

## Supplementary material

### Modular synthesis of triphenylphosphine-derived cage ligands for rhodium-catalyzed hydroformylation applications

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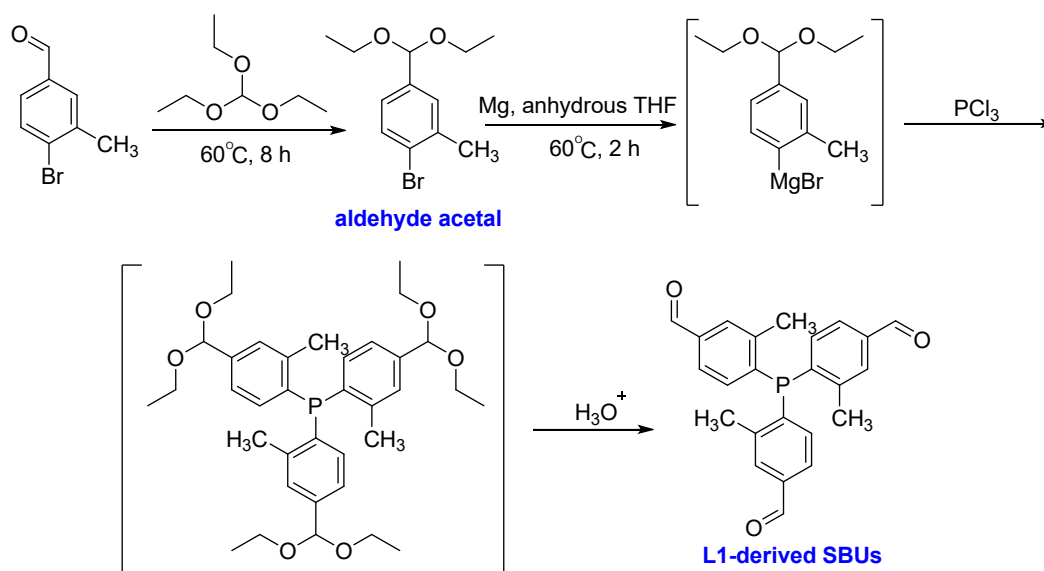
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## 1. General remarks

All quantum mechanical calculations were conducted by employing DFT with the Gaussian 09 package<sup>1</sup>. Molecular structures were optimized using the B3LYP functional<sup>2</sup>. The 6-31G(*d,p*) basis set was used for all elements except for Rh or Ni, for which the LANL2DZ basis set was employed with an extra *f*-polarization function ( $\zeta_f = 1.350$  for Rh,  $\zeta_f = 3.130$  for Ni). Vibrational frequency calculations at the same level were performed to verify that each stationary point was a minimum (no imaginary frequency) or a transition state (only one imaginary frequency). The SMD solvent model<sup>3</sup> was utilized, and toluene was chosen as the solvent. Intrinsic reaction coordinate calculations were conducted to verify the transition-state structures. Single-point calculations were performed at a higher theoretical level, M06-L<sup>4</sup>, with the def2-TZVP basis set for Rh, and the 6-311+G(*d,p*) basis set for all the other atoms to determine the free energies for use at the B3LYP-optimized geometries. Empirical D3 dispersion corrections<sup>5</sup> were included in the single-point calculations.

## 2. Synthesis of L1-derived SBUs



**Synthesis of aldehyde acetal.** 4-bromo-3-methylbenzaldehyde (5.53 g, 25 mmol) and triethyl orthoformate (4.89 g, 33 mmol) were dissolved in 50 mL of anhydrous ethanol, and then a drop of concentrated sulphuric acid was added as a catalyst. The mixture was magnetically stirred and refluxed for 8 h. After the completion of the

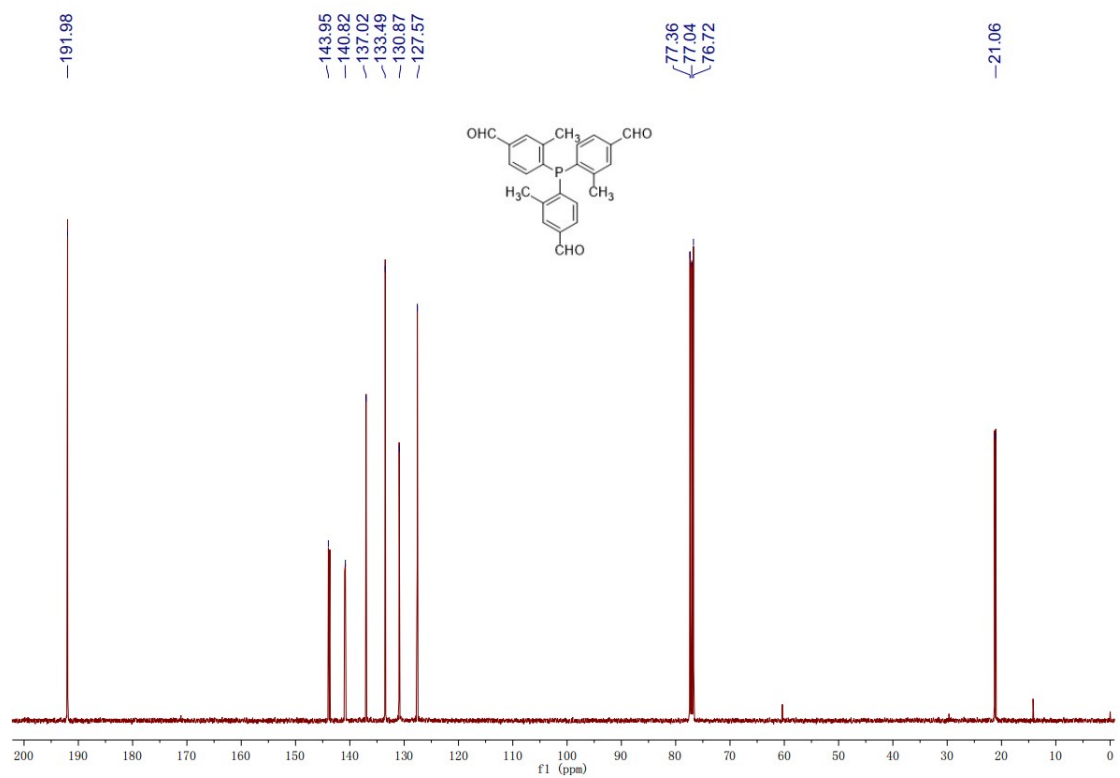
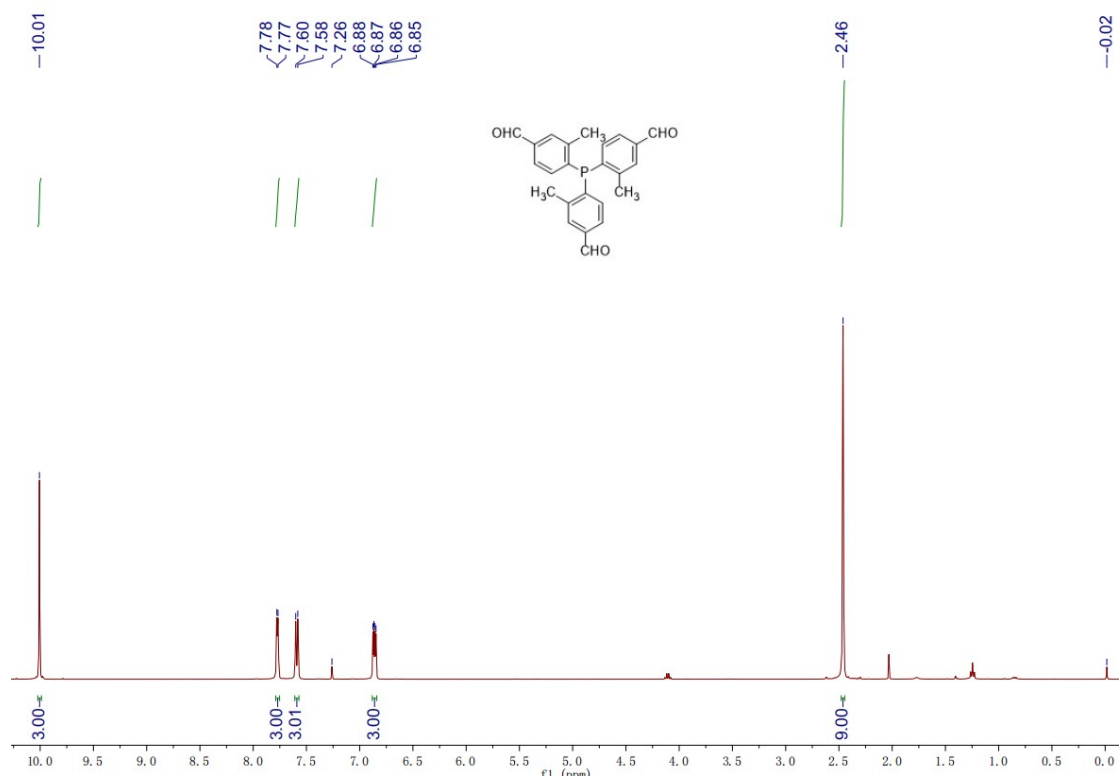
reaction, the mixture was cooled to room temperature and 30 mL of NaHCO<sub>3</sub> solution (0.5 M) was added, then the mixture was transferred to the separation funnel. The aqueous phase was extracted with ethyl acetate (3 × 100 mL), the combined organic extract was washed with saturated brine (3 × 100 mL), dried over anhydrous magnesium sulfate (MgSO<sub>4</sub>, 50 g) and concentrated to afford aldehyde acetal product as a clear oil (6.49 g, 95% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.21 (t, 6 H, *J* = 8.0 Hz), 2.34 (s, 3 H), 3.46-3.60 (m, 4 H), 5.50 (s, 1 H), 7.30 (d, 2 H, 8.0 Hz), 7.44 (d, 2 H, 8.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 15.2, 23.0, 61.1, 101.0, 124.8, 125.7, 129.1, 132.1, 137.7, 138.4.

**Synthesis of Grignard reagent.** An oven-dried 100 mL three-necked, round-bottomed flask was loaded with magnesium powder (0.58 g, 24 mmol) and a crystal of iodine. Anhydrous THF (20 mL) was charged into this flask under an atmosphere of nitrogen. The synthesized aldehyde acetal product (5.46 g, 20 mmol) was dissolved in 30 mL of anhydrous THF, 10 mL of this solvent was directly charged to the Schlenk flask under an atmosphere of nitrogen. The flask was connected with a condenser-west tube and the mixture was magnetically stirred and heated to 60 °C, the Grignard reaction could be easily initiated. Then, this flask was equipped with a 50 mL dropping funnel filled with the before mentioned aldehyde acetal in THF solution (the remaining 20 mL), the solution was added dropwise within 10-15 min under an atmosphere of nitrogen. After the completion of the addition, the mixture was further refluxed for 2 h to afford the fresh Grignard reagent.

**Synthesis of the final L1-derived SBUs.** The above-prepared fresh Grignard reagent was cooled to -5 °C using an ice-salt bath. Then, PCl<sub>3</sub> (0.916 g, 6.67 mmol) was diluted with 10 mL anhydrous THF, the diluted PCl<sub>3</sub> solution was added to the Grignard reagent via a dropping funnel under an atmosphere of nitrogen, the reaction temperature was kept below 0 °C. After the completion of the addition process, the mixture was heated to 60 °C and stirred for another 2 h. After the reaction, the mixture was cooled to 0 °C using an ice bath, 10 mL of saturated NH<sub>4</sub>Cl solution was added dropwise to quench the reaction mixture, after the addition of saturated NH<sub>4</sub>Cl solution, the mixture was stirred overnight at room temperature. Then the solution was transferred to a separation funnel, after shaking, the solution was separated into

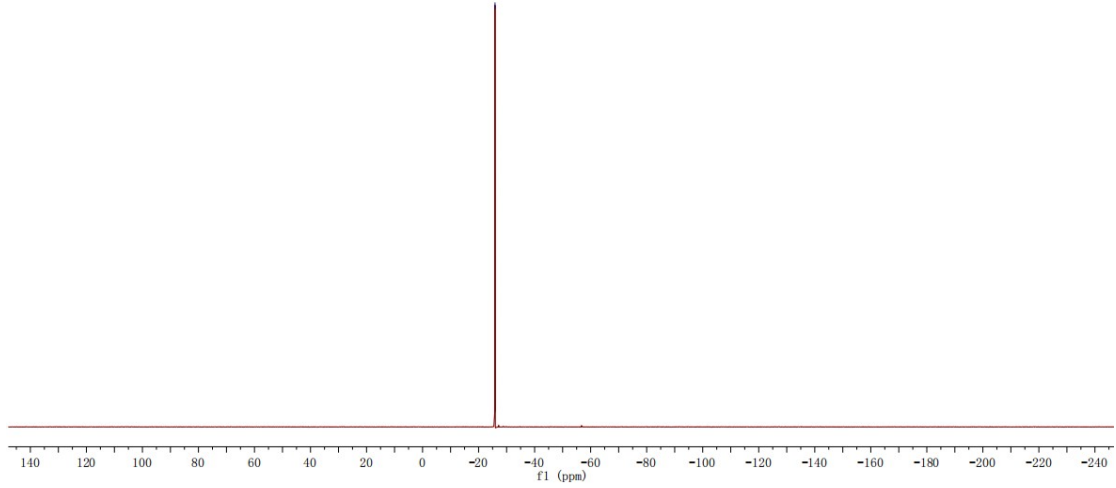
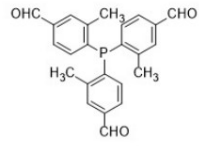
two layers, the organic phase was collected. The water phase was extracted with ethyl acetate (15 mL  $\times$  3), the combined organic phase was further washed with saturated aqueous NaCl solution (100 mL  $\times$  2), dried over anhydrous MgSO<sub>4</sub>, filtered through fluted filter paper in a glass funnel, and concentrated on a rotary evaporator to afford crude product of yellow powder. The crude product was further purified through column chromatography with an eluent of hexane/EtOAc = 4/1 to afford the pure product as a light yellow powder (1.42 g, 55% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.46 (s, 9 H), 6.85-6.88 (q, 3 H,  $J$  = 4.0 Hz), 7.59 (d, 3 H,  $J$  = 8.0 Hz), 7.78 (d, 3 H,  $J$  = 4.0 Hz), 10.01 (s, 3 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  21.1, 127.6, 130.9, 133.5, 137.0, 140.8, 144.0, 192.0. <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  -25.9. HRMS  $m/z$  (ESI) calcd for C<sub>24</sub>H<sub>22</sub>O<sub>3</sub>P [M+H]<sup>+</sup> 389.1307, found 389.1280.

# $^1\text{H}$ , $^{13}\text{C}$ , $^{31}\text{P}$ NMR spectra of synthetic intermediates



<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ -25.86.

---25.86



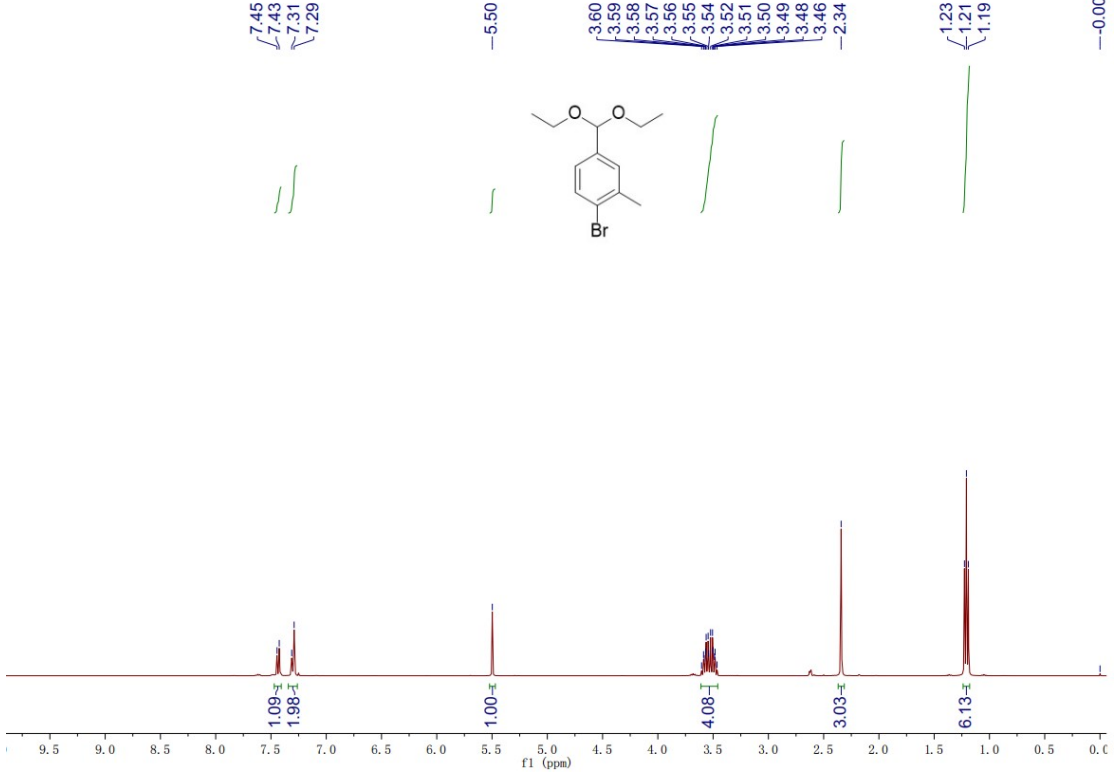
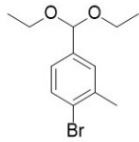
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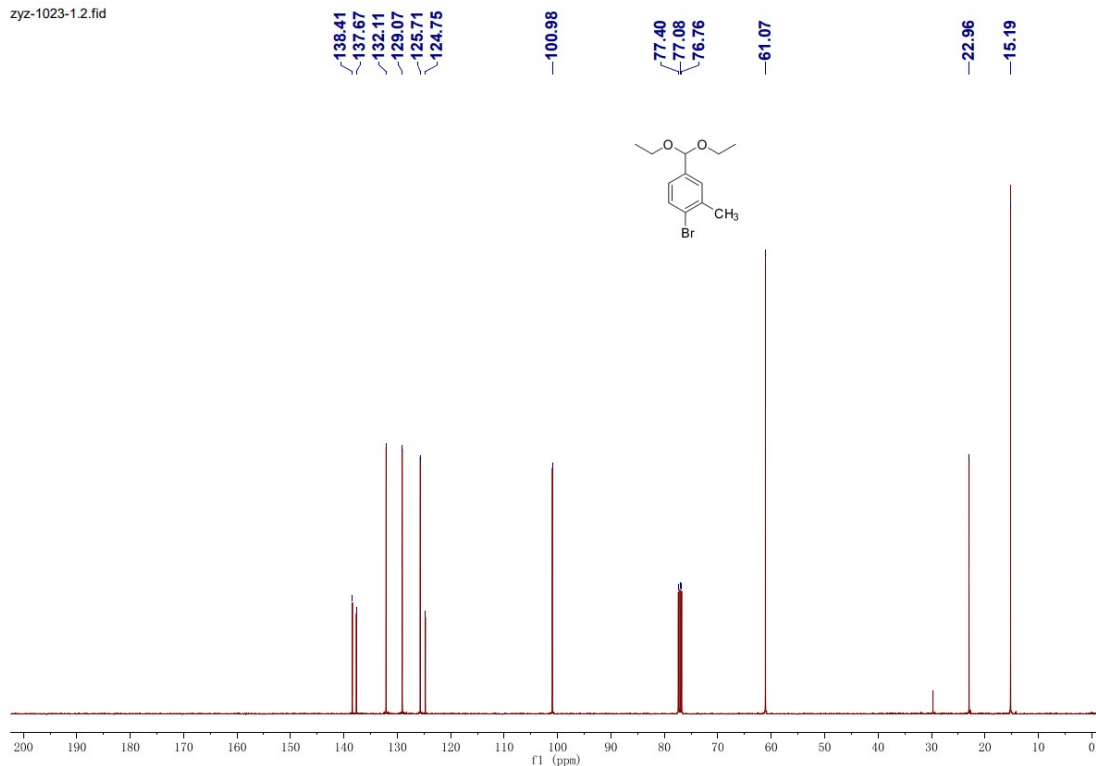
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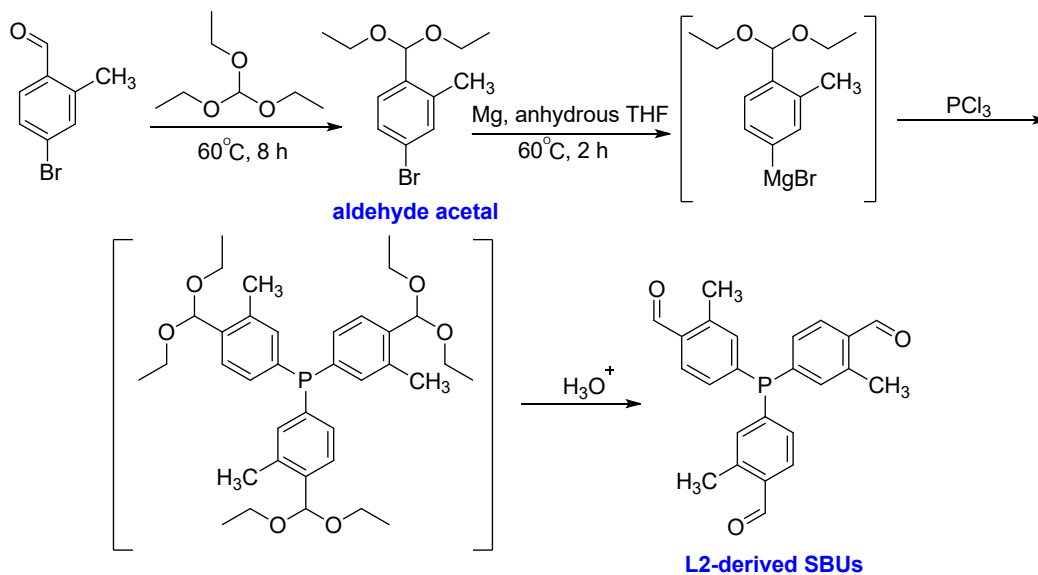
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### 3. Synthesis of L2-derived SBUs and Cage-L2



**Synthesis of aldehyde acetal.** 4-bromo-2-methylbenzaldehyde (5.53 g, 25 mmol) and triethyl orthoformate (4.89 g, 33 mmol) were dissolved in 50 mL of anhydrous ethanol, and then a drop of concentrated sulphuric acid was added as a catalyst. The mixture was magnetically stirred and refluxed for 8 h. After the completion of the reaction, the mixture was cooled to room temperature and 30 mL of  $\text{NaHCO}_3$  solution



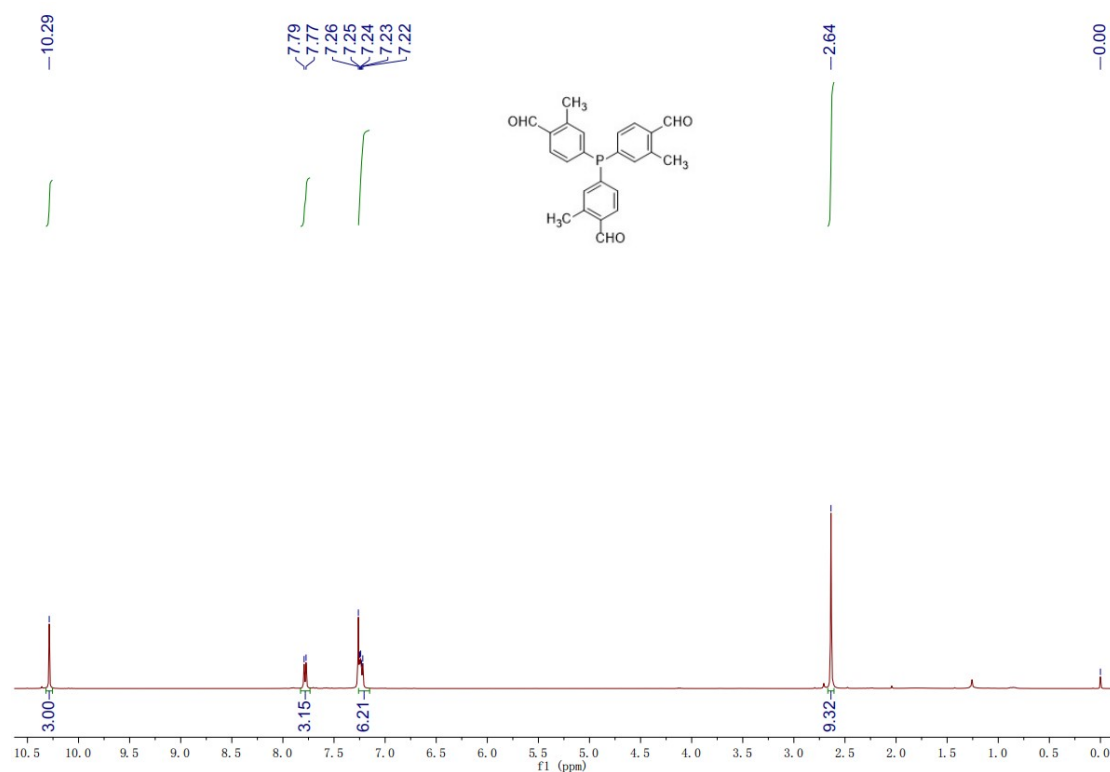
(0.5 M) was added, then the mixture was transferred to the separation funnel. The aqueous phase was extracted with ethyl acetate (3 × 100 mL), the combined organic extract was washed with saturated brine (3 × 100 mL), dried over anhydrous magnesium sulfate (MgSO<sub>4</sub>, 50 g) and concentrated to afford aldehyde acetal product as a clear oil (6.56 g, 96% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.22 (t, 6 H, *J* = 8.0 Hz), 2.35 (s, 3 H), 3.47-3.61 (m, 4 H), 5.50 (s, 1 H), 7.32 (d, 2 H, 8.0 Hz), 7.44 (d, 2 H, 8.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 15.2, 22.9, 60.9, 100.8, 124.7, 125.7, 129.1, 132.0, 137.5, 138.5.

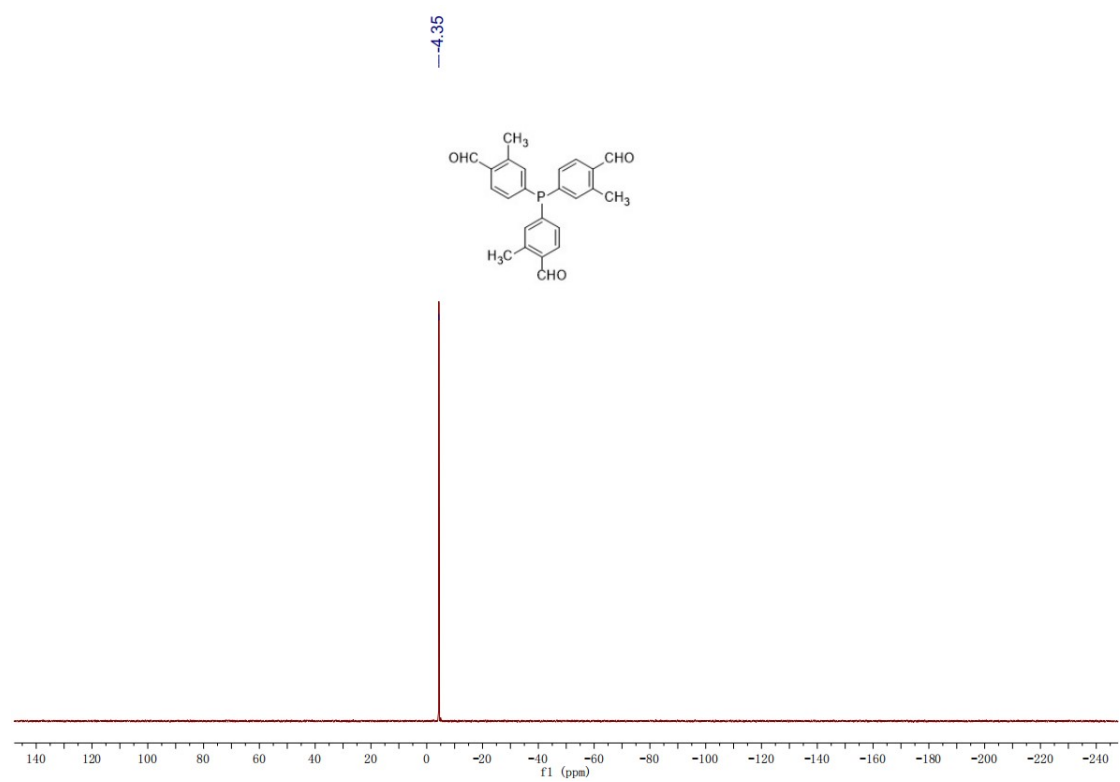
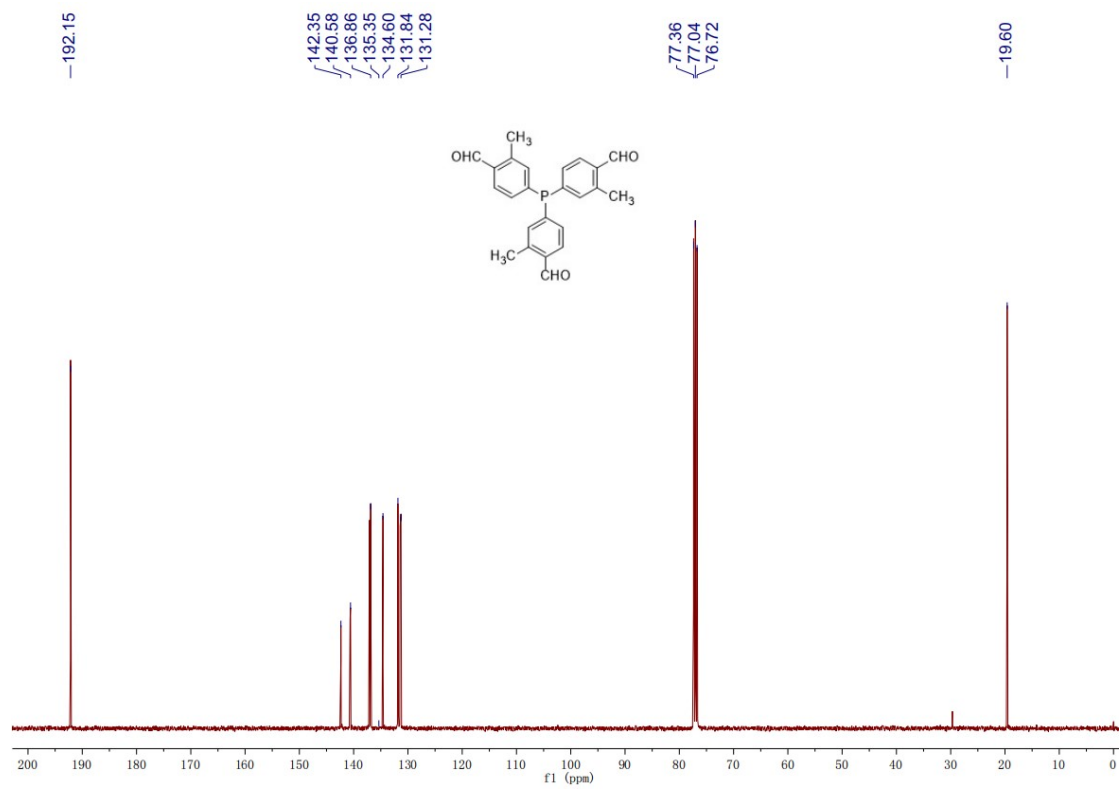
**Synthesis of Grignard reagent.** An oven-dried 100 mL three-necked, round-bottomed flask was loaded with magnesium powder (0.58 g, 24 mmol) and a crystal of iodine. Anhydrous THF (20 mL) was charged into this flask under an atmosphere of nitrogen. The synthesized aldehyde acetal product (5.46 g, 20 mmol) was dissolved in 30 mL of anhydrous THF, 10 mL of this solvent was directly charged to the Schlenk flask under an atmosphere of nitrogen. The flask was connected with a condenser-west tube and the mixture was magnetically stirred and heated to 60 °C, the Grignard reaction could be easily initiated. Then, this flask was equipped with a 50 mL dropping funnel filled with the before mentioned aldehyde acetal in THF solution (the remaining 20 mL), the solution was added dropwise within 10-15 min under an atmosphere of nitrogen. After the completion of the addition, the mixture was further refluxed for 2 h to afford the fresh Grignard reagent.

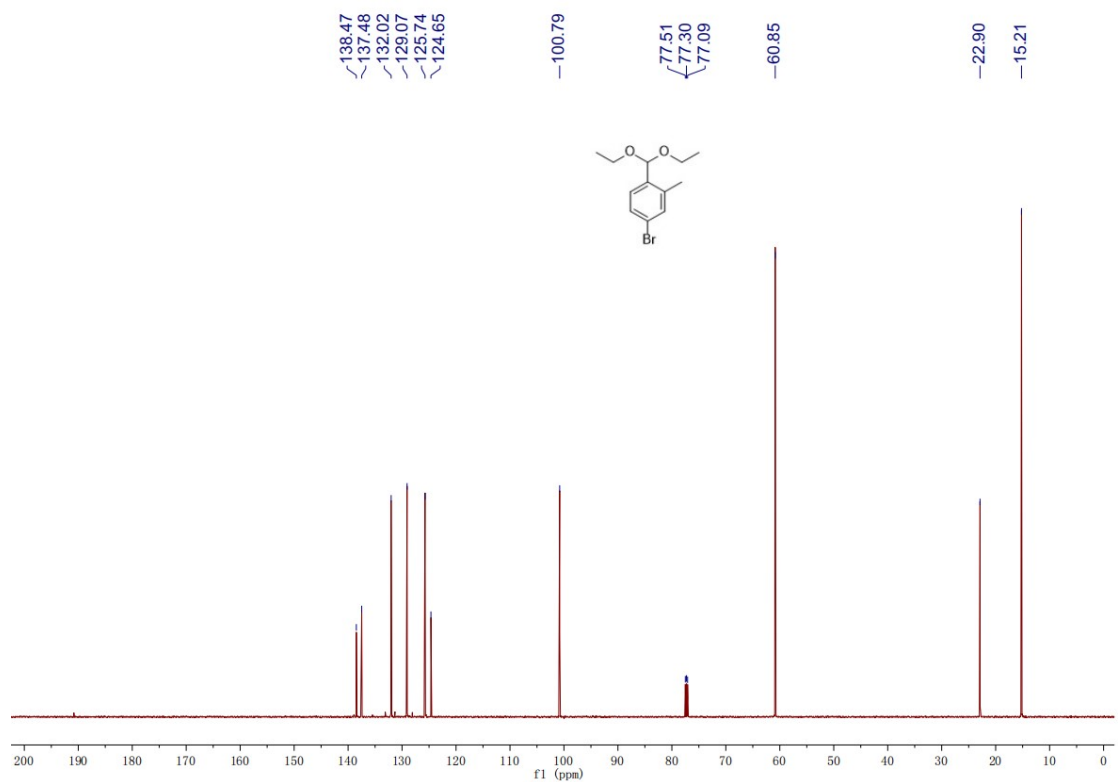
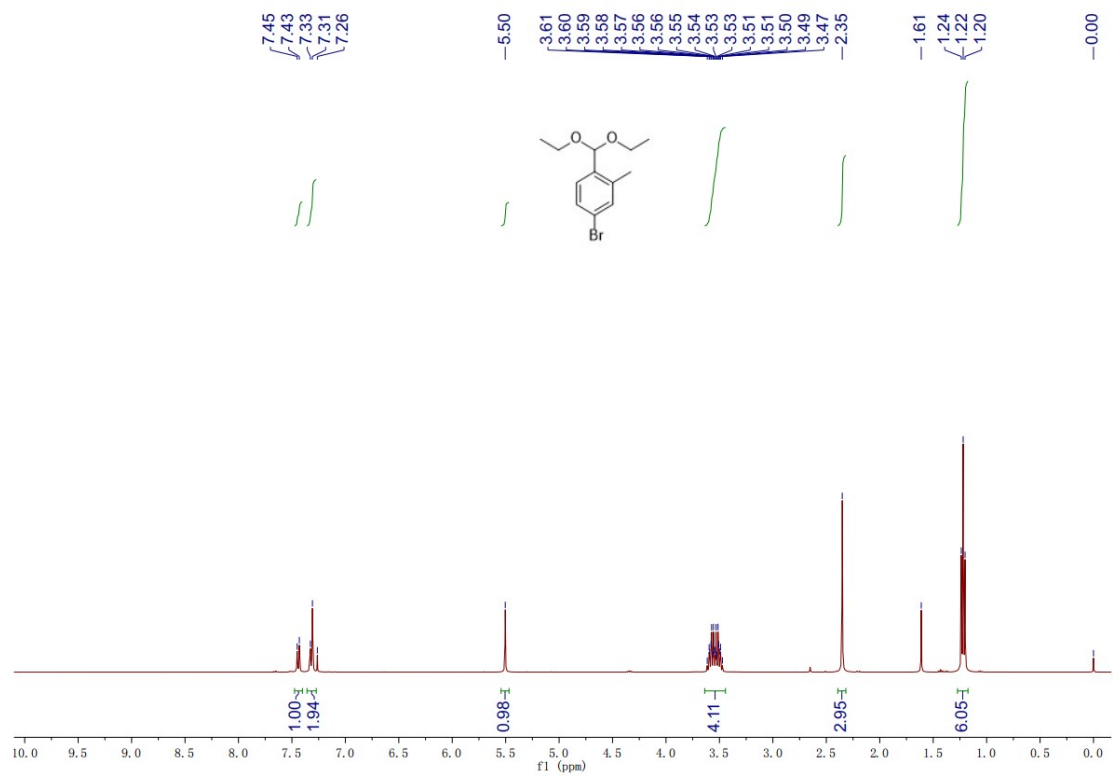
**Synthesis of the final L2-derived SBUs.** The above-prepared fresh Grignard reagent was cooled to -5 °C using an ice-salt bath. Then, PCl<sub>3</sub> (0.916 g, 6.67 mmol) was diluted with 10 mL anhydrous THF, the diluted PCl<sub>3</sub> solution was added to the Grignard reagent via a dropping funnel under an atmosphere of nitrogen, the reaction temperature was kept below 0 °C. After the completion of the addition process, the mixture was heated to 60 °C and stirred for another 2 h. After the reaction, the mixture was cooled to 0 °C using an ice bath, 10 mL of saturated NH<sub>4</sub>Cl solution was added dropwise to quench the reaction mixture, after the addition of saturated NH<sub>4</sub>Cl solution, the mixture was stirred overnight at room temperature. Then the solution was transferred to a separation funnel, after shaking, the solution was separated into two layers, the organic phase was collected. The water phase was extracted with ethyl

acetate (15 mL  $\times$  3), the combined organic phase was further washed with saturated aqueous NaCl solution (100 mL  $\times$  2), dried over anhydrous MgSO<sub>4</sub>, filtered through fluted filter paper in a glass funnel, and concentrated on a rotary evaporator to afford crude product of yellow powder. The crude product was further purified through column chromatography with an eluent of hexane/EtOAc = 4/1 to afford the pure product as a light yellow powder (1.5 g, 58% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.64 (s, 9 H), 7.22-7.25 (q, 6 H,  $J$  = 4.0 Hz), 7.78 (d, 3 H,  $J$  = 8.0 Hz), 10.29 (s, 3 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  19.6, 131.6, 134.6, 135.4, 136.9, 140.6, 142.4, 192.2. <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  -4.35. HRMS  $m/z$  (ESI) calcd for C<sub>24</sub>H<sub>22</sub>O<sub>3</sub>P [M+H]<sup>+</sup> 389.1307, found 389.1306. Note: the two peaks at 131.28 and 131.84 ppm are both split from the same carbon.

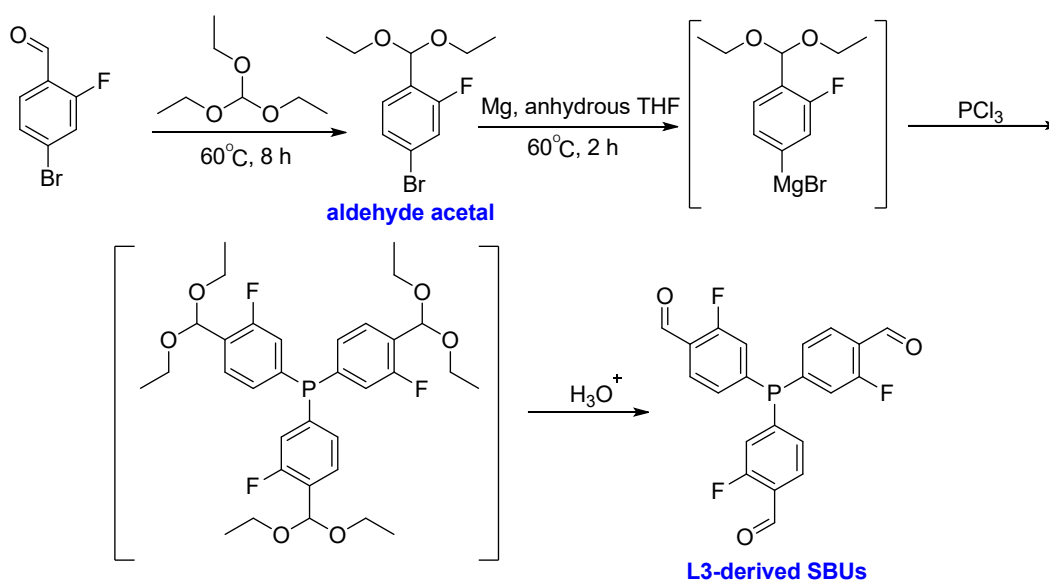
### <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR spectra of synthetic intermediates







#### 4. Synthesis of L3-derived SBUs



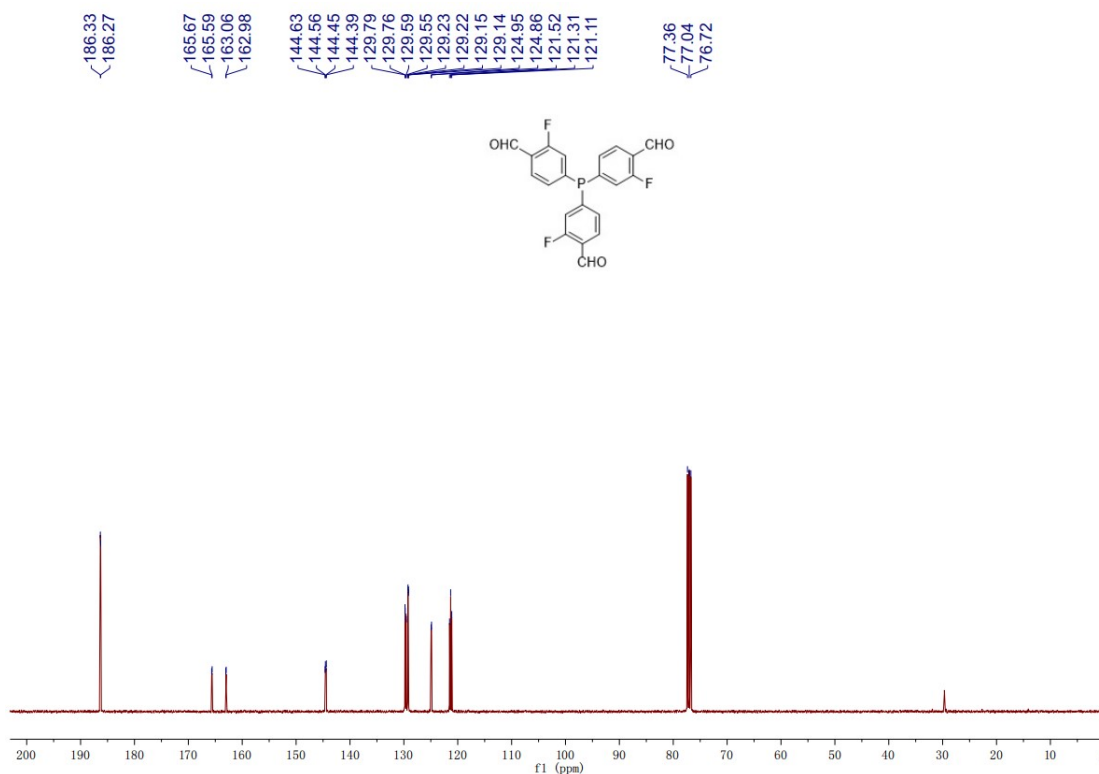
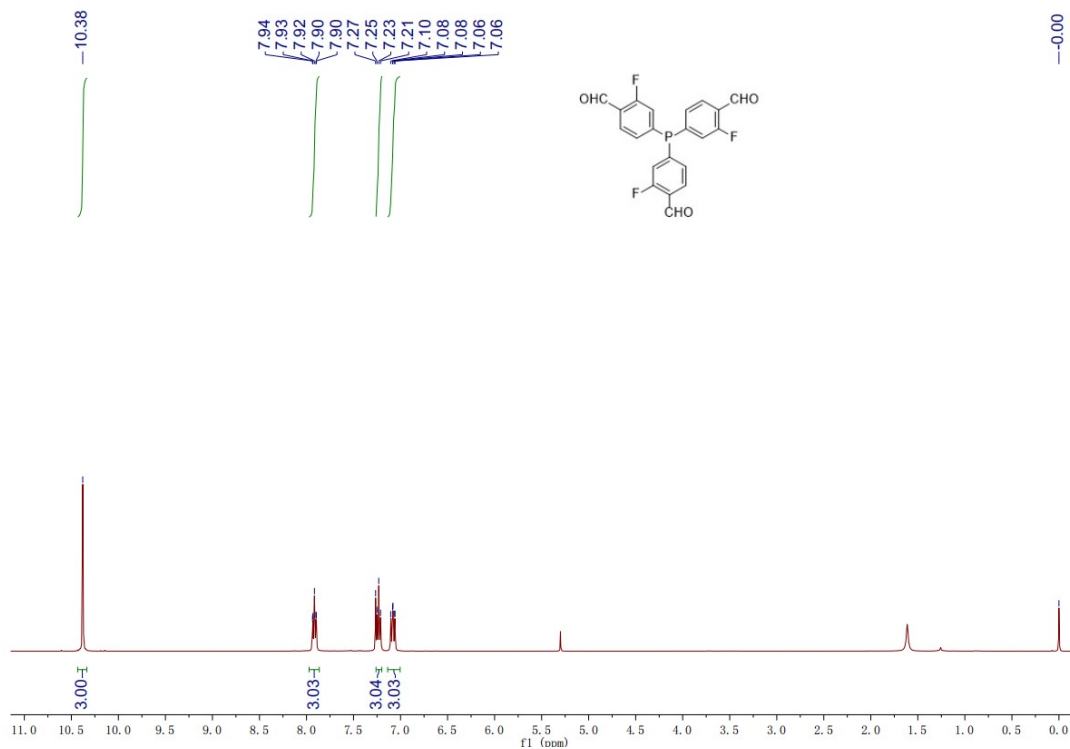
**Synthesis of aldehyde acetal.** 4-bromo-2-fluorobenzaldehyde (5.08 g, 25 mmol) and triethyl orthoformate (4.89 g, 33 mmol) were dissolved in 50 mL of anhydrous ethanol, and then a drop of concentrated sulphuric acid was added as a catalyst. The mixture was magnetically stirred and refluxed for 8 h. After the completion of the reaction, the mixture was cooled to room temperature and 30 mL of NaHCO<sub>3</sub> solution (0.5 M) was added, then the mixture was transferred to the separation funnel. The aqueous phase was extracted with ethyl acetate (3 × 100 mL), the combined organic extract was washed with saturated brine (3 × 100 mL), dried over anhydrous magnesium sulfate (MgSO<sub>4</sub>, 50 g) and concentrated to afford aldehyde acetal product as a yellow oil (6.65 g, 96% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.23 (t, 6 H, *J* = 8.0 Hz), 3.51-3.59 (m, 2 H), 3.61-3.69 (m, 2 H), 5.66 (s, 1 H), 7.22 (d, 1 H, *J* = 8.0 Hz), 7.29 (d, 1 H, *J* = 8.0 Hz), 7.48 (t, 1 H, *J* = 8.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 15.1, 61.9, 96.2, 118.8, 122.4, 125.8, 127.1, 129.3, 160.1. Note: the two peaks at 115.50 and 115.69 ppm are both split from the same carbon; The four peaks at 159.85, 159.91, 161.55 and 161.61 ppm are all split from the same carbon (C-F).

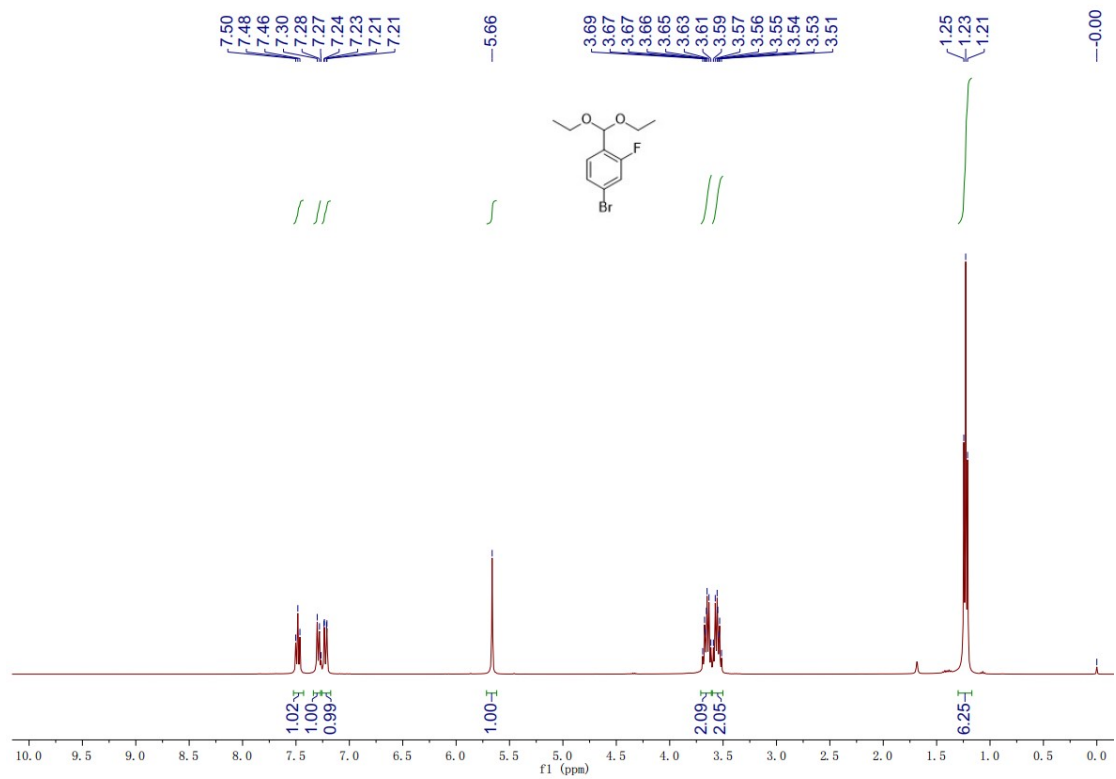
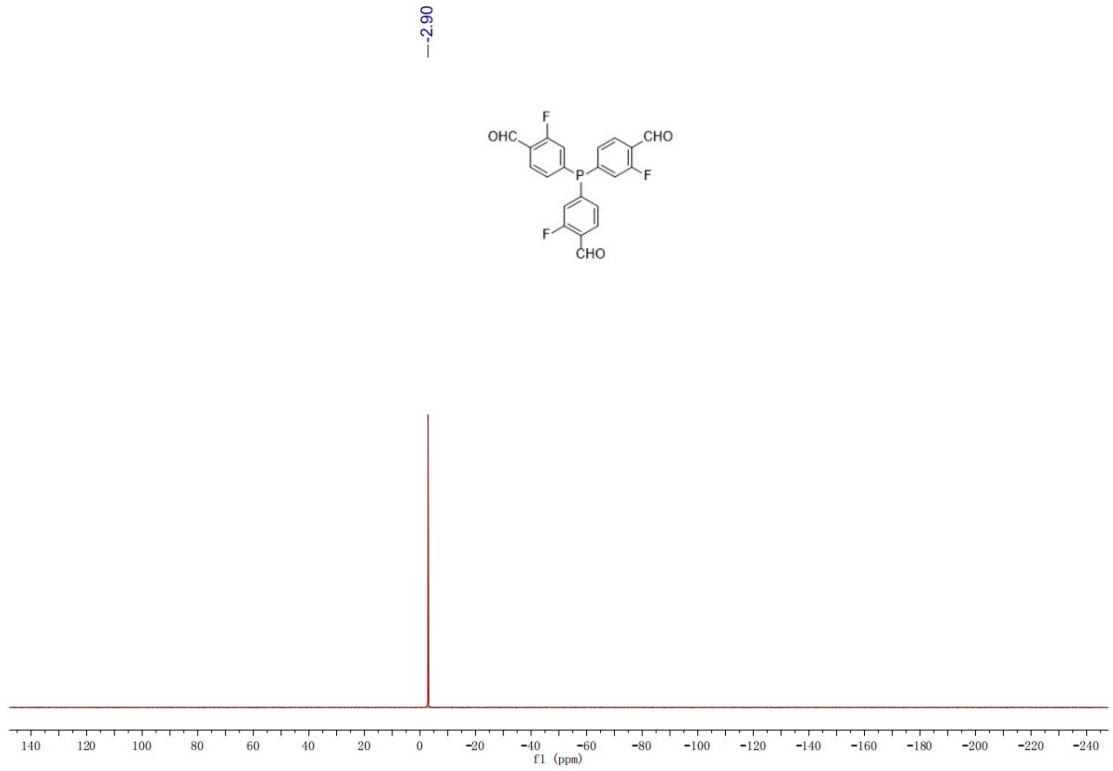
**Synthesis of Grignard reagent.** An oven-dried 100 mL three-necked, round-bottomed flask was loaded with magnesium powder (0.58 g, 24 mmol) and a crystal of iodine. Anhydrous THF (20 mL) was charged into this flask under an atmosphere of nitrogen. The synthesized aldehyde acetal product (5.54 g, 20 mmol) was dissolved

in 30 mL of anhydrous THF, 10 mL of this solvent was directly charged to the Schlenk flask under an atmosphere of nitrogen. The flask was connected with a condenser-west tube and the mixture was magnetically stirred and heated to 60 °C, the Grignard reaction could be easily initiated. Then, this flask was equipped with a 50 mL dropping funnel filled with the before mentioned aldehyde acetal in THF solution (the remaining 20 mL), the solution was added dropwise within 10-15 min under an atmosphere of nitrogen. After the completion of the addition, the mixture was further refluxed for 2 h to afford the fresh Grignard reagent.

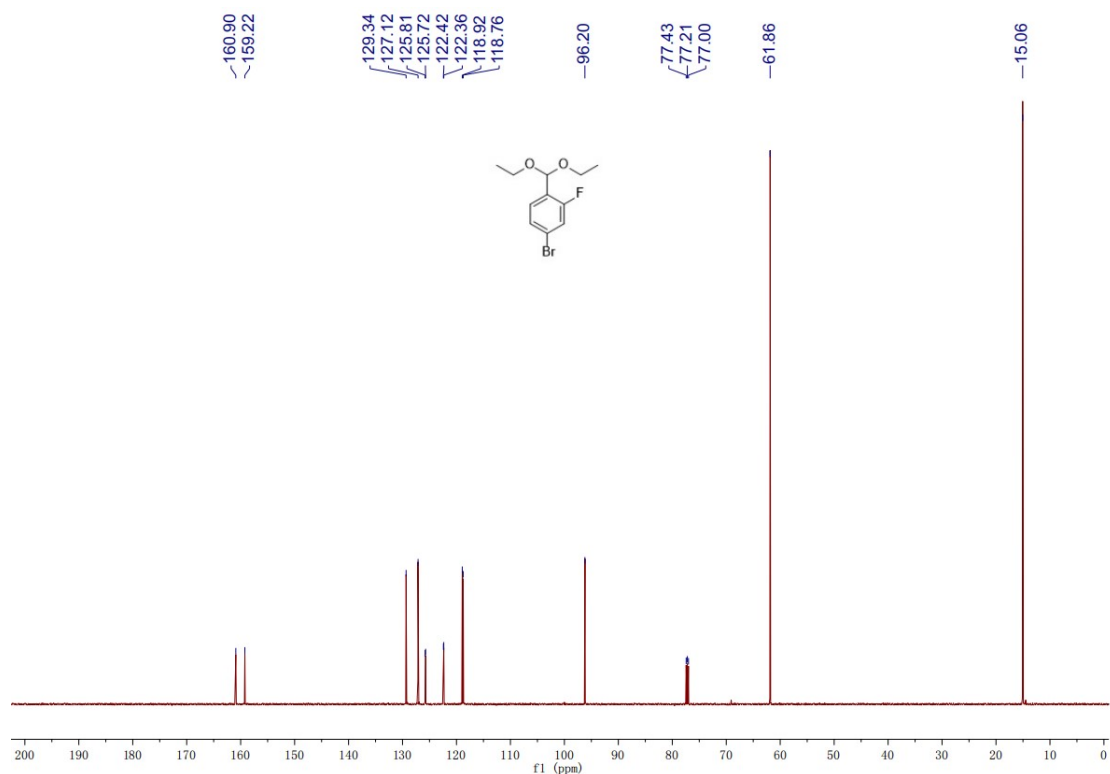
**Synthesis of the final L3-derived SBUs.** The above-prepared fresh Grignard reagent was cooled to -5 °C using an ice-salt bath. Then, PCl<sub>3</sub> (0.916 g, 6.67 mmol) was diluted with 10 mL anhydrous THF, the diluted PCl<sub>3</sub> solution was added to the Grignard reagent via a dropping funnel under an atmosphere of nitrogen, the reaction temperature was kept below 0 °C. After the completion of the addition process, the mixture was heated to 60 °C and stirred for another 2 h. After the reaction, the mixture was cooled to 0 °C using an ice bath, 10 mL of saturated NH<sub>4</sub>Cl solution was added dropwise to quench the reaction mixture, after the addition of saturated NH<sub>4</sub>Cl solution, the mixture was stirred overnight at room temperature. Then the solution was transferred to a separation funnel, after shaking, the solution was separated into two layers, the organic phase was collected. The water phase was extracted with ethyl acetate (15 mL × 3), the combined organic phase was further washed with saturated aqueous NaCl solution (100 mL × 2), dried over anhydrous MgSO<sub>4</sub>, filtered through fluted filter paper in a glass funnel, and concentrated on a rotary evaporator to afford crude product of yellow powder. The crude product was further purified through column chromatography with an eluent of hexane/EtOAc = 4/1 to afford the pure product as a light yellow powder (1.36 g, 51% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.08 (t, 3 H, *J* = 8.0 Hz), 7.21-7.27 (m, 3 H, *J* = 8.0 Hz), 7.92 (t, 3 H, *J* = 8.0 Hz), 10.38 (s, 3 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 121.3, 124.9, 129.6, 144.5, 163.0, 165.6, 186.3. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -2.90. HRMS *m/z* (ESI) calcd for C<sub>21</sub>H<sub>13</sub>F<sub>3</sub>O<sub>3</sub>P [M+H]<sup>+</sup> 401.0554, found 401.0524.

# $^1\text{H}$ , $^{13}\text{C}$ , $^{31}\text{P}$ NMR spectra of synthetic intermediates

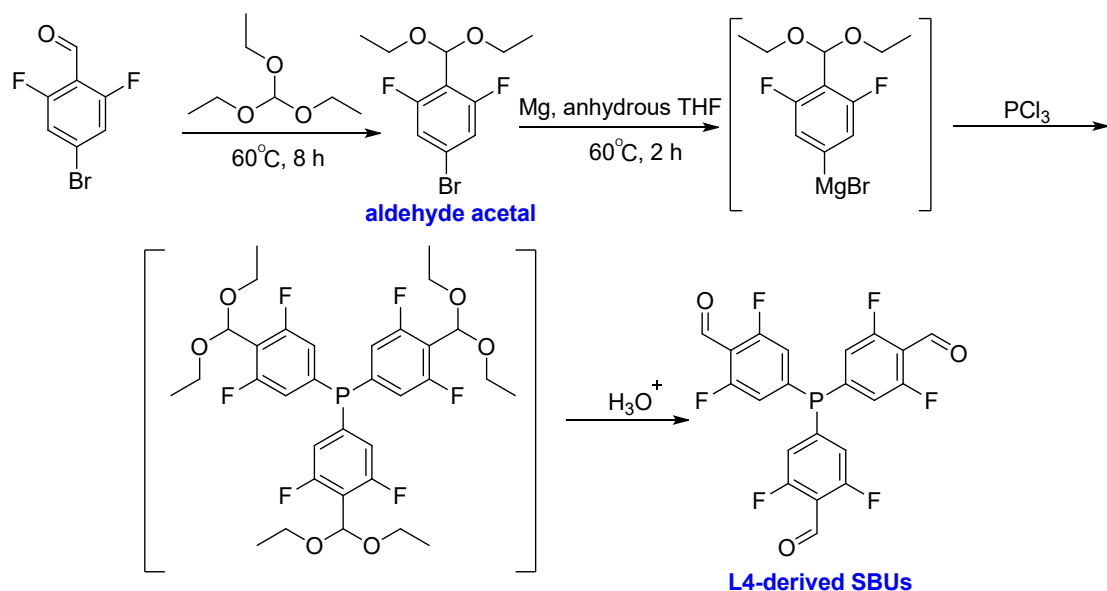








## 5. Synthesis of L4-derived SBUs



**Synthesis of aldehyde acetal.** 4-bromo-2,6-difluorobenzaldehyde (5.53 g, 25 mmol) and triethyl orthoformate (4.89 g, 33 mmol) were dissolved in 50 mL of anhydrous ethanol, and then a drop of concentrated sulphuric acid was added as a catalyst. The mixture was magnetically stirred and refluxed for 8 h. After the completion of the reaction, the mixture was cooled to room temperature and 30 mL of NaHCO<sub>3</sub> solution

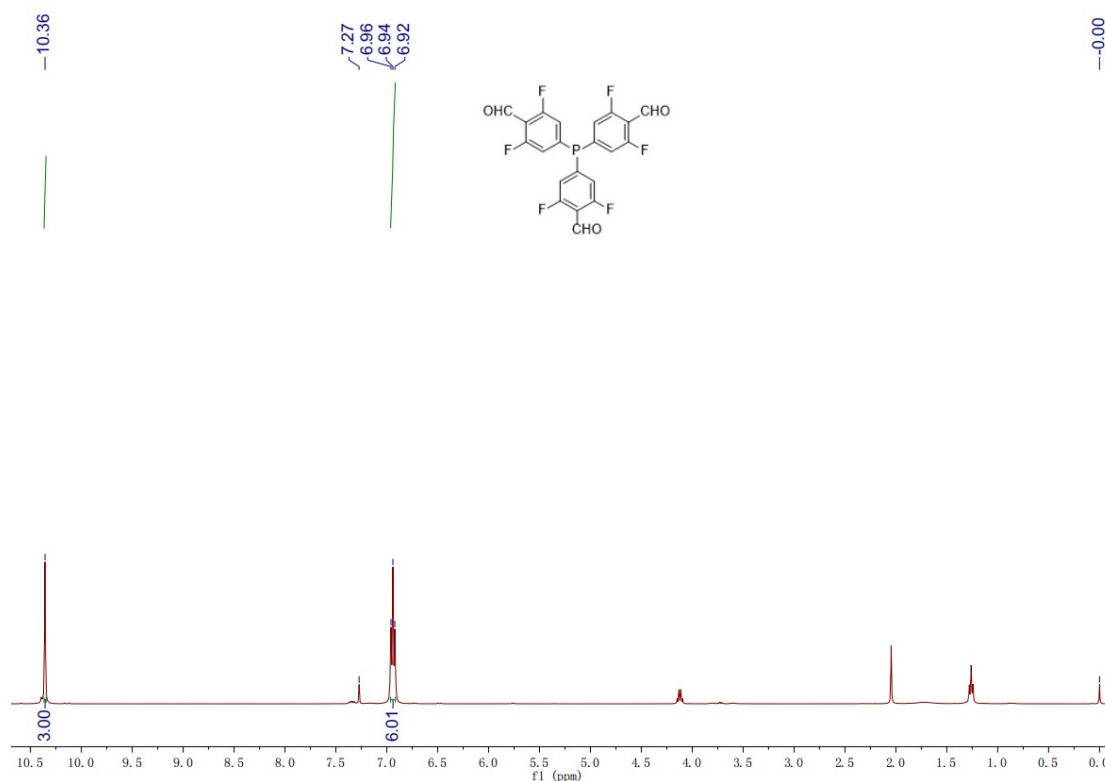
(0.5 M) was added, then the mixture was transferred to the separation funnel. The aqueous phase was extracted with ethyl acetate (3 × 100 mL), the combined organic extract was washed with saturated brine (3 × 100 mL), dried over anhydrous magnesium sulfate (MgSO<sub>4</sub>, 50 g) and concentrated to afford aldehyde acetal product as a yellow oil (7.01 g, 95% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.26 (t, 6 H, *J* = 8.0 Hz, 4.0 Hz), 3.56-3.63 (m, 2 H), 3.75-3.83 (m, 2 H), 5.7 (s, 1 H), 6.82 (t, 2 H, *J* = 8.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.9, 63.2, 96.5, 115.0, 115.5, 115.7, 122.0, 159.9, 161.6.

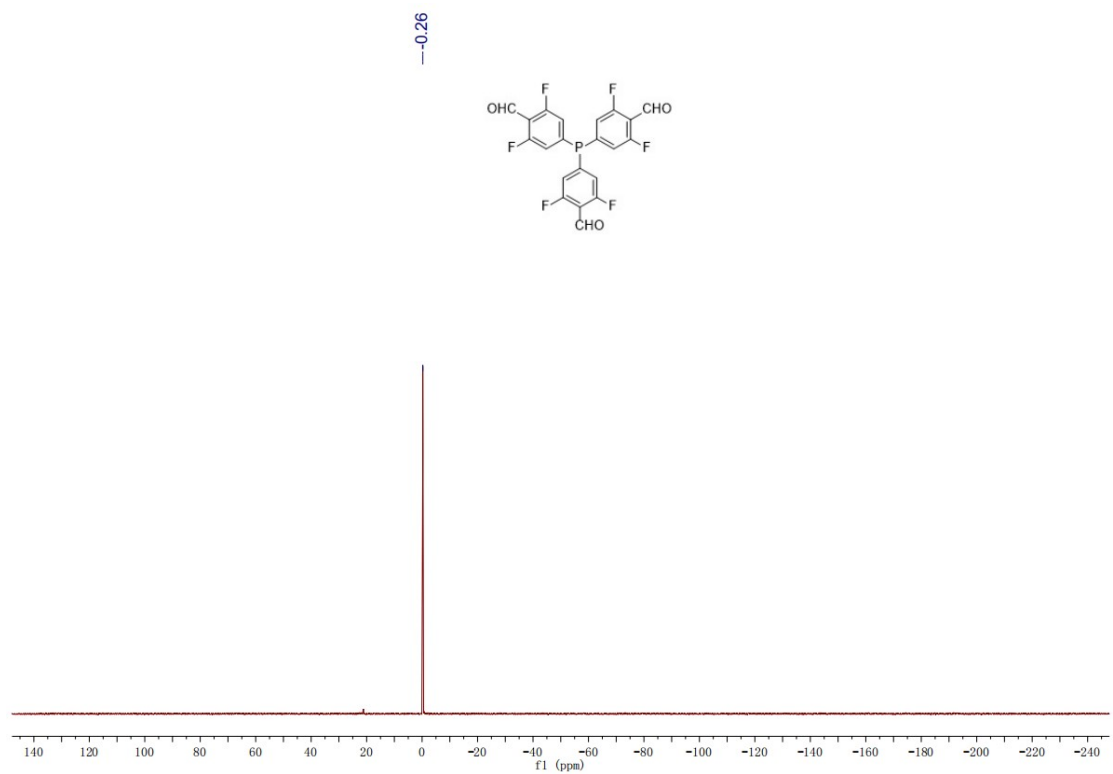
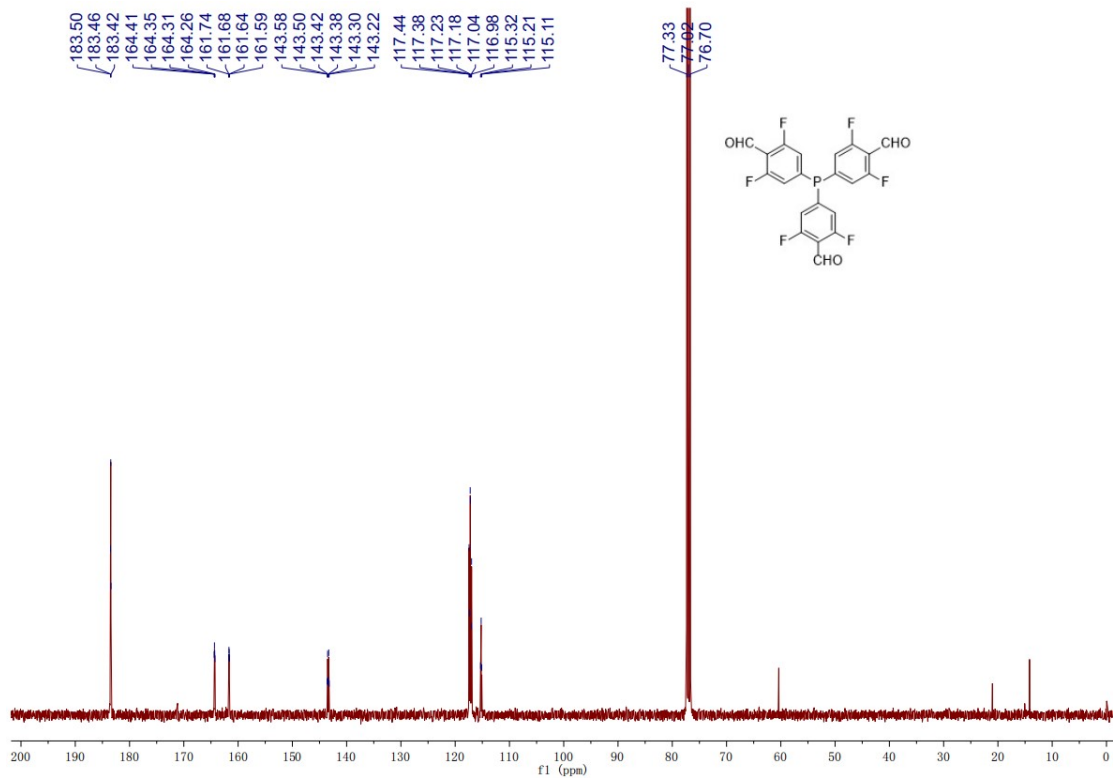
**Synthesis of Grignard reagent.** An oven-dried 100 mL three-necked, round-bottomed flask was loaded with magnesium powder (0.58 g, 24 mmol) and a crystal of iodine. Anhydrous THF (20 mL) was charged into this flask under an atmosphere of nitrogen. The synthesized aldehyde acetal product (5.90 g, 20 mmol) was dissolved in 30 mL of anhydrous THF, 10 mL of this solvent was directly charged to the Schlenk flask under an atmosphere of nitrogen. The flask was connected with a condenser-west tube and the mixture was magnetically stirred and heated to 60 °C, the Grignard reaction could be easily initiated. Then, this flask was equipped with a 50 mL dropping funnel filled with the before mentioned aldehyde acetal in THF solution (the remaining 20 mL), the solution was added dropwise within 10-15 min under an atmosphere of nitrogen. After the completion of the addition, the mixture was further refluxed for 2 h to afford the fresh Grignard reagent.

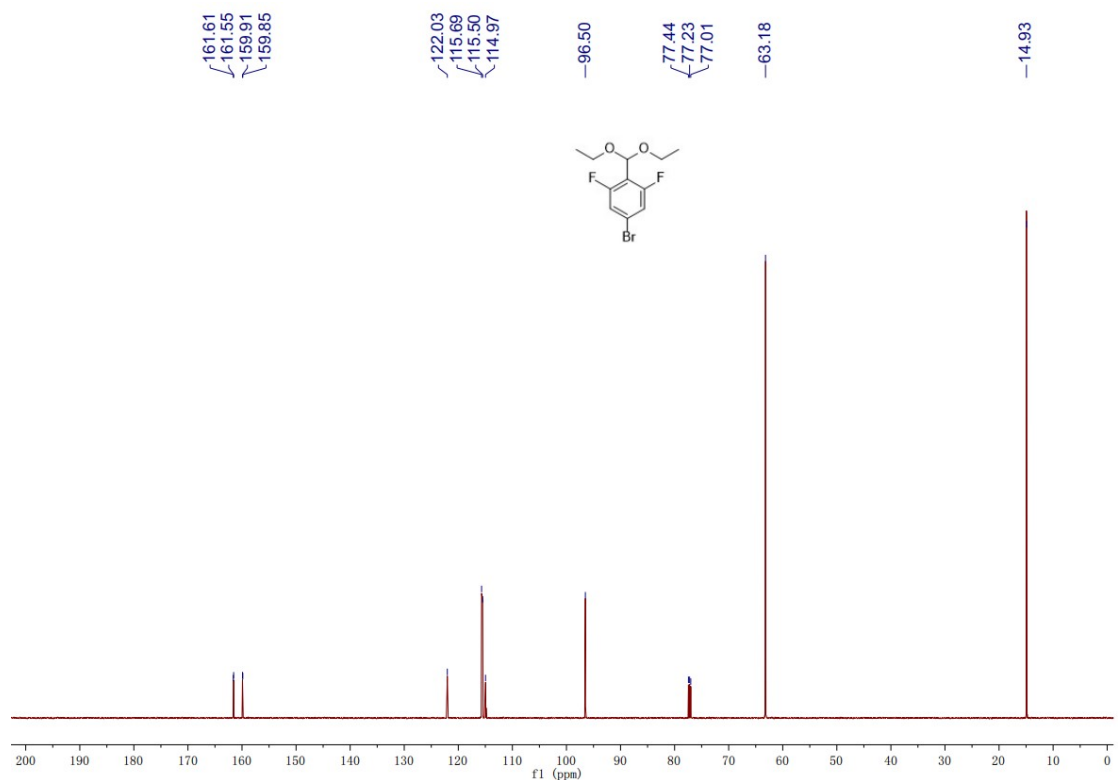
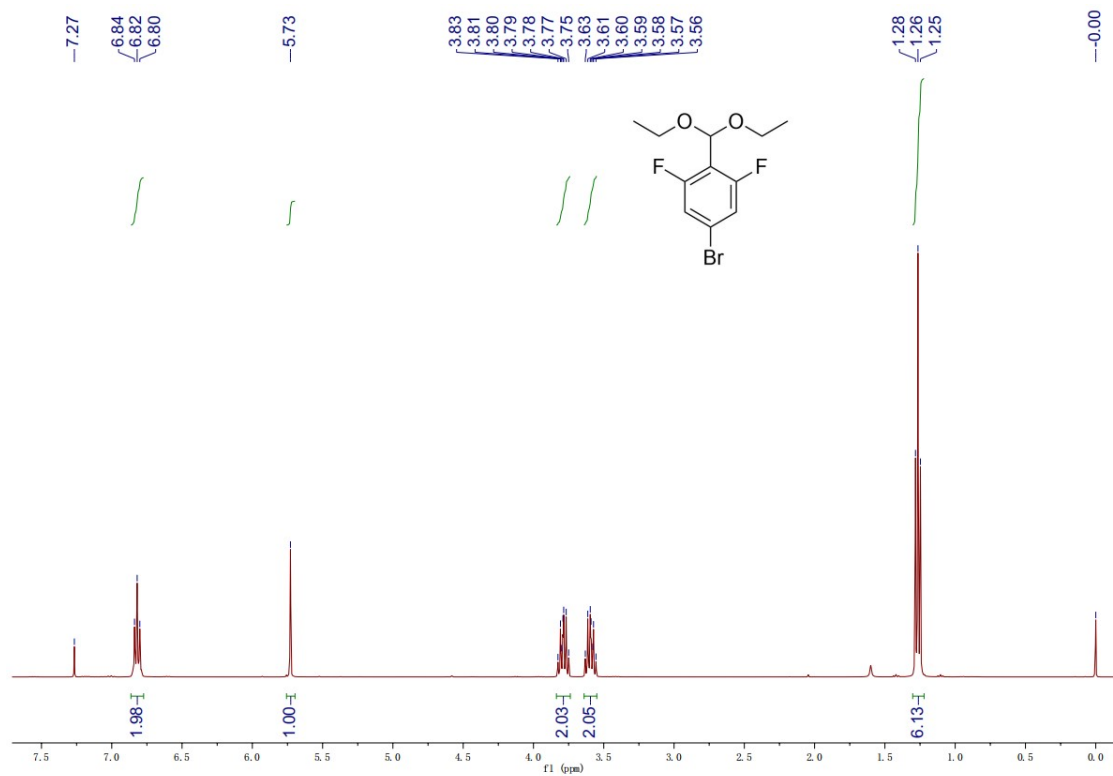
**Synthesis of the final L4-derived SBUs.** The above-prepared fresh Grignard reagent was cooled to -5 °C using an ice-salt bath. Then, PCl<sub>3</sub> (0.916 g, 6.67 mmol) was diluted with 10 mL anhydrous THF, the diluted PCl<sub>3</sub> solution was added to the Grignard reagent via a dropping funnel under an atmosphere of nitrogen, the reaction temperature was kept below 0 °C. After the completion of the addition process, the mixture was heated to 60 °C and stirred for another 2 h. After the reaction, the mixture was cooled to 0 °C using an ice bath, 10 mL of saturated NH<sub>4</sub>Cl solution was added dropwise to quench the reaction mixture, after the addition of saturated NH<sub>4</sub>Cl solution, the mixture was stirred overnight at room temperature. Then the solution was transferred to a separation funnel, after shaking, the solution was separated into two layers, the organic phase was collected. The water phase was extracted with ethyl

acetate (15 mL × 3), the combined organic phase was further washed with saturated aqueous NaCl solution (100 mL × 2), dried over anhydrous MgSO<sub>4</sub>, filtered through fluted filter paper in a glass funnel, and concentrated on a rotary evaporator to afford crude product of yellow powder. The crude product was further purified through column chromatography with an eluent of hexane/EtOAc = 3/1 to afford the pure product as a light yellow powder (1.61 g, 53% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 6.94 (t, 6 H, *J* = 8.0 Hz), 10.36 (s, 3 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 115.2, 117.2, 143.4, 163.0, 183.5. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -0.26. HRMS *m/z* (ESI) calcd for C<sub>21</sub>H<sub>10</sub>F<sub>6</sub>O<sub>3</sub>P [M+H]<sup>+</sup> 455.0272, found 455.0242. Note: due to the presence of F atoms, the splitting of C appears unusually active, and the eight peaks ranging from 161.59 to 164.41 ppm are all split from the same carbon.

### <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR spectra of synthetic intermediates

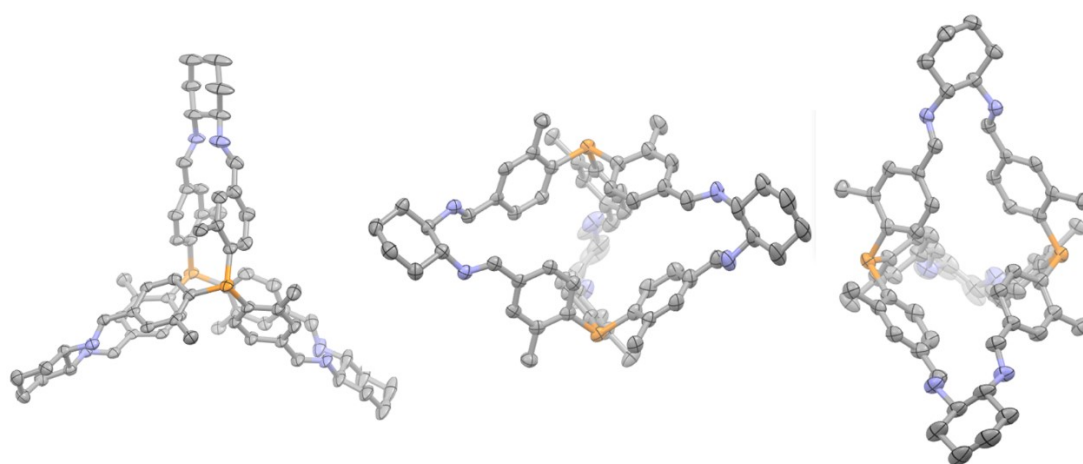






## 6. X-ray single crystallography

The single crystals of compound cage-L1, cage-L3 and cage-L4 were obtained by the slow diffusion methanol to the CH<sub>2</sub>Cl<sub>2</sub> solution of the cage molecule. The detail structures information was uploaded to The Cambridge Crystallographic Data Centre (CCDC) and the data can be obtained free of charge via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

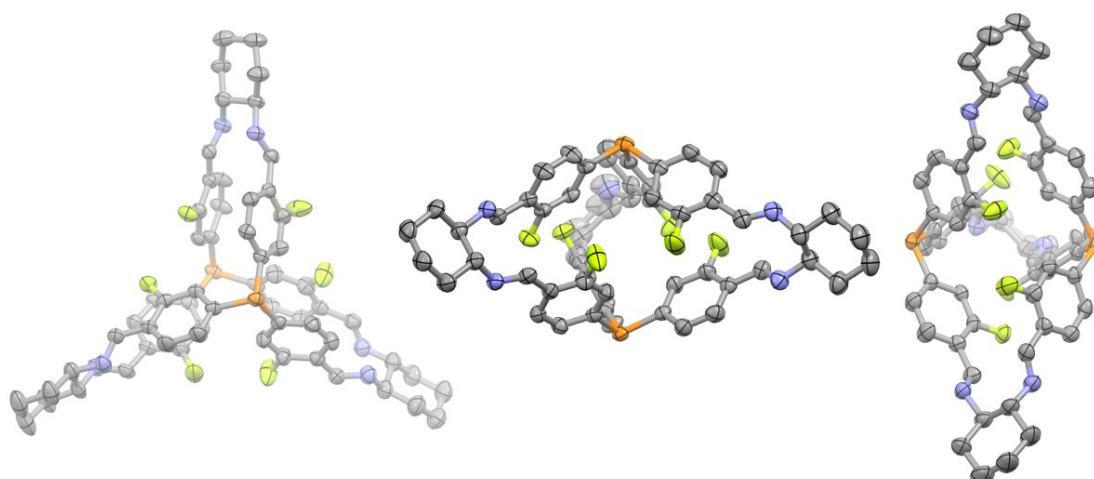


**Figure S1. ORTEP drawing of cage-L1 with 50% probability thermal ellipsoids. (CCDC number: 2070376)**

**Table S1. Crystal data for cage-L1**

Identification code	Cage-L1
Empirical formula	C <sub>66</sub> H <sub>72</sub> N <sub>6</sub> P <sub>2</sub>
Formula weight	1011.23
Temperature/K	100.00(10)
Crystal system	tetragonal
Space group	P4 <sub>1</sub> 22
a/Å	17.1786(5)
b/Å	17.1786(5)
c/Å	24.7552(6)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	7305.3(4)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	0.919
μ/mm <sup>-1</sup>	0.809

F(000)	2160.0
Crystal size/mm <sup>3</sup>	0.13 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	5.144 to 147.518
Index ranges	-20 ≤ h ≤ 17, -20 ≤ k ≤ 15, -30 ≤ l ≤ 25
Reflections collected	25027
Independent reflections	7230 [R <sub>int</sub> = 0.0796, R <sub>sigma</sub> = 0.0620]
Data/restraints/parameters	7230/0/337
Goodness-of-fit on F <sup>2</sup>	1.071
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0679, wR <sub>2</sub> = 0.1824
Final R indexes [all data]	R <sub>1</sub> = 0.0785, wR <sub>2</sub> = 0.1946
Largest diff. peak/hole/eÅ <sup>-3</sup>	0.33/-0.41
Flack parameter	0.00(2)

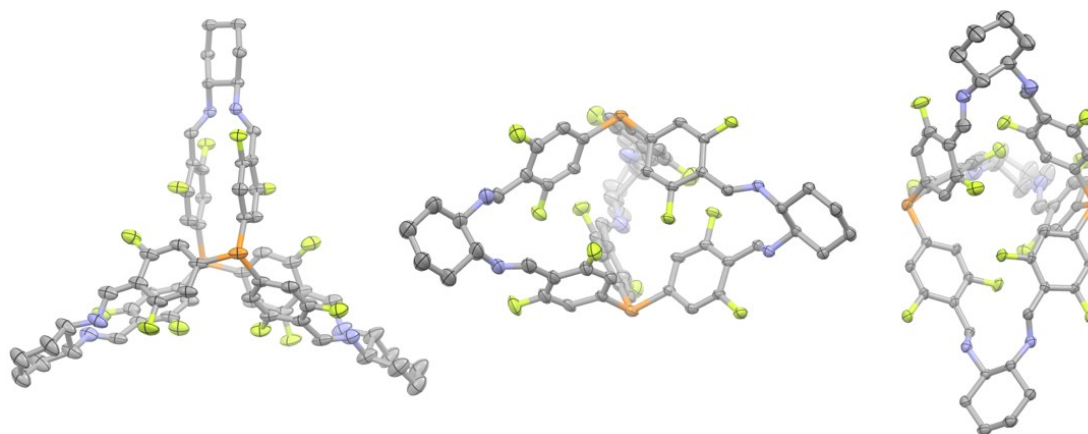


**Figure S2. ORTEP drawing of cage-L3 with 50% probability thermal ellipsoids. (CCDC number: 2070380).**

**Table S2. Crystal data for cage-L3**

Identification code	Cage-L3
Empirical formula	$C_{61.33}H_{55.33}Cl_4F_6N_6P_2$
Formula weight	1194.19
Temperature/K	229.97
Crystal system	triclinic
Space group	P1
a/Å	15.478(6)
b/Å	17.328(8)
c/Å	20.278(9)
$\alpha/^\circ$	76.67(3)
$\beta/^\circ$	85.24(2)
$\gamma/^\circ$	64.164(15)
Volume/Å <sup>3</sup>	4762(4)
Z	3
$\rho_{\text{calc}}/\text{cm}^3$	1.249
$\mu/\text{mm}^{-1}$	0.296
F(000)	1852.0
Crystal size/mm <sup>3</sup>	0.11 × 0.12 × 0.14
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\theta$ range for data collection/ $^\circ$	4.406 to 54.998
Index ranges	$-19 \leq h \leq 20, -22 \leq k \leq 22, -26 \leq l \leq 26$
Reflections collected	104371
Independent reflections	41971 [ $R_{\text{int}} = 0.0372, R_{\text{sigma}} = 0.0514$ ]
Data/restraints/parameters	41971/18/2143
Goodness-of-fit on F <sup>2</sup>	1.016
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0691, wR_2 = 0.1855$
Final R indexes [all data]	$R_1 = 0.0998, wR_2 = 0.2152$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.70/-0.68
Flack parameter	0.058(14)





**Figure S3. ORTEP drawing of cage-L4 with 15% probability thermal ellipsoids. (CCDC number: 2070417).**

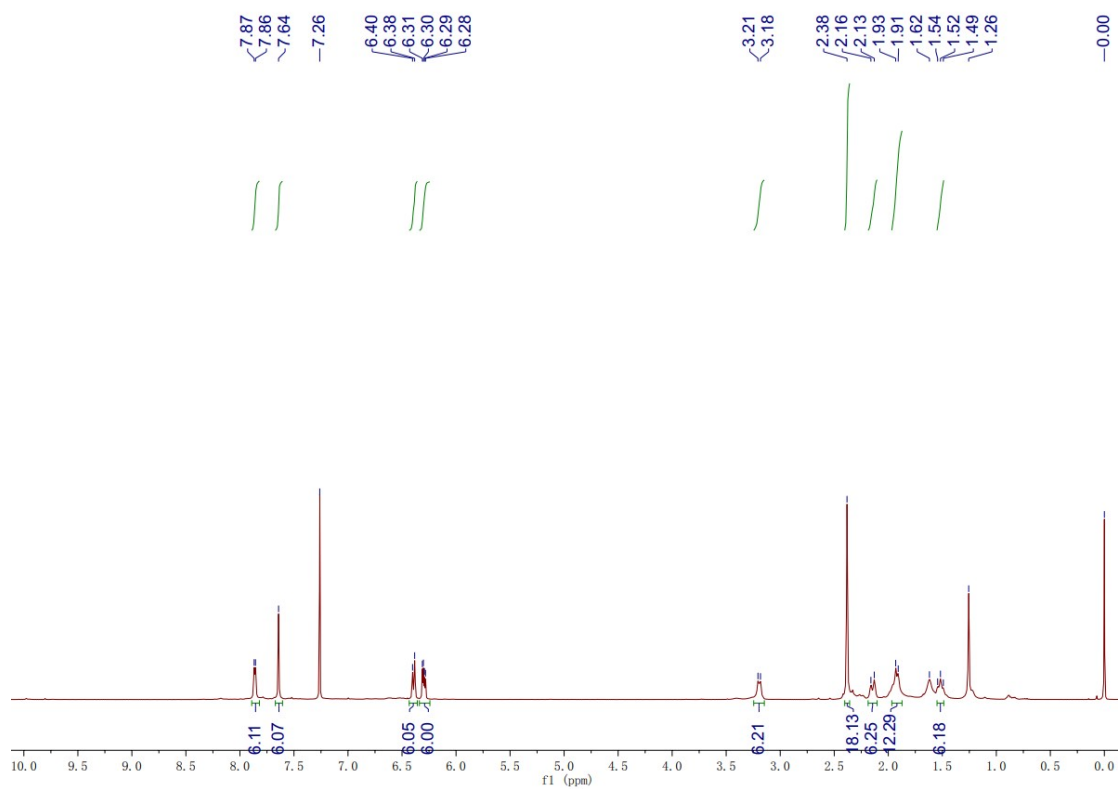
**Table S3. Crystal data for cage-L4**

Identification code	Cage-L4
Empirical formula	$C_{61}H_{42}Cl_2F_{12}N_6P_2$
Formula weight	1219.84
Temperature/K	250.01
Crystal system	hexagonal
Space group	$P6_322$
a/Å	23.8636(12)
b/Å	23.8636(12)
c/Å	22.2433(10)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	120
Volume/Å <sup>3</sup>	10969.9(12)
Z	6
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.108
$\mu/\text{mm}^{-1}$	0.199
F(000)	3732.0
Crystal size/mm <sup>3</sup>	0.12 × 0.1 × 0.08
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/ $^\circ$	4.346 to 55.144
Index ranges	-31 ≤ h ≤ 20, -13 ≤ k ≤ 31, -28 ≤ l ≤ 18
Reflections collected	37707

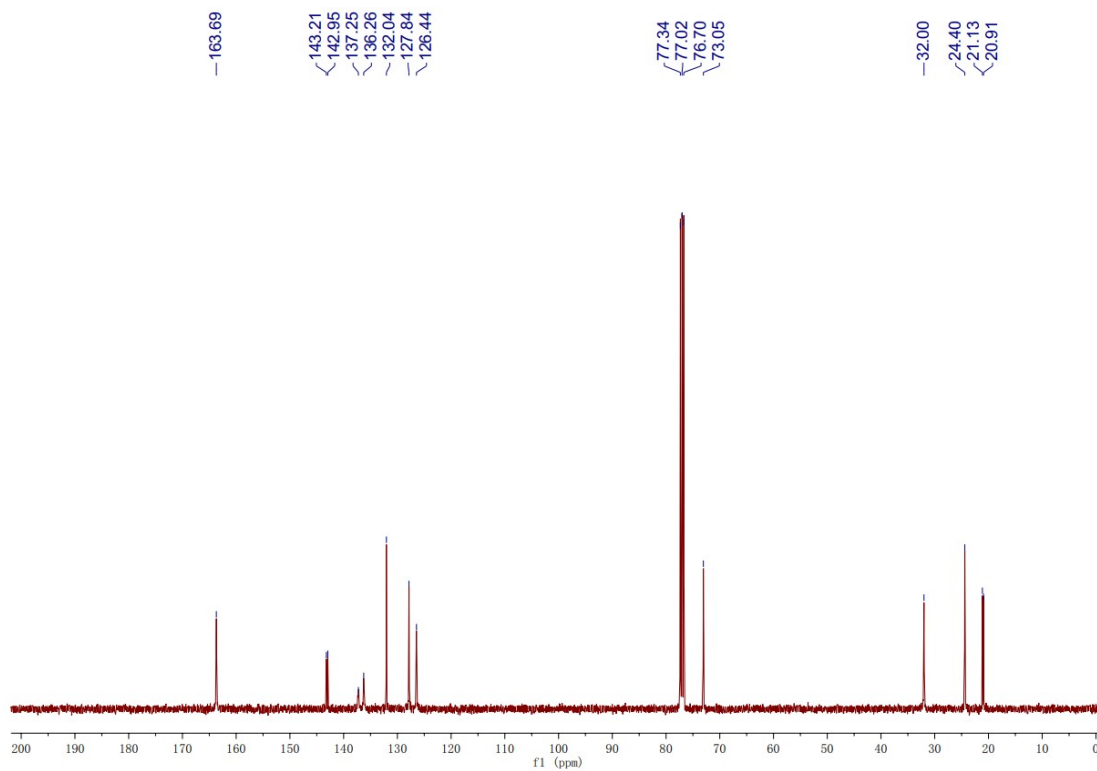
Independent reflections	8447 [ $R_{\text{int}} = 0.0529$ , $R_{\text{sigma}} = 0.0574$ ]
Data/restraints/parameters	8447/109/363
Goodness-of-fit on $F^2$	0.985
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0596$ , $wR_2 = 0.1689$
Final R indexes [all data]	$R_1 = 0.1406$ , $wR_2 = 0.2096$
Largest diff. peak/hole/ $e \text{ \AA}^{-3}$	0.17/-0.18
Flack/Hooft parameter	0.02(3)/0.08(3)

## 7. NMR and ESI-HRMS characterizations of cage-L1

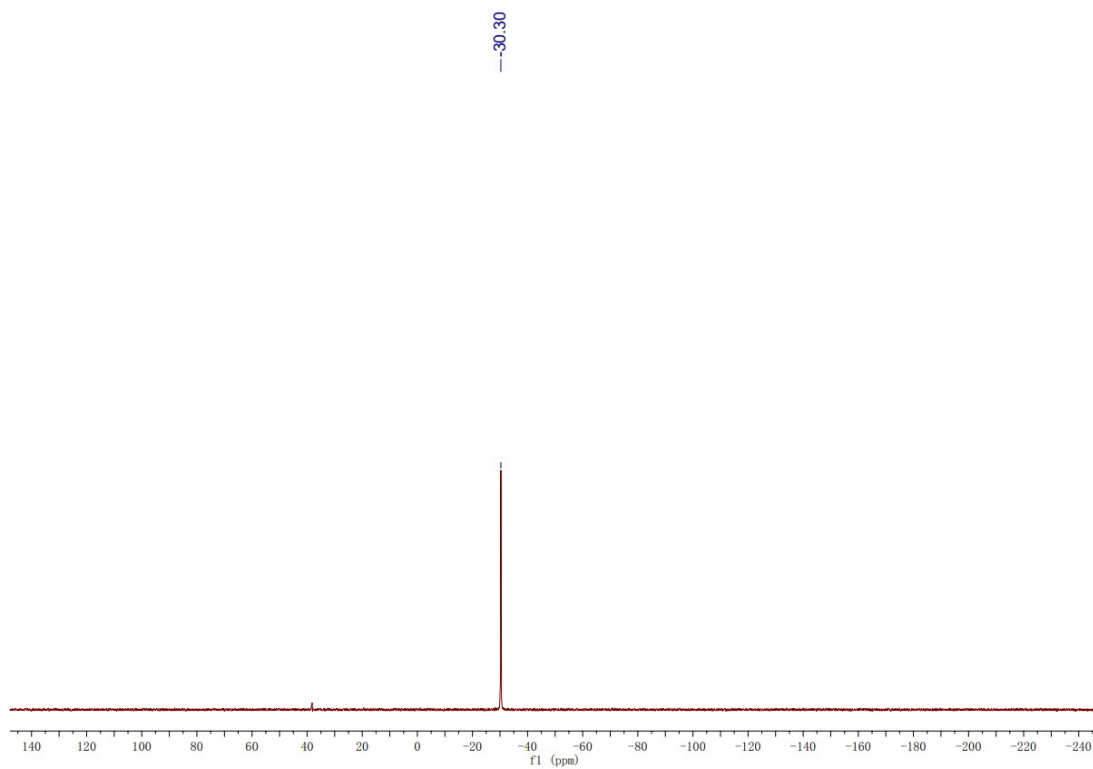
### $^1\text{H}$ NMR for cage-L1



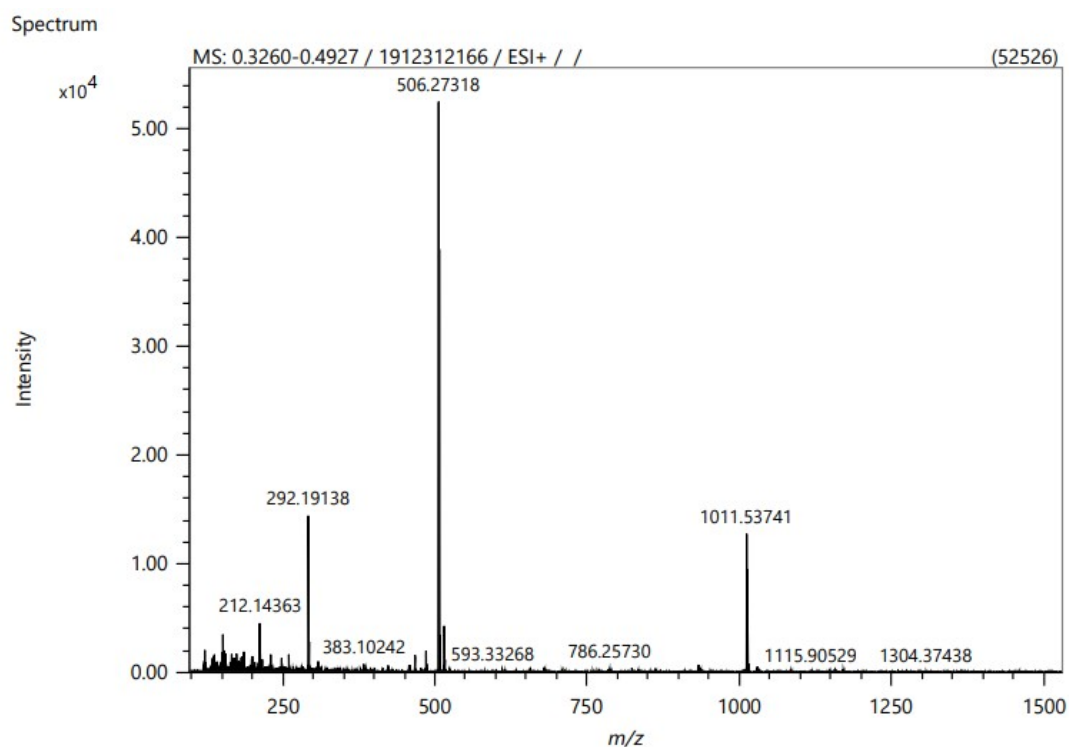
### $^{13}\text{C}$ NMR for cage-L1



### <sup>31</sup>P NMR for cage-L1



### ESI-HRMS spectrum for cage-L1



#### Elemental Composition

##### Parameters

Tolerance:  $\pm 5.00$  ppm  
 Electron: Odd/Even  
 Charge: +1  
 DBE: -1.5 - 200.0

##### Elements Set 1:

Symbol	C	H	N	O	Na	S	Cl	Br
Min	0	0	0	0	0	0	0	0
Max	120	120	6	0	0	0	0	0

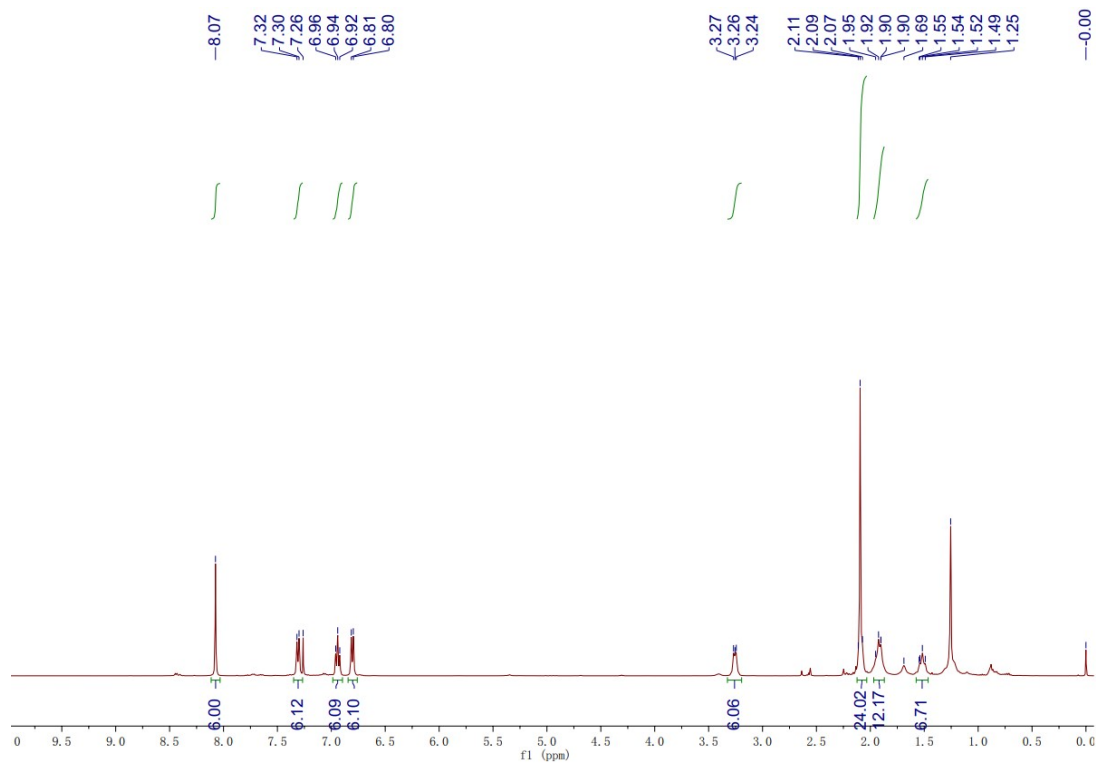
Symbol	F	Si	P	Ir
Min	0	0	2	0
Max	0	0	2	0

#### Results

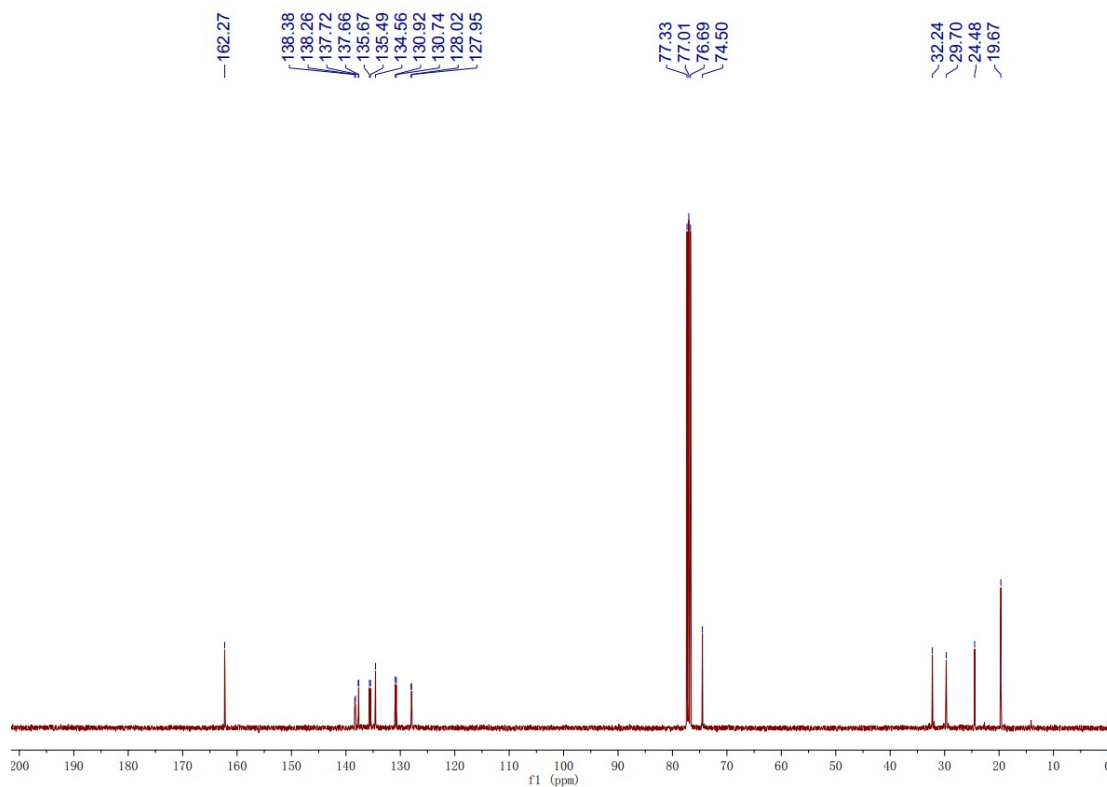
Mass	Intensity	Intensity [%]	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
1011.53741	12749.21	24.27	C66 H73 N6 P2	1011.53665	0.76	0.76	34.5

## 8. NMR and ESI-HRMS characterizations of cage-L2

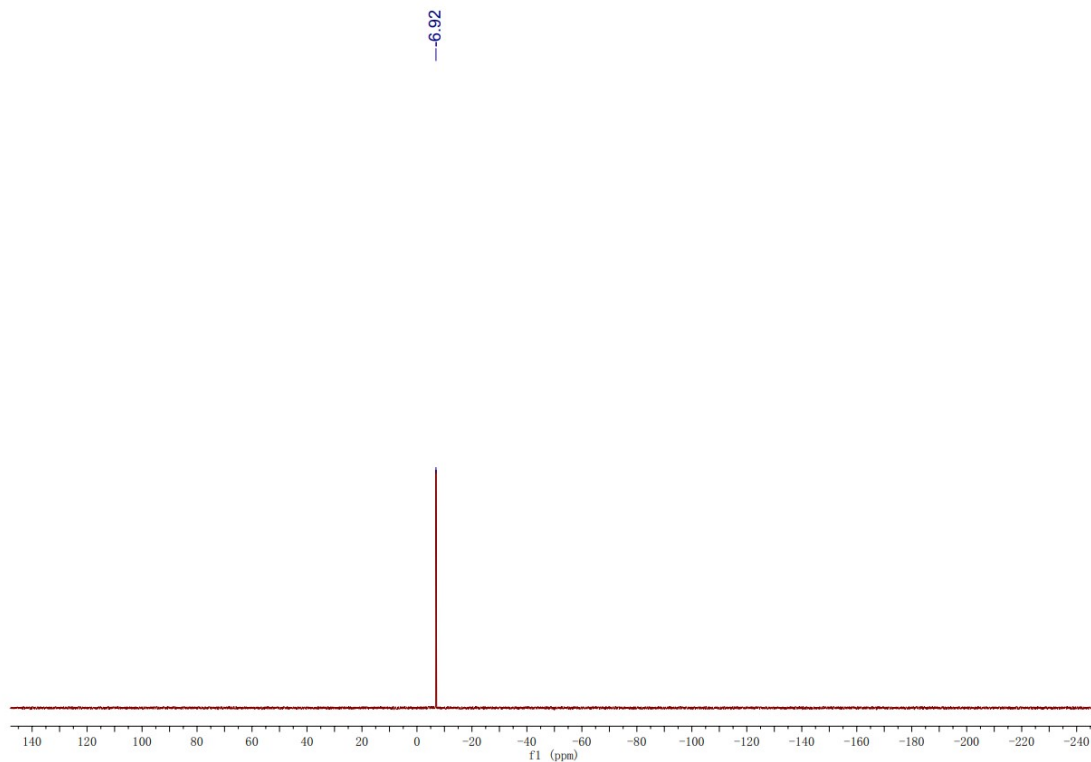
### <sup>1</sup>H NMR for cage-L2



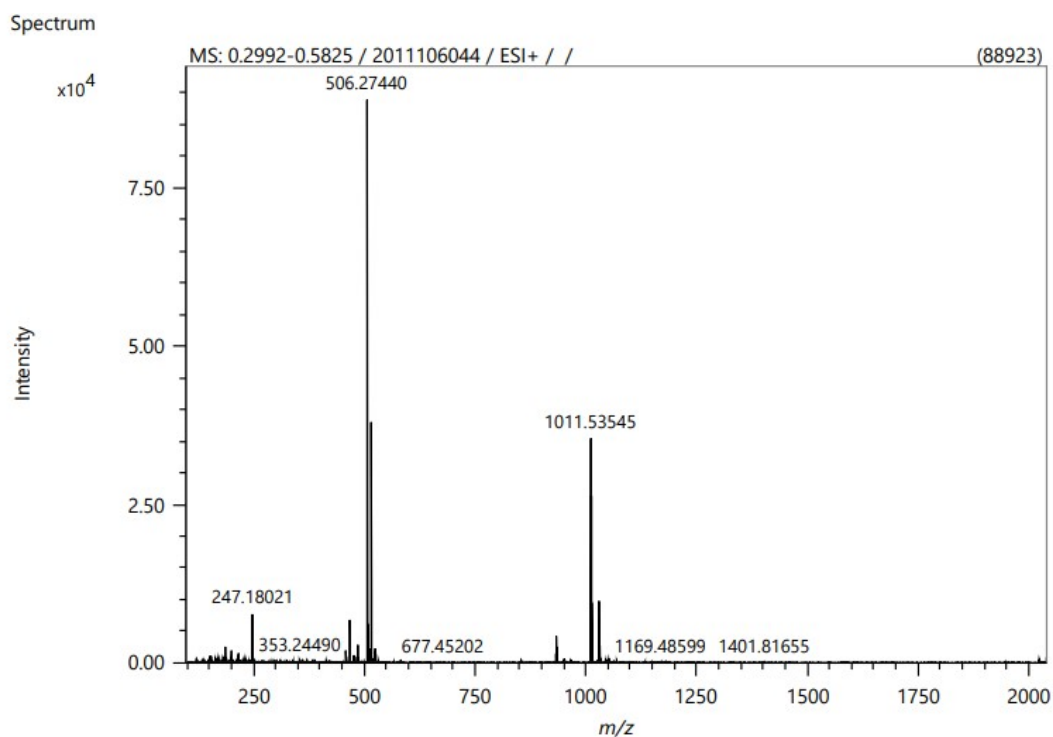
### <sup>13</sup>C NMR for cage-L2



### <sup>31</sup>P NMR for cage-L2



**ESI-HRMS spectrum for cage-L2**



#### Elemental Composition

##### Parameters

Tolerance:  $\pm 5.00$  ppm  
 Electron: Odd/Even  
 Charge: +1  
 DBE: -1.5 - 200.0

##### Elements Set 1:

Symbol	C	H	N	O	Na	S	Cl	Br
Min	0	0	0	0	0	0	0	0
Max	200	200	6	0	0	0	0	0

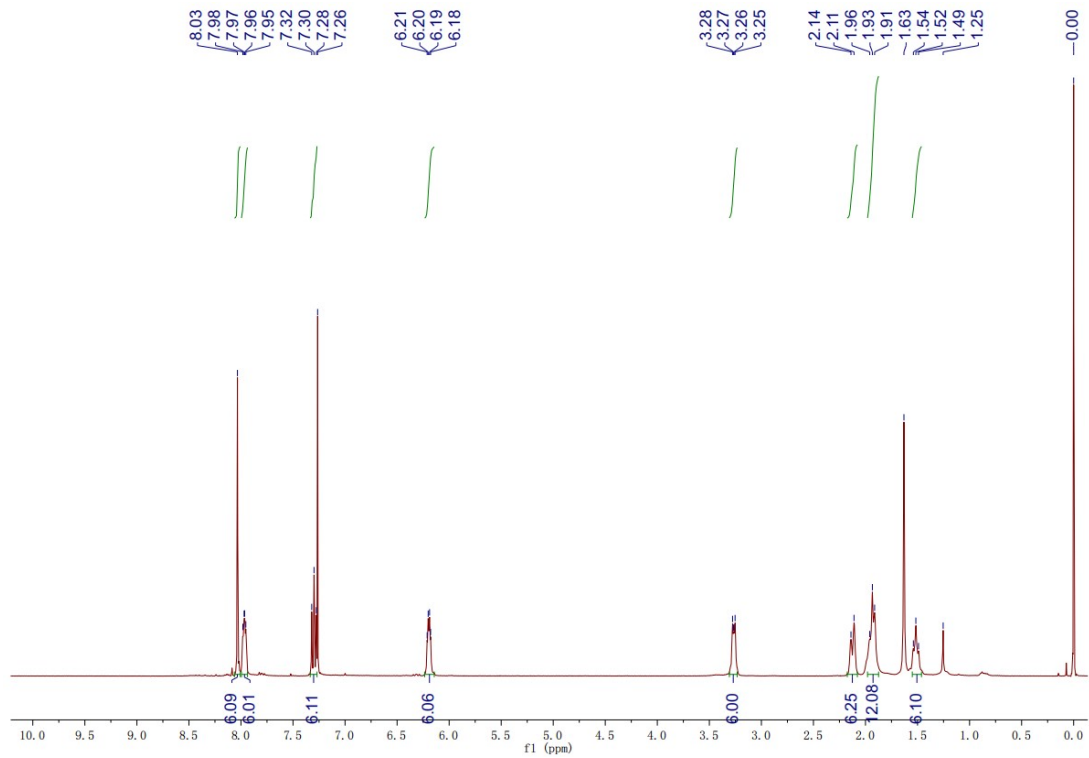
Symbol	F	P
Min	0	2
Max	0	2

#### Results

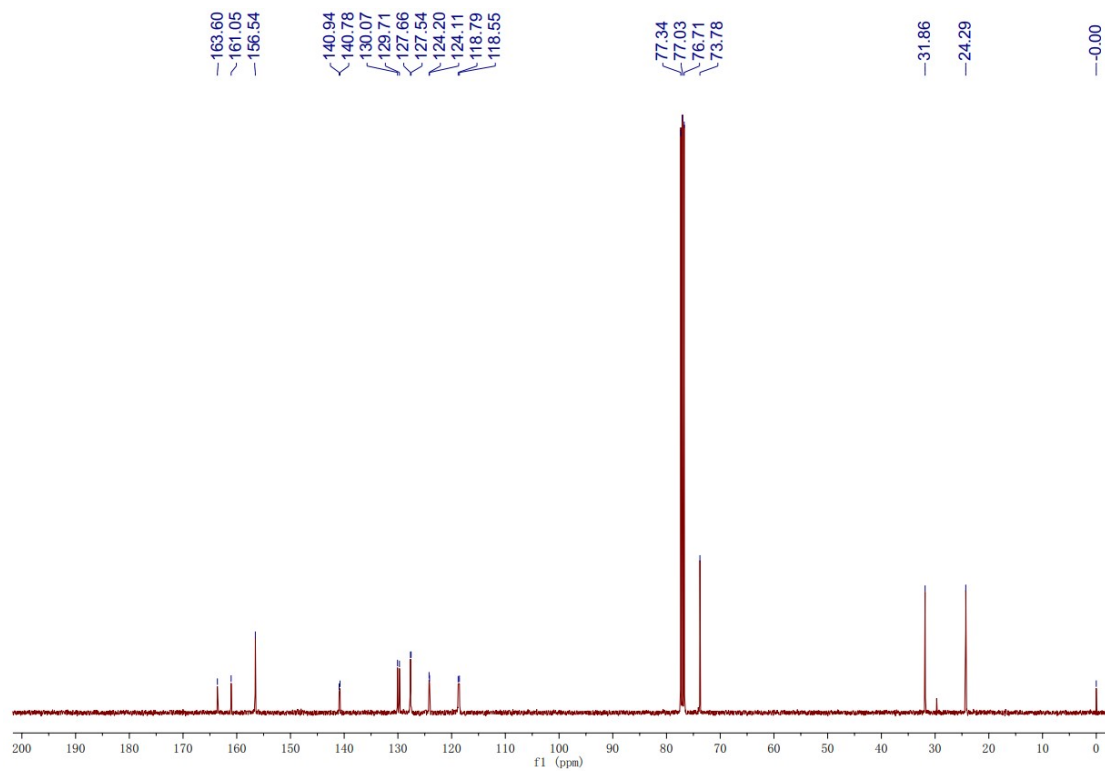
Mass	Intensity	Intensity [%]	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
1011.53545	35462.13	39.88	C <sub>66</sub> H <sub>73</sub> N <sub>6</sub> P <sub>2</sub>	1011.53665	-1.20	-1.19	34.5

## 9. NMR and ESI-HRMS characterizations of cage-L3

### <sup>1</sup>H NMR for cage-L3

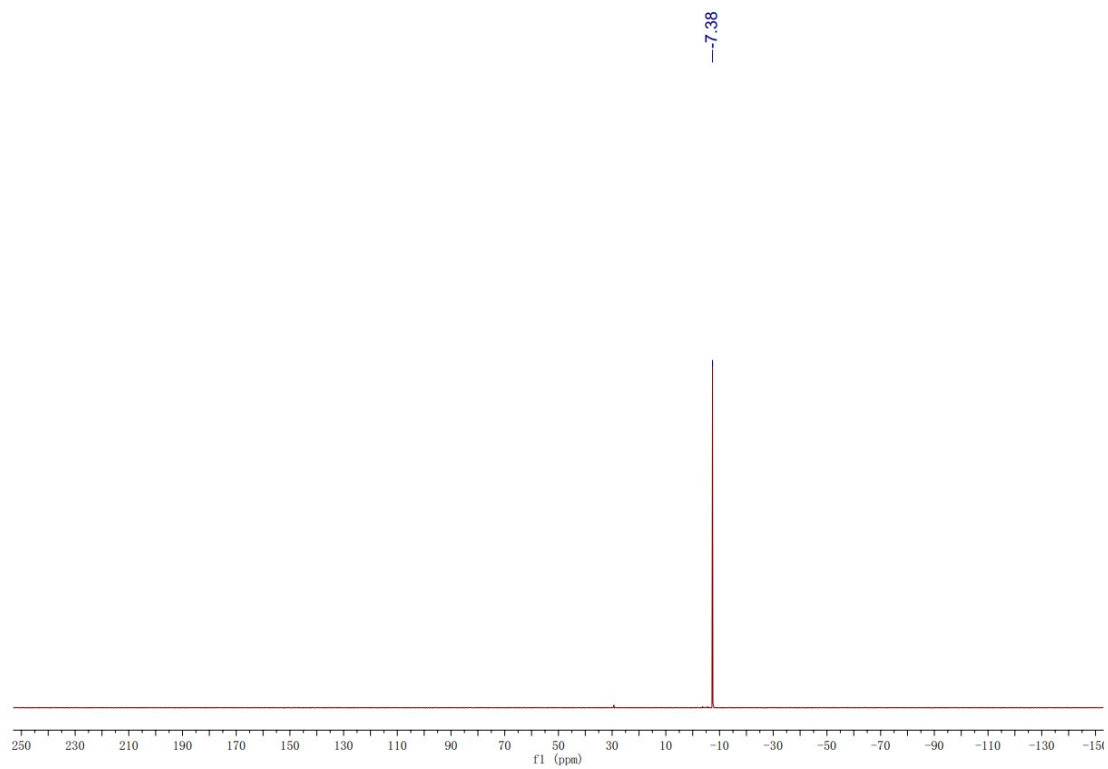


**<sup>13</sup>C NMR for cage-L3**

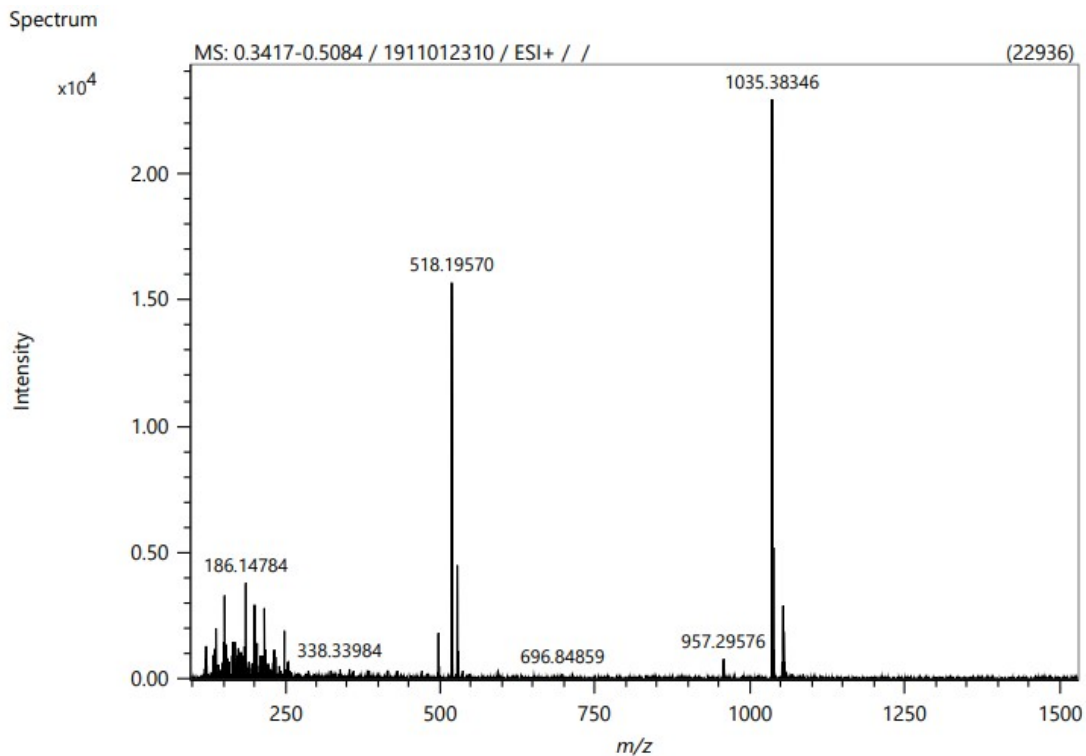


**<sup>31</sup>P NMR for cage-L3**





### ESI-HRMS spectrum for cage-L3



#### Elemental Composition

##### Parameters

Tolerance:  $\pm 5.00$  ppm  
 Electron: Odd/Even  
 Charge: +1  
 DBE: -1.5 - 200.0

##### Elements Set 1:

Symbol	C	H	N	O	Na	S	Cl	Br
Min	0	0	0	0	0	0	0	0
Max	120	120	6	0	0	0	0	0

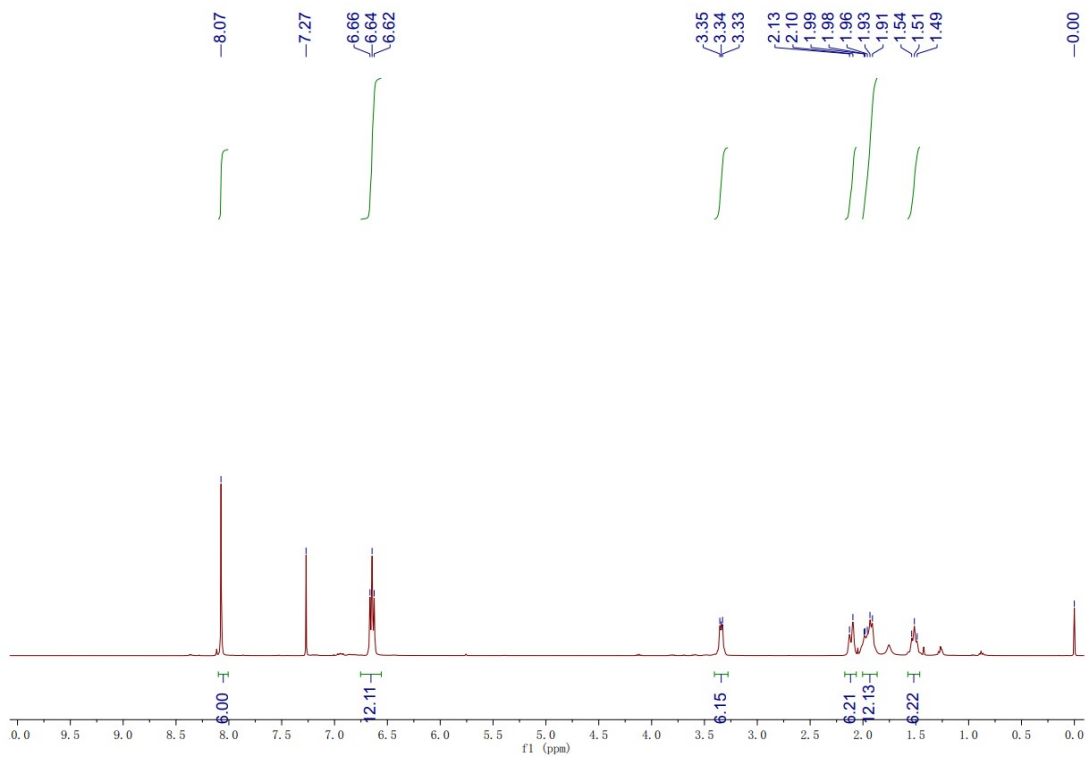
Symbol	F	P	I	Si
Min	6	0	0	0
Max	6	2	0	0

#### Results

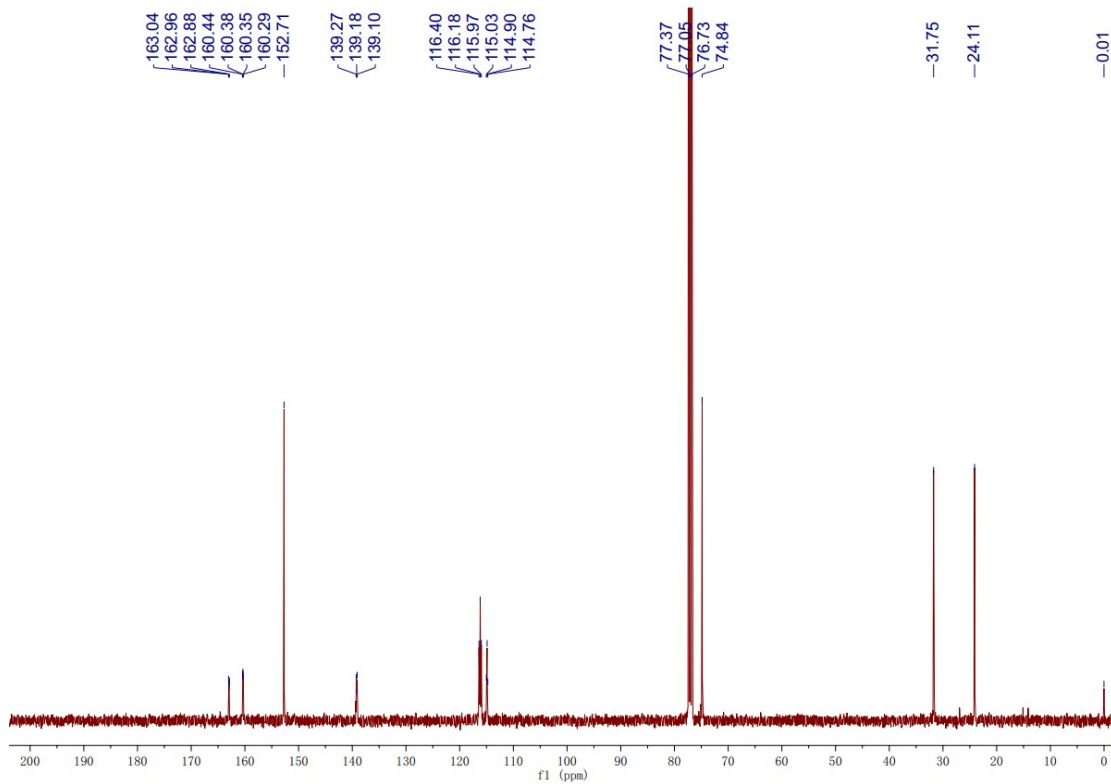
Mass	Intensity	Intensity [%]	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
1035.38346	22935.82	100.00	C <sub>68</sub> H <sub>49</sub> N <sub>4</sub> F <sub>6</sub>	1035.38559	-2.14	-2.06	43.5
			C <sub>64</sub> H <sub>52</sub> N <sub>5</sub> F <sub>6</sub> P	1035.38590	-2.45	-2.36	39.0
			C <sub>60</sub> H <sub>55</sub> N <sub>6</sub> F <sub>6</sub> P <sub>2</sub>	1035.38621	-2.76	-2.66	34.5

## 10. NMR and ESI-HRMS characterizations of cage-L4

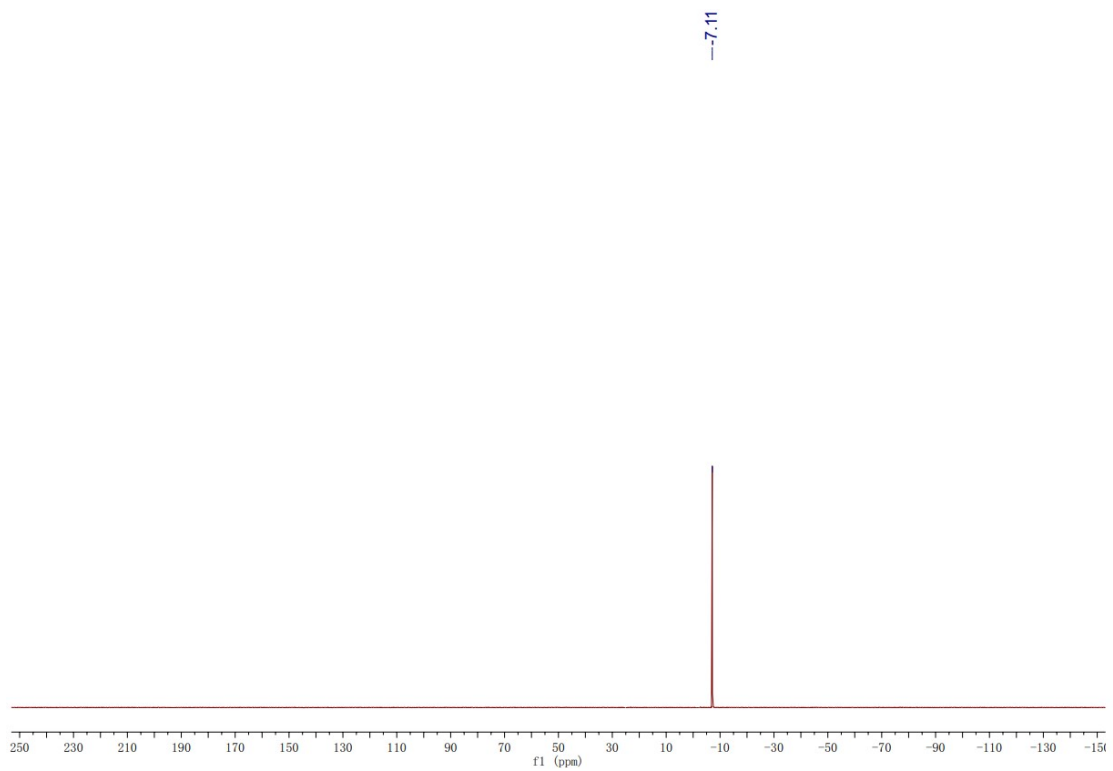
### <sup>1</sup>H NMR for cage-L4



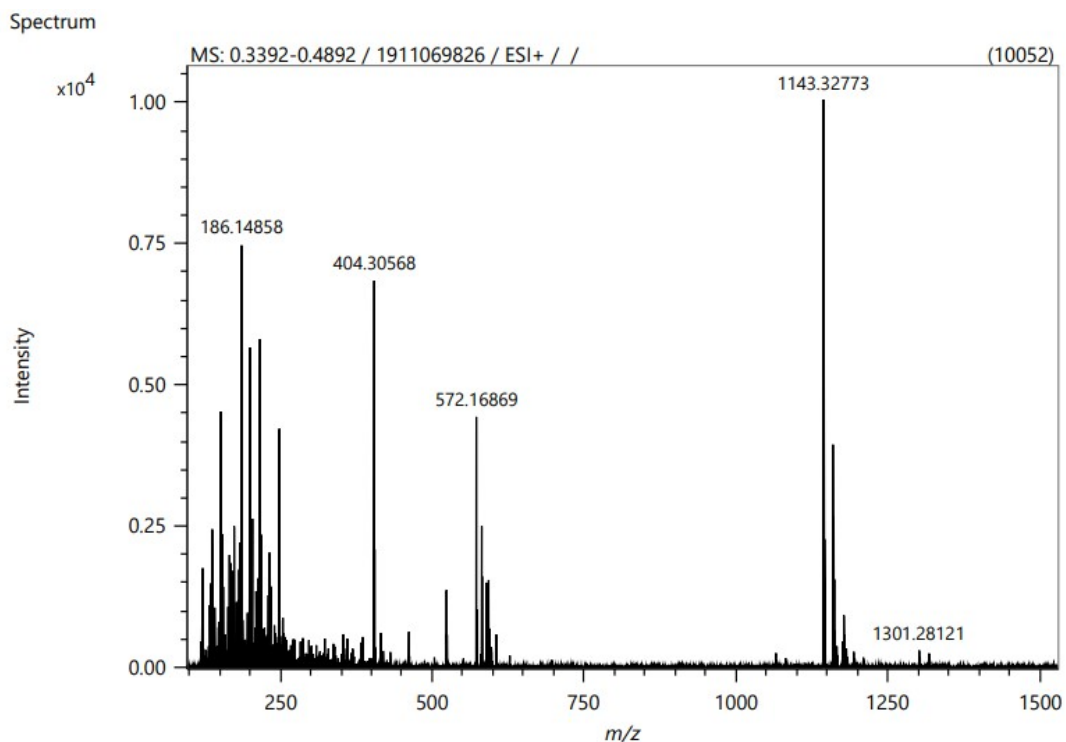
### <sup>13</sup>C NMR for cage-L4



### <sup>31</sup>P NMR for cage-L4



**ESI-HRMS spectrum for cage-L4**



#### Elemental Composition

##### Parameters

Tolerance:  $\pm 5.00$  ppm  
 Electron: Odd/Even  
 Charge: +1  
 DBE: -1.5 - 200.0

##### Elements Set 1:

Symbol	C	H	N	O	Na	S	Cl	Br
Min	0	0	0	0	0	0	0	0
Max	120	120	6	0	0	0	0	0

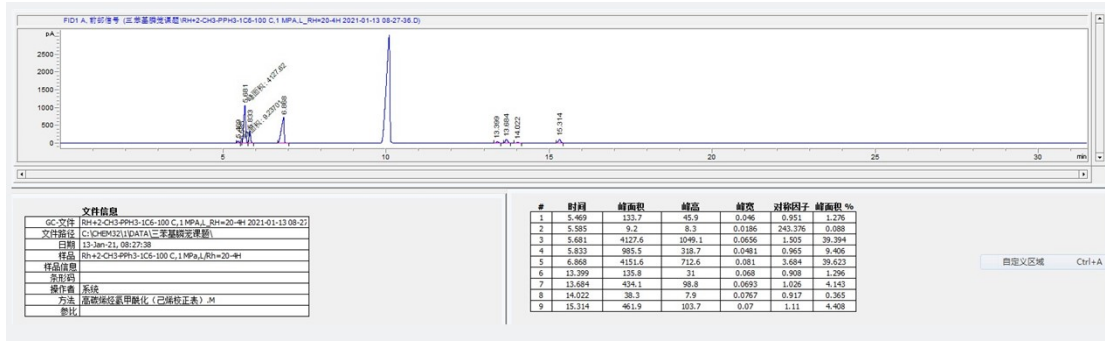
Symbol	F	P	I	Si
Min	12	2	0	0
Max	12	2	0	0

#### Results

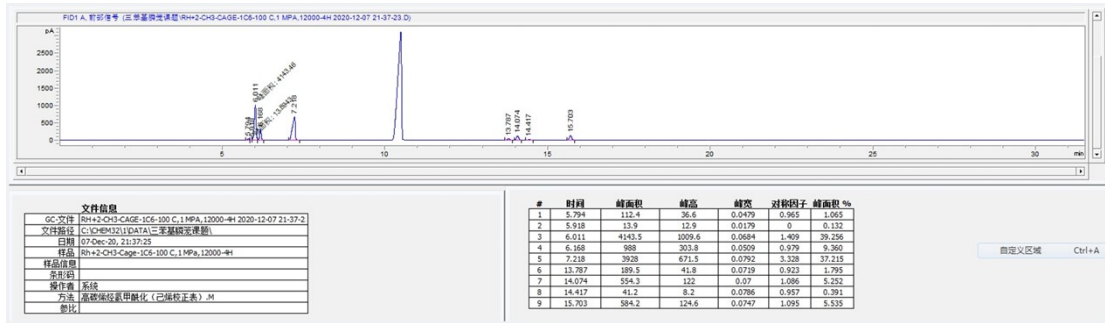
Mass	Intensity	Intensity [%]	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
1143.32773	10052.15	100.00	C <sub>60</sub> H <sub>49</sub> N <sub>6</sub> F <sub>12</sub> P <sub>2</sub>	1143.32968	-1.96	-1.71	34.5

## 11. Gas chromatography spectra

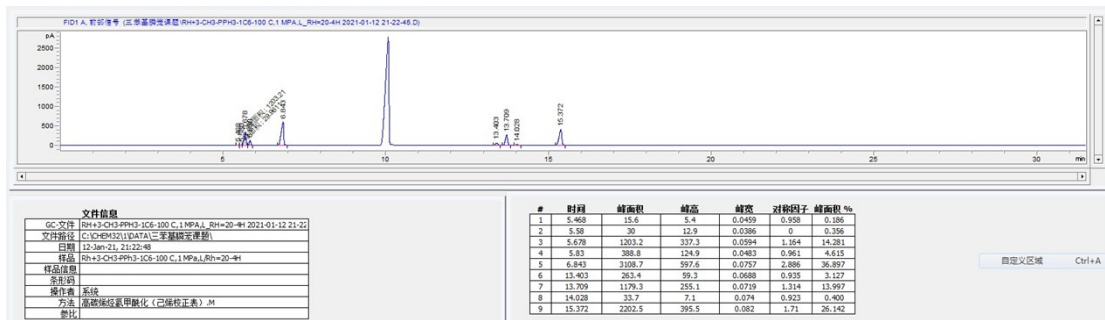
### Gas chromatography spectrum for L1 in Table 1



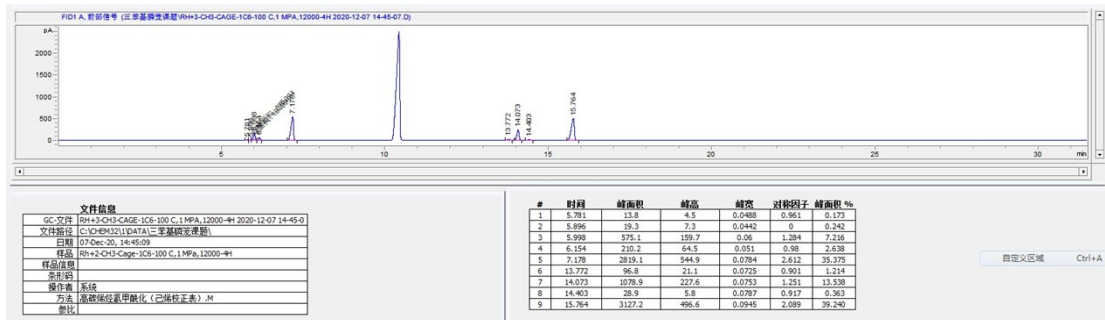
Gas chromatography spectrum for Cage-L1 in Table 1



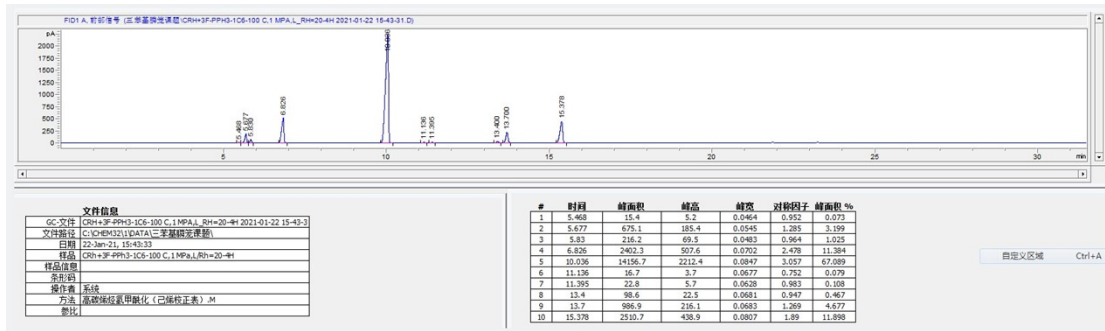
Gas chromatography spectrum for L2 in Table 1



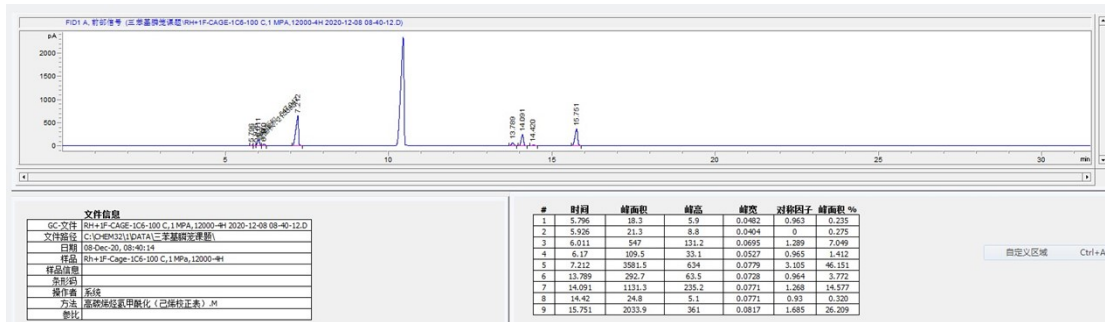
Gas chromatography spectrum for Cage-L2 in Table 1



Gas chromatography spectrum for L3 in Table 1



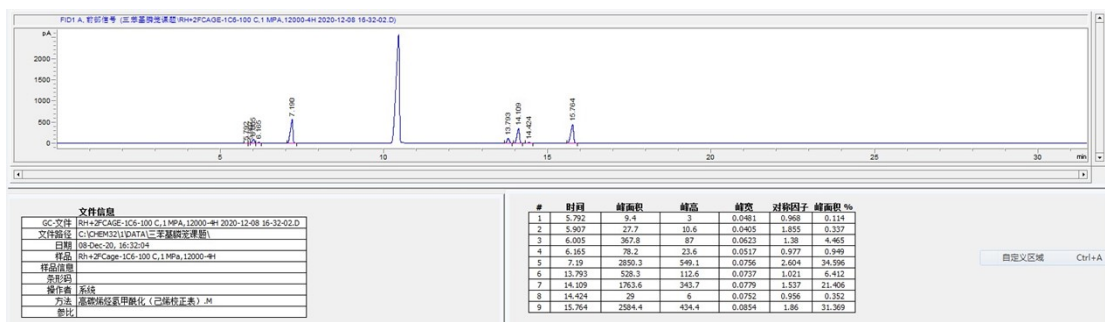
Gas chromatography spectrum for Cage-L3 in Table 1



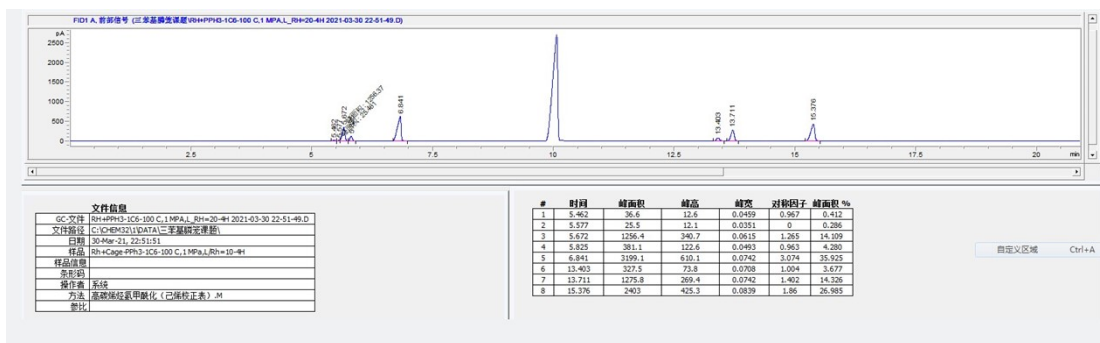
Gas chromatography spectrum for L4 in Table 1



Gas chromatography spectrum for Cage-L4 in Table 1



Gas chromatography spectrum for PPh3 in Table 1



Gas chromatography spectrum for Cage-PPh<sub>3</sub> in Table 1



## 12. References

- (1) Frisch, M. J. *et al.* Gaussian 09, revision D.01; Gaussian, Inc.: Pittsburgh, PA, **2009**.
- (2) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623-11627.
- (3) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B*, **2009**, *113*, 6378-6396.
- (4) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101-194118.
- (5) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.*, **2010**, *132*, 154104.