Supporting information

for

Phosphate Binding to the [Au(IPr)] Moiety: Inner vs Outer Sphere Coordination Behaviour

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Table of Content

Part 1: Preparation of compounds 2-5

General Considerations. All reactions were carried out in air unless otherwise stated. Technical solvents were used and purchased from Aldrich. NMR spectra were recorded on a 300 MHz or 400 MHz Brucker spectrometer. Elemental analyses were performed by the analytical services at the University of St Andrews. For optical properties, measurement were performed on Perkin Elmer Model 341 polarimeter (wavelength = 589 nm, T = 20°C, solvent = $CHCl_3$). Compounds **1**[1] and **2**[2] were prepared and characterized by comparison with the ^1H NMR data reported in the literature.

Synthesis of [Λ-TRISPHAT-N]·[HN^{n}Bu$_3$] (*Λ*-3). [*rac*-TRISPHAT-N]·[*n*-Bu_3NH] (600 mg, 0.7 mmol) was dissolved in 21 mL of chloroform. *N*-benzylcinchonidinium chloride (296 mg, 0.7 mmol) was added in one portion to the clear solution. The alkaloid dissolved immediately upon stirring and 2 min later the formation of a white precipitate was observed. The reaction was stirred at 25 °C for 24 hours to ensure maximum precipitation of [Δ-TRISPHAT-N] [*N*-benzylcinchonidinium]. The crude reaction mixture was filtered over Millipore system filtration XX15 047 00 (Whatman filter paper type 595, 4-7 µm, 45 mm diameter). The white powder was washed with cold $CHCl_3$ and collected. The mother liquor was concentrated, dissolved in $CHCl_3$ (6 mL) and filtered over a Millipore. The resulting mother liquor was concentrated, filtered on Al_2O_3 (elution CH_2Cl_2) and precipitated in $CHCl_3$/pentane. [Λ-TRISPHAT-N]·[HN^{n}Bu$_3$] *Λ*-**3** was isolated as a white solid (53% yield, 159 mg). mp > 248 °C (decomposition); ^1H NMR (400 MHz, CD_3CN): δ 7.52 (d, *J* = 2.2 Hz, 1H, C*H* aromatic), 7.11-7.08 (m, 1H, C*H* aromatic), 6.70 (s broad, 1H, N*H*), 3.11-2.99 (m, 6H, N(CH_2)$_3$), 1.67-1.57 (m, 6H, N(CH_2CH_2)$_3$), 1.41-1.29 (m, 6H, N($CH_2CH_2CH_2$)$_3$), 0.95 (t, *J* = 7.4 Hz, 9H, N($CH_2CH_2CH_2CH_3$)$_3$) ppm; ^{31}P NMR (162 Hz, CD_3CN): -84.4 ppm; ^{13}C NMR (100 MHz, CD_3CN): δ 154.5 (d, *J* = 12.0 Hz, 1C), 142.8-142.6 (m, 4C), 140.3 (s, 1C), 136.7 (s, 1CH),

[1] S. Gaillard, A. M. Z. Slawin and S. P. Nolan, *Chem. Commun.* 2010, **46**, 2742-2744.
[2] J. Lacour, C. Ginglinger, C. Grivet and G. Bernardinelli *Angew. Chem. Int. Ed.* 1997, **36**, 608-610.

124.5 (s, 1C), 123.4 (d, J = 4.6 Hz, 1C), 123.4 (s, 1C), 118.6 (s, 1C), 117.2 (d, J = 17.7 Hz, 1CH), 114.6 (d, J = 19.3 Hz, 1C), 114.6 (d, J = 19.7 Hz, 1C), 114.6 (d, J = 19.3 Hz, 1C), 114.5 (d, J = 19.6 Hz, 1C), 114.5 (d, J = 19.6 Hz, 1C), 54.0 (s, $3CH_2$), 26.2 (s, $3CH_2$), 20.4 (s, $3CH_2$), 13.7 (s, $3CH_3$); $[\alpha]_D^{20}$ = +335 (MeOH, c = 0.101); IR (neat): 2964, 1593, 1445, 1388, 1234, 990, 819, 655 cm^{-1}; HRMS (ESI positif): *m/z* calculated for $C_{12}H_{28}N$ 186.2216 observed 186.2211; HRMS (ESI negatif): *m/z* calculated for $C_{17}H_2N_1O_6P_1Cl_9$ 661.6811 observed 661.6787; UV/Vis (CH_3CN, $1.01 \cdot 10^{-5}$ M) λ_{max} (ε) 217 ($5.18 \cdot 10^4$), 295 ($1.8 \cdot 10^3$); CD (CH_3CN, $1.01 \cdot 10^{-5}$ M, 20 °C) λ ($\Delta\varepsilon$) 210 (-14), 220 (+28), 242 (+3).

Synthesis of [Au(IPr)(Bu_3N)][*rac*-TRISPHAT] (4). [Au(OH)(IPr)] **1** (20 mg, 0.033 mmol) and [*rac*-TRISPHAT]·**[**HN^nBu_3] **2** (31.7 mg, 0.033 mmol) were introduced into a vial containing benzene (0.33 mL). The reaction was stirred at room temperature for 14h. Solvent was reduced by half under vacuum and pentane (4 mL) was added and the resulting precipitate was collected on a frit. Solid was washed with pentane (3 x 3 mL) and dried under vacuum to afford crude **4** as a white microcrystalline solid. Solid was recrystallized by slow gas diffusion of pentane into a solution containing crude **4** in dichloromethane to give pure **4** as colorless crystals (47.1 mg, 93%). **Synthesis of [Au(IPr)(Bu_3N)][*Λ*-TRISPHAT] (*Λ*-4).** [Au(OH)(IPr)] **1** (136.6 mg, 0.227 mmol) and [*Λ*-TRISPHAT]·[HN^nBu_3] *Λ*-**2** (216.6 mg, 0.227 mmol) were introduced into a vial containing benzene (2.2 mL). The reaction was stirred at room temperature for 14h. Solvent was reduced by half under vacuum and pentane (4 mL) was added and the resulting precipitate was collected on a frit. Solid was washed with pentane (3 x 3 mL) and dried under vacuum to afford crude *Λ*-**4** as a white microcrystalline solid. Solid was recrystallized by slow gas diffusion of pentane into a solution containing crude *Λ*-**4** in dichloromethane to give pure *Λ*-**4** as colorless crystals (324.5 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (t, J = 7.8 Hz, 2H, C*H* aromatic IPr), 7.51 (s, 2H, C*H* imidazole IPr), 7.33 (d, J = 7.8 Hz, 4H, C*H* aromatic IPr), 2.56-2.44 (m, 10H, 4 C*H* C*H*$(CH_3)_2$ and 6 N-CH_2 of Bu_3N), 1.29-1.13 (m, 30H, 24 CH(CH_3)$_2$ and 6 CH_2 of Bu_3N),

1.10-0.98 (m, 6H, CH_2 of Bu_3N), 0.75 (t, J = 7.2 Hz, 9H, CH_3 of Bu_3N) ppm. ^{31}P NMR (162 Hz, $CDCl_3$): -81.0 (s, TRISPHAT) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7 (s, C carbene), 145.6 (s, *C* aromatic IPr), 142.1 (d, J = 6.5 Hz, *C*Cl TRISPHAT), 133.5 (s, *C* aromatic IPr), 131.3 (s, *C*H imidazole IPr), 124.8 (*C*H aromatic IPr), 124.4 (s, *C*H aromatic IPr), 122.2 (s, *C*Cl TRISPHAT), 113.8 (d, J = 19.8 Hz, *C*O TRIPSHAT), 59.2 (s, N-*C*H_2 Bu_3N), 28.9 (s, *C*H$(CH_3)_2$), 28.4 (s, *C*H_2 Bu_3N), 24.4 (s, CH(*C*H_3)$_2$), 24.1 (s, CH(*C*H_3)$_2$), 20.2 (s, *C*H_2 Bu_3N), 13.6 (s, *C*H_3 Bu_3N) ppm. $[\alpha]^{20}_D$ = +207 (C = , $CHCl_3$). Anal. Calcd for $C_{57}H_{63}AuCl_{12}N_3O_6P$: C, 44.47; H, 4.12; N, 2.73. Found: C, 44.73; H, 3.75; N, 2.42.

Synthesis of [Au(IPr)][*rac*-TRISPHAT-N] (5). [Au(OH)(IPr)] **1** (30 mg, 0.0498 mmol) and [*rac*-TRISPHAT-N]**[**HN^nBu_3] **3** (42.5 mg, 0.0498 mmol) were introduced into a vial containing benzene (0.5 mL). The reaction was stirred at 60°C for 14h. Solvent was reduced by half under vacuum and pentane (4 mL) was added and the resulting precipitate was collected on a frit. Solid was washed with pentane (3 x 3 mL) and dried under vacuum to afford crude **5** as a white microcrystalline solid. Solid was recrystallized by slow gas diffusion of pentane into a solution containing crude **5** in dichloromethane to give pure **5** as colorless crystals (60.0 mg, 97%). **Synthesis of [Au(IPr)][*Λ*-TRISPHAT-N] (*Λ*-5).** [Au(OH)(IPr)] **1** (35.5 mg, 0.0589 mmol) and [*Λ*-TRISPHAT-N]**[**HN^nBu_3] *Λ*-**3** (50 mg, 0.0589 mmol) were introduced into a vial containing benzene (0.6 mL). The reaction was stirred at 60°C for 14h. Solvent was reduced by half under vacuum and pentane (4 mL) was added and the resulting precipitate was collected on a frit. Solid was washed with pentane (3 x 3 mL) and dried under vacuum to afford crude *Λ*-**5** as a white microcrystalline solid. Solid was recrystallized by slow gas diffusion of pentane into a solution containing crude *Λ*-**5** in dichloromethane to give pure *Λ*-**5** as colorless crystals (67.8 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (t, J = 7.8 Hz, 2H, C*H* aromatic IPr), 7.33 (dd, J = 7.8, 1.1 Hz, 2H, C*H* aromatic IPr), 7.27 (s, 2H, TRISPHAT-N), 7.24 (dd, J = 7.8, 1.1 Hz, 2H, C*H* aromatic IPr), 6.95 (dd, J = 2.0, 1.1 Hz,

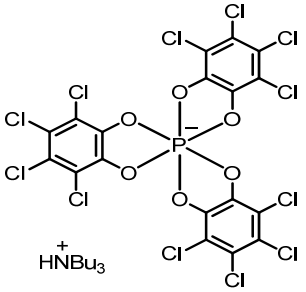
1H, C*H* imidazole IPr), 6.81 (dd, *J* = 2.01, 0.5 Hz, 1H, C*H* imidazole IPr), 2.53 (sept, *J* = 6.9 Hz, 2H, C*H*(CH_3)$_2$ IPr), 2.42 (sept, *J* = 6.9 Hz, 2H, C*H*(CH_3)$_2$ IPr), 1.43 (d, *J* = 6.9 Hz, 6 CH(C*H*$_3$)$_2$ IPr), 1.23 (t, *J* = 6.4 Hz, 12 CH(C*H*$_3$)$_2$ IPr), 1.04 (d, *J* = 6.9 Hz, 6 CH(C*H*$_3$)$_2$ IPr) ppm. ^{31}P NMR (121 Hz, $CDCl_3$): -83.6 (s, TRISPHAT-N) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5 (s, C carbene), 155.5 (d, *J* = 14.0 Hz, *C*O pyr TRISPHAT-N), 145.8 (s, *C* aromatic IPr), 145.4 (s, *C* aromatic IPr), 142.4 (s, *C*Cl pyr TRISPHAT-N), 141.5 (d, *J* = 6.8 Hz, 2x*C*Cl TRISPHAT-N), 141.5 (d, *J* = 6.8 Hz, 2x*C*Cl TRISPHAT-N), 141.4 (d, *J* = 6.7 Hz, *C*Cl TRISPHAT-N), 141.3 (d, *J* = 7.2 Hz, *C*Cl TRISPHAT), 133.3 (s, *C* aromatic IPr), 132.7 (s, C*H* pyr TRISPHAT-N), 131.3 (s, *C*H imidazole IPr), 124.6 (*C*H aromatic IPr), 124.3 (*C*H aromatic IPr), 124.0 (*C*H aromatic IPr), 123.0 (s, *C*Cl TRISPHAT-N), 122.9 (d, *J* = 23.7 Hz, *C*O Pyr TRIPHAT-N), 114.5 (d, *J* = 19.6 Hz, *C*O TRIPSHAT-N), 114.1 (d, *J* = 20.2 Hz, *C*O TRIPSHAT-N), 114.0 (d, *J* = 20.5 Hz, *C*O TRIPSHAT-N), 113.9 (d, *J* = 20.2 Hz, *C*O TRIPSHAT-N), 29.0 (s, *C*H(CH_3)$_2$), 28.8 (s, *C*H(CH_3)$_2$), 24.8 (s, CH(*C*H$_3$)$_2$), 24.4 (s, CH(*C*H$_3$)$_2$), 24.1 (s, CH(*C*H$_3$)$_2$), 23.6 (s, CH(*C*H$_3$)$_2$) ppm. Anal. Calcd for $C_{44}H_{39}AuCl_9N_3O_6P$: C, 42.22; H, 3.06; N, 3.36. Found: C, 42.35; H, 2.75; N, 3.25.

Part 2: Crystallographic data of complexes 4 and 5.

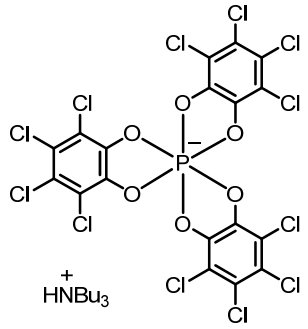
	[Au(IPr)][TRISPHAT] **4**	[Au(IPr)][TRISPHAT-N] **5**
Formula	$C_{25}H_{63}AuCl_{12}N_3O_6P$, CH_2Cl_2	$C_{44}H_{38}AuCl_9N_3O_6P$, $2CH_2Cl_2$
M/g.mol^{-1}	1624.37	1421.61
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a/ Å	15.203(2)	13.280(5)
b/ Å	20.357(3)	13.599(5)
c/ Å	24.945(4)	16.803(5)
α/ °	110.743(8)	79.10(3)
β/ °	98.496(7)	68.36(2)
γ/ °	94.591(7)	81.50(3)
V/ Å^3	7066.8(19)	2759.8(16)
Z	4	4
$\rho calcd$/ g.cm^{-3}	1.527	1.711
μ(Mo K_α)/ mm^{-1}	2.681	3.372
T/ K	93(2)	93(2)
No of reflections	45358	16903
No of unique reflections	25107	6537
R_{int}	0.0488	0.1414
*R*1, wR_2 (I > 2σ(I))	0.0690, 0.1855	0.1743, 04154
*R*1, wR_2 (all data)	0.0997, 0.2146	0.2107, 0.4632
GOF	1.077	1.442

[*rac*-TRISPHAT]·[$HNBu_3$] **2**

[*rac*-TRISPHAT]·[$HNBu_3$], ^1H NMR, CD_2Cl_2

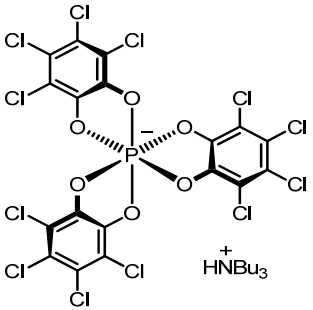


[*rac*-TRISPHAT]·[$HNBu_3$], ^{31}P NMR, CD_2Cl_2

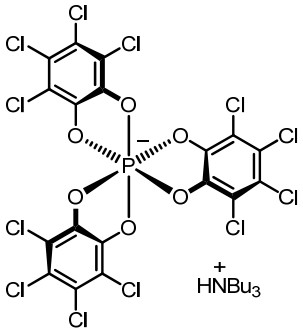


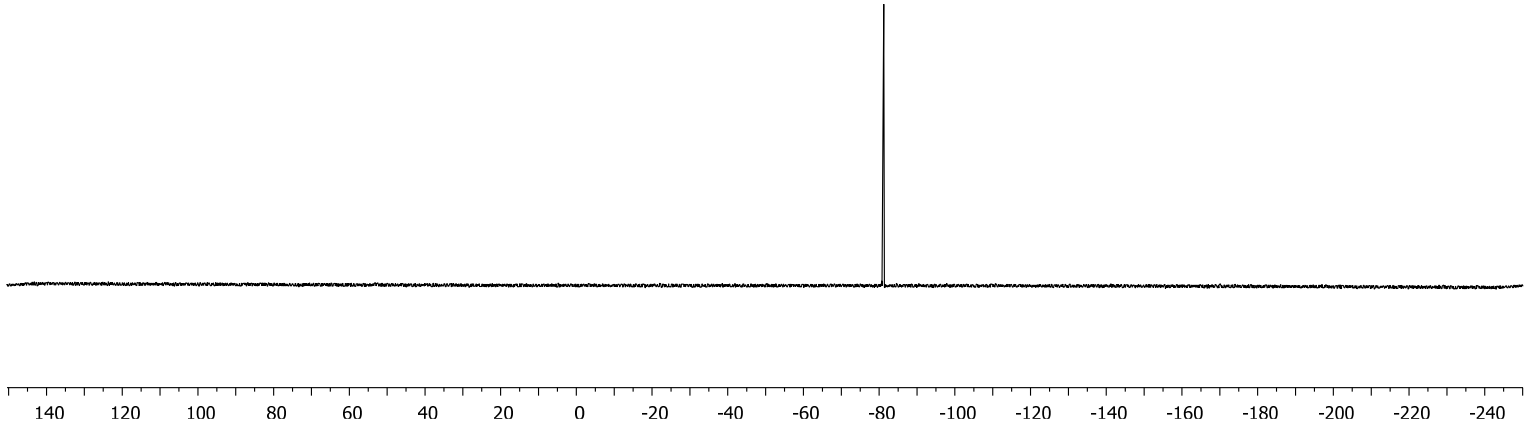
[Λ-TRISPHAT]·[$HNBu_3$] **Λ–2**

[Λ-TRISPHAT]·[$HNBu_3$], ^{1}H NMR, CD_2Cl_2



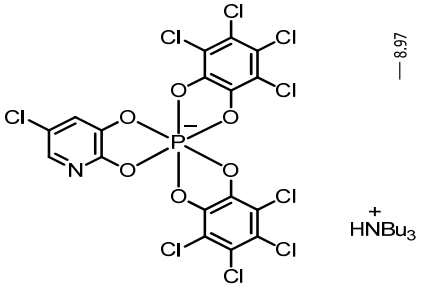
[Λ-TRISPHAT]·[$HNBu_3$], ^{31}P NMR, CD_2Cl_2

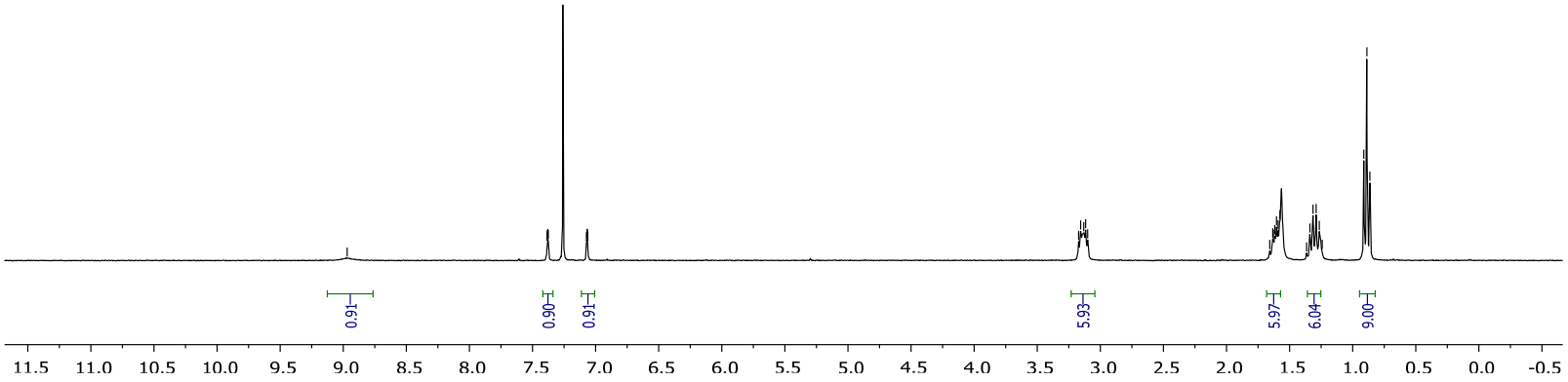




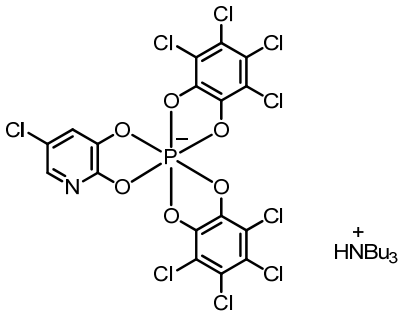
[*rac*-TRISPHAT-N]·[$HNBu_3$] **3**

[*rac*-TRISPHAT-N]·[$HNBu_3$], ^1H NMR, CD_2Cl_2

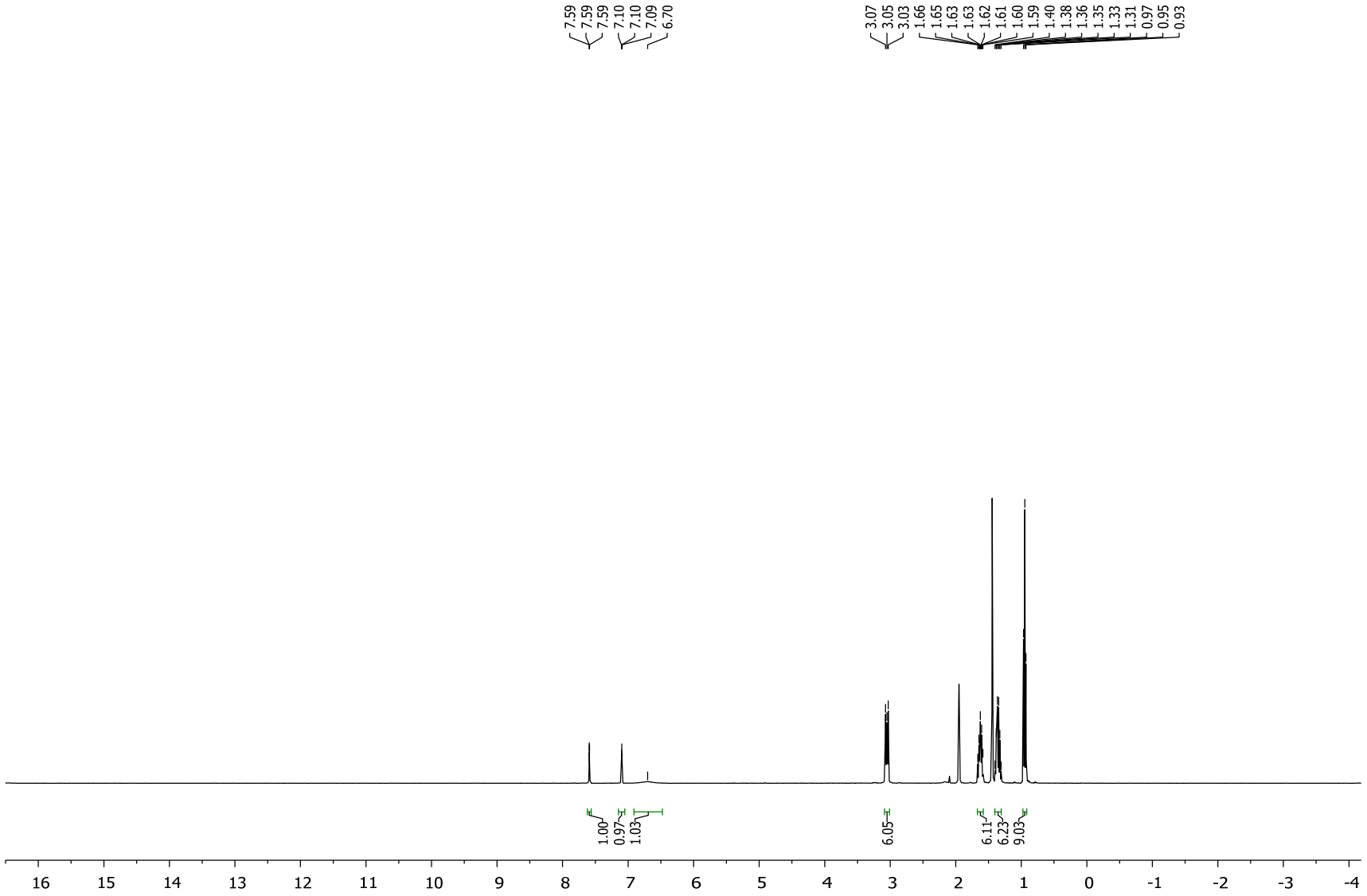


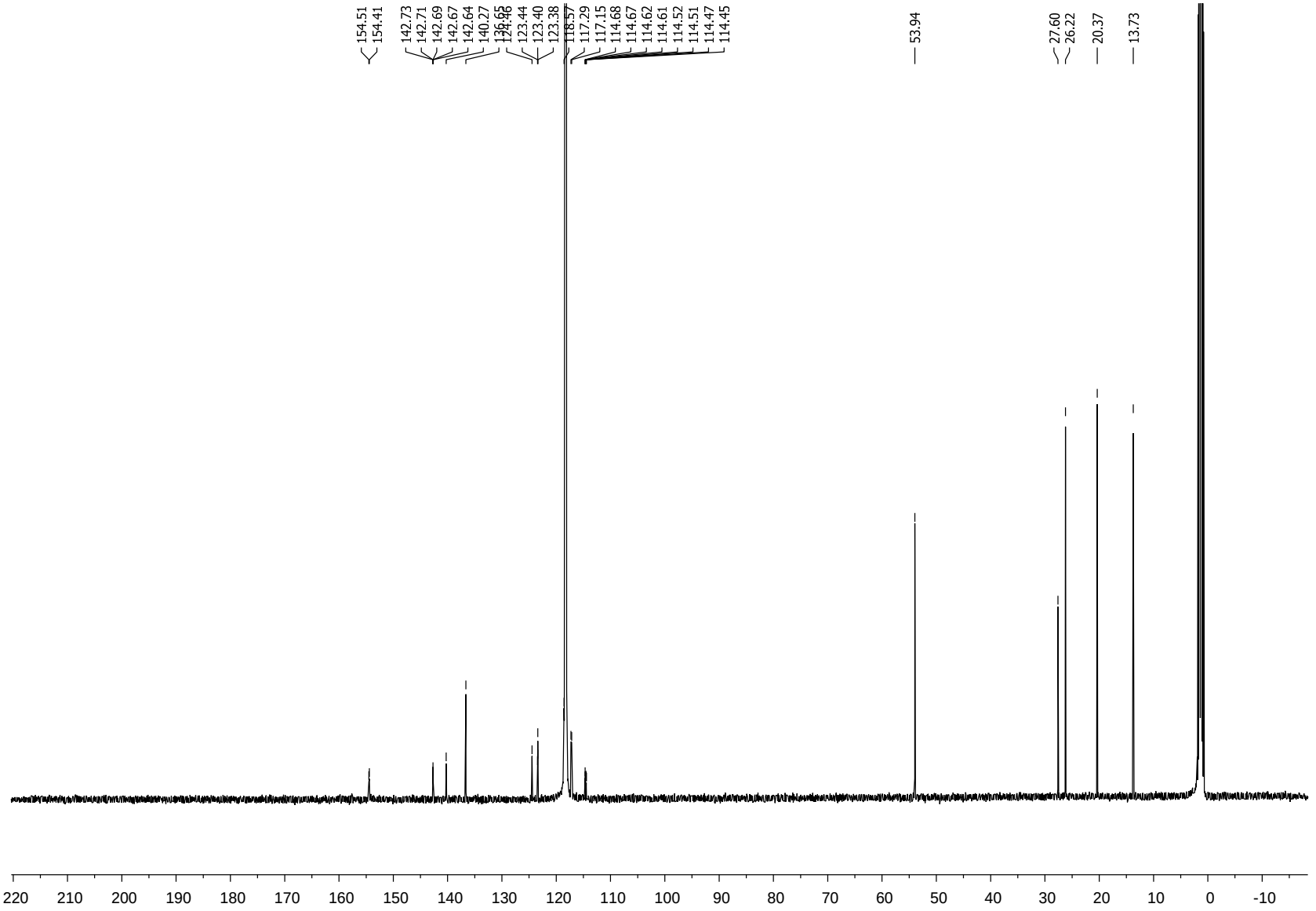


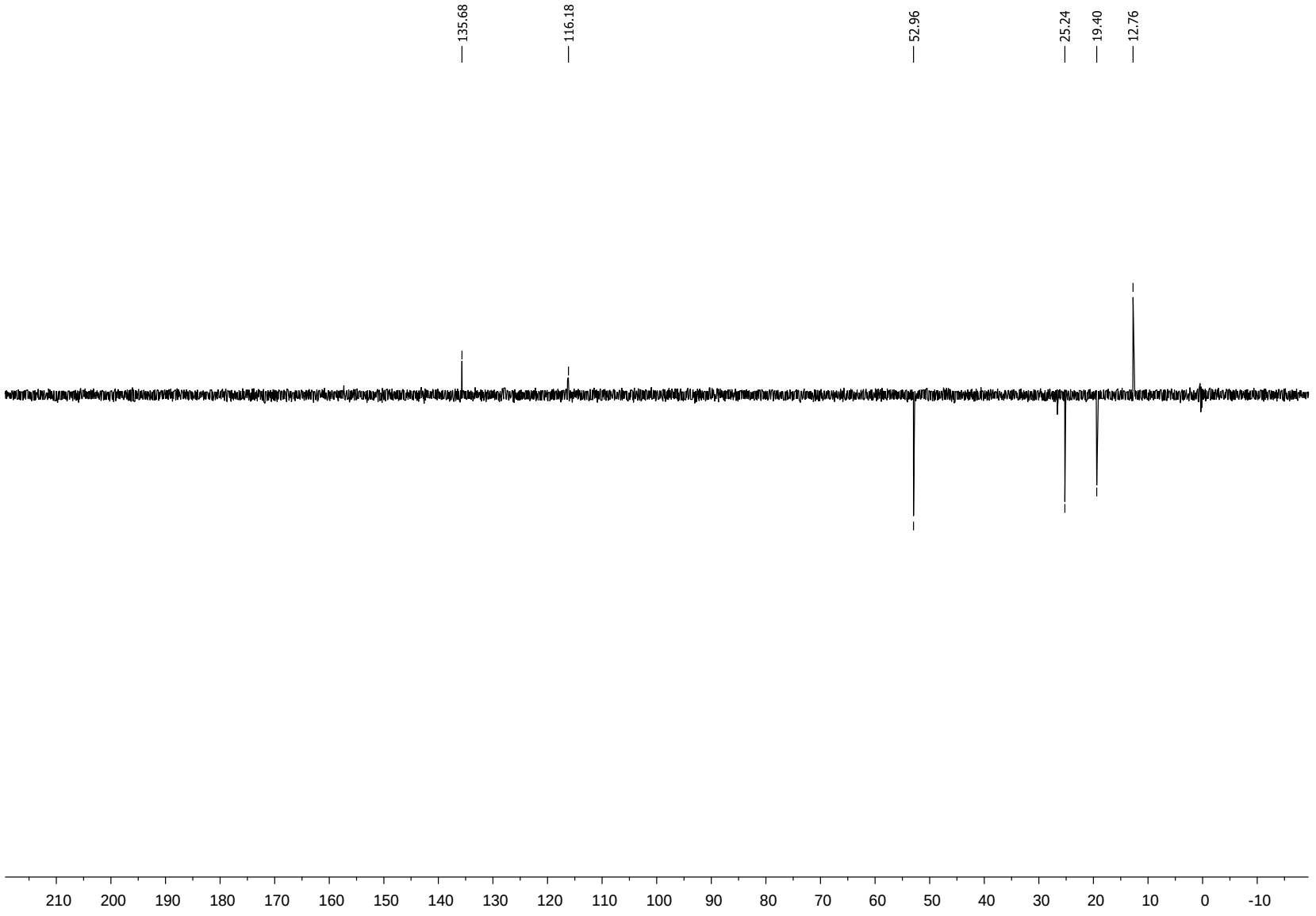
[*rac*-TRISPHAT-N]·[$HNBu_3$], ^{31}P NMR, CD_2Cl_2

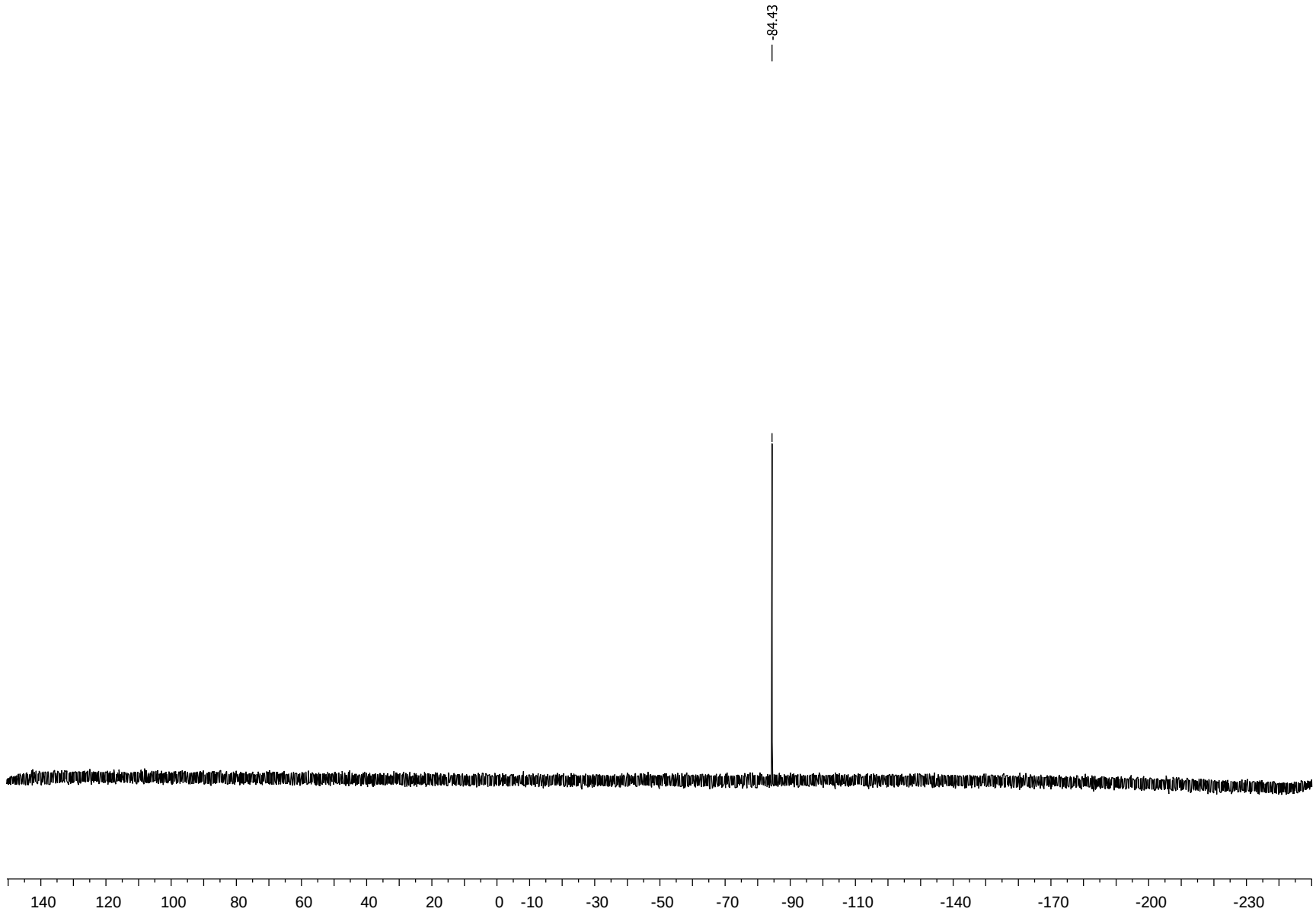


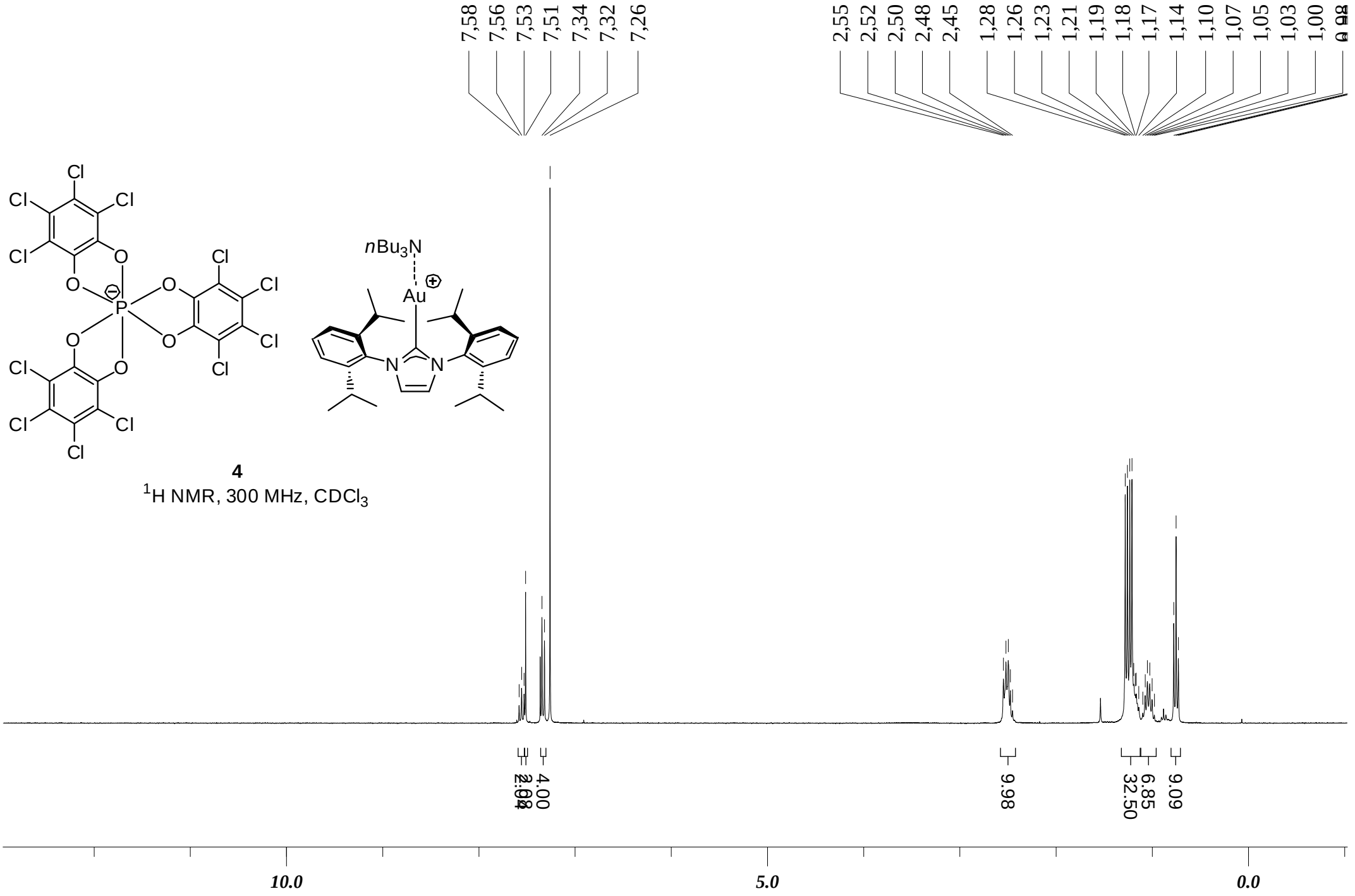
[*Λ*-TRISPHAT-N]·[HNBu$_3$] ***Λ*–3**





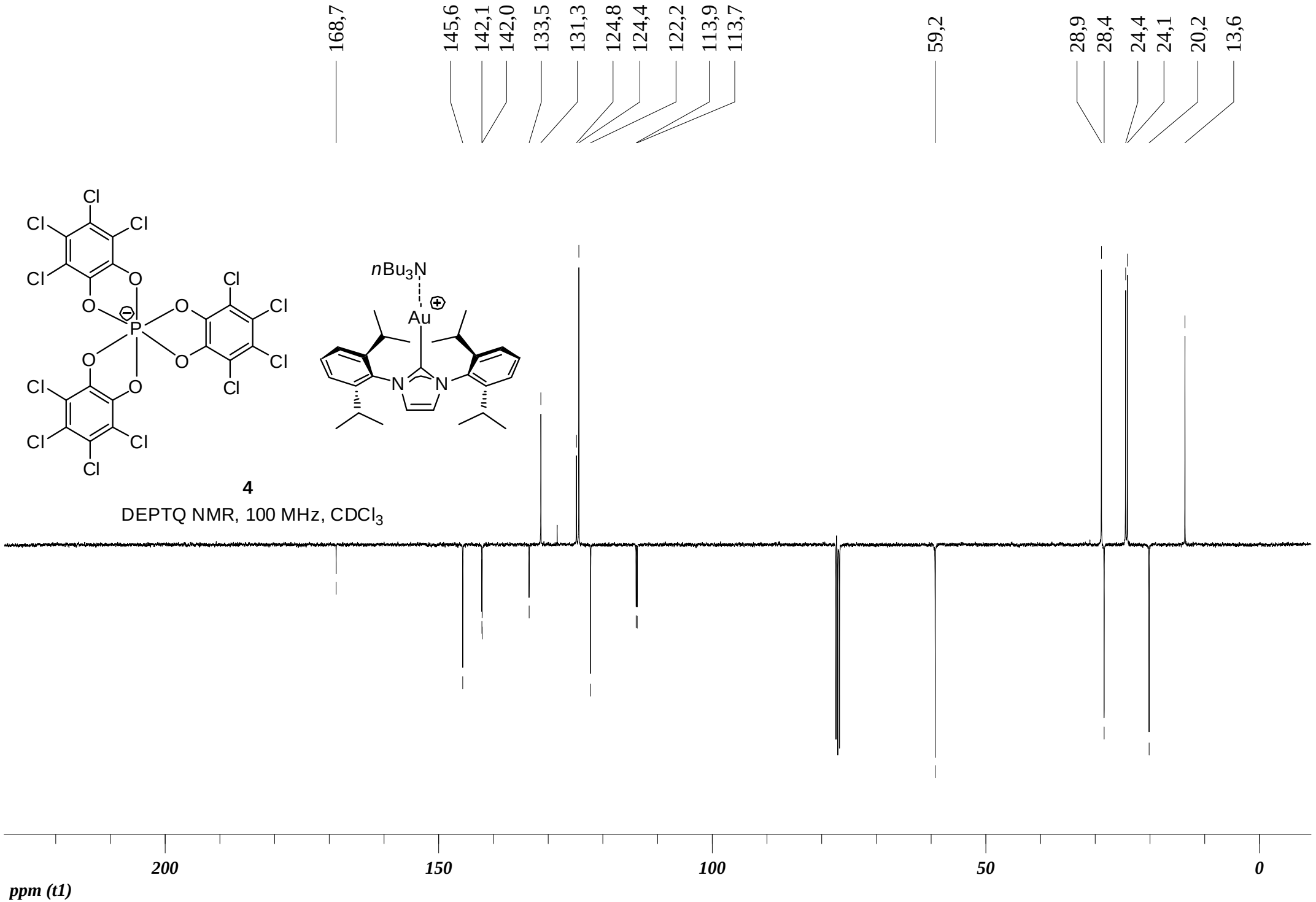


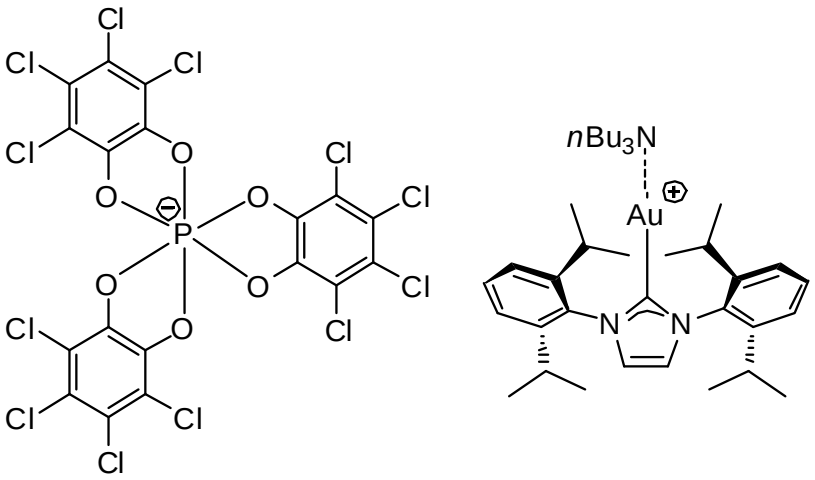




4

^{1}H NMR, 300 MHz, $CDCl_3$





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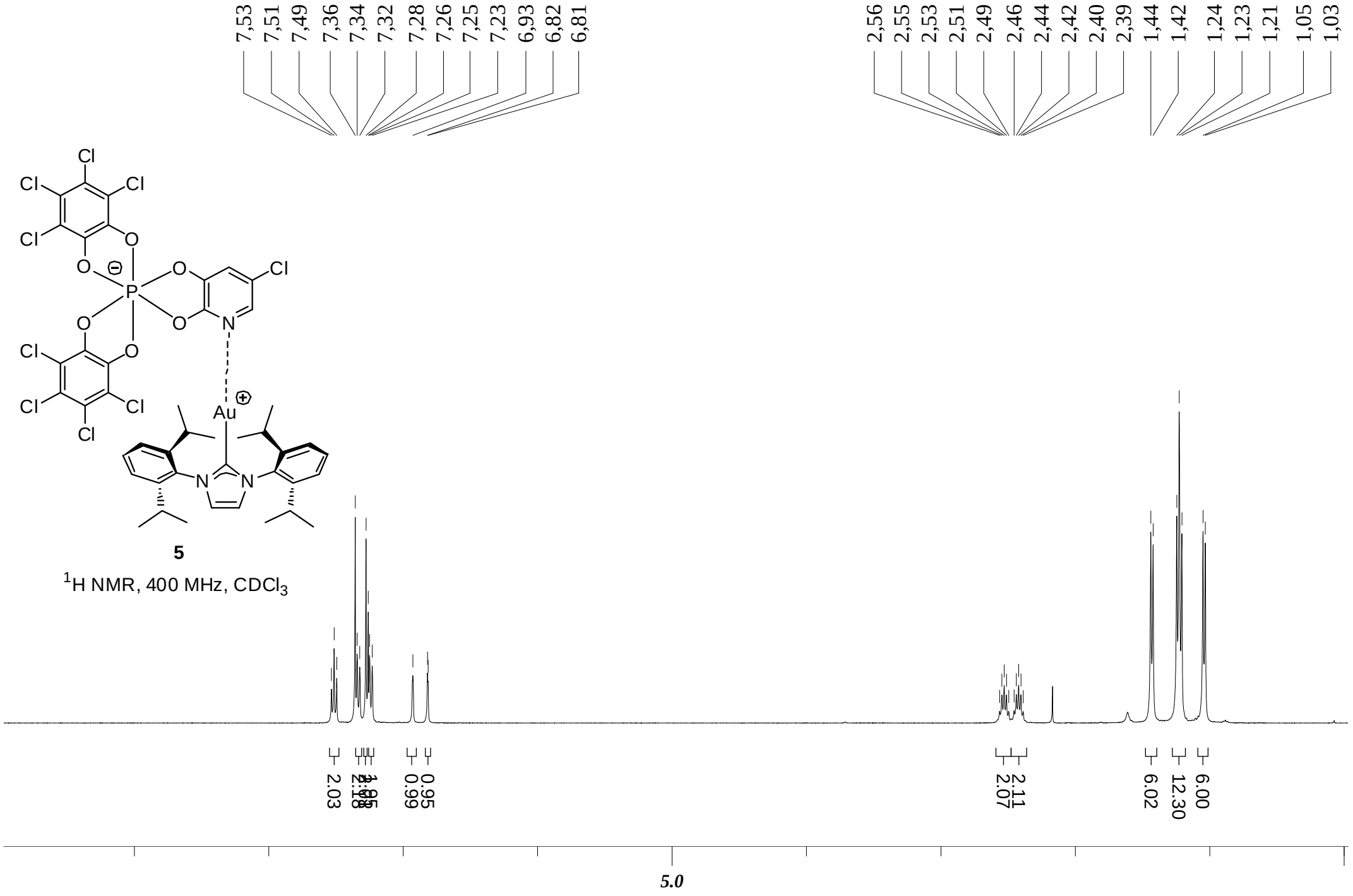
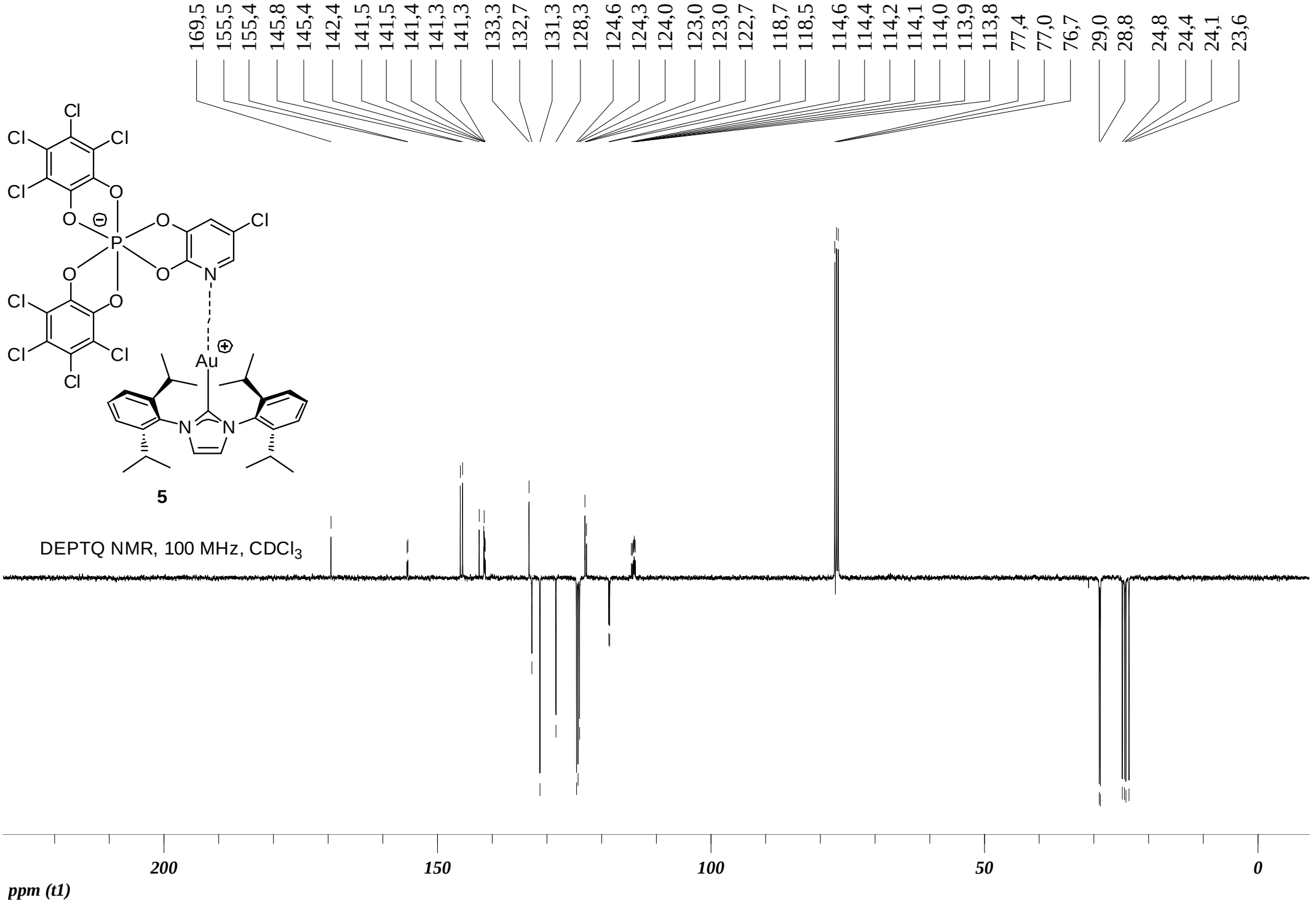
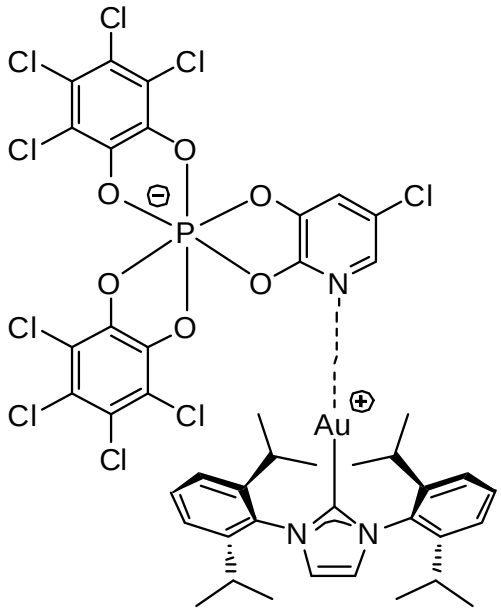
^{31}P NMR, 162 MHz, $CDCl_3$



5

^{1}H NMR, 400 MHz, $CDCl_3$





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^{31}P NMR, 162 MHz, $CDCl_3$