Electronic Supplementary Material (ESI) for New Journal of Chemistry.


# Supporting Information

## Investigating Stimuli-Responsive Luminescence and Aggregation-Induced Emission Properties of *o*-Carborane-Based Luminophores Modified with Phenanthrene or Anthracene

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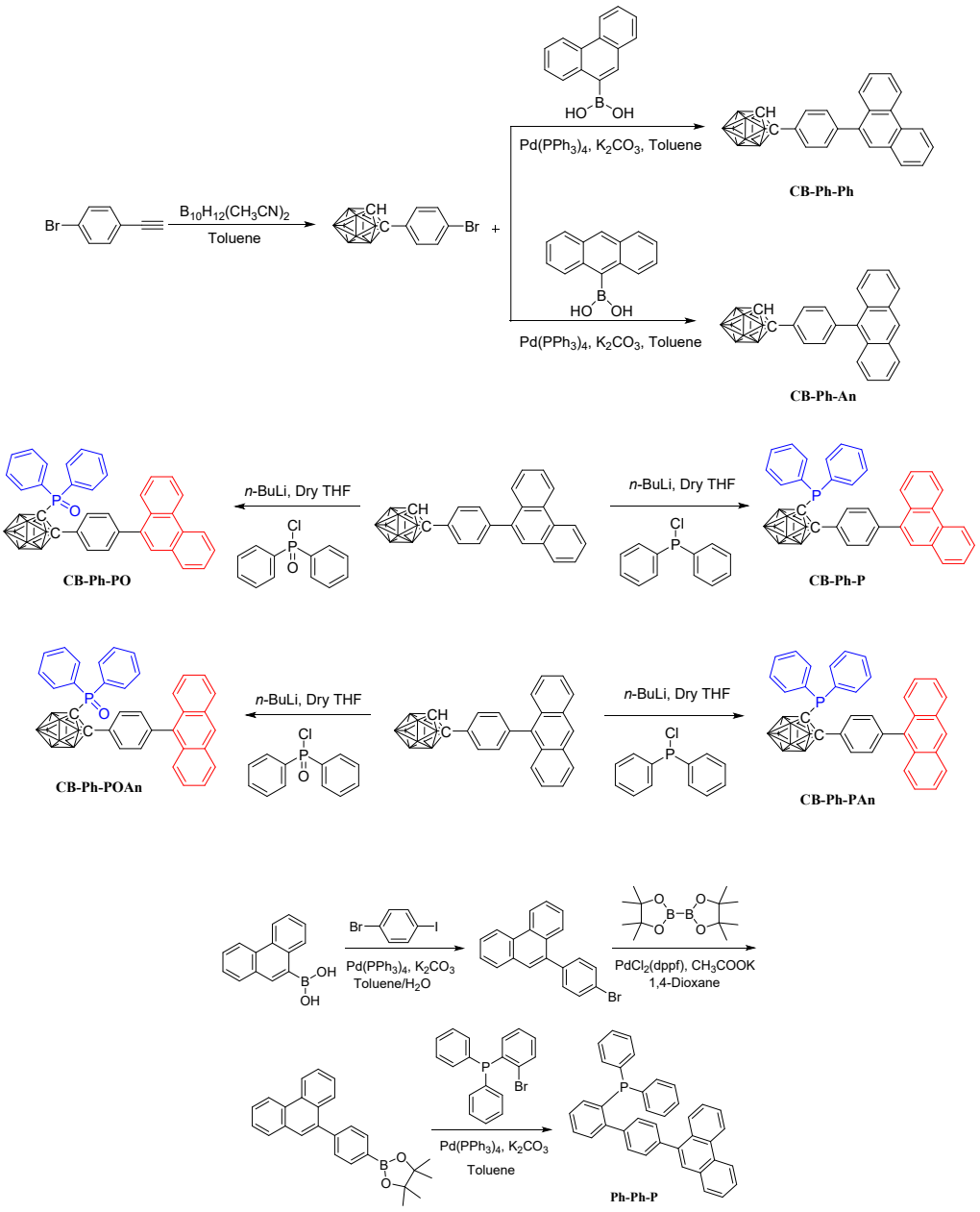
# I. Synthesis




**Scheme S1** Synthesis routes for target compounds and **Ph-Ph-P**.

Synthesis of **CB-Ph-Ph**: The compound was synthesized according to the previous literature[1]. White solid, with a yield of 49%. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.79 (d, *J* = 8.3 Hz, 1H), 8.73 (d, *J* = 8.3 Hz, 1H), 7.89 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.76-7.66 (m, 2H), 7.66-7.59 (m, 4H), 7.59-7.47 (m, 3H), 4.06 (s, 1H), 3.15-1.87 (m, 10H, carborane-H).

Synthesis of **CB-Ph-An**: The compound was synthesized according to previous literature[1]. White solid, with a yield of 79%. $^1$H NMR (500 MHz, Chloroform-*d*) δ

8.53 (s, 1H), 8.06 (ddt, *J* = 8.5, 1.3, 0.7 Hz, 2H), 7.73-7.67 (m, 2H), 7.55 (dq, *J* = 8.9, 1.0 Hz, 2H), 7.51-7.44 (m, 2H), 7.44-7.34 (m, 4H), 4.11 (s, 1H)，3.36-1.90 (m, 10H, carborane-H).

Synthesis of **CB-Ph-P**: To a solution of **CB-Ph-Ph** (90 mg, 0.2 mmol) in anhydrous THF was added *n*-BuLi (1.2 M, 2.4 mmol) dropwise at -78 °C and stirred for 2 h. Inject Chlorodiphenylphosphine and react for two hours. Add a drop of water to quench the reaction, dry with anhydrous $Na_2SO_4$. Remove the solvent by rotary evaporation under reduced pressure. The crude product was purified by silica gel column chromatography (pure PE) to give a white solid 103 mg, yield 78%. M.p. :157.1 ℃. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.80 (dd, *J* = 26.1, 8.3 Hz, 2H), 7.95 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.77-7.58 (m, 11H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.50-7.36 (m, 6H), 3.25-1.66 (m, 10H, carborane-H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 143.30, 137.34, 135.65, 135.38, 132.90, 132.75, 131.97, 131.40, 131.06, 130.78, 130.66, 130.29, 130.25, 130.20, 129.93, 128.83, 128.67, 128.57, 127.82, 127.12, 127.06, 126.78, 126.74, 126.50, 123.18, 122.66, 85.80, 85.62, 83.68, 82.96. $^{11}$B NMR (128 MHz, Chloroform-*d*) δ −2.88 (3 B), −13.88 (7 B). $^{31}$P NMR (162 MHz, Chloroform-*d*) δ 12.00. HRMS (ESI): m/z: $[M+H]^+$ Calcd for $C_{34}H_{33}B_{10}P$: 581.3396 ; Found: 581.3392.

Synthesis of **CB-Ph-PO**: To a solution of **CB-Ph-Ph** in anhydrous THF was added *n*-BuLi (1.2 M, 2.4 mmol) dropwise at -78 °C and stirred for 2 h. Inject diphenylphosphinyl Chloride and react for two hours. Add a drop of water to quench the reaction, dry with anhydrous $Na_2SO_4$. Remove the solvent by rotary evaporation under reduced pressure. The crude product was purified by silica gel column chromatography (DCM: PE = 2: 1) to give a white solid of 455 mg, yield 58%. M.p. :241.5 ℃. $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.80 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.77-8.71 (m, 1H), 7.98-7.88 (m, 6H), 7.74-7.50 (m, 9H), 7.46 (td, *J* = 7.7, 3.8 Hz, 4H), 7.38-7.32 (m, 2H), 3.75-1.76 (m, 10H, carborane-H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 143.16, 137.46, 133.11, 132.66, 132.59, 132.00, 131.46, 130.79, 130.63, 130.21, 129.67, 129.62, 129.58, 128.88, 128.75, 128.50, 128.40, 127.88, 127.86, 127.15, 127.08, 126.83, 126.79, 126.67, 123.19, 122.70, 85.31, 79.11, 78.67. $^{11}$B NMR (128 MHz, Chloroform-*d*) δ −2.9 (2 B), −15.8 (8 B). $^{31}$PNMR (202 MHz, Chloroform-*d*) δ 19.86. HRMS (ESI): m/z: $[M+H]^+$ Calcd for $C_{34}H_{33}B_{10}PO$: 597.3345 ; Found: 597.3342.

Synthesis of **CB-Ph-PAn**: Following a similar procedure to **CB-Ph-P**. A white

solid was obtained with a yield of 68%. M.p. :237.2 ℃. $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 8.08 (d, *J* = 8.6 Hz, 2H), 7.74-7.67 (m, 8H), 7.52-7.38 (m, 12H)，3.52-1.76 (m, 10H, carborane-H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 141.58, 135.69, 135.47, 135.40, 132.95, 132.83, 132.12, 131.44, 131.32, 131.17, 130.50, 130.46, 130.05, 128.78, 128.71, 128.67, 127.32, 126.37, 125.86, 125.38, 85.78, 85.64, 83.65, 83.08. $^{11}$B NMR (160 MHz, Chloroform-*d*) δ – 2.00(2 B), – 4.43(2 B), – 10.87(6 B). $^{31}$PNMR (202 MHz, Chloroform-*d*) δ 12.41. HRMS (ESI): m/z: $[M+H]^+$ Calcd for $C_{34}H_{33}B_{10}P$: 581.3396 ; Found: 581.3404.

Synthesis of **CB-Ph-POAn**: Following a similar procedure to **CB-Ph-PO**. A white solid was obtained with a yield of 86%. M.p. :279.1 ℃. $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 8.06 (d, *J* = 8.5 Hz, 2H), 8.02-7.94 (m, 4H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.60-7.53 (m, 4H), 7.48 (dt, *J* = 8.9, 5.6 Hz, 6H), 7.40 (ddd, *J* = 8.2, 6.5, 1.3 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 3.85-1.68 (m, 10H, carborane-H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 141.36, 135.48, 133.21, 133.18, 132.68, 132.61, 132.06, 131.40, 130.91, 129.98, 129.74, 128.87, 128.55, 128.45, 127.17, 126.52, 125.76, 125.34, 85.40, 79.07, 78.64. $^{11}$B NMR (160 MHz, Chloroform-*d*) δ 0.35(2 B), -3.14(2 B), -10.61(6 B). $^{31}$P NMR (202 MHz, Chloroform-*d*) δ 20.29. HRMS (ESI): m/z: $[M+H]^+$ Calcd for $C_{34}H_{33}B_{10}P$: 597.3345 ; Found: 597.3354.

Synthesis of **Ph-Ph-P**: (2-bromophenyl) diphenylphosphine (273 mg, 0.8 mmol), phenanthrene-9-ylboronic acid (400 mg, 1.1 mmol), $K_2CO_3$ (310 mg, 2.2 mmol) and $Pd(PPh_3)_4$ (92 mg, 0.1 mmol) were added to a 150 mL three-necked flask, and the Schlenk technique was used to deoxygenate. The temperature was raised to 80 °C, and the reaction was carried out for 24 hours. After post-treatment, the mixture was extracted twice with dichloromethane, extracted once with saturated brine, and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure, 100-200 mesh silica gel column chromatography. A white solid was obtained with a yield of 35%. $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.78 (dd, *J* = 27.1, 8.2 Hz, 2H), 7.94 (dd, *J* = 11.8, 7.9 Hz, 2H), 7.77-7.57 (m, 5H), 7.53-7.31 (m, 17H), 7.15 (dd, *J* = 7.8, 3.9 Hz, 1H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 147.87, 147.66, 140.84, 139.58, 138.70, 137.57, 137.48, 136.52, 136.40, 134.37, 134.21, 133.98, 131.73, 131.26, 130.76, 130.38, 130.35, 130.07, 129.83, 129.79, 129.44, 128.87, 128.82, 128.75, 128.60, 128.55, 127.67, 127.58, 127.23, 126.98, 126.69, 126.58, 123.01, 122.68. $^{31}$P NMR (202 MHz, Chloroform-*d*) δ -11.28. HRMS (ESI): m/z: $[M+H]^+$ Calcd for $C_{38}H_{27}P$: 515.1923 ; Found: 515.1927.

## II.Crystal data

**Table S1** A summary of crystallographic data of target compounds.

| Name | **P-crystal** | **O-crystal** | **CB-Ph-PO** | **CB-Ph-POAn** |
|---|---|---|---|---|
| Formula | $C_{34}H_{33}B_{10}P$ | $C_{34}H_{33}B_{10}P$ | $C_{34}H_{33}B_{10}$ OP | $C_{34}H_{33}B_{10}OP$ |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| Formula weight | 580.86 | 580.86 | 596.67 | 596.67 |
| Temperature(K) | 296.15 | 296.15 | 296.15 | 296.15 |
| Crystal system | triclinic | monoclinic | triclinic | triclinic |
| Space group | *P*-1 | *C*2/*c* | *P*-1 | *P*-1 |
| *a*(Å) | 8.615(5) | 20.073(10) | 11.424(14) | 11.4493(12) |
| *b*(Å) | 11.155(6) | 22.990(10) | 13.228(17) | 12.8915(14) |
| *c*(Å) | 17.890(11) | 16.078(7) | 13.267(15) | 13.2464(14) |
| *α*(°) | 80.41(3) | 90 | 117.72(6) | 63.033(3) |
| *β*(°) | 79.43(3) | 113.578(14) | 97.28(7) | 88.703(4) |
| *γ*(°) | 67.43(3) | 90 | 91.11(8) | 76.711(4) |
| Volume(Å$^3$) | 1551.9(16) | 6801(5) | 1753(4) | 1688.4(3) |
| Z | 2 | 116 | 2 | 2 |
| Density(g/cm$^3$) | 1.243 | 1.205 | 1.130 | 1.291 |
| *μ/mm$^{-1}$* | 0.114 | 0.109 | 0.105 | 0.230 |
| *F*(000) | 604.5 | 2577.6 | 620.0 | 678.9 |
| $R_1$ (I>2σ(I)) | 0.0474 | 0.0477 | 0.0696 | 0.0518 |
| $wR_2$ (I>2σ(I)) | 0.1042 | 0.1128 | 0.1629 | 0.1205 |
| GOOF | 1.0573 | 1.024 | 1.050 | 1.044 |

**Table S2** The photophysical properties of target compounds.

| Sample | $\lambda_{ex}$[a] (nm) | $\lambda_{em}$[a] (nm) | $\tau_F$[a] (ns) | $\Phi_F$[e] (%) | | |
|---|---|---|---|---|---|---|
| | | | | Sol[b] | Agg[c] | Solid[a] |
| **P-crystal** | 387 | 426 | 0.72 | n.d.[d] | n.d.[d] | 0.6 |
| **O-crystal** | 356 | 596 | 4.54 | n.d.[d] | n.d.[d] | 3.3 |
| **Recrystallization** | 367 | 423 | 0.799 | n.d.[d] | n.d.[d] | ＜0.1 |
| **ground-1** | 364 | 608 | 3.96 | n.d.[d] | n.d.[d] | 3.5 |
| **CB-Ph-P** | 373 | 421 | 1.03 | n.d.[d] | 3.28 | 4.5 |
| **CB-Ph-PO** | 388 | 624 | 11..13 | n.d.[d] | 26.57 | 65.3 |
| **CB-Ph-PAn** | 258 | 393 | 1.91 | n.d.[d] | 2.92 | 1.3 |
| **ground-2** | 417 | 623 | 3.66 | n.d.[d] | n.d.[d] | n.d.[d] |
| **CB-Ph-POAn** | 373 | 672 | 4.42 | n.d.[d] | 3.71 | 5.4 |

[a] In the amorphous state. [b] Measured in THF solution ($10^{-5}$ mol $L^{-1}$) at room temperature. [c] $f_w$ = 99%. [d] Not detected. [e] Determined as a fluorescence quantum efficiency.

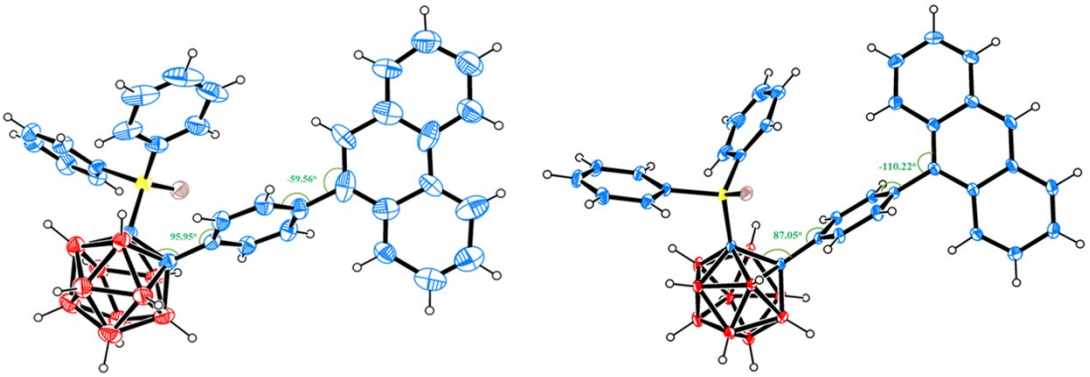


**Figure S1** ORTEP diagram (30% probability level) of **CB-Ph-PO** (left) and **CB-Ph-POAn** (right).

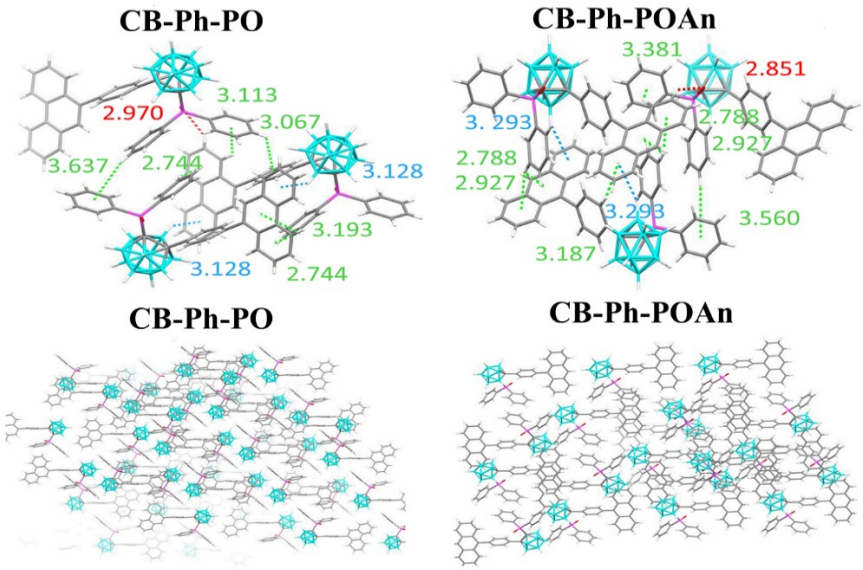



**Figure S2** The intermolecular interactions between adjacent molecules in **CB-Ph-PO** and **CB-Ph-POAn**.

## III. Photophysical Properties.

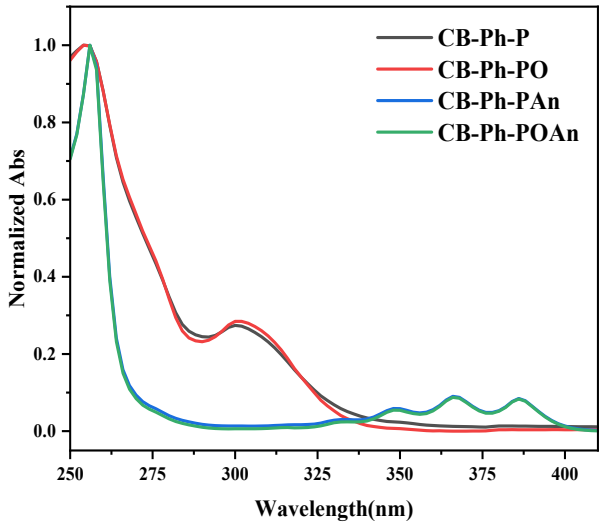


**Figure S3** UV–vis absorption spectra of **CB-Ph-P**, **CB-Ph-PO, CB-Ph-PAn** and **CB-Ph-POAn** in THF solution ($1\times10^{-5}$ mol $L^{-1}$).

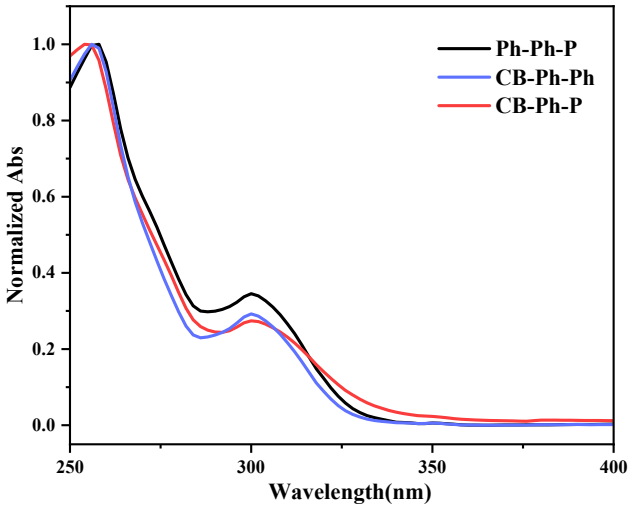



**Figure S4** UV–vis absorption spectra of **CB-Ph-P**, **CB-Ph-Ph**, **Ph-Ph-P** in THF solution ($1\times10^{-5}$ mol $L^{-1}$).

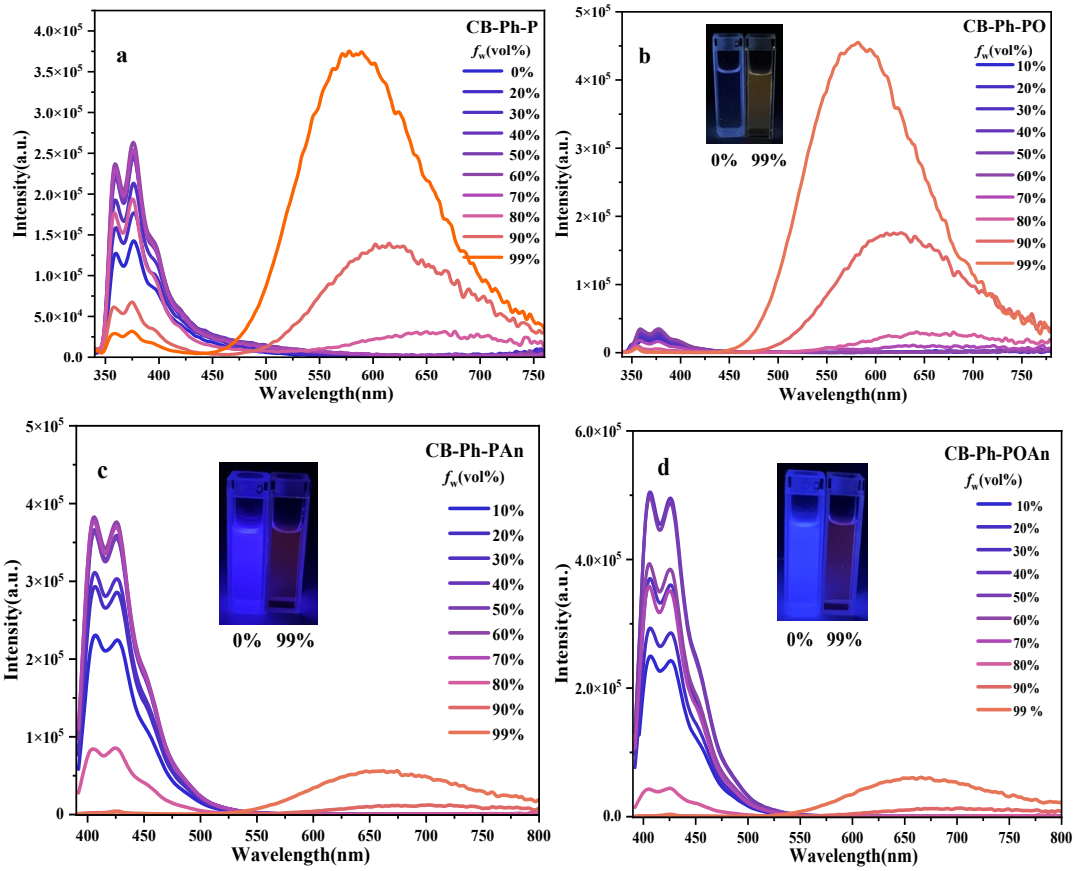



**Figure S5** Fluorescence emission spectra of (a) **CB-Ph-P**; (b)**CB-Ph-PO**; (c) **CB-Ph-PAn**; (d) **CB-Ph-POAn** in THF and $H_2O$ solvents with different water fractions.

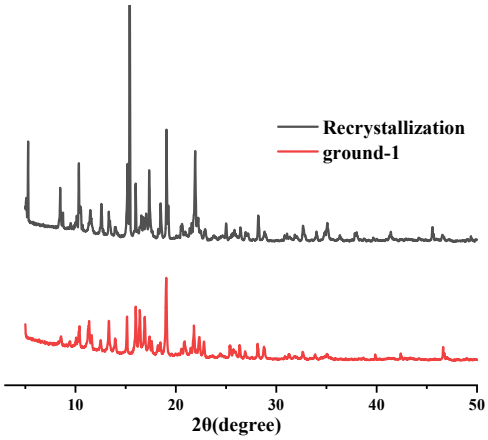



**Figure S6** The PXRD diagram of the original and ground for the recrystallized solid of **CB-Ph-P**.

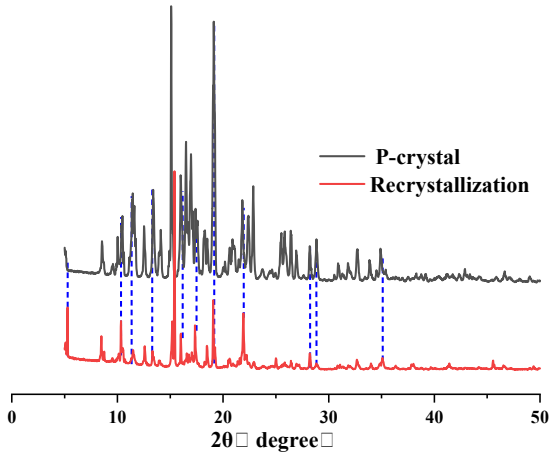
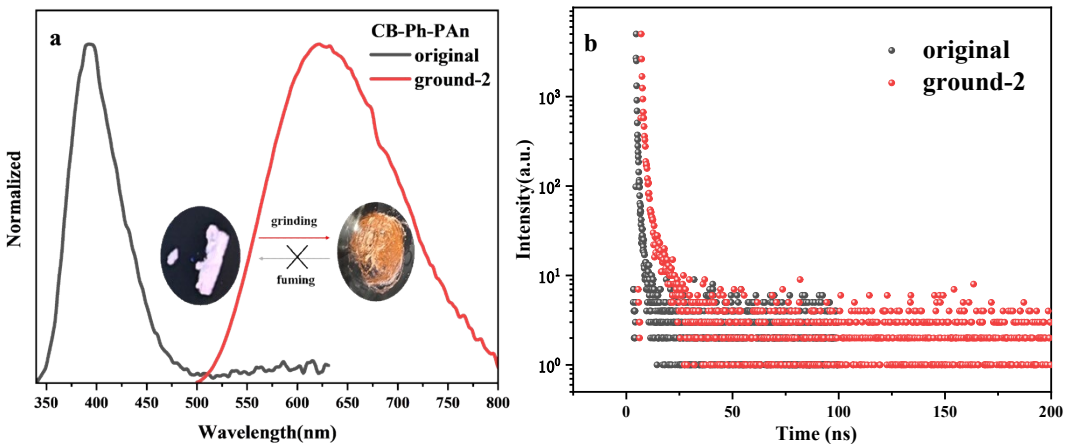



**Figure S7** The PXRD diagram of the P-crystal and the recrystallized solid.



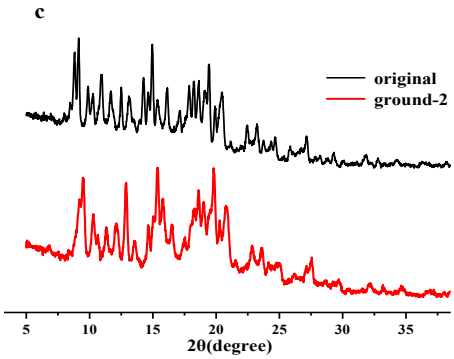



**Figure S8** (a) Fluorescence spectra; (b) lifetime; (c) PXRD of the original sample and the ground sample for **CB-Ph-PAn**.

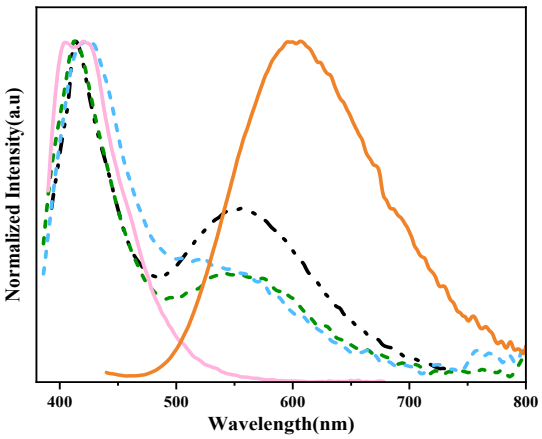



**Figure S9** The recrystallized solid (solid pink line) and the O-crystal (solid orange line) emission spectra of **CB-Ph-P**; the crystal state (black dashed line); the ground sample (green dashed line) and the amorphous powder state sample (blue dashed line) emission spectra of **CB-Ph-Ph**.

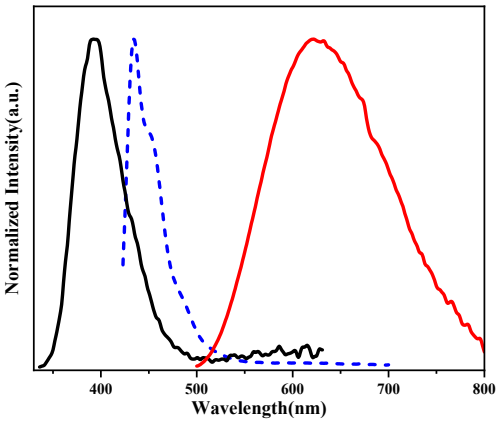



**Figure S10** The powdered state (solid black line) and the ground sample(solid red line) emission spectra of **CB-Ph-PAn**, the amorphous powder state sample (blue dashed line) emission spectra of **CB-Ph-An**.

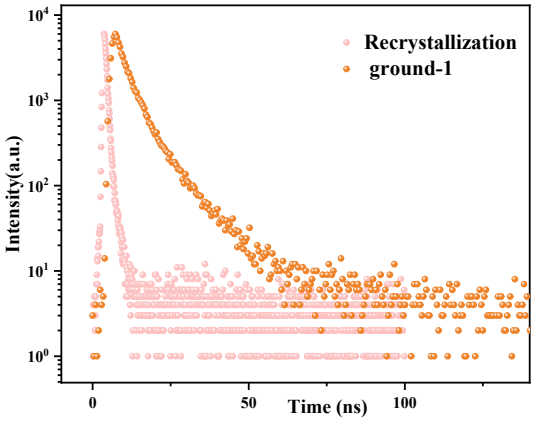



**Figure S11** Fluorescence lifetime of the recrystallized solid and the ground sample for **CB-Ph-P**.

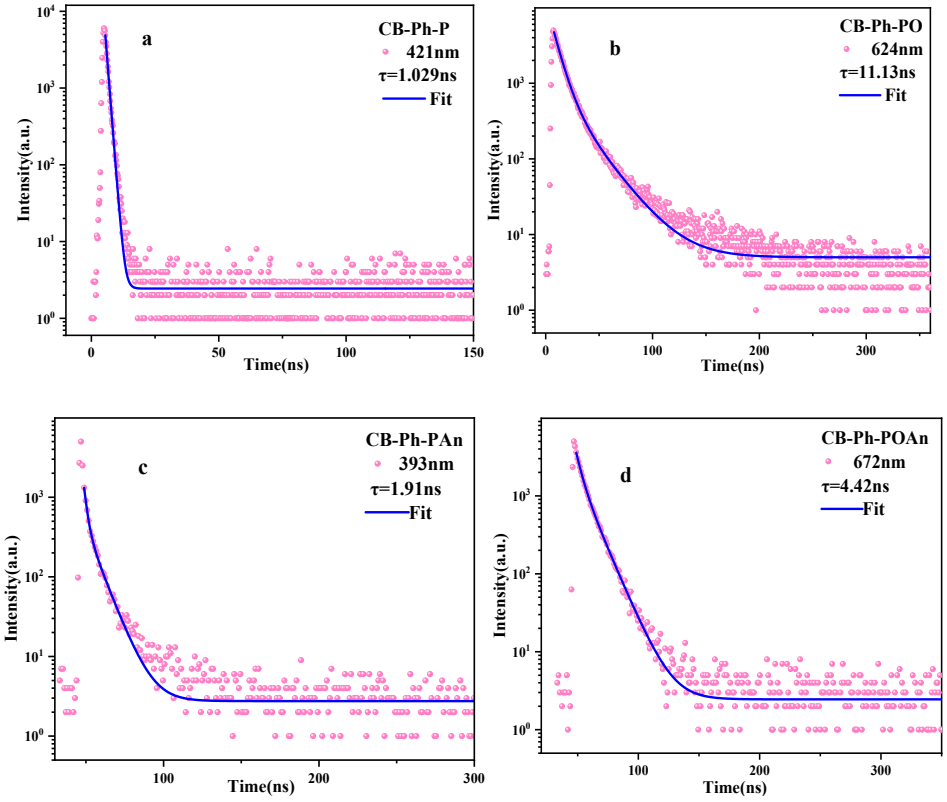



**Figure S12** The fluorescence lifetime of **CB-Ph-P** (a); **CB-Ph-PO** (b); **CB-Ph-PAn** (c) and **CB-Ph-POAn** (d).

# IV. NMR spectra and HRMS of new compounds

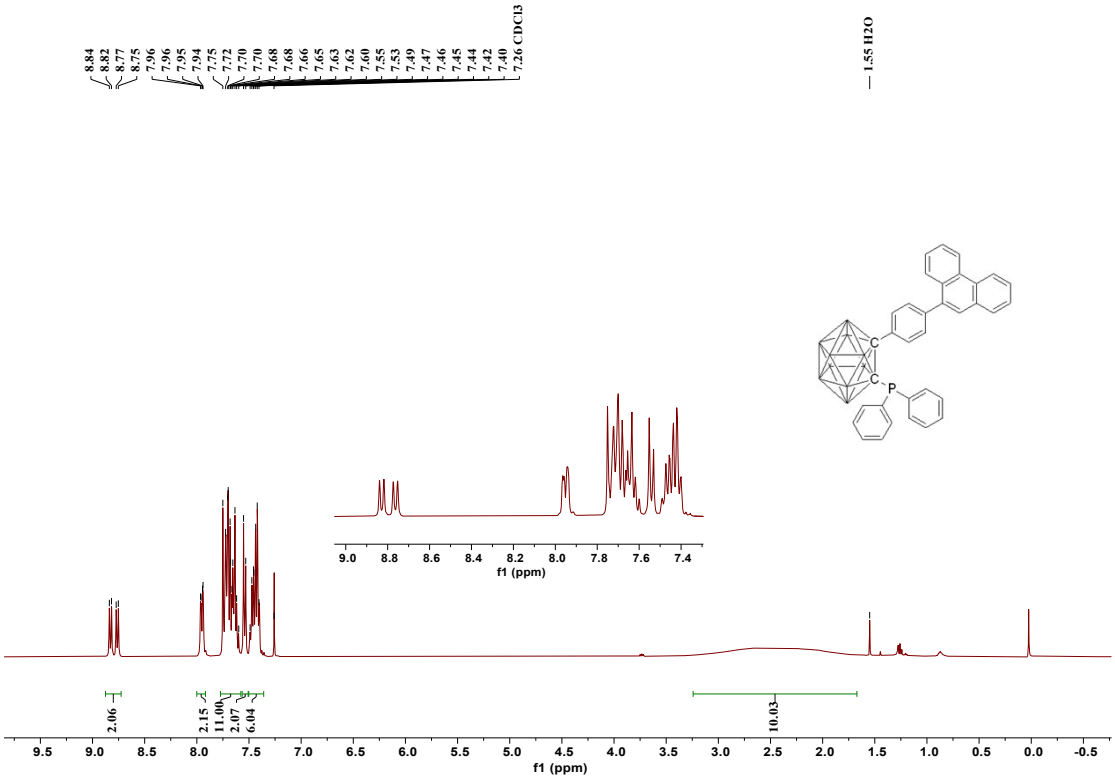



**Figure S13** $^{1}$H NMR spectrum of **CB-Ph-P** in $CDCl_3$.

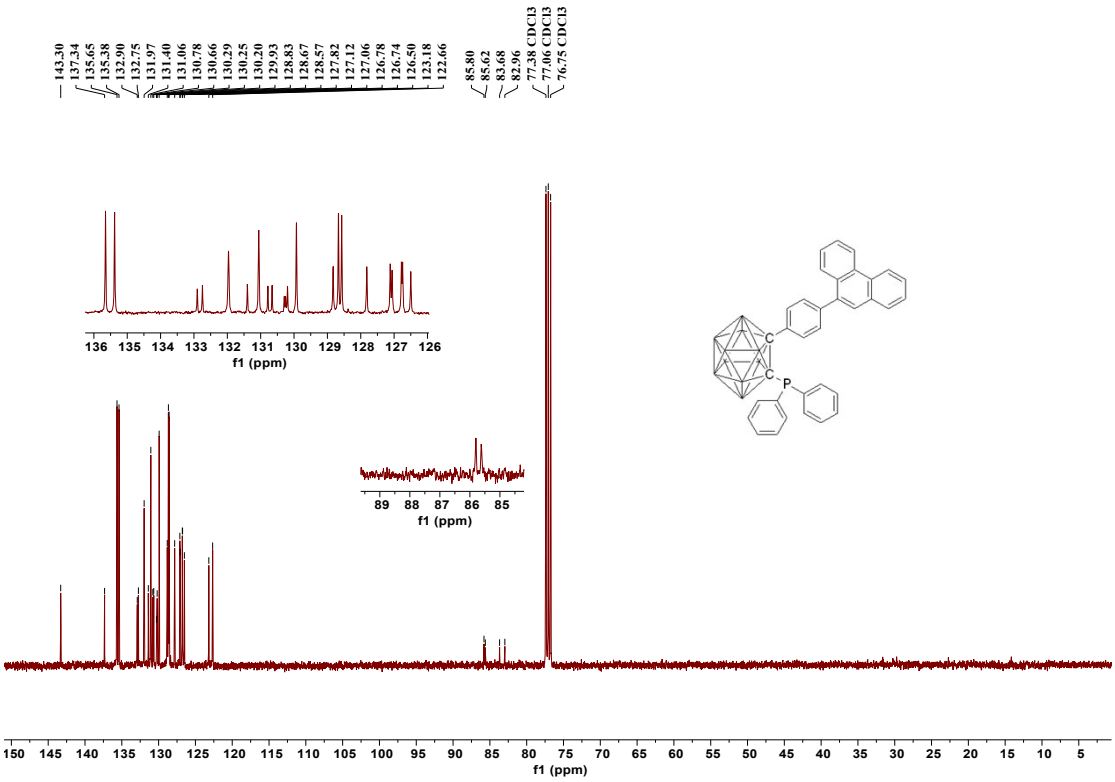



**Figure S14** $^{13}$C NMR spectrum of **CB-Ph-P** in $CDCl_3$.

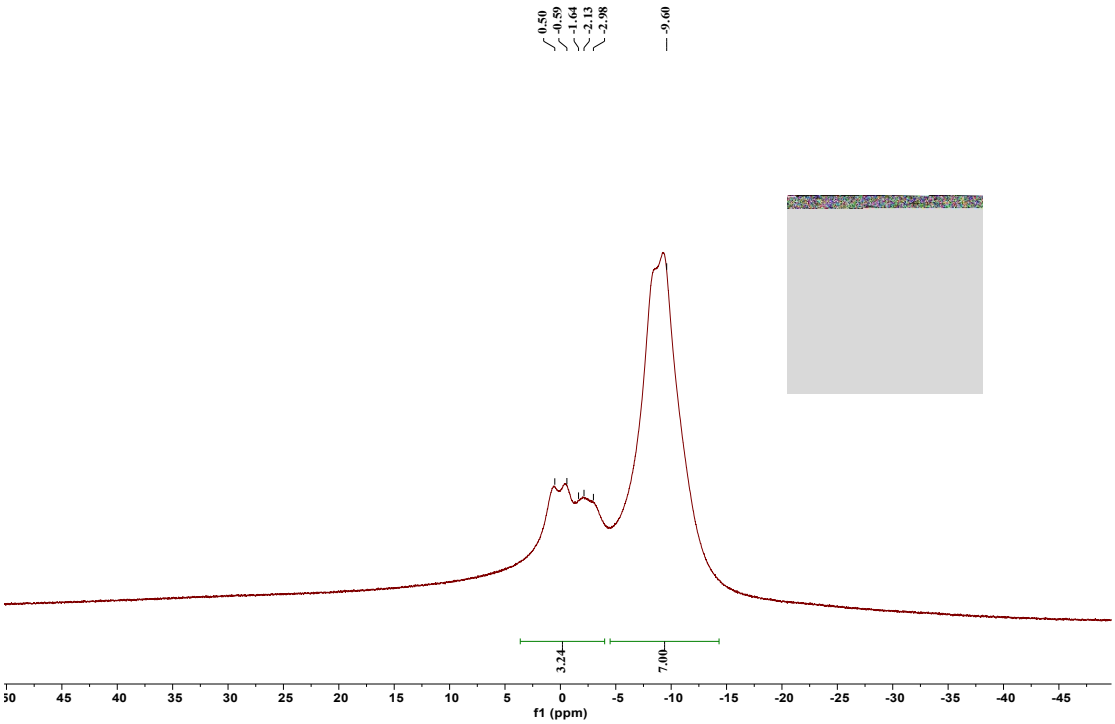



**Figure S15** $^{11}$B NMR spectrum of **CB-Ph-P** in $CDCl_3$.

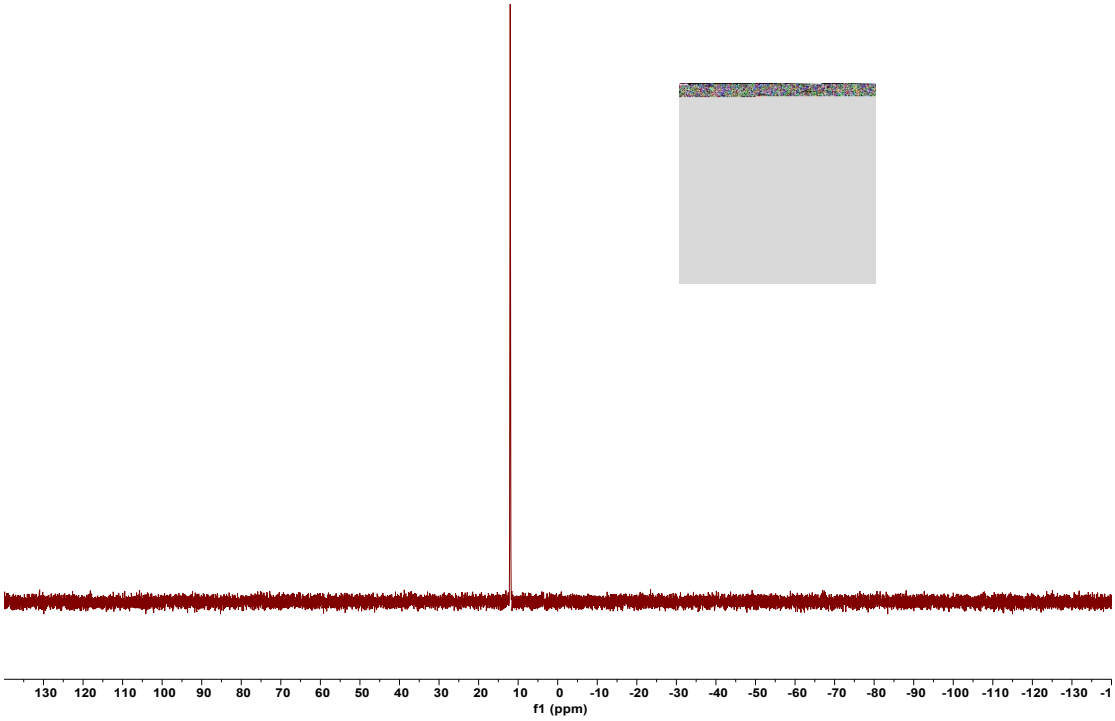



**Figure S16** $^{31}$P NMR spectrum of **CB-Ph-P** in $CDCl_3$.

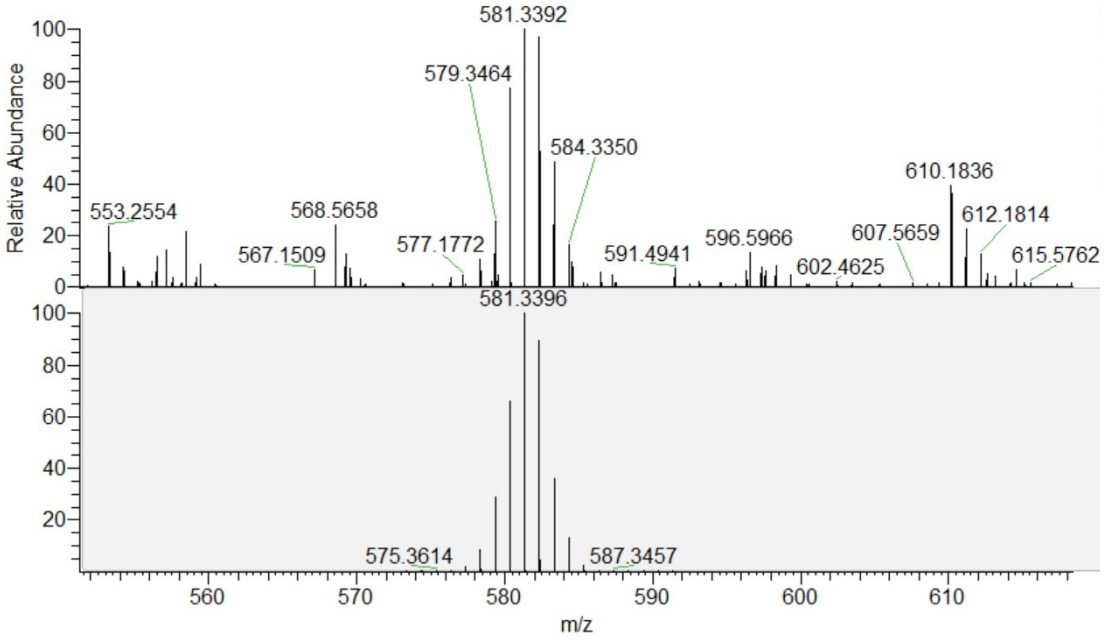



**Figure S17** HRMS spectrum of **CB-Ph-P**.

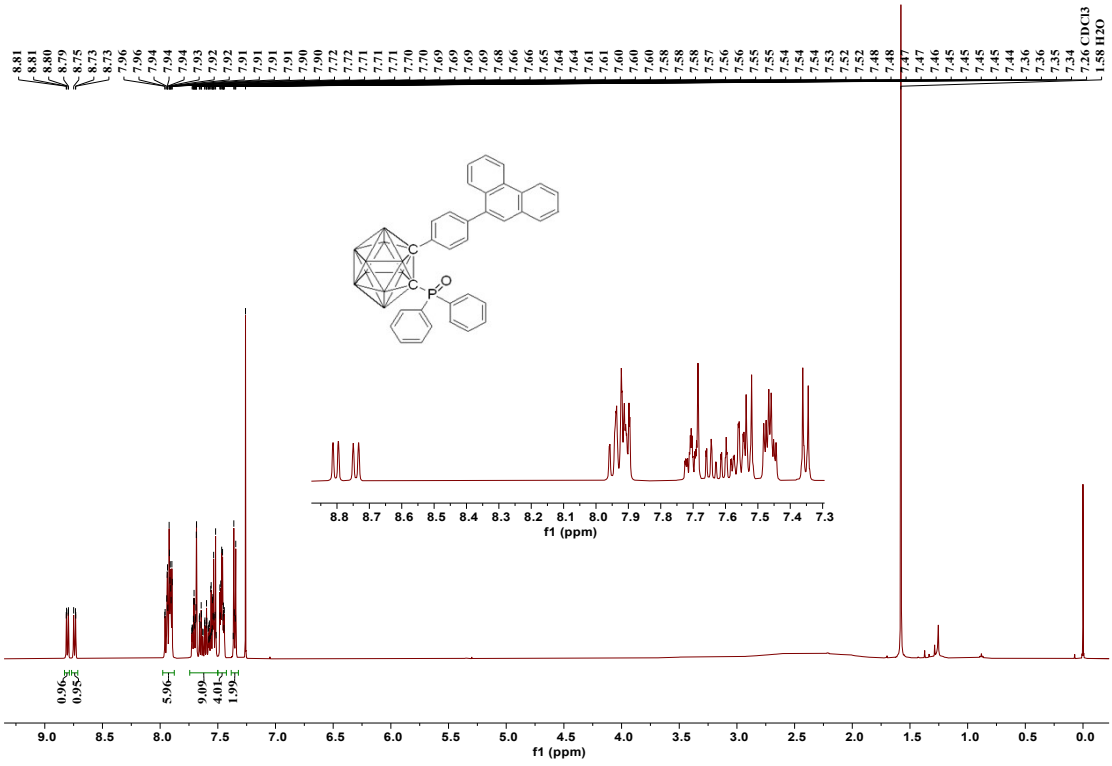



**Figure S18** $^{1}$H NMR spectrum of **CB-Ph-PO** in $CDCl_3$.

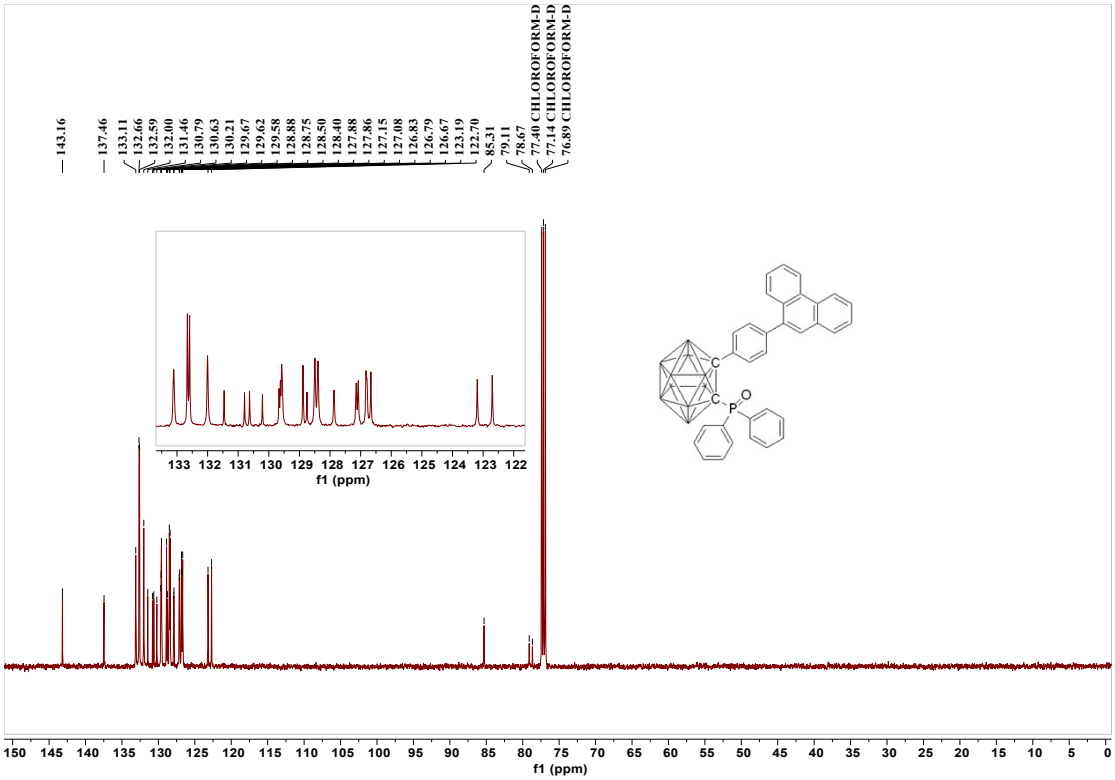



**Figure S19** $^{13}$C NMR spectrum of **CB-Ph-PO** in $CDCl_3$.

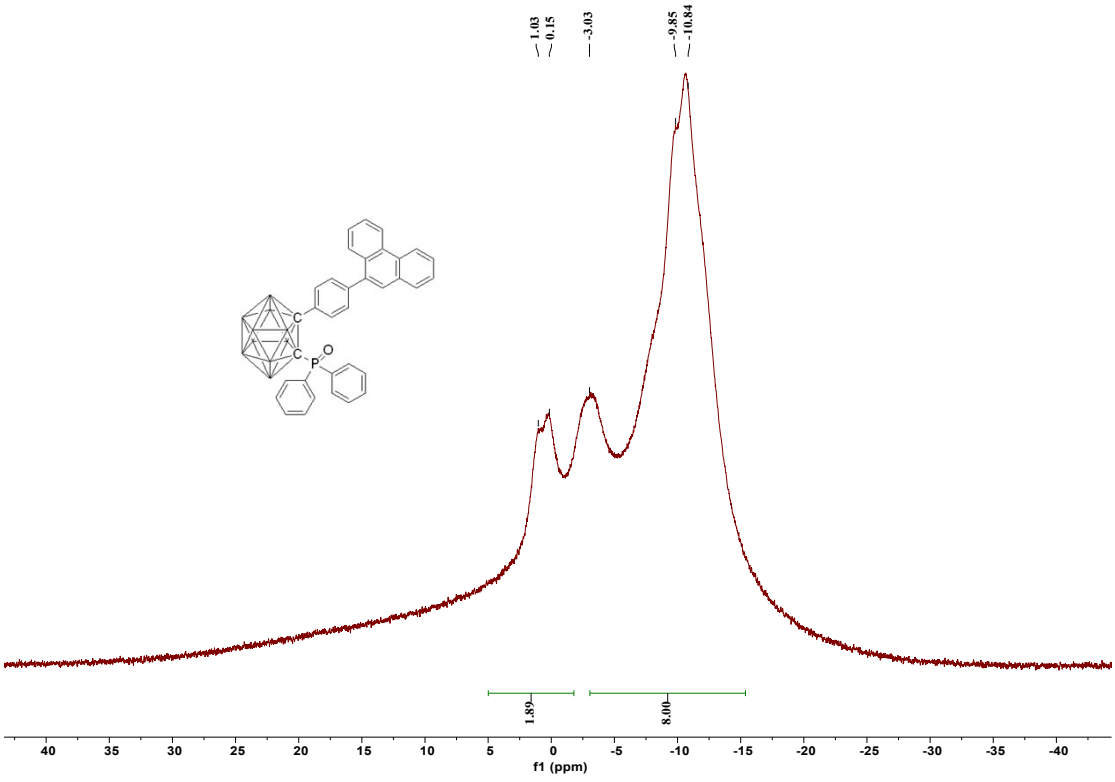



**Figure S20** $^{11}$B NMR spectrum of **CB-Ph-PO** in $CDCl_3$.

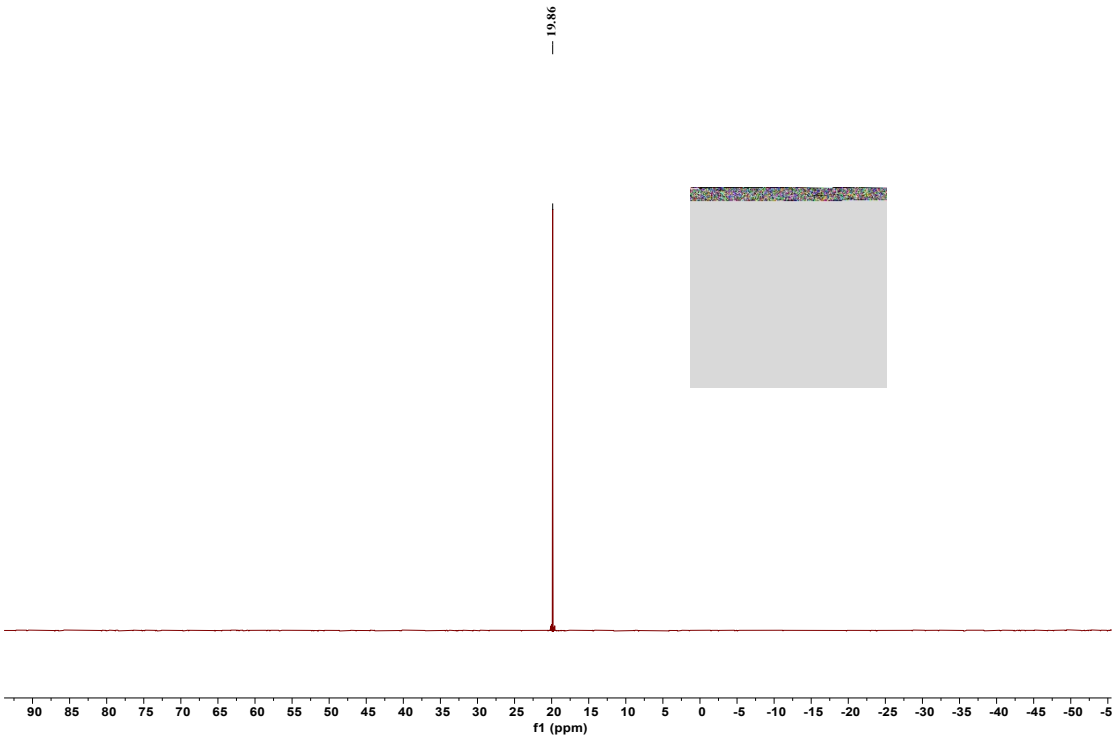



**Figure S21** $^{31}$P NMR spectrum of **CB-Ph-PO** in $CDCl_3$.

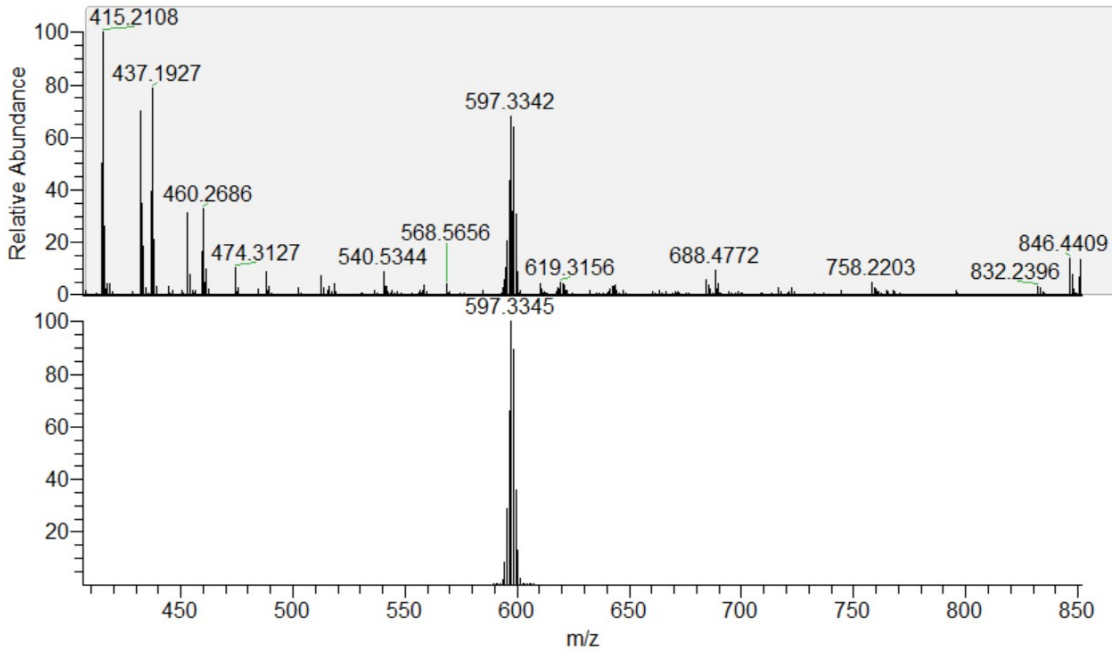



**Figure S22** HRMS spectrum of **CB-Ph-PO**.

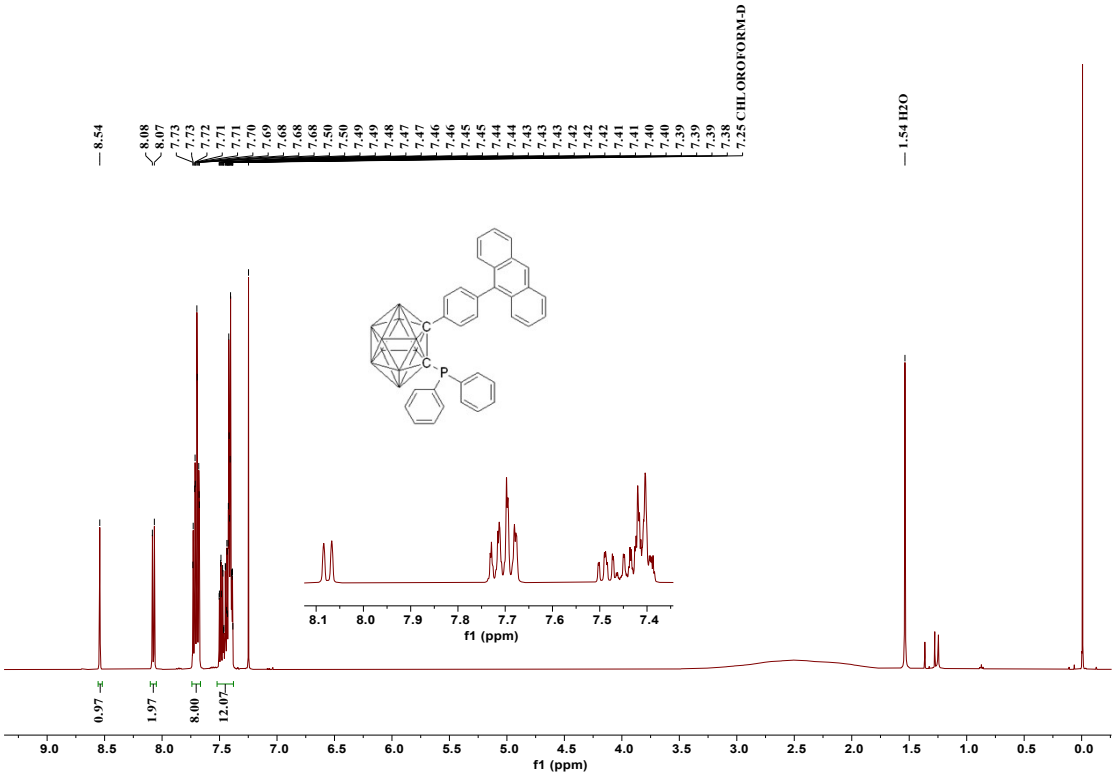



**Figure S23** $^{1}$H NMR spectrum of **CB-Ph-PAn** in $CDCl_3$.

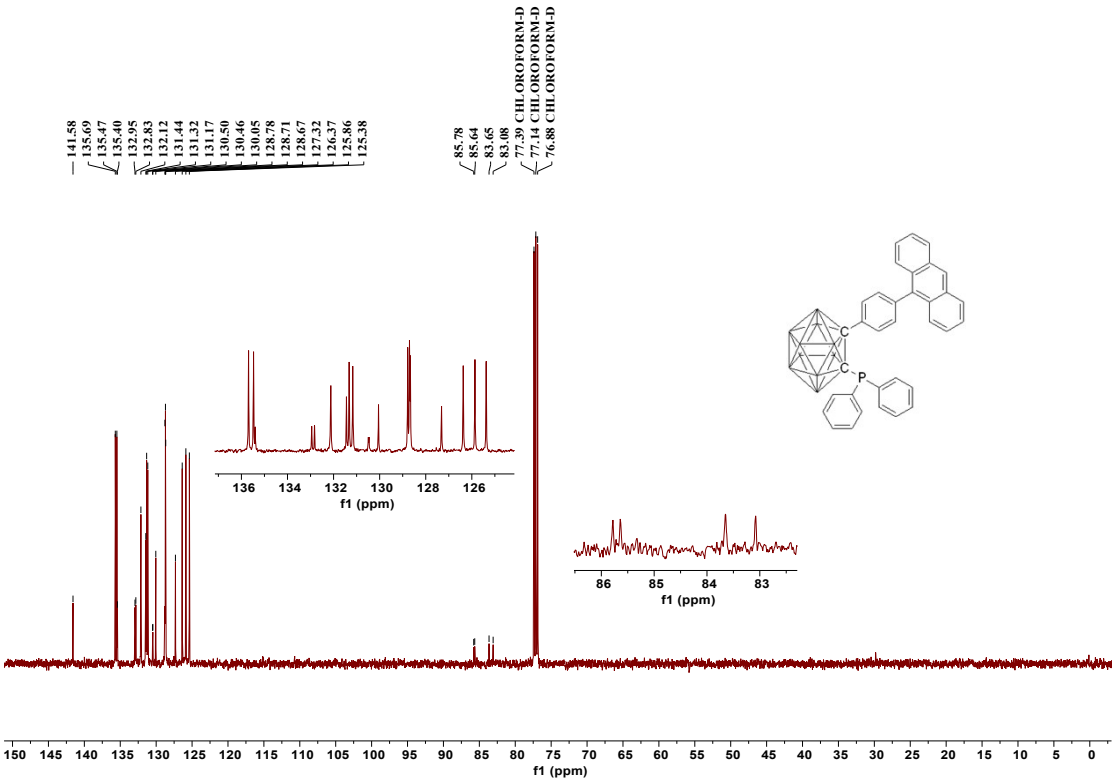



**Figure S24** $^{13}$C NMR spectrum of **CB-Ph-PAn** in $CDCl_3$.

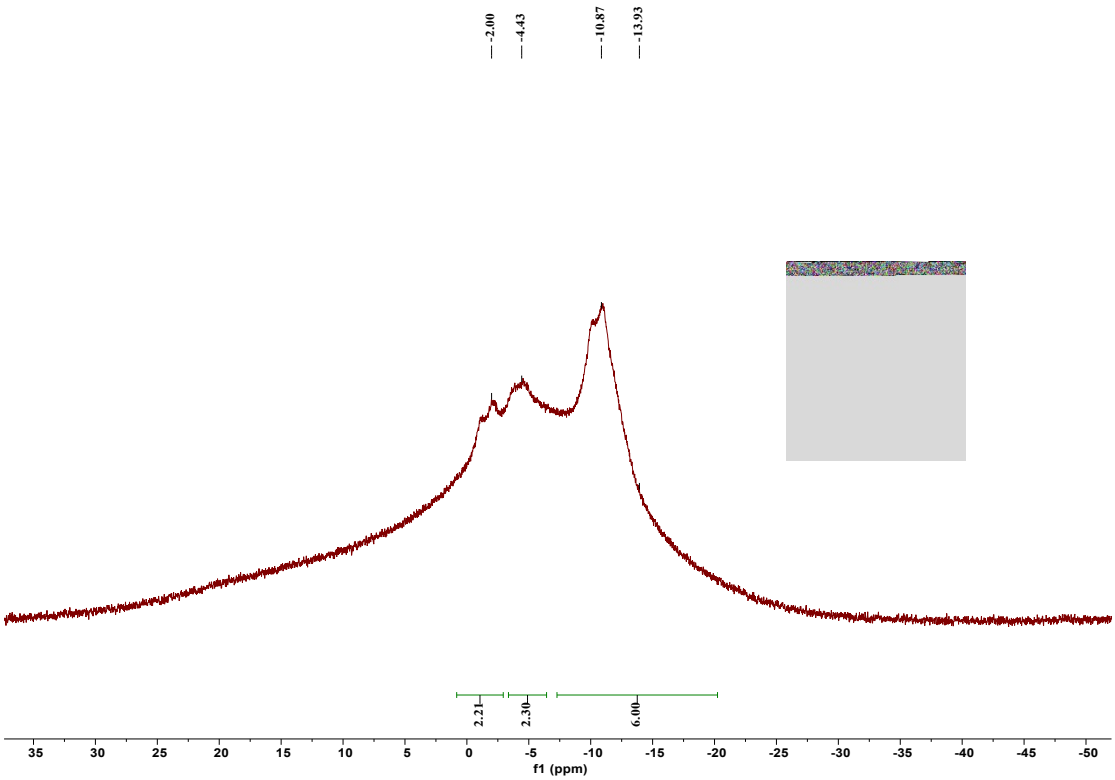



**Figure 25** $^{11}$B NMR spectrum of **CB-Ph-PAn** in $CDCl_3$.

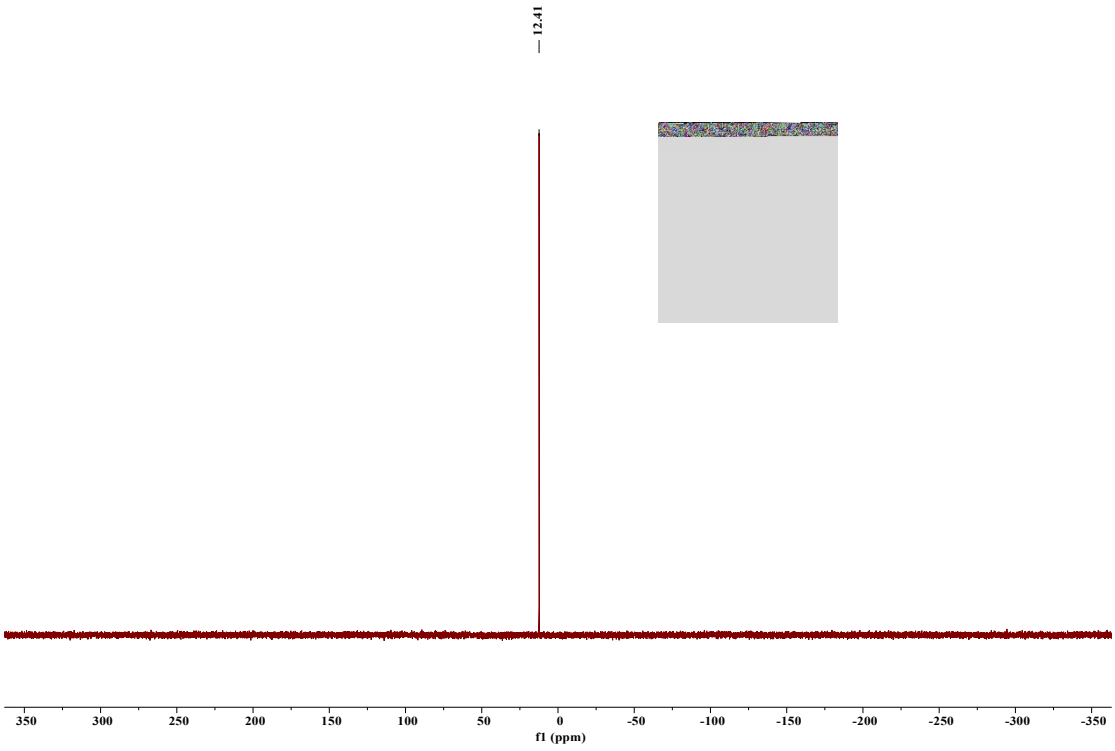



**Figure S26** $^{31}$P NMR spectrum of **CB-Ph-PAn** in $CDCl_3$.

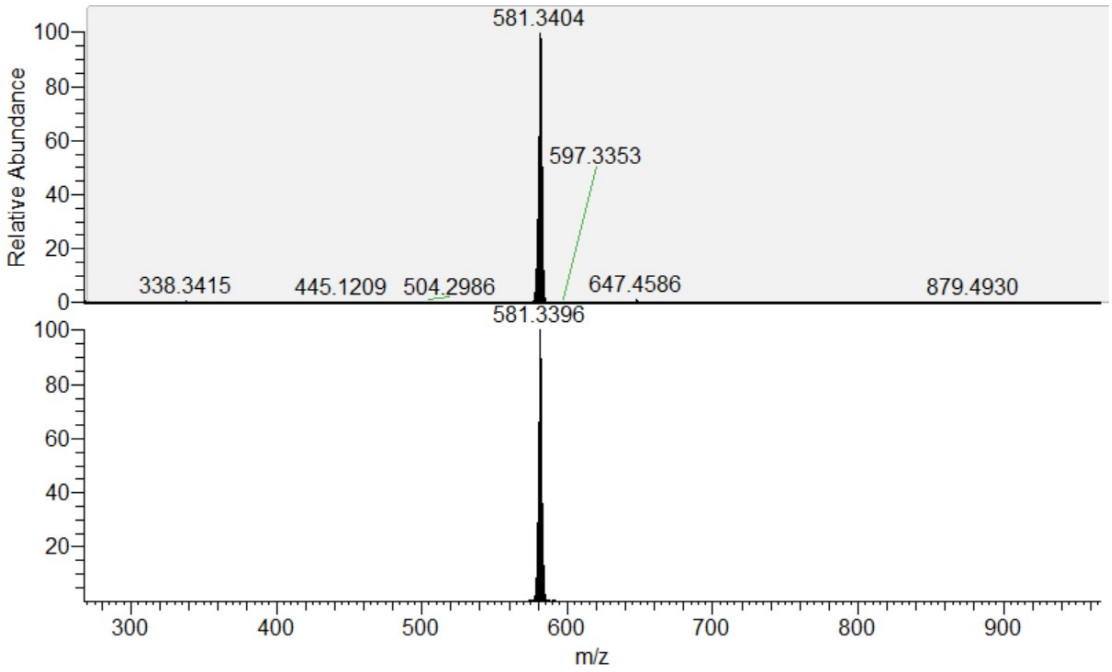



**Figure S27** HRMS spectrum of **CB-Ph-PAn**.

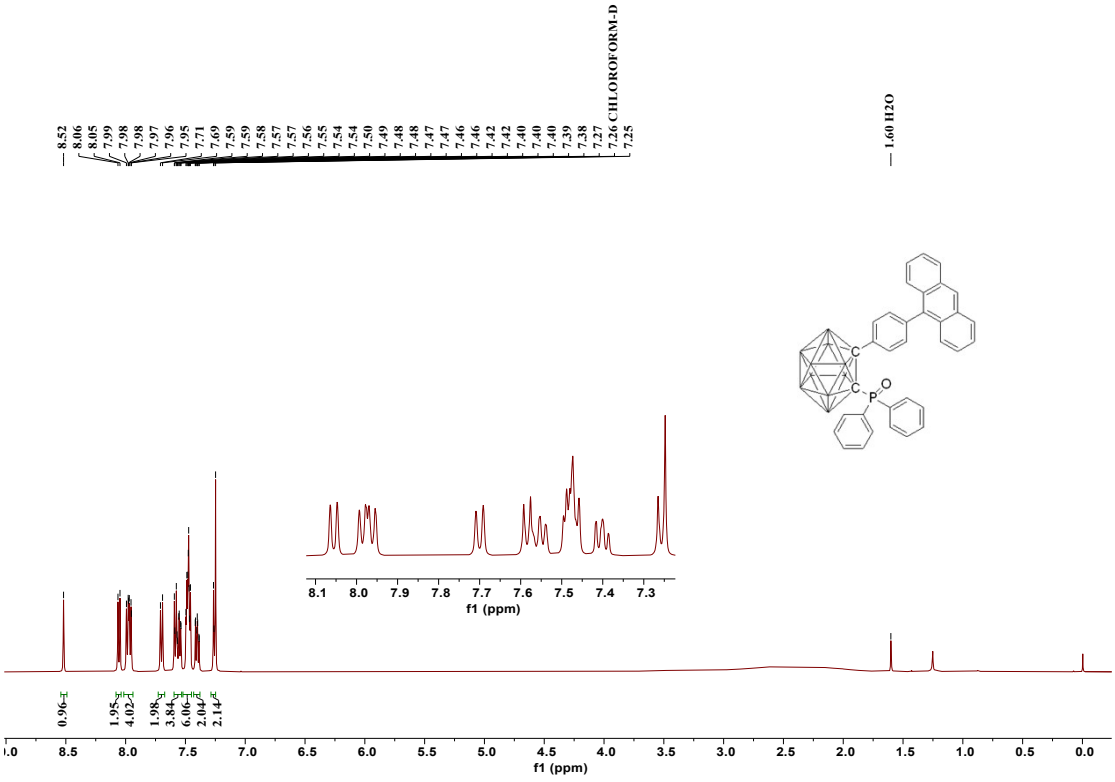



**Figure S28** $^{1}$H NMR spectrum of **CB-Ph-POAn** in $CDCl_3$.

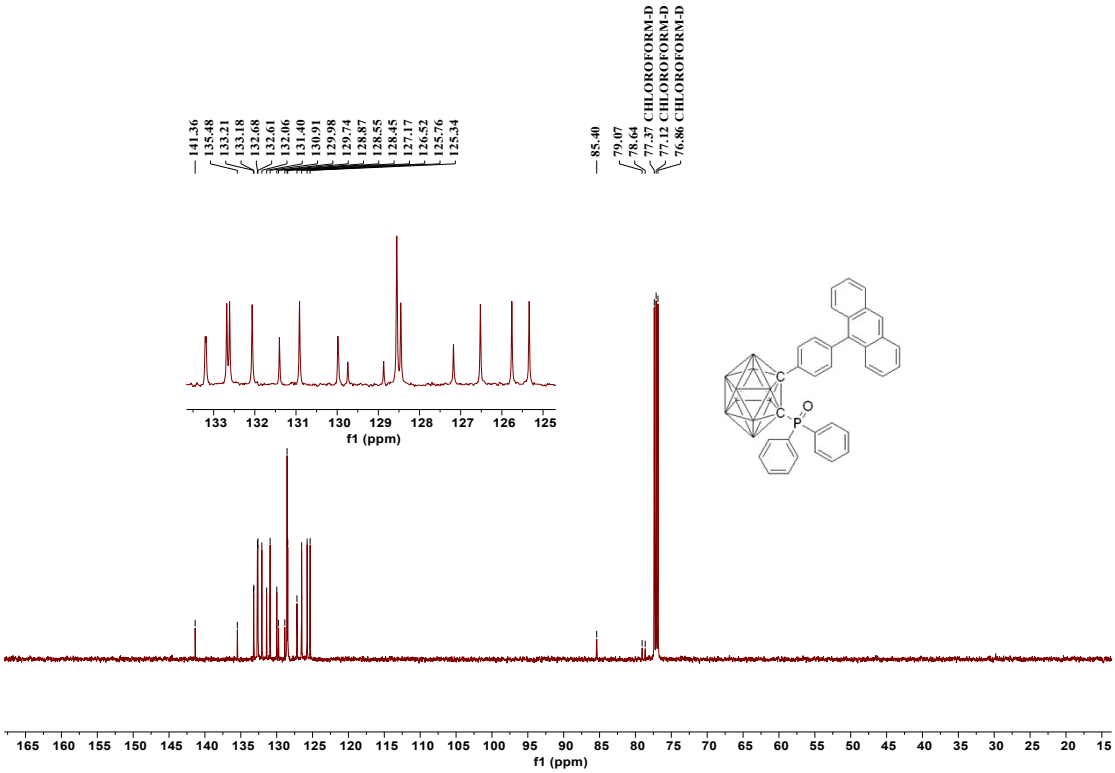



**Figure S29** $^{13}$C NMR spectrum of **CB-Ph-POAn** in $CDCl_3$.

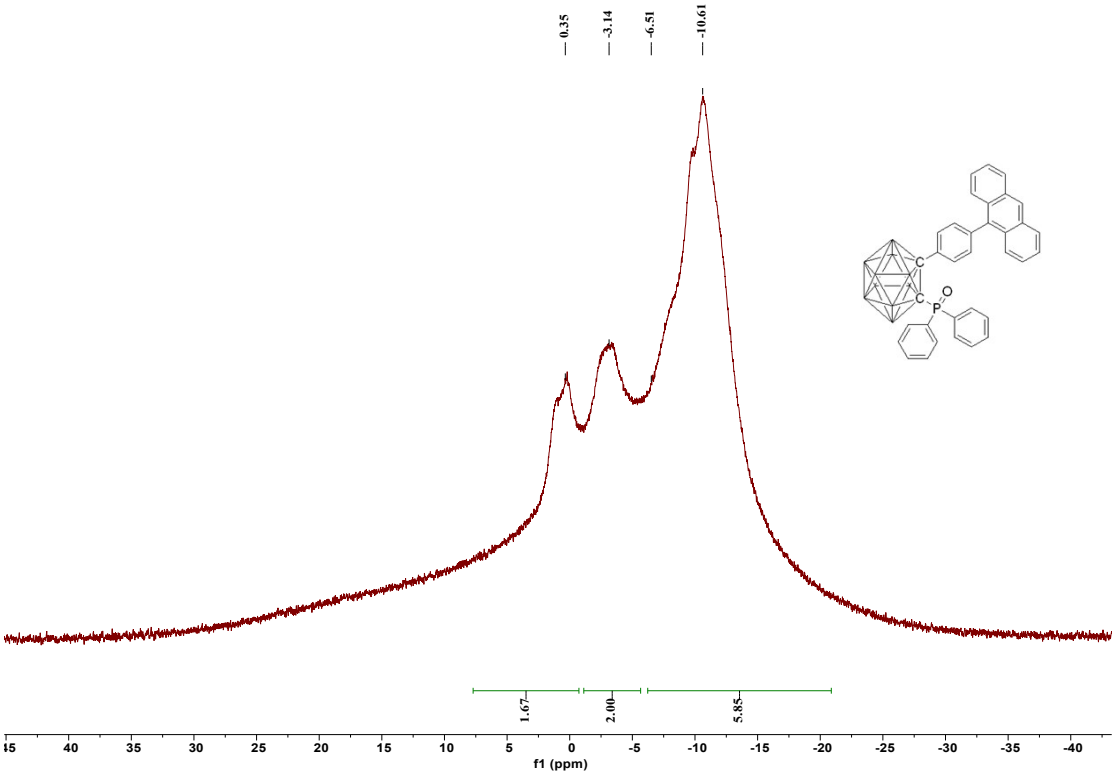



**Figure S30** $^{11}$B NMR spectrum of **CB-Ph-POAn** in $CDCl_3$.

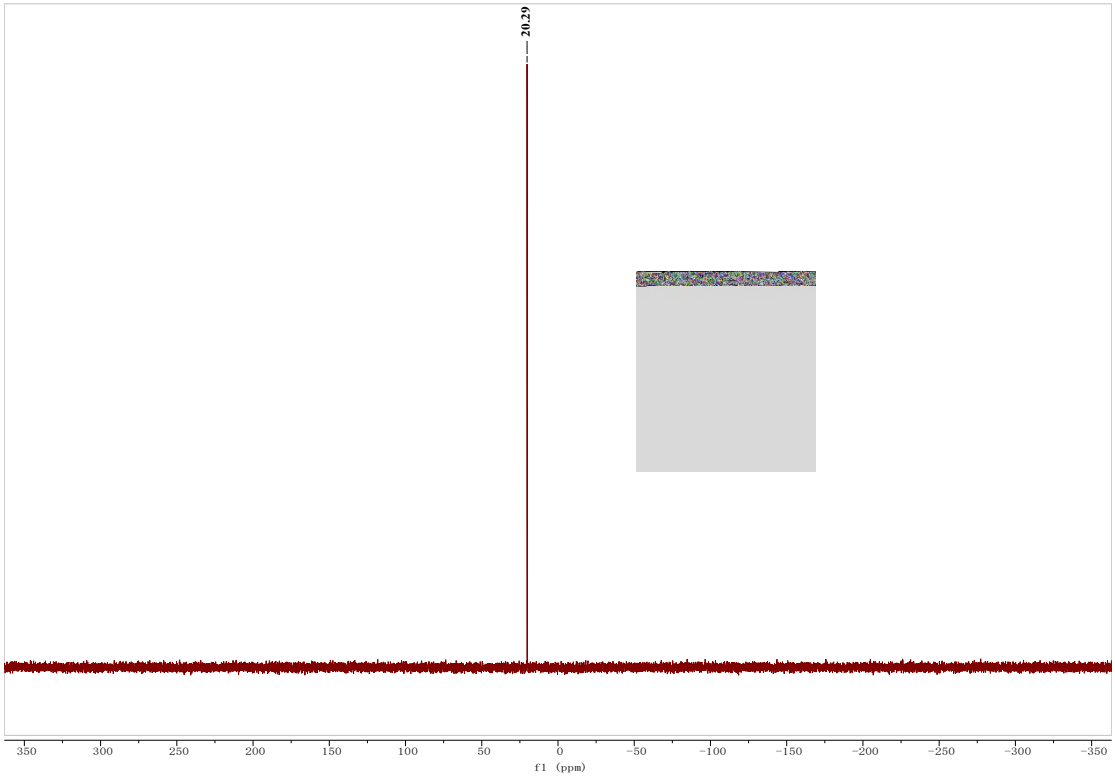



**Figure S31** $^{31}$P NMR spectrum of **CB-Ph-POAn** in $CDCl_3$.

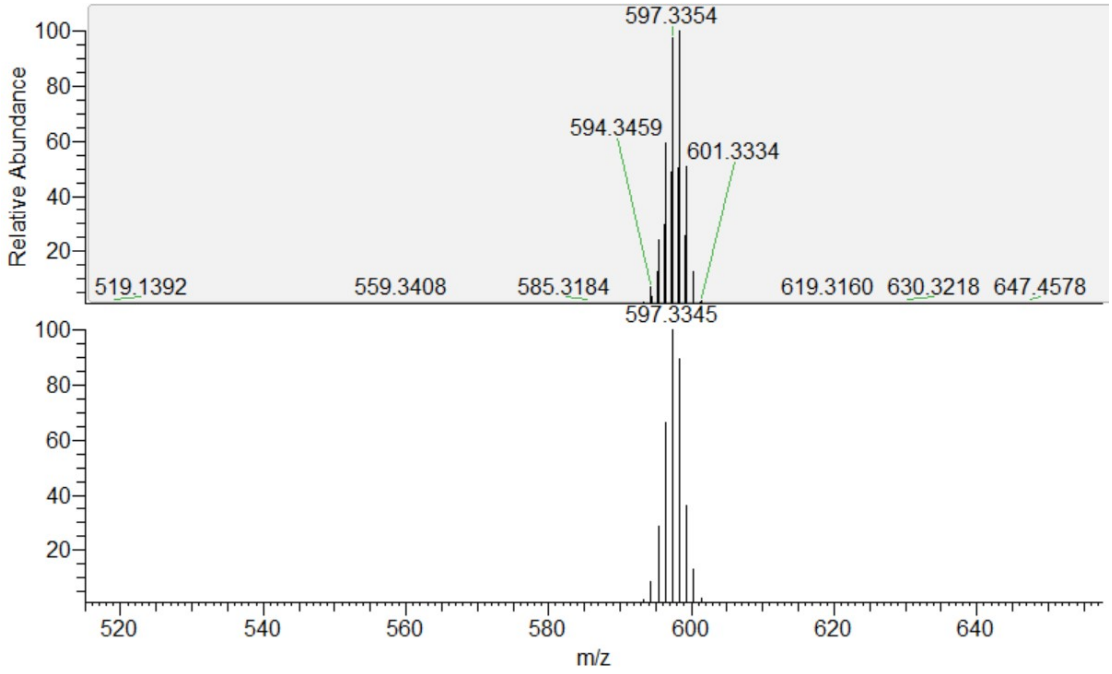



**Figure S32** HRMS spectrum of **CB-Ph-POAn**.

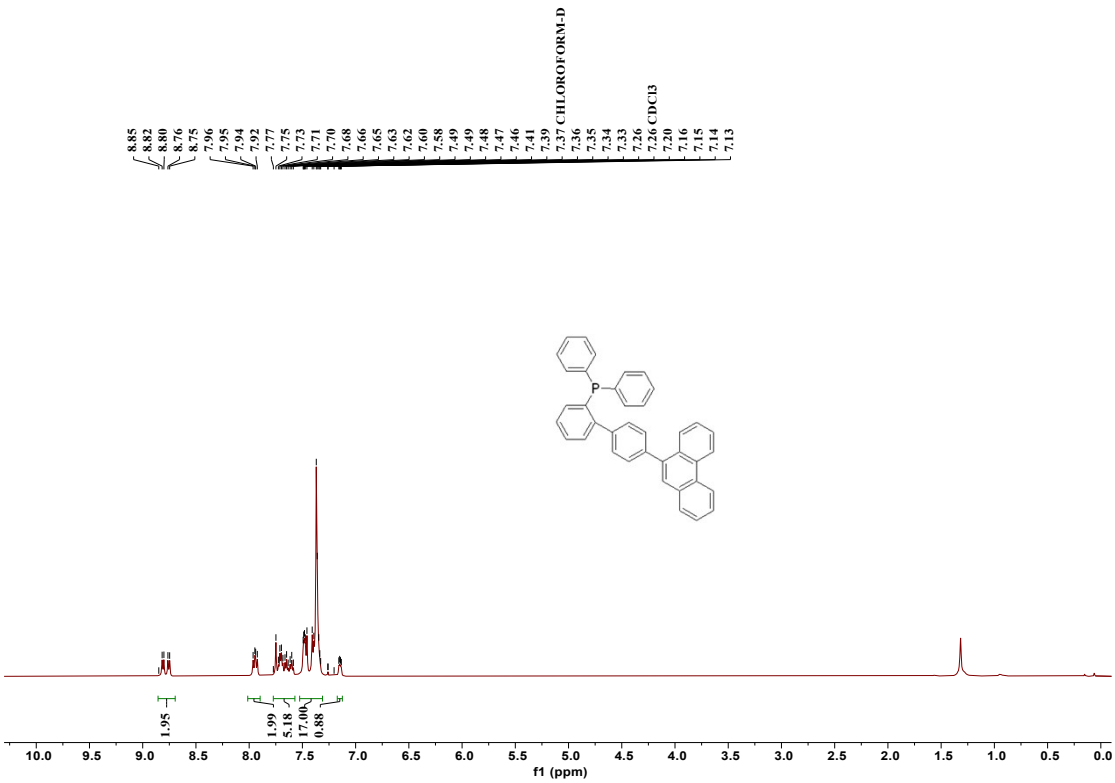



**Figure S33** $^{1}$H NMR spectrum of **Ph-Ph-P** in $CDCl_3$.

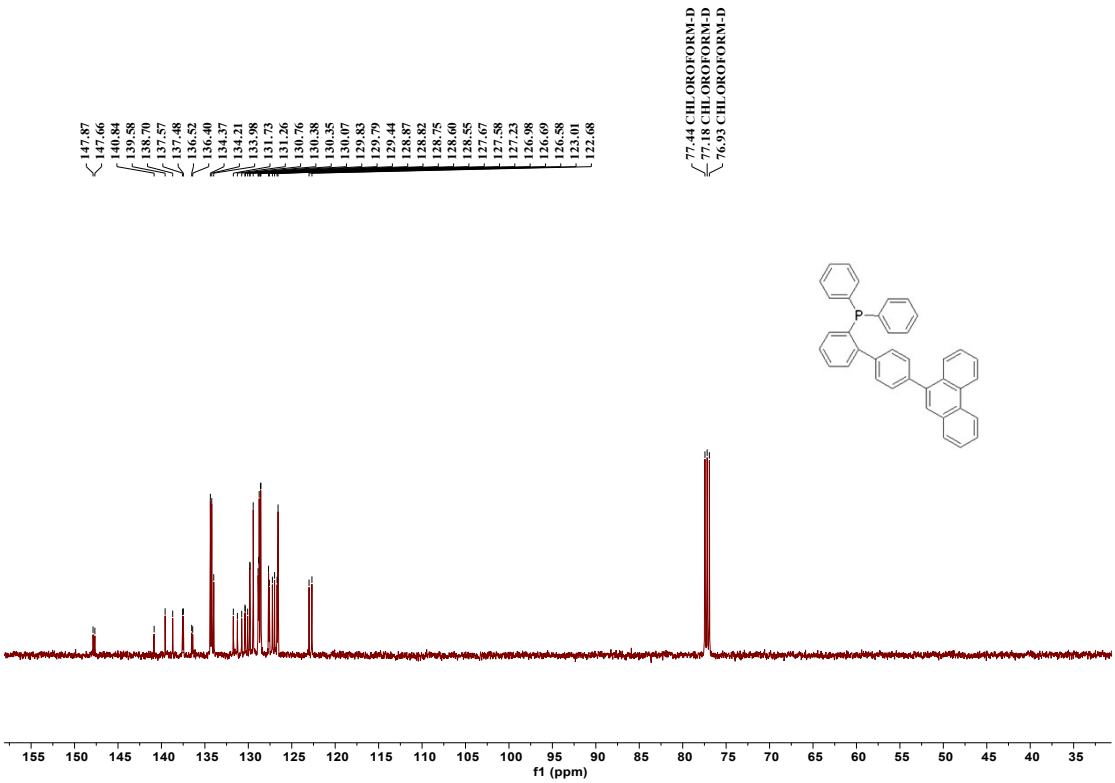



**Figure S34** $^{13}$C NMR spectrum of **Ph-Ph-P** in $CDCl_3$.

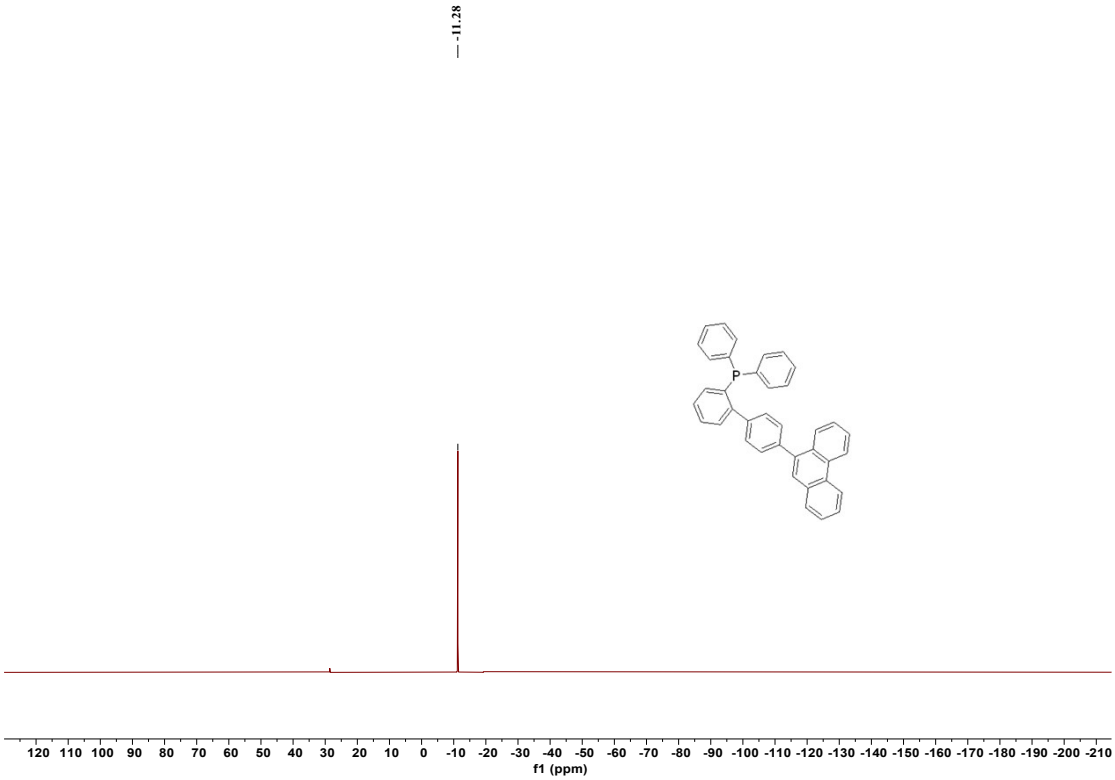



**Figure S35** $^{31}$P NMR spectrum of **Ph-Ph-P** in $CDCl_3$.

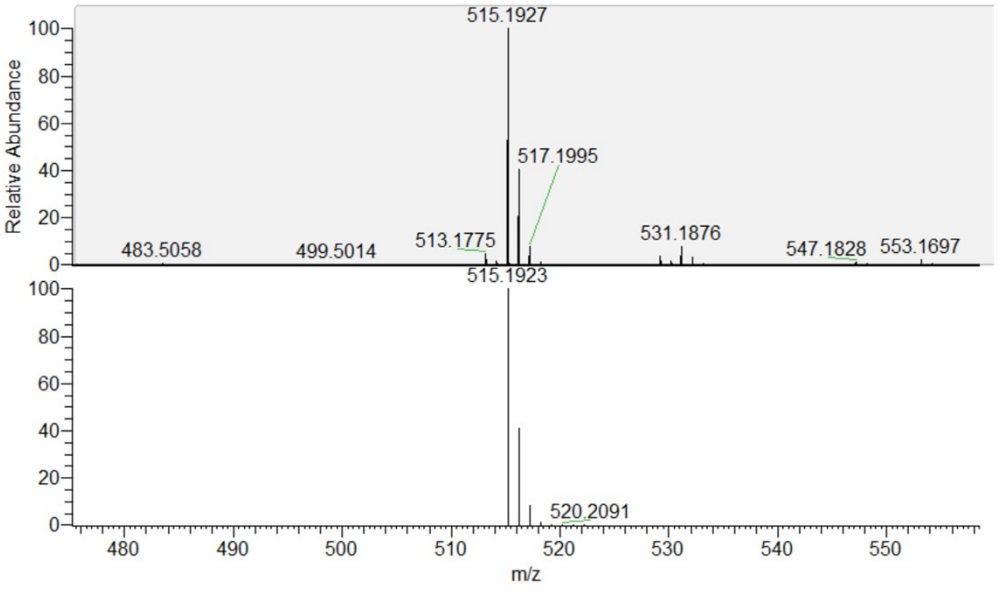



**Figure S36** HRMS spectrum of **Ph-Ph-P**.

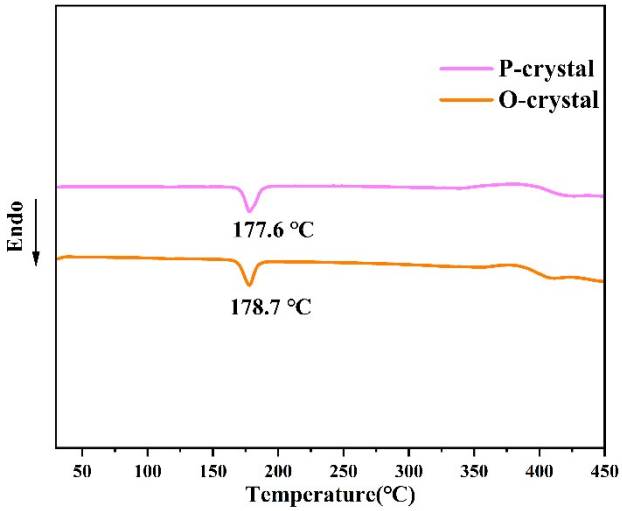



**Figure S37** DSC curves of P-crystal and O-crystal under nitrogen.

## V References

1. D. Tu, P. Leong, S. Guo, H. Yan, C. Lu and Q. Zhao, *Angew Chem Int Ed*, 2017, **56**, 11370-11374.