

Electronic Supplementary Information

Synthesis and Structure of Metallocarboranes Bearing Carborane-Fused Cyclopentenyl and Dicarbolyl-Fused Cyclopentene Ligands

Tek Long Chan, Zhenpin Lu and Zuowei Xie*

*Department of Chemistry and State Key Laboratory of Synthetic Chemistry,
The Chinese University of Hong Kong, Shatin, N. T., Hong Kong, China
Email: zxie@cuhk.edu.hk*

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Table S1. Crystal Data and Summary of Data Collection and Refinement for **2**, **3**, **4**, **5**, **6** and **7**.

Compound	2	3	5	6
Formula	C ₆ H ₁₆ B ₁₀	C ₉ H ₂₆ B ₉ N	C ₁₆ H ₂₉ B ₉ Ru	C ₁₁ H ₂₀ B ₉ Co
MW	196.29	245.60	419.75	308.49
Crystal size (mm ³)	0.50×0.40×0.30	0.50×0.40×0.30	0.40×0.30×0.20	0.50×0.40×0.30
Crystal system	Triclinic	Orthorhombic	Monoclinic	Orthorhombic
Space Group	<i>P</i> -1	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Pnma</i>
a, Å	7.132(1)	14.562(2)	18.251(4)	13.117(2)
b, Å	7.981(1)	14.779(2)	14.637(3)	7.507(1)
c, Å	11.866(2)	14.875(2)	16.567(3)	15.274(2)
α, deg	75.05(1)	90	90	90
β, deg	86.24(1)	90	114.00(1)	90
γ, deg	69.07(1)	90	90	90
<i>V</i> , Å ³	609.2(2)	3201.3(5)	4042.8(2)	1504.2(3)
<i>Z</i>	2	8	8	4
<i>D</i> _{calcd} mg/m ³	1.070	1.019	1.379	1.362
Radiation (Å)	0.71073	0.71073	0.71073	0.71073
2θrange, deg	5.64 to 50.50	4.78 to 50.50	2.44 to 50.50	4.10 to 55.94
μ, mm ⁻¹	0.048	0.050	0.772	1.119
<i>F</i> (000)	204	1056	1712	632
No. of obsd reflns	2172	2892	7319	1938
No. of params refnd	146	176	469	109
Goodness of fit	1.034	1.026	1.071	1.201
R1	0.0877	0.0698	0.0501	0.0704
wR2	0.2358	0.2002	0.1192	0.1811

Compound	7	4
Formula	C ₃₃ H ₄₁ B ₉ NiP ₂	C ₂₂ H ₃₄ B ₁₀ Ru
MW	655.60	507.66
Crystal size (mm ³)	0.50×0.40×0.30	0.26×0.22×0.20
Crystal system	Monoclinic	Monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
a, Å	11.342(1)	14.425(2)
b, Å	19.989(1)	9.746(2)
c, Å	15.969(1)	18.373(3)
α, deg	90	90
β, deg	110.23(1)	102.41(1)
γ, deg	90	90
<i>V</i> , Å ³	3397.2(2)	2522.5(6)
<i>Z</i>	4	4
<i>D</i> _{calcd} mg/m ³	1.282	1.337
Radiation (Å)	0.71073	0.71073
2θrange, deg	3.40 to 50.50	2.89 to 61.14
μ, mm ⁻¹	0.689	0.631
<i>F</i> (000)	1368	1040
No. of obsd reflns	6148	7717
No. of params refnd	416	298
Goodness of fit	1.022	1.011
R1	0.0454	0.0271
wR2	0.1011	0.0734

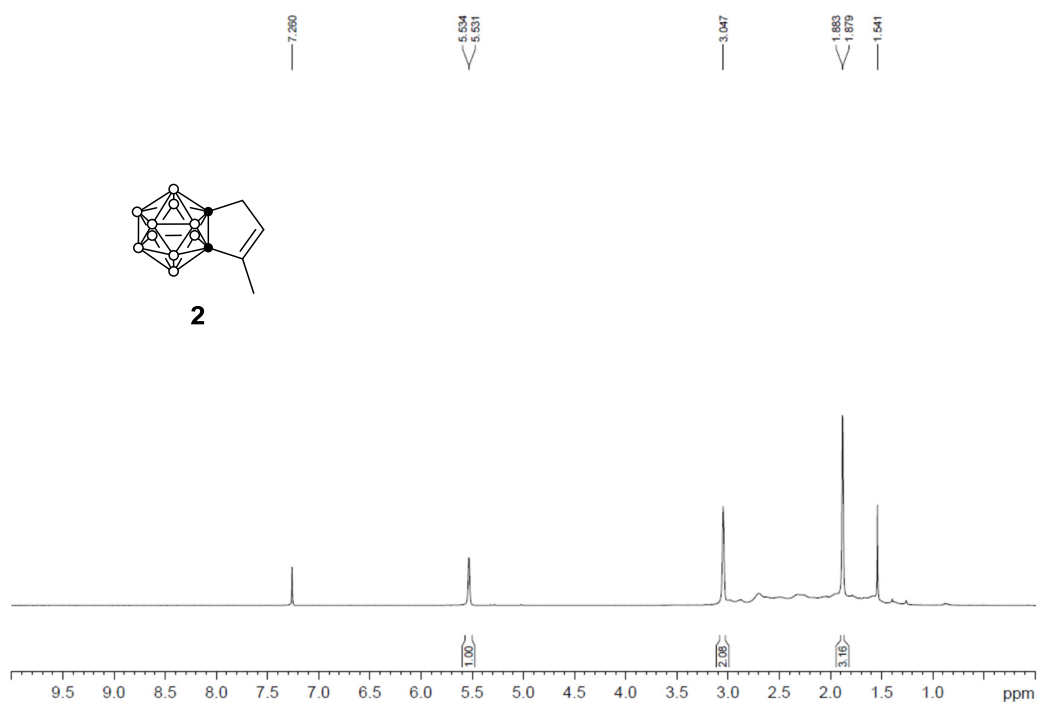


Figure S1. ^1H NMR spectrum of **2** in CDCl_3 .

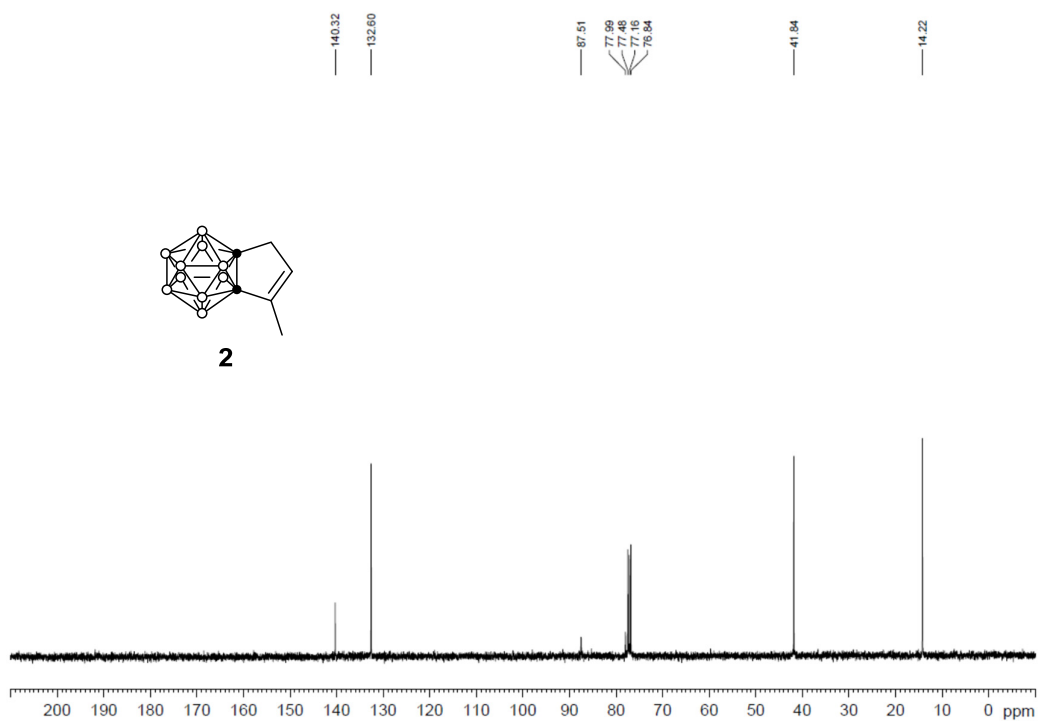


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** in CDCl_3 .

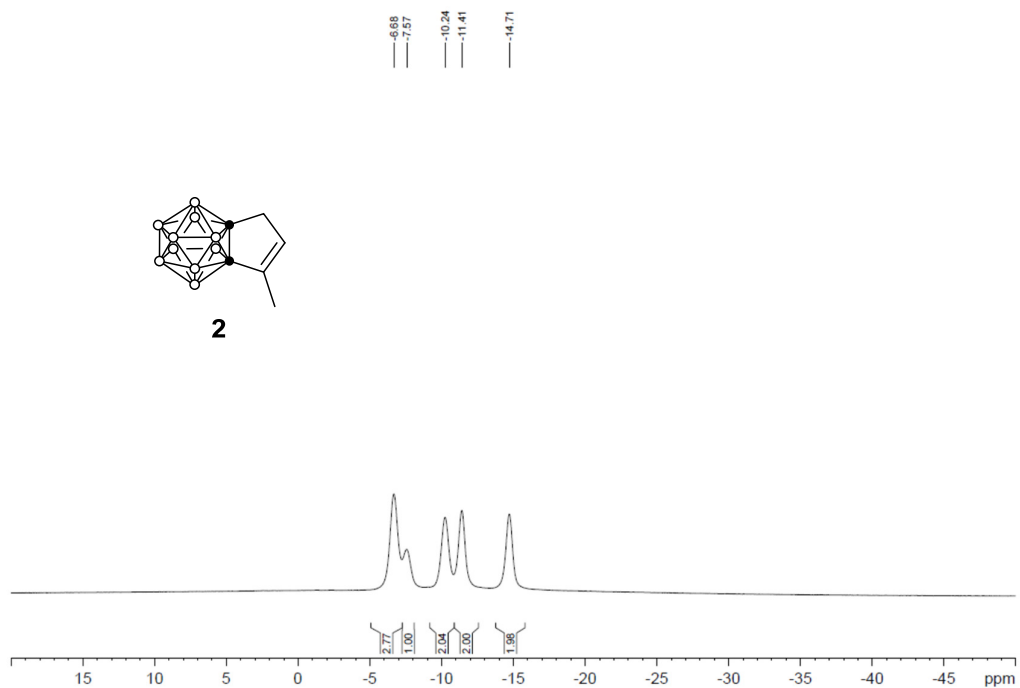


Figure S3. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **2** in CDCl_3 .

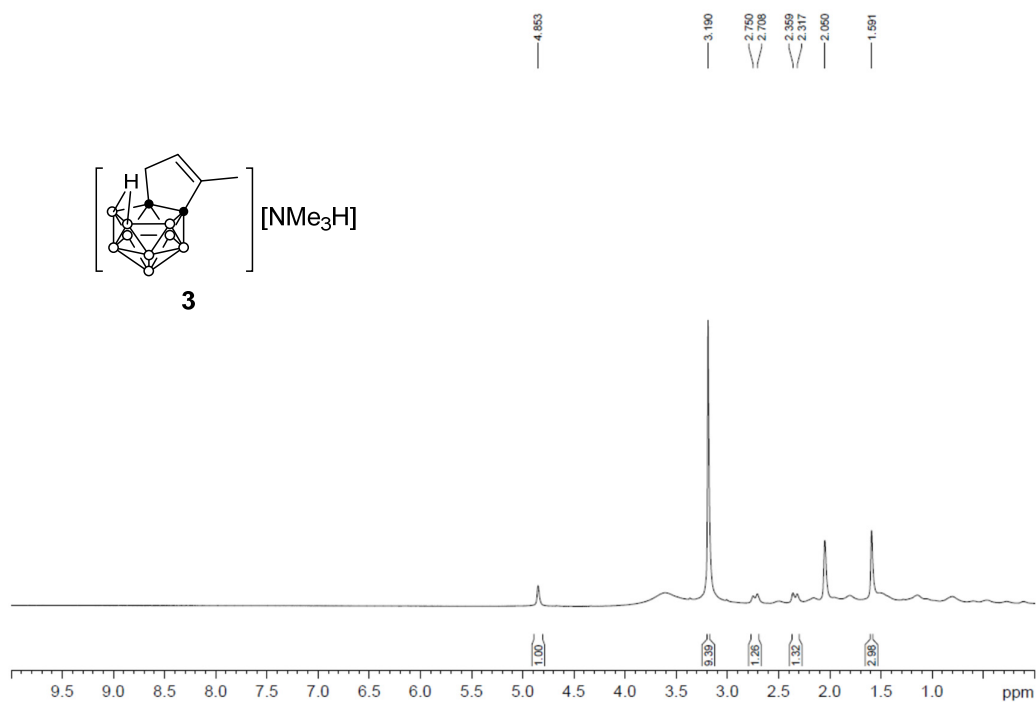


Figure S4. ^1H NMR spectrum of **3** in d_6 -acetone.

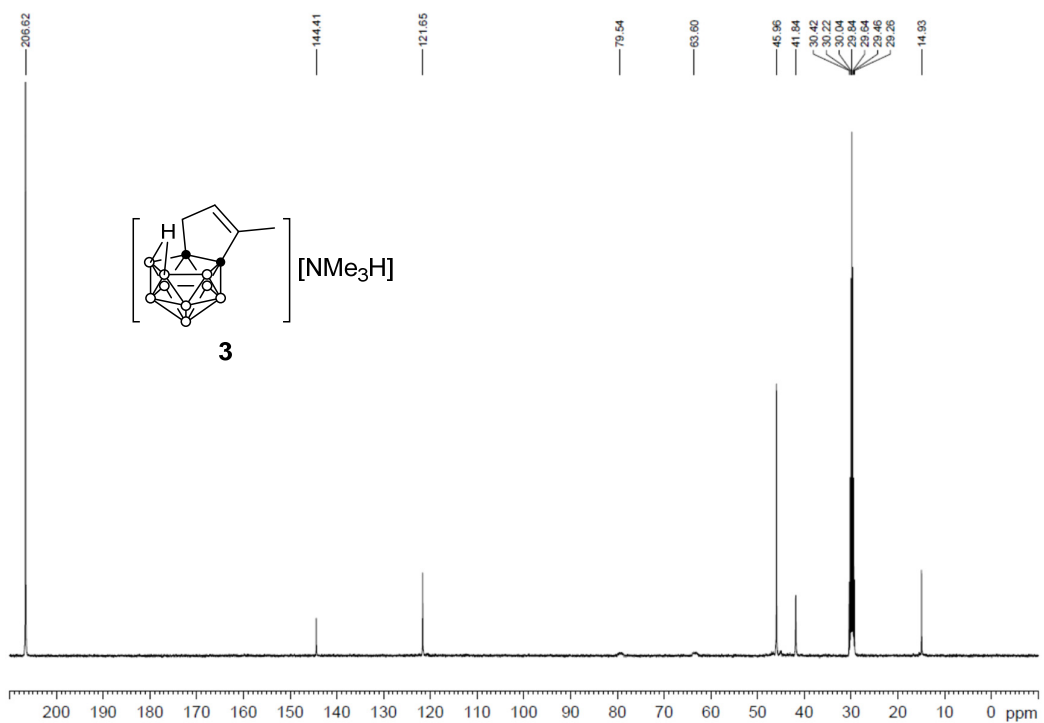


Figure S5. ¹³C{¹H} NMR spectrum of **3** in *d*₆-acetone.

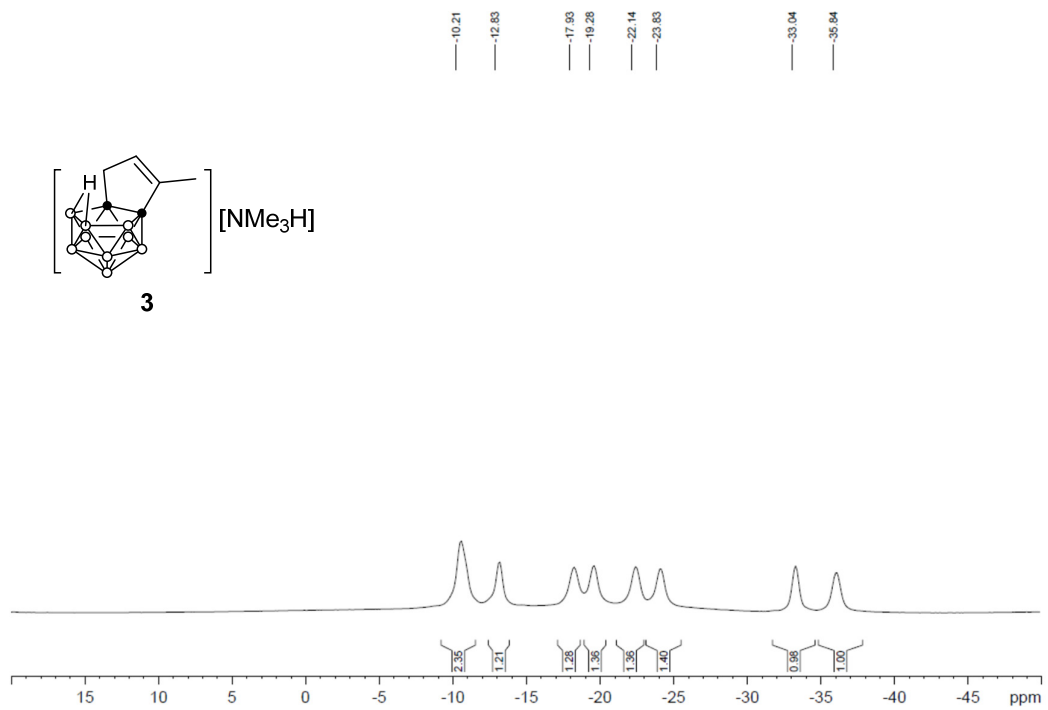


Figure S6. ¹¹B{¹H} NMR spectrum of **3** in *d*₆-acetone.

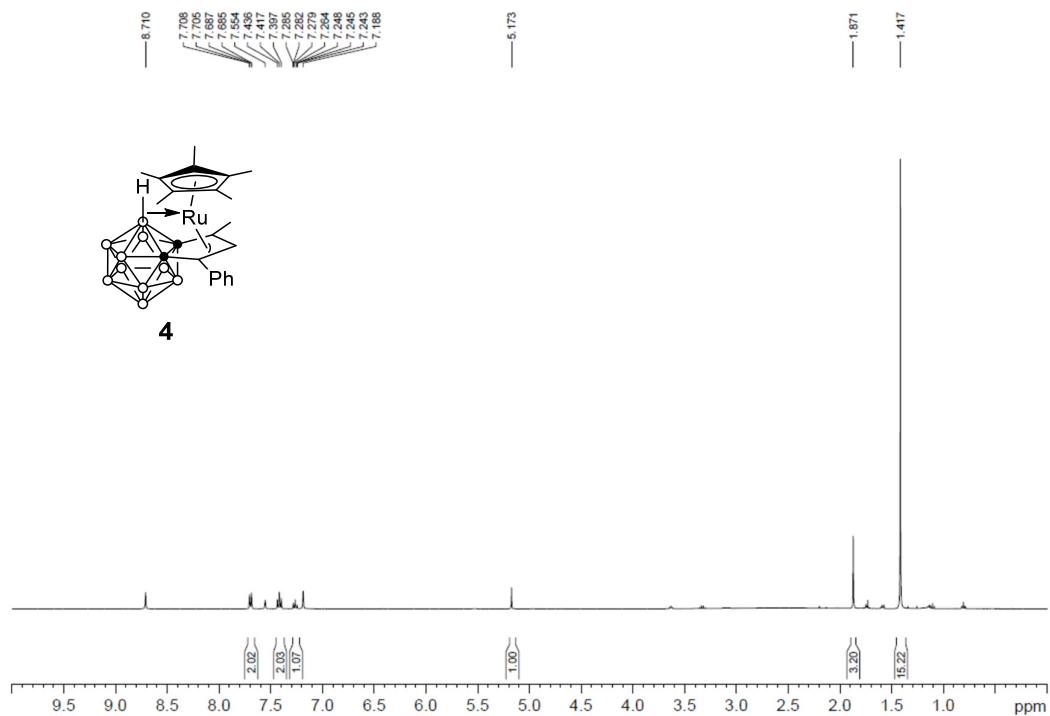


Figure S7. ¹H NMR spectrum of **4** in *d*₅-pyridine.

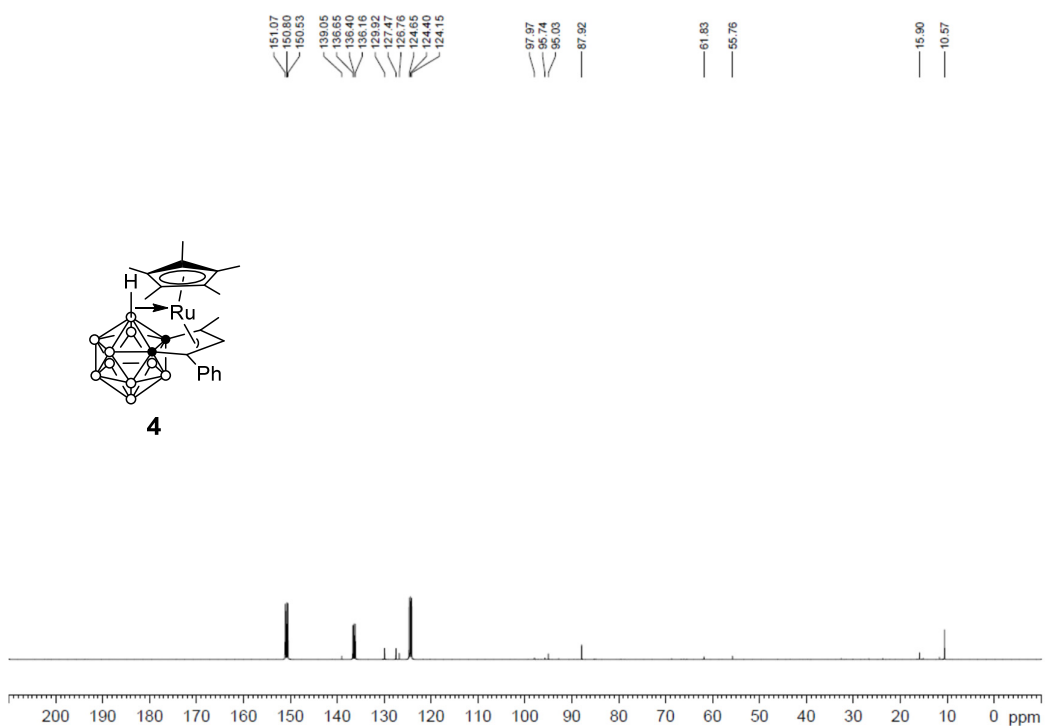


Figure S8. ¹³C{¹H} NMR spectrum of **4** in *d*₅-pyridine.

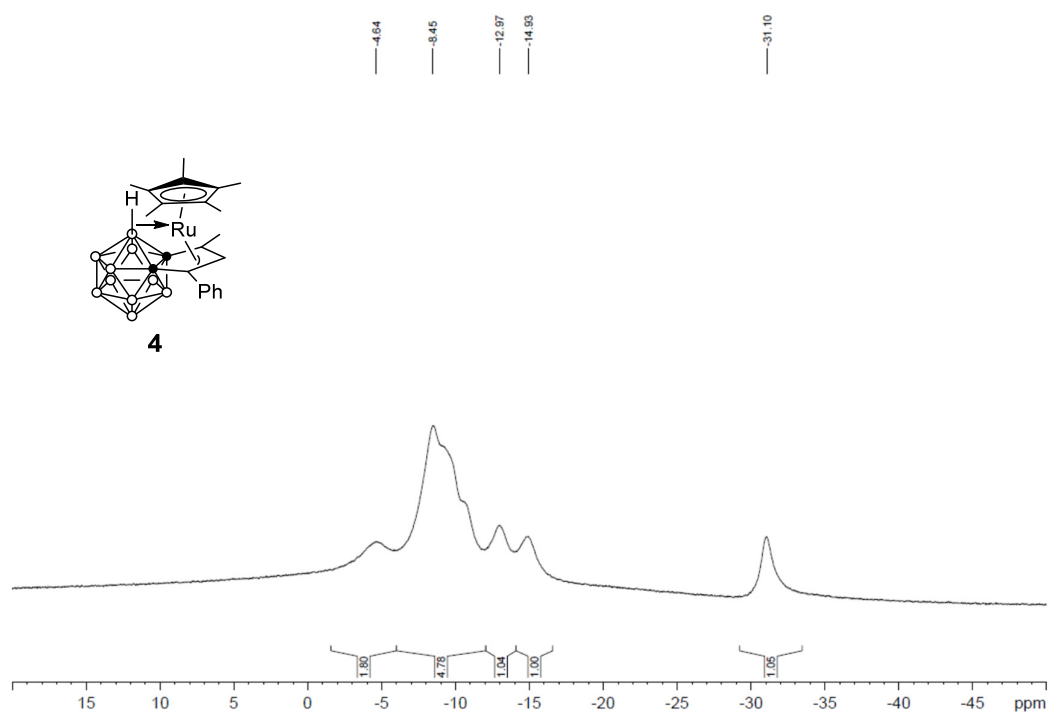


Figure S9. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4** in d_5 -pyridine.

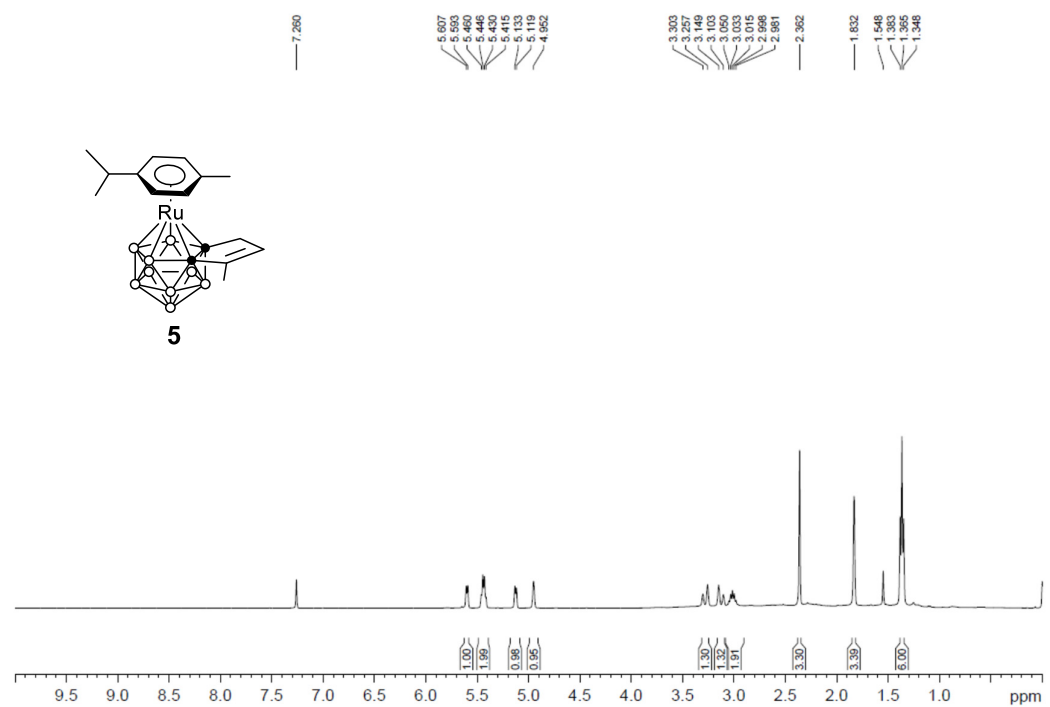


Figure S10. ^1H NMR spectrum of **5** in CDCl_3 .

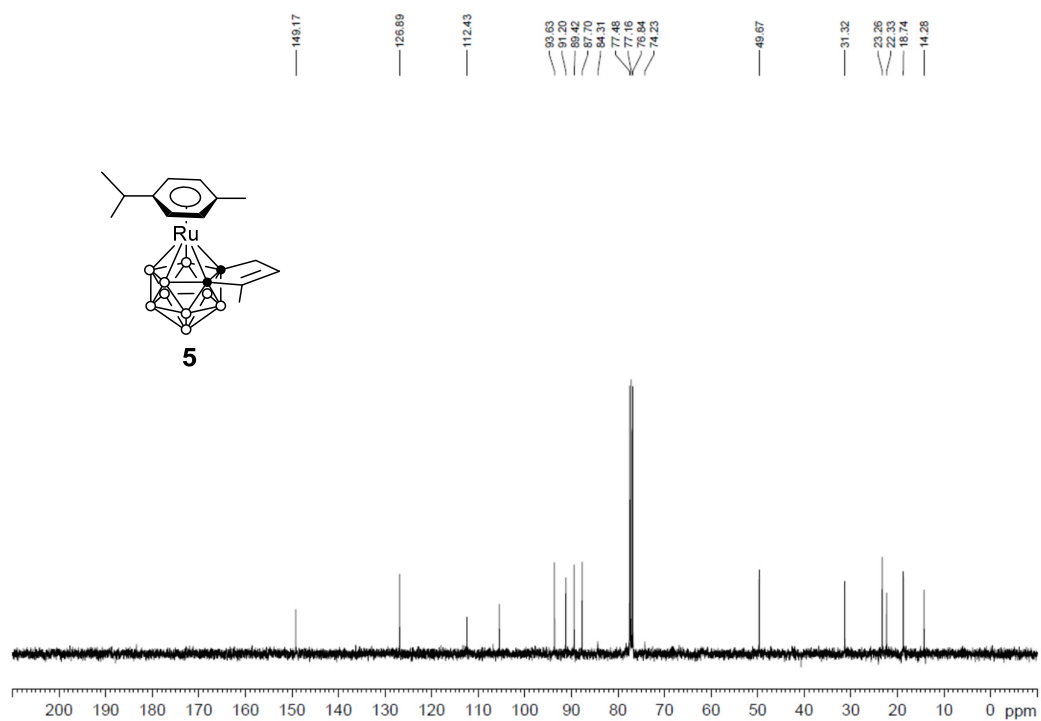


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** in CDCl_3 .

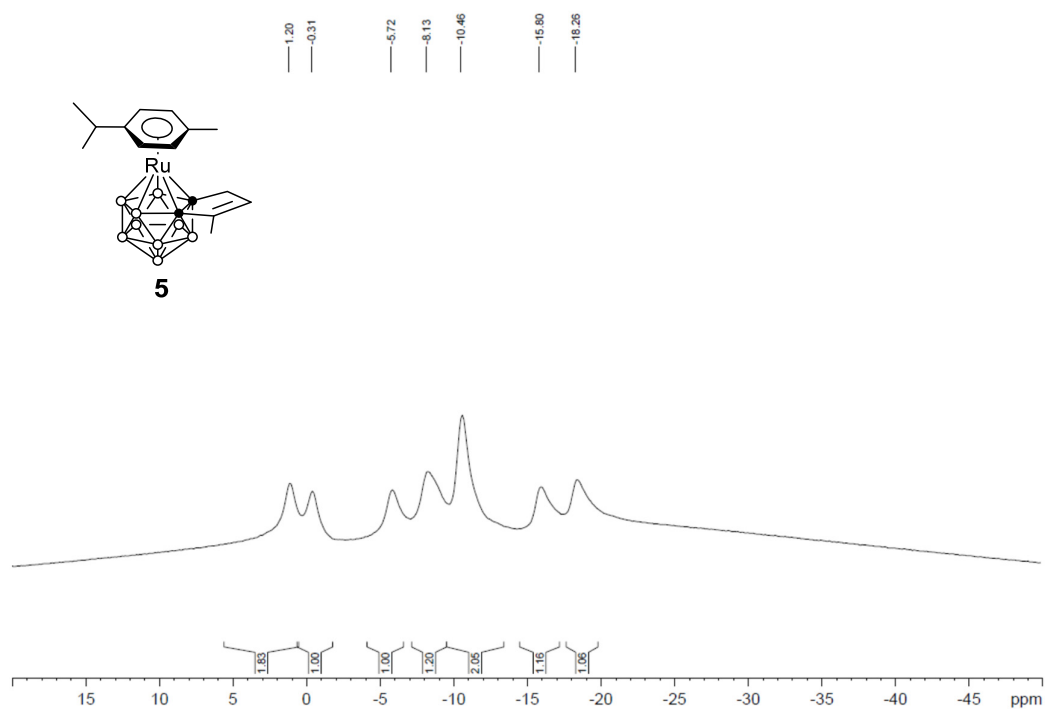


Figure S12. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **5** in CDCl_3 .

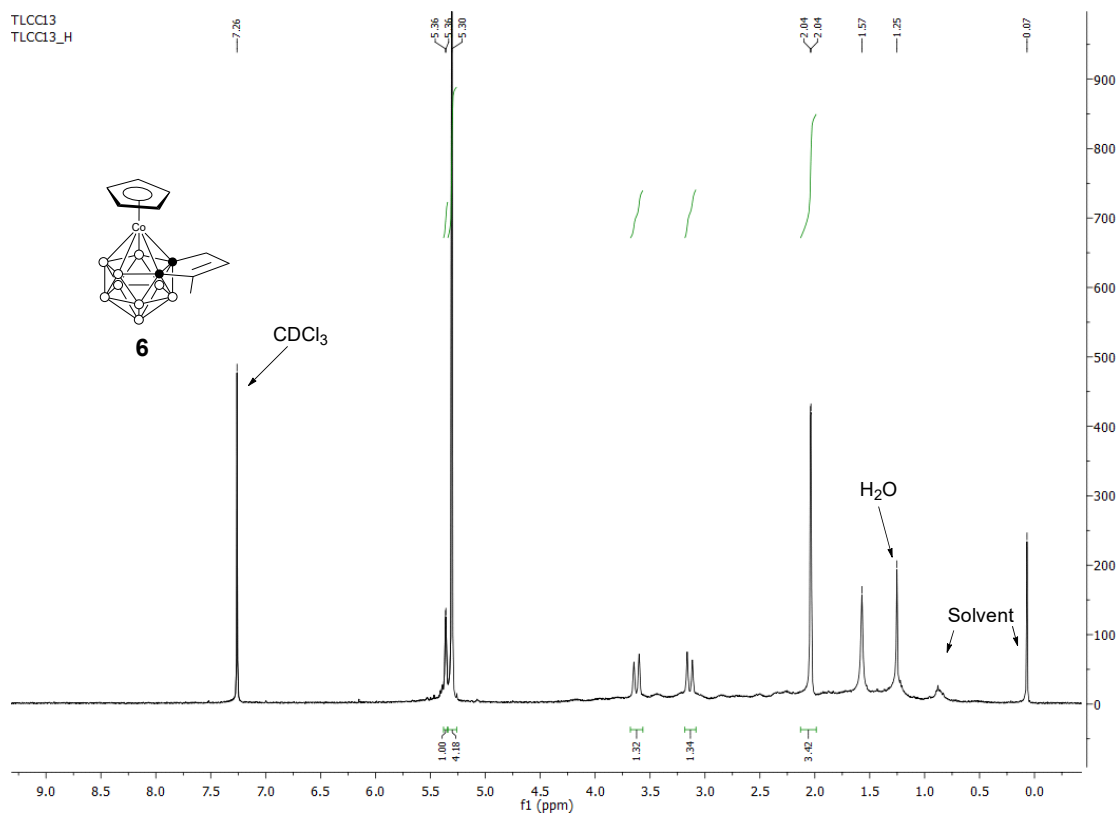


Figure S13. ¹H NMR spectrum of **6** in CDCl₃.

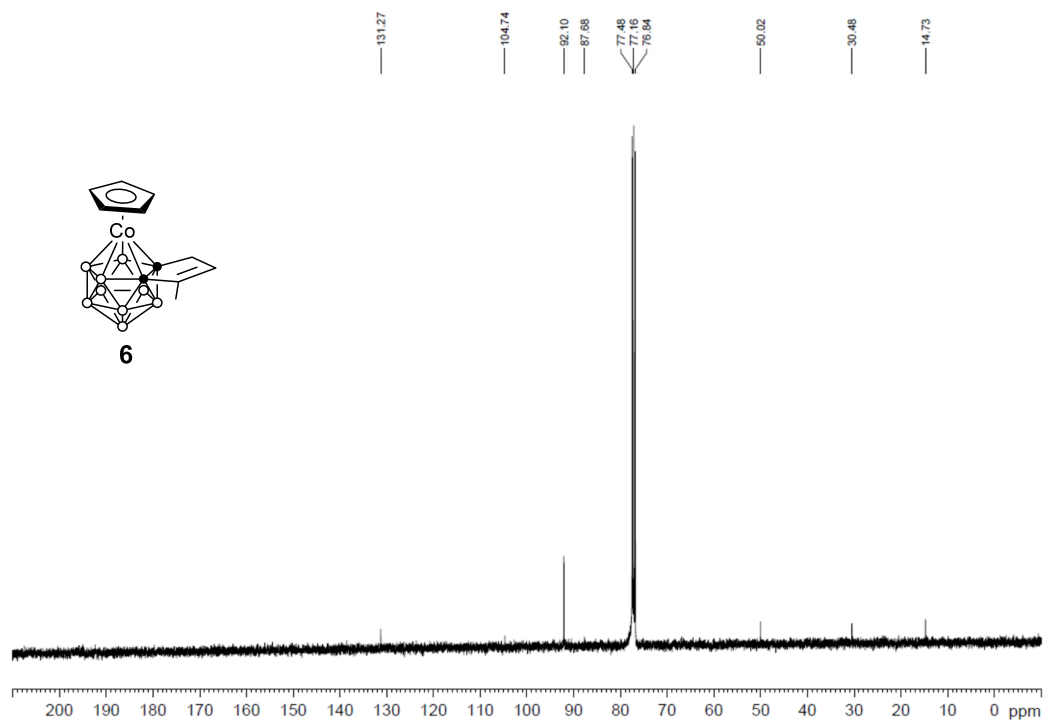


Figure S14. ¹³C{¹H} NMR spectrum of **6** in CDCl₃.

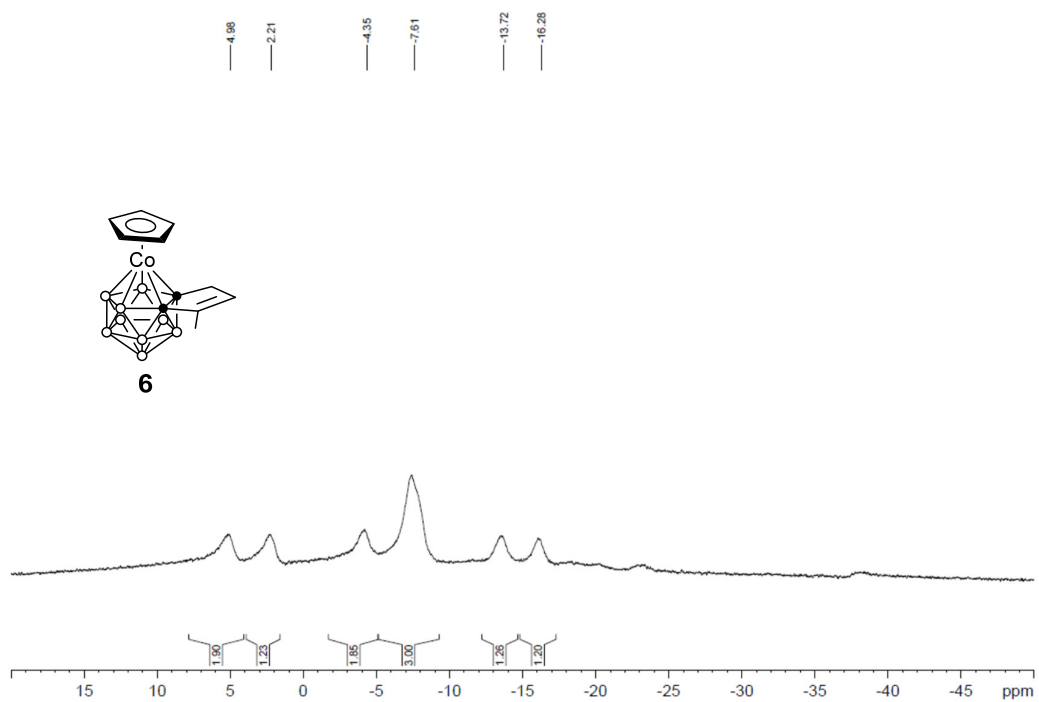


Figure S15. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **6** in CDCl_3 .

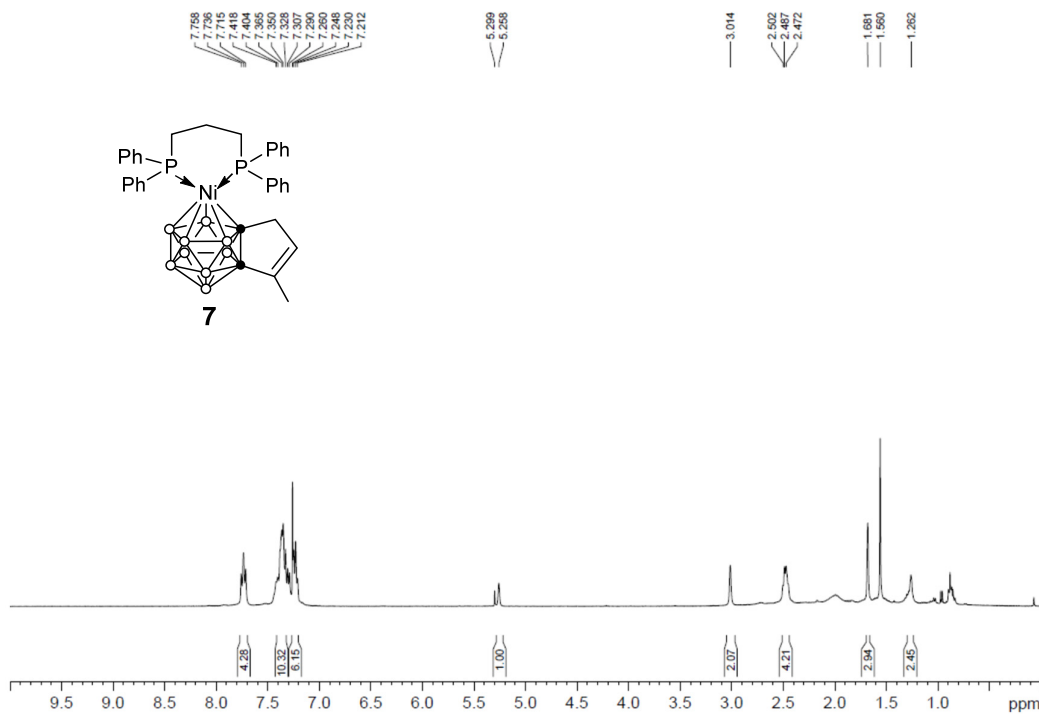


Figure S16. ^1H NMR spectrum of **7** in CDCl_3 .

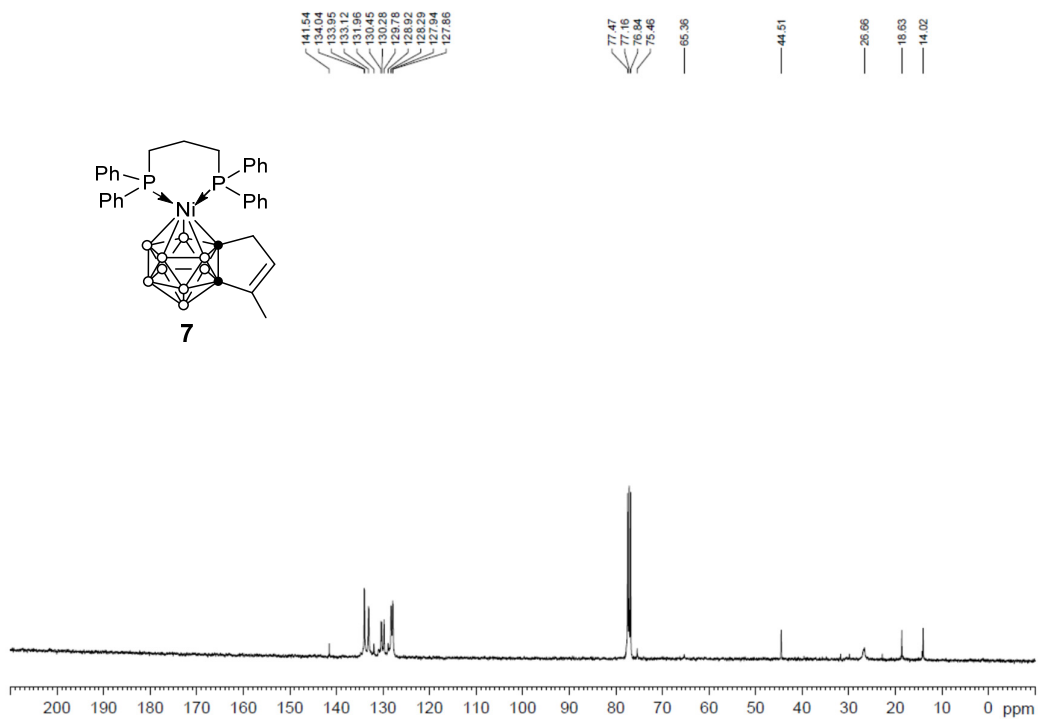


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7** in CDCl_3 .

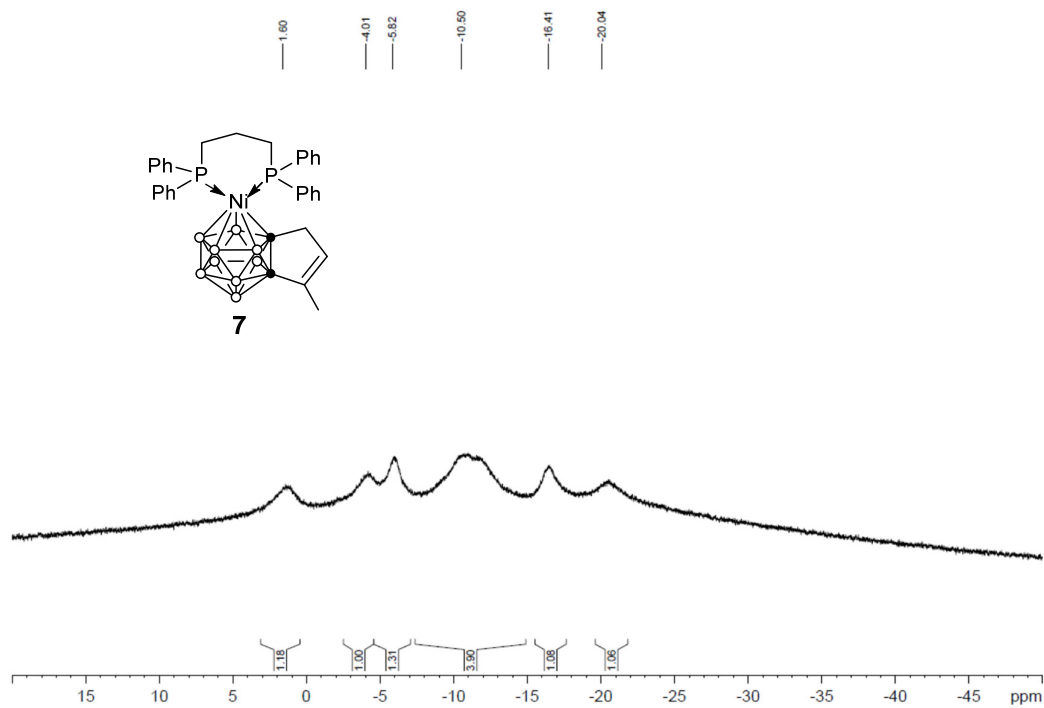


Figure S18. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **7** in CDCl_3 .

zwx2512 #17 RT: 1.49 AV: 1 NL: 1.96E6
T: + c EI Full ms [79.50-800.50]

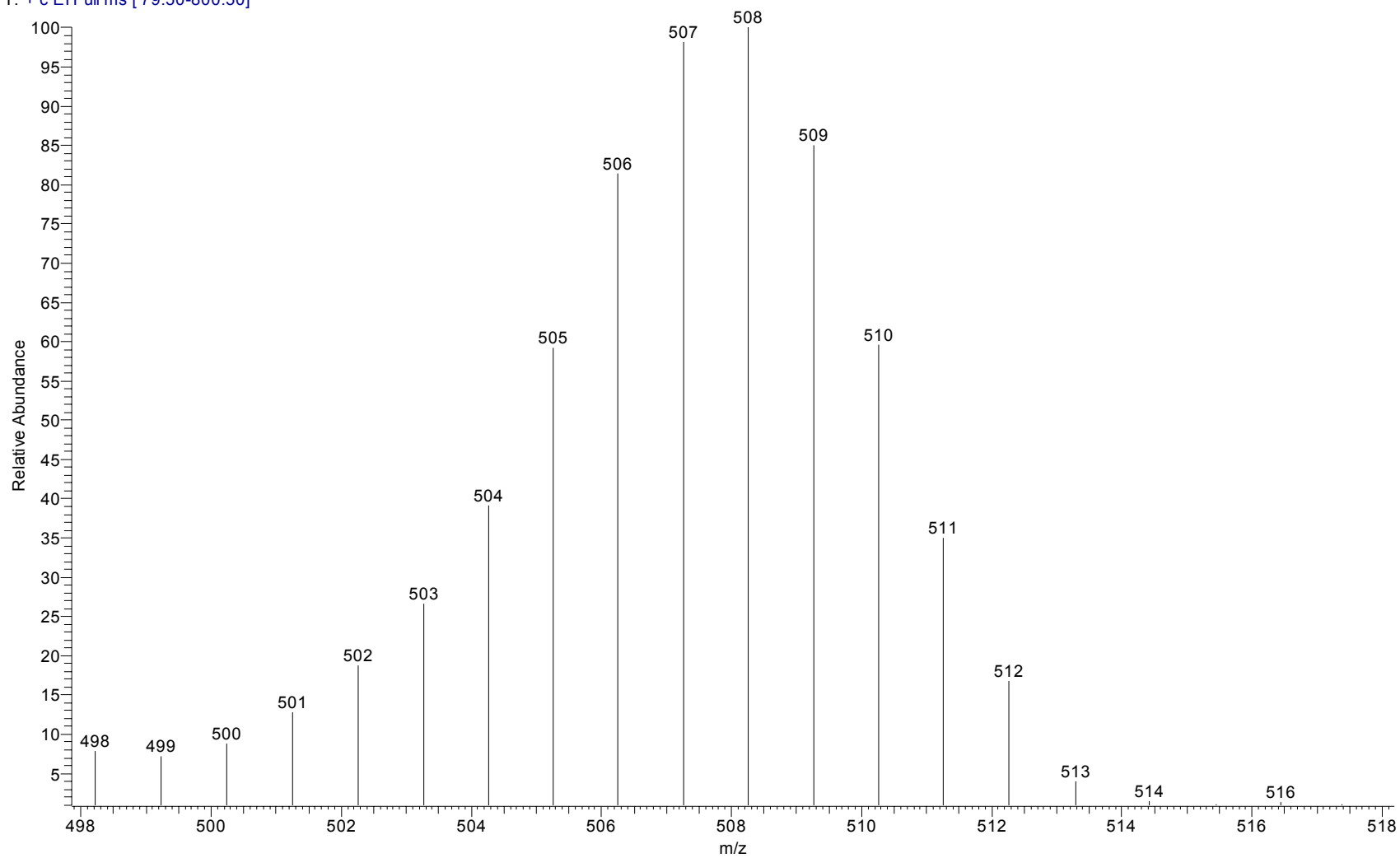
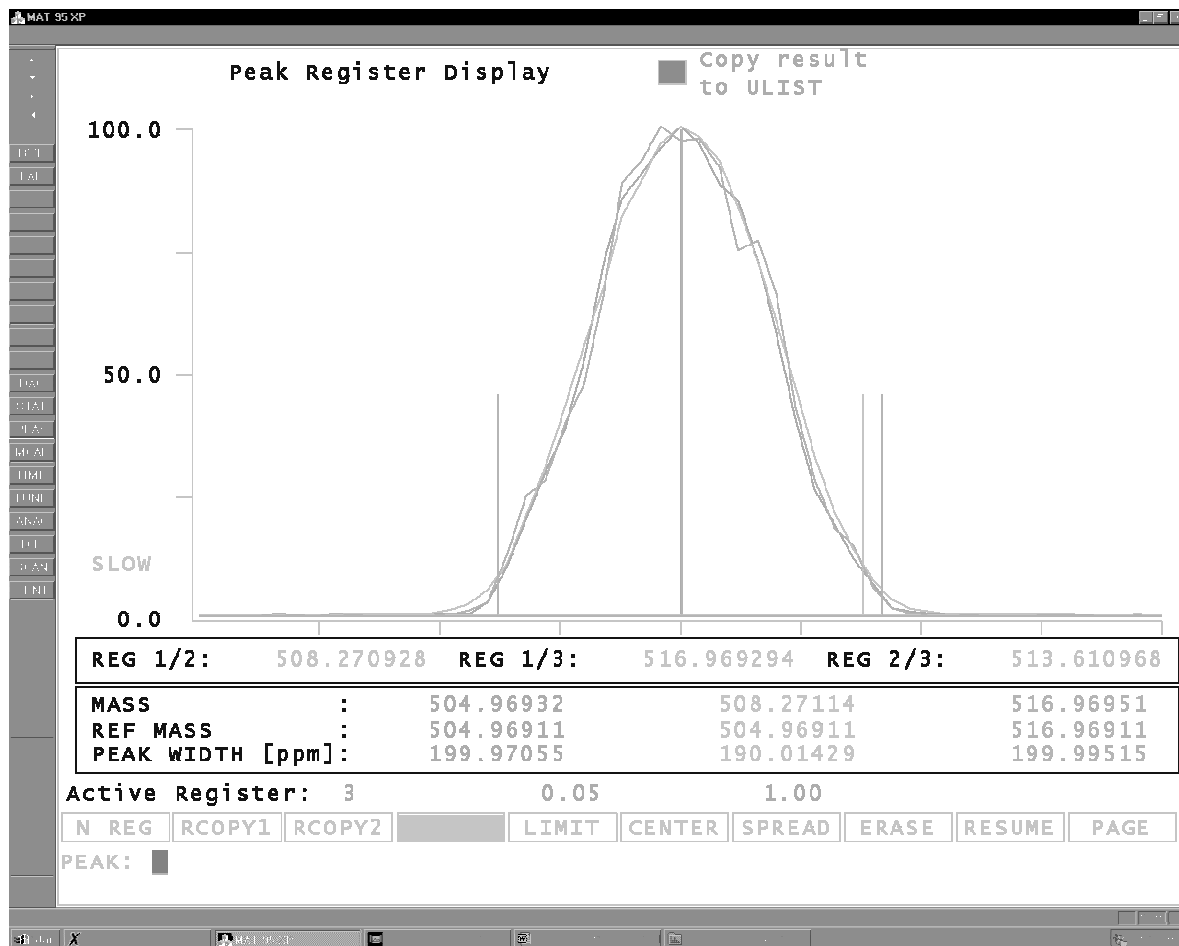


Figure S19. HRMS data of compound 4.

Accurate Mass Measurement



Molecular formula
 $C_{22}H_{34}B_{10}Ru$
 $[M]^+$ (theoretical)
= 508.2708

Figure S20. HRMS data of compound 4.

zwx1062 #21 RT: 1.62 AV: 1 NL: 5.51E7
T: + c EI Full ms [79.50-600.50]

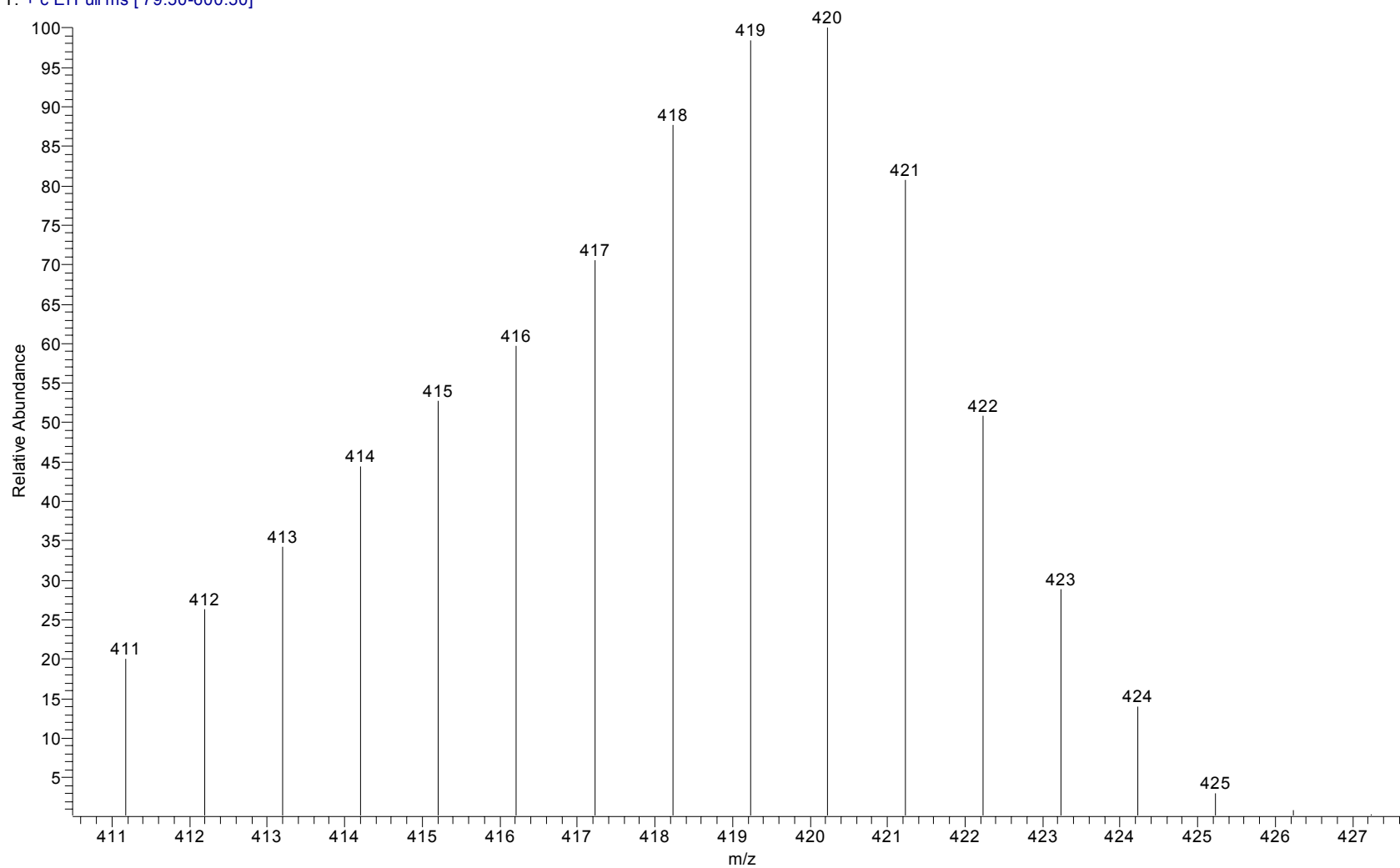
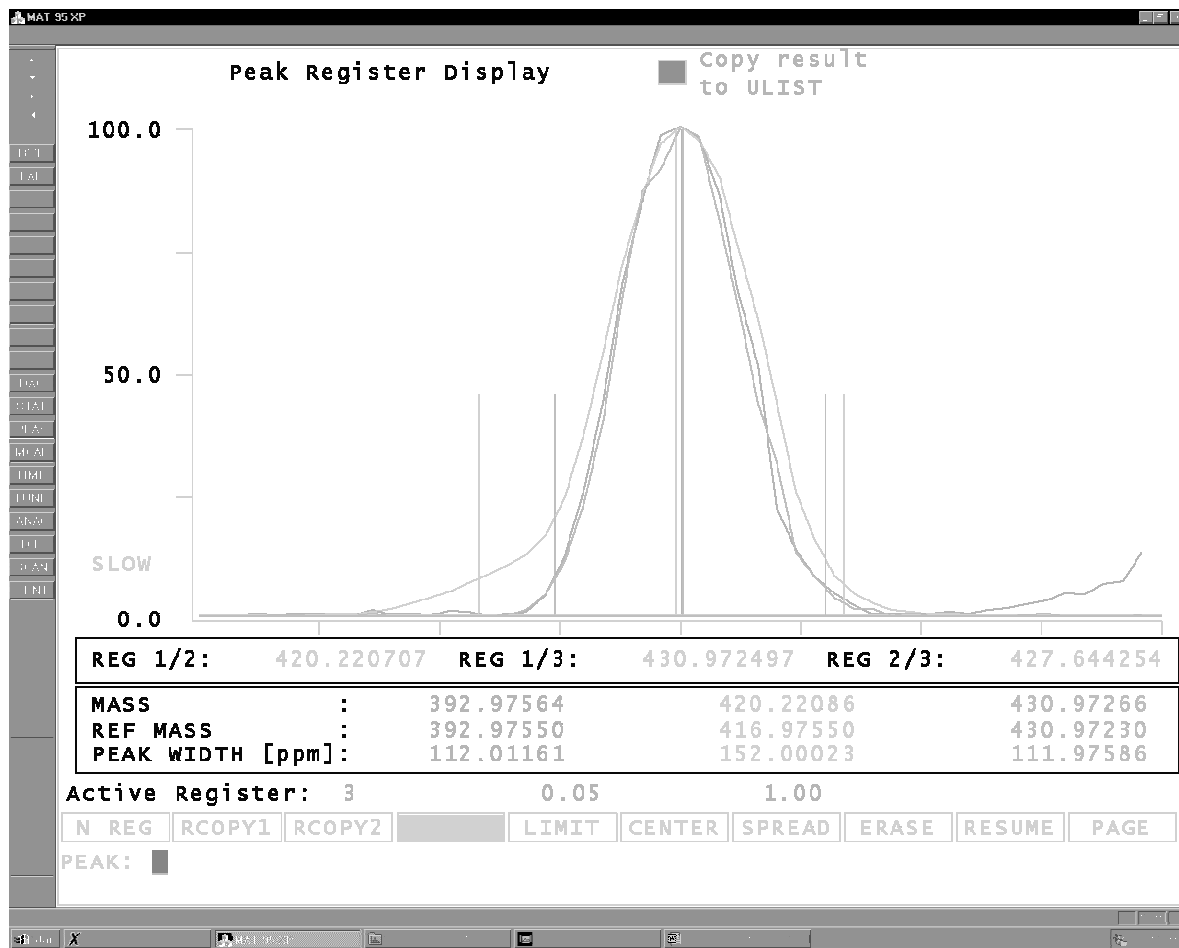


Figure S21. HRMS data of compound **5**.

Accurate Mass Measurement



Molecular formula
 $\text{RuC}_{16}\text{H}_{29}\text{B}_9$
 $[\text{M}]^+$ (theoretical)
= 420.2216

Figure S22. HRMS data of compound 5.

zwx1063 #29 RT: 2.28 AV: 1 NL: 2.32E7
T: + c EI Full ms [79.50-600.50]

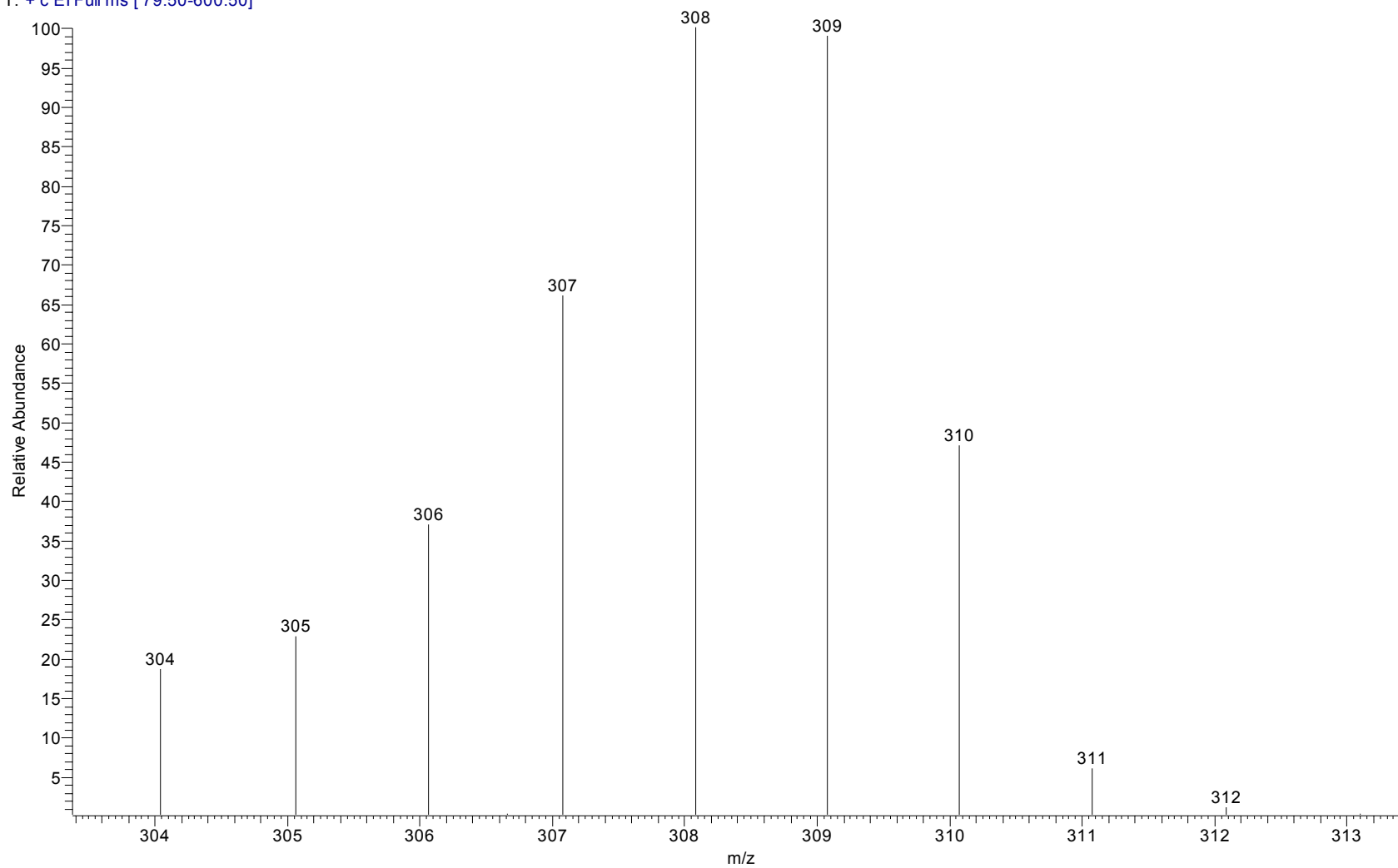
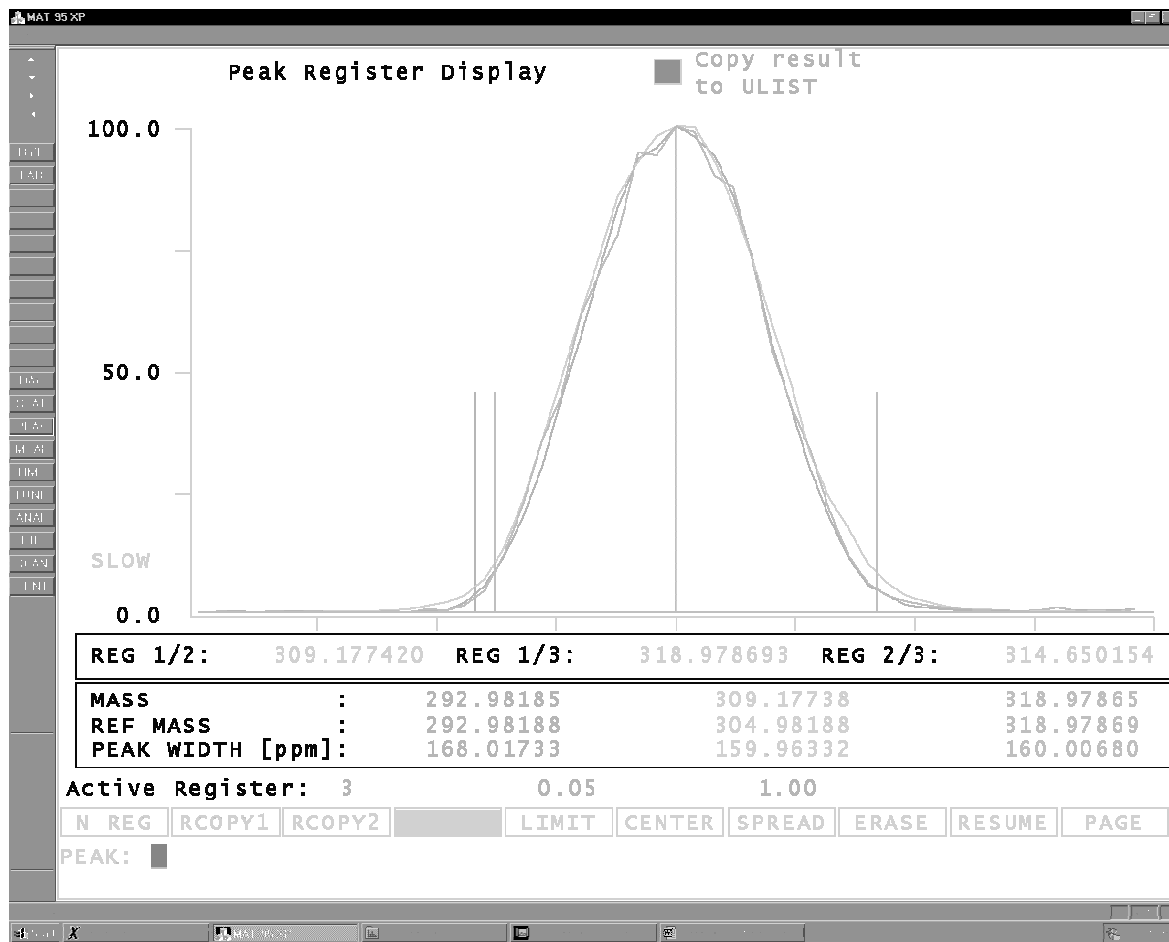


Figure S23. HRMS data of compound **6** .

Accurate Mass Measurement



Molecular formula
 $\text{CoC}_{11}\text{H}_{20}\text{B}_9$
 $[\text{M}]^+$ (theoretical)
= 309.1773

Figure S24. HRMS data of compound 6 .

zwx2508_161104153038 #23 RT: 1.81 AV: 1 NL: 3.56E3
T: + c EI Full ms [79.50-800.50]

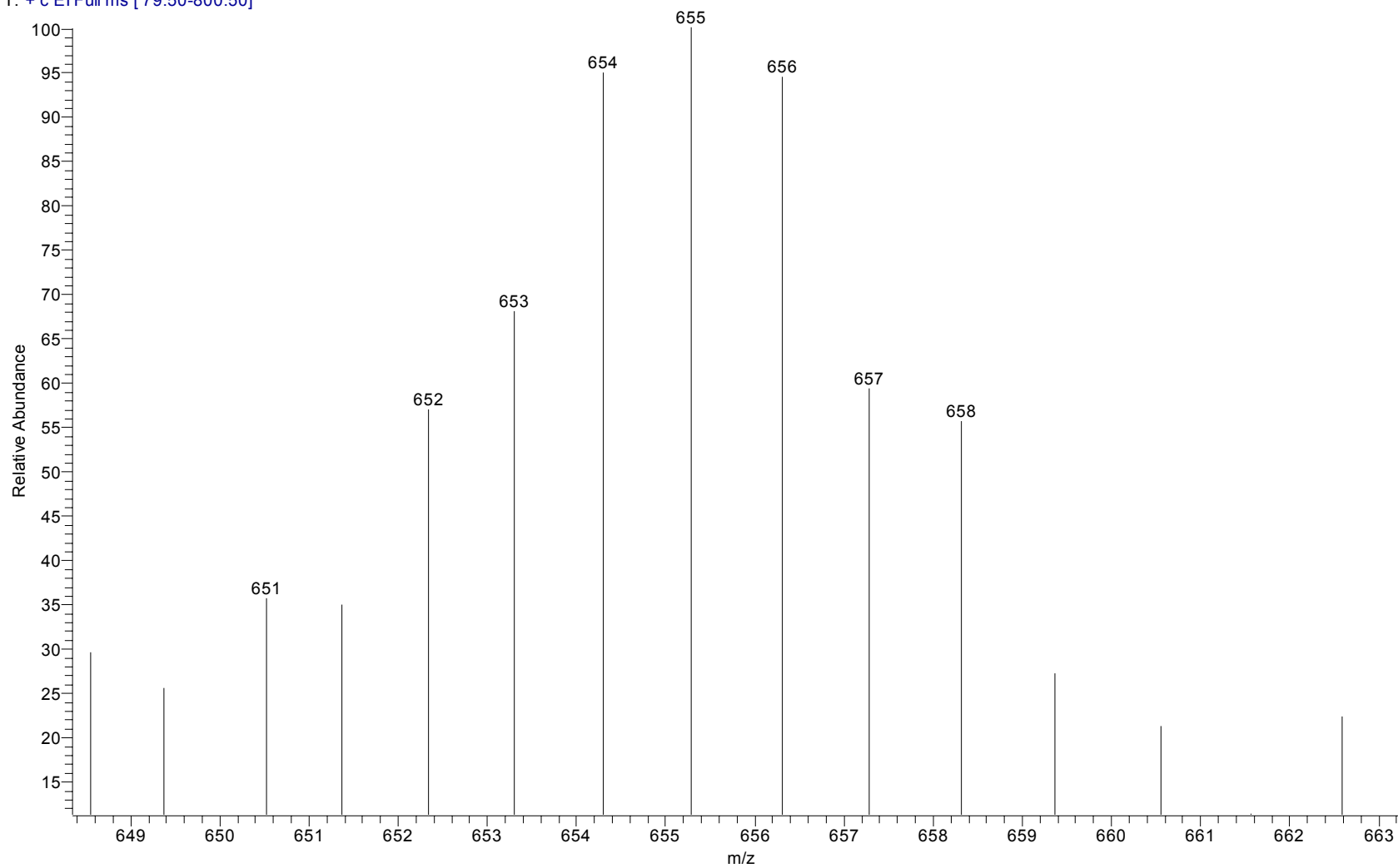
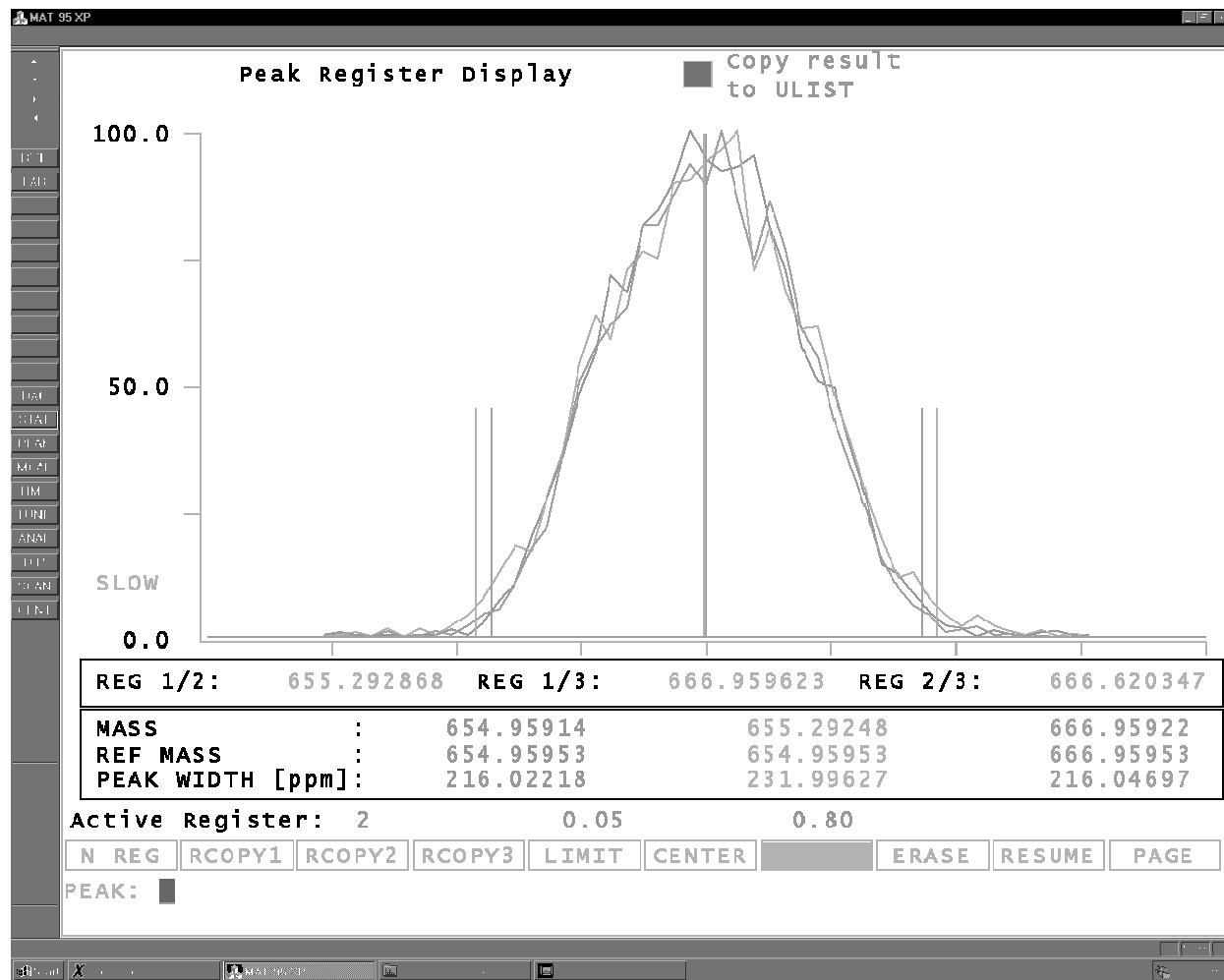


Figure S25. HRMS data of compound 7.

Accurate Mass Measurement



Molecular formula
 $C_{33}H_{41}B_9NiP_2$
 $[M]^+$ (theoretical)
= 655.2929

Figure S26. HRMS data of compound 7.