Supporting Information

Highly Efficient Room-Temperature Phosphorescence Achieved Employing Gadolinium Complexes

Boxun Sun,[a] Chen Wei,*[a] Huibo Wei,*[b] Zelun Cai,[a] Huanyu Liu,[a] Zhiyu Zang,[a] Wenchao Yan,[a] Zhiwei Liu,[a] Zuqiang Bian*[a] and Chunhui Huang[a]

[a]College of Chemistry and Molecular Engineering, Peking University, 202 Chengfu Road, Beijing 100871, P. R. China.
[b]Jiangsu JITRI Molecular Engineering Institute Co., Ltd., 88 Xianshi Road, Changshu 215500, P. R. China.

*Corresponding to:

Table of Contents

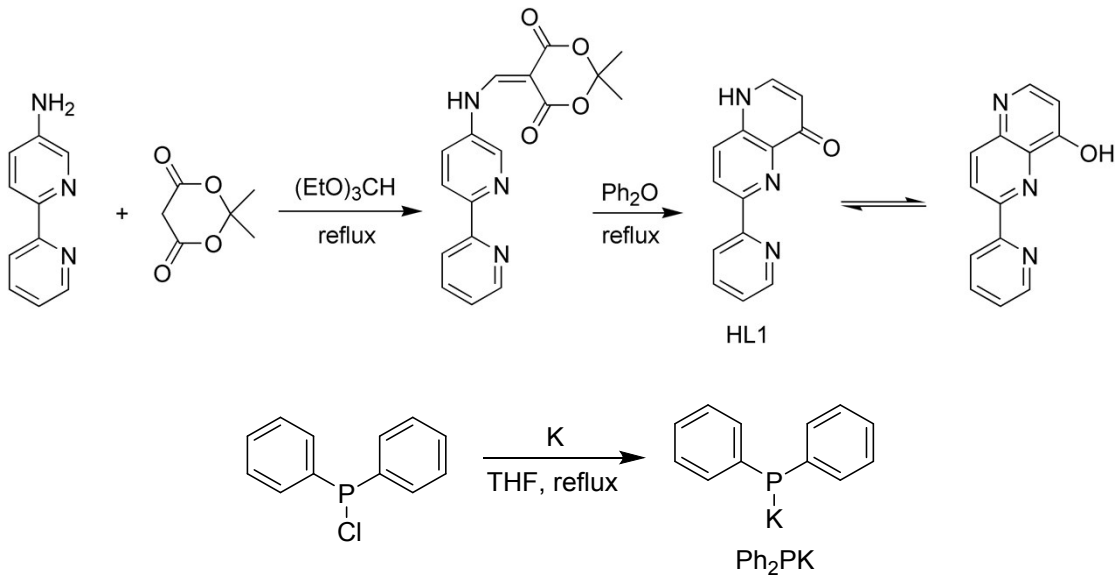
Experimental Section

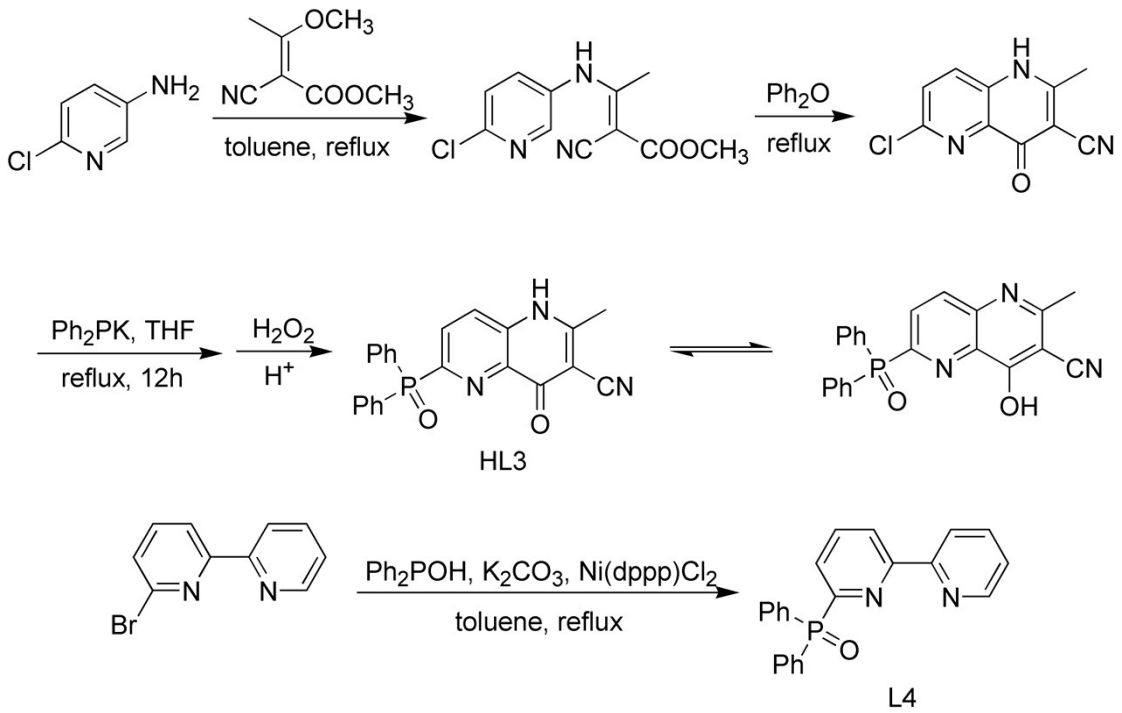
General Information. ^{1}H spectra were recorded on Bruker 400MHz NMR spectrometer. ^{31}P spectra were recorded on Bruker 500MHz NMR spectrometer. Electrospray ionization mass spectra (ESI-MS) were performed in positive ion mode on Bruker Apex IV Fourier transform ion cyclotron resonance mass spectrometer. Elemental analyses were conducted on a VARIO elemental analyzer from Elementar Analysensysteme GmbH. UV-visible absorption spectra were measured by a Perkin-Elmer Lambda 35 spectrometer. Emission and low temperature phosphorescence spectra were recorded on Edinburgh FLS980 fluorescence spectrophotometer. Luminescence lifetimes were obtained on a single photon counting spectrometer from Edinburgh FLS980 with micro-second pulse lamp and nano-second pulse lamp as the excitation source. The data were analyzed by tail fit of the decay profile using a software package provided by Edinburgh Instruments. Absolute quantum yields were measured using Hamamatsu C9920-02 PL quantum yield measurement system with integrating sphere for all the complexes. The photophysical properties of the complexes were carried out in PMMA films (w/w 1%) at room temperature or ethanol solutions (containing 5% methanol and 5% isopropanol, 1×10^{-5} mol·L^{-1}) from room temperature to 77 K.

The synthesis of Ligands and their complexes

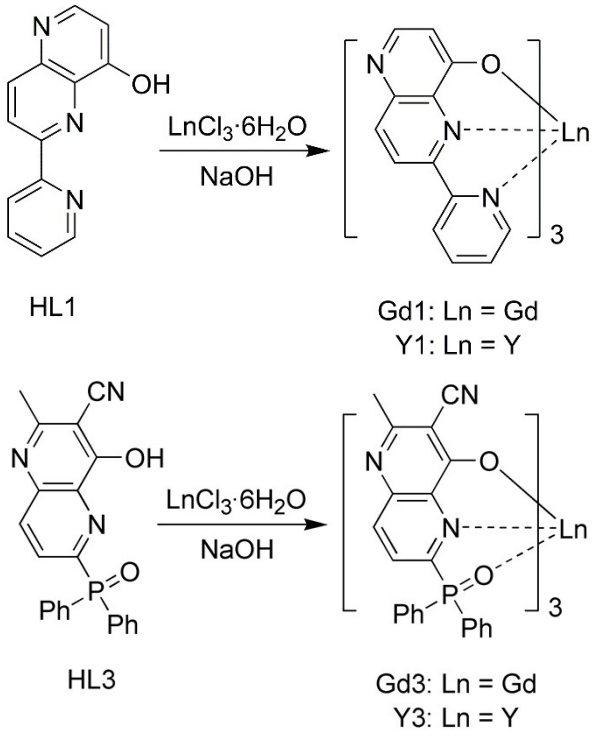
The synthesis of HL1, HL3 and L4 was according to previous work[1,2].

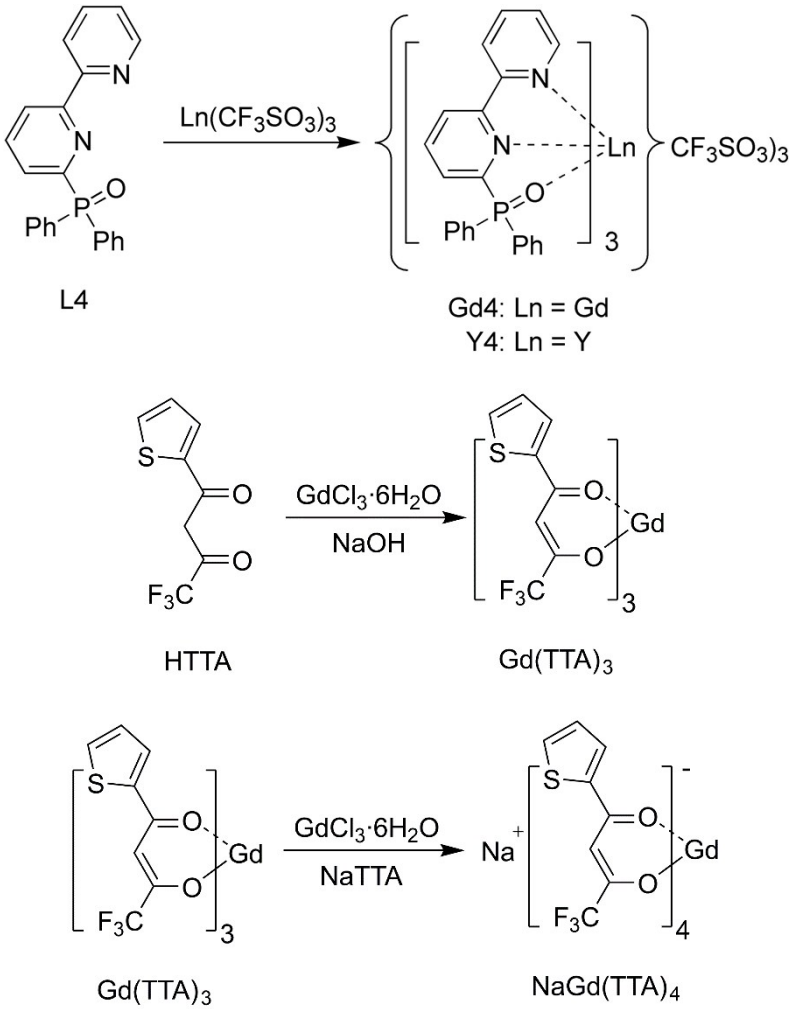
Scheme S1. Synthetic routes of HL1, HL3 and L4.





Scheme S2. Synthetic routes of Ln1, Ln3, Ln4 (Ln = Y and Gd) and NaGd(TTA)$_4$.





Gd1. A mixture of HL1 (69 mg, 0.30 mmol), NaOH (12 mg, 0.30 mmol) and $GdCl_3 \cdot 6H_2O$ (37 mg, 0.10 mmol) in methanol was heated to reflux for 60 minutes. the solid by vacuum-filtered was separated and washed 2 times with methanol. The product was dried under vacuum. The product is yellow solid. Yield: 72 % (59 mg). MS (m/z, ESI): calcd for $C_{39}H_{24}GdN_9O_3$ 824.1, found 825.1 ($M + H^+$). Anal. calcd for $C_{39}H_{24}GdN_9O_3 \cdot 3H_2O$ (found): N: 14.36 (14.40), C: 53.35 (53.62), H: 3.44(2.78).

Gd3. **Gd3** was synthesized in the same manner as **Eu3** in work 2. Yield: 72 % (94 mg). MS (m/z, ESI): calcd for $C_{66}H_{45}GdN_9O_6P_3$ 1310.2, found 1310.3 ($M + H^+$). Anal. calcd for $C_{66}H_{45}GdN_9O_6P_3 \cdot H_2O$ (found): N: 9.26 (9.49), C: 59.14 (59.68), H: 3.36 (3.57).

Gd4. **Gd4** was synthesized in the same manner as **Eu4** in work 2. Yield: 85 % (142 mg). MS (m/z, ESI): calcd for $C_{69}H_{52}F_9GdN_6O_{12}P_3S_3$ 1674.1, found 1524.3 $(M\text{-}OTf^-)^+$ and 1168.1 $(M\text{-}L3\text{-}OTf^-)^+$. Anal. calcd for $C_{66}H_{45}GdN_9O_6P_3 \cdot 5H_2O$ (found): N: 4.77 (4.68), C: 46.99 (46.86), H: 3.49 (2.88).

Y1. **Y1** was synthesized in the same manner as **Gd1**. Yield: 53 % (40 mg). MS (m/z, ESI): calcd for $C_{39}H_{24}YN_9O_3$ 755.1, found 756.1 ($M + H^+$).

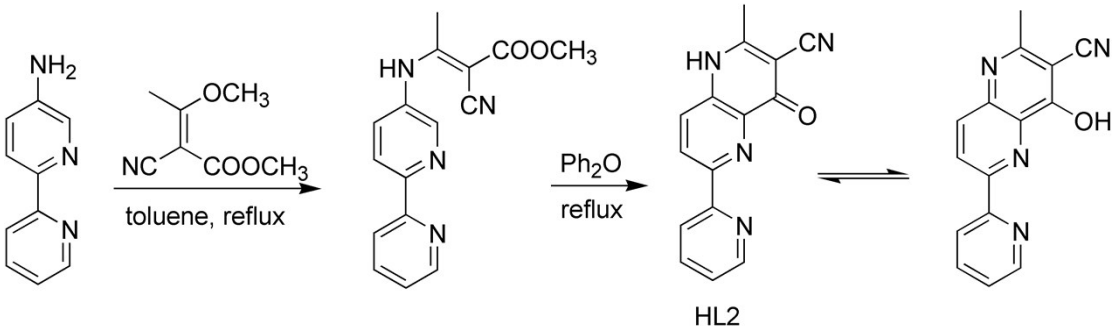
Y3. **Y3** was synthesized in the same manner as **Gd3**. Yield: 50 % (62 mg). MS (m/z, ESI): calcd

for $C_{66}H_{45}YN_9O_6P_3$ 1241.2, found 1242.2 ($M + H^+$).

Y4. **Y4** was synthesized in the same manner as **Gd4**. Yield: 73 % (117 mg). MS (m/z, ESI): calcd for $C_{69}H_{52}F_9YN_6O_{12}P_3S_3$ 1605.1, found 1455.2$(M\text{-}OTf^-)^+$ and 1099.1 $(M\text{-}L3\text{-}OTf^-)^+$.

NaGd(TTA)$_4$. The methanol solution of $GdCl_3 \cdot 6H_2O$ (185 mg, 0.50 mmol) was added into the methanol solution of NaOH(60 mg, 1.5 mmol) and 4,4,4-trifluoro-1-(thiophen-2-yl)butane-1,3-dione(TTA, 333 mg, 1.50 mmol). The solvent was separated by vacuum distillation and the complex of 3:1 was extracted by acetone leaching. Then the methanol solution of NaOH(20 mg, 0.50 mmol) and 4,4,4-trifluoro-1-(thiophen-2-yl)butane-1,3-dione(TTA, 111 mg, 0.50 mmol) was added into the complex of 3:1 and the solvent was separated by vacuum distillation. The final product was The product was dried under vacuum. The product is ivory white solid. Yield: 78% (416 mg) MS (m/z, ESI): calcd for $C_{32}H_{16}F_{12}GdO_8S_4Na$ 1064.9, found 1041.9 ($M - Na^+$). Anal. calcd for $C_{32}H_{16}F_{12}GdO_8S_4Na$ (found): C: 36.09 (36.14), H: 1.51 (1.63).

Scheme S3. Synthetic Routes of HL2.



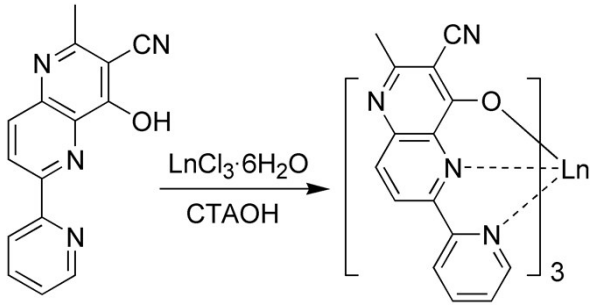
Methyl-3-([2,2'-bipyridin]-5-ylamino)-2-cyanobut-2-enoate. A mixture of 5-amino-2,2′-bipyridine (1.08 g, 6.3 mmol) and methyl-2-cyano-3-methoxybut-2-enoate (3.10 g, 20.0 mmol) was added into 15 mL xylene. The mixture was heated to reflux for 8 hours and the methanol generated from the reaction was removed from distillation. A majority amount of xylene was removed by rotary evaporation and 15 mL methanol was added into the reaction system. Put the reaction system into fridge and a large amount of product was separated out. The precipitation was isolated by filtration and washed with cold methanol. The intermediate product was obtained as a white powder. Yield: 59 % (1.09 g). ^{1}H NMR (400 MHz, d^6-DMSO): δ 2.29 (s, 3H), 3.76 (s, 3H), 7.45-7.52 (m, 1H), 7.91-8.02 (m, 2H), 8.39 (d, J = 7.9 Hz, 1H), 8.44 (d, J = 8.5 Hz, 1H), 8.67 (d, J = 1.8 Hz, 1H), 8.71 (d, J = 4.1 Hz, 1H), 11.37 (s, 1H). MS (m/z, ESI): calcd for $C_{16}H_{14}N_4O_2$ 294.1, found 295.1 ($M + H^+$).

4-hydroxy-2-methyl-6-(pyridin-2-yl)-1,5-naphthyridine-3-carbonitrile (HL2). Pre-HL4 (1.70 g 5.8 mmol) was added into diphenyl ether (100 mL), and then heat the mixture to reflux under nitrogen atmosphere for 3 hours. The crude product was separated through vacuum-filtered and washed 3 times with acetone. The crude product was brown and purified by thermal gradient sublimation and recrystallized by N,N-dimethylformamide (DMF). The intermediate product (HL4)

was obtained as a ivory-white powder. Yield: 64 % (0.97 g). ^{1}H NMR (400 MHz, d^6-DMSO): δ 12.80 (s, 1H), 8.73 (d, J = 7.3 Hz, 2H), 8.49 (d, J = 7.9 Hz, 1H), 8.15 (d, J = 8.8 Hz, 1H), 8.03 (t, J = 7.7 Hz, 1H), 7.57 – 7.44 (m, 1H), 2.62 (s, 3H). MS (m/z, ESI): calcd for $C_{15}H_{10}N_4O$ 261.1, found 260.1 (M - H^+). Anal. calcd for $C_{15}H_{10}N_4O$ (found): N: 21.36 (21.32), C: 68.69 (68.47), H: 3.68 (3.84).

^{1}H NMR (400 MHz, d^6-DMSO): δ 12.80 (s, 1H), 8.73 (d, J = 7.3 Hz, 2H), 8.49 (d, J = 7.9 Hz, 1H), 8.15 (d, J = 8.8 Hz, 1H), 8.03 (t, J = 7.7 Hz, 1H), 7.57 – 7.44 (m, 1H), 2.62 (s, 3H).

Scheme S4. Synthetic Routes of Gd2 and Y2.



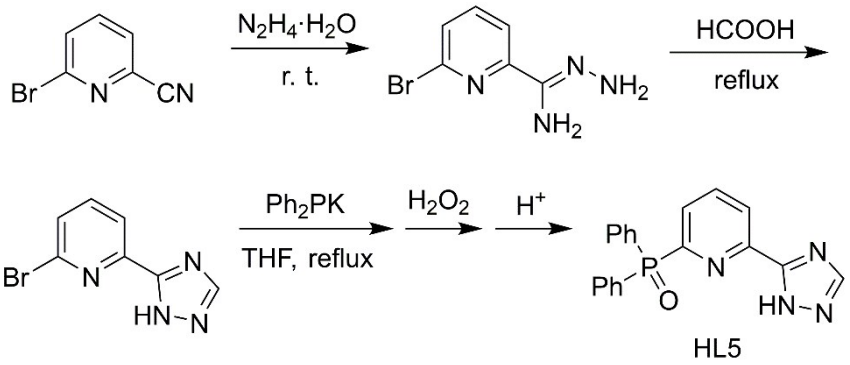
HL2 Gd2: Ln = Gd Y2: Ln = Y

CTAOH. Cetyl trimethyl ammonium chloride (CTAC, 16.00 g, 50.00 mmol) was dissolved in 30 mL alcohol while sodium hydroxide (NaOH, 2.00 g, 50 mmol) was dissolved in 30 mL hot alcohol. Cool the NaOH solution down and drip it into CTAC solution. Insoluble sodium chloride was separated by vacuum-filtered and washed 3 times with a little alcohol. The solution was transferred into a 100 mL volume and diluted to 100 mL. The concentration is 0.50 mol/L.

Gd2. A mixture of HL2 (4, 79 mg, 0.30 mmol), CTAOH solution (5, 600 μL, 0.30 mmol) and $GdCl_3·6H_2O$ (37 mg, 0.10 mmol) in methanol was heated to reflux for 60 minutes. Separated the solid by vacuum-filtered and wash it 3 times with methanol. The product was dried under vacuum. The product is ivory white solid. Yield: 72 % (68 mg). MS (m/z, ESI): calcd for $C_{45}H_{27}N_{12}O_3Gd$ 941.2, found 942.2 (M + H^+). Anal. calcd for $C_{45}H_{27}N_{12}O_3Gd·H_2O$ (found): N: 17.53 (17.48), C: 56.36 (56.13), H: 3.05 (2.83).

Y2. **Y2** was synthesized in the same manner as **Gd2**. Yield: 77 % (67 mg). MS (m/z, ESI): calcd for $C_{45}H_{27}N_{12}O_3Y$ 872.2, found 873.2 (M + H^+).

Scheme S5. Synthetic Routes of HL5.

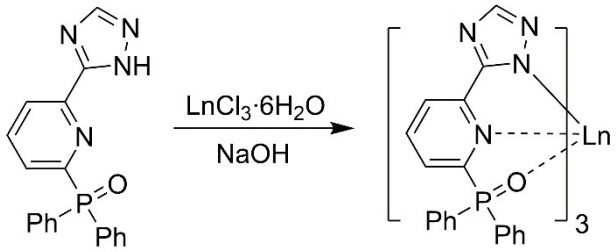


6-bromopicolinohydrazonamide. 6-bromopicolinonitrile (1, 9.15g, 50.0 mmol) was added into hydrazine hydrate (20 mL) and stirred for 30 minutes at room temperature (about 298 K）. Then the product was separated through vacuum-filtered and washed 3 times with water. The product was yellowish white after dried under vacuum. Yield: 97 % (10.48 g). MS (m/z, ESI): calcd for $C_6H_7BrN_4$ 214.0 (^{79}Br) and 216.0 (^{81}Br) , found 215.0 (^{79}Br, M + H^+) and 217.0 (^{81}Br, M + H^+).^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.71 (s, 2H), 5.16 (s, 2H), 7.45 (d, J = 7.7 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.99 (d, J = 7.7 Hz, 1H).

2-bromo-6-(4H-1,2,4-triazol-3-yl)pyridine. 6-bromopicolinohydrazonamide (2, 800 mg, 3.72 mmol) was added into methane acid and heated to reflux for 2 hours. Then methane acid was separated by vacuum distillation and neutralized by sodium bicarbonate. The crude product was separated by vacuum-filtered and recrystallized by water. The pure product is white solid. Yield: 97 %(800 mg). MS (m/z, ESI): calcd for $C_7H_5BrN_4$ 224.0 (^{79}Br) and 226.0 (^{81}Br) , found 225.0 (^{79}Br M + H^+) and 227.0 (^{81}Br M + H^+). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.66 (d, J = 7.9 Hz, 1H), 7.86 (t, J = 7.8 Hz, 1H), 8.09 (d, J = 7.6 Hz, 1H), 8.35 (s, 1H).

(6-(4H-1,2,4-triazol-3-yl)pyridin-2-yl)diphenyl phosphine oxide (HL5). Potassium diphenylphosphanide (about 15.1 mmol) was prepared by adding tetrahydrofuran solution of potassium tert-butoxide (6.72 g, 50.0 mmol) to tetrahydrofuran solution of diphenylphosphane (2.80 g, 15.1 mmol). The orange color of diphenylphosphine anion can be seen in tetrahydrofuran solution. Then the tetrahydrofuran solution of 2-bromo-6-(4H-1,2,4-triazol-3-yl)pyridine (3, 1.90 g, 8.44 mmol) was added to potassium diphenylphosphanide. The solution was heated to reflux for 30 minutes and cooled down to room temperature. 2 mL 30 % hydrogen peroxide (diluted with 10 mL of water) was added to the mixture to oxidize trivalent phosphorus to pentavalent. The remaining base was neutralized by ammonium chloride. Tetrahydrofuran was removed by vacuum distillation and the crude product was separated by extracting with dichloromethane. The product was purified by recrystallized by methanol. The pure product is white solid. Yield: 36 % (1.04 g).MS (m/z, ESI): calcd for $C_{19}H_{15}N_4OP$ 346.1, found 347.1 (M + H^+). ^{1}H NMR (400 MHz, DMSO, δ): 14.56 (s, 1H), 8.47 (s, 1H), 8.23 (dd, *J* = 18.2, 7.0 Hz, 2H), 8.20 – 8.14 (m, 1H), 8.11 – 7.93 (m, 4H), 7.64 – 7.57 (m, 2H), 7.53 (ddd, *J* = 7.1, 5.3, 2.1 Hz, 4H). ^{31}P NMR (202 MHz, $CDCl_3$, δ): 22.88 (s). Anal. calcd for $C_{19}H_{15}N_4OP$ (found): C 65.89 (65.72), H 4.37 (4.21), N 16.18 (16.20).

Scheme S6. Synthetic Routes of Gd5 and Y5.



HL5 Gd5: Ln = Gd
Y5: Ln = Y

Gd5. A mixture of HL5 (4, 104 mg, 0.30 mmol), NaOH (12 mg, 0.30 mmol) and $GdCl_3 \cdot 6H_2O$ (37 mg, 0.10 mmol) in methanol was heated to reflux for 60 minutes. Separated the solid by vacuum-filtered and wash it 3 times with methanol. The product was dried under vacuum. The product is white solid. Yield: 59 % (70 mg). MS (m/z, ESI): calcd for $C_{58}H_{46}N_{12}O_3P_3Gd$ 1209.2, found 1210.2 ($M + H^+$). Anal. calcd for $C_{45}H_{27}N_{12}O_3Gd \cdot 3H_2O$ (found): N: 13.48 (13.18), C: 54.89 (54.32), H: 3.88 (3.60).

Y5. Y5 was synthesized in the same manner as **Gd5**. Yield: 59 % (70 mg). MS (m/z, ESI): calcd for $C_{58}H_{46}N_{12}O_3P_3Y$ 1140.2, found 1140.3 ($M + H^+$).

Crystallographic Data

Table S2. Crystallographic Data for Gd3

Compound	**Gd3**
chemical formula	$C_{66}H_{45}GdN_9O_6P_3$
formula weight	1310.27
crystal size (mm)	0.28×0.22×0.20
temperature (K)	180.0(1)
radiation	0.71073
crystal system	Cubic
space group	Pa-3
a(Å)	23.92840(10)
b(Å)	23.92840(10)
c(Å)	23.92840(10)
α(°)	90.00
β(°)	90.00
γ(°)	90.00
V(Å^3)	13700.64(17)
Z	8
$\rho_{(calc)}$ (g/cm^3)	1.270
F (000)	5288
absorption coefficient (mm^{-1})	1.091
θ range (deg)	2.823 to 27.474
reflections collected	86639 (R_{int} = 0.0281)
independent reflections	5223
reflections obs. [$I>2\sigma(I)$]	3598
data/restraints/paras	5223/38/252
GOF	1.038
R_1/wR_2 [$I>2\sigma(I)$]	0.0427/0.1086
R_1/wR_2 (all data)	0.0774/0.1411
large peak and hole(e/Å^3)	1.156/-0.485

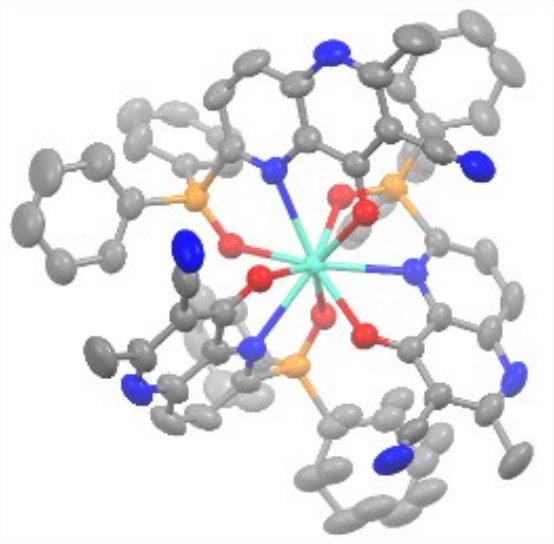


Fig. S1. Perspective view of **Gd3** at 50% probability level, with Gd in cyan, N in blue, O in red, P in orange and C in gray. Hydrogen atoms are omitted for clarity.

Photophysical Properties

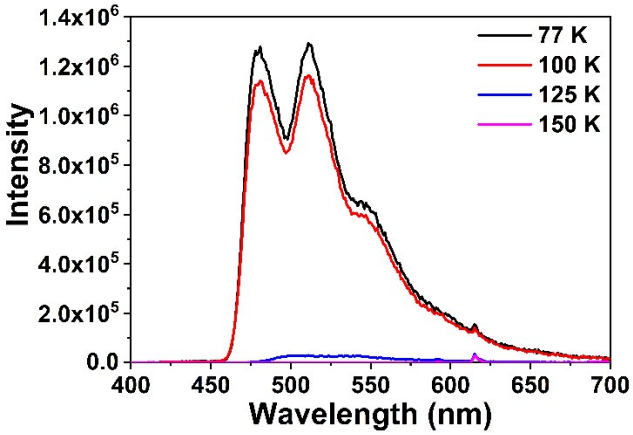


Fig. S2. The phosphorescent emission spectra of **Gd3**(b) in ethanol solutions (containing 5% methanol and 5% isopropanol, 1×10^{-5} mol·L^{-1}) at varied temperatures.

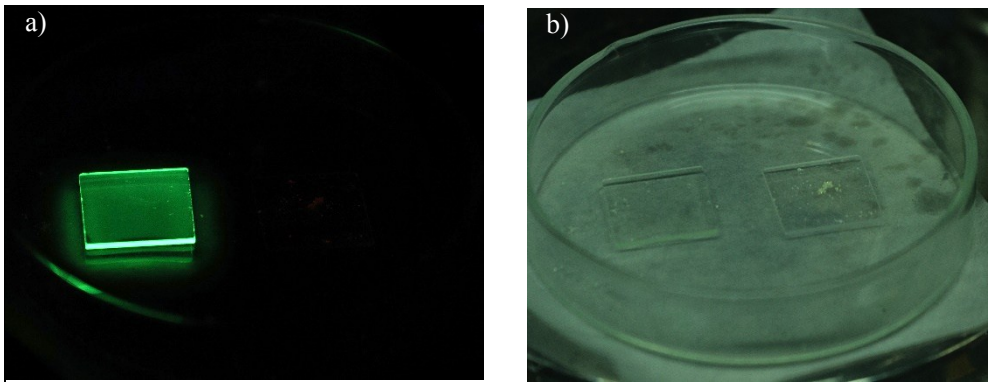


Fig. S3. Comparisons of PMMA film (right slice) and powder (left slice) of **Gd3** at nitrogen atmosphere under ultraviolet (365 nm, a) and visible light (b).

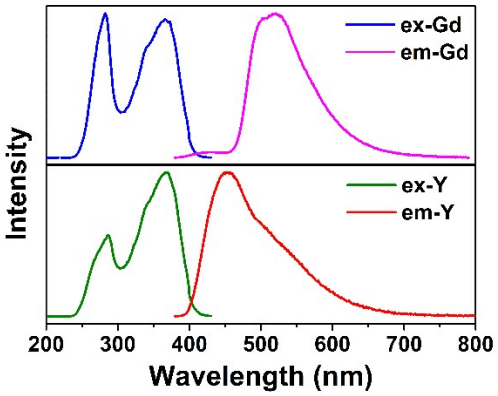


Fig. S4. The excitation and emission spectra **Gd3** and **Y3** in PMMA films encapsulated with wax. (0.5%, w/w)

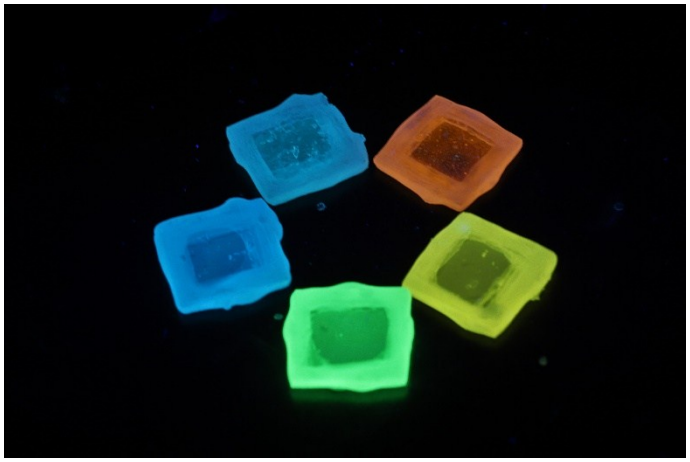


Fig. S5. Photograph of the encapsulated PMMA film doped with title gadolinium(III) complexes under UV 254/365 nm excitation.

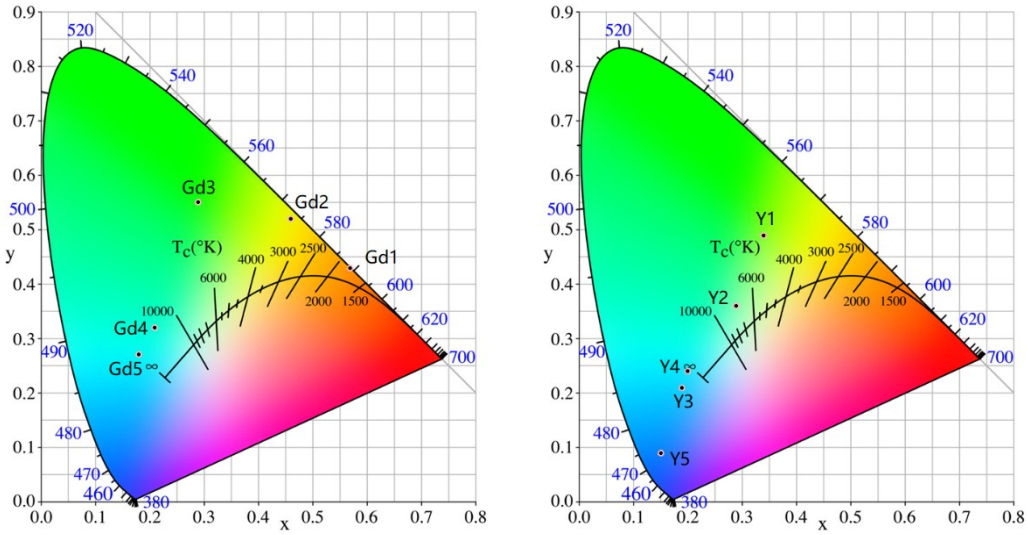


Fig. S6. CIE coordinates of **Gd1**/**Y1** to **Gd5**/**Y5** in PMMA films. The line is the isotemperature line of black-body radiation.

Table S3. Photoluminescent quantum yields of Gadolinium(III) complexes in PMMA films encapsulated with wax

Concentration	**Gd1**	**Gd2**	**Gd3**	**Gd4**	**Gd5**
0.1 %	15	20	41	20	47
0.2 %	18	19	52	21	**54**
0.5 %	**18**	20	**66**	**22**	41
1 %	18	**24**	64	21	21
2 %	15	11	63	17	17

Preparation of PMMA films containing Gd(III) complexes

The solution of gadolinium complexes can be used to achieve the triplet energy of the ligand via low temperature emission spectra, which means we can obtain the phosphorescence of ligands by using their gadolinium complexes at room temperature as well. Both complexes and PMMA are easy to be dissolved in dichloromethane, so we prepared PMMA-dichloromethane solution with the concentration of 0.10 g/mL, which can be called PMMA-CH_2Cl_2 solution in this essay. When 1.0 mg complex is dissolved in 1.0 mL PMMA-CH_2Cl_2 solution, spreaded on a quartz slice and dichloromethane evaporates, the doping ratio is 1.0 %. If these films are encapsulated by wax, these films can also show phosphorescence emission when these films are took out of the glove box, which can make convenient for us to obtain the spectrum of these complexes at room temperature. In this way we get the films which can emit phosphorescence at room temperature.

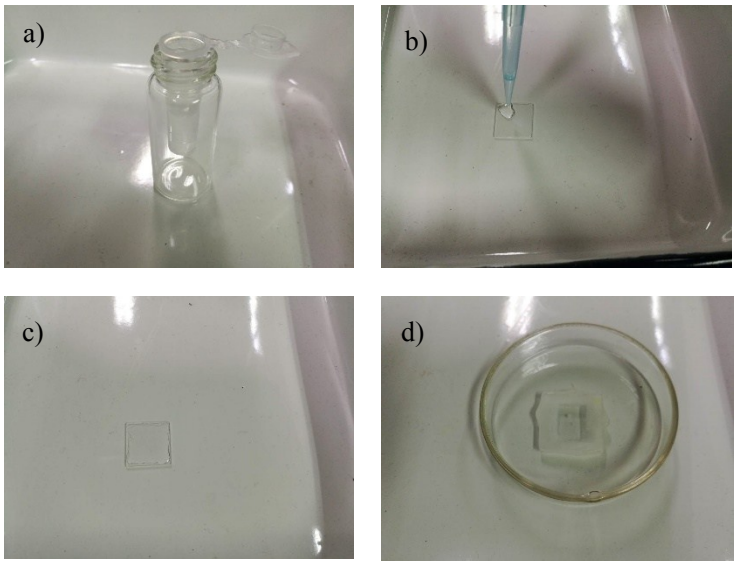


Fig. S7. Method for fabricating PMMA films containing Gd(III) complexes: a) preparing the solution containing Gd(III) complex, PMMA and CH_2Cl_2; b) drop casting the solution by pipette onto a silica; c) drying the PMMA film by evaporation of CH_2Cl_2; d) encapsulation by another silica on top and wax around the gaps.

Photophysical properties of diketone complexes

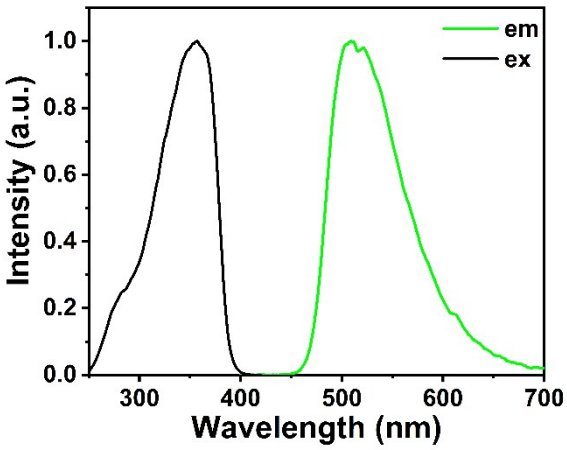


Fig. S8. The excitation and emission spectra **NaGd(TTA)$_4$** in PMMA films encapsulated with wax. (0.5%, w/w)

Table S4. Photoluminescent quantum yields of Gadolinium(III) complexes in PMMA films encapsulated with wax

Concentration	0.1%	0.2%	0.5%	1%	2%
PLQY (%)	17	15	16	15	16
τ (ms)	2.83	2.57	2.66	2.93	2.18

^{1}H and ^{31}P NMR spectra

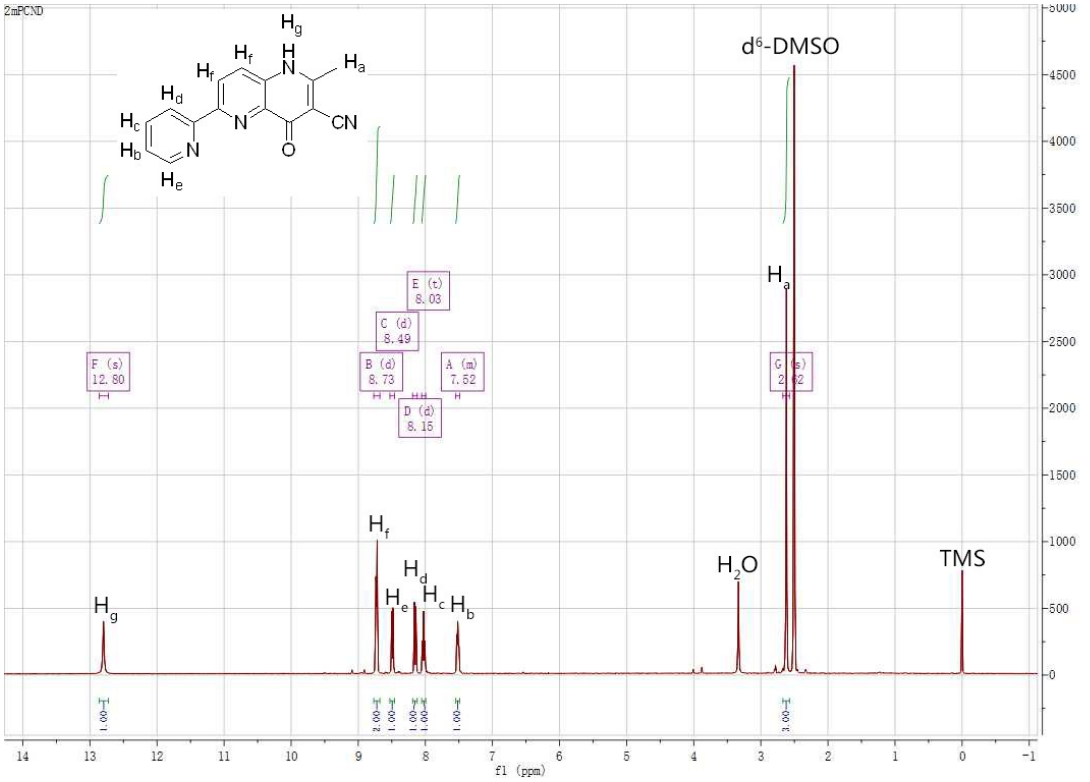
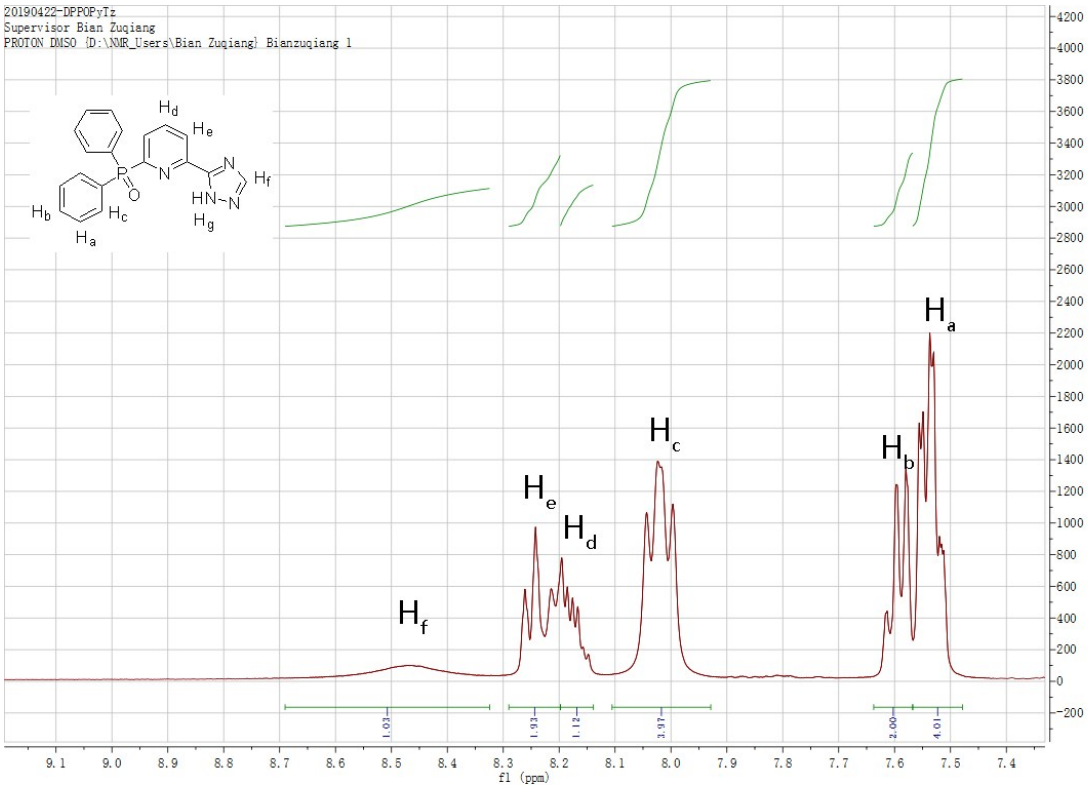


Fig. S9. ^{1}H NMR spectrum of HL2 in d^{6}-DMSO



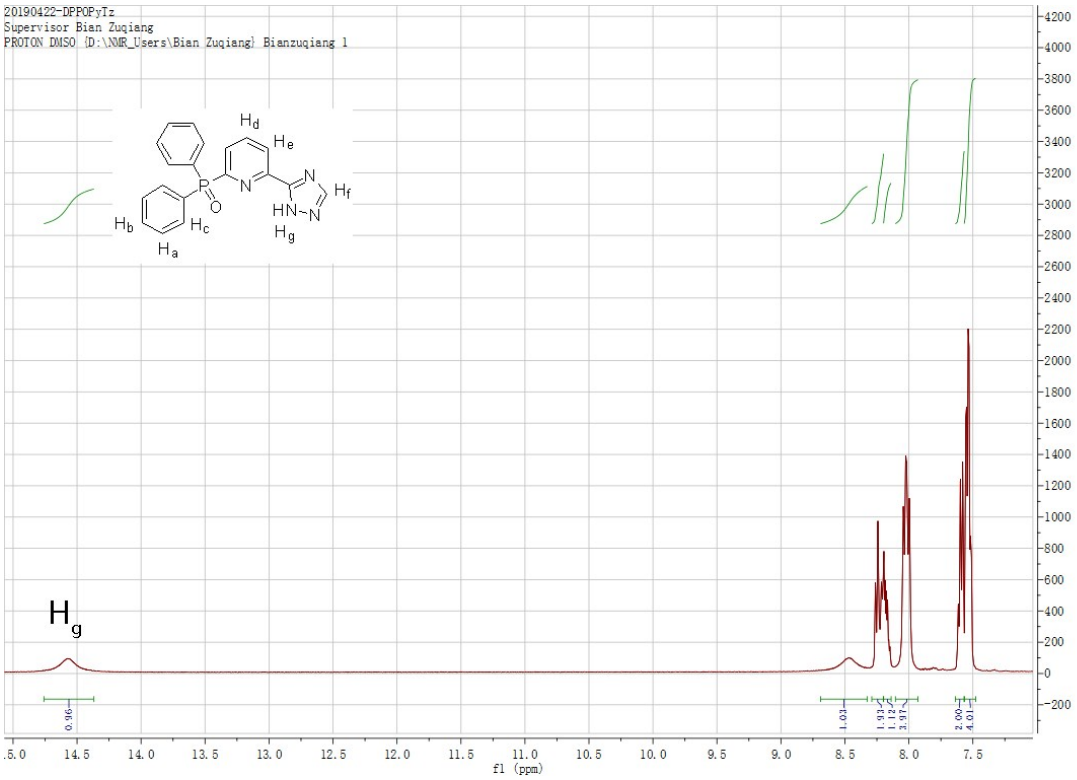


Fig. S10. ^{1}H NMR spectrum of HL5 in d^{6}-DMSO

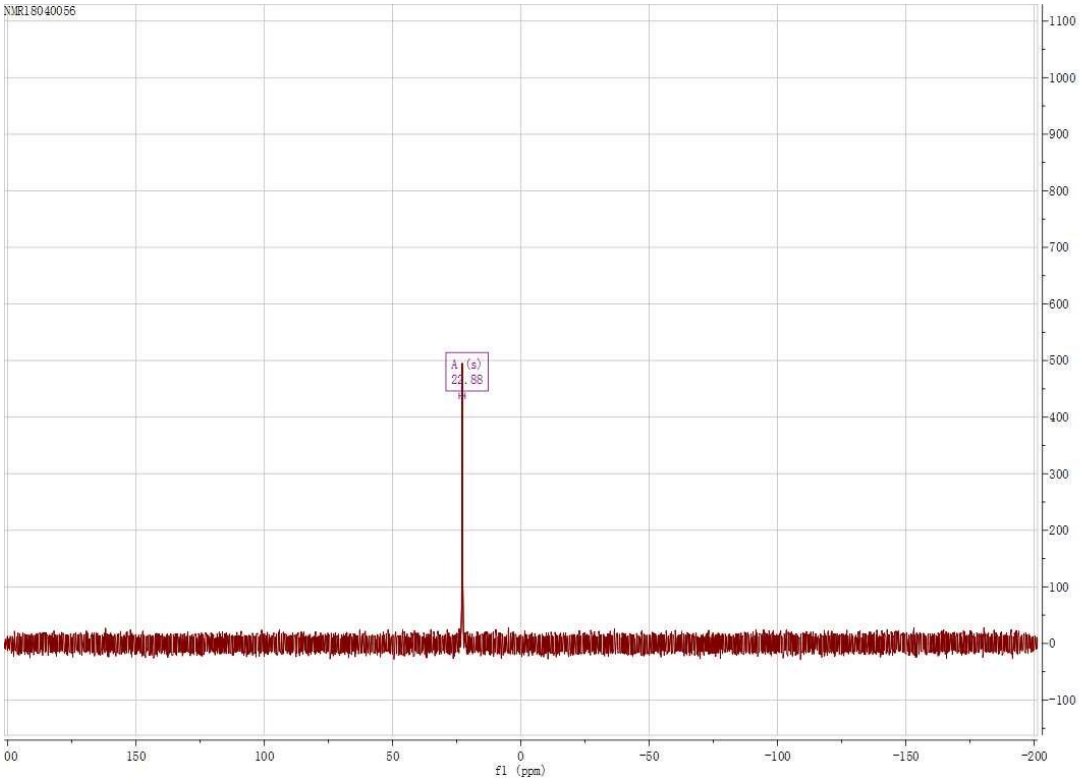


Fig. S11. ^{31}P NMR spectrum of HL5 in $CDCl_3$

References

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