

**Supplemental information**

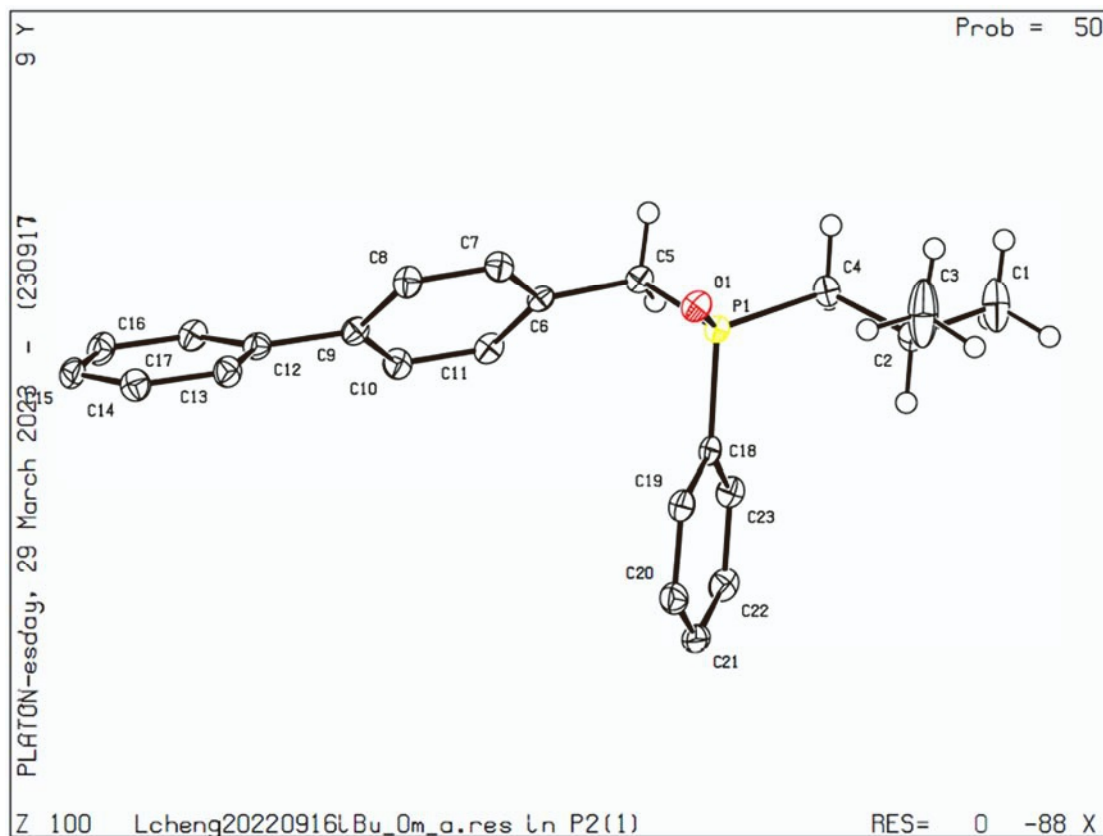
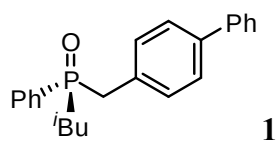
**Copper-catalyzed doubly enantioconvergent radical  
C(sp<sup>3</sup>)–P cross-coupling for the construction  
of P- and P,C-stereogenic centers**

**Cheng Luan, Chang-Jiang Yang, Pei-Jie Huang, Cong-Qiao Xu, Xin-Ran Dong, Chi Zhang, Jin-Min Xiang, Li-Wen Fan, Chen-Yu Xiao, Si-Yuan Chen, Lin Liu, Fu-Li Wang, Zhong-Liang Li, Li-Lei Wang, Ang Gao, Qiang-Shuai Gu, Jun Li, and Xin-Yuan Liu**

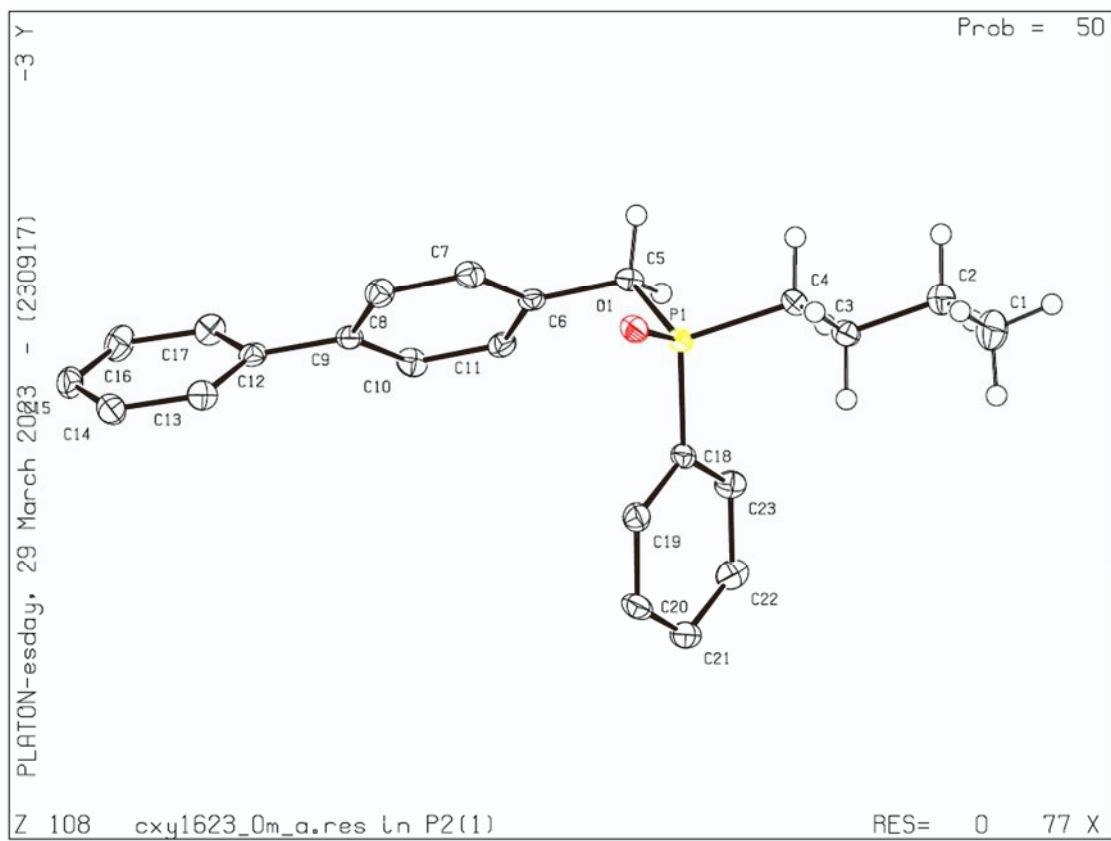
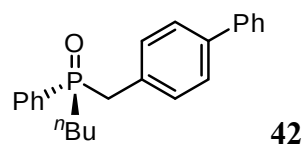
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## Supplemental Figures

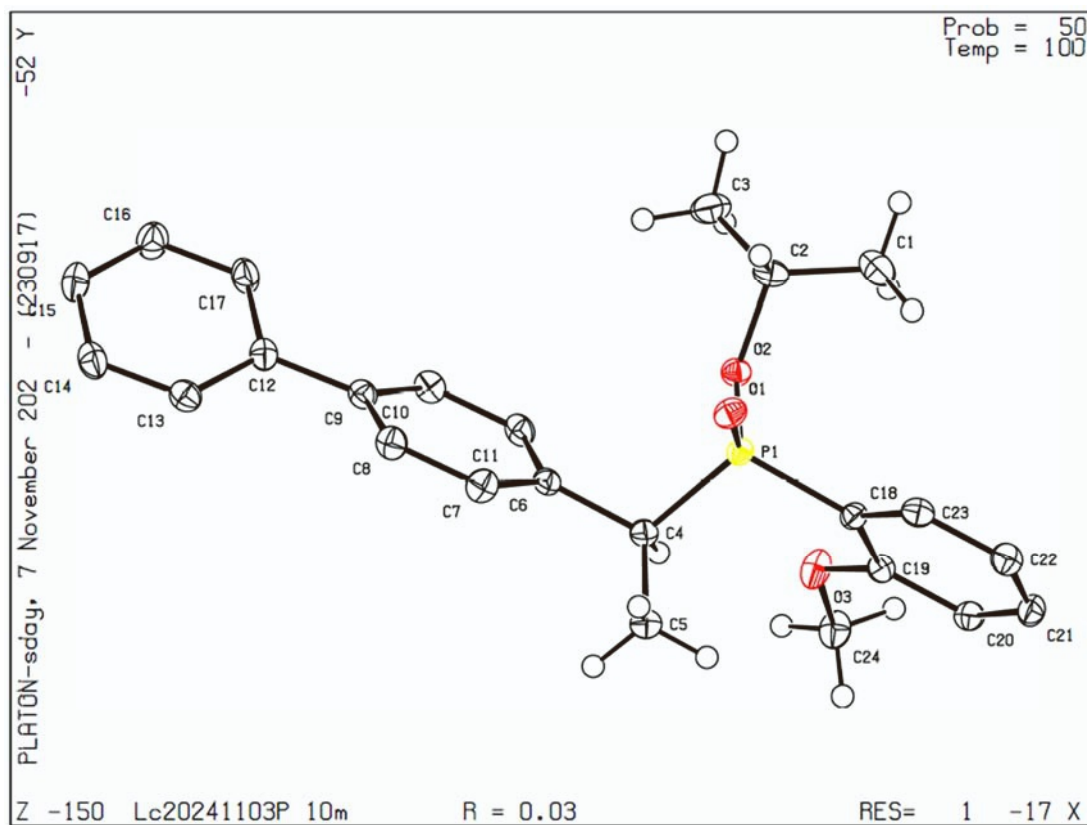
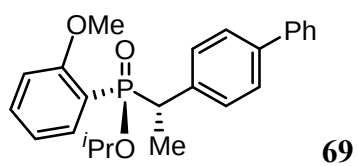


**Figure S1.** The X-ray structure of **1** (CCDC 2235110, 50% probability ellipsoids) Related to Scheme 2.

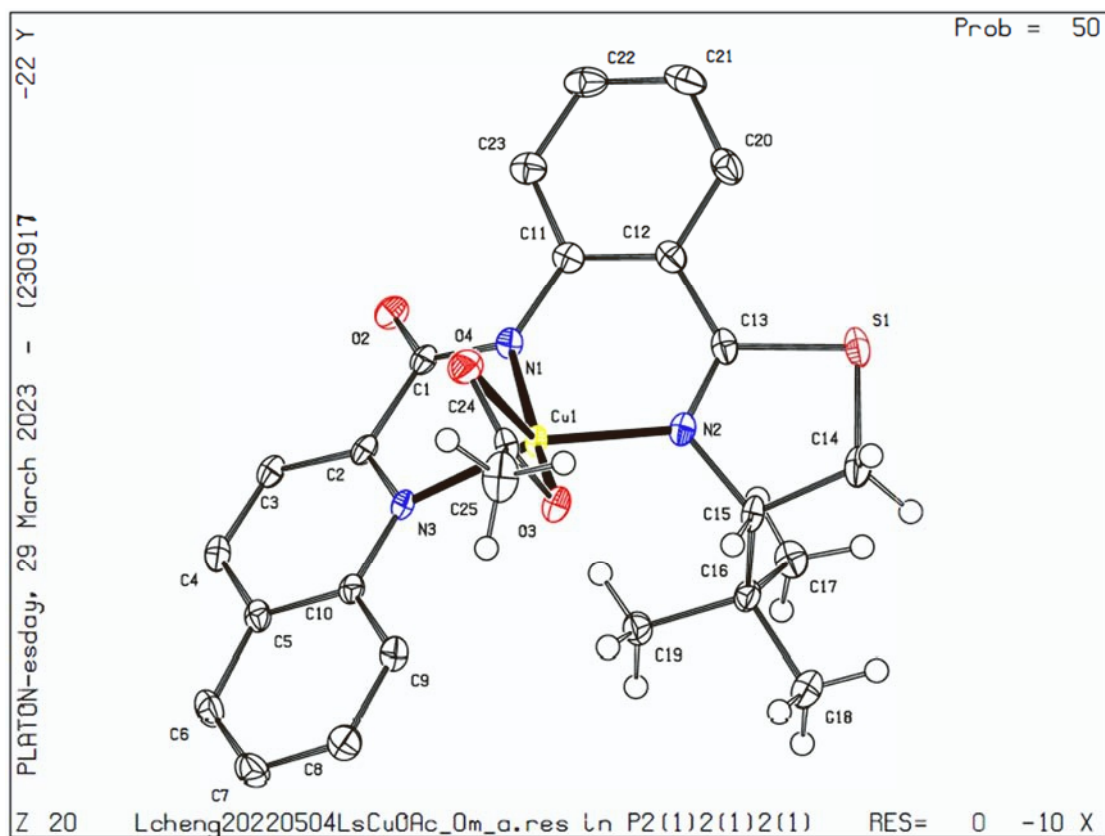
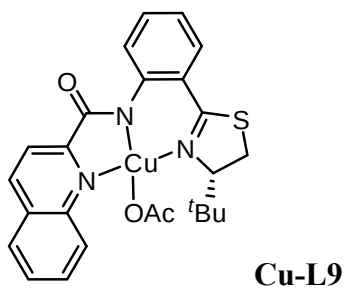


**Figure S2.** The X-ray structure of **42** (CCDC 2235111, 50% probability ellipsoids) Related to Scheme 3.

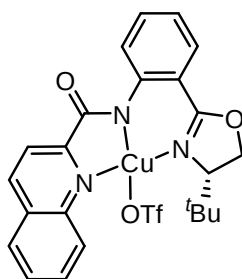




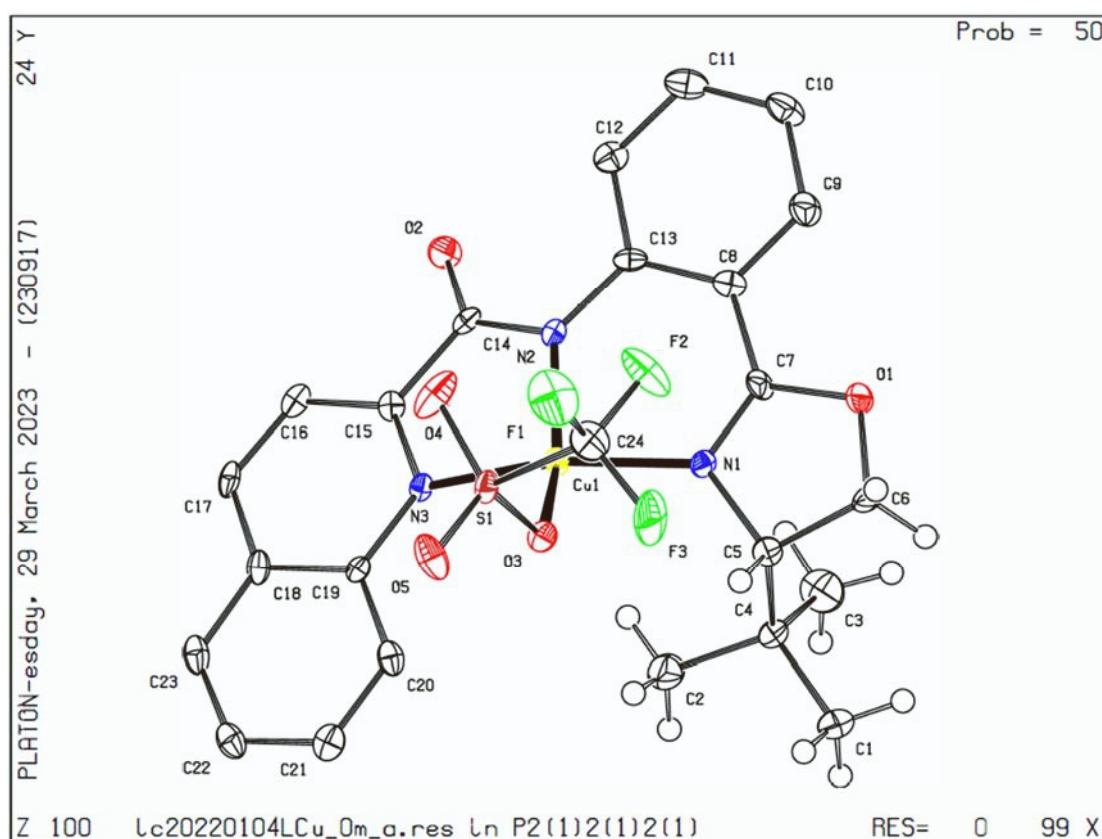
**Figure S3.** The X-ray structure of **69** (CCDC 2396572, 50% probability ellipsoids) Related to Scheme 4.



**Figure S4. The X-ray structure of Cu-L9 (CCDC 2235107, 50% probability ellipsoids)**  
 Related to Scheme 6.

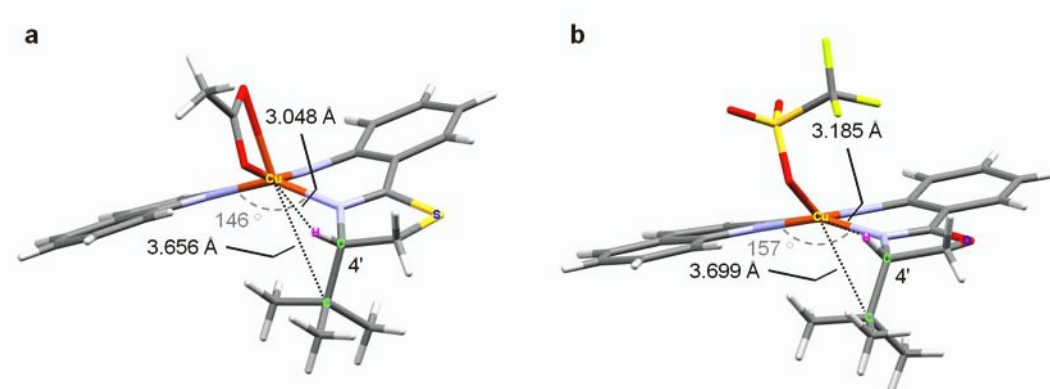


**Cu-L6**



**Figure S5. The X-ray structure of Cu-L6 (CCDC 2235106, 50% probability ellipsoids)**

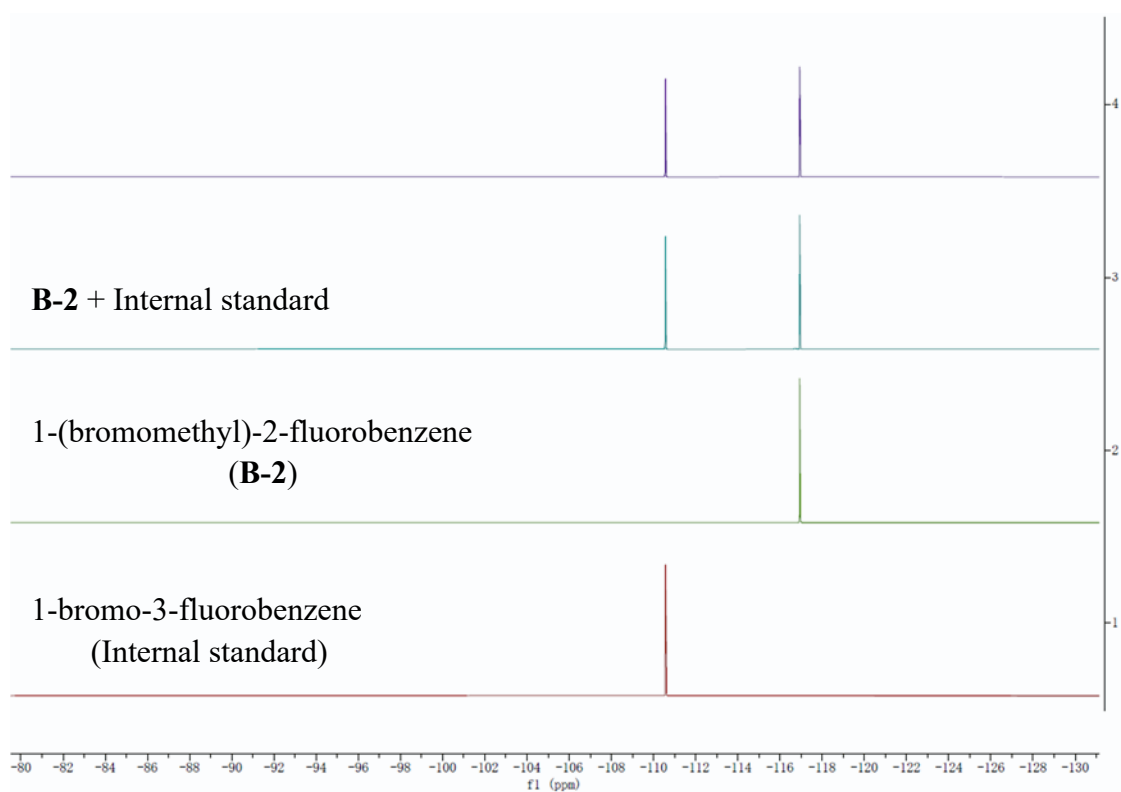
Related to Scheme 6.



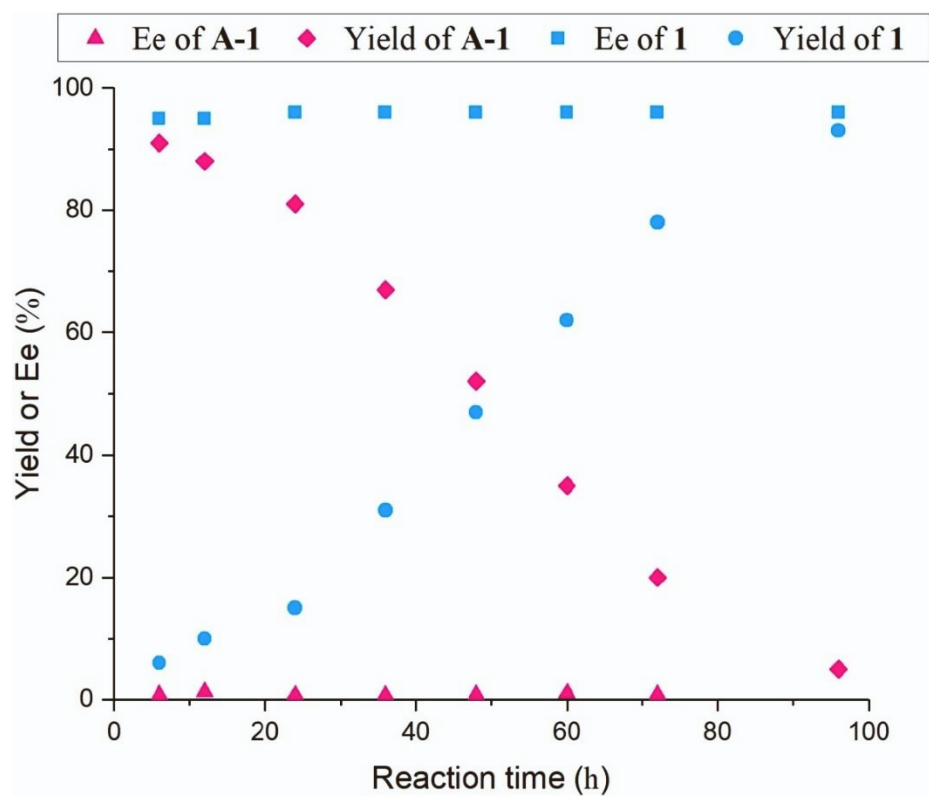
**Figure S6. The O-to-S replacement pushes the C4' stereocenter closer to the copper center**

**a** and **b**, X-ray structures of **Cu-L9** and **Cu-L6**, respectively, with the labelled distances between the copper centers and the C4' substituents. Angles of N(quinoline)–Cu–N(oxazoline/thiazoline) were shown in grey.

Related to Scheme 6.

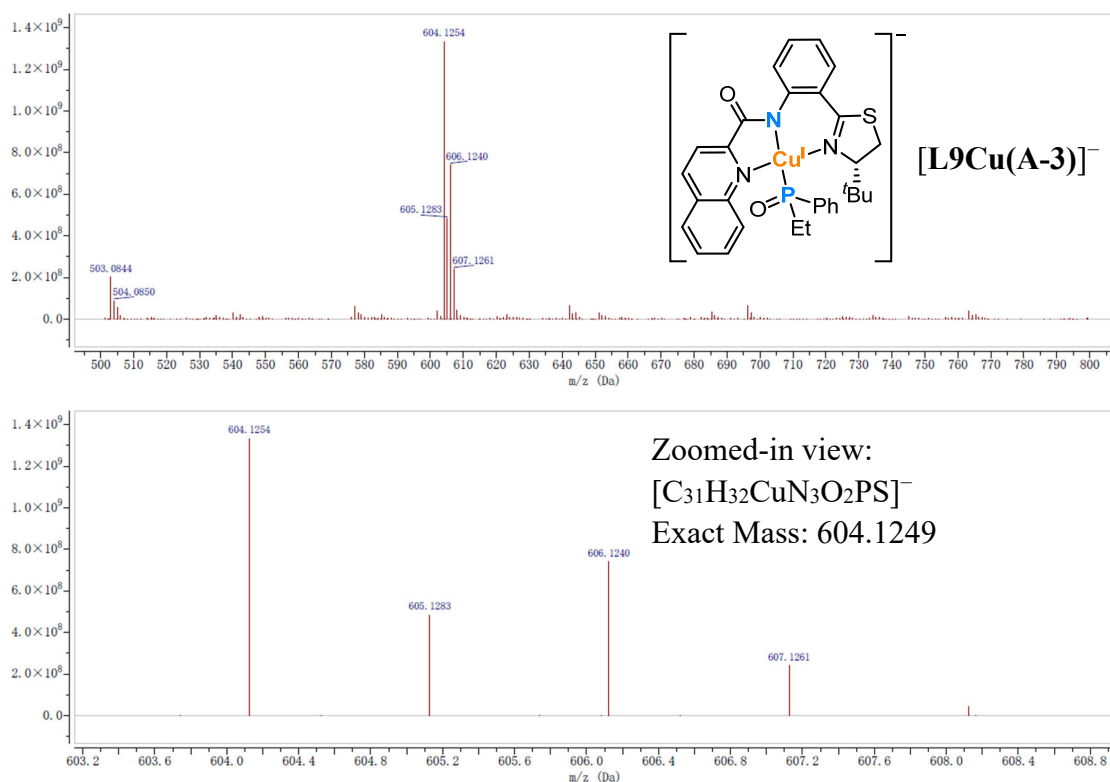


**Figure S7. The stacked  $^{19}\text{F}$  NMR spectra (376 MHz,  $\text{CDCl}_3$ )**  
Related to Scheme 6.

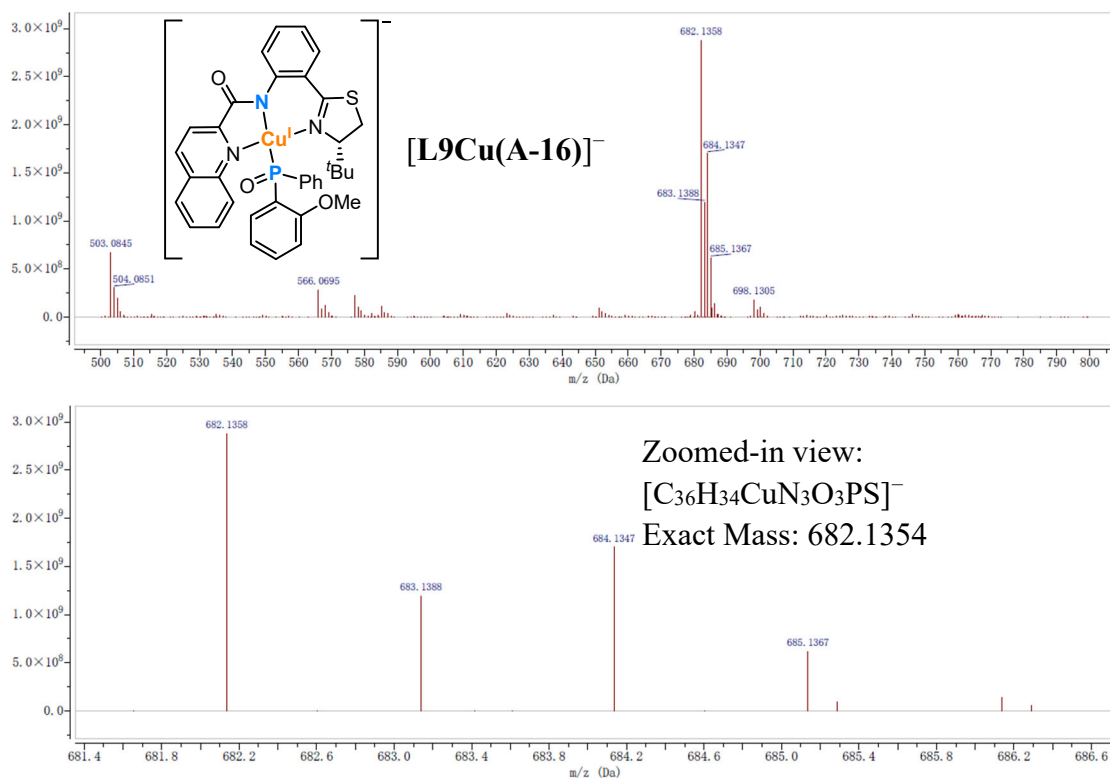


**Figure S8. Stereochemical outcome of the reaction (stereochemistry of the SPO and the product)**

Related to Scheme 6.

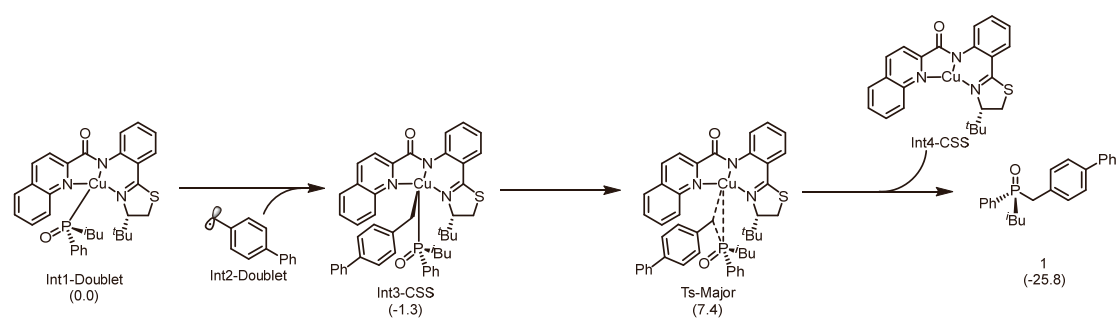


**Figure S9. High-resolution mass spectrum (HRMS) of the L9Cu(A-3) complex**  
 Related to Scheme 6.

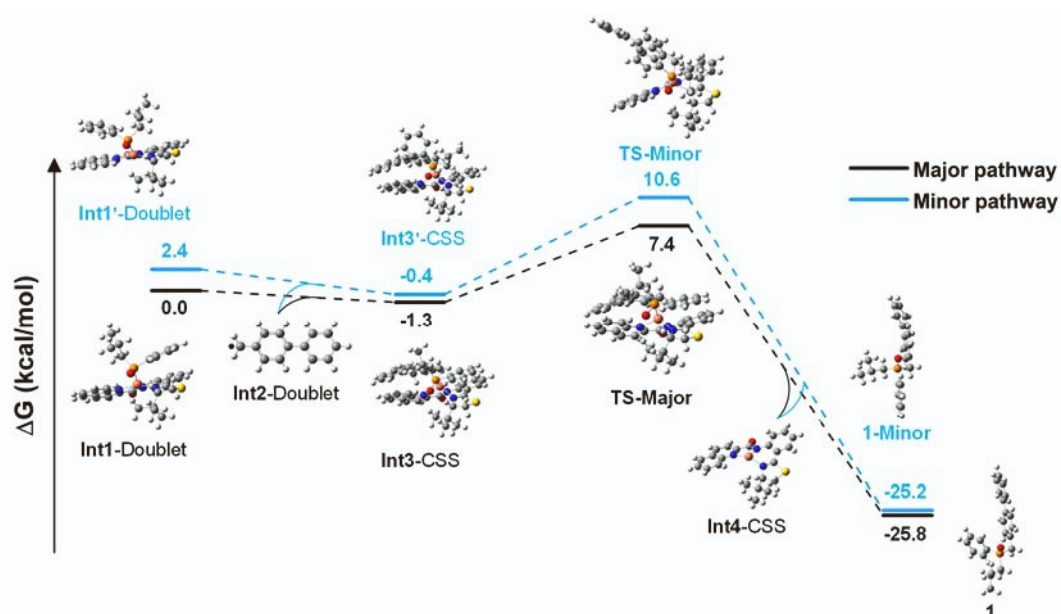


**Figure S10. HRMS spectrum of the L9Cu(A-16) complex**  
Related to Scheme 6.





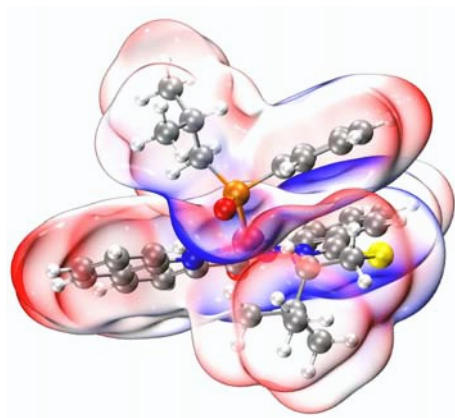
**Figure S11. Schematic reaction mechanism for C–P coupling leading to product 1**  
Related to Scheme 6.



**Figure S12. Proposed free-energy profiles for the enantioselective C-P coupling reactions, together with the optimized structures**

The major pathway corresponds to formation of product **1**, whereas the minor pathway corresponds to formation of the minor enantiomer (**1-Minor**).

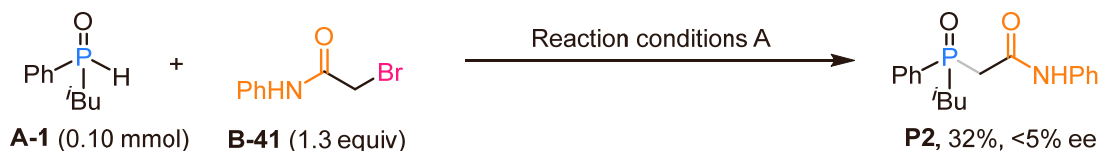
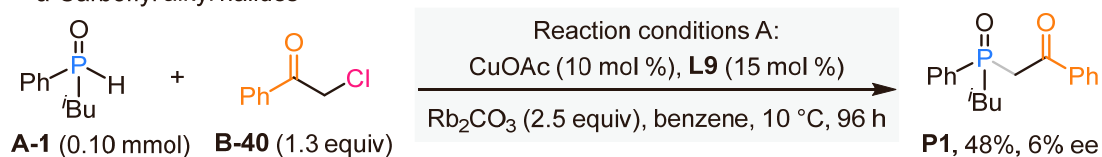
Related to Scheme 6.



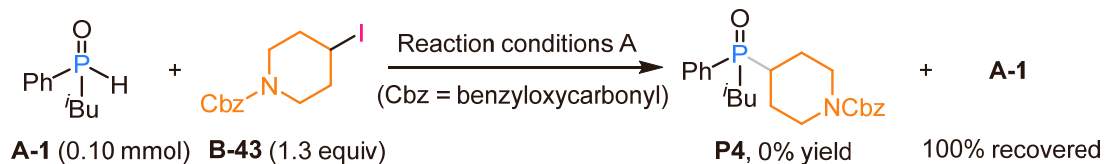
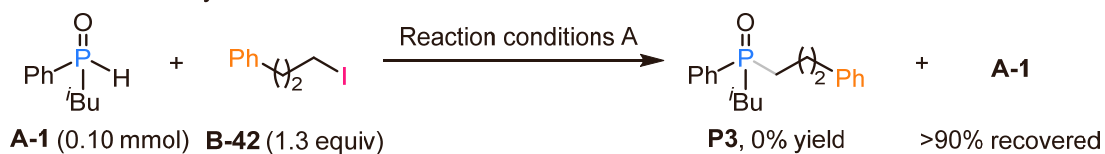
**Figure S13. Penetration map of Int1 with the electrostatic potential mapped onto the van der Waals surface**  
Related to Scheme 6.

## Supplemental Schemes

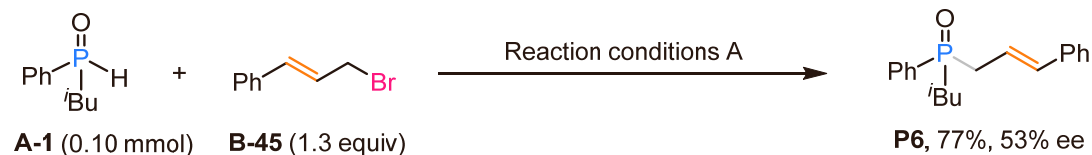
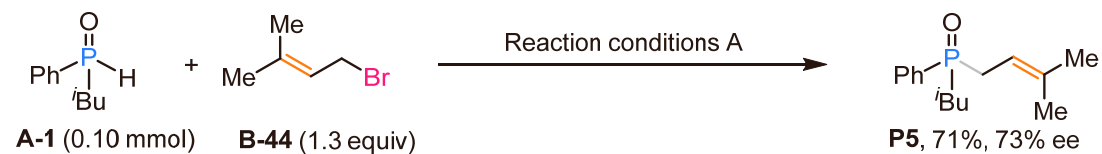
### A $\alpha$ -Carbonyl alkyl halides



### B Unactivated alkyl iodides

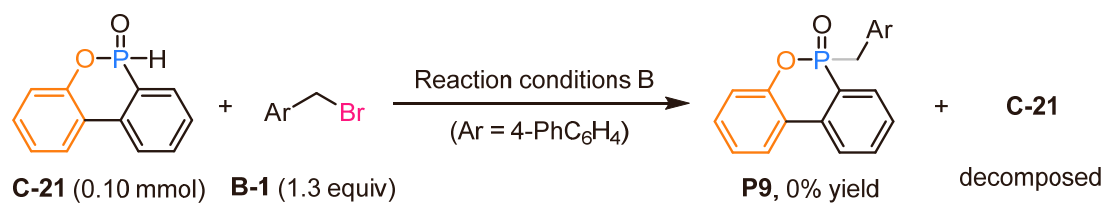
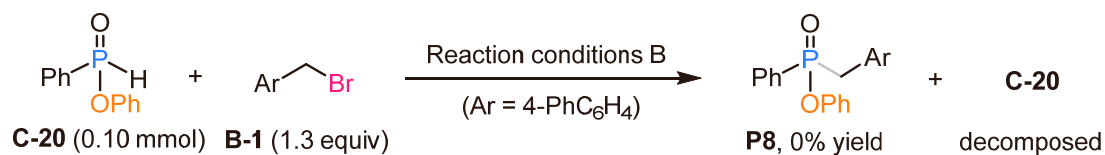
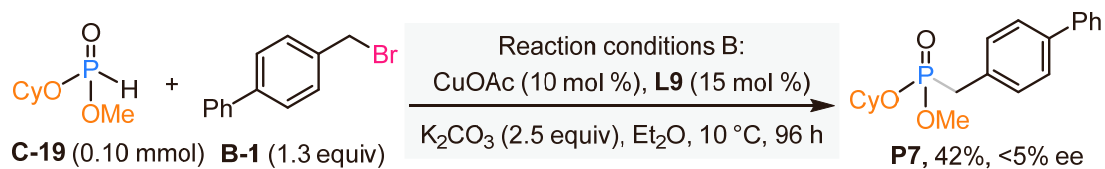


### C Allylic bromides



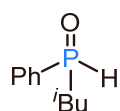
## Scheme S1. Results for other types of alkyl halides

Related to Scheme 2.

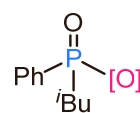
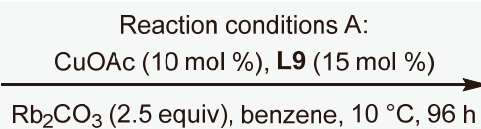


### Scheme S2. Results for other types of SPOs

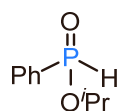
Related to Scheme 3.

**A****A-1** (0.050 mmol)

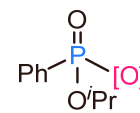
[O]



N.P.

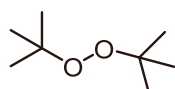
**C-1** (0.050 mmol)

[O]

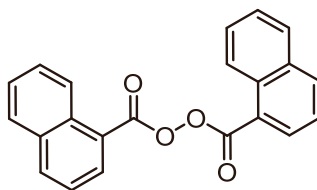


N.P.

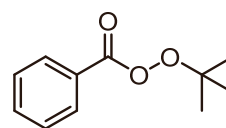
[O] =



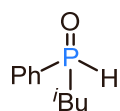
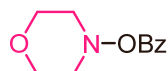
pOx.1



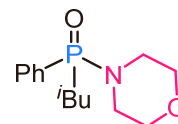
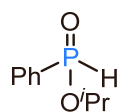
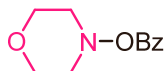
pOx.2



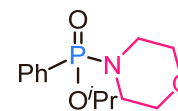
pOx.3

**B****A-1** (0.050 mmol)

Reaction conditions A

**P10**, N.P.**C-1** (0.050 mmol)

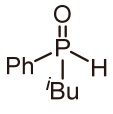
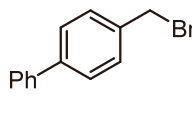
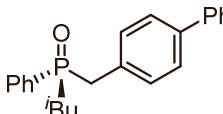
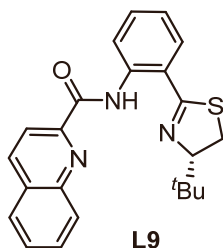
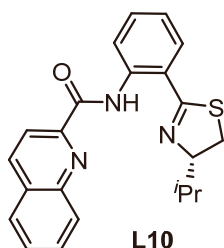
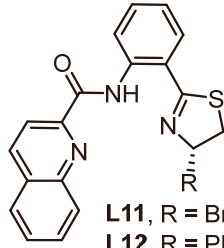
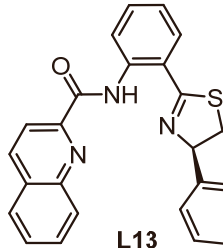
Reaction conditions C:

CuCN (10 mol %), **L3** (15 mol %)Cs<sub>2</sub>CO<sub>3</sub> (2.0 equiv), THF, rt, 36 h**P11**, 14%, 54% ee**Scheme S3. Results with oxygen- and nitrogen-centered radicals**

Related to Scheme 2.

## Supplemental Tables

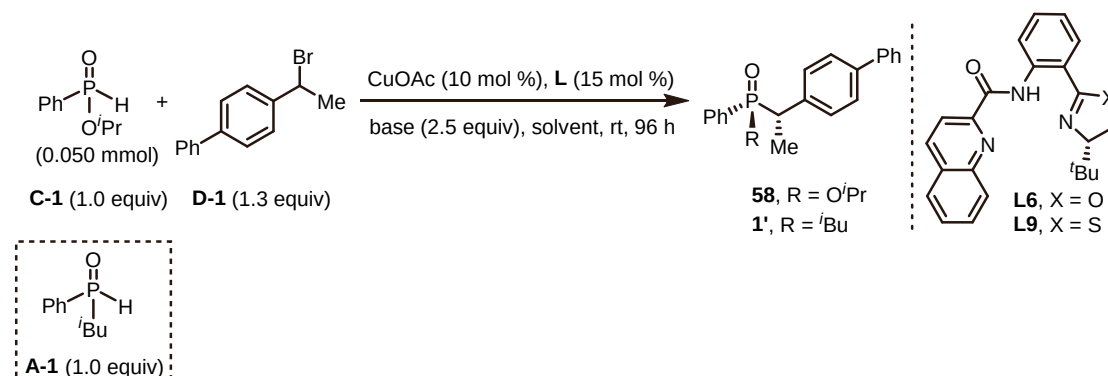
**Table S1. Optimization of reaction conditions**

| <div style="display: flex; align-items: center; justify-content: space-around;"> <div style="text-align: center;">  <p><b>A-1</b></p> </div> <div>+</div> <div style="text-align: center;">  <p><b>B-1</b> (1.3 equiv.)</p> </div> <div style="border: 1px solid black; padding: 5px; text-align: center; background-color: #f0f0f0;"> <p>Standard conditions:<br/>CuOAc (10 mol %), <b>L9</b> (15 mol %)<br/>Rb<sub>2</sub>CO<sub>3</sub> (2.5 equiv),<br/>benzene, 10 °C, 96 h</p> </div> <div style="text-align: center;">  <p><b>1</b></p> </div> </div> |                                                                              |                        |                     |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------|------------------------|---------------------|
| <div style="display: flex; justify-content: space-around; align-items: flex-end;"> <div style="text-align: center;">  <p><b>L9</b></p> </div> <div style="text-align: center;">  <p><b>L10</b></p> </div> <div style="text-align: center;">  <p><b>L11</b>, R = Bn<br/><b>L12</b>, R = Ph</p> </div> <div style="text-align: center;">  <p><b>L13</b></p> </div> </div>                                                                                                    |                                                                              |                        |                     |
| Entry                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | Variation from standard conditions <sup>a</sup>                              | Yield (%) <sup>b</sup> | Ee (%) <sup>c</sup> |
| 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | none                                                                         | 95                     | 96                  |
| 2                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | At rt for 48h                                                                | 88                     | 93                  |
| 3                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | <b>L10</b> , instead of <b>L9</b>                                            | 63                     | 92                  |
| 4                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | <b>L11</b> , instead of <b>L9</b>                                            | 41                     | 77                  |
| 5                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | <b>L12</b> , instead of <b>L9</b>                                            | 16                     | 75                  |
| 6                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | <b>L13</b> , instead of <b>L9</b>                                            | 55                     | –71                 |
| 7                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | CuI, instead of CuOAc                                                        | 61                     | 86                  |
| 8                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | CuTc, instead of CuOAc                                                       | 47                     | 87                  |
| 9                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | Cu(MeCN) <sub>4</sub> PF <sub>6</sub> , instead of CuOAc                     | 43                     | 79                  |
| 10                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Cu(OAc) <sub>2</sub> , instead of CuOAc                                      | 63                     | 85                  |
| 11                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | K <sub>2</sub> CO <sub>3</sub> , instead of Rb <sub>2</sub> CO <sub>3</sub>  | 67                     | 91                  |
| 12                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Cs <sub>2</sub> CO <sub>3</sub> , instead of Rb <sub>2</sub> CO <sub>3</sub> | 85                     | 93                  |
| 13                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | K <sub>3</sub> PO <sub>4</sub> , instead of Rb <sub>2</sub> CO <sub>3</sub>  | 65                     | 83                  |
| 14                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | LiO <sup>t</sup> Bu, instead of Rb <sub>2</sub> CO <sub>3</sub>              | 0                      | –                   |
| 15                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Dioxane, instead of benzene, at rt for 48h                                   | 95                     | 89                  |
| 16                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | DCM, instead of benzene                                                      | 12                     | 86                  |
| 17                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | EtOAc, instead of benzene                                                    | 62                     | 92                  |
| 18                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | PhMe, instead of benzene                                                     | 73                     | 95                  |
| 19                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | PhCl, instead of benzene                                                     | 38                     | 94                  |
| 20                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | PhF, instead of benzene                                                      | 45                     | 94                  |
| 21                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 1.2 equiv of <b>B-1</b>                                                      | 89                     | 96                  |
| 22                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 1.4 equiv of <b>B-1</b>                                                      | 95                     | 95                  |
| 23                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 2.0 equiv of Rb <sub>2</sub> CO <sub>3</sub>                                 | 90                     | 96                  |
| 24                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 3.0 equiv of Rb <sub>2</sub> CO <sub>3</sub>                                 | 95                     | 96                  |
| 25                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 5.0 mol % of CuOAc and 7.5 mol % of <b>L9</b>                                | 75                     | 95                  |
| 26                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 2.5 mol % of CuOAc and 3.75 mol % of <b>L9</b>                               | 53                     | 91                  |
| 27                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Without CuOAc                                                                | 0                      | –                   |
| 28                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Without <b>L9</b>                                                            | 0                      | –                   |
| 29                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Without Rb <sub>2</sub> CO <sub>3</sub>                                      | 0                      | –                   |

<sup>a</sup>Standard conditions: racemic **A-1** (0.025 mmol), *p*-phenylbenzyl bromide **B-1** (1.3 equiv), CuOAc (10 mol %), **L9** (15 mol %) and Rb<sub>2</sub>CO<sub>3</sub> (2.5 equiv) in benzene (0.50 mL) at 10 °C under argon stirred for 96 h. <sup>b</sup>Yields were based on <sup>31</sup>P NMR analysis using trimethyl phosphate as an internal standard. <sup>c</sup>Ee values were determined by chiral HPLC analysis. Tc, 2-thiophenecarboxylato.  
Related to Figure 1.



**Table S2. Condition optimization for doubly enantioconvergent C–P cross-coupling<sup>a</sup>**



| Entry           | L         | Base                                | Solvent                        | Yield (%) <sup>b</sup> | Dr <sup>c</sup> | Ee1 (%) <sup>d</sup> | Ee2 (%) <sup>d</sup> |
|-----------------|-----------|-------------------------------------|--------------------------------|------------------------|-----------------|----------------------|----------------------|
| 1 <sup>e</sup>  | <b>L9</b> | Rb <sub>2</sub> CO <sub>3</sub>     | benzene                        | 27                     | 5:1             | 90                   | 19                   |
| 2 <sup>f</sup>  | <b>L9</b> | Rb <sub>2</sub> CO <sub>3</sub>     | benzene                        | 50                     | 6:1             | 91                   | 85                   |
| 3 <sup>f</sup>  | <b>L6</b> | Rb <sub>2</sub> CO <sub>3</sub>     | benzene                        | 30                     | 16:1            | 98                   | 65                   |
| 4               | <b>L6</b> | Rb <sub>2</sub> CO <sub>3</sub>     | benzene                        | 41                     | 14:1            | 96                   | 42                   |
| 5               | <b>L6</b> | Rb <sub>2</sub> CO <sub>3</sub>     | DCM                            | 66                     | 8:1             | 97                   | 60                   |
| 6               | <b>L6</b> | Rb <sub>2</sub> CO <sub>3</sub>     | THF                            | 60                     | 8:1             | 98                   | 63                   |
| 7               | <b>L6</b> | Rb <sub>2</sub> CO <sub>3</sub>     | dioxane                        | 49                     | 11:1            | 96                   | 61                   |
| 8               | <b>L6</b> | Rb <sub>2</sub> CO <sub>3</sub>     | Et <sub>2</sub> O              | 52                     | 20:1            | 99                   | 46                   |
| 9               | <b>L6</b> | Rb <sub>2</sub> CO <sub>3</sub>     | <i>i</i> Pr <sub>2</sub> O     | 32                     | >20:1           | 94                   | —                    |
| 10              | <b>L6</b> | K <sub>2</sub> CO <sub>3</sub>      | <i>i</i> Pr <sub>2</sub> O     | 26                     | 10:1            | 79                   | 45                   |
| 11              | <b>L6</b> | <b>Cs<sub>2</sub>CO<sub>3</sub></b> | <b><i>i</i>Pr<sub>2</sub>O</b> | <b>70</b>              | <b>&gt;20:1</b> | <b>99</b>            | —                    |
| 12 <sup>g</sup> | <b>L6</b> | Cs <sub>2</sub> CO <sub>3</sub>     | <i>i</i> Pr <sub>2</sub> O     | 0                      | —               | —                    | —                    |
| 13              | —         | Cs <sub>2</sub> CO <sub>3</sub>     | <i>i</i> Pr <sub>2</sub> O     | 0                      | —               | —                    | —                    |
| 14              | <b>L6</b> | —                                   | <i>i</i> Pr <sub>2</sub> O     | 0                      | —               | —                    | —                    |

<sup>a</sup>Reaction conditions: racemic *H*-phosphinate **C-1** (0.050 mmol, 1.0 equiv), 4-(1-bromoethyl)-1,1'-biphenyl **D-1** (1.3 equiv), CuOAc (10 mol %), **L** (15 mol %) and base (2.5 equiv) in solvent (0.50 mL) at rt under argon stirred for 96 h. <sup>b</sup>Isolated yields based on preparative thin-layer chromatography (PTLC) analysis and referred to as total yields of the diastereomeric products. <sup>c</sup>Dr values were determined by crude <sup>31</sup>P NMR analysis. <sup>d</sup>Ee values were determined by chiral HPLC analysis, with ee1 corresponding to the major isomer and ee2 corresponding to the minor isomer. <sup>e</sup>Racemic **A-1** (0.050 mmol, 1.0 equiv) was used instead of **C-1** and the reaction was performed at 10 °C. <sup>f</sup>Reaction was performed at 10 °C. <sup>g</sup>Without CuOAc.

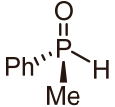
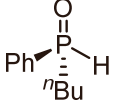
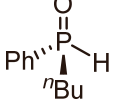
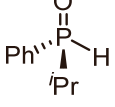
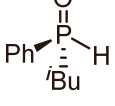
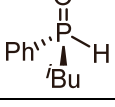
Related to Scheme 4.

**Table S3. Results of stereochemical studies**

| Time (h) | Yield of <b>A-1</b> (%) | Ee of <b>A-1</b> (%) | Yield of <b>1</b> (%) | Ee of <b>1</b> (%) |
|----------|-------------------------|----------------------|-----------------------|--------------------|
| 6        | 91                      | 0.8                  | 6                     | 95                 |
| 12       | 88                      | 1.3                  | 10                    | 95                 |
| 24       | 81                      | 0.7                  | 15                    | 96                 |
| 36       | 67                      | 0.7                  | 31                    | 96                 |
| 48       | 52                      | 0.8                  | 47                    | 96                 |
| 60       | 35                      | 1.0                  | 62                    | 96                 |
| 72       | 20                      | 0.8                  | 78                    | 96                 |
| 96       | <5                      | —                    | 93                    | 96                 |

Related to Scheme 6.

**Table S4. Optical rotation data of A in literature**

| Entry | Absolute configuration                                                                            | $[\alpha]$                                                        | Reference      |
|-------|---------------------------------------------------------------------------------------------------|-------------------------------------------------------------------|----------------|
| 1     |  <b>(S)-A-2</b>  | $[\alpha]_{589}^{31} = -21.6$<br>$(c = 0.23, \text{CHCl}_3)$      | <i>Ref.</i> 16 |
| 2     |  <b>(R)-A-4</b>  | $[\alpha]_{589}^{25} = +20.5$<br>$(c = 0.58, \text{CHCl}_3)$      | <i>Ref.</i> 16 |
| 3     |  <b>(S)-A-4</b>  | $[\alpha]_{589}^{31} = -22.0$<br>$(c = 0.60, \text{CHCl}_3)$      | <i>Ref.</i> 16 |
| 4     |  <b>(S)-A-6</b>  | $[\alpha]_{589}^{24} = -48.8$<br>$(c = 0.42, \text{CHCl}_3)$      | <i>Ref.</i> 16 |
| 5     |  <b>(R)-A-1</b>  | $[\alpha]_{\text{D}}^{20} = +16.0$<br>$(c = 0.50, \text{CHCl}_3)$ | This work      |
| 6     |  <b>(S)-A-1</b> | $[\alpha]_{\text{D}}^{20} = -21.1$<br>$(c = 1.00, \text{CHCl}_3)$ | This work      |

Related to Scheme 6.

**Table S5. Results of control experiments on the racemization of A-1**

| Entry | Condition variation                                          | Ee of recovered <b>A-1</b> (%) |
|-------|--------------------------------------------------------------|--------------------------------|
| 1     | None                                                         | 2                              |
| 2     | Without <b>L9</b>                                            | 43                             |
| 3     | Without Rb <sub>2</sub> CO <sub>3</sub>                      | 86                             |
| 4     | Without <b>L9</b> , Rb <sub>2</sub> CO <sub>3</sub>          | 79                             |
| 5     | Without CuOAc                                                | 95                             |
| 6     | Without CuOAc, Rb <sub>2</sub> CO <sub>3</sub>               | 96                             |
| 7     | Without CuOAc, <b>L9</b>                                     | 96                             |
| 8     | Without CuOAc, <b>L9</b> and Rb <sub>2</sub> CO <sub>3</sub> | 96                             |

Related to Scheme 6.

**Table S6. Energy decomposition analysis of Int1 (major pathway to product 1) and Int1' (minor pathway to the minor enantiomer, 1-Minor)**

| Energy term <sup>a</sup>    | Energy (kcal/mol) |         |
|-----------------------------|-------------------|---------|
|                             | Int1              | Int1'   |
| $\Delta E_{\text{int}}$     | -158.98           | -157.13 |
| $\Delta E_{\text{Pauli}}$   | 151.89            | 150.08  |
| $\Delta E_{\text{elestat}}$ | -201.08           | -197.26 |
| $\Delta E_{\text{orb}}$     | -85.24            | -84.00  |
| $\Delta E_{\text{dis}}$     | -24.54            | -25.94  |

<sup>a</sup> $\Delta E_{\text{int}}$ ,  $\Delta E_{\text{Pauli}}$ ,  $\Delta E_{\text{elestat}}$ ,  $\Delta E_{\text{orb}}$ , and  $\Delta E_{\text{dis}}$  represent the total interaction energy, Pauli repulsion, electrostatic interaction, orbital interaction, and dispersion interaction, respectively, between the cationic Cu fragment and the anionic P fragment, where  $\Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elestat}} + \Delta E_{\text{orb}} + \Delta E_{\text{dis}}$ .

Related to Scheme 6.

## Supplemental Methods

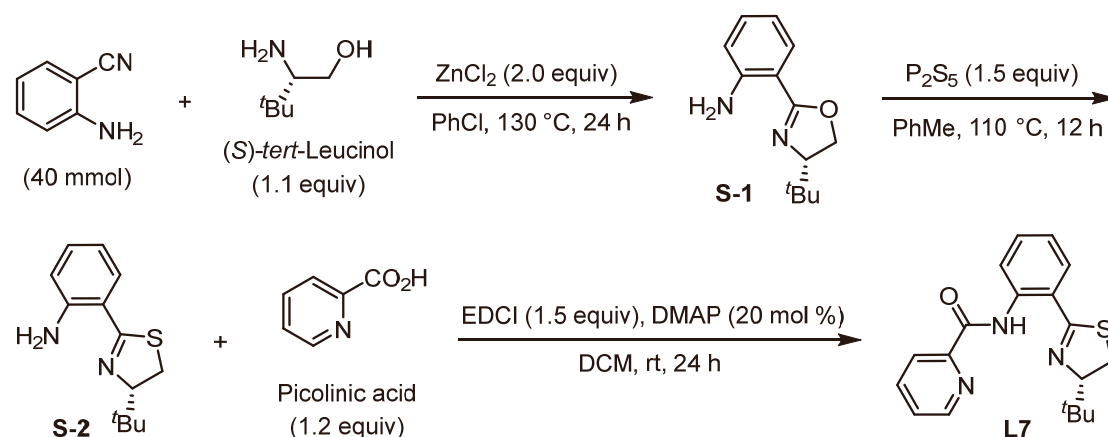
### General information

Reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. CuOAc (CAS No. 598–54–9), CuBr (CAS No. 7787–70–4) and Cu(OTf)<sub>2</sub> (CAS No. 34946–82–2) were purchased from TCI Shanghai Development Co., Ltd. Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (CAS No. 64443–05–6) was purchased from Adamas Reagent Co., Ltd. Rb<sub>2</sub>CO<sub>3</sub> was purchased from Shanghai Maclin Biochemical Co., Ltd, and pretreated prior to use by heating at 100 °C under reduced pressure for 2 h. K<sub>2</sub>CO<sub>3</sub> was purchased from Shanghai Titan Scientific Co., Ltd, and pretreated prior to use by heating at 100 °C under reduced pressure for 2 h. NaOTMS and <sup>t</sup>BuOLi were purchased from Shanghai Maclin Biochemical Co., Ltd. Anhydrous benzene and 1,4-dioxane were purchased from Beijing J&K Scientific Co., Ltd. Anhydrous diethyl ether (Et<sub>2</sub>O) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd, which was pretreated by 4 Å molecular sieve and distilled after refluxing with sodium and benzophenone prior to use.

Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm), iodine on silica gel or basic KMnO<sub>4</sub> indicator. NMR spectra were recorded on Bruker DRX-400 spectrometer at 400 MHz for <sup>1</sup>H NMR, 100 MHz for <sup>13</sup>C NMR, 162 MHz for <sup>31</sup>P NMR and 376 MHz for <sup>19</sup>F NMR, respectively, in CDCl<sub>3</sub> with tetramethylsilane (TMS) as an internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for <sup>1</sup>H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet; m, multiplet; br, broad), coupling constant (Hz), integration. Data for <sup>13</sup>C NMR were reported in terms of chemical shift (δ, ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS. Enantiomeric excess (ee) was determined using SHIMADZU LC-20AD with SPD-20AV detector (at appropriate wavelength). Column conditions were documented in the experimental section that followed. X-ray diffraction was measured on a 'Bruker APEX-II CCD' diffractometer with Cu-Kα radiation.

## General procedure for the synthesis of chiral ligands

The synthesis of **L7** was outlined as the general procedure, and **L8–L13** were prepared by analogy.



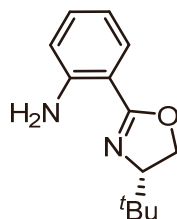
According to the modified literature procedure.<sup>[S1]</sup> To a solution of 2-aminobenzonitrile (4.72 g, 40 mmol, 1.0 equiv) and (*S*)-*tert*-leucinol (5.16 g, 44 mmol, 1.1 equiv) in chlorobenzene (100 mL) was added  $\text{ZnCl}_2$  (10.91 g, 80 mmol, 2.0 equiv) at room temperature. The resulting mixture was stirred at 130 °C for 24 h. Upon completion (monitored by TLC), the reaction mixture was cooled to approximate 60 °C and quenched with water (20 mL) and tetramethyl ethylenediamine (TMEDA, 20 mL). The resulting mixture was then stirred at 60 °C for 30 min before being cooled to room temperature. Then saturated  $\text{NH}_4\text{Cl}$  (40 mL) was added under stirring until the mixture becomes clear. The reaction mixture was extracted with EtOAc (100 mL  $\times$  2). The combined organic layers were washed with water (200 mL) and brine (200 mL  $\times$  2), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to give **S-1** as a white solid (8.12 g, 93% yield).

To a solution of **S-1** (4.37 g, 20 mmol, 1.0 equiv) in toluene (60 mL) was added  $\text{P}_2\text{S}_5$  (6.67 g, 30 mmol, 1.5 equiv) at room temperature. The reaction mixture was stirred at 110 °C for 12 h. Upon completion (monitored by TLC), the mixture was diluted with EtOAc (40 mL) and quenched with NaOH (2 M, 20 mL). The resulting mixture was stirred at room temperature for 30 min and extracted with EtOAc (50 mL  $\times$  2). The combined organic layers were washed with water (100 mL) and brine (100 mL  $\times$  2), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to give **S-2** as a yellow oil (2.82 g, 60% yield).

To a solution of **S-2** (1.17 g, 5.0 mmol, 1.0 equiv), picolinic acid (0.74 g, 6.0 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 122.2 mg, 1.0 mmol, 20 mol %) in anhydrous DCM (20 mL) was added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 1.44 g, 7.5 mmol, 1.5 equiv) in portions at room temperature. The reaction mixture was then stirred at room temperature for 24 h. Upon completion (monitored by TLC), the mixture was quenched with water (20 mL) and extracted with DCM (20 mL  $\times$  2). The combined organic layers were washed with brine (50 mL  $\times$  2),

dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) to give **L7** as a colorless oil, which was slowly solidified during storage at room temperature (1.62 g, 95% yield).

**(S)-2-(4-(*tert*-butyl)-4,5-dihydrooxazol-2-yl)aniline (S-1)**



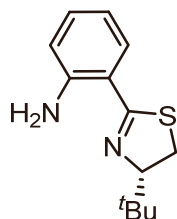
**S-1** is a known compound.<sup>[S2]</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 (dd,  $J$  = 7.9, 1.7 Hz, 1H), 7.24 – 7.15 (m, 1H), 6.70 (d,  $J$  = 8.2 Hz, 1H), 6.68 – 6.61 (m, 1H), 6.15 (br s, 2H), 4.28 – 4.19 (m, 1H), 4.15 – 4.04 (m, 2H), 0.93 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  163.4, 148.6, 131.8, 129.5, 115.9, 115.6, 109.1, 76.3, 66.8, 33.8, 25.9.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>13</sub>H<sub>19</sub>N<sub>2</sub>O [M + H]<sup>+</sup> 219.1492, found 219.1488.

**(S)-2-(4-(*tert*-butyl)-4,5-dihydrothiazol-2-yl)aniline (S-2)**

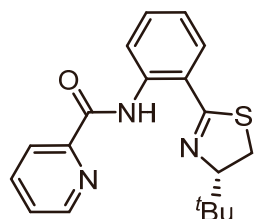


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 (dd,  $J$  = 7.9, 1.5 Hz, 1H), 7.16 (ddd,  $J$  = 8.4, 7.1, 1.5 Hz, 1H), 6.72 – 6.61 (m, 2H), 6.24 (br s, 2H), 4.39 (dd,  $J$  = 10.8, 8.6 Hz, 1H), 3.20 (dd,  $J$  = 10.8, 8.6 Hz, 1H), 3.06 (t,  $J$  = 10.8 Hz, 1H), 1.05 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  167.2, 147.6, 132.1, 131.3, 116.1, 115.9, 115.0, 88.1, 35.0, 32.2, 26.9.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>13</sub>H<sub>19</sub>N<sub>2</sub>S [M + H]<sup>+</sup> 235.1263, found 235.1258.

**(S)-N-(2-(4-(*tert*-butyl)-4,5-dihydrothiazol-2-yl)phenyl)picolinamide (L7)**



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  13.20 (br s, 1H), 8.98 (dd,  $J$  = 8.4, 1.2 Hz, 1H), 8.65 – 8.57 (m, 1H), 8.33 – 8.24 (m, 1H), 7.87 (td,  $J$  = 7.7, 1.7 Hz, 1H), 7.70 (dd,  $J$  = 7.8, 1.6

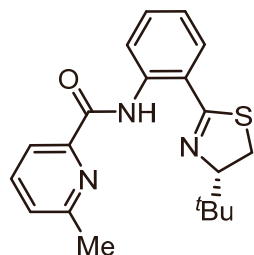


Hz, 1H), 7.53 – 7.39 (m, 2H), 7.15 (td,  $J = 7.6, 1.2$  Hz, 1H), 4.54 (dd,  $J = 11.0, 8.6$  Hz, 1H), 3.27 (dd,  $J = 11.0, 8.6$  Hz, 1H), 3.15 (t,  $J = 11.0$  Hz, 1H), 1.17 (s, 9H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.5, 164.2, 150.9, 148.1, 137.9, 137.2, 131.6, 131.5, 126.1, 123.1, 122.9, 121.0, 120.8, 89.1, 35.2, 32.6, 26.9.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{22}\text{N}_3\text{OS}$   $[\text{M} + \text{H}]^+$  340.1478, found 340.1471.

**(S)-N-(2-(4-(*tert*-butyl)-4,5-dihydrothiazol-2-yl)phenyl)-6-methylpicolinamide (L8)**



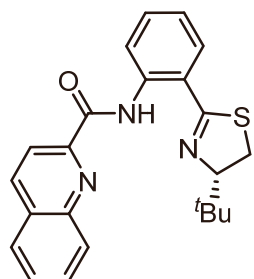
According to the general procedure, **L8** was prepared as a white solid (1.61 g, 91% yield in the final step).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.85 (br s, 1H), 8.86 – 8.75 (m, 1H), 8.06 (d,  $J = 7.7$  Hz, 1H), 7.75 (t,  $J = 7.7$  Hz, 1H), 7.67 (dd,  $J = 7.9, 1.6$  Hz, 1H), 7.52 – 7.42 (m, 1H), 7.30 (d,  $J = 7.6$  Hz, 1H), 7.19 – 7.09 (m, 1H), 4.66 (t,  $J = 8.8$  Hz, 1H), 3.31 (dd,  $J = 11.0, 8.8$  Hz, 1H), 3.21 (dd,  $J = 11.0, 8.8$  Hz, 1H), 2.65 (s, 3H), 0.99 (s, 9H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 164.7, 157.3, 150.9, 137.9, 137.3, 131.5, 131.4, 125.9, 123.1, 121.3, 121.0, 120.4, 88.5, 35.8, 32.2, 26.7, 24.7.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{24}\text{N}_3\text{OS}$   $[\text{M} + \text{H}]^+$  354.1635, found 354.1627.

**(S)-N-(2-(4-(*tert*-butyl)-4,5-dihydrothiazol-2-yl)phenyl)quinoline-2-carboxamide (L9)**



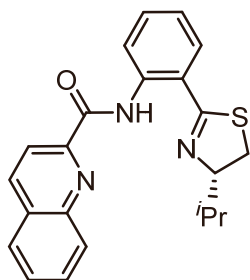
According to the general procedure, **L9** was prepared as a slightly yellow oil, which was slowly solidified during storage at room temperature (1.85 g, 95% yield in the final step).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  13.20 (br s, 1H), 8.89 (dd,  $J = 8.4, 1.2$  Hz, 1H), 8.37 – 8.30 (m, 2H), 8.21 (d,  $J = 8.5$  Hz, 1H), 7.89 (dd,  $J = 8.1, 1.4$  Hz, 1H), 7.79 (ddd,  $J = 8.5, 6.9, 1.5$  Hz, 1H), 7.71 (dd,  $J = 7.9, 1.6$  Hz, 1H), 7.63 (ddd,  $J = 8.2, 6.9, 1.2$  Hz, 1H), 7.55 – 7.47 (m, 1H), 7.17 (td,  $J = 7.8, 1.2$  Hz, 1H), 4.72 (t,  $J = 9.0$  Hz, 1H), 3.33 (dd,  $J = 11.0, 9.0$  Hz, 1H), 3.22 (dd,  $J = 11.0, 9.0$  Hz, 1H), 0.95 (s, 9H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 164.7, 151.4, 146.5, 138.0, 137.4, 131.6, 131.5, 130.3, 129.7, 129.3, 127.9, 127.8, 123.2, 121.2, 120.9, 119.6, 88.6, 35.7, 32.2, 26.8.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{23}\text{H}_{24}\text{N}_3\text{OS}$   $[\text{M} + \text{H}]^+$  390.1635, found 390.1627.

**(S)-N-(2-(4-isopropyl-4,5-dihydrothiazol-2-yl)phenyl)quinoline-2-carboxamide (L10)**



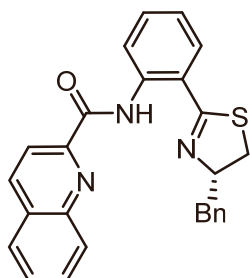
According to the general procedure, **L10** was prepared as a white solid (1.74 g, 93% yield in the final step).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 13.74 (br s, 1H), 8.99 (d, *J* = 8.4, Hz, 1H), 8.41 – 8.29 (m, 2H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.83 – 7.75 (m, 1H), 7.70 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.55 – 7.46 (m, 1H), 7.20 – 7.12 (m, 1H), 4.91 (ddd, *J* = 9.0, 7.8, 5.7 Hz, 1H), 3.39 (dd, *J* = 10.9, 9.0 Hz, 1H), 3.18 (dd, *J* = 10.9, 7.8 Hz, 1H), 2.43 – 2.29 (m, *J* = 6.6 Hz, 1H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 167.3, 164.5, 151.2, 146.6, 138.3, 137.4, 131.7, 131.6, 129.9, 129.8, 129.3, 127.9, 127.8, 123.0, 120.8, 120.5, 119.5, 84.4, 32.9, 32.8, 19.7, 18.1.

**HRMS** (ESI) *m/z* calcd. for C<sub>22</sub>H<sub>22</sub>N<sub>3</sub>OS [M + H]<sup>+</sup> 376.1478, found 376.1470.

**(S)-N-(2-(4-benzyl-4,5-dihydrothiazol-2-yl)phenyl)quinoline-2-carboxamide (L11)**



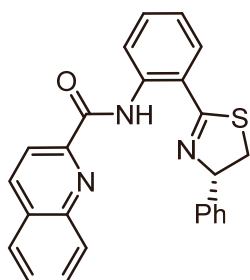
According to the general procedure, **L11** was prepared as a white solid (1.93 g, 91% yield in the final step).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 14.06 (br s, 1H), 9.06 (d, *J* = 8.4 Hz, 1H), 8.43 – 8.29 (m, 2H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.80 – 7.68 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.30 – 7.05 (m, 6H), 5.39 – 5.28 (m, 1H), 3.48 (dd, *J* = 13.7, 4.7 Hz, 1H), 3.32 (dd, *J* = 11.0, 8.3 Hz, 1H), 3.17 (dd, *J* = 11.0, 5.7 Hz, 1H), 2.93 (dd, *J* = 13.7, 9.5 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 168.5, 164.4, 151.0, 146.6, 138.5, 137.9, 137.4, 132.0, 131.9, 129.9, 129.8, 129.3, 128.5, 127.9, 127.8, 126.5, 123.0, 120.6, 120.1, 119.4, 79.1, 40.1, 35.4.

**HRMS** (ESI) *m/z* calcd. for C<sub>26</sub>H<sub>22</sub>N<sub>3</sub>OS [M + H]<sup>+</sup> 424.1478, found 424.1471.

**(S)-N-(2-(4-phenyl-4,5-dihydrothiazol-2-yl)phenyl)quinoline-2-carboxamide (L12)**



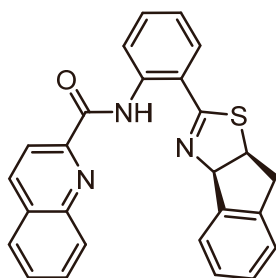
According to the general procedure, **L12** was prepared as a white solid (1.84 g, 90% yield in the final step).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 14.06 (br s, 1H), 9.11 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 8.5 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.42 (m, 4H), 7.37 – 7.26 (m, 4H), 7.23 – 7.16 (m, 1H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.00 (dd, *J* = 10.7, 8.5 Hz, 1H), 3.76 (dd, *J* = 10.7, 8.5 Hz, 1H), 3.23 (t, *J* = 10.7 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.1, 164.5, 150.4, 146.4, 142.0, 138.7, 137.2, 132.3, 132.2, 129.9, 129.5, 128.9, 128.8, 127.8, 127.7, 127.2, 126.9, 123.0, 120.7, 120.1, 119.0, 81.7, 40.0.

**HRMS** (ESI) *m/z* calcd. for C<sub>25</sub>H<sub>20</sub>N<sub>3</sub>OS [M + H]<sup>+</sup> 410.1322, found 410.1313.

**N-(2-(((3aR,8aS)-3a,8a-dihydro-8H-indeno[1,2-d]thiazol-2-yl)phenyl)quinoline-2-carboxamide (L13)**



According to the general procedure, **L13** was prepared as a white solid (1.83 g, 87% yield in the final step).

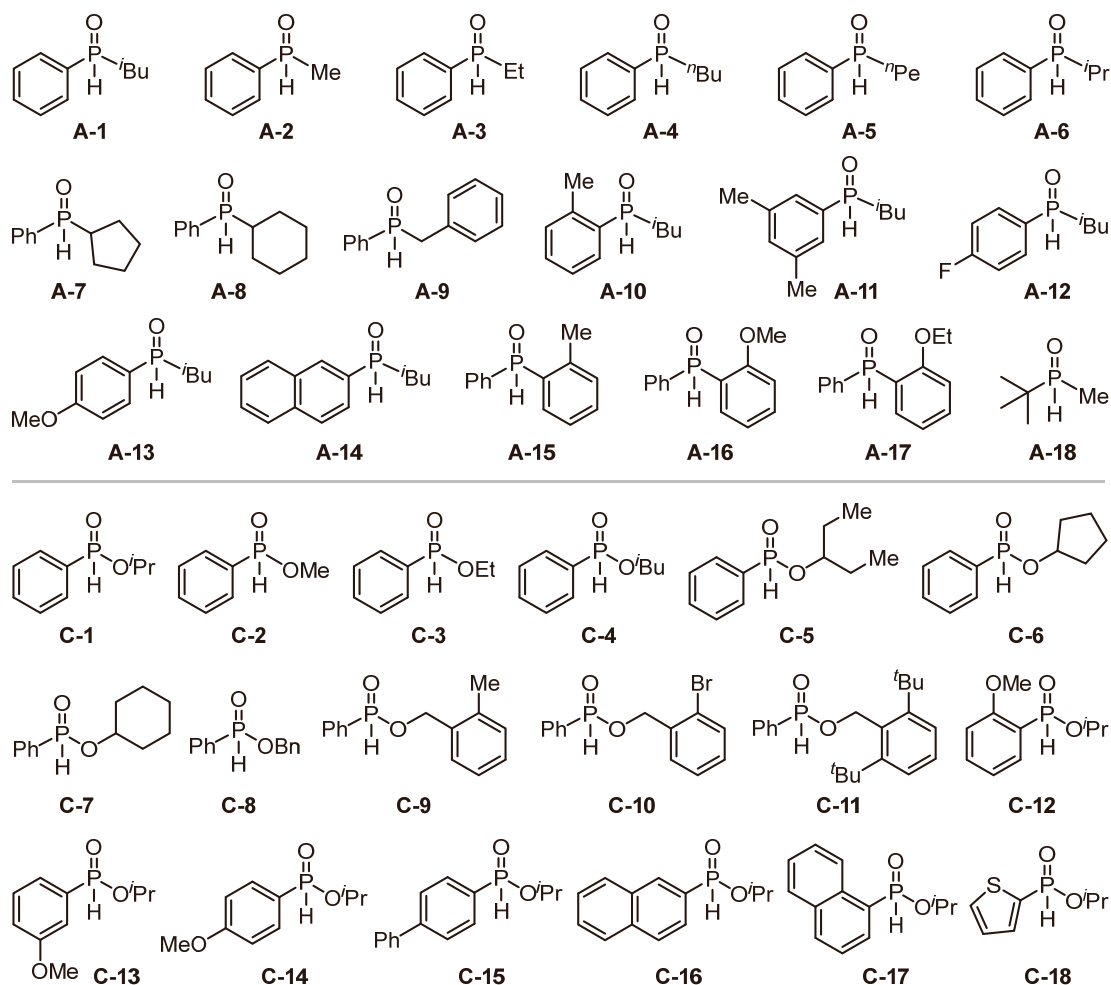
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 14.32 (br s, 1H), 9.06 (d, *J* = 8.4 Hz, 1H), 8.48 – 8.30 (m, 3H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.69 – 7.58 (m, 2H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.31 – 7.18 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 4.88 – 4.77 (m, 1H), 3.63 (dd, *J* = 17.2, 7.4 Hz, 1H), 3.39 (d, *J* = 17.2 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 168.6, 164.3, 151.1, 146.7, 141.0, 139.6, 138.7, 137.5, 132.0, 131.9, 130.2, 130.0, 129.4, 128.5, 128.0, 127.9, 127.5, 125.7, 125.1, 122.9, 120.5, 119.9, 119.5, 88.4, 50.5, 39.6.

**HRMS** (ESI) *m/z* calcd. for C<sub>26</sub>H<sub>20</sub>N<sub>3</sub>OS [M + H]<sup>+</sup> 422.1322, found 422.1314.

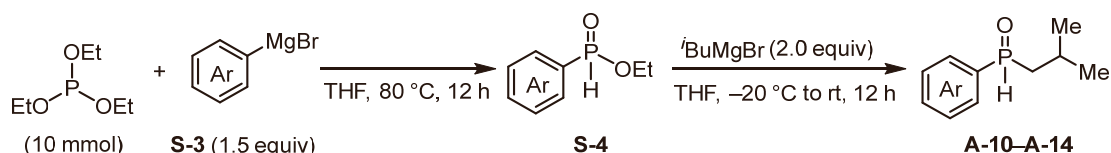
## General procedure for the synthesis of substrates

### 1. The structures and synthesis of racemic SPOs and *H*-phosphinates



The racemic secondary phosphine oxides **A-1–A-9** and **A-15–A-18**, and *H*-phosphinates **C-1–C-18** were prepared according to the literature procedure, and the analytical data were consistent with those reported in the literature.<sup>[S3–S7]</sup>

#### General procedure for the synthesis of **A-10–A-14**

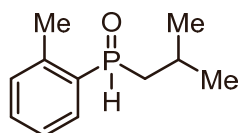


According to the modified literature procedure.<sup>[S8]</sup> To a solution of the freshly prepared Grignard reagent **S-3** (15 mmol, 1.5 equiv) in anhydrous THF (40 mL) was added triethyl phosphite (1.71 mL, 10 mmol, 1.0 equiv) at room temperature. The resulting mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was quenched with HCl (1 M) to approximate pH = 2 before being filtered through a pad of celite. The filtrate was concentrated under reduced pressure to

remove the organic solvent. Then the remaining aqueous phase was diluted with DCM (50 mL), washed with saturated water (50 mL) and brine (50 mL  $\times$  2). The organic layer was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (DCM/MeOH 80:1) to afford the pure product **S-4** as a colorless oil.

To a solution of above prepared **S-4** in anhydrous THF (20 mL) was dropwise added *t*BuMgBr (2.0 M solution in THF, 10 mL, 20 mmol, 2.0 equiv) at  $-20\text{ }^{\circ}\text{C}$  under argon atmosphere. Then the resulting mixture was warmed to room temperature and stirred for 12 h. Upon completion (monitored by TLC), the reaction mixture was quenched by saturated NH<sub>4</sub>Cl (20 mL) and concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (20 mL  $\times$  3). The combined organic layers were washed with brine (50 mL  $\times$  2), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 1:1) to give the desired product.

#### **isobutyl(*o*-tolyl)phosphine oxide (A-10)**



According to the general procedure, **A-10** was prepared as a colorless oil (0.72 g, 37% yield over two steps).

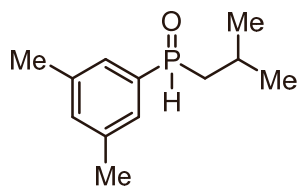
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 (ddd,  $J = 15.1, 7.6, 1.5$  Hz, 1H), 7.56 (ddd,  $J = 461.8, 5.9, 2.0$  Hz, 1H), 7.39 – 7.32 (m, 1H), 7.27 – 7.20 (m, 1H), 7.18 (dd,  $J = 7.7, 4.7$  Hz, 1H), 2.47 (s, 3H), 2.16 – 2.03 (m, 1H), 2.03 – 1.90 (m, 1H), 1.79 – 1.68 (m, 1H), 1.01 (d,  $J = 6.6$  Hz, 3H), 0.99 (dd,  $J = 6.6, 1.0$  Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.7 (d,  $J = 11.4$  Hz), 132.8 (d,  $J = 9.1$  Hz), 132.3 (d,  $J = 2.6$  Hz), 131.1 (d,  $J = 9.1$  Hz), 129.3 (d,  $J = 96.1$  Hz), 125.4 (d,  $J = 11.9$  Hz), 38.7 (d,  $J = 67.1$  Hz), 24.2 (d,  $J = 10.3$  Hz), 23.4 (d,  $J = 8.6$  Hz), 23.2 (d,  $J = 3.7$  Hz), 21.3 (d,  $J = 3.2$  Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  25.2.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>11</sub>H<sub>18</sub>OP [M + H]<sup>+</sup> 197.1090, found 197.1090.

#### **(3,5-dimethylphenyl)(isobutyl)phosphine oxide (A-11)**



According to the general procedure, **A-11** was prepared as a colorless oil (0.98 g, 47% yield over two steps).

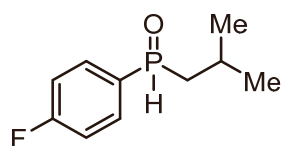
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.51 (ddd, *J* = 461.7, 5.8, 1.8 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.18 (s, 1H), 2.37 (s, 6H), 2.25 – 2.12 (m, 1H), 2.05 – 1.92 (m, 1H), 1.85 – 1.75 (m, 1H), 1.12 (d, *J* = 6.6 Hz, 3H), 1.07 (dd, *J* = 6.6, 1.1 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 138.6 (d, *J* = 13.0 Hz), 134.0 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 96.9 Hz), 127.2 (d, *J* = 10.9 Hz), 39.3 (d, *J* = 67.4 Hz), 24.2 (d, *J* = 10.3 Hz), 23.4 (d, *J* = 8.2 Hz), 23.1 (d, *J* = 3.7 Hz), 21.1.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 25.4.

**HRMS** (ESI) *m/z* calcd. for C<sub>12</sub>H<sub>20</sub>OP [M + H]<sup>+</sup> 211.1246, found 211.1245.

#### (4-fluorophenyl)(isobutyl)phosphine oxide (**A-12**)



According to the general procedure, **A-12** was prepared as a colorless oil (0.89 g, 45% yield over two steps).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.80 – 7.65 (m, 2H), 7.59 (ddd, *J* = 465.2, 5.7, 1.7 Hz, 1H), 7.27 – 7.14 (m, 2H), 2.26 – 2.10 (m, 1H), 2.05 – 1.92 (m, 1H), 1.89 – 1.77 (m, 1H), 1.12 (d, *J* = 6.6 Hz, 3H), 1.07 (d, *J* = 6.6 Hz, 3H).

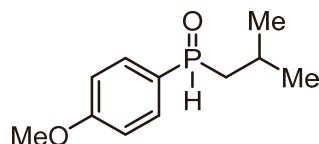
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 165.0 (dd, *J* = 253.5, 3.3 Hz), 132.0 (dd, *J* = 12.2, 8.8 Hz), 127.2 (dd, *J* = 98.5, 3.4 Hz), 116.1 (dd, *J* = 21.6, 13.4 Hz), 39.4 (d, *J* = 68.2 Hz), 24.1 (d, *J* = 10.8 Hz), 23.3 (d, *J* = 8.6 Hz), 23.2 (d, *J* = 3.8 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 23.5.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -106.1.

**HRMS** (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>13</sub>FOP [M + H]<sup>+</sup> 201.0839, found 201.0838.

#### isobutyl(4-methoxyphenyl)phosphine oxide (**A-13**)



According to the general procedure, **A-13** was prepared as a colorless oil (0.71 g, 33% yield over two steps).

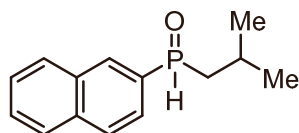
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.55 (dd, *J* = 12.6, 8.7 Hz, 2H), 7.45 (ddd, *J* = 460.9, 5.5, 1.9 Hz, 1H), 6.93 (dd, *J* = 8.7, 2.1 Hz, 2H), 3.76 (s, 3H), 2.15 – 2.00 (m, 1H), 1.95 – 1.81 (m, 1H), 1.79 – 1.67 (m, 1H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.96 (dd, *J* = 6.6, 1.0 Hz, 3H).

**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.2 (d,  $J = 3.0$  Hz), 132.8 (d,  $J = 11.5$  Hz), 122.1 (d,  $J = 103.0$  Hz), 114.5 (d,  $J = 13.5$  Hz), 55.3, 39.5 (d,  $J = 68.3$  Hz), 24.2 (d,  $J = 10.3$  Hz), 23.5 (d,  $J = 8.6$  Hz), 23.4 (d,  $J = 3.7$  Hz).

**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )  $\delta$  24.2.

**HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{11}\text{H}_{18}\text{O}_2\text{P}$   $[\text{M} + \text{H}]^+$  213.1039, found 213.1037.

**isobutyl(naphthalen-2-yl)phosphine oxide (A-14)**



According to the general procedure, **A-14** was prepared as a white solid (1.24 g, 53% yield over two steps).

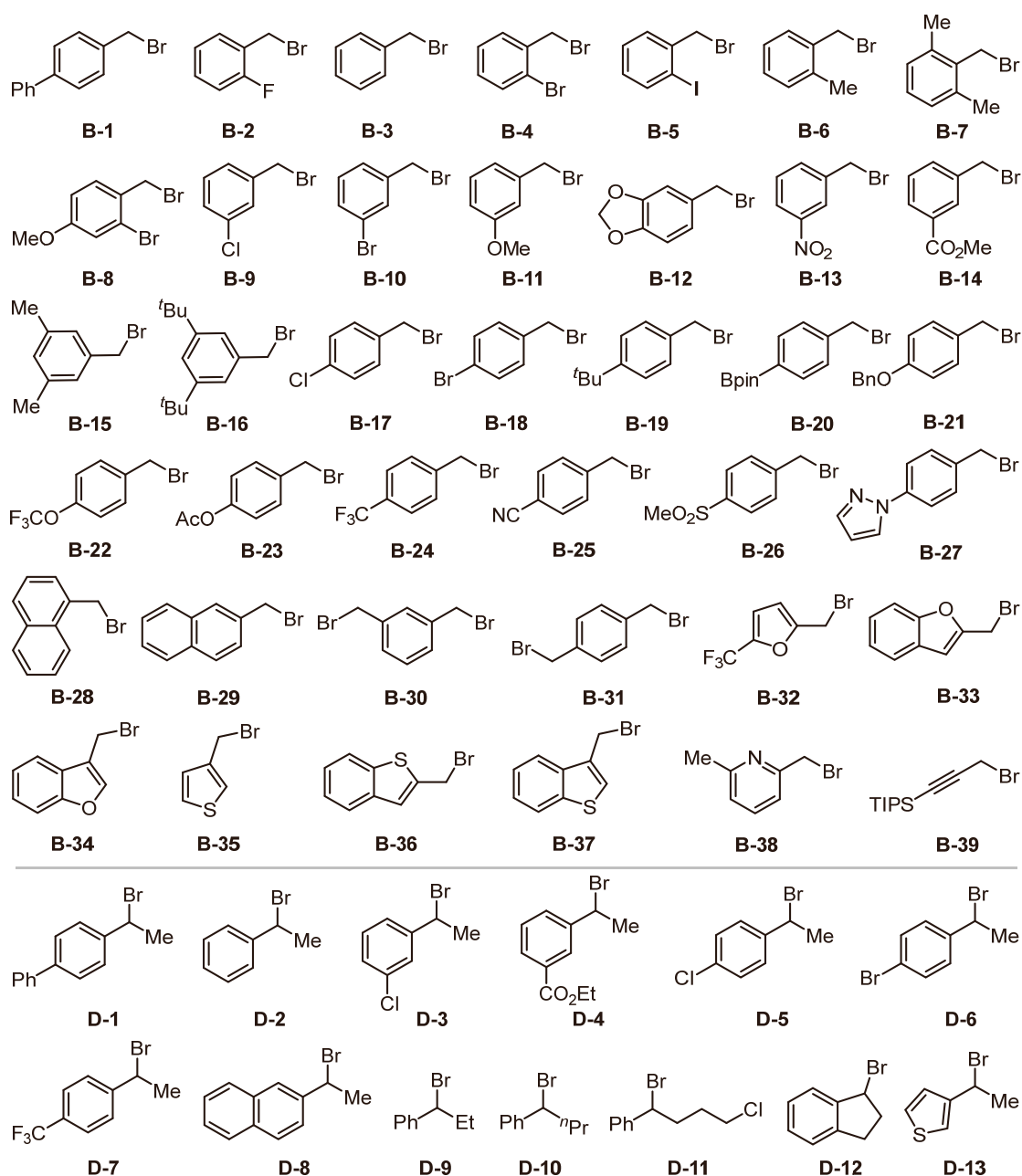
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 – 8.29 (m, 1H), 8.00 – 7.86 (m, 3H), 7.71 (ddd,  $J = 463.2, 5.5, 1.8$  Hz, 1H), 7.67 – 7.55 (m, 3H), 2.29 – 2.15 (m, 1H), 2.12 – 2.00 (m, 1H), 1.97 – 1.87 (m, 1H), 1.14 (d,  $J = 6.6$  Hz, 3H), 1.07 (dd,  $J = 6.6, 1.1$  Hz, 3H).

**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  134.9 (d,  $J = 2.6$  Hz), 132.6 (d,  $J = 13.2$  Hz), 131.9 (d,  $J = 9.9$  Hz), 128.8 (d,  $J = 12.3$  Hz), 128.5 (d,  $J = 96.6$  Hz), 128.7, 128.2, 127.9, 127.1, 124.2 (d,  $J = 11.8$  Hz), 39.6 (d,  $J = 67.6$  Hz), 24.4 (d,  $J = 10.9$  Hz), 23.6 (d,  $J = 8.8$  Hz), 23.5 (d,  $J = 4.0$  Hz).

**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )  $\delta$  24.6.

**HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{18}\text{OP}$   $[\text{M} + \text{H}]^+$  233.1090, found 233.1088.

## 2. The structures of alkyl bromides

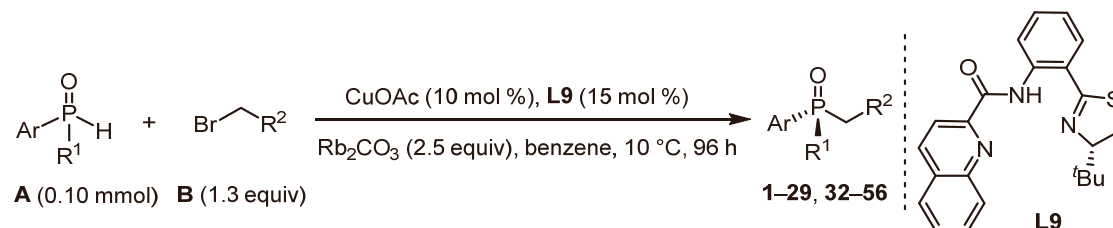


The (hetero)benzyl bromides **B-1–B-38** and **D-1–D-13** are commercially available, or can be readily prepared following the literature procedure.<sup>[S9,S10]</sup> Propargyl bromide **B-39** was prepared according to a known method,<sup>[S11]</sup> and the analytical data were consistent with those reported in the literature.



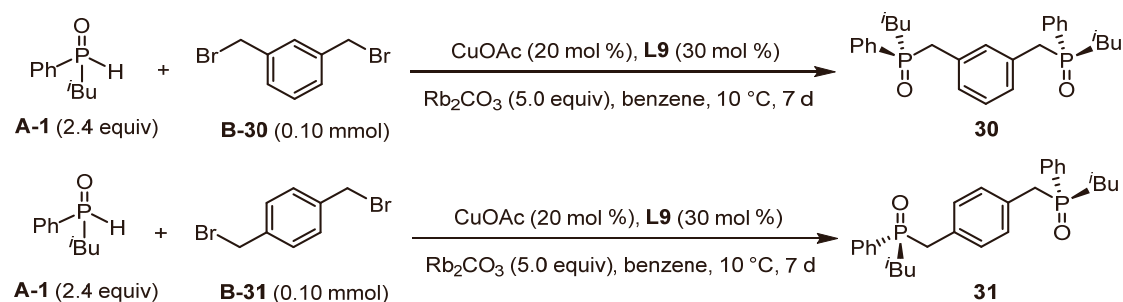
## General procedure for the synthesis of products

### General procedure A



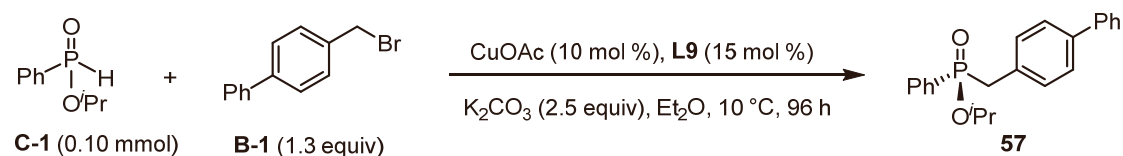
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (1.2 mg, 0.010 mmol, 10 mol %), **L9** (5.8 mg, 0.015 mmol, 15 mol %), Rb<sub>2</sub>CO<sub>3</sub> (57.7 mg, 0.25 mmol, 2.5 equiv) and anhydrous benzene (2.0 mL). The mixture was stirred at room temperature for 30 min. After that, racemic secondary phosphine oxide **A** (0.10 mmol, 1.0 equiv) and bromide **B** (0.13 mmol, 1.3 equiv) were sequentially added into the mixture. The resulting mixture was stirred at 10 °C for 96 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL) and DCM (5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: DCM/MeOH 100:1–50:1) to afford the desired product.

### General procedure B



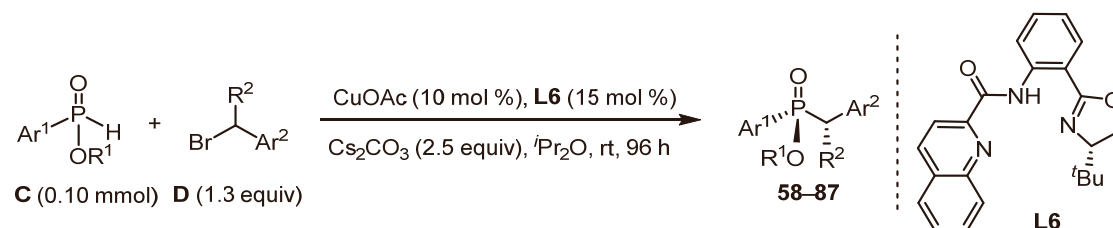
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (2.5 mg, 0.020 mmol, 20 mol %), **L9** (11.7 mg, 0.030 mmol, 30 mol %), Rb<sub>2</sub>CO<sub>3</sub> (115.5 mg, 0.50 mmol, 5.0 equiv) and anhydrous benzene (4.0 mL). The mixture was stirred at room temperature for 30 min. After that, racemic secondary phosphine oxide **A-1** (43.7 mg, 0.24 mmol, 2.4 equiv) and bromide **B-30** or **B-31** (26.4 mg, 0.10 mmol, 1.0 equiv) were sequentially added into the mixture. The resulting mixture was stirred at 10 °C for 7 d. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL) and DCM (5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: DCM/MeOH 50:1–25:1) to afford the product **30** or **31**.

### General procedure C



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (1.2 mg, 0.010 mmol, 10 mol %), **L9** (5.8 mg, 0.015 mmol, 15 mol %), K<sub>2</sub>CO<sub>3</sub> (34.6 mg, 0.25 mmol, 2.5 equiv) and anhydrous Et<sub>2</sub>O (2.0 mL). The mixture was stirred at room temperature for 30 min. After that, racemic *H*-phosphinate **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and bromide **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were sequentially added into the mixture. The resulting mixture was stirred at 10 °C for 96 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL) and DCM (5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: DCM/MeOH 200:1–120:1) to afford the product **57**.

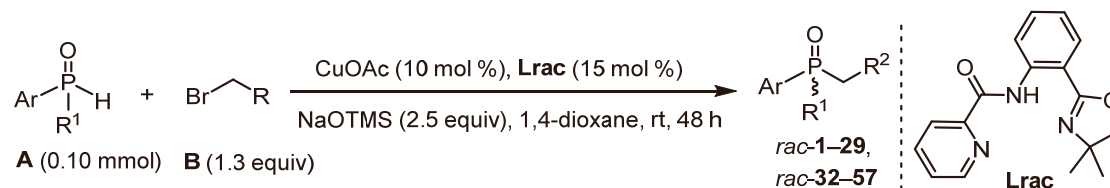
### General procedure D



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (1.2 mg, 0.010 mmol, 10 mol %), **L6** (5.6 mg, 0.015 mmol, 15 mol %), Cs<sub>2</sub>CO<sub>3</sub> (81.5 mg, 0.25 mmol, 2.5 equiv) and anhydrous *t*Pr<sub>2</sub>O (2.0 mL). The mixture was stirred at room temperature for 30 min. After that, racemic *H*-phosphinate **C** (0.10 mmol, 1.0 equiv) and bromide **D** (0.13 mmol, 1.3 equiv) were sequentially added into the mixture. The resulting mixture was stirred at room temperature for 96 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL) and DCM (5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: hexane/EA 4:1–2:1) to afford the desired product.

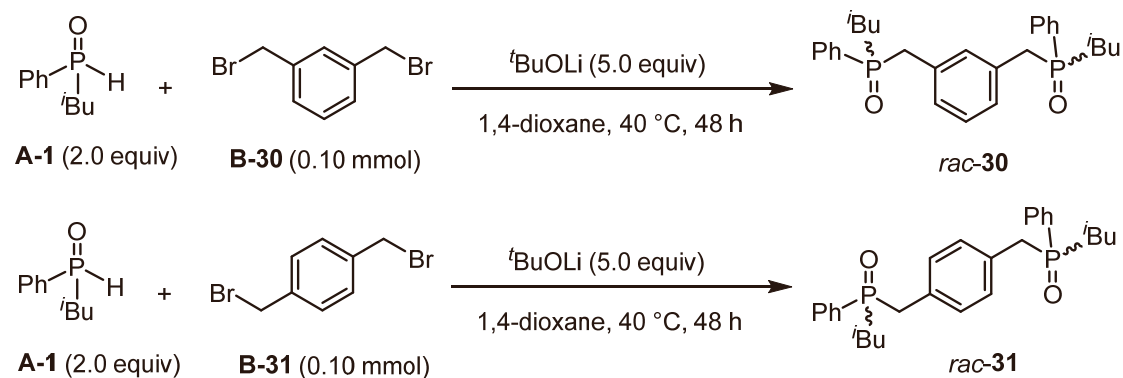
## General procedure for the synthesis of racemates

### General procedure E



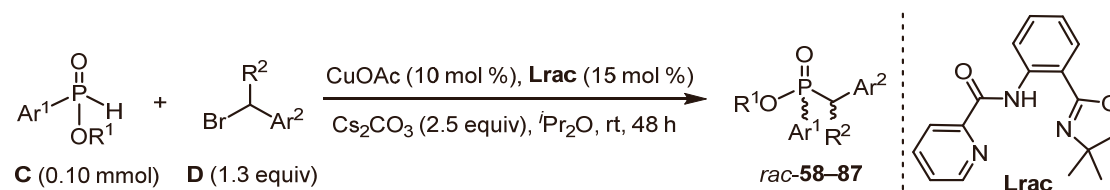
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (1.2 mg, 0.010 mmol, 10 mol %), **Lrac** (4.4 mg, 0.015 mmol, 15 mol %), NaOTMS (28.0 mg, 0.25 mmol, 2.5 equiv) and anhydrous 1,4-dioxane (2.0 mL). The mixture was stirred at room temperature for 30 min. After that, racemic secondary phosphine oxide **A** (0.10 mmol, 1.0 equiv) and bromide **B** (0.13 mmol, 1.3 equiv) were sequentially added into the mixture. The resulting mixture was stirred at room temperature for 48 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL) and DCM (5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: DCM/MeOH 100:1–50:1) to afford the racemic product.

### General procedure F



To a mixture of racemic secondary phosphine oxide **A-1** (36.4 mg, 0.20 mmol, 2.0 equiv) and bromide **B-30** or **B-31** (26.4 mg, 0.10 mmol, 1.0 equiv) in anhydrous 1,4-dioxane (2.0 mL) was added *t*BuOLi (40.0 mg, 0.50 mmol, 5.0 equiv). The reaction mixture was then stirred at 40 °C for 48 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL) and DCM (5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: DCM/MeOH 50:1–25:1) to afford the *rac-30* or *rac-31*.

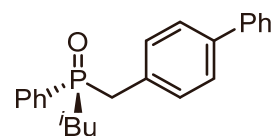
## General procedure G



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (1.2 mg, 0.010 mmol, 10 mol %), **Lrac** (4.4 mg, 0.015 mmol, 15 mol %), Cs<sub>2</sub>CO<sub>3</sub> (81.5 mg, 0.25 mmol, 2.5 equiv) and anhydrous *i*Pr<sub>2</sub>O (2.0 mL). The mixture was stirred at room temperature for 30 min. After that, racemic *H*-phosphinate **C** (0.10 mmol, 1.0 equiv) and bromide **D** (0.13 mmol, 1.3 equiv) were sequentially added into the mixture. The resulting mixture was stirred at room temperature for 48 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL) and DCM (5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: hexane/EA 4:1–2:1) to afford the racemic product.

## Analytical data for products

### (*R*)-([1,1'-biphenyl]-4-ylmethyl)(isobutyl)(phenyl)phosphine oxide (**1**)



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **1** as a white solid (31.2 mg, 90% yield, 96% ee).

**HPLC** analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 10.139 min,  $t_R$  (minor) = 18.347 min.

$[\alpha]_D^{25}$  = -46.2 (*c* 1.0, CHCl<sub>3</sub>).

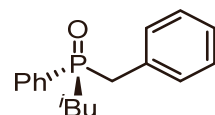
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.66 – 7.59 (m, 2H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.53 – 7.39 (m, 7H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.14 (dd, *J* = 8.1, 2.2 Hz, 2H), 3.32 (d, *J* = 14.3 Hz, 2H), 2.12 – 1.93 (m, 2H), 1.91 – 1.81 (m, 1H), 1.05 (d, *J* = 6.4 Hz, 3H), 0.87 (d, *J* = 6.4 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.6 (d, *J* = 1.3 Hz), 139.5 (d, *J* = 3.1 Hz), 132.4 (d, *J* = 92.4 Hz), 131.5 (d, *J* = 2.9 Hz), 130.8 (d, *J* = 7.8 Hz), 130.7 (d, *J* = 8.6 Hz), 130.2 (d, *J* = 4.9 Hz), 128.7, 128.4 (d, *J* = 11.2 Hz), 127.2, 127.1 (d, *J* = 2.7 Hz), 126.9, 39.6 (d, *J* = 62.3 Hz), 36.9 (d, *J* = 68.2 Hz), 24.6 (d, *J* = 9.0 Hz), 24.5 (d, *J* = 8.5 Hz), 23.4 (d, *J* = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  36.9.

**HRMS** (ESI) *m/z* calcd. for C<sub>23</sub>H<sub>26</sub>OP [M + H]<sup>+</sup> 349.1716, found 349.1713.

### (*R*)-benzyl(isobutyl)(phenyl)phosphine oxide (**2**)



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-3** (22.2 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **2** as a white solid (21.1 mg, 78% yield, 95% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 220 nm),  $t_R$  (major) = 14.855 min,  $t_R$  (minor) = 19.448 min.

$[\alpha]_D^{25}$  = -20.8 (*c* 1.0, CHCl<sub>3</sub>).

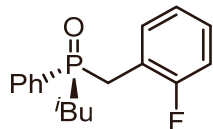
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 – 7.54 (m, 2H), 7.52 – 7.47 (m, 1H), 7.45 – 7.39 (m, 2H), 7.25 – 7.17 (m, 3H), 7.09 – 7.03 (m, 2H), 3.30 (t, *J* = 15.2 Hz, 1H), 3.26 (t, *J* = 15.2 Hz, 1H), 2.10 – 1.89 (m, 2H), 1.87 – 1.78 (m, 1H), 1.03 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 6.5 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  132.3 (d, *J* = 92.6 Hz), 131.8 (d, *J* = 7.6 Hz), 131.5 (d, *J* = 3.0 Hz), 130.7 (d, *J* = 8.7 Hz), 129.8 (d, *J* = 5.0 Hz), 128.4 (d, *J* = 2.5 Hz), 128.3 (d, *J* = 11.3 Hz), 126.7 (d, *J* = 3.0 Hz), 39.9 (d, *J* = 62.5 Hz), 36.8 (d, *J* = 68.4 Hz), 24.6 (d, *J* = 9.1 Hz), 24.5 (d, *J* = 8.6 Hz), 23.4 (d, *J* = 4.1 Hz).

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 37.0.

HRMS (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>22</sub>OP [M + H]<sup>+</sup> 273.1403, found 273.1392.

**(*R*)-(2-fluorobenzyl)(isobutyl)(phenyl)phosphine oxide (3)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-2** (24.6 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **3** as a white solid (23.0 mg, 79% yield, 93% ee).

HPLC analysis: Chiralpak IF (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 220 nm), *t<sub>R</sub>* (major) = 29.179 min, *t<sub>R</sub>* (minor) = 32.353 min.

[α]<sub>D</sub><sup>25</sup> = −24.4 (*c* 1.0, CHCl<sub>3</sub>).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.66 – 7.58 (m, 2H), 7.54 – 7.48 (m, 1H), 7.46 – 7.40 (m, 2H), 7.25 – 7.15 (m, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 9.1 Hz, 1H), 3.41 – 3.24 (m, 2H), 2.09 – 1.81 (m, 3H), 1.03 (d, *J* = 6.4 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H).

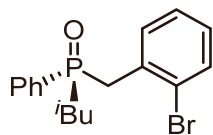
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.5 (dd, *J* = 245.2, 5.7 Hz), 132.2 (d, *J* = 93.0 Hz), 132.0 (t, *J* = 3.9 Hz), 131.6 (d, *J* = 2.9 Hz), 130.6 (d, *J* = 8.8 Hz), 128.5 (dd, *J* = 8.2, 3.1 Hz), 128.3 (d, *J* = 11.3 Hz), 124.2 (t, *J* = 3.2 Hz), 119.2 (dd, *J* = 15.5, 7.4 Hz), 115.2 (dd, *J* = 22.1, 2.5 Hz), 36.9 (d, *J* = 68.5 Hz), 32.3 (dd, *J* = 63.0, 2.2 Hz), 24.5 (d, *J* = 9.4 Hz), 24.4 (d, *J* = 8.5 Hz), 23.4 (d, *J* = 4.2 Hz).

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 37.2 (d, *J* = 3.5 Hz).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ −117.1 (d, *J* = 3.5 Hz).

HRMS (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>21</sub>FOP [M + H]<sup>+</sup> 291.1309, found 291.1395.

**(*R*)-(2-bromobenzyl)(isobutyl)(phenyl)phosphine oxide (4)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-4** (32.5 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **4** as a colorless oil (28.5 mg, 81% yield, 96% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 220 nm), *t<sub>R</sub>* (major) = 10.001 min, *t<sub>R</sub>* (minor) = 11.892 min.

[α]<sub>D</sub><sup>25</sup> = −26.6 (*c* 1.0, CHCl<sub>3</sub>).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70 – 7.64 (m, 2H), 7.55 – 7.49 (m, 2H), 7.48 – 7.40 (m, 3H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.12 – 7.05 (m, 1H), 3.66 – 3.57 (m, 1H), 3.50 – 3.40 (m, 1H), 2.02 – 1.88 (m, 3H), 1.00 (d, *J* = 6.3 Hz, 3H), 0.82 (d, *J* = 6.3 Hz, 3H).

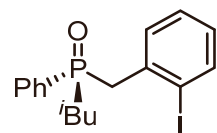
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 132.8 (d, *J* = 2.5 Hz), 132.5 (d, *J* = 93.0 Hz), 132.1 (d, *J* = 7.4 Hz), 131.8 (d, *J* = 4.1 Hz), 131.6 (d, *J* = 2.8 Hz), 130.7 (d, *J* = 9.0 Hz), 128.5 (d,

$J = 3.1$  Hz), 128.4 (d,  $J = 11.4$  Hz), 127.6 (d,  $J = 2.7$  Hz), 124.8 (d,  $J = 6.6$  Hz), 39.3 (d,  $J = 61.8$  Hz), 37.1 (d,  $J = 68.2$  Hz), 24.5 (d,  $J = 9.7$  Hz), 24.4 (d,  $J = 8.8$  Hz), 23.4 (d,  $J = 4.2$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.6.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{21}\text{BrOP}$   $[\text{M} + \text{H}]^+$  351.0508, found 351.0505.

**(*R*)-(2-iodobenzyl)(isobutyl)(phenyl)phosphine oxide (5)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-5** (38.6 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **5** as a slightly yellow oil (31.0 mg, 78% yield, 96% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda = 220$  nm),  $t_R$  (major) = 7.016 min,  $t_R$  (minor) = 8.703 min.

$[\alpha]_D^{25} = -33.7$  ( $c$  1.0,  $\text{CHCl}_3$ ).

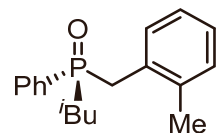
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J = 8.0$  Hz, 1H), 7.73 – 7.65 (m, 2H), 7.56 – 7.42 (m, 4H), 7.32 – 7.27 (m, 1H), 6.91 (t,  $J = 7.7$  Hz, 1H), 3.66 – 3.56 (m, 1H), 3.49 (t,  $J = 15.4$  Hz, 1H), 2.03 – 1.87 (m, 3H), 1.00 (d,  $J = 6.2$  Hz, 3H), 0.82 (d,  $J = 6.2$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.6 (d,  $J = 2.3$  Hz), 135.7 (d,  $J = 7.3$  Hz), 132.4 (d,  $J = 92.8$  Hz), 131.6 (d,  $J = 2.9$  Hz), 130.8 (d,  $J = 4.5$  Hz), 130.7 (d,  $J = 9.2$  Hz), 128.6 (d,  $J = 1.9$  Hz), 128.5 (d,  $J = 2.3$  Hz), 128.4 (d,  $J = 11.3$  Hz), 101.7 (d,  $J = 7.1$  Hz), 44.2 (d,  $J = 61.4$  Hz), 37.3 (d,  $J = 68.1$  Hz), 24.5 (d,  $J = 9.4$  Hz), 24.4 (d,  $J = 8.5$  Hz), 23.4 (d,  $J = 4.2$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.5.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{21}\text{IOP}$   $[\text{M} + \text{H}]^+$  399.0369, found 399.0380.

**(*R*)-isobutyl(2-methylbenzyl)(phenyl)phosphine oxide (6)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-6** (24.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **6** as a slightly yellow solid (24.2 mg, 85% yield, 94% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda = 220$  nm),  $t_R$  (major) = 11.163 min,  $t_R$  (minor) = 14.410 min.

$[\alpha]_D^{25} = -20.0$  ( $c$  1.0,  $\text{CHCl}_3$ ).

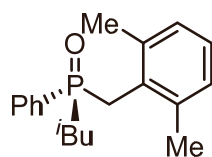
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.47 (m, 3H), 7.44 – 7.37 (m, 2H), 7.14 – 7.02 (m, 4H), 3.39 – 3.23 (m, 2H), 2.08 (d, *J* = 1.4 Hz, 3H), 2.07 – 1.94 (m, 2H), 1.93 – 1.83 (m, 1H), 1.05 (d, *J* = 6.4 Hz, 3H), 0.85 (d, *J* = 6.4 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 137.1 (d, *J* = 5.1 Hz), 132.6 (d, *J* = 91.7 Hz), 131.4 (d, *J* = 2.8 Hz), 130.6 (d, *J* = 8.7 Hz), 130.5 (d, *J* = 3.0 Hz), 130.4 (d, *J* = 7.6 Hz), 130.2 (d, *J* = 4.4 Hz), 128.3 (d, *J* = 11.2 Hz), 126.8 (d, *J* = 3.2 Hz), 125.8 (d, *J* = 2.9 Hz), 37.1 (d, *J* = 62.5 Hz), 36.8 (d, *J* = 68.0 Hz), 24.5 (d, *J* = 9.0 Hz), 24.4 (d, *J* = 8.6 Hz), 23.4 (d, *J* = 4.1 Hz), 19.9 (d, *J* = 1.3 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 37.3.

**HRMS** (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>24</sub>OP [M + H]<sup>+</sup> 287.1559, found 287.1559.

**(*R*)-(2,6-dimethylbenzyl)(isobutyl)(phenyl)phosphine oxide (7)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-7** (25.9 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **7** as a white solid (22.3 mg, 74% yield, 93% ee).

**HPLC** analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 220 nm), *t<sub>R</sub>* (major) = 17.375 min, *t<sub>R</sub>* (minor) = 24.594 min.

[α]<sub>D</sub><sup>25</sup> = −15.5 (*c* 1.0, CHCl<sub>3</sub>).

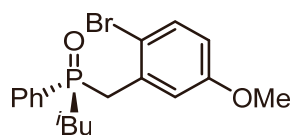
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.57 (m, 2H), 7.53 – 7.47 (m, 1H), 7.45 – 7.39 (m, 2H), 7.05 – 6.93 (m, 3H), 3.39 (d, *J* = 14.6 Hz, 2H), 2.21 (s, 6H), 2.06 – 1.93 (m, 2H), 1.92 – 1.82 (m, 1H), 1.03 (d, *J* = 6.3 Hz, 3H), 0.83 (d, *J* = 6.3 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 137.3 (d, *J* = 4.7 Hz), 133.6 (d, *J* = 90.8 Hz), 131.4 (d, *J* = 2.7 Hz), 130.5 (d, *J* = 8.6 Hz), 129.6 (d, *J* = 8.2 Hz), 128.4 (d, *J* = 10.9 Hz), 128.3 (d, *J* = 2.9 Hz), 126.5 (d, *J* = 3.3 Hz), 37.7 (d, *J* = 67.1 Hz), 34.7 (d, *J* = 62.8 Hz), 24.6 (d, *J* = 9.0 Hz), 24.5 (d, *J* = 8.3 Hz), 23.5 (d, *J* = 4.3 Hz), 21.0 (d, *J* = 1.4 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 37.8.

**HRMS** (ESI) *m/z* calcd. for C<sub>19</sub>H<sub>26</sub>OP [M + H]<sup>+</sup> 301.1716, found 301.1726.

**(*R*)-(2-bromo-5-methoxybenzyl)(isobutyl)(phenyl)phosphine oxide (8)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-8** (36.4 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **8** as a colorless oil (30.6 mg, 80% yield, 95% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 220 nm), *t<sub>R</sub>* (major) = 11.572 min, *t<sub>R</sub>* (minor) = 13.265 min.



$[\alpha]_D^{25} = -30.4$  ( $c$  1.0,  $\text{CHCl}_3$ ).

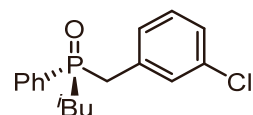
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 – 7.65 (m, 2H), 7.55 – 7.49 (m, 1H), 7.49 – 7.42 (m, 2H), 7.37 (d,  $J = 8.8$  Hz, 1H), 6.96 – 6.93 (m, 1H), 6.66 (ddd,  $J = 8.8, 3.1, 1.8$  Hz, 1H), 3.72 (s, 3H), 3.61 – 3.52 (m, 1H), 3.47 – 3.36 (m, 1H), 2.04 – 1.88 (m, 3H), 1.01 (d,  $J = 6.3$  Hz, 3H), 0.83 (d,  $J = 6.4$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7 (d,  $J = 2.9$  Hz), 133.2 (d,  $J = 2.5$  Hz), 133.0 (d,  $J = 7.3$  Hz), 132.5 (d,  $J = 92.8$  Hz), 131.6 (d,  $J = 2.8$  Hz), 130.7 (d,  $J = 9.0$  Hz), 128.4 (d,  $J = 11.3$  Hz), 116.1 (d,  $J = 4.1$  Hz), 115.5 (d,  $J = 2.9$  Hz), 115.1 (d,  $J = 6.7$  Hz), 55.4, 39.5 (d,  $J = 61.6$  Hz), 37.1 (d,  $J = 68.1$  Hz), 24.5 (d,  $J = 9.1$  Hz), 24.4 (d,  $J = 8.7$  Hz), 23.4 (d,  $J = 4.3$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.7.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{23}\text{BrO}_2\text{P}$   $[\text{M} + \text{H}]^+$  381.0614/383.0593, found 381.0610/383.0587.

### (*R*)-(3-chlorobenzyl)(isobutyl)(phenyl)phosphine oxide (**9**)



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-9** (26.7 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **9** as a white solid (24.5 mg, 80% yield, 90% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda = 220$  nm),  $t_R$  (major) = 16.186 min,  $t_R$  (minor) = 19.804 min.

$[\alpha]_D^{25} = -19.7$  ( $c$  1.0,  $\text{CHCl}_3$ ).

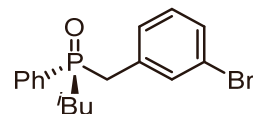
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.56 (m, 2H), 7.52 (t,  $J = 7.4$  Hz, 1H), 7.48 – 7.42 (m, 2H), 7.21 – 7.11 (m, 2H), 7.02 (d,  $J = 2.2$  Hz, 1H), 7.00 – 6.95 (m, 1H), 3.33 – 3.16 (m, 2H), 2.13 – 1.91 (m, 2H), 1.90 – 1.79 (m, 1H), 1.05 (d,  $J = 6.6$  Hz, 3H), 0.88 (d,  $J = 6.5$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  134.1 (d,  $J = 3.0$  Hz), 133.8 (d,  $J = 7.4$  Hz), 131.9 (d,  $J = 93.6$  Hz), 131.7 (d,  $J = 2.9$  Hz), 130.6 (d,  $J = 8.8$  Hz), 129.7 (d,  $J = 5.0$  Hz), 129.6 (d,  $J = 2.8$  Hz), 128.4 (d,  $J = 11.8$  Hz), 127.9 (d,  $J = 4.9$  Hz), 126.9 (d,  $J = 2.9$  Hz), 39.5 (d,  $J = 62.1$  Hz), 36.9 (d,  $J = 68.7$  Hz), 24.5 (d,  $J = 8.5$  Hz), 24.4 (d,  $J = 8.0$  Hz), 23.4 (d,  $J = 4.3$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  36.6.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{21}\text{ClOP}$   $[\text{M} + \text{H}]^+$  307.1013, found 307.0999.

### (*R*)-(3-bromobenzyl)(isobutyl)(phenyl)phosphine oxide (**10**)



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-10** (32.5 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **10** as a white solid (28.4 mg, 81% yield, 89% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 220 nm),  $t_R$  (major) = 9.607 min,  $t_R$  (minor) = 11.156 min.

$[\alpha]_D^{25} = -22.5$  (*c* 1.0, CHCl<sub>3</sub>).

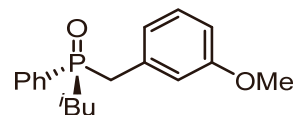
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 – 7.50 (m, 3H), 7.48 – 7.42 (m, 2H), 7.35 – 7.30 (m, 1H), 7.17 – 7.14 (m, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 7.05 – 7.00 (m, 1H), 3.30 – 3.16 (m, 2H), 2.12 – 1.83 (m, 3H), 1.05 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  134.1 (d, *J* = 7.7 Hz), 132.6 (d, *J* = 5.1 Hz), 131.9 (d, *J* = 93.4 Hz), 131.7 (d, *J* = 2.8 Hz), 130.6 (d, *J* = 8.7 Hz), 129.9 (d, *J* = 2.8 Hz), 129.8 (d, *J* = 3.1 Hz), 128.5 (d, *J* = 11.4 Hz), 128.4 (d, *J* = 5.0 Hz), 122.3 (d, *J* = 3.1 Hz), 39.5 (d, *J* = 61.6 Hz), 36.9 (d, *J* = 68.6 Hz), 24.5 (d, *J* = 9.2 Hz), 24.4 (d, *J* = 8.5 Hz), 23.4 (d, *J* = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  36.5.

**HRMS** (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>21</sub>BrOP [M + H]<sup>+</sup> 351.0508, found 351.0504.

#### (*R*)-isobutyl(3-methoxybenzyl)(phenyl)phosphine oxide (**11**)



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-11** (26.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **11** as a slightly yellow solid (25.3 mg, 84% yield, 90% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 220 nm),  $t_R$  (major) = 10.615 min,  $t_R$  (minor) = 15.273 min.

$[\alpha]_D^{25} = -27.1$  (*c* 1.0, CHCl<sub>3</sub>).

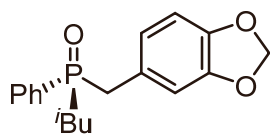
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 – 7.48 (m, 2H), 7.45 – 7.40 (m, 1H), 7.39 – 7.32 (m, 2H), 7.06 (t, *J* = 7.9 Hz, 1H), 6.70 – 6.64 (m, 1H), 6.58 (d, *J* = 7.7 Hz, 1H), 6.52 – 6.47 (m, 1H), 3.61 (s, 3H), 3.25 – 3.12 (m, 2H), 2.04 – 1.83 (m, 2H), 1.81 – 1.71 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.79 (d, *J* = 6.5 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.4 (d, *J* = 2.7 Hz), 133.2 (d, *J* = 7.5 Hz), 132.4 (d, *J* = 92.7 Hz), 131.5 (d, *J* = 2.8 Hz), 130.7 (d, *J* = 8.7 Hz), 129.3 (d, *J* = 2.6 Hz), 128.3 (d, *J* = 11.3 Hz), 122.1 (d, *J* = 5.1 Hz), 115.0 (d, *J* = 4.9 Hz), 112.7 (d, *J* = 3.0 Hz), 55.0, 40.0 (d, *J* = 62.3 Hz), 36.7 (d, *J* = 68.4 Hz), 24.5 (d, *J* = 9.1 Hz), 24.4 (d, *J* = 8.6 Hz), 23.4 (d, *J* = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  37.0.

**HRMS** (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>24</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 303.1508, found 303.1494.

**(R)-(benzo[d][1,3]dioxol-5-ylmethyl)(isobutyl)(phenyl)phosphine oxide (12)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-12** (28.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **12** as a white solid (23.9 mg, 76% yield, 92% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 220 nm),  $t_R$  (major) = 19.656 min,  $t_R$  (minor) = 25.004 min.

$[\alpha]_D^{25} = -54.7$  (*c* 1.0, CHCl<sub>3</sub>).

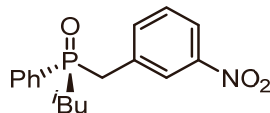
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.66 – 7.57 (m, 2H), 7.55 – 7.49 (m, 1H), 7.48 – 7.41 (m, 2H), 6.67 (d,  $J$  = 7.9 Hz, 1H), 6.59 (t,  $J$  = 1.8 Hz, 1H), 6.50 (dt,  $J$  = 8.0, 2.2 Hz, 1H), 5.91 (s, 2H), 3.20 (d,  $J$  = 13.9 Hz, 2H), 2.11 – 1.89 (m, 2H), 1.87 – 1.76 (m, 1H), 1.04 (d,  $J$  = 6.5 Hz, 3H), 0.86 (d,  $J$  = 6.5 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  147.6 (d,  $J$  = 2.6 Hz), 146.4 (d,  $J$  = 3.0 Hz), 132.3 (d,  $J$  = 92.9 Hz), 131.5 (d,  $J$  = 2.8 Hz), 130.7 (d,  $J$  = 8.7 Hz), 128.4 (d,  $J$  = 11.3 Hz), 125.1 (d,  $J$  = 8.0 Hz), 122.9 (d,  $J$  = 5.8 Hz), 110.2 (d,  $J$  = 4.4 Hz), 108.2 (d,  $J$  = 2.7 Hz), 100.9, 39.4 (d,  $J$  = 63.2 Hz), 36.8 (d,  $J$  = 68.2 Hz), 24.5 (d,  $J$  = 9.1 Hz), 24.4 (d,  $J$  = 8.5 Hz), 23.4 (d,  $J$  = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  37.0.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>18</sub>H<sub>22</sub>O<sub>3</sub>P [M + H]<sup>+</sup> 317.1301, found 317.1292.

**(R)-isobutyl(3-nitrobenzyl)(phenyl)phosphine oxide (13)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-13** (28.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **13** as a white solid (20.1 mg, 63% yield, 87% ee).

**HPLC** analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 23.629 min,  $t_R$  (minor) = 30.453 min.

$[\alpha]_D^{25} = -25.4$  (*c* 1.0, CHCl<sub>3</sub>).

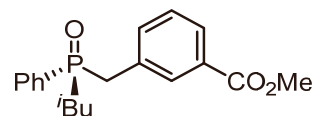
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 – 8.02 (m, 1H), 7.82 (d,  $J$  = 2.1 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.55 – 7.43 (m, 4H), 7.40 (t,  $J$  = 7.9 Hz, 1H), 3.44 (t,  $J$  = 14.5 Hz, 1H), 3.31 (dd,  $J$  = 14.5, 12.0 Hz, 1H), 2.15 – 1.98 (m, 2H), 1.96 – 1.87 (m, 1H), 1.06 (d,  $J$  = 6.4 Hz, 3H), 0.90 (d,  $J$  = 6.5 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.0 (d,  $J$  = 2.7 Hz), 136.0 (d,  $J$  = 4.4 Hz), 133.9 (d,  $J$  = 7.8 Hz), 132.0 (d,  $J$  = 2.8 Hz), 131.4 (d,  $J$  = 94.2 Hz), 130.5 (d,  $J$  = 8.8 Hz), 129.3 (d,  $J$  = 2.5 Hz), 128.7 (d,  $J$  = 11.5 Hz), 124.4 (d,  $J$  = 5.1 Hz), 121.8 (d,  $J$  = 2.8 Hz), 39.4 (d,  $J$  = 60.7 Hz), 37.4 (d,  $J$  = 68.5 Hz), 24.5 (d,  $J$  = 9.3 Hz), 24.4 (d,  $J$  = 8.6 Hz), 23.5 (d,  $J$  = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  36.5.

**HRMS** (ESI)  $m/z$  calcd. for  $C_{17}H_{21}NO_3P$   $[M + H]^+$  318.1254, found 318.1247.

**methyl (R)-3-((isobutyl(phenyl)phosphoryl)methyl)benzoate (14)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-14** (29.8 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **14** as a white solid (19.2 mg, 58% yield, 86% ee).

**HPLC** analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 230 nm),  $t_R$  (major) = 16.747 min,  $t_R$  (minor) = 22.720 min.

$[\alpha]_D^{25} = -24.4$  ( $c$  1.0,  $CHCl_3$ ).

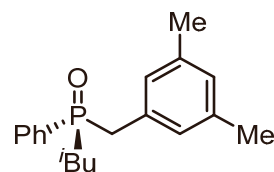
**$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.91 – 7.85 (m, 1H), 7.71 (d,  $J$  = 2.2 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.54 – 7.48 (m, 1H), 7.47 – 7.40 (m, 2H), 7.33 – 7.29 (m, 2H), 3.88 (s, 3H), 3.39 – 3.25 (m, 2H), 2.12 – 1.97 (m, 2H), 1.91 – 1.80 (m, 1H), 1.04 (d,  $J$  = 6.6 Hz, 3H), 0.87 (d,  $J$  = 6.6 Hz, 3H).

**$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  166.8, 134.3 (d,  $J$  = 4.6 Hz), 132.3 (d,  $J$  = 7.6 Hz), 132.0 (d,  $J$  = 93.1 Hz), 131.6 (d,  $J$  = 2.9 Hz), 130.7 (d,  $J$  = 5.2 Hz), 130.6 (d,  $J$  = 8.7 Hz), 130.2 (d,  $J$  = 2.5 Hz), 128.5 (d,  $J$  = 2.4 Hz), 128.5 (d,  $J$  = 11.2 Hz), 128.0 (d,  $J$  = 2.8 Hz), 52.1, 39.6 (d,  $J$  = 61.8 Hz), 36.9 (d,  $J$  = 68.4 Hz), 24.5 (d,  $J$  = 9.1 Hz), 24.4 (d,  $J$  = 8.5 Hz), 23.4 (d,  $J$  = 4.2 Hz).

**$^{31}P$  NMR** (162 MHz,  $CDCl_3$ )  $\delta$  36.8.

**HRMS** (ESI)  $m/z$  calcd. for  $C_{19}H_{24}O_3P$   $[M + H]^+$  331.1458, found 331.1455.

**(R)-(3,5-dimethylbenzyl)(isobutyl)(phenyl)phosphine oxide (15)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-15** (25.9 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **15** as a white solid (26.1 mg, 87% yield, 91% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 220 nm),  $t_R$  (major) = 10.860 min,  $t_R$  (minor) = 13.671 min.

$[\alpha]_D^{25} = -16.1$  ( $c$  1.0,  $CHCl_3$ ).

**$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.62 – 7.55 (m, 2H), 7.53 – 7.47 (m, 1H), 7.46 – 7.40 (m, 2H), 6.83 (s, 1H), 6.65 (t,  $J$  = 2.3 Hz, 2H), 3.29 – 3.11 (m, 2H), 2.21 (s, 6H), 2.11 – 1.99 (m, 1H), 1.98 – 1.88 (m, 1H), 1.85 – 1.75 (m, 1H), 1.03 (d,  $J$  = 6.6 Hz, 3H), 0.86 (d,  $J$  = 6.6 Hz, 3H).

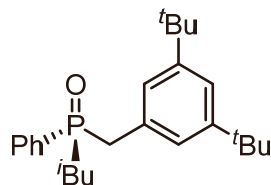
**$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  137.8 (d,  $J$  = 2.6 Hz), 132.6 (d,  $J$  = 92.3 Hz), 131.5 (d,  $J$  = 7.5 Hz), 131.4 (d,  $J$  = 2.8 Hz), 130.8 (d,  $J$  = 8.6 Hz), 128.3 (d,  $J$  = 3.1 Hz), 128.2 (d,

$J = 11.3$  Hz), 127.7 (d,  $J = 5.0$  Hz), 39.8 (d,  $J = 62.7$  Hz), 36.5 (d,  $J = 68.3$  Hz), 24.5 (d,  $J = 8.8$  Hz), 24.4 (d,  $J = 8.6$  Hz), 23.4 (d,  $J = 4.2$  Hz), 21.1.

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.1.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{26}\text{OP}$   $[\text{M} + \text{H}]^+$  301.1716, found 301.1725.

**(*R*)-(3,5-di-*tert*-butylbenzyl)(isobutyl)(phenyl)phosphine oxide (16)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-16** (36.8 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **16** as a white solid (32.7 mg, 85% yield, 90% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda = 220$  nm),  $t_R$  (major) = 6.880 min,  $t_R$  (minor) = 9.300 min.

$[\alpha]_D^{25} = -14.8$  ( $c$  1.0,  $\text{CHCl}_3$ ).

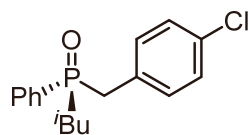
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.43 (m, 3H), 7.42 – 7.35 (m, 2H), 7.24 – 7.20 (m, 1H), 6.78 (t,  $J = 2.1$  Hz, 2H), 3.39 – 3.21 (m, 2H), 2.17 – 2.05 (m, 1H), 2.04 – 1.93 (m, 1H), 1.89 – 1.78 (m, 1H), 1.22 (s, 18H), 1.06 (d,  $J = 6.6$  Hz, 3H), 0.89 (d,  $J = 6.6$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.6 (d,  $J = 2.7$  Hz), 132.4 (d,  $J = 92.7$  Hz), 131.3 (d,  $J = 2.8$  Hz), 130.8 (d,  $J = 8.5$  Hz), 130.7 (d,  $J = 7.9$  Hz), 128.2 (d,  $J = 11.2$  Hz), 124.2 (d,  $J = 4.9$  Hz), 120.4 (d,  $J = 3.2$  Hz), 40.4 (d,  $J = 62.4$  Hz), 36.4 (d,  $J = 68.0$  Hz), 34.6, 31.3, 24.6 (d,  $J = 8.9$  Hz), 24.5 (d,  $J = 8.5$  Hz), 23.4 (d,  $J = 4.1$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.5.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{25}\text{H}_{38}\text{OP}$   $[\text{M} + \text{H}]^+$  385.2655, found 385.2660.

**(*R*)-(4-chlorobenzyl)(isobutyl)(phenyl)phosphine oxide (17)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-17** (26.7 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **17** as a white solid (25.5 mg, 83% yield, 90% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda = 220$  nm),  $t_R$  (major) = 9.471 min,  $t_R$  (minor) = 12.397 min.

$[\alpha]_D^{25} = -33.4$ . ( $c$  1.0,  $\text{CHCl}_3$ ).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 – 7.55 (m, 2H), 7.54 – 7.48 (m, 1H), 7.47 – 7.40 (m, 2H), 7.18 (d,  $J = 8.4$  Hz, 2H), 6.99 (dd,  $J = 8.5, 2.2$  Hz, 2H), 3.32 – 3.16 (m, 2H),

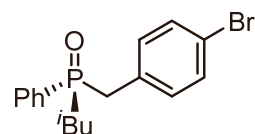
2.11 – 1.99 (m, 1H), 1.98 – 1.78 (m, 2H), 1.04 (d,  $J = 6.6$  Hz, 3H), 0.87 (d,  $J = 6.6$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  132.7 (d,  $J = 3.7$  Hz), 132.0 (d,  $J = 93.0$  Hz), 131.6 (d,  $J = 2.9$  Hz), 131.0 (d,  $J = 4.9$  Hz), 130.6 (d,  $J = 8.7$  Hz), 130.3 (d,  $J = 7.8$  Hz), 128.5 (d,  $J = 2.6$  Hz), 128.4 (d,  $J = 11.3$  Hz), 39.1 (d,  $J = 62.2$  Hz), 37.0 (d,  $J = 68.4$  Hz), 24.5 (d,  $J = 9.0$  Hz), 24.4 (d,  $J = 8.5$  Hz), 23.4 (d,  $J = 4.1$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  36.6.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{21}\text{ClOP}$   $[\text{M} + \text{H}]^+$  307.1013, found 307.1011.

#### (*R*)-(4-bromobenzyl)(isobutyl)(phenyl)phosphine oxide (**18**)



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-18** (32.5 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **18** as a white solid (26.6 mg, 76% yield, 92% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda = 230$  nm),  $t_R$  (major) = 17.446 min,  $t_R$  (minor) = 23.486 min.

$[\alpha]_D^{25} = -25.2$  ( $c$  1.0,  $\text{CHCl}_3$ ).

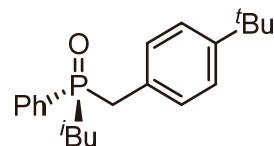
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 – 7.55 (m, 2H), 7.54 – 7.48 (m, 1H), 7.47 – 7.41 (m, 2H), 7.33 (d,  $J = 8.3$  Hz, 2H), 6.94 (dd,  $J = 8.5, 2.2$  Hz, 2H), 3.31 – 3.15 (m, 2H), 2.12 – 1.78 (m, 3H), 1.04 (d,  $J = 6.6$  Hz, 3H), 0.86 (d,  $J = 6.6$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  132.0 (d,  $J = 93.0$  Hz), 131.6 (d,  $J = 2.8$  Hz), 131.5 (d,  $J = 2.6$  Hz), 131.4 (d,  $J = 5.0$  Hz), 130.8 (d,  $J = 7.7$  Hz), 130.6 (d,  $J = 8.7$  Hz), 128.4 (d,  $J = 11.3$  Hz), 120.8 (d,  $J = 3.8$  Hz), 39.2 (d,  $J = 62.0$  Hz), 37.0 (d,  $J = 68.4$  Hz), 24.5 (d,  $J = 9.1$  Hz), 24.4 (d,  $J = 8.6$  Hz), 23.4 (d,  $J = 4.2$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  36.5.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{21}\text{BrOP}$   $[\text{M} + \text{H}]^+$  351.0508, found 351.0507.

#### (*R*)-(4-(*tert*-butyl)benzyl)(isobutyl)(phenyl)phosphine oxide (**19**)



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-19** (29.5 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **19** as a white solid (25.8 mg, 79% yield, 92% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda = 220$  nm),  $t_R$  (major) = 10.944 min,  $t_R$  (minor) = 14.140 min.

$[\alpha]_D^{25} = -27.7$  ( $c$  1.0,  $\text{CHCl}_3$ ).

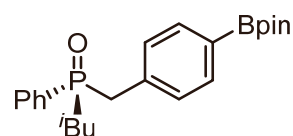
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.64 – 7.56 (m, 2H), 7.53 – 7.47 (m, 1H), 7.46 – 7.39 (m, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.01 (dd, *J* = 8.3, 2.3 Hz, 2H), 3.34 – 3.16 (m, 2H), 2.10 – 1.89 (m, 2H), 1.87 – 1.75 (m, 1H), 1.28 (s, 9H), 1.02 (d, *J* = 6.4 Hz, 3H), 0.84 (d, *J* = 6.4 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 149.6 (d, *J* = 3.3 Hz), 132.6 (d, *J* = 92.1 Hz), 131.4 (d, *J* = 2.8 Hz), 130.7 (d, *J* = 8.7 Hz), 129.4 (d, *J* = 4.9 Hz), 128.6 (d, *J* = 7.7 Hz), 128.3 (d, *J* = 11.2 Hz), 125.4 (d, *J* = 2.7 Hz), 39.3 (d, *J* = 63.1 Hz), 36.8 (d, *J* = 68.2 Hz), 34.3, 31.3, 24.5 (d, *J* = 9.0 Hz), 24.4 (d, *J* = 8.5 Hz), 23.4 (d, *J* = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 37.0.

**HRMS** (ESI) *m/z* calcd. for C<sub>21</sub>H<sub>30</sub>OP [M + H]<sup>+</sup> 329.2029, found 329.2023.

**(*R*)-isobutyl(phenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)phosphine oxide (20)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-20** (38.6 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **20** as a white solid (29.0 mg, 73% yield, 93% ee).

**HPLC** analysis: Chiralpak IG (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 230 nm), *t<sub>R</sub>* (minor) = 48.736 min, *t<sub>R</sub>* (major) = 51.710 min.

[α]<sub>D</sub><sup>25</sup> = −43.6 (*c* 1.0, CHCl<sub>3</sub>).

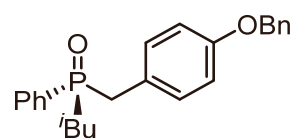
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 7.7 Hz, 2H), 7.60 – 7.53 (m, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.38 (m, 2H), 7.06 (dd, *J* = 8.1, 2.1 Hz, 2H), 3.40 – 3.24 (m, 2H), 2.12 – 1.88 (m, 2H), 1.86 – 1.75 (m, 1H), 1.33 (s, 12H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 135.0 (d, *J* = 7.5 Hz), 134.8 (d, *J* = 2.6 Hz), 132.1 (d, *J* = 93.9 Hz), 131.5 (d, *J* = 2.6 Hz), 130.7 (d, *J* = 8.7 Hz), 129.2 (d, *J* = 5.0 Hz), 128.3 (d, *J* = 11.3 Hz), 83.7, 40.2 (d, *J* = 61.6 Hz), 36.6 (d, *J* = 68.4 Hz), 24.8, 24.7, 24.5 (d, *J* = 9.4 Hz), 24.4 (d, *J* = 8.2 Hz), 23.3 (d, *J* = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 37.0.

**HRMS** (ESI) *m/z* calcd. for C<sub>23</sub>H<sub>33</sub>BO<sub>3</sub>P [M + H]<sup>+</sup> 399.2255, found 399.2251.

**(*R*)-(4-(benzyloxy)benzyl)(isobutyl)(phenyl)phosphine oxide (21)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-21** (36.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **21** as a white solid (26.8 mg, 71% yield, 92% ee).

**HPLC** analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 220 nm),  $t_R$  (major) = 14.450 min,  $t_R$  (minor) = 19.382 min.

$[\alpha]_D^{25} = -30.5$  ( $c$  1.0, CHCl<sub>3</sub>).

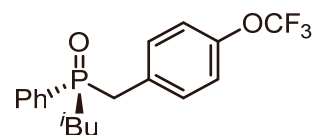
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 – 7.54 (m, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.28 (m, 7H), 6.97 (dd,  $J$  = 8.7, 2.3 Hz, 2H), 6.84 (d,  $J$  = 8.6 Hz, 2H), 5.01 (s, 2H), 3.29 – 3.14 (m, 2H), 2.11 – 1.87 (m, 2H), 1.86 – 1.75 (m, 1H), 1.03 (d,  $J$  = 6.6 Hz, 3H), 0.85 (d,  $J$  = 6.6 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  157.6 (d,  $J$  = 3.0 Hz), 136.8, 132.4 (d,  $J$  = 92.2 Hz), 131.4 (d,  $J$  = 2.7 Hz), 130.7 (d,  $J$  = 5.2 Hz), 130.6 (d,  $J$  = 8.9 Hz), 128.5, 128.3 (d,  $J$  = 11.1 Hz), 127.9, 127.4, 123.9 (d,  $J$  = 7.7 Hz), 114.8 (d,  $J$  = 2.6 Hz), 69.9, 38.8 (d,  $J$  = 63.5 Hz), 36.7 (d,  $J$  = 68.1 Hz), 24.5 (d,  $J$  = 9.0 Hz), 24.4 (d,  $J$  = 8.6 Hz), 23.3 (d,  $J$  = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  37.2.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>24</sub>H<sub>28</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 379.1821, found 379.1819.

**(*R*)-isobutyl(phenyl)(4-(trifluoromethoxy)benzyl)phosphine oxide (22)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-22** (33.2 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **22** as a white solid (29.1 mg, 82% yield, 90% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 220 nm),  $t_R$  (major) = 11.064 min,  $t_R$  (minor) = 15.056 min.

$[\alpha]_D^{25} = -21.1$  ( $c$  1.0, CHCl<sub>3</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 – 7.55 (m, 2H), 7.54 – 7.48 (m, 1H), 7.47 – 7.40 (m, 2H), 7.13 – 7.03 (m, 4H), 3.37 – 3.18 (m, 2H), 2.12 – 1.99 (m, 1H), 1.99 – 1.81 (m, 2H), 1.05 (d,  $J$  = 6.6 Hz, 3H), 0.87 (d,  $J$  = 6.5 Hz, 3H).

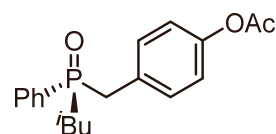
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.0 (d,  $J$  = 1.7 Hz), 131.9 (d,  $J$  = 93.1 Hz), 131.7 (d,  $J$  = 2.7 Hz), 131.0 (d,  $J$  = 4.8 Hz), 130.6 (d,  $J$  = 7.1 Hz), 130.5 (d,  $J$  = 8.8 Hz), 128.5 (d,  $J$  = 11.4 Hz), 120.9 (d,  $J$  = 2.5 Hz), 120.3 (q,  $J$  = 257.1 Hz), 39.0 (d,  $J$  = 62.1 Hz), 37.1 (d,  $J$  = 68.4 Hz), 24.5 (d,  $J$  = 9.5 Hz), 24.4 (d,  $J$  = 8.8 Hz), 23.4 (d,  $J$  = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  36.6.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -57.9.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>18</sub>H<sub>21</sub>F<sub>3</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 357.1226, found 357.1220.

**(*R*)-4-((isobutyl(phenyl)phosphoryl)methyl)phenyl acetate (23)**





According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-23** (29.8 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **23** as a white solid (22.9 mg, 69% yield, 95% ee).

**HPLC** analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 220 nm),  $t_R$  (major) = 14.544 min,  $t_R$  (minor) = 20.332 min.

$[\alpha]_D^{25} = -26.8$  ( $c$  1.0, CHCl<sub>3</sub>).

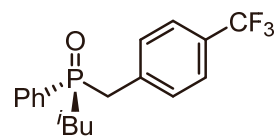
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 – 7.55 (m, 2H), 7.54 – 7.48 (m, 1H), 7.47 – 7.40 (m, 2H), 7.07 (dd,  $J$  = 8.6, 2.2 Hz, 2H), 6.95 (d,  $J$  = 8.5 Hz, 2H), 3.28 (d,  $J$  = 14.1 Hz, 2H), 2.27 (s, 3H), 2.13 – 1.90 (m, 2H), 1.89 – 1.78 (m, 1H), 1.04 (d,  $J$  = 6.5 Hz, 3H), 0.86 (d,  $J$  = 6.5 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.4, 149.5 (d,  $J$  = 3.4 Hz), 132.0 (d,  $J$  = 93.4 Hz), 131.6 (d,  $J$  = 2.6 Hz), 130.7 (d,  $J$  = 9.0 Hz), 130.6 (d,  $J$  = 4.9 Hz), 129.4 (d,  $J$  = 7.4 Hz), 128.4 (d,  $J$  = 11.3 Hz), 121.6 (d,  $J$  = 2.8 Hz), 39.2 (d,  $J$  = 62.3 Hz), 36.9 (d,  $J$  = 68.5 Hz), 24.5 (d,  $J$  = 9.1 Hz), 24.4 (d,  $J$  = 8.6 Hz), 23.4 (d,  $J$  = 4.1 Hz), 21.1.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  37.0.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>P [M + H]<sup>+</sup> 331.1458, found 331.1460.

#### (*R*)-isobutyl(phenyl)(4-(trifluoromethyl)benzyl)phosphine oxide (**24**)



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-24** (31.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **24** as a white solid (25.8 mg, 76% yield, 90% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 220 nm),  $t_R$  (major) = 7.555 min,  $t_R$  (minor) = 10.216 min.

$[\alpha]_D^{25} = -16.7$  ( $c$  1.0, CHCl<sub>3</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 – 7.56 (m, 2H), 7.53 (t,  $J$  = 7.2 Hz, 1H), 7.49 – 7.41 (m, 4H), 7.18 (d,  $J$  = 7.9 Hz, 2H), 3.42 – 3.24 (m, 2H), 2.13 – 1.99 (m, 1H), 1.98 – 1.82 (m, 2H), 1.05 (d,  $J$  = 6.5 Hz, 3H), 0.87 (d,  $J$  = 6.5 Hz, 3H).

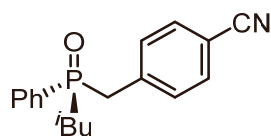
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.0 (d,  $J$  = 8.0 Hz), 131.9 (d,  $J$  = 93.5 Hz), 131.8 (d,  $J$  = 2.8 Hz), 130.6 (d,  $J$  = 8.9 Hz), 130.0 (d,  $J$  = 4.9 Hz), 129.0 (qd,  $J$  = 32.7, 3.4 Hz), 128.6 (d,  $J$  = 11.4 Hz), 125.3 (dq,  $J$  = 3.3, 6.9 Hz), 124.1 (qd,  $J$  = 271.8, 1.4 Hz), 39.7 (d,  $J$  = 61.1 Hz), 37.2 (d,  $J$  = 68.5 Hz), 24.5 (d,  $J$  = 9.5 Hz), 24.4 (d,  $J$  = 8.7 Hz), 23.5 (d,  $J$  = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  36.6.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.5 (d,  $J$  = 2.0 Hz).

**HRMS** (ESI)  $m/z$  calcd. for C<sub>18</sub>H<sub>21</sub>F<sub>3</sub>OP [M + H]<sup>+</sup> 341.1277, found 341.1260.

**(R)-4-((isobutyl(phenyl)phosphoryl)methyl)benzonitrile (25)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-25** (25.5 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **25** as a white solid (19.2 mg, 65% yield, 92% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 230 nm),  $t_R$  (minor) = 33.951 min,  $t_R$  (major) = 38.534 min.

$[\alpha]_D^{25} = -131.3$  ( $c$  1.0, CHCl<sub>3</sub>).

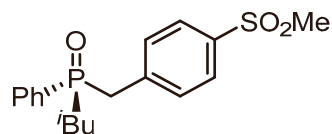
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 – 7.41 (m, 7H), 7.23 – 7.12 (m, 2H), 3.48 – 3.20 (m, 2H), 2.14 – 1.83 (m, 1H), 1.06 (d,  $J$  = 6.4 Hz, 3H), 0.89 (d,  $J$  = 6.3 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.6 (d,  $J$  = 8.0 Hz), 132.0 (d,  $J$  = 2.6 Hz), 131.9 (d,  $J$  = 2.8 Hz), 131.5 (d,  $J$  = 93.7 Hz), 130.5 (d,  $J$  = 8.6 Hz), 130.4 (d,  $J$  = 4.5 Hz), 128.6 (d,  $J$  = 11.6 Hz), 118.7 (d,  $J$  = 1.7 Hz), 110.6 (d,  $J$  = 3.3 Hz), 40.0 (d,  $J$  = 60.1 Hz), 37.5 (d,  $J$  = 68.6 Hz), 24.5 (d,  $J$  = 9.3 Hz), 24.4 (d,  $J$  = 8.5 Hz), 23.5 (d,  $J$  = 4.2 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  36.4.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>18</sub>H<sub>21</sub>NOP [M + H]<sup>+</sup> 298.1355, found 298.1353.

**(R)-isobutyl(4-(methylsulfonyl)benzyl)(phenyl)phosphine oxide (26)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-26** (32.4 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **26** as a white solid (23.6 mg, 67% yield, 91% ee).

**HPLC** analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min,  $\lambda$  = 230 nm),  $t_R$  (major) = 25.888 min,  $t_R$  (minor) = 30.733 min.

$[\alpha]_D^{25} = -23.1$  ( $c$  1.0, CHCl<sub>3</sub>).

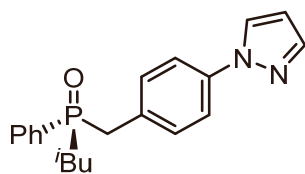
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78 (d,  $J$  = 8.2 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.56 – 7.50 (m, 1H), 7.49 – 7.42 (m, 2H), 7.28 (dd,  $J$  = 8.5, 2.1 Hz, 2H), 3.47 – 3.26 (m, 2H), 3.02 (s, 3H), 2.11 – 2.01 (m, 1H), 1.99 – 1.85 (m, 2H), 1.05 (d,  $J$  = 6.5 Hz, 3H), 0.88 (d,  $J$  = 6.5 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.8 (d,  $J$  = 3.3 Hz), 138.5 (d,  $J$  = 7.8 Hz), 131.9 (d,  $J$  = 2.7 Hz), 131.5 (d,  $J$  = 94.0 Hz), 130.6 (d,  $J$  = 4.7 Hz), 130.5 (d,  $J$  = 9.0 Hz), 128.6 (d,  $J$  = 11.4 Hz), 127.4 (d,  $J$  = 2.5 Hz), 44.4, 39.7 (d,  $J$  = 60.1 Hz), 37.5 (d,  $J$  = 68.6 Hz), 24.5 (d,  $J$  = 9.4 Hz), 24.4 (d,  $J$  = 8.4 Hz), 23.5 (d,  $J$  = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  36.4.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>18</sub>H<sub>24</sub>O<sub>3</sub>PS [M + H]<sup>+</sup> 351.1178, found 351.1176.

**(R)-(4-(1H-pyrazol-1-yl)benzyl)(isobutyl)(phenyl)phosphine oxide (27)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-27** (30.8 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **27** as a white solid (28.4 mg, 84% yield, 95% ee).

**HPLC** analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 18.285 min,  $t_R$  (minor) = 26.444 min.

$[\alpha]_D^{25} = -45.5$  ( $c$  1.0, CHCl<sub>3</sub>).

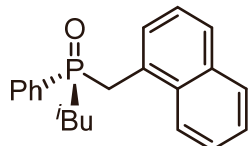
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d,  $J$  = 2.5 Hz, 1H), 7.70 (d,  $J$  = 1.7 Hz, 1H), 7.64 – 7.53 (m, 4H), 7.53 – 7.48 (m, 1H), 7.47 – 7.41 (m, 2H), 7.15 (dd,  $J$  = 8.7, 2.2 Hz, 2H), 6.45 (t,  $J$  = 2.1 Hz, 1H), 3.38 – 3.23 (m, 2H), 2.13 – 1.91 (m, 2H), 1.90 – 1.81 (m, 1H), 1.05 (d,  $J$  = 6.5 Hz, 3H), 0.87 (d,  $J$  = 6.5 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.0, 138.9 (d,  $J$  = 3.3 Hz), 132.0 (d,  $J$  = 92.5 Hz), 131.6 (d,  $J$  = 2.8 Hz), 130.7 (d,  $J$  = 4.6 Hz), 130.6 (d,  $J$  = 8.4 Hz), 130.0 (d,  $J$  = 7.9 Hz), 128.4 (d,  $J$  = 11.3 Hz), 126.6, 119.1 (d,  $J$  = 2.7 Hz), 107.5, 39.2 (d,  $J$  = 62.4 Hz), 37.0 (d,  $J$  = 68.3 Hz), 24.5 (d,  $J$  = 9.1 Hz), 24.4 (d,  $J$  = 8.5 Hz), 23.4 (d,  $J$  = 4.2 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  36.8.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>OP [M + H]<sup>+</sup> 339.1621, found 339.1617.

**(R)-isobutyl(naphthalen-1-ylmethyl)(phenyl)phosphine oxide (28)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-28** (28.7 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **28** as a white solid (27.0 mg, 84% yield, 91% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 220 nm),  $t_R$  (major) = 9.276 min,  $t_R$  (minor) = 13.709 min.

$[\alpha]_D^{25} = -30.6$  ( $c$  1.0, CHCl<sub>3</sub>).

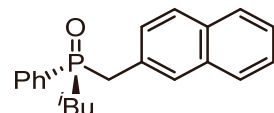
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d,  $J$  = 7.9 Hz, 1H), 7.80 (d,  $J$  = 8.2 Hz, 1H), 7.72 (d,  $J$  = 8.0 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.46 – 7.38 (m, 3H), 7.37 – 7.30 (m, 3H), 7.27 – 7.23 (m, 1H), 3.85 – 3.67 (m, 2H), 2.06 – 1.91 (m, 2H), 1.90 – 1.79 (m, 1H), 0.98 (d,  $J$  = 6.2 Hz, 3H), 0.81 (d,  $J$  = 6.2 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  133.7 (d,  $J$  = 2.2 Hz), 132.4 (d,  $J$  = 92.1 Hz), 132.0 (d,  $J$  = 3.9 Hz), 131.4 (d,  $J$  = 2.8 Hz), 130.6 (d,  $J$  = 8.7 Hz), 128.5 (d,  $J$  = 8.5 Hz), 128.4, 128.3 (d,  $J$  = 4.1 Hz), 128.2 (d,  $J$  = 11.0 Hz), 127.5 (d,  $J$  = 3.6 Hz), 125.9, 125.6, 125.1 (d,  $J$  = 3.3 Hz), 124.1 (d,  $J$  = 1.4 Hz), 36.9 (d,  $J$  = 62.4 Hz), 36.8 (d,  $J$  = 68.2 Hz), 24.5 (d,  $J$  = 9.1 Hz), 24.4 (d,  $J$  = 8.4 Hz), 23.4 (d,  $J$  = 4.1 Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.5.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{24}\text{OP}$   $[\text{M} + \text{H}]^+$  323.1559, found 323.1545.

**(*R*)-isobutyl(naphthalen-2-ylmethyl)(phenyl)phosphine oxide (29)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-29** (28.7 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **29** as a white solid (27.9 mg, 87% yield, 90% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 220 nm),  $t_R$  (major) = 11.130 min,  $t_R$  (minor) = 15.020 min.

$[\alpha]_D^{25} = -39.4$  ( $c$  1.0,  $\text{CHCl}_3$ ).

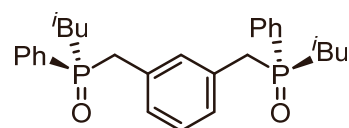
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 – 7.75 (m, 1H), 7.73 – 7.67 (m, 2H), 7.64 – 7.55 (m, 2H), 7.54 – 7.46 (m, 2H), 7.46 – 7.37 (m, 4H), 7.19 (d,  $J$  = 8.6 Hz, 1H), 3.52 – 3.36 (m, 2H), 2.13 – 1.91 (m, 2H), 1.90 – 1.79 (m, 1H), 1.03 (d,  $J$  = 6.5 Hz, 3H), 0.85 (d,  $J$  = 6.5 Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.3 (d,  $J$  = 2.7 Hz), 132.3 (d,  $J$  = 92.6 Hz), 132.1 (d,  $J$  = 2.2 Hz), 131.5 (d,  $J$  = 2.7 Hz), 130.7 (d,  $J$  = 8.6 Hz), 129.4 (d,  $J$  = 7.7 Hz), 128.5 (d,  $J$  = 6.5 Hz), 128.3 (d,  $J$  = 11.2 Hz), 128.0 (d,  $J$  = 2.2 Hz), 127.9 (d,  $J$  = 3.8 Hz), 127.5 (d,  $J$  = 1.4 Hz), 127.4 (d,  $J$  = 1.3 Hz), 126.0, 125.6 (d,  $J$  = 1.2 Hz), 40.1 (d,  $J$  = 62.3 Hz), 36.8 (d,  $J$  = 68.3 Hz), 24.5 (d,  $J$  = 9.1 Hz), 24.4 (d,  $J$  = 8.5 Hz), 23.4 (d,  $J$  = 4.1 Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.0.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{24}\text{OP}$   $[\text{M} + \text{H}]^+$  323.1559, found 323.1557.

**(1*R*,1'*R*)-(1,3-phenylenebis(methylene))bis(isobutyl(phenyl)phosphine oxide) (30)**



According to the **general procedure B**, substrates **A-1** (43.7 mg, 0.24 mmol, 2.4 equiv) and **B-30** (26.4 mg, 0.10 mmol, 1.0 equiv) were employed to yield the product **30** as a white solid (29.7 mg, 64% yield, 99% ee, >20:1 dr as determined by  $^{31}\text{P}$  NMR analysis of the isolated product).

HPLC analysis: Chiralpak IF (hexane/*i*-PrOH = 75/25, flow rate 1.0 mL/min,  $\lambda$  = 220 nm),  $t_R$  (major) = 21.494 min,  $t_R$  (*meso*-) = 27.416 min,  $t_R$  (minor) = 34.849 min.

$[\alpha]_D^{25} = -165.5$  ( $c$  1.0,  $\text{CHCl}_3$ ).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 – 7.52 (m, 4H), 7.51 – 7.46 (m, 2H), 7.45 – 7.38 (m, 4H), 7.08 – 7.02 (m, 1H), 6.97 – 6.86 (m, 3H), 3.21 (d,  $J$  = 14.0 Hz, 4H), 2.06 – 1.95 (m, 2H), 1.94 – 1.76 (m, 4H), 1.05 – 0.99 (m, 6H), 0.88 – 0.82 (m, 6H).

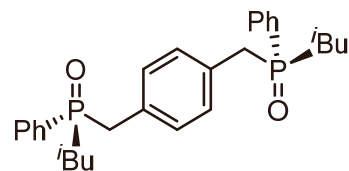
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  132.3 (d,  $J$  = 92.7 Hz), 132.1 – 131.9 (m), 131.6 – 131.3 (m), 131.3 – 131.1 (m), 130.6 (d,  $J$  = 8.4 Hz), 128.6 – 128.4 (m), 128.3 (d,  $J$  = 3.3 Hz),

128.2 – 128.1 (m), 39.6 (d,  $J = 62.4$  Hz), 36.9 (d,  $J = 68.4$  Hz), 24.5 (d,  $J = 9.1$  Hz), 24.4 (d,  $J = 8.4$  Hz), 23.4 (d,  $J = 4.0$  Hz), 23.3 (d,  $J = 3.9$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.0.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{28}\text{H}_{37}\text{O}_2\text{P}_2$   $[\text{M} + \text{H}]^+$  467.2263, found 467.2261.

**(1*R*,1'*R*)-(1,4-phenylenebis(methylene))bis(isobutyl(phenyl)phosphine oxide) (31)**



According to the **general procedure B**, substrates **A-1** (43.7 mg, 0.24 mmol, 2.4 equiv) and **B-31** (26.4 mg, 0.10 mmol, 1.0 equiv) were employed to yield the product **31** as a white solid (26.7 mg, 57% yield, 99% ee, 15:1 dr as determined by  $^{31}\text{P}$  NMR analysis of the isolated product).

HPLC analysis: Chiralpak IF (hexane/*i*-PrOH = 75/25, flow rate 1.0 mL/min,  $\lambda = 220$  nm),  $t_R$  (major) = 31.583 min,  $t_R$  (*meso*-) = 40.411 min,  $t_R$  (minor) = 51.648 min.

$[\alpha]_D^{25} = -114.6$  ( $c$  1.0,  $\text{CHCl}_3$ ).

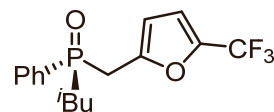
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 – 7.47 (m, 6H), 7.45 – 7.38 (m, 4H), 6.95 – 6.89 (m, 4H), 3.23 (d,  $J = 13.7$  Hz, 4H), 2.08 – 1.98 (m, 2H), 1.94 – 1.86 (m, 2H), 1.83 – 1.74 (m, 2H), 1.03 (d,  $J = 6.6$  Hz, 6H), 0.85 (d,  $J = 6.5$  Hz, 6H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  131.6 – 131.5 (m), 130.7 (d,  $J = 8.5$  Hz), 130.4 – 130.2 (m), 130.0 – 129.8 (m), 128.4 (d,  $J = 11.1$  Hz), 39.41 (d,  $J = 62.3$  Hz), 36.8 (d,  $J = 67.8$  Hz), 24.5 (d,  $J = 9.4$  Hz), 24.4 (d,  $J = 9.0$  Hz), 23.4 (d,  $J = 4.0$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.0.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{28}\text{H}_{37}\text{O}_2\text{P}_2$   $[\text{M} + \text{H}]^+$  467.2263, found 467.2262.

**(*R*)-isobutyl(phenyl)((5-(trifluoromethyl)furan-2-yl)methyl)phosphine oxide (32)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-32** (29.8 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **32** as a white solid (26.9 mg, 82% yield, 90% ee).

HPLC analysis: Chiralpak IF (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda = 220$  nm),  $t_R$  (major) = 19.164 min,  $t_R$  (minor) = 21.507 min.

$[\alpha]_D^{25} = -83.3$  ( $c$  1.0,  $\text{CHCl}_3$ ).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.51 (m, 3H), 7.50 – 7.42 (m, 2H), 6.68 (d,  $J = 3.3$  Hz, 1H), 6.23 – 6.13 (m, 1H), 3.50 – 3.31 (m, 2H), 2.18 – 1.99 (m, 2H), 1.98 – 1.87 (m, 1H), 1.08 (d,  $J = 6.5$  Hz, 3H), 0.92 (d,  $J = 6.5$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.4 (dq,  $J = 7.9, 1.4$  Hz), 141.0 (qd,  $J = 42.8, 3.1$  Hz), 132.0 (d,  $J = 2.7$  Hz), 131.7 (d,  $J = 94.7$  Hz), 130.4 (d,  $J = 8.9$  Hz), 128.6 (d,  $J = 11.6$  Hz).

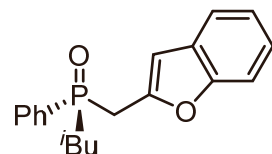
Hz), 118.9 (qd,  $J = 266.7$ , 0.9 Hz), 112.9 (dq,  $J = 5.6$ , 2.7 Hz), 109.5 (d,  $J = 5.9$  Hz), 37.4 (d,  $J = 68.7$  Hz), 32.7 (d,  $J = 62.8$  Hz), 24.5 (d,  $J = 9.2$  Hz), 24.4 (d,  $J = 8.8$  Hz), 23.5 (d,  $J = 4.1$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  35.2.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.1 (d,  $J = 2.5$  Hz).

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{19}\text{F}_3\text{O}_2\text{P}$   $[\text{M} + \text{H}]^+$  331.1069, found 331.1069.

### (*R*)-(benzofuran-2-ylmethyl)(isobutyl)(phenyl)phosphine oxide (**33**)



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-33** (27.4 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **33** as a white solid (23.0 mg, 74% yield, 81% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda = 254$  nm),  $t_R$  (major) = 16.851 min,  $t_R$  (minor) = 19.979 min.

$[\alpha]_D^{25} = -54.7$  ( $c$  1.0,  $\text{CHCl}_3$ ).

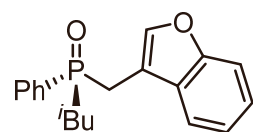
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 – 7.59 (m, 2H), 7.55 – 7.49 (m, 1H), 7.49 – 7.37 (m, 4H), 7.26 – 7.16 (m, 2H), 6.46 (dd,  $J = 3.5$ , 0.9 Hz, 1H), 3.62 – 3.41 (m, 2H), 2.17 – 2.05 (m, 2H), 1.99 – 1.89 (m, 1H), 1.07 (d,  $J = 6.1$  Hz, 3H), 0.90 (d,  $J = 6.4$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.7, 149.3 (d,  $J = 8.5$  Hz), 132.1 (d,  $J = 94.2$  Hz), 131.8 (d,  $J = 2.8$  Hz), 130.6 (d,  $J = 8.9$  Hz), 128.6 (d,  $J = 2.5$  Hz), 128.5 (d,  $J = 11.4$  Hz), 123.8, 122.8, 120.6, 110.8, 105.7 (d,  $J = 6.9$  Hz), 37.4 (d,  $J = 68.6$  Hz), 33.4 (d,  $J = 63.0$  Hz), 24.6 (d,  $J = 9.2$  Hz), 24.5 (d,  $J = 8.8$  Hz), 23.5 (d,  $J = 4.1$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  35.6.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{22}\text{O}_2\text{P}$   $[\text{M} + \text{H}]^+$  313.1352, found 313.1349.

### (*R*)-(benzofuran-3-ylmethyl)(isobutyl)(phenyl)phosphine oxide (**34**)



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-34** (27.4 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **34** as a white solid (25.5 mg, 82% yield, 90% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min,  $\lambda = 254$  nm),  $t_R$  (major) = 7.172 min,  $t_R$  (minor) = 10.040 min.

$[\alpha]_D^{25} = -37.1$  ( $c$  1.0,  $\text{CHCl}_3$ ).

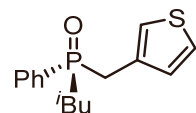
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 – 7.62 (m, 2H), 7.53 – 7.46 (m, 2H), 7.45 – 7.34 (m, 4H), 7.29 – 7.22 (m, 1H), 7.19 – 7.13 (m, 1H), 3.40 – 3.23 (m, 2H), 2.13 – 1.96 (m, 2H), 1.94 – 1.83 (m, 1H), 1.04 (d,  $J = 6.4$  Hz, 3H), 0.86 (d,  $J = 6.4$  Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 154.8, 143.1 (d, *J* = 7.4 Hz), 132.2 (d, *J* = 93.2 Hz), 131.7 (d, *J* = 2.8 Hz), 130.6 (d, *J* = 8.6 Hz), 128.5 (d, *J* = 11.3 Hz), 127.7 (d, *J* = 4.0 Hz), 124.3, 122.5, 119.5, 111.3, 110.7 (d, *J* = 7.9 Hz), 37.1 (d, *J* = 68.4 Hz), 27.5 (d, *J* = 66.0 Hz), 24.5 (d, *J* = 9.1 Hz), 24.4 (d, *J* = 8.7 Hz), 23.5 (d, *J* = 4.2 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 37.0.

**HRMS** (ESI) *m/z* calcd. for C<sub>19</sub>H<sub>22</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 313.1352, found 313.1348.

**(*R*)-isobutyl(phenyl)(thiophen-3-ylmethyl)phosphine oxide (35)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-35** (23.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **35** as a white solid (22.6 mg, 81% yield, 88% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm), *t<sub>R</sub>* (major) = 11.744 min, *t<sub>R</sub>* (minor) = 13.643 min.

[α]<sub>D</sub><sup>25</sup> = -62.3 (*c* 1.0, CHCl<sub>3</sub>).

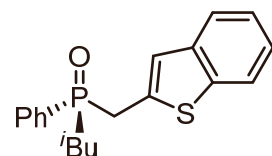
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.64 – 7.56 (m, 2H), 7.54 – 7.48 (m, 1H), 7.47 – 7.40 (m, 2H), 7.21 (dd, *J* = 4.9, 3.1 Hz, 1H), 6.93 (d, *J* = 3.1 Hz, 1H), 6.83 (d, *J* = 4.9 Hz, 1H), 3.41 – 3.25 (m, 2H), 2.13 – 1.89 (m, 2H), 1.88 – 1.77 (m, 1H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 132.4 (d, *J* = 92.4 Hz), 131.5 (d, *J* = 2.7 Hz), 131.1 (d, *J* = 7.5 Hz), 130.6 (d, *J* = 8.6 Hz), 129.0 (d, *J* = 3.3 Hz), 128.4 (d, *J* = 11.2 Hz), 125.6 (d, *J* = 1.6 Hz), 123.0 (d, *J* = 7.2 Hz), 36.9 (d, *J* = 68.5 Hz), 34.3 (d, *J* = 64.4 Hz), 24.5 (d, *J* = 9.1 Hz), 24.4 (d, *J* = 8.8 Hz), 23.4 (d, *J* = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 36.5.

**HRMS** (ESI) *m/z* calcd. for C<sub>15</sub>H<sub>20</sub>OPS [M + H]<sup>+</sup> 279.0967, found 279.0954.

**(*R*)-(benzo[*b*]thiophen-2-ylmethyl)(isobutyl)(phenyl)phosphine oxide (36)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-36** (29.5 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **36** as a white solid (23.5 mg, 72% yield, 85% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm), *t<sub>R</sub>* (major) = 8.768 min, *t<sub>R</sub>* (minor) = 11.083 min.

[α]<sub>D</sub><sup>25</sup> = -76.4 (*c* 1.0, CHCl<sub>3</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.75 – 7.61 (m, 4H), 7.56 – 7.49 (m, 1H), 7.49 – 7.41 (m, 2H), 7.33 – 7.22 (m, 2H), 7.04 (dd, *J* = 3.2, 0.9 Hz, 1H), 3.57 (d, *J* = 13.9 Hz, 2H),



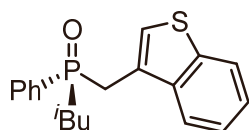
2.15 – 2.01 (m, 2H), 1.96 – 1.86 (m, 1H), 1.06 (d,  $J = 6.2$  Hz, 3H), 0.89 (d,  $J = 6.3$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9 (d,  $J = 2.8$  Hz), 139.7 (d,  $J = 1.6$  Hz), 133.7 (d,  $J = 8.6$  Hz), 131.9 (d,  $J = 93.7$  Hz), 131.8 (d,  $J = 2.9$  Hz), 130.7 (d,  $J = 8.8$  Hz), 128.5 (d,  $J = 11.5$  Hz), 124.2, 124.1 (d,  $J = 7.1$  Hz), 123.9 (d,  $J = 1.1$  Hz), 123.1 (d,  $J = 1.1$  Hz), 121.9 (d,  $J = 0.7$  Hz), 37.0 (d,  $J = 68.6$  Hz), 34.8 (d,  $J = 63.4$  Hz), 24.5 (d,  $J = 9.2$  Hz), 24.4 (d,  $J = 8.5$  Hz), 23.5 (d,  $J = 4.1$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  36.0.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{22}\text{OPS}$   $[\text{M} + \text{H}]^+$  329.1123, found 329.1121.

**(*R*)-(benzo[*b*]thiophen-3-ylmethyl)(isobutyl)(phenyl)phosphine oxide (37)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-37** (29.5 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **37** as a white solid (25.7 mg, 78% yield, 88% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min,  $\lambda = 220$  nm),  $t_R$  (major) = 7.464 min,  $t_R$  (minor) = 10.499 min.

$[\alpha]_D^{25} = -98.5$  ( $c$  1.0,  $\text{CHCl}_3$ ).

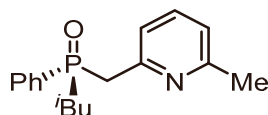
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.77 (m, 1H), 7.65 – 7.55 (m, 3H), 7.49 – 7.43 (m, 1H), 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.20 (d,  $J = 3.4$  Hz, 1H), 3.62 – 3.46 (m, 2H), 2.12 – 1.94 (m, 2H), 1.92 – 1.81 (m, 1H), 1.02 (d,  $J = 6.4$  Hz, 3H), 0.84 (d,  $J = 6.4$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8, 138.7 (d,  $J = 3.8$  Hz), 132.3 (d,  $J = 93.0$  Hz), 131.6 (d,  $J = 2.8$  Hz), 130.6 (d,  $J = 8.7$  Hz), 128.4 (d,  $J = 11.3$  Hz), 126.0 (d,  $J = 7.7$  Hz), 124.6 (d,  $J = 7.2$  Hz), 124.3, 124.0, 122.7, 121.7, 37.0 (d,  $J = 68.2$  Hz), 32.3 (d,  $J = 64.5$  Hz), 24.5 (d,  $J = 9.1$  Hz), 24.4 (d,  $J = 8.5$  Hz), 23.5 (d,  $J = 4.2$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  36.9.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{22}\text{OPS}$   $[\text{M} + \text{H}]^+$  329.1123, found 329.1121.

**(*R*)-isobutyl((6-methylpyridin-2-yl)methyl)(phenyl)phosphine oxide (38)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-38** (24.2 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **38** as a slightly yellow oil (18.6 mg, 65% yield, 73% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda = 220$  nm),  $t_R$  (major) = 7.589 min,  $t_R$  (minor) = 8.624 min.

$[\alpha]_D^{25} = -67.9$  ( $c$  1.0,  $\text{CHCl}_3$ ).



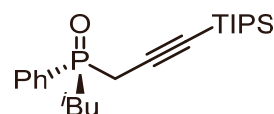
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.69 – 7.60 (m, 2H), 7.53 – 7.39 (m, 4H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 3.57 – 3.42 (m, 2H), 2.49 (s, 3H), 2.13 – 1.85 (m, 3H), 1.01 (d, *J* = 6.1 Hz, 3H), 0.85 (d, *J* = 6.0 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.0 (d, *J* = 2.2 Hz), 152.2 (d, *J* = 7.4 Hz), 136.8 (d, *J* = 2.4 Hz), 132.6 (d, *J* = 93.0 Hz), 131.5 (d, *J* = 2.8 Hz), 130.6 (d, *J* = 8.8 Hz), 128.3 (d, *J* = 11.4 Hz), 121.7 (d, *J* = 4.1 Hz), 121.3 (d, *J* = 2.7 Hz), 42.4 (d, *J* = 60.4 Hz), 37.2 (d, *J* = 68.3 Hz), 24.5 (d, *J* = 9.0 Hz), 24.4 (d, *J* = 8.8 Hz), 24.3, 23.3 (d, *J* = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 37.5.

**HRMS** (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>23</sub>NOP [M + H]<sup>+</sup> 288.1512, found 288.1501.

**(*R*)-isobutyl(phenyl)(3-(triisopropylsilyl)prop-2-yn-1-yl)phosphine oxide (39)**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-39** (35.8 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **39** as a colorless oil (24.6 mg, 65% yield, 87% ee).

**HPLC** analysis: Chiralpak IC (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 214 nm), *t<sub>R</sub>* (major) = 24.928 min, *t<sub>R</sub>* (minor) = 28.225 min.

[α]<sub>D</sub><sup>25</sup> = −11.8 (*c* 1.0, CHCl<sub>3</sub>).

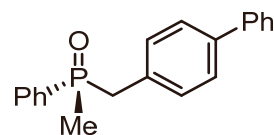
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.96 – 7.89 (m, 2H), 7.58 – 7.53 (m, 1H), 7.50 – 7.44 (m, 2H), 3.13 (t, *J* = 17.6 Hz, 1H), 2.99 (t, *J* = 17.6 Hz, 1H), 2.33 – 2.23 (m, 1H), 2.21 – 2.08 (m, 2H), 1.11 (d, *J* = 6.3 Hz, 3H), 1.06 (s, 21H), 0.99 (d, *J* = 6.3 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 132.3 (d, *J* = 94.0 Hz), 132.0 (d, *J* = 2.8 Hz), 130.7 (d, *J* = 8.6 Hz), 128.4 (d, *J* = 11.6 Hz), 99.0 (d, *J* = 8.4 Hz), 85.6 (d, *J* = 7.0 Hz), 36.3 (d, *J* = 70.4 Hz), 24.7 (d, *J* = 64.6 Hz), 24.5 (d, *J* = 8.2 Hz), 24.4 (d, *J* = 7.6 Hz), 23.5 (d, *J* = 4.1 Hz), 18.5, 11.2.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 36.1.

**HRMS** (ESI) *m/z* calcd. for C<sub>22</sub>H<sub>38</sub>OPSi [M + H]<sup>+</sup> 377.2424, found 377.2421.

**(*R*)-([1,1'-biphenyl]-4-ylmethyl)(methyl)(phenyl)phosphine oxide (40)**



According to the **general procedure A**, substrates **A-2** (14.0 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **40** as a white solid (22.3 mg, 73% yield, 82% ee).

**HPLC** analysis: Chiralcel OJ-3 (hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 254 nm), *t<sub>R</sub>* (major) = 11.617 min, *t<sub>R</sub>* (minor) = 15.224 min.

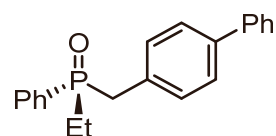
[α]<sub>D</sub><sup>25</sup> = −29.3 (*c* 1.0, CHCl<sub>3</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.69 – 7.61 (m, 2H), 7.59 – 7.39 (m, 9H), 7.36 – 7.30 (m, 1H), 7.17 (dd, *J* = 8.2, 2.1 Hz, 2H), 3.44 – 3.25 (m, 2H), 1.71 (d, *J* = 12.7 Hz, 3H).  
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.5 (d, *J* = 1.2 Hz), 139.7 (d, *J* = 3.3 Hz), 132.9 (d, *J* = 96.7 Hz), 131.8 (d, *J* = 2.7 Hz), 130.7 (d, *J* = 7.9 Hz), 130.3 (d, *J* = 9.1 Hz), 130.1 (d, *J* = 5.1 Hz), 128.7, 128.5 (d, *J* = 11.6 Hz), 127.3, 127.2 (d, *J* = 3.1 Hz), 126.9, 40.0 (d, *J* = 64.3 Hz), 14.7 (d, *J* = 71.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 35.3.

**HRMS** (ESI) *m/z* calcd. for C<sub>20</sub>H<sub>20</sub>OP [M + H]<sup>+</sup> 307.1246, found 307.1245.

**(*R*)-([1,1'-biphenyl]-4-ylmethyl)(ethyl)(phenyl)phosphine oxide (41)**



According to the **general procedure A**, substrates **A-3** (15.4 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **41** as a white solid (28.1 mg, 88% yield, 90% ee).

**HPLC** analysis: Chiralcel OJ-3 (hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 254 nm), *t<sub>R</sub>* (major) = 9.886 min, *t<sub>R</sub>* (minor) = 27.488 min.

[α]<sub>D</sub><sup>25</sup> = −28.4 (*c* 1.0, CHCl<sub>3</sub>).

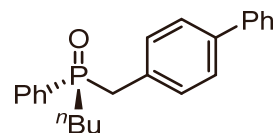
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.67 – 7.59 (m, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.52 – 7.37 (m, 7H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.17 (dd, *J* = 8.2, 2.2 Hz, 2H), 3.44 – 3.28 (m, 2H), 2.11 – 1.84 (m, 2H), 1.17 – 1.05 (m, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.6 (d, *J* = 1.1 Hz), 139.6 (d, *J* = 3.2 Hz), 131.6 (d, *J* = 2.8 Hz), 131.2 (d, *J* = 91.8 Hz), 130.8 (d, *J* = 8.7 Hz), 130.7 (d, *J* = 7.7 Hz), 130.1 (d, *J* = 5.0 Hz), 128.7, 128.4 (d, *J* = 11.3 Hz), 127.2, 127.1 (d, *J* = 2.6 Hz), 126.9, 38.0 (d, *J* = 62.3 Hz), 21.2 (d, *J* = 70.3 Hz), 5.3 (d, *J* = 5.2 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 39.7.

**HRMS** (ESI) *m/z* calcd. for C<sub>21</sub>H<sub>22</sub>OP [M + H]<sup>+</sup> 321.1403, found 321.1400.

**(*R*)-([1,1'-biphenyl]-4-ylmethyl)(*n*-butyl)(phenyl)phosphine oxide (42)**



According to the **general procedure A**, substrates **A-4** (18.2 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **42** as a white solid (27.5 mg, 89% yield, 80% ee).

**HPLC** analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), *t<sub>R</sub>* (major) = 10.531 min, *t<sub>R</sub>* (minor) = 13.327 min.

[α]<sub>D</sub><sup>25</sup> = −37.3 (*c* 1.0, CHCl<sub>3</sub>).

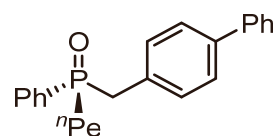
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.66 – 7.58 (m, 2H), 7.58 – 7.54 (m, 2H), 7.53 – 7.50 (m, 1H), 7.49 – 7.39 (m, 6H), 7.36 – 7.30 (m, 1H), 7.16 (dd, *J* = 8.3, 2.2 Hz, 2H), 3.43 – 3.28 (m, 2H), 2.08 – 1.86 (m, 2H), 1.70 – 1.56 (m, 1H), 1.49 – 1.31 (m, 3H), 0.85 (t, *J* = 7.2 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.6 (d, *J* = 1.0 Hz), 139.6 (d, *J* = 3.3 Hz), 131.8 (d, *J* = 92.9 Hz), 131.6 (d, *J* = 2.7 Hz), 130.8 (d, *J* = 7.6 Hz), 130.7 (d, *J* = 8.5 Hz), 130.2 (d, *J* = 5.0 Hz), 128.7, 128.4 (d, *J* = 11.3 Hz), 127.2 (d, *J* = 2.6 Hz), 127.1, 126.9, 38.6 (d, *J* = 62.1 Hz), 28.0 (d, *J* = 69.4 Hz), 24.0 (d, *J* = 14.6 Hz), 23.3 (d, *J* = 4.2 Hz), 13.6.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 38.1.

**HRMS** (ESI) *m/z* calcd. for C<sub>23</sub>H<sub>26</sub>OP [M + H]<sup>+</sup> 349.1716, found 349.1714.

**(R)-([1,1'-biphenyl]-4-ylmethyl)(n-pentyl)(phenyl)phosphine oxide (43)**



According to the **general procedure A**, substrates **A-5** (19.6 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **43** as a white solid (26.8 mg, 74% yield, 89% ee).

**HPLC** analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), *t<sub>R</sub>* (major) = 18.936 min, *t<sub>R</sub>* (minor) = 23.217 min.

[α]<sub>D</sub><sup>25</sup> = −40.3 (*c* 1.0, CHCl<sub>3</sub>).

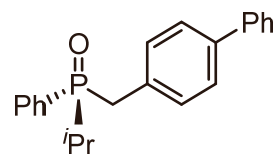
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.59 (m, 2H), 7.58 – 7.54 (m, 2H), 7.53 – 7.39 (m, 7H), 7.36 – 7.30 (m, 1H), 7.19 – 7.13 (m, 2H), 3.42 – 3.28 (m, 2H), 2.07 – 1.83 (m, 2H), 1.69 – 1.57 (m, 1H), 1.51 – 1.38 (m, 1H), 1.36 – 1.26 (m, 4H), 0.83 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.6 (d, *J* = 1.2 Hz), 139.6 (d, *J* = 3.4 Hz), 131.8 (d, *J* = 93.1 Hz), 131.7 (d, *J* = 2.9 Hz), 130.8 (d, *J* = 7.9 Hz), 130.7 (d, *J* = 8.7 Hz), 130.2 (d, *J* = 5.1 Hz), 128.7, 128.5 (d, *J* = 11.2 Hz), 127.3, 127.2 (d, *J* = 2.8 Hz), 126.9, 38.6 (d, *J* = 62.1 Hz), 33.1 (d, *J* = 14.2 Hz), 28.3 (d, *J* = 69.3 Hz), 22.1, 20.9 (d, *J* = 4.2 Hz), 13.8.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 38.1.

**HRMS** (ESI) *m/z* calcd. for C<sub>24</sub>H<sub>28</sub>OP [M + H]<sup>+</sup> 363.1872, found 363.1869.

**(S)-([1,1'-biphenyl]-4-ylmethyl)(isopropyl)(phenyl)phosphine oxide (44)**



According to the **general procedure A**, substrates **A-6** (16.8 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **44** as a white solid (30.1 mg, 90% yield, 93% ee).

**HPLC** analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 11.887 min,  $t_R$  (minor) = 19.337 min.

$[\alpha]_D^{25} = -47.5$  (*c* 1.0, CHCl<sub>3</sub>).

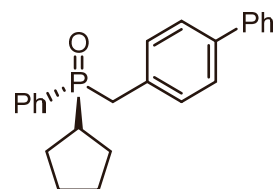
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 – 7.57 (m, 2H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.46 – 7.37 (m, 6H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.21 – 7.15 (m, 2H), 3.47 (t, *J* = 14.7 Hz, 1H), 3.42 – 3.32 (m, 1H), 2.24 – 2.10 (m, 1H), 1.30 (dd, *J* = 15.6, 7.1 Hz, 3H), 1.07 (dd, *J* = 16.5, 7.1 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.6 (d, *J* = 1.2 Hz), 139.4 (d, *J* = 3.0 Hz), 131.5 (d, *J* = 2.7 Hz), 131.2 (d, *J* = 8.0 Hz), 130.8 (d, *J* = 7.4 Hz), 130.3 (d, *J* = 90.1 Hz), 130.2 (d, *J* = 5.0 Hz), 128.6, 128.2 (d, *J* = 11.0 Hz), 127.1, 127.1 (d, *J* = 2.5 Hz), 126.9, 35.0 (d, *J* = 60.3 Hz), 27.1 (d, *J* = 69.4 Hz), 15.8 (d, *J* = 2.4 Hz), 15.0 (d, *J* = 3.2 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  43.5.

**HRMS** (ESI) *m/z* calcd. for C<sub>22</sub>H<sub>24</sub>OP [M + H]<sup>+</sup> 335.1559, found 335.1557.

**(S)-([1,1'-biphenyl]-4-ylmethyl)(cyclopentyl)(phenyl)phosphine oxide (45)**



According to the **general procedure A**, substrates **A-7** (19.4 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **45** as a white solid (27.8 mg, 77% yield, 91% ee).

**HPLC** analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 28.035 min,  $t_R$  (minor) = 46.369 min.

$[\alpha]_D^{25} = -55.1$  (*c* 1.0, CHCl<sub>3</sub>).

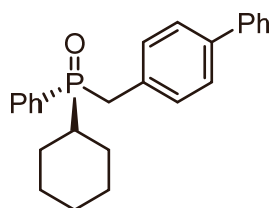
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 – 7.52 (m, 4H), 7.51 – 7.37 (m, 7H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.15 – 7.08 (m, 2H), 3.38 (d, *J* = 14.5 Hz, 2H), 2.44 – 2.31 (m, 1H), 2.10 – 1.88 (m, 2H), 1.79 – 1.58 (m, 5H), 1.56 – 1.46 (m, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.6 (d, *J* = 1.1 Hz), 139.4 (d, *J* = 3.2 Hz), 131.7 (d, *J* = 91.8 Hz), 131.4 (d, *J* = 2.6 Hz), 131.1 (d, *J* = 8.2 Hz), 130.2 (d, *J* = 4.9 Hz), 128.7, 128.2 (d, *J* = 11.0 Hz), 127.2, 127.0 (d, *J* = 2.7 Hz), 126.9, 37.5 (d, *J* = 60.9 Hz), 36.3 (d, *J* = 72.3 Hz), 26.9 (d, *J* = 8.5 Hz), 26.7 (d, *J* = 1.5 Hz), 26.4 (d, *J* = 9.1 Hz), 25.8 (d, *J* = 1.9 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  41.6.

**HRMS** (ESI) *m/z* calcd. for C<sub>24</sub>H<sub>26</sub>OP [M + H]<sup>+</sup> 361.1716, found 361.1713.

**(S)-([1,1'-biphenyl]-4-ylmethyl)(cyclohexyl)(phenyl)phosphine oxide (46)**



According to the **general procedure A**, substrates **A-8** (20.8 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **46** as a white solid (27.6 mg, 74% yield, 90% ee).

**HPLC** analysis: Chiralcel OJ-3 (hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 9.476 min,  $t_R$  (minor) = 12.098 min.

$[\alpha]_D^{25} = -16.9$  ( $c$  1.0, CHCl<sub>3</sub>).

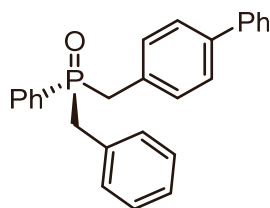
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 – 7.37 (m, 11H), 7.31 (t,  $J$  = 7.3 Hz, 1H), 7.20 – 7.14 (m, 2H), 3.46 (t,  $J$  = 14.8 Hz, 1H), 3.40 – 3.31 (m, 1H), 2.17 – 2.08 (m, 1H), 2.05 – 1.83 (m, 3H), 1.80 – 1.62 (m, 3H), 1.55 – 1.41 (m, 1H), 1.39 – 1.30 (m, 1H), 1.24 – 1.13 (m, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.6, 139.4 (d,  $J$  = 3.0 Hz), 131.5 (d,  $J$  = 2.8 Hz), 131.2 (d,  $J$  = 8.1 Hz), 130.8 (d,  $J$  = 7.3 Hz), 130.4 (d,  $J$  = 90.9 Hz), 130.2 (d,  $J$  = 4.8 Hz), 128.7, 128.2 (d,  $J$  = 11.0 Hz), 127.2, 127.1 (d,  $J$  = 2.5 Hz), 126.9, 37.4 (d,  $J$  = 69.5 Hz), 34.7 (d,  $J$  = 60.4 Hz), 26.2 (d,  $J$  = 13.3 Hz), 25.7, 25.4 (d,  $J$  = 2.6 Hz), 24.8 (d,  $J$  = 3.3 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  40.7.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>25</sub>H<sub>28</sub>OP [M + H]<sup>+</sup> 375.1872, found 375.1871.

**(R)-([1,1'-biphenyl]-4-ylmethyl)(benzyl)(phenyl)phosphine oxide (47)**



According to the **general procedure A**, substrates **A-9** (21.6 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **47** as a white solid (25.9 mg, 68% yield, 87% ee).

**HPLC** analysis: Chiralcel OJ-3 (hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min,  $\lambda$  = 254 nm),  $t_R$  (minor) = 23.765 min,  $t_R$  (major) = 39.179 min.

$[\alpha]_D^{25} = -52.2$  ( $c$  1.0, CHCl<sub>3</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 – 7.51 (m, 4H), 7.50 – 7.36 (m, 7H), 7.32 (t,  $J$  = 7.2 Hz, 1H), 7.26 – 7.16 (m, 5H), 7.15 – 7.10 (m, 2H), 3.45 – 3.33 (m, 4H).

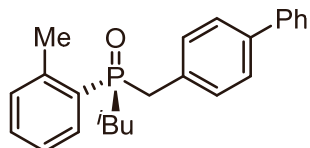
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.5, 139.6 (d,  $J$  = 3.5 Hz), 131.7 (d,  $J$  = 2.8 Hz), 131.3 (d,  $J$  = 7.6 Hz), 131.0 (d,  $J$  = 8.5 Hz), 130.9 (d,  $J$  = 98.7 Hz), 130.4 (d,  $J$  = 7.9 Hz), 130.3 (d,  $J$  = 5.3 Hz), 129.9 (d,  $J$  = 5.2 Hz), 128.7, 128.5 (d,  $J$  = 2.5 Hz), 128.3 (d,

$J = 11.4$  Hz), 127.2 (d,  $J = 3.1$  Hz), 127.1, 126.9, 126.8 (d,  $J = 3.2$  Hz), 37.5 (d,  $J = 63.4$  Hz), 36.9 (d,  $J = 63.4$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  35.0.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{26}\text{H}_{24}\text{OP}$   $[\text{M} + \text{H}]^+$  383.1559, found 383.1556.

**(*R*)-([1,1'-biphenyl]-4-ylmethyl)(isobutyl)(*o*-tolyl)phosphine oxide (48)**



According to the **general procedure A**, substrates **A-10** (19.6 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **48** as a white solid (27.8 mg, 77% yield, 95% ee).

HPLC analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min,  $\lambda = 254$  nm),  $t_R$  (major) = 20.910 min,  $t_R$  (minor) = 27.769 min.

$[\alpha]_D^{25} = -36.5$  ( $c$  1.0,  $\text{CHCl}_3$ ).

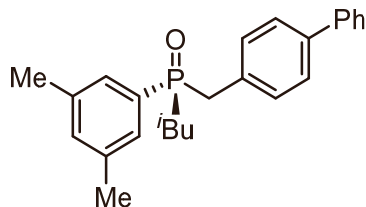
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 – 7.52 (m, 3H), 7.48 – 7.35 (m, 5H), 7.35 – 7.29 (m, 1H), 7.25 – 7.19 (m, 2H), 7.13 (dd,  $J = 8.3, 2.2$  Hz, 2H), 3.49 – 3.27 (m, 2H), 2.57 (d,  $J = 1.2$  Hz, 3H), 2.15 – 2.03 (m, 1H), 2.02 – 1.88 (m, 2H), 1.04 (d,  $J = 6.5$  Hz, 3H), 0.94 (d,  $J = 6.6$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.3 (d,  $J = 8.3$  Hz), 140.6 (d,  $J = 1.1$  Hz), 139.5 (d,  $J = 3.2$  Hz), 132.3 (d,  $J = 9.5$  Hz), 131.8 (d,  $J = 10.6$  Hz), 131.5 (d,  $J = 2.7$  Hz), 131.1 (d,  $J = 7.8$  Hz), 130.3 (d,  $J = 89.3$  Hz), 130.2 (d,  $J = 5.0$  Hz), 128.7, 127.2, 127.0 (d,  $J = 2.7$  Hz), 126.9, 125.5 (d,  $J = 11.3$  Hz), 39.3 (d,  $J = 61.5$  Hz), 37.4 (d,  $J = 68.0$  Hz), 24.6 (d,  $J = 9.6$  Hz), 24.4 (d,  $J = 7.8$  Hz), 23.6 (d,  $J = 3.9$  Hz), 21.6 (d,  $J = 2.7$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  39.3.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{24}\text{H}_{28}\text{OP}$   $[\text{M} + \text{H}]^+$  363.1872, found 363.1870.

**(*R*)-([1,1'-biphenyl]-4-ylmethyl)(3,5-dimethylphenyl)(isobutyl)phosphine oxide (49)**



According to the **general procedure A**, substrates **A-11** (21.0 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **49** as a white solid (24.1 mg, 64% yield, 91% ee).

HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda = 254$  nm),  $t_R$  (major) = 7.907 min,  $t_R$  (minor) = 14.993 min.

$[\alpha]_D^{25} = -15.4$  ( $c$  1.0,  $\text{CHCl}_3$ ).

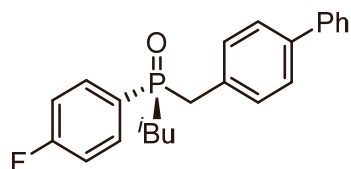
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.54 (m, 2H), 7.50 – 7.39 (m, 4H), 7.36 – 7.30 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 11.2 Hz, 2H), 7.15 (dd, *J* = 8.3, 2.2 Hz, 2H), 7.13 (s, 1H), 3.39 – 3.21 (m, 2H), 2.33 (s, 6H), 2.11 – 2.00 (m, 1H), 1.99 – 1.90 (m, 1H), 1.87 – 1.78 (m, 1H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.7 (d, *J* = 1.1 Hz), 139.6 (d, *J* = 3.3 Hz), 138.0 (d, *J* = 11.9 Hz), 133.3 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 92.5 Hz), 131.1 (d, *J* = 7.7 Hz), 130.3 (d, *J* = 5.1 Hz), 128.7, 128.4 (d, *J* = 8.7 Hz), 127.2, 127.1 (d, *J* = 2.7 Hz), 127.0, 39.7 (d, *J* = 62.0 Hz), 36.8 (d, *J* = 68.0 Hz), 24.7 (d, *J* = 9.4 Hz), 24.6 (d, *J* = 8.9 Hz), 23.4 (d, *J* = 4.0 Hz), 21.3.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 37.3.

**HRMS** (ESI) *m/z* calcd. for C<sub>25</sub>H<sub>30</sub>OP [M + H]<sup>+</sup> 377.2029, found 377.2028.

**(*R*)-([1,1'-biphenyl]-4-ylmethyl)(4-fluorophenyl)(isobutyl)phosphine oxide (50)**



According to the **general procedure A**, substrates **A-12** (20.0 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **50** as a white solid (19.8 mg, 54% yield, 89% ee).

**HPLC** analysis: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), *t<sub>R</sub>* (major) = 11.765 min, *t<sub>R</sub>* (minor) = 14.853 min.

[α]<sub>D</sub><sup>25</sup> = −14.3 (*c* 1.0, CHCl<sub>3</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.64 – 7.53 (m, 4H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.36 – 7.30 (m, 1H), 7.16 – 7.08 (m, 4H), 3.31 (d, *J* = 14.5 Hz, 2H), 2.12 – 2.02 (m, 1H), 2.01 – 1.94 (m, 1H), 1.89 – 1.79 (m, 1H), 1.06 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 6.5 Hz, 3H).

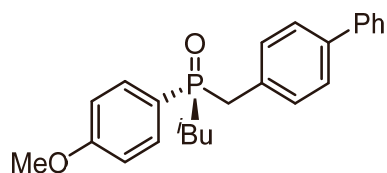
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 164.8 (dd, *J* = 252.8, 3.3 Hz), 140.5 (d, *J* = 1.4 Hz), 139.6 (d, *J* = 3.3 Hz), 133.2 (dd, *J* = 10.0, 8.6 Hz), 130.6 (d, *J* = 7.7 Hz), 130.2 (d, *J* = 5.0 Hz), 128.7, 128.2 (dd, *J* = 94.6, 3.4 Hz), 127.3, 127.2 (d, *J* = 2.8 Hz), 126.9, 115.7 (dd, *J* = 21.3, 12.2 Hz), 39.7 (d, *J* = 62.8 Hz), 37.1 (d, *J* = 68.6 Hz), 24.6 (d, *J* = 2.9 Hz), 24.5 (d, *J* = 2.6 Hz), 23.5 (d, *J* = 4.2 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 36.4.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ −107.4.

**HRMS** (ESI) *m/z* calcd. for C<sub>23</sub>H<sub>25</sub>FOP [M + H]<sup>+</sup> 367.1622, found 367.1620.

**(*R*)-([1,1'-biphenyl]-4-ylmethyl)(isobutyl)(2-methoxyphenyl)phosphine oxide (51)**



According to the **general procedure A**, substrates **A-13** (21.2 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **51** as a white solid (34.1 mg, 90% yield, 93% ee).

**HPLC** analysis: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (minor) = 26.933 min,  $t_R$  (major) = 29.575 min.

$[\alpha]_D^{25} = -22.6$  ( $c$  1.0, CHCl<sub>3</sub>).

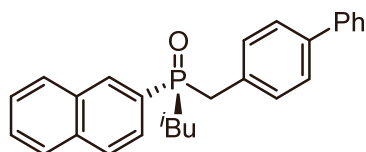
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.60 – 7.49 (m, 4H), 7.49 – 7.38 (m, 4H), 7.36 – 7.29 (m, 1H), 7.13 (dd,  $J$  = 8.3, 2.2 Hz, 2H), 6.94 (dd,  $J$  = 8.8, 2.2 Hz, 2H), 3.84 (s, 3H), 3.29 (d,  $J$  = 14.5 Hz, 2H), 2.11 – 2.01 (m, 1H), 1.99 – 1.89 (m, 1H), 1.86 – 1.76 (m, 1H), 1.05 (d,  $J$  = 6.6 Hz, 3H), 0.87 (d,  $J$  = 6.6 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.1 (d,  $J$  = 2.9 Hz), 140.6 (d,  $J$  = 1.4 Hz), 139.4 (d,  $J$  = 3.3 Hz), 132.6 (d,  $J$  = 9.9 Hz), 131.1 (d,  $J$  = 7.6 Hz), 130.2 (d,  $J$  = 4.9 Hz), 128.7, 127.2, 127.1 (d,  $J$  = 2.7 Hz), 126.9, 123.2 (d,  $J$  = 98.5 Hz), 113.9 (d,  $J$  = 12.2 Hz), 55.2, 39.8 (d,  $J$  = 62.7 Hz), 37.1 (d,  $J$  = 68.7 Hz), 24.6 (d,  $J$  = 8.9 Hz), 24.5 (d,  $J$  = 8.5 Hz), 23.4 (d,  $J$  = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  36.9.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>24</sub>H<sub>28</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 379.1821, found 379.1818.

**(*R*)-([1,1'-biphenyl]-4-ylmethyl)(isobutyl)(naphthalen-2-yl)phosphine oxide (**52**)**



According to the **general procedure A**, substrates **A-14** (23.2 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **52** as a white solid (27.9 mg, 70% yield, 93% ee).

**HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 23.293 min,  $t_R$  (minor) = 48.408 min.

$[\alpha]_D^{25} = -30.3$  ( $c$  1.0, CHCl<sub>3</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 (d,  $J$  = 12.7 Hz, 1H), 7.93 – 7.84 (m, 3H), 7.63 – 7.47 (m, 5H), 7.47 – 7.37 (m, 4H), 7.31 (t,  $J$  = 7.3 Hz, 1H), 7.20 – 7.11 (m, 2H), 3.40 (d,  $J$  = 14.3 Hz, 2H), 2.13 – 2.02 (m, 2H), 2.00 – 1.90 (m, 1H), 1.07 (d,  $J$  = 6.2 Hz, 3H), 0.86 (d,  $J$  = 6.2 Hz, 3H).

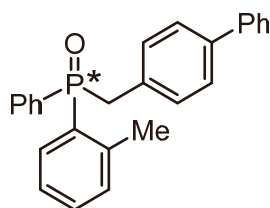
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.6 (d,  $J$  = 1.2 Hz), 139.6 (d,  $J$  = 3.3 Hz), 134.5 (d,  $J$  = 2.4 Hz), 133.3 (d,  $J$  = 7.2 Hz), 132.5 (d,  $J$  = 12.2 Hz), 130.8 (d,  $J$  = 7.7 Hz), 130.2 (d,  $J$  = 5.0 Hz), 129.4 (d,  $J$  = 92.4 Hz), 128.8, 128.7, 128.1 (d,  $J$  = 11.3 Hz), 128.0, 127.7, 127.2, 127.1 (d,  $J$  = 3.0 Hz), 126.9, 126.8 (d,  $J$  = 3.6 Hz), 125.3 (d,  $J$  = 10.4 Hz), 39.5 (d,  $J$  = 62.5 Hz), 37.0 (d,  $J$  = 68.3 Hz), 24.6 (d,  $J$  = 9.1 Hz), 24.5 (d,  $J$  = 8.5 Hz), 23.5 (d,  $J$  = 4.1 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  36.9.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>25</sub>H<sub>30</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 399.1872, found 399.1871.



**([1,1'-biphenyl]-4-ylmethyl)(phenyl)(*o*-tolyl)phosphine oxide (53)**



According to the **general procedure A**, substrates **A-15** (21.6 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **53** as a white solid (26.7 mg, 70% yield, 82% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 13.326 min,  $t_R$  (minor) = 25.620 min.

$[\alpha]_D^{25} = -25.4$  ( $c$  1.0, CHCl<sub>3</sub>).

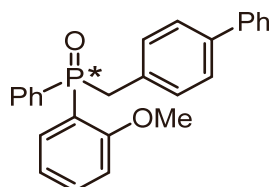
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (ddd,  $J$  = 12.7, 7.7, 1.3 Hz, 1H), 7.57 – 7.49 (m, 4H), 7.49 – 7.35 (m, 8H), 7.34 – 7.27 (m, 2H), 7.23 (dd,  $J$  = 7.7, 4.1 Hz, 1H), 7.15 (dd,  $J$  = 8.2, 2.2 Hz, 2H), 3.82 (t,  $J$  = 14.6 Hz, 1H), 3.73 – 3.62 (m, 1H), 2.38 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.9 (d,  $J$  = 7.6 Hz), 140.7 (d,  $J$  = 1.1 Hz), 139.5 (d,  $J$  = 3.1 Hz), 133.0 (d,  $J$  = 98.3 Hz), 132.1 (d,  $J$  = 10.1 Hz), 132.0 (d,  $J$  = 2.1 Hz), 131.5 (d,  $J$  = 2.9 Hz), 131.4 (d,  $J$  = 10.9 Hz), 131.0 (d,  $J$  = 9.5 Hz), 130.6 (d,  $J$  = 5.2 Hz), 130.5 (d,  $J$  = 97.3 Hz), 130.2 (d,  $J$  = 7.8 Hz), 128.7, 128.3 (d,  $J$  = 11.8 Hz), 127.1, 126.9, 125.4 (d,  $J$  = 12.0 Hz), 37.3 (d,  $J$  = 66.5 Hz), 21.3 (d,  $J$  = 4.2 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  30.8.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>26</sub>H<sub>24</sub>OP [M + H]<sup>+</sup> 383.1559, found 383.1556.

**([1,1'-biphenyl]-4-ylmethyl)(2-methoxyphenyl)(phenyl)phosphine oxide (54)**



According to the **general procedure A**, substrates **A-16** (23.2 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **54** as a white solid (31.5 mg, 79% yield, 86% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (minor) = 22.373 min,  $t_R$  (major) = 26.772 min.

$[\alpha]_D^{25} = -18.1$  ( $c$  1.0, CHCl<sub>3</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 (ddd,  $J$  = 12.9, 7.5, 1.7 Hz, 1H), 7.82 – 7.74 (m, 2H), 7.55 – 7.43 (m, 4H), 7.43 – 7.33 (m, 6H), 7.29 (d,  $J$  = 7.2 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.06 – 6.98 (m, 1H), 6.92 (dd,  $J$  = 8.3, 5.4 Hz, 1H), 3.97 – 3.88 (m, 1H), 3.86 (s, 3H), 3.81 (t,  $J$  = 15.2 Hz, 1H).

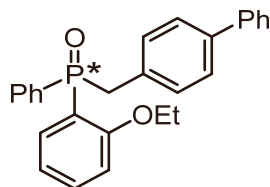
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.4 (d,  $J$  = 4.5 Hz), 140.7 (d,  $J$  = 1.1 Hz), 139.2 (d,  $J$  = 3.3 Hz), 134.9 (d,  $J$  = 5.1 Hz), 133.9 (d,  $J$  = 2.2 Hz), 133.6 (d,  $J$  = 100.7 Hz), 131.3 (d,  $J$  = 2.8 Hz), 131.0 (d,  $J$  = 8.7 Hz), 130.7 (d,  $J$  = 9.6 Hz), 130.2 (d,  $J$  = 5.5 Hz), 128.5,

128.0 (d,  $J = 11.8$  Hz), 127.0, 126.9 (d,  $J = 2.9$  Hz), 126.8, 121.1 (d,  $J = 10.8$  Hz), 119.5 (d,  $J = 97.7$  Hz), 110.5 (d,  $J = 6.9$  Hz), 55.2, 36.7 (d,  $J = 67.6$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  29.2.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{26}\text{H}_{24}\text{O}_2\text{P}$   $[\text{M} + \text{H}]^+$  399.1508, found 399.1508.

**([1,1'-biphenyl]-4-ylmethyl)(2-ethoxyphenyl)(phenyl)phosphine oxide (55)**



According to the **general procedure A**, substrates **A-17** (24.6 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **55** as a white solid (26.4 mg, 64% yield, 77% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda = 254$  nm),  $t_R$  (minor) = 17.343 min,  $t_R$  (major) = 21.337 min.

$[\alpha]_D^{25} = -16.5$  (c 1.0,  $\text{CHCl}_3$ ).

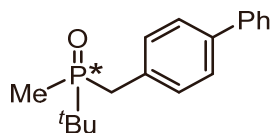
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (ddd,  $J = 12.8, 7.5, 1.7$  Hz, 1H), 7.82 – 7.72 (m, 2H), 7.55 – 7.48 (m, 2H), 7.48 – 7.33 (m, 8H), 7.28 (t,  $J = 7.3$  Hz, 1H), 7.26 – 7.19 (m, 2H), 7.04 – 6.97 (m, 1H), 6.87 (dd,  $J = 8.3, 5.5$  Hz, 1H), 4.20 – 4.11 (m, 1H), 4.06 – 3.98 (m, 1H), 3.98 – 3.79 (m, 2H), 1.35 (t,  $J = 7.0$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7 (d,  $J = 4.6$  Hz), 140.7 (d,  $J = 1.3$  Hz), 139.2 (d,  $J = 3.4$  Hz), 135.0 (d,  $J = 4.9$  Hz), 133.8 (d,  $J = 101.0$  Hz), 133.9 (d,  $J = 2.1$  Hz), 131.2 (d,  $J = 2.9$  Hz), 131.0 (d,  $J = 8.7$  Hz), 130.7 (d,  $J = 9.6$  Hz), 130.2 (d,  $J = 5.5$  Hz), 128.5, 128.0 (d,  $J = 11.9$  Hz), 127.0, 126.9 (d,  $J = 2.8$  Hz), 126.8, 120.9 (d,  $J = 10.9$  Hz), 119.2 (d,  $J = 98.3$  Hz), 111.0 (d,  $J = 6.9$  Hz), 63.7, 36.4 (d,  $J = 67.5$  Hz), 14.4.

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  29.3.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{27}\text{H}_{26}\text{O}_2\text{P}$   $[\text{M} + \text{H}]^+$  413.1665, found 413.1667.

**([1,1'-biphenyl]-4-ylmethyl)(*tert*-butyl)(methyl)phosphine oxide (56)**



According to the **general procedure A**, substrates **A-18** (12.0 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **56** as a colorless oil (25.4 mg, 89% yield, 97% ee).

HPLC analysis: Chiralpak IF (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda = 254$  nm),  $t_R$  (major) = 25.623 min,  $t_R$  (minor) = 31.664 min.

$[\alpha]_D^{25} = -21.1$  (c 1.0,  $\text{CHCl}_3$ ).

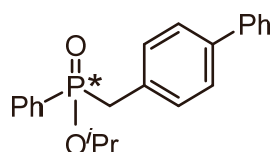
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.53 (m, 4H), 7.47 – 7.37 (m, 4H), 7.36 – 7.31 (m, 1H), 3.31 – 3.20 (m, 1H), 2.99 (dd, *J* = 14.4, 7.4 Hz, 1H), 1.25 (d, *J* = 10.8 Hz, 3H), 1.24 (d, *J* = 14.6 Hz, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.8 (d, *J* = 1.0 Hz), 139.7 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 8.0 Hz), 130.3 (d, *J* = 4.8 Hz), 128.8, 127.4 (d, *J* = 2.4 Hz), 127.2, 127.0, 32.9 (d, *J* = 63.0 Hz), 32.3 (d, *J* = 72.9 Hz), 24.5, 9.0 (d, *J* = 64.7 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 52.9.

**HRMS** (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>24</sub>OP [M + H]<sup>+</sup> 287.1559, found 287.1558.

**isopropyl ([1,1'-biphenyl]-4-ylmethyl)(phenyl)phosphinate (57)**



According to the **general procedure C**, substrates **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **57** as a white solid (28.6 mg, 82% yield, 71% ee).

**HPLC** analysis: Chiralpak IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), *t<sub>R</sub>* (major) = 8.673 min, *t<sub>R</sub>* (minor) = 12.433 min.

[α]<sub>D</sub><sup>25</sup> = −23.4 (*c* 1.0, CHCl<sub>3</sub>).

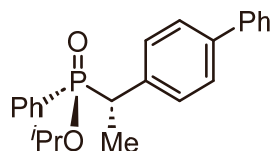
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.70 – 7.62 (m, 2H), 7.58 – 7.54 (m, 2H), 7.53 – 7.48 (m, 1H), 7.47 – 7.38 (m, 6H), 7.35 – 7.29 (m, 1H), 7.17 (dd, *J* = 8.3, 2.5 Hz, 2H), 4.63 – 4.50 (m, 1H), 3.30 (d, *J* = 17.7 Hz, 2H), 1.34 (d, *J* = 6.2 Hz, 3H), 1.18 (d, *J* = 6.1 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.7 (d, *J* = 1.5 Hz), 139.4 (d, *J* = 3.7 Hz), 132.1 (d, *J* = 2.9 Hz), 131.9 (d, *J* = 9.6 Hz), 131.6 (d, *J* = 7.8 Hz), 131.0 (d, *J* = 125.6 Hz), 130.4 (d, *J* = 5.8 Hz), 128.7, 128.2 (d, *J* = 12.5 Hz), 127.2, 127.0, 126.9, 70.1 (d, *J* = 6.8 Hz), 38.2 (d, *J* = 95.5 Hz), 24.5 (d, *J* = 3.4 Hz), 24.0 (d, *J* = 4.8 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 38.5.

**HRMS** (ESI) *m/z* calcd. for C<sub>22</sub>H<sub>24</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 351.1508, found 351.1512.

**isopropyl (*S*)-((*S*)-1-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)phosphinate (58)**



According to the **general procedure D**, substrates **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **58** as a white solid (29.2 mg, 79% yield, 99% ee, >20:1 dr).

**HPLC** analysis: Chiralpak IG (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), *t<sub>R</sub>* (major) = 20.985 min, *t<sub>R</sub>* (minor) = 29.593 min.

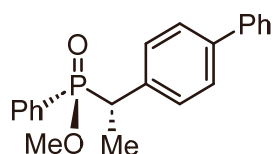
[α]<sub>D</sub><sup>25</sup> = −48.1 (*c* 1.0, CHCl<sub>3</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.69 – 7.59 (m, 4H), 7.55 – 7.50 (m, 3H), 7.49 – 7.41 (m, 4H), 7.39 – 7.34 (m, 1H), 7.32 – 7.27 (m, 2H), 4.60 – 4.48 (m, 1H), 3.32 – 3.21 (m, 1H), 1.54 (dd, *J* = 17.5, 7.4 Hz, 3H), 1.24 (d, *J* = 6.1 Hz, 3H), 1.17 (d, *J* = 6.1 Hz, 3H).  
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.8 (d, *J* = 1.5 Hz), 139.6 (d, *J* = 3.2 Hz), 137.0 (d, *J* = 7.0 Hz), 132.3 (d, *J* = 9.2 Hz), 132.0 (d, *J* = 2.7 Hz), 130.7 (d, *J* = 121.9 Hz), 129.4 (d, *J* = 5.5 Hz), 128.7, 128.1 (d, *J* = 12.2 Hz), 127.2, 127.0, 126.7 (d, *J* = 2.7 Hz), 69.9 (d, *J* = 7.0 Hz), 41.6 (d, *J* = 95.2 Hz), 24.2 (d, *J* = 3.7 Hz), 24.0 (d, *J* = 4.5 Hz), 14.5 (d, *J* = 2.4 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 42.5 (isomer), δ 41.6.

**HRMS** (ESI) *m/z* calcd. for C<sub>23</sub>H<sub>26</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 365.1665, found 365.1660.

### methyl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)phosphinate (**59**)



According to the **general procedure D**, substrates **C-2** (15.6 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **59** as a white solid (18.5 mg, 55% yield, 95% ee, >20:1 dr).

**HPLC** analysis: Chiralpak ADH (hexane/*i*-PrOH = 94/6, flow rate 0.8 mL/min, λ = 254 nm), *t<sub>R</sub>* (major) = 24.531 min, *t<sub>R</sub>* (minor) = 51.642 min.

[α]<sub>D</sub><sup>25</sup> = −56.7 (*c* 1.0, CHCl<sub>3</sub>).

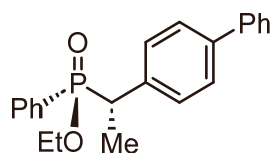
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.69 – 7.60 (m, 4H), 7.58 – 7.52 (m, 3H), 7.49 – 7.42 (m, 4H), 7.39 – 7.34 (m, 1H), 7.34 – 7.29 (m, 2H), 3.60 (d, *J* = 10.7 Hz, 3H), 3.33 (dd, *J* = 17.2, 7.4 Hz, 1H), 1.55 (dd, *J* = 17.7, 7.4 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.7 (d, *J* = 1.1 Hz), 139.8 (d, *J* = 3.2 Hz), 136.6 (d, *J* = 7.0 Hz), 132.4 (d, *J* = 9.2 Hz), 132.3 (d, *J* = 2.7 Hz), 129.3 (d, *J* = 5.6 Hz), 128.8 (d, *J* = 120.8 Hz), 128.6 (d, *J* = 12.2 Hz), 127.1 (d, *J* = 2.8 Hz), 51.7 (d, *J* = 7.0 Hz), 41.0 (d, *J* = 95.3 Hz), 14.7 (d, *J* = 2.2 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 45.0 (isomer), δ 45.7.

**HRMS** (ESI) *m/z* calcd. for C<sub>21</sub>H<sub>22</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 337.1352, found 337.1347.

### ethyl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)phosphinate (**60**)



According to the **general procedure D**, substrates **C-3** (17.0 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **60** as a white solid (19.7 mg, 59% yield, 95% ee, 12:1 dr).

**HPLC** analysis: Chiralpak IG (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), *t<sub>R</sub>* (major) = 28.986 min, *t<sub>R</sub>* (minor) = 54.784 min.

$[\alpha]_{\text{D}}^{25} = -78.7$  ( $c$  1.0,  $\text{CHCl}_3$ ).

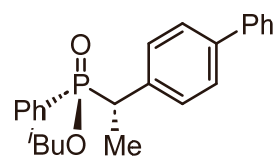
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.57 (m, 4H), 7.53 – 7.47 (m, 3H), 7.46 – 7.39 (m, 4H), 7.37 – 7.31 (m, 1H), 7.30 – 7.24 (m, 2H), 4.04 – 3.94 (m, 1H), 3.90 – 3.80 (m, 1H), 3.34 – 3.24 (m, 1H), 1.53 (dd,  $J = 17.6, 7.4$  Hz, 3H), 1.22 (t,  $J = 7.0$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.7 (d,  $J = 1.1$  Hz), 139.7 (d,  $J = 3.2$  Hz), 136.8 (d,  $J = 6.9$  Hz), 132.3 (d,  $J = 9.2$  Hz), 132.1 (d,  $J = 2.7$  Hz), 129.3 (d,  $J = 5.5$  Hz), 128.7, 128.2 (d,  $J = 12.1$  Hz), 127.2, 126.9, 126.8 (d,  $J = 2.7$  Hz), 61.0 (d,  $J = 6.9$  Hz), 41.3 (d,  $J = 95.0$  Hz), 16.3 (d,  $J = 6.3$  Hz), 14.6 (d,  $J = 2.5$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  43.9 (isomer),  $\delta$  43.2.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{24}\text{O}_2\text{P}$   $[\text{M} + \text{H}]^+$  351.1504, found 351.1508.

### isobutyl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)phosphinate (61)



According to the **general procedure D**, substrates **C-4** (19.8 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **61** as a white solid (23.1 mg, 65% yield, 94% ee, 12:1 dr).

HPLC analysis: Chiralpak IG (hexane/*i*-PrOH = 96/4, flow rate 0.8 mL/min,  $\lambda = 254$  nm),  $t_{\text{R}}$  (major) = 29.979 min,  $t_{\text{R}}$  (minor) = 43.036 min.

$[\alpha]_{\text{D}}^{25} = -119.3$  ( $c$  1.0,  $\text{CHCl}_3$ ).

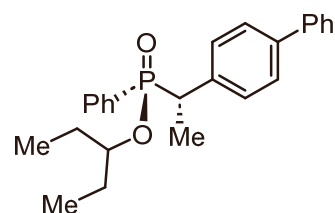
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 – 7.56 (m, 4H), 7.53 – 7.48 (m, 3H), 7.46 – 7.38 (m, 4H), 7.36 – 7.31 (m, 1H), 7.30 – 7.25 (m, 2H), 3.79 – 3.67 (m, 1H), 3.50 – 3.42 (m, 1H), 3.36 – 3.24 (m, 1H), 1.92 – 1.81 (m, 1H), 1.55 (dd,  $J = 17.5, 7.4$  Hz, 3H), 0.86 (dd,  $J = 6.7, 3.9$  Hz, 6H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8 (d,  $J = 1.1$  Hz), 139.8 (d,  $J = 3.4$  Hz), 136.8 (d,  $J = 7.1$  Hz), 132.4 (d,  $J = 9.1$  Hz), 132.2 (d,  $J = 2.7$  Hz), 129.5 (d,  $J = 5.5$  Hz), 129.4 (d,  $J = 120.7$  Hz), 128.8, 128.3 (d,  $J = 12.1$  Hz), 127.2, 127.0, 126.9 (d,  $J = 2.7$  Hz), 70.7 (d,  $J = 7.3$  Hz), 41.4 (d,  $J = 95.4$  Hz), 29.3 (d,  $J = 6.6$  Hz), 18.8 (d,  $J = 10.4$  Hz), 14.5 (d,  $J = 2.6$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  43.5 (isomer),  $\delta$  42.6.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{24}\text{H}_{28}\text{O}_2\text{P}$   $[\text{M} + \text{H}]^+$  379.1821, found 379.1815.

### pentan-3-yl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)phosphinate (62)



According to the **general procedure D**, substrates **C-5** (21.2 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **62** as a white solid (23.4 mg, 63% yield, 88% ee, 10:1 dr).

**HPLC** analysis: Chiralpak AZ3 (hexane/*i*-PrOH = 94/6, flow rate 0.8 mL/min,  $\lambda$  = 254 nm),  $t_R$  (minor) = 37.484 min,  $t_R$  (major) = 47.462 min.

$[\alpha]_D^{25} = -70.4$  (*c* 1.0, CHCl<sub>3</sub>).

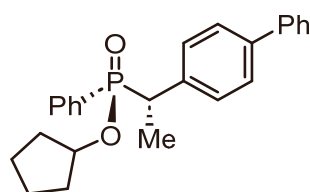
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.68 – 7.57 (m, 4H), 7.53 – 7.49 (m, 3H), 7.47 – 7.39 (m, 4H), 7.35 – 7.28 (m, 3H), 4.27 – 4.17 (m, 1H), 3.32 – 3.21 (m, 1H), 1.57 – 1.40 (m, 7H), 0.72 (t, *J* = 7.4 Hz, 6H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.8(d, *J* = 1.1 Hz), 139.6 (d, *J* = 3.3 Hz), 137.1 (d, *J* = 7.2 Hz), 132.2 (d, *J* = 9.2 Hz), 131.9 (d, *J* = 2.7 Hz), 130.9 (d, *J* = 121.7 Hz), 129.5 (d, *J* = 5.6 Hz), 128.7 (d, *J* = 3.8 Hz), 128.1 (d, *J* = 12.2 Hz), 127.1, 127.0, 126.8 (d, *J* = 2.6 Hz), 78.8 (d, *J* = 7.5 Hz), 41.6 (d, *J* = 95.7 Hz), 26.9 (d, *J* = 3.4 Hz), 26.7 (d, *J* = 4.0 Hz), 14.7 (d, *J* = 2.1 Hz), 8.9, 8.5.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  42.1 (isomer),  $\delta$  41.2.

**HRMS** (ESI) *m/z* calcd. for C<sub>25</sub>H<sub>30</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 393.1978, found 393.1972.

#### cyclopentyl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)phosphinate (**63**)



According to the **general procedure D**, substrates **C-6** (21.0 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **63** as a white solid (24.2 mg, 65% yield, 92% ee, 14:1 dr).

**HPLC** analysis: Chiralpak IG (hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 84.899 min,  $t_R$  (minor) = 115.909 min.

$[\alpha]_D^{25} = -96.7$  (*c* 1.0, CHCl<sub>3</sub>).

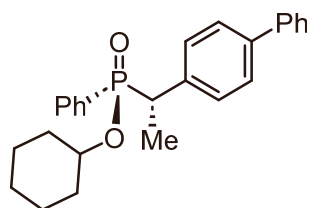
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 – 7.56 (m, 4H), 7.53 – 7.47 (m, 3H), 7.47 – 7.38 (m, 4H), 7.36 – 7.30 (m, 1H), 7.29 – 7.23 (m, 2H), 4.76 – 4.66 (m, 1H), 3.28 – 3.17 (m, 1H), 1.86 – 1.56 (m, 7H), 1.51 (dd, *J* = 17.5, 7.4 Hz, 4H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.8(d, *J* = 1.1 Hz), 139.6 (d, *J* = 3.3 Hz), 137.1 (d, *J* = 7.2 Hz), 132.2 (d, *J* = 9.2 Hz), 131.9 (d, *J* = 2.7 Hz), 130.9 (d, *J* = 121.7 Hz), 129.5 (d, *J* = 5.6 Hz), 128.7 (d, *J* = 3.8 Hz), 128.1 (d, *J* = 12.2 Hz), 127.1, 127.0, 126.8 (d, *J* = 2.6 Hz), 78.8 (d, *J* = 7.5 Hz), 41.6 (d, *J* = 95.7 Hz), 26.9 (d, *J* = 3.4 Hz), 26.7 (d, *J* = 4.0 Hz), 14.7 (d, *J* = 2.1 Hz), 8.9, 8.5.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  42.6 (isomer),  $\delta$  41.7.

**HRMS** (ESI) *m/z* calcd. for C<sub>25</sub>H<sub>28</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 391.1821, found 391.1815.

**cyclohexyl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)phosphinate (64)**



According to the **general procedure D**, substrates **C-7** (22.4 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **64** as a white solid (24.7 mg, 61% yield, 91% ee, 14:1 dr).

**HPLC** analysis: Chiral resolution was achieved by using two tandem Chiralpak IG (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 57.233 min,  $t_R$  (minor) = 71.720 min.

$[\alpha]_D^{25} = -89.5$  (*c* 1.0, CHCl<sub>3</sub>).

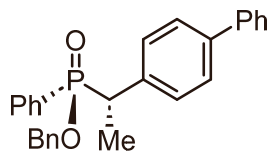
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.66 – 7.57 (m, 4H), 7.53 – 7.48 (m, 3H), 7.47 – 7.38 (m, 4H), 7.36 – 7.31 (m, 1H), 7.30 – 7.25 (m, 2H), 4.31 – 4.21 (m, 1H), 3.30 – 3.19 (m, 1H), 1.53 (dd, *J* = 17.5, 7.4 Hz, 3H), 1.68 – 1.15 (m, 10H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.8 (d, *J* = 1.3 Hz), 139.6 (d, *J* = 3.3 Hz), 137.1 (d, *J* = 7.1 Hz), 132.2 (d, *J* = 9.3 Hz), 131.9 (d, *J* = 2.8 Hz), 130.8 (d, *J* = 121.9 Hz), 129.4 (d, *J* = 5.4 Hz), 128.7, 128.1 (d, *J* = 12.2 Hz), 127.1, 126.9, 126.7 (d, *J* = 2.6 Hz), 74.5 (d, *J* = 7.3 Hz), 41.6 (d, *J* = 95.4 Hz), 33.7 (d, *J* = 3.3 Hz), 33.5 (d, *J* = 4.1 Hz), 25.2, 23.3 (d, *J* = 5.3 Hz), 14.4 (d, *J* = 2.5 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  42.5 (isomer),  $\delta$  41.6.

**HRMS** (ESI) *m/z* calcd. for C<sub>26</sub>H<sub>30</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 405.1978, found 405.1974.

**benzyl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)phosphinate (65)**



According to the **general procedure D**, substrates **C-8** (23.2 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **65** as a white solid (27.6 mg, 67% yield, 96% ee, 10:1 dr).

**HPLC** analysis: Chiral resolution was achieved by using two tandem Chiralpak ADH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 49.117 min,  $t_R$  (minor) = 79.312 min.

$[\alpha]_D^{25} = -70.4$  (*c* 1.0, CHCl<sub>3</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 – 7.62 (m, 2H), 7.62 – 7.57 (m, 2H), 7.54 – 7.48 (m, 3H), 7.45 – 7.40 (m, 3H), 7.37 – 7.25 (m, 7H), 7.22 – 7.16 (m, 2H), 4.98 (dd, *J* = 12.0, 6.8 Hz, 1H), 4.75 (dd, *J* = 12.0, 6.3 Hz, 1H), 3.41 – 3.30 (m, 1H), 1.54 (dd, *J* = 17.8, 7.4 Hz, 3H).

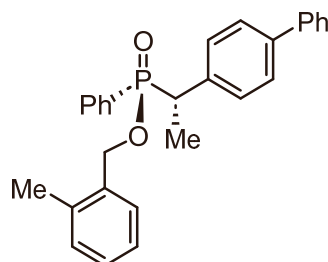
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.8 (d, *J* = 1.5 Hz), 139.9 (d, *J* = 3.3 Hz), 136.6 (dd, *J* = 7.3, 7.3 Hz), 132.4, 132.4 (d, *J* = 9.2 Hz), 132.4, 129.5 (d, *J* = 5.5 Hz), 128.8, 128.4

(t,  $J = 6.1$  Hz), 128.1, 127.5, 127.3, 127.0, 127.0 (d,  $J = 2.8$  Hz), 66.2 (d,  $J = 6.6$  Hz), 41.4 (d,  $J = 94.2$  Hz), 14.6 (d,  $J = 2.1$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  45.0 (isomer),  $\delta$  44.2.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{27}\text{H}_{26}\text{O}_2\text{P}$   $[\text{M} + \text{H}]^+$  413.1665, found 413.1659.

### 2-methylbenzyl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)phosphinate (66)



According to the **general procedure D**, substrates **C-9** (24.6 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **66** as a white solid (25.6 mg, 60% yield, 94% ee, 11:1 dr).

**HPLC** analysis: Chiralpak IG (hexane/*i*-PrOH = 94/6, flow rate 0.8 mL/min,  $\lambda = 254$  nm),  $t_R$  (major) = 95.447 min,  $t_R$  (minor) = 135.572 min.

$[\alpha]_D^{25} = -43.4$  ( $c$  1.0,  $\text{CHCl}_3$ ).

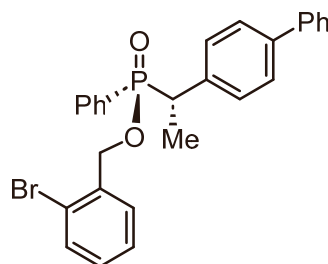
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 – 7.62 (m, 2H), 7.61 – 7.57 (m, 2H), 7.52 – 7.48 (m, 2H), 7.47 – 7.40 (m, 4H), 7.38 – 7.27 (m, 4H), 7.21 – 7.09 (m, 4H), 4.99 (dd,  $J = 12.1, 6.1$  Hz, 1H), 4.75 (dd,  $J = 12.1, 6.0$  Hz, 1H), 3.40 – 3.29 (m, 1H), 2.16 (s, 3H), 1.54 (dd,  $J = 17.9, 7.4$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8 (d,  $J = 1.5$  Hz), 139.9 (d,  $J = 3.2$  Hz), 136.6 (d,  $J = 8.1$  Hz), 136.5, 134.6 (d,  $J = 7.1$  Hz), 132.4 (d,  $J = 9.4$  Hz), 132.4 (d,  $J = 2.8$  Hz), 130.2, 129.5 (d,  $J = 5.6$  Hz), 129.3 (d,  $J = 121.1$  Hz), 128.8, 128.5, 128.4, 128.3 (d,  $J = 5.1$  Hz), 127.3, 127.0, 127.0 (d,  $J = 2.8$  Hz), 125.9, 64.6 (d,  $J = 6.5$  Hz), 41.4 (d,  $J = 94.3$  Hz), 18.7, 14.6 (d,  $J = 2.0$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  45.0 (isomer),  $\delta$  44.2.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{28}\text{H}_{28}\text{O}_2\text{P}$   $[\text{M} + \text{H}]^+$  427.1821, found 427.1815.

### 2-bromobenzyl (1-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)phosphinate (67)



According to the **general procedure D**, substrates **C-10** (31.1 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **67** as a white solid (25.1 mg, 51% yield, 92% ee, 12:1 dr).



**HPLC** analysis: Chiral resolution was achieved by using two tandem Chiralpak IG (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 106.421 min,  $t_R$  (minor) = 136.734 min.

$[\alpha]_D^{25} = -34.2$  (*c* 1.0, CHCl<sub>3</sub>).

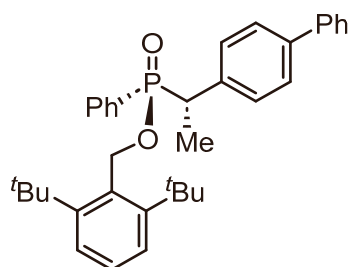
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.75 – 7.64 (m, 2H), 7.62 – 7.41 (m, 10H), 7.39 – 7.32 (m, 3H), 7.21 – 7.17 (m, 2H), 7.15 – 7.06 (m, 1H), 5.02 (dd, *J* = 13.1, 7.3 Hz, 1H), 4.85 (dd, *J* = 13.1, 6.4 Hz, 1H), 3.44 – 3.33 (m, 1H), 1.57 (dd, *J* = 17.9, 7.4 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.8 (d, *J* = 0.9 Hz), 136.5 (d, *J* = 7.2 Hz), 132.5, 132.4 (d, *J* = 9.4 Hz), 129.5 (d, *J* = 5.6 Hz), 129.4, 129.2 (d, *J* = 120.7 Hz), 129.0, 128.8, 128.5 (d, *J* = 12.3 Hz), 127.4, 127.3, 127.1, 122.3, 65.6 (d, *J* = 6.0 Hz), 41.4 (d, *J* = 94.4 Hz), 14.7 (d, *J* = 1.8 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  45.3 (isomer),  $\delta$  44.5.

**HRMS** (ESI) *m/z* calcd. for C<sub>27</sub>H<sub>25</sub>BrO<sub>2</sub>P [M + H]<sup>+</sup> 490.0697, found 490.0694.

**2,6-di-*tert*-butylbenzyl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(phenyl)phosphinate (68)**



According to the **general procedure D**, substrates **C-11** (34.4 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **68** as a white solid (27.8 mg, 53% yield, 93% ee, 9:1 dr).

**HPLC** analysis: Chiralpak IG (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 11.566 min,  $t_R$  (minor) = 35.875 min.

$[\alpha]_D^{25} = -23.6$  (*c* 1.0, CHCl<sub>3</sub>).

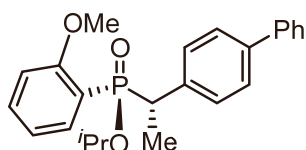
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 – 7.56 (m, 4H), 7.53 – 7.49 (m, 3H), 7.46 – 7.36 (m, 5H), 7.34 – 7.30 (m, 3H), 7.08 (d, *J* = 1.9 Hz, 2H), 4.99 (dd, *J* = 11.9, 6.8 Hz, 1H), 4.78 (dd, *J* = 11.9, 6.3 Hz, 1H), 3.41 – 3.30 (m, 1H), 1.55 (dd, *J* = 17.8, 7.4 Hz, 3H), 1.28 (s, 18H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.9, 132.5, 132.4, 132.2, 129.4 (d, *J* = 5.6 Hz), 128.7, 128.3, 127.7 (d, *J* = 103.2 Hz), 126.9 (d, *J* = 4.0 Hz), 122.0, 121.7, 34.8, 31.4 (d, *J* = 2.9 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  44.7 (isomer),  $\delta$  43.9.

**HRMS** (ESI) *m/z* calcd. for C<sub>35</sub>H<sub>42</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 525.2917, found 525.2914.

**isopropyl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(2-methoxyphenyl)phosphinate (69)**



According to the **general procedure D**, substrates **C-12** (21.4 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **69** as a white solid (26.8 mg, 68% yield, 99% ee, >20:1 dr).

**HPLC** analysis: Chiralpak AZ3 (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 41.215 min,  $t_R$  (minor) = 54.113 min.

$[\alpha]_D^{25} = -188.1$  ( $c$  1.0, CHCl<sub>3</sub>).

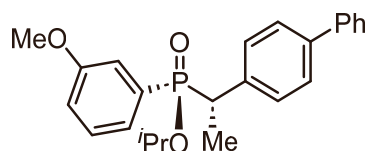
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 – 7.89 (m, 1H), 7.63 – 7.56 (m, 2H), 7.55 – 7.48 (m, 3H), 7.46 – 7.39 (m, 4H), 7.36 – 7.29 (m, 1H), 7.07 – 7.00 (m, 1H), 6.96 – 6.89 (m, 1H), 4.47 – 4.37 (m, 1H), 3.89 (s, 3H), 3.69 – 3.58 (m, 1H), 1.42 (dd,  $J$  = 19.2, 7.5 Hz, 3H), 1.09 (d,  $J$  = 6.2 Hz, 3H), 1.04 (d,  $J$  = 6.2 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.6 (d,  $J$  = 4.6 Hz), 141.0 (d,  $J$  = 1.3 Hz), 139.3 (d,  $J$  = 3.2 Hz), 137.5 (d,  $J$  = 8.5 Hz), 136.0 (d,  $J$  = 5.8 Hz), 134.0 (d,  $J$  = 2.2 Hz), 129.6 (d,  $J$  = 5.8 Hz), 128.6, 127.0 (d,  $J$  = 6.1 Hz), 126.6 (d,  $J$  = 2.6 Hz), 120.6 (d,  $J$  = 11.2 Hz), 118.9 (d,  $J$  = 117.8 Hz), 110.6 (d,  $J$  = 7.5 Hz), 69.3 (d,  $J$  = 7.4 Hz), 55.4, 40.0 (d,  $J$  = 97.7 Hz), 24.1 (d,  $J$  = 4.0 Hz), 23.6 (d,  $J$  = 4.3 Hz), 14.5.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  41.0 (isomer),  $\delta$  40.5.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>24</sub>H<sub>28</sub>O<sub>3</sub>P [M + H]<sup>+</sup> 395.1771, found 395.1764.

**isopropyl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(3-methoxyphenyl)phosphinate (70)**



According to the **general procedure D**, substrates **C-13** (21.4 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **70** as a white solid (24.9 mg, 63% yield, 91% ee, 14:1 dr).

**HPLC** analysis: Chiralpak AZ3 (hexane/*i*-PrOH = 94/6, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (minor) = 71.416 min,  $t_R$  (major) = 89.772 min.

$[\alpha]_D^{25} = -93.9$  ( $c$  1.0, CHCl<sub>3</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 – 7.56 (m, 2H), 7.53 – 7.48 (m, 2H), 7.46 – 7.41 (m, 2H), 7.36 – 7.26 (m, 4H), 7.25 – 7.18 (m, 1H), 7.09 – 7.01 (m, 2H), 4.58 – 4.46 (m, 1H), 3.72 (s, 3H), 3.28 – 3.18 (m, 1H), 1.53 (dd,  $J$  = 17.5, 7.4 Hz, 3H), 1.23 (d,  $J$  = 6.2 Hz, 3H), 1.15 (d,  $J$  = 6.2 Hz, 3H).

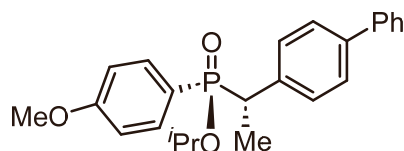
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.1 (d,  $J$  = 15.3 Hz), 140.8 (d,  $J$  = 1.4 Hz), 139.6 (d,  $J$  = 3.3 Hz), 137.1 (d,  $J$  = 6.9 Hz), 132.0 (d,  $J$  = 120.9 Hz), 129.4 (d,  $J$  = 5.5 Hz), 129.3 (d,  $J$  = 14.4 Hz), 128.7, 127.2, 126.9, 126.7 (d,  $J$  = 2.6 Hz), 124.5 (d,  $J$  = 8.8 Hz), 118.6

(d,  $J = 2.8$  Hz), 116.5 (d,  $J = 10.3$  Hz), 69.9 (d,  $J = 7.2$  Hz), 55.2, 41.6 (d,  $J = 95.4$  Hz), 24.2 (d,  $J = 3.5$  Hz), 24.0 (d,  $J = 4.6$  Hz), 14.5 (d,  $J = 2.6$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  42.5 (isomer),  $\delta$  41.5.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{24}\text{H}_{28}\text{O}_3\text{P}$   $[\text{M} + \text{H}]^+$  395.1771, found 395.1767.

**isopropyl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(4-methoxyphenyl)phosphinate (71)**



According to the **general procedure D**, substrates **C-14** (21.4 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **71** as a white solid (24.5 mg, 62% yield, 91% ee, 12:1 dr).

HPLC analysis: Chiralpak IG (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda = 254$  nm),  $t_R$  (minor) = 31.786 min,  $t_R$  (major) = 36.070 min.

$[\alpha]_D^{25} = -51.7$  ( $c$  1.0,  $\text{CHCl}_3$ ).

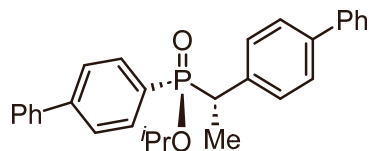
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 – 7.58 (m, 2H), 7.55 – 7.48 (m, 4H), 7.46 – 7.41 (m, 2H), 7.36 – 7.31 (m, 1H), 7.29 – 7.23 (m, 2H), 6.92 – 6.86 (m, 2H), 4.55 – 4.44 (m, 1H), 3.84 (s, 3H), 3.26 – 3.16 (m, 1H), 1.52 (dd,  $J = 17.4, 7.4$  Hz, 3H), 1.23 (d,  $J = 6.1$  Hz, 3H), 1.14 (d,  $J = 6.1$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5 (d,  $J = 2.9$  Hz), 140.8 (d,  $J = 1.2$  Hz), 139.5 (d,  $J = 3.3$  Hz), 137.3 (d,  $J = 6.8$  Hz), 134.2 (d,  $J = 10.5$  Hz), 129.4 (d,  $J = 5.5$  Hz), 128.7, 127.1, 126.9, 126.7 (d,  $J = 2.7$  Hz), 121.8 (d,  $J = 128.6$  Hz), 113.6 (d,  $J = 13.1$  Hz), 69.6 (d,  $J = 7.0$  Hz), 55.2, 41.8 (d,  $J = 96.4$  Hz), 24.3 (d,  $J = 3.6$  Hz), 24.0 (d,  $J = 4.6$  Hz), 14.6 (d,  $J = 2.6$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  42.8 (isomer),  $\delta$  41.9.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{24}\text{H}_{28}\text{O}_3\text{P}$   $[\text{M} + \text{H}]^+$  395.1771, found 395.1765.

**isopropyl (S)-[1,1'-biphenyl]-4-yl((S)-1-([1,1'-biphenyl]-4-yl)ethyl)phosphinate (72)**



According to the **general procedure D**, substrates **C-15** (26.0 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **72** as a white solid (30.8 mg, 70% yield, 92% ee, >20:1 dr).

HPLC analysis: Chiralpak AZ3 (hexane/*i*-PrOH = 94/6, flow rate 1.0 mL/min,  $\lambda = 254$  nm),  $t_R$  (minor) = 65.718 min,  $t_R$  (major) = 84.322 min.

$[\alpha]_D^{25} = -36.1$  ( $c$  1.0,  $\text{CHCl}_3$ ).

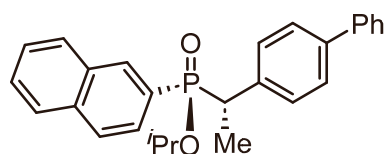
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.71 – 7.59 (m, 8H), 7.55 – 7.50 (m, 2H), 7.49 – 7.39 (m, 5H), 7.37 – 7.28 (m, 3H), 4.60 – 4.48 (m, 1H), 3.35 – 3.21 (m, 1H), 1.55 (dd, *J* = 17.6, 7.4 Hz, 3H), 1.24 (d, *J* = 6.1 Hz, 3H), 1.17 (d, *J* = 6.2 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 144.6 (d, *J* = 2.8 Hz), 140.7 (d, *J* = 1.1 Hz), 139.9, 139.6 (d, *J* = 3.3 Hz), 137.0 (d, *J* = 6.7 Hz), 132.8 (d, *J* = 9.5 Hz), 129.5 (d, *J* = 5.6 Hz), 128.9, 128.7, 128.1, 127.2 (d, *J* = 4.4 Hz), 127.0, 126.8 (d, *J* = 2.6 Hz), 126.7 (d, *J* = 12.4 Hz), 70.0 (d, *J* = 7.3 Hz), 41.6 (d, *J* = 95.6 Hz), 24.2 (d, *J* = 3.7 Hz), 24.0 (d, *J* = 4.5 Hz), 14.6 (d, *J* = 2.6 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 42.6 (isomer), δ 41.7.

**HRMS** (ESI) *m/z* calcd. for C<sub>29</sub>H<sub>30</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 441.1978, found 441.1974.

**isopropyl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(naphthalen-2-yl)phosphinate (73)**



According to the **general procedure D**, substrates **C-16** (23.4 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **73** as a white solid (29.4 mg, 71% yield, 90% ee, 10:1 dr).

**HPLC** analysis: Chiralpak AZ3 (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), *t<sub>R</sub>* (minor) = 28.048 min, *t<sub>R</sub>* (major) = 31.173 min.

[α]<sub>D</sub><sup>25</sup> = −41.1 (*c* 1.0, CHCl<sub>3</sub>).

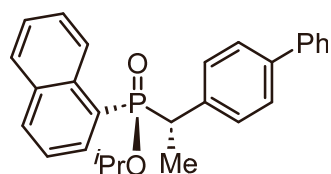
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.29 (d, *J* = 12.9 Hz, 1H), 7.92 – 7.80 (m, 3H), 7.62 – 7.49 (m, 7H), 7.47 – 7.41 (m, 2H), 7.37 – 7.28 (m, 3H), 4.59 – 4.50 (m, 1H), 3.38 – 3.27 (m, 1H), 1.55 (dd, *J* = 17.6, 7.4 Hz, 3H), 1.24 (d, *J* = 6.2 Hz, 3H), 1.14 (d, *J* = 6.1 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.8 (d, *J* = 1.1 Hz), 139.6 (d, *J* = 3.3 Hz), 137.0 (d, *J* = 7.1 Hz), 134.8 (d, *J* = 1.1 Hz), 134.6 (d, *J* = 2.5 Hz), 132.3 (d, *J* = 13.4 Hz), 129.5 (d, *J* = 5.4 Hz), 129.0, 128.7, 128.1, 127.9 (d, *J* = 120.7 Hz), 127.8 (d, *J* = 6.8 Hz), 127.7, 127.2, 126.7, 126.8 (d, *J* = 2.6 Hz), 126.7, 70.0 (d, *J* = 6.9 Hz), 41.6 (d, *J* = 95.8 Hz), 24.2 (d, *J* = 3.6 Hz), 24.0 (d, *J* = 4.5 Hz), 14.6 (d, *J* = 2.4 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 42.5 (isomer), δ 41.6.

**HRMS** (ESI) *m/z* calcd. for C<sub>27</sub>H<sub>28</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 415.1821, found 415.1817.

**isopropyl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(naphthalen-1-yl)phosphinate (74)**



According to the **general procedure D**, substrates **C-17** (23.4 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **74** as a white solid (24.0 mg, 57% yield, 95% ee, 12:1 dr).

**HPLC** analysis: Chiralpak IG (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 20.018 min,  $t_R$  (minor) = 51.503 min.

$[\alpha]_D^{25} = -41.6$  ( $c$  1.0, CHCl<sub>3</sub>).

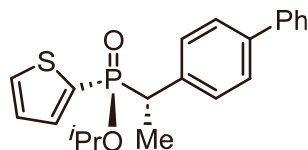
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.69 – 8.62 (m, 1H), 8.18 – 8.08 (m, 1H), 8.05 – 7.99 (m, 1H), 7.93 – 7.88 (m, 1H), 7.59 – 7.41 (m, 9H), 7.37 – 7.30 (m, 3H), 4.70 – 4.58 (m, 1H), 3.51 – 3.38 (m, 1H), 1.42 (dd,  $J$  = 18.2, 7.4 Hz, 3H), 1.19 (d,  $J$  = 6.1 Hz, 3H), 1.11 (d,  $J$  = 6.2 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.9 (d,  $J$  = 1.1 Hz), 139.6 (d,  $J$  = 3.1 Hz), 137.1 (d,  $J$  = 7.9 Hz), 134.8 (d,  $J$  = 7.6 Hz), 133.6 (d,  $J$  = 10.7 Hz), 133.3, 133.2 (d,  $J$  = 3.2 Hz), 129.5 (d,  $J$  = 5.5 Hz), 128.9 (d,  $J$  = 1.3 Hz), 128.7, 128.3 (d,  $J$  = 57.9 Hz), 127.1 (d,  $J$  = 1.7 Hz), 127.0, 126.8 (d,  $J$  = 2.6 Hz), 126.5 (d,  $J$  = 2.9 Hz), 126.1, 124.5 (d,  $J$  = 13.2 Hz), 70.4 (d,  $J$  = 7.1 Hz), 42.1 (d,  $J$  = 94.1 Hz), 24.2 (d,  $J$  = 4.0 Hz), 23.9 (d,  $J$  = 4.3 Hz), 14.6 (d,  $J$  = 1.4 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  42.7 (isomer),  $\delta$  42.2.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>27</sub>H<sub>28</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 415.1821, found 415.1814.

**isopropyl (S)-((S)-1-([1,1'-biphenyl]-4-yl)ethyl)(thiophen-2-yl)phosphinate (75)**



According to the **general procedure D**, substrates **C-18** (19.0 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **75** as a white solid (27.0 mg, 73% yield, 96% ee, 10:1 dr).

**HPLC** analysis: Chiralpak IG (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 23.001 min,  $t_R$  (minor) = 32.969 min.

$[\alpha]_D^{25} = -170.5$  ( $c$  1.0, CHCl<sub>3</sub>).

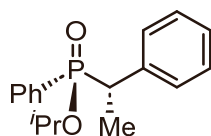
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.68 – 7.61 (m, 1H), 7.63 – 7.56 (m, 2H), 7.55 – 7.47 (m, 2H), 7.48 – 7.36 (m, 3H), 7.37 – 7.26 (m, 3H), 7.15 – 7.08 (m, 1H), 4.65 – 4.50 (m, 1H), 3.35 – 3.21 (m, 1H), 1.59 (dd,  $J$  = 18.2, 7.4 Hz, 3H), 1.25 (d,  $J$  = 6.2 Hz, 3H), 1.19 (d,  $J$  = 6.2 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.6 (d,  $J$  = 1.5 Hz), 139.7 (d,  $J$  = 3.4 Hz), 136.8 (d,  $J$  = 9.9 Hz), 136.7 (d,  $J$  = 6.9 Hz), 133.5 (d,  $J$  = 5.1 Hz), 130.6 (d,  $J$  = 131.7 Hz), 129.3 (d,  $J$  = 5.9 Hz), 127.9 (d,  $J$  = 14.4 Hz), 127.2, 126.9, 126.7 (d,  $J$  = 2.8 Hz), 70.5 (d,  $J$  = 7.4 Hz), 42.4 (d,  $J$  = 103.2 Hz), 24.2 (d,  $J$  = 3.3 Hz), 23.8 (d,  $J$  = 4.9 Hz), 14.6 (d,  $J$  = 3.2 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  37.0 (isomer),  $\delta$  36.3.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 371.1229, found 371.1223.

**isopropyl (S)-phenyl((S)-1-phenylethyl)phosphinate (76)**



According to the **general procedure D**, substrates **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and **D-2** (24.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **76** as a white solid (18.5 mg, 47% yield, 90% ee, 9:1 dr).

**HPLC** analysis: Chiral resolution was achieved by using two tandem Chiralpak IG (hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min,  $\lambda$  = 230 nm),  $t_R$  (major) = 62.888 min,  $t_R$  (minor) = 70.960 min.

$[\alpha]_D^{25} = -59.4$  (*c* 1.0, CHCl<sub>3</sub>).

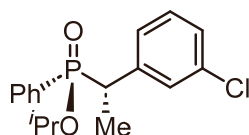
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 – 7.54 (m, 2H), 7.52 – 7.47 (m, 1H), 7.41 – 7.35 (m, 2H), 7.28 – 7.18 (m, 5H), 4.54 – 4.43 (m, 1H), 3.24 – 3.13 (m, 1H), 1.49 (dd, *J* = 17.5, 7.4 Hz, 3H), 1.19 (d, *J* = 6.2 Hz, 3H), 1.13 (d, *J* = 6.2 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.9 (d, *J* = 6.8 Hz), 132.2 (d, *J* = 9.1 Hz), 131.9 (d, *J* = 2.8 Hz), 130.6 (d, *J* = 121.9 Hz), 129.0 (d, *J* = 5.5 Hz), 128.1 (d, *J* = 4.9 Hz), 128.0 (d, *J* = 4.7 Hz), 126.8 (d, *J* = 3.0 Hz), 69.9 (d, *J* = 7.1 Hz), 41.9 (d, *J* = 95.4 Hz), 24.1 (d, *J* = 3.6 Hz), 23.9 (d, *J* = 4.5 Hz), 14.5 (d, *J* = 2.5 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  42.8 (isomer),  $\delta$  41.8.

**HRMS** (ESI) *m/z* calcd. for C<sub>21</sub>H<sub>22</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 289.1352, found 289.1348.

**isopropyl (S)-((S)-1-(3-chlorophenyl)ethyl)(phenyl)phosphinate (77)**



According to the **general procedure D**, substrates **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and **D-3** (28.6 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **77** as a white solid (17.1 mg, 53% yield, 91% ee, 9:1 dr).

**HPLC** analysis: Chiral resolution was achieved by using two tandem Chiralpak IG (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 230 nm),  $t_R$  (major) = 23.875 min,  $t_R$  (minor) = 27.095 min.

$[\alpha]_D^{25} = -56.3$  (*c* 1.0, CHCl<sub>3</sub>).

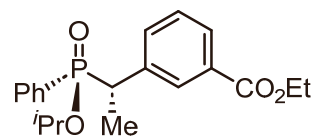
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 – 7.56 (m, 2H), 7.56 – 7.50 (m, 1H), 7.45 – 7.38 (m, 2H), 7.25 – 7.14 (m, 3H), 7.13 – 7.08 (m, 1H), 4.57 – 4.43 (m, 1H), 3.21 – 3.11 (m, 1H), 1.46 (dd, *J* = 17.5, 7.4 Hz, 3H), 1.21 (d, *J* = 6.2 Hz, 3H), 1.14 (d, *J* = 6.2 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.0 (d, *J* = 6.9 Hz), 133.8 (d, *J* = 2.8 Hz), 132.2 (d, *J* = 9.1 Hz), 132.2 (d, *J* = 3.1 Hz), 130.3 (d, *J* = 122.8 Hz), 129.3 (d, *J* = 2.6 Hz), 129.1 (d, *J* = 5.5 Hz), 128.2 (d, *J* = 12.2 Hz), 127.2 (d, *J* = 5.4 Hz), 126.9 (d, *J* = 3.0 Hz), 70.1 (d, *J* = 7.0 Hz), 41.6 (d, *J* = 95.2 Hz), 24.1 (d, *J* = 3.6 Hz), 23.9 (d, *J* = 4.7 Hz), 14.3 (d, *J* = 2.4 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  41.8 (isomer),  $\delta$  41.0.

**HRMS** (ESI)  $m/z$  calcd. for  $C_{17}H_{21}O_2P$   $[M + H]^+$  323.0962, found 323.0958.

**ethyl 3-((S)-1-((S)-isopropoxy(phenyl)phosphoryl)ethyl)benzoate (78)**



According to the **general procedure D**, substrates **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and **D-4** (31.6 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **78** as a white solid (21.6 mg, 55% yield, 85% ee, 10:1 dr).

**HPLC** analysis: Chiral resolution was achieved by using two tandem Chiralpak ADH (hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min,  $\lambda$  = 230 nm),  $t_R$  (major) = 38.447 min,  $t_R$  (minor) = 43.238 min.

$[\alpha]_D^{25} = -28.7$  ( $c$  1.0,  $CHCl_3$ ).

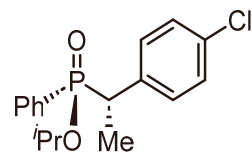
**$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.95 – 7.89 (m, 1H), 7.89 – 7.85 (m, 1H), 7.64 – 7.57 (m, 2H), 7.54 – 7.49 (m, 1H), 7.43 – 7.31 (m, 4H), 4.55 – 4.45 (m, 1H), 4.40 – 4.33 (m, 2H), 3.30 – 3.21 (m, 1H), 1.50 (dd,  $J$  = 17.5, 7.4 Hz, 3H), 1.39 (t,  $J$  = 7.2 Hz, 3H), 1.19 (d,  $J$  = 6.1 Hz, 3H), 1.13 (d,  $J$  = 6.2 Hz, 3H).

**$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  166.5, 138.4 (d,  $J$  = 6.8 Hz), 133.4 (d,  $J$  = 5.2 Hz), 132.2 (d,  $J$  = 9.3 Hz), 132.1 (d,  $J$  = 2.6 Hz), 130.5 (d,  $J$  = 122.0 Hz), 130.3 (d,  $J$  = 2.3 Hz), 130.2 (d,  $J$  = 6.3 Hz), 128.2 (d,  $J$  = 12.2 Hz), 128.0 (d,  $J$  = 2.9 Hz), 70.1 (d,  $J$  = 7.2 Hz), 60.9, 41.7 (d,  $J$  = 95.3 Hz), 24.2 (d,  $J$  = 3.7 Hz), 23.9 (d,  $J$  = 4.7 Hz), 14.4 (d,  $J$  = 2.5 Hz), 14.3.

**$^{31}P$  NMR** (162 MHz,  $CDCl_3$ )  $\delta$  42.0 (isomer),  $\delta$  41.1.

**HRMS** (ESI)  $m/z$  calcd. for  $C_{20}H_{26}O_4P$   $[M + H]^+$  361.1563, found 361.1558.

**isopropyl (S)-((S)-1-(4-chlorophenyl)ethyl)(phenyl)phosphinate (79)**



According to the **general procedure D**, substrates **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and **D-5** (28.5 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **79** as a white solid (20.7 mg, 64% yield, 92% ee, 11:1 dr).

**HPLC** analysis: Chiral resolution was achieved by using two tandem Chiralpak IA (hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min,  $\lambda$  = 230 nm),  $t_R$  (major) = 33.423 min,  $t_R$  (minor) = 41.290 min.

$[\alpha]_D^{25} = -44.9$  ( $c$  1.0,  $CHCl_3$ ).

**$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.66 – 7.56 (m, 2H), 7.55 – 7.49 (m, 1H), 7.45 – 7.37 (m, 2H), 7.27 – 7.20 (m, 2H), 7.16 – 7.11 (m, 2H), 4.55 – 4.44 (m, 1H), 3.22 – 3.11 (m, 1H), 1.45 (dd,  $J$  = 17.4, 7.4 Hz, 3H), 1.21 (d,  $J$  = 6.1 Hz, 3H), 1.13 (d,  $J$  = 6.2 Hz, 3H).

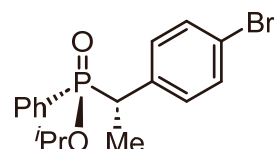


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.5 (d,  $J = 6.9$  Hz), 132.6 (d,  $J = 3.6$  Hz), 132.2 (d,  $J = 9.3$  Hz), 132.1 (d,  $J = 2.8$  Hz), 130.4 (d,  $J = 121.4$  Hz), 130.3 (d,  $J = 5.5$  Hz), 128.2 (d,  $J = 5.0$  Hz), 128.2 (d,  $J = 4.8$  Hz), 70.0 (d,  $J = 7.2$  Hz), 41.2 (d,  $J = 95.6$  Hz), 24.2 (d,  $J = 3.5$  Hz), 23.9 (d,  $J = 4.7$  Hz), 14.5 (d,  $J = 2.4$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  42.0 (isomer),  $\delta$  41.2.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{21}\text{ClO}_2\text{P}$   $[\text{M} + \text{H}]^+$  323.0962, found 323.0957.

#### isopropyl (S)-((S)-1-(4-bromophenyl)ethyl)(phenyl)phosphinate (80)



According to the **general procedure D**, substrates **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and **D-6** (34.3 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **80** as a white solid (19.8 mg, 54% yield, 91% ee, 12:1 dr).

**HPLC** analysis: Chiral resolution was achieved by using two tandem Chiralpak IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda = 230$  nm),  $t_R$  (major) = 16.800 min,  $t_R$  (minor) = 20.195 min.

$[\alpha]_D^{25} = -50.8$  ( $c$  1.0,  $\text{CHCl}_3$ ).

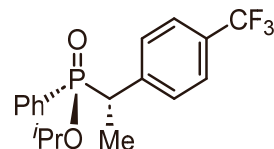
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 – 7.56 (m, 2H), 7.54 – 7.49 (m, 1H), 7.45 – 7.35 (m, 4H), 7.13 – 7.02 (m, 2H), 4.55 – 4.44 (m, 1H), 3.20 – 3.10 (m, 1H), 1.44 (dd,  $J = 17.5, 7.4$  Hz, 3H), 1.21 (d,  $J = 6.2$  Hz, 3H), 1.13 (d,  $J = 6.2$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.0 (d,  $J = 6.9$  Hz), 132.2 (d,  $J = 9.2$  Hz), 132.1 (d,  $J = 2.8$  Hz), 131.1 (d,  $J = 2.5$  Hz), 130.7 (d,  $J = 5.5$  Hz), 130.3 (d,  $J = 121.4$  Hz), 128.2 (d,  $J = 12.3$  Hz), 120.7 (d,  $J = 3.9$  Hz), 70.0 (d,  $J = 7.1$  Hz), 41.3 (d,  $J = 95.4$  Hz), 24.2 (d,  $J = 3.4$  Hz), 23.9 (d,  $J = 4.7$  Hz), 14.4 (d,  $J = 2.5$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  41.8 (isomer),  $\delta$  41.0.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{21}\text{BrO}_2\text{P}$   $[\text{M} + \text{H}]^+$  367.0457, found 367.0453.

#### isopropyl (S)-phenyl((S)-1-(4-(trifluoromethyl)phenyl)ethyl)phosphinate (81)



According to the **general procedure D**, substrates **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and **D-7** (32.9 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **81** as a white solid (21.0 mg, 59% yield, 93% ee, 8:1 dr).

**HPLC** analysis: Chiral resolution was achieved by using two tandem Chiralpak IA (hexane/*i*-PrOH = 96/4, flow rate 0.8 mL/min,  $\lambda = 230$  nm),  $t_R$  (major) = 32.109 min,  $t_R$  (minor) = 44.263 min.

$[\alpha]_D^{25} = -30.1$  ( $c$  1.0,  $\text{CHCl}_3$ ).



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.66 – 7.57 (m, 2H), 7.55 – 7.50 (m, 3H), 7.44 – 7.40 (m, 2H), 7.36 – 7.32 (m, 2H), 4.56 – 4.45 (m, 1H), 3.31 – 3.21 (m, 1H), 1.48 (dd, *J* = 17.4, 7.4 Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 3H), 1.13 (d, *J* = 6.2 Hz, 3H).

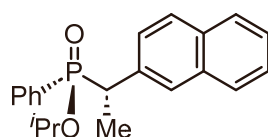
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) 142.3 (d, *J* = 6.9 Hz), 132.2, 132.1, 130.3 (d, *J* = 122.9 Hz), 129.3 (d, *J* = 5.4 Hz), 128.3, 128.2, 125.0 – 124.8 (m), 70.2 (d, *J* = 7.1 Hz), 42.3, 41.3, 24.1 (d, *J* = 3.5 Hz), 23.9 (d, *J* = 4.6 Hz), 14.4 (d, *J* = 2.3 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 42.5 (isomer), δ 41.7.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ –62.4 (d, *J* = 2.3 Hz), –62.5 (d, *J* = 2.1 Hz) (isomer).

**HRMS** (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>21</sub>F<sub>3</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 357.1226, found 357.1220.

### isopropyl (S)-((S)-1-(naphthalen-2-yl)ethyl)(phenyl)phosphinate (**82**)



According to the **general procedure D**, substrates **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and **D-8** (30.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **82** as a white solid (23.0 mg, 68% yield, 80% ee, 7:1 dr).

**HPLC** analysis: Chiral resolution was achieved by using two tandem Chiralpak IG (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), *t<sub>R</sub>* (major) = 56.059 min, *t<sub>R</sub>* (minor) = 125.898 min.

[α]<sub>D</sub><sup>25</sup> = –41.9 (*c* 1.0, CHCl<sub>3</sub>).

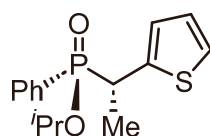
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.83 – 7.78 (m, 1H), 7.77 – 7.71 (m, 2H), 7.64 – 7.57 (m, 3H), 7.51 – 7.47 (m, 1H), 7.46 – 7.42 (m, 2H), 7.40 – 7.34 (m, 3H), 4.55 – 4.45 (m, 1H), 3.41 – 3.32 (m, 1H), 1.57 (dd, *J* = 17.5, 7.4 Hz, 3H), 1.17 (d, *J* = 6.1 Hz, 3H), 1.12 (d, *J* = 6.2 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 135.6 (d, *J* = 7.1 Hz), 133.2 (d, *J* = 2.6 Hz), 132.4 (d, *J* = 2.4 Hz), 132.3, 132.2, 132.0 (d, *J* = 2.6 Hz), 130.7 (d, *J* = 122.0 Hz), 128.1 (d, *J* = 12.1 Hz), 127.7 (d, *J* = 3.3 Hz), 127.6 (d, *J* = 3.7 Hz), 127.5, 127.4 (d, *J* = 4.3 Hz), 125.9, 125.6, 70.0 (d, *J* = 7.0 Hz), 42.0 (d, *J* = 95.4 Hz), 24.2 (d, *J* = 3.7 Hz), 24.0 (d, *J* = 4.6 Hz), 14.7 (d, *J* = 2.4 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 42.5 (isomer), δ 41.7.

**HRMS** (ESI) *m/z* calcd. for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 339.1508, found 339.1504.

### isopropyl (S)-phenyl((S)-1-(thiophen-2-yl)ethyl)phosphinate (**83**)



According to the **general procedure D**, substrates **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and **D-13** (24.8 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **87** as a white solid (19.3 mg, 64% yield, 98% ee, 10:1 dr).

**HPLC** analysis: Chiral resolution was achieved by using two tandem Chiralpak IC (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 230 nm),  $t_R$  (major) = 62.074 min,  $t_R$  (minor) = 66.642 min.

$[\alpha]_D^{25} = -45.7$  ( $c$  1.0, CHCl<sub>3</sub>).

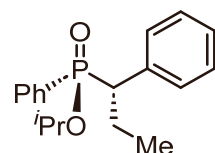
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 – 7.51 (m, 2H), 7.51 – 7.46 (m, 1H), 7.42 – 7.35 (m, 2H), 7.26 – 7.20 (m, 1H), 7.05 – 6.99 (m, 1H), 6.97 – 6.92 (m, 1H), 4.58 – 4.50 (m, 1H), 3.41 – 3.29 (m, 1H), 1.47 (dd,  $J$  = 17.2, 7.4 Hz, 3H), 1.27 (d,  $J$  = 6.2 Hz, 3H), 1.16 (d,  $J$  = 6.2 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.0 (d,  $J$  = 6.7 Hz), 132.2 (d,  $J$  = 9.1 Hz), 131.9 (d,  $J$  = 2.8 Hz), 130.4 (d,  $J$  = 122.4 Hz), 128.4 (d,  $J$  = 3.4 Hz), 128.0 (d,  $J$  = 12.2 Hz), 124.8 (d,  $J$  = 1.8 Hz), 122.2 (d,  $J$  = 8.2 Hz), 69.9 (d,  $J$  = 7.1 Hz), 37.5 (d,  $J$  = 97.6 Hz), 24.3 (d,  $J$  = 3.5 Hz), 24.0 (d,  $J$  = 4.7 Hz), 14.6 (d,  $J$  = 2.6 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  42.1 (isomer),  $\delta$  41.3.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>PS [M + H]<sup>+</sup> 295.0916, found 295.0913

#### isopropyl (S)-phenyl((S)-1-phenylpropyl)phosphinate (**84**)



According to the **general procedure D**, substrates **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and **D-9** (25.88 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **84** as a white solid (16.7 mg, 55% yield, 92% ee, 10:1 dr).

**HPLC** analysis: Chiral resolution was achieved by using two tandem Chiralpak ADH (hexane/*i*-PrOH = 96/4, flow rate 0.8 mL/min,  $\lambda$  = 230 nm),  $t_R$  (major) = 28.791 min,  $t_R$  (minor) = 34.137 min.

$[\alpha]_D^{25} = -42.8$  ( $c$  1.0, CHCl<sub>3</sub>).

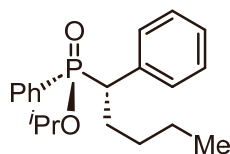
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.60 – 7.53 (m, 2H), 7.50 – 7.45 (m, 1H), 7.40 – 7.34 (m, 2H), 7.28 – 7.23 (m, 3H), 7.20 – 7.15 (m, 2H), 4.50 – 4.41 (m, 1H), 2.94 – 2.85 (m, 1H), 1.97 – 1.90 (m, 2H), 1.16 (d,  $J$  = 6.2 Hz, 3H), 1.10 (d,  $J$  = 6.2 Hz, 3H), 0.77 (t, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.0 (d,  $J$  = 6.7 Hz), 132.2 (d,  $J$  = 9.1 Hz), 131.8 (d,  $J$  = 2.7 Hz), 131.1 (d,  $J$  = 113.3 Hz), 129.7 (d,  $J$  = 5.9 Hz), 128.1 (d), 128.0 (d,  $J$  = 11.0 Hz), 126.8 (d,  $J$  = 3.0 Hz), 69.7 (d,  $J$  = 7.2 Hz), 50.1 (d,  $J$  = 95.5 Hz), 24.1 (d,  $J$  = 3.6 Hz), 23.9 (d,  $J$  = 4.7 Hz), 21.7, 12.6 (d,  $J$  = 15.5 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  42.2 (isomer),  $\delta$  40.8.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>18</sub>H<sub>24</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 303.1508, found 303.1504.

**isopropyl (S)-phenyl((S)-1-phenylbutyl)phosphinate (85)**



According to the **general procedure D**, substrates **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and **D-10** (27.7 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **85** as a white solid (16.1 mg, 51% yield, 92% ee, 10:1 dr).

**HPLC** analysis: Chiral resolution was achieved by using two tandem Chiralpak IA (hexane/*i*-PrOH = 96/4, flow rate 0.8 mL/min,  $\lambda$  = 230 nm),  $t_R$  (major) = 31.304 min,  $t_R$  (minor) = 34.886 min.

$[\alpha]_D^{25} = -52.2$  ( $c$  1.0, CHCl<sub>3</sub>).

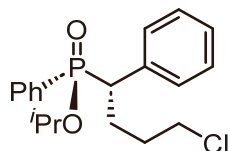
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 – 7.52 (m, 2H), 7.49 – 7.45 (m, 1H), 7.39 – 7.33 (m, 2H), 7.27 – 7.22 (m, 3H), 7.19 – 7.15 (m, 2H), 4.50 – 4.41 (m, 1H), 3.05 – 2.96 (m, 1H), 1.98 – 1.91 (m, 2H), 1.28 – 1.19 (m, 2H), 1.17 (d,  $J$  = 6.1 Hz, 3H), 1.10 (d,  $J$  = 6.2 Hz, 3H), 0.79 (t,  $J$  = 7.3 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.2 (d,  $J$  = 6.9 Hz), 132.2 (d,  $J$  = 9.1 Hz), 131.8 (d,  $J$  = 2.7 Hz), 131.1 (d,  $J$  = 121.9 Hz), 129.6 (d,  $J$  = 5.9 Hz), 128.1, 128.0 (d,  $J$  = 10.5 Hz), 126.7 (d,  $J$  = 3.0 Hz), 69.7 (d,  $J$  = 7.2 Hz), 48.0 (d,  $J$  = 95.5 Hz), 30.2 (d,  $J$  = 1.7 Hz), 24.1 (d,  $J$  = 3.6 Hz), 23.9 (d,  $J$  = 4.7 Hz), 20.8 (d,  $J$  = 15.0 Hz), 13.6.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  42.3 (isomer),  $\delta$  41.0.

**HRMS** (ESI)  $m/z$  calcd. for C<sub>20</sub>H<sub>28</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 317.1665, found 317.1661.

**isopropyl (S)-((S)-4-chloro-1-phenylbutyl)(phenyl)phosphinate (86)**



According to the **general procedure D**, substrates **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and **D-11** (32.2 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **86** as a white solid (20.7 mg, 59% yield, 93% ee, 8:1 dr).

**HPLC** analysis: Chiral resolution was achieved by using two tandem Chiralpak IA (hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min,  $\lambda$  = 230 nm),  $t_R$  (major) = 35.056 min,  $t_R$  (minor) = 44.766 min.

$[\alpha]_D^{25} = -28.0$  ( $c$  1.0, CHCl<sub>3</sub>).

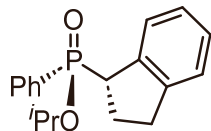
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 – 7.52 (m, 2H), 7.50 – 7.47 (m, 1H), 7.40 – 7.34 (m, 2H), 7.28 – 7.23 (m, 3H), 7.18 – 7.14 (m, 2H), 4.52 – 4.42 (m, 1H), 3.41 (t,  $J$  = 6.9 Hz, 2H), 3.05 – 2.95 (m, 1H), 2.17 – 2.05 (m, 2H), 1.67 – 1.56 (m, 2H), 1.18 (d,  $J$  = 6.1 Hz, 3H), 1.11 (d,  $J$  = 6.1 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  135.6 (d,  $J$  = 6.9 Hz), 132.2 (d,  $J$  = 9.2 Hz), 132.0 (d,  $J$  = 2.8 Hz), 130.7 (d,  $J$  = 123.0 Hz), 129.5 (d,  $J$  = 5.8 Hz), 128.3 (d,  $J$  = 2.5 Hz), 128.1 (d,  $J$  = 12.3 Hz), 127.1 (d,  $J$  = 3.0 Hz), 70.0 (d,  $J$  = 7.1 Hz), 47.7 (d,  $J$  = 95.6 Hz), 44.4, 30.7 (d,  $J$  = 14.9 Hz), 25.7, 24.1 (d,  $J$  = 3.5 Hz), 23.9 (d,  $J$  = 4.6 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 41.7 (isomer), δ 40.2.

**HRMS** (ESI) *m/z* calcd. for C<sub>19</sub>H<sub>25</sub>ClO<sub>2</sub>P [M + H]<sup>+</sup> 351.1275, found 351.1272.

**isopropyl (S)-((S)-2,3-dihydro-1H-inden-1-yl)(phenyl)phosphinate (87)**



According to the **general procedure D**, substrates **C-1** (18.4 mg, 0.10 mmol, 1.0 equiv) and **D-12** (25.6 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **87** as a white solid (18.0 mg, 62% yield, 86% ee, 6:1 dr).

**HPLC** analysis: Chiralpak ID (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), *t<sub>R</sub>* (major) = 16.081 min, *t<sub>R</sub>* (minor) = 20.997 min.

[α]<sub>D</sub><sup>25</sup> = +8.4 (*c* 1.0, CHCl<sub>3</sub>).

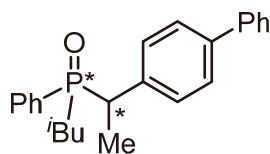
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.70 – 7.63 (m, 2H), 7.51 – 7.48 (m, 1H), 7.46 – 7.36 (m, 3H), 7.17 – 7.12 (m, 3H), 4.70 – 4.61 (m, 1H), 3.71 – 3.62 (m, 1H), 2.82 – 2.73 (m, 2H), 2.32 – 2.15 (m, 2H), 1.41 (d, *J* = 6.1 Hz, 3H), 1.24 (d, *J* = 6.2 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 144.9 (d, *J* = 7.1 Hz), 138.2 (d, *J* = 6.0 Hz), 132.3 (d, *J* = 9.1 Hz), 132.2 (d, *J* = 9.1 Hz), 132.0 (d, *J* = 2.7 Hz), 130.8 (d, *J* = 121.5 Hz), 128.2 (d, *J* = 11.9 Hz), 127.2 (d, *J* = 3.0 Hz), 126.1 (d, *J* = 2.8 Hz), 126.0 (d, *J* = 3.5 Hz), 124.5 (d, *J* = 2.5 Hz), 69.9 (d, *J* = 6.8 Hz), 46.1 (d, *J* = 99.3 Hz), 31.6 (d, *J* = 2.7 Hz), 26.2, 24.5 (d, *J* = 3.4 Hz), 24.1 (d, *J* = 4.7 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 41.0, δ 41.6 (isomer).

**HRMS** (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>22</sub>O<sub>2</sub>P [M + H]<sup>+</sup> 301.1352, found 301.1348.

**(1-([1,1'-biphenyl]-4-yl)ethyl)(isobutyl)(phenyl)phosphine oxide (1')**



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and **D-1** (34.0 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **1'** as a white solid (9.8 mg, 27% yield, dr 5:1, 90% ee for the major isomer, 19% ee for the minor isomer).

**HPLC** analysis: Chiralpak IG (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), *t<sub>R</sub>* (1) = 57.426 min, *t<sub>R</sub>* (2) = 64.487 min, *t<sub>R</sub>* (major) = 69.941 min, *t<sub>R</sub>* (minor) = 130.733 min.

[α]<sub>D</sub><sup>25</sup> = −9.2 (*c* 0.5, CHCl<sub>3</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.75 – 7.67 (m, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2.2H), 7.55 – 7.41 (m, 6.6H), 7.40 – 7.32 (m, 3.6H), 7.02 (dd, *J* = 8.4, 2.2 Hz, 0.4H), 3.40 – 3.28 (m, 0.2H), 3.19 – 3.07 (m, 1H), 2.11 – 2.01 (m, 0.4H), 1.88 – 1.79 (m, 2H), 1.78 – 1.76 (m, 0.2H), 1.74 – 1.71 (m, 1H), 1.59 (dd, *J* = 15.2, 7.3 Hz,

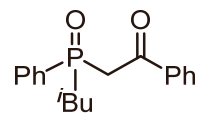
0.6H), 1.43 (dd,  $J = 15.5, 7.4$  Hz, 3H), 1.09 (d,  $J = 6.2$  Hz, 0.6H), 0.92 (d,  $J = 6.5$  Hz, 3H), 0.87 (d,  $J = 6.4$  Hz, 0.6H), 0.74 (d,  $J = 6.5$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.7 (d,  $J = 1.0$  Hz), 139.9 (d,  $J = 2.9$  Hz), 137.6 (d,  $J = 5.5$  Hz), 132.2 (d,  $J = 87.9$  Hz), 131.4 (d,  $J = 2.8$  Hz), 131.0 (d,  $J = 8.3$  Hz), 129.2 (d,  $J = 5.3$  Hz), 128.8, 128.5 (d,  $J = 10.9$  Hz), 127.3, 127.0, 126.9 (d,  $J = 9.4$  Hz), 42.5 (d,  $J = 63.8$  Hz), 35.8 (d,  $J = 67.8$  Hz), 24.7 (d,  $J = 9.8$  Hz), 24.2 (d,  $J = 7.6$  Hz), 23.4 (d,  $J = 4.1$  Hz), 14.8 (d,  $J = 2.9$  Hz). Selected signals for the minor isomer: 131.6 (d,  $J = 8.0$  Hz), 129.1 (d,  $J = 4.8$  Hz), 128.7, 127.9 (d,  $J = 11.2$  Hz), 126.7 (d,  $J = 2.6$  Hz), 42.4 (d,  $J = 62.2$  Hz), 23.6 (d,  $J = 4.2$  Hz), 14.0 (d,  $J = 3.0$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  42.0 (minor), 41.3 (major).

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{24}\text{H}_{28}\text{OP}$   $[\text{M} + \text{H}]^+$  363.1872, found 363.1869.

### 2-(isobutyl(phenyl)phosphoryl)-1-phenylethan-1-one (P1)



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and 2-chloro-1-phenylethan-1-one **B-40** (20.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **P1** as a white solid (14.3 mg, 48% yield, 6% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min,  $\lambda = 254$  nm),  $t_R$  (1) = 9.652 min,  $t_R$  (2) = 13.836 min.

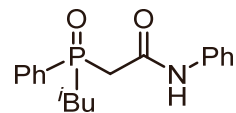
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 – 7.85 (m, 2H), 7.78 – 7.67 (m, 2H), 7.58 – 7.33 (m, 6H), 3.84 – 3.68 (m, 2H), 2.29 – 2.15 (m, 1H), 2.13 – 1.98 (m, 2H), 1.06 (d,  $J = 6.2$  Hz, 3H), 0.90 (d,  $J = 6.2$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  193.8 (d,  $J = 5.1$  Hz), 136.9 (d,  $J = 1.4$  Hz), 133.6, 132.2 (d,  $J = 95.6$  Hz), 131.9 (d,  $J = 2.8$  Hz), 130.6 (d,  $J = 9.2$  Hz), 129.0, 128.6 (d,  $J = 11.7$  Hz), 128.5, 44.6 (d,  $J = 53.5$  Hz), 37.9 (d,  $J = 69.6$  Hz), 24.5 (d,  $J = 9.9$  Hz), 24.4 (d,  $J = 9.0$  Hz), 23.5 (d,  $J = 4.1$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  34.3.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{22}\text{O}_2\text{P}$   $[\text{M} + \text{H}]^+$  301.1352, found 301.1355.

### 2-(isobutyl(phenyl)phosphoryl)-*N*-phenylacetamide (P2)



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and 2-bromo-*N*-phenylacetamide **B-41** (27.8 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **P2** as a white solid (10.1 mg, 32% yield, 3% ee).

HPLC analysis: Chiralpak IG (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min,  $\lambda = 254$  nm),  $t_R$  (1) = 10.810 min,  $t_R$  (2) = 12.135 min.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.08 (br s, 1H), 7.86 – 7.74 (m, 2H), 7.66 – 7.59 (m, 1H), 7.59 – 7.49 (m, 4H), 7.37 – 7.28 (m, 2H), 7.16 – 7.08 (m, 1H), 4.49 (dd,  $J = 15.0$ ,

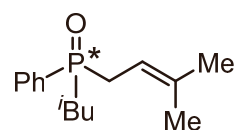
9.2 Hz, 1H), 4.28 (dd,  $J = 14.9, 11.6$  Hz, 1H), 2.22 – 1.92 (m, 3H), 1.12 (d,  $J = 6.5$  Hz, 3H), 1.01 (d,  $J = 6.5$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7 (d,  $J = 5.0$  Hz), 137.2, 133.1 (d,  $J = 2.8$  Hz), 131.5 (d,  $J = 10.2$  Hz), 129.2 (d,  $J = 120.7$  Hz), 129.1 (d,  $J = 12.5$  Hz), 129.0, 124.6, 119.9, 64.3 (d,  $J = 7.3$  Hz), 38.0 (d,  $J = 97.6$  Hz), 24.3 (d,  $J = 7.4$  Hz), 24.2 (d,  $J = 6.2$  Hz), 23.4 (d,  $J = 3.3$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  49.8.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{23}\text{NO}_2\text{P}$   $[\text{M} + \text{H}]^+$  316.1461, found 316.1463.

### isobutyl(3-methylbut-2-en-1-yl)(phenyl)phosphine oxideisobutyl(3-methylbut-2-en-1-yl)(phenyl)phosphine oxide (P5)



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and 1-bromo-3-methylbut-2-ene **B-44** (19.37 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **P5** as a colorless oil (17.8 mg, 71% yield, 73% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 95/05, flow rate 0.8 mL/min,  $\lambda = 214$  nm),  $t_R$  (major) = 25.883 min,  $t_R$  (minor) = 38.422 min.

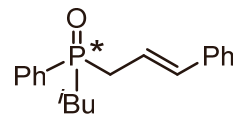
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.76 – 7.63 (m, 2H), 7.56 – 7.41 (m, 3H), 5.13 (q,  $J = 7.2$  Hz, 1H), 2.80 – 2.59 (m, 2H), 2.14 – 2.02 (m, 1H), 2.01 – 1.91 (m, 1H), 1.86 – 1.77 (m, 1H), 1.69 (d,  $J = 4.6$  Hz, 3H), 1.43 (d,  $J = 3.4$  Hz, 3H), 1.06 (d,  $J = 6.6$  Hz, 3H), 0.88 (d,  $J = 6.6$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  137.0 (d,  $J = 11.6$  Hz), 133.2 (d,  $J = 91.3$  Hz), 131.3 (d,  $J = 2.7$  Hz), 130.5 (d,  $J = 8.5$  Hz), 128.4 (d,  $J = 11.0$  Hz), 112.9 (d,  $J = 8.4$  Hz), 37.2 (d,  $J = 67.7$  Hz), 32.4 (d,  $J = 66.6$  Hz), 25.8 (d,  $J = 2.8$  Hz), 24.6 (dd,  $J = 10.4, 8.7$  Hz), 23.4 (d,  $J = 4.2$  Hz), 17.9 (d,  $J = 2.4$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  38.4.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{23}\text{OP}$   $[\text{M} + \text{H}]^+$  251.1559, found 251.1557.

### cinnamyl(isobutyl)(phenyl)phosphine oxide (P6)



According to the **general procedure A**, substrates **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and cinnamyl bromide **B-45** (15.73 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **P6** as a colorless oil (25.62 mg, 77% yield, 53% ee).

HPLC analysis: Chiralpak IH (hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min,  $\lambda = 254$  nm),  $t_R$  (major) = 11.732 min,  $t_R$  (minor) = 16.989 min.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.81 – 7.68 (m, 2H), 7.59 – 7.46 (m, 3H), 7.32 (d, 2H), 7.29 (d, 2H), 7.25 (q,  $J = 4.4$  Hz, 1H), 6.42 (dd,  $J = 15.8, 4.5$  Hz, 1H), 6.21 –

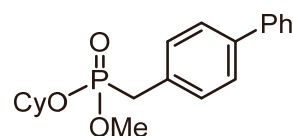
6.06 (m, 1H), 2.94 (d,  $J = 15.3, 7.7$  Hz, 2H), 2.19 – 2.09 (m, 1H), 2.08 – 2.01 (m, 1H), 1.93 – 1.83 (m, 1H), 1.09 (d,  $J = 6.4$  Hz, 3H), 0.92 (d,  $J = 6.5$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  136.8 (d,  $J = 3.1$  Hz), 135.1 (d,  $J = 11.7$  Hz), 132.8 (d,  $J = 92.2$  Hz), 131.6 (d,  $J = 2.8$  Hz), 130.6 (d,  $J = 8.6$  Hz), 128.6 (d,  $J = 7.1$  Hz), 128.5 (d,  $J = 4.0$  Hz), 127.6, 126.2 (d,  $J = 1.8$  Hz), 119.1 (d,  $J = 9.3$  Hz), 37.5 (d,  $J = 11.0$  Hz), 36.9 (d,  $J = 7.2$  Hz), 24.6 (dd,  $J = 11.8, 8.7$  Hz), 23.5 (d,  $J = 4.1$  Hz).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.3.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{23}\text{OP}$   $[\text{M} + \text{H}]^+$  299.1559, found 299.1558.

### cyclohexyl methyl ([1,1'-biphenyl]-4-ylmethyl)phosphonate (P7)



According to the **general procedure C**, substrates cyclohexyl methyl phosphonate **C-19** (17.8 mg, 0.10 mmol, 1.0 equiv) and **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were employed to yield the product **P7** as a white solid (14.4 mg, 42% yield, 3% ee).

HPLC analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda = 254$  nm),  $t_R$  (1) = 8.567 min,  $t_R$  (2) = 11.276 min.

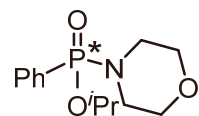
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.49 (m, 4H), 7.48 – 7.28 (m, 5H), 4.46 – 4.29 (m, 1H), 3.67 (d,  $J = 10.9$  Hz, 3H), 3.20 (d,  $J = 21.7$  Hz, 2H), 1.97 – 1.84 (m, 1H), 1.82 – 1.61 (m, 3H), 1.53 – 1.15 (m, 6H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.7 (d,  $J = 1.4$  Hz), 139.7 (d,  $J = 3.9$  Hz), 130.7 (d,  $J = 9.2$  Hz), 130.2 (d,  $J = 6.6$  Hz), 128.7, 127.3, 127.2, 127.0, 75.9 (d,  $J = 7.0$  Hz), 52.5 (d,  $J = 6.9$  Hz), 33.8 (d,  $J = 3.3$  Hz), 33.5 (d,  $J = 4.8$  Hz), 33.4 (d,  $J = 139.1$  Hz), 25.1.

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  26.7.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{26}\text{O}_3\text{P}$   $[\text{M} + \text{H}]^+$  345.1614, found 345.1617.

### isopropyl morpholino(phenyl)phosphinate (P11)



According to the **general procedure A**, substrates **C-1** (9.2 mg, 0.050 mmol, 1.0 equiv) and 4-benzoyloxymorpholine (1.3 equiv) were employed to yield the product **P11** as a white solid (2.8 mg, 14% yield, 54% ee).

HPLC analysis: Chiralpak IG-3 (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda = 234$  nm),  $t_R$  (minor) = 23.836 min,  $t_R$  (major) = 31.272 min.

$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.81 – 7.68 (m, 2H), 7.54 – 7.40 (m, 3H), 4.88 – 4.72 (m, 1H), 3.69 – 3.55 (m, 4H), 3.16 – 3.01 (m,  $J = 3.8$  Hz, 4H), 1.39 (t,  $J = 6.0$  Hz, 6H).

$^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  131.6 (d,  $J = 3.0$  Hz), 131.1 (d,  $J = 9.4$  Hz), 130.4 (d,  $J = 174.7$  Hz), 128.3 (d,  $J = 14.1$  Hz), 69.3 (d,  $J = 6.0$  Hz), 66.8 (d,  $J = 5.9$

Hz), 44.1 (d,  $J = 1.3$  Hz), 24.14 (d,  $J = 4.2$  Hz), 23.97 (d,  $J = 4.5$  Hz).

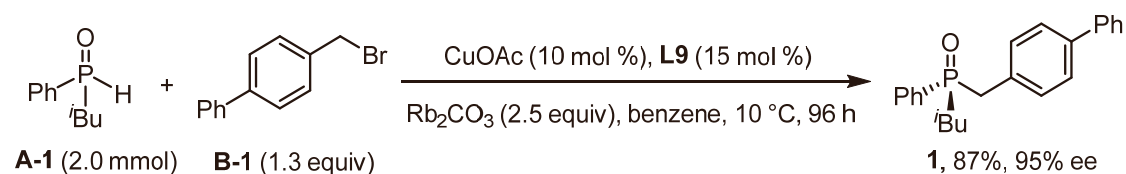
**$^{31}\text{P}$  NMR** (162 MHz, Chloroform-*d*)  $\delta$  19.8.

**HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{20}\text{NO}_3\text{P}$   $[\text{M} + \text{H}]^+$  270.1254, found 270.1252.



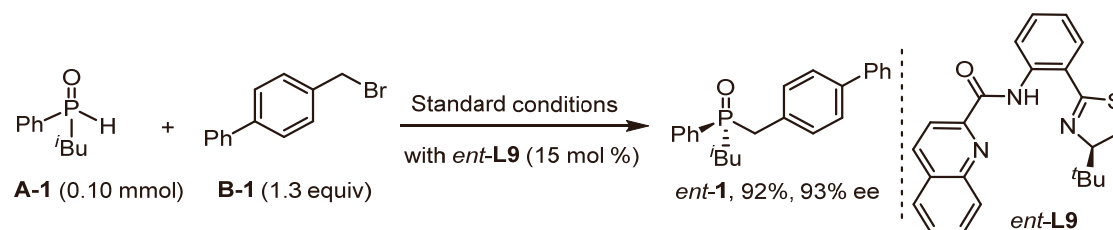
## Scalability and synthetic utility

### 1. Large scale synthesis (Scheme 5A)



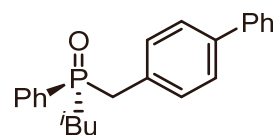
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (24.5 mg, 0.20 mmol, 10 mol %), **L9** (116.9 mg, 0.30 mmol, 15 mol %), Rb<sub>2</sub>CO<sub>3</sub> (1.15 g, 5.0 mmol, 2.5 equiv) and anhydrous benzene (40 mL). The mixture was stirred at room temperature for 1 h. After that, racemic secondary phosphine oxide **A-1** (364.4 mg, 2.0 mmol, 1.0 equiv) and bromide **B-1** (642.6 mg, 2.6 mmol, 1.3 equiv) were sequentially added into the mixture, and the resulting mixture was stirred at 10 °C for 96 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (20 mL) and DCM (20 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: DCM/MeOH 100:1–50:1) to afford the product **1** as a white solid (603.7 mg, 87% yield, 95% ee). **HPLC** analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (major) = 9.914 min,  $t_R$  (minor) = 18.597 min.

## 2. The synthesis of antipode product *ent*-1 (Scheme 5B)



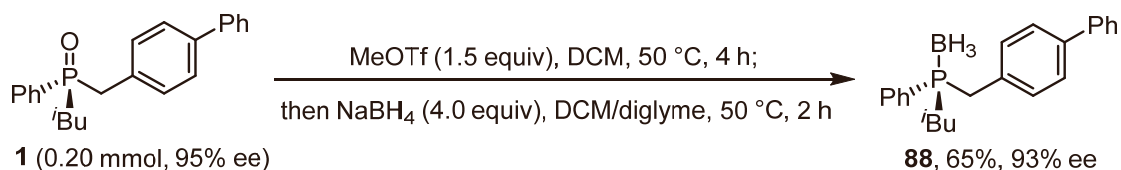
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (1.2 mg, 0.010 mmol, 10 mol %), *ent*-**L9** (5.8 mg, 0.015 mmol, 15 mol %), Rb<sub>2</sub>CO<sub>3</sub> (57.7 mg, 0.25 mmol, 2.5 equiv) and anhydrous benzene (2.0 mL). The mixture was stirred at room temperature for 30 min. After that, racemic secondary phosphine oxide **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and bromide **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) were sequentially added into the mixture, and the resulting mixture was stirred at 10 °C for 96 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL) and DCM (5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: DCM/MeOH 100:1–50:1) to afford the antipode product *ent*-1 as a white solid (32.0 mg, 92% yield, 93% ee).

### (S)-([1,1'-biphenyl]-4-ylmethyl)(isobutyl)(phenyl)phosphine oxide (*ent*-1)



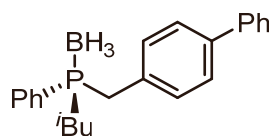
**HPLC** analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (minor) = 10.287 min,  $t_R$  (major) = 19.214 min.  $[\alpha]_D^{25}$  = +10.9 (*c* 0.5, CHCl<sub>3</sub>).

### 3. Stereospecific reduction of chiral phosphine oxide (Scheme 5C)



According to the modified literature procedure.<sup>[S11]</sup> To a stirred solution of **1** (95% ee, 69.7 mg, 0.20 mmol, 1.0 equiv) in anhydrous DCM (2 mL) was dropwise added MeOTf (34  $\mu$ L, 0.30 mmol, 1.5 equiv) under argon atmosphere at room temperature. The reaction mixture was stirred at 50 °C for 4 h. After cooling to room temperature, a dispersion of NaBH<sub>4</sub> (30.2 mg, 0.80 mmol, 4.0 equiv) in diglyme (0.5 mL) was slowly added into the mixture. The resulting mixture was then stirred at 50 °C for 2 h before being cooled to room temperature and diluted with DCM (2 mL). The reaction mixture was slowly quenched by water (5 mL) and extracted with DCM (5 mL  $\times$  2). The combined organic layers were washed with water (10 mL) and brine (10 mL). The organic layer was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/DCM 5:1) to give the product **88** as a white solid (44.8 mg, 65% yield over two steps, 93% ee).

#### (S)-([1,1'-biphenyl]-4-ylmethyl)(isobutyl)(phenyl)phosphine borane (**88**)



**HPLC** analysis: Chiralpak IF (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min,  $\lambda$  = 254 nm),  $t_R$  (minor) = 10.469 min,  $t_R$  (major) = 12.436 min.

$[\alpha]_D^{25}$  = +41.2 (*c* 1.0, CHCl<sub>3</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 – 7.58 (m, 2H), 7.57 – 7.54 (m, 2H), 7.48 (td, *J* = 7.3, 1.5 Hz, 1H), 7.45 – 7.37 (m, 6H), 7.32 (t, *J* = 7.3 Hz, 1H), 6.97 (dd, *J* = 8.3, 2.1 Hz, 2H), 3.29 – 3.12 (m, 2H), 2.09 – 1.97 (m, 1H), 1.96 – 1.86 (m, 1H), 1.84 – 1.76 (m, 1H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.77 (d, *J* = 6.6 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.4 (d, *J* = 1.3 Hz), 139.6 (d, *J* = 3.0 Hz), 132.4 (d, *J* = 8.7 Hz), 131.4 (d, *J* = 6.9 Hz), 131.3 (d, *J* = 2.5 Hz), 130.3 (d, *J* = 4.1 Hz), 128.7, 128.5 (d, *J* = 9.7 Hz), 128.3 (d, *J* = 50.5 Hz), 127.2, 126.9, 126.7 (d, *J* = 2.5 Hz), 35.7 (d, *J* = 31.8 Hz), 32.4 (d, *J* = 33.3 Hz), 24.9 (d, *J* = 9.1 Hz), 24.4, 24.3 (d, *J* = 6.5 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)  $\delta$  14.4 (d, *J* = 74.9 Hz).

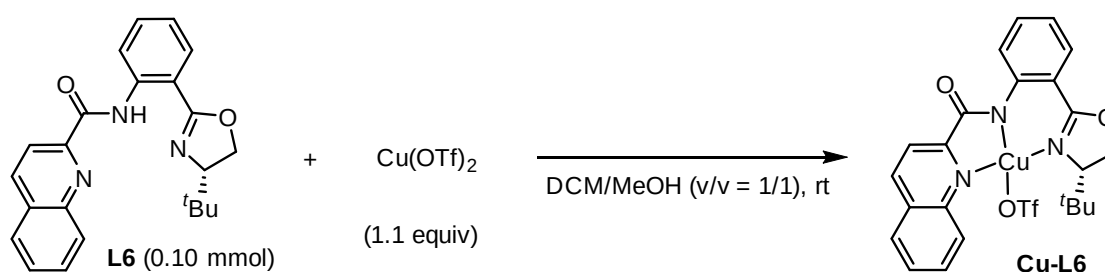
**<sup>11</sup>B NMR** (128 MHz, CDCl<sub>3</sub>)  $\delta$  -39.3 – -41.2 (m).

**HRMS** (ESI) *m/z* calcd. for C<sub>23</sub>H<sub>28</sub>BP [M – BH<sub>3</sub> + H]<sup>+</sup> 333.1767, found 333.1768.

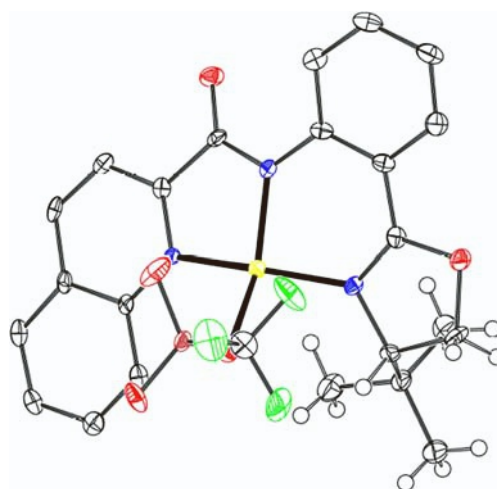
## Experimental mechanistic studies

### 1. Preparation and catalytic efficiency of copper/chiral ligand complex

#### (1) The synthesis Cu-L6 complex



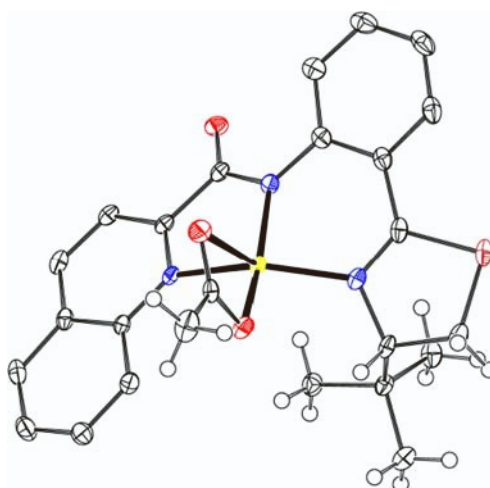
To a solution of **L6** (37.3 mg, 0.10 mmol) in DCM/MeOH (v/v = 1:1, 2 mL) was added  $\text{Cu}(\text{OTf})_2$  (39.8 mg, 0.11 mmol). The reaction mixture was stirred at room temperature for overnight. The mixture was filtered through a short pad of celite and rinsed with DCM. The filtrate was slowly diffused with  $\text{Et}_2\text{O}$  and recrystallized to give the pure **Cu-L6** complex as blue crystals (44.6 mg, 76% yield). The structure of **Cu-L6** was confirmed by X-ray diffraction analysis.



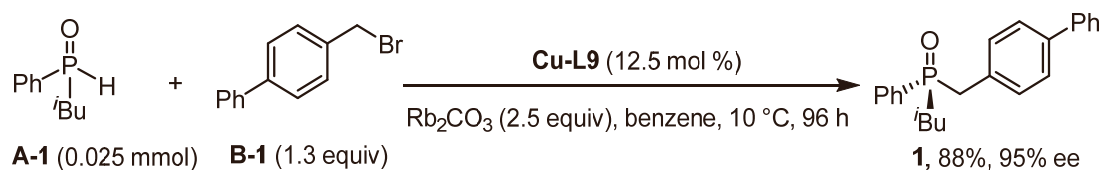
## (2) The synthesis Cu-L9 complex (Scheme 6A)



To a solution of **L9** (39.0 mg, 0.10 mmol) in DCM/MeOH (v/v = 1:1, 2 mL) was added CuOAc (13.5 mg, 0.11 mmol). The reaction mixture was stirred at room temperature for overnight. The mixture was filtered through a short pad of celite and rinsed with DCM. The filtrate was slowly diffused with Et<sub>2</sub>O and recrystallized to give the pure **Cu-L9** complex as blue crystals (42.5 mg, 83% yield). The structure of **Cu-L9** was confirmed by X-ray diffraction analysis.



### (3) The catalytic activity of Cu-L9 complex (Scheme 6B)

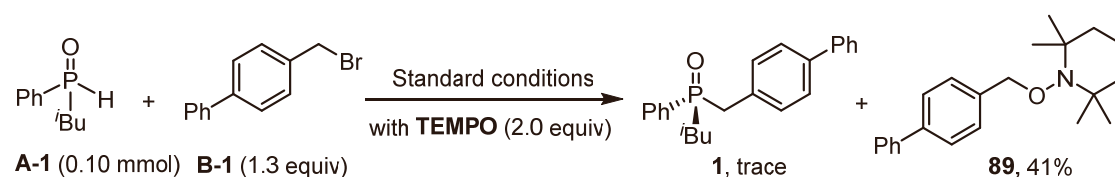


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **Cu-L9** (1.6 mg, 0.0031 mmol, 12.5 mol %),  $\text{Rb}_2\text{CO}_3$  (14.5 mg, 0.063 mmol, 2.5 equiv), bromide **B-1** (8.2 mg, 0.033 mmol, 1.3 equiv) and anhydrous benzene (0.5 mL). The racemic secondary phosphine oxide **A-1** (4.6 mg, 0.025 mmol, 1.0 equiv) was added into the mixture. The resulting mixture was stirred at  $10^\circ\text{C}$  for 96 h. The reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (1 mL) and DCM (1 mL). The filtrate was concentrated under reduced pressure. The residue was initially subjected to  $^{31}\text{P}$  NMR analysis, employing trimethyl phosphate as an internal standard for the determination of the yield of product **1** (88% yield based on  $^{31}\text{P}$  NMR analysis). The crude product was then purified by preparative TLC on silica gel (DCM/MeOH 100:1) to afford the pure product **1** for HPLC analysis (95% ee).

HPLC conditions: Chiralcel OJ-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min,  $\lambda = 254\text{ nm}$ ),  $t_{\text{R}}$  (major) = 9.980 min,  $t_{\text{R}}$  (minor) = 18.740 min.

## 2. Radical inhibition experiments

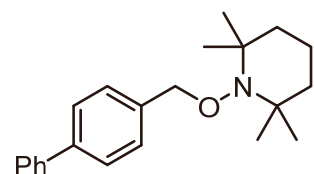
### (1) Radical trap experiment with TEMPO (Scheme 6C)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (1.2 mg, 0.010 mmol, 10 mol %), **L9** (5.8 mg, 0.015 mmol, 15 mol %), Rb<sub>2</sub>CO<sub>3</sub> (57.7 mg, 0.25 mmol, 2.5 equiv) and anhydrous benzene (2.0 mL). The mixture was stirred at room temperature for 30 min. After that, racemic secondary phosphine oxide **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv), bromide **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) and 2,2,6,6-tetramethylpiperidinoxy (**TEMPO**, 31.3 mg, 0.20 mmol, 2.0 equiv) were sequentially added into the mixture. The resulting mixture was stirred at 10 °C for 96 h. The reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL) and DCM (5 mL). The filtrate was concentrated under reduced pressure. The residue was initially subjected to <sup>31</sup>P NMR analysis using trimethyl phosphate as an internal standard. The results demonstrated that the intended reaction was completely inhibited, and product **1** was not detected. The crude product was then purified by column chromatography on silica gel (gradient eluent: petroleum ether 100% to petroleum ether/EtOAc 50:1) to afford the product **89** as a white solid (17.1 mg, 41% yield based on the dosage of **B-1**).

Product **89** is a known compound.<sup>[S12]</sup>

#### 1-([1,1'-biphenyl]-4-ylmethoxy)-2,2,6,6-tetramethylpiperidine (**89**)

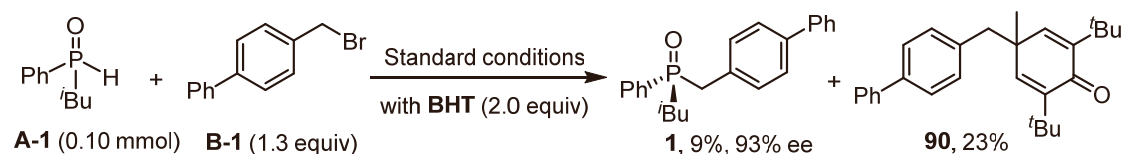


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.54 (m, 4H), 7.48 – 7.39 (m, 4H), 7.37 – 7.30 (m, 1H), 4.87 (s, 2H), 1.65 – 1.45 (m, 5H), 1.40 – 1.32 (m, 1H), 1.28 (s, 6H), 1.17 (s, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.0, 140.3, 137.3, 128.7, 127.9, 127.2, 127.1, 127.0, 78.4, 60.0, 39.7, 33.1, 20.3, 17.1.

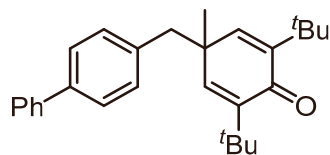
HRMS (ESI) *m/z* calcd. for C<sub>22</sub>H<sub>30</sub>NO [M + H]<sup>+</sup> 324.2322, found 324.2324.

## (2) Radical trap experiment with BHT (Scheme 6D)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (1.2 mg, 0.010 mmol, 10 mol %), **L9** (5.8 mg, 0.015 mmol, 15 mol %), Rb<sub>2</sub>CO<sub>3</sub> (57.7 mg, 0.25 mmol, 2.5 equiv) and anhydrous benzene (2.0 mL). The mixture was stirred at room temperature for 30 min. After that, racemic secondary phosphine oxide **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv), bromide **B-1** (32.1 mg, 0.13 mmol, 1.3 equiv) and butylated hydroxytoluene (**BHT**, 44.1 mg, 0.20 mmol, 2.0 equiv) were sequentially added into the mixture. The resulting mixture was stirred at 10 °C for 96 h. The reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL) and DCM (5 mL). The filtrate was concentrated under reduced pressure. The residue was initially subjected to <sup>31</sup>P NMR analysis using trimethyl phosphate as an internal standard. The results revealed that the intended reaction was largely inhibited, and the product **1** was detected (13% yield based on <sup>31</sup>P NMR analysis). Subsequently, the crude product was purified by column chromatography on silica gel (gradient eluent: petroleum ether 100% to petroleum ether/EtOAc 50:1 for the isolation of **90**, and then DCM/MeOH 100:1–50:1 for the isolation of **1**) to afford the product **90** as a slightly yellow semi-solid (11.6 mg, 23% yield based on the dosage of **B-1**) and the product **1** as a white solid (3.0 mg, 9% yield, 93% ee based on HPLC analysis).

### 4-([1,1'-biphenyl]-4-ylmethyl)-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dien-1-one (**90**)

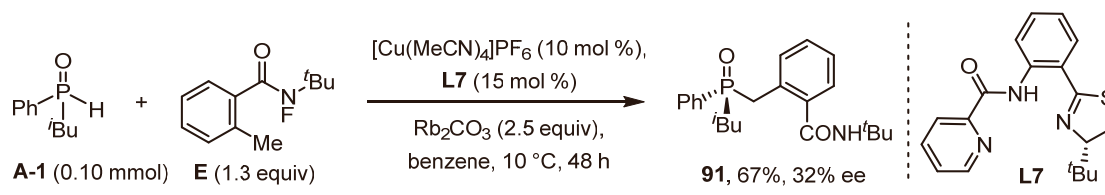


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54 – 7.49 (m, 2H), 7.44 – 7.38 (m, 4H), 7.34 – 7.28 (m, 1H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.50 (s, 2H), 2.86 (s, 2H), 1.29 (s, 3H), 1.16 (s, 18H).  
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 186.0, 146.1, 145.9, 140.9, 139.5, 135.9, 130.5, 128.7, 127.1, 127.0, 126.2, 47.6, 40.9, 34.6, 29.3, 26.1.

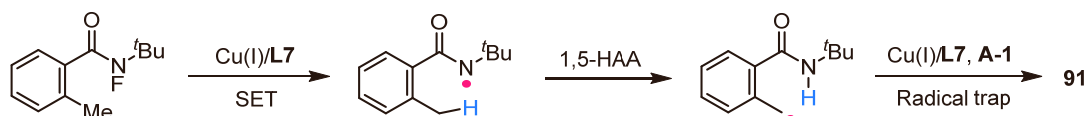
HRMS (ESI) *m/z* calcd. for C<sub>28</sub>H<sub>35</sub>O [M + H]<sup>+</sup> 387.2682, found 387.2688.



### 3. Alternative benzyl radical generation via an intramolecular 1,5-hydrogen atom abstraction (HAA) process (Scheme 6E)



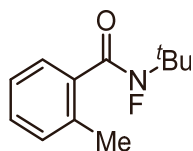
Possible mechanism: benzyl radical generated via 1,5-HAA process



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  (3.7 mg, 0.010 mmol, 10 mol %), **L7** (5.1 mg, 0.015 mmol, 15 mol %),  $\text{Rb}_2\text{CO}_3$  (57.7 mg, 0.25 mmol, 2.5 equiv) and anhydrous benzene (2.0 mL). The mixture was stirred at room temperature for 30 min. After that, racemic secondary phosphine oxide **A-1** (18.2 mg, 0.10 mmol, 1.0 equiv) and substrate **E** (27.2 mg, 0.13 mmol, 1.3 equiv) were sequentially added into the mixture. The resulting mixture was stirred at 10 °C for 48 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL) and DCM (5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: DCM/MeOH 100:1–50:1) to afford the product **91** as a slightly yellow solid (24.8 mg, 67% yield, 32% ee).

Substrate **E** was prepared following the literature procedure.<sup>[S13]</sup>

#### *N*-(*tert*-butyl)-*N*-fluoro-2-methylbenzamide (**E**)



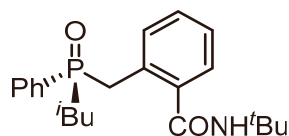
<sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.27 (m, 2H), 7.24 – 7.17 (m, 2H), 2.40 (s, 3H), 1.55 (d,  $J$  = 2.0 Hz, 9H).

<sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  175.0 (d,  $J$  = 10.9 Hz), 135.3 (d,  $J$  = 2.4 Hz), 135.0, 130.4, 129.9 (d,  $J$  = 1.1 Hz), 127.1 (d,  $J$  = 4.4 Hz), 125.3, 64.4 (d,  $J$  = 10.5 Hz), 27.2 (d,  $J$  = 5.7 Hz), 19.3.

<sup>19</sup>F NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –64.7.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{12}\text{H}_{17}\text{FNO}$   $[\text{M} + \text{H}]^+$  210.1289, found 210.1291.

**(R)-N-(tert-butyl)-2-((isobutyl(phenyl)phosphoryl)methyl)benzamide (91)**



**HPLC** analysis: Chiralpak IF (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min,  $\lambda$  = 220 nm),  $t_R$  (major) = 9.043 min,  $t_R$  (minor) = 11.964 min.

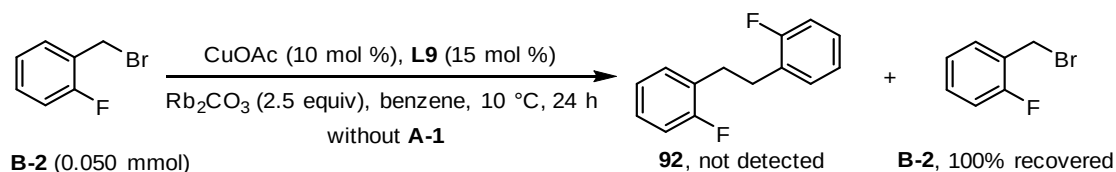
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (br s, 1H), 7.72 – 7.65 (m, 2H), 7.60 – 7.55 (m, 1H), 7.54 – 7.47 (m, 3H), 7.24 – 7.18 (m, 1H), 7.09 (td,  $J$  = 7.6, 1.4 Hz, 1H), 6.62 (d,  $J$  = 7.5 Hz, 1H), 3.66 – 3.56 (m, 1H), 3.33 – 3.22 (m, 1H), 2.07 – 1.96 (m, 3H), 1.49 (s, 9H), 1.04 (d,  $J$  = 6.1 Hz, 3H), 0.86 (d,  $J$  = 6.0 Hz, 3H).

**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.8, 139.8 (d,  $J$  = 5.1 Hz), 131.9 (d,  $J$  = 2.8 Hz), 131.6 (d,  $J$  = 93.4 Hz), 130.7 (d,  $J$  = 9.0 Hz), 130.0 (d,  $J$  = 4.1 Hz), 129.0 (d,  $J$  = 2.7 Hz), 128.8 (d,  $J$  = 3.0 Hz), 128.7 (d,  $J$  = 11.4 Hz), 127.3 (d,  $J$  = 8.7 Hz), 127.0 (d,  $J$  = 3.1 Hz), 51.8, 37.8 (d,  $J$  = 67.7 Hz), 36.7 (d,  $J$  = 61.5 Hz), 28.8, 24.7 (d,  $J$  = 9.9 Hz), 24.4 (d,  $J$  = 7.6 Hz), 23.4 (d,  $J$  = 4.2 Hz).

**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )  $\delta$  39.6.

**HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{31}\text{NO}_2\text{P}$   $[\text{M} + \text{H}]^+$  372.2087, found 372.2091.

#### 4. Control experiment without racemic SPO (Scheme 6F)

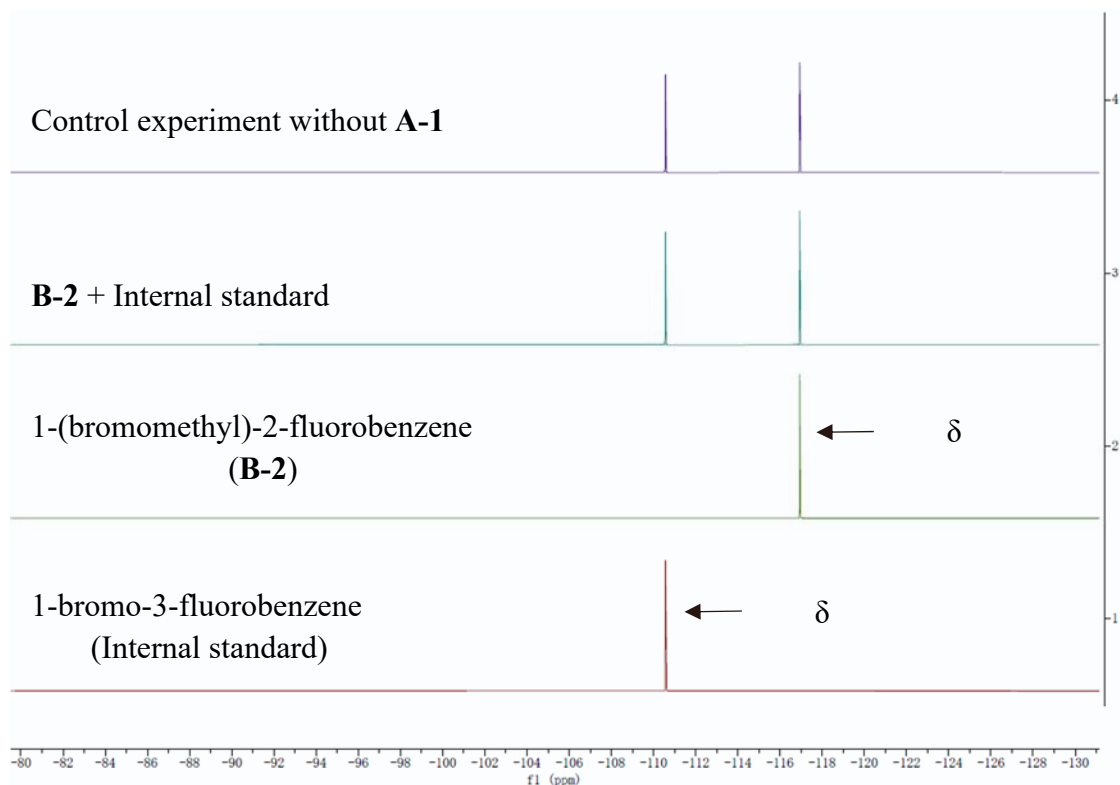


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (0.6 mg, 0.0050 mmol, 10 mol %), **L9** (2.9 mg, 0.0075 mmol, 15 mol %), Rb<sub>2</sub>CO<sub>3</sub> (28.9 mg, 0.125 mmol, 2.5 equiv) and anhydrous benzene (1.0 mL). The mixture was stirred at room temperature for 30 min. After that, 1-(bromomethyl)-2-fluorobenzene **B-2** (9.5 mg, 0.050 mmol, 1.0 equiv) was added into the mixture. The resulting mixture was stirred at 10 °C for 24 h. Then **1-bromo-3-fluorobenzene** (8.8 mg, 0.050 mmol, 1.0 equiv) was added as an internal standard, and the reaction mixture was filtered through a short pad of celite and rinsed with CDCl<sub>3</sub> (2 mL). The filtrate was directly subjected to <sup>19</sup>F NMR analysis. The results revealed that the anticipated radical dimerization product **92** was not detected, and **B-2** was fully recovered.

1,2-Bis(2-fluorophenyl)ethane (**92**) is a known compound, and the literature reported <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -119.0 – -119.1 (m).<sup>[S14]</sup>

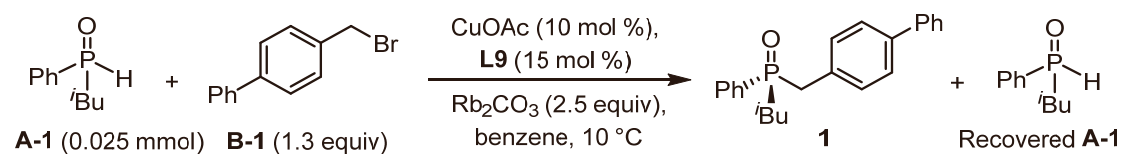
1-(bromomethyl)-2-fluorobenzene (**B-2**): <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -116.9.

**1-bromo-3-fluorobenzene** (internal standard): <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -110.6.



**Figure S7.** The stacked <sup>19</sup>F NMR spectra (376 MHz, CDCl<sub>3</sub>)

## 5. The stereochemistry of SPO and product during the reaction (Scheme 6G)

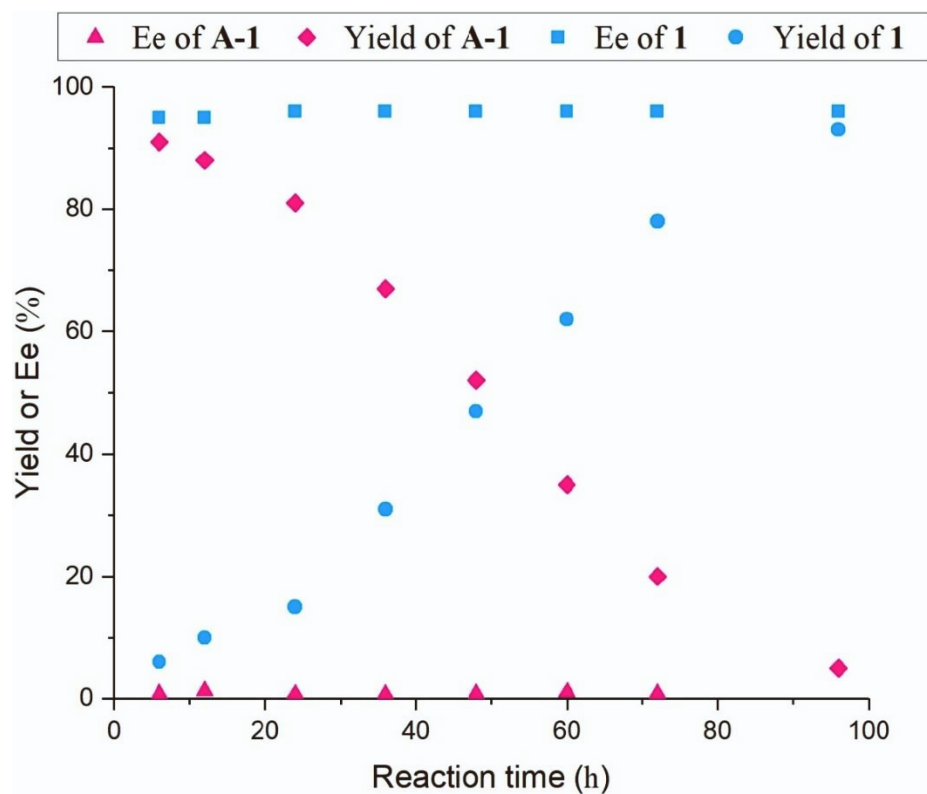


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (0.3 mg, 0.0025 mmol, 10 mol %), **L9** (1.5 mg, 0.0038 mmol, 15 mol %), Rb<sub>2</sub>CO<sub>3</sub> (14.5 mg, 0.063 mmol, 2.5 equiv) and anhydrous benzene (0.5 mL). The mixture was stirred at room temperature for 30 min. After that, racemic secondary phosphine oxide **A-1** (4.6 mg, 0.025 mmol, 1.0 equiv) and bromide **B-1** (8.2 mg, 0.033 mmol, 1.3 equiv) were sequentially added into the mixture. The resulting mixture was stirred at 10 °C for a specified period of time. The reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (1 mL) and DCM (1 mL). The filtrate was concentrated under reduced pressure. The residue was initially subjected to <sup>31</sup>P NMR analysis using trimethyl phosphate as an internal standard. The crude product was then purified by preparative thin-layer chromatography (PTLC) on silica gel (DCM/MeOH 100:1), resulting in the recovery of **A-1** and the isolation of the desired product **1**.

The ee values of the recovered **A-1** and the product **1** were determined by HPLC analysis. HPLC conditions for **A-1**: Chiralpak AD-H, hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min, λ = 214 nm. HPLC conditions for product **1**: Chiralcel OJ-H, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm.

**Table S3. Results of stereochemical studies**

| Time (h) | Yield of <b>A-1</b> (%) | Ee of <b>A-1</b> (%) | Yield of <b>1</b> (%) | Ee of <b>1</b> (%) |
|----------|-------------------------|----------------------|-----------------------|--------------------|
| 6        | 91                      | 0.8                  | 6                     | 95                 |
| 12       | 88                      | 1.3                  | 10                    | 95                 |
| 24       | 81                      | 0.7                  | 15                    | 96                 |
| 36       | 67                      | 0.7                  | 31                    | 96                 |
| 48       | 52                      | 0.8                  | 47                    | 96                 |
| 60       | 35                      | 1.0                  | 62                    | 96                 |
| 72       | 20                      | 0.8                  | 78                    | 96                 |
| 96       | <5                      | —                    | 93                    | 96                 |

**Figure S8. Stereochemical outcome of the reaction (stereochemistry of the SPO and the product)**

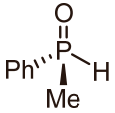
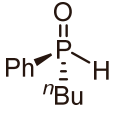
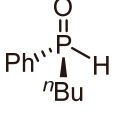
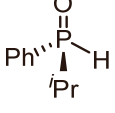
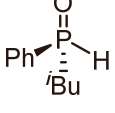
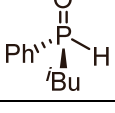
## 6. Control experiments with enantioenriched SPOs (Scheme 6H)

### (1) The preparation of enantioenriched SPOs

The enantioenriched secondary phosphine oxides (*R*)-**A-1** and (*S*)-**A-1** were prepared from the racemic **A-1** by semi-preparative HPLC separation using a preparative Daicel Chiralpak AD-H column (Conditions: hexane/*i*-PrOH = 95/5, flow rate 5.0 mL/min,  $\lambda$  = 214 nm).

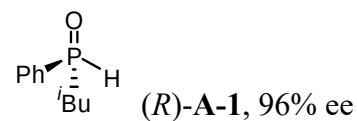
The absolute configuration of (*R*)-**A-1** and (*S*)-**A-1** was assigned by comparison with the optical rotation data of **A**, as reported in the literature.<sup>[S15]</sup>

**Table S4. Optical rotation data of **A** in literature**

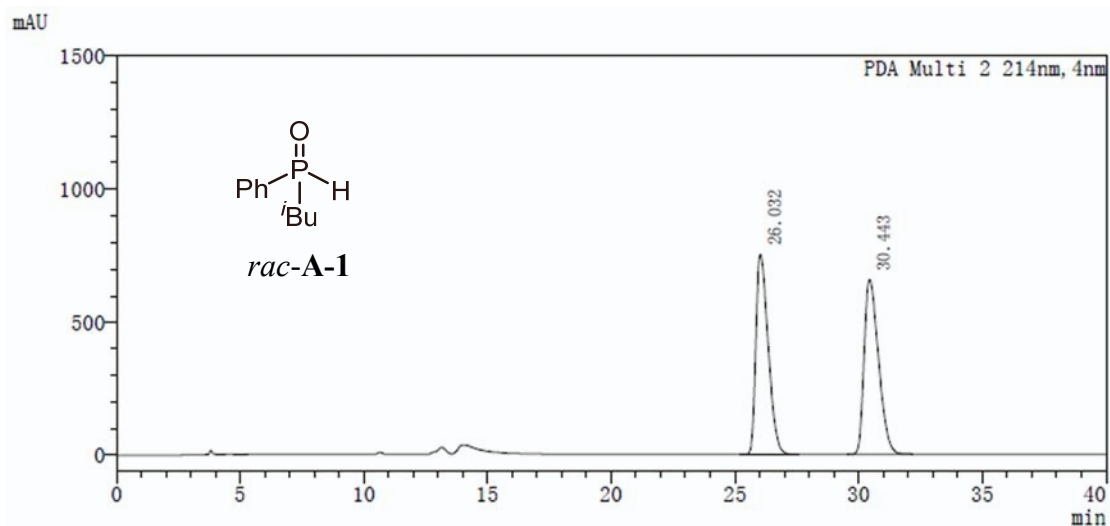
| Entry | Absolute configuration                                                                                       | $[\alpha]$                                                                   | Reference      |
|-------|--------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------|----------------|
| 1     |  ( <i>S</i> )- <b>A-2</b>   | $[\alpha]_{589}^{31} = -21.6$<br>( <i>c</i> = 0.23, CHCl <sub>3</sub> )      | <i>Ref.</i> 16 |
| 2     |  ( <i>R</i> )- <b>A-4</b>  | $[\alpha]_{589}^{25} = +20.5$<br>( <i>c</i> = 0.58, CHCl <sub>3</sub> )      | <i>Ref.</i> 16 |
| 3     |  ( <i>S</i> )- <b>A-4</b> | $[\alpha]_{589}^{31} = -22.0$<br>( <i>c</i> = 0.60, CHCl <sub>3</sub> )      | <i>Ref.</i> 16 |
| 4     |  ( <i>S</i> )- <b>A-6</b> | $[\alpha]_{589}^{24} = -48.8$<br>( <i>c</i> = 0.42, CHCl <sub>3</sub> )      | <i>Ref.</i> 16 |
| 5     |  ( <i>R</i> )- <b>A-1</b> | $[\alpha]_{\text{D}}^{20} = +16.0$<br>( <i>c</i> = 0.50, CHCl <sub>3</sub> ) | This work      |
| 6     |  ( <i>S</i> )- <b>A-1</b> | $[\alpha]_{\text{D}}^{20} = -21.1$<br>( <i>c</i> = 1.00, CHCl <sub>3</sub> ) | This work      |

HPLC analysis of (*R*)-**A-1** and (*S*)-**A-1**:

**(*R*)-isobutyl(phenyl)phosphine oxide ((*R*)-**A-1**)**



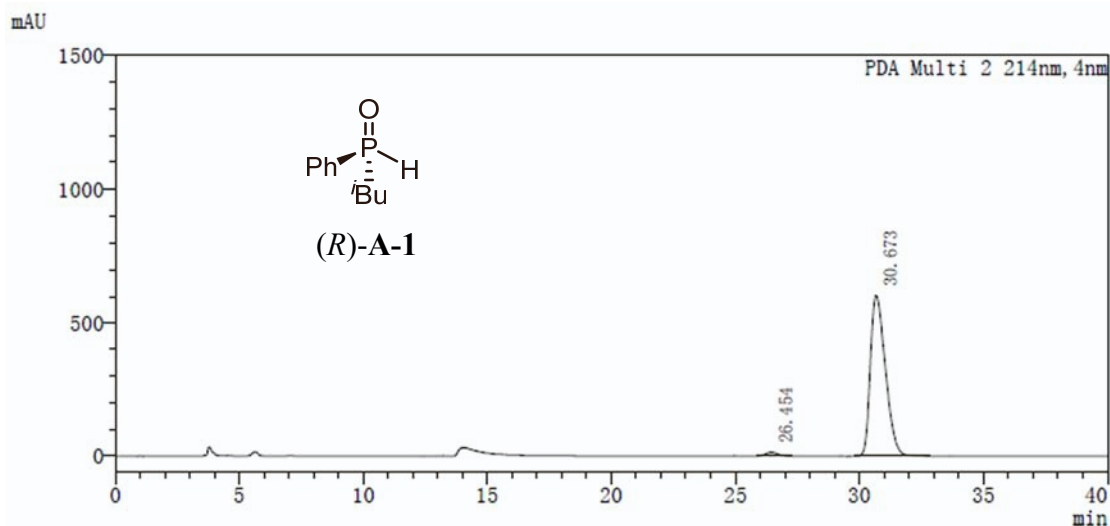
**HPLC** analysis: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min,  $\lambda$  = 214 nm),  $t_R$  (minor) = 26.454 min,  $t_R$  (major) = 30.673 min.



Peak Table

PDA Ch2 214nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 26.032    | 26012073 | 49.492 |
| 2     | 30.443    | 26546513 | 50.508 |

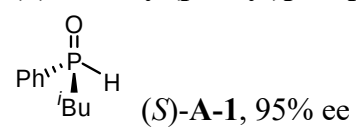


Peak Table

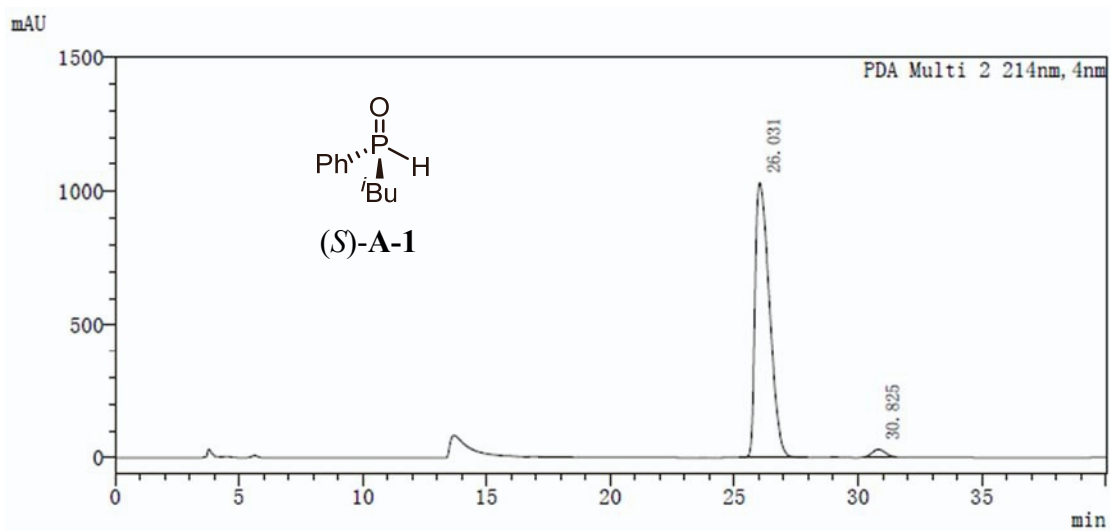
PDA Ch2 214nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 26.454    | 455741   | 1.758  |
| 2     | 30.673    | 25465949 | 98.242 |

**(S)-isobutyl(phenyl)phosphine oxide ((S)-A-1)**



**HPLC analysis:** Chiralpak AD-H (hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min,  $\lambda$  = 214 nm),  $t_R$  (major) = 26.031 min,  $t_R$  (minor) = 30.825 min.



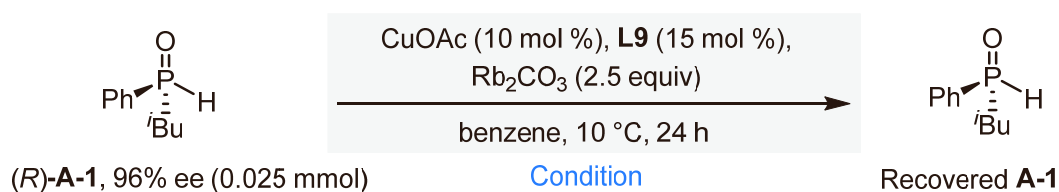
Peak Table

PDA Ch2 214nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 26.031    | 41533642 | 97.608 |
| 2     | 30.825    | 1017855  | 2.392  |



## (2) Control experiments for the racemization of enantioenriched SPO



General procedure for the reaction under **Condition:**

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (0.3 mg, 0.0025 mmol, 10 mol %), **L9** (1.5 mg, 0.0038 mmol, 15 mol %), Rb<sub>2</sub>CO<sub>3</sub> (14.5 mg, 0.063 mmol, 2.5 equiv) and anhydrous benzene (0.5 mL). The mixture was stirred at room temperature for 30 min. After that, enantioenriched secondary phosphine oxide (*R*)-**A-1** (4.6 mg, 0.025 mmol, 1.0 equiv) was added into the mixture. The resulting mixture was stirred at 10 °C for 24 h. The reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (1 mL) and DCM (1 mL). The filtrate was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (PTLC) on silica gel (DCM/MeOH 100:1) to afford the pure recovered **A-1** for HPLC analysis (HPLC conditions: Chiralpak AD-H, hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min, λ = 214 nm).

The procedure for the reactions under **Condition variation** was identical to that described above, except that modified conditions as stated below were employed in a specified reaction system.

**Table S5. Results of control experiments on the racemization of A-1**

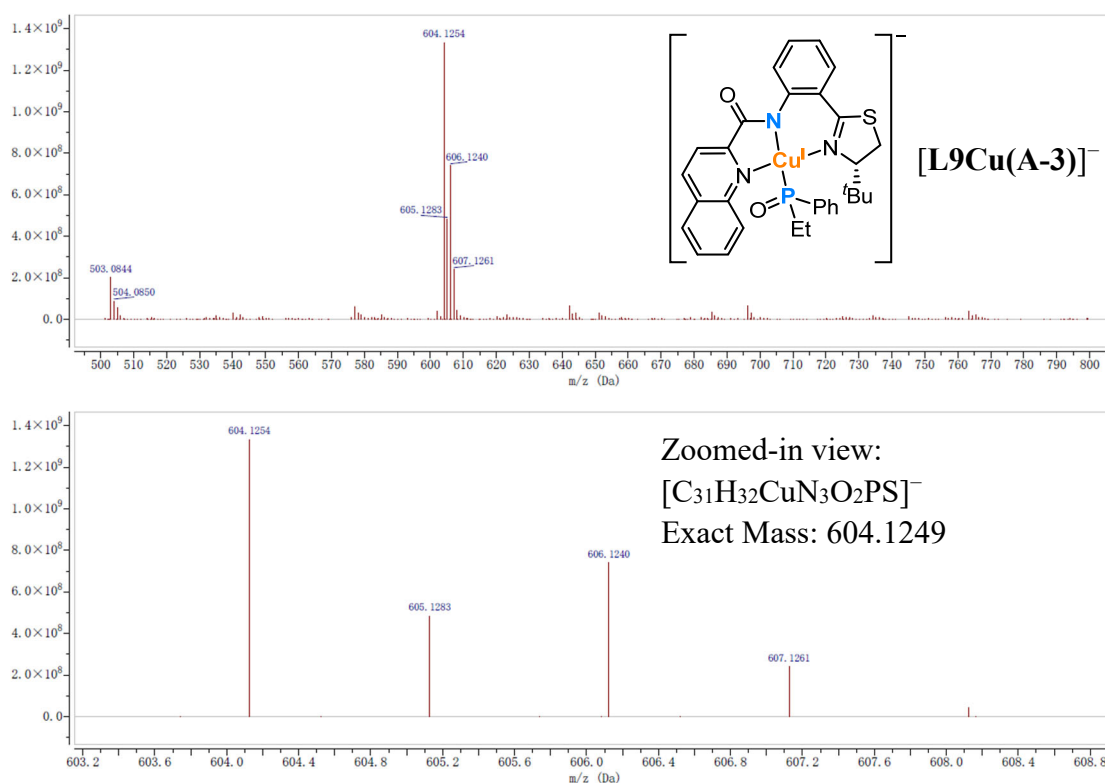
| Entry | Condition variation                                          | Ee of recovered <b>A-1</b> (%) |
|-------|--------------------------------------------------------------|--------------------------------|
| 1     | None                                                         | 2                              |
| 2     | Without <b>L9</b>                                            | 43                             |
| 3     | Without Rb <sub>2</sub> CO <sub>3</sub>                      | 86                             |
| 4     | Without <b>L9</b> , Rb <sub>2</sub> CO <sub>3</sub>          | 79                             |
| 5     | Without CuOAc                                                | 95                             |
| 6     | Without CuOAc, Rb <sub>2</sub> CO <sub>3</sub>               | 96                             |
| 7     | Without CuOAc, <b>L9</b>                                     | 96                             |
| 8     | Without CuOAc, <b>L9</b> and Rb <sub>2</sub> CO <sub>3</sub> | 96                             |

## 7. HRMS analysis of L9Cu(A) complex

### (1) HRMS analysis of L9Cu(A-3) complex

A mixture of **A-3** (7.7 mg, 0.05 mmol, 1.0 equiv), **L9**-Rb salt (1.0 equiv), CuOAc (1.0 equiv) and Rb<sub>2</sub>CO<sub>3</sub> (1.0 equiv) in anhydrous THF (1.0 mL) was stirred at room temperature for 1 h. The resulting mixture was directly subjected to HRMS analysis.

The desired **L9Cu(A-3)** complex was successfully detected: **HRMS** (ESI) *m/z* calcd. for [C<sub>31</sub>H<sub>32</sub>CuN<sub>3</sub>O<sub>2</sub>PS]<sup>−</sup> 604.1249, found 604.1254.

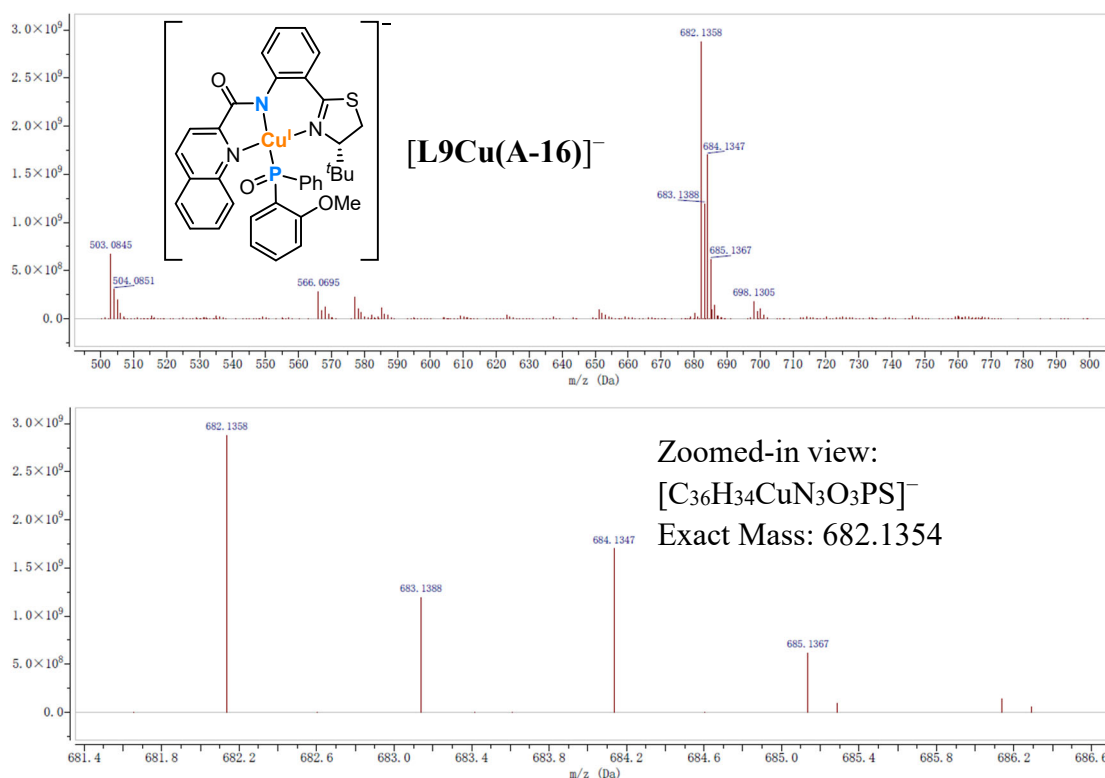


**Figure S9. High-resolution mass spectrum (HRMS) of the L9Cu(A-3) complex**

## (2) HRMS analysis of L9Cu(A-16) complex

A mixture of **A-16** (11.6 mg, 0.05 mmol, 1.0 equiv), **L9**-Rb salt (1.0 equiv), CuOAc (1.0 equiv) and Rb<sub>2</sub>CO<sub>3</sub> (1.0 equiv) in anhydrous THF (1.0 mL) was stirred at room temperature for 1 h. The resulting mixture was directly subjected to HRMS analysis.

The desired **L9Cu(A-16)** complex was successfully detected: **HRMS** (ESI)  $m/z$  calcd. for [C<sub>36</sub>H<sub>34</sub>CuN<sub>3</sub>O<sub>3</sub>PS]<sup>−</sup> 682.1354, found 682.1358.



**Figure S10. HRMS spectrum of the L9Cu(A-16) complex**

## Computational mechanistic studies

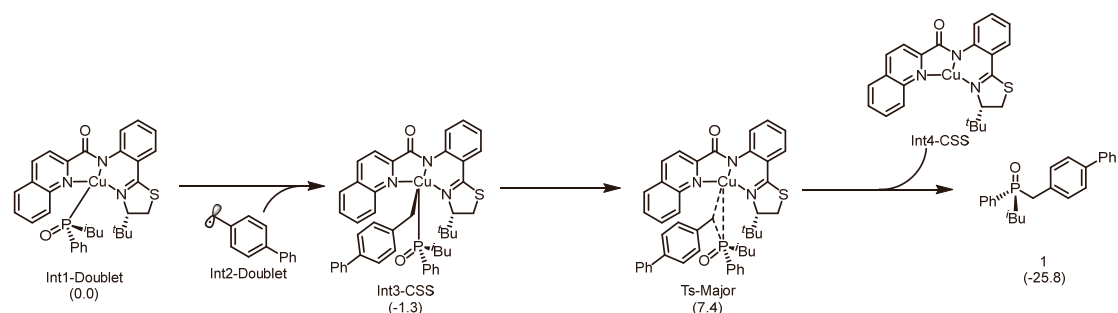
### 1. Computational details

Quantum chemical calculations based on density functional theory (DFT) were performed using the Gaussian 16 program.<sup>[S16]</sup> The structures were optimized with the B3LYP exchange-correlation functional,<sup>[S17,S18]</sup> together with Grimme's dispersion correction<sup>[S19]</sup> with Becke-Johnson damping (D3-BJ).<sup>[S20]</sup> The LANL2DZ basis set was applied for Cu and the 6-31G(d) basis set was used for all other atoms. Unrestricted calculations were carried out for open-shell species. Vibrational frequency calculations were conducted to confirm the nature of the stationary points: transition states have one imaginary frequency, whereas reactants, intermediates, and products have no imaginary frequencies. Single-point energies were then calculated for all of the optimized structures with the SDD basis set<sup>[S21]</sup> and pseudopotential for Cu and 6-311+G(d,p) for all other atoms, including solvation effects using the solvation model based on density (SMD)<sup>[S22]</sup> with benzene as the solvent. The Gibbs free energies in solution were corrected by 1.89 kcal/mol, which is the Gibbs free energy change from 1 atm in gas phase to 1 mol/L in solution phase at 298.15 K. Energy decomposition analysis (EDA) was carried out for selected optimized structures at the B3LYP-D3BJ level of theory using ADF 2019.304 program, along with a small-core TZP basis set.<sup>[S23,S24]</sup> Electrostatic potential (ESP) was evaluated using Multiwfn 3.8 program.<sup>[S25,S26]</sup>

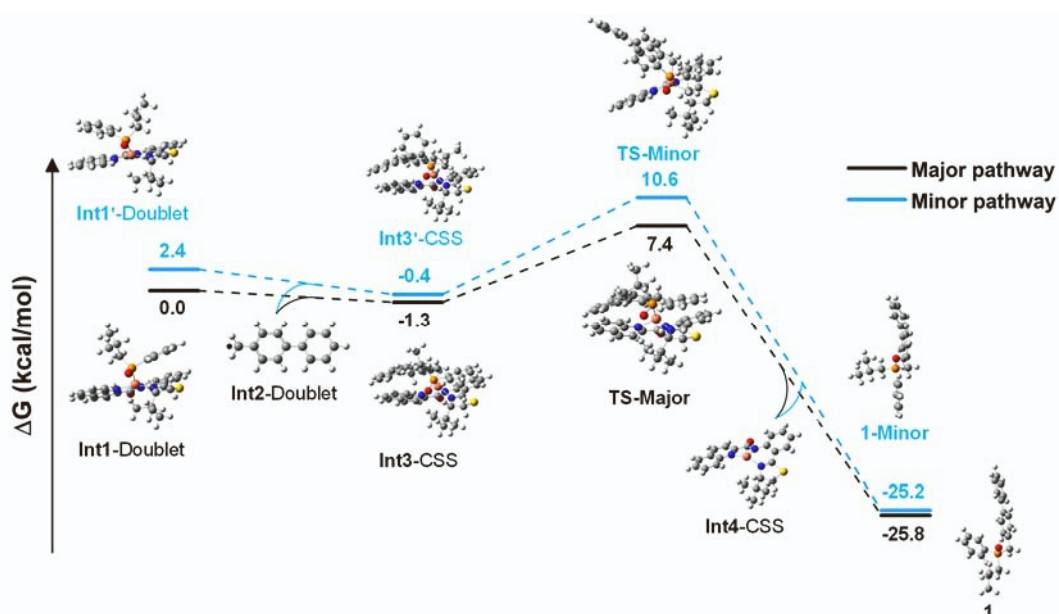
### 2. Discussion on Cu<sup>I</sup>-P Mediated C-P Bonding Mechanism of Benzyl Radical and SPOs

Theoretical studies employing DFT calculations were conducted to elucidate the reaction mechanism and the origin of enantioselectivity in the synthesis of product **1** using racemic SPO **A-1**, *p*-phenylbenzyl bromide **B-1** and **L9** ligand. As illustrated in Figures S11 and S12, during the SET process between the phosphinito Cu<sup>I</sup> complex and alkyl halides, the phosphinito Cu<sup>II</sup> complex (**Int1**) and an alkyl radical (**Int2**) are generated. Subsequently, they associate through a Cu-C interaction to form the closed-shell singlet (CSS) intermediate **Int3**. The C-P coupling then proceeds via the transition state **TS-Major**, yielding product **1** and the Cu<sup>I</sup> complex for the subsequent reaction cycle. The formation of the C-P bond entails a free energy barrier of 8.7 kcal/mol, suggesting superior catalytic activity towards product **1**.

The formation of the minor enantiomer of product **1** (**1-Minor**) was also analyzed to explain the observed enantioselectivity, as shown in Scheme 2 in the main text. In this scenario, the C–P coupling has to overcome a higher free energy barrier of 11.0 kcal/mol, which aligns well with the high experimental ee value of product **1**. Notably, the phenyl ring on the phosphinito fragment and the thiazoline ring coordinated to Cu are arranged in parallel throughout the reaction pathway for product **1**. To investigate the interaction mechanism, ESP was mapped onto the van der Waals (vdW) surface of **Int1**, and the resulting penetration map was examined (Figure S13). An apparent penetrating region is observed between the phenyl ring on the phosphinito fragment and the thiazoline ring coordinated to Cu, suggesting a marked electrostatic interaction that enhances the stability of this distinct structure and contributes to the excellent enantioselectivity. Energy decomposition analyses (EDA) of **Int1** and **Int1'** in Table S6 further validate that the increased electrostatic attraction serves as the driving force for enantioselectivity.

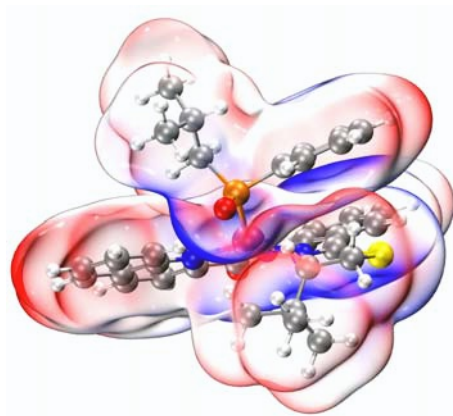


**Figure S11. Schematic reaction mechanism for C–P coupling leading to product **1****



**Figure S12. Proposed free-energy profiles for the enantioselective C-P coupling reactions, together with the optimized structures**

The major pathway corresponds to formation of product **1**, whereas the minor pathway corresponds to formation of the minor enantiomer (**1-Minor**).



**Figure S13. Penetration map of Int1 with the electrostatic potential mapped onto the van der Waals surface**

**Table S6. Energy decomposition analysis of Int1 (major pathway to product 1) and Int1' (minor pathway to the minor enantiomer, 1-Minor)**

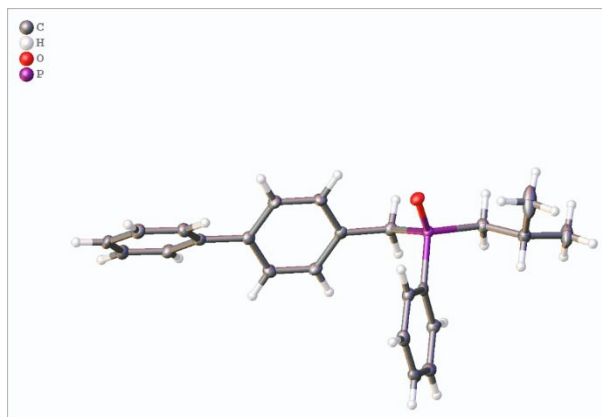
| Energy term <sup>a</sup>    | Energy (kcal/mol) |              |
|-----------------------------|-------------------|--------------|
|                             | <b>Int1</b>       | <b>Int1'</b> |
| $\Delta E_{\text{int}}$     | −158.98           | −157.13      |
| $\Delta E_{\text{Pauli}}$   | 151.89            | 150.08       |
| $\Delta E_{\text{elestat}}$ | −201.08           | −197.26      |
| $\Delta E_{\text{orb}}$     | −85.24            | −84.00       |
| $\Delta E_{\text{dis}}$     | −24.54            | −25.94       |

<sup>a</sup> $\Delta E_{\text{int}}$ ,  $\Delta E_{\text{Pauli}}$ ,  $\Delta E_{\text{elestat}}$ ,  $\Delta E_{\text{orb}}$ , and  $\Delta E_{\text{dis}}$  represent the total interaction energy, Pauli repulsion, electrostatic interaction, orbital interaction, and dispersion interaction, respectively, between the cationic Cu fragment and the anionic P fragment, where  $\Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elestat}} + \Delta E_{\text{orb}} + \Delta E_{\text{dis}}$ .

**Data S2. X-Ray crystallographic data**

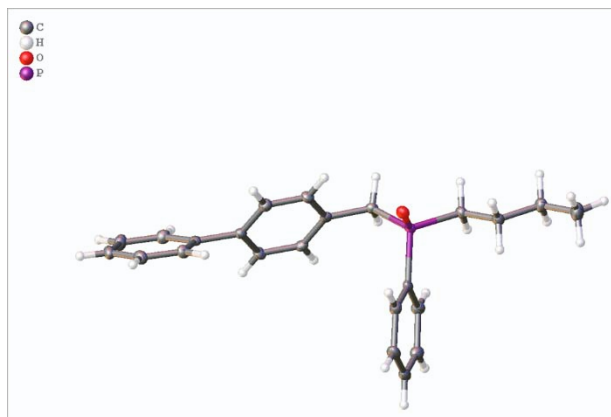
The X-ray crystallographic data were collected on a Bruker D8 VENTURE diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) at 100(2) K. Data collection and reduction were performed using the Bruker APEX3/SAINT software package. The structures were solved using SHELXT and refined using SHELXL within the Olex2 graphical interface. Refinement was carried out on  $F^2$  by full-matrix least-squares minimization.





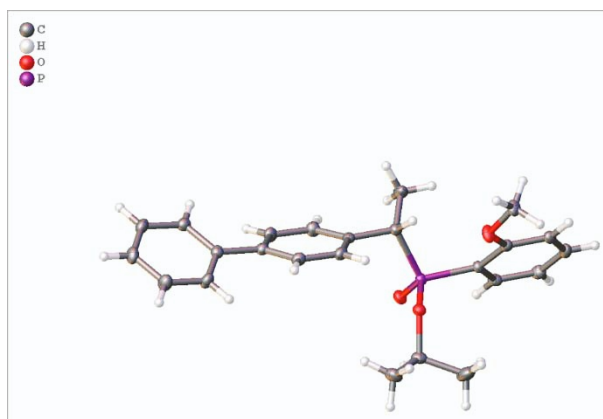
### Crystal data and structure refinement for CIF\_of\_Product\_1.

|                                             |                                                               |
|---------------------------------------------|---------------------------------------------------------------|
| Identification code                         | CIF_of_Product_1                                              |
| Empirical formula                           | C <sub>23</sub> H <sub>25</sub> OP                            |
| Formula weight                              | 348.40                                                        |
| Temperature/K                               | 100.0(2)                                                      |
| Crystal system                              | monoclinic                                                    |
| Space group                                 | P2 <sub>1</sub>                                               |
| a/Å                                         | 12.0625(15)                                                   |
| b/Å                                         | 5.8857(5)                                                     |
| c/Å                                         | 13.1841(14)                                                   |
| α/°                                         | 90                                                            |
| β/°                                         | 93.434(8)                                                     |
| γ/°                                         | 90                                                            |
| Volume/Å <sup>3</sup>                       | 934.34(17)                                                    |
| Z                                           | 2                                                             |
| ρ <sub>calc</sub> /cm <sup>3</sup>          | 1.238                                                         |
| μ/mm <sup>-1</sup>                          | 1.342                                                         |
| F(000)                                      | 372.0                                                         |
| Crystal size/mm <sup>3</sup>                | 0.1 × 0.1 × 0.1                                               |
| Radiation                                   | CuKα (λ = 1.54184)                                            |
| 2θ range for data collection/°              | 6.716 to 137.16                                               |
| Index ranges                                | -14 ≤ h ≤ 14, -7 ≤ k ≤ 7, -15 ≤ l ≤ 15                        |
| Reflections collected                       | 13838                                                         |
| Independent reflections                     | 3394 [R <sub>int</sub> = 0.0502, R <sub>sigma</sub> = 0.0402] |
| Data/restraints/parameters                  | 3394/1/228                                                    |
| Goodness-of-fit on F <sup>2</sup>           | 1.068                                                         |
| Final R indexes [I ≥ 2σ (I)]                | R <sub>1</sub> = 0.0296, wR <sub>2</sub> = 0.0765             |
| Final R indexes [all data]                  | R <sub>1</sub> = 0.0301, wR <sub>2</sub> = 0.0770             |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 0.22/-0.41                                                    |
| Flack parameter                             | 0.066(8)                                                      |



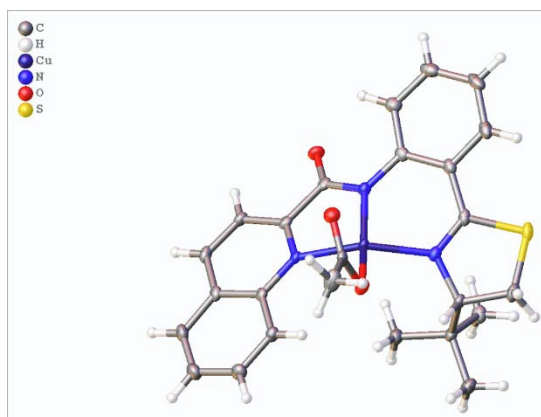
### Crystal data and structure refinement for CheckCIF\_of\_Product\_42.

|                                             |                                                               |
|---------------------------------------------|---------------------------------------------------------------|
| Identification code                         | CheckCIF_of_Product_42                                        |
| Empirical formula                           | C <sub>23</sub> H <sub>25</sub> OP                            |
| Formula weight                              | 348.40                                                        |
| Temperature/K                               | 100.01                                                        |
| Crystal system                              | monoclinic                                                    |
| Space group                                 | P21                                                           |
| a/Å                                         | 12.3738(13)                                                   |
| b/Å                                         | 5.7549(6)                                                     |
| c/Å                                         | 13.2212(13)                                                   |
| $\alpha$ /°                                 | 90                                                            |
| $\beta$ /°                                  | 95.098(3)                                                     |
| $\gamma$ /°                                 | 90                                                            |
| Volume/Å <sup>3</sup>                       | 937.76(17)                                                    |
| Z                                           | 2                                                             |
| $\rho$ <sub>calc</sub> /cm <sup>3</sup>     | 1.234                                                         |
| $\mu$ /mm <sup>-1</sup>                     | 0.154                                                         |
| F(000)                                      | 372.0                                                         |
| Crystal size/mm <sup>3</sup>                | 0.33 × 0.31 × 0.24                                            |
| Radiation                                   | MoK $\alpha$ ( $\lambda$ = 0.71073)                           |
| 2 $\theta$ range for data collection/°      | 4.322 to 55.058                                               |
| Index ranges                                | -16 ≤ h ≤ 16, -7 ≤ k ≤ 7, -17 ≤ l ≤ 17                        |
| Reflections collected                       | 12757                                                         |
| Independent reflections                     | 4313 [R <sub>int</sub> = 0.0433, R <sub>sigma</sub> = 0.0540] |
| Data/restraints/parameters                  | 4313/1/227                                                    |
| Goodness-of-fit on F <sup>2</sup>           | 1.048                                                         |
| Final R indexes [I ≥ 2 $\sigma$ (I)]        | R <sub>1</sub> = 0.0435, wR <sub>2</sub> = 0.0908             |
| Final R indexes [all data]                  | R <sub>1</sub> = 0.0555, wR <sub>2</sub> = 0.0963             |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 0.31/-0.30                                                    |
| Flack parameter                             | -0.06(7)                                                      |



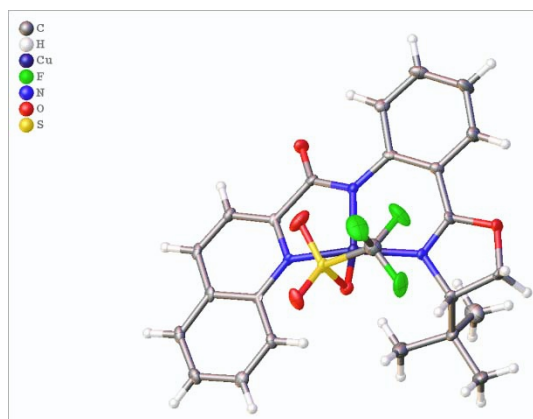
### Crystal data and structure refinement for CheckCIF\_of\_Product\_69.

|                                             |                                                               |
|---------------------------------------------|---------------------------------------------------------------|
| Identification code                         | CheckCIF_of_Product_69                                        |
| Empirical formula                           | C <sub>24</sub> H <sub>27</sub> O <sub>3</sub> P              |
| Formula weight                              | 394.42                                                        |
| Temperature/K                               | 100.0(2)                                                      |
| Crystal system                              | monoclinic                                                    |
| Space group                                 | P2 <sub>1</sub>                                               |
| a/Å                                         | 7.5834(9)                                                     |
| b/Å                                         | 16.3940(14)                                                   |
| c/Å                                         | 9.3741(13)                                                    |
| α/°                                         | 90                                                            |
| β/°                                         | 111.867(8)                                                    |
| γ/°                                         | 90                                                            |
| Volume/Å <sup>3</sup>                       | 1081.6(2)                                                     |
| Z                                           | 2                                                             |
| ρ <sub>calc</sub> /cm <sup>3</sup>          | 1.211                                                         |
| μ/mm <sup>-1</sup>                          | 1.288                                                         |
| F(000)                                      | 420.0                                                         |
| Crystal size/mm <sup>3</sup>                | 0.1 × 0.1 × 0.1                                               |
| Radiation                                   | CuKα (λ = 1.54178)                                            |
| 2θ range for data collection/°              | 10.792 to 144.072                                             |
| Index ranges                                | -9 ≤ h ≤ 9, -20 ≤ k ≤ 19, -11 ≤ l ≤ 11                        |
| Reflections collected                       | 31933                                                         |
| Independent reflections                     | 4105 [R <sub>int</sub> = 0.0396, R <sub>sigma</sub> = 0.0253] |
| Data/restraints/parameters                  | 4105/1/257                                                    |
| Goodness-of-fit on F <sup>2</sup>           | 1.060                                                         |
| Final R indexes [I ≥ 2σ (I)]                | R <sub>1</sub> = 0.0244, wR <sub>2</sub> = 0.0632             |
| Final R indexes [all data]                  | R <sub>1</sub> = 0.0246, wR <sub>2</sub> = 0.0633             |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 0.30/-0.22                                                    |
| Flack parameter                             | 0.049(4)                                                      |



### Crystal data and structure refinement for CheckCIF\_of\_Product\_Cu-L9.

|                                             |                                                                   |
|---------------------------------------------|-------------------------------------------------------------------|
| Identification code                         | CheckCIF_of_Product_Cu-L9                                         |
| Empirical formula                           | C <sub>25</sub> H <sub>25</sub> CuN <sub>3</sub> O <sub>3</sub> S |
| Formula weight                              | 511.08                                                            |
| Temperature/K                               | 293.15                                                            |
| Crystal system                              | orthorhombic                                                      |
| Space group                                 | P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>                     |
| a/Å                                         | 9.0502(2)                                                         |
| b/Å                                         | 9.5202(4)                                                         |
| c/Å                                         | 26.9293(14)                                                       |
| $\alpha$ /°                                 | 90                                                                |
| $\beta$ /°                                  | 90                                                                |
| $\gamma$ /°                                 | 90                                                                |
| Volume/Å <sup>3</sup>                       | 2320.22(16)                                                       |
| Z                                           | 4                                                                 |
| $\rho_{\text{calc}}$ /cm <sup>3</sup>       | 1.463                                                             |
| $\mu$ /mm <sup>-1</sup>                     | 2.437                                                             |
| F(000)                                      | 1060.0                                                            |
| Crystal size/mm <sup>3</sup>                | 0.1 × 0.1 × 0.1                                                   |
| Radiation                                   | CuK $\alpha$ ( $\lambda$ = 1.54184)                               |
| 2 $\theta$ range for data collection/°      | 11.782 to 136.738                                                 |
| Index ranges                                | -10 ≤ h ≤ 9, -11 ≤ k ≤ 11, -24 ≤ l ≤ 32                           |
| Reflections collected                       | 17809                                                             |
| Independent reflections                     | 4192 [R <sub>int</sub> = 0.0212, R <sub>sigma</sub> = 0.0199]     |
| Data/restraints/parameters                  | 4192/0/303                                                        |
| Goodness-of-fit on F <sup>2</sup>           | 1.122                                                             |
| Final R indexes [I ≥ 2 $\sigma$ (I)]        | R <sub>1</sub> = 0.0195, wR <sub>2</sub> = 0.0532                 |
| Final R indexes [all data]                  | R <sub>1</sub> = 0.0197, wR <sub>2</sub> = 0.0533                 |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 0.21/-0.35                                                        |
| Flack parameter                             | 0.035(17)                                                         |

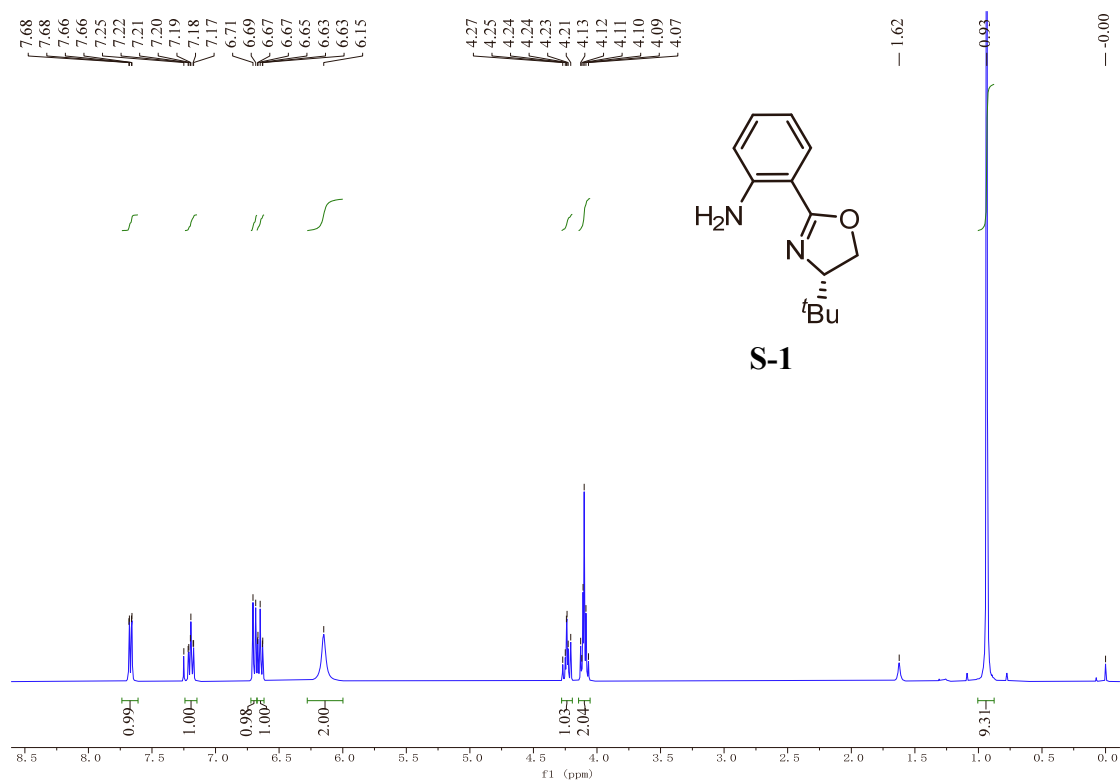


### Crystal data and structure refinement for CheckCIF\_of\_Product\_Cu-L6.

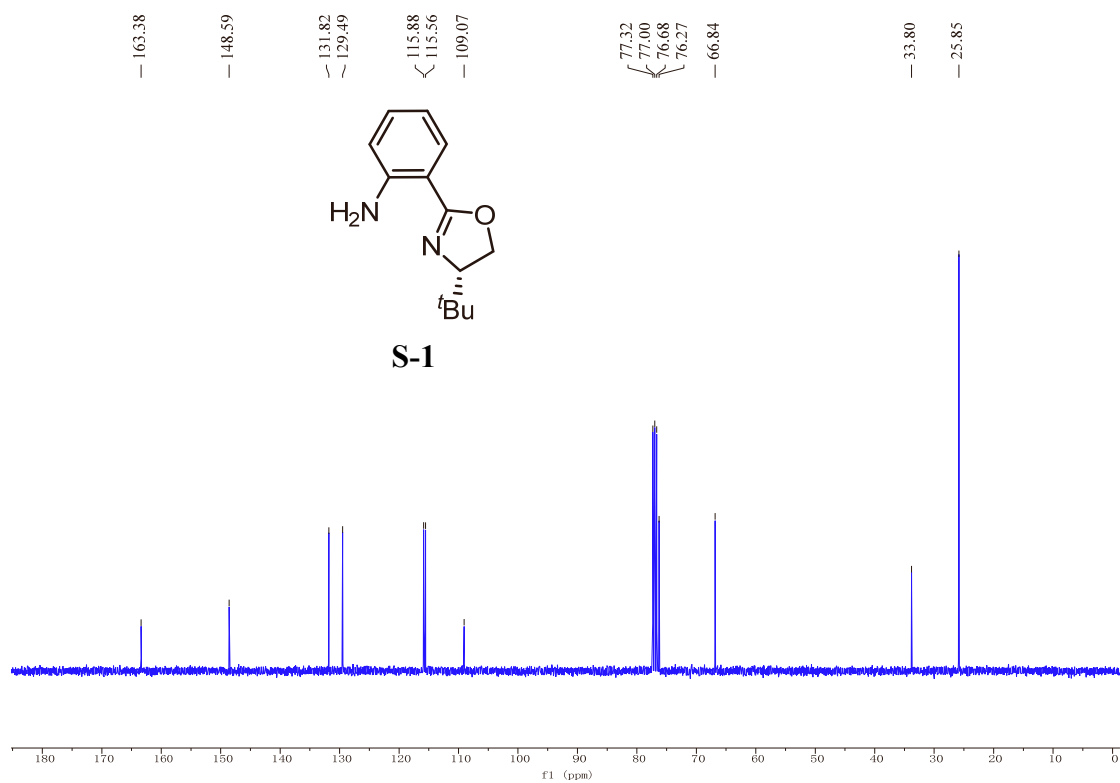
|                                             |                                                                                  |
|---------------------------------------------|----------------------------------------------------------------------------------|
| Identification code                         | CheckCIF_of_Product_Cu-L6                                                        |
| Empirical formula                           | C <sub>24</sub> H <sub>22</sub> CuF <sub>3</sub> N <sub>3</sub> O <sub>5</sub> S |
| Formula weight                              | 585.04                                                                           |
| Temperature/K                               | 293.15                                                                           |
| Crystal system                              | orthorhombic                                                                     |
| Space group                                 | P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>                                    |
| a/Å                                         | 10.3556(5)                                                                       |
| b/Å                                         | 12.8024(7)                                                                       |
| c/Å                                         | 18.2703(10)                                                                      |
| α/°                                         | 90                                                                               |
| β/°                                         | 90                                                                               |
| γ/°                                         | 90                                                                               |
| Volume/Å <sup>3</sup>                       | 2422.2(2)                                                                        |
| Z                                           | 4                                                                                |
| ρ <sub>calc</sub> /cm <sup>3</sup>          | 1.604                                                                            |
| μ/mm <sup>-1</sup>                          | 1.053                                                                            |
| F(000)                                      | 1196.0                                                                           |
| Crystal size/mm <sup>3</sup>                | 0.1 × 0.1 × 0.1                                                                  |
| Radiation                                   | MoKα (λ = 0.71073)                                                               |
| 2θ range for data collection/°              | 4.458 to 55.084                                                                  |
| Index ranges                                | -13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -22 ≤ l ≤ 23                                         |
| Reflections collected                       | 35244                                                                            |
| Independent reflections                     | 5540 [R <sub>int</sub> = 0.1278, R <sub>sigma</sub> = 0.1039]                    |
| Data/restraints/parameters                  | 5540/0/338                                                                       |
| Goodness-of-fit on F <sup>2</sup>           | 1.020                                                                            |
| Final R indexes [I ≥ 2σ (I)]                | R <sub>1</sub> = 0.0579, wR <sub>2</sub> = 0.1027                                |
| Final R indexes [all data]                  | R <sub>1</sub> = 0.0973, wR <sub>2</sub> = 0.1181                                |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 0.64/-0.89                                                                       |
| Flack parameter                             | 0.04(3)                                                                          |

## Data S3. NMR spectra

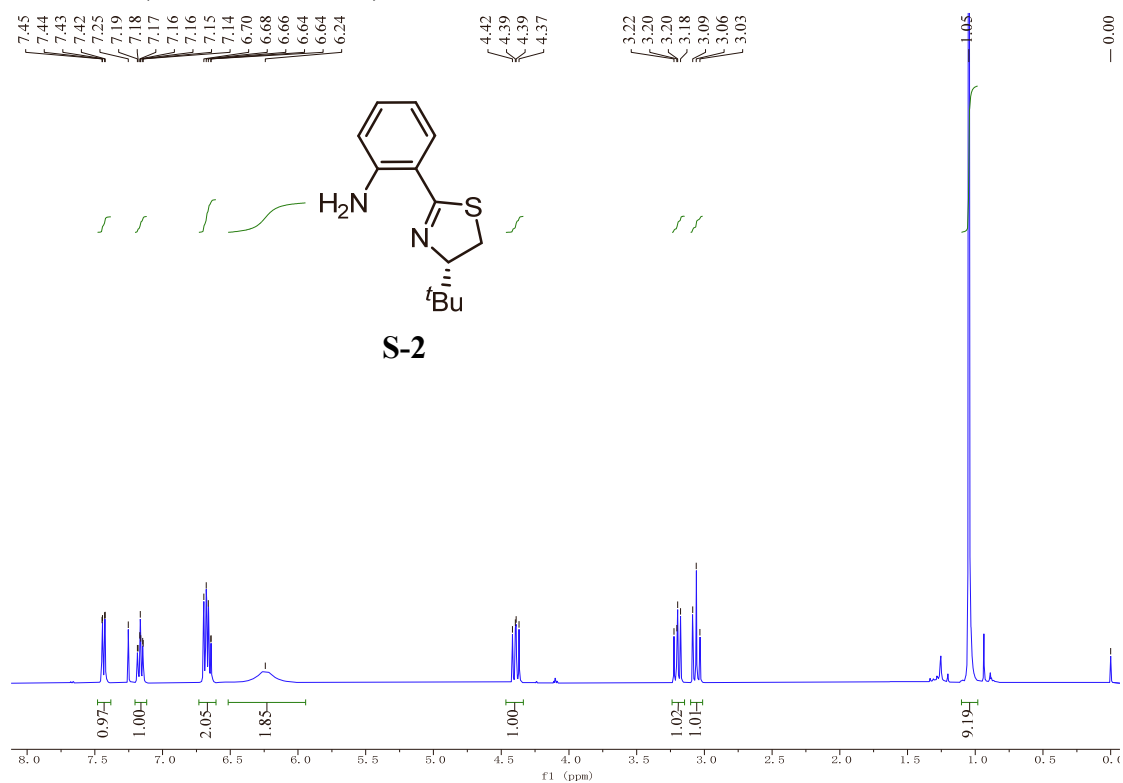
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



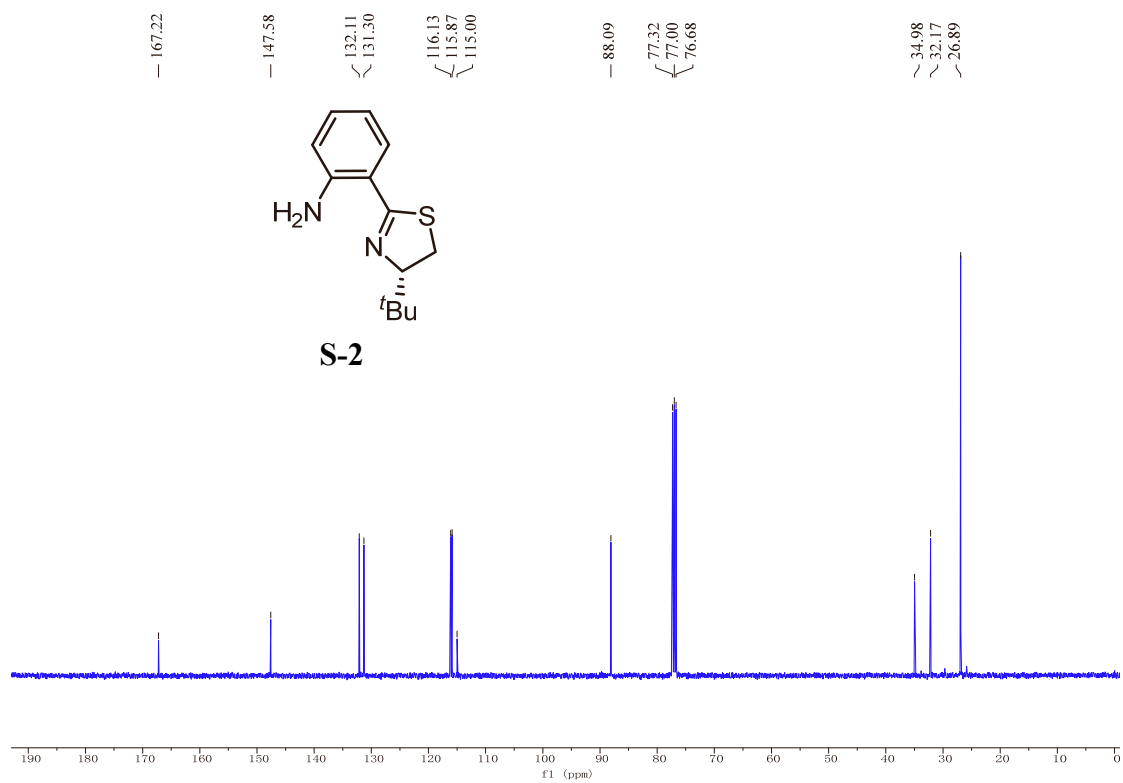
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



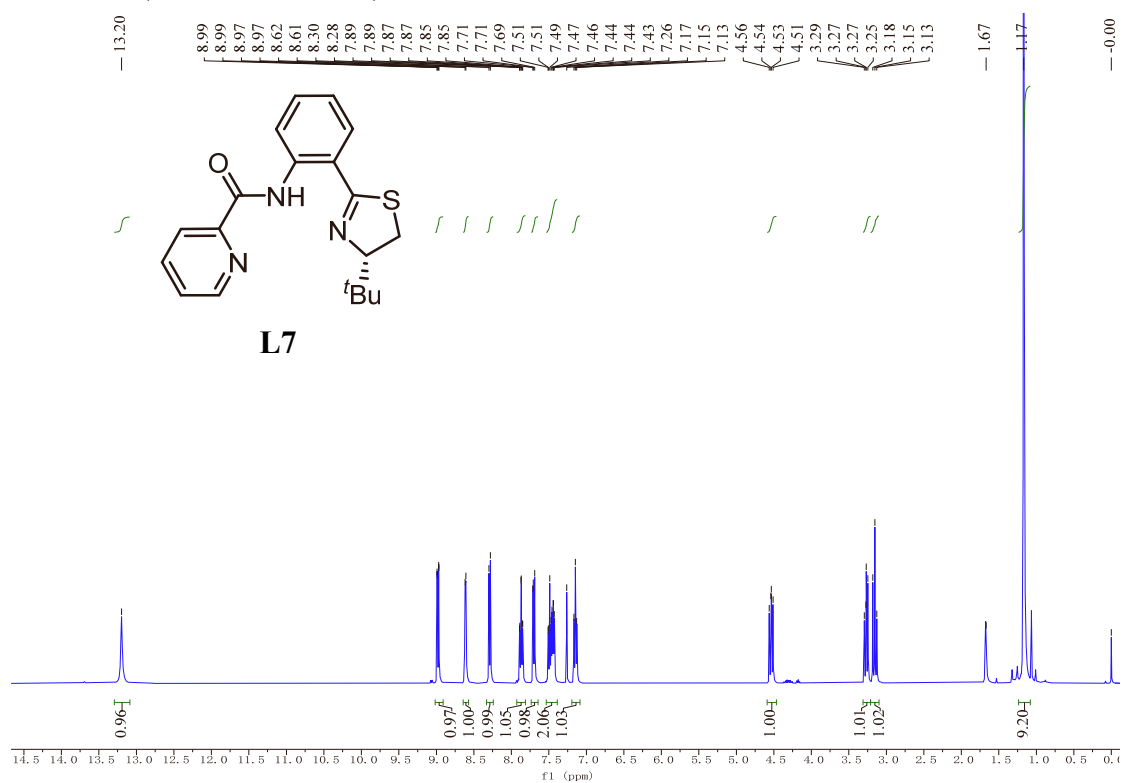
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



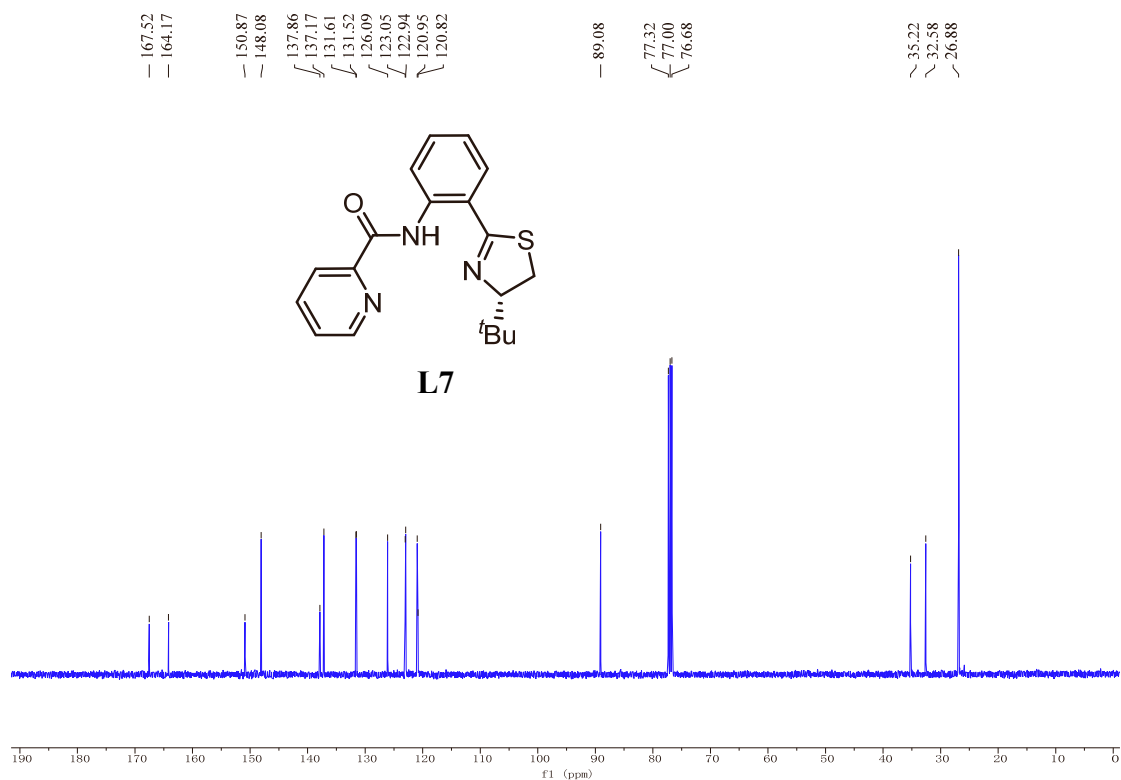
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

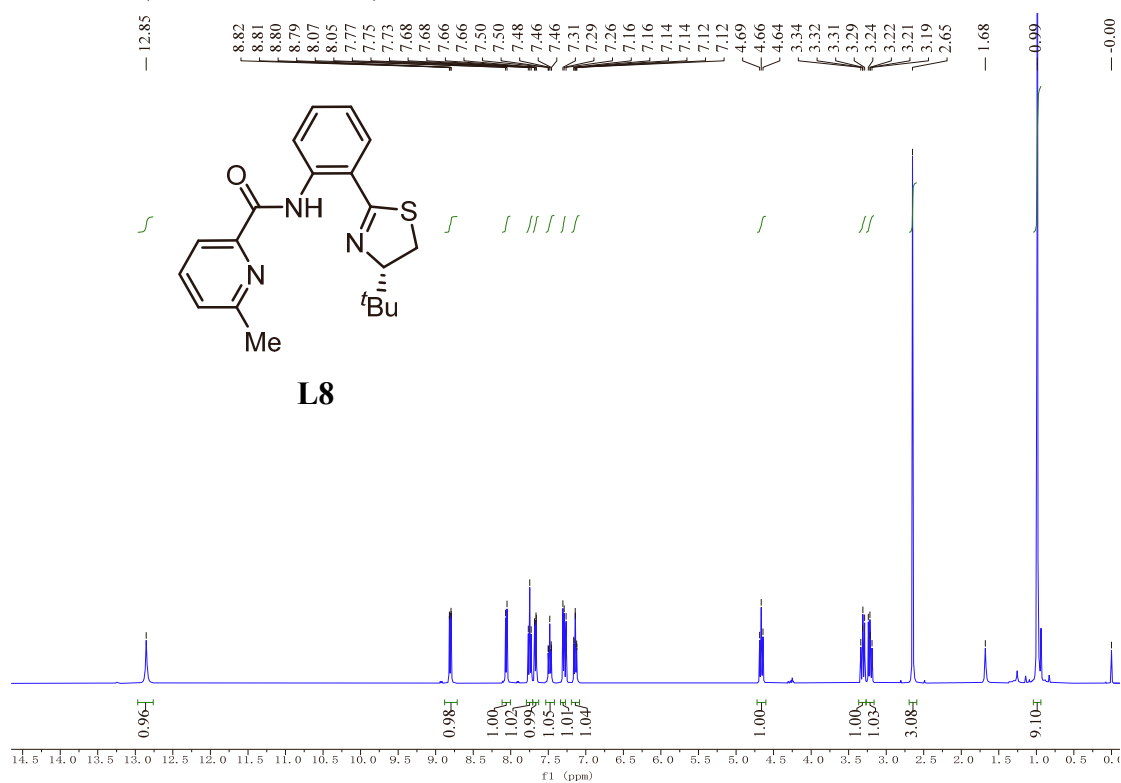


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

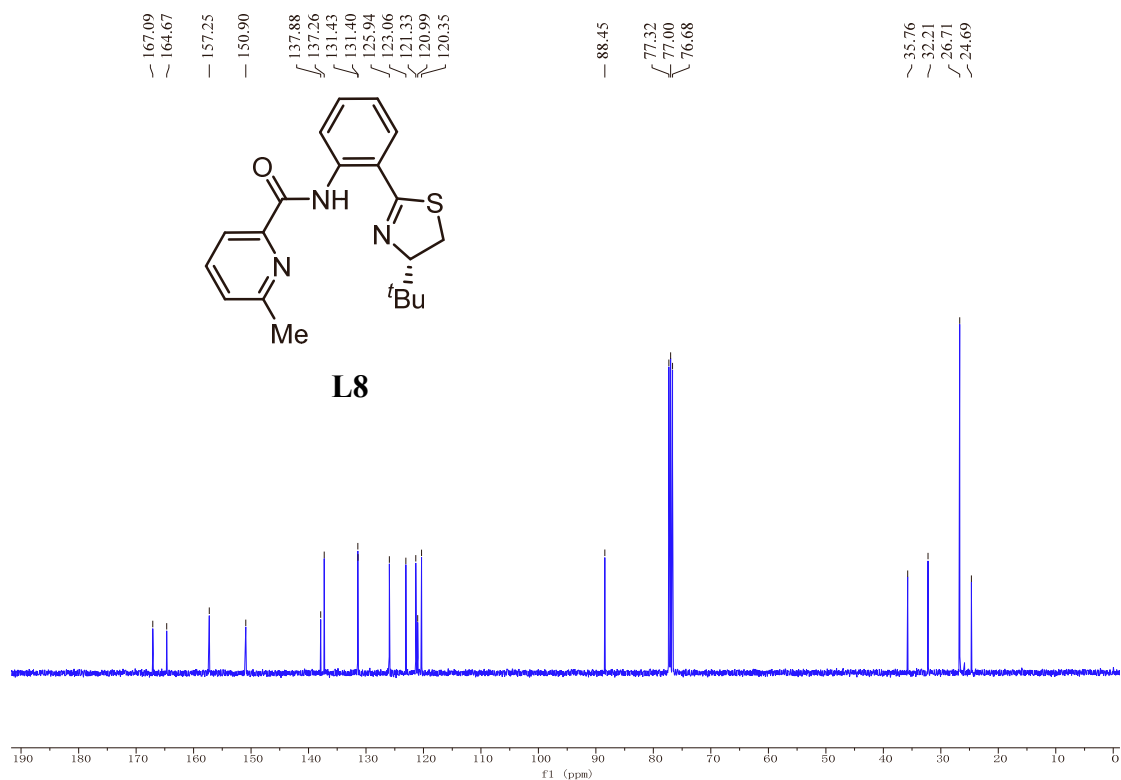




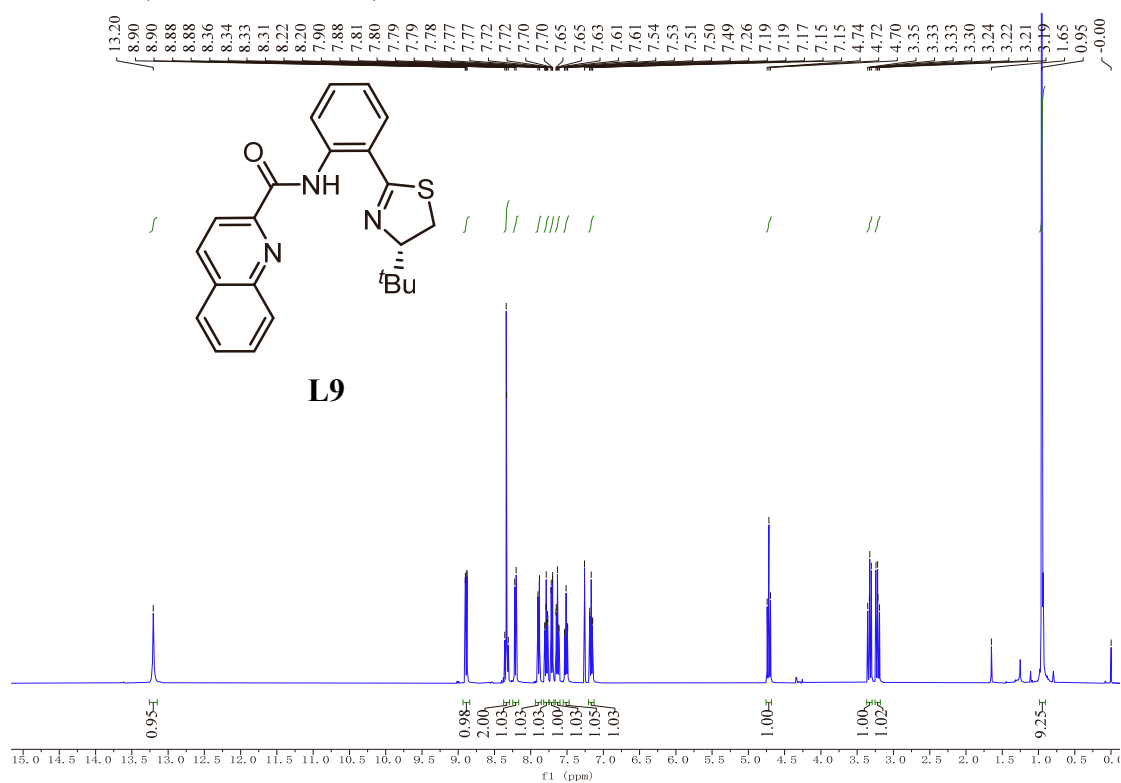
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



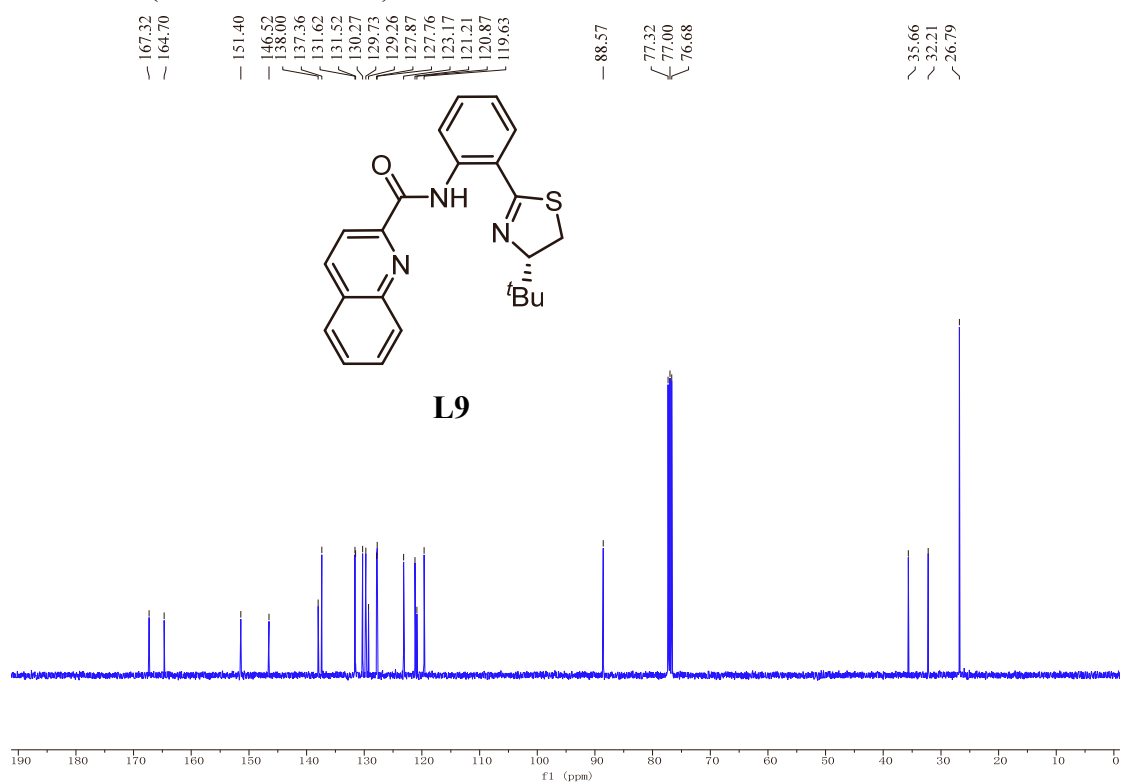
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



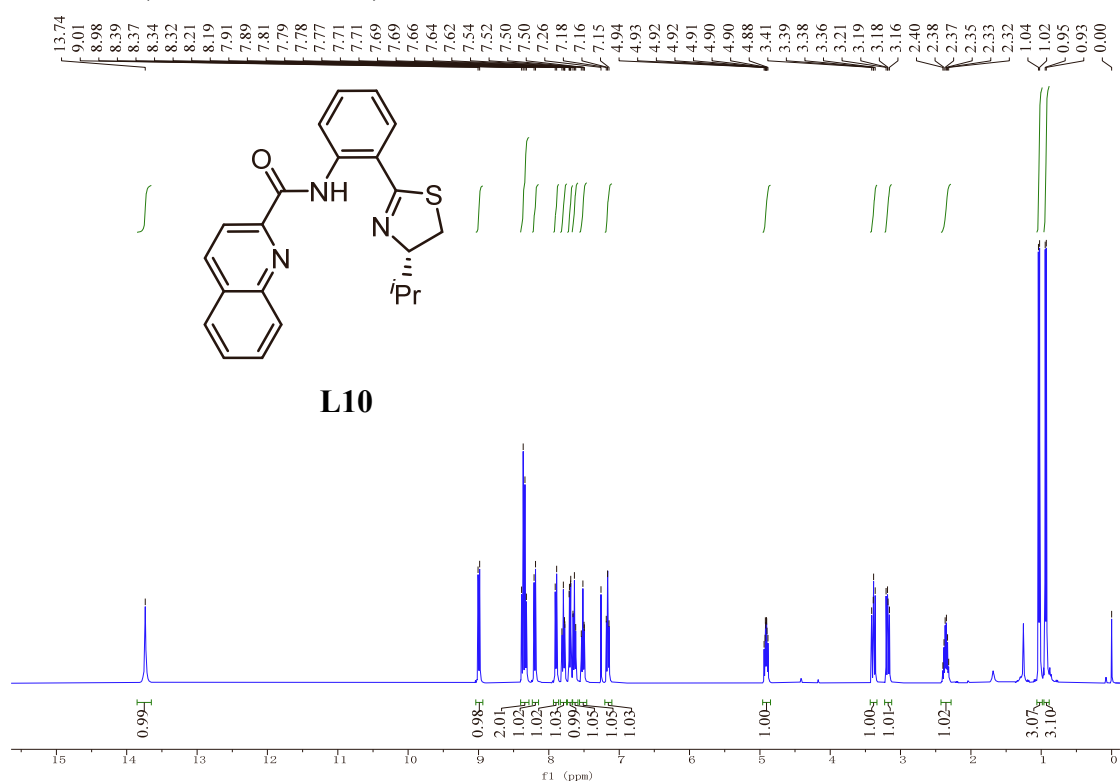
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



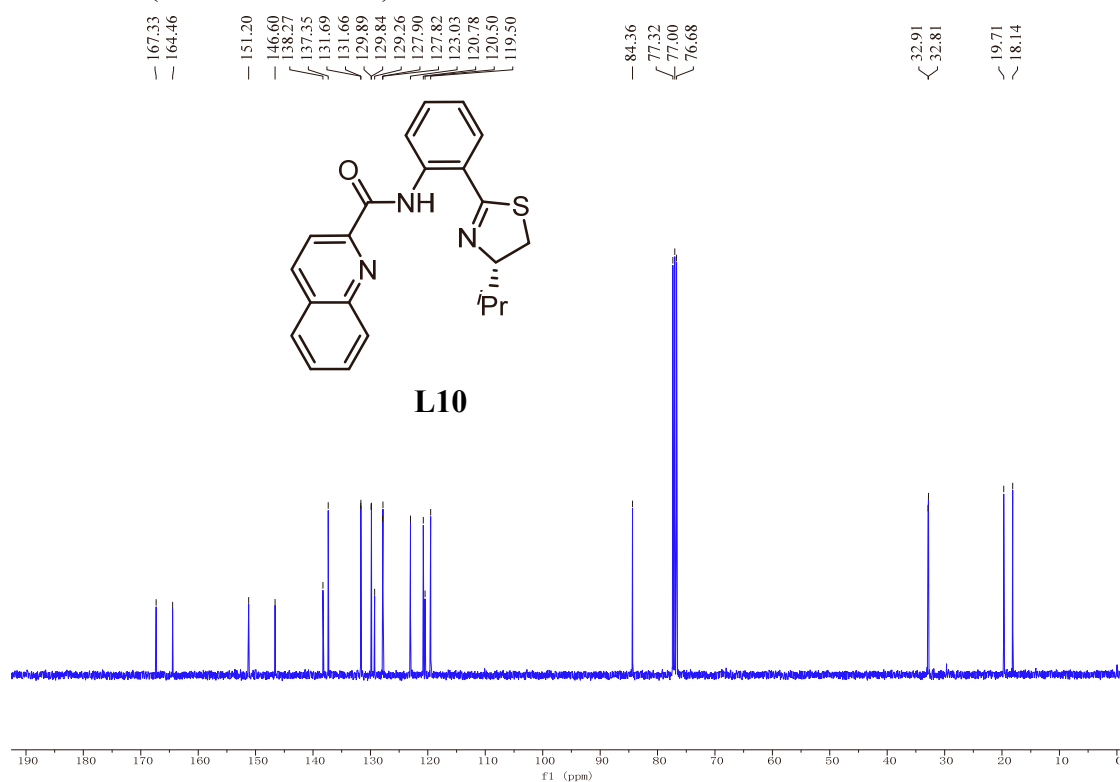
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



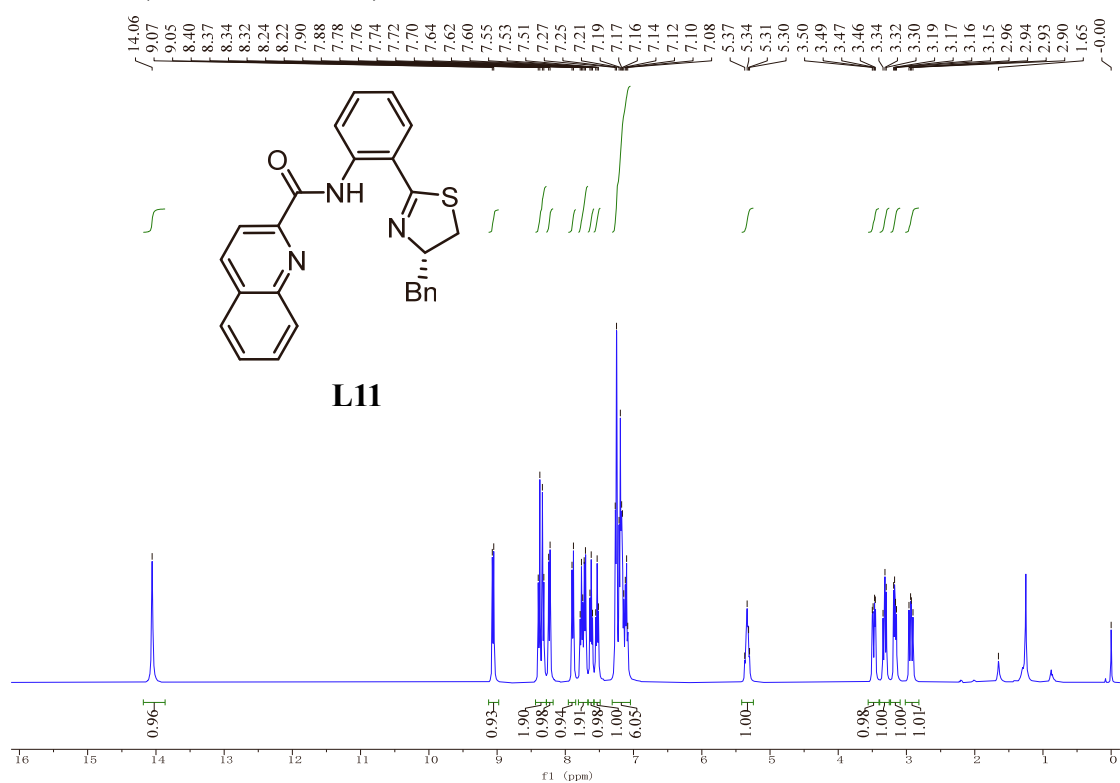
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



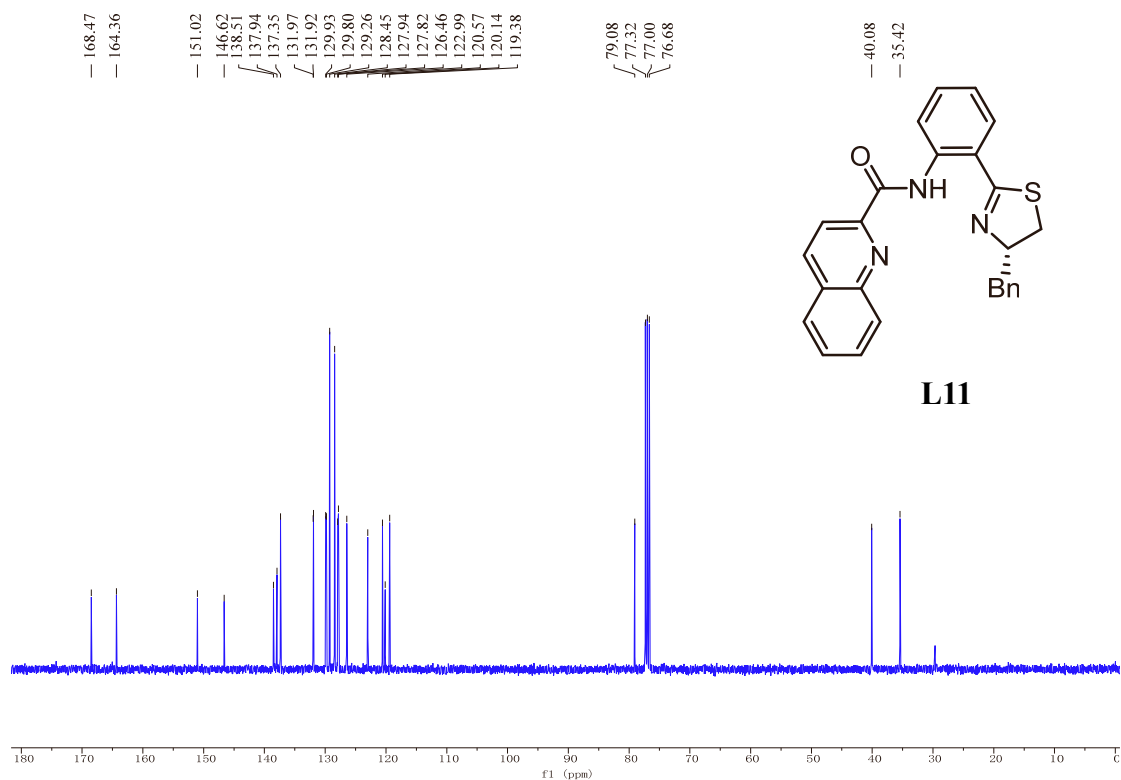
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



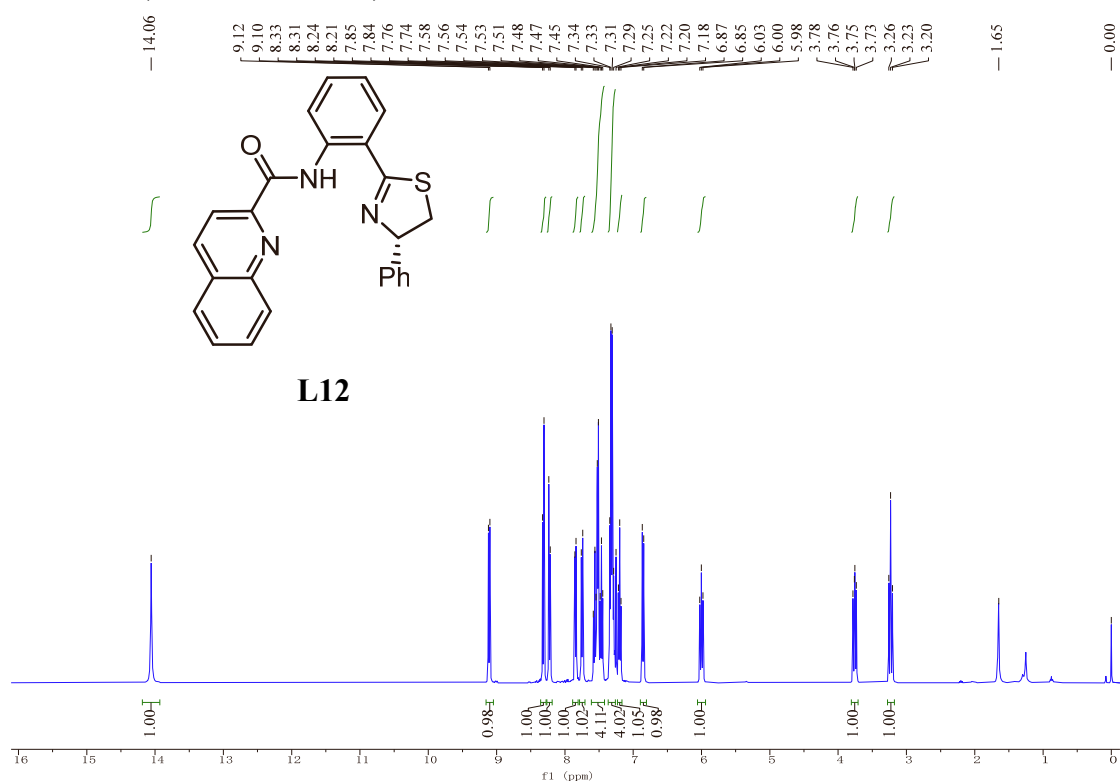
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



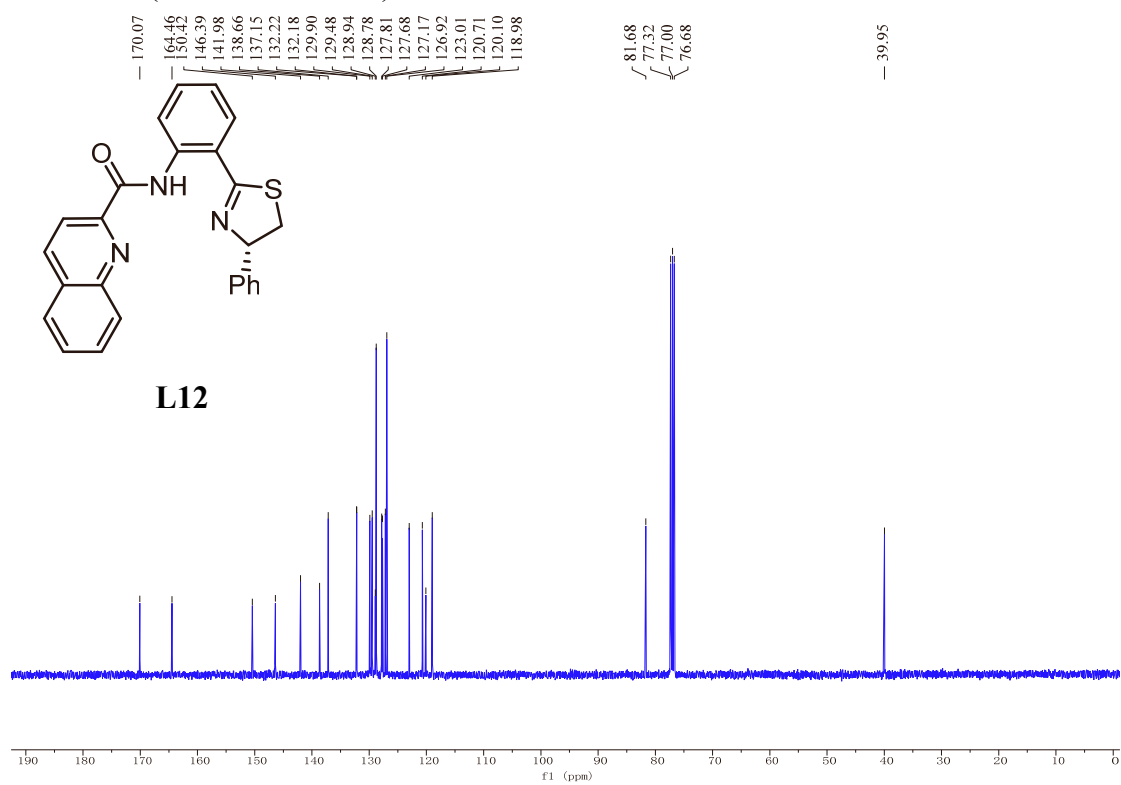
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



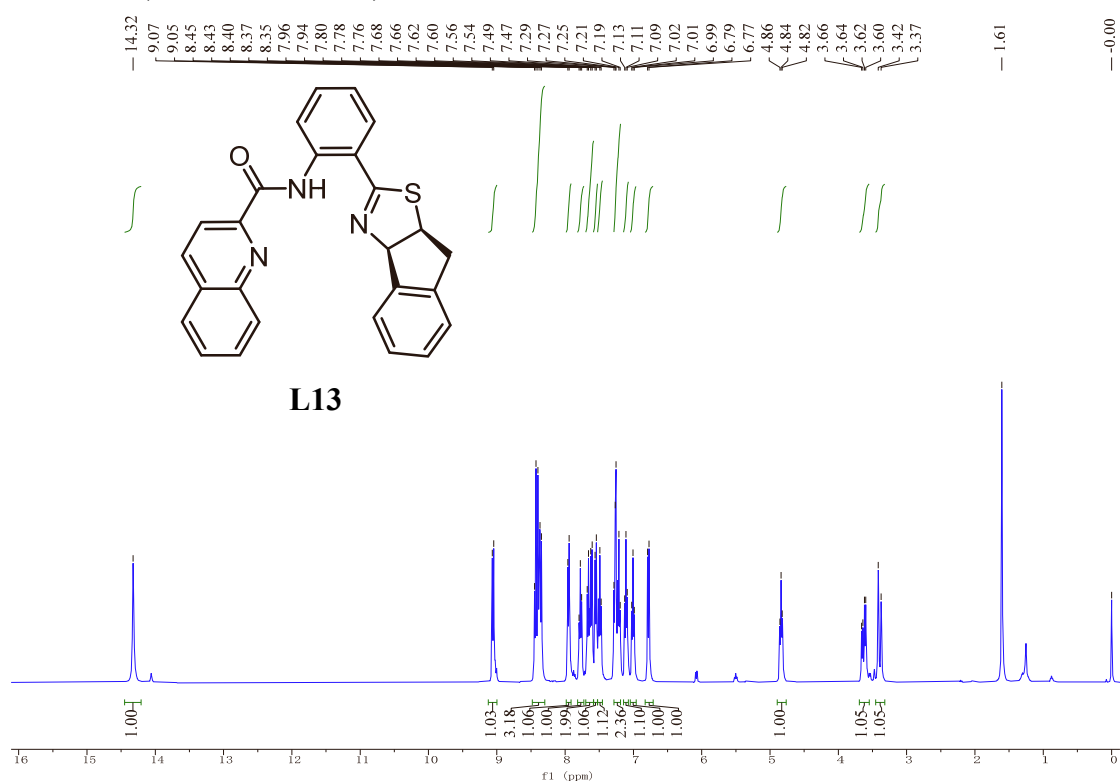
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



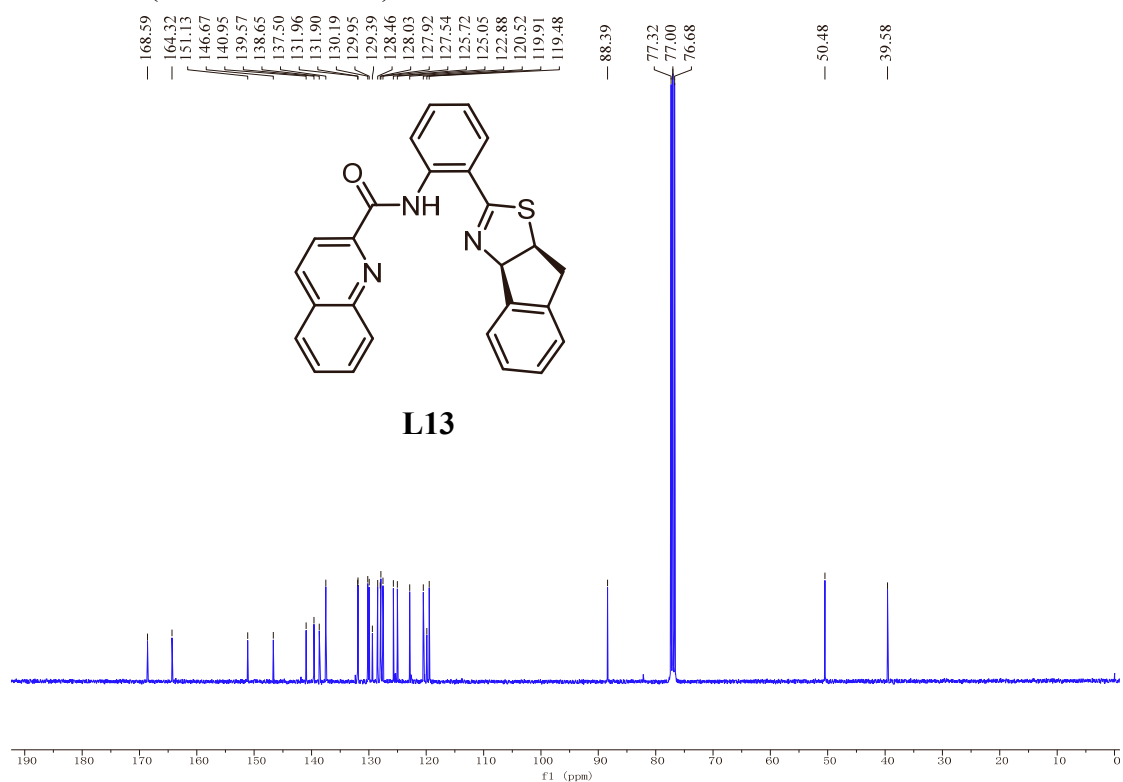
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



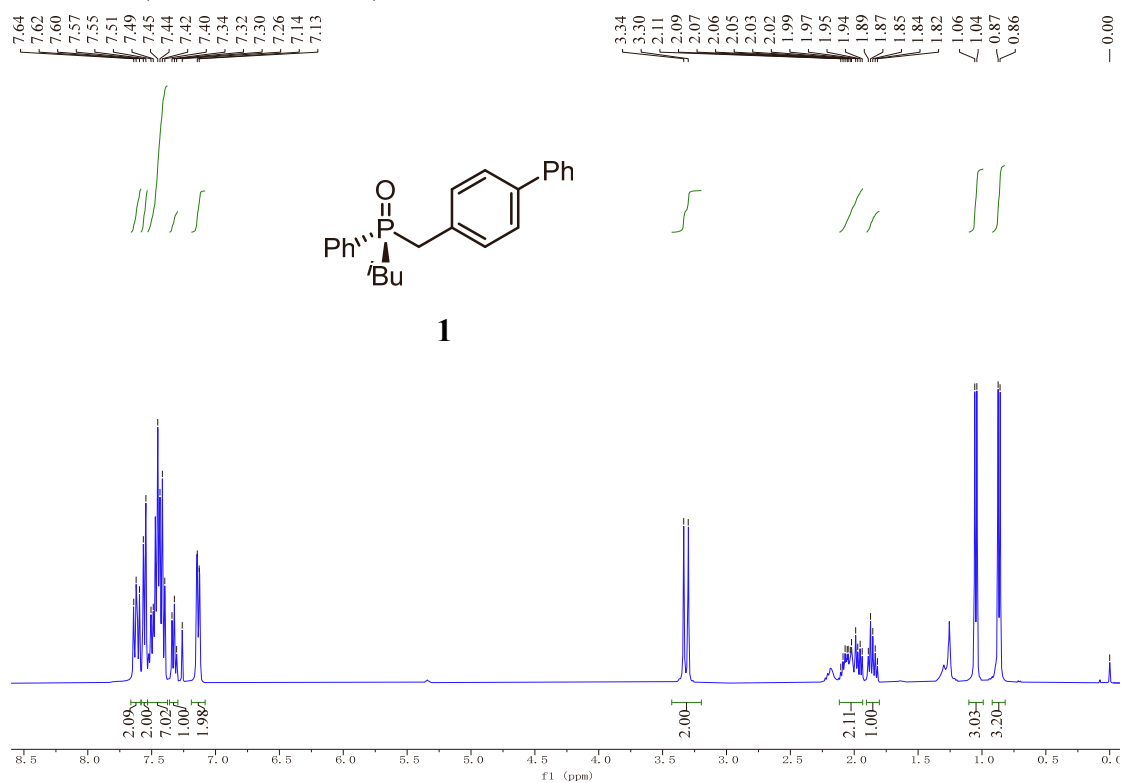
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



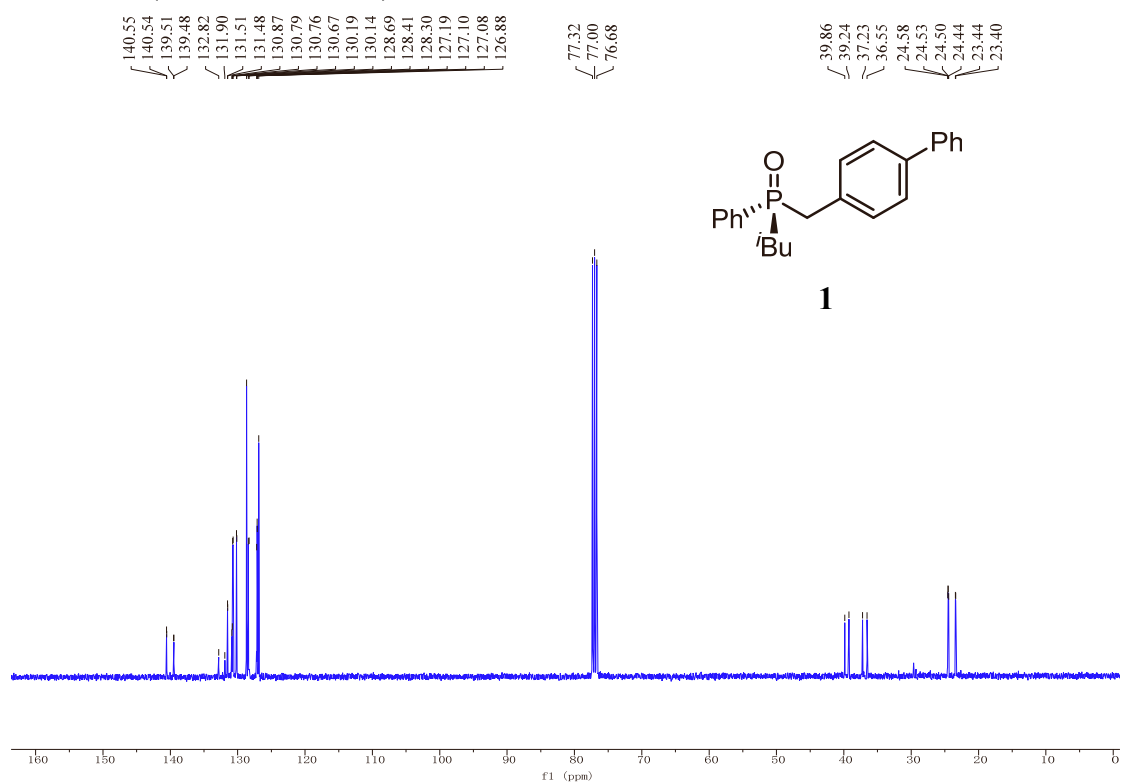
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



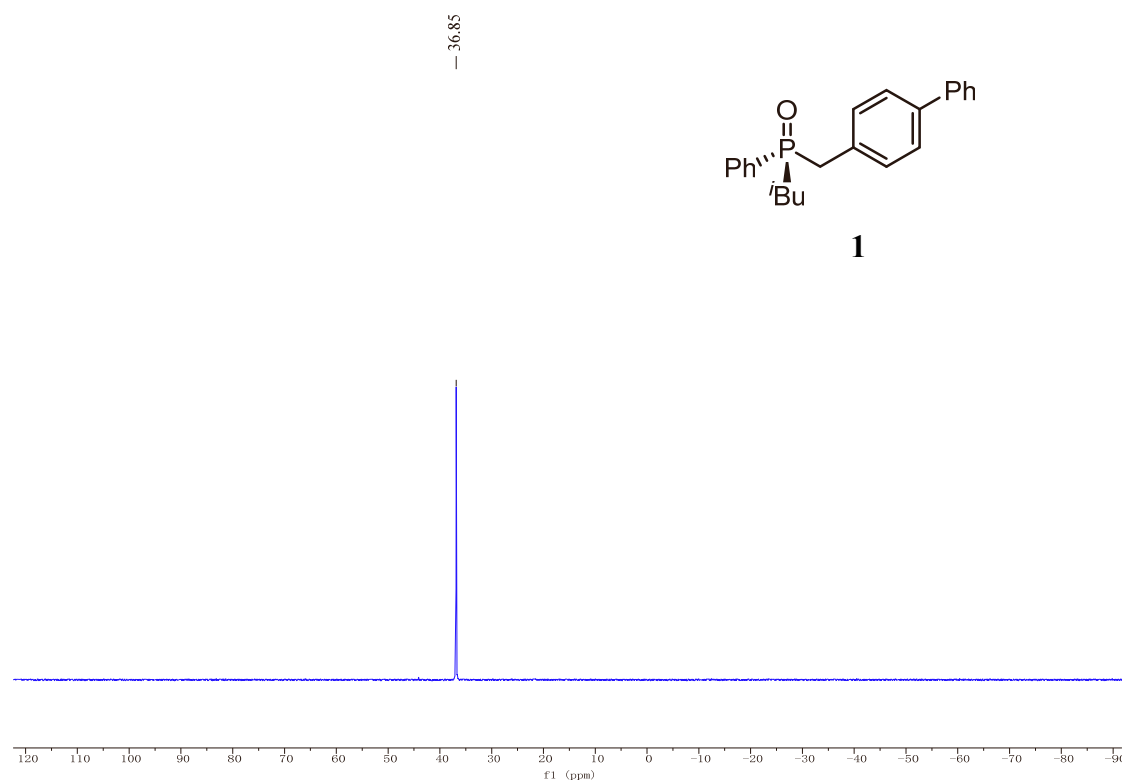
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

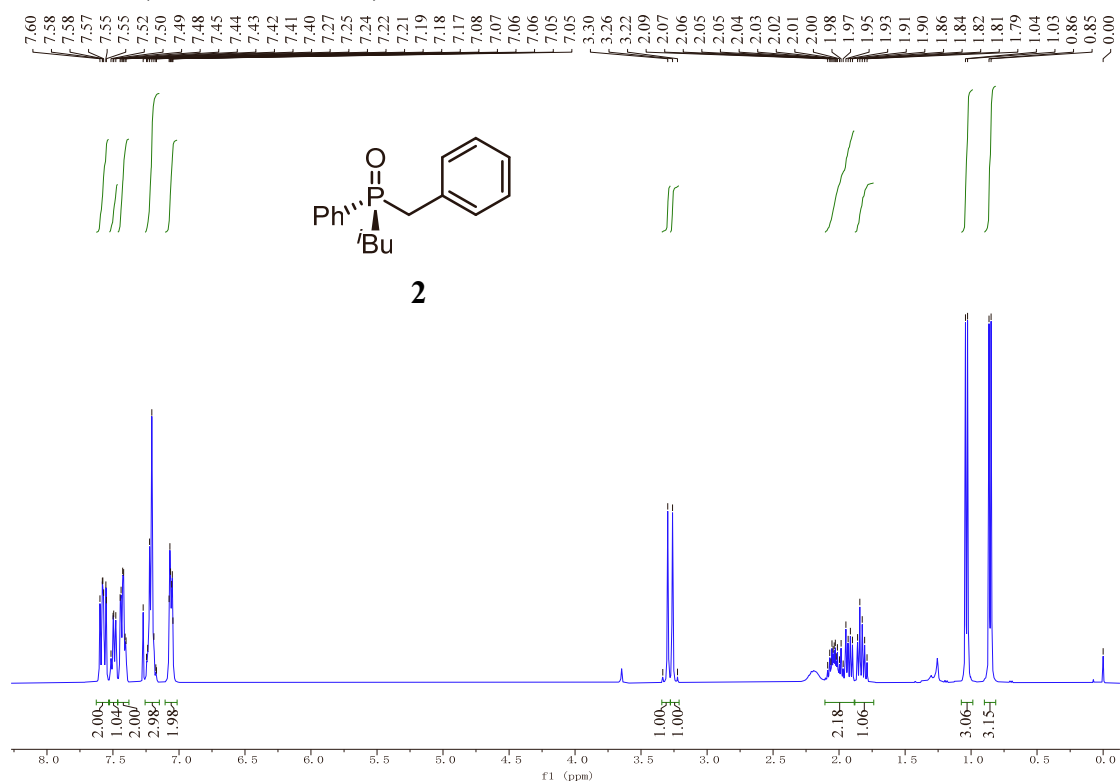


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

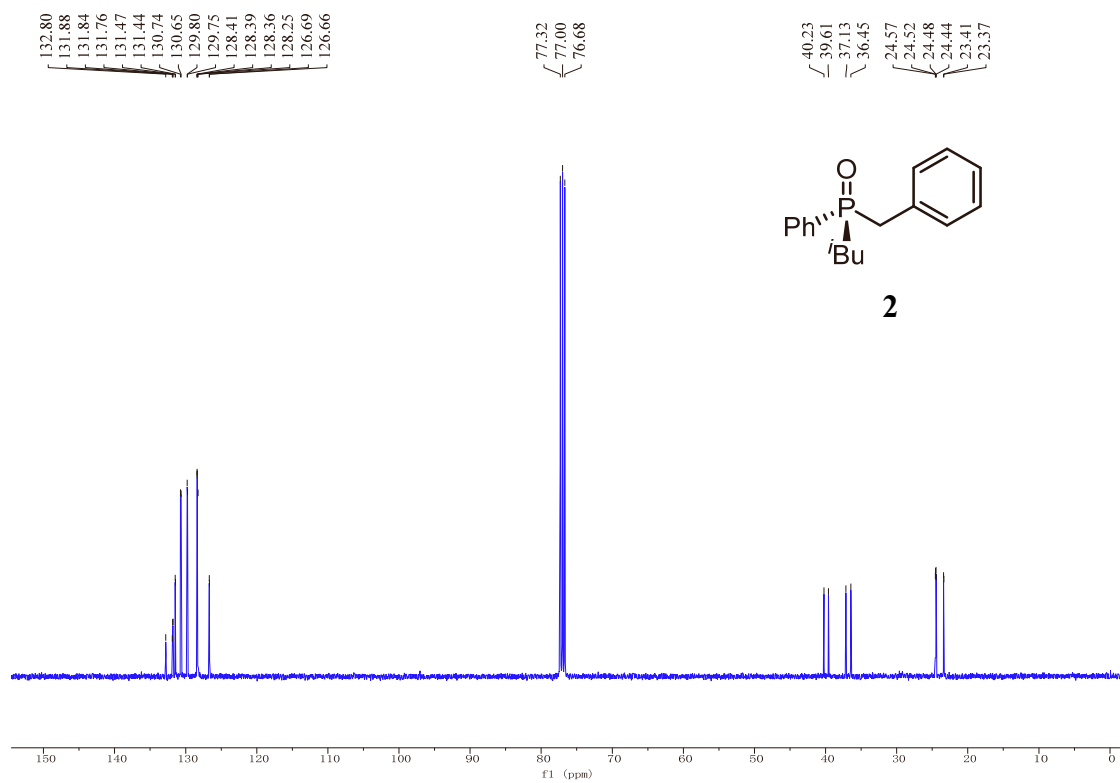




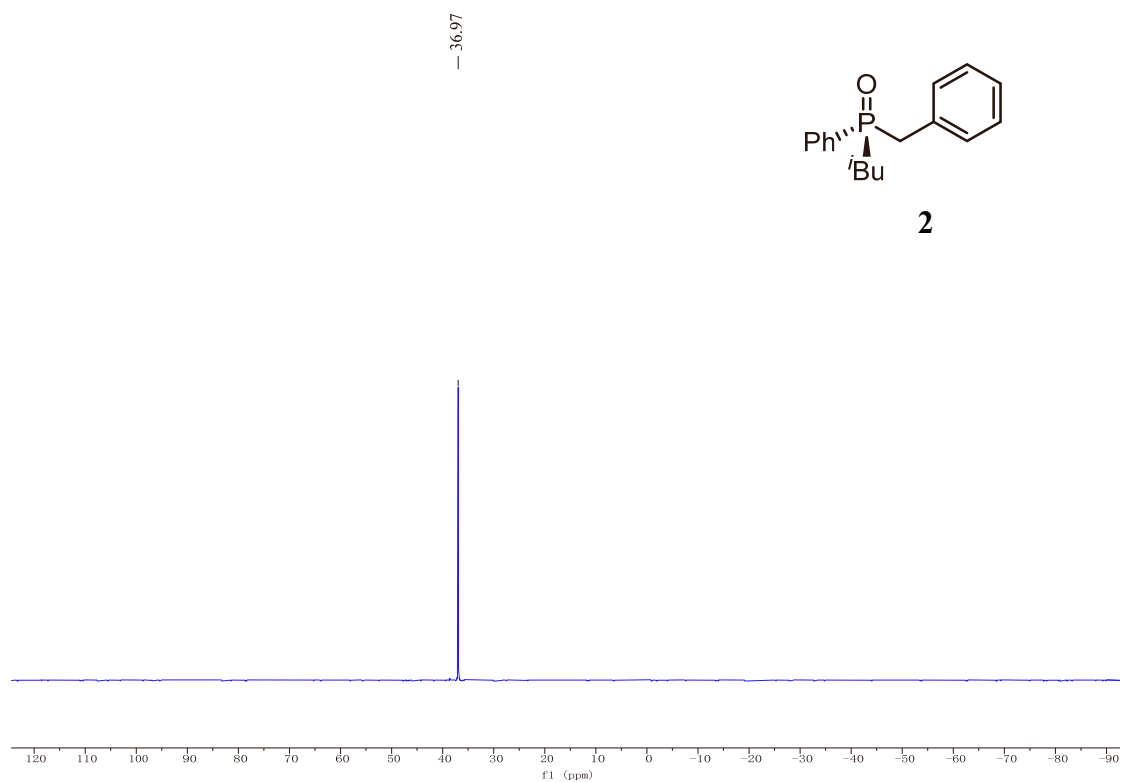
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



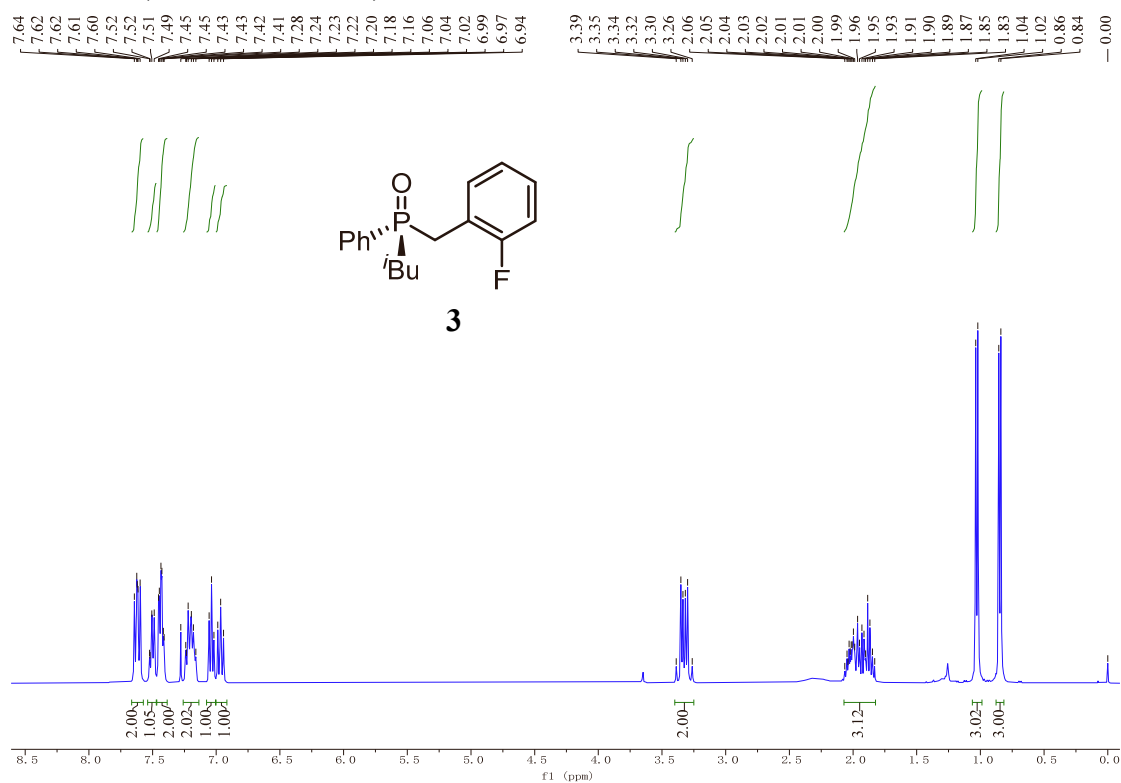
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



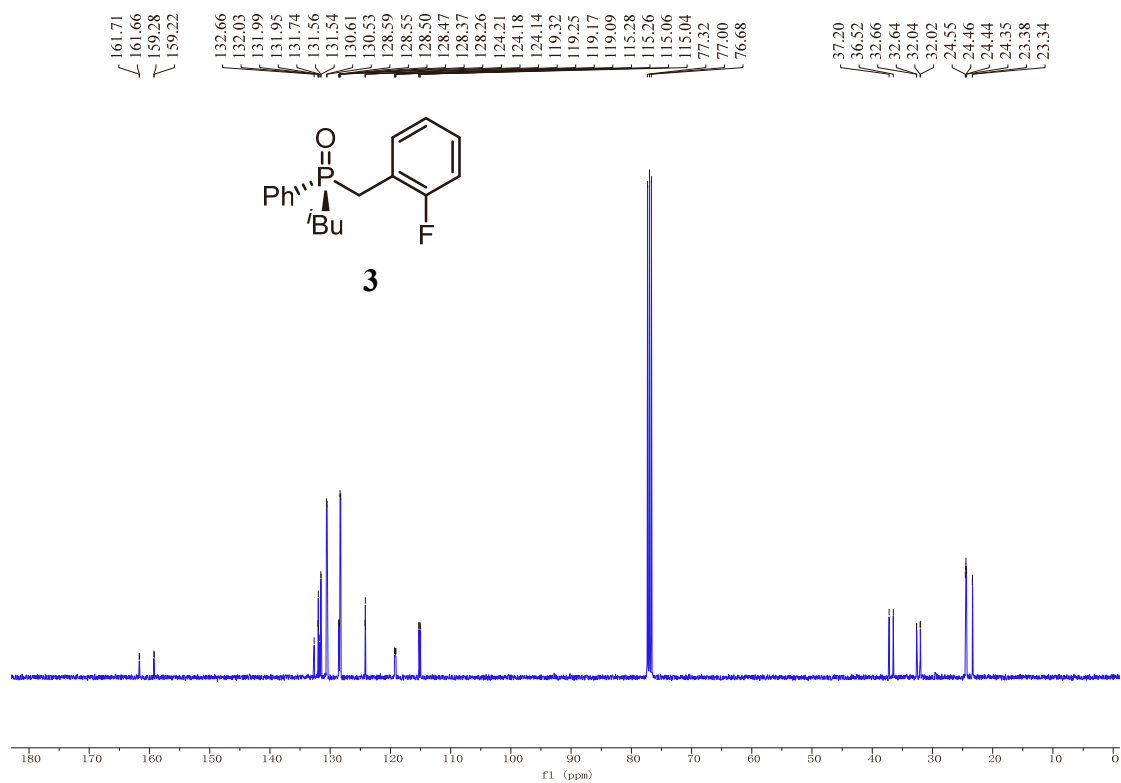
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

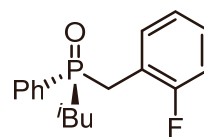


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

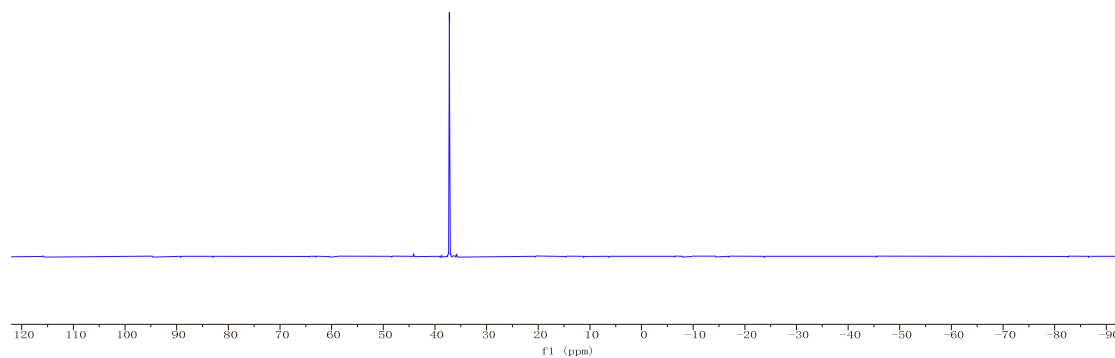


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

37.20  
37.18

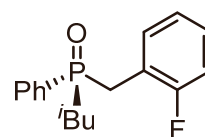


**3**

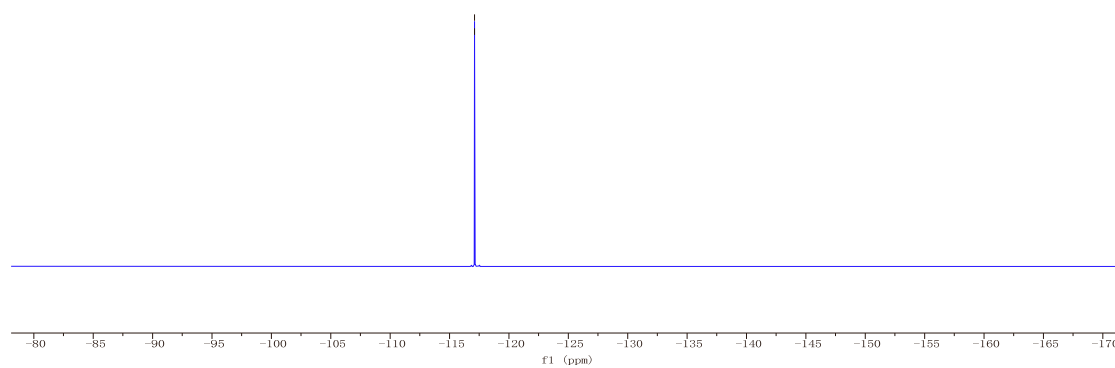


**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )

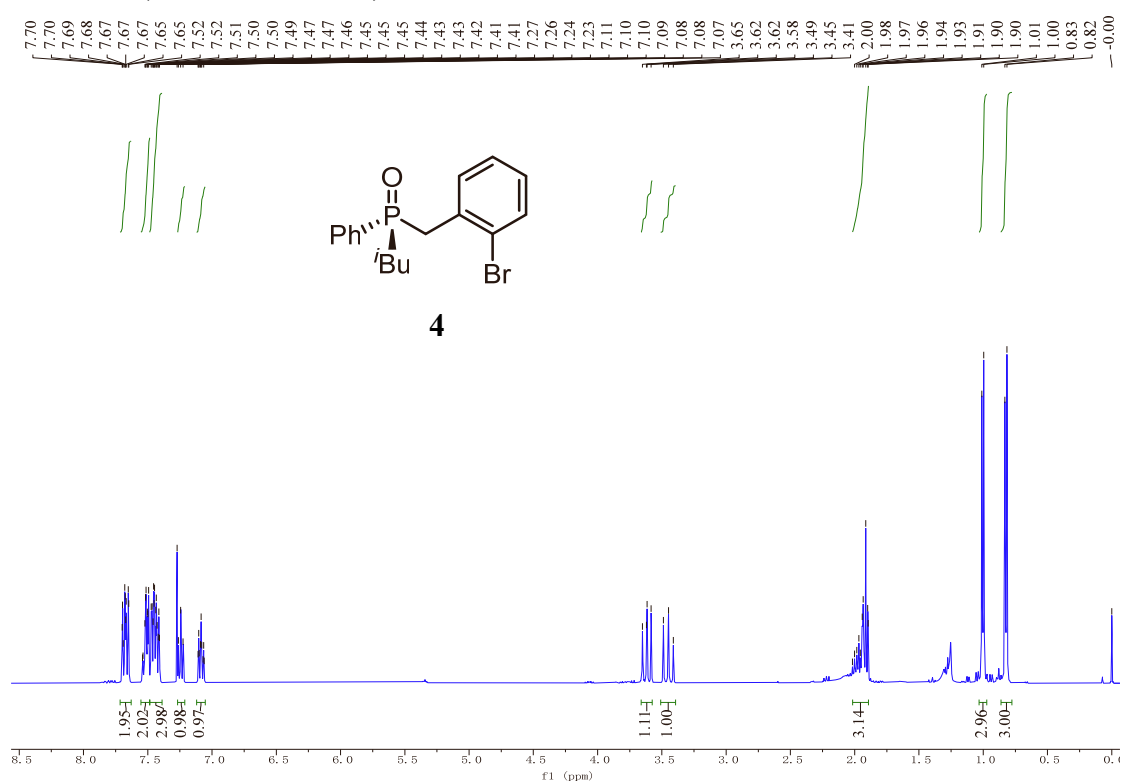
-117.10  
-117.11



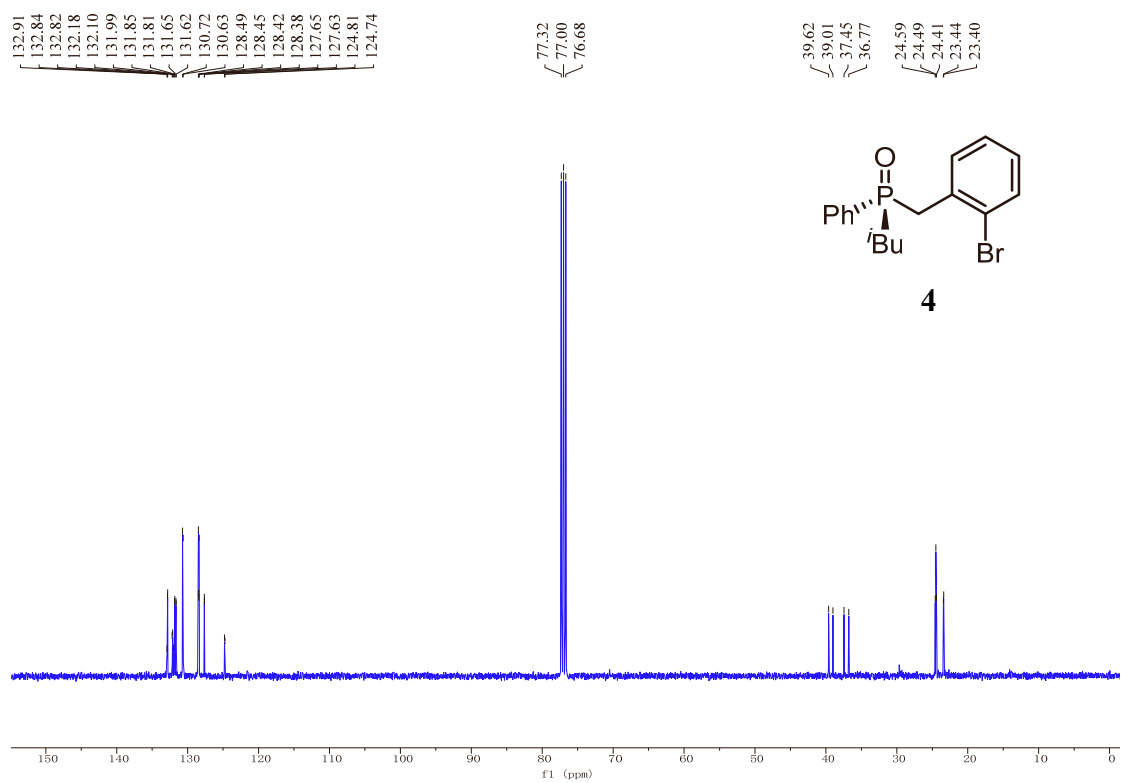
**3**



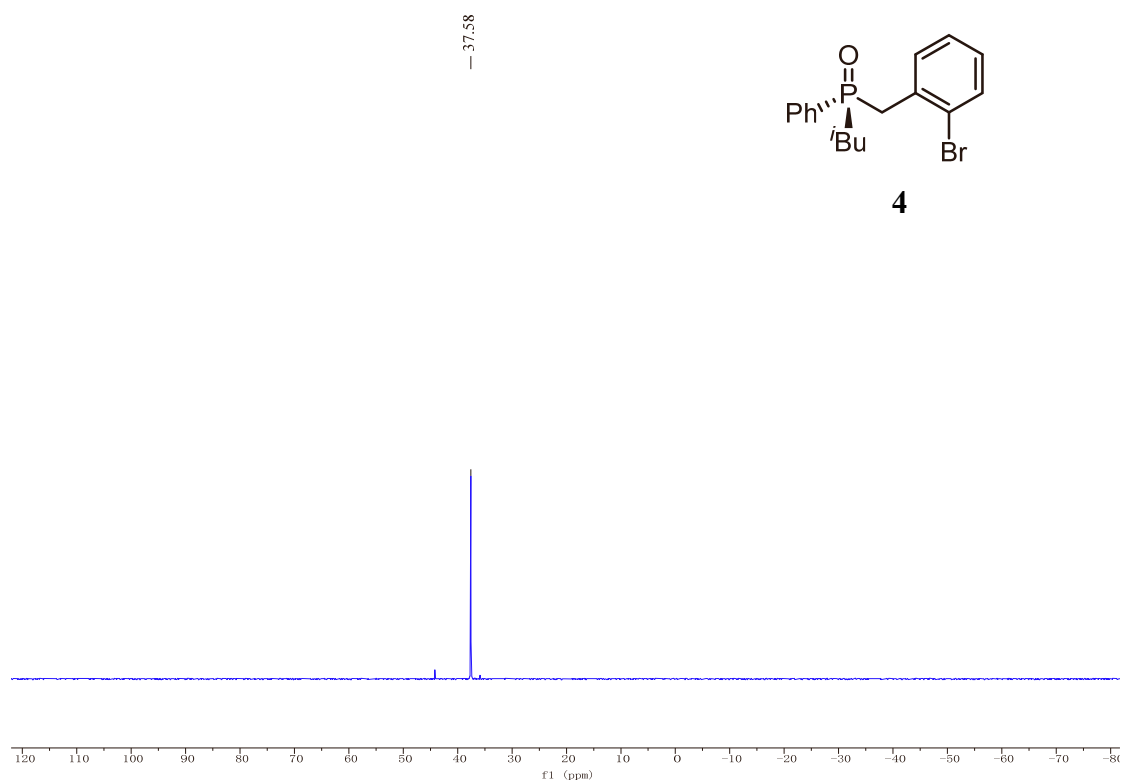
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



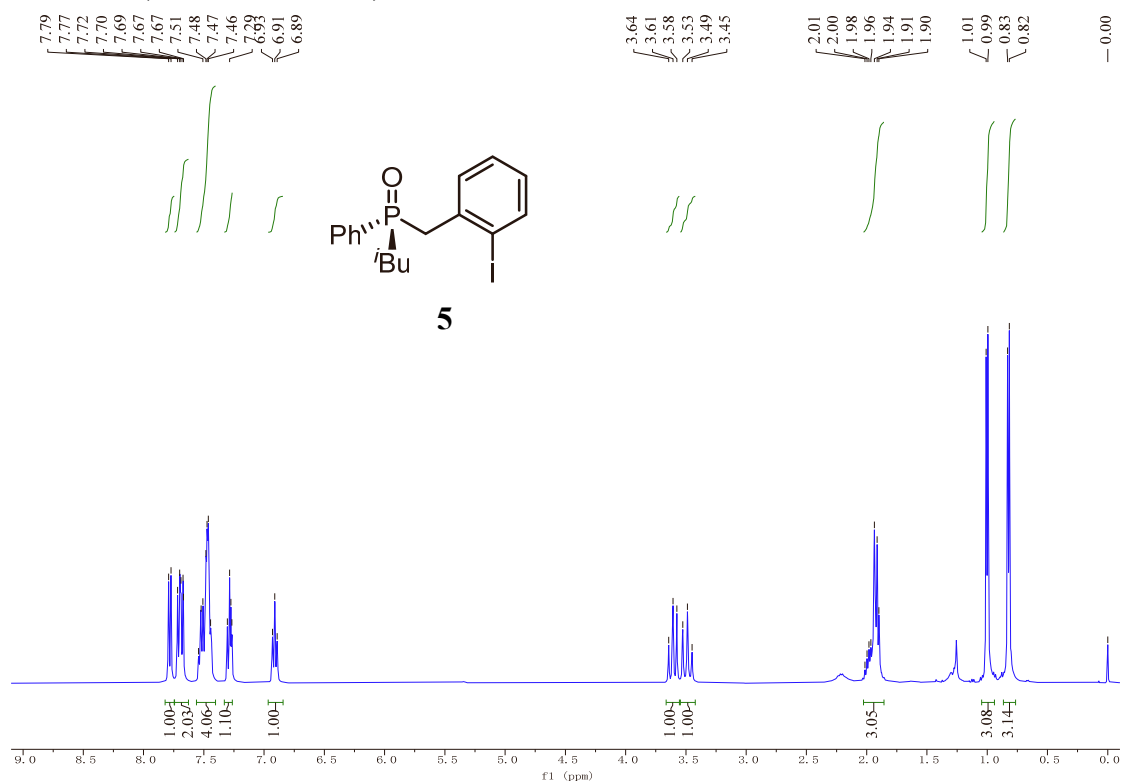
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



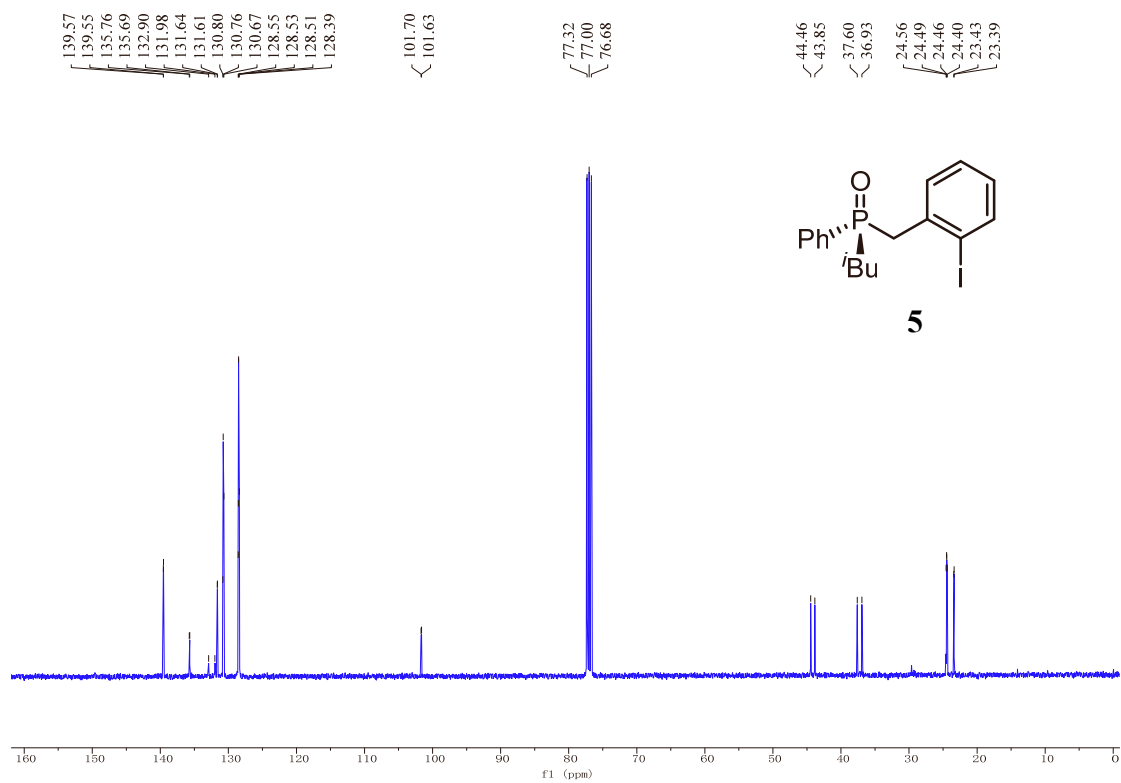
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



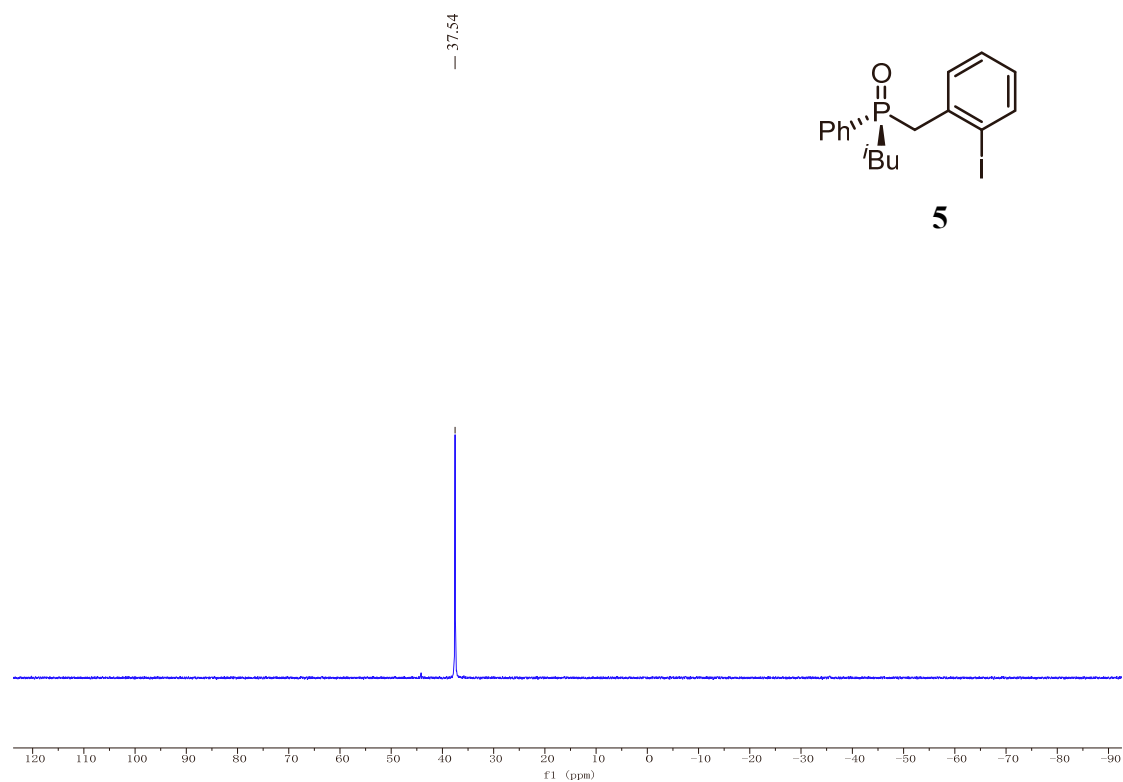
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

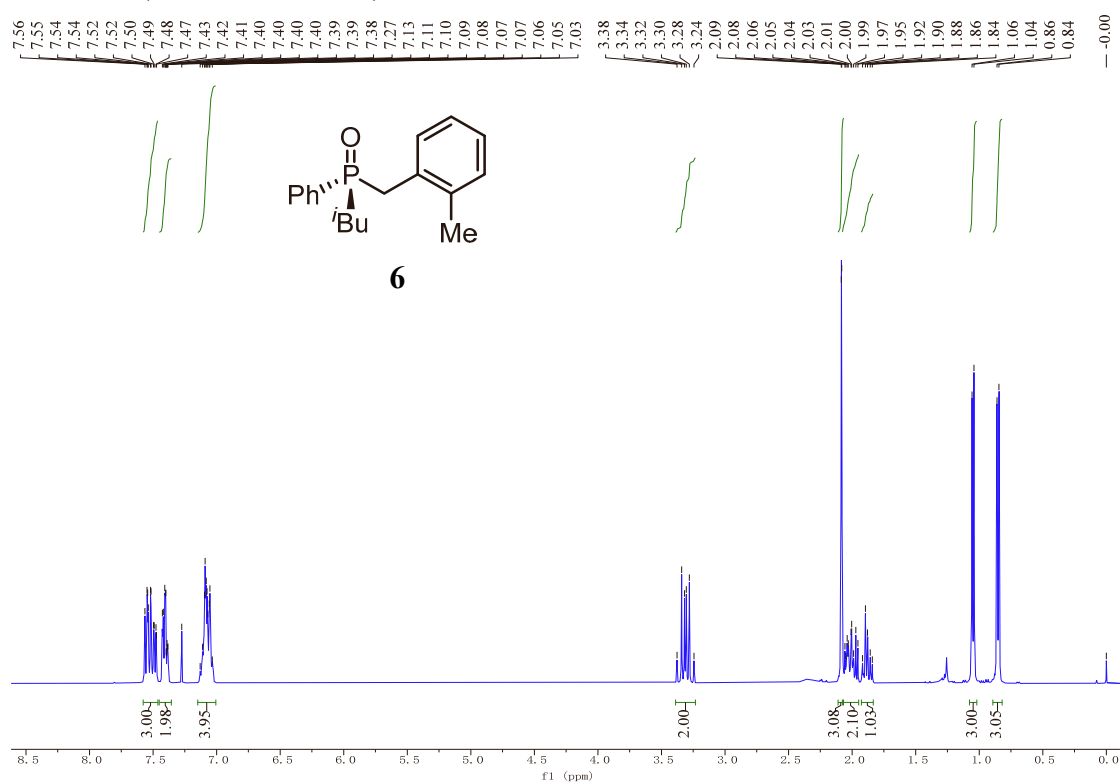


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

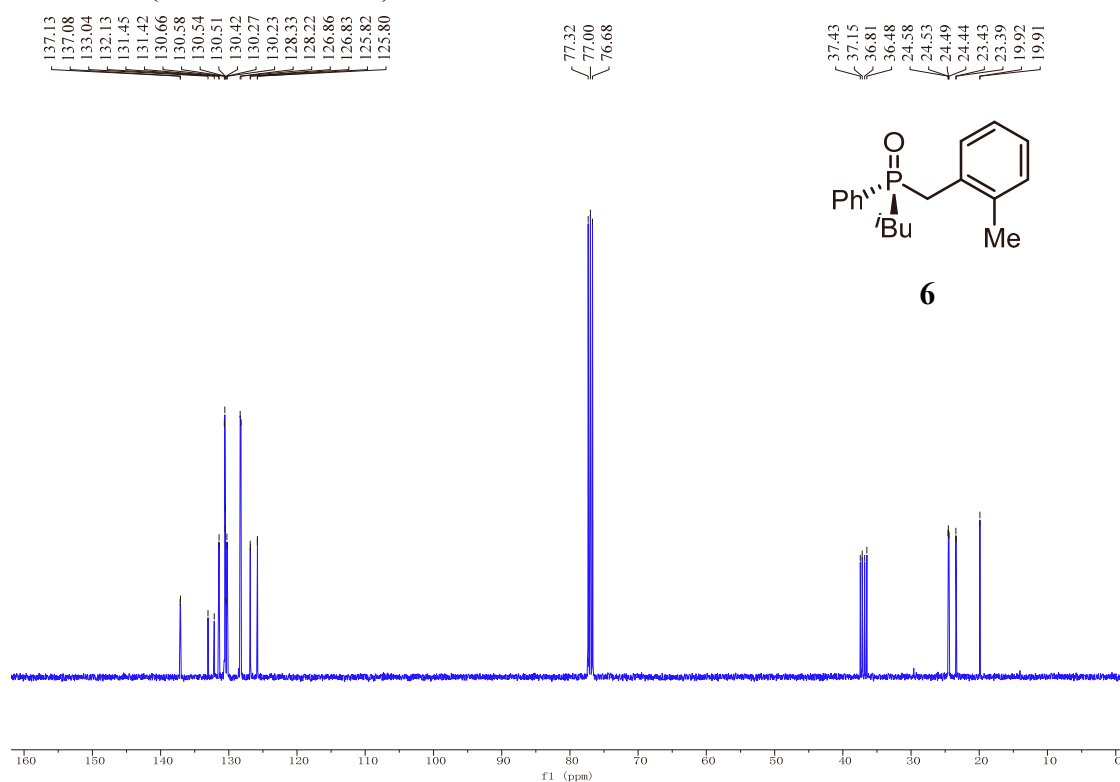




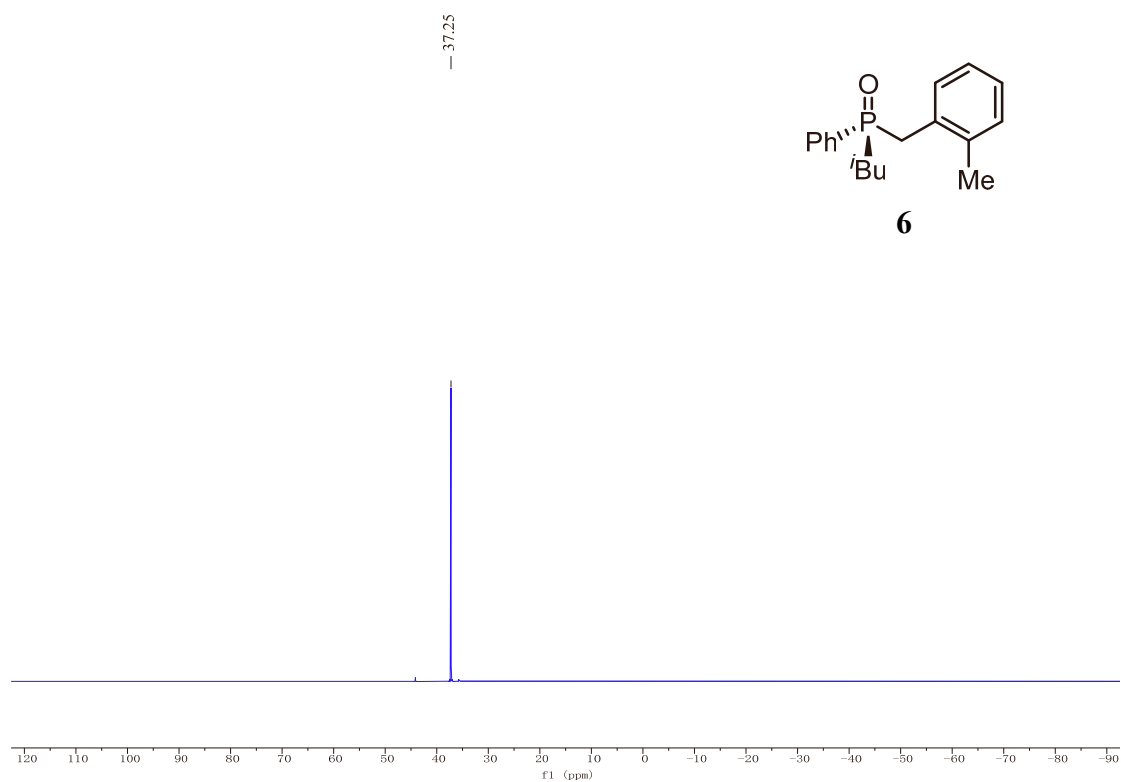
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



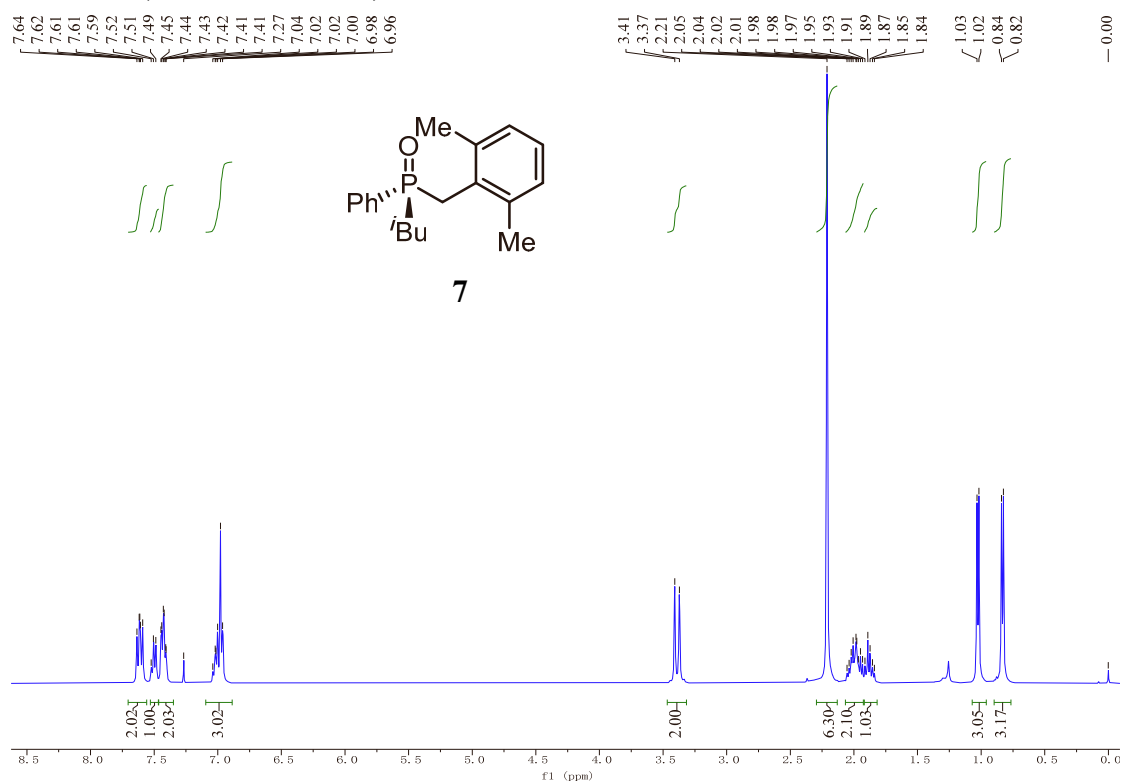
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



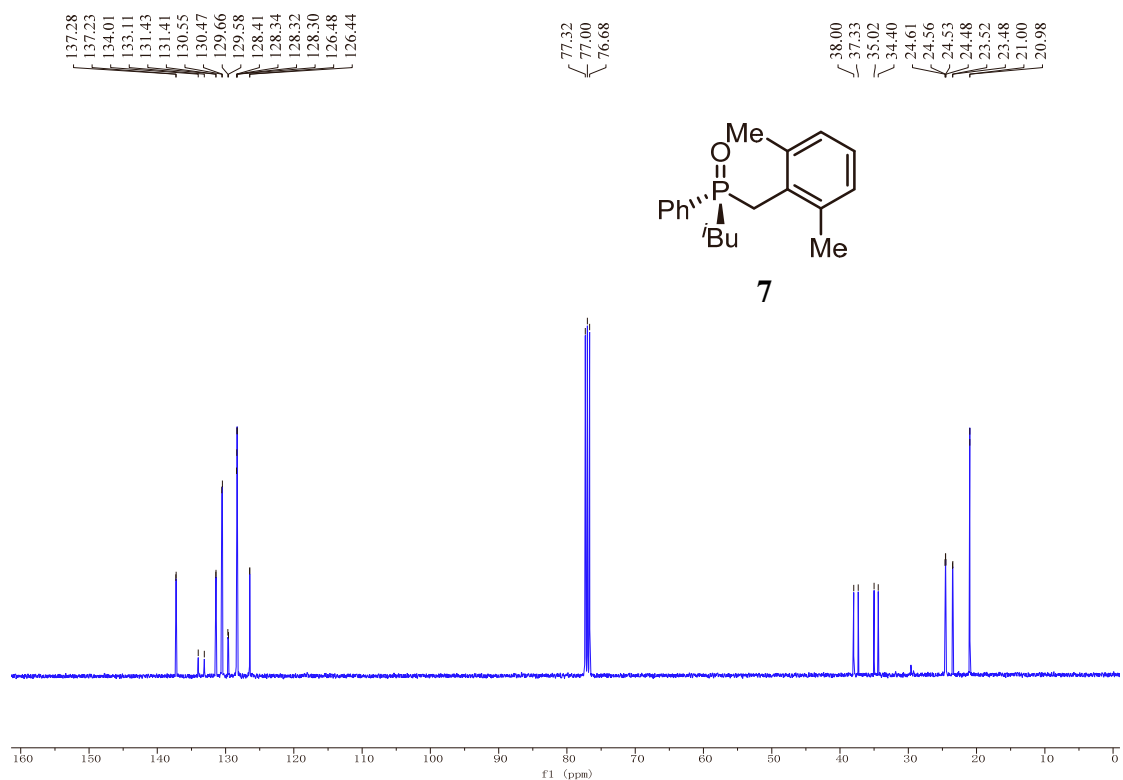
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



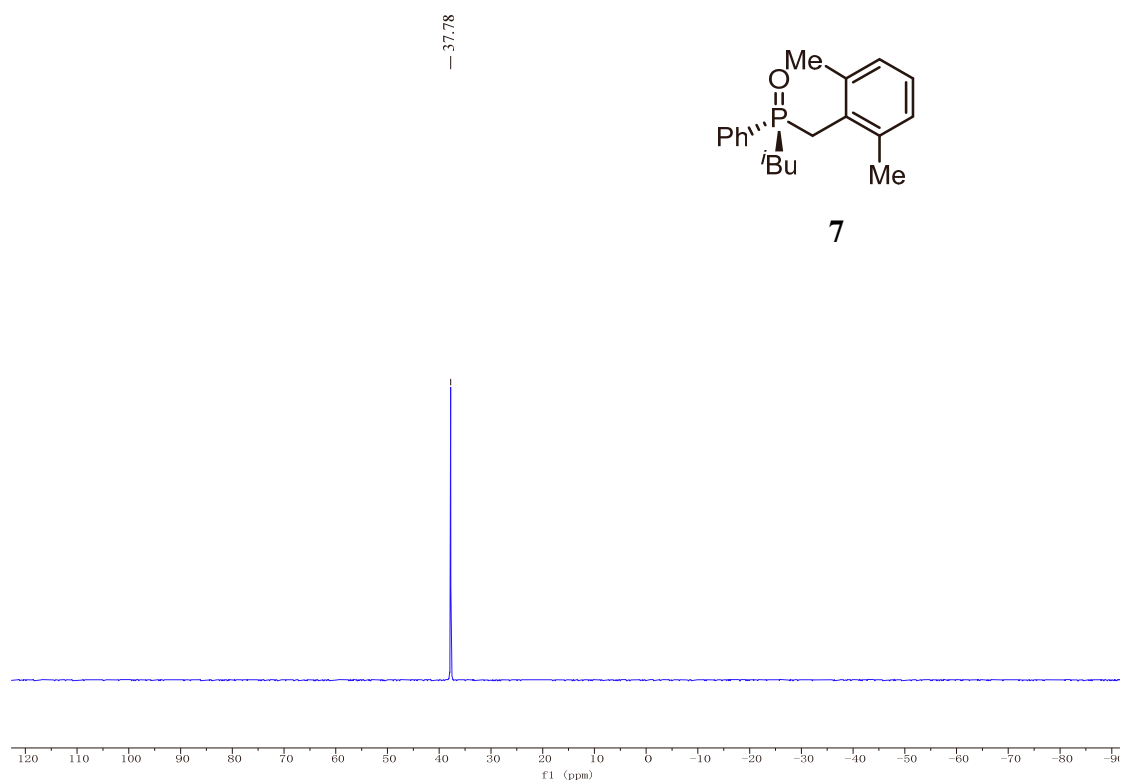
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



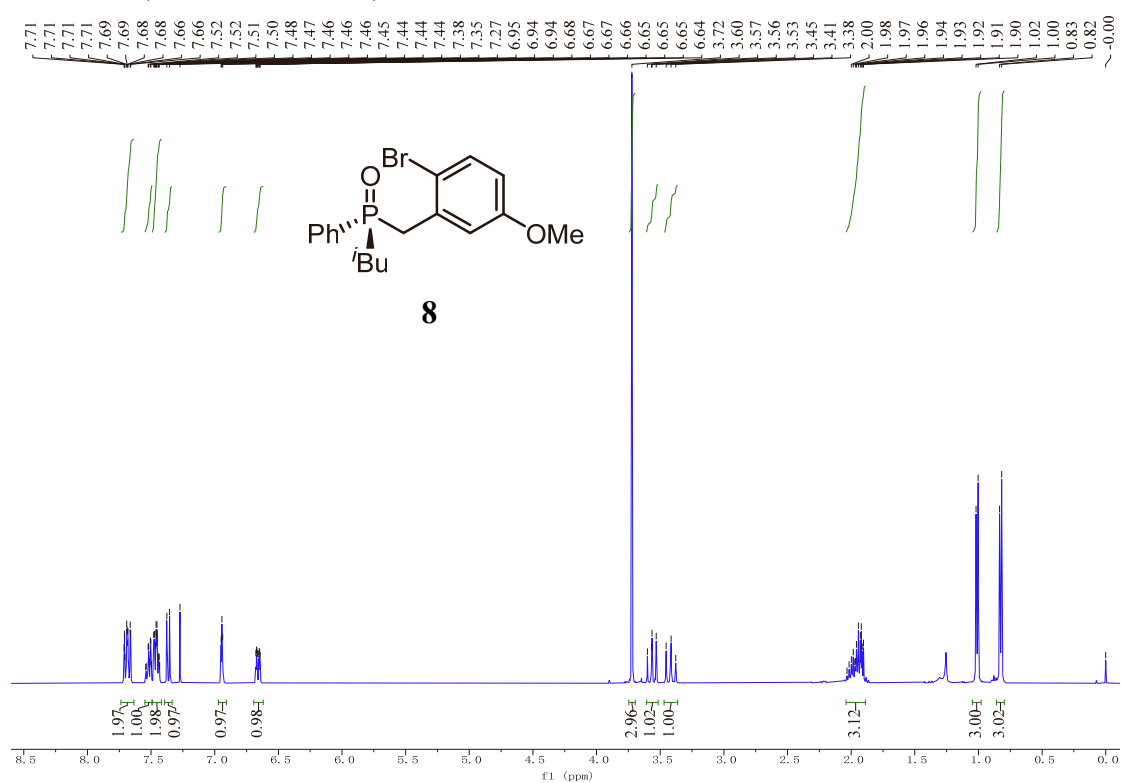
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



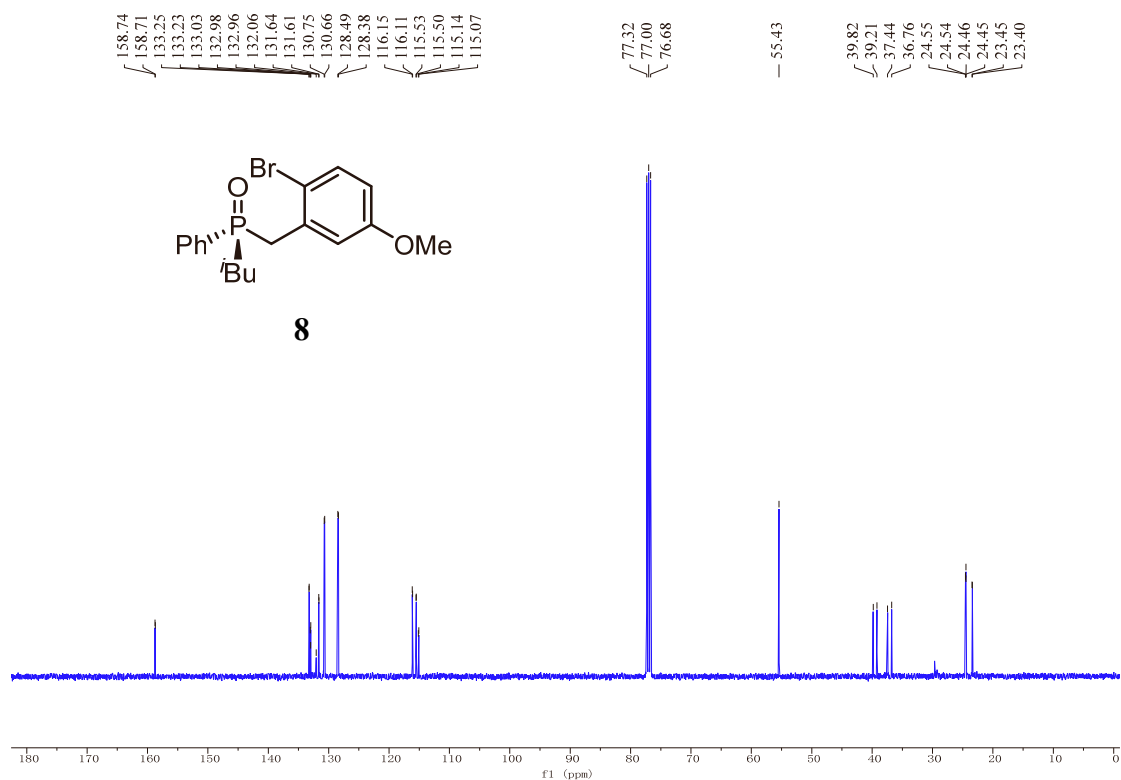
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



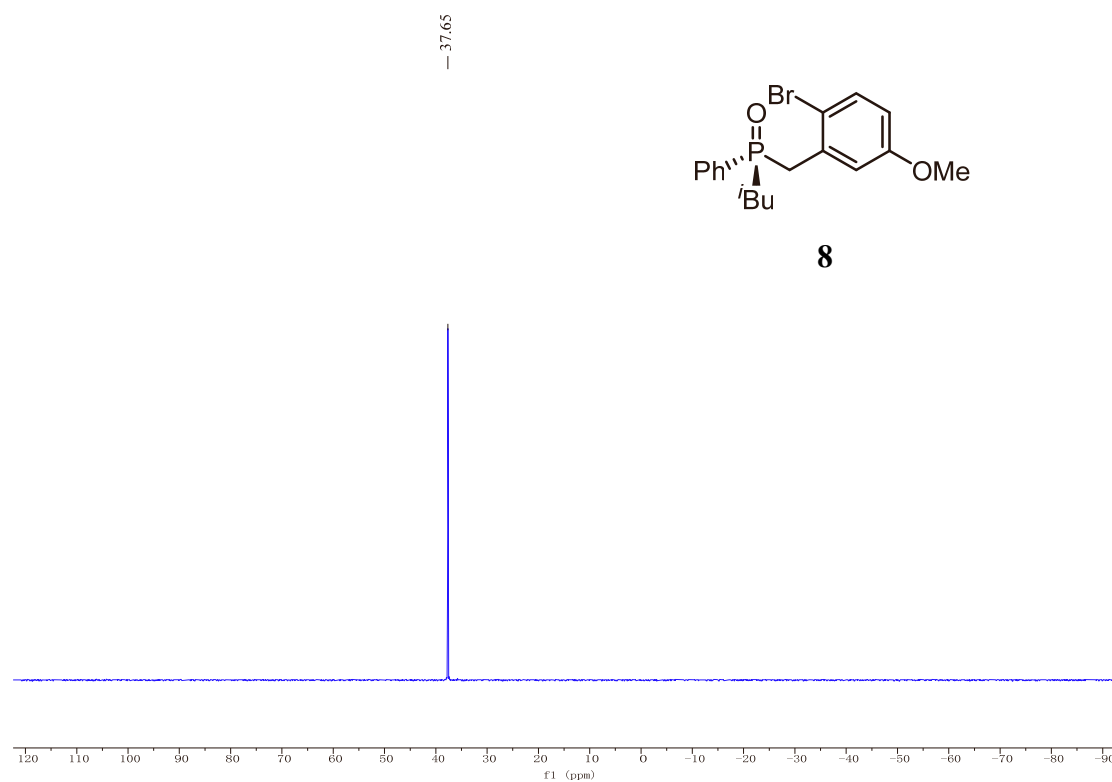
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



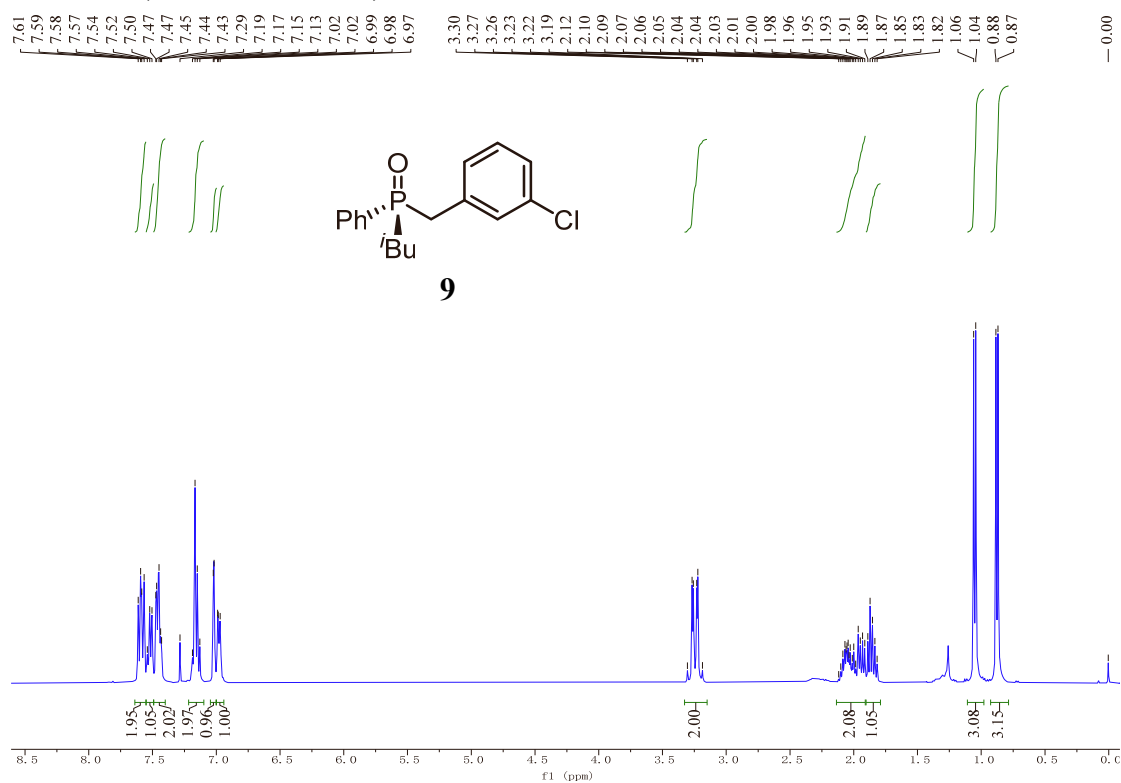
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



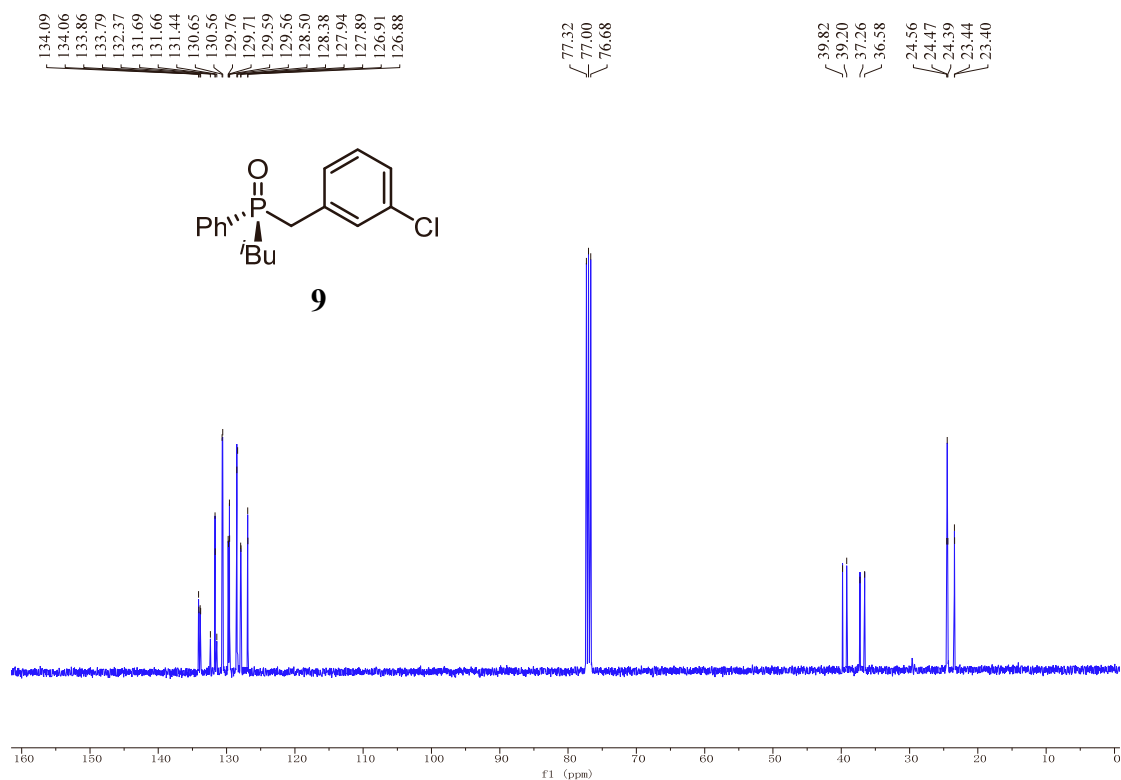
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



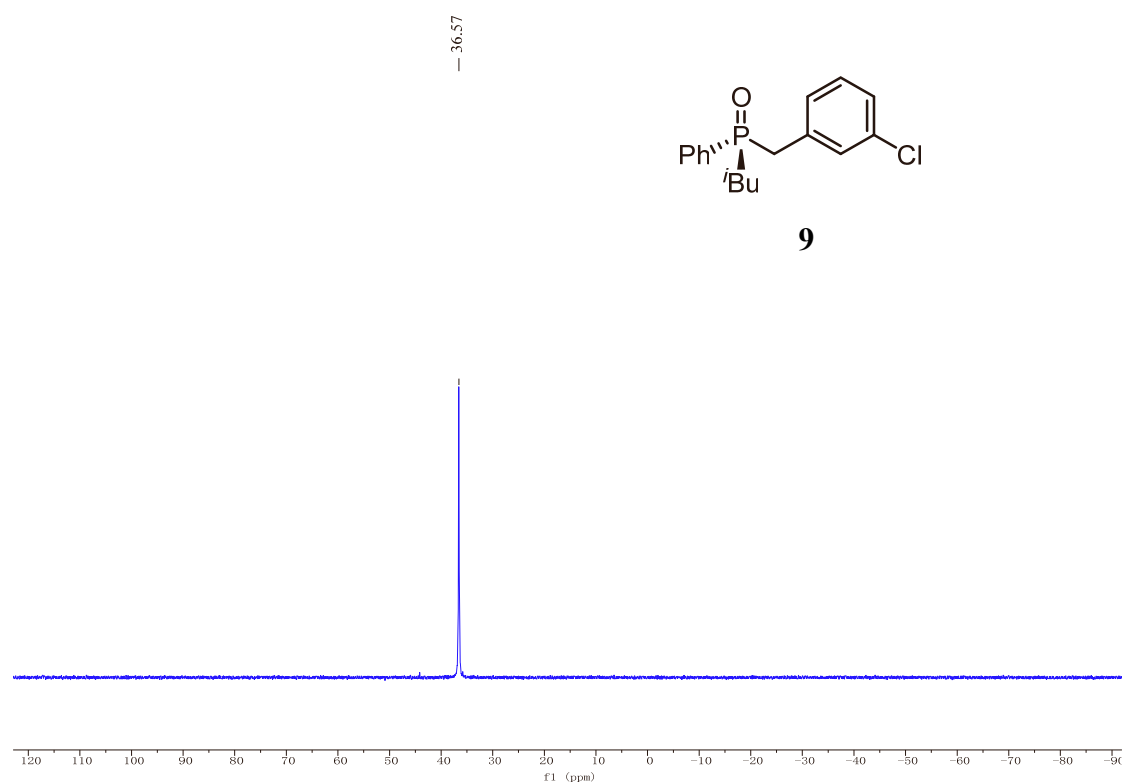
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

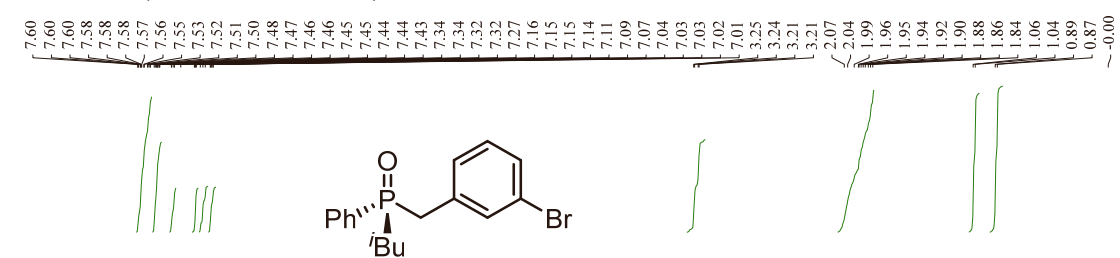


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

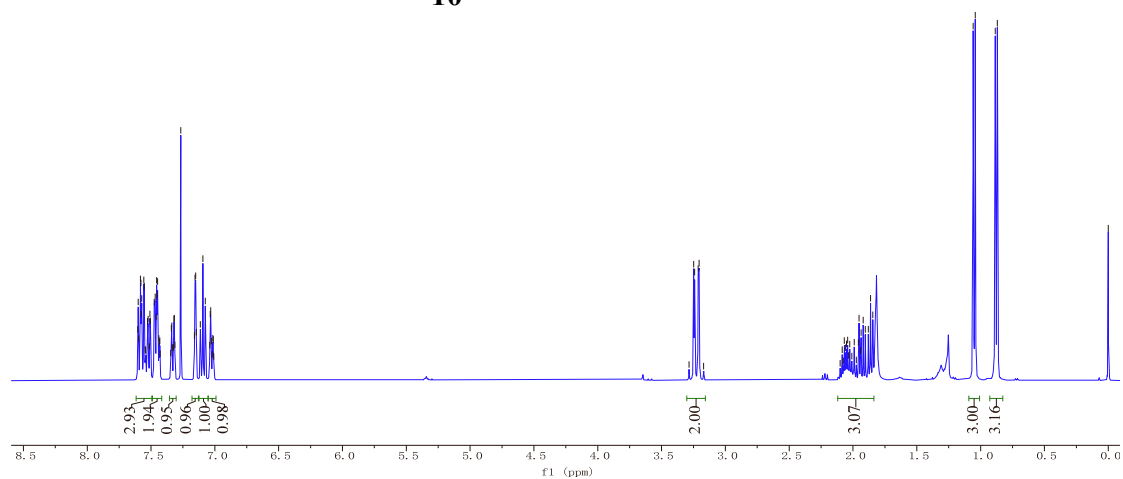




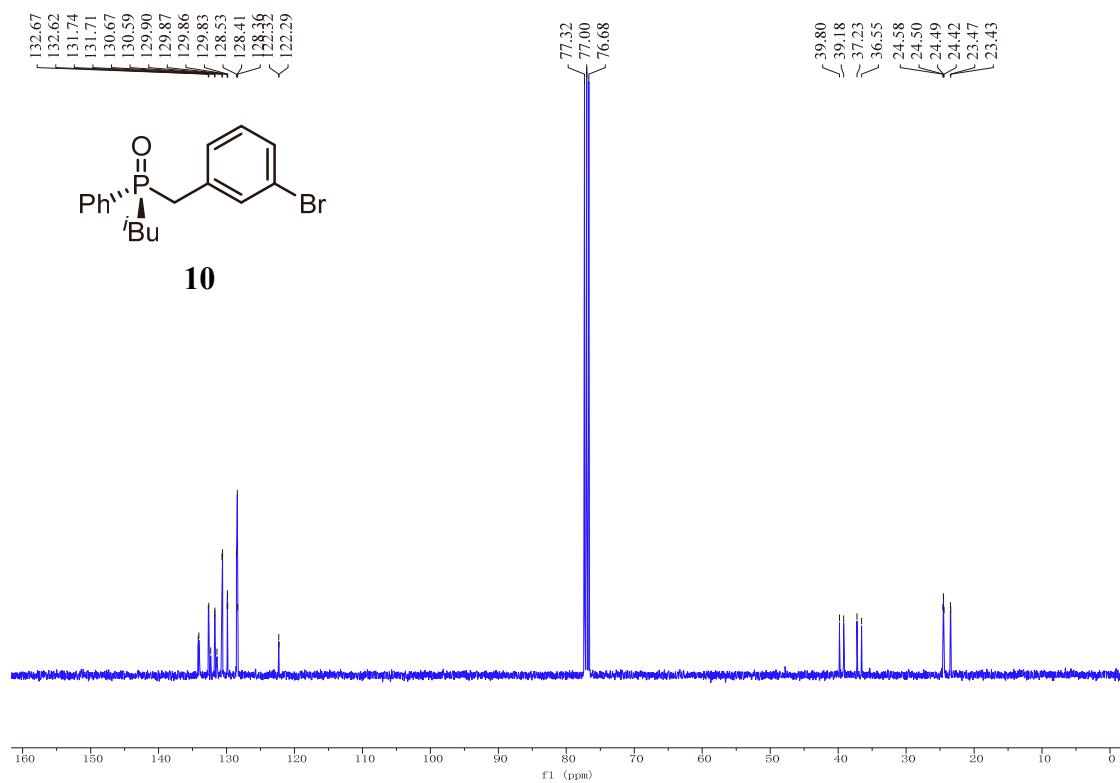
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**10**

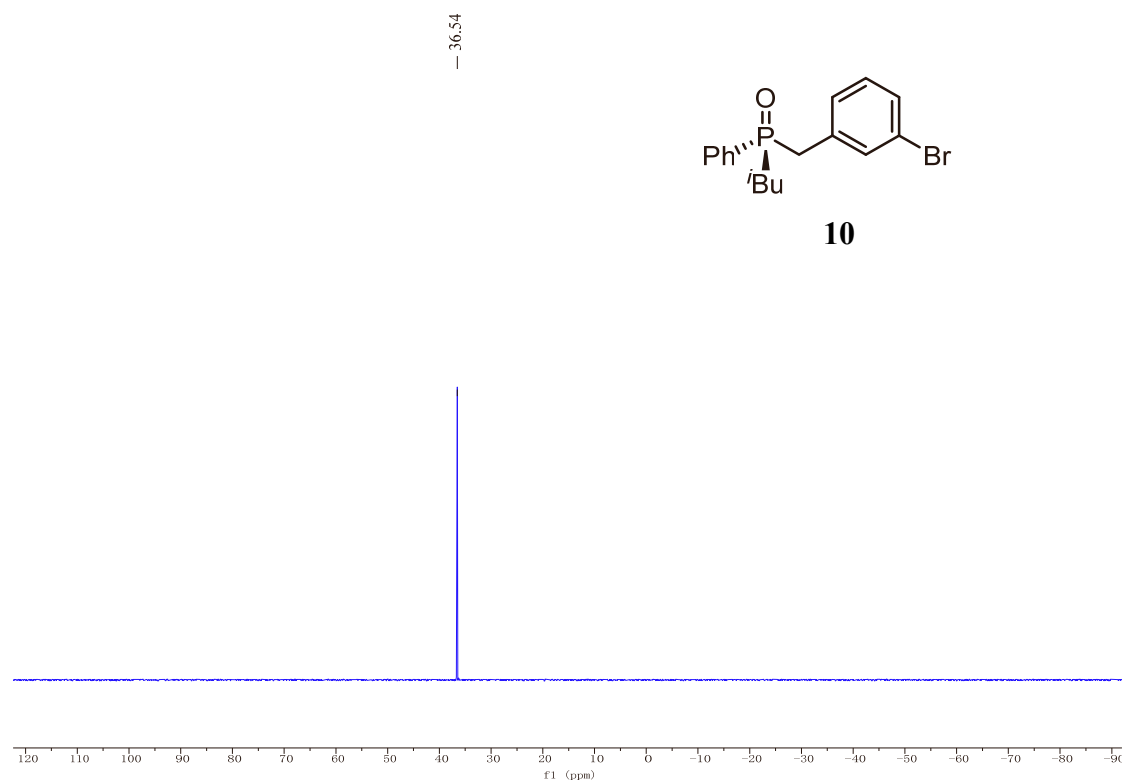


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

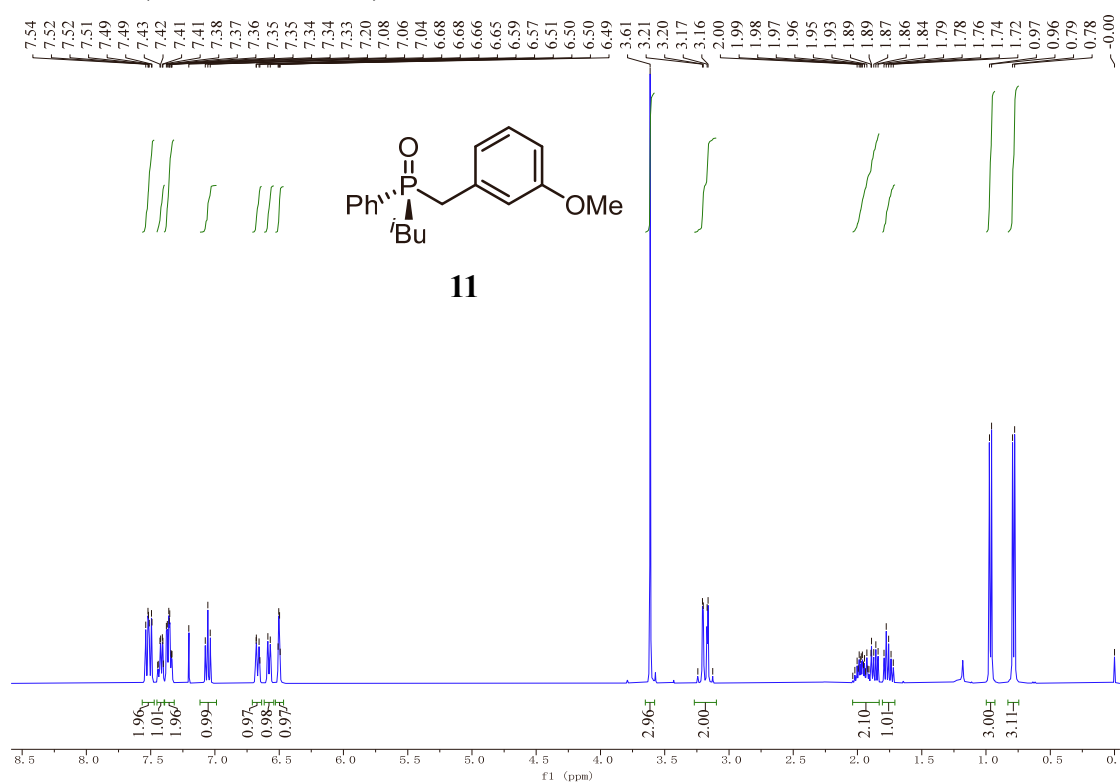


**10**

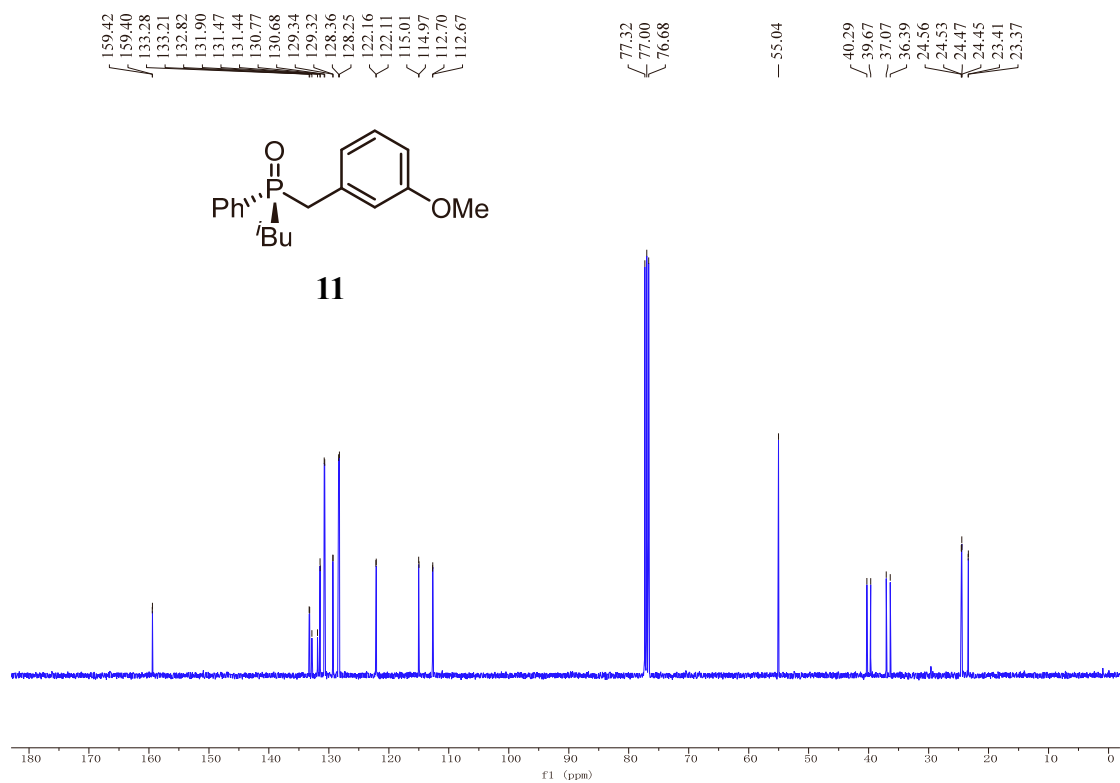
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



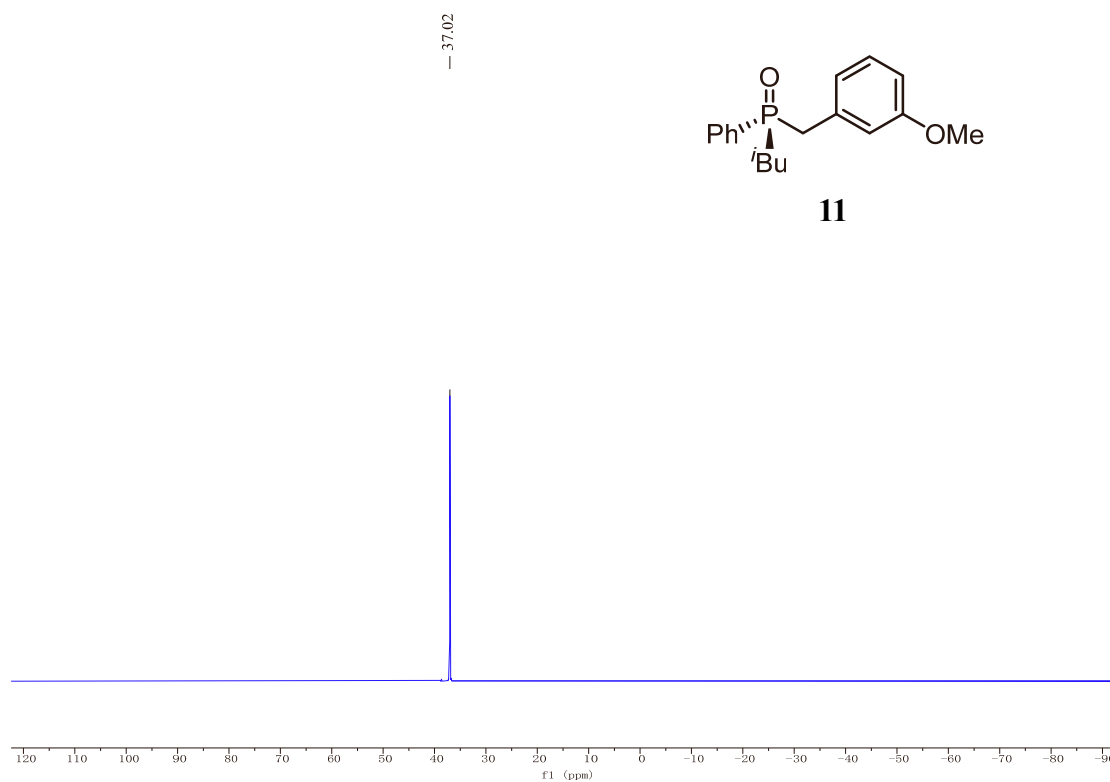
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



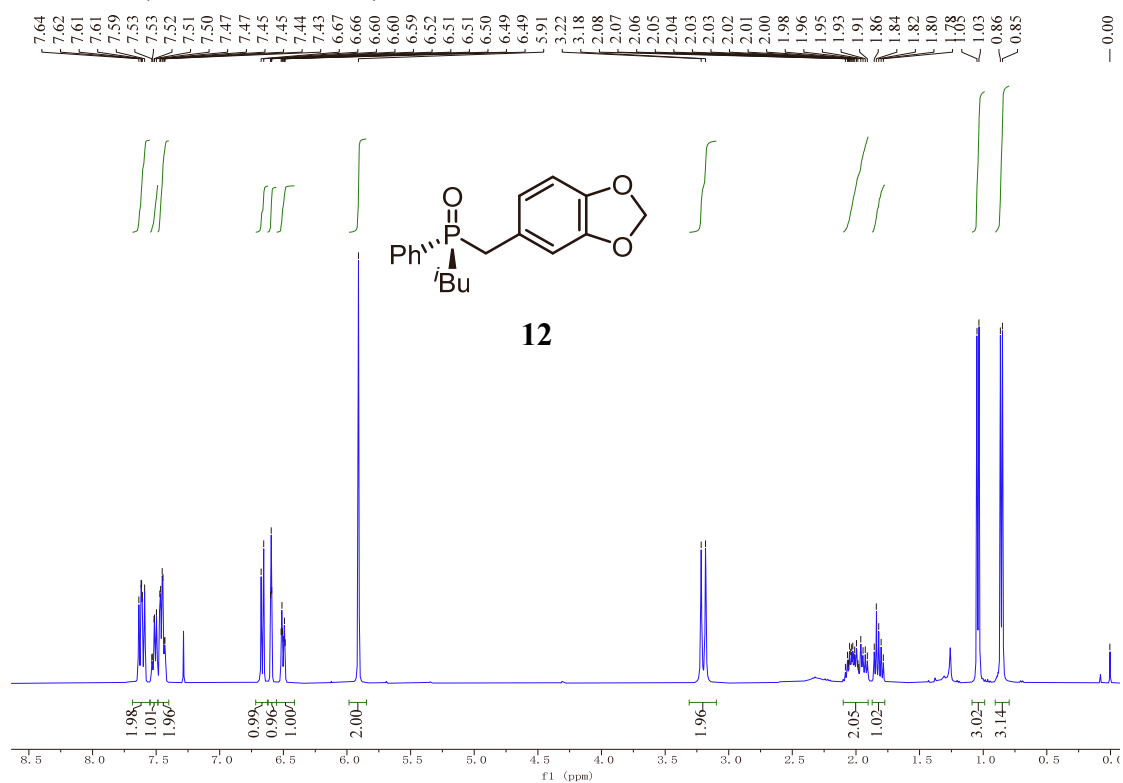
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



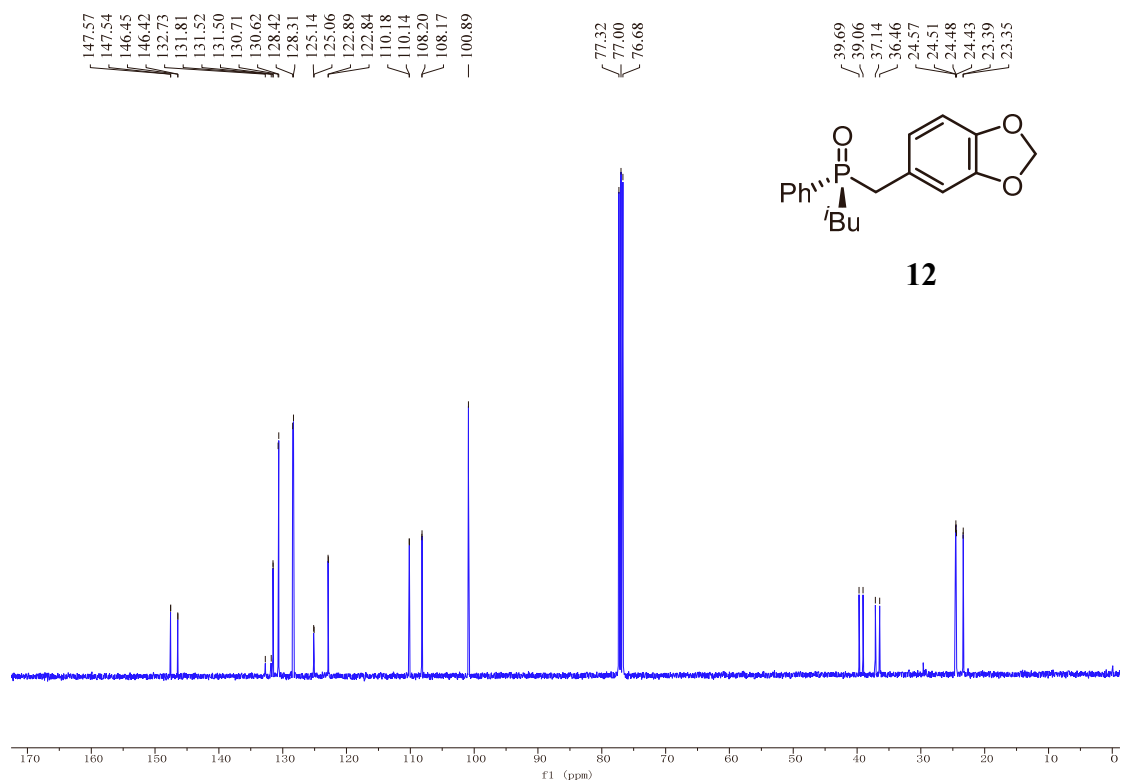
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



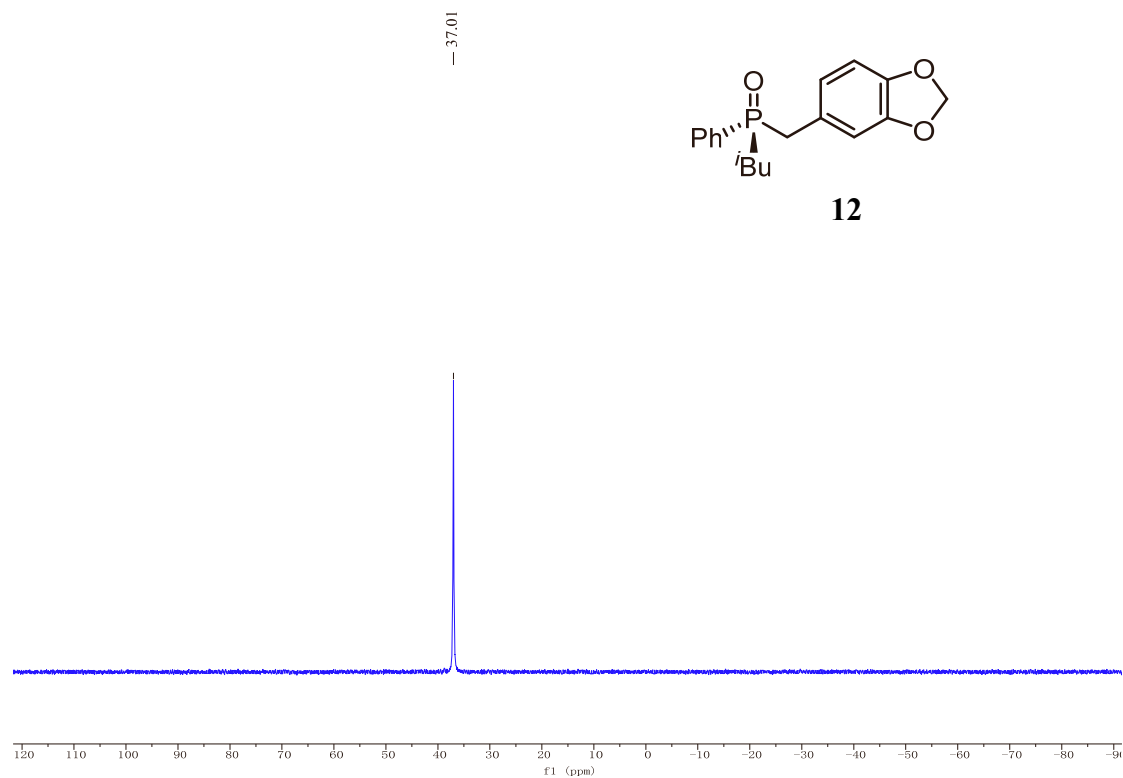
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



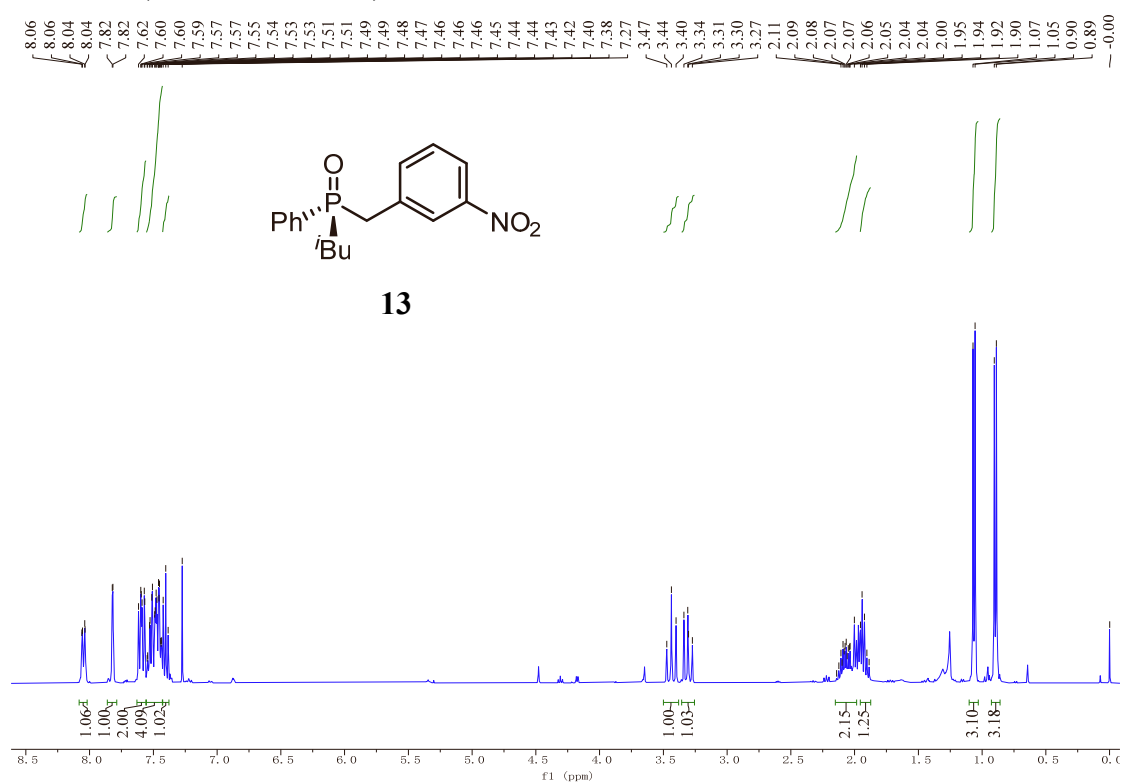
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



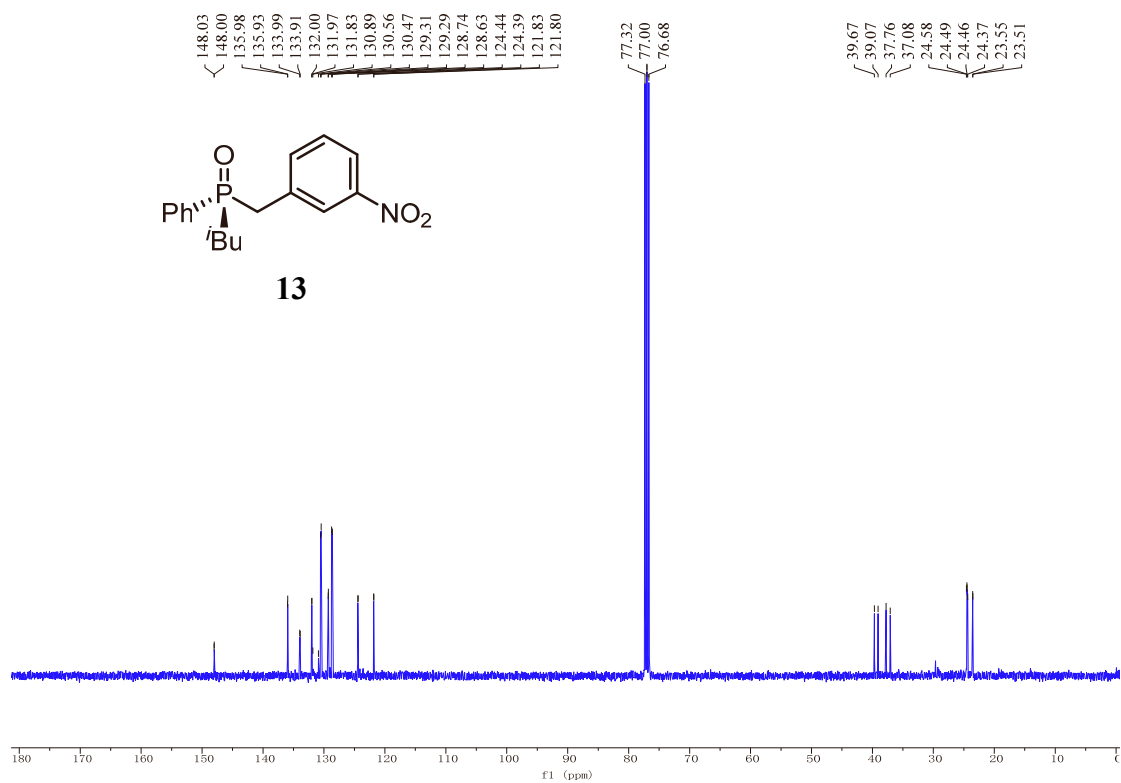
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



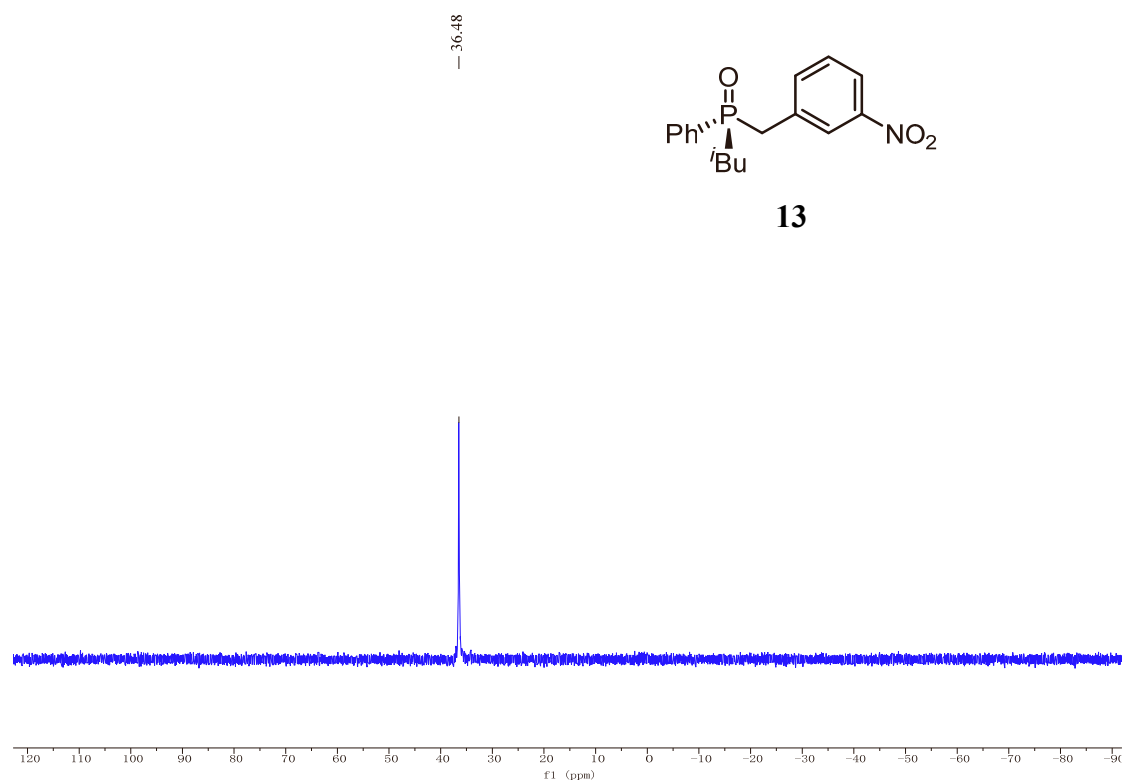
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

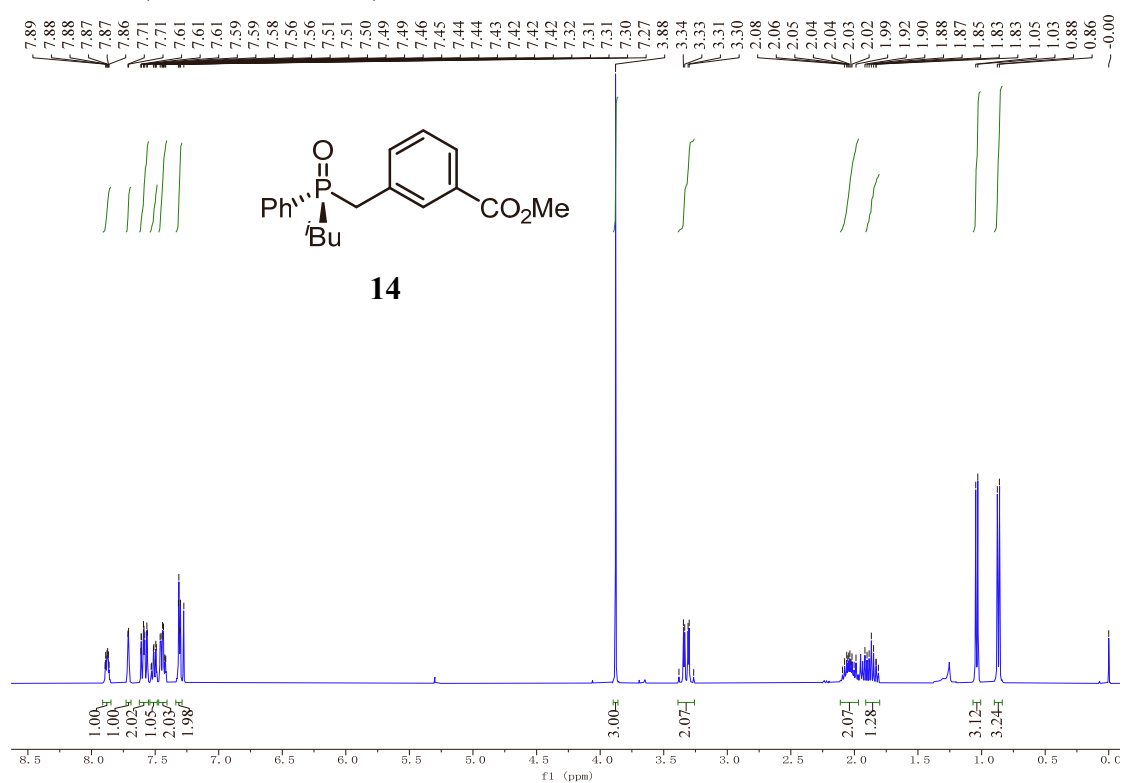


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

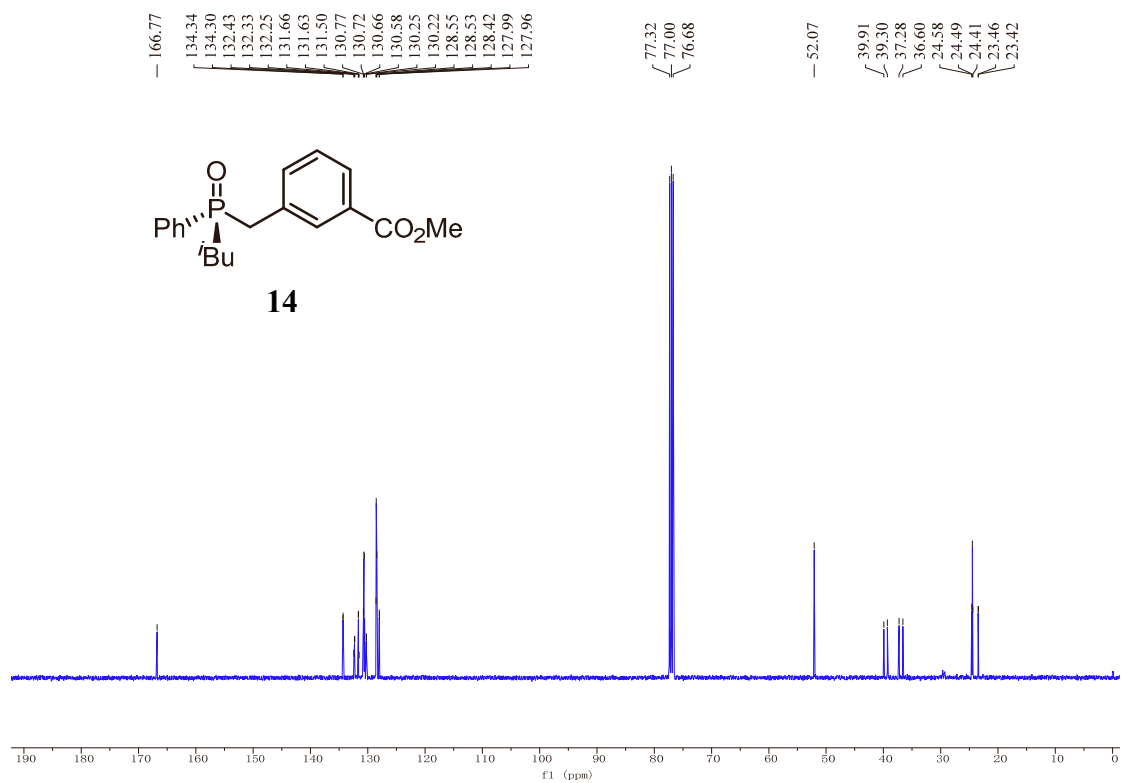




**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

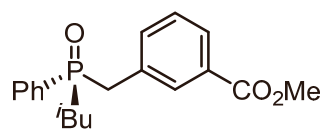


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

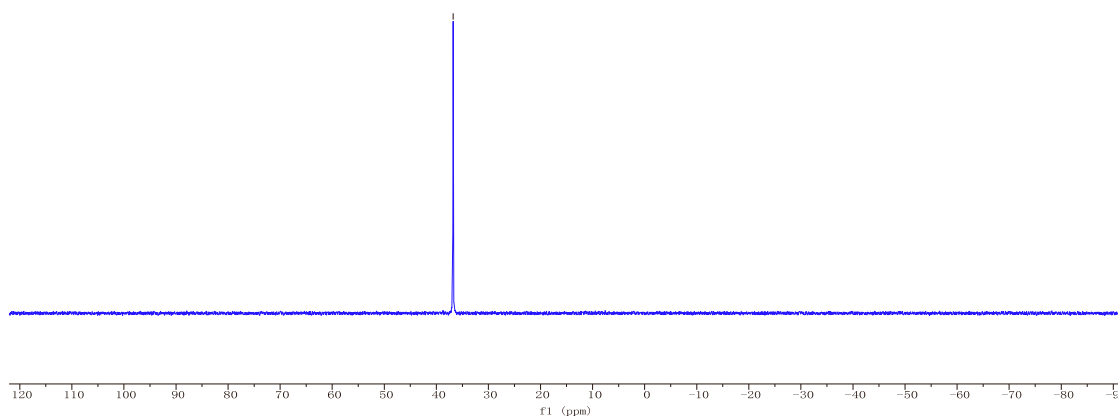


**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)

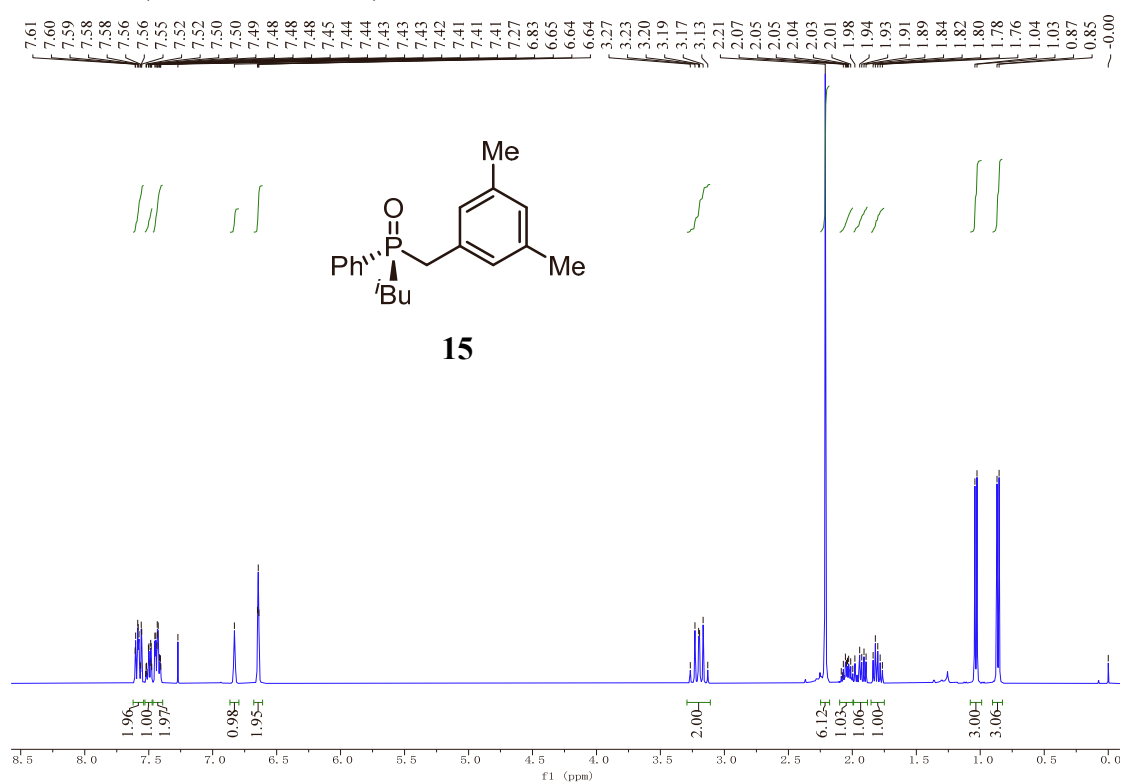
— 36.78



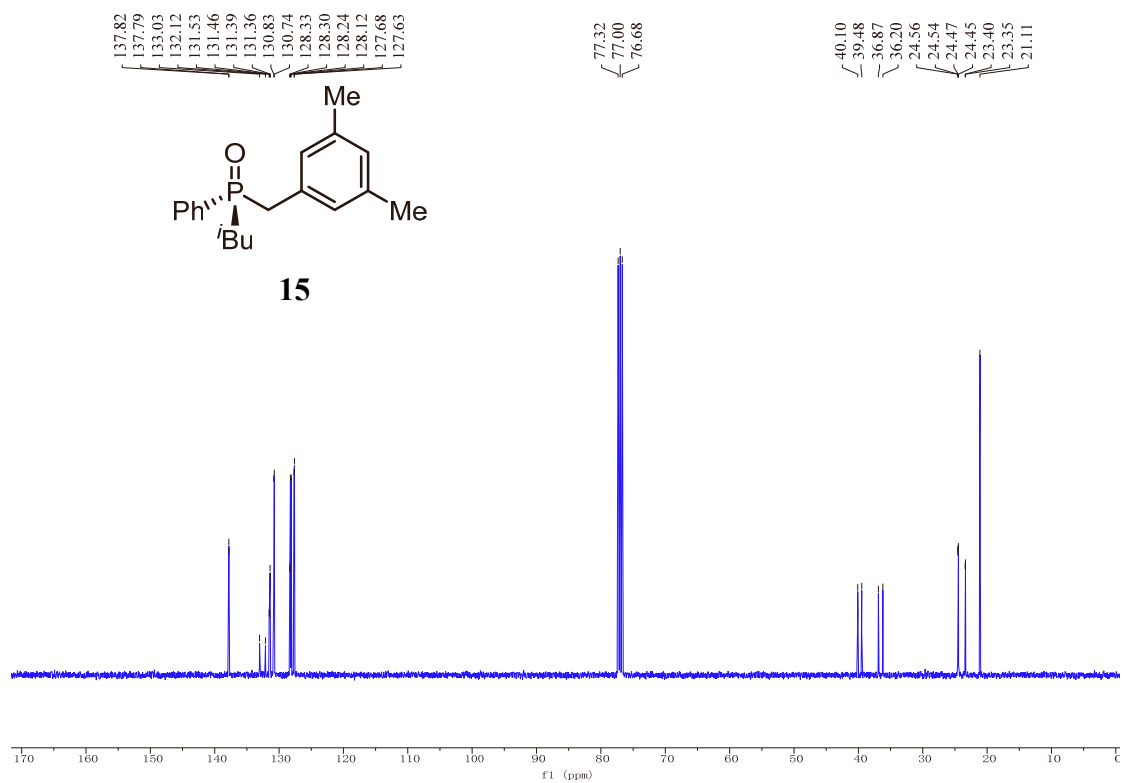
**14**



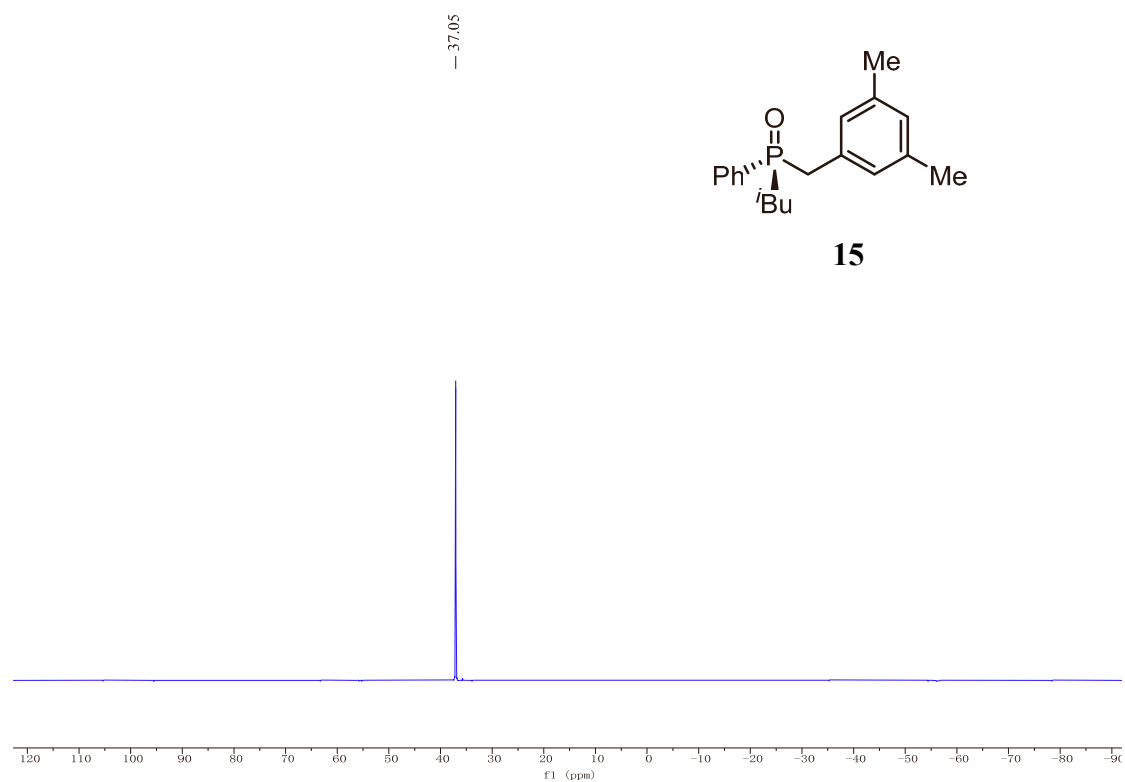
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



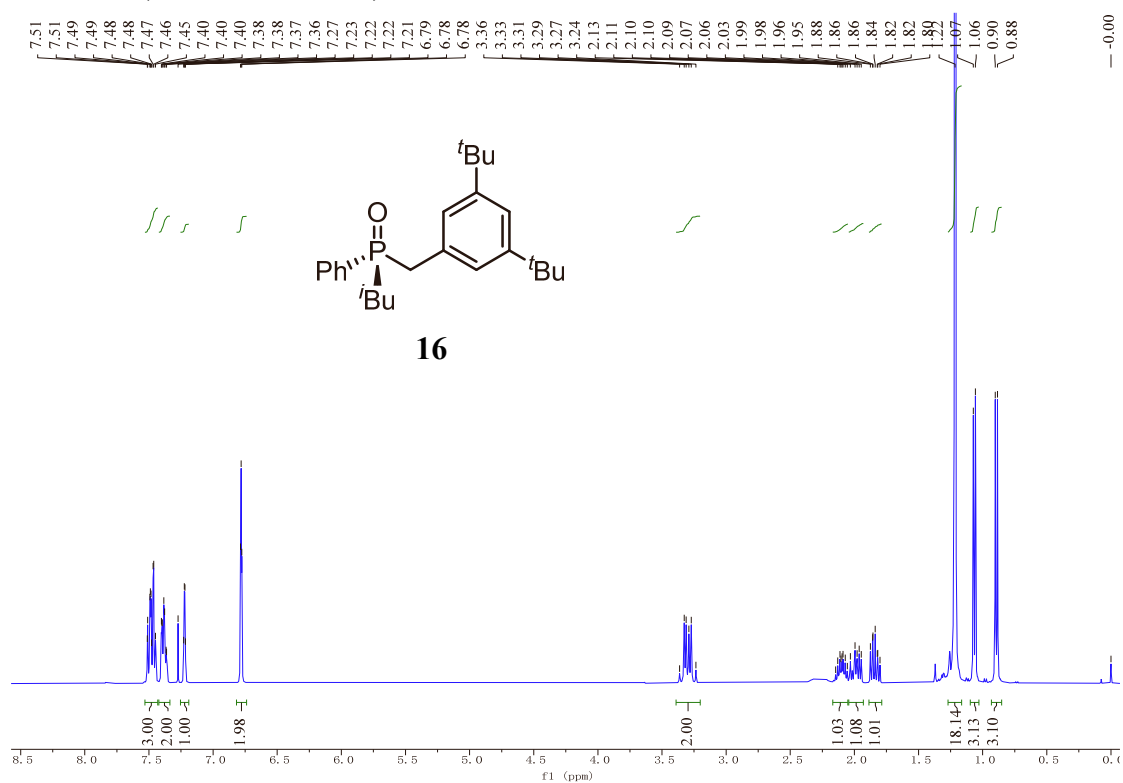
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



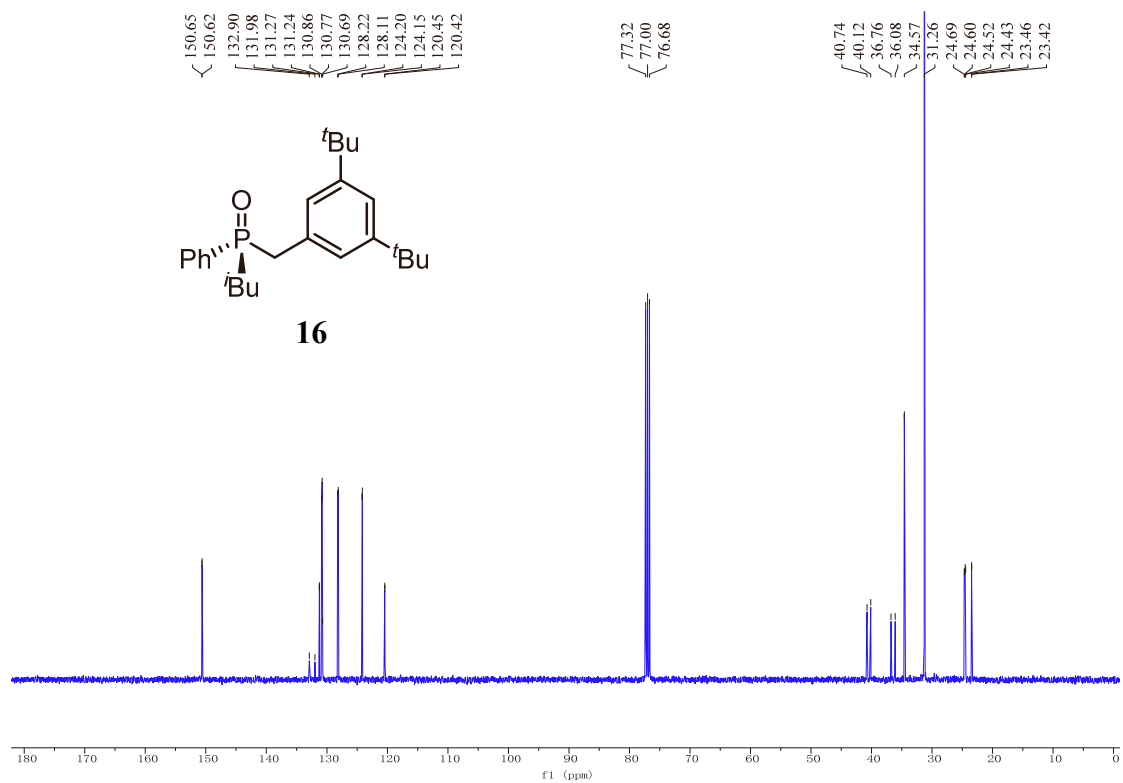
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



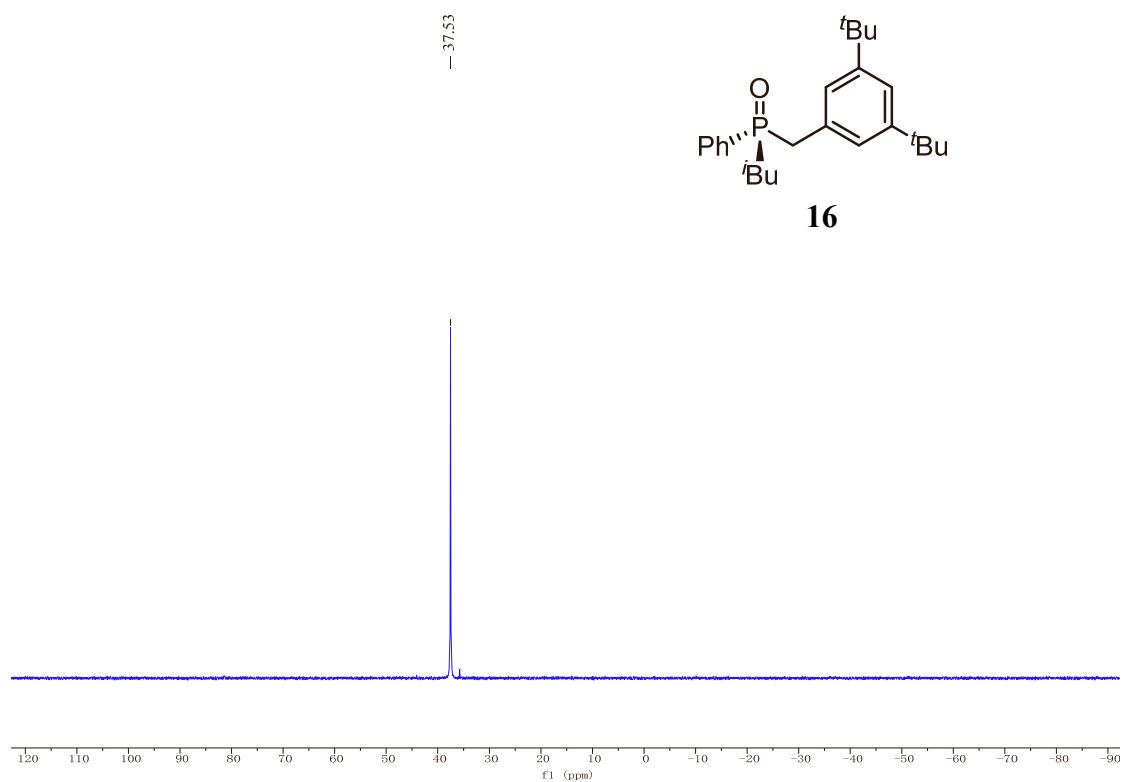
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



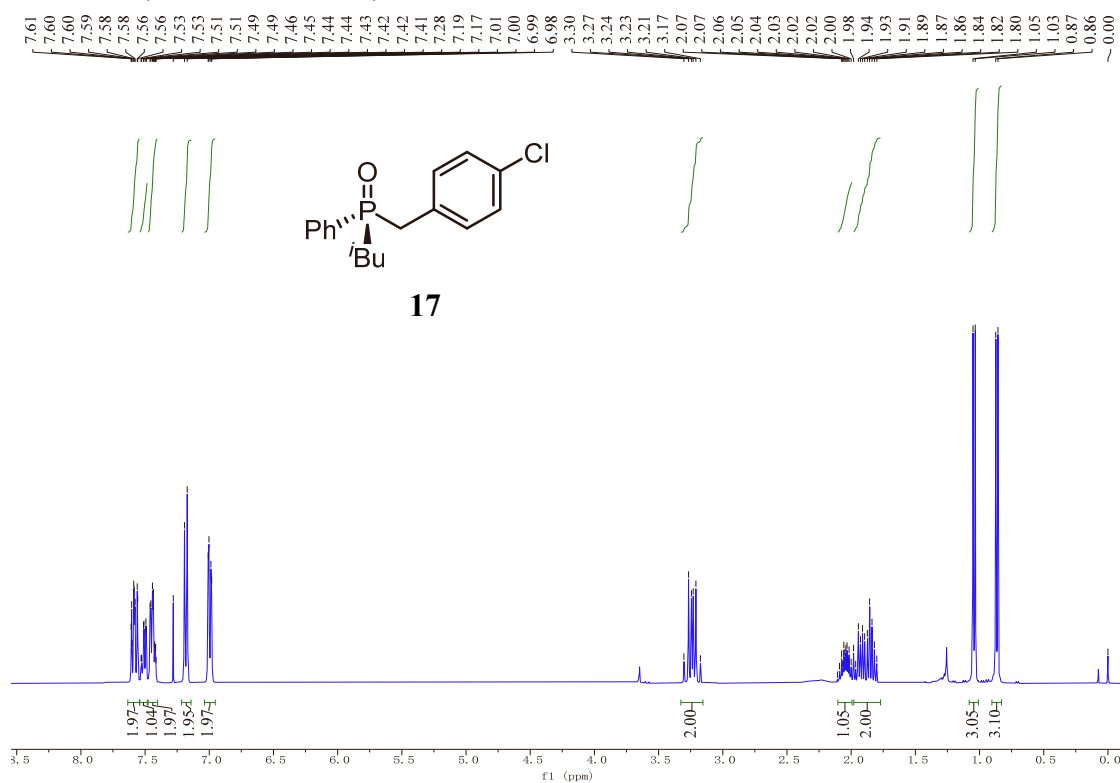
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



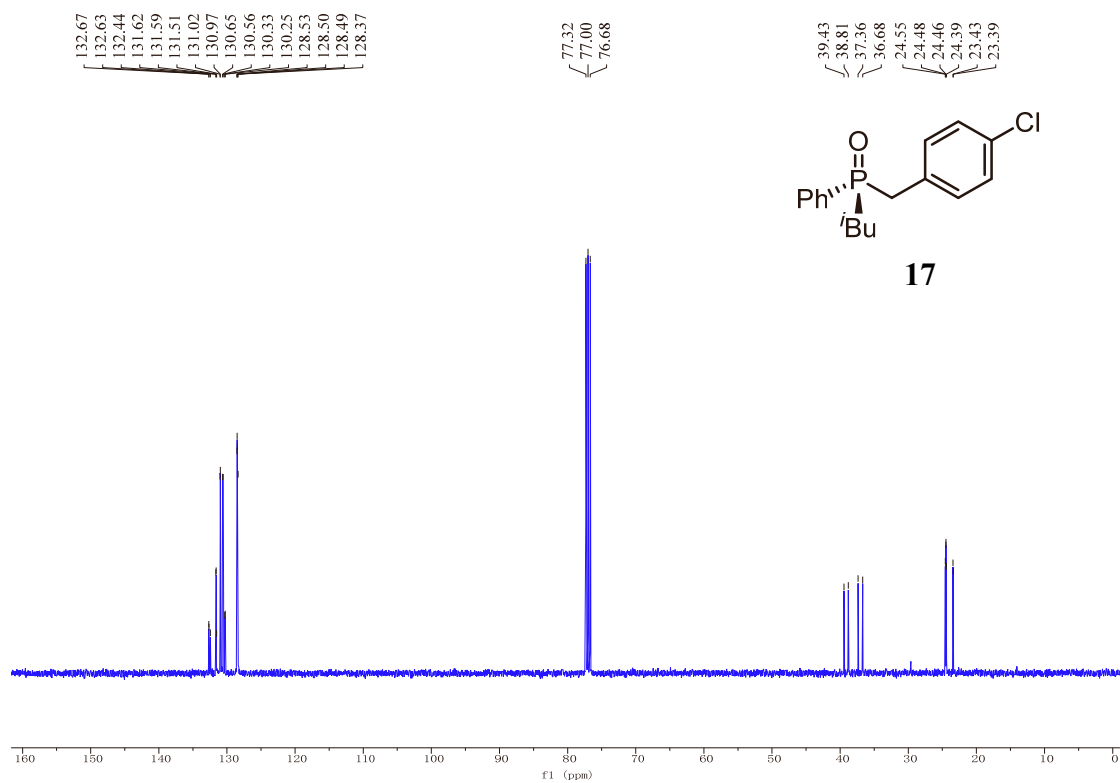
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



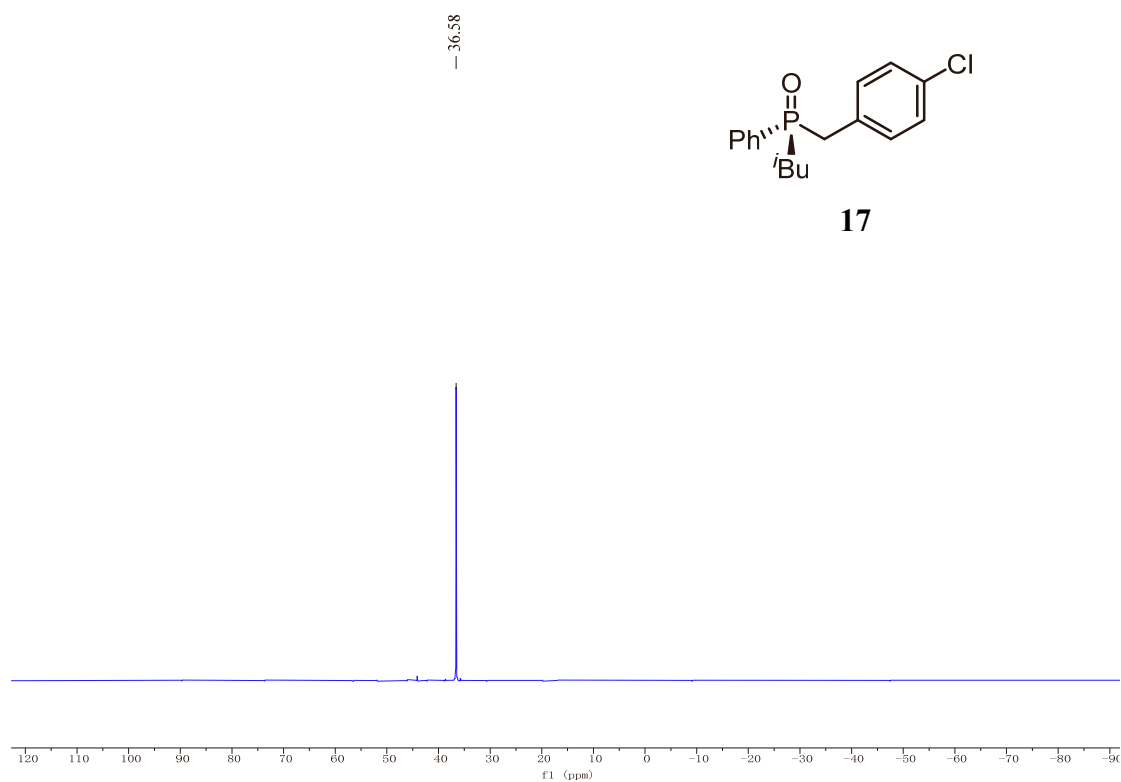
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

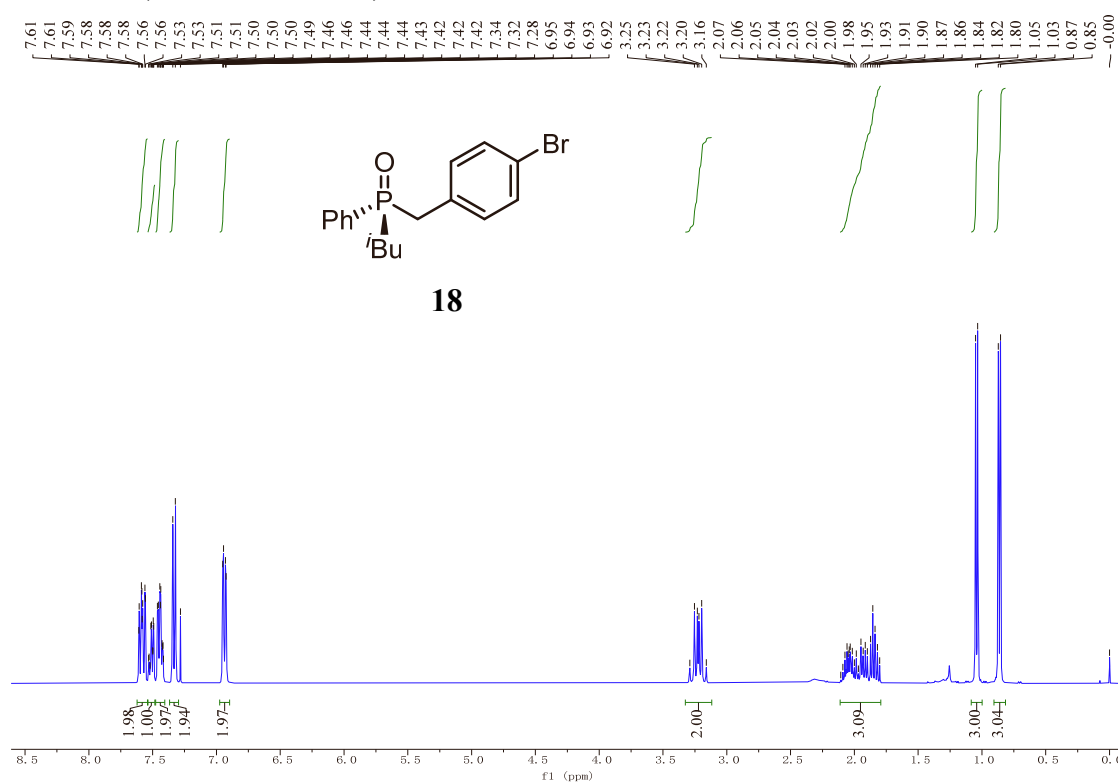


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

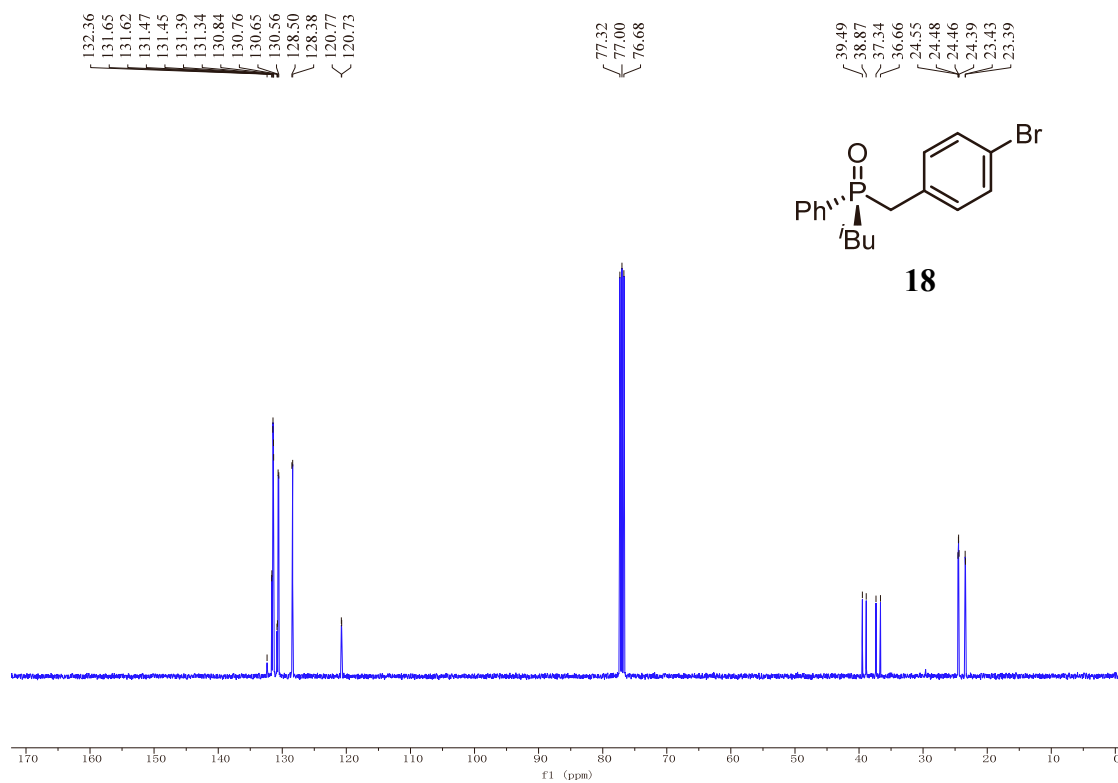




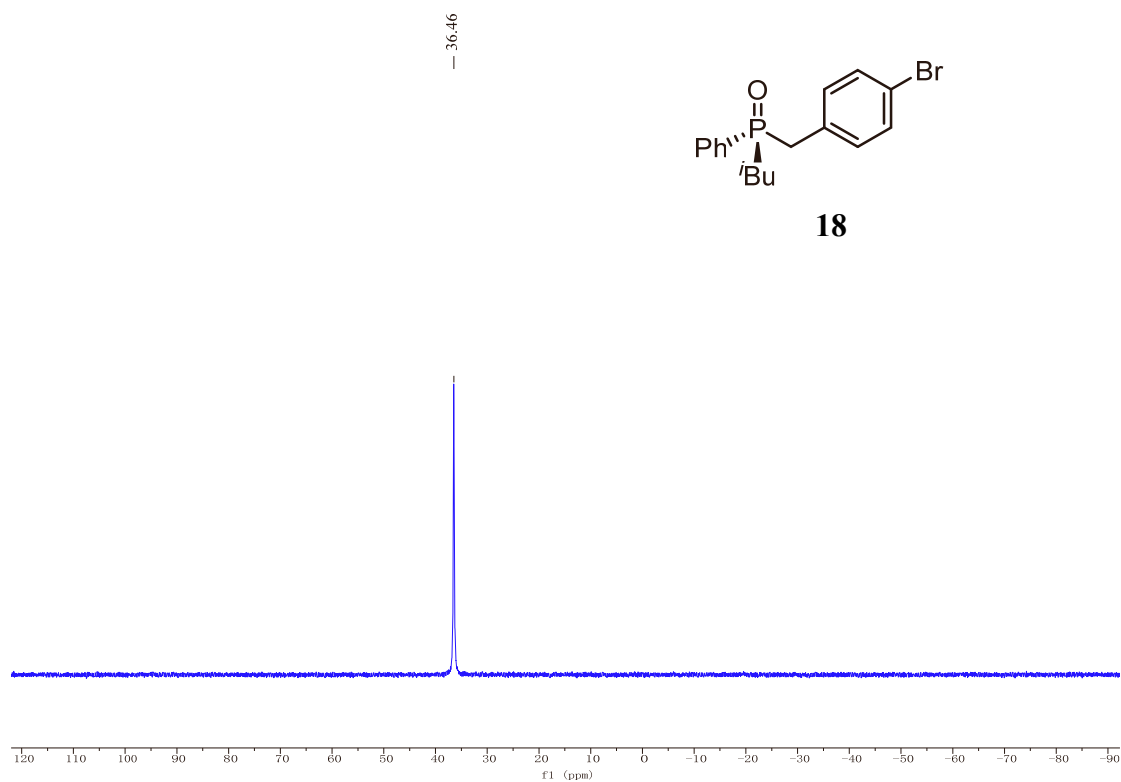
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



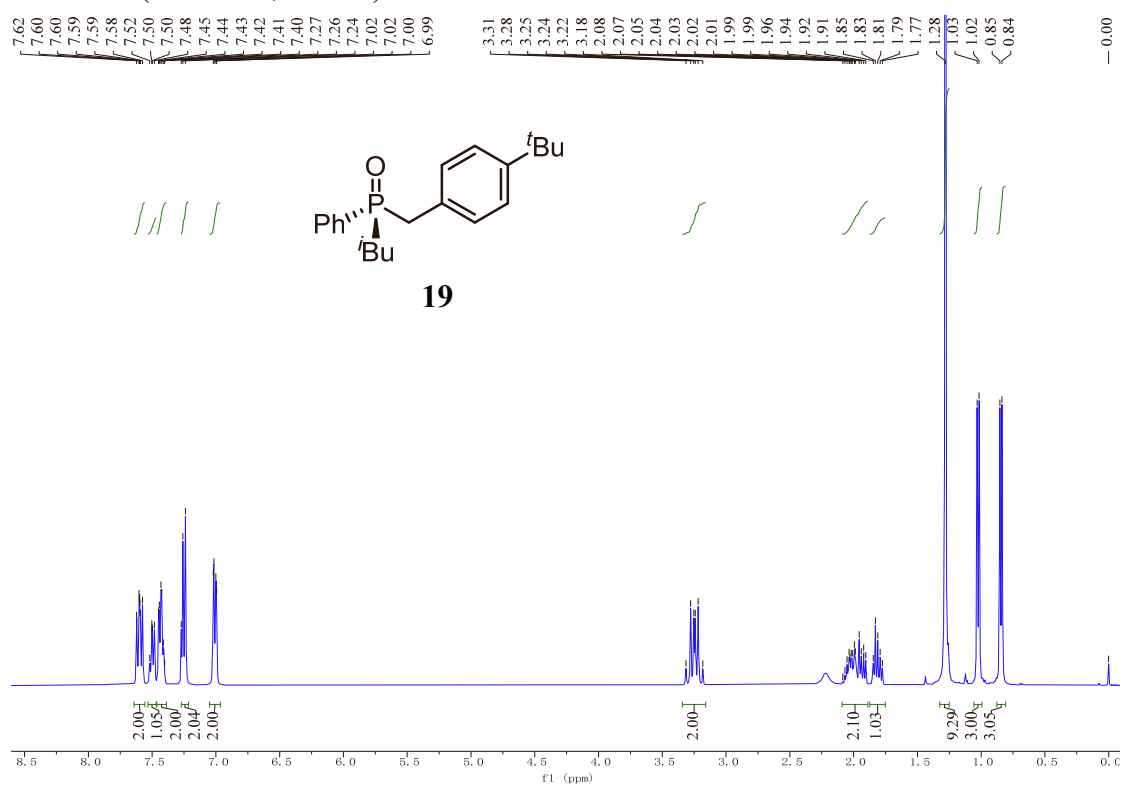
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



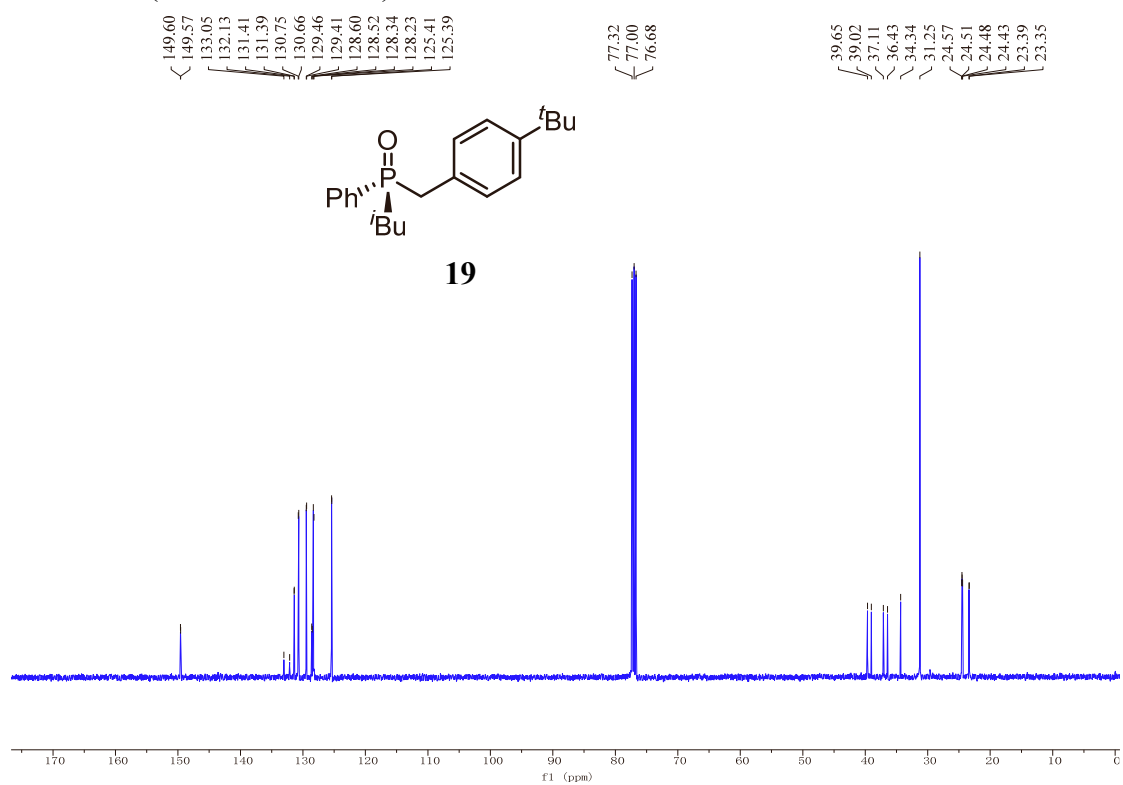
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



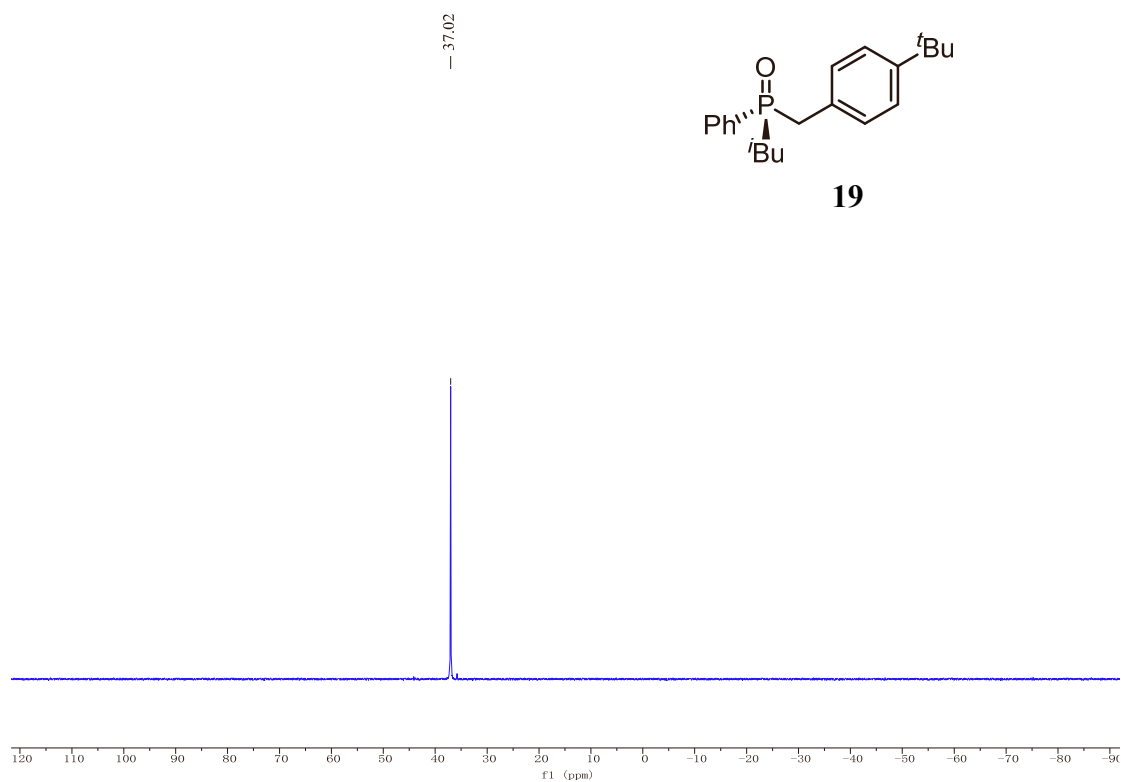
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



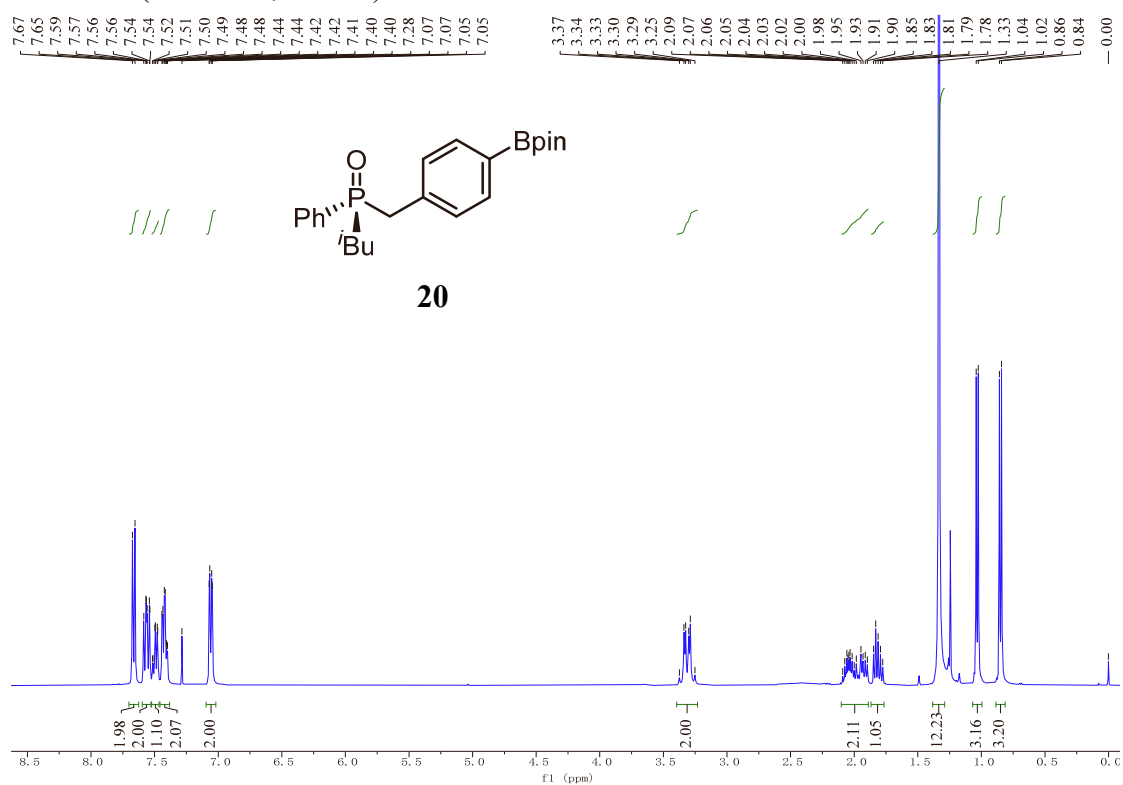
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



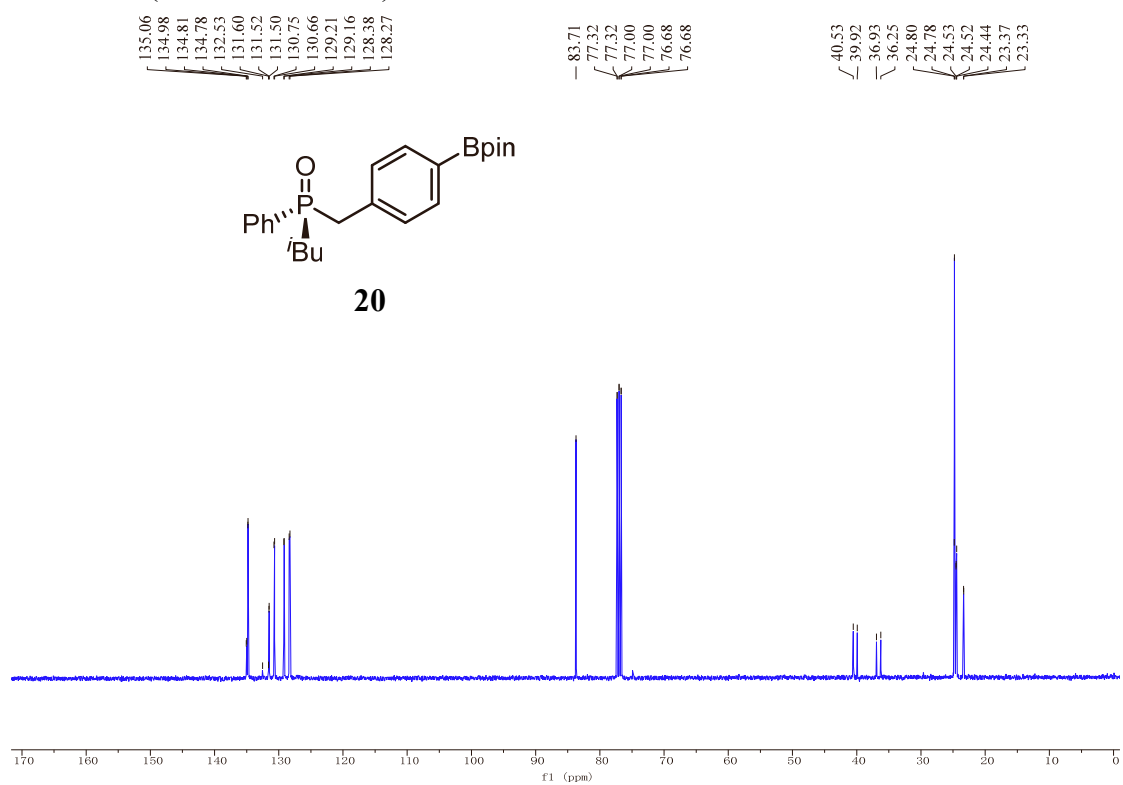
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



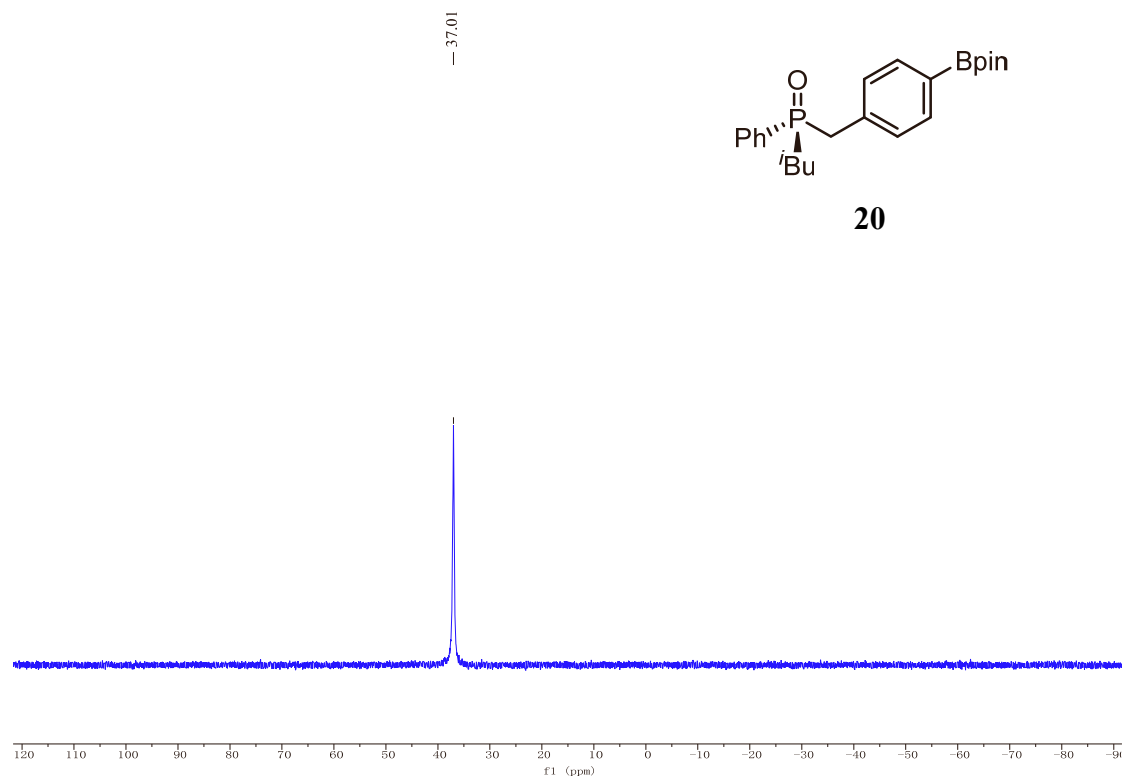
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



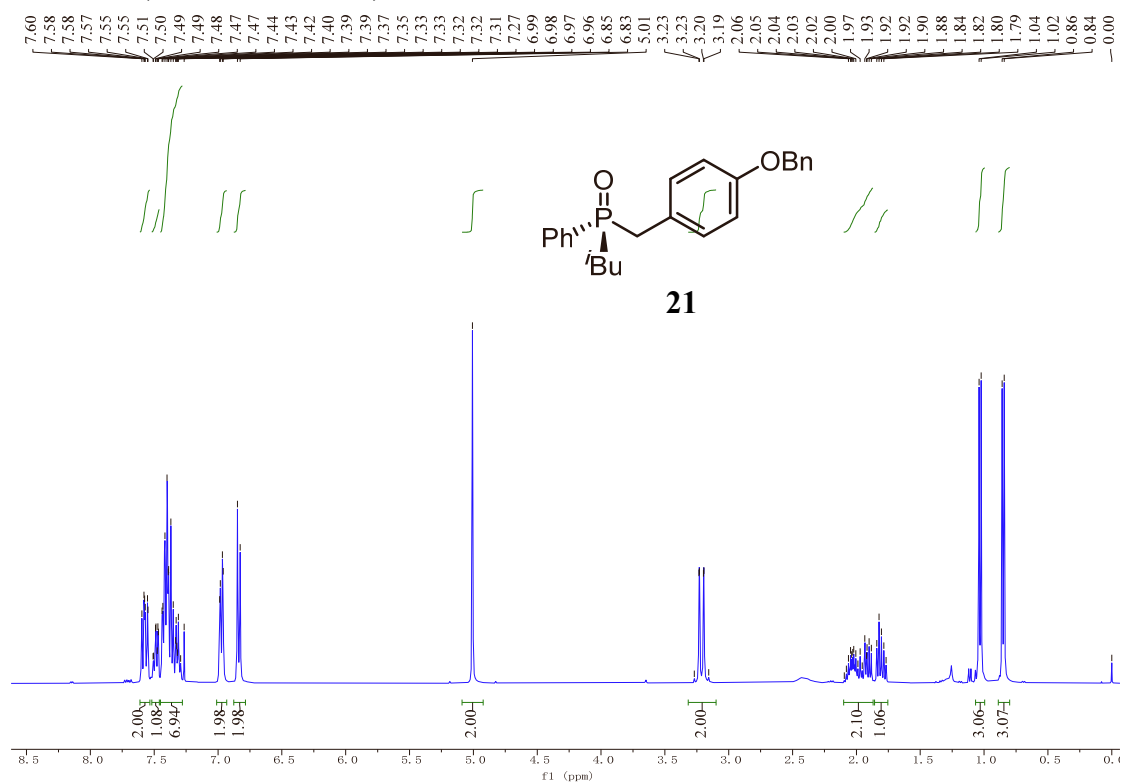
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



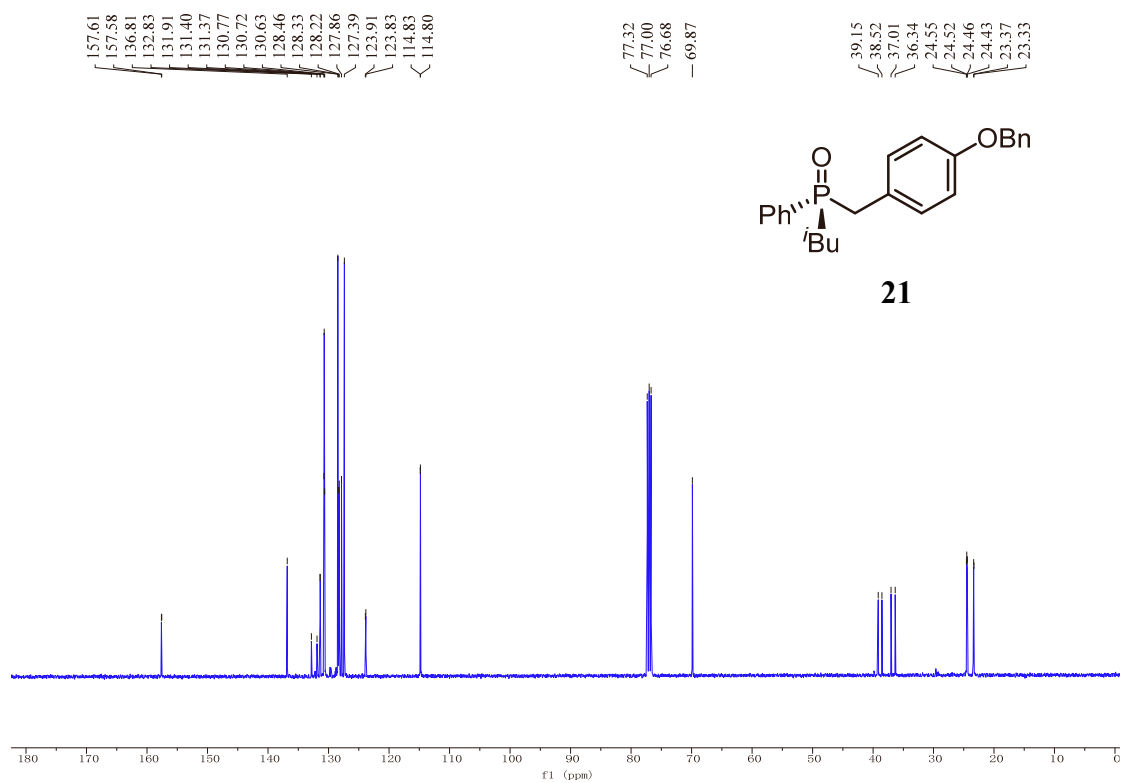
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



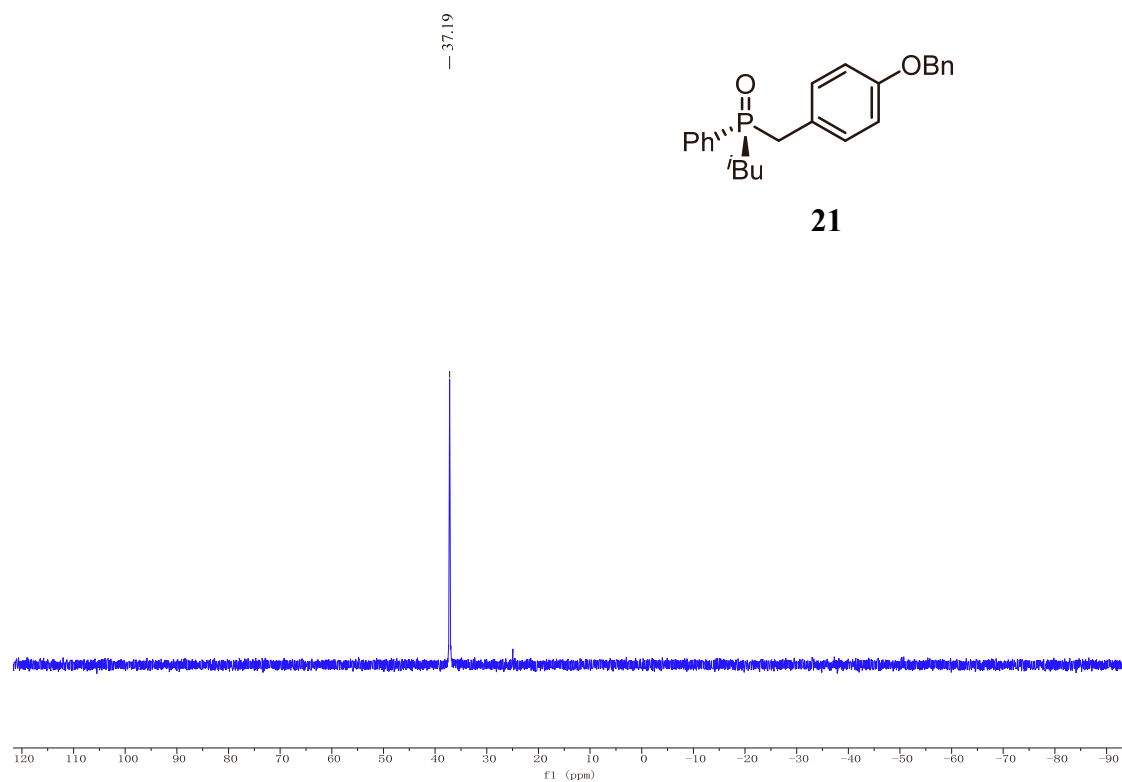
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

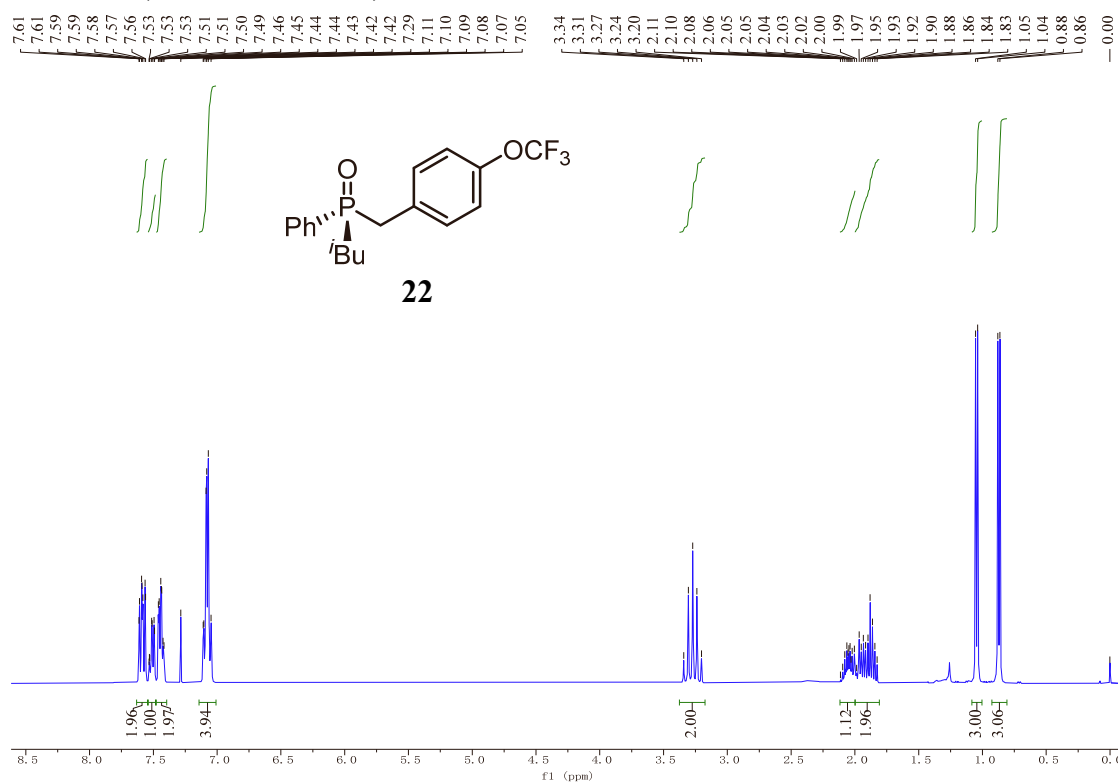


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

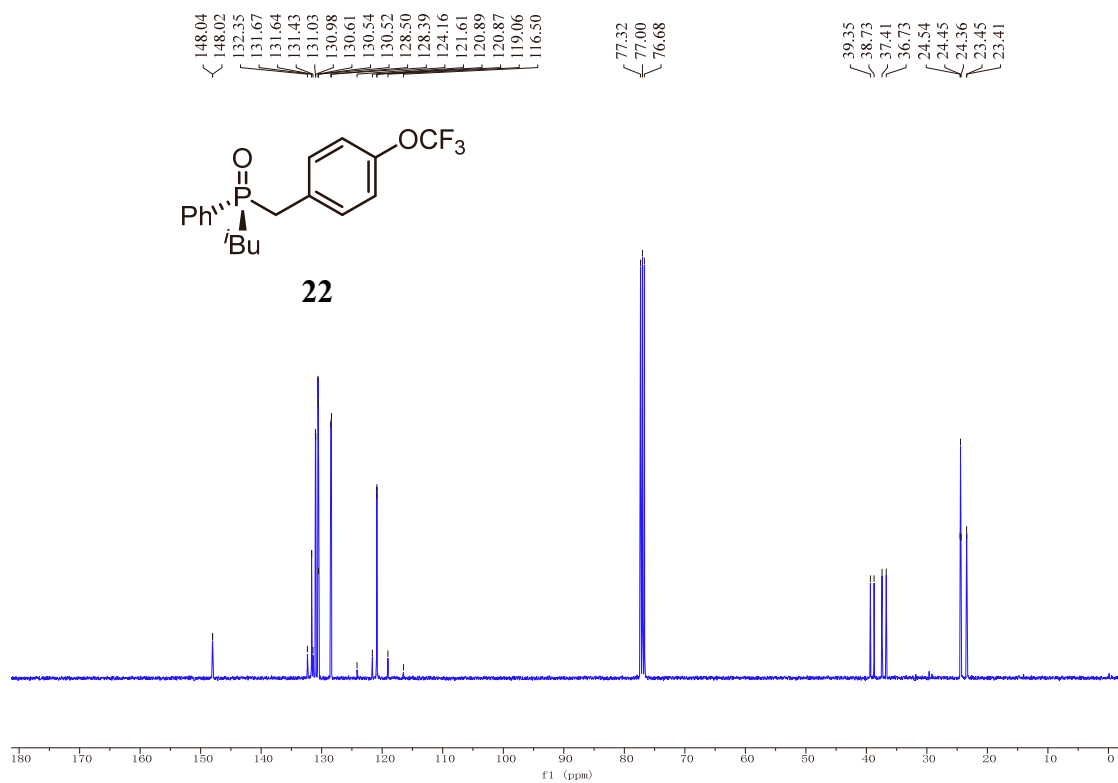




**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

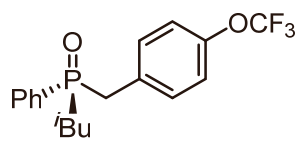


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

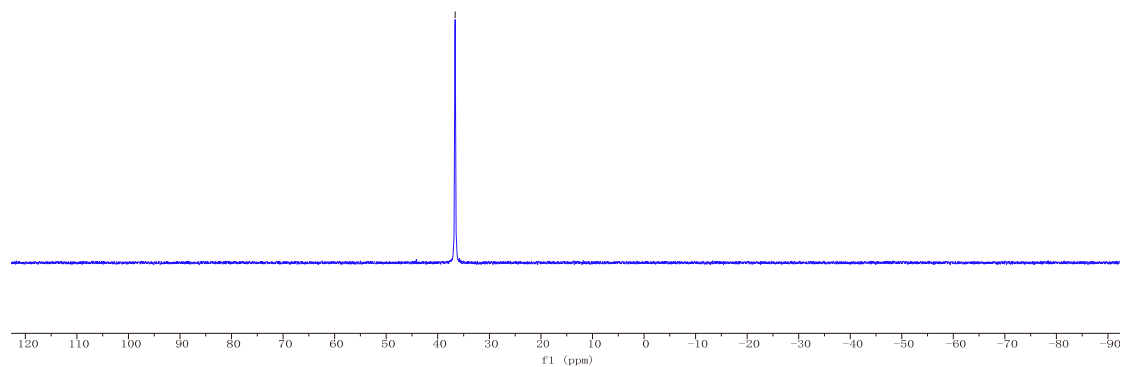


**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>)

— 36.63

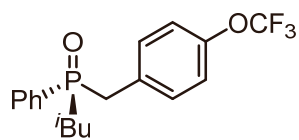


**22**

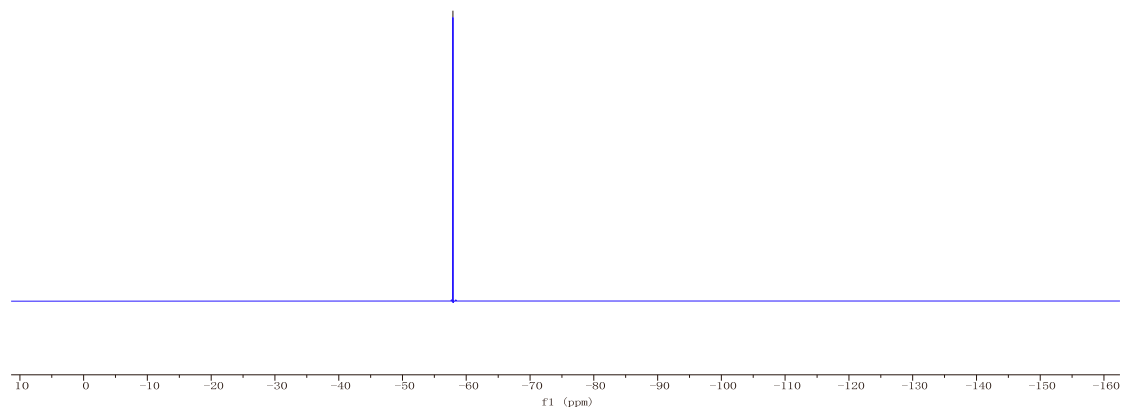


**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)

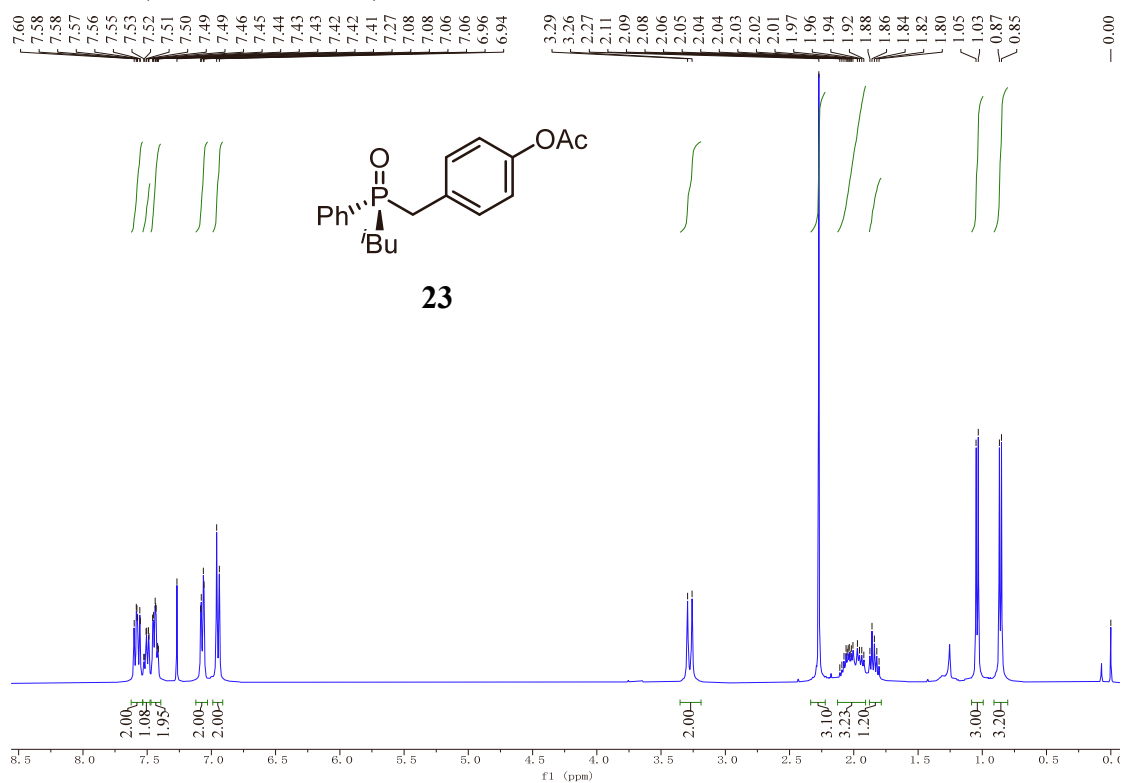
— -57.91



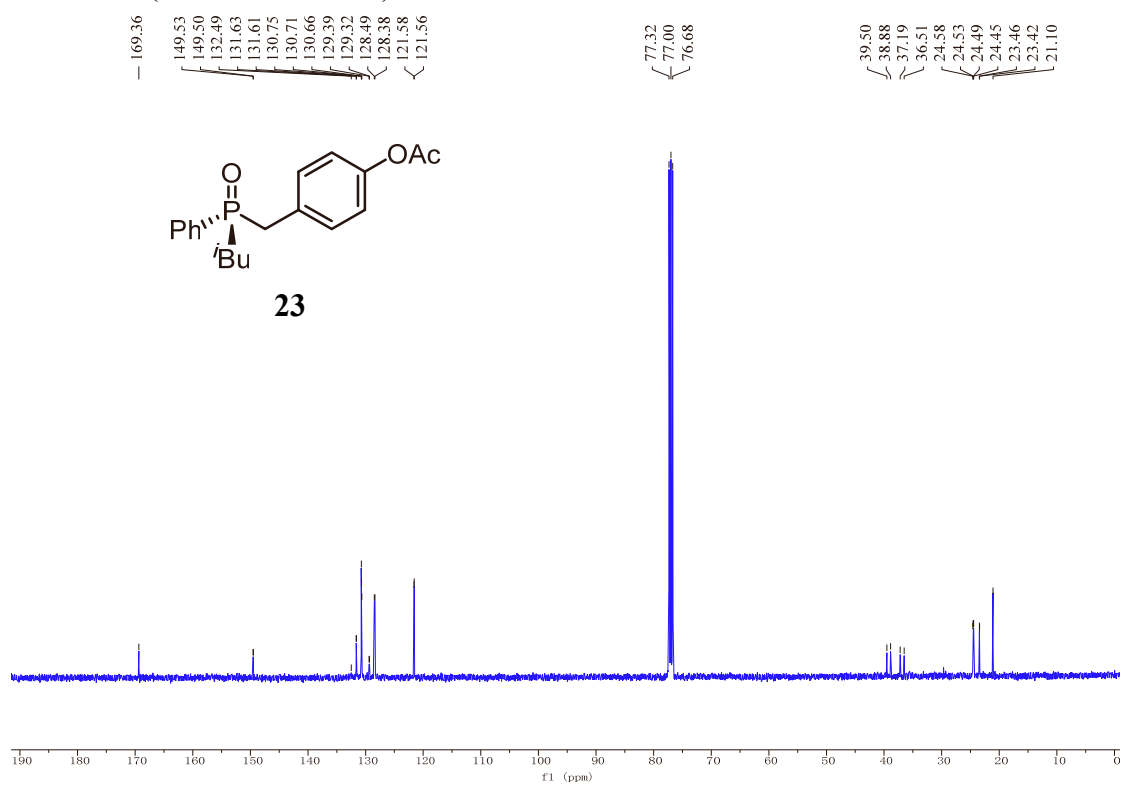
**22**



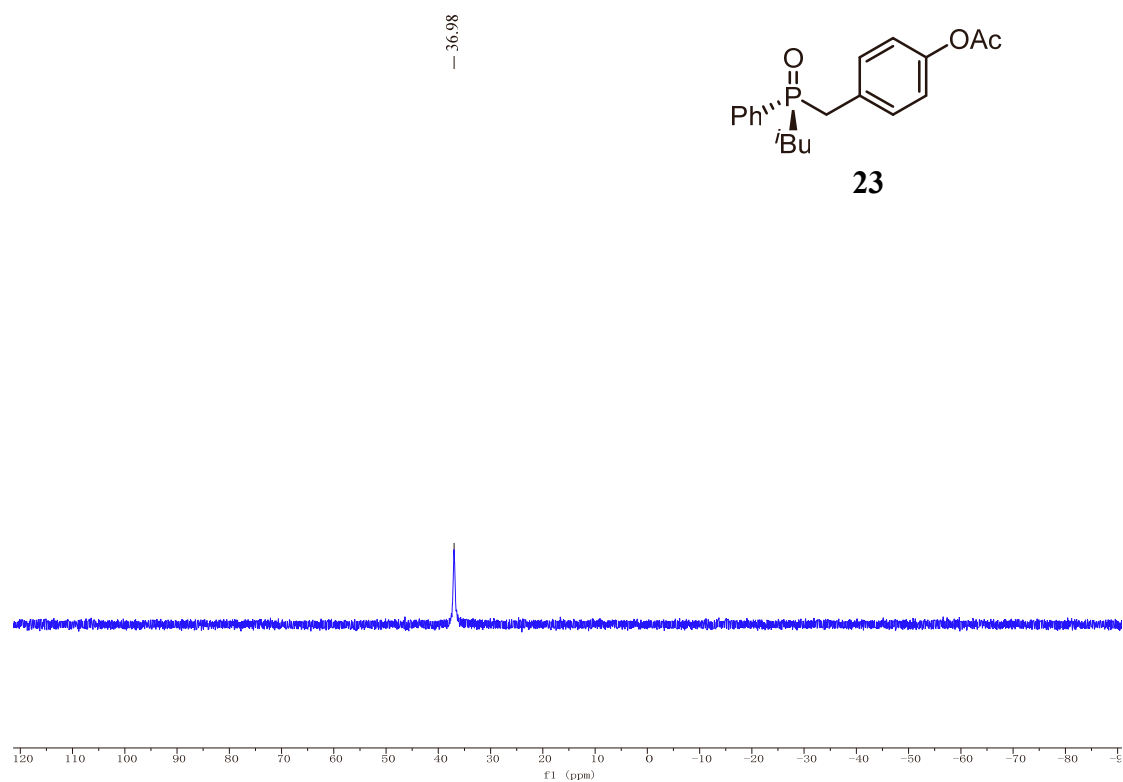
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



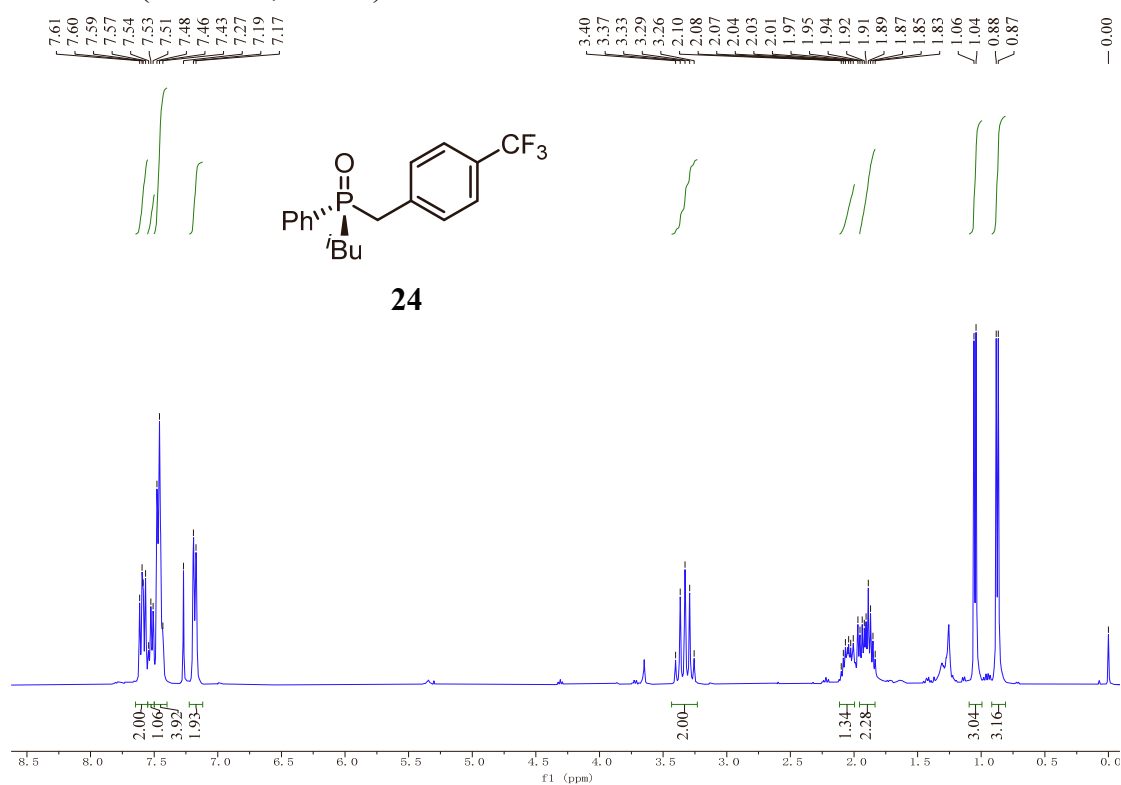
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



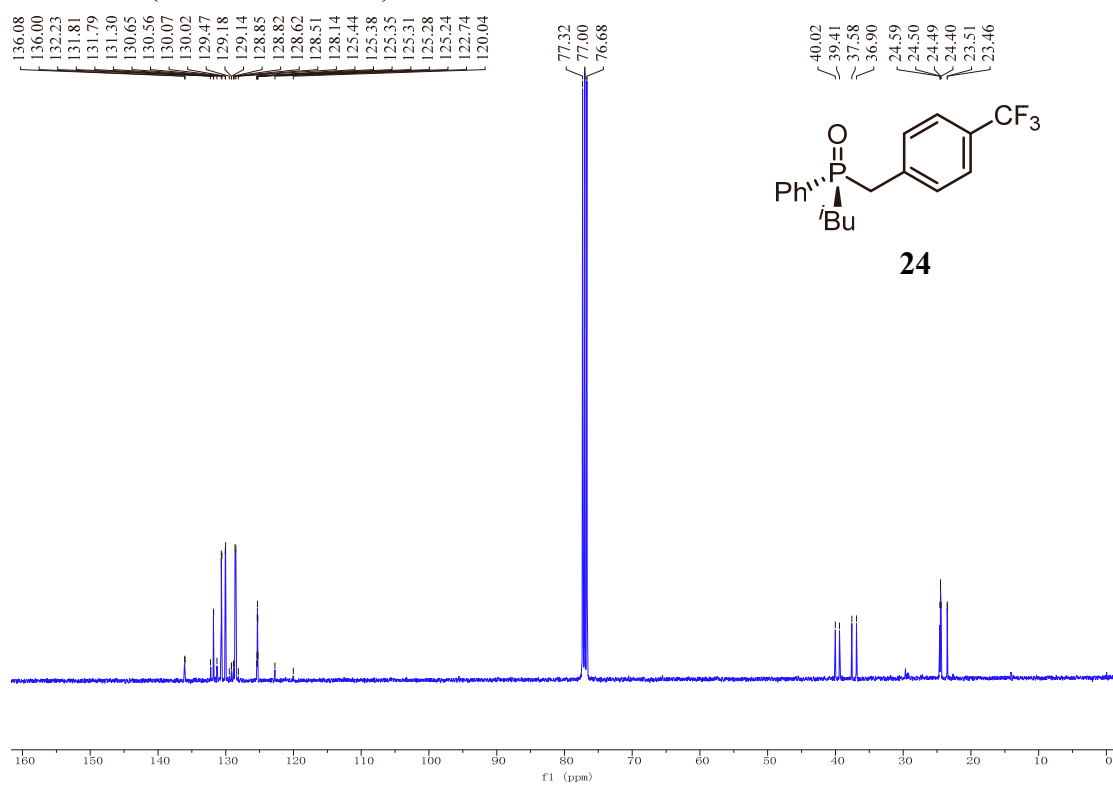
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



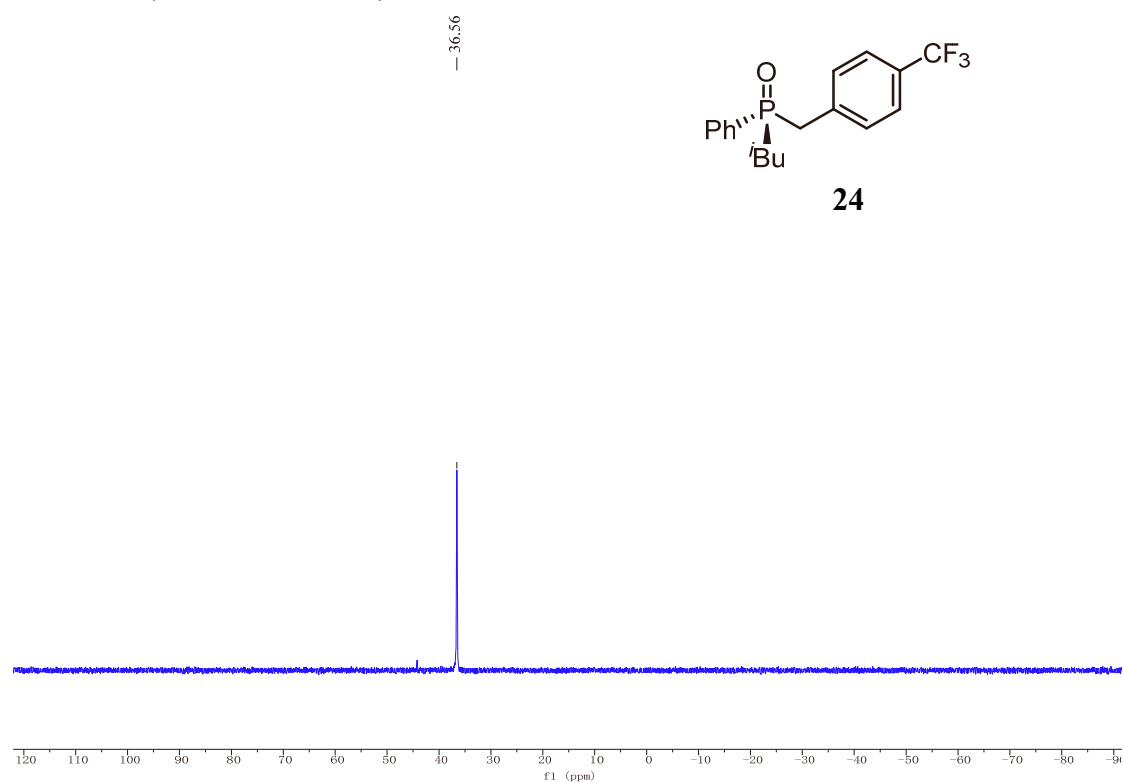
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



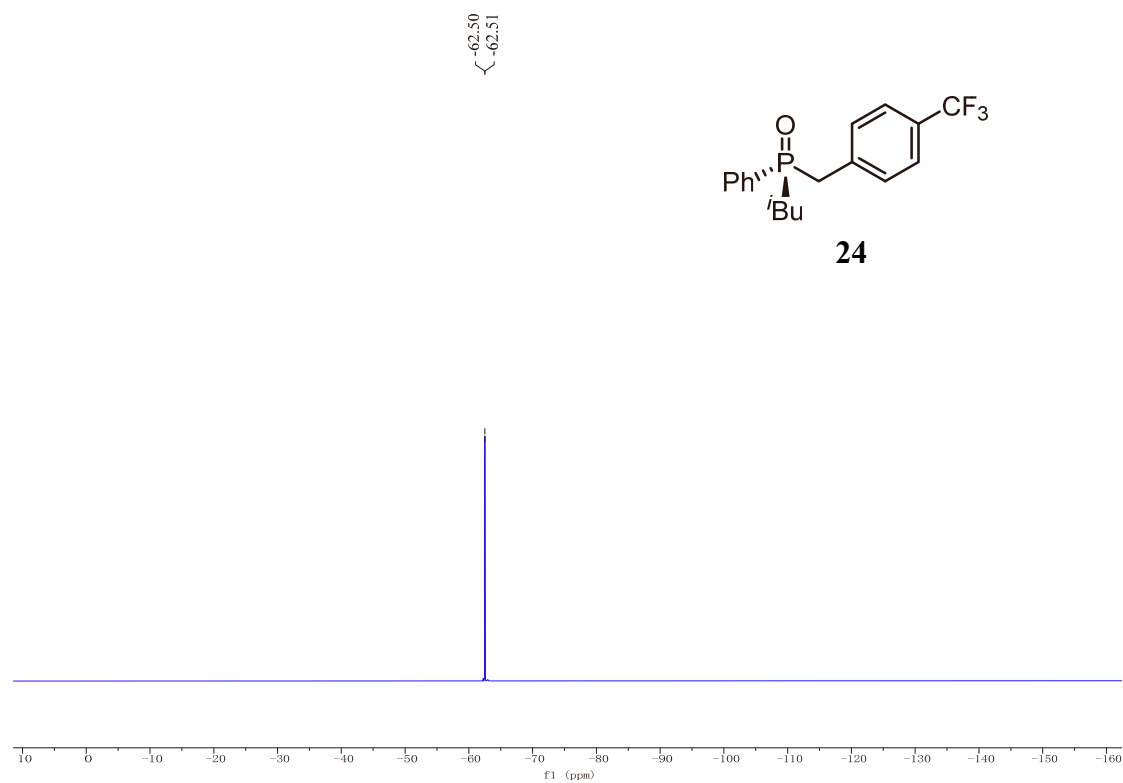
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



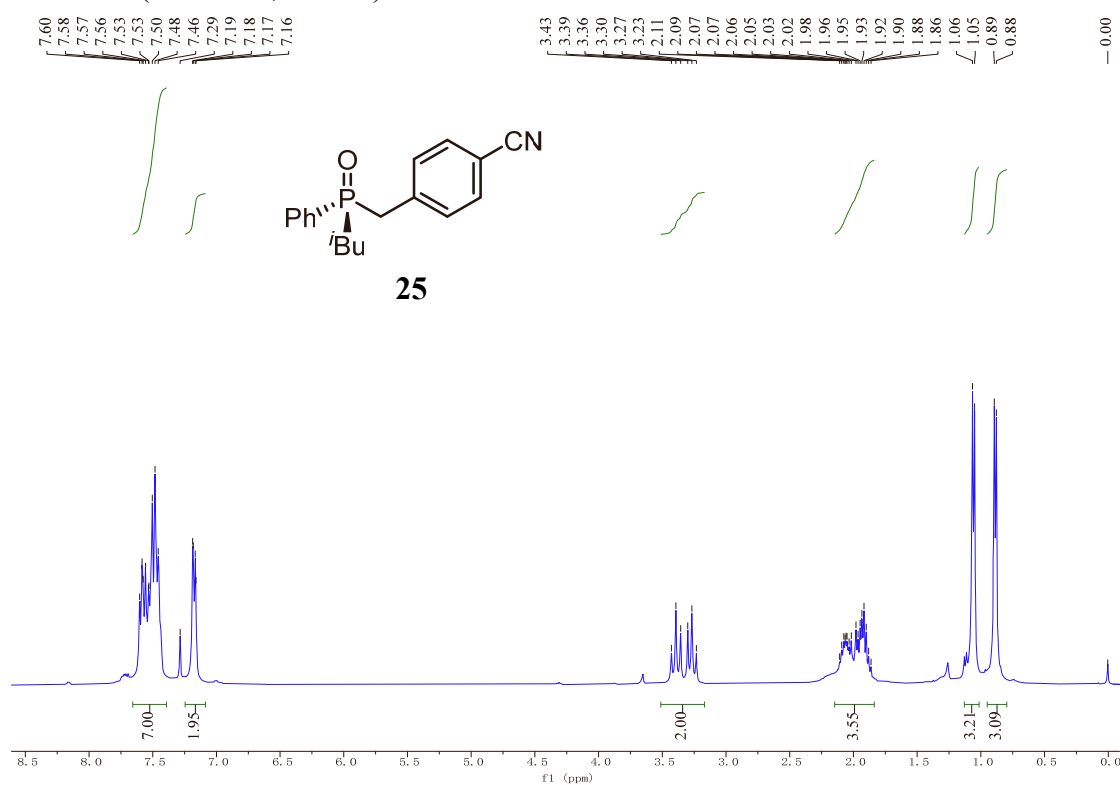
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



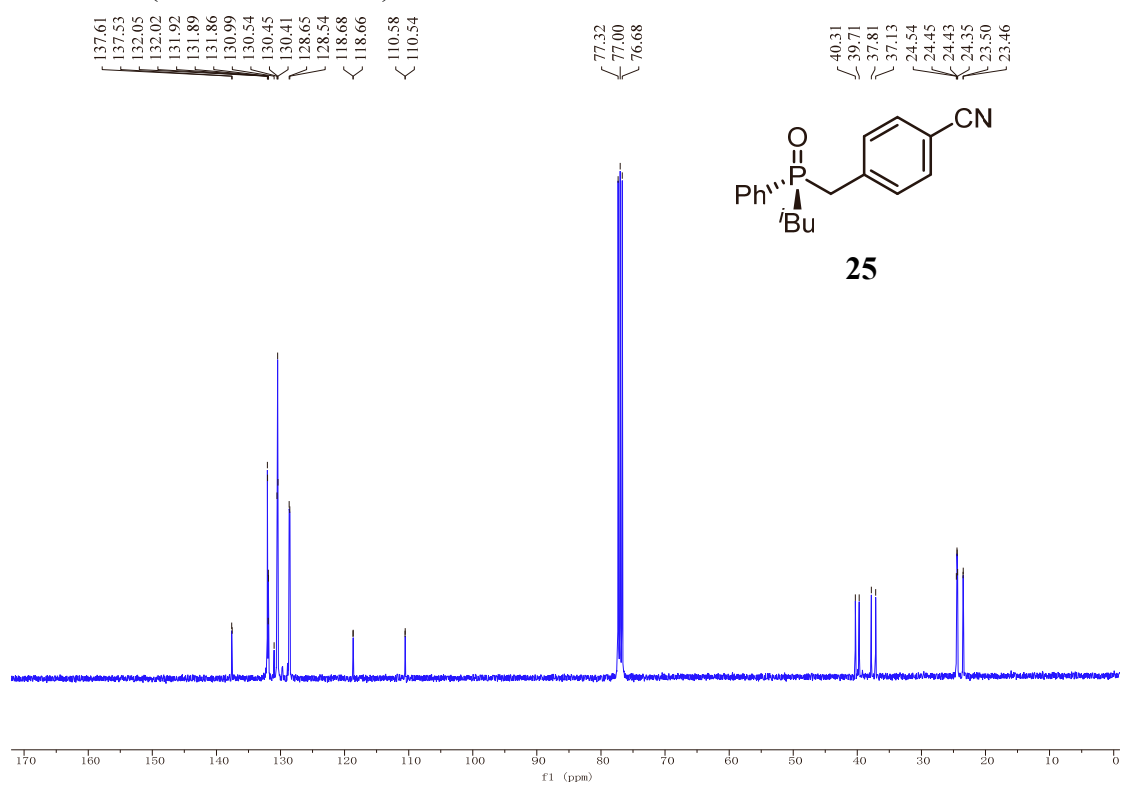
**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )



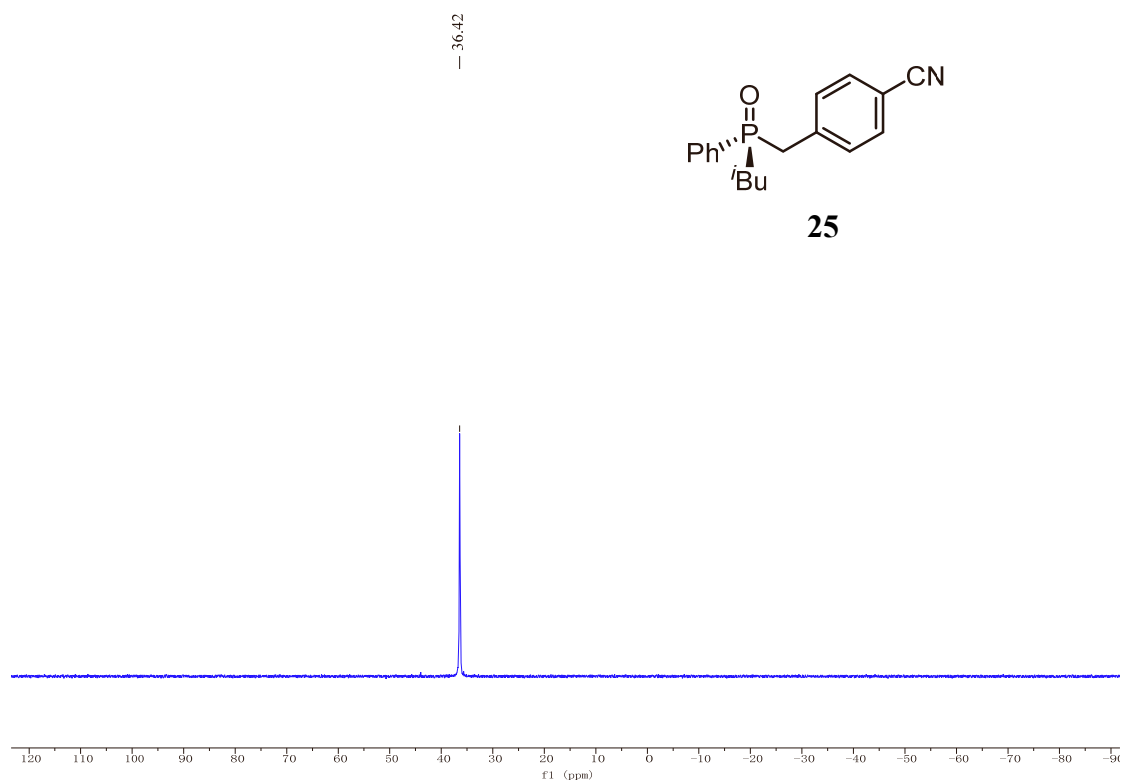
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

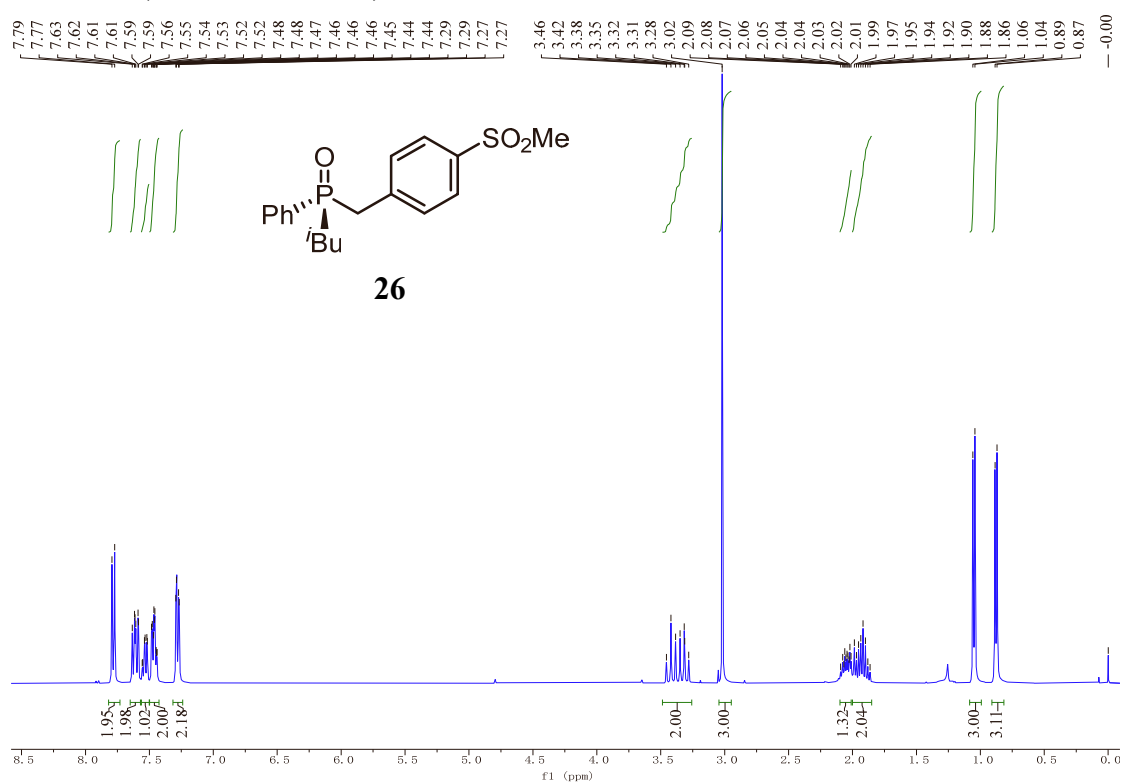


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

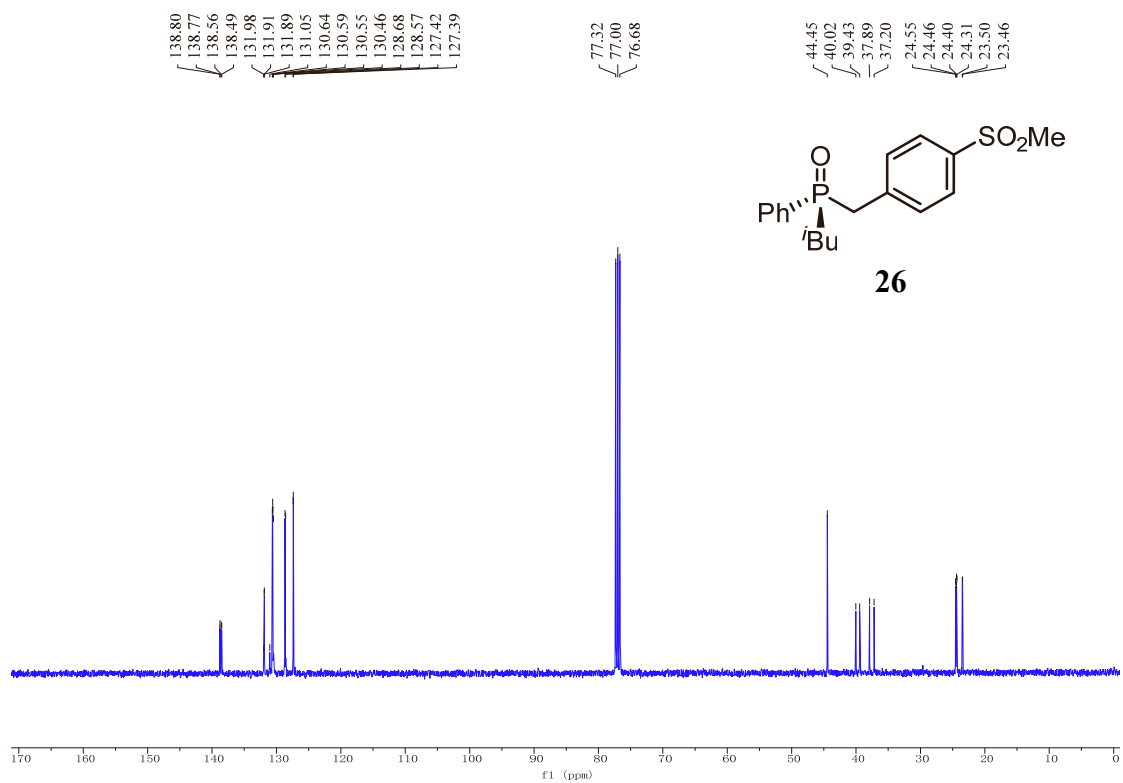




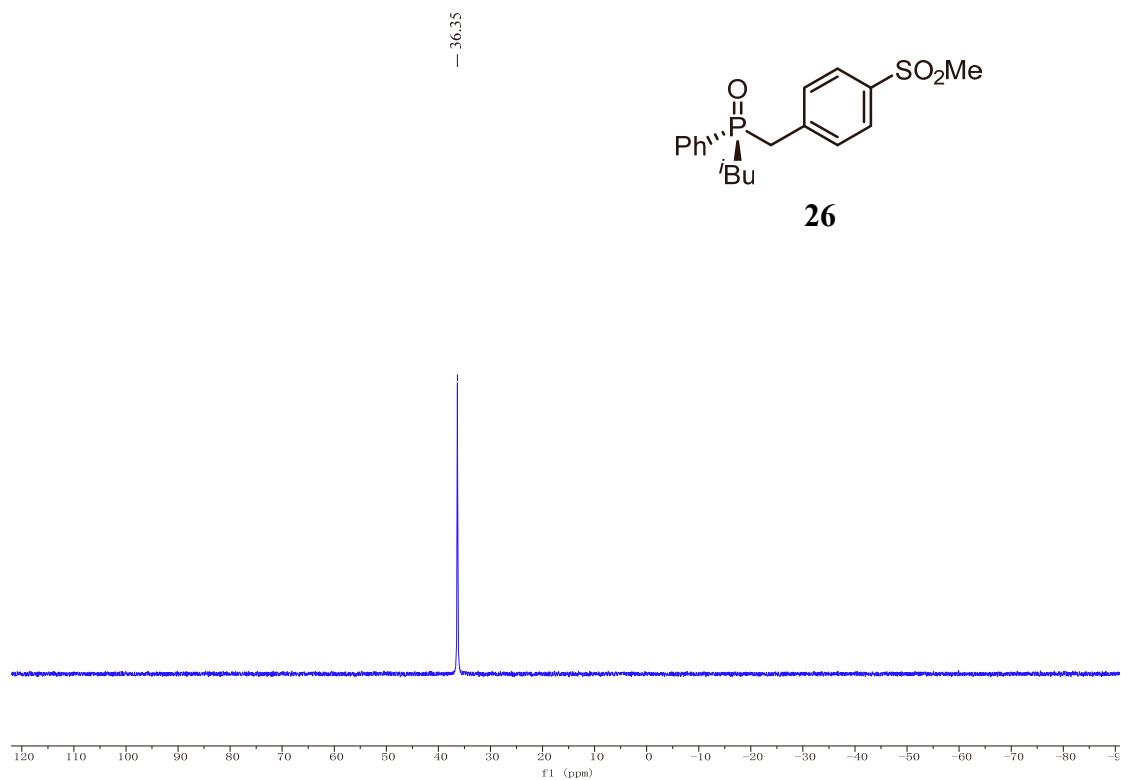
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



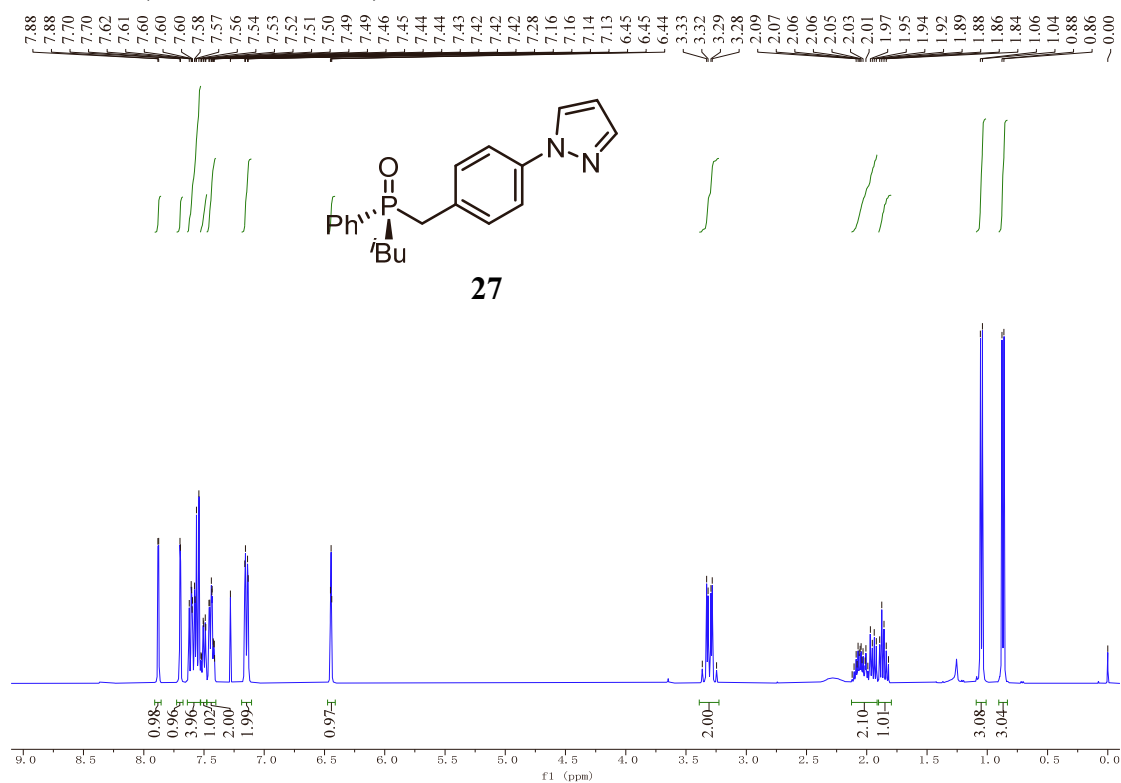
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



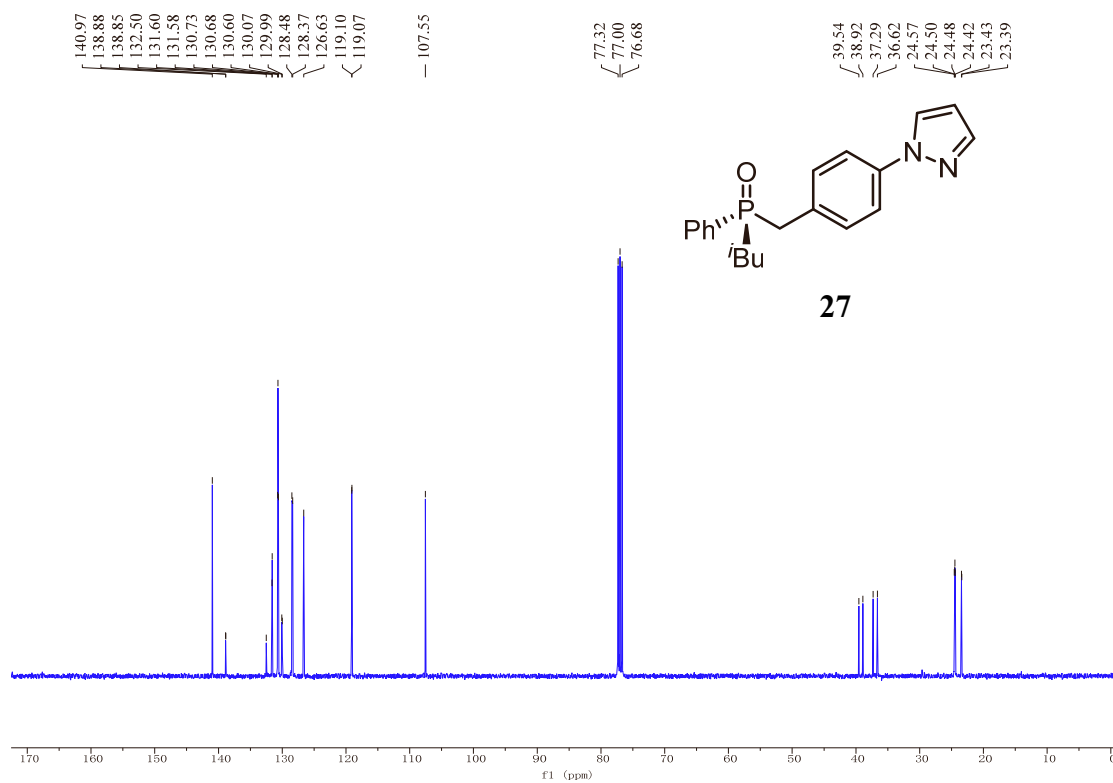
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



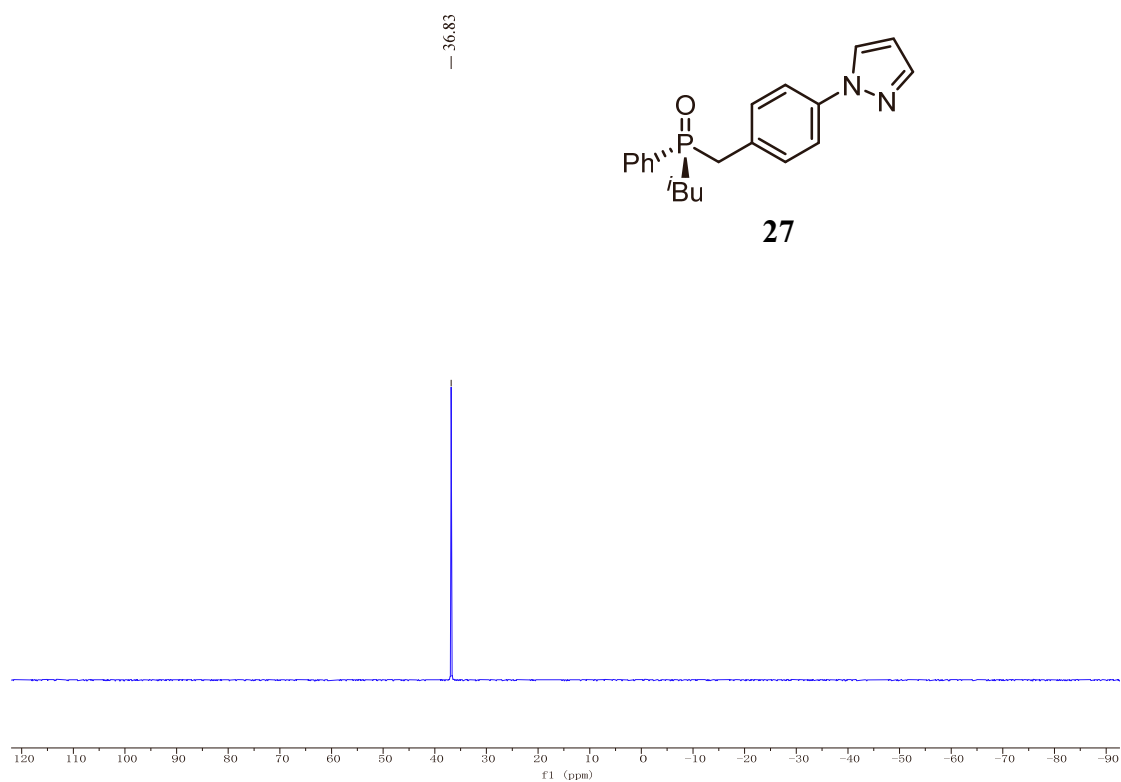
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



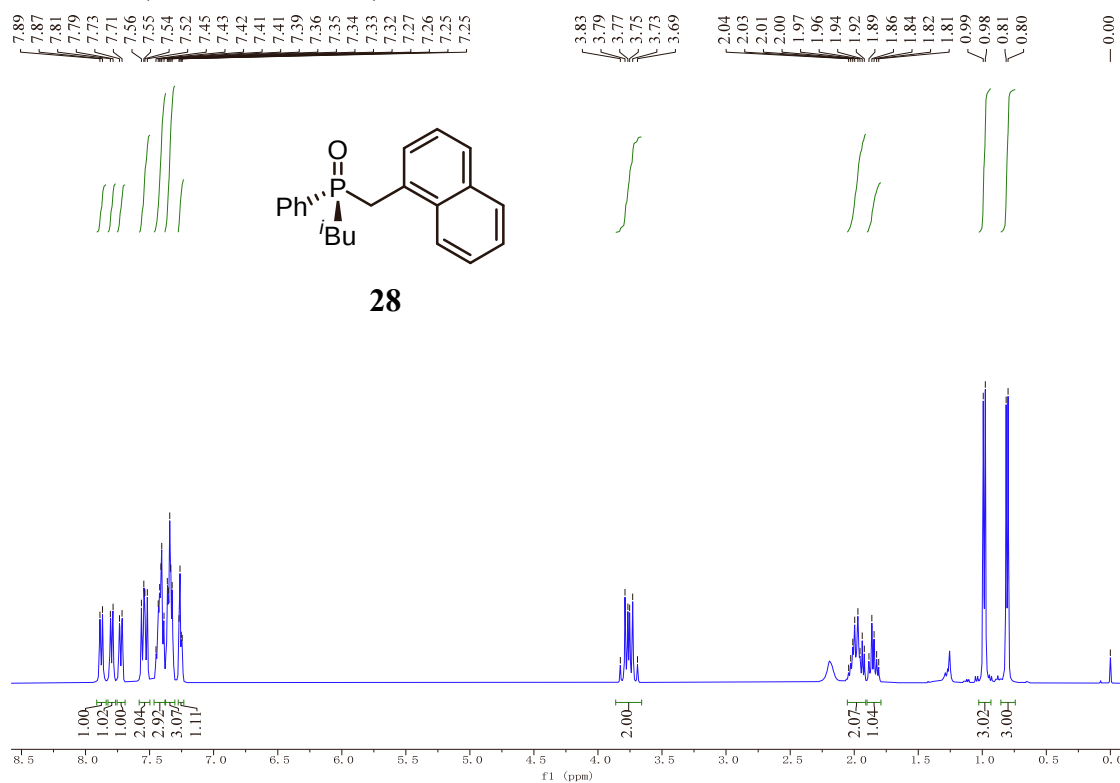
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



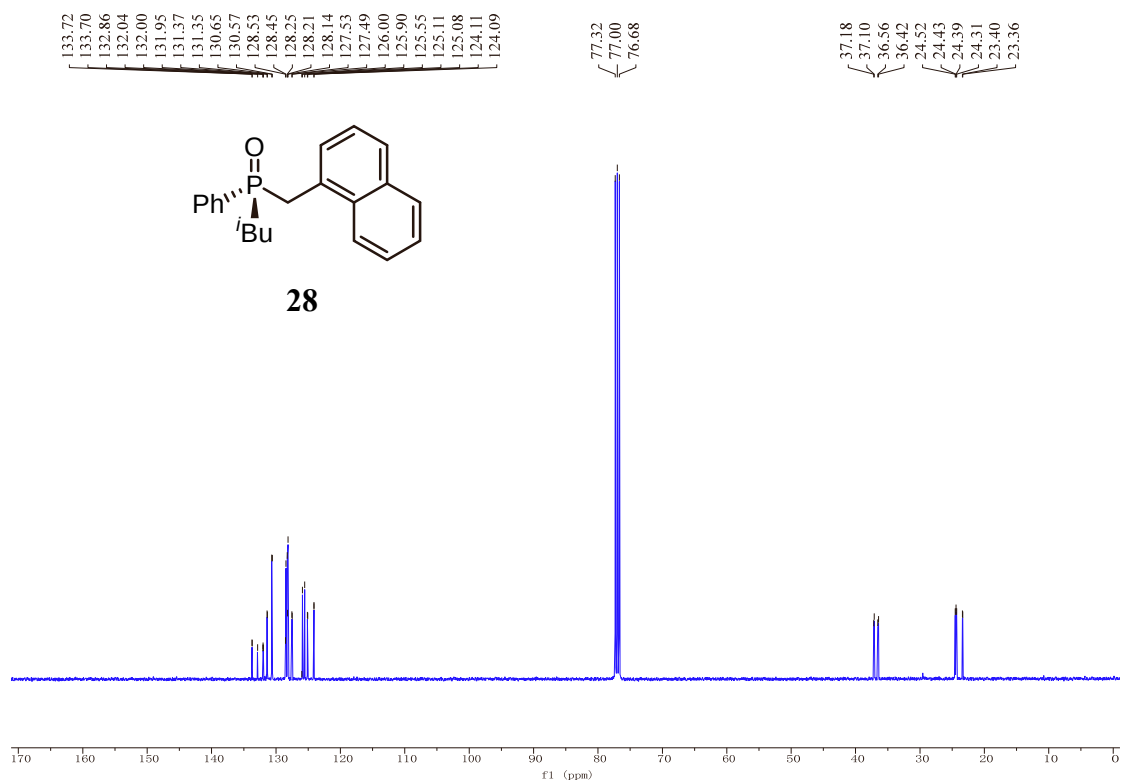
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



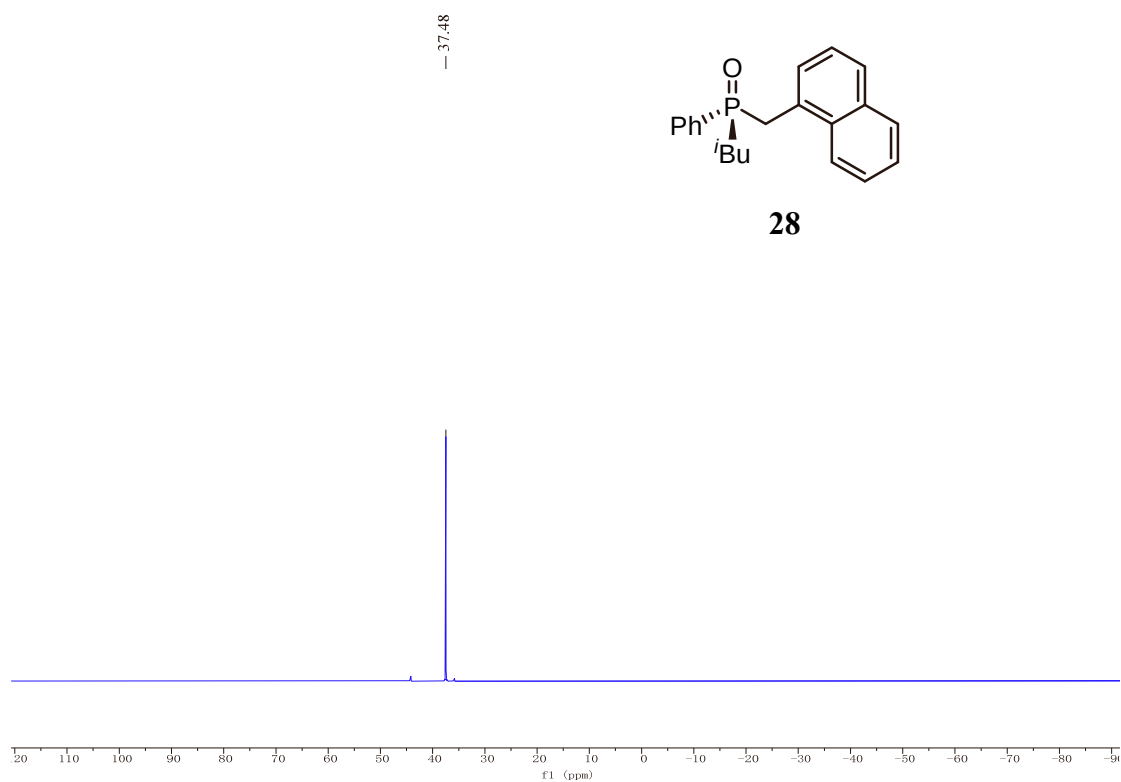
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



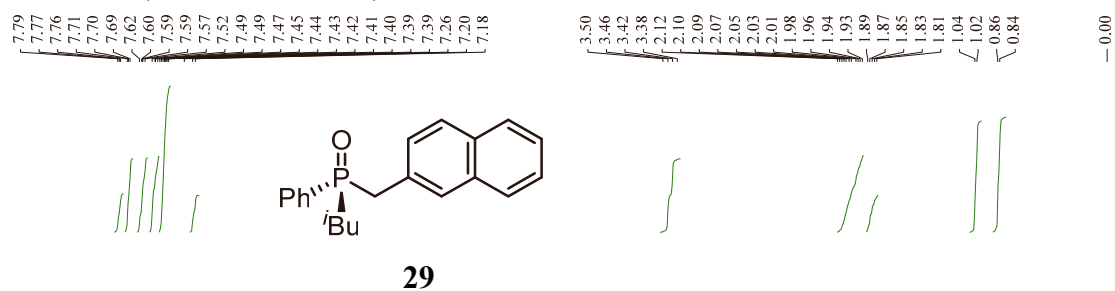
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



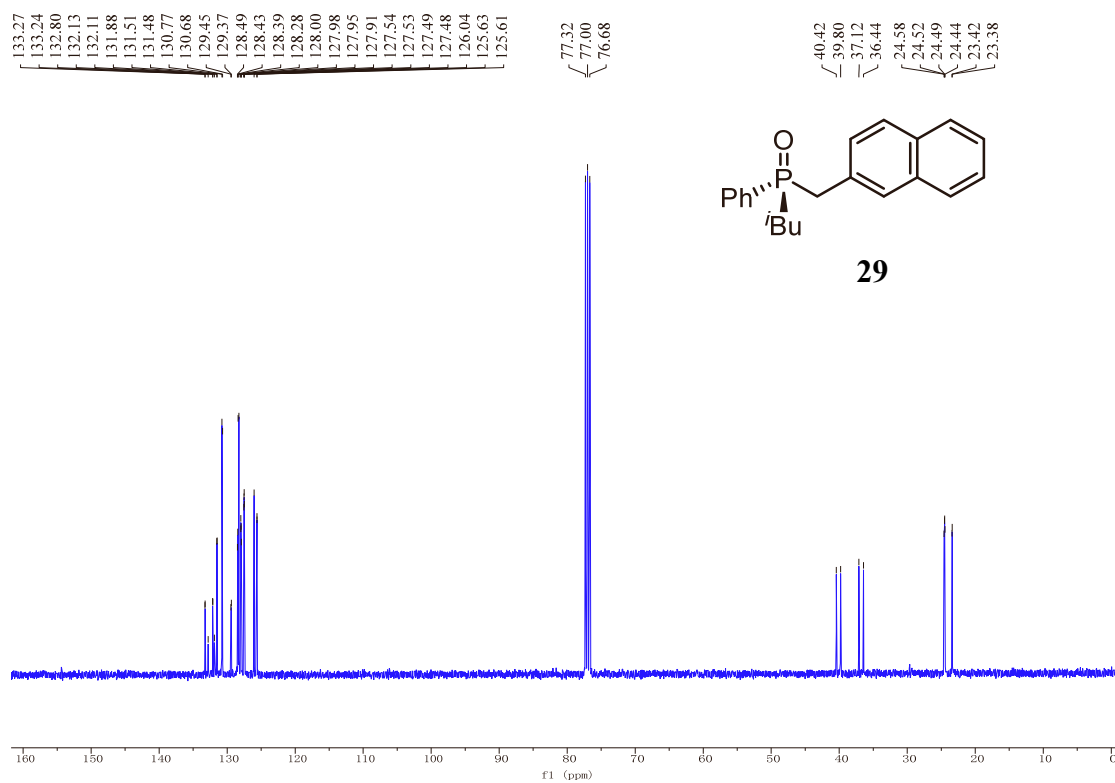
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



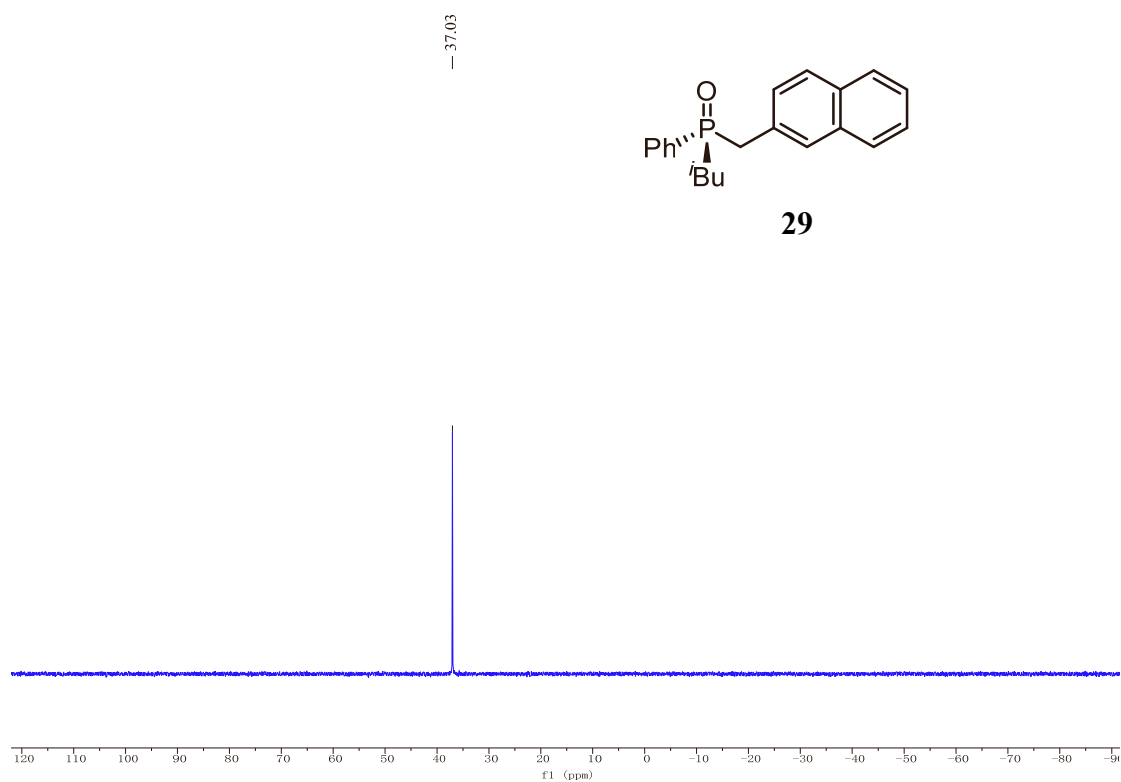
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

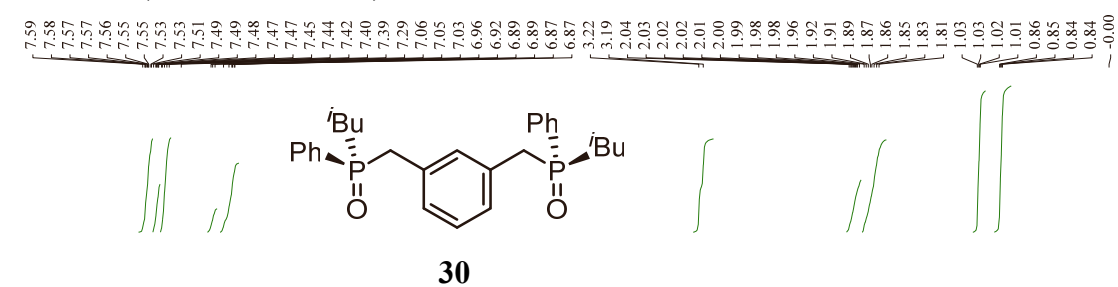


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

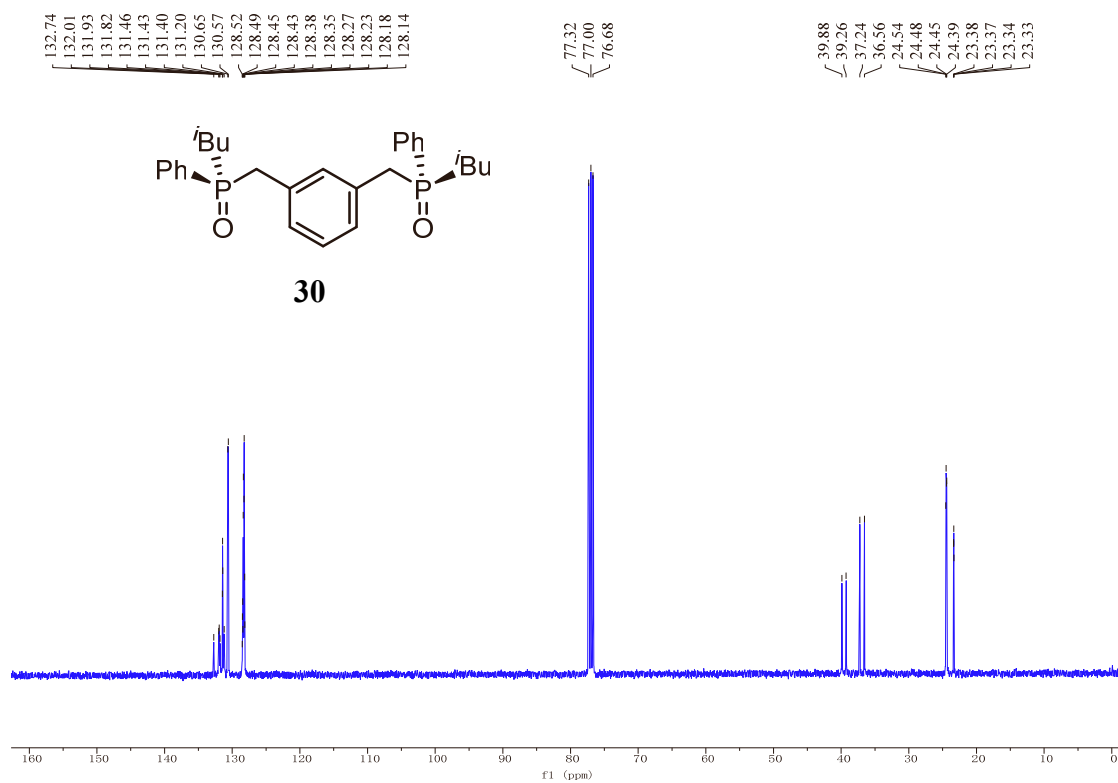




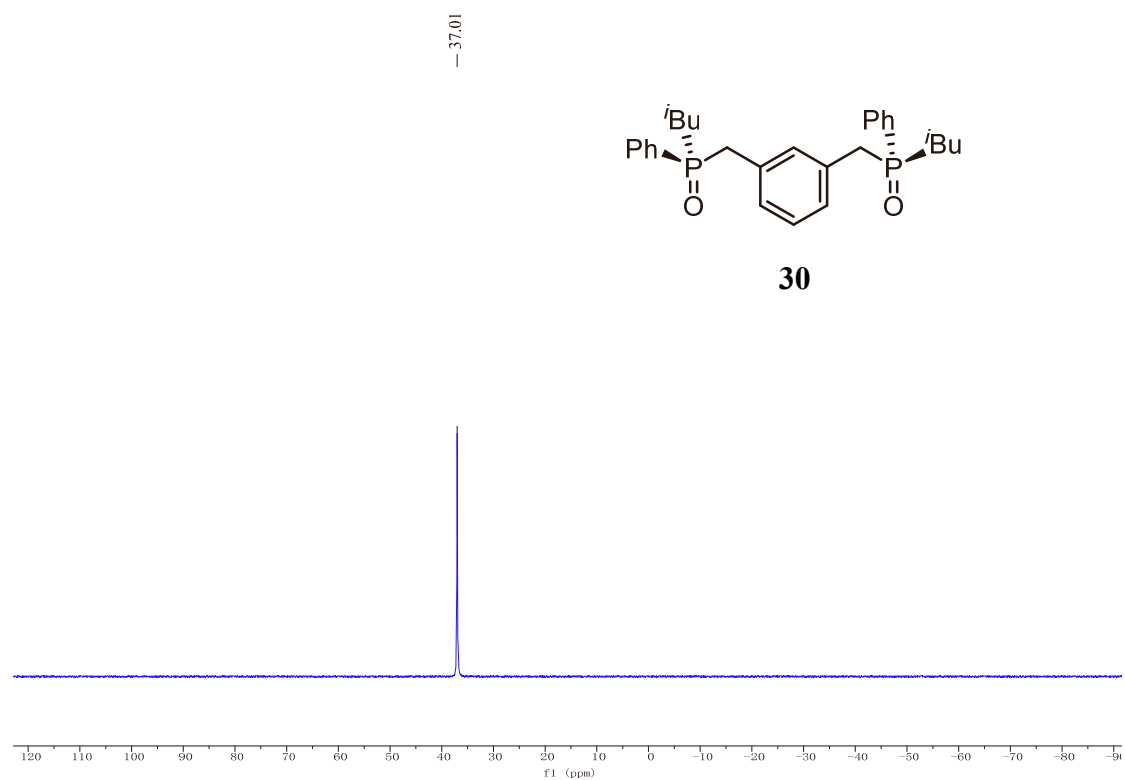
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



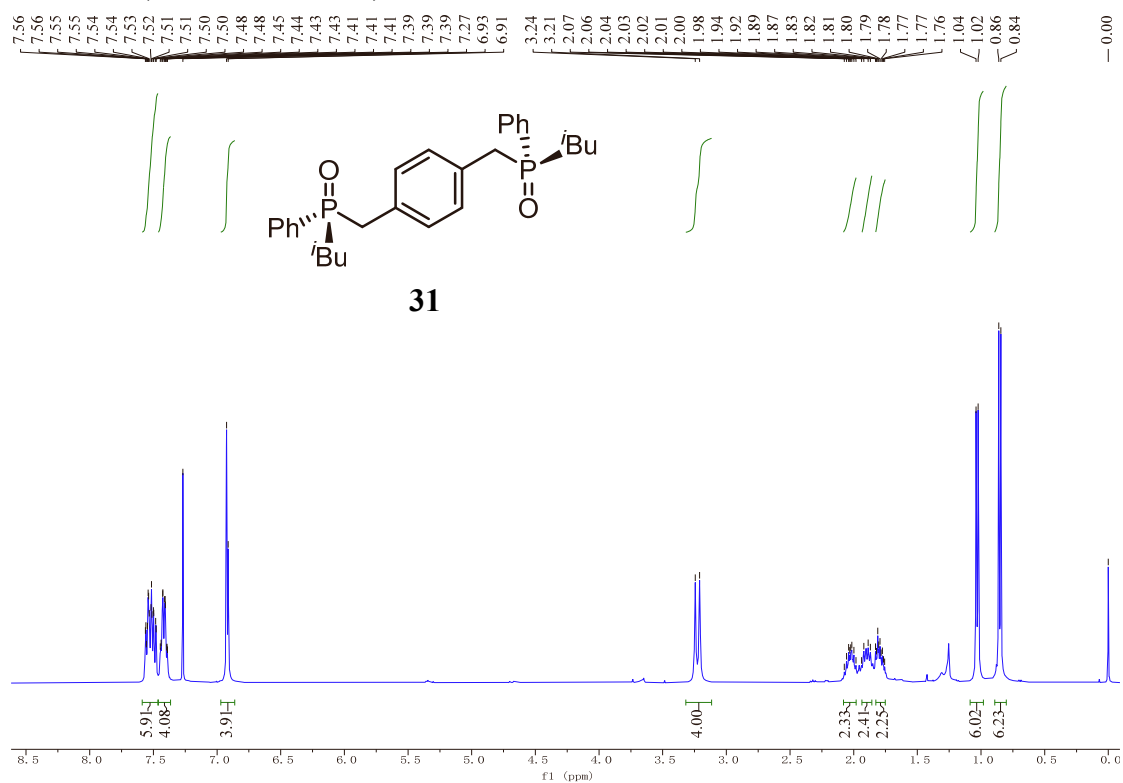
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



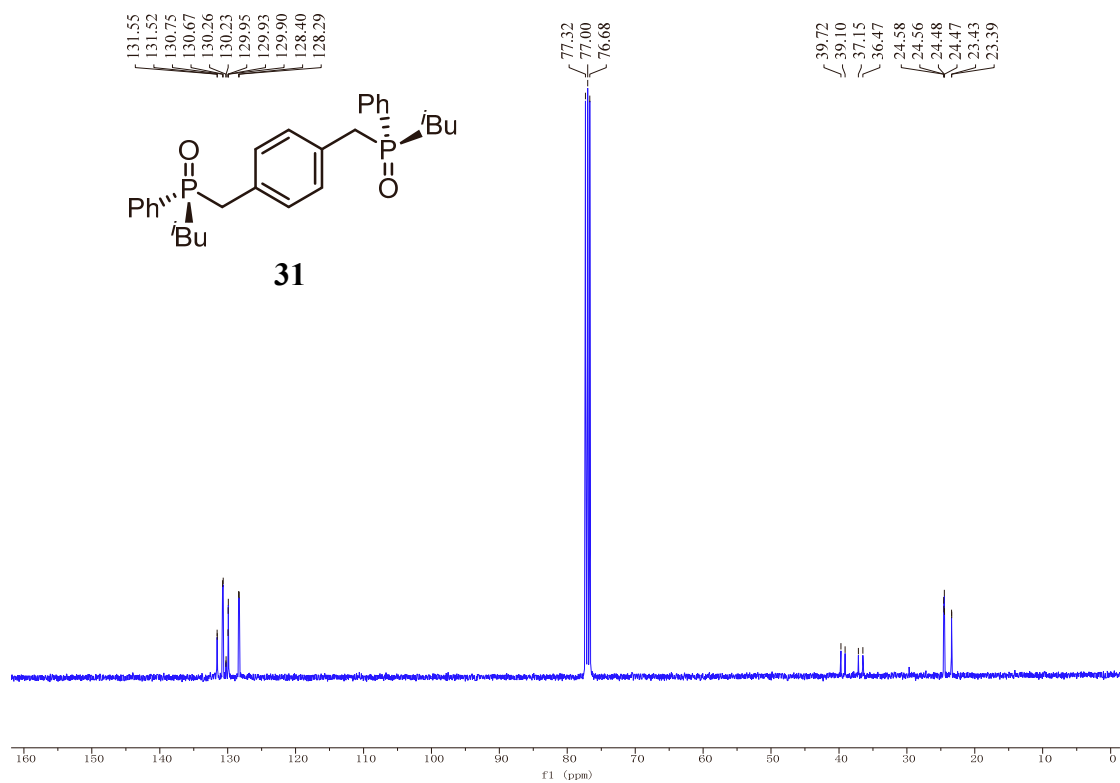
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



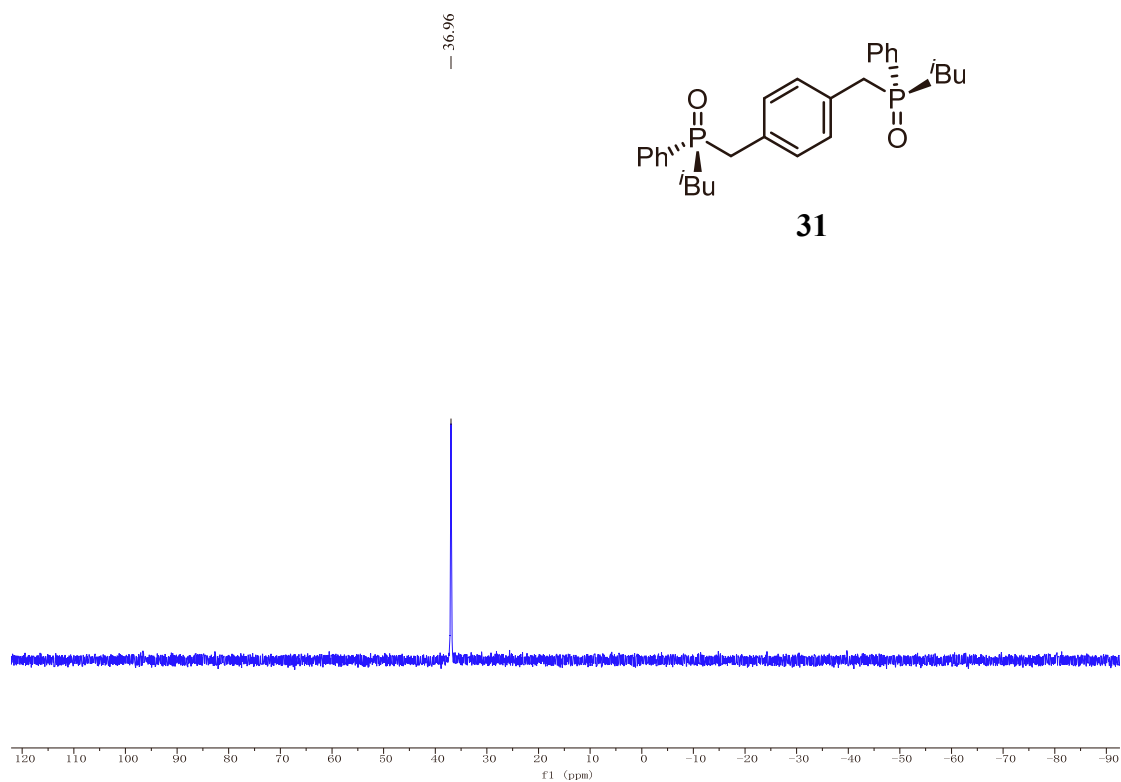
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



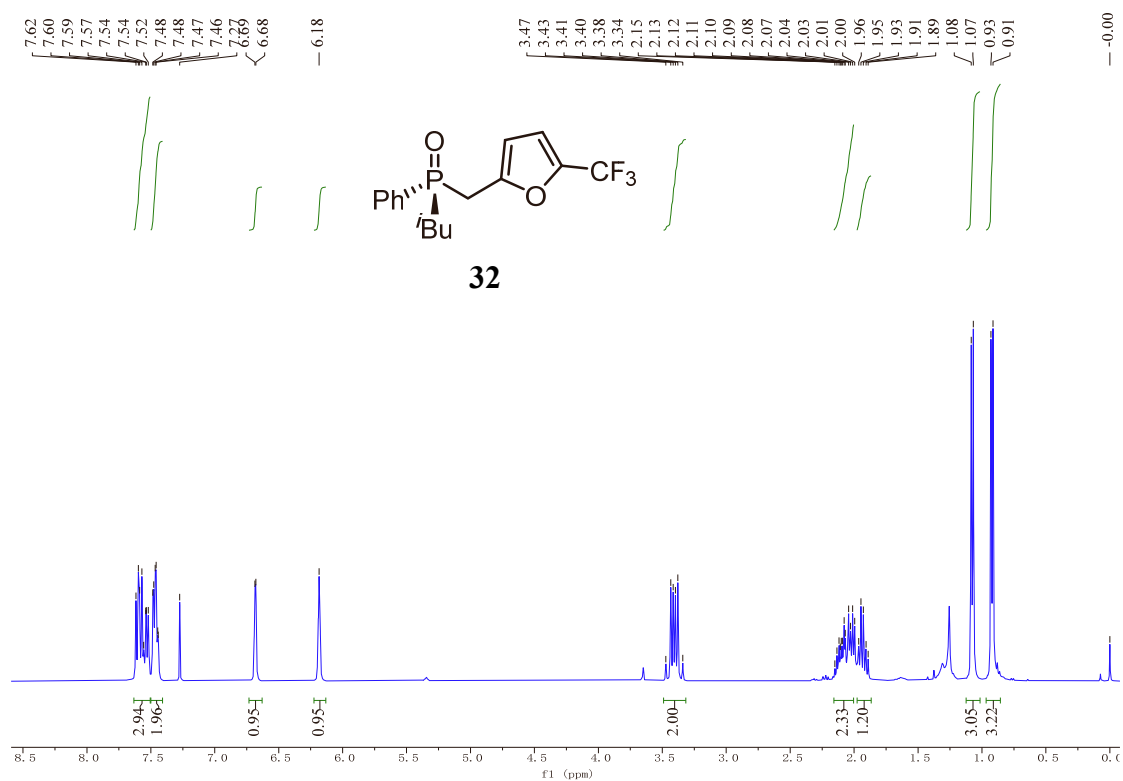
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



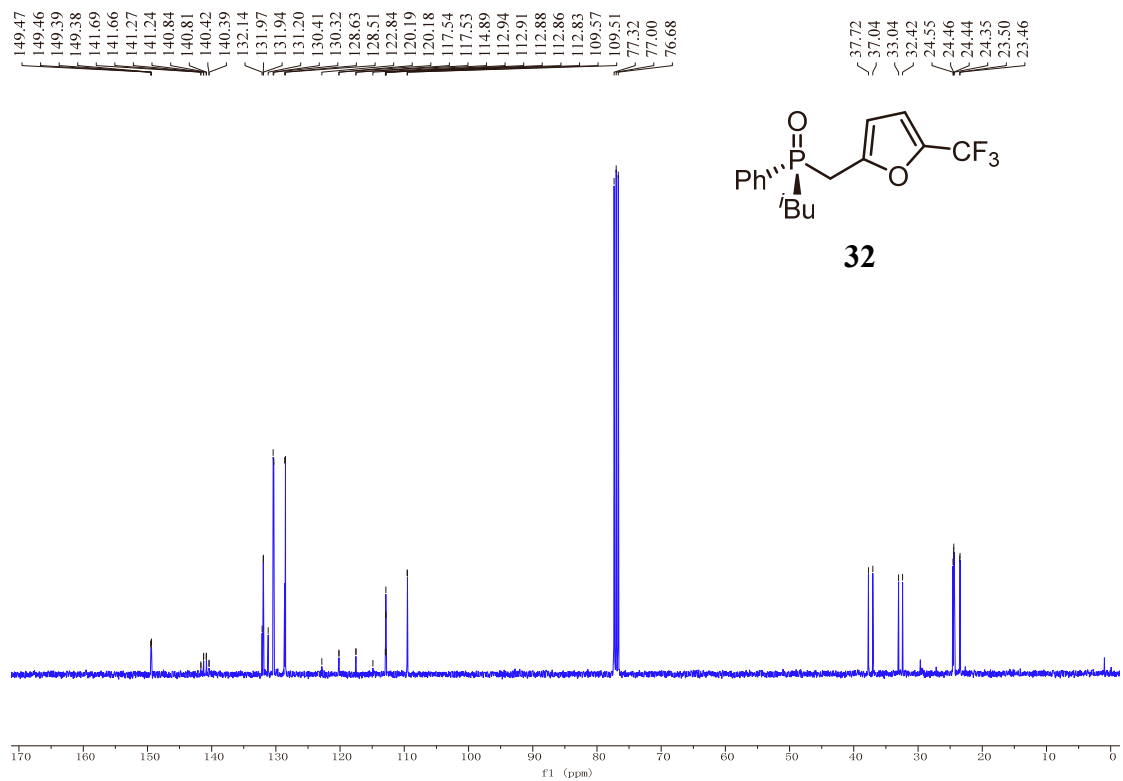
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



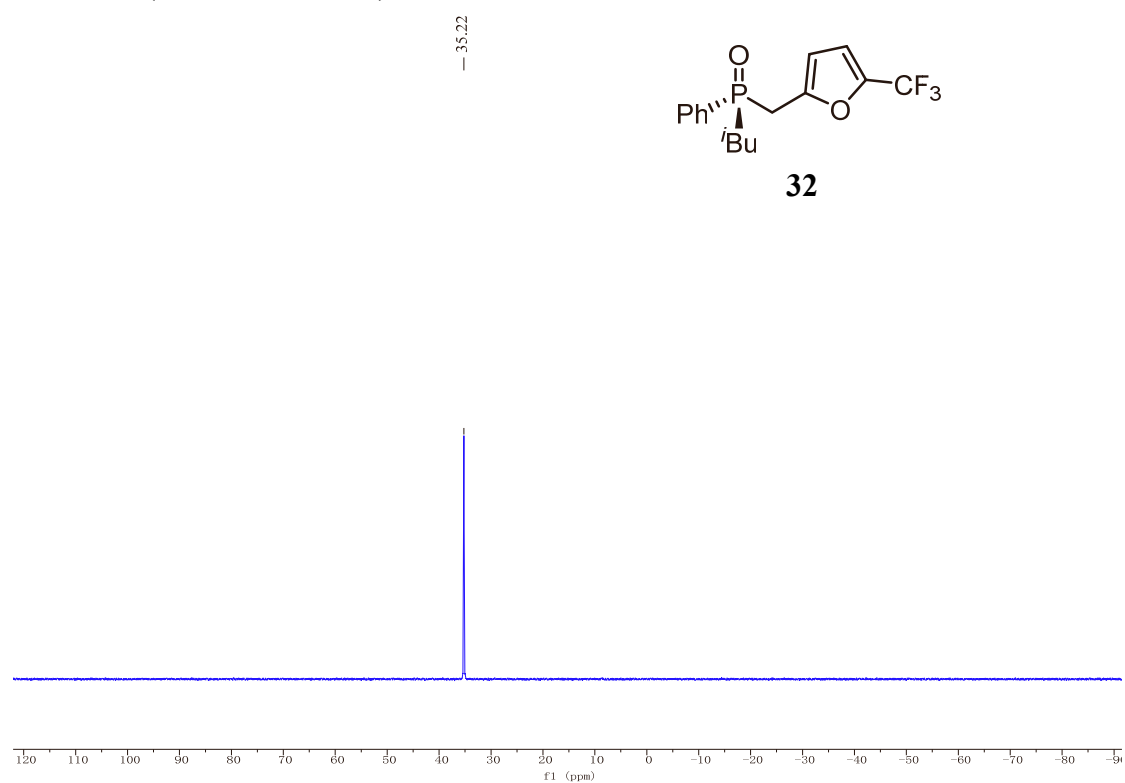
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



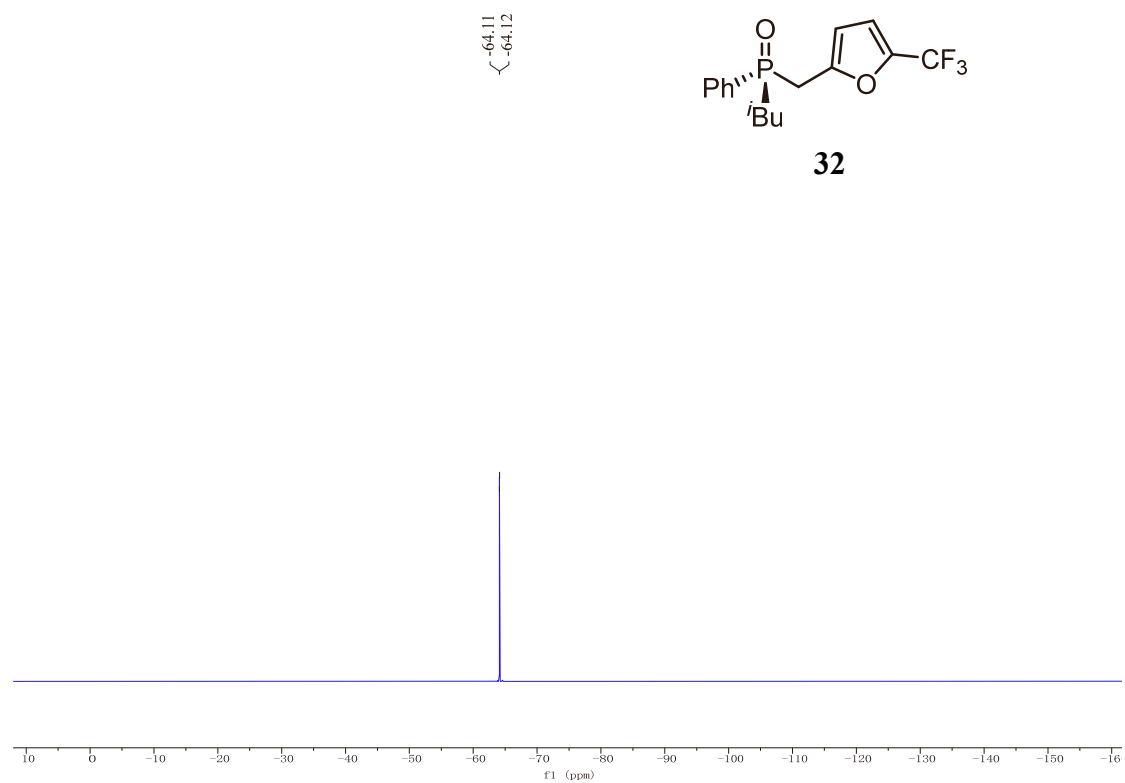
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



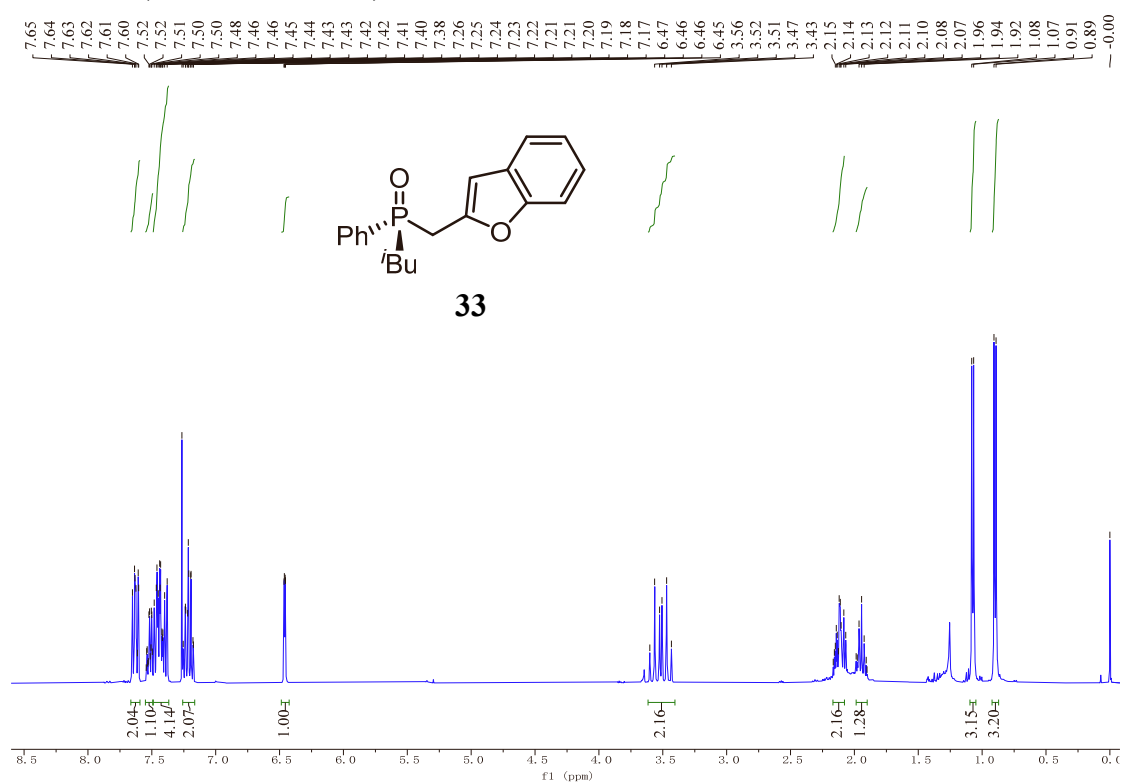
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



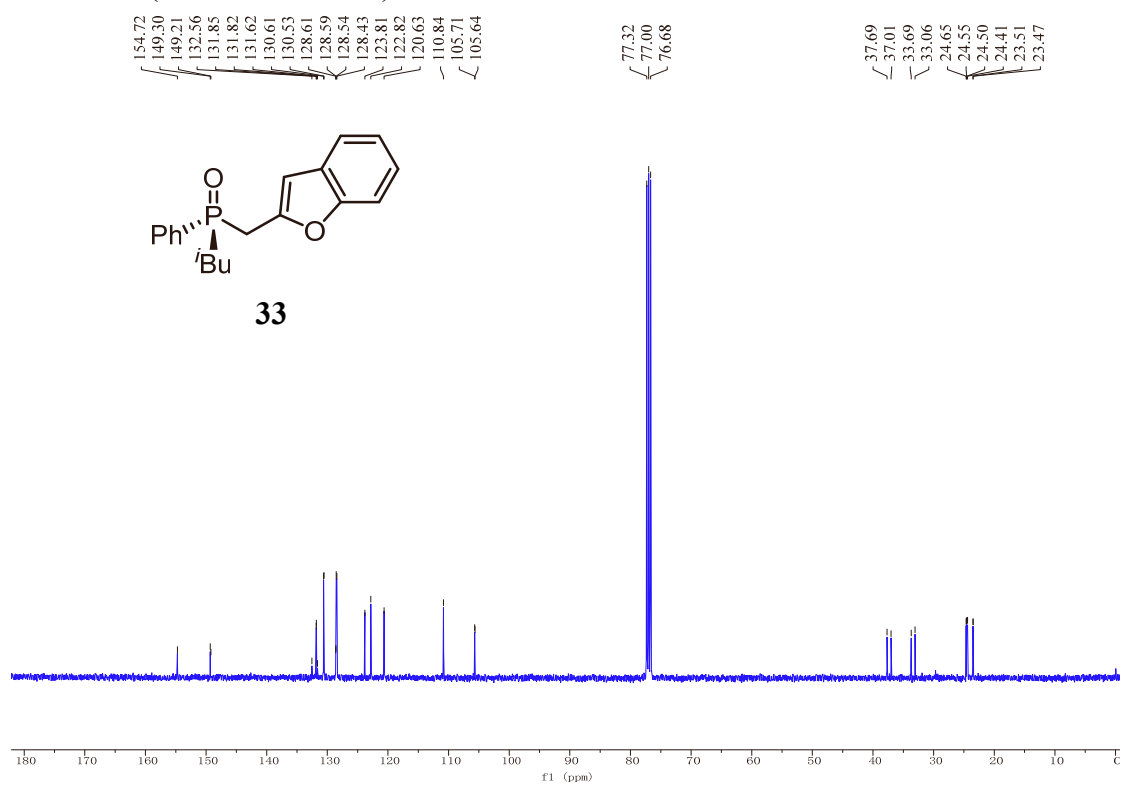
**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )



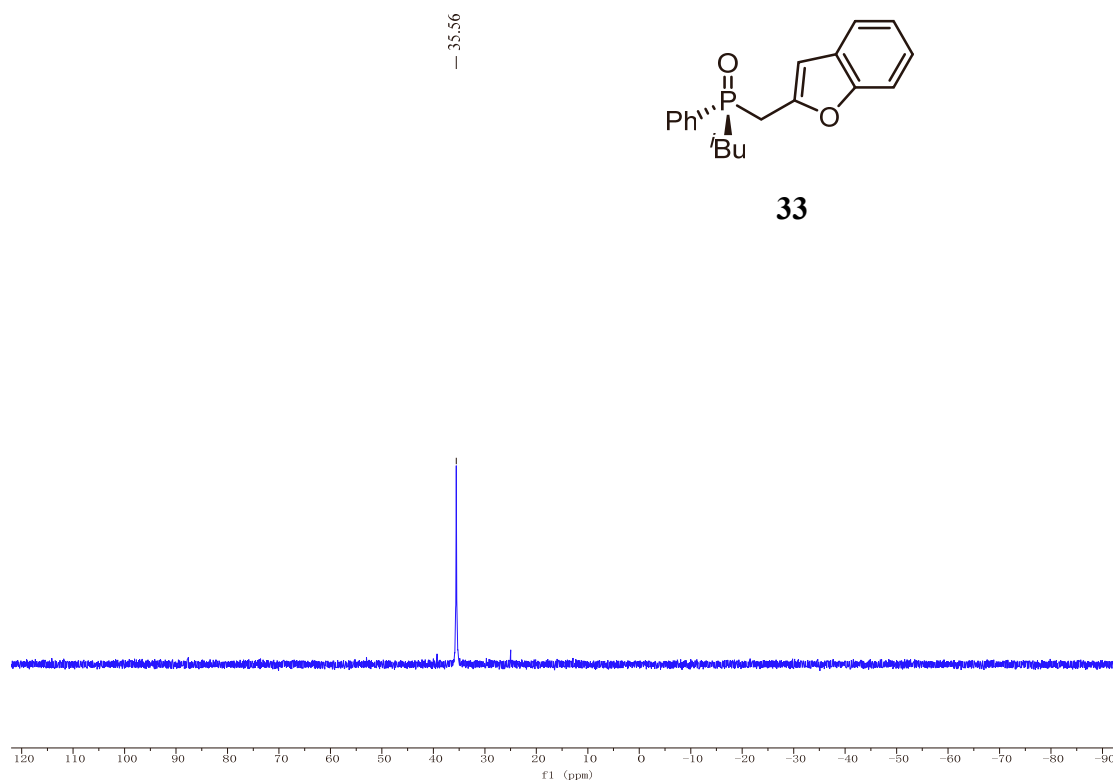
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

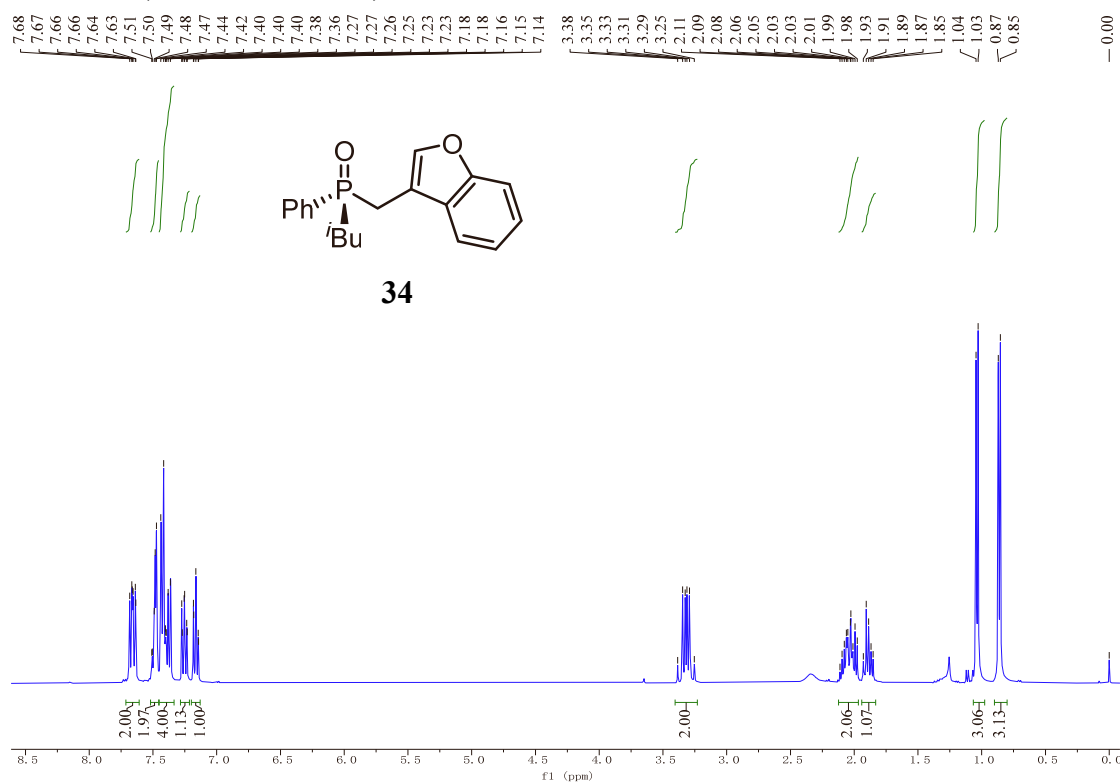


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

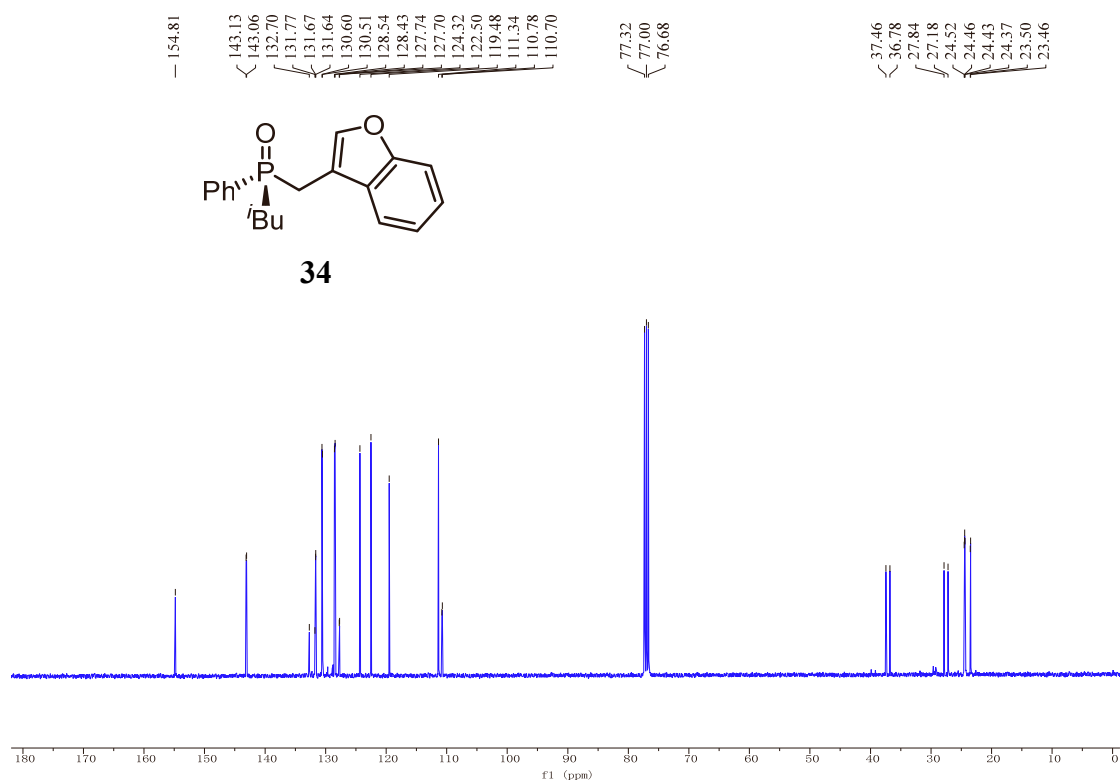




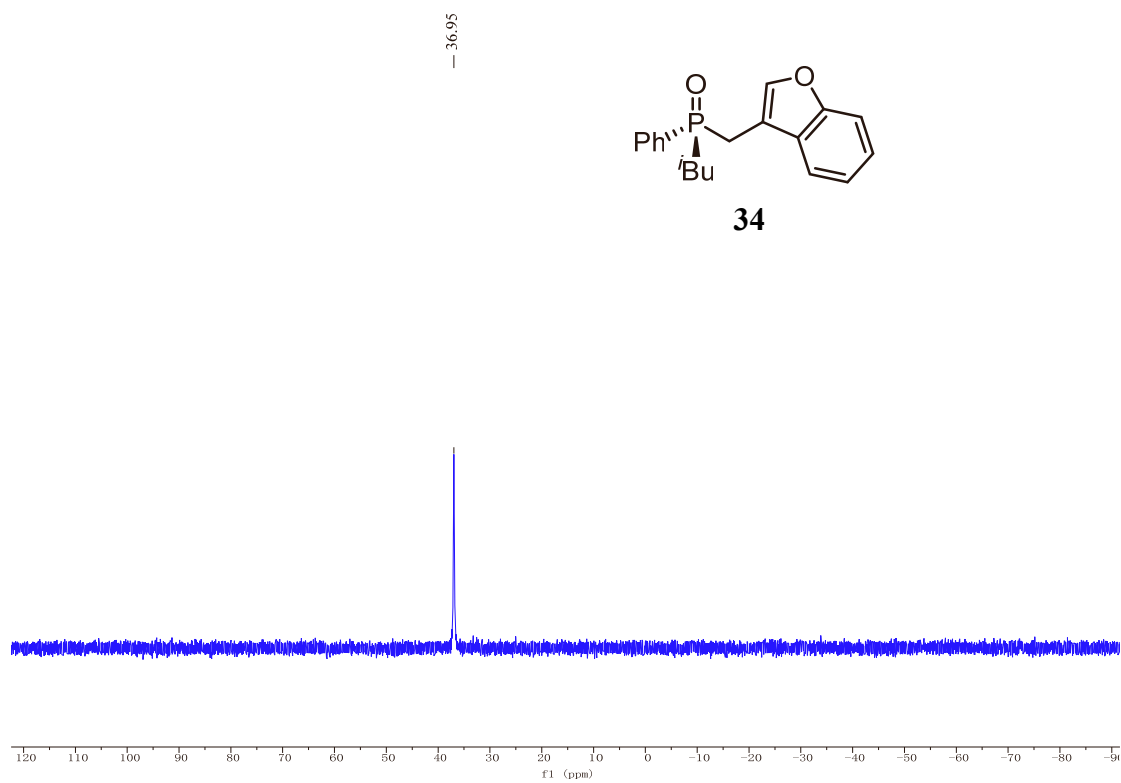
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



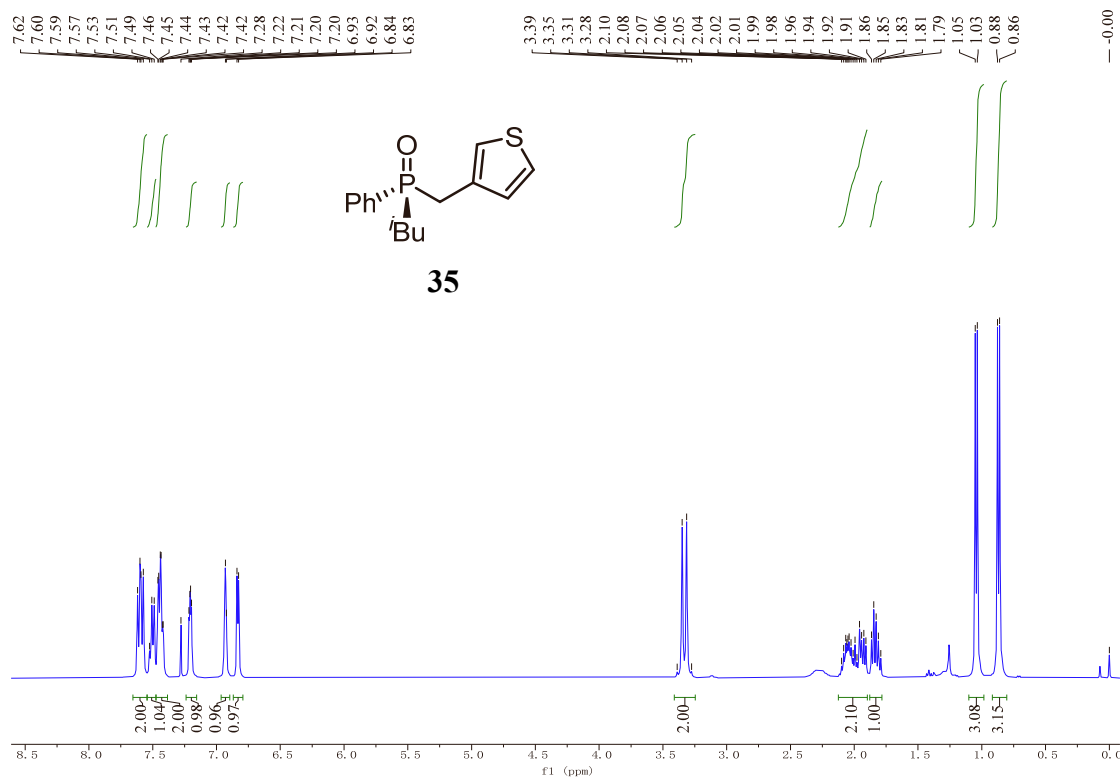
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



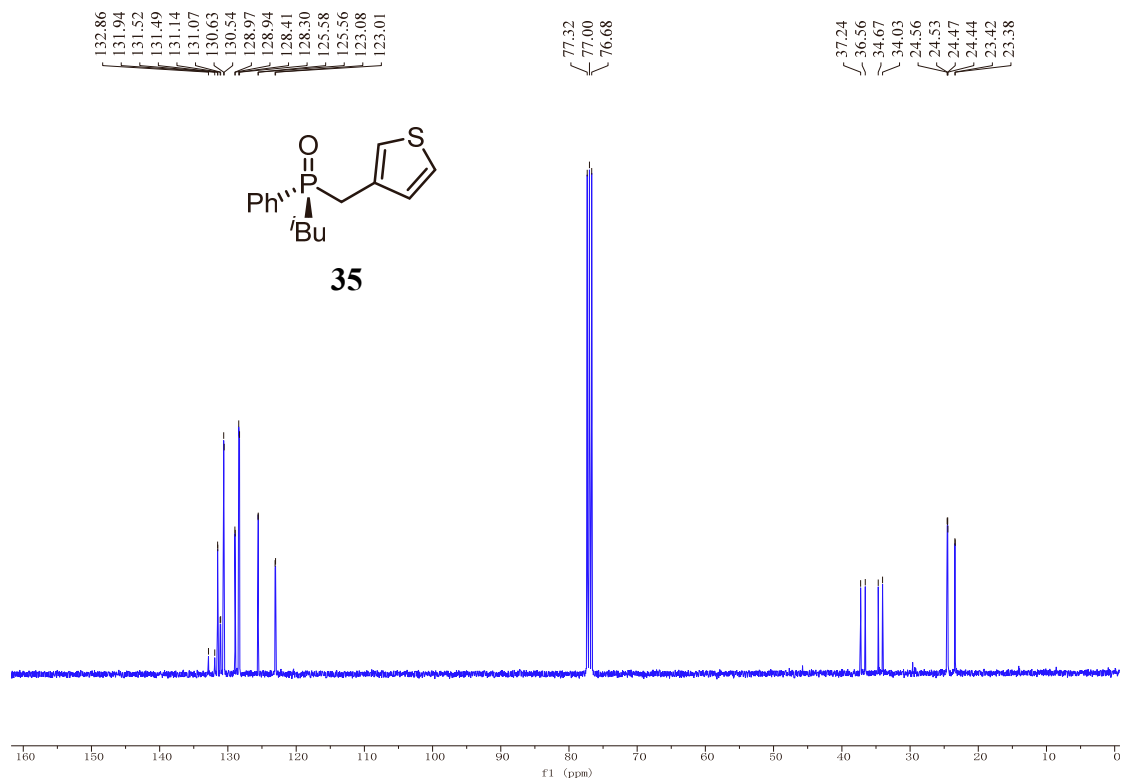
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



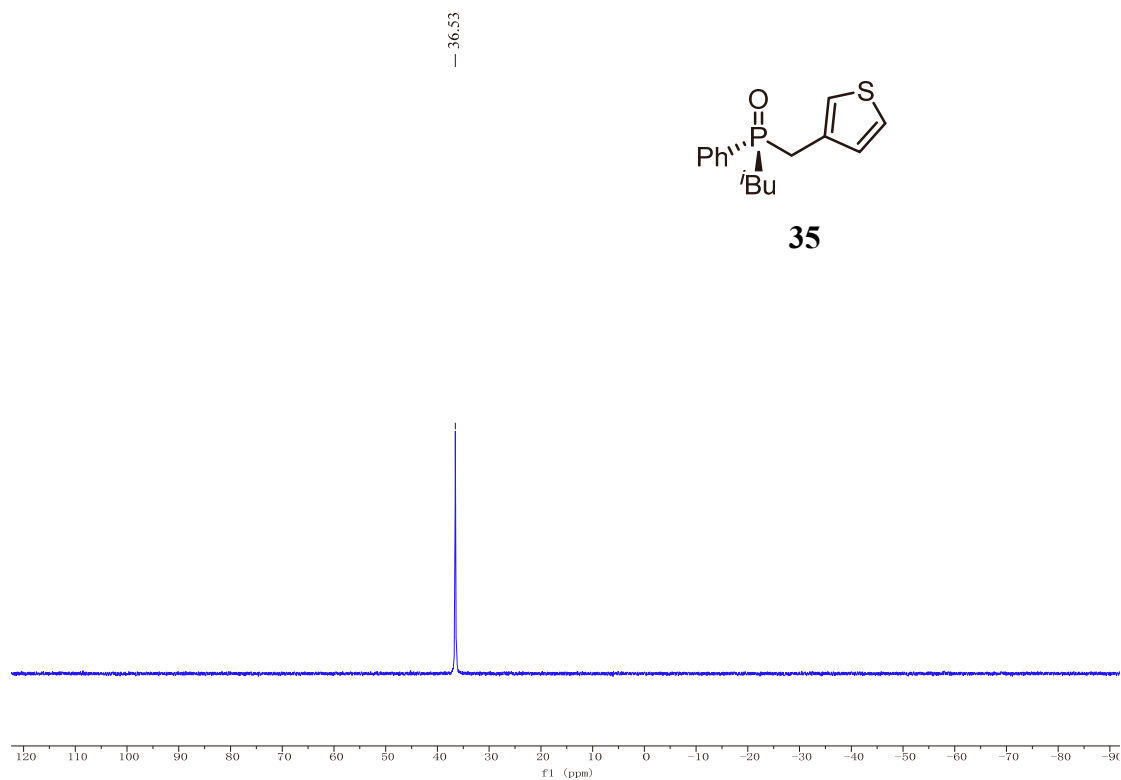
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



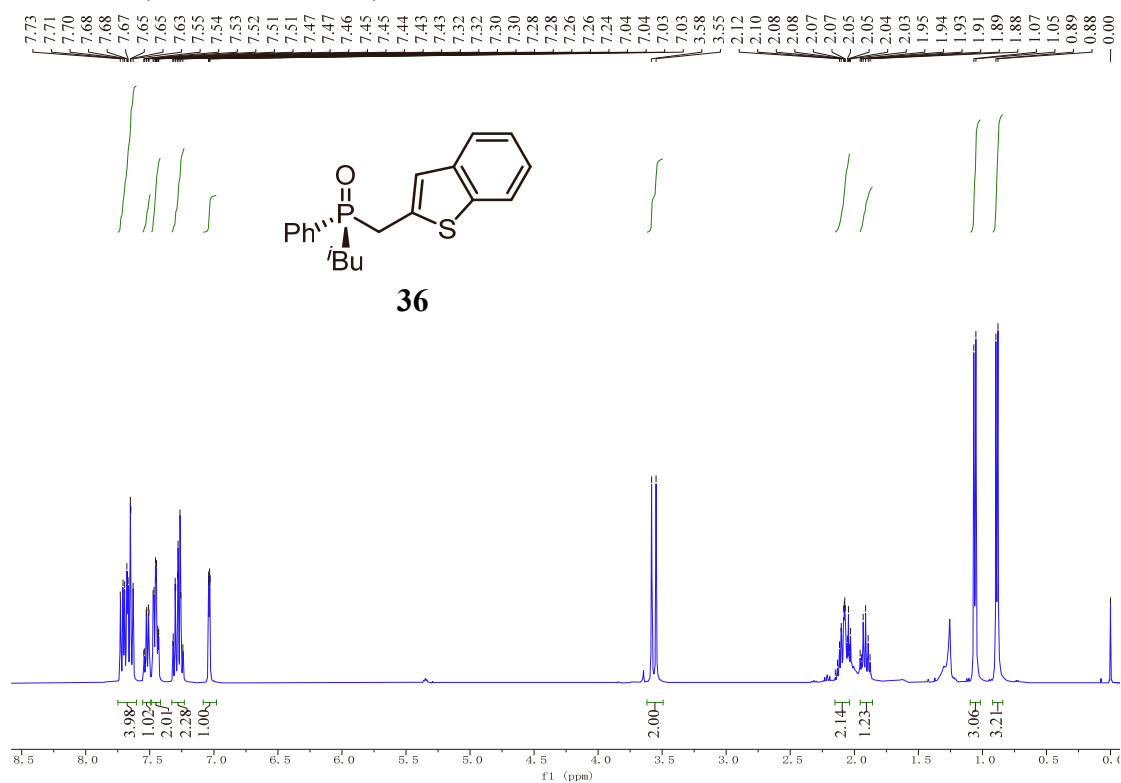
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



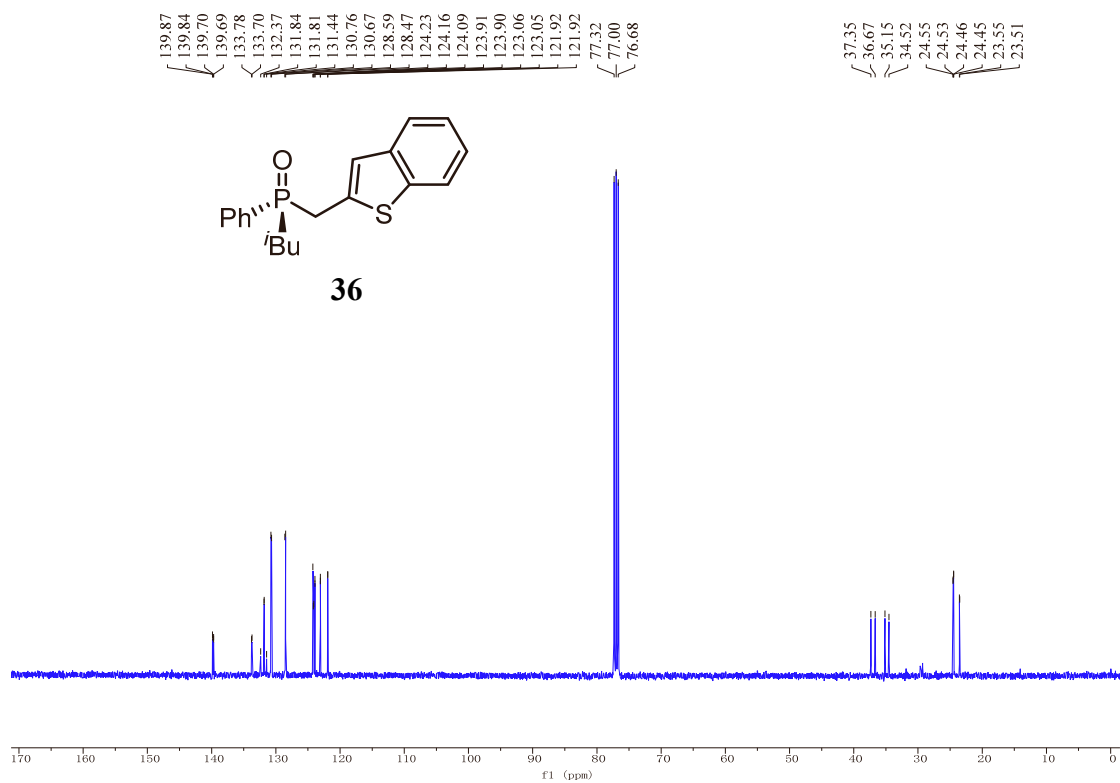
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



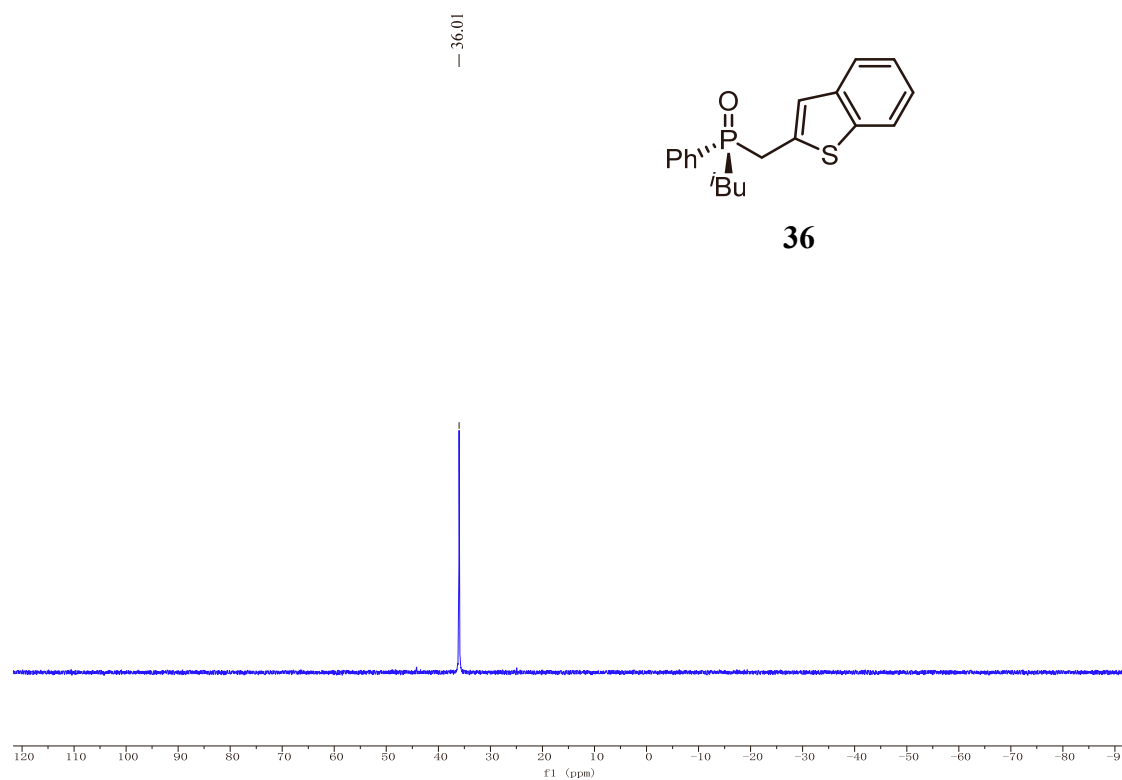
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



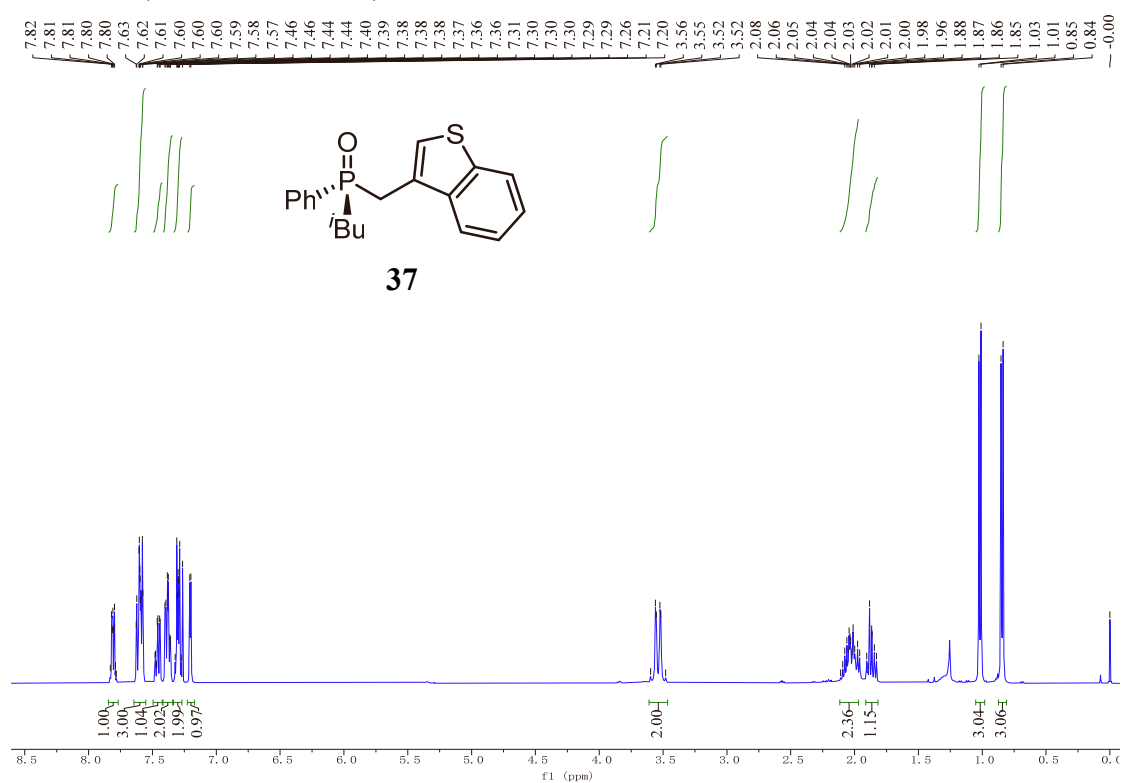
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



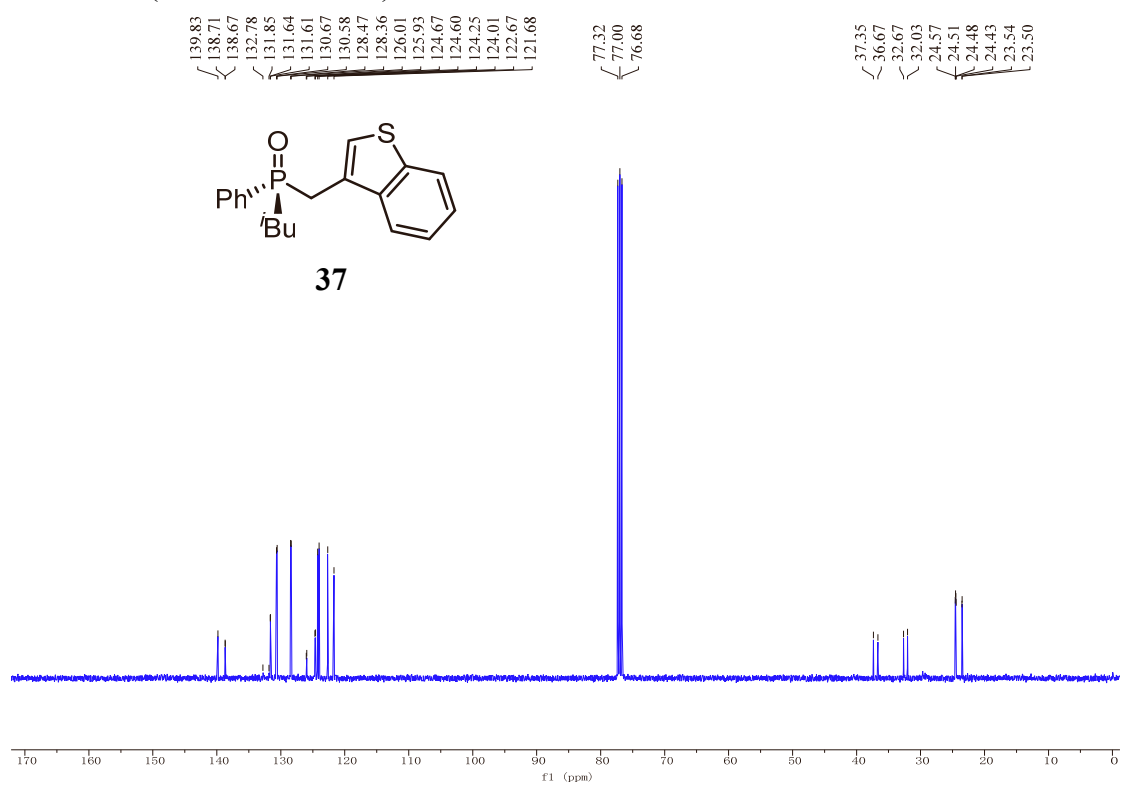
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



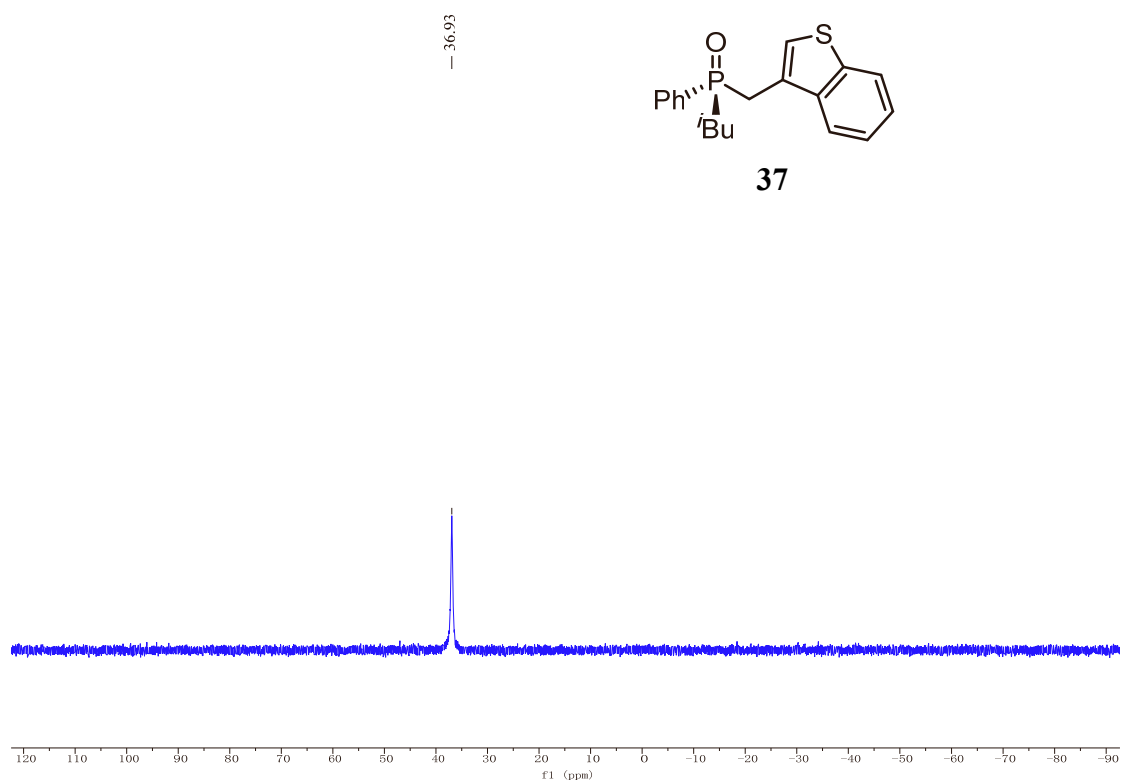
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

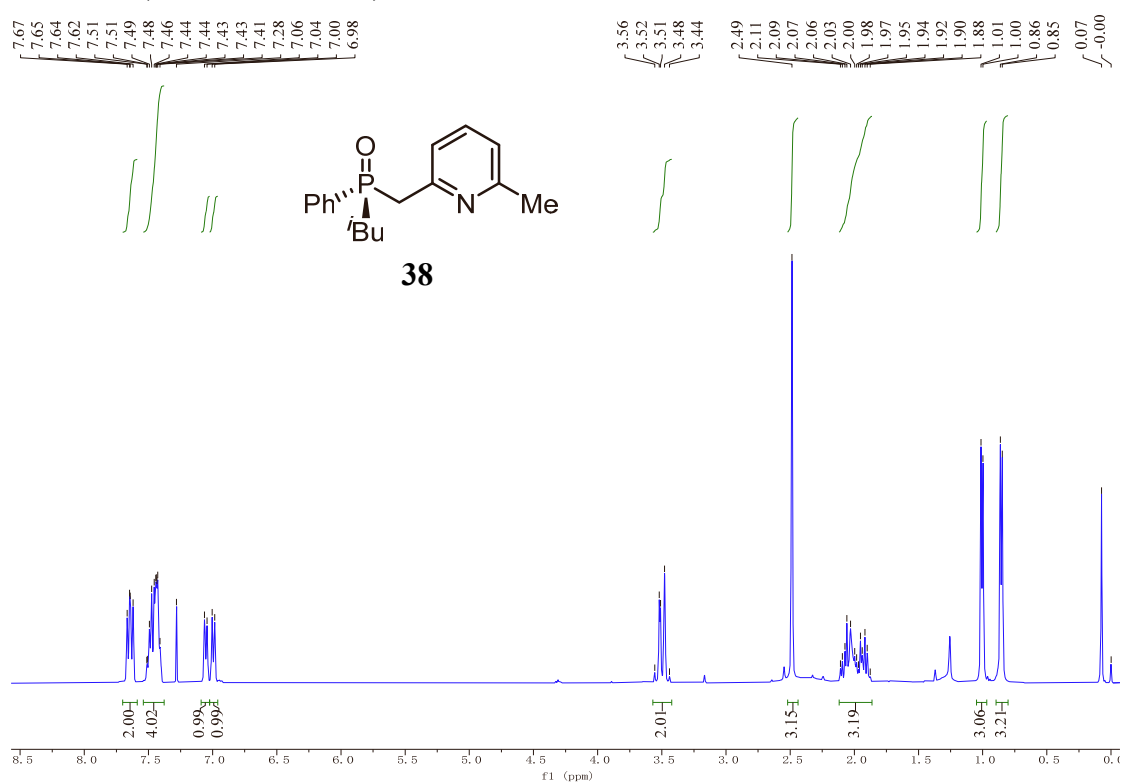


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

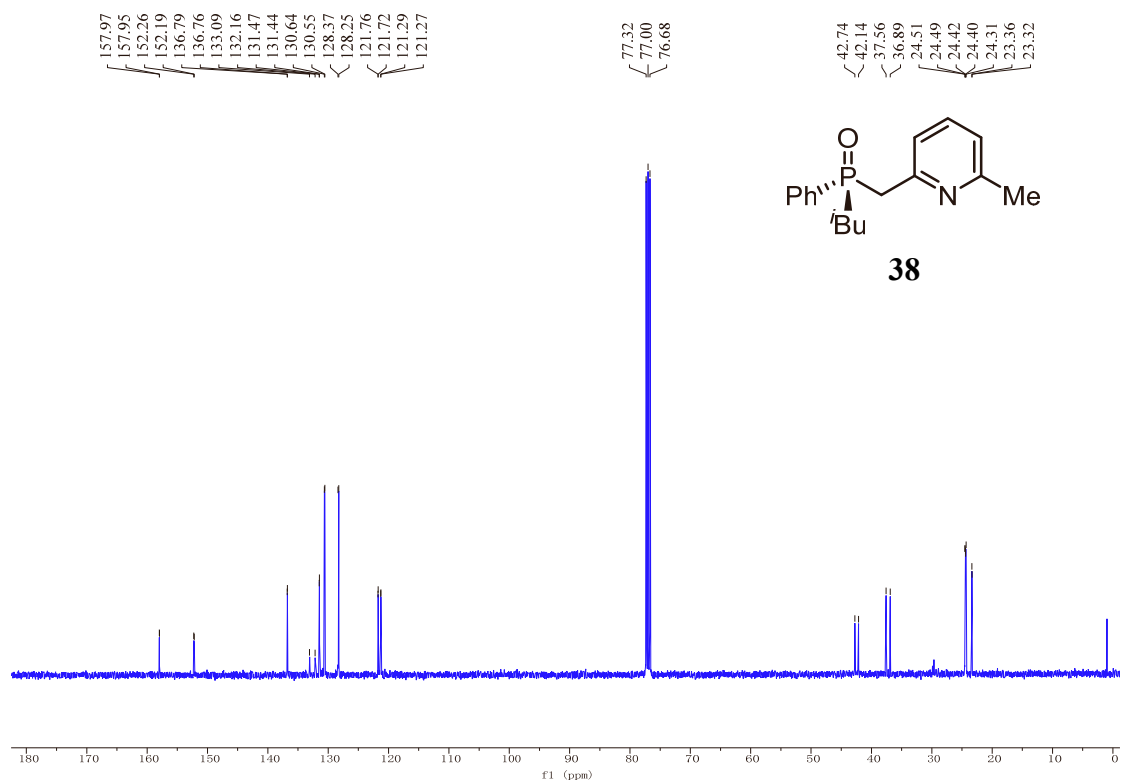




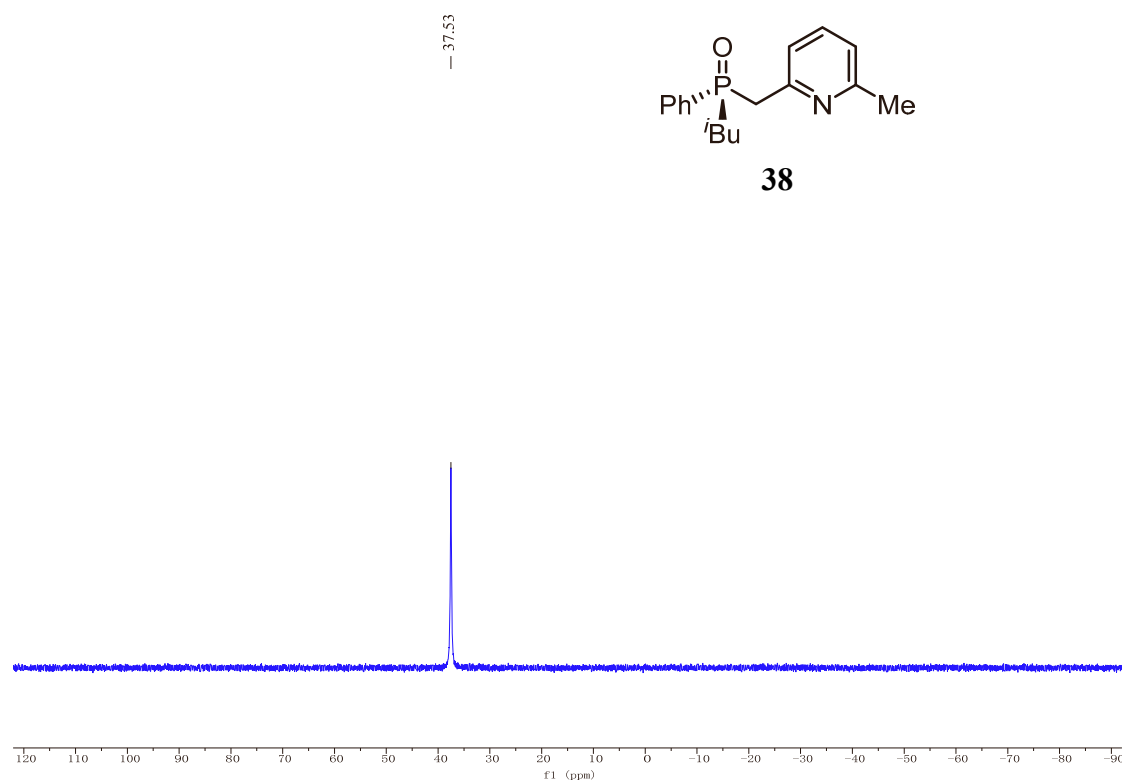
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



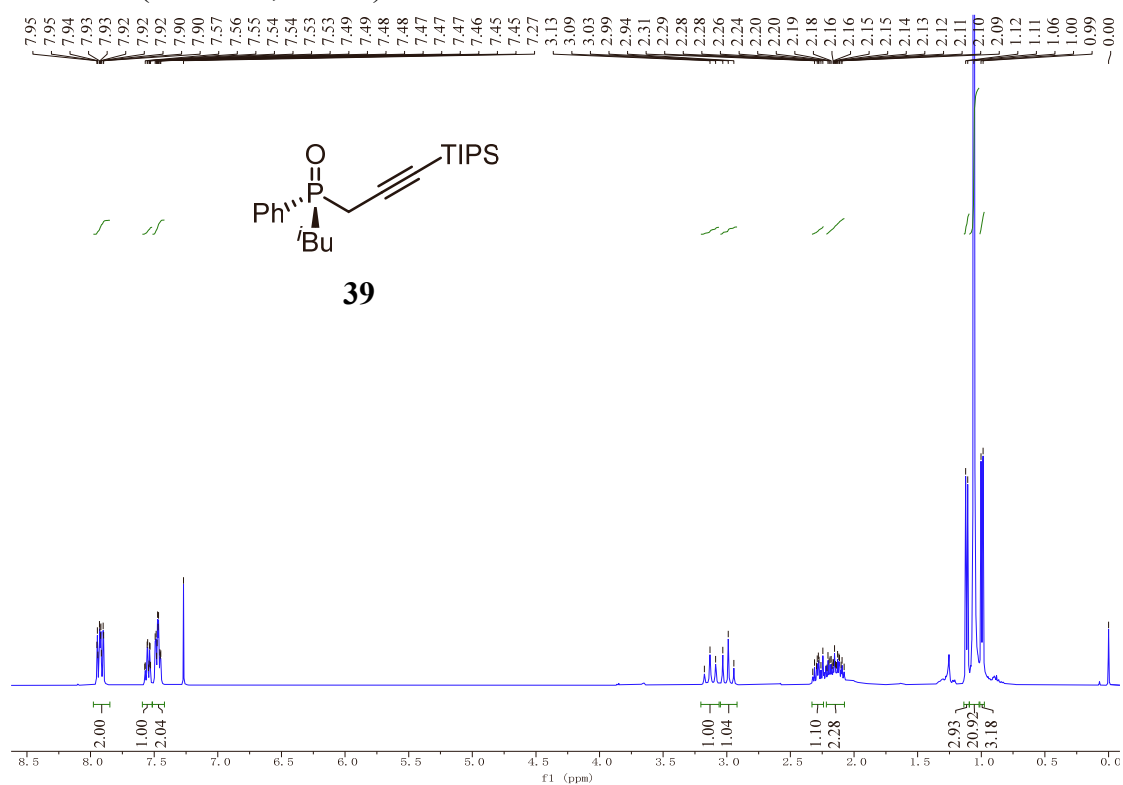
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



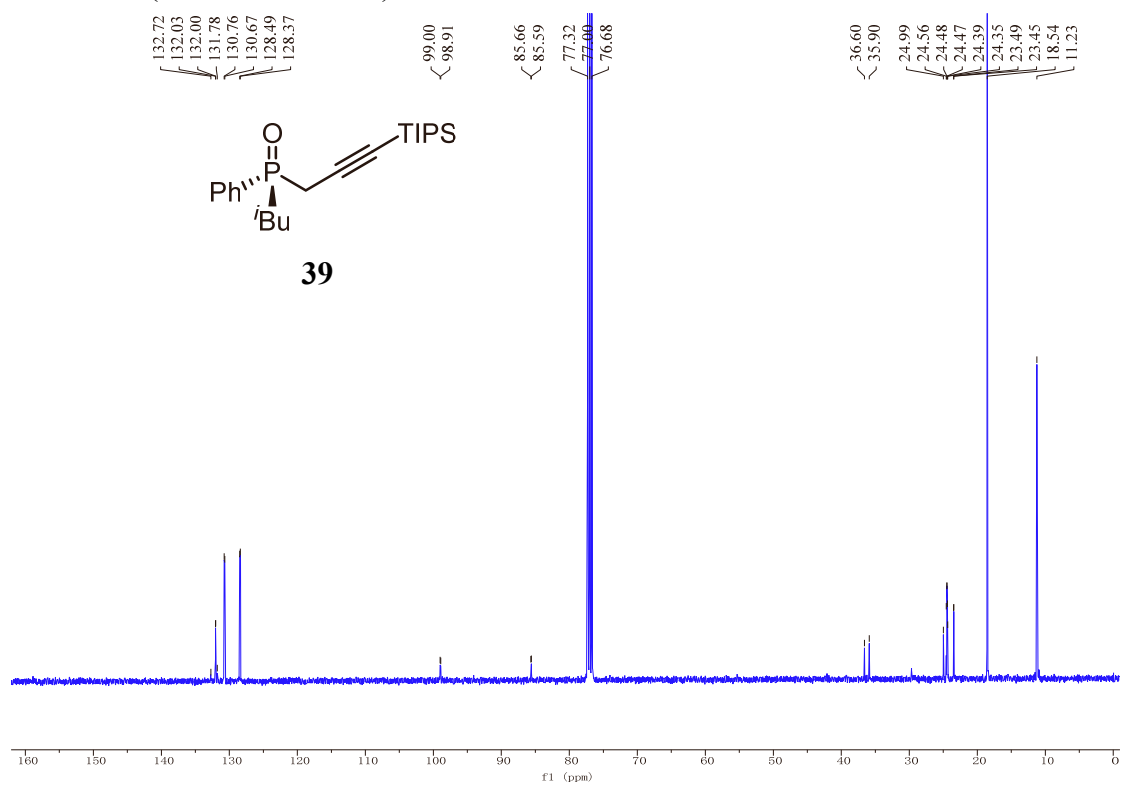
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

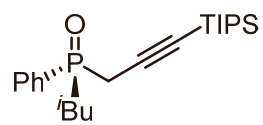


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

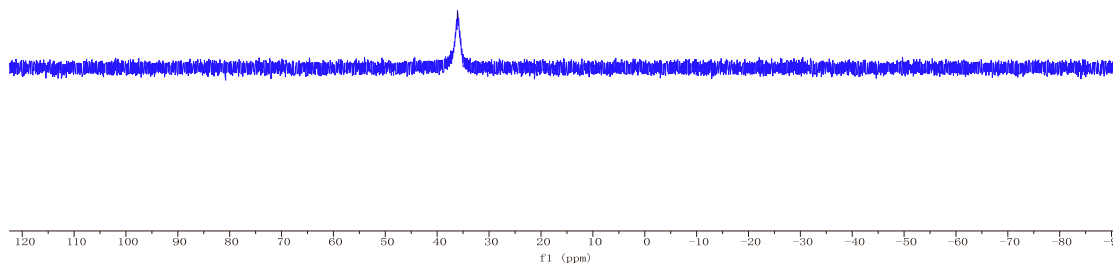


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

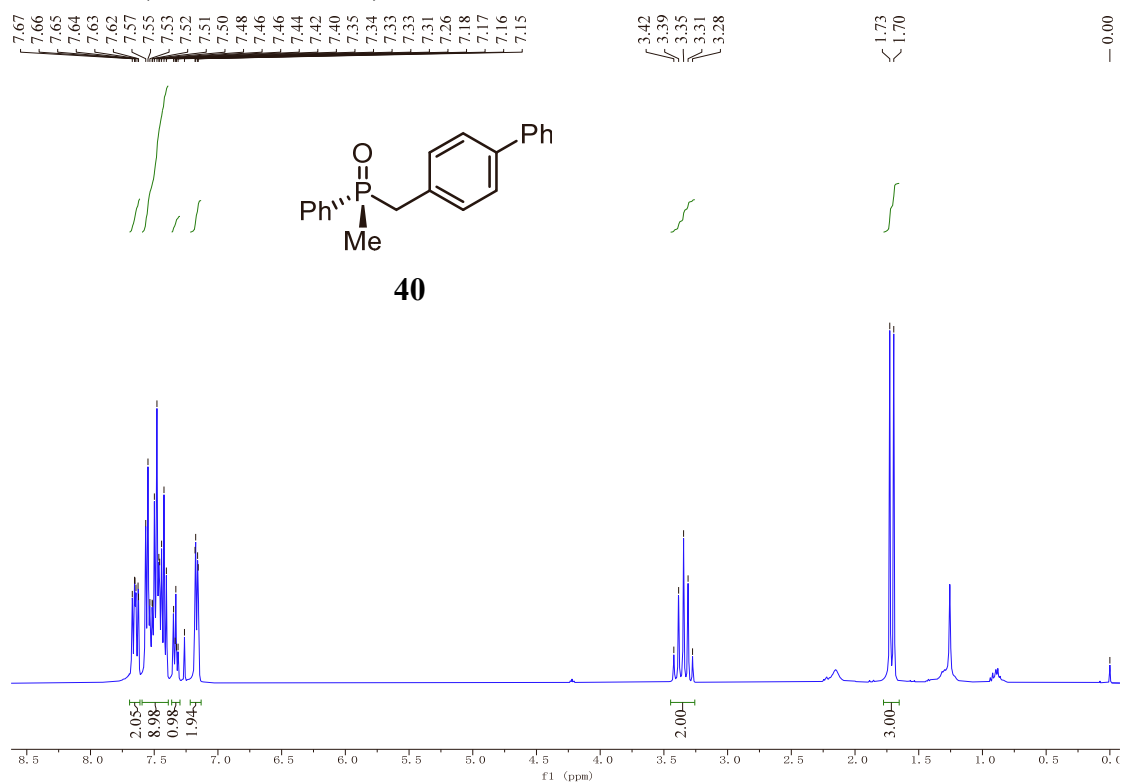
36.06  
|



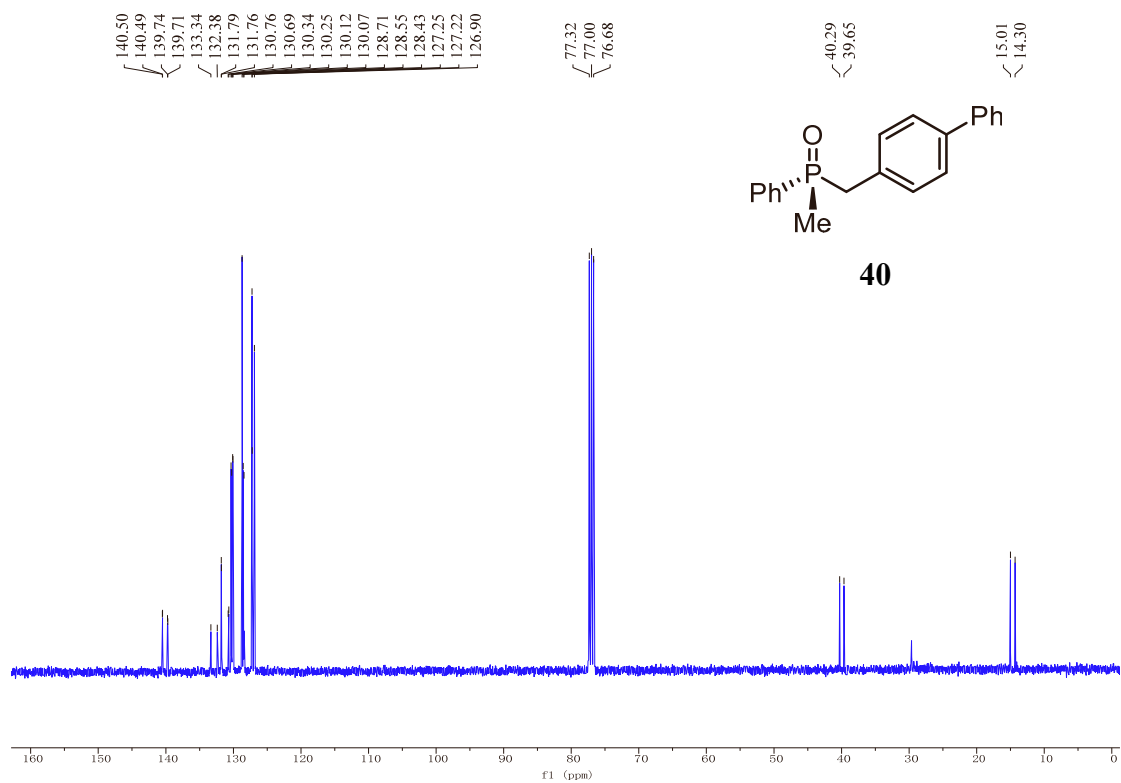
**39**



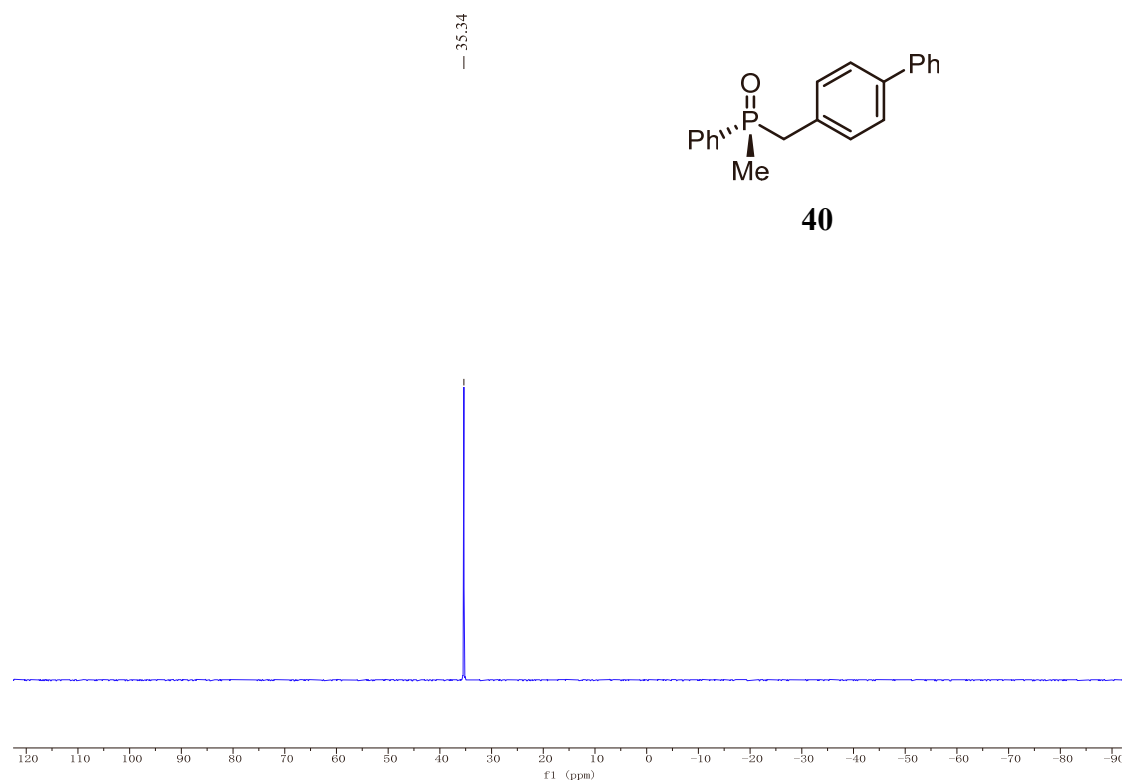
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



Chemical structure of compound **41** is shown above the spectrum. The structure is (S)-1-((S)-1-ethoxy-1-oxo-2-phenylethyl)-4-phenylbutane.

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound **41** is displayed below the structure. The x-axis represents the chemical shift in ppm (f1), ranging from 0.00 to 7.65. The spectrum shows several peaks, with integration values indicated below the baseline.

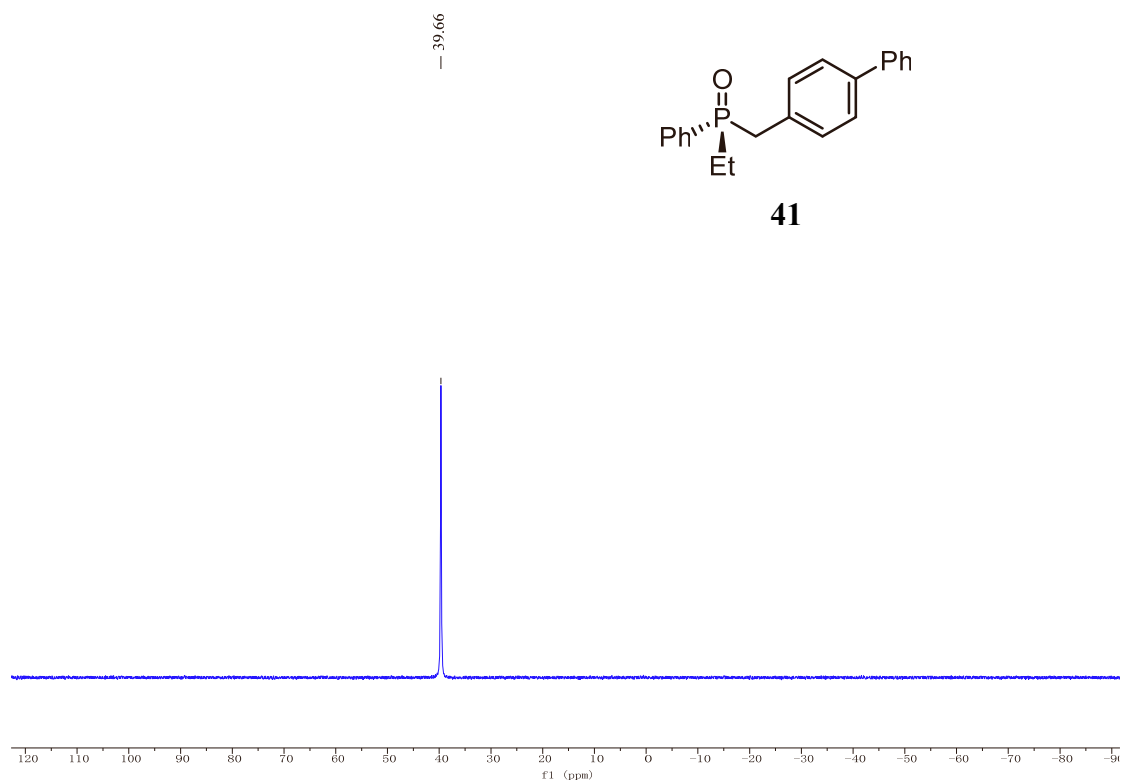
Integration values (from left to right): 2.00, 2.02, 7.05, 1.00, 2.00, 2.00, 2.00, 2.05, 3.00.

Chemical structure of **41**: CC(P(=O)(c1ccccc1)Cc2ccc(cc2)c3ccccc3)C4=CC=CC=C4

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of compound **41**. The spectrum shows peaks corresponding to the structure, with the following chemical shifts (ppm) labeled above the peaks:

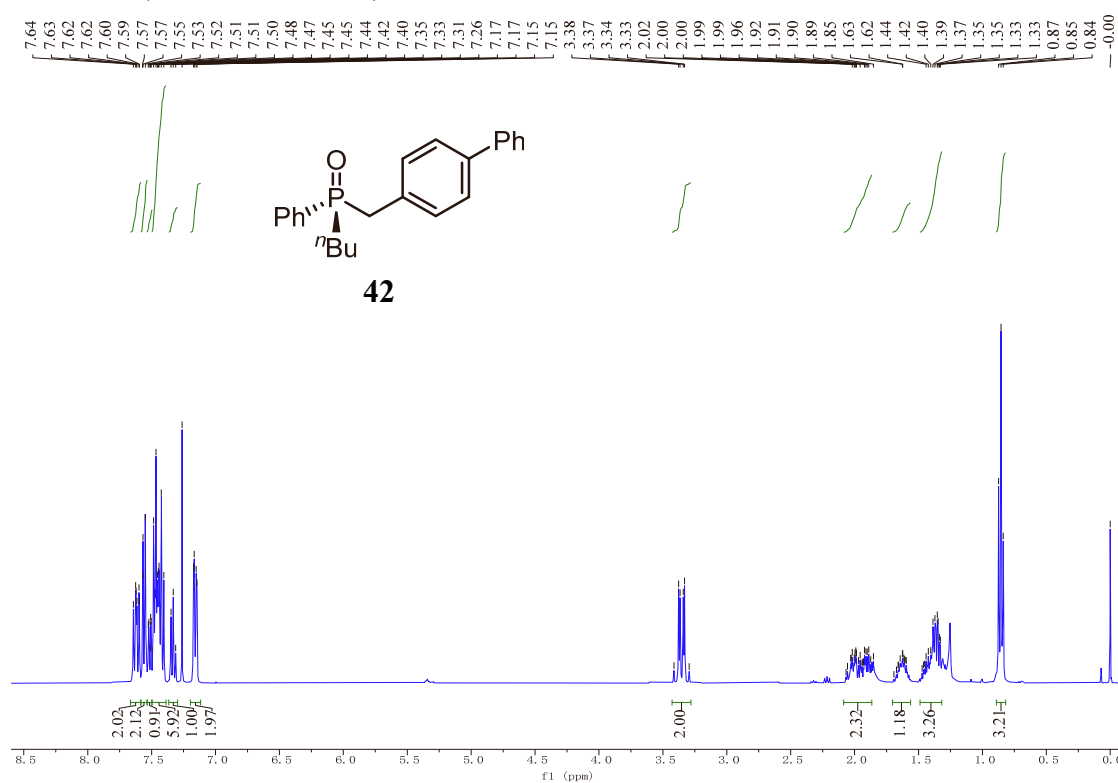
- 140.49, 140.48, 139.59, 139.56, 131.65, 131.62, 130.78, 130.74, 130.69, 130.66, 130.63, 130.13, 130.08, 128.67, 128.46, 128.35, 127.18, 127.15, 127.13, 126.85
- 77.32, 77.00, 76.68 (CDCl<sub>3</sub> solvent triplet)
- 38.33, 37.71 (ethyl group carbons)
- 21.51, 20.81 (ethyl group carbons)
- 5.31, 5.26 (ethyl group carbons)

**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

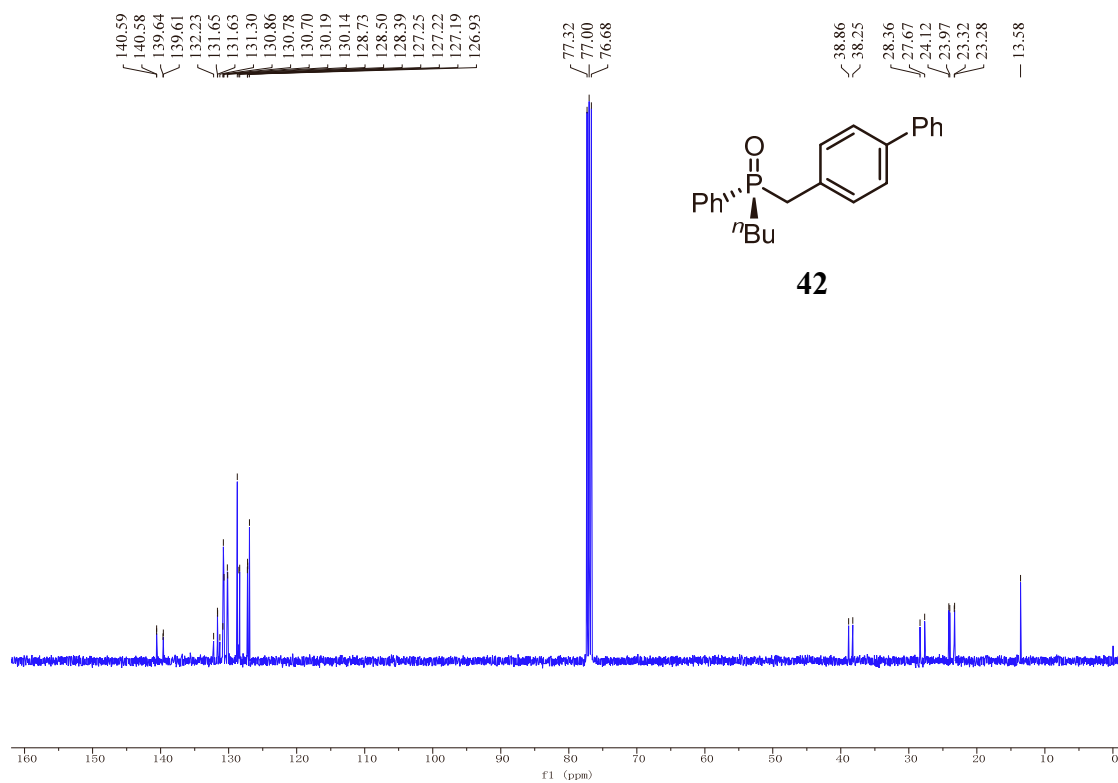




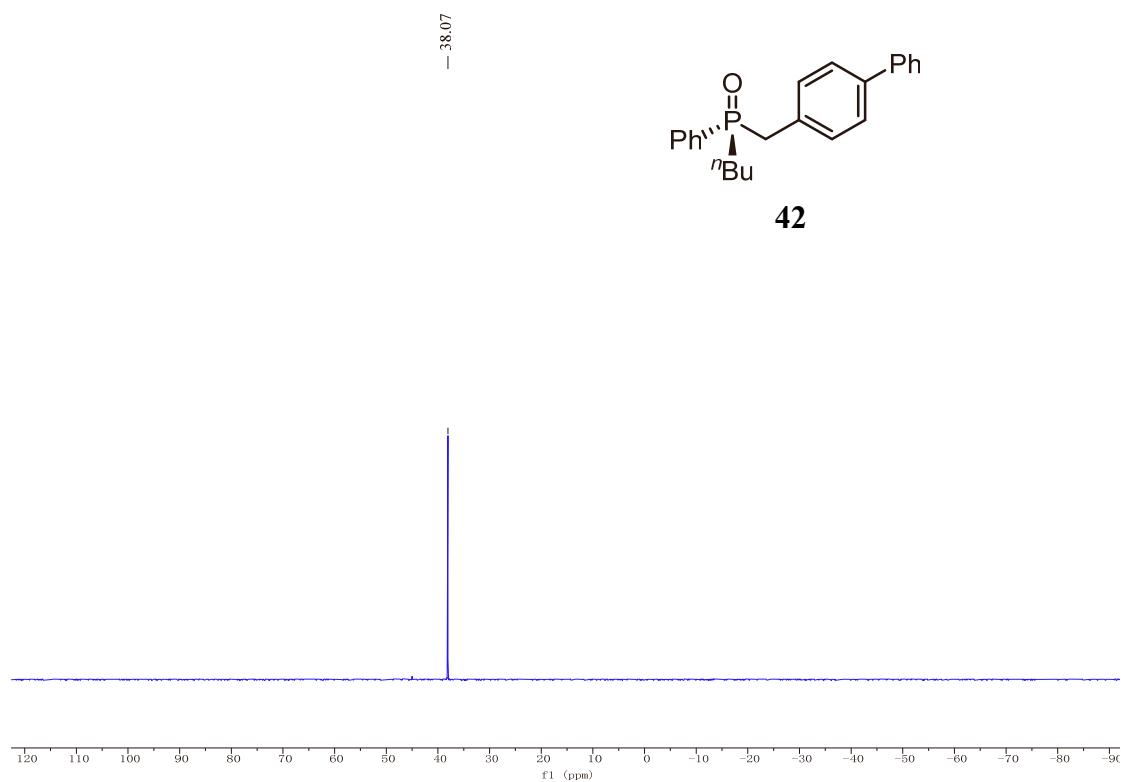
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



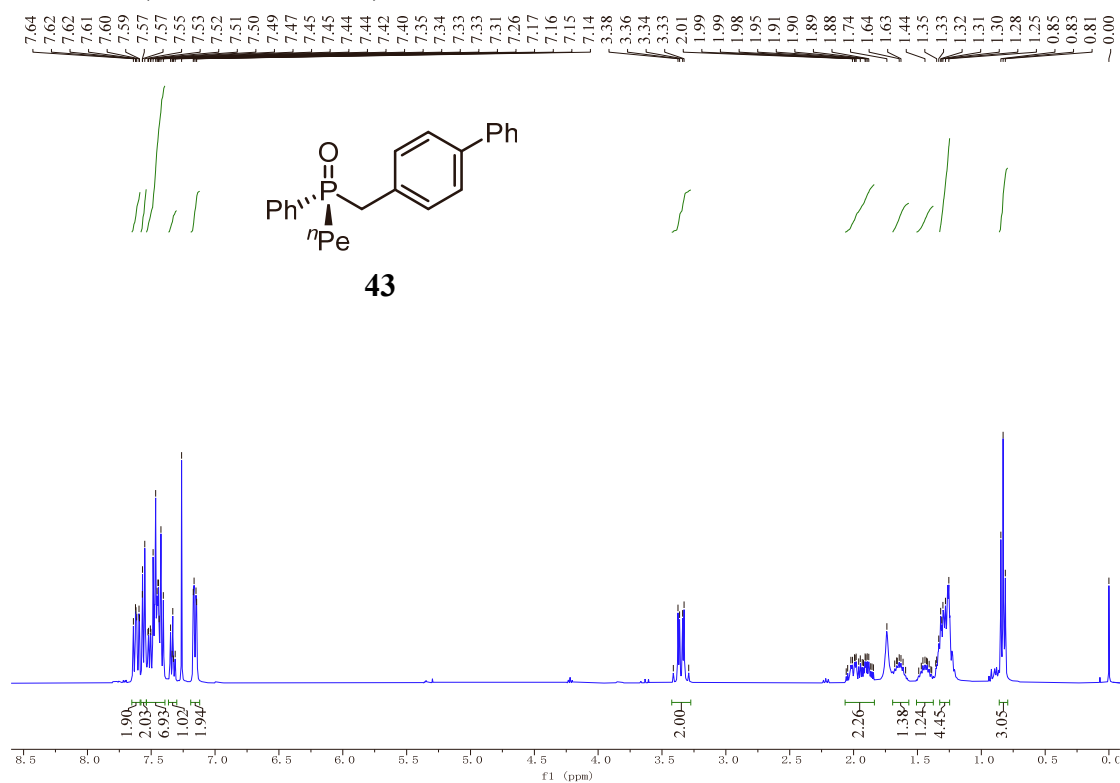
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



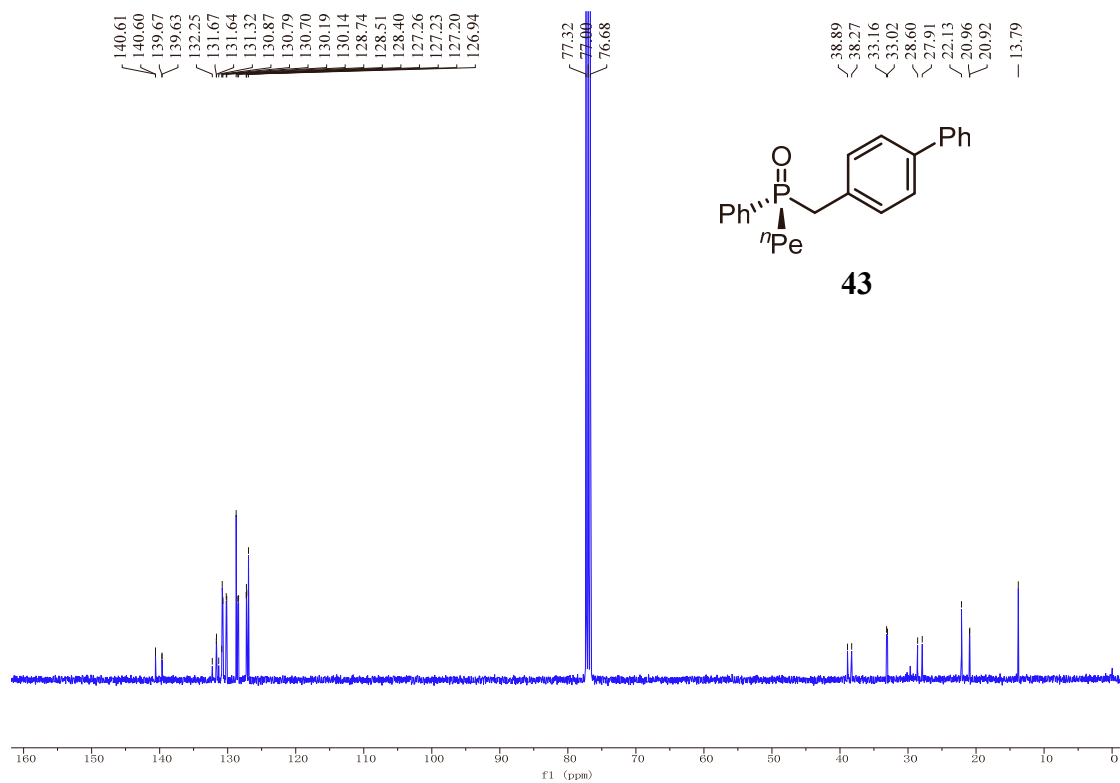
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



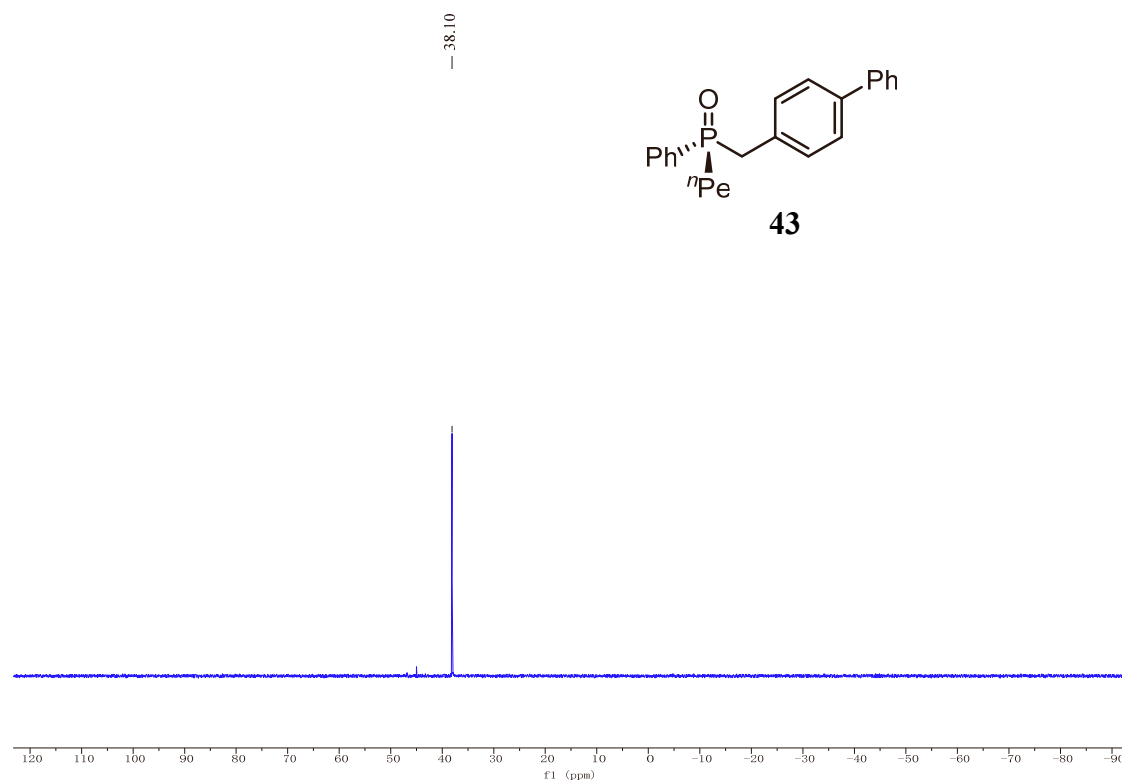
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



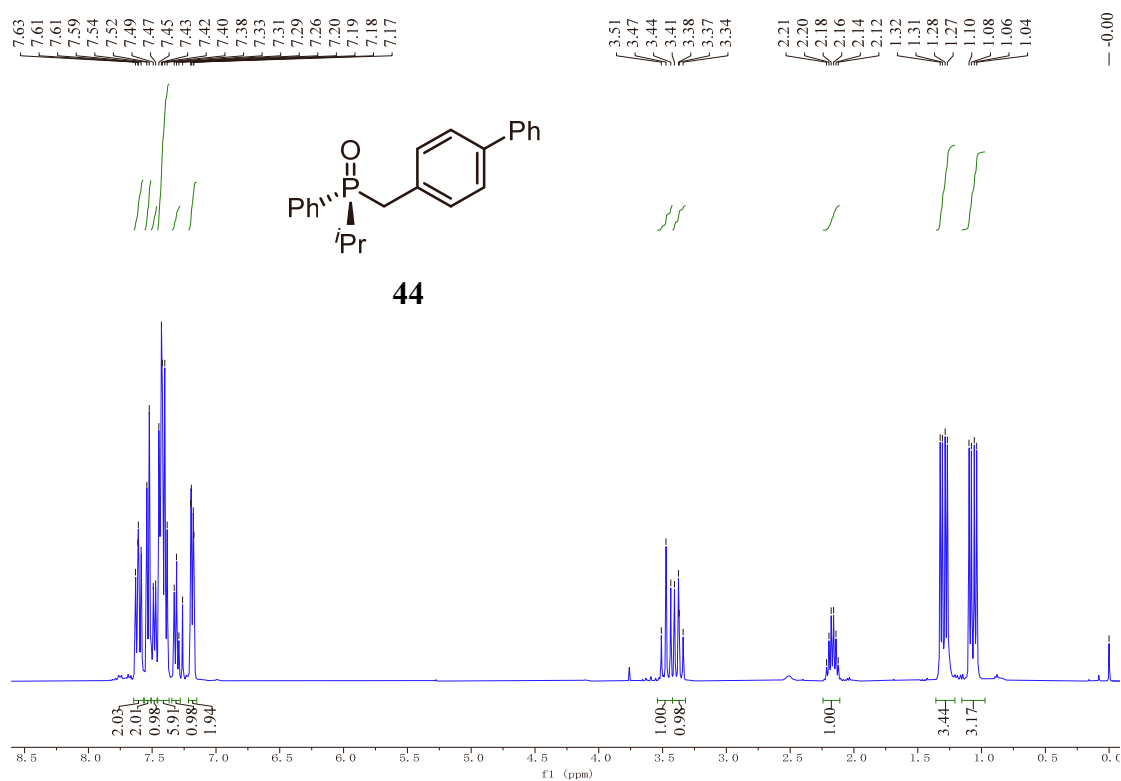
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**



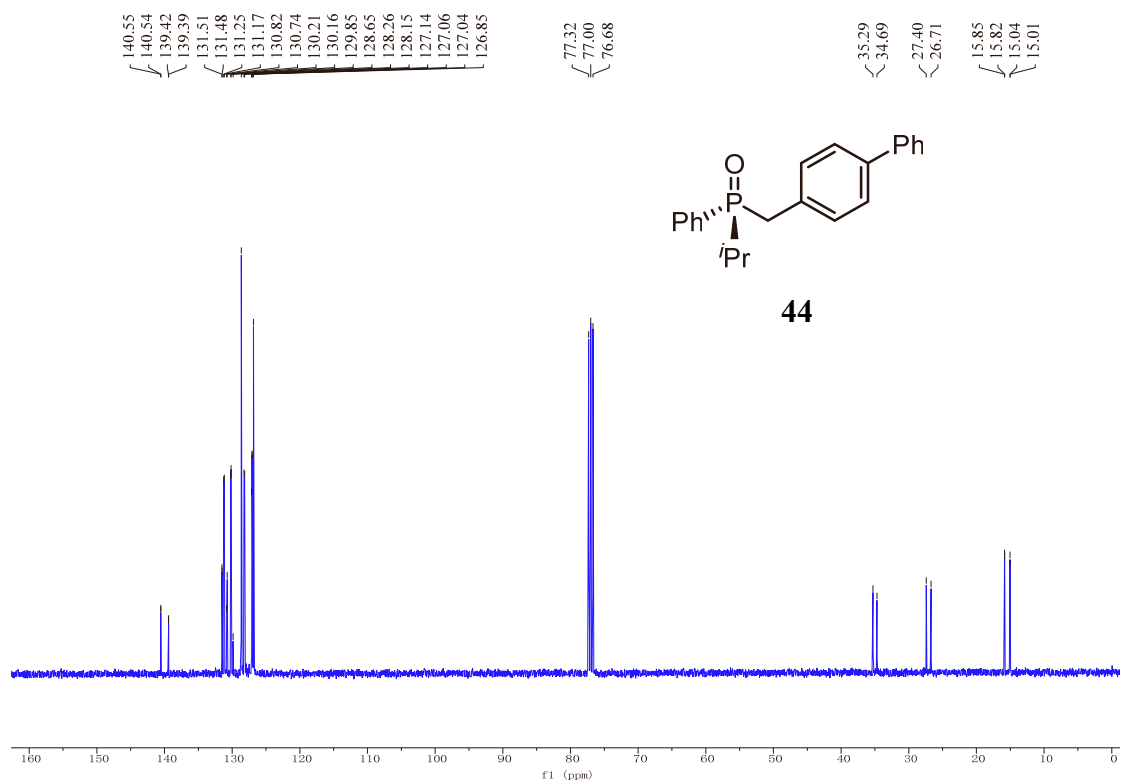
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



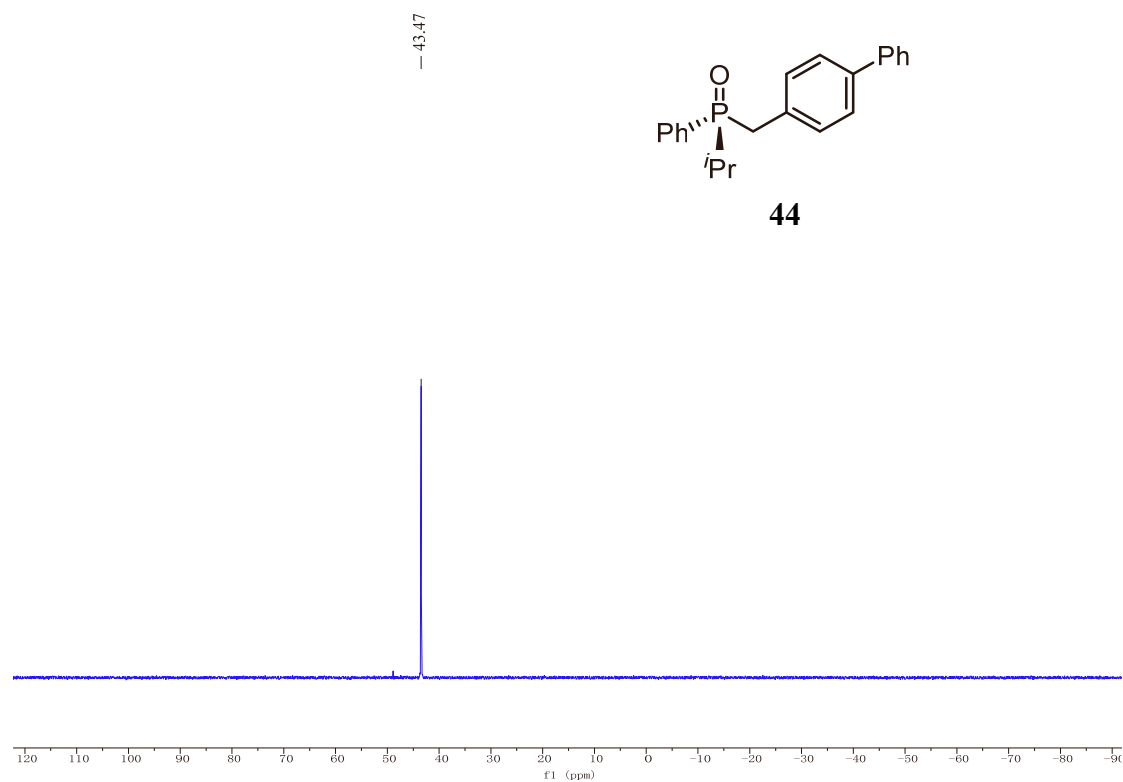
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



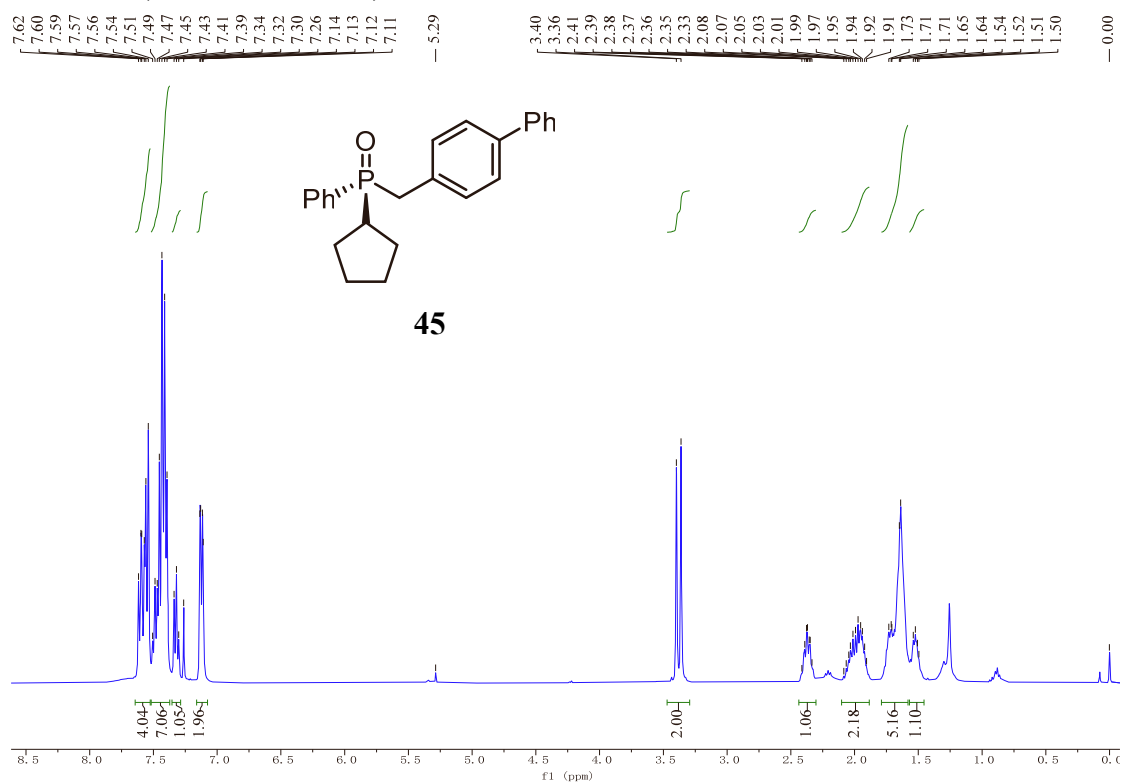
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



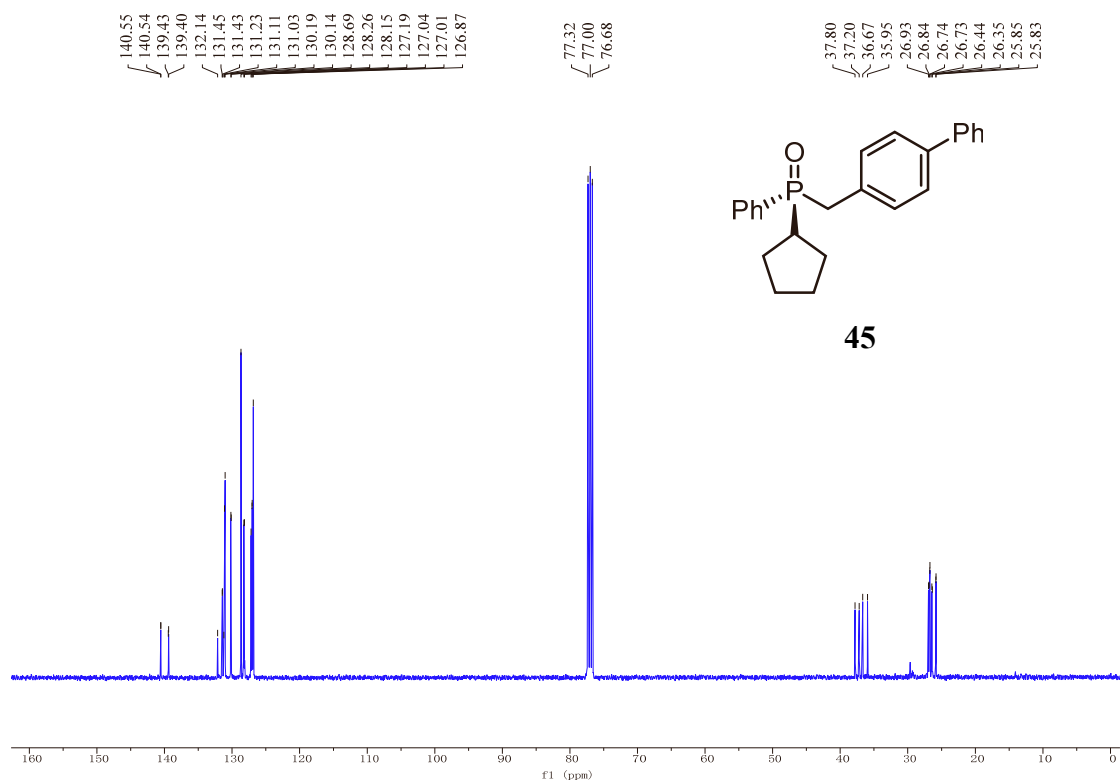
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



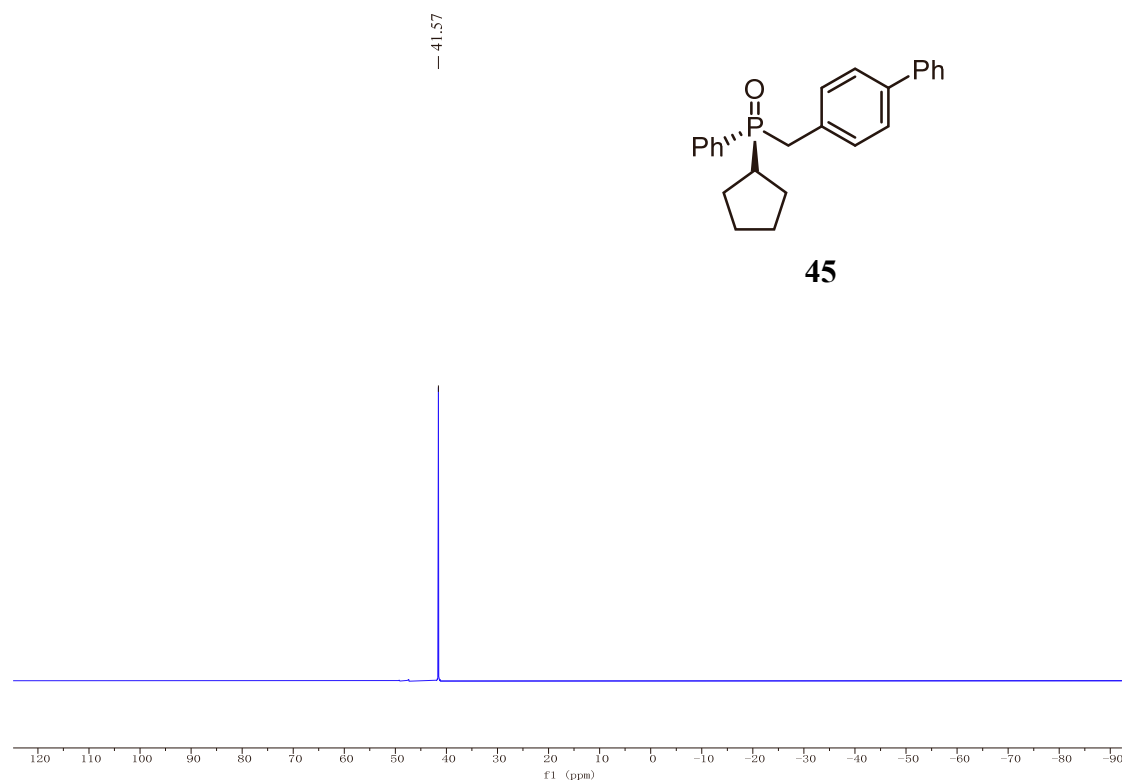
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

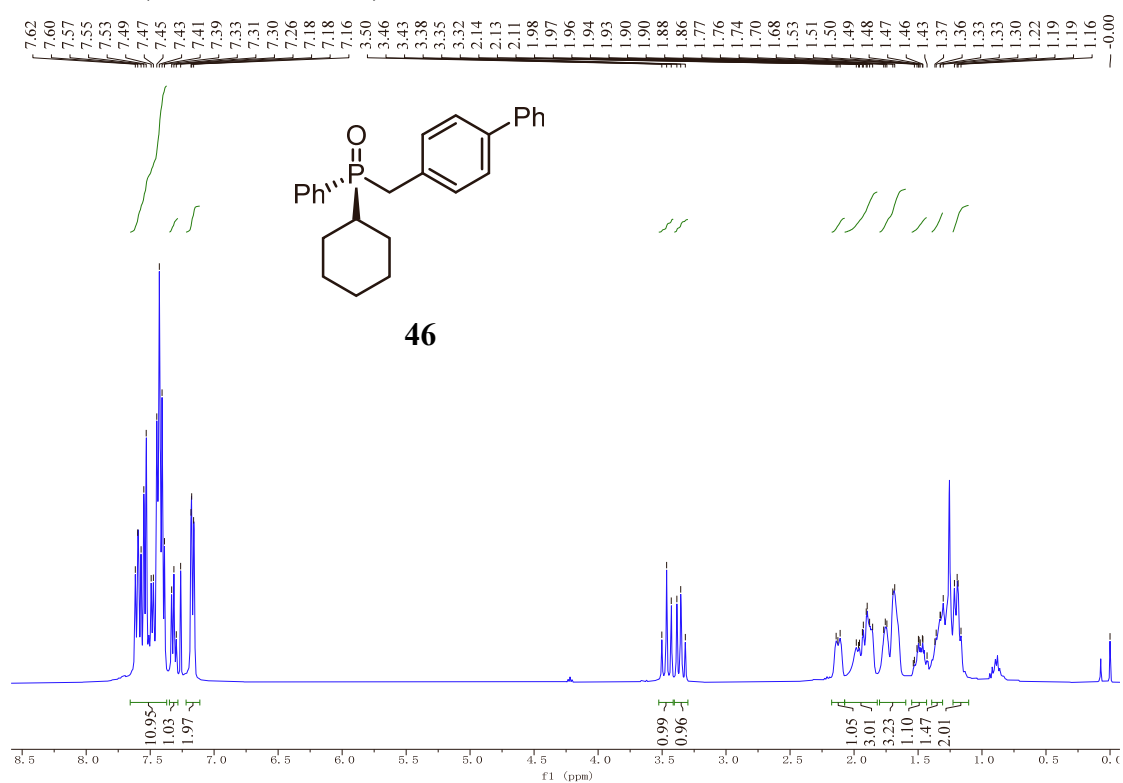


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

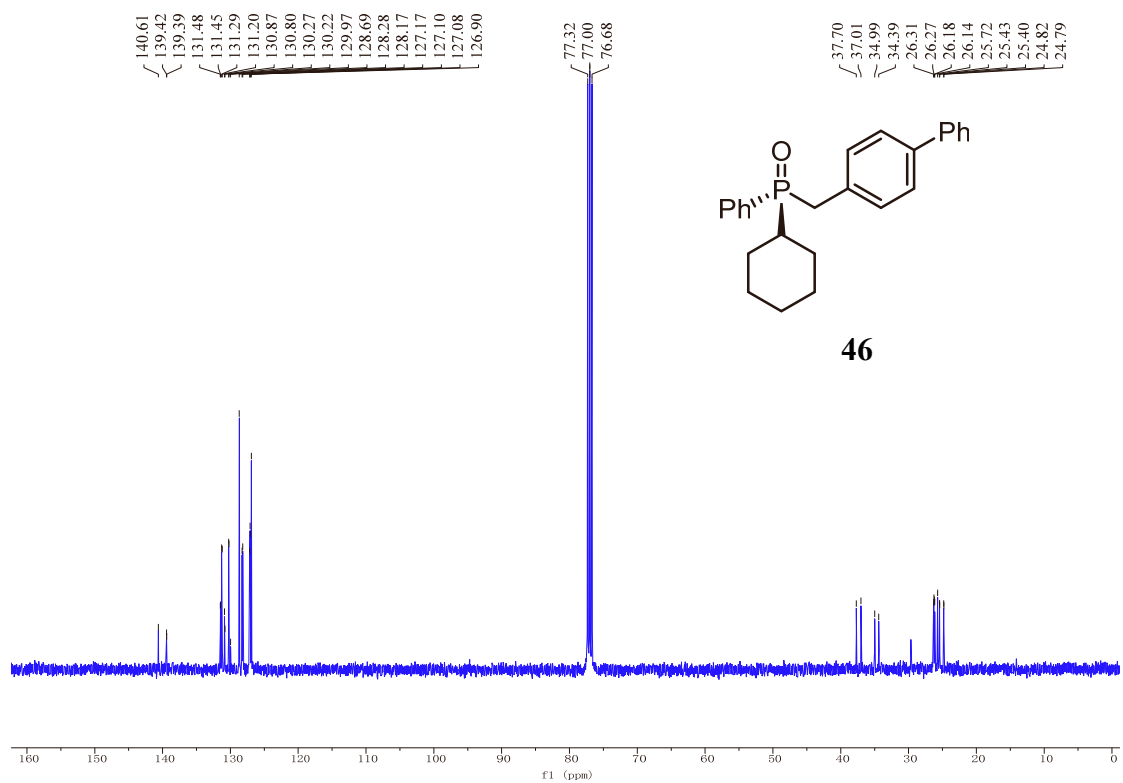




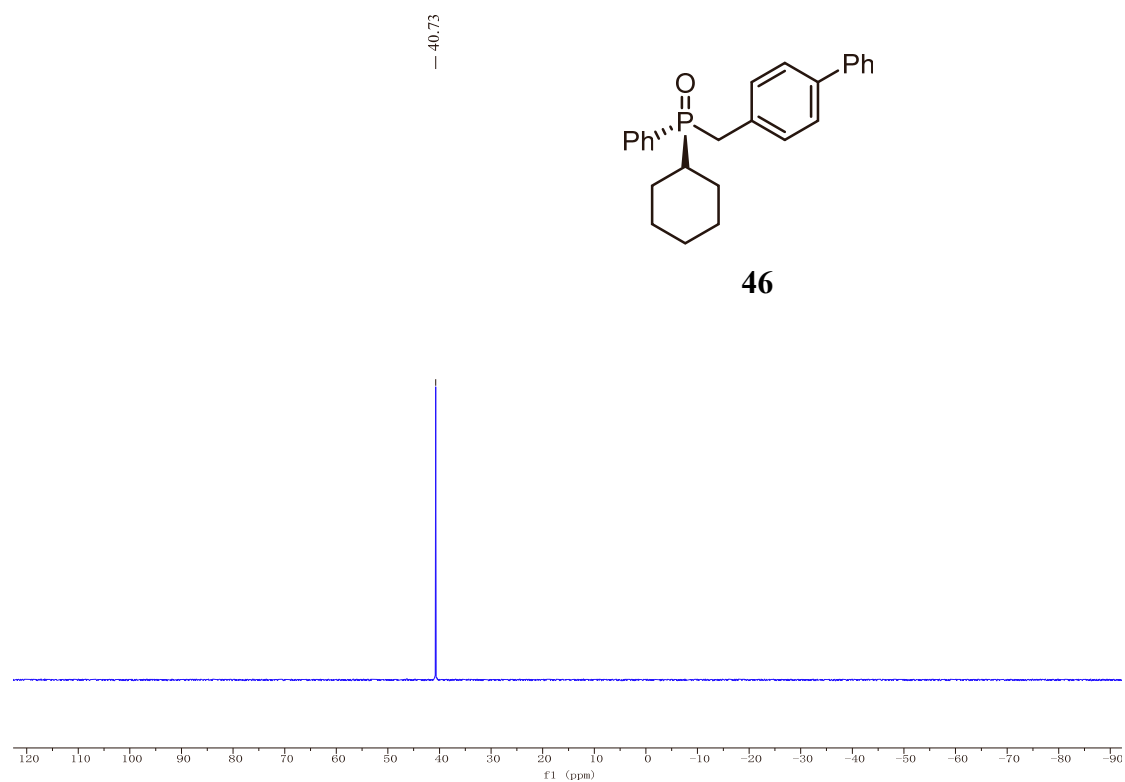
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



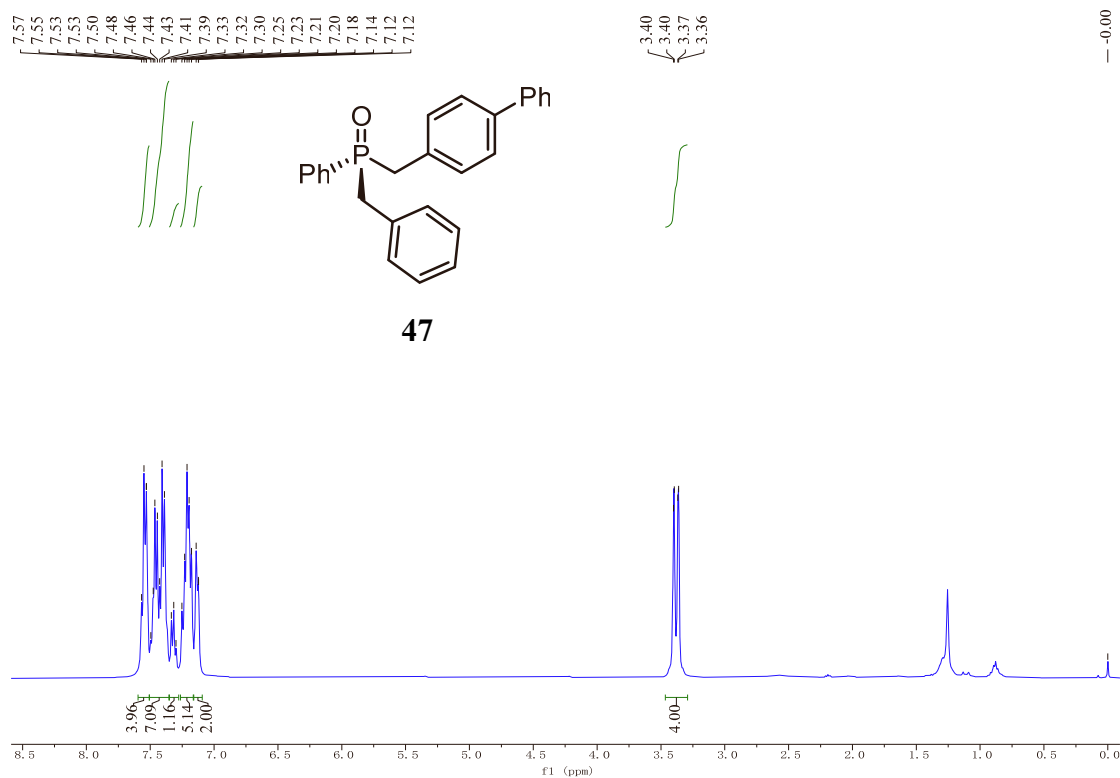
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**



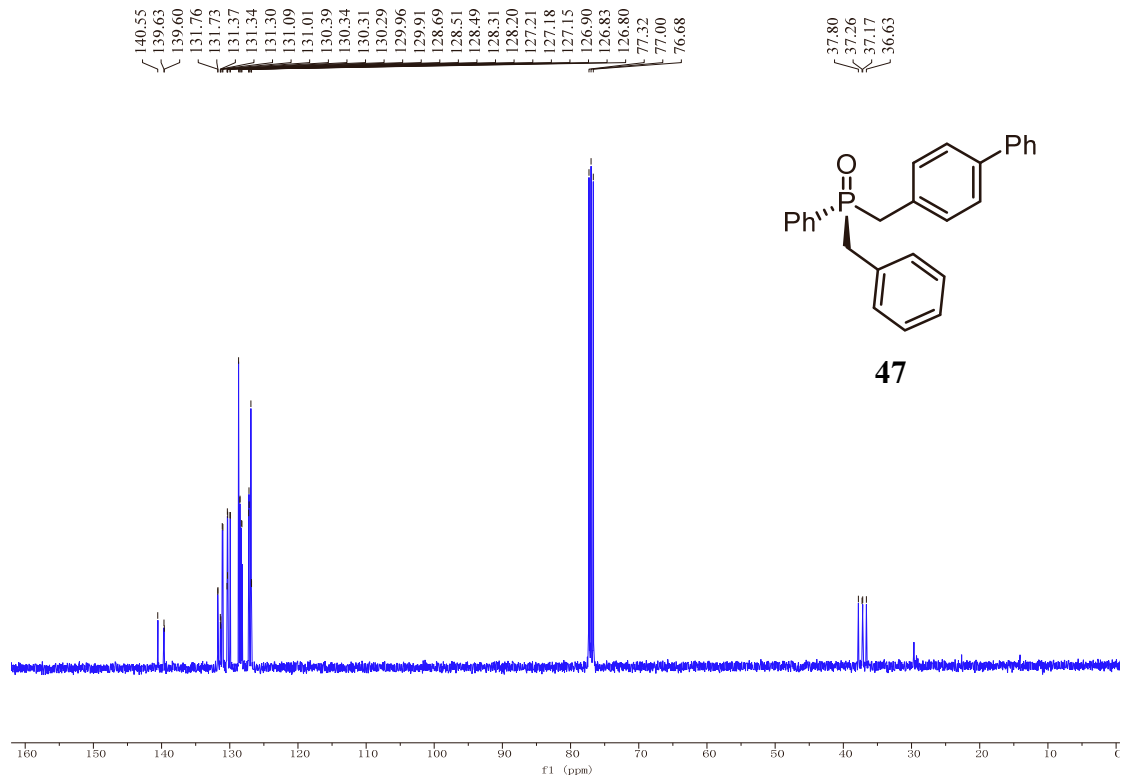
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



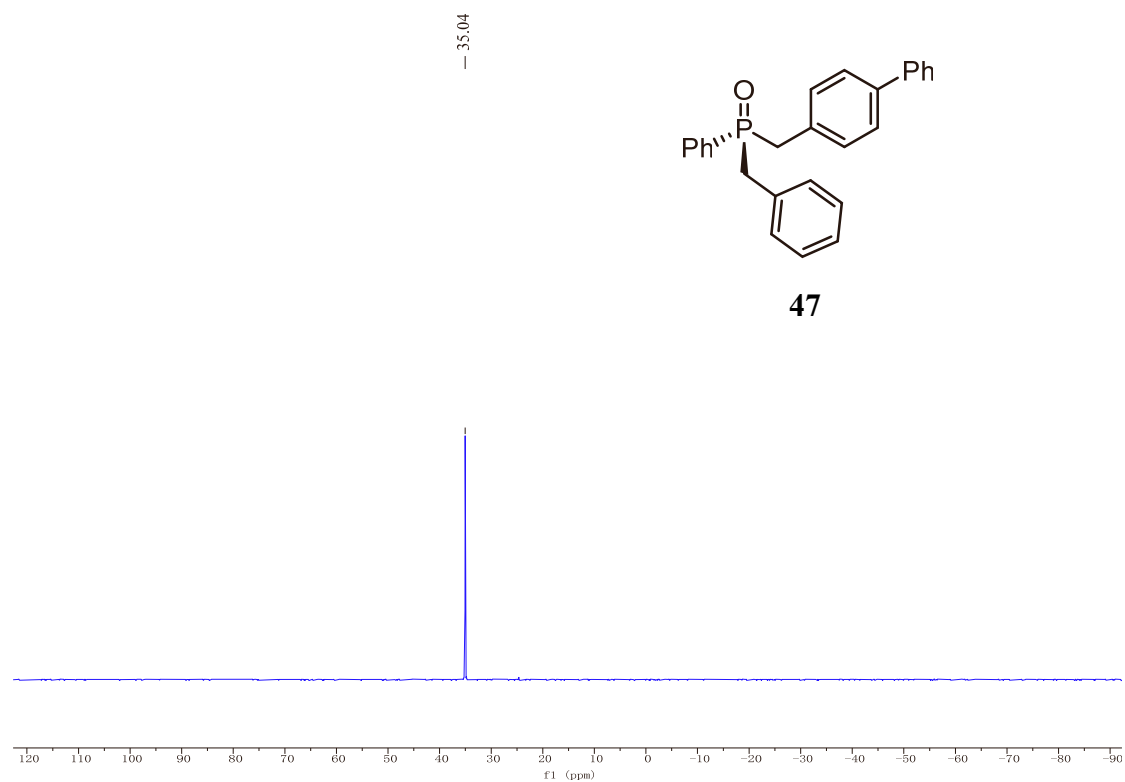
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



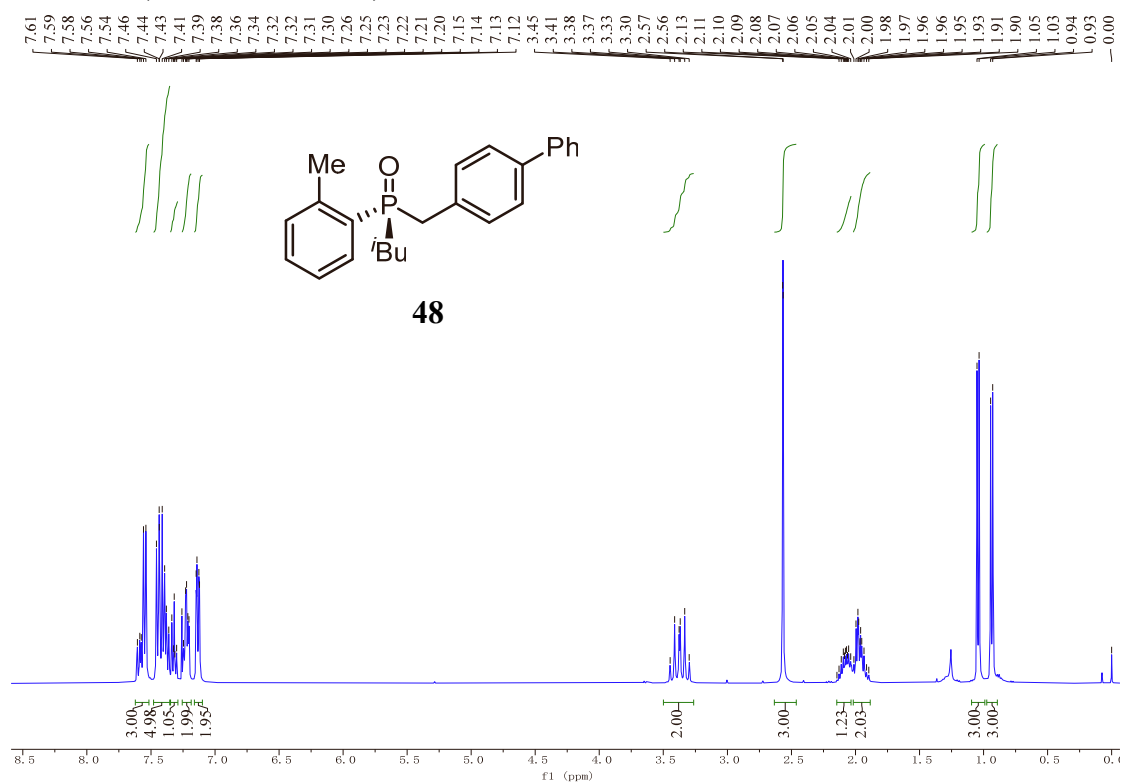
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



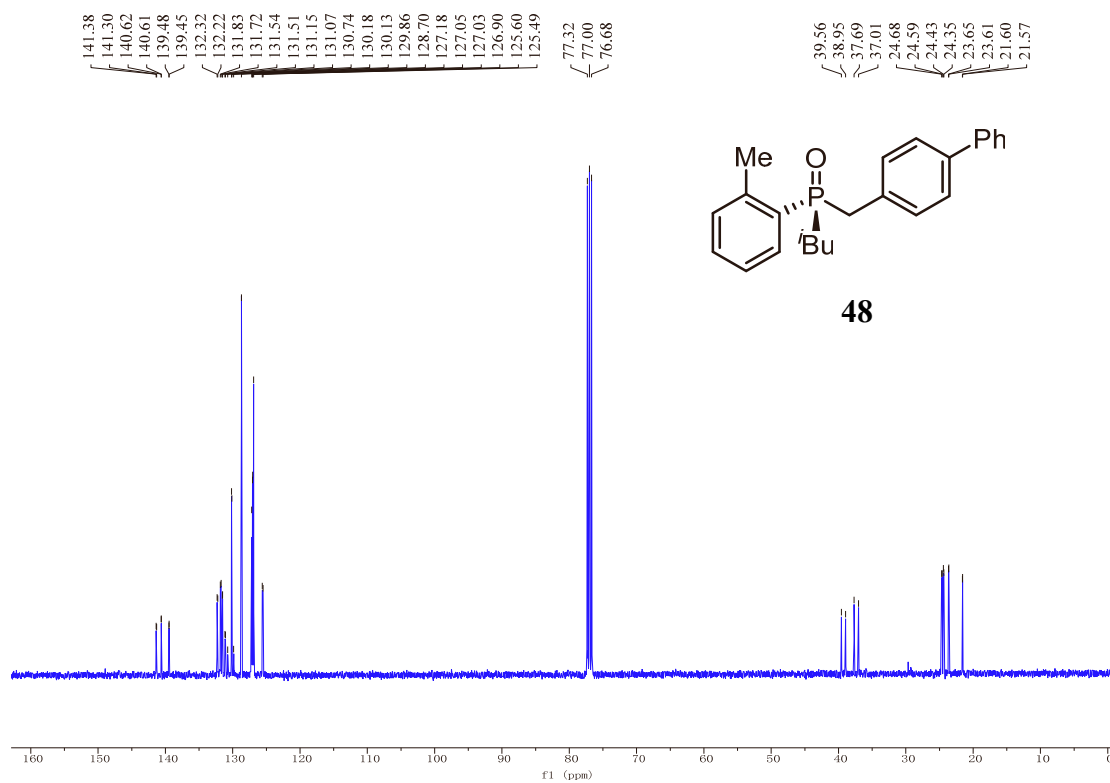
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



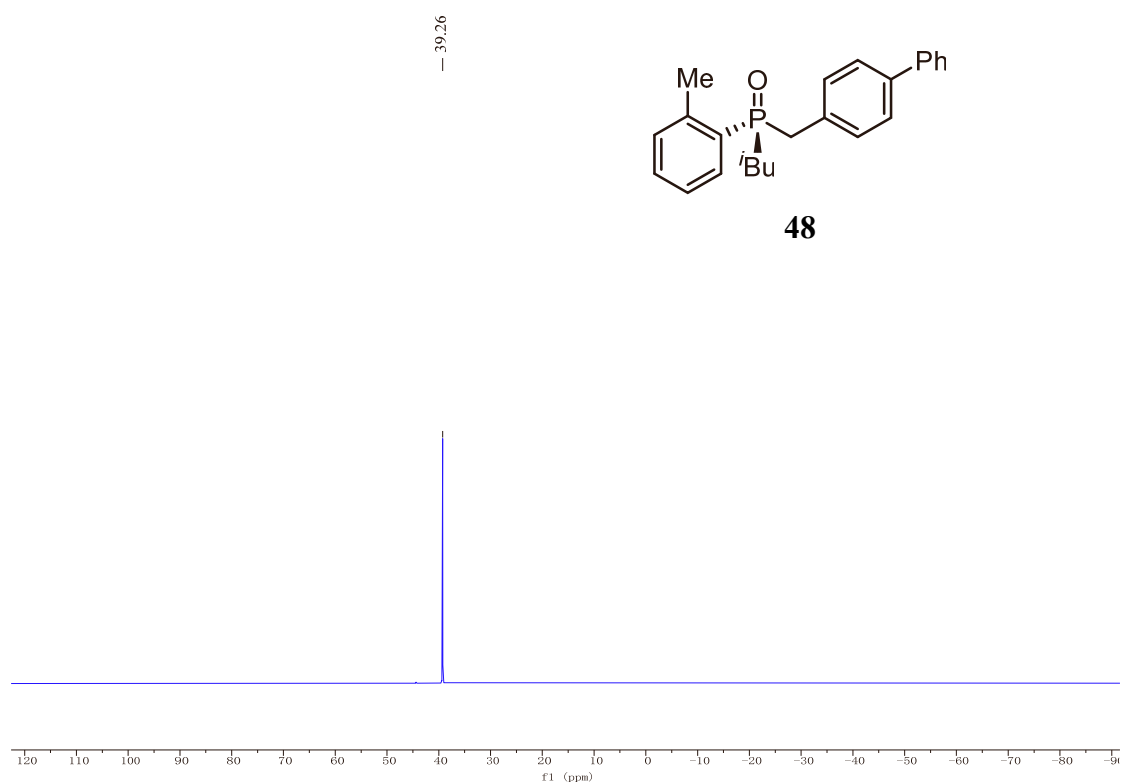
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



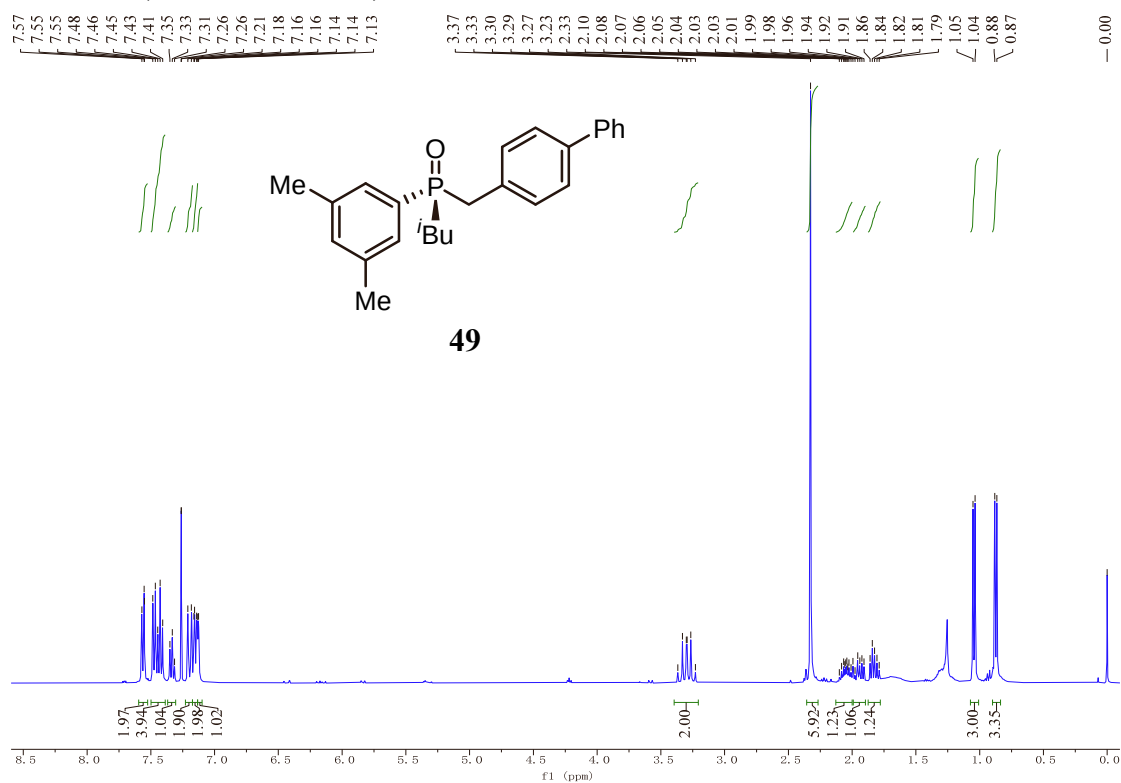
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



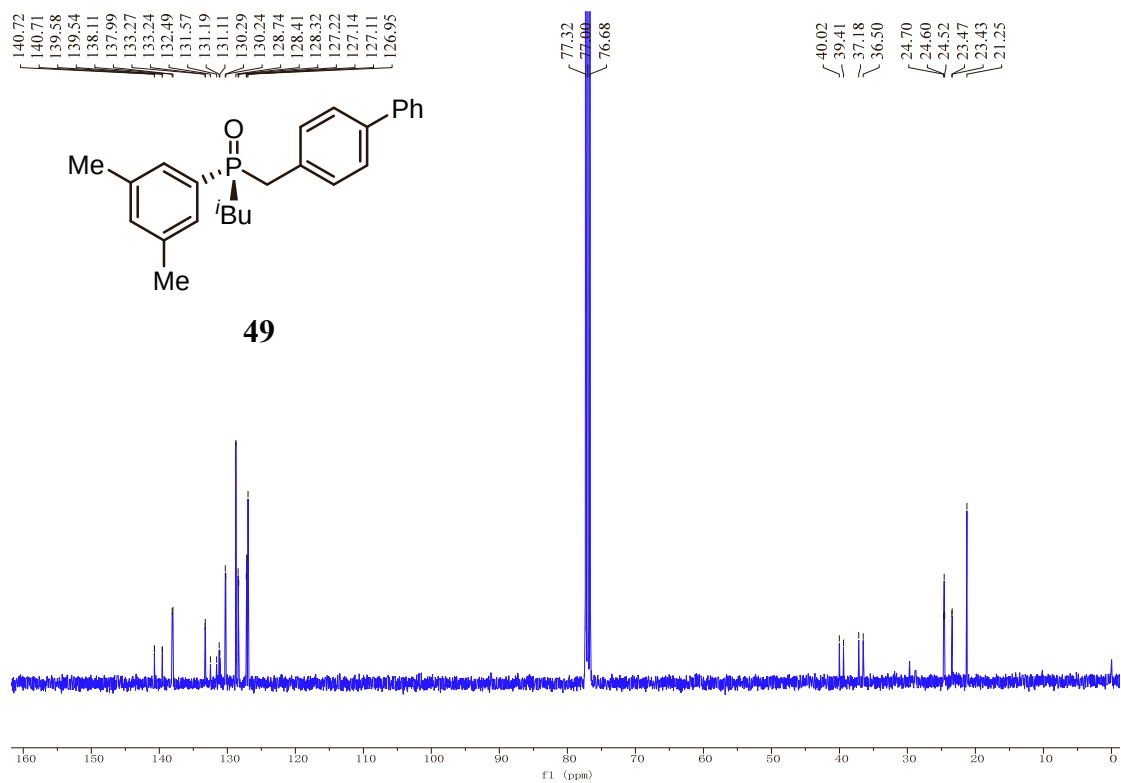
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



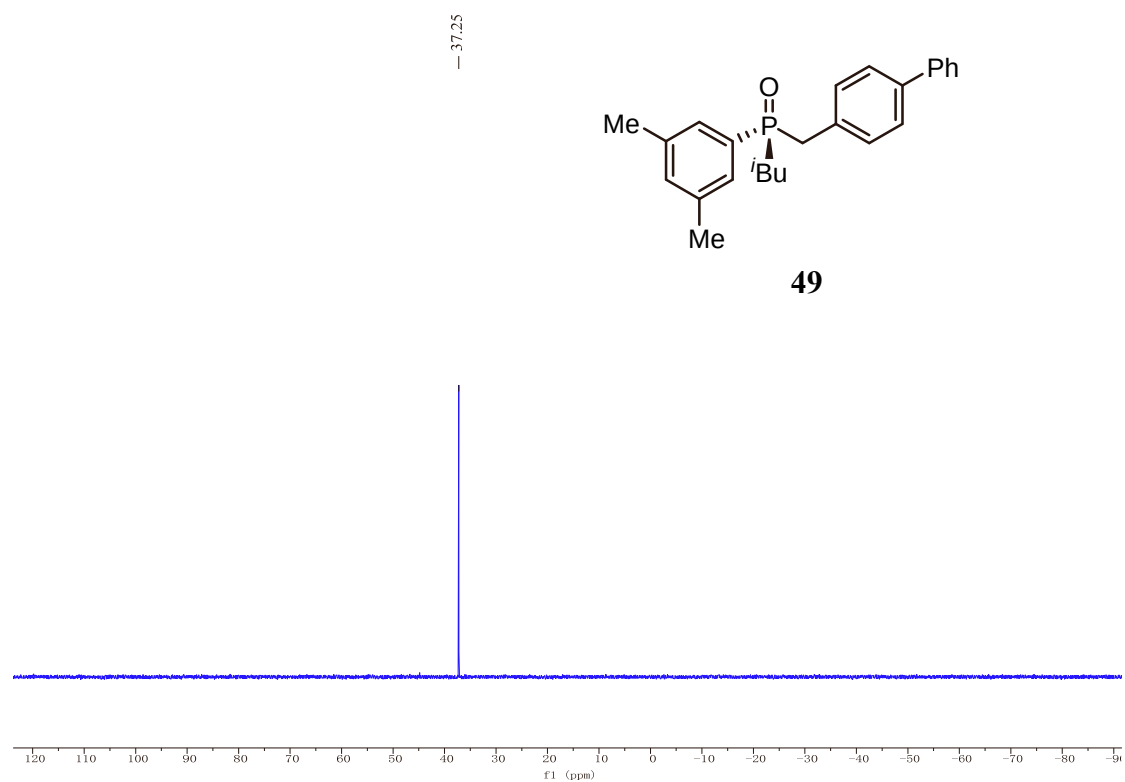
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

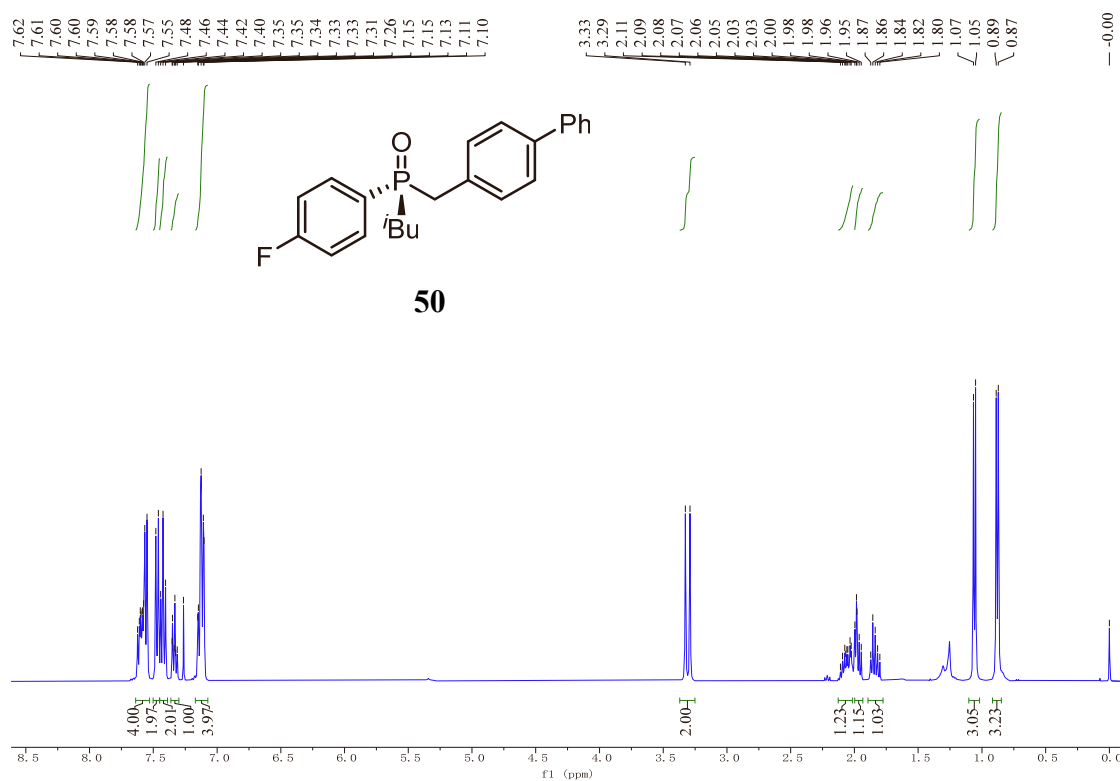


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

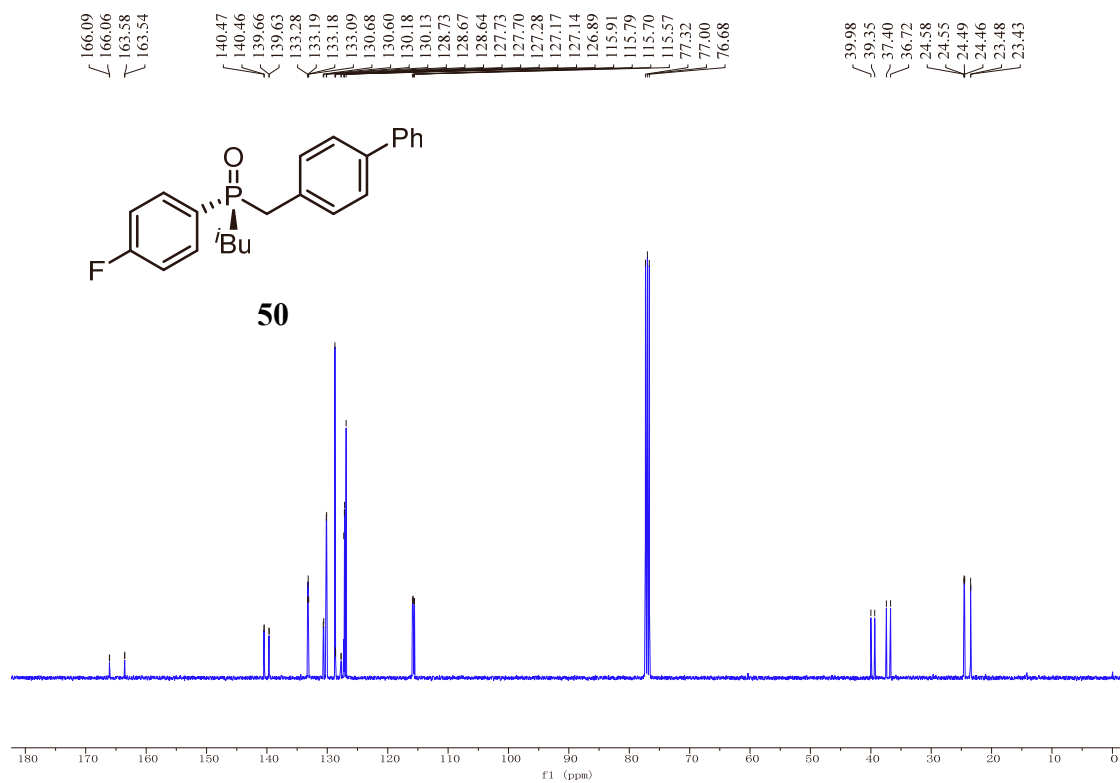




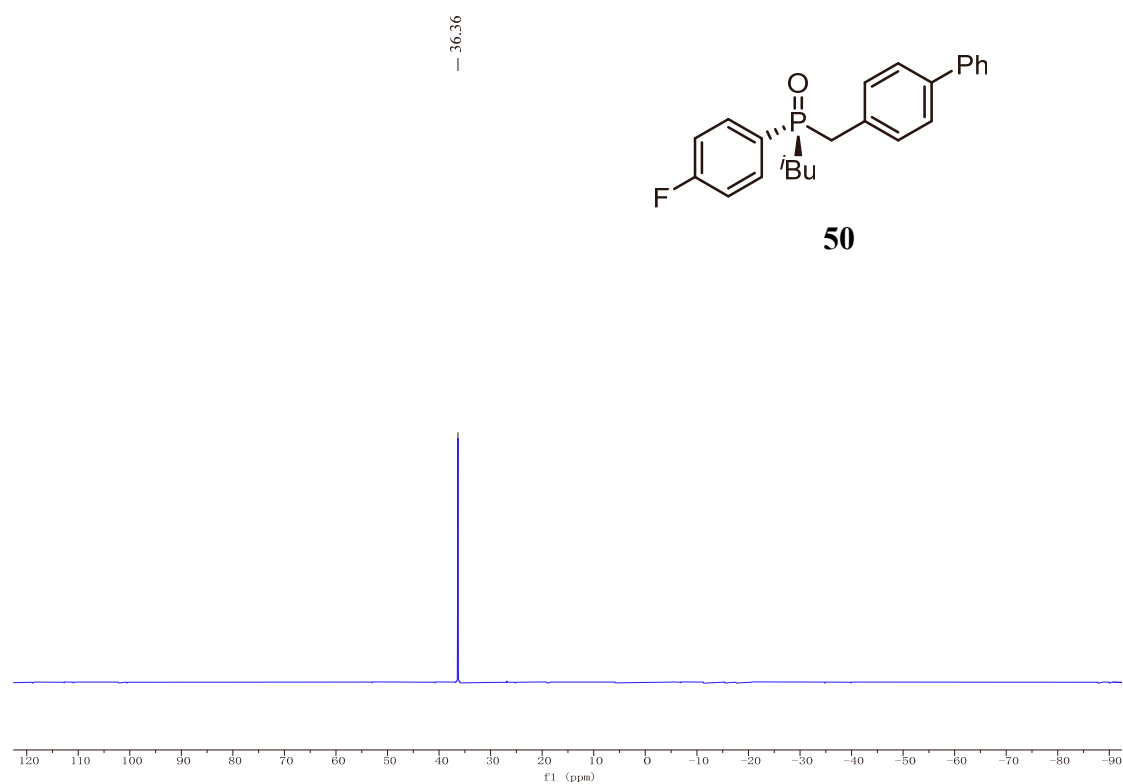
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



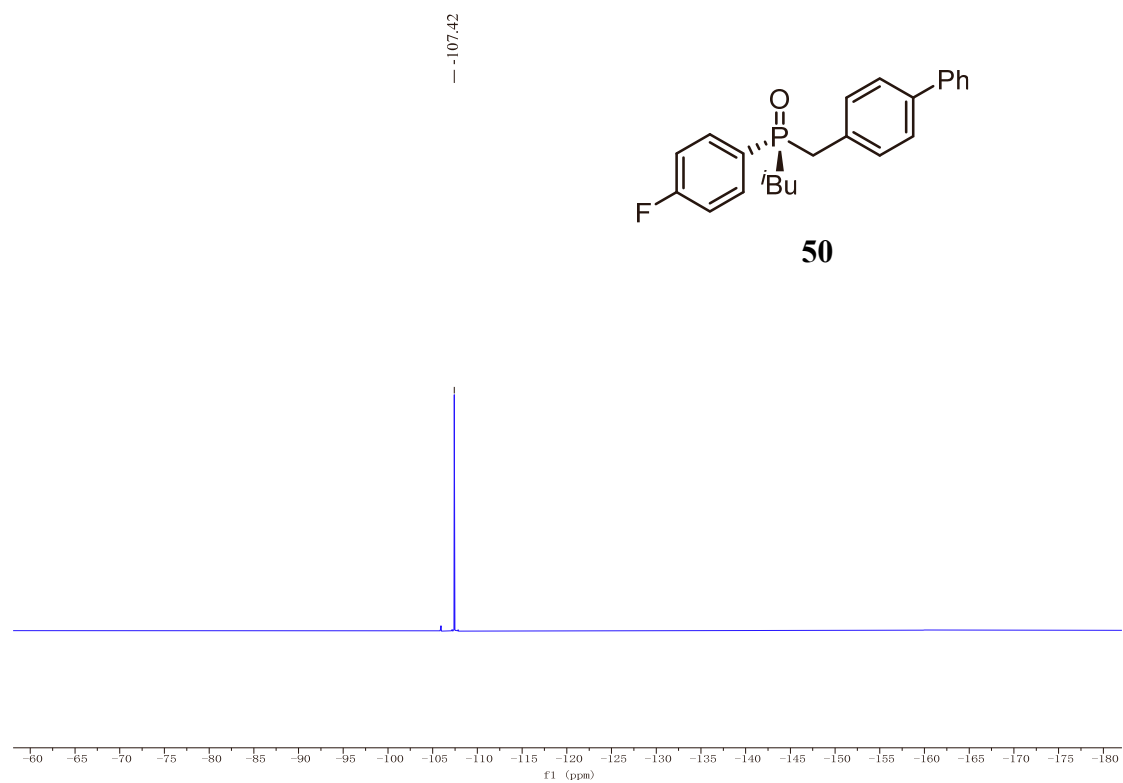
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



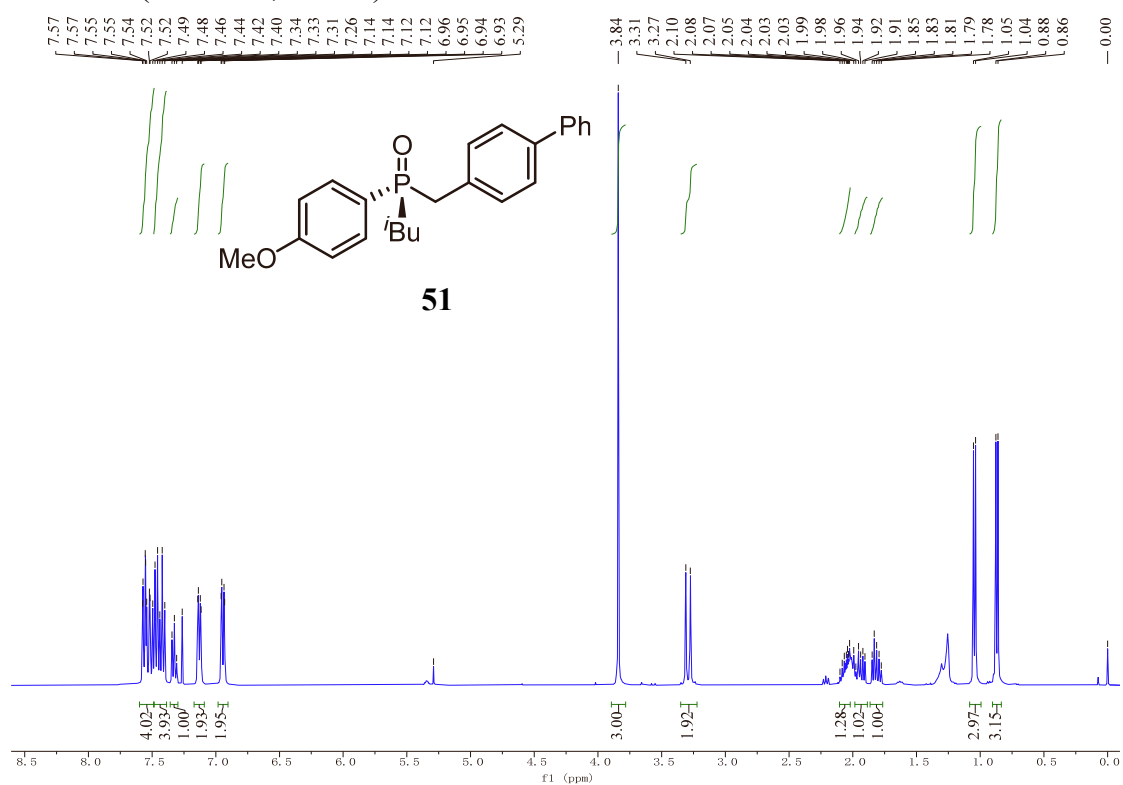
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



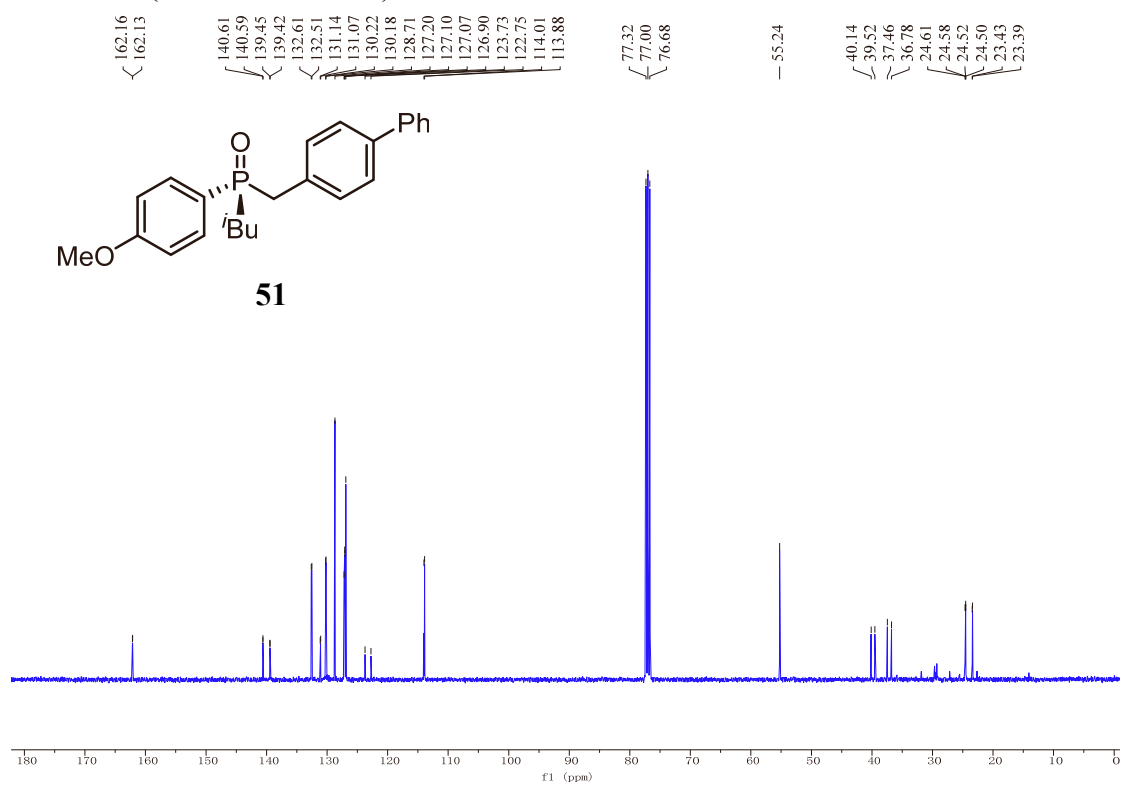
**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )



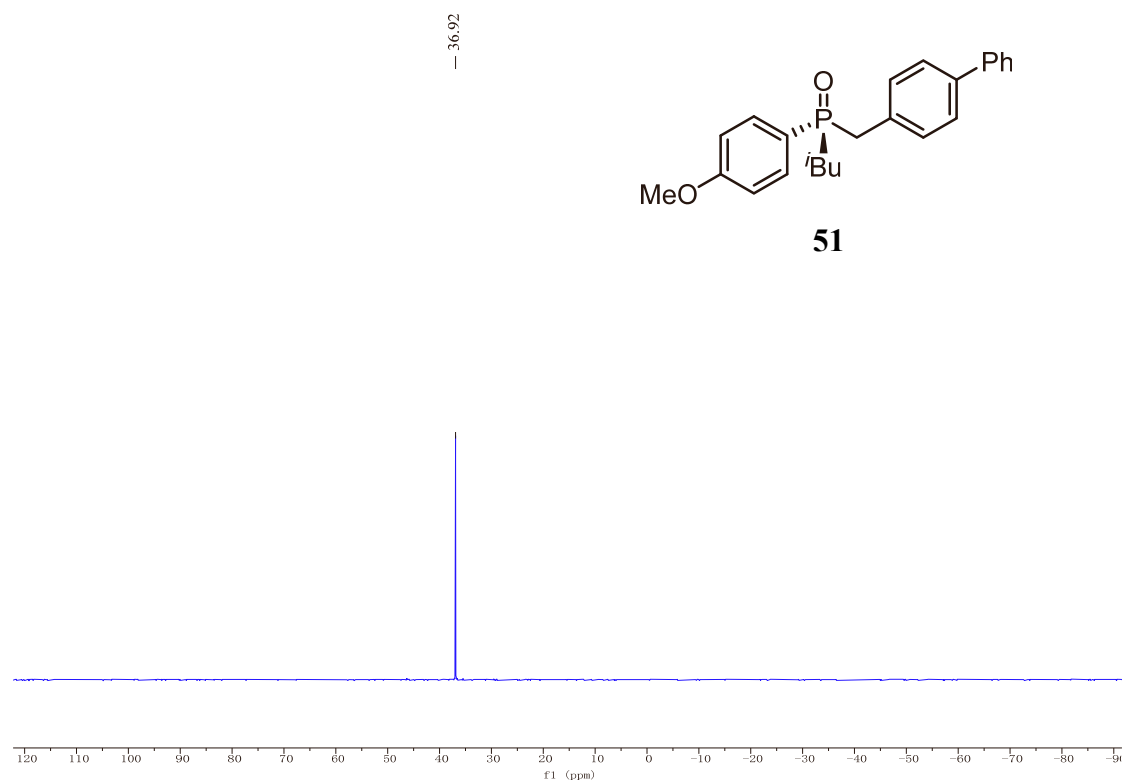
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



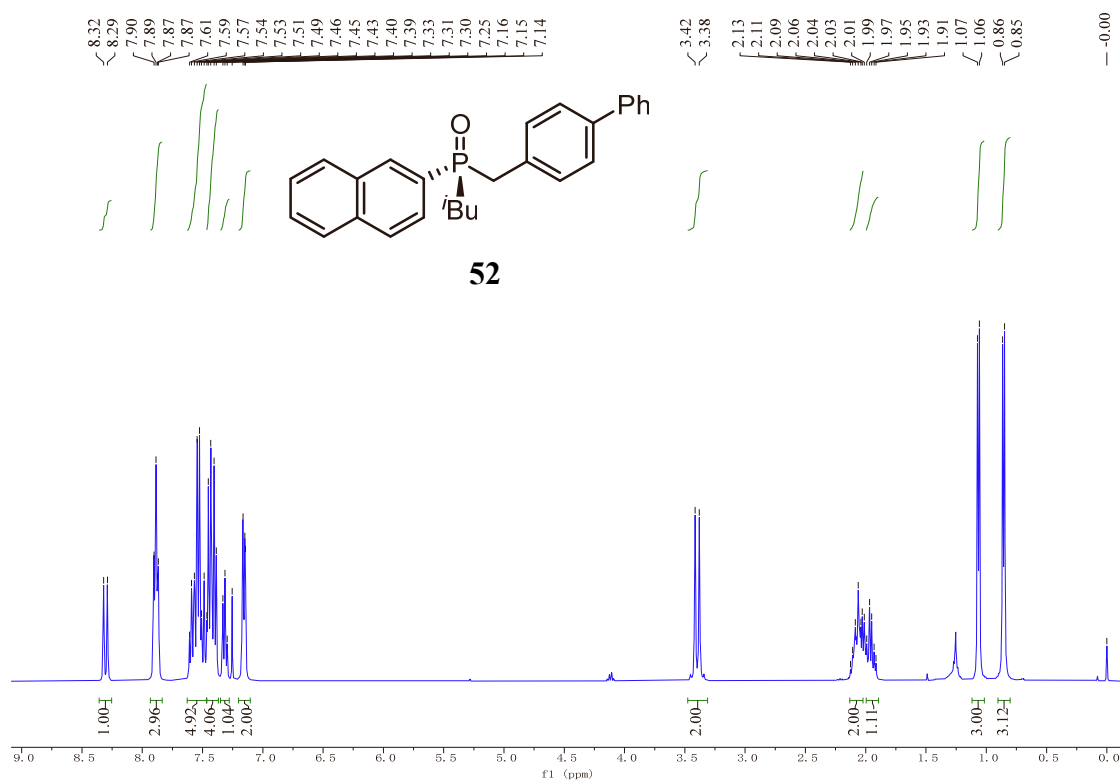
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



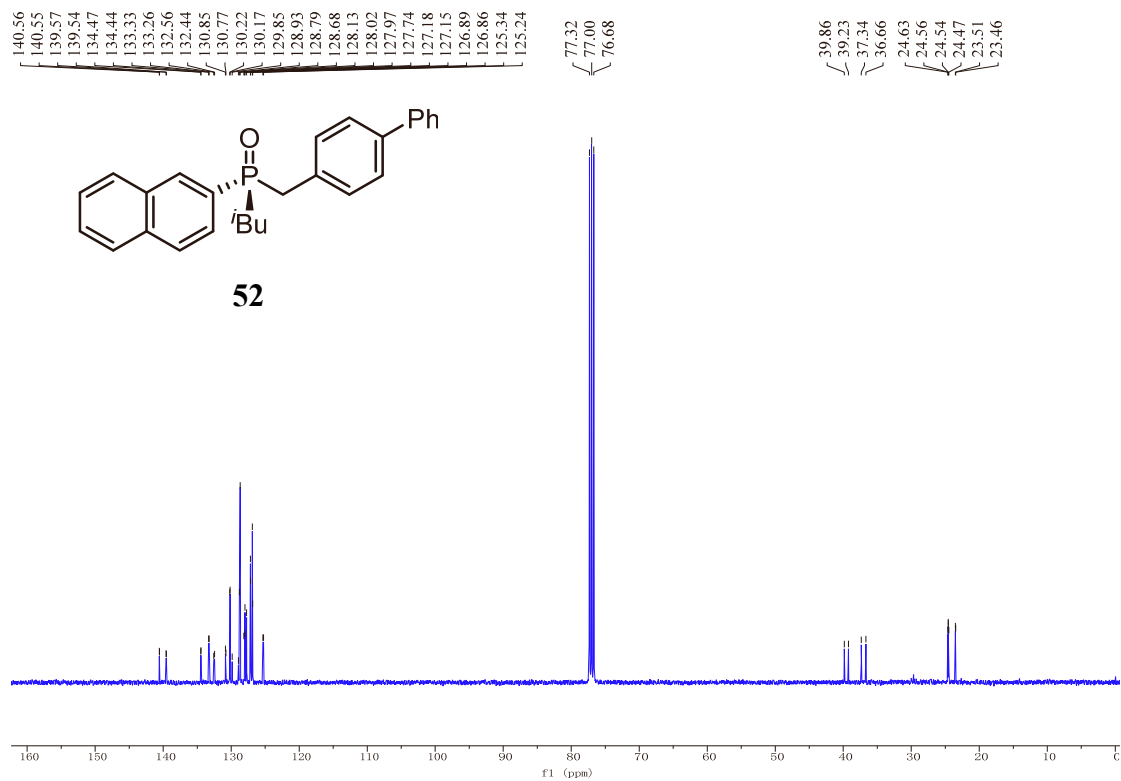
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



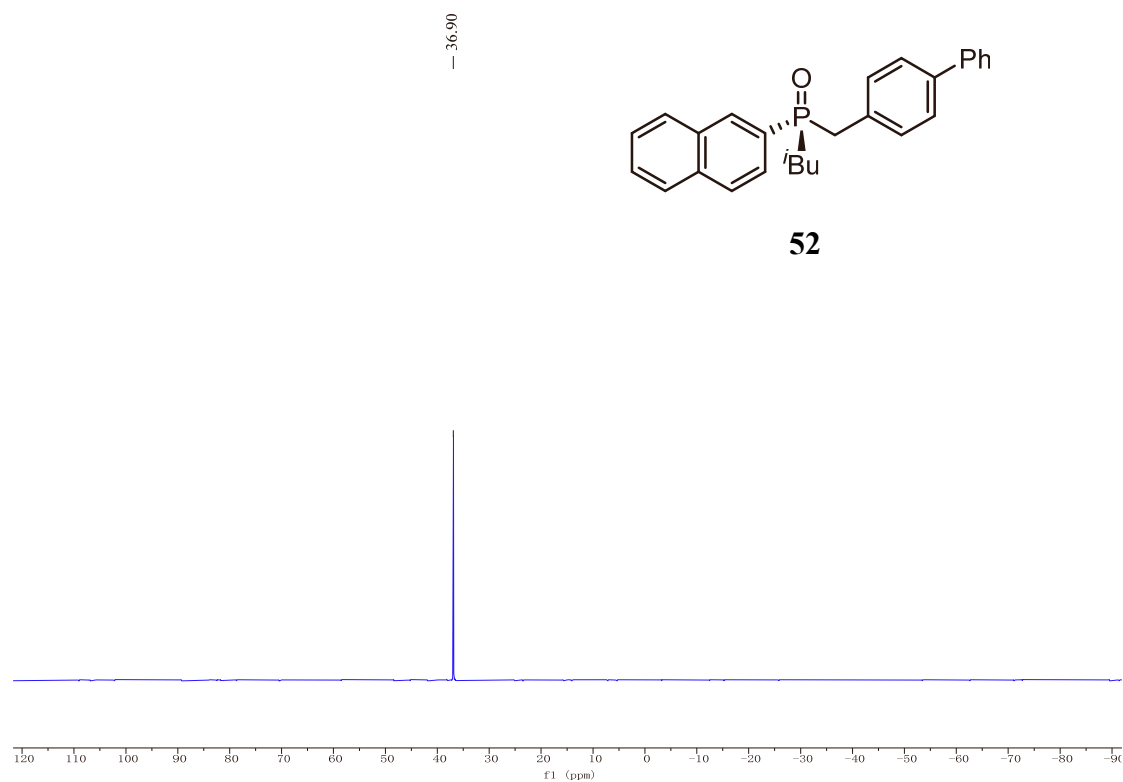
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



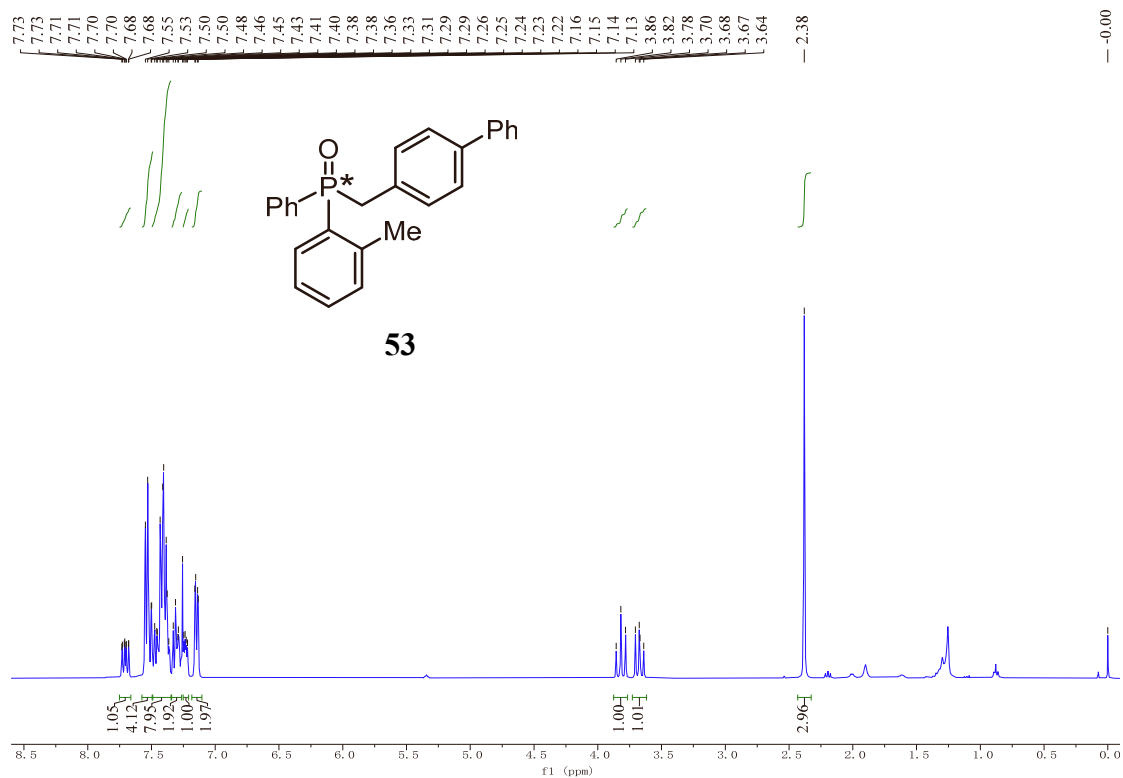
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



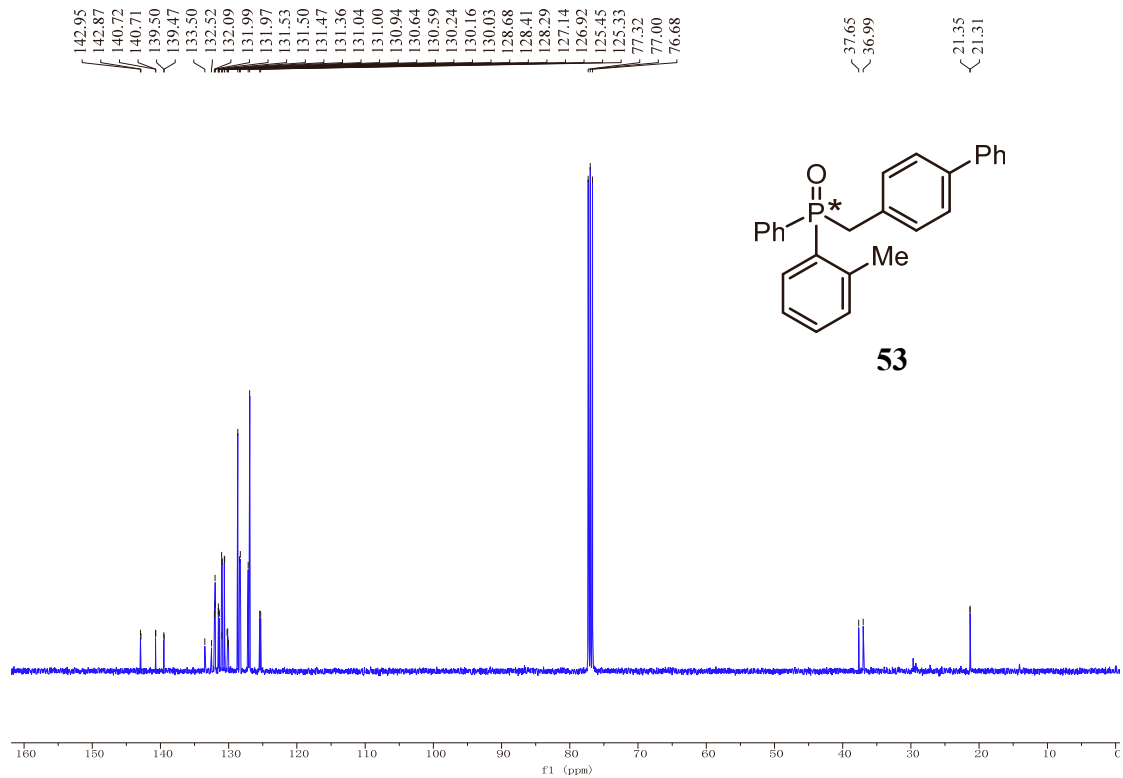
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



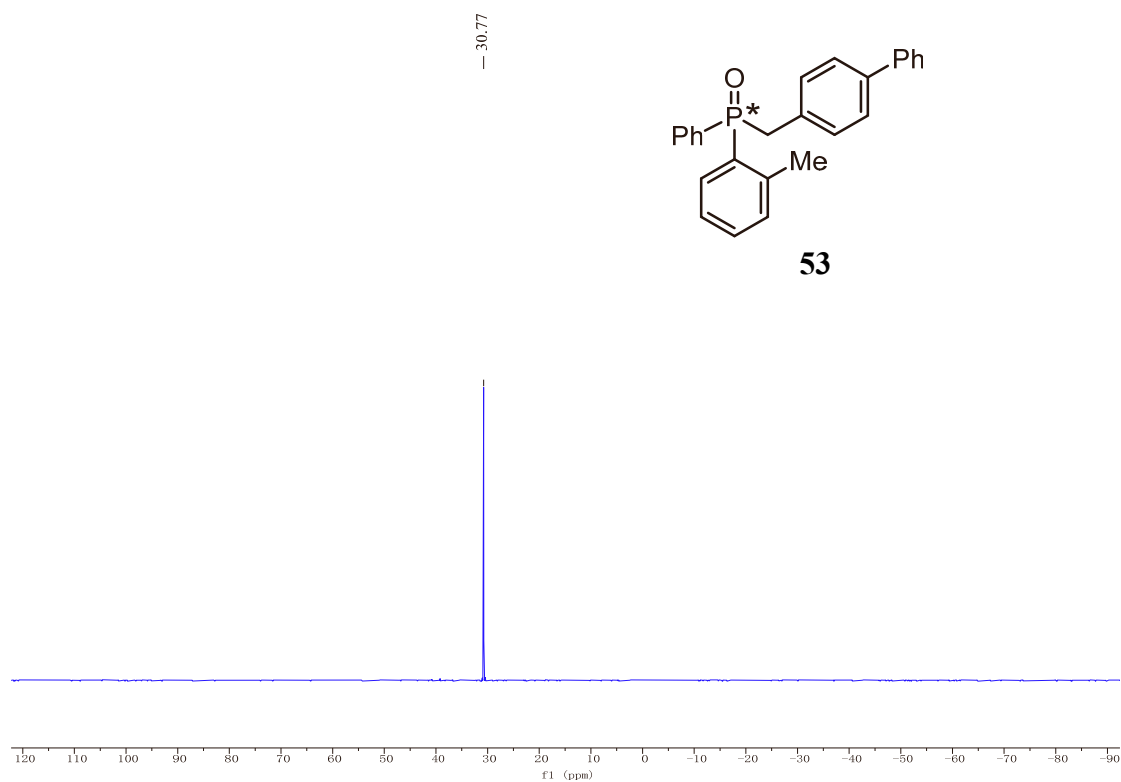
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

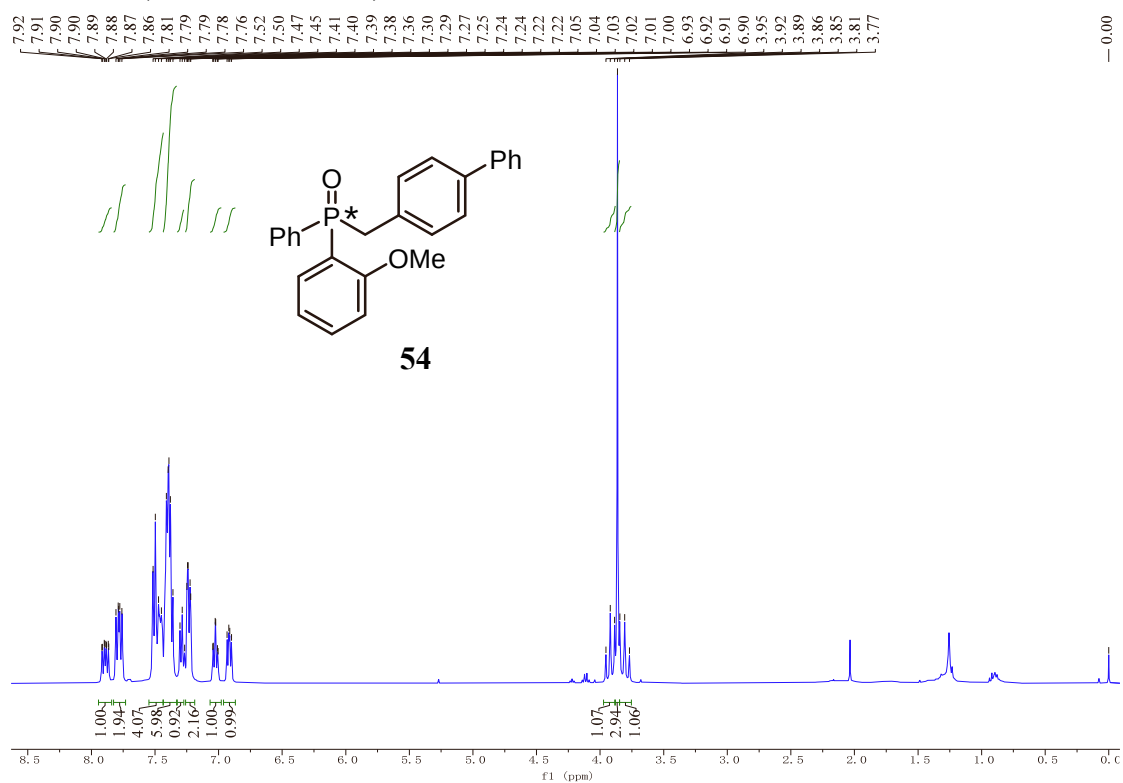


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

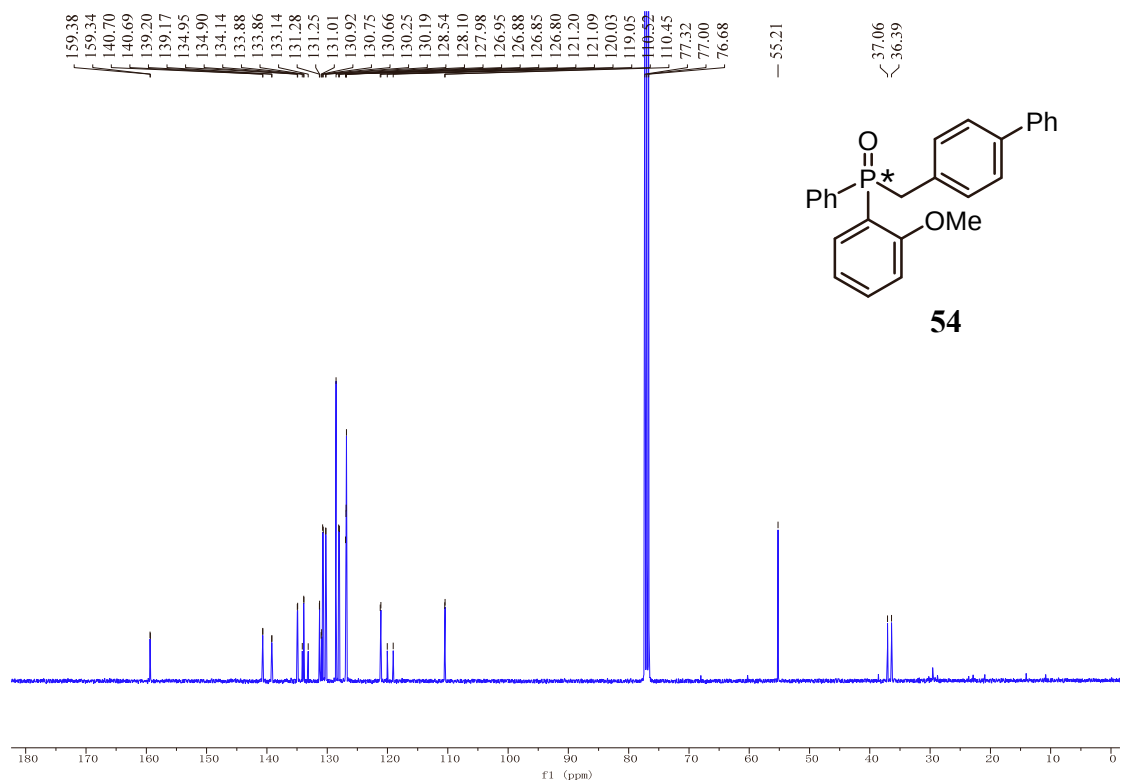




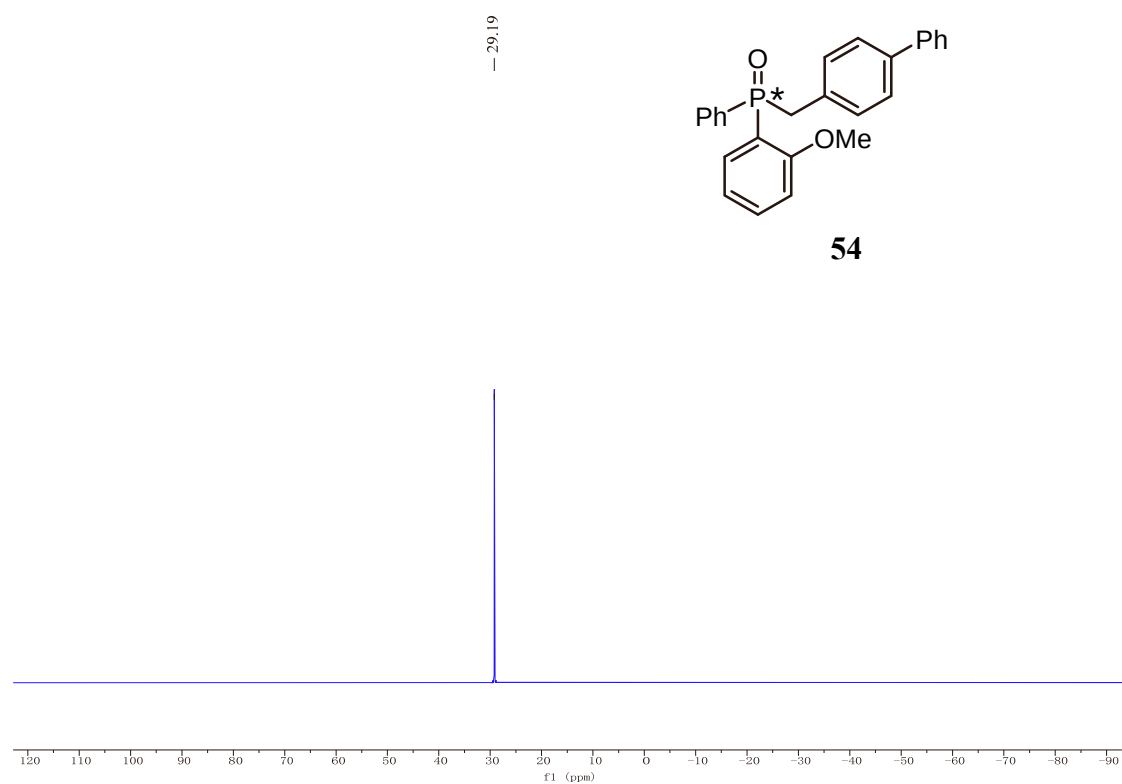
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



[illegible]

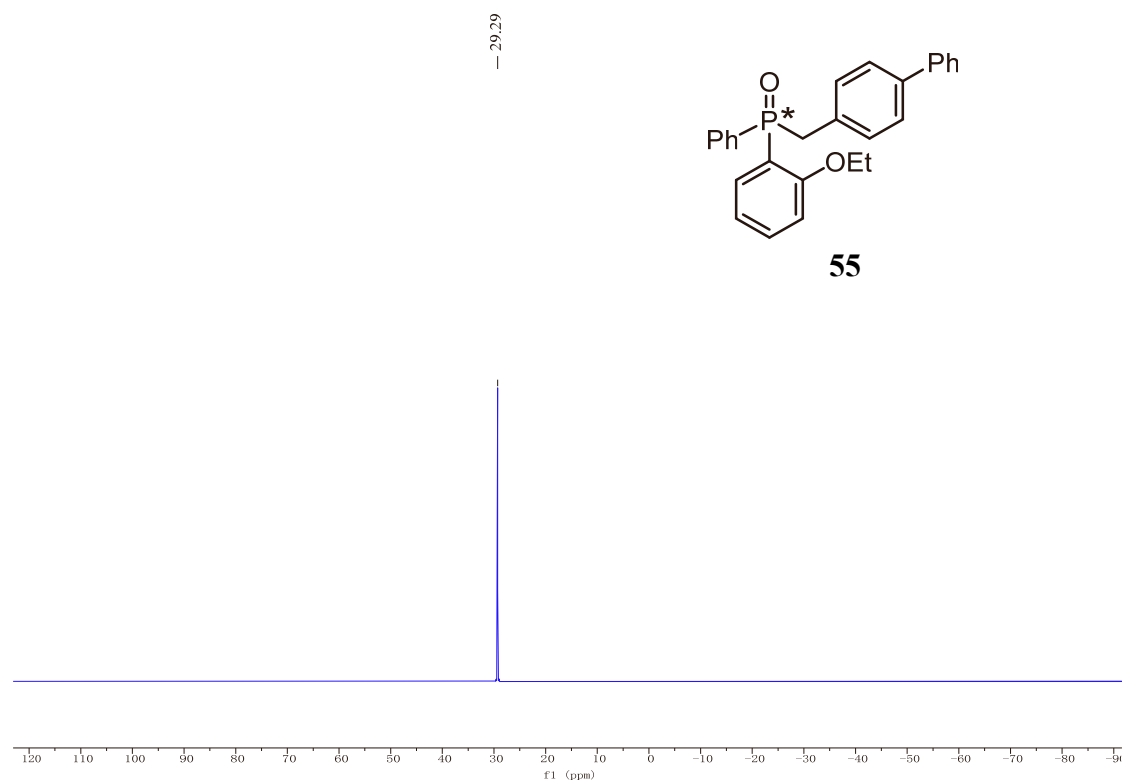
Chemical structure of compound **55** is shown as an inset: CCOP(=O)(c1ccccc1)Cc2ccccc2.

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound **55** is displayed below the structure. The x-axis represents the chemical shift in ppm (f1), ranging from 0 to 180. The spectrum shows several peaks, with integration values indicated above the baseline.

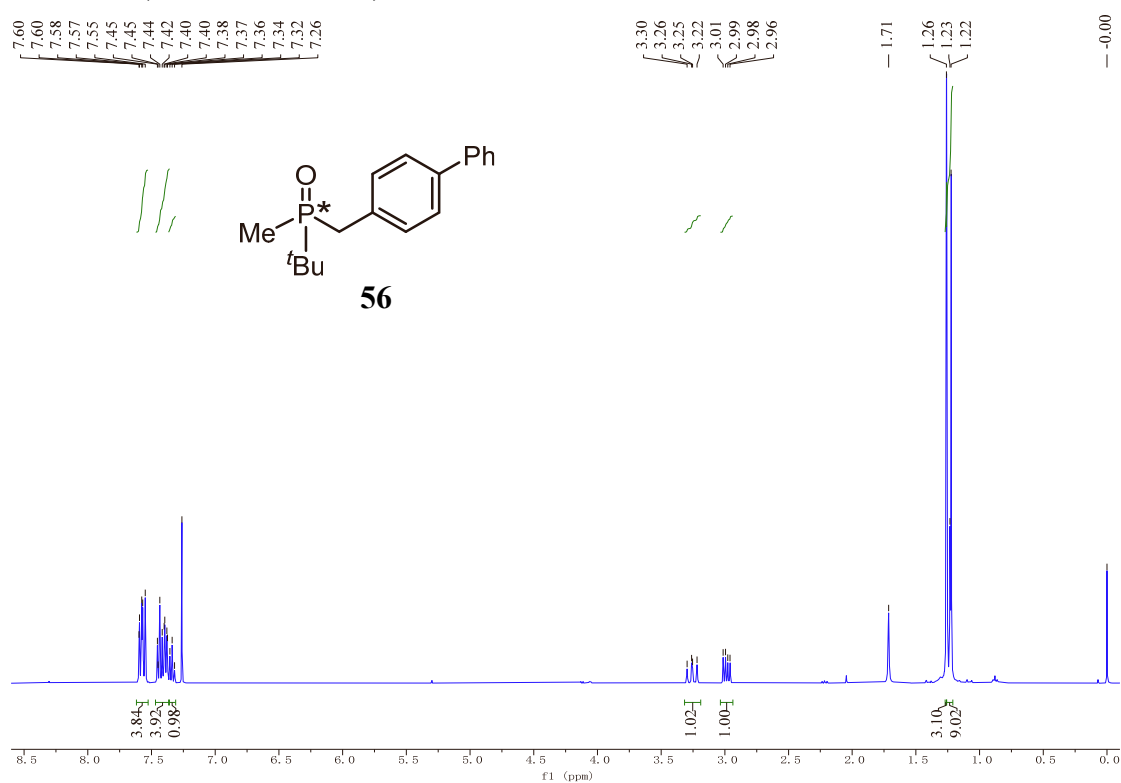
Integration values (from left to right):

- 1.58, 7.4
- 1.58, 6.9
- 1.40, 6.9
- 1.40, 6.8
- 1.39, 2.2
- 1.39, 1.9
- 1.34, 9.8
- 1.34, 9.3
- 1.34, 3.2
- 1.33, 8.6
- 1.33, 8.4
- 1.33, 3.1
- 1.31, 2.6
- 1.31, 2.3
- 1.31, 0.1
- 1.30, 9.2
- 1.30, 7.2
- 1.30, 6.3
- 1.30, 2.5
- 1.30, 2.0
- 1.28, 5.4
- 1.28, 0.4
- 1.27, 9.2
- 1.26, 9.6
- 1.26, 8.9
- 1.26, 8.7
- 1.26, 8.0
- 1.20, 9.4
- 1.20, 8.3
- 1.19, 6.6
- 1.18, 6.8
- 1.10, 9.9
- 1.10, 9.2
- 77.32
- 77.00
- 76.68
- 63.73
- 36.77
- 36.10
- 14.44

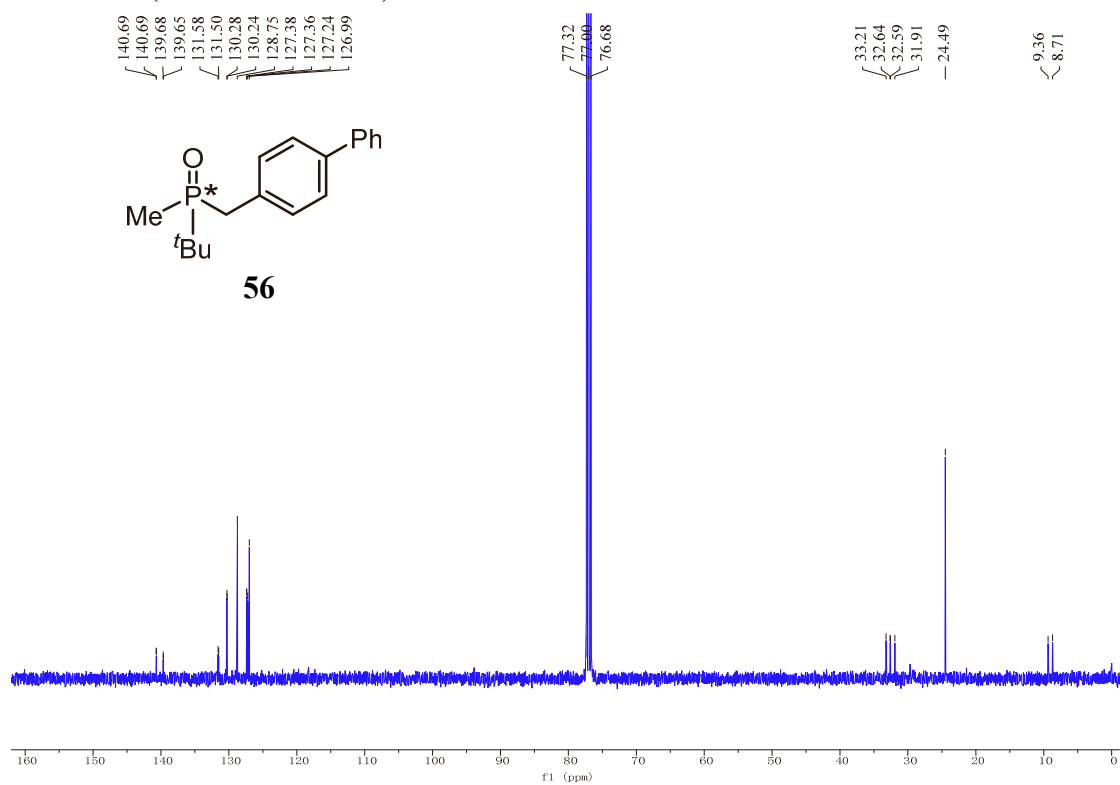
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



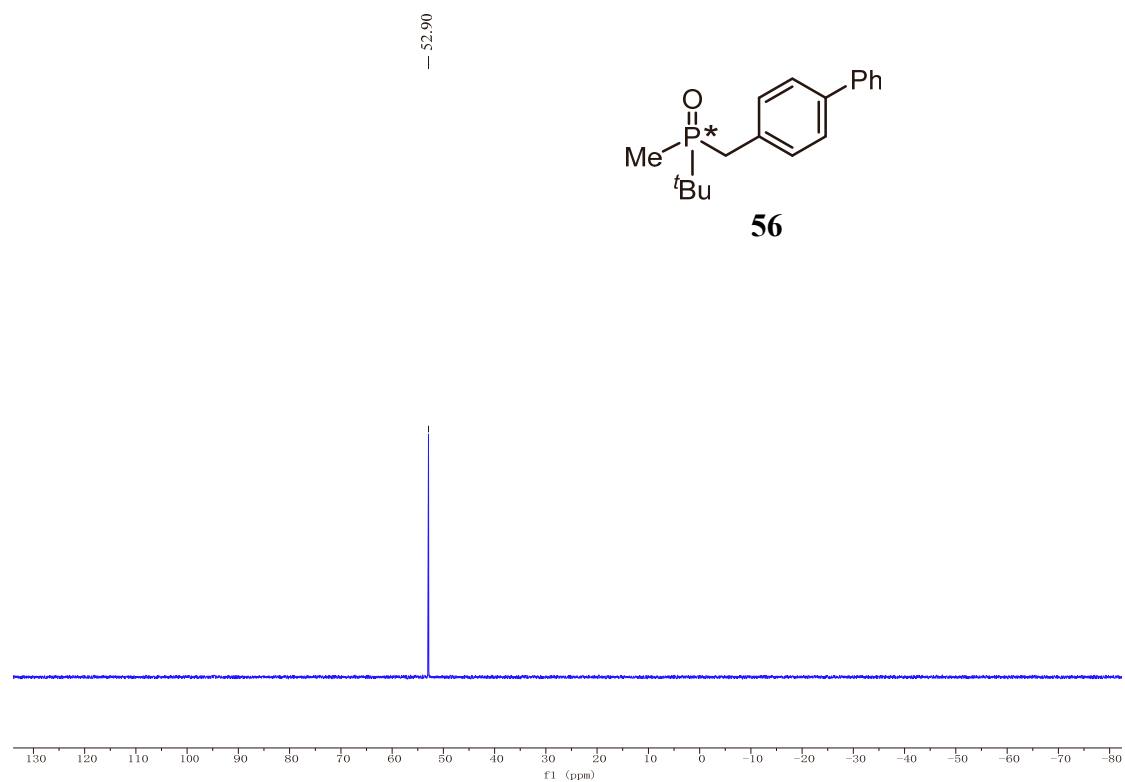
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



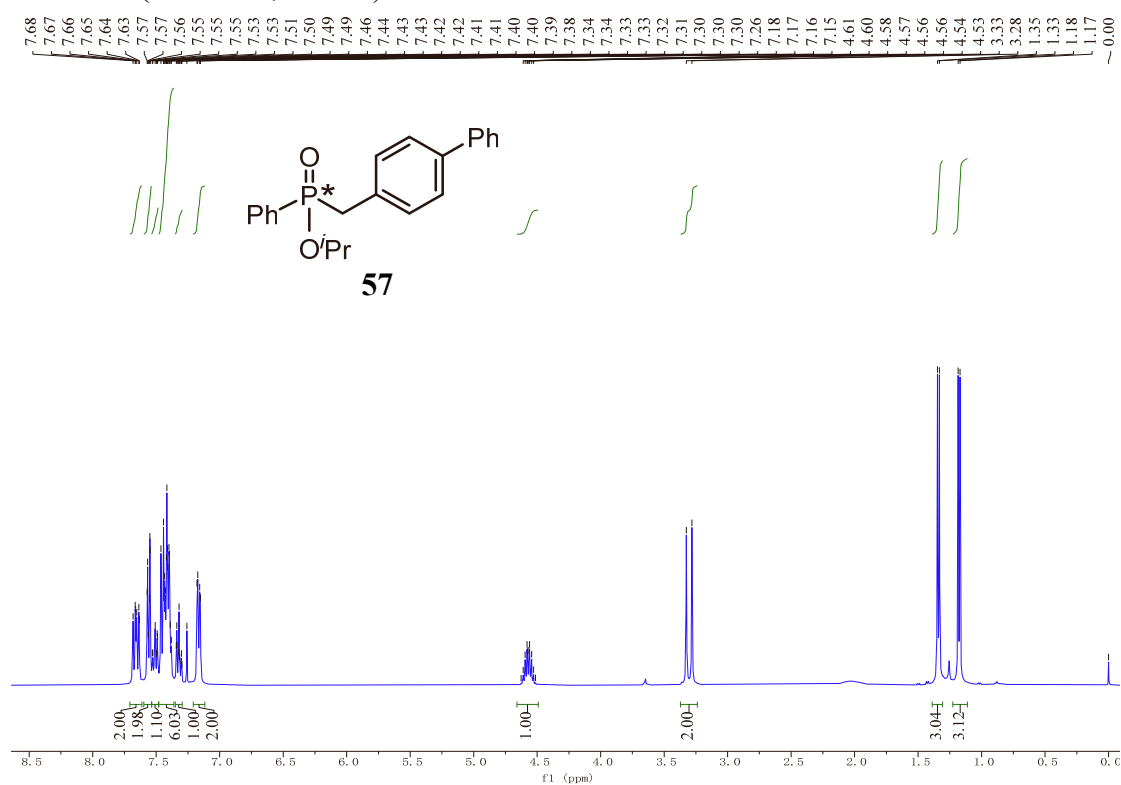
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



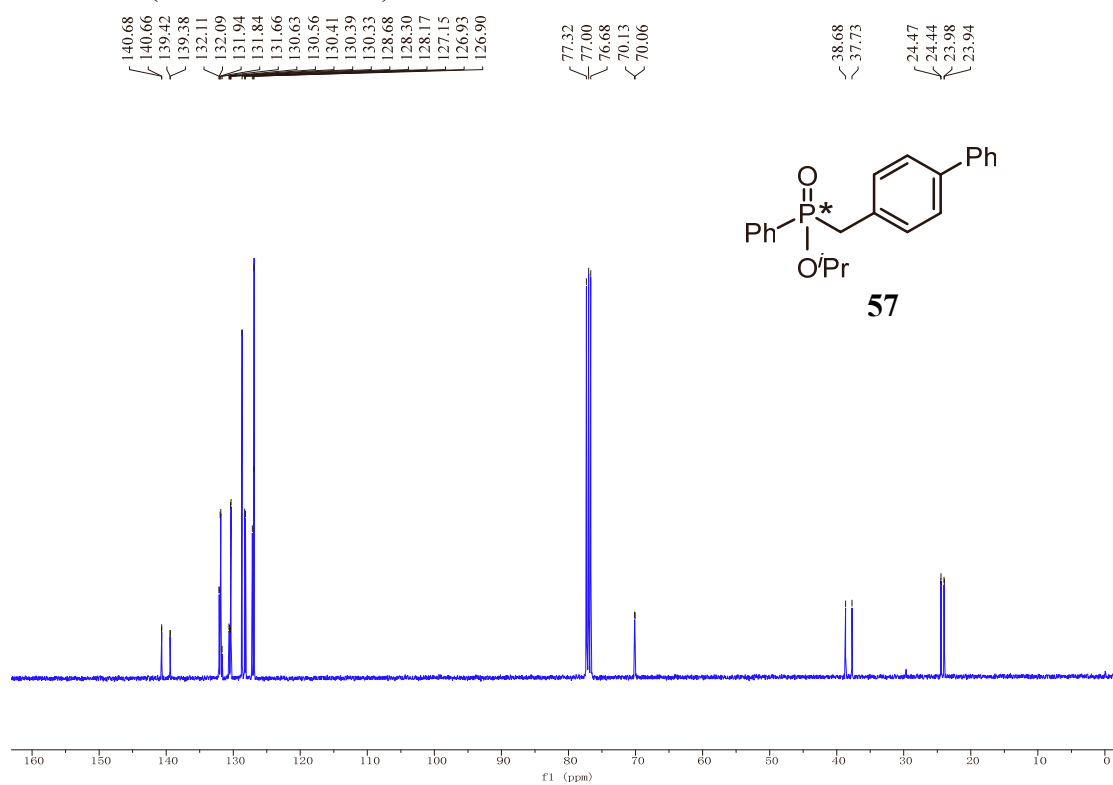
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



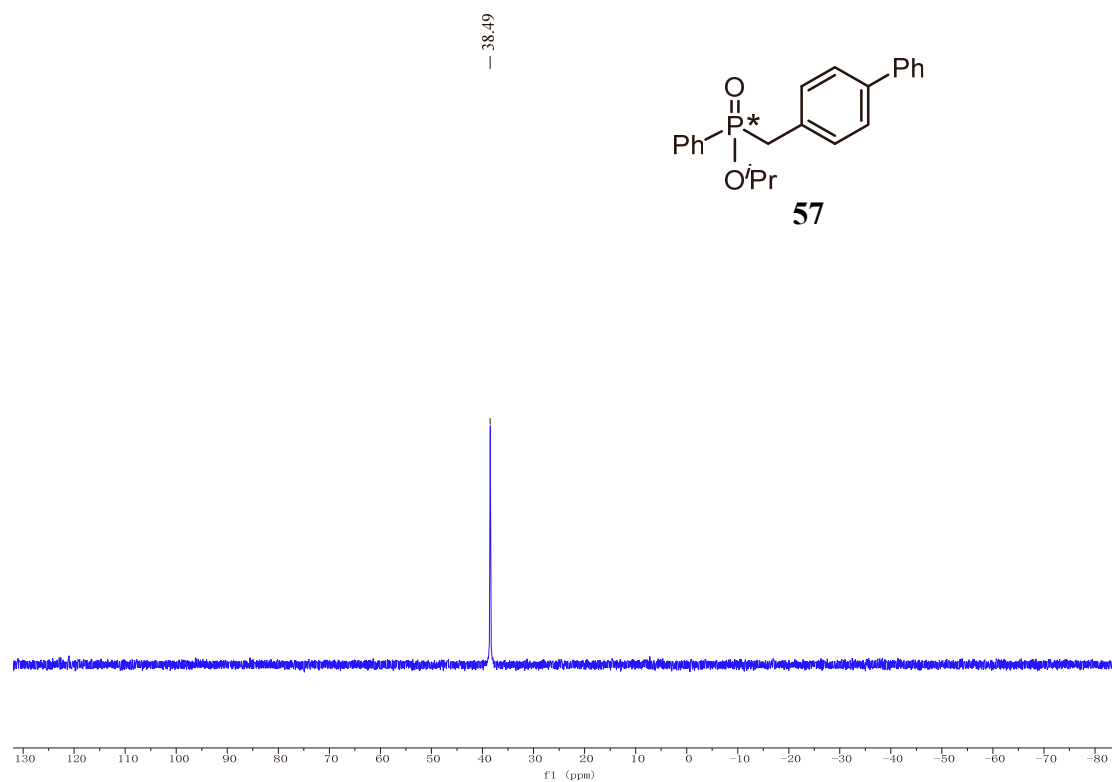
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )





<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of compound **58**. The chemical structure of **58** is shown above the spectrum. The spectrum displays peaks in the aromatic region (7.1-7.7 ppm) and aliphatic region (1.1-1.6 ppm). Integration values are provided below the peaks.

Chemical structure of **58**: CC(C)OP(=O)(c1ccccc1)Cc2ccccc2

<sup>1</sup>H NMR peaks (ppm): 7.67, 7.67, 7.67, 7.65, 7.65, 7.65, 7.64, 7.63, 7.63, 7.62, 7.61, 7.55, 7.55, 7.55, 7.54, 7.53, 7.53, 7.52, 7.51, 7.48, 7.46, 7.46, 7.44, 7.43, 7.43, 7.42, 7.41, 7.41, 7.38, 7.38, 7.38, 7.36, 7.34, 7.31, 7.30, 7.29, 7.29, 7.28, 7.28, 4.56, 4.55, 4.54, 4.54, 3.30, 3.30, 3.28, 3.25, 3.23, 1.57, 1.55, 1.53, 1.51, 1.51, 1.25, 1.23, 1.17, 1.16.

Integration values: 3.95, 2.98, 4.00, 1.16, 2.44, 1.00, 1.00, 2.98, 2.95, 2.95.

A "Minor isomer" is indicated in the spectrum.

CC(C)P(=O)(c1ccccc1)c2ccc(cc2)C3=CC=CC=C3

**58**

140.79  
 139.61  
 139.57  
 137.06  
 136.99  
 132.31  
 132.22  
 131.96  
 131.94  
 131.34  
 130.13  
 129.44  
 128.72  
 128.68  
 128.15  
 128.03  
 127.17  
 126.95  
 126.90  
 126.74  
 126.71

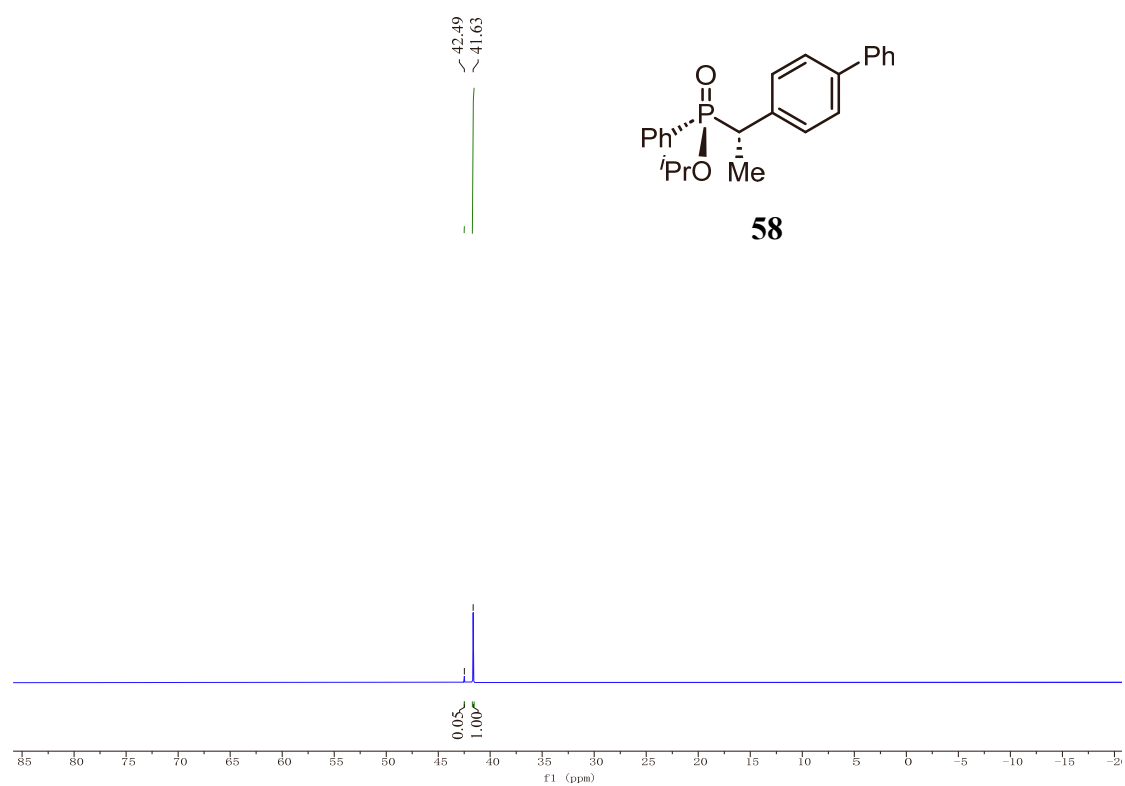
69.97  
 69.91

42.05  
 41.10

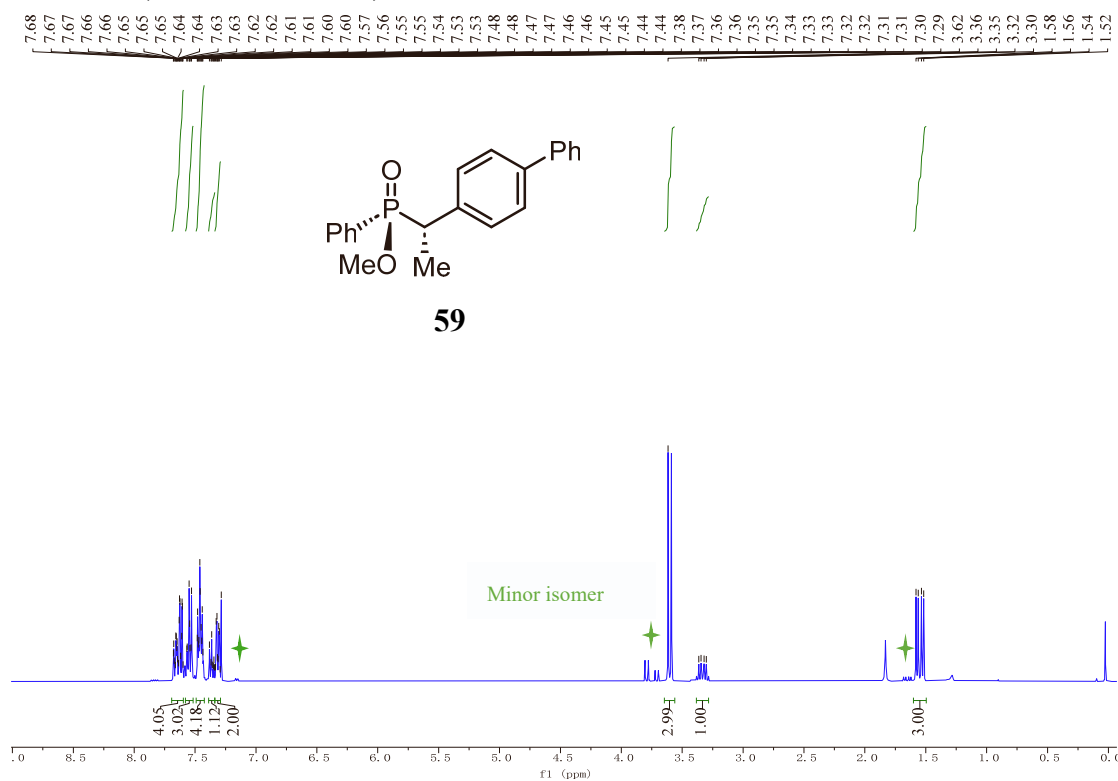
24.23  
 24.19  
 24.00  
 23.95

14.51  
 14.49

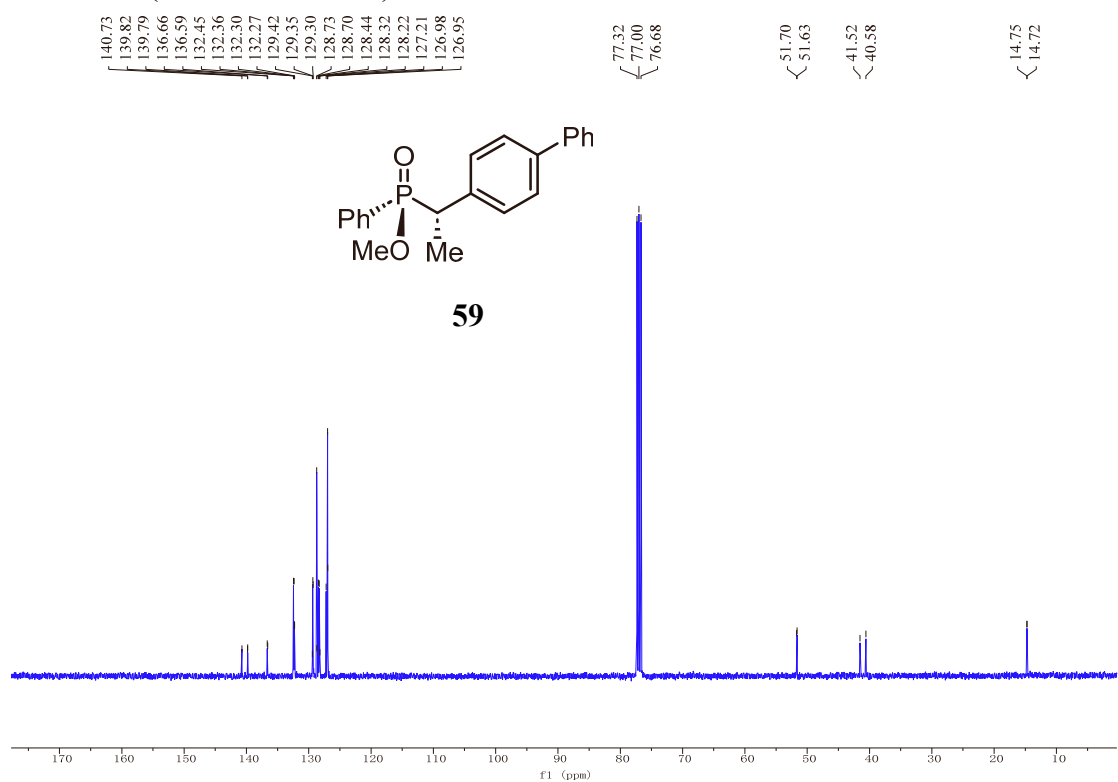
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



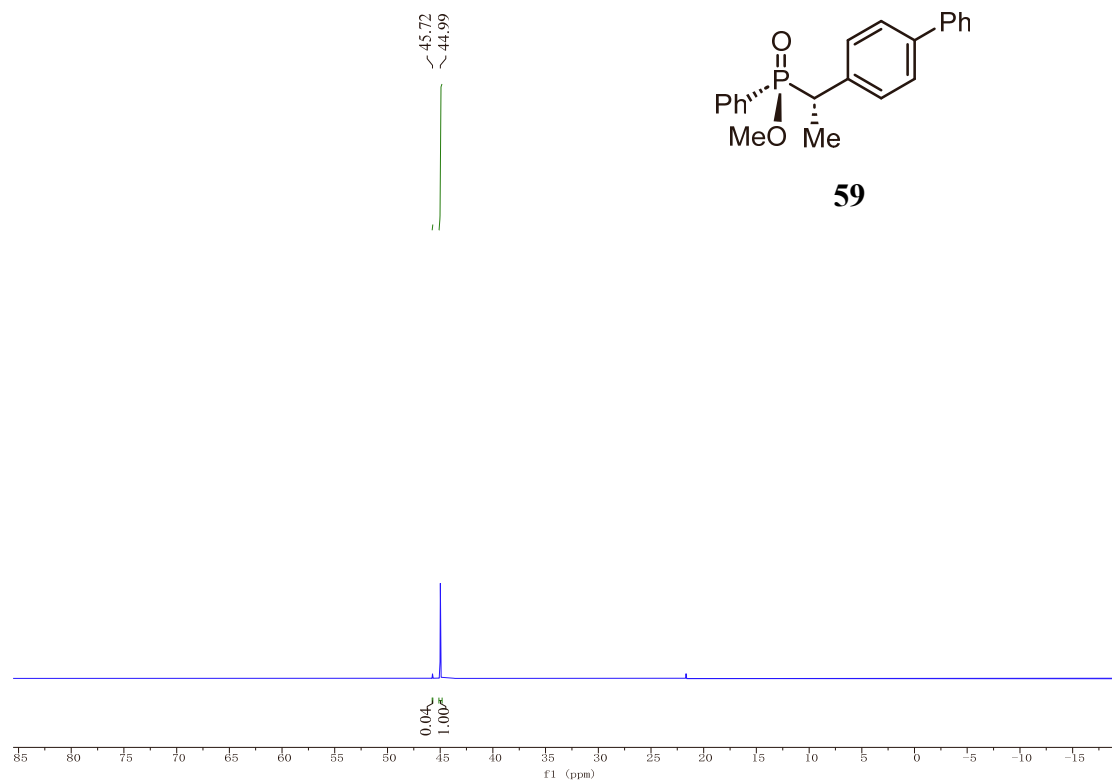
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



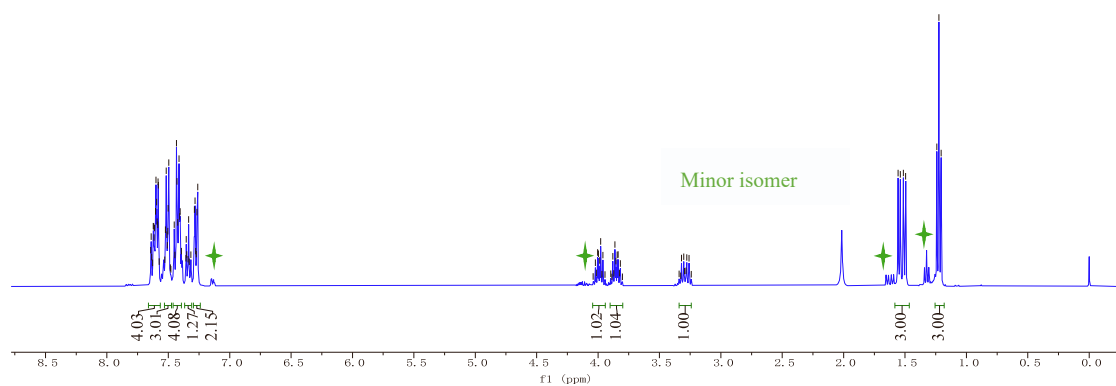
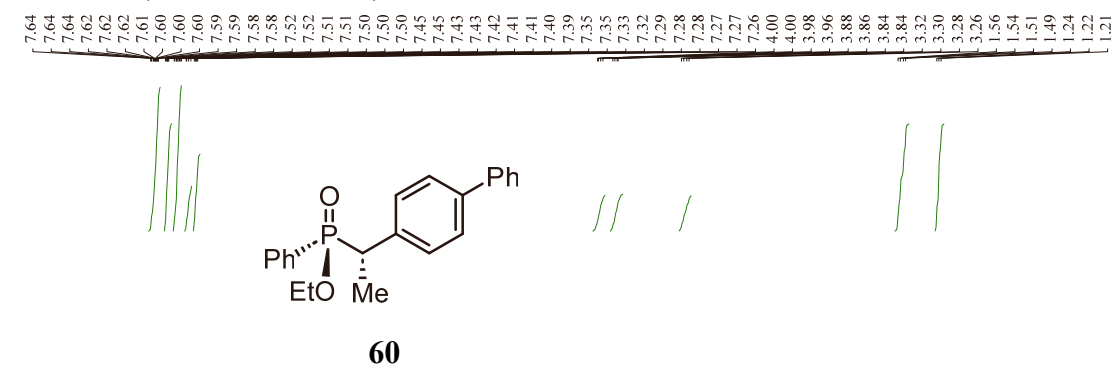
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



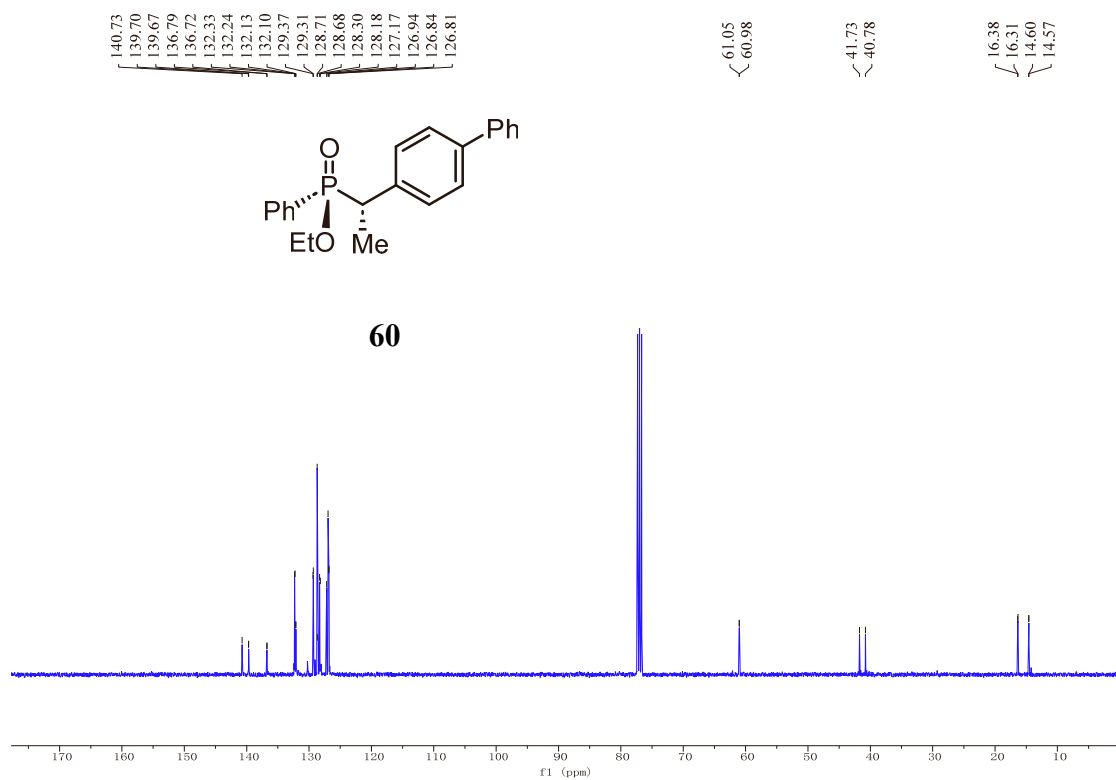
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



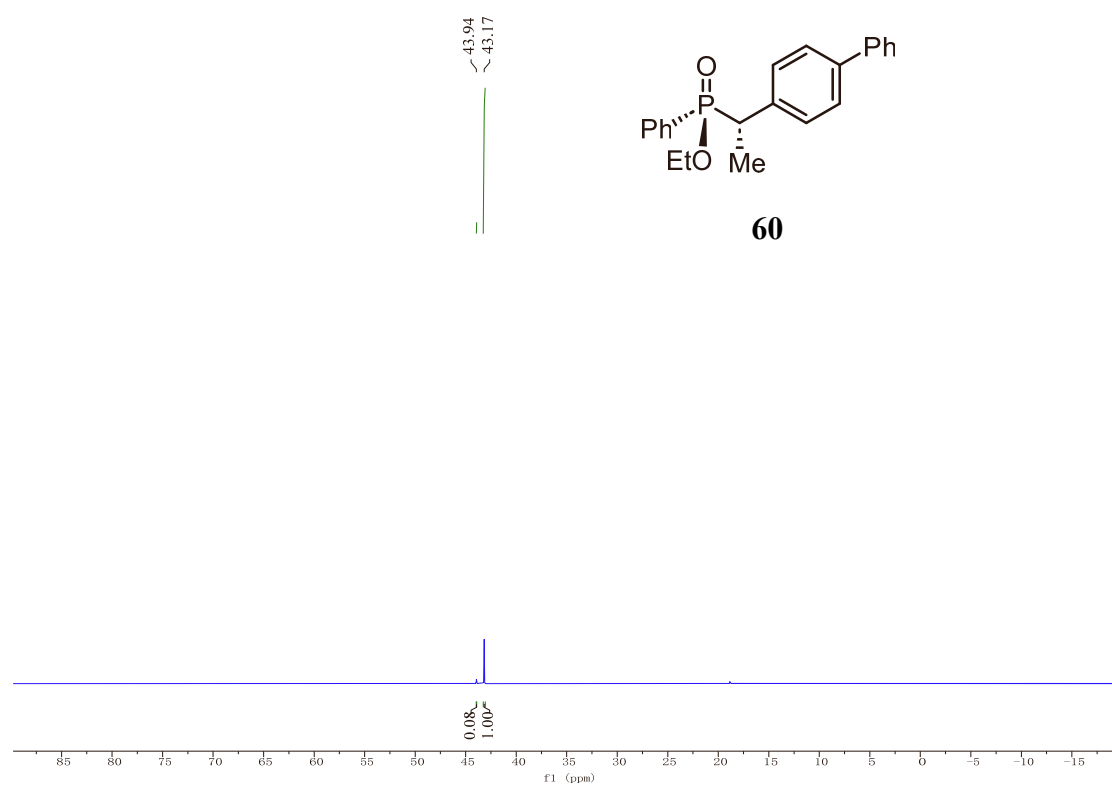
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



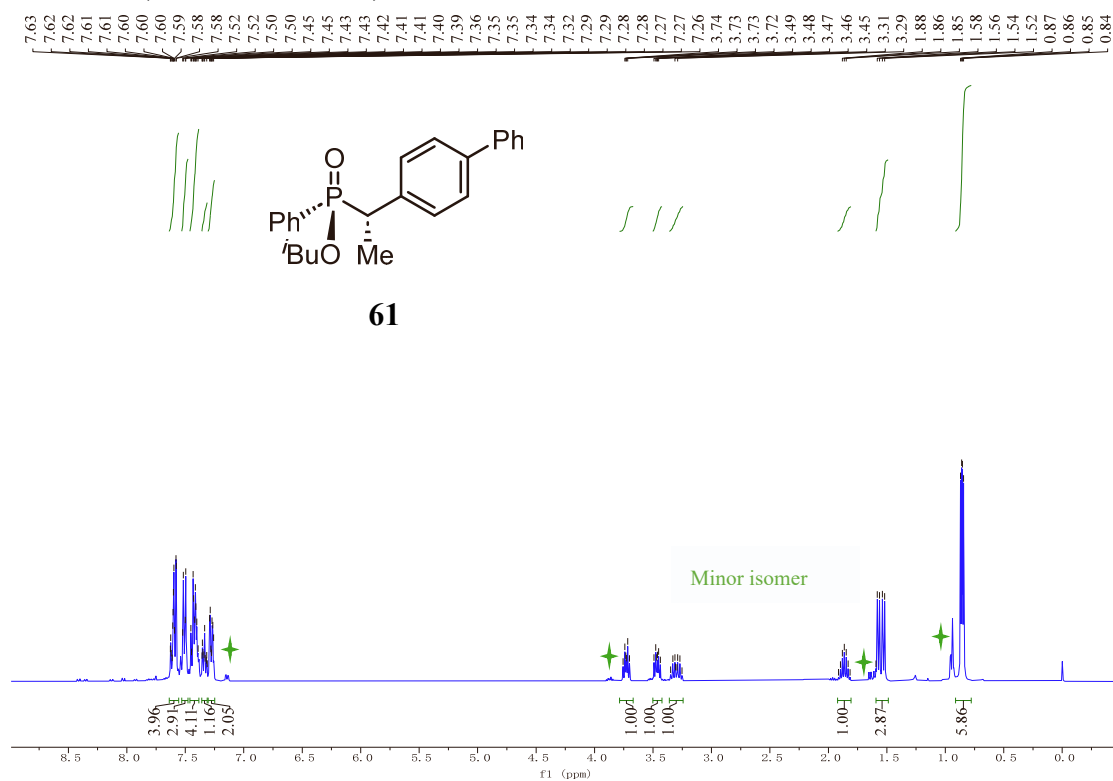
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



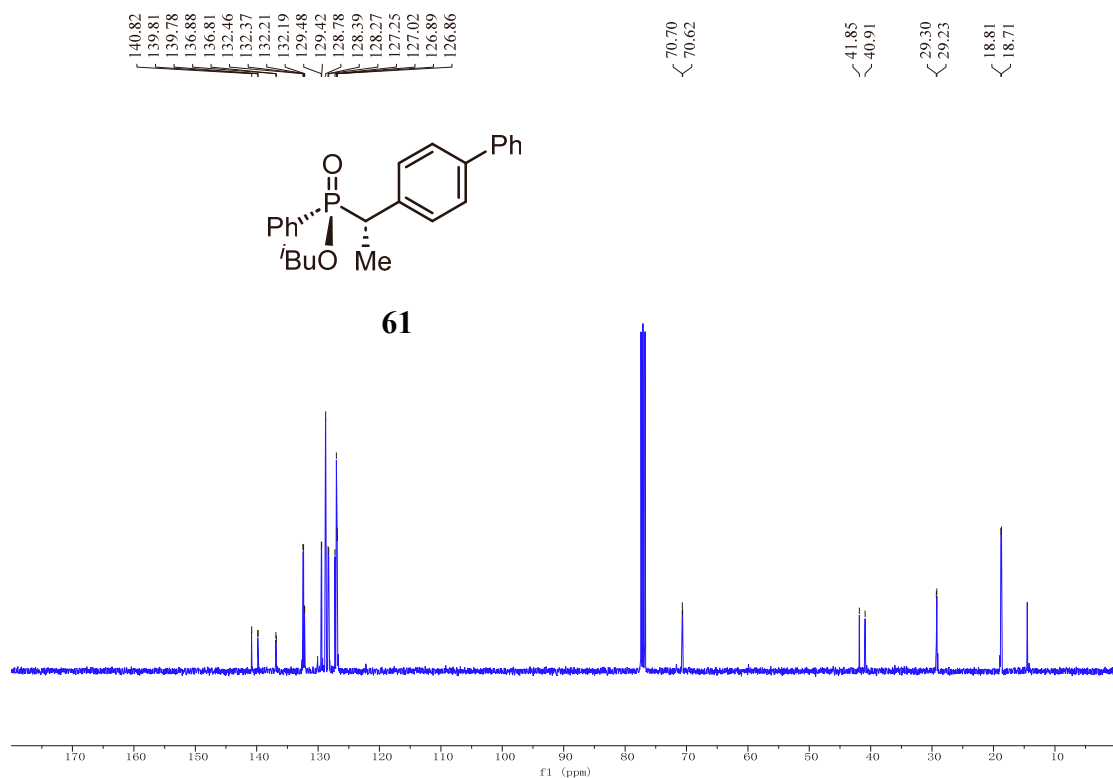
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



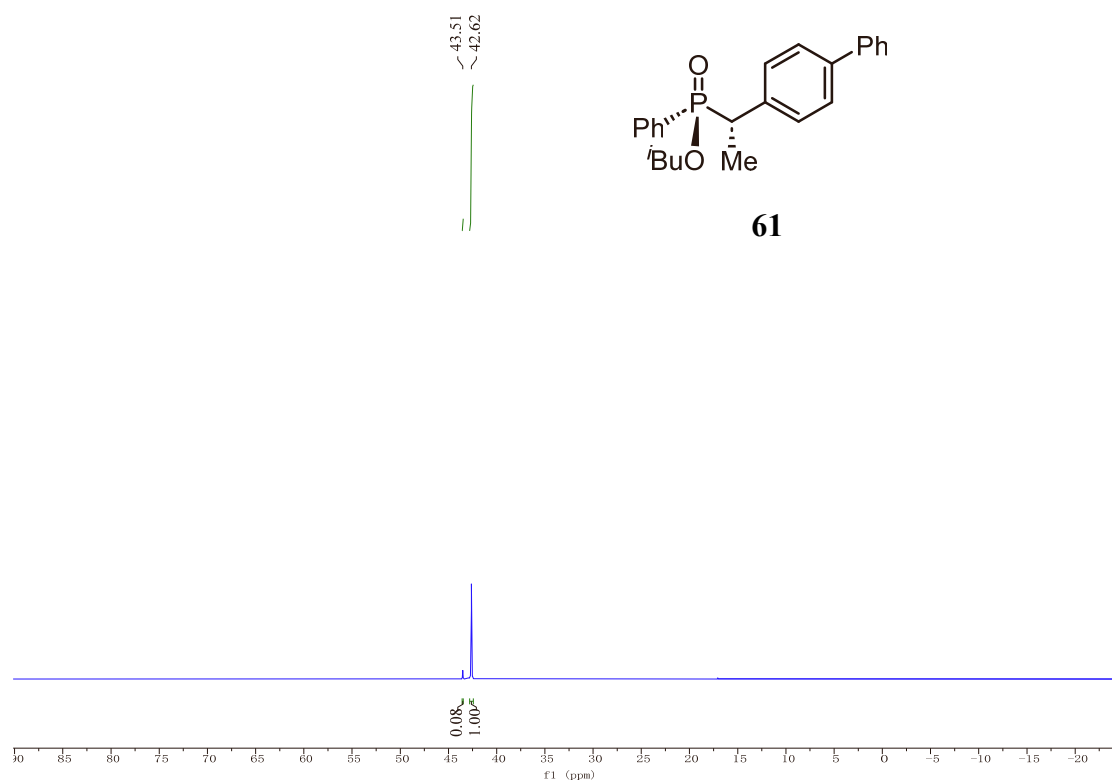
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

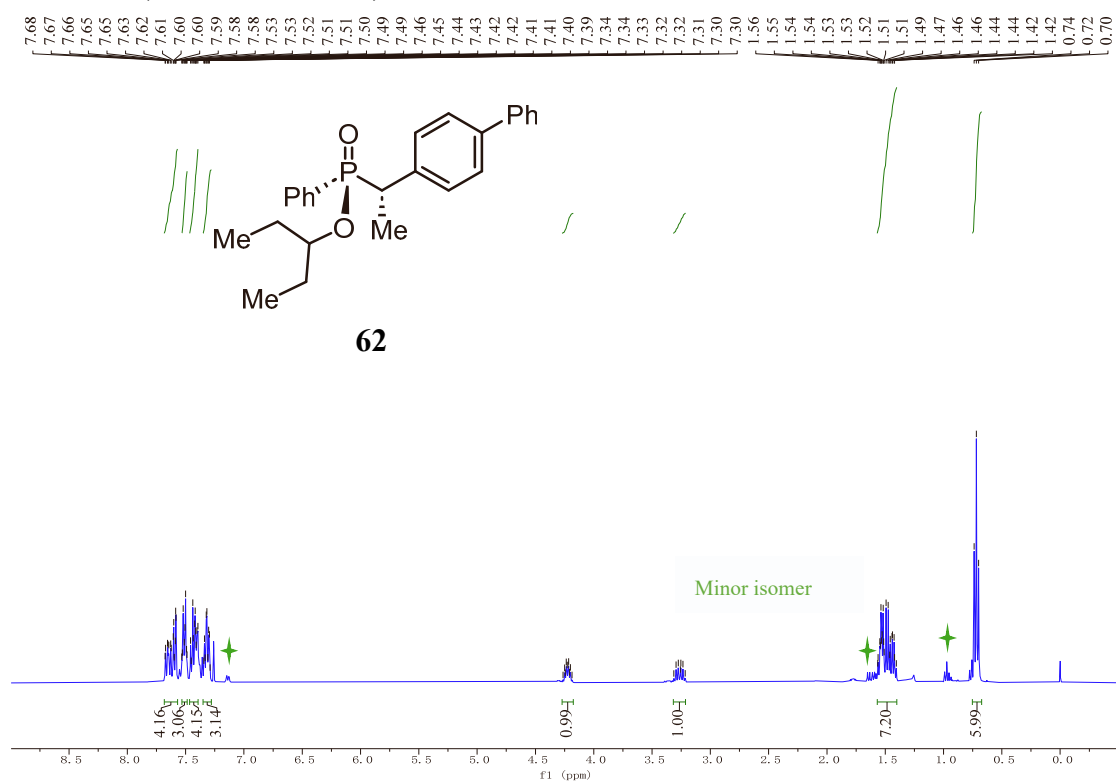


**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**

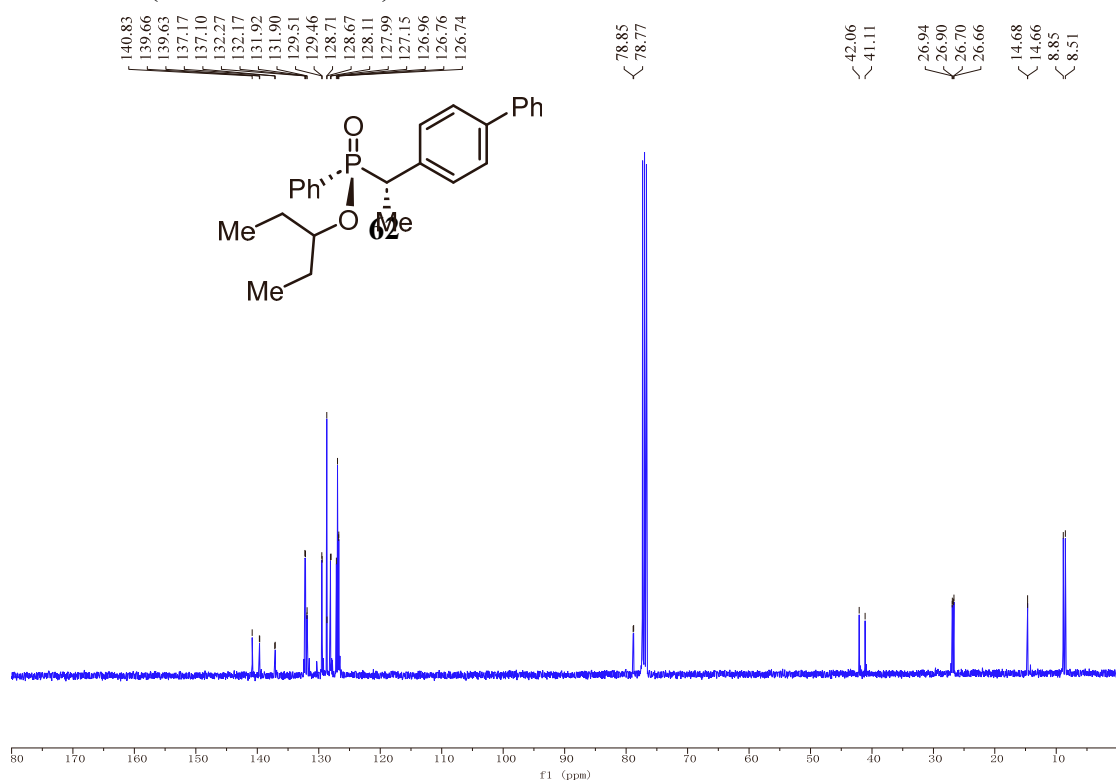




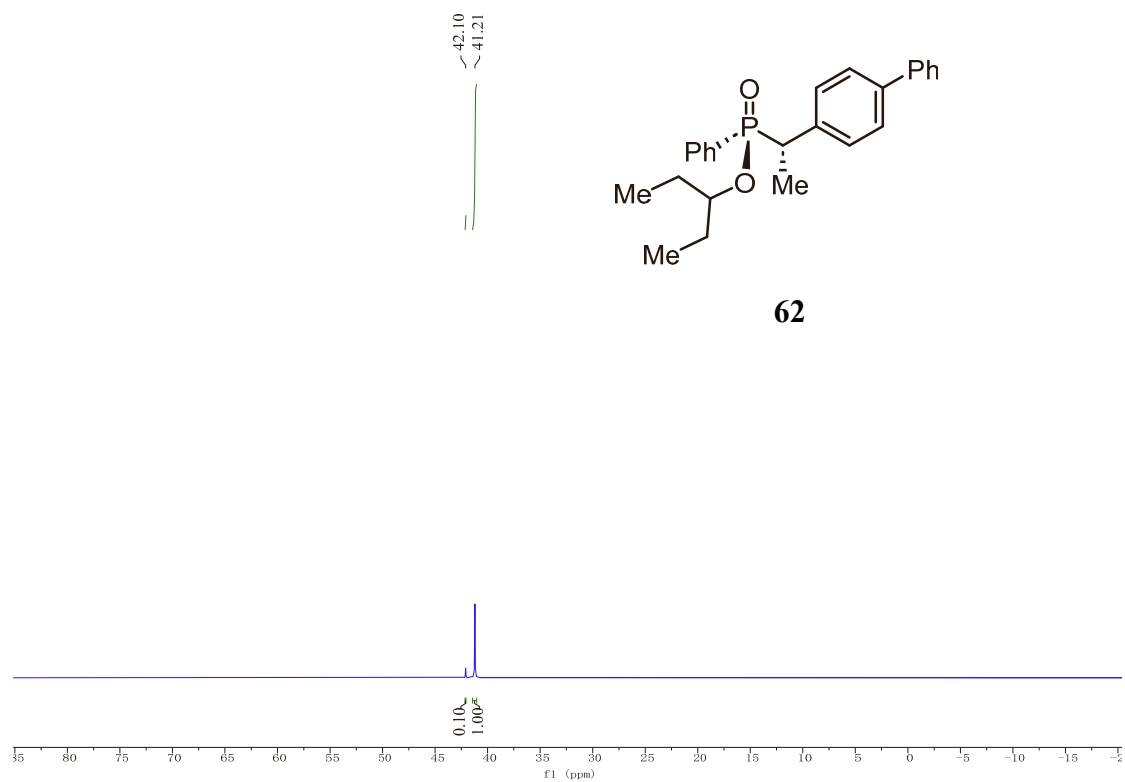
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



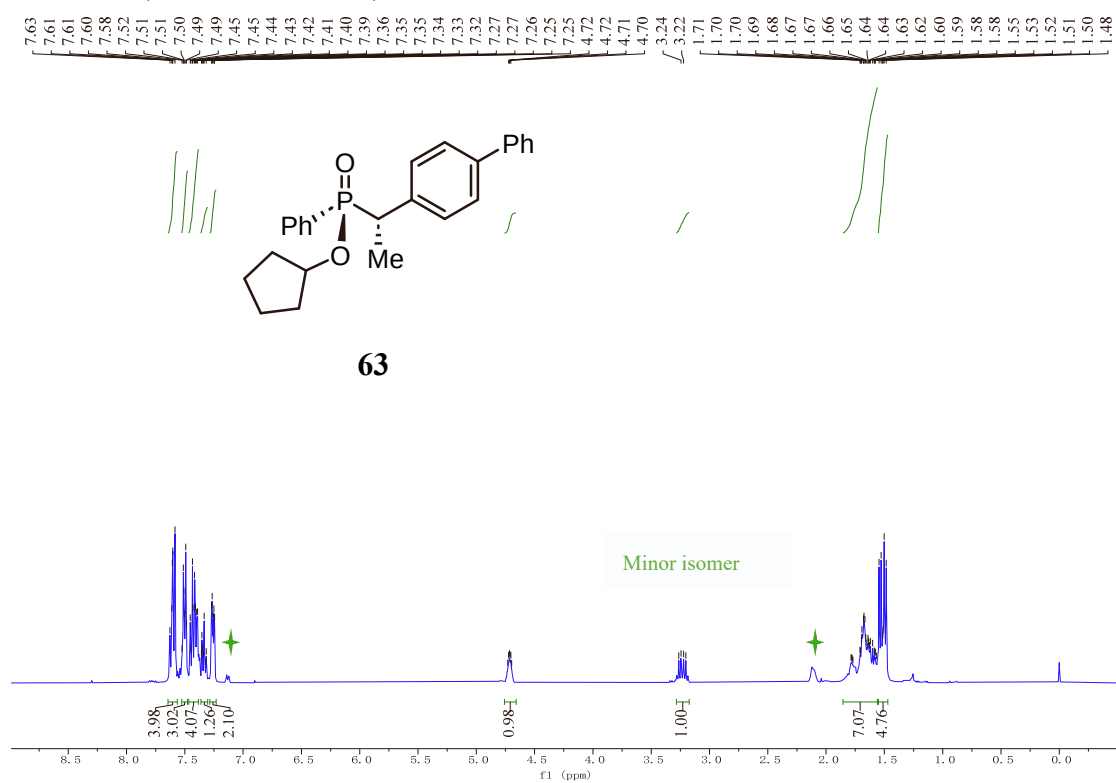
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**



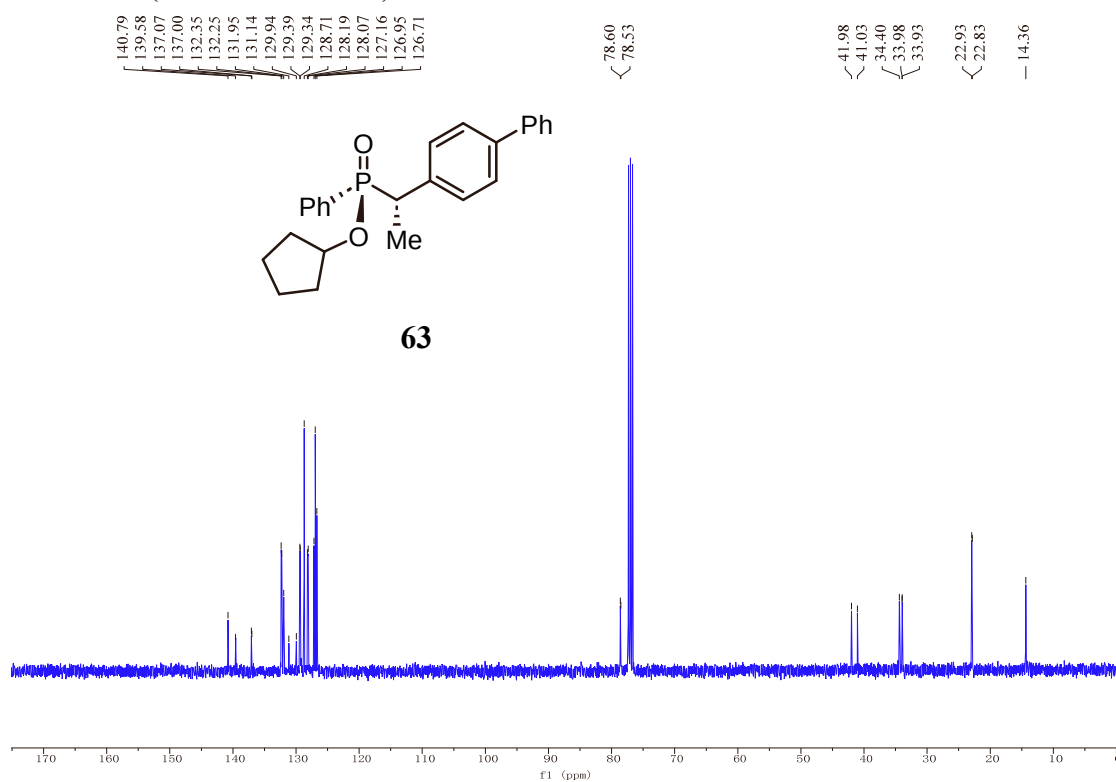
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



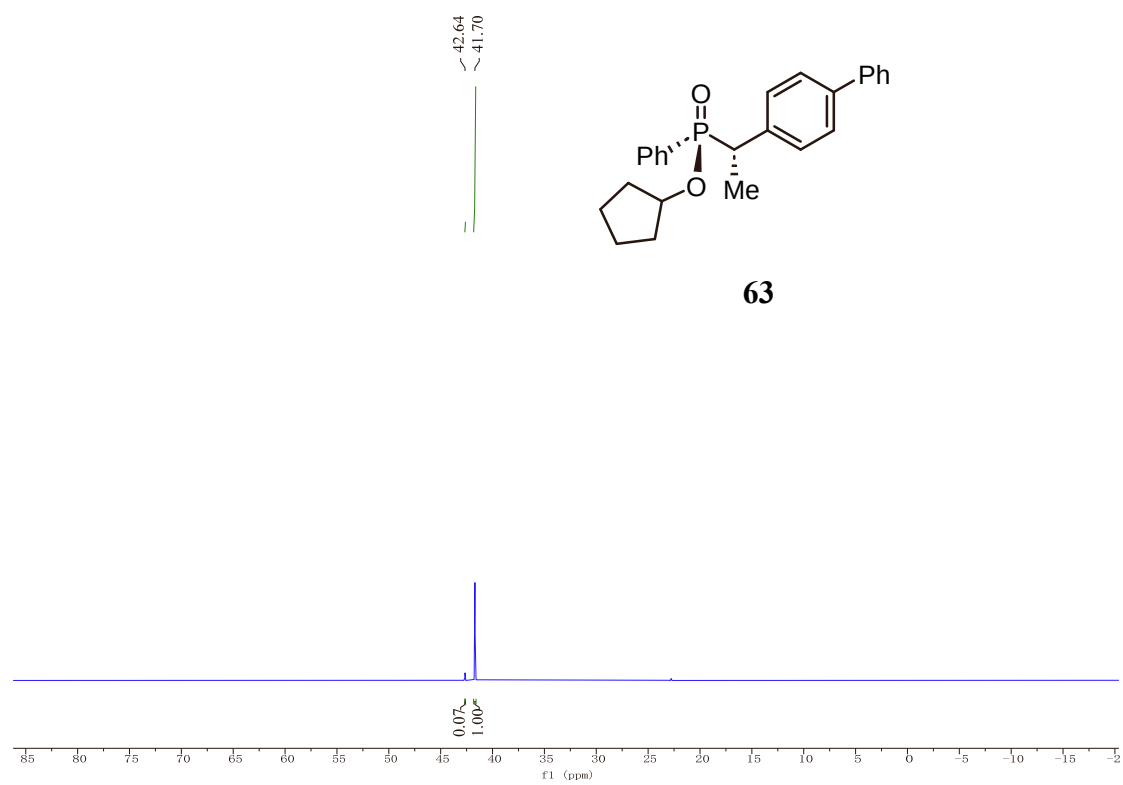
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



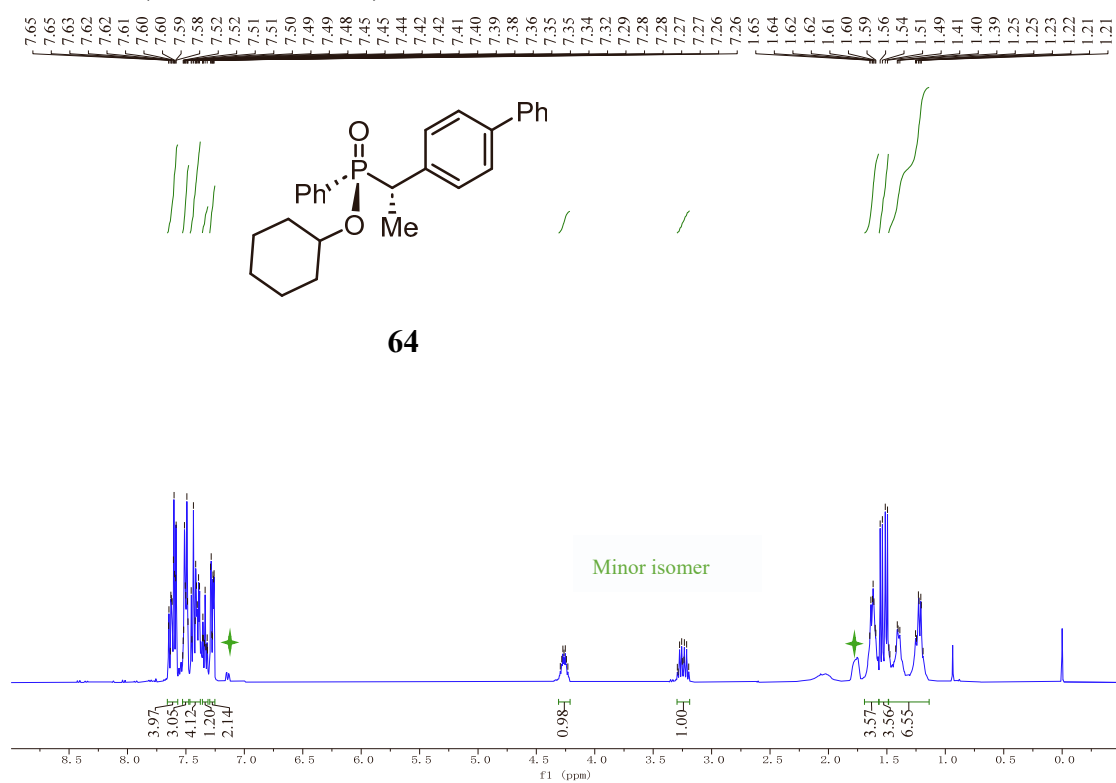
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**



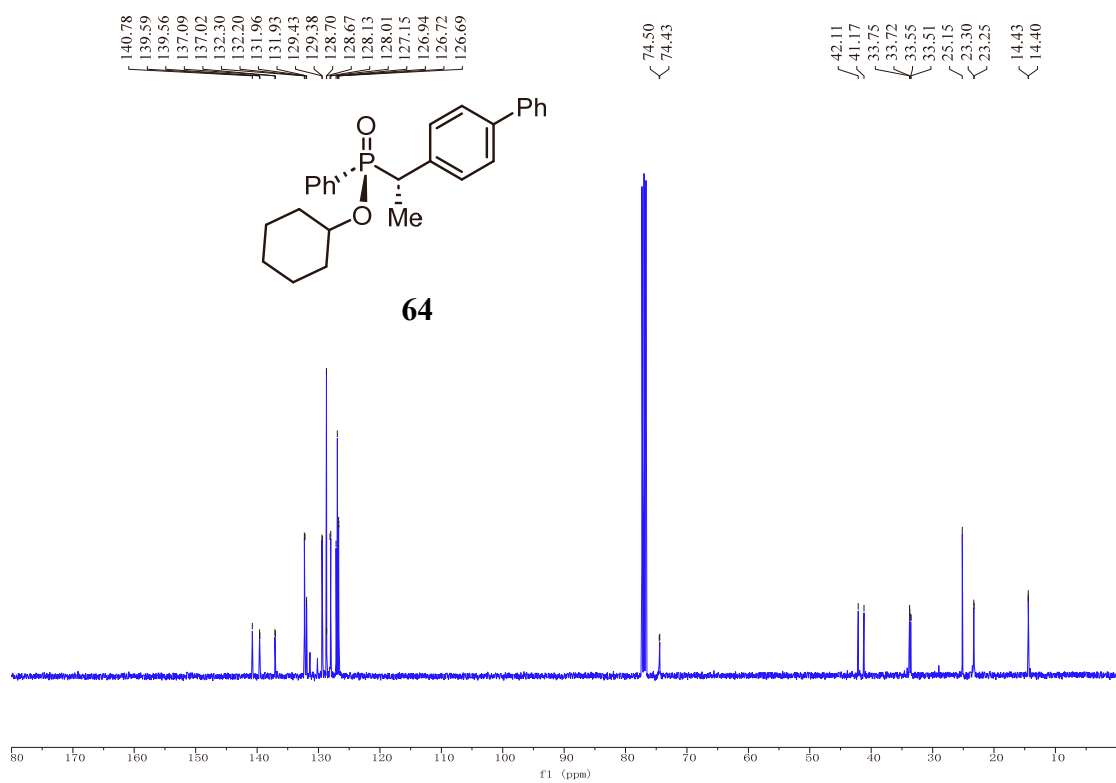
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



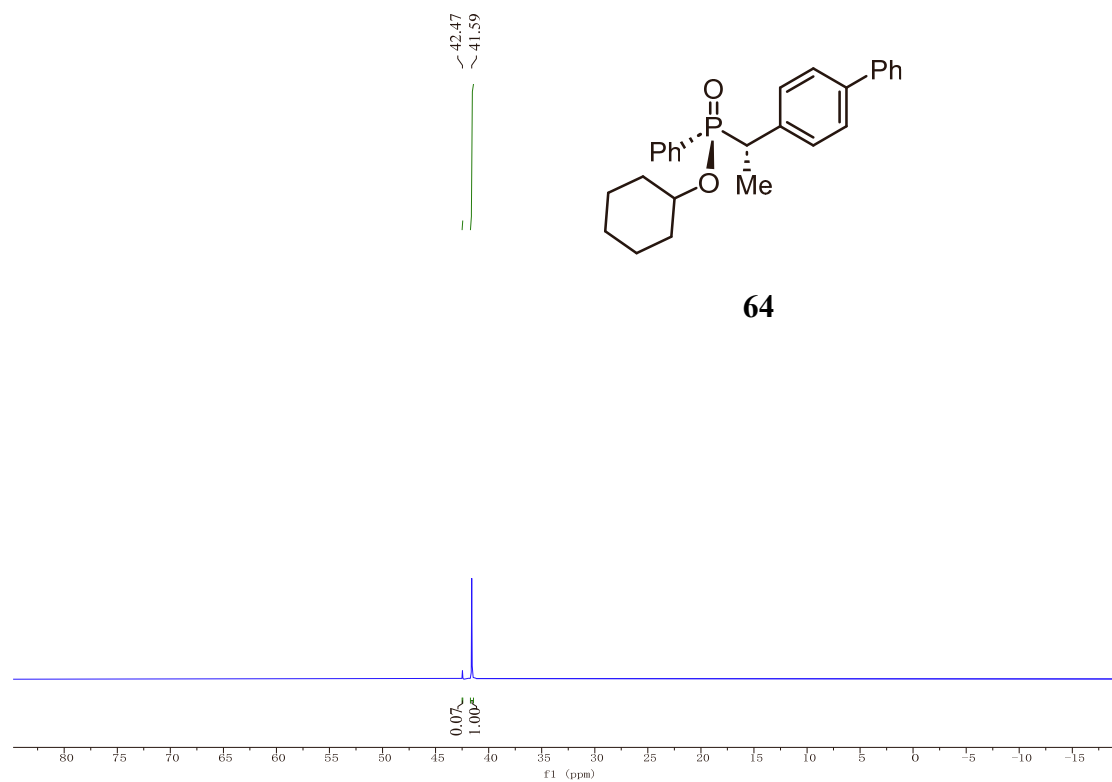
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



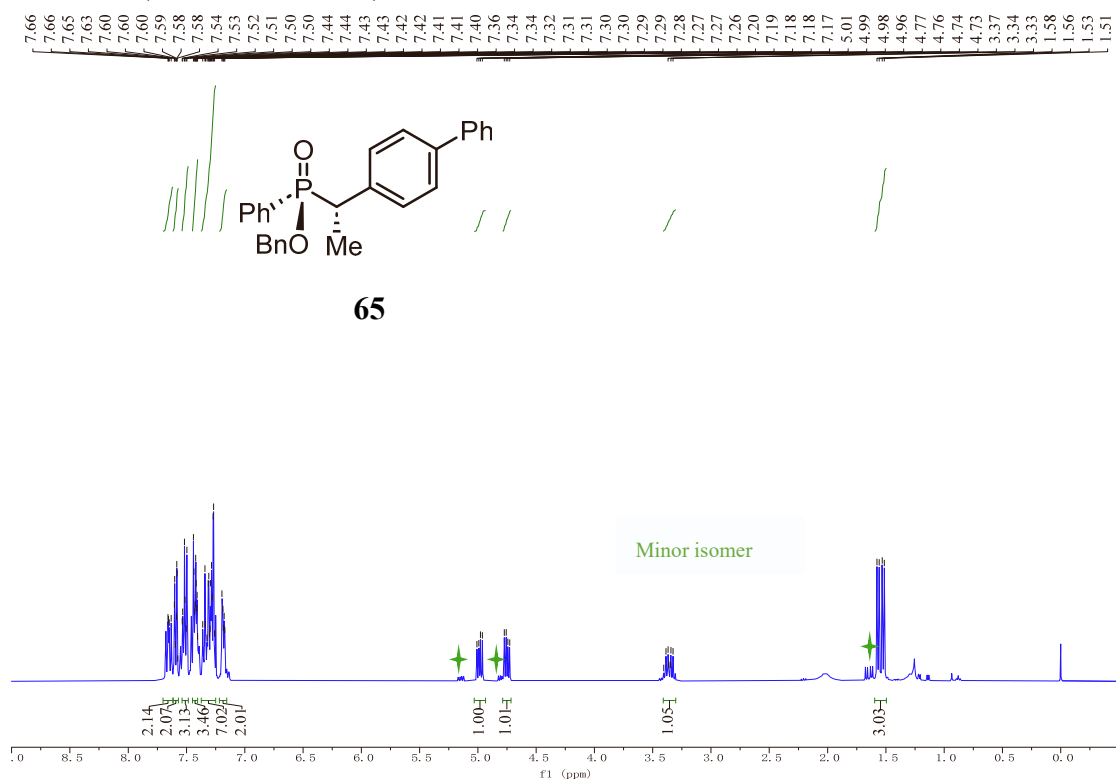
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**



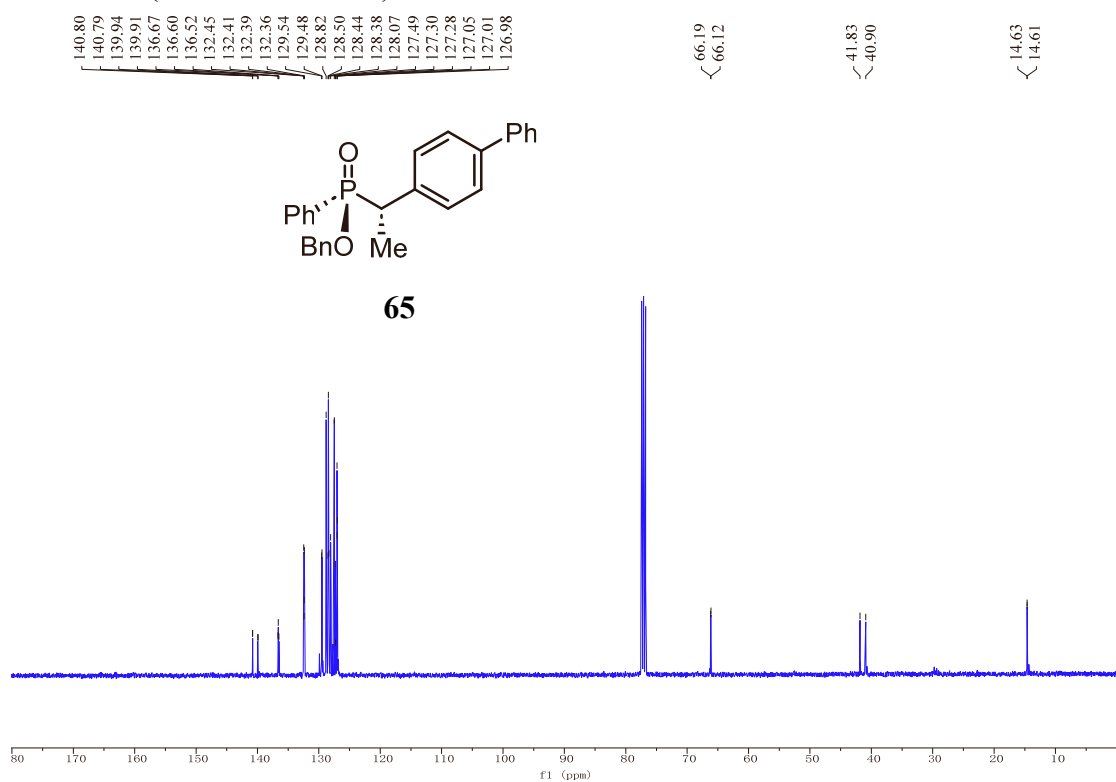
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



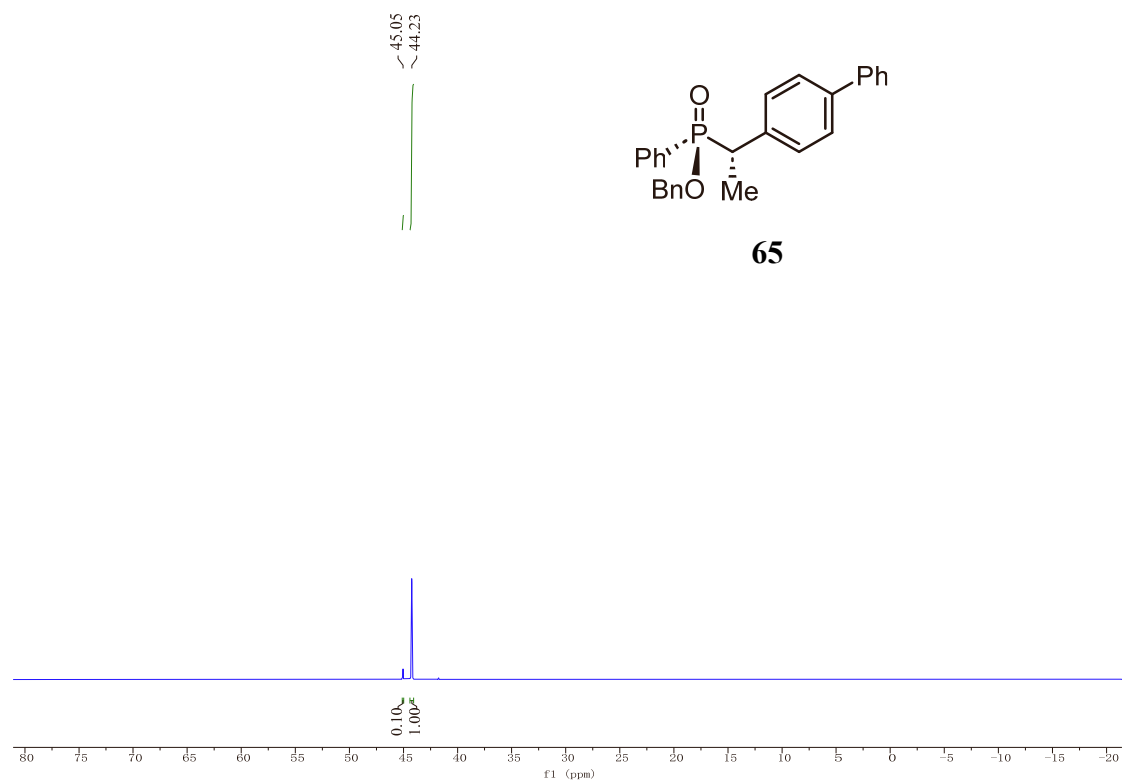
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

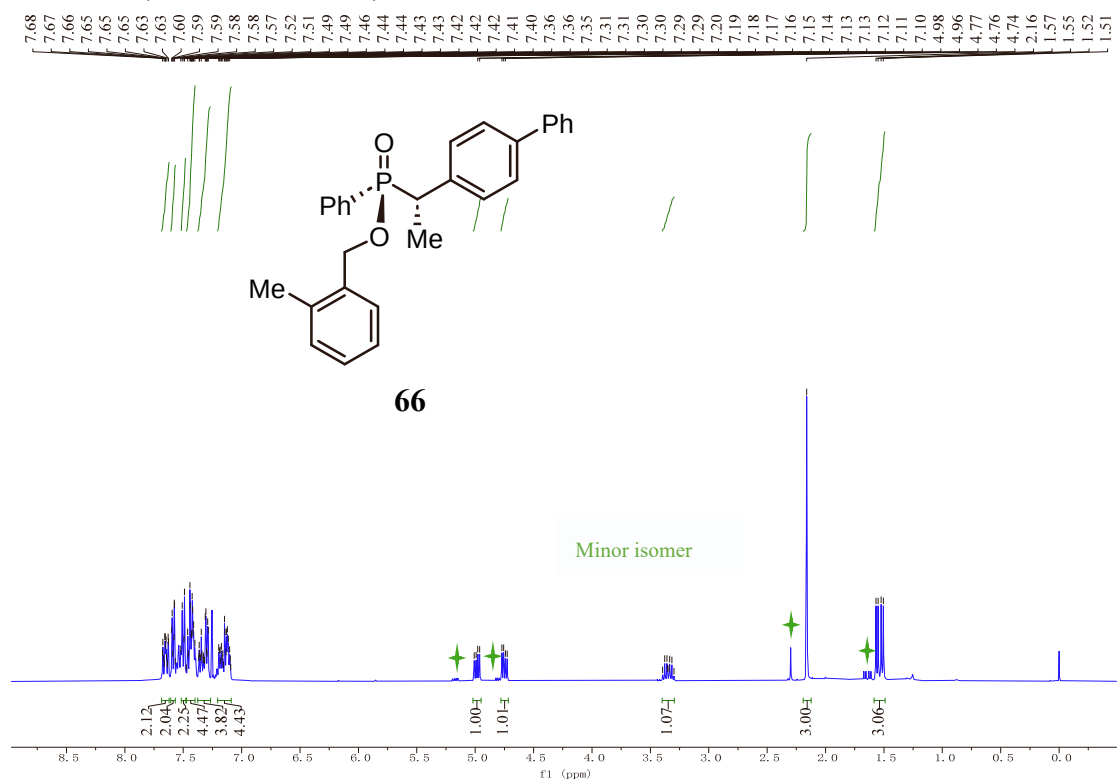


**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**

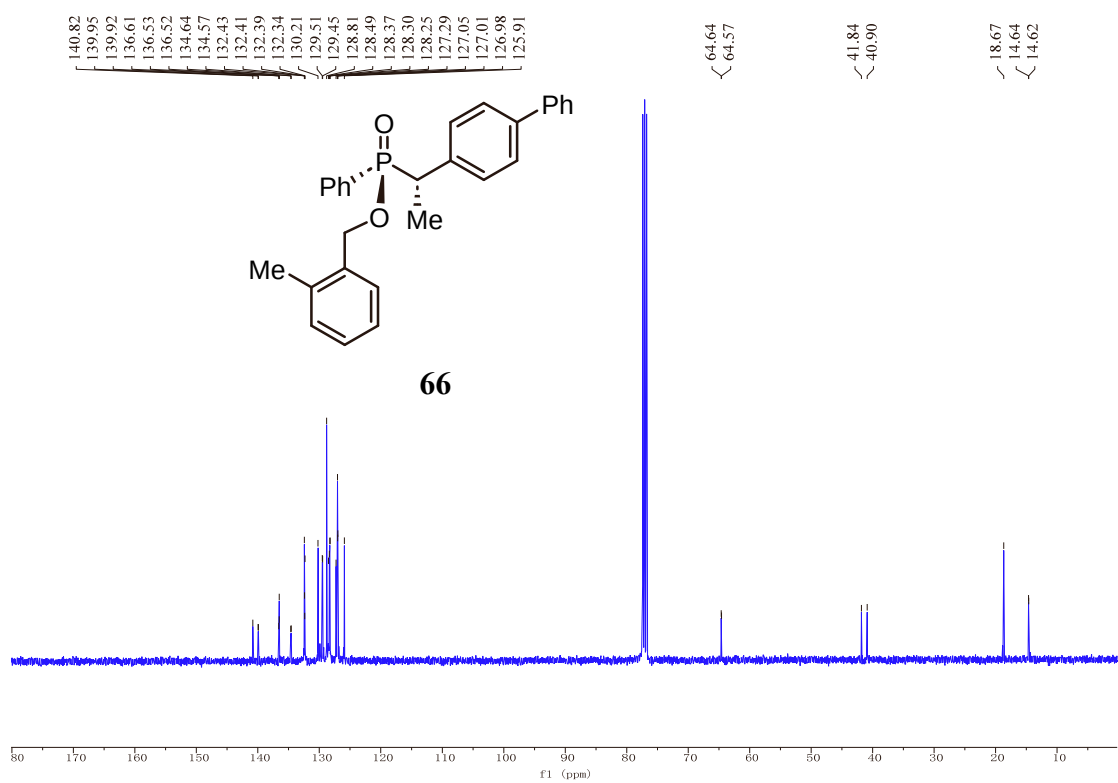




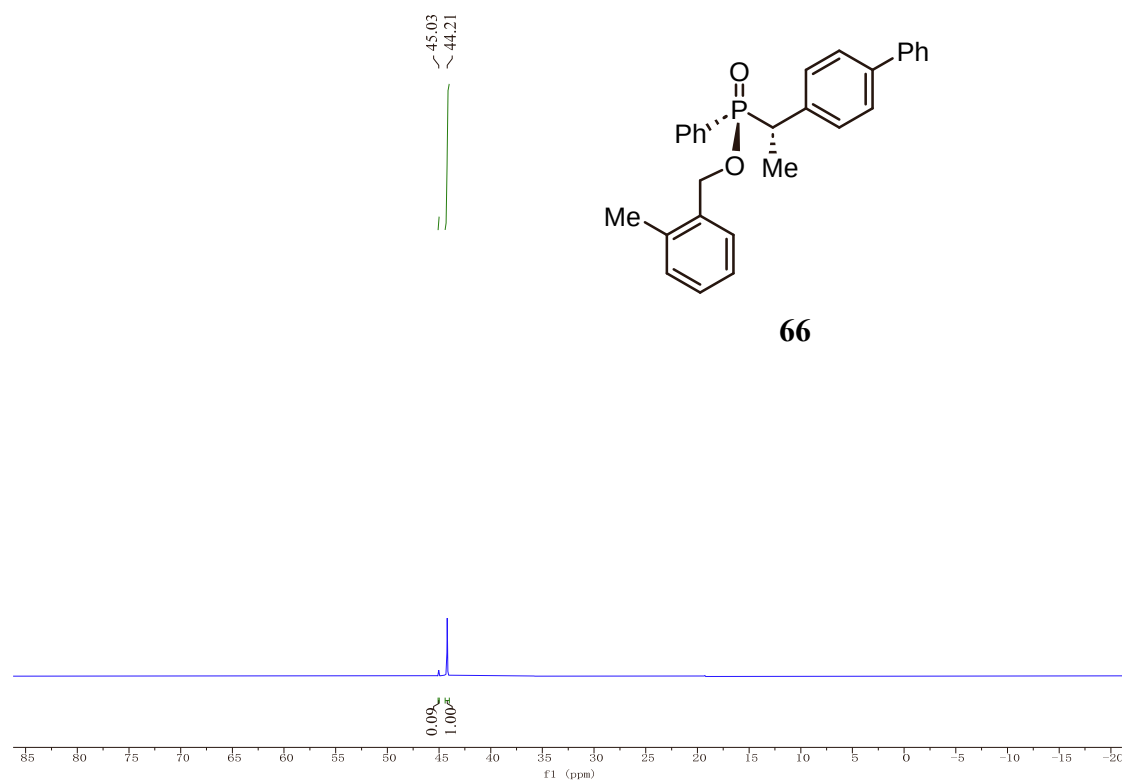
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



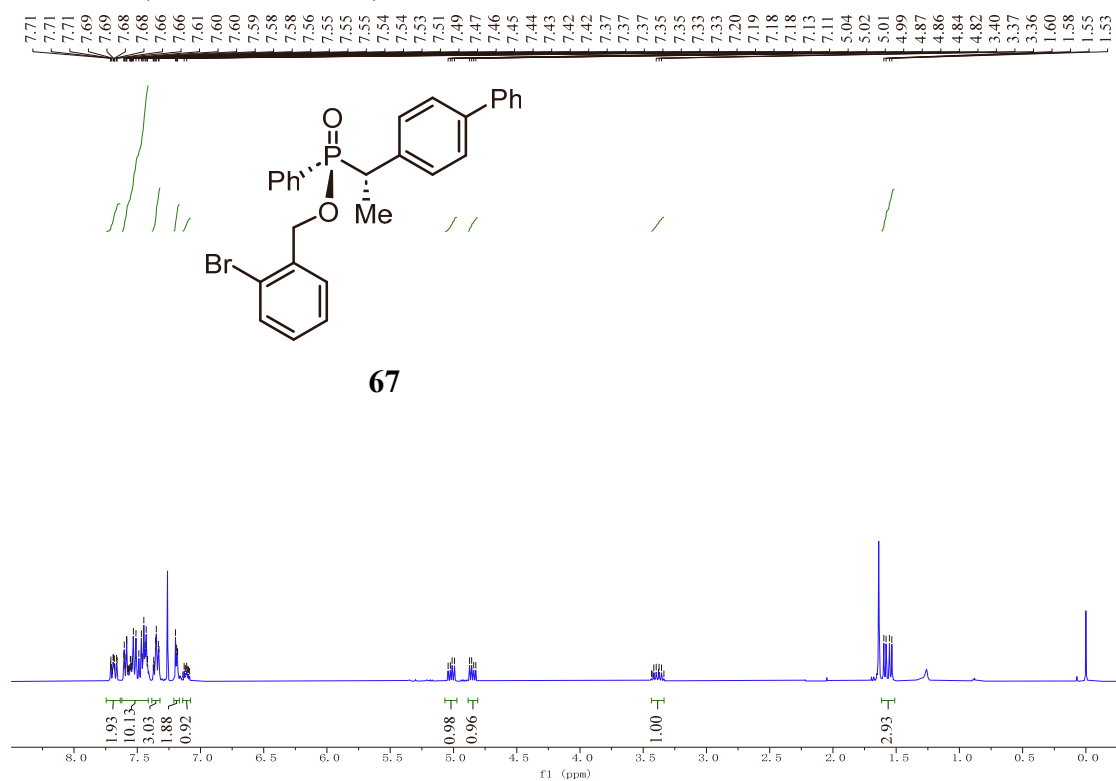
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



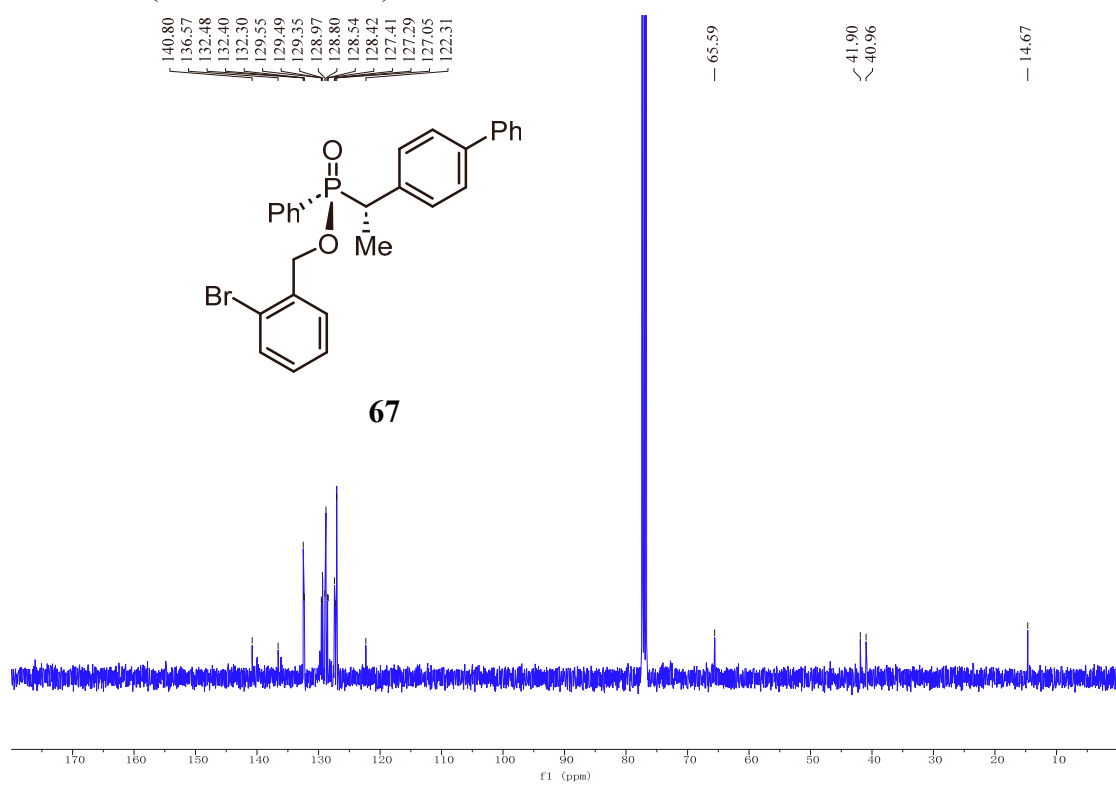
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



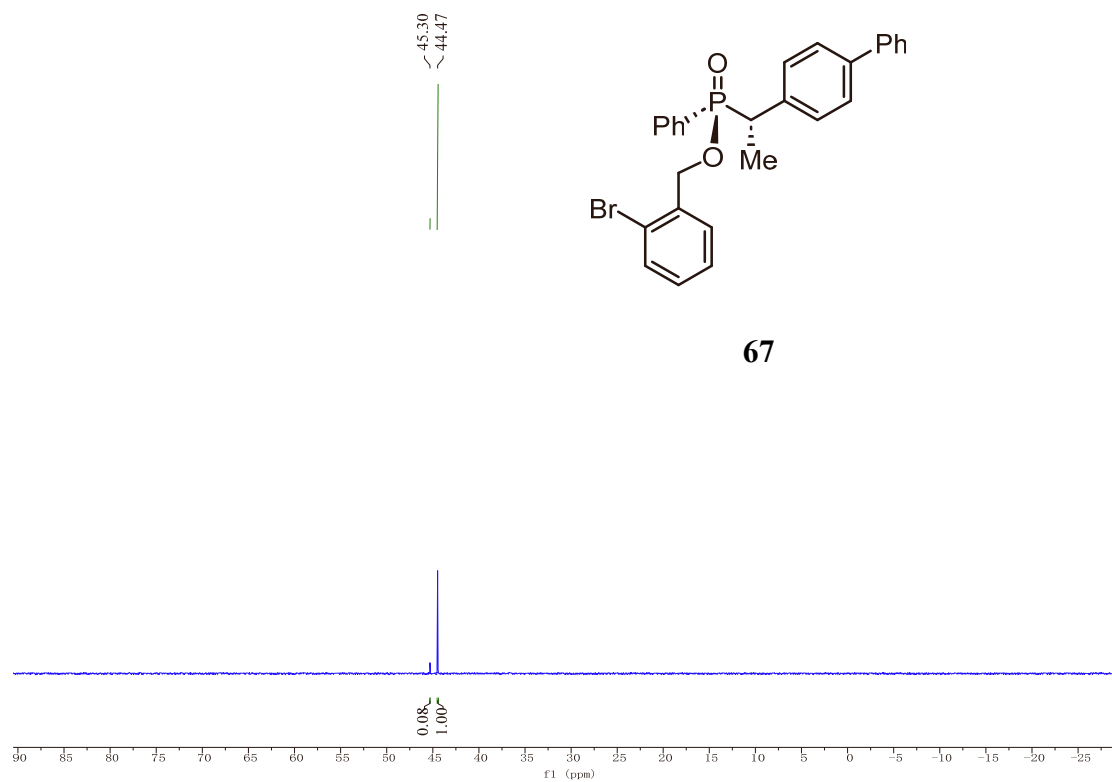
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



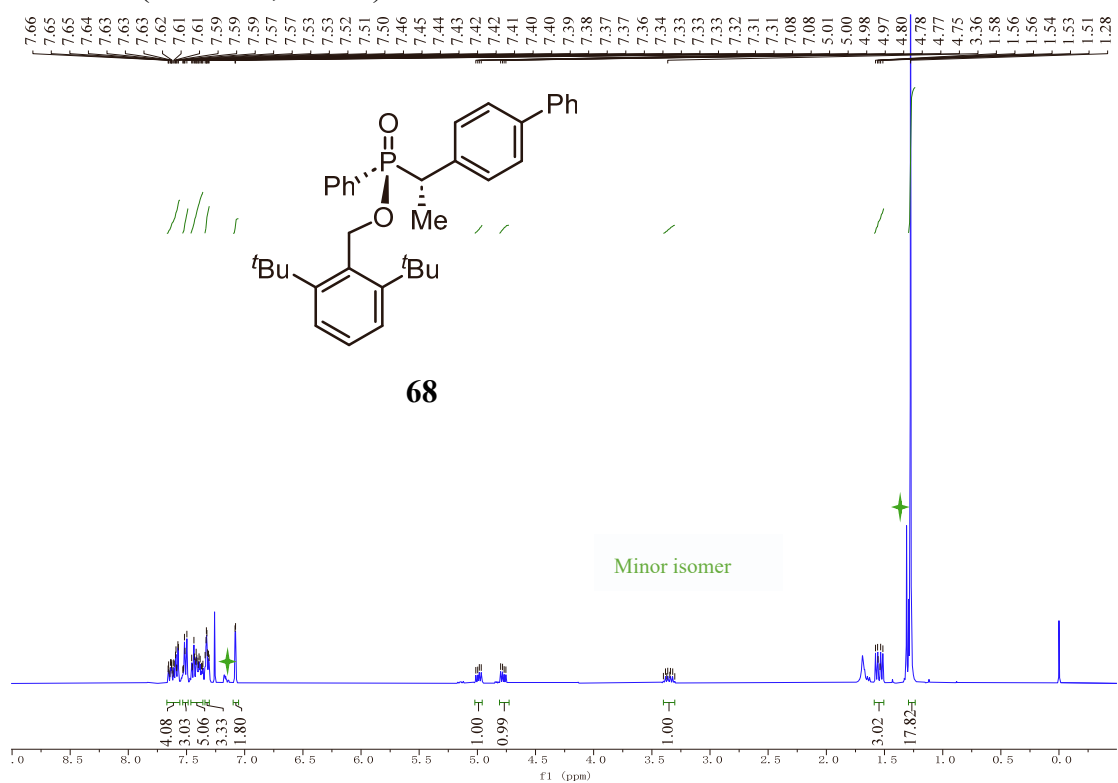
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



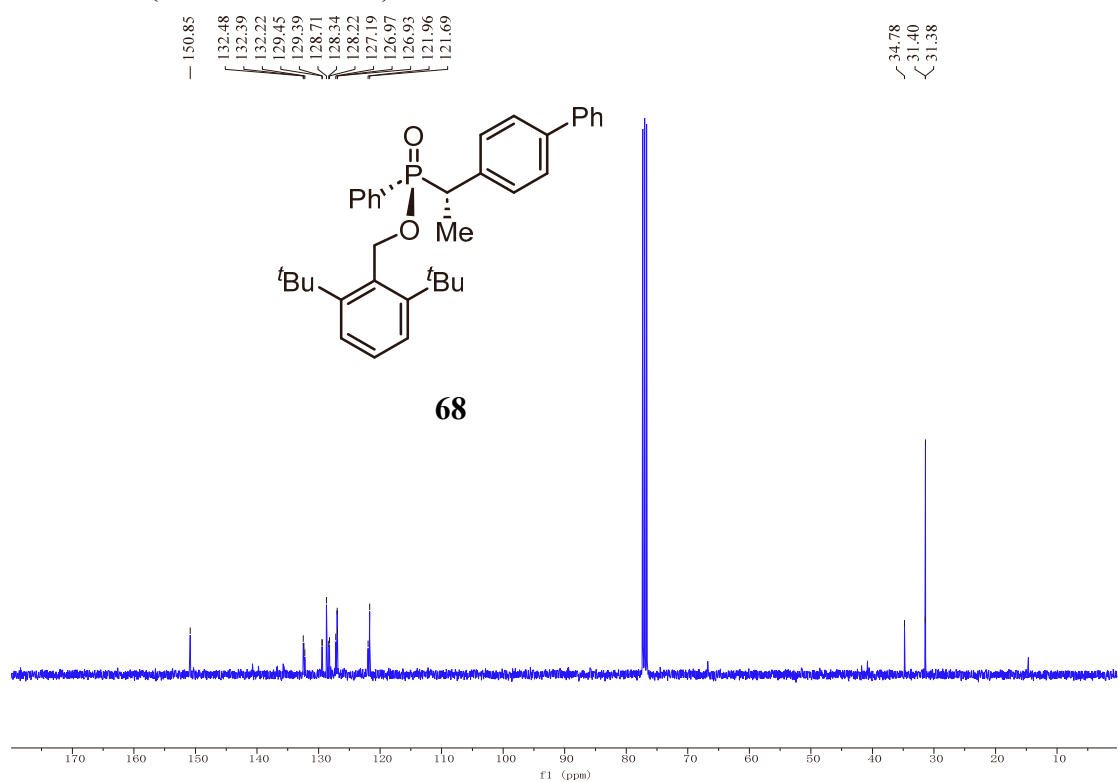
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



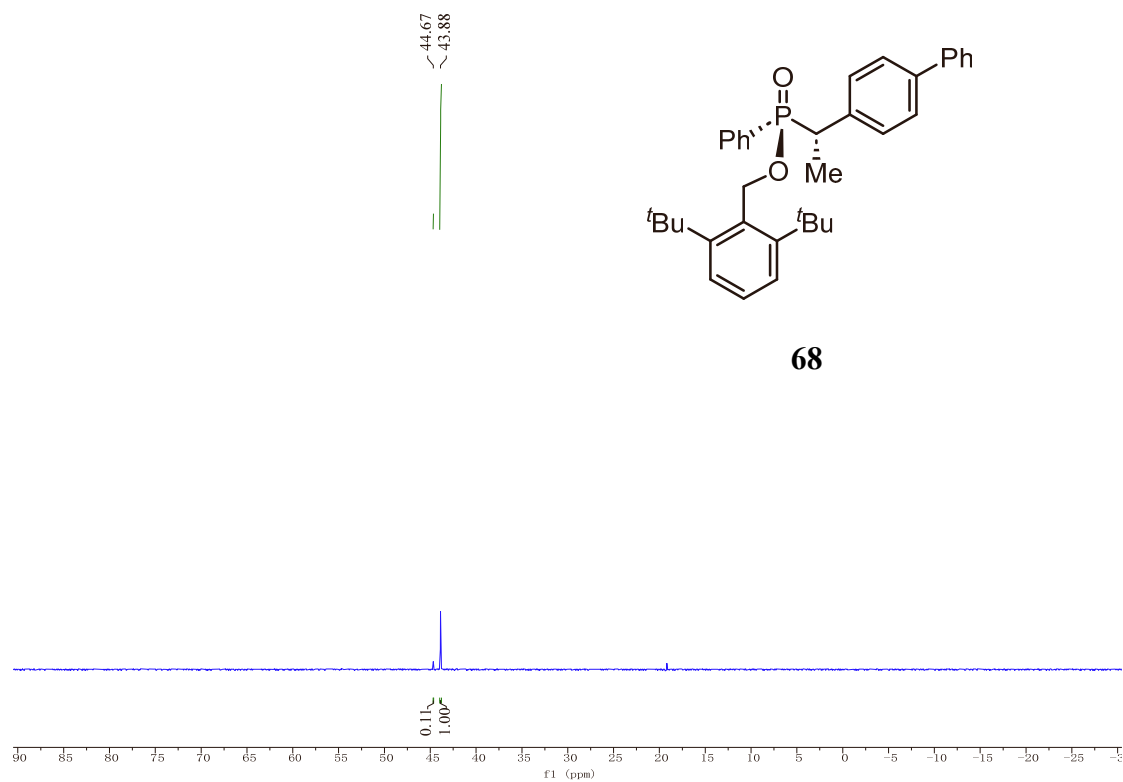
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



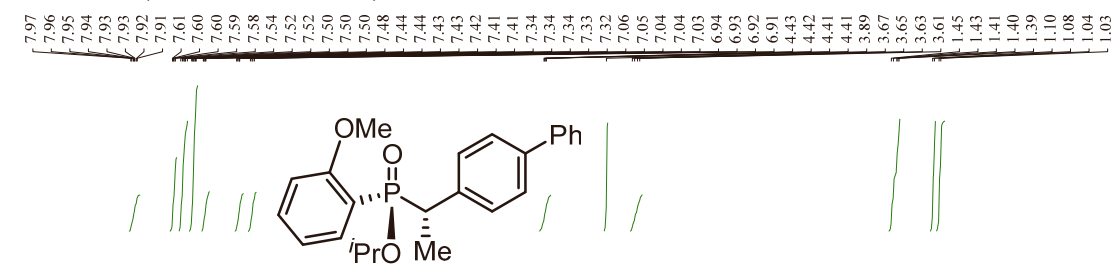
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



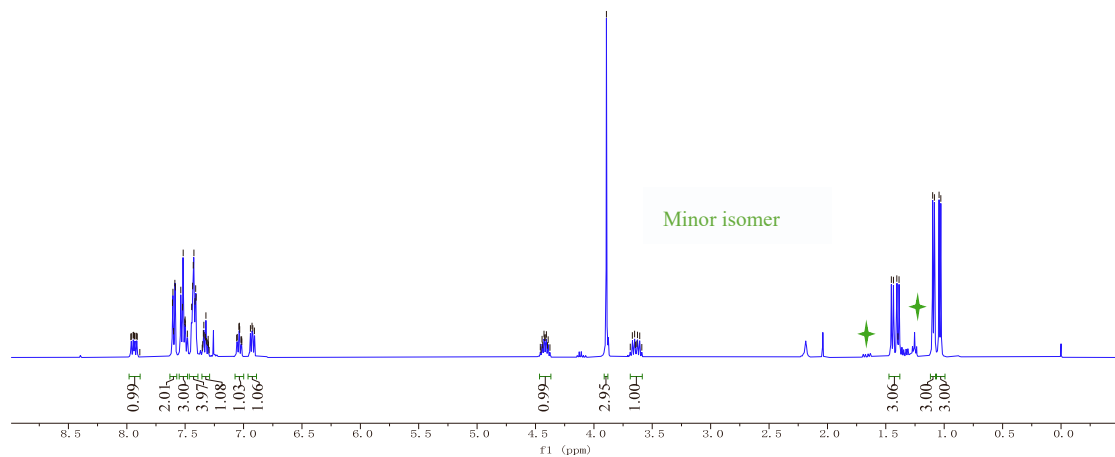
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



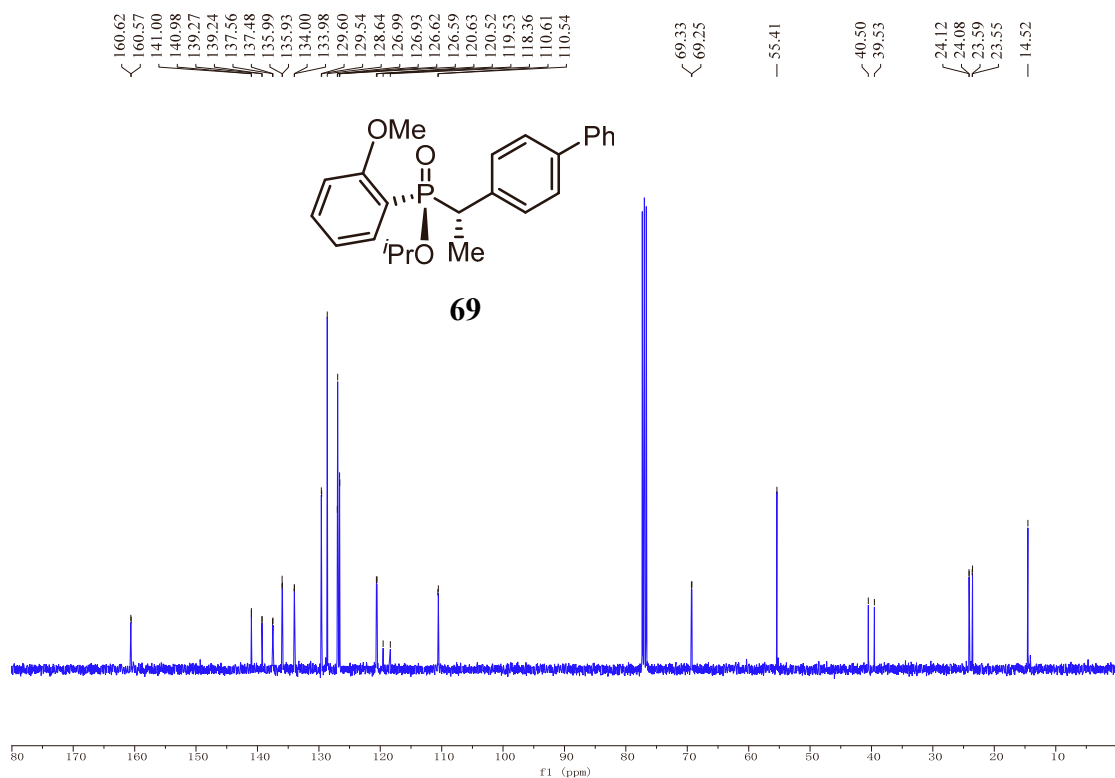
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



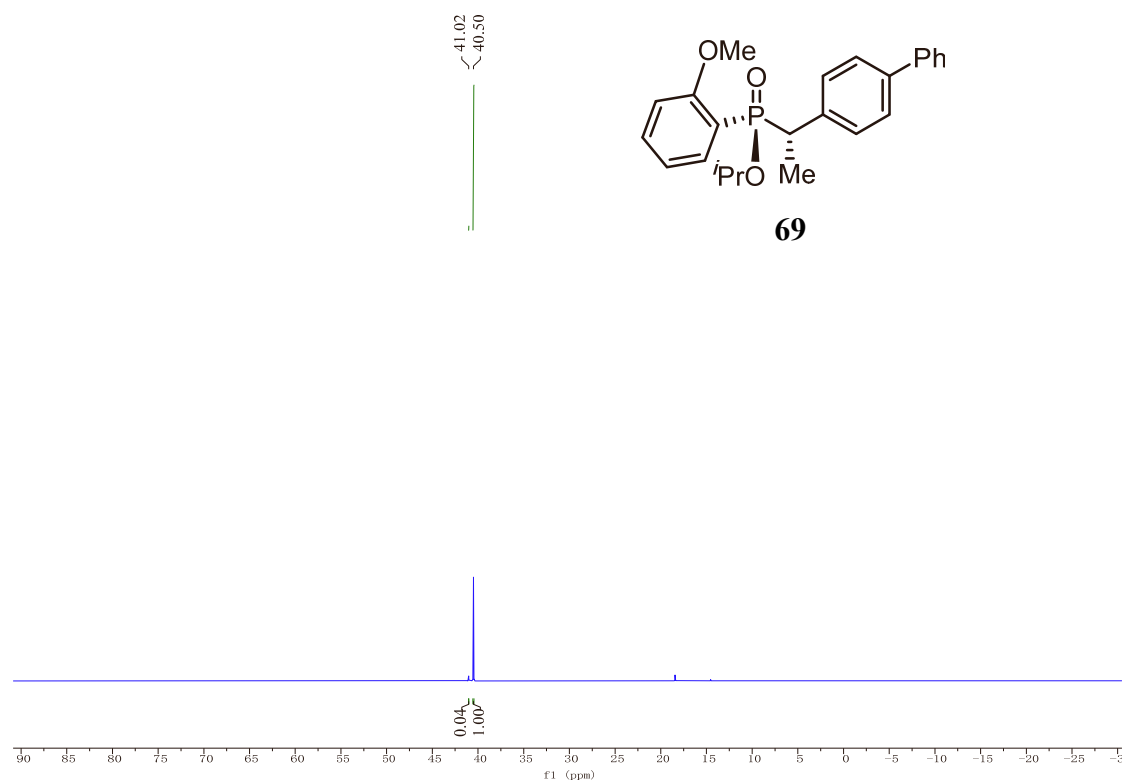
**69**



**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**

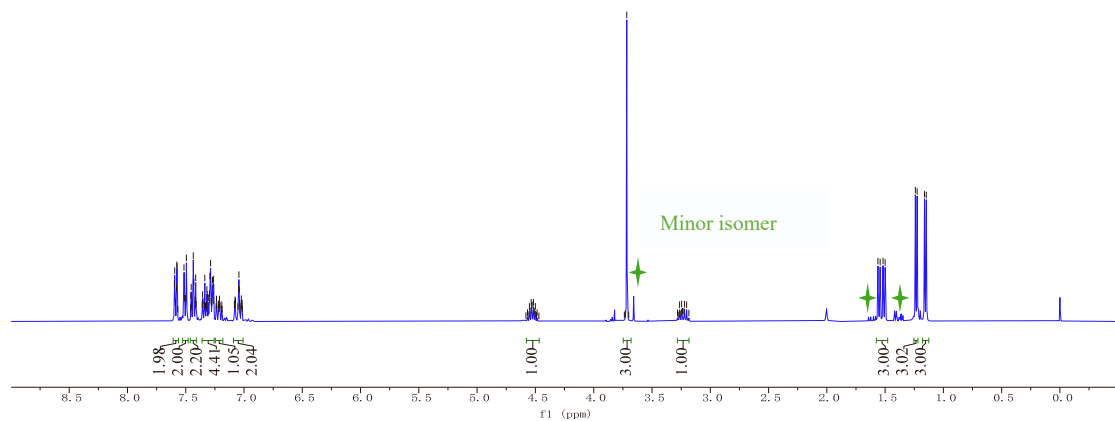
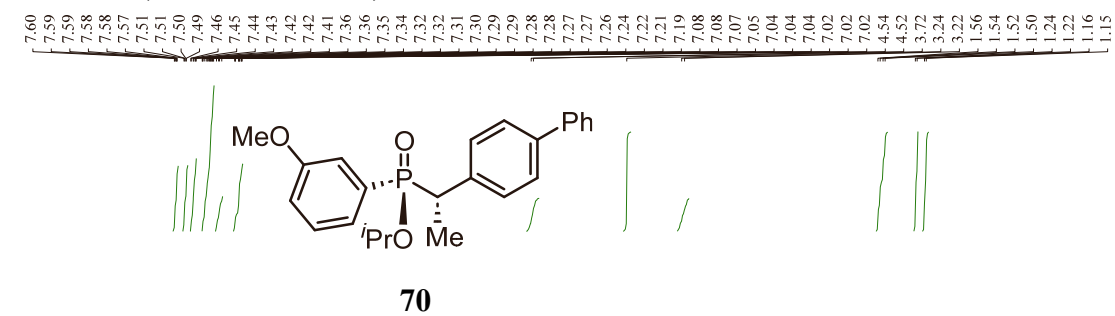


**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**

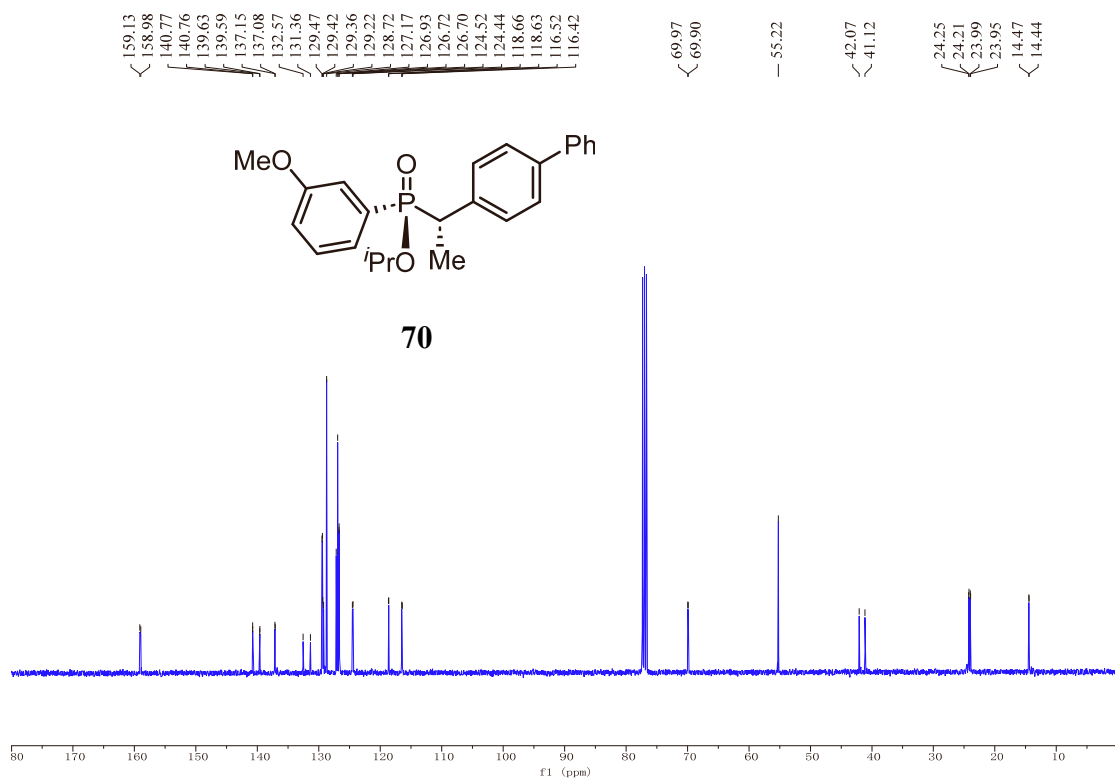




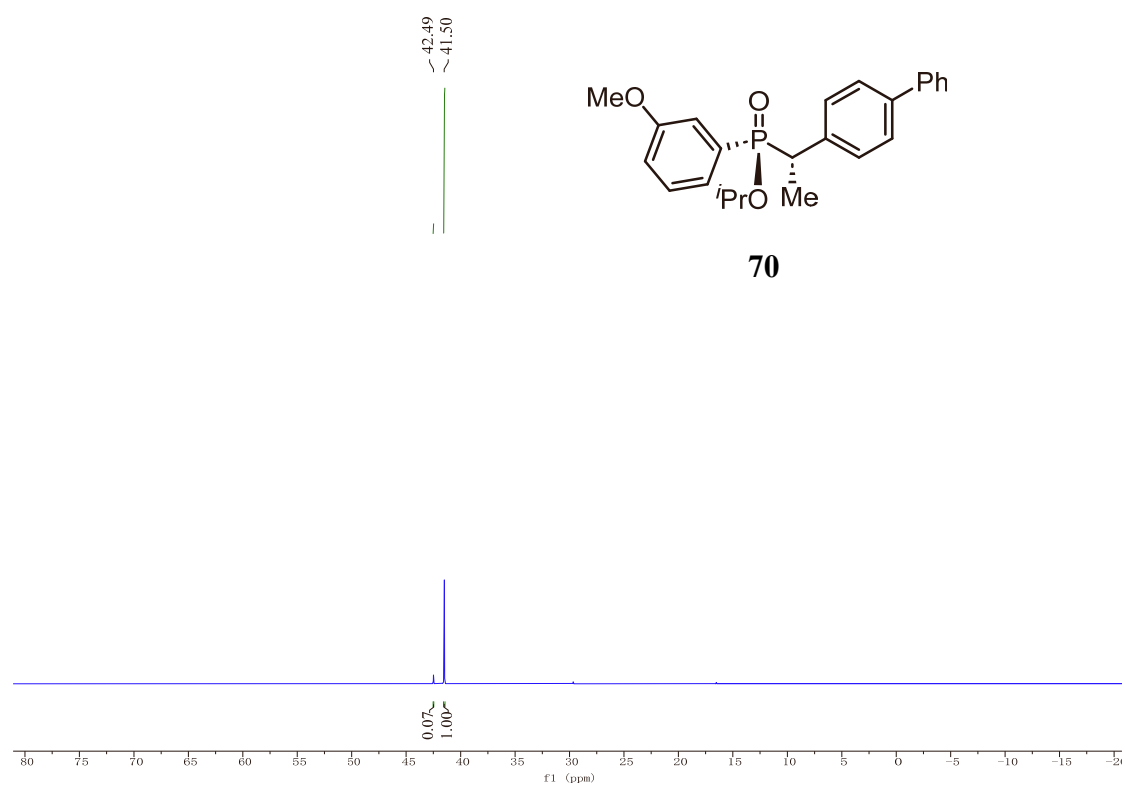
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



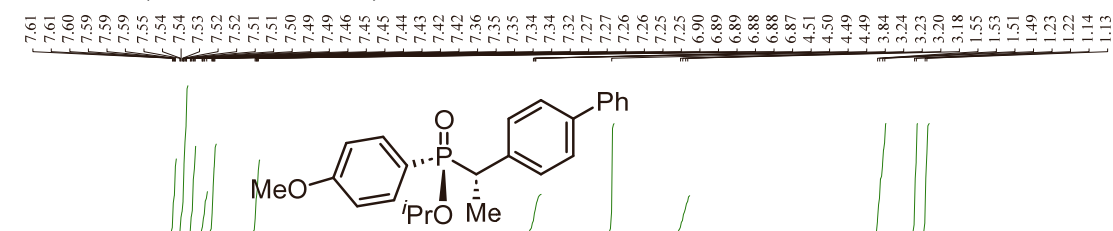
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



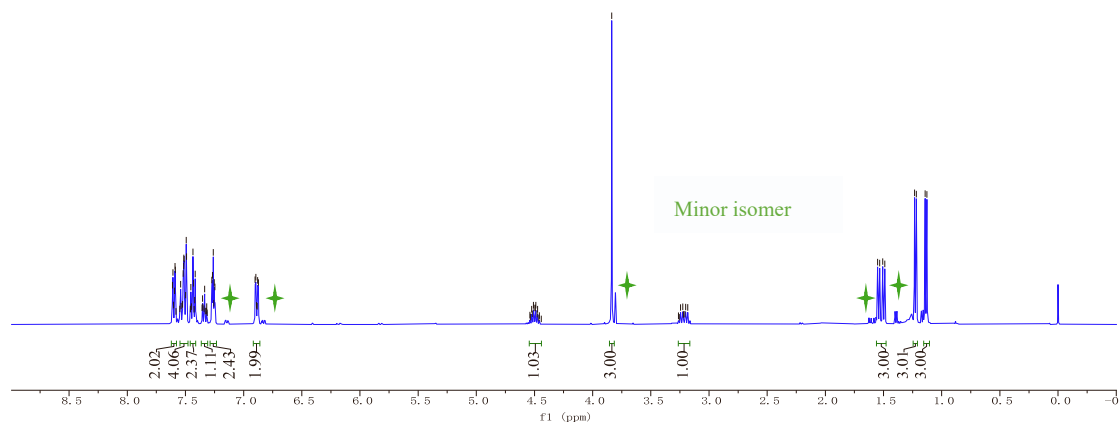
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



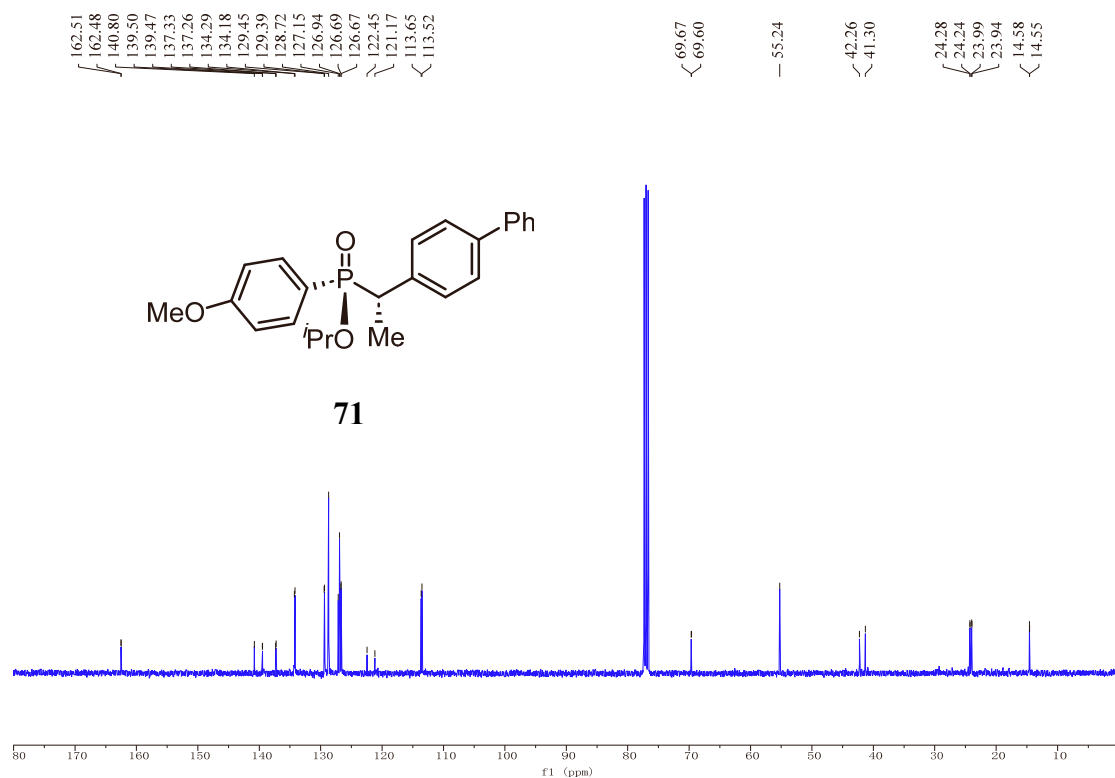
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



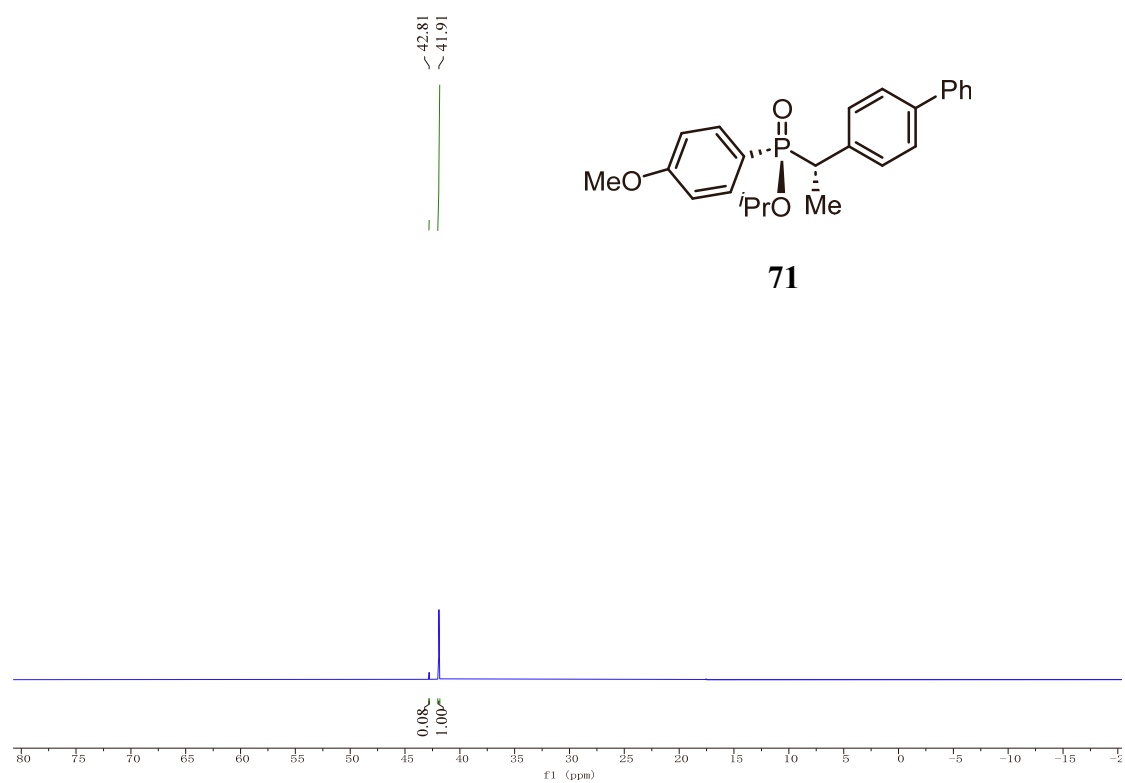
**71**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



7.71  
7.69  
7.68  
7.68  
7.66  
7.64  
7.63  
7.62  
7.61  
7.61  
7.60  
7.59  
7.53  
7.53  
7.52  
7.51  
7.49  
7.47  
7.46  
7.46  
7.45  
7.44  
7.44  
7.43  
7.42  
7.42  
7.41  
7.41  
7.41  
7.39  
7.36  
7.36  
7.36  
7.34  
7.32  
7.32  
7.31  
7.31  
7.30  
7.30  
4.56  
1.57  
1.54  
1.52  
1.26  
1.24  
1.23  
1.22  
1.18  
1.16

Ph

Ph

72

Minor isomer

8.02  
2.05  
5.32  
3.07

1.00

1.00

3.00

3.08

3.00

f1 (ppm)

144.64  
140.74  
139.91  
139.63  
139.59  
137.04  
132.88  
132.78  
129.50  
129.44  
128.90  
128.73  
128.09  
127.23  
127.19  
126.96  
126.80  
126.76  
126.74  
126.68

70.04  
69.97

42.11  
41.16

24.26  
24.23  
24.06  
24.01

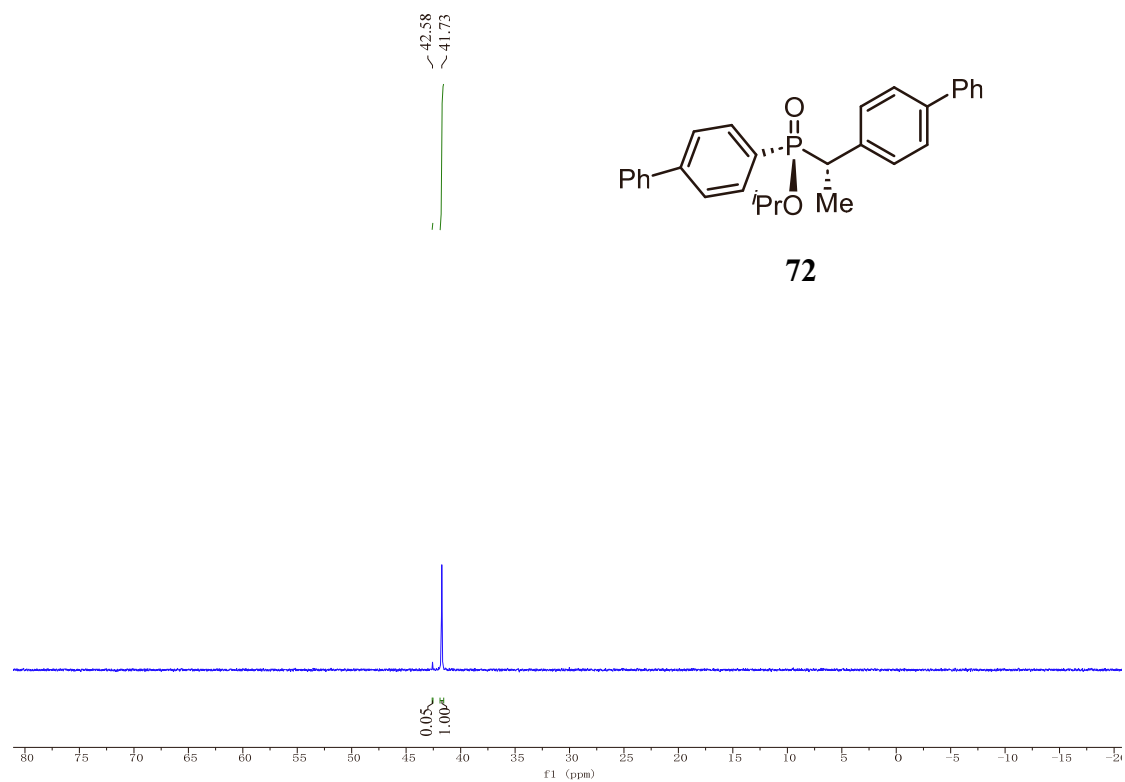
14.58  
14.55

72

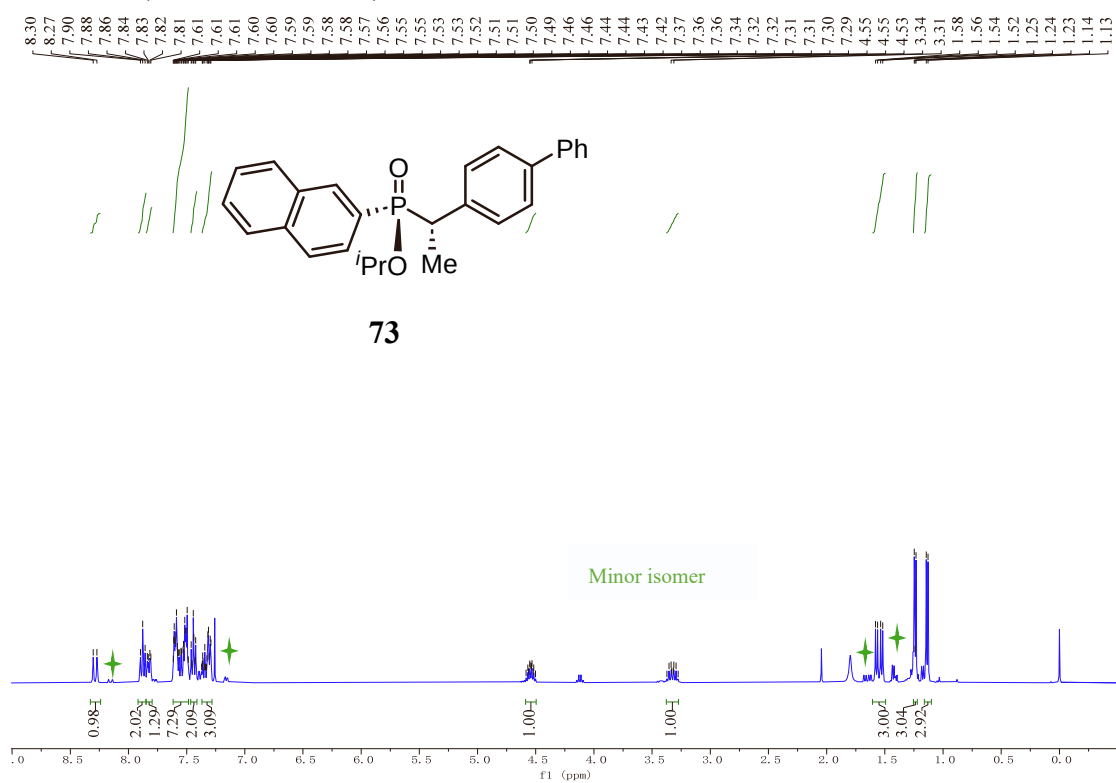
CC(C(=O)OC1=CC=C(C=C1)C2=CC=CC=C2)C3=CC=C(C=C3)C4=CC=CC=C4

f1 (ppm)

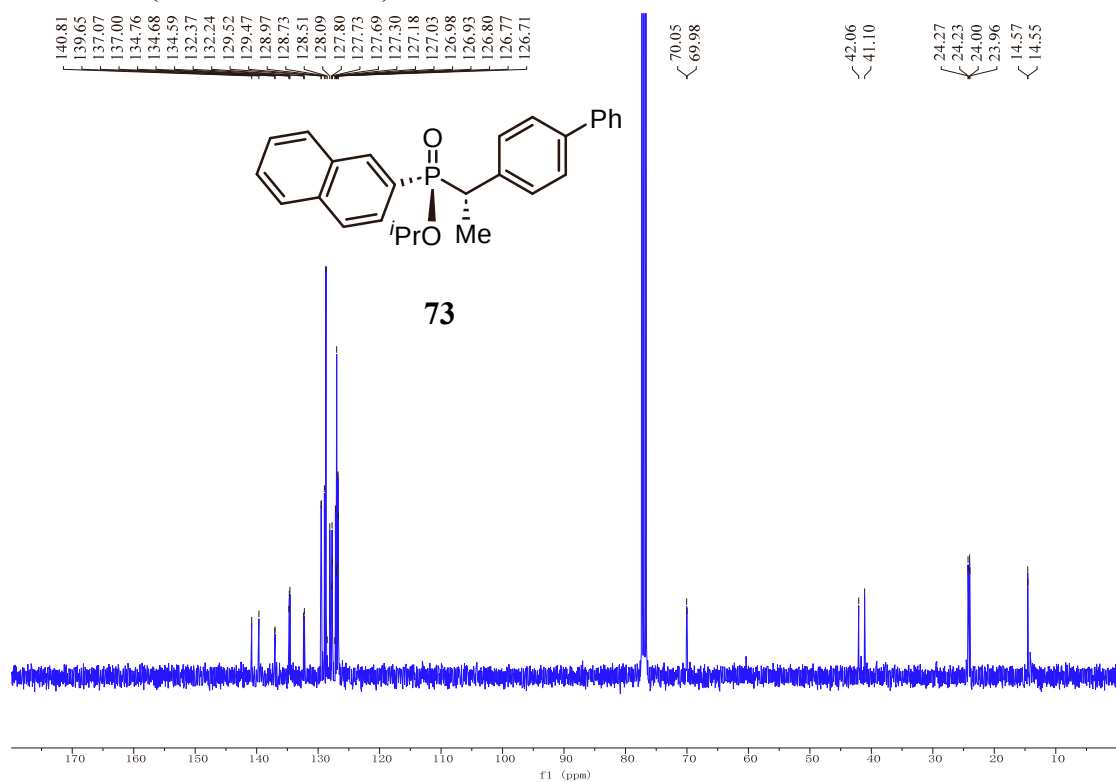
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



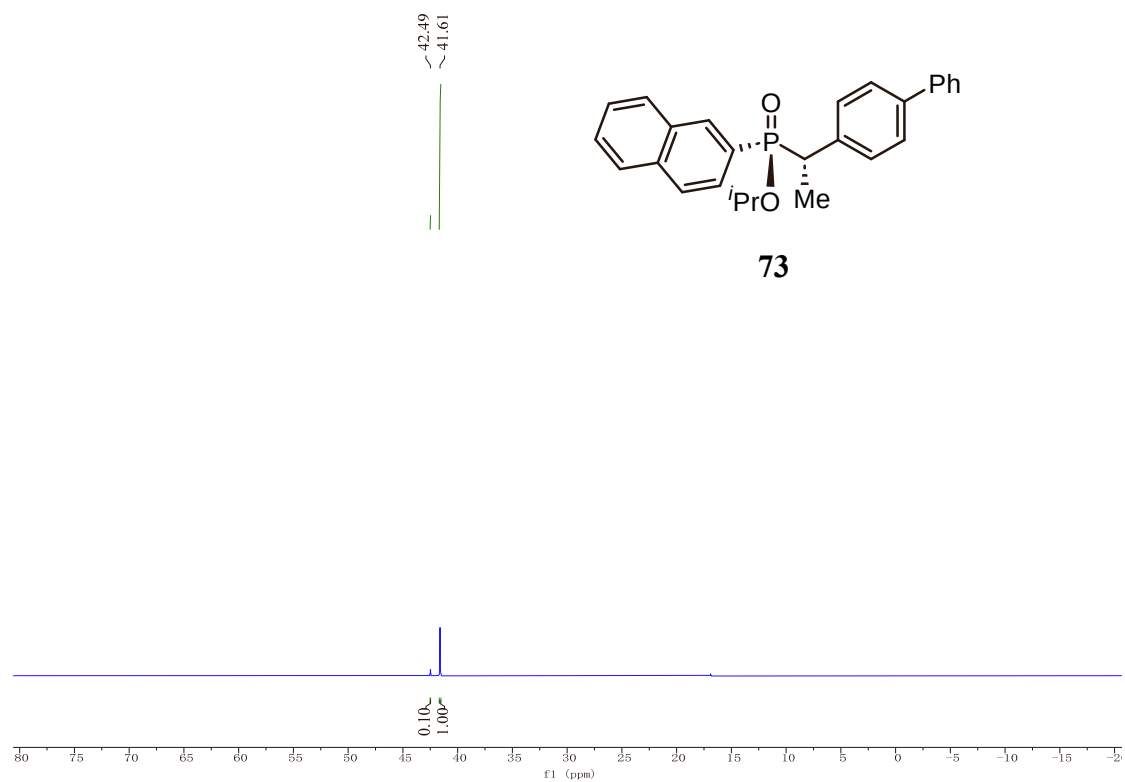
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**

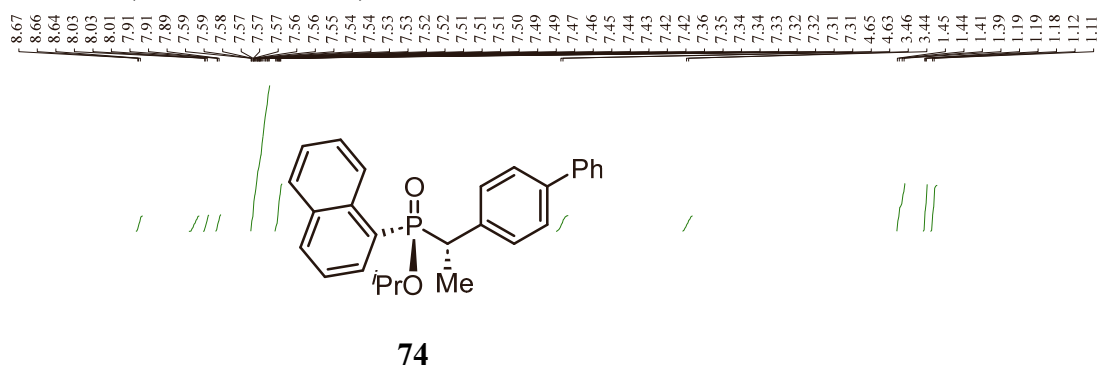


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

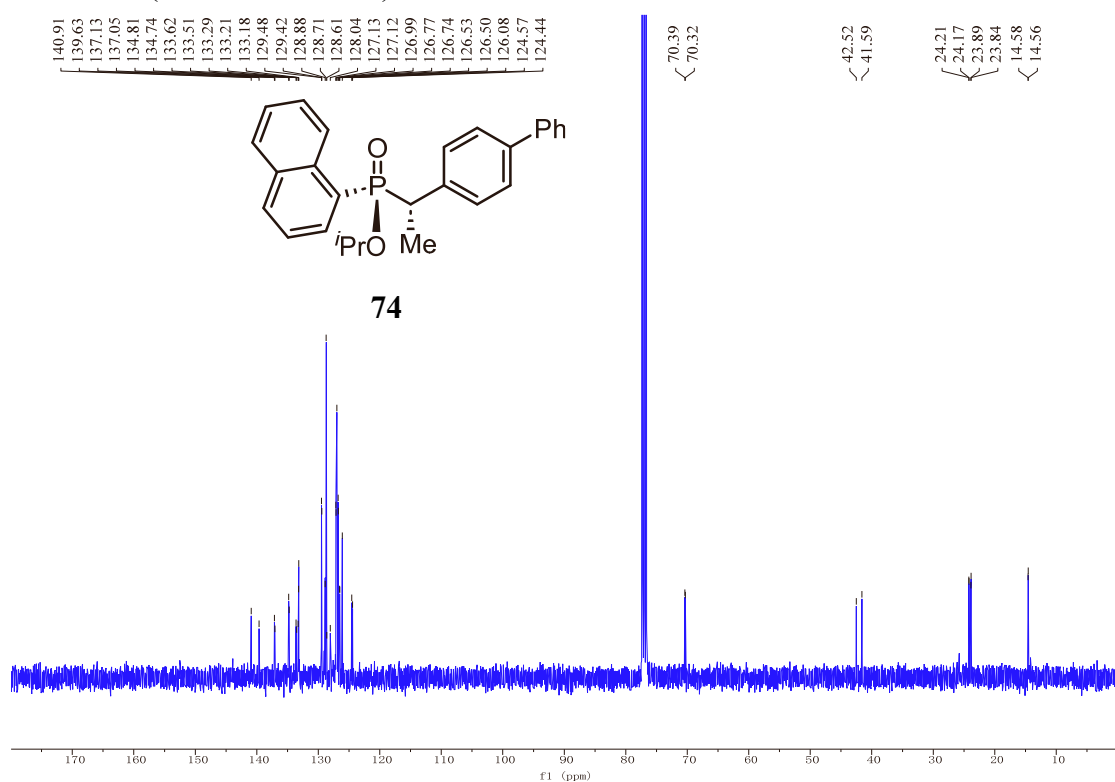




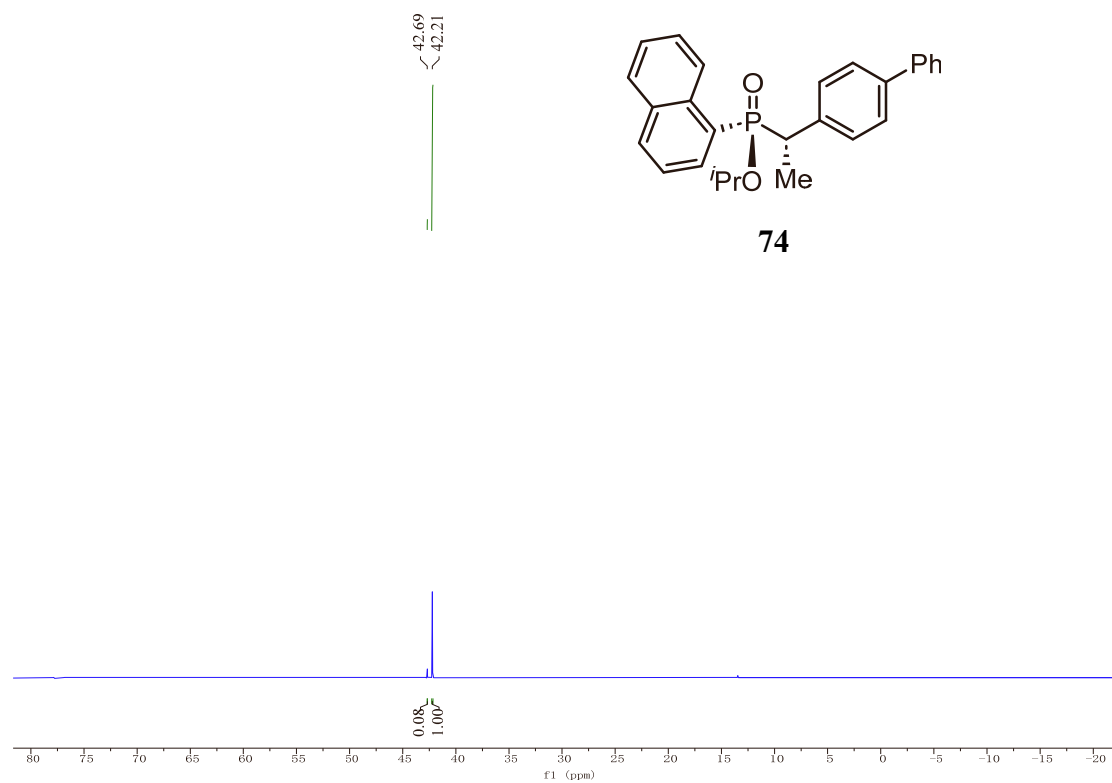
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



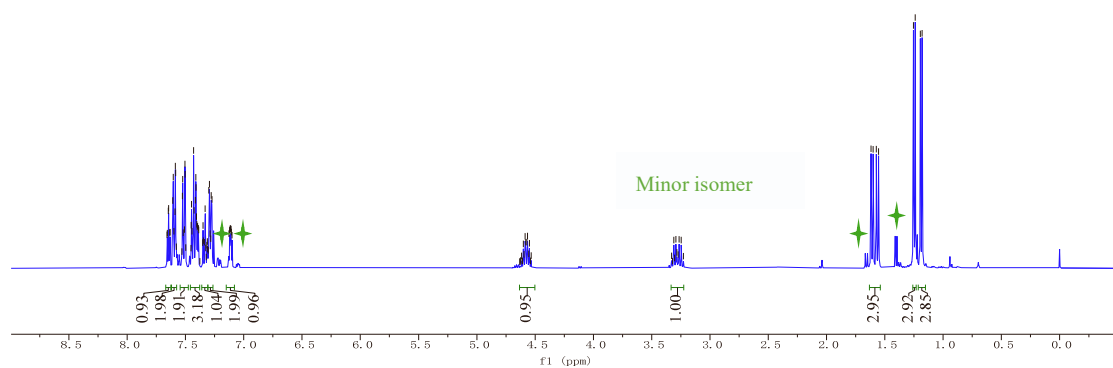
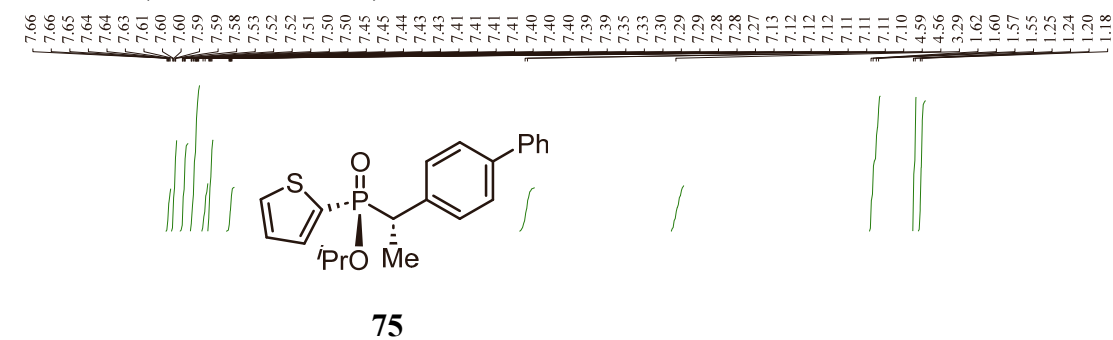
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



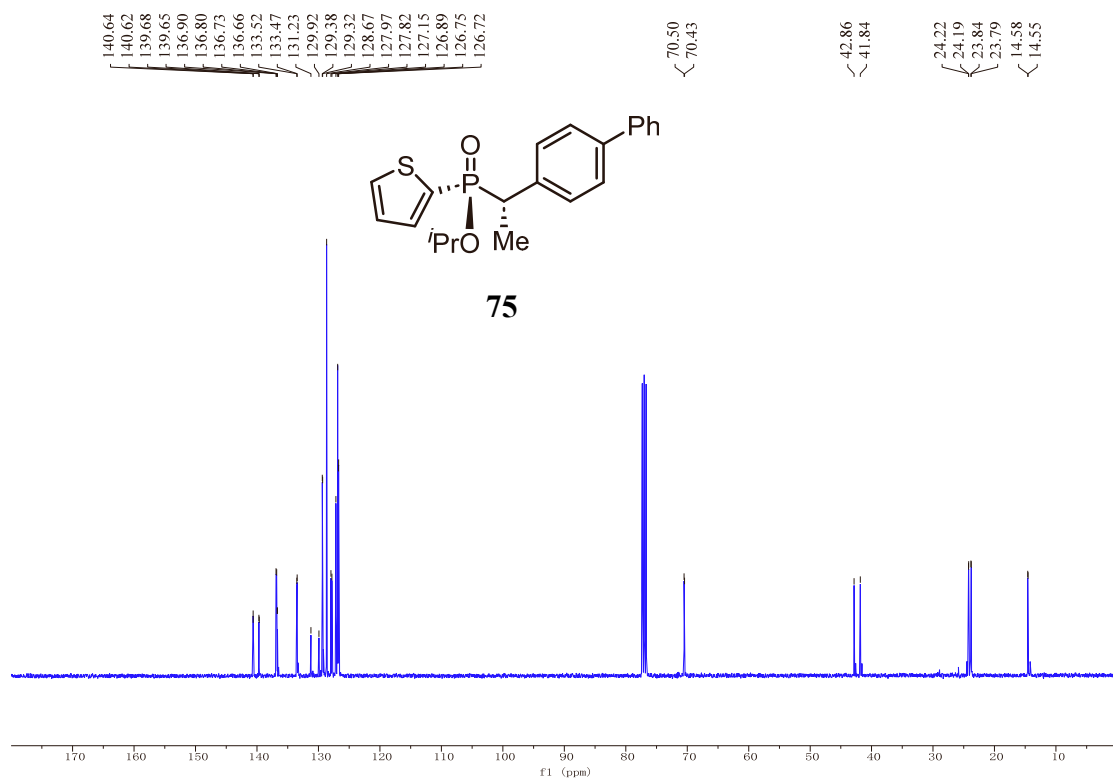
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



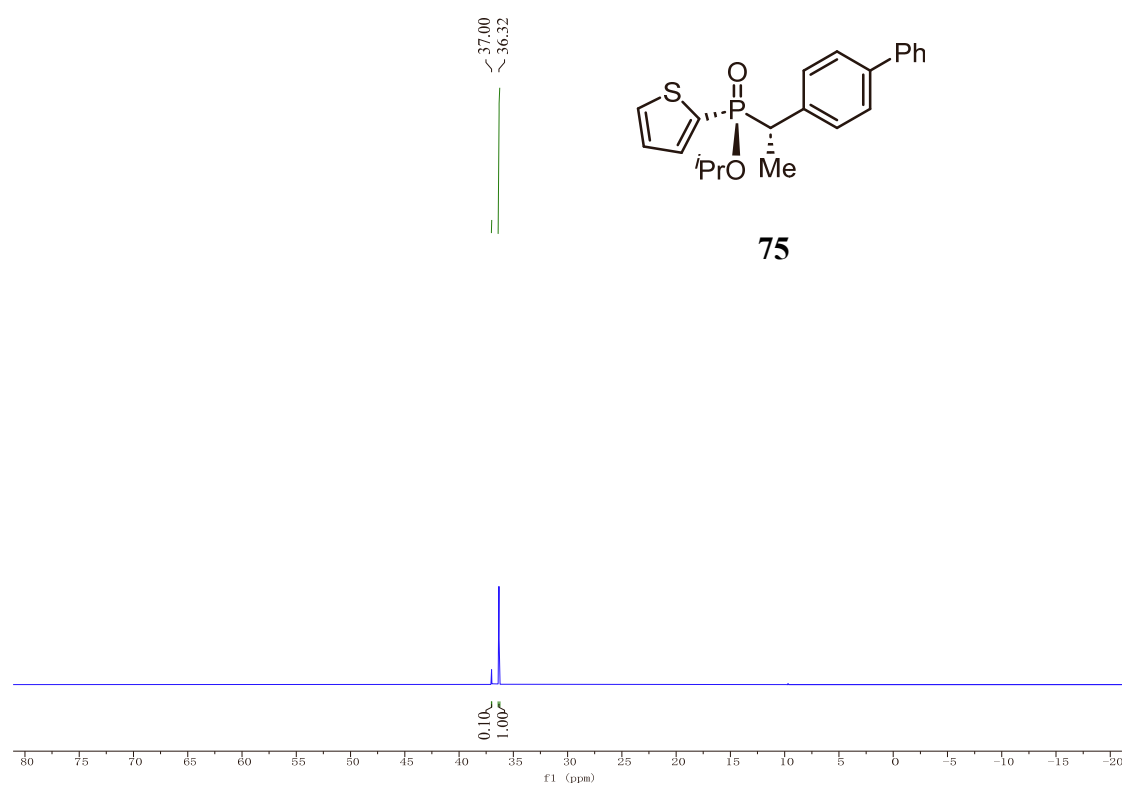
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



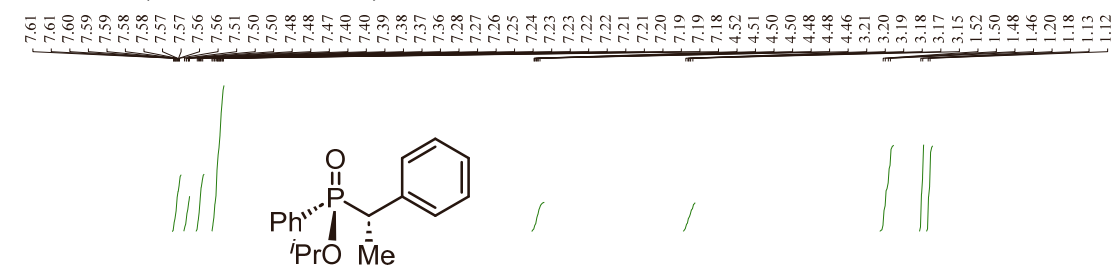
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



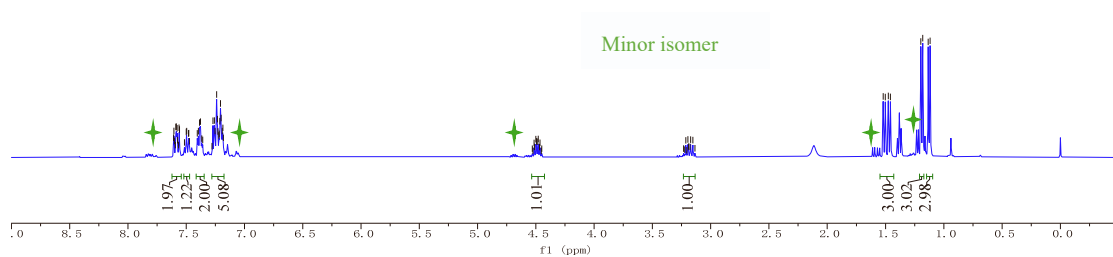
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



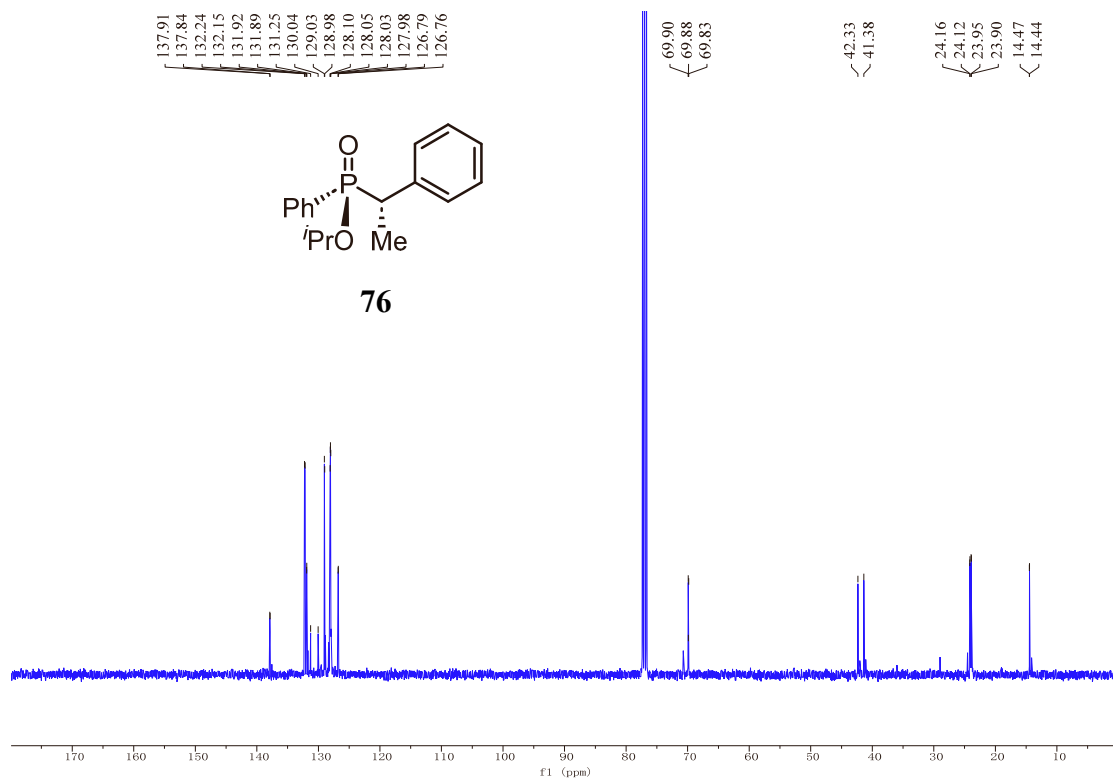
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



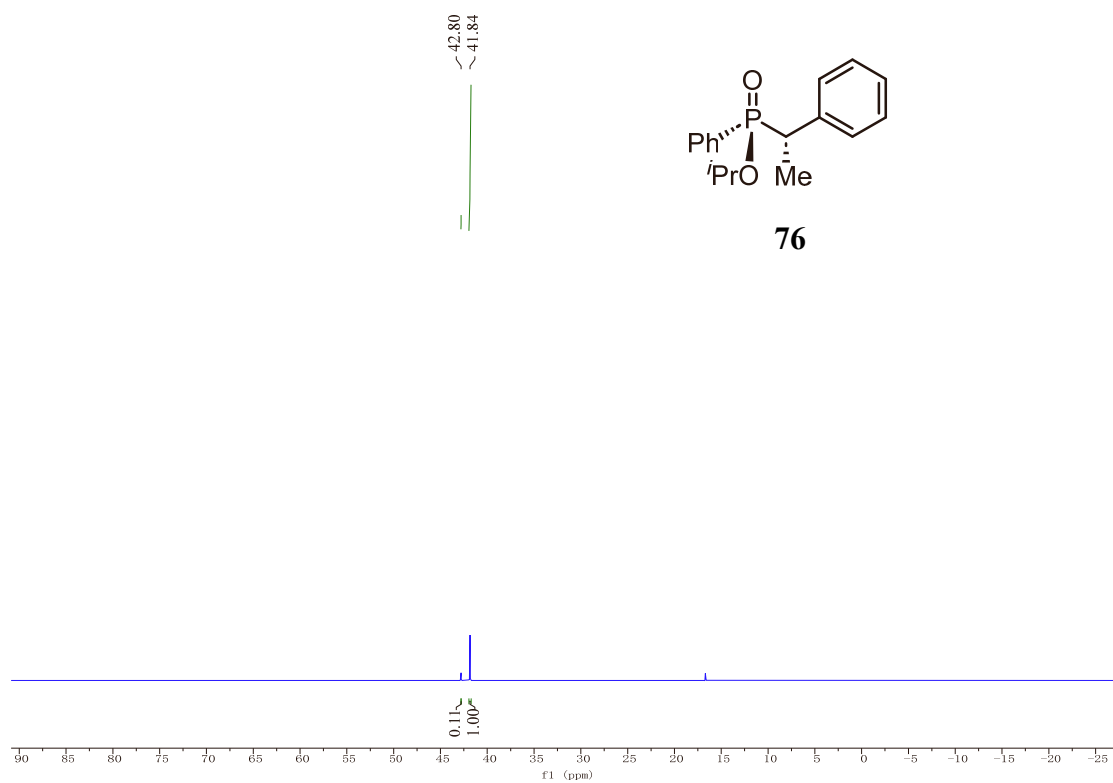
**76**



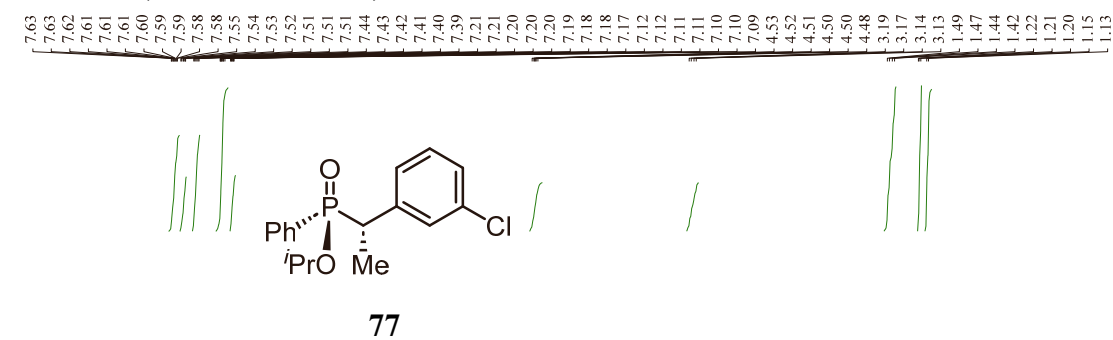
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**



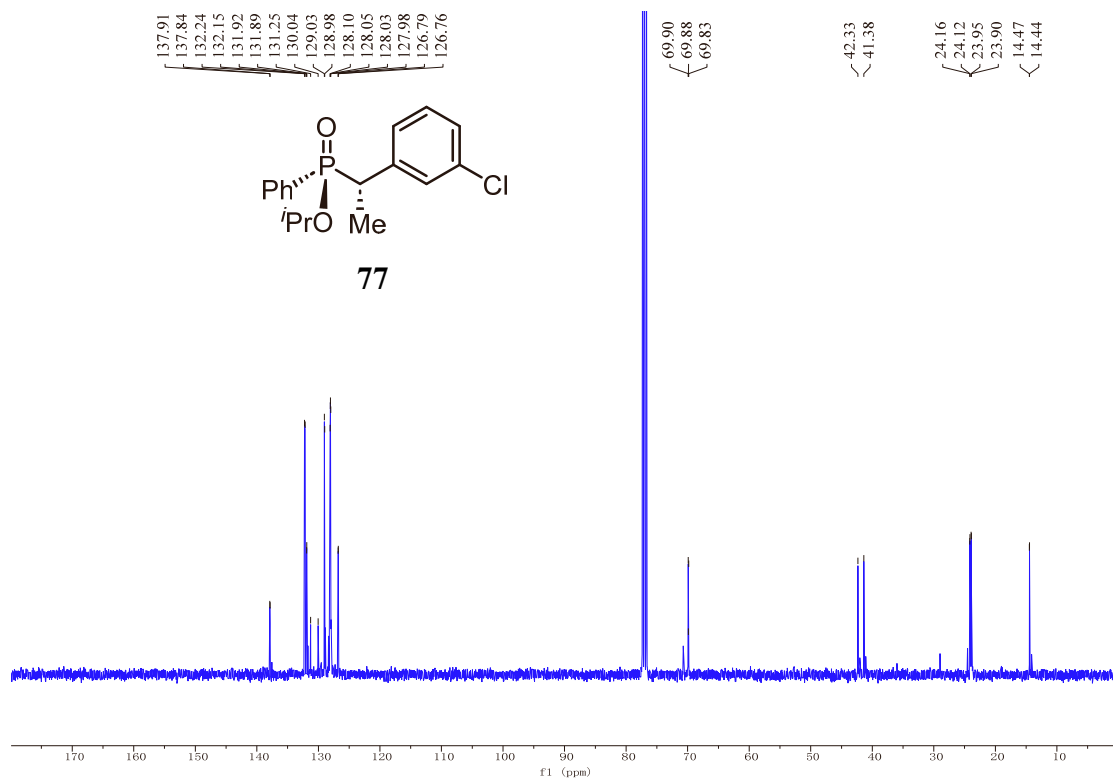
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



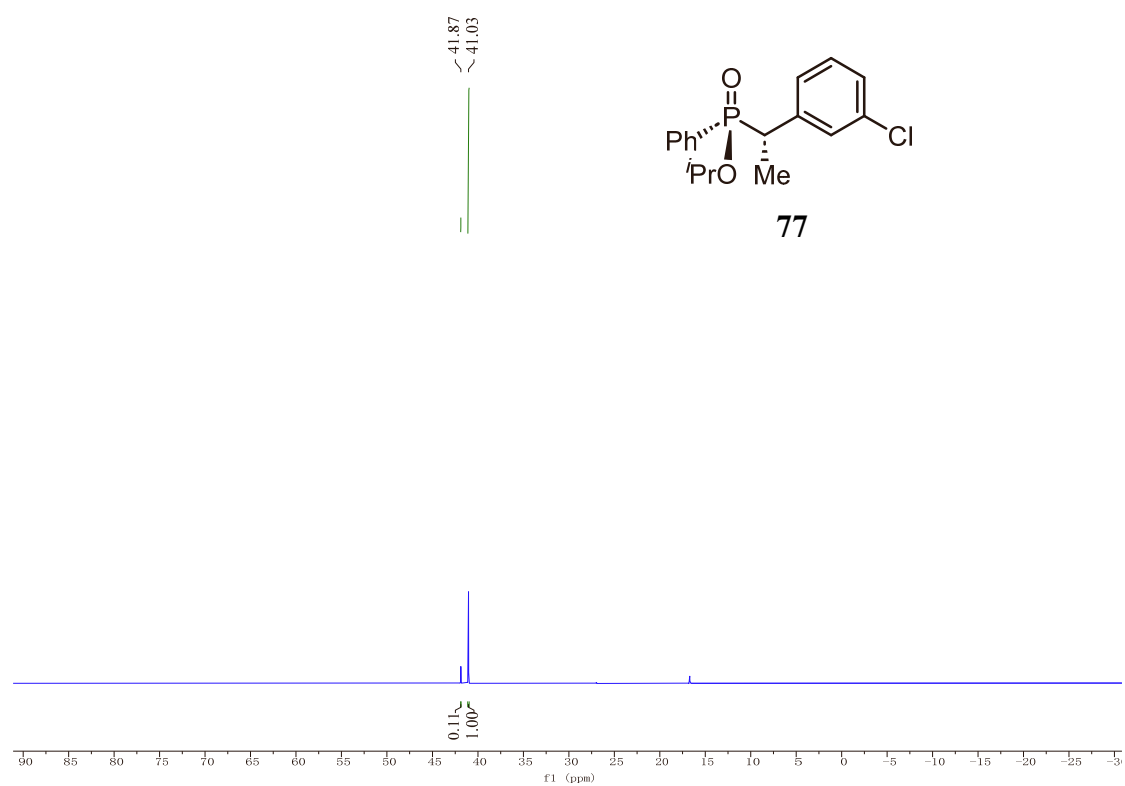
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

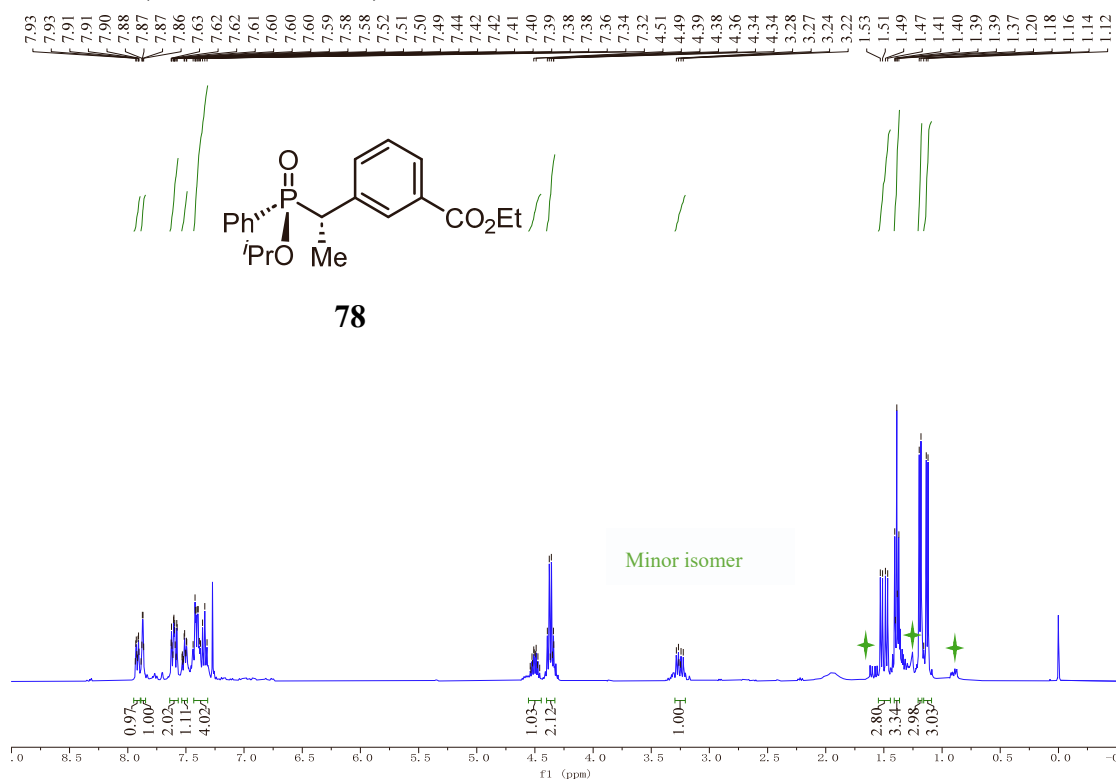


**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**

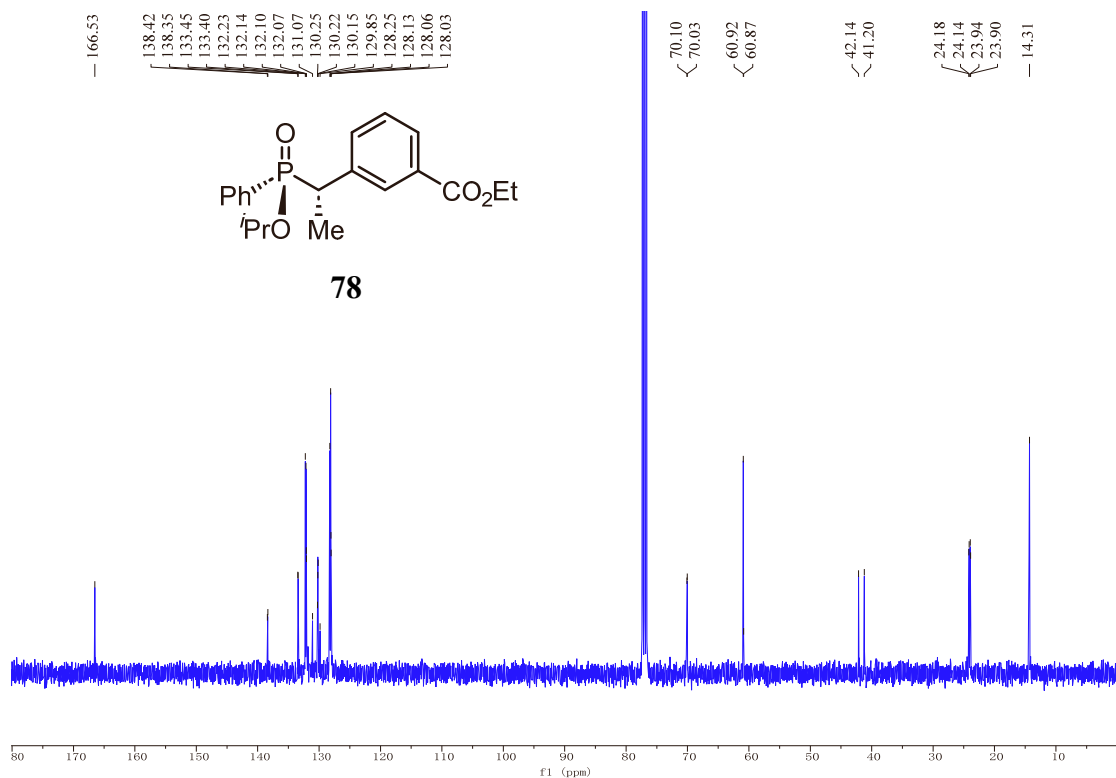




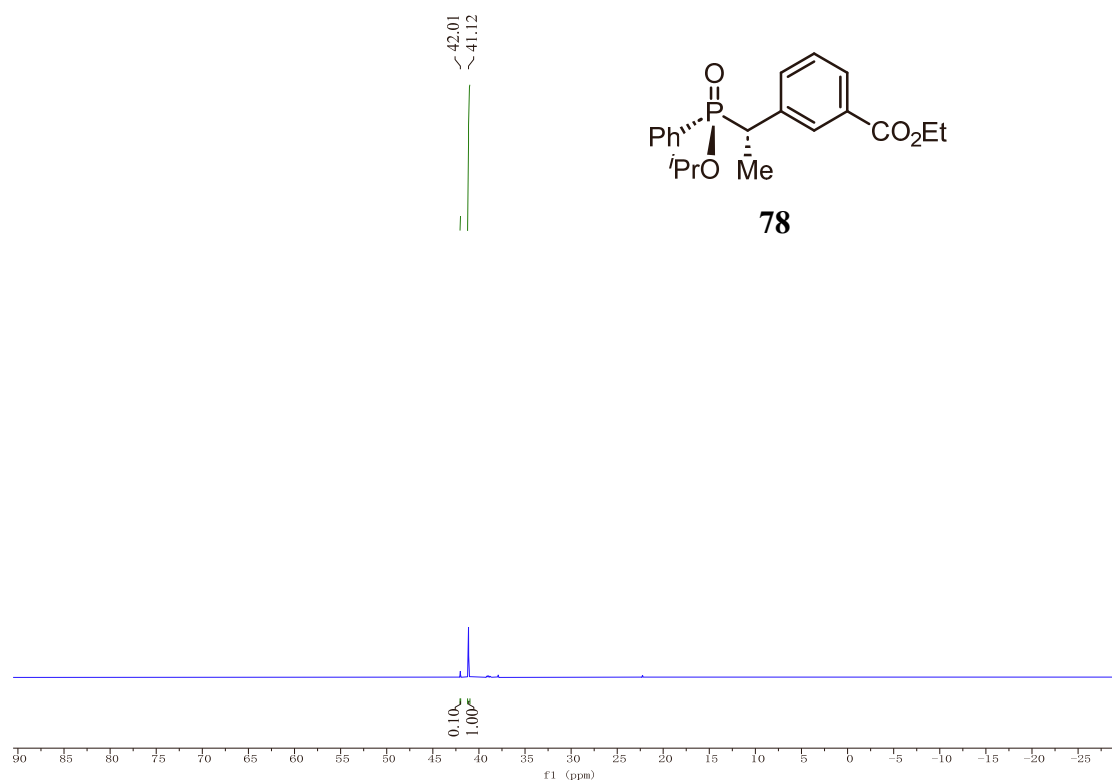
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



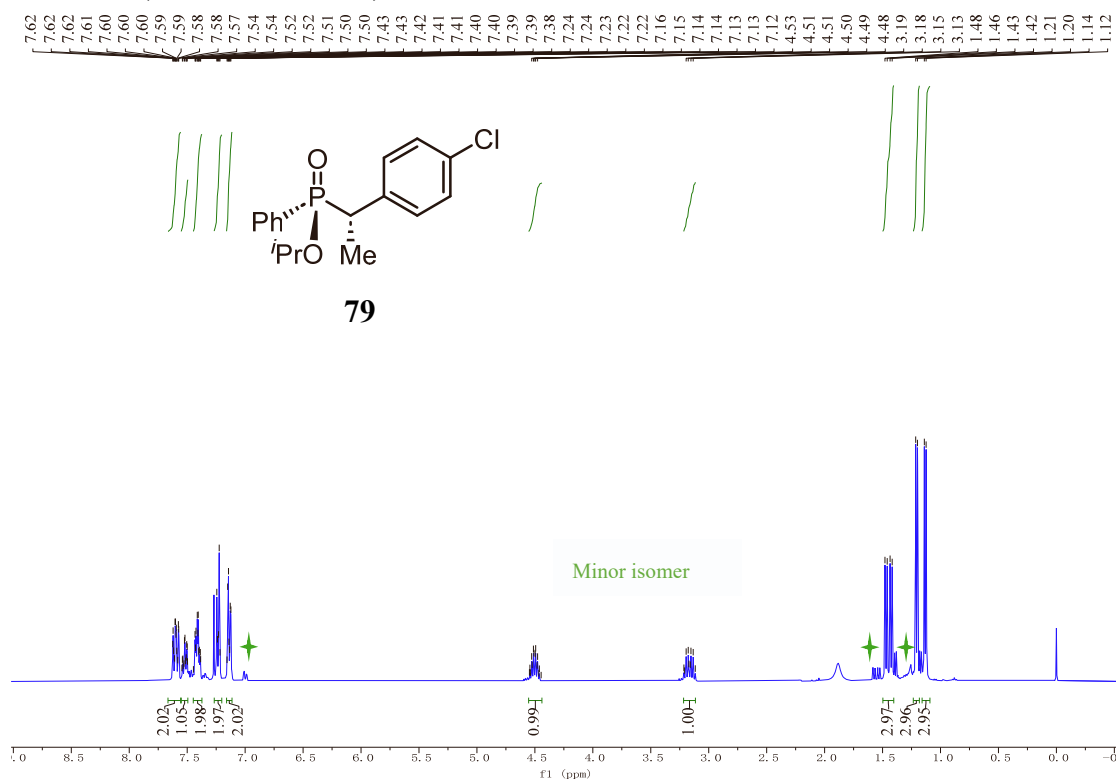
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



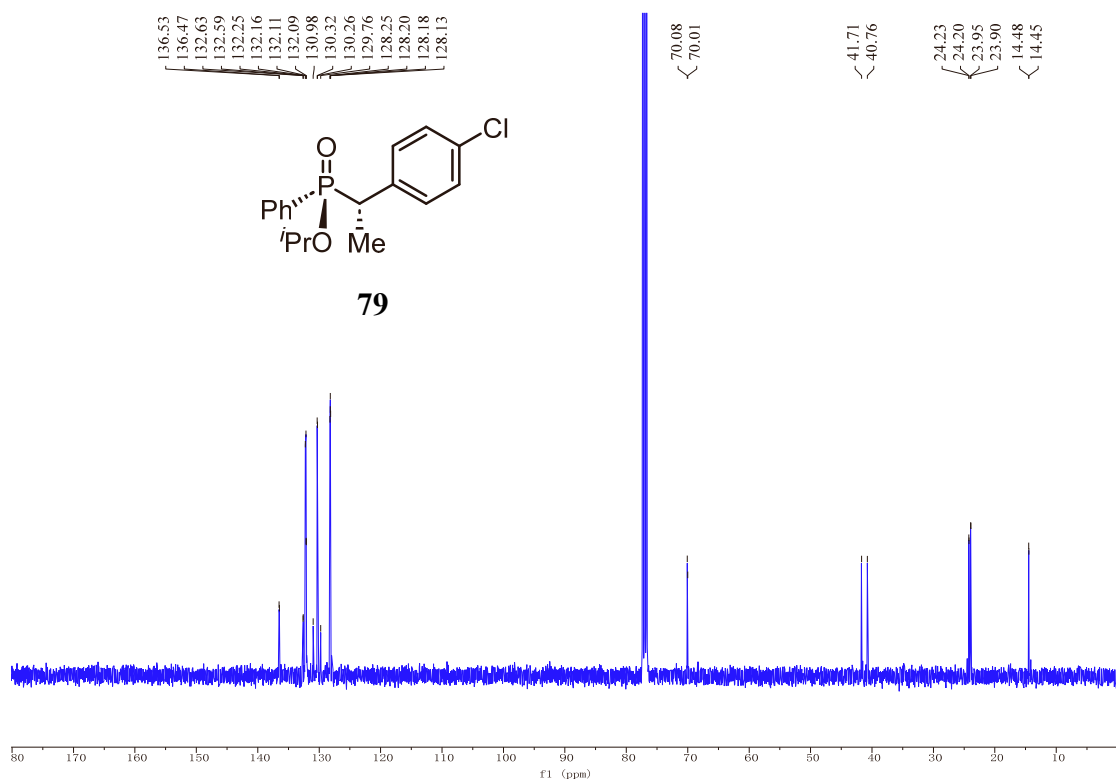
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



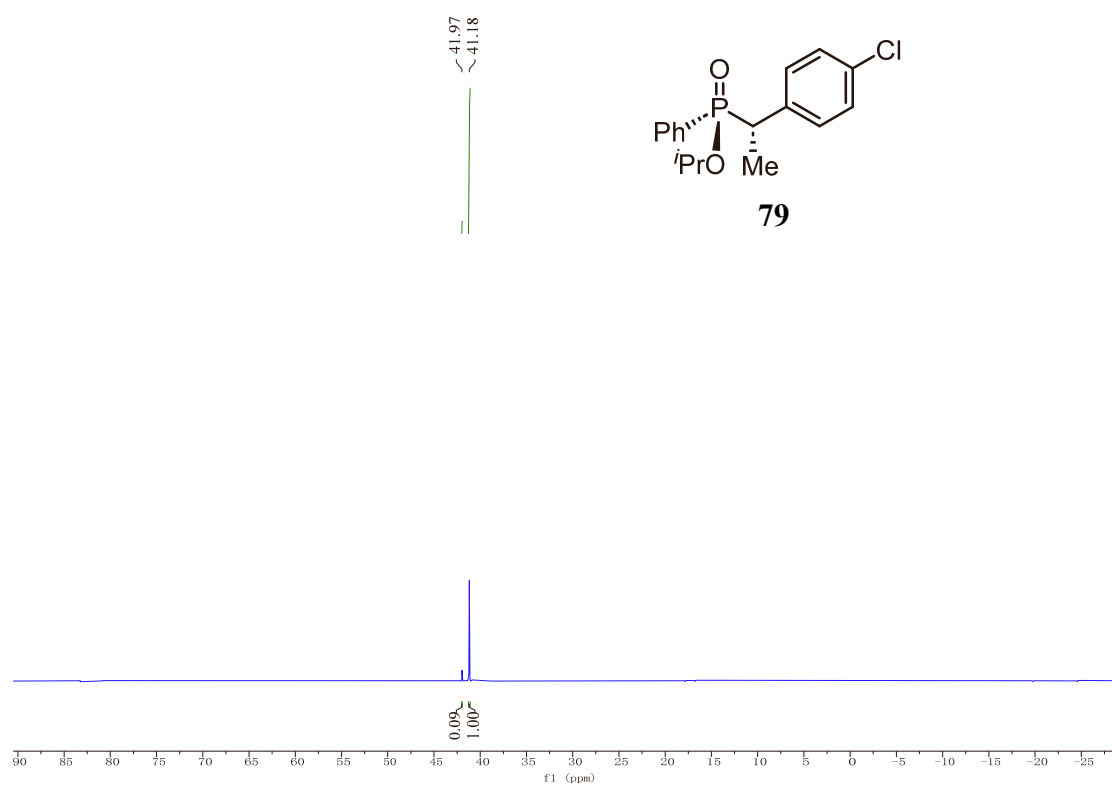
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



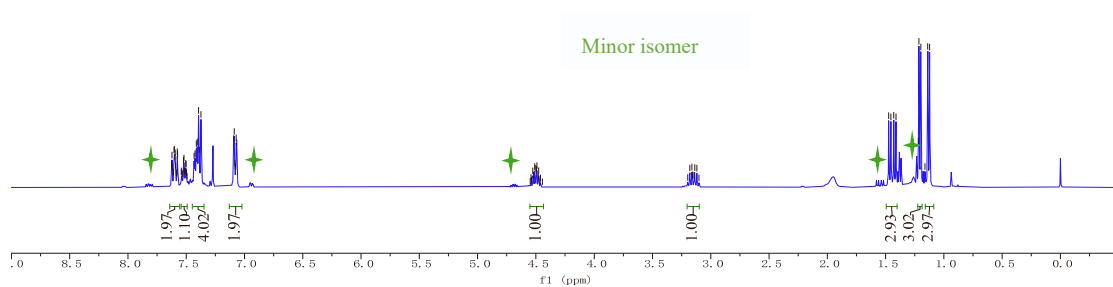
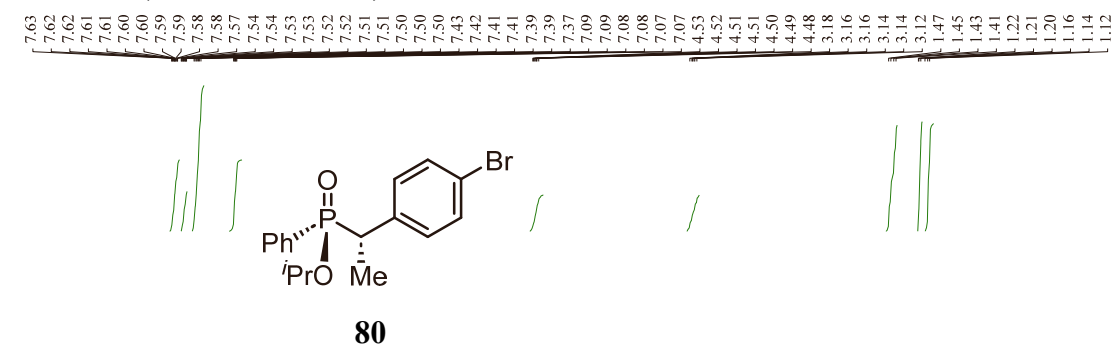
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



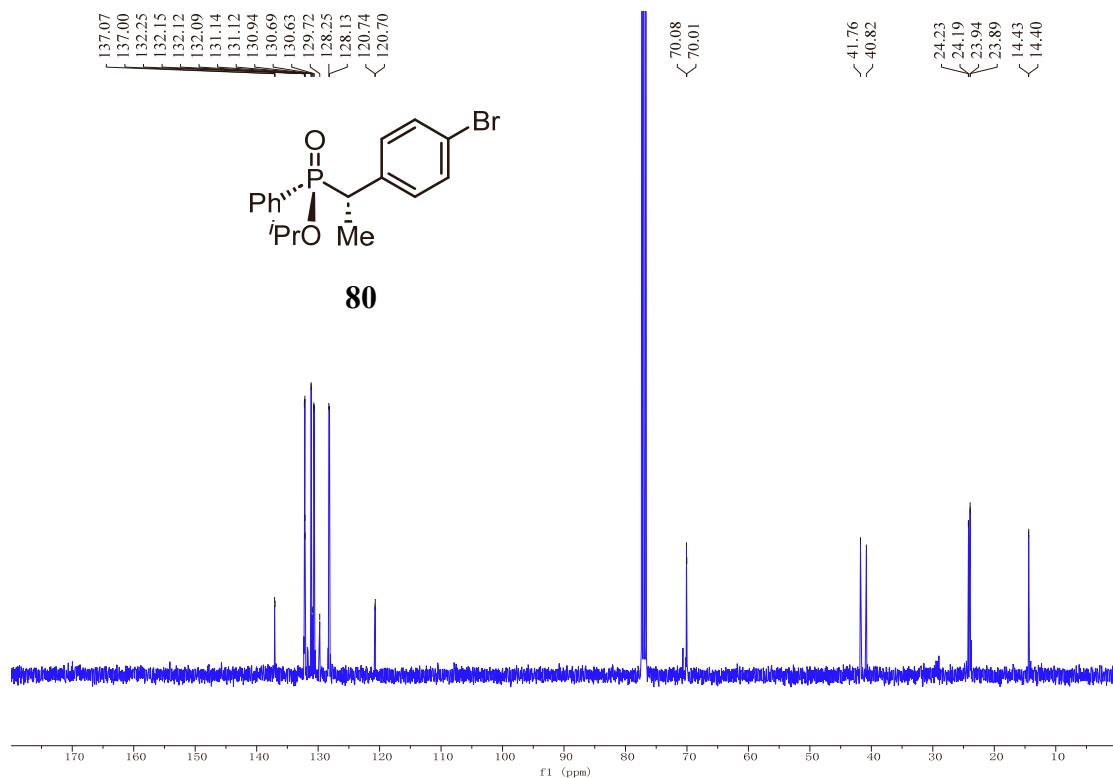
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



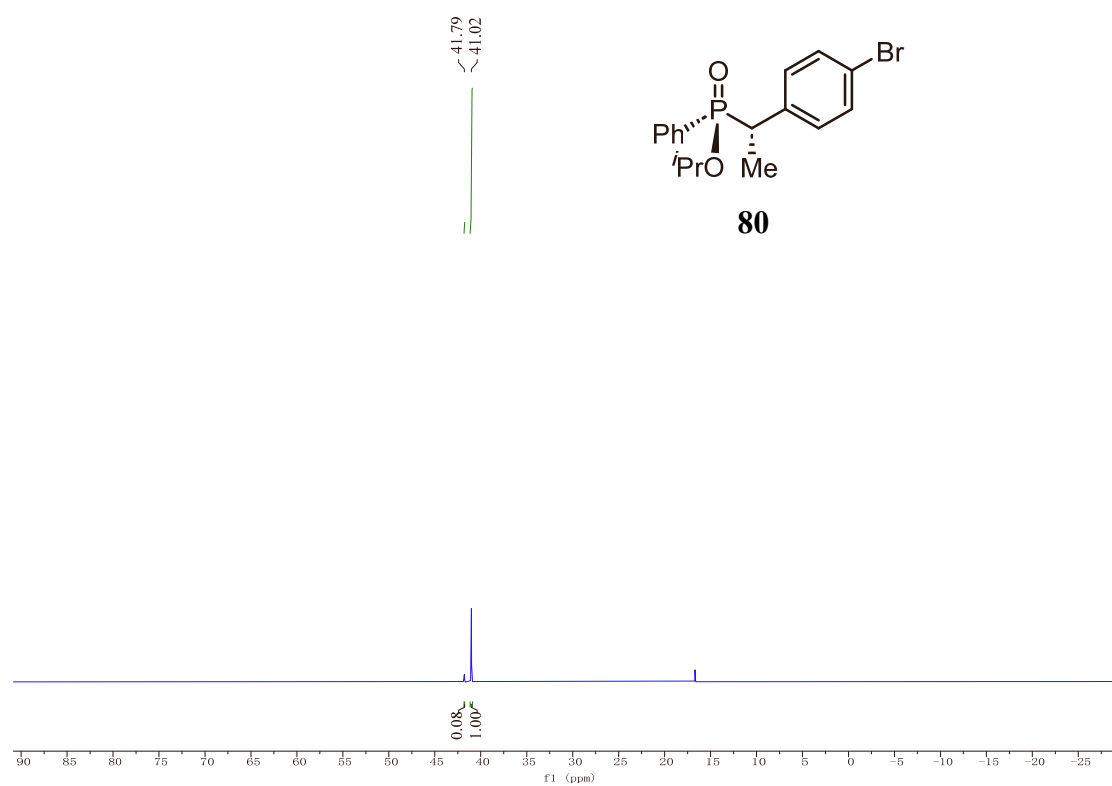
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



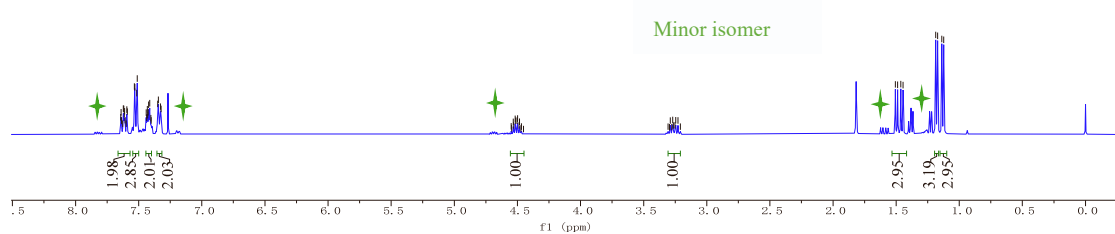
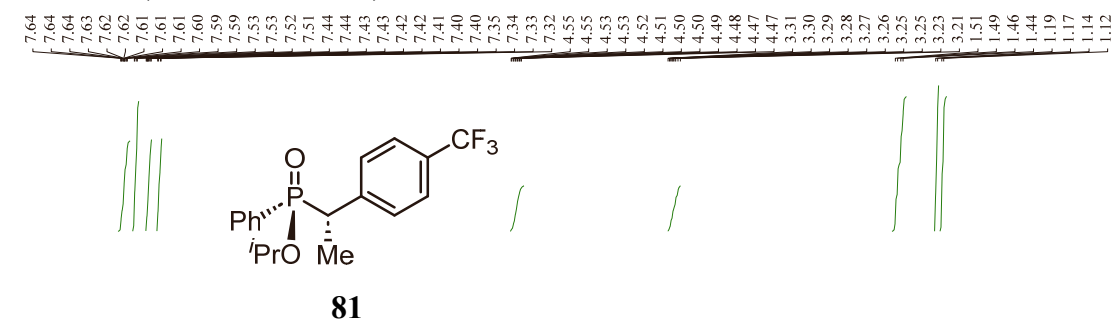
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



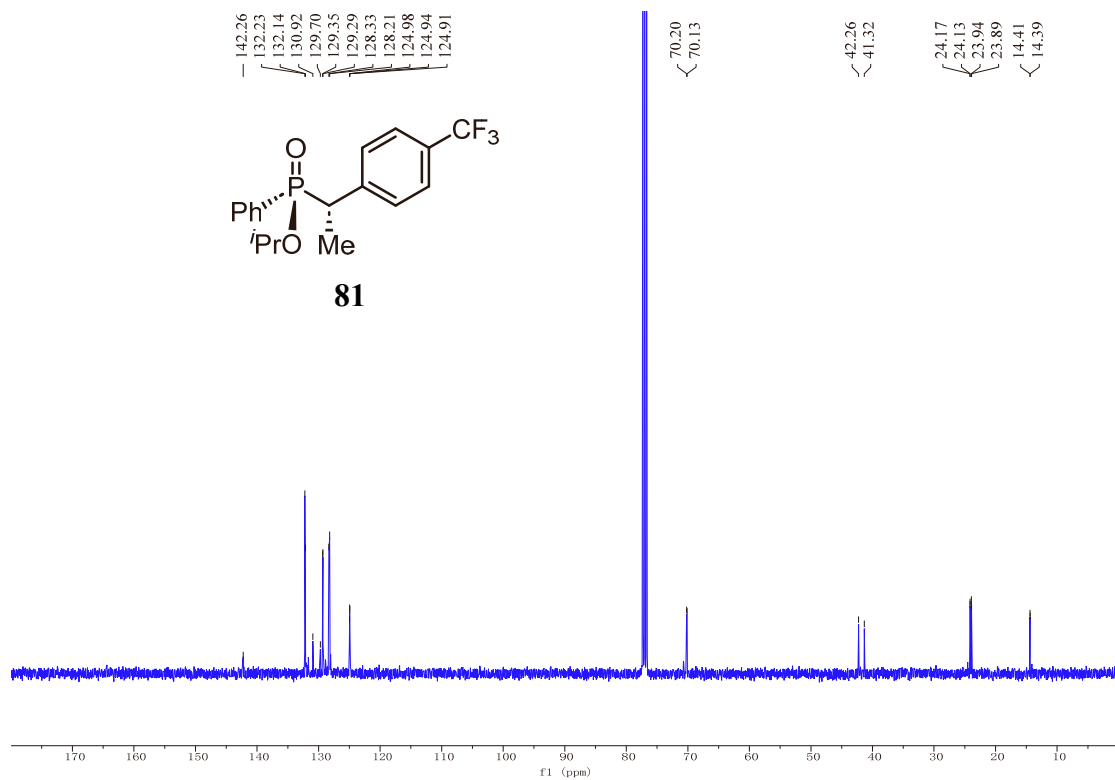
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



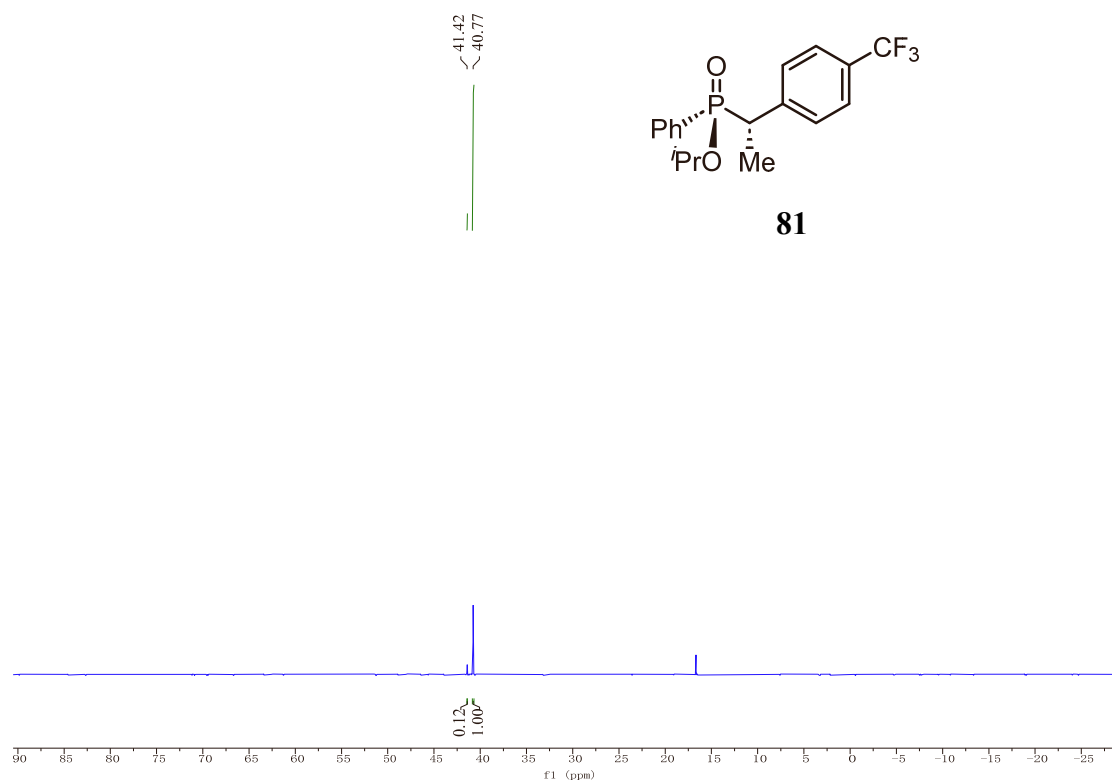
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

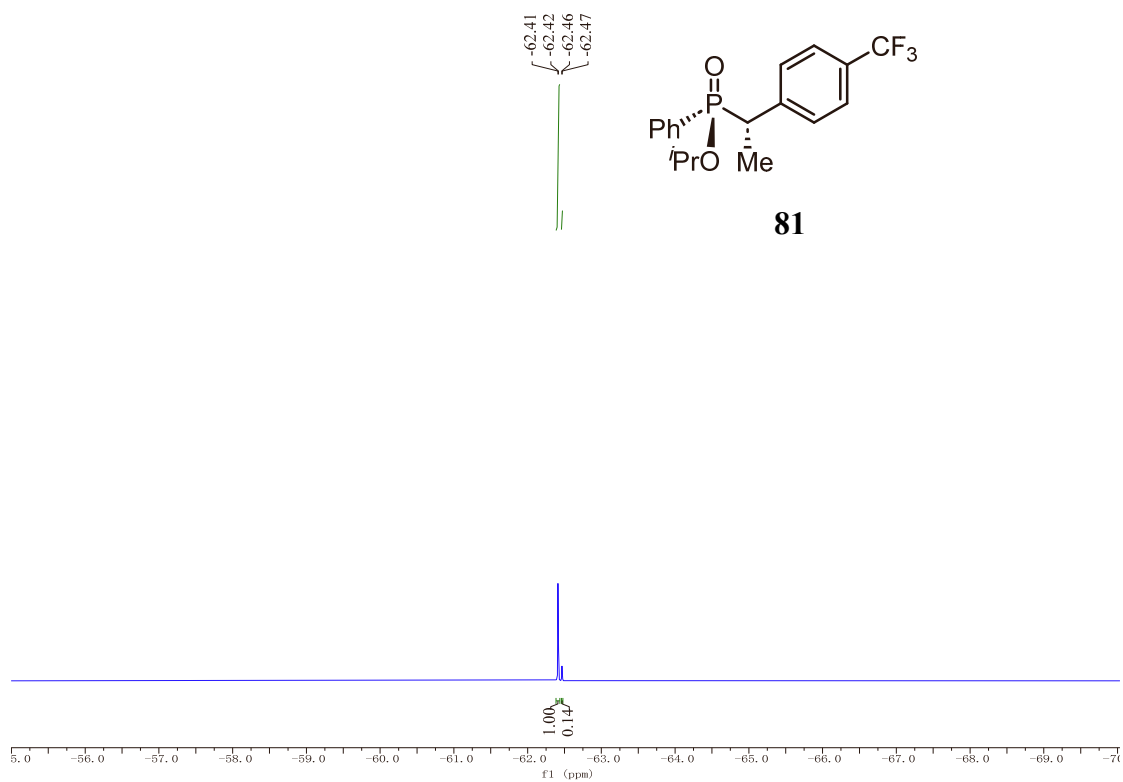


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

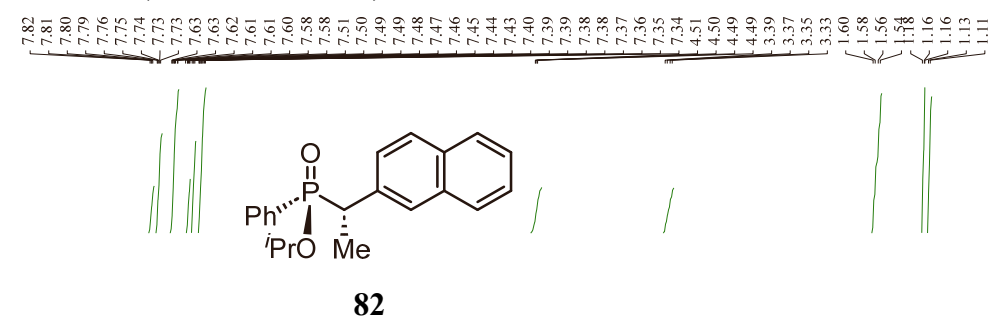


**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )

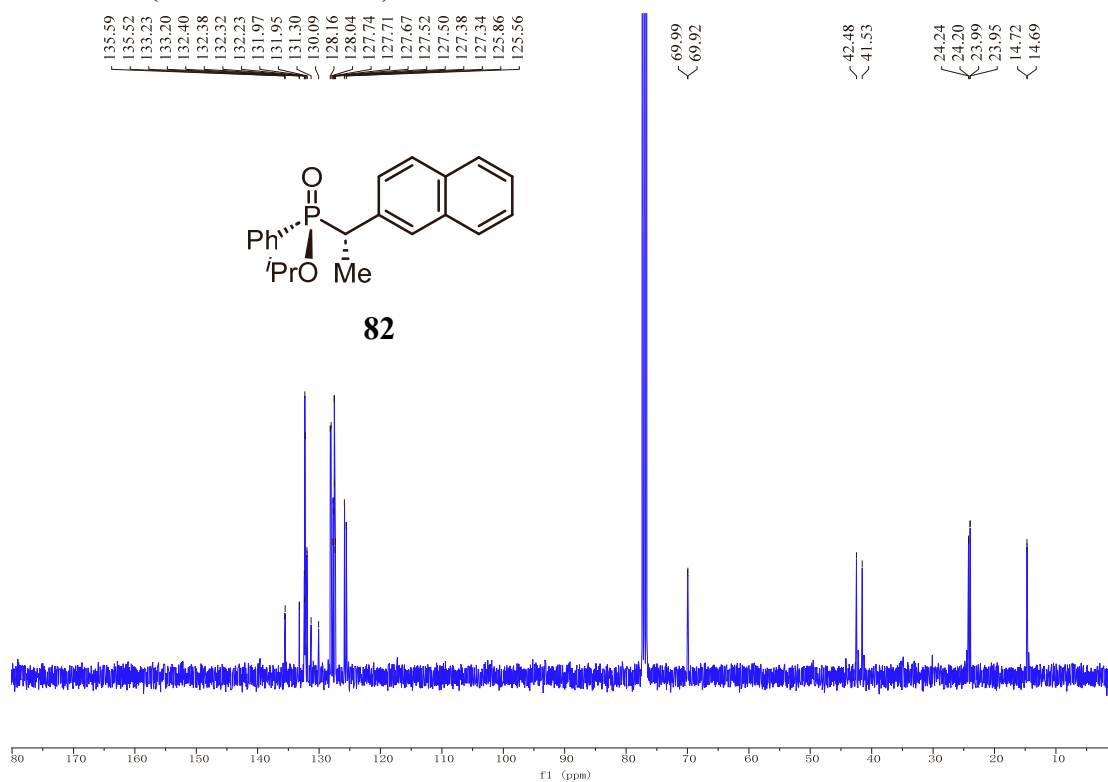




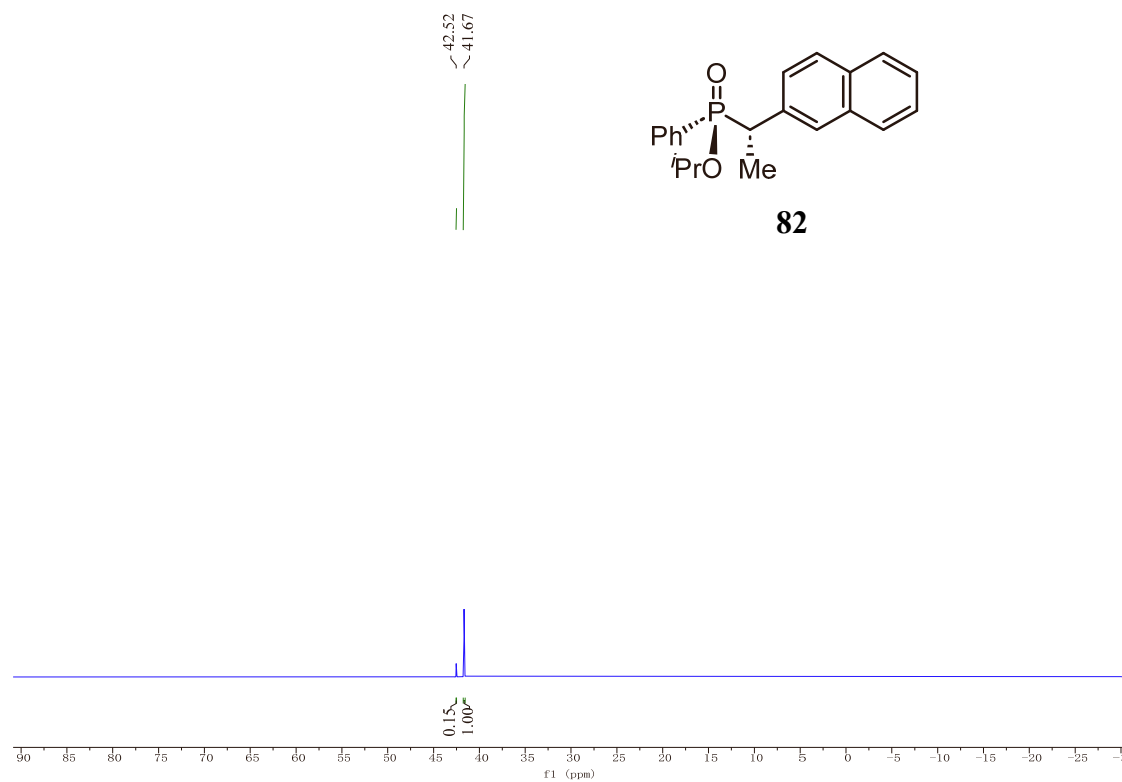
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



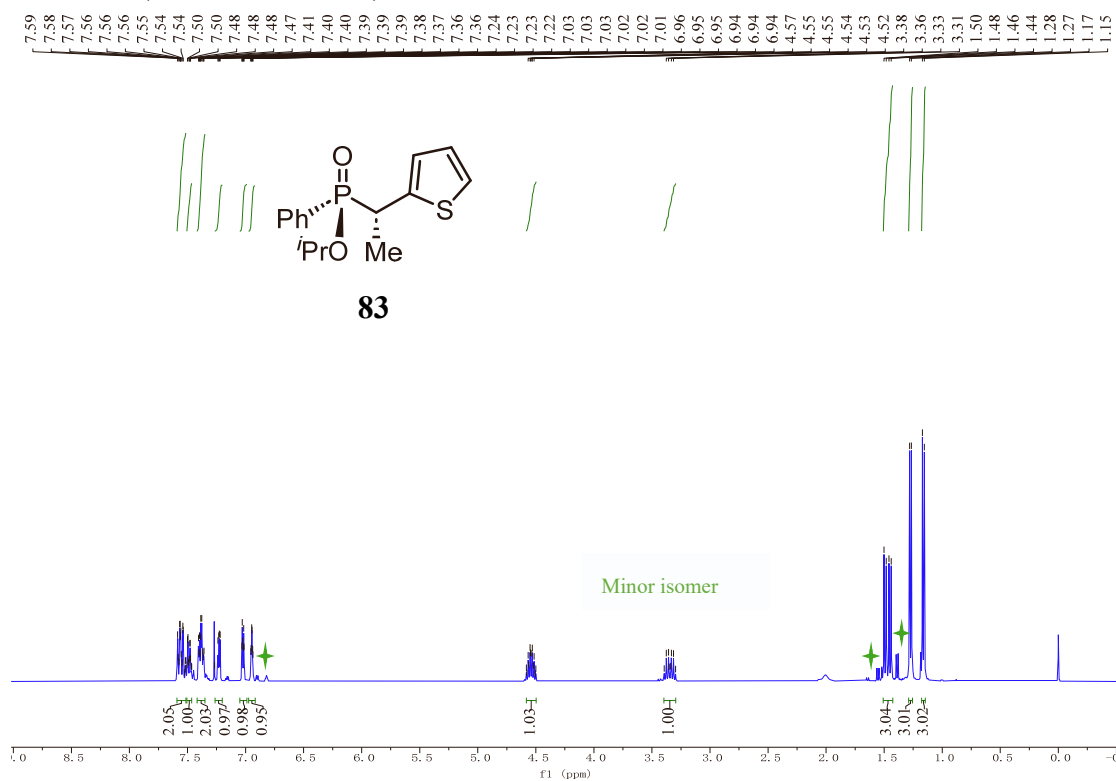
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



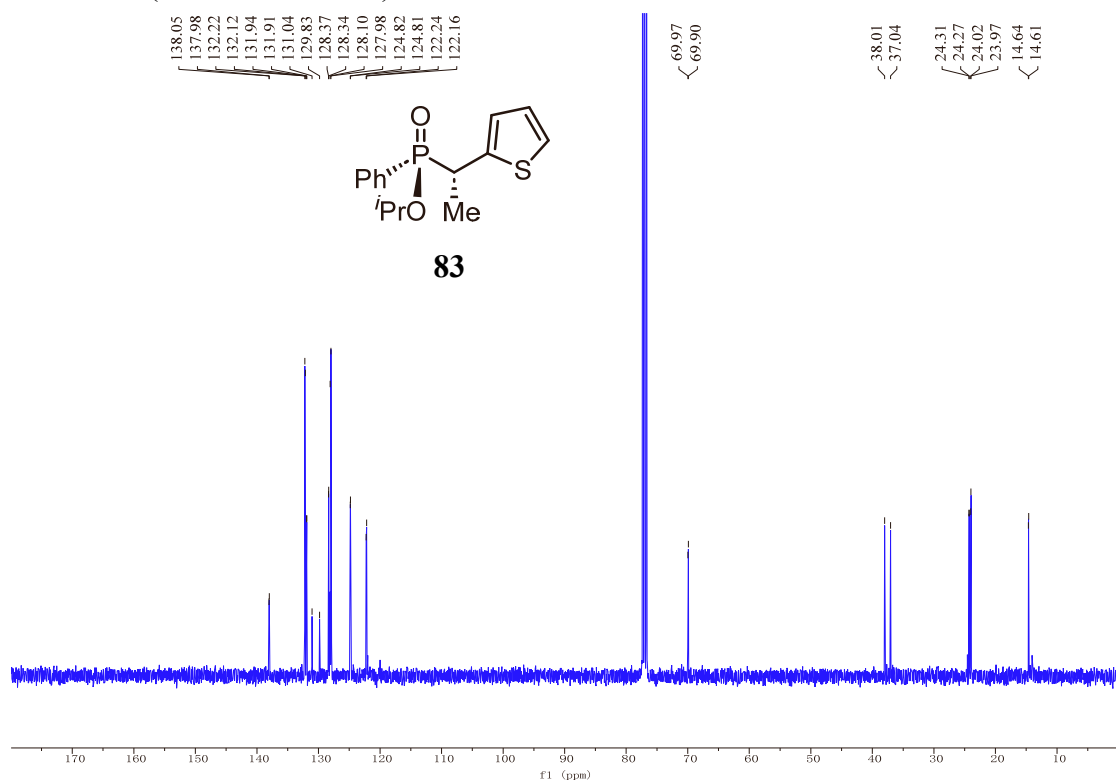
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**

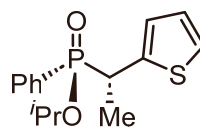


**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**

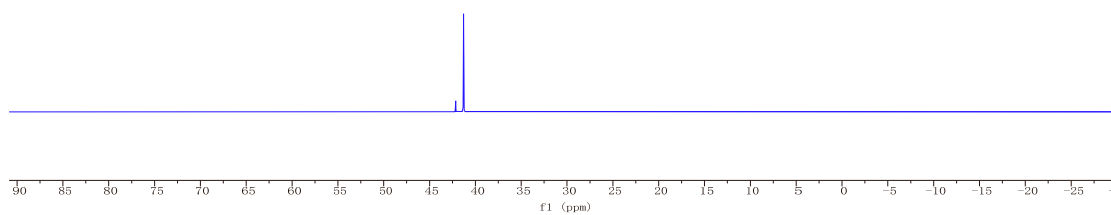


**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**

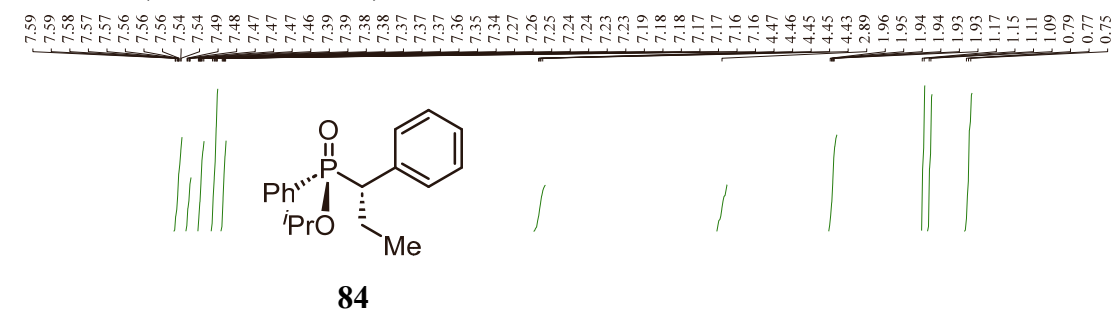
~42.15  
~41.30



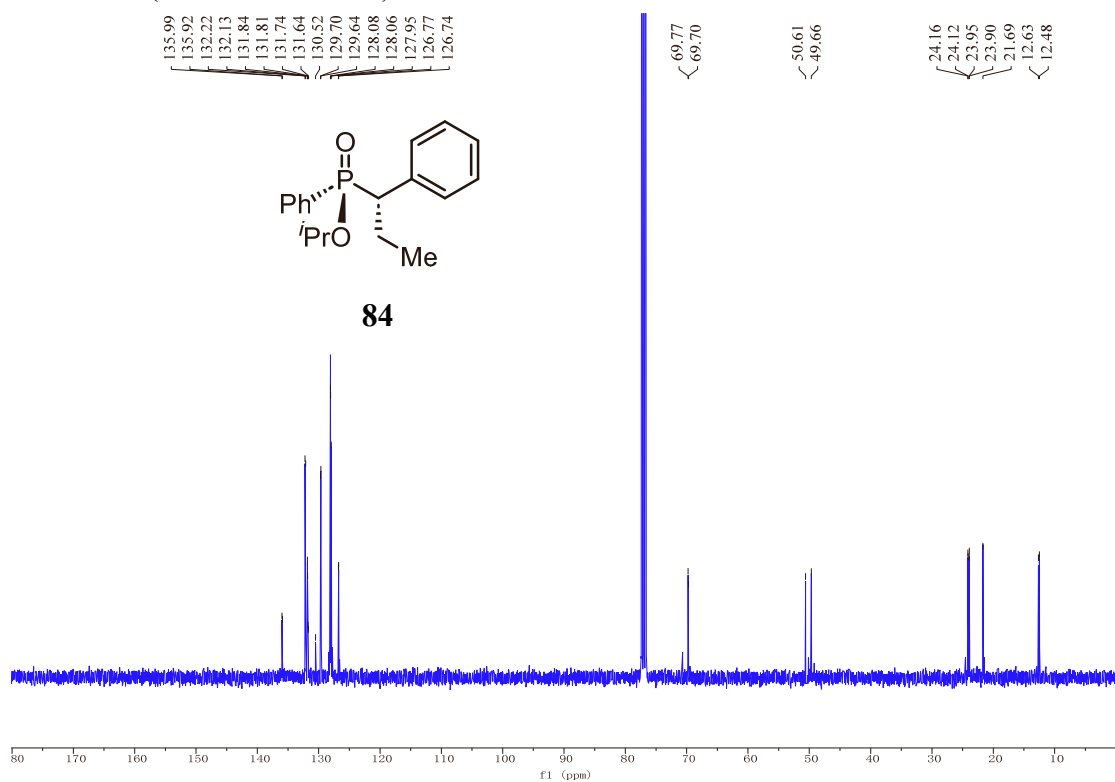
**83**



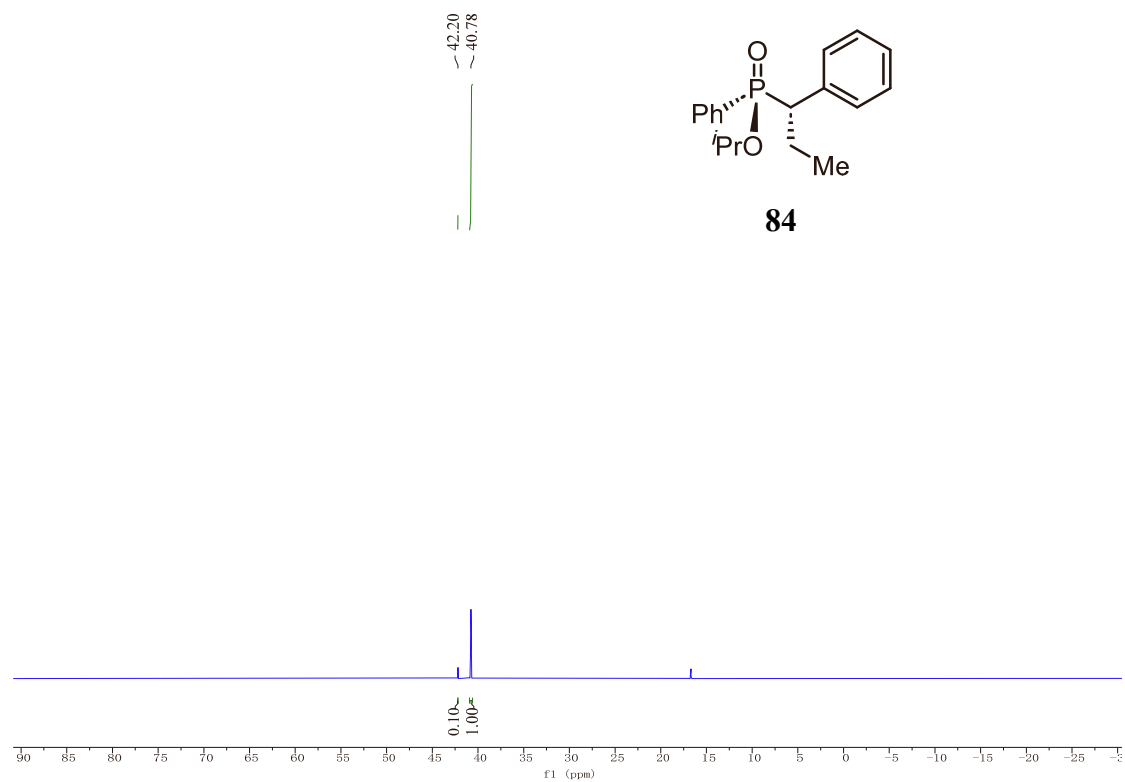
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



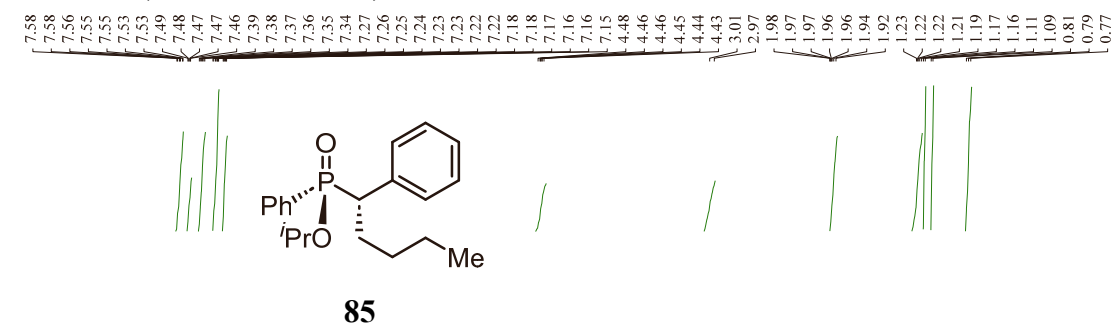
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**



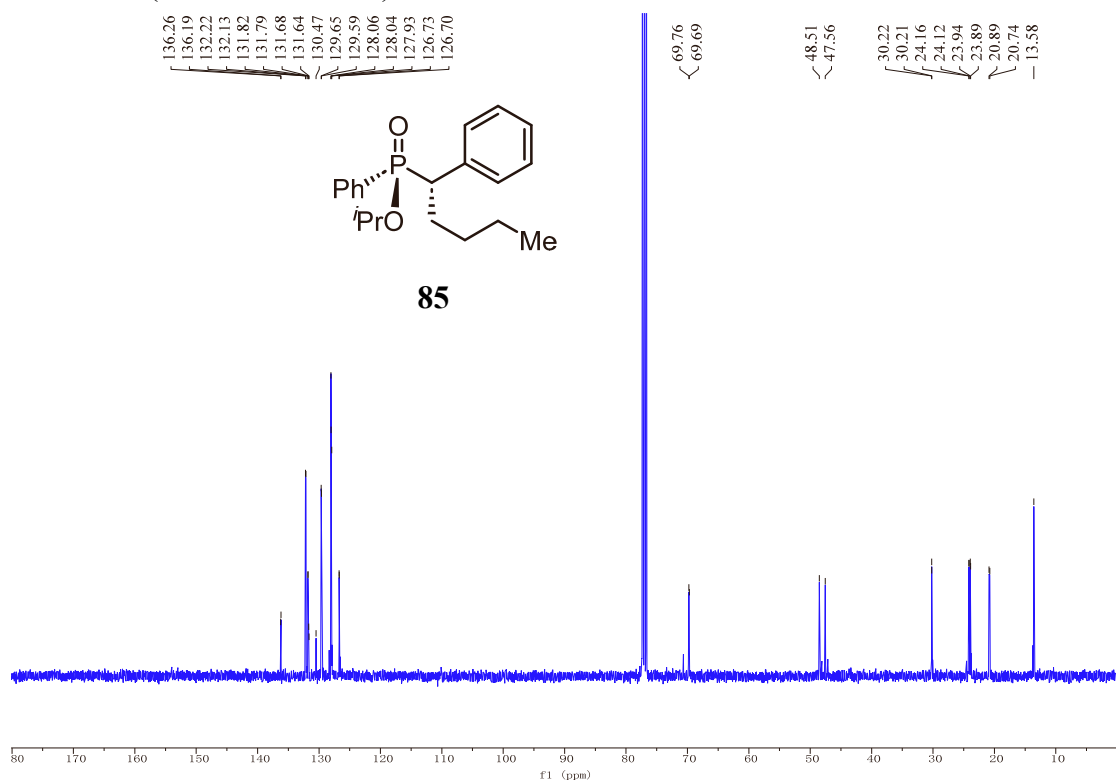
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

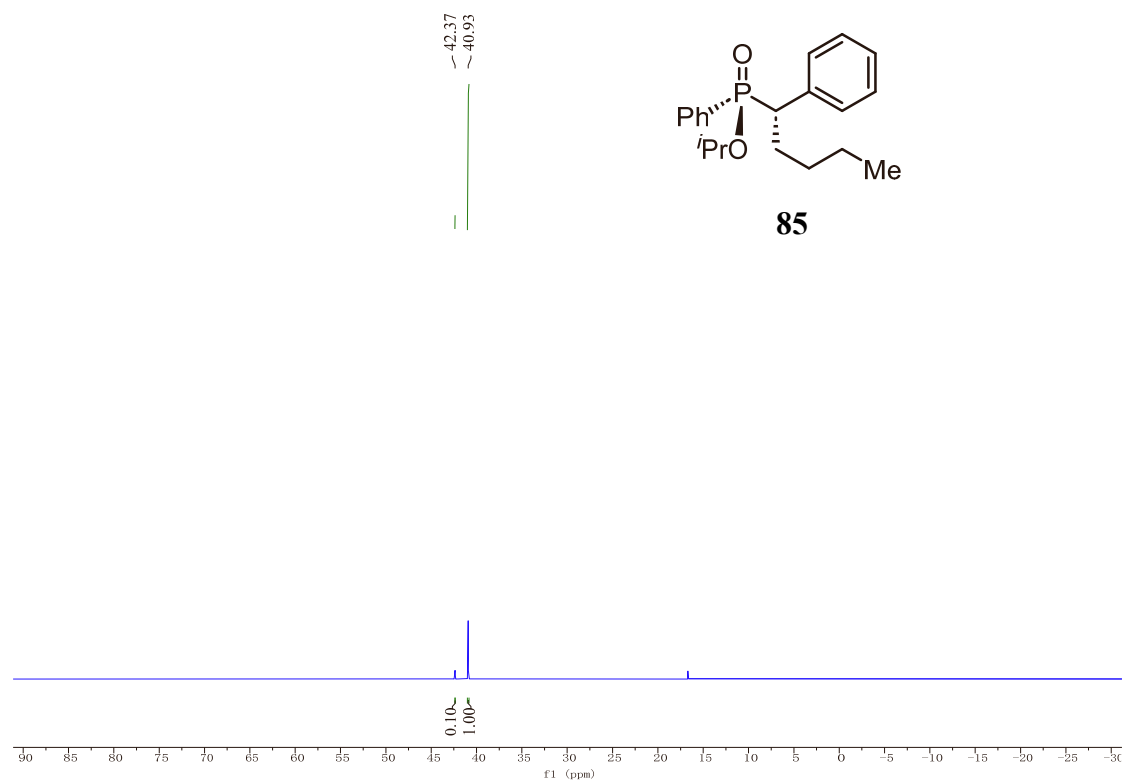


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

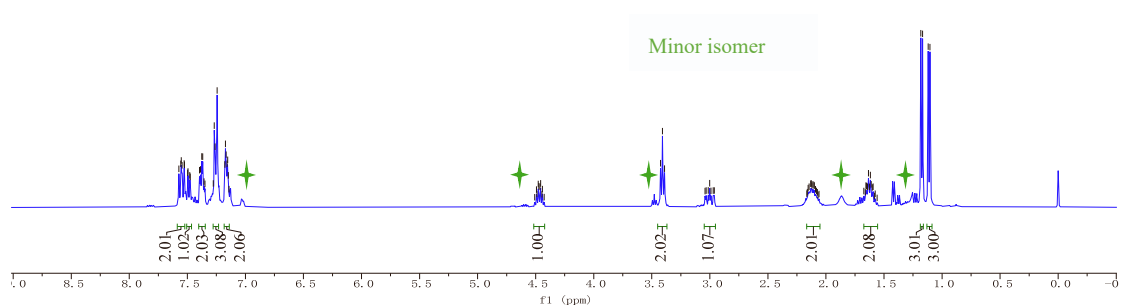
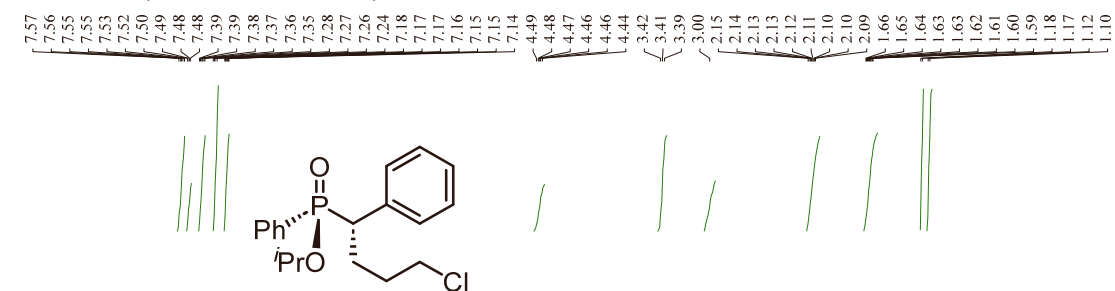




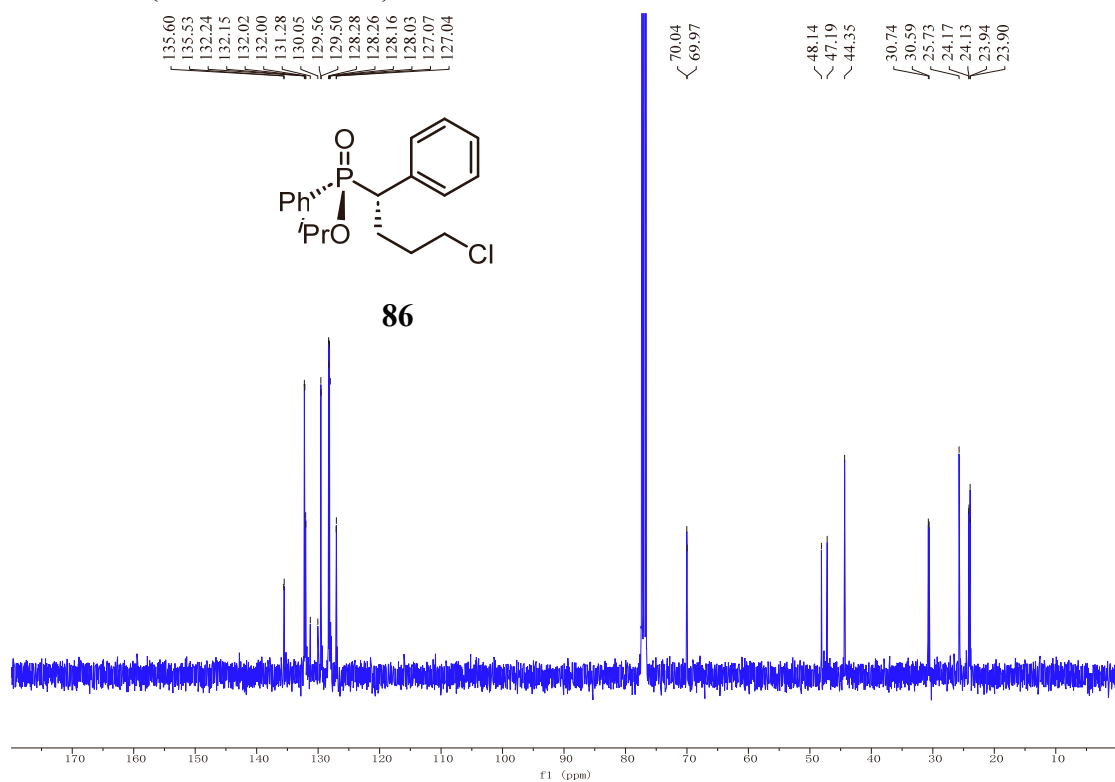
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



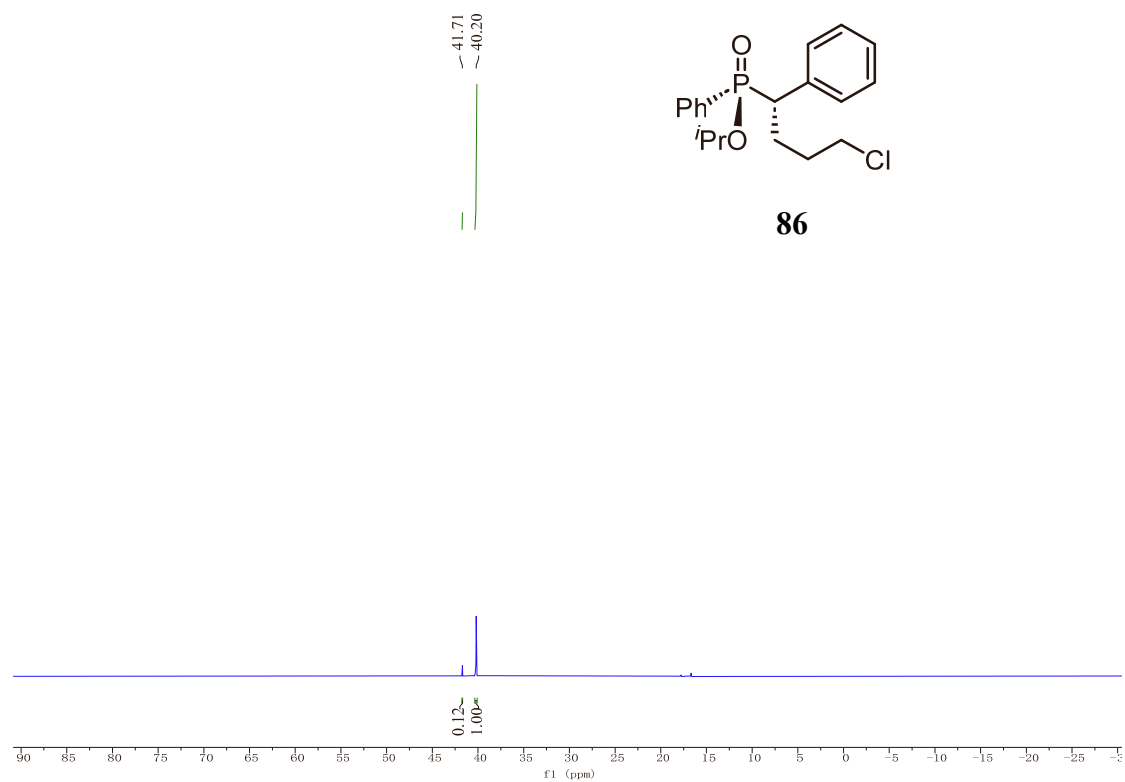
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



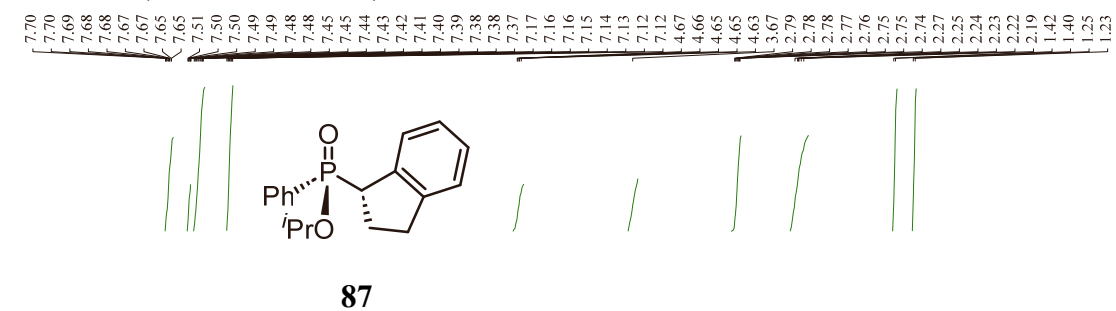
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**



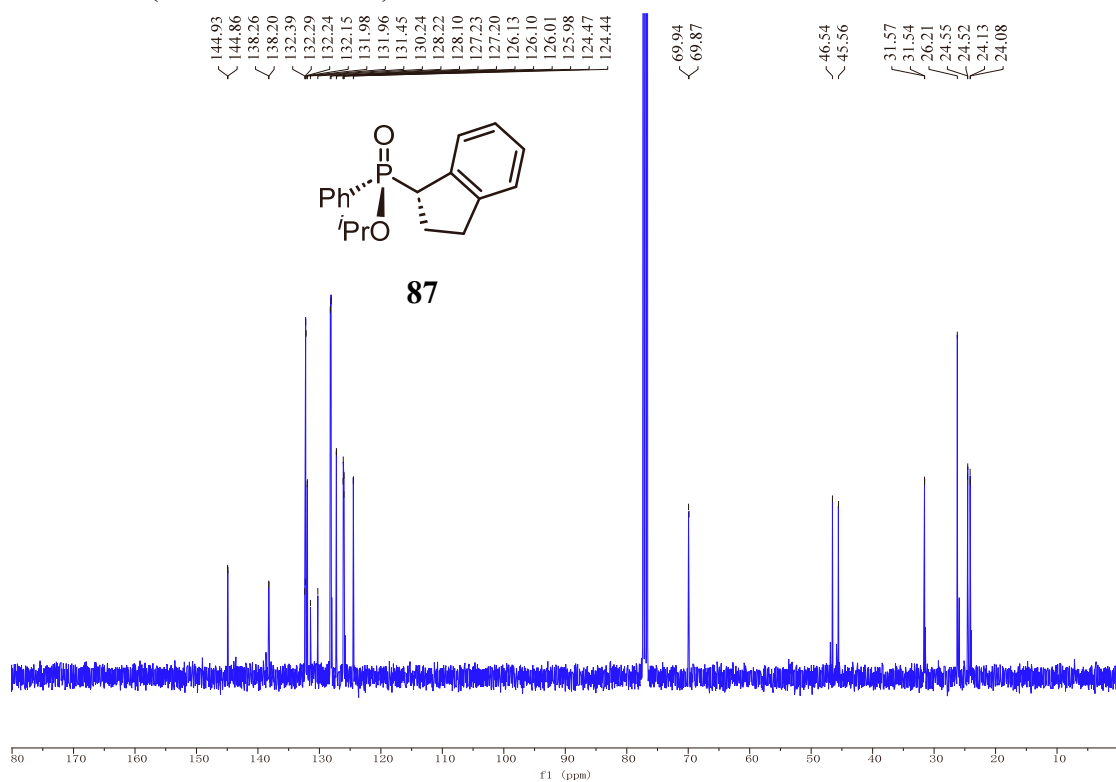
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



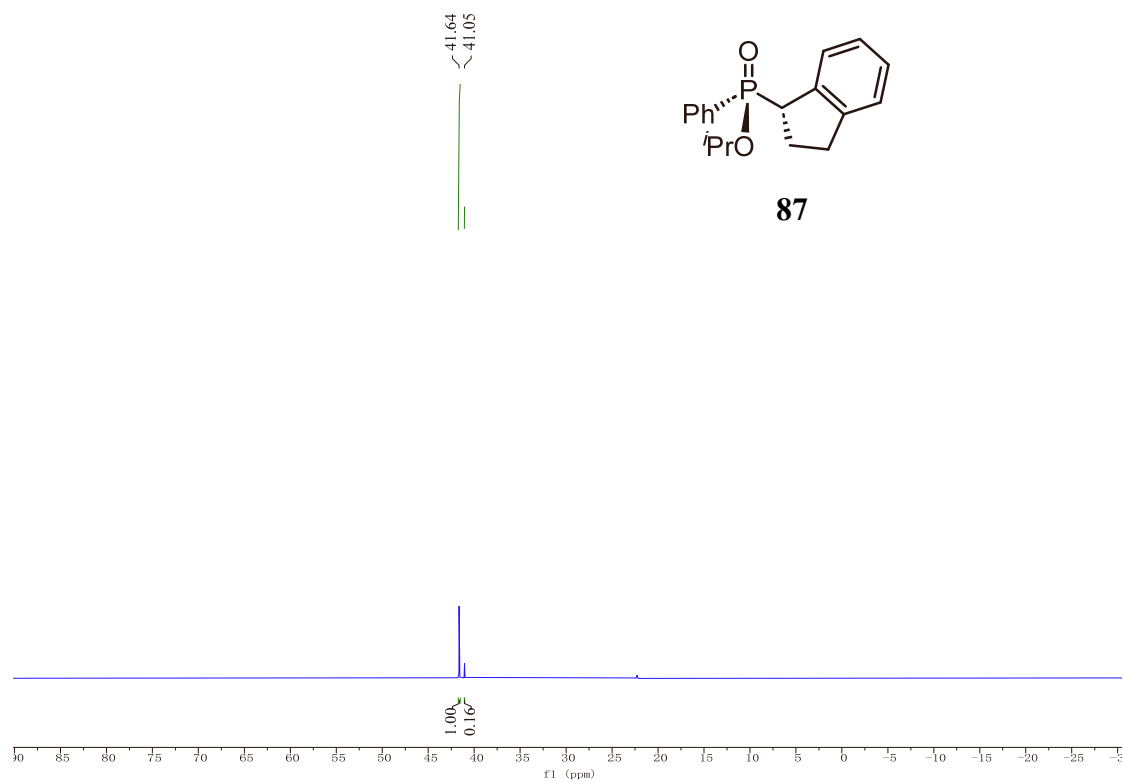
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**



**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



CC1(BH3)P(c2ccccc2)C(c3ccccc3)C1

**88**

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound **88**. The spectrum displays peaks in the aromatic region (7.0–7.6 ppm) and aliphatic region (0.0–2.1 ppm). Integration values are shown below the baseline.

140.42  
140.41  
139.57  
132.41  
132.32  
131.43  
131.36  
131.33  
131.31  
130.32  
130.28  
128.71  
128.50  
128.40  
128.01  
127.24  
126.85  
126.74  
126.71

77.32  
77.00  
76.68

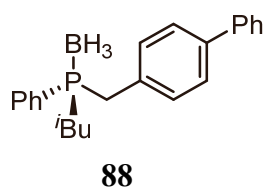
35.84  
35.53  
32.52  
32.18  
24.93  
24.84  
24.44  
24.31  
24.24

88

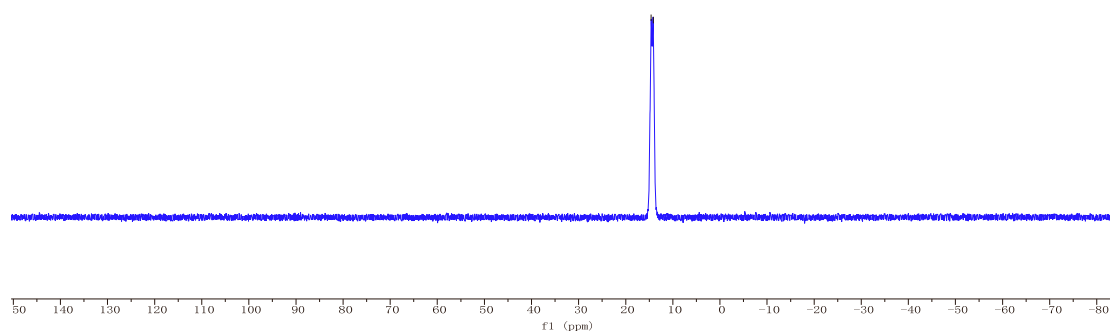
CC(P(=O)(c1ccccc1)C(=O)c2ccccc2)Cc3ccc(cc3)C(=O)c4ccccc4

Figure S10. <sup>13</sup>C NMR spectrum of compound 88 in CDCl<sub>3</sub>. The spectrum shows peaks in the aromatic region (126.71–140.42 ppm), a solvent triplet (76.68–77.32 ppm), and aliphatic region (24.24–35.84 ppm).

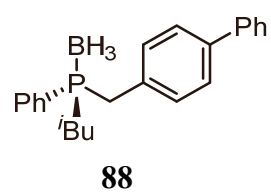
**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



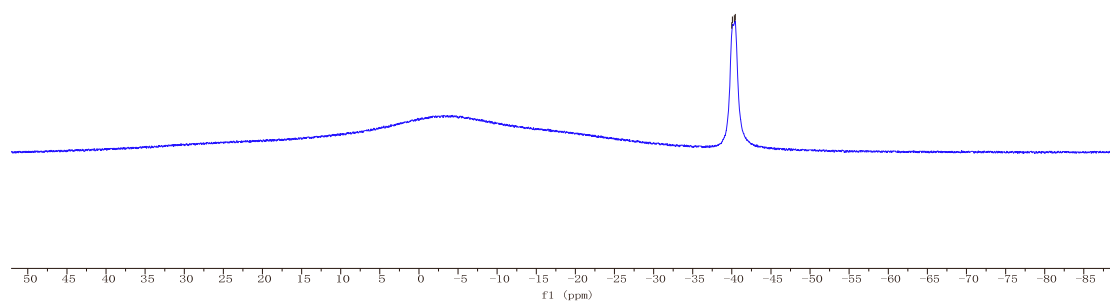
14.61  
14.14



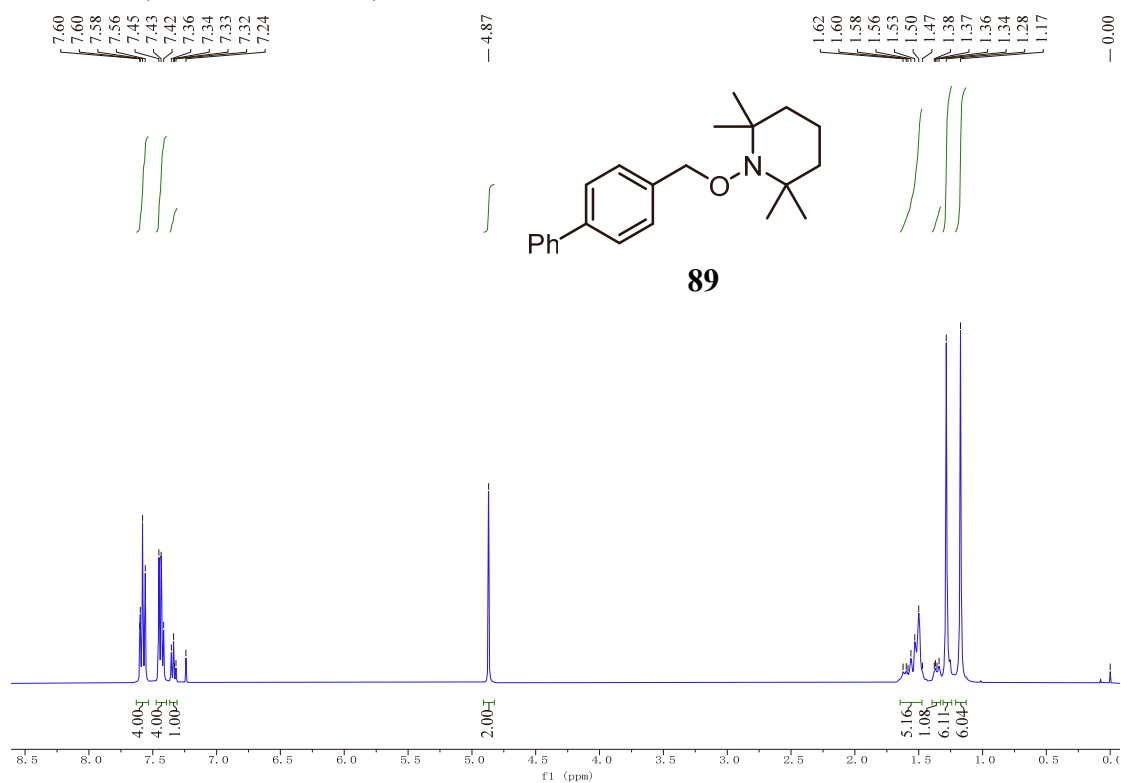
**$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )**



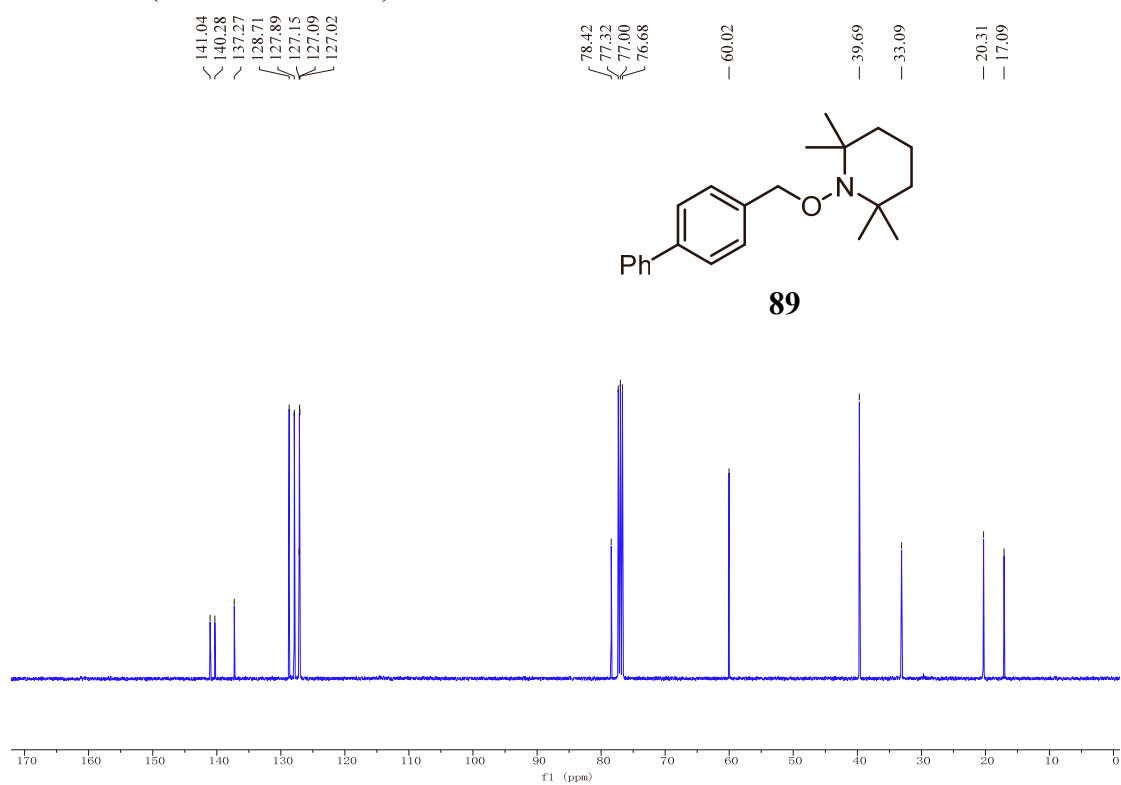
-40.00  
-40.08  
-40.32  
-40.45



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

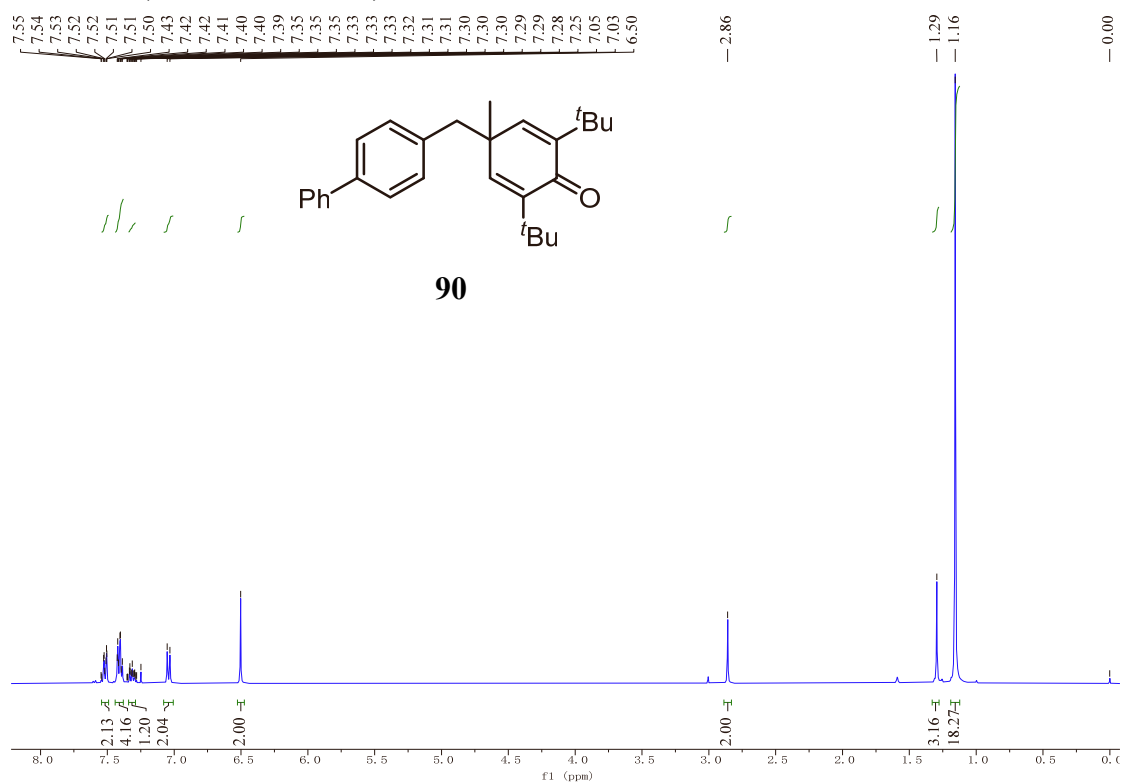


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

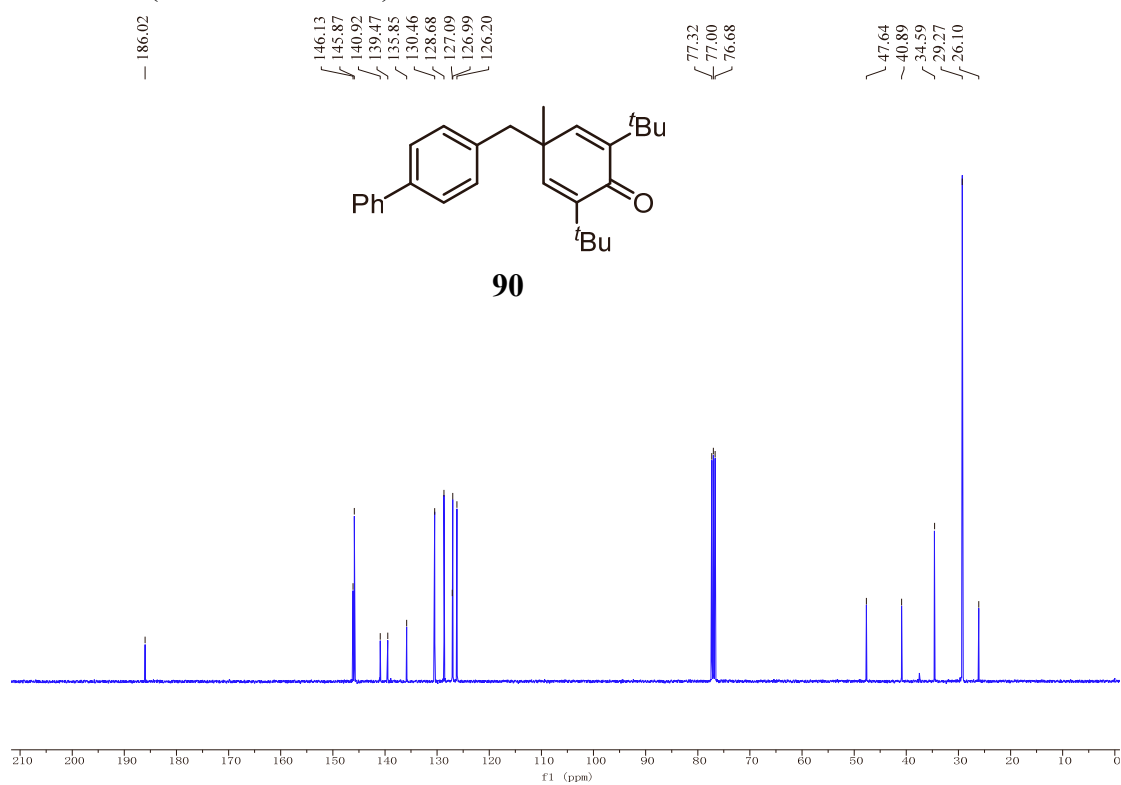




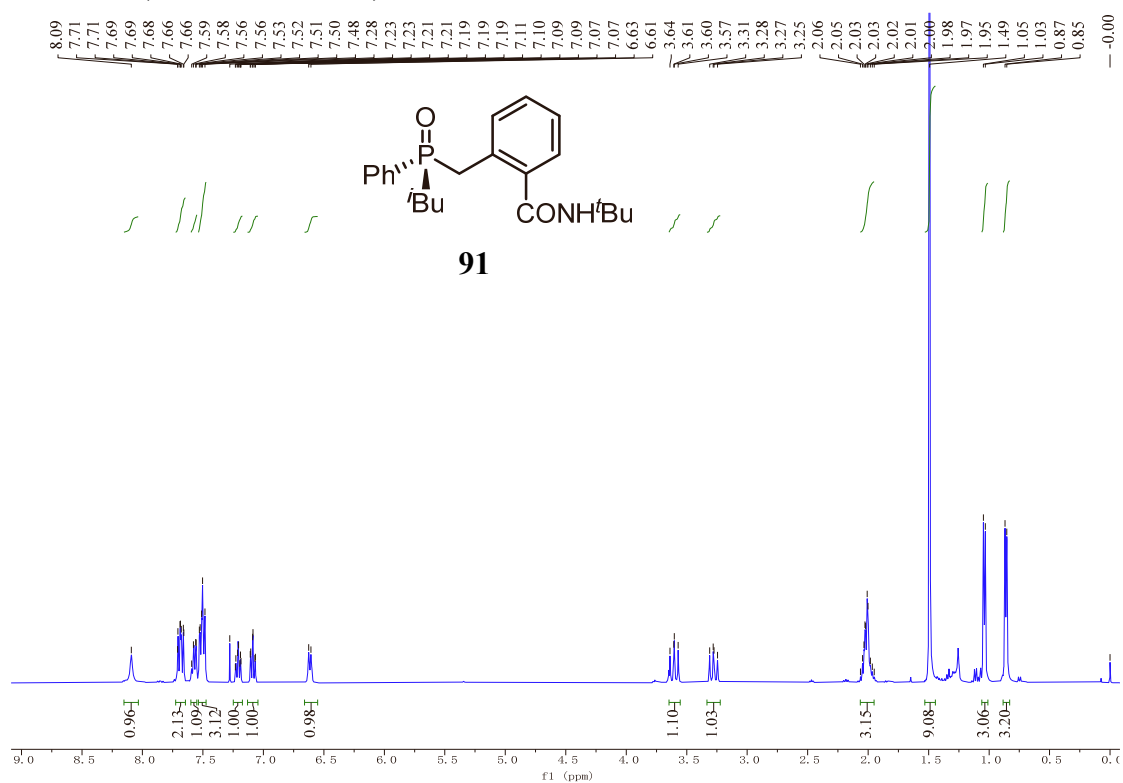
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



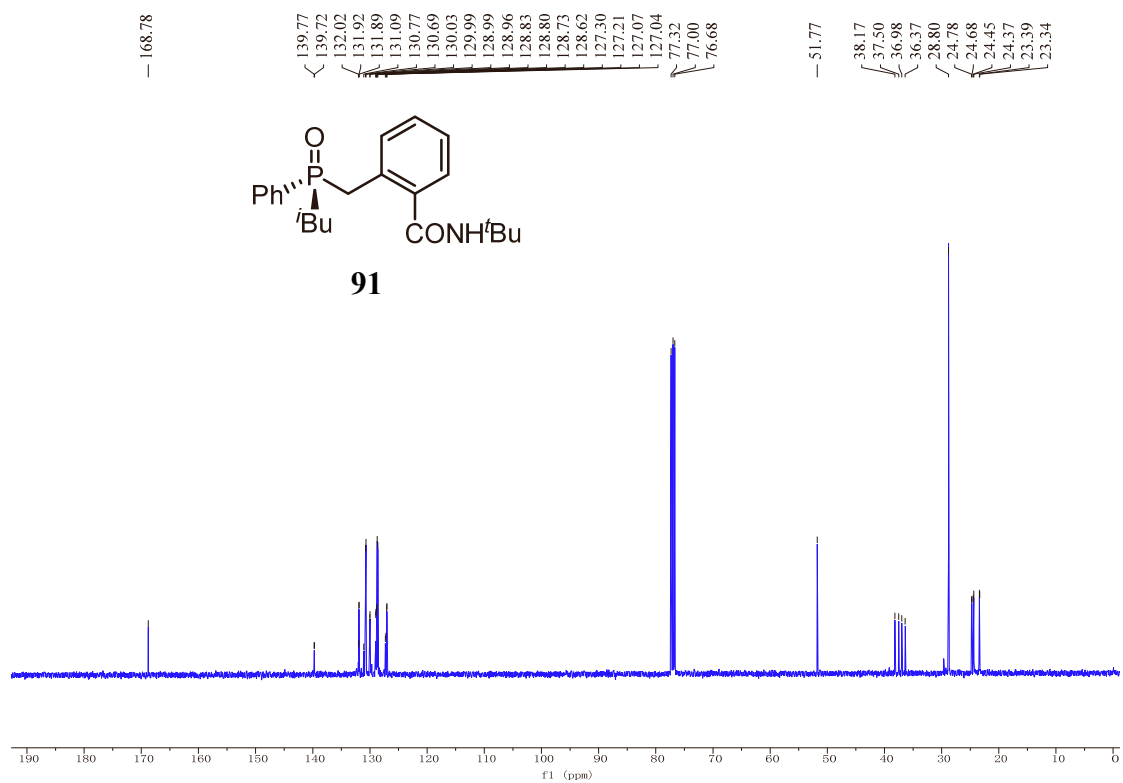
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



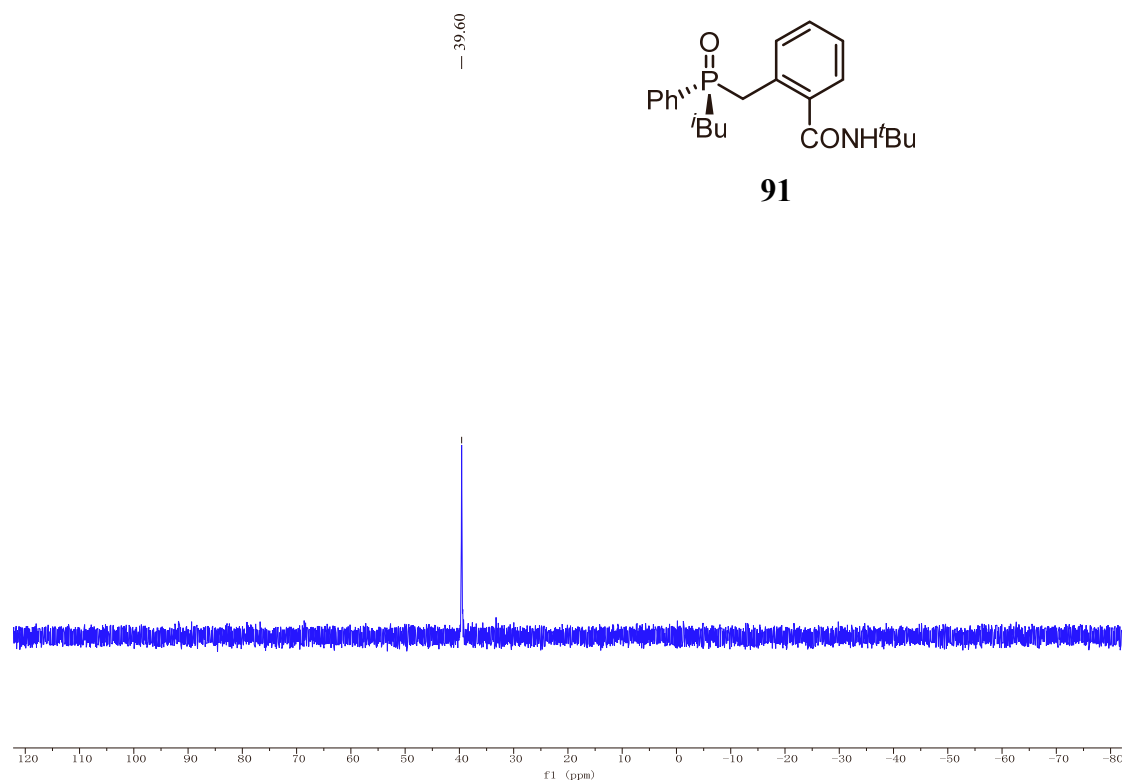
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



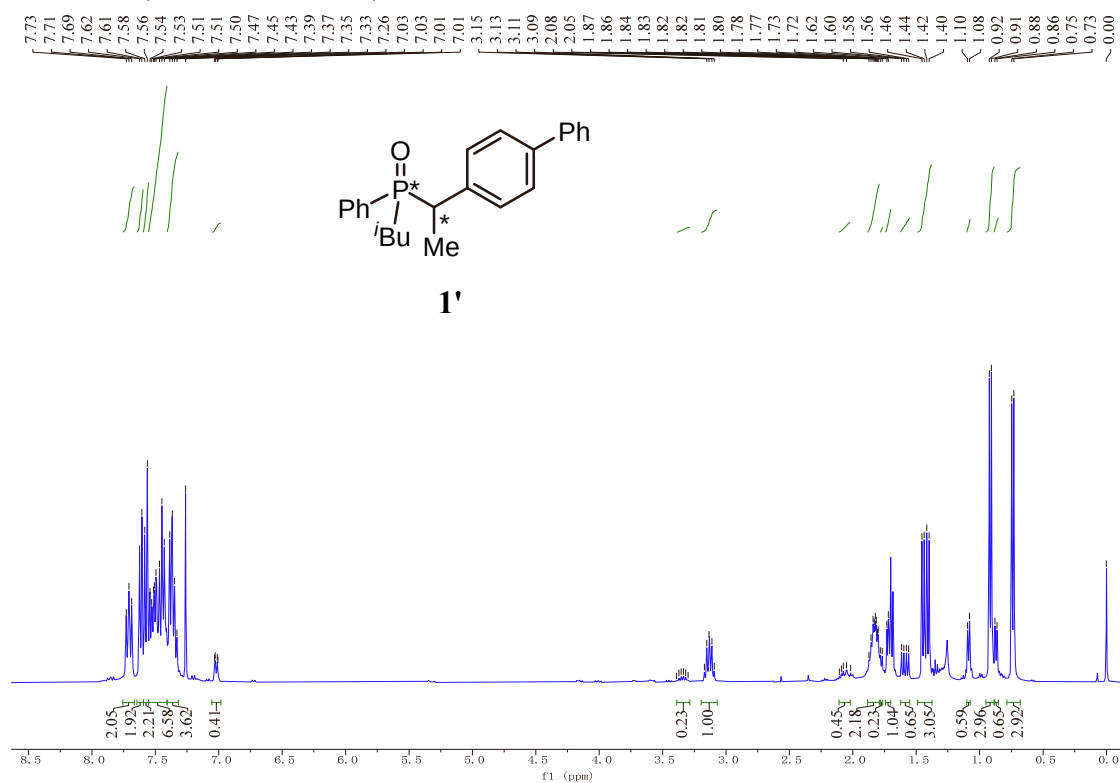
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



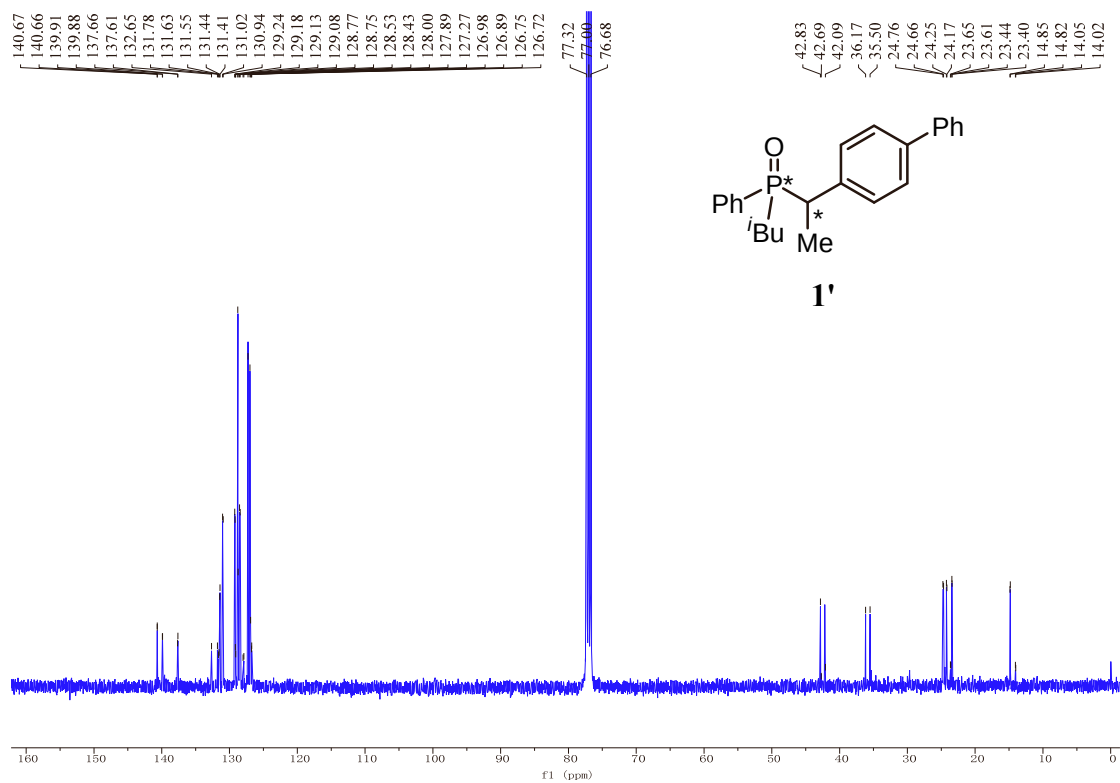
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



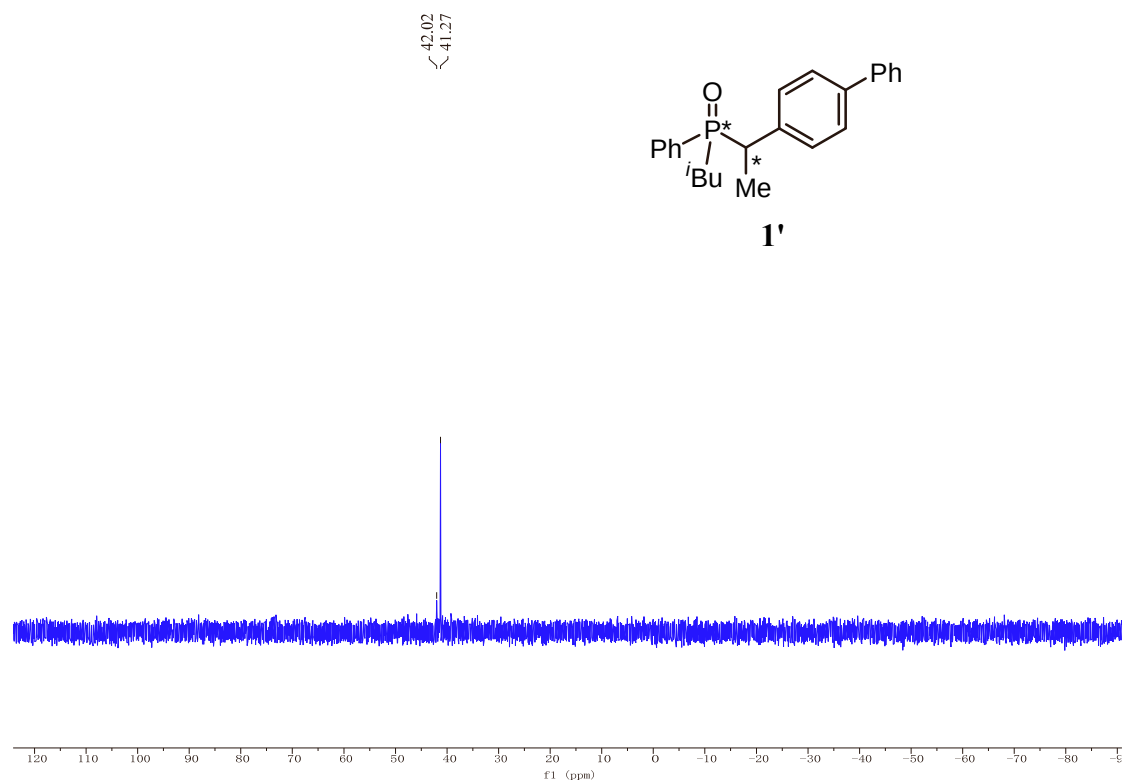
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



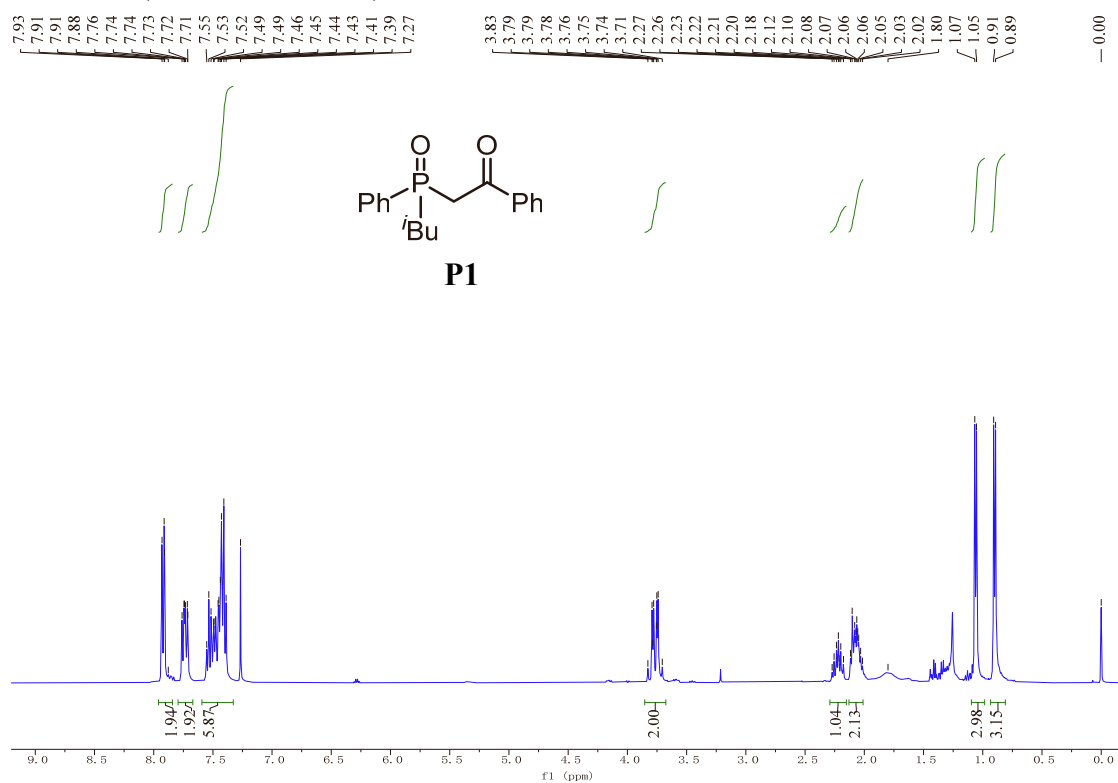
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



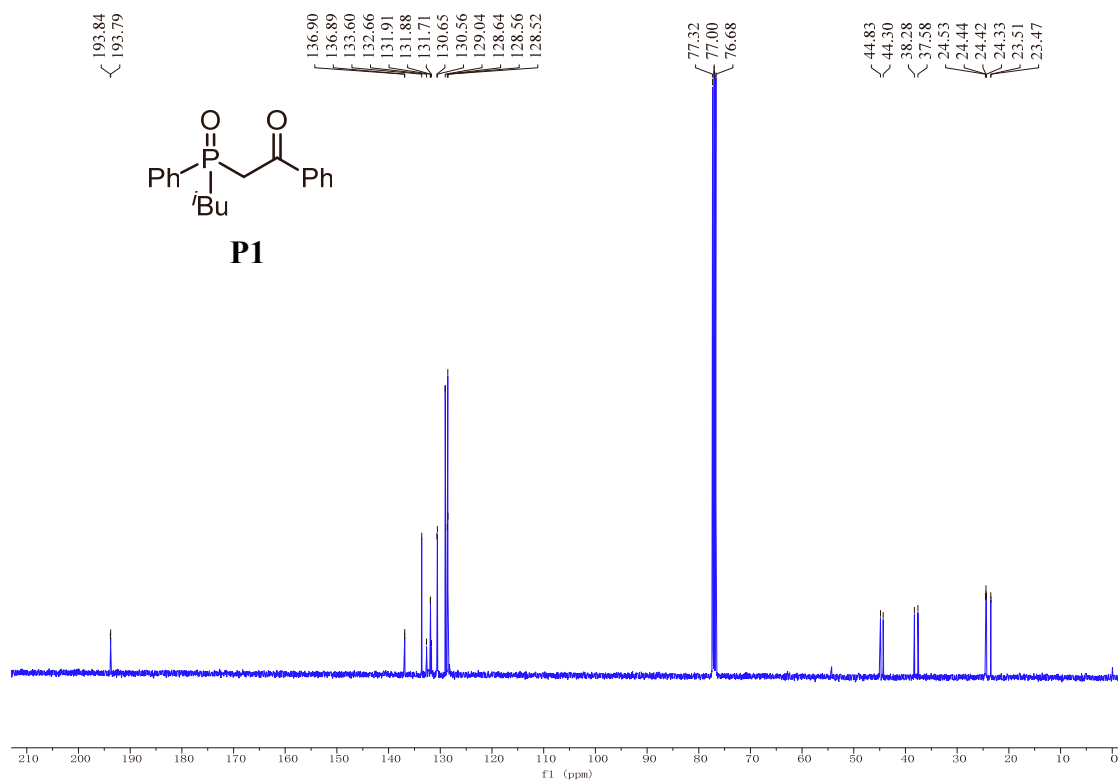
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



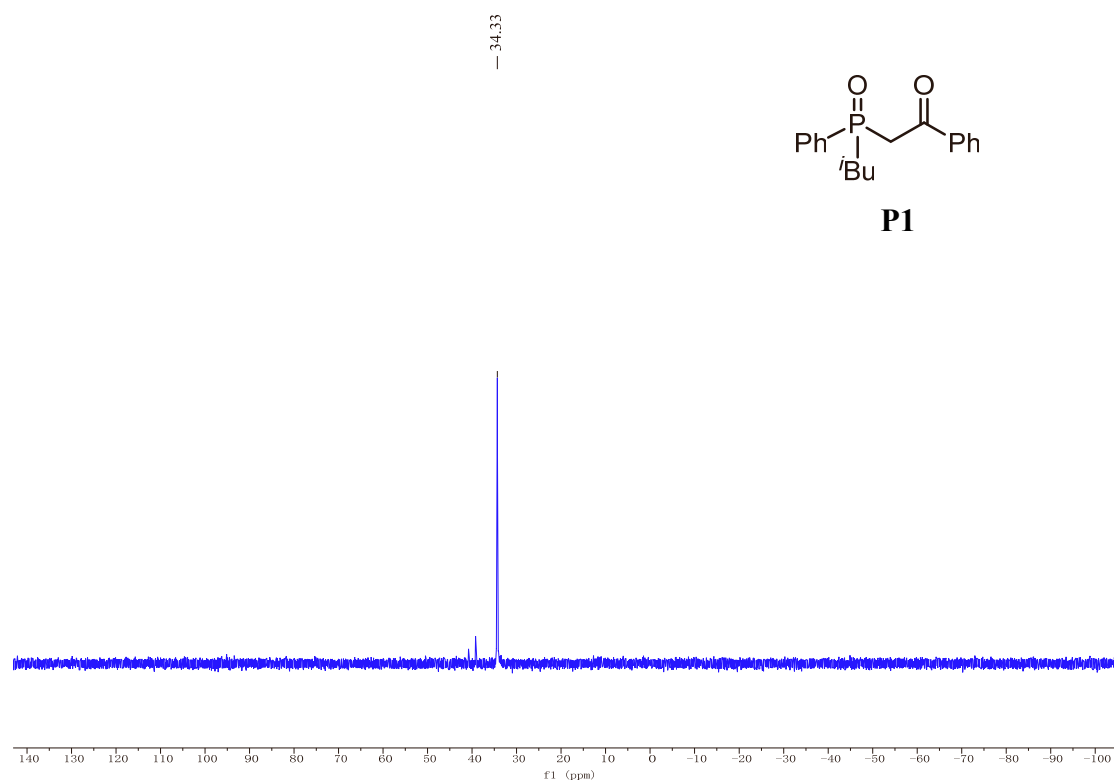
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



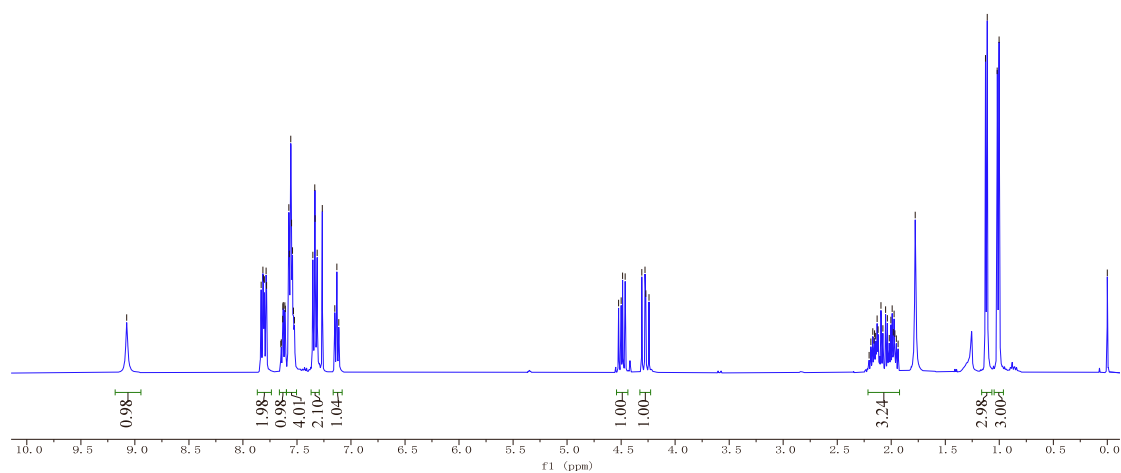
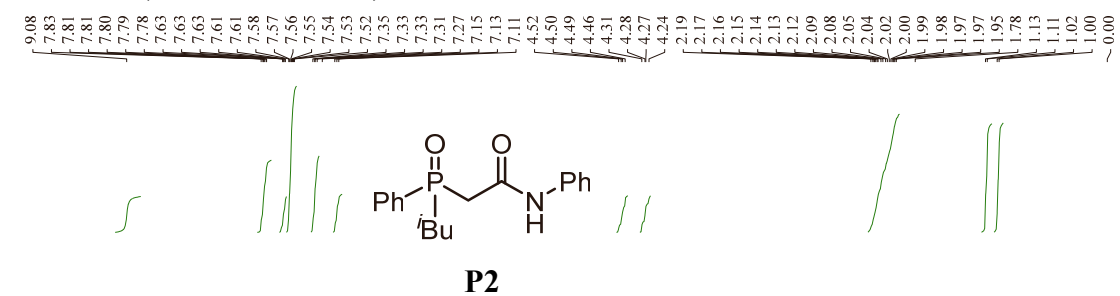
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

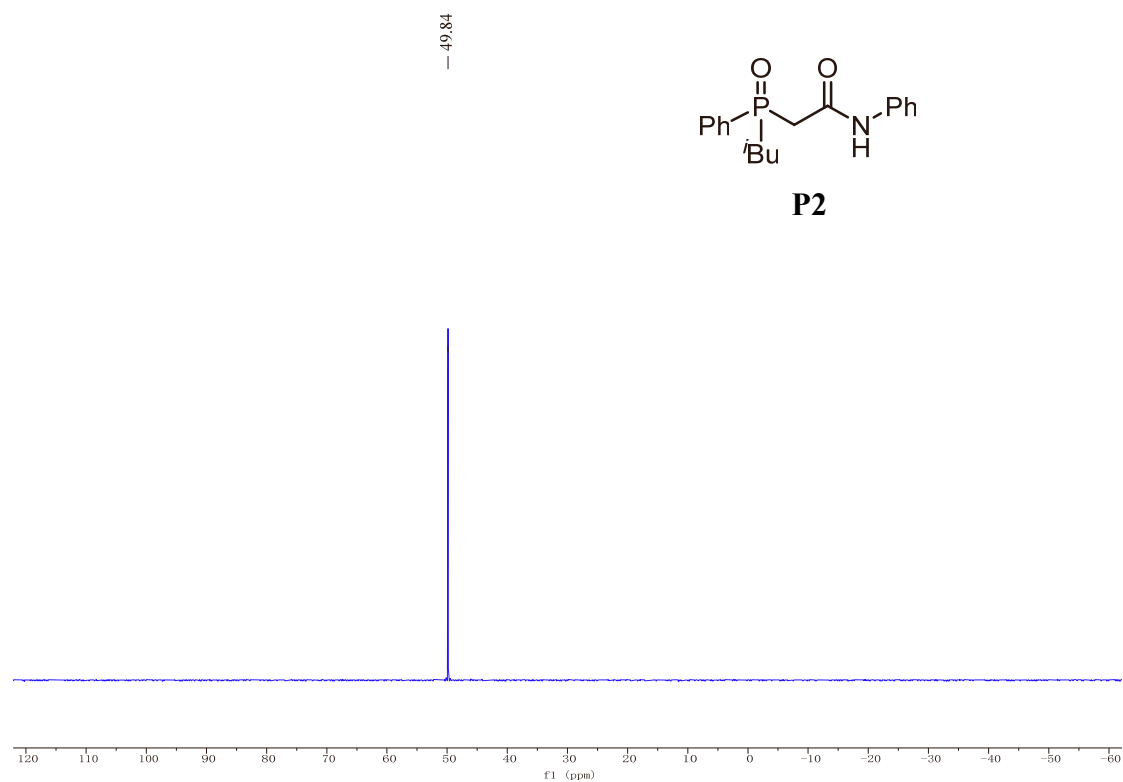


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

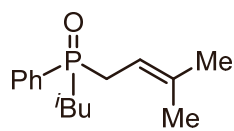
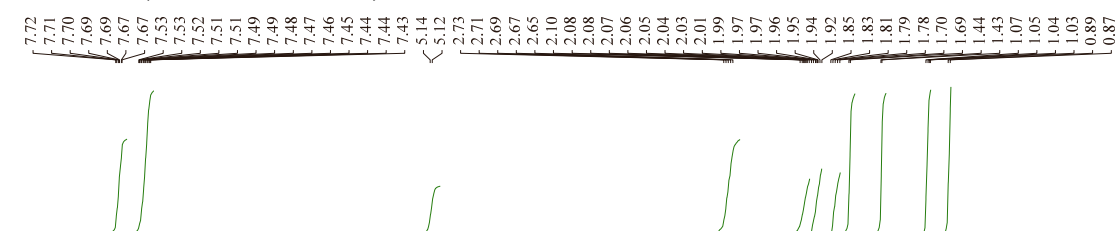




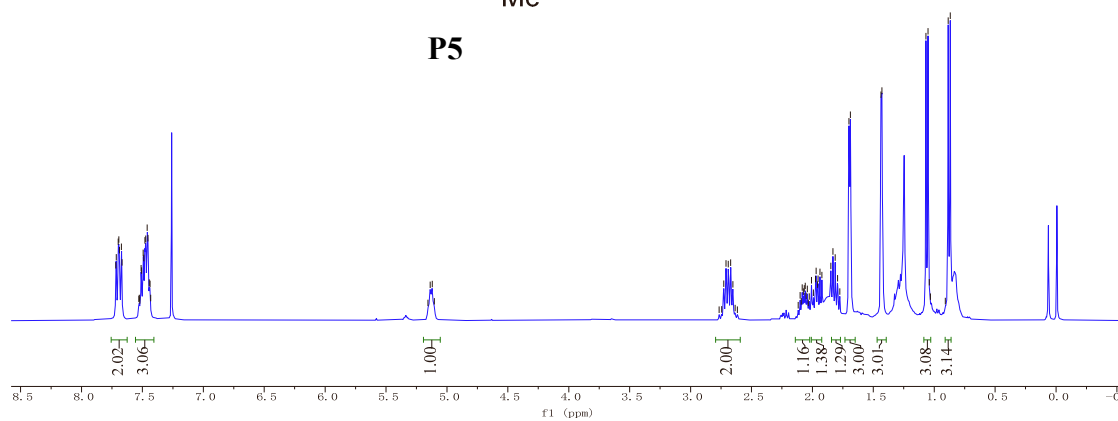
**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )



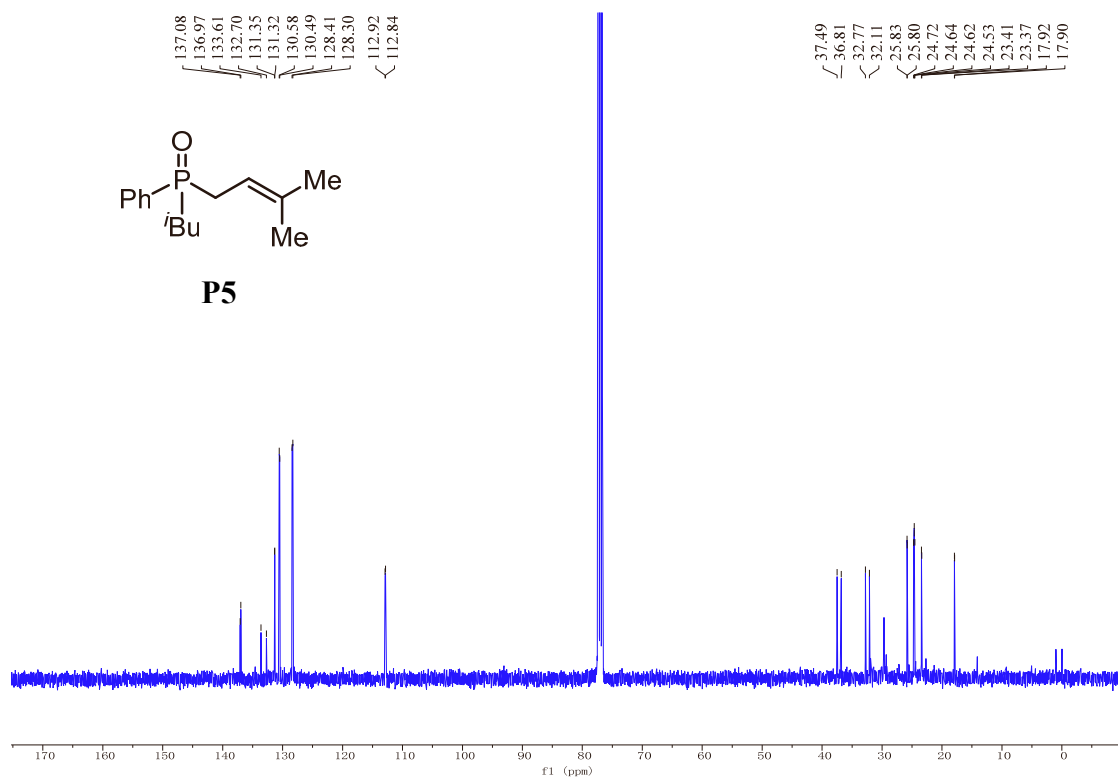
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**P5**

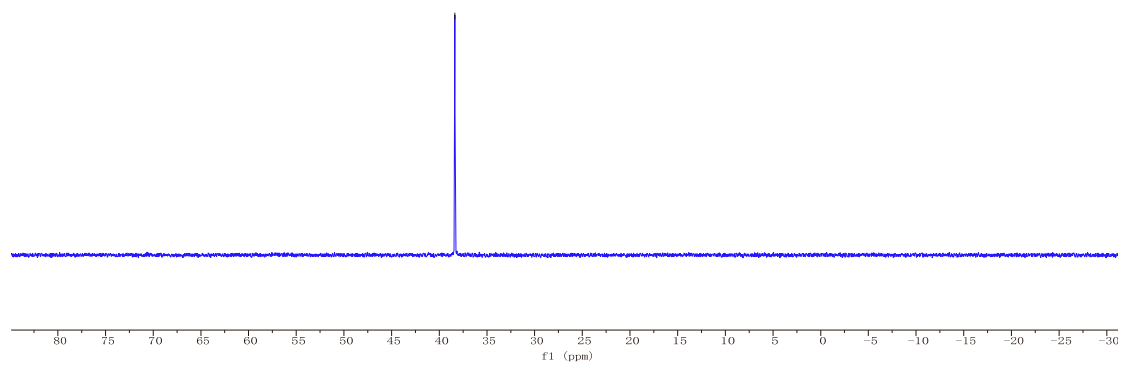
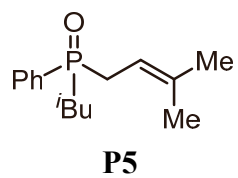


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

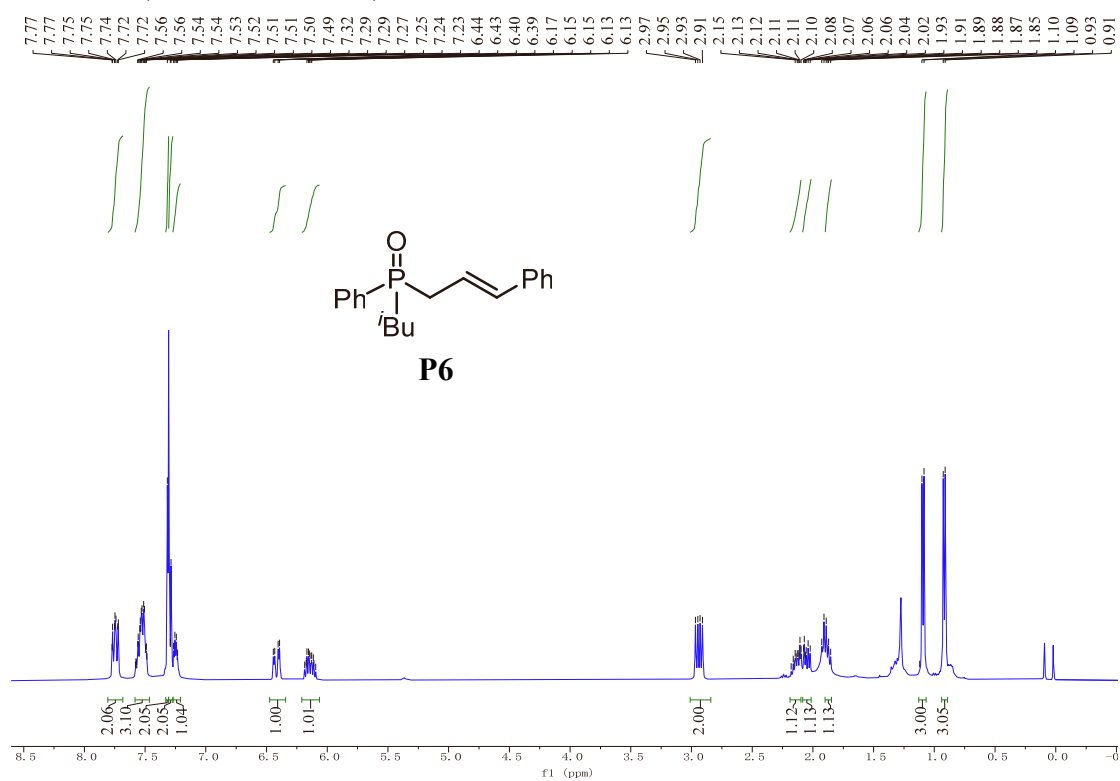


**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**

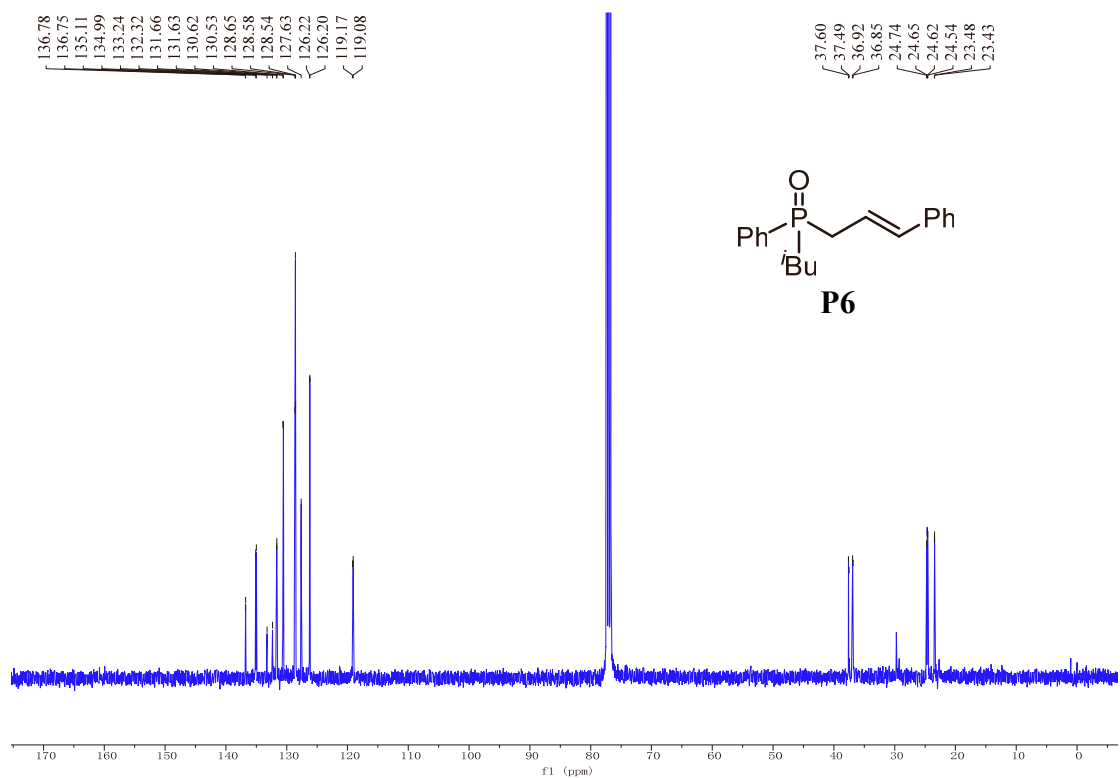
— 38.37



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

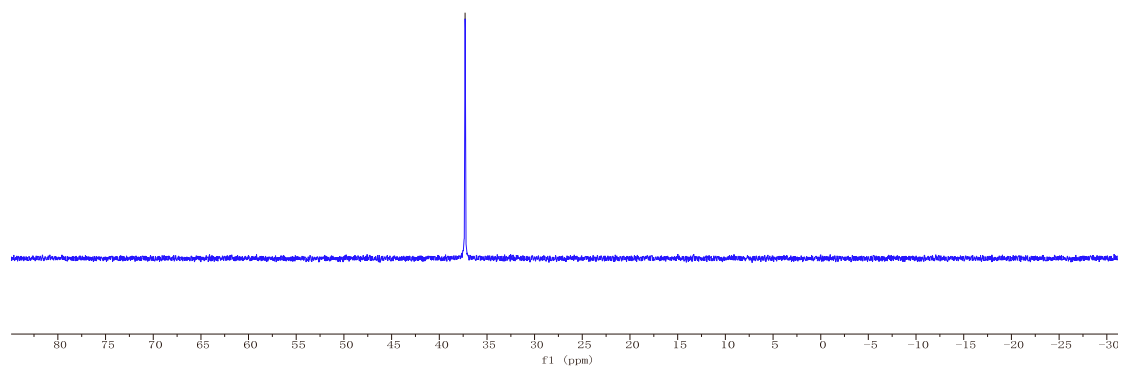
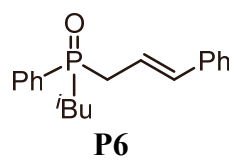


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

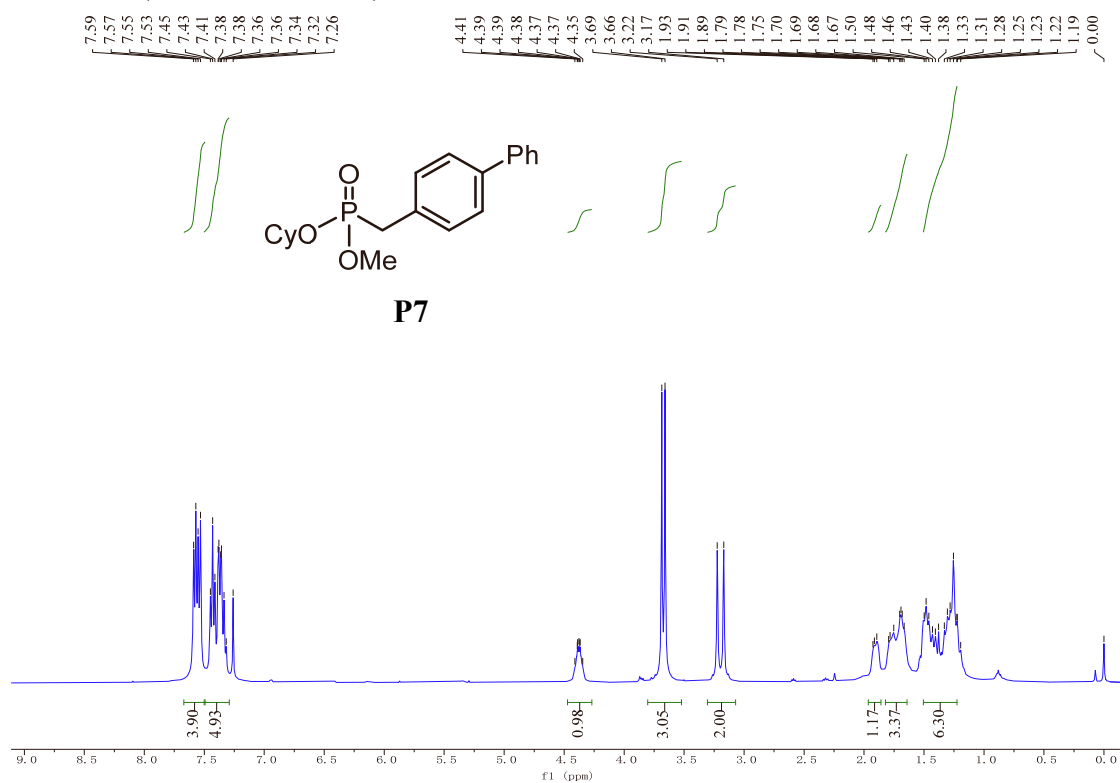


**$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )**

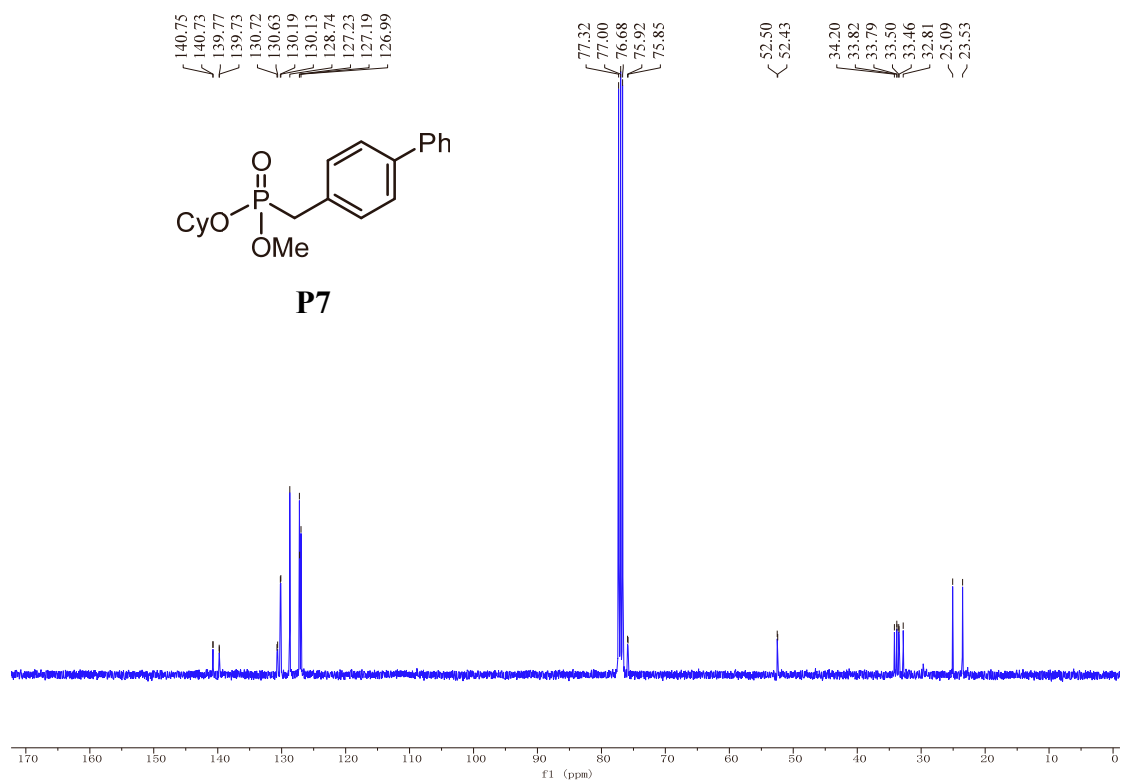
— 37.29



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

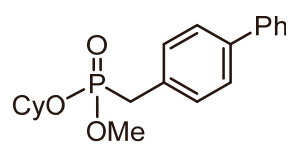


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

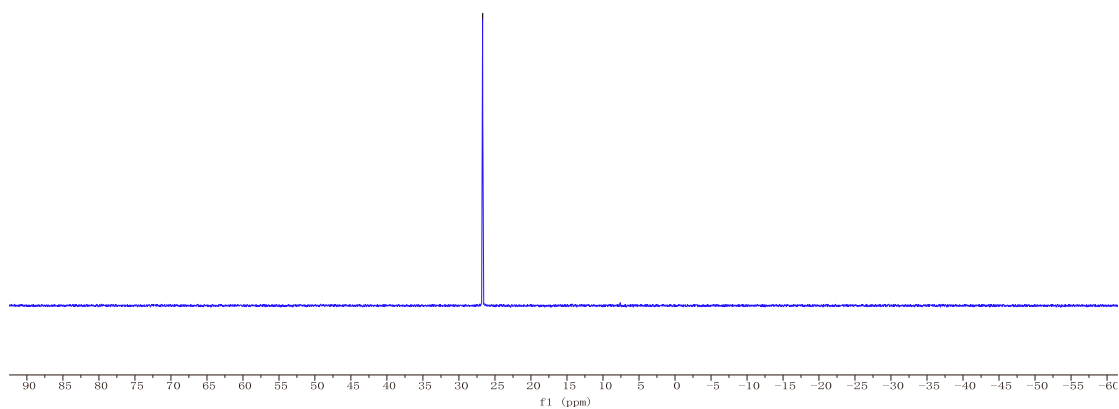


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

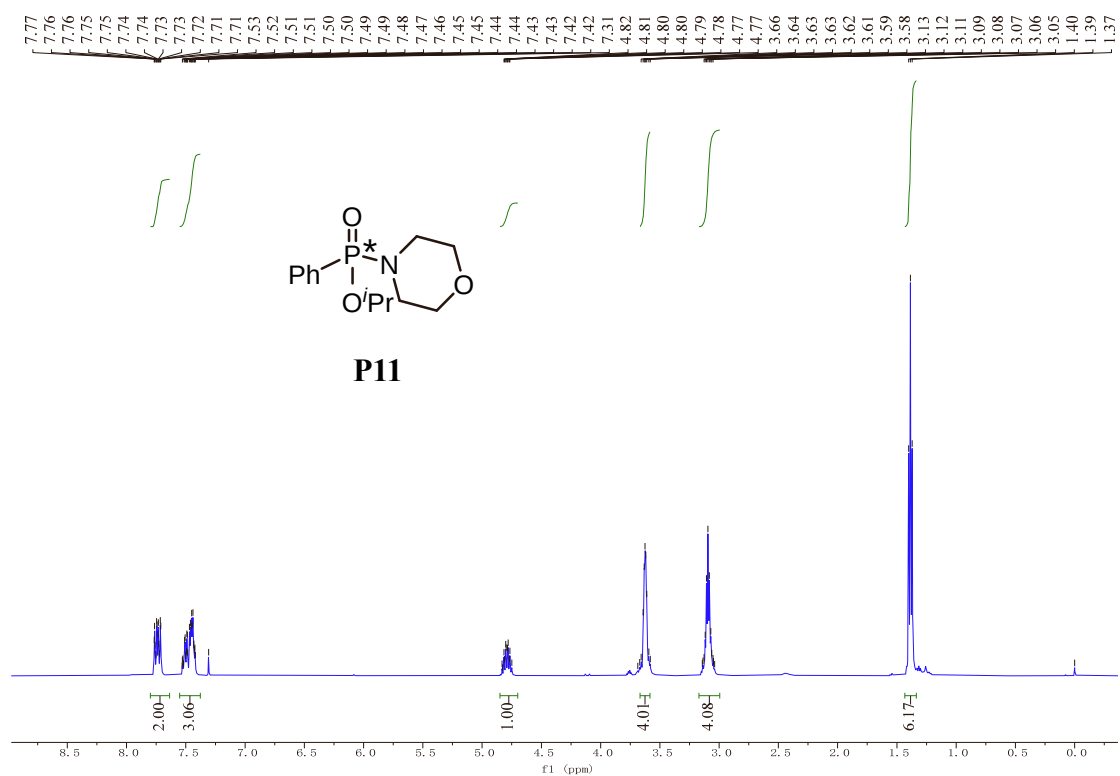
— 26.71



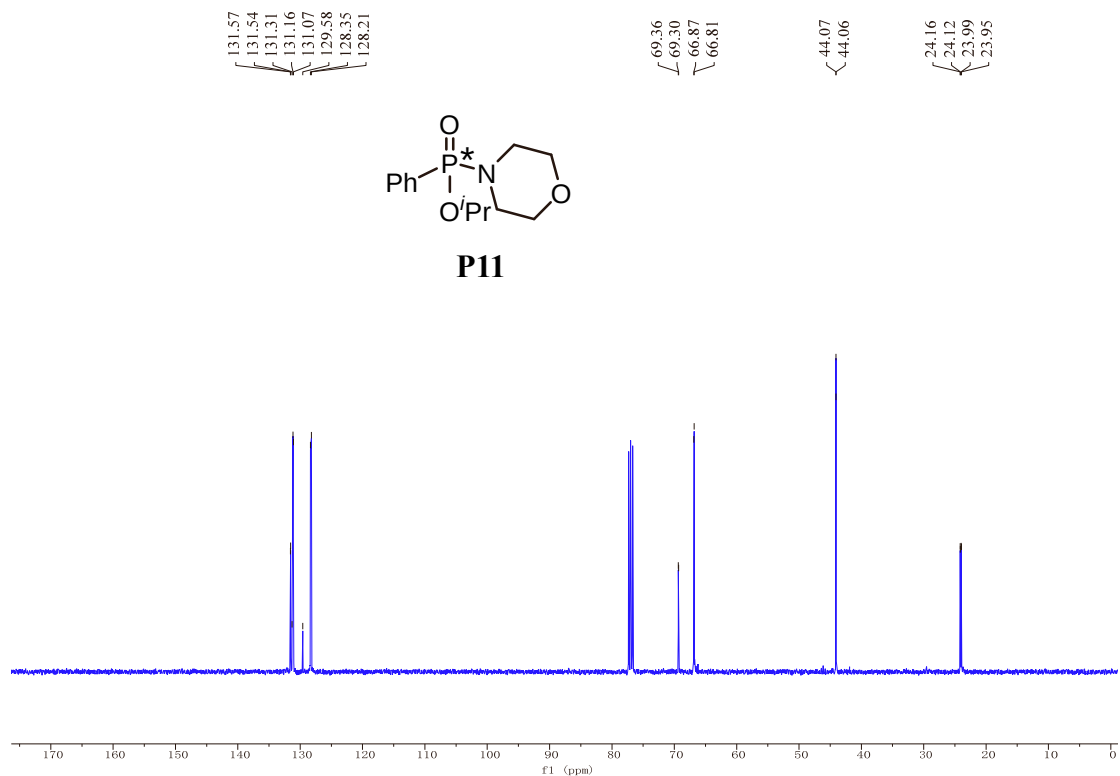
**P7**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



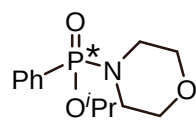
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



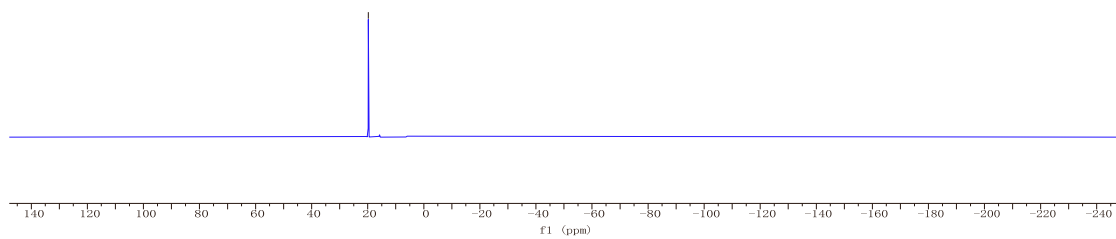


**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )

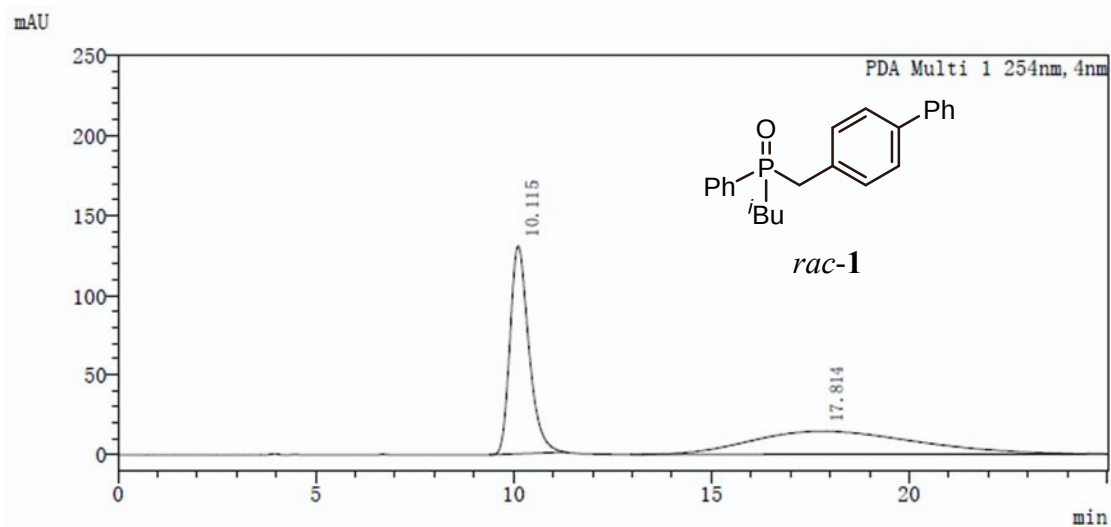
19.80  
—



**P11**



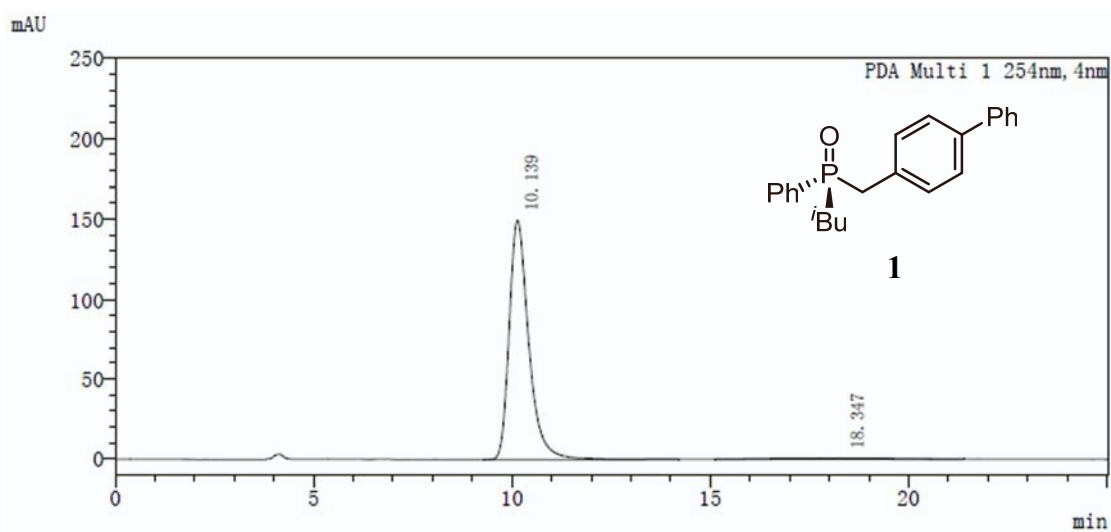
## Data S4. HPLC spectra



Peak Table

PDA Ch1 254nm

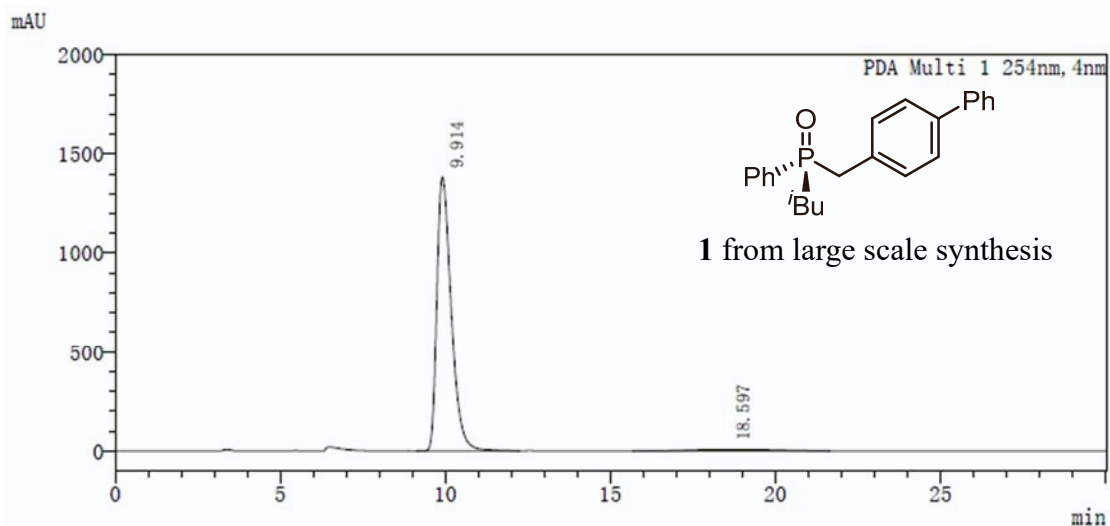
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 10.115    | 4318374 | 50.620 |
| 2     | 17.814    | 4212603 | 49.380 |



Peak Table

PDA Ch1 254nm

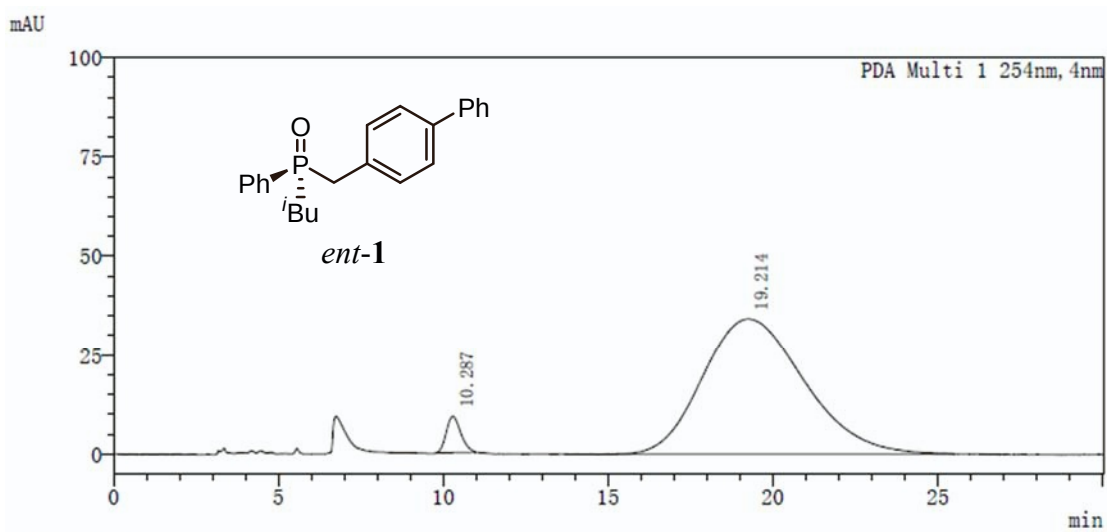
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 10.139    | 5127146 | 97.995 |
| 2     | 18.347    | 104916  | 2.005  |



Peak Table

PDA Ch1 254nm

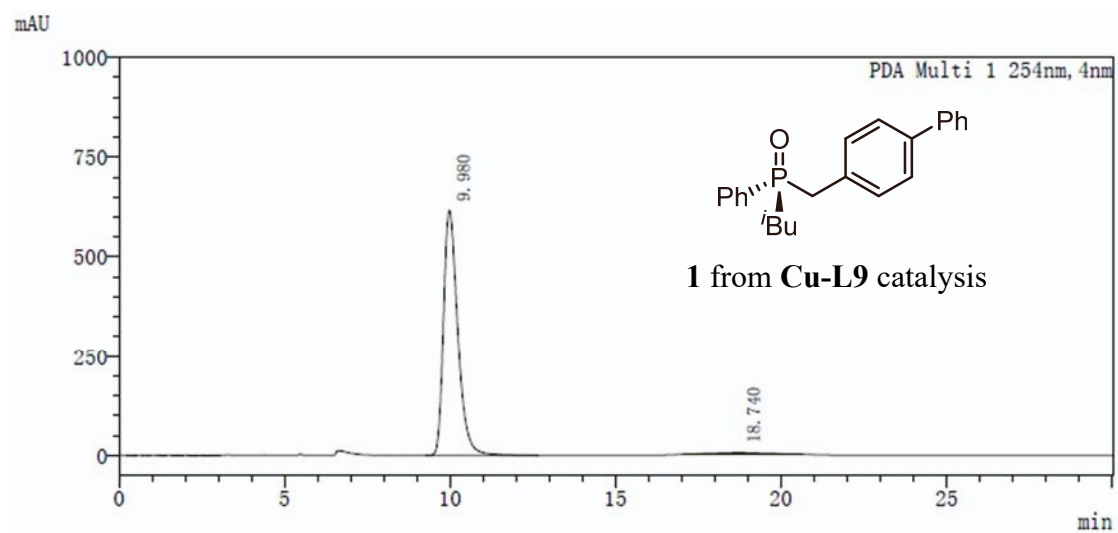
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 9.914     | 41825432 | 97.523 |
| 2     | 18.597    | 1062164  | 2.477  |



Peak Table

PDA Ch1 254nm

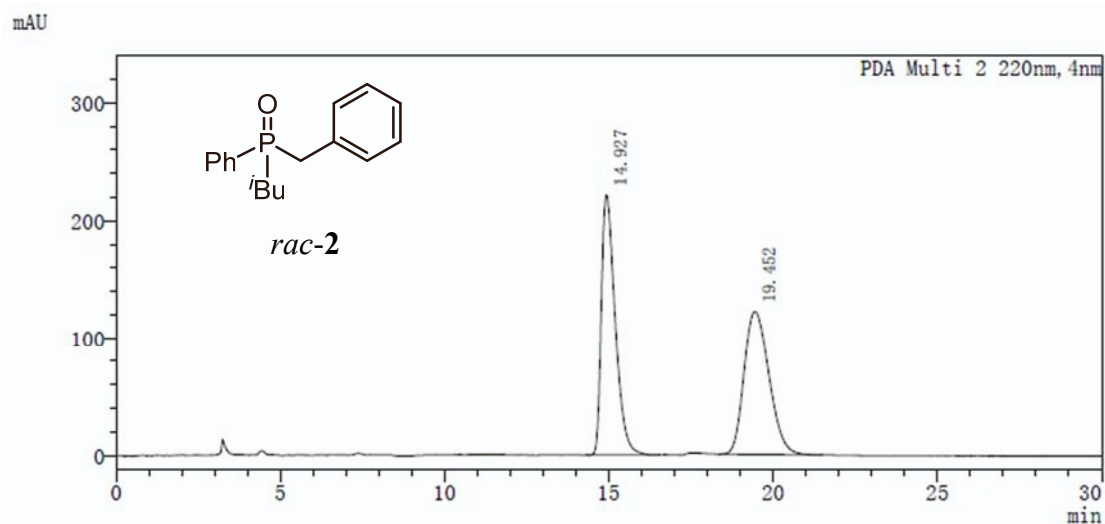
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 10.287    | 276965  | 3.660  |
| 2     | 19.214    | 7289365 | 96.340 |



Peak Table

PDA Ch1 254nm

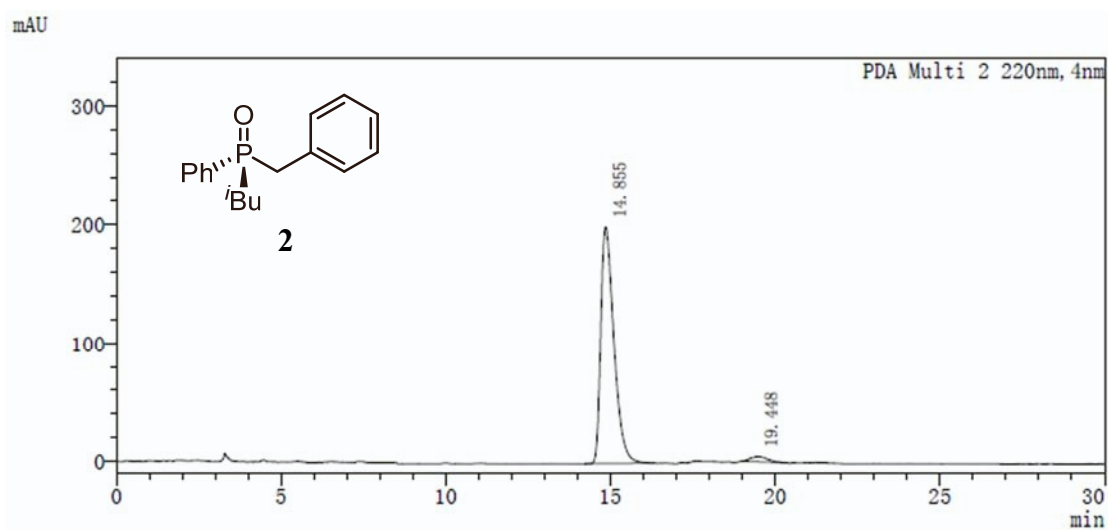
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 9.980     | 18458050 | 97.331 |
| 2     | 18.740    | 506203   | 2.669  |



Peak Table

PDA Ch2 220nm

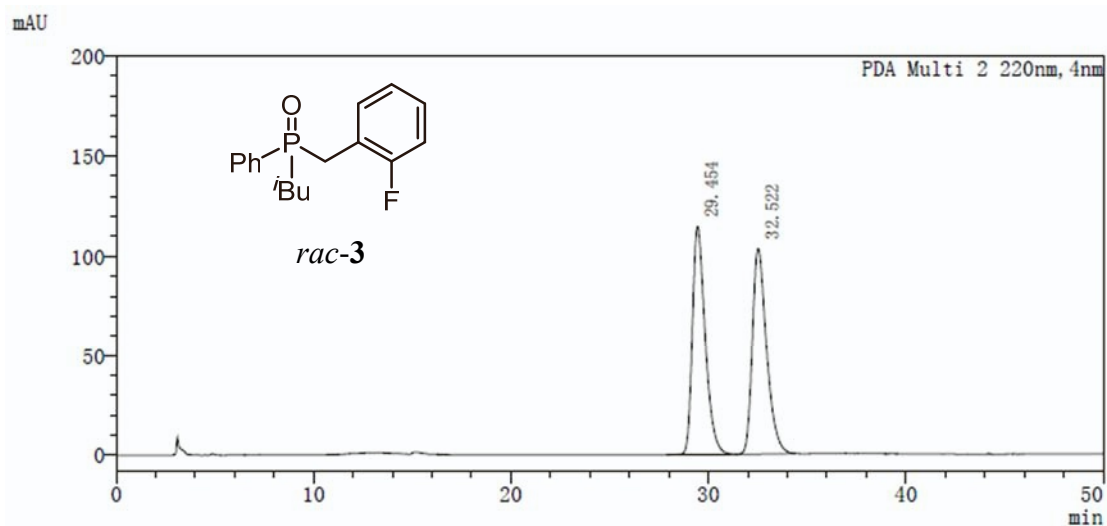
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 14.927    | 6478132 | 50.140 |
| 2     | 19.452    | 6441854 | 49.860 |



Peak Table

PDA Ch2 220nm

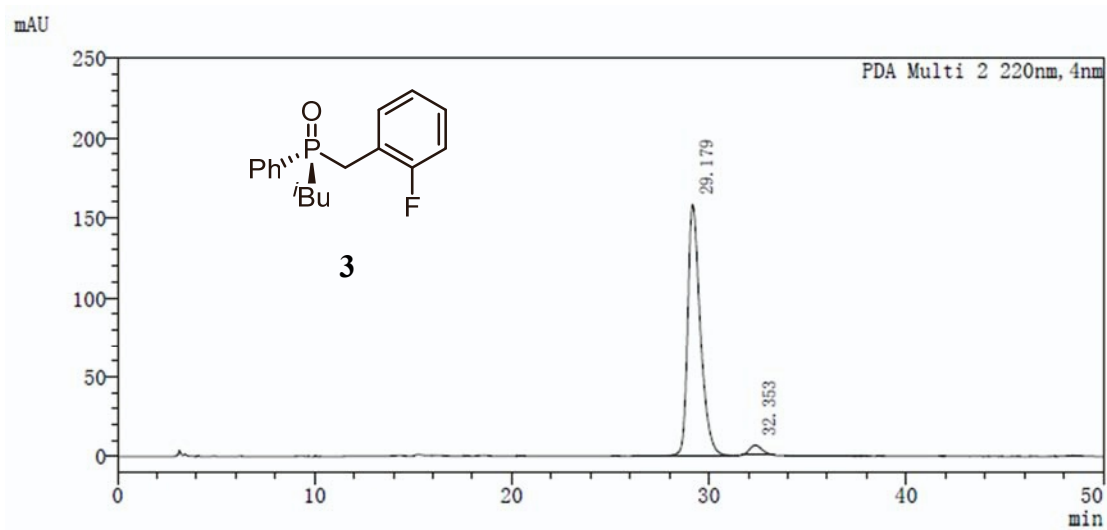
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 14.855    | 5544847 | 97.353 |
| 2     | 19.448    | 150768  | 2.647  |



Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 29.454    | 5168075 | 49.997 |
| 2     | 32.522    | 5168642 | 50.003 |

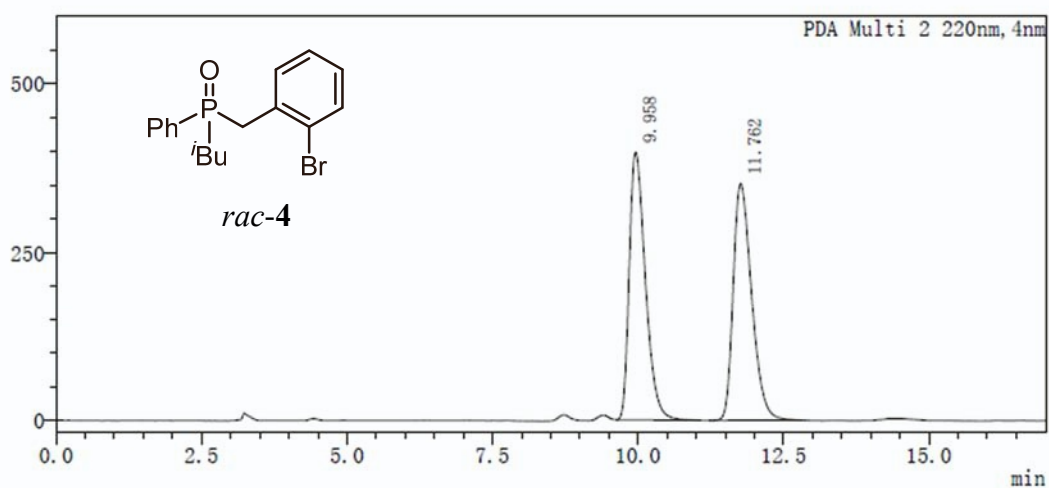


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 29.179    | 7082535 | 96.252 |
| 2     | 32.353    | 275756  | 3.748  |

mAU

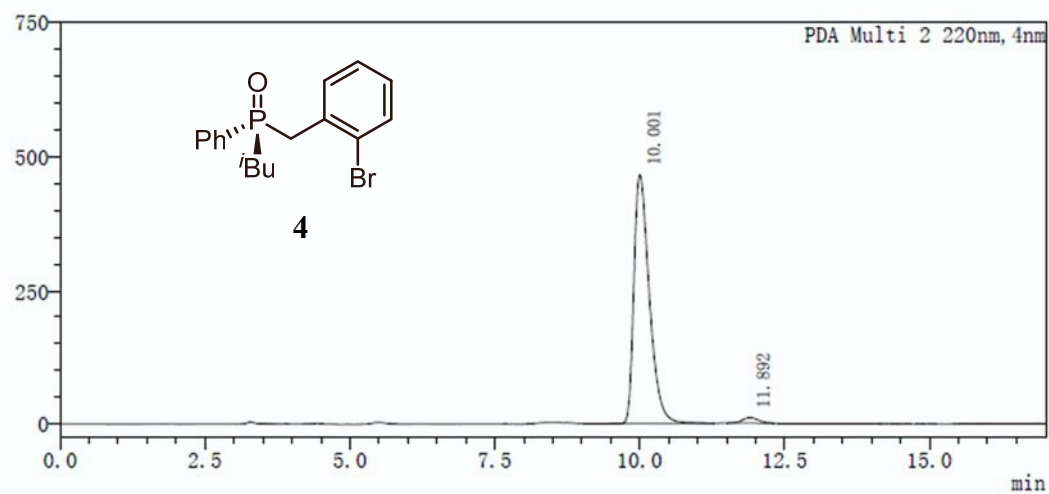


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 9.958     | 7687476 | 49.712 |
| 2     | 11.762    | 7776535 | 50.288 |

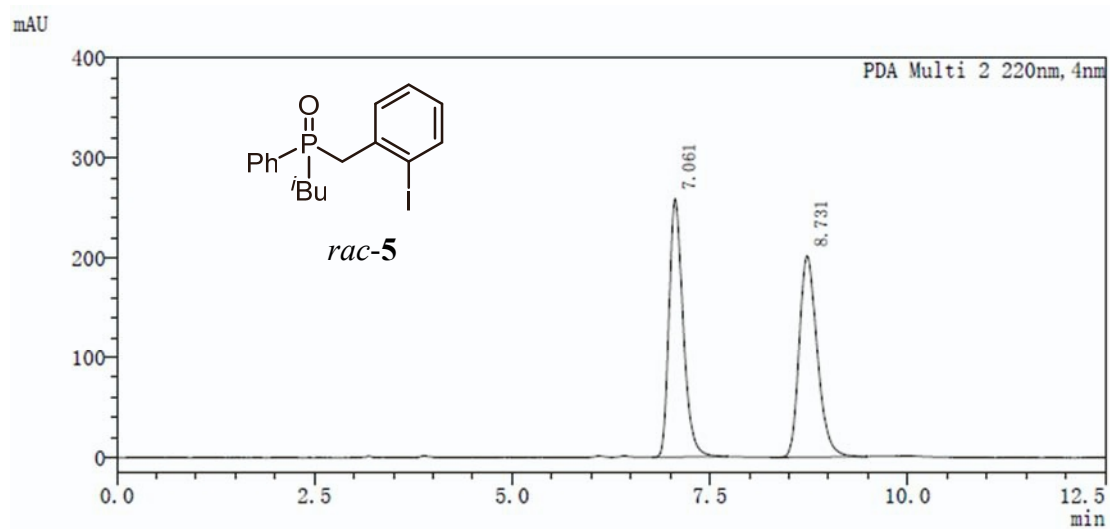
mAU



Peak Table

PDA Ch2 220nm

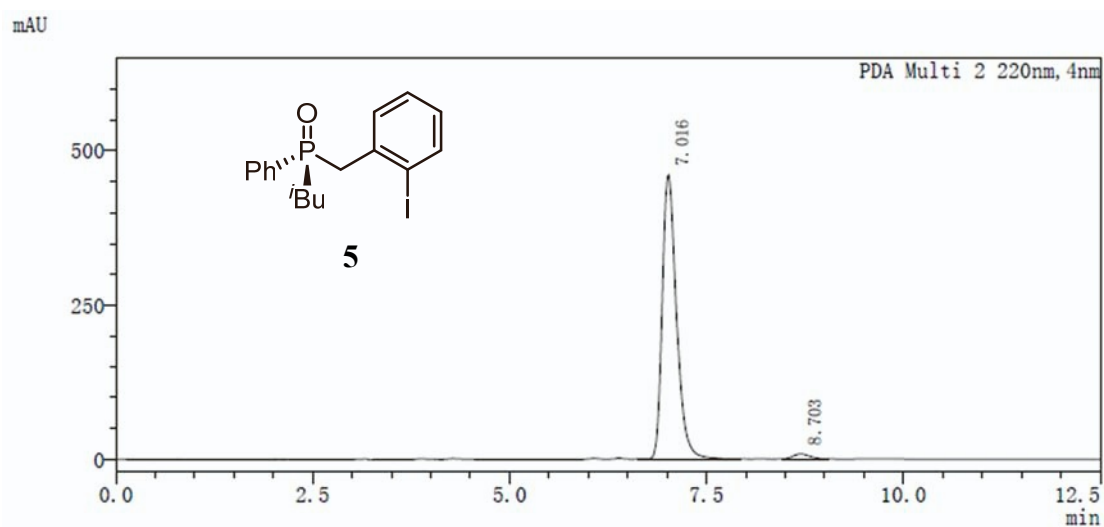
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 10.001    | 8589809 | 97.798 |
| 2     | 11.892    | 193437  | 2.202  |



Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 7.061     | 3209160 | 49.950 |
| 2     | 8.731     | 3215634 | 50.050 |

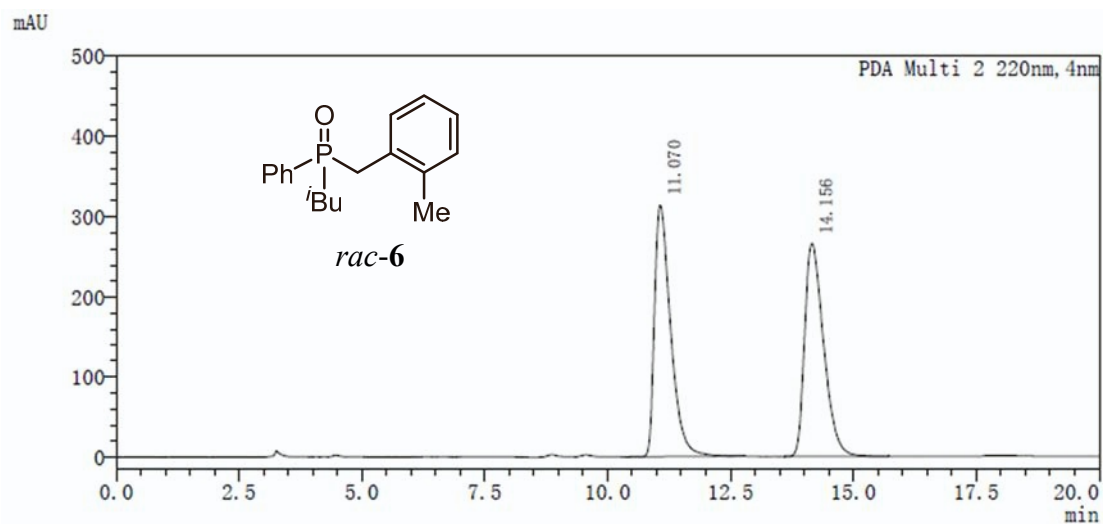


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 7.016     | 5788948 | 98.012 |
| 2     | 8.703     | 117390  | 1.988  |

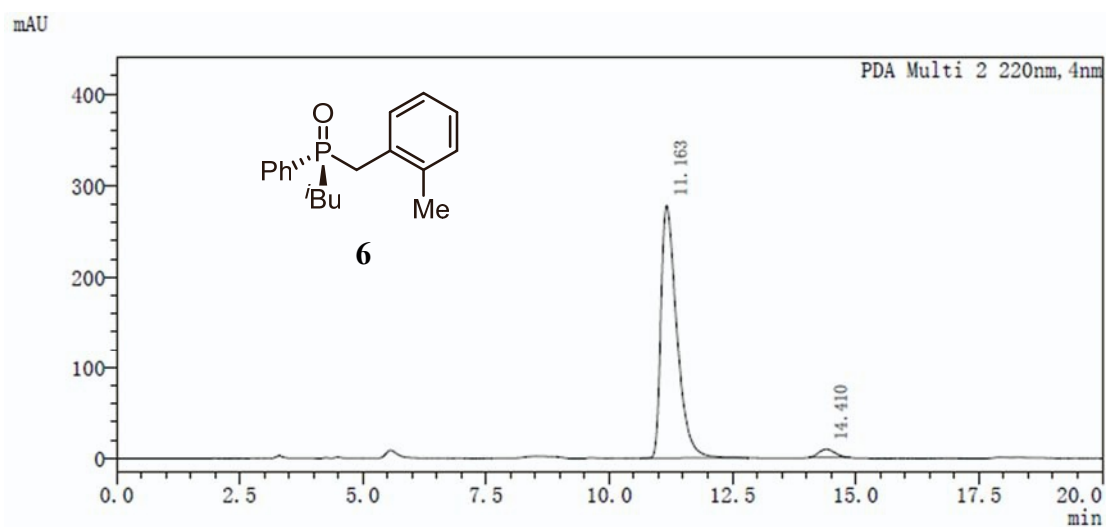




Peak Table

PDA Ch2 220nm

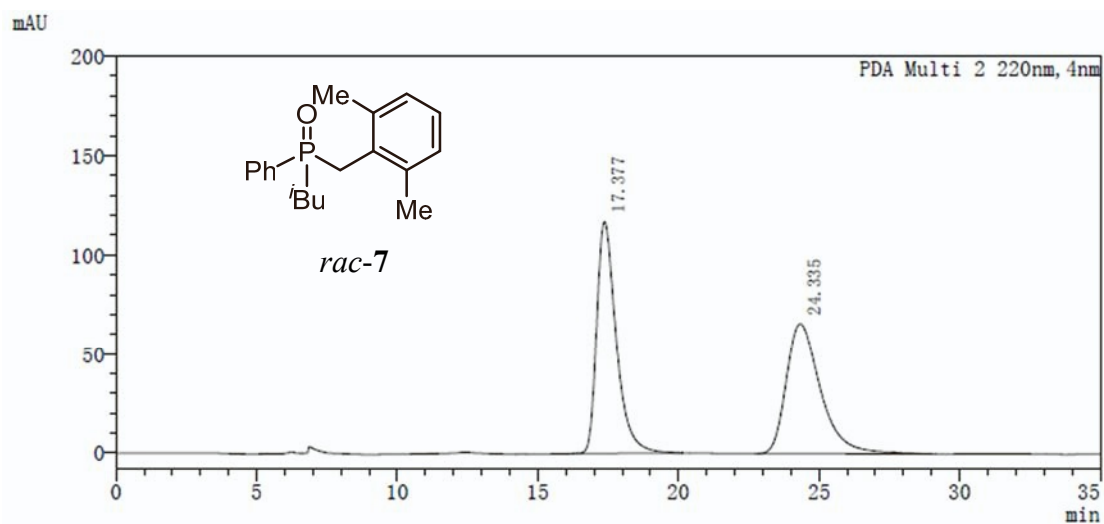
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 11.070    | 7181413 | 50.062 |
| 2     | 14.156    | 7163555 | 49.938 |



Peak Table

PDA Ch2 220nm

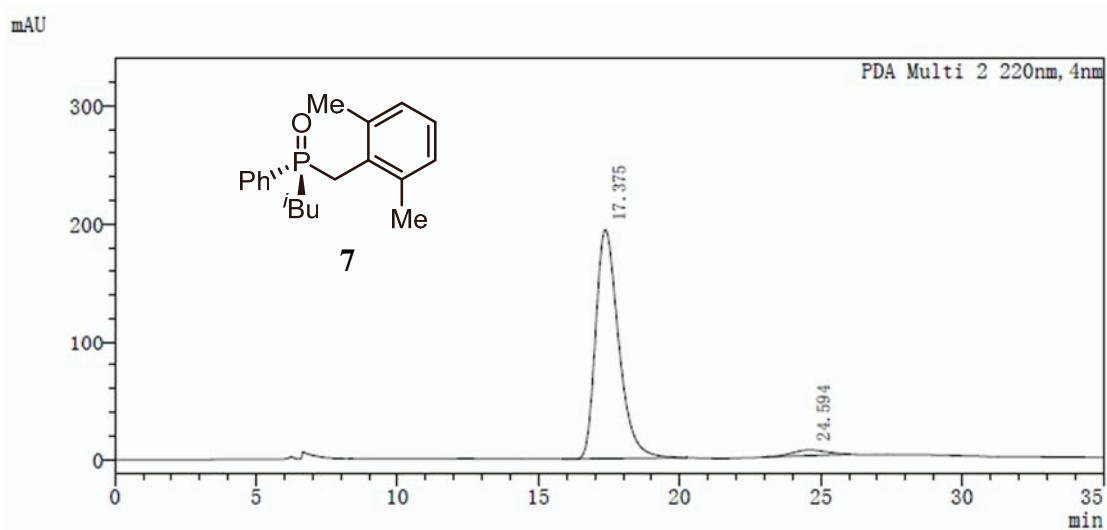
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 11.163    | 6246275 | 96.788 |
| 2     | 14.410    | 207256  | 3.212  |



Peak Table

PDA Ch2 220nm

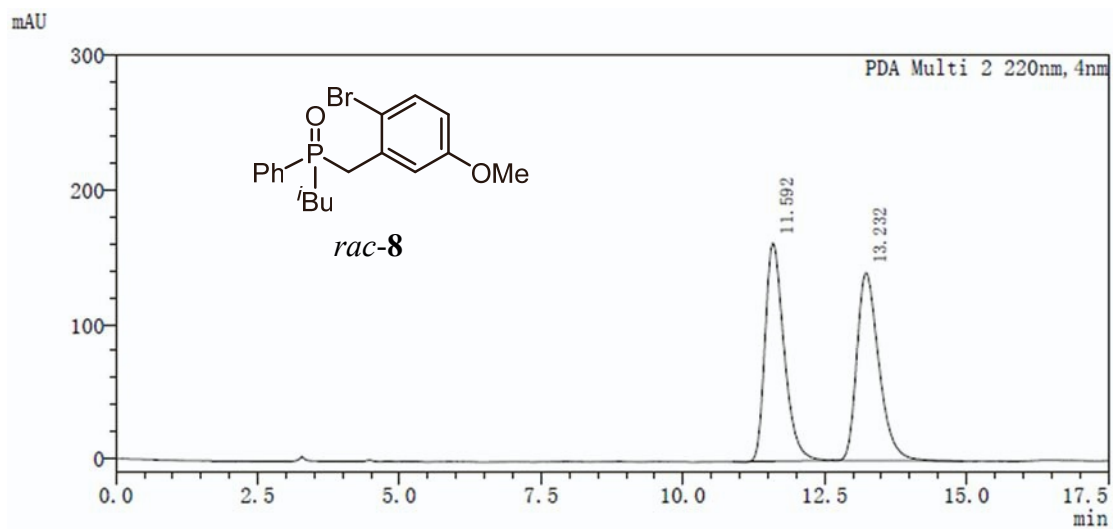
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 17.377    | 5651589 | 50.468 |
| 2     | 24.335    | 5546841 | 49.532 |



Peak Table

PDA Ch2 220nm

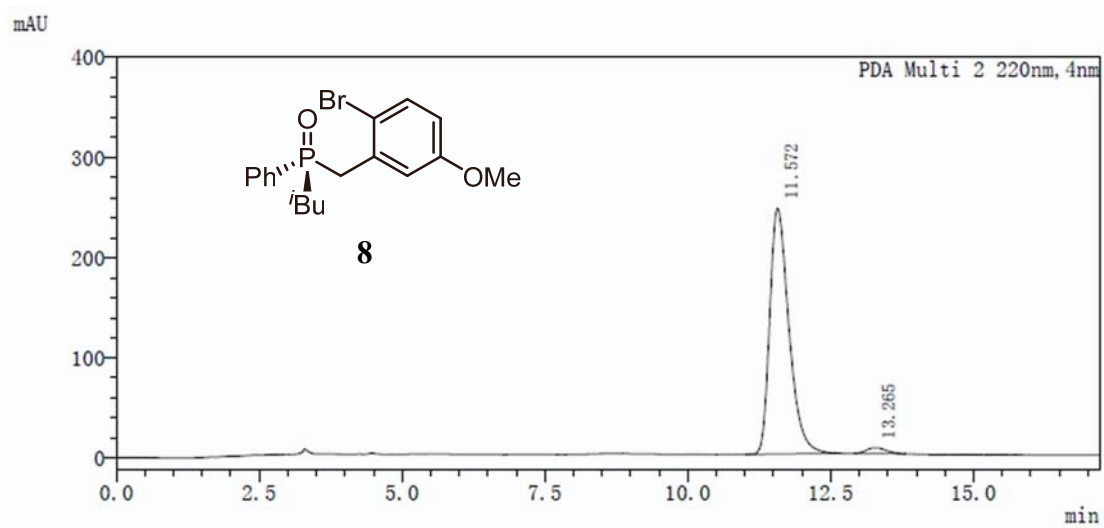
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 17.375    | 10992611 | 96.543 |
| 2     | 24.594    | 393609   | 3.457  |



Peak Table

PDA Ch2 220nm

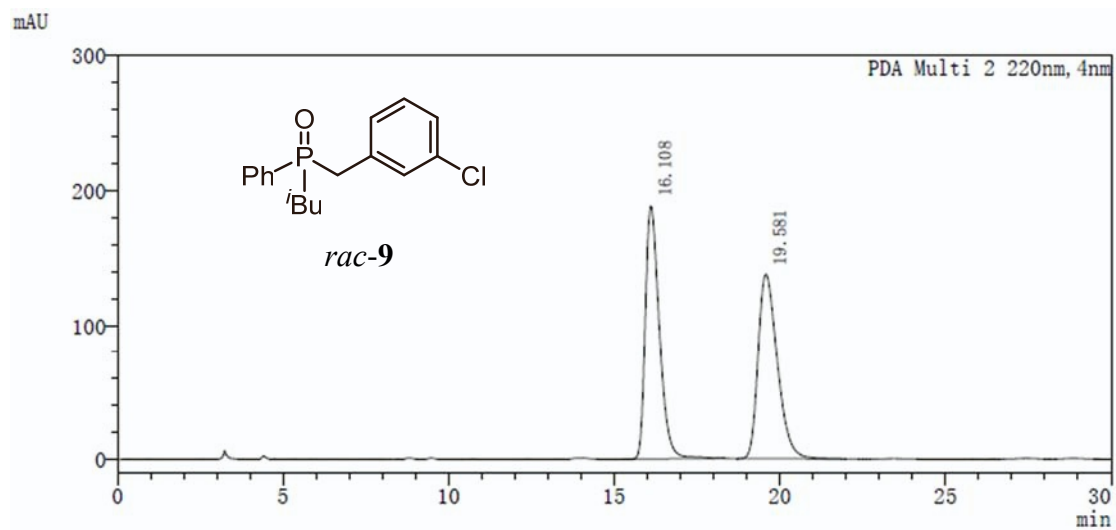
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 11.592    | 3788231 | 49.945 |
| 2     | 13.232    | 3796503 | 50.055 |



Peak Table

PDA Ch2 220nm

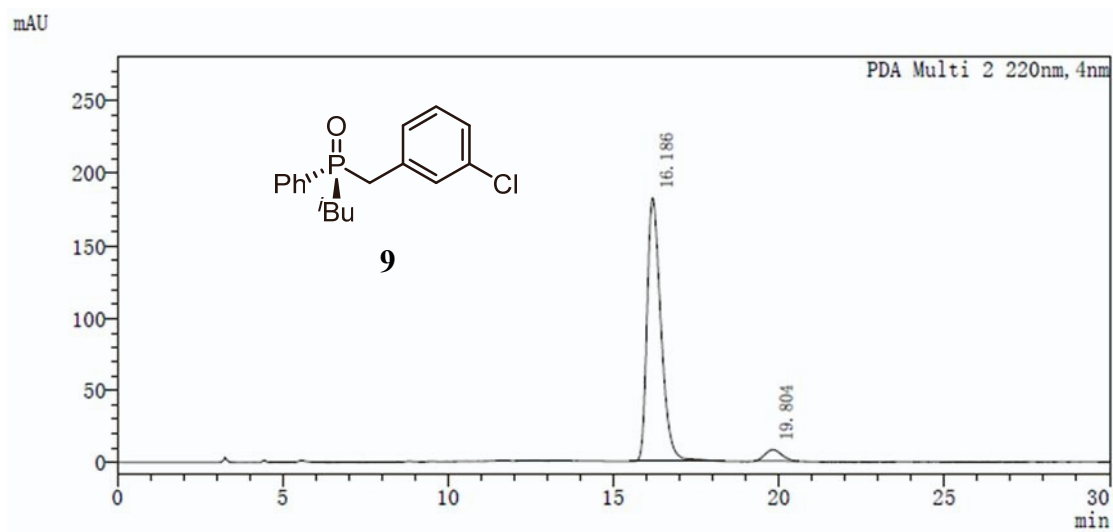
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 11.572    | 5723665 | 97.550 |
| 2     | 13.265    | 143732  | 2.450  |



Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 16.108    | 5562436 | 50.031 |
| 2     | 19.581    | 5555649 | 49.969 |

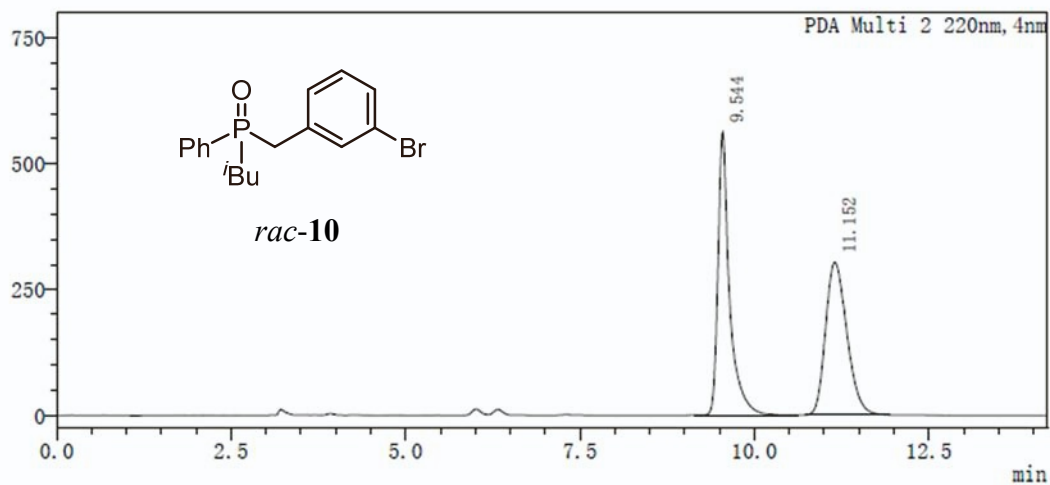


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 16.186    | 5337697 | 95.041 |
| 2     | 19.804    | 278488  | 4.959  |

mAU

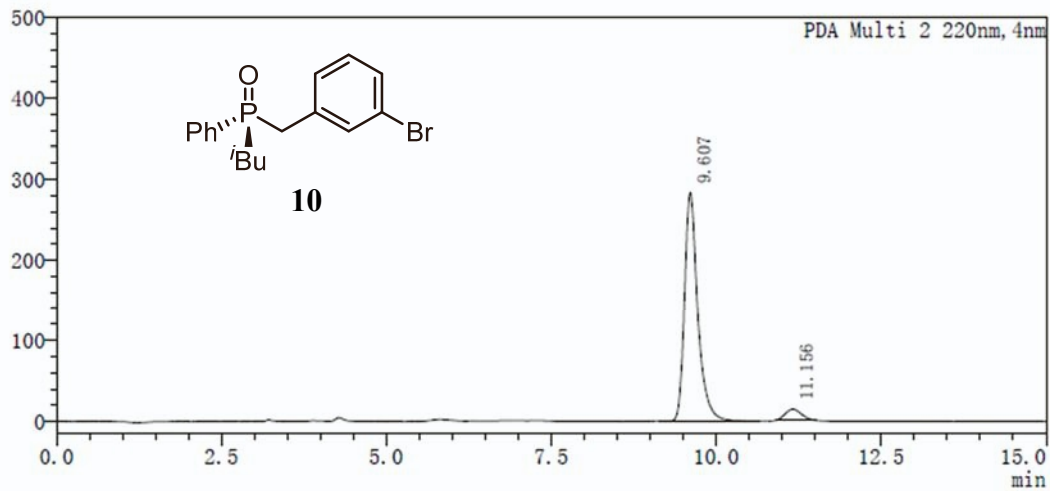


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 9.544     | 6462056 | 49.991 |
| 2     | 11.152    | 6464430 | 50.009 |

mAU

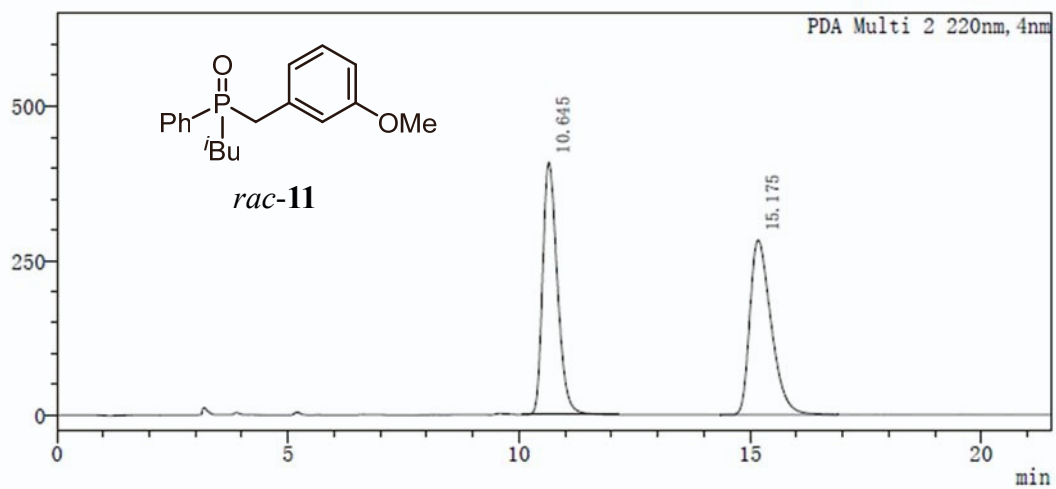


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 9.607     | 3950434 | 94.358 |
| 2     | 11.156    | 236219  | 5.642  |

mAU

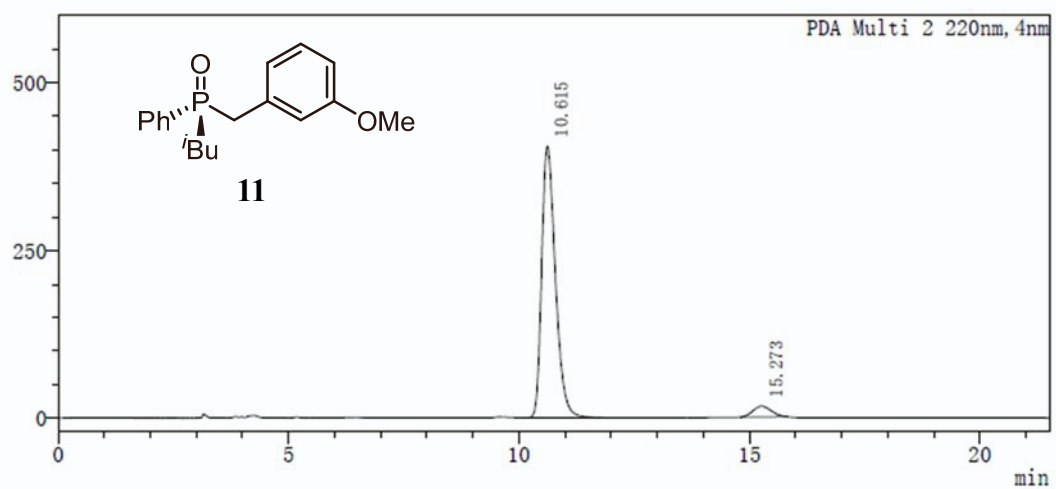


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 10.645    | 9035972 | 49.918 |
| 2     | 15.175    | 9065816 | 50.082 |

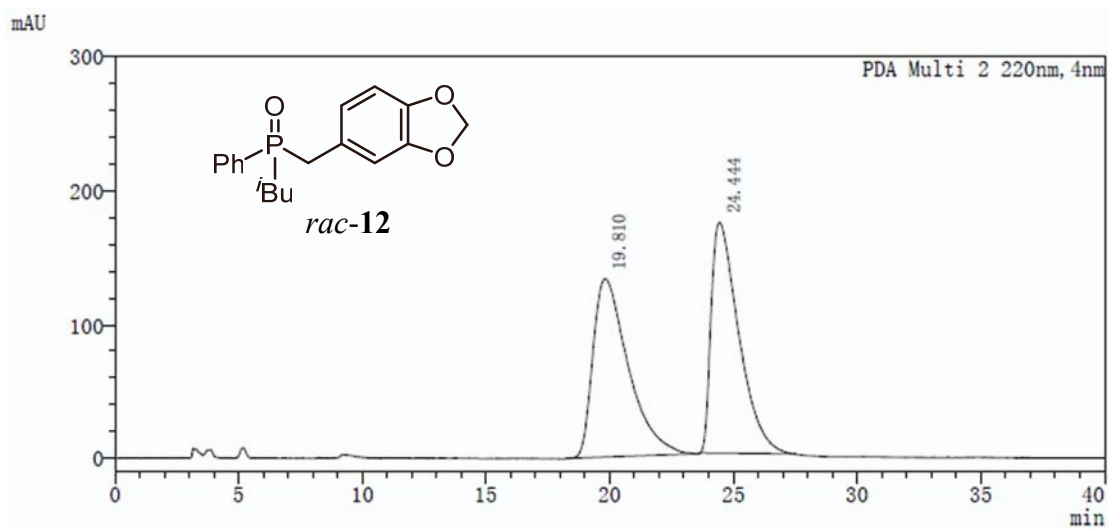
mAU



Peak Table

PDA Ch2 220nm

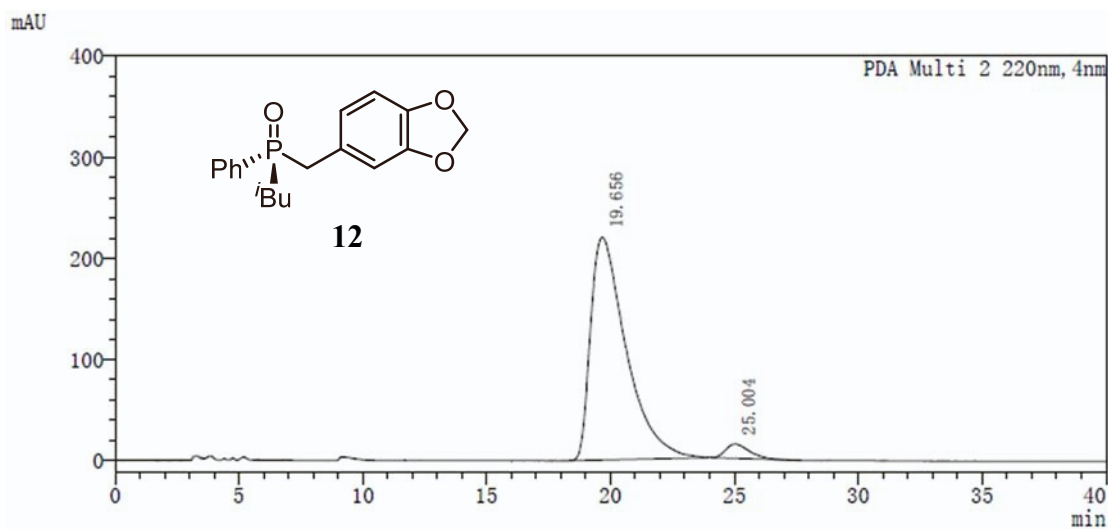
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 10.615    | 8377946 | 95.025 |
| 2     | 15.273    | 438584  | 4.975  |



Peak Table

PDA Ch2 220nm

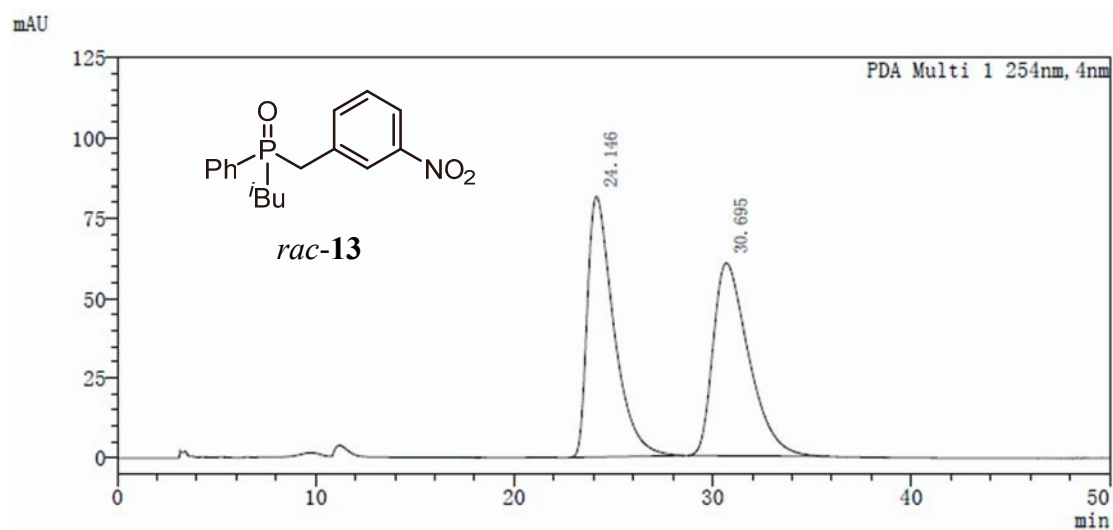
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 19.810    | 13264618 | 49.765 |
| 2     | 24.444    | 13390089 | 50.235 |



Peak Table

PDA Ch2 220nm

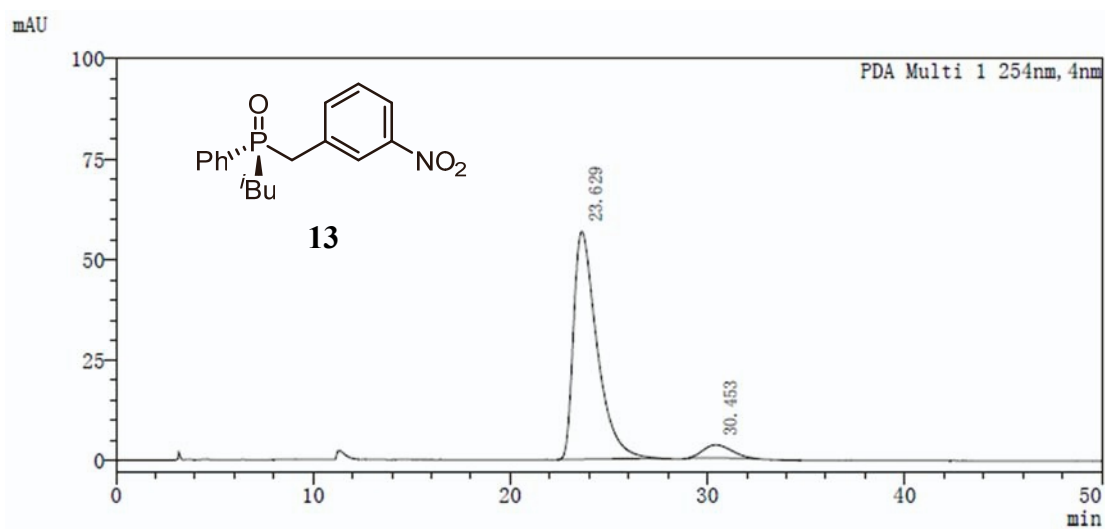
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 19.656    | 22046162 | 95.852 |
| 2     | 25.004    | 954130   | 4.148  |



Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 24.146    | 7552505 | 50.079 |
| 2     | 30.695    | 7528550 | 49.921 |

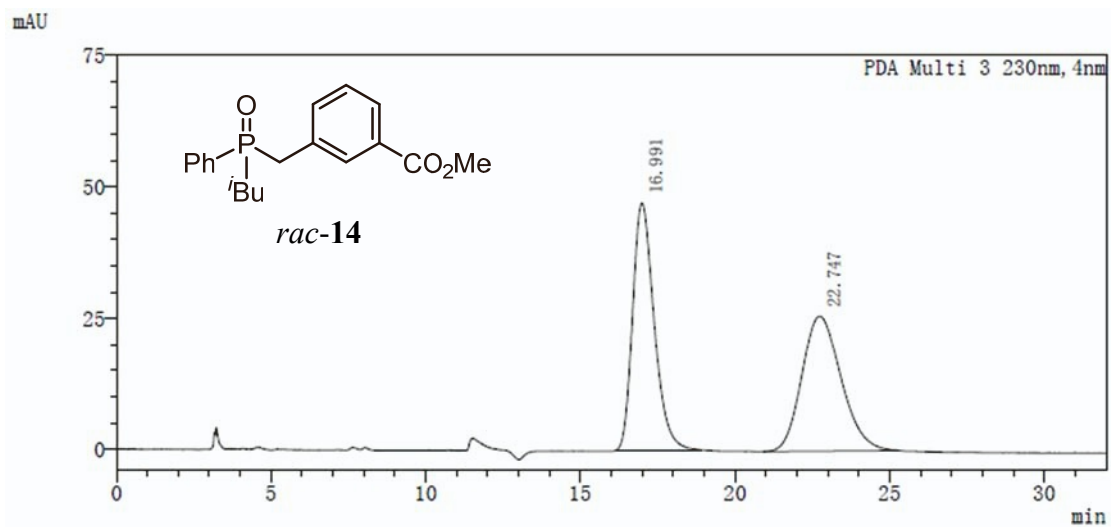


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 23.629    | 4721583 | 93.486 |
| 2     | 30.453    | 329006  | 6.514  |

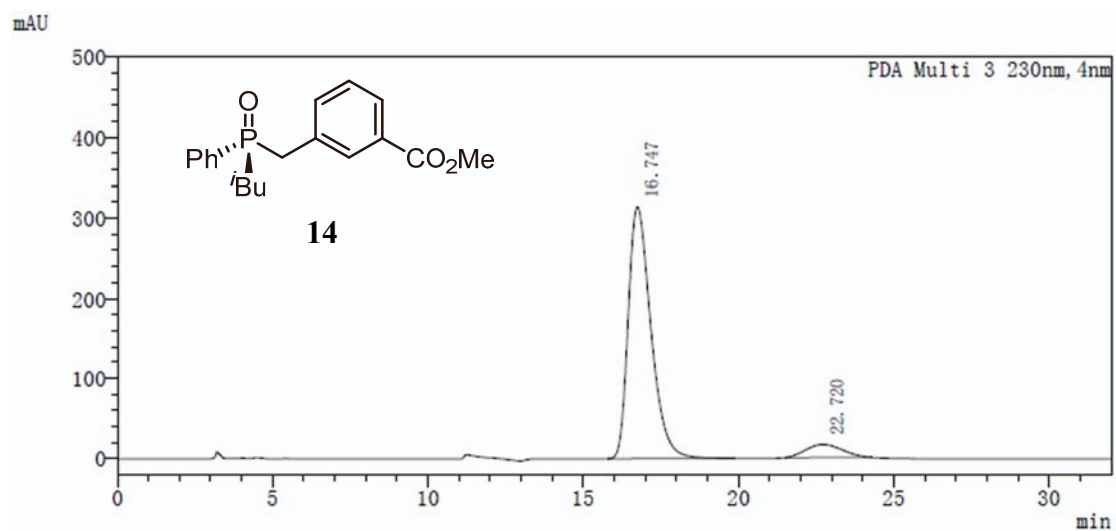




Peak Table

PDA Ch3 230nm

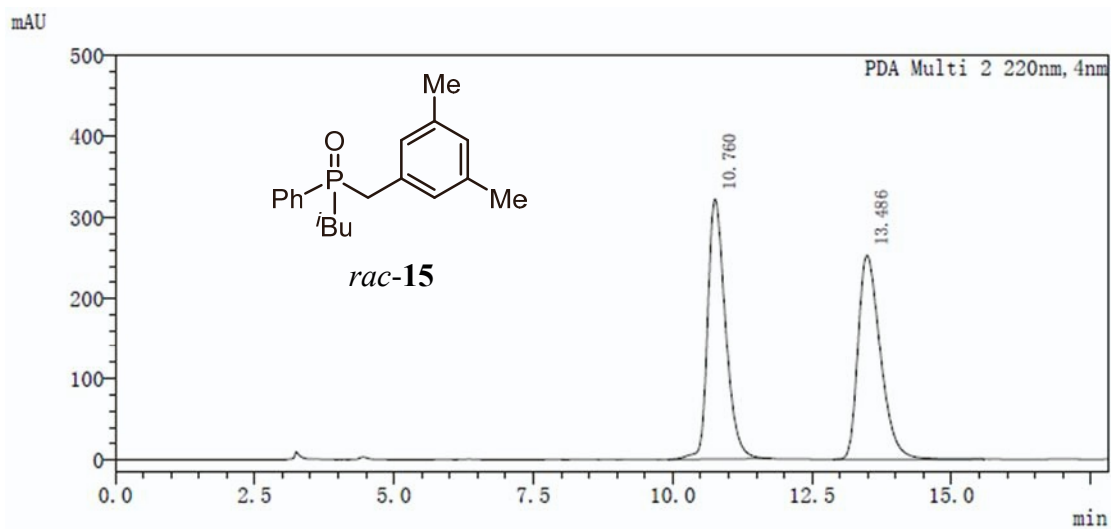
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 16.991    | 2270636 | 50.000 |
| 2     | 22.747    | 2270646 | 50.000 |



Peak Table

PDA Ch3 230nm

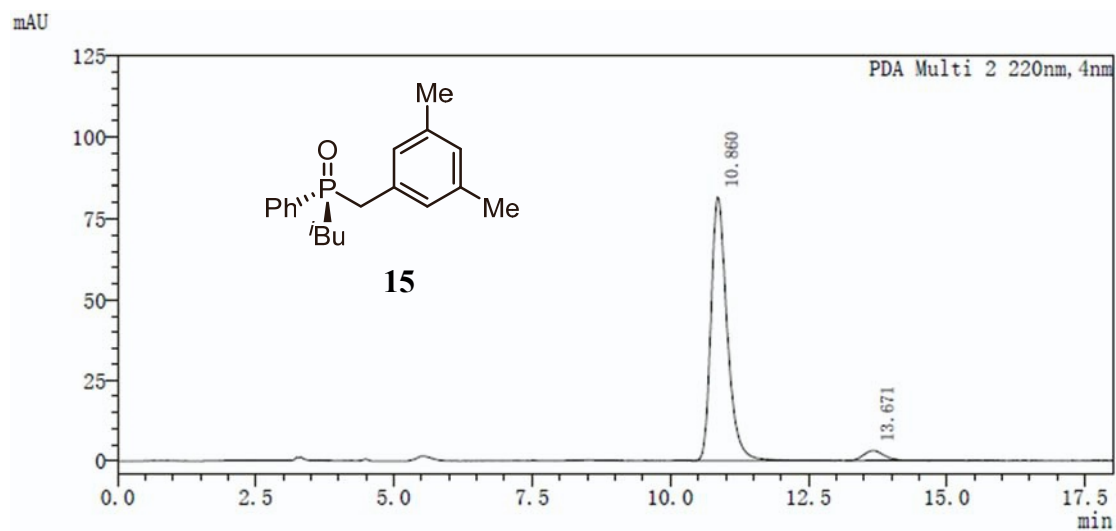
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 16.747    | 15941973 | 92.334 |
| 2     | 22.720    | 1323615  | 7.666  |



Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 10.760    | 7154104 | 50.331 |
| 2     | 13.486    | 7059930 | 49.669 |

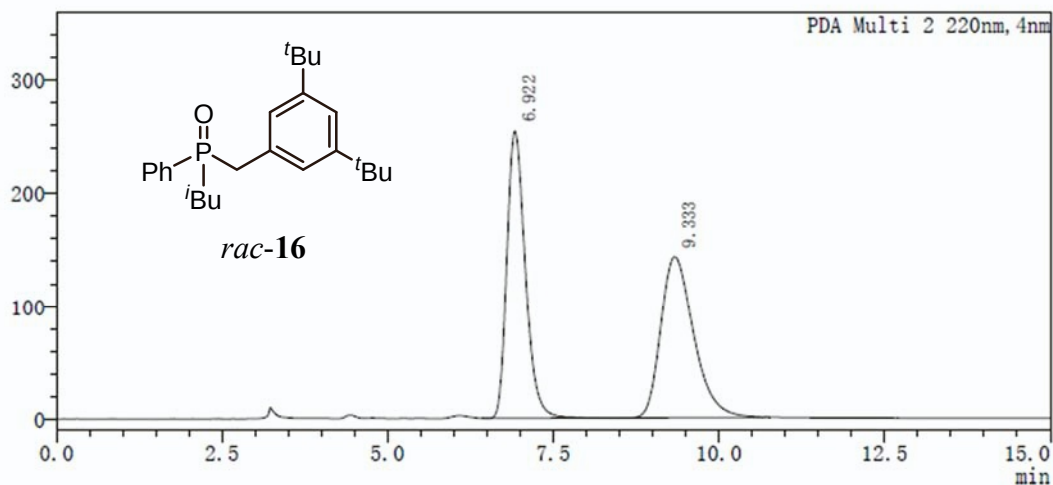


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 10.860    | 1655216 | 95.520 |
| 2     | 13.671    | 77627   | 4.480  |

mAU

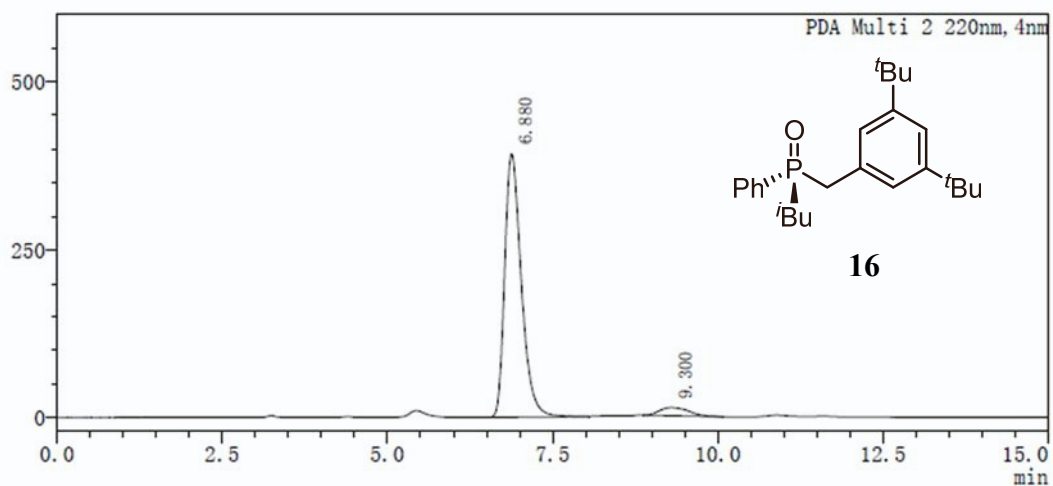


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 6.922     | 4933140 | 49.982 |
| 2     | 9.333     | 4936625 | 50.018 |

mAU

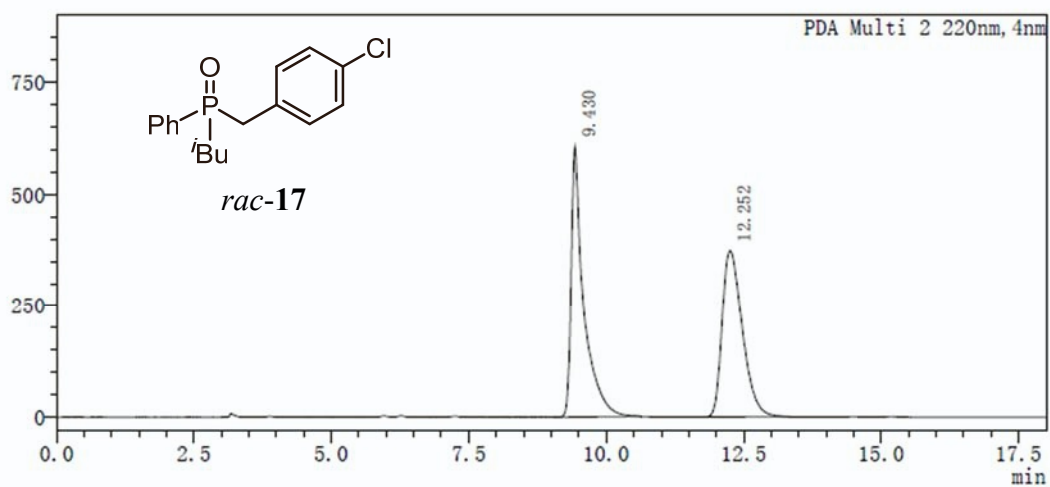


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 6.880     | 6555784 | 94.935 |
| 2     | 9.300     | 365761  | 5.065  |

mAU

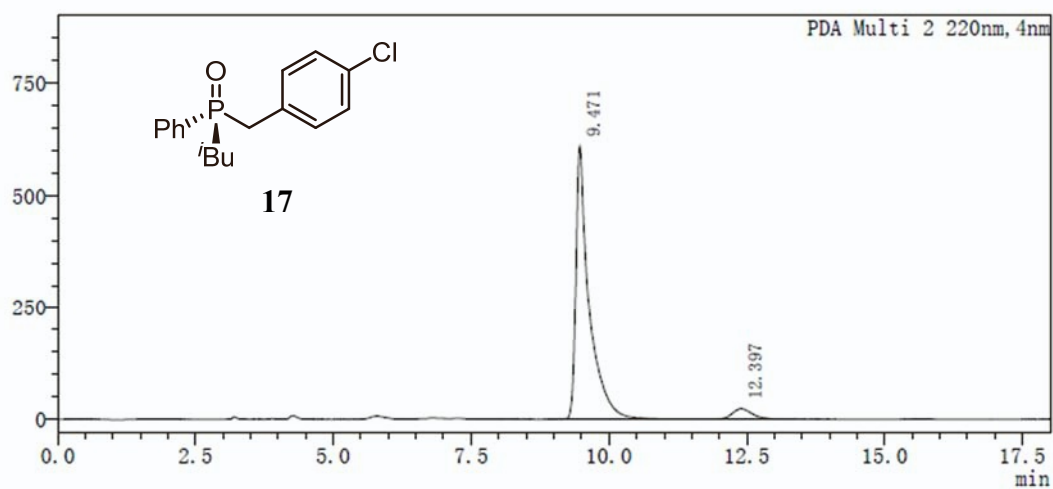


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 9.430     | 9573942 | 50.032 |
| 2     | 12.252    | 9561692 | 49.968 |

mAU

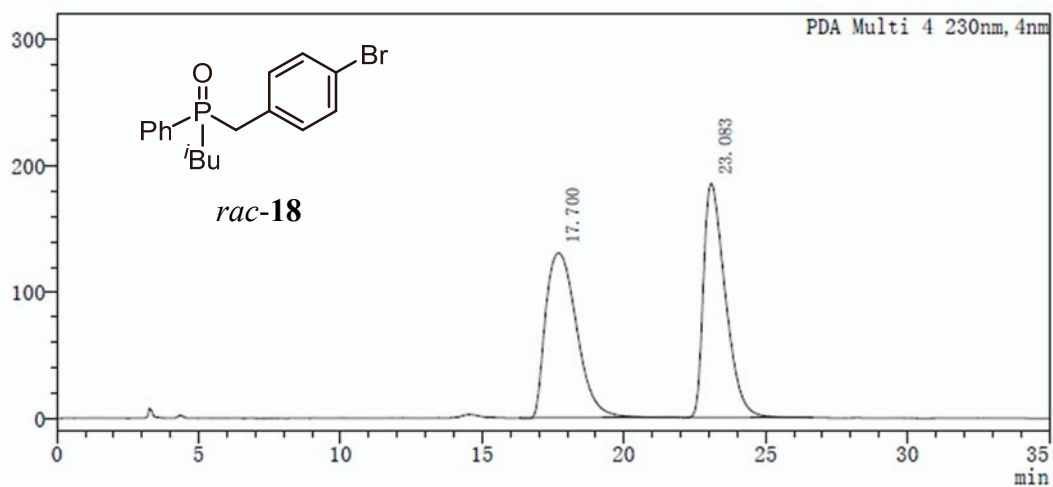


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 9.471     | 10142350 | 94.963 |
| 2     | 12.397    | 538021   | 5.037  |

mAU

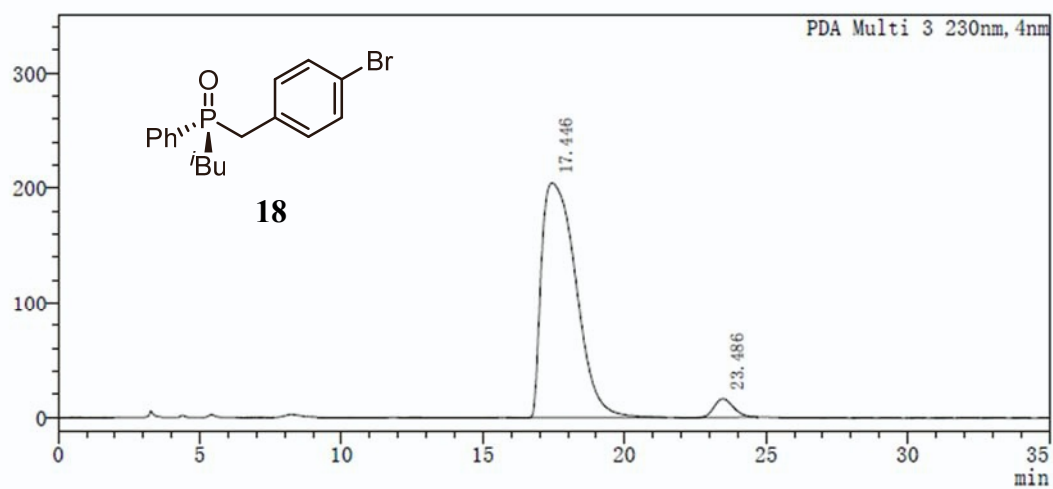


Peak Table

PDA Ch4 230nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 17.700    | 9968839 | 50.033 |
| 2     | 23.083    | 9955764 | 49.967 |

mAU

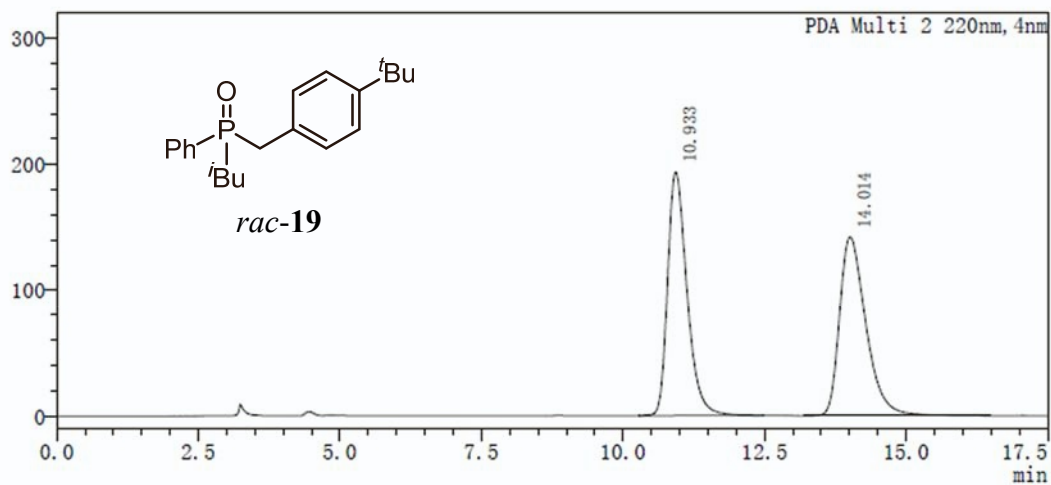


Peak Table

PDA Ch3 230nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 17.446    | 17346671 | 95.758 |
| 2     | 23.486    | 768401   | 4.242  |

mAU

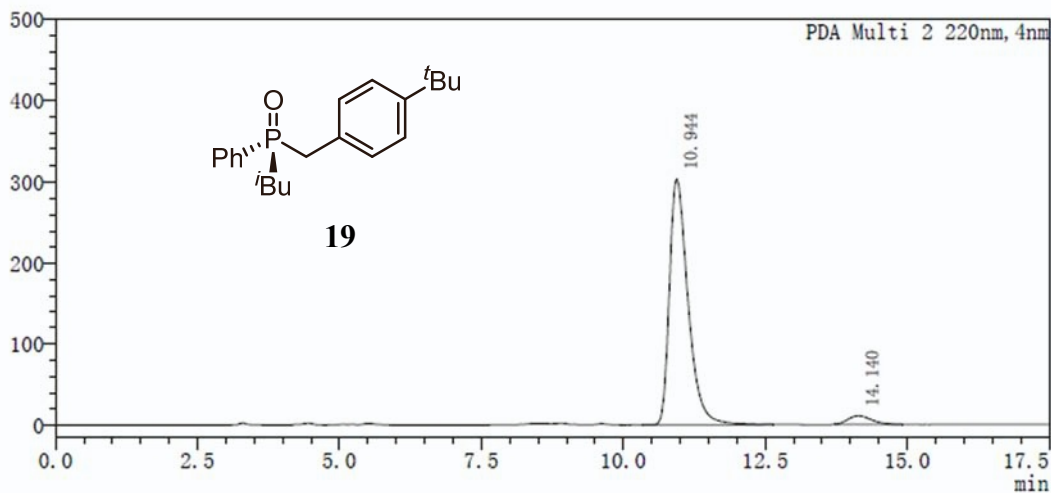


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 10.933    | 4610657 | 50.145 |
| 2     | 14.014    | 4583956 | 49.855 |

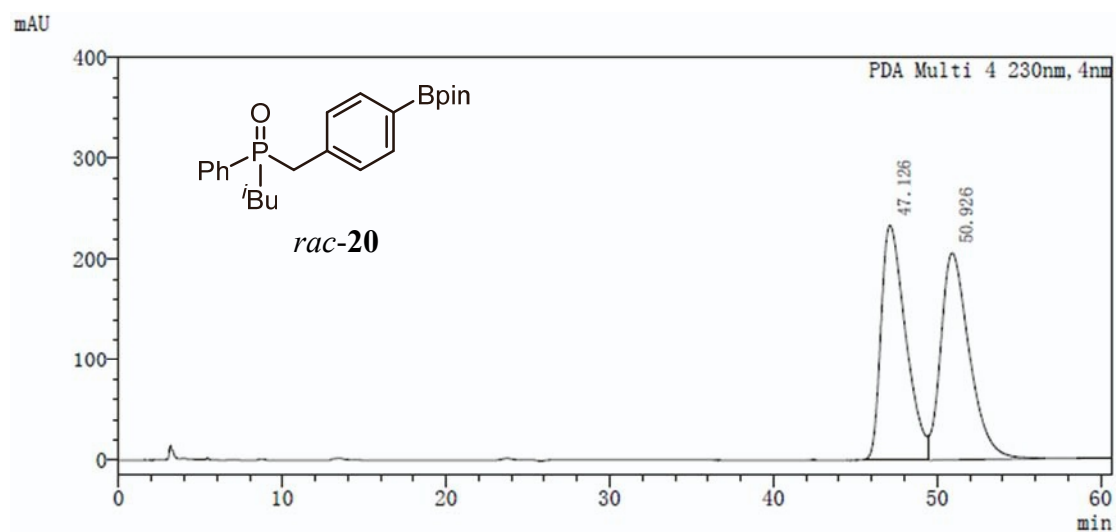
mAU



Peak Table

PDA Ch2 220nm

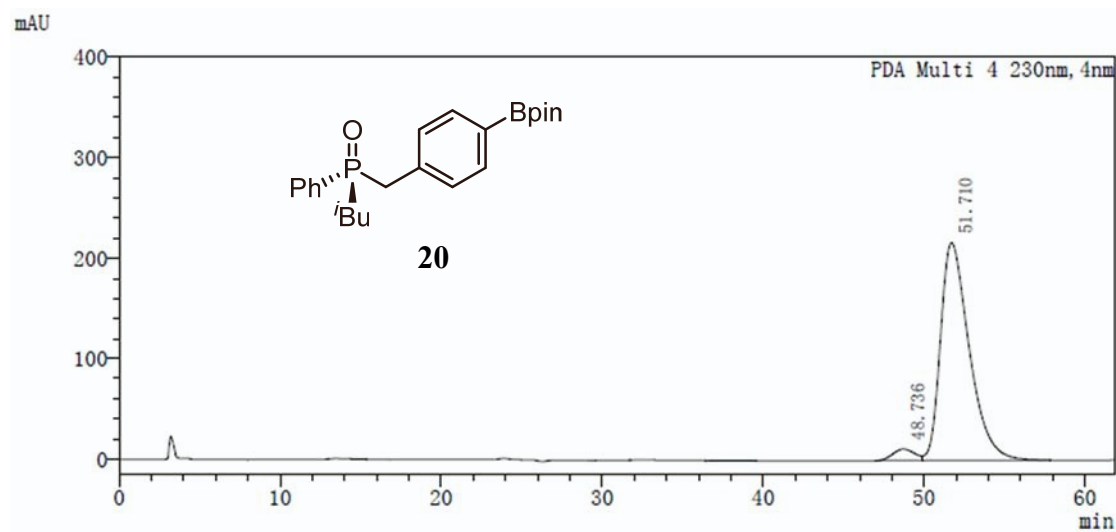
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 10.944    | 6899348 | 95.787 |
| 2     | 14.140    | 303421  | 4.213  |



Peak Table

PDA Ch4 230nm

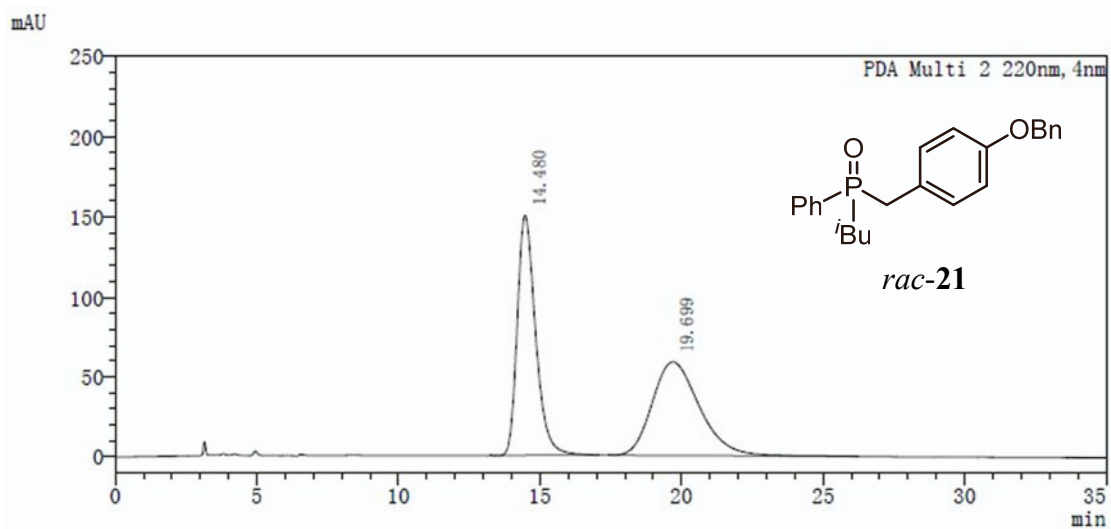
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 47.126    | 24439449 | 49.469 |
| 2     | 50.926    | 24963687 | 50.531 |



Peak Table

PDA Ch4 230nm

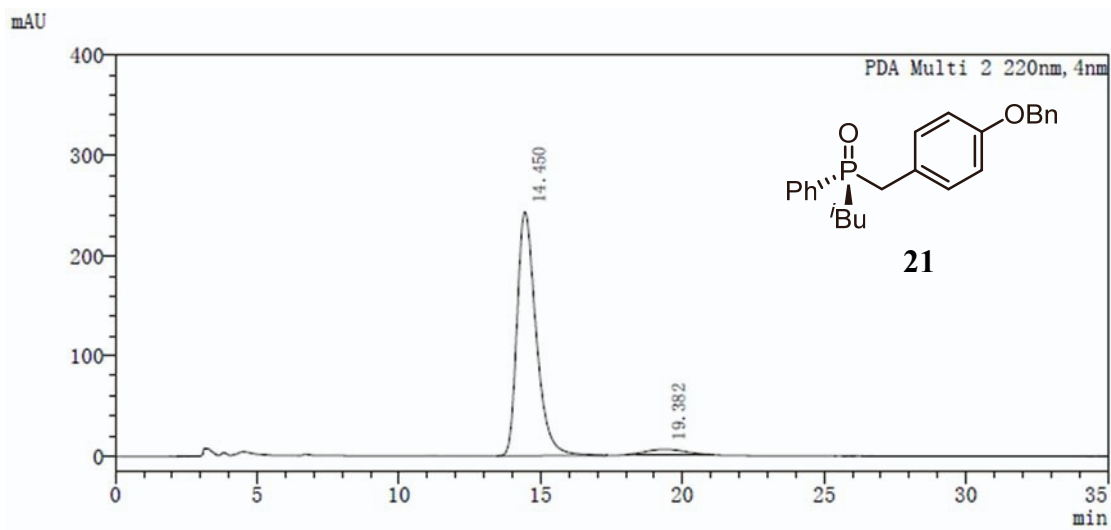
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 48.736    | 1042096  | 3.732  |
| 2     | 51.710    | 26878659 | 96.268 |



Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 14.480    | 6750274 | 50.008 |
| 2     | 19.699    | 6748016 | 49.992 |

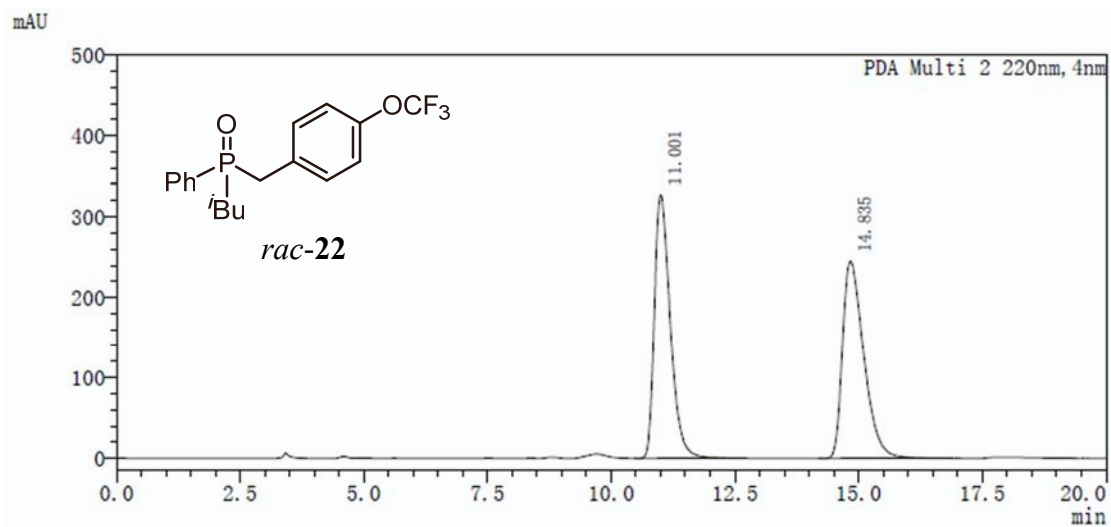


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 14.450    | 11358969 | 95.826 |
| 2     | 19.382    | 494728   | 4.174  |

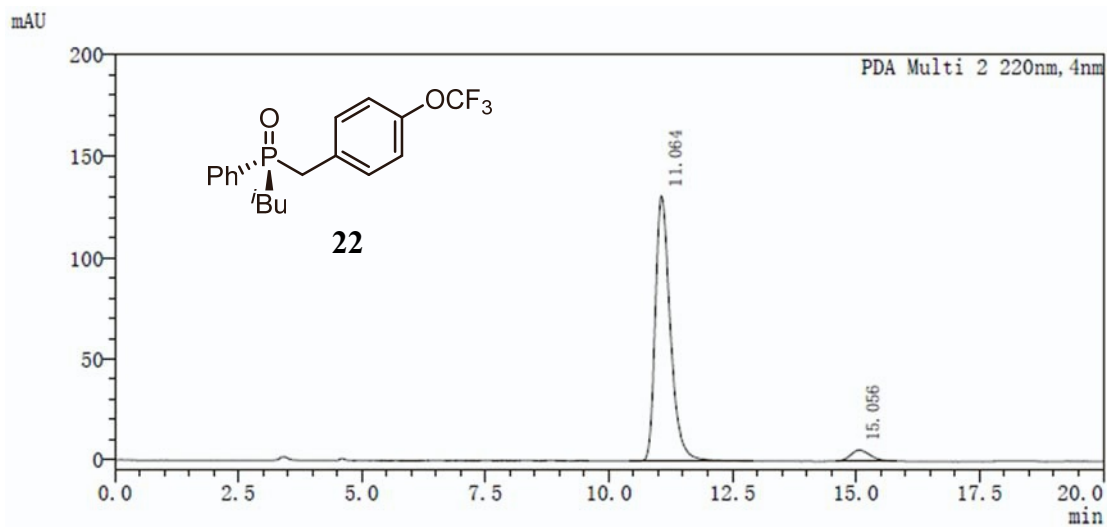




Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 11.001    | 7310081 | 49.961 |
| 2     | 14.835    | 7321412 | 50.039 |

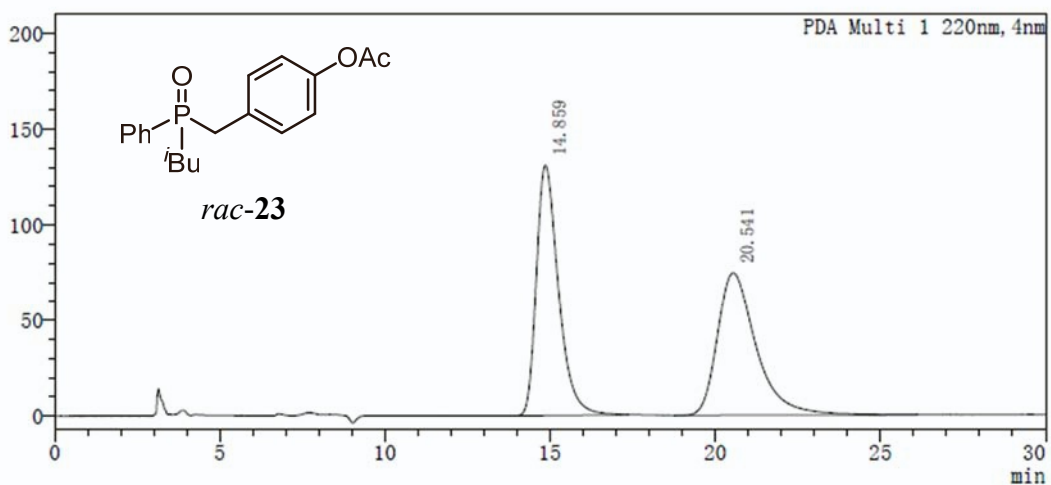


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 11.064    | 2771490 | 94.821 |
| 2     | 15.056    | 151386  | 5.179  |

mAU

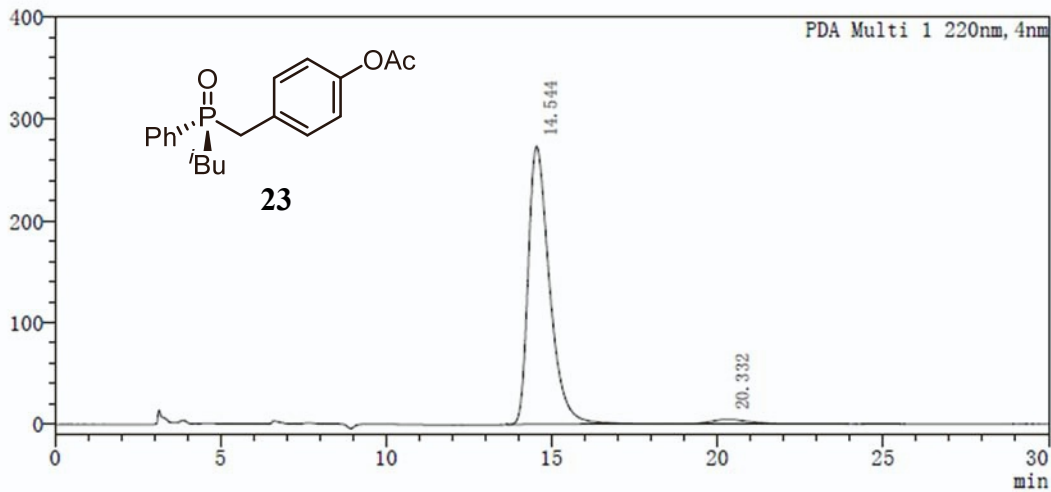


Peak Table

PDA Ch1 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 14.859    | 6095941 | 50.086 |
| 2     | 20.541    | 6075026 | 49.914 |

mAU

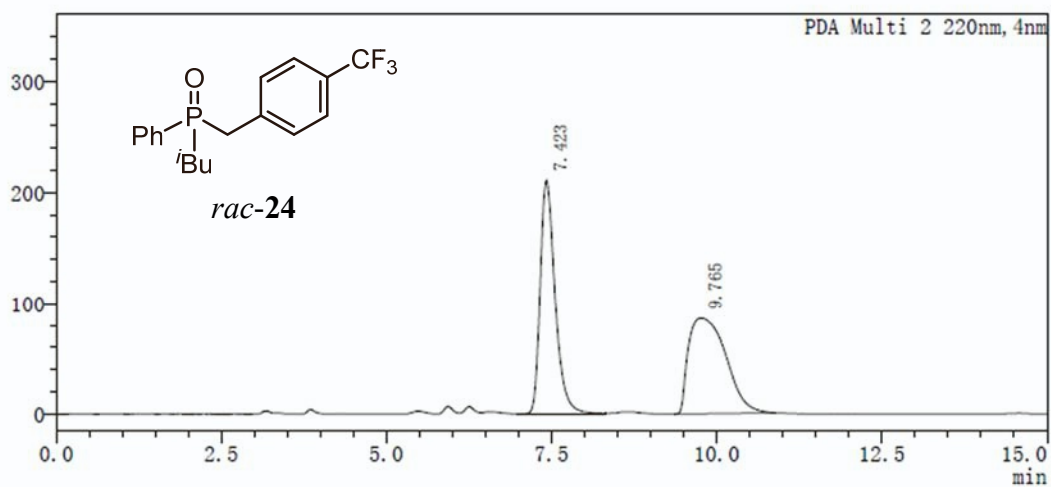


Peak Table

PDA Ch1 220nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 14.544    | 12169168 | 97.386 |
| 2     | 20.332    | 326671   | 2.614  |

mAU

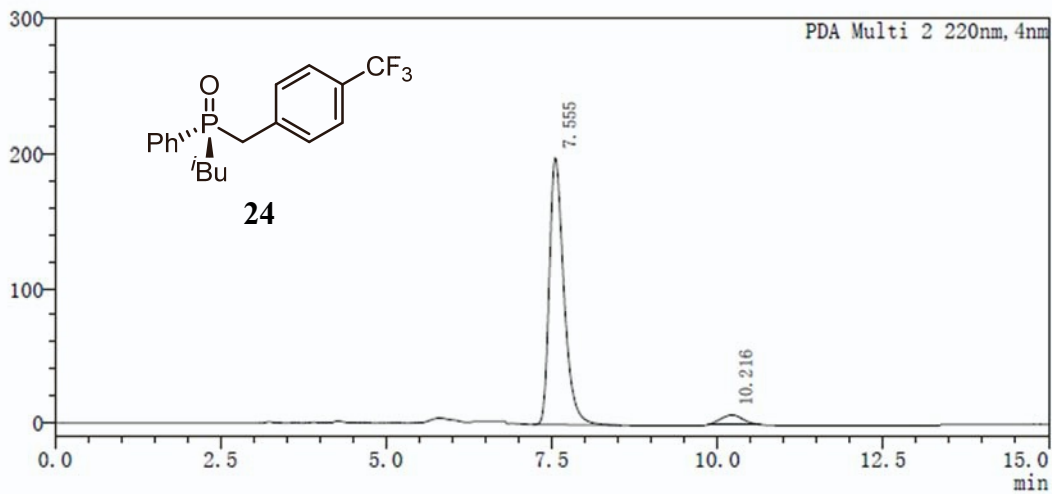


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 7.423     | 3321618 | 49.498 |
| 2     | 9.765     | 3389020 | 50.502 |

mAU

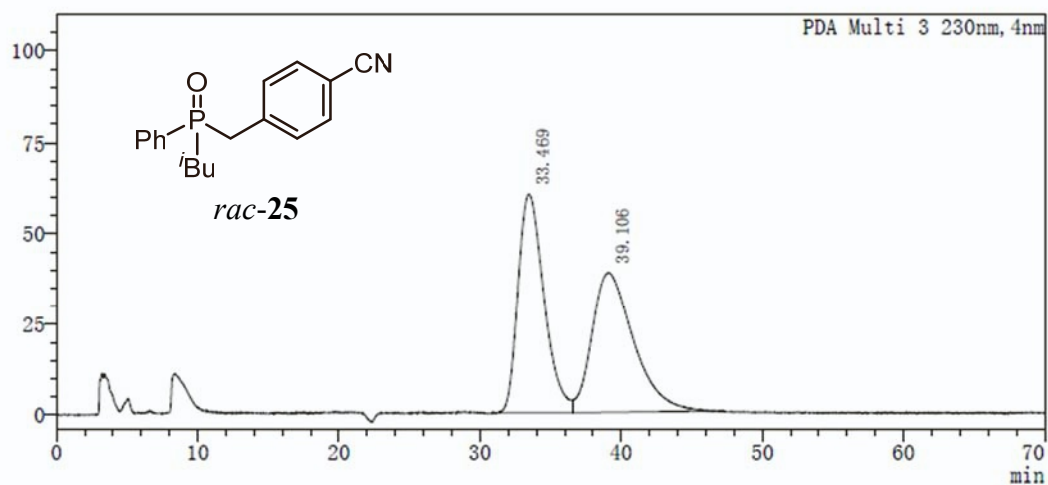


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 7.555     | 3028499 | 94.798 |
| 2     | 10.216    | 166195  | 5.202  |

mAU

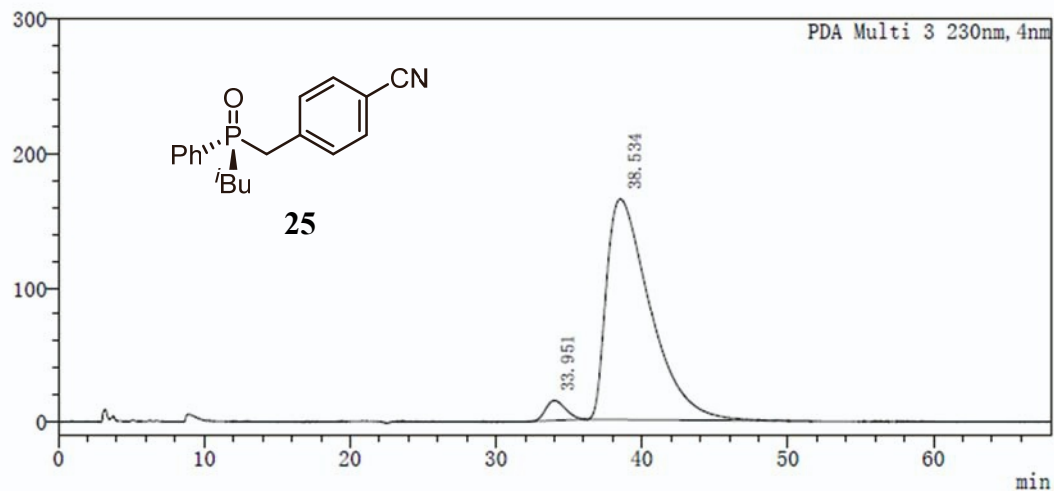


Peak Table

PDA Ch3 230nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 33.469    | 7708530 | 49.356 |
| 2     | 39.106    | 7909820 | 50.644 |

mAU

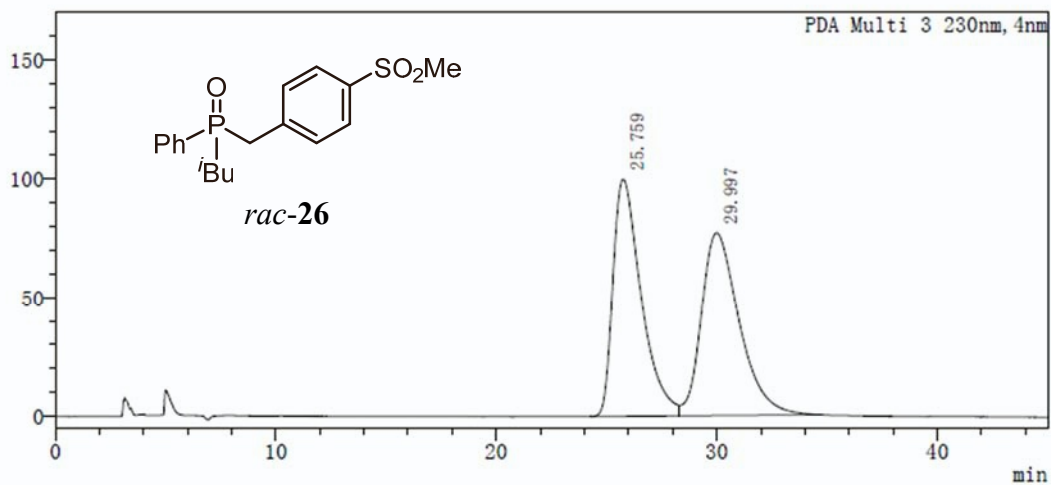


Peak Table

PDA Ch3 230nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 33.951    | 1415672  | 3.960  |
| 2     | 38.534    | 34335115 | 96.040 |

mAU

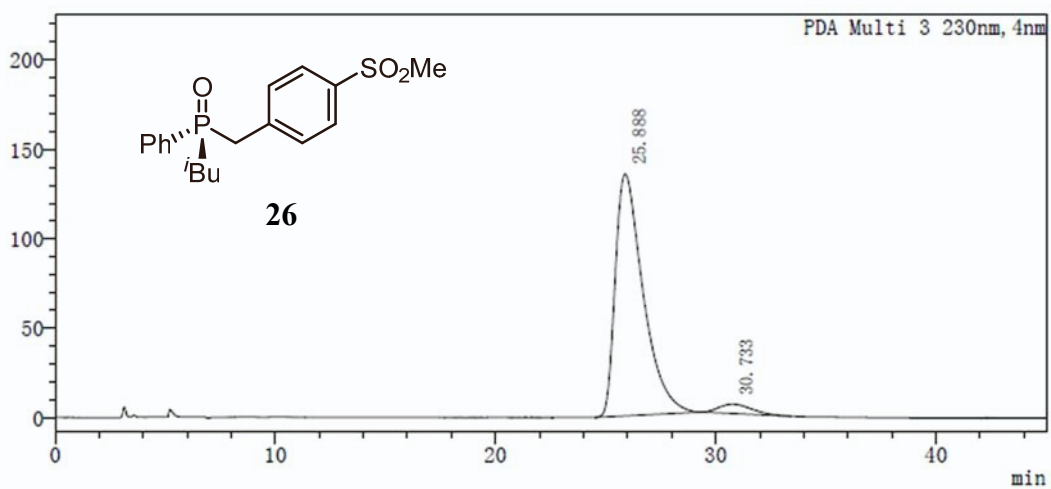


Peak Table

PDA Ch3 230nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 25.759    | 8894215 | 49.242 |
| 2     | 29.997    | 9168134 | 50.758 |

mAU

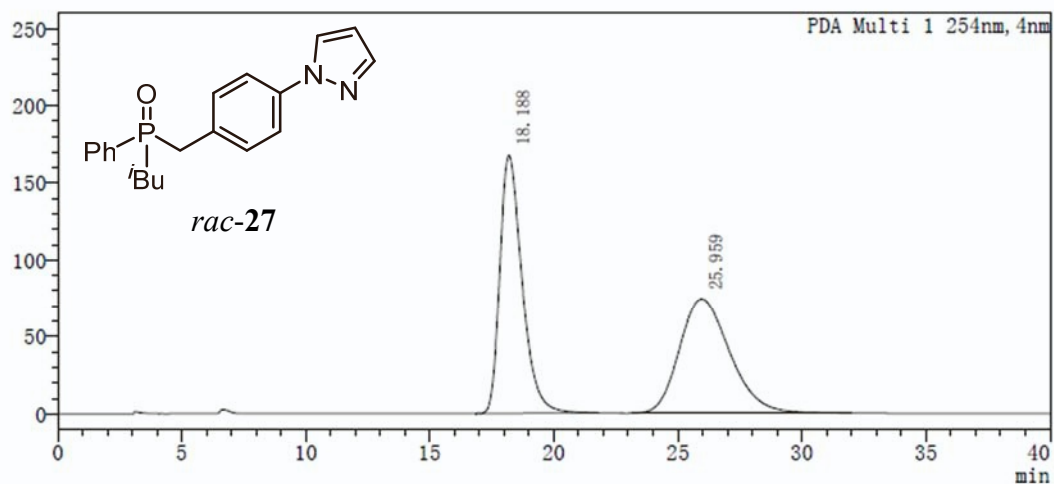


Peak Table

PDA Ch3 230nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 25.888    | 11892801 | 95.695 |
| 2     | 30.733    | 535069   | 4.305  |

mAU

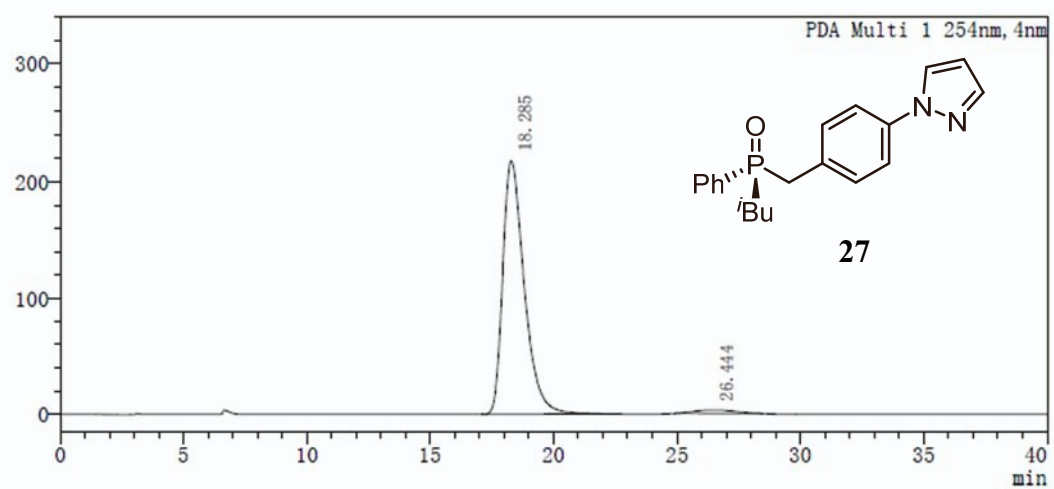


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 18.188    | 10459464 | 50.064 |
| 2     | 25.959    | 10432585 | 49.936 |

mAU

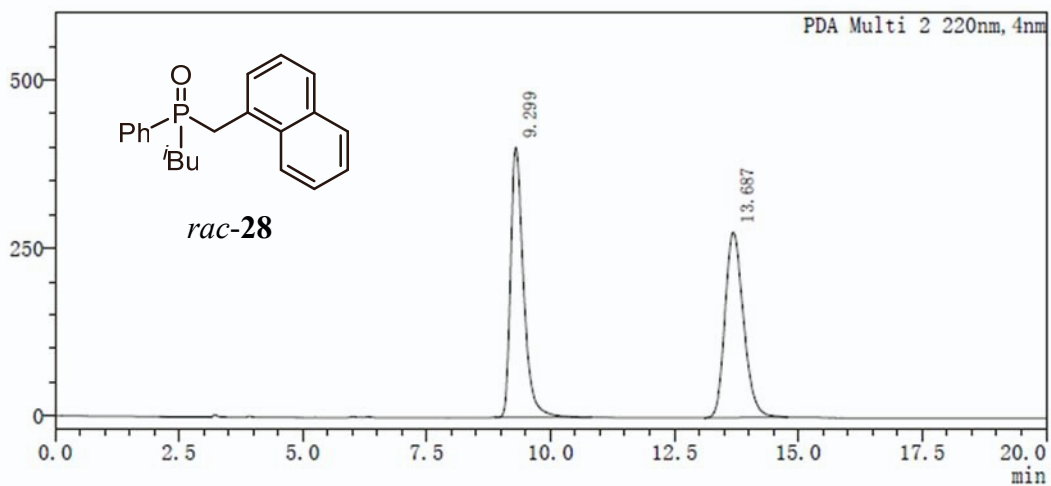


Peak Table

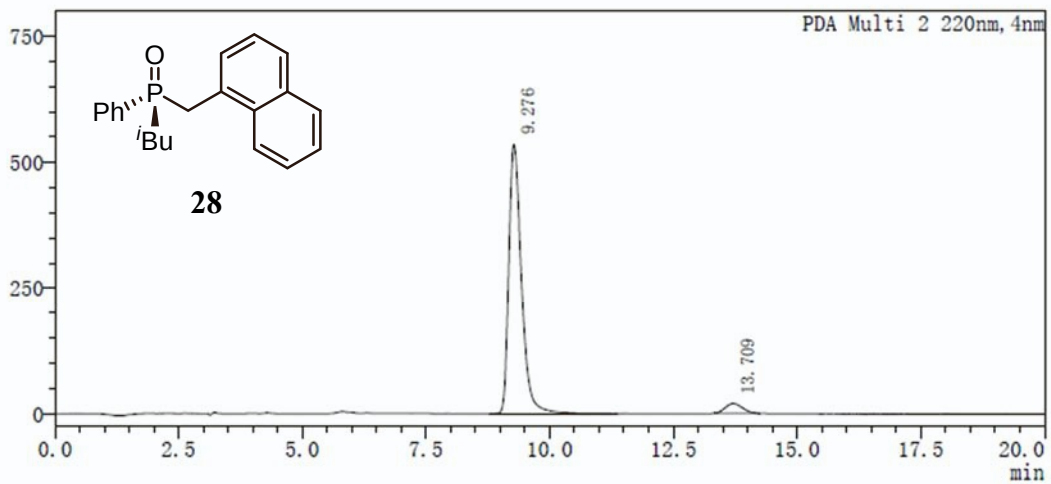
PDA Ch1 254nm

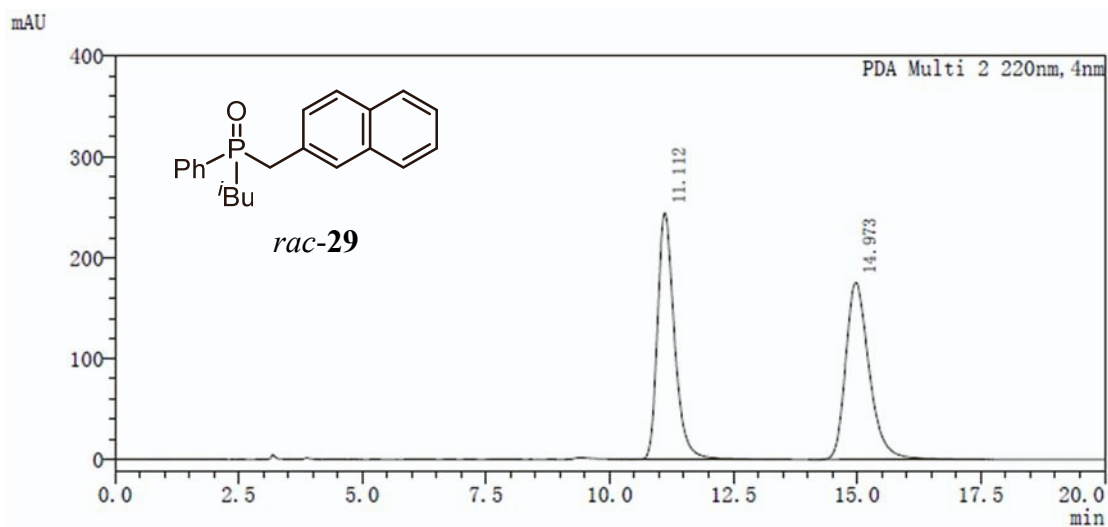
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 18.285    | 13200014 | 97.515 |
| 2     | 26.444    | 336439   | 2.485  |

mAU



mAU

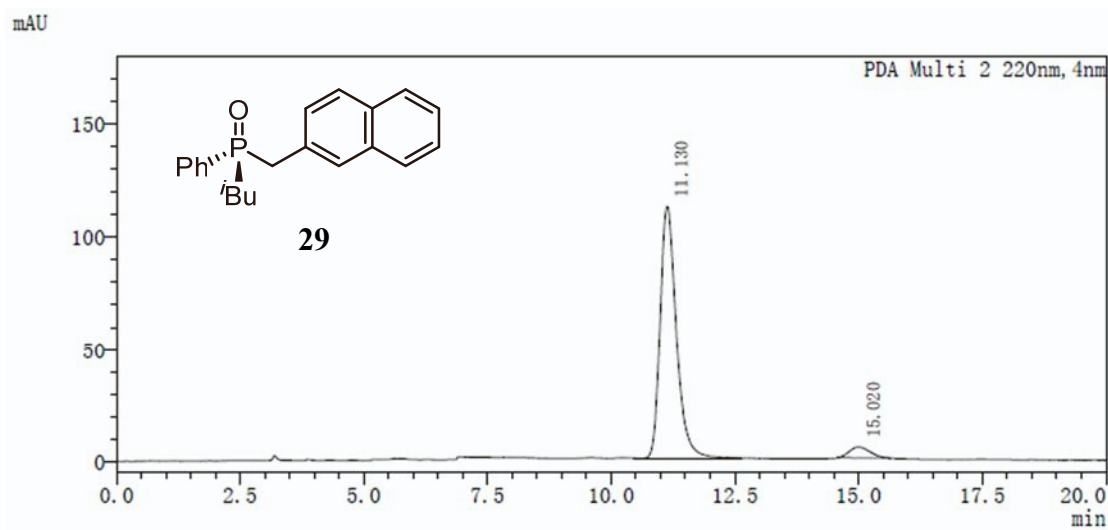




Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 11.112    | 5797994 | 50.062 |
| 2     | 14.973    | 5783710 | 49.938 |

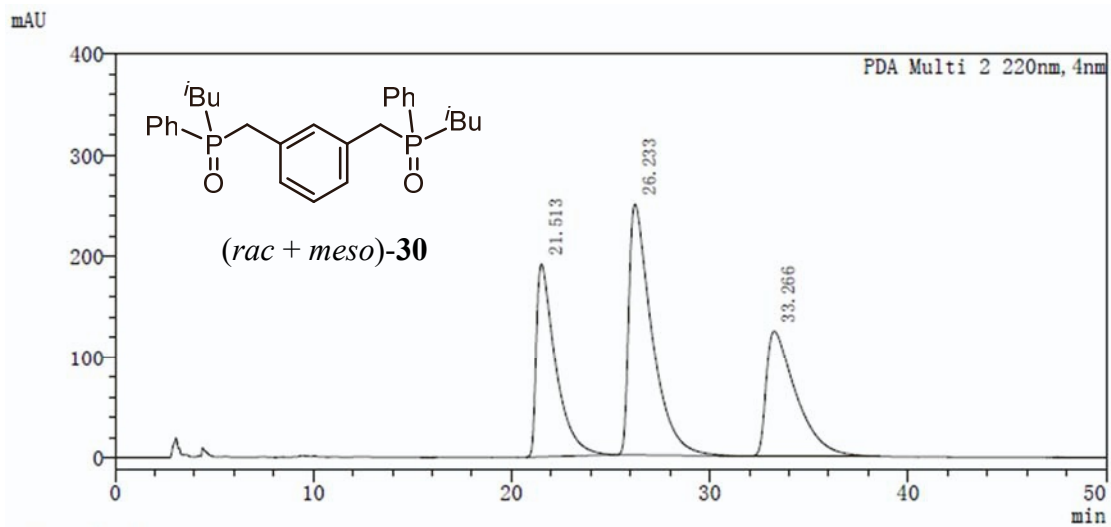


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 11.130    | 2553993 | 94.759 |
| 2     | 15.020    | 141244  | 5.241  |

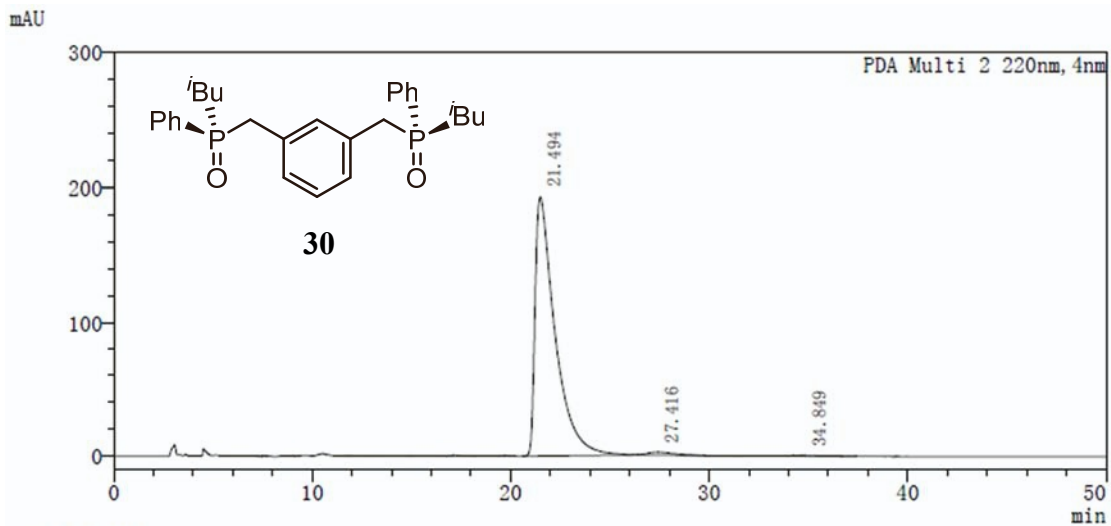




Peak Table

PDA Ch2 220nm

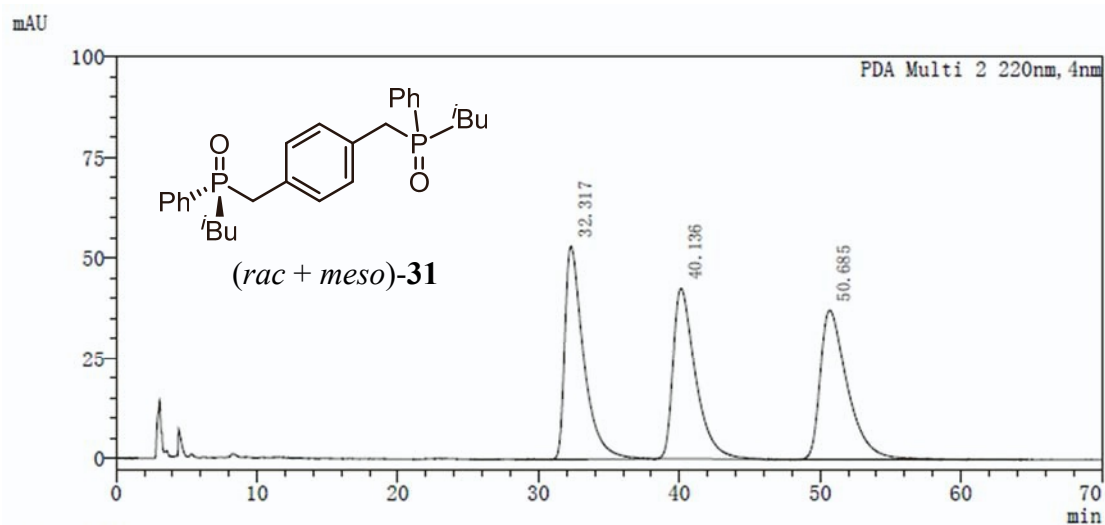
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 21.513    | 12962913 | 28.122 |
| 2     | 26.233    | 20196871 | 43.815 |
| 3     | 33.266    | 12935556 | 28.063 |



Peak Table

PDA Ch2 220nm

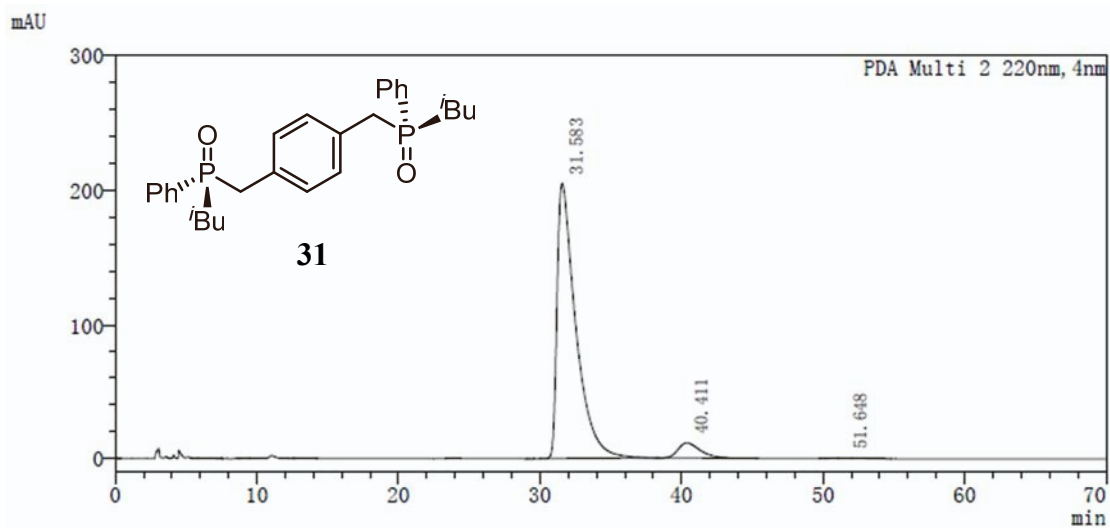
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 21.494    | 13482471 | 98.117 |
| 2     | 27.416    | 198240   | 1.443  |
| 3     | 34.849    | 60560    | 0.441  |



Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 32.317    | 4954496 | 33.870 |
| 2     | 40.136    | 4718115 | 32.255 |
| 3     | 50.685    | 4955153 | 33.875 |

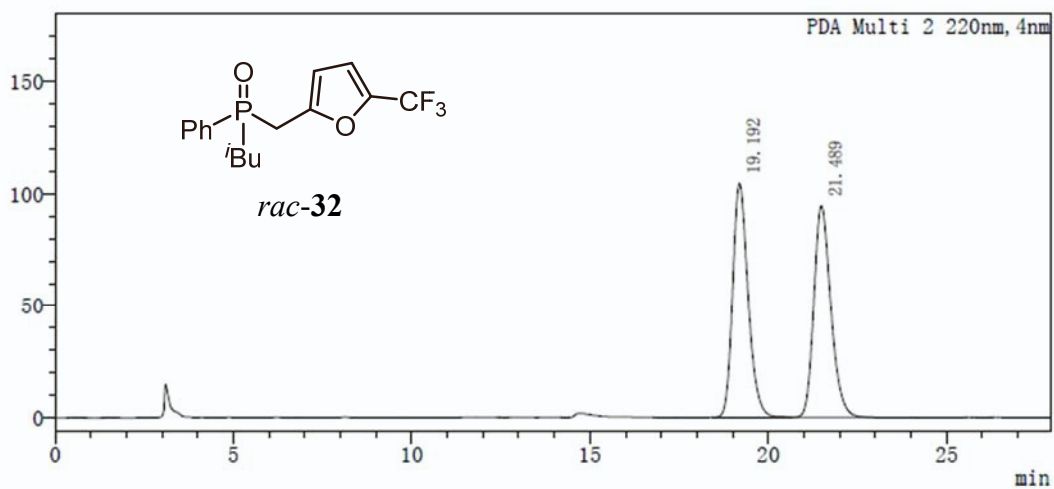


Peak Table

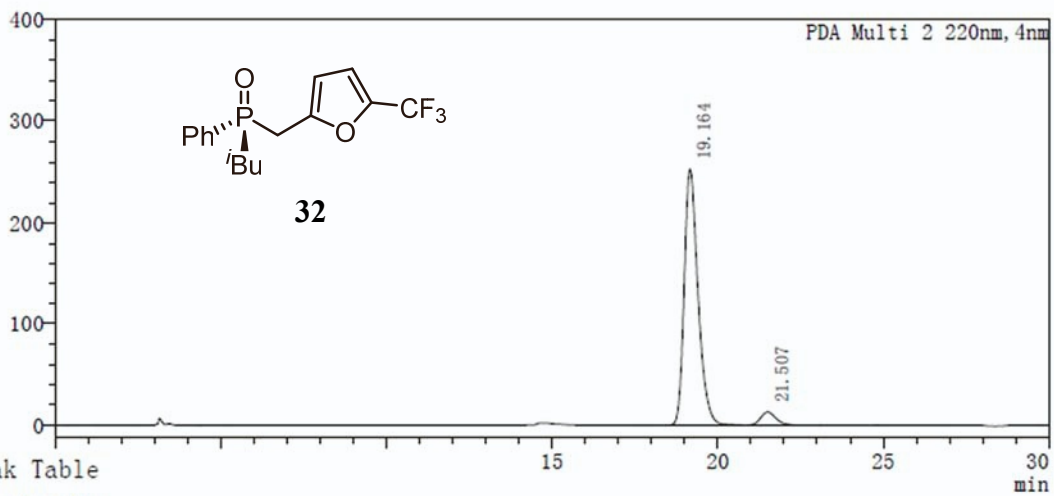
PDA Ch2 220nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 31.583    | 18838015 | 93.614 |
| 2     | 40.411    | 1230546  | 6.115  |
| 3     | 51.648    | 54419    | 0.270  |

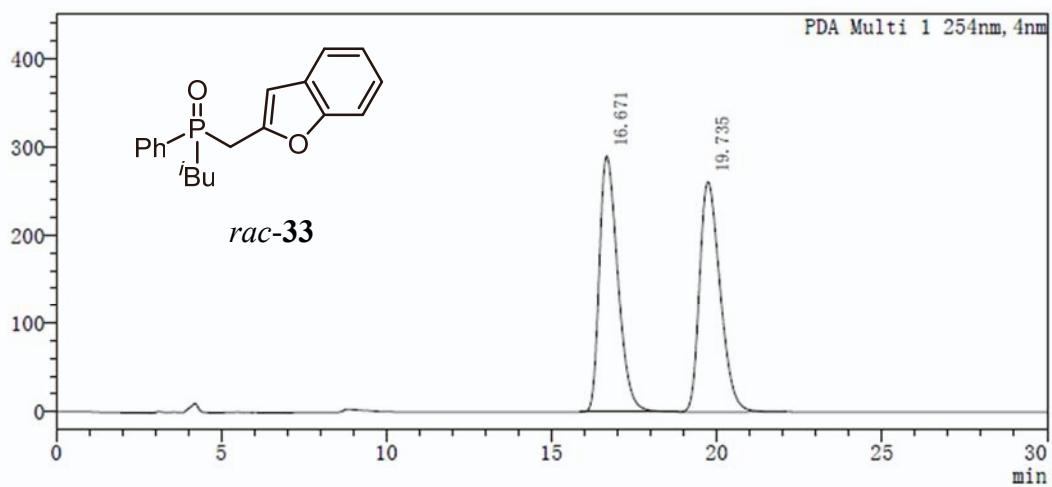
mAU



mAU



mAU

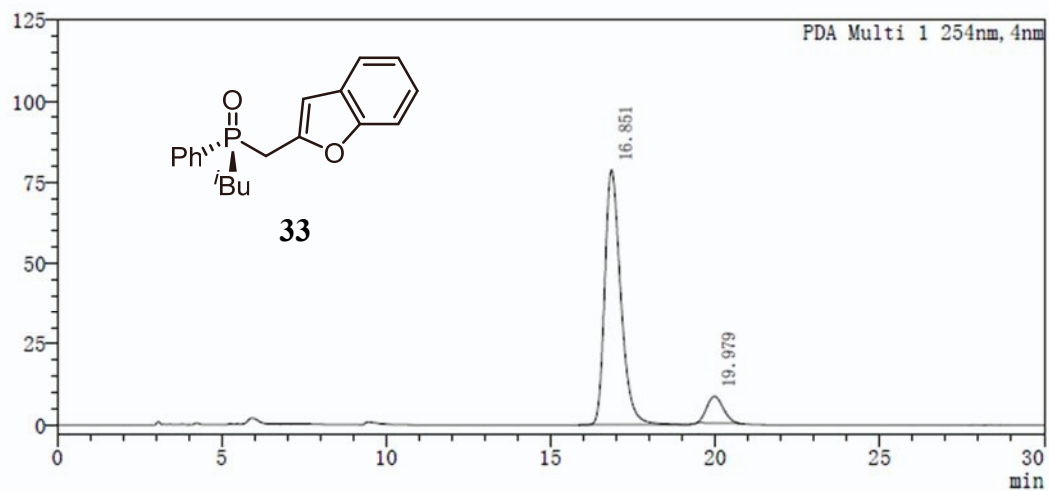


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 16.671    | 11295555 | 50.003 |
| 2     | 19.735    | 11294414 | 49.997 |

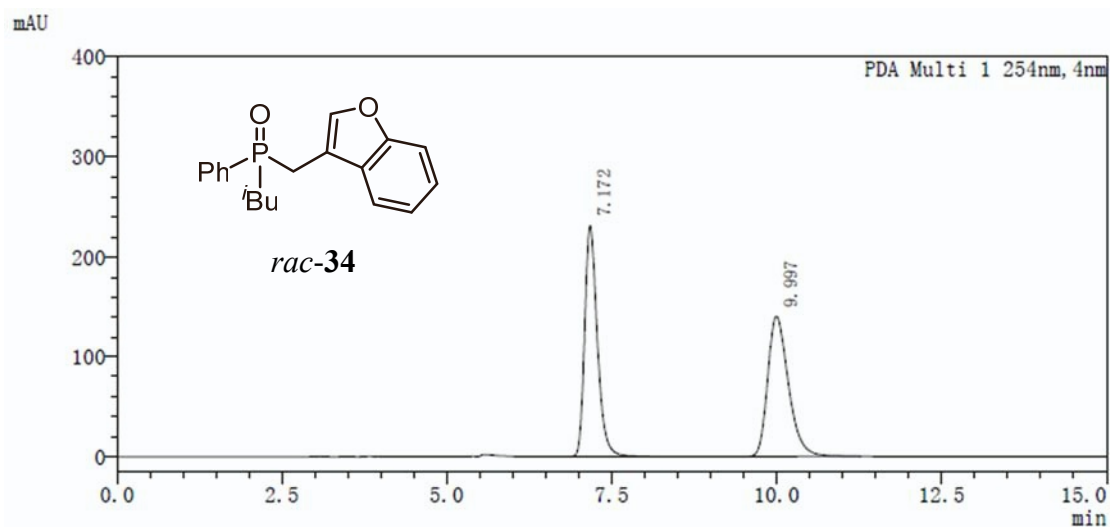
mAU



Peak Table

PDA Ch1 254nm

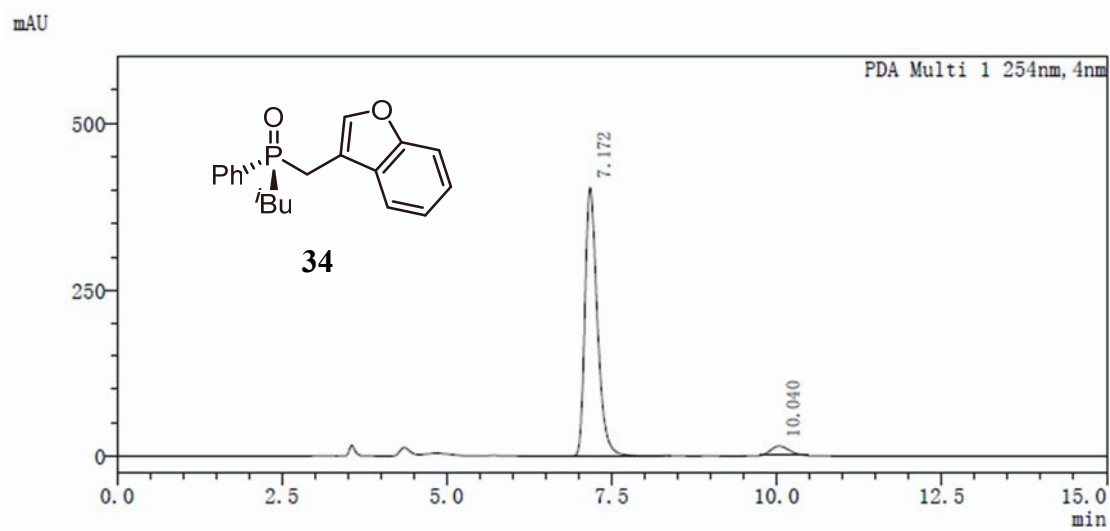
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 16.851    | 2653815 | 90.261 |
| 2     | 19.979    | 286353  | 9.739  |



Peak Table

PDA Ch1 254nm

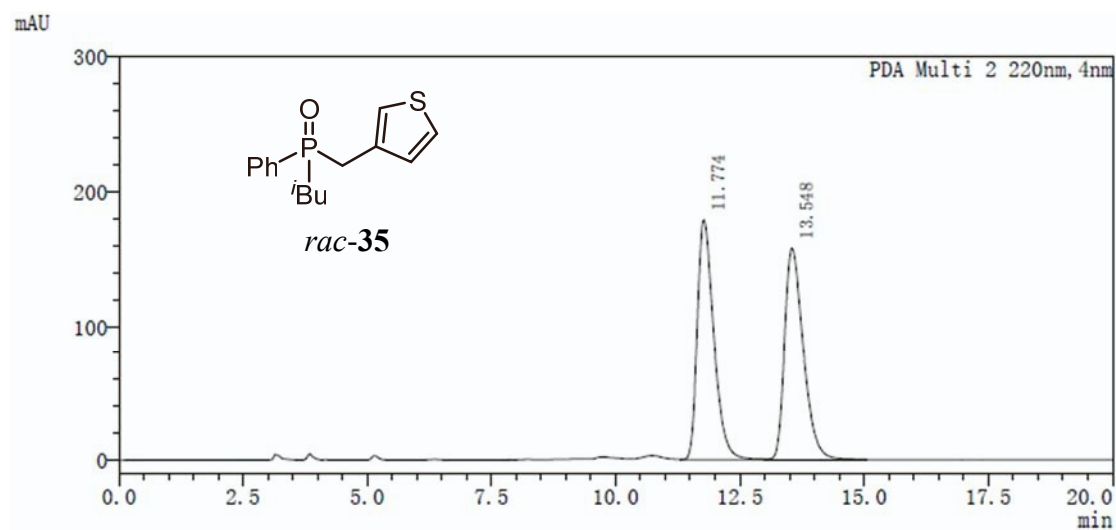
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 7.172     | 3082020 | 50.089 |
| 2     | 9.997     | 3071053 | 49.911 |



Peak Table

PDA Ch1 254nm

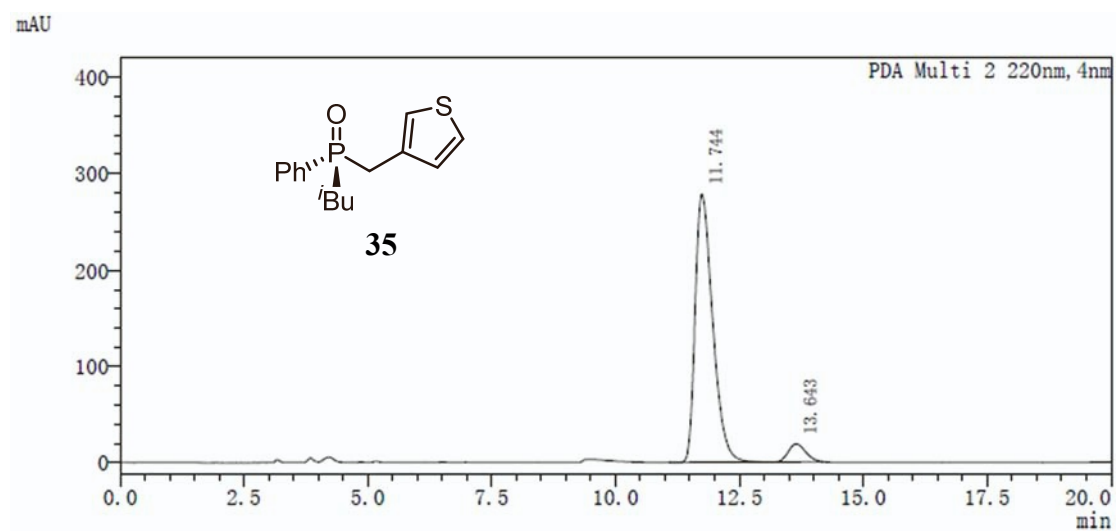
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 7.172     | 5294933 | 95.068 |
| 2     | 10.040    | 274672  | 4.932  |



Peak Table

PDA Ch2 220nm

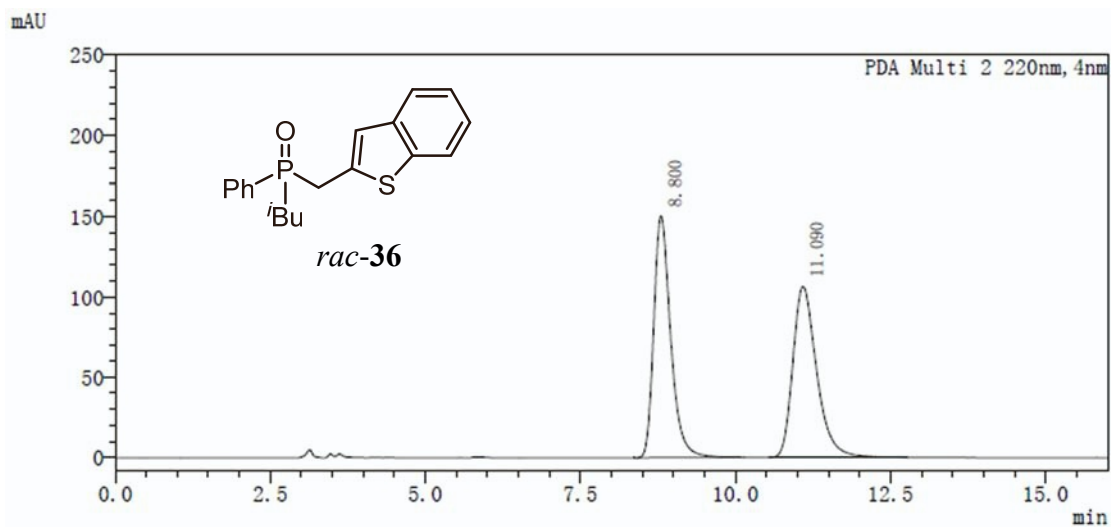
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 11.774    | 4132157 | 49.975 |
| 2     | 13.548    | 4136356 | 50.025 |



Peak Table

PDA Ch2 220nm

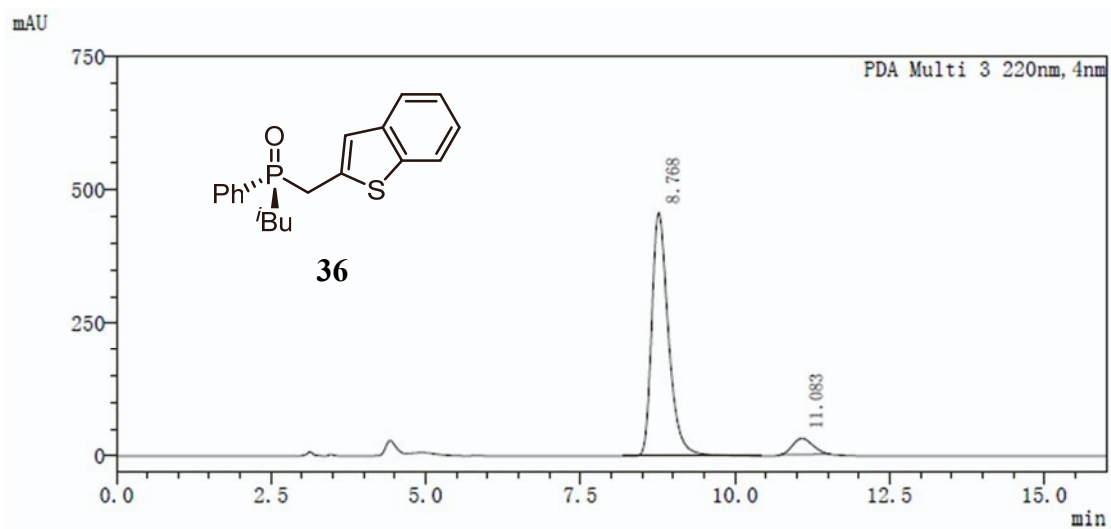
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 11.744    | 6870655 | 93.763 |
| 2     | 13.643    | 457040  | 6.237  |



Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 8.800     | 2842886 | 50.036 |
| 2     | 11.090    | 2838749 | 49.964 |

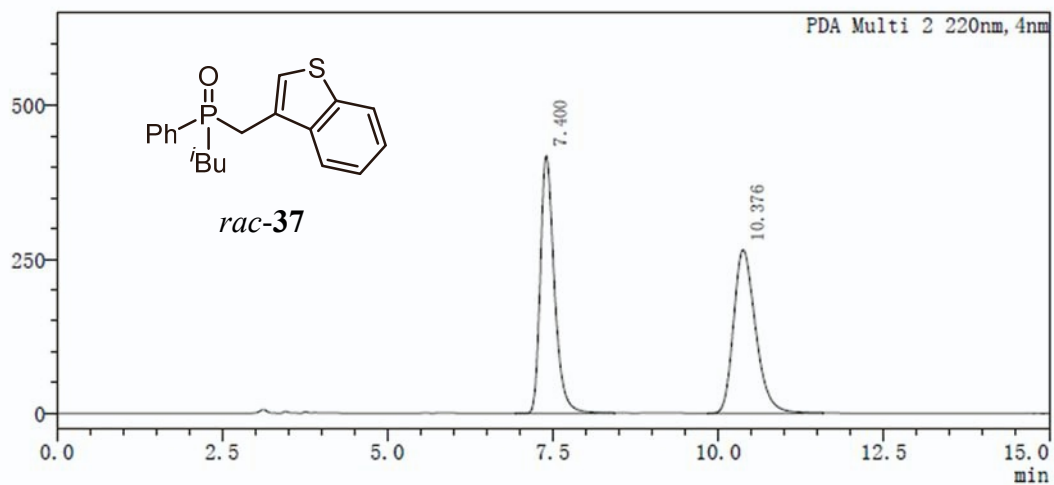


Peak Table

PDA Ch3 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 8.768     | 8573748 | 92.721 |
| 2     | 11.083    | 673056  | 7.279  |

mAU

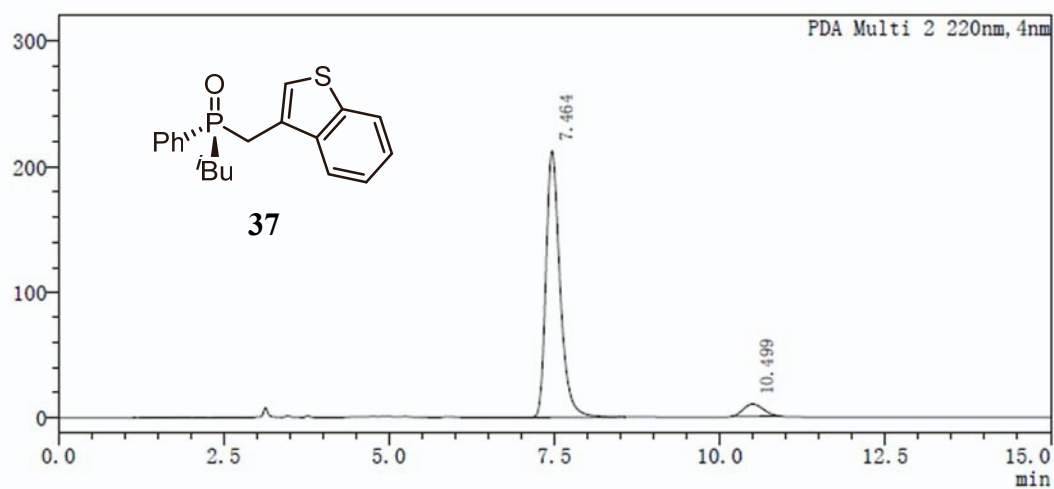


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 7.400     | 6162705 | 50.033 |
| 2     | 10.376    | 6154489 | 49.967 |

mAU

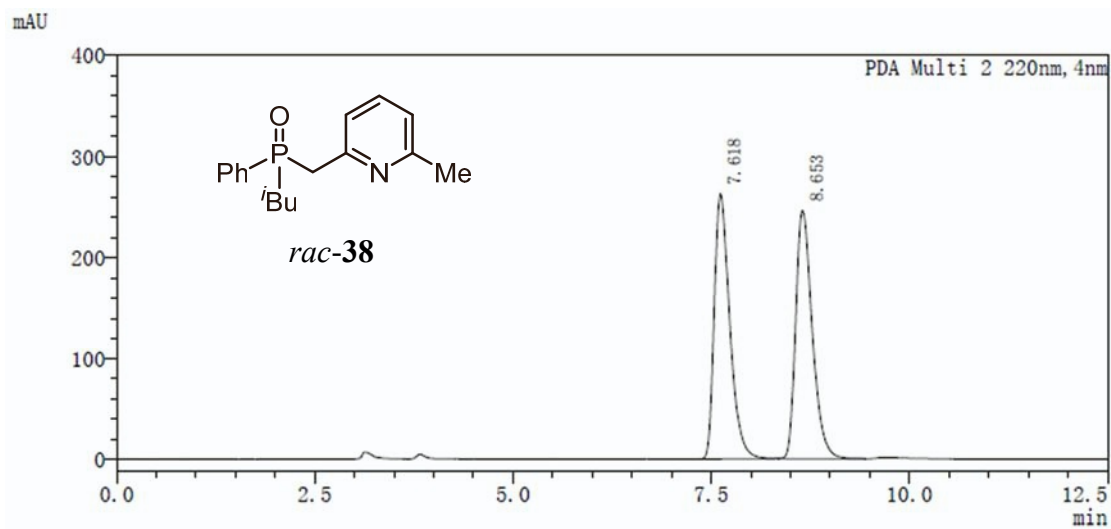


Peak Table

PDA Ch2 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 7.464     | 3143471 | 93.864 |
| 2     | 10.499    | 205505  | 6.136  |

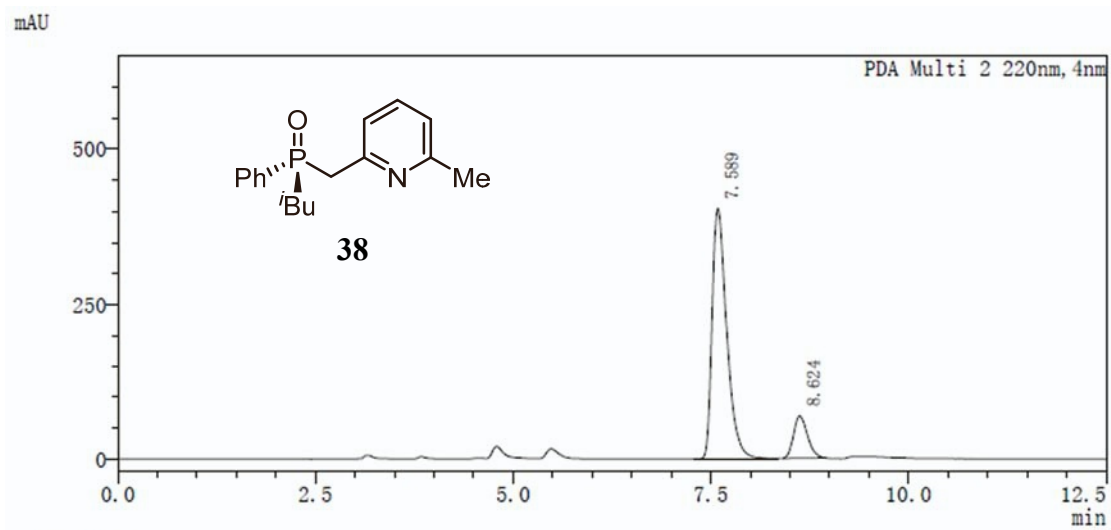




Peak Table

PDA Ch2 220nm

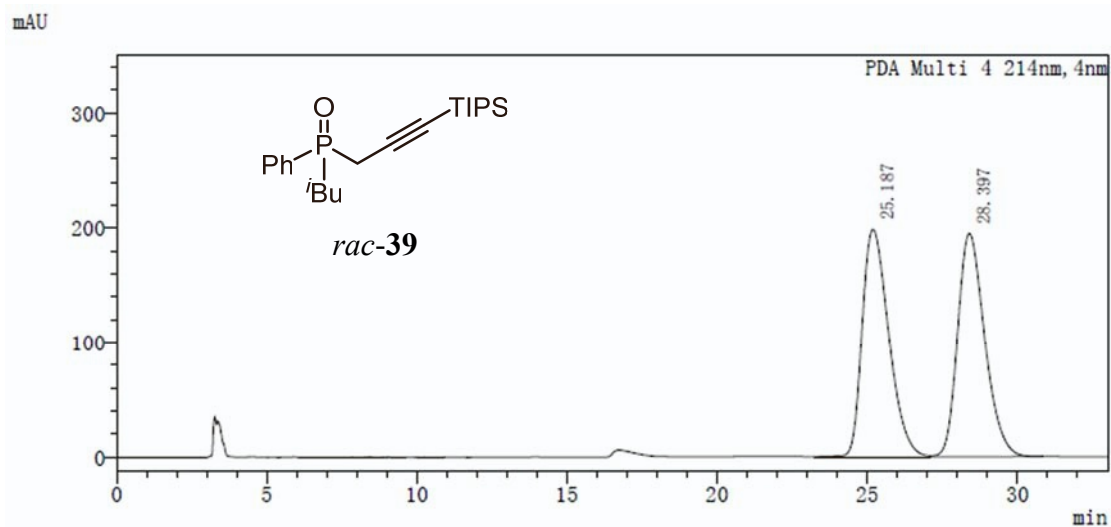
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 7.618     | 3574440 | 49.942 |
| 2     | 8.653     | 3582784 | 50.058 |



Peak Table

PDA Ch2 220nm

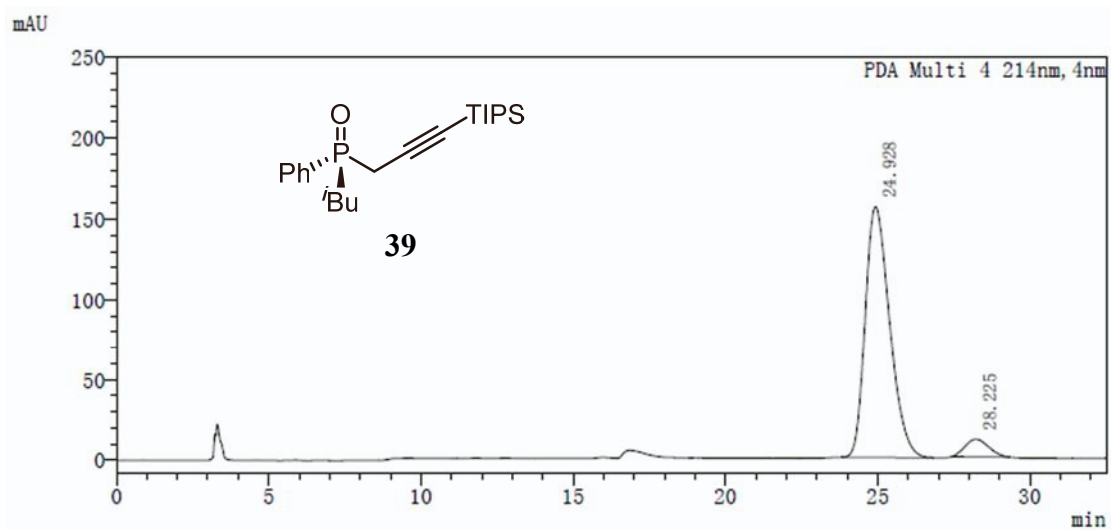
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 7.589     | 5230458 | 86.266 |
| 2     | 8.624     | 832704  | 13.734 |



Peak Table

PDA Ch4 214nm

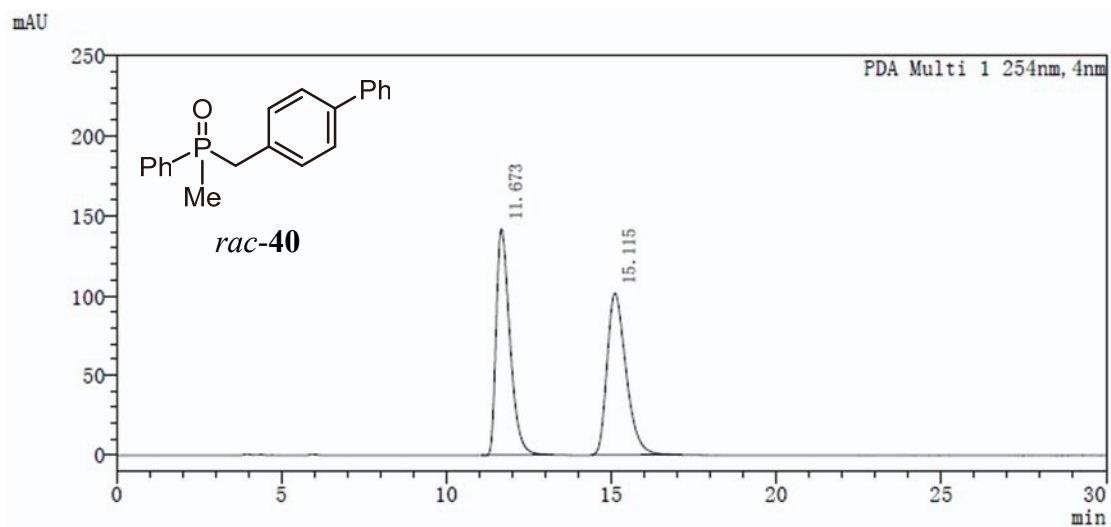
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 25.187    | 12204885 | 49.996 |
| 2     | 28.397    | 12207014 | 50.004 |



Peak Table

PDA Ch4 214nm

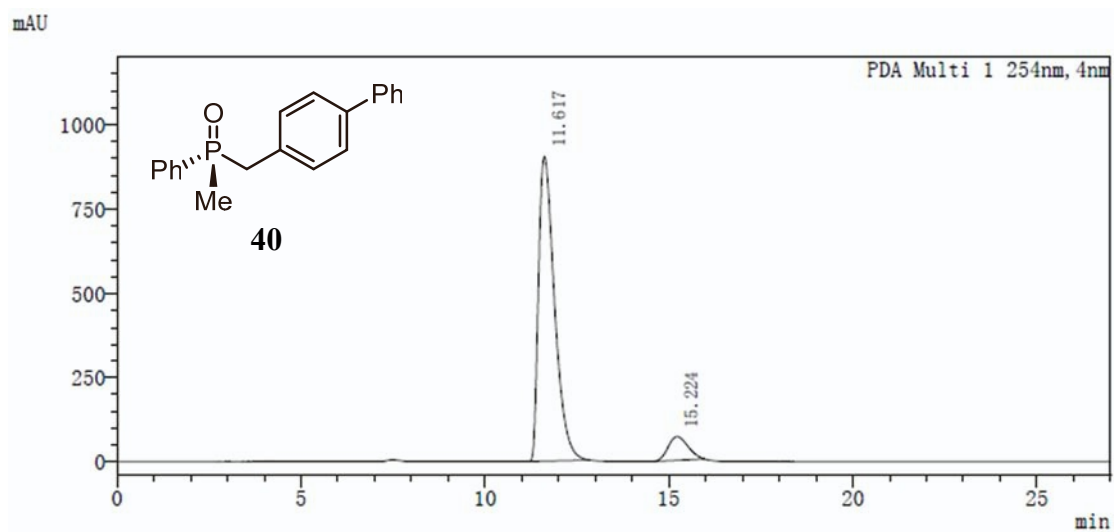
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 24.928    | 8693672 | 93.589 |
| 2     | 28.225    | 595496  | 6.411  |



Peak Table

PDA Ch1 254nm

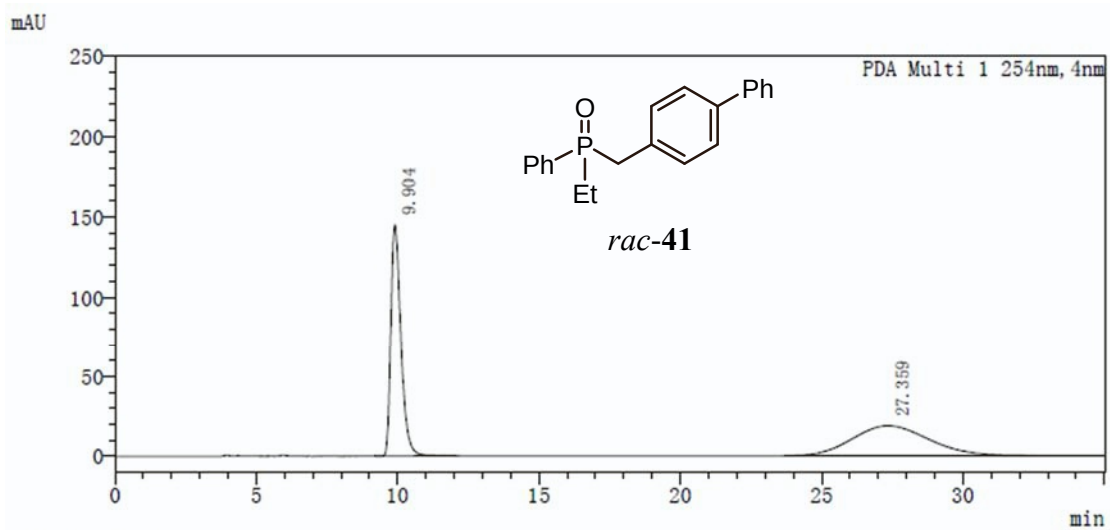
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 11.673    | 4083822 | 50.095 |
| 2     | 15.115    | 4068375 | 49.905 |



Peak Table

PDA Ch1 254nm

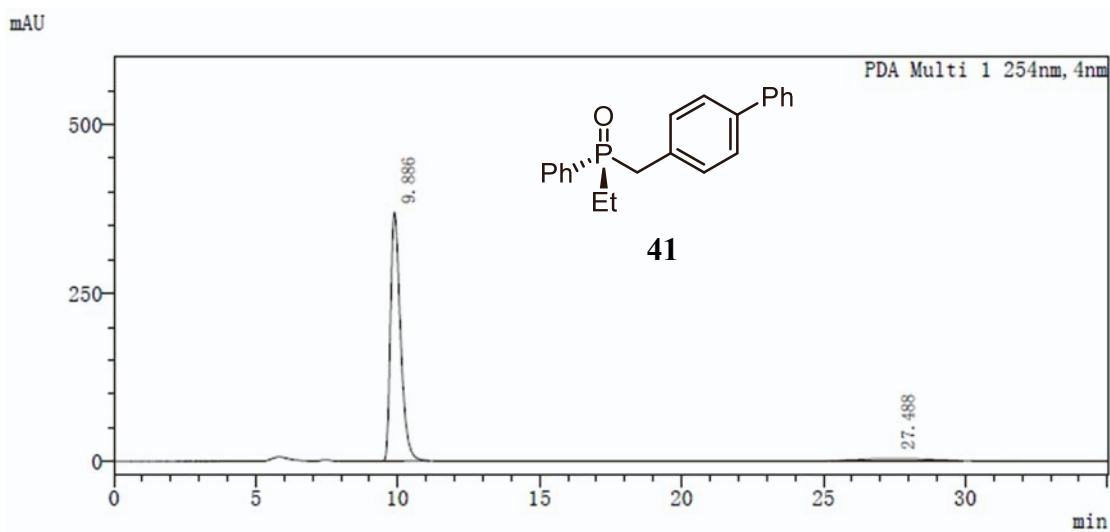
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 11.617    | 27390626 | 91.196 |
| 2     | 15.224    | 2644128  | 8.804  |



Peak Table

PDA Ch1 254nm

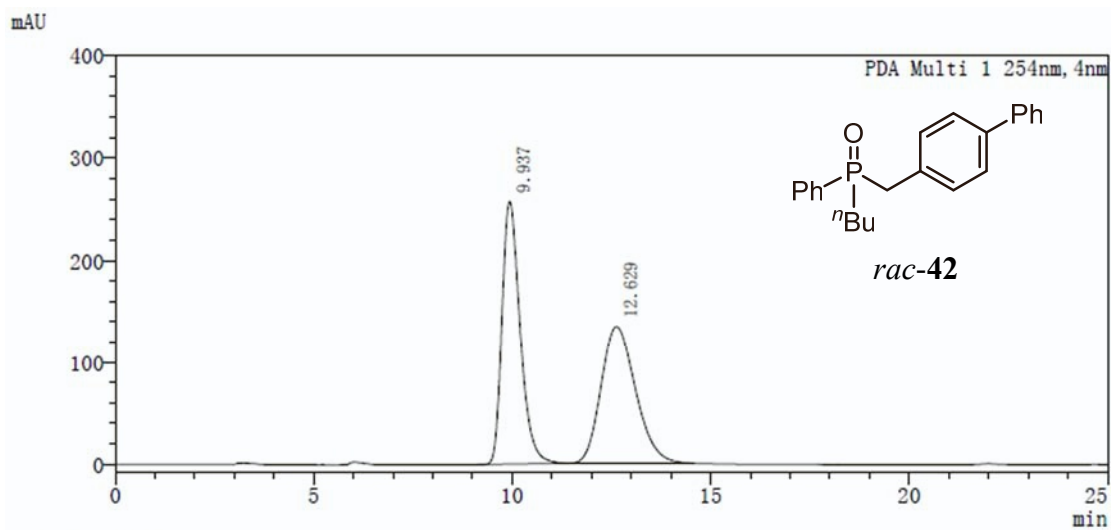
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 9.904     | 3581538 | 50.243 |
| 2     | 27.359    | 3546880 | 49.757 |



Peak Table

PDA Ch1 254nm

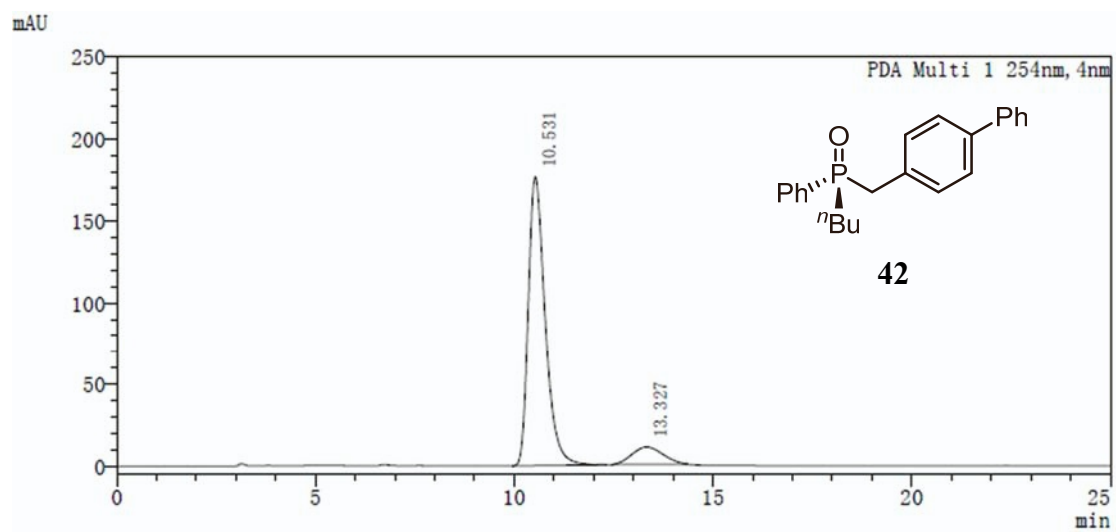
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 9.886     | 9050173 | 95.160 |
| 2     | 27.488    | 460341  | 4.840  |



Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 9.937     | 8171615 | 50.231 |
| 2     | 12.629    | 8096301 | 49.769 |

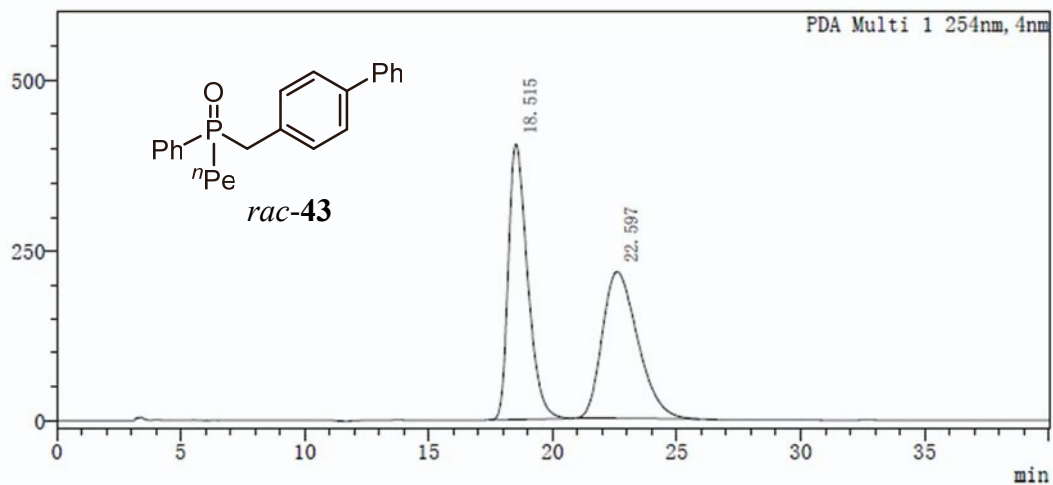


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 10.531    | 5227859 | 90.172 |
| 2     | 13.327    | 569764  | 9.828  |

mAU

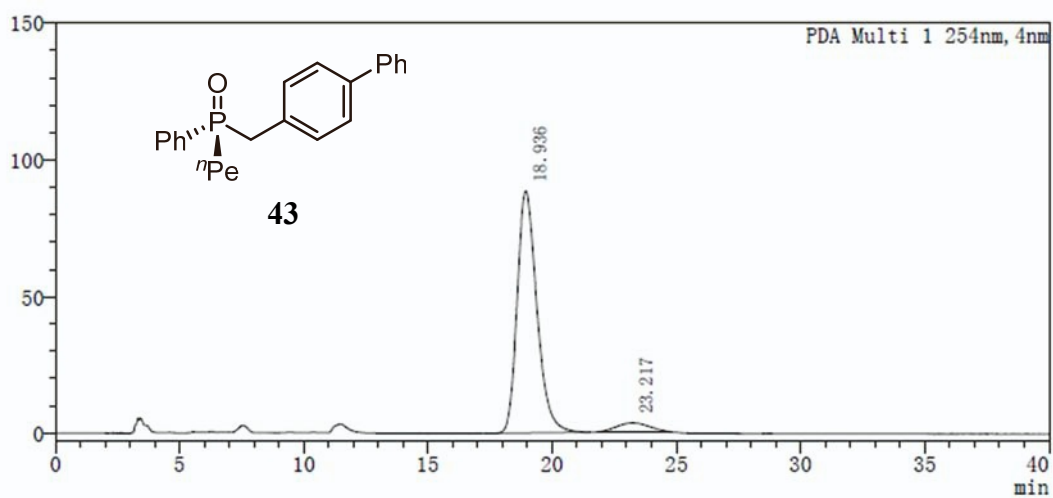


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 18.515    | 21883366 | 50.452 |
| 2     | 22.597    | 21491014 | 49.548 |

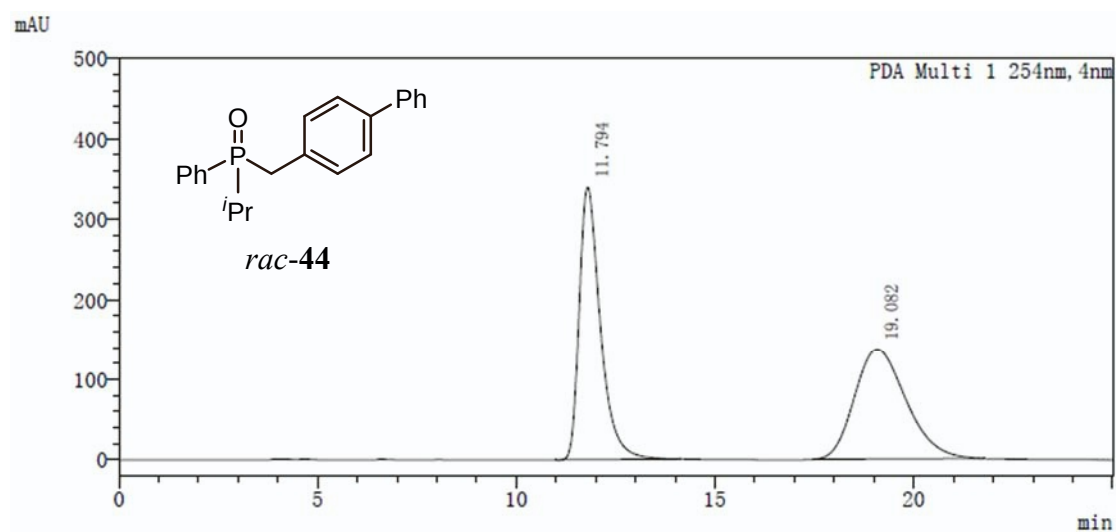
mAU



Peak Table

PDA Ch1 254nm

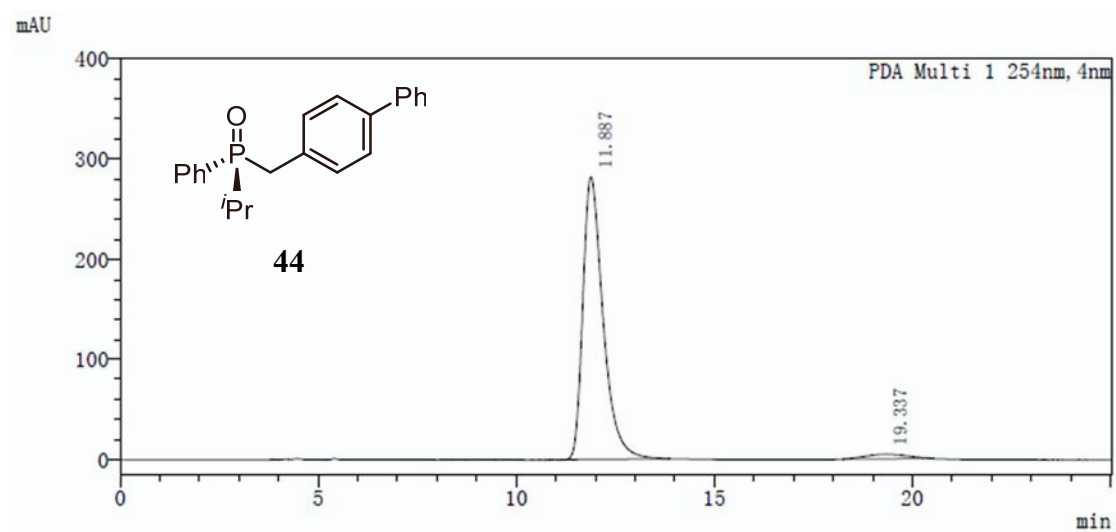
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 18.936    | 4910875 | 94.626 |
| 2     | 23.217    | 278884  | 5.374  |



Peak Table

PDA Ch1 254nm

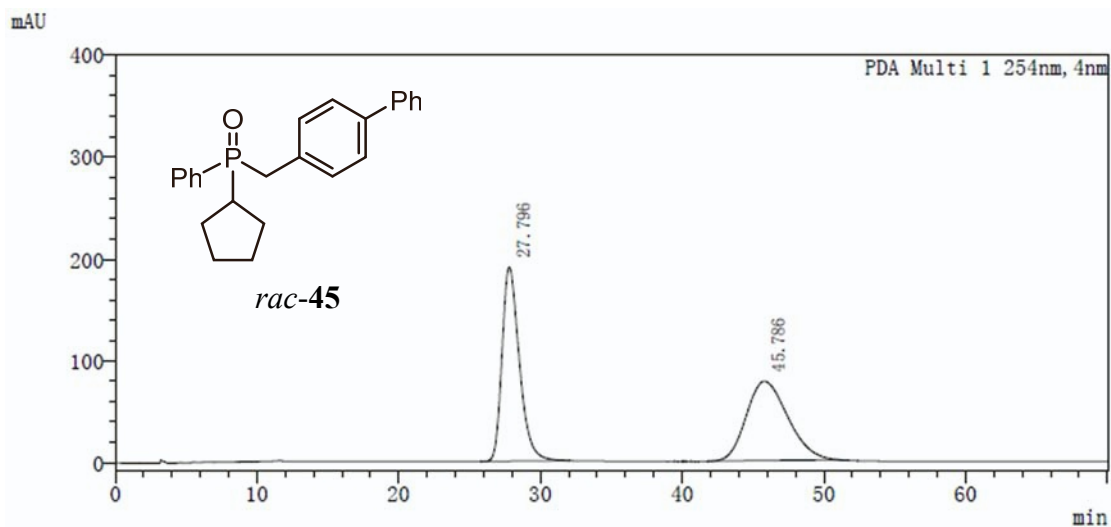
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 11.794    | 12556964 | 50.493 |
| 2     | 19.082    | 12311824 | 49.507 |



Peak Table

PDA Ch1 254nm

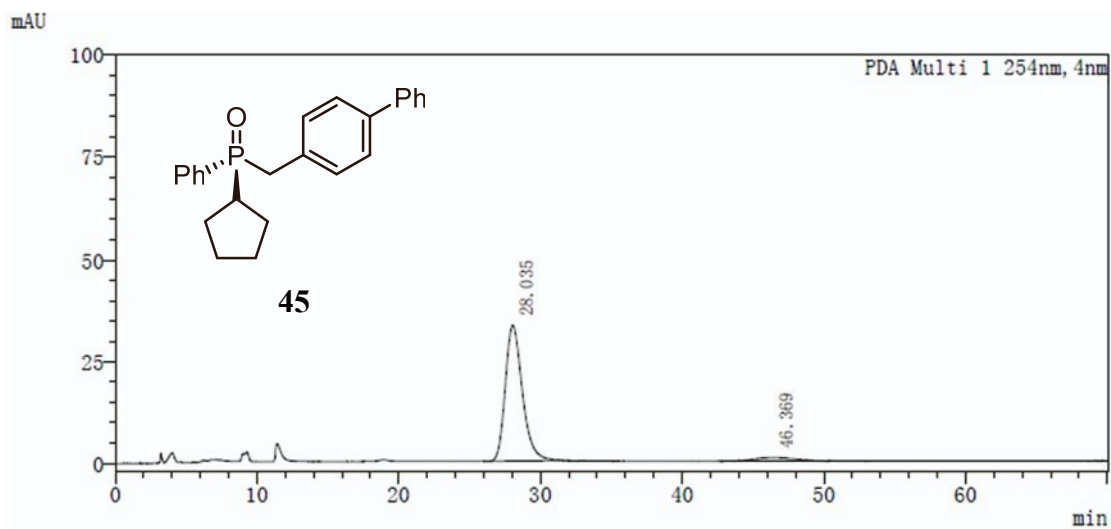
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 11.887    | 10015260 | 96.700 |
| 2     | 19.337    | 341766   | 3.300  |



Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 27.796    | 16196595 | 50.575 |
| 2     | 45.786    | 15828332 | 49.425 |

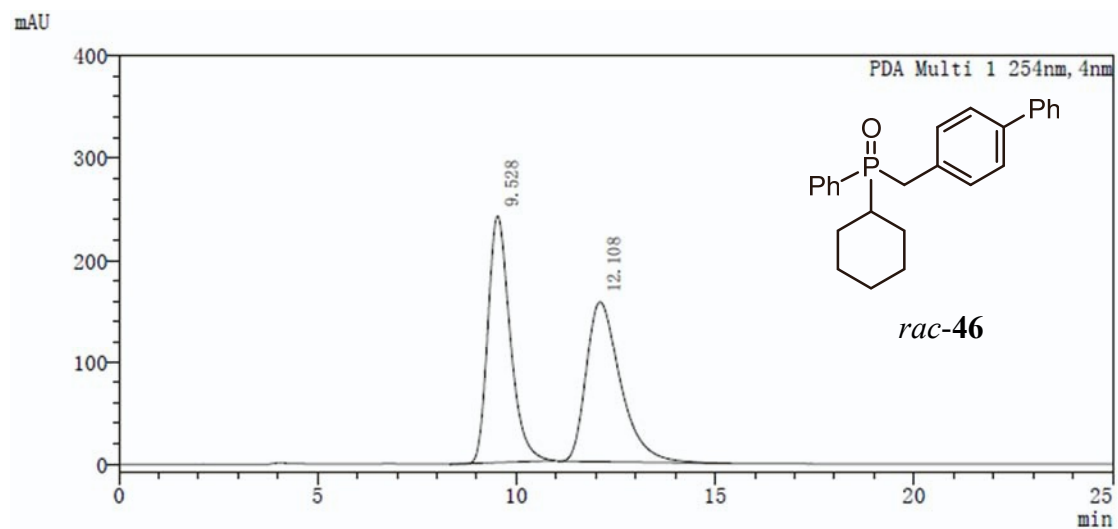


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 28.035    | 2799727 | 95.644 |
| 2     | 46.369    | 127505  | 4.356  |

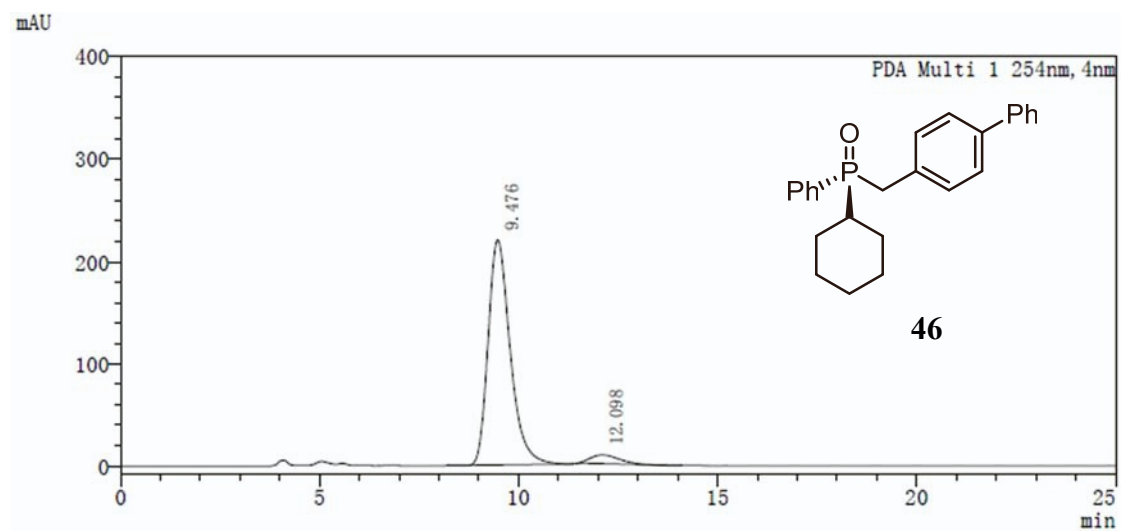




Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 9.528     | 9396377 | 50.012 |
| 2     | 12.108    | 9391872 | 49.988 |

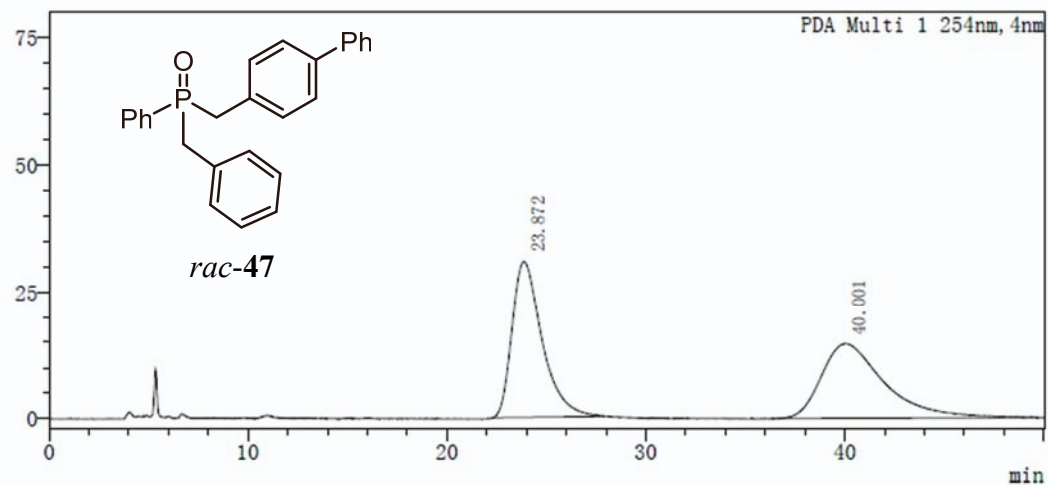


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 9.476     | 8493003 | 95.092 |
| 2     | 12.098    | 438373  | 4.908  |

mAU

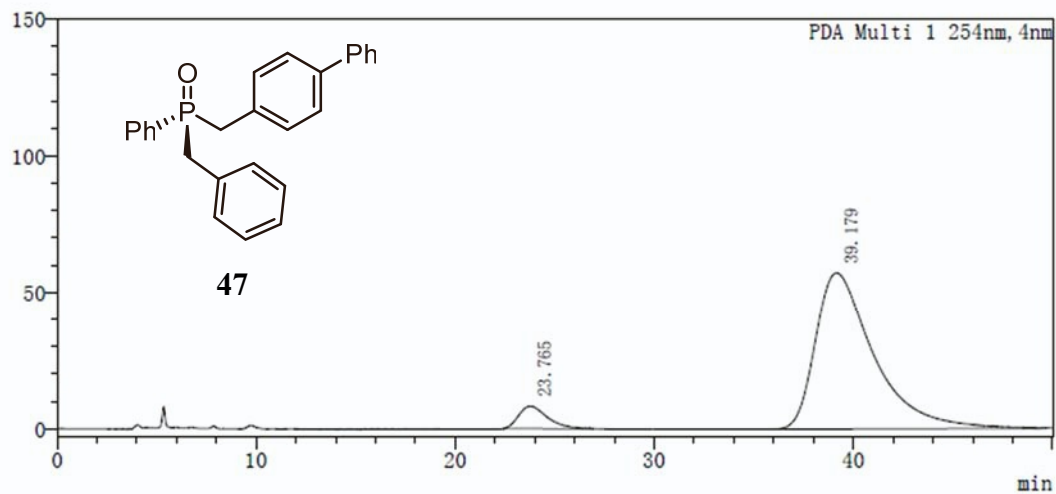


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 23.872    | 3224687 | 50.107 |
| 2     | 40.001    | 3210926 | 49.893 |

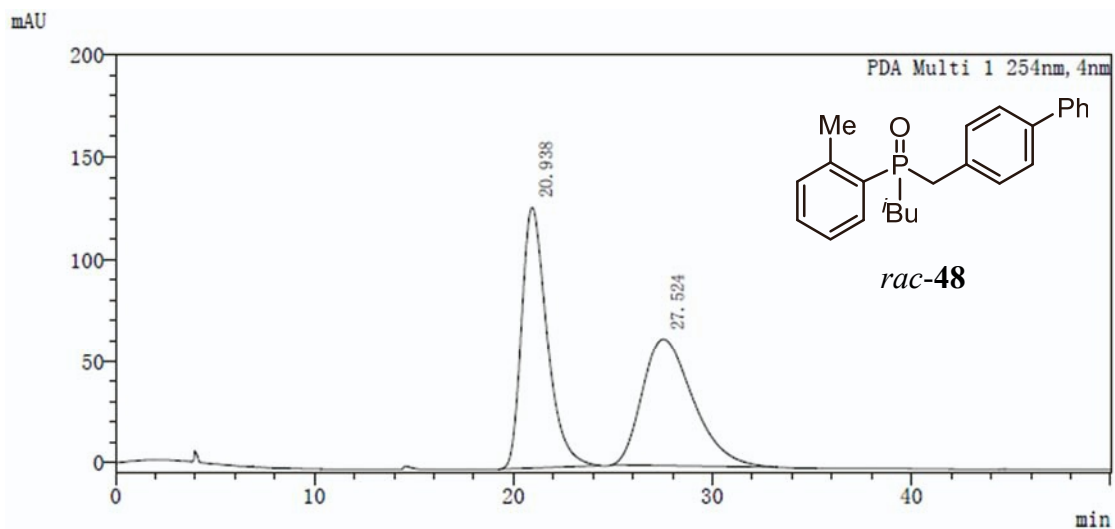
mAU



Peak Table

PDA Ch1 254nm

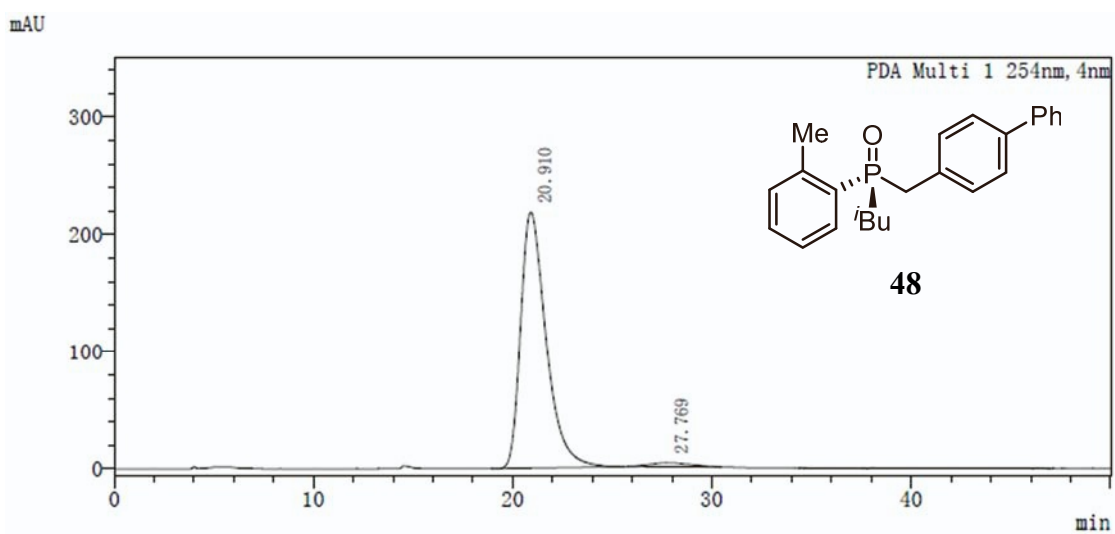
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 23.765    | 820422   | 6.591  |
| 2     | 39.179    | 11627455 | 93.409 |



Peak Table

PDA Ch1 254nm

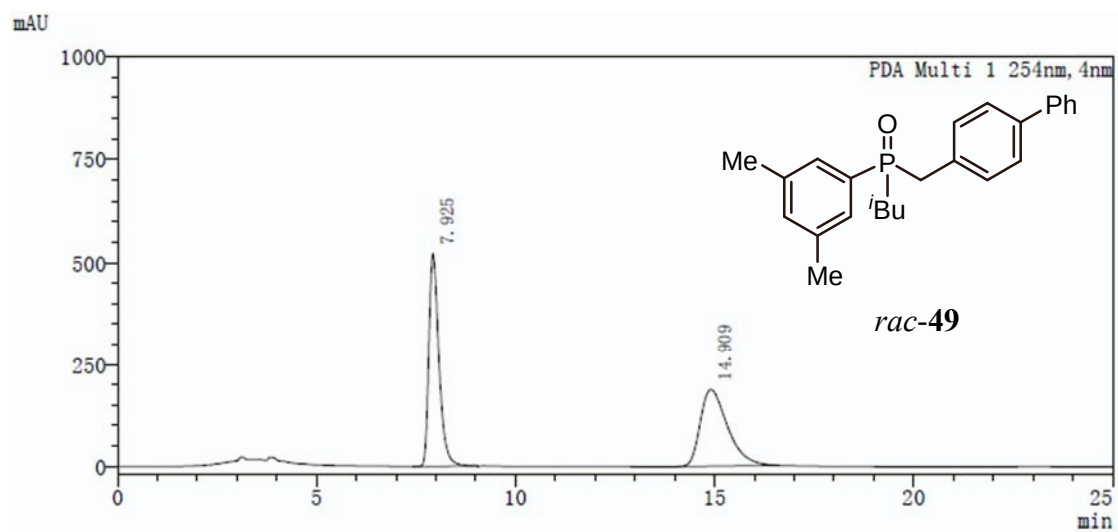
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 20.938    | 11423014 | 50.804 |
| 2     | 27.524    | 11061309 | 49.196 |



Peak Table

PDA Ch1 254nm

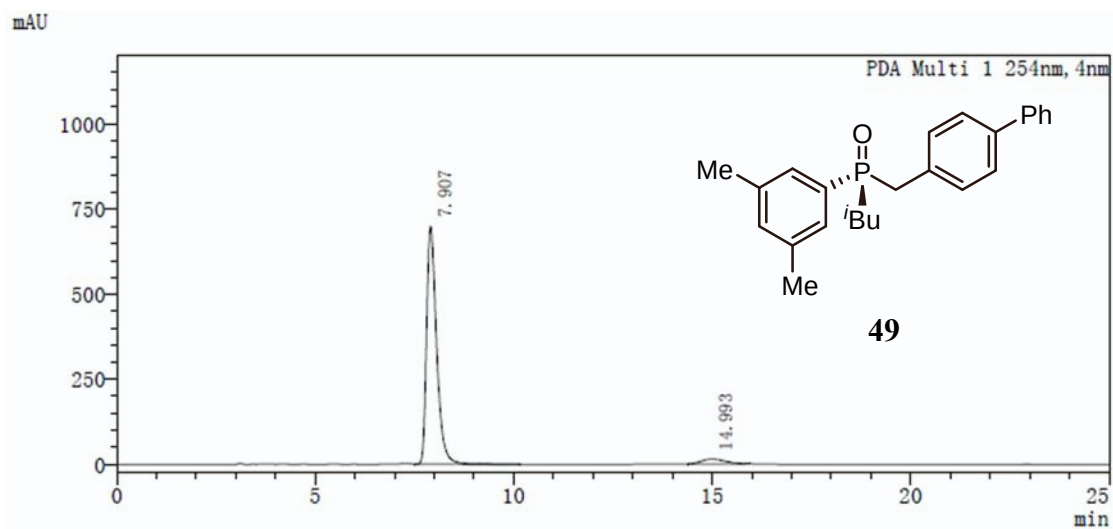
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 20.910    | 19411804 | 97.660 |
| 2     | 27.769    | 465211   | 2.340  |



Peak Table

PDA Ch1 254nm

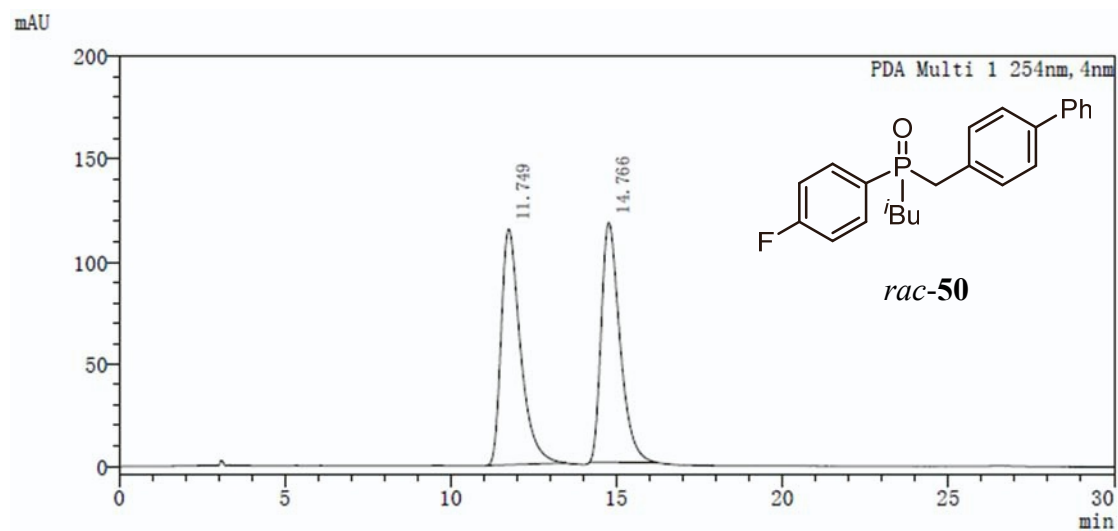
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 7.925     | 9212249 | 50.752 |
| 2     | 14.909    | 8939321 | 49.248 |



Peak Table

PDA Ch1 254nm

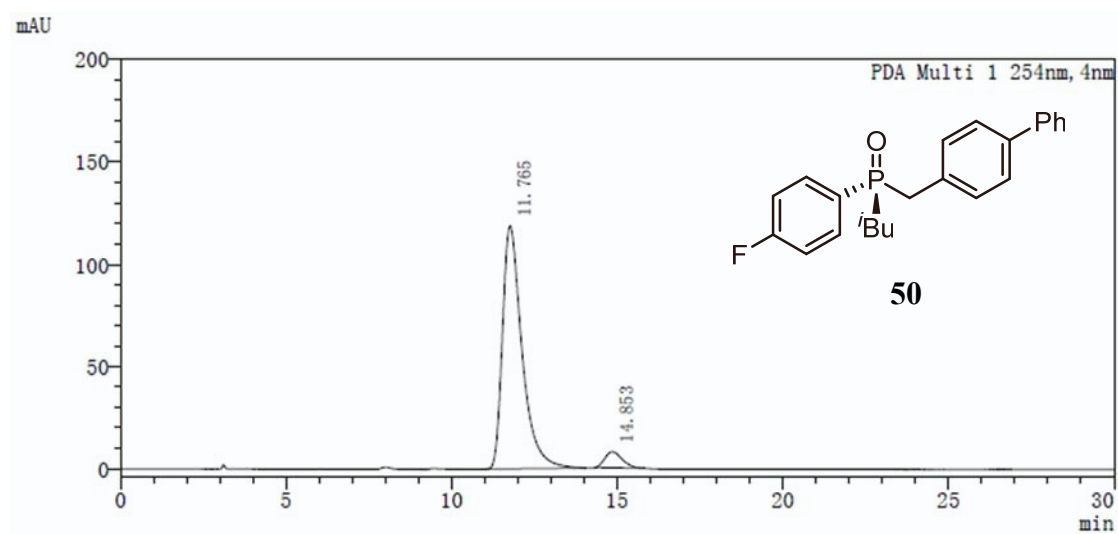
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 7.907     | 12246253 | 95.260 |
| 2     | 14.993    | 609410   | 4.740  |



Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 11.749    | 4656555 | 50.458 |
| 2     | 14.766    | 4572049 | 49.542 |

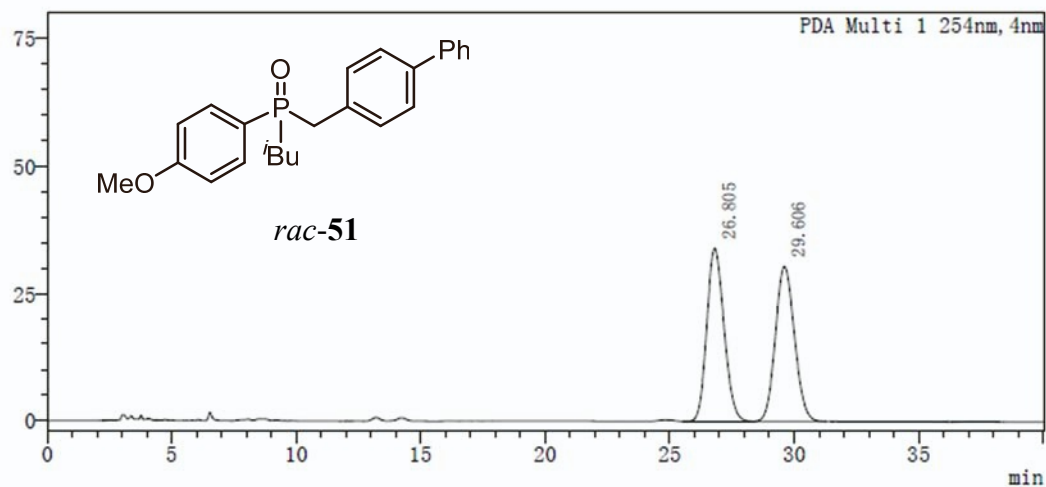


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 11.765    | 4874298 | 94.503 |
| 2     | 14.853    | 283525  | 5.497  |

mAU

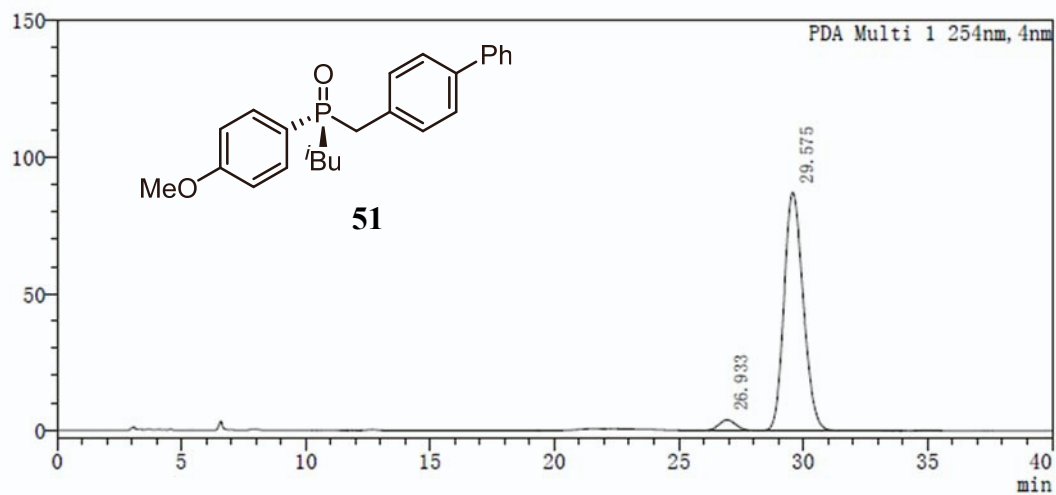


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 26.805    | 1629939 | 50.184 |
| 2     | 29.606    | 1617967 | 49.816 |

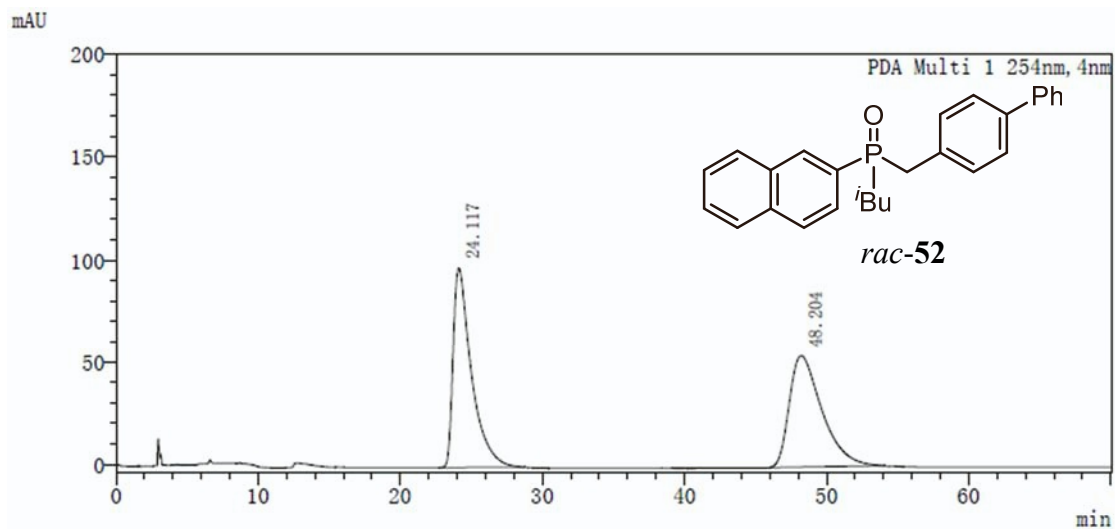
mAU



Peak Table

PDA Ch1 254nm

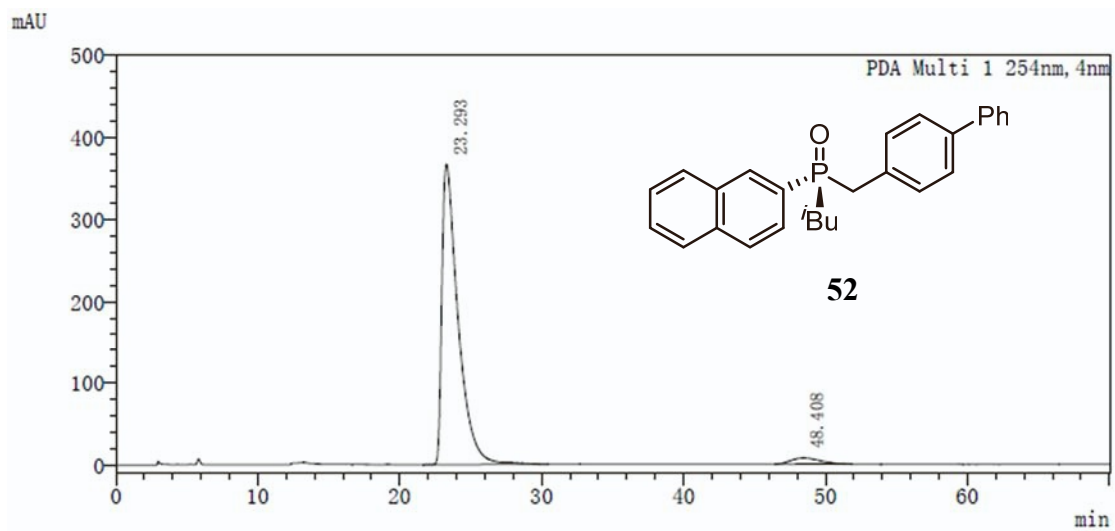
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 26.933    | 169575  | 3.486  |
| 2     | 29.575    | 4694499 | 96.514 |



Peak Table

PDA Ch1 254nm

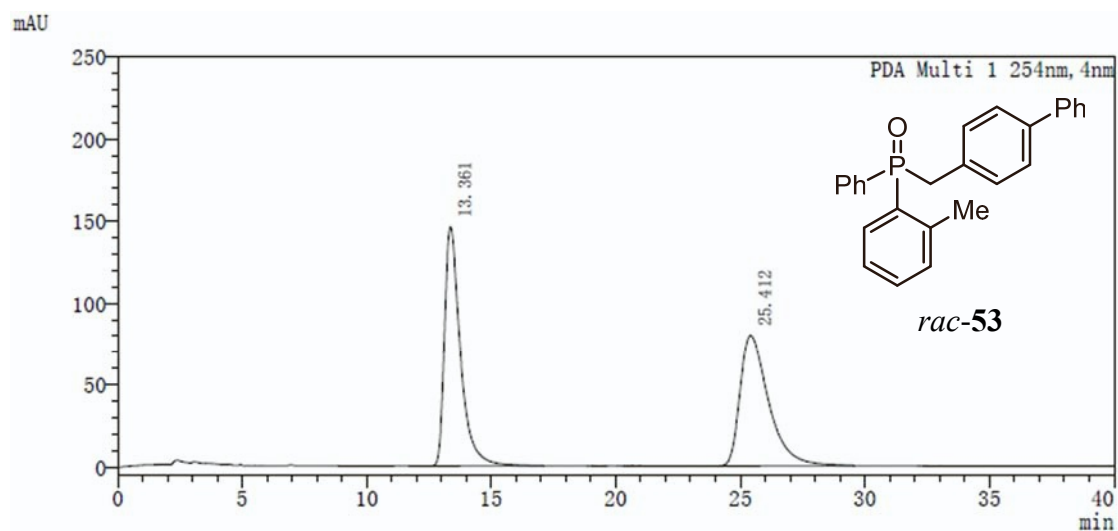
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 24.117    | 8734348 | 50.282 |
| 2     | 48.204    | 8636330 | 49.718 |



Peak Table

PDA Ch1 254nm

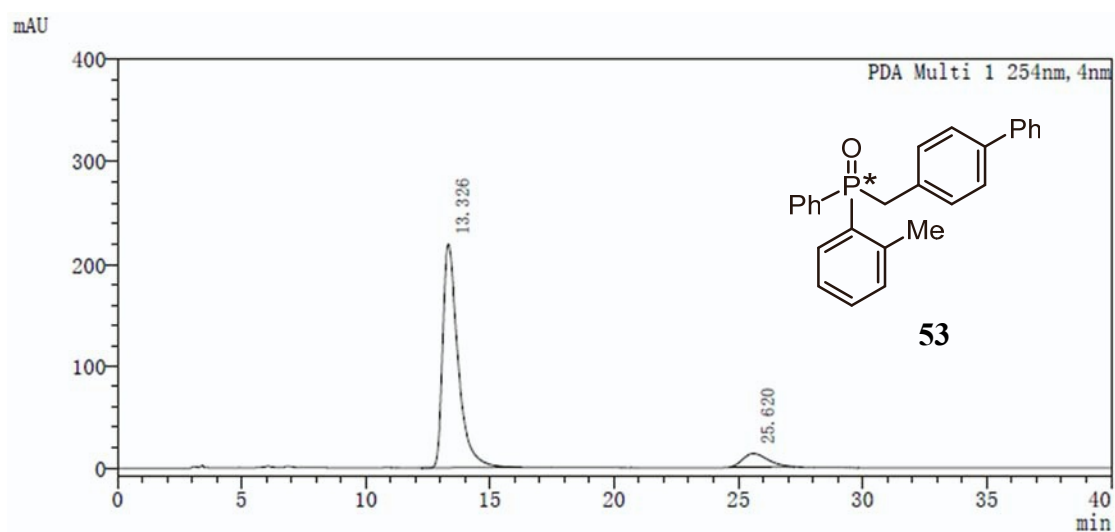
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 23.293    | 29115007 | 96.523 |
| 2     | 48.408    | 1048931  | 3.477  |



Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 13.361    | 6430462 | 50.398 |
| 2     | 25.412    | 6328869 | 49.602 |

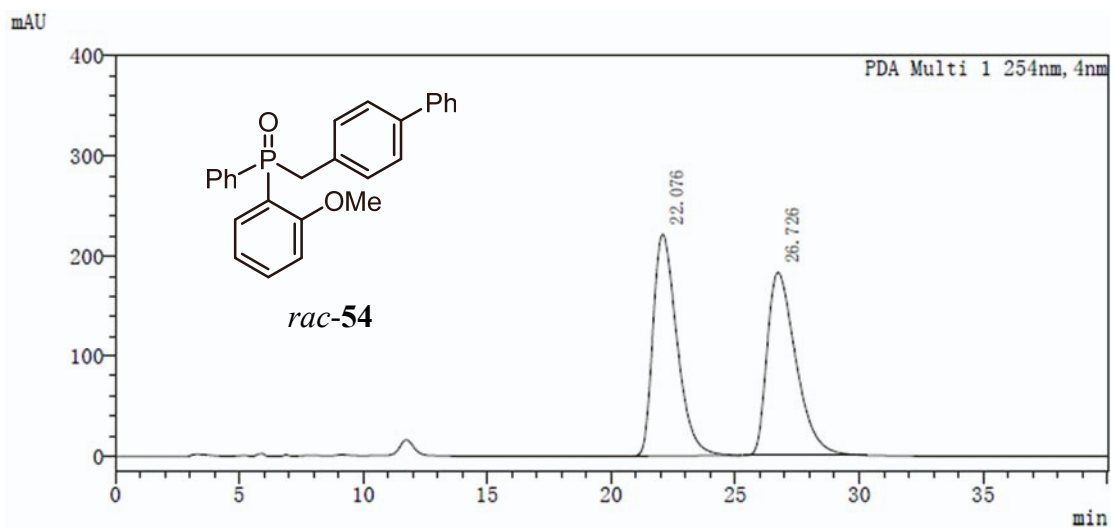


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 13.326    | 9360632 | 91.040 |
| 2     | 25.620    | 921289  | 8.960  |

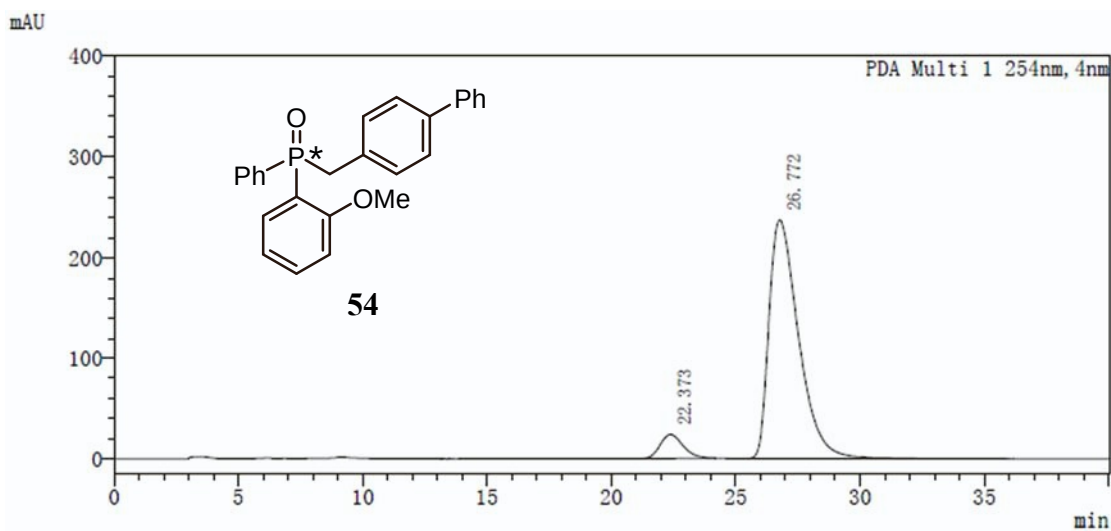




Peak Table

PDA Ch1 254nm

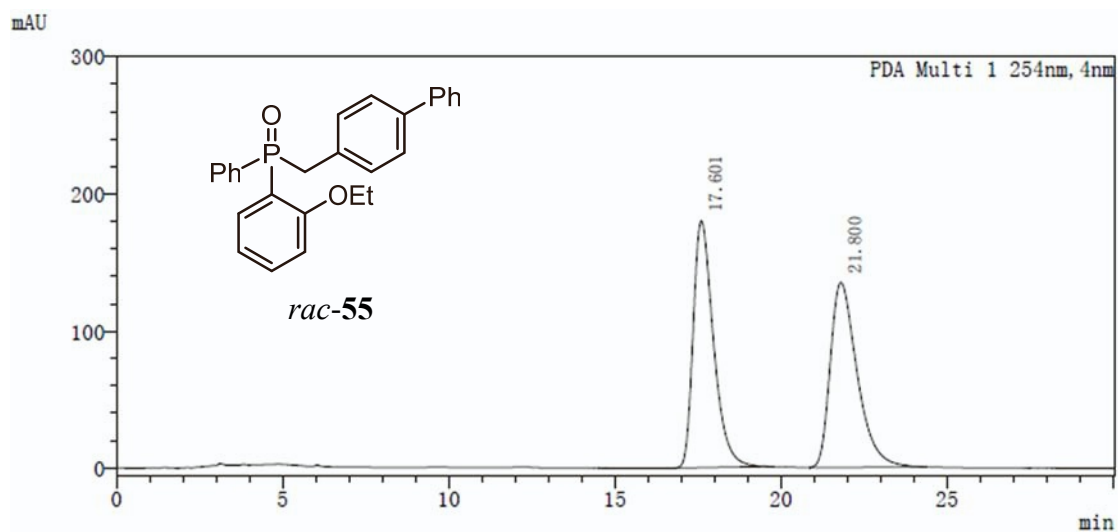
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 22.076    | 14888936 | 50.155 |
| 2     | 26.726    | 14796877 | 49.845 |



Peak Table

PDA Ch1 254nm

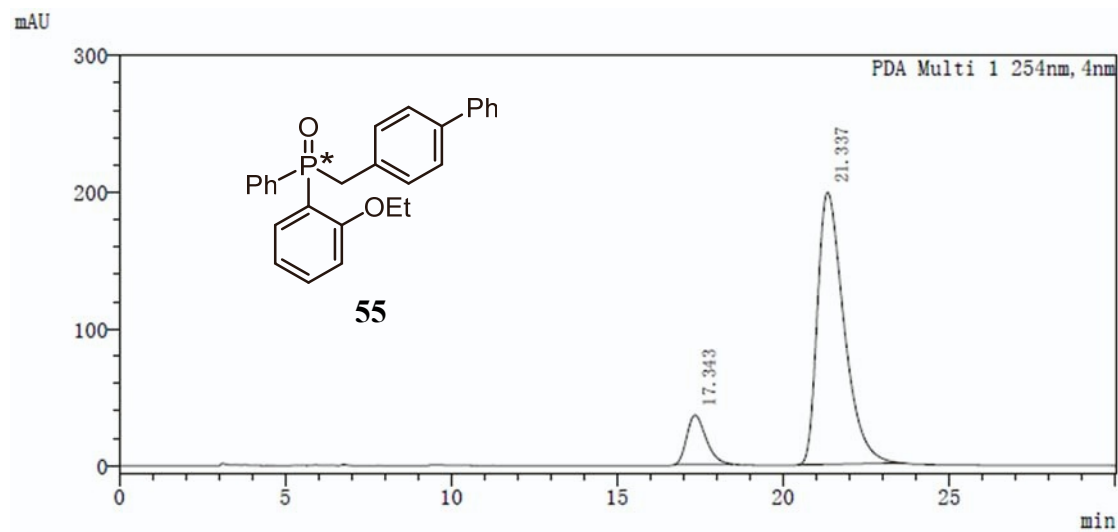
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 22.373    | 1530417  | 7.211  |
| 2     | 26.772    | 19692310 | 92.789 |



Peak Table

PDA Ch1 254nm

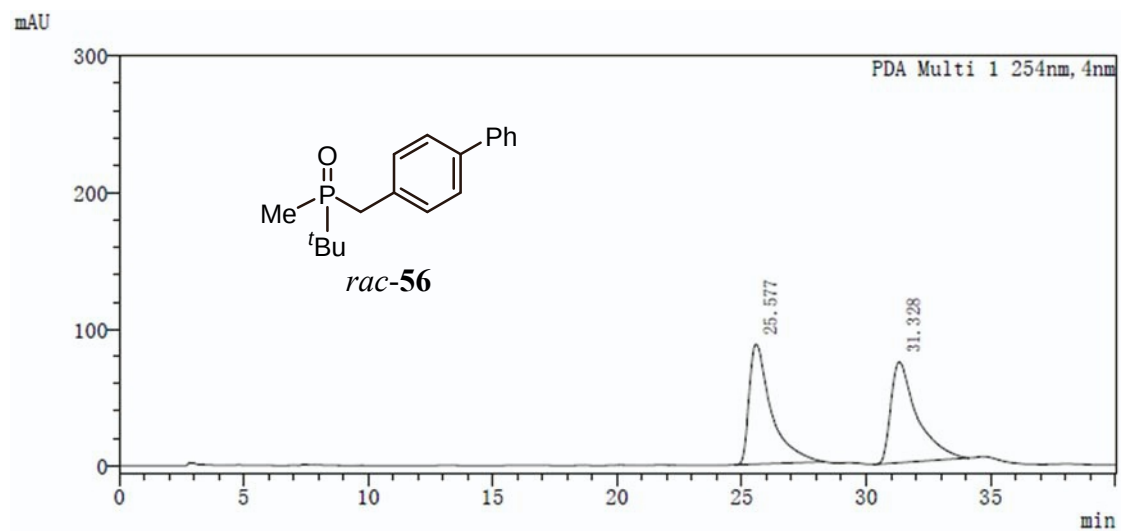
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 17.601    | 7674398 | 50.194 |
| 2     | 21.800    | 7615052 | 49.806 |



Peak Table

PDA Ch1 254nm

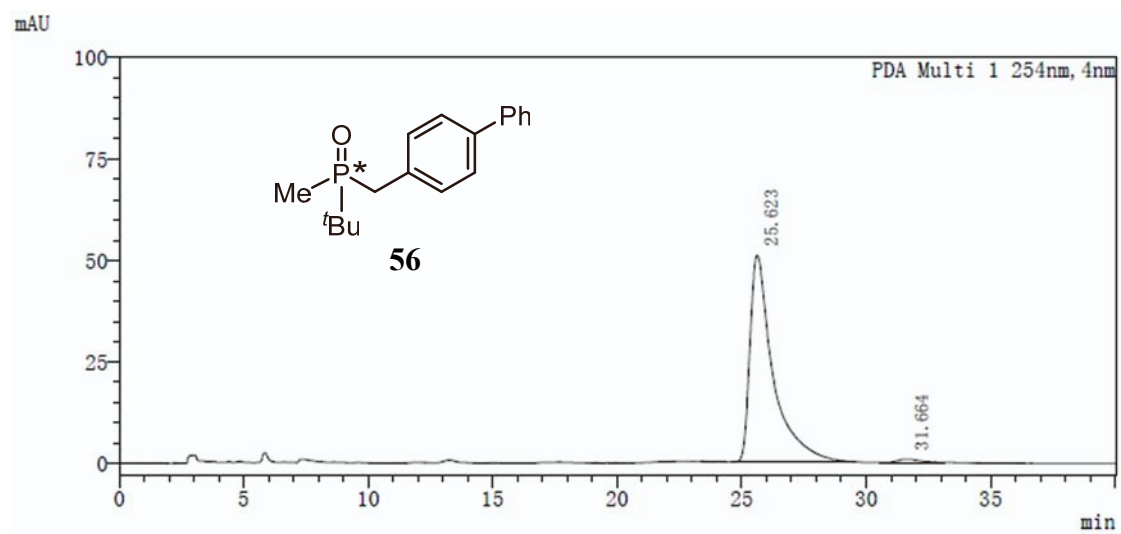
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 17.343    | 1431708  | 11.435 |
| 2     | 21.337    | 11088292 | 88.565 |



Peak Table

PDA Ch1 254nm

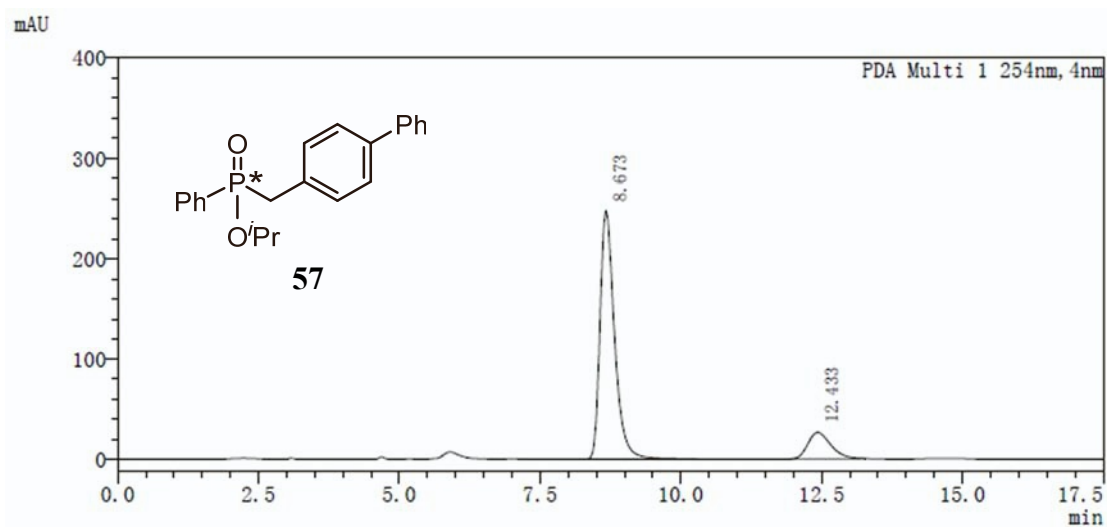
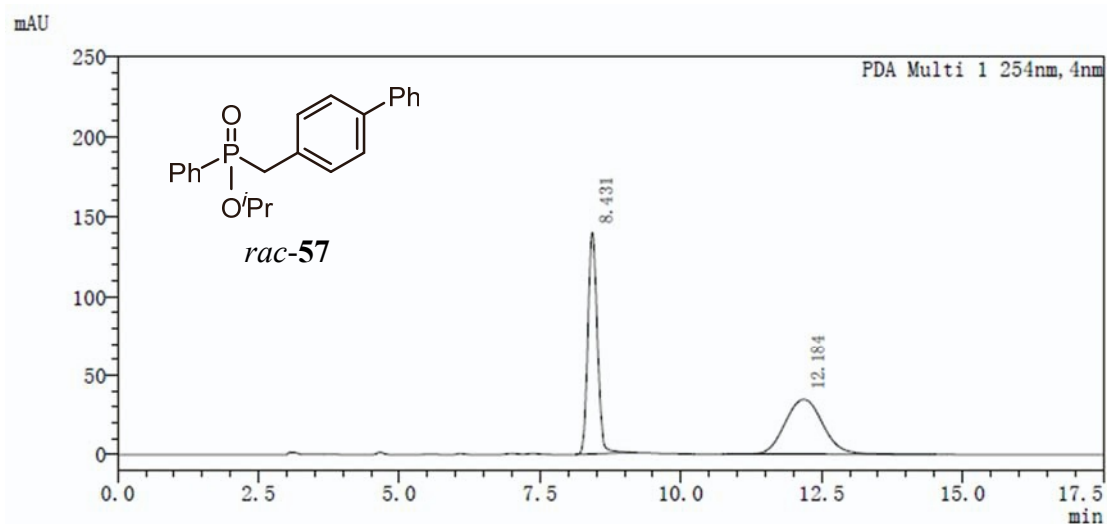
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 25.577    | 5432795 | 50.381 |
| 2     | 31.328    | 5350651 | 49.619 |



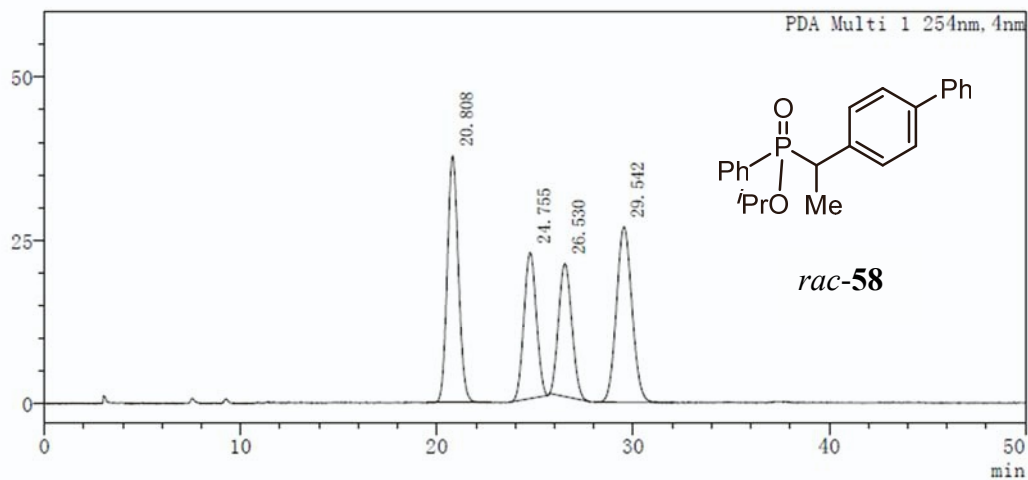
Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 25.623    | 3293042 | 98.487 |
| 2     | 31.664    | 50577   | 1.513  |



mAU

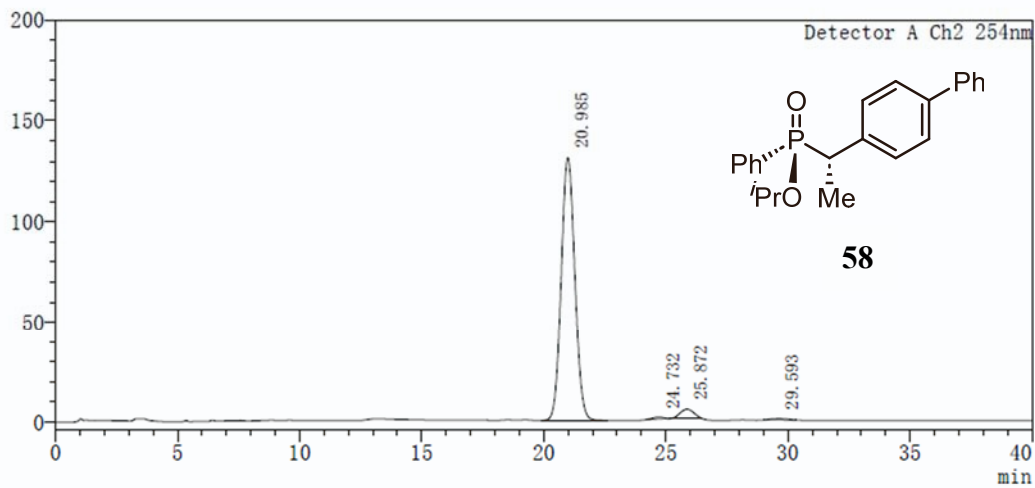


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 20.808    | 1486928 | 30.151 |
| 2     | 24.755    | 993231  | 20.140 |
| 3     | 26.530    | 965164  | 19.571 |
| 4     | 29.542    | 1486351 | 30.139 |

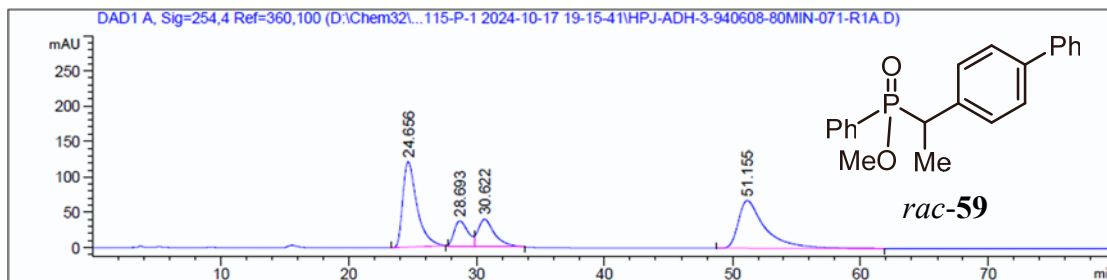
mV



Peak Table

Detector A Ch2 254nm

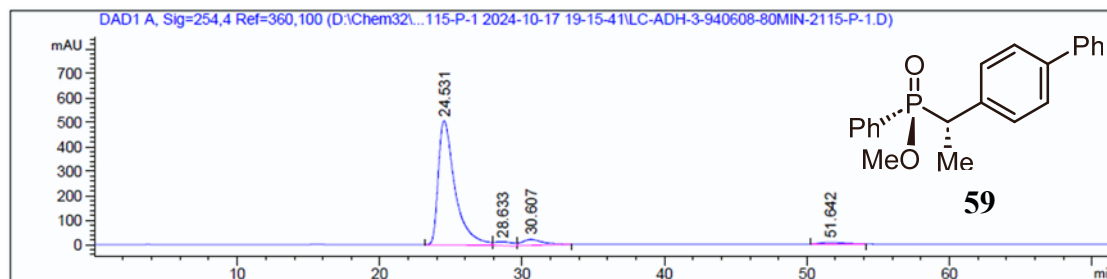
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 20.985    | 5092297 | 95.737 |
| 2     | 24.732    | 24585   | 0.462  |
| 3     | 25.872    | 171581  | 3.226  |
| 4     | 29.593    | 30592   | 0.575  |



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 24.656        | BB   | 1.1666      | 9365.63574   | 121.32452    | 36.9002 |
| 2      | 28.693        | MM R | 1.2522      | 2736.17944   | 36.41858     | 10.7804 |
| 3      | 30.622        | MM R | 1.4673      | 3413.40405   | 38.77080     | 13.4487 |
| 4      | 51.155        | BB   | 2.0593      | 9865.78809   | 67.89376     | 38.8708 |

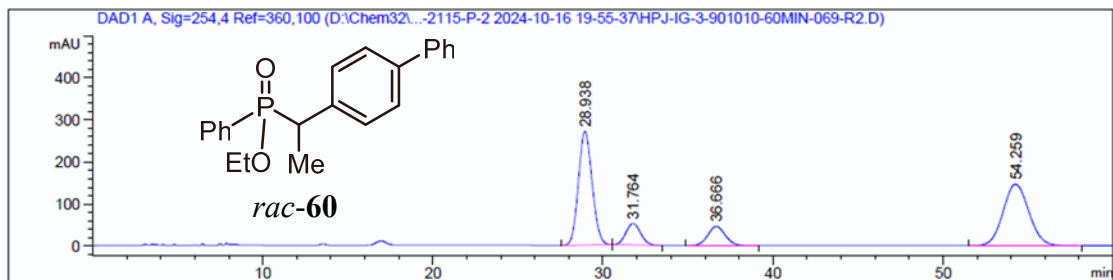
Totals : 2.53810e4 264.40767



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 24.531        | MM R | 1.3648      | 4.15894e4    | 507.89819    | 88.8362 |
| 2      | 28.633        | MM R | 1.5422      | 1444.31299   | 15.60857     | 3.0851  |
| 3      | 30.607        | MM R | 1.7106      | 2551.12988   | 24.85641     | 5.4493  |
| 4      | 51.642        | MM R | 2.3069      | 1230.97937   | 8.89338      | 2.6294  |

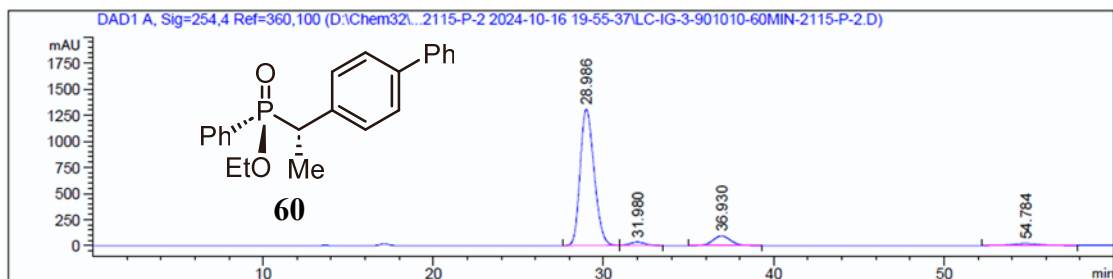
Totals : 4.68158e4 557.25656



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 28.938        | BB   | 0.8796      | 1.51956e4    | 269.58945    | 41.2383 |
| 2      | 31.764        | BB   | 0.9483      | 3111.00439   | 51.53547     | 8.4427  |
| 3      | 36.666        | BB   | 1.1076      | 3194.42432   | 45.14307     | 8.6691  |
| 4      | 54.259        | BB   | 1.6289      | 1.53472e4    | 146.18185    | 41.6498 |

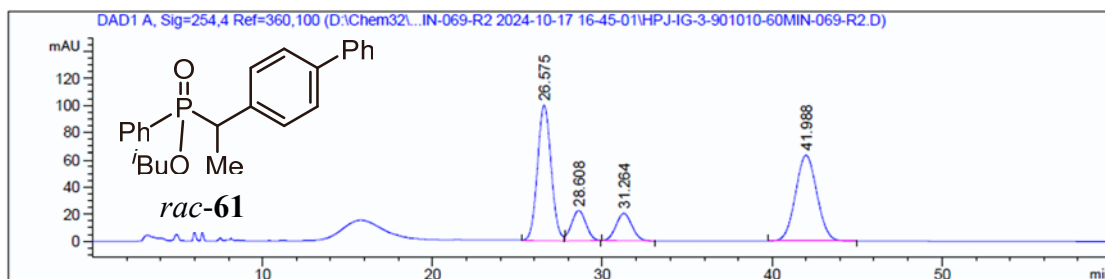
Totals : 3.68483e4 512.44985



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 28.986        | BB   | 0.8877      | 7.44298e4    | 1304.41589   | 87.7724 |
| 2      | 31.980        | BB   | 0.9308      | 1804.24194   | 30.56097     | 2.1277  |
| 3      | 36.930        | BB   | 1.1167      | 6539.55225   | 91.84570     | 7.7119  |
| 4      | 54.784        | BB   | 1.6323      | 2025.04761   | 18.86603     | 2.3881  |

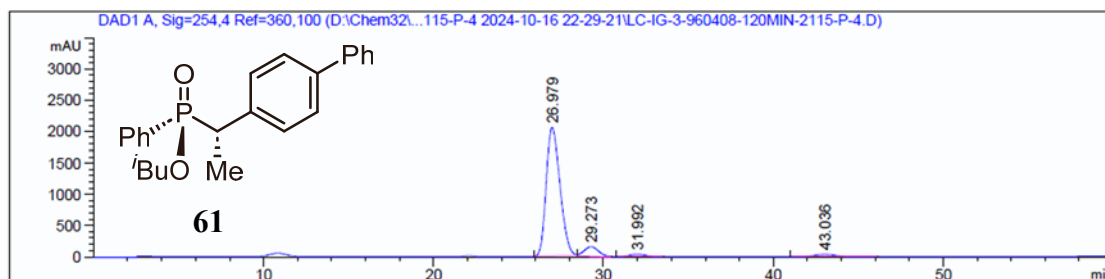
Totals : 8.47986e4 1445.68860



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 26.575        | MM R | 0.9334      | 5590.31836   | 99.81669     | 40.6489 |
| 2      | 28.608        | MM R | 0.9866      | 1324.00684   | 22.36656     | 9.6273  |
| 3      | 31.264        | BB   | 1.0010      | 1300.50769   | 20.14944     | 9.4564  |
| 4      | 41.988        | BB   | 1.3742      | 5537.85938   | 63.32793     | 40.2675 |

Totals : 1.37527e4 205.66061

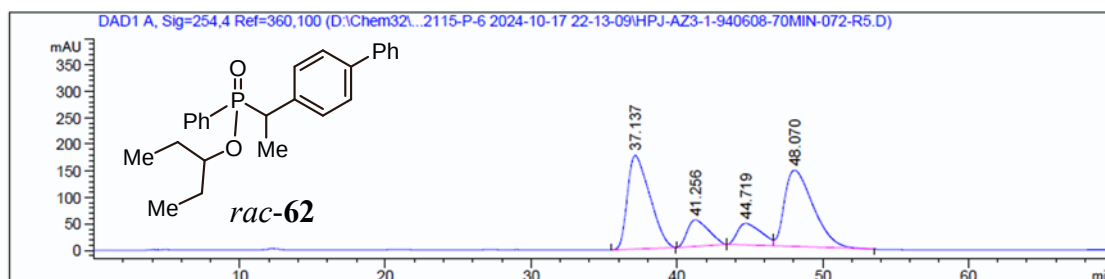


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 26.979        | MM R | 0.9381      | 1.15167e5    | 2046.20093   | 88.3445 |
| 2      | 29.273        | MM R | 0.9938      | 9258.58203   | 155.26587    | 7.1023  |
| 3      | 31.992        | BB   | 1.0043      | 2554.61572   | 39.72242     | 1.9596  |
| 4      | 43.036        | BB   | 1.3779      | 3381.00903   | 38.00635     | 2.5936  |

Totals : 1.30361e5 2279.19556

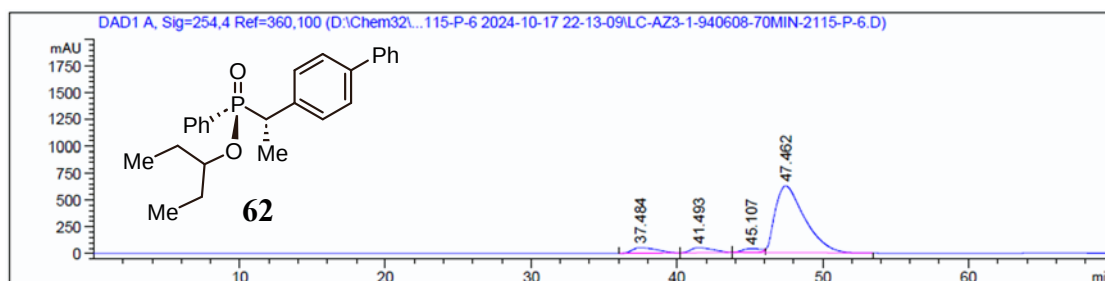




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 37.137        | BB   | 1.5652      | 1.88722e4    | 177.10635    | 38.9733 |
| 2      | 41.256        | BB   | 1.5150      | 5038.50635   | 50.02895     | 10.4051 |
| 3      | 44.719        | BV   | 1.6593      | 4661.32861   | 40.84851     | 9.6262  |
| 4      | 48.070        | VB   | 2.0762      | 1.98514e4    | 144.73044    | 40.9954 |

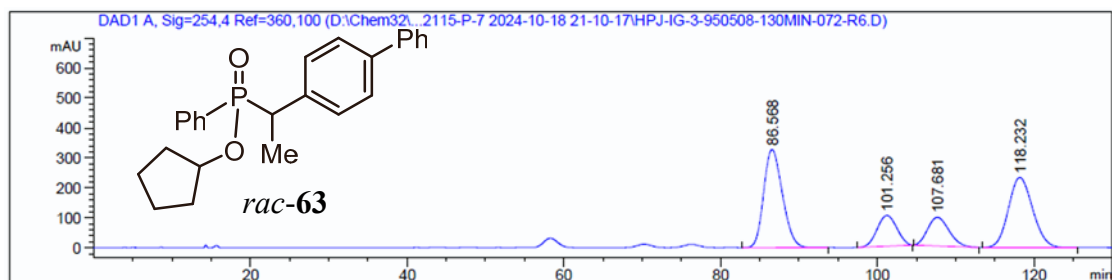
Totals : 4.84235e4 412.71425



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 37.484        | BB   | 1.8359      | 5936.03076   | 51.15084     | 5.7743  |
| 2      | 41.493        | BB   | 1.5476      | 5020.10449   | 47.47585     | 4.8833  |
| 3      | 45.107        | BV E | 1.3108      | 3119.84888   | 37.18665     | 3.0348  |
| 4      | 47.462        | VB R | 2.1522      | 8.87251e4    | 626.52502    | 86.3075 |

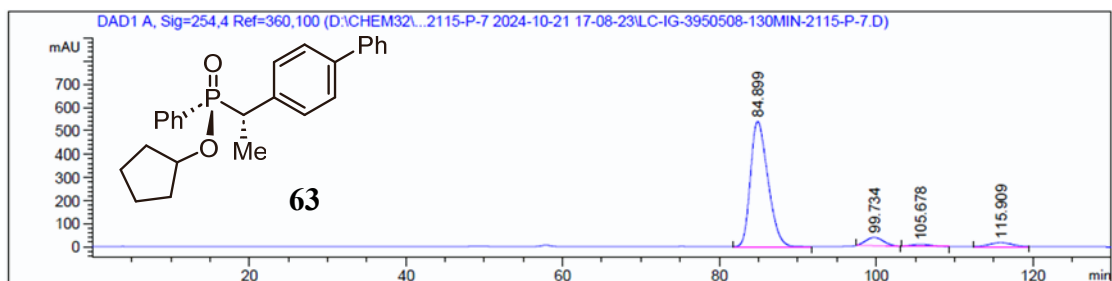
Totals : 1.02801e5 762.33836



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 86.568        | BB   | 2.5681      | 5.43974e4    | 327.45193    | 38.6634 |
| 2      | 101.256       | BB   | 2.7208      | 1.80349e4    | 103.00050    | 12.8185 |
| 3      | 107.681       | BB   | 2.7800      | 1.81266e4    | 95.43171     | 12.8836 |
| 4      | 118.232       | BB   | 3.3227      | 5.01360e4    | 233.15517    | 35.6345 |

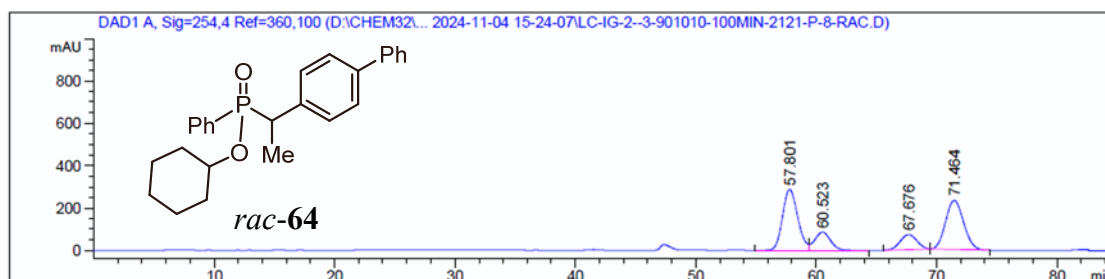
Totals : 1.40695e5 759.03931



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 84.899        | BB   | 2.3095      | 8.34828e4    | 538.83594    | 88.8314 |
| 2      | 99.734        | BB   | 2.1956      | 5514.51221   | 35.31912     | 5.8678  |
| 3      | 105.678       | MM R | 2.6994      | 1412.07715   | 8.71855      | 1.5025  |
| 4      | 115.909       | MM R | 3.3893      | 3569.57886   | 17.55322     | 3.7983  |

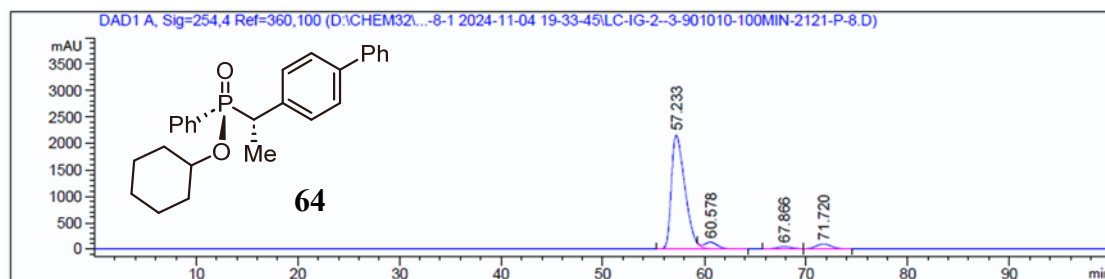
Totals : 9.39790e4 600.42683



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 57.801        | BV   | 1.3710      | 2.52643e4    | 289.24078    | 39.4174 |
| 2      | 60.523        | VB   | 1.3974      | 7766.55566   | 85.68923     | 12.1174 |
| 3      | 67.676        | BB   | 1.5057      | 6832.65967   | 71.06494     | 10.6603 |
| 4      | 71.464        | BB   | 1.6543      | 2.42308e4    | 232.79332    | 37.8049 |

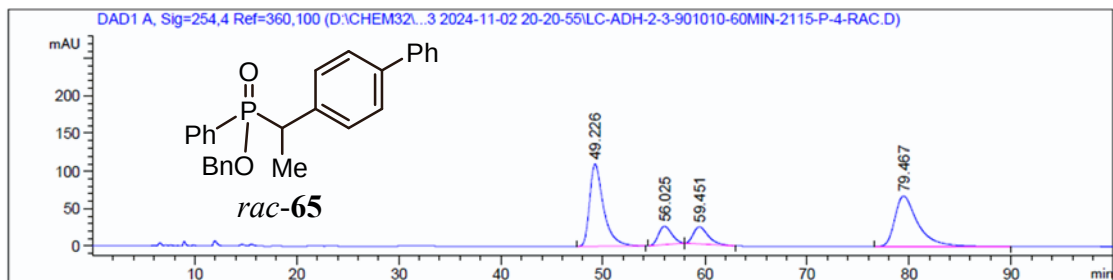
Totals : 6.40942e4 678.78828



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 57.233        | BV R | 1.4514      | 2.00968e5    | 2144.37866   | 89.3191 |
| 2      | 60.578        | VB E | 1.3430      | 1.04964e4    | 120.88974    | 4.6651  |
| 3      | 67.866        | BB   | 1.5208      | 4078.34302   | 41.56396     | 1.8126  |
| 4      | 71.720        | BB   | 1.6494      | 9457.18652   | 90.33115     | 4.2032  |

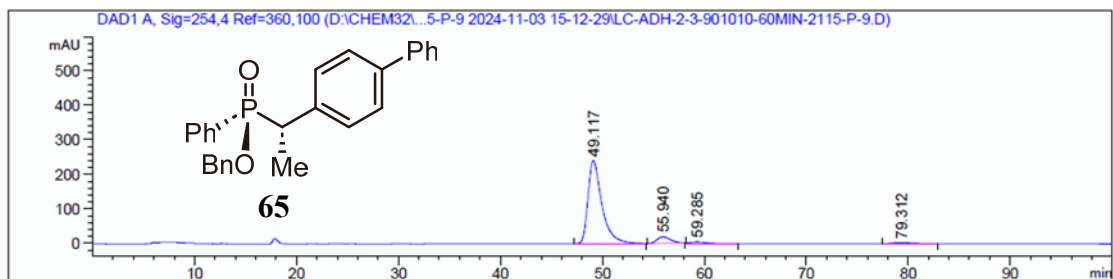
Totals : 2.25000e5 2397.16351



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.601         | BB   | 0.2772      | 68.82755     | 4.03125      | 0.2659  |
| 2      | 8.951         | BB   | 0.2394      | 98.16512     | 6.17762      | 0.3792  |
| 3      | 9.858         | BB   | 0.2511      | 19.81226     | 1.19689      | 0.0765  |
| 4      | 11.959        | BB   | 0.4112      | 187.69742    | 6.94716      | 0.7251  |
| 5      | 49.226        | BB   | 1.4243      | 1.04387e4    | 110.08164    | 40.3238 |
| 6      | 56.025        | BB   | 1.3820      | 2228.09204   | 24.71033     | 8.6069  |
| 7      | 59.451        | BB   | 1.4978      | 2300.53735   | 22.86599     | 8.8868  |
| 8      | 79.467        | BB   | 2.3073      | 1.05453e4    | 67.40092     | 40.7358 |

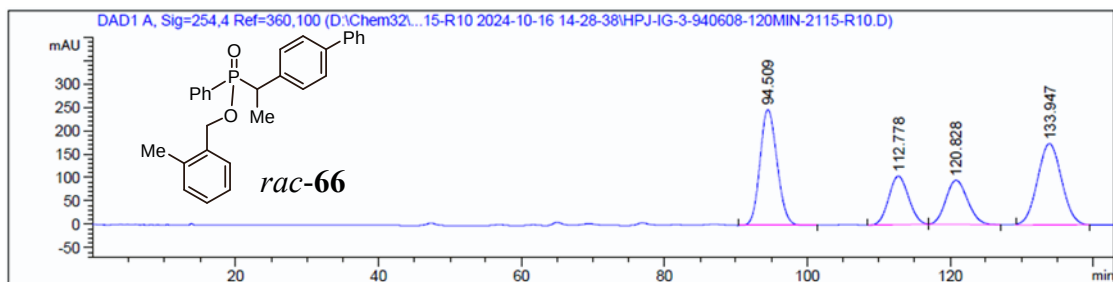
Totals : 2.58872e4 243.41180



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 49.117        | BB   | 1.4135      | 2.29612e4    | 242.30580    | 89.0403 |
| 2      | 55.940        | BB   | 1.3770      | 1719.88782   | 18.70096     | 6.6695  |
| 3      | 59.285        | MM R | 2.0848      | 688.09668    | 5.50092      | 2.6683  |
| 4      | 79.312        | MM R | 2.0721      | 418.22992    | 3.36402      | 1.6218  |

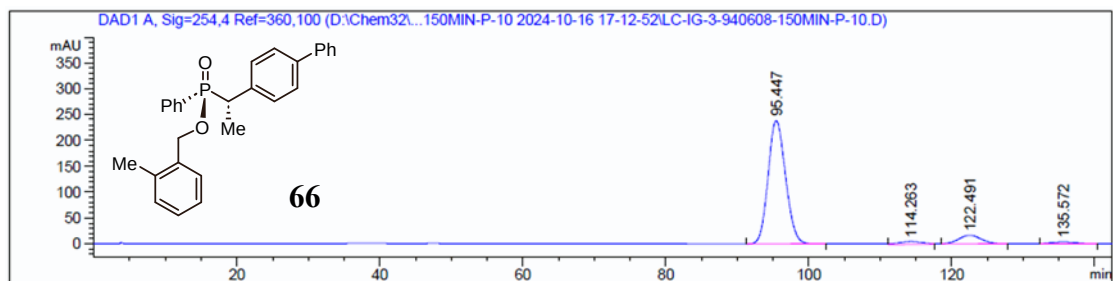
Totals : 2.57874e4 269.87170



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 94.509        | BB   | 2.5634      | 4.10770e4    | 247.61099    | 33.7950 |
| 2      | 112.778       | BB   | 2.8602      | 1.99352e4    | 103.81992    | 16.4011 |
| 3      | 120.828       | BB   | 3.1410      | 1.97197e4    | 94.01809     | 16.2239 |
| 4      | 133.947       | MM R | 3.9113      | 4.08156e4    | 173.92014    | 33.5799 |

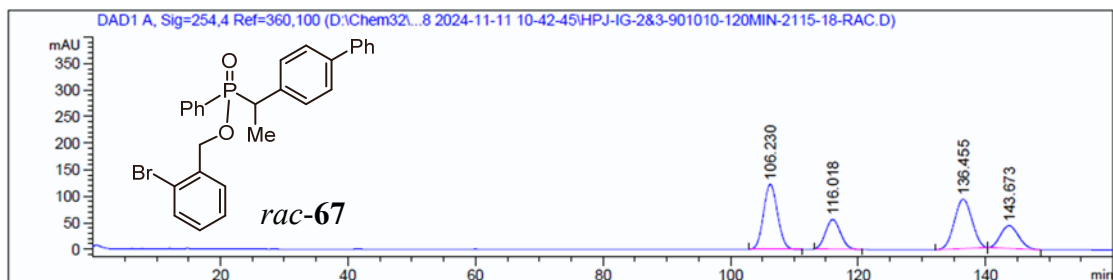
Totals : 1.21547e5 619.36914



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 95.447        | BB   | 2.5517      | 4.05377e4    | 238.65341    | 86.2981 |
| 2      | 114.263       | MM R | 2.8200      | 1410.38635   | 5.85077      | 3.0025  |
| 3      | 122.491       | MM R | 3.6810      | 3770.18384   | 17.07033     | 8.0261  |
| 4      | 135.572       | MM R | 4.5539      | 1255.78088   | 4.59603      | 2.6733  |

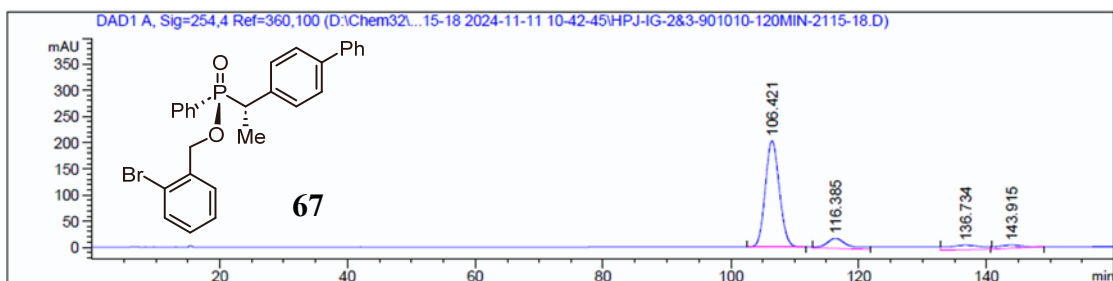
Totals : 4.69741e4 266.17054



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 106.421       | BB   | 2.2951      | 3.11074e4    | 203.30426    | 77.9934 |
| 2      | 116.385       | MM R | 3.6689      | 4230.47168   | 19.21782     | 10.6067 |
| 3      | 136.734       | MM R | 5.8690      | 3040.09424   | 8.63323      | 7.6222  |
| 4      | 143.915       | MM R | 3.0684      | 1506.71790   | 5.73998      | 3.7777  |

Totals : 3.98847e4 236.89529

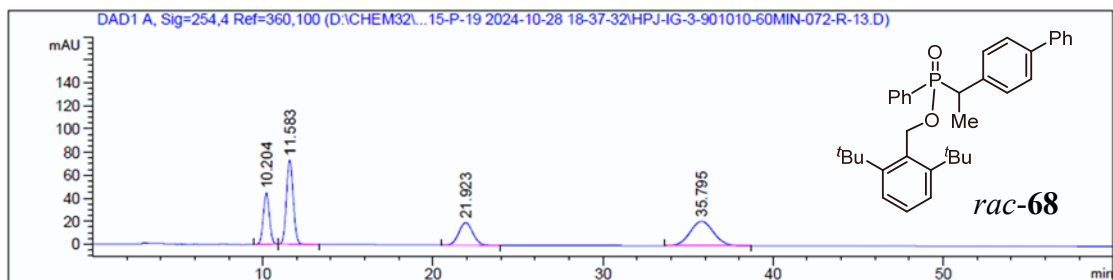


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 106.230       | BB   | 2.2591      | 1.88784e4    | 123.51855    | 34.7617 |
| 2      | 116.018       | BB   | 2.2887      | 9084.93359   | 55.70630     | 16.7285 |
| 3      | 136.455       | BB   | 2.8082      | 1.79011e4    | 93.30986     | 32.9620 |
| 4      | 143.673       | BB   | 2.5748      | 8443.72559   | 42.92826     | 15.5478 |

Totals : 5.43082e4 315.46297

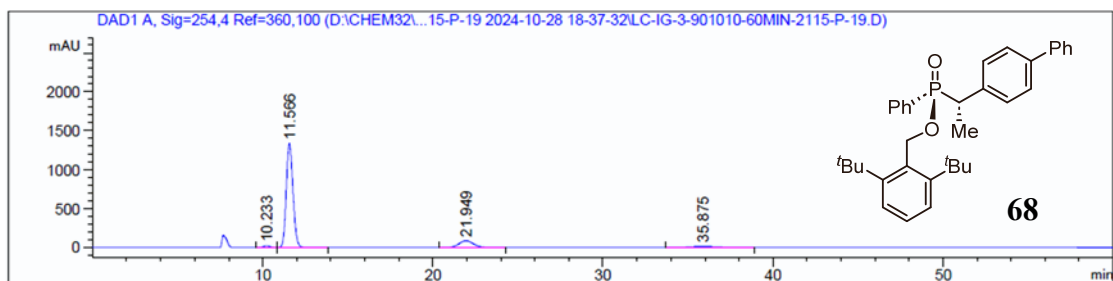




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 10.204        | BB   | 0.3911      | 1120.26843   | 44.58593     | 17.7108 |
| 2      | 11.583        | BB   | 0.4341      | 2038.22400   | 73.36964     | 32.2231 |
| 3      | 21.923        | BB   | 0.8869      | 1124.01331   | 19.66316     | 17.7700 |
| 4      | 35.795        | BB   | 1.4452      | 2042.85059   | 21.25703     | 32.2962 |

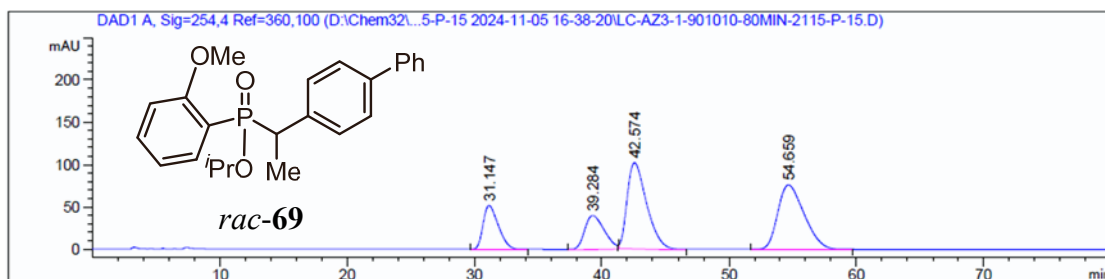
Totals : 6325.35632 158.87577



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 10.233        | BB   | 0.3721      | 498.49472    | 20.91133     | 1.1458  |
| 2      | 11.566        | BB   | 0.4293      | 3.67029e4    | 1332.72058   | 84.3650 |
| 3      | 21.949        | BB   | 0.8944      | 5007.10156   | 87.39074     | 11.5093 |
| 4      | 35.875        | BB   | 1.3987      | 1296.36975   | 13.14323     | 2.9798  |

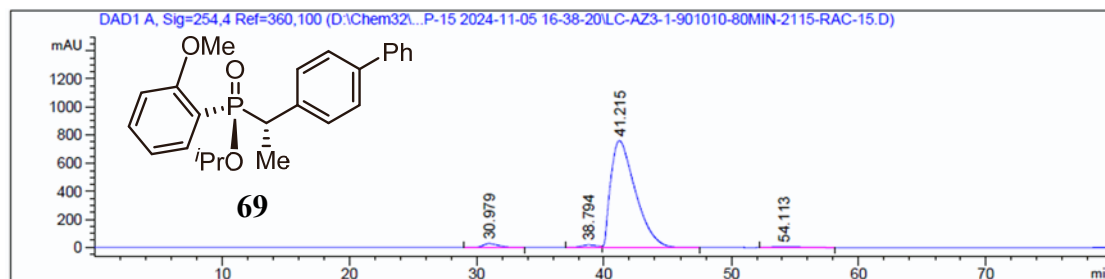
Totals : 4.35048e4 1454.16589



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 31.147        | BB   | 1.2518      | 4307.25098   | 51.92133     | 14.1088 |
| 2      | 39.284        | MM R | 1.7837      | 4330.71387   | 40.46642     | 14.1857 |
| 3      | 42.574        | MM R | 1.7894      | 1.09723e4    | 102.19923    | 35.9409 |
| 4      | 54.659        | BB   | 2.1707      | 1.09185e4    | 76.24689     | 35.7646 |

Totals : 3.05287e4 270.83386

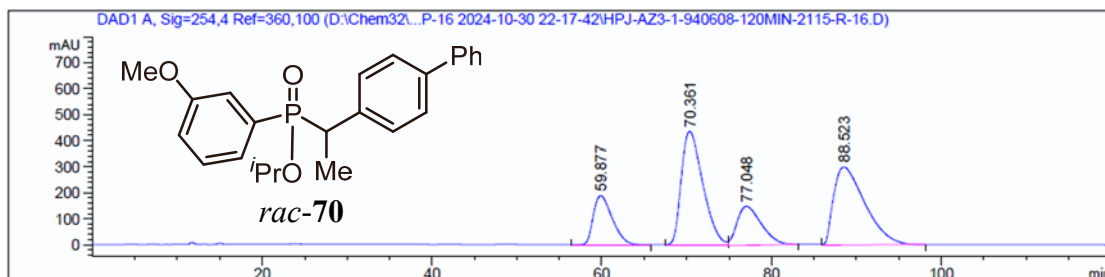


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 30.979        | BB   | 1.2135      | 2158.33960   | 26.68939     | 2.0146  |
| 2      | 38.794        | BV E | 1.2720      | 1408.20117   | 16.76409     | 1.3144  |
| 3      | 41.215        | VB R | 2.1458      | 1.02280e5    | 758.19824    | 95.4683 |
| 4      | 54.113        | MM R | 2.7896      | 1288.52295   | 7.69844      | 1.2027  |

Totals : 1.07135e5 809.35016

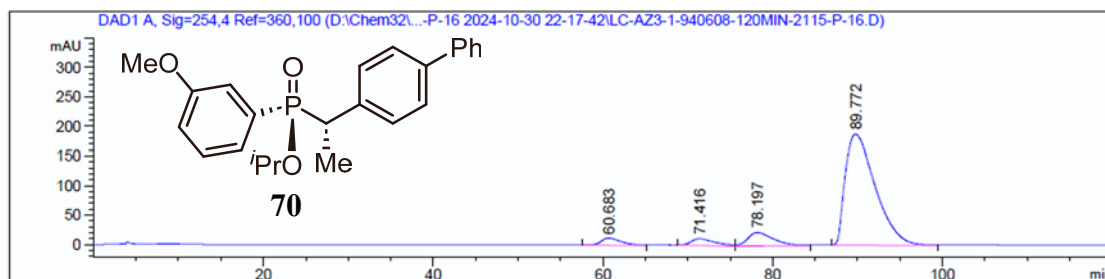




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 59.877        | MM R | 2.7055      | 3.13802e4    | 193.31223    | 14.4818 |
| 2      | 70.361        | MM R | 2.9749      | 7.83843e4    | 439.14105    | 36.1741 |
| 3      | 77.048        | MM R | 3.3368      | 3.00955e4    | 150.32265    | 13.8890 |
| 4      | 88.523        | MM R | 4.2538      | 7.68262e4    | 301.00897    | 35.4551 |

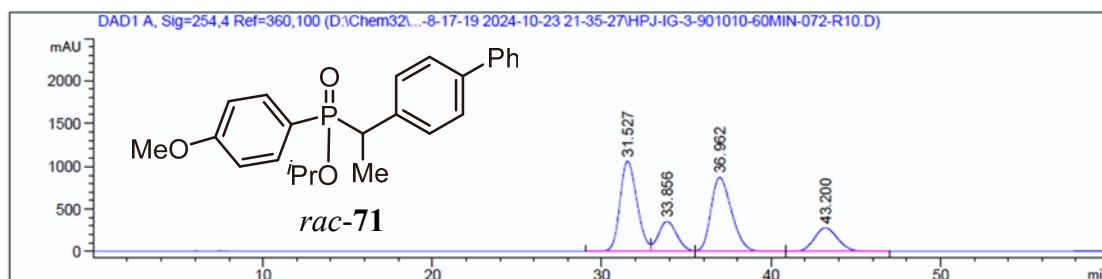
Totals : 2.16686e5 1083.78490



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 60.683        | MM R | 2.8789      | 2162.62891   | 12.51995     | 3.8716  |
| 2      | 71.416        | MM R | 3.3510      | 2309.56738   | 11.48695     | 4.1347  |
| 3      | 78.197        | MM R | 3.5841      | 5011.60742   | 23.30502     | 8.9719  |
| 4      | 89.772        | MM R | 4.1225      | 4.63750e4    | 187.48628    | 83.0218 |

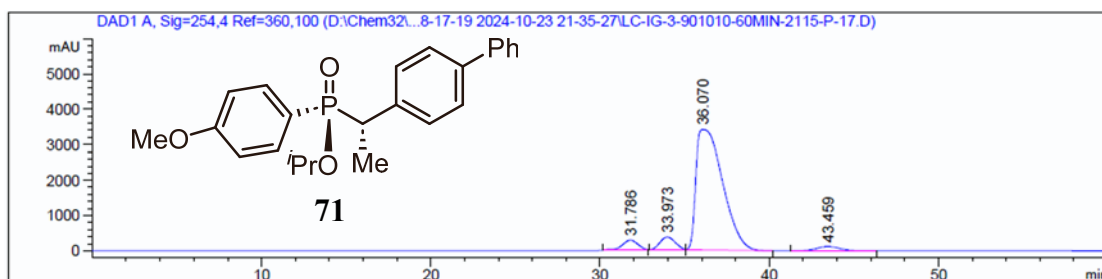
Totals : 5.58588e4 234.79821



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 31.527        | BV   | 1.0848      | 7.41567e4    | 1061.86609   | 36.8683 |
| 2      | 33.856        | VV   | 1.1752      | 2.67546e4    | 352.62299    | 13.3015 |
| 3      | 36.962        | VB   | 1.3221      | 7.37069e4    | 870.28839    | 36.6447 |
| 4      | 43.200        | BB   | 1.4896      | 2.65211e4    | 276.36734    | 13.1854 |

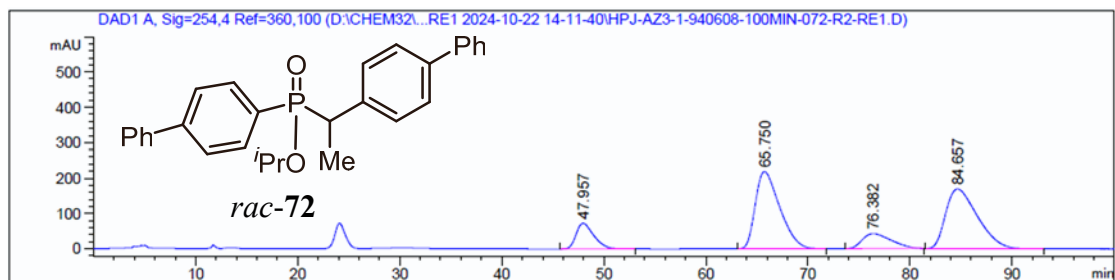
Totals : 2.01139e5 2561.14481



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 31.786        | MM R | 1.0574      | 1.74487e4    | 275.03326    | 4.1094  |
| 2      | 33.973        | BV R | 1.0025      | 2.27094e4    | 362.69684    | 5.3484  |
| 3      | 36.070        | VB   | 1.2902      | 3.73027e5    | 3404.81152   | 87.8538 |
| 4      | 43.459        | BB   | 1.5014      | 1.14148e4    | 119.18035    | 2.6884  |

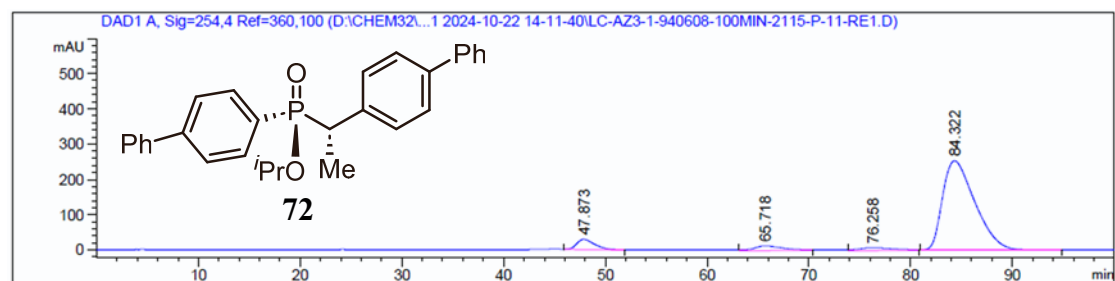
Totals : 4.24599e5 4161.72198



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 47.957        | BB   | 1.8196      | 8701.50879   | 72.63874     | 9.6168  |
| 2      | 65.750        | MM R | 2.7944      | 3.68774e4    | 219.94859    | 40.7566 |
| 3      | 76.382        | MM R | 3.2612      | 8303.31543   | 42.43480     | 9.1768  |
| 4      | 84.657        | BB   | 3.0143      | 3.65997e4    | 169.29091    | 40.4497 |

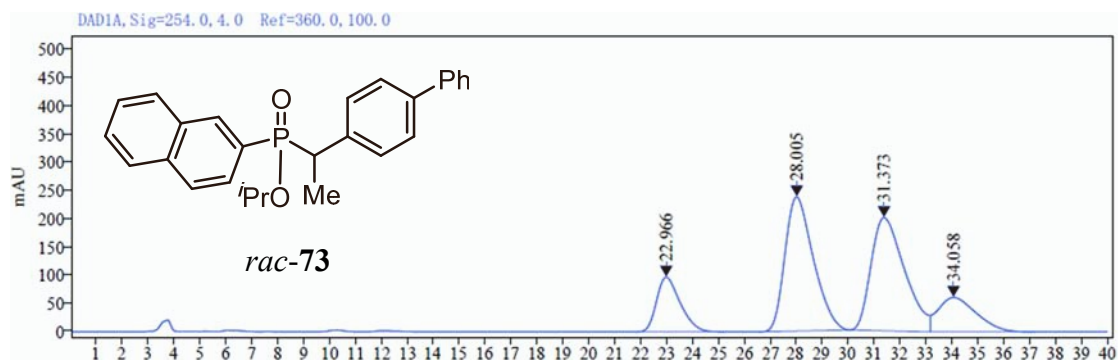
Totals : 9.04819e4 504.31305



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

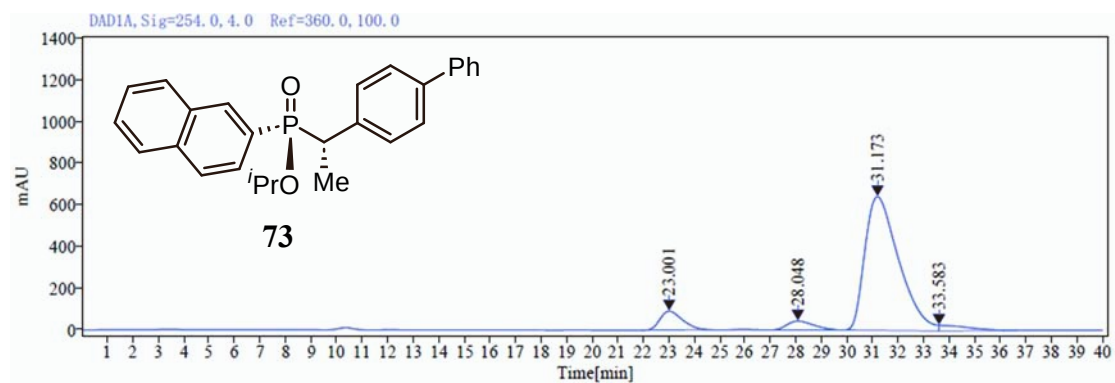
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 47.873        | BB   | 1.7251      | 3361.89575   | 28.52241     | 5.3177  |
| 2      | 65.718        | MM R | 3.2513      | 2495.32202   | 12.79155     | 3.9470  |
| 3      | 76.258        | MM R | 2.7549      | 1799.25354   | 7.64414      | 2.8460  |
| 4      | 84.322        | BB   | 3.0865      | 5.55640e4    | 253.37054    | 87.8892 |

Totals : 6.32204e4 302.32864



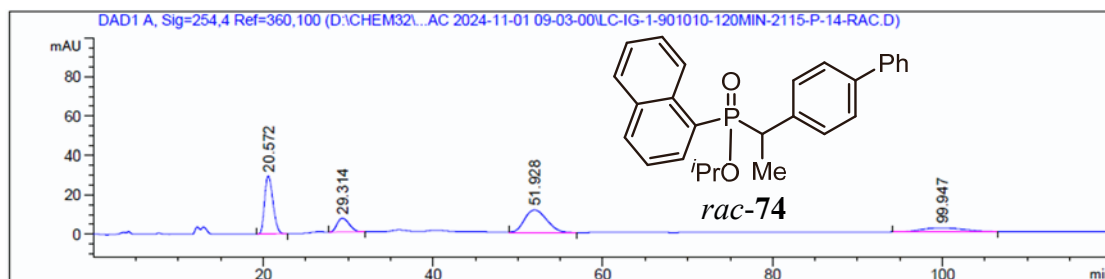
Signal 1: DAD1A, Sig=254.0, 4.0 Ref=360.0, 100.0

| RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area% |
|---------------|------|-------------|--------------|--------------|-------|
| 22.966        | MM m | 3.40        | 6127.50      | 96.77        | 12.62 |
| 28.005        | MM m | 3.59        | 18119.03     | 237.56       | 37.31 |
| 31.373        | MM m | 3.06        | 18042.83     | 200.22       | 37.16 |
| 34.058        | MM m | 4.09        | 6269.91      | 61.18        | 12.91 |
| Totals        |      | 14.13       | 48559.26     |              |       |



Signal 1: DAD1A, Sig=254.0, 4.0 Ref=360.0, 100.0

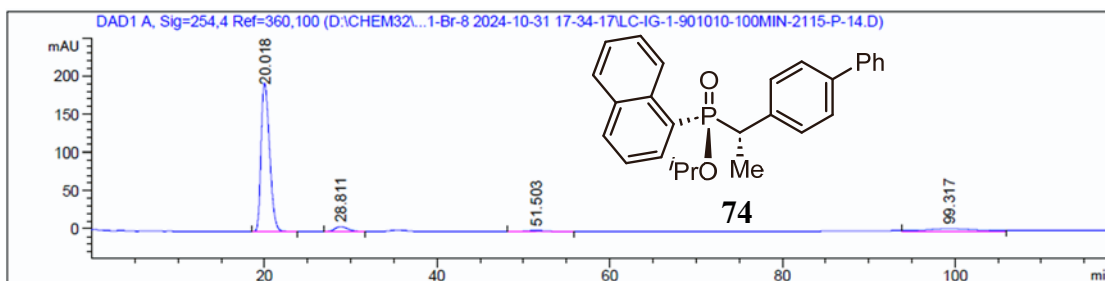
| RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area% |
|---------------|------|-------------|--------------|--------------|-------|
| 23.001        | MM m | 2.60        | 5503.86      | 90.99        | 7.84  |
| 28.048        | MM m | 3.06        | 3141.61      | 43.19        | 4.47  |
| 31.173        | MM m | 3.70        | 59454.17     | 643.58       | 84.64 |
| 33.583        | MM m | 3.06        | 2143.63      | 26.92        | 3.05  |
| Totals        |      | 12.41       | 70243.27     |              |       |



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 20.572        | BB   | 1.0816      | 2038.41101   | 29.66718     | 35.9796 |
| 2      | 29.314        | BB   | 1.3908      | 703.30585    | 7.06843      | 12.4139 |
| 3      | 51.928        | MM R | 3.0657      | 2123.19434   | 11.54262     | 37.4761 |
| 4      | 99.947        | MM R | 6.2794      | 800.55518    | 2.12482      | 14.1304 |

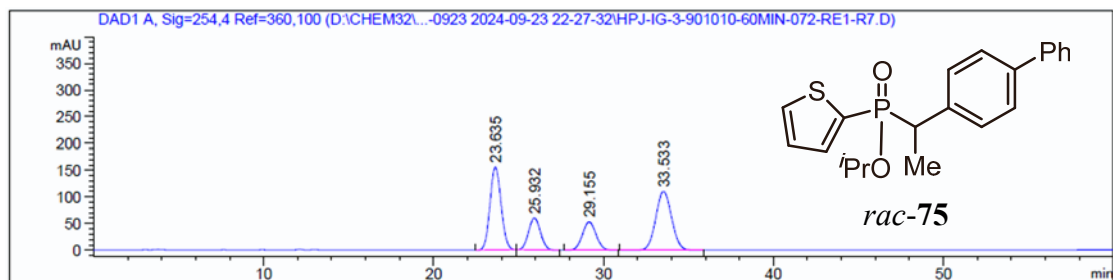
Totals : 5665.46637 50.40304



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 20.018        | BB   | 1.0880      | 1.33160e4    | 194.19543    | 86.3919 |
| 2      | 28.811        | BB   | 1.2914      | 611.17334    | 6.24728      | 3.9652  |
| 3      | 51.503        | MM R | 3.8535      | 346.36206    | 1.49805      | 2.2471  |
| 4      | 99.317        | MM R | 6.5436      | 1139.94287   | 2.90346      | 7.3957  |

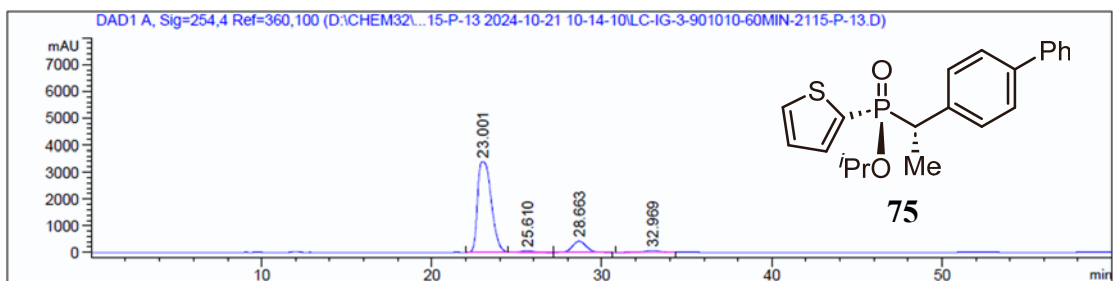
Totals : 1.54135e4 204.84422



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 23.635        | BB   | 0.7056      | 7080.00000   | 155.96280    | 35.0984 |
| 2      | 25.932        | BB   | 0.7657      | 2953.18677   | 60.05820     | 14.6401 |
| 3      | 29.155        | BB   | 0.8722      | 2976.85181   | 53.24809     | 14.7574 |
| 4      | 33.533        | BB   | 1.0105      | 7161.82861   | 110.73772    | 35.5040 |

Totals : 2.01719e4 380.00680

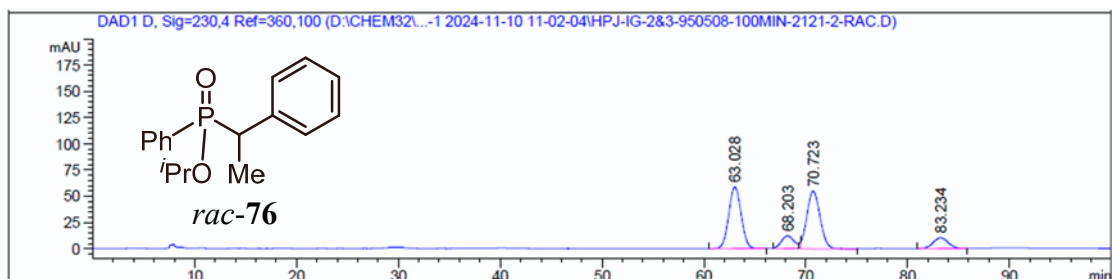


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 23.001        | BV R | 0.7635      | 1.89587e5    | 3384.81201   | 85.9659 |
| 2      | 25.610        | VB E | 0.7962      | 3264.09644   | 63.24083     | 1.4801  |
| 3      | 28.663        | BB   | 0.8827      | 2.35955e4    | 417.91110    | 10.6991 |
| 4      | 32.969        | BB   | 0.9880      | 4090.82861   | 64.66629     | 1.8549  |

Totals : 2.20537e5 3930.63023

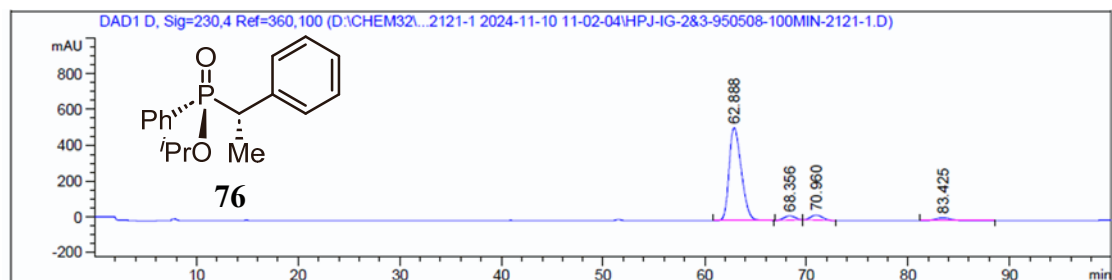




Signal 4: DAD1 D, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 63.028        | BB   | 1.3239      | 4966.08398   | 58.76769     | 41.0505 |
| 2      | 68.203        | MM R | 1.4515      | 1053.11218   | 12.09203     | 8.7052  |
| 3      | 70.723        | MM R | 1.5251      | 5028.12451   | 54.94693     | 41.5633 |
| 4      | 83.234        | BB   | 1.4075      | 1050.18188   | 10.31732     | 8.6810  |

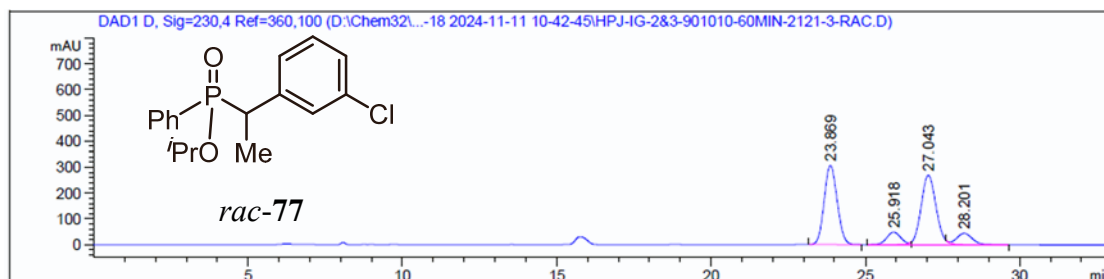
Totals : 1.20975e4 136.12396



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 62.888        | BB   | 1.3090      | 4.34741e4    | 518.07446    | 87.9310 |
| 2      | 68.356        | BB   | 1.1620      | 1788.68555   | 23.82317     | 3.6178  |
| 3      | 70.960        | BB   | 1.2742      | 2289.87769   | 28.29456     | 4.6315  |
| 4      | 83.425        | BB   | 1.5822      | 1888.49255   | 17.18360     | 3.8197  |

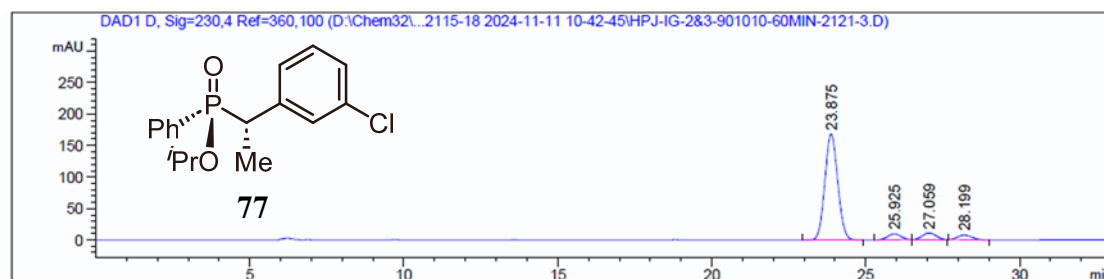
Totals : 4.94411e4 587.37579



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 23.869        | BB   | 0.4563      | 8974.87012   | 307.66663    | 42.5663 |
| 2      | 25.918        | BV E | 0.4852      | 1489.36792   | 48.37277     | 7.0638  |
| 3      | 27.043        | VV R | 0.5264      | 9119.82324   | 269.78183    | 43.2538 |
| 4      | 28.201        | VB E | 0.5367      | 1500.38721   | 43.68887     | 7.1161  |

Totals : 2.10844e4 669.51010

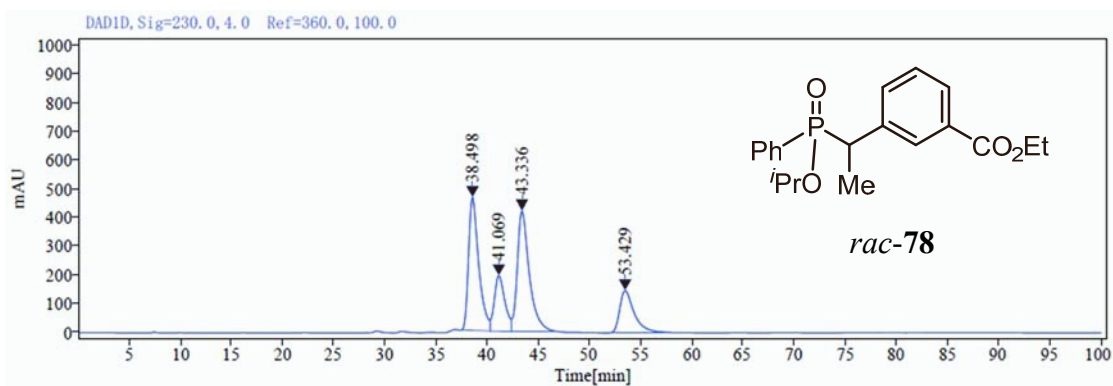


Signal 4: DAD1 D, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 23.875        | BB   | 0.4558      | 4889.33350   | 167.85957    | 85.1910 |
| 2      | 25.925        | BB   | 0.4699      | 280.49728    | 9.40759      | 4.8873  |
| 3      | 27.059        | BB   | 0.4873      | 326.16187    | 10.65093     | 5.6830  |
| 4      | 28.199        | BB   | 0.5218      | 243.26869    | 7.43274      | 4.2387  |

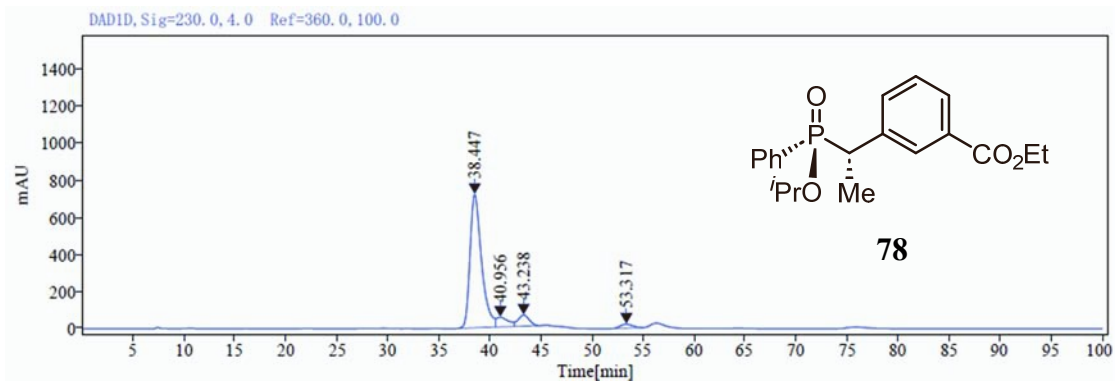
Totals : 5739.26134 195.35083





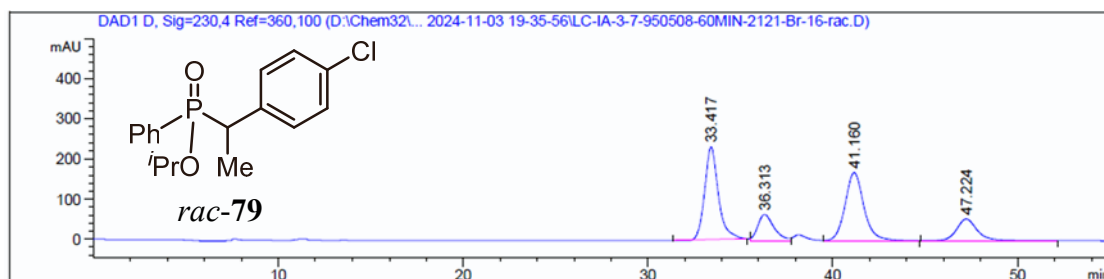
Signal 1: DAD1D, Sig=230.0, 4.0 Ref=360.0, 100.0

| RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area% |
|---------------|------|-------------|--------------|--------------|-------|
| 38.498        | MM m | 2.77        | 32049.07     | 462.94       | 33.73 |
| 41.069        | MM m | 2.10        | 14078.44     | 194.21       | 14.82 |
| 43.336        | MM m | 4.39        | 34403.72     | 421.22       | 36.21 |
| 53.429        | MM m | 6.59        | 14492.62     | 147.36       | 15.25 |
| Totals        |      | 15.85       | 95023.85     |              |       |



Signal 1: DAD1D, Sig=230.0, 4.0 Ref=360.0, 100.0

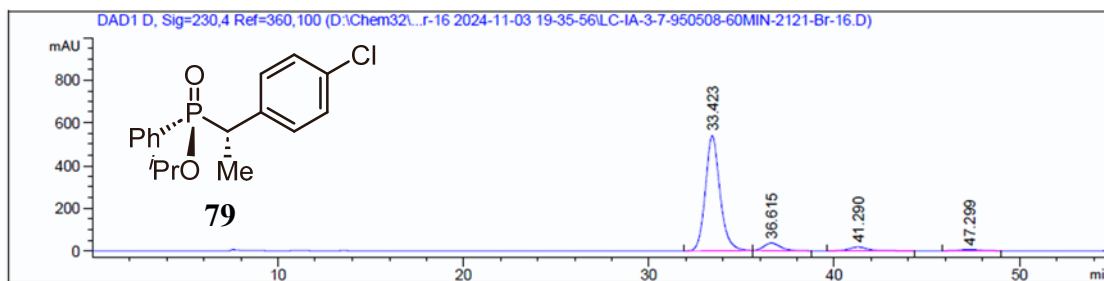
| RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area% |
|---------------|------|-------------|--------------|--------------|-------|
| 38.447        | MM m | 3.73        | 56531.38     | 718.00       | 84.24 |
| 40.956        | MM m | 1.84        | 4268.21      | 51.48        | 6.36  |
| 43.238        | MM m | 2.36        | 4543.83      | 59.98        | 6.77  |
| 53.317        | MM m | 2.96        | 1765.88      | 21.20        | 2.63  |
| Totals        |      | 10.89       | 67109.30     |              |       |



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 33.417        | MM R | 0.8621      | 1.18725e4    | 229.51671    | 37.0731 |
| 2      | 36.313        | MM R | 1.0161      | 3998.12402   | 65.58031     | 12.4845 |
| 3      | 41.160        | BB   | 1.0663      | 1.19277e4    | 169.63269    | 37.2455 |
| 4      | 47.224        | BB   | 1.1704      | 4226.24219   | 54.16002     | 13.1968 |

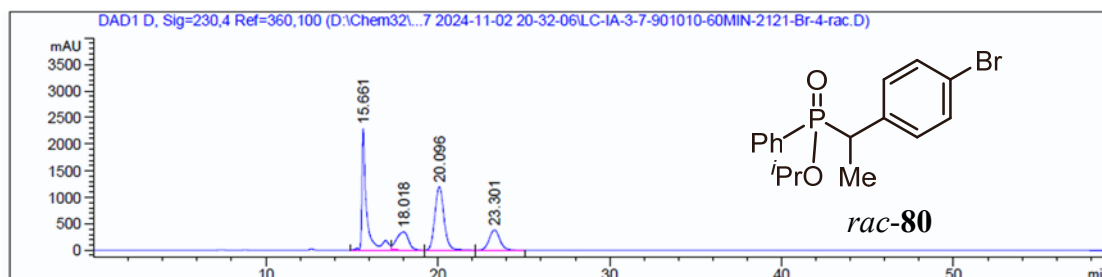
Totals : 3.20246e4 518.88973



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 33.423        | BB   | 0.8299      | 2.95032e4    | 537.86145    | 88.5947 |
| 2      | 36.615        | BB   | 0.9302      | 2102.28149   | 34.82885     | 6.3129  |
| 3      | 41.290        | BB   | 1.0127      | 1241.73889   | 18.23034     | 3.7288  |
| 4      | 47.299        | BB   | 0.9853      | 454.10962    | 6.69545      | 1.3636  |

Totals : 3.33013e4 597.61609

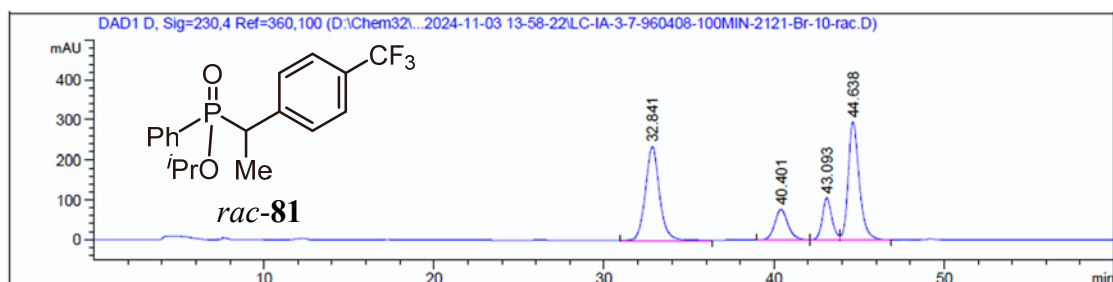


Signal 4: DAD1 D, Sig=230,4 Ref=360,100

|          |           |            |
|----------|-----------|------------|
| Totals : | 1.21746e5 | 4222.94824 |
|----------|-----------|------------|

Signal 4: DAD1 D, Sig=230,4 Ref=360,100

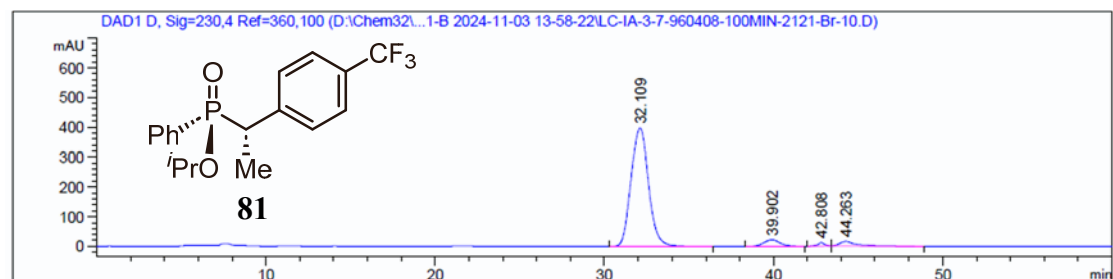
Totals : 1.02678e5 3248.38381



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 32.841        | BB   | 0.8683      | 1.34389e4    | 233.90918    | 38.1865 |
| 2      | 40.401        | BB   | 0.8212      | 4189.17969   | 77.43036     | 11.9035 |
| 3      | 43.093        | BV   | 0.5922      | 4164.70117   | 106.04324    | 11.8339 |
| 4      | 44.638        | VB   | 0.6865      | 1.34001e4    | 295.78366    | 38.0761 |

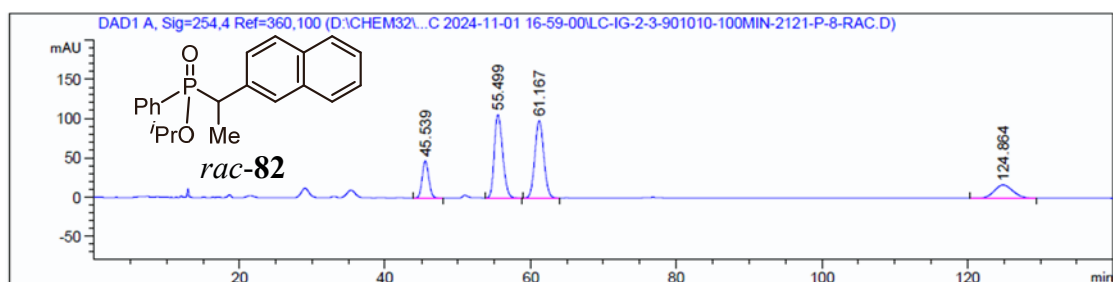
Totals : 3.51929e4 713.16644



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 32.109        | BB   | 1.1475      | 2.85056e4    | 397.07935    | 90.9474 |
| 2      | 39.902        | BB   | 1.0227      | 1485.51001   | 22.20029     | 4.7395  |
| 3      | 42.808        | BB   | 0.3369      | 311.62894    | 12.76294     | 0.9943  |
| 4      | 44.263        | BB   | 0.9924      | 1040.22095   | 15.16248     | 3.3188  |

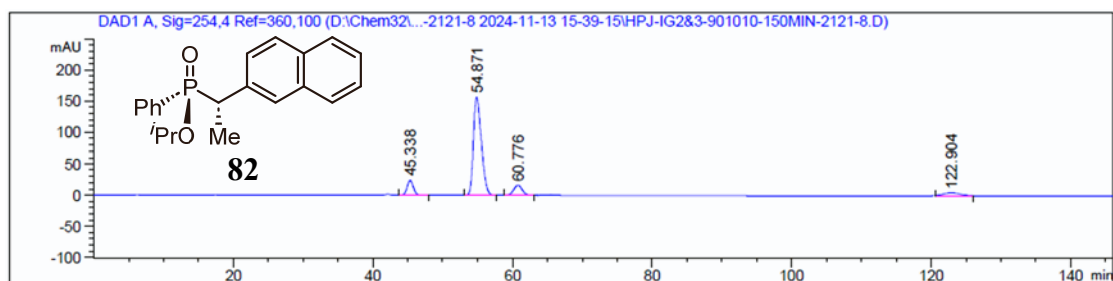
Totals : 3.13430e4 447.20505



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 45.539        | BB   | 0.9731      | 2956.08569   | 47.43071     | 13.0325 |
| 2      | 55.499        | BB   | 1.2378      | 8383.43164   | 105.64564    | 36.9600 |
| 3      | 61.167        | BB   | 1.3387      | 8371.86719   | 97.79945     | 36.9090 |
| 4      | 124.864       | MM R | 2.9580      | 2971.05933   | 16.74036     | 13.0985 |

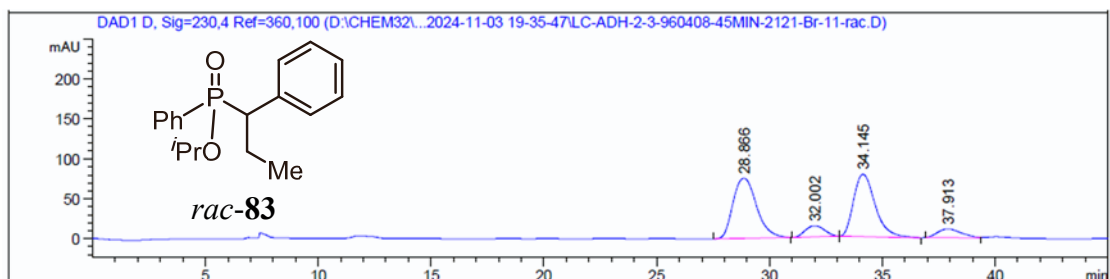
Totals : 2.26824e4 267.61616



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 45.338        | BB   | 0.9610      | 1460.44629   | 23.76394     | 9.0897  |
| 2      | 54.871        | BB   | 1.2207      | 1.23320e4    | 156.26704    | 76.7535 |
| 3      | 60.776        | BB   | 1.2834      | 1344.71448   | 16.05179     | 8.3694  |
| 4      | 122.904       | MM R | 2.9390      | 929.85895    | 5.27312      | 5.7874  |

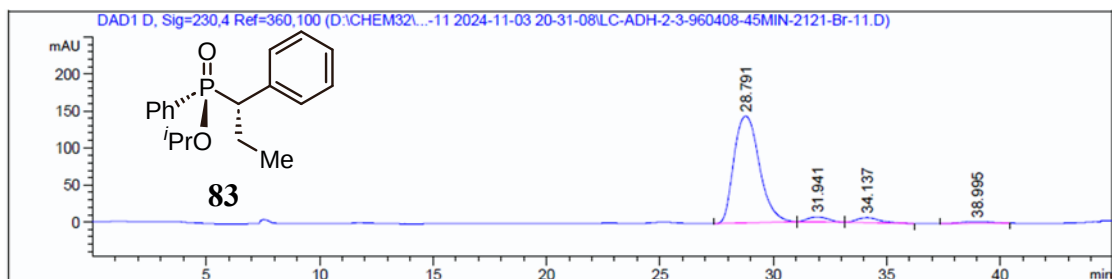
Totals : 1.60670e4 201.35589



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 28.866        | BB   | 1.1539      | 5479.32324   | 75.57388     | 44.2717 |
| 2      | 32.002        | BB   | 0.9455      | 840.21539    | 14.09373     | 6.7887  |
| 3      | 34.145        | BB   | 1.0436      | 5237.81104   | 78.58275     | 42.3203 |
| 4      | 37.913        | MM R | 1.2364      | 819.24323    | 11.04324     | 6.6193  |

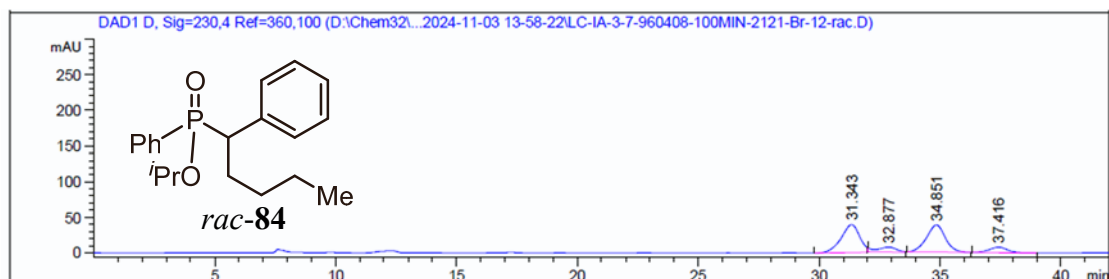
Totals : 1.23766e4 179.29360



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 28.791        | BB   | 1.2493      | 1.12827e4    | 144.12801    | 90.5570 |
| 2      | 31.941        | BB   | 1.0353      | 429.43347    | 6.73995      | 3.4467  |
| 3      | 34.137        | BB   | 1.1090      | 485.46204    | 6.81587      | 3.8964  |
| 4      | 38.995        | MM R | 1.5748      | 261.62656    | 2.76881      | 2.0999  |

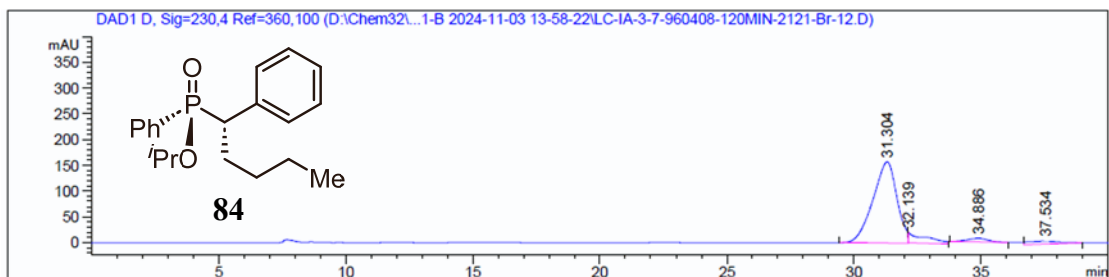
Totals : 1.24592e4 160.45264



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 31.343        | MM R | 0.8911      | 2109.32007   | 39.45320     | 42.4413 |
| 2      | 32.877        | MM R | 0.9624      | 398.80463    | 6.90656      | 8.0243  |
| 3      | 34.851        | BB   | 0.8116      | 2062.48999   | 38.22116     | 41.4990 |
| 4      | 37.416        | BB   | 0.7785      | 399.35468    | 7.65636      | 8.0354  |

Totals : 4969.96936 92.23727

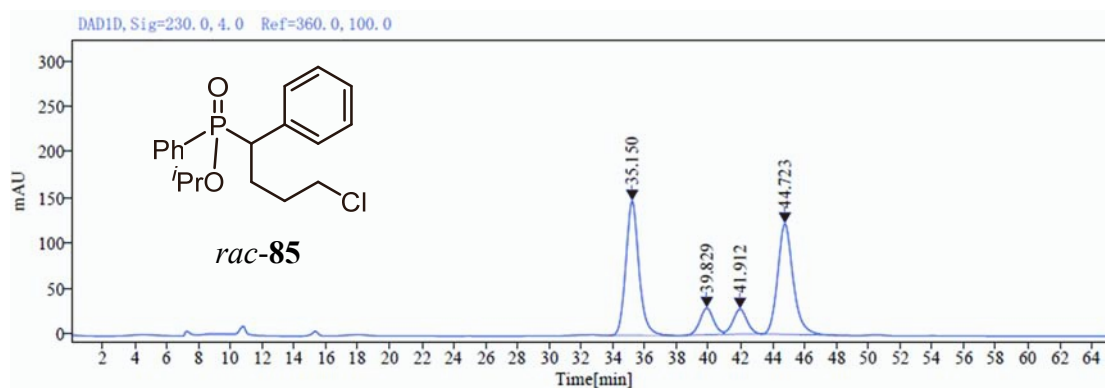


Signal 4: DAD1 D, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 31.304        | MM R | 1.0865      | 1.02977e4    | 157.96910    | 85.0989 |
| 2      | 32.139        | MM R | 0.6803      | 922.63812    | 20.40920     | 7.6245  |
| 3      | 34.886        | BB   | 0.8475      | 407.10431    | 7.20121      | 3.3642  |
| 4      | 37.534        | MM R | 1.4053      | 473.42346    | 5.61457      | 3.9123  |

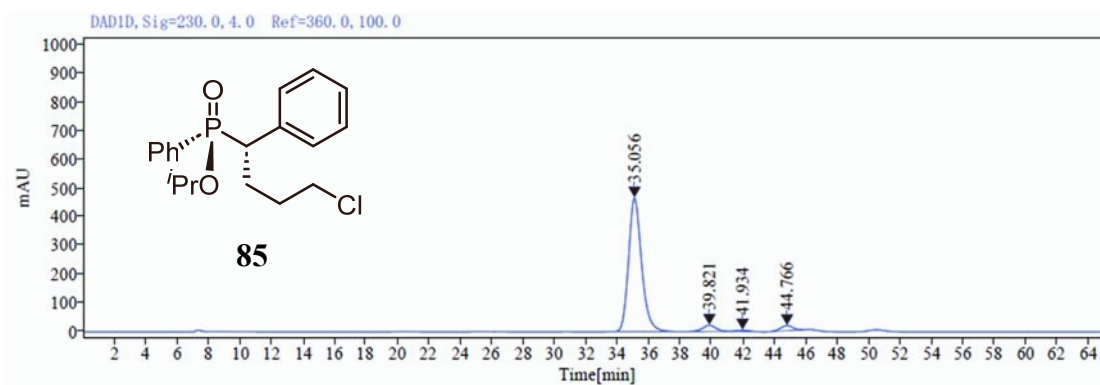
Totals : 1.21009e4 191.19409





Signal 1: DAD1D, Sig=230.0, 4.0 Ref=360.0, 100.0

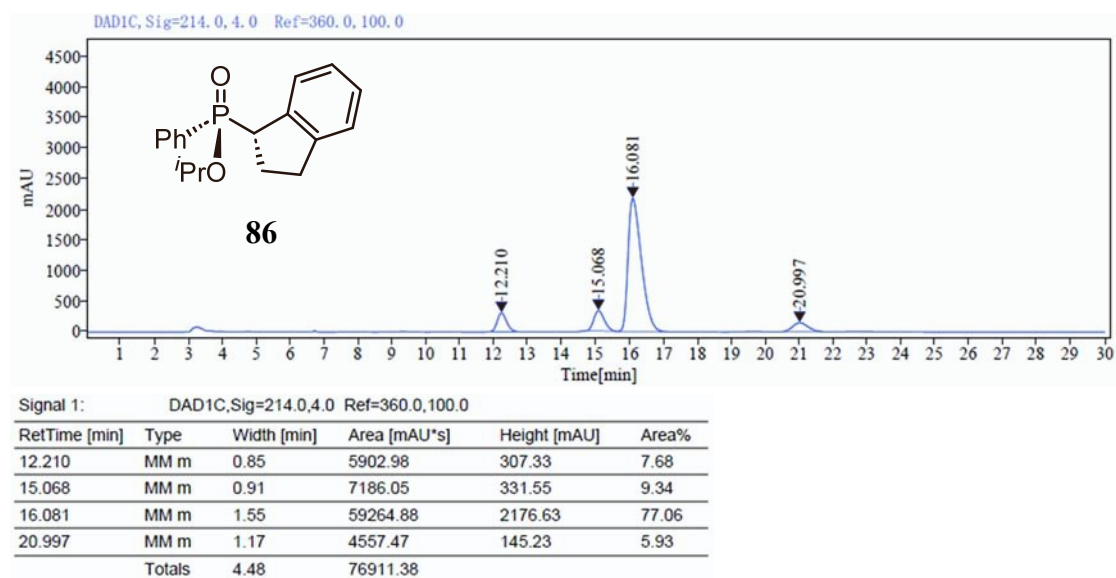
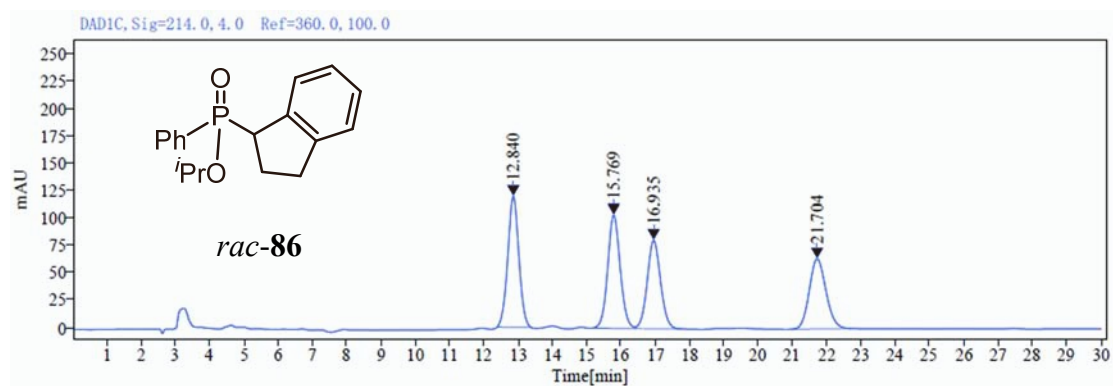
| RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area% |
|---------------|------|-------------|--------------|--------------|-------|
| 35.150        | MM m | 4.05        | 8433.17      | 147.43       | 42.03 |
| 39.829        | MM m | 2.44        | 1757.55      | 29.32        | 8.76  |
| 41.912        | MM m | 2.29        | 1662.77      | 27.52        | 8.29  |
| 44.723        | MM m | 4.79        | 8210.53      | 121.31       | 40.92 |
| Totals        |      | 13.57       | 20064.03     |              |       |

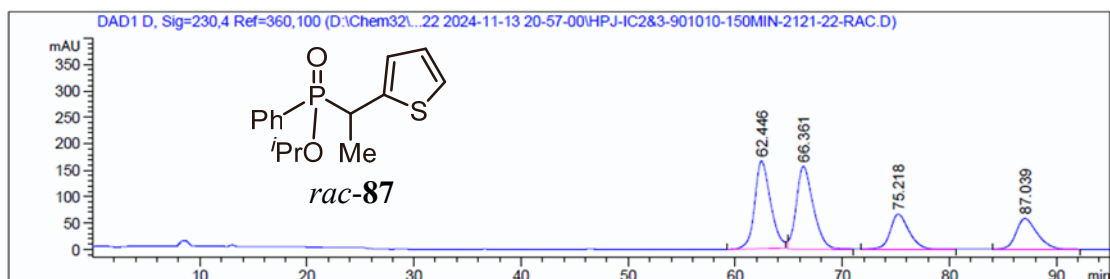


Signal 1: DAD1D, Sig=230.0, 4.0 Ref=360.0, 100.0

| RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area% |
|---------------|------|-------------|--------------|--------------|-------|
| 35.056        | MM m | 4.97        | 26926.91     | 465.54       | 91.69 |
| 39.821        | MM m | 2.67        | 1250.39      | 21.28        | 4.26  |
| 41.934        | MM m | 2.11        | 246.32       | 4.79         | 0.84  |
| 44.766        | MM m | 2.05        | 944.87       | 17.39        | 3.22  |
| Totals        |      | 11.79       | 29368.50     |              |       |



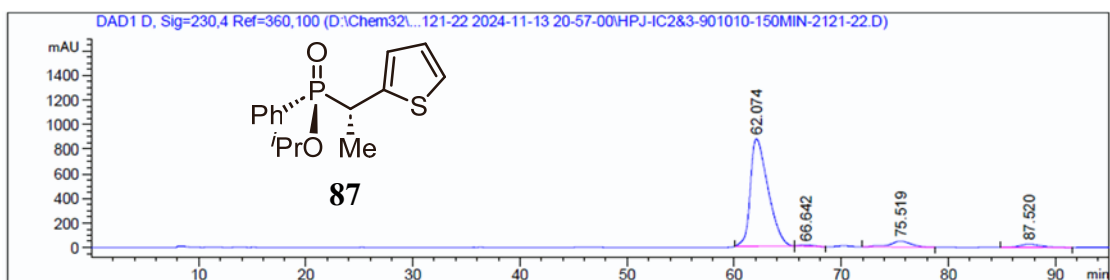




Signal 4: DAD1 D, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 62.446        | MM R | 1.7267      | 1.72919e4    | 166.91017    | 34.1889 |
| 2      | 66.361        | MM R | 1.8428      | 1.73872e4    | 157.25206    | 34.3774 |
| 3      | 75.218        | BB   | 1.7576      | 8015.46533   | 66.52740     | 15.8479 |
| 4      | 87.039        | BB   | 1.9857      | 7882.87305   | 58.14432     | 15.5857 |

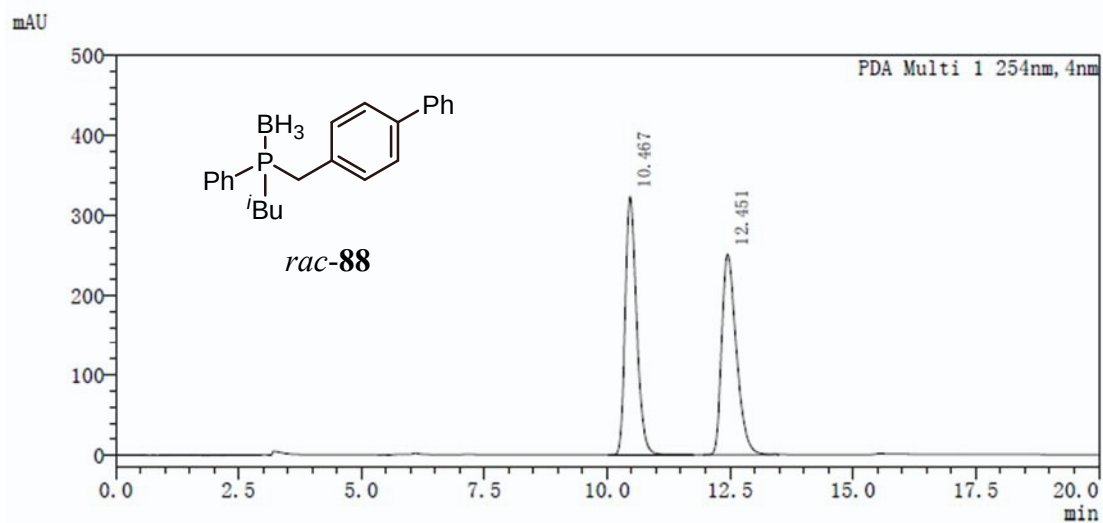
Totals : 5.05775e4 448.83395



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 62.074        | BB   | 1.7003      | 1.00143e5    | 870.39984    | 89.9224 |
| 2      | 66.642        | BB   | 1.1700      | 948.16034    | 11.52328     | 0.8514  |
| 3      | 75.519        | BB   | 1.9919      | 6844.99512   | 49.60318     | 6.1464  |
| 4      | 87.520        | BB   | 1.9503      | 3429.88647   | 25.16136     | 3.0798  |

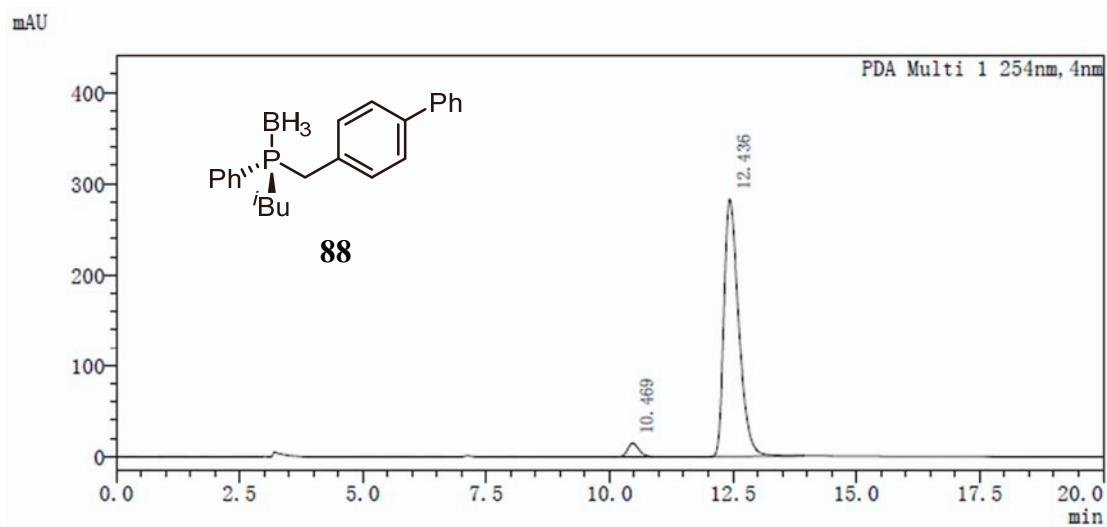
Totals : 1.11367e5 956.68766



Peak Table

PDA Ch1 254nm

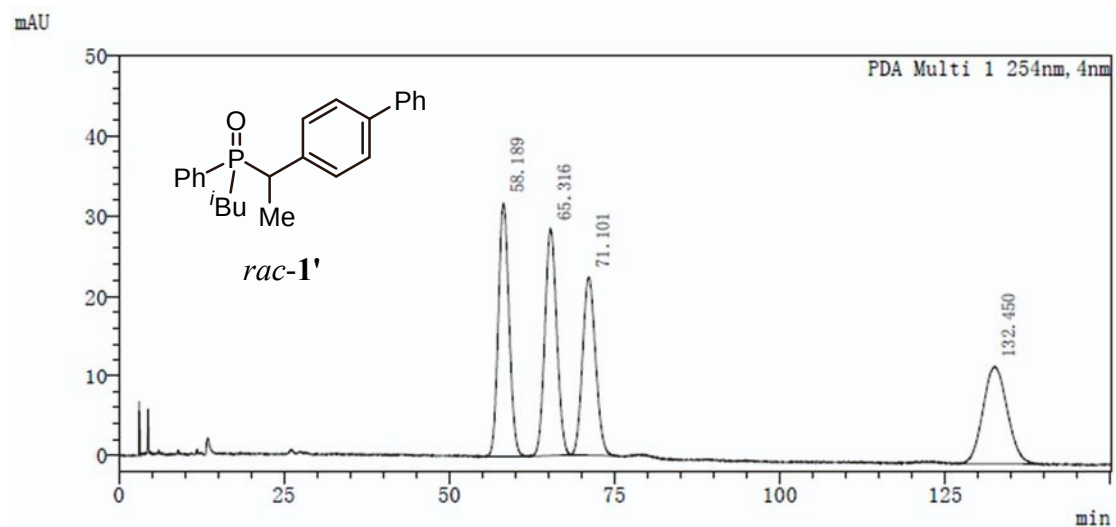
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 10.467    | 5197078 | 49.992 |
| 2     | 12.451    | 5198832 | 50.008 |



Peak Table

PDA Ch1 254nm

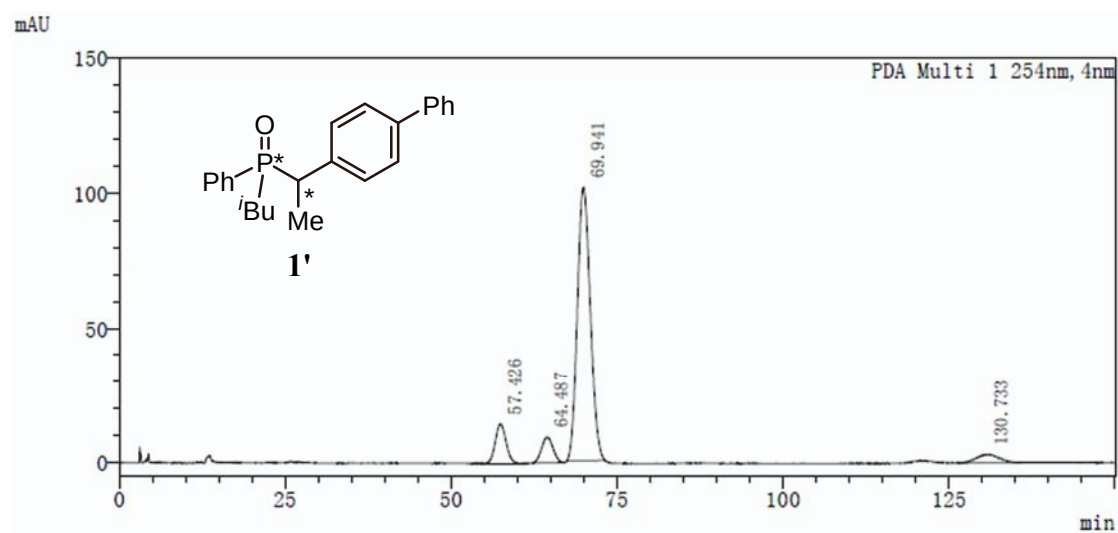
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 10.469    | 219689  | 3.591  |
| 2     | 12.436    | 5897980 | 96.409 |



Peak Table

PDA Ch1 254nm

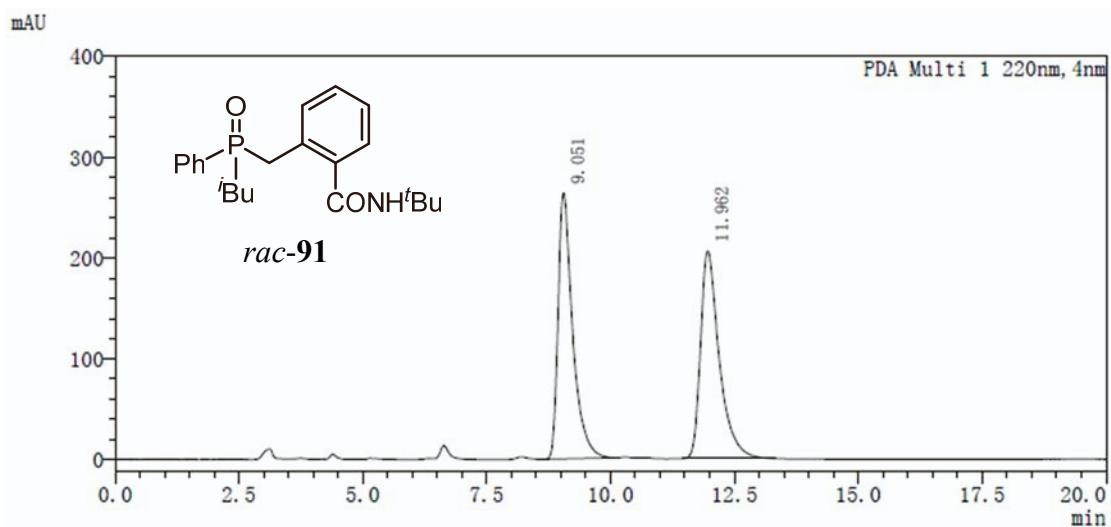
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 58.189    | 3591331 | 26.981 |
| 2     | 65.316    | 3566449 | 26.794 |
| 3     | 71.101    | 3061776 | 23.002 |
| 4     | 132.450   | 3091171 | 23.223 |



Peak Table

PDA Ch1 254nm

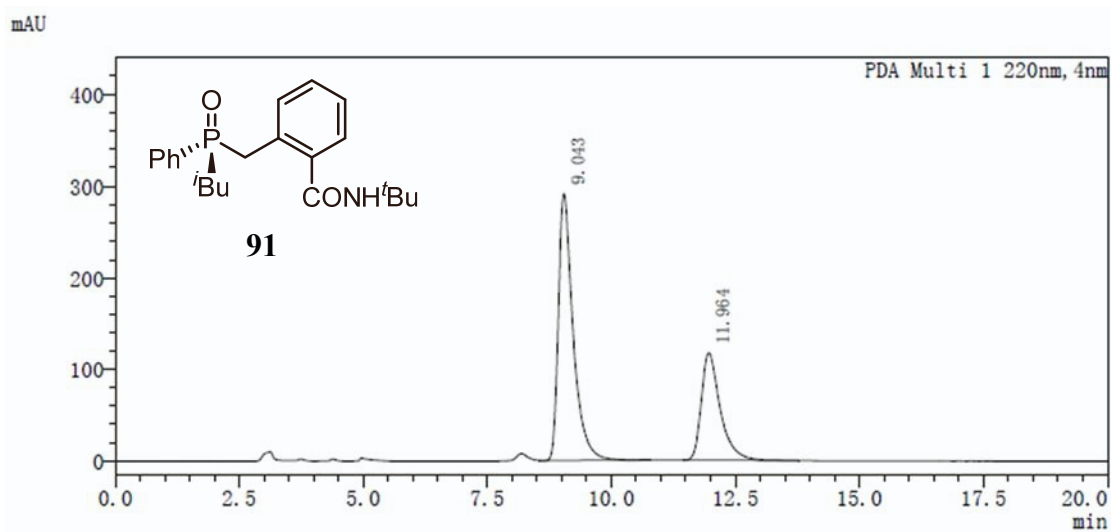
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 57.426    | 1654201  | 9.574  |
| 2     | 64.487    | 1130215  | 6.542  |
| 3     | 69.941    | 13736412 | 79.505 |
| 4     | 130.733   | 756573   | 4.379  |



Peak Table

PDA Ch1 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 9.051     | 5385184 | 49.906 |
| 2     | 11.962    | 5405480 | 50.094 |

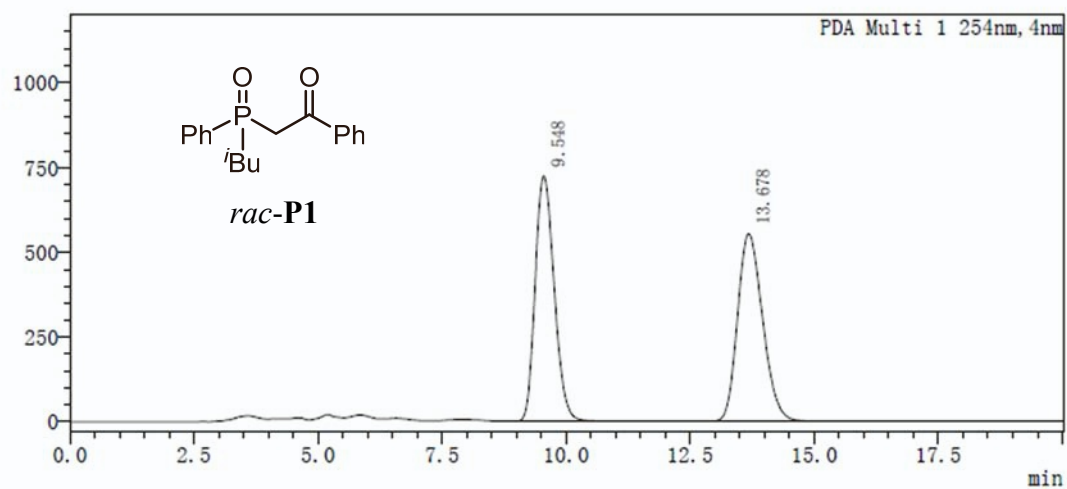


Peak Table

PDA Ch1 220nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 9.043     | 5986674 | 65.977 |
| 2     | 11.964    | 3087207 | 34.023 |

mAU

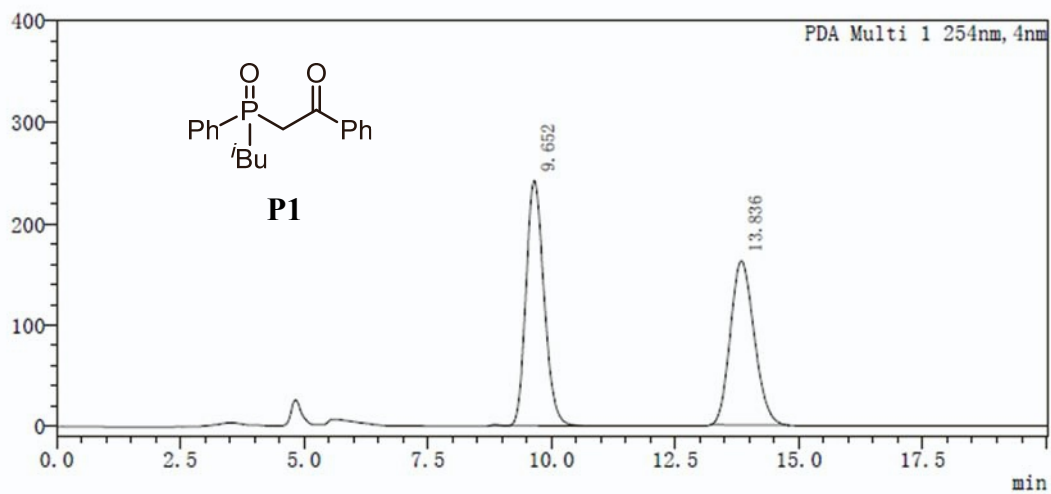


Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 9.548     | 19251004 | 49.787 |
| 2     | 13.678    | 19416104 | 50.213 |

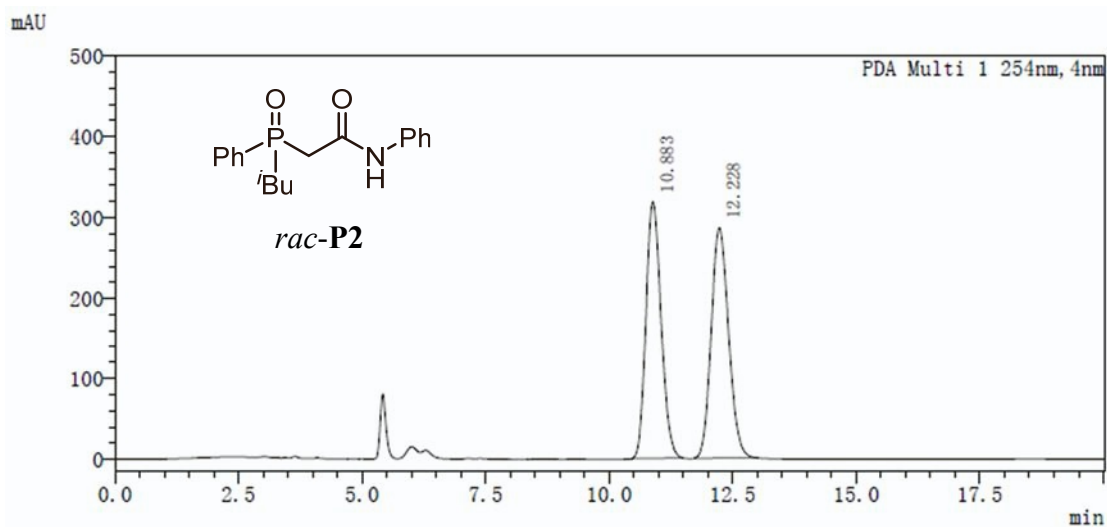
mAU



Peak Table

PDA Ch1 254nm

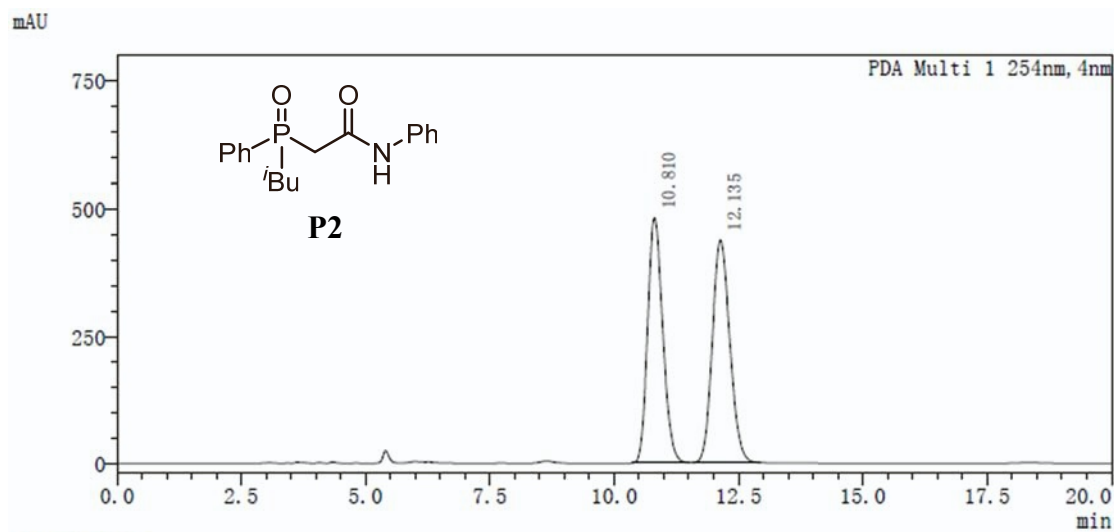
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 9.652     | 6136378 | 52.972 |
| 2     | 13.836    | 5447846 | 47.028 |



Peak Table

PDA Ch1 254nm

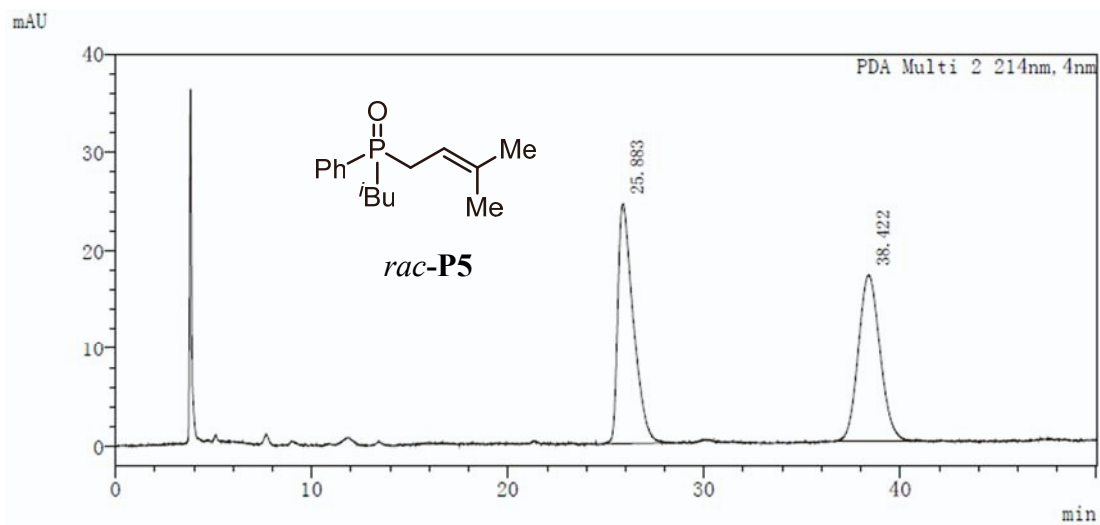
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 10.883    | 6785454 | 49.209 |
| 2     | 12.228    | 7003566 | 50.791 |



Peak Table

PDA Ch1 254nm

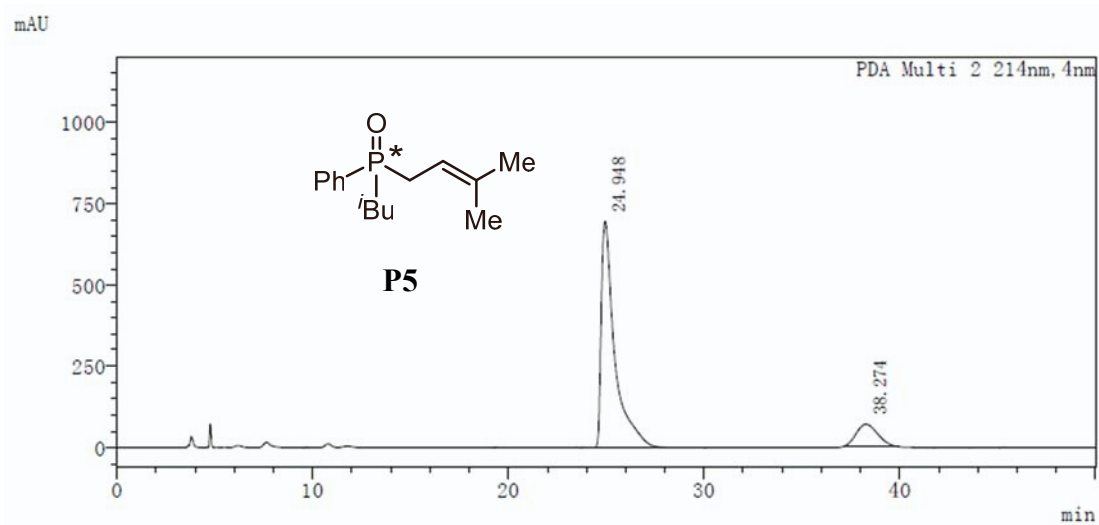
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 10.810    | 10226480 | 48.688 |
| 2     | 12.135    | 10777508 | 51.312 |



Peak Table

PDA Ch2 214nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 25.883    | 1343351 | 50.911 |
| 2     | 38.422    | 1295276 | 49.089 |

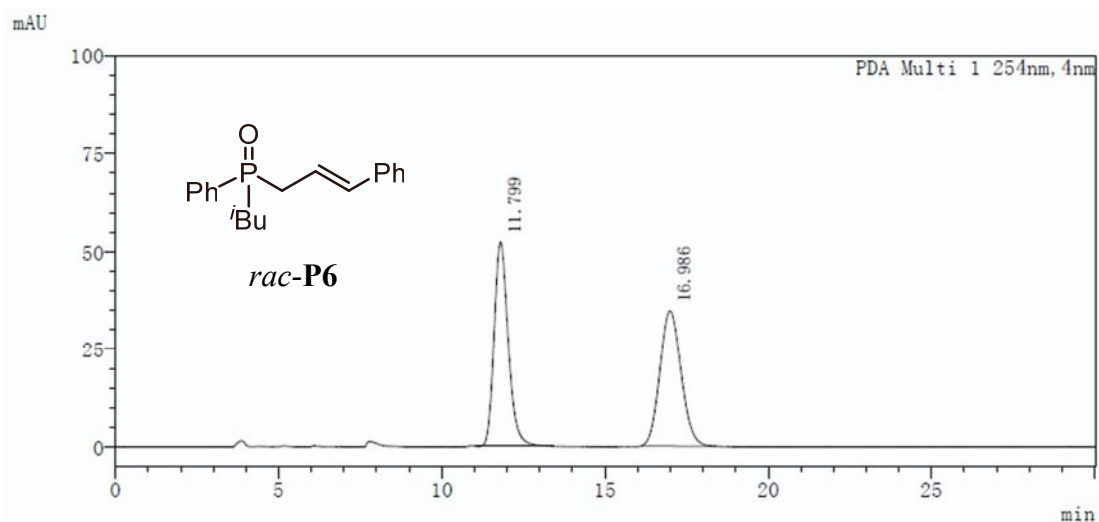


Peak Table

PDA Ch2 214nm

| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 24.948    | 33209277 | 86.378 |
| 2     | 38.274    | 5237187  | 13.622 |

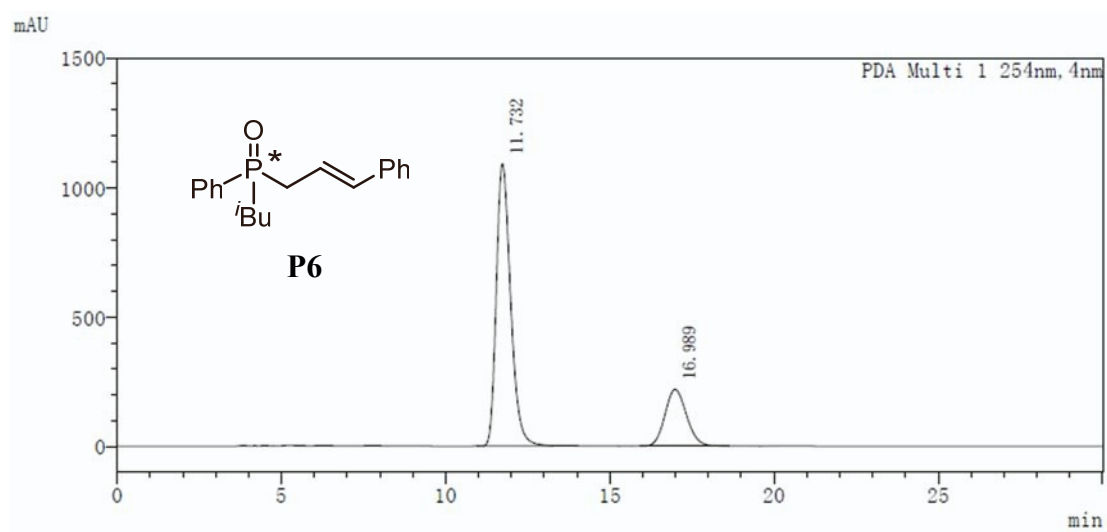




Peak Table

PDA Ch1 254nm

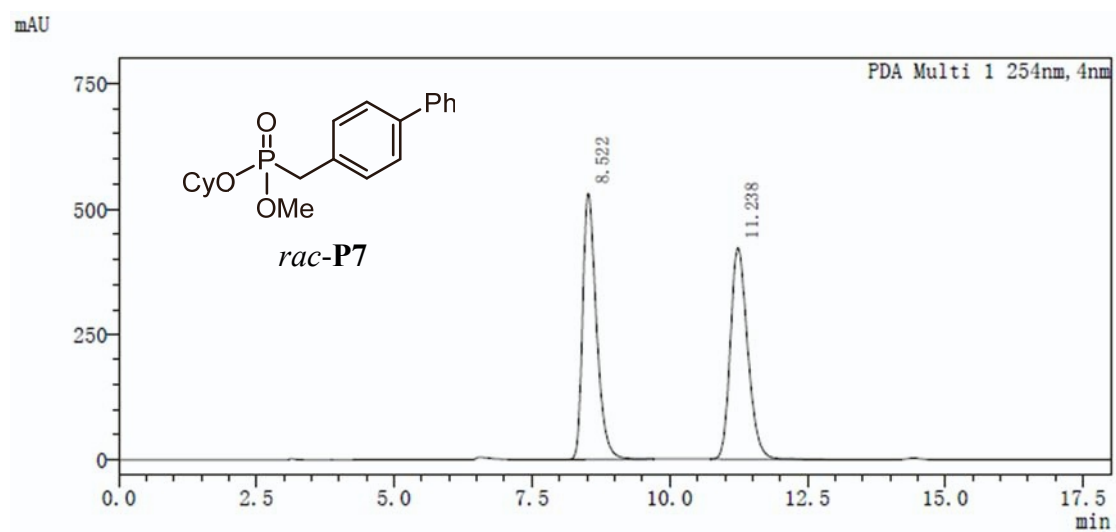
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 11.799    | 1572125 | 50.150 |
| 2     | 16.986    | 1562739 | 49.850 |



Peak Table

PDA Ch1 254nm

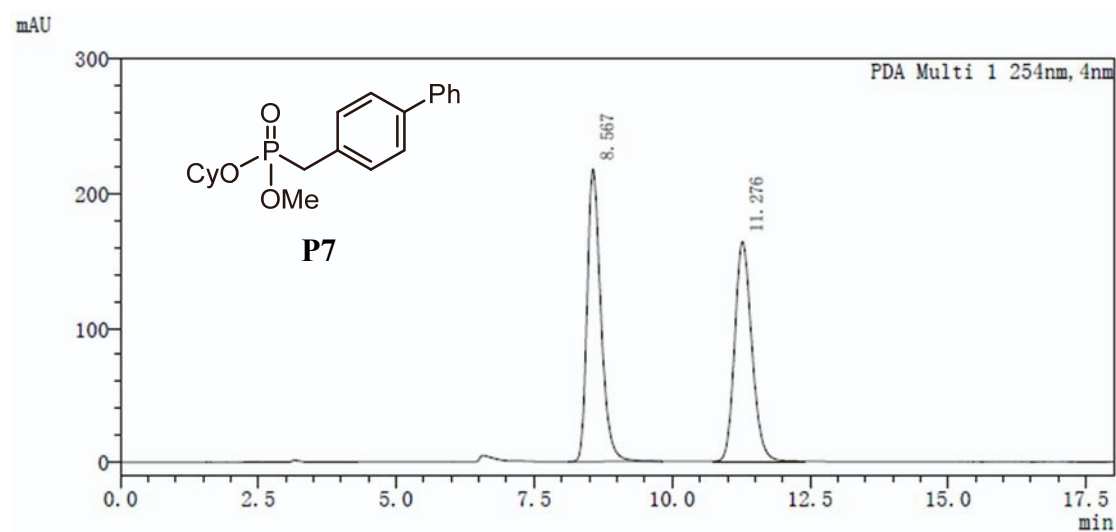
| Peak# | Ret. Time | Area     | Area%  |
|-------|-----------|----------|--------|
| 1     | 11.732    | 33113332 | 76.771 |
| 2     | 16.989    | 10019412 | 23.229 |



Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 8.522     | 9229827 | 50.035 |
| 2     | 11.238    | 9216907 | 49.965 |

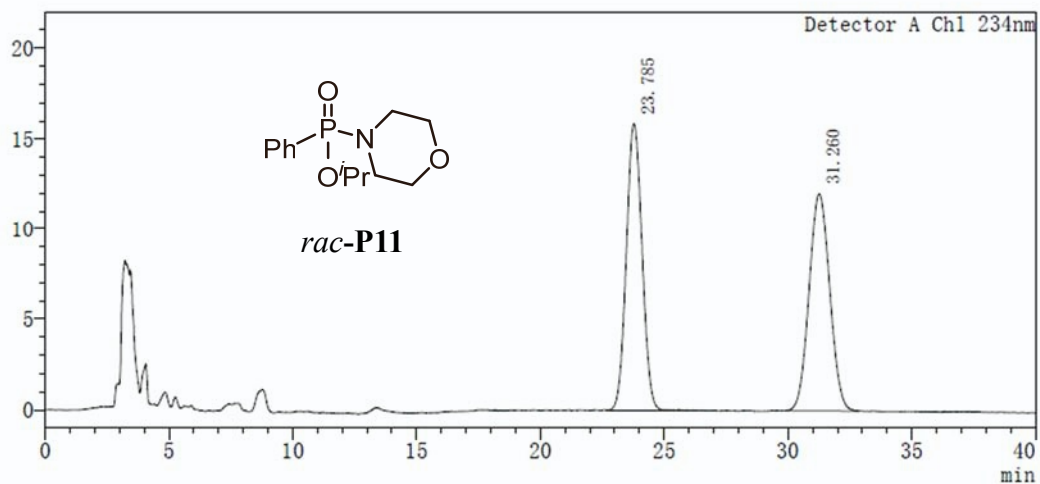


Peak Table

PDA Ch1 254nm

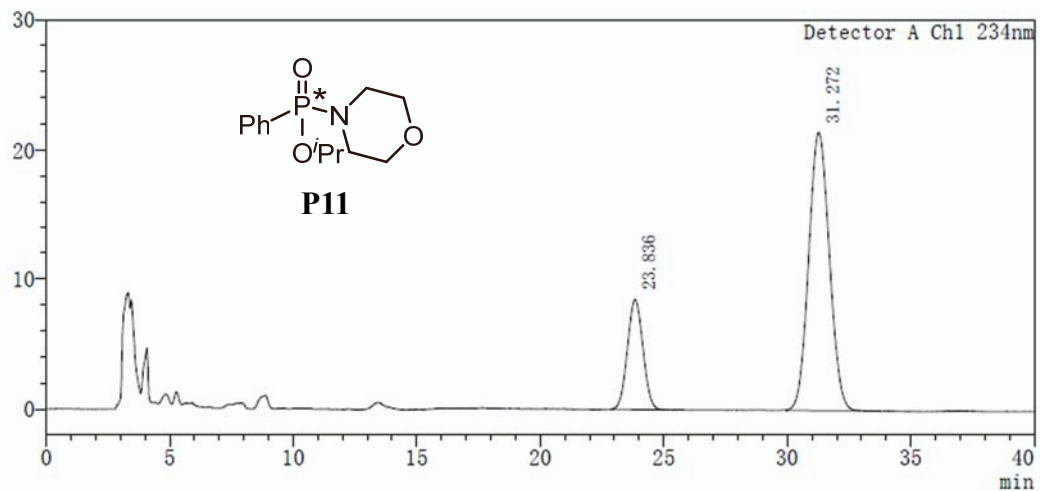
| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 8.567     | 3768856 | 51.606 |
| 2     | 11.276    | 3534278 | 48.394 |

mV



| Peak# | Ret. Time | Area   | Area%  |
|-------|-----------|--------|--------|
| 1     | 23.785    | 701824 | 50.167 |
| 2     | 31.260    | 697159 | 49.833 |

mV



| Peak# | Ret. Time | Area    | Area%  |
|-------|-----------|---------|--------|
| 1     | 23.836    | 368062  | 22.783 |
| 2     | 31.272    | 1247416 | 77.217 |

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