

Supporting Information

Arene displacement, C-H activation and acetonitrile insertion reactions enabled by coordination of a functionalized iminophosphorane to Ru^{II}-*p*-cymene scaffold

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Crystal structure determination of complexes 2-5

Single-crystal X-ray diffraction suitable crystal of compounds **2-5** and **7** was mounted on a cryoloop with a drop of paratone oil and placed in the cold nitrogen stream on a Bruker D8 Venture diffractometer. Data was collected at 150(2) K, 300 K or 100 K using Bruker D8 Venture diffractometer with a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) with ‘phi–omega scan’ techniques and were scaled and reduced using CrysAlisPro Red 171.41_64.93a software. The crystal structures of all the compounds were solved using Olex21.5¹ with the ShelXT² structure solution program using intrinsic phasing and refined with the ShelXL³ refinement package using least-square minimization. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included as riding contributions, with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2302590 (compound **3**), 2302591 (compound **4**), 2302664 (compound **5**) and 2344271 (compound **7**). The details of X-ray structural determinations are given in Table S1.

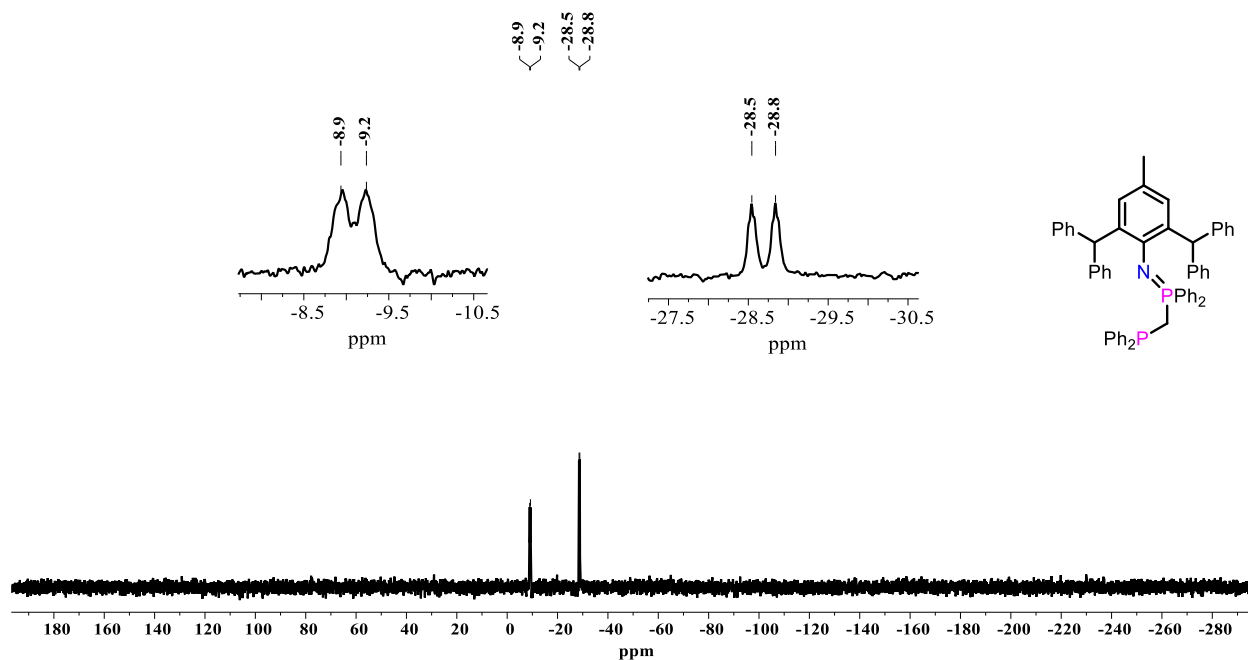
Crystallographic information of complexes 2-5 and 7

Table S1. Crystallographic information of complexes 2-5 and 7

	2	3.(0.9CH₂Cl₂)(1.6C₄H₁₀O)	4.(1.21CH₂Cl₂)	5.(1.6CH₂Cl₂)	7
Empirical formula	C ₆₈ H ₆₃ Cl ₂ NP ₂ Ru	C _{65.3} H _{65.8} Cl _{2.8} NO _{2.6} P ₂ Ru	C _{59.23} H _{50.46} Cl _{3.46} NO P ₂ Ru	C _{67.6} H _{64.2} B ₂ Cl _{3.2} F ₈ N ₅ P ₂ Ru	C ₄₁ H ₄₁ Cl ₂ NP ₂ Ru
Formula weight	1128.18	1169.039	1077.85	1396.793	781.66
T (K)	100	150	300	150	150
Cryst. System	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	P-1	P-1	P 2 ₁ /c	P 2 ₁ /c	P 2 ₁ /c
a/Å	15.7093(6)	13.1607(2)	14.4145(8)	13.422(4)	18.7777(2)
b/Å	19.6268(7)	13.4638(3)	15.8158(8)	21.209(5)	11.3055(10)
c/Å	20.6953(10)	18.5572(3)	23.9074(13)	24.410(47)	17.3485(2)
α/°	75.523(4)	74.144(2)	90	90	90
β/°	76.473(4)	70.026(2)	102.198	99.495(11)	100.6520(10)
γ/°	89.531(3)	67.700(2)	90	90	90
V, Å³	5998.3(5)	2820.02(11)	5327.3(5)	6854(3)	3619.47
Z	2	2	4	4	4
ρ_{calc} g/cm³	1.343	1.376	1.344	1.354	1.434
μ (Mo Ka), mm⁻¹	0.535	0.514	0.568	0.465	0.700
F(000)	2512.0	1214.0	2215.0	2860.0	1608.0
crystal size, mm	0.056 x 0.043 x 0.024	0.089 × 0.078 × 0.045	0.091 × 0.071 × 0.046	0.090 × 0.068 × 0.036	0.089 × 0.073 × 0.043
2θ range, deg	3.336 to 50	3.642 to 60	3.678 to 49.998	3.78 to 50	4.414 to 59.996
Refl. collected	54698	165754	98307	155476	82029
Indep. reflections	20861 [R _{int} = 0.0670]	16437 [R _{int} = 0.0632]	9368 [R _{int} = 0.1146]	12061 [R _{int} = 0.1602]	10519 [R _{int} = 0.0658]
Goodness-of-fit on F²	1.037	1.025	1.064	1.057	1.035
R₁	0.1155	0.0431	0.0776	0.0664	0.0485
wR₂	0.2104	0.0918	0.1317	0.1342	0.0946

Table S2. Selected bond lengths and bond angles of compound **2**

Bond distance (Å)	2	Bond angles (°)	2
N1–P1	1.524(4)	N1–P1–C46	109.0(3)
P1–C46	1.838(6)	P1–C46–P2	132.6(3)
C46–P2	1.837(6)	P2–Ru1–C11	84.85(5)
Ru1–P2	2.3662(16)	P2–Ru1–C12	88.21(5)
Ru1–C11	2.3942(15)	C11–Ru1–C12	88.09(5)
Ru1–C12	2.4222(16)		

NMR and HRMS spectra of compounds 1-7**Figure S1.** $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in CDCl_3 (202 MHz).

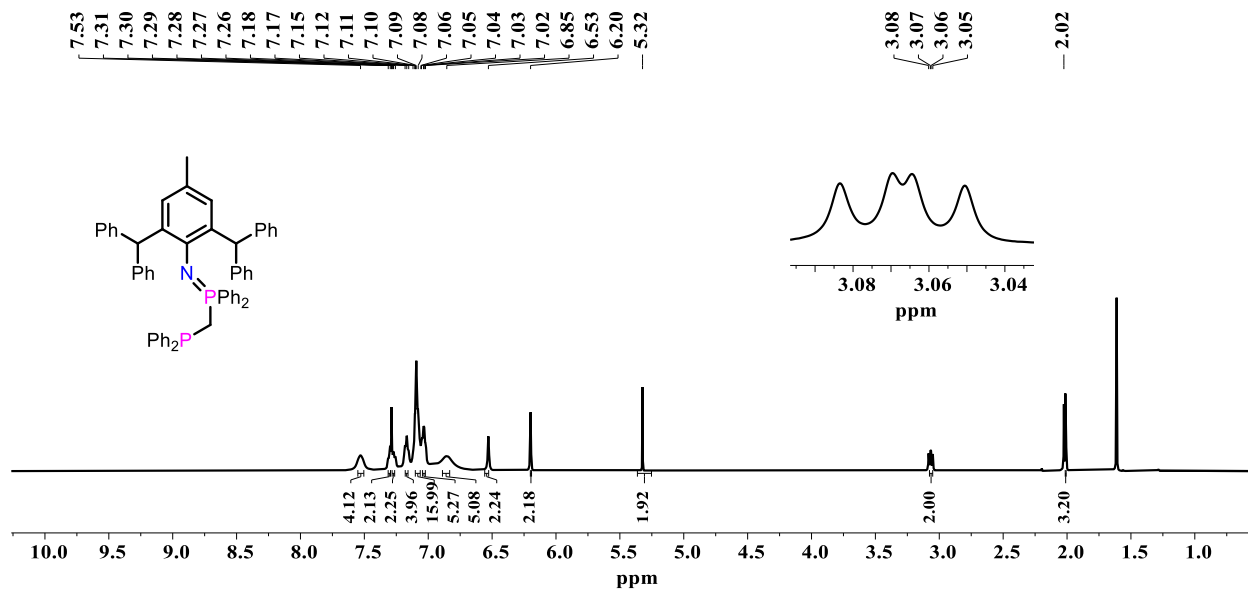


Figure S2. ^1H NMR spectrum of **1** in CDCl_3 (500 MHz).

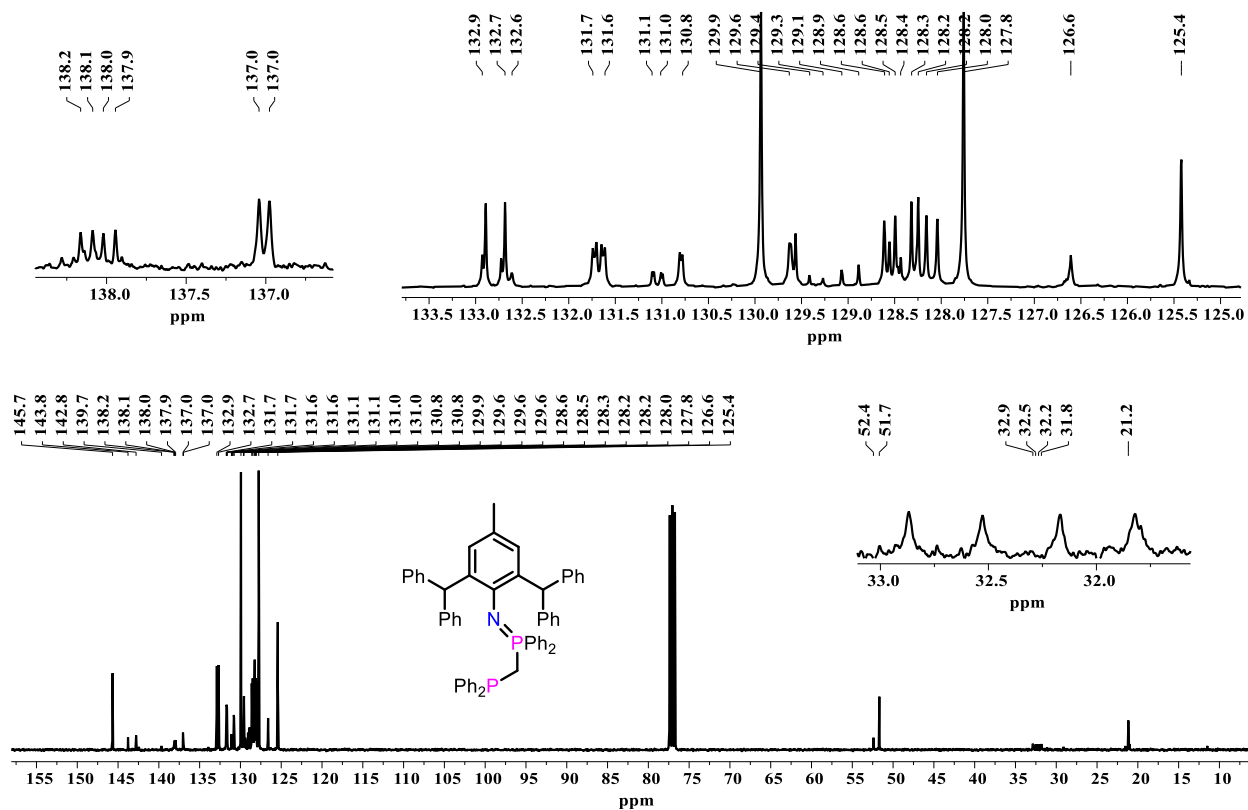


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** in CDCl_3 (101 MHz).

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Analysis Info

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 Sample Name MSB-RG-A-4
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Acquisition Date 5/17/2022 7:41:45 PM

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 Instrument maXis impact 282001.00081

Acquisition Parameter

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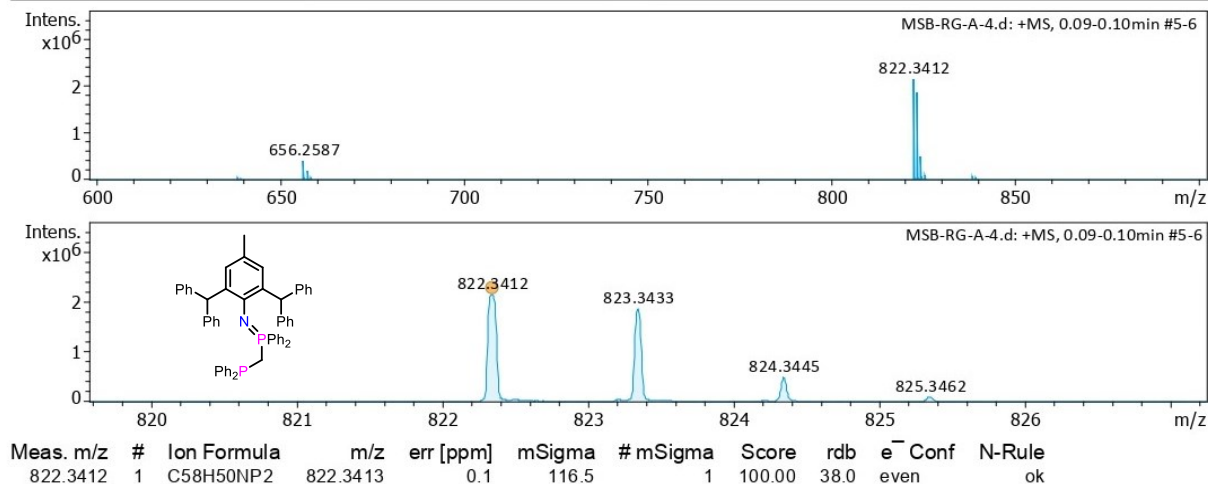


Figure S4. HRMS spectrum of 1.

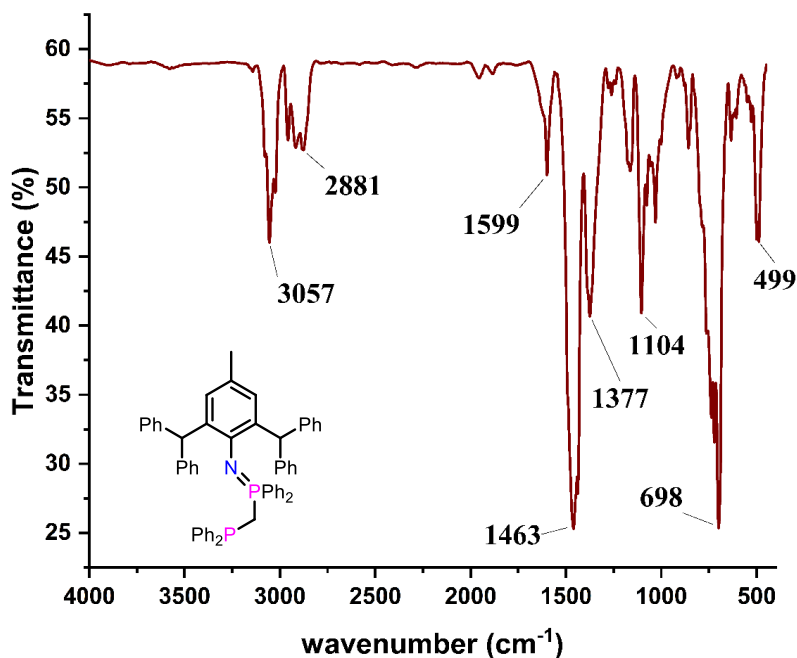


Figure S5. FT-IR spectrum of 1.

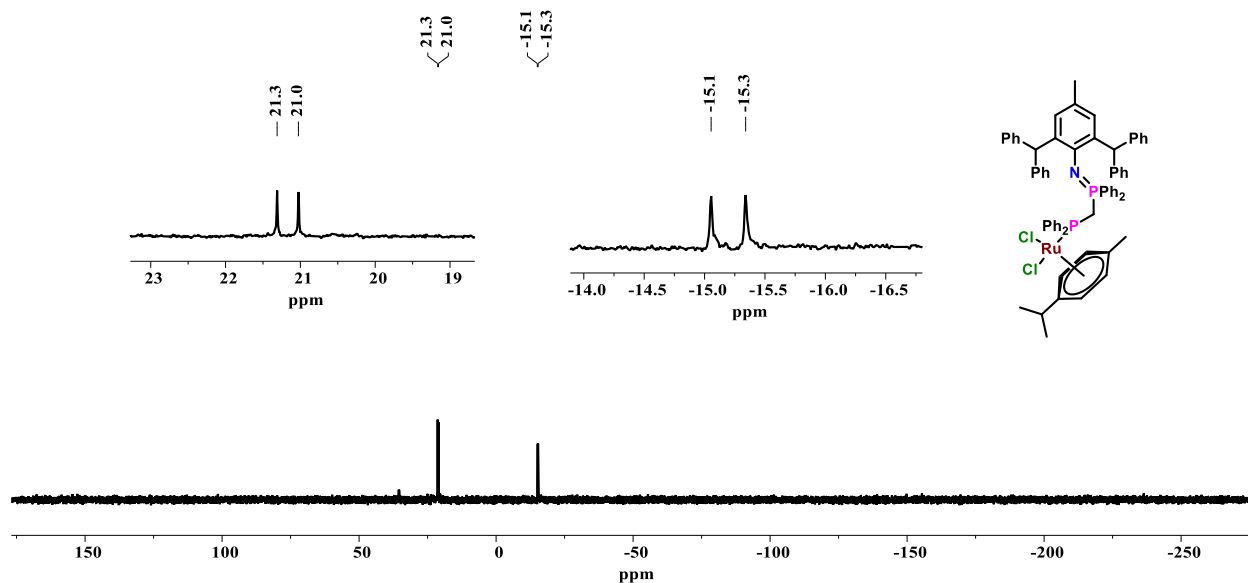


Figure S6. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in CDCl_3 (162 MHz).

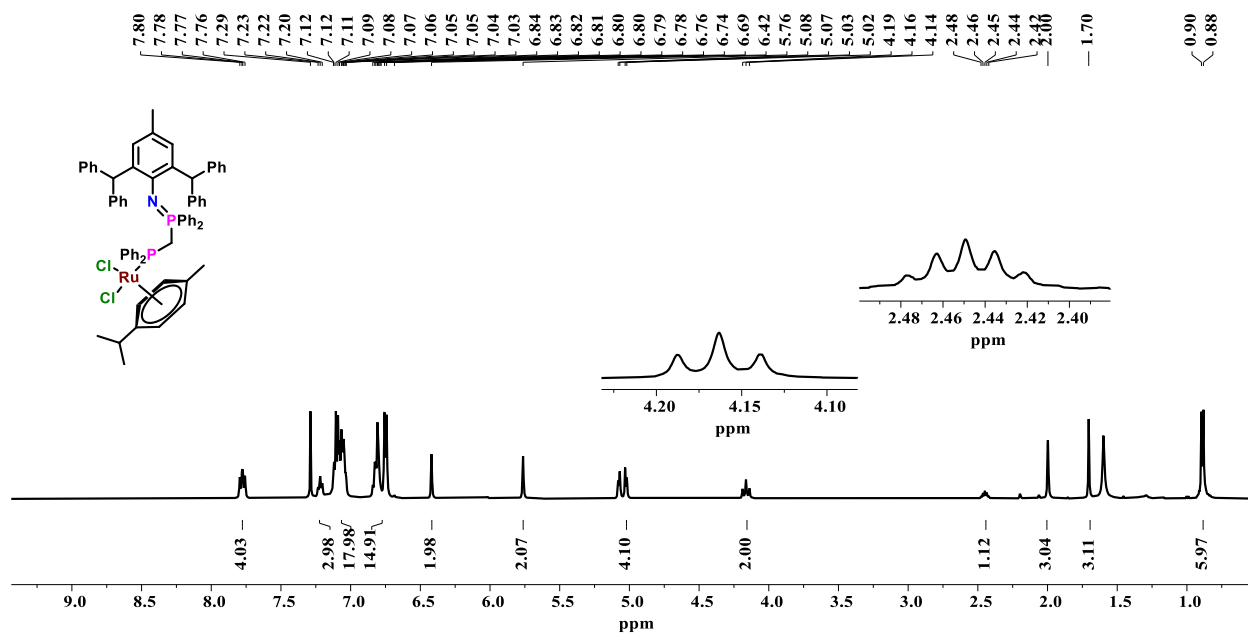


Figure S7. ^1H NMR spectrum of **2** in CDCl_3 (400 MHz).

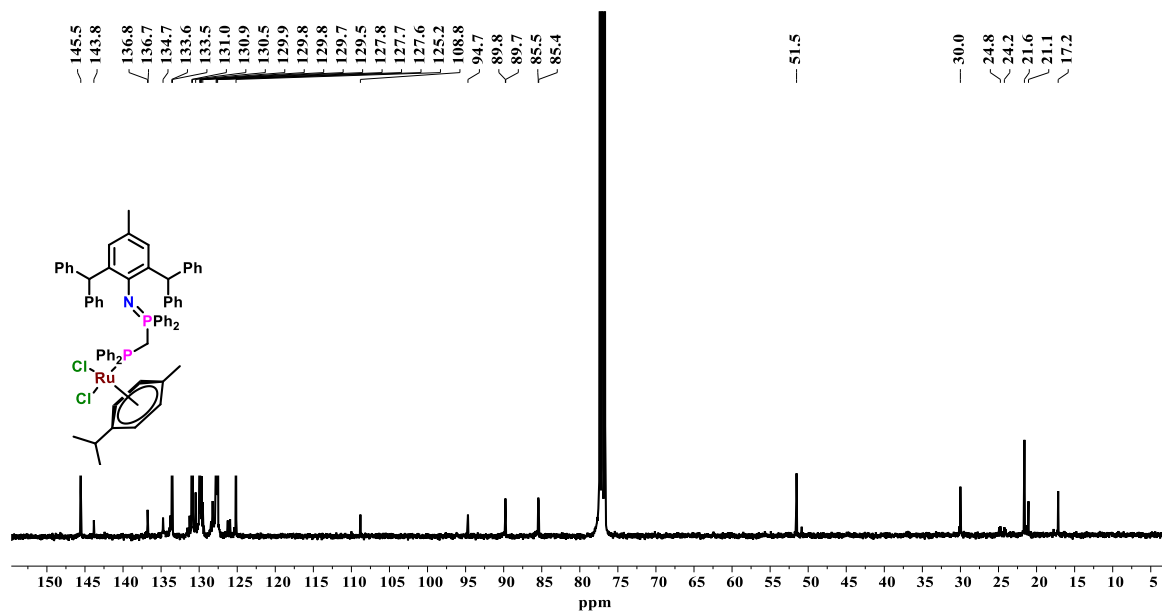


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** in CDCl_3 (101 MHz).

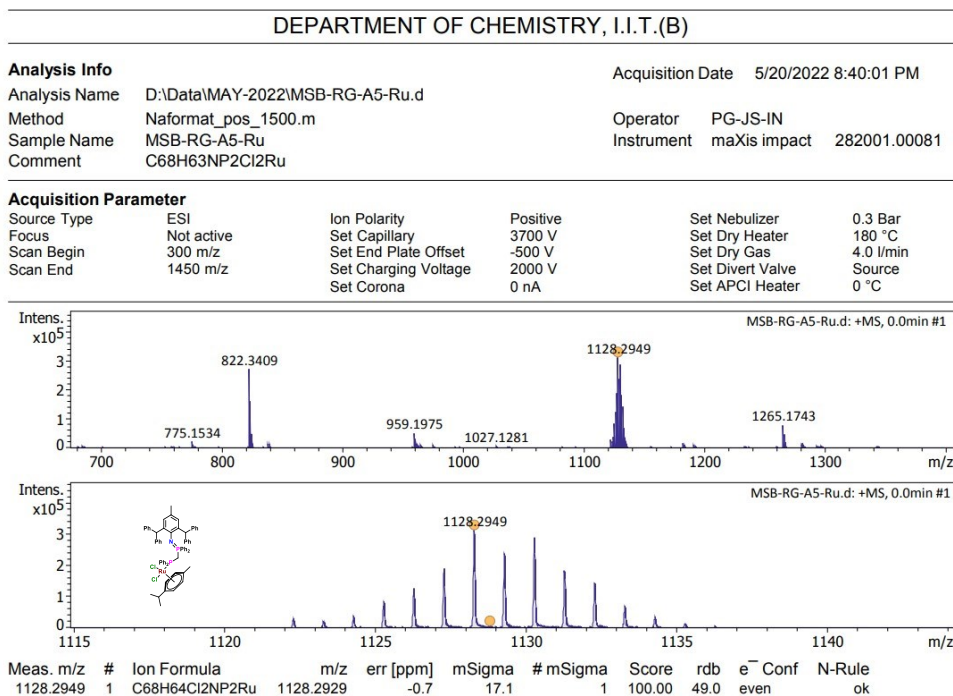


Figure S9. HRMS spectrum of **2**.

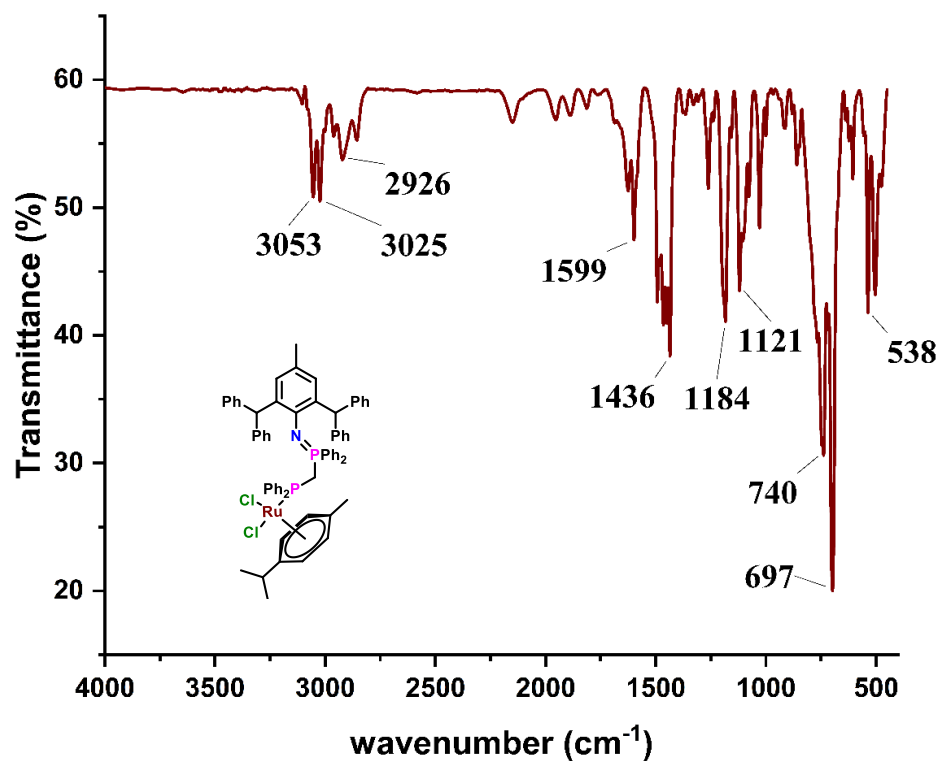


Figure S10. FT-IR spectrum of **2**.

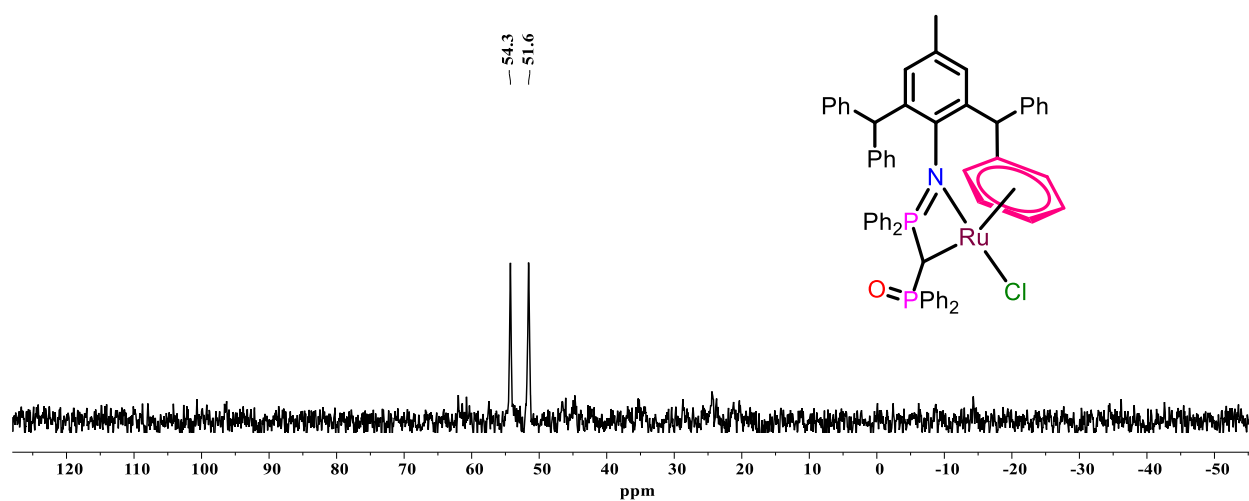


Figure S11. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** in CDCl_3 (162 MHz).

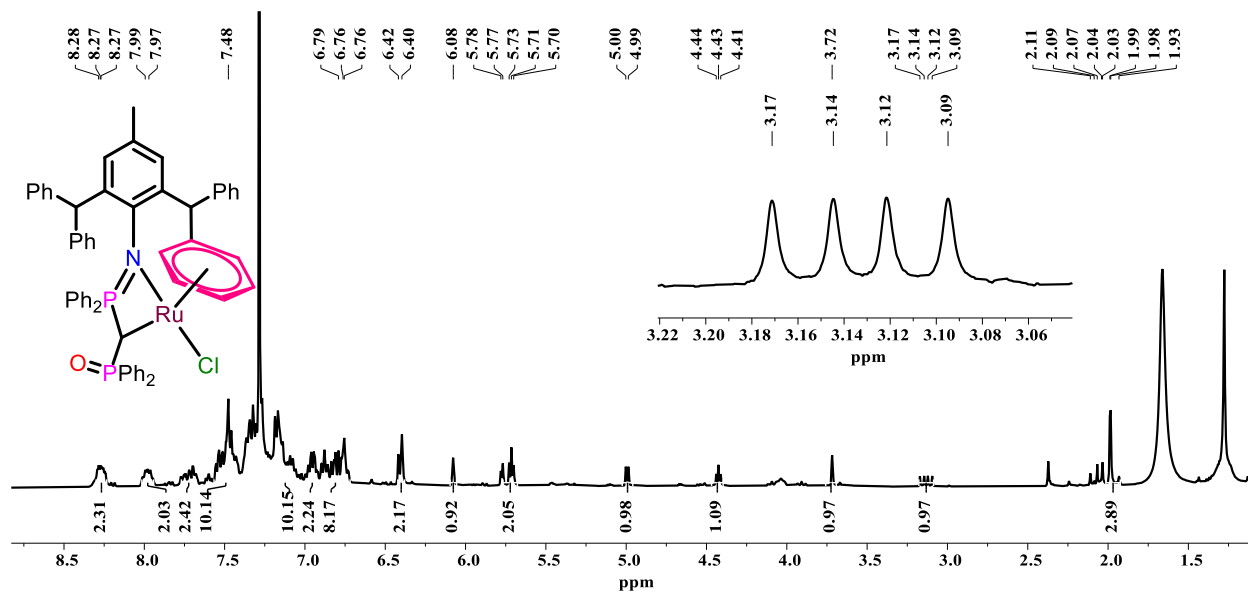


Figure S12. ^1H NMR spectrum of **2** in CDCl_3 (400 MHz).

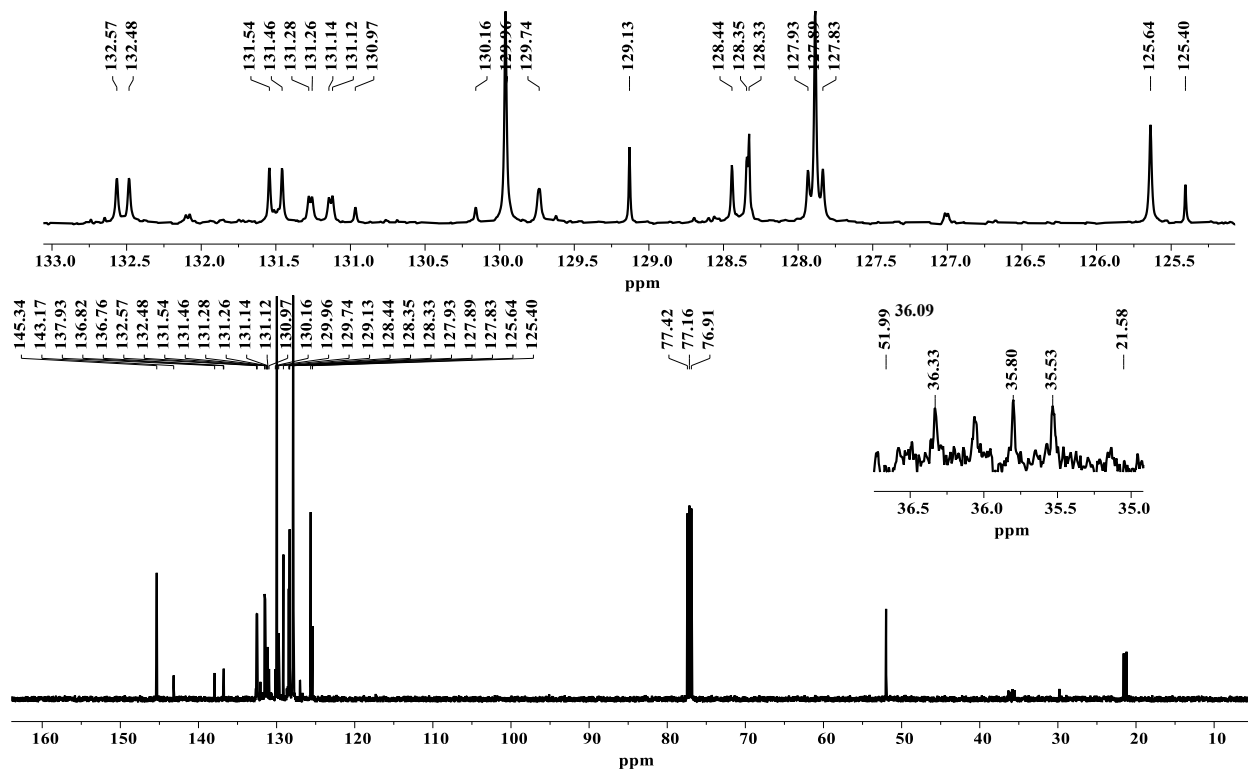


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** in CDCl_3 (126 MHz).

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Analysis Info

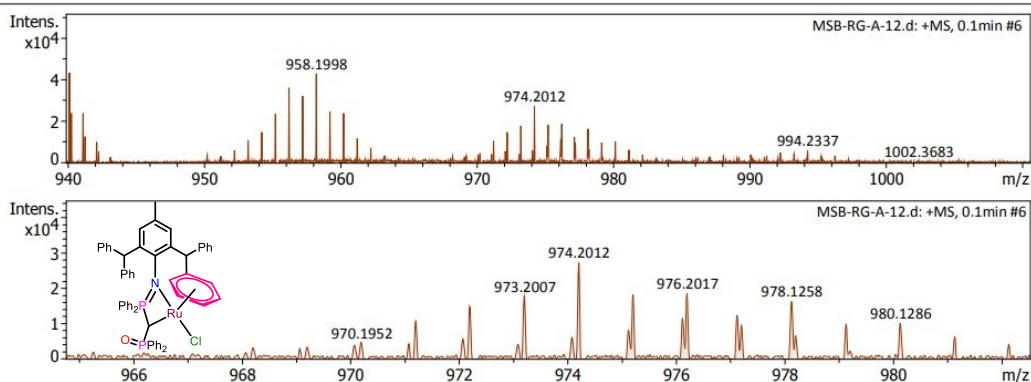
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Operator MSB-IN
 Instrument maXis impact 282001.00081

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Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
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Figure S14. HRMS spectrum of 3.

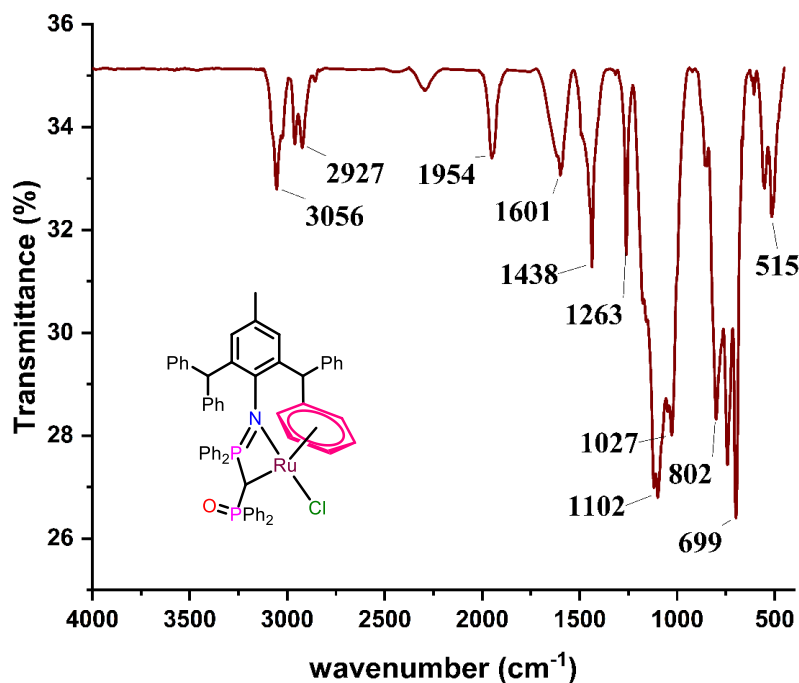


Figure S15. FT-IR spectrum of 3.

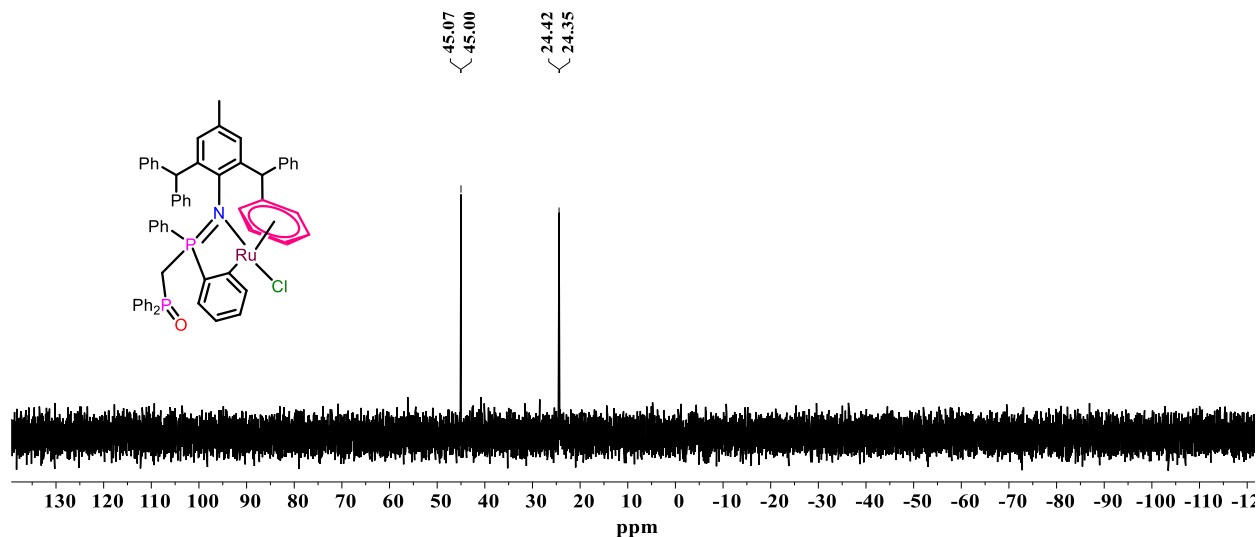


Figure S16. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** in CDCl_3 (202 MHz)

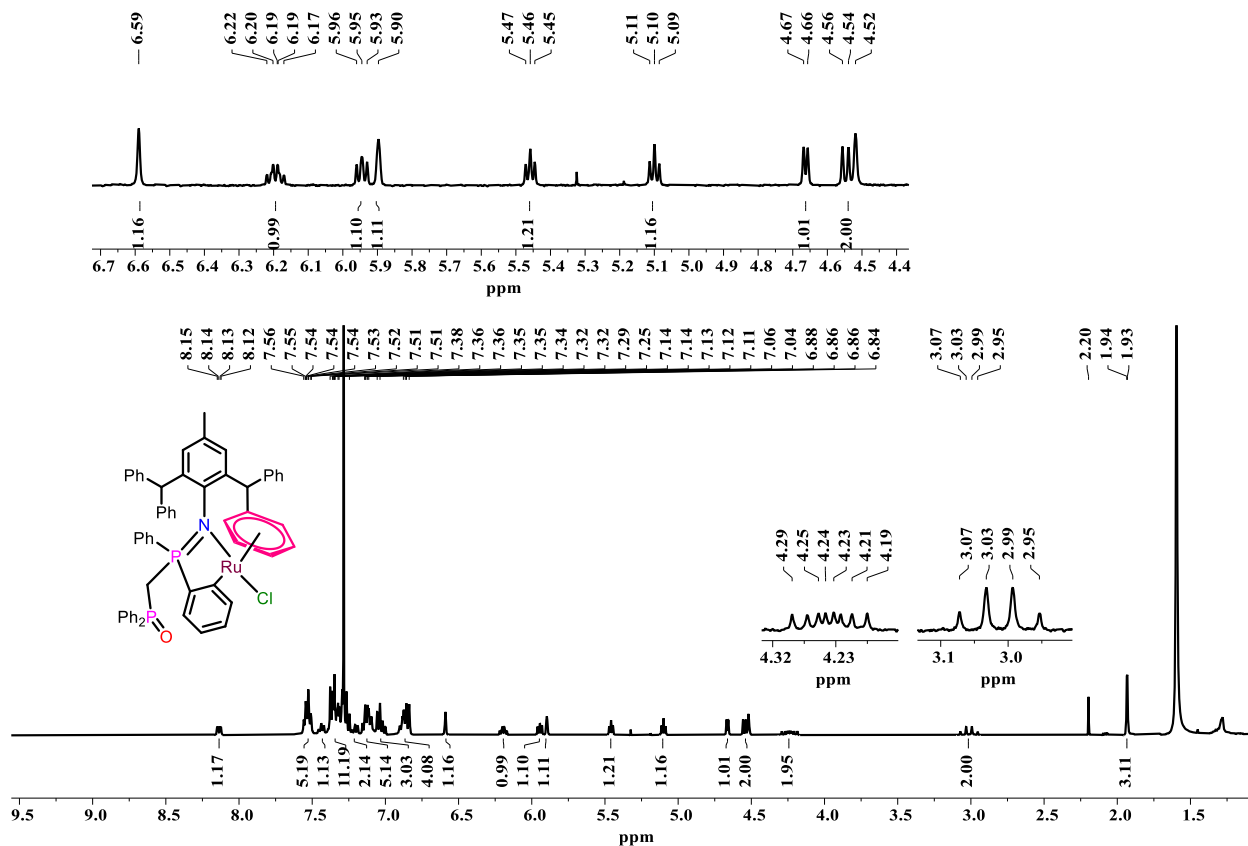


Figure S17. ^1H NMR spectrum of **4** in CDCl_3 (400 MHz).

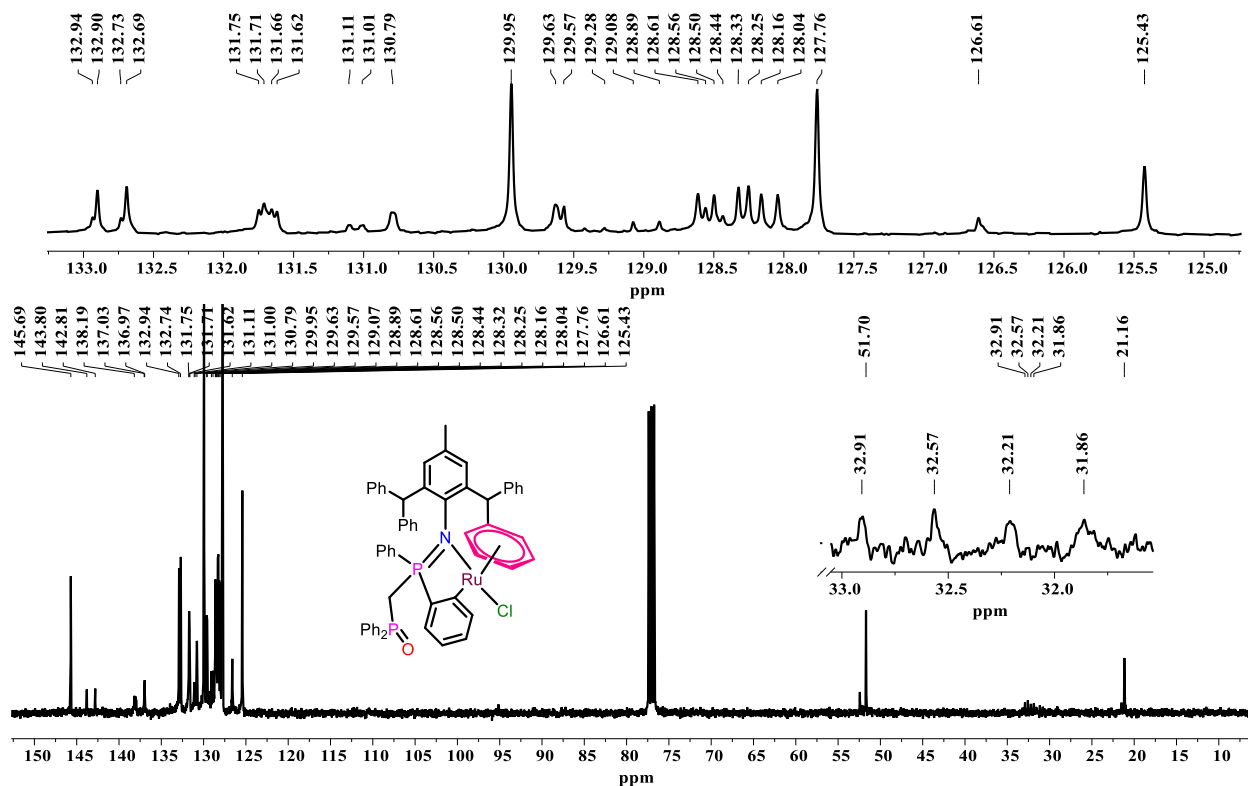


Figure S18. ^{13}C NMR spectrum of **4** in CDCl_3 (202 MHz).

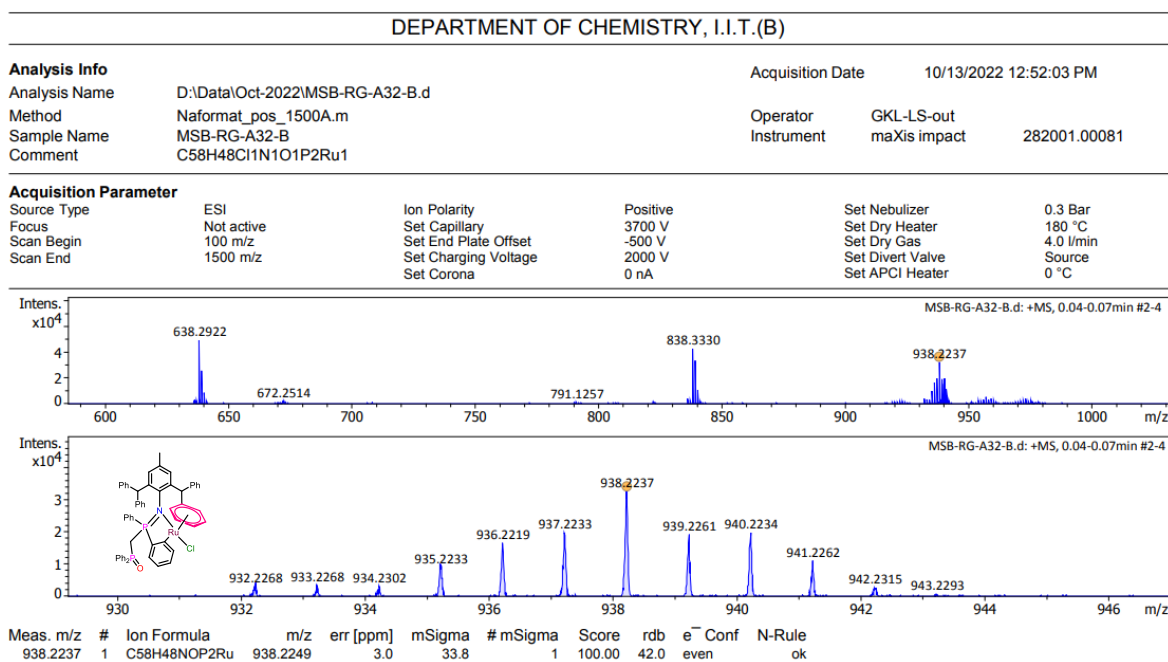


Figure S19. HRMS spectrum of **4**.

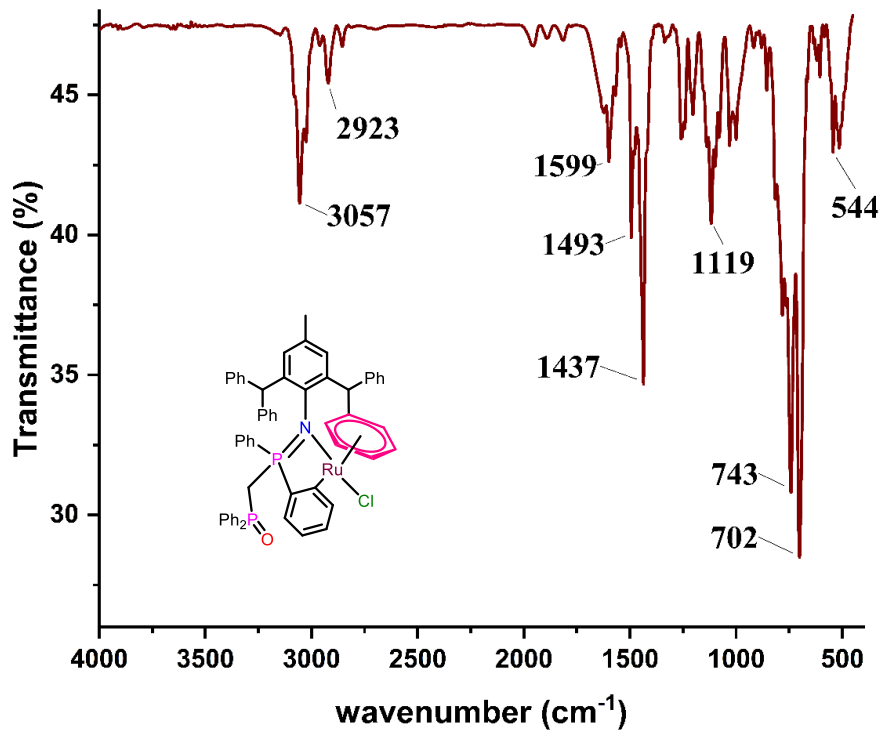


Figure S20. FT-IR spectrum of 4.

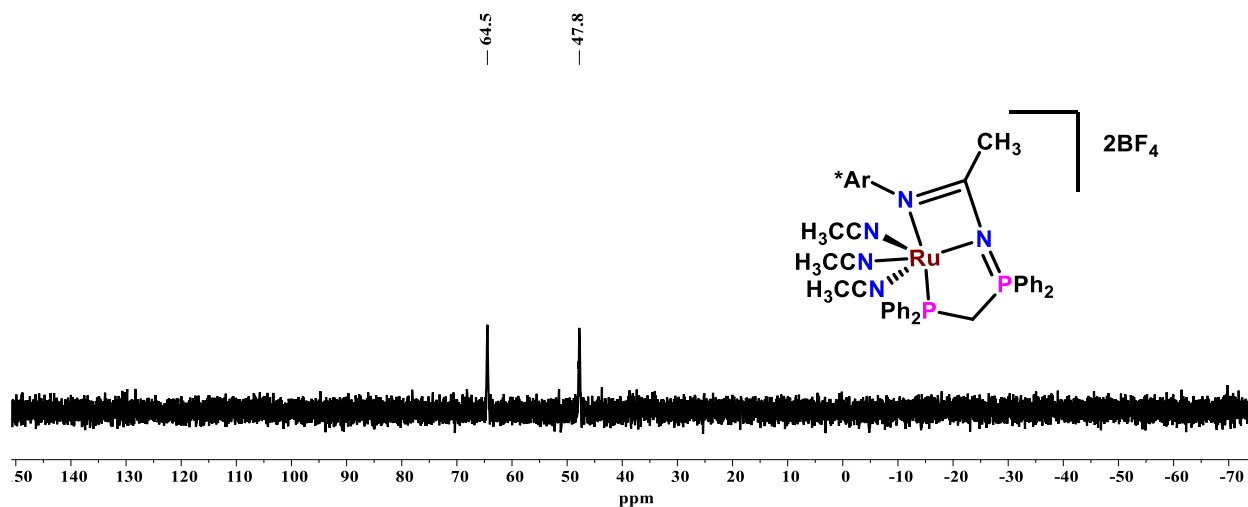


Figure S21. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 5 in CDCl_3 (162 MHz).

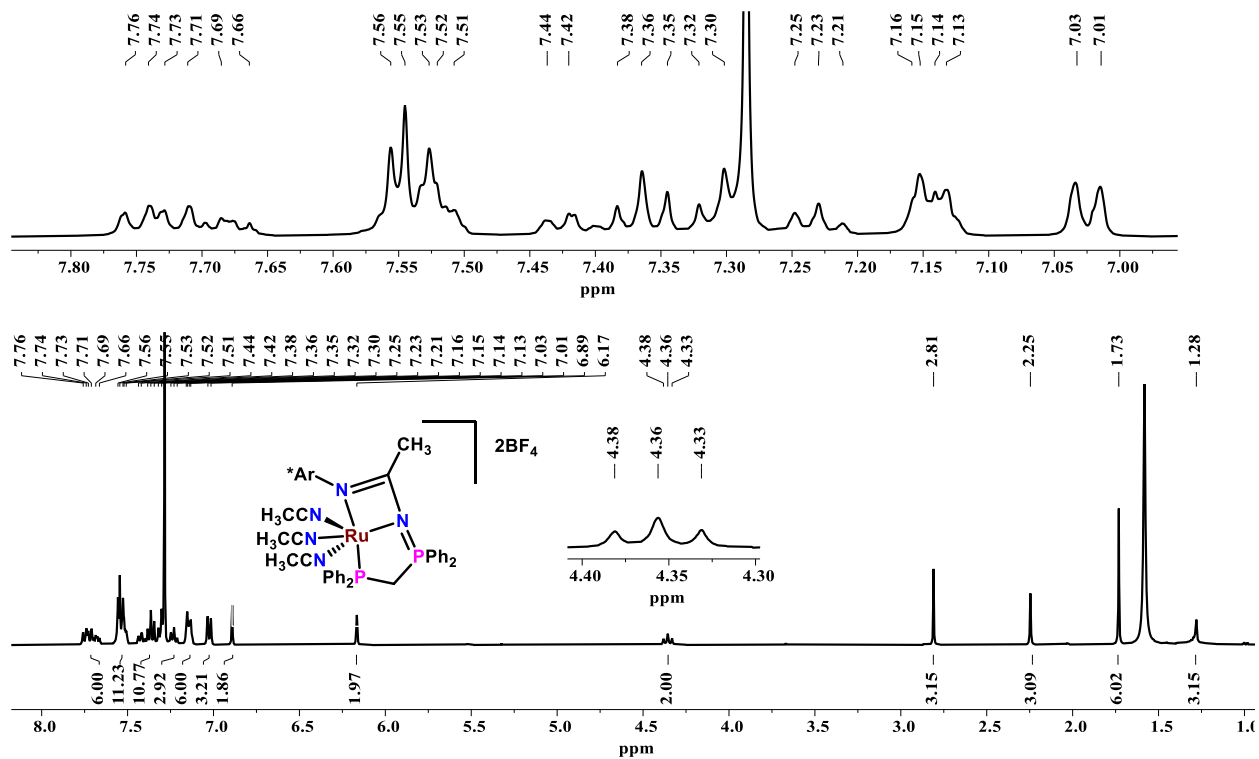


Figure S22. ^1H NMR spectrum of **5** in CDCl_3 (400 MHz).

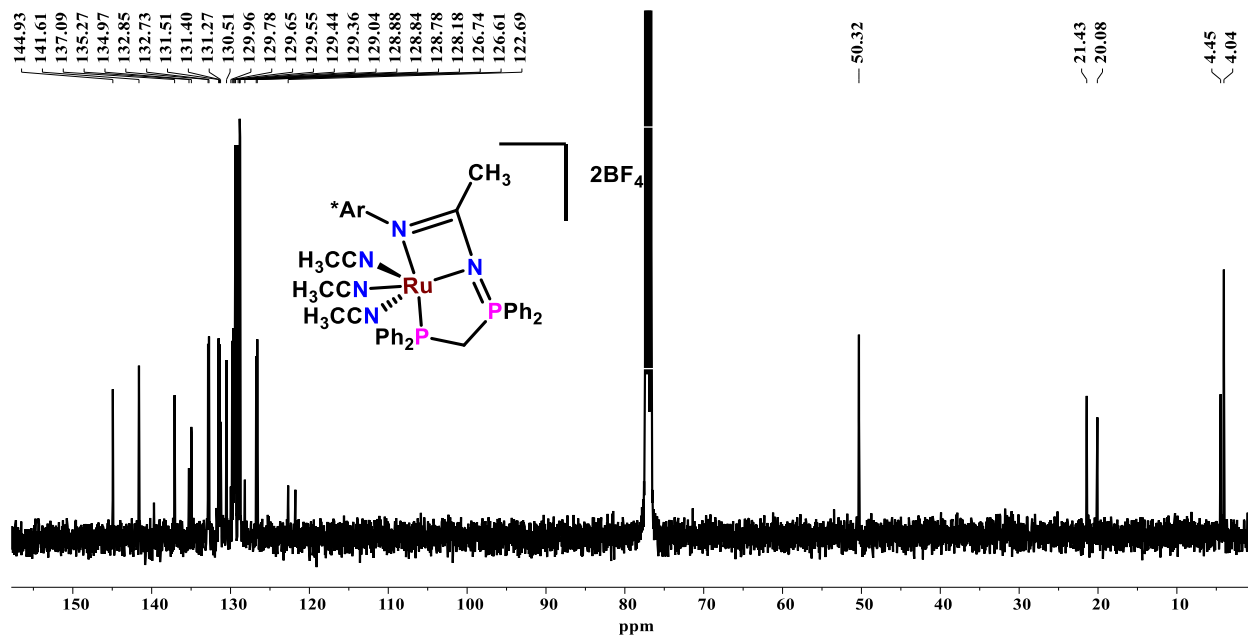


Figure S23. ^{13}C NMR spectrum of **5** in CDCl_3 (101 MHz).

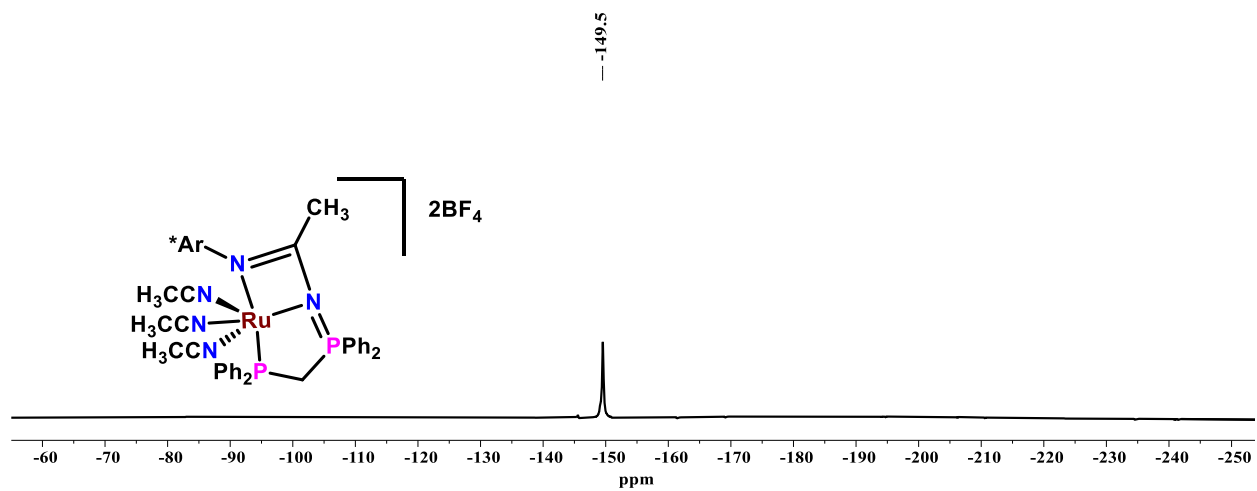


Figure S24. ^{19}F NMR spectrum of **5** in CDCl_3 (377 MHz).

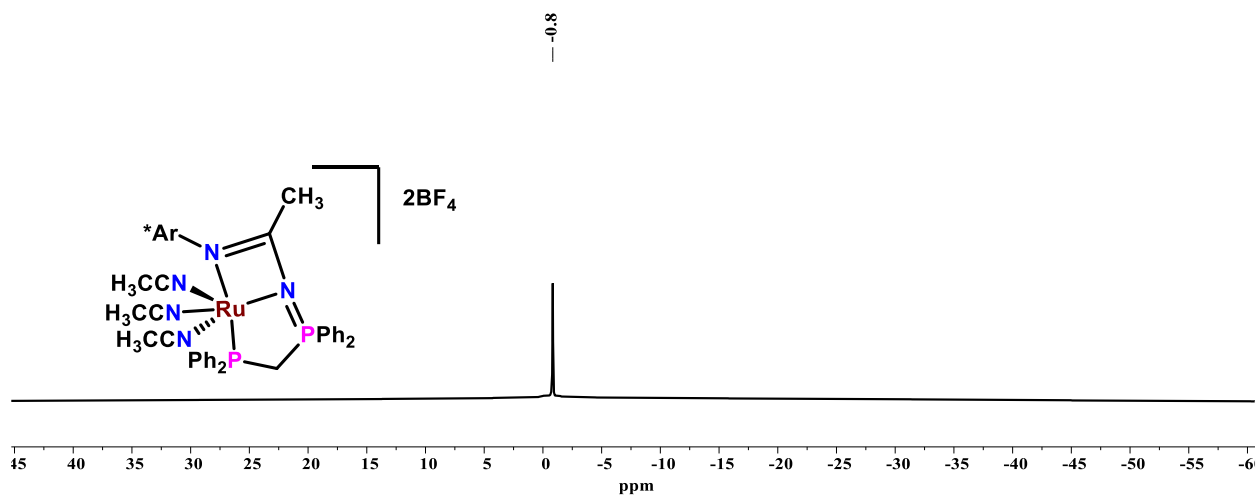


Figure S25. ^{11}B NMR spectrum of **5** in CDCl_3 (128 MHz).

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Analysis Info

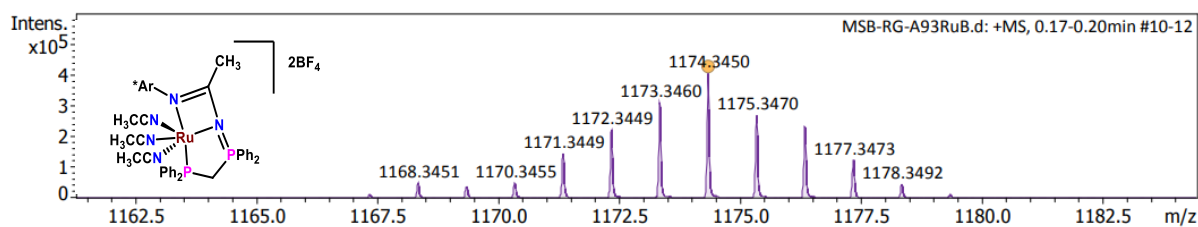
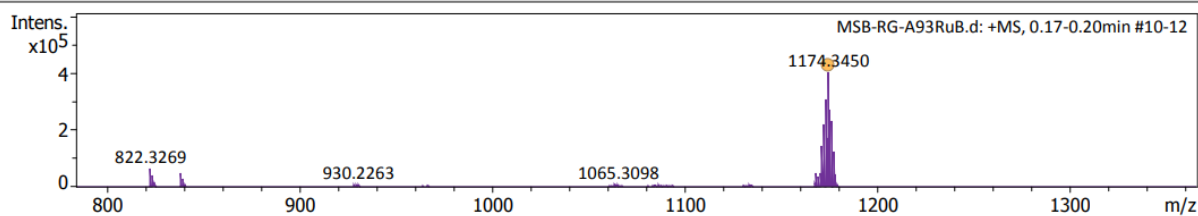
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Operator PG-JS-IN
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Acquisition Parameter

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		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
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Figure S26. HRMS spectrum of **5**.

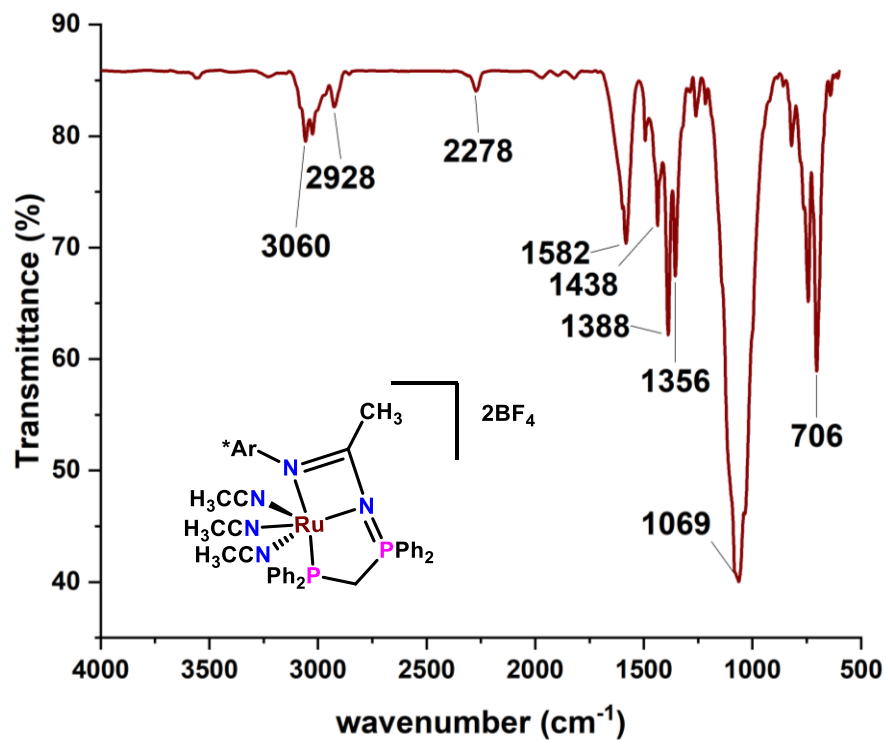


Figure S27. FT-IR spectrum of **5**.

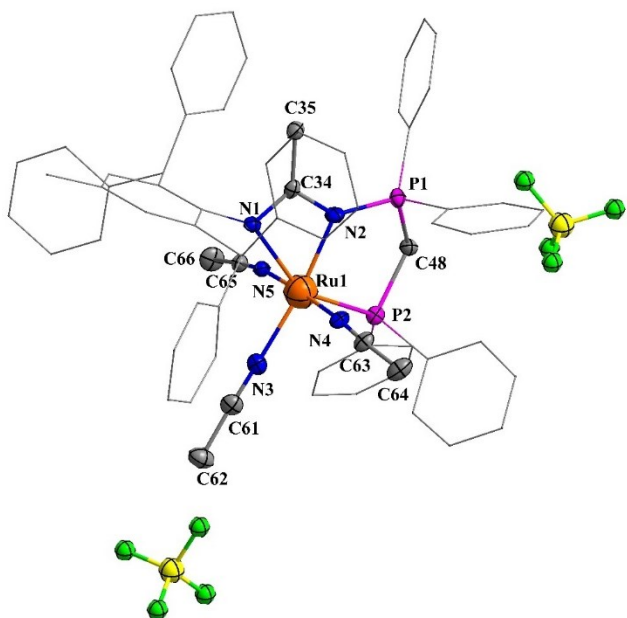


Figure S28. Molecular structure of **5**. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

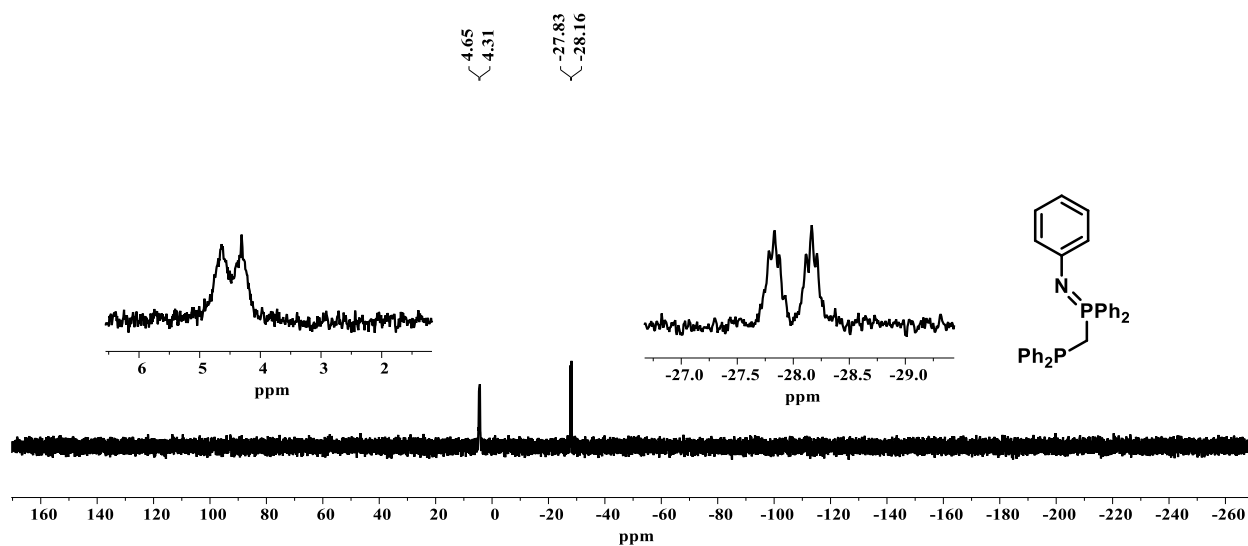


Figure S29. ³¹P{¹H} NMR spectrum of **6** in CDCl₃ (162 MHz) .

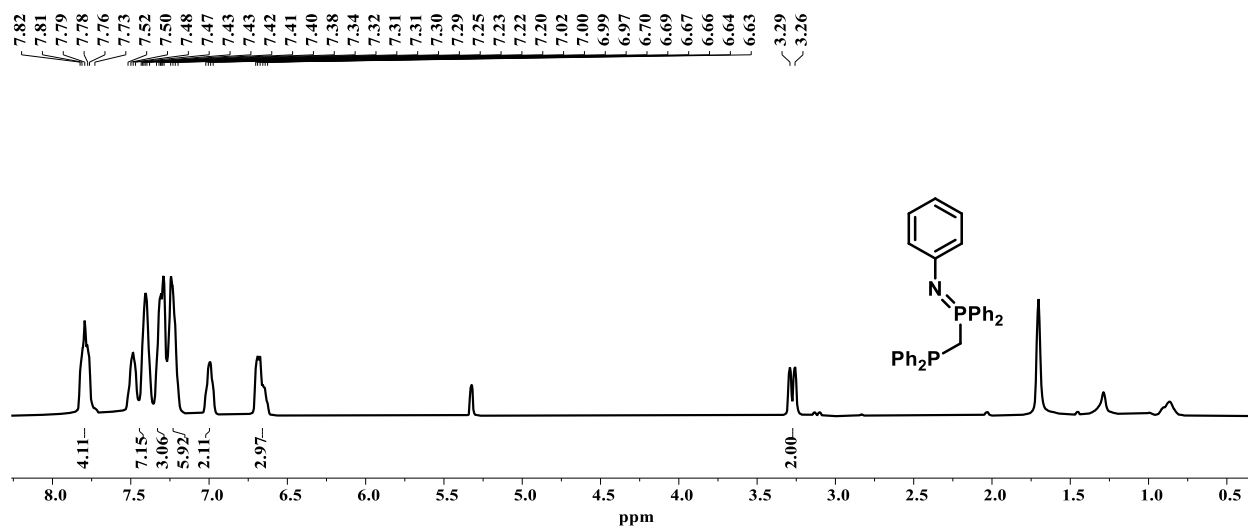


Figure S30. ¹H NMR spectrum of **6** in CDCl₃ (400 MHz).

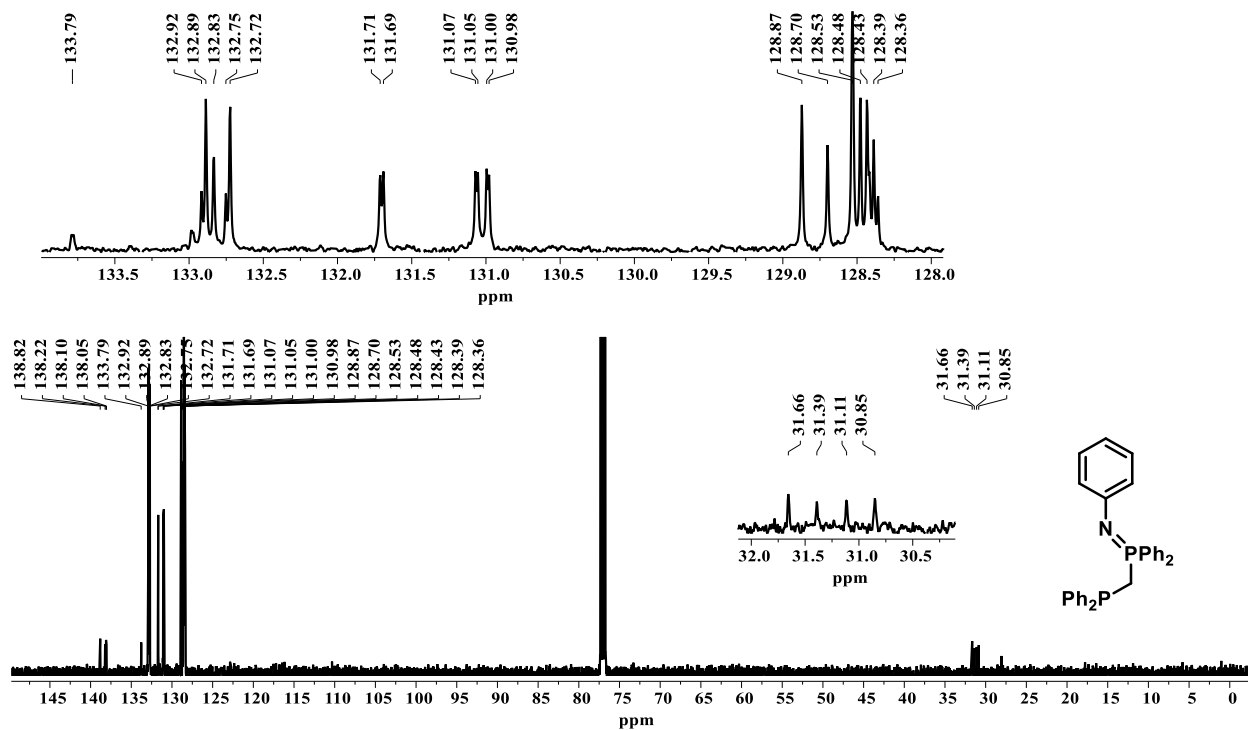


Figure S31. ¹³C NMR spectrum of **6** in CDCl₃ (126 MHz).

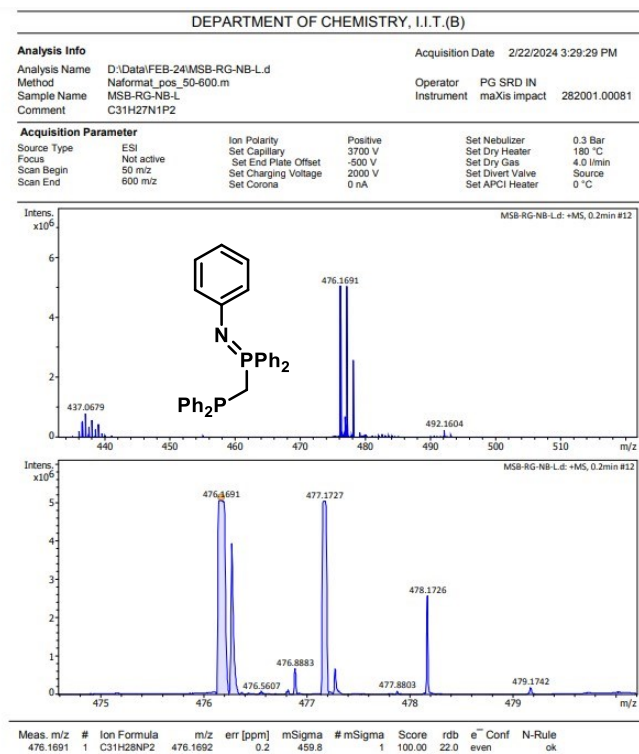


Figure S32. HRMS spectrum of **6**.

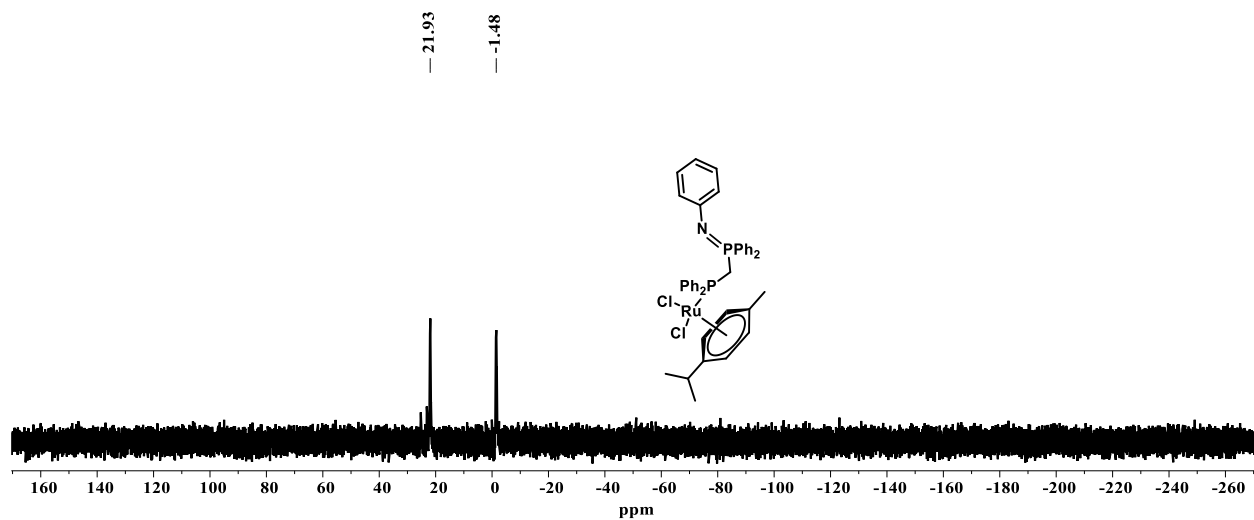


Figure S33. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 7 in CDCl_3 (162 MHz).

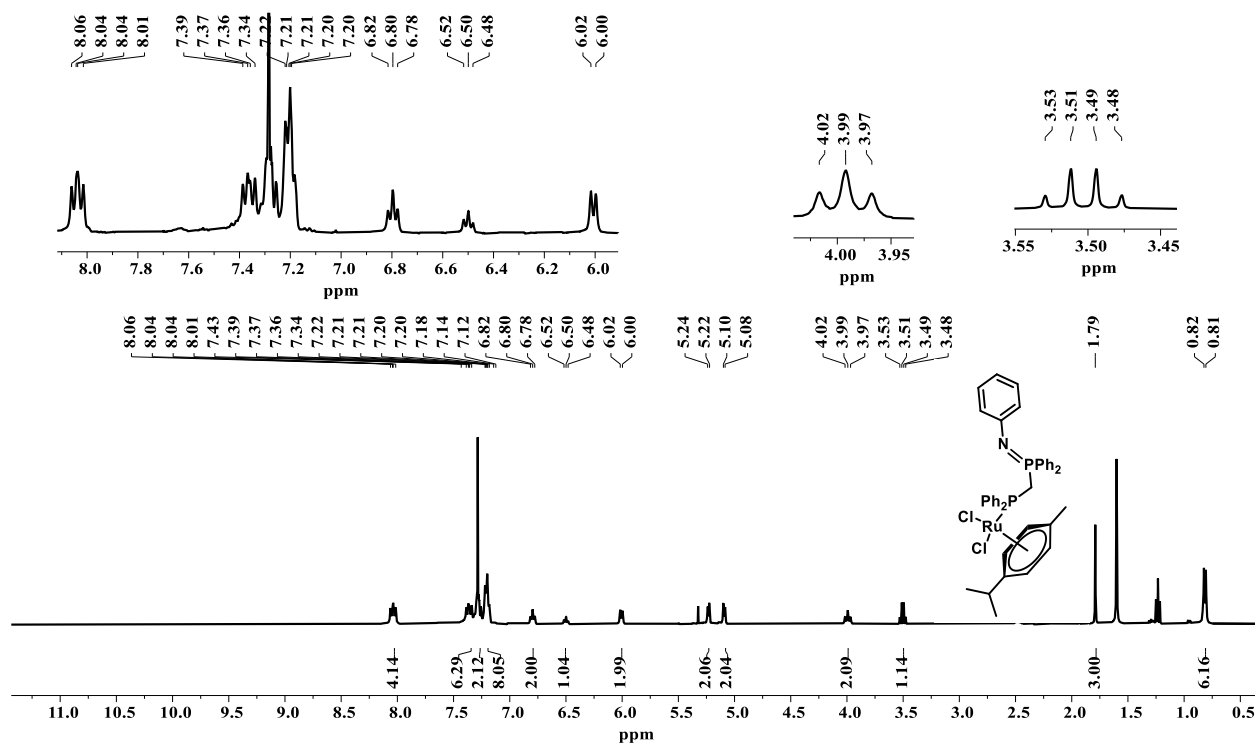


Figure S34. ^1H NMR spectrum of 7 in CDCl_3 (400 MHz).

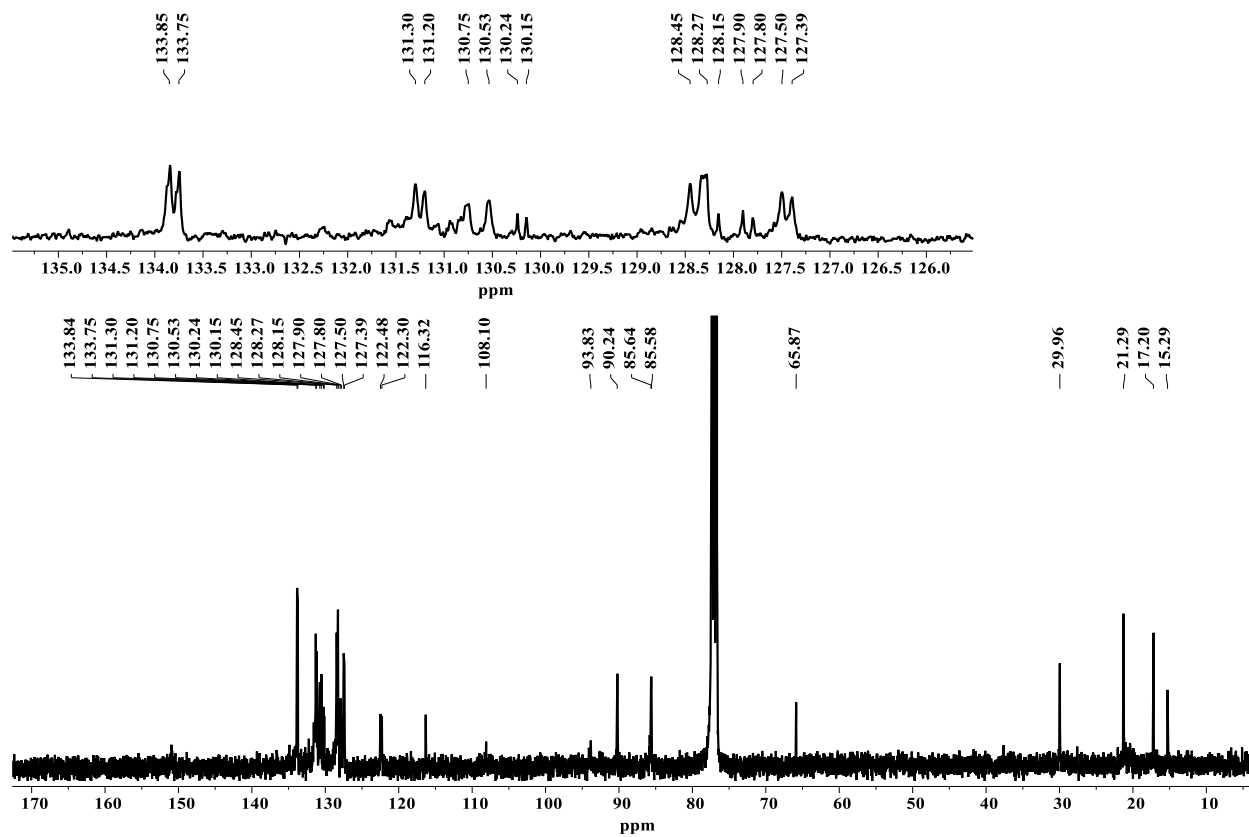


Figure S35. ^{13}C NMR spectrum of 7 in CDCl_3 (101 MHz).

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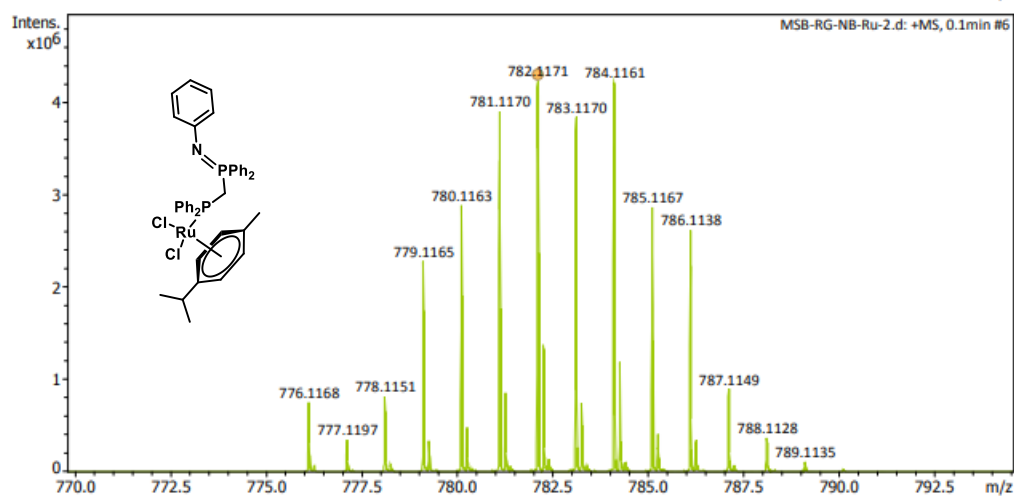
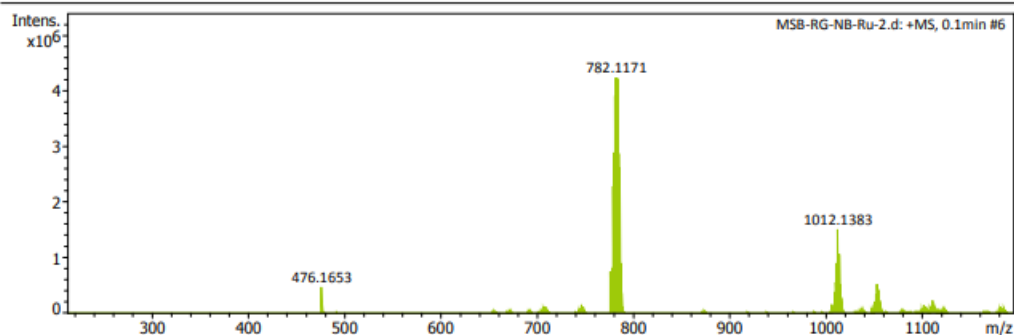
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		Set Corona	0 nA	Set APCI Heater	0 °C

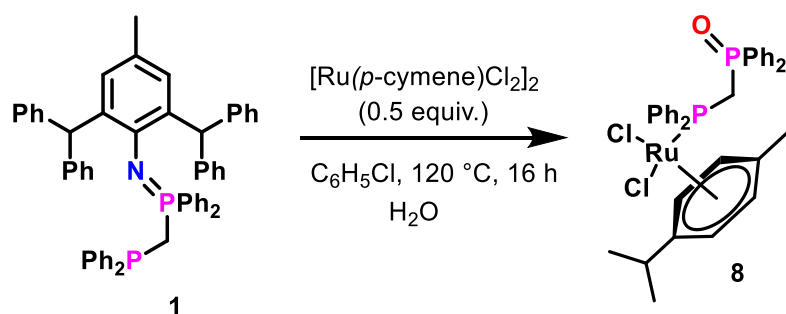


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
782.1171	1	C41H42Cl2NP2Ru	782.1208	5.3	188.0	1	100.00	33.0	even	ok

Figure S36. HRMS spectrum of 7.

Synthesis of $[\text{RuCl}_2\{(\eta^6\text{-}p\text{-cymene})(\text{PPh}_2\text{CH}_2\text{Ph}_2\text{P}=\text{O})\text{-}\kappa^1\text{-P}\}](\mathbf{8})$

The mixture of **1** (0.04 g, 0.04866 mmol) and $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (0.014 g, 0.02433 mmol) in chlorobenzene along with few drops of water was stirred at 120 °C for 16 h. The solution was allowed to cool to room temperature, the resulting reaction mixture was evaporated and washed with petroleum ether twice (2 x 15 ml) followed by vacuum evaporation which yielded compound **8**. ^{31}P NMR (162 MHz, CDCl_3) δ 24.98, 23.05. ^1H NMR (400 MHz, CDCl_3) δ 8.08 – 7.93 (m, 4H), 7.38 (dd, $J = 11.8, 8.4$ Hz, 4H), 7.19 (t, $J = 7.3$ Hz, 4H), 5.26 (d, $J = 8.0$ Hz, 2H), 5.11 (d, $J = 6.3$ Hz, 2H), 3.87 (dd, $J = 10.4, 9.2$ Hz, 2H), 2.49 (p, $J = 6.9$ Hz, 1H), 1.83 (s, 3H), 0.80 (d, $J = 7.0$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 134.93, 133.82 (d, $J = 9.7$ Hz), 131.58, 131.12, 130.87 (dd, $J = 10.2, 2.6$ Hz), 130.18 (d, $J = 9.3$ Hz), 128.20 (d, $J = 12.0$ Hz), 127.83 (d, $J = 10.3$ Hz), 108.27, 94.04, 90.17 (d, $J = 4.4$ Hz), 85.78 (d, $J = 6.1$ Hz), 30.01, 21.25, 17.28.



Scheme S1. Synthesis of complex **8**.

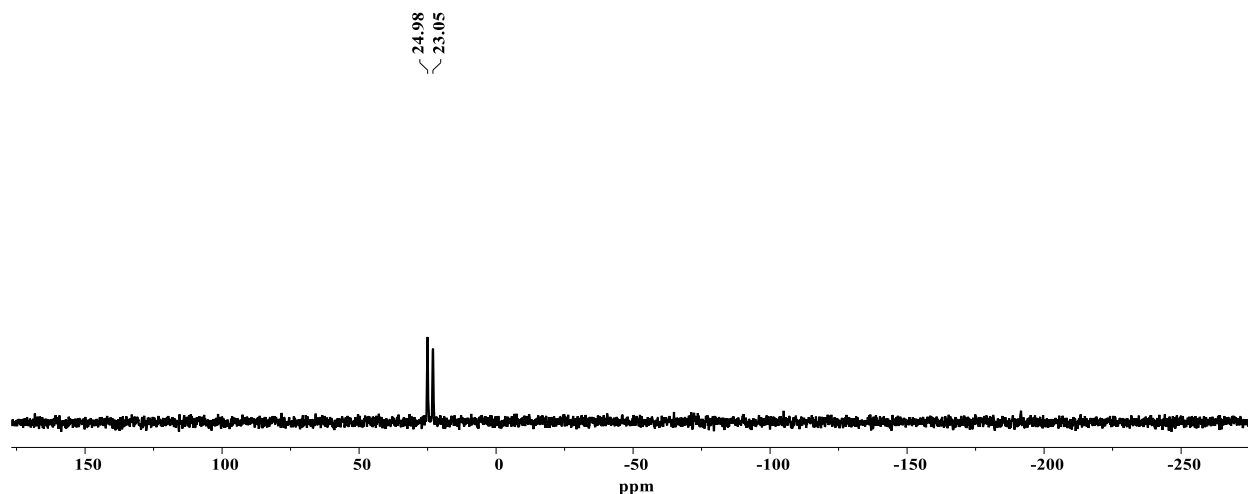


Figure S37. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** in CDCl_3 (162 MHz).

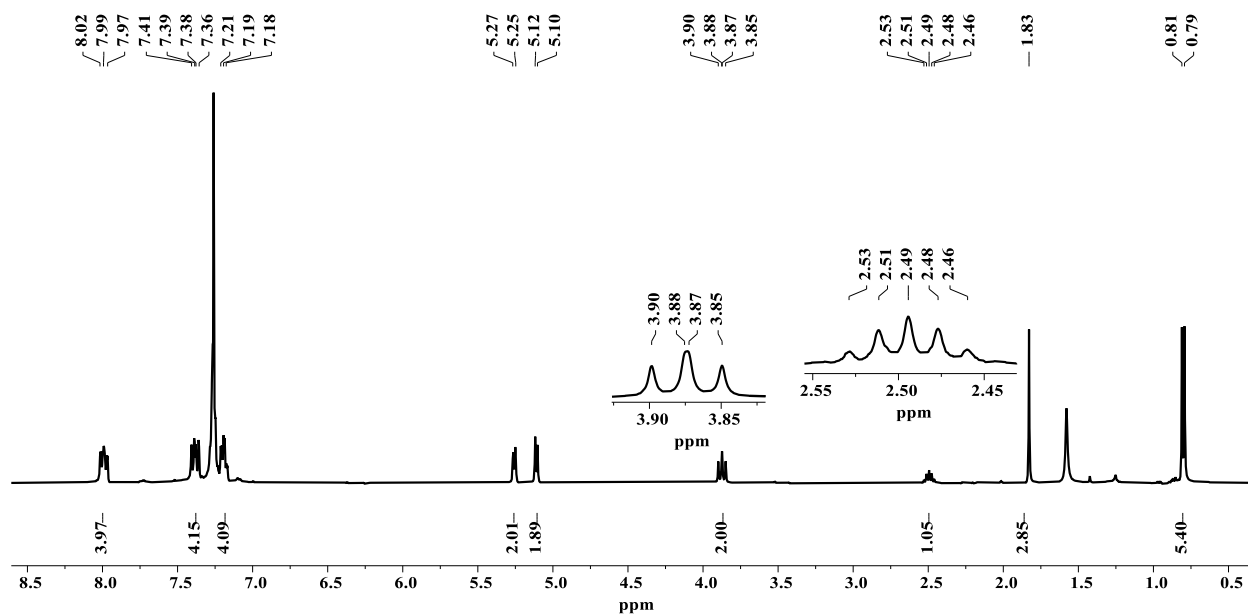


Figure S38. ^1H NMR spectrum of **8** in CDCl_3 (400 MHz).

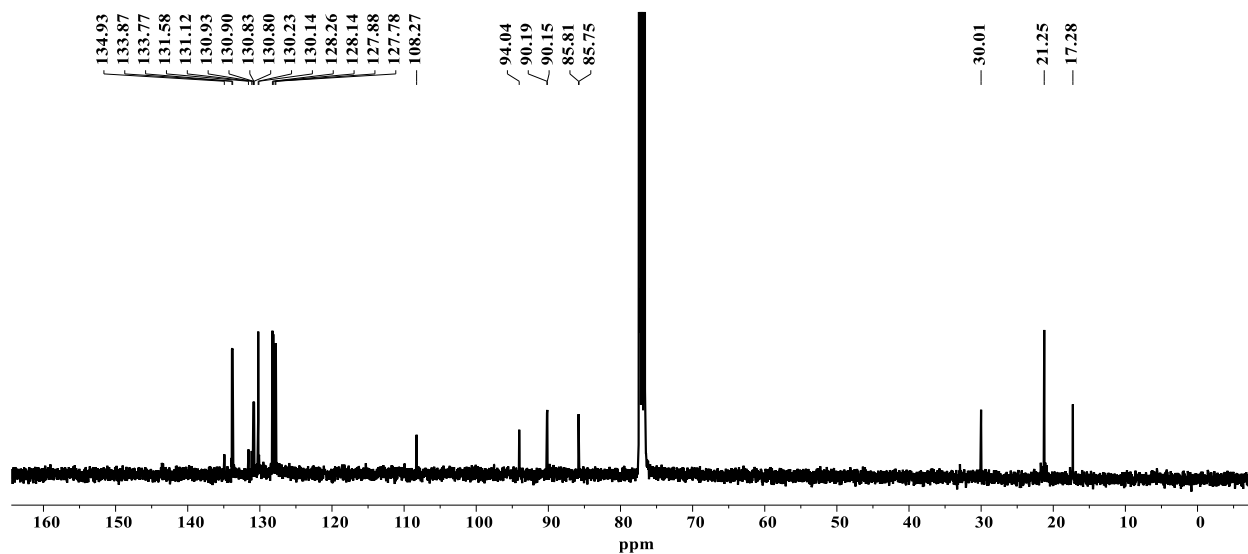
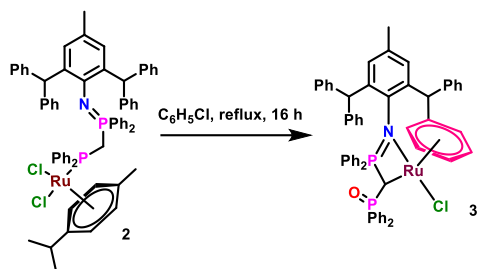


Figure S39. ^{13}C NMR spectrum of **8** in CDCl_3 (101 MHz).

Synthesis of complex 3 from 2



Scheme S2. Formation of complex 3 from 2.

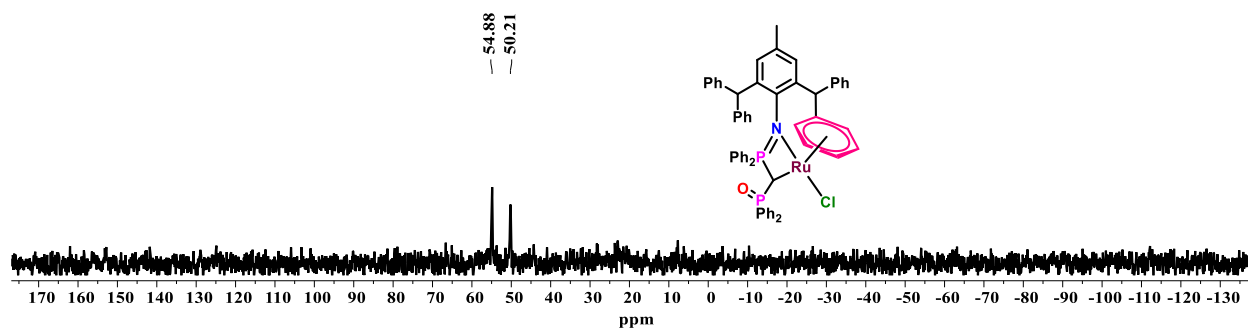
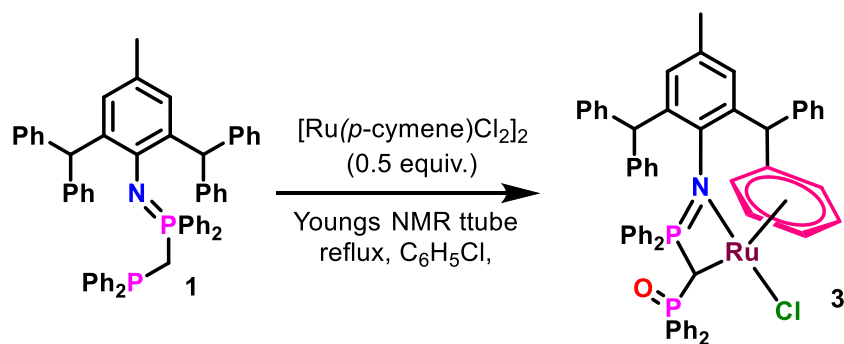


Figure S40. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 3 in CDCl_3 (162 MHz).

Formation of C-H activated Ru^{II} complex 3

The reaction of compound 1 (0.0121 mmol) with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (0.00609 mmol) in chlorobenzene was carried out in a J Youngs NMR tube. The progression of the reaction was monitored using ^{31}P NMR spectroscopy and mass spectrometry.



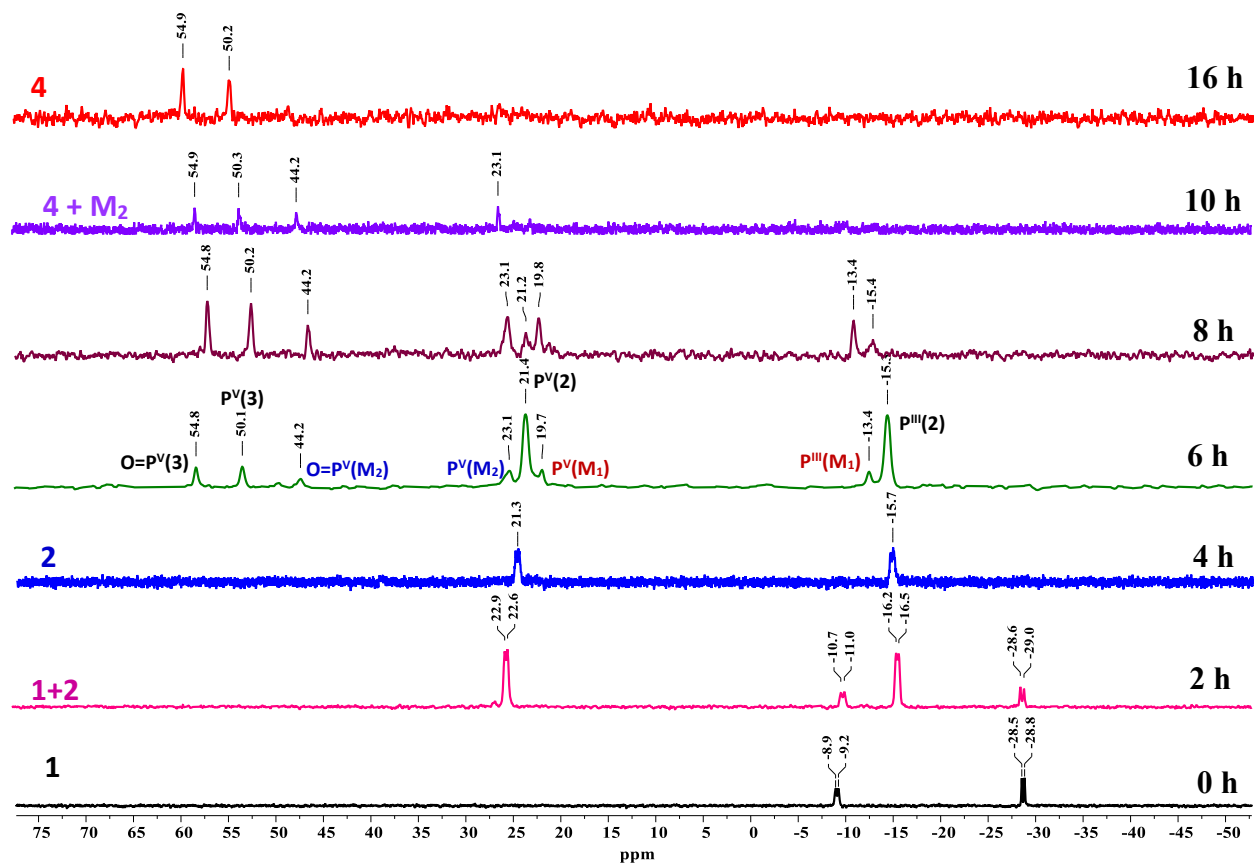
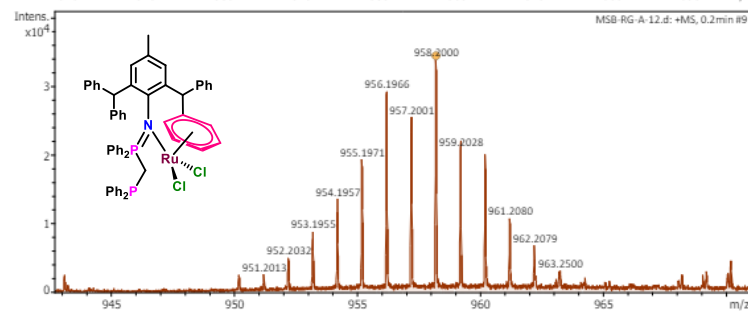
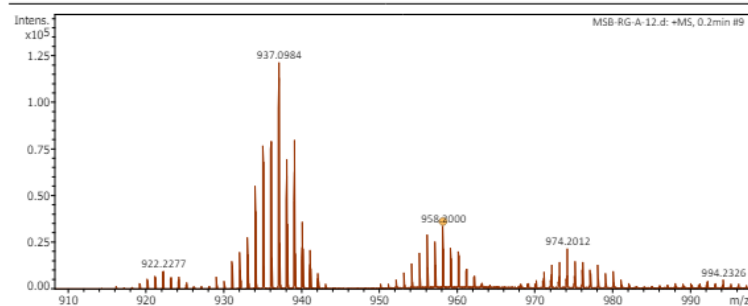


Figure S41. ^{31}P variable time NMR spectra for the formation of **3** in $\text{C}_6\text{H}_5\text{Cl}$.

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Analysis Info
 Analysis Name D:\Data\JULY-2022\MSB-RG-A-12.d Acquisition Date 7/19/2022 7:28:29 PM
 Method NaFormat_pos_1500.m Operator MSB-IN
 Sample Name MSB-RG-A-12 Instrument maXis impact 282001.00081
 Comment C58H48NP2O1Ru1Cl1

Acquisition Parameter
 Source Type ESI Ion Polarity Positive Set Nebulizer 0.3 Bar
 Set Capillary 3700 V Set Dry Heater 180 °C
 Focus Not active Set End Plate Offset -500 V Set Dry Gas 4.0 l/min
 Scan Begin 100 m/z Set Charging Voltage 2000 V Set Divert Valve Source
 Scan End 1500 m/z Set Corona 0 nA Set AP/CI Heater 0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
958.2000	1	C54H49ClNO3P2Ru	958.1914	-7.7	188.9	1	100.00	40.0	even	ok

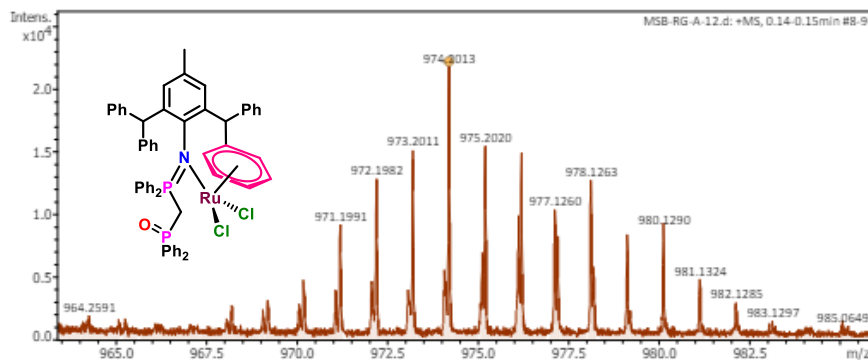
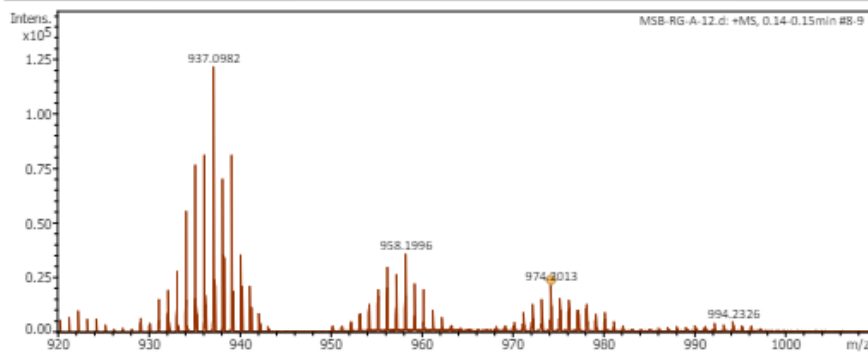
Figure S42. HRMS spectrum of **M₁**. (HRMS (ESI) of C₅₈H₄₉Cl₂NP₂Ru calc for [M-Cl]⁺ : 958.1914, Found: 958.2000.)

DEPARTMENT OF CHEMISTRY, I.I.T.(B)

Analysis Info Acquisition Date 7/19/2022 7:28:29 PM
 Analysis Name D:\Data\JULY-2022\MSB-RG-A-12.d
 Method Naformat_pos_1500.m Operator MSB-IN
 Sample Name MSB-RG-A-12 Instrument maXis impact 282001.00081
 Comment C58H48NP2O1Ru1Cl1

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
974.2013	1	C ₅₈ H ₄₉ Cl ₂ INOP ₂ Ru	974.2016	1.6	78.0	1	100.00	44.0	even	ok

MSB-RG-A-12.d

Bruker Compass DataAnalysis 5.1

printed: 5/6/2024 4:03:35 PM

by: iitb

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Figure S43. HRMS spectrum of **M₂**. (HRMS (ESI) of C₅₈H₄₉Cl₂NOP₂Ru calc for [M-Cl]⁺ : 974.2016, Found: 974.2013.)

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Analysis Info
Analysis Name D:\Data\OCT-2023\MSB-RG-RU-I-1.d Acquisition Date 10/5/2023 12:08:44 PM
Method NaICsl_pos_2000.m Operator SJG-OUT
Sample Name MSB-RG-RU-I-1 Instrument maXis impact 282001.00081
Comment HRMS

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.5 l/min
Scan End	2000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

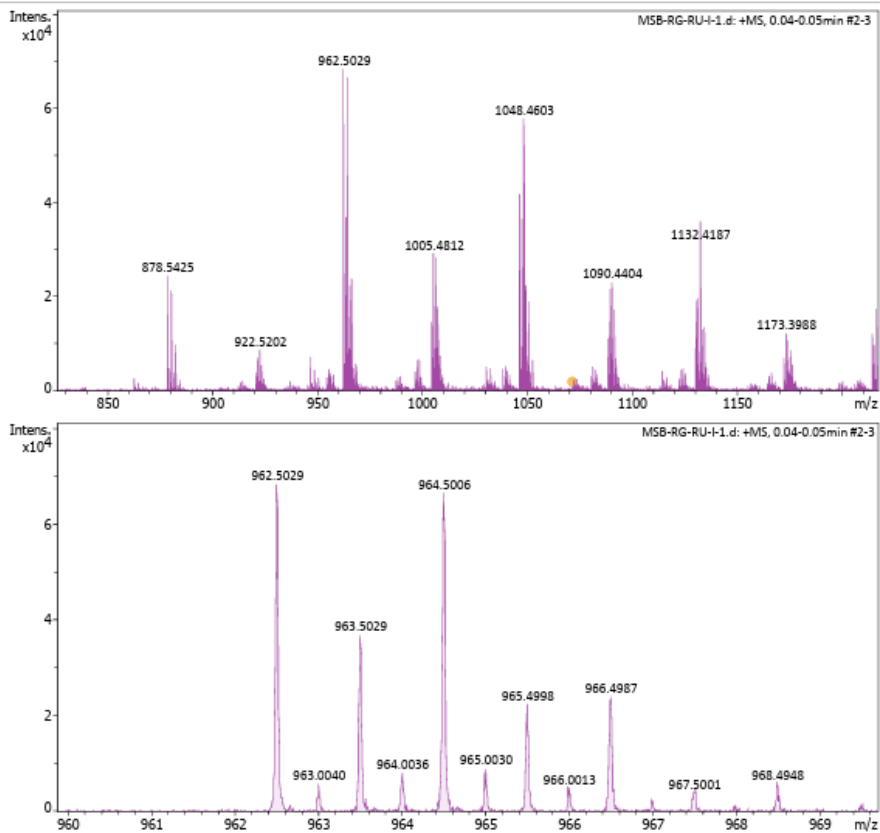
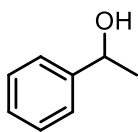
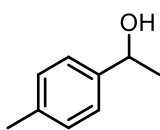


Figure S44. LRMS spectrum of intermediate **B** of transfer hydrogenation reaction.

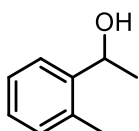
NMR spectral data of catalytic products



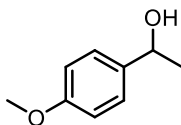
1-phenylethan-1-ol (**a1**). The compound was isolated as a colorless liquid. Yield: 97%. ^1H NMR (500 MHz, CDCl_3) δ 7.68 – 6.84 (m, 1H), 4.86 (q, J = 6.5 Hz, 1H), 3.19 – 2.97 (d, J = 5.7 Hz, 1H), 1.51 (d, J = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 145.99, 128.48, 127.39, 125.52, 70.23, 25.20.



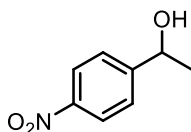
1-(p-tolyl)ethan-1-ol (**a2**). The compound was isolated as a colorless liquid. Yield: 95%. ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.16 (m, 4H), 4.90 – 4.80 (m, 1H), 3.20 – 3.13 (m, 1H), 2.43 (s, 3H), 1.50 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.10, 136.96, 129.15, 125.51, 70.07, 25.17, 21.17.



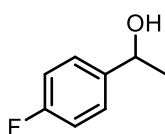
1-(o-tolyl)ethan-1-ol (**a3**). The compound was isolated as a colorless liquid. Yield: 94%. ^1H NMR (400 MHz, CDCl_3) δ 7.51 (dd, J = 7.7, 1.5 Hz, 1H), 7.27 – 7.09 (m, 3H), 5.12 (q, J = 6.4 Hz, 1H), 2.35 (s, 3H), 2.01 (s, 1H), 1.46 (d, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.87, 130.38, 127.18, 126.39, 124.50, 66.80, 23.94, 18.93.



1-(4-methoxyphenyl)ethan-1-ol (**a4**). The compound was isolated as a colorless liquid. Yield: 89%. ^1H NMR (500 MHz, CDCl_3) δ 7.28 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 4.82 (t, J = 6.5 Hz, 1H), 3.80 (s, 3H), 2.72 (s, 1H), 1.46 (d, J = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 158.85, 138.16, 126.71, 113.80, 69.79, 55.27, 25.05.

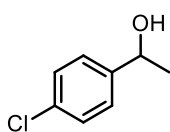


1-(4-nitrophenyl)ethan-1-ol (**a5**). The compound was isolated as a colorless liquid. Yield: 93%. ^1H NMR (500 MHz, CDCl_3) δ 8.13 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 4.99 (q, J = 6.7 Hz, 1H), 2.97 (s, 1H), 1.48 (d, J = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 153.37, 146.98, 126.16, 123.67, 69.37, 25.38.

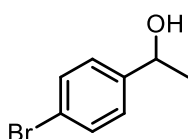


1-(4-fluorophenyl)ethan-1-ol (**a6**). The compound was isolated as a colorless liquid. Yield: 92%. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (ddd, J = 8.9, 5.4, 0.6 Hz, 2H), 7.02 (t, J = 8.8 Hz, 2H), 4.84 (qd, J = 6.3, 2.3 Hz, 1H), 2.68 (d, J = 3.1 Hz, 1H), 1.45 (d, J = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ

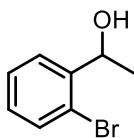
163.29, 160.86, 141.57, 141.54, 127.11, 127.02, 115.30, 115.09, 69.65, 25.22.



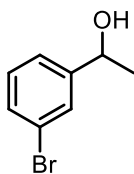
1-(4-chlorophenyl)ethan-1-ol (**a7**). The compound was isolated as a yellowish liquid. Yield: 90%. ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, $J = 10.7$ Hz, 4H), 4.79 (q, $J = 4.7$ Hz, 1H), 3.03 – 2.98 (m, 1H), 1.42 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.29, 132.95, 128.54, 126.84, 69.57, 25.20.



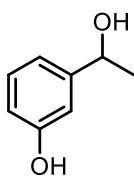
1-(4-bromophenyl)ethan-1-ol (**a8**). The compound was isolated as a yellow liquid. Yield: 89%. ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.41 (m, 2H), 7.28 – 7.18 (m, 2H), 4.83 (d, $J = 6.4$ Hz, 1H), 2.22 (s, 1H), 1.45 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.77, 131.55, 127.18, 121.15, 69.75, 25.24.



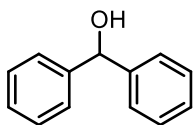
1-(2-bromophenyl)ethan-1-ol (**a9**). The compound was isolated as a white solid. Yield: 87%. ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 2.0$ Hz, 1H), 7.37 (dt, $J = 7.8, 1.6$ Hz, 1H), 7.24 (d, $J = 7.7$ Hz, 2H), 4.79 (d, $J = 6.5$ Hz, 1H), 2.64 (s, 1H), 1.43 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.14, 130.43, 130.11, 128.57, 124.06, 122.58, 69.66, 25.22.



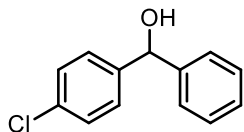
1-(3-bromophenyl)ethan-1-ol (**a10**). The compound was isolated as a yellowish liquid. Yield: 88%. ^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.45 (m, 2H), 7.31 (td, $J = 7.6, 1.3$ Hz, 1H), 7.10 (td, $J = 7.7, 1.8$ Hz, 1H), 5.20 (q, $J = 6.4$ Hz, 1H), 2.73 (d, $J = 12.2$ Hz, 1H), 1.44 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.68, 132.63, 128.74, 127.87, 126.71, 121.67, 69.13, 23.61.



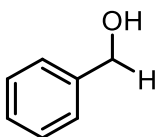
1-(1-hydroxyethyl)phenol (**a11**). The compound was isolated as a colorless liquid. Yield: 91%. ^1H NMR (400 MHz, DMSO) δ 9.24 (s, 1H), 7.05 (t, $J = 7.8$ Hz, 1H), 6.76 – 6.67 (m, 2H), 6.60 – 6.53 (m, 1H), 5.05 (d, $J = 4.2$ Hz, 1H), 4.59 (dd, $J = 6.5, 4.2$ Hz, 1H), 1.25 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 157.59, 149.46, 129.35, 116.41, 113.81, 112.61, 68.47, 26.40.



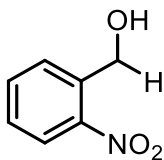
Diphenylmethanol (**a12**). The compound was isolated as a white solid. Yield: 88%. ^1H NMR (500 MHz, CDCl_3) δ 7.61 – 6.95 (m, 10H), 5.88 (d, J = 3.3 Hz, 1H), 2.34 (d, J = 3.6 Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.83, 128.53, 127.60, 126.57, 76.28.



(4-chlorophenyl)(phenyl)methanol (**a13**). The compound was isolated as a colorless liquid. Yield: 86%. ^1H NMR (500 MHz, CDCl_3) δ 7.46 – 7.24 (m, 9H), 5.77 (s, 1H), 2.80 (d, J = 12.2 Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.46, 142.27, 133.26, 131.56, 130.03, 128.70, 128.67, 128.62, 128.48, 127.95, 127.87, 126.58, 75.57.



Phenylmethanol (**a14**). The compound was isolated as a colorless liquid. Yield: 89%. ^1H NMR (400 MHz, CDCl_3) δ 7.37 (s, 5H), 4.64 (s, 2H), 2.94 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.92, 128.55, 127.60, 127.06, 65.08, 65.05.



(2-nitrophenyl)methanol (**a15**). The compound was isolated as a white solid. Yield: 90%. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (dd, J = 8.2, 1.3 Hz, 1H), 7.78 – 7.63 (m, 2H), 7.48 (ddd, J = 8.7, 7.4, 1.6 Hz, 1H), 4.98 (s, 2H), 2.59 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.78, 134.17, 130.02, 128.54, 125.05, 62.58.

NMR spectra of substrates

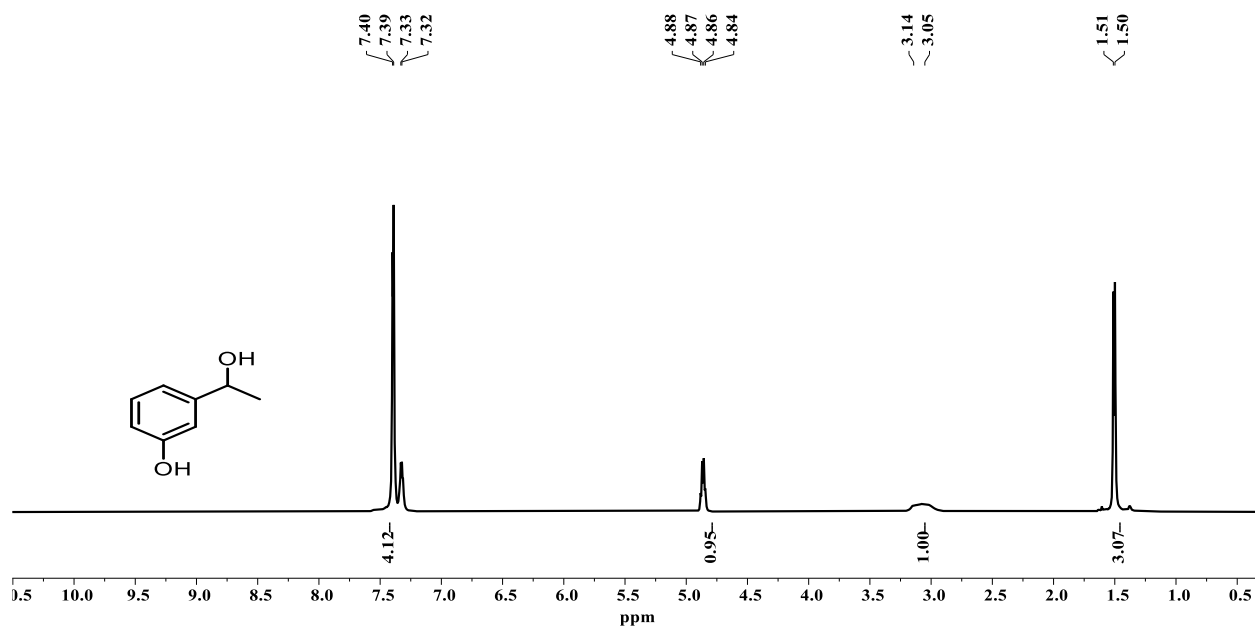


Figure S45. ^1H NMR spectrum of **a1** in CDCl_3 (500 MHz).

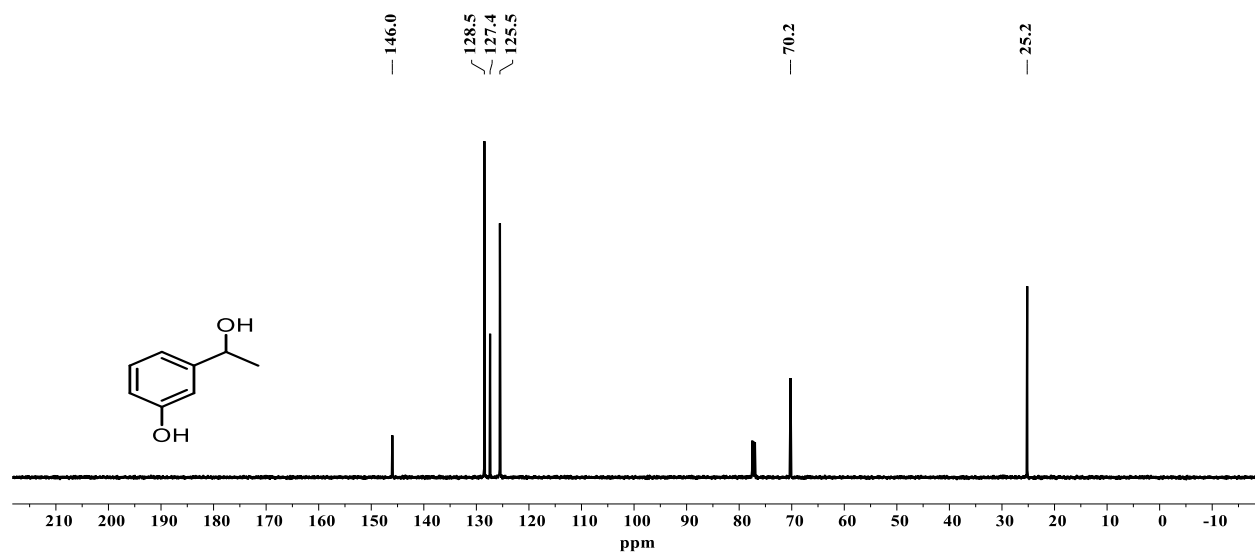


Figure S46. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a1** in CDCl_3 (126 MHz).

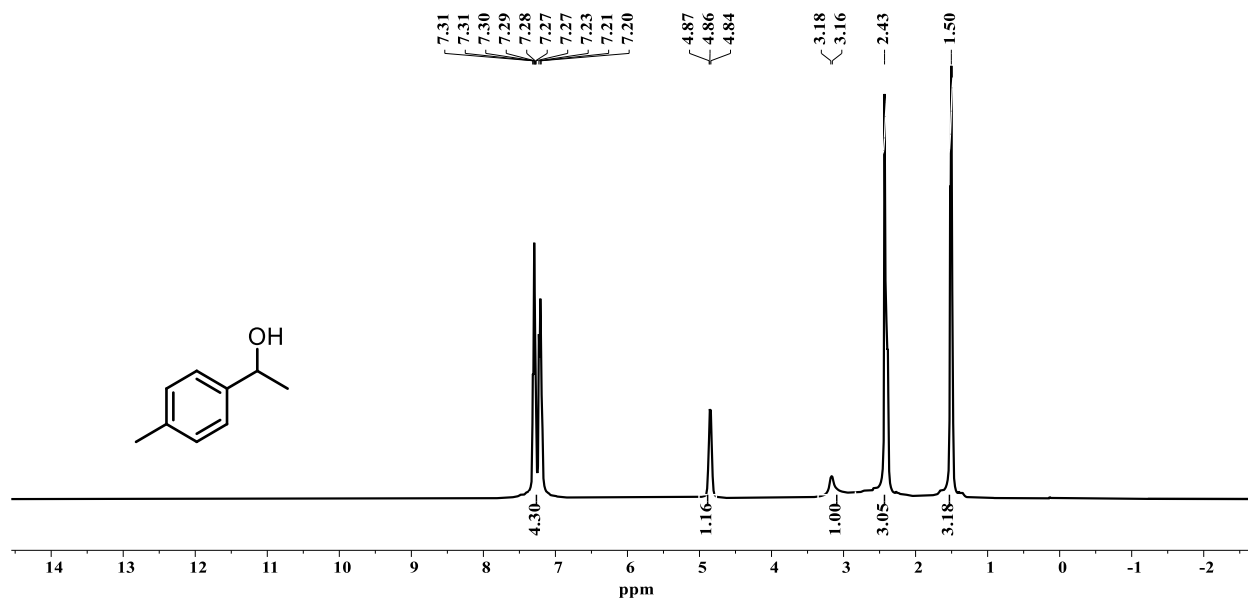


Figure S47. ^1H NMR spectrum of **a2** in CDCl_3 (400 MHz).

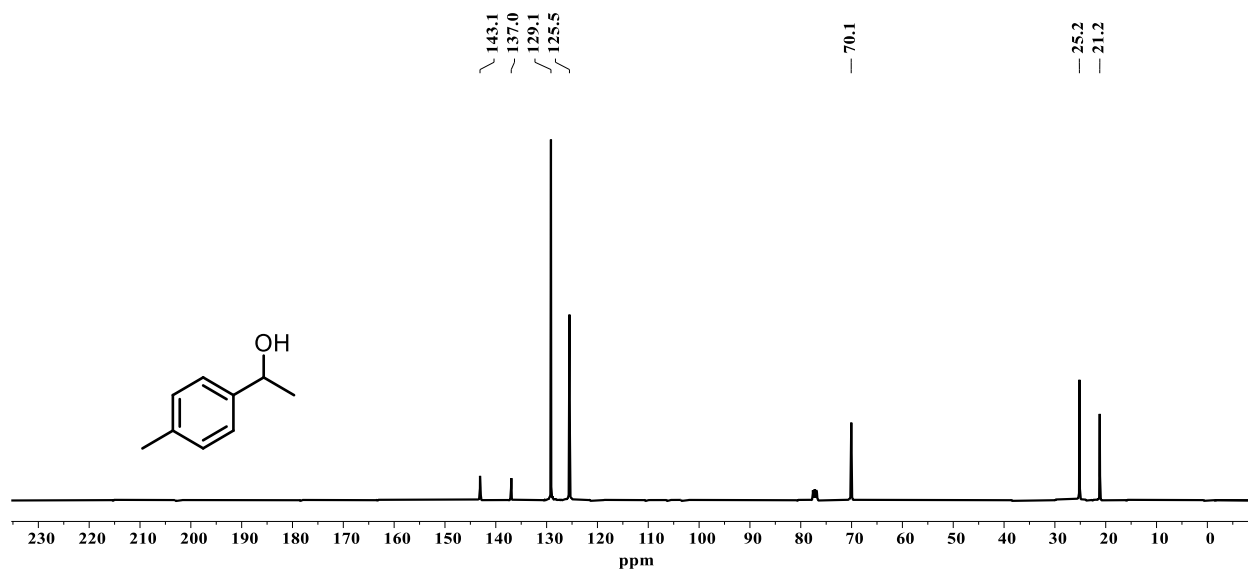


Figure S48. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a2** in CDCl_3 (101 MHz).

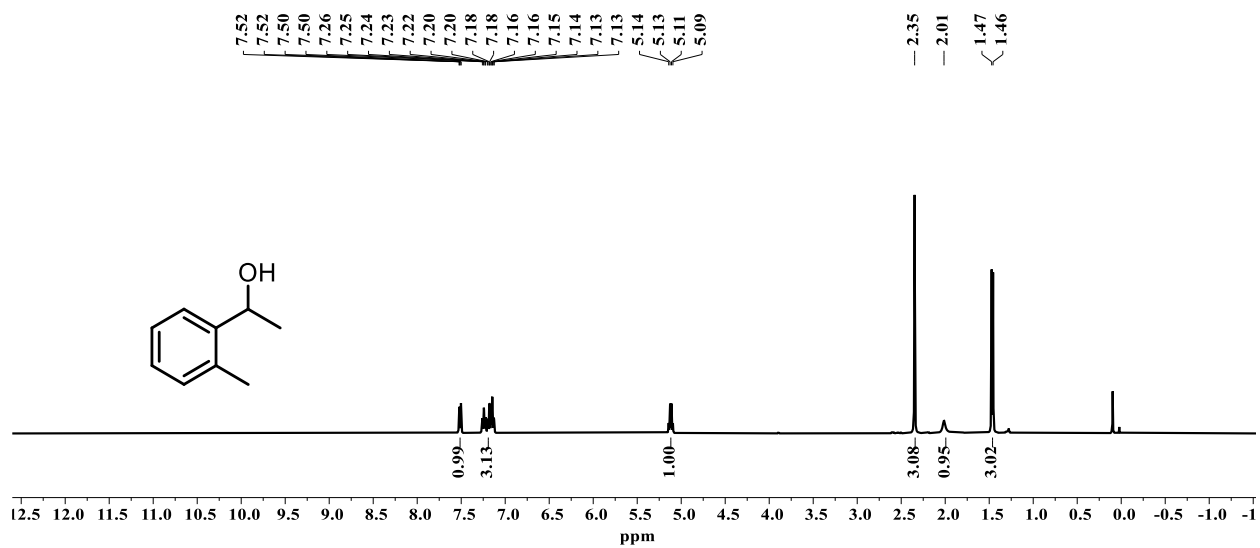


Figure S49. ^1H NMR spectrum of **a3** in CDCl_3 (400 MHz).

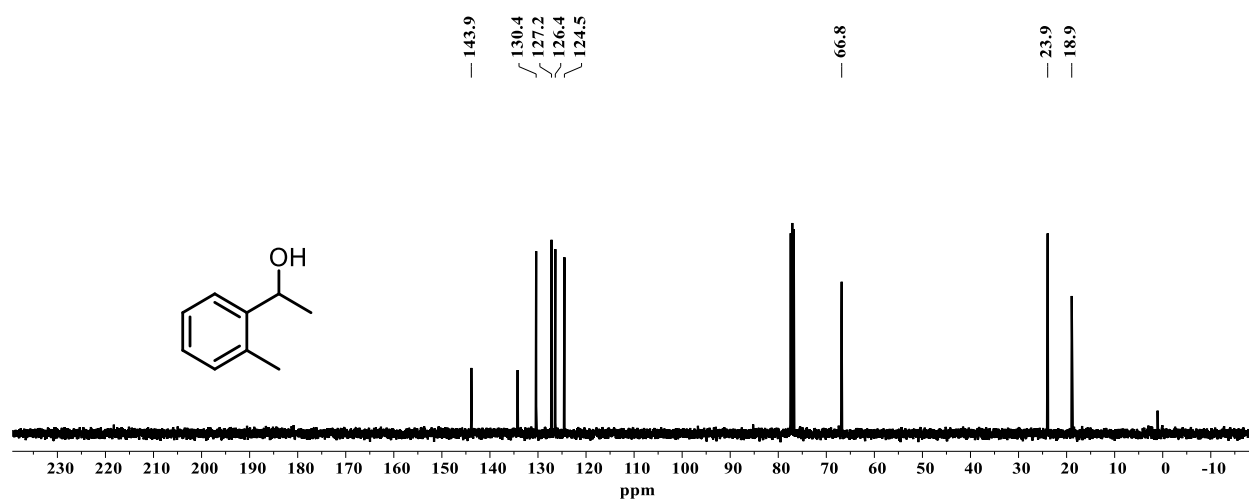


Figure S50. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a3** in CDCl_3 (101 MHz).

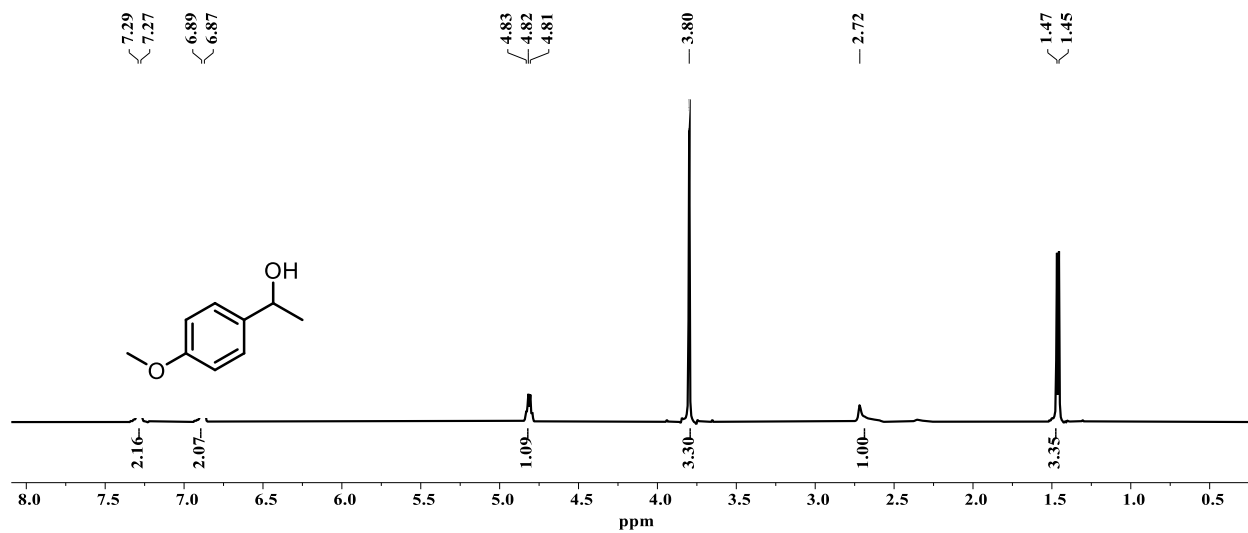


Figure S51. ^1H NMR spectrum of **a4** in CDCl_3 (500 MHz).

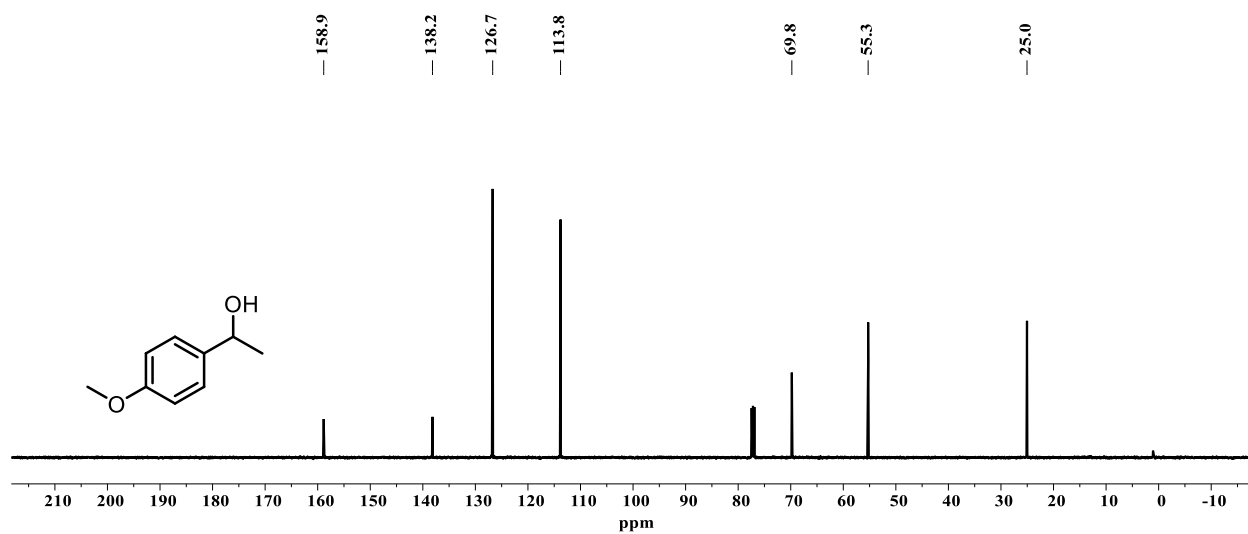


Figure S52. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a4** in CDCl_3 (126 MHz).

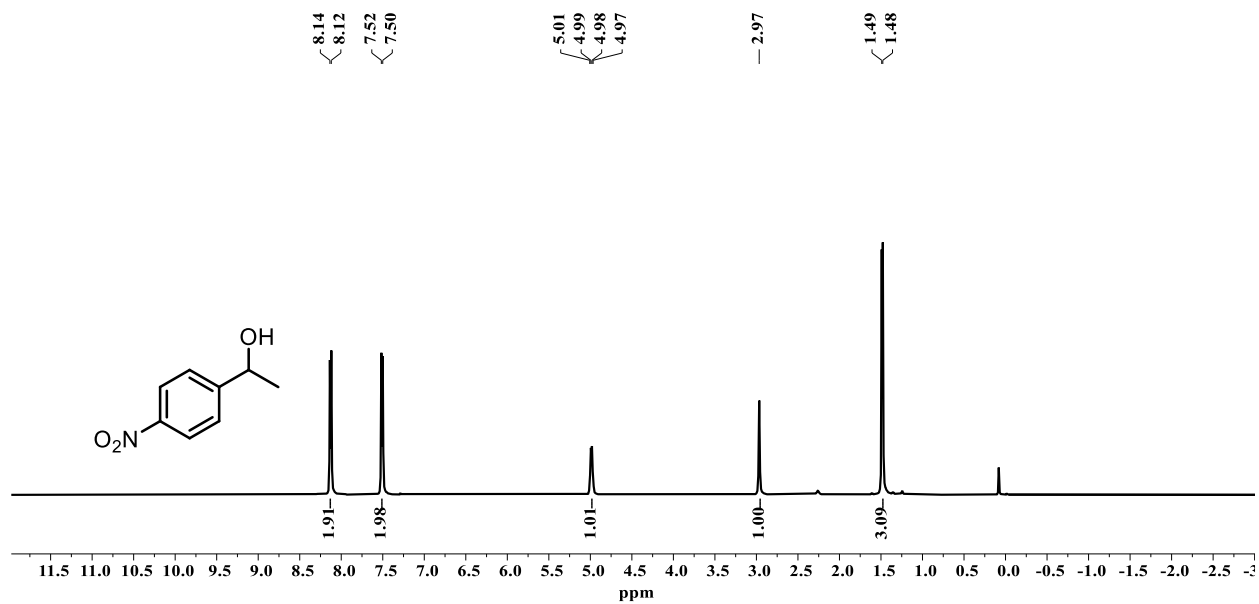


Figure S53. ^1H NMR spectrum of **5a** in CDCl_3 (500 MHz).

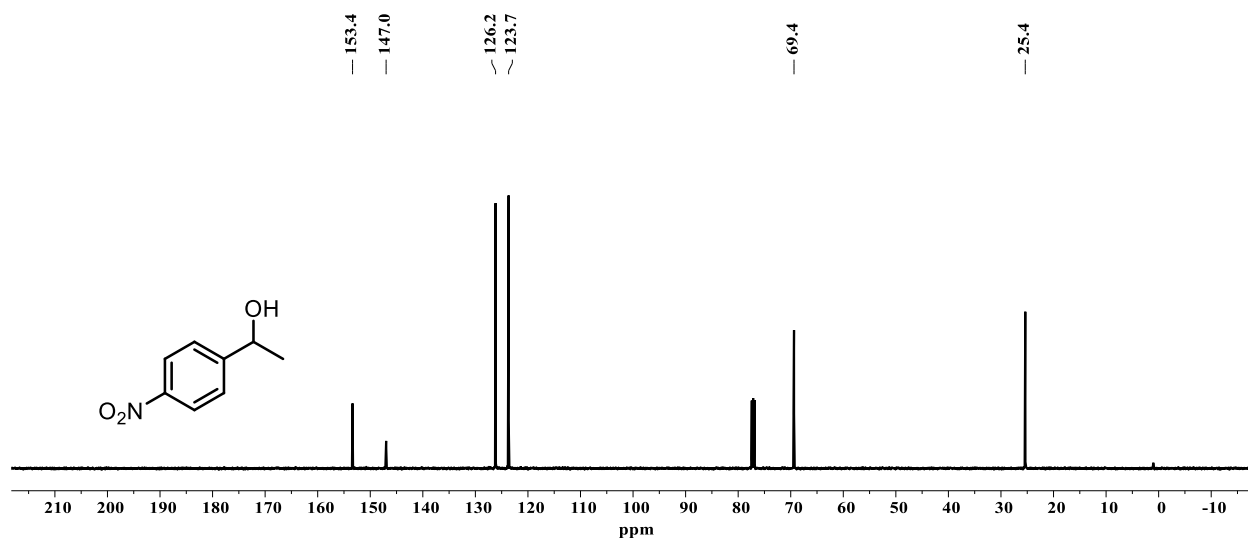


Figure S54. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5a** in CDCl_3 (126 MHz).

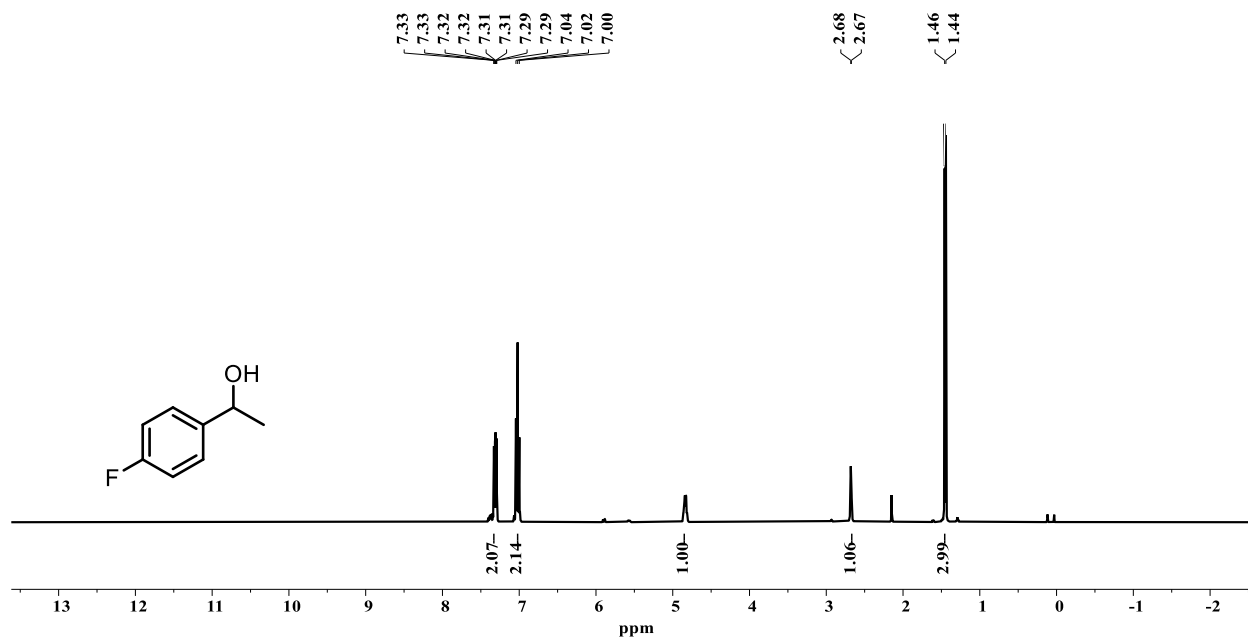


Figure S55. ^1H NMR spectrum of **a**₆ in CDCl_3 (400 MHz).

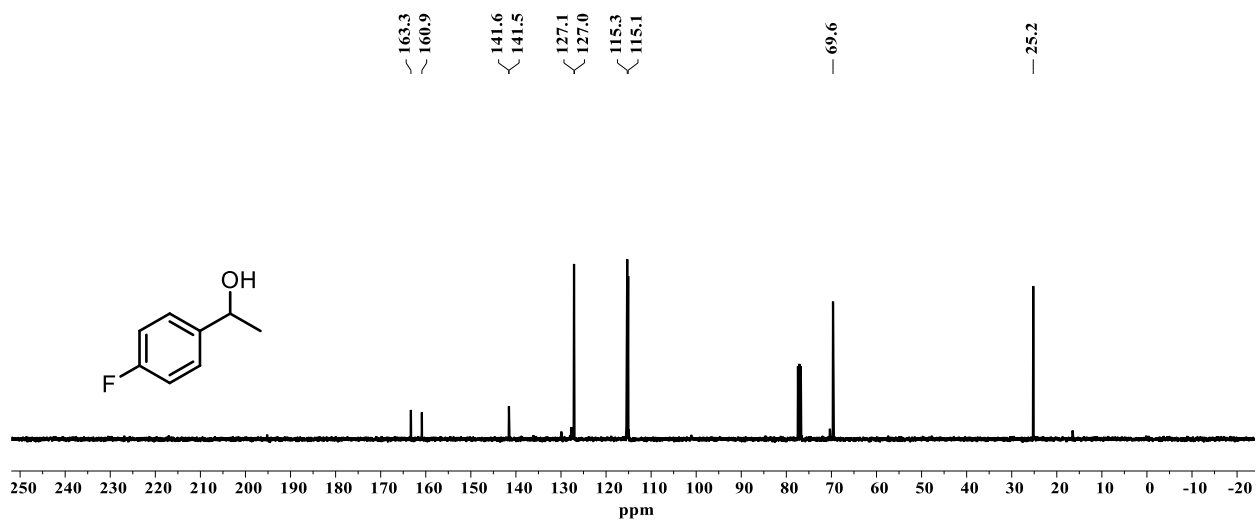


Figure S56. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a**₆ in CDCl_3 (101 MHz).

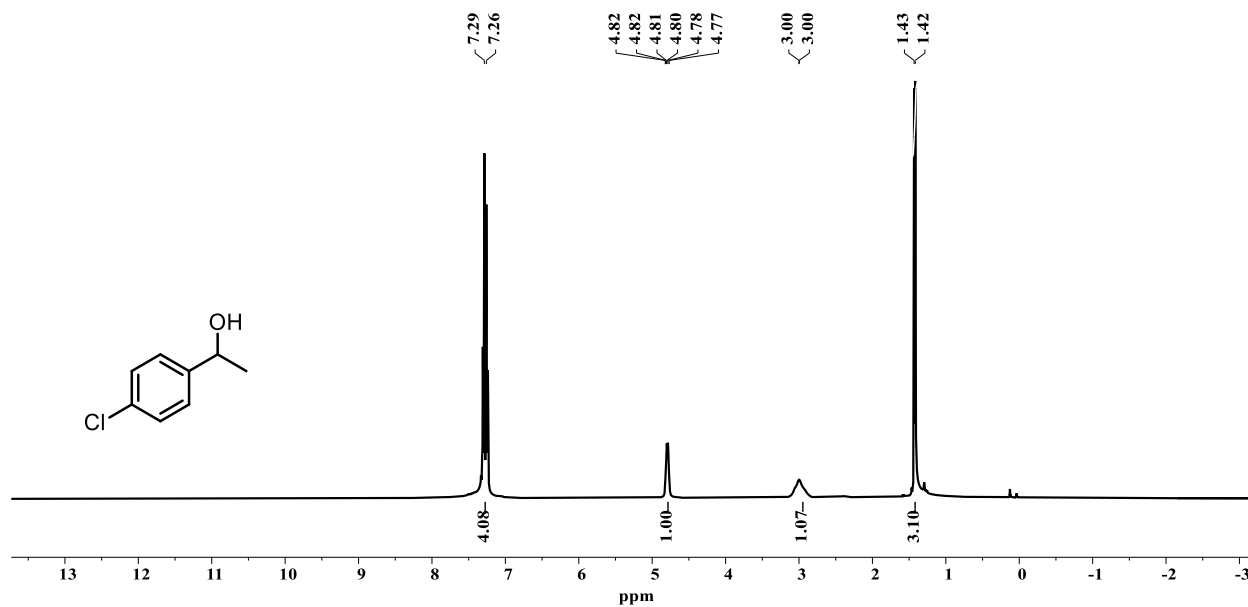


Figure S57. ^1H NMR spectrum of **a7** in CDCl_3 (400 MHz).

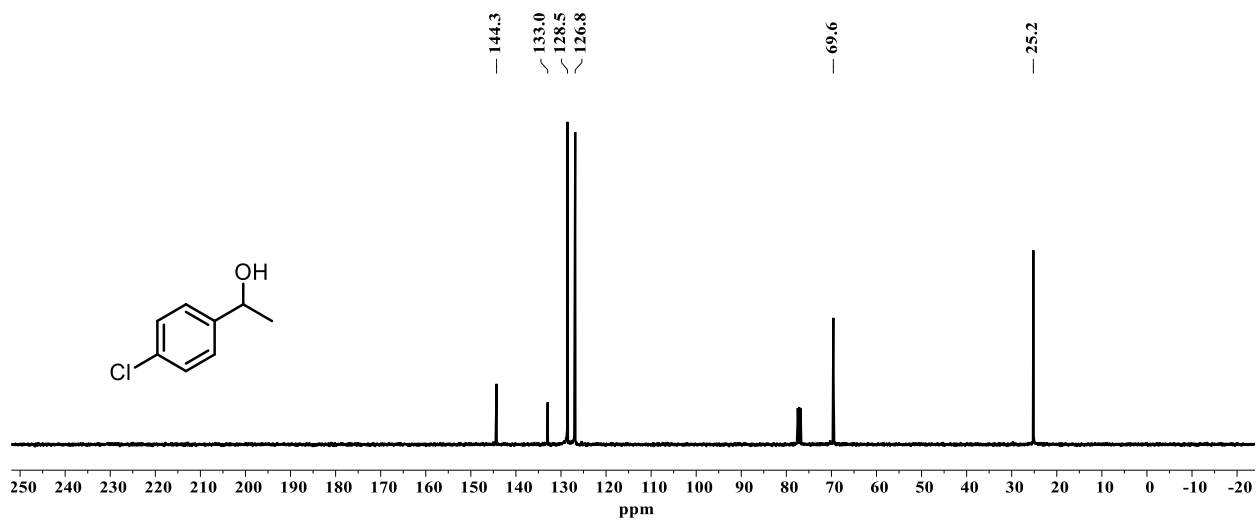


Figure S58. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a7** in CDCl_3 (101 MHz).

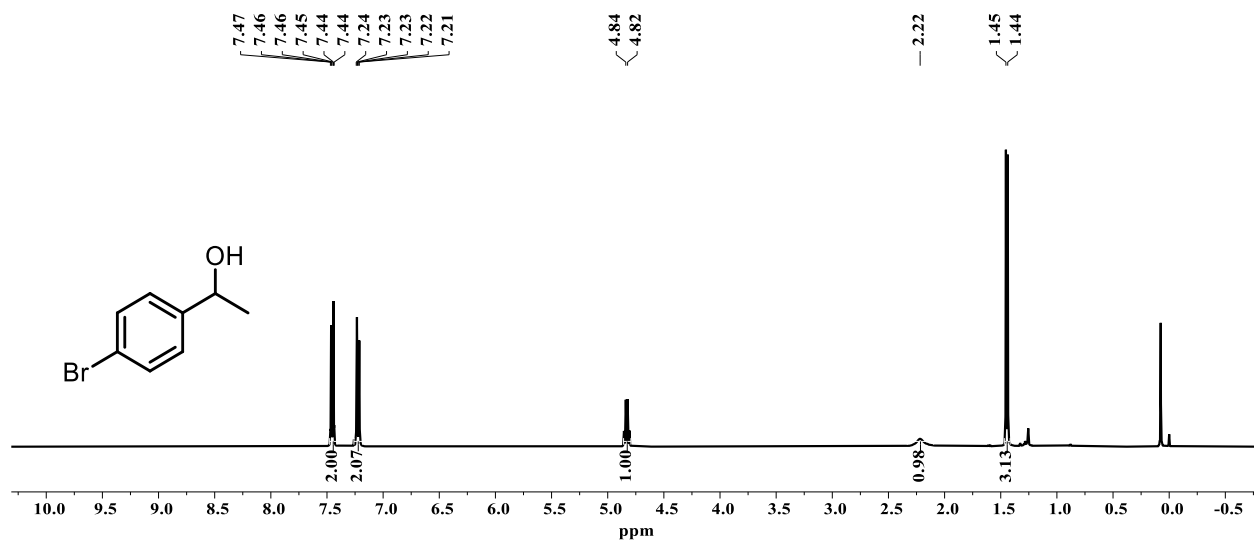


Figure S59. ^1H NMR spectrum of **as** in CDCl_3 (400 MHz).

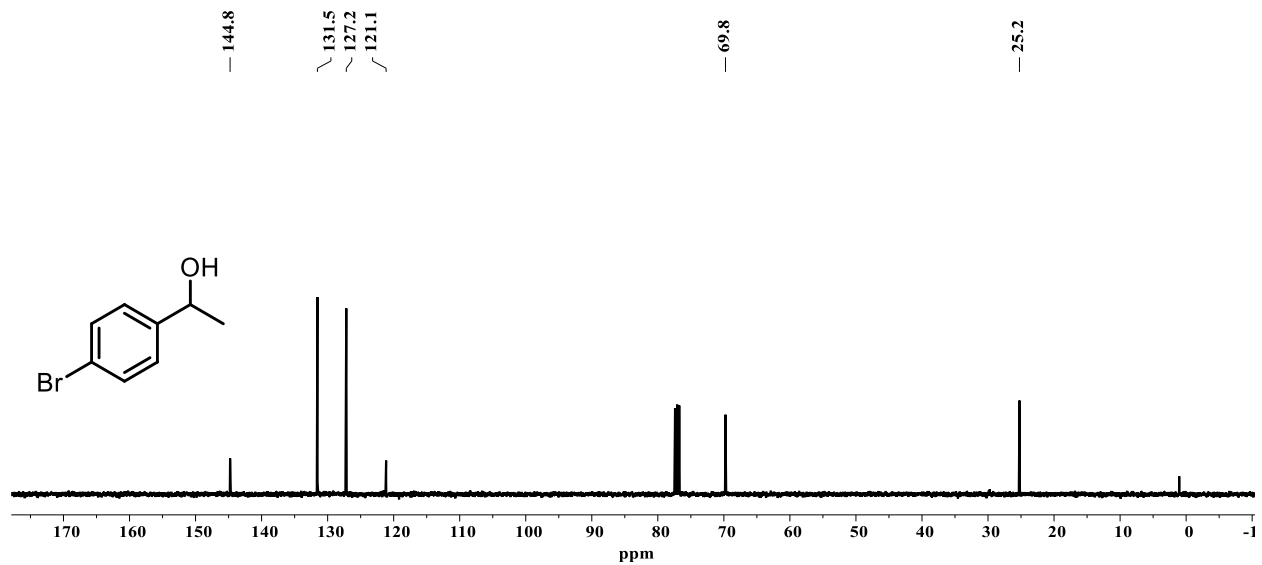


Figure S60. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **as** in CDCl_3 (101 MHz).

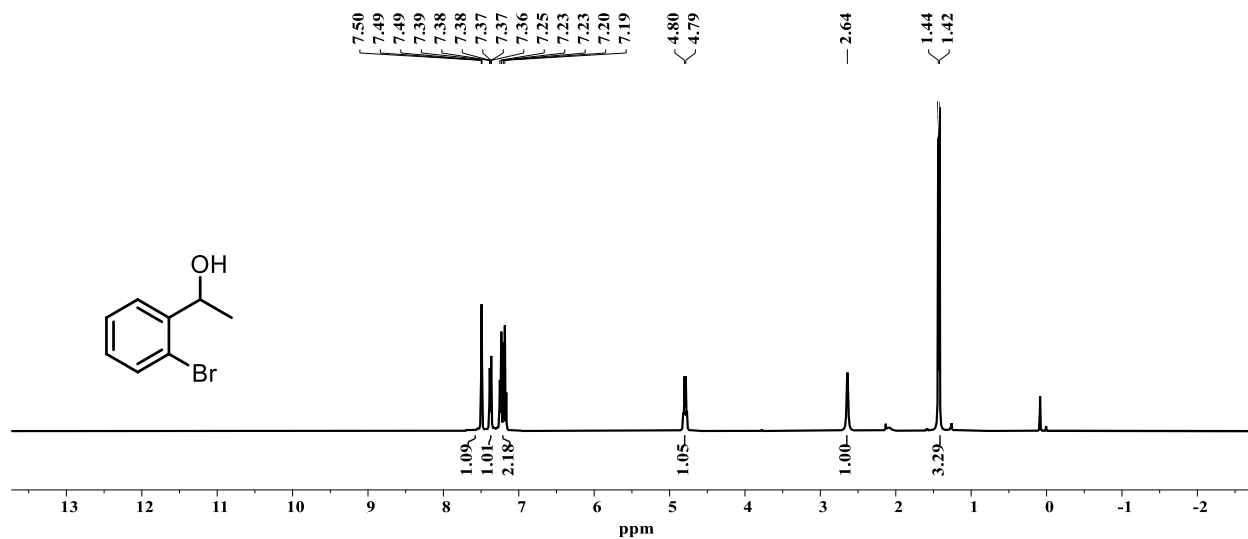


Figure S61. ^1H NMR spectrum of **a9** in CDCl_3 (400 MHz).

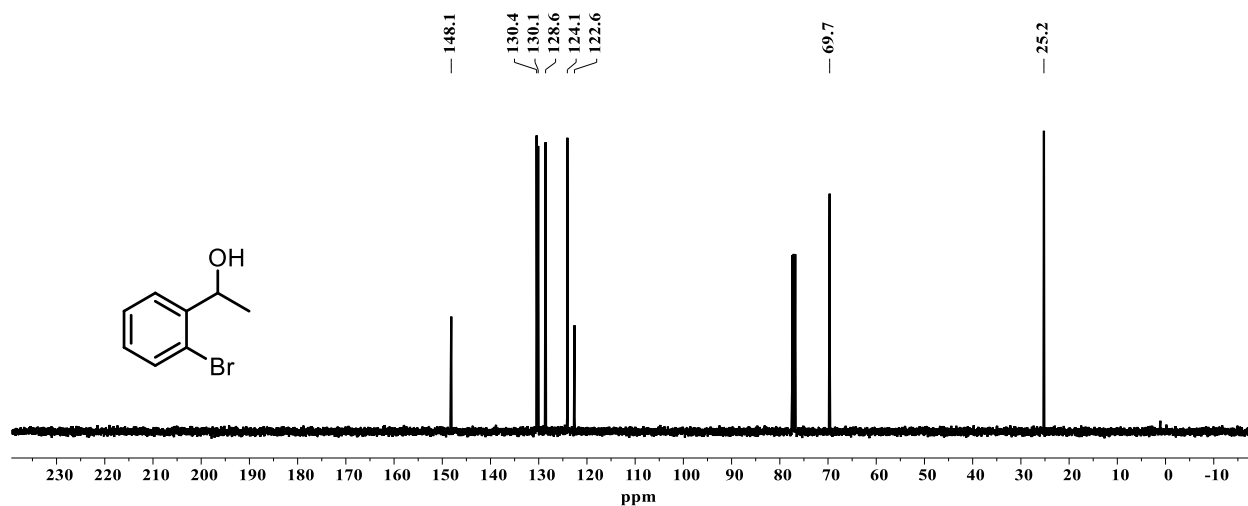


Figure S62. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a9** in CDCl_3 (101 MHz).

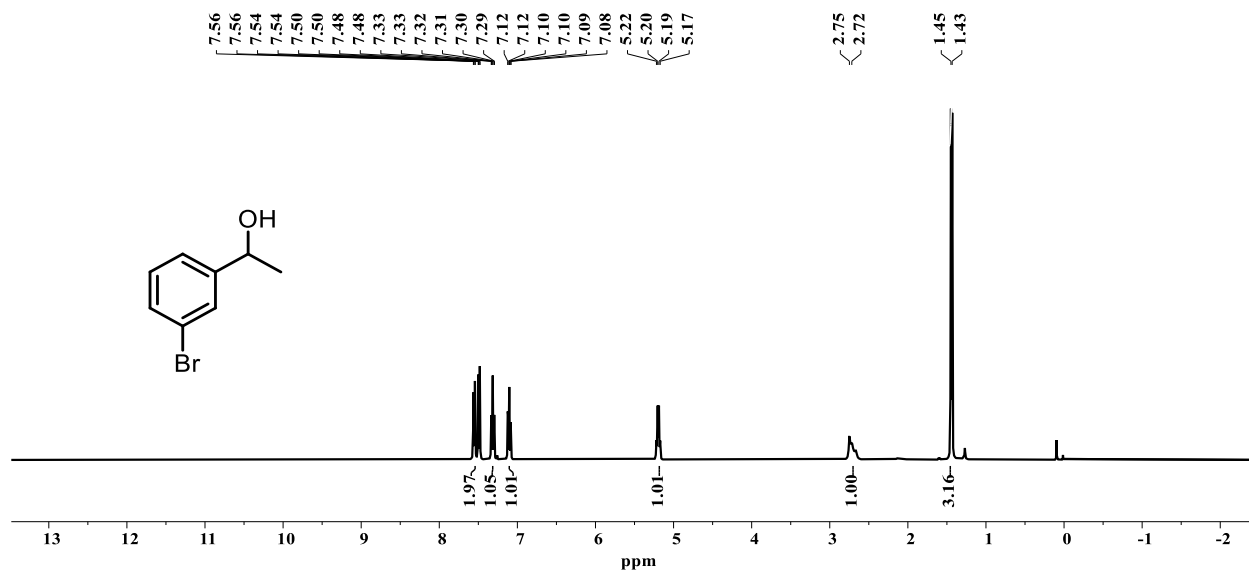


Figure S63. ^1H NMR spectrum of **a10** in CDCl_3 (400 MHz).

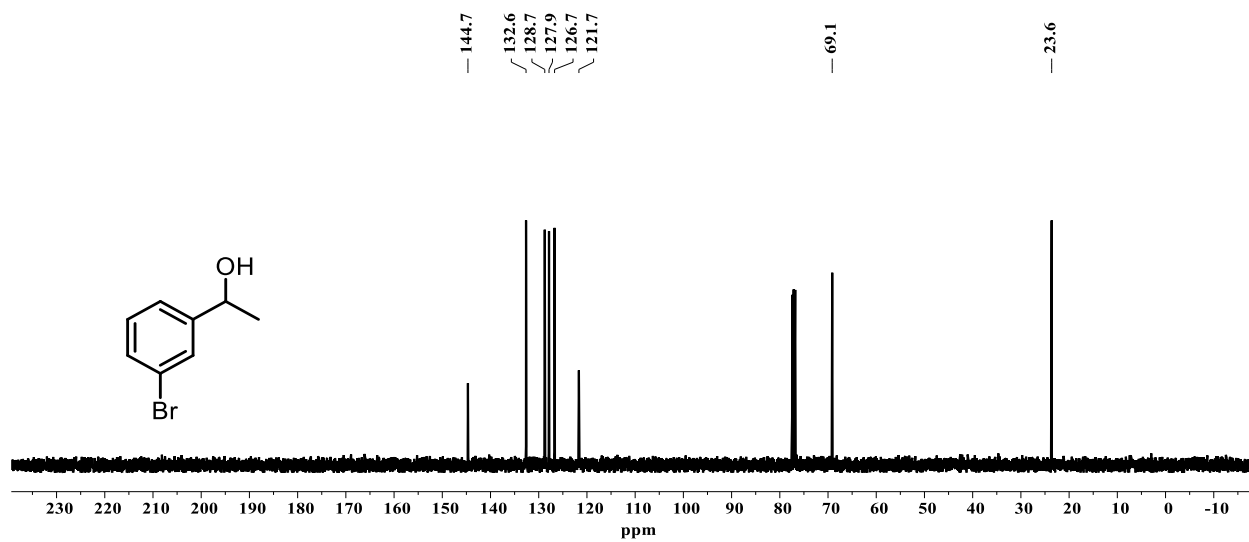


Figure S64. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a10** in CDCl_3 (101 MHz).

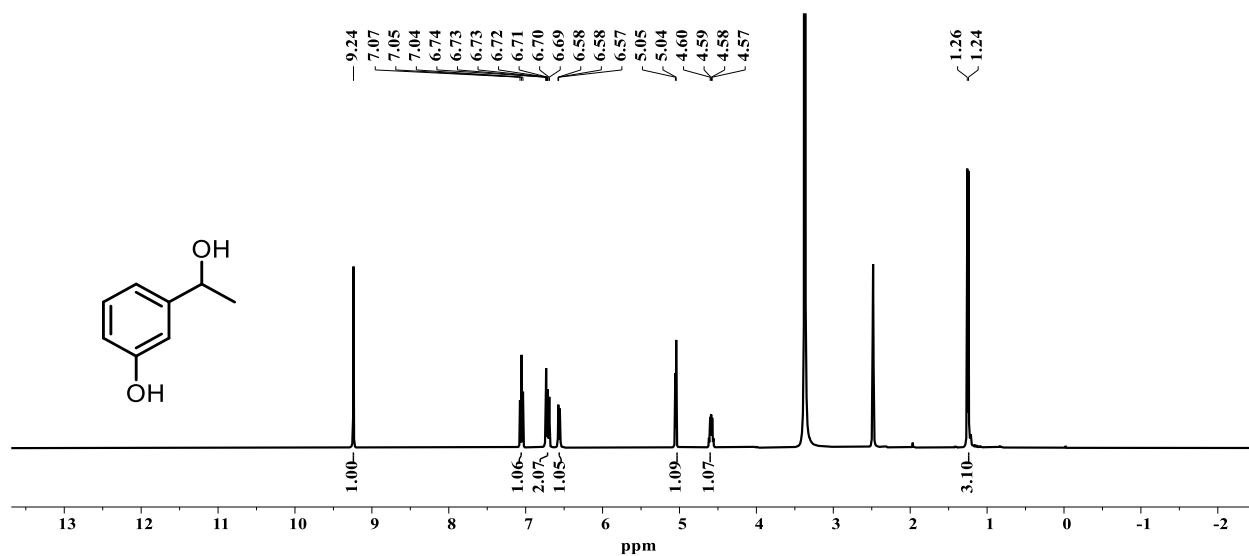


Figure S65. ¹H NMR spectrum of a₁₁ in CDCl₃ (400 MHz).

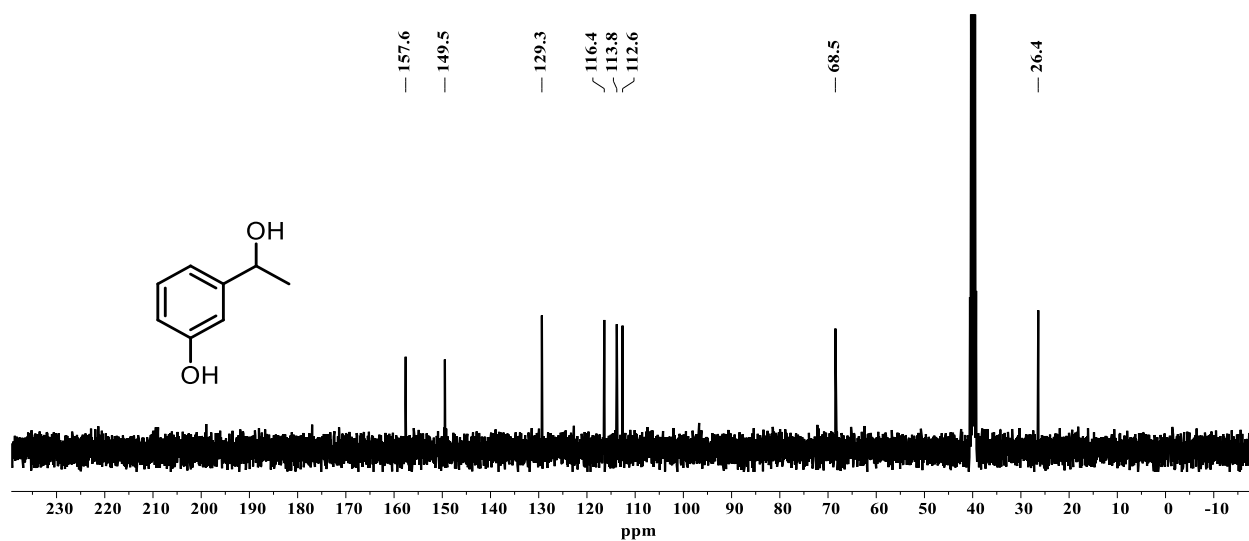


Figure S66. ¹³C {¹H} NMR spectrum of a₁₁ in CDCl₃ (101 MHz).

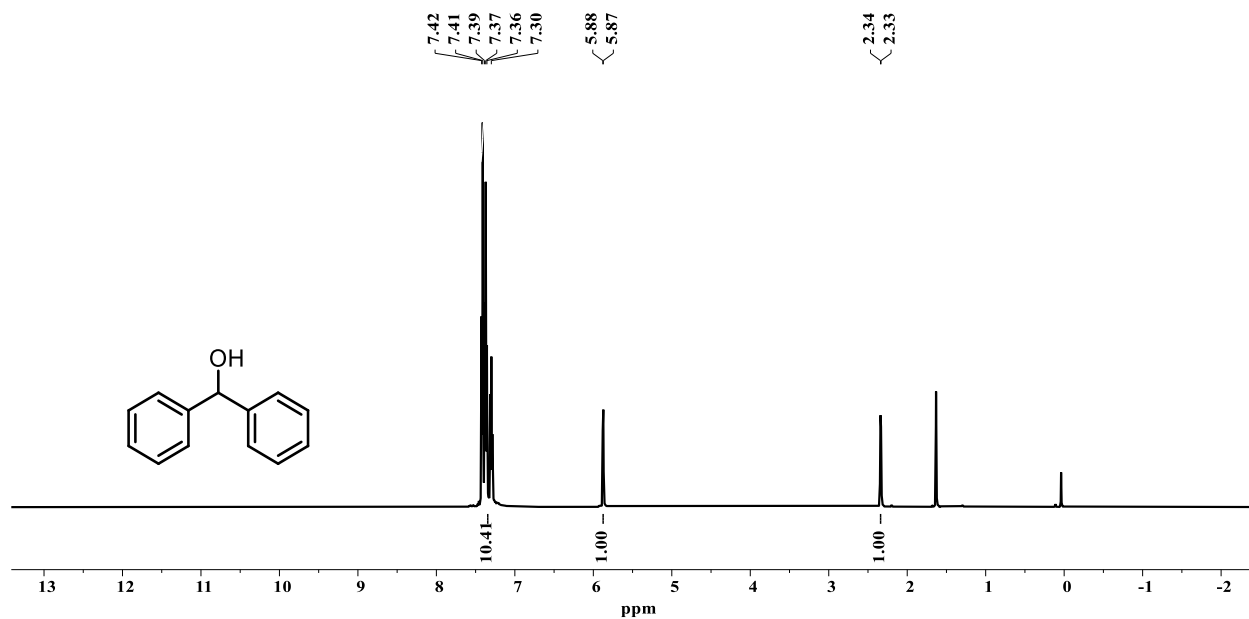


Figure S67. ^1H NMR spectrum of **a12** in CDCl_3 (500 MHz).

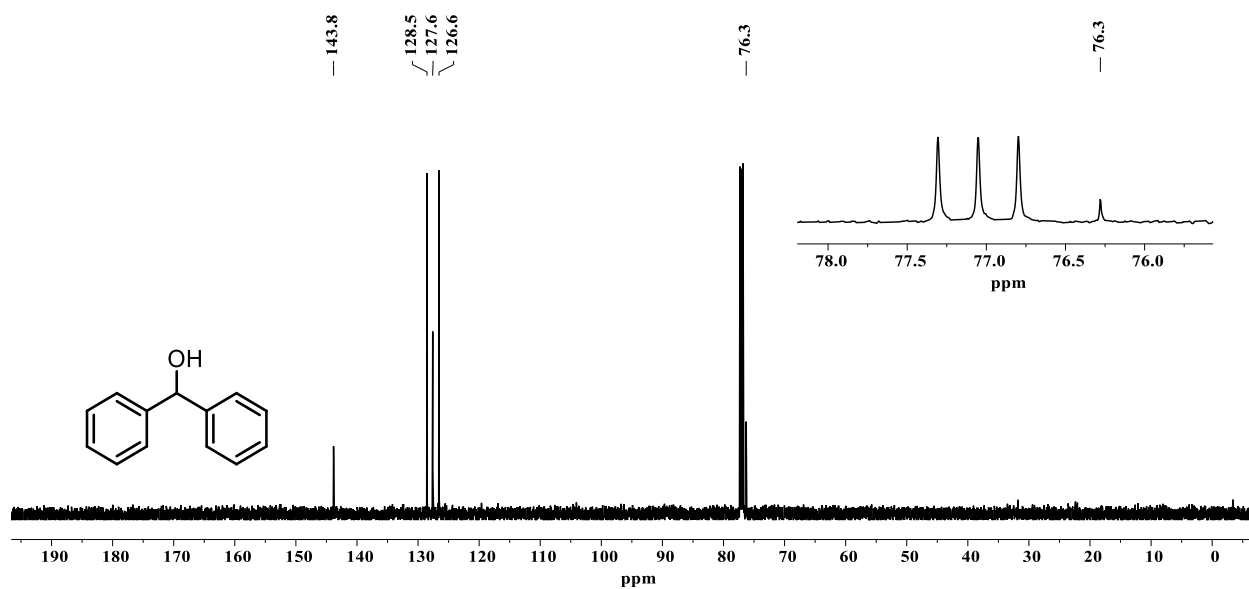


Figure S68. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a12** in CDCl_3 (126 MHz).

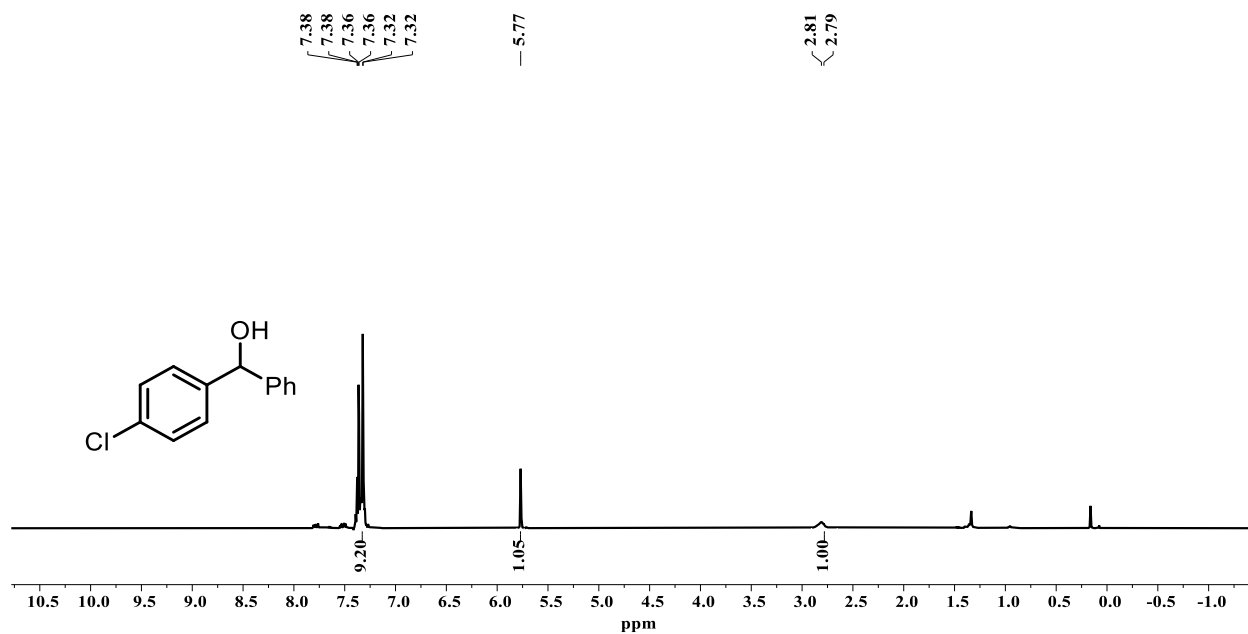


Figure S69. ^1H NMR spectrum of **a13** in CDCl_3 (500 MHz).

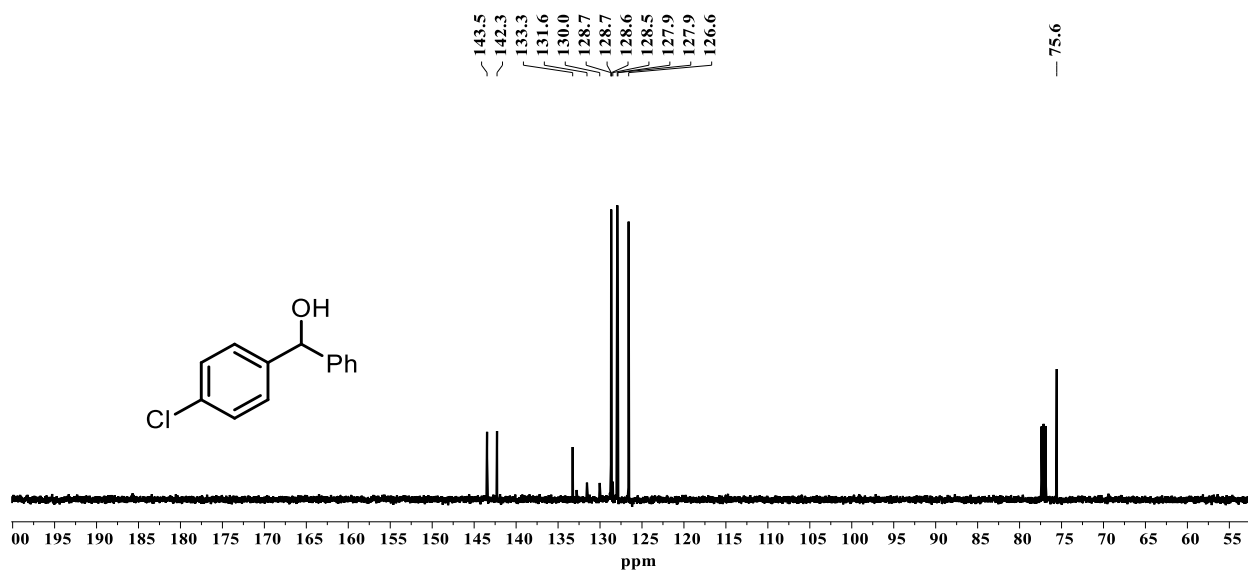


Figure S70. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a13** in CDCl_3 (126 MHz).

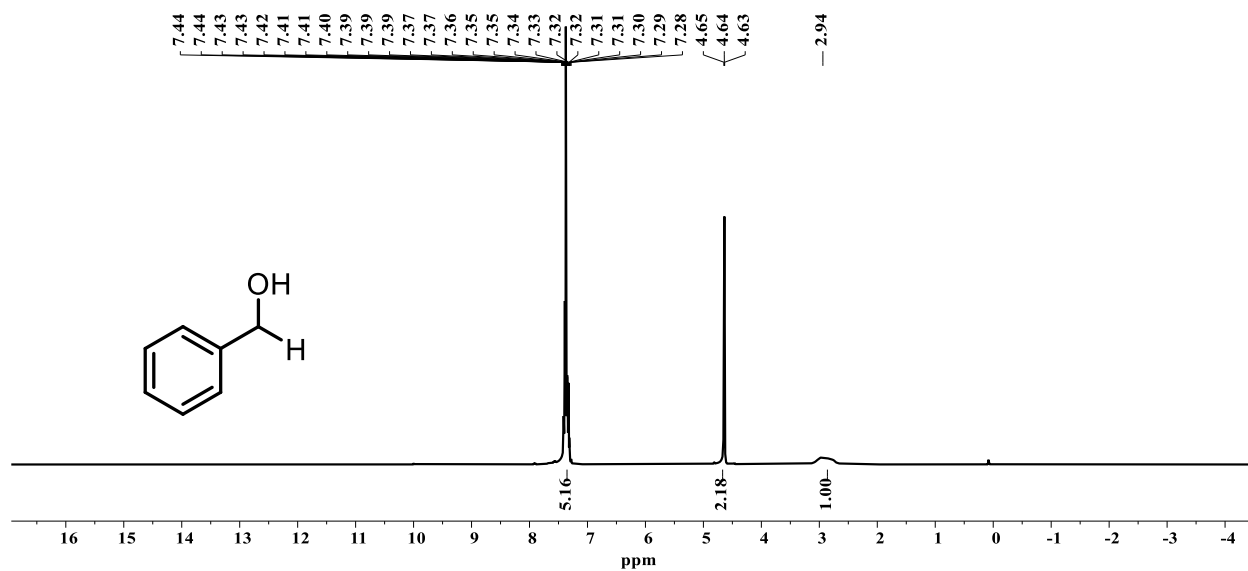


Figure S71. ^1H NMR spectrum of **a14** in CDCl_3 (400 MHz).

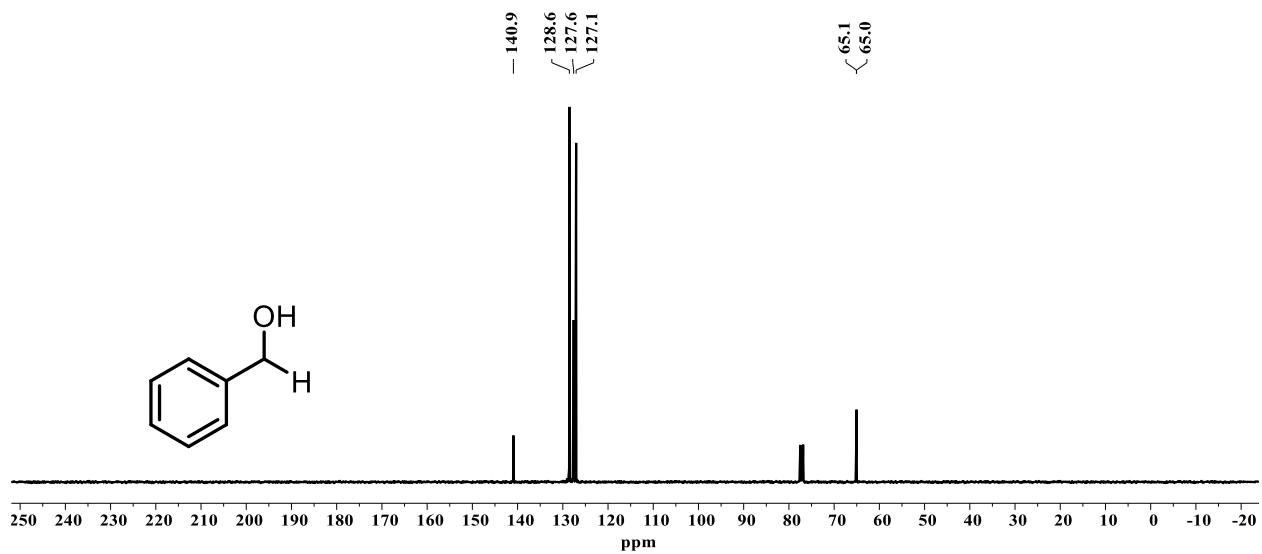


Figure S72. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a14** in CDCl_3 (101 MHz).

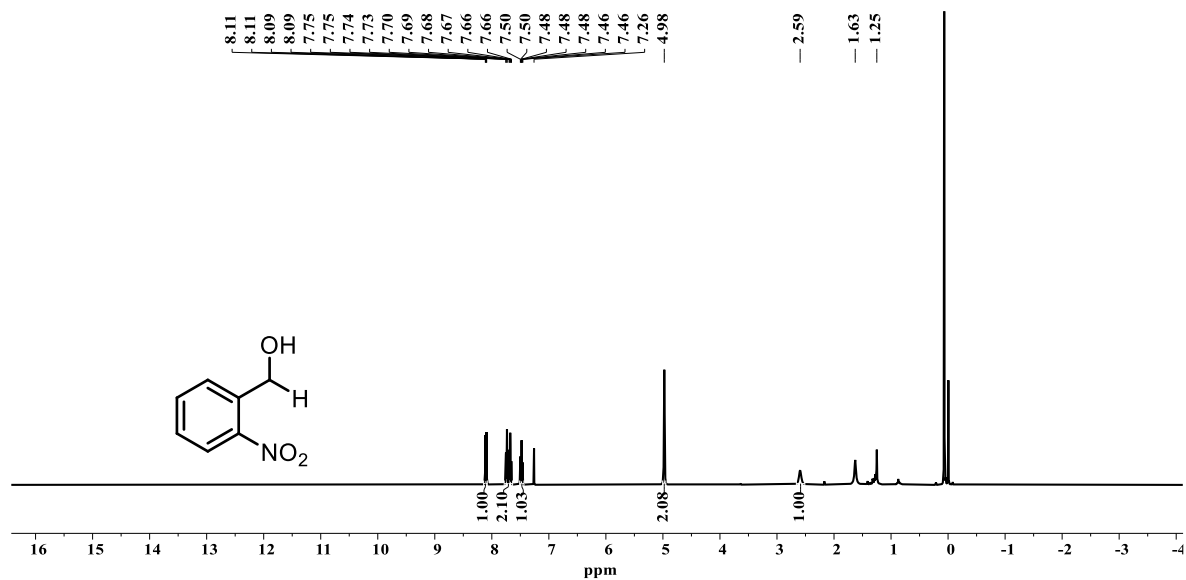


Figure S73. ^1H NMR spectrum of **a15** in CDCl_3 (400 MHz).

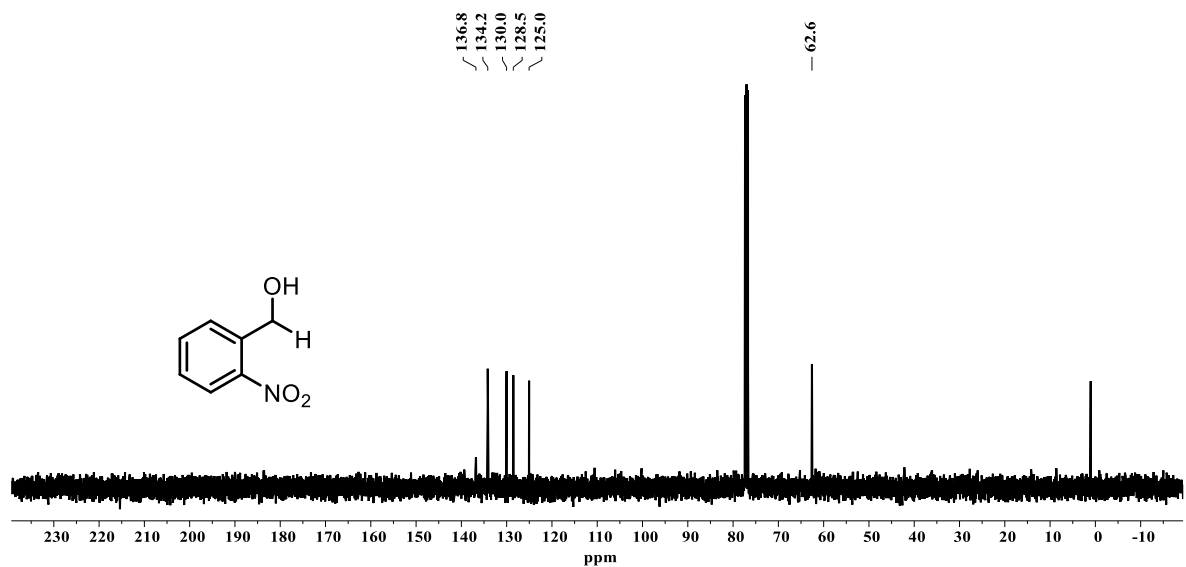


Figure S74. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a15** in CDCl_3 (101 MHz).

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