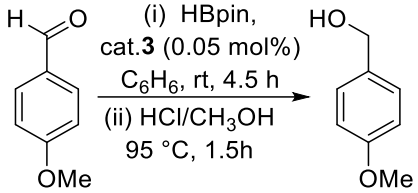


8p was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8p**) was obtained

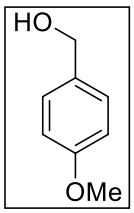


by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent. (28.3 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$); δ= 7.39 – 7.33 (m, 1H, Ar*H*), 7.20 (dt, *J* = 8.6, 4.7 Hz, 3H, Ar*H*), 4.68 (s, 2H, Ar-CH_2), 2.36 (s, 3H, Ar-CH_3), 1.90 (s, 1H, O*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 138.8 (Ar*C*), 136.2 (Ar*C*), 130.4 (Ar*C*), 127.9 (Ar*C*), 127.7 (Ar*C*), 126.2 (Ar*C*), 63.6 (Ar-*C*H_2), and 18.7 (Ar-*C*H_3) ppm.

Preparation of alcohol (8q)[3]

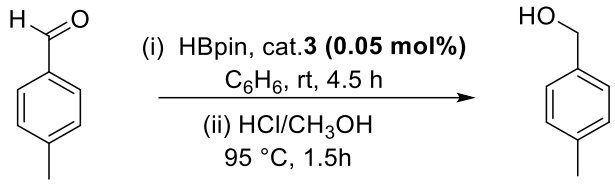


8q was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (**8q**) was obtained

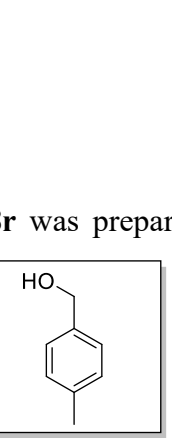


by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent. (23 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.29 (d, *J* = 8.5 Hz, 2H, Ar*H*), 6.89 (d, *J* = 8.5 Hz, 2H, Ar*H*), 4.61 (s, 2H, Ar-CH_2), 3.81 (s, 3H, Ar-OCH_3), 1.74 (s, 1H, O*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 159.3 (Ar*C*), 133.2 (Ar*C*), 128.8 (Ar*C*), 114.1 (Ar*C*), 65.2 (Ar-*C*H_2), and 55.4 (Ar-O*C*H_3) ppm.

Preparation of alcohol (8r)[3]



8r was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohol (8r) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane (1:1) mixture as eluent. (51 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 7.4 Hz, 2H), 7.20 (d, J = 7.6 Hz, 2H), 4.67 (s, 2H), 2.39 (s, 3H), 1.84 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.0 (Aryl), 137.5 (Aryl), 129.4 (Aryl), 127.2 (Aryl), 65.4 (Aryl-CH_2), and 21.3 (Aryl-CH_3) ppm.



Supporting spectral data of primary alcohols

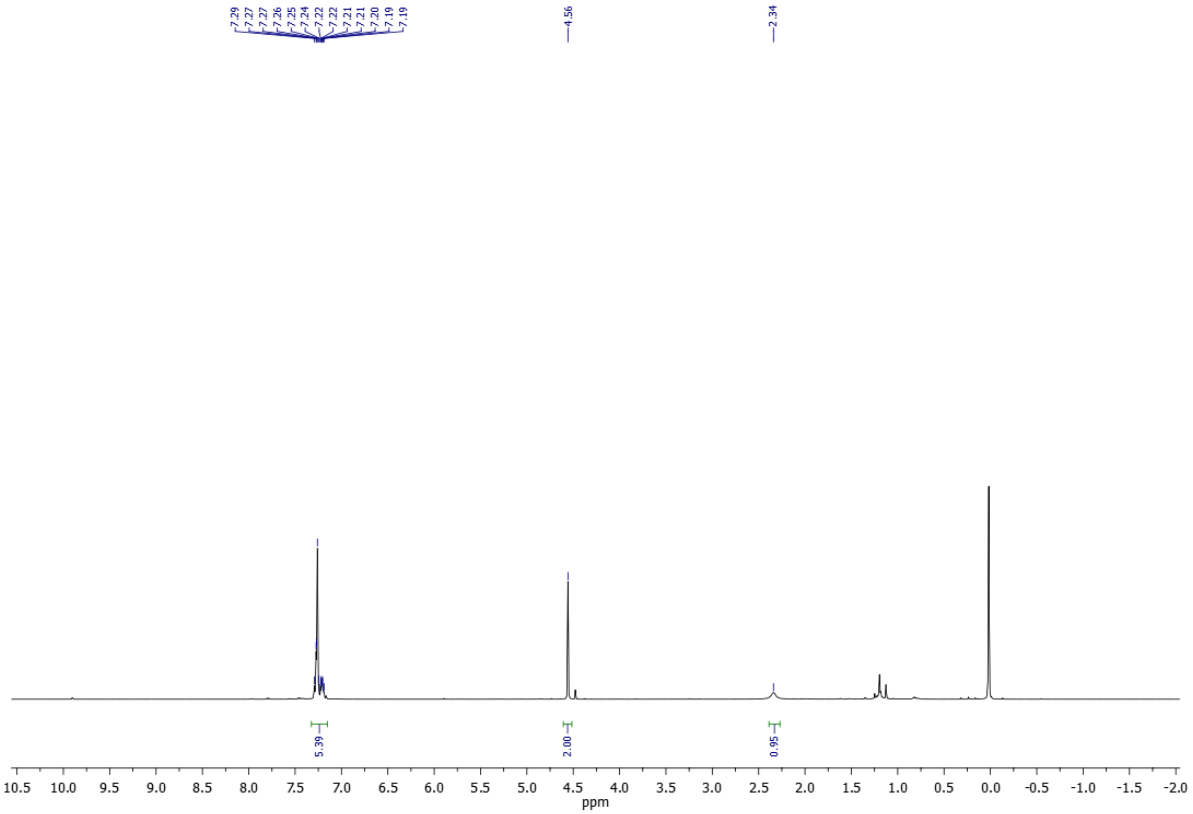


Figure S68. ^{1}H NMR spectrum of **8a** measured in $CDCl_3$.

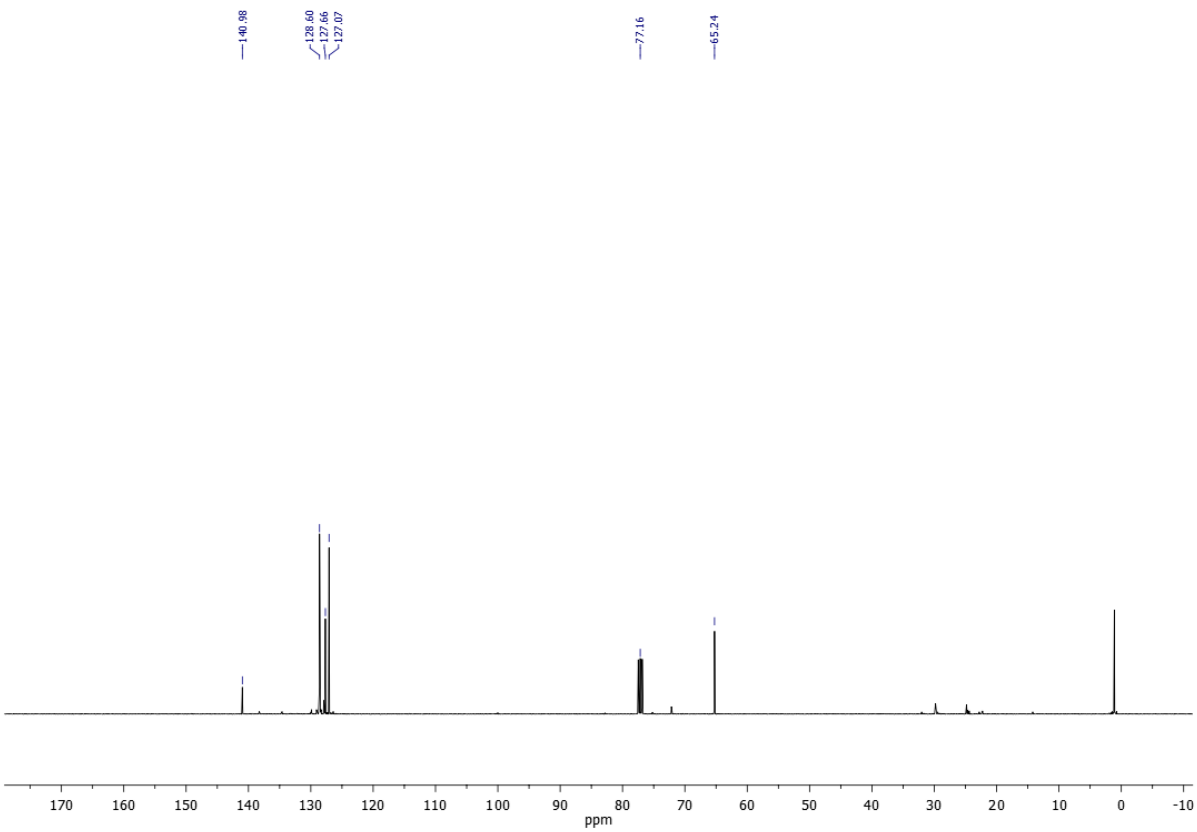


Figure S69. ^{13}C NMR spectrum of **8a** measured in $CDCl_3$.

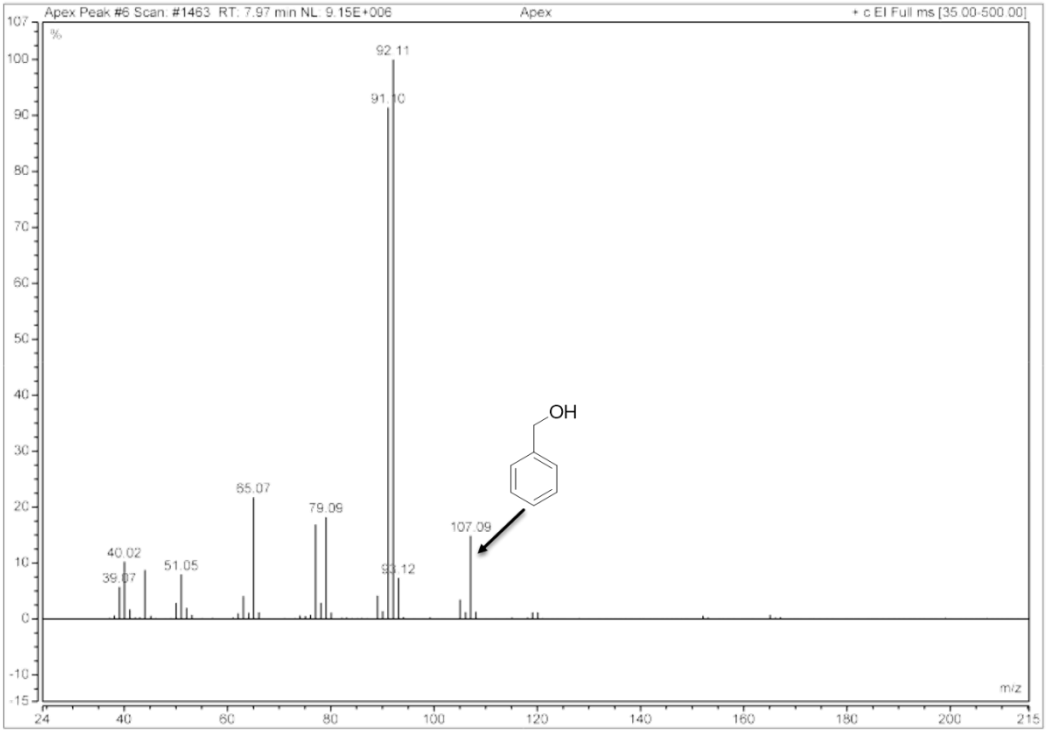


Figure S70. GC-MS spectrum of **8a** measured in ethyl acetate.

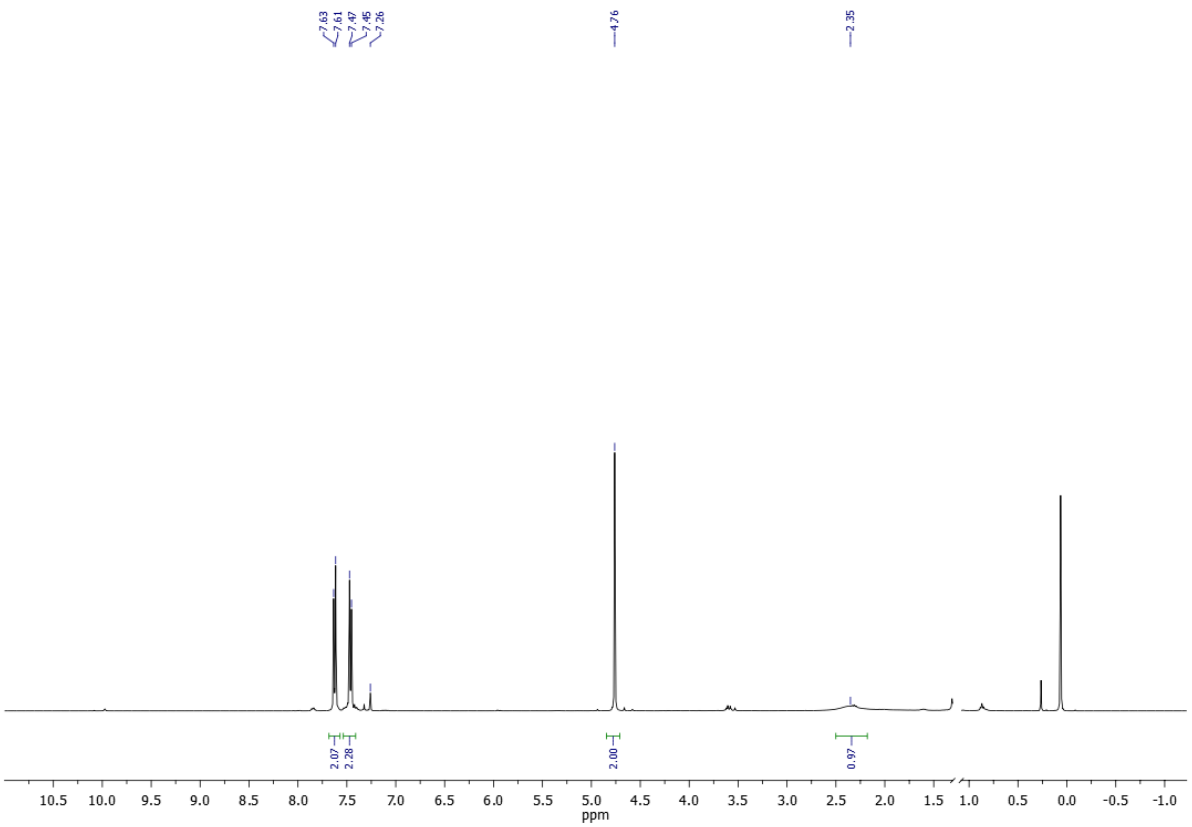


Figure S71. ^{1}H NMR spectrum of **8b** measured in $CDCl_3$.

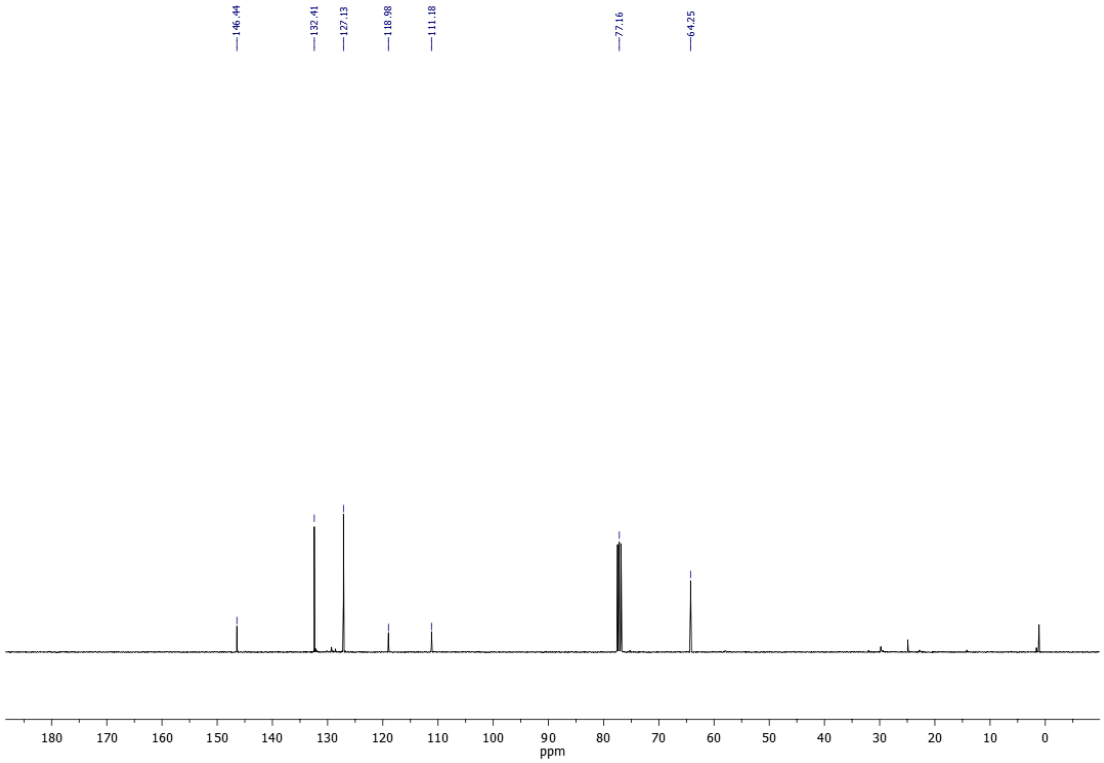


Figure S72. ^{13}C NMR spectrum of **8b** measured in $CDCl_3$.

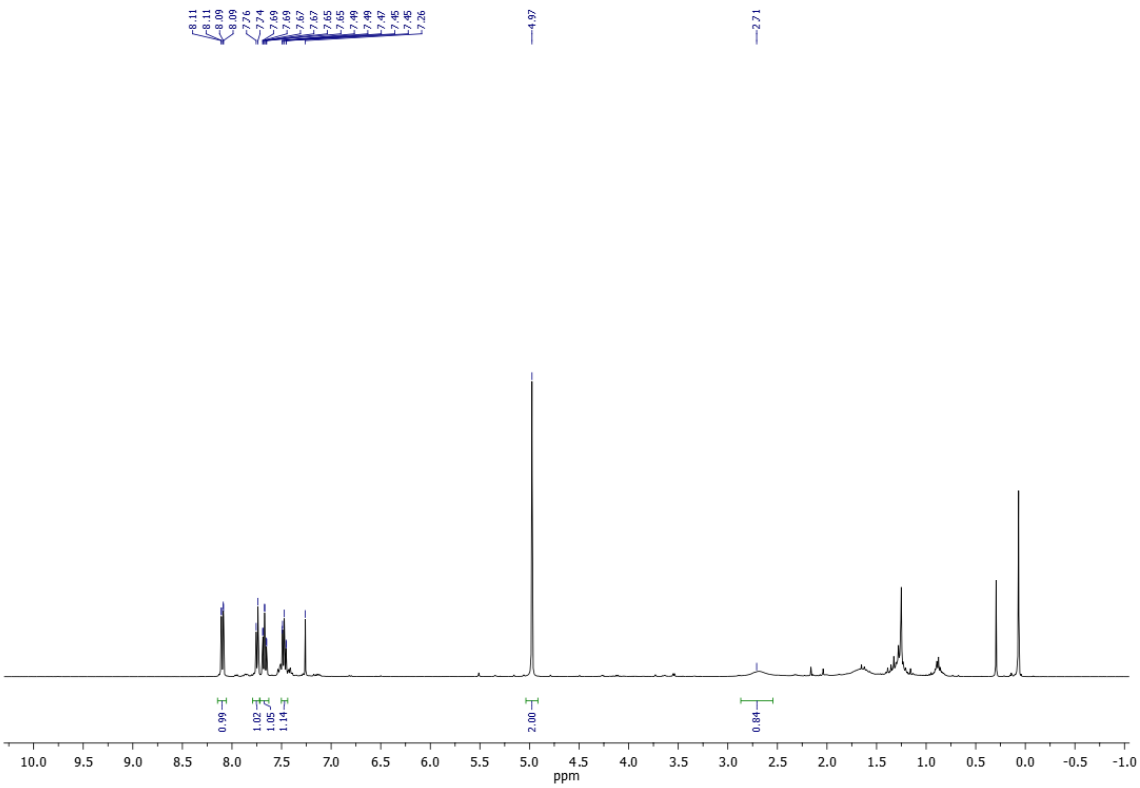


Figure S73. ^{1}H NMR spectrum of **8c** measured in $CDCl_3$.

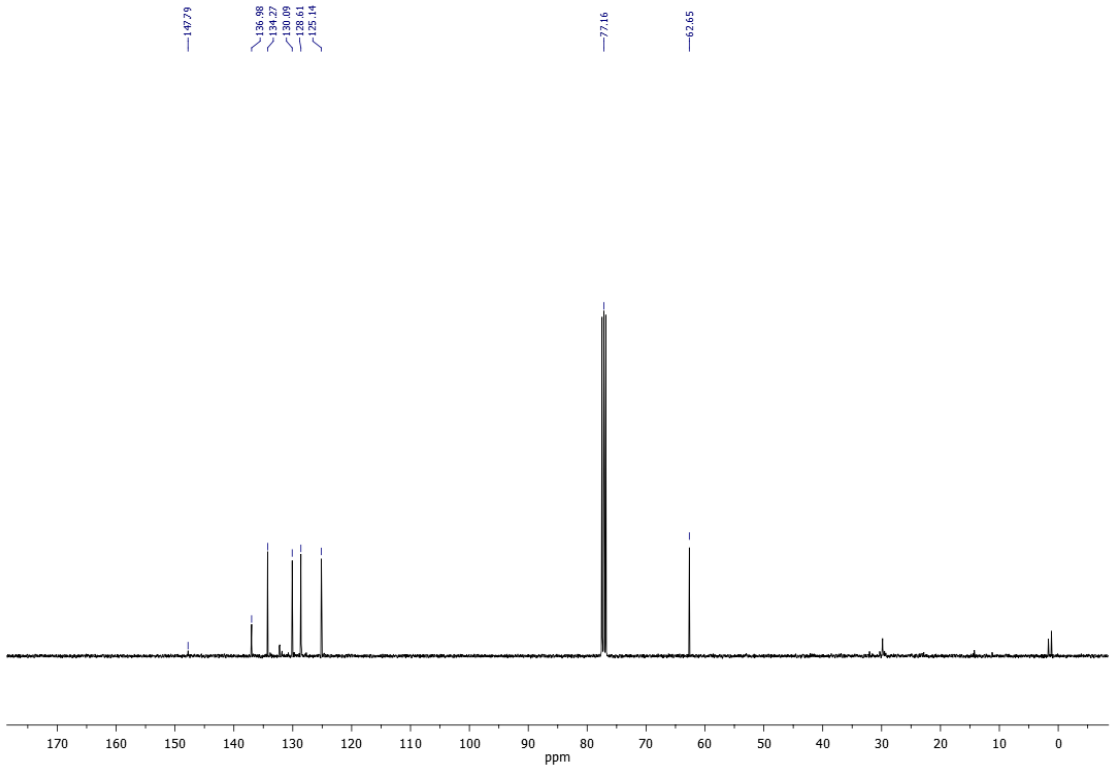


Figure S74. ^{13}C NMR spectrum of **8c** measured in $CDCl_3$.

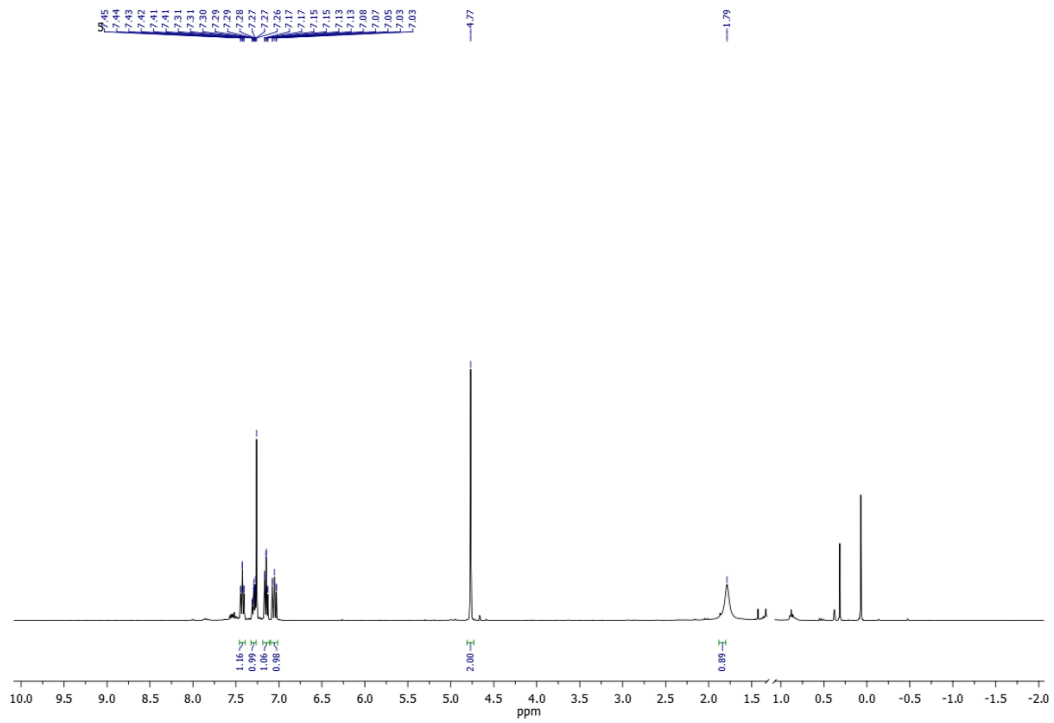


Figure S75. ^{1}H NMR spectrum of **8d** measured in $CDCl_3$.

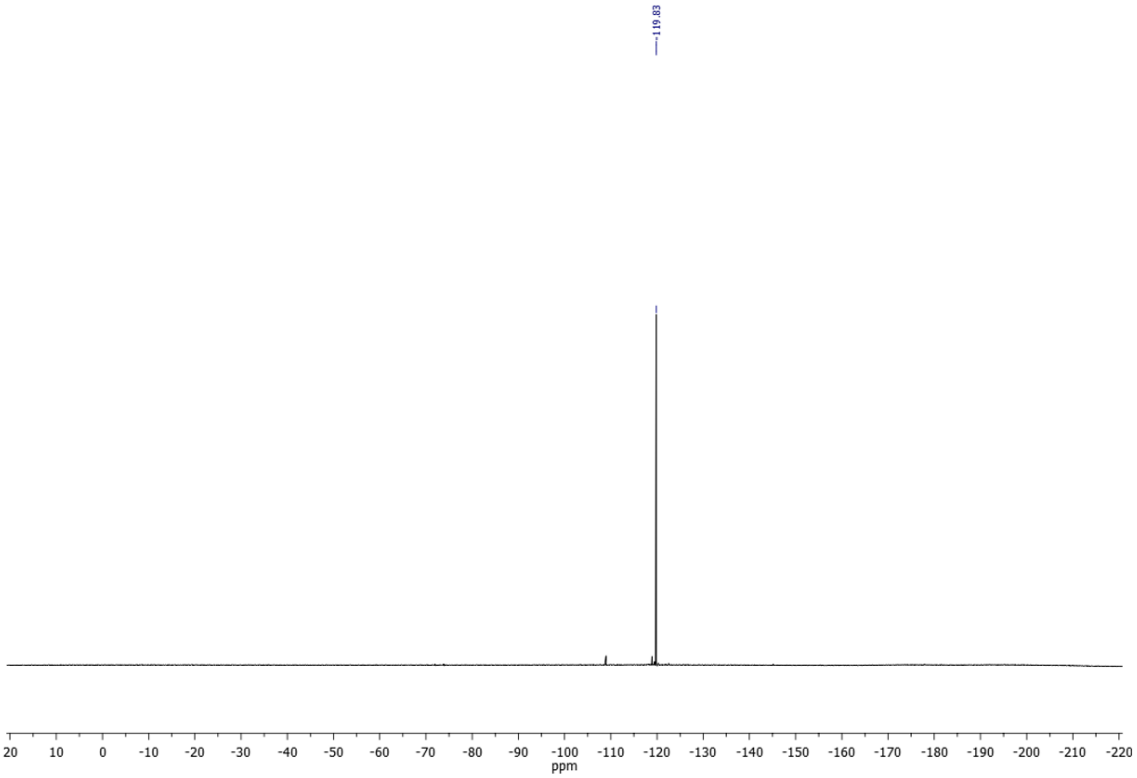


Figure S76. ^{19}F NMR spectrum of **8d** measured in $CDCl_3$.

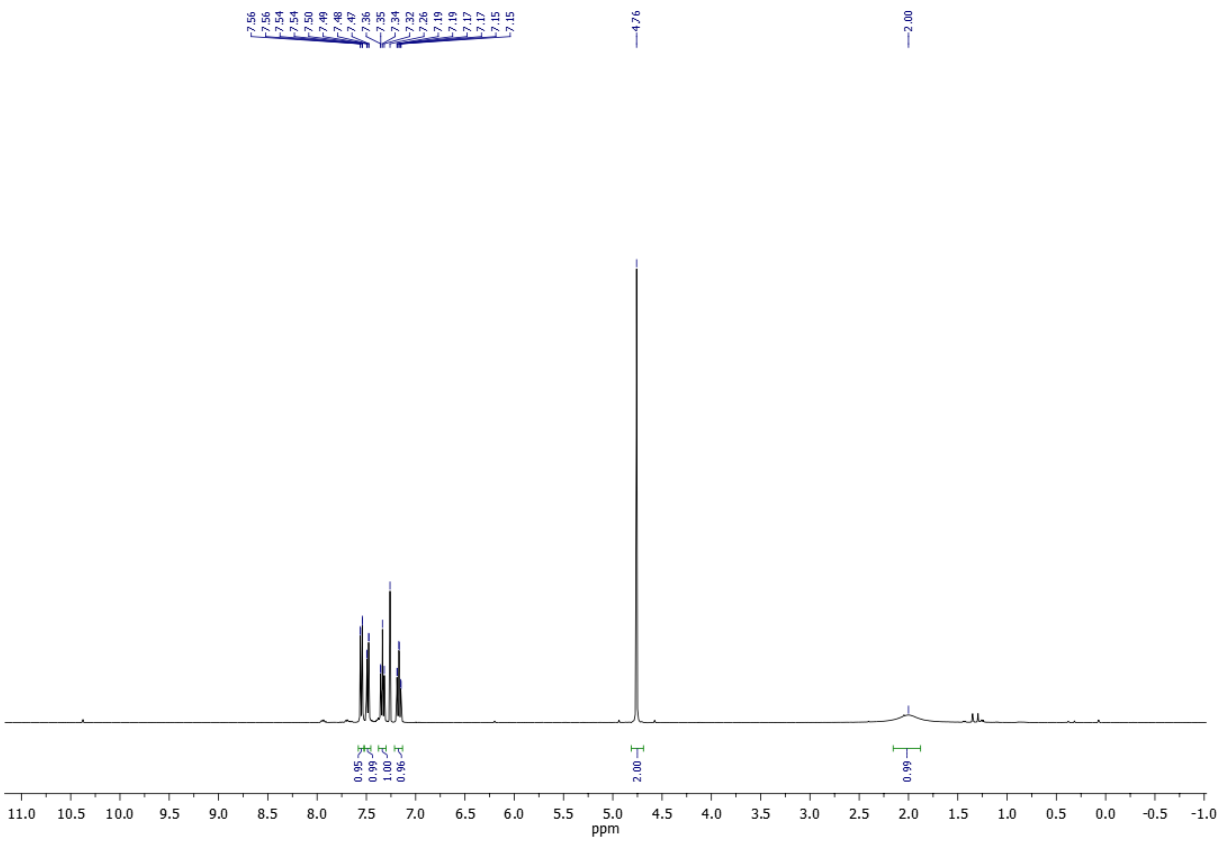


Figure S77. ^{1}H NMR spectrum of **8e** measured in $CDCl_3$.

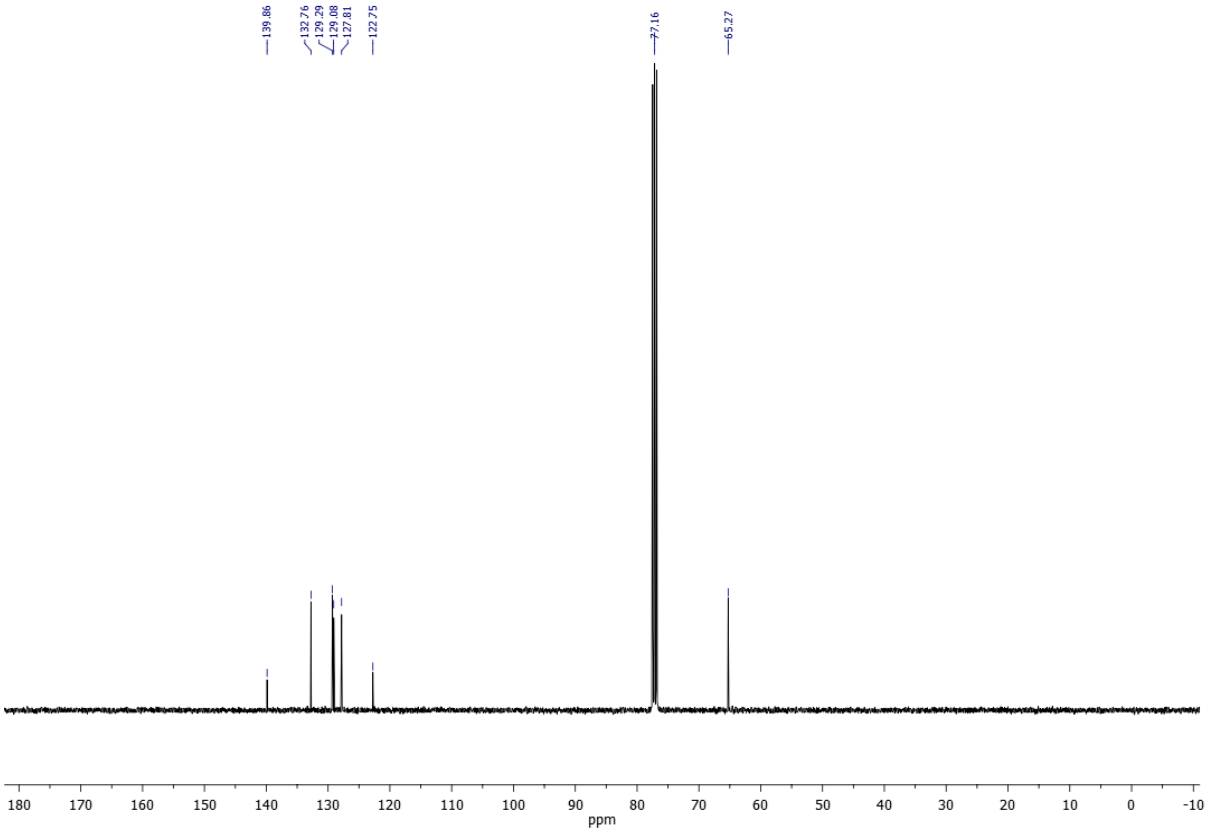


Figure S78. ^{13}C NMR spectrum of **8e** measured in $CDCl_3$.

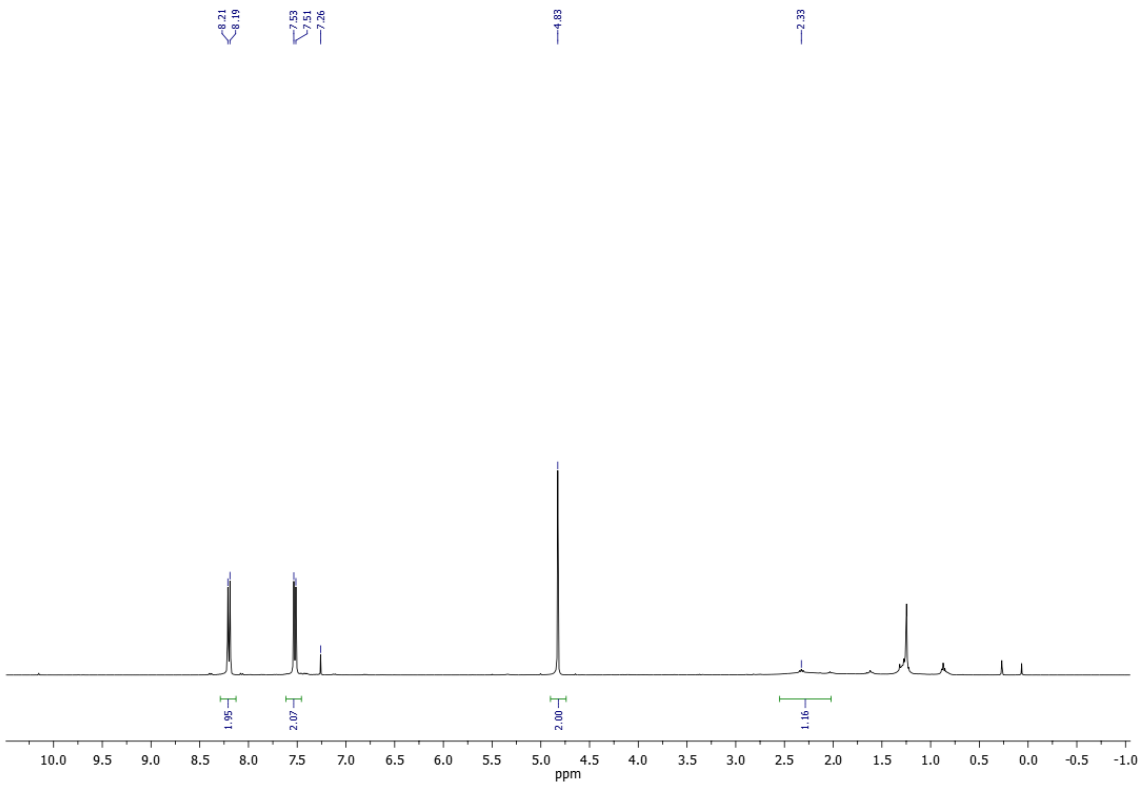


Figure S79. ^{1}H NMR spectrum of **8f** measured in $CDCl_3$.

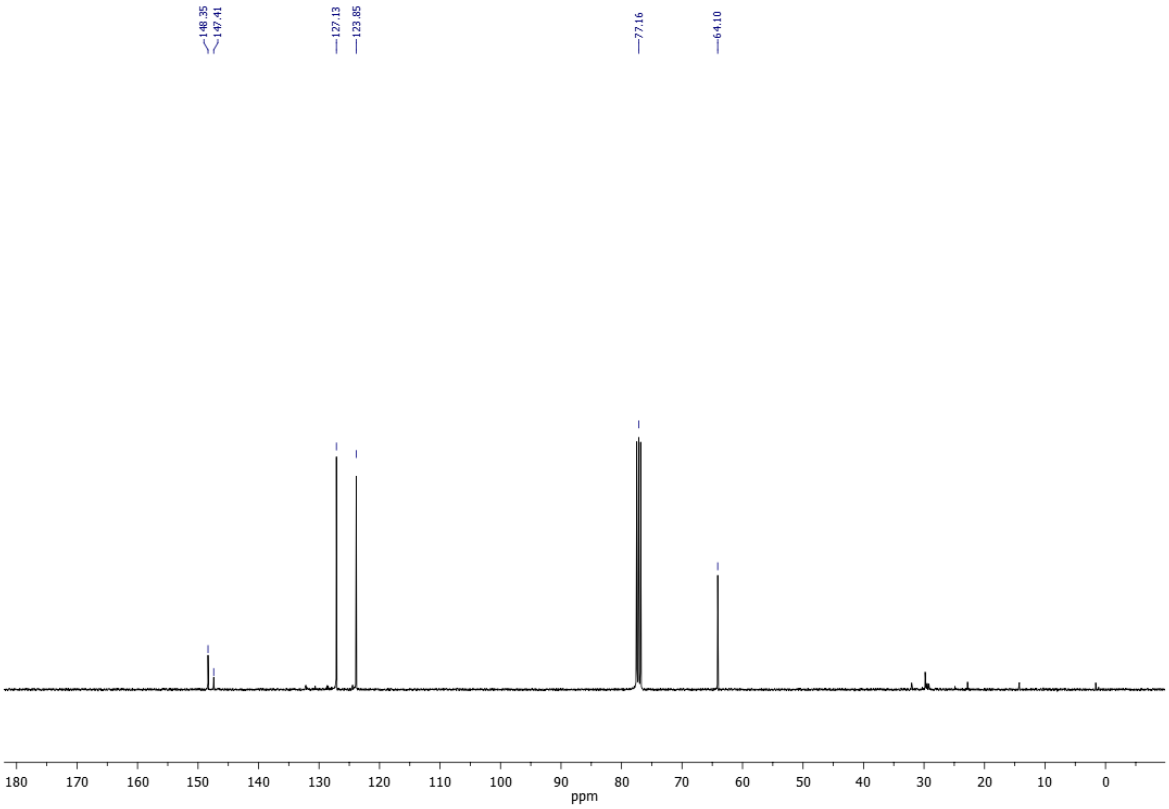


Figure S80. ^{13}C NMR spectrum of **8f** measured in $CDCl_3$.

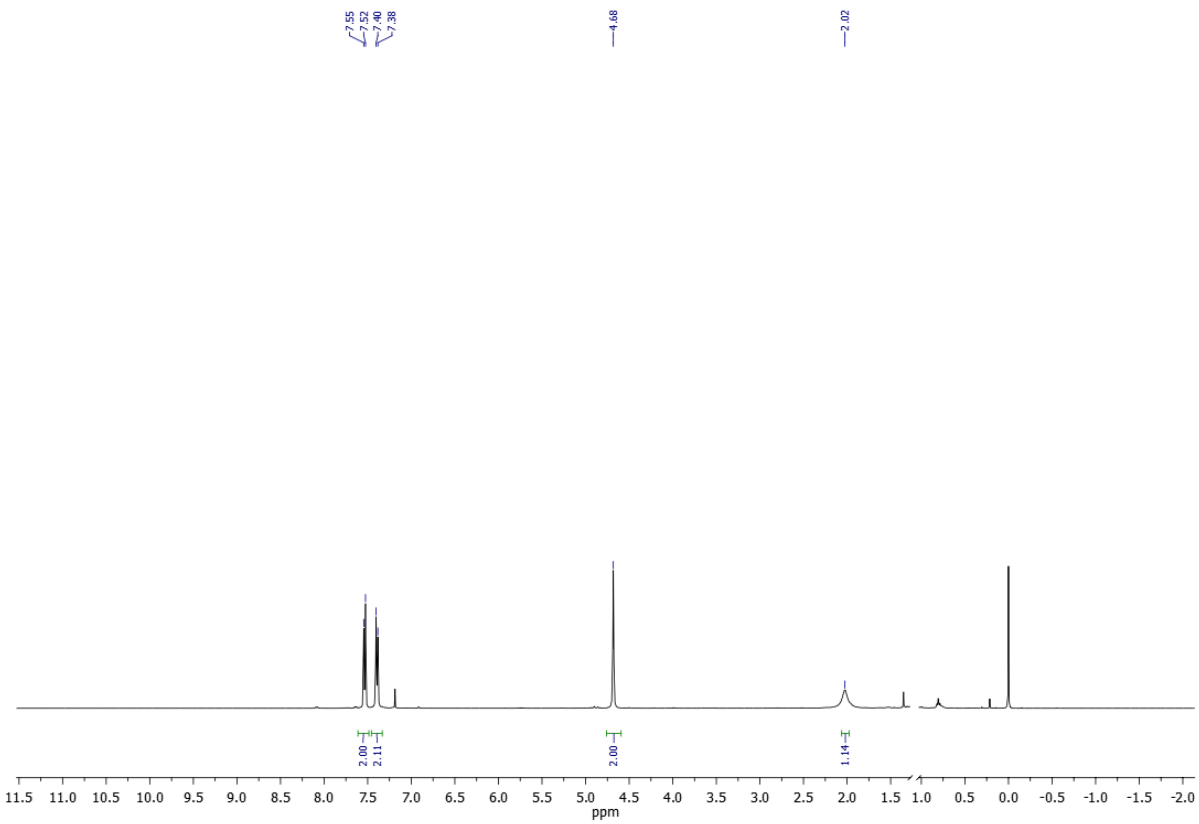


Figure S81. ^{1}H NMR spectrum of **8g** measured in $CDCl_3$.

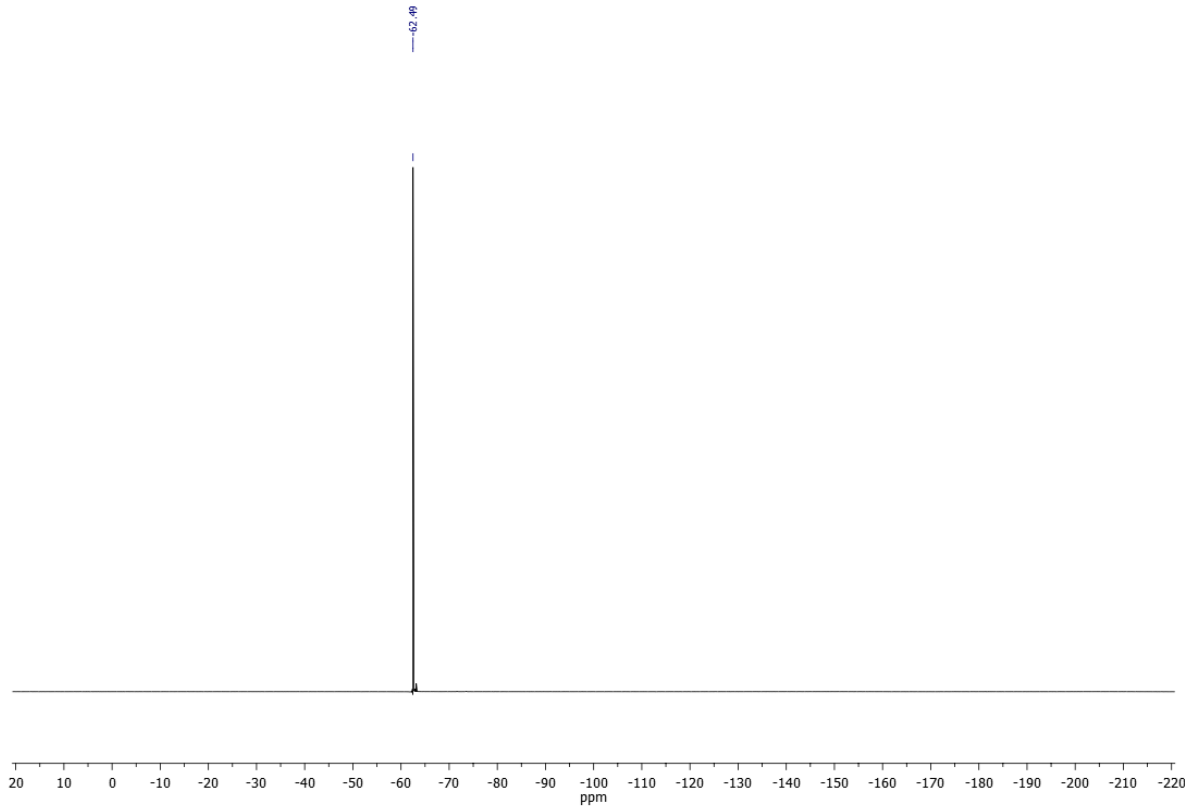


Figure S82. ^{19}F NMR spectrum of **8g** measured in $CDCl_3$.

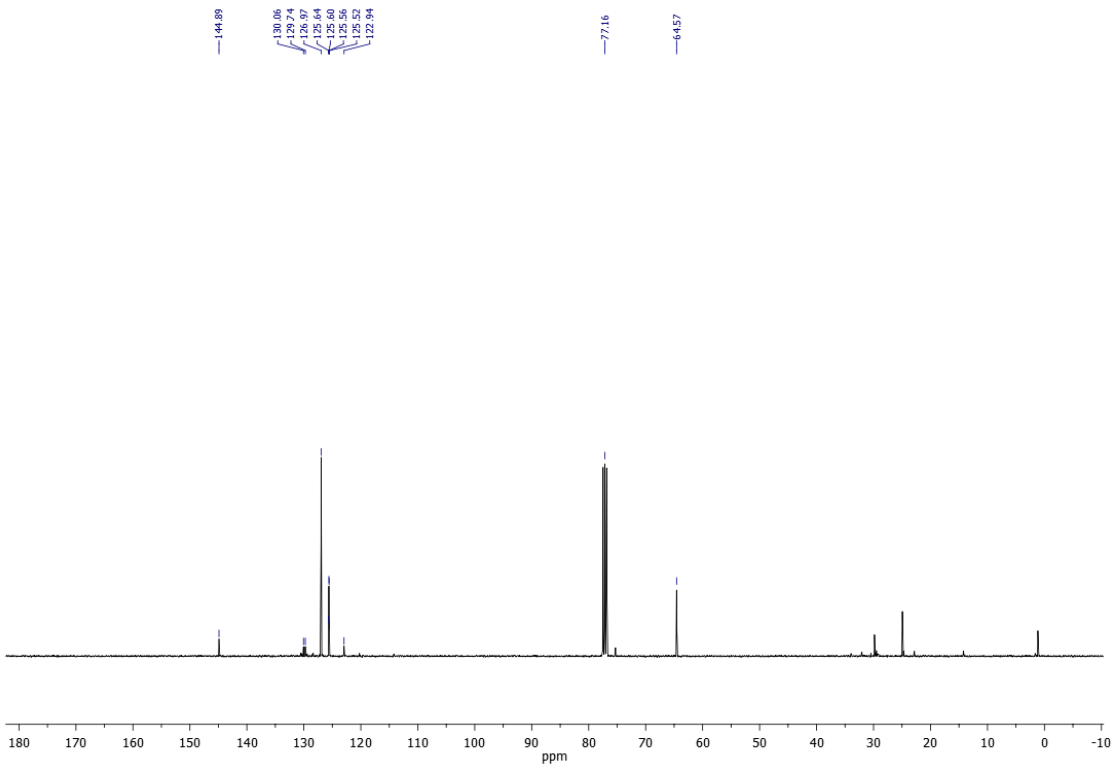


Figure S83. ^{13}C NMR spectrum of **8g** measured in $CDCl_3$.

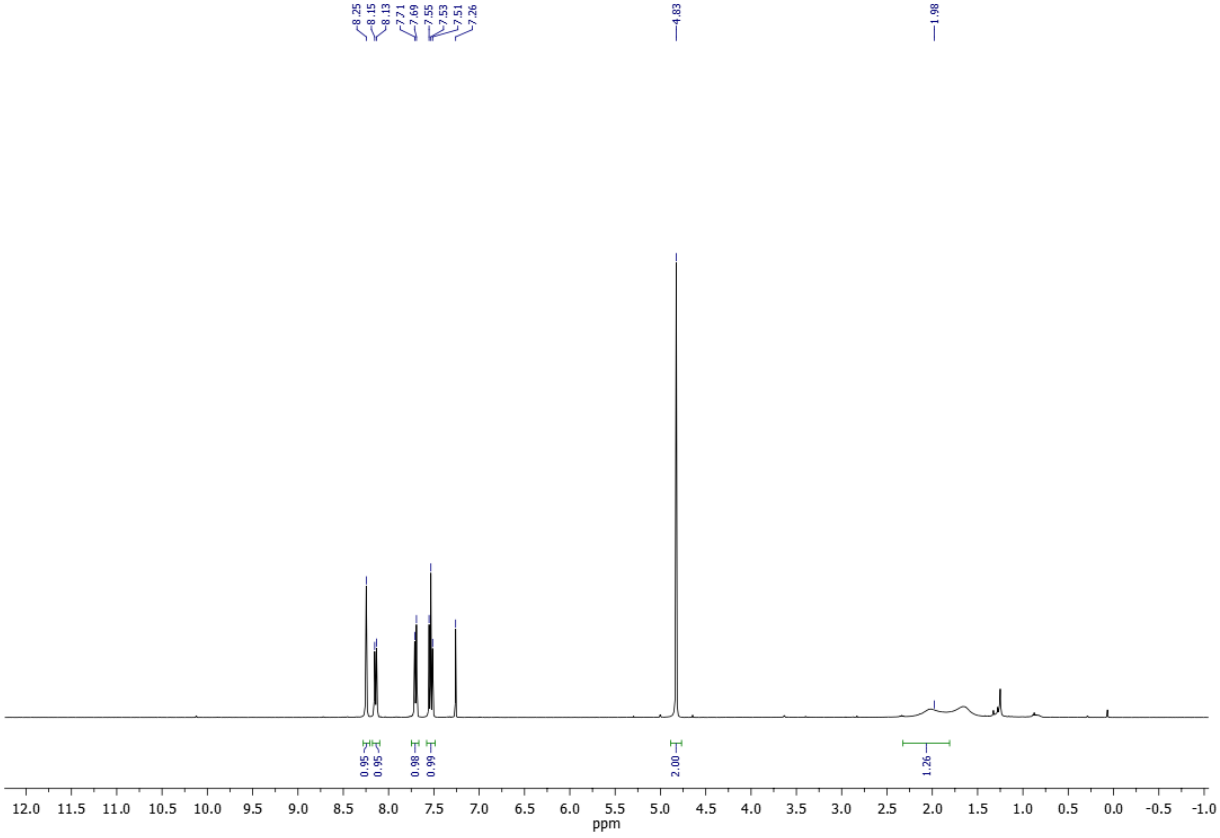


Figure S84. ^{1}H NMR spectrum of **8h** measured in $CDCl_3$.

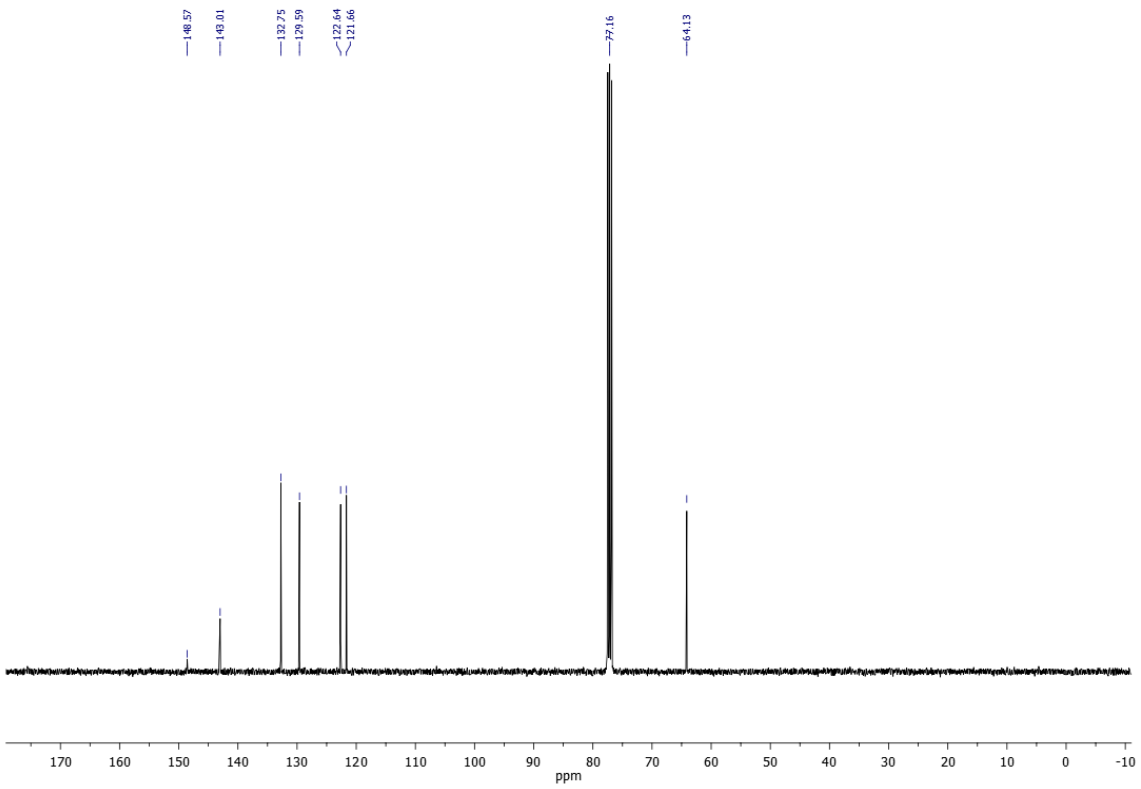


Figure S85. ^{13}C NMR spectrum of **8h** measured in $CDCl_3$.

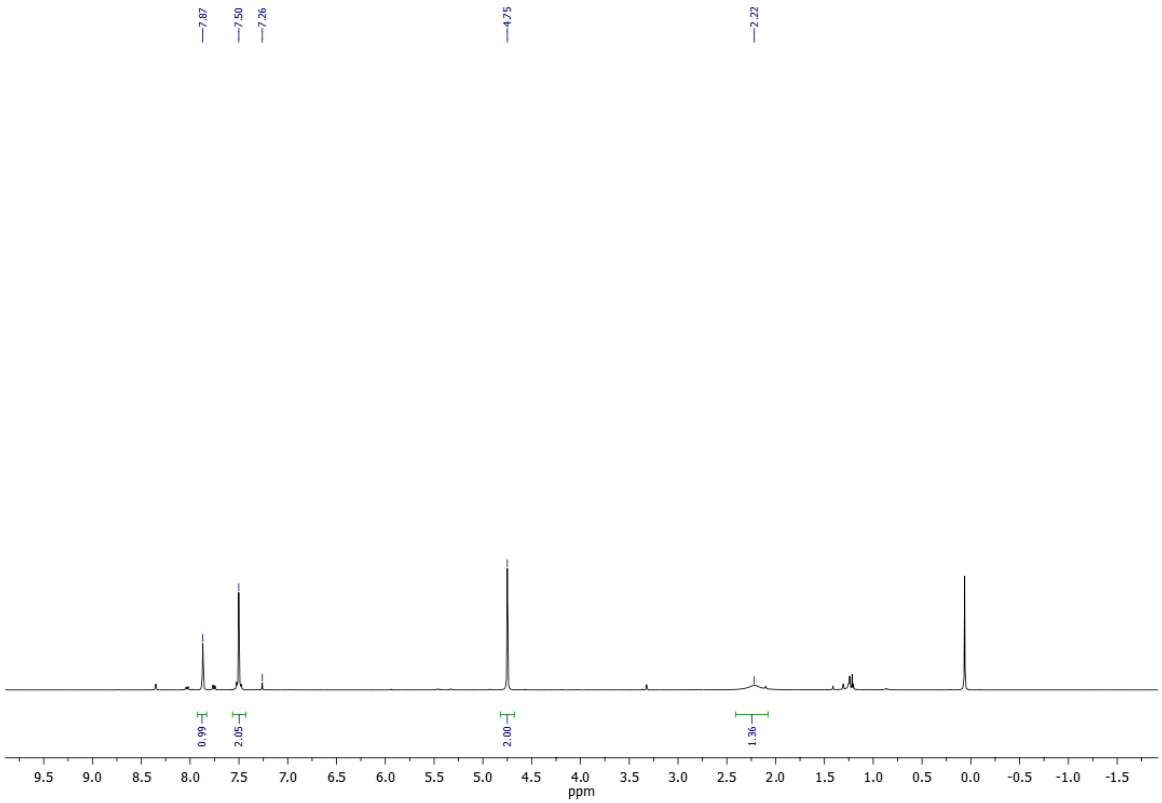


Figure S86. ^{1}H NMR spectrum of **8i** measured in $CDCl_3$.

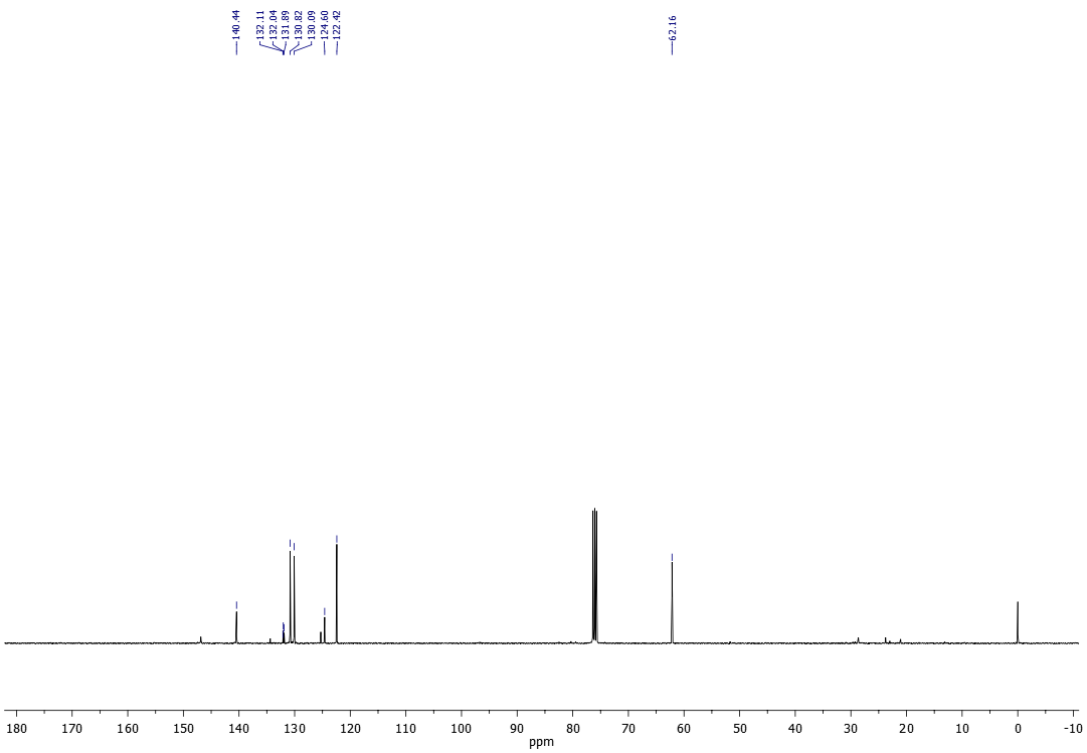


Figure S87. ^{13}C NMR spectrum of **8i** measured in $CDCl_3$.

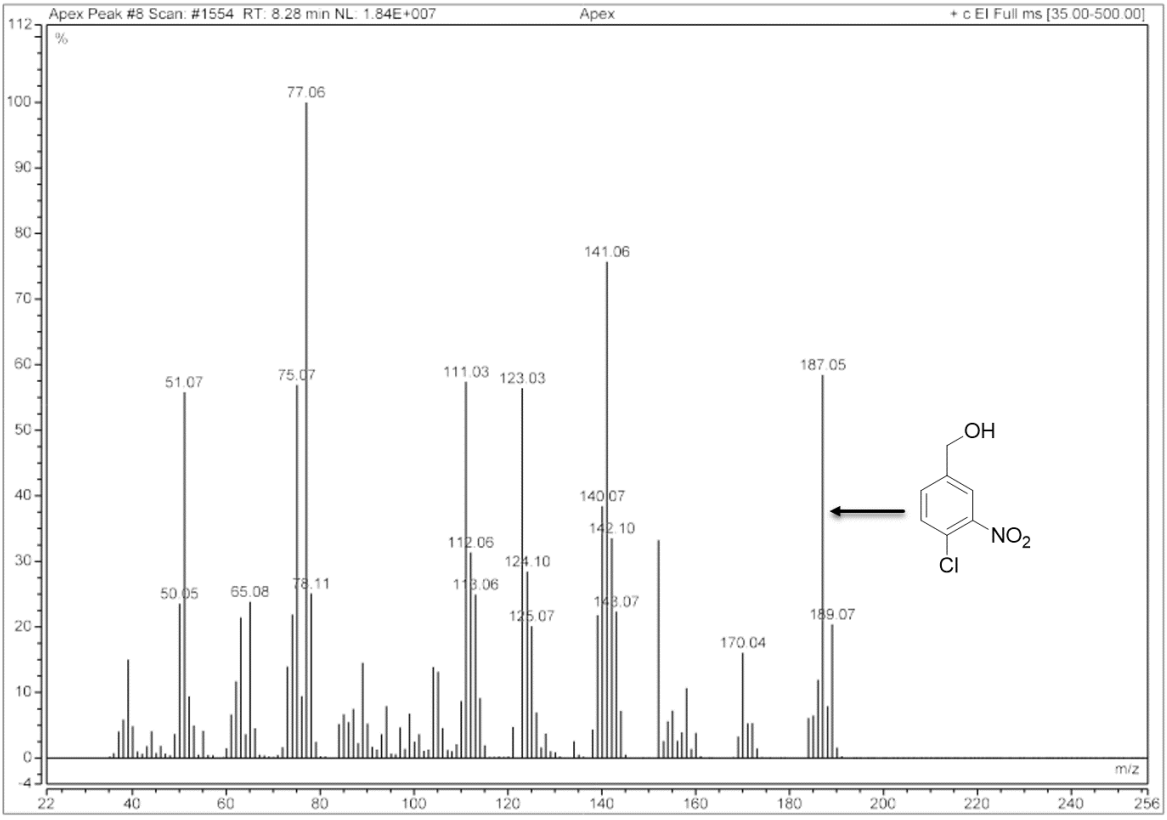


Figure S88. GC-MS spectrum of **8i** measured in ethyl acetate.

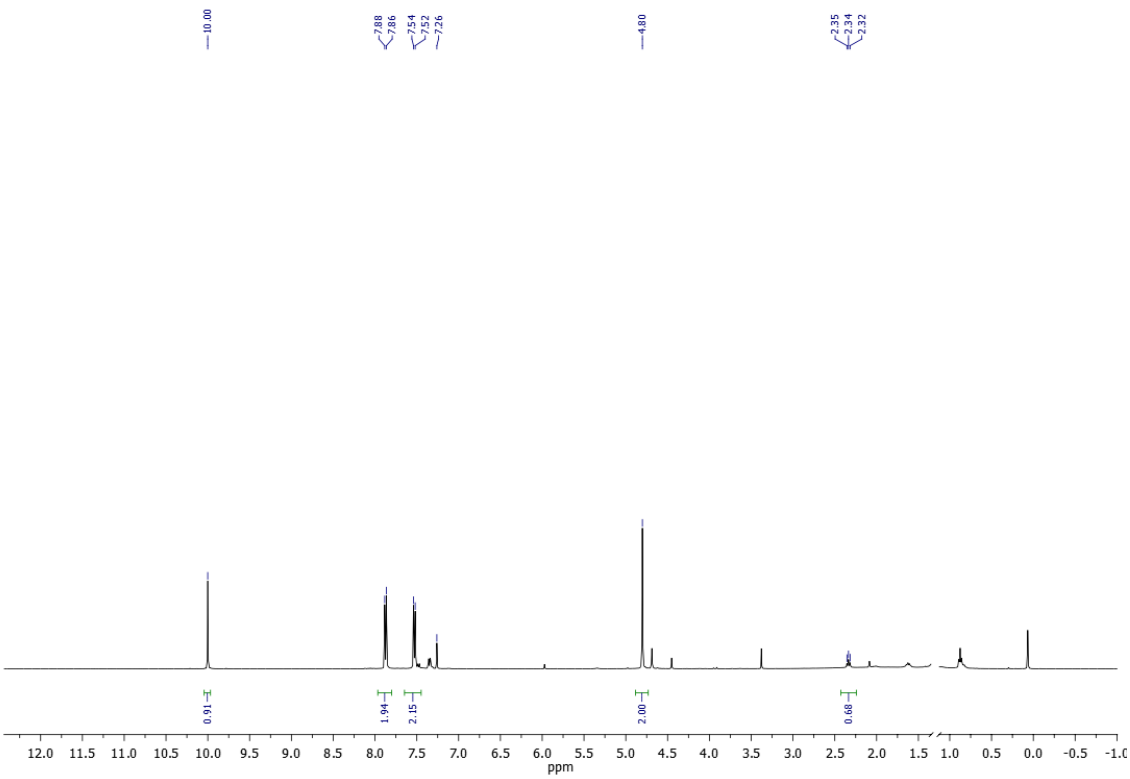


Figure S89. ^{1}H NMR spectrum of **8j** measured in $CDCl_3$.

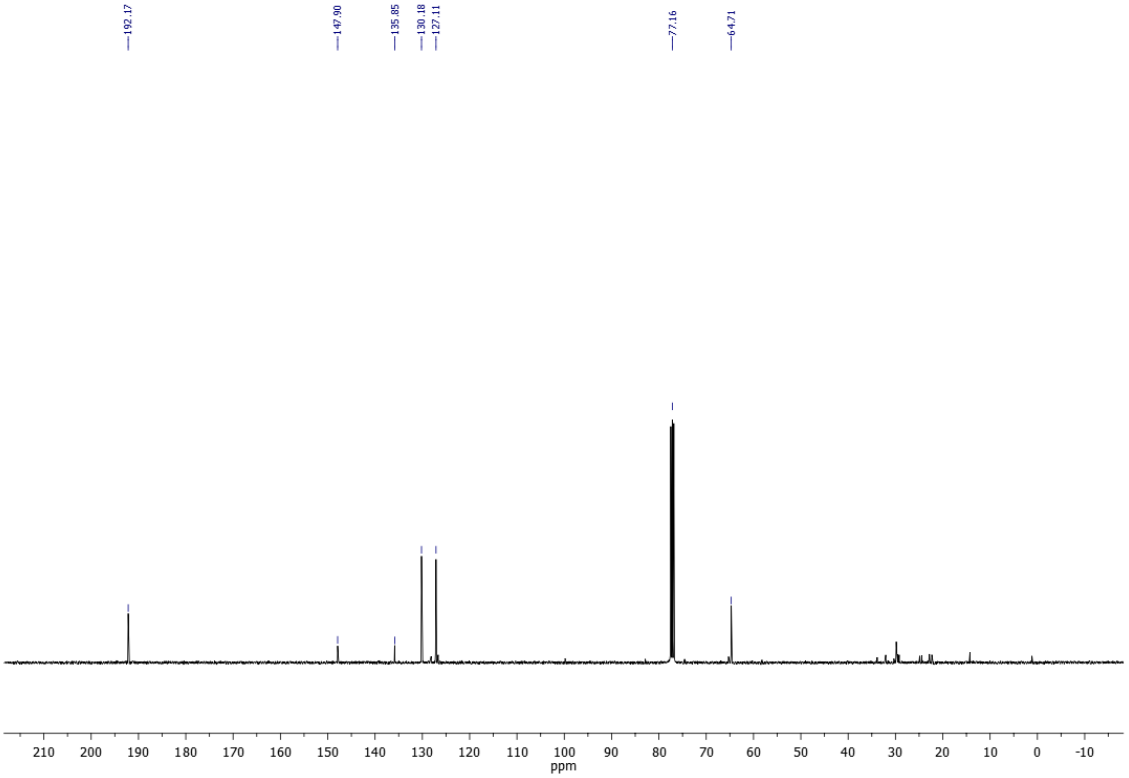


Figure S90. ^{13}C NMR spectrum of **8j** measured in $CDCl_3$.

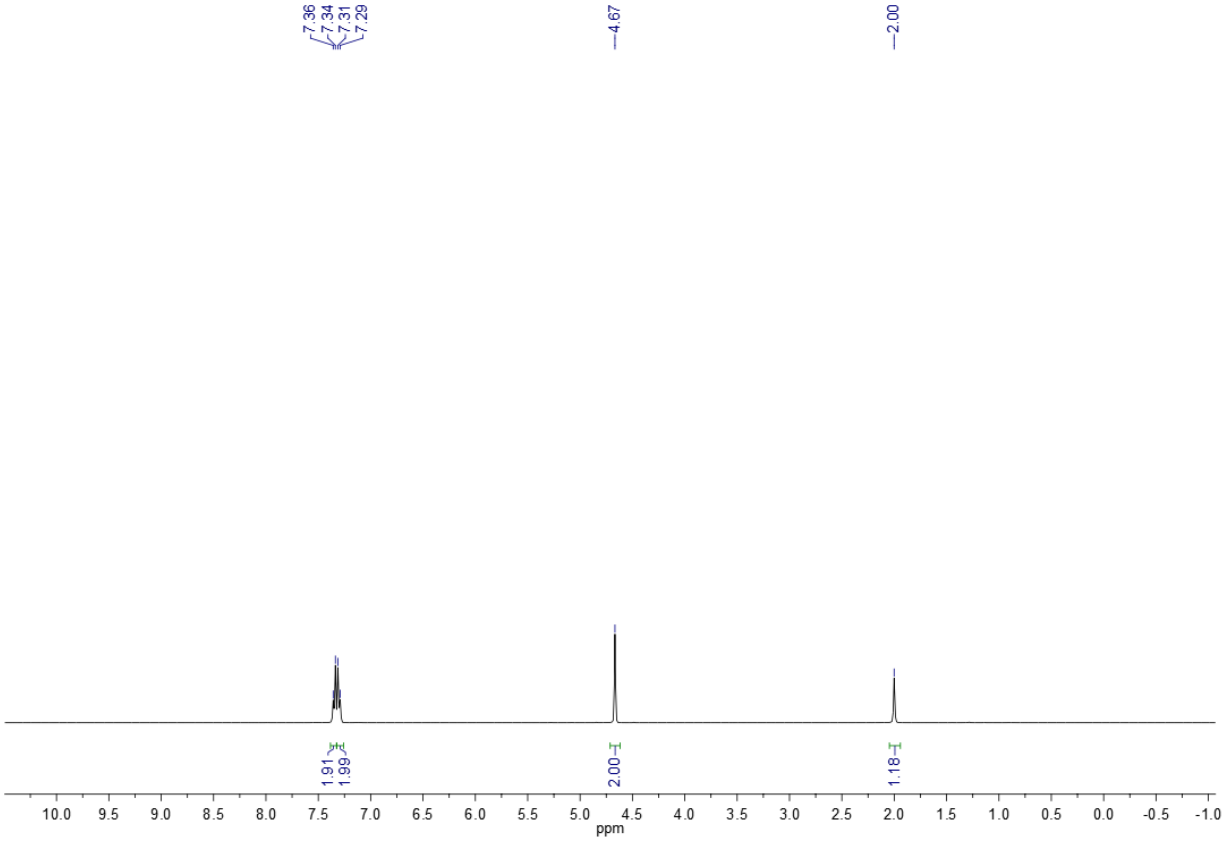


Figure S91. ^{1}H NMR spectrum of **8k** measured in $CDCl_3$.

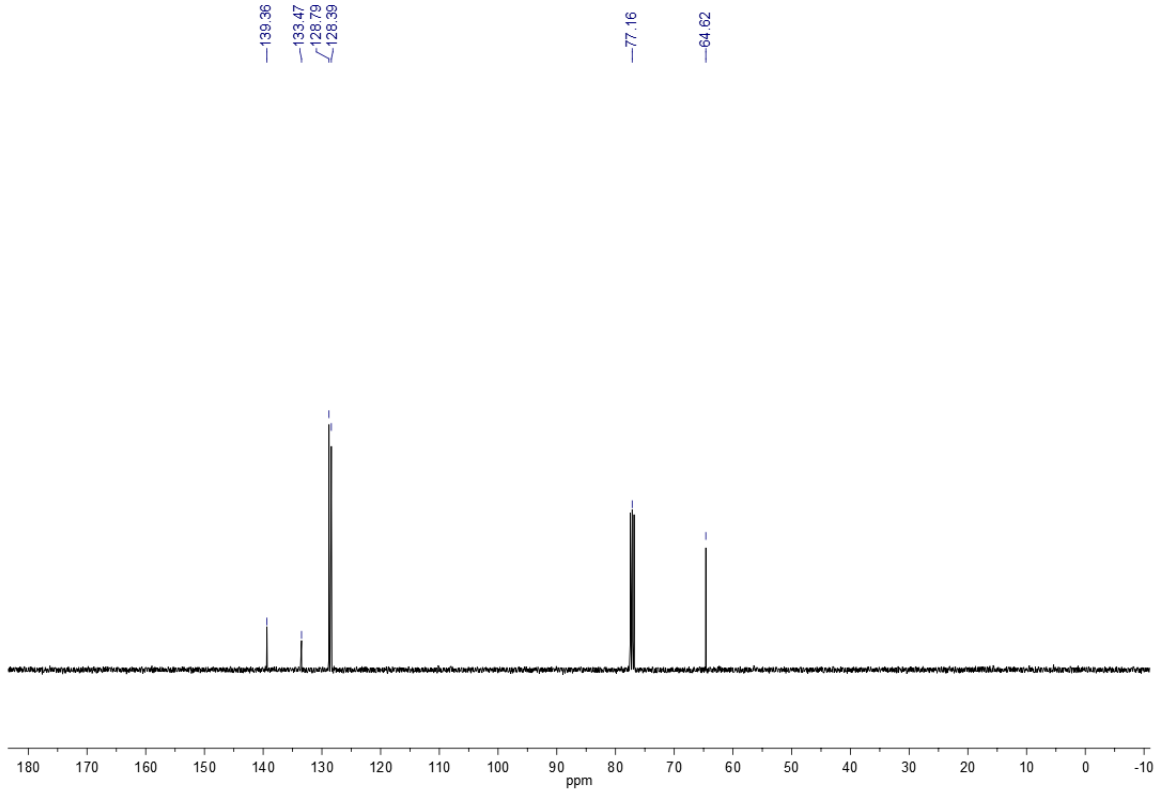


Figure S92. ^{13}C NMR spectrum of **8k** measured in $CDCl_3$.

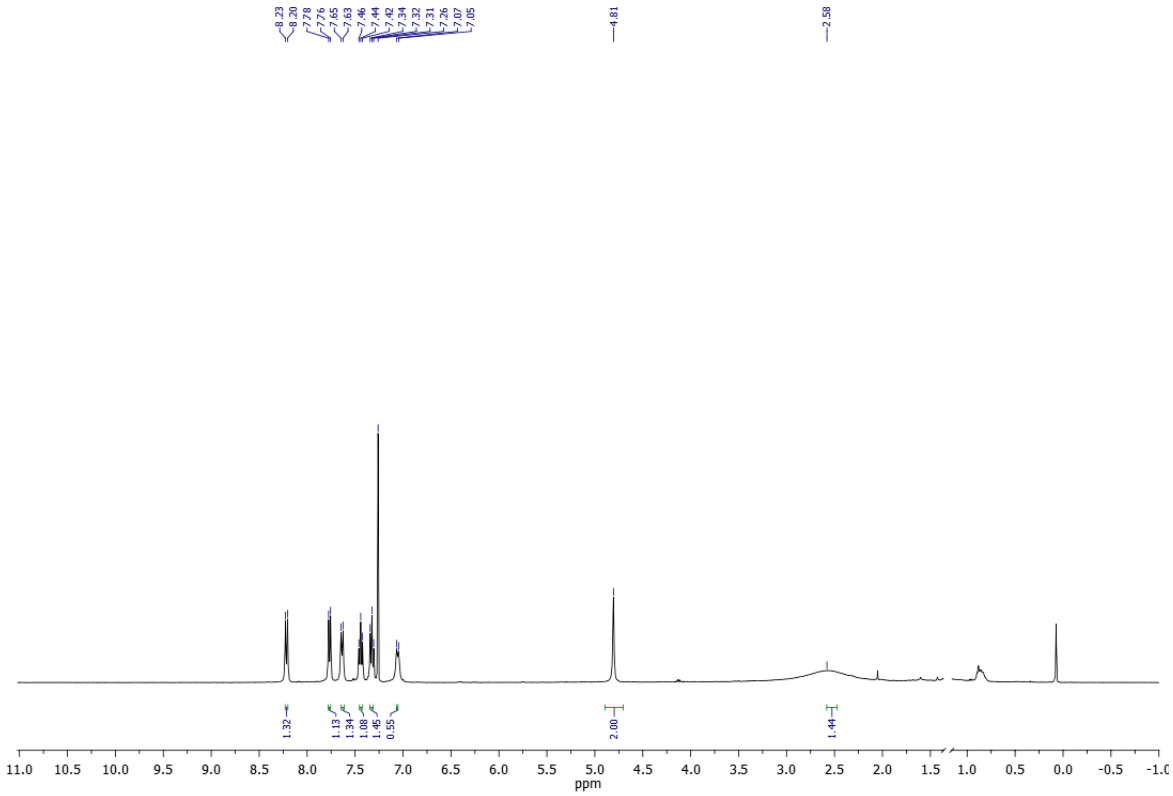


Figure S93. ^{1}H NMR spectrum of **8l** measured in $CDCl_3$.

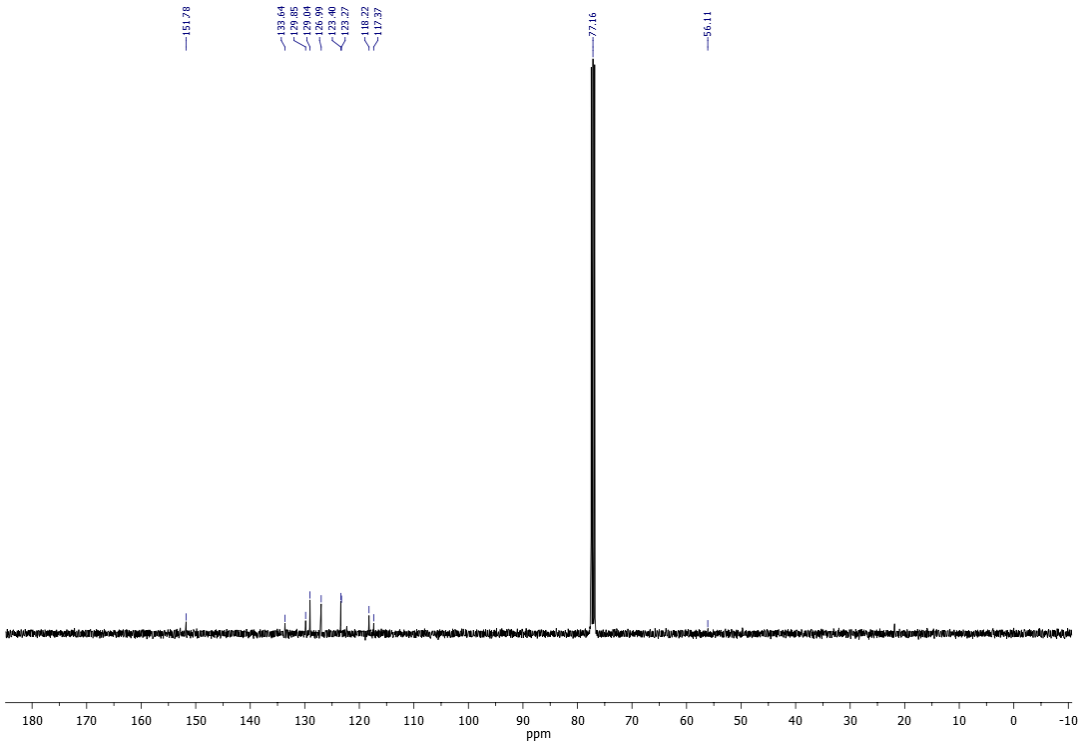


Figure S94. ^{13}C NMR spectrum of **8l** measured in $CDCl_3$.

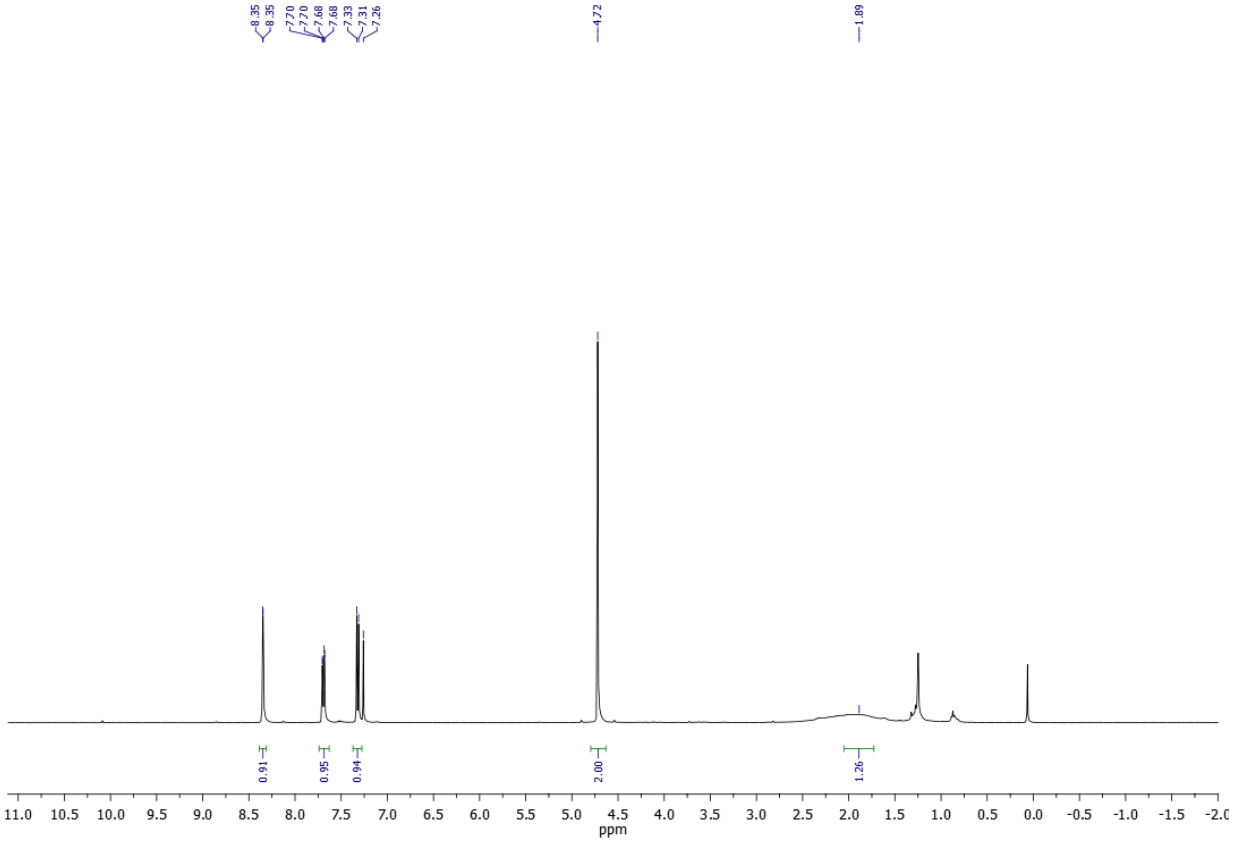


Figure S95. ^{1}H NMR spectrum of **8m** measured in $CDCl_3$.

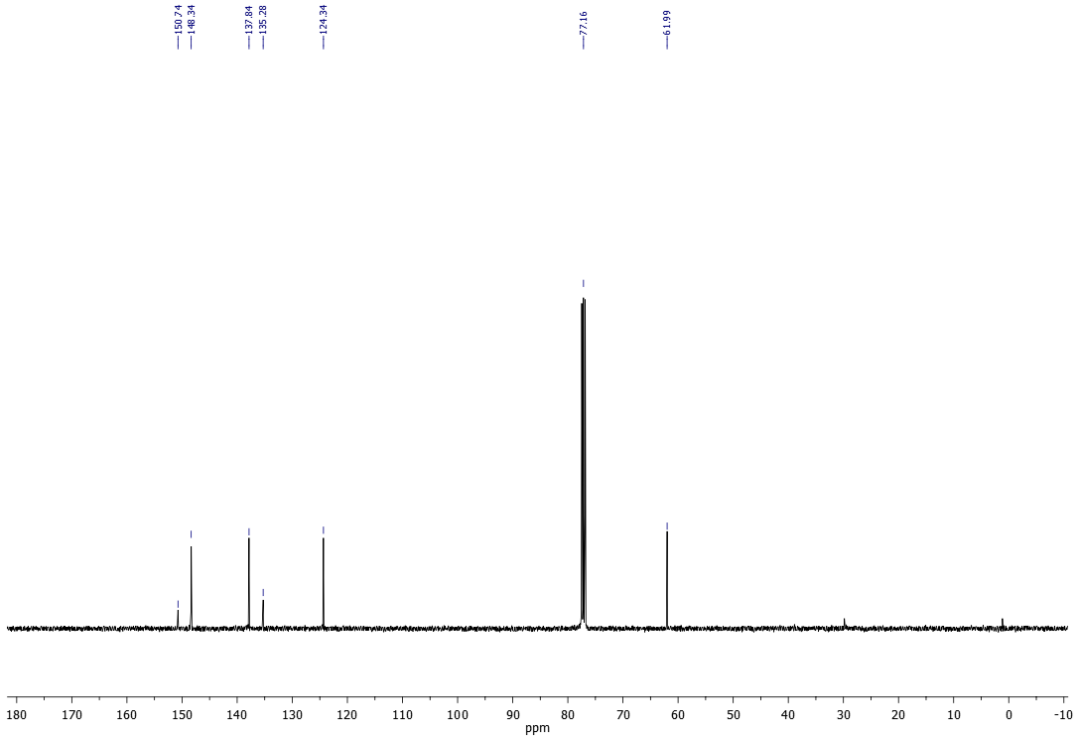


Figure S96. ^{13}C NMR spectrum of **8m** measured in $CDCl_3$.

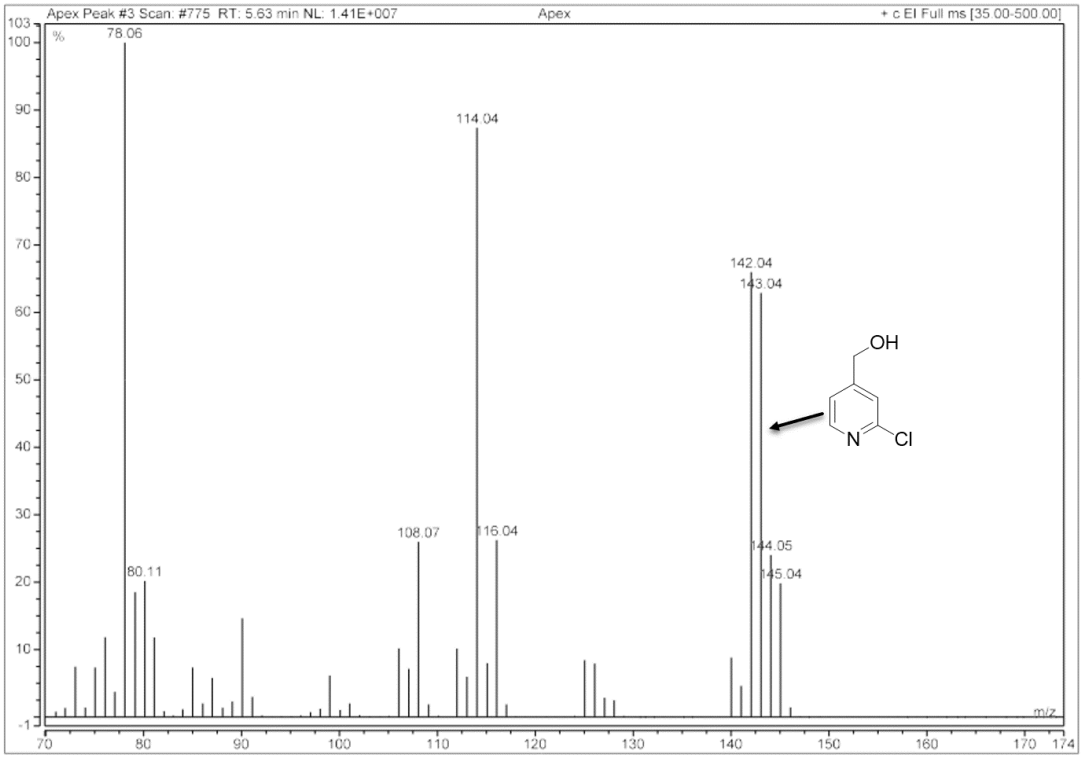


Figure S97. GC-MS spectrum of **8m** measured in ethyl acetate.

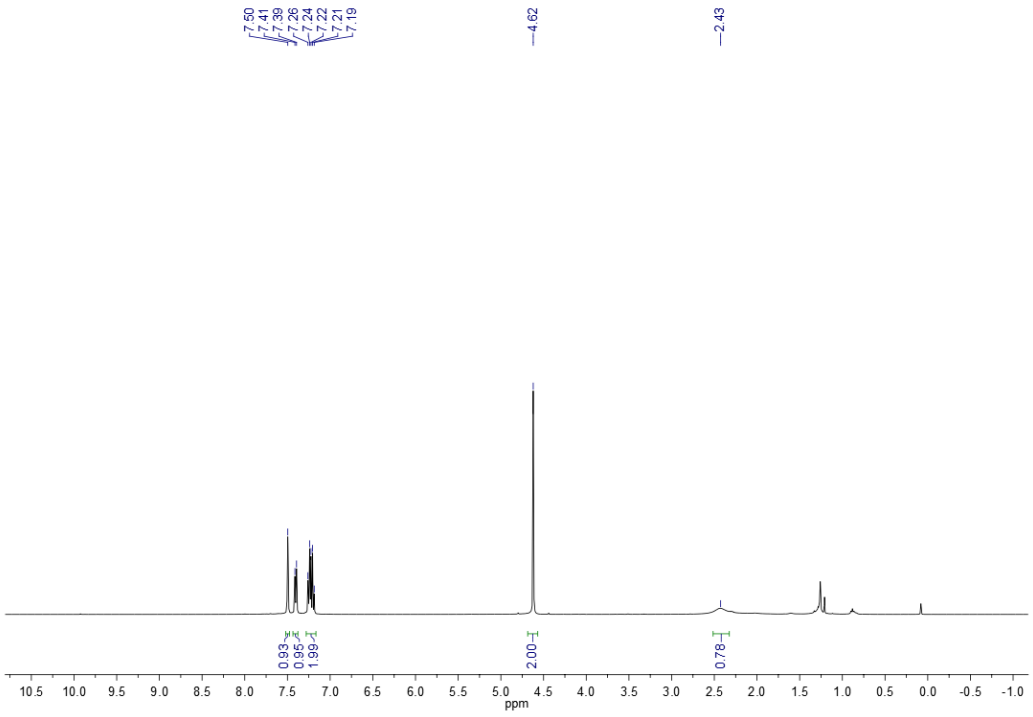


Figure S98. ^{1}H NMR spectrum of **8n** measured in $CDCl_3$.

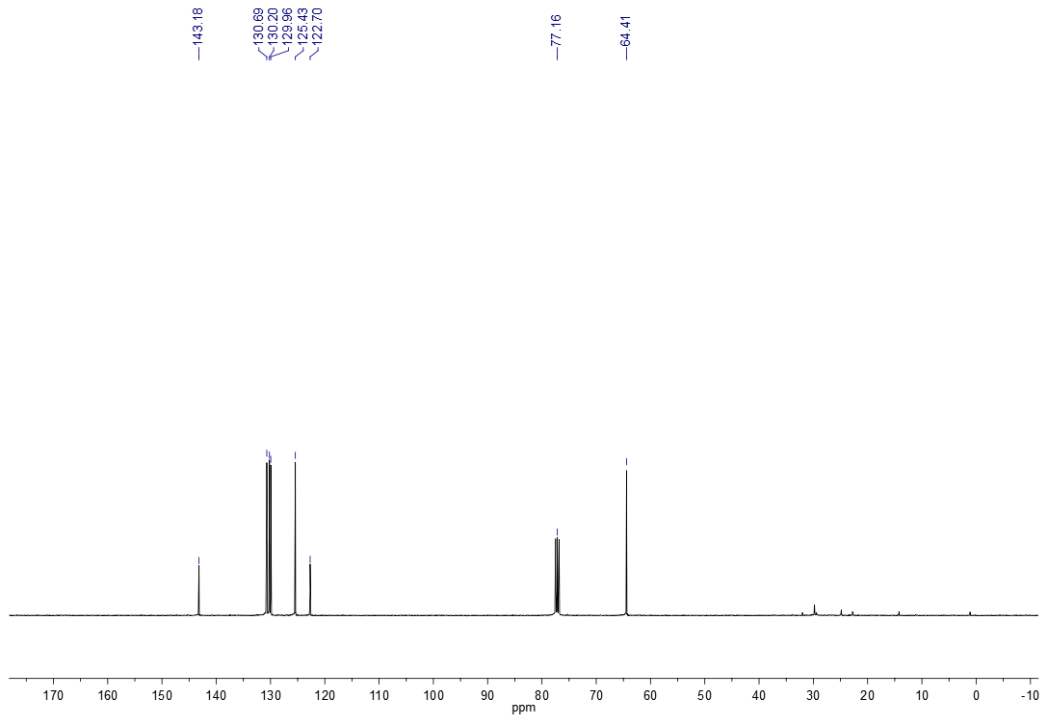


Figure S99. ^{13}C NMR spectrum of **8n** measured in $CDCl_3$.

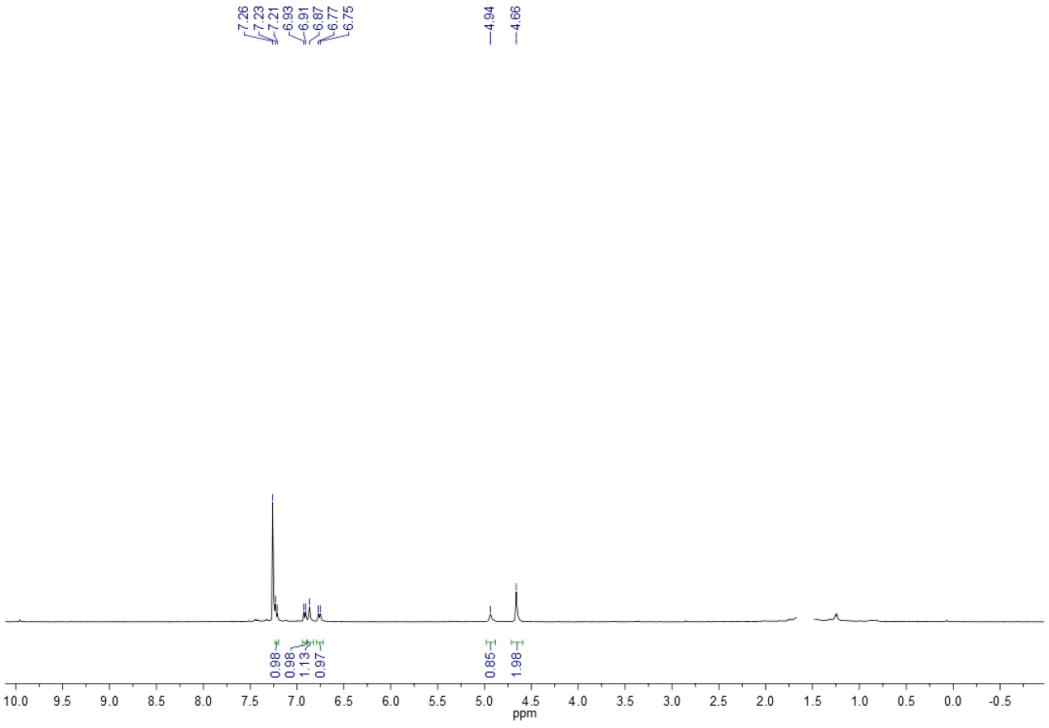


Figure S100. ^{1}H NMR spectrum of **8o** measured in $CDCl_3$.

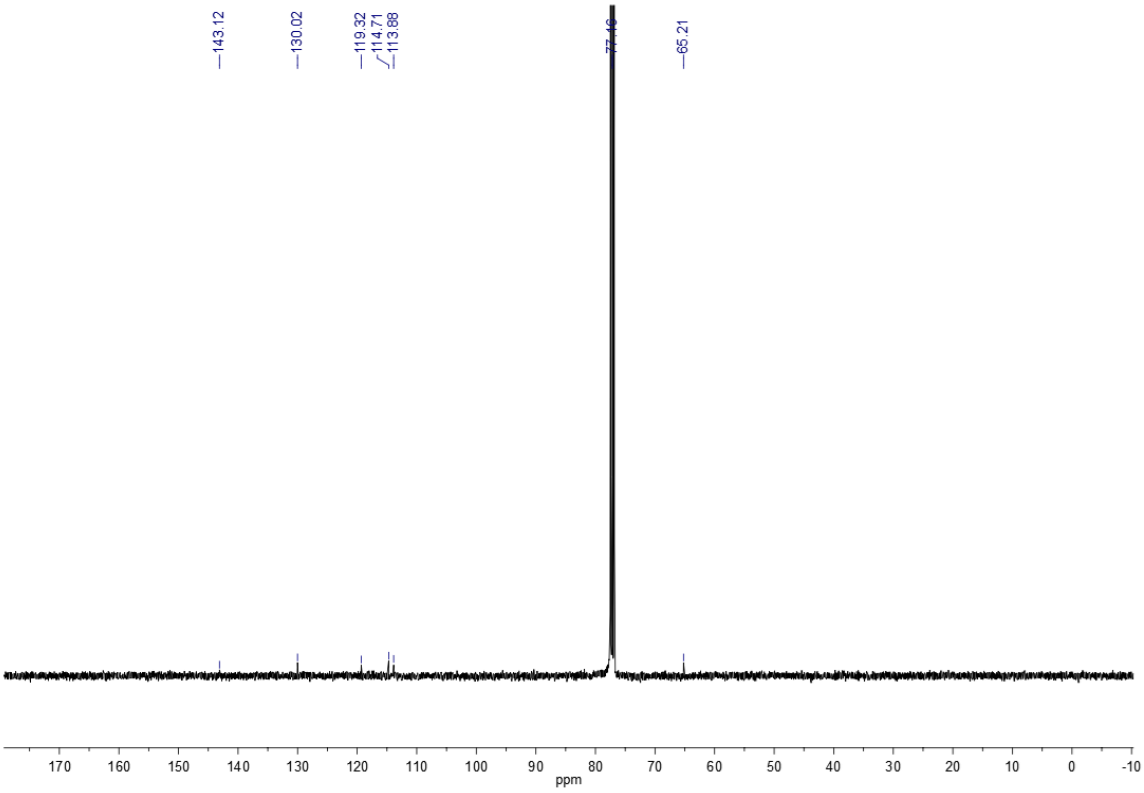


Figure S101. ^{13}C NMR spectrum of **8o** measured in $CDCl_3$.

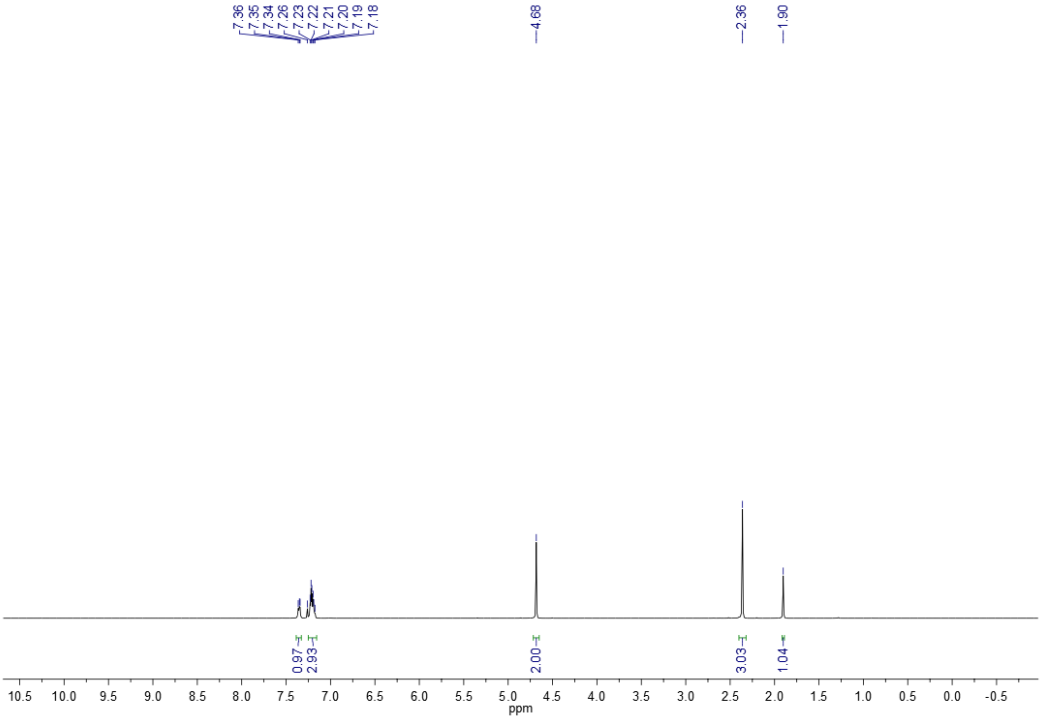


Figure S102. ^{1}H NMR spectrum of **8p** measured in $CDCl_3$.

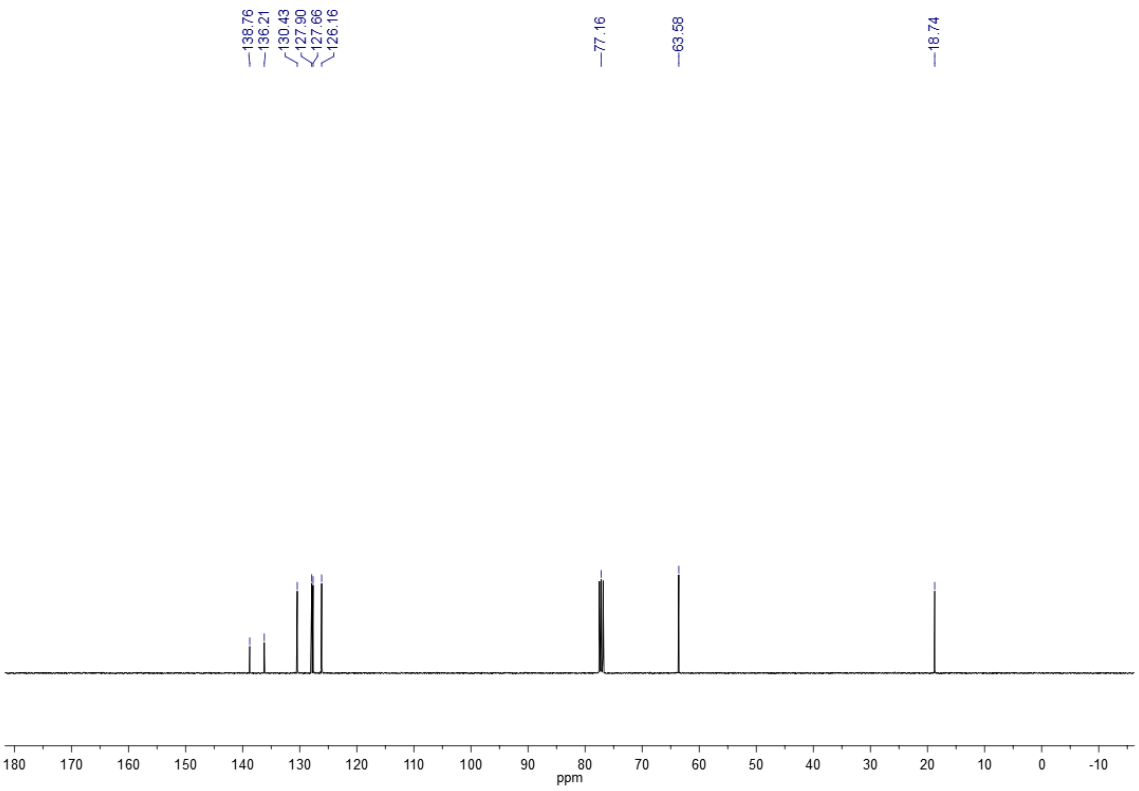


Figure S103. ^{13}C NMR spectrum of **8p** measured in $CDCl_3$.

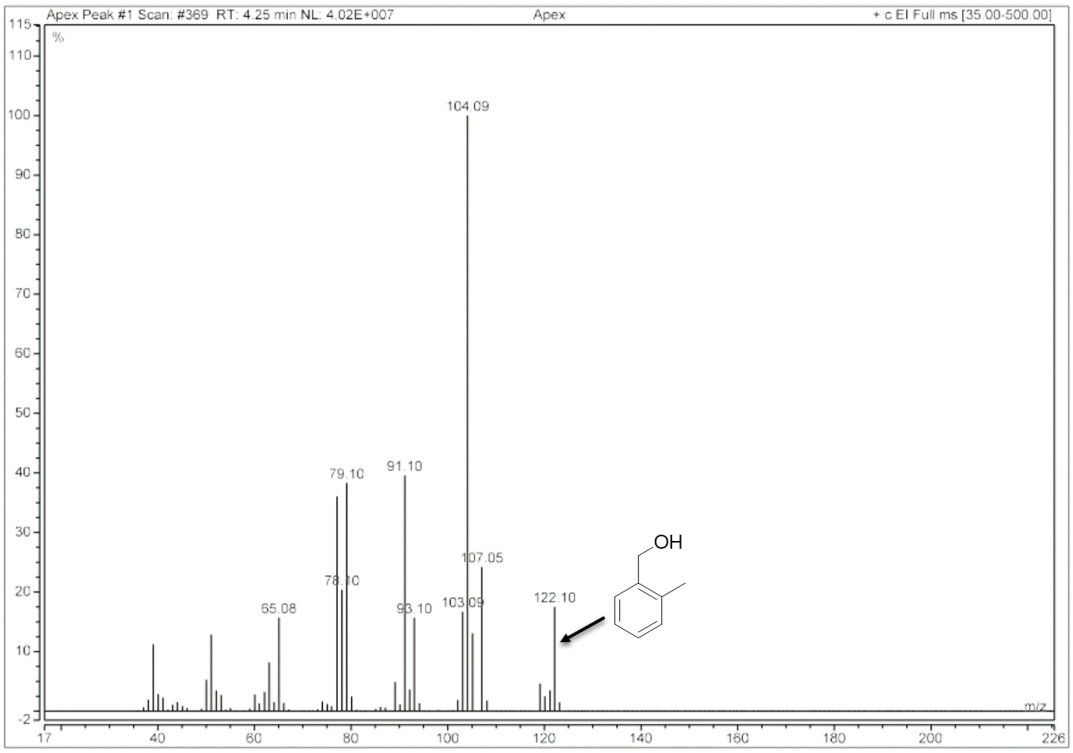


Figure S104. GC-MS spectrum of **8p** measured in ethyl acetate.

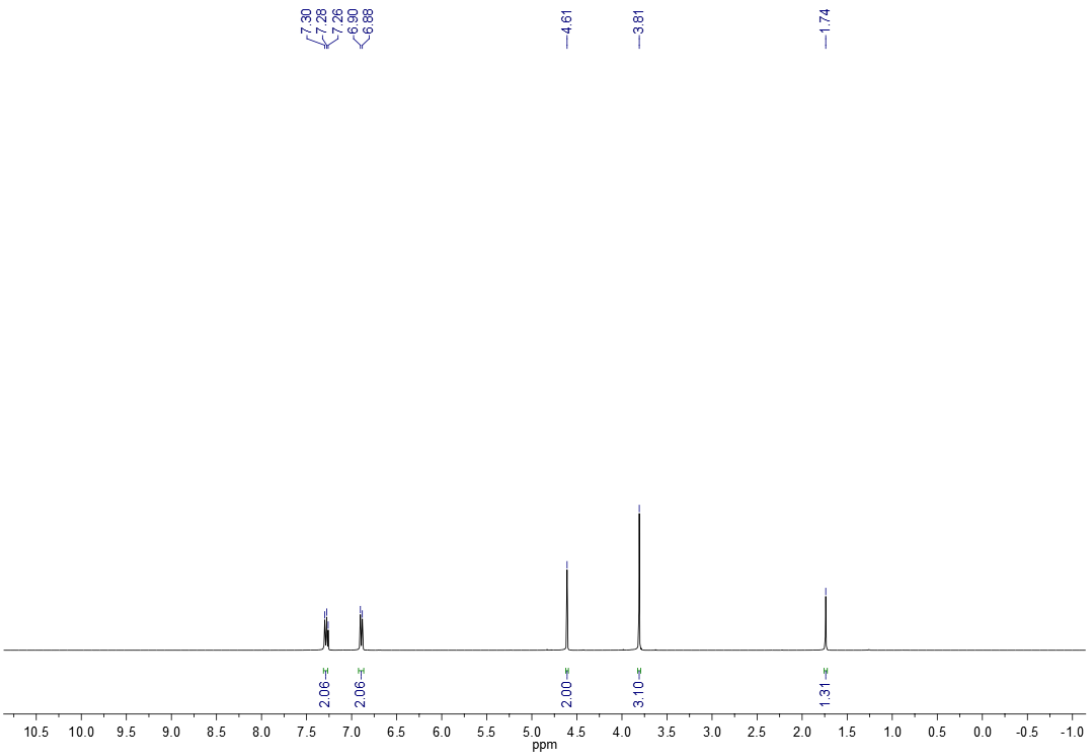


Figure S105. ^{1}H NMR spectrum of **8q** measured in $CDCl_3$.

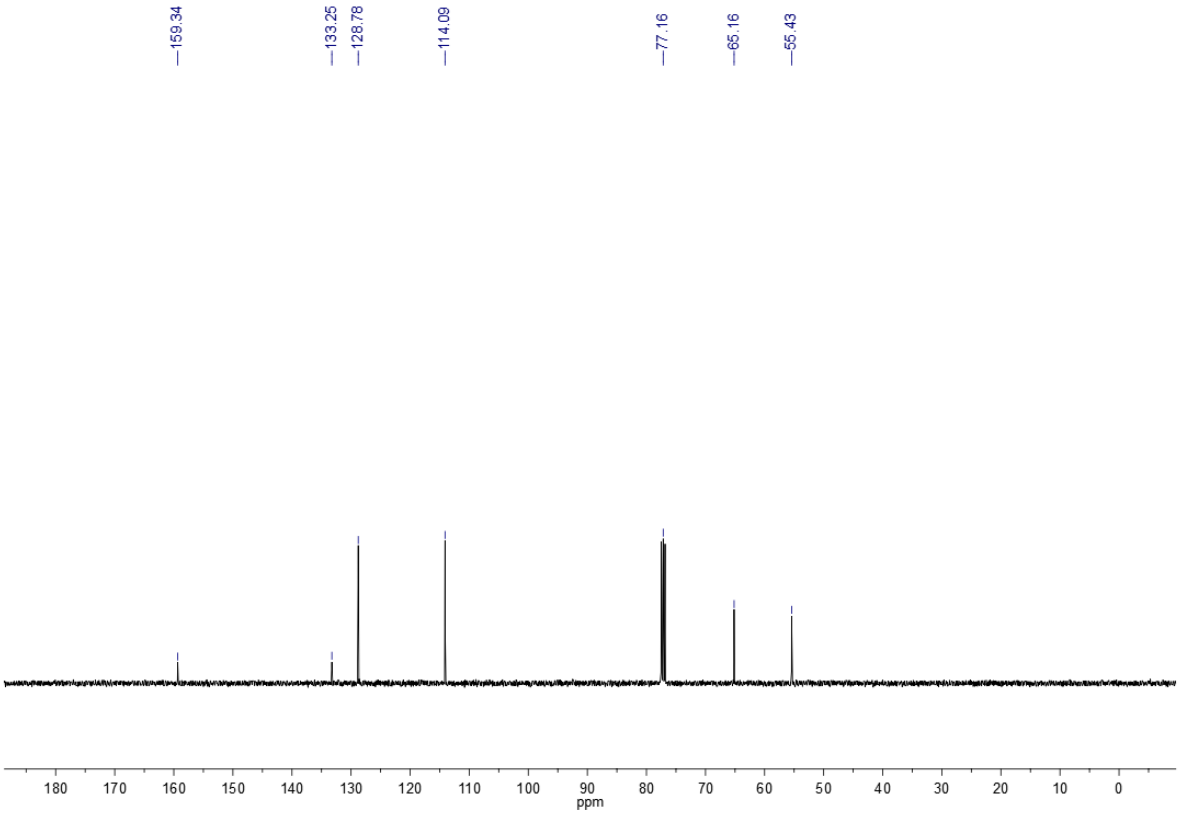


Figure S106. ^{13}C NMR spectrum of **8q** measured in $CDCl_3$.

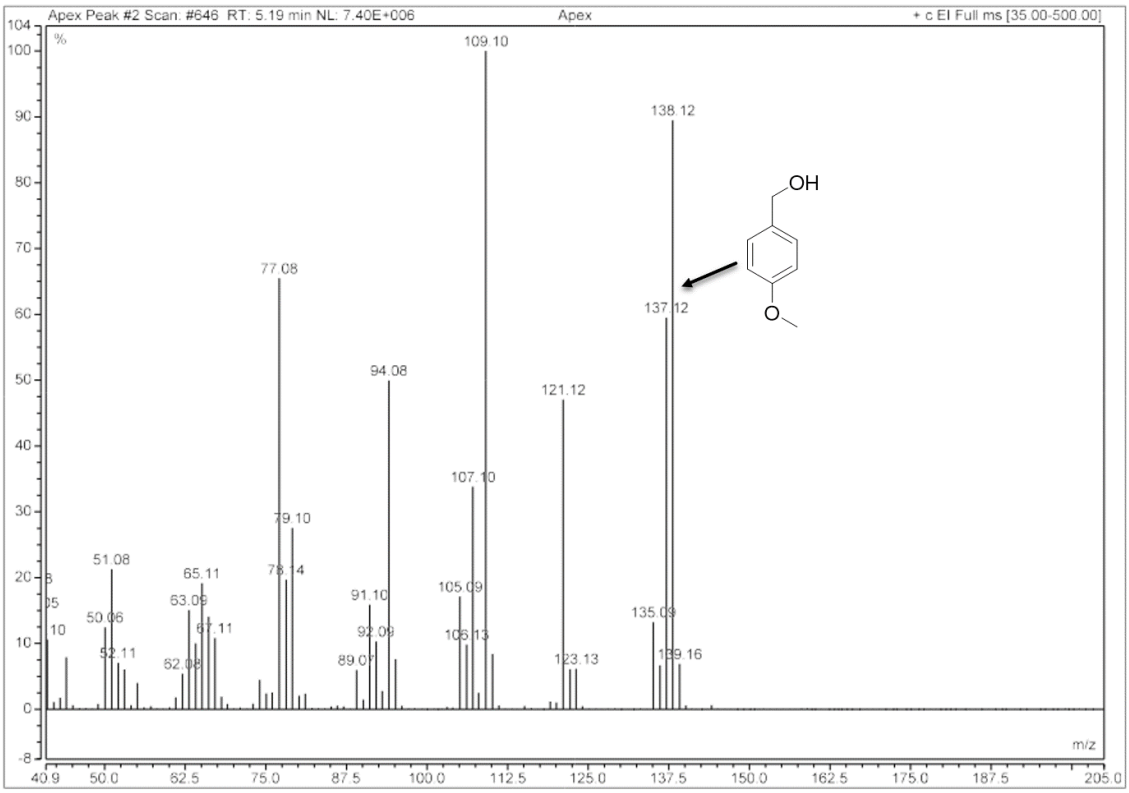


Figure S107. GC-MS spectrum of **8q** measured in ethyl acetate.

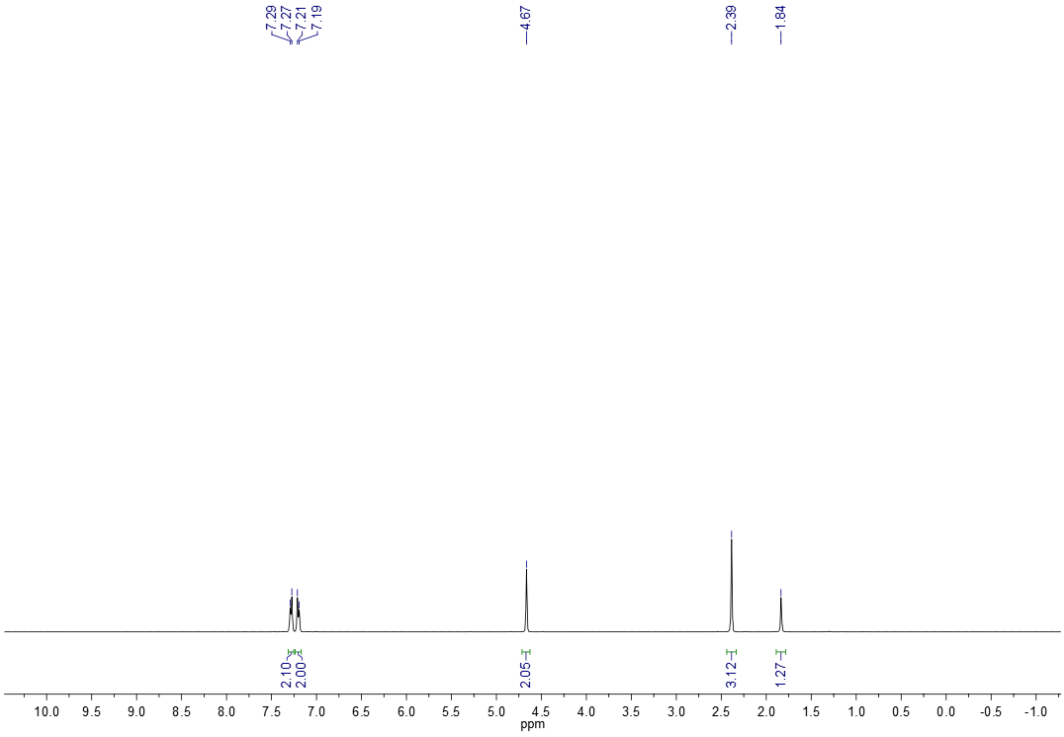


Figure S108. ^{1}H NMR spectrum of **8r** measured in $CDCl_3$.

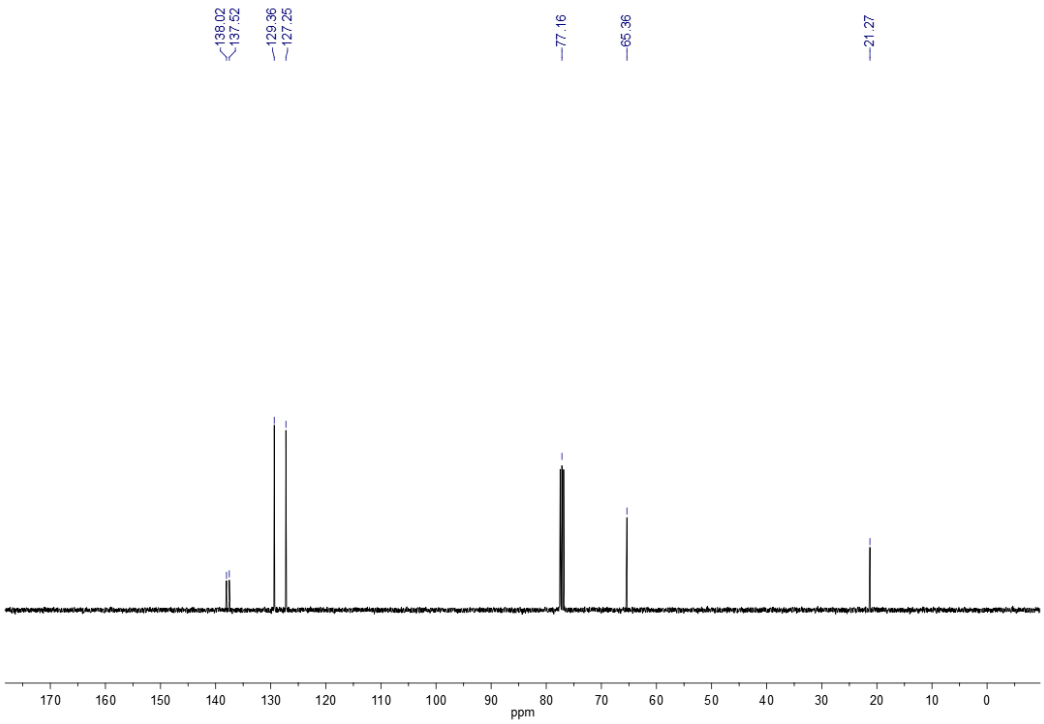
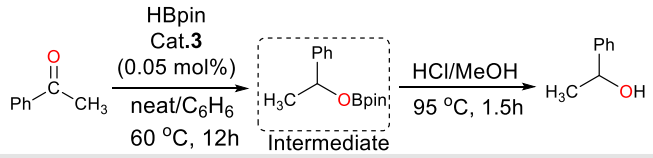


Figure S109. ^{13}C NMR spectrum of **8r** measured in $CDCl_3$.



entry	deviation from the standard conditions	yield of product (%)[b]
1	**none**	81
2	0.1 mol% cat. **3**	80.8
3	1 mol% cat. **3**	81
4	0.5 mol% cat.**3**	80.6
5	24h instead of 13.5h	81
6	10h instead of 13.5h	72
7	8h instead of 13.5h	70

[a]Reaction conditions: **Ketone** (1 equiv.), **HBpin** (1 equiv.), cat.**3** (0.05 mol%), neat/C_6H_6 condition, RT, 13.5 h. [b]Isolated yields.

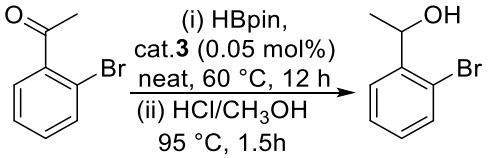
Table S2. Optimisation table for the synthesis of secondary alcohol from ketone.

General Procedure for ketone to secondary alcohol conversion (10a-l)

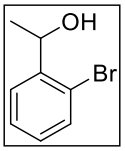
In a nitrogen atmosphere, a 25 mL Schlenk tube was charged with 1 equiv. of ketone, 1 equiv. of pinacolborane, and 0.1 mol% of Cat.**3** [benzene, 1-2 ml, for solid substrates]. For the duration of 12 h, the reaction mixture was stirred at 60 °C. After the reaction was complete, the resulting boronate ester residue was treated with 1.5 h of refluxing methanol and 1 M aqueous HCl. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The

pure secondary alcohols (**10a-l**) were obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent.

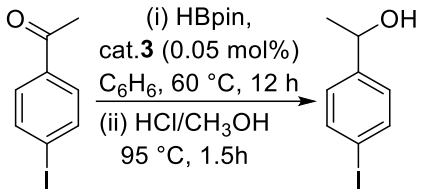
Preparation of secondary alcohol (10a)[16]



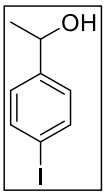
10a was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure secondary alcohol (**10a**) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent (33.5 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.59 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.51 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.34 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.12 (t, *J* = 7.6 Hz, 1H, Ar*H*), 5.24 (q, *J* = 6.4 Hz, 1H, C*H*), 1.48 (d, *J* = 6.4 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 144.7 (Ar*C*), 132.8 (Ar*C*), 128.9 (Ar*C*), 127.9 (Ar*C*), 126.8 (Ar*C*), 121.8 (Ar*C*), 69.3 (Ar*C*CH_3OH), and 23.7 (ArC*C*H_3OH) ppm.



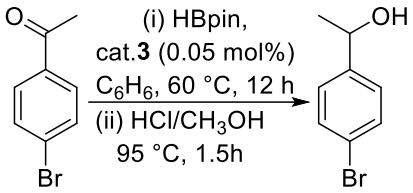
Preparation of secondary alcohol (10b)[17]



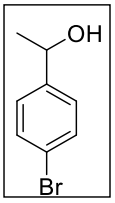
10b was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure secondary alcohol (**10b**) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent (36 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.67 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.13 (d, *J* = 8.2 Hz, 2H, Ar*H*), 4.85 (q, *J* = 6.4 Hz, 1H, C*H*), 1.47 (d, *J* = 6.5 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 145.6 (Ar*C*), 137.6 (Ar*C*), 127.6 (Ar*C*), 92.8 (Ar*C*), 69.9 (Ar*C*CH_3OH), and 25.4 (ArC*C*H_3OH) ppm.



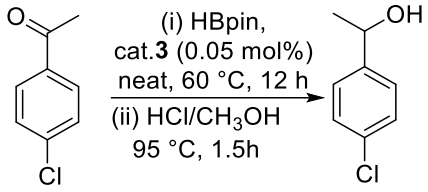
Preparation of secondary alcohol (10c)[18]



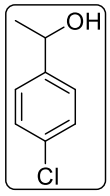
10c was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure secondary alcohol (**10c**) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent (33.5 mg, 83 %). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.47 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.25 (d, *J* = 8.6 Hz, 2H, Ar*H*), 4.87 (q, *J* = 6.4 Hz, 1H, C*H*), 1.47 (d, *J* = 6.5 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$); δ = 144.9 (Ar*C*), 131.7 (Ar*C*), 127.3 (Ar*C*), 121.3 (Ar*C*), 69.9 (Ar*C*CH_3OH), and 25.4 (ArC*C*H_3OH) ppm.



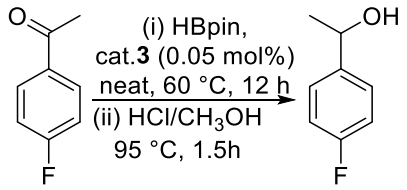
Preparation of secondary alcohol (10d)[11]



10d was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure secondary alcohol (**10d**) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent (33 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.30 (m, 4H, Ar*H*), 4.87 (q, *J* = 6.4 Hz, 1H, C*H*), 1.47 (d, *J* = 6.5 Hz, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 144.4 (Ar*C*), 133.2 (Ar*C*), 128.7 (Ar*C*), 126.9 (Ar*C*), 69.8 (Ar*C*CH_3OH), and 25.4 (ArC*C*H_3OH) ppm.

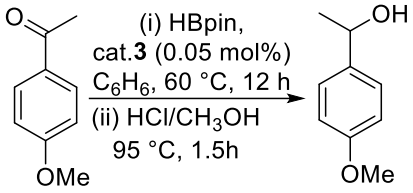


Preparation of secondary alcohol (10e)[18]



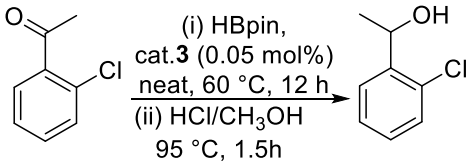
10e was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure secondary alcohol (**10e**) was obtained by drying and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent (36 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.67 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.13 (d, *J* = 8.3 Hz, 2H, Ar*H*), 4.85 (q, *J* = 6.4 Hz, 1H, C*H*), 1.82 (s, 1H, O*H*), 1.47 (d, *J* = 6.5 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 145.6 (Ar*C*), 137.7 (Ar*C*), 127.6 (Ar*C*), 92.8 (Ar*C*), 70.0 (Ar*C*CH_3OH), and 25.4 (ArC*C*H_3OH) ppm.

Preparation of alcohol (10f)[3]



10f was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure secondary alcohol (10f) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent (37 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.30 (d, *J* = 8.6 Hz, 2H, Ar*H*), 6.89 (d, *J* = 8.6 Hz, 2H, Ar*H*), 4.86 (q, *J* = 6.4 Hz, 1H, C*H*), 3.81 (s, 3H, Ar-OCH_3), 1.48 (d, *J* = 6.4 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 159.1 (Ar*C*), 138.1 (Ar*C*), 126.8 (Ar*C*), 114.0 (Ar*C*), 70.1 (Ar*C*CH_3OH), 55.4 (Ar-O*C*H_3), and 25.2 (ArC*C*H_3OH) ppm.

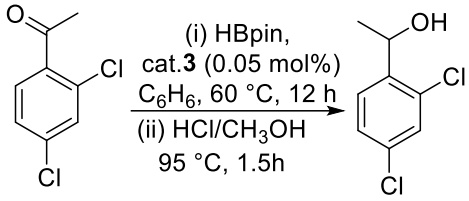
Preparation of alcohol (10g)[3]



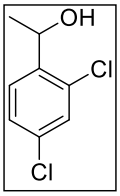
10g was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure secondary alcohol (**10g**) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent. (34.4 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.62 – 7.56 (m, 1H, Ar*H*), 7.31 (dd, *J* = 14.5, 7.7 Hz, 2H, Ar*H*), 7.20 (td, *J* = 7.7, 1.3 Hz, 1H, Ar*H*), 5.29 (q, *J* = 6.4 Hz, 1H, C*H*), 2.05 (s, 1H, OH), 1.49 (d, *J* = 6.4 Hz, 3H, CH_3) ppm. ^{13}C NMR (101

MHz, $CDCl_3$) δ = 143.2 (Ar*C*), 131.8 (Ar*C*), 129.5 (Ar*C*), 128.5 (Ar*C*), 127.3 (Ar*C*), 126.5 (Ar*C*), 67.1 (Ar*C*CH_3OH), and 23.6 (ArC*C*H_3OH) ppm.

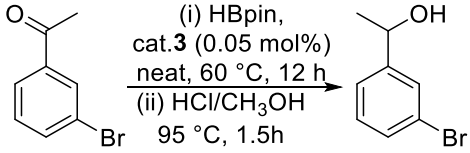
Preparation of secondary alcohol (10h)



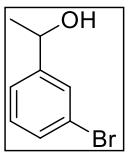
10h was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure secondary alcohol (**10h**) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent. (32.7 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.53 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.33 (d, *J* = 1.2 Hz, 1H, Ar*H*), 7.27 (d, *J* = 7.3 Hz, 1H, Ar*H*), 5.23 (q, *J* = 6.3 Hz, 1H, C*H*), 1.45 (d, *J* = 6.4 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 141.9 (Ar*C*), 133.5 (Ar*C*), 132.3 (Ar*C*), 129.2 (Ar*C*), 127.6 (Ar*C*), 127.5 (Ar*C*), 66.7 (Ar*C*CH_3OH), and 23.7 (ArC*C*H_3OH) ppm.



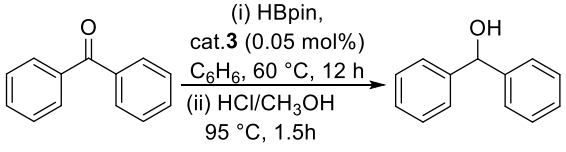
Preparation of secondary alcohol (10i)



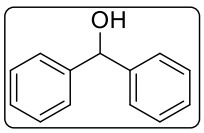
10i was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure secondary alcohol (**10i**) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent. (33 mg, 82%) ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.53 (s, 1H, Ar*H*), 7.39 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.31 – 7.25 (m, 1H, Ar*H*), 7.21 (t, *J* = 7.8 Hz, 1H, Ar*H*), 4.87 (q, *J* = 6.4 Hz, 1H, C*H*), 1.48 (d, *J* = 6.5 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 148.3 (Ar*C*), 130.6 (Ar*C*), 130.2 (Ar*C*), 128.7 (Ar*C*), 124.1 (Ar*C*), 122.7 (Ar*C*), 69.9 (Ar*C*CH_3OH), and 25.4 (ArC*C*H_3OH) ppm.



Preparation of secondary alcohol (10j) [18]

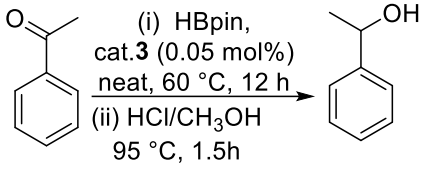


10j was prepared according to the general procedure. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure secondary alcohol (**10j**) was obtained

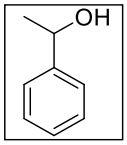


by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent (34.3 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 8H, Ar*H*), 7.33 – 7.27 (m, 2H, Ar*H*), 5.87 (d, *J* = 1.5 Hz, 1H, C*H*), 2.27 (d, *J* = 2.8 Hz, 1H, O*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.9 (Ar*C*), 128.6 (Ar*C*), 127.7 (Ar*C*), 126.7 (Ar*C*), and 76.4 (Ar*C*HAr) ppm.

Preparation of secondary alcohol (10k)[18]

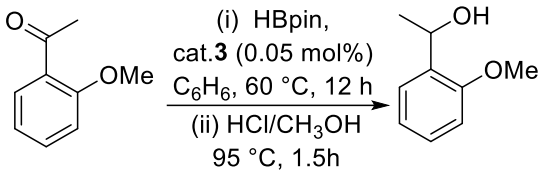


10k was prepared according to the general procedure. The aliquot is then dichloromethane

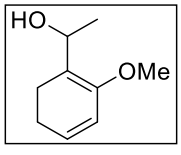


extracted after being evaporated under vacuum. The pure secondary alcohol (**10k**) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent. (33 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.43 – 7.34 (m, 4H, Ar*H*), 7.34 – 7.27 (m, 1H, Ar*H*), 4.90 (q, *J* = 6.5 Hz, 1H, C*H*), 1.51 (d, *J* = 6.5 Hz, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 145.9 (Ar*C*), 128.5 (Ar*C*), 127.5 (Ar*C*), 125.5 (Ar*C*), 70.4 (Ar*C*CH_3OH), and 25.2 (Ar*C*CH_3OH) ppm.

Preparation of secondary alcohol (10l)[18]



10l was prepared according to the general procedure. The aliquot is then dichloromethane



extracted after being evaporated under vacuum. The pure secondary alcohol (**10l**) was obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent. (36 mg, 88%). ^{1}H NMR (700 MHz, $CDCl_3$); δ = 7.38 (d, *J* = 7.5 Hz, 1H, Ar*H*), 7.27 (t, *J* = 7.8 Hz, 1H, Ar*H*), 6.99 (t, *J* = 7.4 Hz, 1H, Ar*H*), 6.91 (d, *J* = 8.2 Hz, 1H, Ar*H*), 5.13 (q, *J* = 6.4 Hz, 1H, C*H*), 3.88 (s, 3H, Ar-OCH_3), 1.53 (d, *J* = 7.3 Hz, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 156.6 (Ar*C*), 133.6 (Ar*C*), 128.3 (Ar*C*),

126.1 (Ar*C*), 120.8 (Ar*C*), 110.5 (Ar*C*), 66.4 (Ar*C*CH_3OH), 55.3 (Ar-O*C*H_3), and 22.9 (ArC*C*H_3OH) ppm.

Supporting spectral data of secondary alcohols

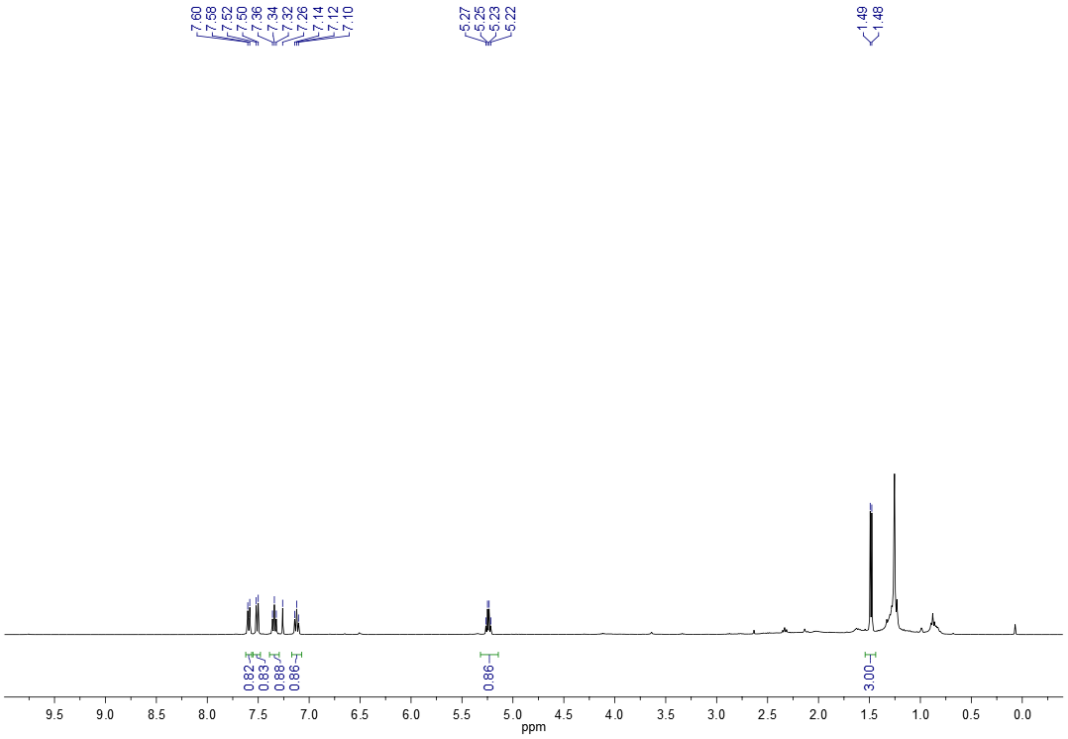


Figure S110. ^{1}H NMR spectrum of **10a** measured in $CDCl_3$.

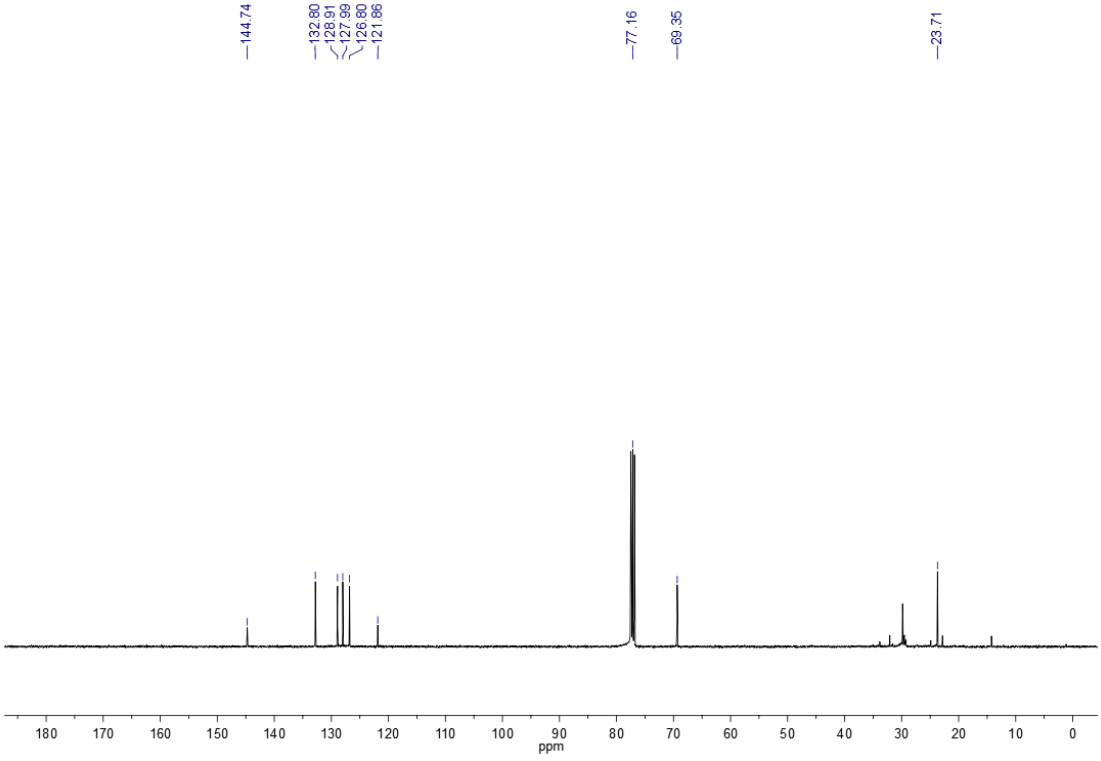


Figure S111. ^{13}C NMR spectrum of **10a** measured in $CDCl_3$.

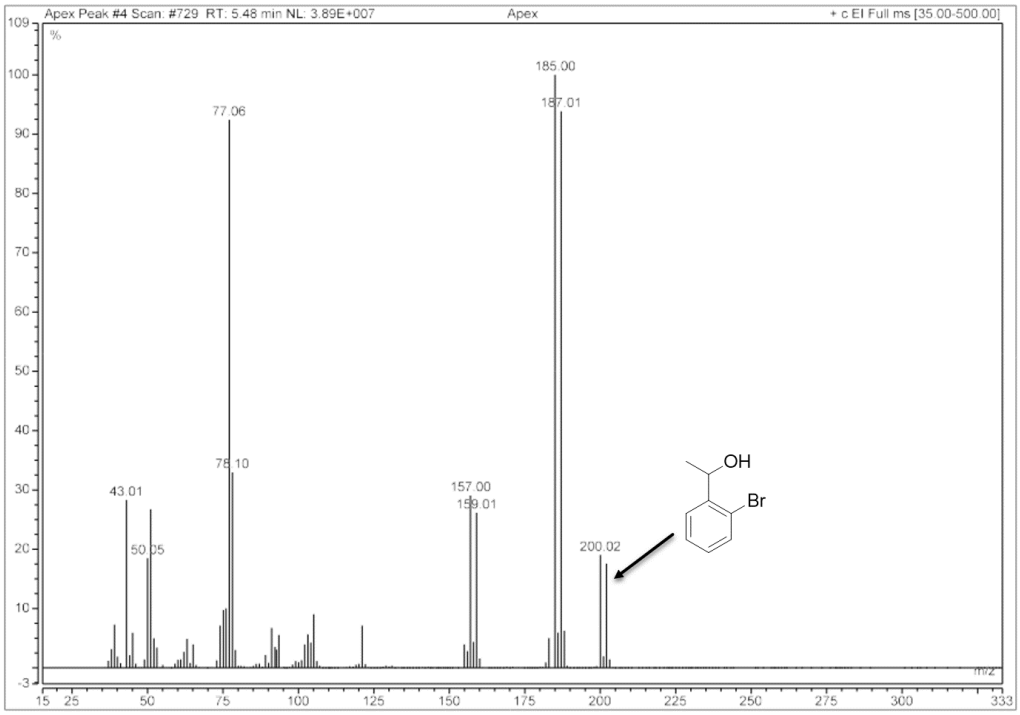


Figure S112. GC-MS of **10a** measured in ethyl acetate.

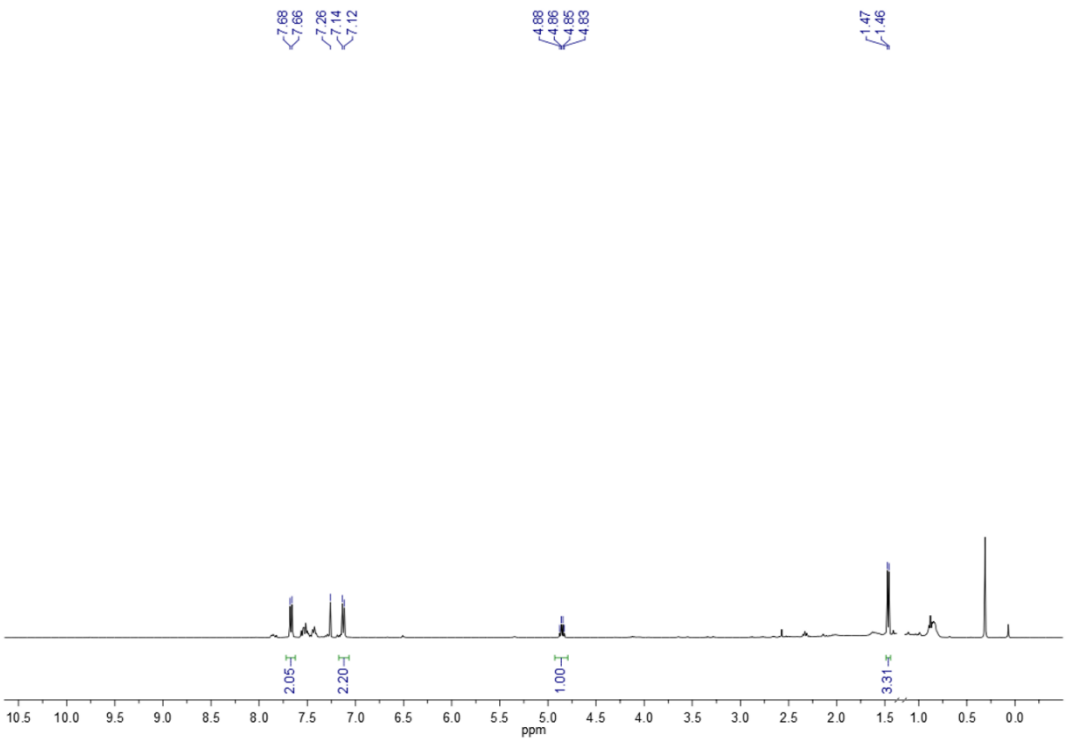


Figure S113. ^{1}H NMR spectrum of **10b** measured in $CDCl_3$.

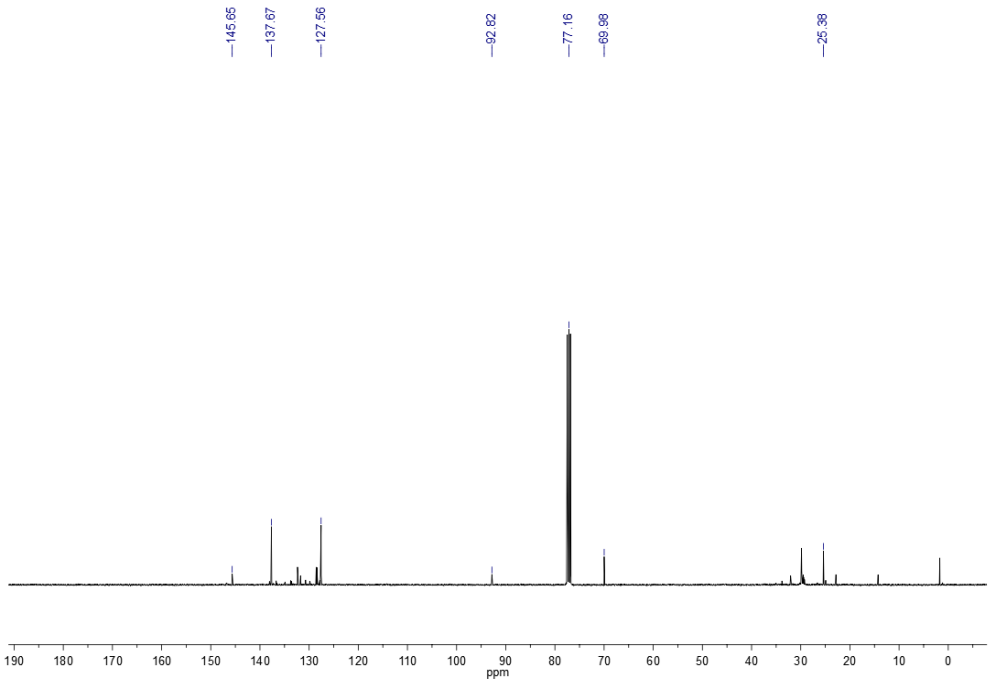


Figure S114. ^{13}C NMR spectrum of **10b** measured in $CDCl_3$.

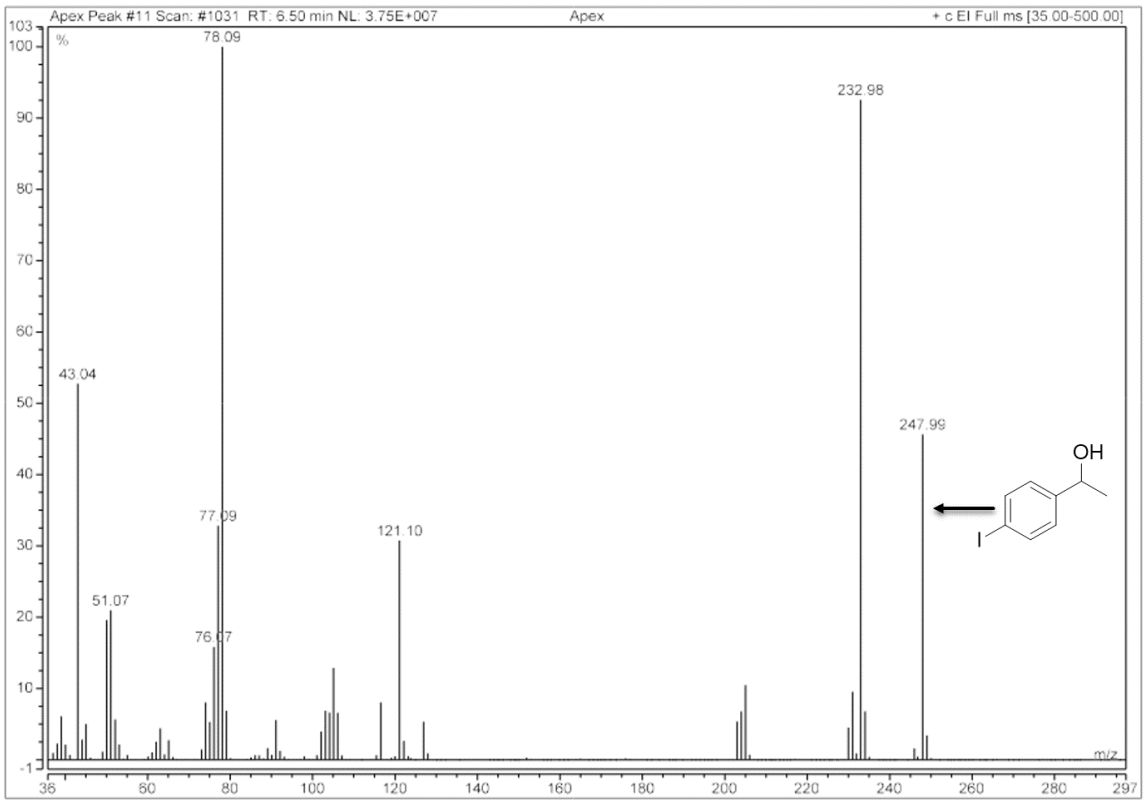


Figure S115. GC-MS spectrum of **10b** measured in ethyl acetate.

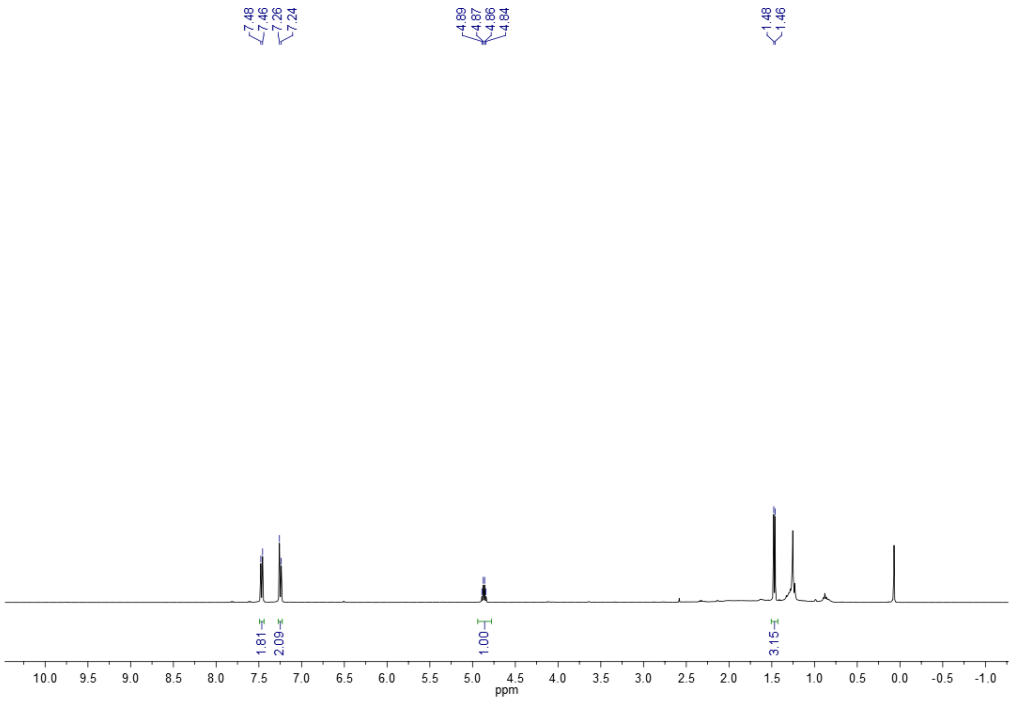


Figure S116. ^{1}H NMR spectrum of **10c** measured in $CDCl_3$.

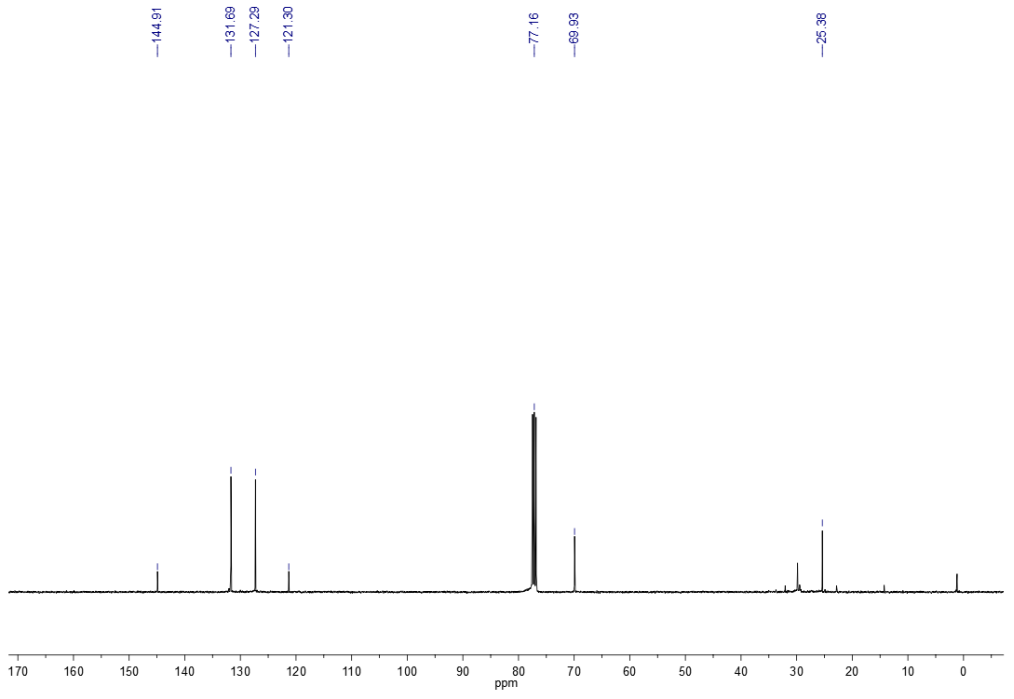


Figure S117. ^{13}C NMR spectrum of **10c** measured in $CDCl_3$.

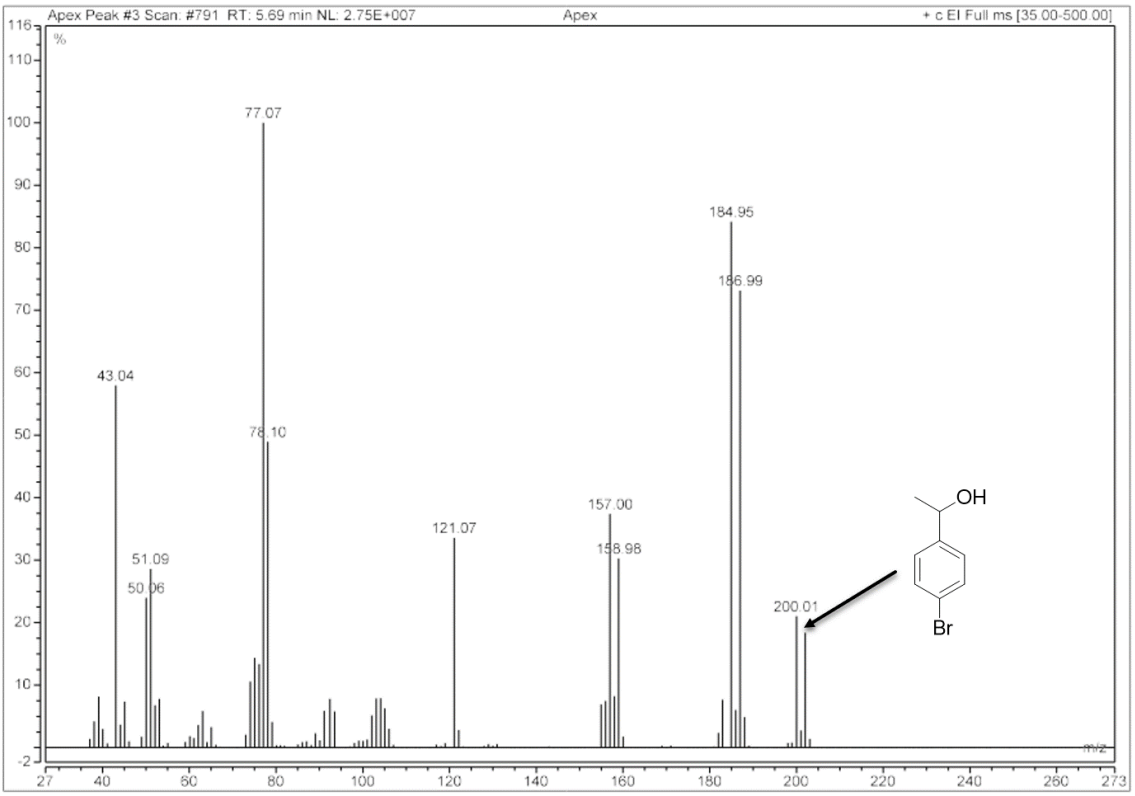


Figure S118. GC-MS spectrum of **10c** measured in ethyl acetate.

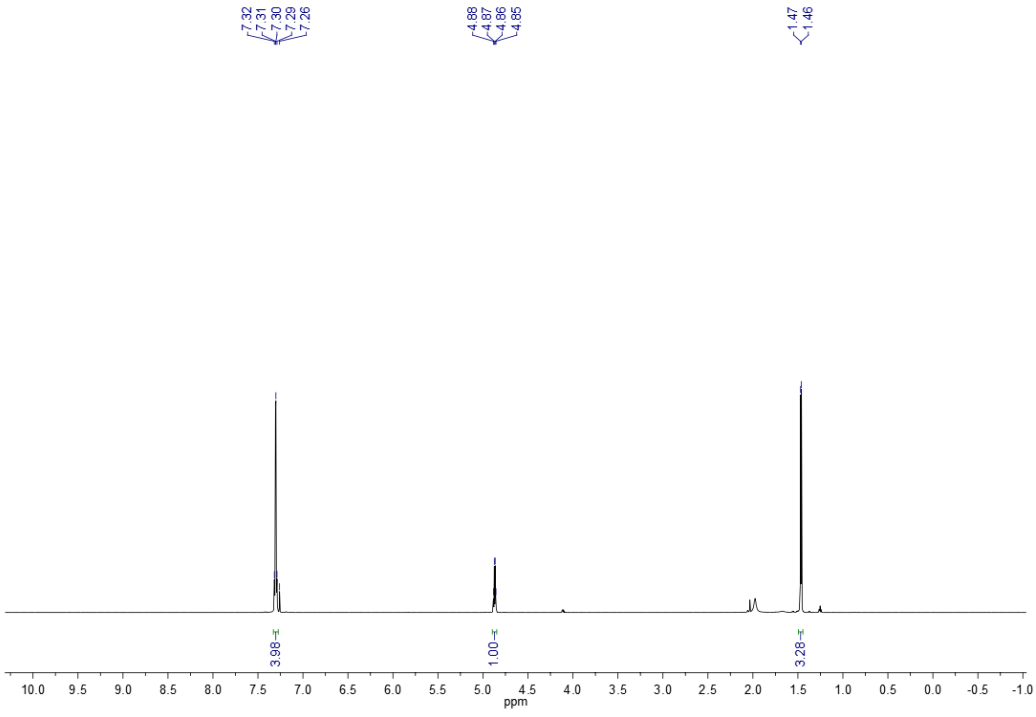


Figure S119. ^{1}H NMR spectrum of **10d** measured in $CDCl_3$.

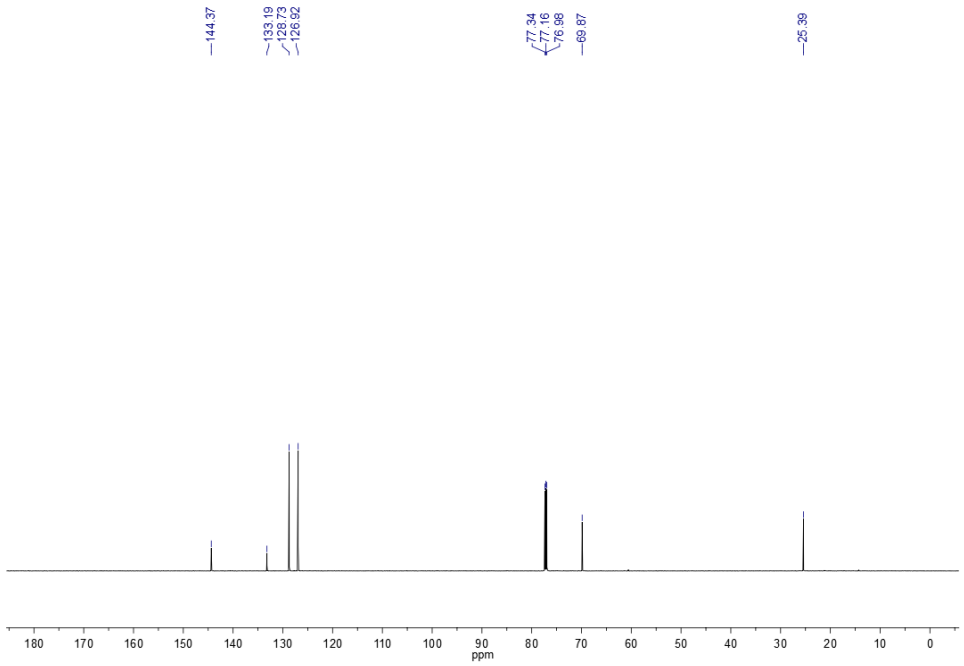


Figure S120. ^{13}C NMR spectrum of **10d** measured in $CDCl_3$.

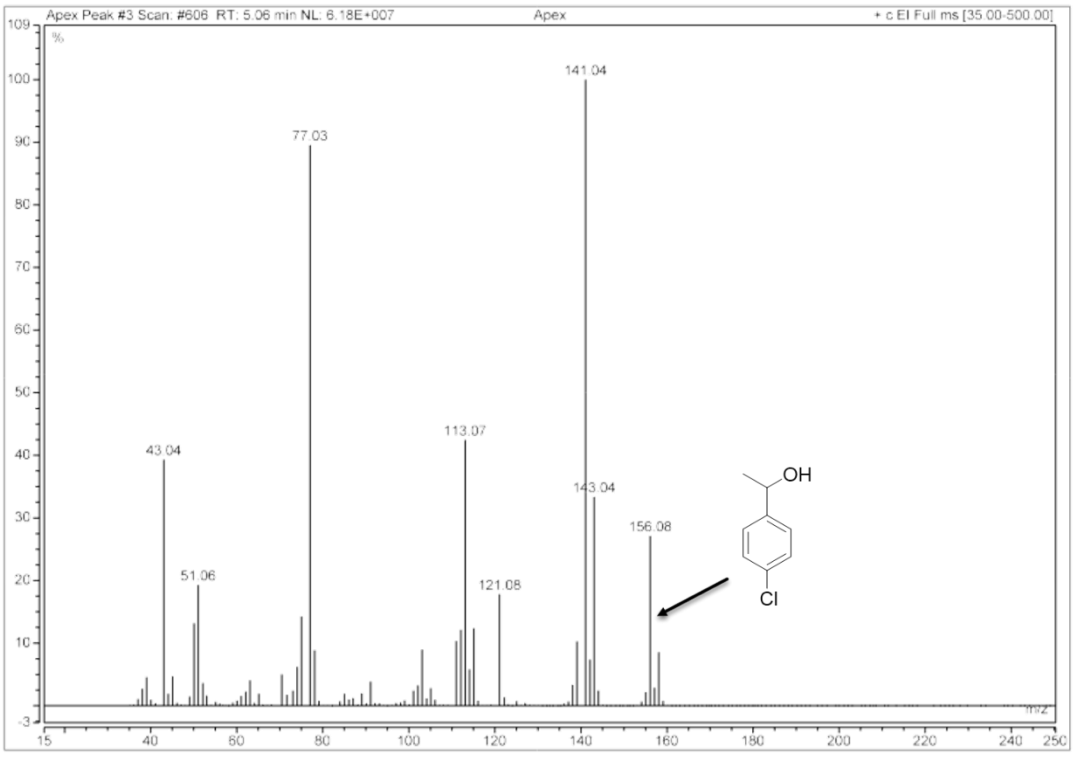


Figure S121. GC-MS spectrum of **10d** measured in ethyl acetate.

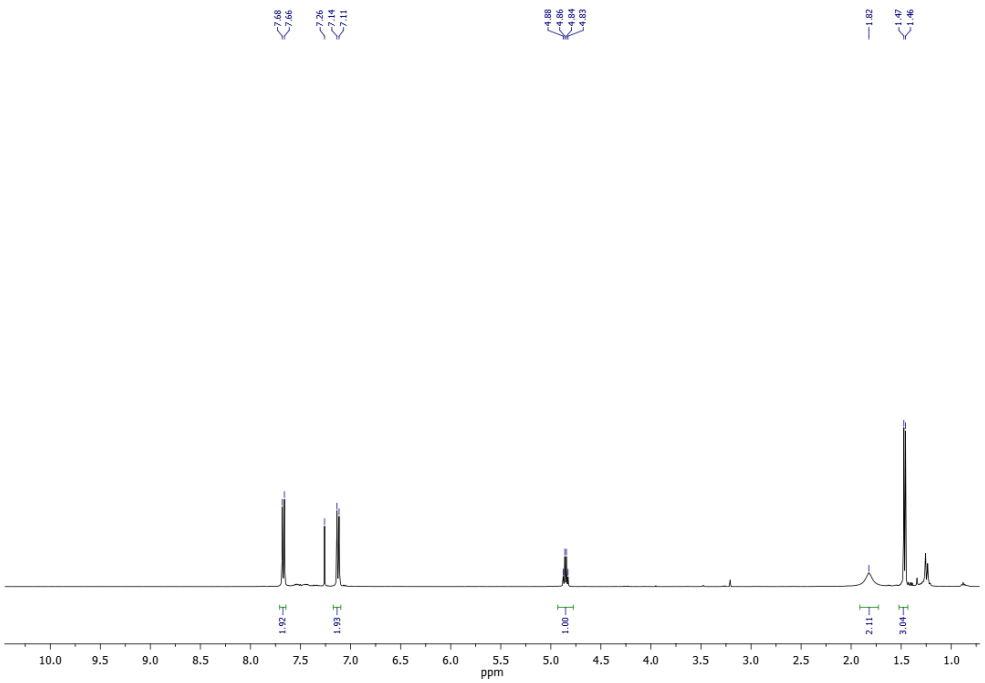


Figure S122. ^{1}H NMR spectrum of **10e** measured in $CDCl_3$.

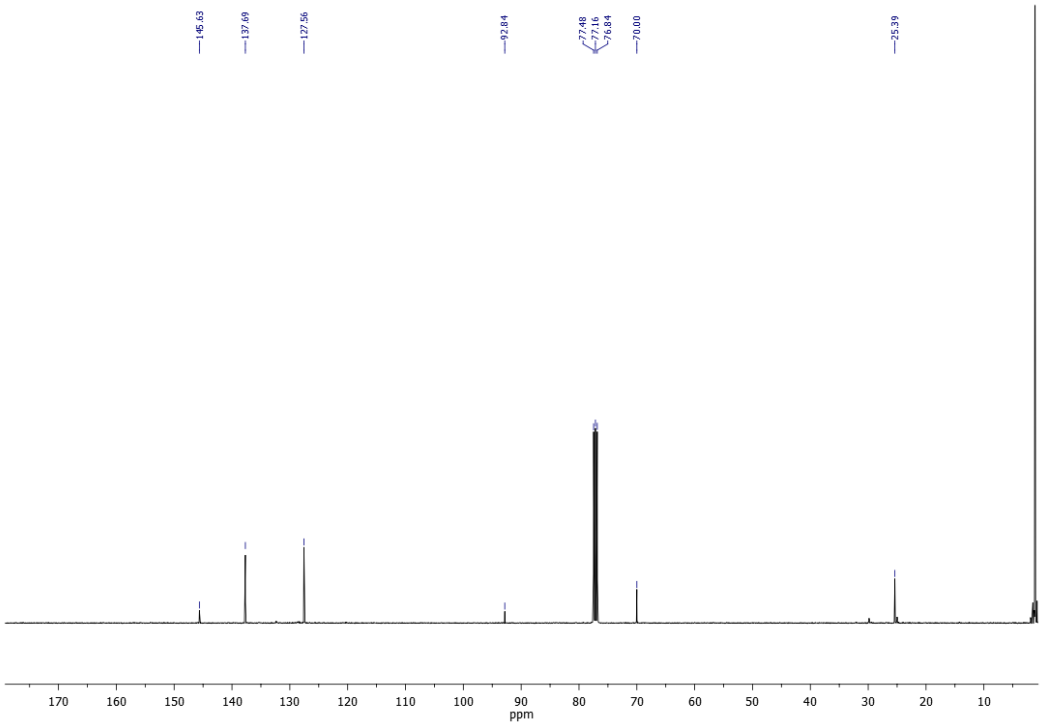


Figure S123. ^{13}C NMR spectrum of **10e** measured in $CDCl_3$.

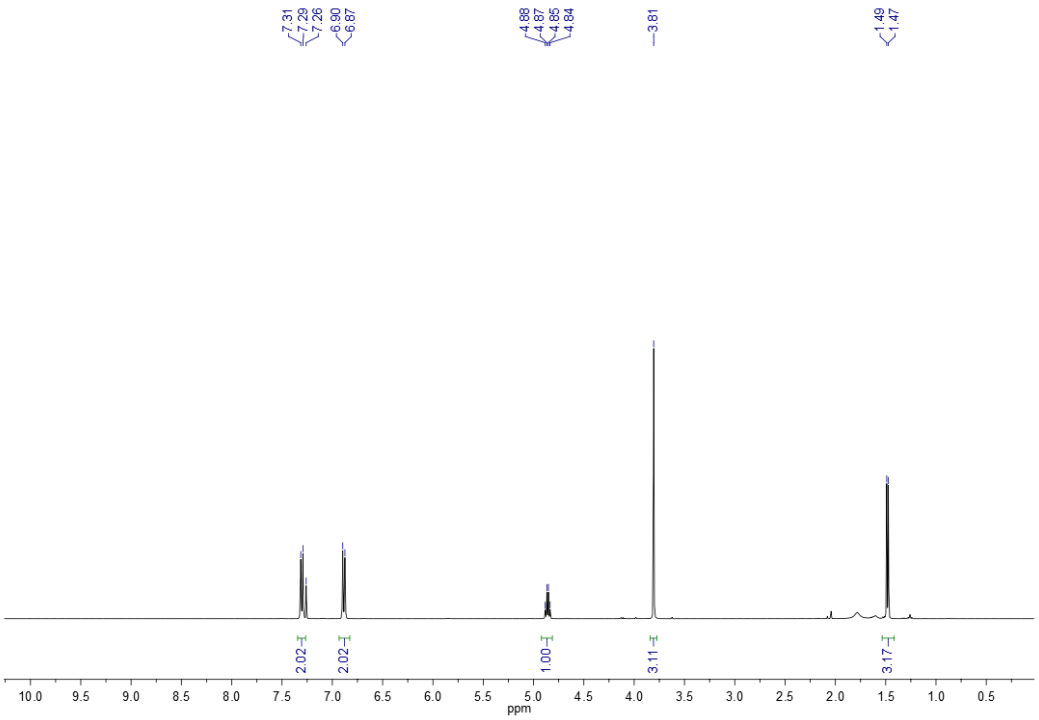


Figure S124. ^{1}H NMR spectrum of **10f** measured in $CDCl_3$.

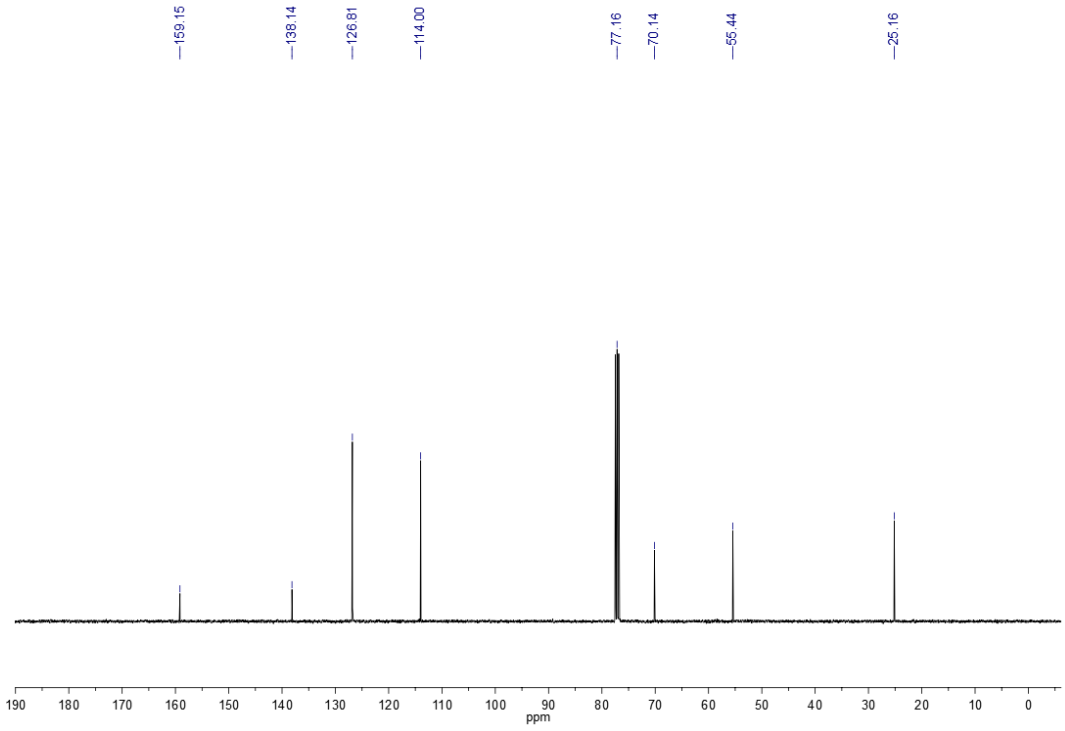


Figure S125. ^{13}C NMR spectrum of **10f** measured in $CDCl_3$.

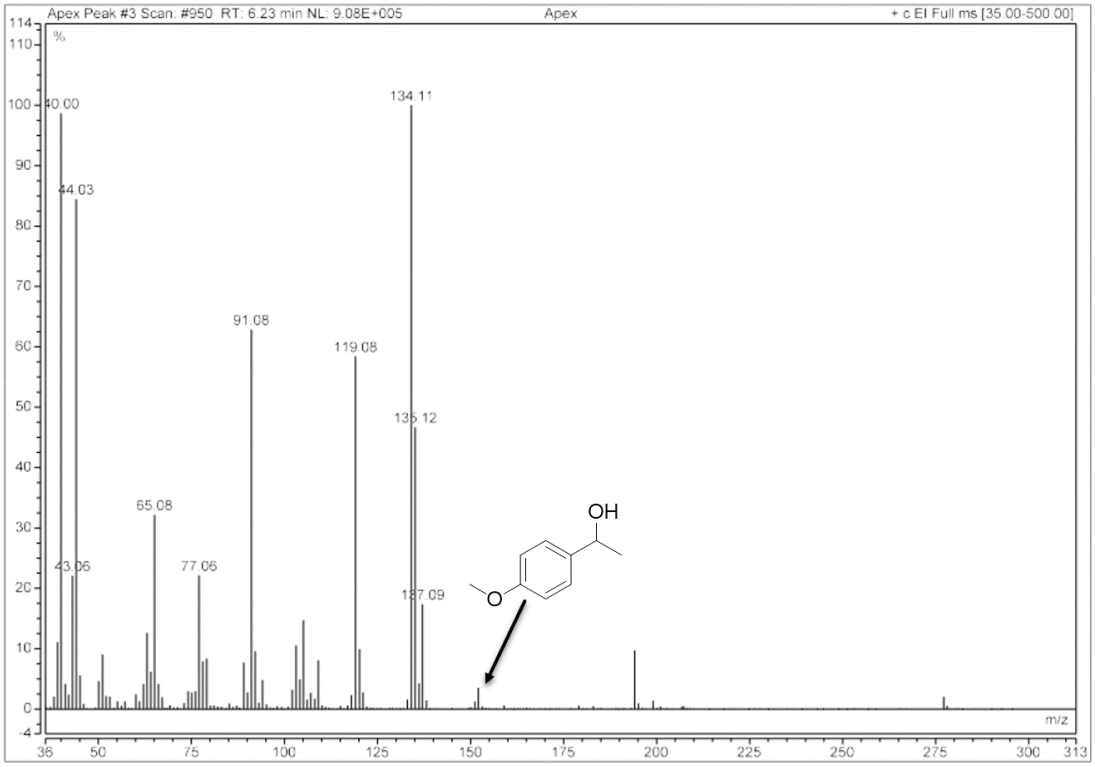


Figure S126. GC-MS spectrum of **10f** measured in ethyl acetate.

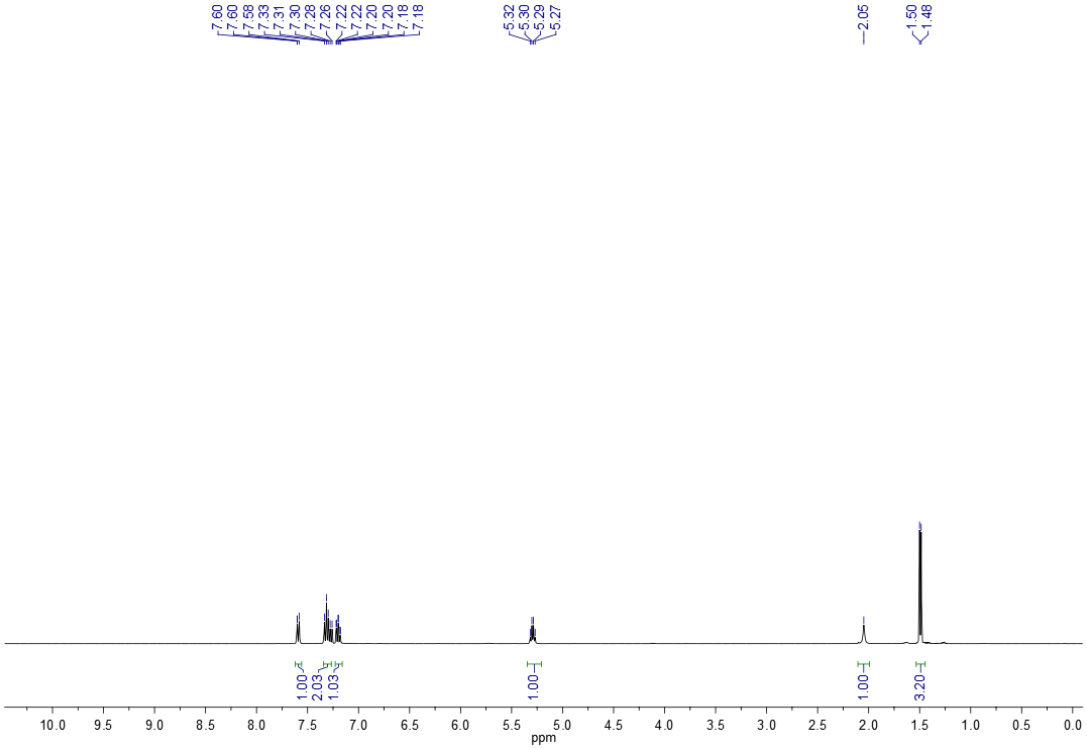


Figure S127. ^{1}H NMR spectrum of **10g** measured in $CDCl_3$.

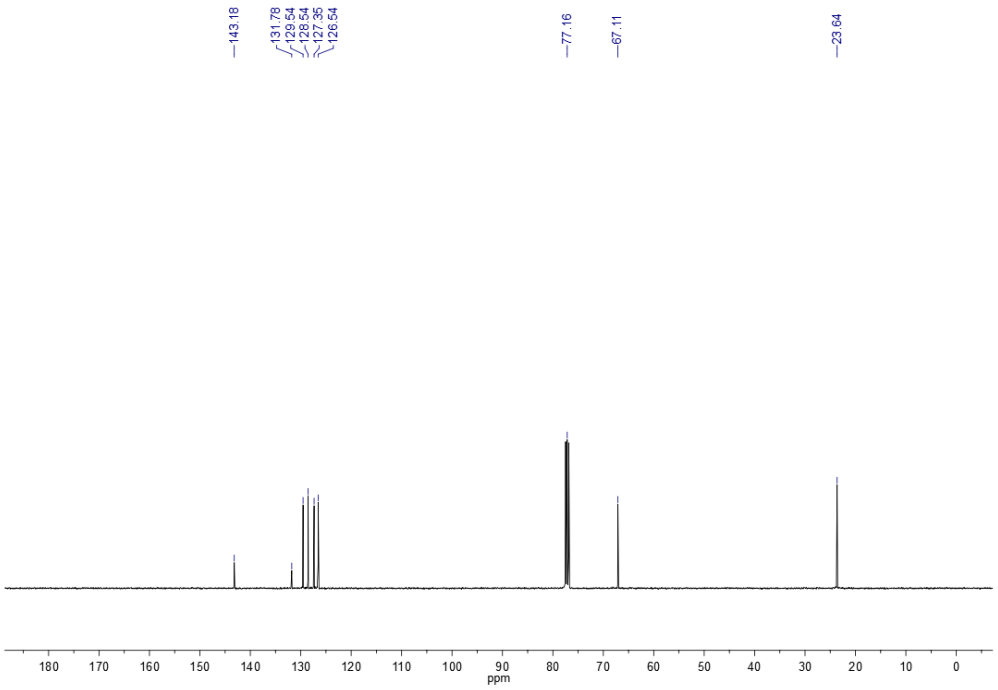


Figure S128. ^{13}C NMR spectrum of **10g** measured in $CDCl_3$.

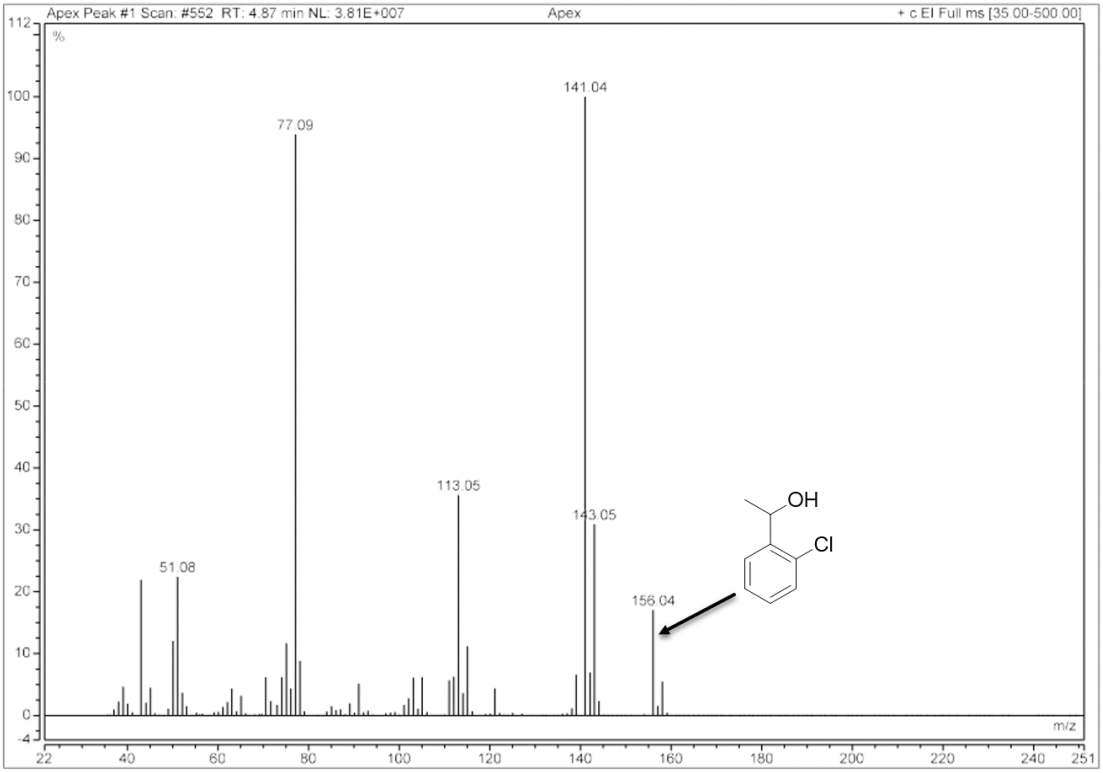


Figure S129. GC-MS spectrum of **10g** measured in $CDCl_3$.

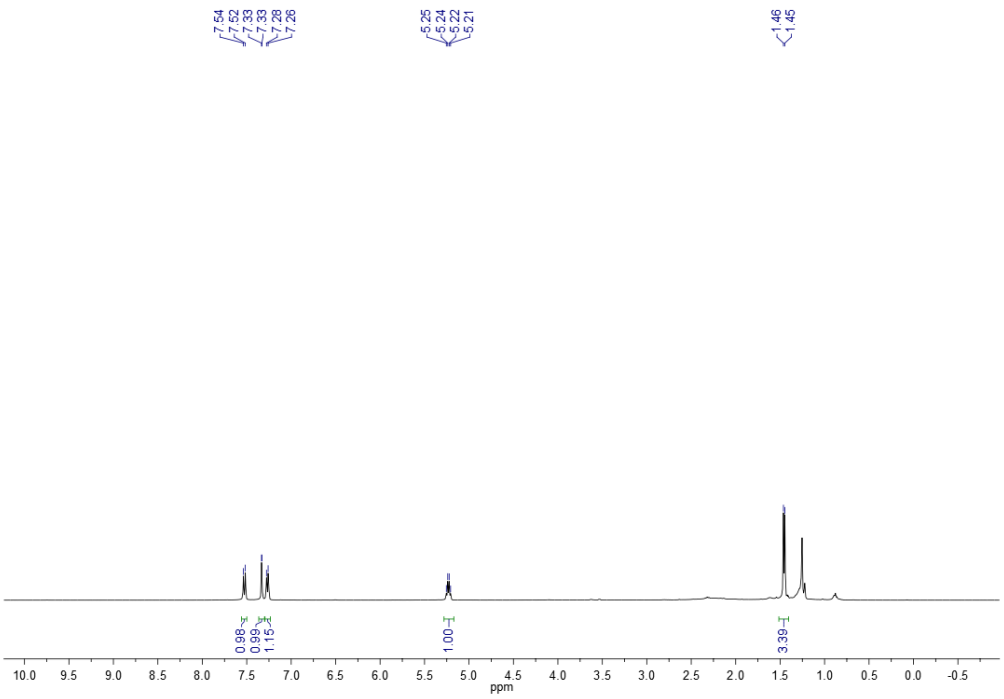


Figure S130. ^{1}H NMR spectrum of **10h** measured in $CDCl_3$.

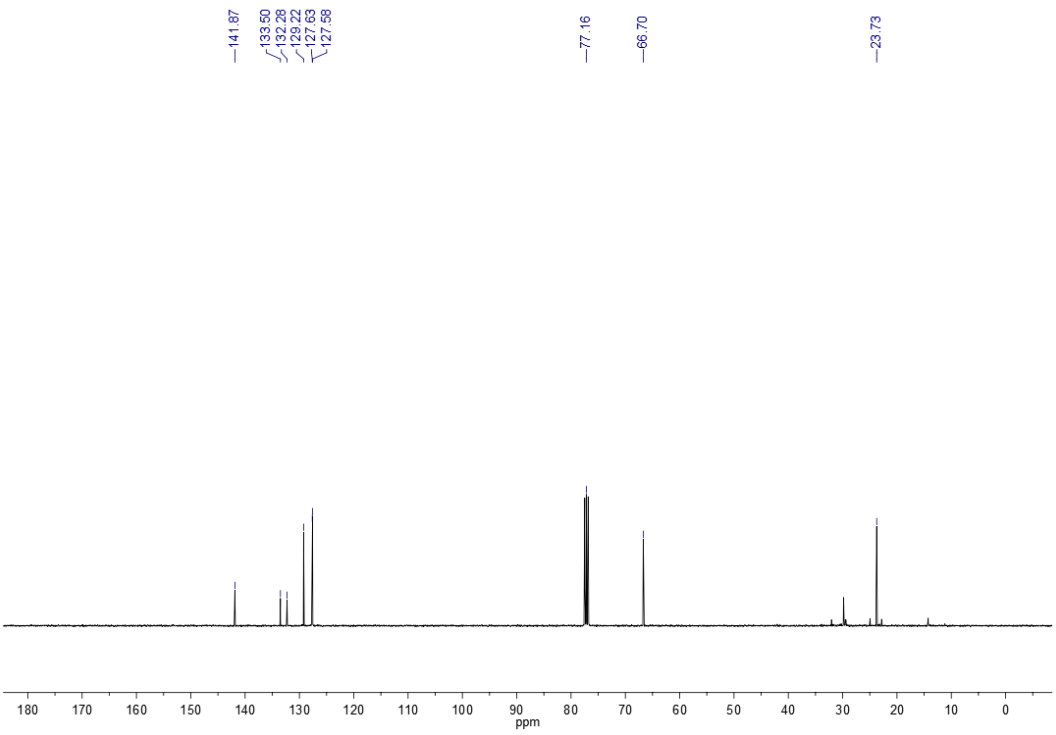


Figure S131. ^{13}C NMR spectrum of **10h** measured in $CDCl_3$.

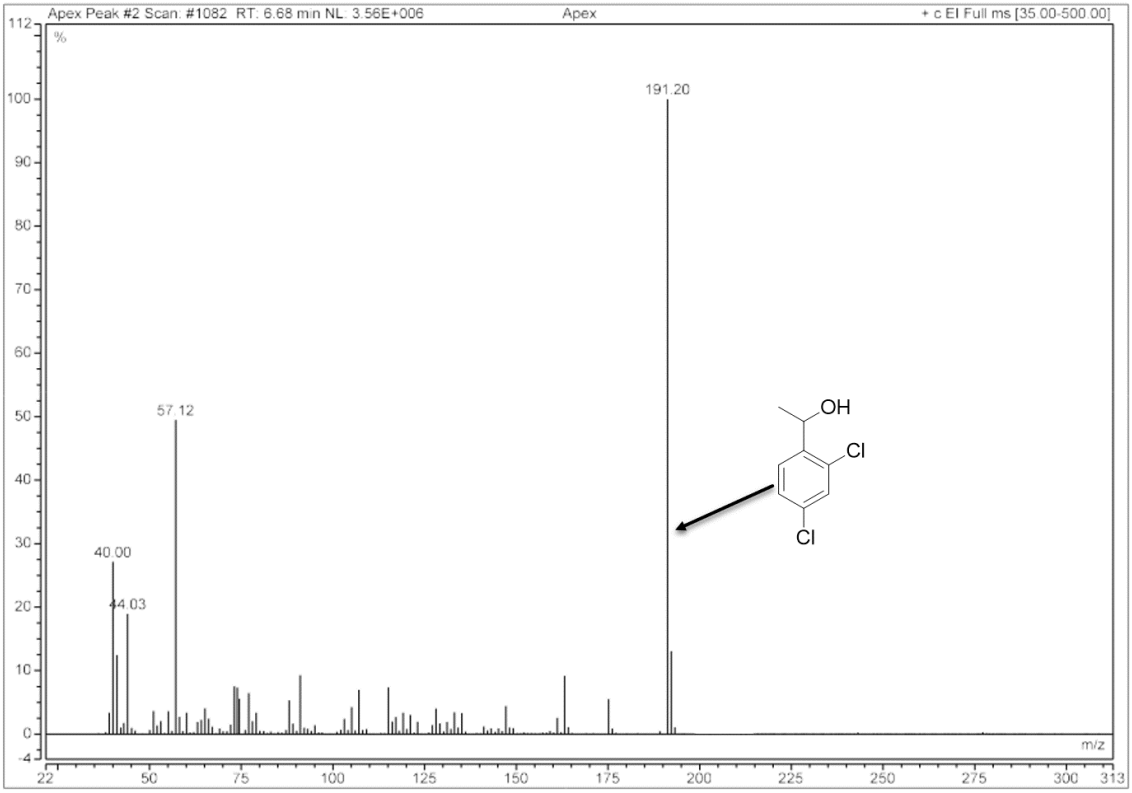


Figure S132. GC-MS spectrum of **10h** measured in ethyl acetate.

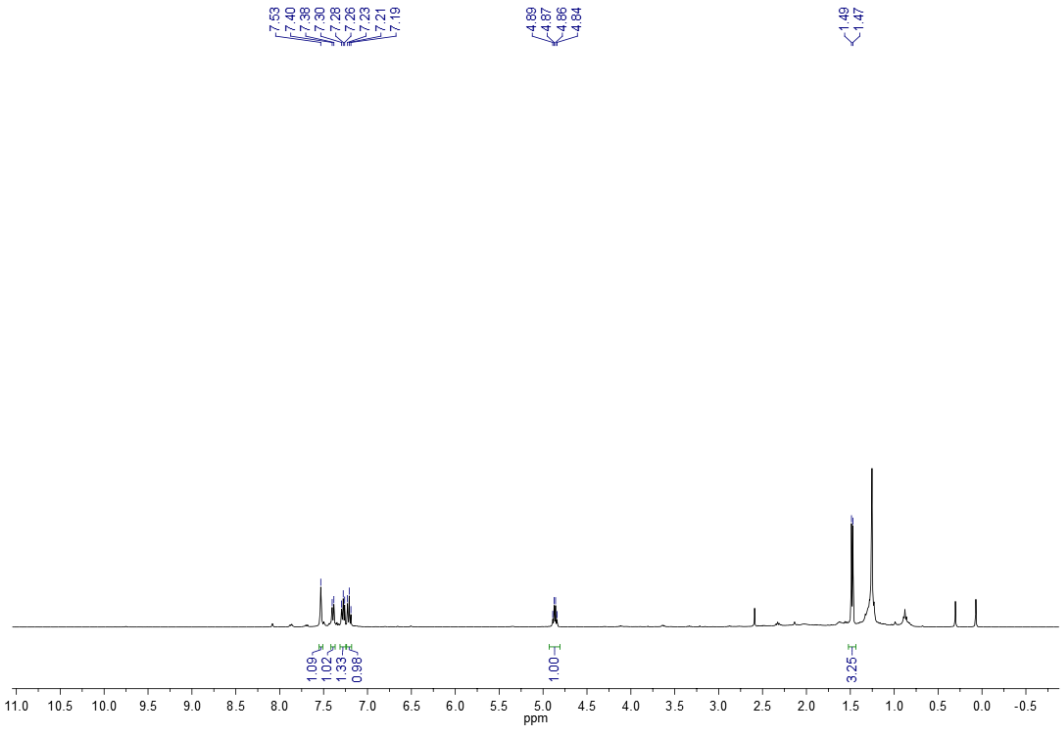


Figure S133. ^{1}H NMR spectrum of **10i** measured in $CDCl_3$.

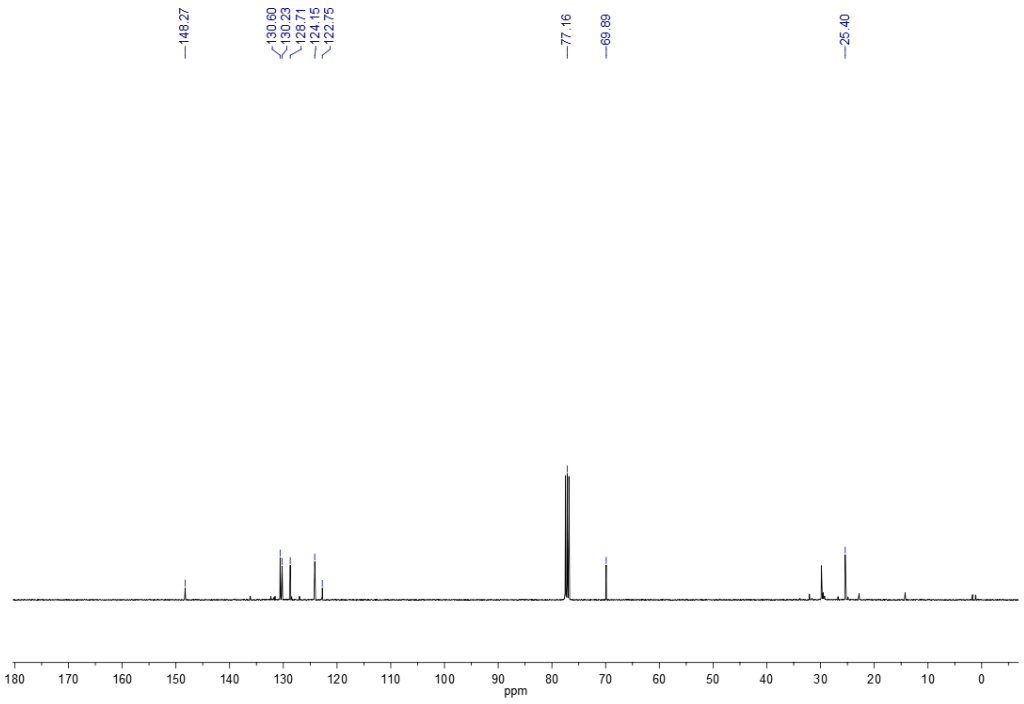


Figure S134. ^{13}C NMR spectrum of **10i** measured in $CDCl_3$.

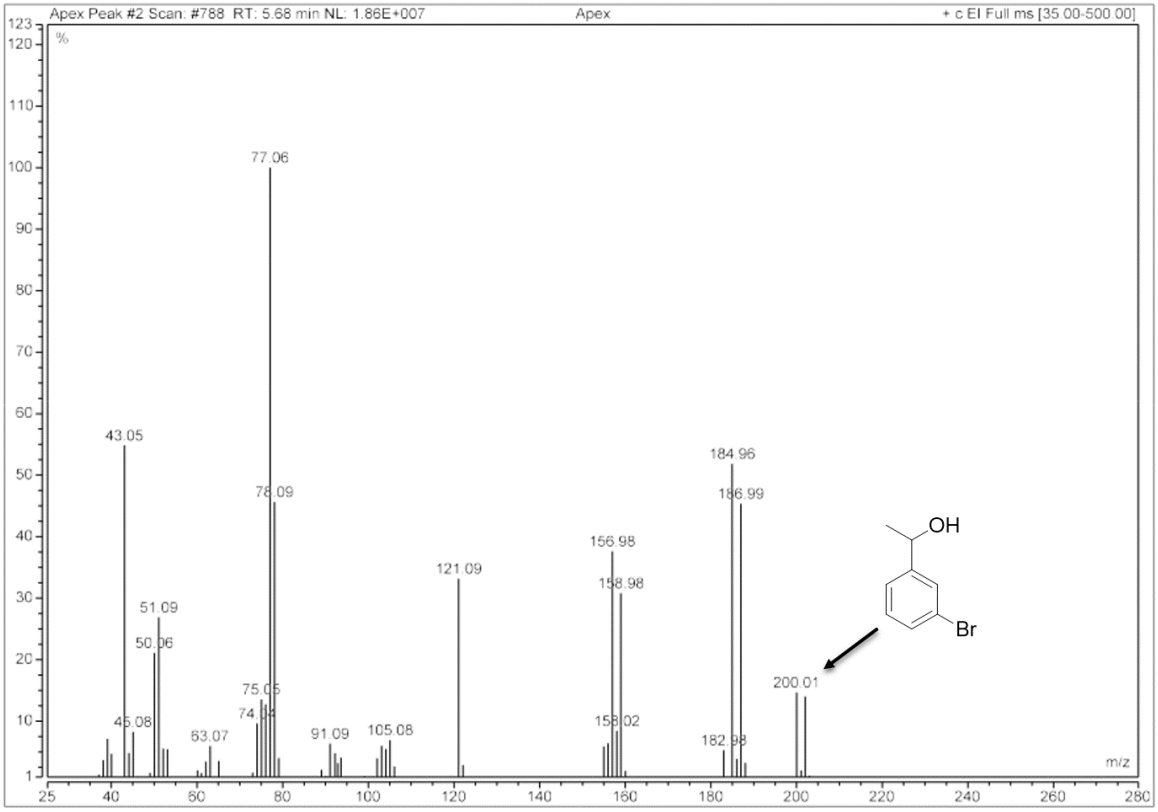


Figure S135. GC-MS spectrum of **10i** measured in ethyl acetate.

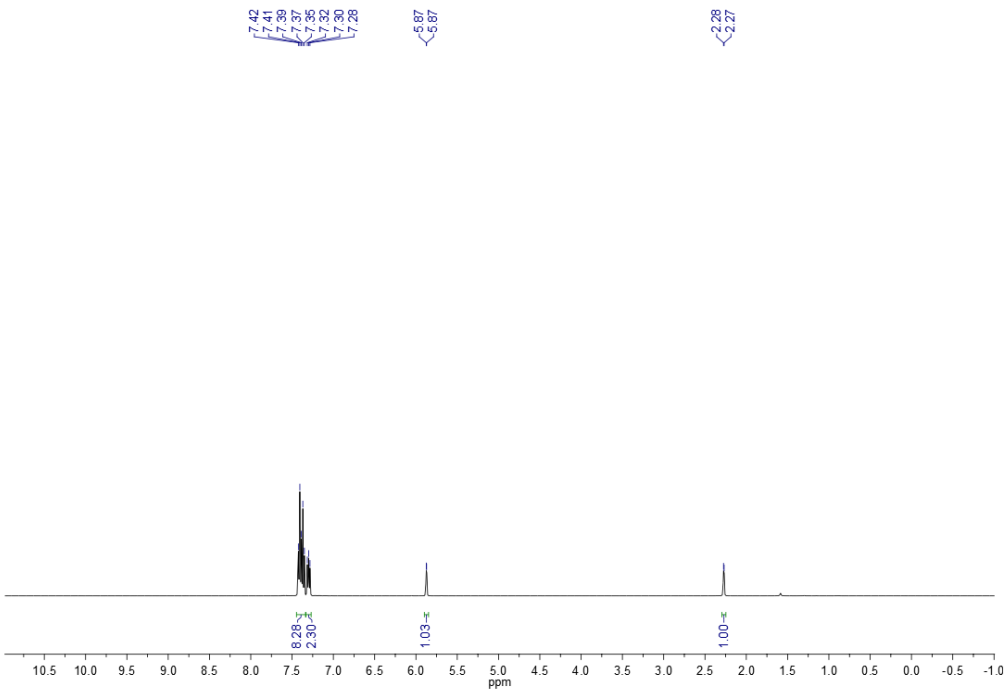


Figure S136. ^{1}H NMR spectrum of **10j** measured in $CDCl_3$.

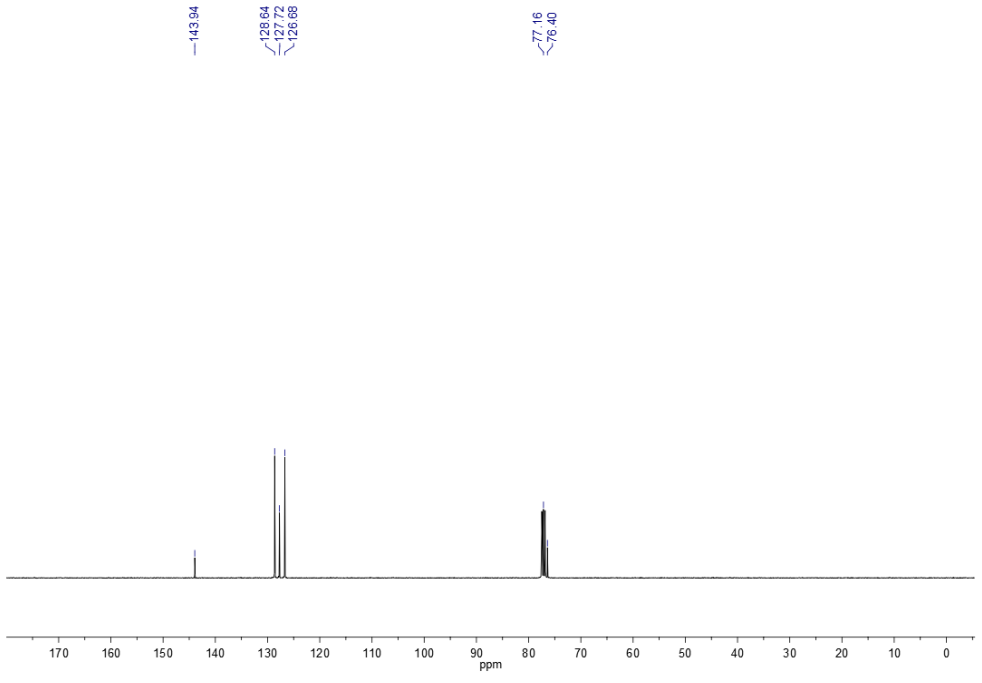


Figure S137. ^{13}C NMR spectrum of **10j** measured in $CDCl_3$.

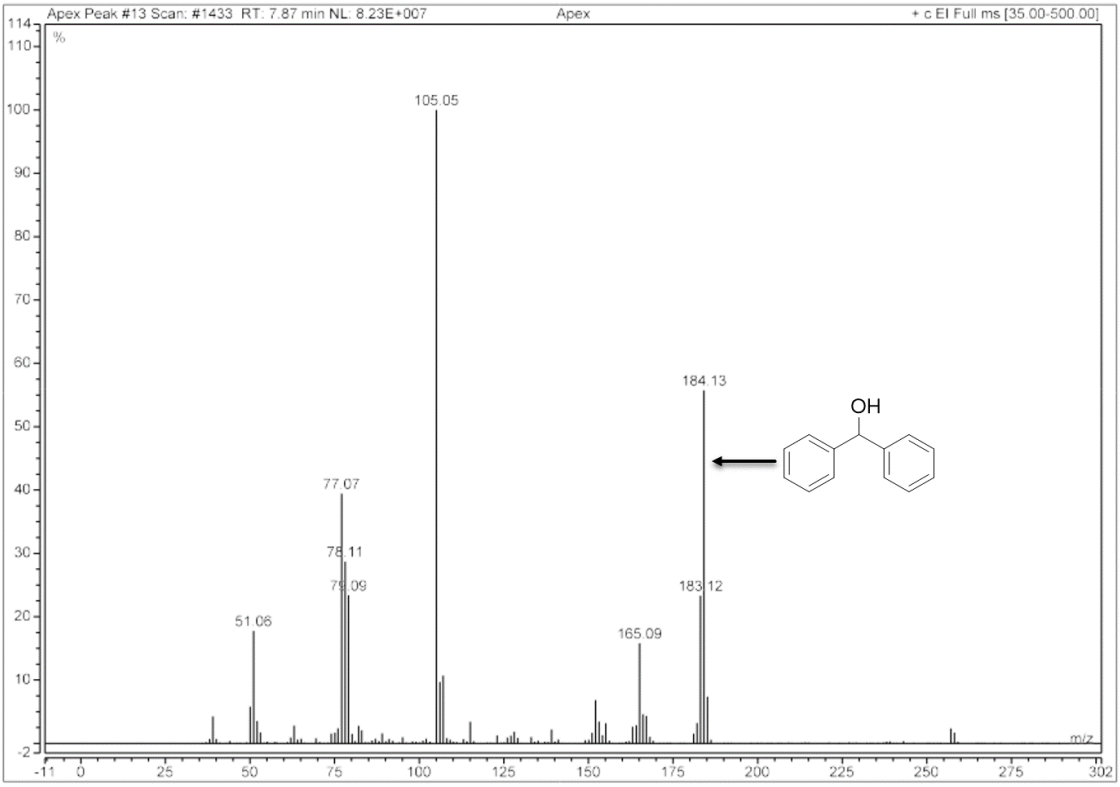


Figure S138. GC-MS spectrum of **10j** measured in ethyl acetate.

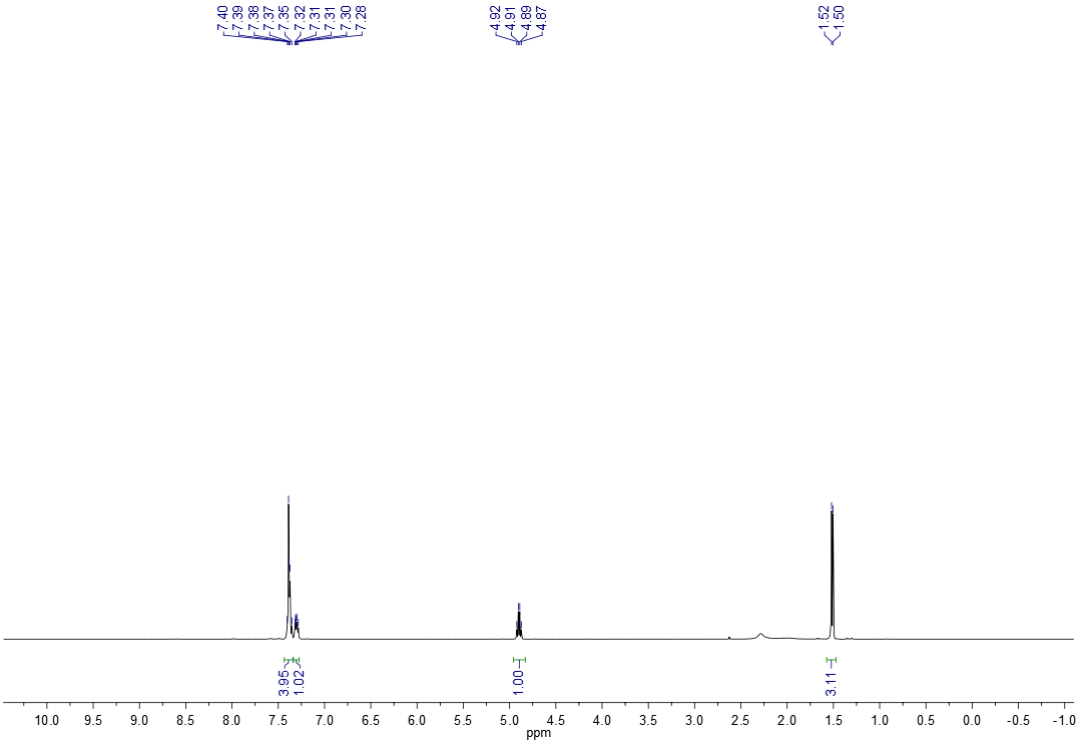


Figure S139. ^{1}H NMR spectrum of **10k** measured in $CDCl_3$.

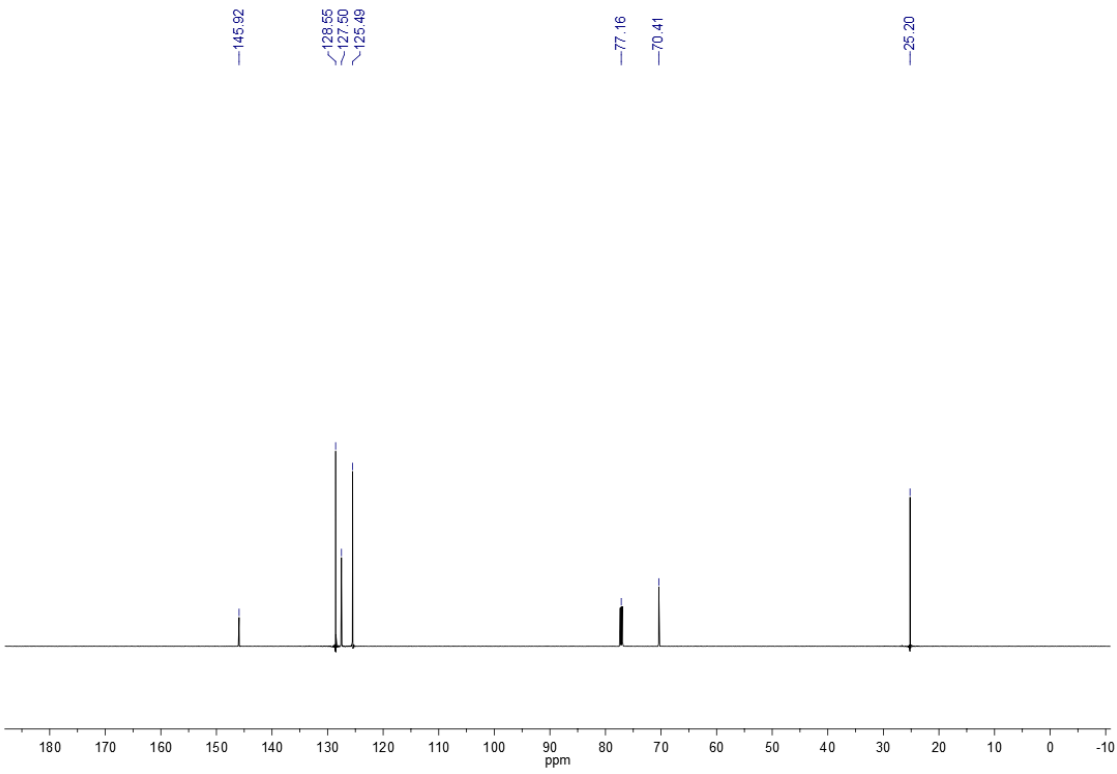


Figure S140. ^{13}C NMR spectrum of **10k** measured in $CDCl_3$.

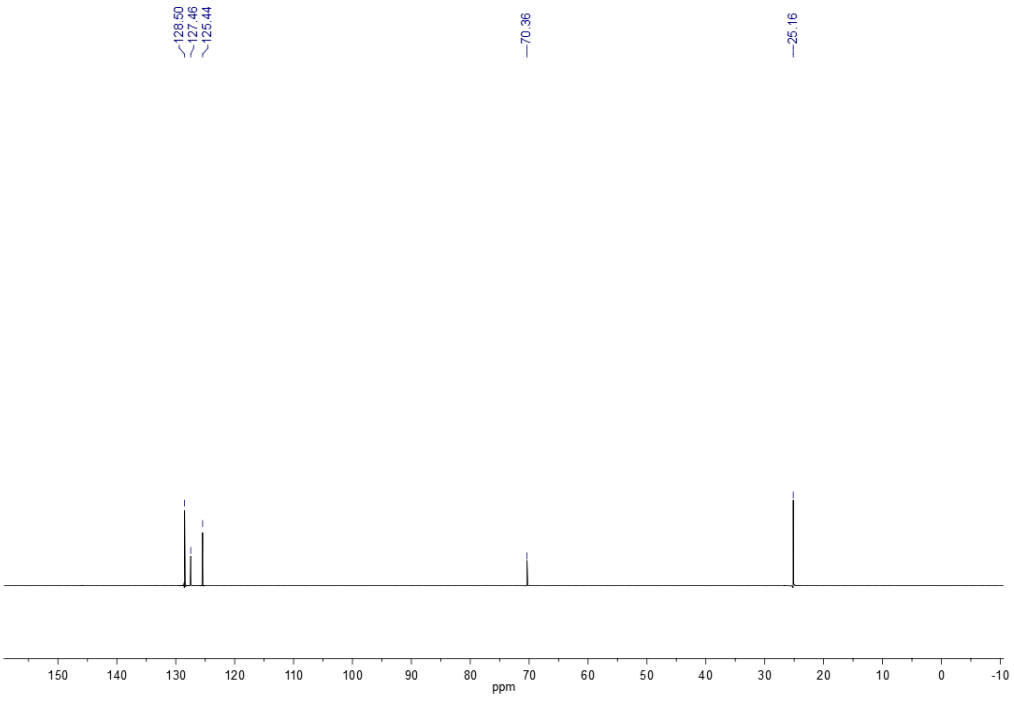


Figure S141. DEPT-135{^{13}C} NMR spectrum of **10k** measured in $CDCl_3$.

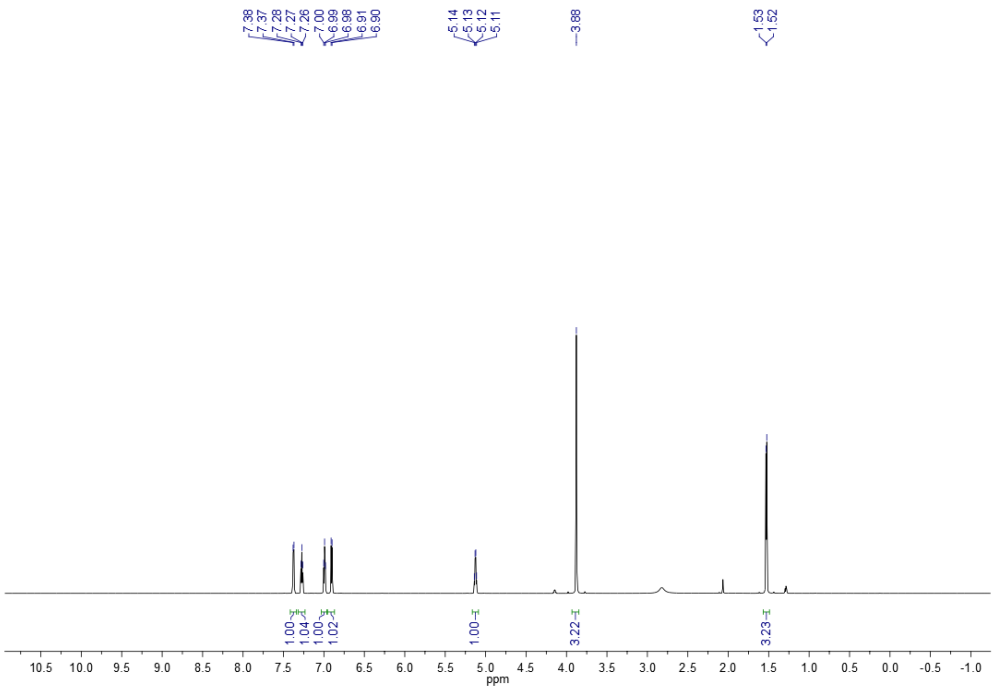


Figure S142. ^{1}H NMR spectrum of **10l** measured in $CDCl_3$.

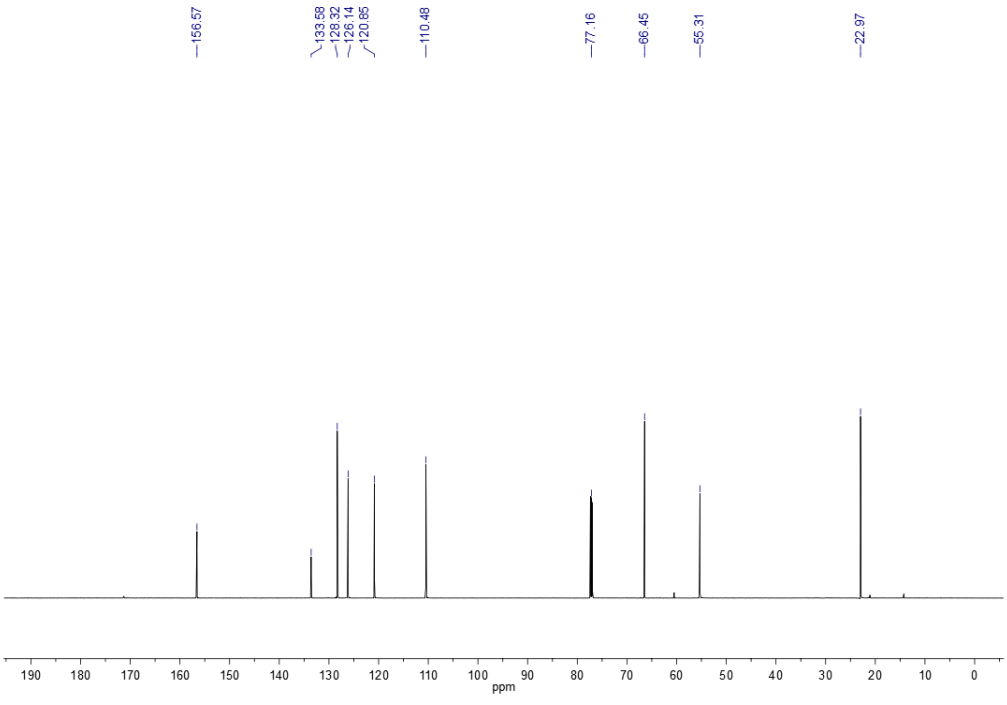


Figure S143. ^{13}C NMR spectrum of **10l** measured in $CDCl_3$.

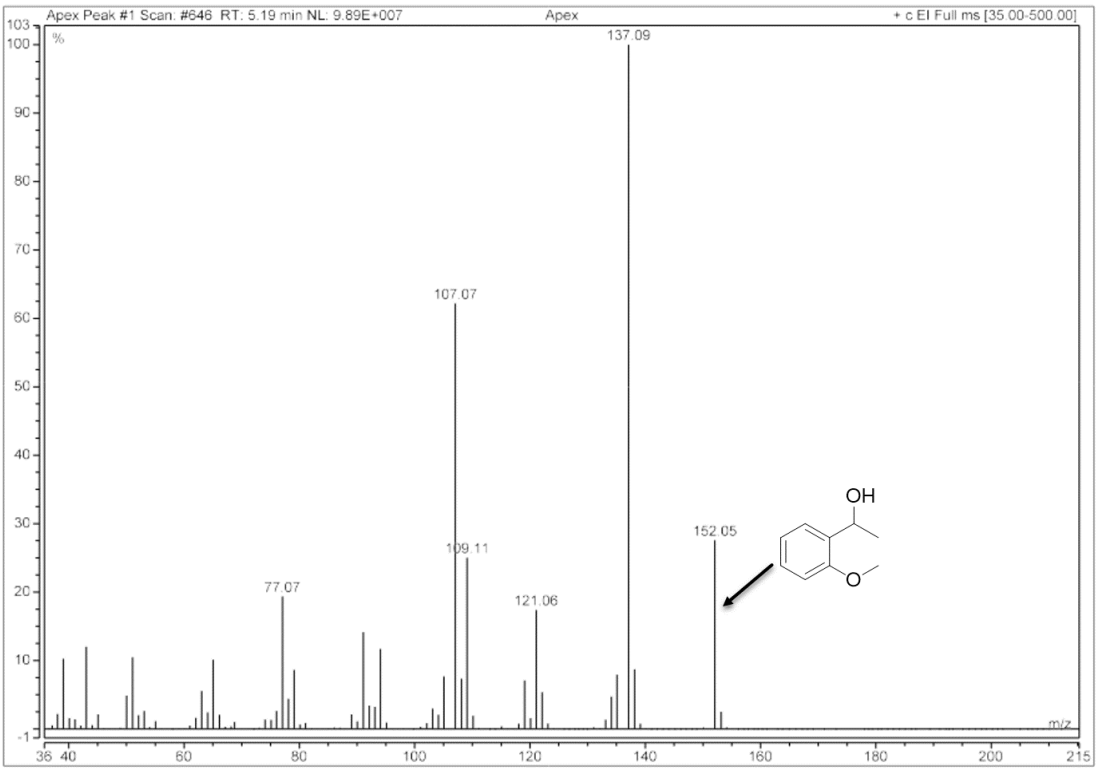
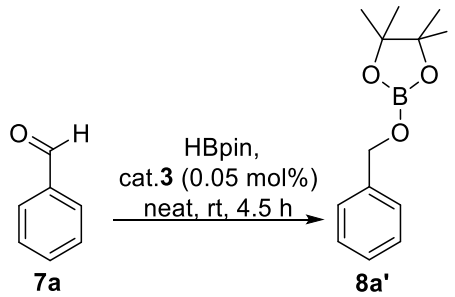


Figure S144. GC-MS spectrum of **10l** measured in ethyl acetate.

General procedure to isolate boronate esters

In a nitrogen atmosphere, a 25 mL Schlenk tube was charged with 1 equiv. of aldehydes or 1 equiv. of ketones, 1 equiv. of pinacolborane, and 0.05 mol% of Cat. **3**. For the duration of 4.5 hours (12 h in case of ketone derivatives), the reaction mixture was stirred at room temperature (50 °C in case of ketones). After the reaction was complete, the resulting reaction mixture was dissolved in diethyl ether and passed through a short neutral alumina column. The eluent was collected and removal of solvent afforded the corresponding boronate esters.

Preparation of boronate ester (8a')[19]



8a' was prepared according to the general procedure. The reaction mixture was dissolved in diethyl ether and passed through an alumina short column and then the collected diethyl ether was evaporated under vacuum to get the boronate ester (**8a'**) (63 mg, 95%). ^{1}H NMR (400

MHz, $CDCl_3$); δ = 7.33 – 7.22 (m, 5H), 4.88 (s, 2H), 1.21 (s, 12H) ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 22.36 (s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 139.3, 128.4, 127.5, 126.8, 83.2, 83.1, 66.8, 24.7, and 24.6 ppm.

NMR spectral data

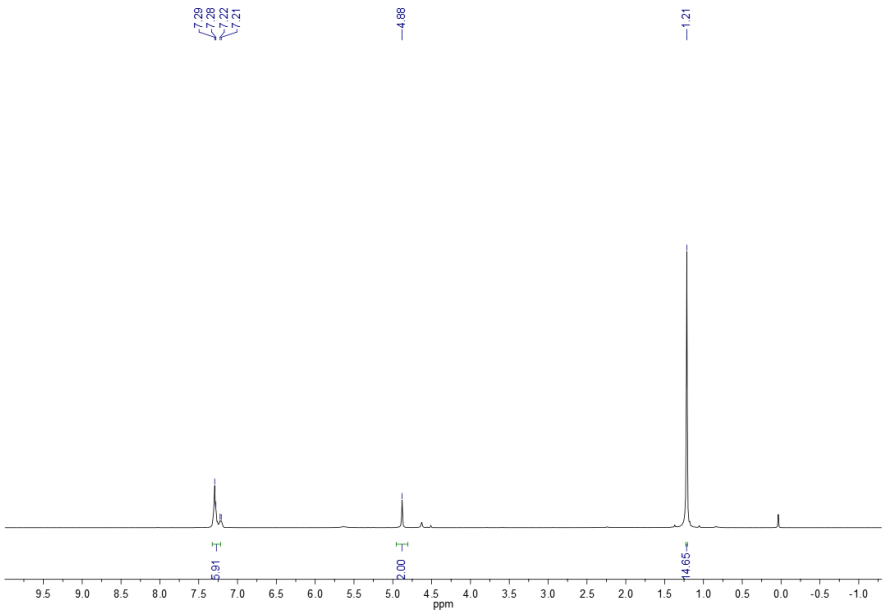


Figure S145. ^1H NMR spectrum of **8a'** measured in $CDCl_3$.

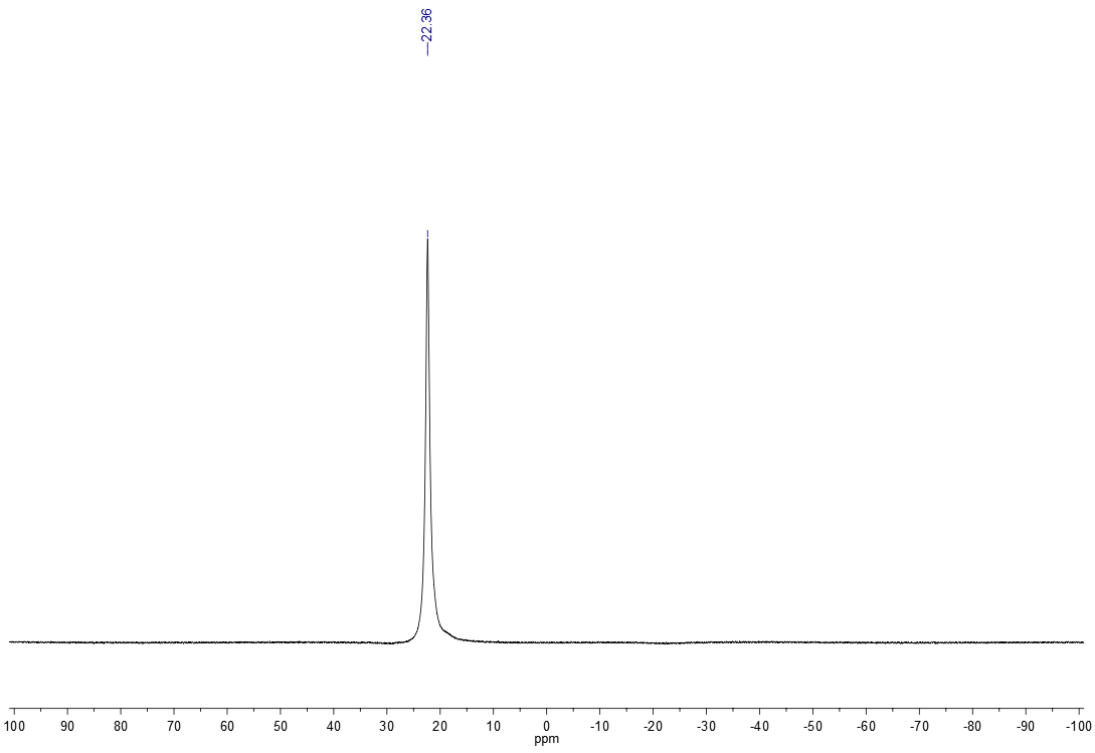


Figure S146. ^{11}B NMR spectrum of **8a'** measured in $CDCl_3$.

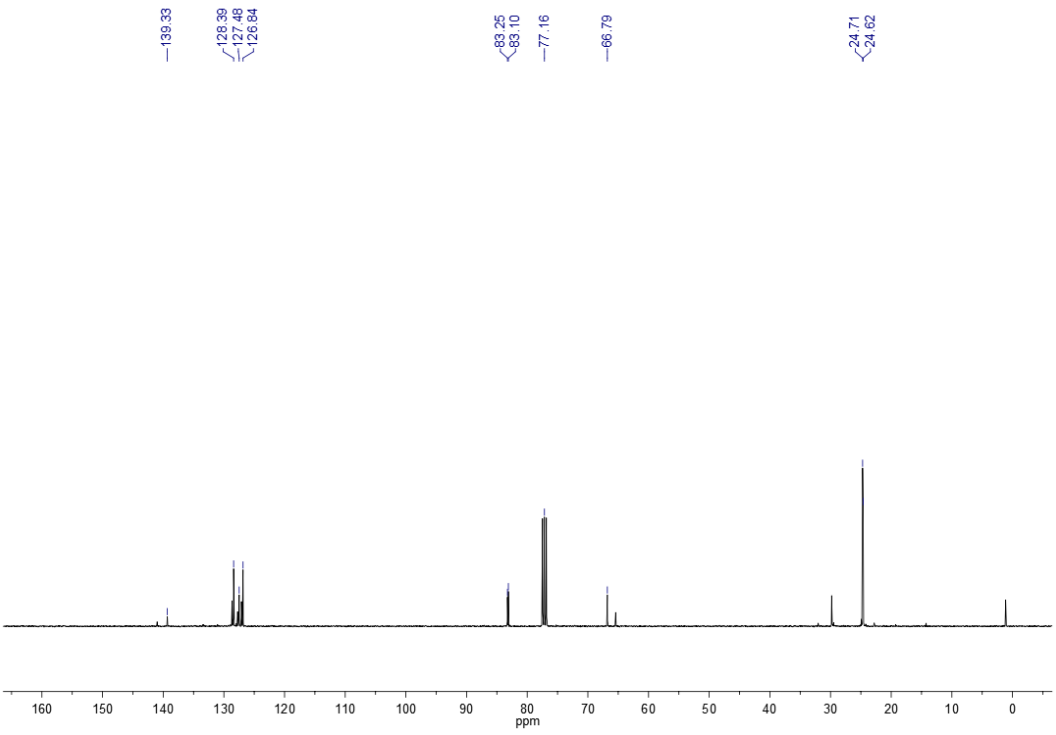
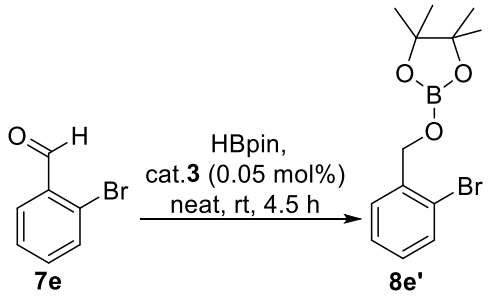


Figure S147. ^{13}C NMR spectrum of **8a'** measured in $CDCl_3$.

Preparation of boronate ester (8e')



8e' was prepared according to the general procedure. The reaction mixture was dissolved in diethyl ether and passed through a alumina short column and then the collected diethyl ether was evaporated under vacuum to get the boronate ester (**8e'**) (63.5 mg, 94%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.50 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 4.97 (s, 2H), 1.28 (s, 12H) ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 22.36 (s) ppm.

NMR spectral data

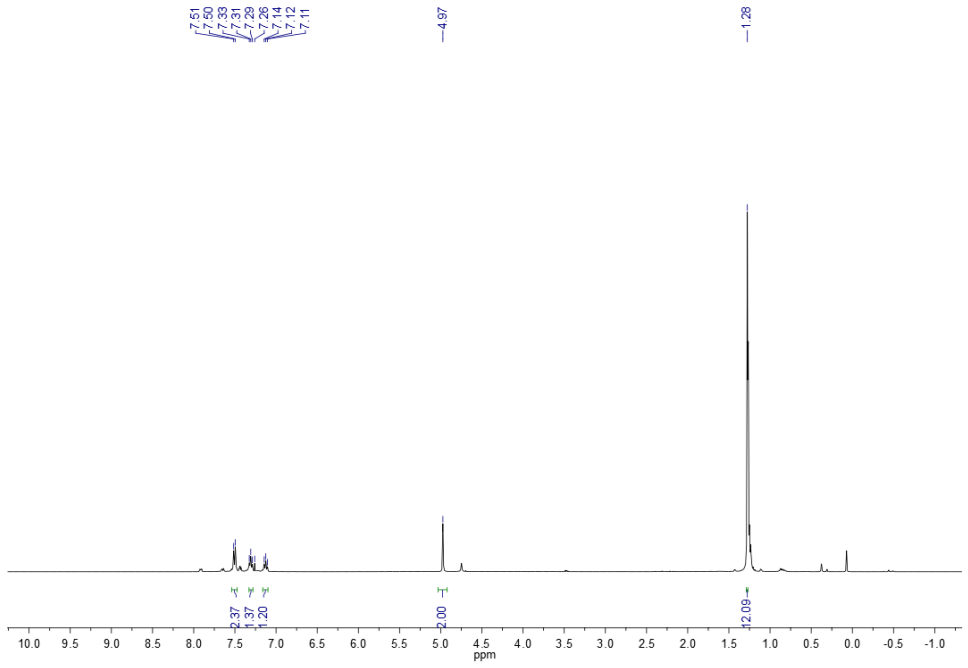


Figure S148. ^{1}H NMR spectrum of **8e'** measured in $CDCl_3$.

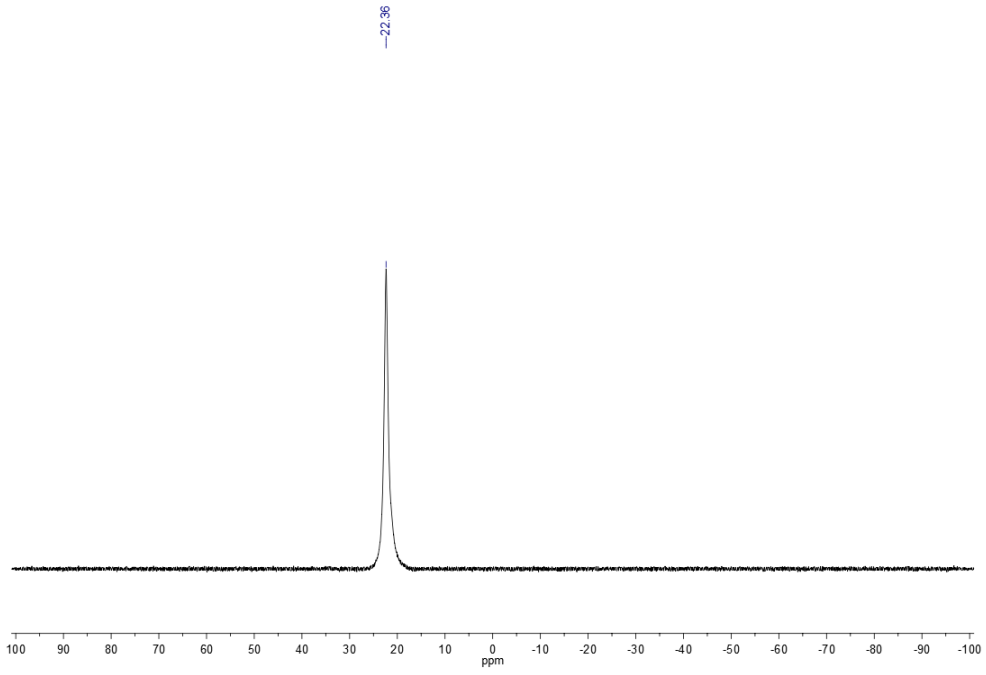
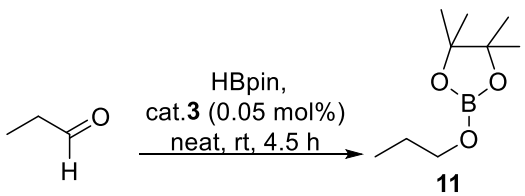


Figure S149. ^{11}B NMR spectrum of **8e'** measured in $CDCl_3$.

Preparation of boronate ester (11)



Compound **11** was prepared according to the general procedure. The reaction mixture was dissolved in diethyl ether and passed through an alumina short column and then the collected diethyl ether was evaporated under vacuum to get the boronate ester (**11**) (310 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.72 (t, *J* = 6.5 Hz, 2H), 1.58 – 1.42 (m, 2H), 1.20 (s, 12H), 0.84 (t, *J* = 7.4 Hz, 3H) ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 22.04 (s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 83.0, 66.5, 24.5, 24.4, and 10.1 ppm.

NMR spectral data

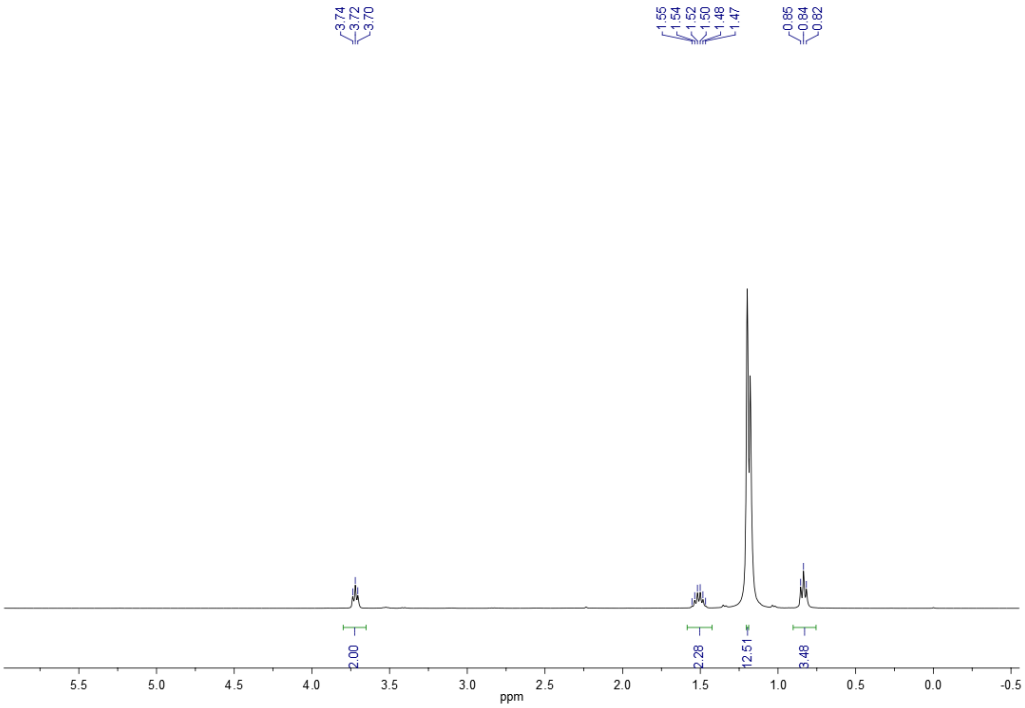


Figure S150. ^{1}H NMR spectrum of **11** measured in $CDCl_3$.

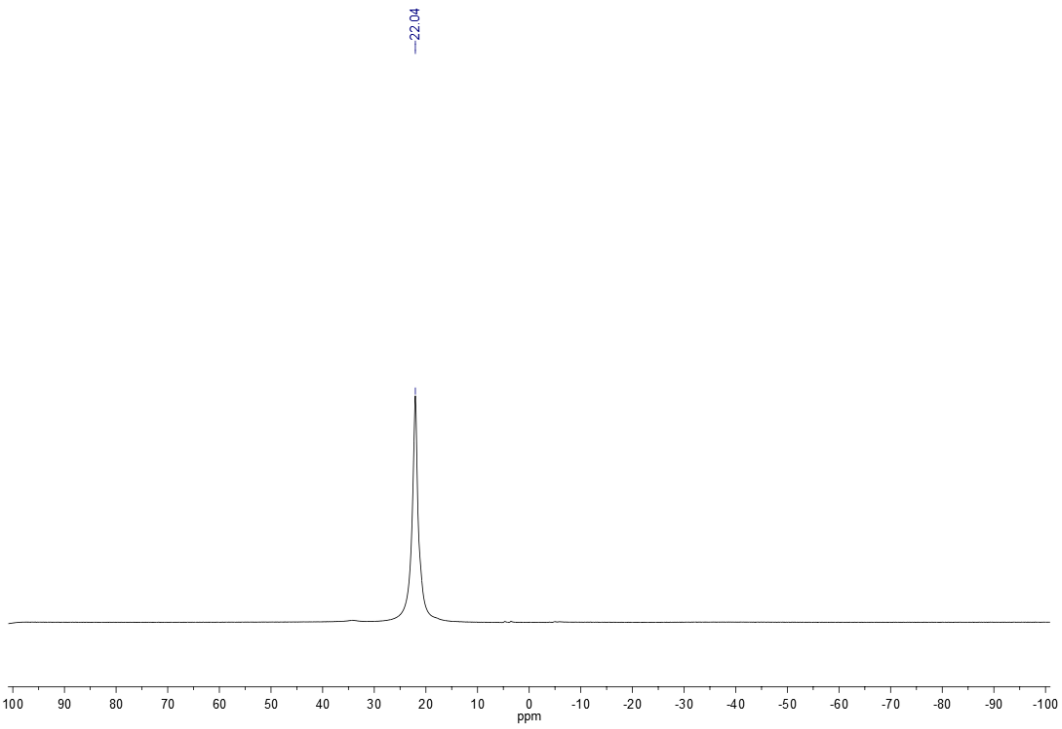


Figure S151. ^{11}B NMR spectrum of **11** measured in $CDCl_3$.

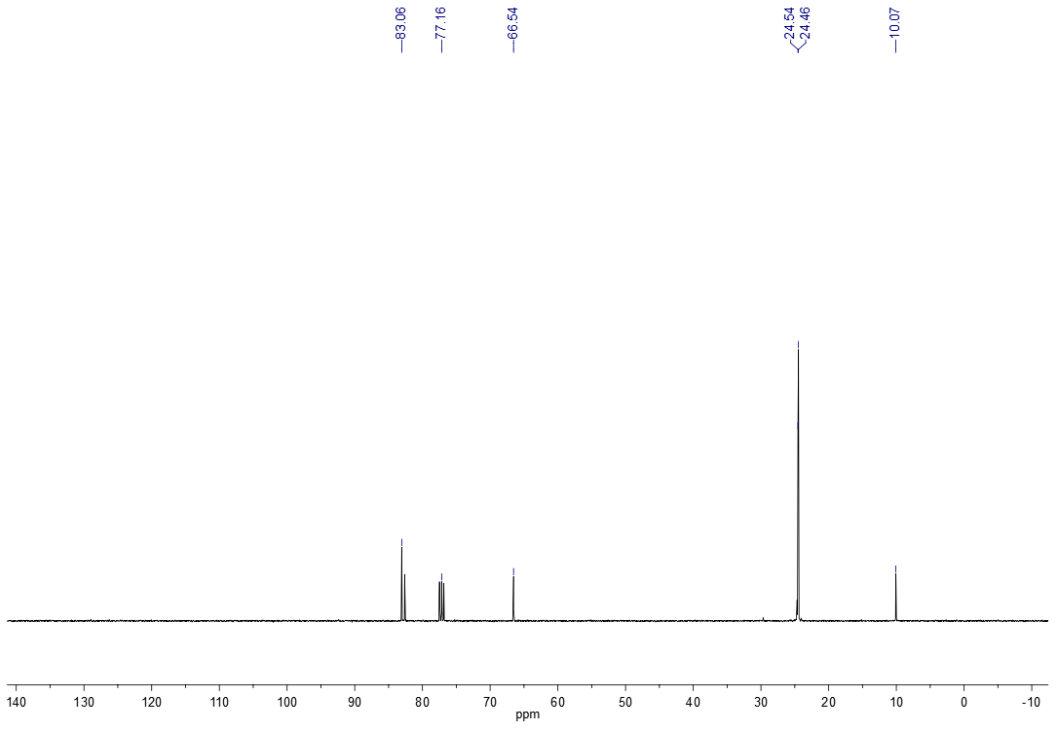
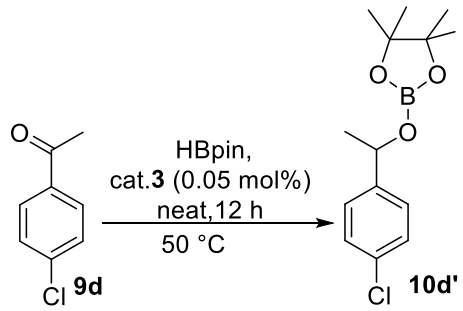


Figure S152. ^{13}C NMR spectrum of **11** measured in $CDCl_3$.

Preparation of boronate ester (10d')



10d' was prepared according to the general procedure. The reaction mixture was dissolved in diethyl ether and passed through a alumina short column and then the collected diethyl ether was evaporated under vacuum to get the boronate ester (**10d'**) (28 mg, 93%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.52 (d, J = 8.5 Hz, 1H), 7.25 (s, 2H), 7.07 (d, J = 8.6 Hz, 1H), 5.33 (d, J = 6.4 Hz, 1H), 1.42 (d, J = 6.5 Hz, 3H) ppm. ^{11}B NMR (128 MHz, C_6D_6) δ = 22.61 (s) ppm.

NMR spectral data

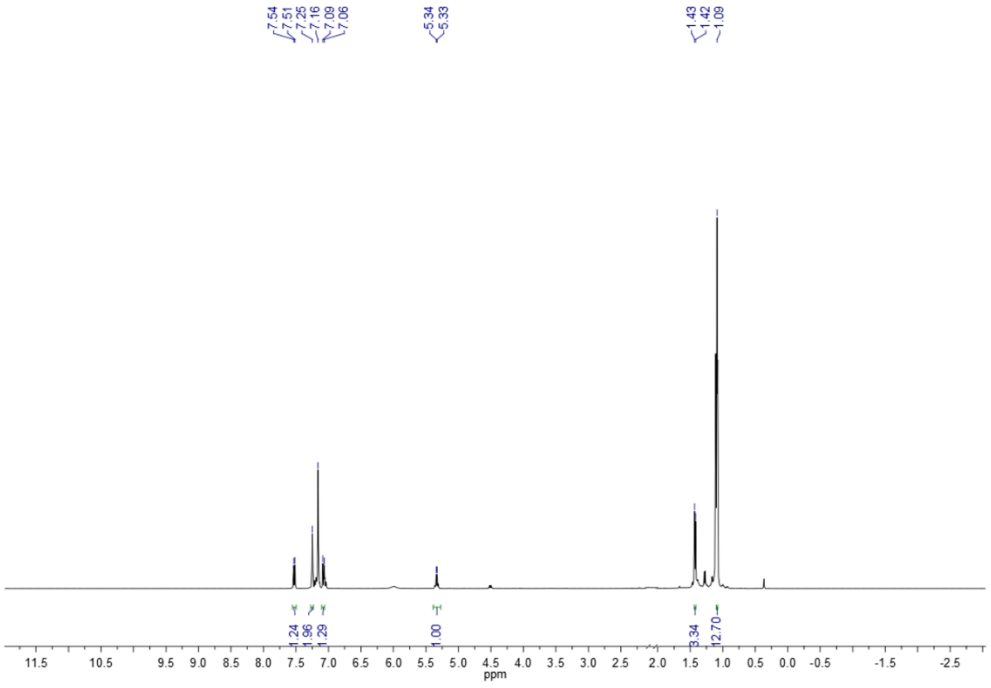


Figure S153. ^{1}H NMR spectrum of **10d'** measured in C_6D_6.

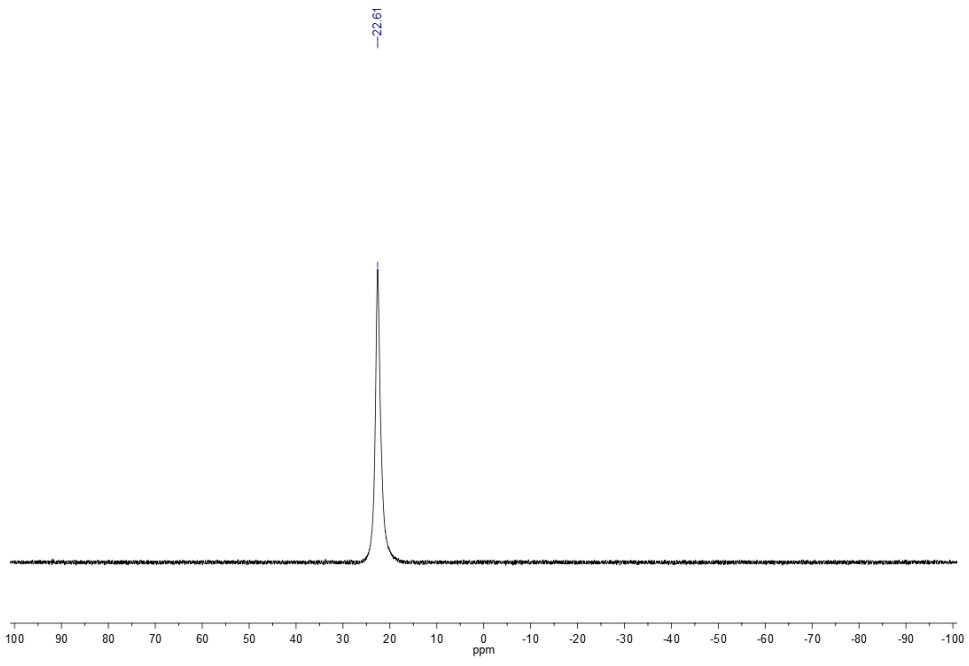
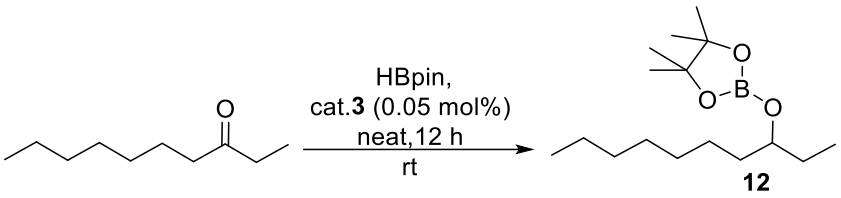


Figure S154. ^{11}B NMR spectrum of **10d'** measured in C_6D_6.

Preparation of boronate ester (12)



12

12 was prepared according to the general procedure. The reaction mixture was dissolved in diethyl ether and passed through a alumina short column and then the collected diethyl ether was evaporated under vacuum to get the boronate ester (**12**) (164 mg, 95%) (NB: Proton NMR is not good due to sensitivity of the of 12). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.94 – 3.82 (m, 1H), 1.45 – 1.34 (m, 4H), 1.19 (s, 10H), 1.17 (s, 12H), 0.81 (m, 6H) ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 22.17 (s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 82.4, 75.9, 36.0, 31.9, 29.6, 29.2, 25.5, 24.5, 22.7, 14.1, and 9.8 ppm.

NMR spectral data

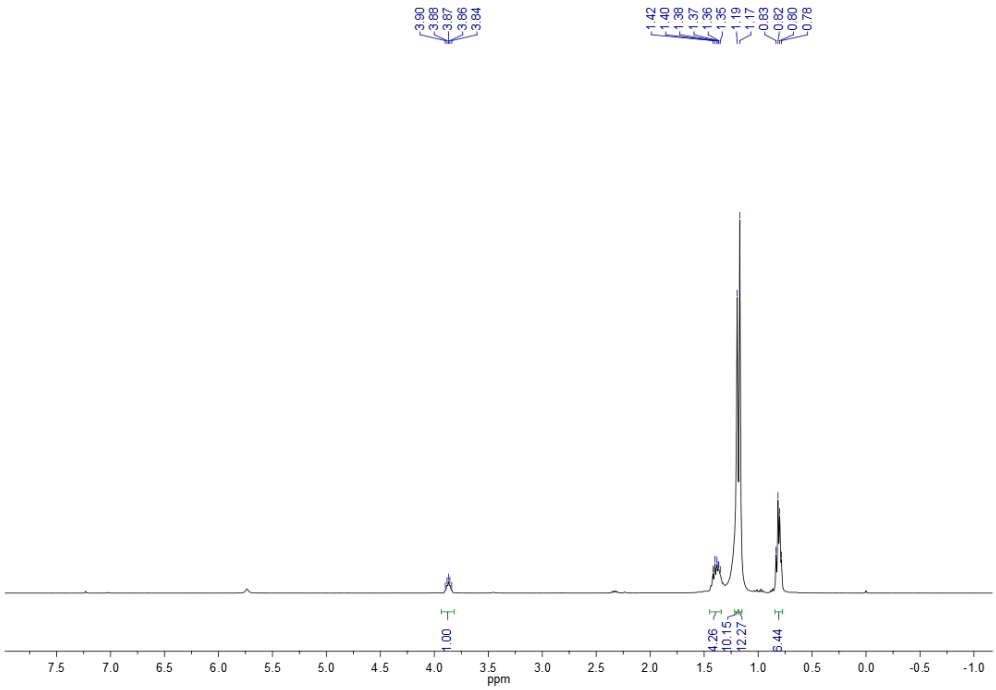


Figure S155. ^{1}H NMR spectrum of **12** measured in $CDCl_3$.

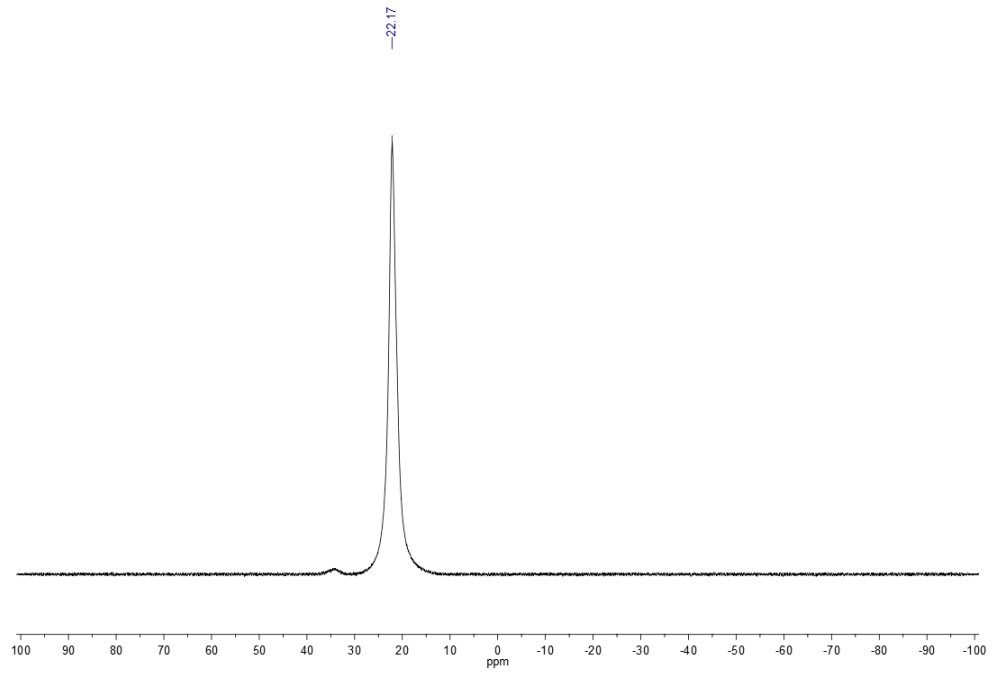


Figure S156. ^{11}B NMR spectrum of **12** measured in $CDCl_3$.

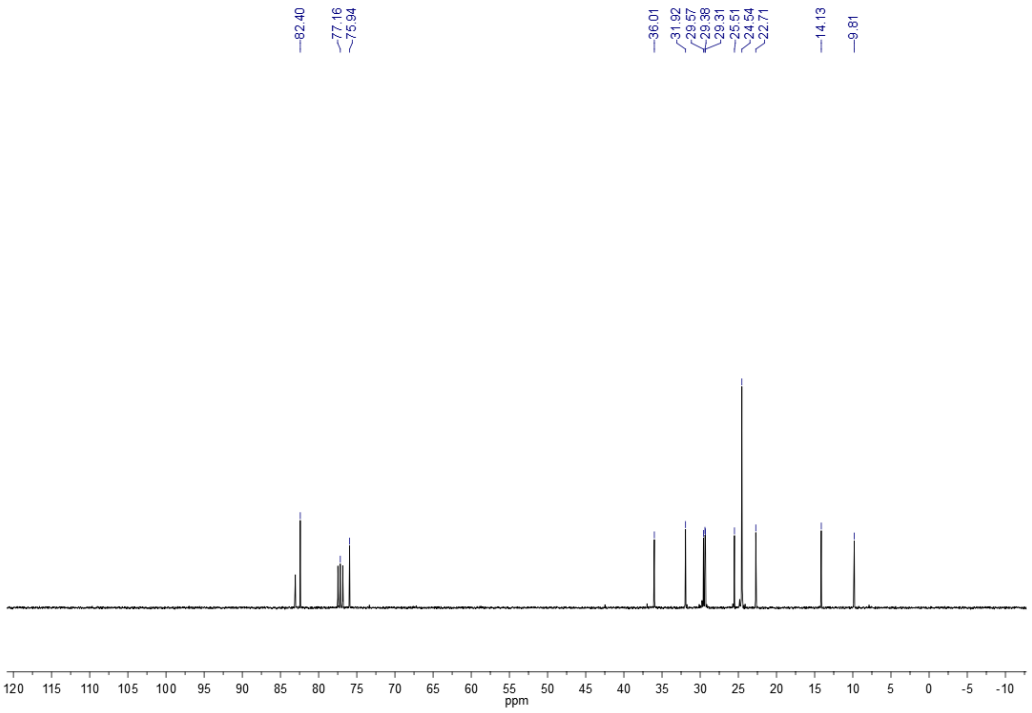
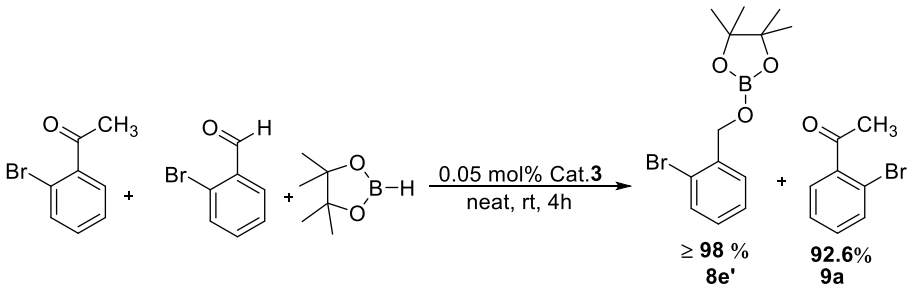


Figure S157. ^{13}C NMR spectrum of **12** measured in $CDCl_3$.

General Procedure for intermolecular competition experiments between aldehyde and ketone

In a nitrogen atmosphere, a 25 mL Schlenk or sealed tube was charged with 1 equiv. of aldehyde, 1 equiv. of ketone, 1 equiv. of pinacolborane, and 0.05 mol% of Cat. **3**. For the duration of 4h, the reaction mixture was stirred at room temperature. After the reaction was complete, the resulting reaction mixture was dissolved in diethyl ether and passed through a short pad of celite filter. The eluent was collected and removal of solvent afforded the corresponding boronate ester and free ketone. Then the NMR was measured by adding 1,3,5-trimethoxy benzene as reference.

Scheme S4



NMR spectral data

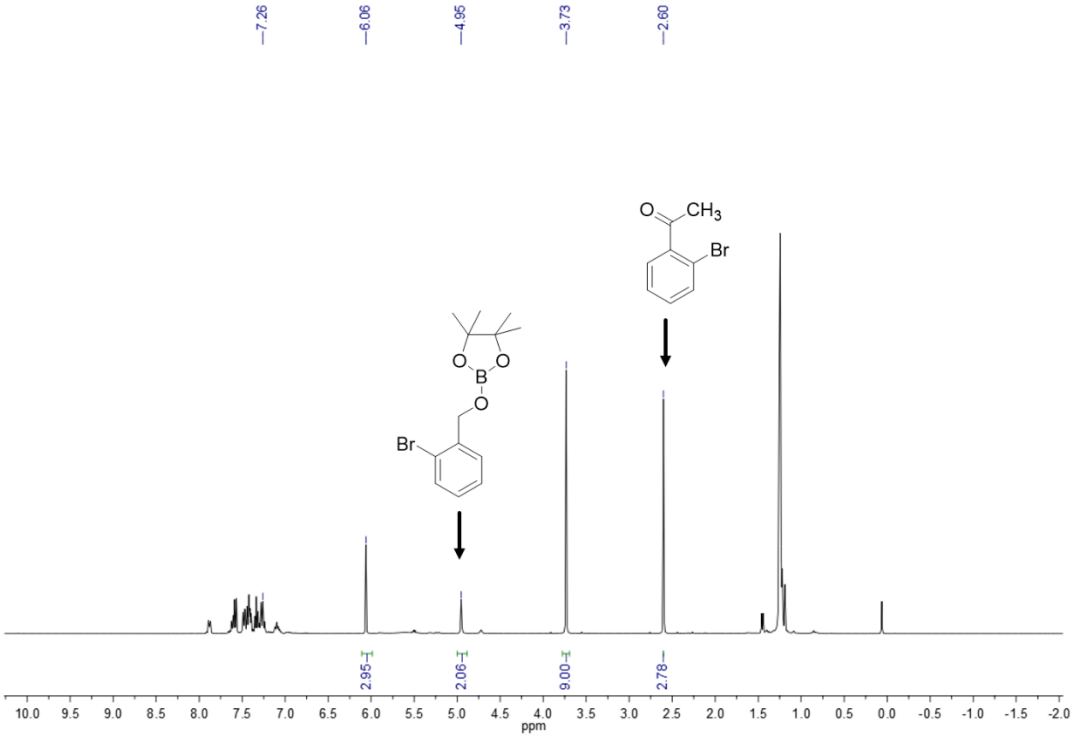


Figure S158. ^{1}H NMR spectrum of intermolecular competition reaction measured in $CDCl_3$.

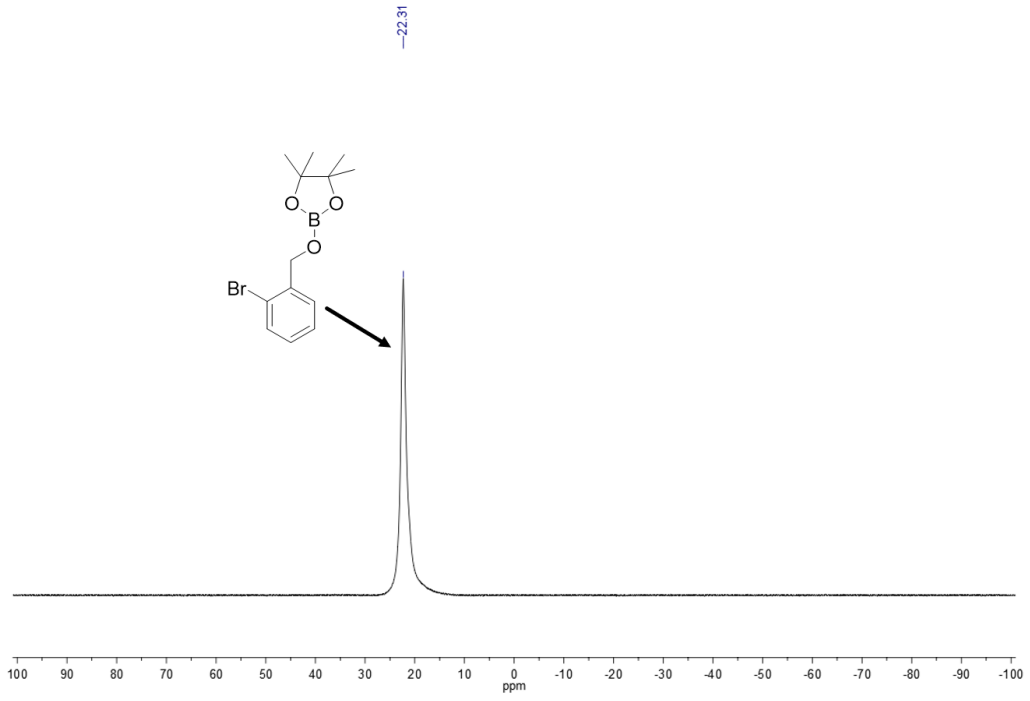
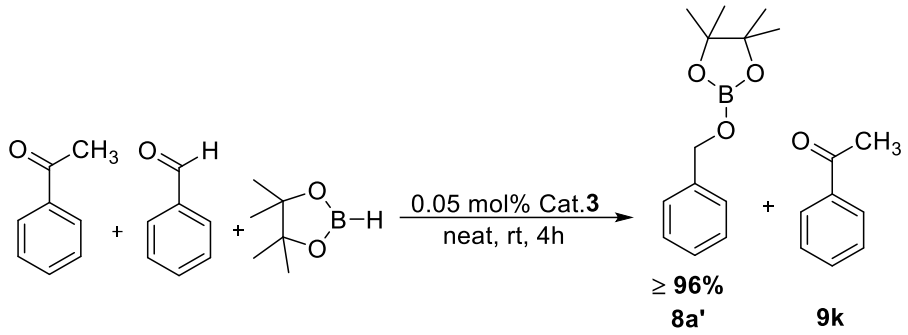


Figure S159. ^{11}B NMR spectrum of intermolecular competition reaction measured in $CDCl_3$.

Scheme S5



NMR spectral data

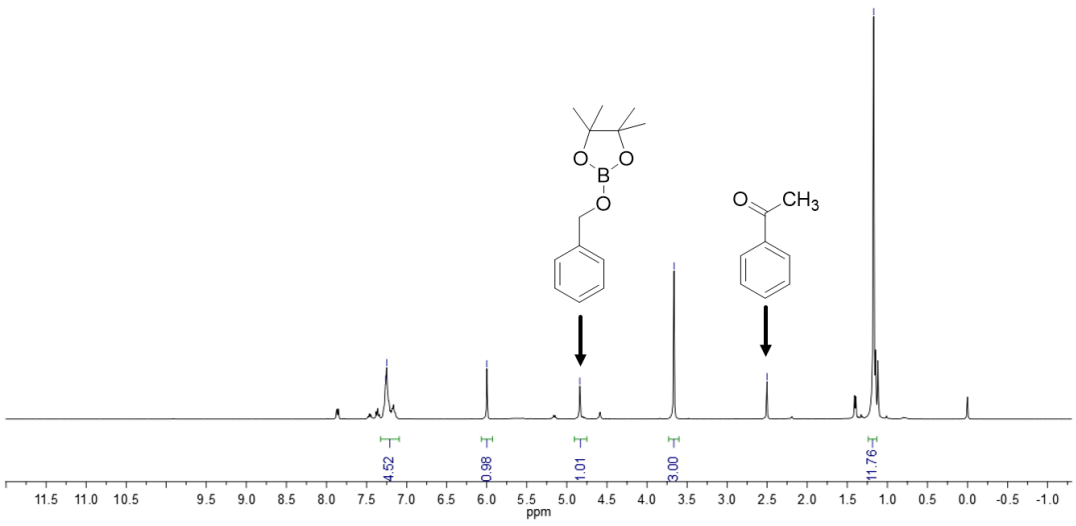


Figure S160. ^{1}H NMR spectrum of intermolecular competition reaction measured in $CDCl_3$.

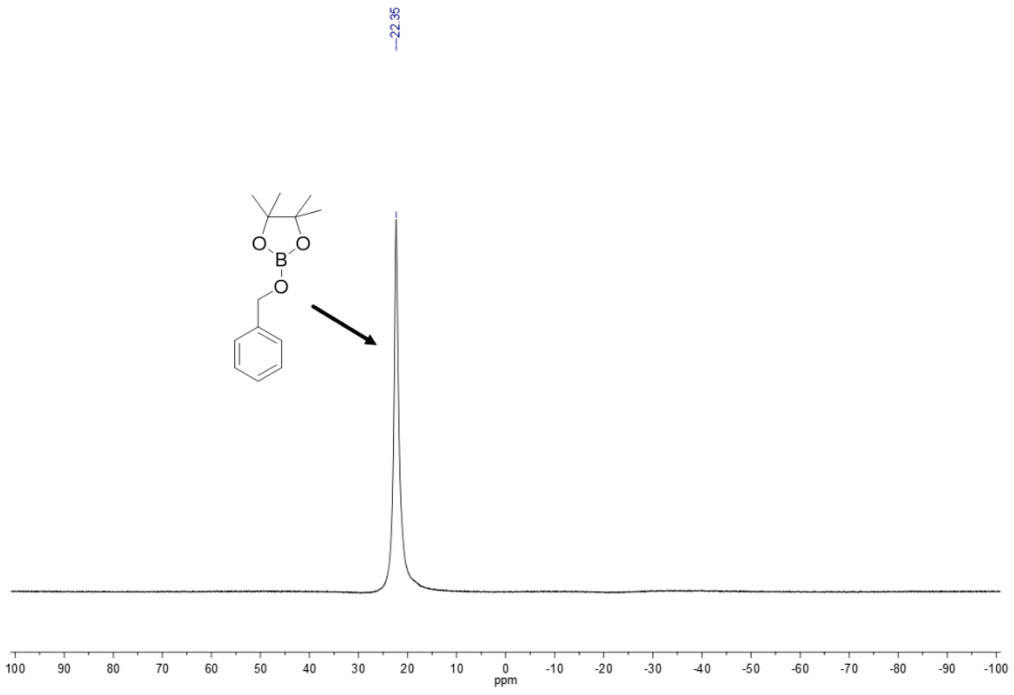
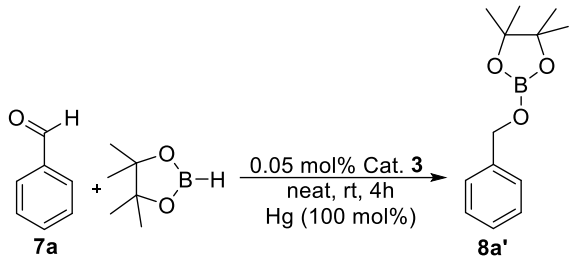


Figure S161. ^{11}B NMR spectrum of intermolecular competition reaction measured in $CDCl_3$.

Procedure for mercury drops experiment to test the homogeneity of the reaction

Scheme S6



In a nitrogen atmosphere, a 25 mL sealed tube was charged with 1 equiv. of benzaldehyde, 1 equiv. of pinacolborane, 1equiv. of mercury and 0.05 mol% of Cat. **3**. For the duration of 4h, the reaction mixture was stirred at room temperature in neat condition. After the reaction was complete, the resulting reaction mixture was dissolved in diethyl ether 15mL and passed through a short pad of celite filter. The eluent was collected and removal of solvent afforded the corresponding boronate ester. full conversion was observed from the NMR, which showed that the reaction is following the homogeneous pathway.

NMR spectral data

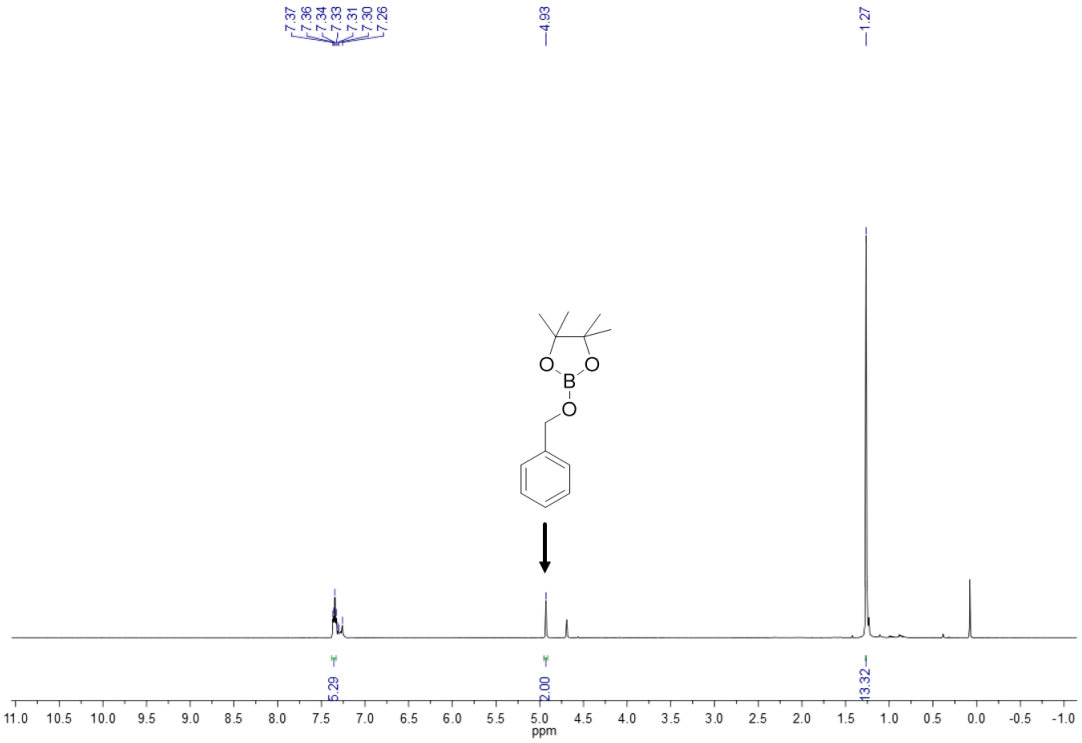


Figure S162. ^{1}H NMR spectrum of mercury drops experiment reaction measured in $CDCl_3$.

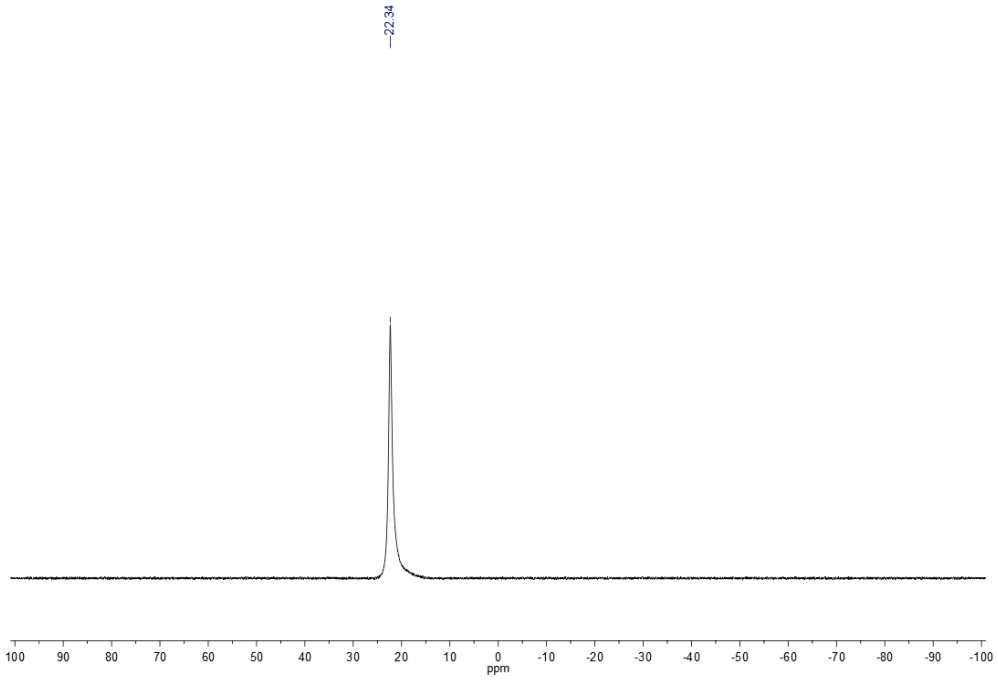
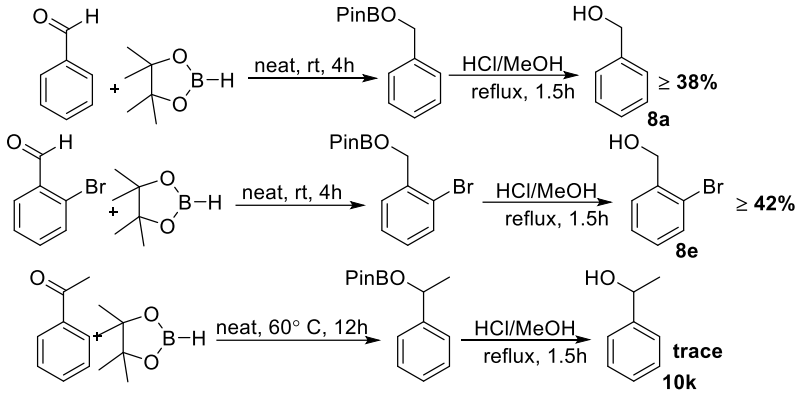


Figure S163. ^{11}B NMR spectrum of mercury drops experiment reaction measured in $CDCl_3$.

General procedure for aldehydes to alcohol conversion without catalyst

In a nitrogen atmosphere, a 25 mL Schlenk tube was charged with 1 equiv. of aldehyde or ketone, 1 equiv. of pinacolborane, and [benzene, 1-2 ml, for solid substrates]. For the duration of 4 hours, the reaction mixture was stirred at room temperature. After the reaction was complete, the resulting boronate ester residue was treated with 1.5 h of refluxing methanol and 1 M aqueous HCl. The aliquot is then dichloromethane extracted after being evaporated under vacuum. The pure primary alcohols and secondary alcohols were obtained by drying, evaporating, and purifying the mixed organic layers through column chromatography over silica-gel (100-200 mesh) with an ethyl acetate/hexane mixture as eluent.

Scheme S7



NMR spectral data

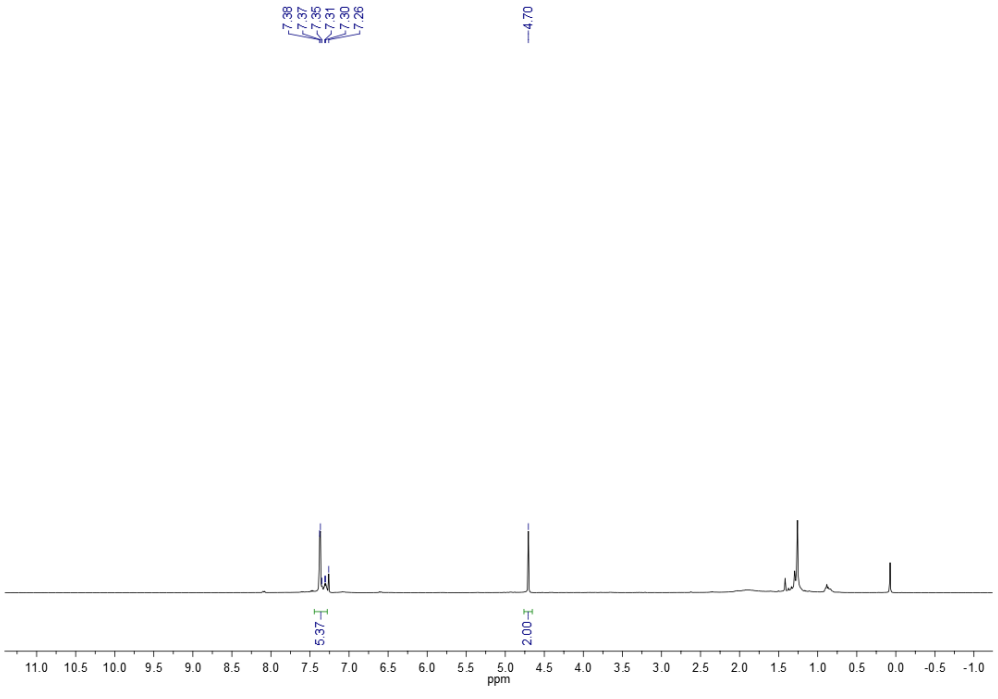


Figure S164. ^{1}H NMR spectrum of **8a** measured in $CDCl_3$.

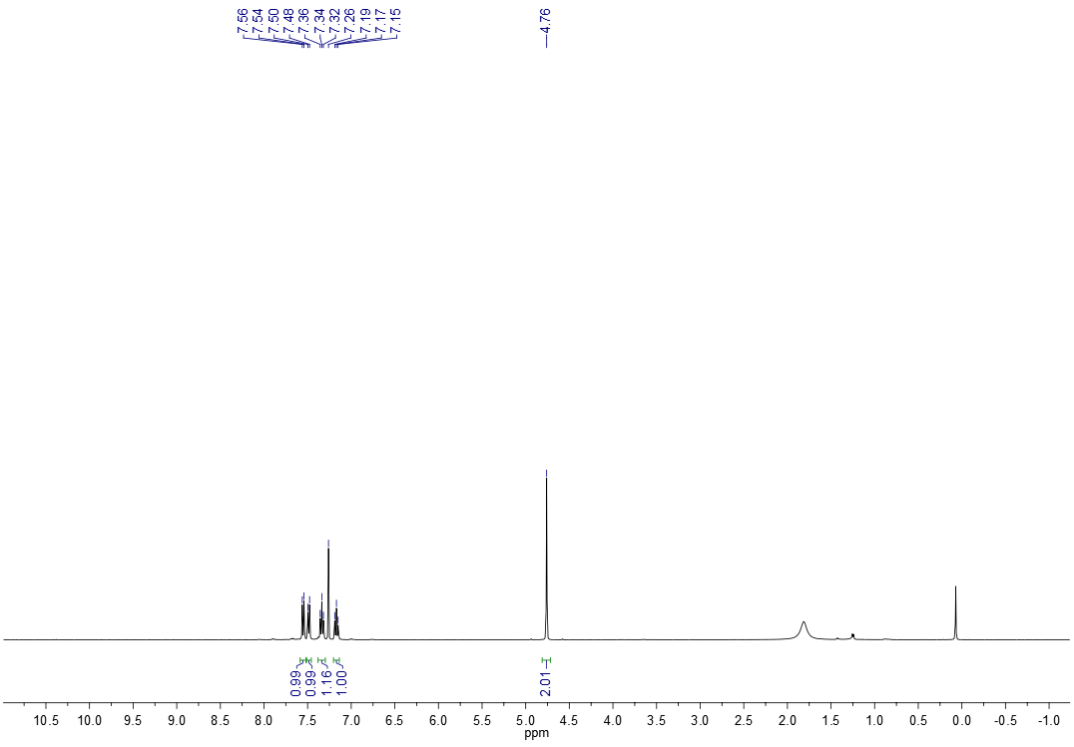


Figure S165. ^{1}H NMR spectrum of **8e** measured in $CDCl_3$.

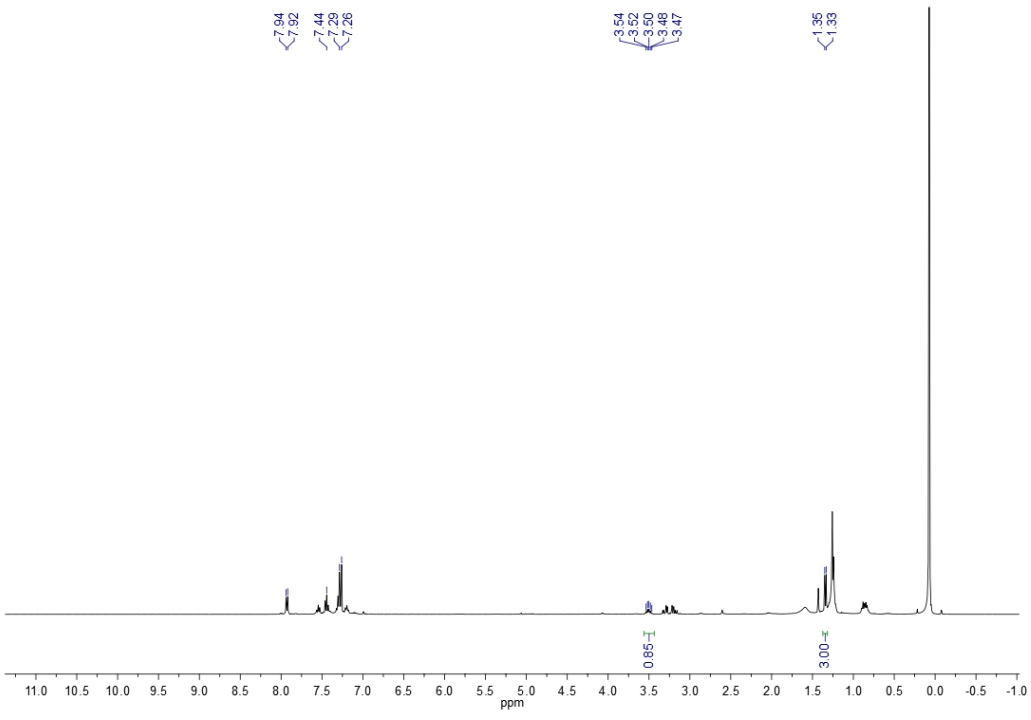
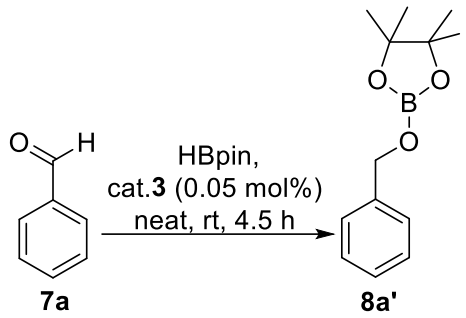


Figure S166. ^{1}H NMR spectrum of **10k** measured in $CDCl_3$

Large scale synthesis of boronate ester (2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (8a')



In a nitrogen atmosphere, a 25 mL Schlenk tube was charged with 1 equiv. of aldehydes (1000 mg, 9.423 mmol), 1 equiv. of pinacolborane (1206 mg, 9.423 mmol), and 0.05 mol% of Cat. **3** (3.7 mg, 0.00471 mmol). For the duration of 4.5 hours the reaction mixture was stirred at room temperature. After the reaction was complete, the resulting reaction mixture was dissolved in diethyl ether and passed through a short pad of celite filter. The eluent was collected and removal of solvent afforded the corresponding boronate ester **8a'** as colourless liquid. Yield: 2130 mg (96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 – 7.27 (m, 5H), 4.94 (s, 2H), and 1.27 (s, 12H) ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 22.38 ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.3, 128.4, 127.5, 126.8, 83.1, 66.8, and 24.7 ppm.

NMR spectral data

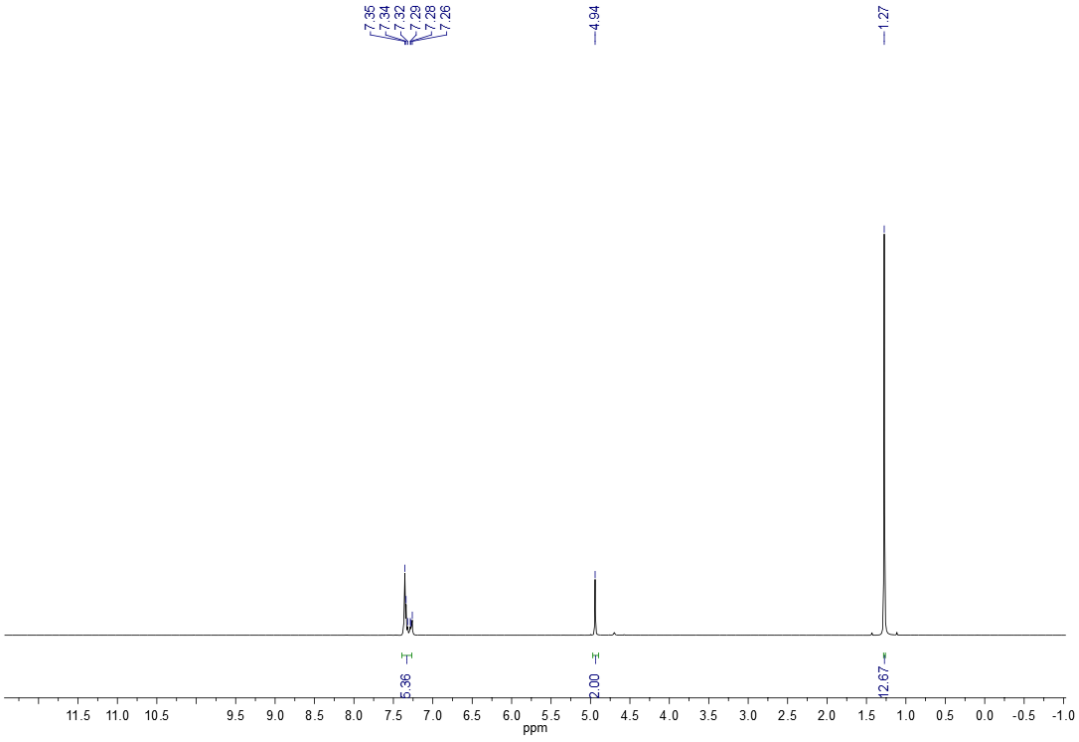


Figure S167. ^{1}H NMR spectrum of **8a'** measured in $CDCl_3$.

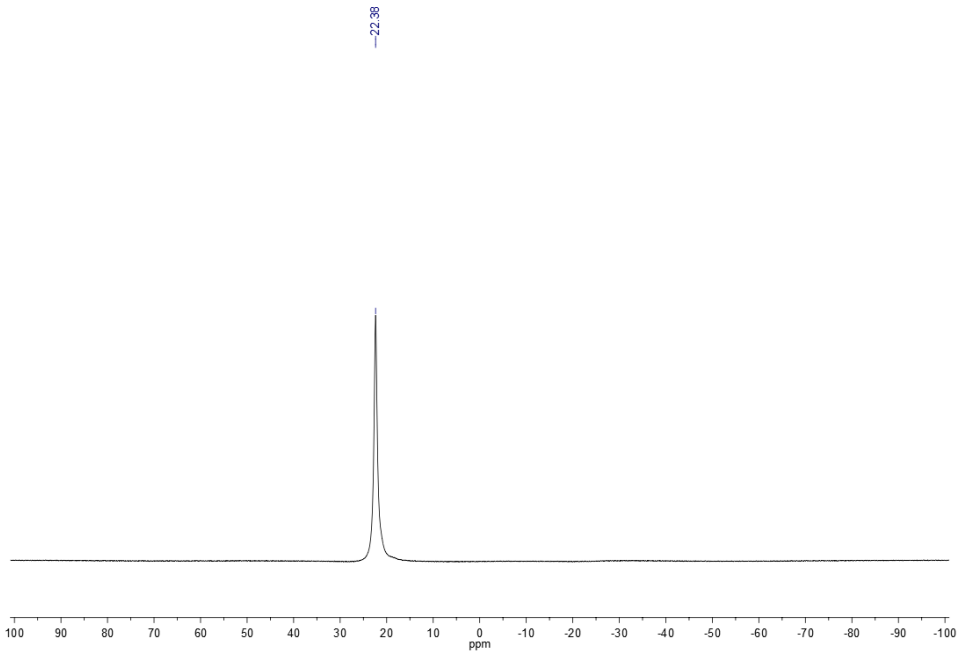


Figure S168. ^{11}B NMR spectrum of **8a'** measured in $CDCl_3$.

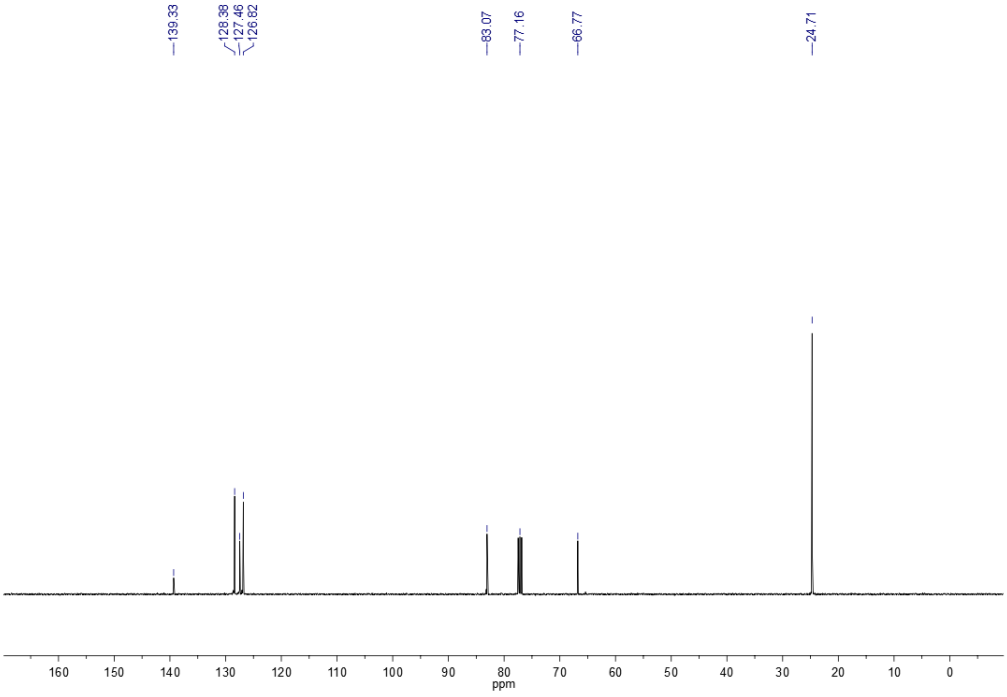
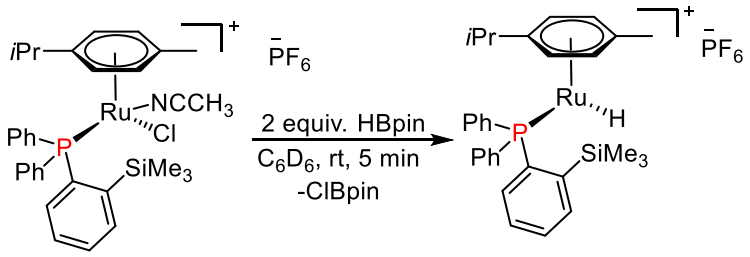


Figure S169. ^{13}C NMR spectrum of **8a'** measured in $CDCl_3$.

Detection of intermediate (III) through NMR experiments

Scheme S8



In an argon filled glovebox, a 5 mL vial was charged with cat **3** (5 mg, 0.0063 mol), To this 0.6 ml of C_6D_6 was added to give yellowish clear solution. Then HBpin (0.003 ml, 0.0189 mmol) was added to the reaction mixture to form a blood red colour clear reaction mixture which was transferred into a NMR tube and hand shaken for 2 minutes. Then the NMR was measured in a regular interval to detect the elusive Ru-H species. A broad singlet was observed at -6.4 ppm which supports the presence of Ru-H species in the reaction mixture.

NMR spectral data

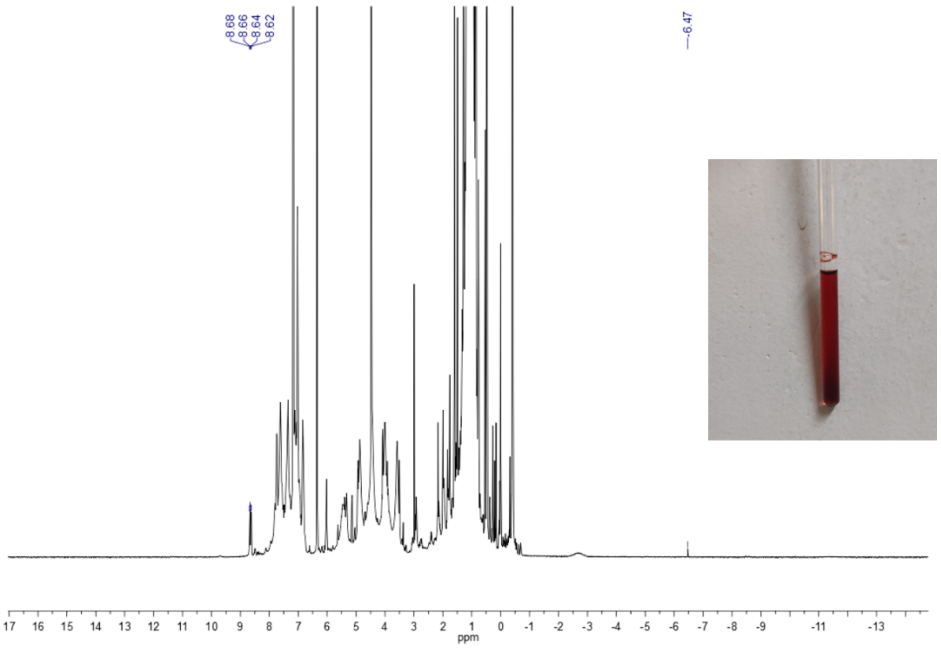


Figure S170. ^{1}H NMR spectrum of **Ru-H** species measured in C_6D_6 after 5 min.

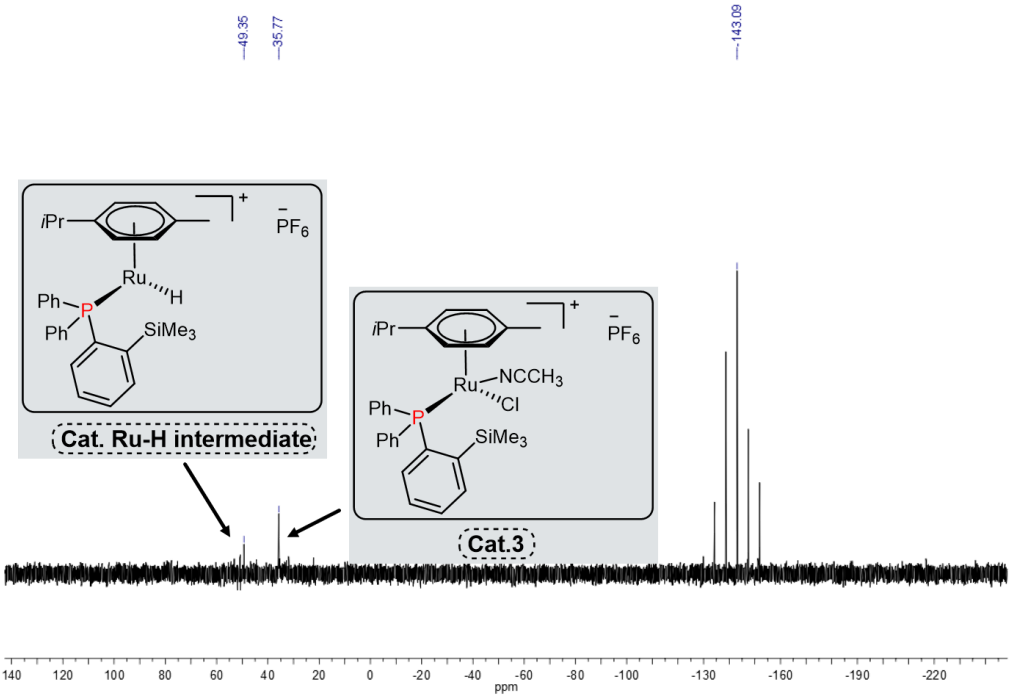


Figure S171. ^{31}P NMR spectrum of **Ru-H** species measured in C_6D_6 after 5 min.

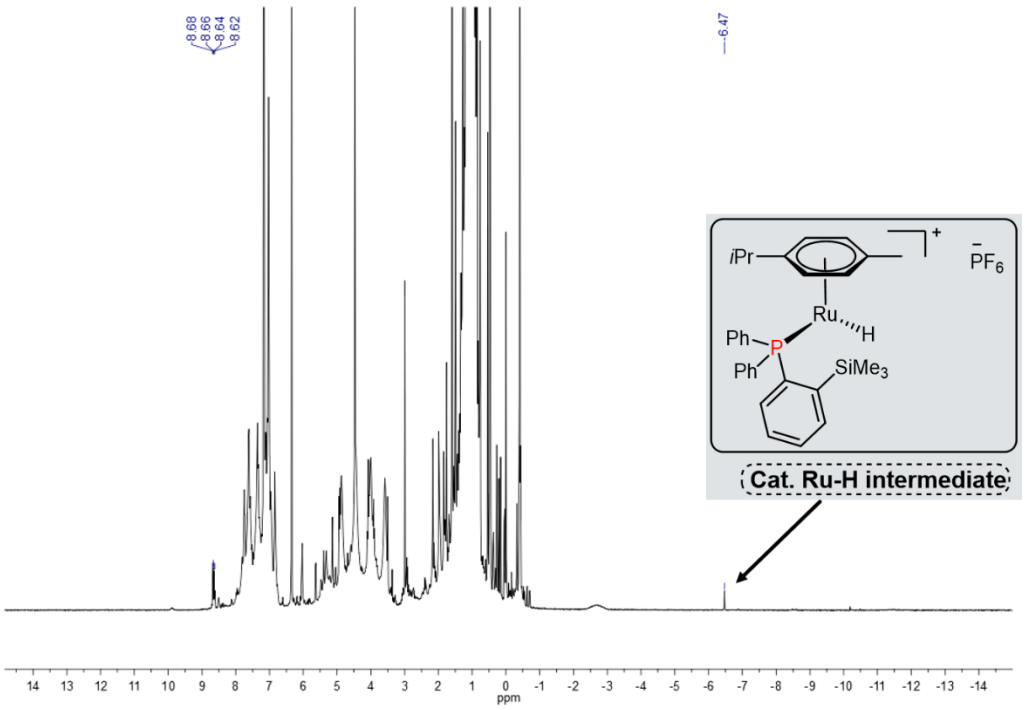


Figure S172. ^{1}H NMR spectrum of **Ru-H** species measured in C_6D_6 after 10 min.

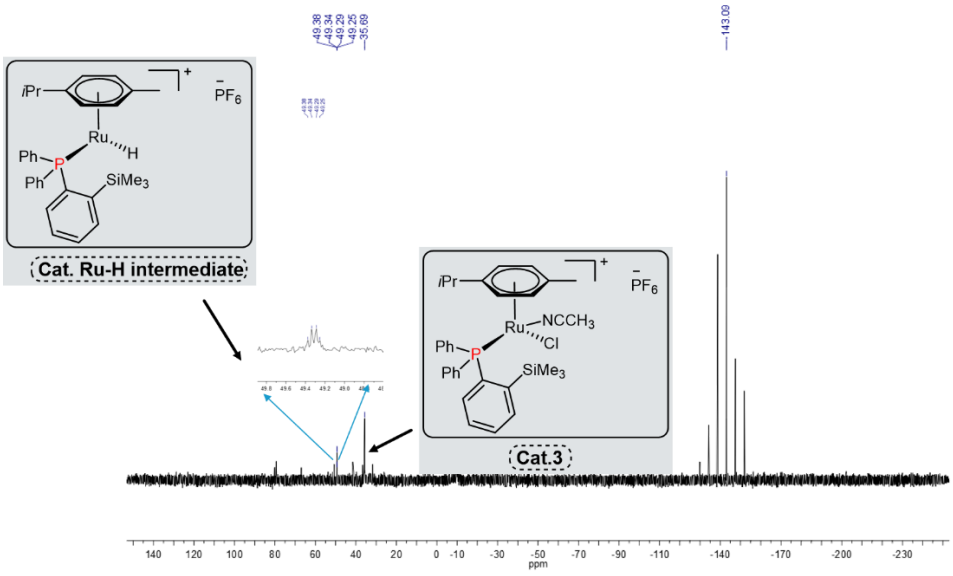


Figure S173. ^{31}P NMR spectrum of **Ru-H** species measured in C_6D_6 after 10 min.

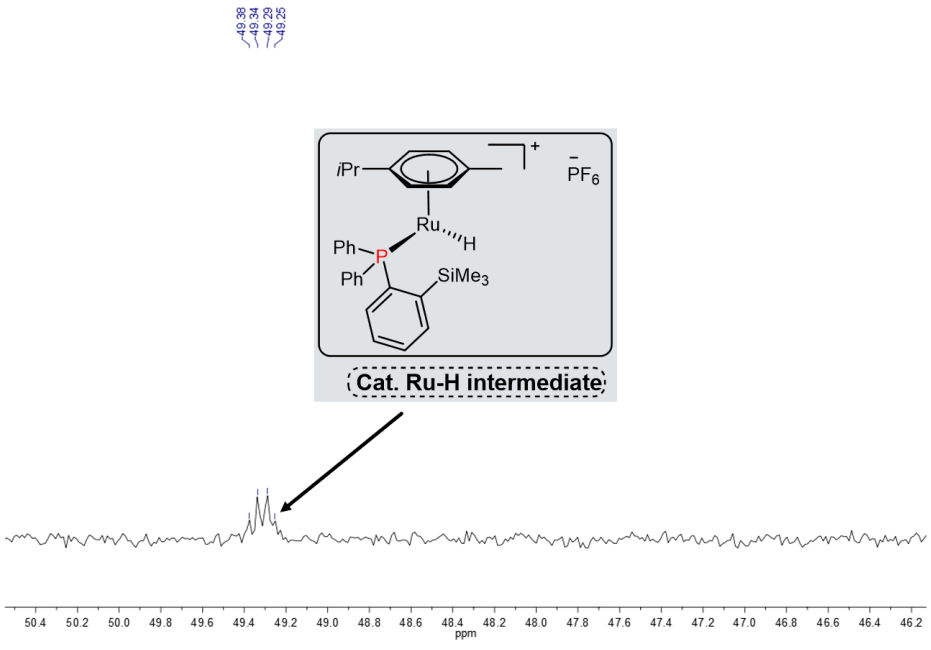
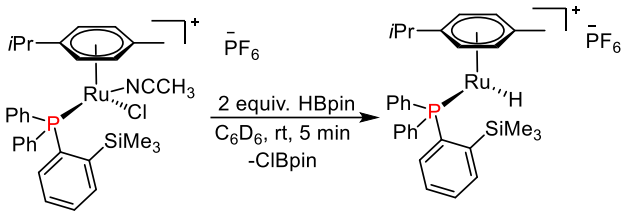


Figure S174. ^{1}H NMR spectrum of **Ru-H** species measured in C_6D_6 after 10 min.

Detection of intermediate through HRMS technique

Scheme S9



In an argon filled glovebox, a 5 mL vial was charged with cat **3** (5 mg, 0.0063 mol), To this 0.6 mL of C_6D_6 was added to give yellowish clear solution. Then HBpin (0.003 ml, 0.0189 mmol) was added to the reaction mixture to form a blood red colour clear reaction mixture which was taken out from the glove box and hand shaken for 2 minutes. Then ESI-mass was measured in a regular interval to detect the elusive Ru-H species. The ESI-mass data showed the *m/z* values at 571.1210 (*calcd* 571.1211) for Ru-H species which can be unambiguously assigned for the presence of cationic ruthenium hydride species in the reaction mixture.

ESI-mass spectral data

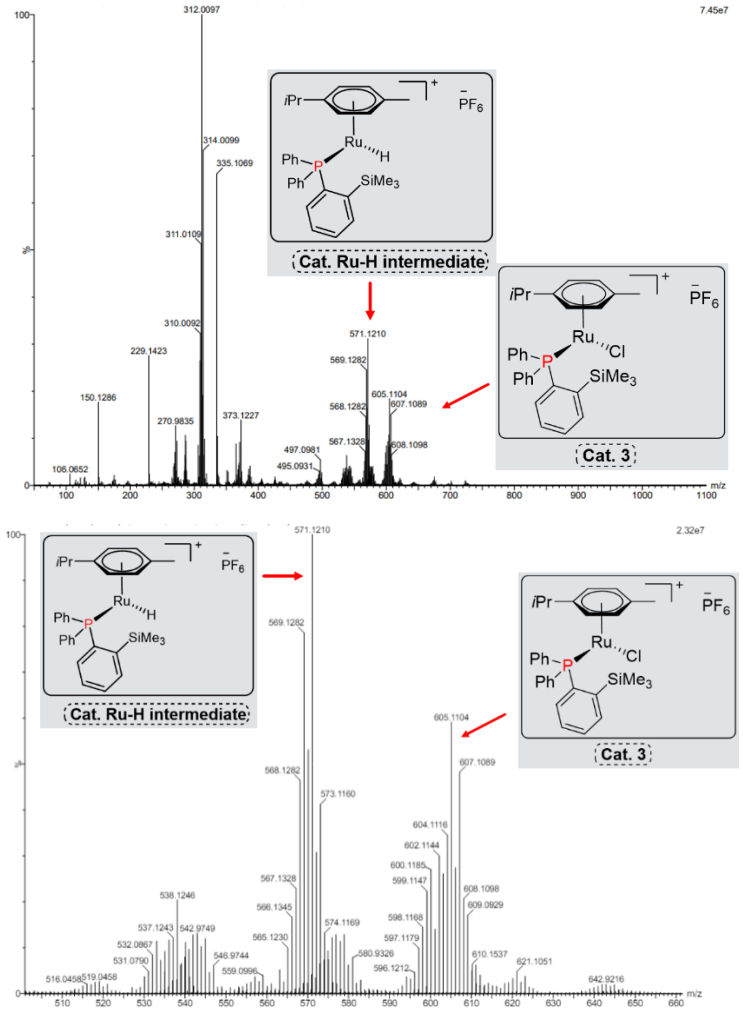


Figure S175. ESI-mass spectrum of reaction mixture showing the presence of both cat **3** and **Ru-H** species measured in acetonitrile.

X-ray crystallographic data of the reported silaylated phosphine and ruthenium metal complexes

Single crystal X-ray structural data of silylated phosphine 1b

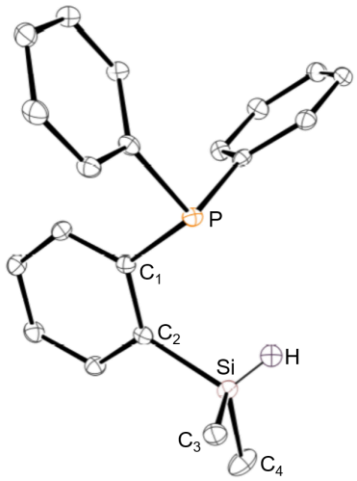


Figure S176. ORTEP view of **1b** with 30% ellipsoid probability. hydrogen atoms except **Si-H** are omitted for clarity. Important bond lengths [Å] and angles [°]; P–C_1; 1.848(3), Si-C_2; 1.891(3), P···Si; 3.283, P-C_1-C_2; 118.5(2), C_2-Si-C_3; 109.83(16), and C_3-Si-C_4; 109.09(17). **Crystallization Method;** *single crystals suitable for XRD measurements were grown by the slow evaporation of diethyl ether solution of the **1b** at room temperature.*

Table S3. Crystal data and structure refinement parameters of **1b**

CCDC identification number	2368156
Empirical formula	$C_{20}H_{21}PSi$
Formula weight	320.43
Temperature/K	99.97
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.49780(10)
b/Å	20.0084(2)
c/Å	24.0485(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3607.73(8)
Z	8
ρ_{calc}g/cm^3	1.180
μ/mm^{-1}	1.921

F(000)	1360.0
Crystal size/mm^3	0.36 × 0.3 × 0.24
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.58 to 155.644
Index ranges	-8 ≤ h ≤ 9, -25 ≤ k ≤ 25, -20 ≤ l ≤ 30
Reflections collected	37246
Independent reflections	7507 [R_{int} = 0.0672, R_{sigma} = 0.0438]
Data/restraints/parameters	7507/0/401
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0391, wR_2 = 0.1002
final R indexes [all data]	R1 = 0.0414, wR2 = 0.1020
Largest diff. peak/hole / e Å-3	0.37/-0.45
Flack parameter	0.346(10)

Single crystal X-ray structural data of ruthenium complex 3

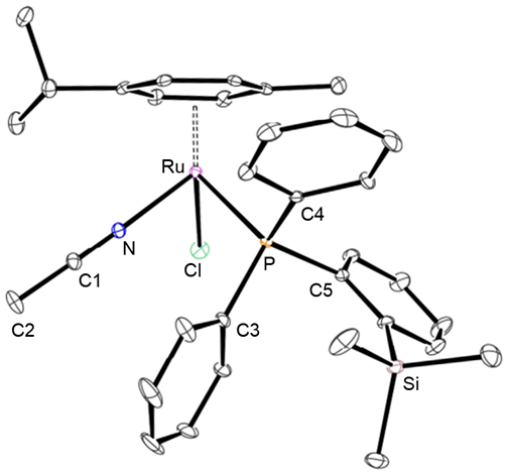


Figure S177. Solid-state structure of the cationic part of complex **3**. Ellipsoids are shown at the 30% probability level; hydrogen atoms, solvent molecule and counter anion are omitted for clarity. Selected bond lengths [Å], angles, and dihedral angles [°]: P−Ru, 2.3771 (6); Ru−Cl, 2.3962(7); Ru−N, 2.040 (2); P−C4, 1.862(3); P−C3, 1.823(3); P−C5, 1.832(3), P−Ru−Cl 89.79(2); P−Ru−N 86.26(7); Cl−Ru−N 83.06(7)

Crystallization Method; *single crystals suitable for XRD measurements were grown by the vapor diffusion of n-hexane over benzene solution of the complex **3** at room temperature.*

Table S4. Crystal data and structure refinement parameters of **3**

CCDC identification number	2368150
Empirical formula	$C_{36}H_{43}ClF_6NP_2RuSi$
Formula weight	830.26
Temperature/K	100.0(2)

Crystal system	triclinic
Space group	P-1
a/Å	9.6071(2)
b/Å	13.6074(2)
c/Å	15.4123(3)
α/°	92.9040(10)
β/°	94.8830(10)
γ/°	102.109(2)
Volume/Å^3	1957.97(6)
Z	2
ρ_{calc}g/cm^3	1.408
μ/mm^{-1}	5.403
F(000)	850.0
Crystal size/mm^3	0.29 × 0.24 × 0.21
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.502 to 156.75
Index ranges	-11 ≤ h ≤ 12, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19
Reflections collected	31178
Independent reflections	8210 [R_{int} = 0.0614, R_{sigma} = 0.0425]
Data/restraints/parameters	8210/0/440
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0467, wR_2 = 0.1248
Final R indexes [all data]	R_1 = 0.0469, wR_2 = 0.1252
Largest diff. peak/hole / e Å^{-3}	2.43/-2.10

Single crystal X-ray structural data of intermediate ruthenium complex (A)

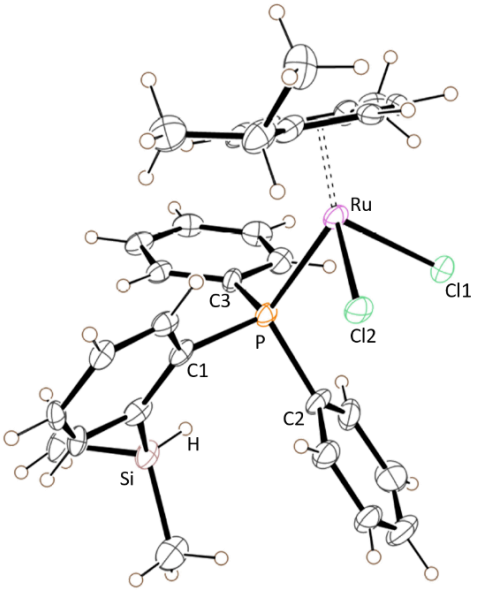


Figure S178. Solid-state structure of **A**. Ellipsoids are shown at the 30% probability level. Selected bond lengths [Å], angles, and dihedral angles [°]: P−Ru, 2.363(3); Ru−Cl_1, 2.406(3); Ru−Cl_2, 2.384(3); P−C_1, 1.849(13); P−Ru−Cl_1 86.35(11); P−Ru−Cl_2 84.77(10).

Crystallization Method; *single crystals suitable for XRD measurements were grown by the vapor diffusion of diethyl ether over benzene solution of the reaction mixture at room temperature.*

Table S5. Crystal data and structure refinement parameters of **int. A**

CCDC identification number	2387230
Empirical formula	$C_{30}H_{35}Cl_2PRuSi$
Formula weight	626.61
Temperature/K	99.98
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	9.7686(2)
b/Å	27.1132(6)
c/Å	12.3737(3)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	3277.27(13)
Z	4
$\rho_{calc}g/cm^3$	1.270
μ/mm^{-1}	6.292
F(000)	1288.0
Crystal size/mm^3	0.26 × 0.24 × 0.22
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.624 to 155.65
Index ranges	$-12 \leq h \leq 11$, $-33 \leq k \leq 29$, $-14 \leq l \leq 15$
Reflections collected	14237
Independent reflections	5911 [R_{int} = 0.0679, R_{sigma} = 0.0612]
Data/restraints/parameters	5911/1/315
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0746, wR_2 = 0.1957
Final R indexes [all data]	R_1 = 0.0793, wR_2 = 0.1995
Largest diff. peak/hole / e $Å^{-3}$	1.44/-1.43
Flack parameter	0.077(13)

Single crystal X-ray structural data of ruthenium complex 5

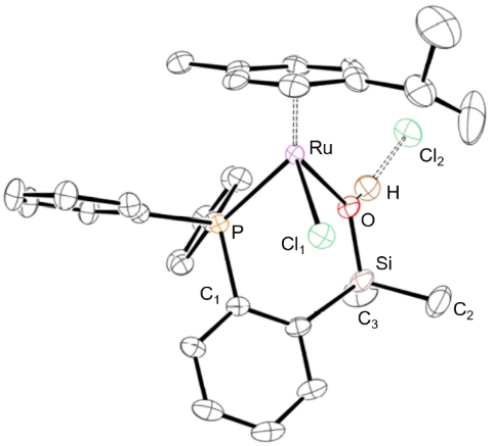


Figure S179. Solid-state structure of complex **5**. Ellipsoids are shown at the 30% probability level; hydrogen atoms except **Si-O-H** are omitted for clarity. Selected bond lengths [Å], angles, and dihedral angles [°]: P−Ru, 2.3599 (8); Ru−Cl_1, 2.3955(8); Ru−O 2.144 (2); P−C_1, 1.837(3); Si-O, 1.659(3); Si-C_2, 1.853(5); Si-C_3, 1.859(5); P−Ru−Cl_1 87.20(3); P−Ru−O 80.11(7); Cl_1−Ru−O 86.92(7); Si-O-Ru 132.75(13).

Crystallization Method; *single crystals suitable for XRD measurements were grown by the vapor diffusion of n-hexane over dichloromethane solution of the complex* ***5*** *at room temperature.*

Table S6. Crystal data and structure refinement parameters of **5**

CCDC identification number	2368152
Empirical formula	$C_{31}H_{37}Cl_4OPRuSi$
Formula weight	727.53
Temperature/K	250(6)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.6049(2)
b/Å	23.5234(4)
c/Å	13.4560(2)
α/°	90
β/°	95.060(2)
γ/°	90
Volume/$Å^3$	3343.70(10)
Z	4
$\rho_{calc}g/cm^3$	1.445
μ/mm^{-1}	7.707
F(000)	1488.0
Crystal size/mm^3	0.3 × 0.29 × 0.26

Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.592 to 156.58
Index ranges	-13 ≤ h ≤ 12, -29 ≤ k ≤ 21, -17 ≤ l ≤ 14
Reflections collected	26806
Independent reflections	7026 [R_{int} = 0.0541, R_{sigma} = 0.0343]
Data/restraints/parameters	7026/0/358
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0496, wR_2 = 0.1293
Final R indexes [all data]	R_1 = 0.0514, wR_2 = 0.1310
Largest diff. peak/hole / e $Å^{-3}$	0.61/-1.94

Single crystal X-ray structural data of ruthenium complex 5'

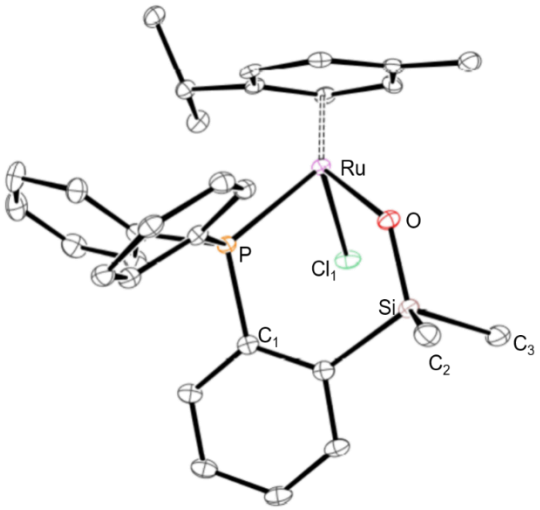


Figure S180. Solid-state structure of **5'**. Ellipsoids are shown at the 30% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles, and dihedral angles [°]: P−Ru, 2.3295(13); Ru−Cl_1, 2.4159(12); Ru−O, 2.070(3); P−C_1, 1.840(5); Si-O, 1.602(4); P−Ru−Cl_1 86.95(4); P−Ru−O 80.94(10); Cl_1−Ru−O 90.25(10), and Si-O-Ru 130.9(2).

Crystallization Method; *single crystals suitable for XRD measurements were grown by the vapor diffusion of n-hexane over dichloromethane solution of the complex* ***5'*** *at 5˚C.*

Table S7. Crystal data and structure refinement parameters of **5'**

CCDC identification number	2368154
Empirical formula	$C_{34.5}H_{44.5}ClOPRuSi$
Formula weight	670.78
Temperature/K	100.03
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.7334(2)

b/Å	8.79540(10)
c/Å	19.4148(2)
α/°	90
β/°	109.4670(10)
γ/°	90
Volume/Å^3	3016.06(6)
Z	4
ρ_{calc}g/cm^3	1.477
μ/mm^{-1}	6.104
F(000)	1398.0
Crystal size/mm^3	0.31 × 0.21 × 0.18
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.284 to 156.05
Index ranges	-23 ≤ h ≤ 23, -11 ≤ k ≤ 10, -24 ≤ l ≤ 23
Reflections collected	39265
Independent reflections	6279 [R_{int} = 0.0592, R_{sigma} = 0.0310]
Data/restraints/parameters	6279/0/321
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0675, wR_2 = 0.2071
Final R indexes [all data]	R_1 = 0.0700, wR_2 = 0.2106
Largest diff. peak/hole / e Å^{-3}	1.26/-1.12

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