ESI for:

Conformational and Electronic Variability of *N,N',O*-Ligand Documented on its Coordination to Main Group Halides

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Table S1. Crystallographic data for **2**

Crystal data	
Chemical formula	$C_{25}H_{37}ClN_2O_3PGe \cdot Cl_3Ge$
M_r	731.51
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	150
a, *b*, *c* (Å)	8.4329(9), 14.0969(13), 14.9495(14)
α, β, γ (°)	70.465(5), 87.024(5), 73.513(5)
V (Å^3)	1604.2(3)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	2.285
Crystal size (mm)	0.290 × 0.123 × 0.059
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.4879, 0.7456
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	38102, 6290, 4639
R_{int}	0.1034
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.596
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.0652, 0.1580, 1.079
No. of reflections	6290
No. of parameters	362
No. of restraints	292
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.386, -0.783

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.5-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2014*/7 (Sheldrick, 2014), *PLATON* (Spek, 2009).

Table S2. Crystallographic data for **3**·0.5(C_6H_{14})

Crystal data	
Chemical formula	$C_{43}H_{52}ClN_2O_3PSn$·0.5(C_6H_{14})
M_r	873.06
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	150
a, *b*, *c* (Å)	9.7555(3), 10.6048(3), 23.1622(7)
α, β, γ (°)	86.347(2), 81.2130(10), 69.5690(10)
V (Å^3)	2219.01(12)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.712
Crystal size (mm)	0.593 × 0.246 × 0.060
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.6487, 0.7469
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	77217, 9196, 7779
R_{int}	0.0965
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.606
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.0460, 0.0850, 1.060
No. of reflections	9196
No. of parameters	493
No. of restraints	441
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.591, -0.986

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.5-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2014*/7 (Sheldrick, 2014), *PLATON* (Spek, 2009).

Table S3. Crystallographic data for **4**

Crystal data	
Chemical formula	$C_{37}H_{47}Cl_2N_2O_3PSn$
M_r	788.32
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	150
a, *b*, *c* (Å)	8.9582(5), 9.7607(6), 22.8368(14)
α, β, γ (°)	79.246(2), 86.851(3), 75.846(3)
V (Å^3)	1902.1(2)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.890
Crystal size (mm)	0.591 × 0.170 × 0.156
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.5753, 0.7456
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	78519, 8746, 8147
R_{int}	0.0421
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.627
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.0295, 0.0662, 1.112
No. of reflections	8746
No. of parameters	424
No. of restraints	366
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.661, -0.872

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.5-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2014*/7 (Sheldrick, 2014), *PLATON* (Spek, 2009).

Table S4. Crystallographic data for **5**·CH_2Cl_2

Crystal data	
Chemical formula	$C_{25}H_{37}Cl_3InN_2O_3P \cdot CH_2Cl_2$
M_r	750.63
Crystal system, space group	Monoclinic, *P2₁/n*
Temperature (K)	150
a, *b*, *c* (Å)	10.0275(4), 24.3548(9), 14.0572(6)
α, β, γ (°)	90, 100.5700(10), 90
V (Å^3)	3374.8(2)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	1.172
Crystal size (mm)	0.592 × 0.200 × 0.052
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.6529, 0.7456
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	96027, 7772, 5822
R_{int}	0.1476
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0591, 0.1125, 1.058
No. of reflections	7772
No. of parameters	338
No. of restraints	375
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.230, -1.475

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.5-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2014*/7 (Sheldrick, 2014), *PLATON* (Spek, 2009).

Table S5. Crystallographic data for **7**

Crystal data	
Chemical formula	$C_{25}H_{36}Cl_3N_2O_3PTe \cdot C_6H_{14}$
M_r	763.65
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	150
a, *b*, *c* (Å)	10.6757(4), 15.4741(6), 21.0949(7)
α, β, γ (°)	90, 90, 90
V (Å^3)	3484.8(2)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	1.163
Crystal size (mm)	0.495 × 0.224 × 0.142
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.6035, 0.7464
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	33790, 10325, 8671
R_{int}	0.0431
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.713
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.0403, 0.0720, 1.046
No. of reflections	10325
No. of parameters	324
No. of restraints	288
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.035, -0.913

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.5-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2014*/7 (Sheldrick, 2014), *PLATON* (Spek, 2009).

Table S6. Crystallographic data for **8**

Crystal data	
Chemical formula	$C_{25}H_{37}GeN_2O_3P$
M_r	517.12
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	150
a, *b*, *c* (Å)	7.9728(13), 11.803(2), 15.182(3)
α, β, γ (°)	80.580(9), 83.224(9), 71.301(8)
V (Å^3)	1331.8(4)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	1.237
Crystal size (mm)	0.371 × 0.353 × 0.174
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.5384, 0.7456
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25989, 5460, 3990
R_{int}	0.1175
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.606
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.1079, 0.2519, 1.114
No. of reflections	5460
No. of parameters	317
No. of restraints	264
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.563, -1.207

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.5-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2014*/7 (Sheldrick, 2014), *PLATON* (Spek, 2009).

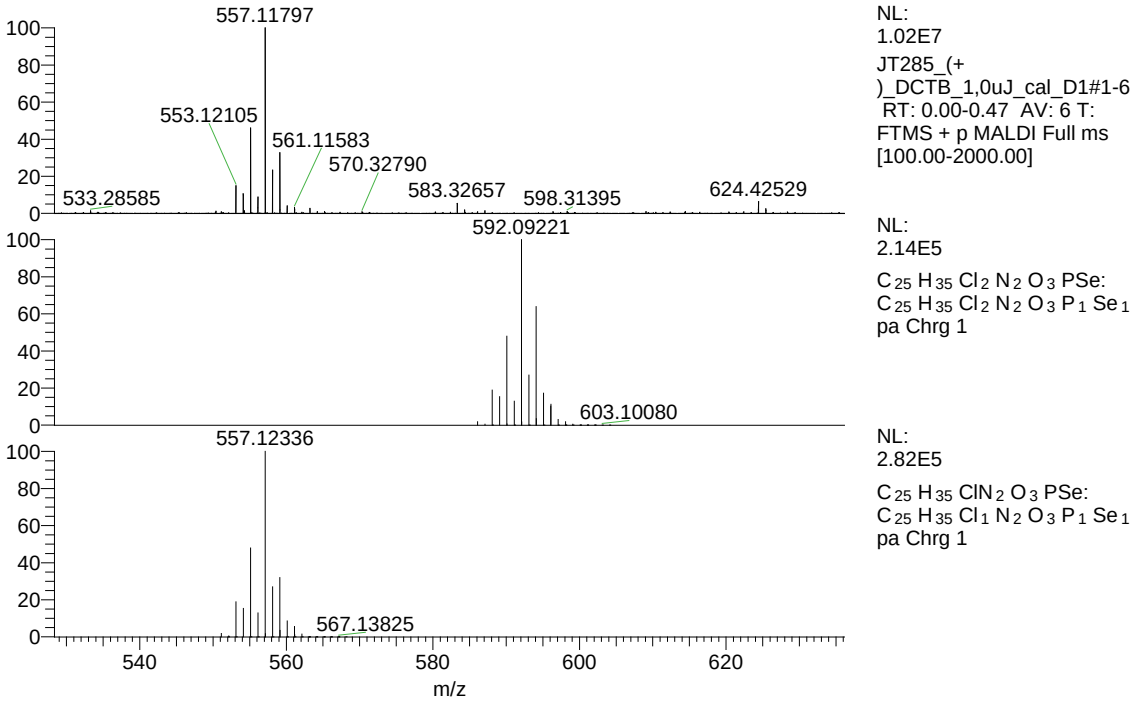

Figure S1. FTMS+ MALDI MS spectrum of **6**

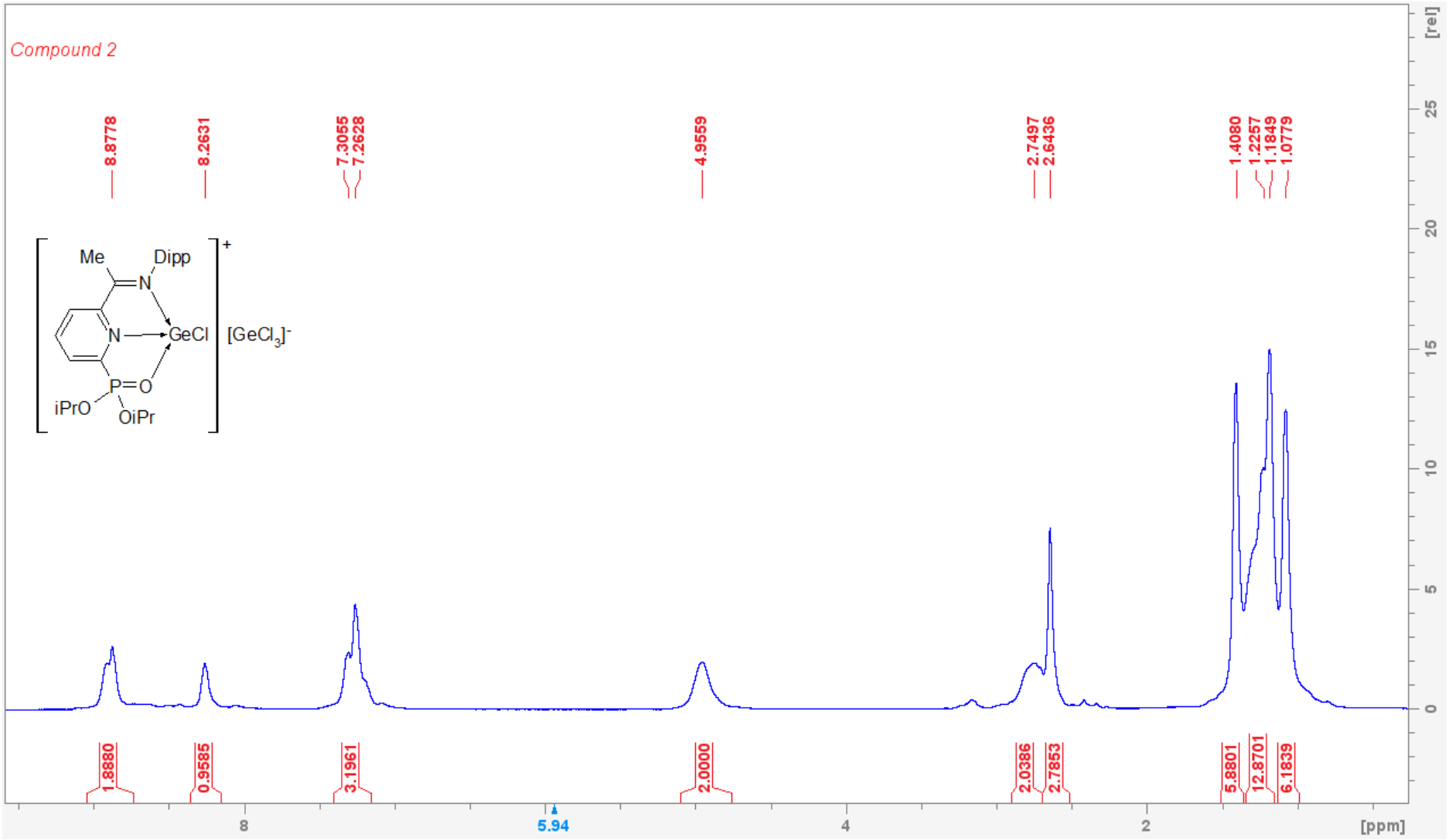

Figure S2. ^{1}H NMR spectrum of **2** in $CDCl_3$

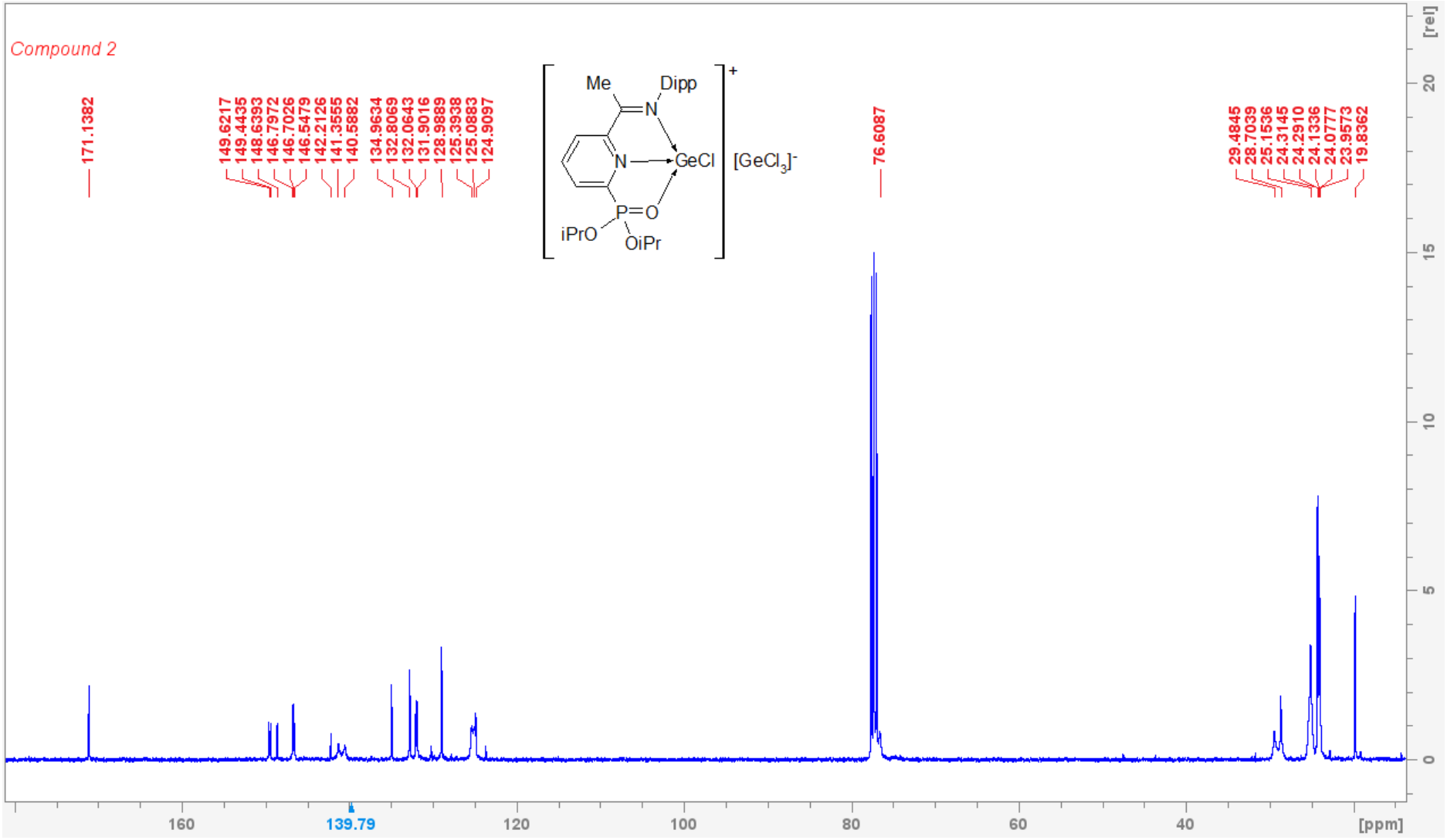

Figure S3. $^{13}C\{H\}$ NMR spectrum of **2** in $CDCl_3$

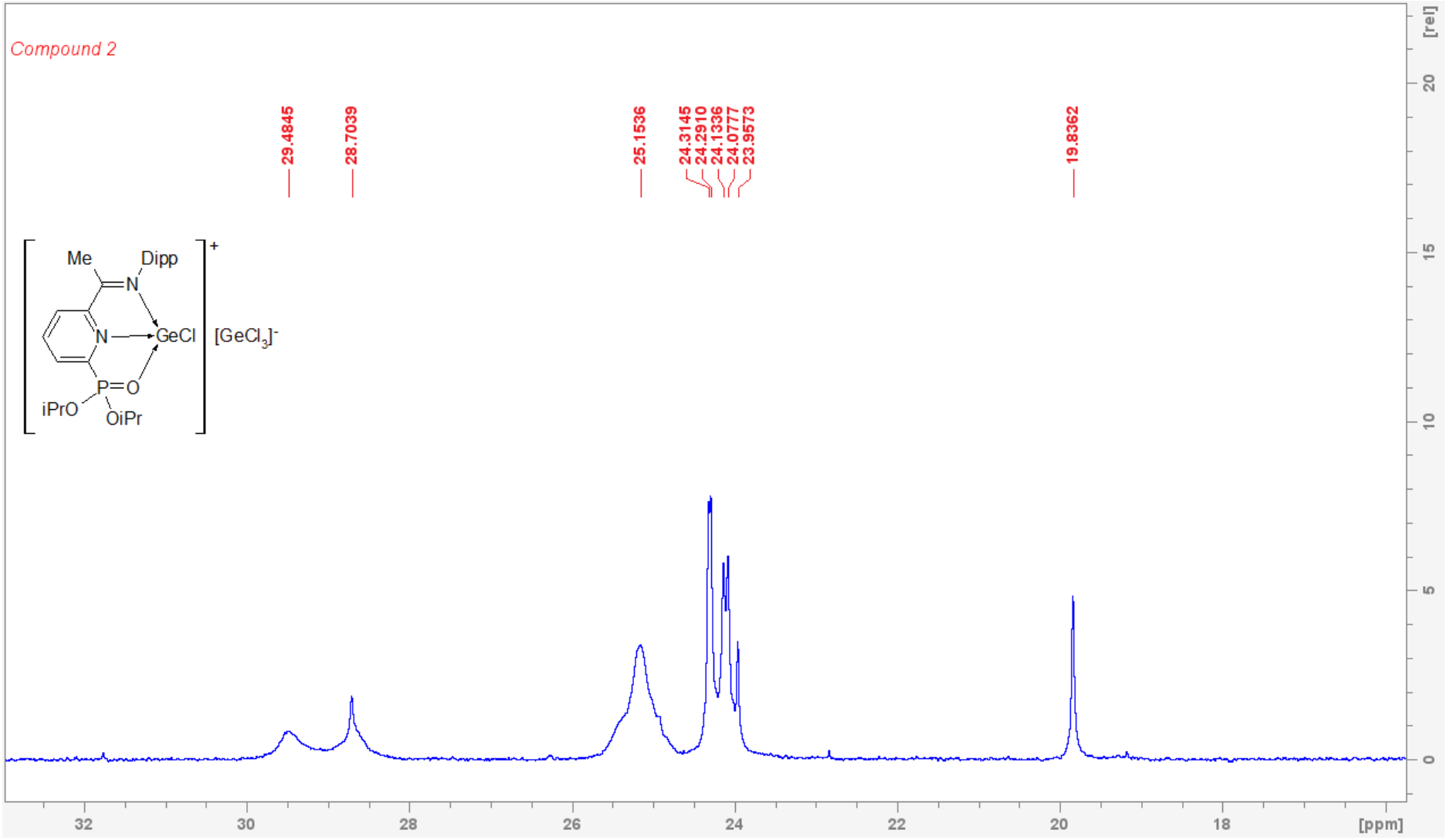

Figure S4. $^{13}C\{H\}$ NMR spectrum of **2** in $CDCl_3$ – aliphatic region

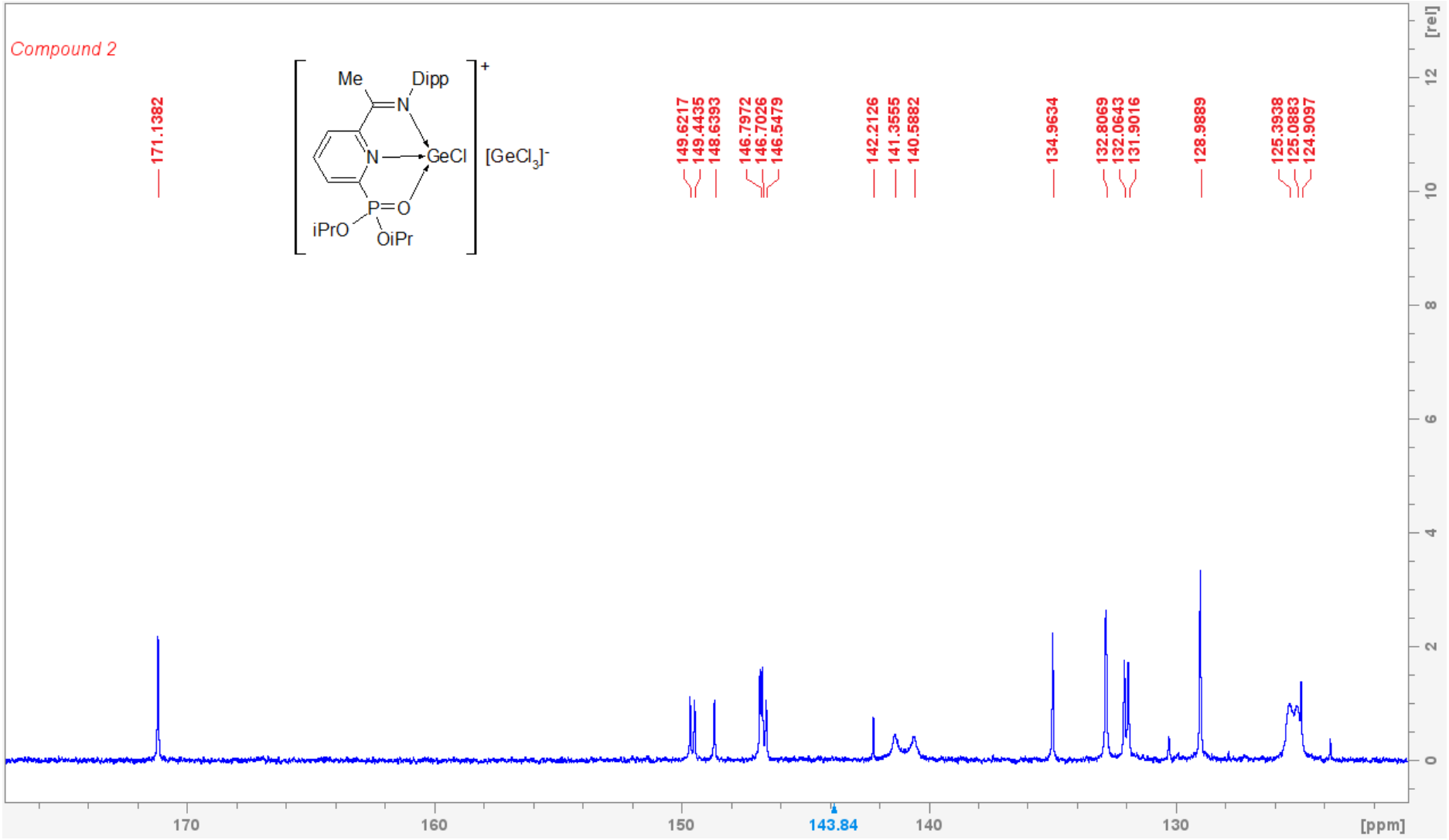

Figure S5. $^{13}C\{H\}$ NMR spectrum of **2** in $CDCl_3$ – aromatic region

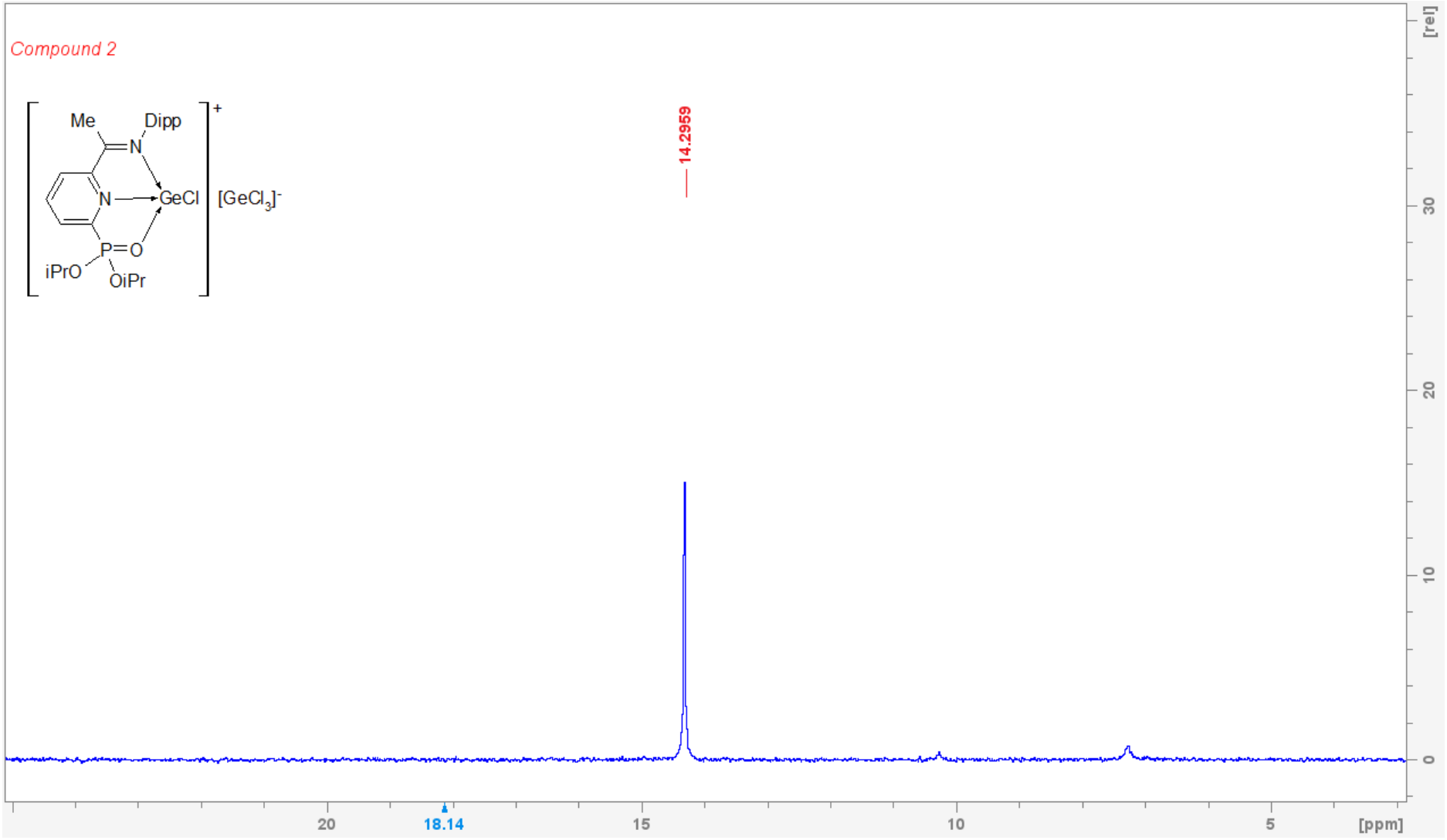

Figure S6. $^{31}P\{H\}$ NMR spectrum of **2** in $CDCl_3$

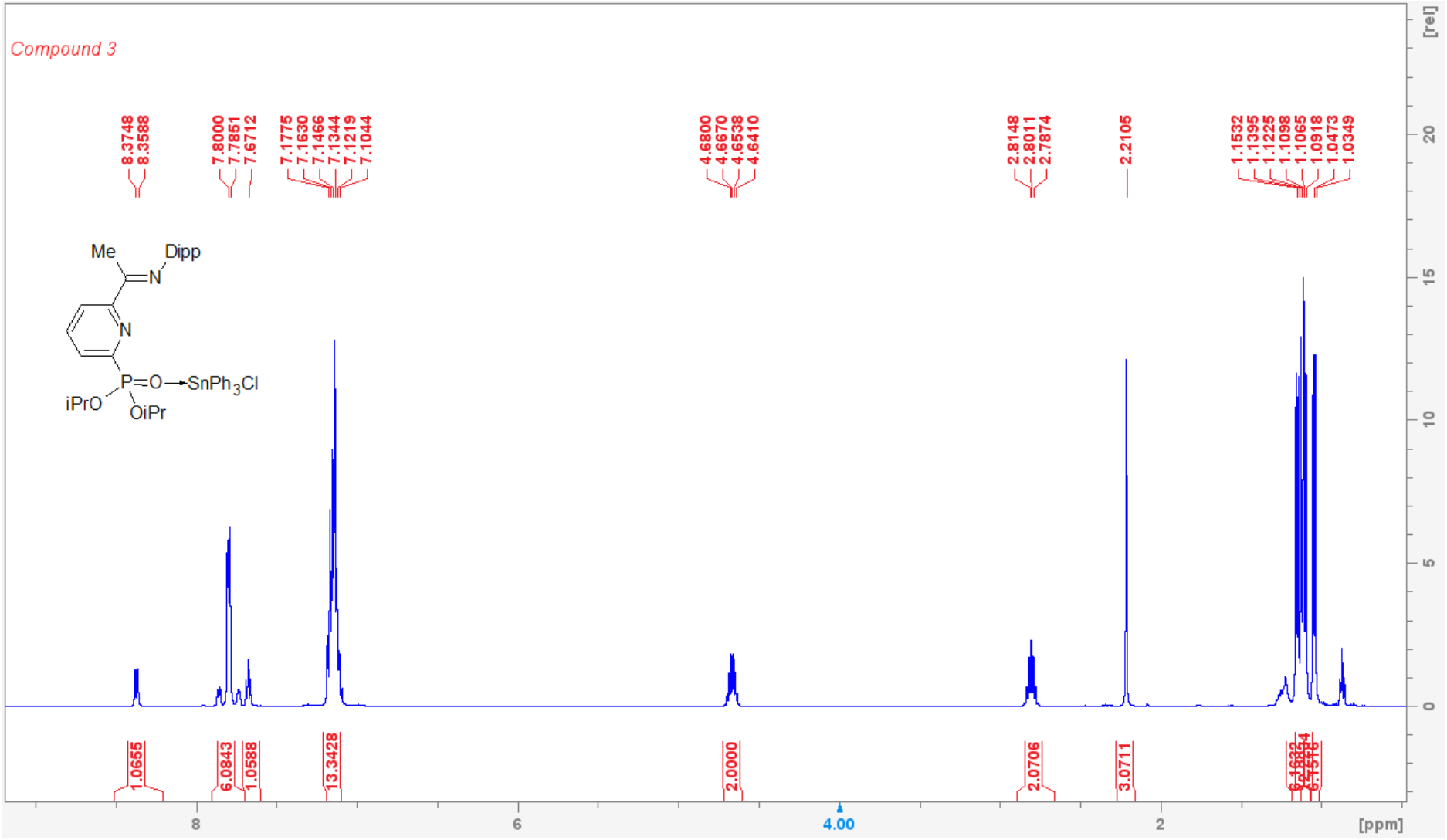

Figure S7. ^{1}H NMR spectrum of **3** in C_6D_6

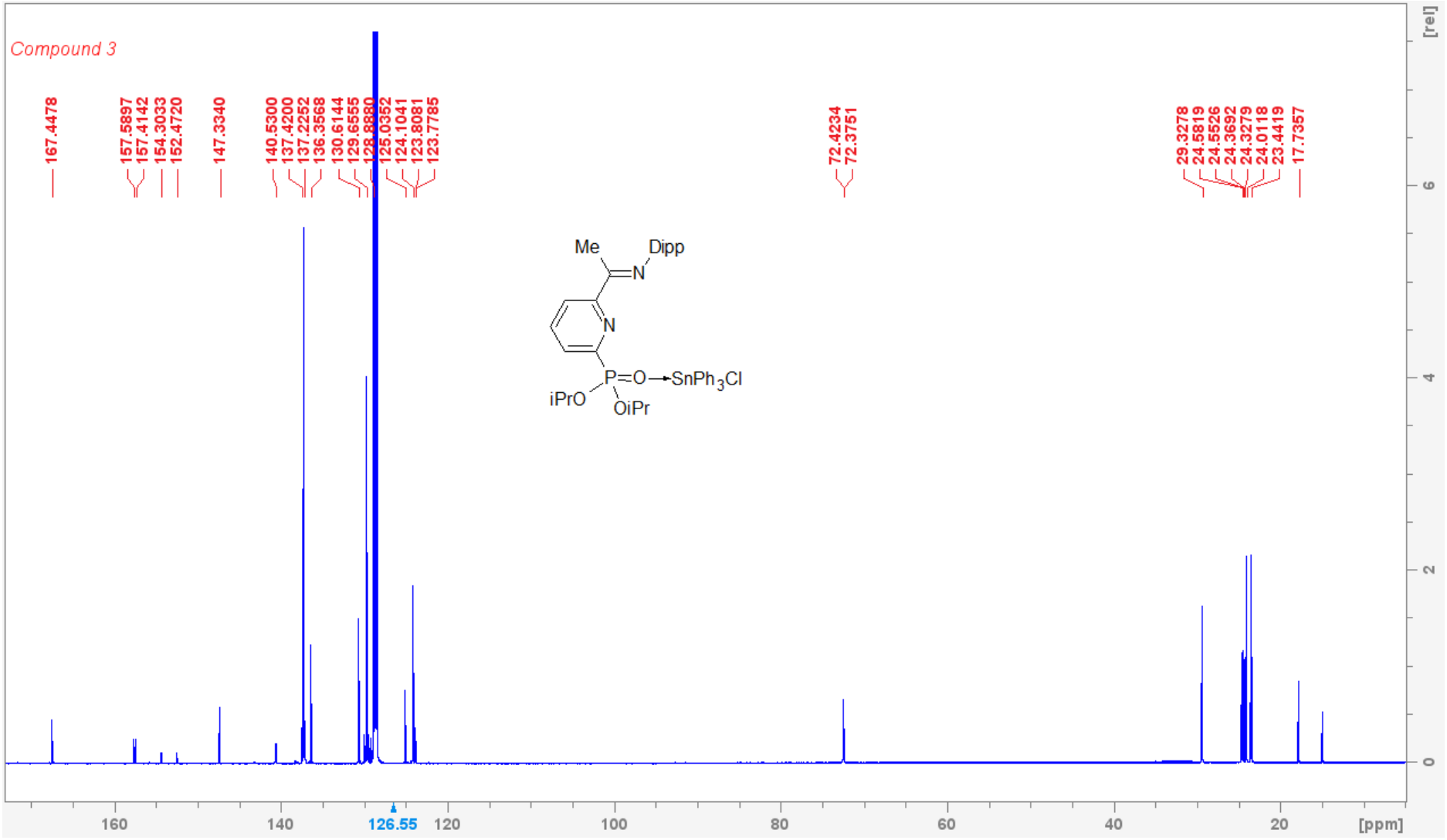

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6

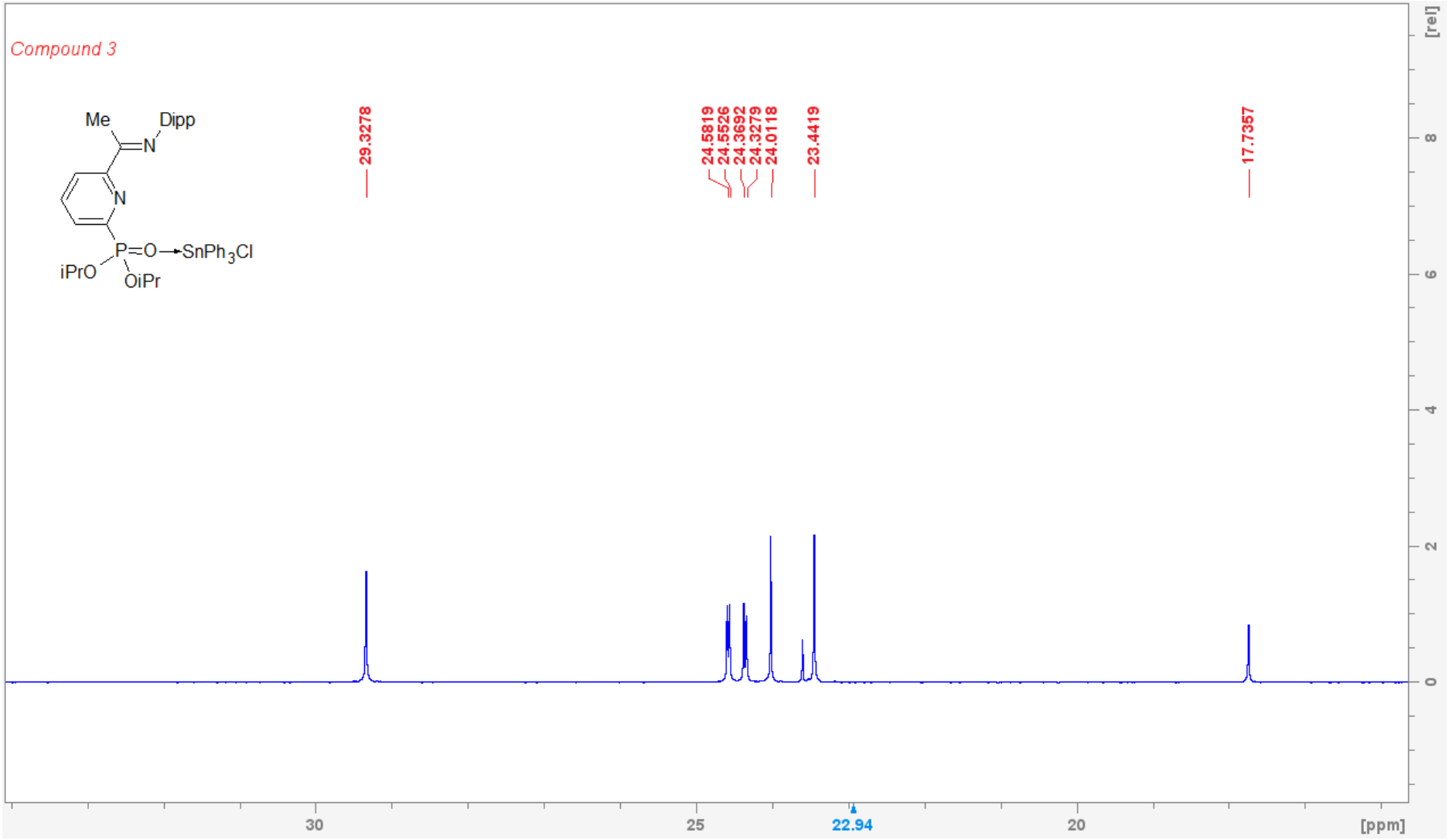

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 – aliphatic region

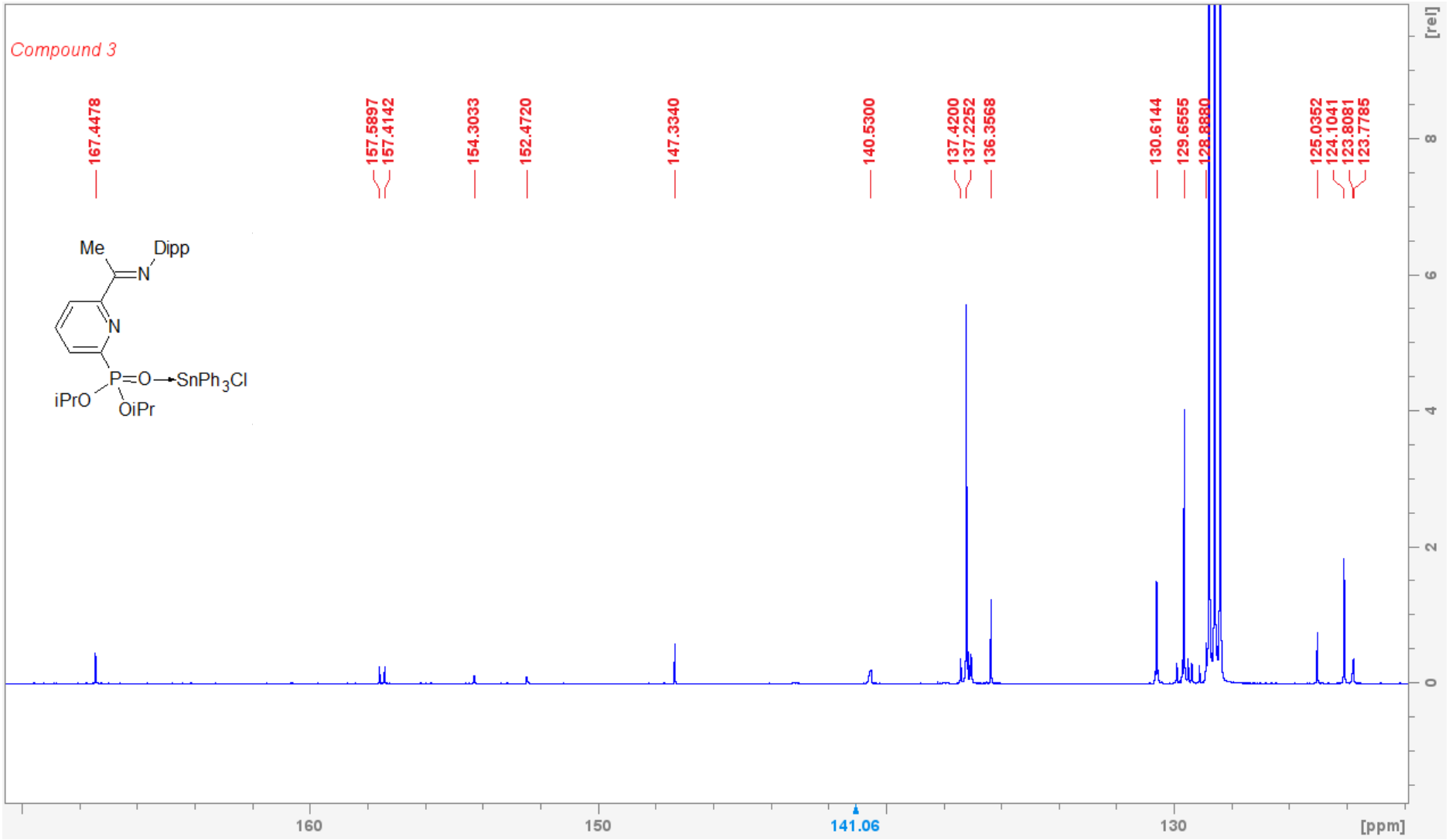

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 – aromatic region

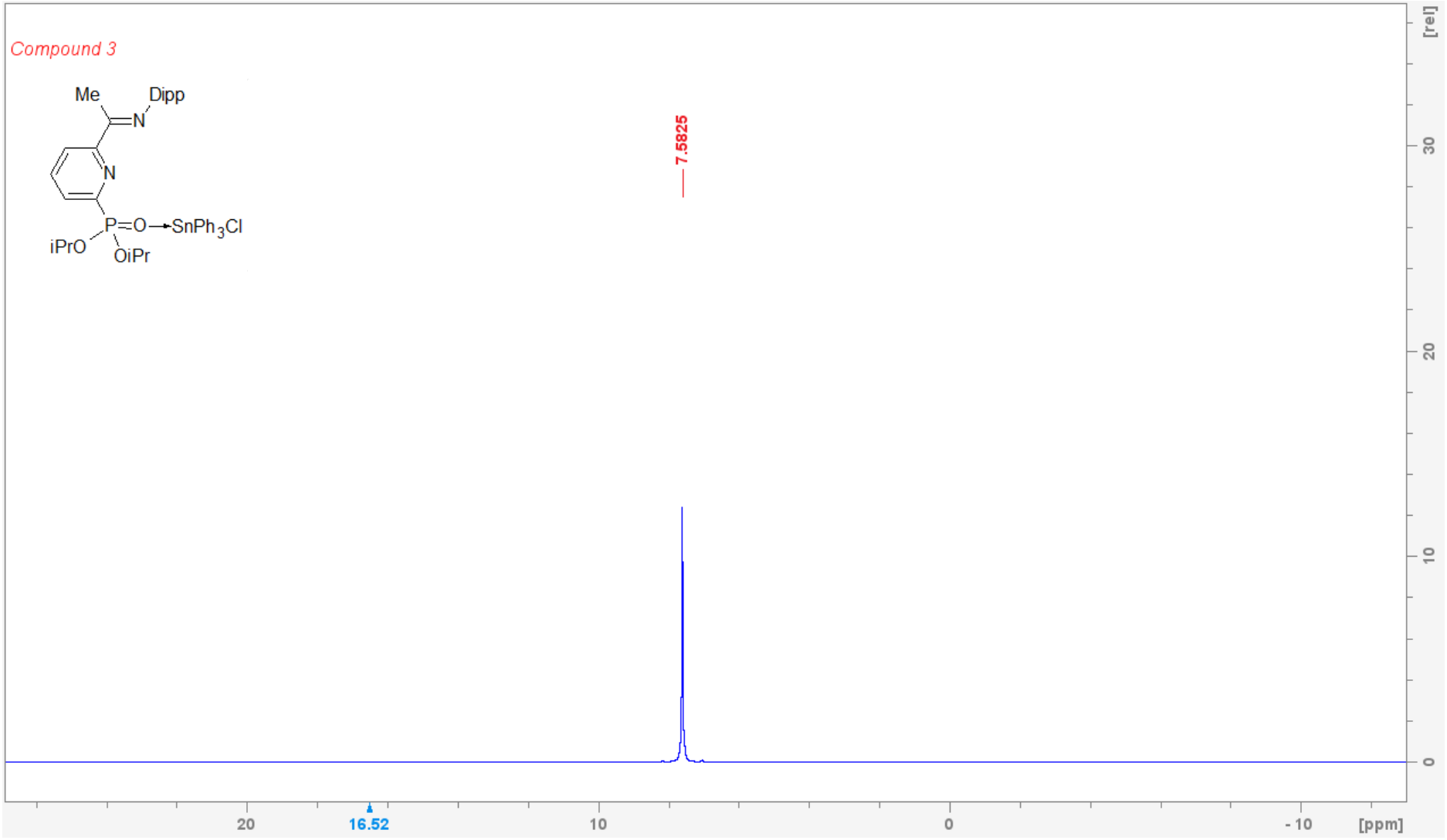

Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in C_6D_6

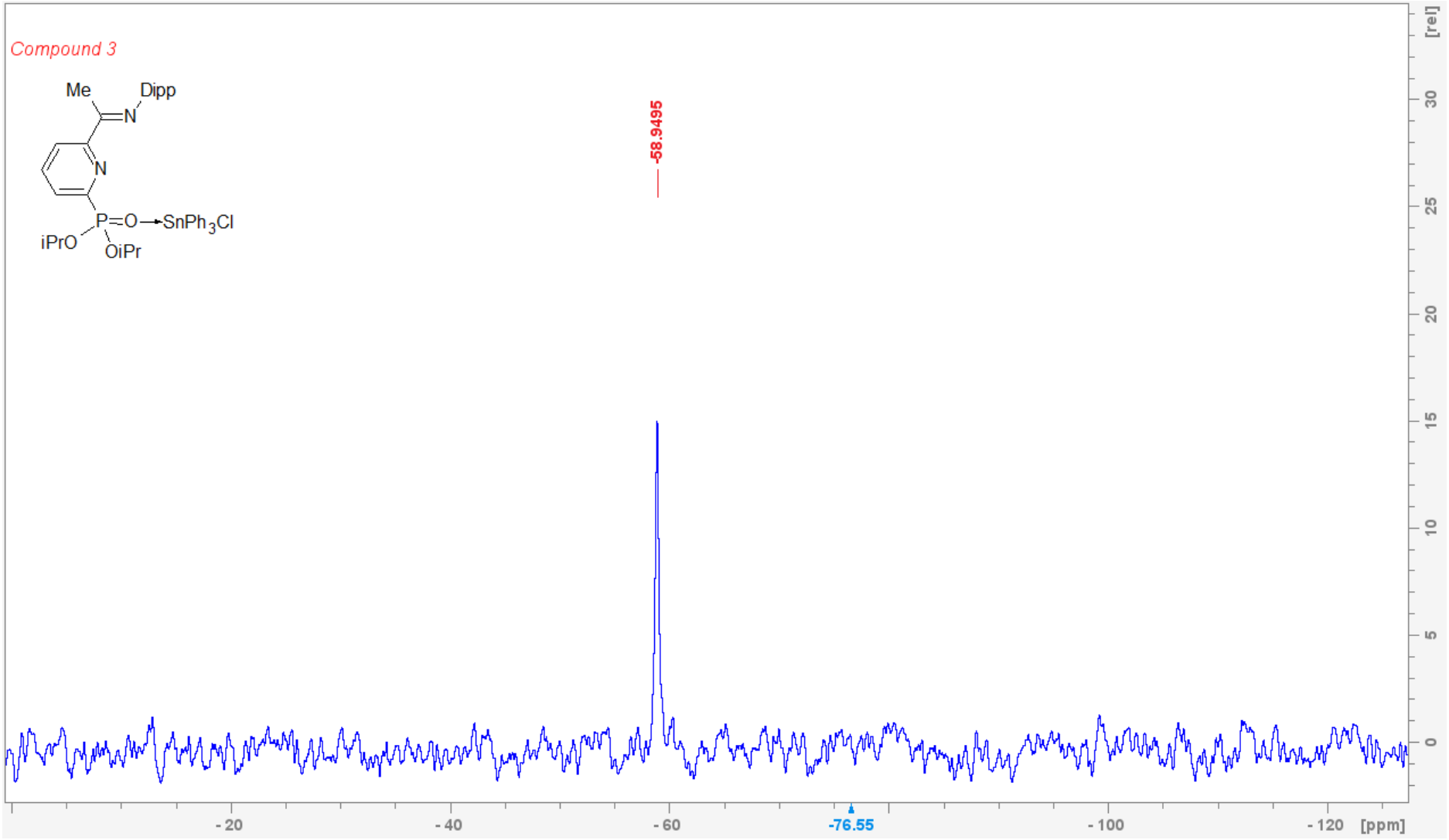

Figure S12. $^{119}Sn\{^{1}H\}$ NMR spectrum of **3** in C_6D_6

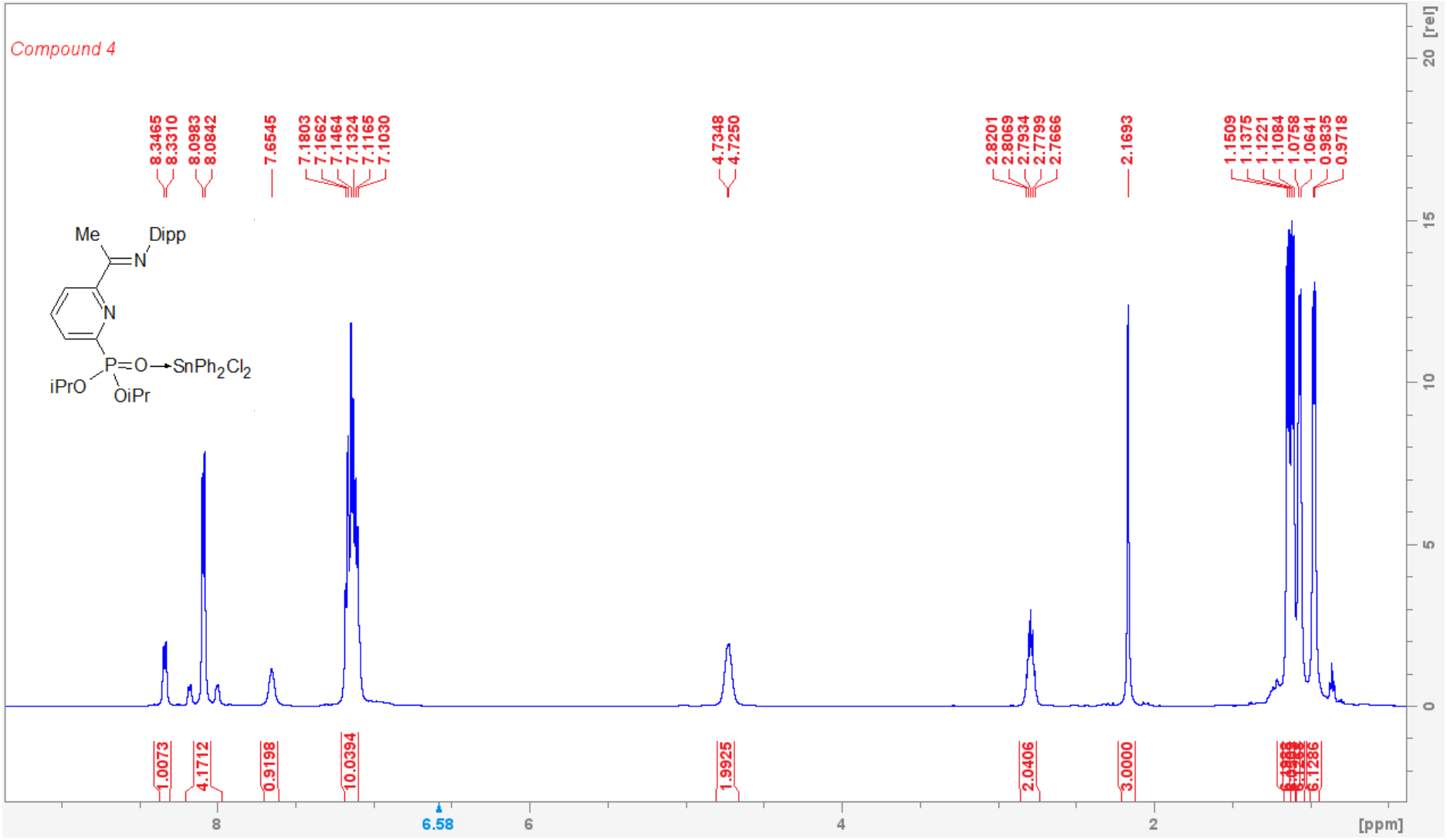

Figure S13. ^{1}H NMR spectrum of **4** in C_6D_6

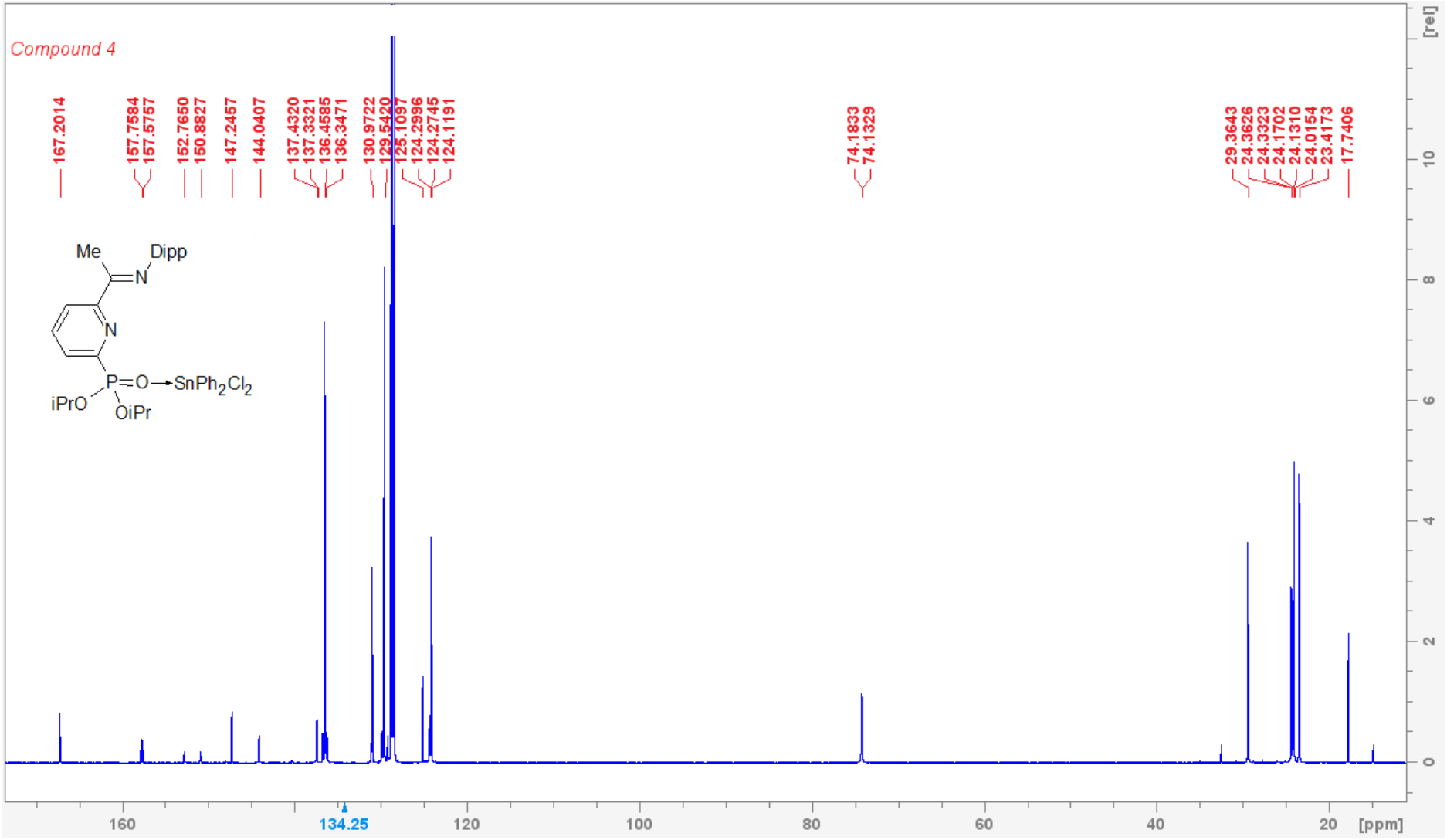

Figure S14. $^{13}C\{H\}$ NMR spectrum of **4** in C_6D_6

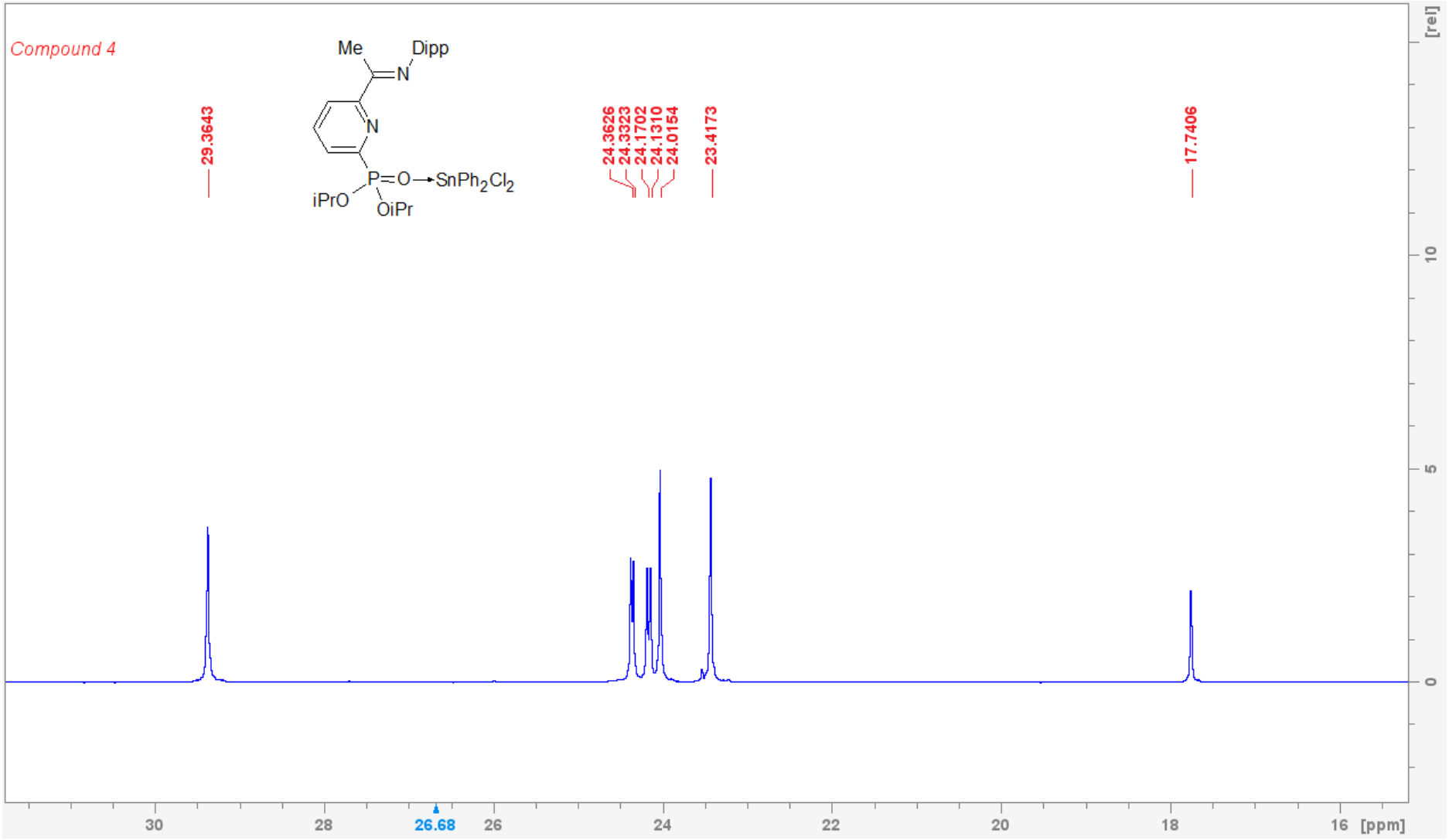

Figure S15. $^{13}C\{H\}$ NMR spectrum of **4** in C_6D_6 – aliphatic region

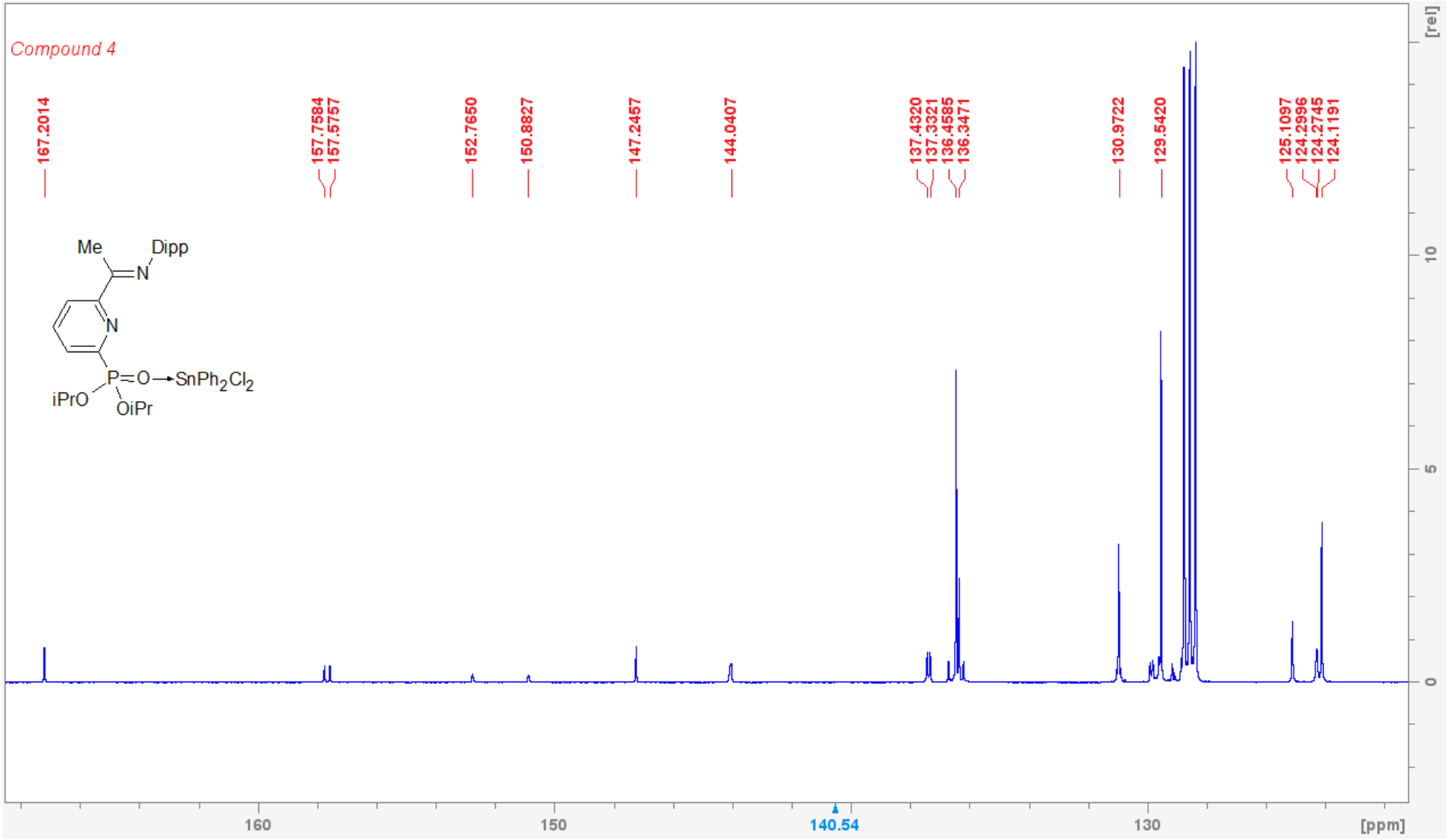

Figure S16. $^{13}C\{H\}$ NMR spectrum of **4** in C_6D_6 – aromatic region

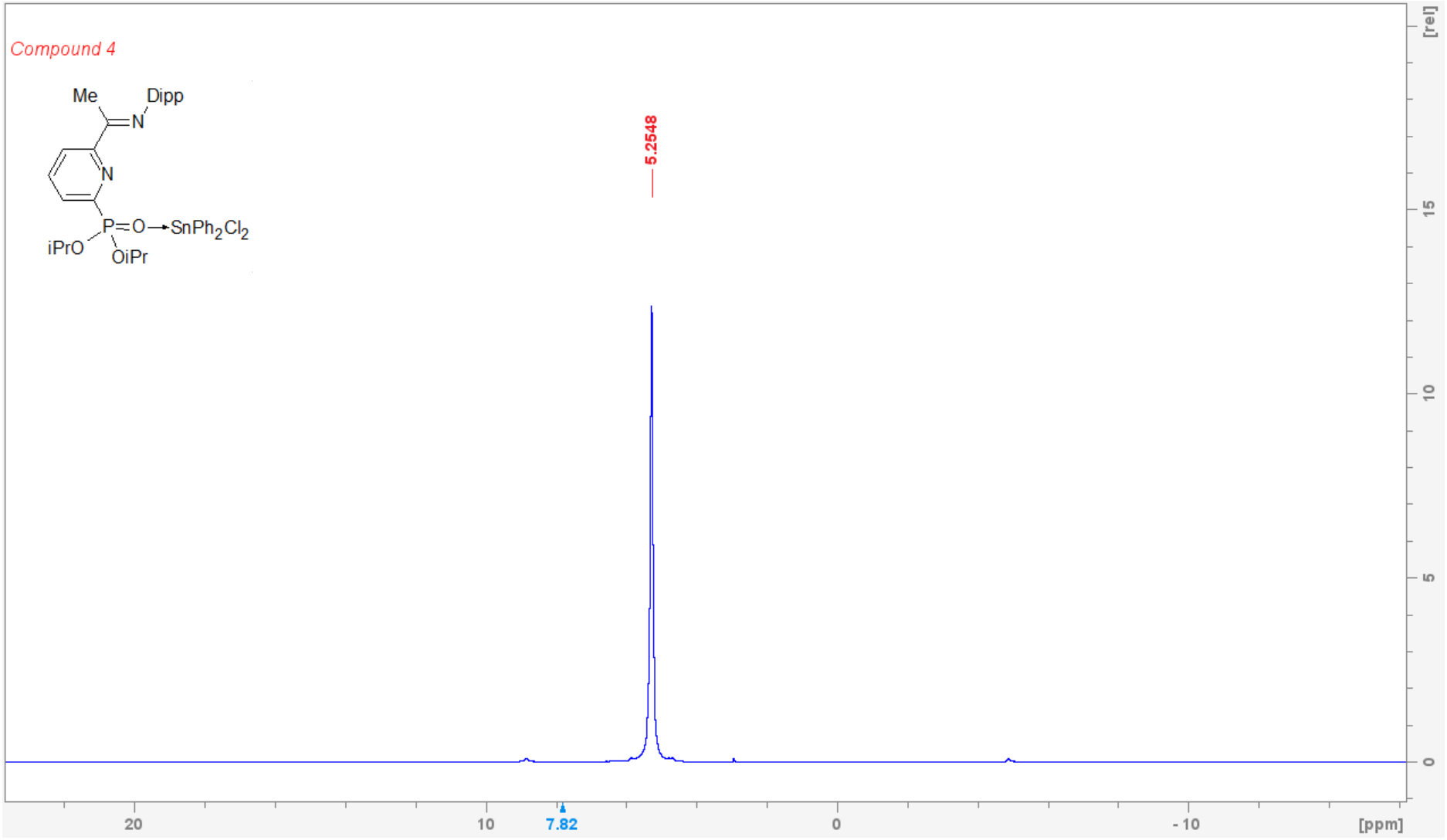

Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of **4** in C_6D_6

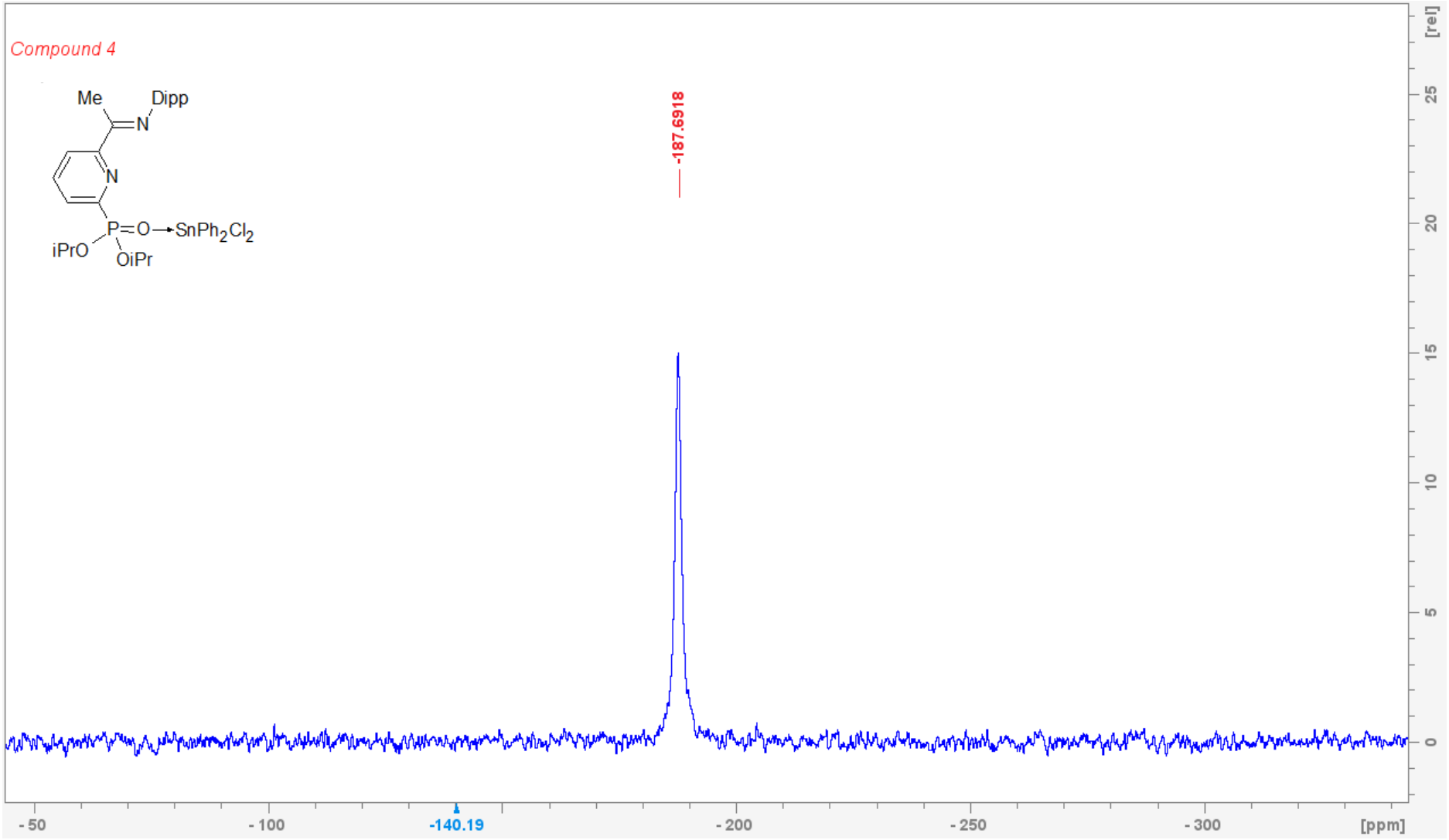

Figure S18. $^{119}Sn\{^{1}H\}$ NMR spectrum of **4** in C_6D_6

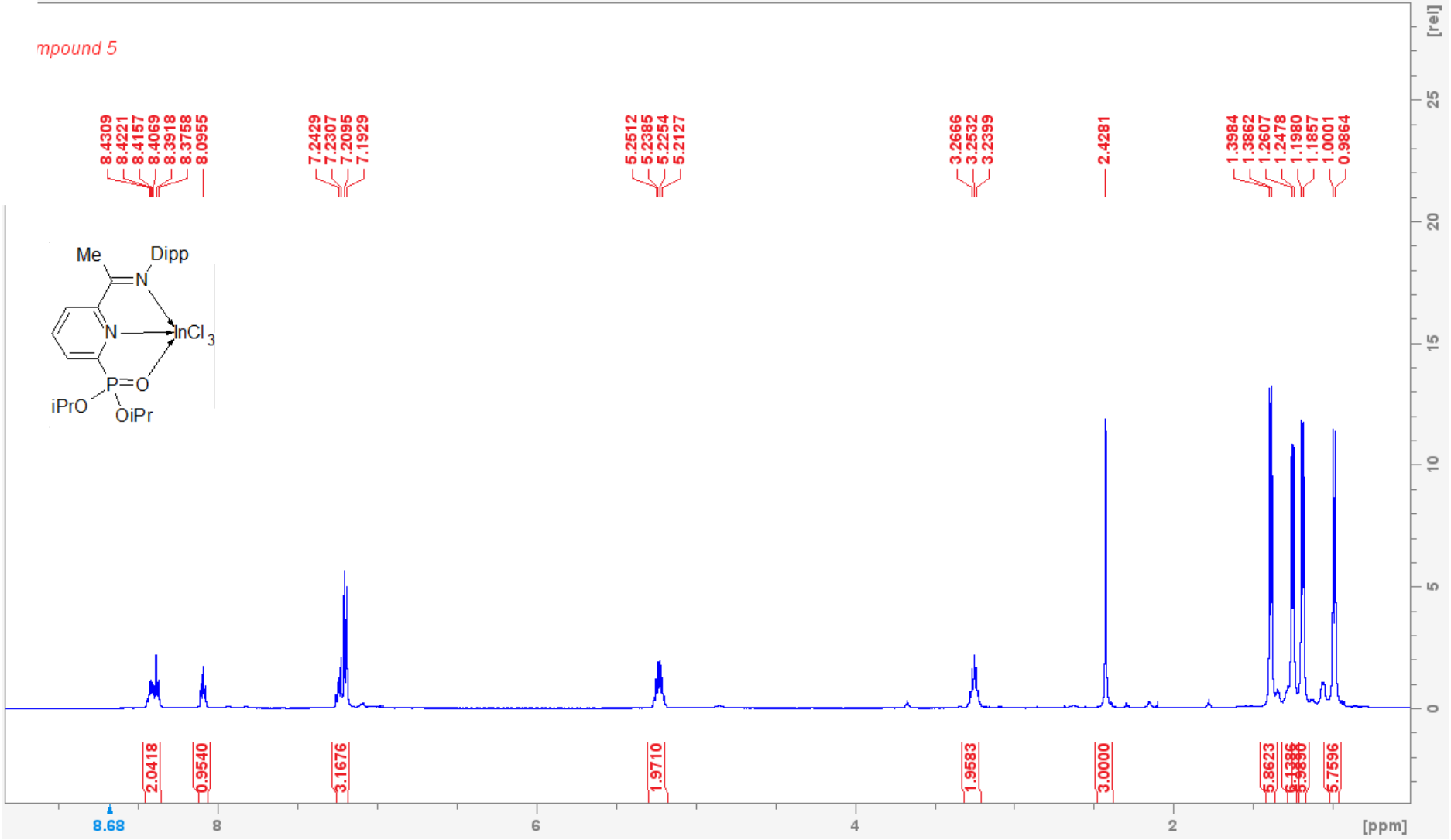

Figure S19. ^{1}H NMR spectrum of **5** in $CDCl_3$

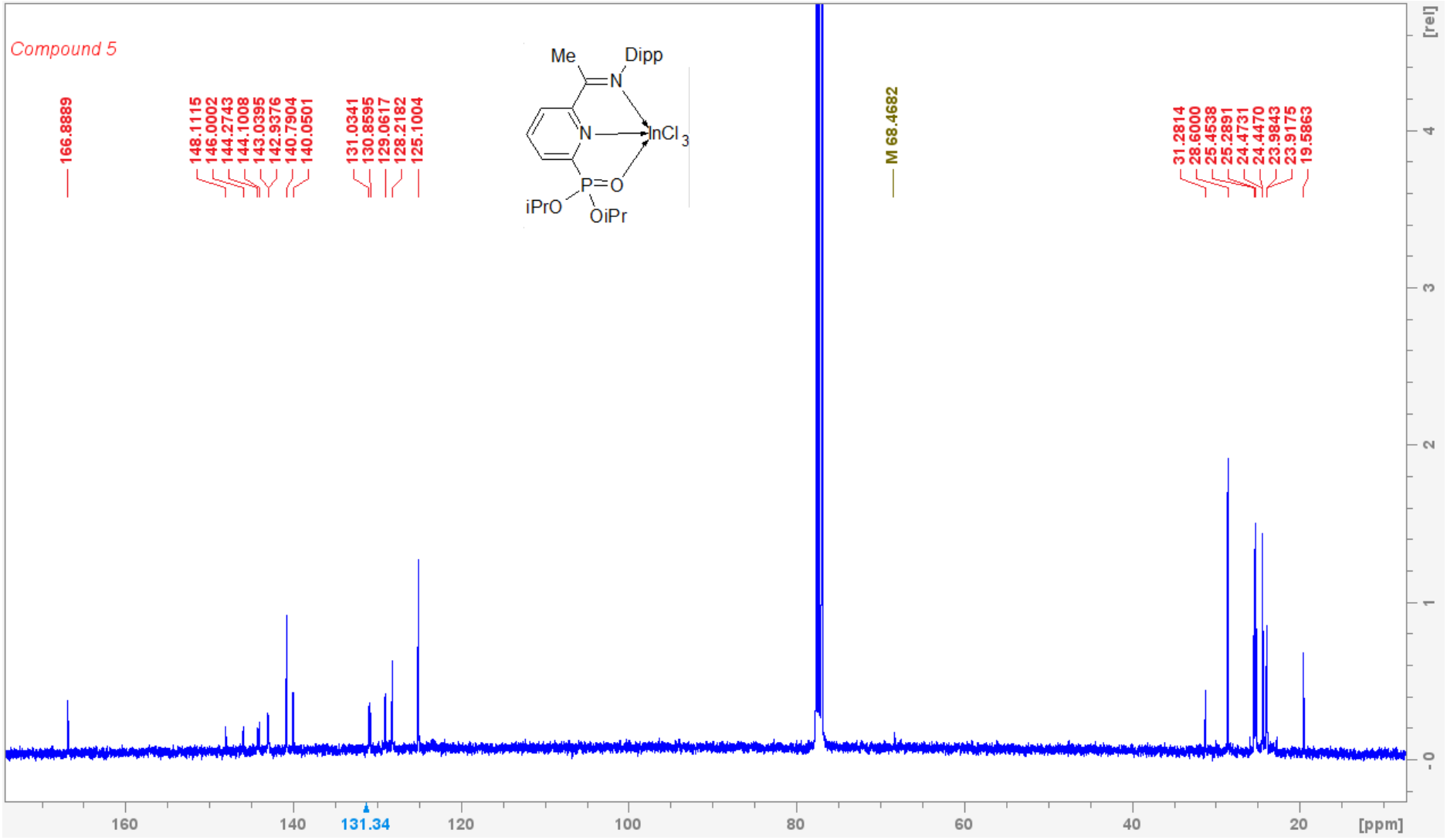

Figure S20. $^{13}C\{H\}$ NMR spectrum of **5** in $CDCl_3$

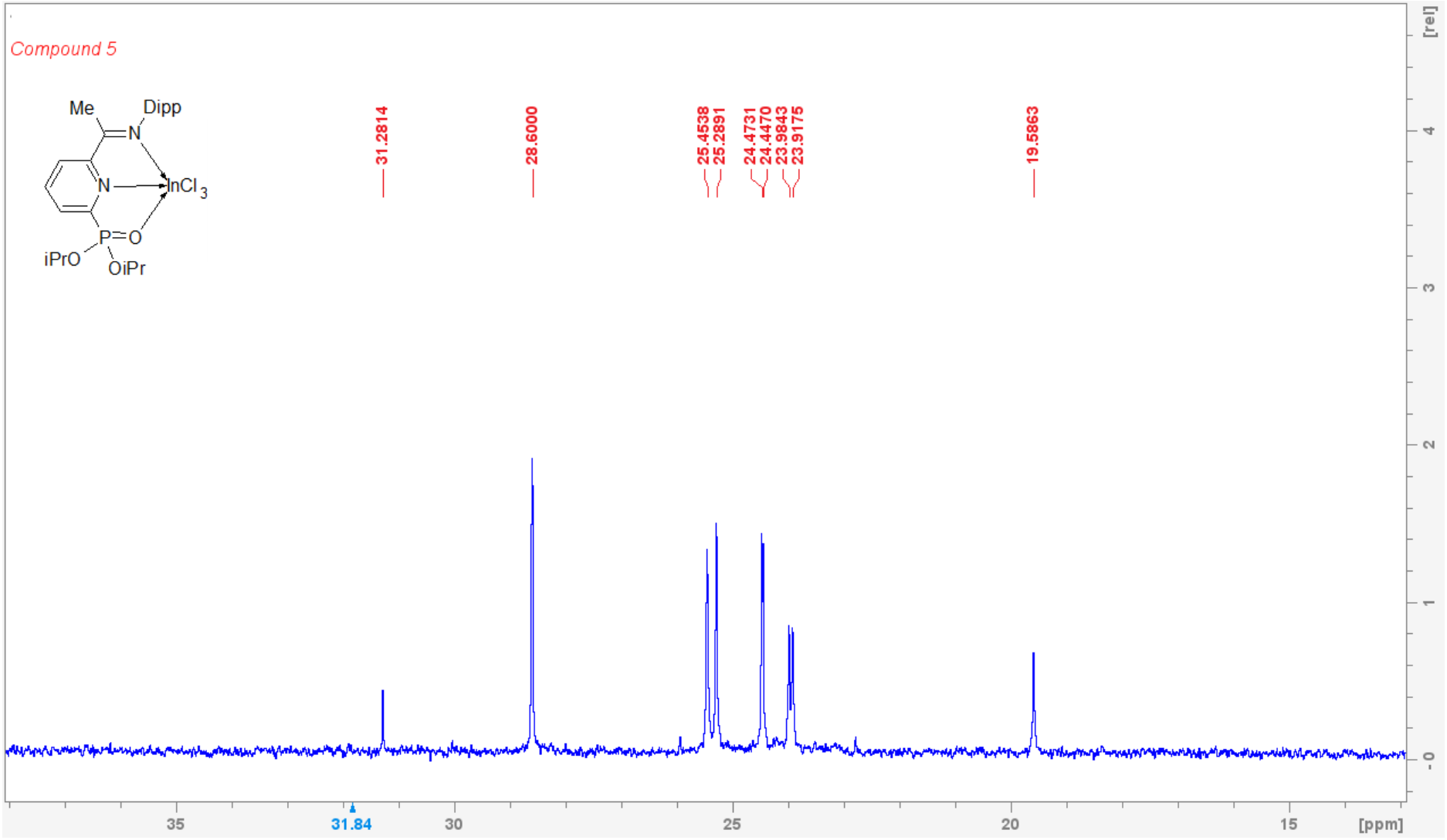

Figure S21. $^{13}C\{H\}$ NMR spectrum of **5** in $CDCl_3$ – aliphatic region

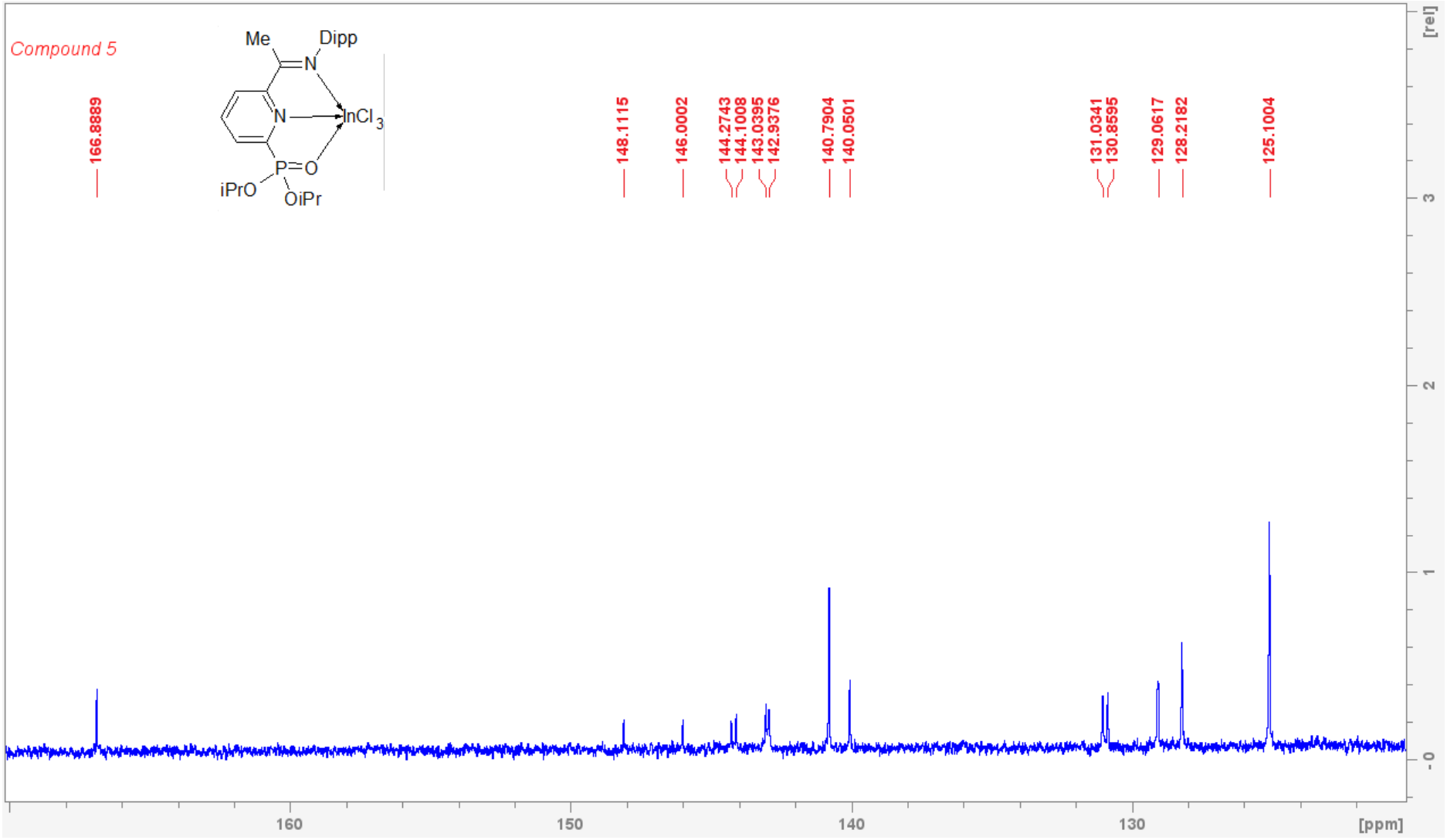

Figure S22. $^{13}C\{H\}$ NMR spectrum of **5** in $CDCl_3$ – aromatic region

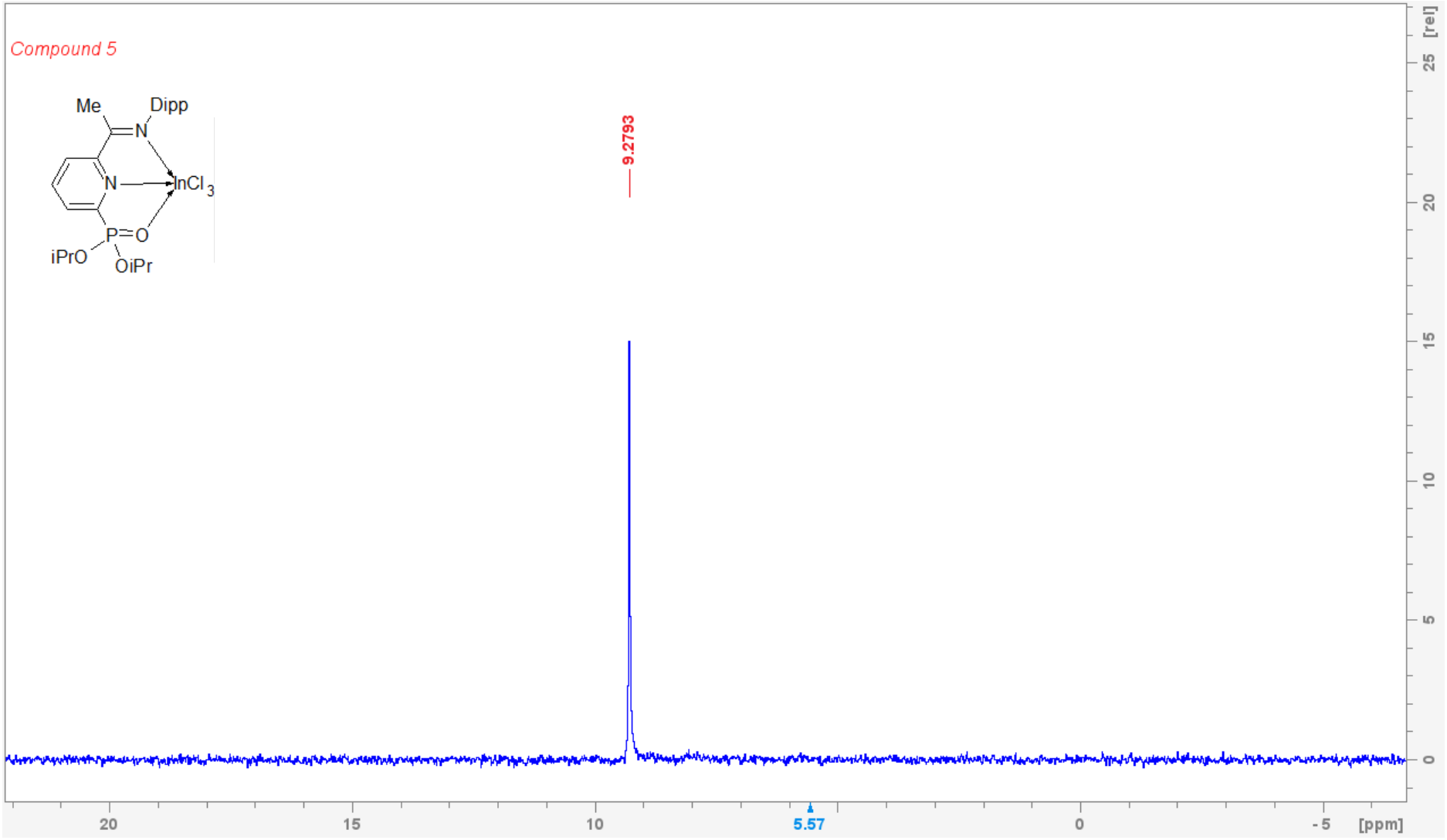

Figure S23. $^{31}P\{H\}$ NMR spectrum of **5** in $CDCl_3$

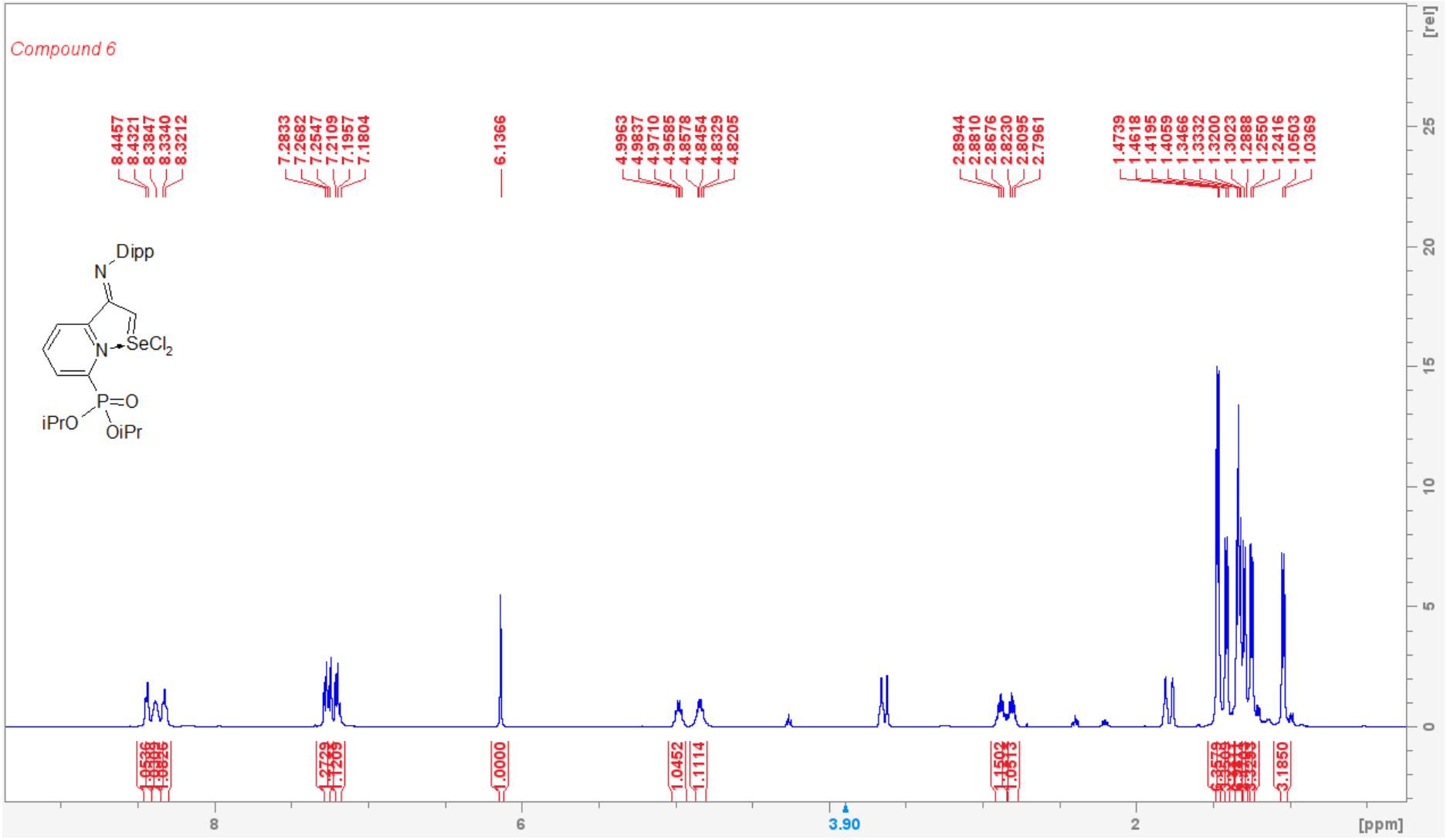

Figure S24. ^{1}H NMR spectrum of **6** in THF-d8

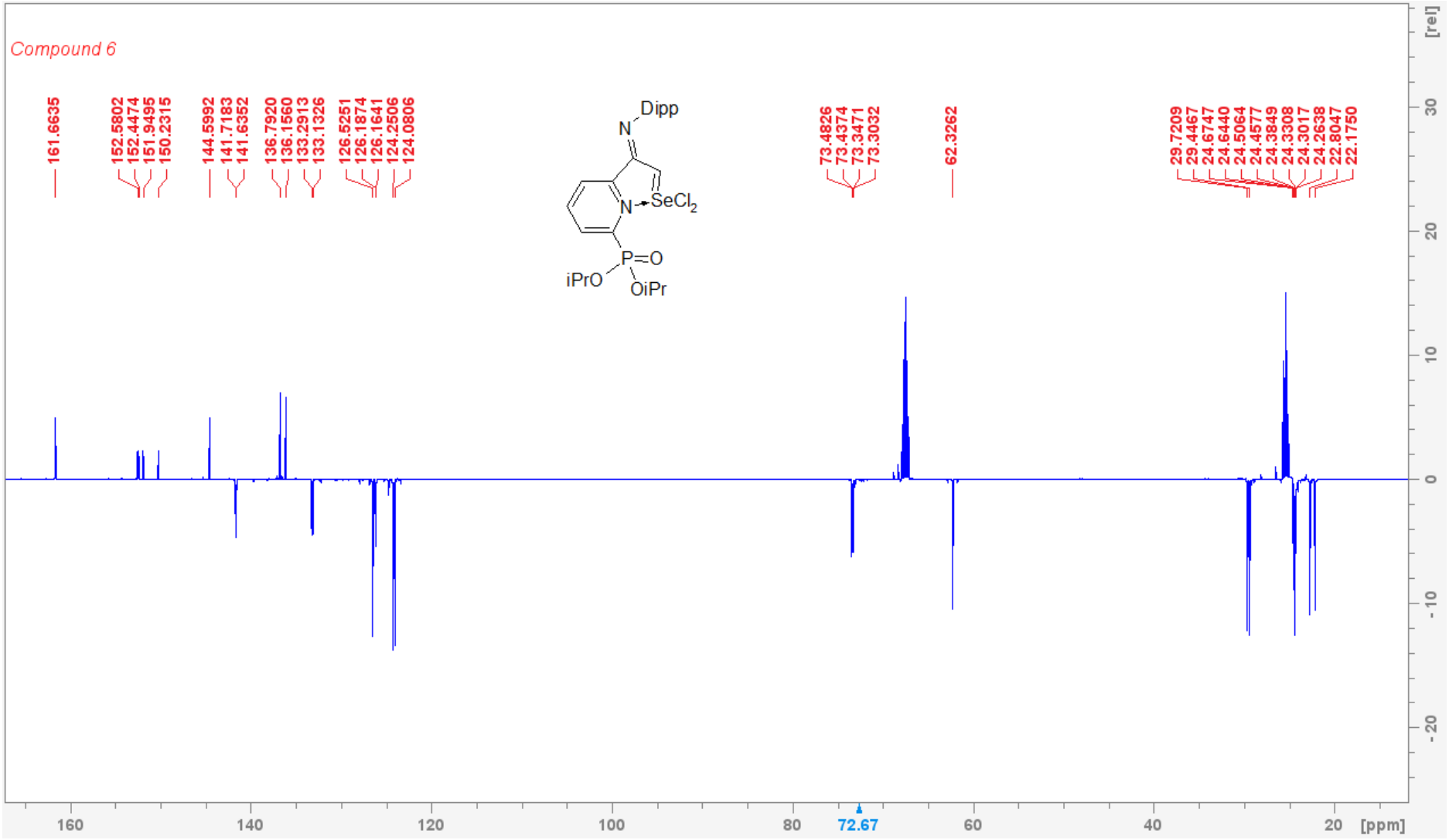

Figure S25. $^{13}C\{H\}$ APT NMR spectrum of **6** in THF-d8

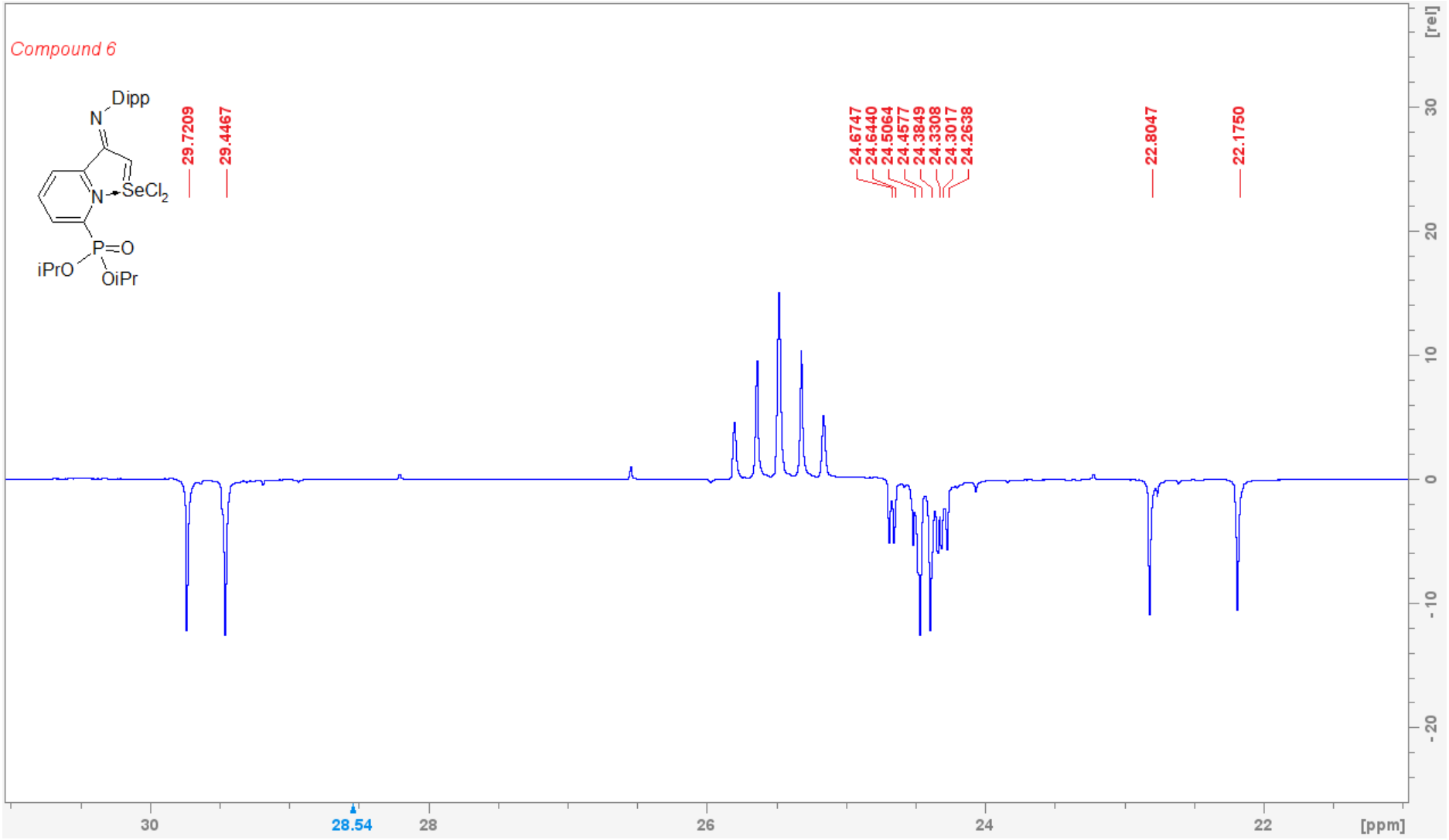

Figure S26. $^{13}C\{H\}$ APT NMR spectrum of **6** in THF-d8 – aliphatic region

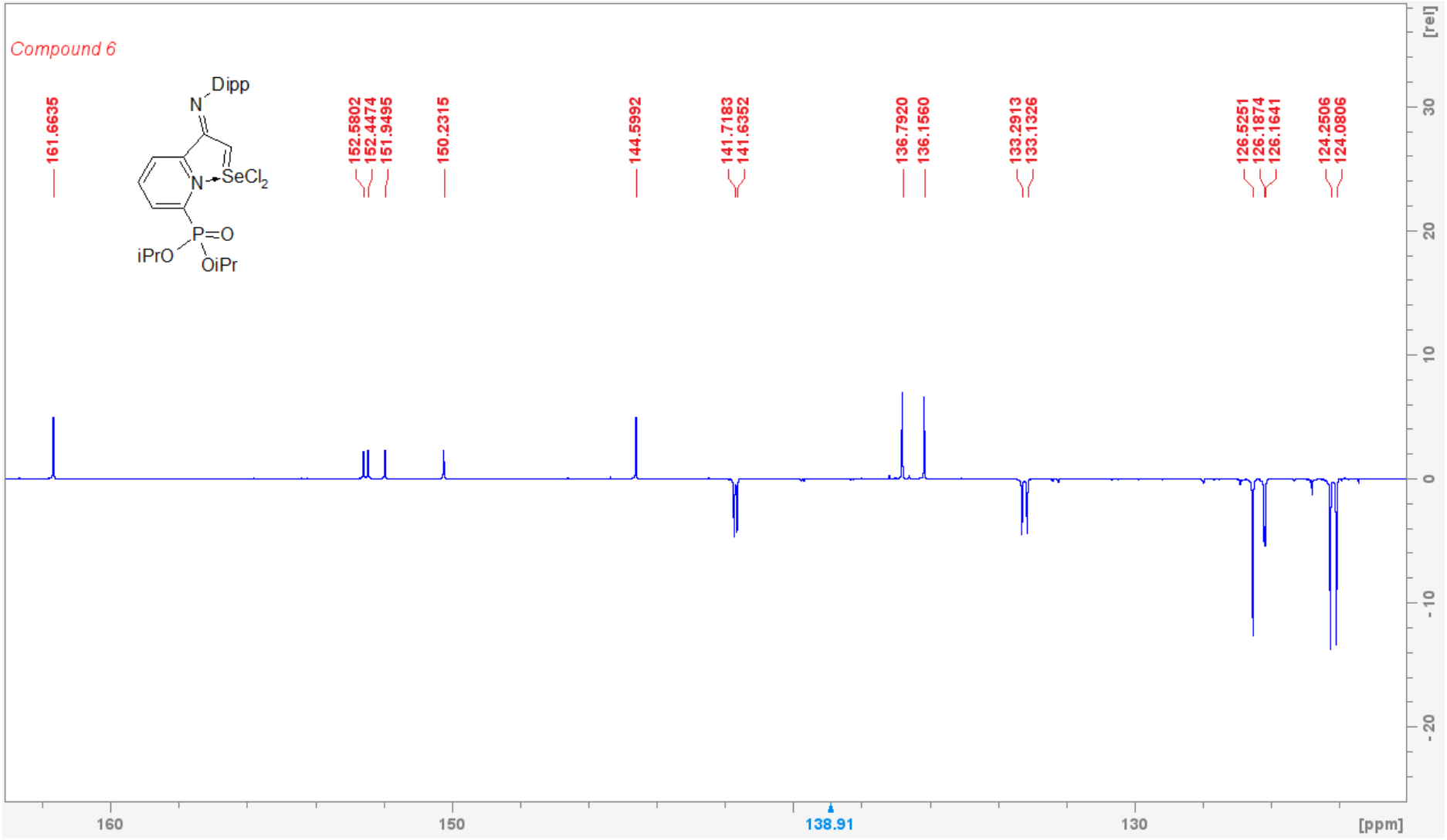

Figure S27. $^{13}C\{H\}$ APT NMR spectrum of **6** in THF-d8 – aromatic region

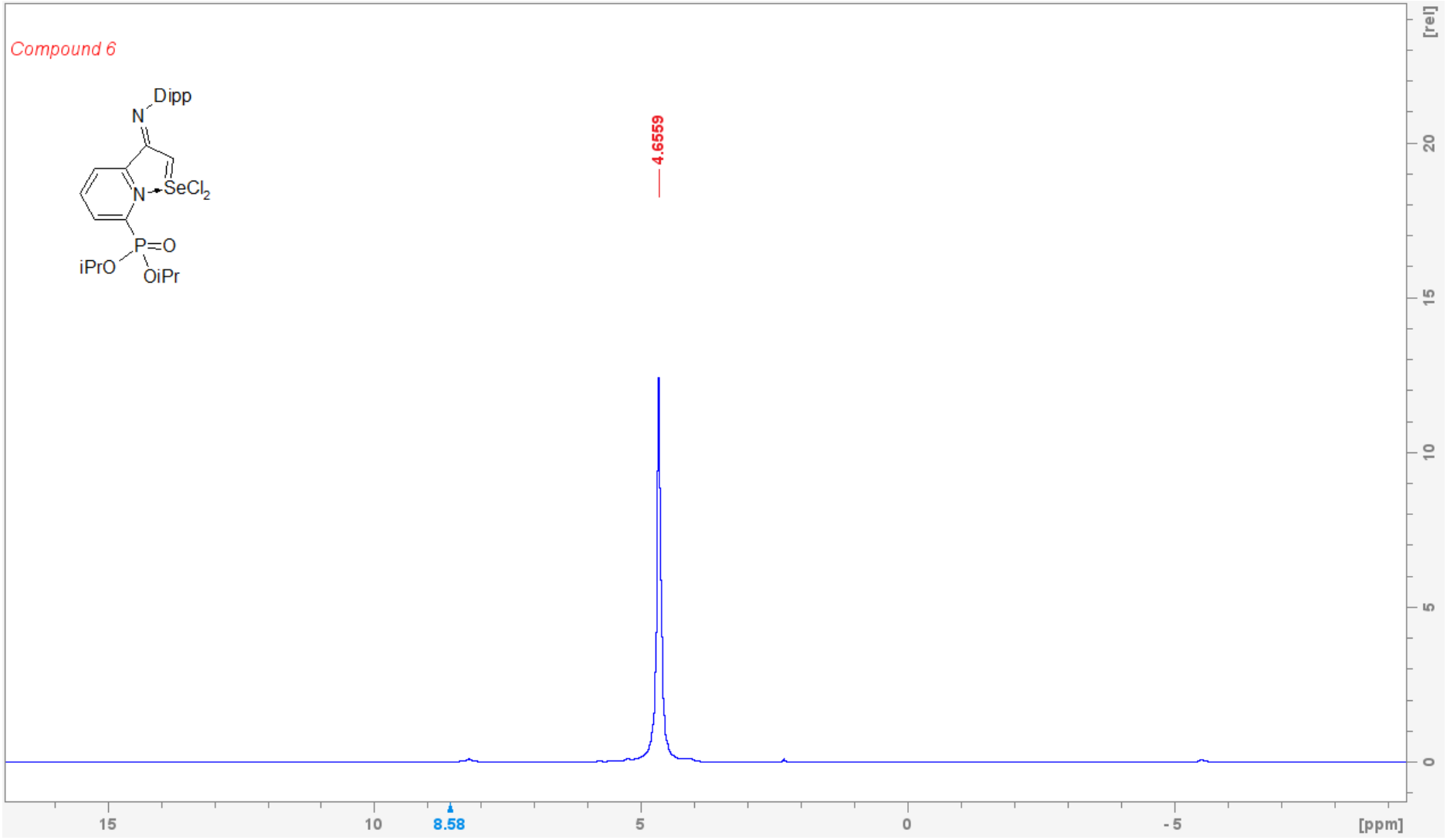

Figure S28. $^{31}P\{H\}$ NMR spectrum of **6** in THF-d8

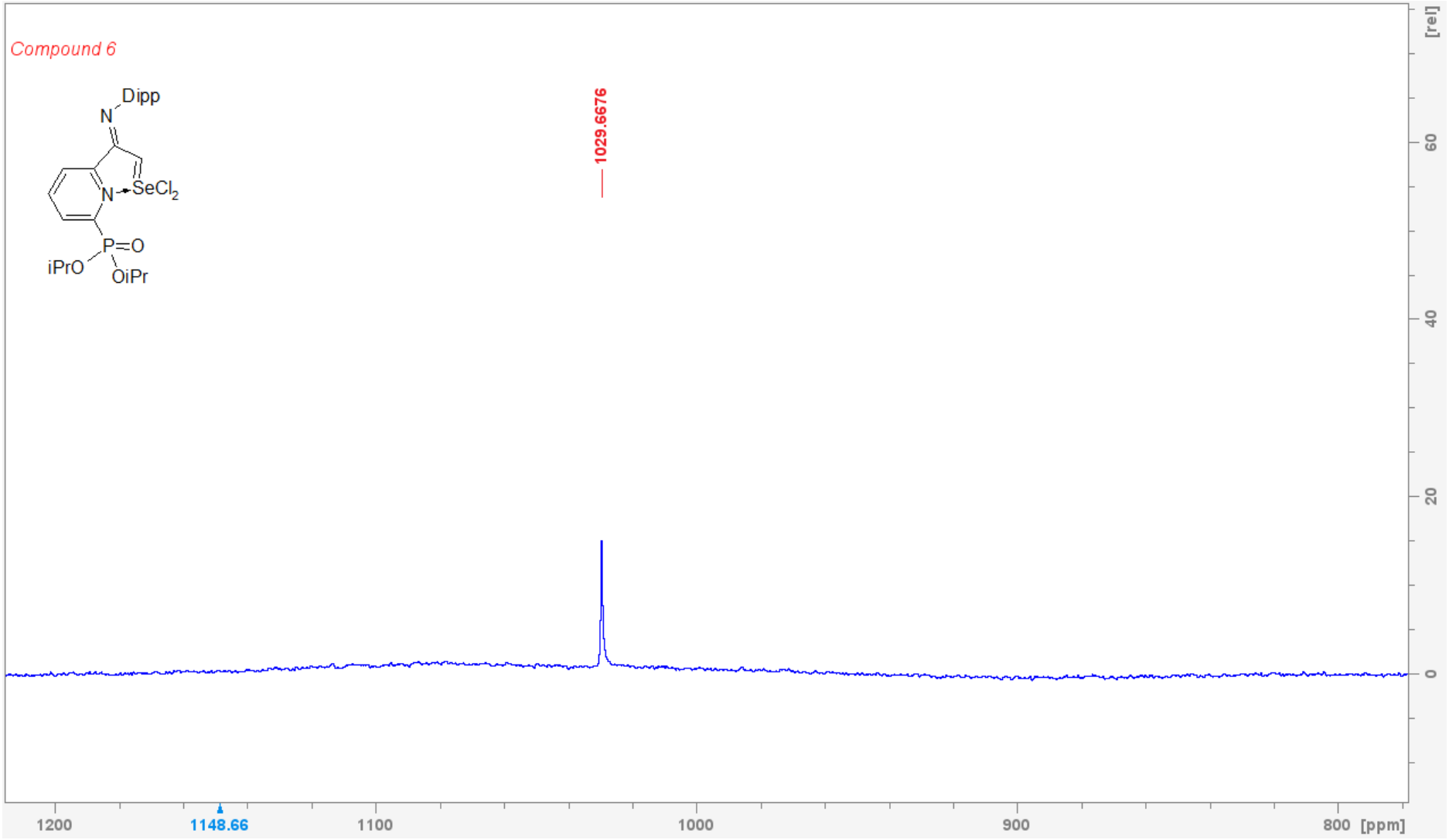

Figure S29. ^{77}Se{H} NMR spectrum of **6** in THF-d8

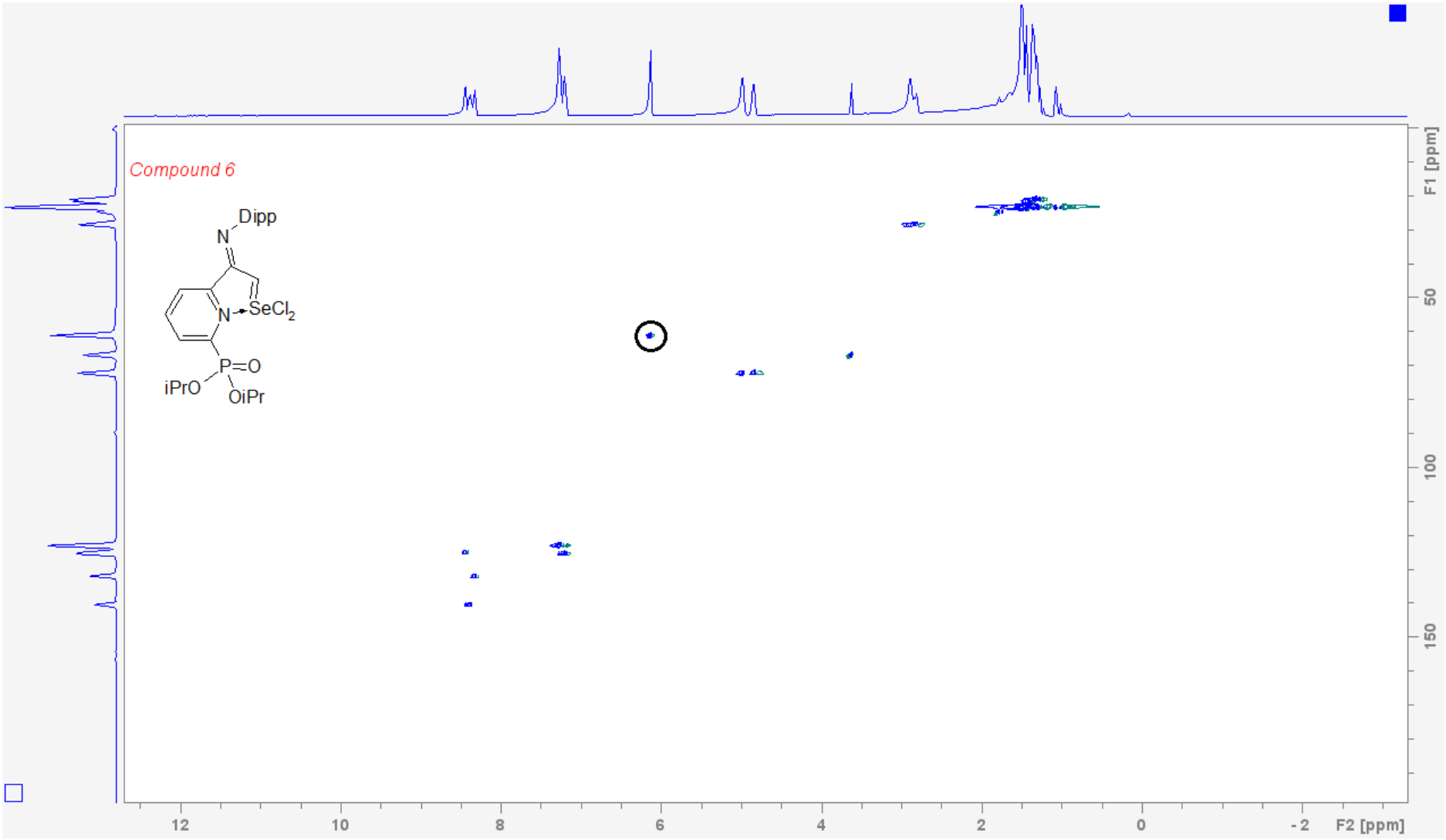

Figure S30. ^{1}H-^{13}C HSQC NMR spectrum of **6** in THF-d8

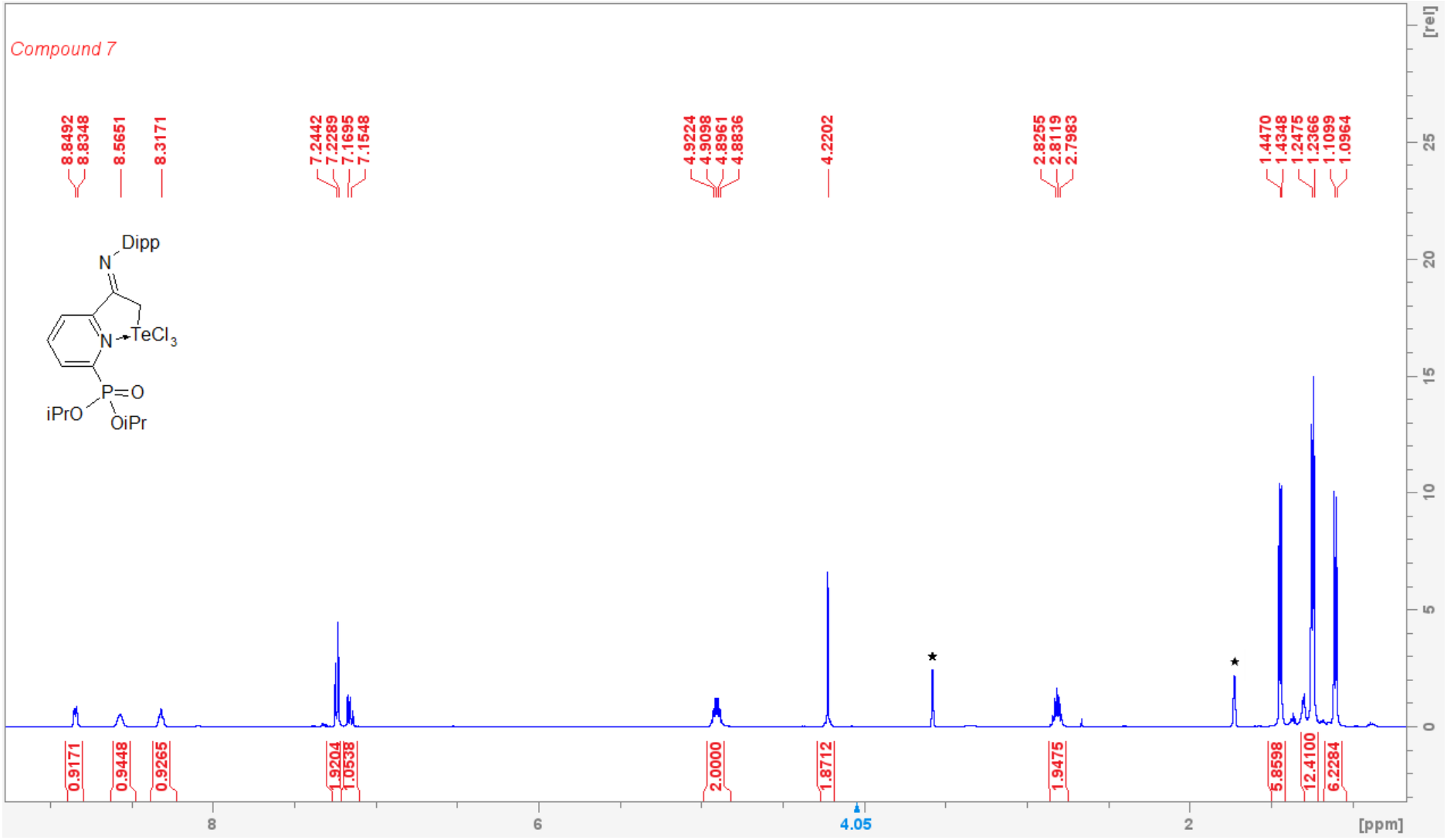

Figure S31. ^{1}H NMR spectrum of **7** in THF-d8 (***** residual signal of THF)

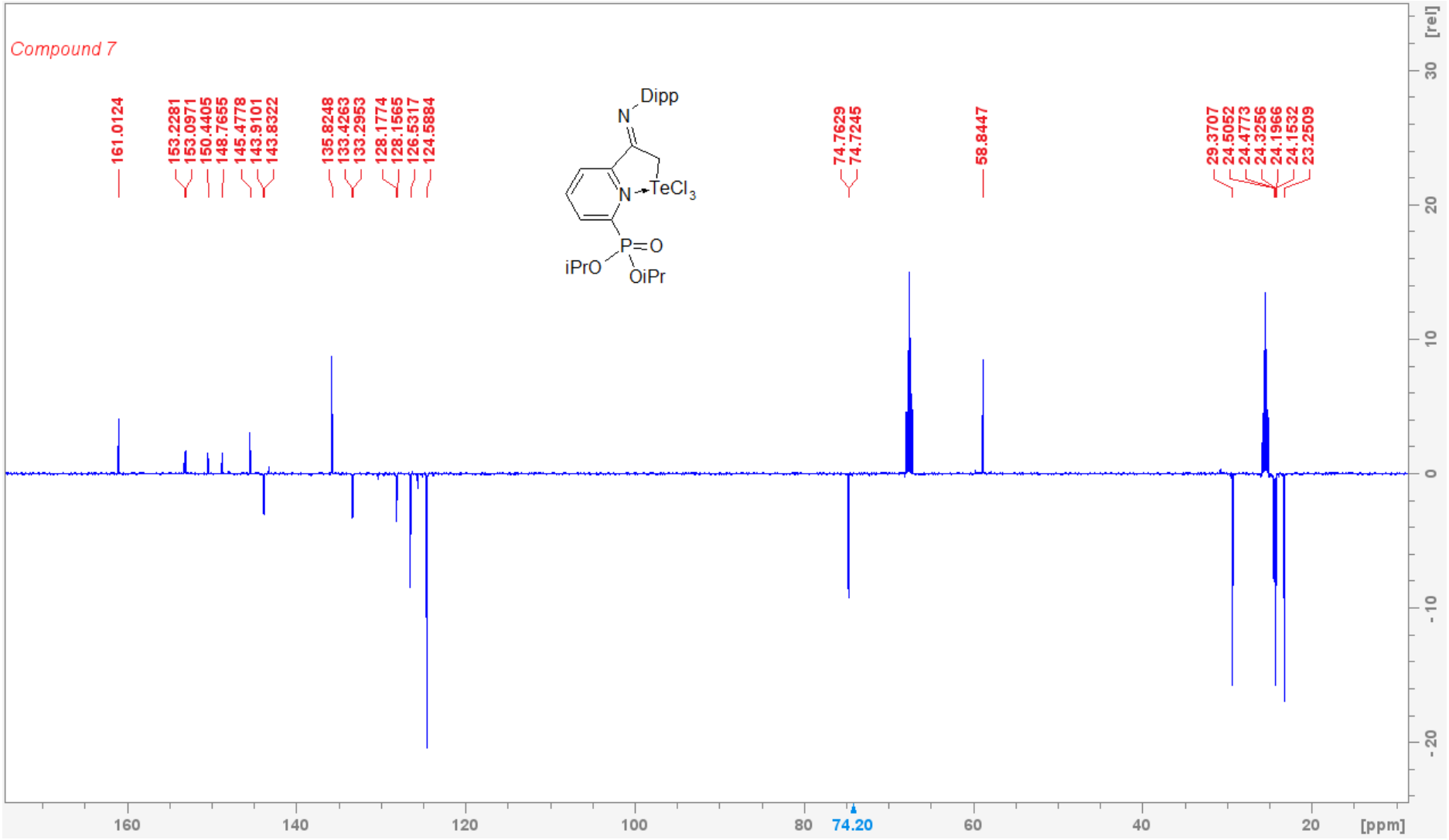

Figure S32. $^{13}C\{H\}$ APT NMR spectrum of **7** in THF-d8

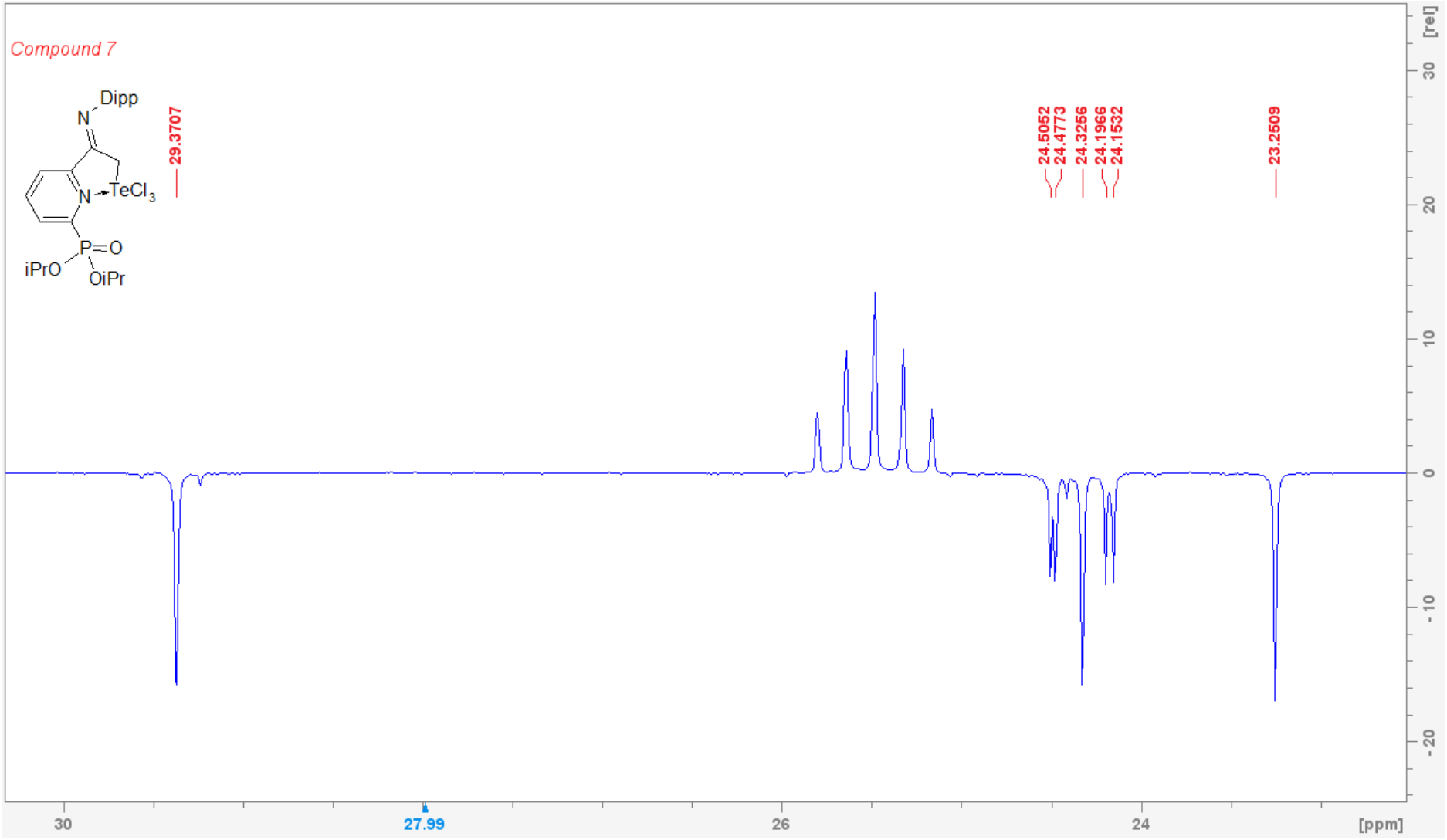

Figure S33. $^{13}C\{H\}$ APT NMR spectrum of **7** in THF-d8 – aliphatic region

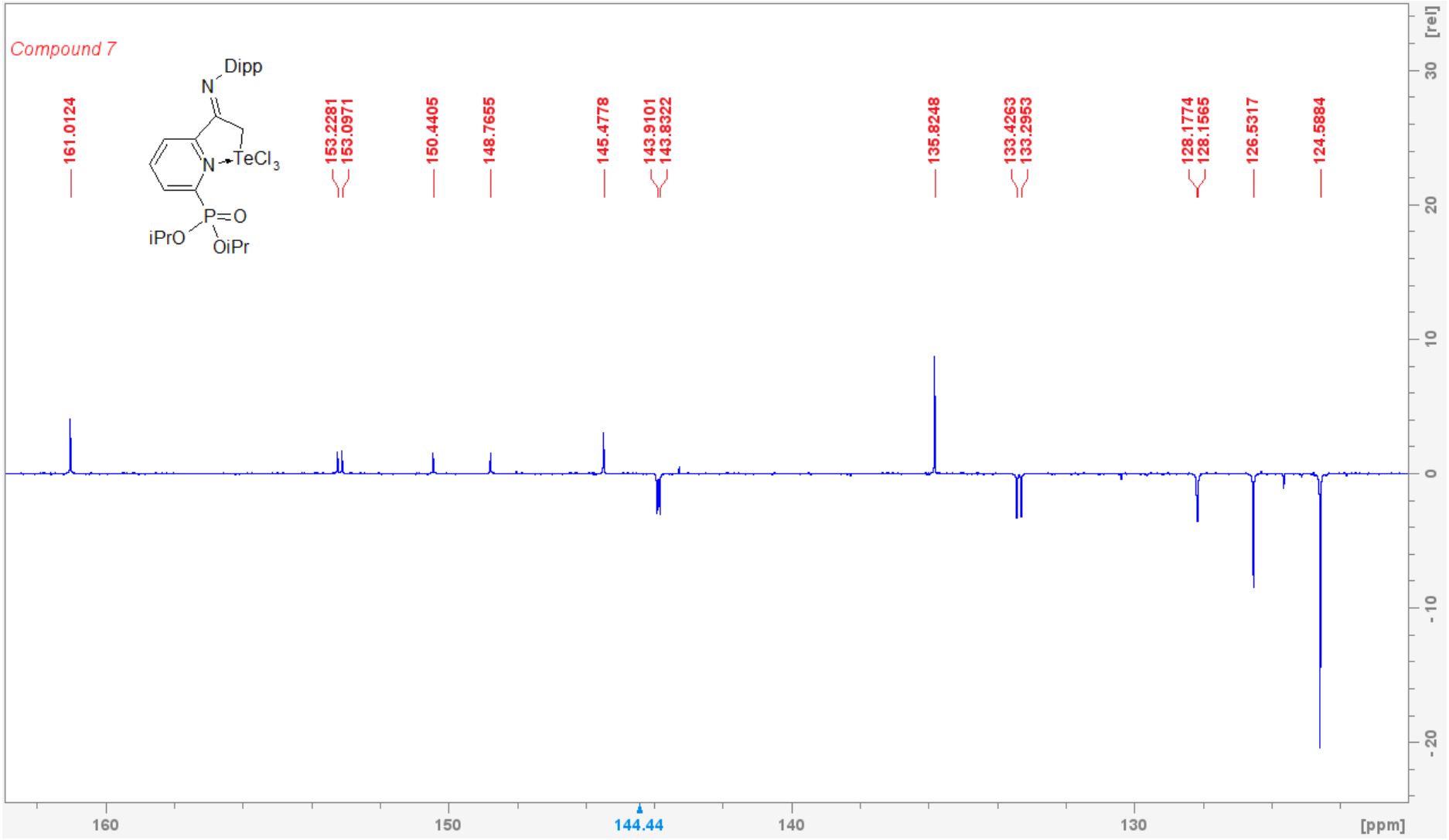

Figure S34. $^{13}C\{H\}$ APT NMR spectrum of **7** in THF-d8 – aromatic region

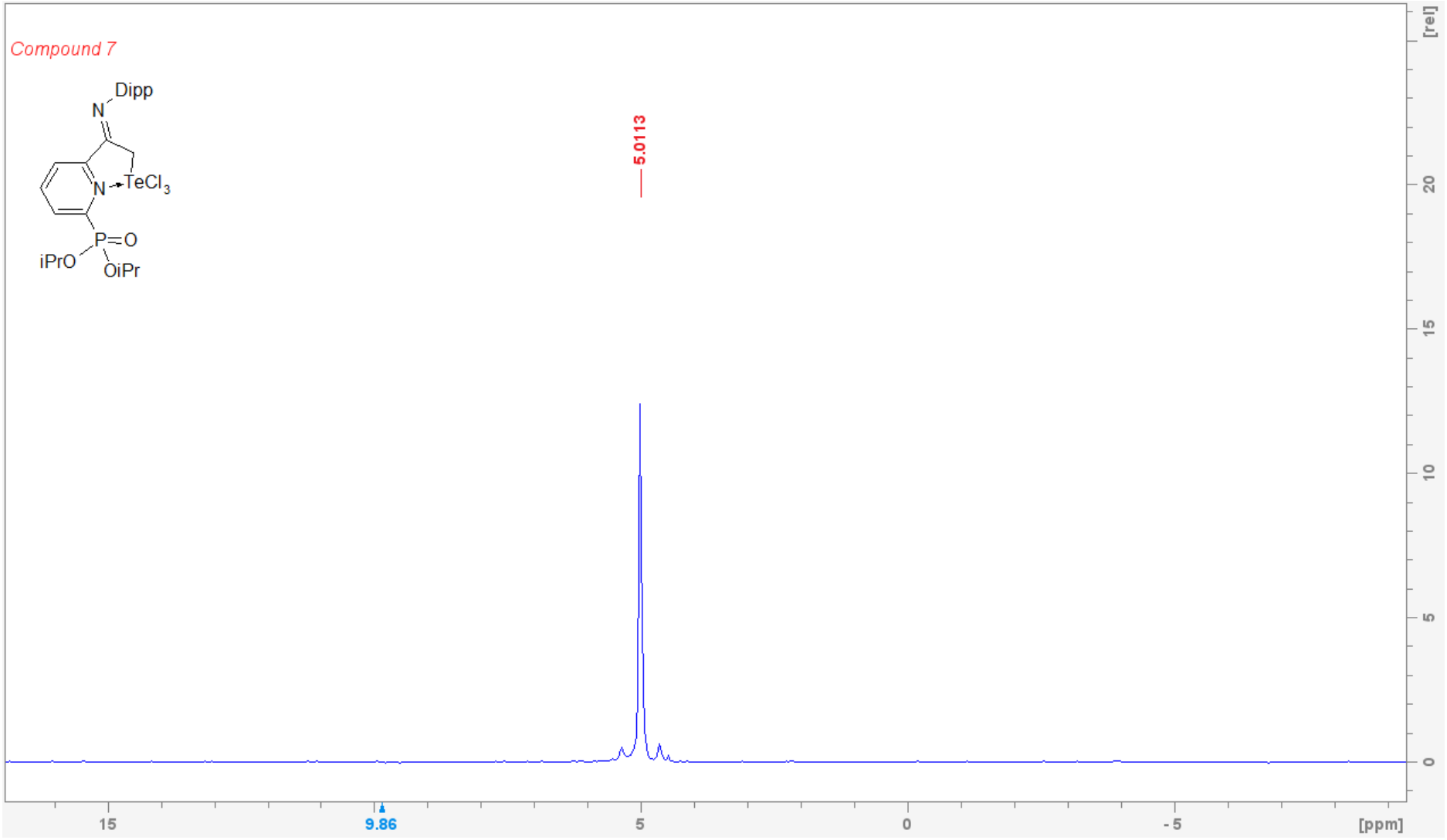

Figure S35. $^{31}P\{H\}$ NMR spectrum of **7** in THF-d8

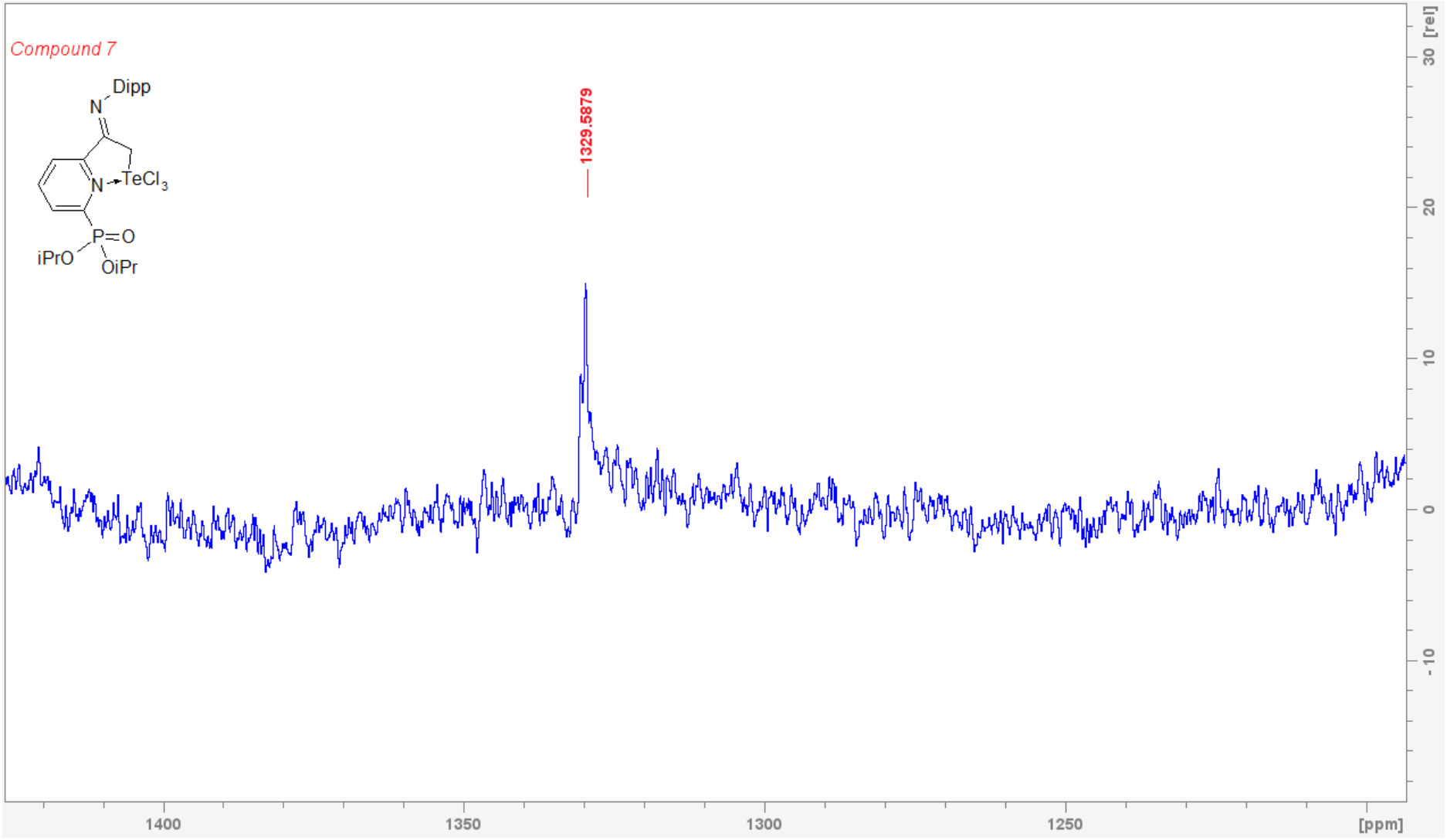

Figure S36. ^{125}Te{H} NMR spectrum of **7** in THF-d8

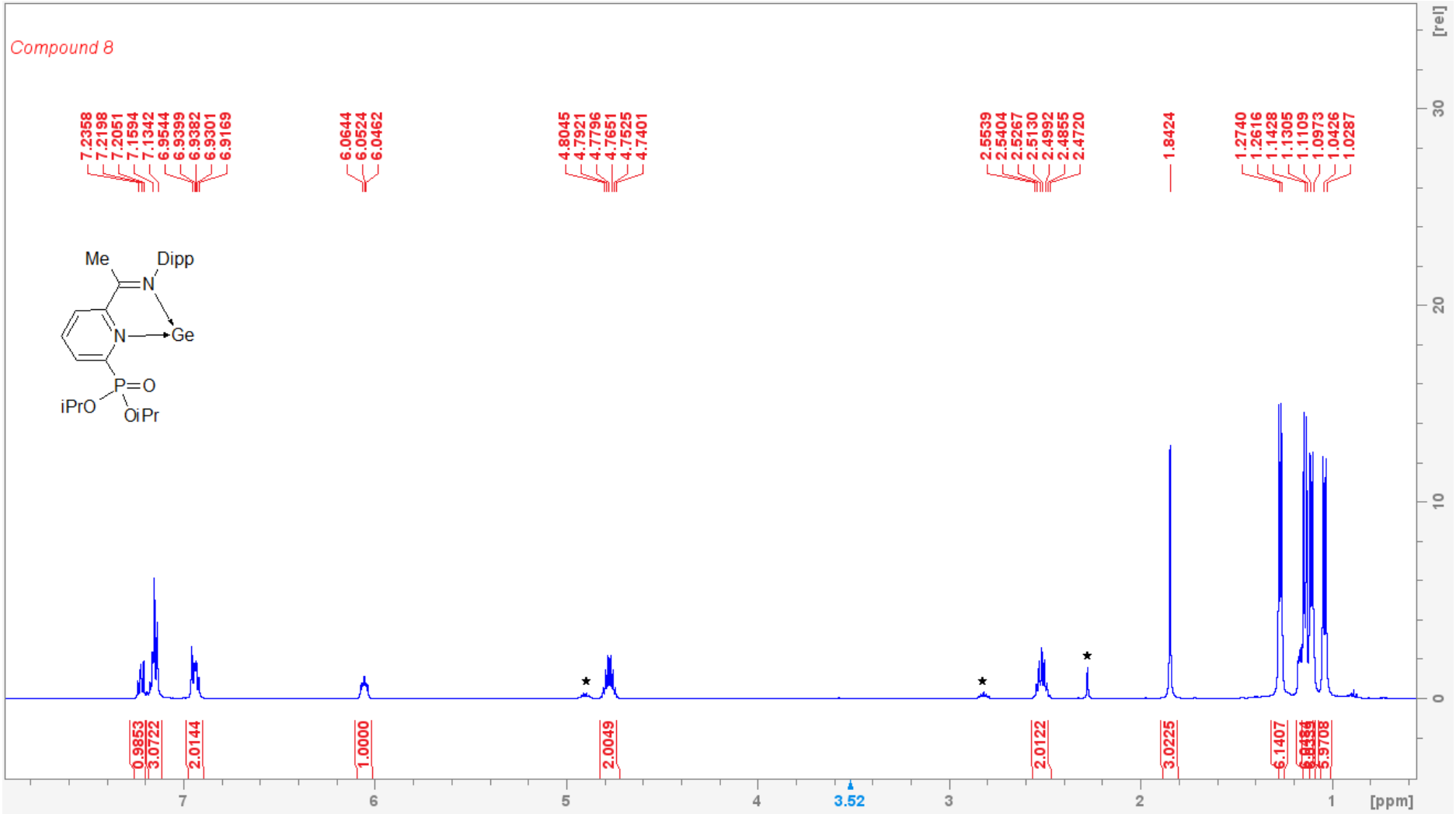

Figure S37. ^{1}H NMR spectrum of **8** in C_6D_6 (***** signal of **L**)

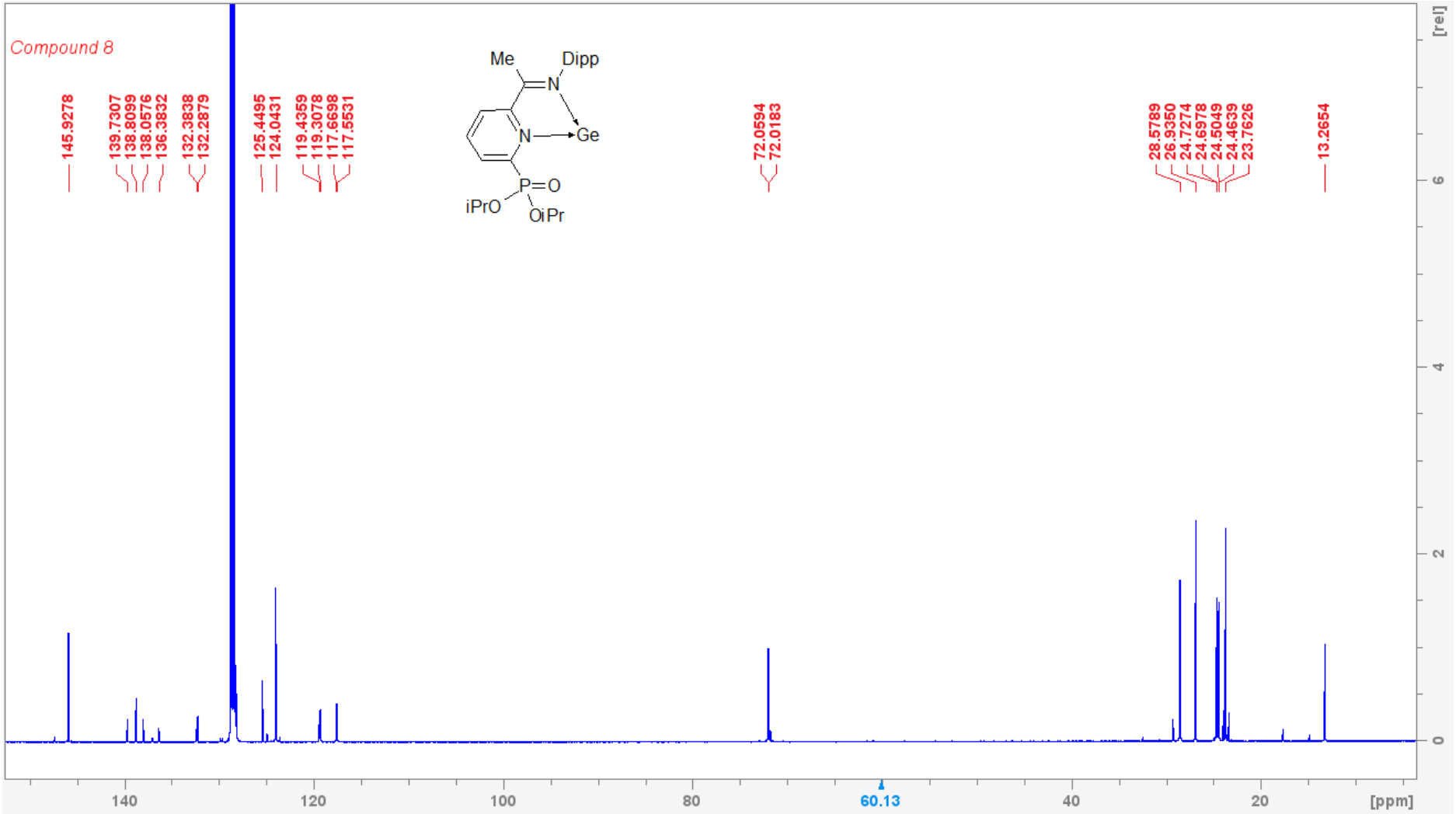

Figure S38. $^{13}C\{H\}$ NMR spectrum of **8** in C_6D_6

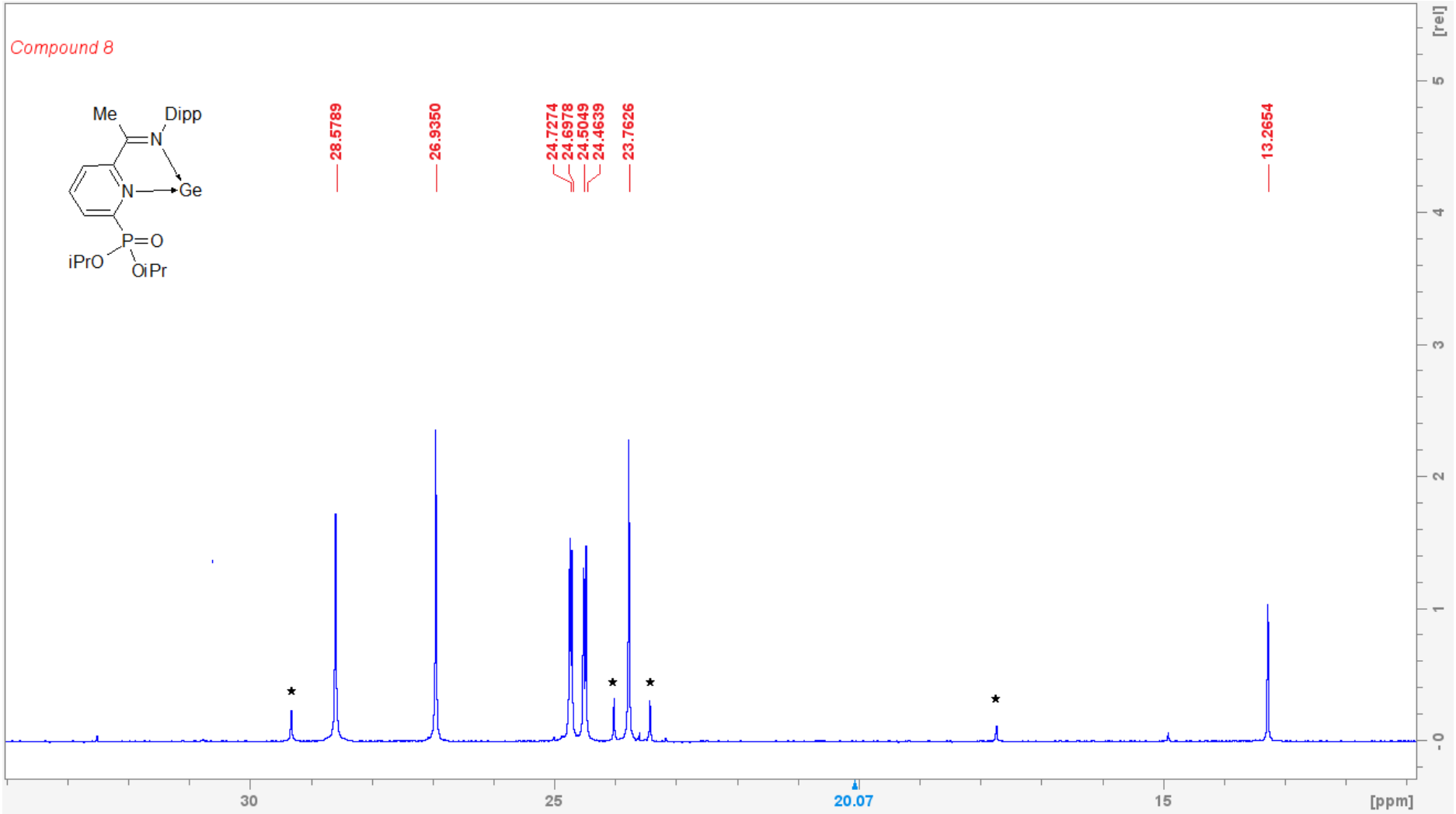

Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of **8** in C_6D_6 – aliphatic region (***** signal of **L**)

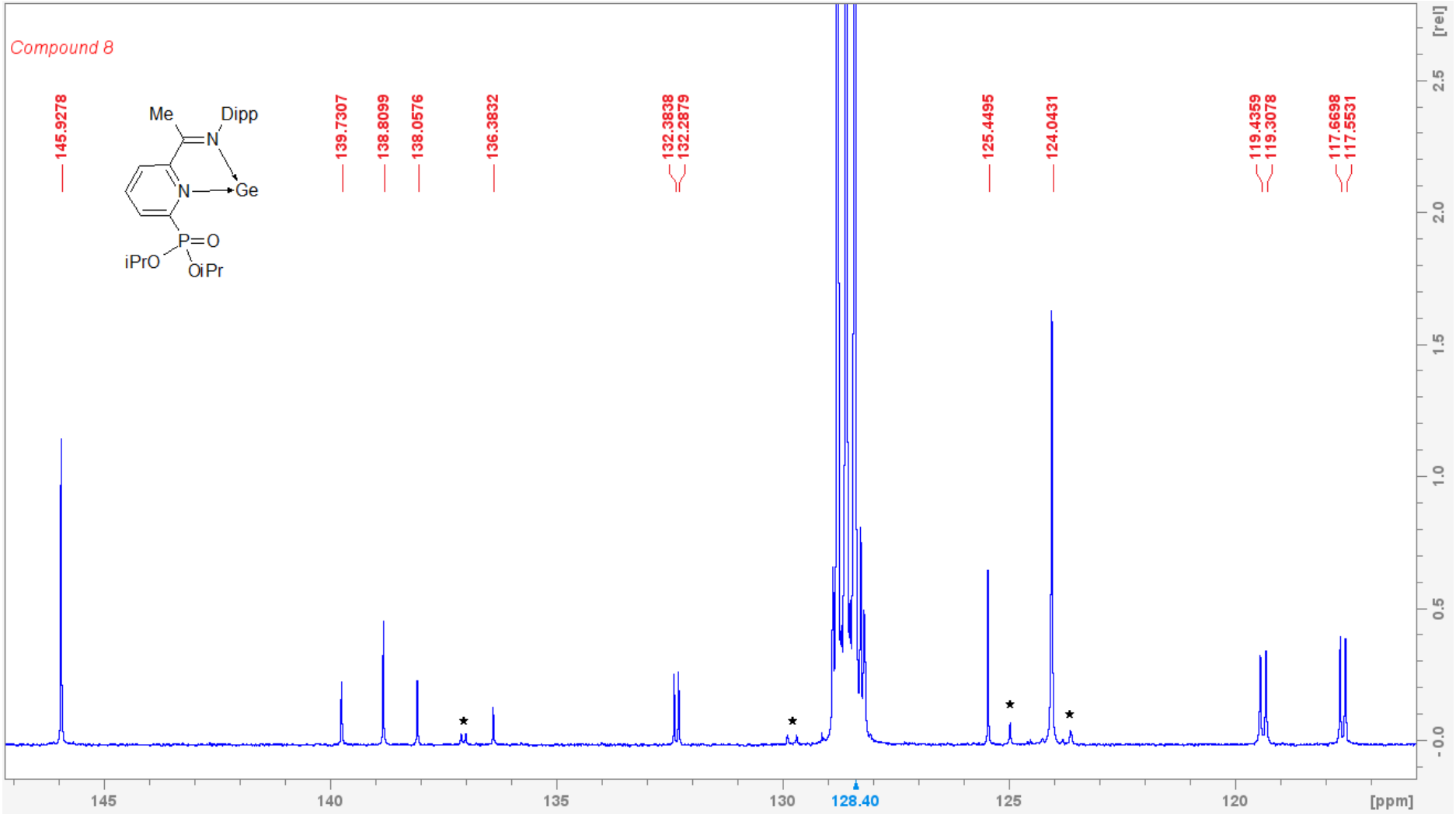

Figure S40. $^{13}C\{H\}$ NMR spectrum of **8** in C_6D_6 – aromatic region (***** signal of **L**)

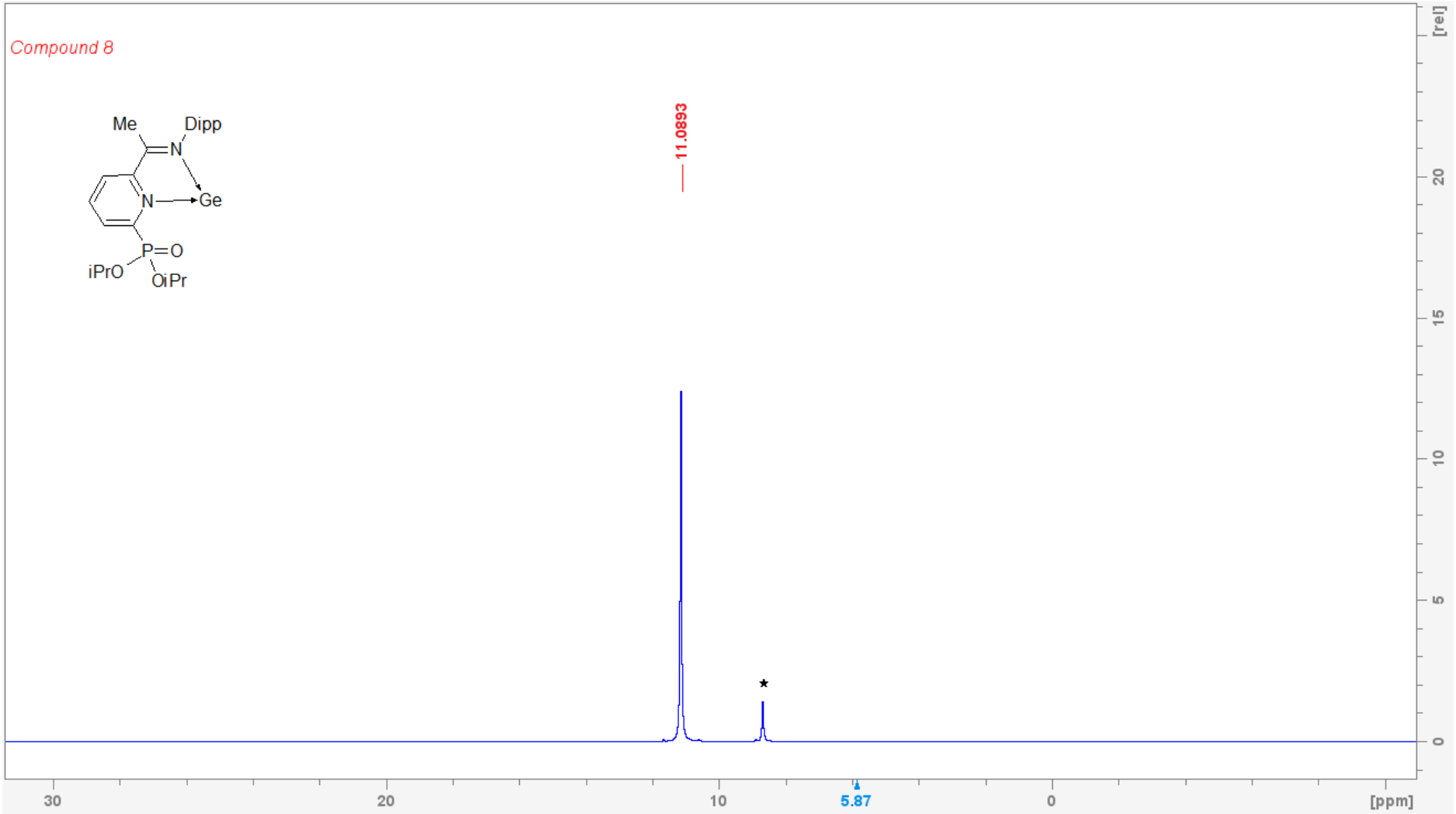

Figure S41. $^{31}P\{H\}$ NMR spectrum of **8** in C_6D_6 (***** signal of **L**).

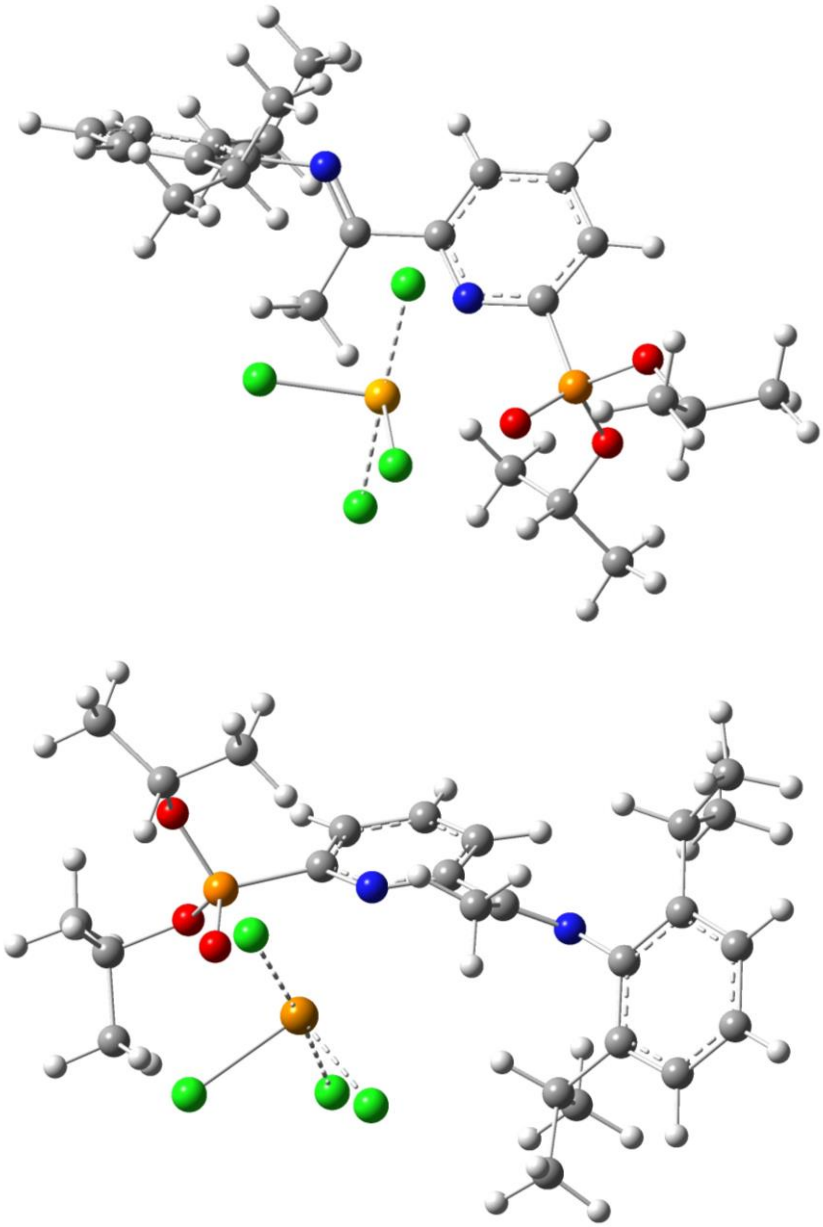

Figure S42. Comparison of optimized structures of **L**→$SeCl_4$ (top) and **L**→$TeCl_4$ (bottom).

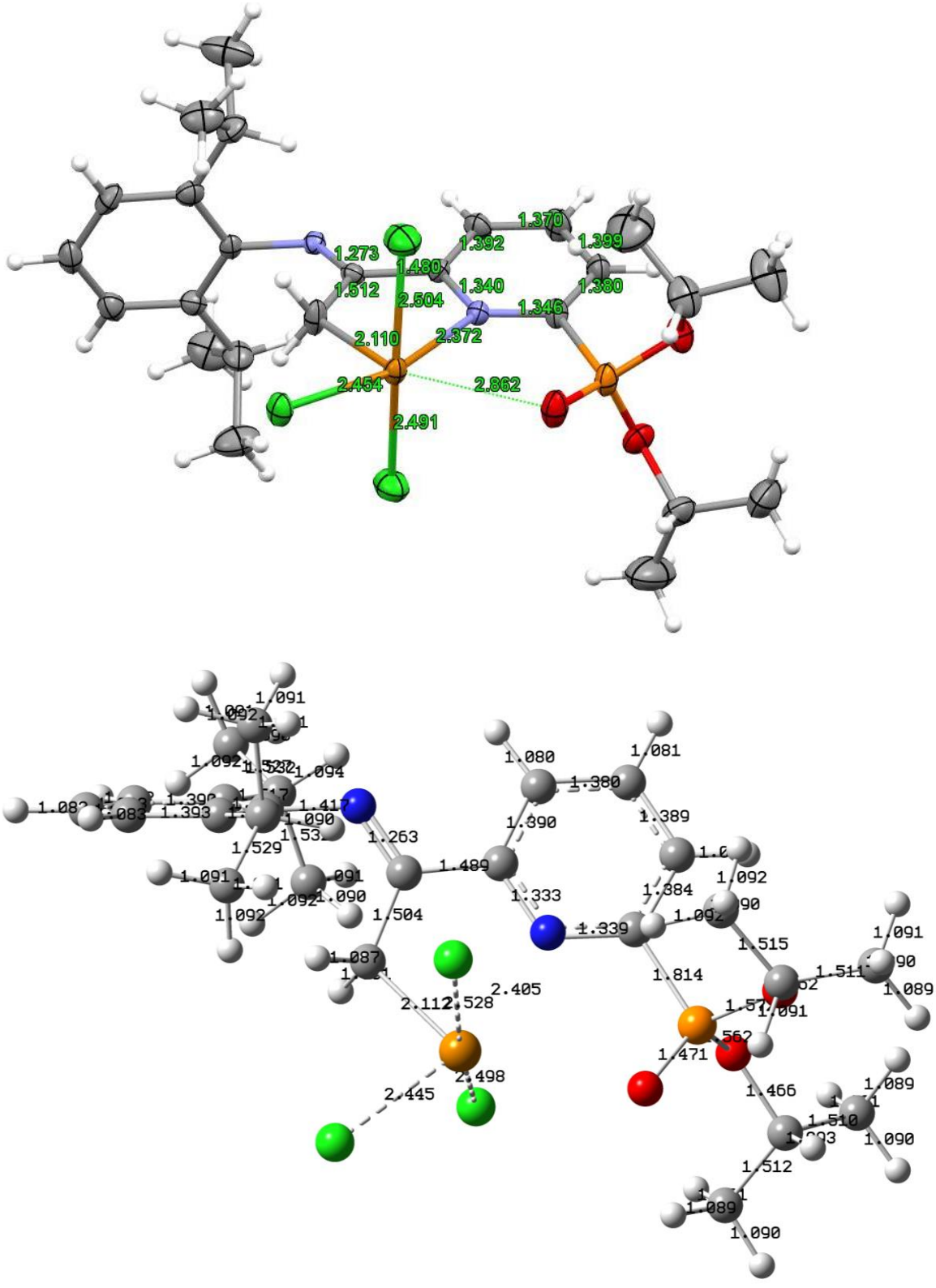

Figure S43. Comparison of molecular structures of **7**, XRD (top) and calculated (bottom, with Te…O 2.913) – bond lengths are given in Å.

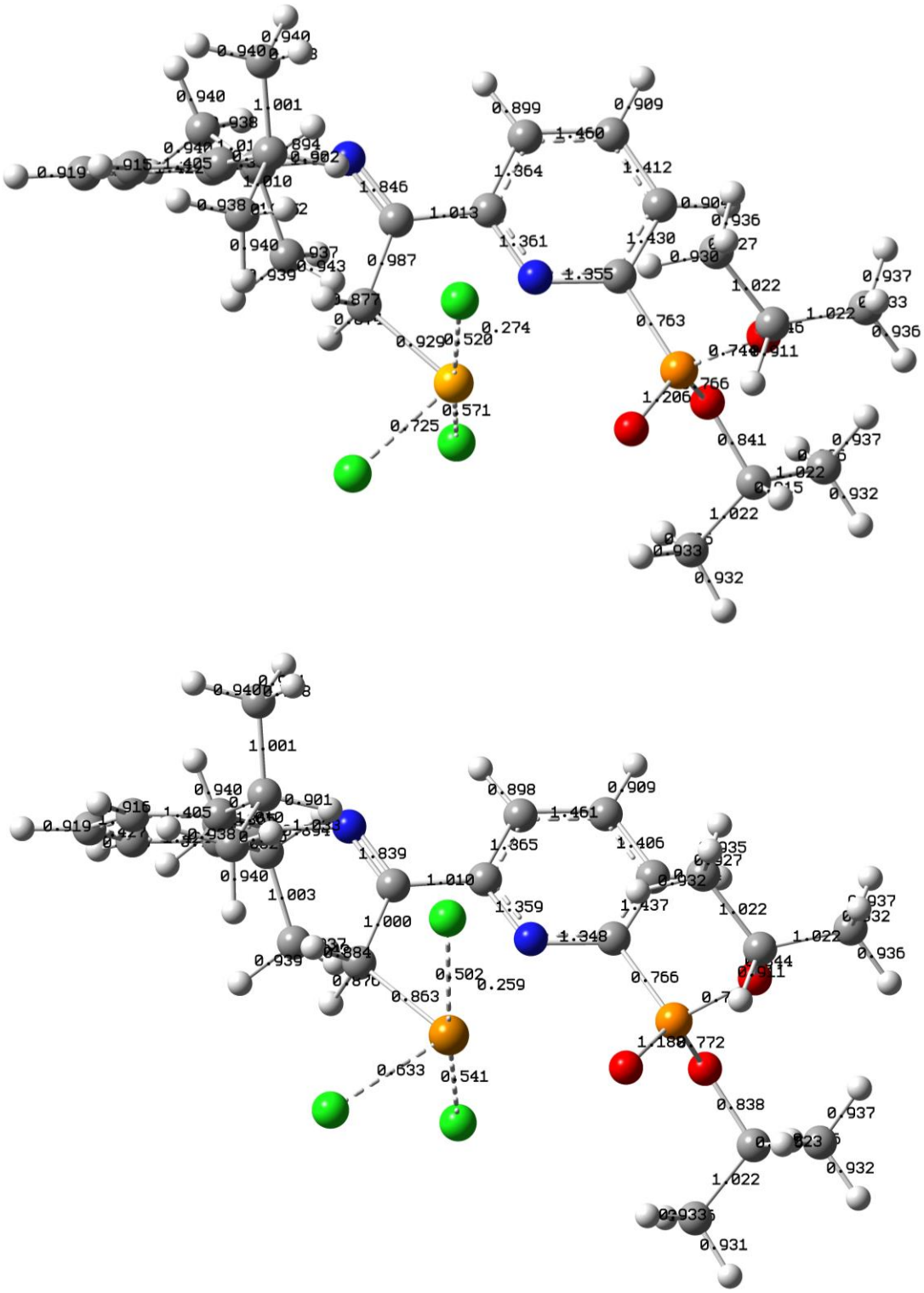

Figure S44. Comparison of optimized structures of **7'**(Se) (top) and **7** (bottom) including WBIs.

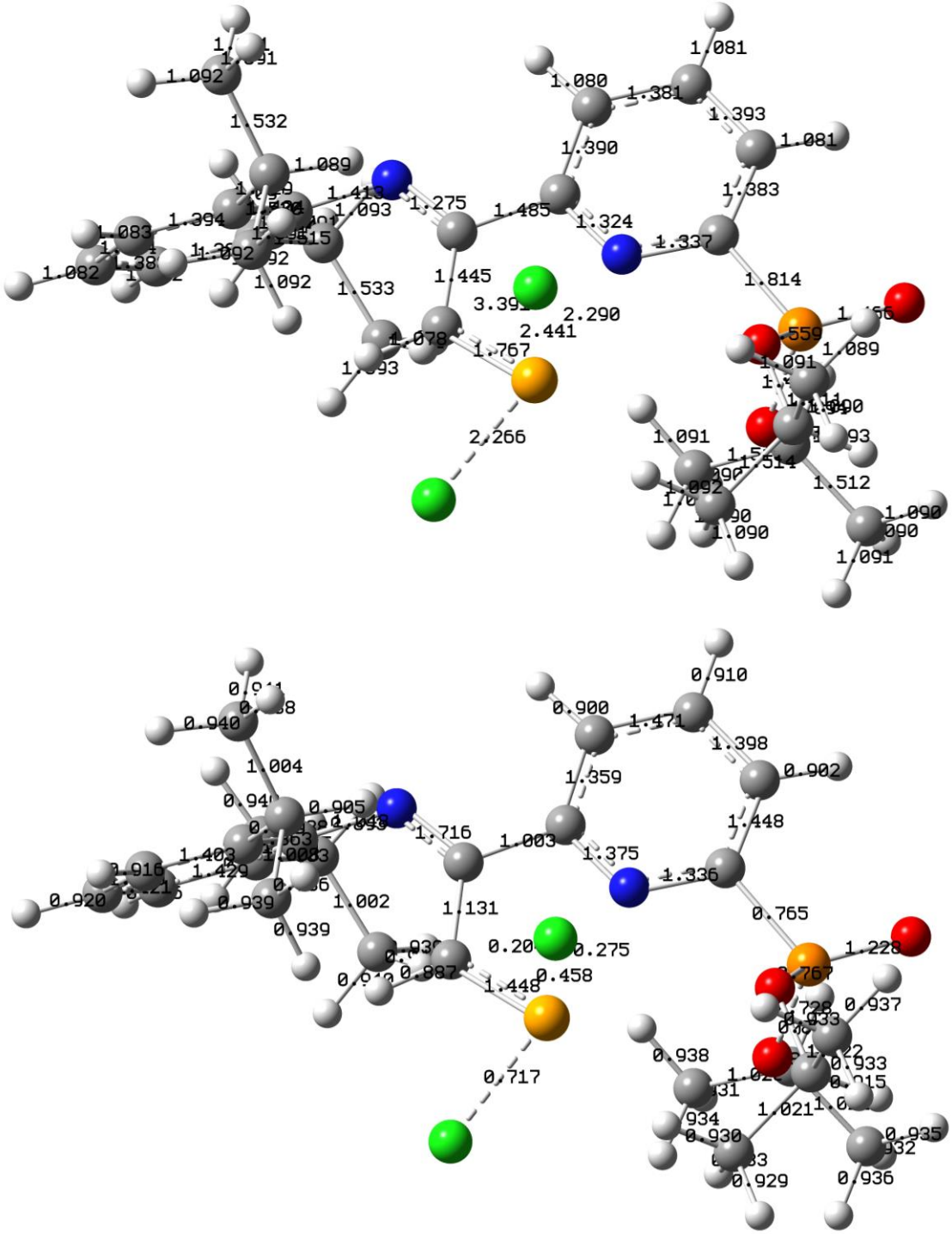

Figure S45. Optimized structure of **6** (top: distances in Å, bottom: WBIs).

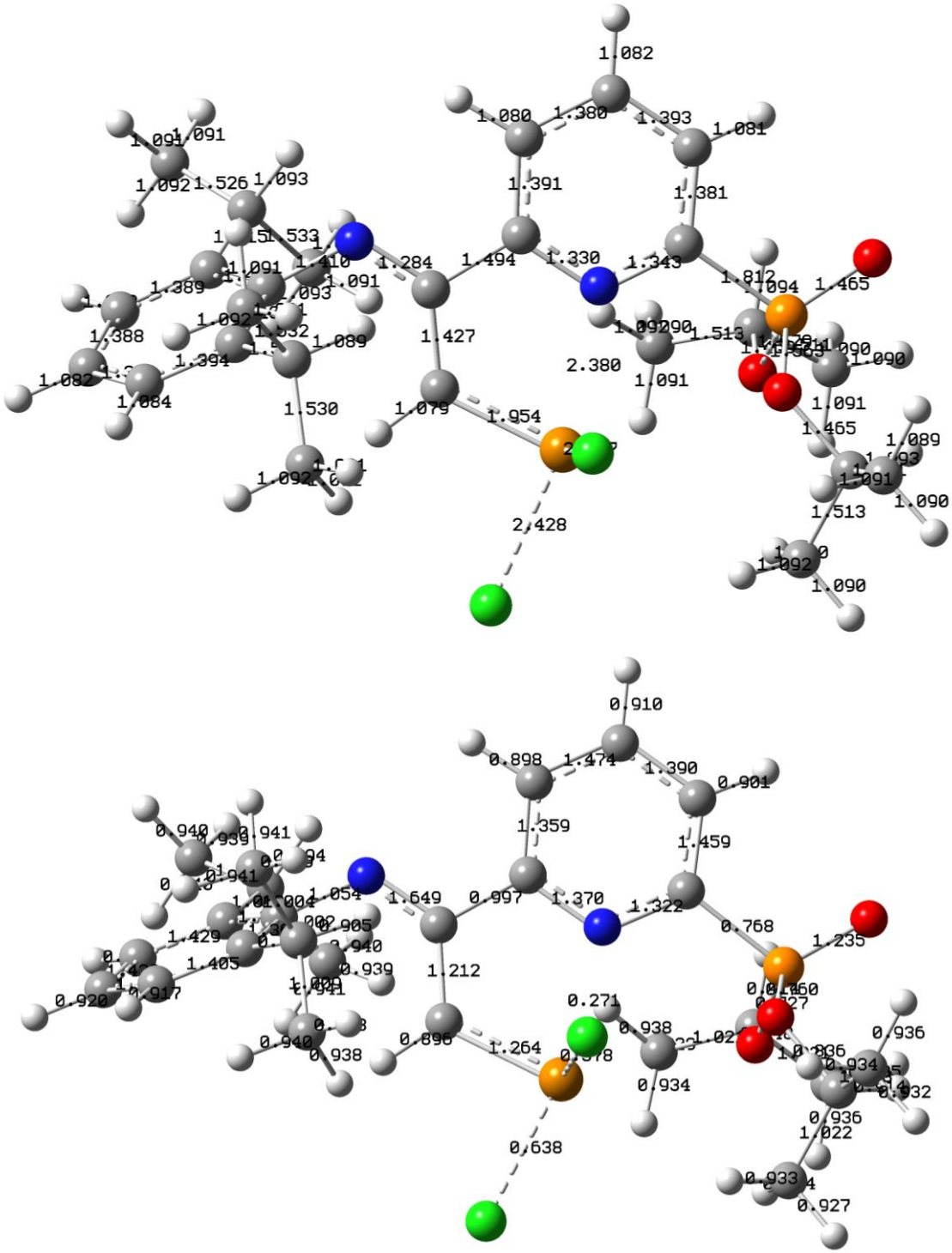

Figure S46. Optimized structure of **6'**(Te) (top: distances in Å, bottom: WBIs).

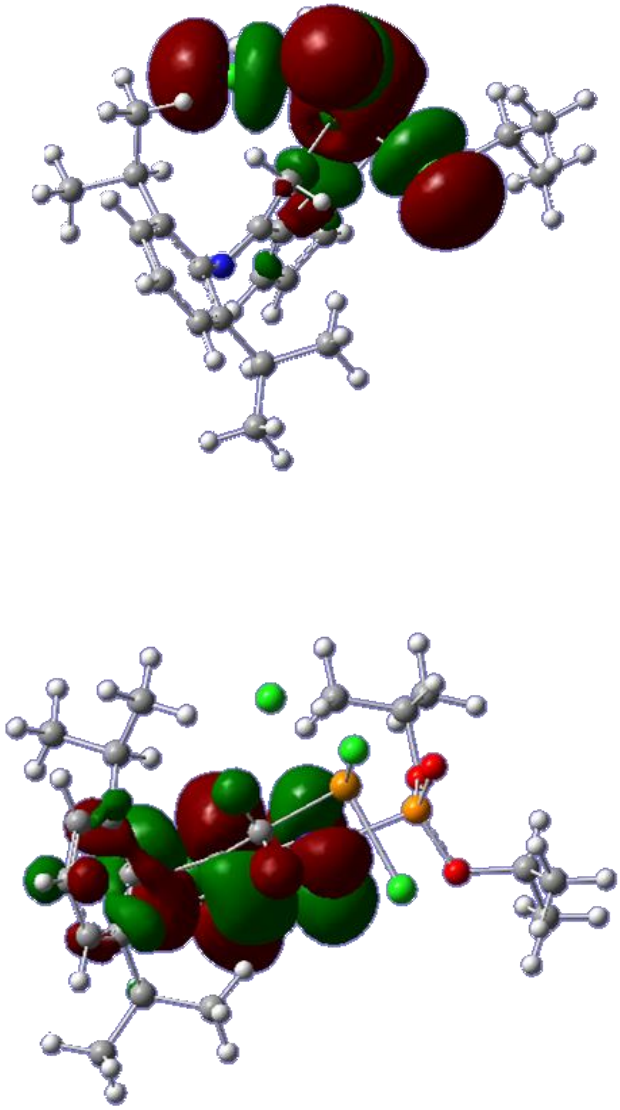

Figure S47. Visualization of HOMO (top) and LUMO (bottom) in **7** and **7'**(Se).

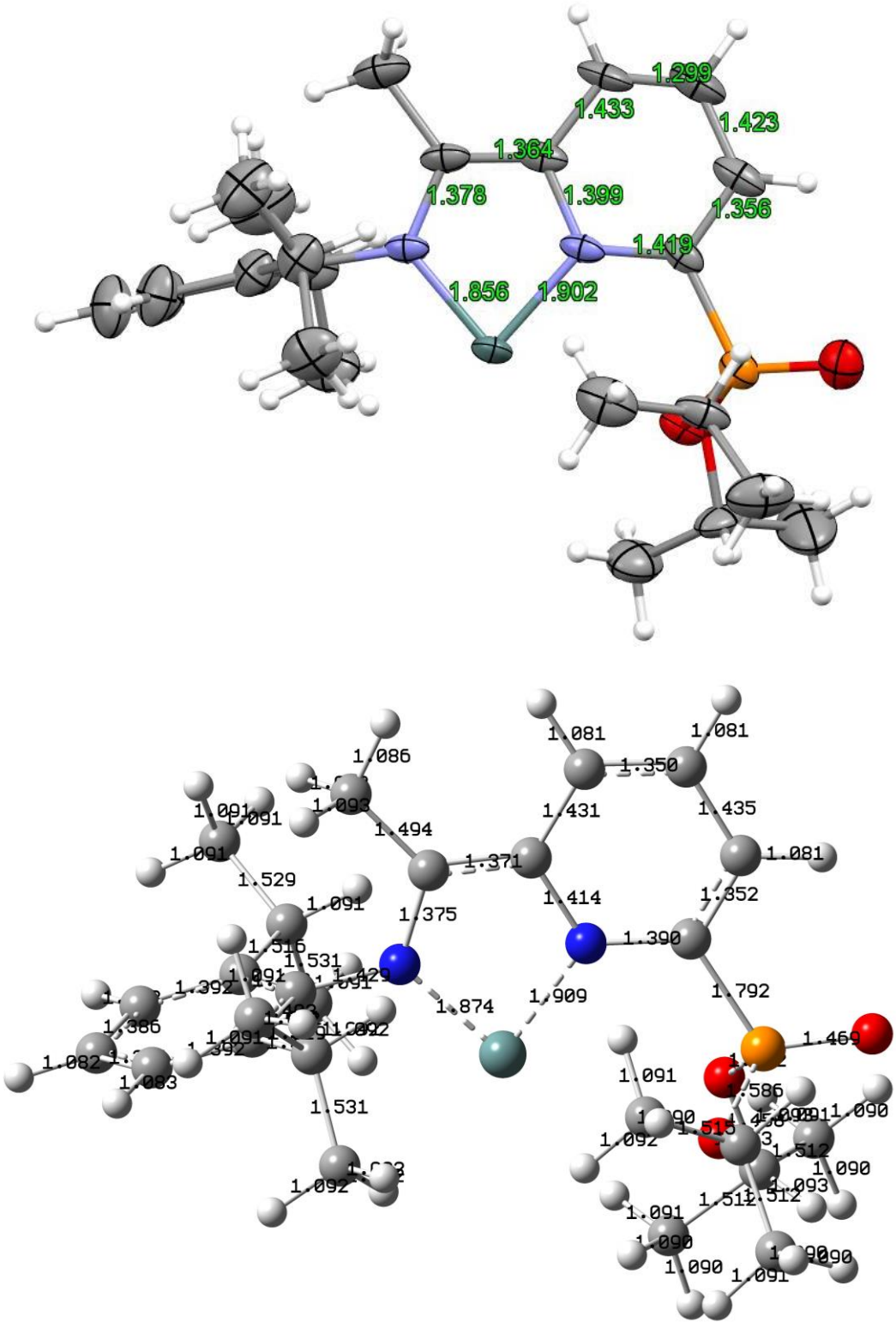

Figure S48. Comparison of molecular structures of **8**, XRD (top) and calculated (bottom) – bond lengths are given in Å.

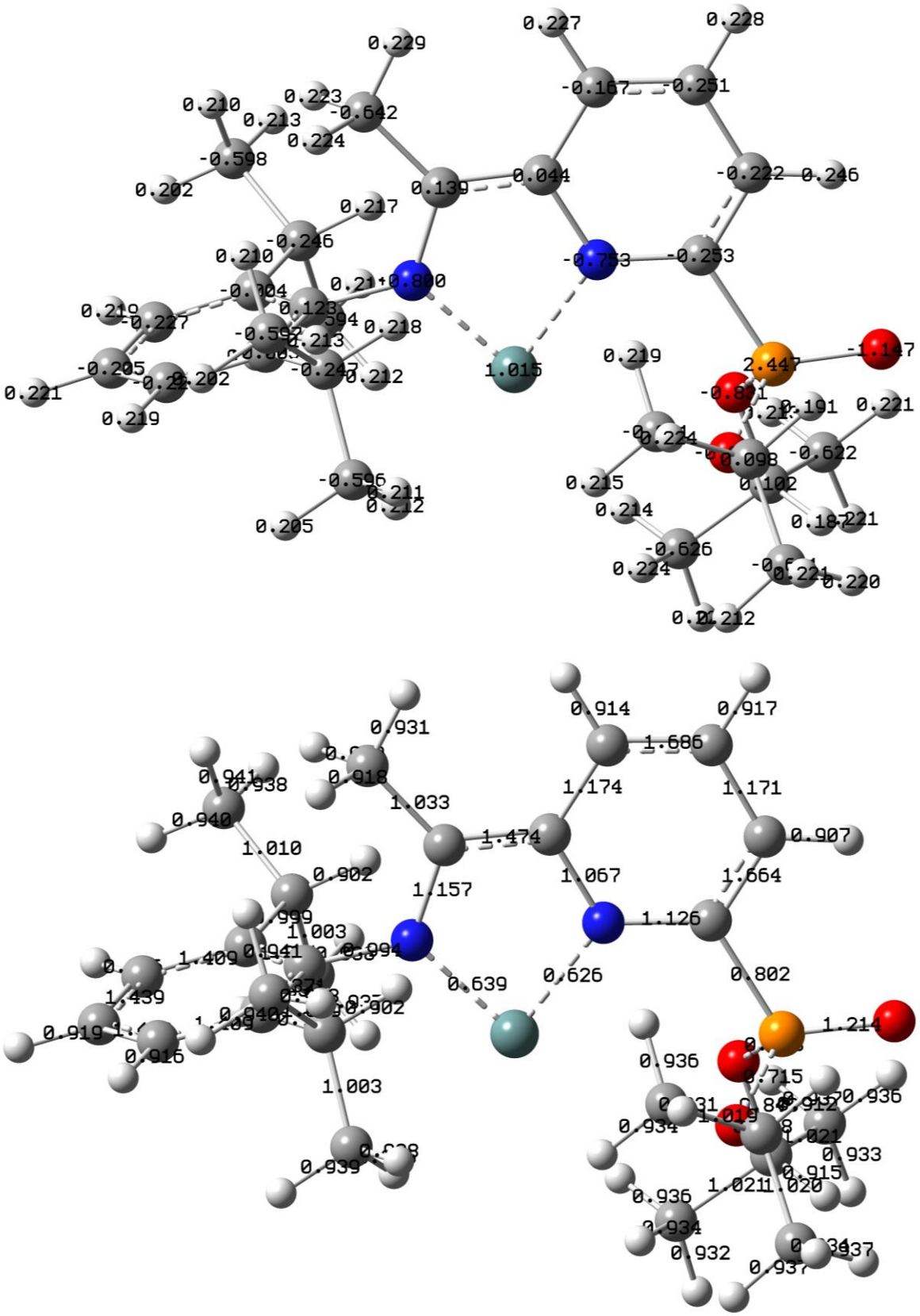

Figure S49. Calculated NBO charges (top) and Wiberg bond indices (bottom) for **8**.

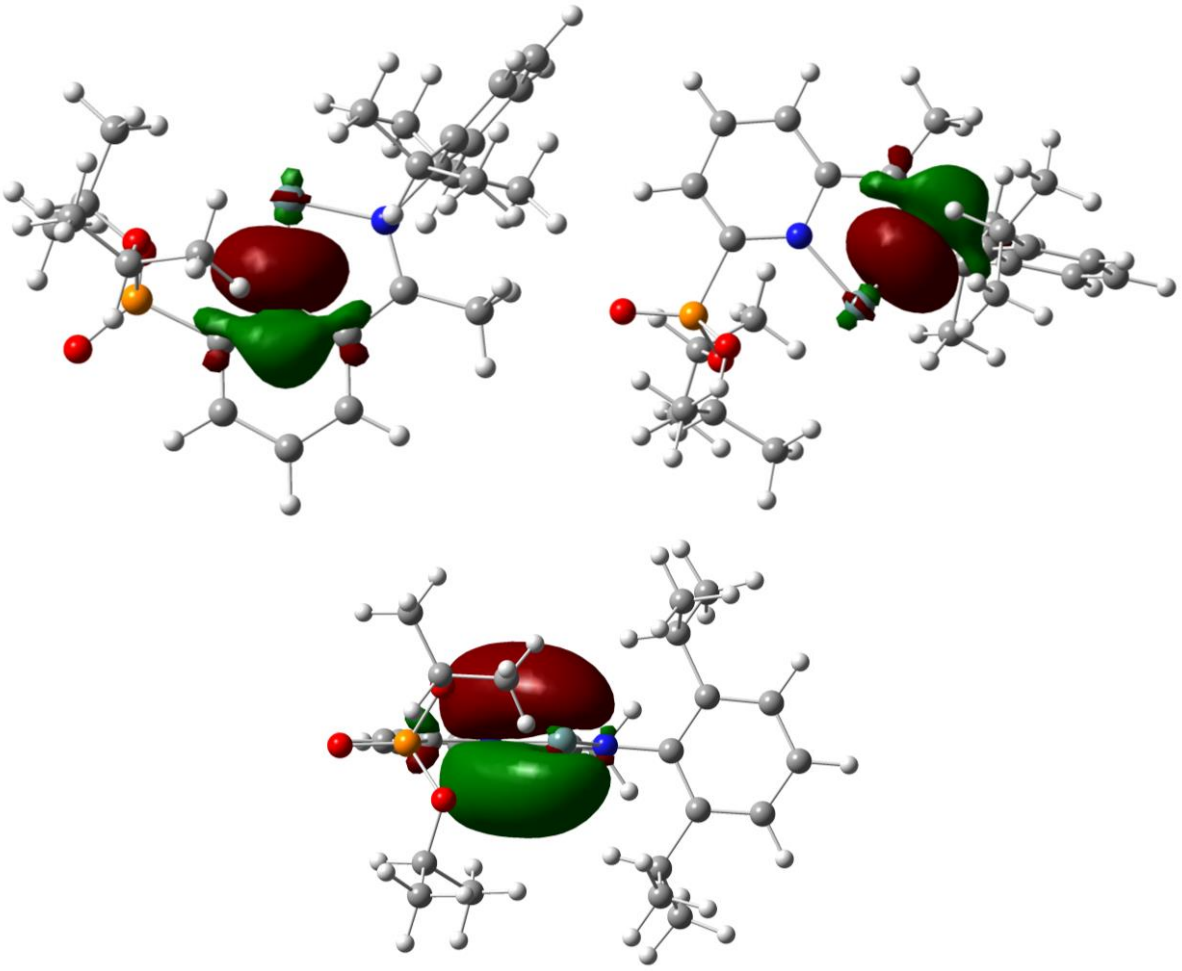

Figure S50. Visualization of HOMO-14 (top-left), HOMO-13 (top-right) and HOMO-5 (bottom) orbitals involved in connection of Ge atom and ligand in **8**.

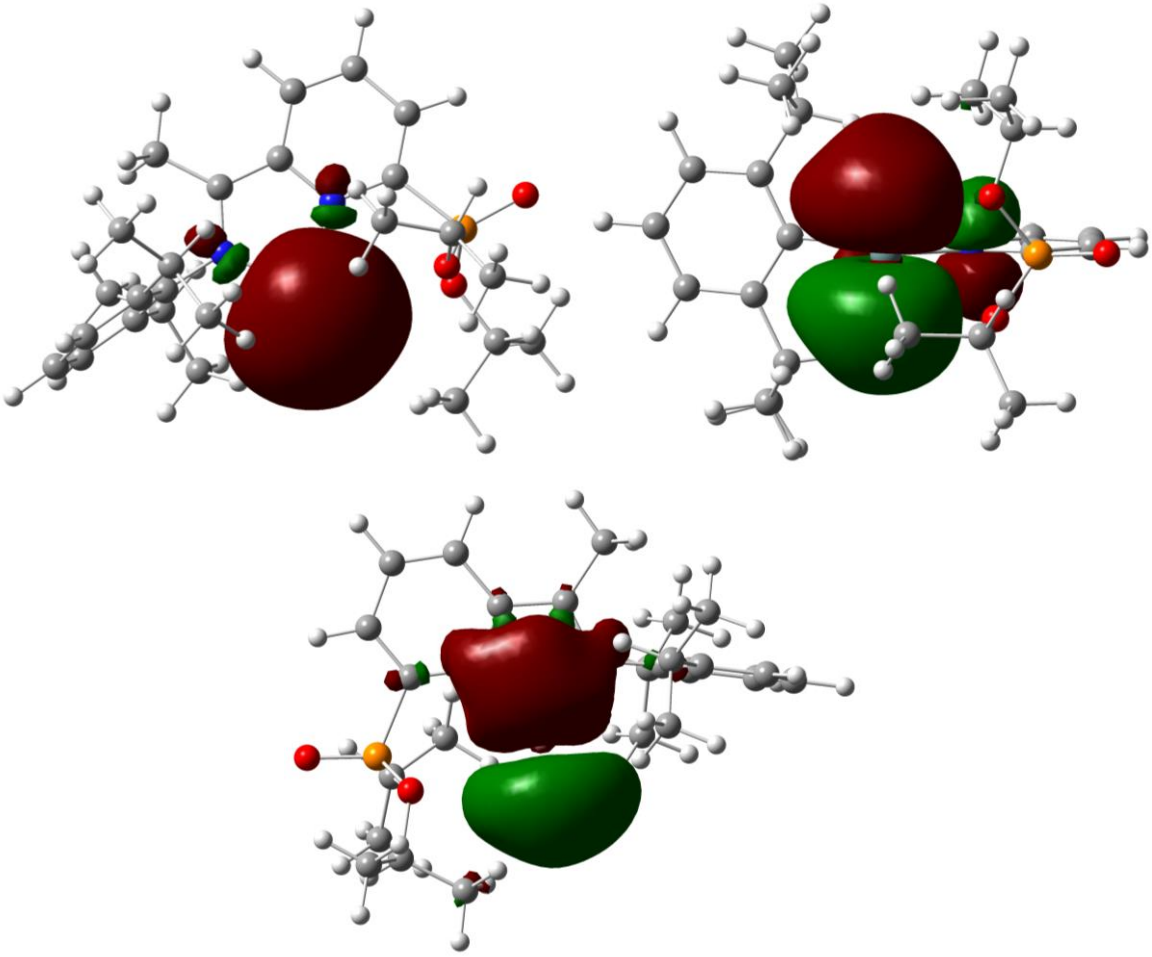

Figure S51. Visualization of HOMO-10 (top-left, lone electron pair on Ge), LUMO (top-right, gap 7.38 eV) and LUMO+8 (bottom) orbitals situated close to Ge atom in **8**.

Table S7. Gibbs‘ free energy in Hartrees

compound	**Gibbs’ free energy**	**complex**	**Gibbs’ free energy**
HCl	-460.811943	$L^{NO}SeCl_4$	-5893.407581
$SeCl_4$	-4242.388935	$L^{CO}SeCl_4$	-5893.404968
$TeCl_4$	-2108.83124	$L^{CO}SeCl_3$	-5432.620862
$L^{CO(ROT)}$	-1651.011969	$L^{CO}SeCl_2$	-4971.767615
L^{CO}	-1651.010611	$L^{CO(ROT)}SeCl_2$	-4971.789719
$L^{NO(ROT)}$	-1651.005528	$L^{NO}TeCl_4$	-3759.862807
L^{NO}	-1651.00387	$L^{CO}TeCl_4$	-3759.858043
		$L^{CO}TeCl_3$	-3299.048927
		$L^{CO}TeCl_2$	-2838.178768
		$L^{CO(ROT)}TeCl_2$	-2838.194775