Isolation and Reactivity of Heteroleptic Magnesium 1,3-Benzazaphospholide Complexes

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S.1 ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR Spectrum

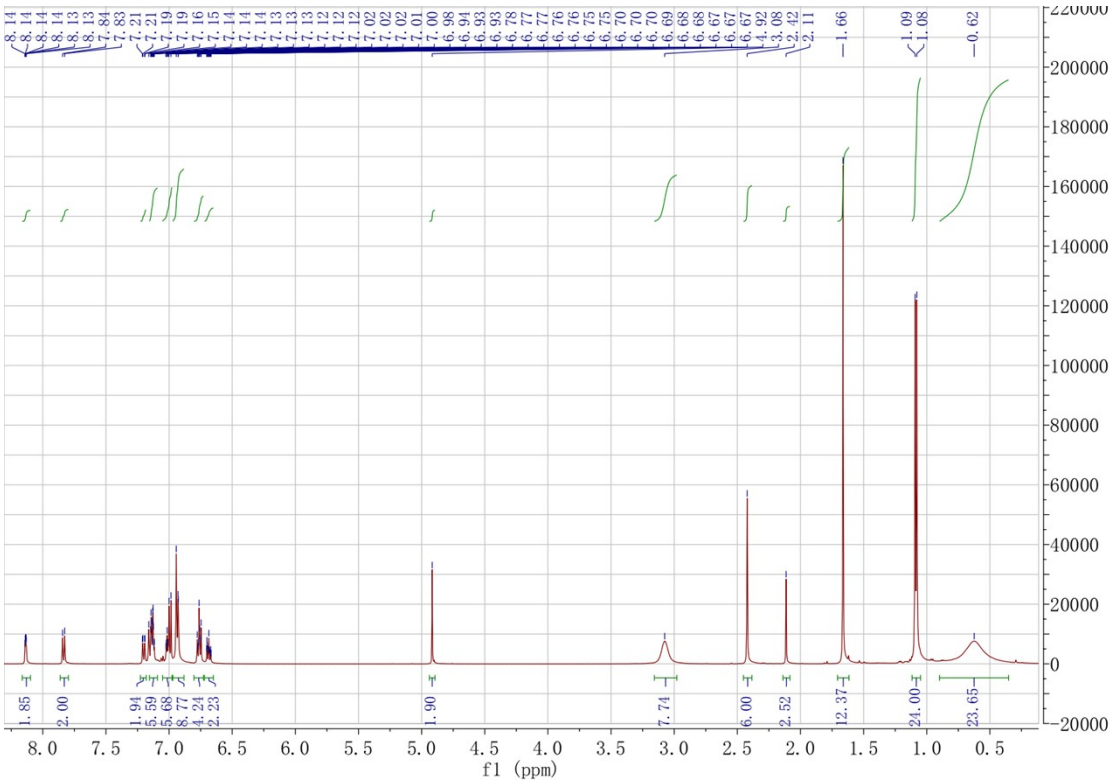


Fig. 1 ^{1}H NMR Spectrum (500 MHz, 298 K, C_6D_6) for compound **2a**

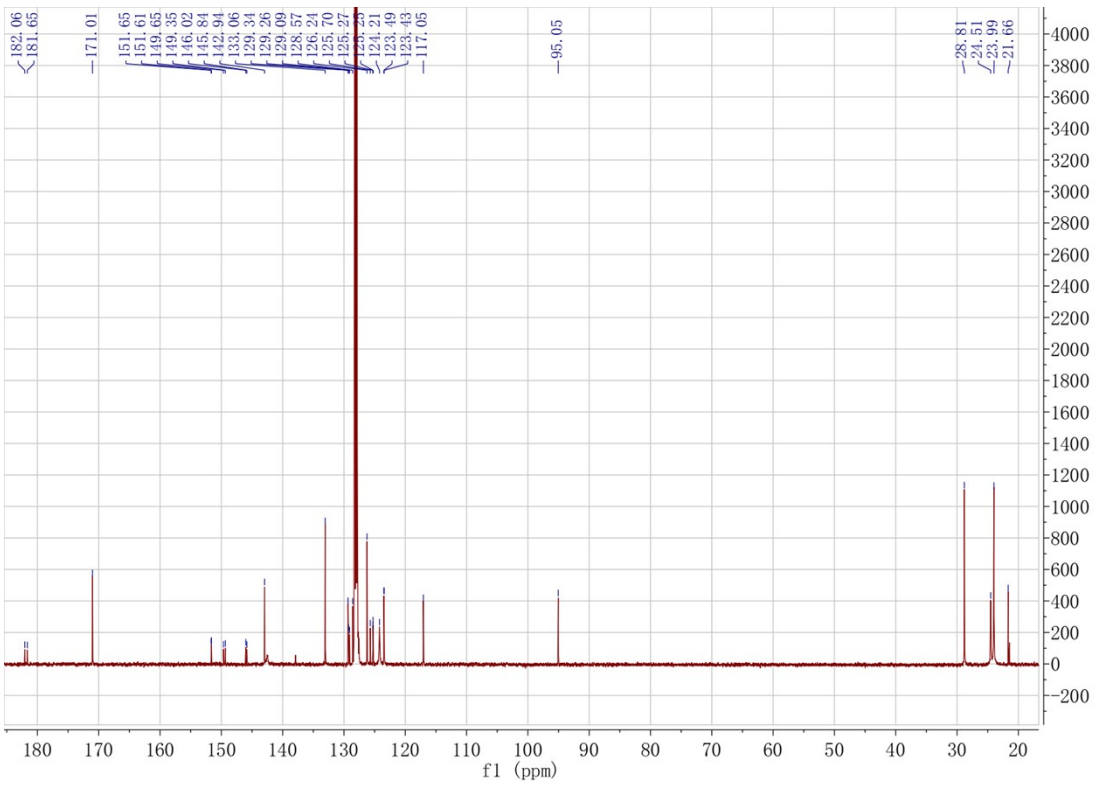
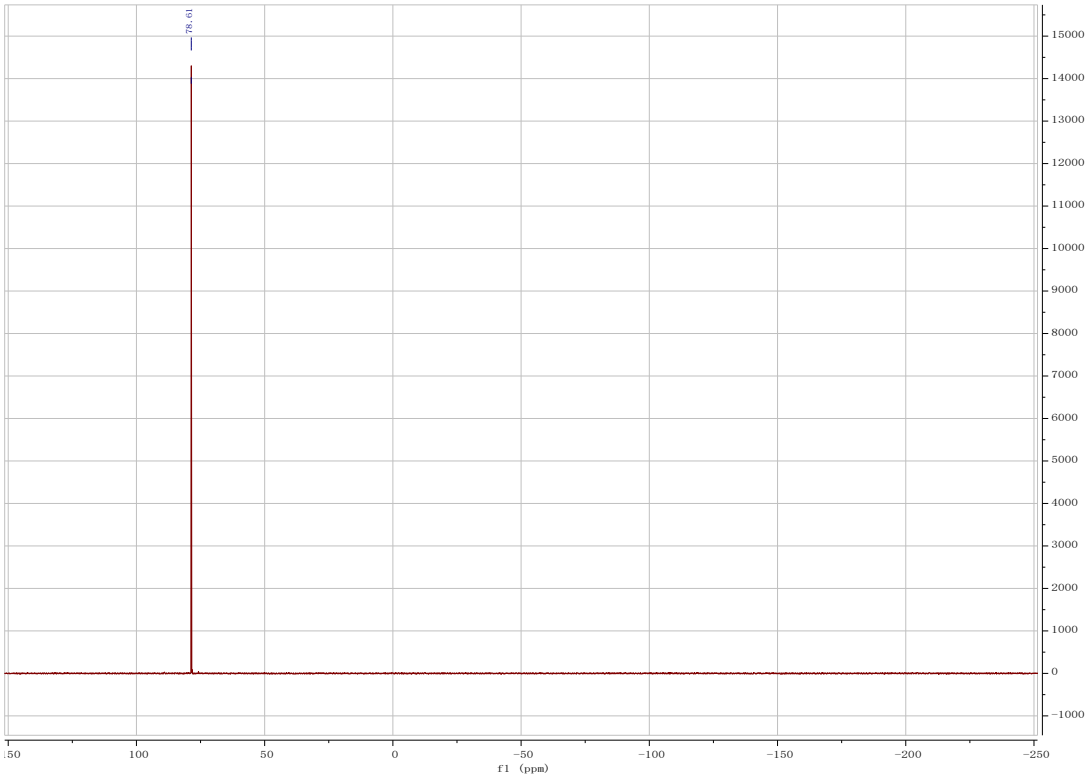


Fig. 2 $^{13}C\{^{1}H\}$ NMR Spectrum (126 MHz, 298 K, C_6D_6) for compound **2a**



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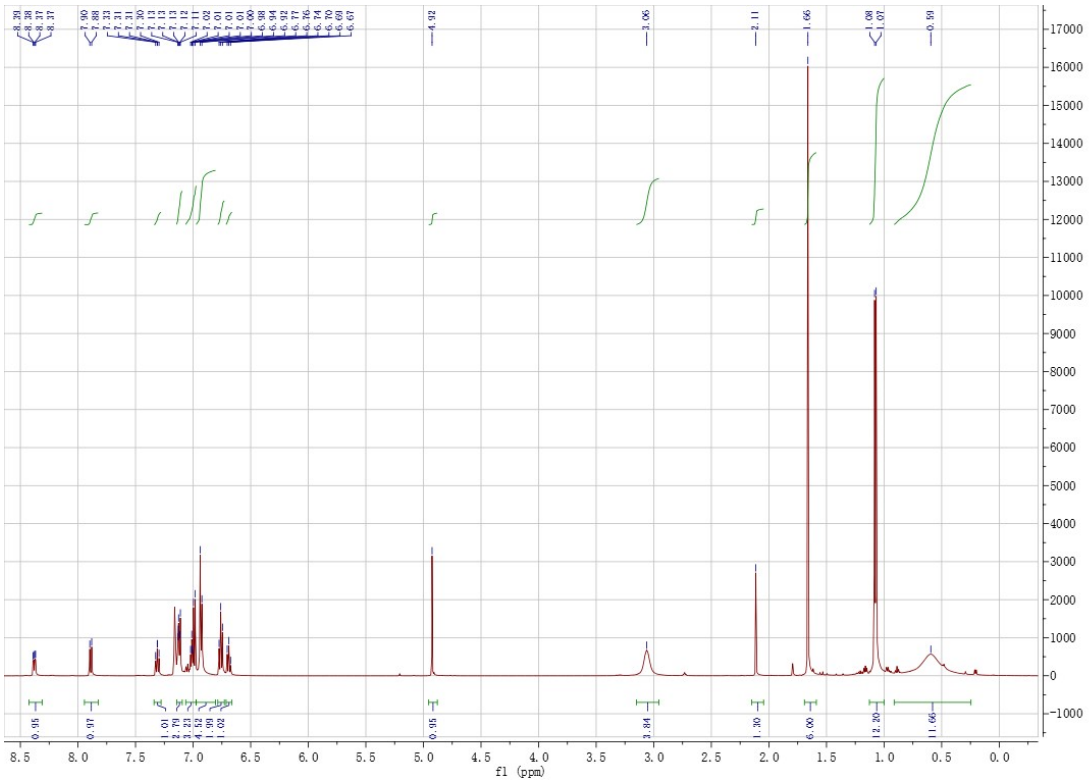


Fig. 4 ^{1}H NMR Spectrum (500 MHz, 298 K, C_6D_6) for compound **2b**

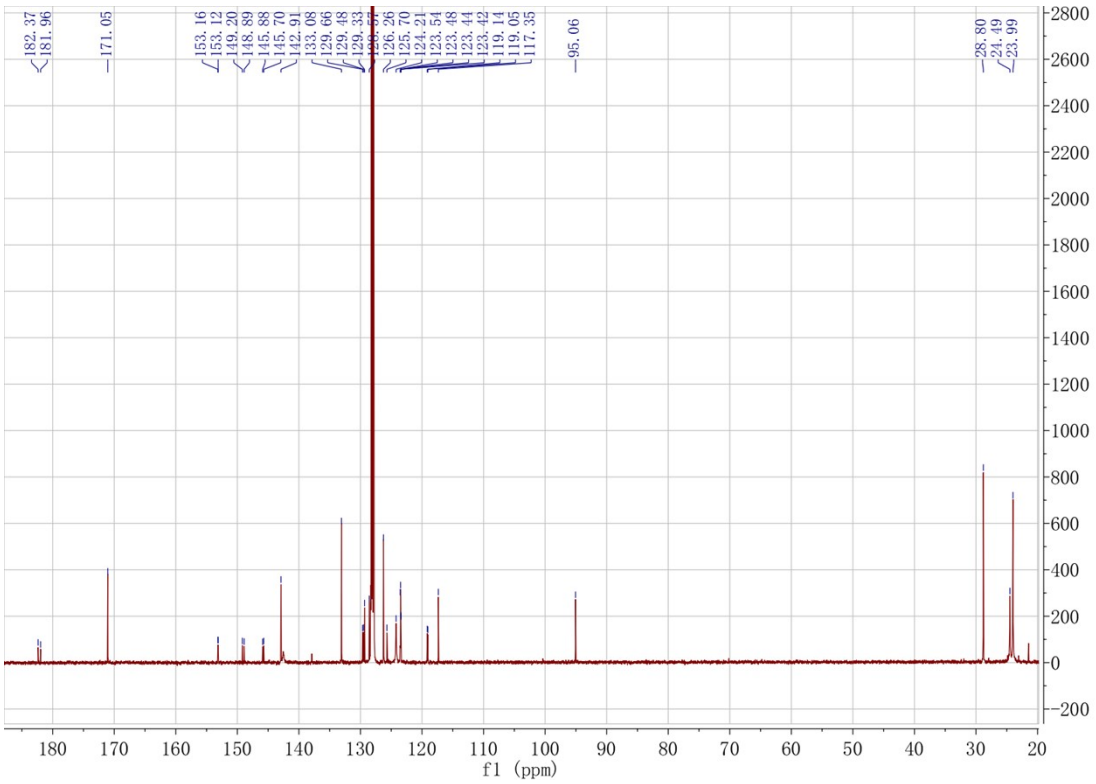


Fig.5 $^{13}C\{^{1}H\}$ NMR Spectrum (126 MHz, 298 K, C_6D_6) for compound **2b**

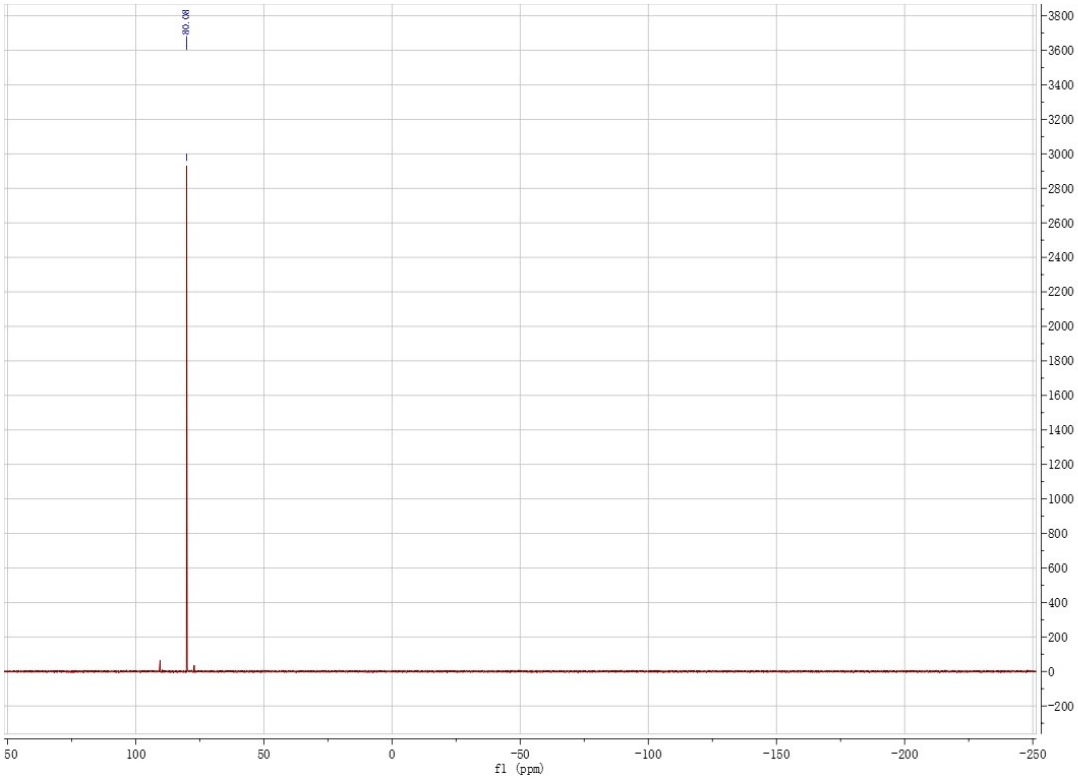


Fig. 6 $^{31}P\{^{1}H\}$ NMR Spectrum (202 MHz, 298 K, C_6D_6) for compound **2b**

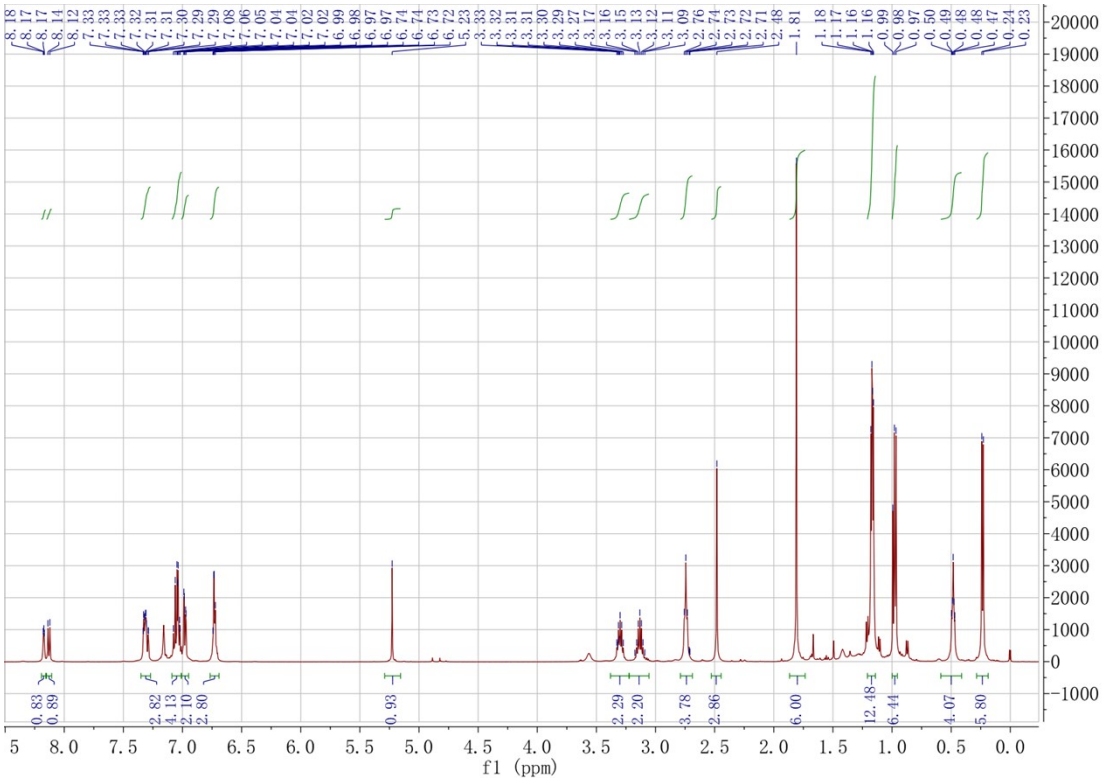
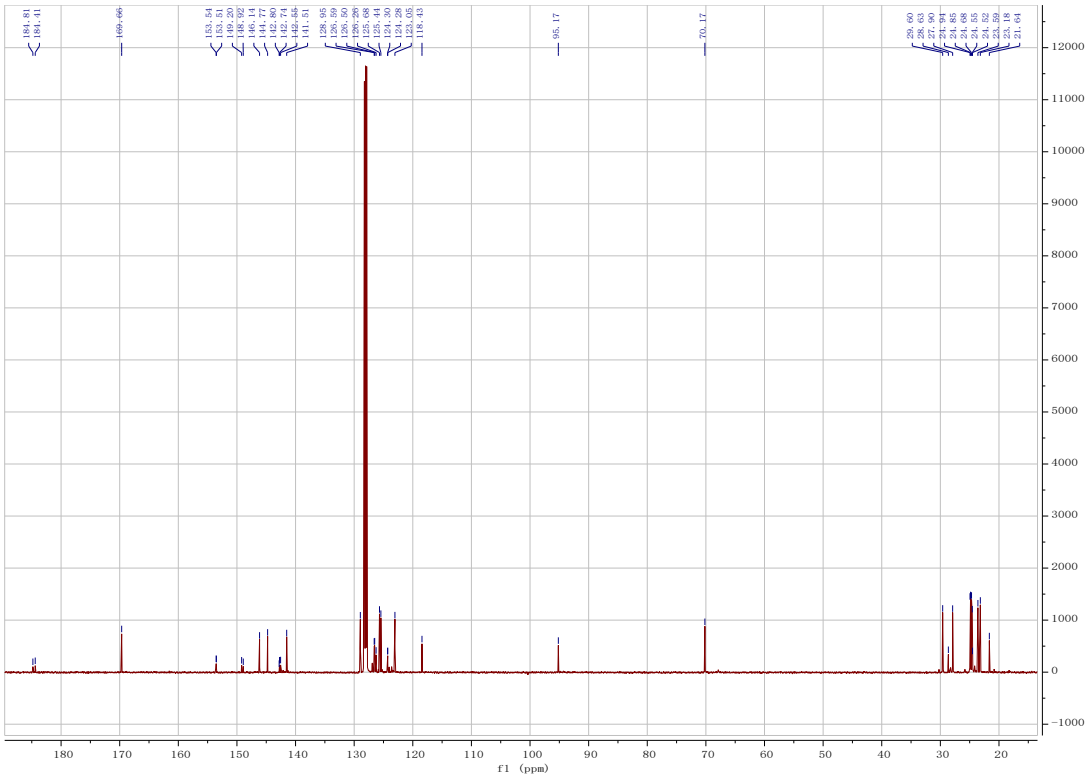


Fig. 7 ^{1}H NMR Spectrum (500 MHz, 298 K, C_6D_6) for compound **3a**



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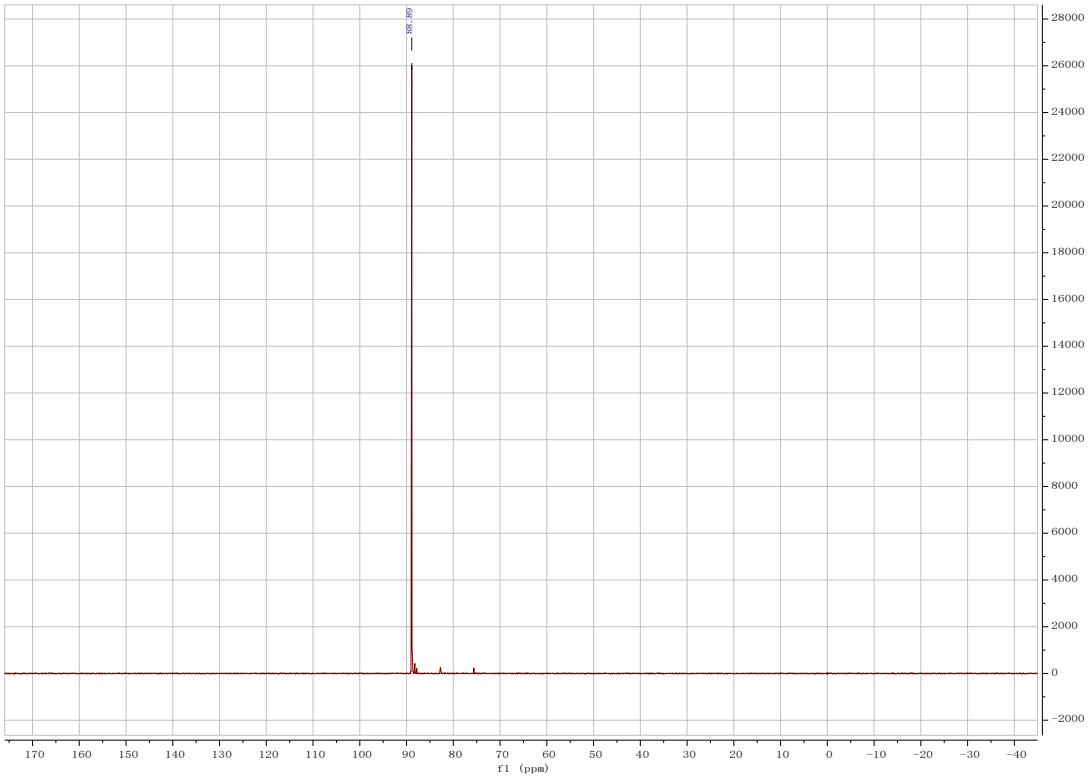
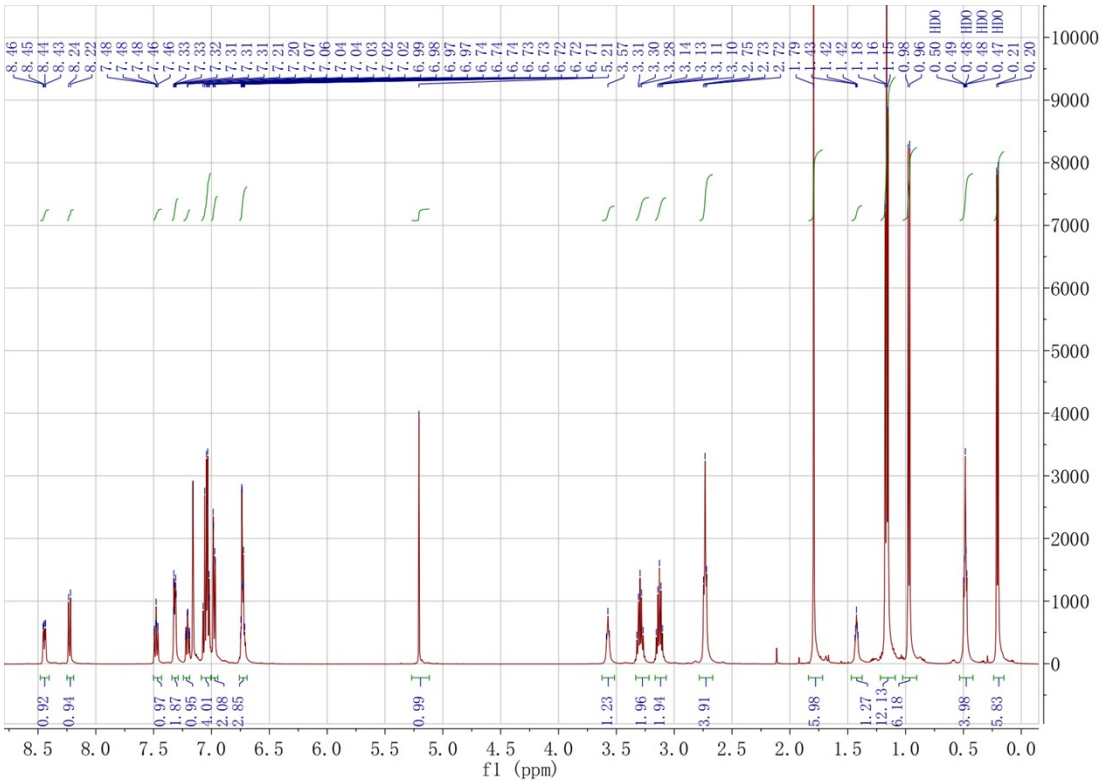


Fig. 9 $^{31}P\{^{1}H\}$ NMR Spectrum (202 MHz, 298 K, C_6D_6) for compound **3a**



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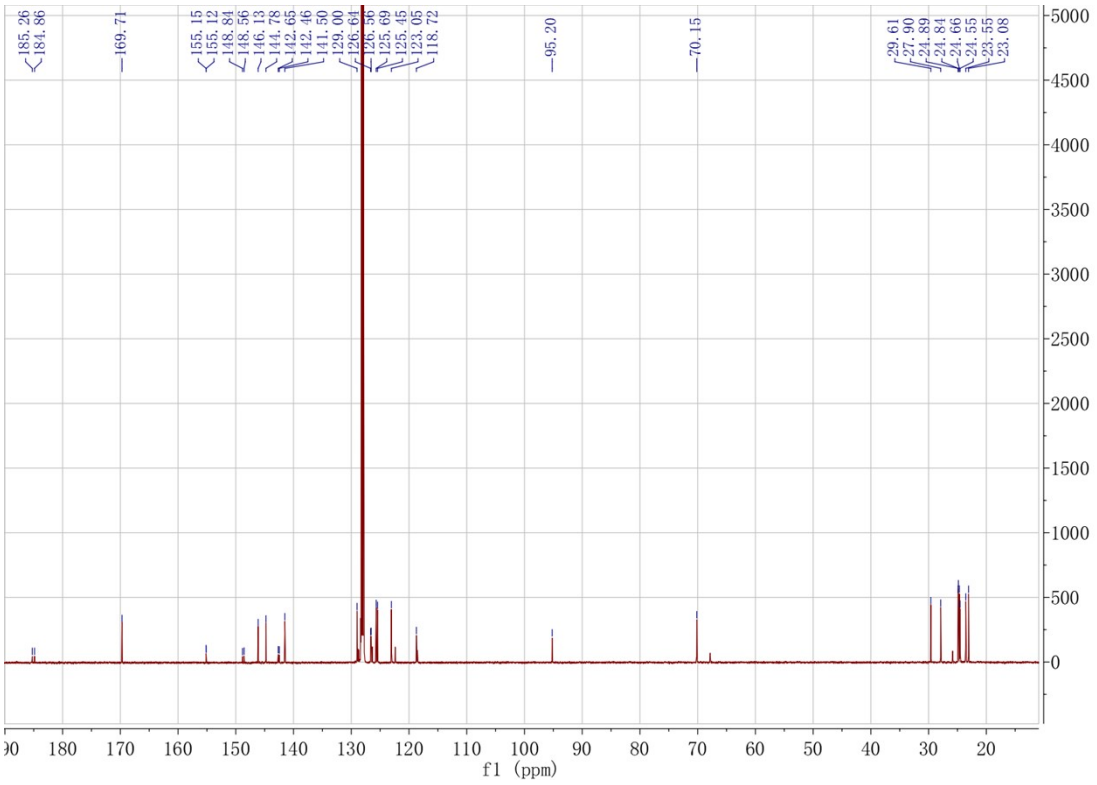

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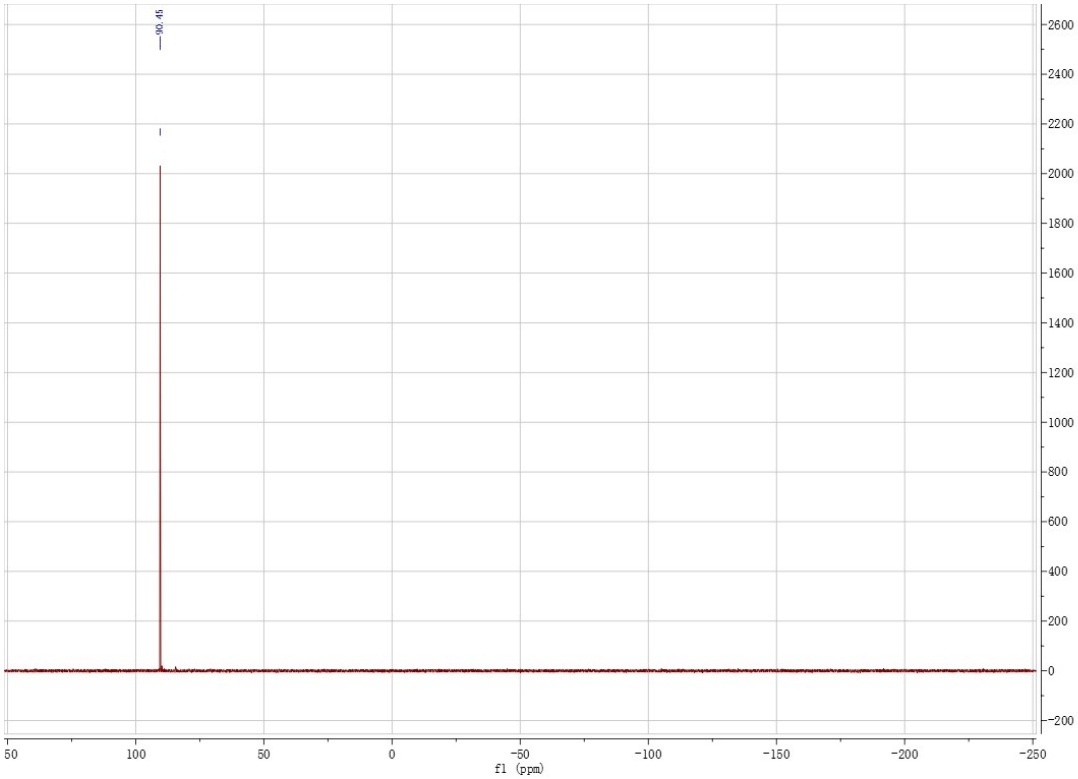


Fig. 12 $^{31}P\{^{1}H\}$ NMR Spectrum (126 MHz, 298 K, C_6D_6) for compound **3b**

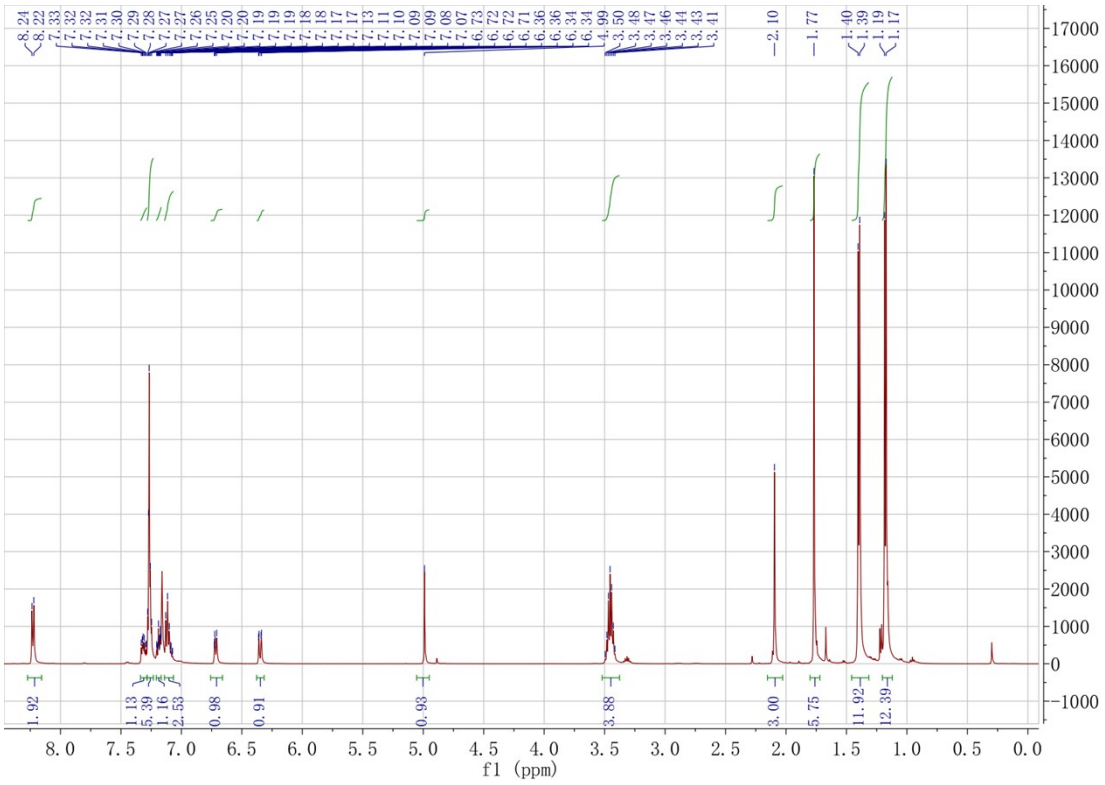


Fig. 13 ^{1}H NMR Spectrum (500 MHz, 298 K, C_6D_6) for compound **4a**

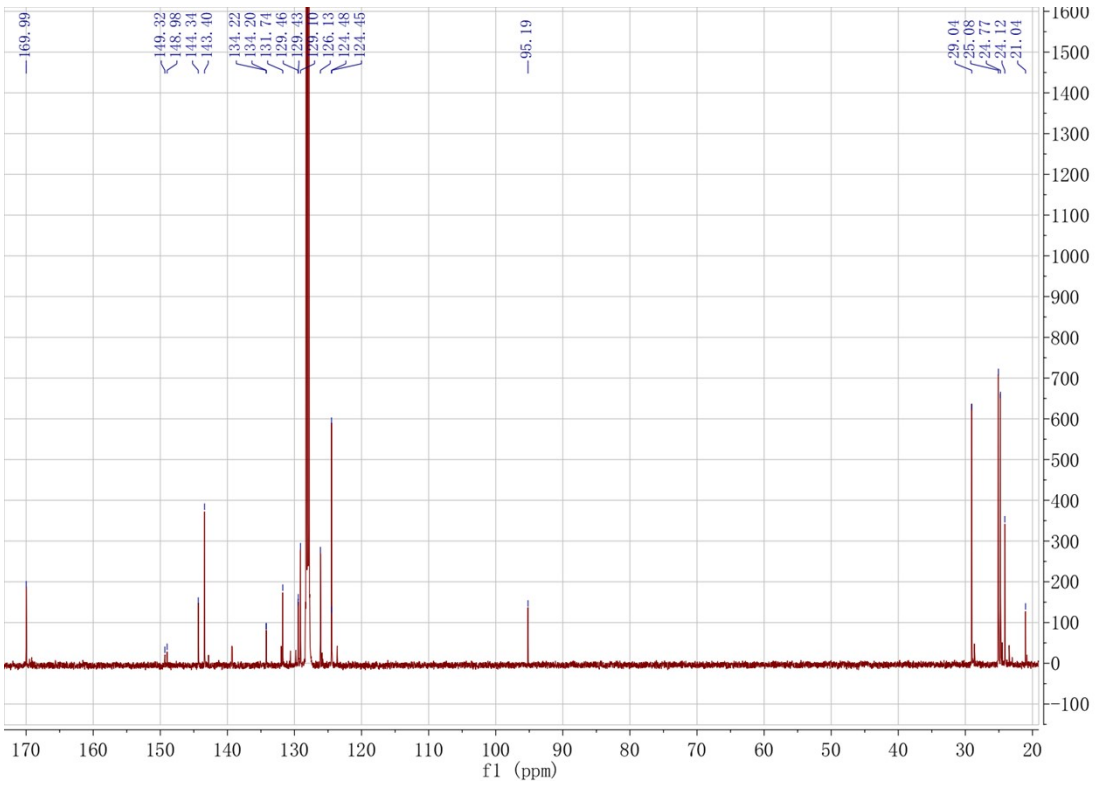
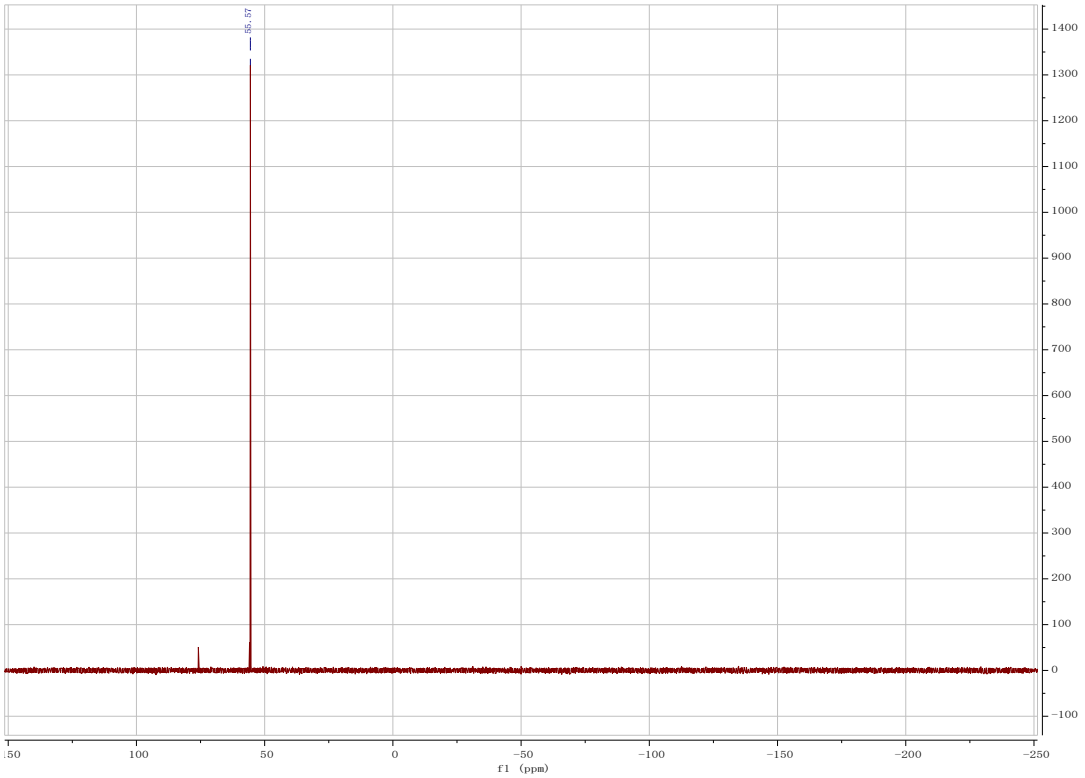


Fig. 14 ^{13}C{^{1}H} NMR Spectrum (126 MHz, 298 K, C_6D_6) for compound **4a**



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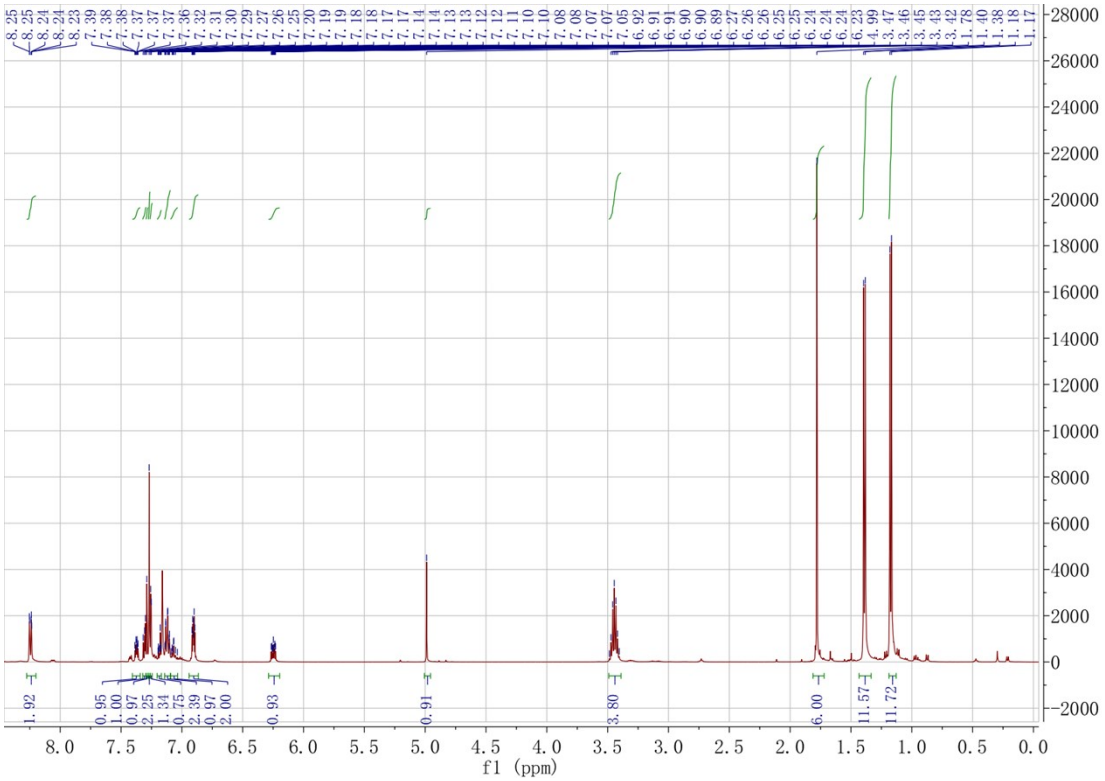

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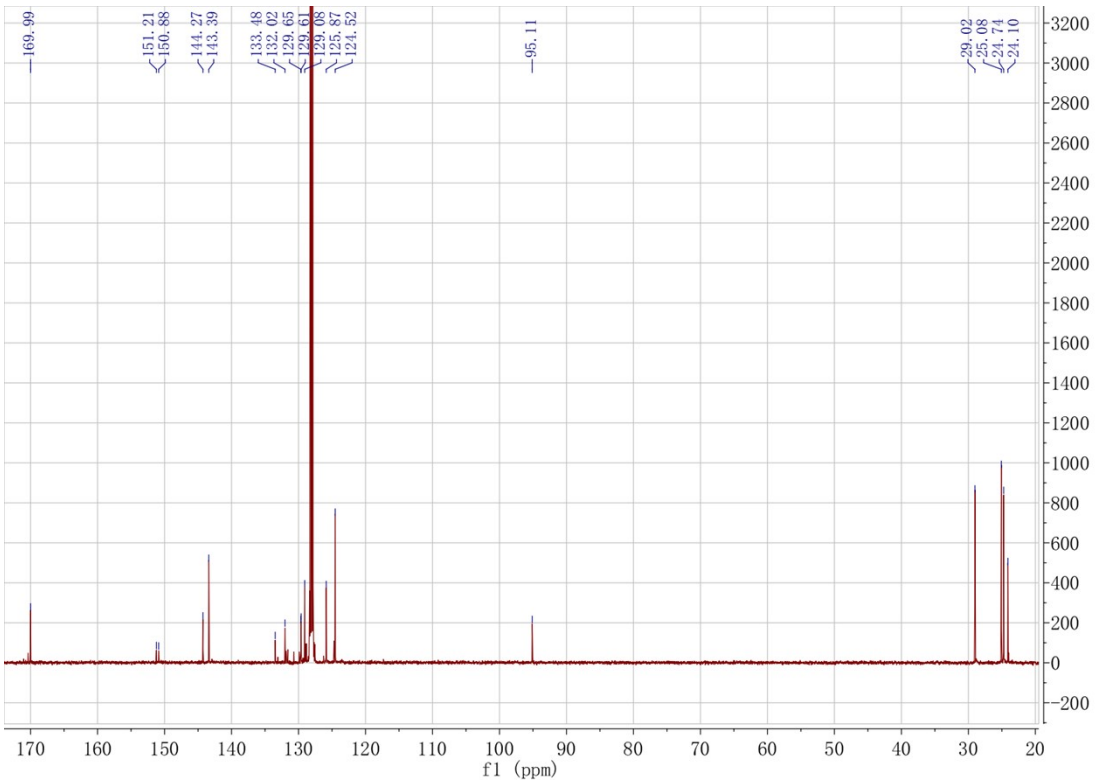

Fig. 17 $^{13}C\{^{1}H\}$ NMR Spectrum (126 MHz, 298 K, C_6D_6) for compound **4b**

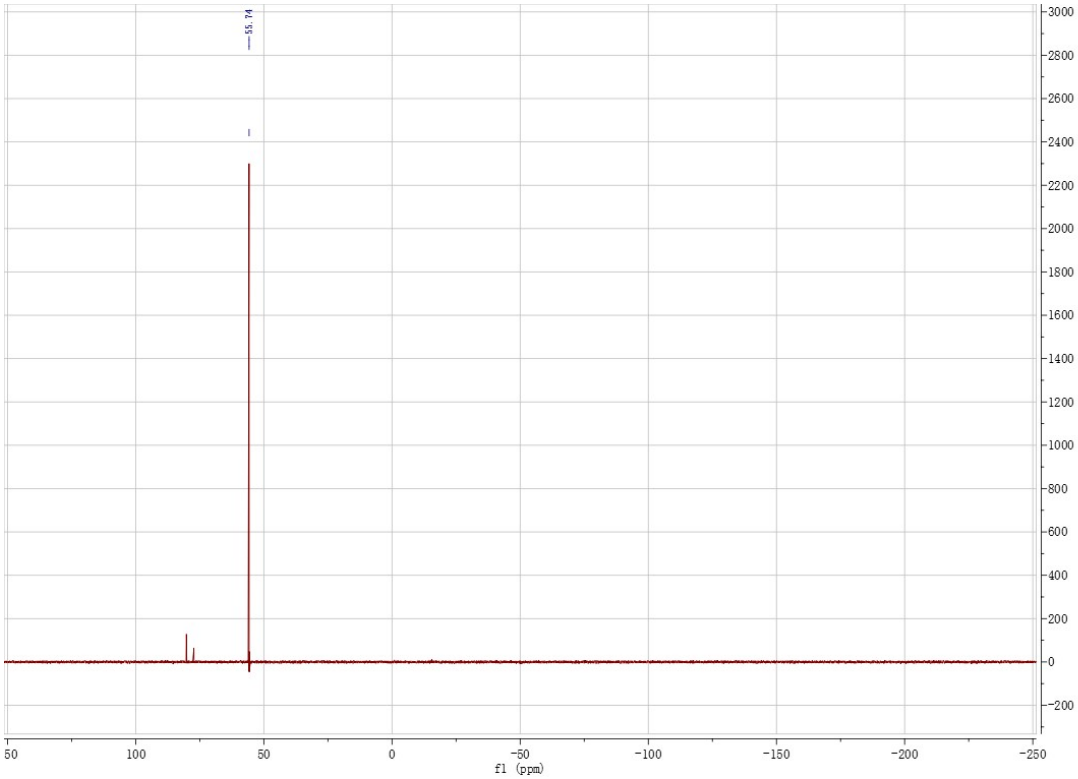

Fig. 18 $^{31}P\{^{1}H\}$ NMR Spectrum (202 MHz, 298 K, C_6D_6) for compound **4b**

Fig. 19 ^{1}H NMR Spectrum (500 MHz, 298 K, $CDCl_3$) for compound rac-**5a.**

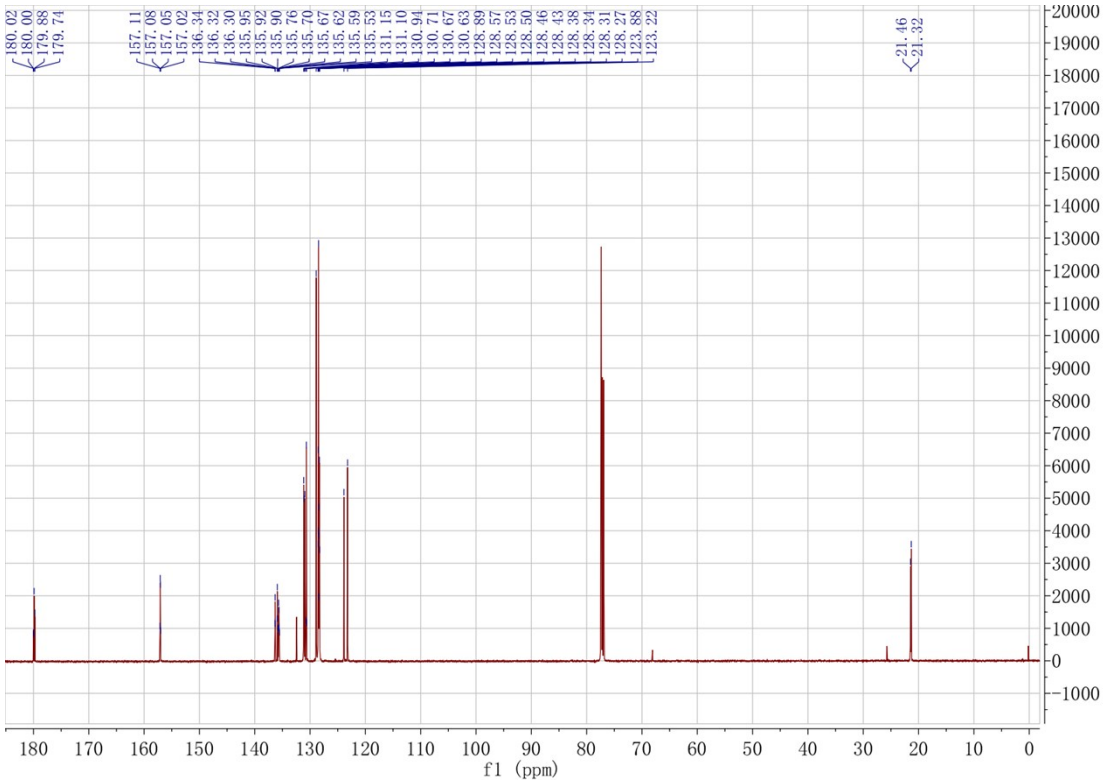

Fig. 20 ^{13}C{^{1}H} NMR Spectrum (126 MHz, 298 K, C_6D_6) for compound **5a**

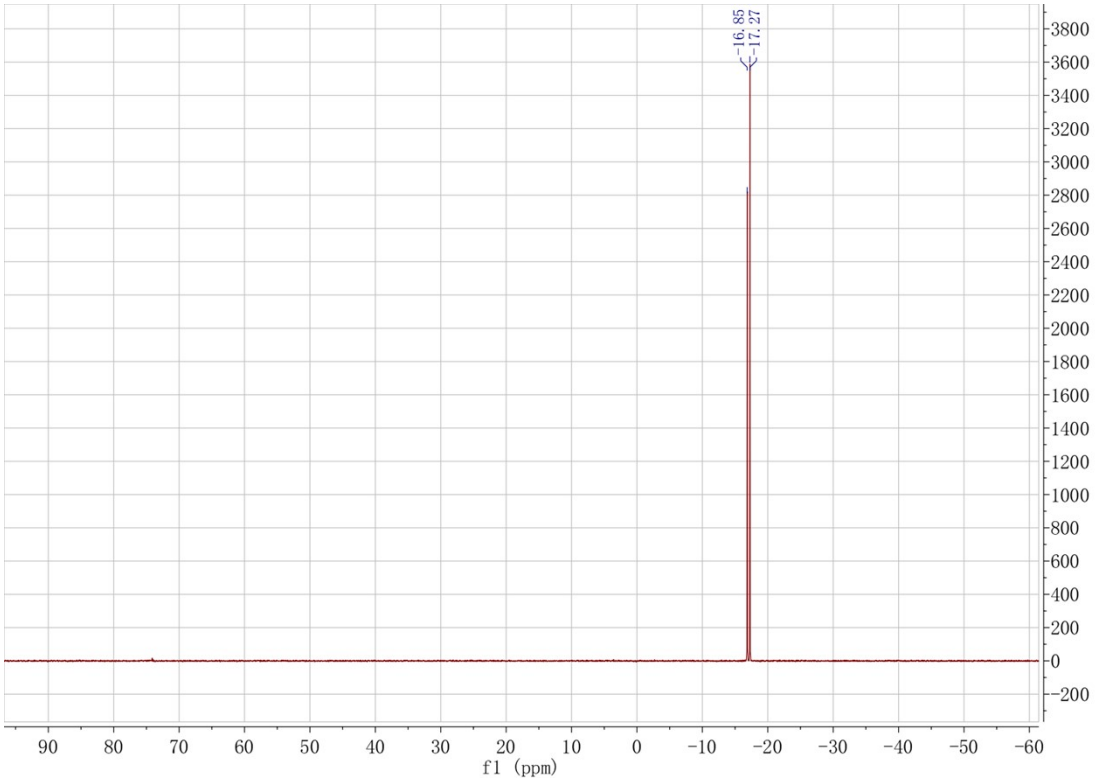

Fig. 21 $^{31}P\{^{1}H\}$ NMR Spectrum (202 MHz, 298 K, $CDCl_3$) for compound rac-**5a**

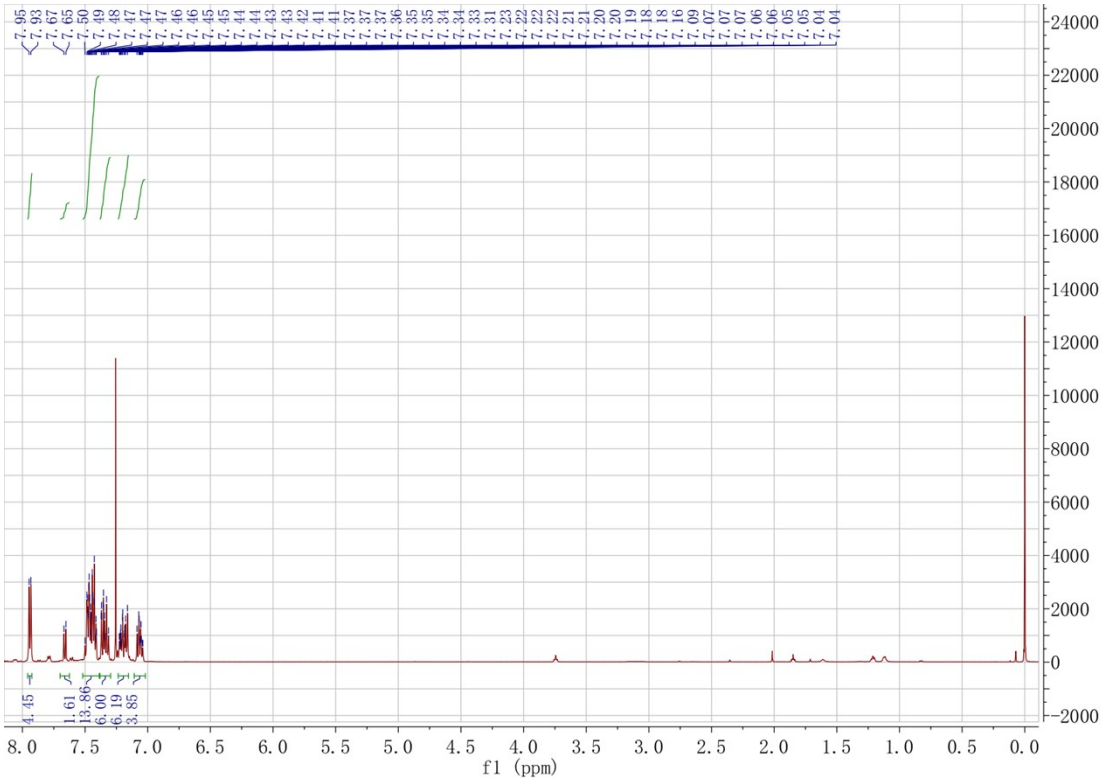

Fig. 22 ^{1}H NMR Spectrum (500 MHz, 298 K, $CDCl_3$) for compounds rac-**5b**

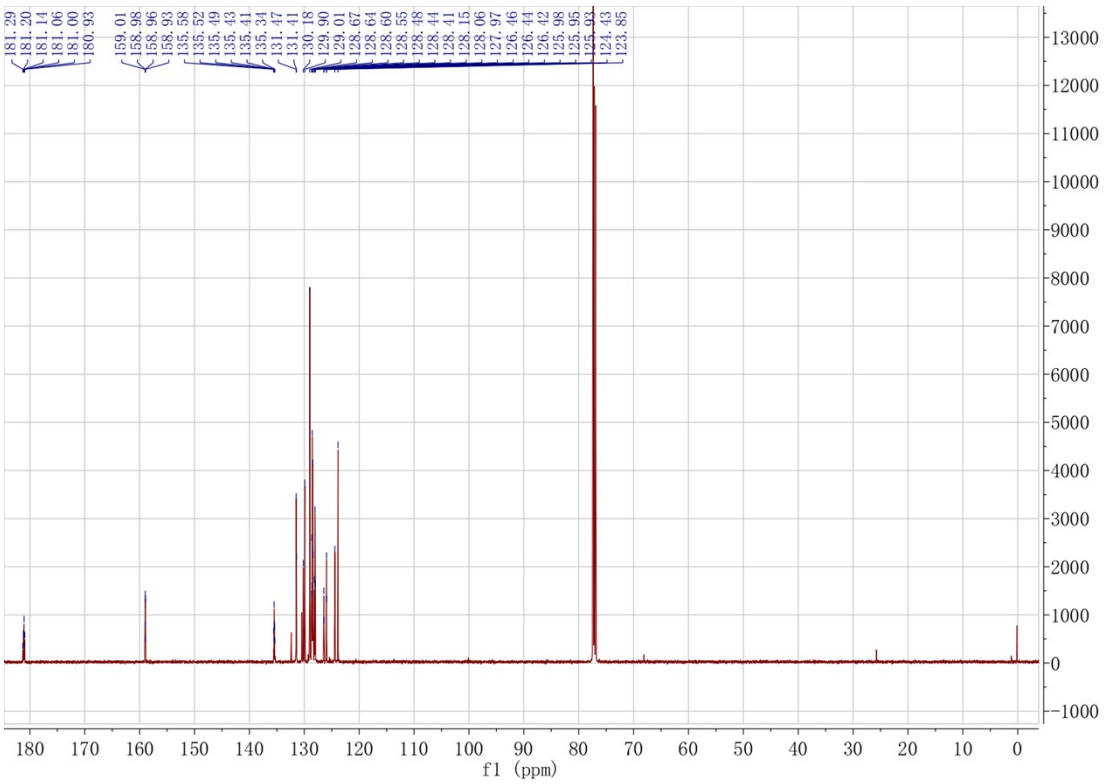

Fig. 23 $^{13}C\{^{1}H\}$ NMR Spectrum (126 MHz, 298 K, $CDCl_3$) for compound rac-**5b.**

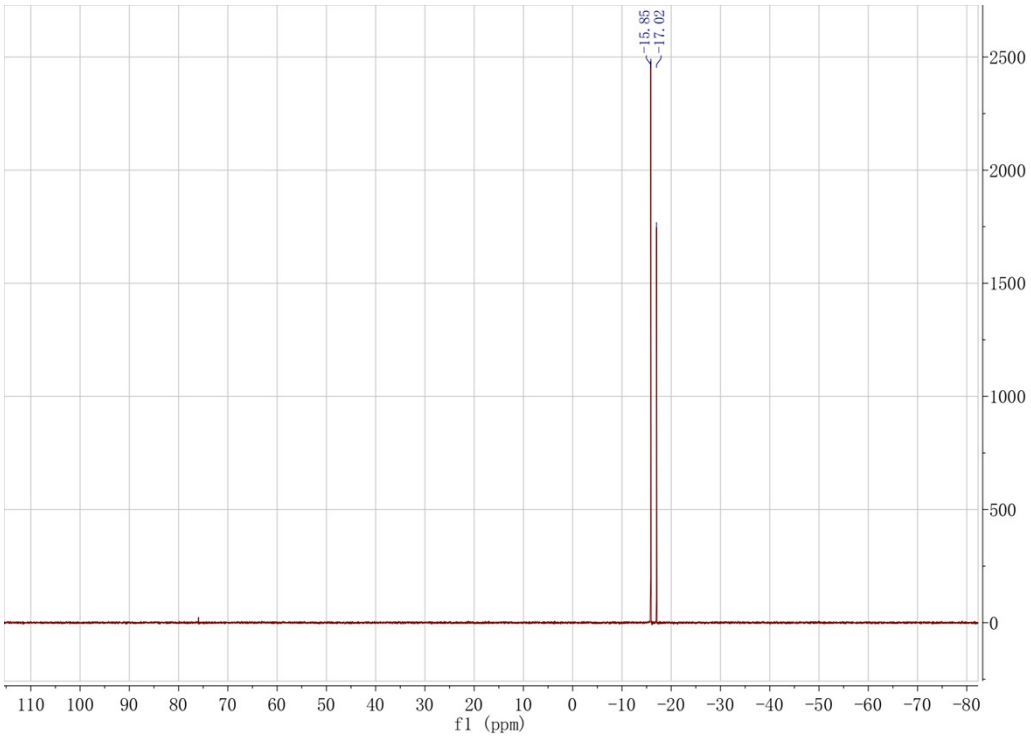

Fig. 24 $^{31}P\{^{1}H\}$ NMR Spectrum (202 MHz, 298 K, $CDCl_3$) for compound rac-**5b**

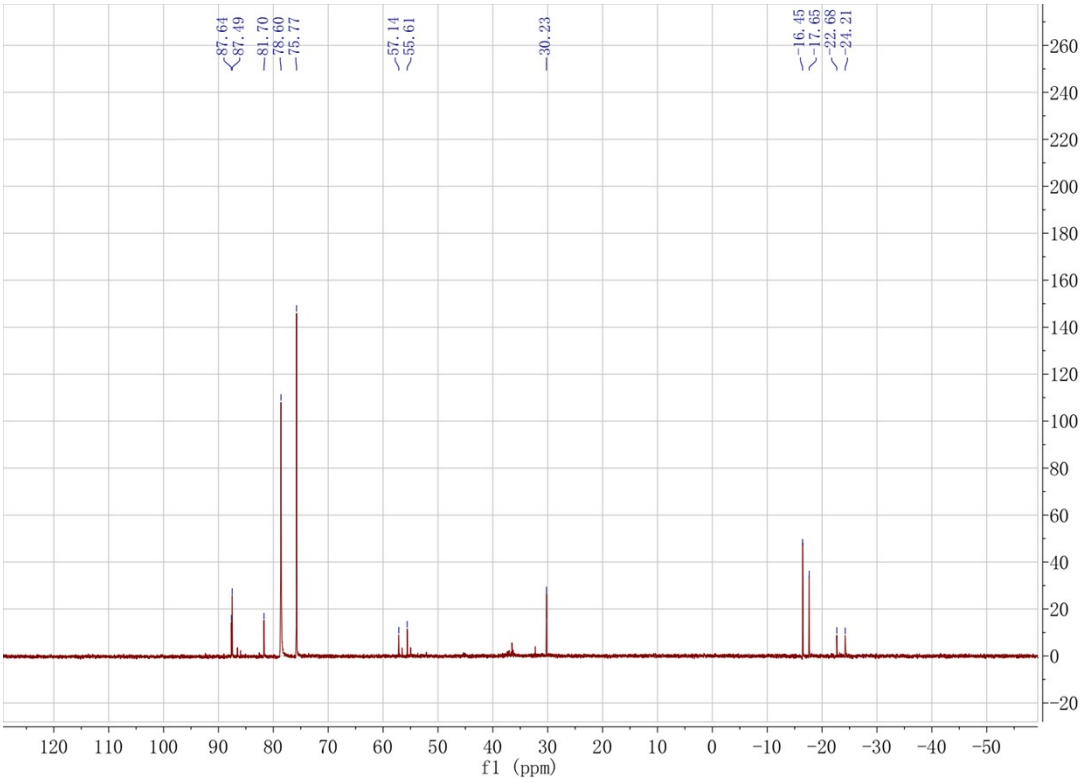

Fig. 25 $^{31}P\{^{1}H\}$ NMR Spectrum (202 MHz, 298 K, C_6D_6) for the C_6D_6 solution of **2a** exposed to air for 5 minutes.

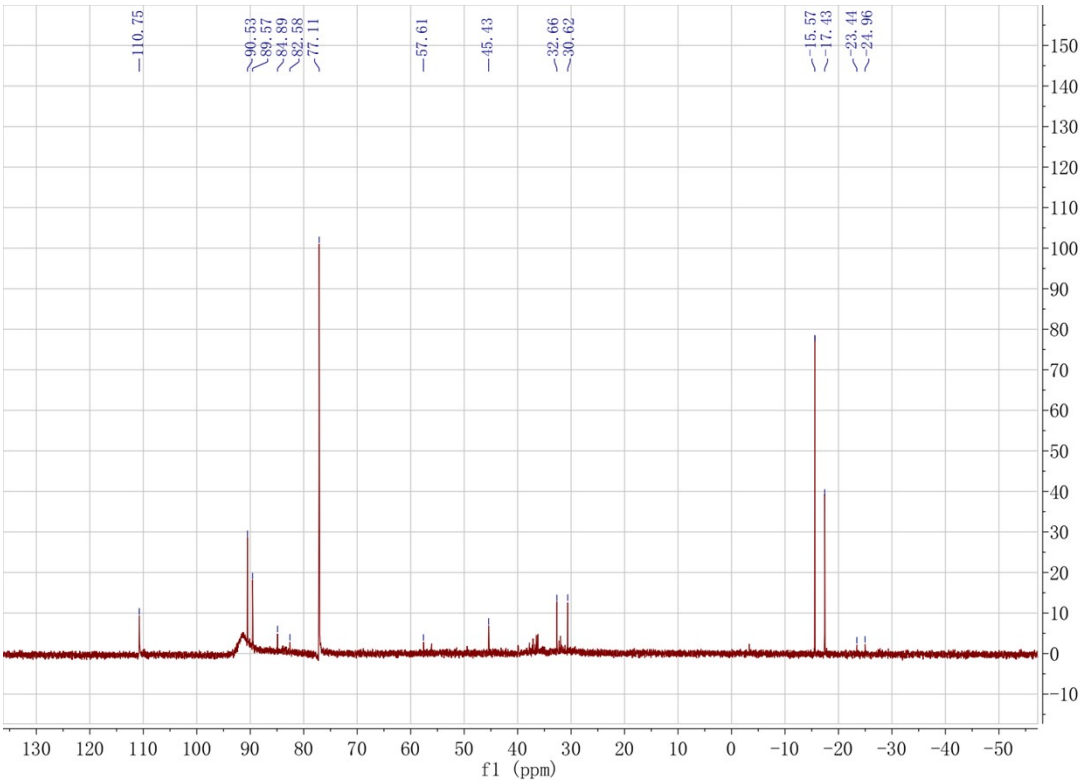

Fig. 26 $^{31}P\{^{1}H\}$ NMR Spectrum (202 MHz, 298 K, C_6D_6) for the C_6D_6 solution of **2b** exposed to air for 5 minutes.

S.2 **Single-Crystal X-ray Structure Determinations**

Suitable single crystals were sealed under N_2 in thin-walled glass capillaries. X-ray diffraction data of compounds **2a**, **2b, 3a**, **3b, 4a** and **5a** were collected on a SMART APEX CCD diffractometer (Bruker, graphite-monochromated Mo-*K*a radiation, φ-ω-scan technique, λ = 0.71073 Å). The intensity data were integrated by means of the SAINT program.[1] SADABS[2] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against F^2 using all reflections with the aid of the SHELXTL package. [3] All non-hydrogen atoms were refined anisotropically. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All non-hydrogen atoms were found from the difference Fourier syntheses. All calculations were performed using the Bruker Smart program. crystallographic data are given below in structural data tables 1, 2. CCDC 2513522 (**2a**), 2513523 (**2b**), 2513524 (**3a**), 2513525 (**3b**) and 2513526 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

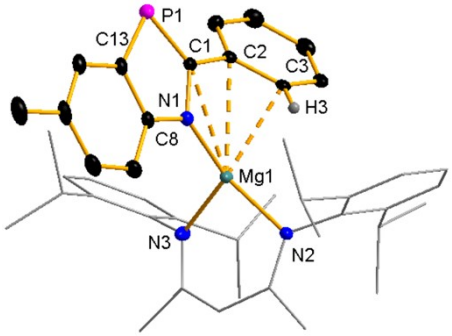

Fig. 27 Thermal ellipsoid (30%) plot of complex **2a**. Hydrogen atoms are omitted except for H3, and some groups are shown in wireframe for clarity. The asymmetric unit contains half of a molecule of free toluene, which is not shown. Selected Bond Lengths (Å) and Angles (°): Mg(1)–N(3) 2.008(2), Mg(1)–N(2) 2.015(2), Mg(1)–N(1) 2.012(2), Mg(1)–C(1) 2.826(2), Mg(1)–C(2) 2.825(2), Mg(1)–C(3) 2.547(2), P(1)–C(1) 1.742(2), P(1)–C(13) 1.780(2), N(1)–C(1) 1.364(2), N(1)–C(8) 1.381(2), C(8)–C(13) 1.413(3), C(1)–C(2) 1.479(3), C(2)–C(3) 1.404(3), C(1)–P(1)–C(13）87.56(9), N(1)–C(1)–P(1) 116.9(1), N(1)–C(8)–C(13) 114.6(2), C(8)–C(13)–P(1) 110.9(1), C(1)–N(1)–C(8) 110.1(2), N(1)–Mg(1)–N(2) 125.2(7), N(1)–Mg(1)–N(3) 122.3(7), N(3)–Mg(1)–N(2) 95.4(7).

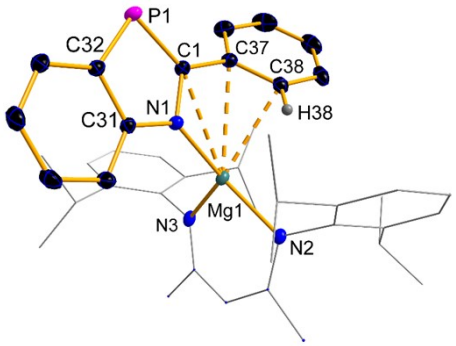

Fig. 28 Thermal ellipsoid (30%) plot of complex **2b**. Hydrogen atoms are omitted except for H38, and some groups are shown in wireframe for clarity. The asymmetric unit contains half of a molecule of free toluene, which is not shown. Selected Bond Lengths (Å) and Angles (°): Mg(1)–N(1) 2.017(1), Mg(1)–N(2) 2.013(1), Mg(1)–N(3) 2.007(2), Mg(1)–C(1) 2.842(3), Mg(1)–C(37) 2.893(3), Mg(1)–C(38) 2.663(3), P(1)–C(1) 1.738(1), N(1)–C(1) 1.367(2), P(1)–C(32) 1.780(2), N(1)–C(31) 1.383(2), C(31)–C(32) 1.423(2), C(1)–C(37) 1.477(2), C(37)–C(38) 1.409(2), C(1)–P(1)–C(32) 87.8(7), C(1)–N(1)–C(31) 110.1(1), N(1)–C(1)–P(1) 117.0(1), N(1)–C(31)–C(32) 114.3(1), C(31)–C(32)–P(1) 110.9(1), N(2)–Mg(1)–N(1) 130.4(6), N(3)–Mg(1)–N(1) 121.1(6), N(3)–Mg(1)–N(2) 96.2(6).

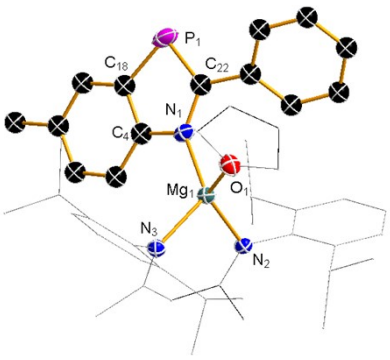

Fig. 29 Thermal ellipsoid (30%) plot of complex **3a**. Hydrogen atoms are omitted, and some groups are shown in wireframe for clarity. Selected Bond Lengths (Å) and Angles (°): Mg(1)–O(1) 2.047(2), Mg(1)–N(3) 2.055(2), Mg(1)–N(1) 2.063(2), Mg(1)–N(2) 2.065 (2), C(4)–N(1) 1.388(3), C(22)–N(1) 1.362(2), C(4)–C(18) 1.420(4), C(18)–P(1) 1.767(3), C(22)–P(1) 1.744(3), N(1)–C(4)–C(18) 114.9 (2), C(4)–C(18)–P(1) 110.5(2), N(1)–C(22)–P(1) 121.82(18), C(22)–N(1)–C(4) 109.6(2), C(22)–P(1)–C(18) 88.2(1), O(1)–Mg(1)–N(3) 101.03(8), O(1)–Mg(1)–N(1) 103.33(8), O(1)–Mg(1)–N(2) 128.43(8), N(3)–Mg(1)–N(1) 122.1(9), N(3)–Mg(1)–N(2) 93.1(8), N(1)–Mg(1)–N(2) 110.3(8).

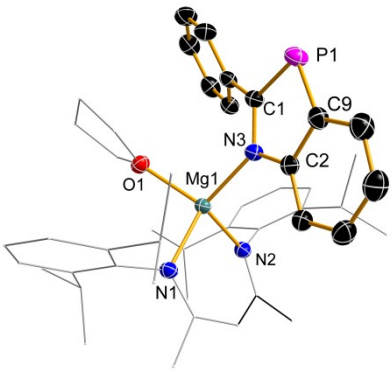

Fig. 30 Thermal ellipsoid (30%) plot of complex **3b**. Hydrogen atoms are omitted, and some groups are shown in wireframe for clarity. The asymmetric unit contains half of a molecule of free thf, which is not shown. Selected Bond Lengths (Å) and Angles (°): Mg(1)–O(1) 2.036(2), Mg(1)–N(2) 2.060(2), Mg(1)–N(3) 2.062(2), Mg(1)–N(1) 2.065(2), C(1)–N(3) 1.370(3), C(1)–P(1) 1.738(2), C(2)–N(3) 1.381(3), C(2)–C(9) 1.415(3), C(9)–P(1) 1.770(2), N(3)–C(1)–P(1) 116.8 (2), N(3)–C(2)–C(9) 115.3(2), C(2)–C(9)–P(1) 110.4(2), C(1)–N(3)–C(2) 109.3(2), C(1)–P(1)–C(9) 88.1(1), O(1)–Mg(1)–N(2) 131.34(7), O(1)–Mg(1)–N(3) 103.00(7), N(2)–Mg(1)–N(3) 107.96(7), O(1)–Mg(1)–N(1) 99.09(7), N(2)–Mg(1)–N(1) 92.13(7), N(3)–Mg(1)–N(1) 125.94(7).

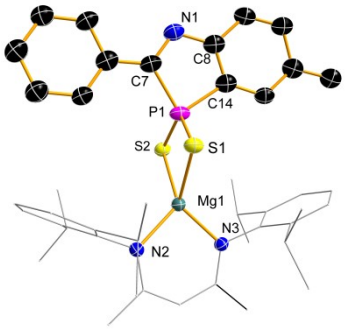

Fig. 31 Thermal ellipsoid (30%) plot of complex **4a**. Hydrogen atoms are omitted, and some groups are shown in wireframe for clarity. Selected Bond Lengths (Å) and Angles (°): S(1)–Mg(1) 2.460(2), S(2)–Mg(1) 2.498(2), Mg(1)–N(3) 2.010(4), Mg(1)–N(2) 2.013(4), P(1)–C(7) 1.836(6), P(1)–C(14) 1.887(7), N(1)–C(7) 1.297(7), N(1)–C(8) 1.400(7), C(8)–C(14) 1.331(8), S(1)–P(1) 1.980(2), S(2)–P(1) 1.994(2), P(1)–S(1)–Mg(1) 81.51(6), P(1)–S(2)–Mg(1) 80.99(6), S(1)–Mg(1)–P(1) 42.09(4), S(2)–Mg(1)–P(1) 42.38(4), S(1)–Mg(1)–S(2) 84.37(6), S(1)–P(1)–S(2) 112.87(8), C(7)–P(1)–Mg(1) 147.5(2), N(3)–Mg(1)–N(2) 94.5(2), C(7)–N(1)–C(8) 113.2(5), C(7)–P(1)–C(14) 88.2(3), C(14)–C(8)–N(1) 120.7(6), N(1)–C(7)–P(1) 112.5(4), C(8)–C(14)–P(1) 105.4(5).

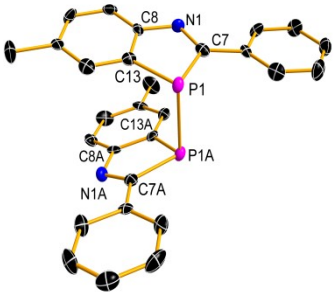

Fig. 32 Thermal ellipsoid (30%) plot of complex rac-**5a**. Hydrogen atoms are omitted, and some groups are shown in wireframe for clarity.

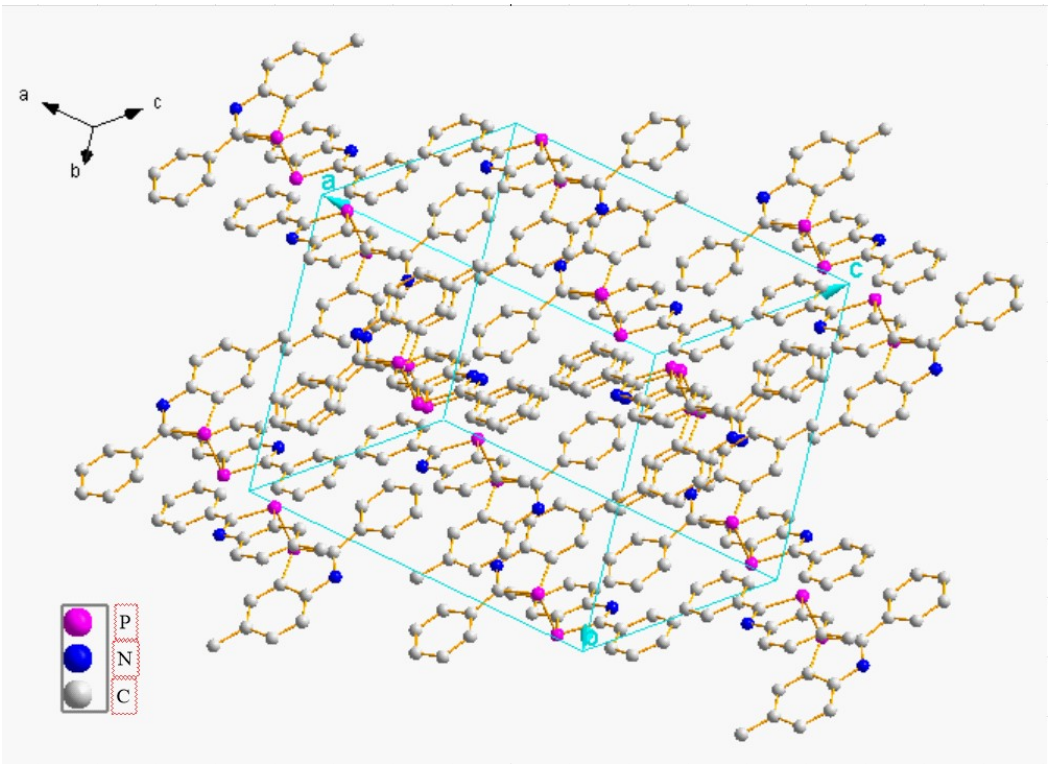

Fig. 33 Unit cell of rac-**5a**, Hydrogen atoms are omitted for clarity.

Table 1. Crystal and Data Collection Parameters of Complexes **2a**, **2b** and **3a**.

	2a·0.5toluene	**2b**·0.5toluene	**3a**
Formula	$C_{46.5}H_{56}MgN_3P$	$C_{45.5}H_{54}MgN_3P$	$C_{47}H_{60}MgN_3OP$
Molecular weight	712.22	698.19	738.26
Crystal dimens (mm)	0.30 × 0.20 × 0.16	0.30 × 0.20 × 0.18	0.20 × 0.16 × 0.11
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	Cc
Unit cell dimensions			
a (Å)	10.8701(15)	10.0667(15)	11.8726(3)
b (Å)	12.3027(17)	11.3787(17)	19.6268(4)
c (Å)	16.905(2)	18.648(3)	18.8009(4)
β (deg)	73.301(2)	96.792(2)	95.9250(10)
V (Å^3)	2062.3(5)	2037.3(5)	4357.60(17)
Z	2	2	4
Dc (g.cm^{-3})	1.147	1.138	1.125
μ (mm^{-1})	0.117	0.117	0.114
F (000)	766.0	750.0	1592.0
Radiation (λ =0.710730Å)	Mo-K_α	Mo-K_α	Mo-K_α
Temperature (K)	296.2	100.0	296.2
h,k,l range	$-12 \le h \le 12$ $-14 \le k \le 14$ $-20 \le l \le 20$	$-12 \le h \le 13$ $-14 \le k \le 14$ $-23 \le l \le 24$	$-14 \le h \le 14$ $-24 \le k \le 24$ $-23 \le l \le 23$
No. of reflections measured	16358	16231	17742
No. of unique reflections	7249 [R_{int} = 0.0250]	8630 [R_{int} = 0.0268]	7913 [R_{int} = 0.0203]
Completeness to θ	99.6% [θ=25.01]	92.7% [θ=27.46]	100 % [θ=26.00]
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F^2	Full-matrix least-squares on F2
Data / restraints / parameters	7249/15/496	8630/84/516	7913/2/507
Goodness-of-fit on F^2	1.015	1.066	1.046
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0437 wR_2 = 0.1138	R1 = 0.0453 wR2 = 0.1237	R1 = 0.0342 wR2 = 0.0851
R indices (all data)	R_1 = 0.0609 wR_2 = 0.1250	R_1 = 0.0594, w*R*2 = 0.1325	R1 = 0.0399 wR2 = 0.0884
Largest diff. peak and hole (e·Å^{-3})	0.28 and -0.45	0.41 and -0.42	0.14 and -0.21

Table 2. Crystal and Data Collection Parameters of Complexes **3b** and **4a** .

	3b·0.5thf	**4a**
Formula	$C_{48}H_{62}MgN_3O_{1.5}P$	$C_{43}H_{52}MgN_3PS_2$
Molecular weight	760.28	730.27
Crystal dimens (mm)	0.20 × 0.20 × 0.18	0.20 × 0.20 × 0.20
Crystal system	Triclinic	Monoclinic
Space group	P-1	C2/c
Unit cell dimensions		
a (Å)	11.1505(5)	38.470(4)
b (Å)	12.2547(5)	13.3630(15)
c (Å)	17.4420(7)	15.7513(17)
β (deg)	81.711(2)	93.695(2)
V (Å^3)	2195.67(16)	8080.4(15)
Z	2	8
Dc (g.cm^{-3})	1.150	1.201
μ (mm^{-1})	0.116	0.220
F (000)	820.0	3120.0
Radiation (λ =0.710730Å)	Mo-K_α	Mo-K_α
Temperature (K)	296.2	100.2
h,k,l range	-13 ≤ h ≤ 13	-45 ≤ *h* ≤ 38
	-12 ≤ k ≤ 14	-15 ≤ *k* ≤ 15
	-19 ≤ l ≤ 20	-18 ≤ *l* ≤ 18
No. of reflections measured	31142	20176
No. of unique reflections	7717 [R_{int} = 0.0315]	7120 [R_{int} = 0.0331]
Completeness to θ	99.8 % [θ=25.00]	99.8% [θ=25.00]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7717/35/544	7120/363/450
Goodness-of-fit on F^2	1.117	1.034
Final R indices [I>2σ (I)]	R_1 = 0.0521	R_1 = 0.0860
	wR_2 = 0.1219	wR_2 = 0.2334
R indices (all data)	R_1 = 0.0637	R_1 = 0.1064
	wR_2 = 0.1302	wR_2 = 0.2560
Largest diff. peak and hole (e·Å^{-3})	0.29 and -0.30	1.30and -0.84

S.3 **References**

1 Bruker (2013) SAINT Data Reduction and Correction Program v. 8.34A, Bruker AXS, Madison, Wisconsin, USA.

2 Sheldrick, G. M. SADABS, A Program for Empirical Absorption Correction; University of Göttingen: Göttingen, Germany, 1996.

3 Sheldrick, G. M. SHELXL-2019/3, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 2015.