Supporting Information for

Amino Group Combined P/Ge and P/Sn Lewis Pairs: Synthesis and Dipolar Addition Reaction to Alkyne and Aldehyde Molecules

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Content:

S1. X-Ray Crystallographic Analysis of Complexes **1**, **7**, and **10**–**14**

Table S1. Crystal data and structure refinements of complexes **1**, **7**, **10**, and **11**[a]

	1	**7**	**10**	**11**
formula	$C_{24}H_{27}Cl_3GeNP$	$C_{27}H_{27}Cl_3GeNO_4P$	$C_{33}H_{42}GeNO_4P$	$C_{31}H_{40}GeNO_2P$
Fw	539.38	639.41	620.24	562.20
crystsyst	Orthorhombic	Monoclinic	Triclinic	Monoclinic
space group	*P2(1)2(1)2(1)*	*P2(1)/c*	*P-1*	*P2(1)/c*
a/Å	12.2706(4)	12.5358(9)	10.5333(6)	11.4190(2)
b/Å	14.1117(7)	13.0789(9)	10.8401(5)	21.2619(2)
c/Å	14.6498(6)	17.8152(13)	15.5515(6)	13.0010(2))
α/deg		90	80.549(4)	90
β/deg	90	102.189(8)	86.245(4)	18.5730(10)
γ/deg		90	68.059(5)	90
V/Å^3	2536.75(18)	1873.40(19)	1624.71(13)	3121.24(8)
Z	4	2	2	4
ρ_{calcd}/g·cm^{-3}	1.412	1.446	1.268	1.196
μ/mm^{-1}	1.598	0.677	1.027	2.007
F(000)	1104	837	652	1184
crystal size/mm^3	0.40×0.30×0.30	0.30×0.30×0.30	0.15×0.15×0.15	0.40×0.30×0.20
θ range/deg	3.13–26.00	3.29–26.00	3.10–26.00	4.02–60.18
index ranges	$-13 \le h \le 15$ $-7 \le k \le 17$ $-18 \le l \le 18$	$-11 \le h \le 12$ $-13 \le k \le 15$ $-20 \le l \le 17$	$-12 \le h \le 12$ $-13 \le k \le 13$ $-19 \le l \le 18$	$-12 \le h \le 12$ $-20 \le k \le 23$ $-14 \le l \le 14$
collected data	7161	14342	11102	12237
unique data	4721 (R_{int} = 0.0304)	7352 (R_{int} = 0.0331)	6372 (R_{int} =0.0210)	4627 (R_{int} = 0.0182)
completeness to θ (%)	99.8	99.8	99.8	99.5
data/restraints/params	4721 / 0 / 275	7352/9/416	6372 / 0 / 370	4627/0/333
GOF on F^2	1.016	1.077	1.029	1.042
final R indices [$I > 2(I)$]	R_1 = 0.0413 wR_2 = 0.0739	R_1 = 0.0724 wR_2 = 0.1751	R_1 = 0.0321 wR_2 = 0.0760	R_1 = 0.0288 wR_2 = 0.0766
R indices (all data)	R_1 = 0.0499 wR_2 = 0.0770	R_1 = 0.0901 wR_2 = 0.1873	R_1 = 0.0375 wR_2 = 0.0781	R_1 = 0.0298 wR_2 = 0.0775
Largest diff peak/hole (e·Å^{-3})	0.462/–0.340	1.291/–1.701	0.405/-0.380	0.309/–0.372

[a]All data were collected at 173(2) K using Mo K_α (λ = 0.71073 Å) radiation. $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)]^{1/2}$, GOF = $[\sum w(F_o^2 - F_c^2)^2/(N_o - N_p)]^{1/2}$.

Table S2. Crystal data and structure refinements of complexes **12–14**[a]

	12$_2$	**13**$_2$·THF	**14**·4THF
Formula	$C_{66}H_{84}Sn_2N_2O_8P_2$	$C_{58}H_{74}Cl_6Ge_2N_2O_3P_2$	$C_{72}H_{92}Cl_6Ge_2N_2O_6P_2$
Fw	1332.67	1267.01	1501.30
Crystsyst	Triclinic	Orthorhombic	Monoclinic
space group	*P-1*	*Pna2(1)*	*P2(1)/c*
a/Å	11.0403(5)	19.2113(2)	13.6361(9)
b/Å	18.5444(9)	9.36270(10)	11.3768(6)
c/Å	18.9549(11)	33.9828(4)	24.1644(13)
α/deg	119.182(6)		90
β/deg	102.169(4)	90	94.974(5)
γ/deg	93.335(4)		90
V/Å^3	3252.6(3)	2855.0(4)	3734.6(4)
Z	2	4	2
ρ_{calcd}/g·cm^{-3}	1.361	1.488	1.335
μ/mm^{-1}	0.870	1.443	1.112
F(000)	1376	1304	1564
crystal size/mm^3	0.15×0.15×0.15	0.40×0.20×0.20	0.10×0.05×0.05
θ range/deg	3.01–26.00	3.00–26.00	1.69–24.06
index ranges	$-13 \le h \le 13$ $-22 \le k \le 15$ $-23 \le l \le 23$	$-15 \le h \le 15$ $-16 \le k \le 9$ $-21 \le l \le 21$	$-15 \le h \le 14$ $-12 \le k \le 14$ $-26 \le l \le 27$
collected data	24079	11876	11609
unique data	12787 (R_{int} = 0.0328)	5595 (R_{int} =0.0395)	5825 (R_{int} = 0.0327)
completeness to θ (%)	99.8	99.9	98.7
data/restraints/params	12787/ 0 / 739	5595 / 0 / 339	5825 / 90 / 425
GOF on F^2	0.998	1.019	1.025
final R indices [$I > 2(I)$]	R_1 = 0.0375 wR_2 = 0.0747	R_1 = 0.0413 wR_2 = 0.0862	R_1 = 0.0463 wR_2 = 0.1262
R indices (all data)	R_1 = 0.0486 wR_2 = 0.0788	R_1 = 0.0568 wR_2 = 0.0918	R_1 = 0.0594 wR_2 = 0.1377
Largest diff peak/hole (e·Å^{-3})	0.393/–0.429	0.426/-0.323	0.513/–0.520

[a]All data were collected at 173(2) K using Mo K$_\alpha$ (λ = 0.71073 Å) radiation. $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)]^{1/2}$, GOF = $[\sum w(F_o^2 - F_c^2)^2/(N_o - N_p)]^{1/2}$.

S2. Important NMR Spectral Data

Table S3. ^{31}P NMR data of complexes **1–5**[a]

Compound	^{31}P
$Ph_2PN(2,6\text{-}iPr_2C_6H_2)GeCl_3$ **(1)**	64.5
$Ph_2PN(2,4,6\text{-}Me_3C_6H_2)GeCl_3$ **(2)**	53.6
$Ph_2PN(C_6H_{11})GeCl_3$ **(3)**	49.3
$Ph_2PN(2,6\text{-}iPr_2C_6H_3)GeMe_3$ **(4)**	58.6
$Ph_2PN(2,6\text{-}iPr_2C_6H_3)SnMe_3$ **(5)**	64.6

[a] Chemical shifts in ppm, δ-scale.

Table S4. ^{31}P NMR data of complexes **6–12**[a]

Compound	^{31}P
$[Ph_2PN(2,6\text{-}iPr_2C_6H_3)GeCl_3](MeO_2CC{=}CCO_2Me)$ **(6)**	15.0
$[Ph_2PN(2,4,6\text{-}Me_3C_6H_2)GeCl_3](MeO_2CC{=}CCO_2Me)$ **(7)**	14.4
$[Ph_2PN(C_6H_{11})GeCl_3](MeO_2CC{=}CCO_2Me)$ **(8)**	11.6
$[Ph_2PN(2,4,6\text{-}Me_3C_6H_2)GeCl_3](HC{=}CCO_2Me)$ **(9)**	11.8
$2,6\text{-}iPr_2C_6H_3N{=}P(Ph_2)C(CO_2Me){=}C(CO_2Me)GeMe_3$ **(10)**	–22.7
$2,6\text{-}iPr_2C_6H_3N{=}P(Ph_2)C(H){=}C(CO_2Me)GeMe_3$ **(11)**	–19.5
$2,6\text{-}iPr_2C_6H_3N{=}P(Ph_2)C(CO_2Me){=}C(CO_2Me)SnMe_3$ **(12)**	–19.2

[a] Chemical shifts in ppm, δ-scale.

Table S5. Selected ^1H and ^{13}C NMR data for the $MeO_2CC{=}CCO_2Me$ group of complexes **6–8**, **10**, and **12**[a]

Compound	**6**	**7**	**8**	**10**	**12**
^1H, $=C(P)CO_2\mathit{Me}$	3.53	3.57	3.56	3.13	3.23
^1H, $=C(M)CO_2\mathit{Me}$	4.03	4.01	3.91	3.73	3.75
^{13}C, $=C(P)CO_2\mathit{Me}$	53.0	53.1	58.2	51.7	51.7
^{13}C, $=C(M)CO_2\mathit{Me}$	53.0	52.9	53.2	52.0	52.0
^{13}C, $=\mathit{C}(P)CO_2Me$	116.1	115.4	123.9	148.1	150.0
^{13}C, $=\mathit{C}(M)CO_2Me$	186.3	187.4	171.8	158.1	160.7
^{13}C, $=C(P)\mathit{C}O_2Me$	160.7	160.8	160.3	167.9	167.7
^{13}C, $=C(M)\mathit{C}O_2Me$	167.6	167.4	166.7	171.2	172.0

[a] Chemical shifts in ppm, δ-scale. M = Ge for **6–8** and **10** and Sn for **12**

Table S6. Selected ^1H and ^{13}C NMR data for the $HC{=}CCO_2Me$ group of complexes **9** and **11**[a]

Compound	**9**	**11**
^1H, $=C(P)\mathit{H}$	7.32	7.92
^1H, $=C(Ge)CO_2\mathit{Me}$	3.98	3.78
^{13}C, $=C(Ge)CO_2\mathit{Me}$	53.0	52.1
^{13}C, $=\mathit{C}(P)H$	122.0	145.8

^{13}C, $=\mathit{C}(Ge)CO_2Me$	173.6	157.1
^{13}C, $=C(Ge)\mathit{C}O_2Me$	166.2	171.3

[a] Chemical shifts in ppm, *δ*-scale.

S3. NMR Spectra of Complexes **1–13**

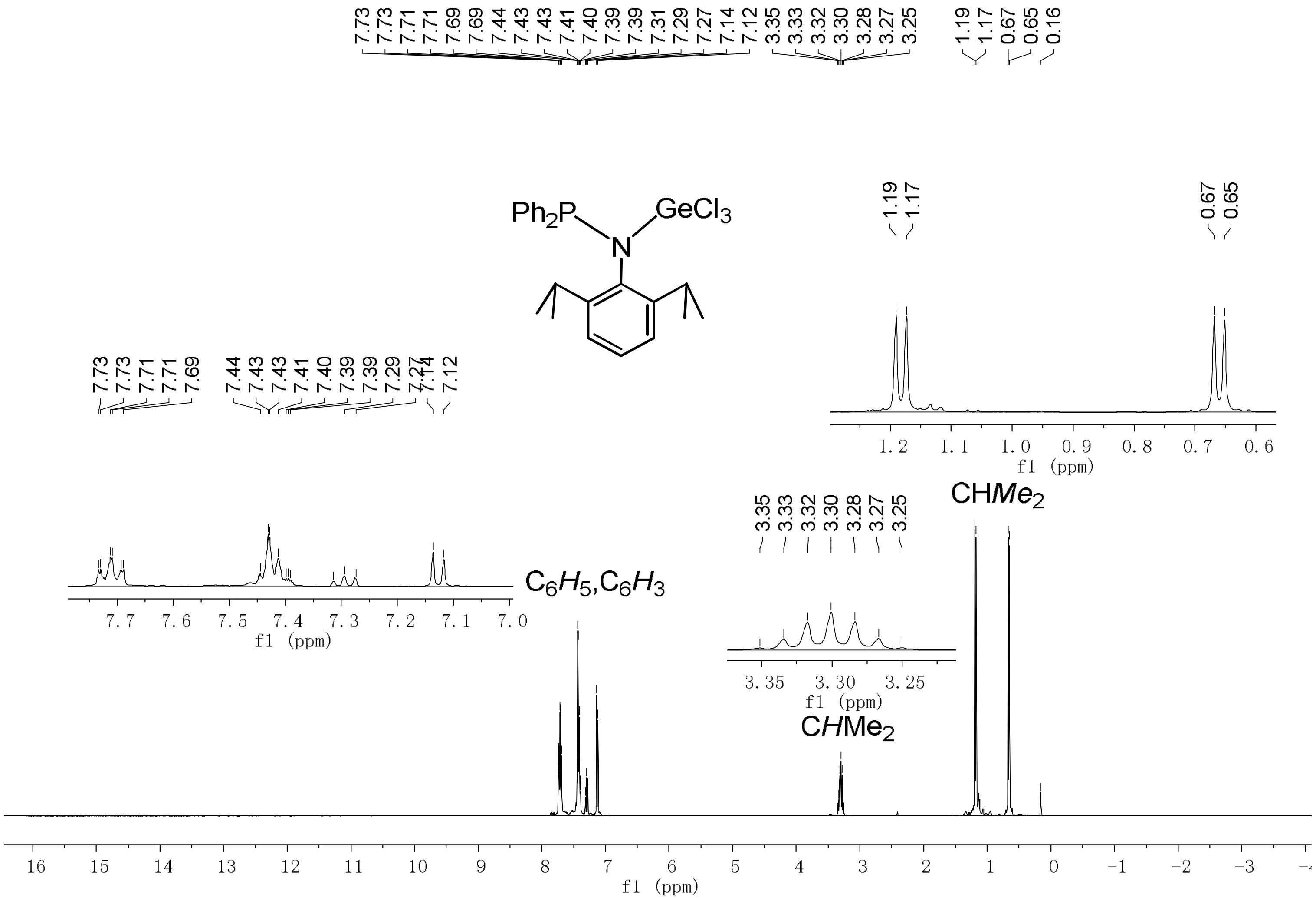

Figure 1s-a. ^{1}H NMR spectrum of **1** in $CDCl_3$

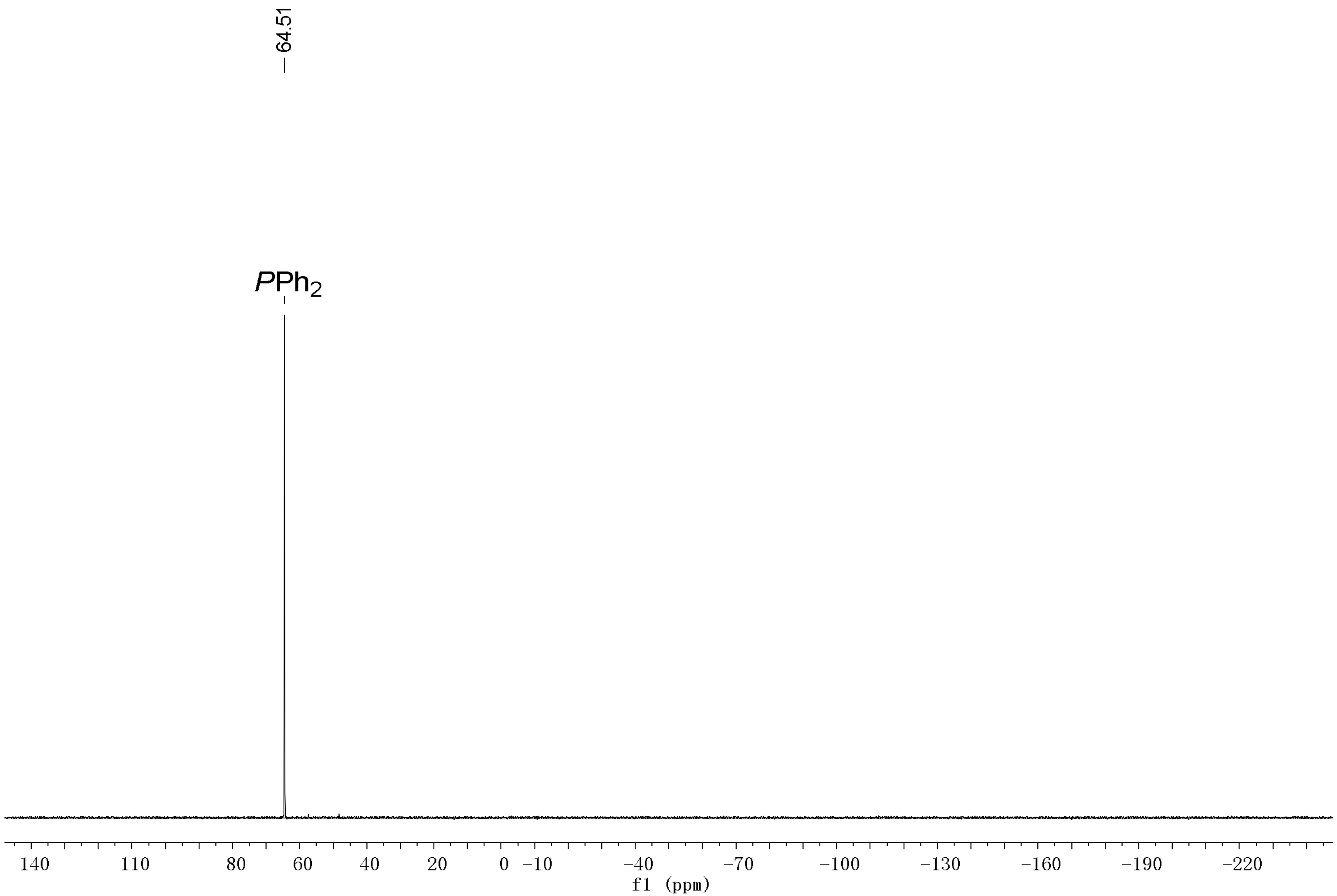

Figure 1s-b. ^{31}P NMR spectrum of **1** in $CDCl_3$

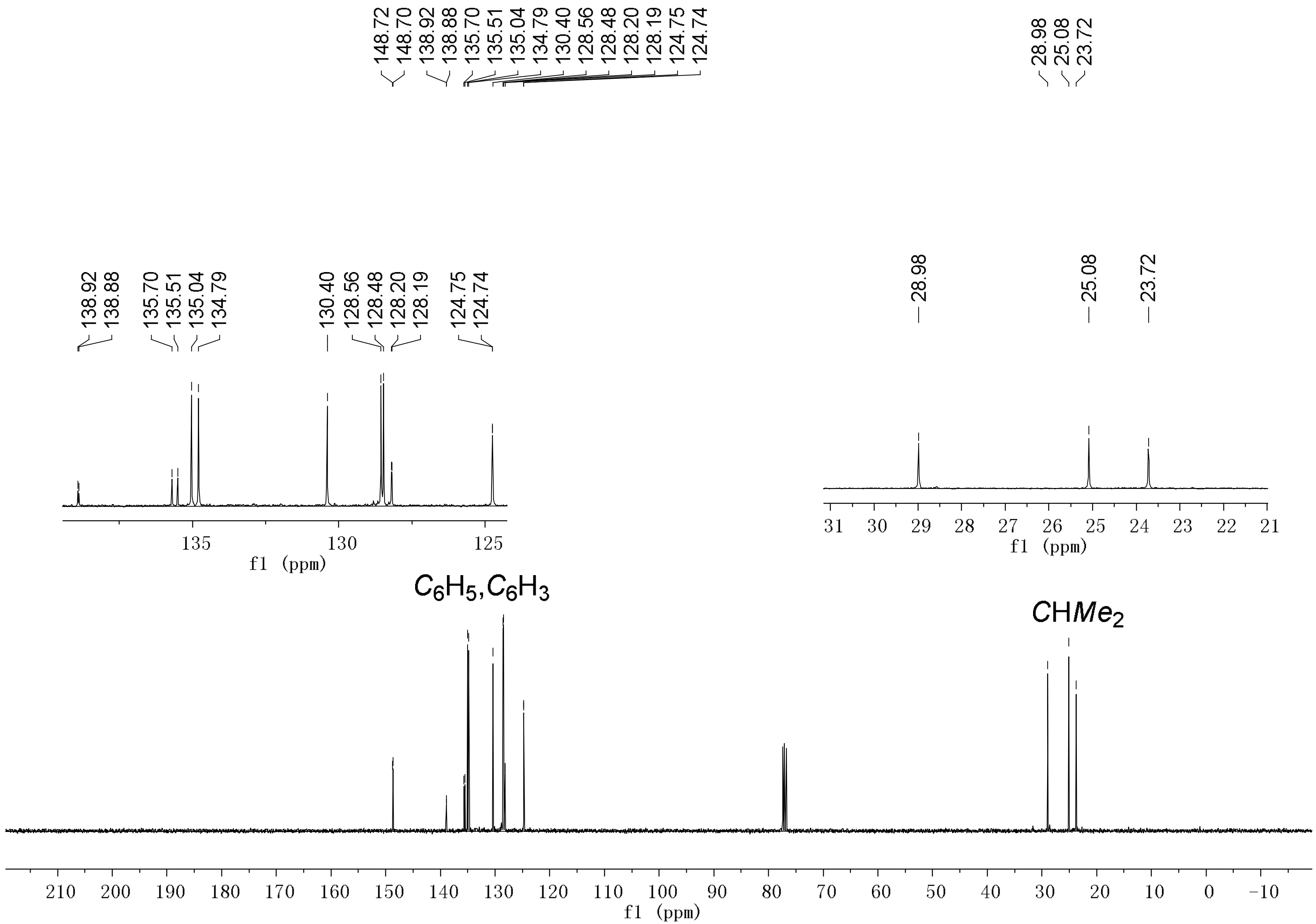

Figure 1s-c. ^{13}C NMR spectrum of **1** in $CDCl_3$

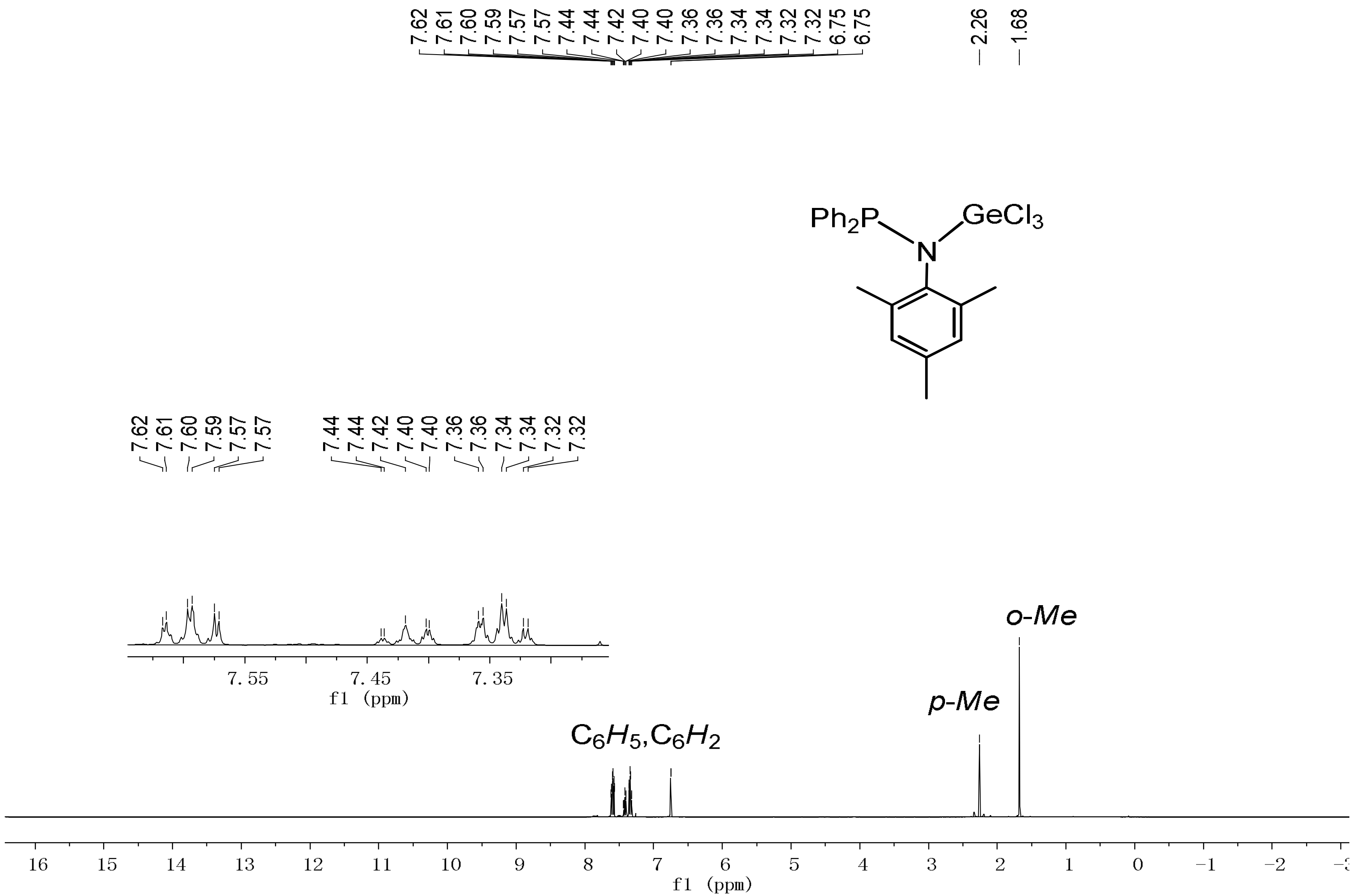

Figure 2s-a. ^{1}H NMR spectrum of **2** in $CDCl_3$

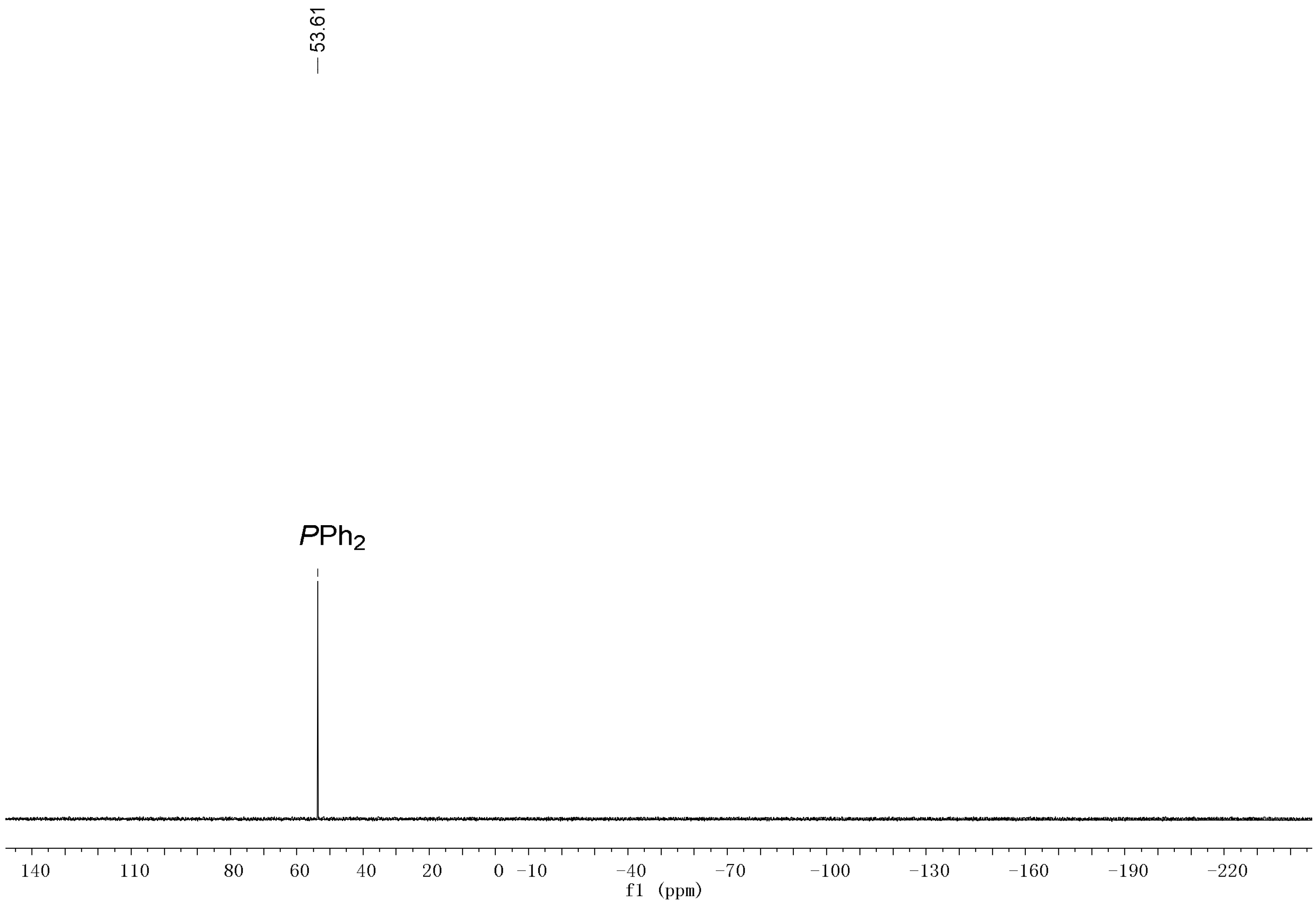

Figure 2s-b. ^{31}P NMR spectrum of **2** in $CDCl_3$

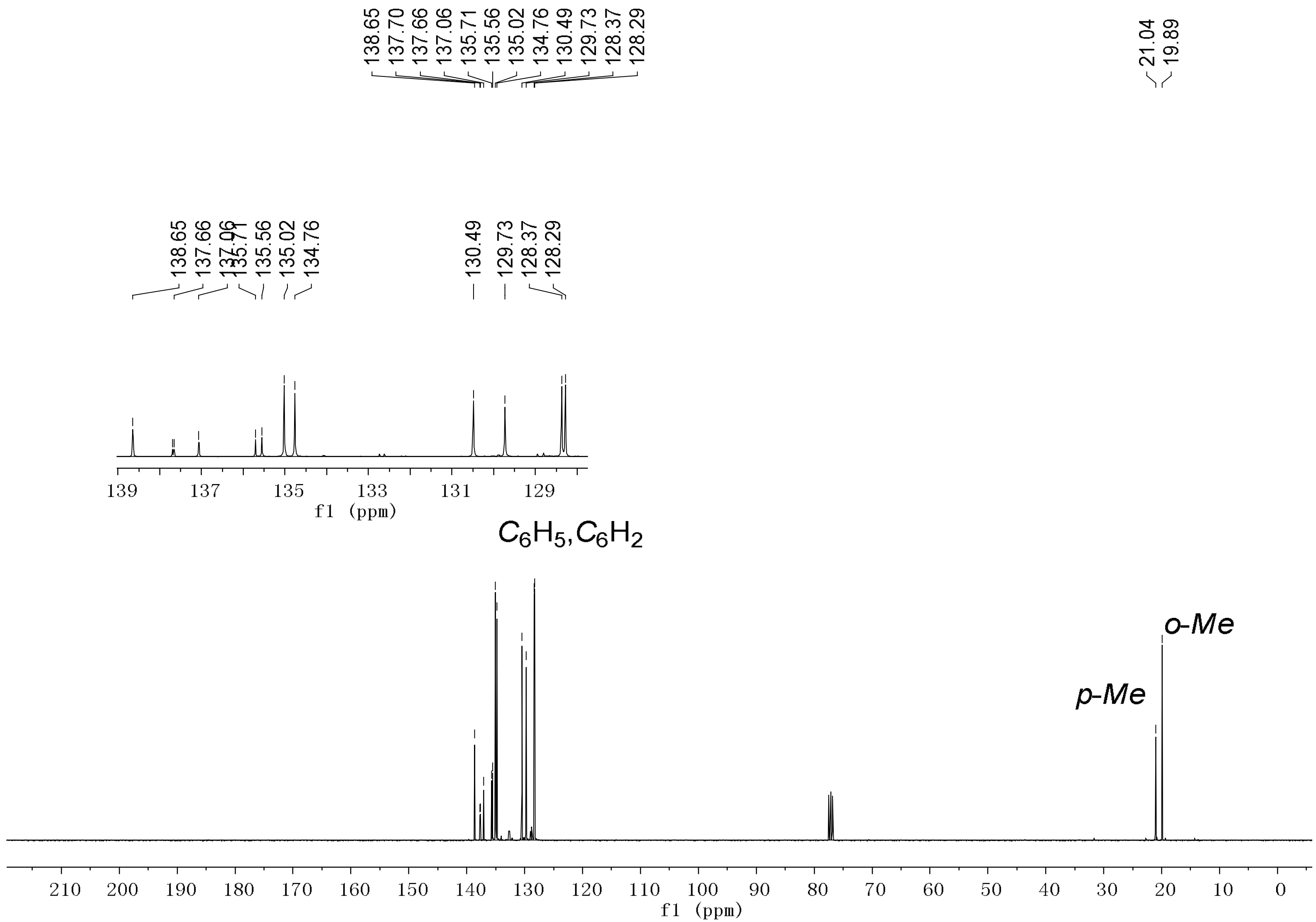

Figure 2s-c. ^{13}C NMR spectrum of **2** in $CDCl_3$

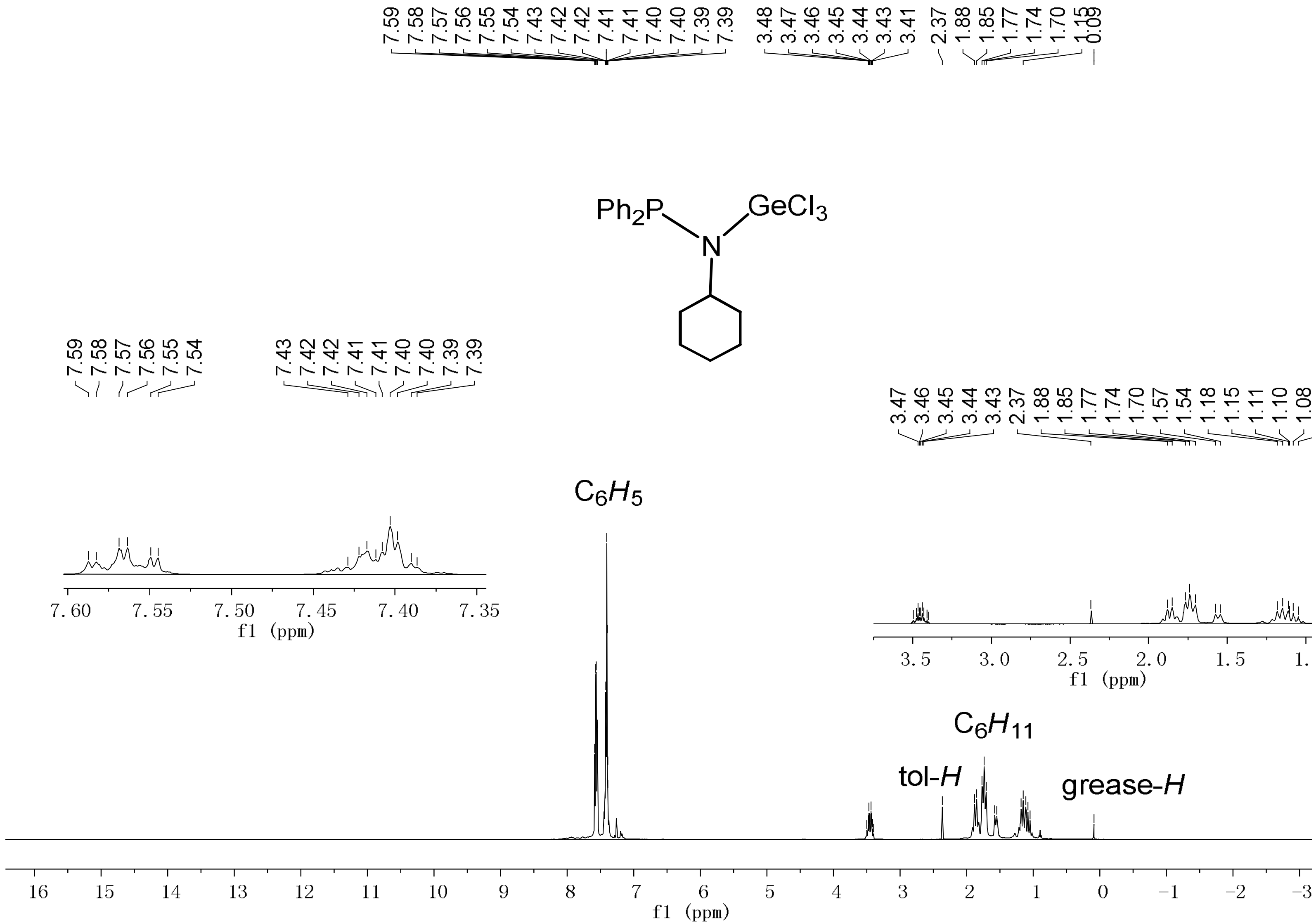

Figure 3s-a. ^{1}H NMR spectrum of **3** in $CDCl_3$

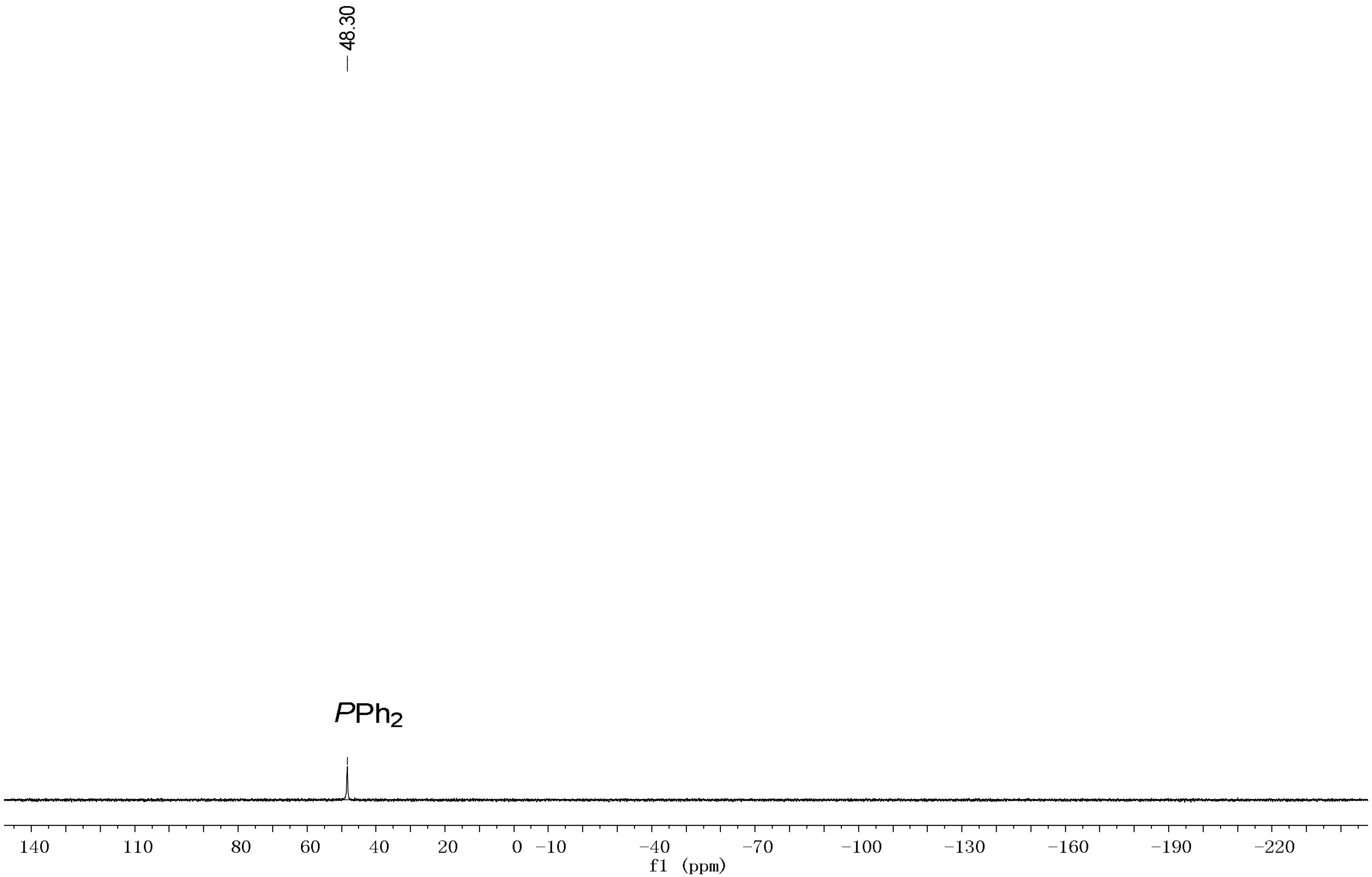

Figure 3s-b. ^{31}P NMR spectrum of **3** in $CDCl_3$

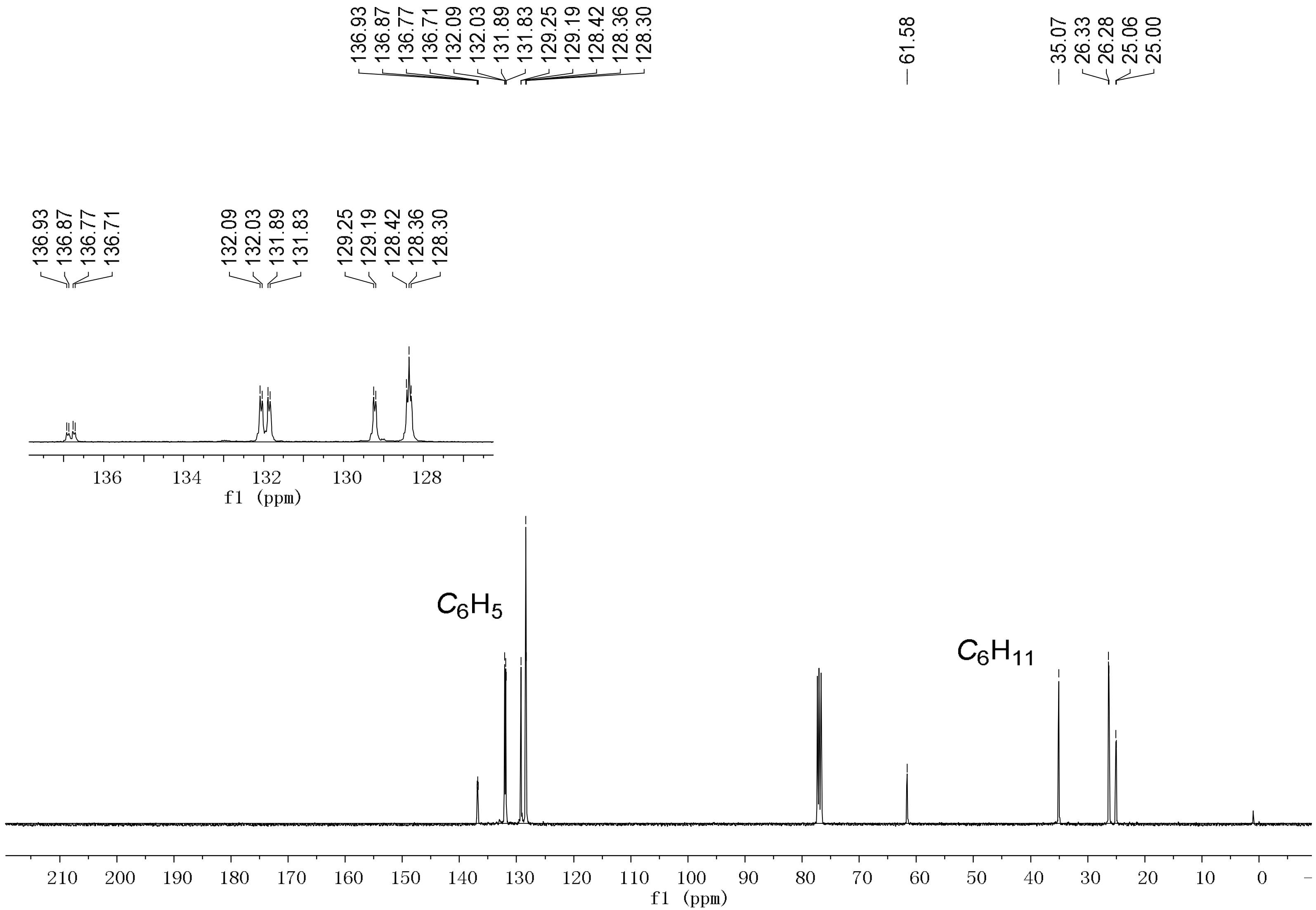

Figure 3s-c. ^{13}C NMR spectrum of **3** in $CDCl_3$

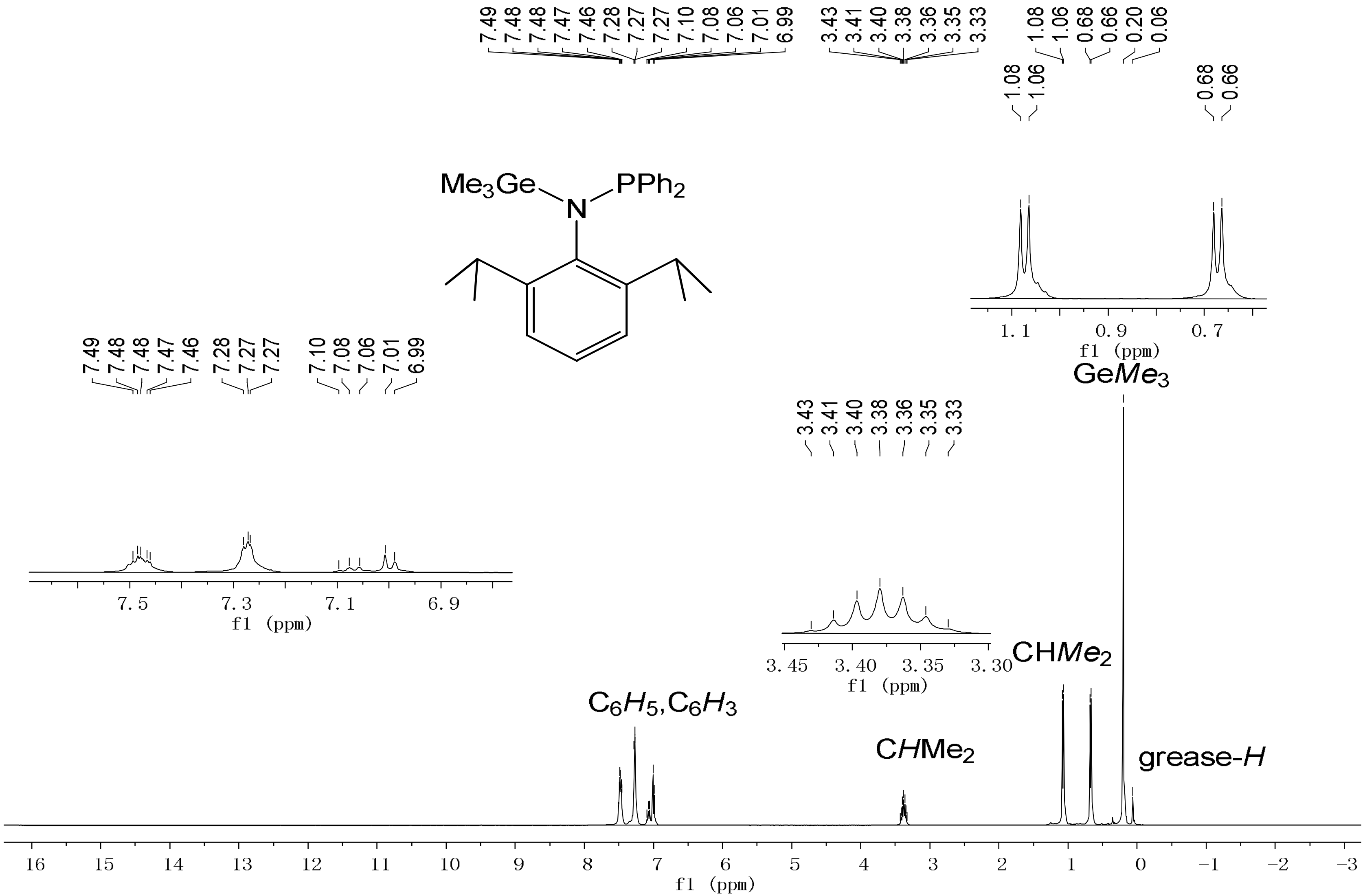

Figure 4s-a. ^{1}H NMR spectrum of **4** in $CDCl_3$

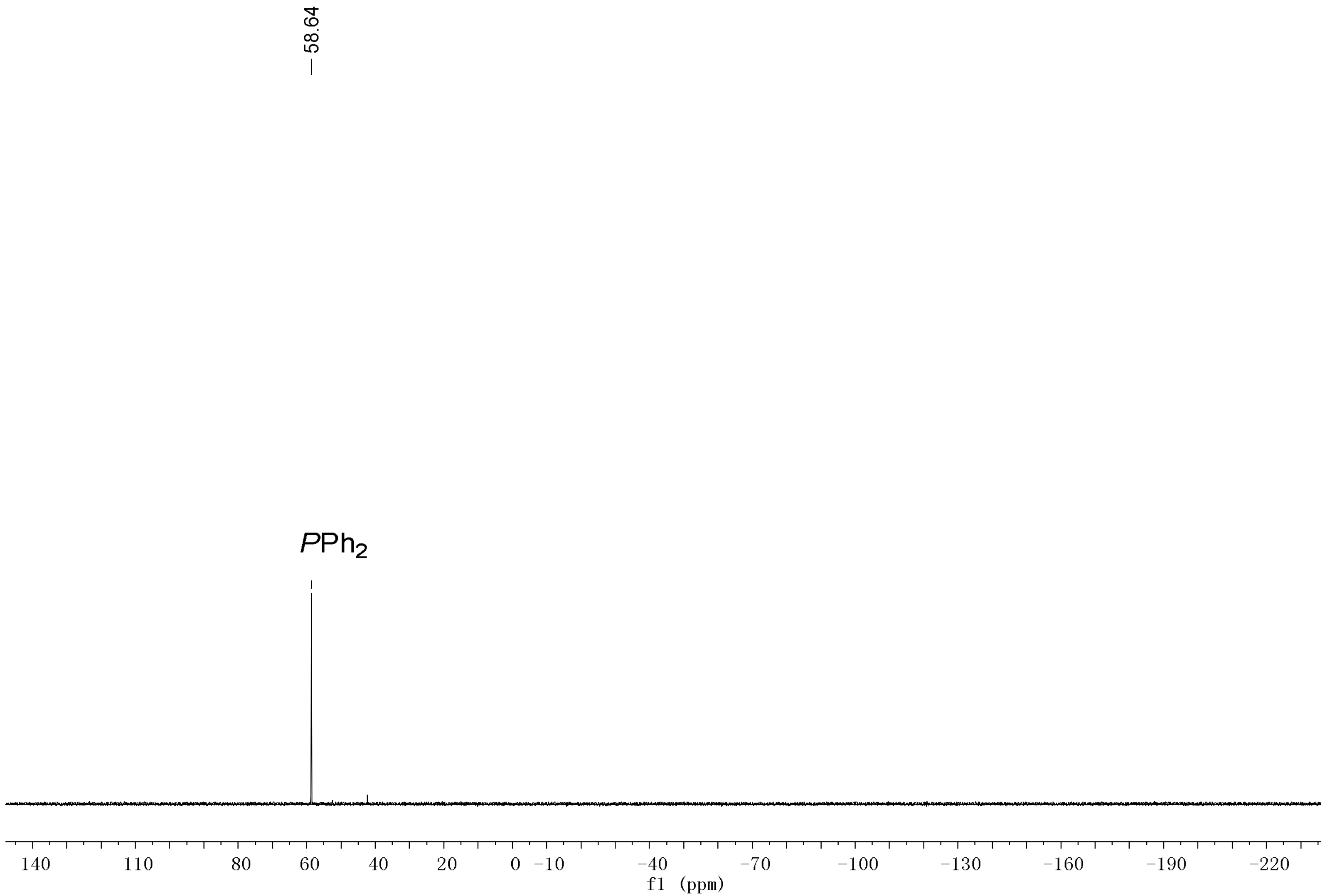

Figure 4s-b. ^{31}P NMR spectrum of **4** in $CDCl_3$

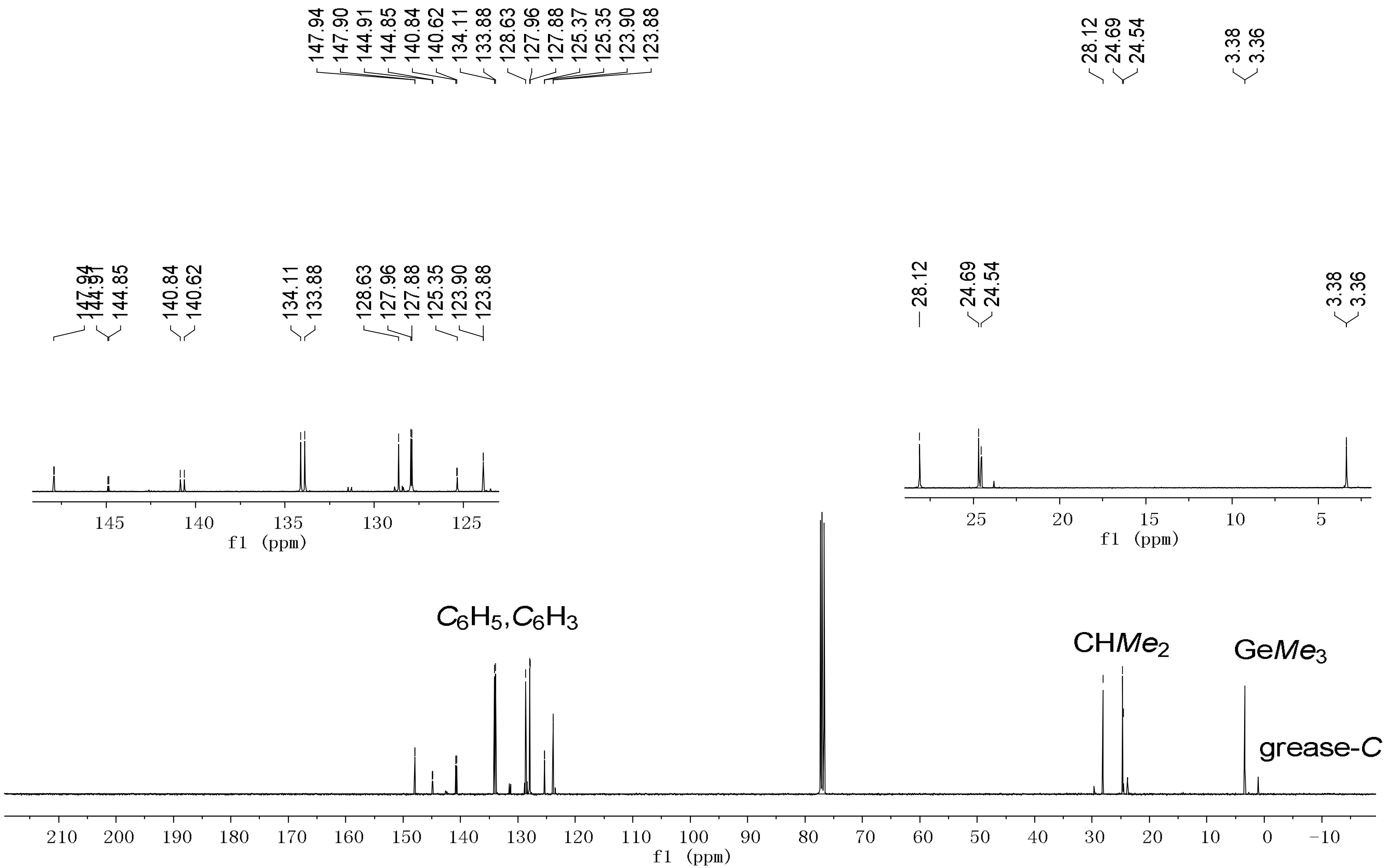

Figure 4s-c. ^{13}C NMR spectrum of **4** in $CDCl_3$

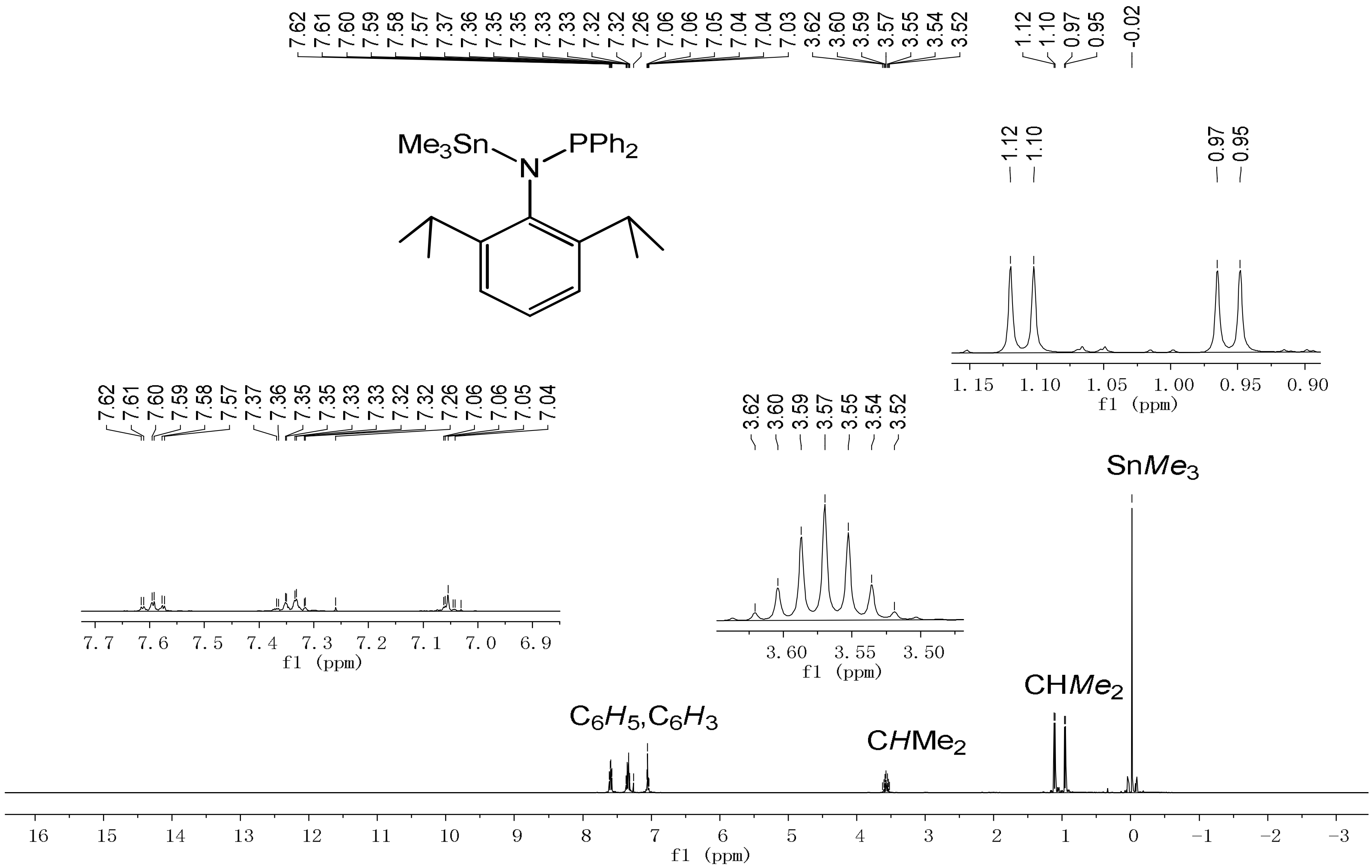

Figure 5s-a. ^{1}H NMR spectrum of **5** in $CDCl_3$

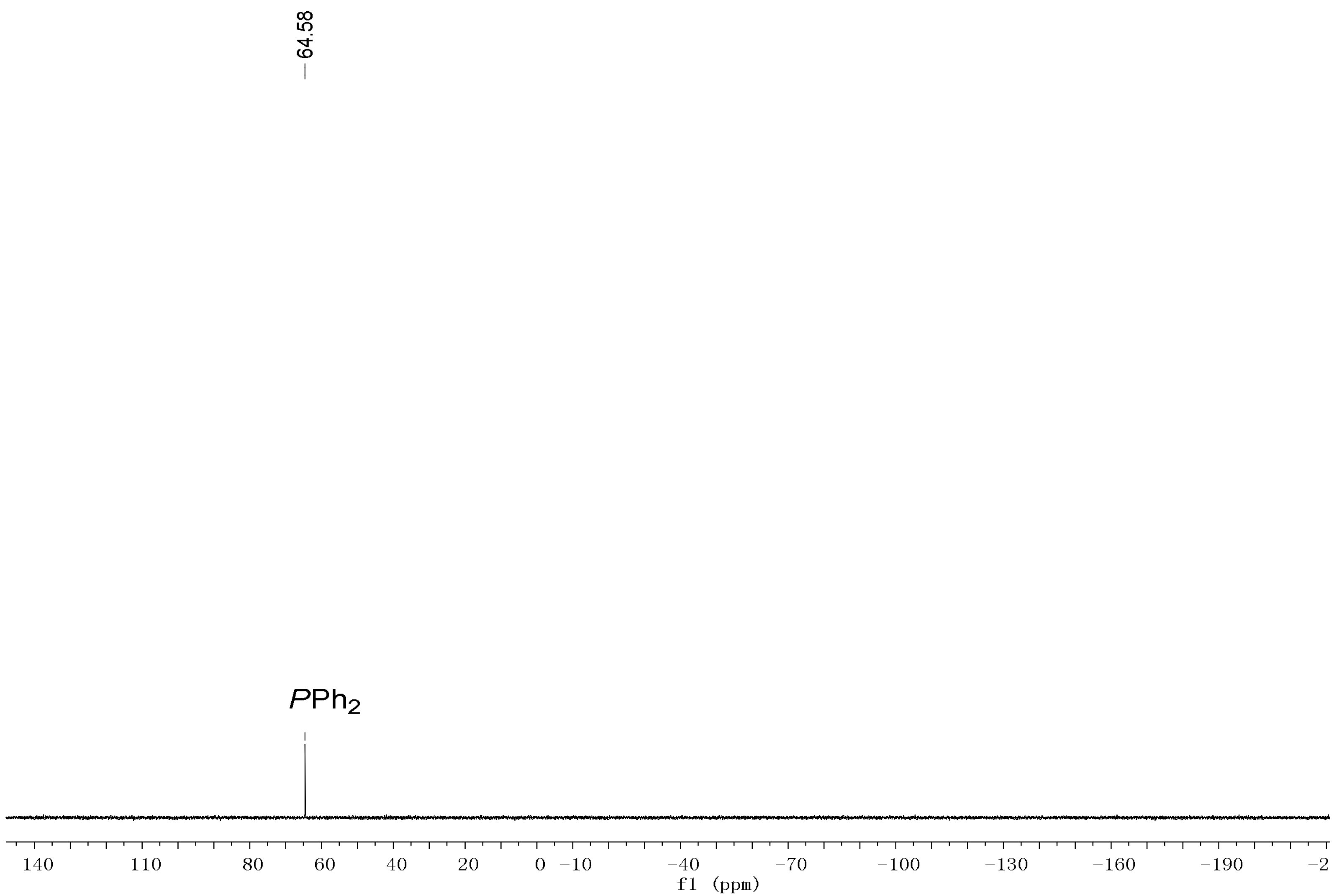

Figure 5s-b. ^{31}P NMR spectrum of **5** in $CDCl_3$

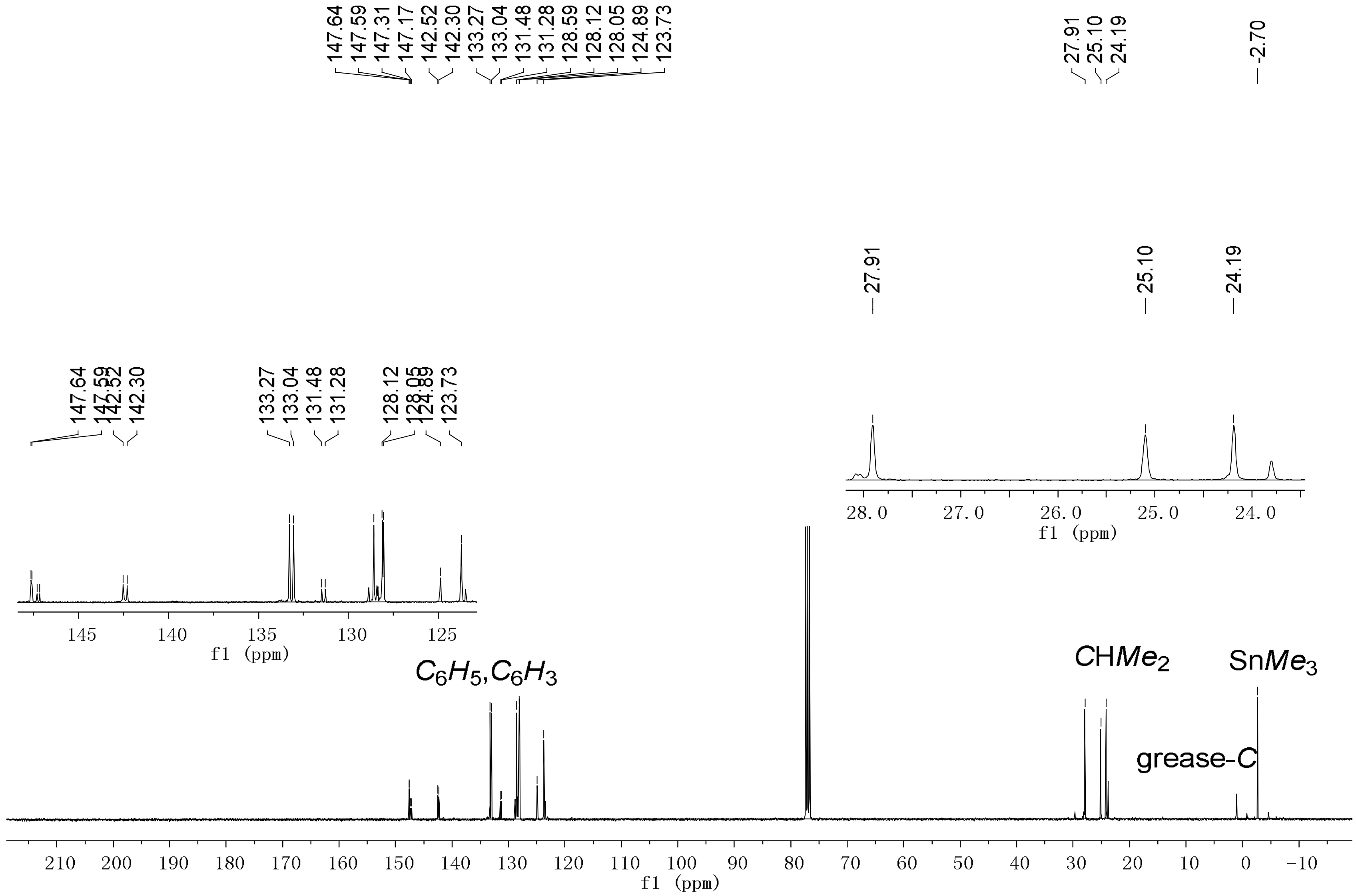

Figure 5s-c. ^{13}C NMR spectrum of **5** in $CDCl_3$

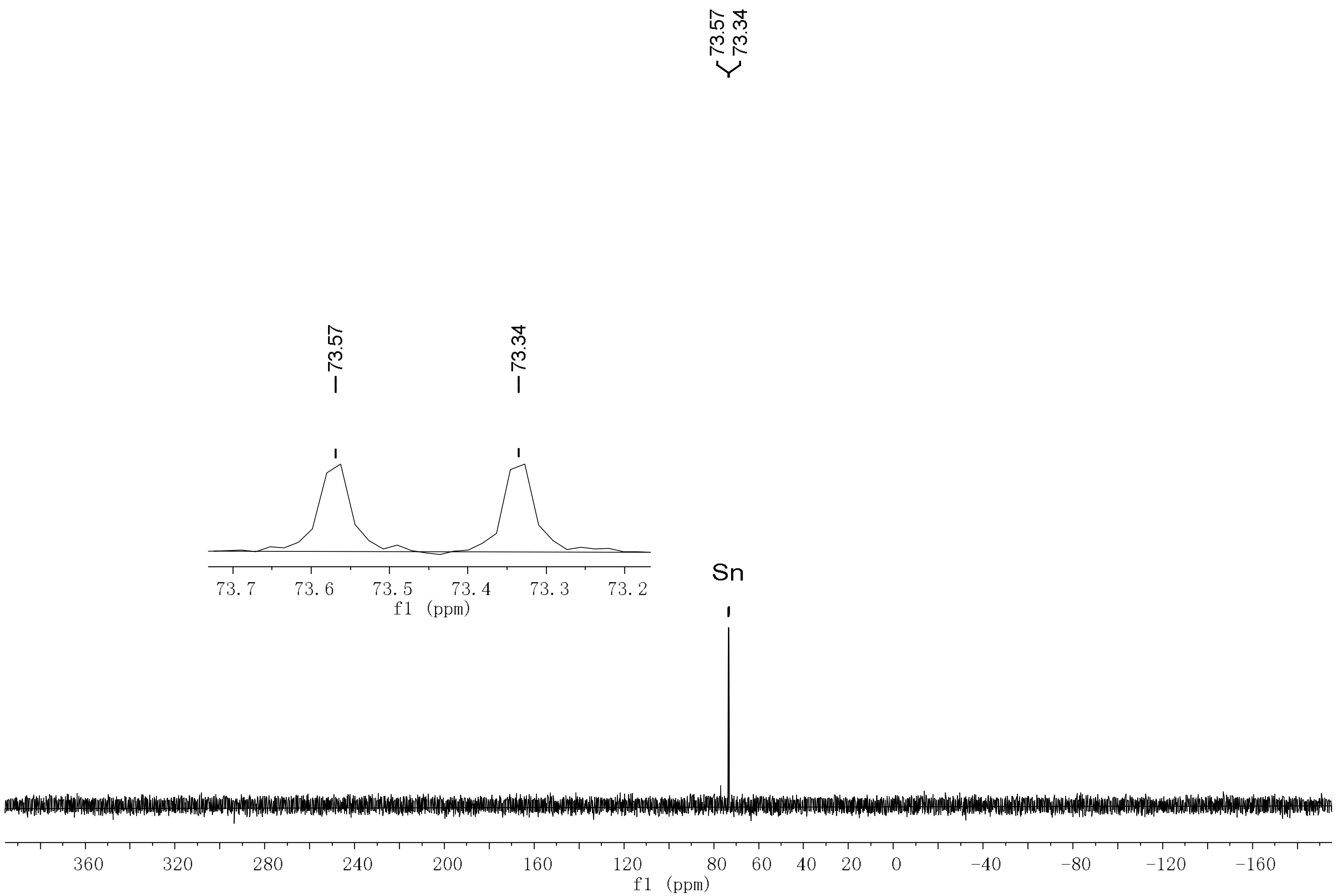

Figure 5s-d. ^{119}Sn NMR spectrum of **5** in $CDCl_3$

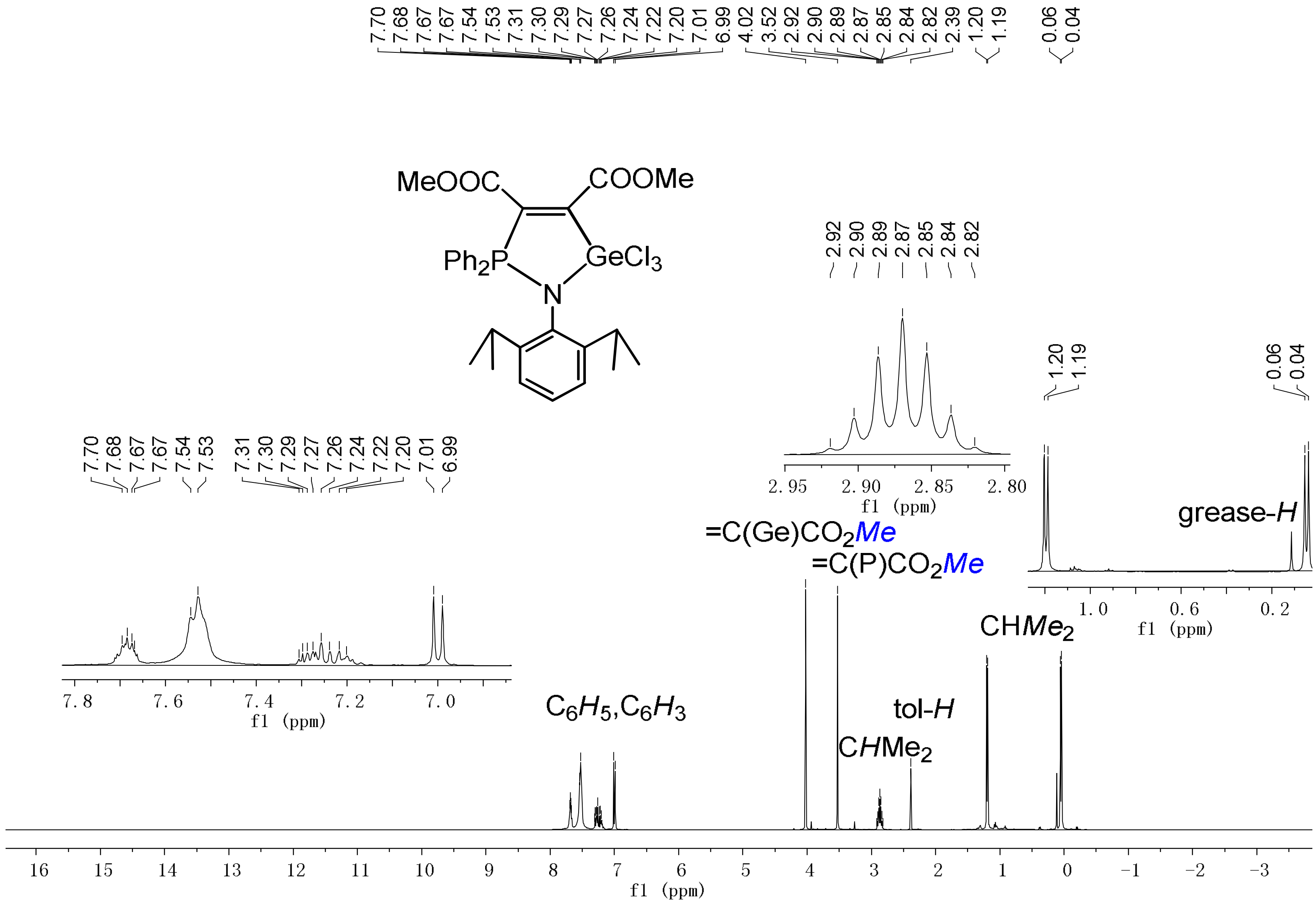

Figure 6s-a. ^{1}H NMR spectrum of **6** in $CDCl_3$

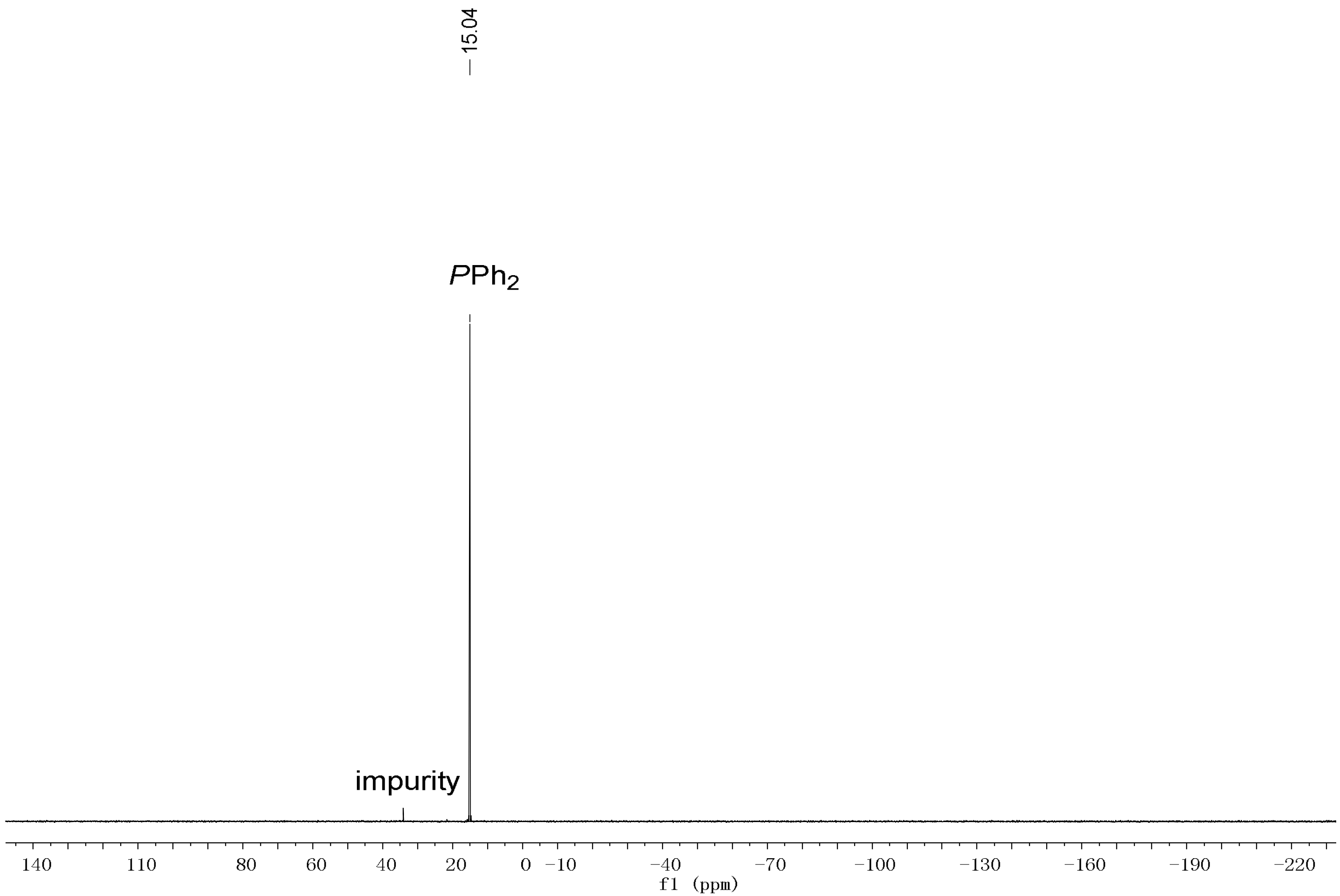

Figure 6s-b. ^{31}P NMR spectrum of **6** in $CDCl_3$

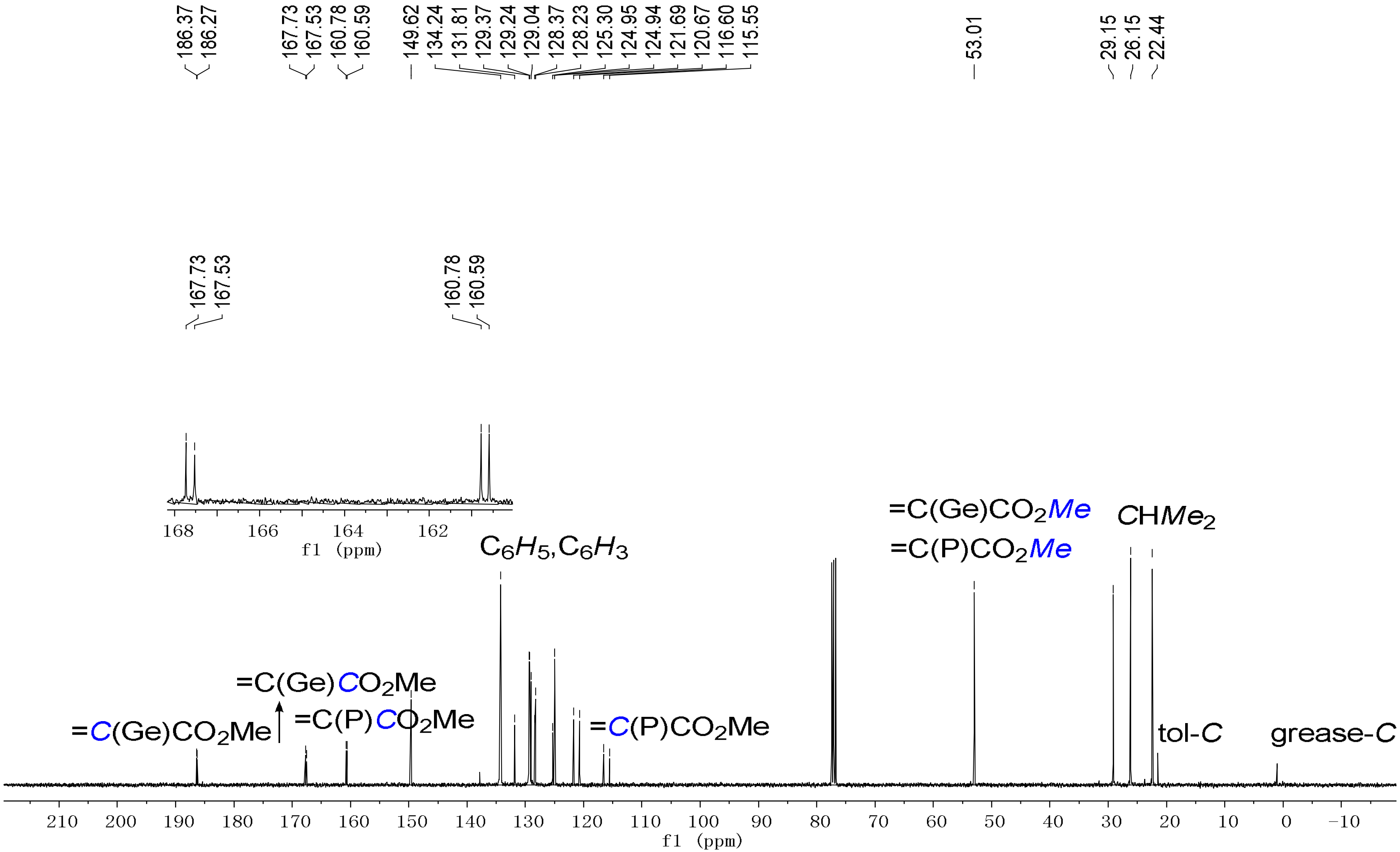

Figure 6s-c. ^{13}C NMR spectrum of **6** in $CDCl_3$

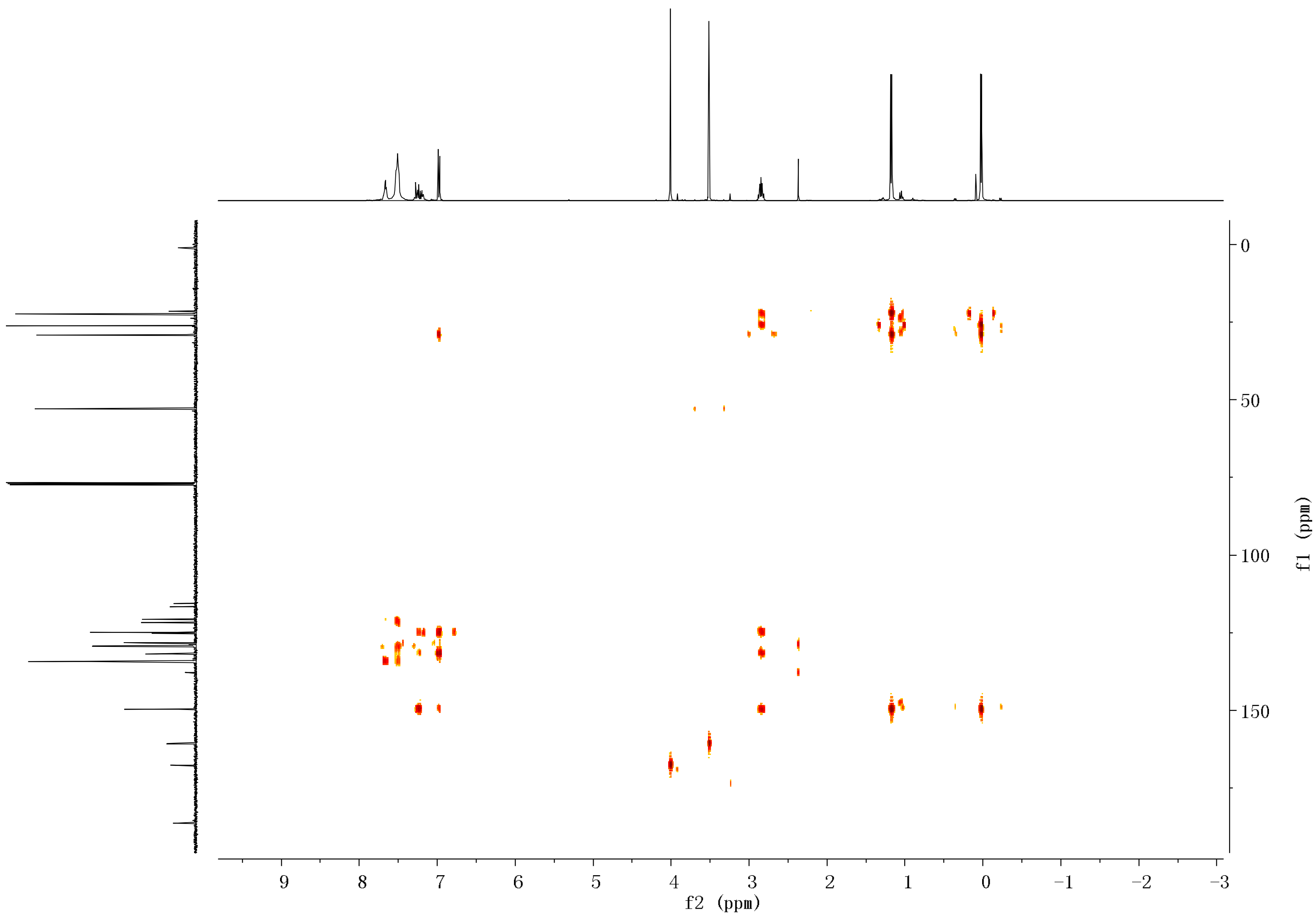

Figure 6s-d. [1]H,[13]C-HMBC spectrum of **6** in $CDCl_3$

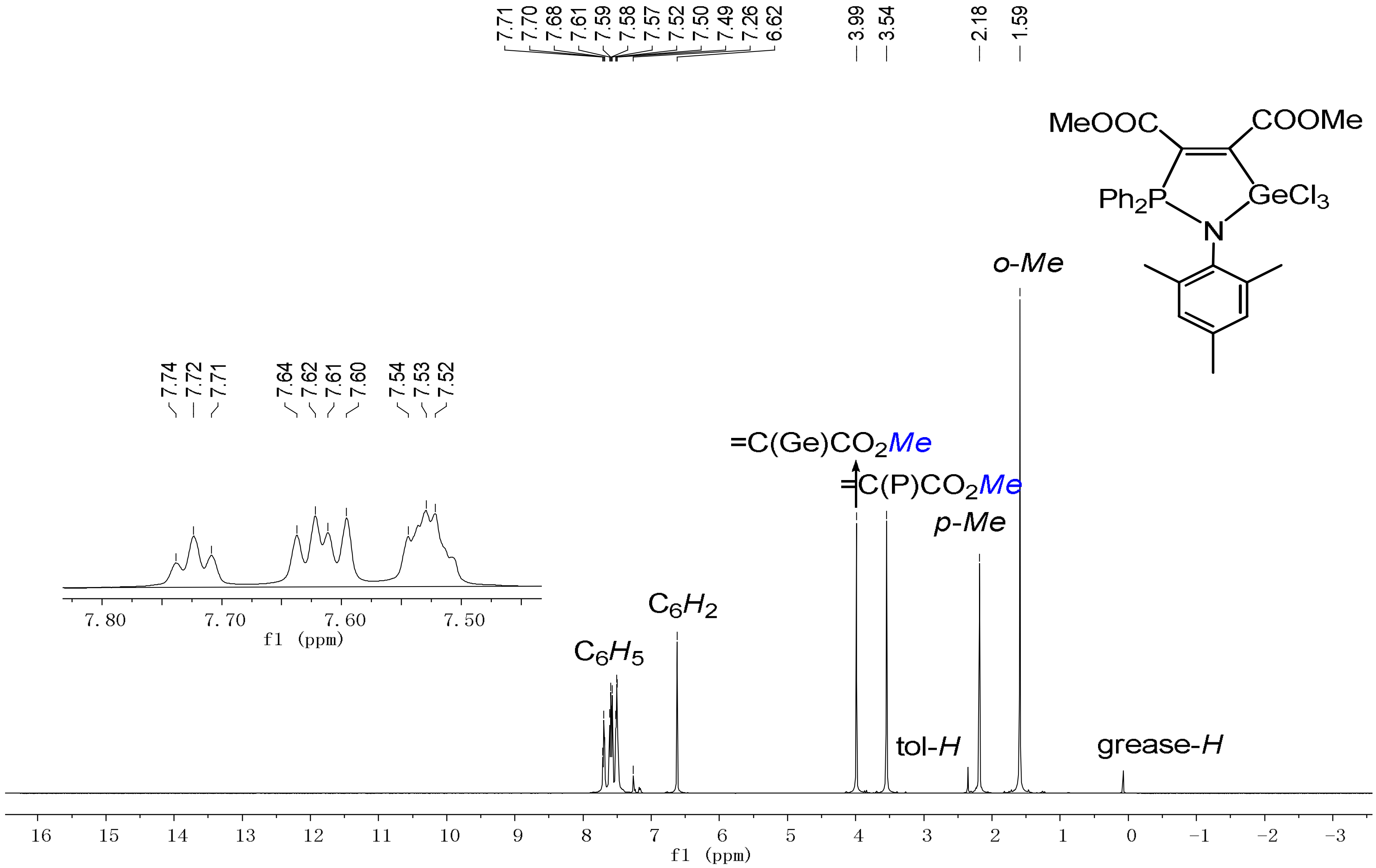

Figure 7s-a. ^{1}H NMR spectrum of **7** in $CDCl_3$

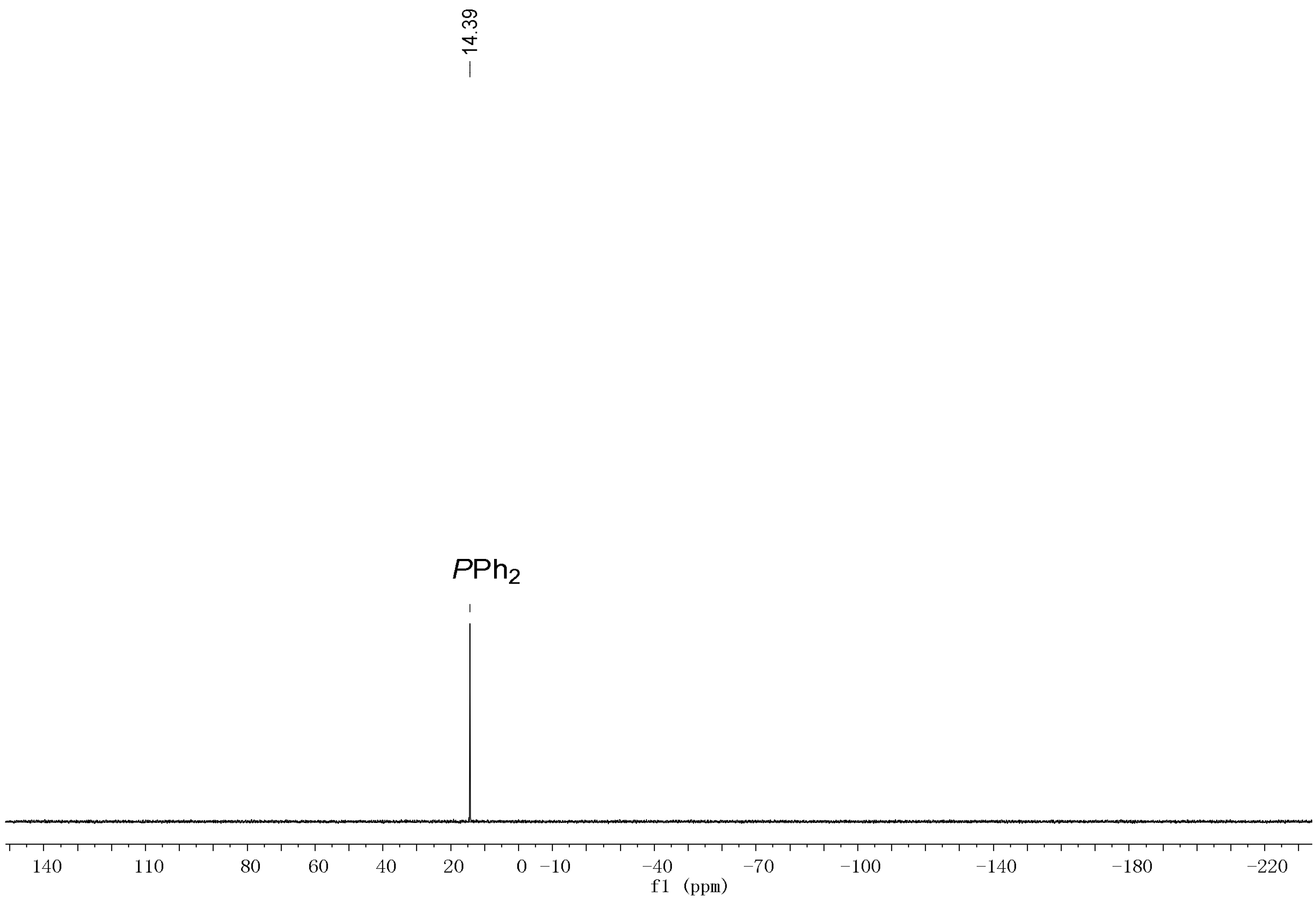

Figure 7s-b. ^{31}P NMR spectrum of **7** in $CDCl_3$

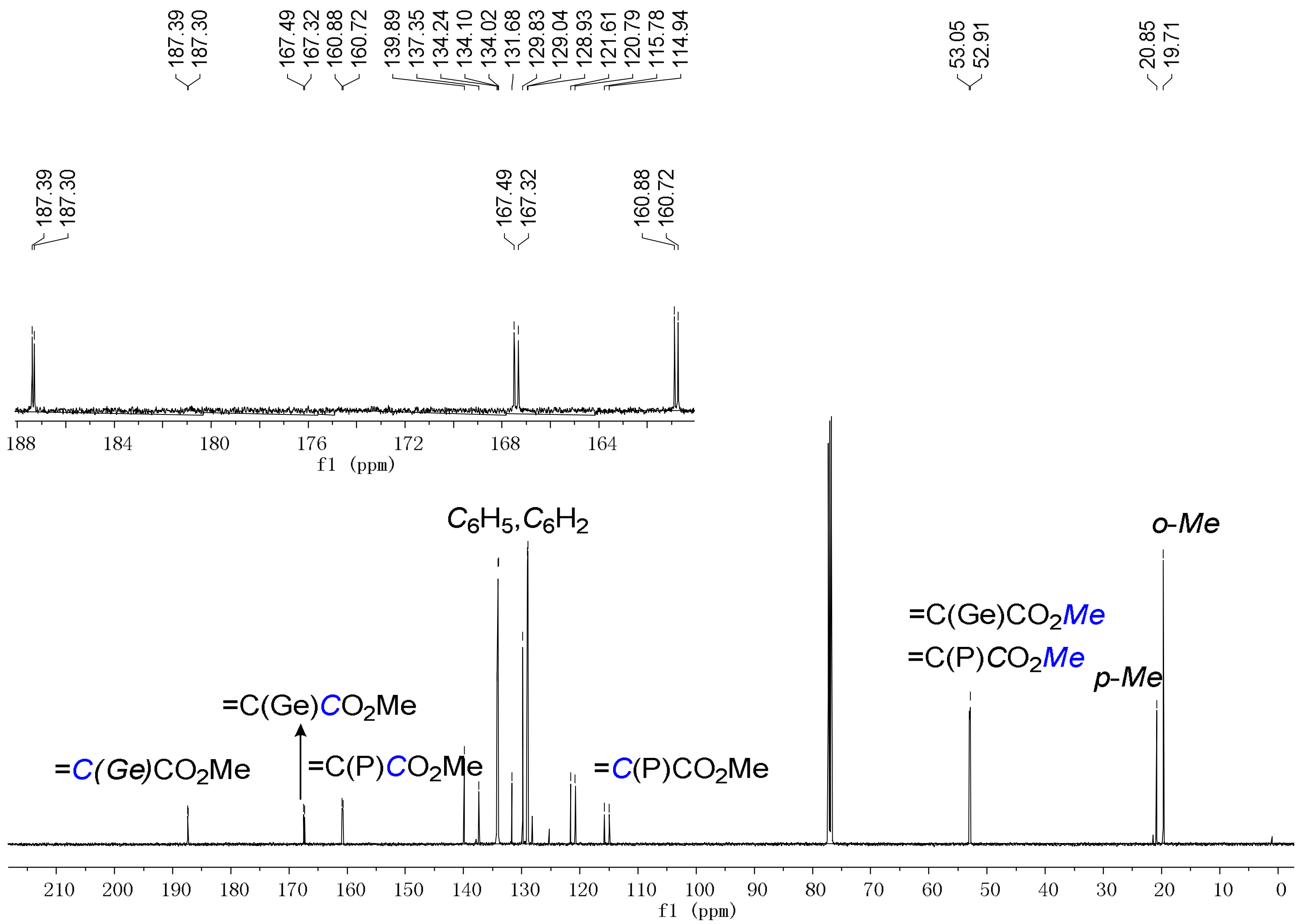

Figure 7s-c. ^{13}C NMR spectrum of **7** in $CDCl_3$

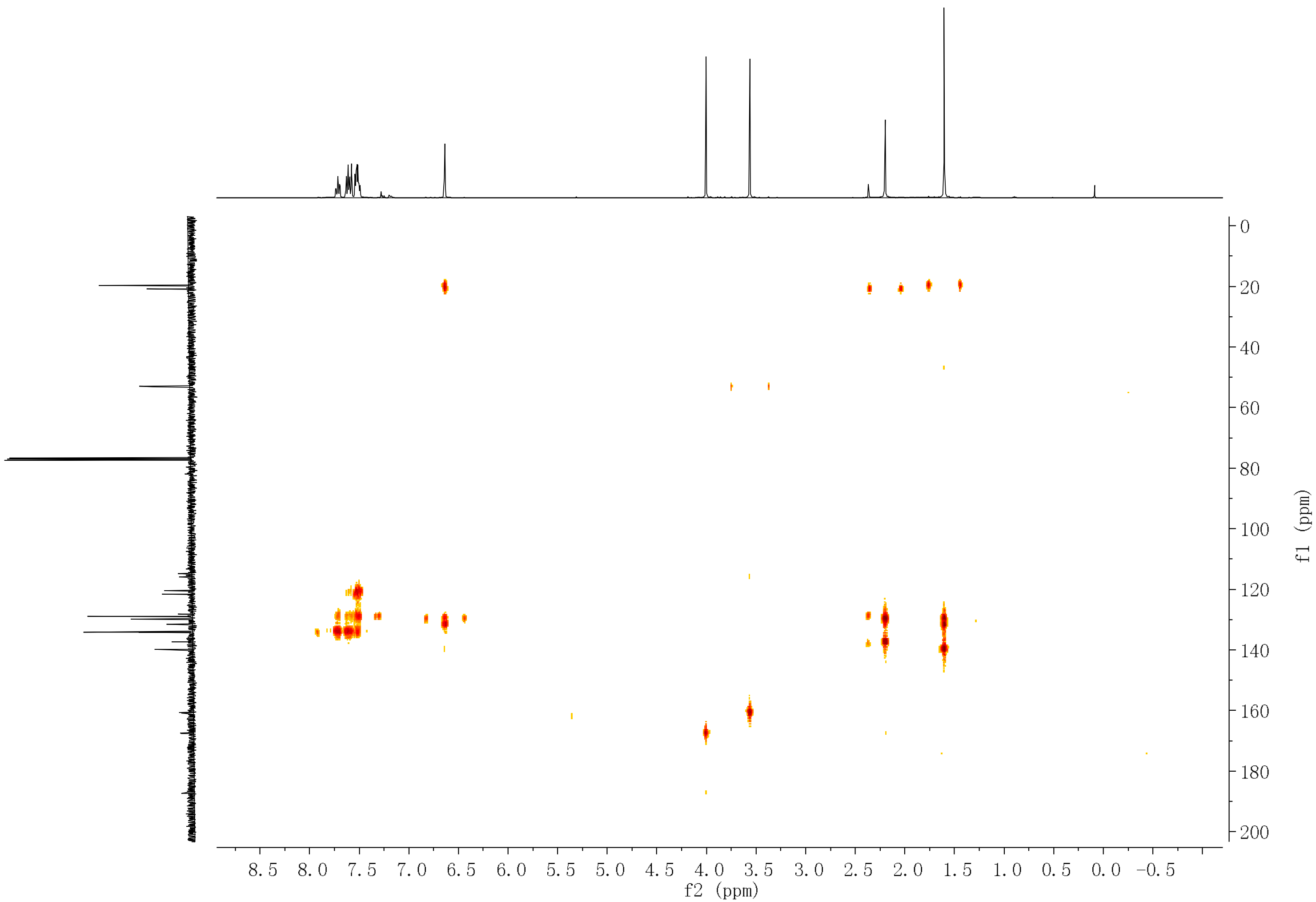

Figure 7s-d. ^{1}H,^{13}C-HMBC spectrum of **7** in $CDCl_3$

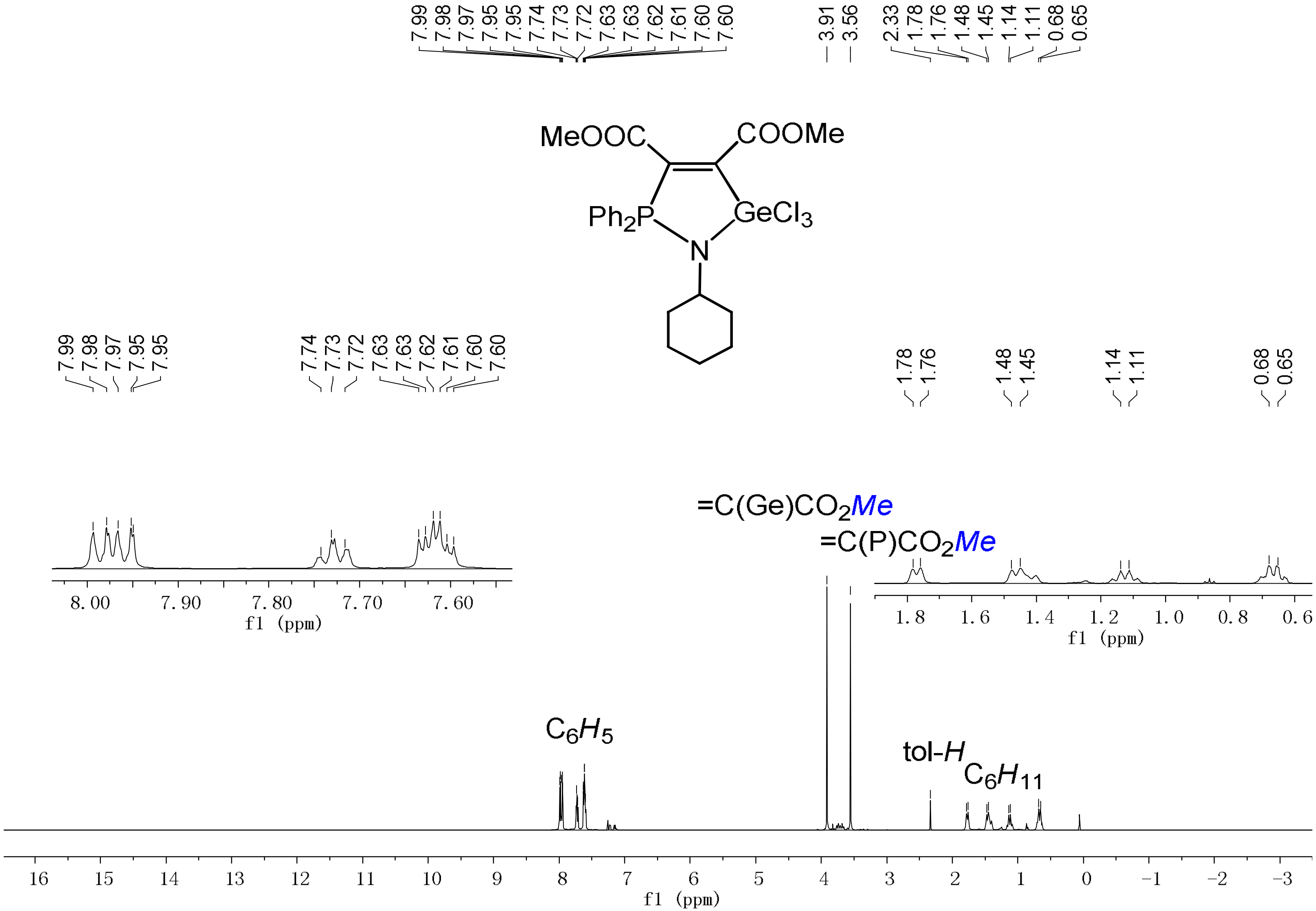

Figure 8s-a. ^{1}H NMR spectrum of **8** in $CDCl_3$

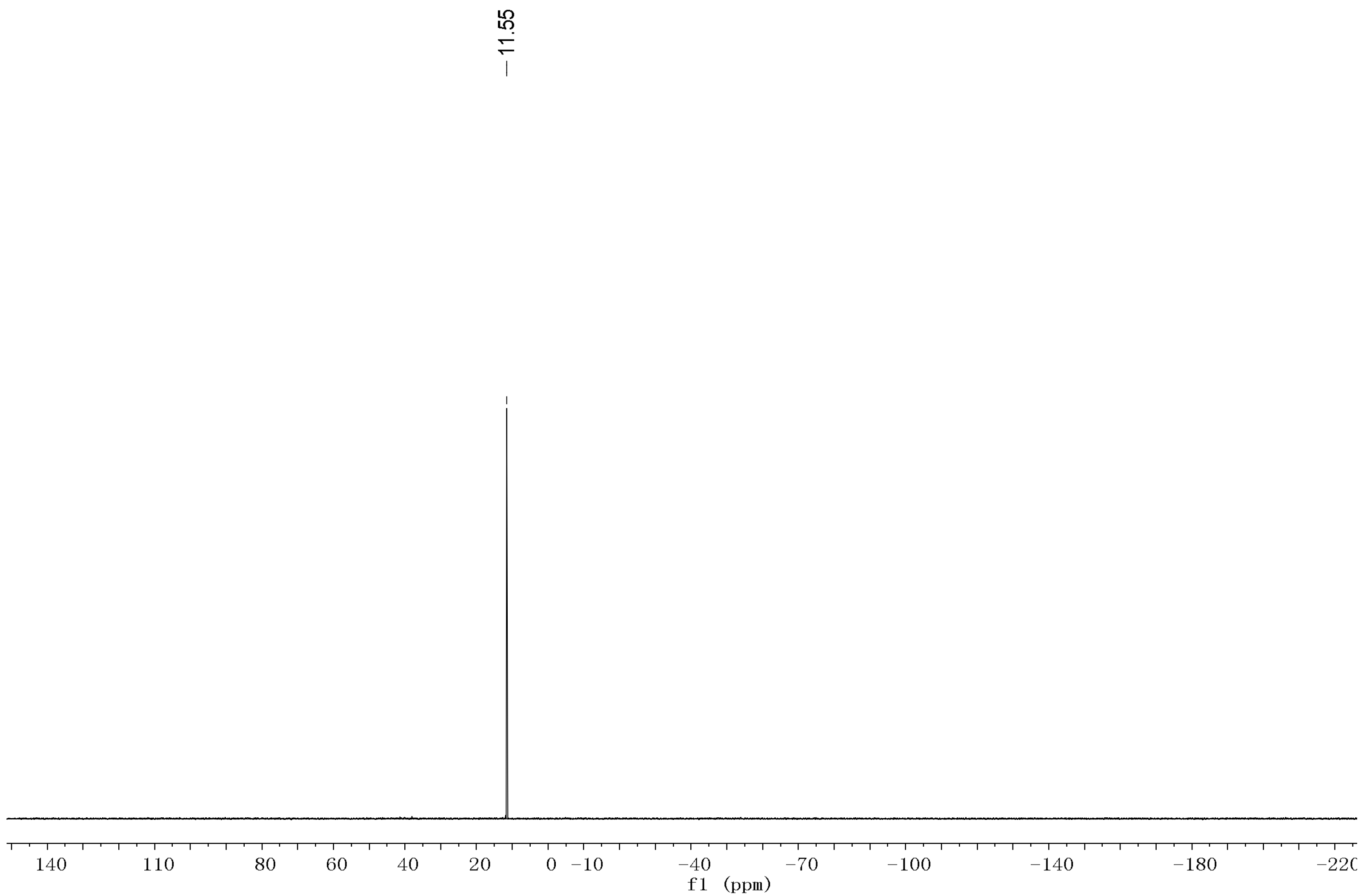

Figure 8s-b. ^{31}P NMR spectrum of **8** in $CDCl_3$

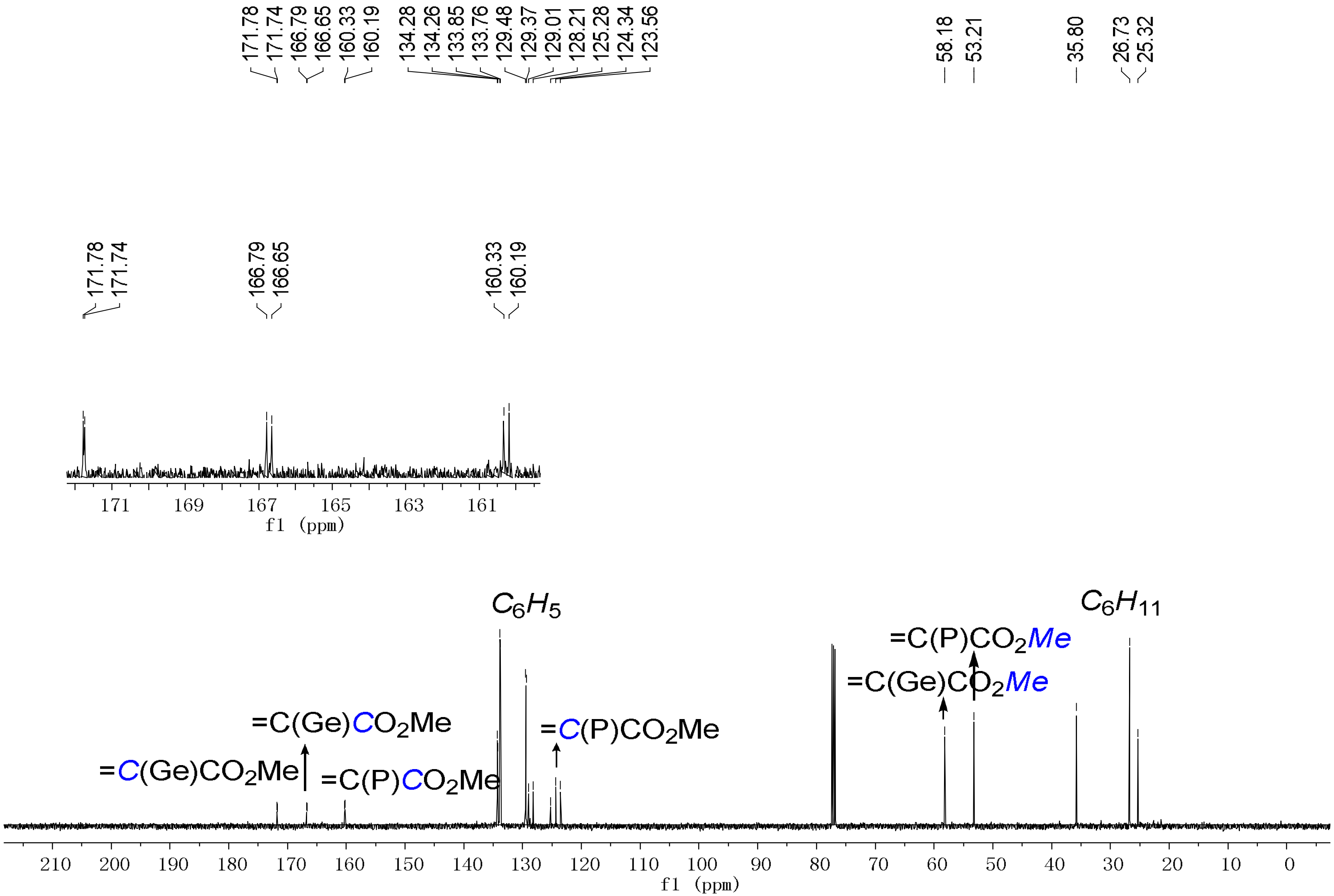

Figure 8s-c. ^{13}C NMR spectrum of **8** in $CDCl_3$

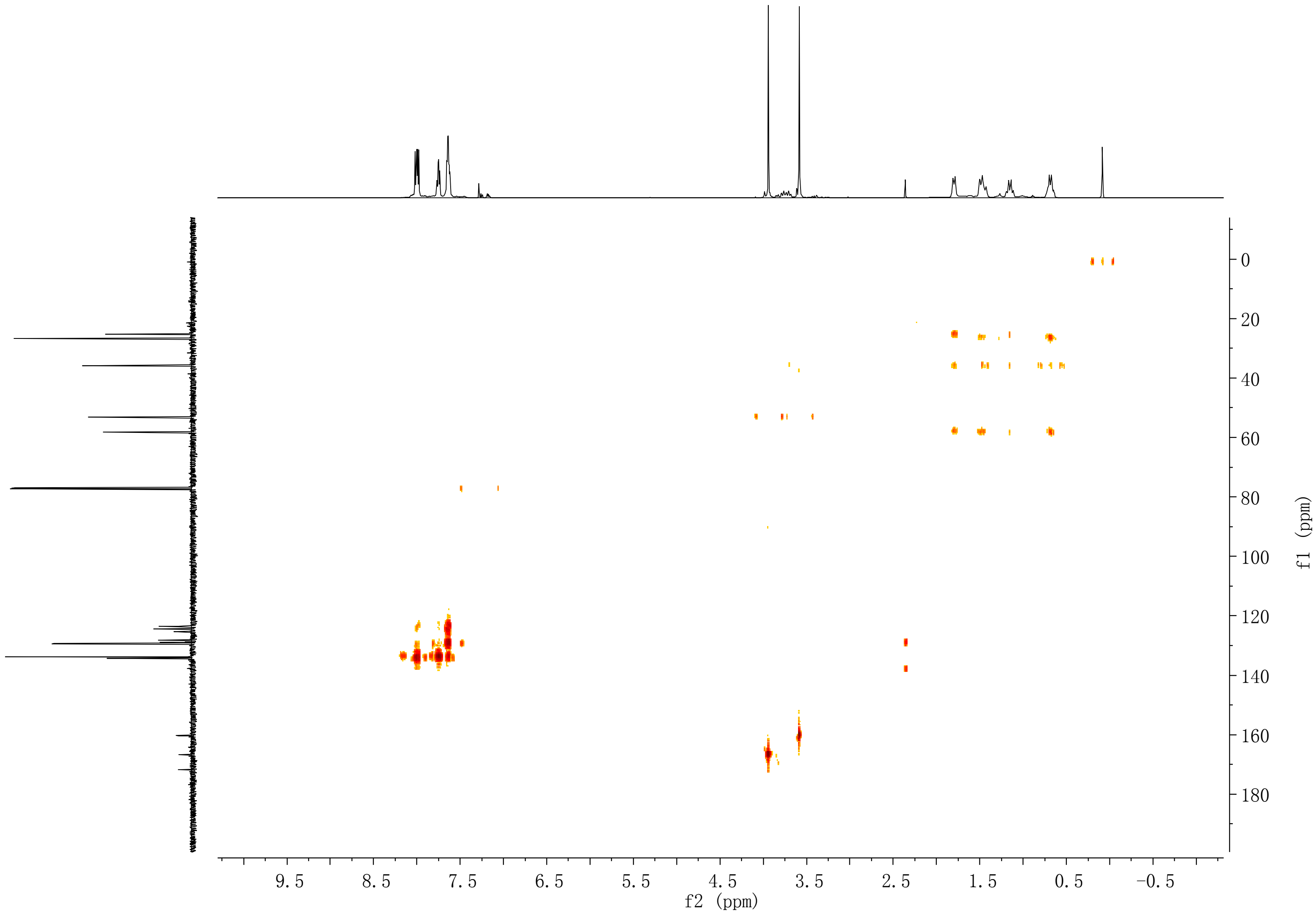

Figure 8s-d. $^{1}H,^{13}C$-HMBC spectrum of **8** in $CDCl_3$

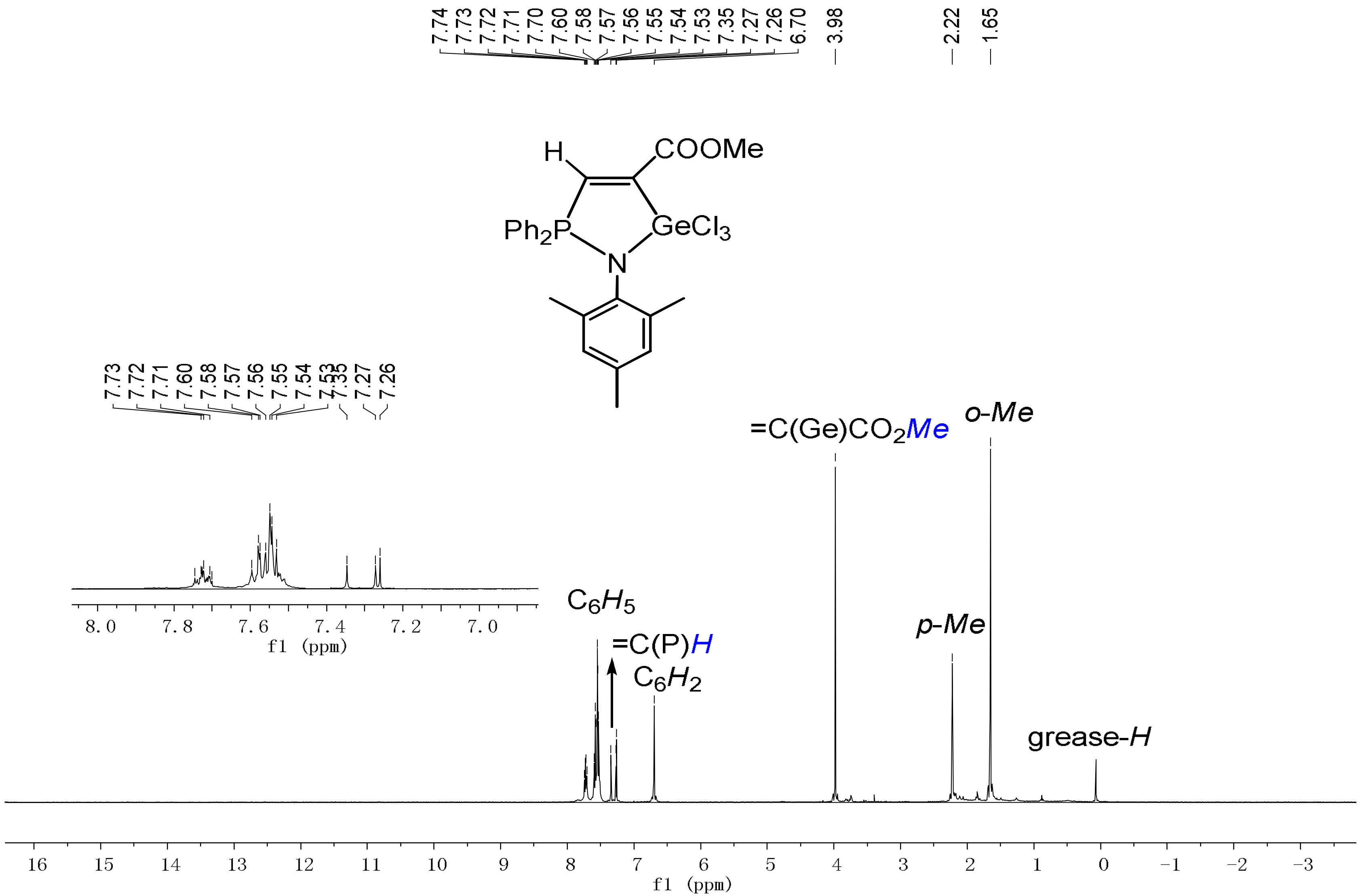

Figure 9s-a. ^{1}H NMR spectrum of **9** in $CDCl_3$

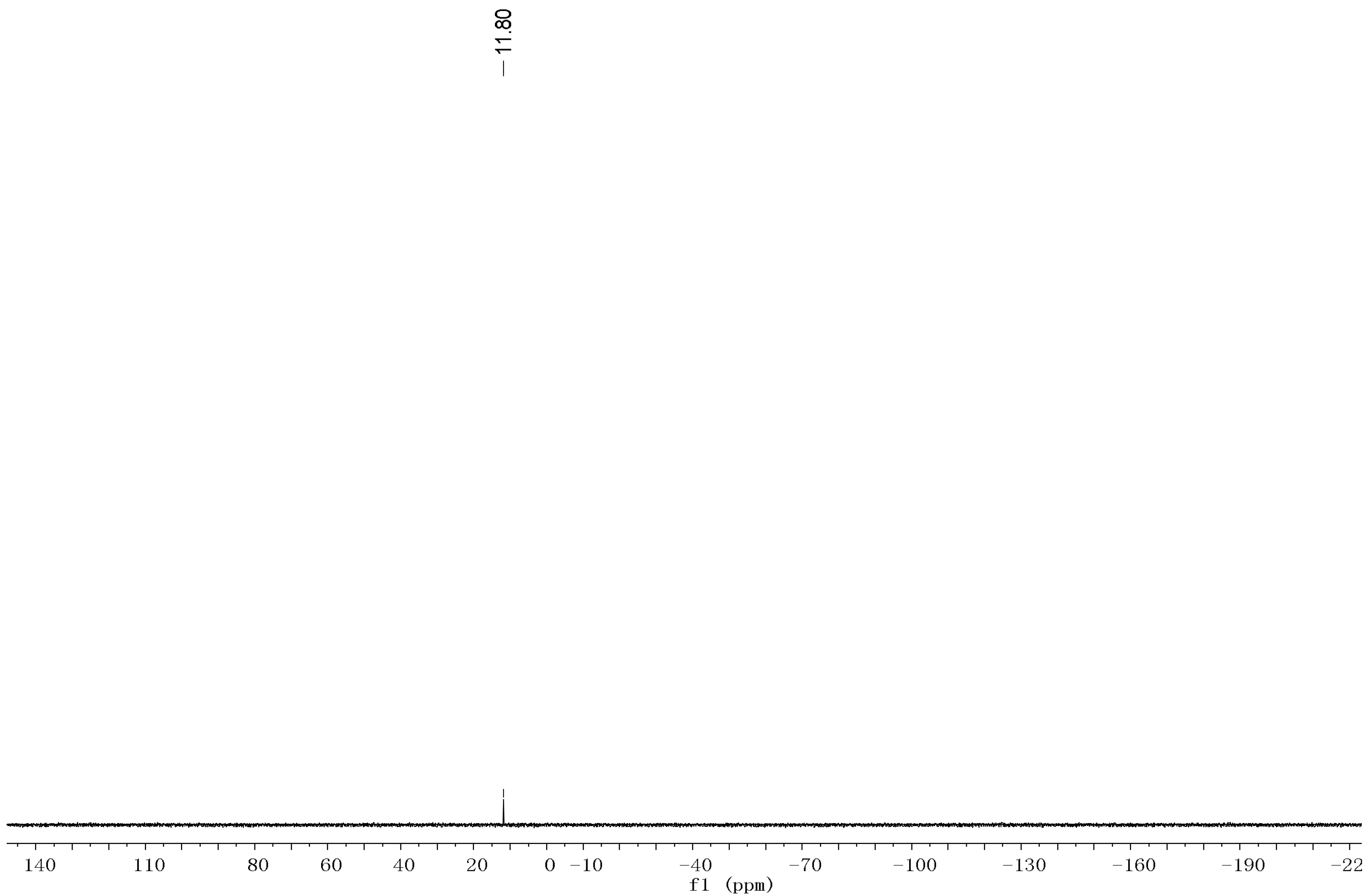

Figure 9s-b. ^{31}P NMR spectrum of **9** in $CDCl_3$

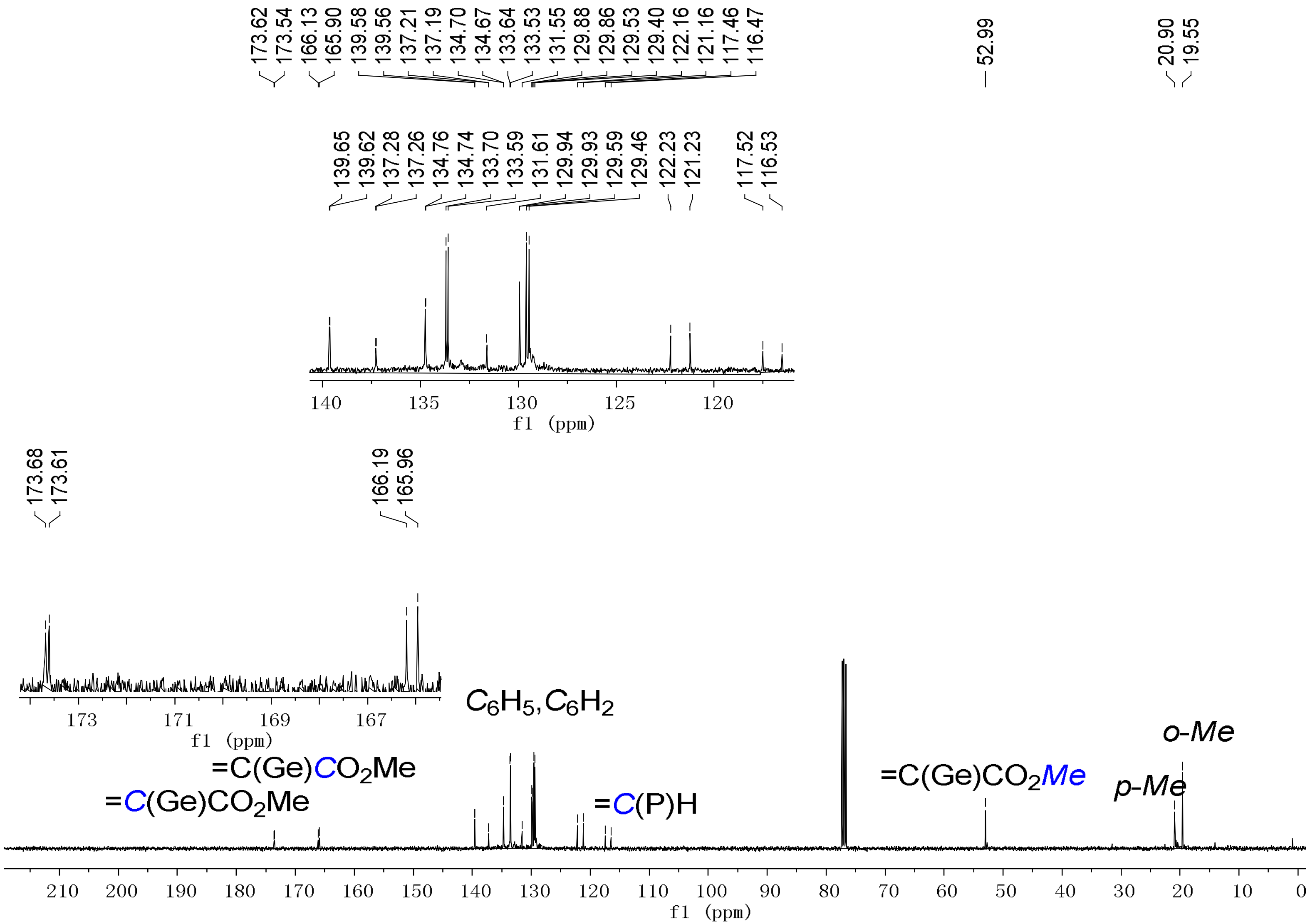

Figure 9s-c. ^{13}C NMR spectrum of **9** in $CDCl_3$

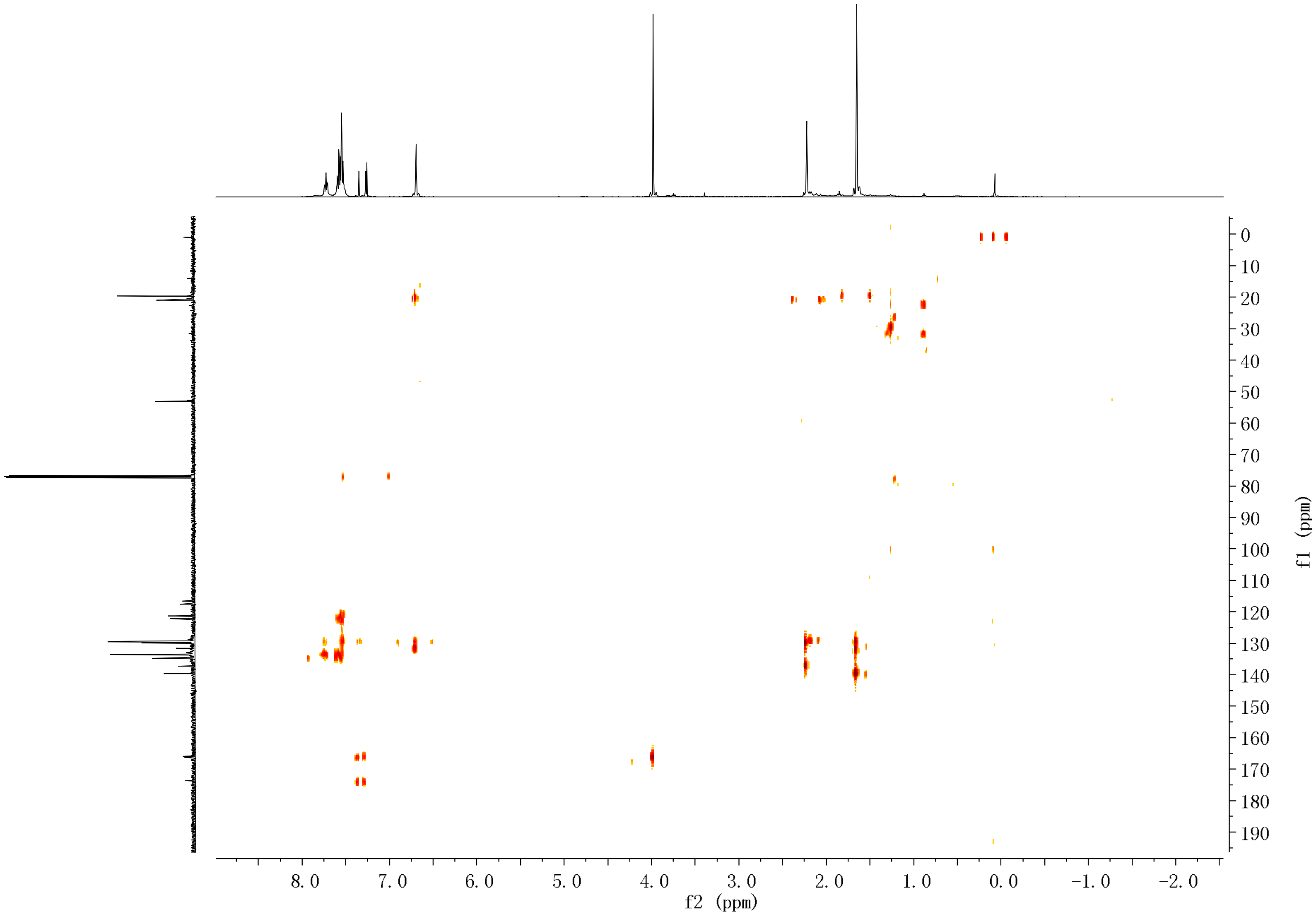

Figure 9s-d. $^{1}H,^{13}C$-HMBC spectrum of **9** in $CDCl_3$

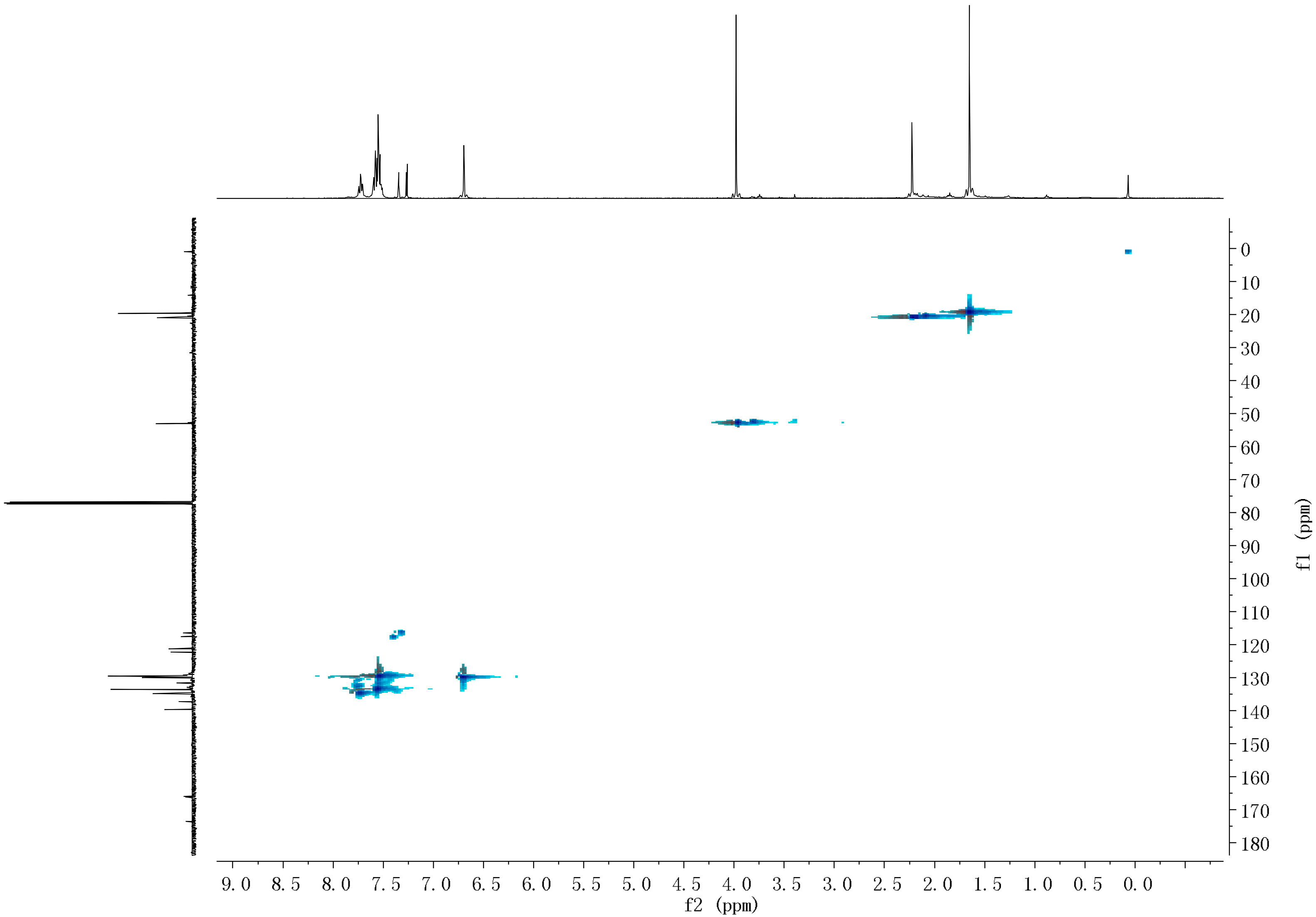

Figure 9s-e. $^{1}H,^{13}C$-HSQC spectrum of **9** in $CDCl_3$

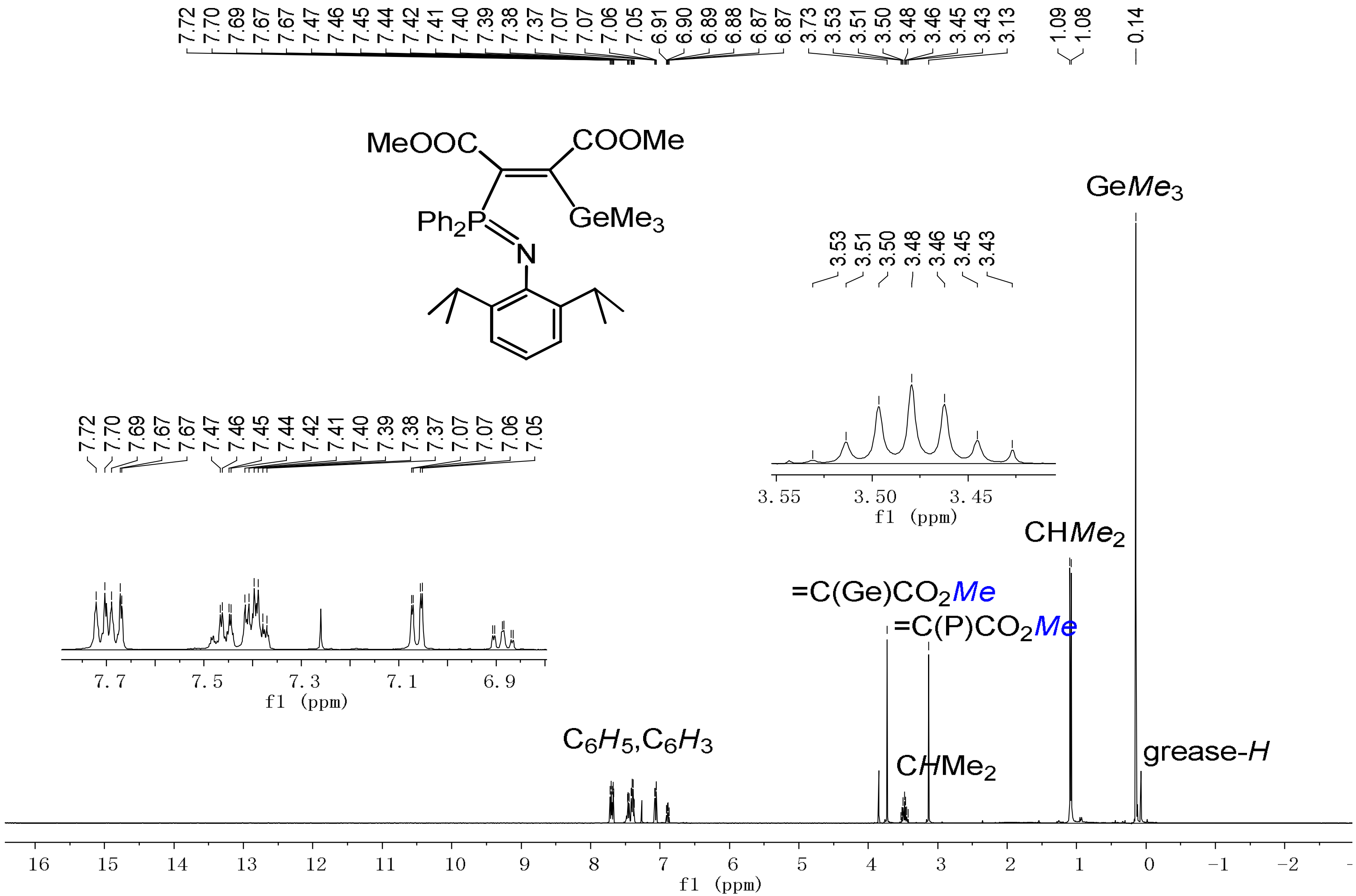

Figure 10s-a. ^{1}H NMR spectrum of **10** in $CDCl_3$

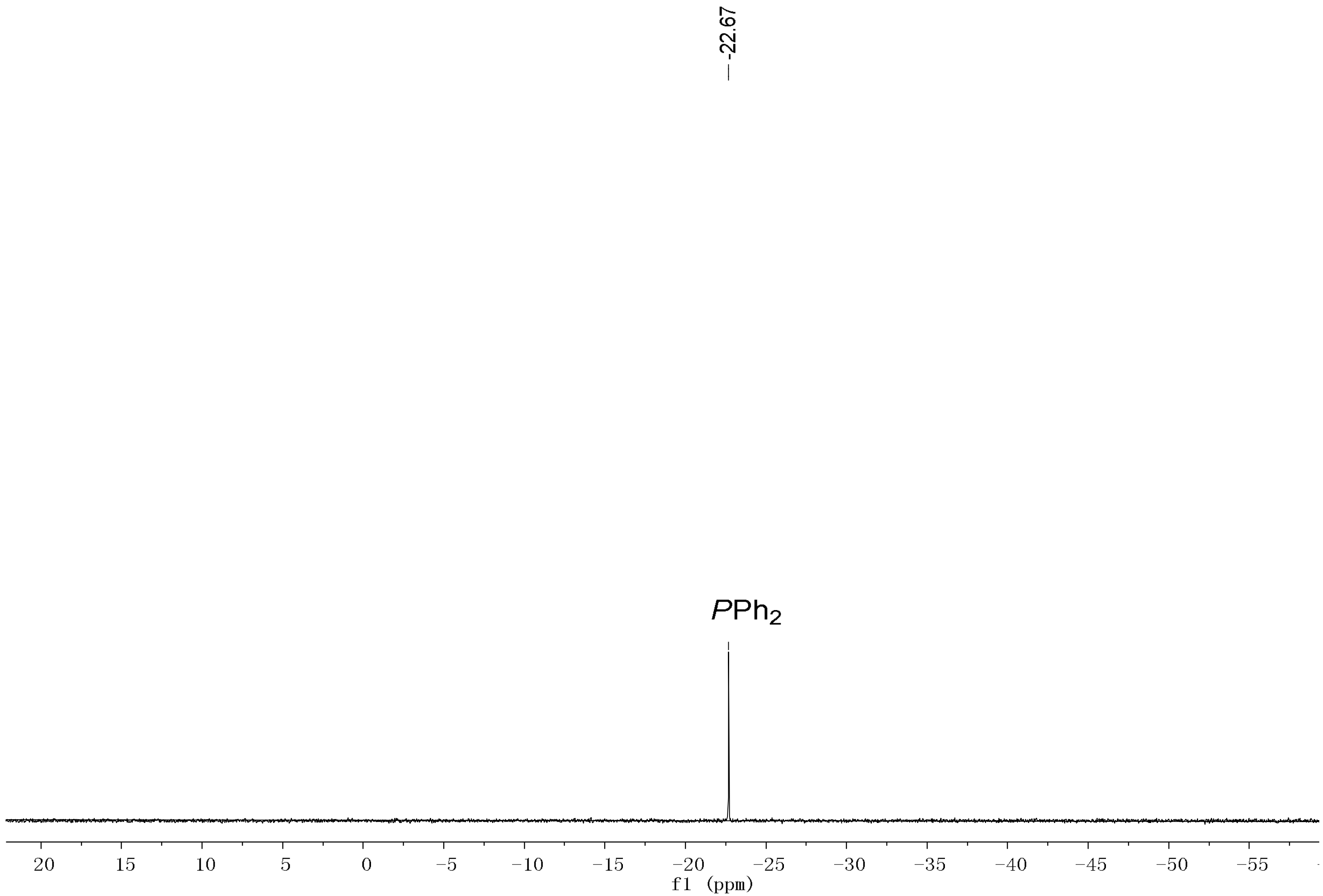

Figure 10s-b. ^{31}P NMR spectrum of **10** in $CDCl_3$

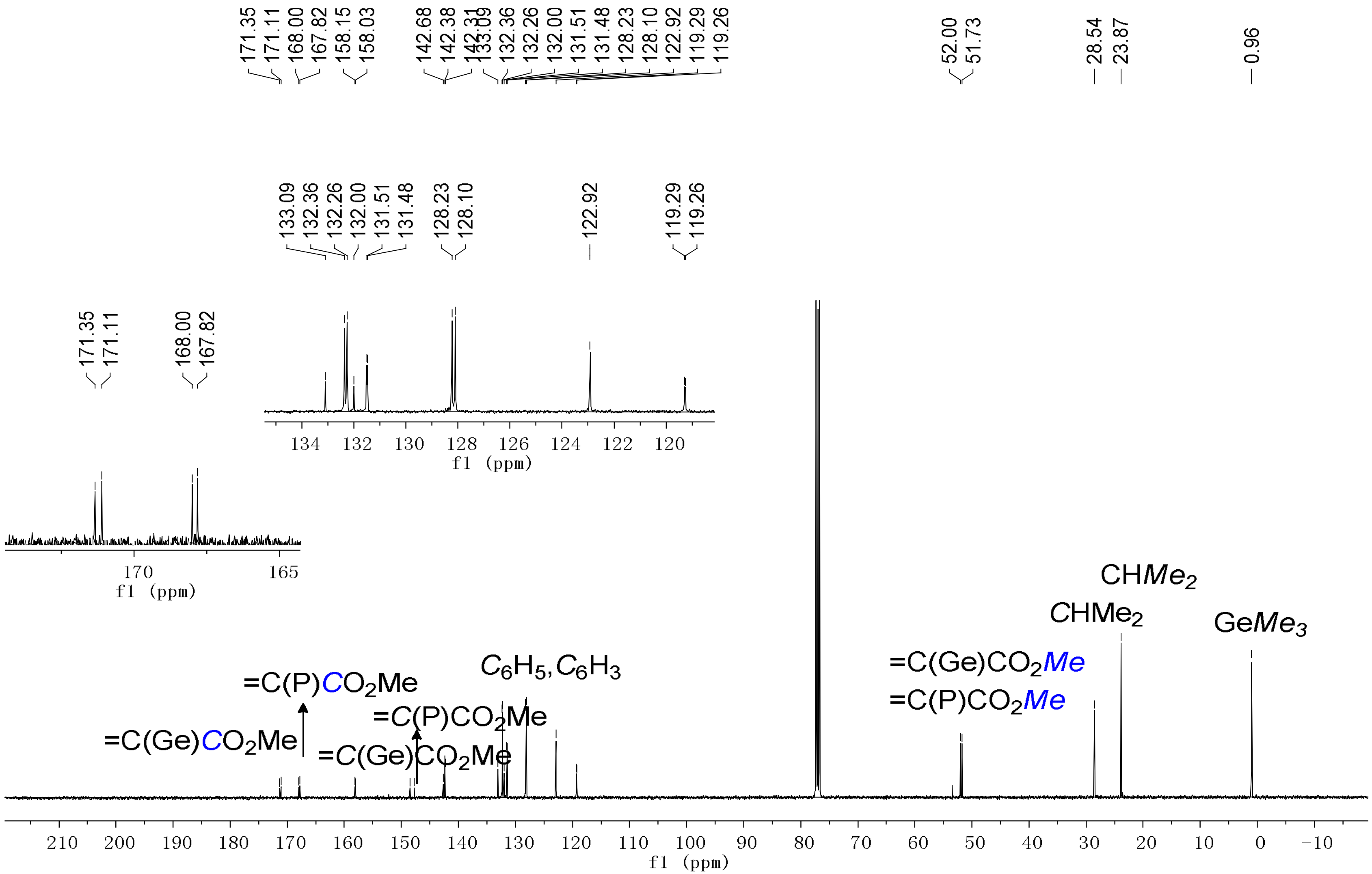

Figure 10s-c. ^{13}C NMR spectrum of **10** in $CDCl_3$

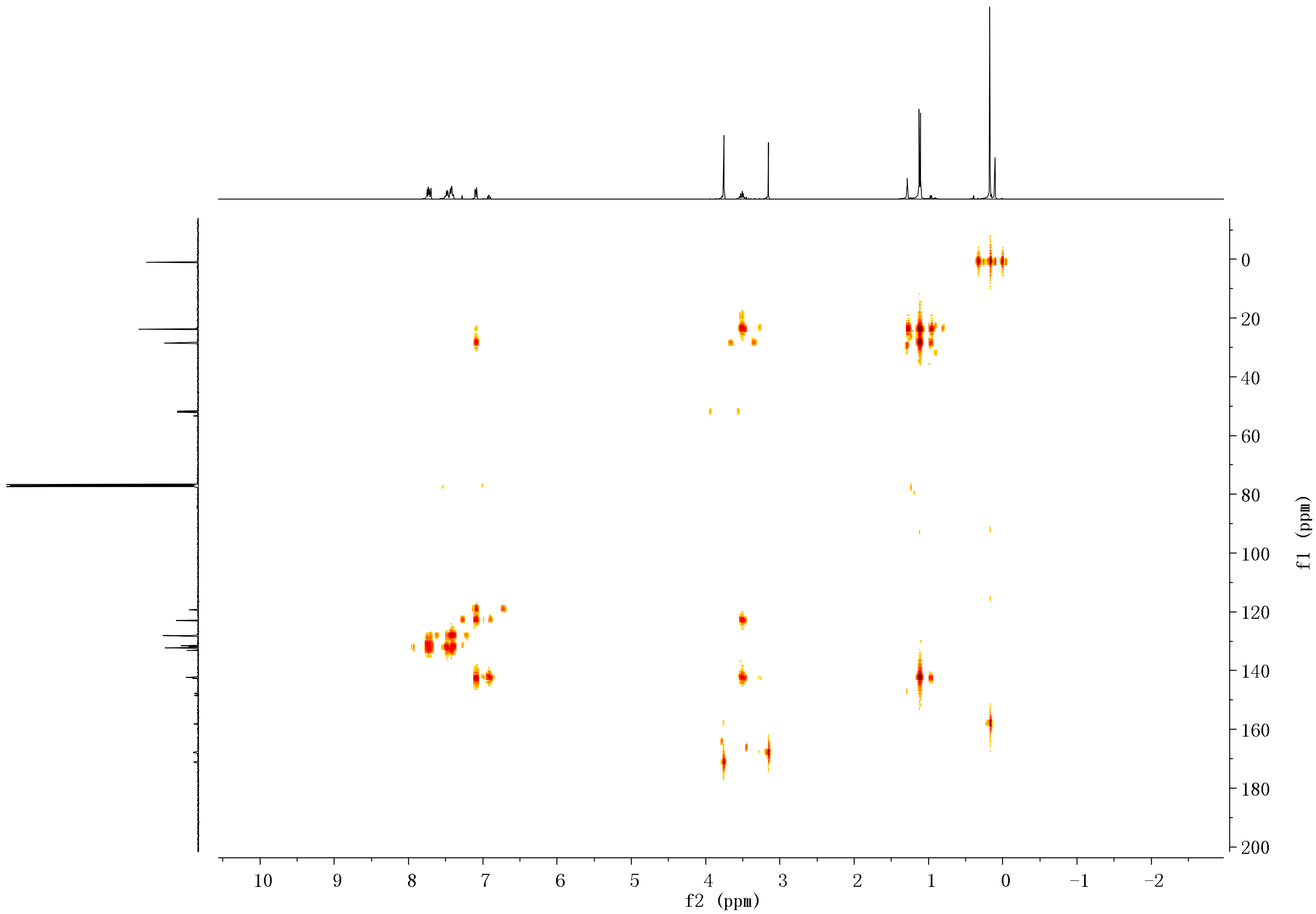

Figure 10s-d. $^{1}H,^{13}C$-HMBC spectrum of **10** in $CDCl_3$

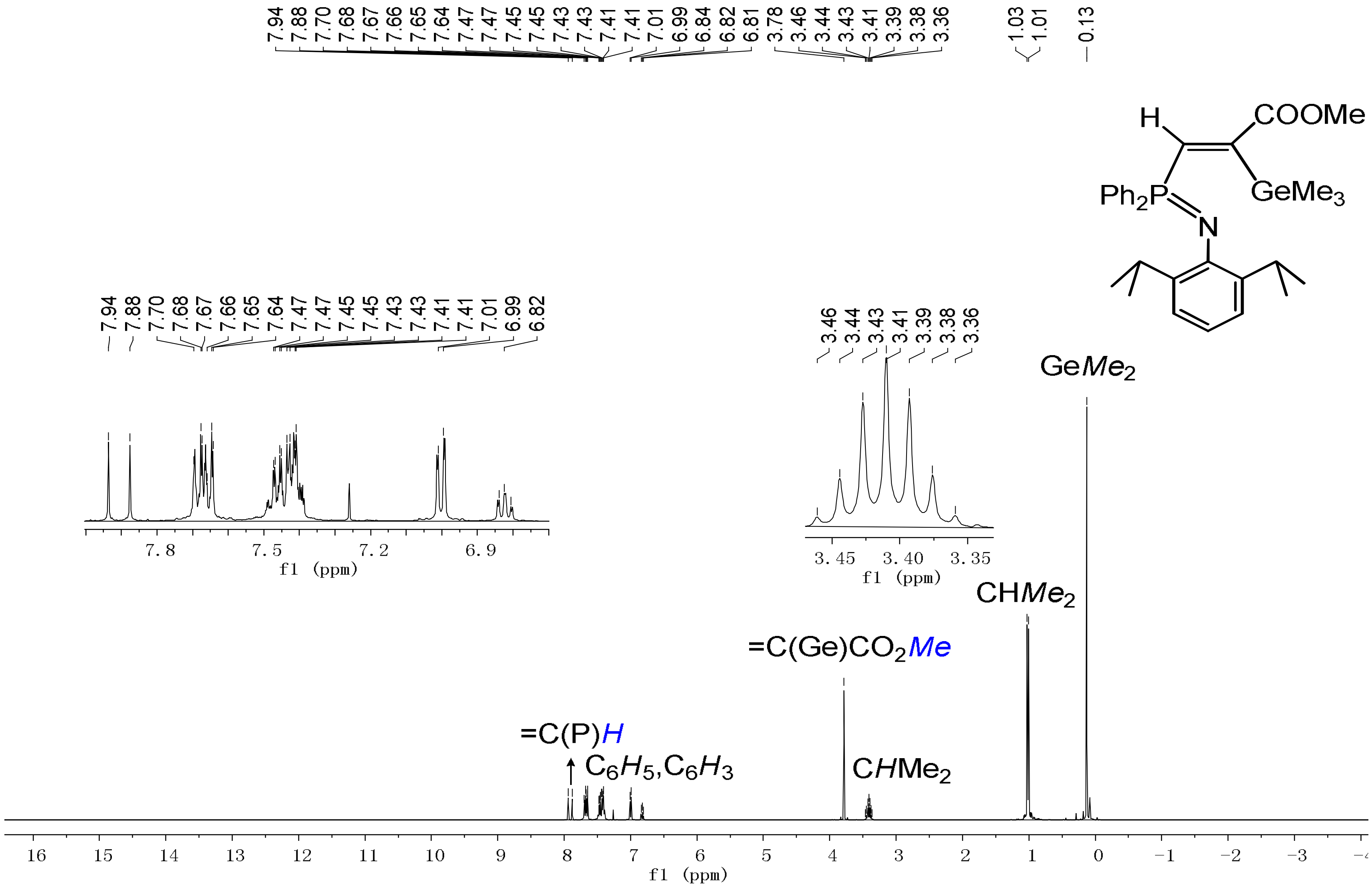

Figure 11s-a. ^{1}H NMR spectrum of **11** in $CDCl_3$

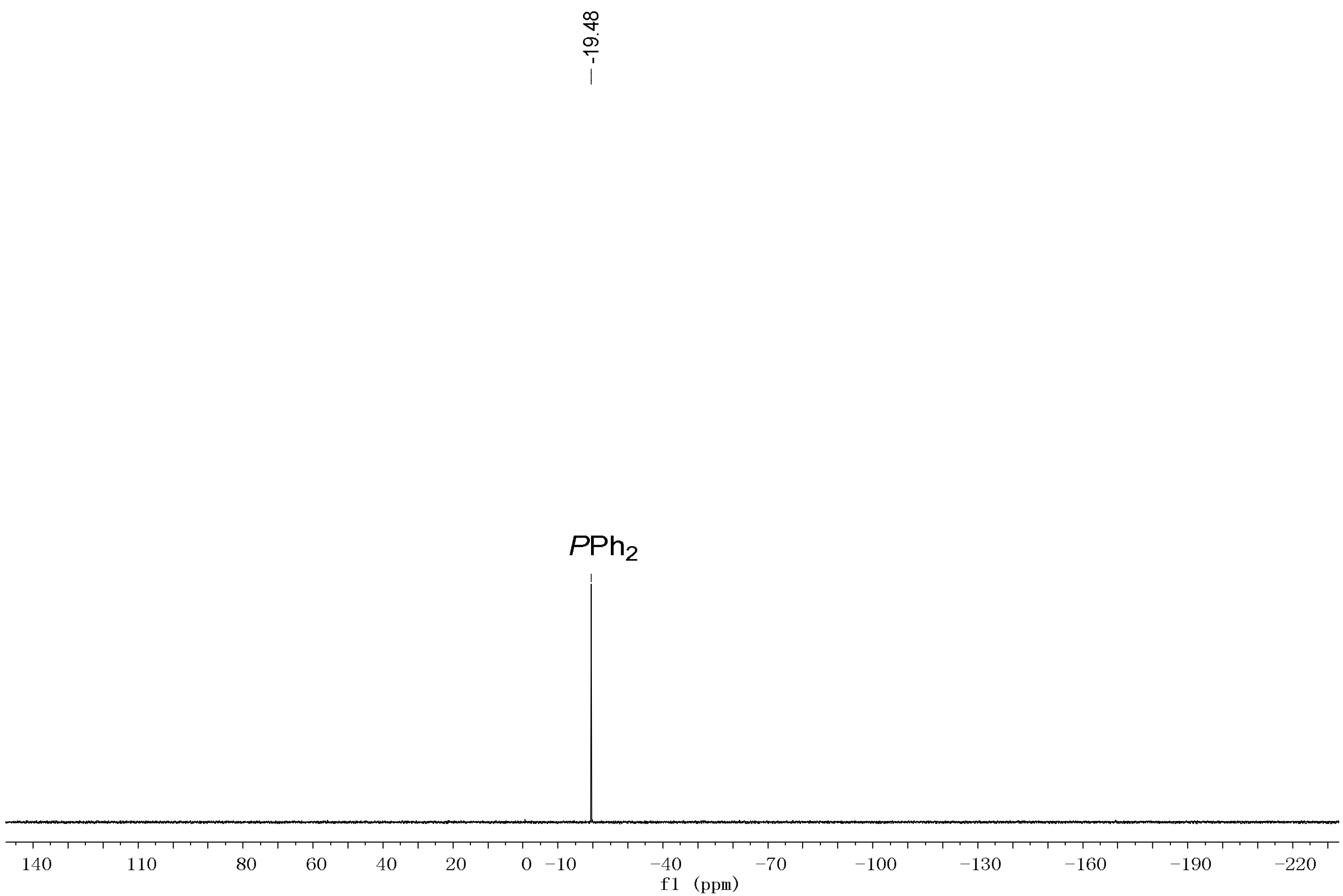

Figure 11s-b. ^{31}P NMR spectrum of **11** in $CDCl_3$

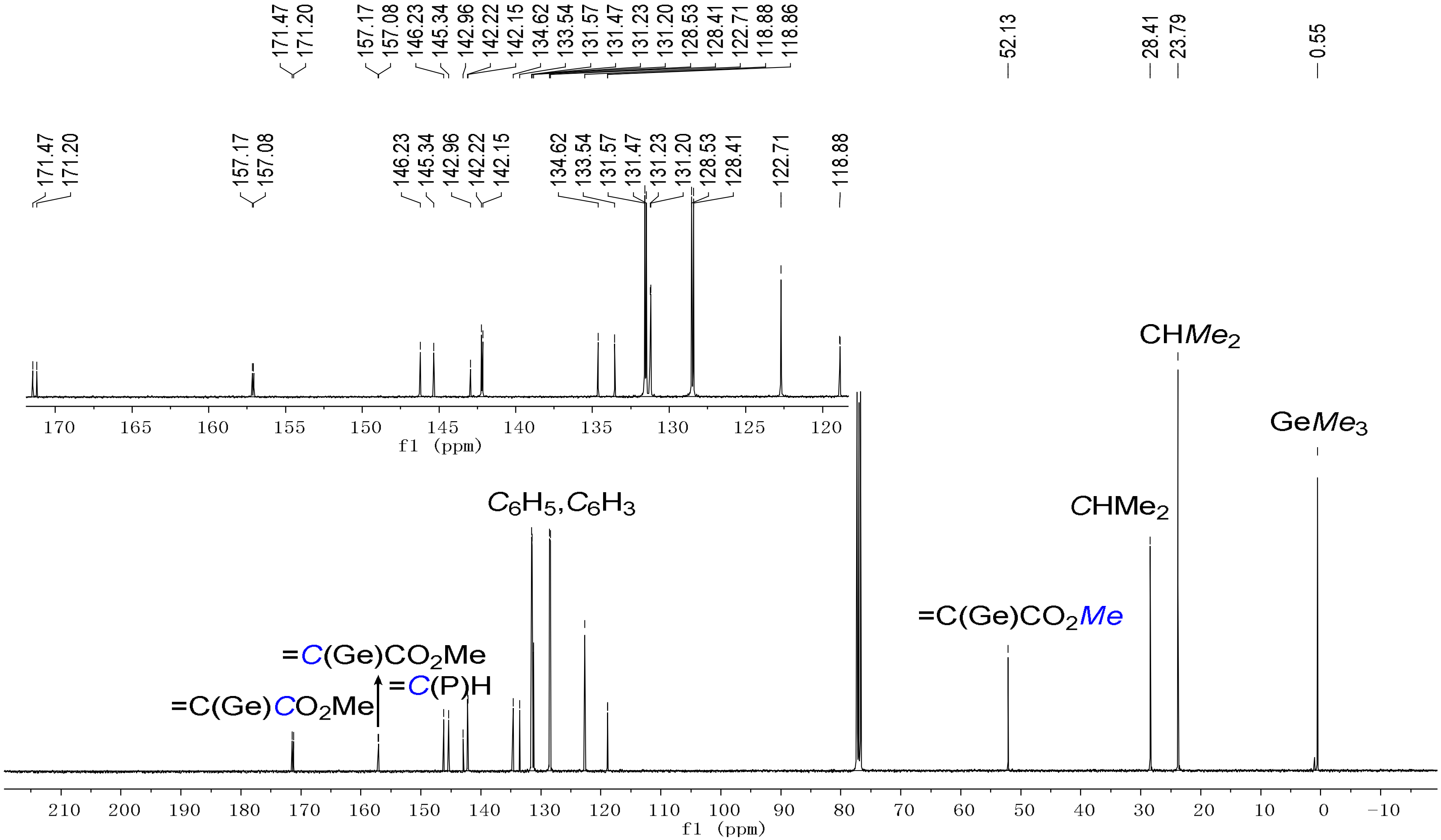

Figure 11s-c. ^{13}C NMR spectrum of **11** in $CDCl_3$

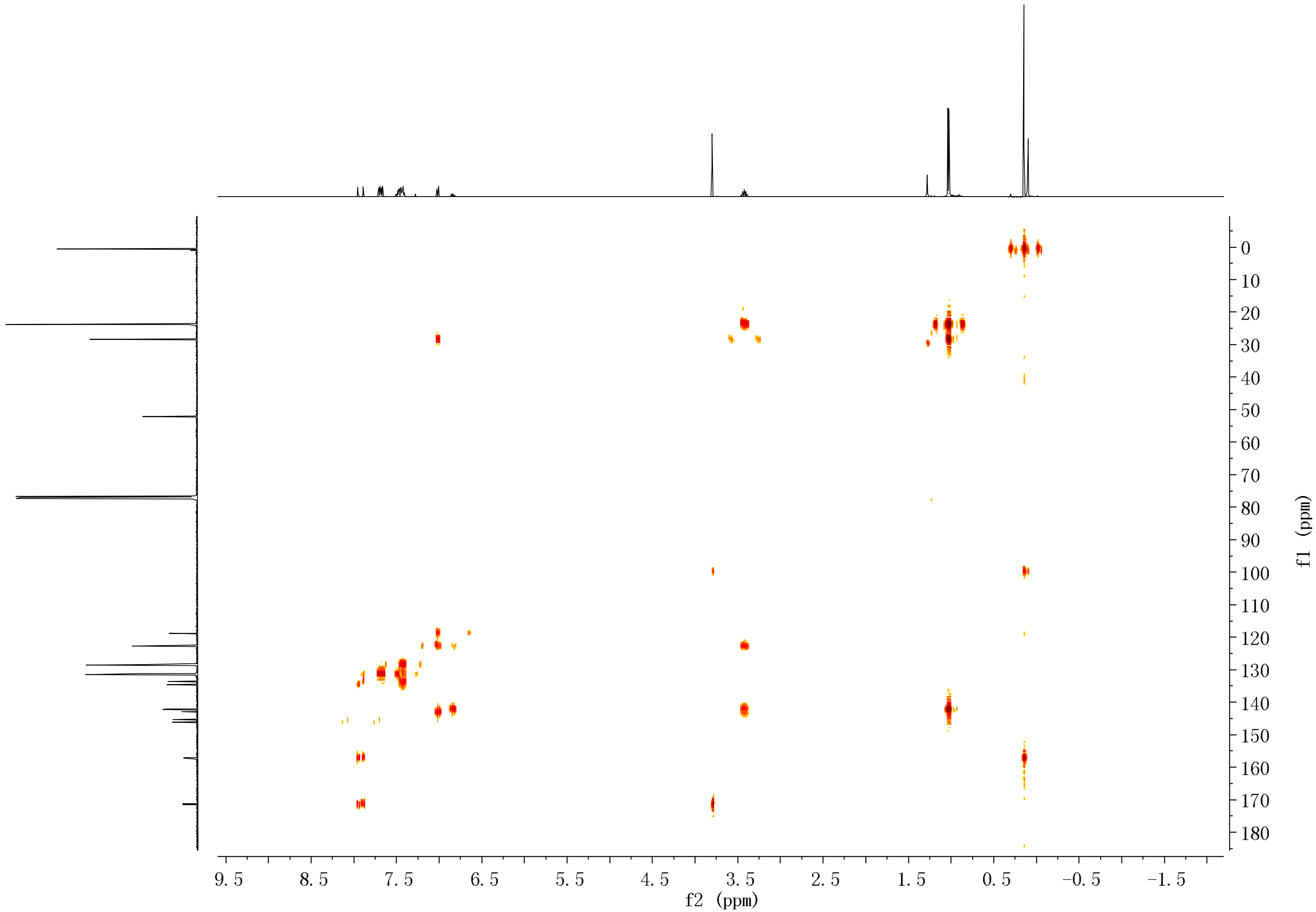

Figure 11s-d. $^{1}H,^{13}C$-HMBC spectrum of **11** in $CDCl_3$

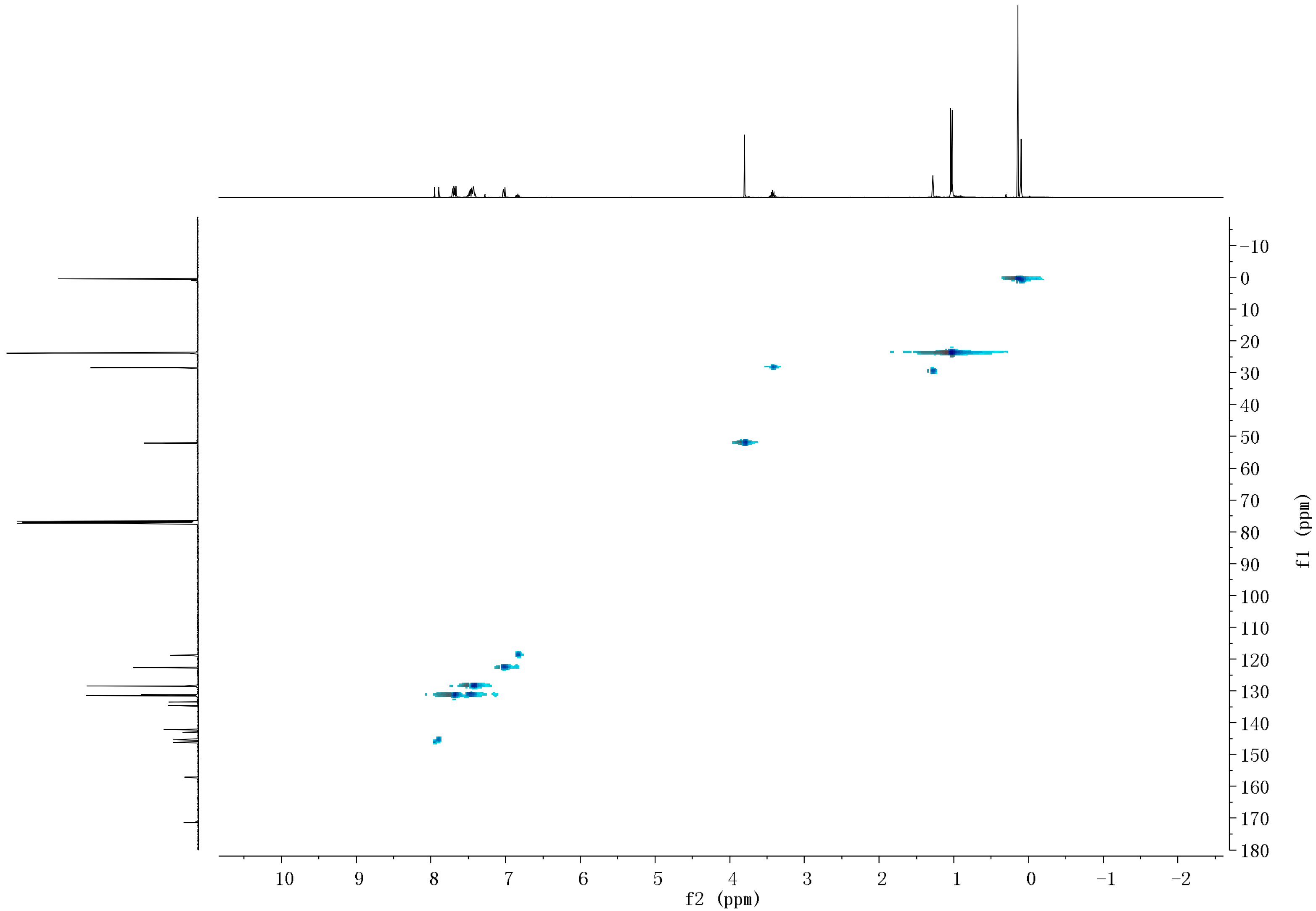

Figure 11s-e. $^{1}H,^{13}C$-HSQC spectrum of **11** in $CDCl_3$

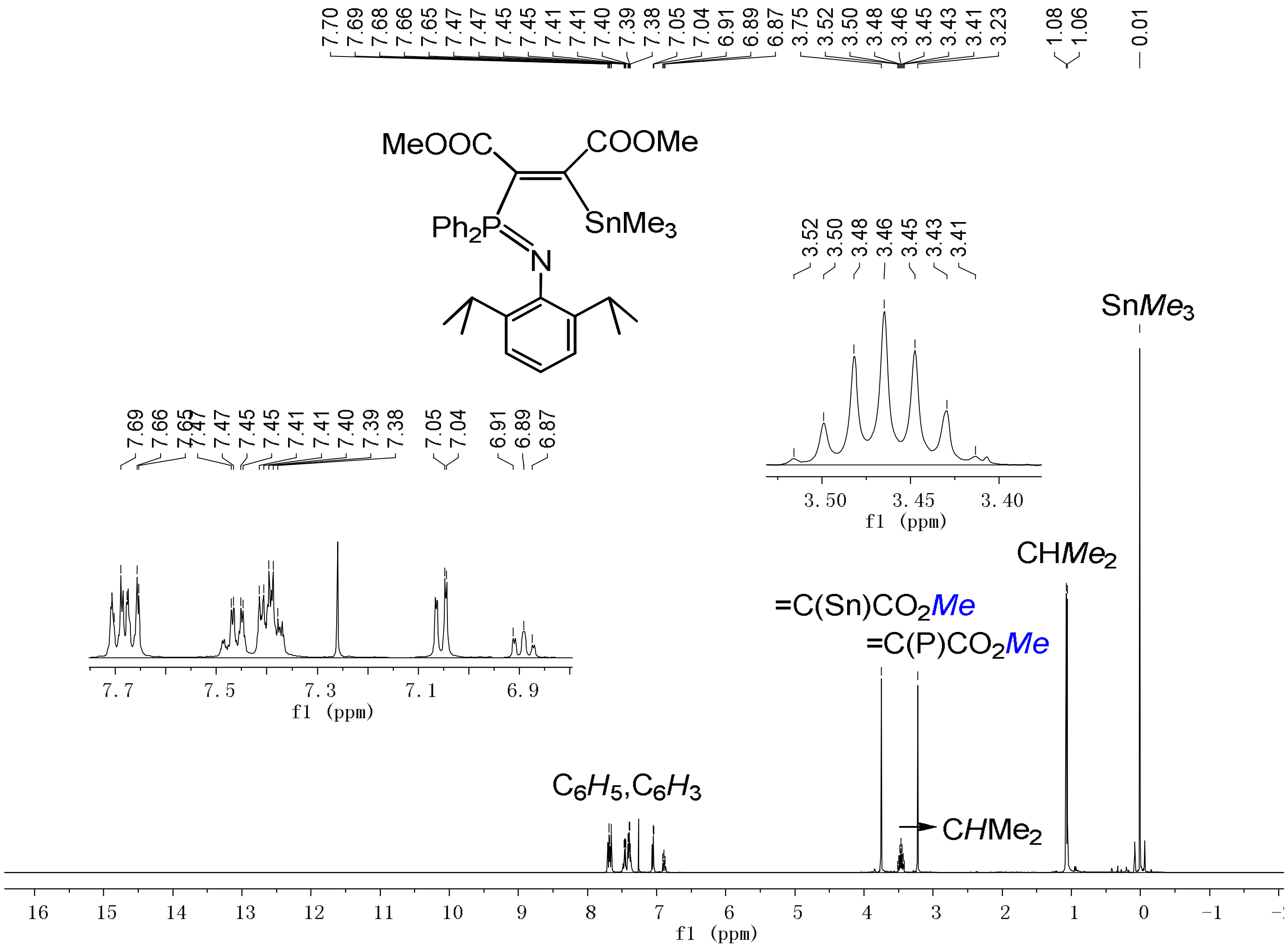

Figure 12s-a. [1]H NMR spectrum of **1** in $CDCl_3$

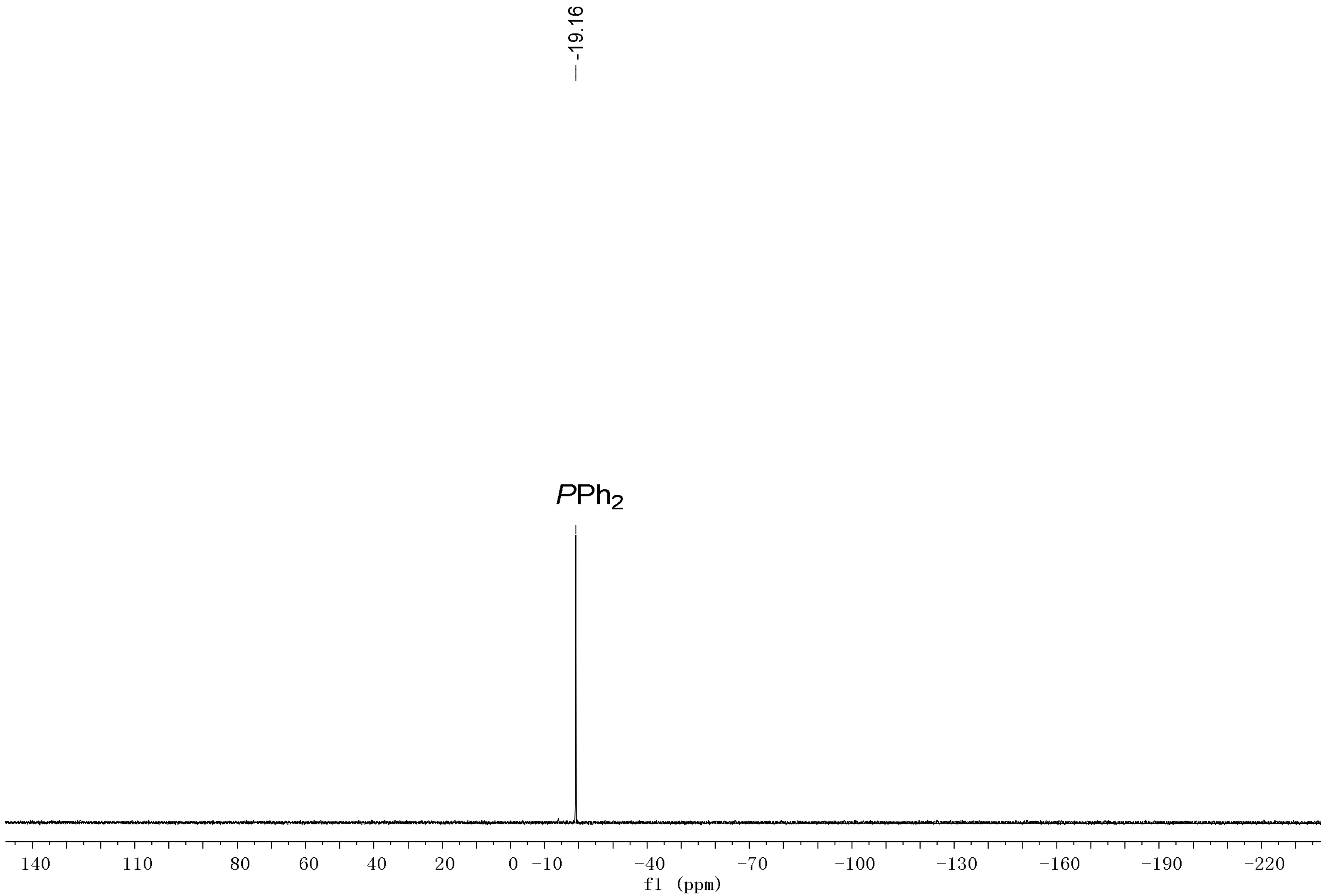

Figure 12s-b. ^{31}P NMR spectrum of **12** in $CDCl_3$

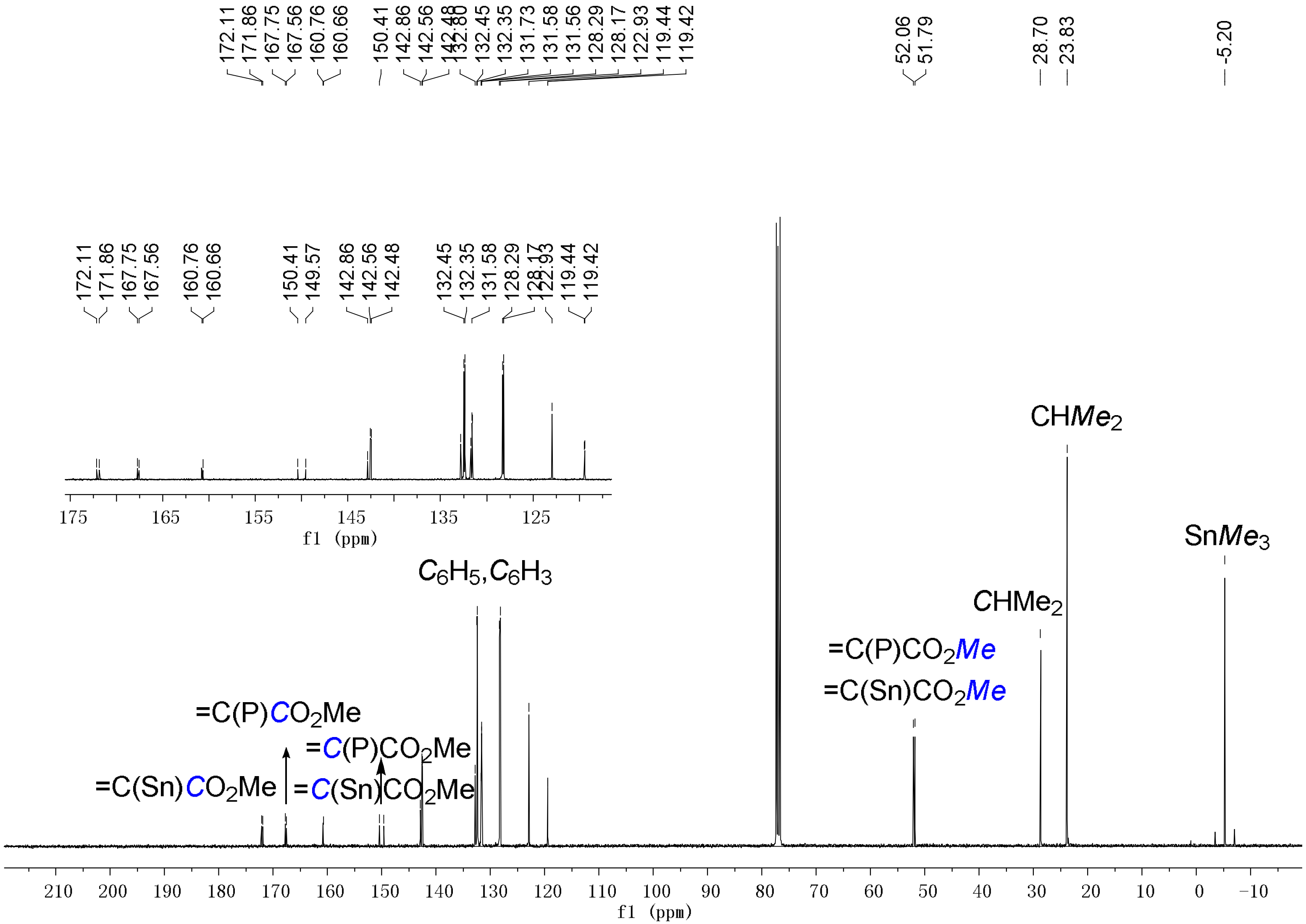

Figure 12s-c. ^{13}C NMR spectrum of **12** in $CDCl_3$

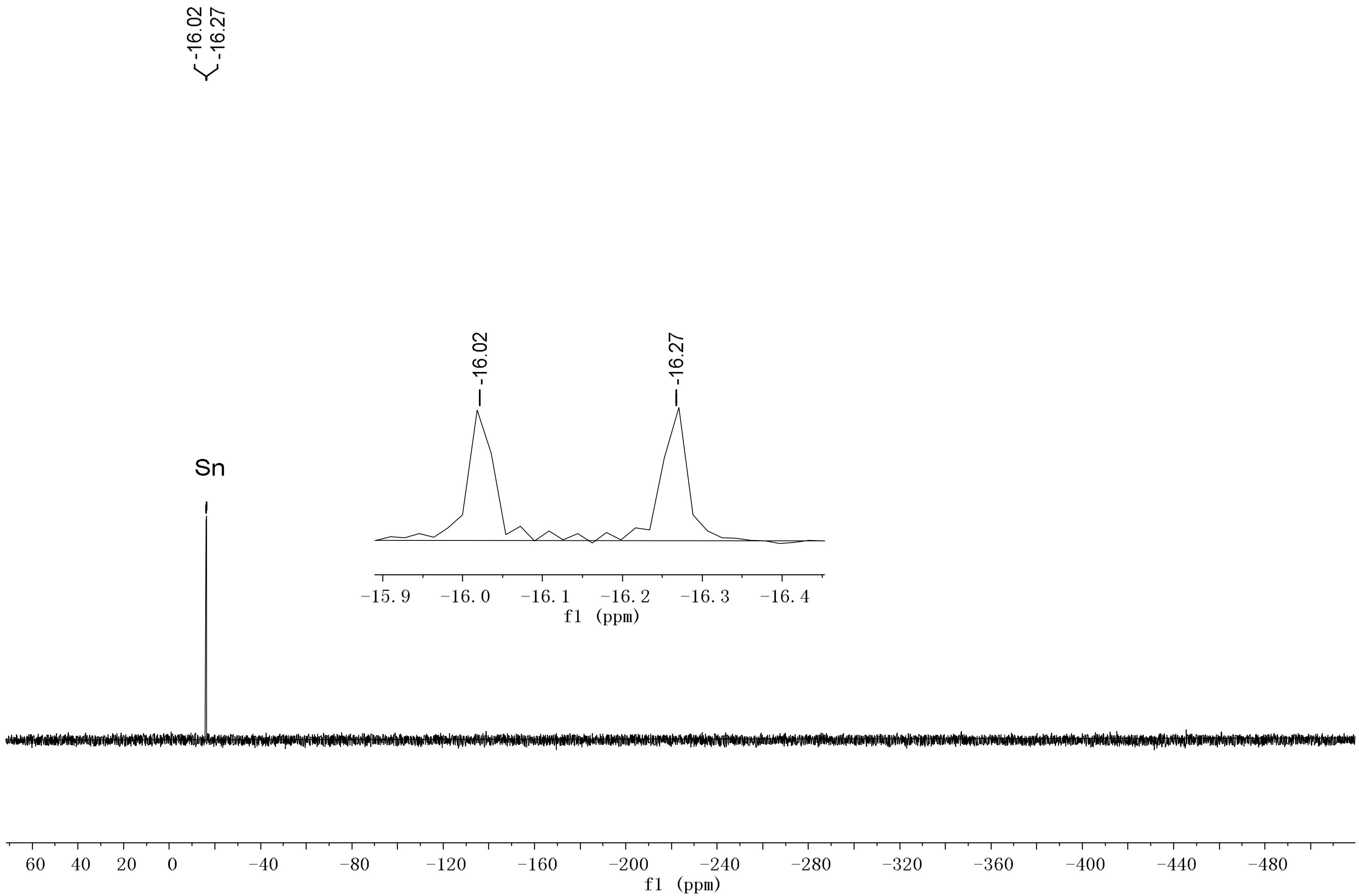

Figure 12s-d. ^{119}Sn NMR spectrum of **12** in $CDCl_3$

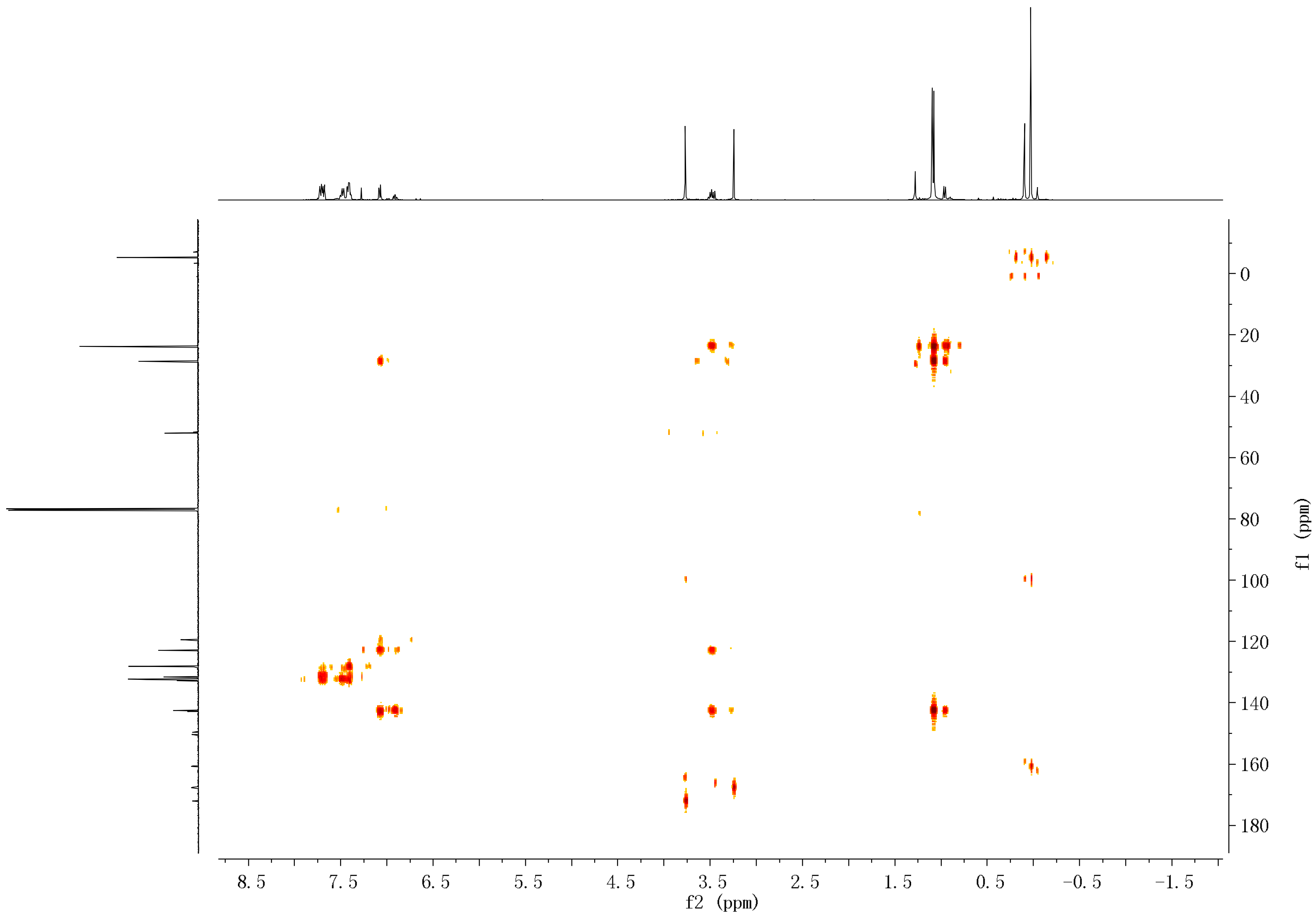

Figure 12s-e. $^{1}H,^{13}C$-HMBC spectrum of **12** in $CDCl_3$

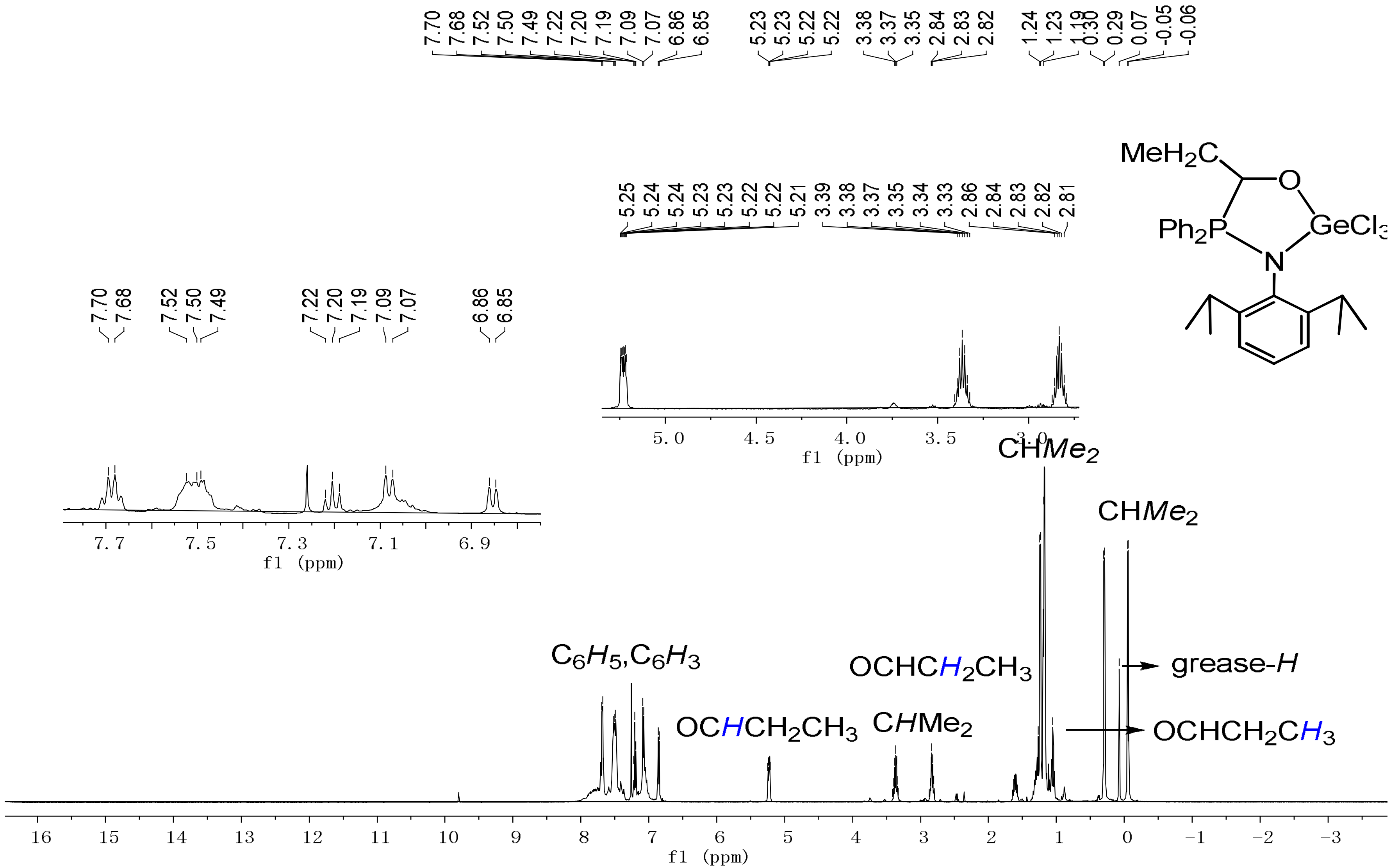

Figure 13s-a. [1]H NMR spectrum of **13** in $CDCl_3$

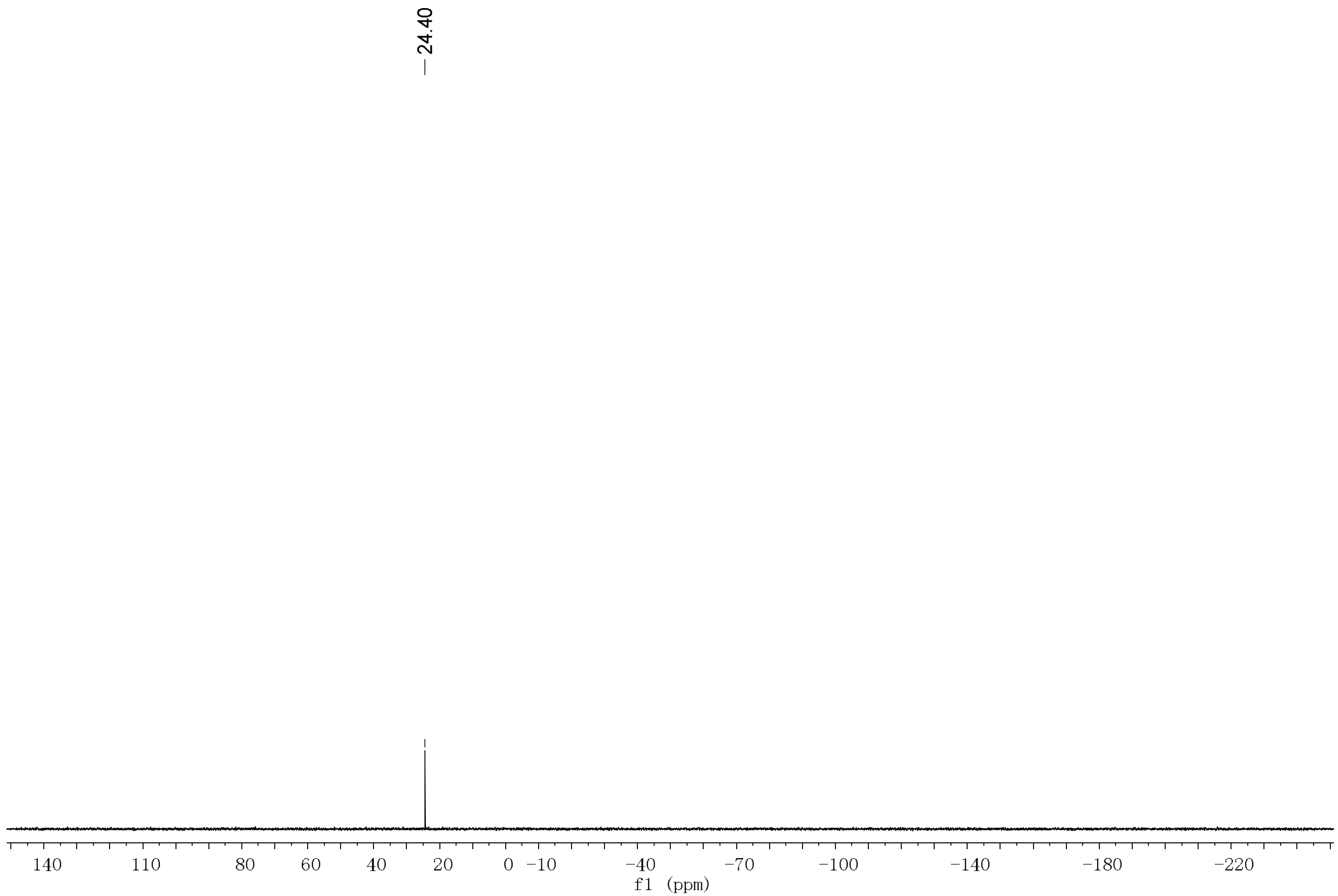

Figure 13s-b. ^{31}P NMR spectrum of **13** in $CDCl_3$

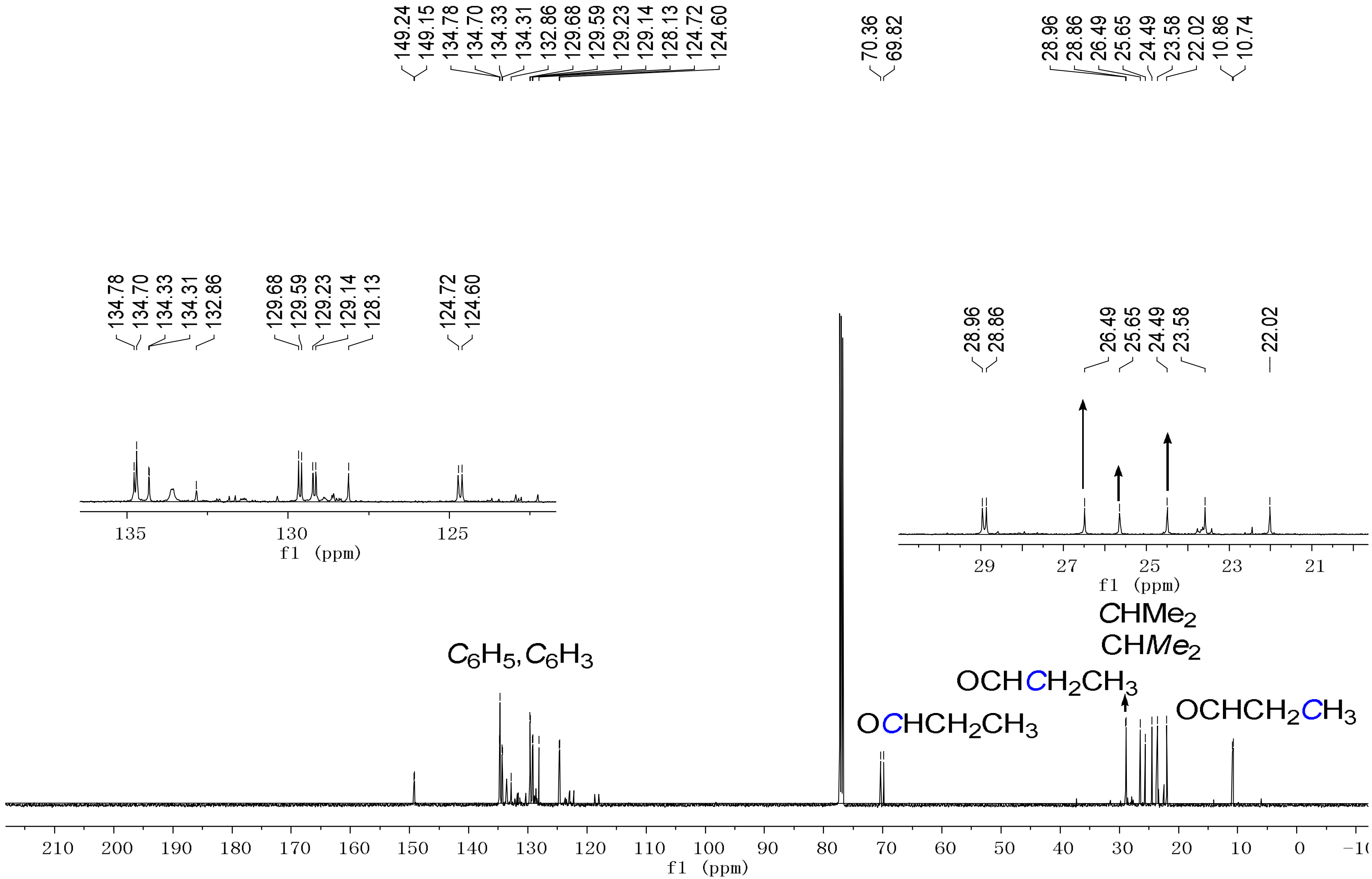

Figure 13s-c. ^{13}C NMR spectrum of **13** in $CDCl_3$

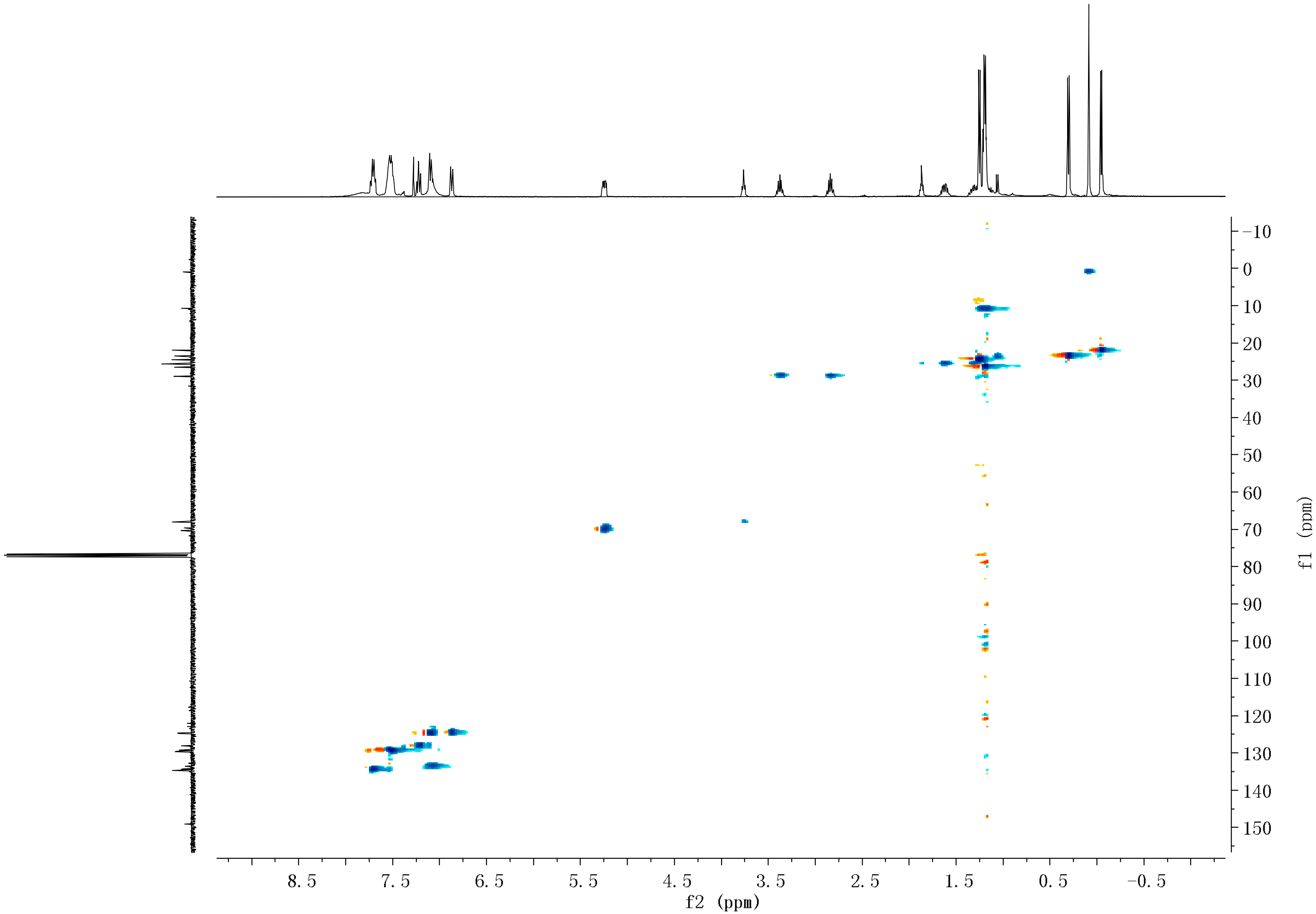

Figure 13s-d. $^{1}H,^{13}C$-HSQC spectrum of **13** in $CDCl_3$