Supporting Information

Role of Ancillary Ligands in Selectivity Towards Acceptorless Dehydrogenation versus Dehydrogenative Coupling of Alcohols and Amines Catalyzed by Cationic Ruthenium(II)-CNC Pincer Complexes

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General Information

Catalysis experiments: Since TH and AAD reactions have been studied with the *N*-Me analogs,[1–3] no substrate scope was investigated again with the new compounds but only a confirmation of the observed trends in terms of the trans effect of ancillary ligands was checked. The catalyst loading may seem high; however, the focus of this manuscript is the effect of ancillary ligands on catalytic performance with a comparison of the four ligands (CO, COD, PPh_3, DMSO) and the unexpected reversal in catalytic activity during the ADC reactions. The CNC pincer ligand platform provides a unique ligand framework with no metal-ligand cooperativity, which allows this comparison between a set of ancillary ligands. New complexes with two bulkier *N*-substituents have allowed us to observe the effect of ancillary ligands and confirmation of these effects in a larger set of compounds as well as characterization of an important Ru-H intermediate with CO ligand positioned trans to the product.

Table S1. Crystal data and structure refinement parameters for **4b** and **6b**.

	4b	**6b**
Empirical formula	$C_{53}H_{55}Br_{0.17}Cl_{0.85}N_5O_{1.5}P_2Ru$	$C_{21}H_{39}Cl_2N_5O_5RuS_2$
T/K	293(2)	293(2)
Crystal System	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/n$
a/ Å	12.3216(2)	11.3804(2)
b/Å	26.5103(11)	11.0157(2)
c/Å	14.8679(3)	24.3528(4)
α/°	90	90
β/°	92.768(2)	96.679(2)
γ/°	90	90
V/Å^3	4850.9(2)	3032.22(9)
Z	4	4
ρ_{calc}g/cm^3	1.360	1.484
λ/Å (Cu-Kα)	1.54184	1.54184
Reflections Collected	21244	13368
Data/restr./param.	8823/0/578	5531/0/342
R (int)	0.0843	0.0897
Final R indices [I>2σ(I)]	R1 = 0.0719, wR2 = 0.1823	R1 = 0.0866, wR2 = 0.2388
R indices (all data)	R1 = 0.0918, wR2 = 0.2003	R1 = 0.0909, wR2 = 0.2488
GOF on F2	1.058	1.039

Table S2. Selected bond lengths and bond angles of complex **4b** and **6b**.

Complex	Bond lengths (Å)	Bond angles (°)
4b	Ru1-N1, 2.058(4) Ru1-C1, 2.022(5) Ru1-C11, 2.049(6) Ru1-P1, 2.3462(14) Ru1-P2, 2.3303(15)	P2-Ru1-P1, 165.04(5) N1-Ru1-P1, 100.75(13) N1-Ru1-P2, 94.21(13) C1-Ru1-P1, 91.58(16) C1-Ru1-P2, 91.81(16) C1-Ru1-N1, 77.5(2) C1-Ru1-C11, 154.5(2) C11-Ru1-P1, 94.09(16) C11-Ru1-P2, 89.10(16) C11-Ru1-N1, 77.0(2)
6b	Ru1-N1, 1.995(5) Ru1-C1, 2.062(6) Ru1-C11, 2.061(6) Ru1-S1, 2.2954(14) Ru1-S2, 2.3138(14) Ru1-Cl1, 2.4296(13)	N1-Ru1-C1, 78.0(2) N1-Ru1-C11, 77.7(2) N1-Ru1-S1, 89.69(14) N1-Ru1-S2, 89.35(14) N1-Ru1-Cl1, 177.23(14) C1-Ru1-S1, 88.29(16) C1-Ru1-S2, 87.69(16) C11-Ru1-Cl1, 101.60(15) C11-Ru1-C1, 155.7(2) C11-Ru1-S1, 91.74(15) C11-Ru1-S2, 91.87(15) C1-Ru1-Cl1, 102.67(16) S1-Ru1-Cl1, 87.65(5) S1-Ru1-S2, 175.98(6) S2-Ru1-Cl1, 93.36(5)

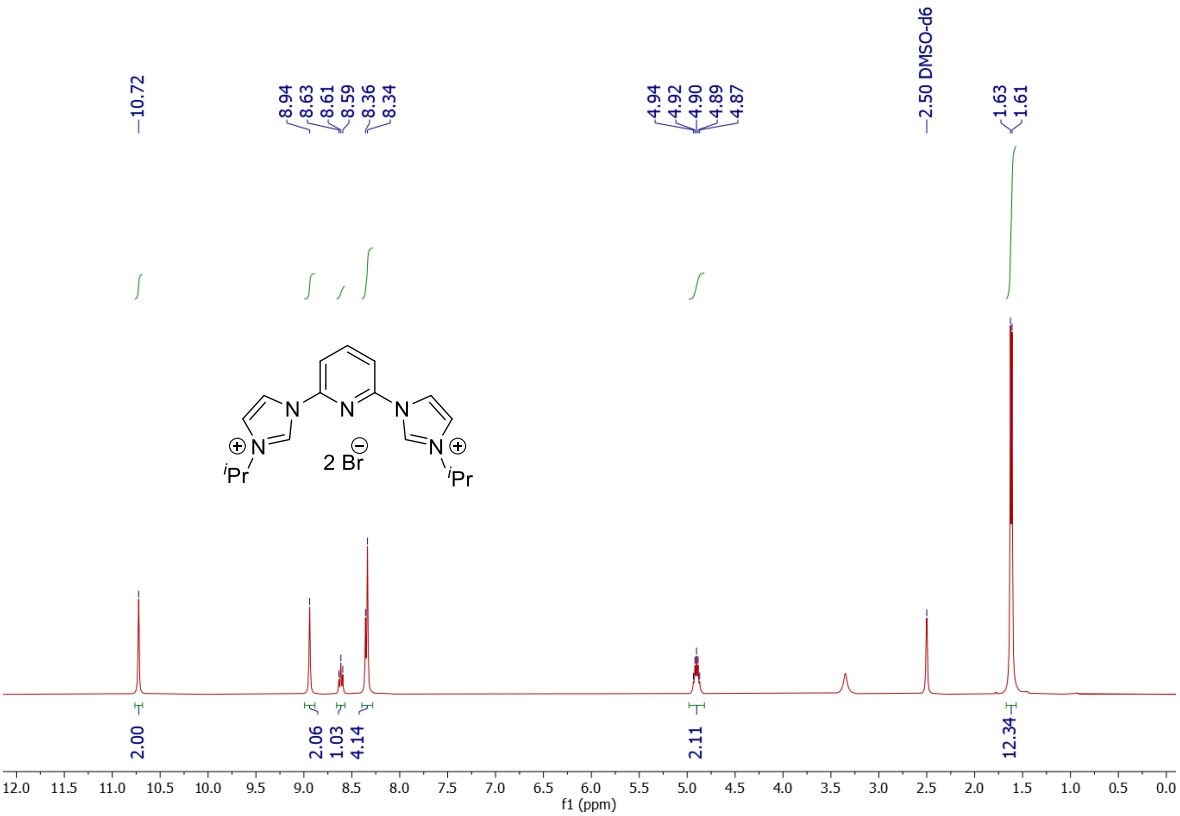

Figure S1. ^{1}H NMR spectrum of **CNC^{iPr}·2HBr**.

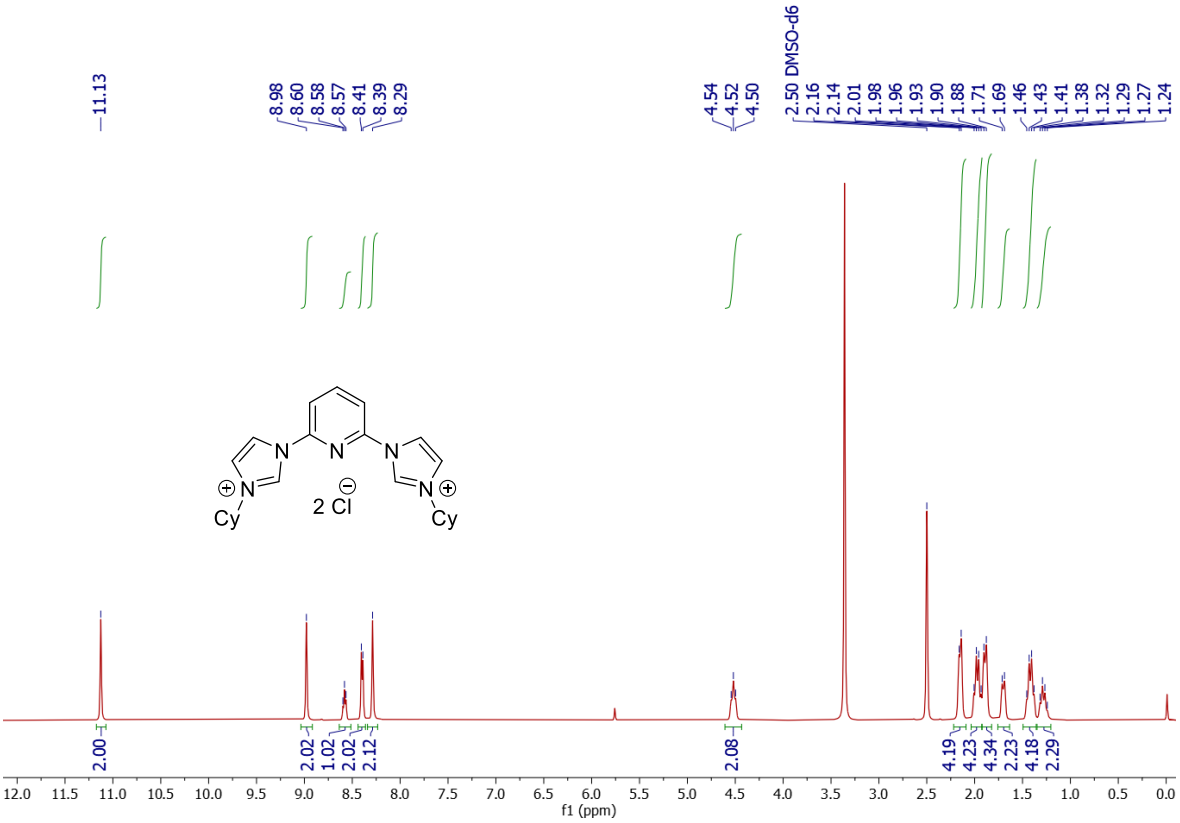

Figure S2. ^{1}H NMR spectrum of **CNC^{Cy}·2HCl**.

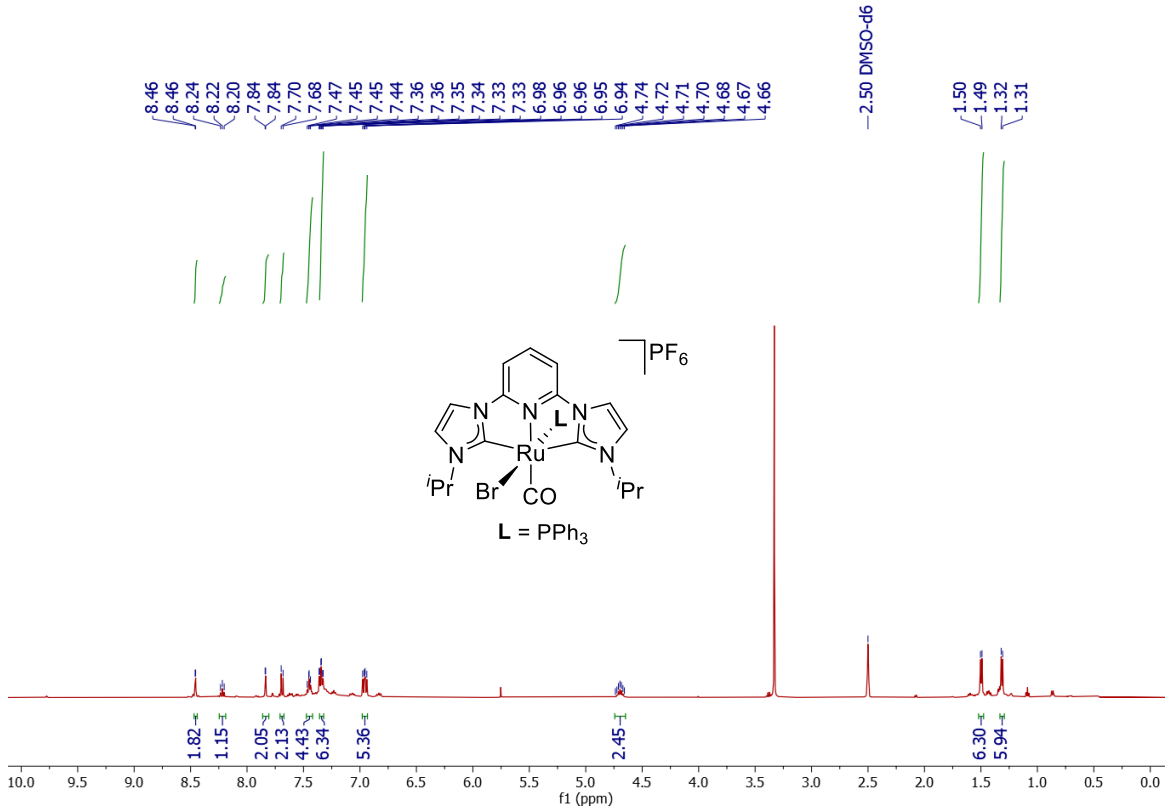

Figure S3. ^{1}H NMR spectrum of Complex **1b**.

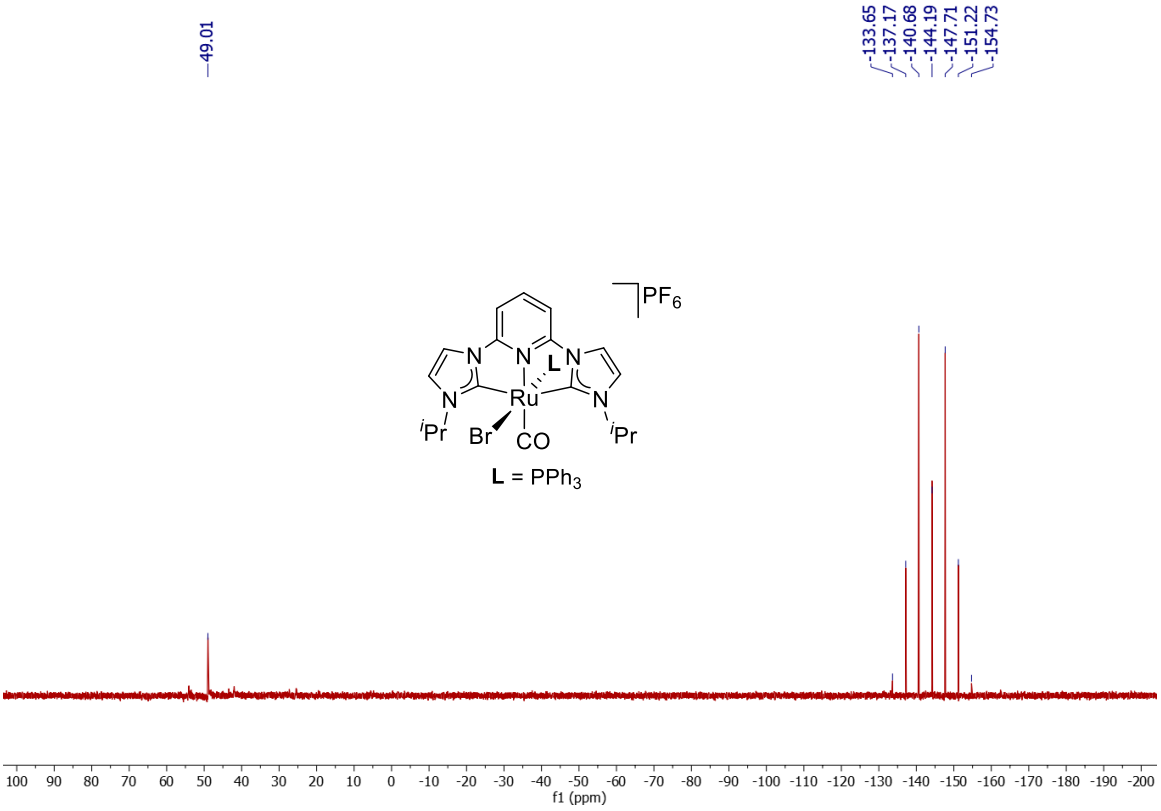

Figure S4. ^{31}P NMR spectrum of Complex **1b**.

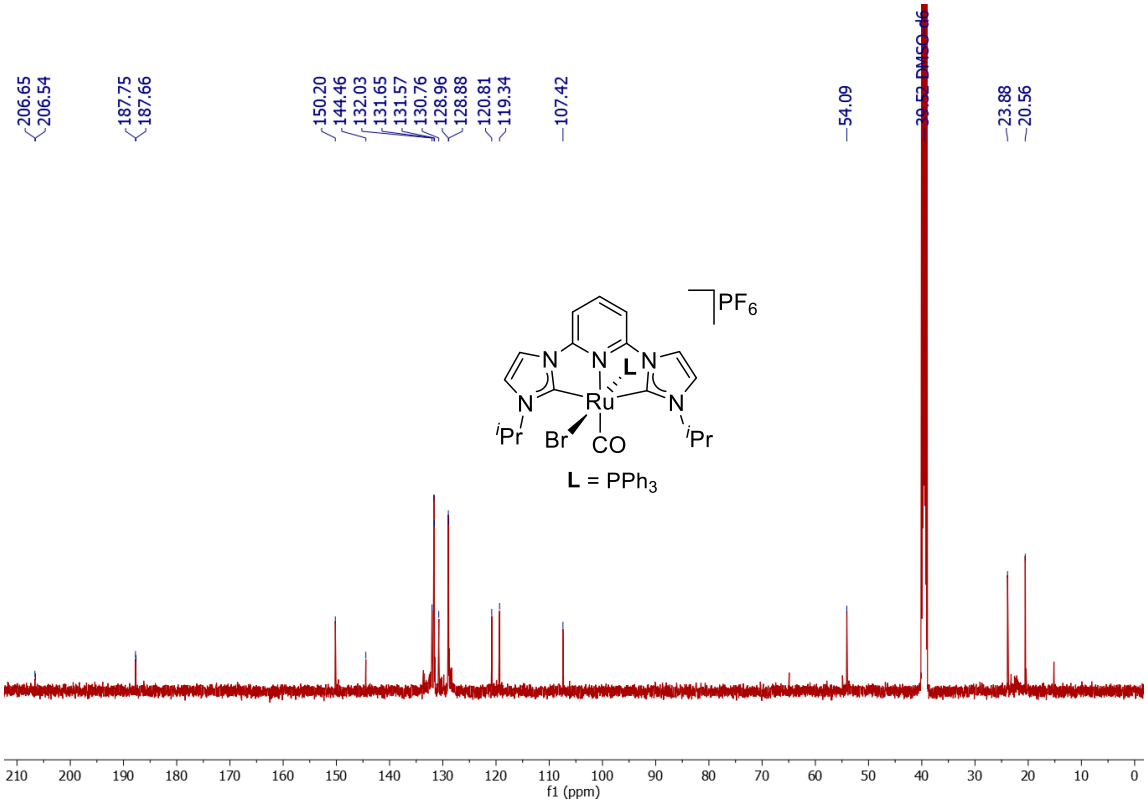

Figure S5. ^{13}C NMR spectrum of Complex **1b**.

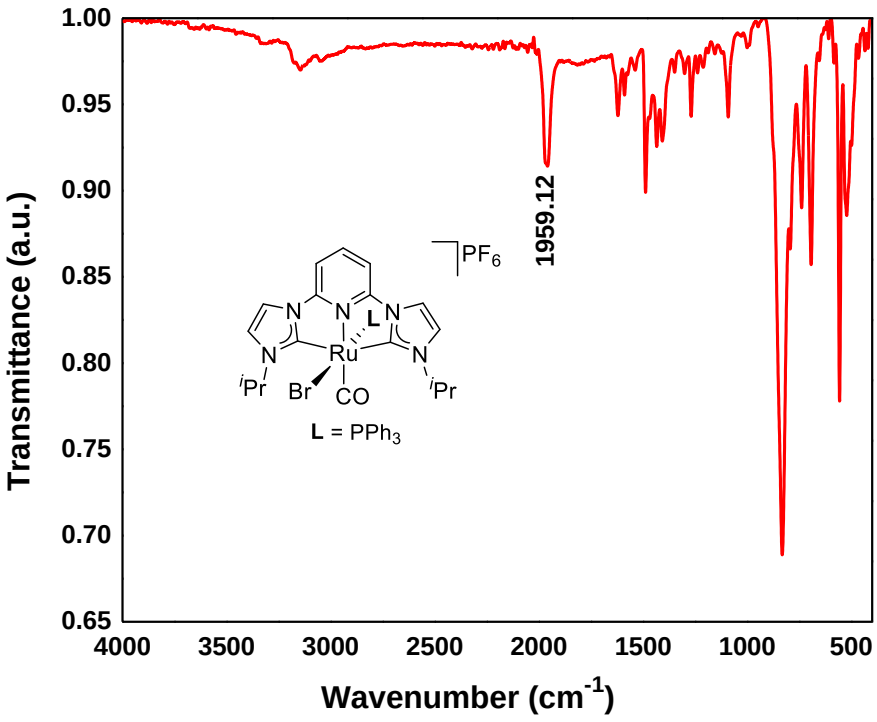

Figure S6. IR spectra of Complex **1b**.

Display Report

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Sample Name	h chem AKS-RKS-200	Instrument	micrOTOF-Q 228888.10348
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
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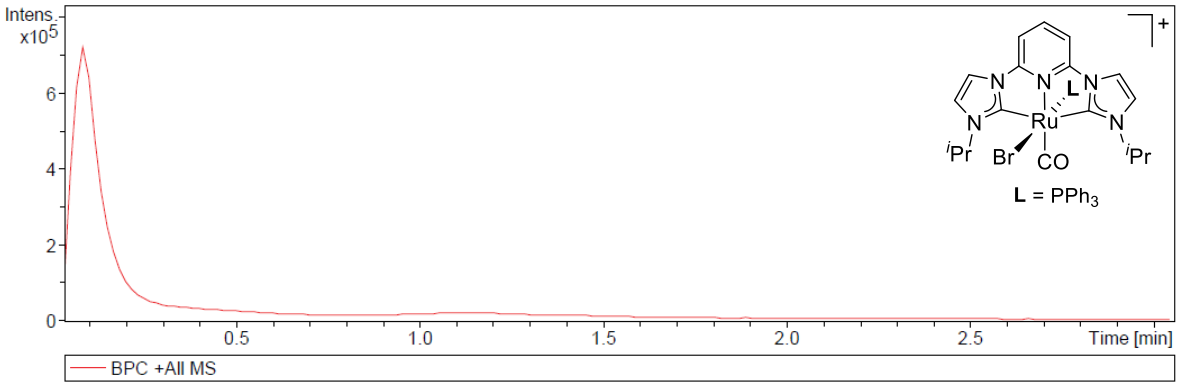

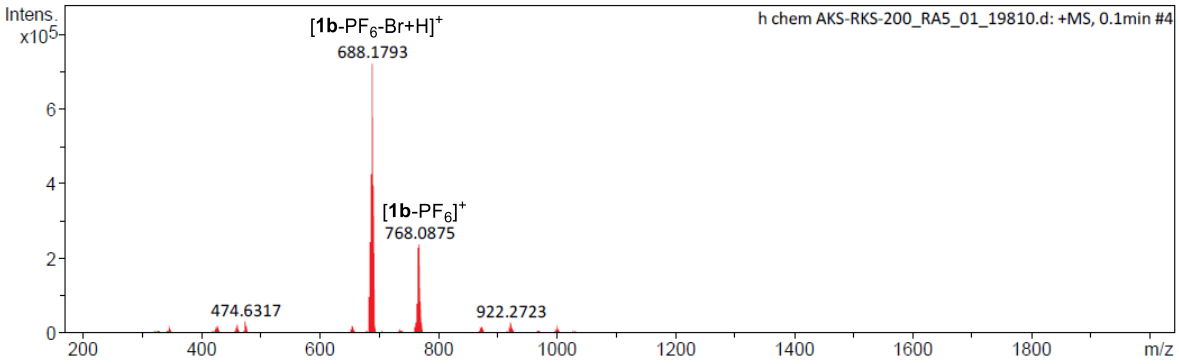

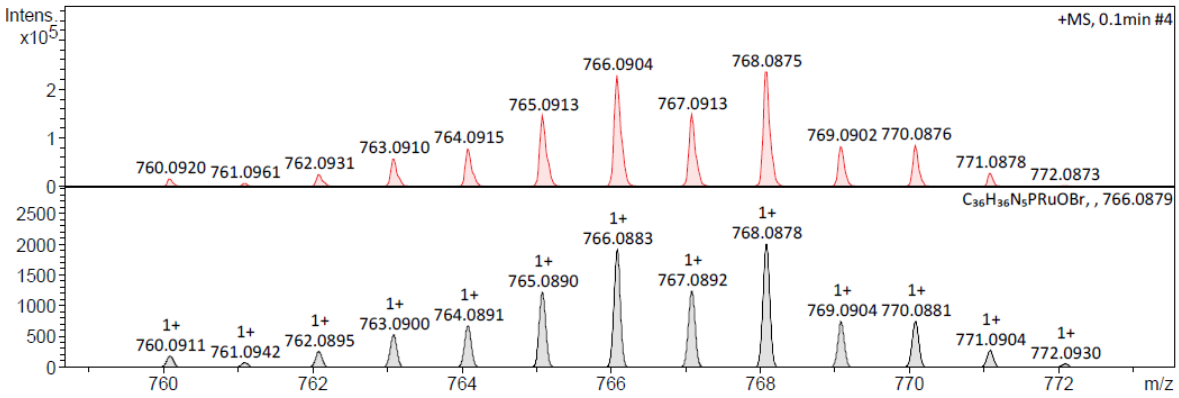

Figure S7. HRMS spectrogram of Complex **1b**.

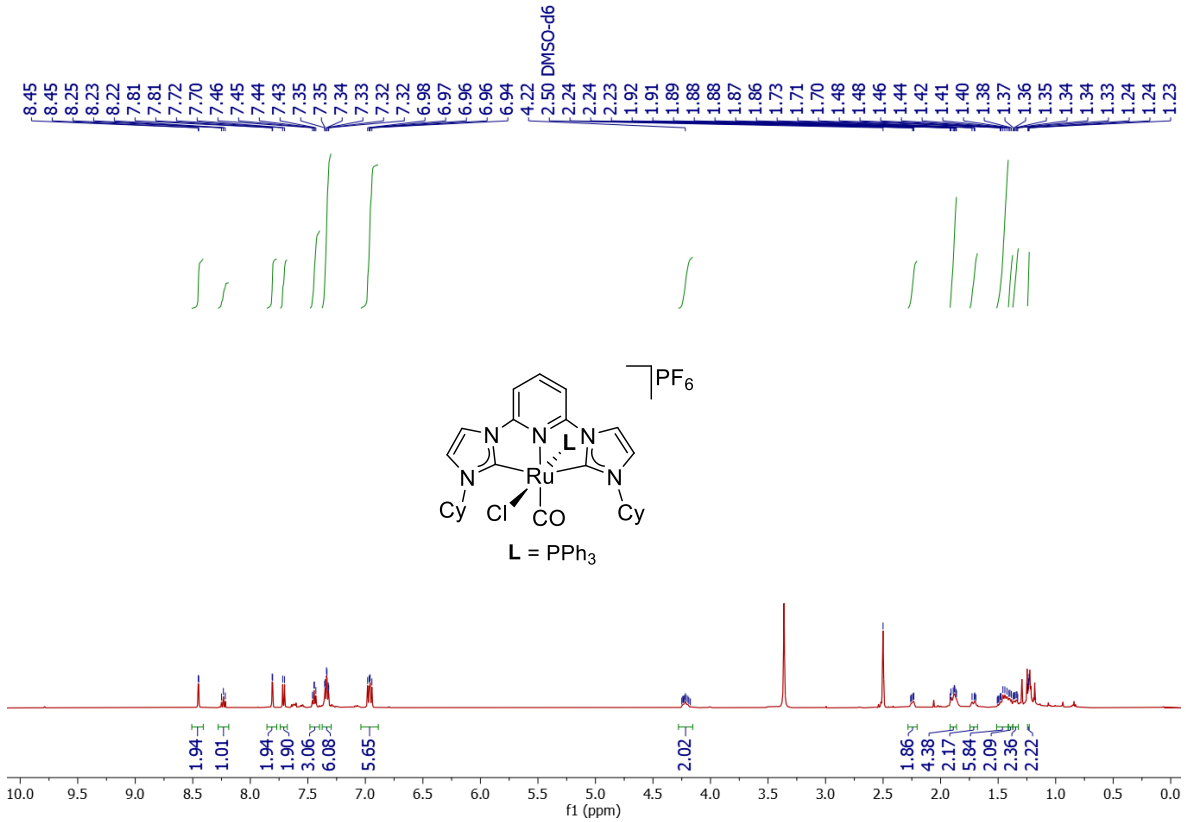

Figure S8. ^{1}H NMR spectrum of Complex **1c**.

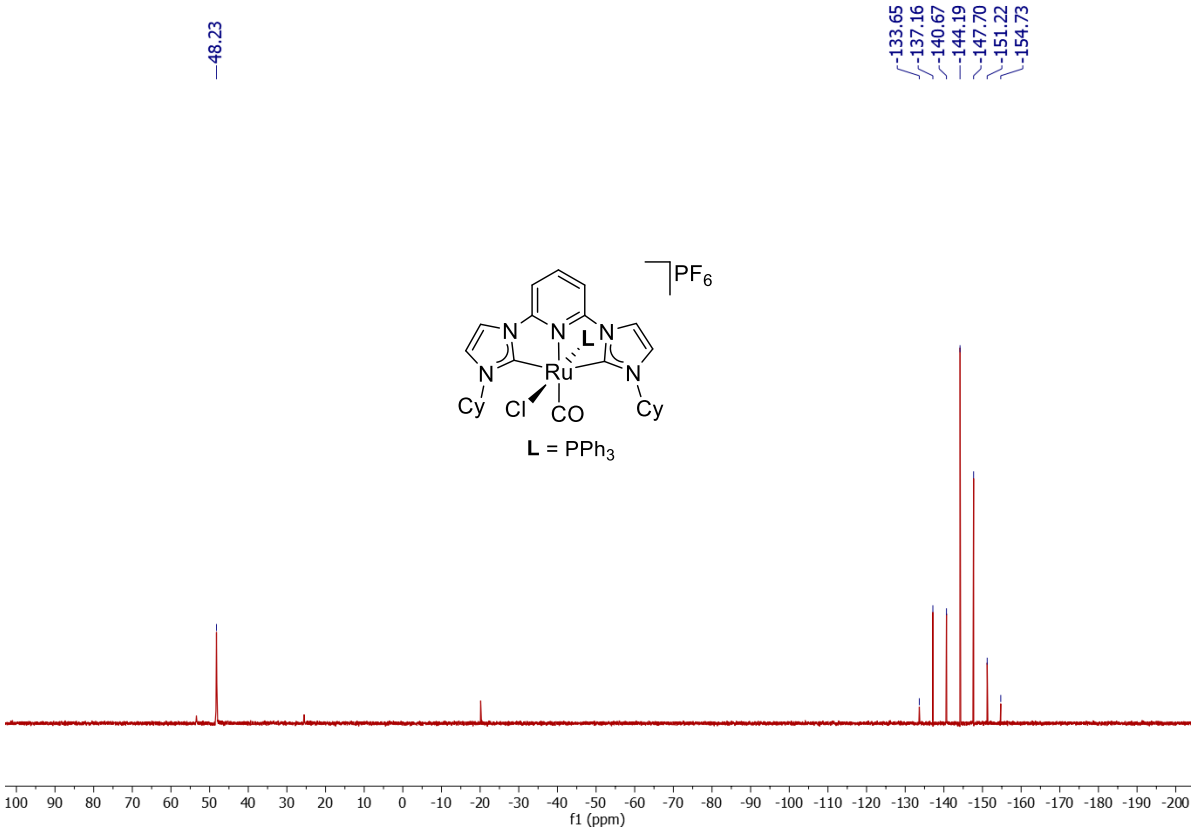

Figure S9. ^{31}P NMR spectrum of Complex **1c**.

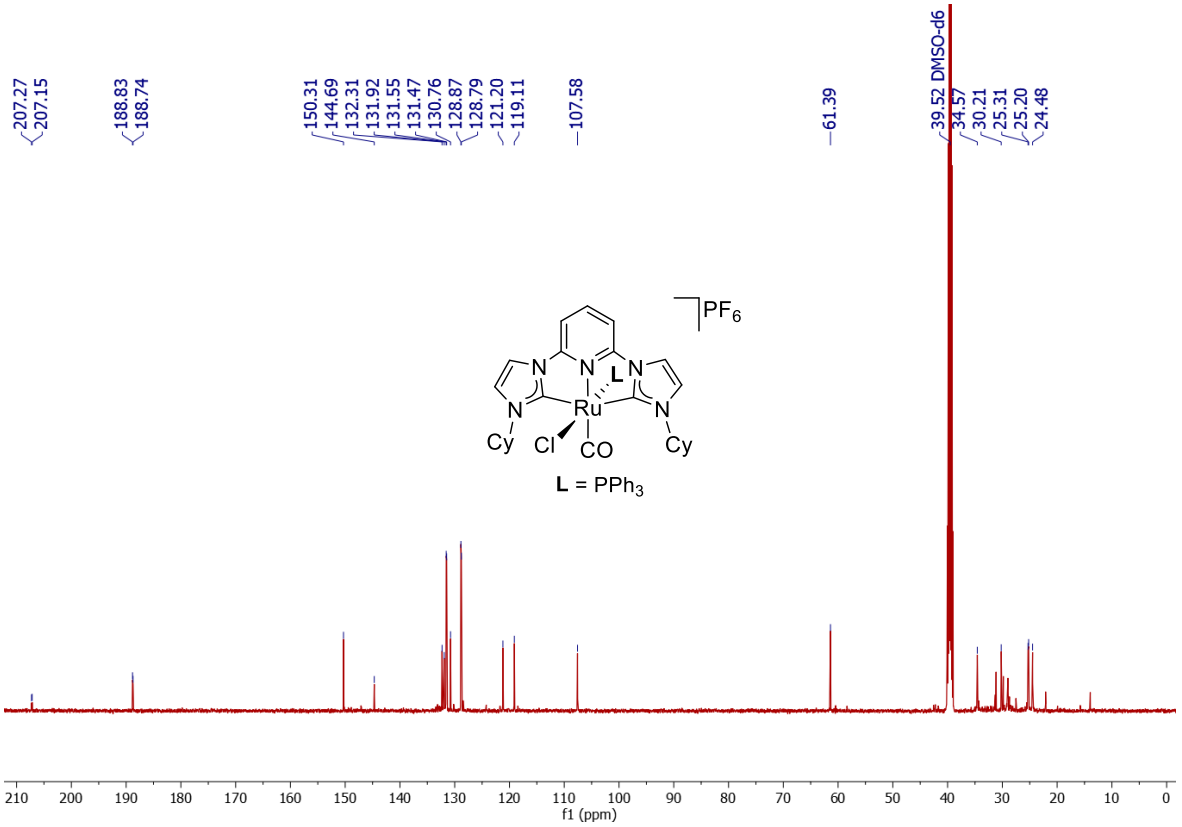

Figure S10. ^{13}C NMR spectrum of Complex **1c**.

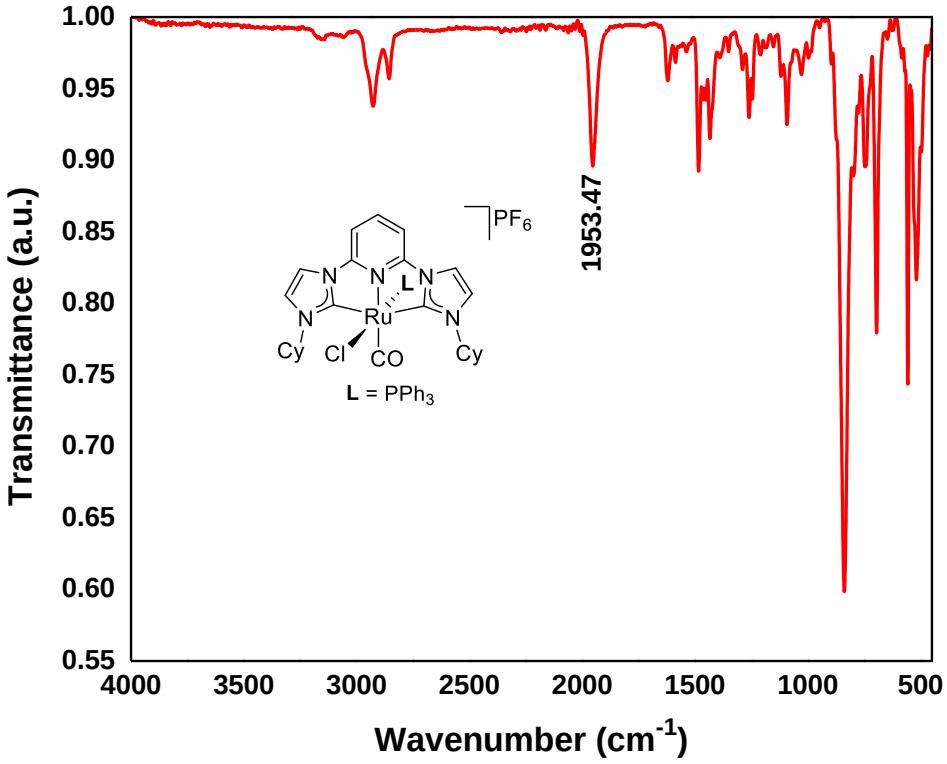

Figure S11. IR spectrum of Complex **1c**.

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Analysis Info

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Sample Name	h chem AKS-RKS-176B	Instrument	micrOTOF-Q 228888.10348
Comment			

Acquisition Parameter

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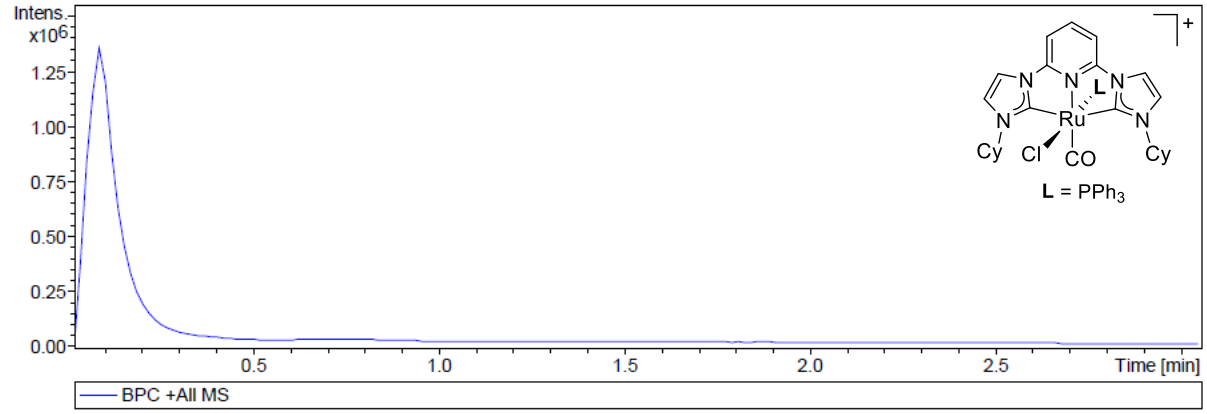

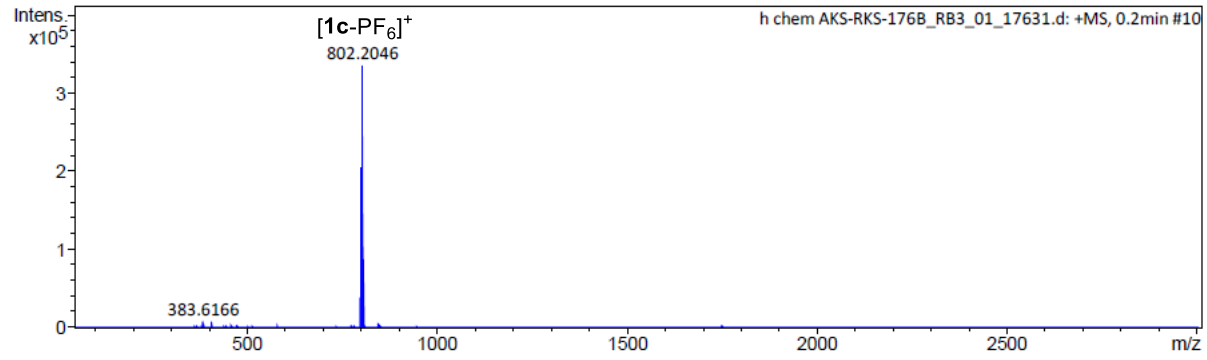

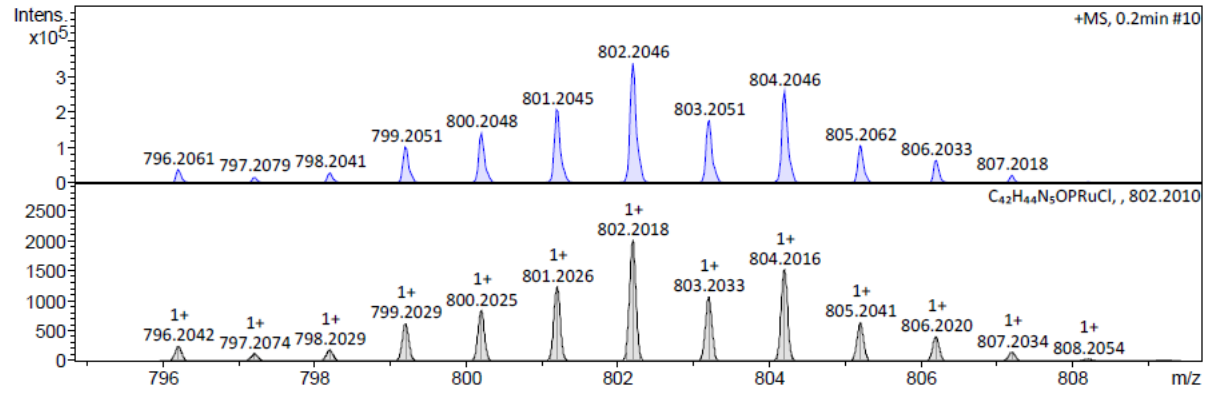

Figure S12. HRMS spectrum of complex **1c**.

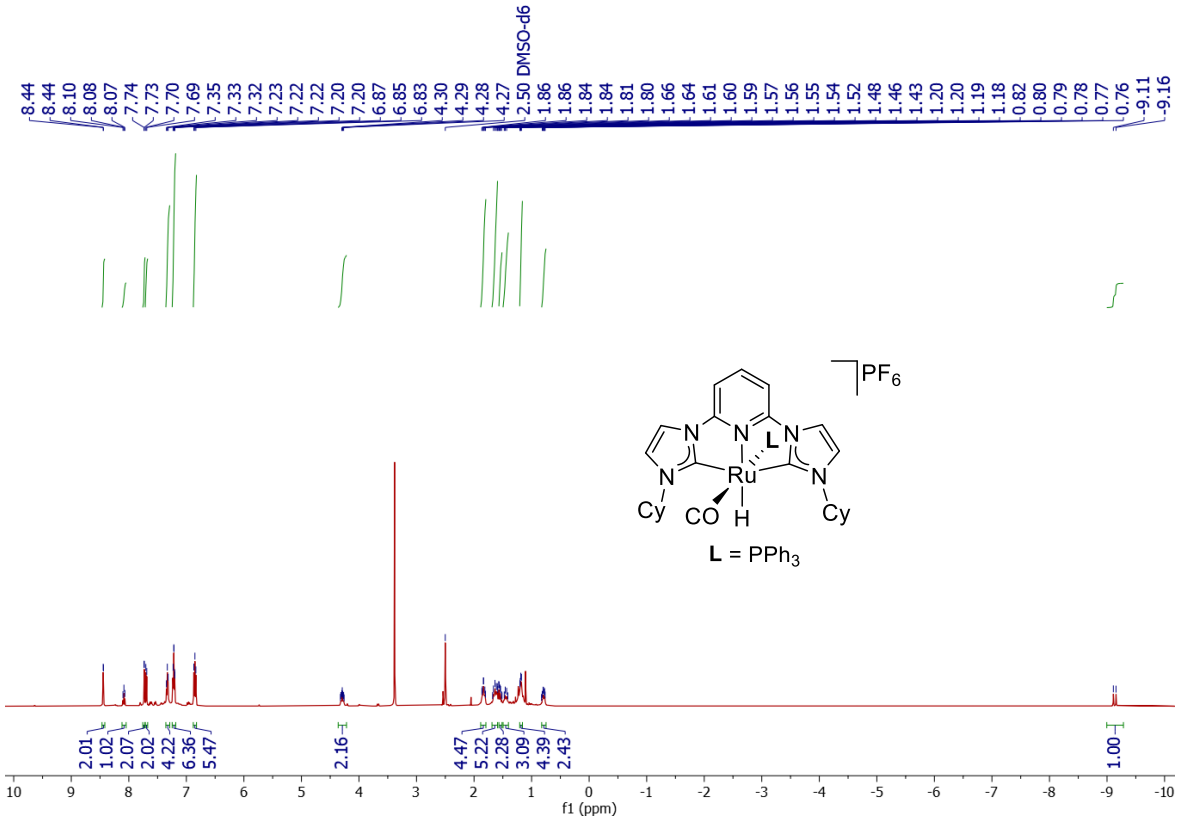

Figure S13. ^{1}H NMR spectrum of Complex **2c**.

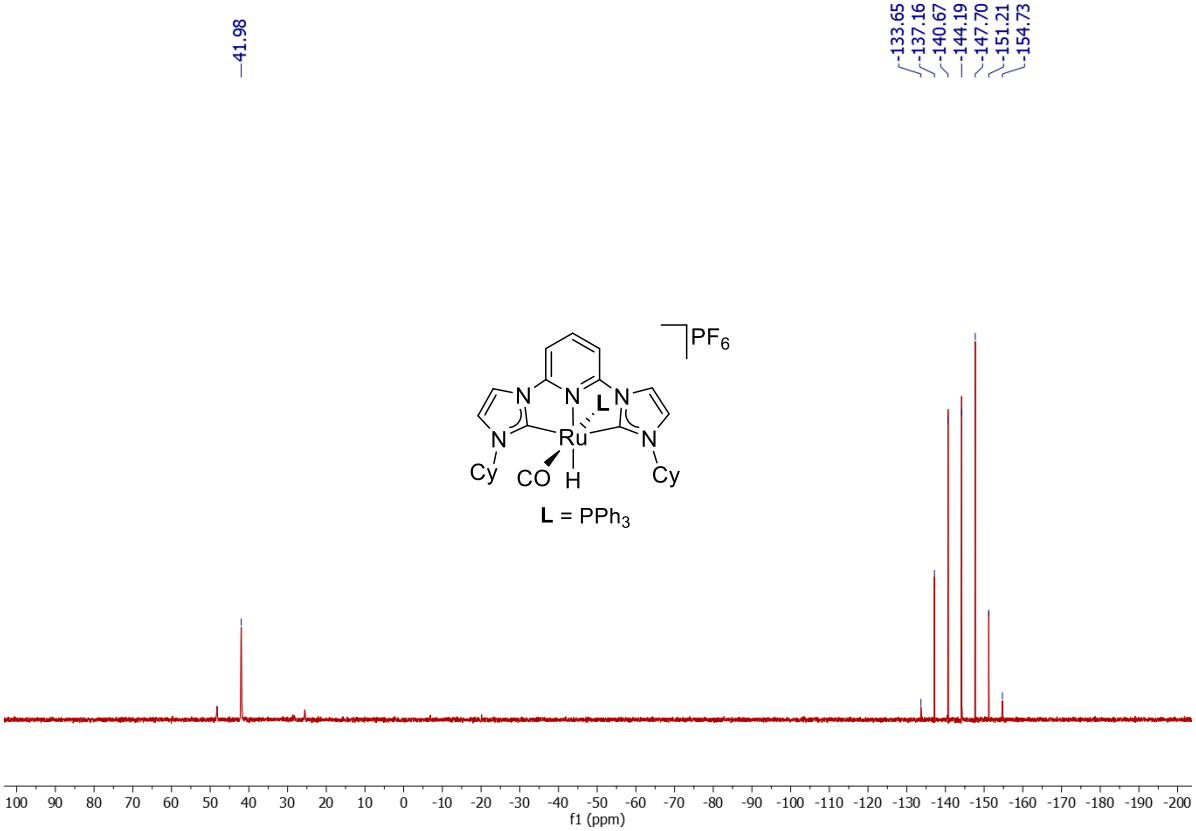

Figure S14. ^{31}P NMR spectrum of Complex **2c**.

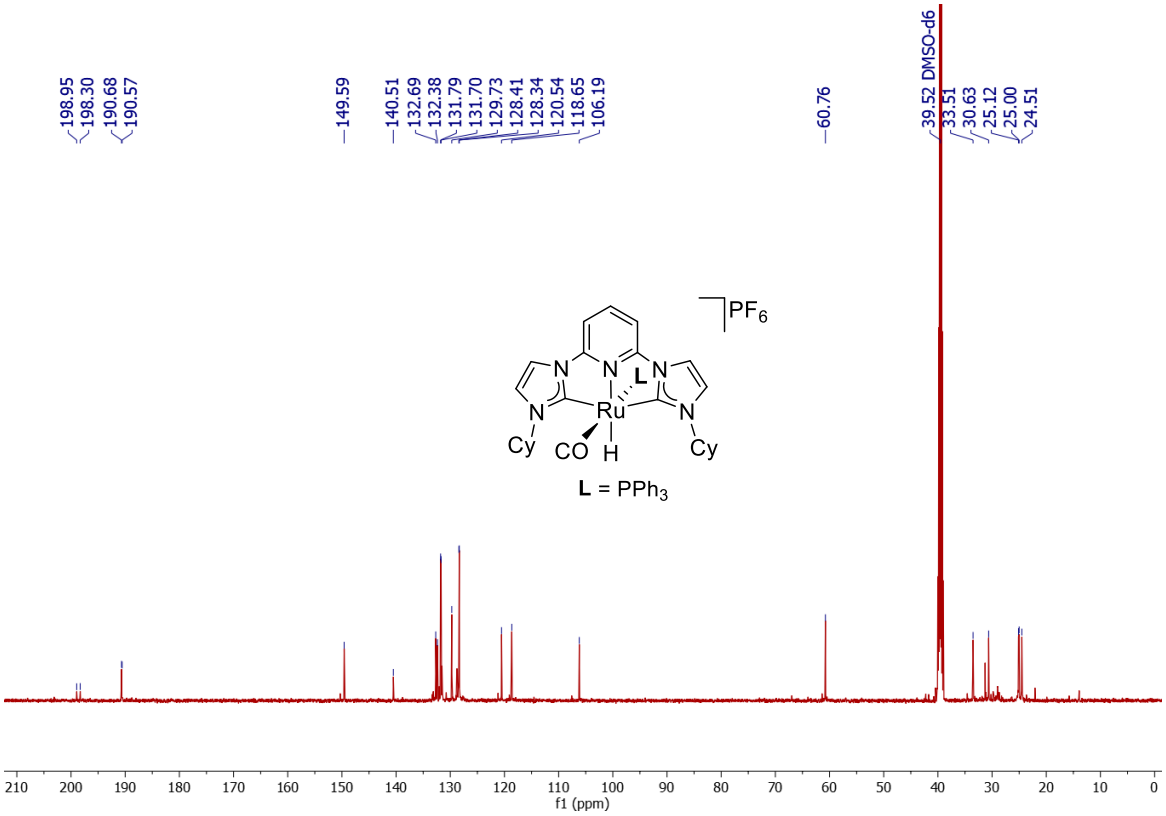

Figure S15. ^{13}C NMR spectrum of Complex **2c**.

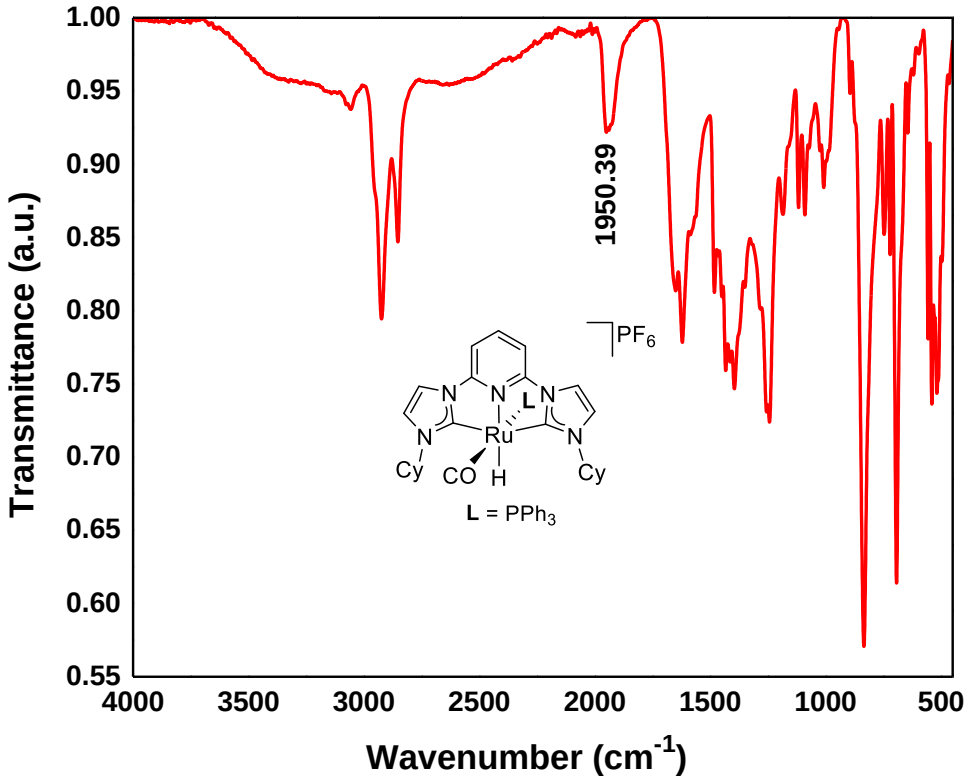

Figure S16. IR spectra of Complex **2c**.

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Method	2. LCMS tune wide ACN.m	Operator	IIT Indore
Sample Name	h chem AKS-RKS-176A	Instrument	micrOTOF-Q 228888.10348
Comment			

Acquisition Parameter

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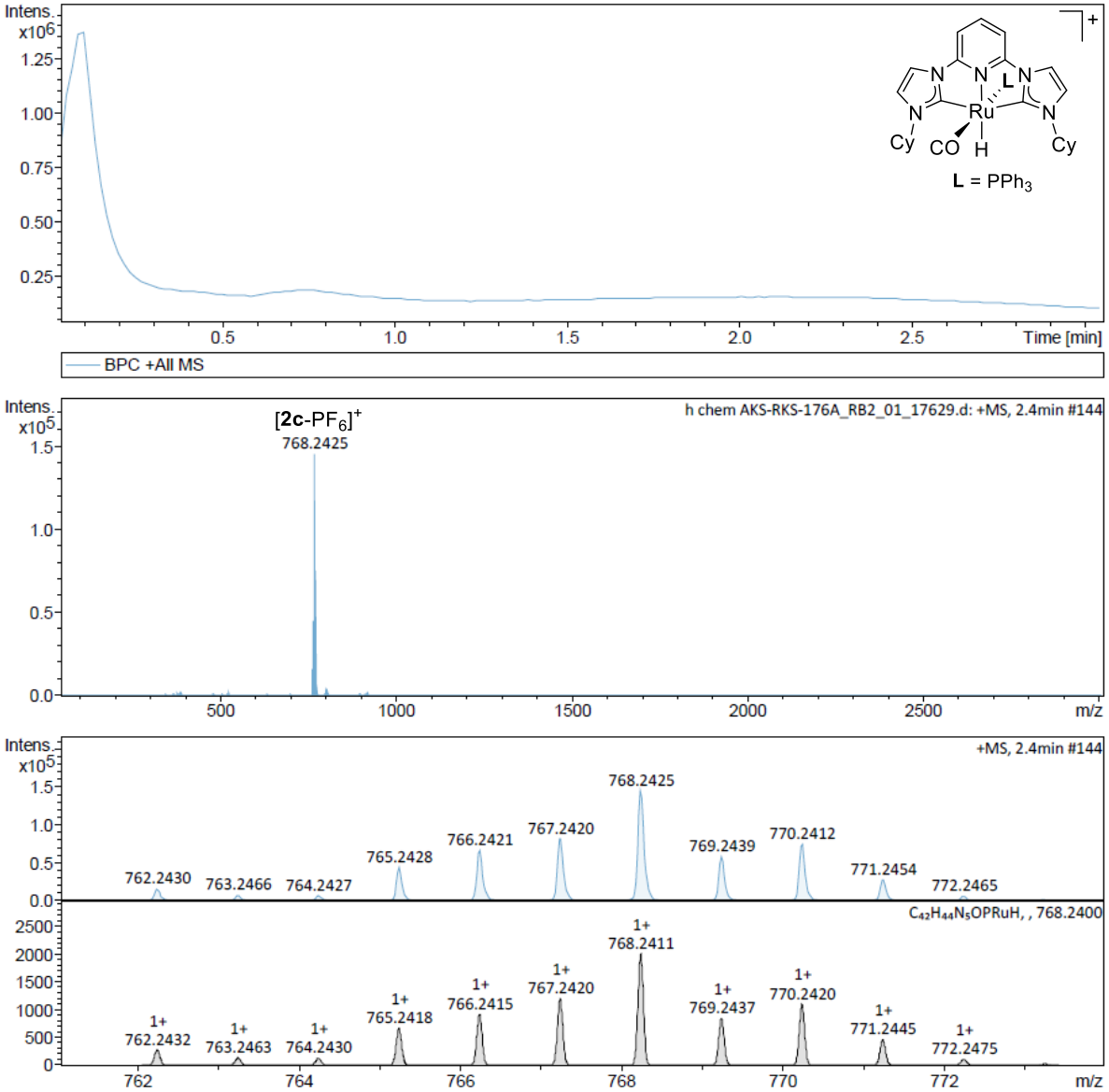

Figure S17. HRMS spectrum of complex **2c**.

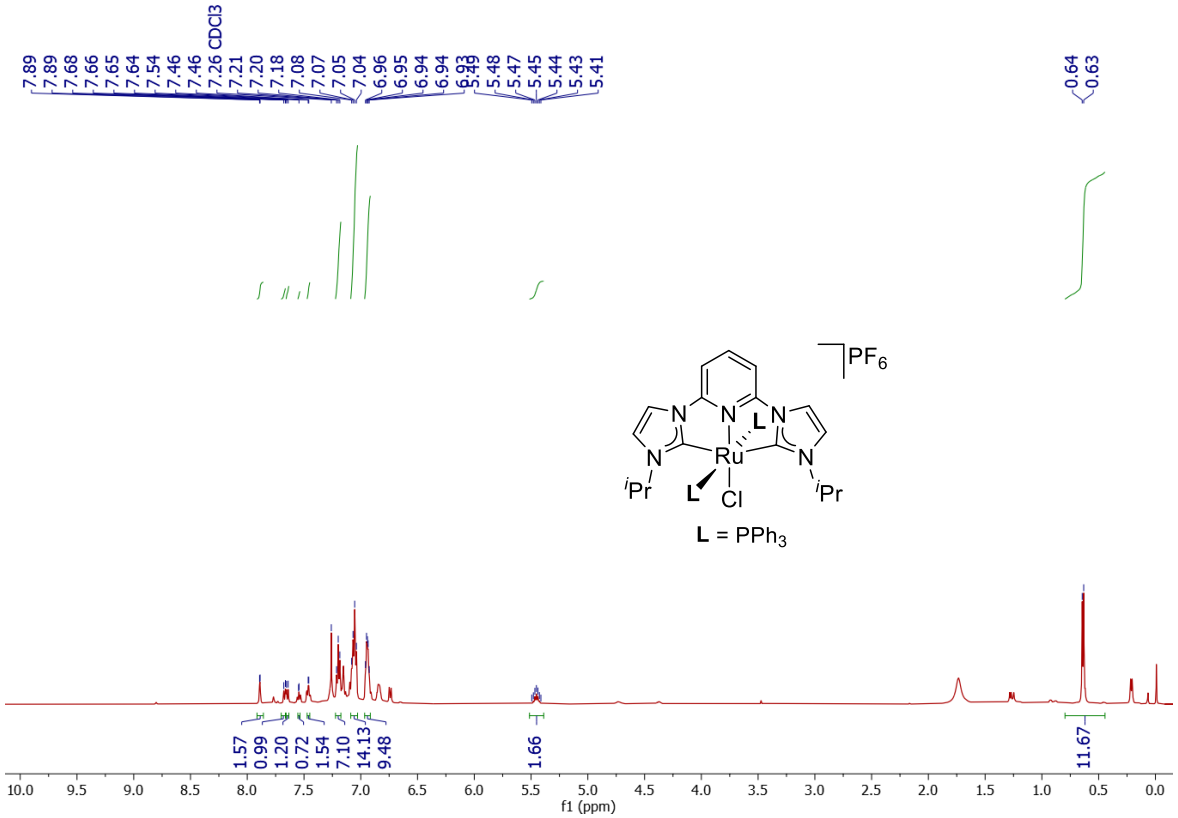

Figure S18. ^{1}H NMR spectrum of Complex **3b**.

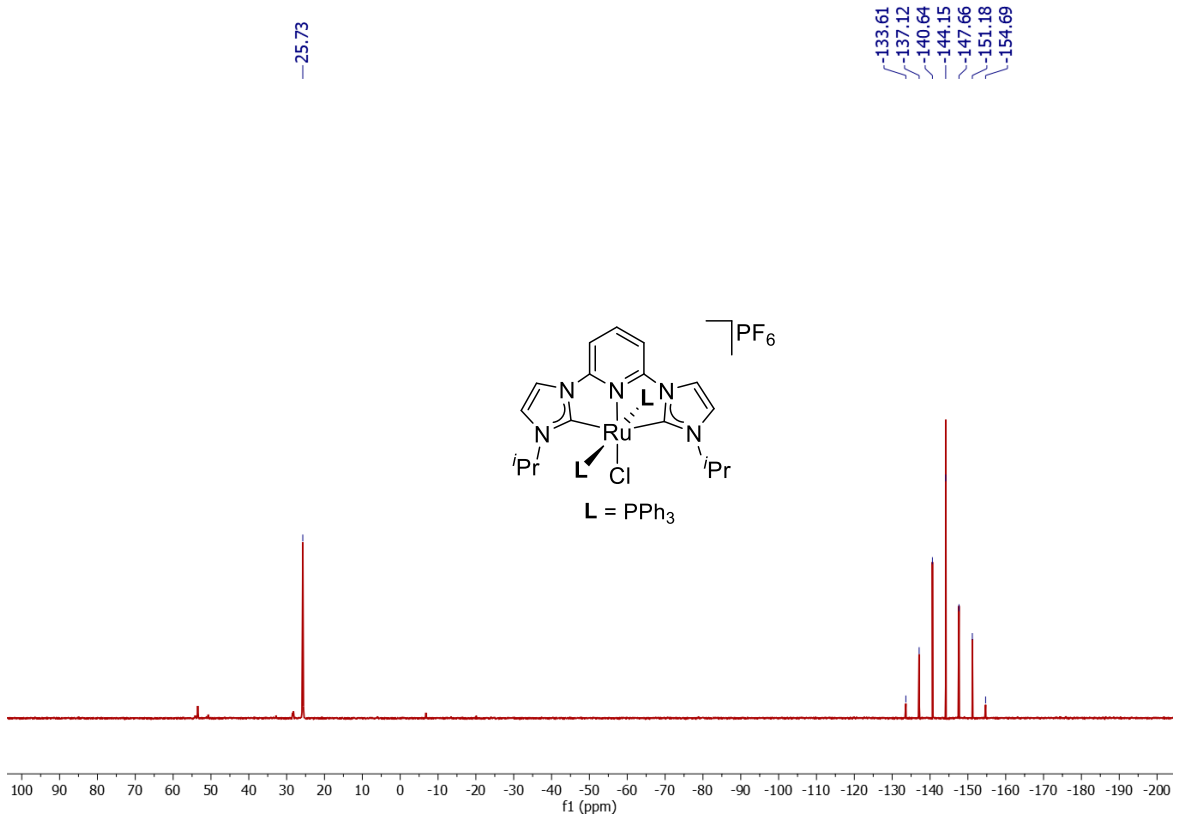

Figure S19. ^{31}P NMR spectrum of Complex **3b**.

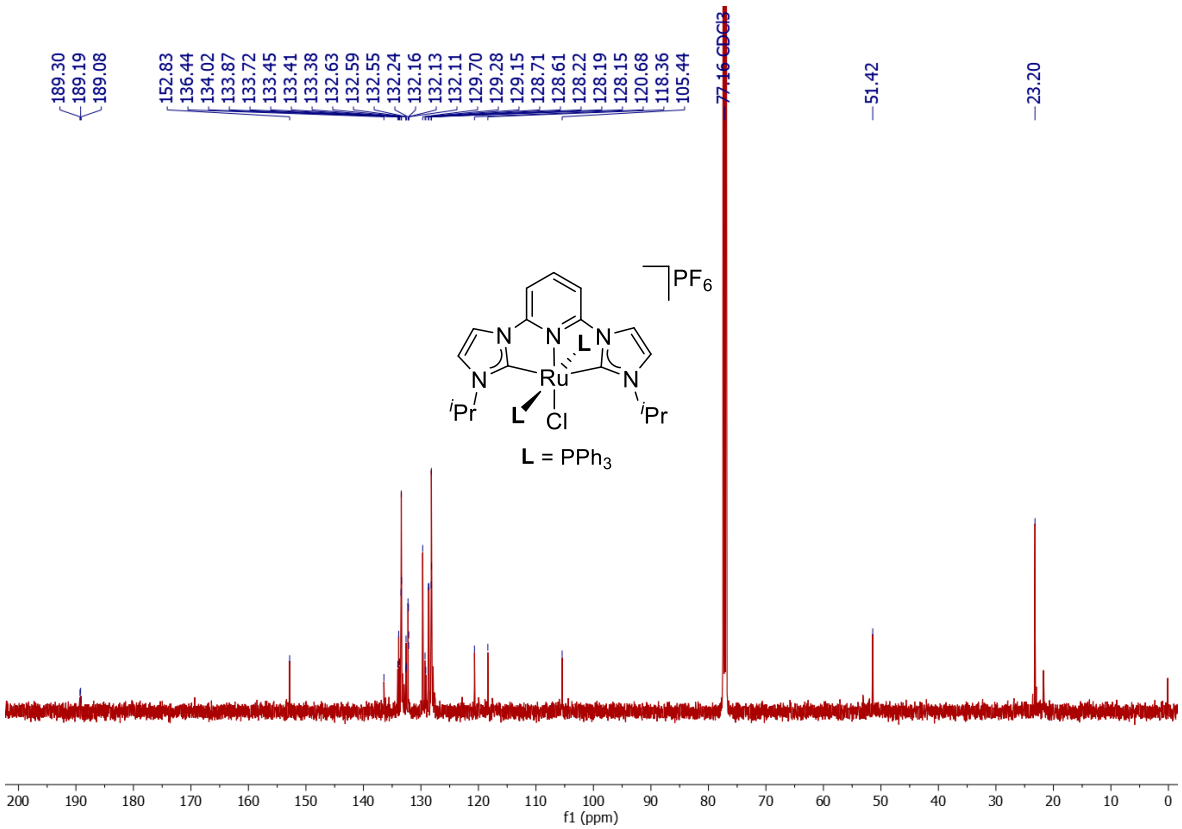

Figure S20. ^{13}C NMR spectrum of Complex **3b**.

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Method	8. LCMS tune wide MeOH.m	Operator	IIT Indore
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Comment			

Acquisition Parameter

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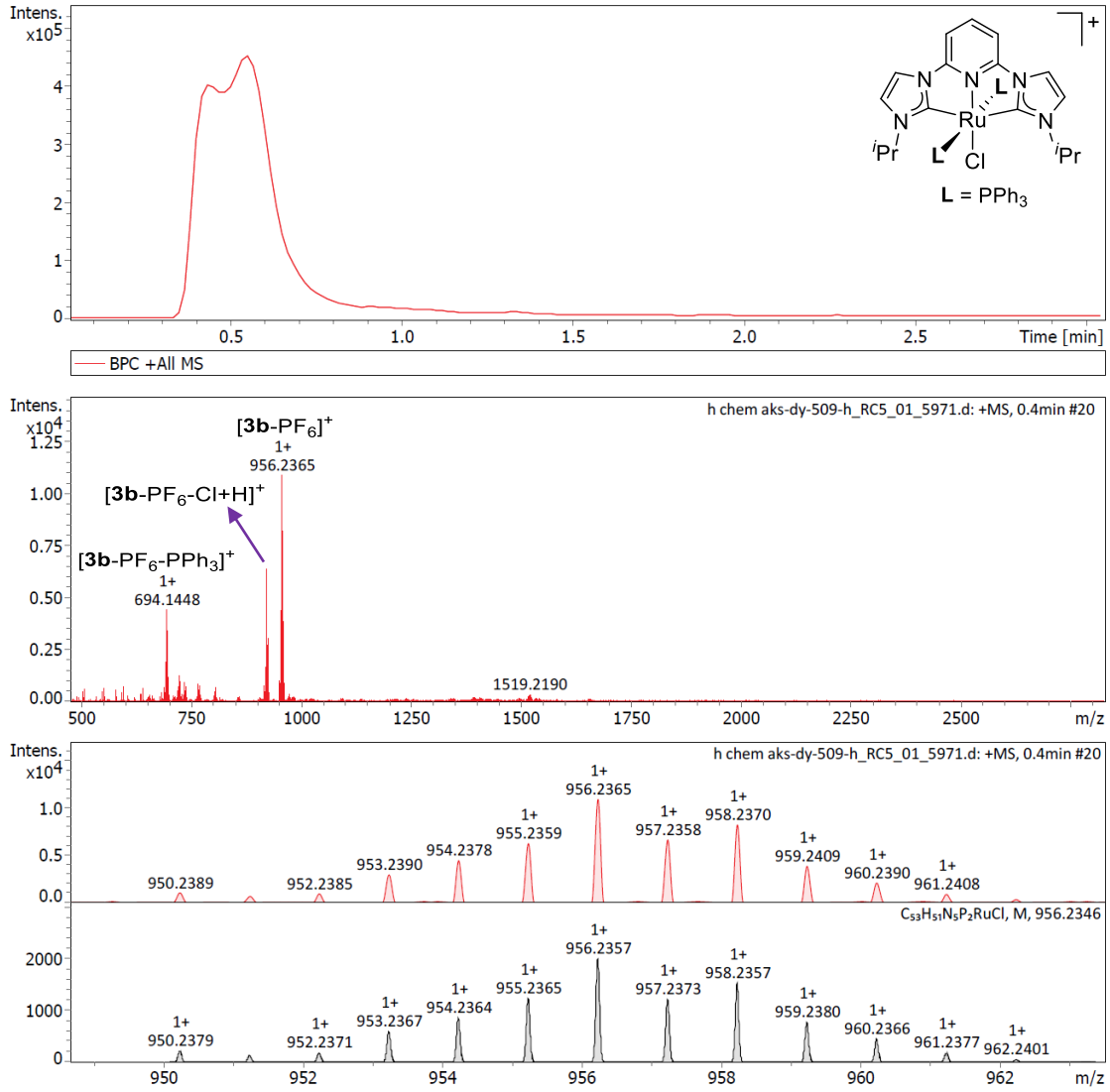

Figure S21. HRMS spectrogram of Complex **3b**.

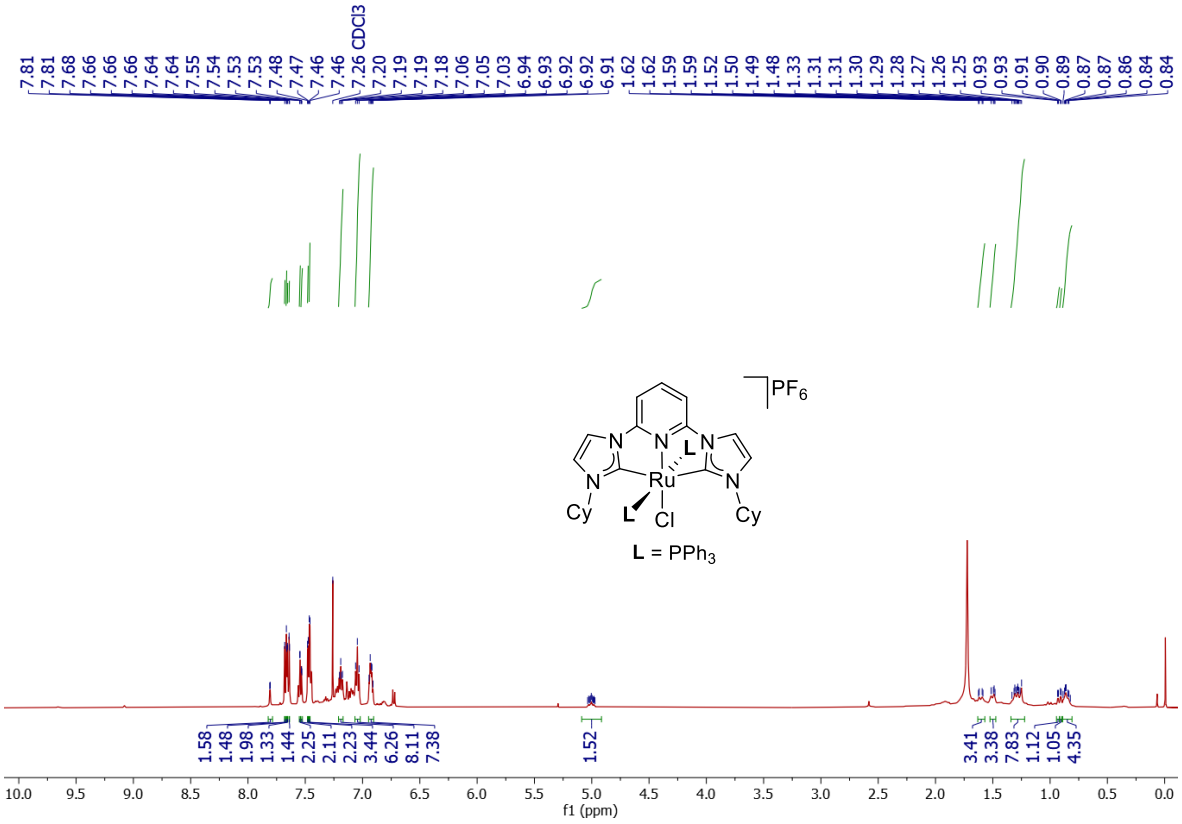

Figure S22. ^{1}H NMR spectrum of Complex **3c**.

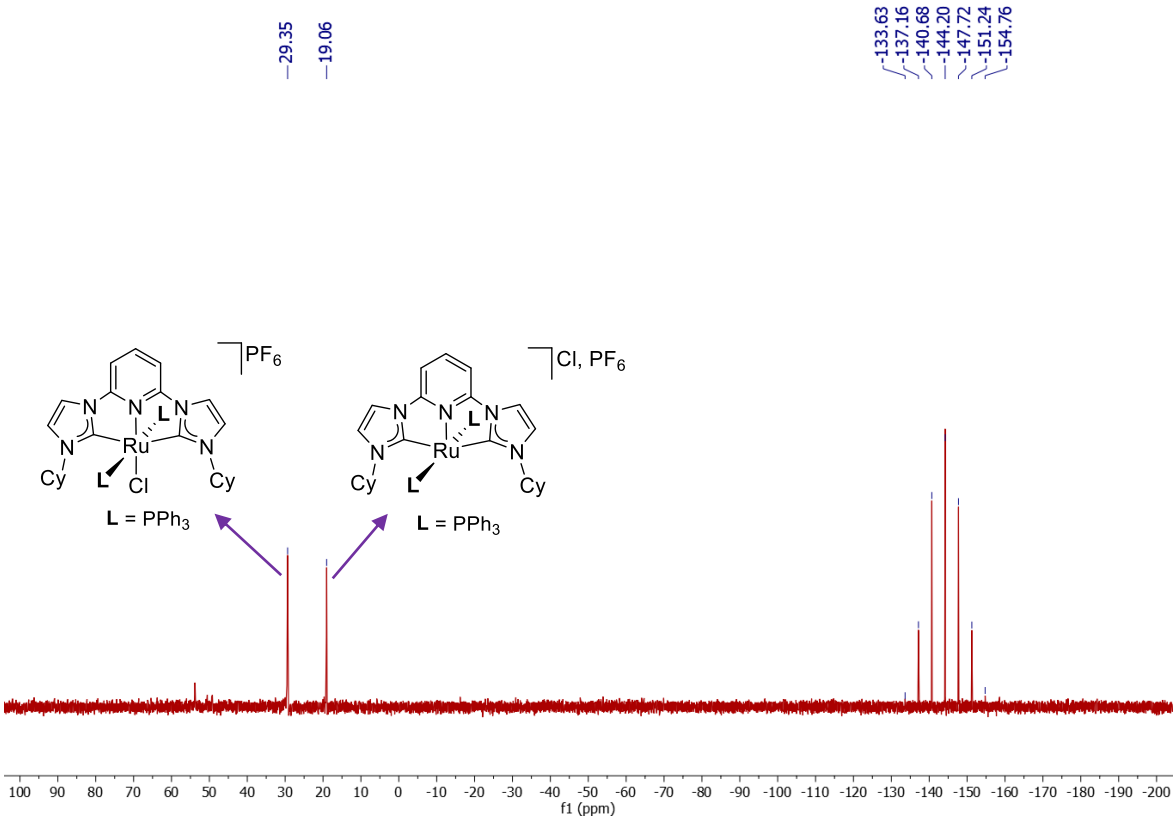

Figure S23. ^{31}P NMR spectrum of Complex **3c**.

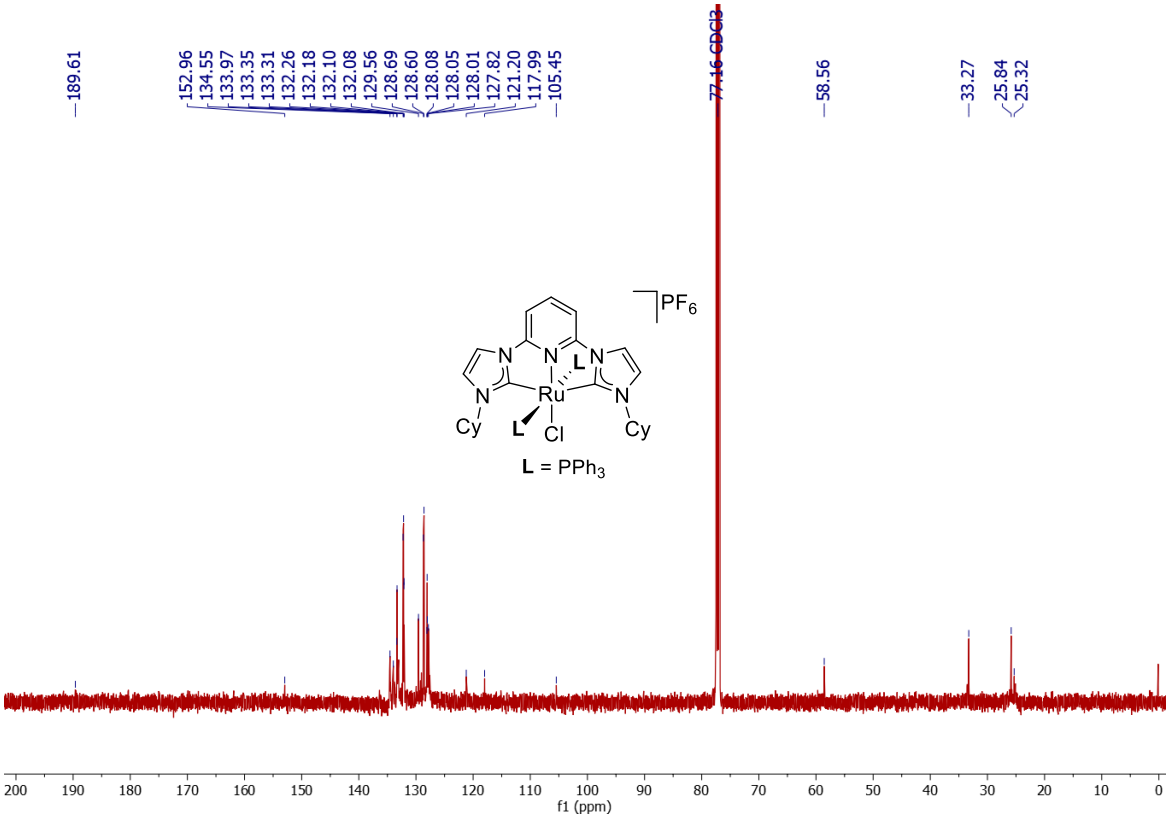

Figure S24. ^{13}C NMR spectrum of Complex **3c**.

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Sample Name	h chem AKS-RKS-177	Instrument	micrOTOF-Q 228888.10348
Comment			

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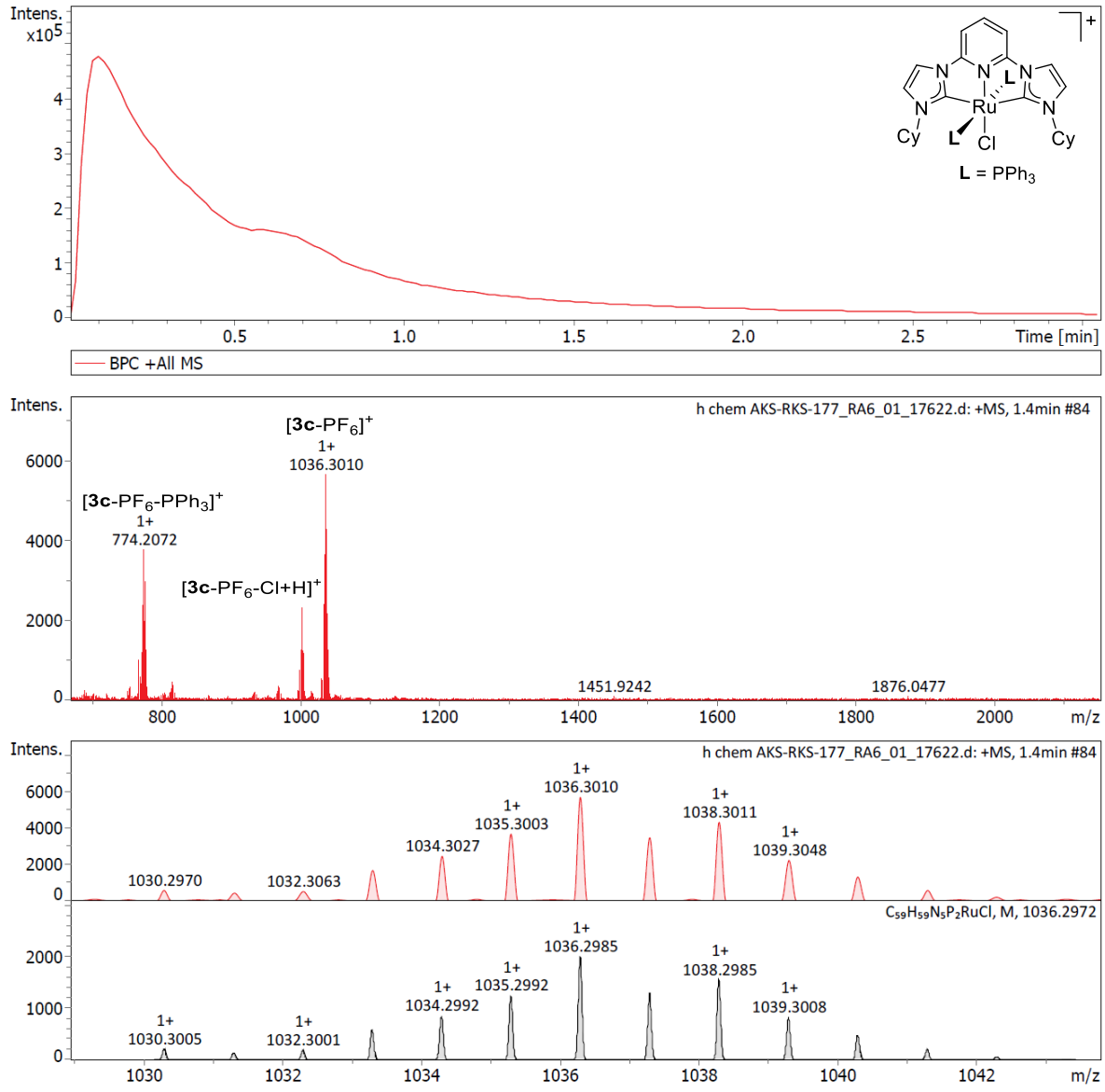

Figure S25. HRMS spectrogram of Complex **3c**.

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Comment			

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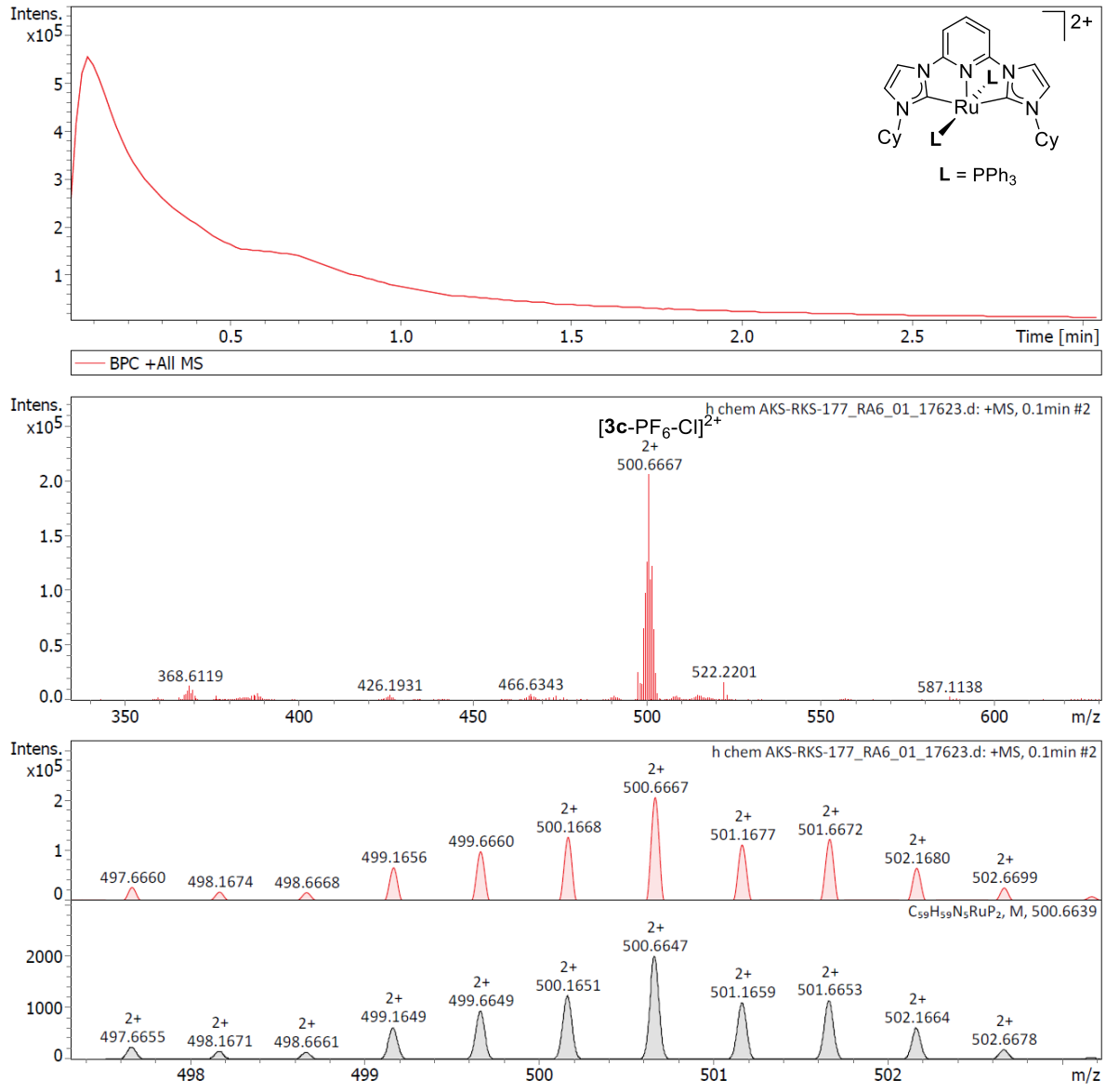

Figure S26. HRMS spectrogram of dicationic complex [**3c**-PF_6-Cl]$^{2+}$.

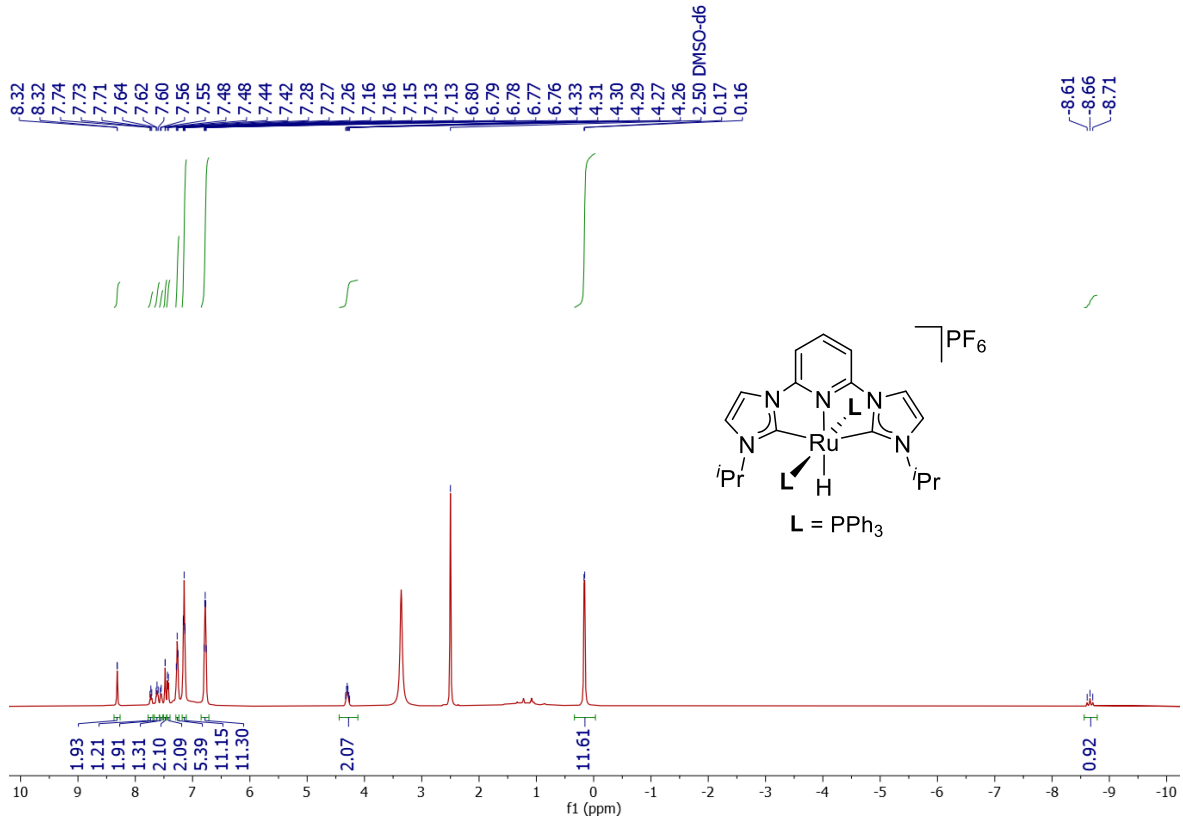

Figure S27. ^{1}H NMR spectrum of Complex **4b**.

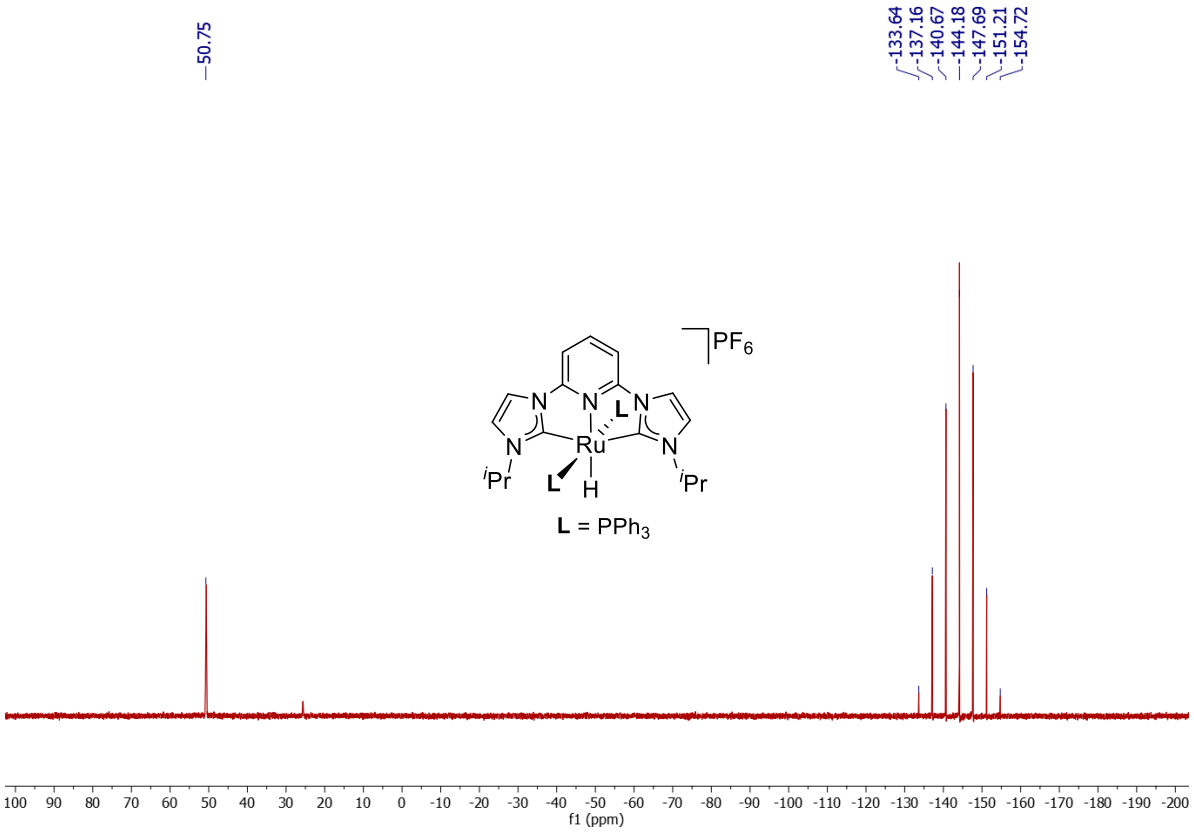

Figure S28. ^{31}P NMR spectrum of Complex **4b**.

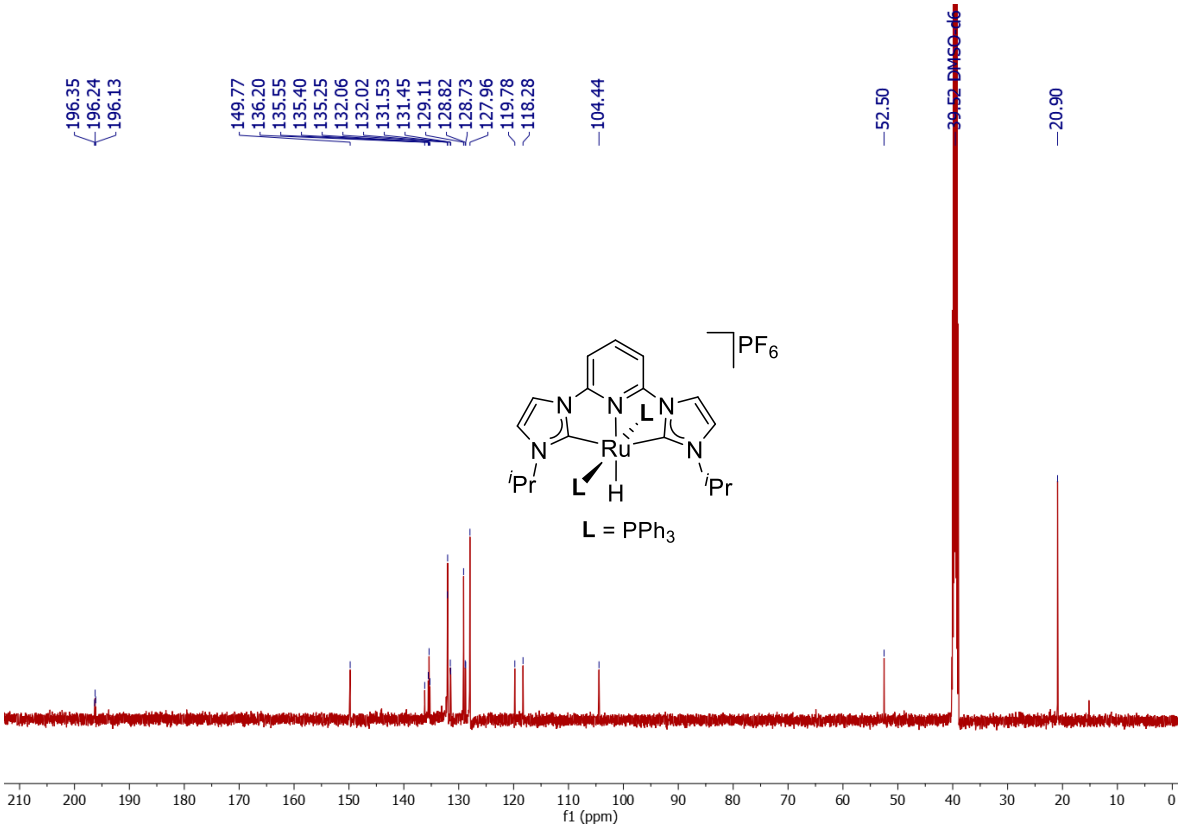

Figure S29. ^{13}C NMR spectrum of Complex **4b**.

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Sample Name	h chem-aks-dy-510-h	Instrument	micrOTOF-Q 228888.10348
Comment			

Acquisition Parameter

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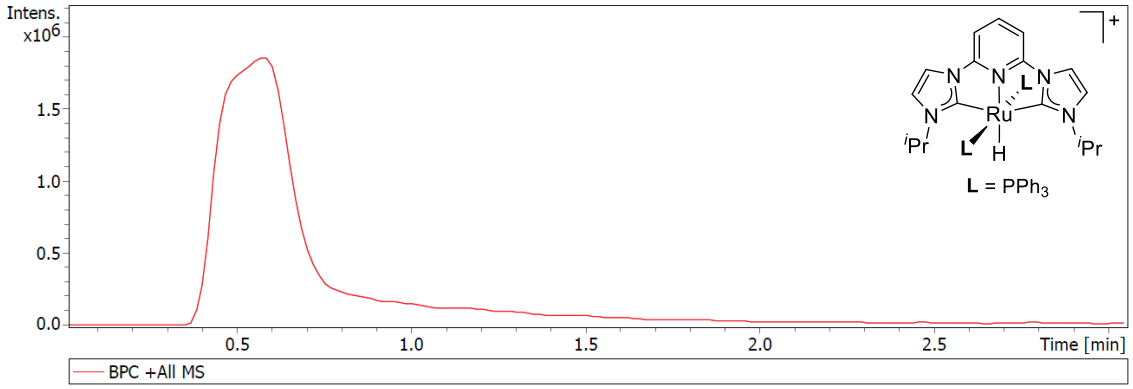
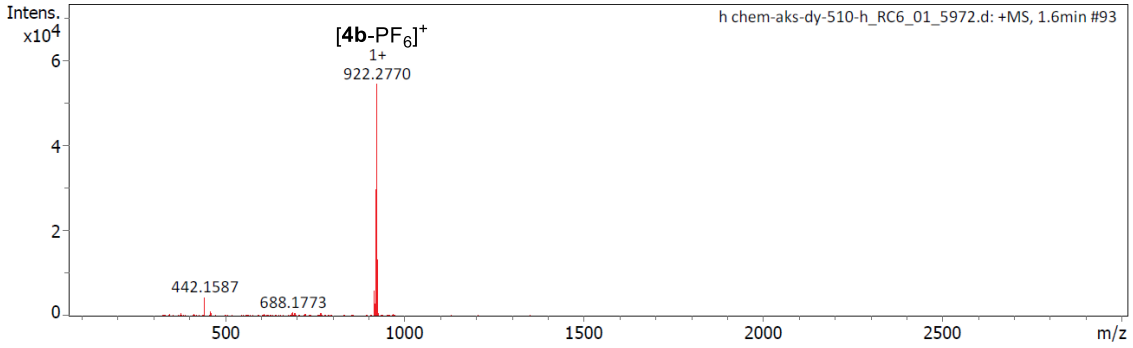




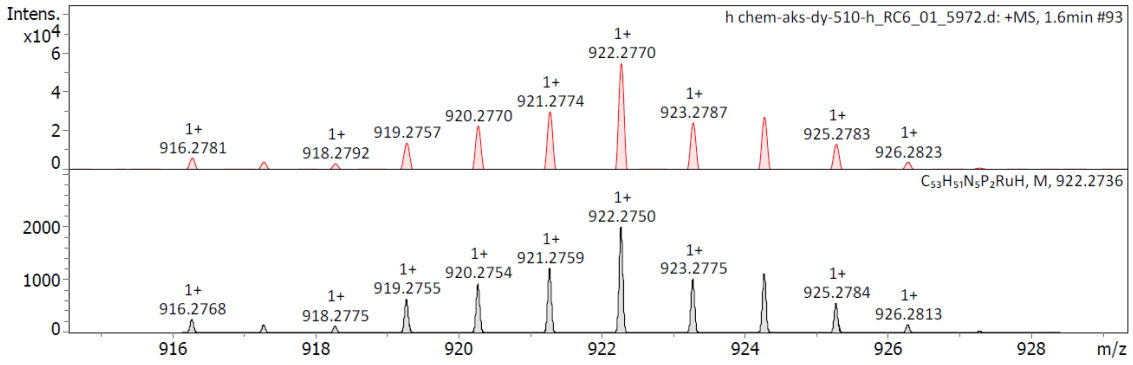


Figure S30. HRMS spectrogram of Complex **4b**.

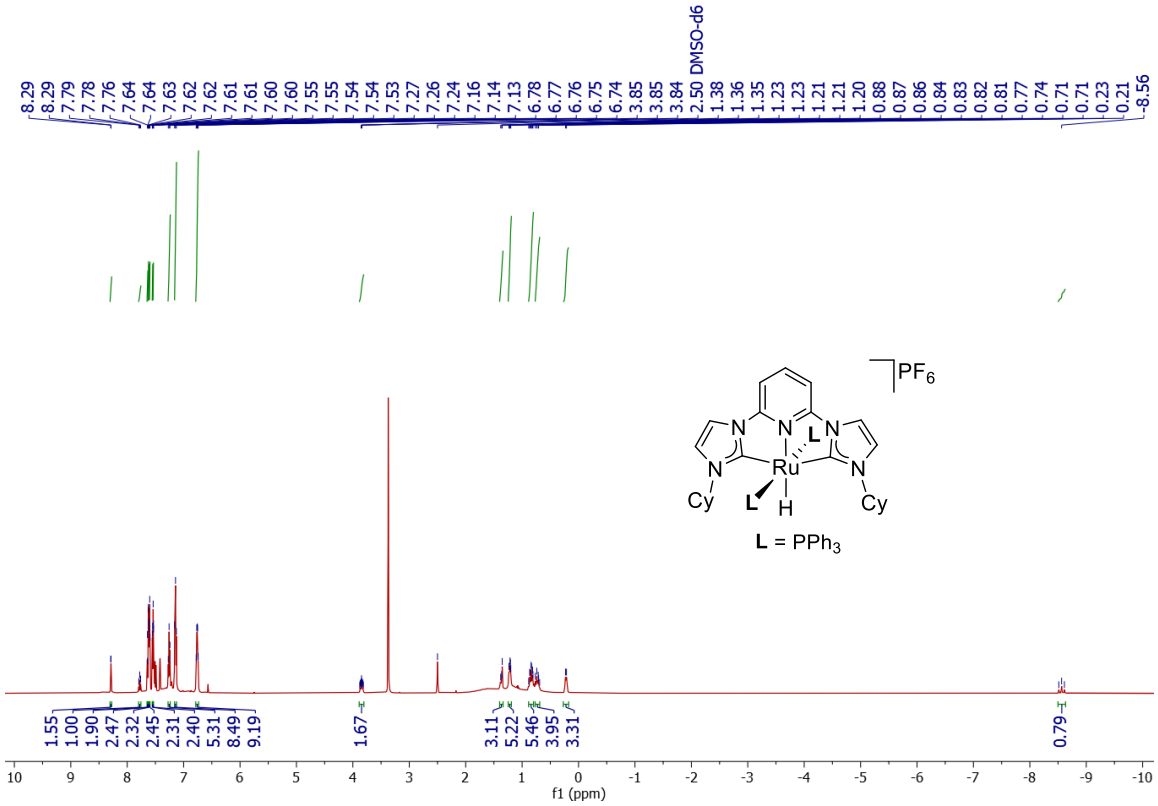


Figure S31. ^{1}H NMR spectrum of Complex **4c**.

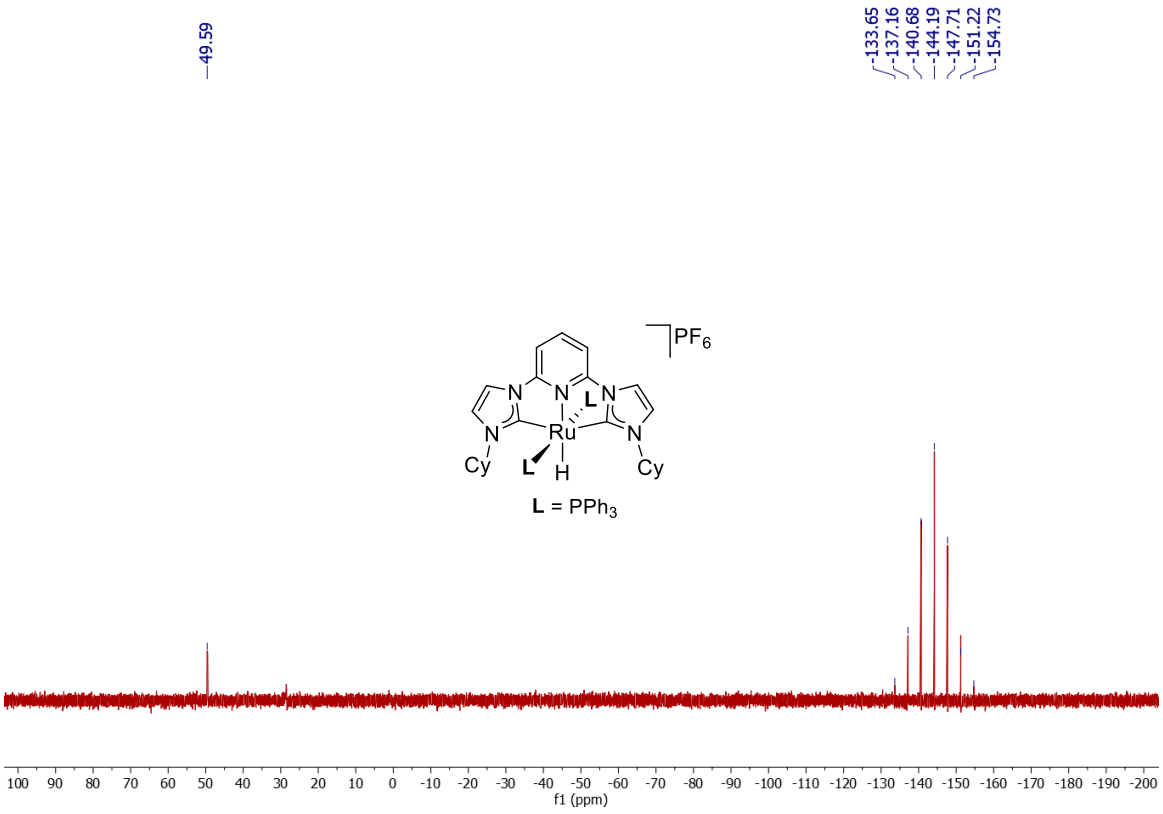


Figure S32. ^{31}P NMR spectrum of Complex **4c**.

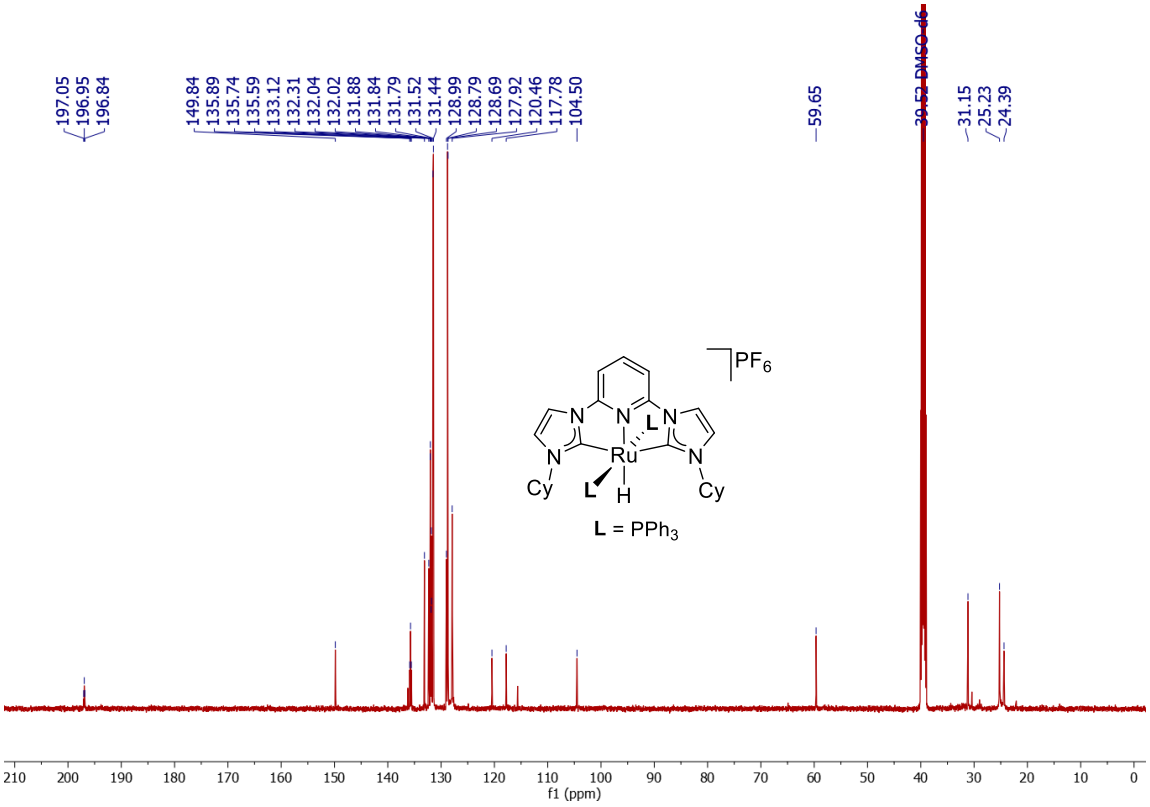


Figure S33. ^{13}C NMR spectrum of Complex **4c**.

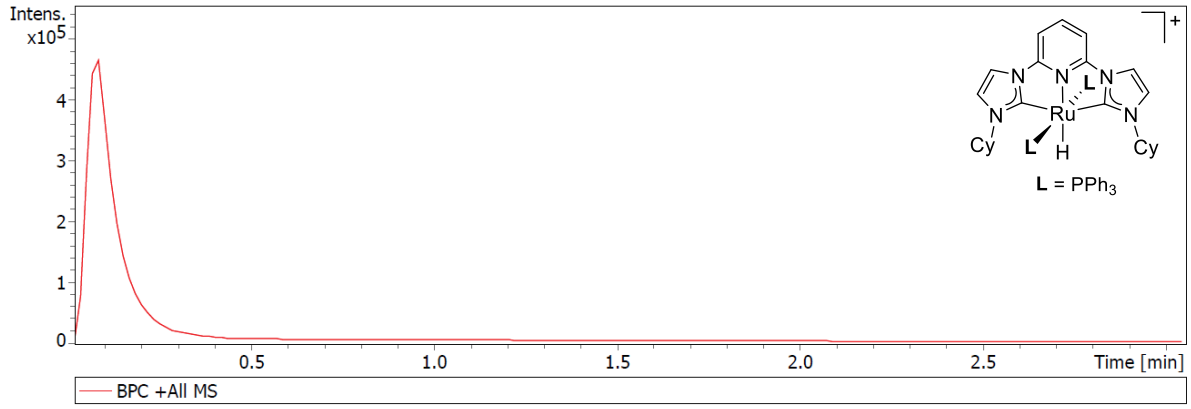
Display Report

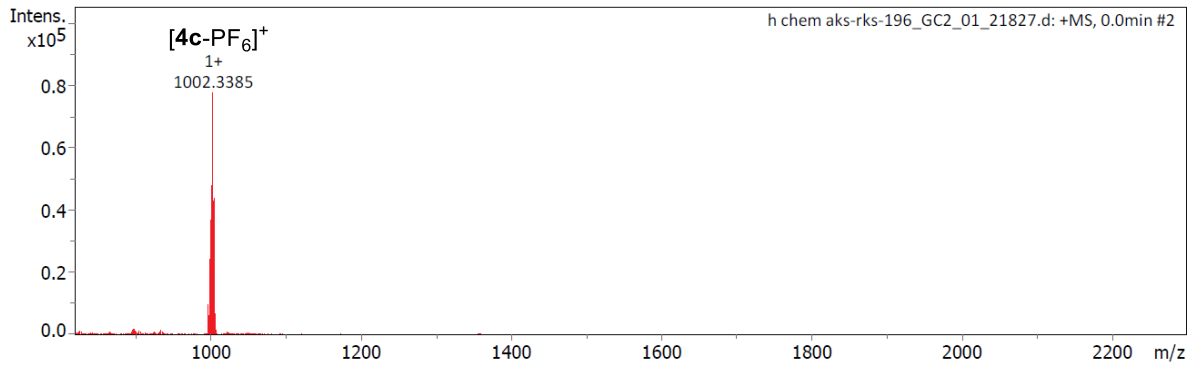
Analysis Info

Analysis Name	C:\Users\Rahul Kumar Singh\Desktop\h chem aks-rks-196_GC2_01_21827.d	Acquisition Date	11-01-2023 15:05:39
Method	2. LCMS tune wide ACN.m	Operator	IIT Indore
Sample Name	h chem aks-rks-196	Instrument	micrOTOF-Q 228888.10348
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	250 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	650.0 Vpp	Set Divert Valve	Waste





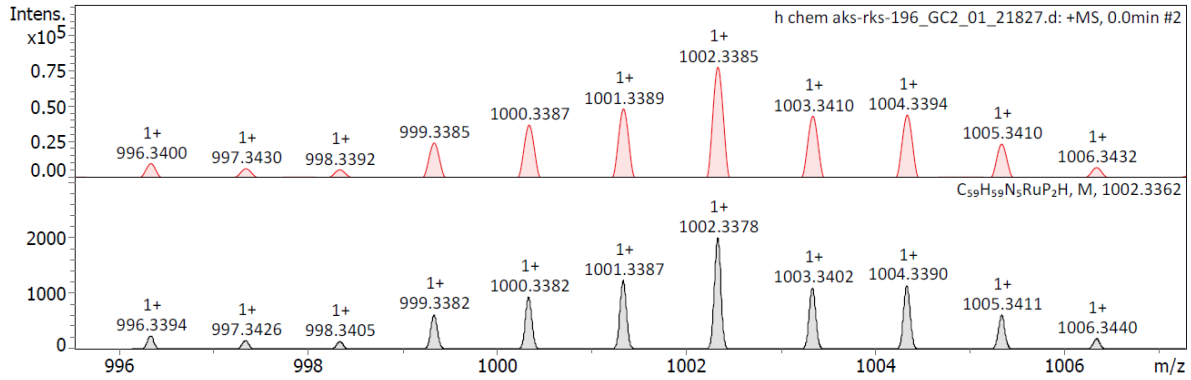


Figure S34. HRMS spectrogram of Complex **4c**.

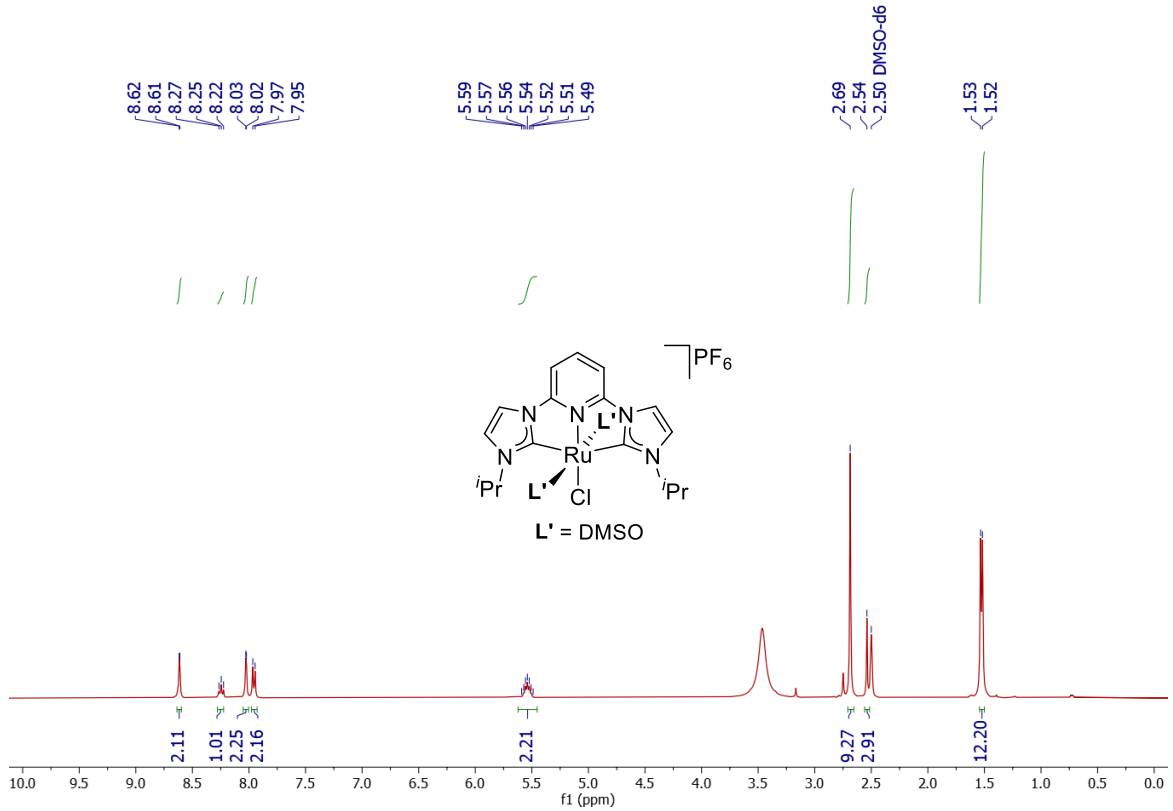


Figure S35. ^{1}H NMR spectrum of Complex **6b**.

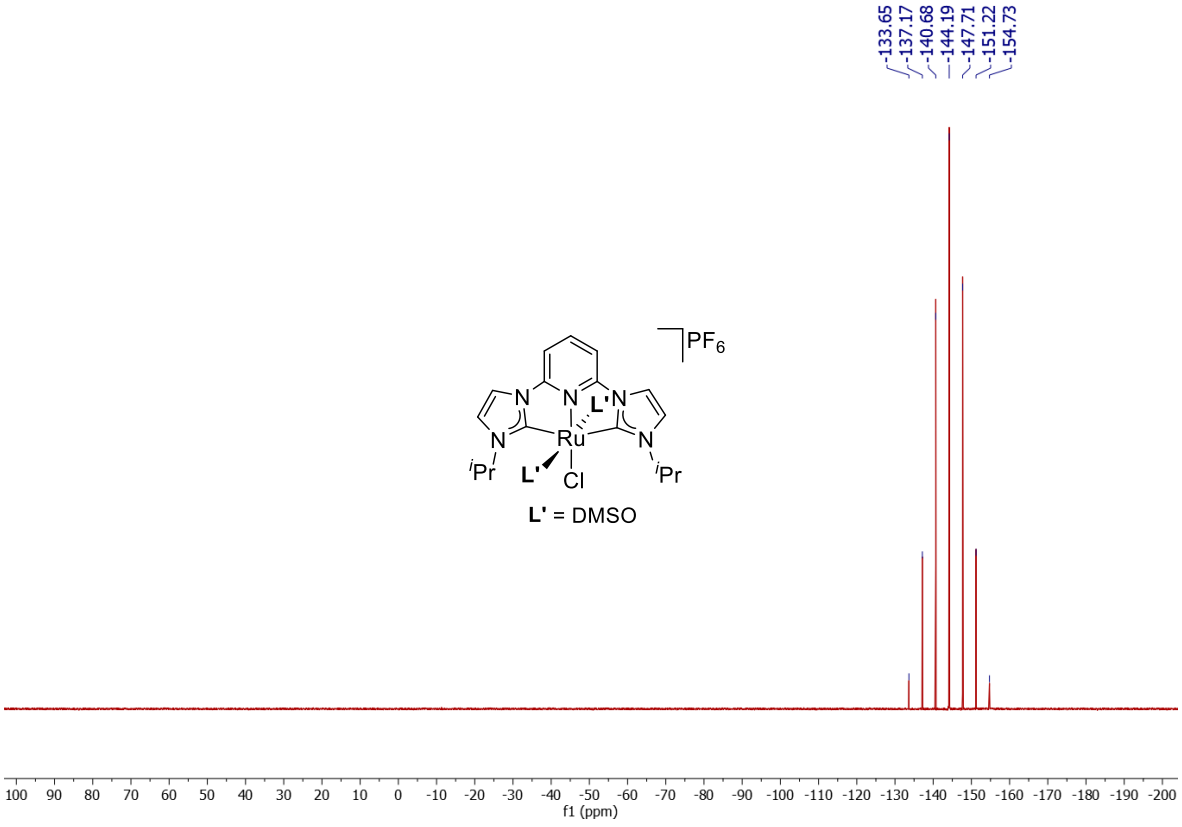


Figure S36. ^{31}P NMR spectrum of Complex **6b**.

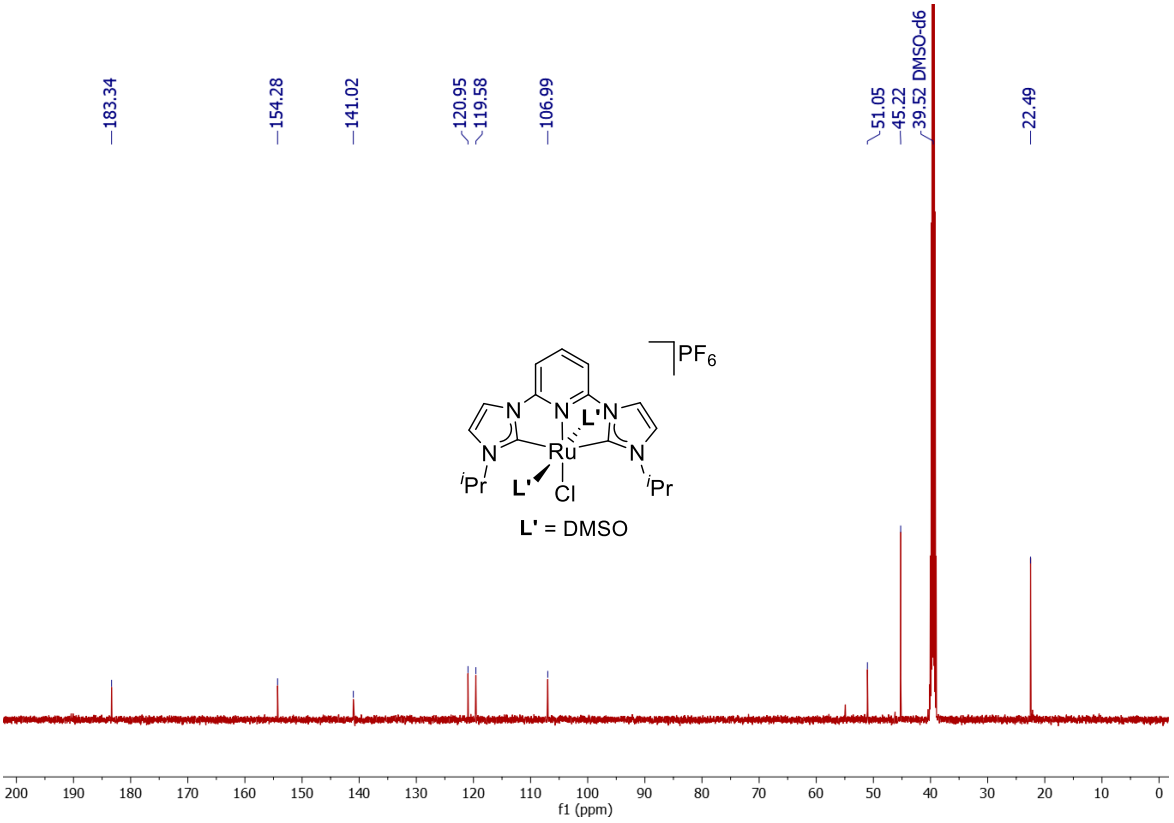


Figure S37. ^{13}C NMR spectrum of Complex **6b**.

Display Report

Analysis Info

Analysis Name	D:\Data\October 2021\h chem AKS-DY-DIPR-a_RA3_01_10202.d	Acquisition Date	10/21/2021 4:07:56 PM
Method	2. LCMS tune wide ACN.m	Operator	IIT Indore
Sample Name	h chem AKS-DY-DIPR-a	Instrument	micrOTOF-Q 228888.10348
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	250 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	650.0 Vpp	Set Divert Valve	Waste

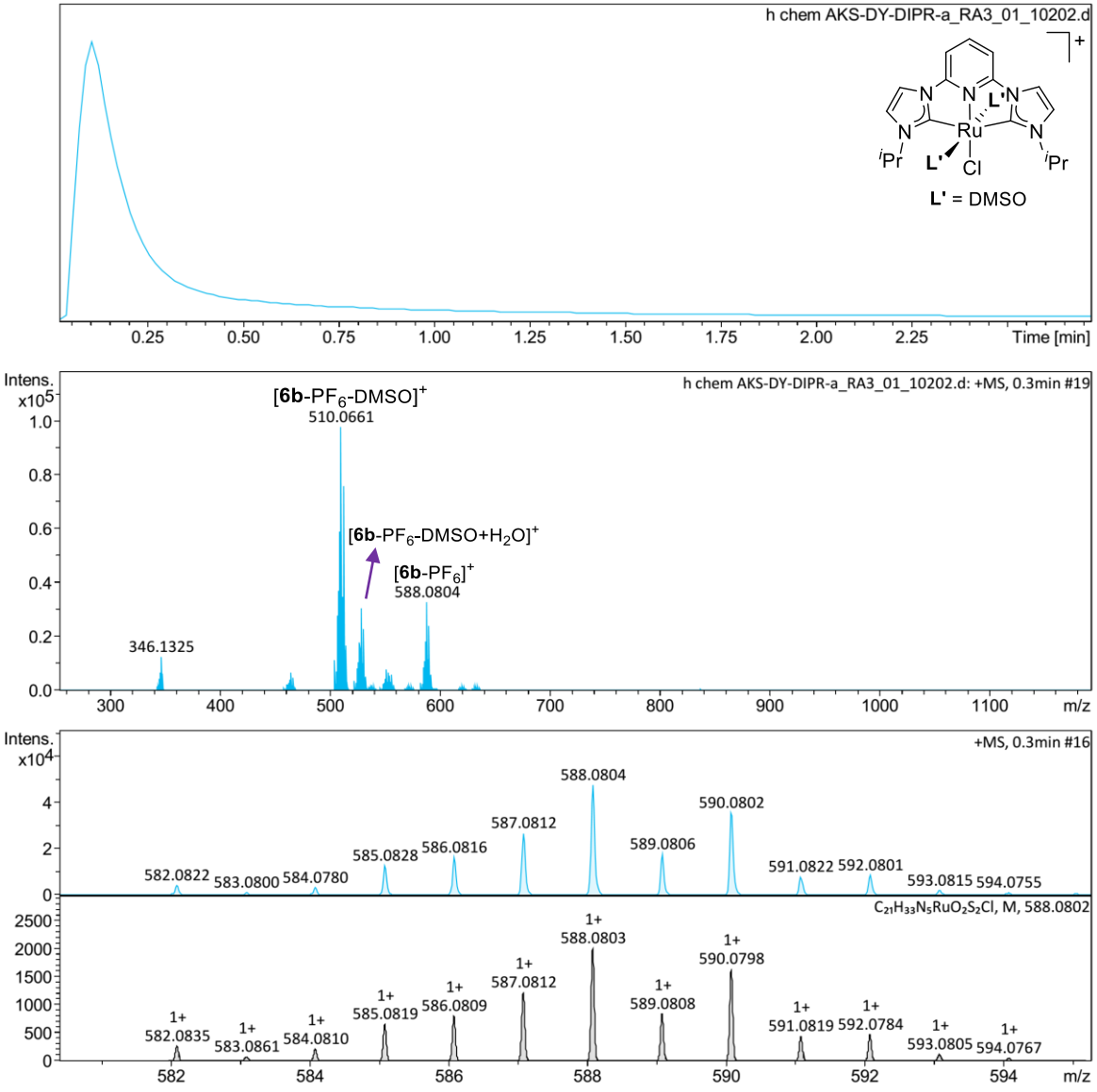


Figure S38. HRMS spectrum of Complex **6b**.

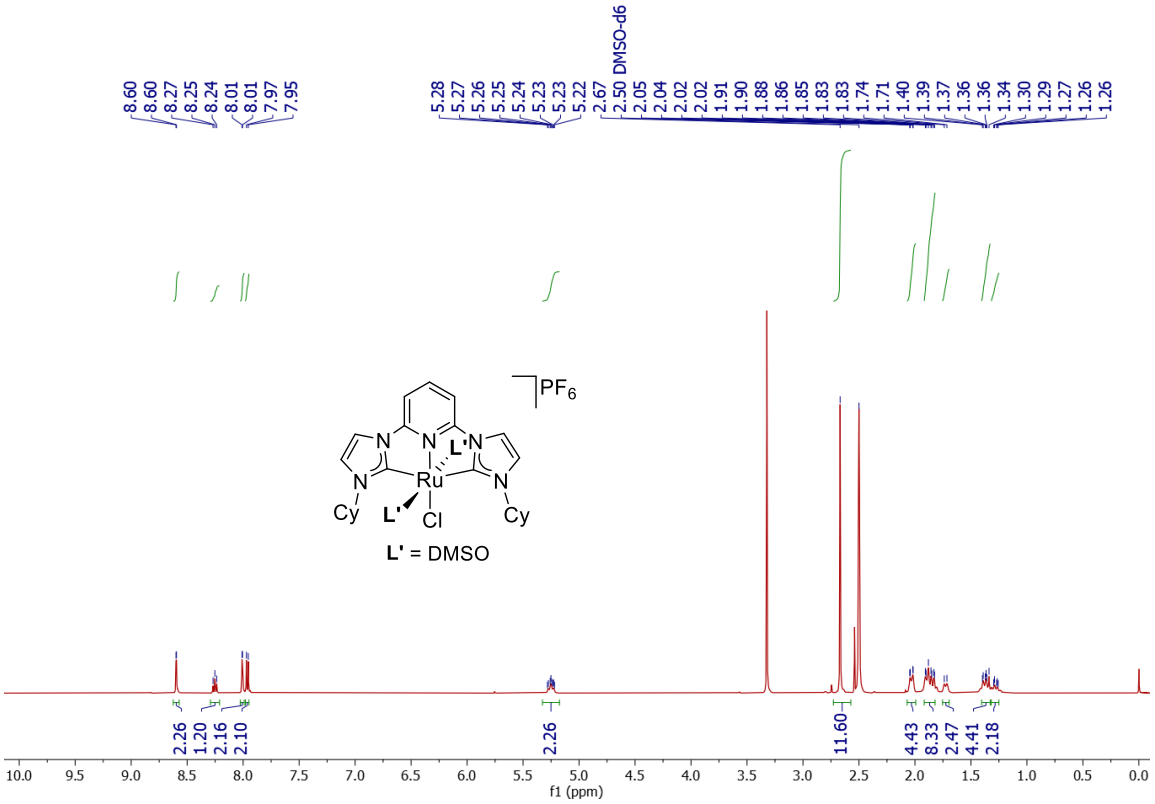


Figure S39. ^{1}H NMR spectrum of Complex **6c**.

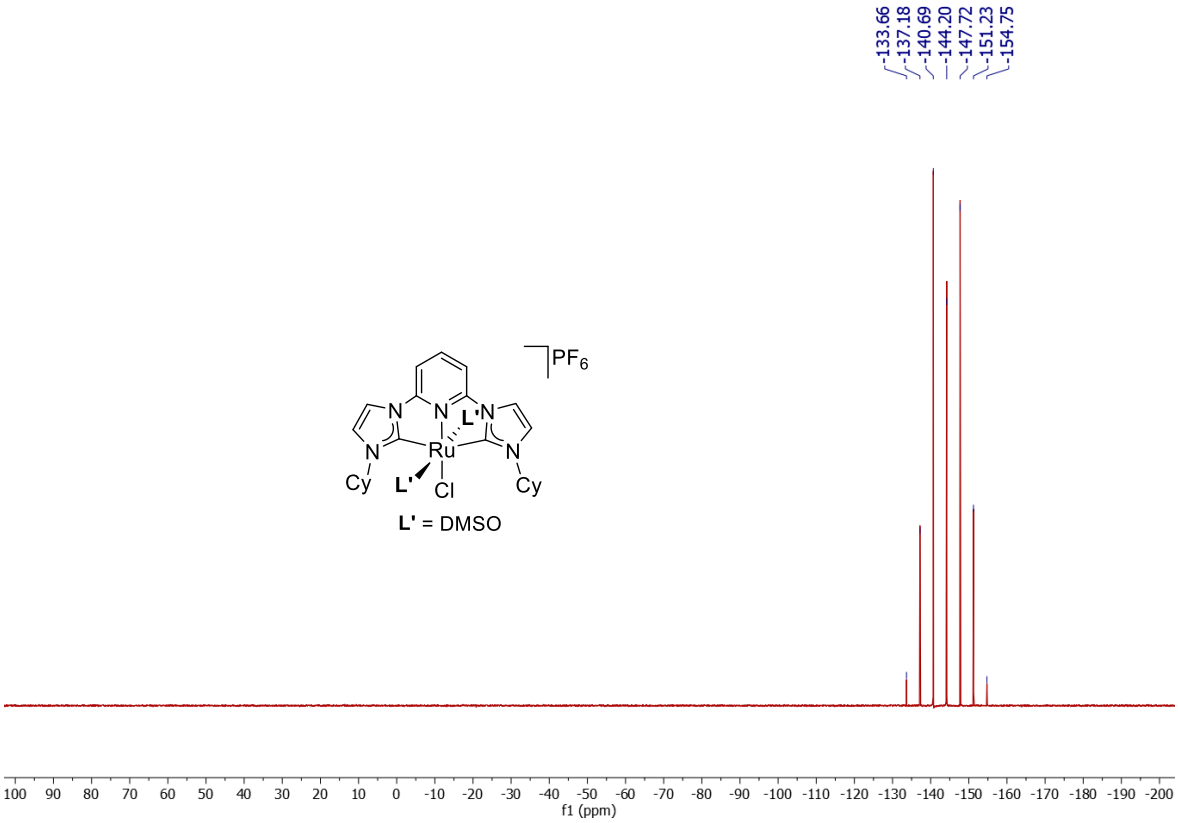


Figure S40. ^{31}P NMR spectrum of Complex **6c**.

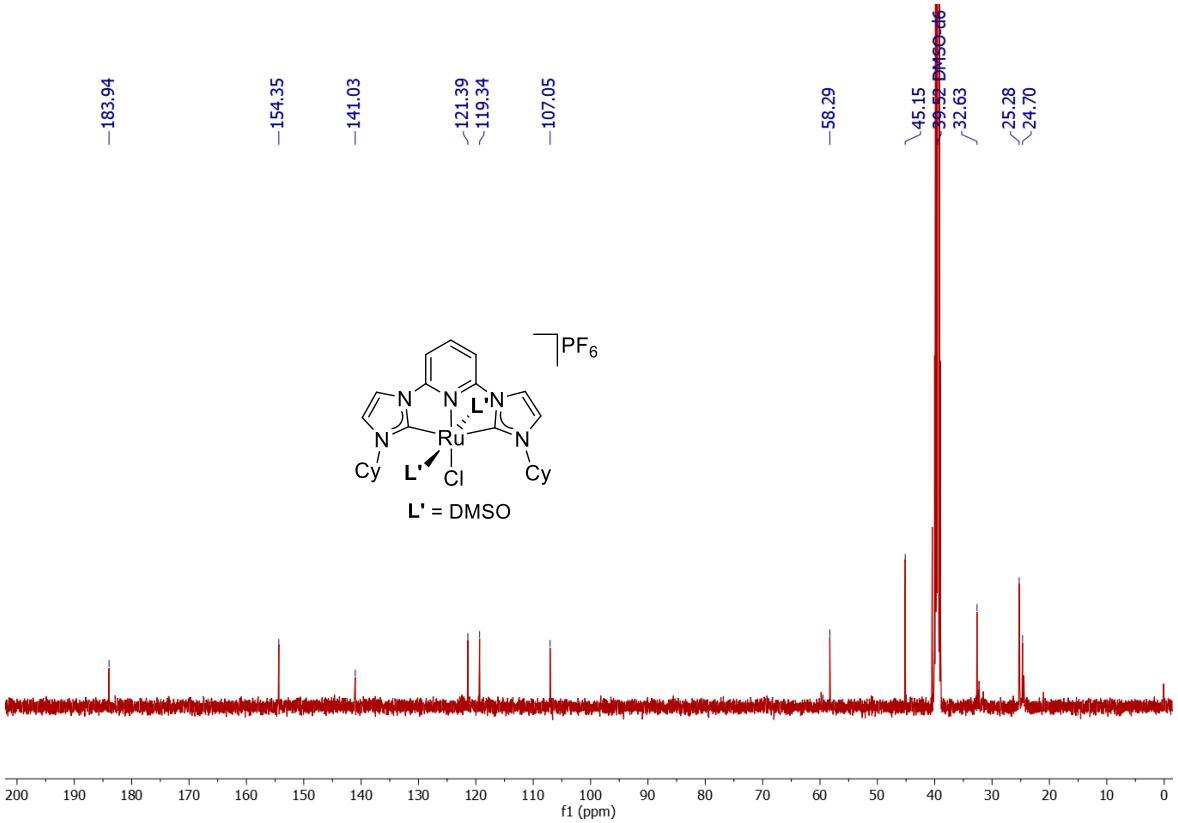


Figure S41. ^{13}C NMR spectrum of Complex **6c**.

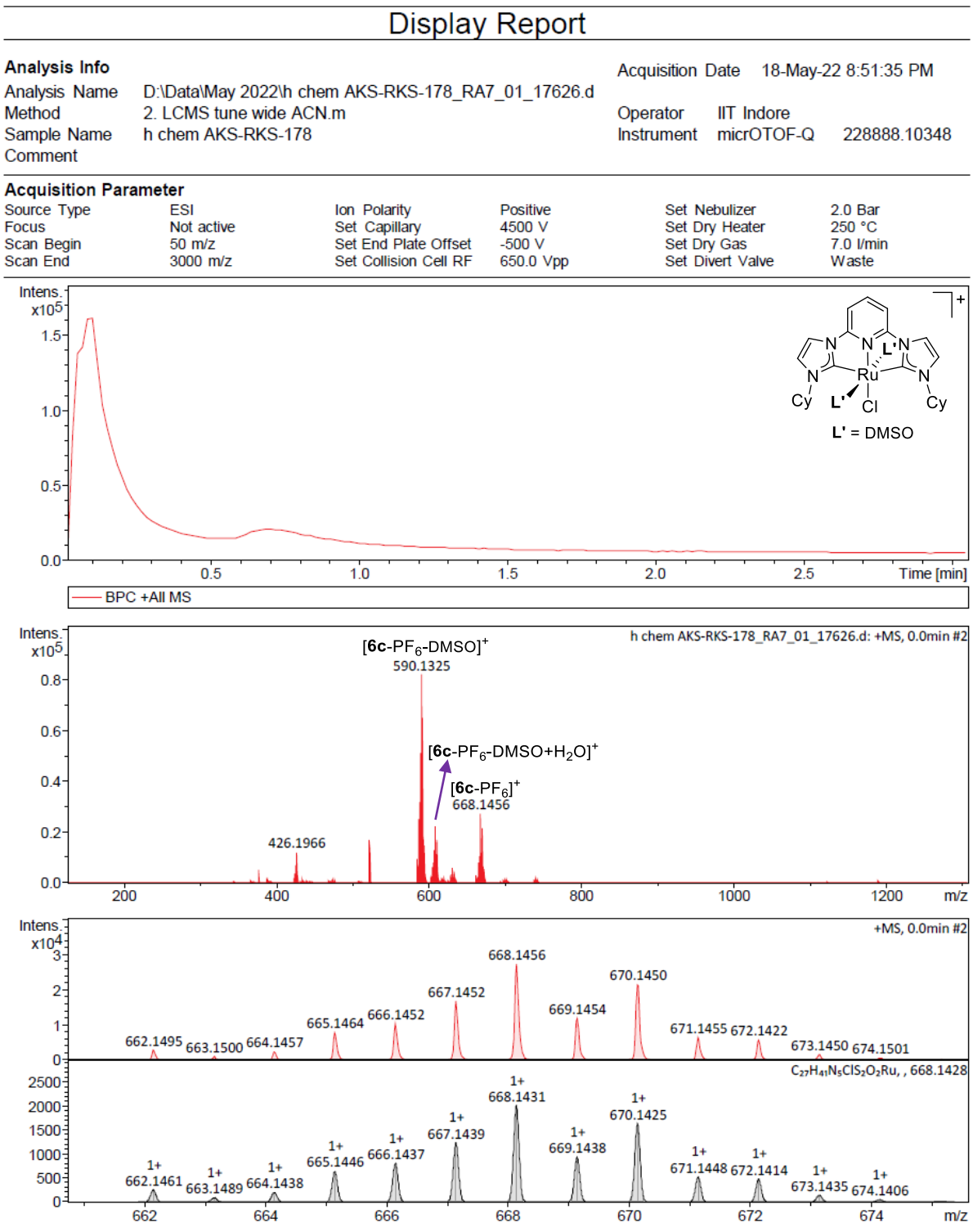


Figure S42. HRMS spectrum of complex **6c**.

Display Report

Analysis Info

Analysis Name	D:\Data\October 2021\h chem AKS-DY-COD-ipr-a2_RA1_01_10207.d	Acquisition Date	10/21/2021 4:53:21 PM
Method	8. LCMS tune wide MeOH.m	Operator	IIT Indore
Sample Name	h chem AKS-DY-COD-ipr-a2	Instrument	micrOTOF-Q 228888.10348
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	250 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	650.0 Vpp	Set Divert Valve	Waste

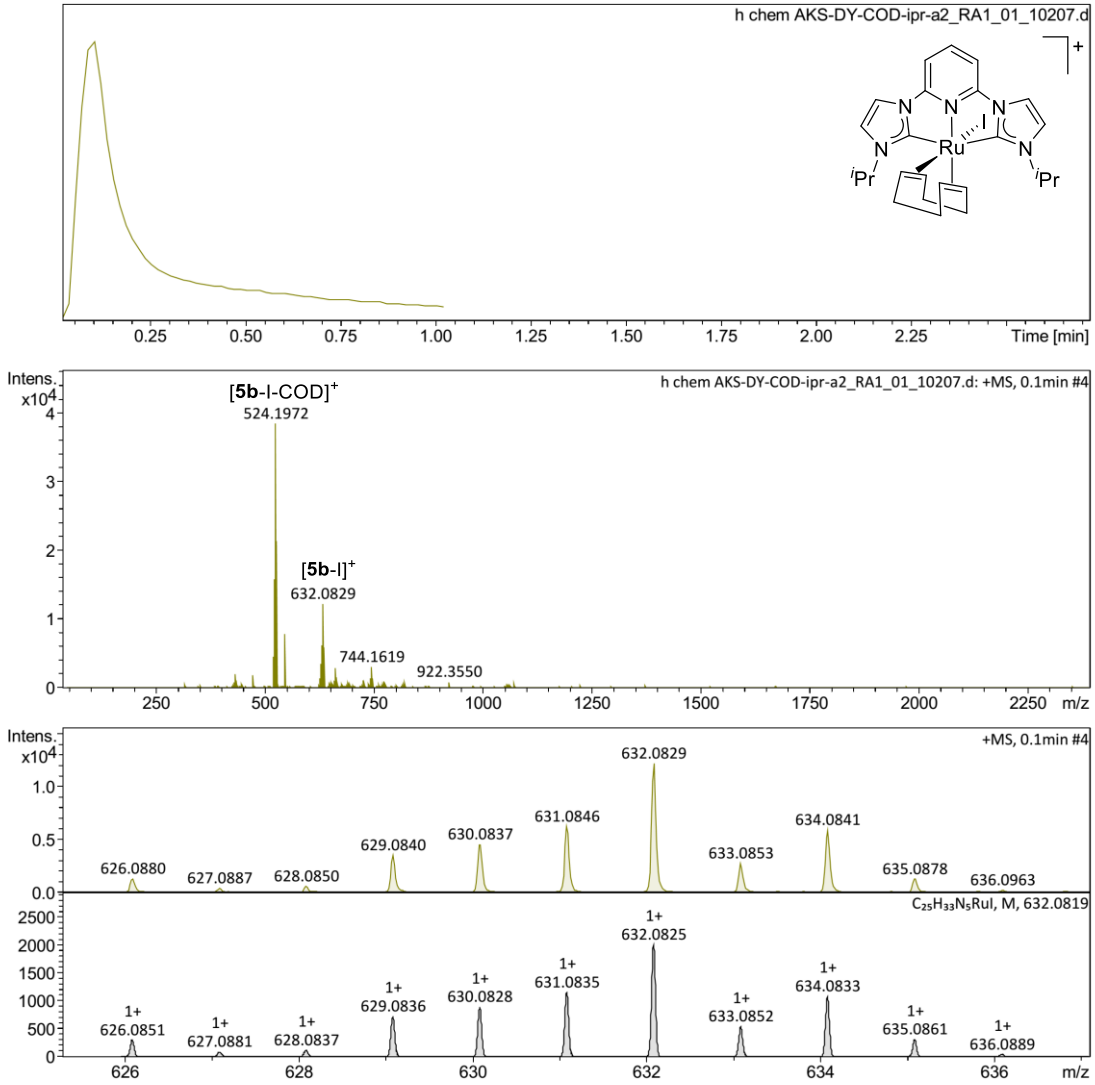


Figure S43. HRMS spectrogram of Complex **5b**.

Mechanism for transfer hydrogenation reaction

A plausible mechanism for transfer hydrogenation is shown, with complex **1c** as the catalyst precursor and **2c** as the Ru-hydride intermediate. The detailed mechanistic investigation for TH reaction with the *N*-methyl complex was previously reported by our group.[1] The ruthenium alkoxide species **A** is produced, when complex **1c** is treated with NaO^{i}Pr. The Ru-H intermediate **2c'** is formed from **A** via β-H elimination by releasing one molecule of acetone, or by dissociation of a PPh_3 ligand if starting from **2c**. The addition of cyclohexanone to the intermediate **2c'** produces another ruthenium alkoxide intermediate **B**, which releases the hydrogenated product upon protonation from ^{i}PrOH resulting in the formation of **A** again.

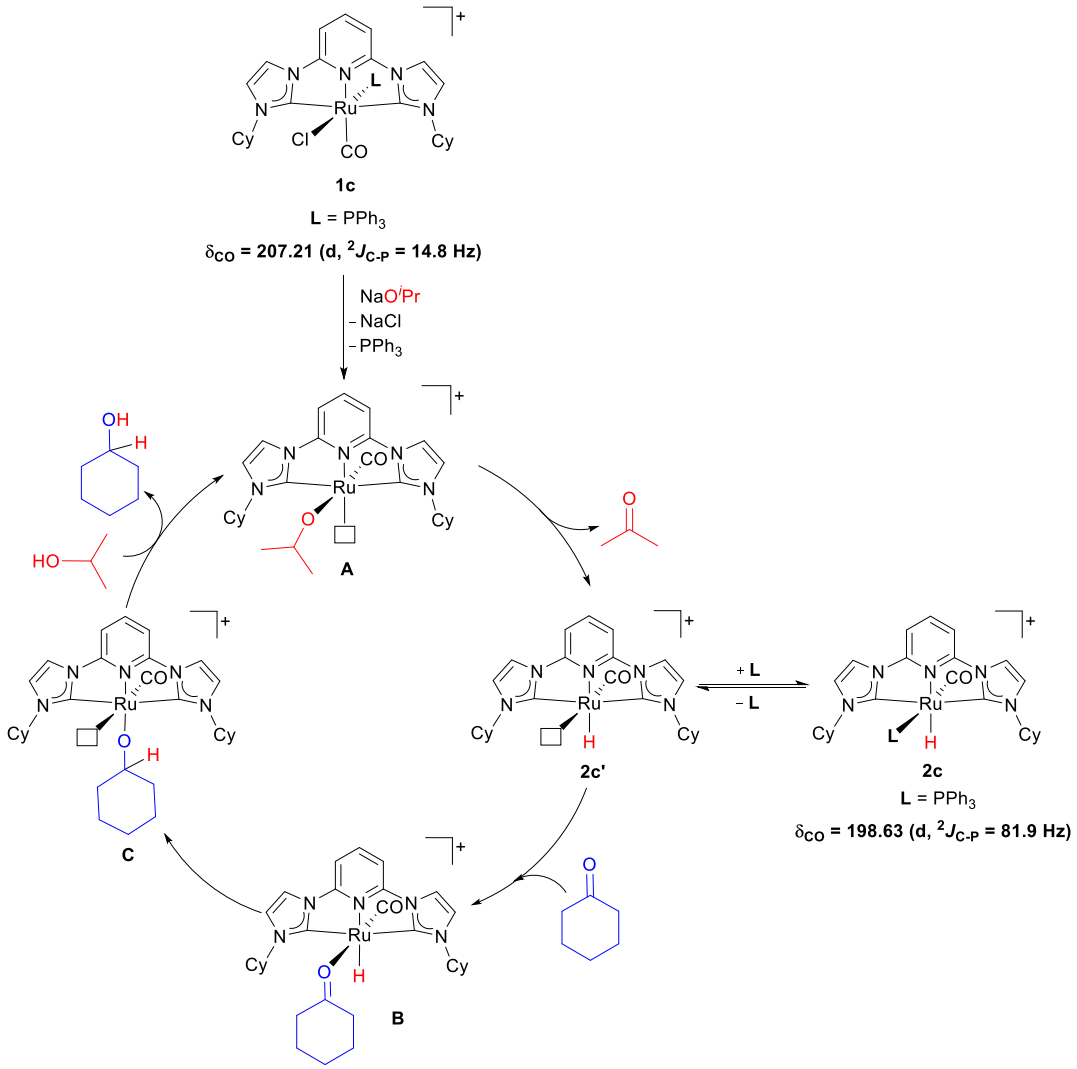


Figure S44. Plausible mechanism for transfer hydrogenation reaction by complex **1c** with key intermediates **2c**.

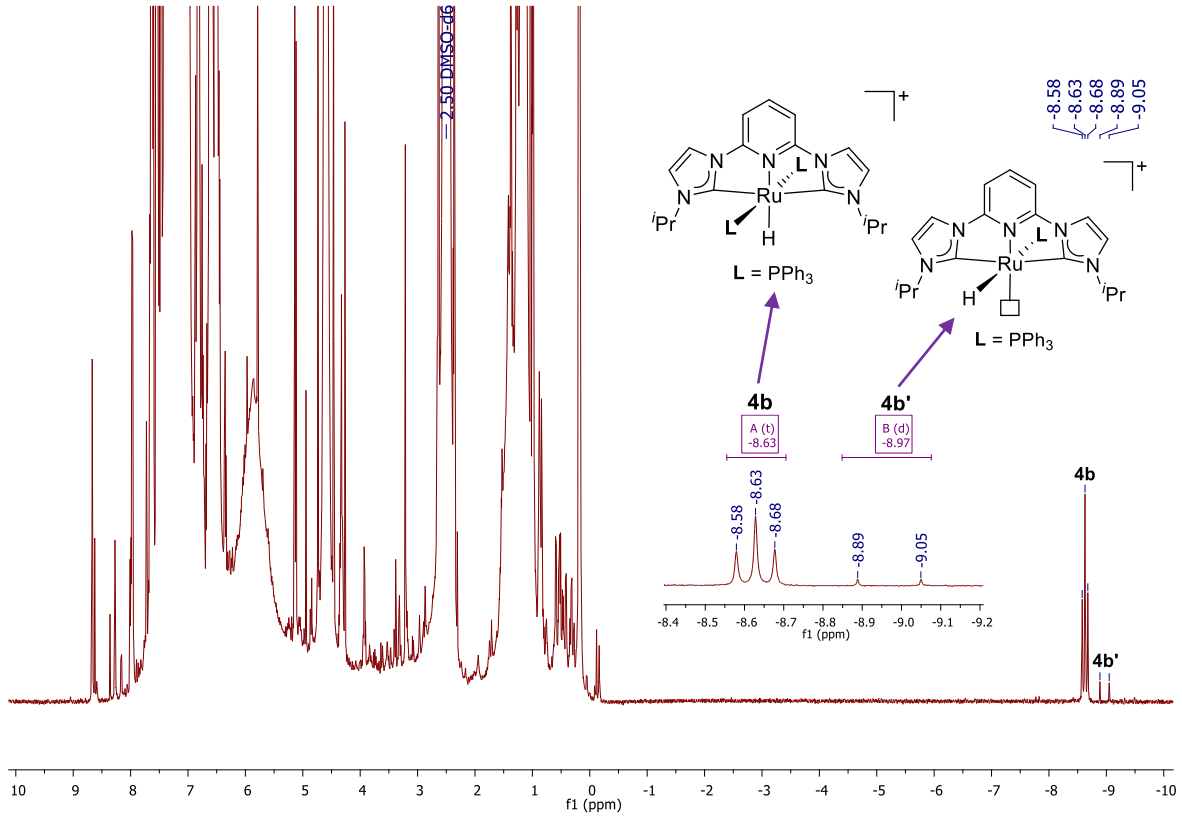


Figure S45. ^{1}H NMR experiment in DMSO-d_6 to observe the generation of ruthenium hydride intermediate from complex **3b** under catalytic reaction conditions.

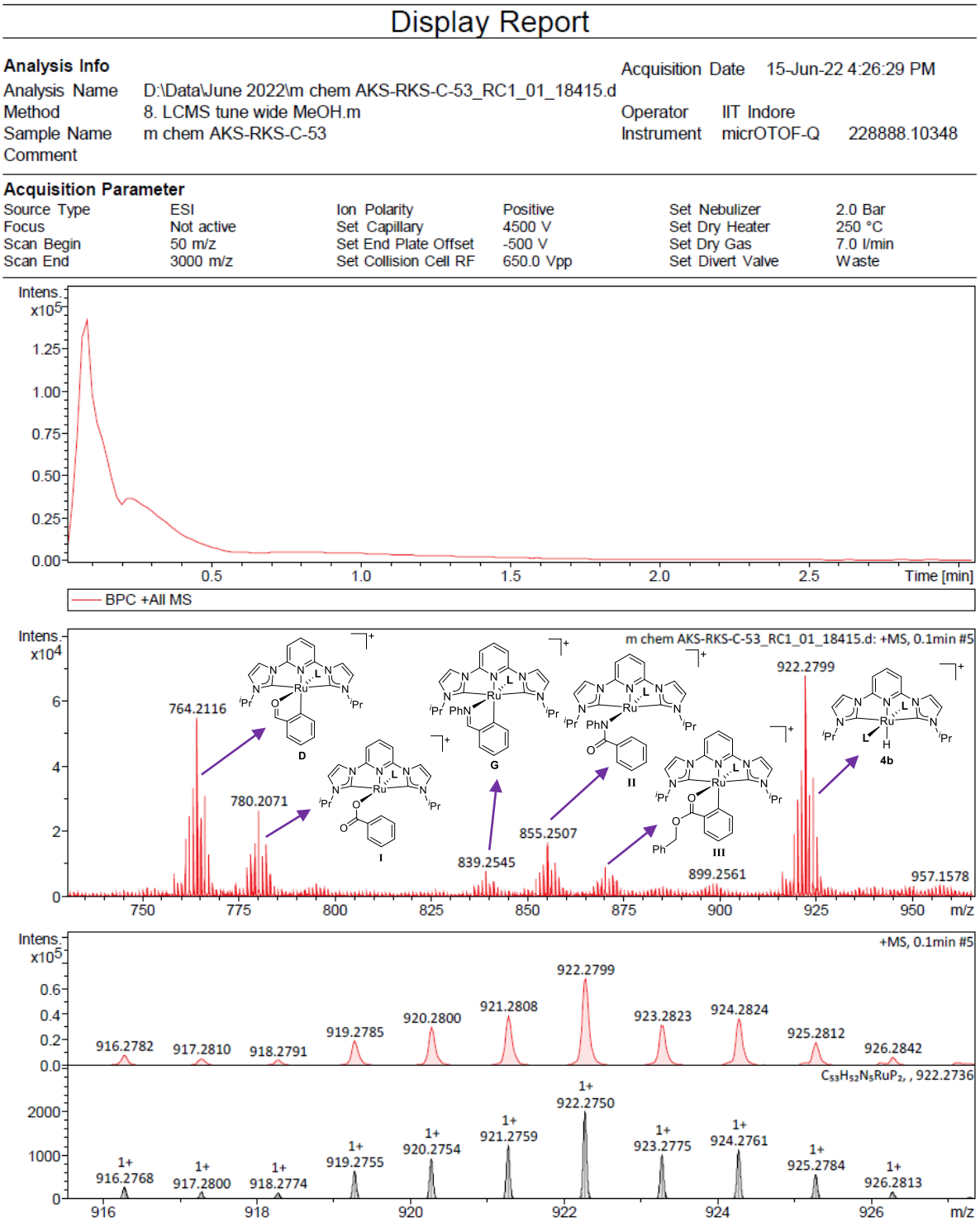


Figure S46. LCMS spectrogram of catalytic reaction mixture (**L** = PPh_3).

Display Report

Analysis Info

Analysis Name	C:\Users\Rahul Kumar Singh\Desktop\NMR and Mass\Mass data\m chem aks-rks-c-110-3h_RA3_01_18656.d	Acquisition Date	22-06-2022 16:24:20
Method	8. LCMS tune wide MeOH.m	Operator	IIT Indore
Sample Name	m chem aks-rks-c-110-3h	Instrument	micrOTOF-Q 228888.10348
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	250 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	650.0 Vpp	Set Divert Valve	Waste

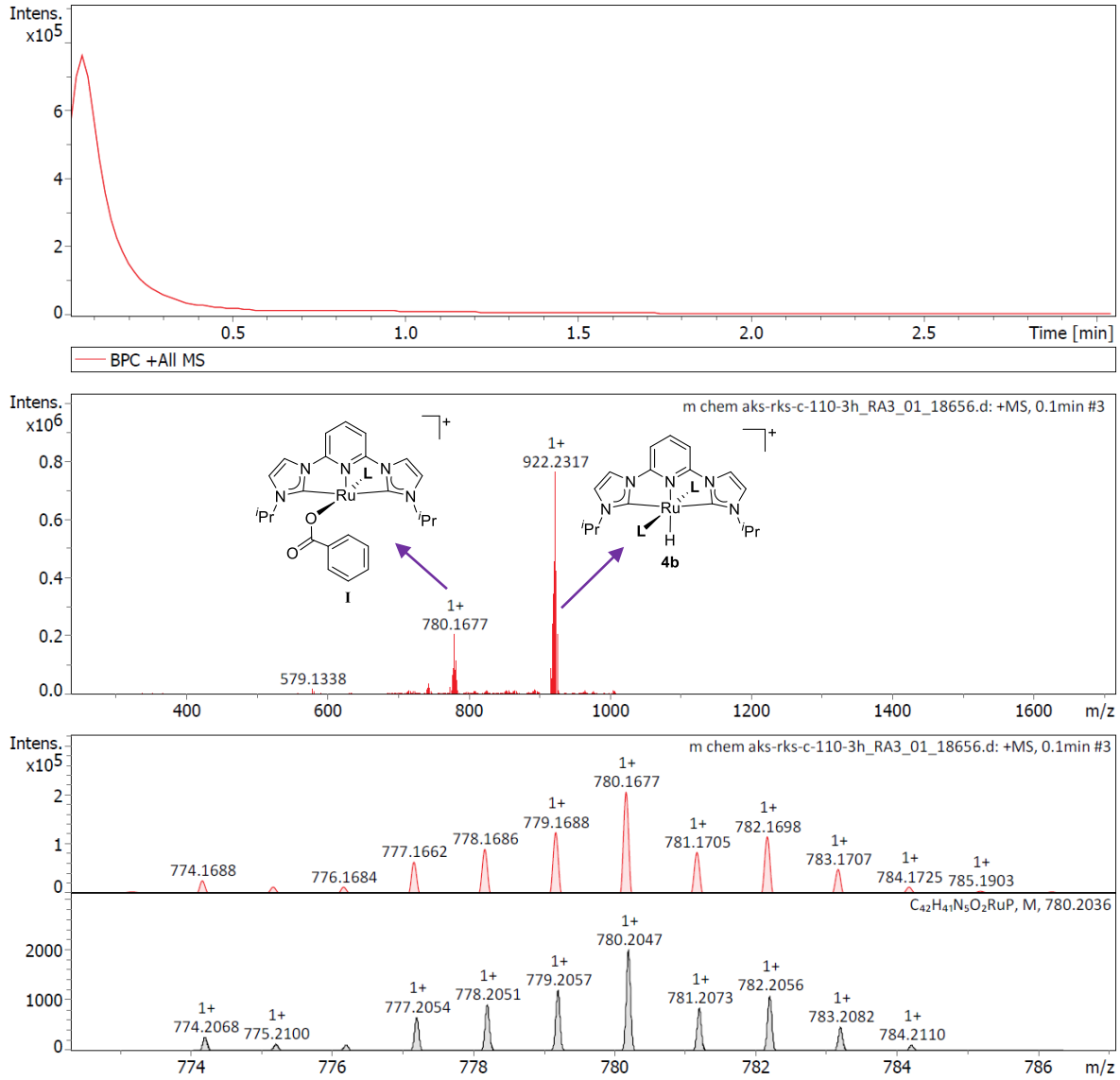


Figure S47. LCMS spectrogram of catalytic reaction mixture with benzaldehyde and catalyst **4b** formed intermediate **I** (**L** = PPh_3).

Formation of other intermediates **I**, **II**, and **III** appeared during the catalytic reactions (Figure S46). Intermediate **I** also appeared in LCMS during the reaction of benzaldehyde with Ru hydride catalyst **4b** (Figure S47). This information suggests that the *ortho* C-H activation of benzaldehyde takes place and generated intermediate **D**, which further reacted with moisture (while recording mass data) and appeared as intermediate **I** (Figure S47).

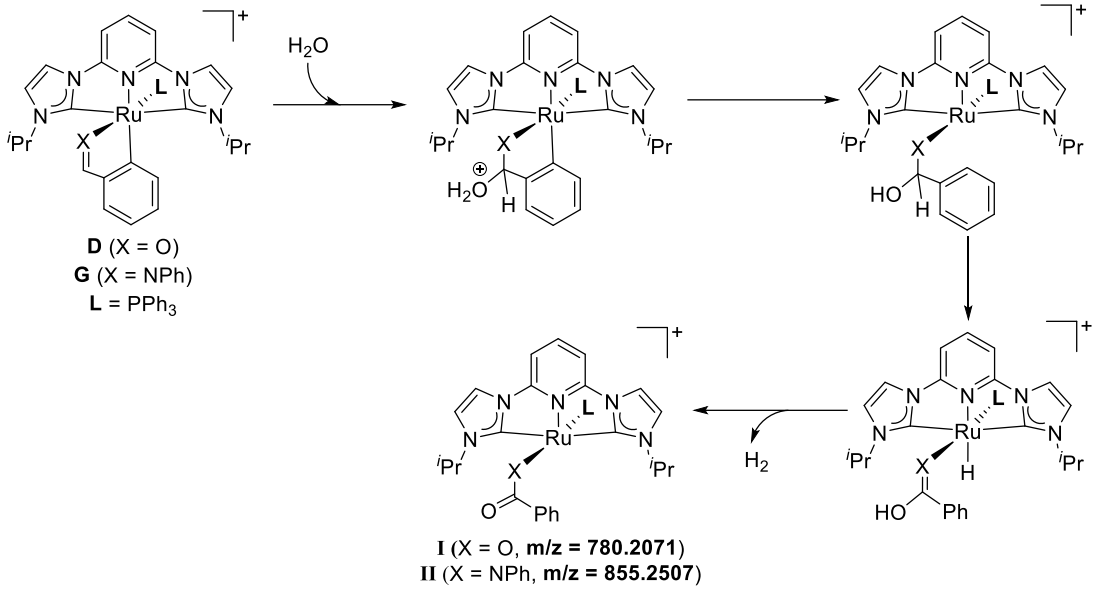


Figure S48. Plausible mechanism for the formation of intermediates **I** and **II** in catalytic reaction mixture by complex **3b**.

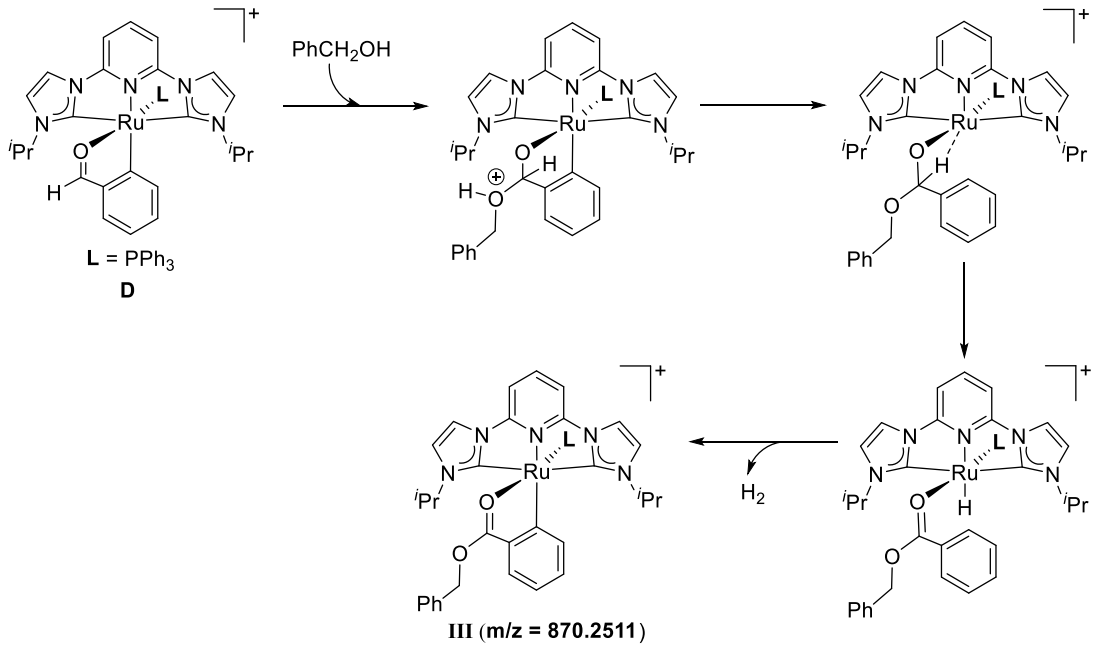


Figure S49. Plausible mechanism for the formation of intermediate **III** in catalytic reaction mixture by complex **3b**.

Determination of % GC yield by gas chromatography

GC Samples were analysed in Shimadzu QP2010 Ultra gas chromatograph. Yields of the product were determined using *n*-decane as an internal standard. Samples were prepared by filtering the reaction mixture through a celite pad with chloroform and further dilution with methanol solution. The additional peaks in some GC-MS traces are of PPh_3 and sometimes $OPPh_3$ due to aerial oxidation in the GC sample. The poor signal separation, only in case of transfer hydrogenation of cyclohexanone, is due to very close retention time of cyclohexanone and cyclohexanol. For uniformity, we have followed the automated integration by the GC-MS software of our instrument. The reactants and products relative response factors (RF) were calculated using *n*-decane as the internal standard. *n*-Decane was added to the reaction mixture prior to start of catalysis. The following equations are used to calculate the % GC yields.[4]

Response factors were calculated using the following equation:

$$\mathrm{RF} = \frac{\text{Area percentage of internal standard} \times \text{Moles of analyte}}{\text{Area percentage of analyte} \times \text{Moles of internal standard}}$$

Moles of remaining reactants and products were calculated using the following equation:

$$\text{Moles of analyte} = \frac{\mathrm{RF} \times \text{Moles of internal standard} \times \text{Area percentage of analyte}}{\text{Area percentage of internal standard}}$$

The products of catalysis experiments (TH and AAD) are characterized by ^{1}H and ^{13}C NMR as well as GC-MS. ADC catalysis experiments are analyzed with GC-MS only as the imine products are prone to hydrolysis during column chromatography.

GC-MS spectra of Transfer hydrogenation of cyclohexanone products for table 1.

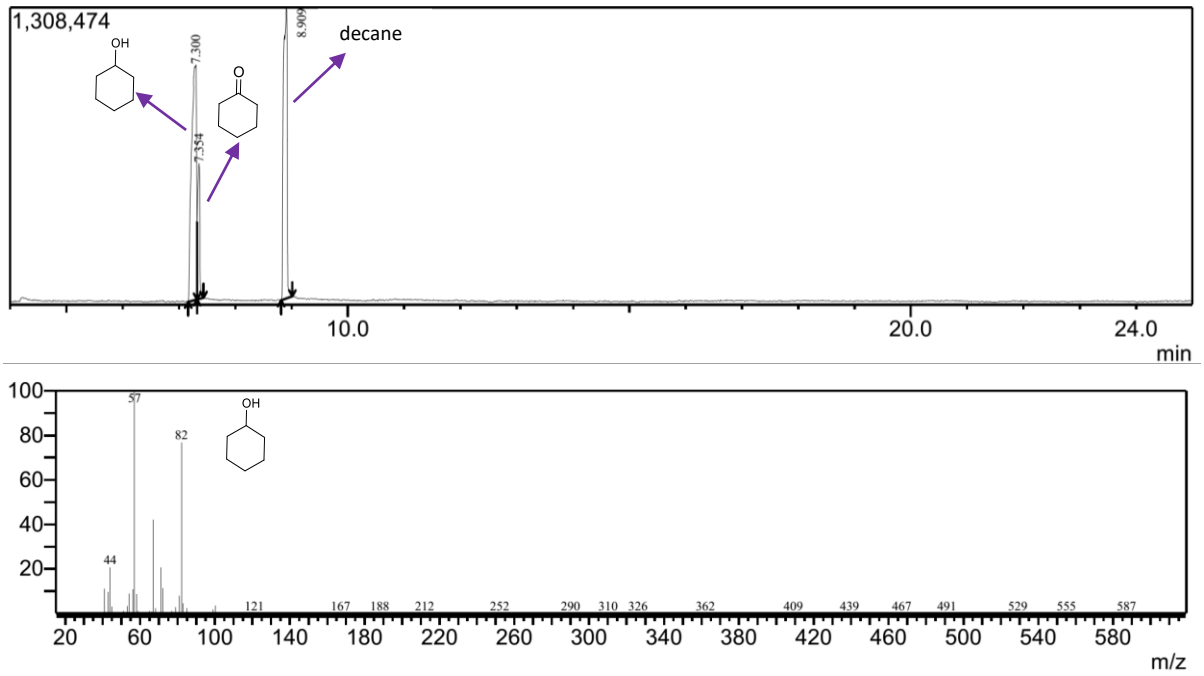


Figure S50. GC-MS spectrum for entry 5 of table 1.

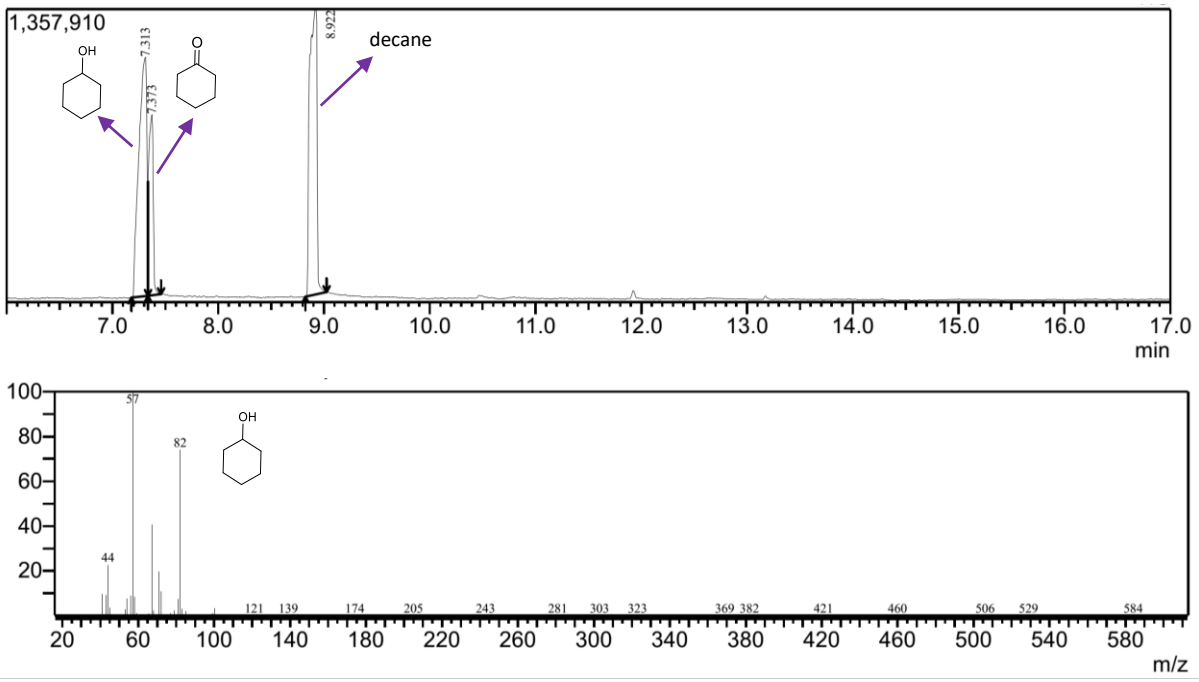


Figure S51. GC-MS spectrum for entry 6 of table 1.

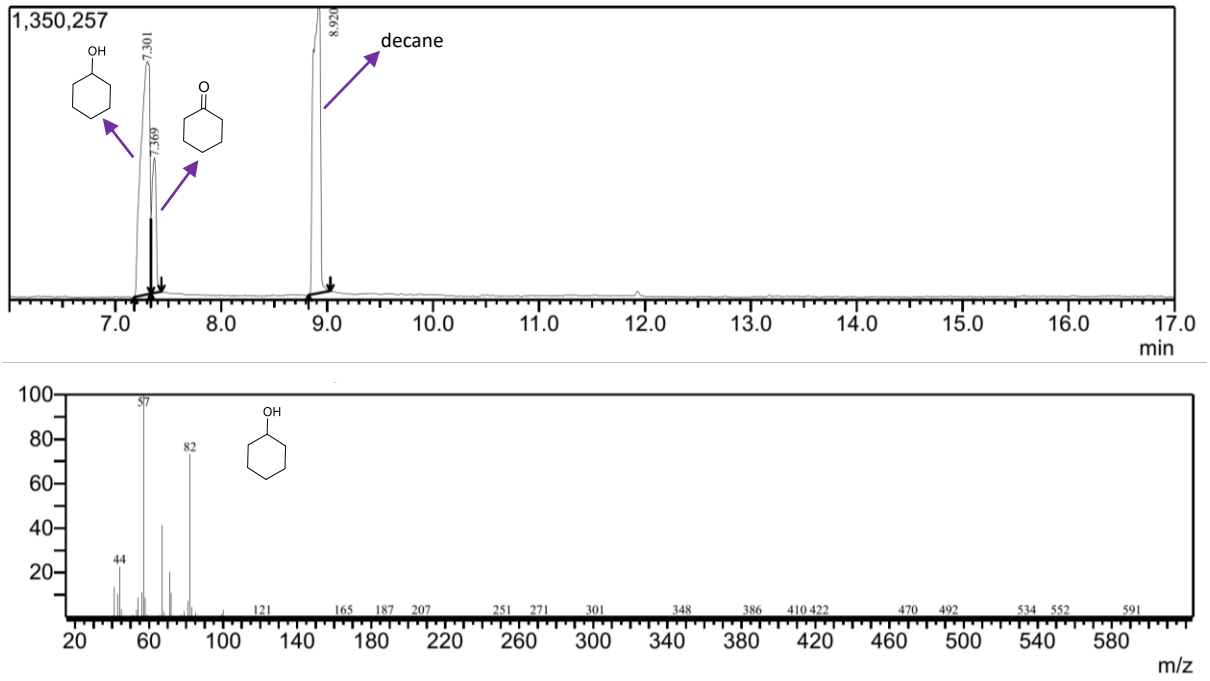


Figure S52. GC-MS spectrum for entry 7 of table 1.

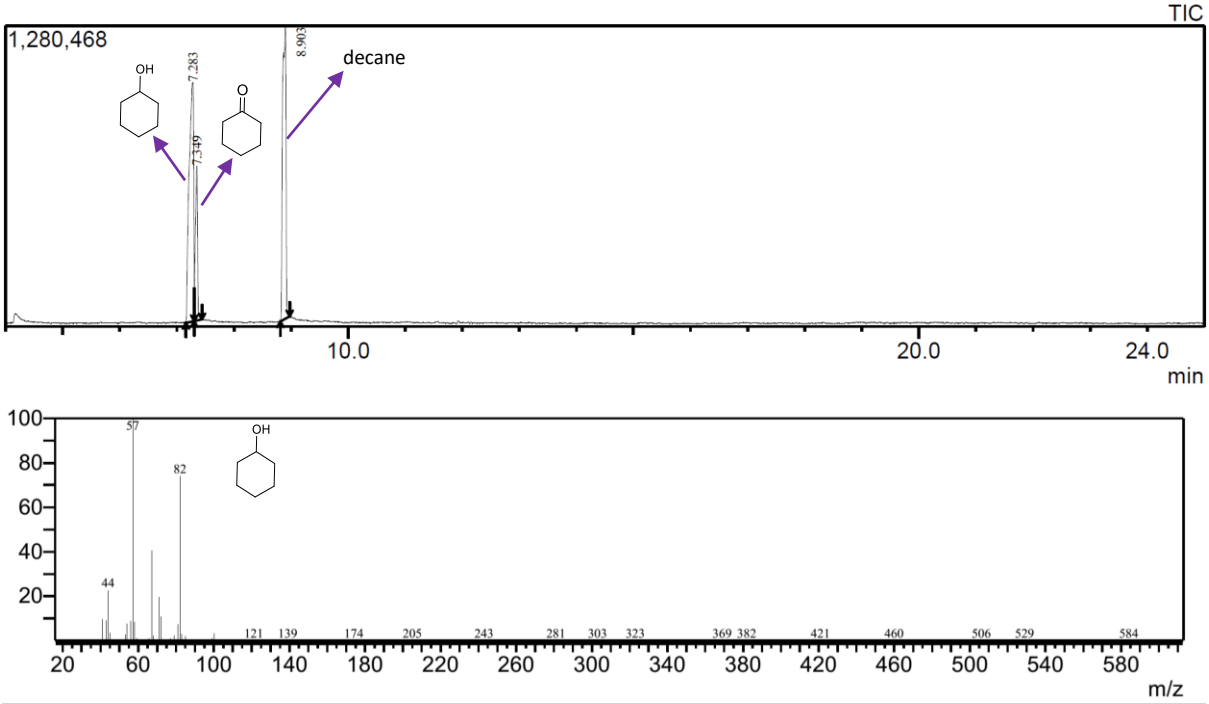


Figure S53. GC-MS spectrum for entry 8 of table 1.

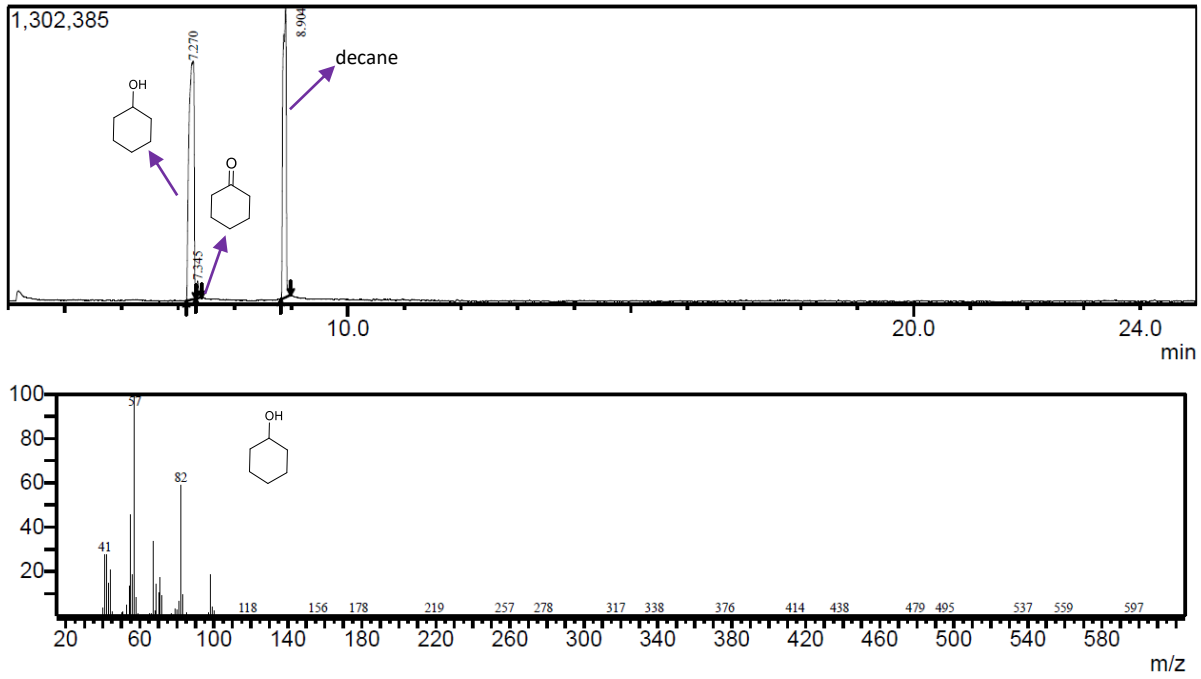


Figure S54. GC-MS spectrum for entry 9 of table 1.

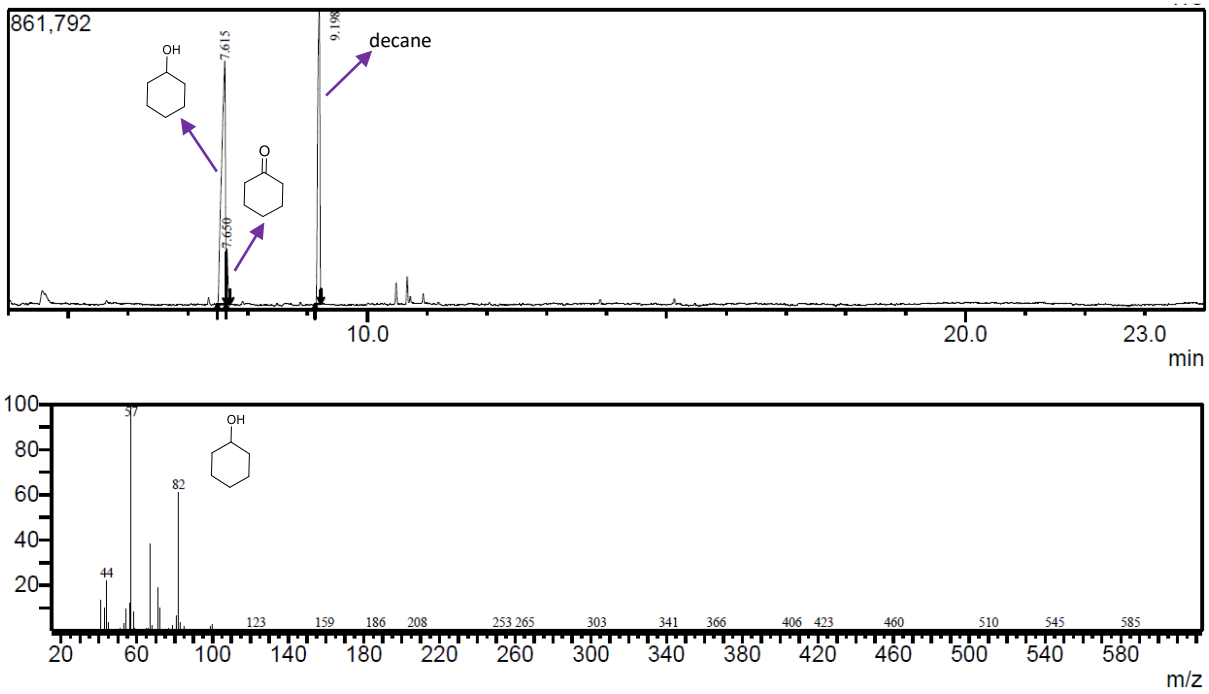


Figure S55. GC-MS spectrum for entry 10 of table 1.

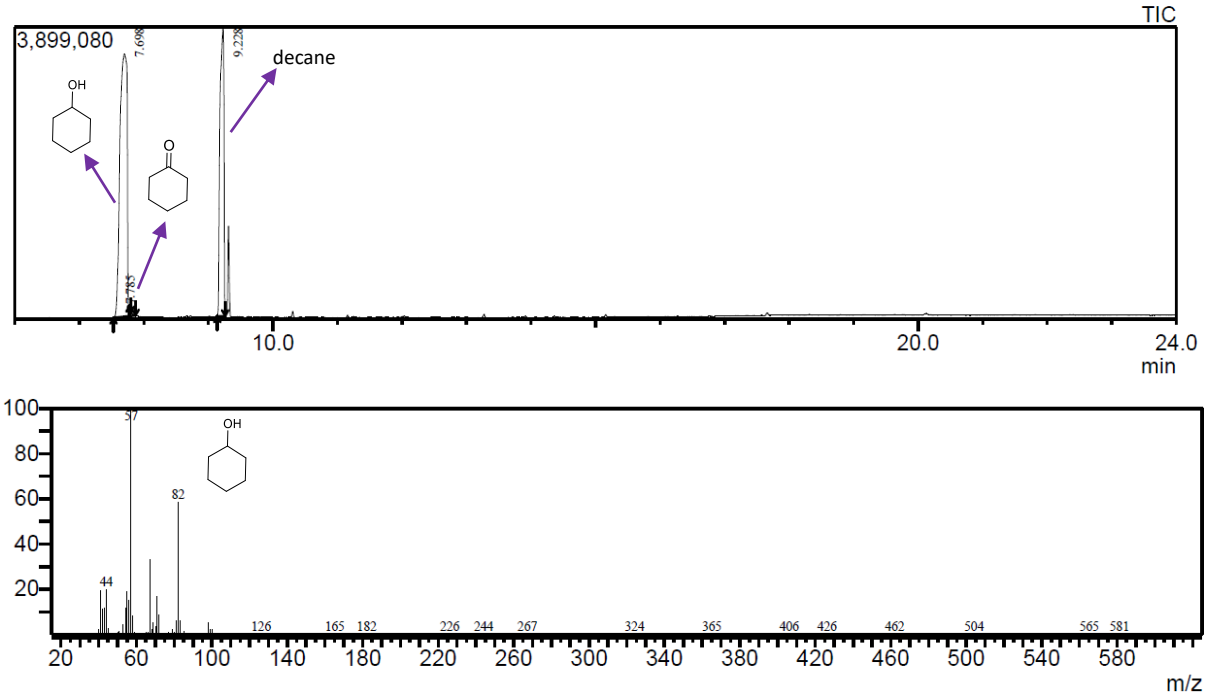


Figure S56. GC-MS spectrum for entry 11 of table 1.

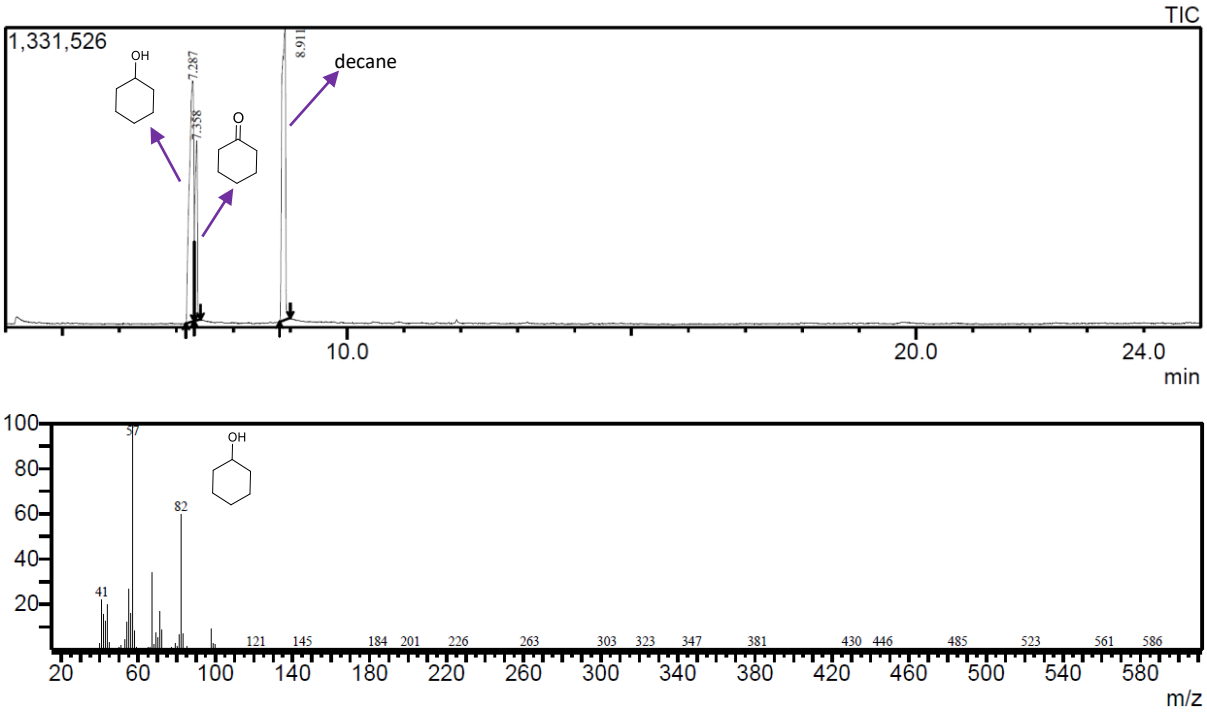


Figure S57. GC-MS spectrum for entry 12 of table 1.

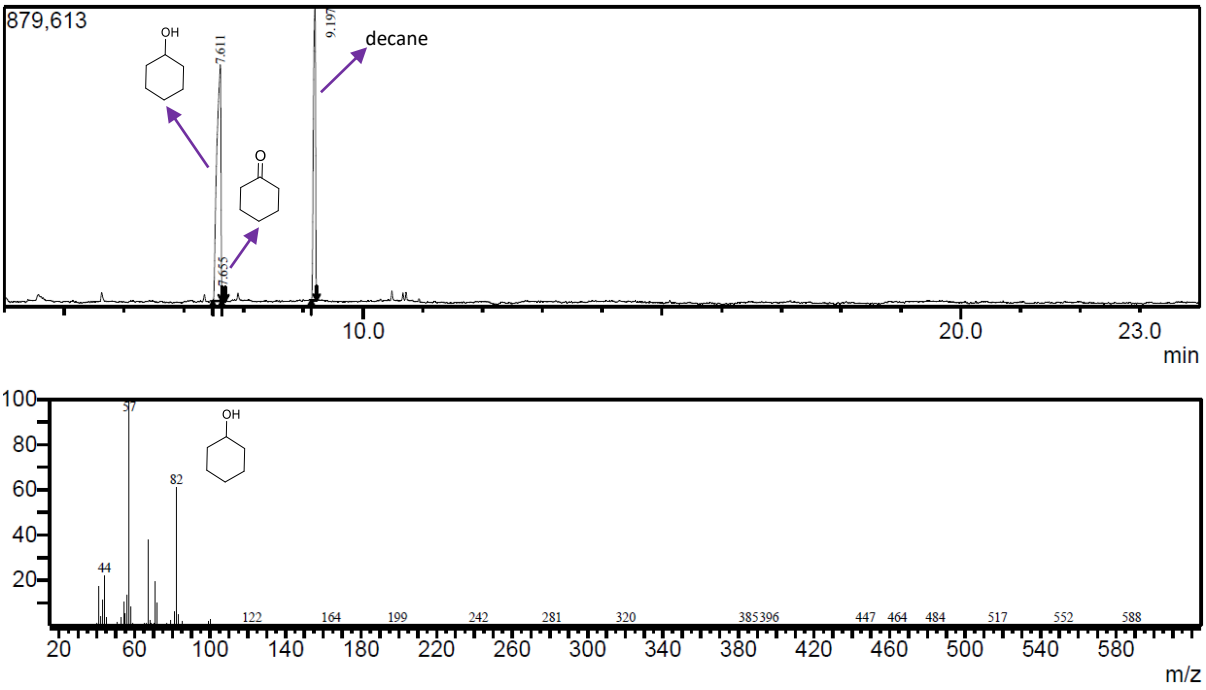


Figure S58. GC-MS spectrum for entry 13 of table 1.

GC-MS spectra of Acceptorless dehydrogenation of benzyl alcohol products for table 2.

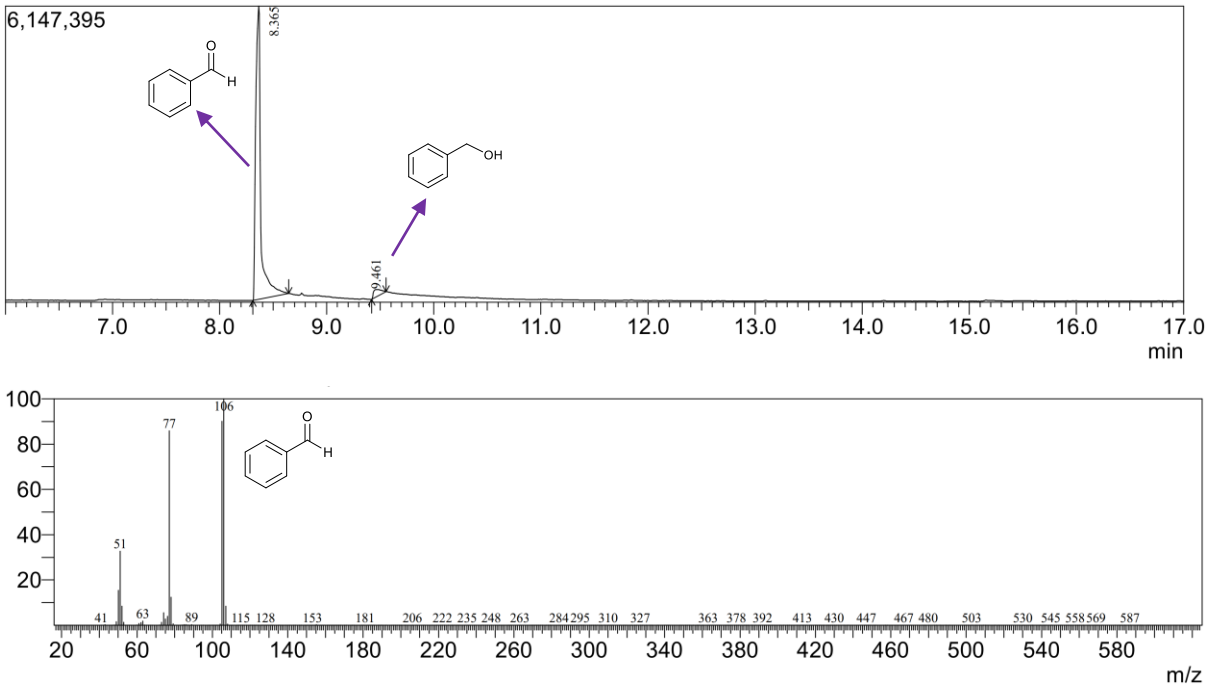


Figure S59. GC-MS spectrum for entry 6 of table 2.

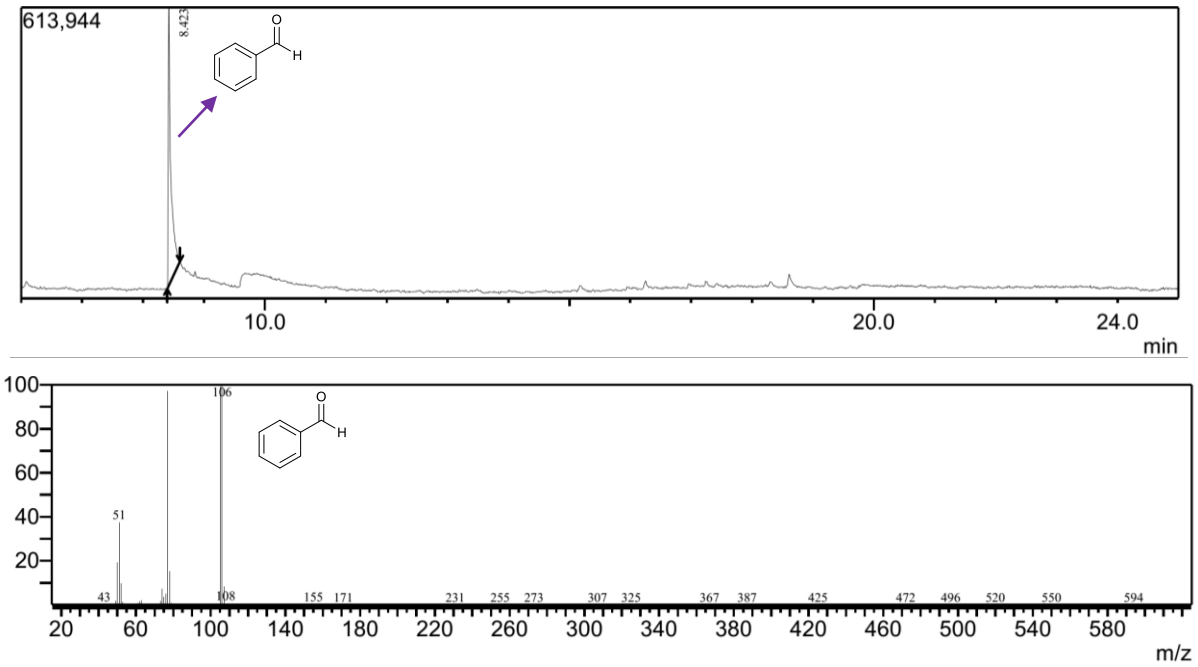


Figure S60. GC-MS spectrum for entry 7 of table 2.

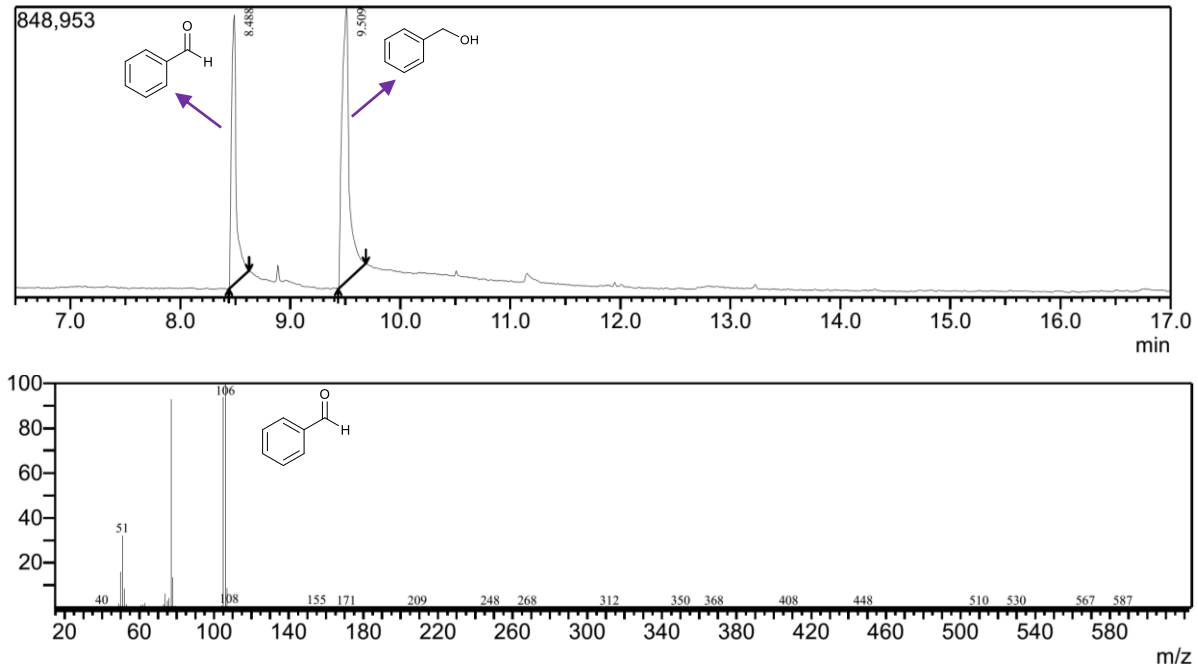


Figure S61. GC-MS spectrum for entry 8 of table 2.

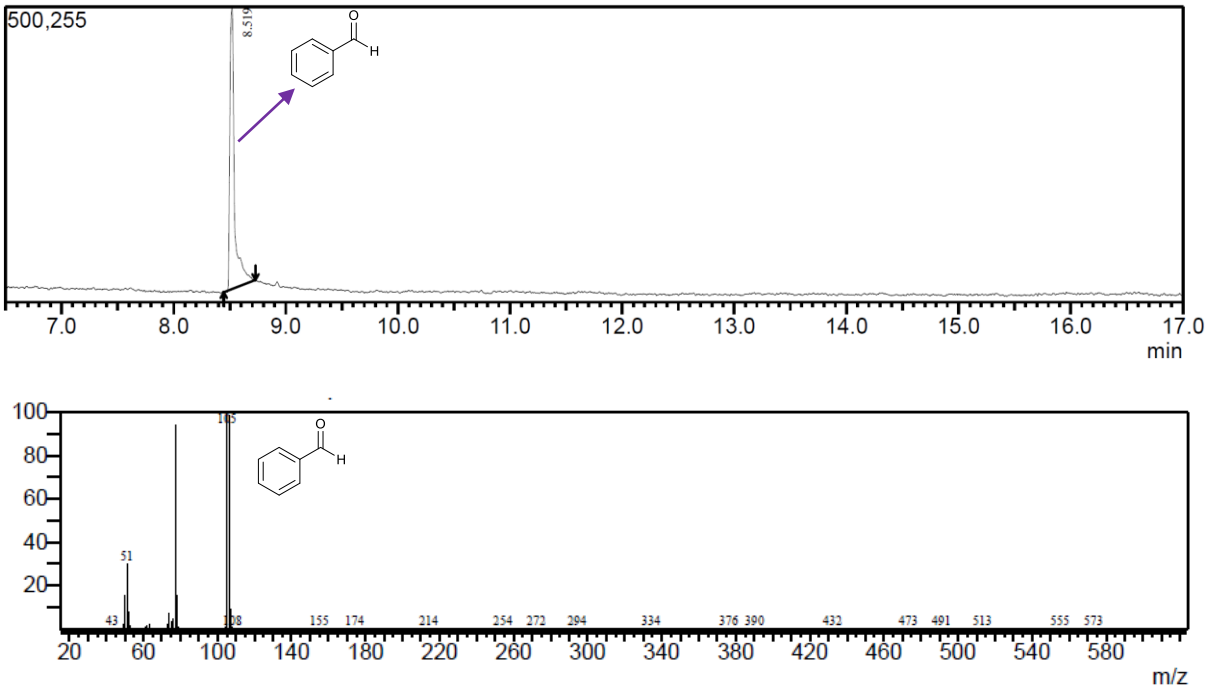


Figure S62. GC-MS spectrum for entry 9 of table 2.

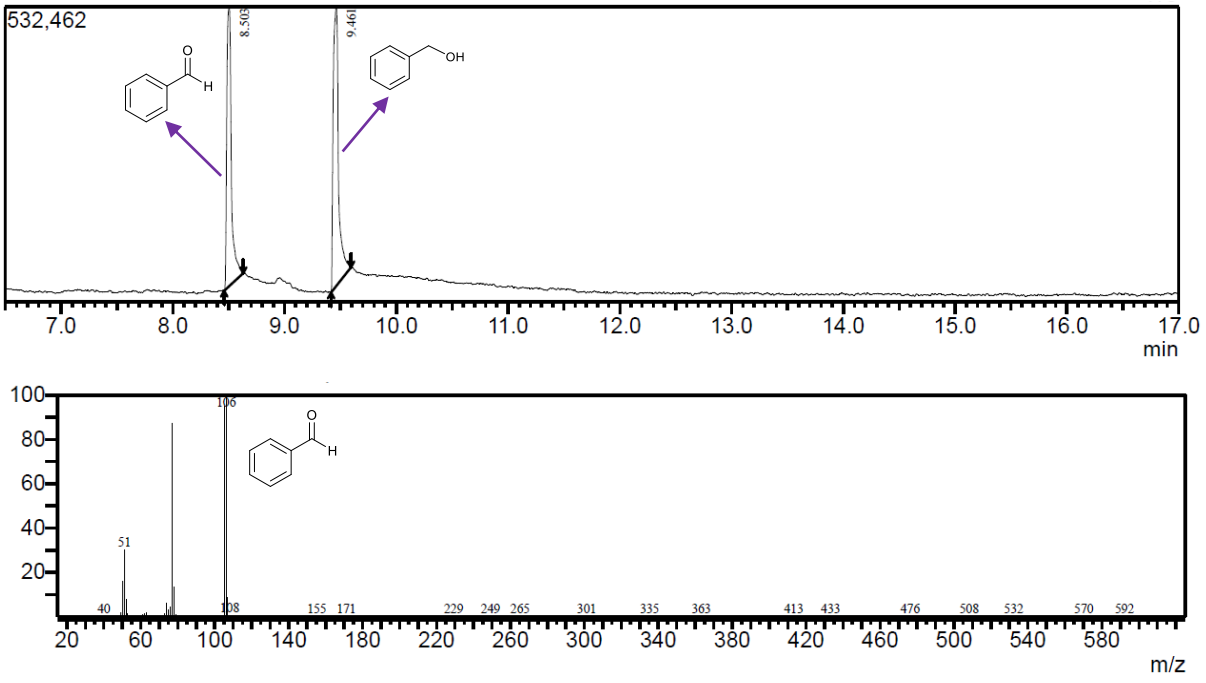


Figure S63. GC-MS spectrum for entry 10 of table 2.

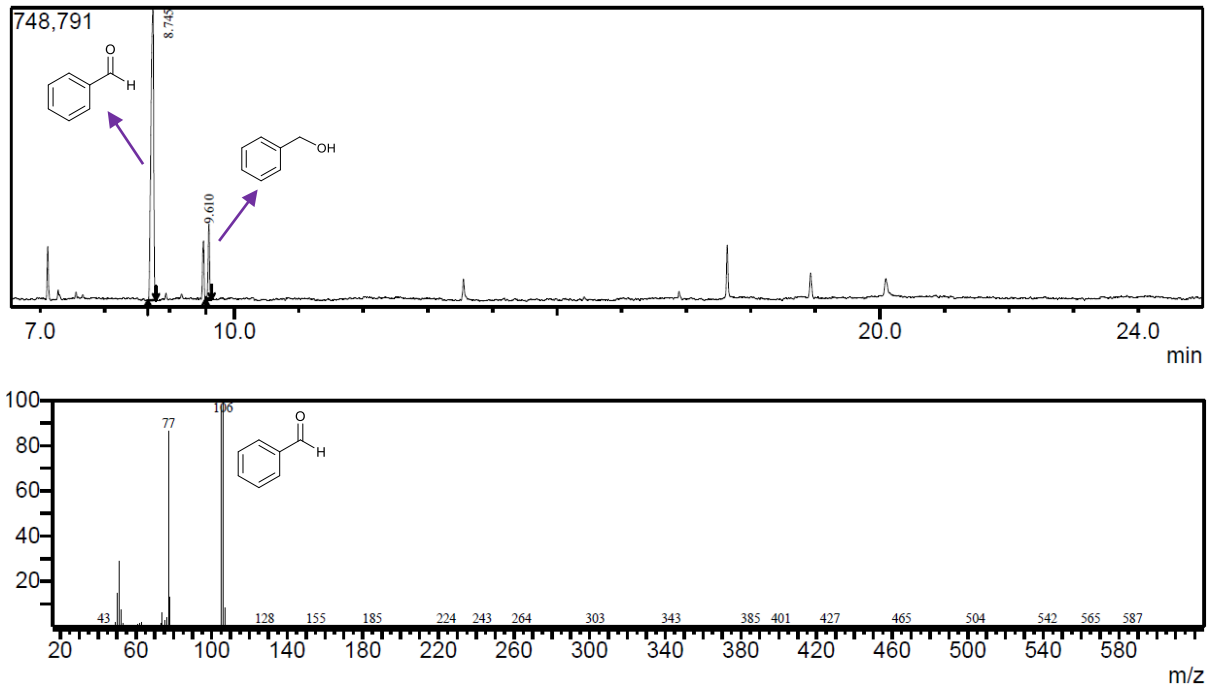


Figure S64. GC-MS spectrum for entry 11 of table 2.

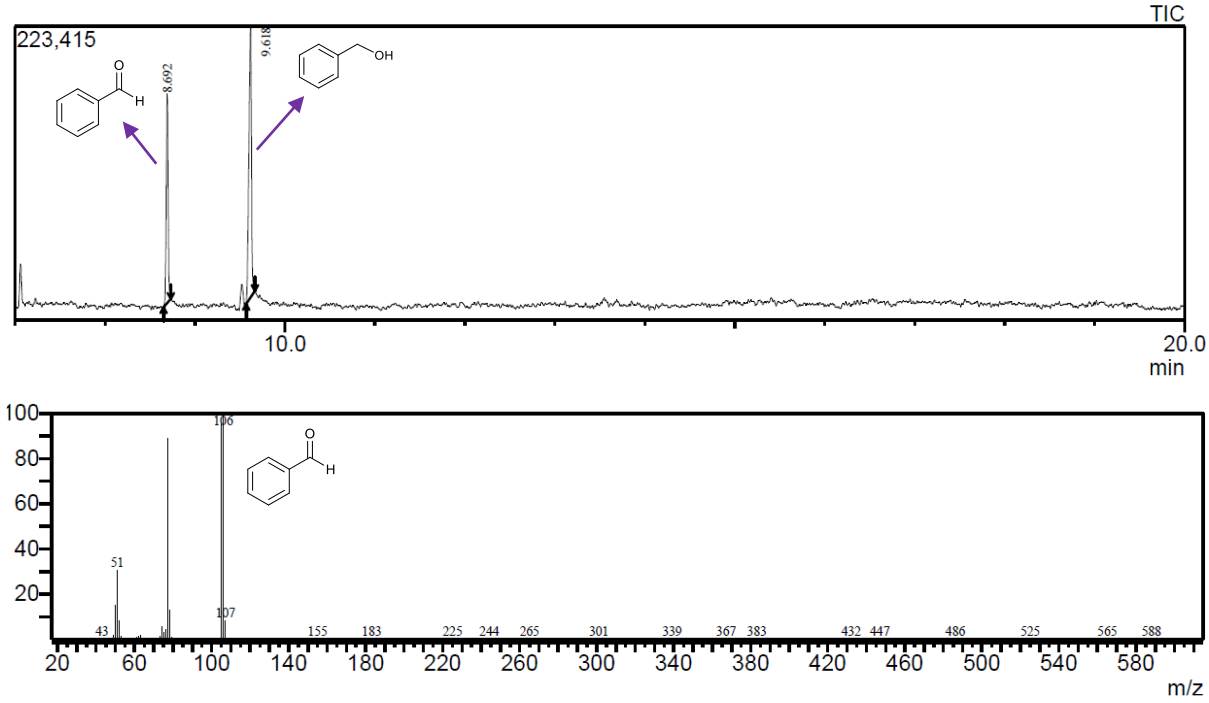


Figure S65. GC-MS spectrum for entry 12 of table 2.

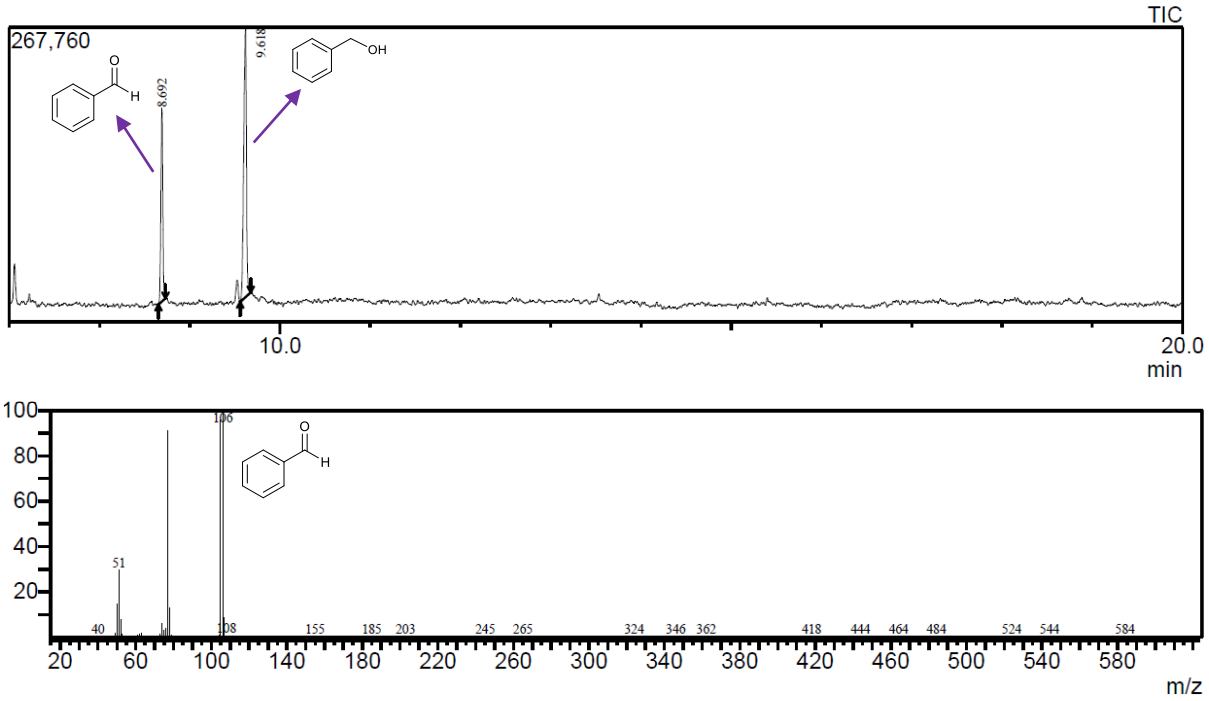


Figure S66. GC-MS spectrum for entry 13 of table 2.

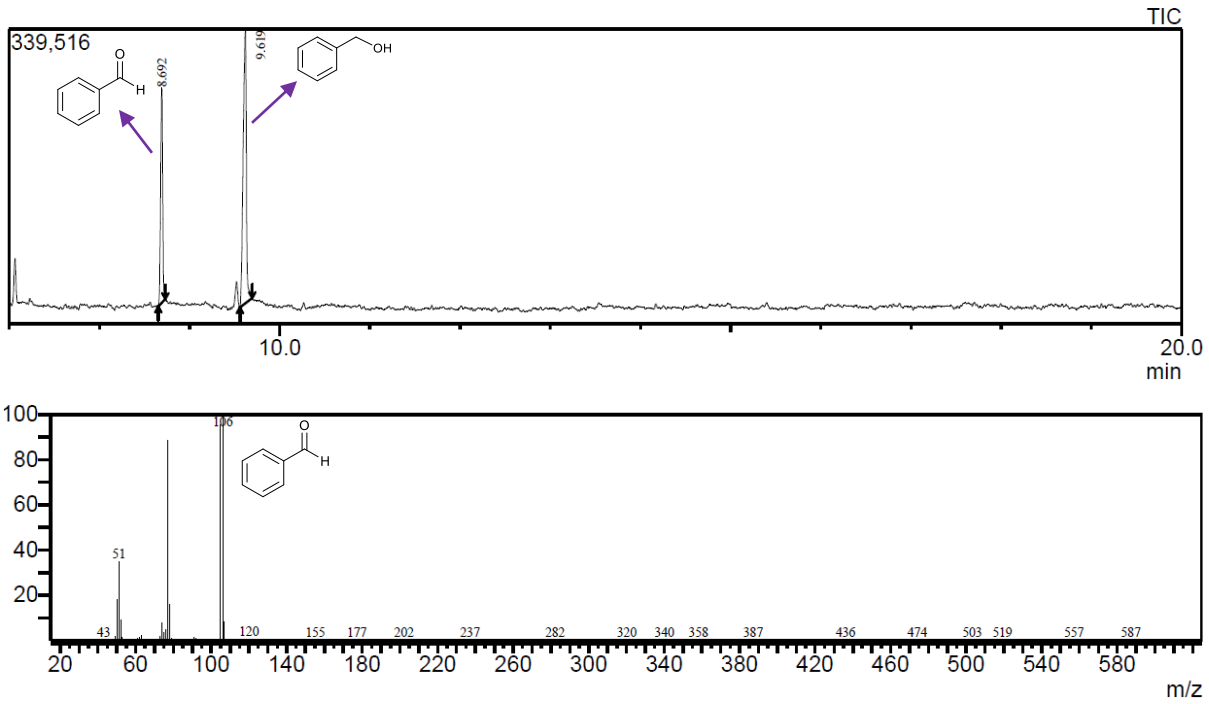


Figure S67. GC-MS spectrum for entry 14 of table 2.

GC-MS spectra of Acceptorless dehydrogenative coupling of aniline and benzyl alcohol products for table 3.

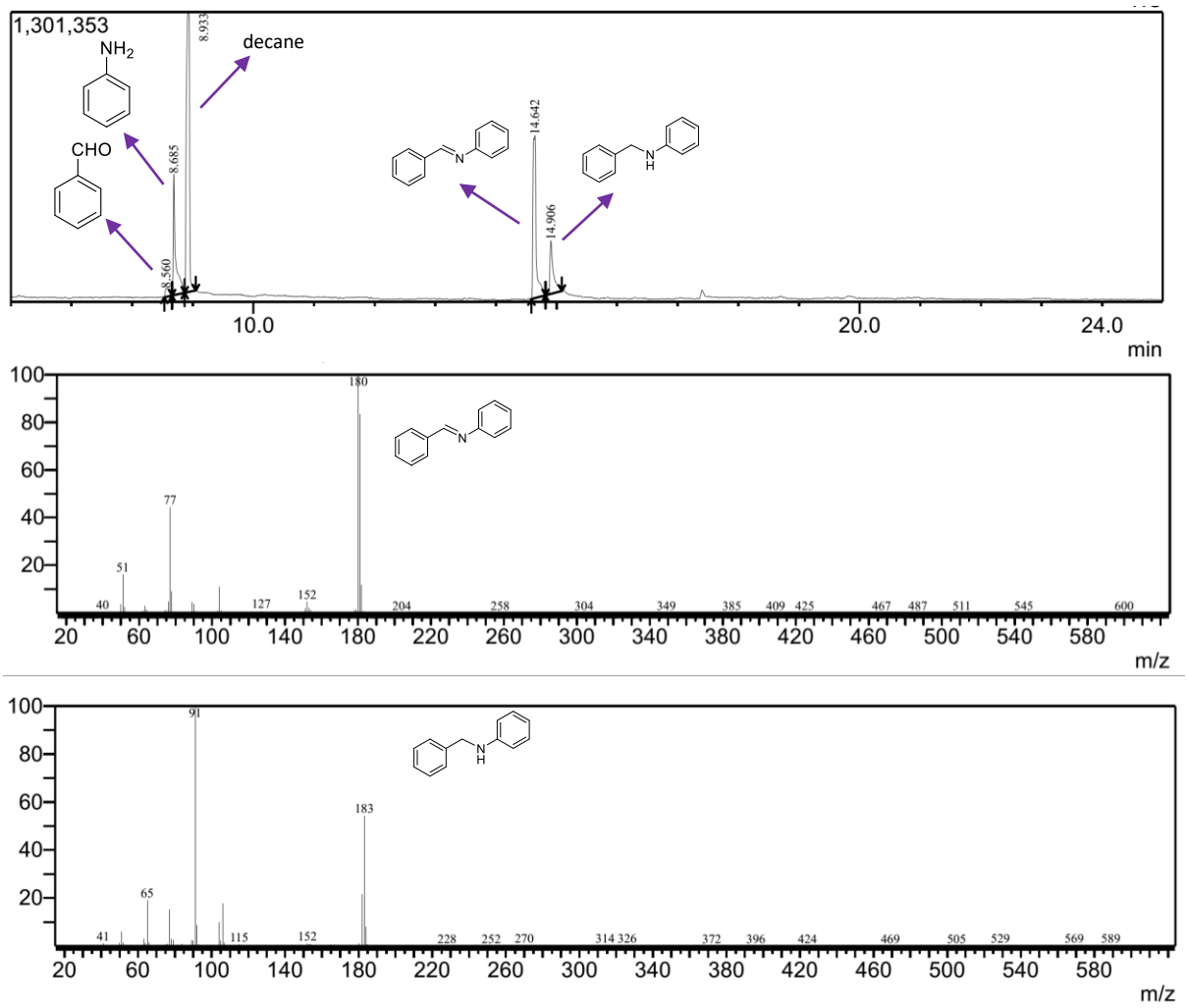


Figure S68. GC-MS spectrum for entry 1 of table 3.

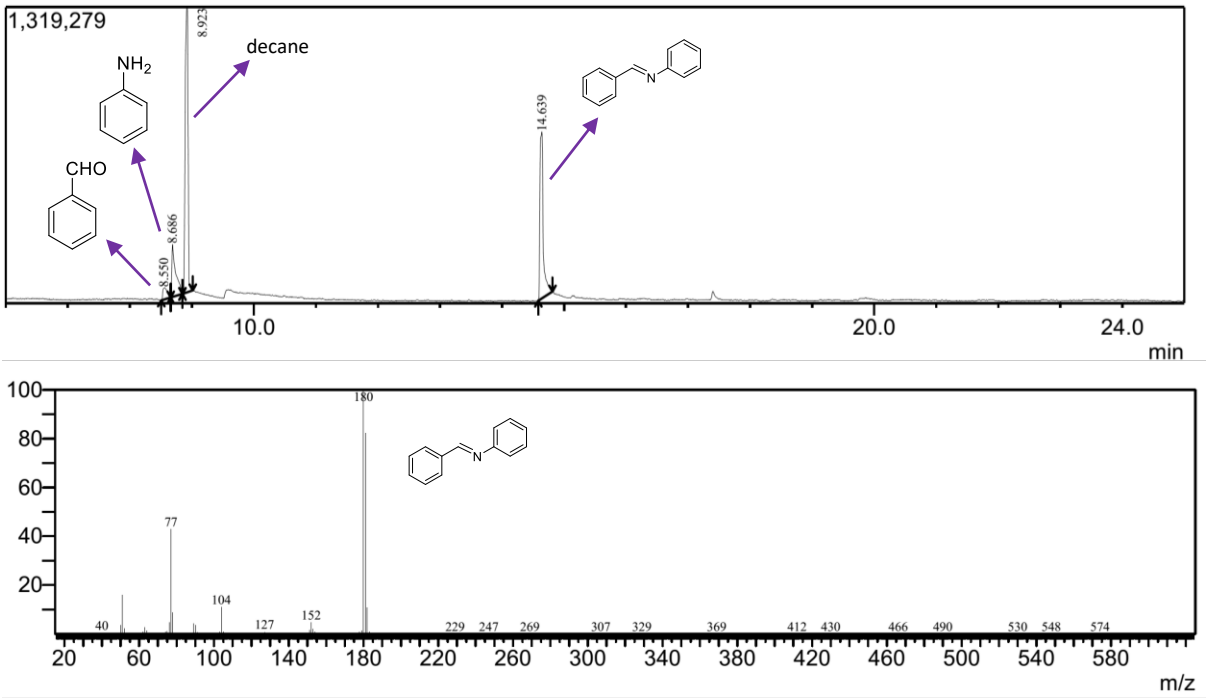
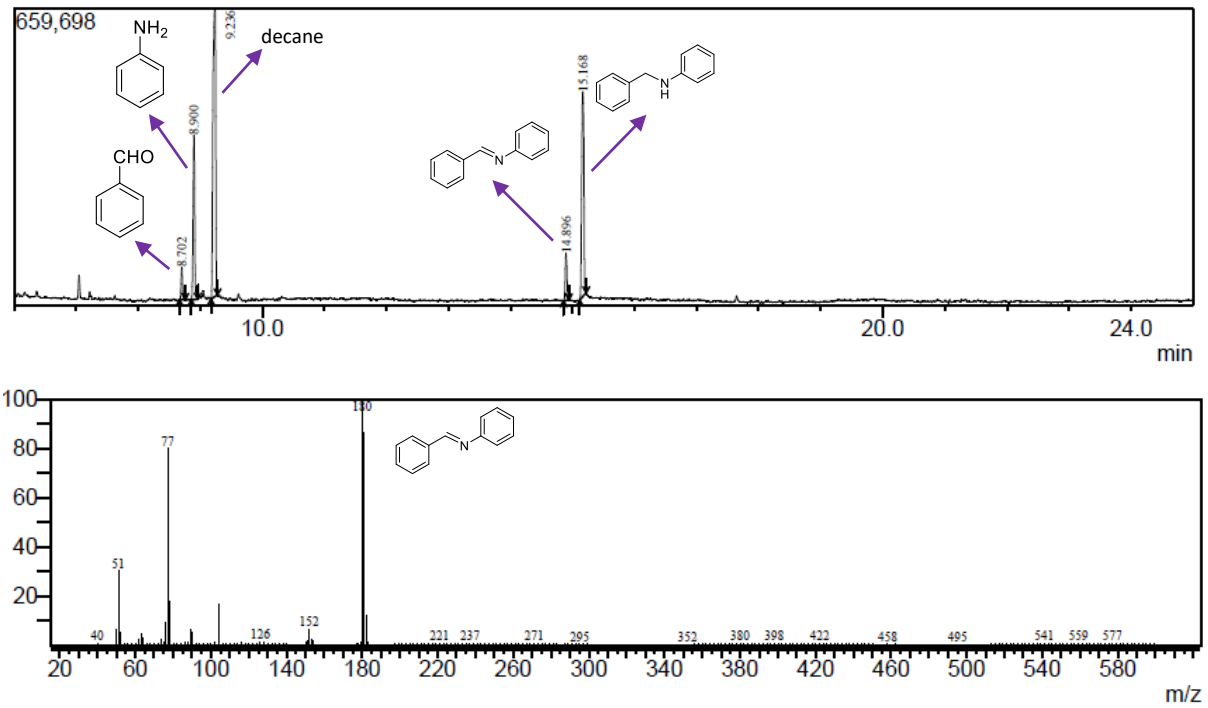


Figure S69. GC-MS spectrum for entry 2 of table 3.



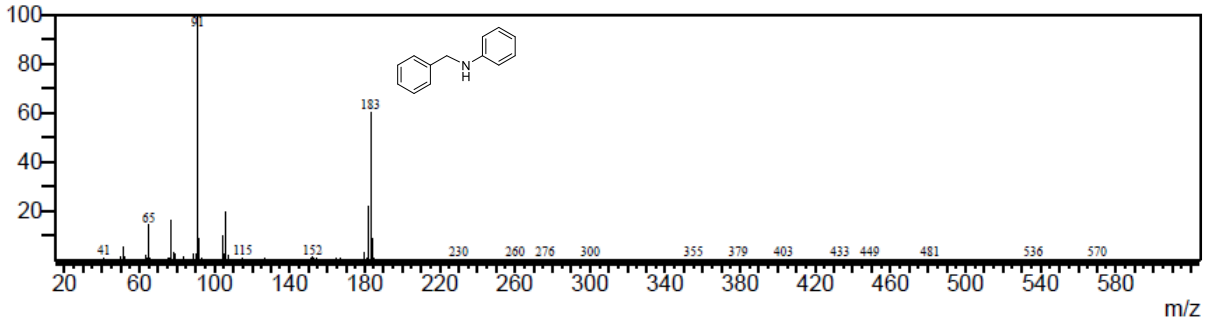


Figure S70. GC-MS spectrum for entry 3 of table 3.

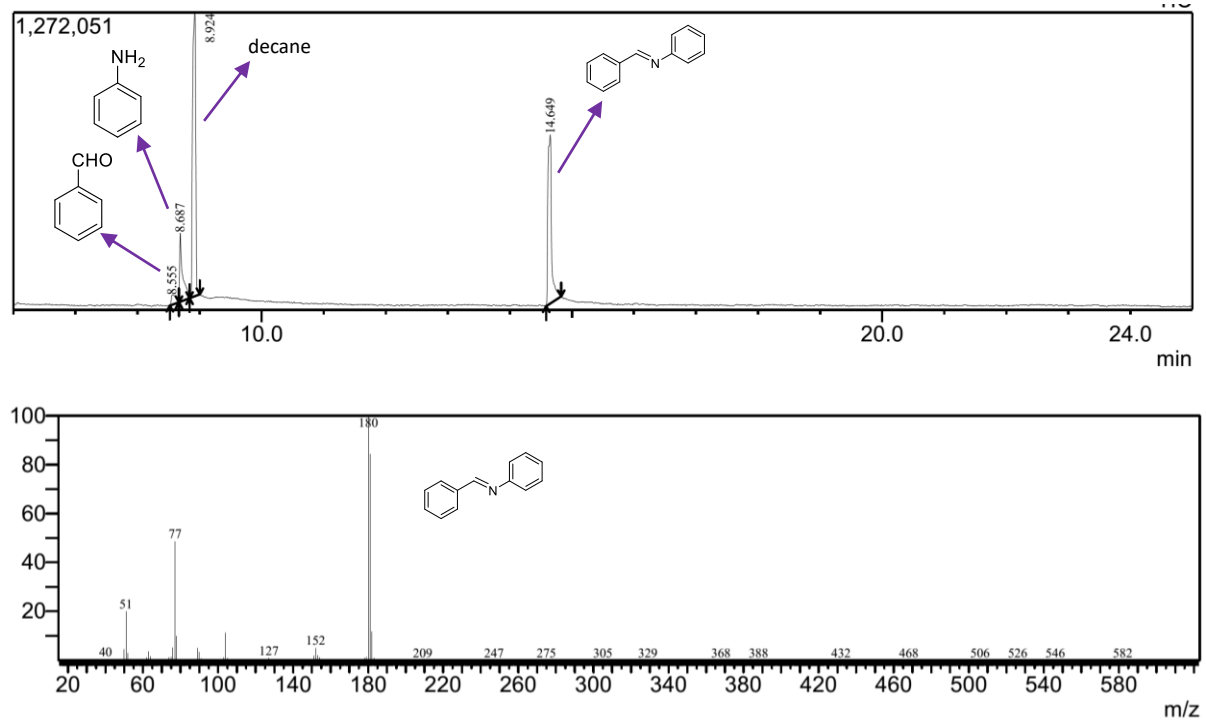
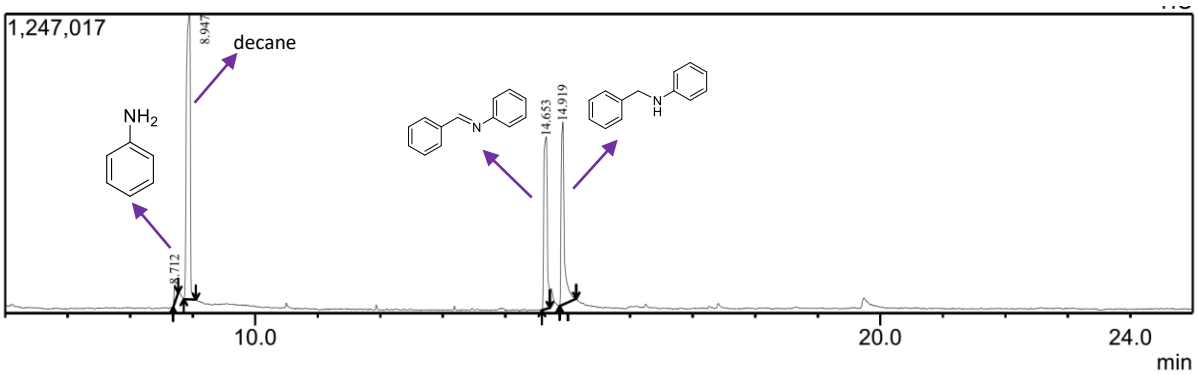


Figure S71. GC-MS spectrum for entry 4 of table 3.



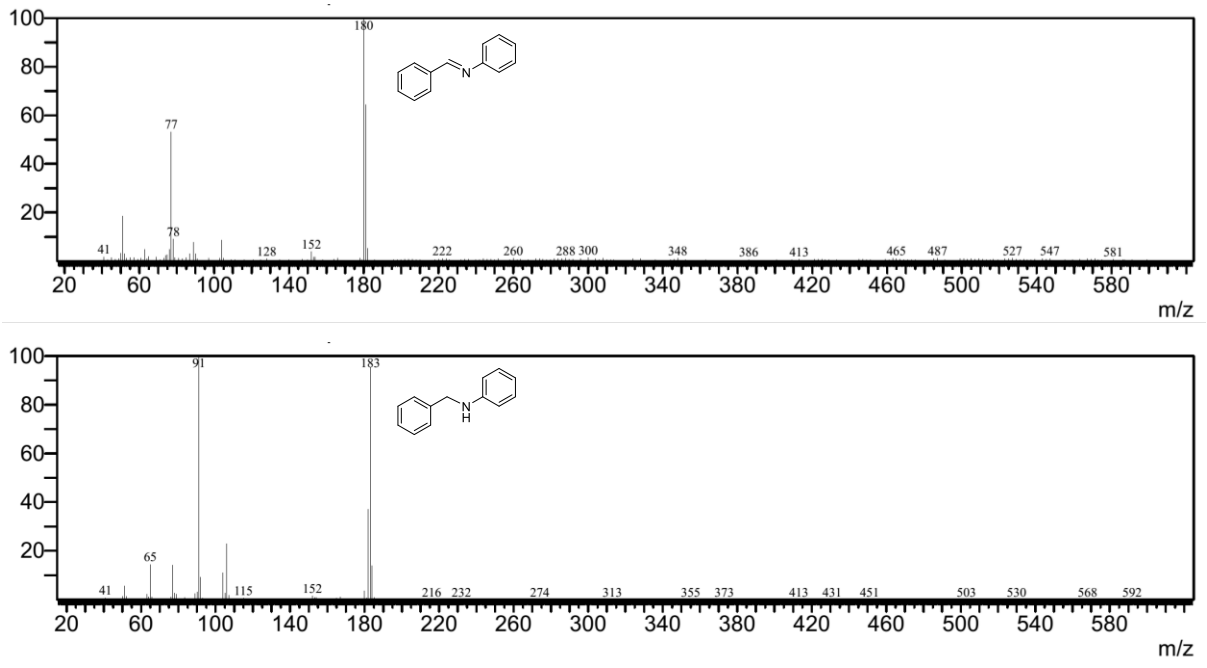
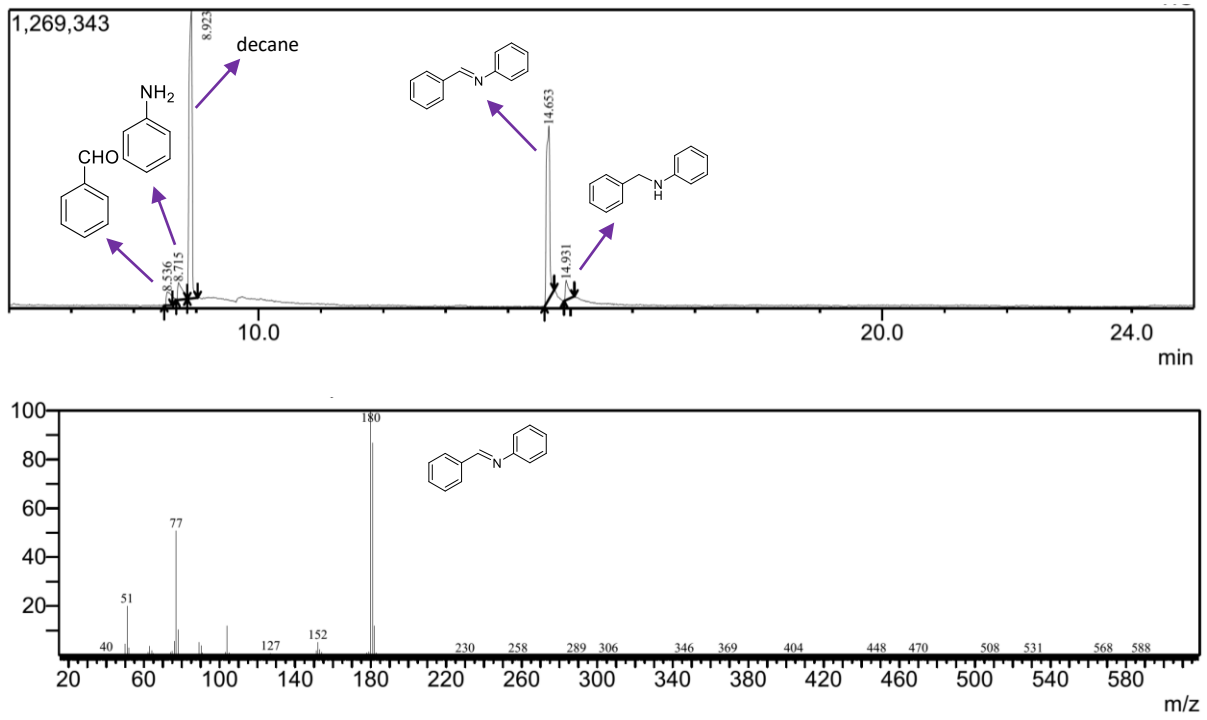


Figure S72. GC-MS spectrum for entry 5 of table 3.



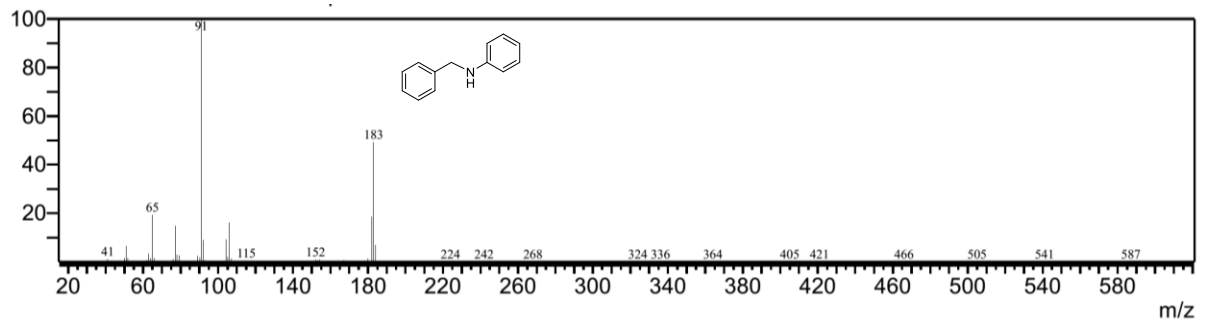


Figure S73. GC-MS spectrum for entry 6 of table 3.

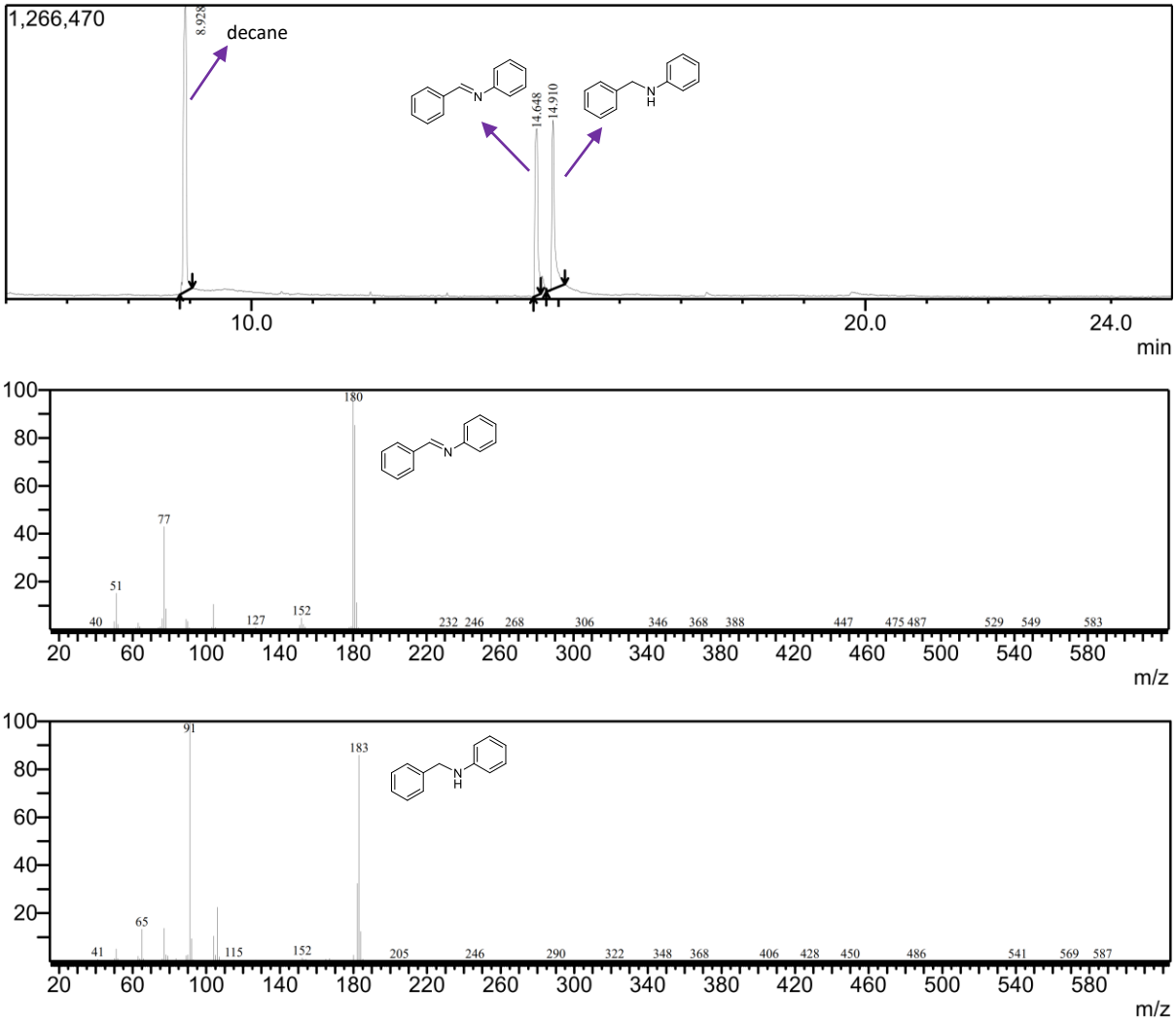


Figure S74. GC-MS spectrum for entry 7 of table 3.

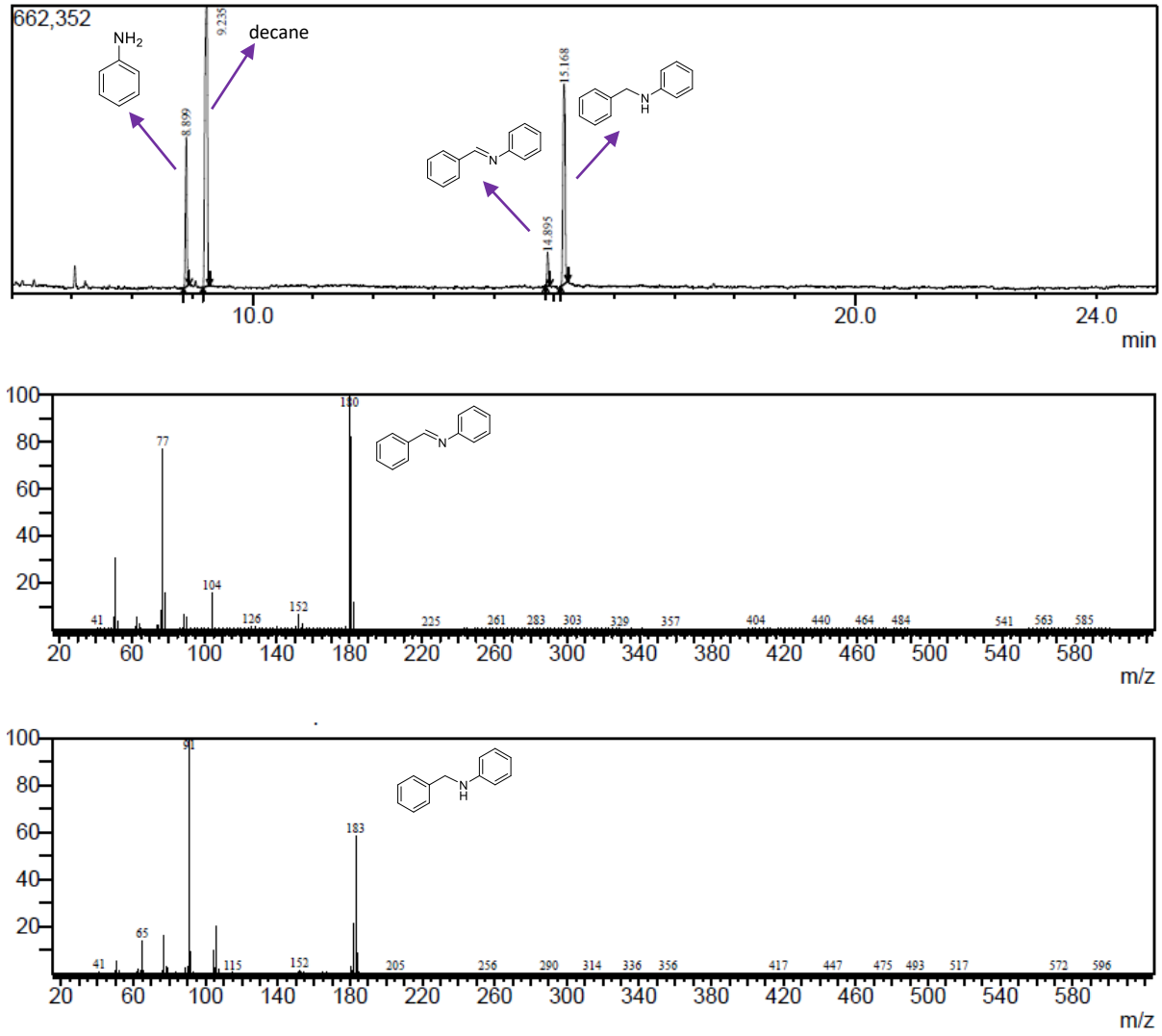
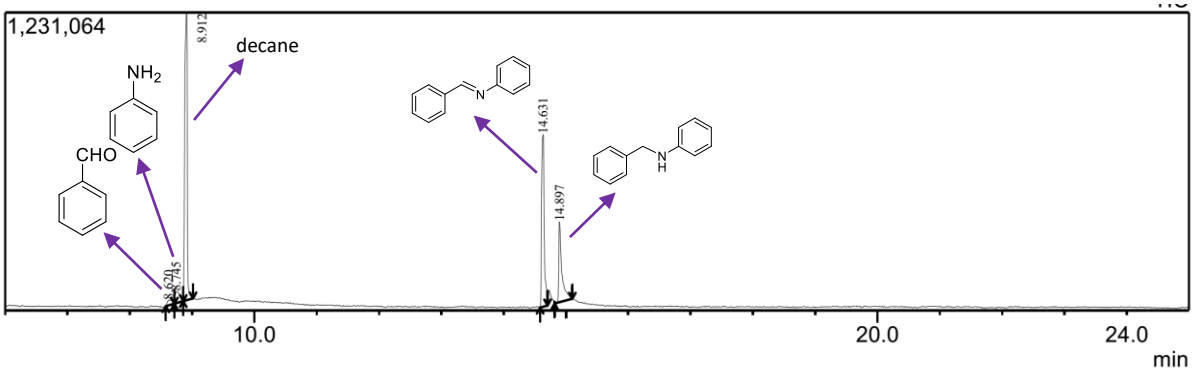


Figure S75. GC-MS spectrum for entry 8 of table 3.



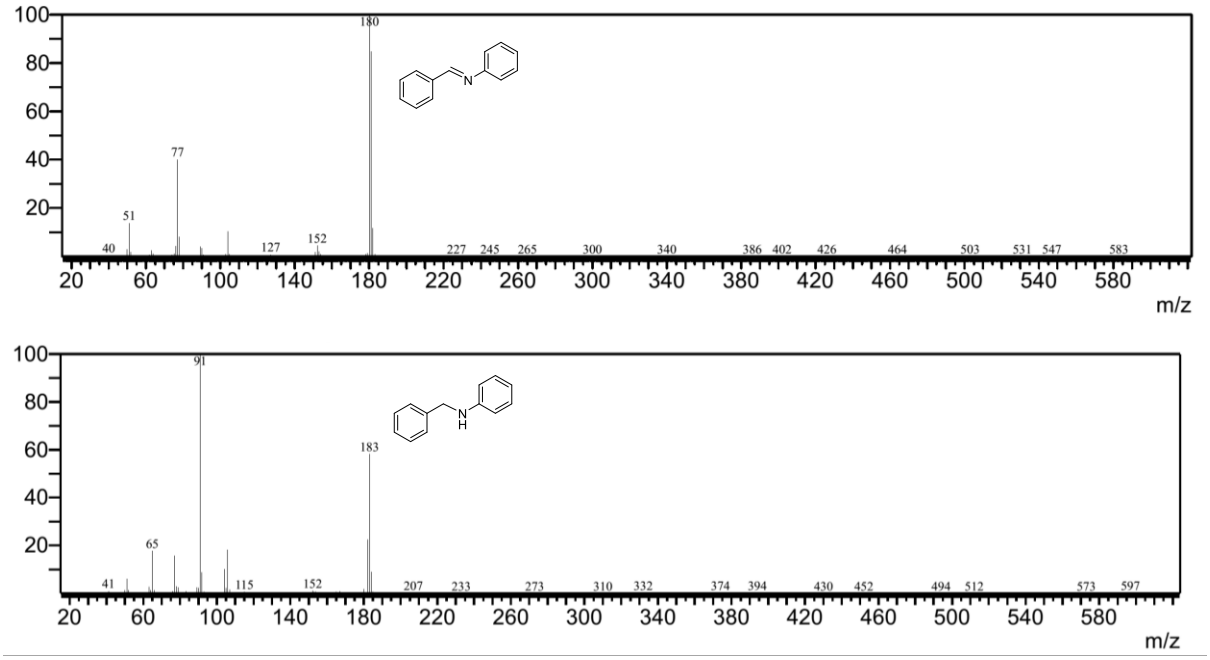
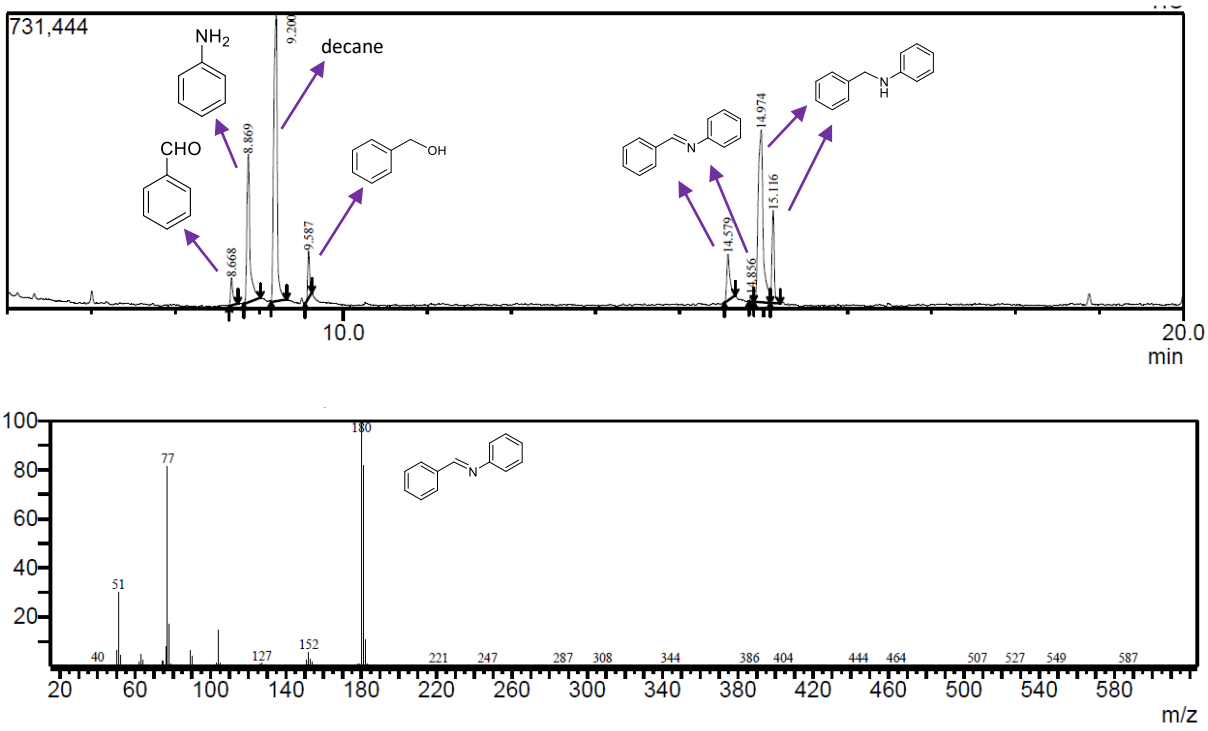


Figure S76. GC-MS spectrum for entry 9 of table 3.



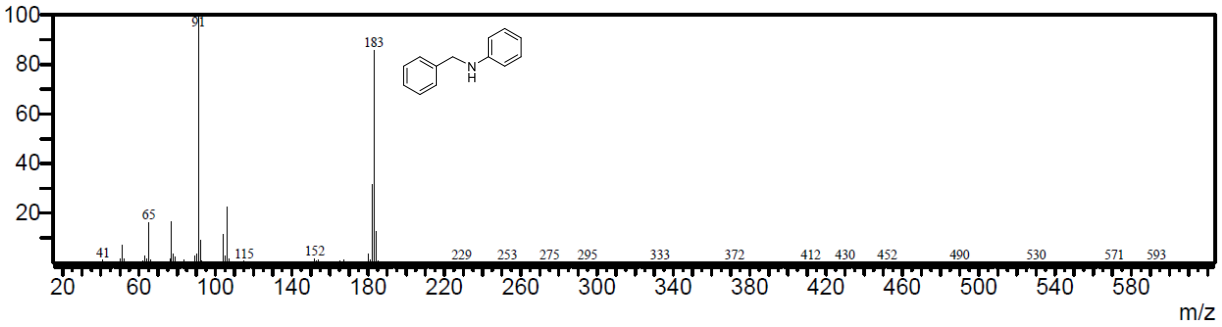


Figure S77. GC-MS spectrum for entry 10 of table 3.

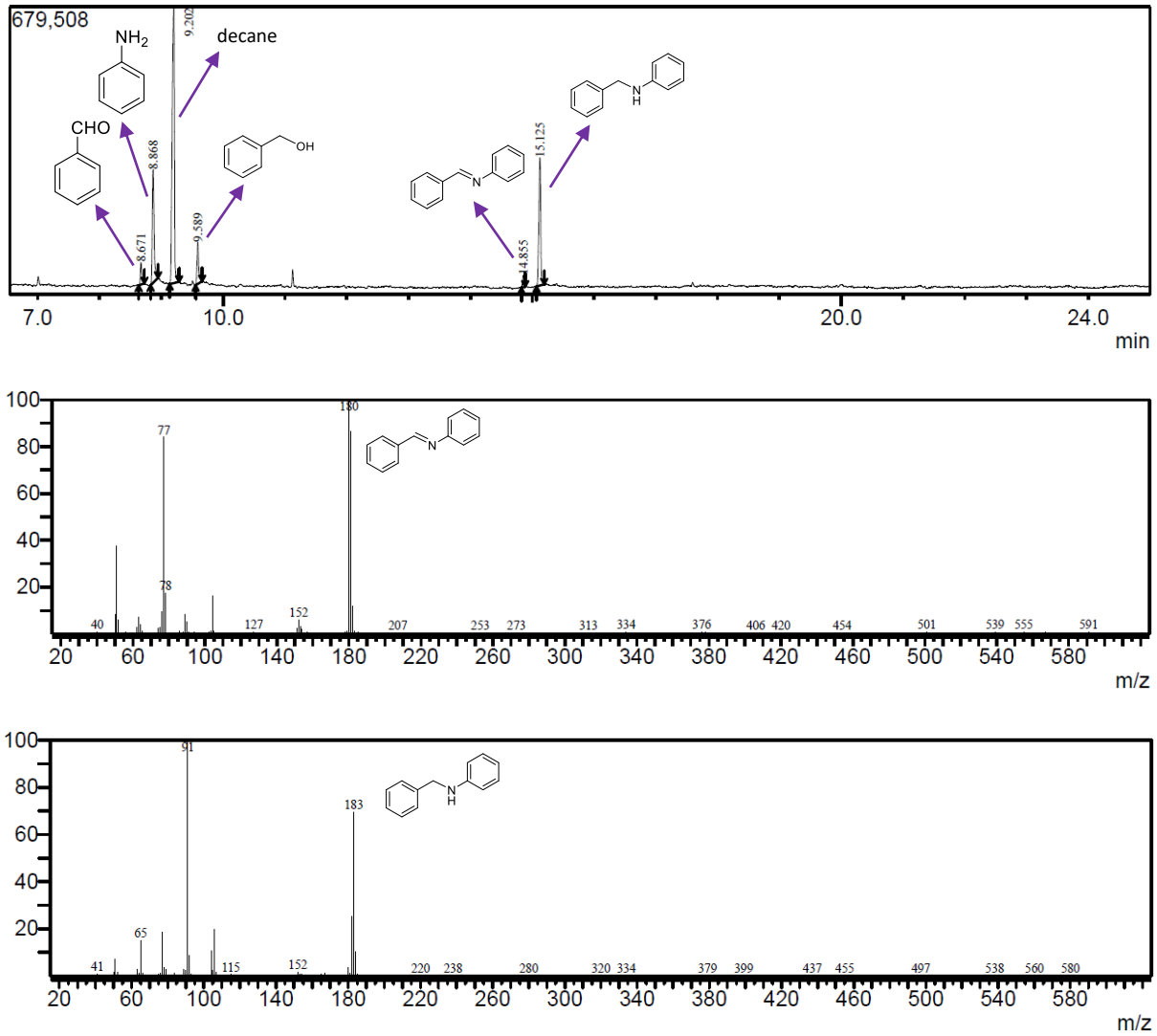


Figure S78. GC-MS spectrum for entry 11 of table 3.

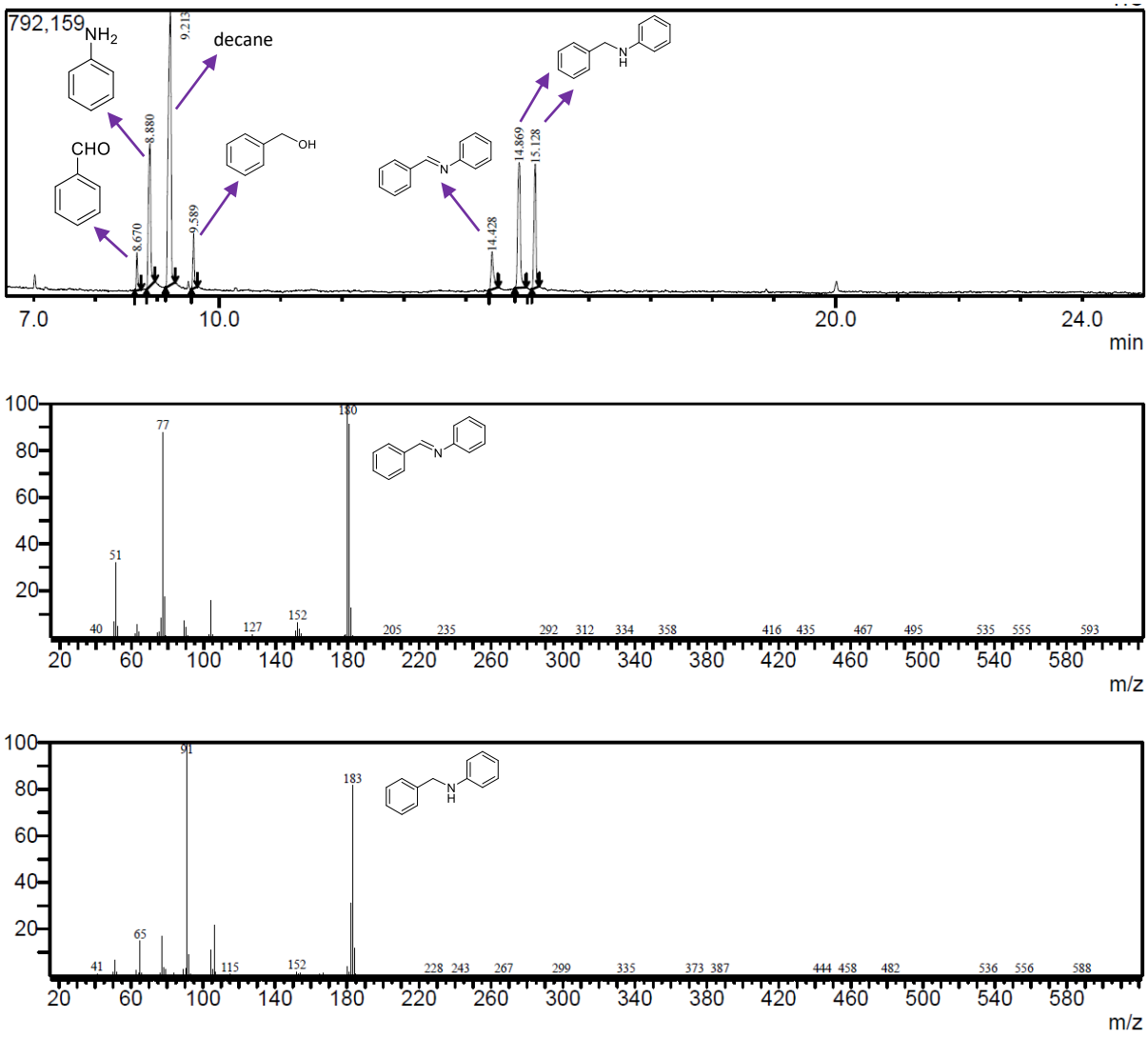
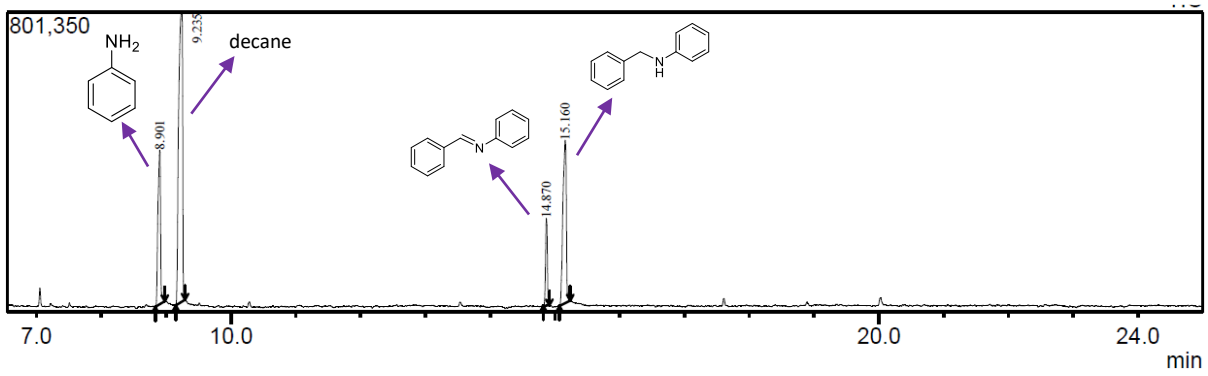


Figure S79. GC-MS spectrum for entry 12 of table 3.



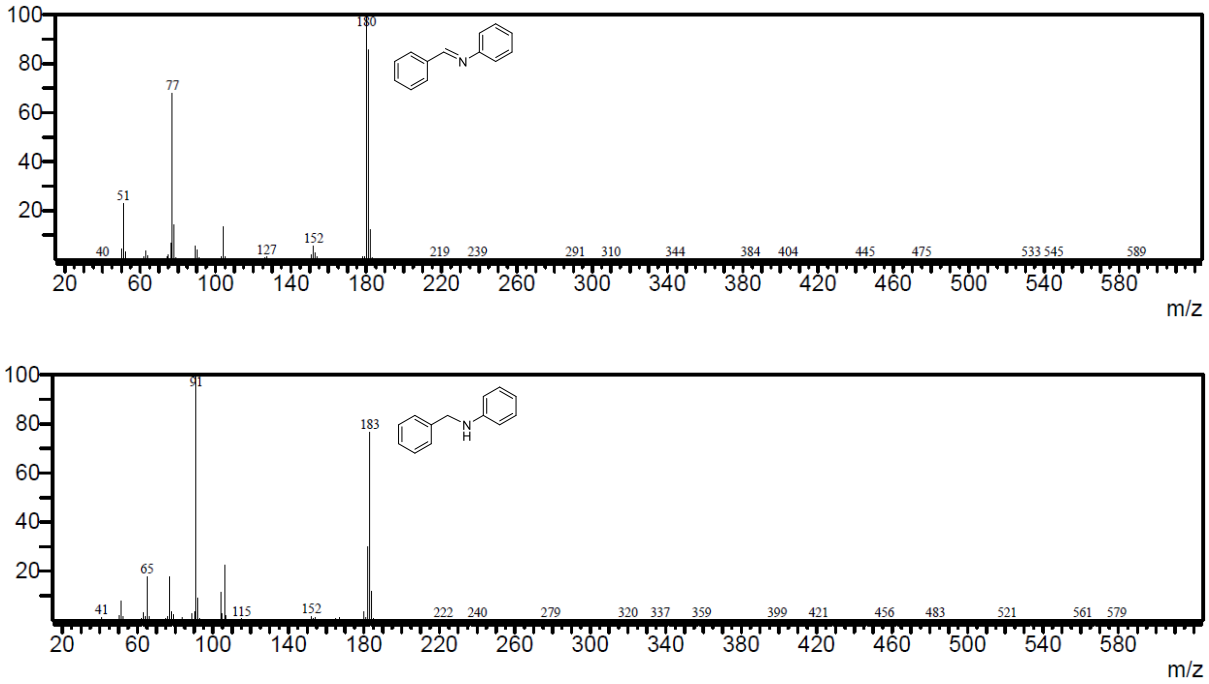
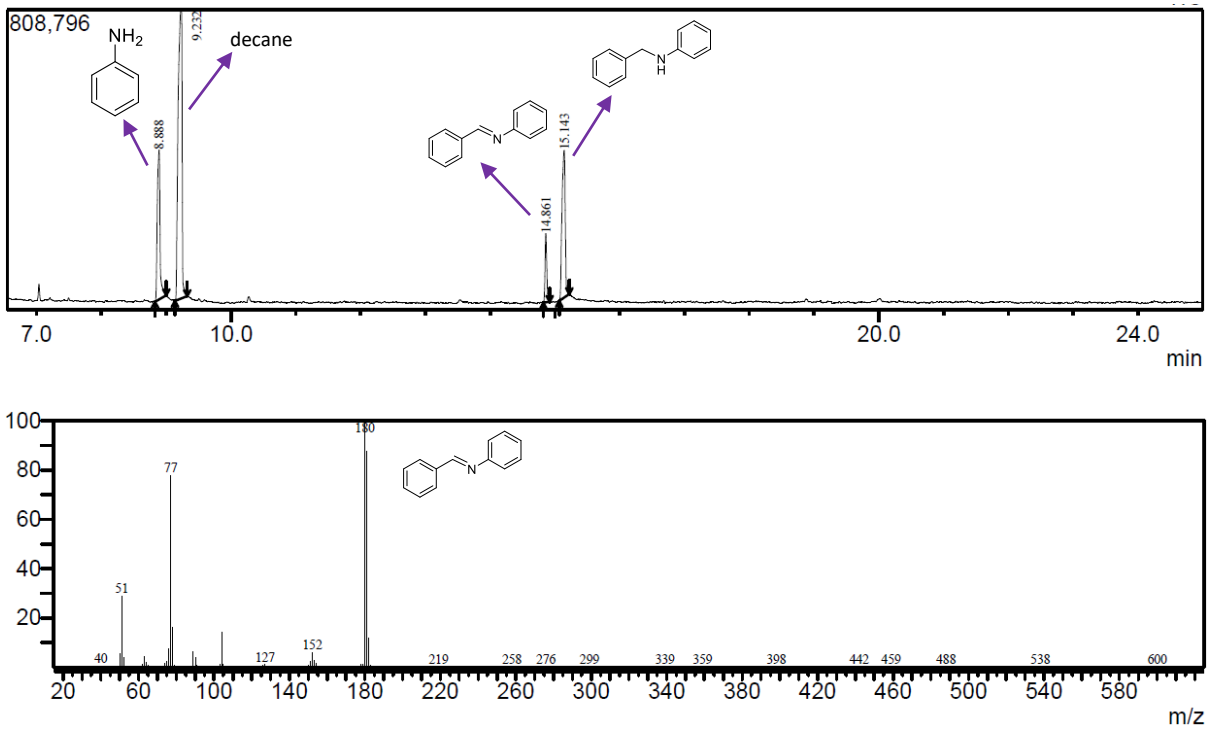


Figure S80. GC-MS spectrum for entry 13 of table 3.



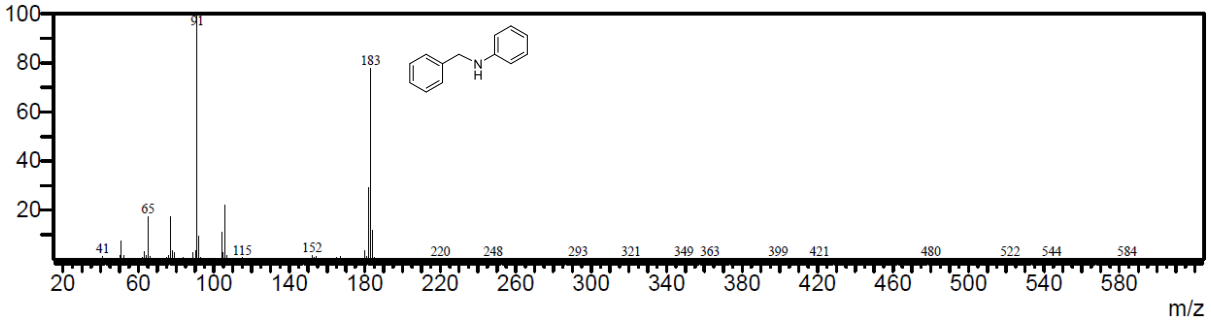


Figure S81. GC-MS spectrum for entry 14 of table 3.

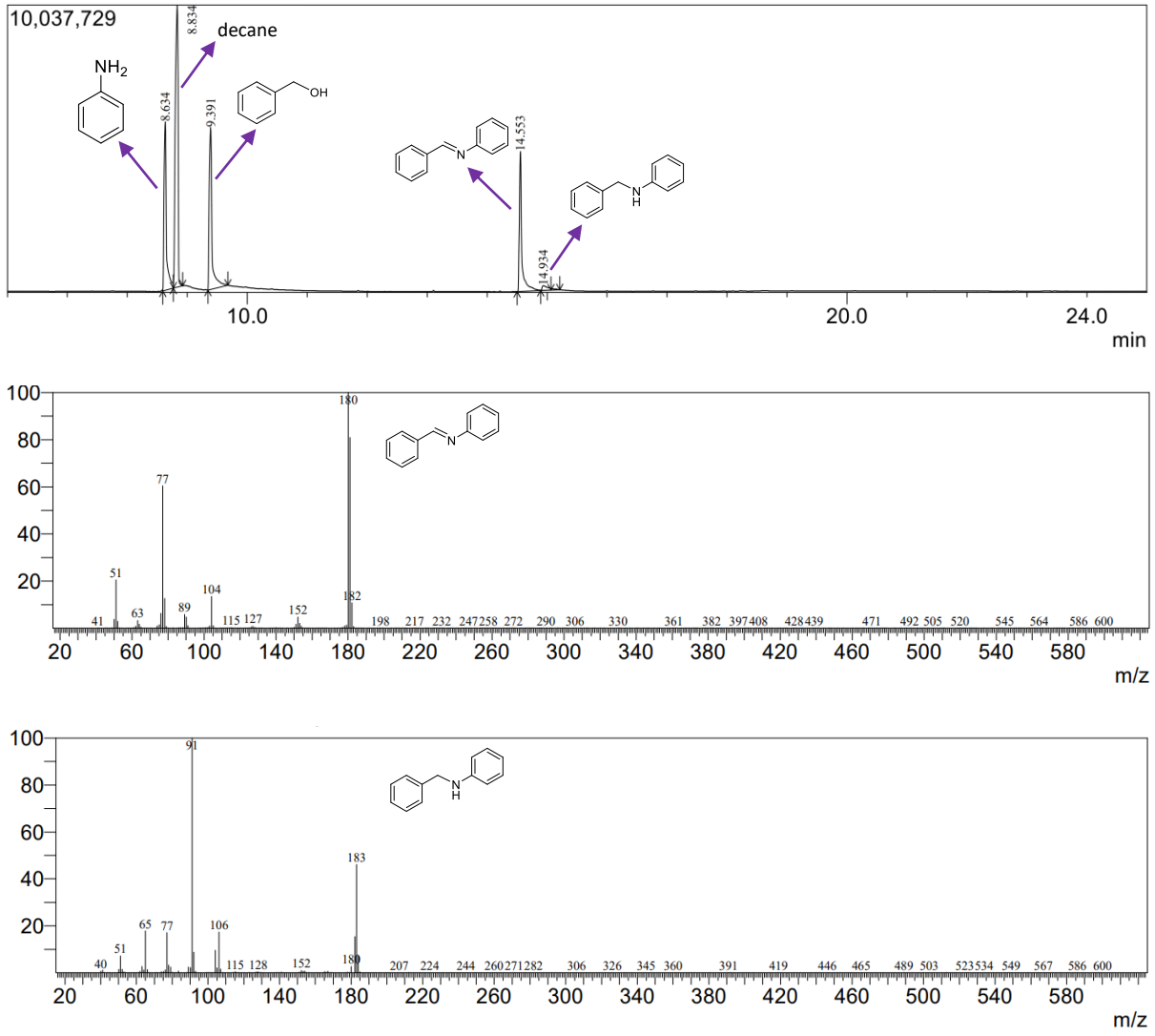


Figure S82. GC-MS spectrum for entry 15 of table 3.

GC-MS spectra of Acceptorless dehydrogenative coupling products for table 4.

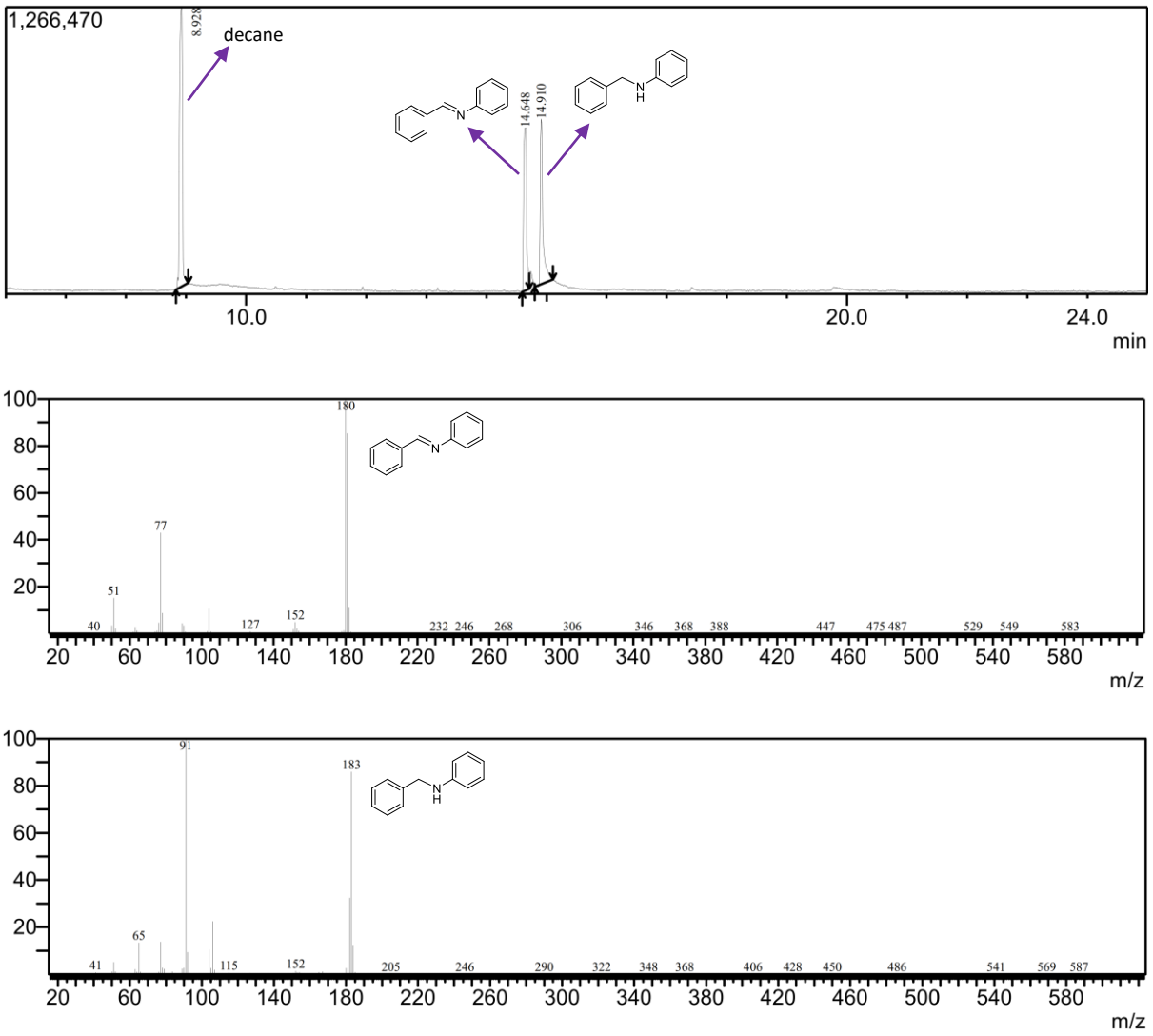
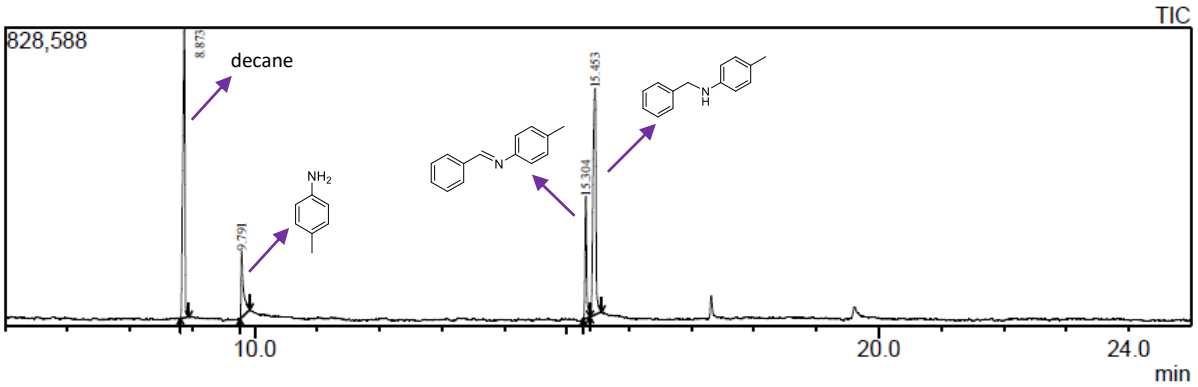


Figure S83. GC-MS spectrum for entry 1 of table 4.



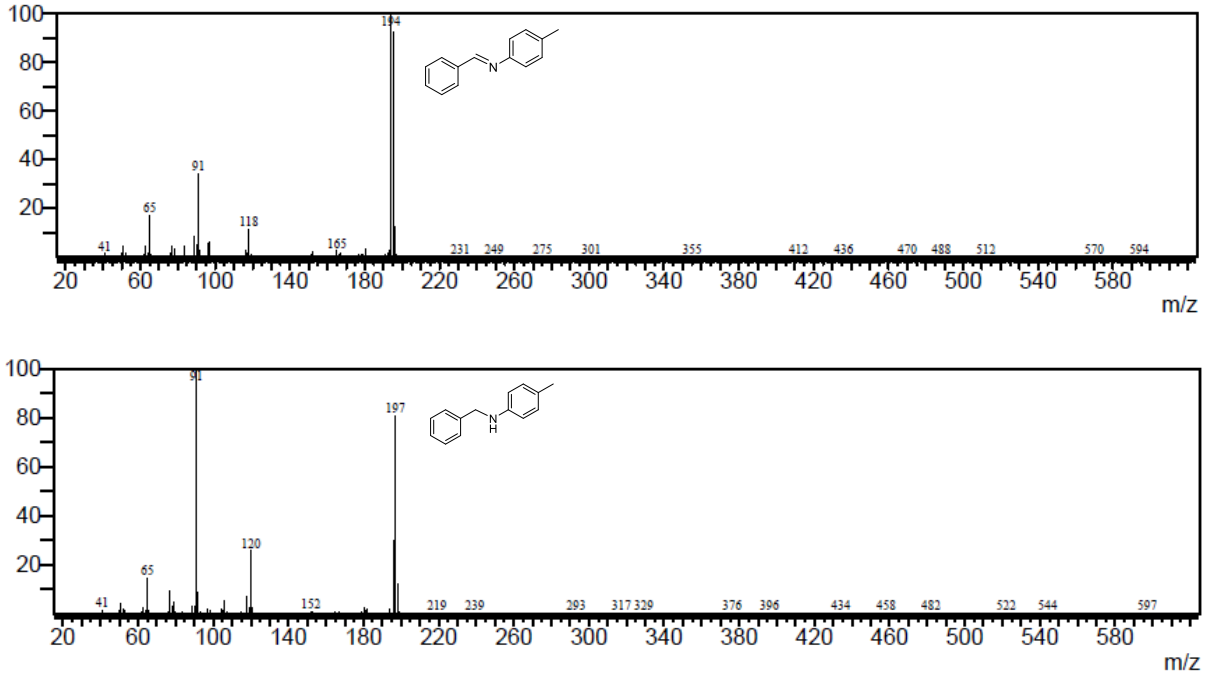
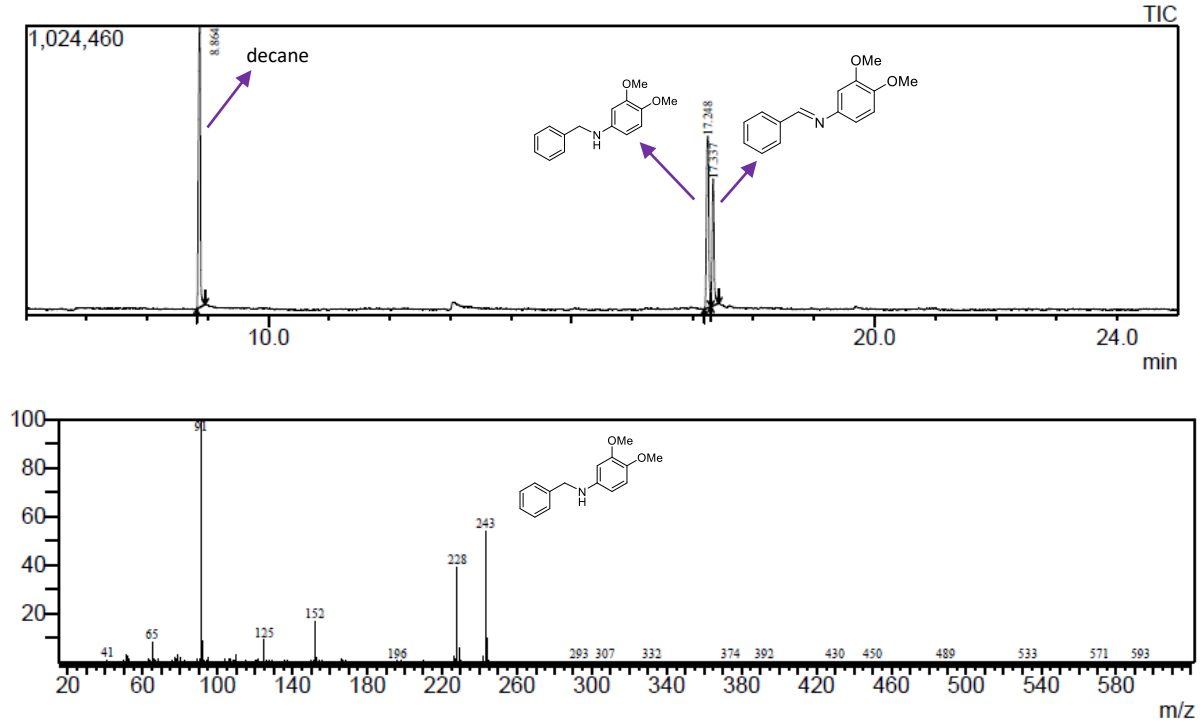


Figure S84. GC-MS spectrum for entry 2 of table 4.



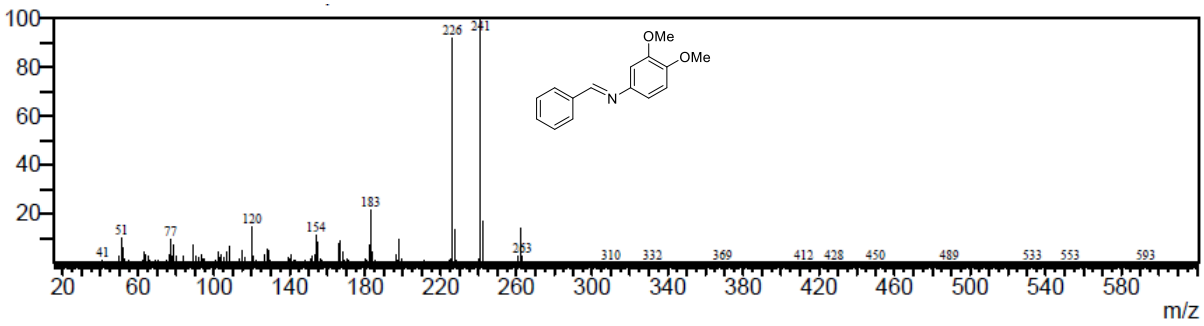


Figure S85. GC-MS spectrum for entry 3 of table 4.

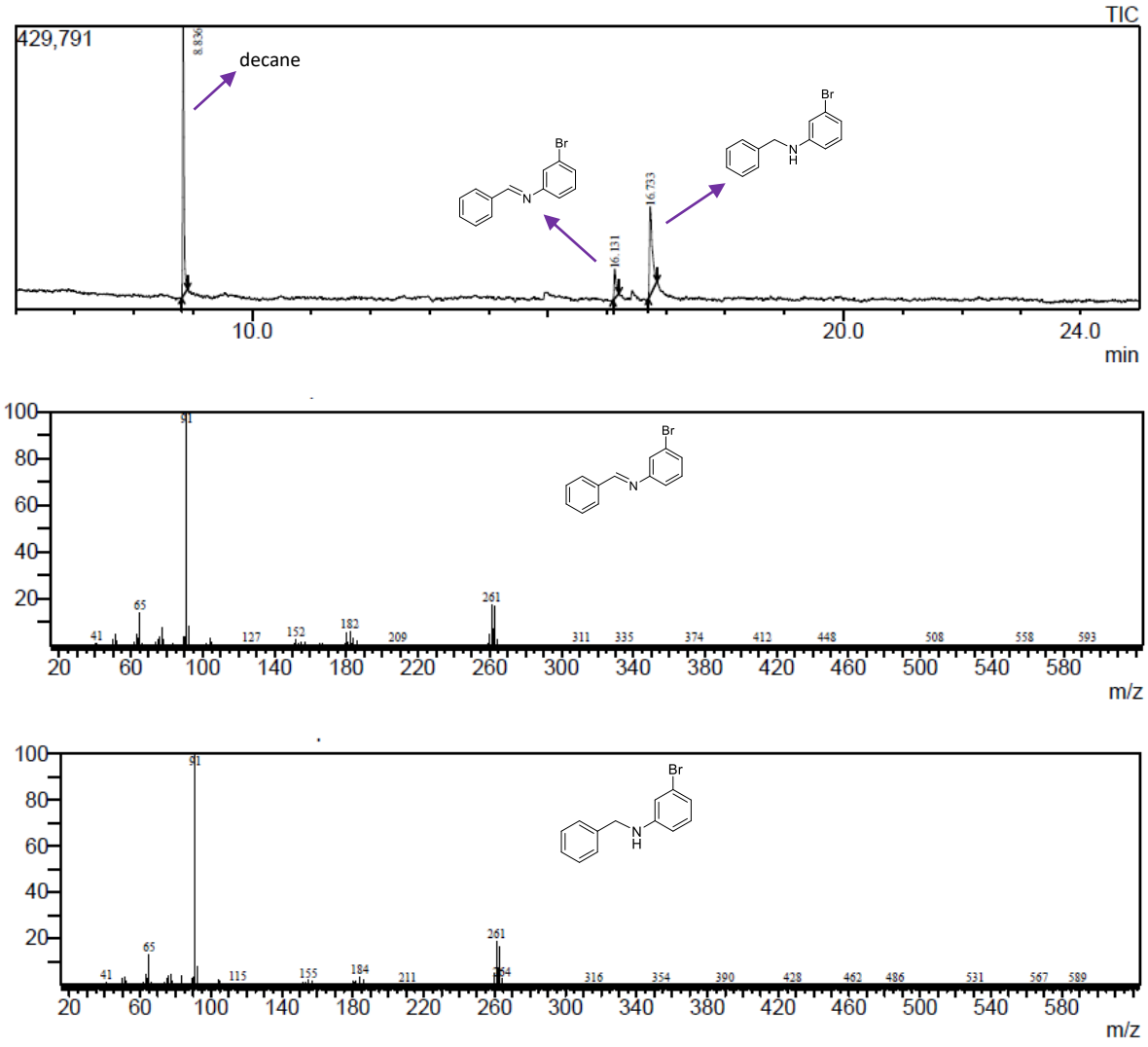


Figure S86. GC-MS spectrum for entry 4 of table 4.

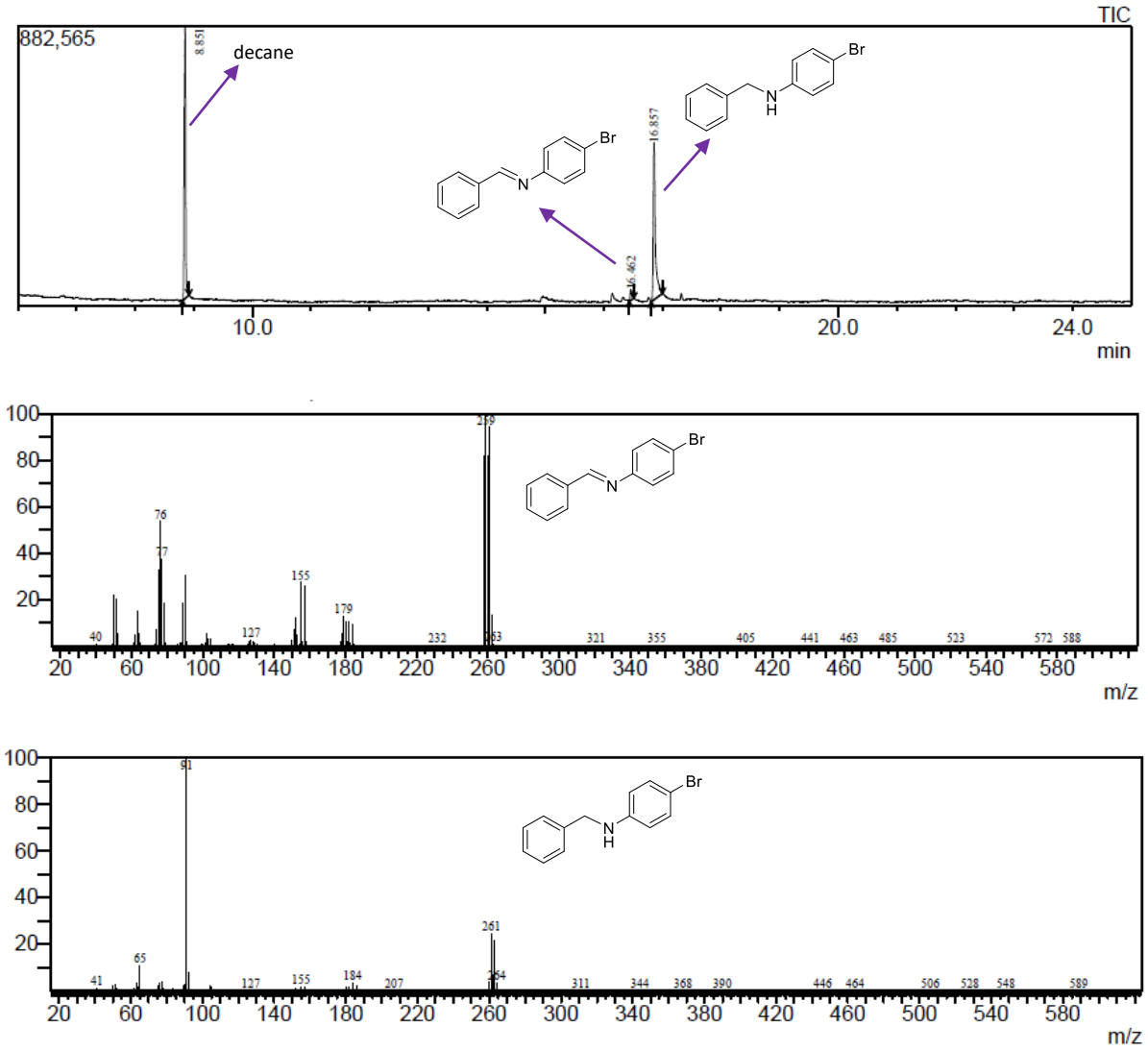
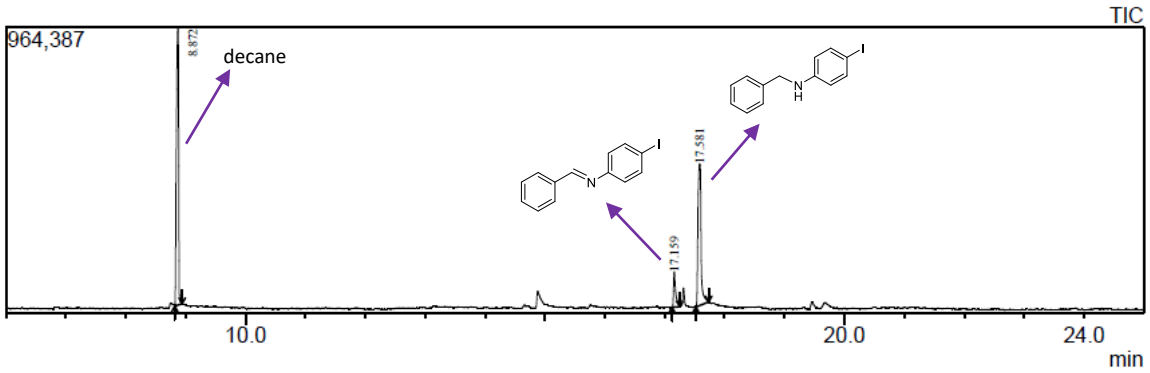


Figure S87. GC-MS spectrum for entry 5 of table 4.



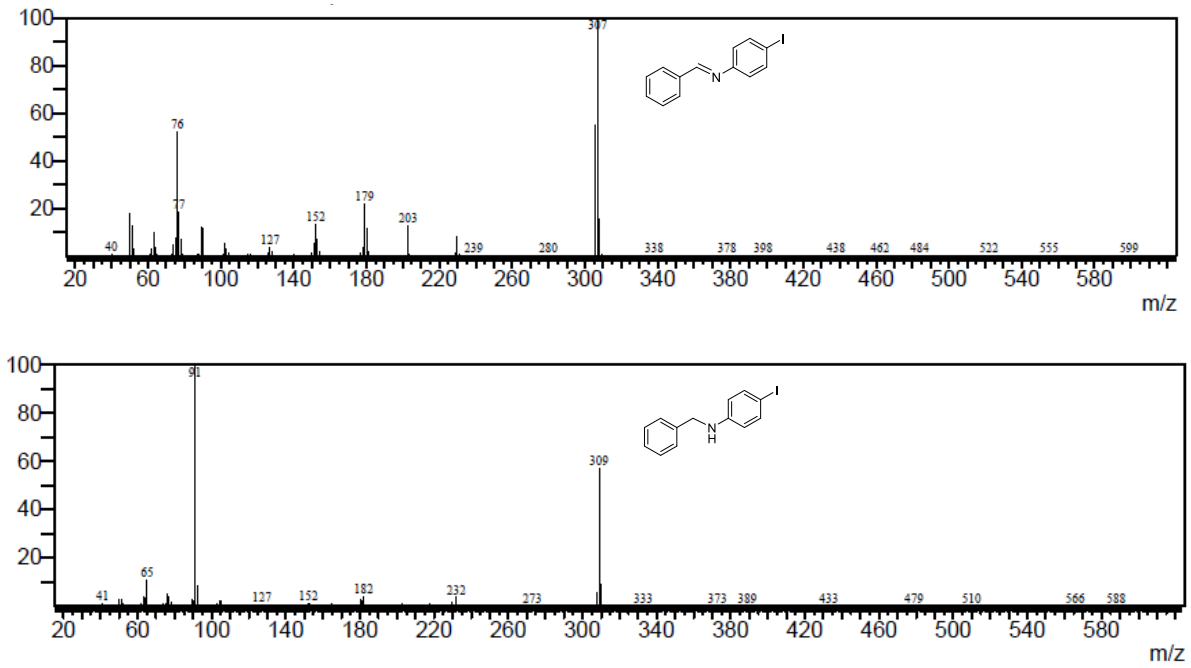


Figure S88. GC-MS spectrum for entry 6 of table 4.

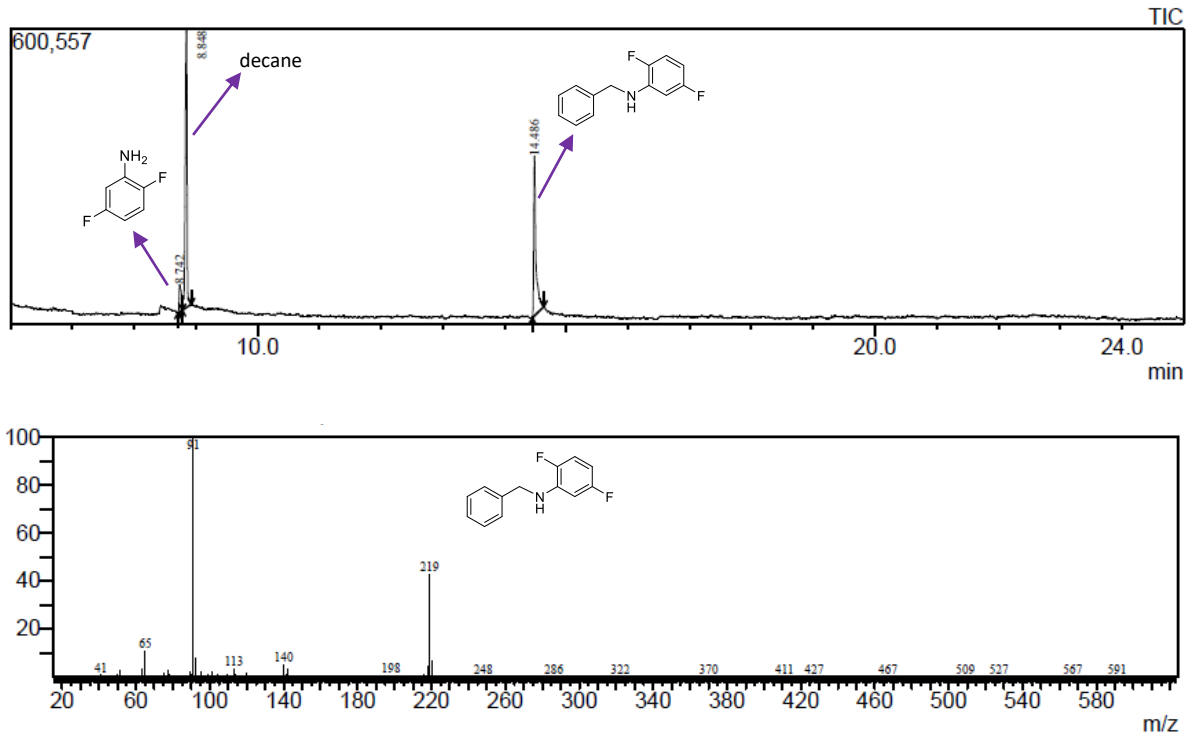


Figure S89. GC-MS spectrum for entry 7 of table 4.

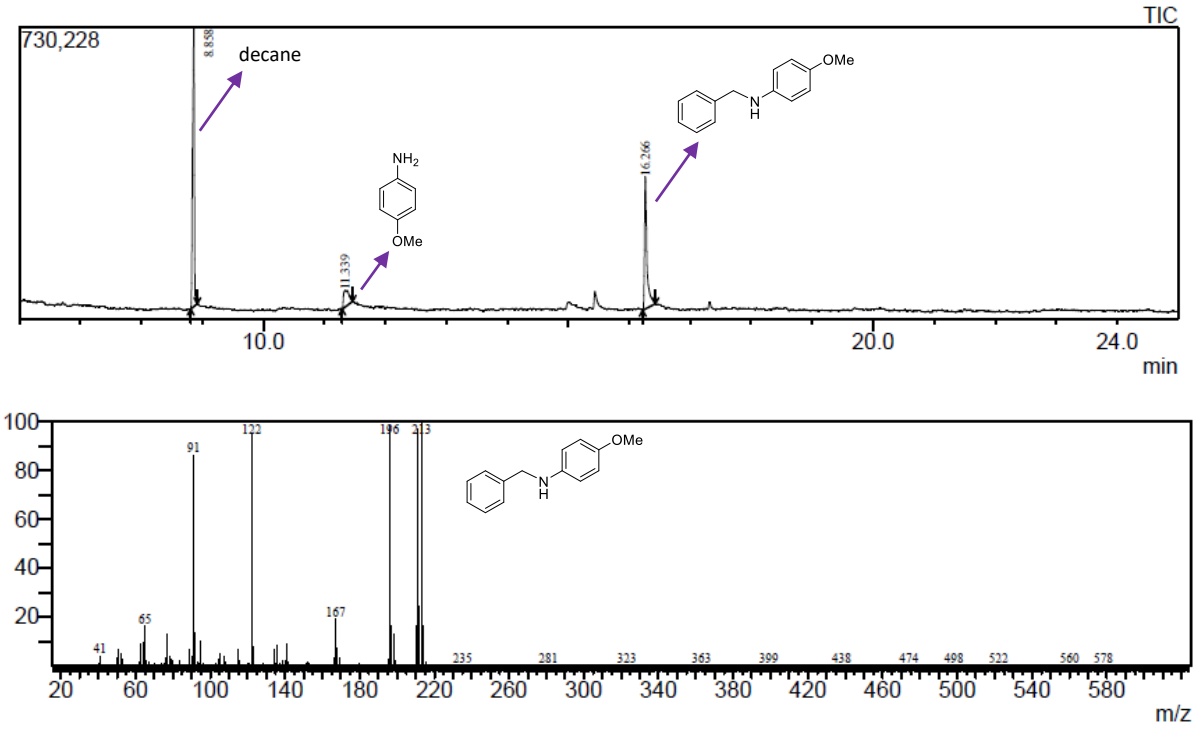


Figure S90. GC-MS spectrum for entry 8 of table 4.

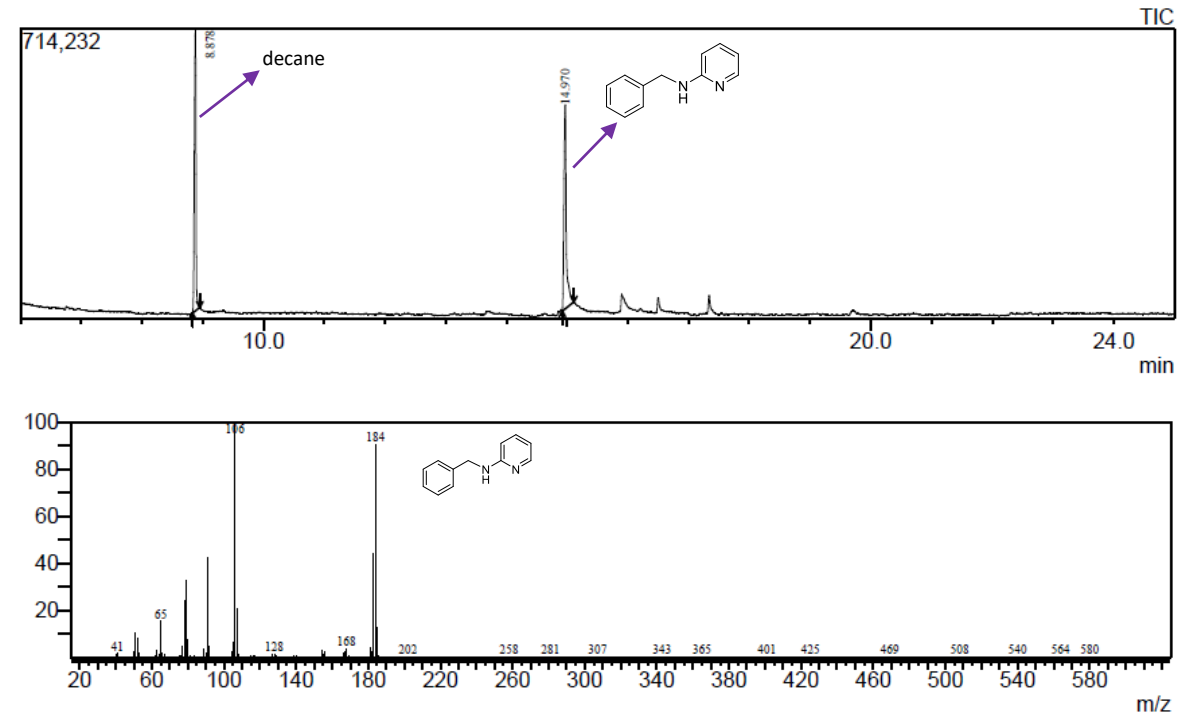


Figure S91. GC-MS spectrum for entry 9 of table 4.

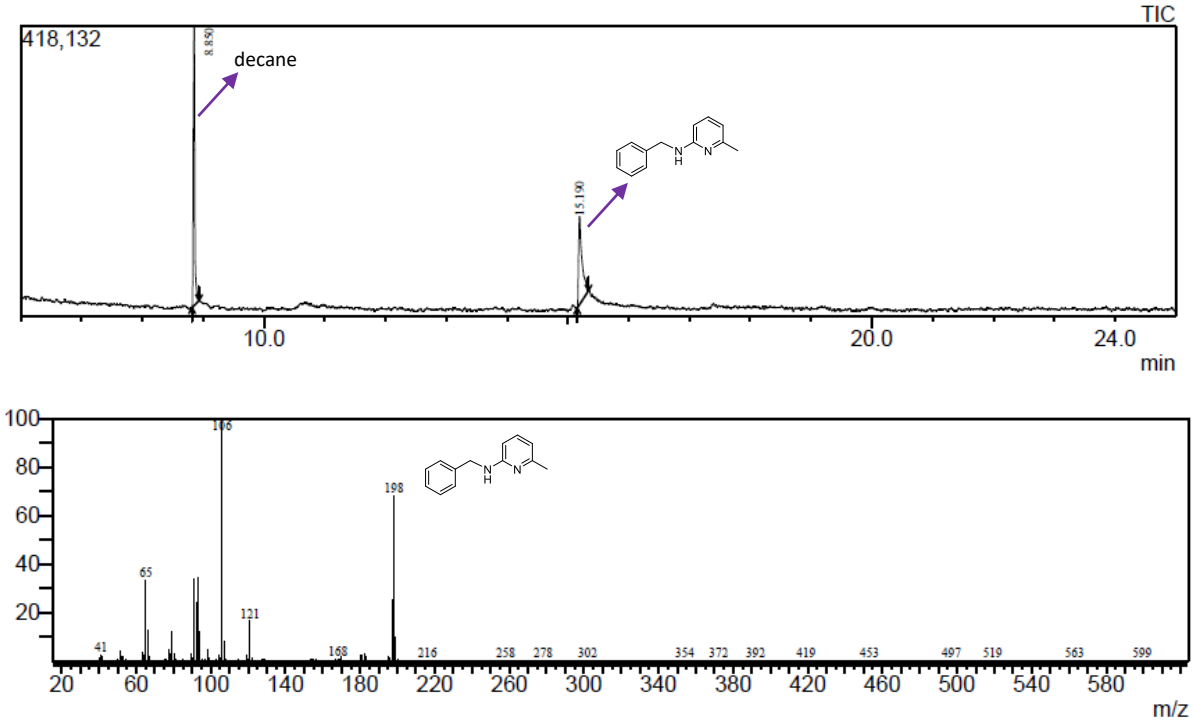


Figure S92. GC-MS spectrum for entry 10 of table 4.

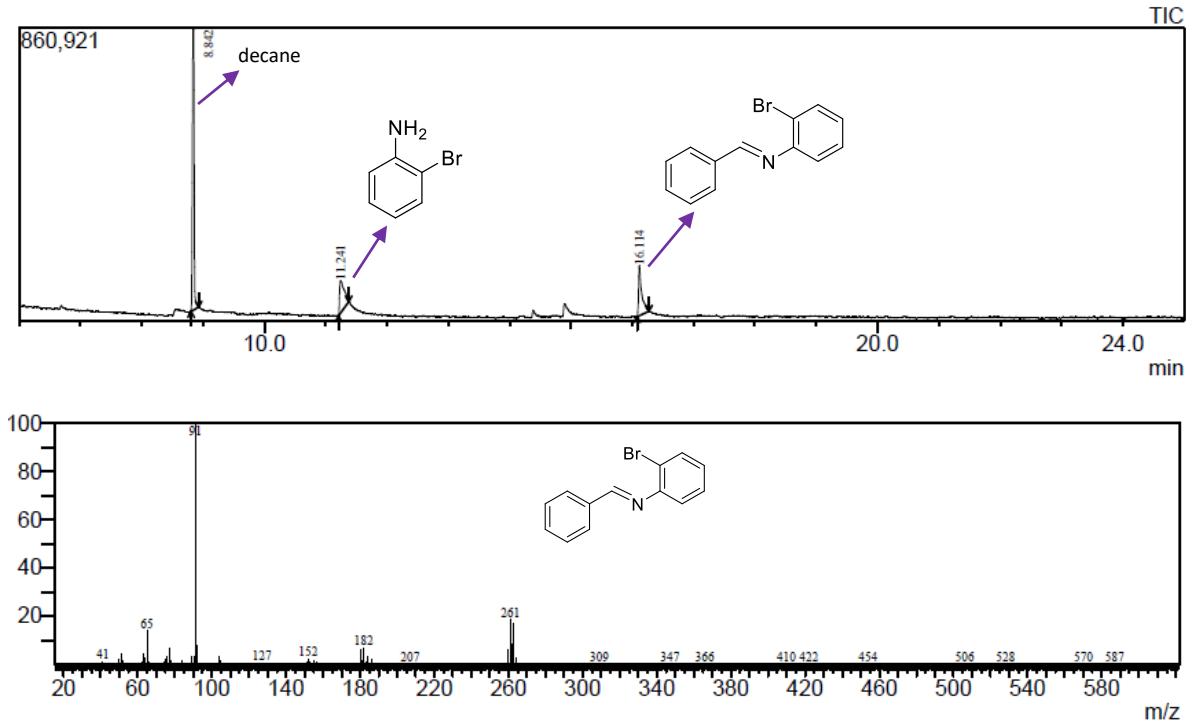


Figure S93. GC-MS spectrum for entry 11 of table 4.

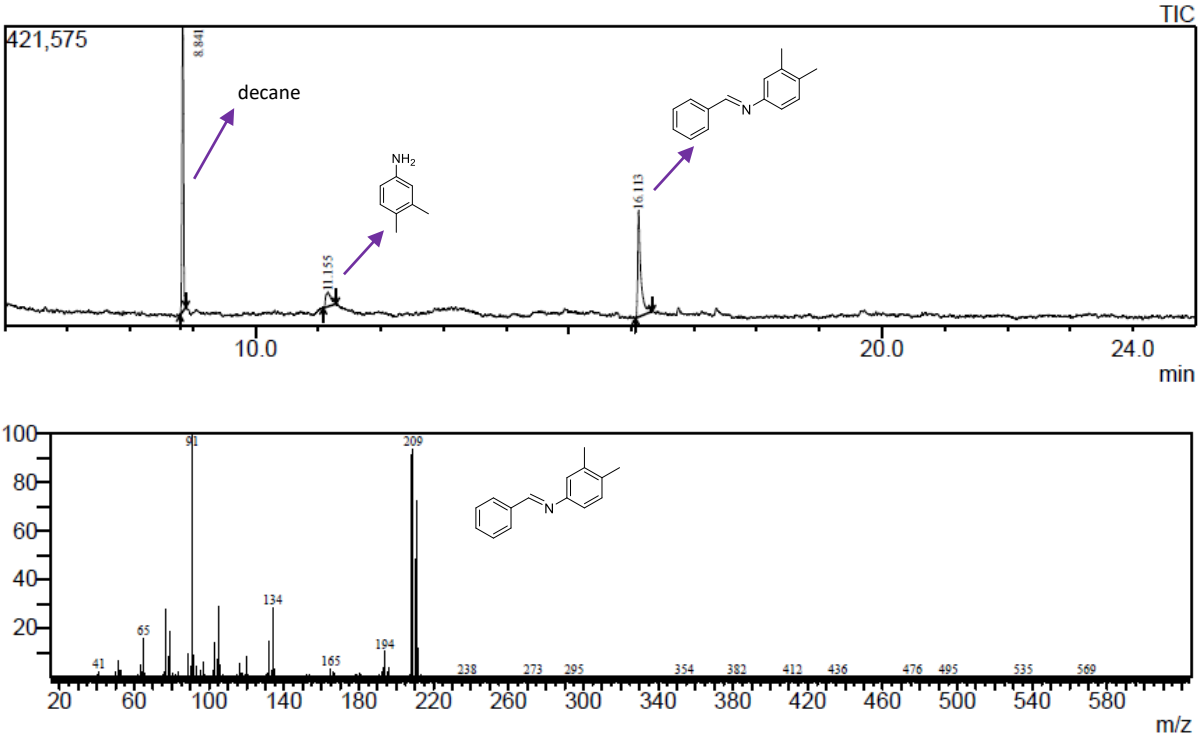


Figure S94. GC-MS spectrum for entry 12 of table 4.

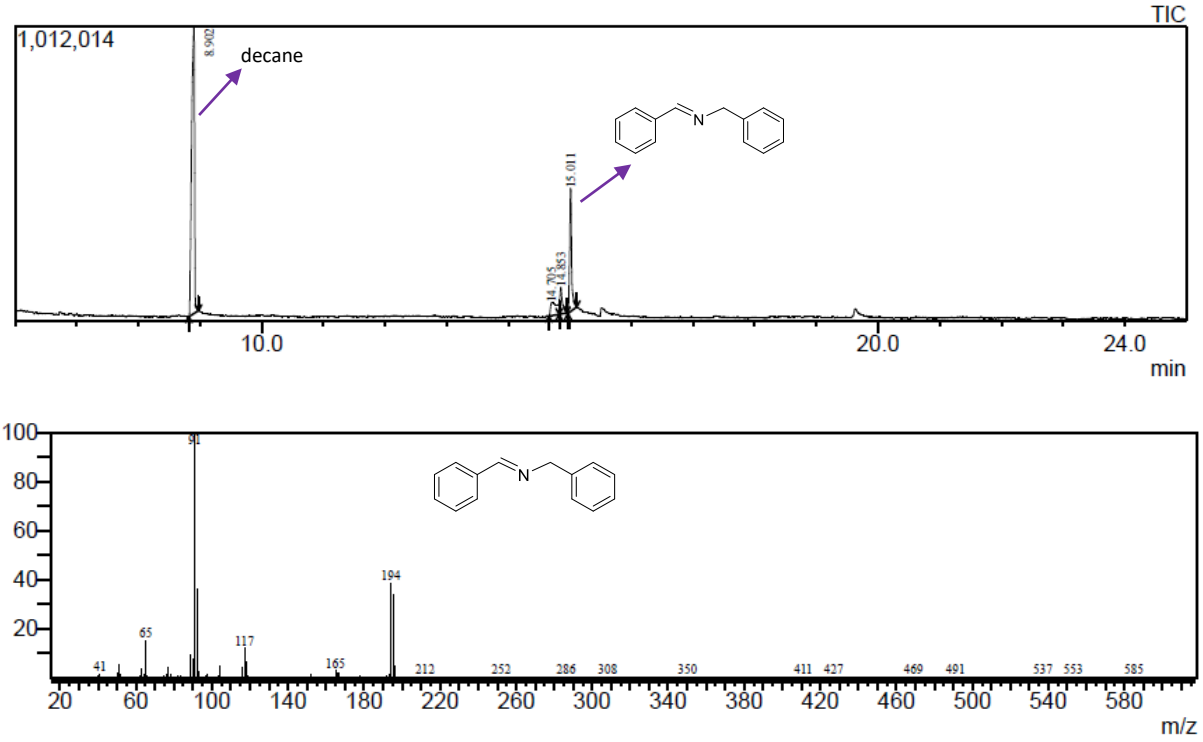


Figure S95. GC-MS spectrum for entry 13 of table 4.

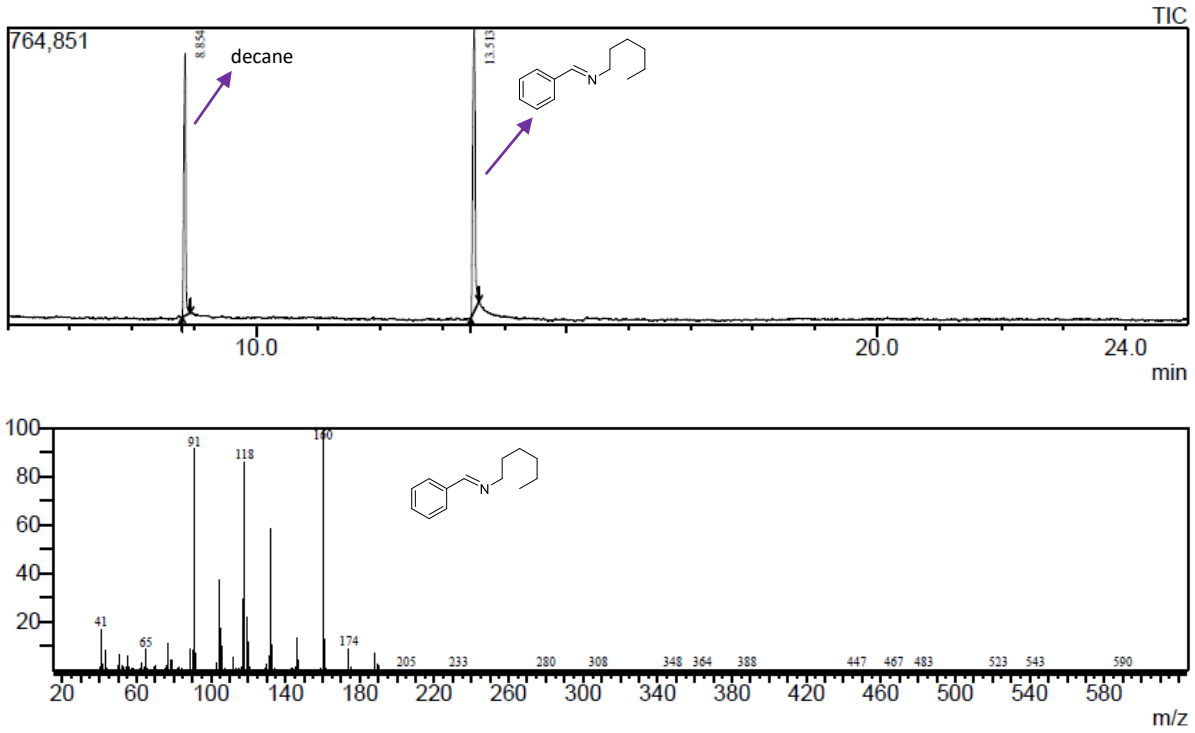


Figure S96. GC-MS spectrum for entry 14 of table 4.

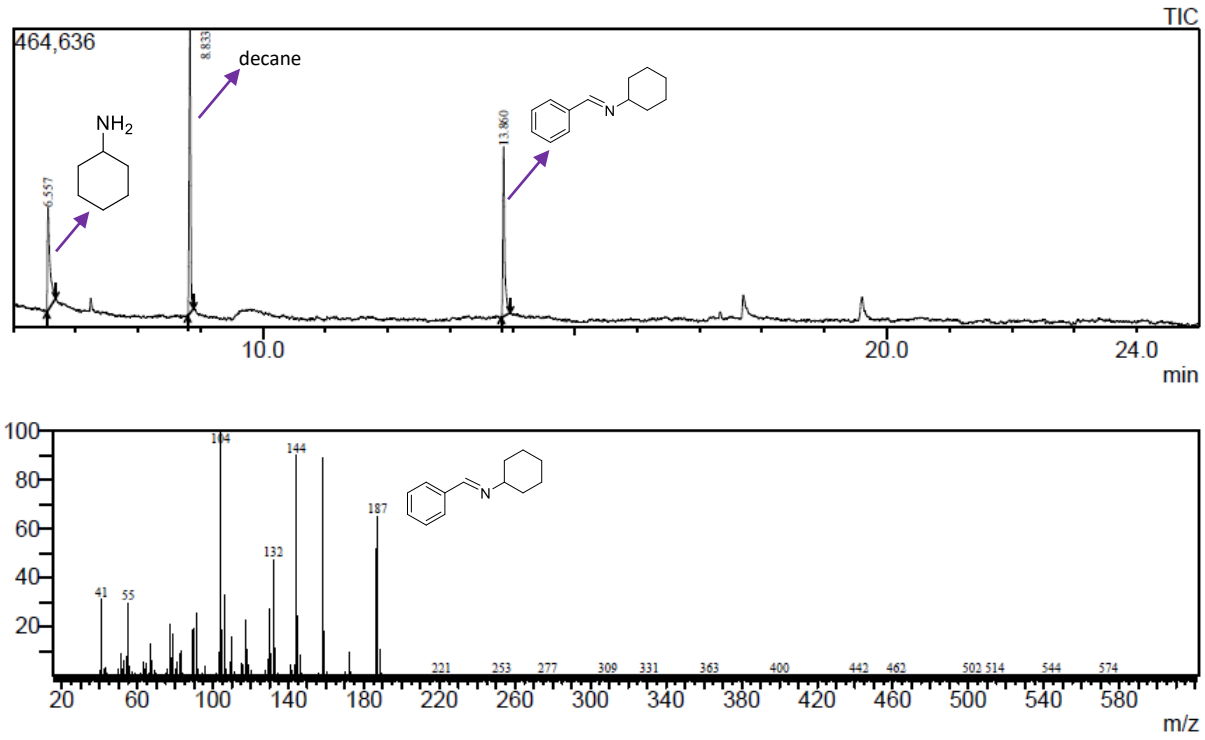


Figure S97. GC-MS spectrum for entry 15 of table 4.

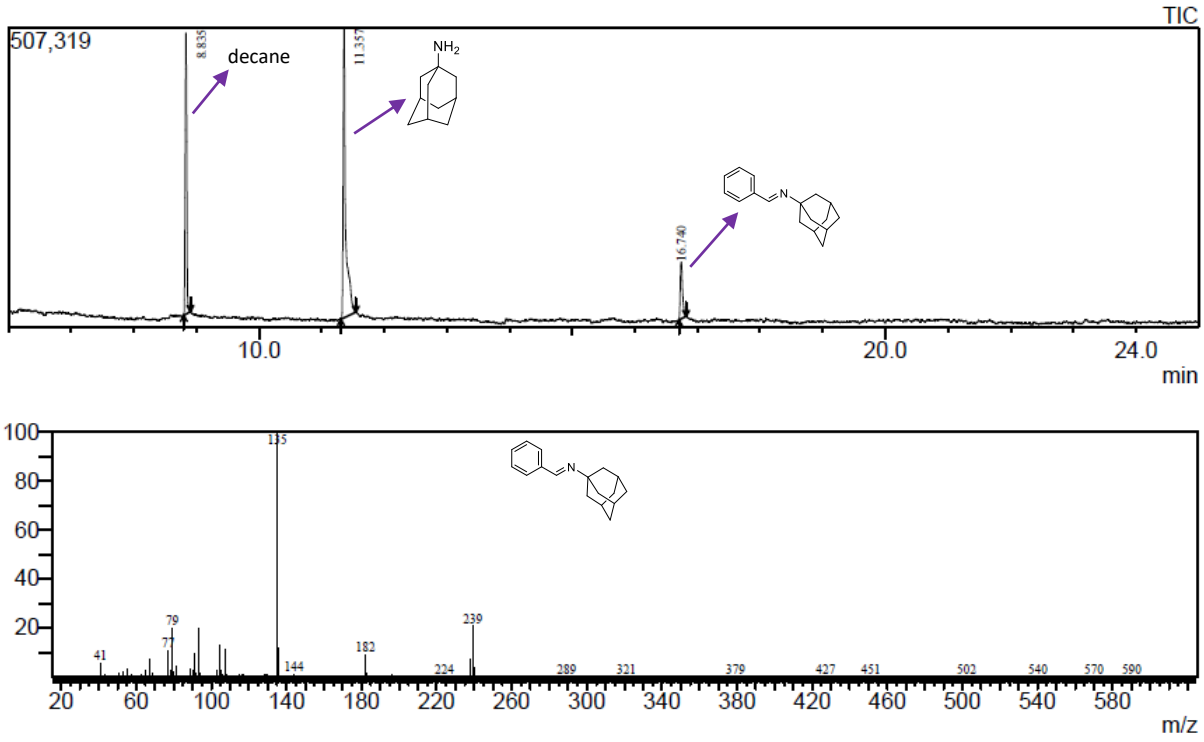


Figure S98. GC-MS spectrum for entry 16 of table 4.

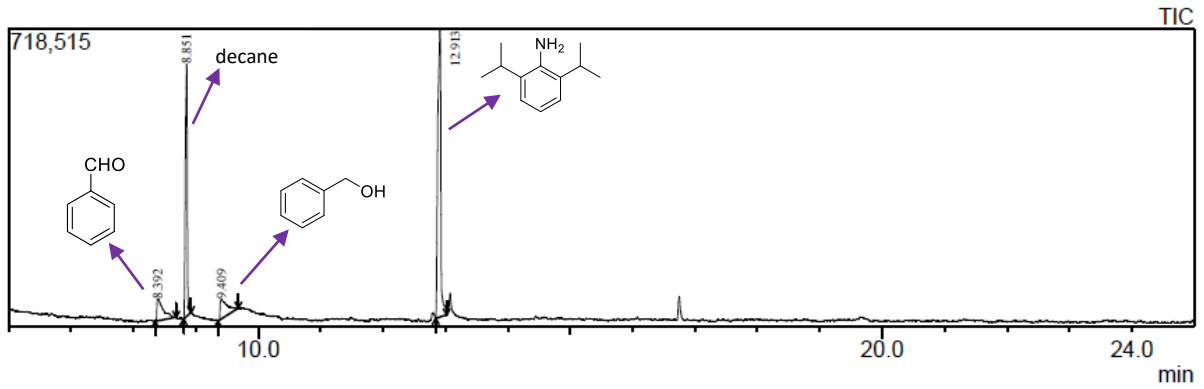


Figure S99. GC-MS spectrum for entry 17 of table 4.

GC-MS spectra of Acceptorless dehydrogenative coupling products for table 5.

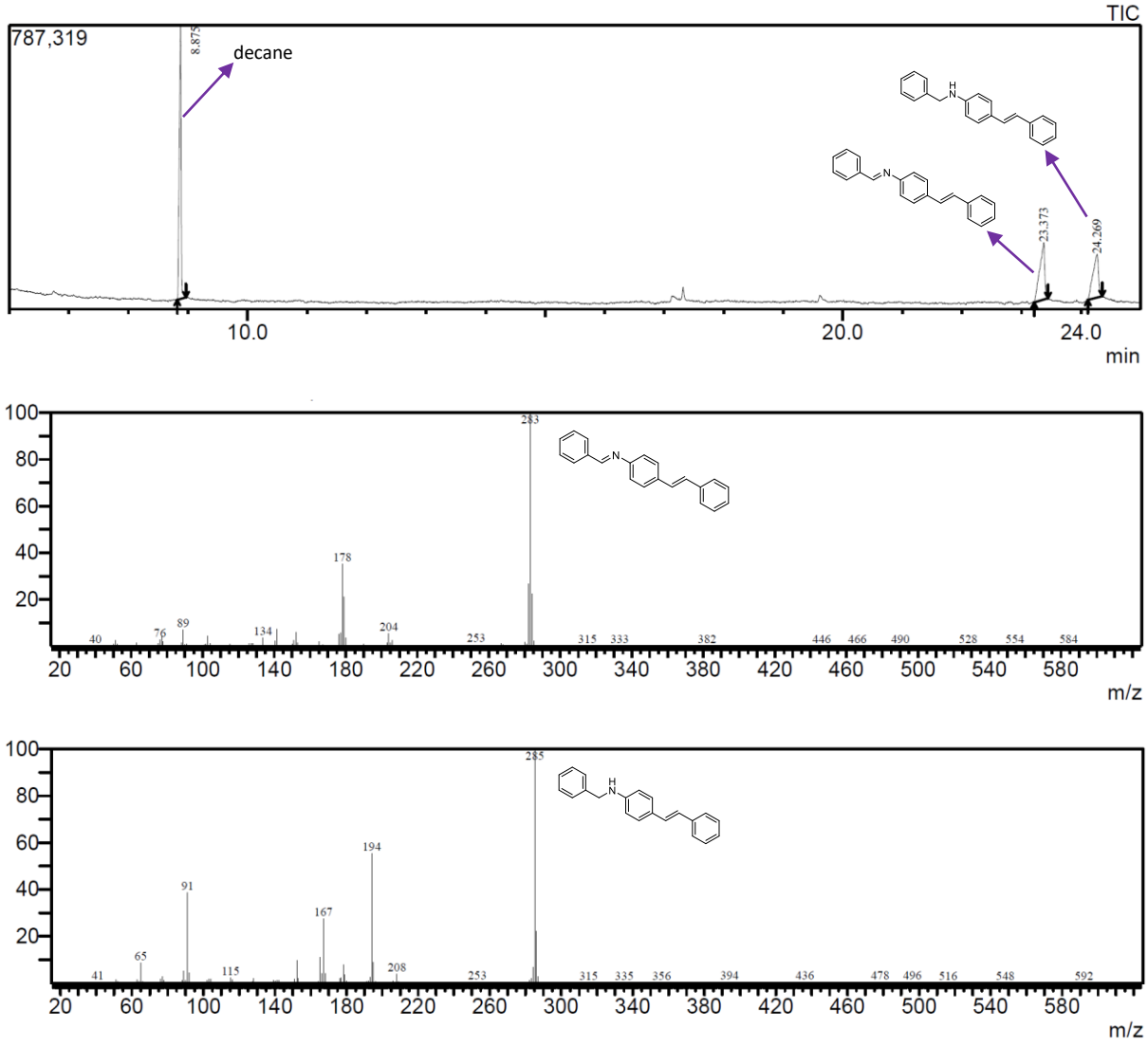
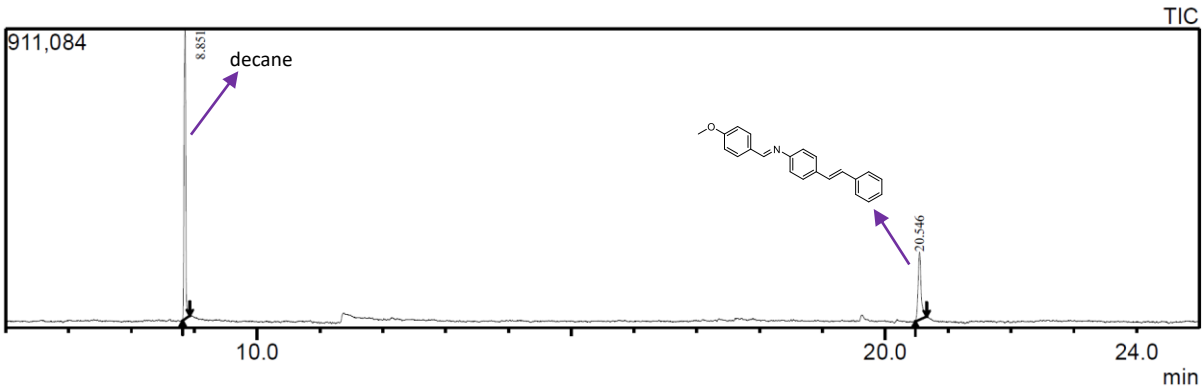


Figure S100. GC-MS spectrum for entry 1 of table 5.



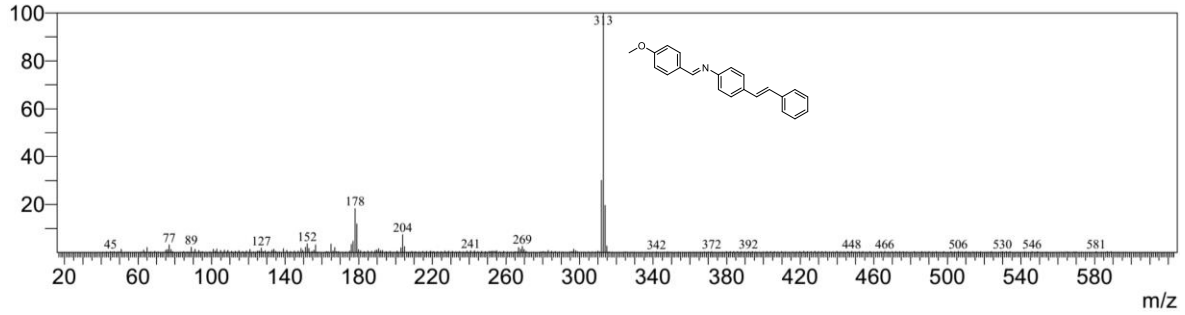


Figure S101. GC-MS spectrum for entry 2 of table 5.

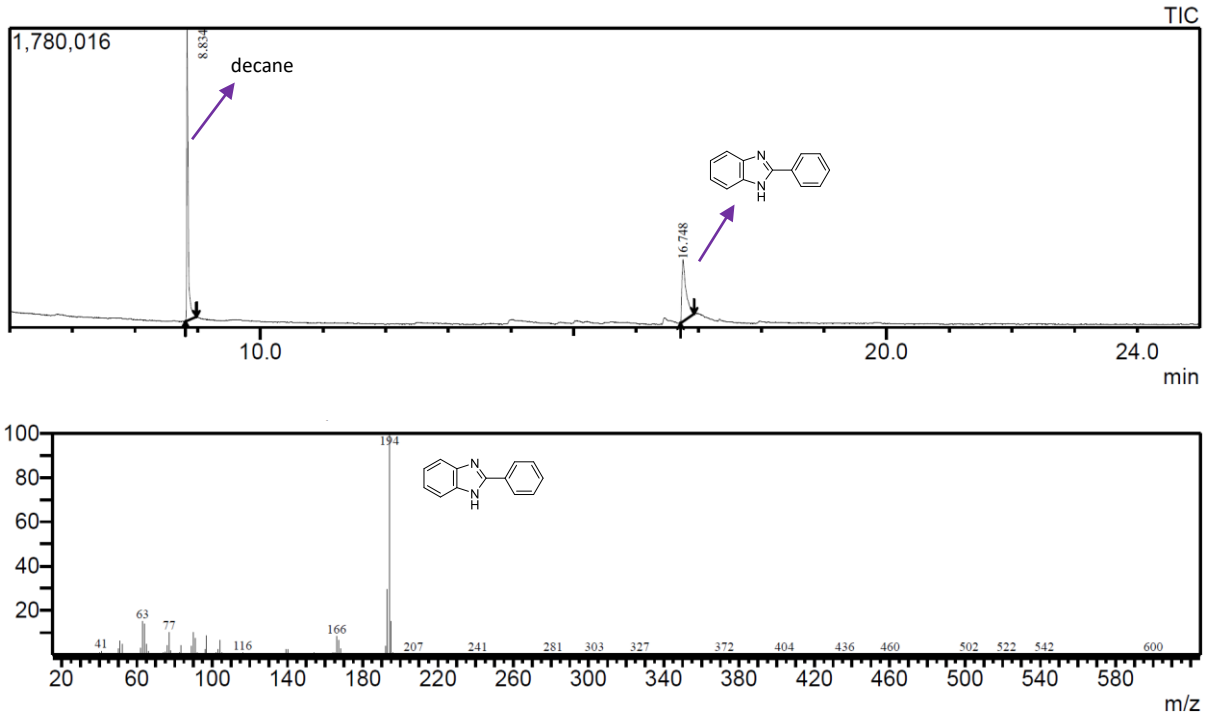
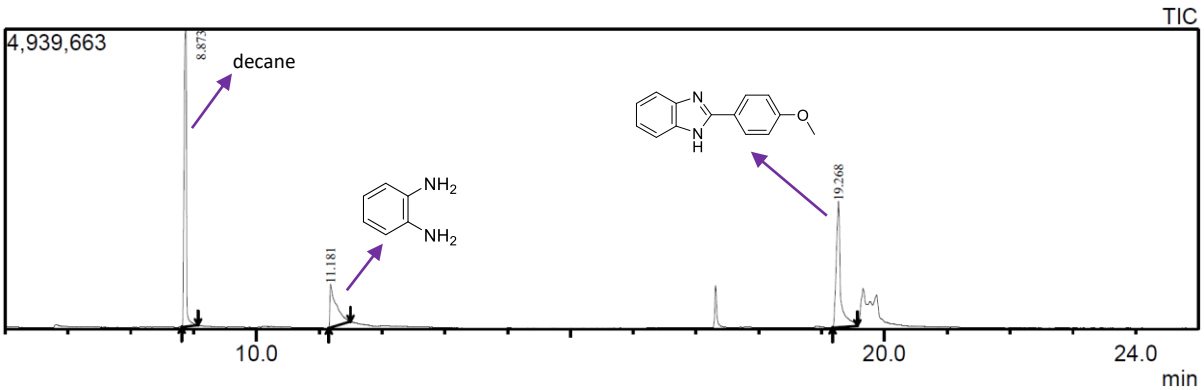


Figure S102. GC-MS spectrum for entry 3 of table 5.



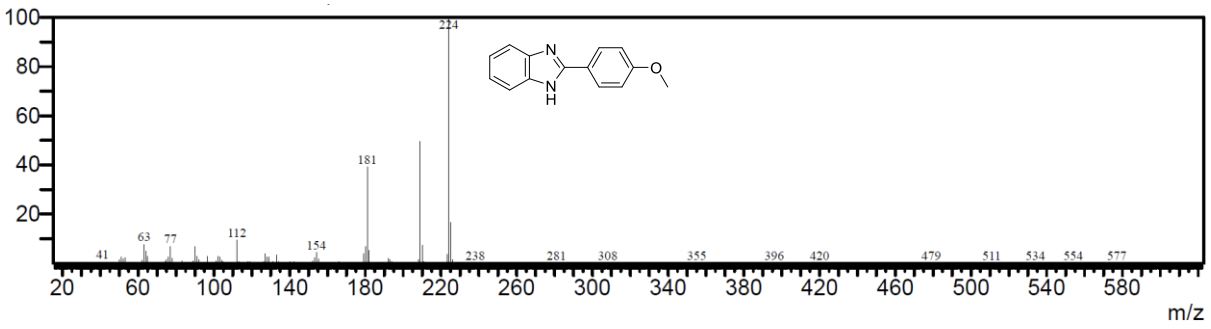


Figure S103. GC-MS spectrum for entry 4 of table 5.

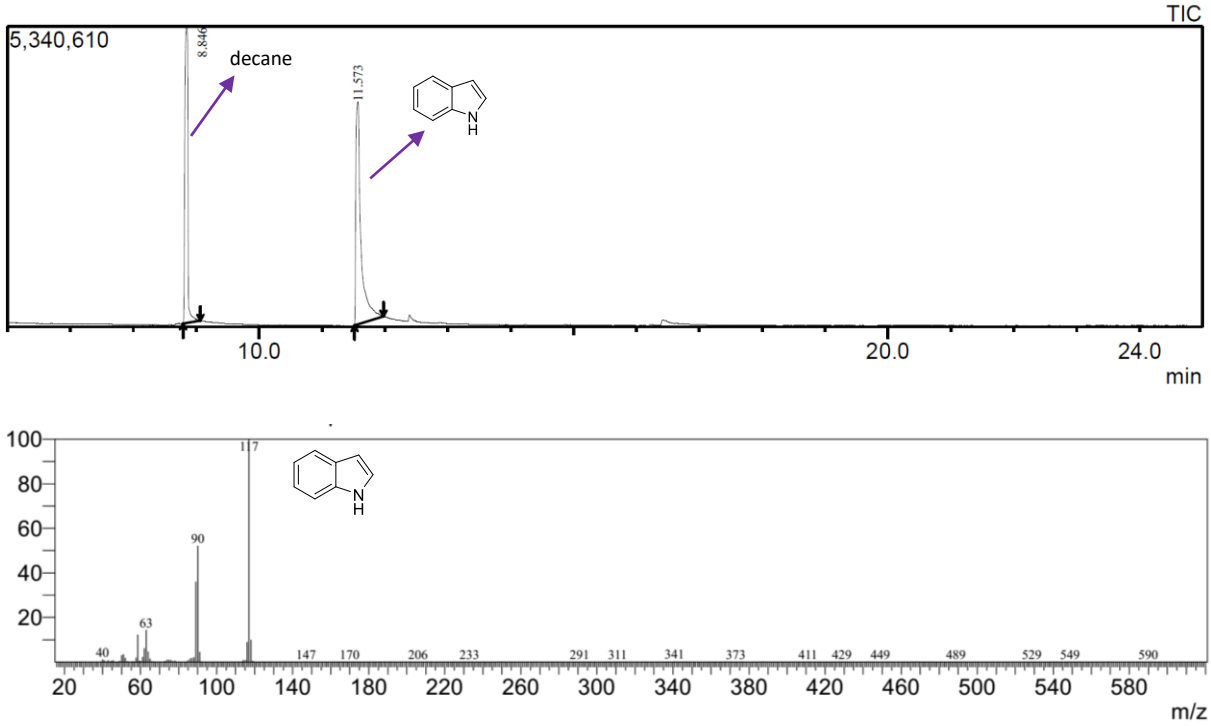


Figure S104. GC-MS spectrum for entry 5 of table 5.

NMR spectra of product after transfer hydrogenation reaction.

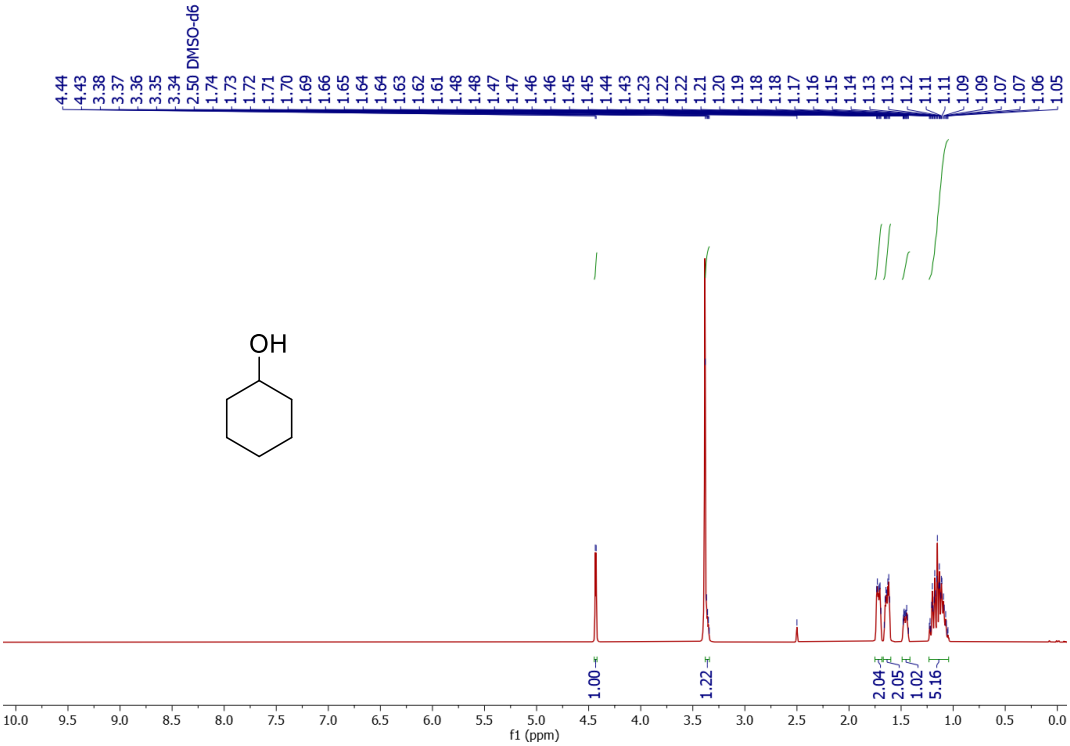


Figure S105. ^{1}H NMR spectrum of cyclohexanol.

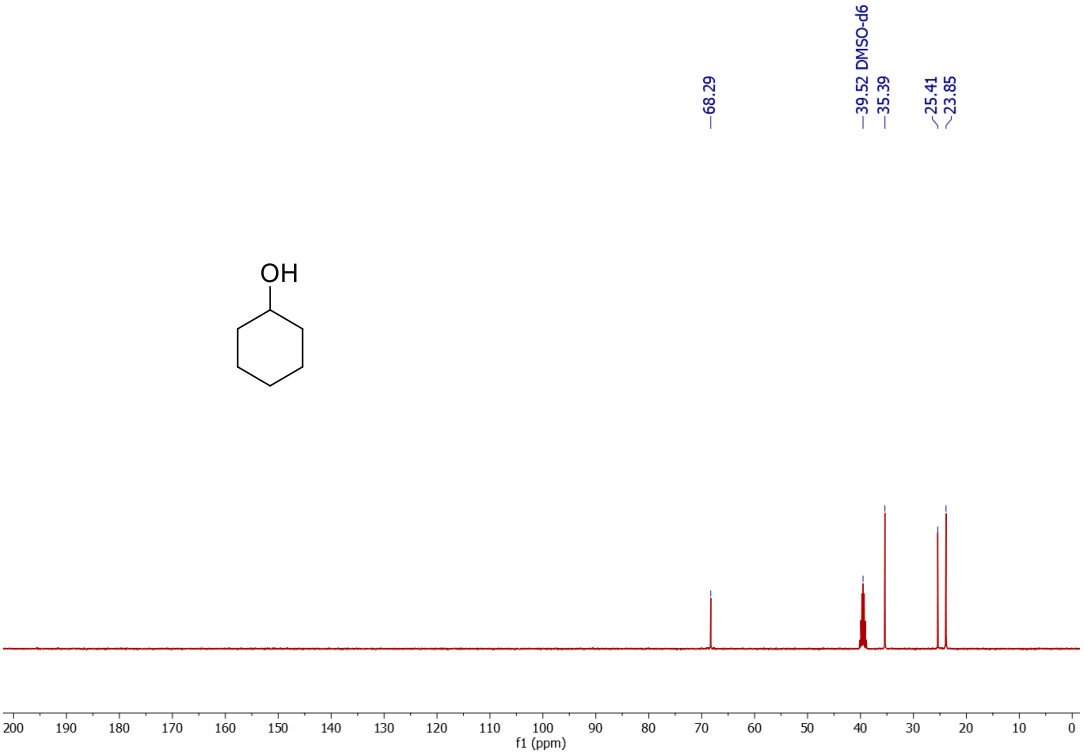


Figure S106. ^{13}C NMR spectrum of cyclohexanol.

NMR spectra of product after acceptorless alcohol dehydrogenation.

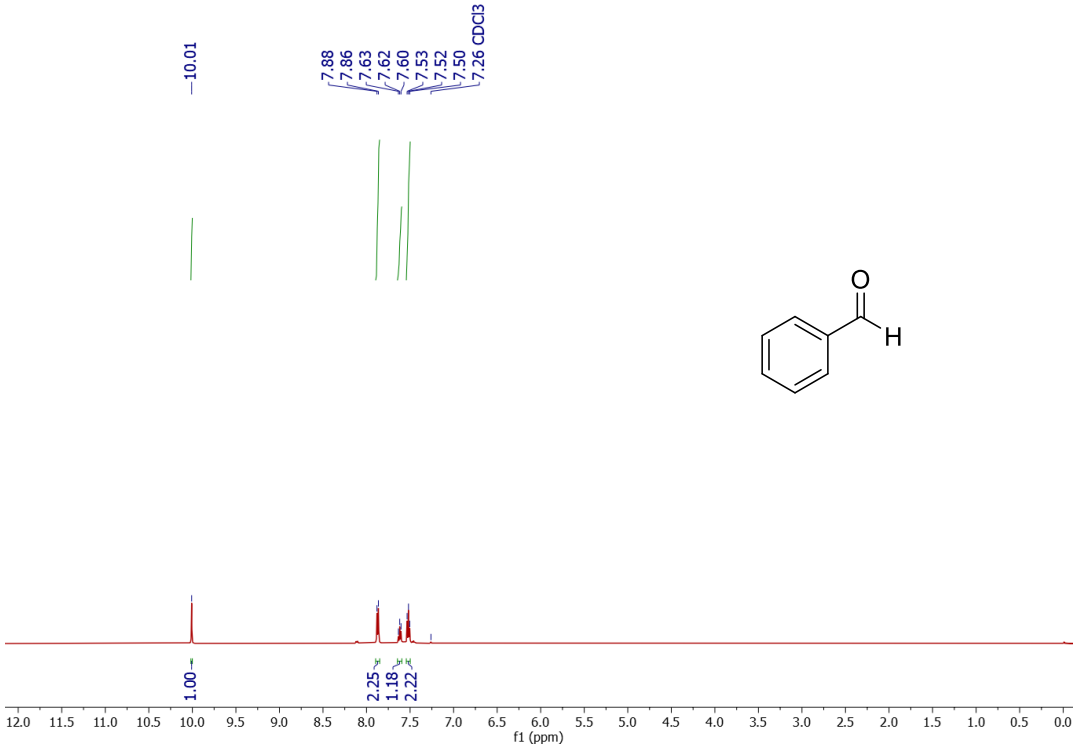


Figure S107. ^{1}H NMR spectrum of benzaldehyde.

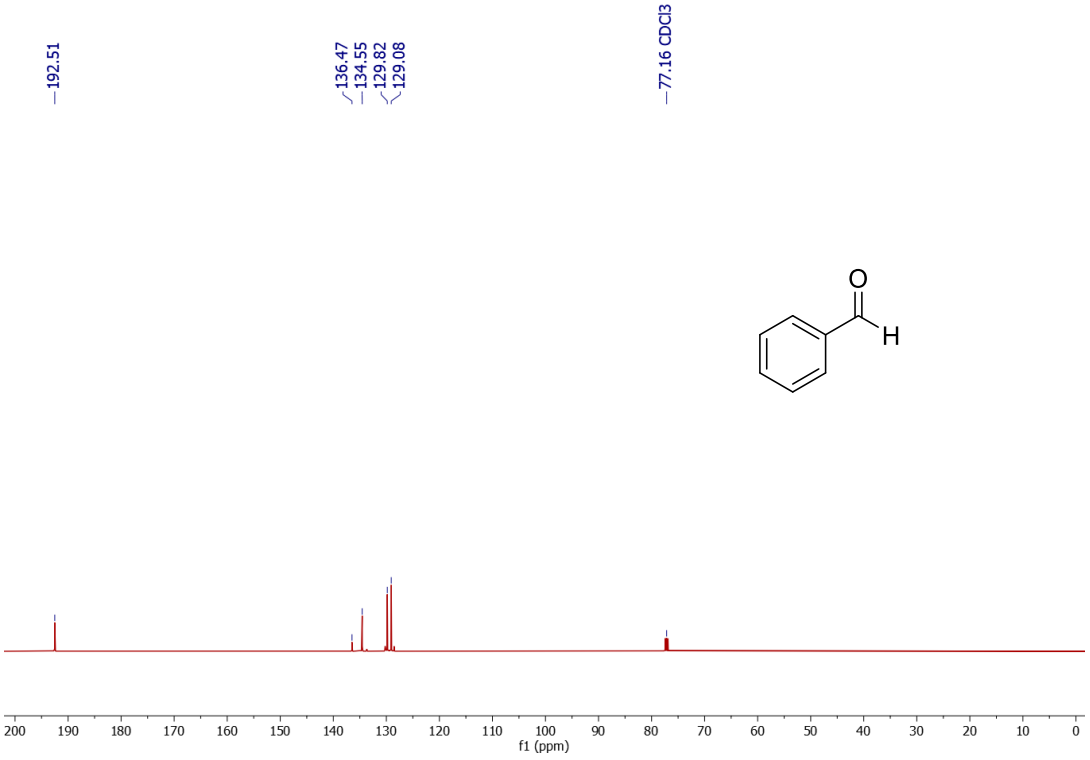


Figure S108. ^{13}C NMR spectrum of benzaldehyde.

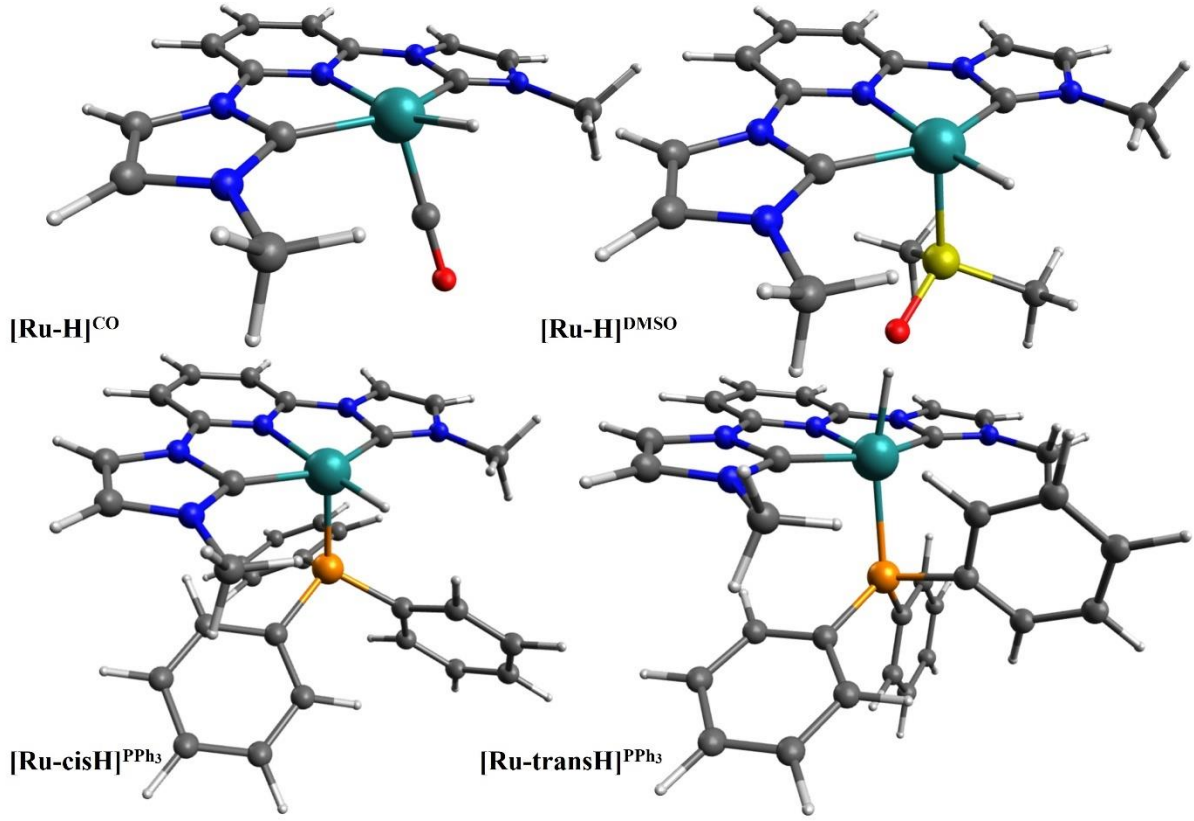


Figure S109. DFT optimized structures of **[Ru-H]^{L}** after aldehyde dissociation from **B^{L}** (**L** = CO, DMSO and PPh_3). For **L** = PPh_3, two structures with hydride position w.r.t. PPh_3 ligand are calculated. The **[Ru-transH]^{PPh_3}** (model for **4b''**, confirmed in ^{1}H NMR) is found -1.7 kcal/mol lower than **[Ru-cisH]^{PPh_3}** (model for **4b'**) possibly due to an agostic interaction between Ru and a phenyl ring of PPh_3 ligand.

Cartesian coordinates of DFT optimized structures

B-CO

Ru	-1.15372206112549	0.97723485532526	0.00700472651732
H	-1.78428764605351	0.32165240741799	1.35010717571905
N	-0.21217954645072	1.84843454058005	-1.64123392543552
N	-0.03021446760500	3.31188843659006	1.96175694434061
N	0.56362526489258	3.32163371694917	-0.10756312207798
N	-2.49509898029893	-1.28604603735579	-1.86986927086123
O	-3.89121220348032	2.16189375233839	0.15371659196936
N	-1.12334350955022	0.11165802602076	-2.76893005709475
C	-0.18578290352311	2.60583946222437	0.82792899217961
C	-1.70092811271409	-0.25016081616334	-1.55009739532875
C	-0.27692718489713	1.22661727259435	-2.82029458032239
C	0.59673694388663	2.89002929456211	-1.43978248158780
C	-2.82440389722069	1.72886008559574	0.07168840573374
C	0.78579098379245	4.42482186452312	1.77022743003579
H	1.02515830339403	5.10933295050600	2.56983741952701
C	0.44214143577264	1.68437504032524	-3.91614508176723
H	0.39304157759952	1.19502207487260	-4.88133534059150
C	1.35626614650844	3.42144170078990	-2.47351955156384
H	2.01441970403031	4.26902009200090	-2.32599841204036
C	-1.56056477190500	-0.71861476612200	-3.79502086463825
H	-1.24481931367083	-0.61668859486426	-4.82095273670268
C	-2.41840896463264	-1.59437518967307	-3.22484889646511
H	-2.98220928152978	-2.40291810344679	-3.66494426525815
C	1.16105760502979	4.43446790636434	0.47246429318946
H	1.78362743499761	5.12827711158688	-0.06930449307091
C	1.25192799393140	2.80134270151571	-3.71741707551693
H	1.83113404344705	3.18791531060387	-4.54964464506400
C	-0.64749217571081	2.95478819624116	3.23605344685193

H	-1.30538710195471	3.76205995131466	3.57079404872831
H	0.12521631156922	2.77567982559966	3.98953570816342
H	-1.23206667100007	2.04700487870003	3.07924089470719
C	-3.29664276257894	-2.02182673489568	-0.89633223871741
H	-2.95065652671720	-3.05845982386968	-0.83866647021412
H	-4.35106763889112	-1.99441549231753	-1.18591101971391
H	-3.16460449099827	-1.53798435162578	0.07283832695381
O	0.82568733297474	-0.04950251184711	0.07540292483926
C	0.27495392674291	-0.81877002496880	0.90758112552435
H	0.26490317552739	-0.54717412671205	1.97728065856173
C	-0.10798930056635	-2.19919578301298	0.58966975555584
C	-0.71987683974946	-2.98577266008129	1.57140513485848
C	0.18546385114629	-2.74933681893820	-0.66427503489637
C	-1.05314072131629	-4.30563988443533	1.29812261805362
H	-0.93621004155599	-2.55520997010817	2.54662279103895
C	-0.14300368701721	-4.06936131447295	-0.93200241320763
H	0.68593904220513	-2.13240804402438	-1.40541450082428
C	-0.76568326506539	-4.84741238640444	0.04663713229069
H	-1.52723273127814	-4.91697066963036	2.05971599820646
H	0.09846192131609	-4.50475630713559	-1.89727417896498
H	-1.01419619970673	-5.88369104303687	-0.16345449161990

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N	-2.17414266515597	-1.14790763499487	-2.34153335412350
N	-0.94993589946208	0.53121461221387	-2.90787361074217
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C	-0.23502822567491	1.71900150539039	-2.73830904382887
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H	0.43055190614618	2.14361479120267	-4.75752908042255
C	1.17256187908087	3.96036691079615	-1.96005840224792
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C	-1.23967558426897	-0.14986675846658	-4.08191900378698
H	-0.88201845430501	0.15408580610390	-5.05249136281090
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H	1.56173242140530	5.12691172960999	0.76254728821430
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H	1.65876510453583	4.17213120190827	-4.03635011944869
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H	-0.09964087627535	1.97085992802610	4.25657959544636
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H	-2.73908372190418	-1.96944563893688	-0.52612844714418
O	0.80880780984151	0.00359448189133	0.02869915607068
C	0.13857504748563	-0.69226954596506	0.86896750645493
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C	-0.10024242473602	-4.04581154407168	-0.83646457742680
H	0.81848548186680	-2.14146604187113	-1.28766213809399
C	-0.86259061244252	-4.76792476302346	0.08055697397207
H	-1.88290577368717	-4.72180093735414	1.97659338195751
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C	-4.71186527660176	0.78228946292763	-0.01622373698848
C	-5.90876162807509	1.16075879377014	-0.63661520835382
C	-4.68494304616104	-0.38706947615630	0.74706719911737
C	-7.04498842949892	0.36824639807374	-0.51462109555915
H	-5.95792038591557	2.07840885970187	-1.21484854697951
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C	-7.00608791738926	-0.80146508470752	0.23887051806509
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H	-5.78926944080579	-2.07966000616026	1.47218616578186
H	-7.89521752152397	-1.41773897308506	0.33477466238994
C	-3.53863636072601	2.81944470491278	-1.66412656817931
C	-3.56052811160024	4.21281276720445	-1.75327363427287
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C	-3.69009458909918	4.83960786087474	-2.99126981623704
H	-3.50397503231079	4.82292265765050	-0.85899056023425
C	-3.82162625081334	2.69583534015228	-4.07002967548677
H	-3.71982715274601	0.98448503958900	-2.79022816002043
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H	-3.71089646806751	5.92428455006830	-3.04056381634296
H	-3.94948701878095	2.09541886806181	-4.96632848779003
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C	-4.64058253905851	2.89462238209671	2.16162910192618
C	-2.79329696115583	4.23890662839561	1.40333235127961
C	-4.85749734541269	3.79147834349647	3.20519416503679
H	-5.28386901394648	2.02616252073592	2.06519323247880
C	-3.02213672386095	5.14106947523580	2.43471193729863
H	-1.97182829198041	4.42455029731958	0.71753100468574
C	-4.05369994055943	4.91692185371413	3.34382260690112
H	-5.66551954517436	3.60859362458492	3.90721652086444
H	-2.39138013348628	6.02067429380775	2.52849547831797
H	-4.23119794309813	5.61922377615147	4.15294137658373

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Ru	-1.09328429010166	0.90013569316317	-0.05559360730452
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N	-0.01287116309214	3.12012246558527	2.04251953922146
N	0.60937940001485	3.25230404554268	-0.01562011190719
N	-2.40260717648785	-1.28314968286995	-2.06397191303269
N	-1.10872337504669	0.23848083212691	-2.87759916706809
C	-0.13604820335859	2.46865920523574	0.87451556397142
C	-1.66254595438160	-0.22302858055008	-1.67194344552360
C	-0.26775338819810	1.35786768519571	-2.86209744025539
C	0.63149000549243	2.91560852881697	-1.37282186991542
C	0.77337737398441	4.26285553755082	1.91919000751796
H	0.98217389277463	4.91150957078214	2.75638123323365
C	0.43927028711447	1.89332361730638	-3.93146113103246
H	0.38008535218338	1.47433397604667	-4.92865391384613
C	1.38248647954223	3.51570753548587	-2.37597962111563
H	2.05296661907904	4.34227201039523	-2.17416972526078
C	-1.50389867619664	-0.55220808706363	-3.95127481333927

H	-1.19106321518169	-0.37828654090638	-4.96848483391856
C	-2.31251464071062	-1.50450101249027	-3.43555298893401
H	-2.82820686346246	-2.31753302135661	-3.92405917207633
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H	1.78198643492179	5.08571691710645	0.13492711325113
C	1.25737716970193	2.98933950361000	-3.66080855013564
H	1.82979764389282	3.43190532286681	-4.46957811592920
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H	-1.42996251554563	3.46927346016602	3.54844865761214
H	0.04256226853458	2.58815453694073	4.07471327487498
H	-1.20376964530450	1.77425451305027	3.07053205401732
C	-3.13865334987944	-2.14066457500193	-1.14043838513634
H	-2.73949807367335	-3.15835519617247	-1.17910277249313
H	-4.20246093482447	-2.15008576733711	-1.39905346680142
H	-2.99620357137127	-1.74184559630763	-0.13471232188665
O	0.84345357143215	-0.06526311219556	-0.06887576295467
C	0.24584435967292	-0.73978047732220	0.83654094243520
H	0.34720402456973	-0.43456793741681	1.89050879179147
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C	-0.81523302394178	-2.85781999249369	1.60939604157768
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H	0.72477110631248	-2.22058732971632	-1.34852167085367
C	-0.80609506403283	-4.82609533439391	0.21976486317067
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H	0.14896956207769	-4.62107190376143	-1.69955868756398
H	-1.04907229648865	-5.87458334834013	0.07385919595196
S	-3.00703283308383	2.06577122129299	0.08266991996288
O	-3.19003186597798	3.00221620546396	1.24059479920903

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H	-4.47066653771707	0.36256639033195	0.86664585887735
H	-5.37360620057901	1.69998649129559	0.07496948081679
C	-3.28154445565648	3.05202277476621	-1.43636567078027
H	-4.24422759684774	3.56159678658835	-1.34275838889803
H	-2.47310346988740	3.78564018219707	-1.48454306417627
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N	0.62447188595128	3.34450912194121	-0.17786594958969
N	-2.48579893716368	-1.24715891921095	-1.88286635140905
O	-3.88662633004641	1.92058483177505	0.60432288288194
N	-1.04351958142099	0.07968966227051	-2.78296473850467
C	-0.17897406238124	2.66786816950785	0.75076375815303
C	-1.66208102558282	-0.23049688628597	-1.56352935954528
C	-0.15785183532992	1.16354015590689	-2.84497396384584
C	0.70915681126614	2.86173693909055	-1.49044244760447
C	-2.80829833642036	1.57655720773182	0.35033841698633
C	0.73074737707493	4.53867301869642	1.65402182835891
H	0.92292724521769	5.26356359917116	2.43066600187157
C	0.59388633857738	1.57865125092365	-3.93550210446195
H	0.55854896577763	1.06671454979608	-4.88940046456840
C	1.49889286518292	3.35198965779634	-2.52135253783310
H	2.15777098536523	4.20151882590705	-2.38937852759005
C	-1.49753660565251	-0.74891507599206	-3.80091260390633
H	-1.15261974303503	-0.68764670630317	-4.82079766906480

C	-2.40282817401053	-1.57690747502413	-3.23144071847922
H	-2.99042325025194	-2.37017482817353	-3.66849663891823
C	1.18197088819102	4.48775358602044	0.37995355307449
H	1.83606880078823	5.15698917550367	-0.15596359816511
C	1.41606811219082	2.68970481933518	-3.74641883429311
H	2.02061956292614	3.04258942281730	-4.57581815815549
C	-0.77427259104173	3.13204122116175	3.11080294987793
H	-1.52594761559931	3.89971829257126	3.31682663438496
H	-0.05042688009754	3.09618463996100	3.92954928575637
H	-1.25937902868498	2.16126995281917	3.00139052540796
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H	-4.41067323874417	-1.71930708671762	-1.17909475643963
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N	0.64705026079382	3.24255588300167	-0.02566047613821
N	-2.38122756992204	-1.27577954565843	-2.08831392438579
N	-1.12080301811611	0.27351669916452	-2.90389512046488
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C	-1.68844175436248	-0.17842751644364	-1.69847040089816
C	-0.25349676539106	1.37598974917624	-2.88203164388028
C	0.67516314743613	2.90698204673510	-1.38269180584466
C	0.81534854812288	4.23683809217471	1.91736367014415
H	1.03664634873524	4.87417194295517	2.76014079123524
C	0.45076852031168	1.91324613613012	-3.95010397501457
H	0.36971062954069	1.51343106674444	-4.95368734908958

C	1.42661021093881	3.50664267929356	-2.38502094310290
H	2.09955731499088	4.33092266847441	-2.18141633611292
C	-1.47421857125622	-0.54346443168602	-3.96943502992227
H	-1.14270583290699	-0.38145376813831	-4.98280649244174
C	-2.26549575202962	-1.51155952170298	-3.45405633367032
H	-2.74681715580114	-2.34688633094680	-3.94020402084628
C	1.23135922205610	4.31790532175544	0.63291343669917
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H	1.86155048932704	3.43738854092520	-4.48258252582363
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H	-1.48162179425209	3.46813756807396	3.47650514693823
H	-0.00125060776971	2.64508249701366	4.07167785213687
H	-1.18658319403821	1.76541541175703	3.05239609164498
C	-3.09177161673468	-2.15132551783506	-1.16004854920449
H	-2.66302576516535	-3.15722503279625	-1.19549104777338
H	-4.15344866419951	-2.20310725656024	-1.42100619223356
H	-2.96612457162888	-1.73738674268070	-0.15757198728901
S	-3.01294350057398	2.07606357258756	0.08053235571056
O	-3.16587532829807	3.07163810714702	1.18842016891223
C	-4.49784019813768	1.01185894938667	0.13803408418511
H	-4.52662818992888	0.38310736833128	-0.75455993374549
H	-4.40744034834533	0.40309333780736	1.03895493620044
H	-5.37138792338594	1.66746877141608	0.19583798849922
C	-3.37385047272996	2.98398229683706	-1.46986263949046
H	-4.33093867881272	3.49935031012426	-1.35110003645640
H	-2.56862030027702	3.71089345516856	-1.60051837796684
H	-3.39643933531262	2.28222084377662	-2.30823204068065

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Ru	-1.20537138174800	0.96555659194820	-0.05851746205130

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N	0.41925326443506	3.33550936077473	0.34082693493847
N	-2.09472352502970	-1.15164419377222	-2.34896694927995
N	-0.94579279085088	0.57945907283069	-2.92739290818835
C	-0.33378721543461	2.40645542903422	1.08230893503633
C	-1.52189477644118	-0.04779107395238	-1.80694223157019
C	-0.23073464747486	1.76779833239963	-2.74918739065530
C	0.49054942204317	3.19214599081181	-1.05018940857977
C	0.57387430115038	4.00513081310325	2.42051202454660
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C	0.40315722950775	2.52518880819710	-3.72442178592422
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H	-0.84241831559385	0.17796460212757	-5.06440027329411
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H	-3.72315607559563	-0.67967525600708	1.25397541661937
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H	-5.74768305369362	-2.08882213320090	1.50573694117609
H	-7.86016480033746	-1.44072289345820	0.37285738017086
C	-3.53702399084222	2.79673024058141	-1.67439619087195
C	-3.55852950446710	4.18984752710187	-1.77469343317344
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H	-3.95484759157557	4.52984154816897	-5.13443815925440
C	-3.56376069216832	3.09689731923072	1.24207570952238
C	-4.57363425433505	2.86547056607866	2.18094757015319
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N	-2.33306178394465	-0.81062672754307	-2.83279676888219
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C	-4.22140628769370	-1.16749347321909	1.09260552896568
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C	-5.57274724044587	-1.37309285324541	0.81675633061419
H	-7.36215538867619	-0.56795606109237	-0.06270340437730
H	-3.63414301743613	-1.93628380860798	1.58618217742015
H	-6.04767228874167	-2.30414088471345	1.11158326294143
C	-4.17749634110776	3.14689380479118	-1.89598656497962
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C	-3.90503476232201	2.59052296214034	-3.14993517420484
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C	-2.69038870680675	5.69804868302097	1.96715391118019
H	-1.76288153637789	4.76709581351692	0.26630789007724
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H	-5.52090921753693	4.60963425545041	3.49710765148053
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H	-3.81628087104649	6.40389398532256	3.66162690554793

PhCHO

O	0.82924960778693	-0.01443492016350	0.22575438720597
C	0.27121011143719	-0.80502922555833	0.95739729329166
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C	-0.73770576187357	-3.00241437694740	1.51259737390072
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H	0.68657605047775	-2.01381644175231	-1.40817997648513
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H	-1.08014623189816	-5.79943091729793	-0.37073999281049

References

1. D. Yadav, S. Misra, D. Kumar, S. Singh and A. K. Singh, *Appl. Organomet. Chem.*, 2021, **35**, e6287.
2. D. Yadav, R. K. Singh, S. Singh, P. M. Shirage and A. K. Singh, *J. Organomet. Chem.,* 2021, **953**, 122061.
3. D. Yadav, R. K. Singh, S. Misra and A. K. Singh, *Appl. Organomet. Chem.*, 2022, e6756.
4. L. M. Dornan and M. J. Muldoon, *Catal. Sci. Technol.*, 2015, **5**, 1428–1432.