

Supporting Information
for
**Synthesis of P-Chiral Phosphonates by Stereoselective
Intramolecular Cyclization**

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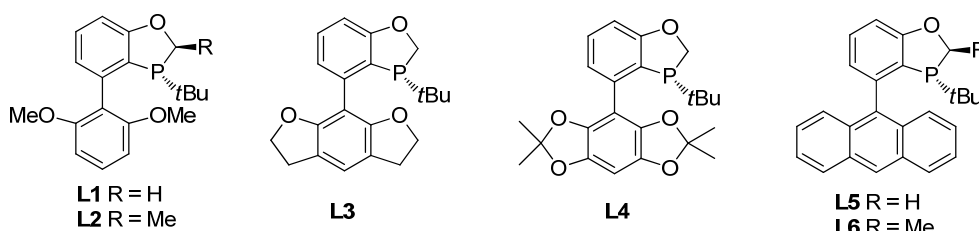
1. General information and materials:

^1H , ^{31}P , ^{19}F and ^{13}C NMR data were recorded on a Bruker DRX500, DRX400. NMR Spectrometer with CDCl_3 as the solvent. ^{31}P shifts were referenced to 85% H_3PO_4 in D_2O at 0.0 ppm as external standard and obtained with ^1H decoupling. ^{13}C shifts were obtained with ^1H decoupling. MS was measured on Agilent 1100 Series LC/MSD mass spectrometer. Enantiomeric excess was determined by chiral HPLC (Agilent Series 1260). Column chromatography was performed with silica gel (300-400 mesh).

All reagents were used as received from commercial sources, unless otherwise specified, or prepared as described in the literature. All solvents were dried and stored under N_2 . All reagents were weighed and handled in air and refilled with nitrogen.

Abbreviations in this text: PE = petroleum ether; EA = ethyl acetate; DCM = dichloromethane;

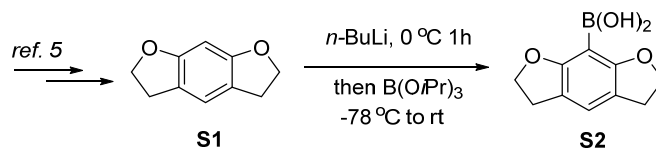
2. Synthetic procedures of ligands L1-L6



The synthesis of **L1** and **L2** were followed according to procedures described in our previous report: (1) W. Tang, A. G. Capacci, X. Wei, W. Li, A. White, N. D. Patel, J. Savoie, J. Gao, S. Rodriguez, B. Qu, N. Haddad, B. Z. Lu, D. Krishnamurthy, N. K. Yee and C. H. Senanayake, *Angew. Chem., Int. Ed.* 2010, **49**, 5879. (2) W. Tang, N. D. Patel, G. Xu, X. Xu, J. Savoie, S. Ma, M.-H. Hao, S. Keshipeddy, A. G. Capacci, X. Wei, Y. Zhang, J. Gao, W. Li, S. Rodriguez, B. Z. Lu, N. K. Yee and C. H. Senanayake, *Org. Lett.* 2012, **14**, 2258.

The syntheses of **L5** and **L6** were followed according to procedures described in our previous report: (3) W. Tang, S. Keshipeddy, Y. Zhang, X. Wei, J. Savoie, N. D. Patel, N. K. Yee and C. H. Senanayake, *Org. Lett.* 2011, **13**, 1366. (4) G. Xu, W. Fu, G. Liu, C. H. Senanayake and W. Tang, *J. Am. Chem. Soc.* 2014, **136**, 570.

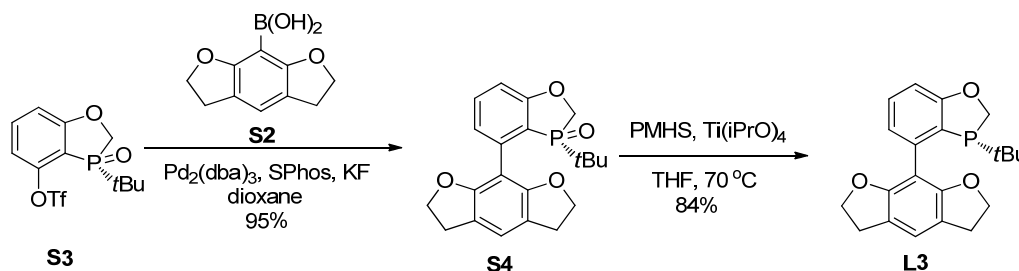
Synthesis of **L3**:



Compound **S1** was synthesized according to the procedure described in reference 5: J. C. González-Gómez, L. Santana and E. Uriarte, *Tetrahedron* 2005, **61**, 4805.

Synthesis of boronic acid **S2**: To a solution of **S1** (2.5g, 15.4 mmol, 1.0 equiv) in THF (150 mL) was added $n\text{-BuLi}$ (6.9 mL, 2.5 M in hexane, 1.1 equiv) dropwise at 0°C over 15 min. After stirred at 0°C for 1 h, the mixture was cooled to -78°C and B(OiPr)_3 (7.1 mL, 30.8 mmol, 2.0 equiv) was added, the resulting mixture was stirred for further 30 min before warmed to room temperature, then saturated NH_4Cl solution (30 mL) was added and the aqueous phase was extracted by EtOAc

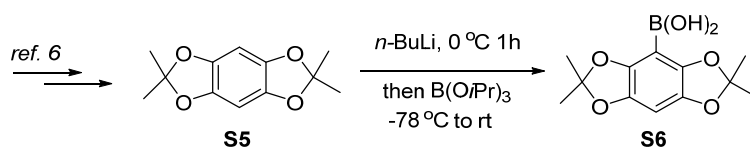
(20 mL X 2), the organic phase was washed with H₂O (20 mL X 2) and brine (15 mL), dried over sodium sulfate, concentrated and purified by silica gel column chromatography (eluent: PE/EA, 2/1) to provide boronic acid **S2** (2.1 g, 10.2mmol, 68 %) as white solid. **S2**: ¹H NMR (400 MHz, CDCl₃) δ 7.07 (s, 1H), 6.16 (s, 2H), 4.65 (t, *J* = 8.6 Hz, 4H), 3.11 (t, *J* = 8.4 Hz, 4H).



Synthesis of **S4**: To a mixture of **S3** (400 mg, 1.12 mmol, 1.0 equiv), **S2** (692 mg, 3.36 mmol, 3.0 equiv), Pd₂(dba)₃ (31 mg, 0.034 mmol, 3%), SPhos (28 mg, 0.067 mmol, 6%) and KF (260 mg, 4.48 mmol, 4.0 equiv) was charged dried dioxane (5 mL). The mixture was stirred under N₂ for 12h at 100 °C, concentrated, partitioned with water (10 mL) and DCM (20 mL), the organic phase was wash with brine and dried over sodium sulfate, concentrated, and purified by silica gel column chromatography (eluent: EtOAc) to provide **S4** (394 mg, 1.06 mmol, 95%) as white solid. **S4**: ¹H NMR (400 MHz, CDCl₃) δ 7.44 (t, *J* = 8.0 Hz, 1H), 6.93-6.96 (m, 2H), 6.86 (dd, *J* = 7.7, 2.6 Hz, 1H), 4.33-4.65 (m, 6H), 3.01-3.17 (m, 4H), 0.88 (d, *J* = 16.0 Hz, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 165.4 (d, *J* = 19.6 Hz), 158.2, 157.2, 136.3 (d, *J* = 5.4 Hz), 134.6, 124.4 (d, *J* = 8.2 Hz), 120.5, 119.3, 117.5, 114.5 (d, *J* = 90.9 Hz), 113.2 (d, *J* = 5.4 Hz), 106.9, 72.3 (d, *J* = 13.4 Hz), 65.5, 64.9, 33.3 (d, *J* = 72.1 Hz), 29.6, 29.4, 23.8. ³¹P NMR (162 MHz, CDCl₃) δ 62.4. ESI-MS: *m/z* 371.6 [M+H]⁺.

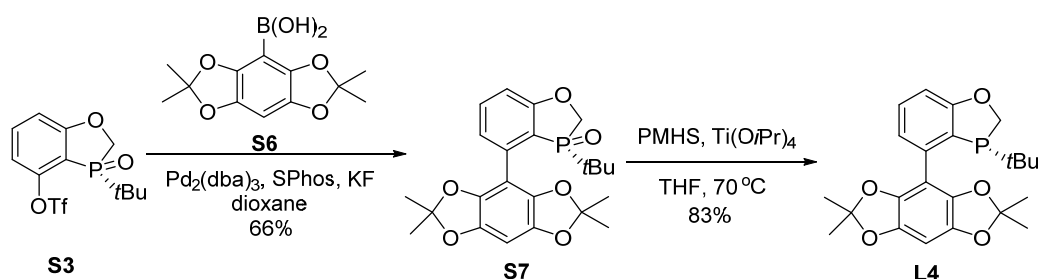
Synthesis of **L3**: To a solution of compound **S4** (400mg, 1.1mmol, 1.0 equiv) in THF (5 mL) at rt was added PMHS (2.5 g) and Ti(OiPr)₄ (1.4 mL, 4.7mmol, 4.3 equiv). The mixture was stirred at reflux for 12 h, and then concentrated under vacuum to remove most THF. 30% aqueous NaOH solution (10 mL) was carefully added to the residue. Gas was generated during addition. The resulting mixture was further stirred at 60 °C for 0.5 h. To the mixture at rt was added ether (8mL X 4). The ether layer was separated and the aqueous layer was further washed with ether (4 mL) under nitrogen. The combined ether solution was dried, concentrated, and purified by passing through a neutral alumina plug to afford the desired product **L3** (326mg, 0.67mmol, 84%) as white solid. **L3**: [α]_D²⁵ = 176.7° (*c* = 0.2, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.34 (t, *J* = 7.8 Hz, 1H), 6.99 (s, 1H), 6.97 (dd, *J* = 7.6, 2.9 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 4.84 (dd, *J* = 12.6, 1.5 Hz, 1H), 4.55-4.66 (m, 4H), 4.41 (q, *J* = 8.9 Hz, 1H), 3.08-3.22(m, 4H), 0.76 (d, *J* = 12.0 Hz, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 163.6, 157.6, 156.6, 136.7 (d, *J* = 17.6 Hz), 131.1, 124.0 (d, *J* = 15.0 Hz), 122.8 (d, *J* = 3.8 Hz), 119.7, 118.9, 118.1, 110.1, 109.1, 72.1, 72.0, 70.1 (d, *J* = 27.7 Hz), 31.1 (d, *J* = 18.9 Hz), 29.7, 26.5 (d, *J* = 13.8 Hz). ³¹P NMR (162 MHz, CDCl₃) δ -8.2. ESI-MS: *m/z* 355.3 [M+H]⁺, 377.4 [M+Na]⁺; HRMS (ESI) calculated for [M+H, C₂₁H₂₄O₃P]⁺: 355.1458; found: 355.1459.

Synthesis of L4



Compound **S5** was synthesized according to the procedures described in reference 6: T. J. Reddy, T. Iwama, H. J. Halpern and V. H. Rawal, *J. Org. Chem.* 2002, **67**, 4635

Synthesis of boronic acid **S6**: To a solution of **S5** (2.0 g, 9.1 mmol, 1.0 equiv) in THF (50 mL) was added dropwise $n\text{-BuLi}$ (4.3 mL, 2.5 M in Hexane, 10.8 mmol, 1.2 equiv) at 0 °C over 15 min. After stirred at 0 °C for 1 h, the mixture was cooled to -78 °C and B(OiPr)_3 (8.4 mL, 36.4 mmol, 4.0 equiv) was added. The resulting mixture was stirred for 30 min and then warmed to room temperature. Saturated NH_4Cl solution (20 mL) was added and the organic phase was separated. The aqueous phase was washed by EtOAc (10 mL X 2) and the combined organic phase was washed with H_2O (10 mL X 2) and brine (10 mL), dried over sodium sulfate, concentrated, and purified by silica gel column chromatography (eluent: PE/EA, 3/1) to provide boronic acid **S6** (1.53 g, 5.75 mmol, 64%) as white solid. **S6**: $^1\text{H NMR}$ (400 MHz, DMSO) δ 7.98 (s, 2H), 6.45 (s, 1H), 1.53 (s, 12 H).



Synthesis of S7

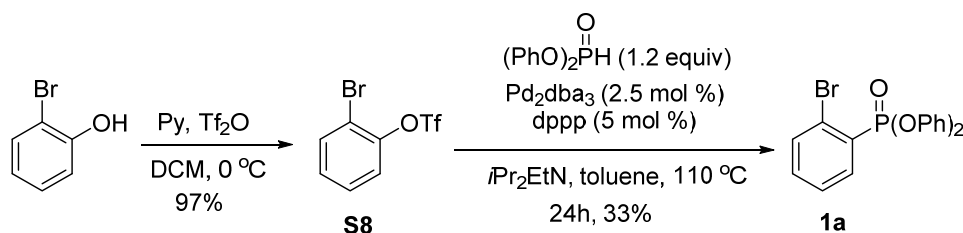
The procedure was similar to that described for the synthesis of **S4**. **S7**: white solid. 66% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.48 (t, $J = 7.8$ Hz, 1H), 6.97 (dd, $J = 7.5, 3.3$ Hz, 1H), 6.94 (dd, $J = 8.5, 3.1$ Hz, 1H), 6.34 (s, 1H), 4.50 (dd, $J = 13.8, 2.0$ Hz, 1H), 4.42 (dd, $J = 13.8, 10.2$ Hz, 1H), 1.75 (s, 3H), 1.64 (s, 3H), 1.62 (s, 3H), 1.54 (s, 3H), 1.00 (d, $J = 16.0$ Hz, 9H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 165.7 (d, $J = 18.9$ Hz), 140.7, 139.6, 139.2, 138.3, 134.6 (d, $J = 1.3$ Hz), 134.1 (d, $J = 6.3$ Hz), 124.6 (d, $J = 7.8$ Hz), 119.1, 117.9, 114.2 (d, $J = 89.4$ Hz), 113.9 (d, $J = 5.0$ Hz), 107.1, 92.5, 65.7 (d, $J = 60.4$ Hz), 33.3 (d, $J = 71.8$ Hz), 26.0 (d, $J = 21.4$ Hz), 25.6, 24.2. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 61.4. ESI-MS: m/z 431.3 $[\text{M}+\text{H}]^+$, 453.4 $[\text{M}+\text{Na}]^+$.

Synthesis of L4

The procedure was similar to that described for the synthesis of **L3**. **L4**: white solid. 83% yield. $[\alpha]_D^{25} = 169.6^\circ$ ($c = 0.25$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.34 (t, $J = 7.8$ Hz, 1H), 6.98 (dd, $J = 7.5, 3.1$ Hz, 1H), 6.92 (dd, $J = 8.1, 0.6$ Hz, 1H), 6.35 (s, 1H), 4.84 (dd, $J = 12.6, 1.8$ Hz, 1H), 4.58 (dd, $J = 25.8, 12.6$ Hz, 1H), 1.72 (s, 6 H), 1.59 (br, 6H), 0.80 (d, $J = 12.0$ Hz, 9H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 163.8, 135.2 (d, $J = 17.6$ Hz), 131.1, 124.2 (d, $J = 18.9$ Hz), 122.9 (d, $J = 5.0$ Hz), 117.9, 110.5, 109.4, 91.9, 70.2 (d, $J = 29.0$ Hz), 31.4 (d, $J = 18.9$ Hz), 26.8 (d, $J = 15.1$ Hz), 25.8 (br). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ -8.8. ESI-MS: m/z 415.5 $[\text{M}+\text{H}]^+$. HRMS (ESI) calculated for $[\text{M}+\text{H}, \text{C}_{23}\text{H}_{28}\text{O}_5\text{P}]^+$: 415.1669; found: 415.1668.

3. Synthetic procedures of Substrates

Procedure A:

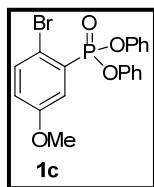


Synthesis of **1a**

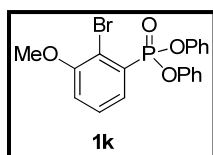
To a solution of 2-bromophenol (7.5 g, 43.1 mmol) and pyridine (4.2 mL, 51.7 mmol) in DCM (50 mL) at 0 °C was charged Tf₂O (8.0 mL, 47.4 mmol). The resulting mixture was stirred for further 20 min and then quenched with water (50 mL). The DCM layer was separated, washed with water (50 mL X 2) and brine (25 mL), dried over sodium sulfate, concentrated, and purified by silica gel column chromatography (eluent: PE/DCM, 5/1) to give the desired product **S8** (12.7 g, 97%) as colorless oil. **S8**: ¹H NMR (400 MHz, CDCl₃) δ 7.69 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.34-7.42 (m, 2H), 7.24-7.28 (m, 1H).

To a mixture of **S8** (3.0 g, 9.8 mmol), (PhO)₂P(O)H (2.8 g, 11.8 mmol), *i*Pr₂EtN (2.6 mL, 14.8 mmol), Pd₂dba₃ (225 mg, 0.25 mmol) and dppp (203 mg, 0.49 mmol) was charged toluene (20 mL). The mixture was stirred at 110 °C for 24 h and then cooled to rt. Water (30 mL) was added and the toluene was separated. The organic phase was washed with water (30 mL X 2) and brine (25 mL), dried over sodium sulfate, concentrated, and purified by silica gel column chromatography (eluent: PE/EA, 10/1 then 5/1) to give the desired product **1a** (1.26 g, 33% yield) as white solid. **1a**: ¹H NMR (500 MHz, CDCl₃) δ 8.23-8.13 (m, 1H), 7.73 (dd, *J* = 8.6, 5.1 Hz, 1H), 7.46-7.36 (m, 2H), 7.28 (m, 8H), 7.16 (d, *J* = 5.4 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 150.2 (d, *J* = 7.5 Hz), 137.2 (d, *J* = 8.7 Hz), 134.6 (d, *J* = 11.2 Hz), 134.5 (d, *J* = 3.7 Hz), 129.7, 128.0 (d, *J* = 197.5 Hz), 127.1 (d, *J* = 15.0 Hz), 125.4 (d, *J* = 3.7 Hz), 125.3 (d, *J* = 1.2 Hz), 120.6 (d, *J* = 5.0 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 7.7; ESI-MS: *m/z* 389.1 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₈H₁₅BrO₃P]⁺: 388.9937; found: 388.9940.

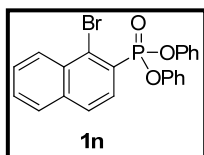
Preparation of **1c**, **1k**, **1n** was carried out according to a procedure similar to that for the synthesis of **1a** with its related arylphenol.



1c: White solid. 31% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.70 (dd, *J* = 16.7, 3.1 Hz, 1H), 7.61 (dd, *J* = 8.7, 6.7 Hz, 1H), 7.35-7.24 (m, 8H), 7.16 (t, *J* = 7.1 Hz, 2H), 6.96 (dd, *J* = 8.8, 3.1 Hz, 1H), 3.80 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 158.5 (d, *J* = 18.2 Hz), 150.2 (d, *J* = 7.6 Hz), 135.5 (d, *J* = 14.1 Hz), 129.7, 128.5 (d, *J* = 195.0 Hz), 125.3 (d, *J* = 1.2 Hz), 122.0 (d, *J* = 10.6 Hz), 121.0 (d, *J* = 3.1 Hz), 120.6 (d, *J* = 4.7 Hz), 115.3 (d, *J* = 3.2 Hz), 55.7; ³¹P NMR (162 MHz, CDCl₃) δ 7.6; ESI-MS: *m/z* 440.8 [M+Na]⁺; HRMS (ESI) calculated for [M+Na; C₁₉H₁₆BrNaO₄P]⁺: 440.9862; found: 440.9867.

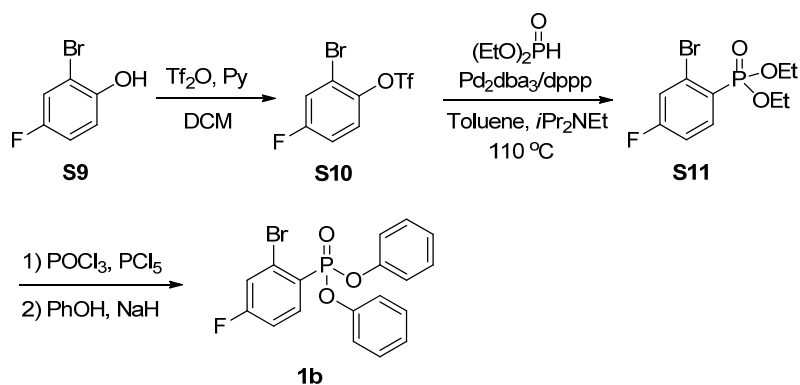


1k: Colorless oil. 32% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.78 (dd, $J = 14.5$, 7.6 Hz, 1H), 7.28-7.37 (m, 9H), 7.12-7.15 (m, 2H), 7.08 (d, $J = 8.1$ Hz, 1H), 3.89 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 156.7 (d, $J = 16.2$ Hz), 150.3 (d, $J = 7.5$ Hz), 129.7, 129.5 (d, $J = 195.0$ Hz), 128.8 (d, $J = 8.7$ Hz), 128.3 (d, $J = 17.5$ Hz), 125.2 (d, $J = 1.2$ Hz), 120.6 (d, $J = 3.7$ Hz), 116.6 (d, $J = 2.5$ Hz), 115.0 (d, $J = 5.0$ Hz), 56.6; $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 7.7; ESI-MS: m/z 419.1 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{19}\text{H}_{16}\text{BrNaO}_4\text{P}]^+$: 440.9862; found: 440.9861.



1n: White solid. 74% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.55 (d, $J = 1.3$ Hz, 1H), 8.18 (m, 1H), 7.90 (m, 2H), 7.70 (m, 2H), 7.30 (m, 8H), 7.15 (m, 2H); $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 8.4; ESI-MS: m/z 439.4 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{22}\text{H}_{16}\text{BrNaO}_3\text{P}]^+$: 460.9913; found: 460.9911.

Procedure B:

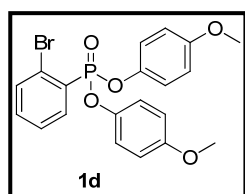


The synthesis of **S10** was carried out according to a procedure similar to that for the synthesis of **S8**.

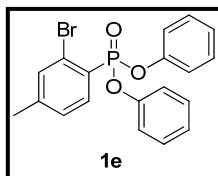
To a mixture of **S8** (2.0 g, 6.2 mmol), $(\text{EtO})_2\text{POH}$ (1.0 g, 7.4 mmol), $i\text{Pr}_2\text{NEt}$ (1.6 mL, 9.3 mmol), Pd_2dba_3 (56 mg, 0.06 mmol), dppp (51 mg, 0.12 mmol) was charged toluene (20 mL). The mixture was stirred at 110 °C for 24 h and then cooled to rt. Water (30 mL) was added and the toluene layer was separated. The organic phase was washed with water (30 mL X 2) and brine (25 mL), dried over sodium sulfate, concentrated, and purified by silica gel column chromatography (eluent: PE/EA, 10/1 then 2/1) to give the desired product **S11** (1.11 g, 58% yield) as colorless oil. To a mixture of **S11** (1.87g, 6.03 mmol) and PCl_5 (2.5 g, 12.06 mmol) was charged POCl_3 (4 mL) in sealed tube, the mixture was heated at 170 °C for 2 h and then cooled to rt, concentrated in vacuum to removed most of the POCl_3 . The residue was dissolved in THF (5 mL) to provide the phosphorus oxychloride solution. To a separated flask was charged PhOH (1.03 g, 10.85 mmol) and THF (10 mL). NaH (60%, 482 mg, 12.06 mmol) was added into the solution at 0 °C and the resulting mixture was stirred for 20 min before added to the aforementioned phosphorus oxychloride solution. The resulting mixture was stirred at rt for 1 h and then quenched with saturated NH_4Cl solution. EtOAc (20 mL) was added and the organic phase was separated, washed with water (25 mL X 2) and brine (15 mL), dried over sodium sulfate, concentrated, and purified by silica gel column chromatography (eluent: PE/EA, 5/1 then 2/1) to give the desired product **1b** (538 mg, 22%) as yellow solid. **1b**: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.19 (m, 1H), 7.50 (m, 1H), 7.32 (m, 4H), 7.26 (m, 4H), 7.17 (m, 3 H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 165.1 (dd, $J = 259.7$, 3.8 Hz), 150.1 (d, $J = 7.5$ Hz), 139.4 (dd,

$J = 10.5, 9.7$ Hz), 129.8, 126.5 (dd, $J = 9.9, 5.2$ Hz), 125.4 (d, $J = 1.2$ Hz), 124.1 (dd, $J = 202.0, 3.4$ Hz), 122.3 (dd, $J = 24.5, 13.1$ Hz), 120.5 (d, $J = 4.7$ Hz), 114.7 (dd, $J = 20.8, 15.7$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 6.9; ESI-MS: m/z 407.2 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{18}\text{H}_{13}\text{FBrNaO}_3\text{P}]^+$: 428.9662; found: 428.9660.

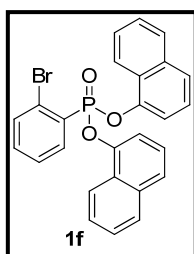
Other substrates were prepared according to procedure B with various substituted phenols. The yields were calculated on the basis of phenols.



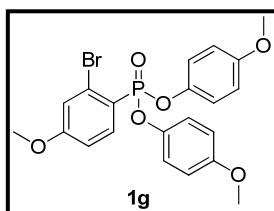
1d: Yellow solid. 17% yield. ^1H NMR (500 MHz, CDCl_3) δ 8.14 (m, 1H), 7.75 (m, 1H), 7.43 (m, 2H), 7.21 (m, 4H), 6.80 (m, 4H), 3.76 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.9, 152.9, 151.0, 143.6 (d, $J = 8.7$ Hz), 137.3 (d, $J = 7.5$ Hz), 137.2 (d, $J = 10.0$ Hz), 134.5 (d, $J = 27.5$ Hz), 127.7 (d, $J = 196.0$ Hz), 127.2 (d, $J = 15.0$ Hz), 125.3 (d, $J = 3.7$ Hz), 121.4 (d, $J = 16.2$ Hz), 114.6 (d, $J = 8.7$ Hz), 55.6, 55.4; ^{31}P NMR (162 MHz, CDCl_3) δ 8.5; ESI-MS: m/z 449.1 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{20}\text{H}_{18}\text{BrNaO}_5\text{P}]^+$: 470.9967; found: 470.9967.



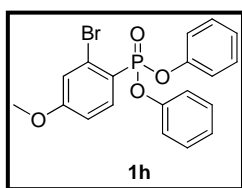
1e: Yellow oil. 15% yield. ^1H NMR (500 MHz, CDCl_3) δ 8.04 (m, 1H), 7.58 (d, $J = 5.0$ Hz), 7.30 (m, 7H), 7.26 (m, 1H), 7.23 (m, 1H), 7.15 (m, 1H), 2.39 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 150.3 (d, $J = 7.4$ Hz), 145.8 (d, $J = 2.9$ Hz), 137.2 (d, $J = 9.7$ Hz), 135.2 (d, $J = 12.1$ Hz), 129.7, 128.0 (d, $J = 14.9$ Hz), 125.1 (d, $J = 0.8$ Hz), 125.1, 124.6 (d, $J = 198.7$ Hz), 120.6 (d, $J = 4.7$ Hz), 21.2; ^{31}P NMR (162 MHz, CDCl_3) δ 8.4; ESI-MS: m/z 403.5 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{19}\text{H}_{16}\text{BrNaO}_3\text{P}]^+$: 424.9913; found: 424.9913.



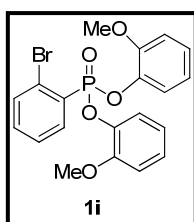
1f: Yellow solid. 21% yield. ^1H NMR (500 MHz, CDCl_3) δ 8.35 (m, 1H), 8.24 (d, $J = 5.0$ Hz, 2H), 7.84 (d, $J = 5.0$ Hz, 2H), 7.81 (m, 1H), 7.66 (d, $J = 10.0$ Hz, 2H), 7.49 (m, 8H), 7.34 (t, $J = 10$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 146.61, 146.56, 137.1, 137.0, 135.0, 134.9, 134.8, 134.7, 134.5, 129.4, 127.8, 127.7, 127.6, 127.4, 127.3, 127.2, 126.8, 126.6, 126.5, 126.3, 125.6, 125.51, 125.48, 125.4, 125.2, 125.0, 122.19, 122.16, 121.7, 121.6, 115.5, 115.3 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets); ^{31}P NMR (162 MHz, CDCl_3) δ 8.2; ESI-MS: m/z 489.4 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{26}\text{H}_{18}\text{BrNaO}_3\text{P}]^+$: 511.0069; found: 511.0054.



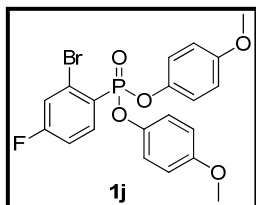
1g: Yellow solid. 10% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.01 (m, 1H), 7.25 (m, 1H), 7.16 (d, $J = 8.0$ Hz, 4H), 6.87 (m, 1H), 6.78 (d, $J = 8$ Hz, 4H), 3.86 (s, 3H), 3.76 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.7 (d, $J = 3.2$ Hz), 156.7 (d, $J = 1.2$ Hz), 143.8 (d, $J = 7.3$ Hz), 138.9 (d, $J = 10.5$ Hz), 126.2 (d, $J = 5.2$ Hz), 121.4 (d, $J = 4.5$ Hz), 120.5 (d, $J = 12.6$ Hz), 118.8 (d, $J = 204.3$ Hz), 114.6, 112.5 (d, $J = 15.3$ Hz), 55.7, 55.5; ^{31}P NMR (162 MHz, CDCl_3) δ 9.6; ESI-MS: m/z 479.2 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{21}\text{H}_{20}\text{BrNaO}_6\text{P}]^+$: 501.0073; found: 501.0075.



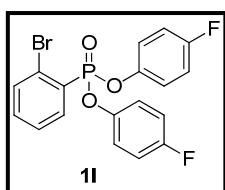
1h: Yellow oil. 11% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.05 (m, 1H), 7.27 (m, 9H), 7.12 (t, $J = 4.8$ Hz, 1H), 6.89 (m, 1H), 3.83 (s, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.8 (d, $J = 3.3$ Hz), 150.3 (d, $J = 7.4$ Hz), 138.8 (d, $J = 10.8$ Hz), 129.7, 126.3 (d, $J = 5.3$ Hz), 125.1, 120.6 (d, $J = 4.8$ Hz), 120.5, 118.9 (d, $J = 205.5$ Hz), 112.6 (d, $J = 15.5$ Hz), 55.7; ^{31}P NMR (162 MHz, CDCl_3) δ 8.8; ESI-MS: m/z 419.1 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{19}\text{H}_{16}\text{BrNaO}_4\text{P}]^+$: 440.9862; found: 440.9863.



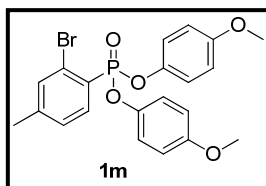
1i: White solid. 17% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.27-8.20 (m, 1H), 7.73 (dd, $J = 8.2, 6.4$ Hz, 1H), 7.42 (ddd, $J = 8.1, 4.8, 2.0$ Hz, 2H), 7.31 (dt, $J = 8.0, 1.4$ Hz, 2H), 7.10 (t, $J = 7.8$ Hz, 2H), 6.90 (d, $J = 8.2$ Hz, 2H), 6.87 (td, $J = 7.9, 1.1$ Hz, 2H), 3.67 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 150.8 (d, $J = 4.6$ Hz), 139.8 (d, $J = 8.5$ Hz), 136.3 (d, $J = 8.8$ Hz), 134.3 (d, $J = 12.1$ Hz), 133.7 (d, $J = 2.9$ Hz), 129.8 (d, $J = 203.4$ Hz), 126.6 (d, $J = 14.7$ Hz), 125.7 (d, $J = 1.4$ Hz), 125.4 (d, $J = 4.1$ Hz), 122.1 (d, $J = 3.5$ Hz), 120.7 (d, $J = 1.4$ Hz), 112.8, 55.8; ^{31}P NMR (162 MHz, CDCl_3) δ 8.1; ESI-MS: m/z 471.0 $[\text{M}+\text{Na}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{20}\text{H}_{18}\text{BrNaO}_5\text{P}]^+$: 470.9967; found: 470.9971.



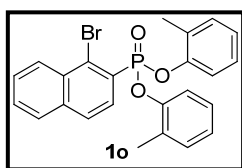
1j: Yellow oil. 15% yield. ^1H NMR (500 MHz, CDCl_3) δ 8.15 (m, 1H), 7.50 (m, 1H), 7.17 (m, 5H), 8.80 (m, 4H), 3.77 (s, 6H); δ 7.78; ^{13}C NMR (125 MHz, CDCl_3) δ 165.1 (dd, $J = 259.5, 3.8$ Hz), 156.9 (d, $J = 1.2$ Hz), 151.0, 143.6 (d, $J = 7.6$ Hz), 139.4 (t, $J = 9.9$ Hz), 126.4 (dd, $J = 9.9, 5.3$ Hz), 124.0 (dd, $J = 200.6, 3.4$ Hz), 122.3 (dd, $J = 24.3, 13.0$ Hz), 121.4 (d, $J = 4.4$ Hz), 114.7, 55.5, 55.4; ^{31}P NMR (162 MHz, CDCl_3) δ 7.8; ESI-MS: m/z 467.2 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{20}\text{H}_{17}\text{FBrNaO}_5\text{P}]^+$: 488.9873; found: 488.9872.



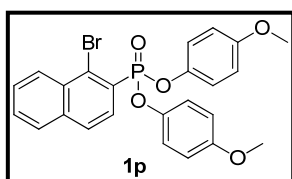
1l: Yellow oil. 19% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.12 (m, 1H), 7.74 (m, 1H), 7.45 (m, 2H), 7.21 (m, 4H), 5.97 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.8 (d, $J = 244.2$ Hz), 145.9 (dd, $J = 7.5, 2.7$ Hz), 137.4 (dd, $J = 14.5, 9.3$ Hz), 134.8 (dd, $J = 22.5, 11.2$ Hz), 134.6 (dd, $J = 22.5, 11.2$ Hz), 127.3 (dd, $J = 31.0, 14.8$ Hz), 127.2 (d, $J = 196.2$ Hz), 125.2, 122.0 (d, $J = 23.4$ Hz), 116.3 (d, $J = 22.5$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 8.6; ESI-MS: m/z 425.1 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{18}\text{H}_{12}\text{BrNaO}_3\text{P}]^+$: 446.9568; found: 446.9569.



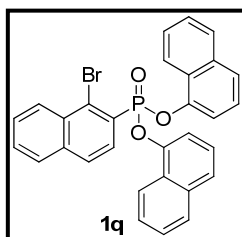
1m: Colorless oil. 19% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.98 (dd, $J = 16.0, 8.0$ Hz, 1H), 7.56 (d, $J = 4.0$ Hz, 1H), 7.17 (m, 5H), 6.77 (m, 4H), 3.74 (s, 6H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.8, 145.7, 143.8 (d, $J = 7.3$ Hz), 137.3 (d, $J = 16.2$ Hz), 135.2 (d, $J = 11.7$ Hz), 127.9 (t, $J = 13.7$ Hz), 125.1 (d, $J = 3.7$ Hz), 124.5 (d, $J = 198.7$ Hz), 121.4 (d, $J = 11.2$ Hz), 114.6 (d, $J = 5.0$ Hz), 55.5, 21.2 (d, $J = 18.4$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 9.2; ESI-MS: m/z 463.5 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{21}\text{H}_{20}\text{BrNaO}_5\text{P}]^+$: 485.0124; found: 485.0126.



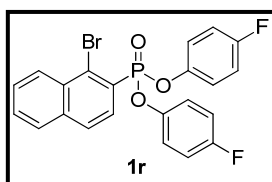
1o: Colorless oil. 18% yield. ^1H NMR (500 MHz, CDCl_3) δ 8.59-8.52 (m, 1H), 8.24 (dd, $J = 13.0, 8.5$ Hz, 1H), 7.96 (dd, $J = 8.5, 3.5$ Hz, 1H), 7.92 (dd, $J = 6.9, 2.5$ Hz, 1H), 7.74-7.66 (m, 2H), 7.27-7.25 (m, 2H), 7.21-7.17 (m, 2H), 7.11-7.03 (m, 4H), 2.31 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 149.2 (d, $J = 7.5$ Hz), 136.3 (d, $J = 2.5$ Hz), 132.6 (d, $J = 12.5$ Hz), 131.5 (d, $J = 16.2$ Hz), 130.3 (d, $J = 8.8$ Hz), 129.7 (d, $J = 6.2$ Hz), 129.2 (d, $J = 23.7$ Hz), 128.6 (d, $J = 6.2$ Hz), 128.5 (d, $J = 2.5$ Hz), 128.4 (d, $J = 7.5$ Hz), 127.9 (d, $J = 13.7$ Hz), 127.3 (d, $J = 197.5$ Hz), 127.0, 125.9, 120.3 (d, $J = 18.7$), 16.9; ^{31}P NMR (162 MHz, CDCl_3) δ 8.2; ESI-MS: m/z 467.3 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{24}\text{H}_{20}\text{BrNaO}_3\text{P}]^+$: 489.0226; found: 489.0226.



1p: Yellow oil. 15% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.53 (d, $J = 8.0$ Hz, 1H), 8.13 (td, $J = 16.0, 8.0$ Hz, 1H), 7.87 (m, 2H), 7.67 (m, 2H), 7.20 (d, $J = 12.0$ Hz, 5.0 Hz, 4H), 6.78 (m, 4H), 3.73 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.8, 143.9 (d, $J = 7.6$ Hz), 136.3, 132.5 (d, $J = 13.4$ Hz), 130.7 (d, $J = 7.5$ Hz), 129.1 (d, $J = 16.2$ Hz), 128.6 (d, $J = 3.7$ Hz), 128.5 (d, $J = 2.5$ Hz), 128.3 (d, $J = 17.5$ Hz), 127.7 (d, $J = 13.7$ Hz), 126.19 (d, $J = 195.6$ Hz), 121.5 (d, $J = 10.0$ Hz), 114.6 (d, $J = 6.2$ Hz), 55.6; ^{31}P NMR (162 MHz, CDCl_3) δ 9.2; ESI-MS: m/z 499.3 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{24}\text{H}_{20}\text{BrNaO}_5\text{P}]^+$: 521.0124; found: 521.0106.

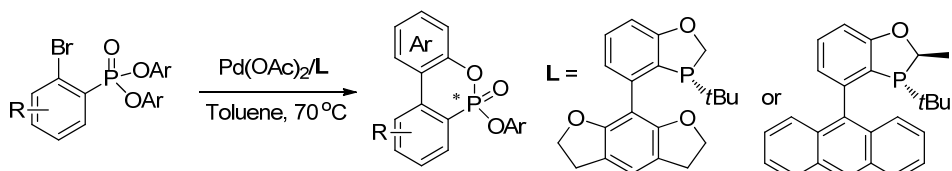


1q: White solid. 19% yield. ^1H NMR (500 MHz, CDCl_3) δ 8.55 (d, $J = 9.8$ Hz, 1H), 8.35 (dd, $J = 13.1, 8.5$ Hz, 1H), 8.25 (d, $J = 8.4$ Hz, 2H), 8.00 (dd, $J = 8.4, 3.6$ Hz, 1H), 7.95-7.90 (m, 1H), 7.83 (d, $J = 8.1$ Hz, 2H), 7.74-7.67 (m, 2H), 7.65 (d, $J = 8.2$ Hz, 2H), 7.55 (dd, $J = 6.6, 1.1$ Hz, 2H), 7.48 (m, 4H), 7.33 (t, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 146.7 (d, $J = 8.0$ Hz), 136.4 (d, $J = 2.5$ Hz), 135.0, 132.6 (d, $J = 13.6$ Hz), 130.3 (d, $J = 9.3$ Hz), 129.4, 129.0 (d, $J = 3.4$ Hz), 128.7, 128.5, 128.4, 128.2, 128.1, 127.8, 126.7, 126.6 (d, $J = 6.4$ Hz), 126.4, 125.5 (d, $J = 1.2$ Hz), 125.1, 122.2, 115.4 (d, $J = 3.5$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 8.8; ESI-MS: m/z 539.2 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{30}\text{H}_{20}\text{BrNaO}_3\text{P}]^+$: 561.0226; found: 561.0210.

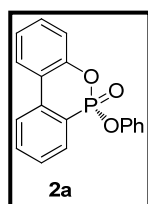


1r: Yellow solid. 17% yield. ^1H NMR (500 MHz, CDCl_3) δ 8.53 (m, 1H), 8.13 (m, 1H), 7.90 (m, 2H), 7.71 (m, 2H), 7.25 (m, 4H), 6.97 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.8, 158.9, 146.0, 136.6, 136.4, 132.5, 132.4, 130.57, 130.5, 130.4, 130.1, 129.91, 129.85, 129.8, 129.5, 129.3, 128.6, 128.54, 128.47, 128.3, 128.1, 128.0, 127.8, 127.2, 126.2, 125.5, 124.6, 122.0, 116.5, 116.3 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets); ^{31}P NMR (126 MHz, CDCl_3) δ 9.3 (d, $J = 21.4$ Hz); ESI-MS: m/z 475 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{H}; \text{C}_{22}\text{H}_{15}\text{BrO}_3\text{F}_2\text{P}]^+$: 474.9905; found: 474.9904.

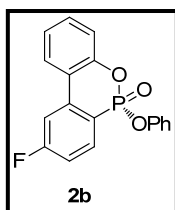
4. General procedure of intramolecular cyclization for constructing the P-chiral center



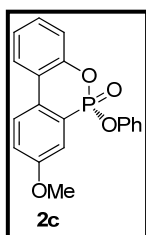
To a mixture of bromide (0.2 mmol), base (0.3 mmol), Pd(OAc)₂ (5 mol%), L (10 mol%) was charged toluene (1 mL). The resulting mixture was stirred at 70 °C under nitrogen for 24 h, and then cooled to room temperature, and concentrated under vacuum. The residue was directly subjected for column chromatography on silica gel to afford the desired product.



2a: Yellow solid; 83% yield. 88% ee; Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 80/20, 254 nm, 15.9 min (*S*), 18.0 min (*R*); $[\alpha]_D^{27} = -28.4^\circ$ ($c = 0.20$, CHCl₃); The absolute configuration was assigned by analogy with compound **2f**. ¹H NMR (400 MHz, CDCl₃) δ 8.08-7.93 (m, 3H), 7.76 (t, $J = 7.8$ Hz, 1H), 7.53 (td, $J = 7.3, 3.6$ Hz, 1H), 7.41 (t, $J = 7.7$ Hz, 1H), 7.35-7.20 (m, 4H), 7.13 (t, $J = 7.0$ Hz, 1H), 7.05 (d, $J = 8.4$ Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 149.9 (d, $J = 8.7$ Hz), 149.8 (d, $J = 8.2$ Hz), 137.1 (d, $J = 7.1$ Hz), 133.9, 130.7, 130.6, 129.7, 128.3 (d, $J = 15.8$ Hz), 125.3, 125.0, 124.2 (d, $J = 12.4$ Hz), 122.5, 122.4, 121.5 (d, $J = 182.0$ Hz), 120.7 (d, $J = 4.2$ Hz), 120.2 (d, $J = 6.8$ Hz); ³¹P NMR (162 MHz, CDCl₃) δ 6.4; ESI-MS: m/z 309.2 [M+H]⁺; HRMS (ESI) calculated for [M+Na; C₁₈H₁₃NaO₃P]⁺: 331.0495; found: 331.0496.

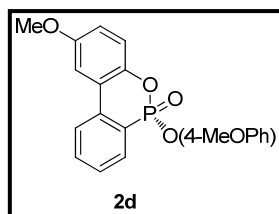


2b: White solid. 83% yield. 84% ee; Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 60/40, 254 nm, 8.3 min (*S*), 9.3 min (*R*); $[\alpha]_D^{27} = -24.1^\circ$ ($c = 0.40$, CHCl₃); The absolute configuration was assigned by analogy with compound **2f**. ¹H NMR (500 MHz, CDCl₃) δ 8.03 (ddd, $J = 14.4, 8.4, 5.9$ Hz, 1H), 7.87 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.66 (ddd, $J = 10.4, 5.4, 2.3$ Hz, 1H), 7.43 (ddd, $J = 8.9, 2.7, 1.4$ Hz, 1H), 7.31 (td, $J = 7.9, 0.8$ Hz, 1H), 7.28-7.19 (m, 4H), 7.17-7.11 (m, 1H), 7.06-7.01 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 166.3 (dd, $J = 254.3, 3.6$ Hz), 150.1 (d, $J = 8.3$ Hz), 149.7 (d, $J = 8.5$ Hz), 140.3 (t, $J = 8.7$ Hz), 133.6 (dd, $J = 10.5, 9.7$ Hz), 131.4, 129.7 (d, $J = 1.0$ Hz), 128.6 (d, $J = 28.6$ Hz), 125.4 (dd, $J = 3.2, 1.1$ Hz), 125.1, 121.7 (d, $J = 11.8$ Hz), 120.6 (d, $J = 4.4$ Hz), 120.4 (d, $J = 7.1$ Hz), 117.7 (d, $J = 186.8$ Hz), 116.0 (dd, $J = 22.1, 16.9$ Hz), 111.3 (dd, $J = 23.5, 13.6$ Hz); ³¹P NMR (162 MHz, CDCl₃) δ 5.8; ESI-MS: m/z 327.2 [M+H]⁺; HRMS (ESI) calculated for [M+Na; C₁₈H₁₂FNaO₃P]⁺: 349.0400; found: 349.0407.

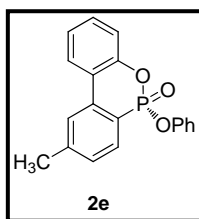


2c: White solid. 61% yield. 87% ee; Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 80/20, 254 nm, 18.4 min (*S*), 21.7 min (*R*); $[\alpha]_D^{27} = -19.3^\circ$ ($c = 0.40$, CHCl₃); The absolute configuration was assigned by analogy with compound **2f**. ¹H NMR (500 MHz, CDCl₃) δ 7.90 (dd, $J = 8.7, 7.9$ Hz, 1H), 7.87 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.47 (dd, $J = 16.5, 2.8$ Hz, 1H), 7.35-7.30 (m, 1H), 7.29-7.23 (m, 4H), 7.20 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.15-7.10 (m, 1H), 7.07-7.02 (m, 2H), 3.87 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.4 (d,

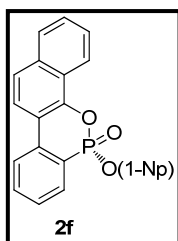
$J = 19.4$ Hz), 149.8 (d, $J = 8.8$ Hz), 149.3 (d, $J = 8.3$ Hz), , 129.6 (d, $J = 1.0$ Hz), 129.5, 128.7, 126.0 (d, $J = 14.8$ Hz), 125.3 (d, $J = 1.3$ Hz), 124.9, 124.7, 122.7 (d, $J = 180.0$ Hz), 122.6 (d, $J = 12.0$ Hz), 121.5 (d, $J = 2.9$ Hz), 120.7 (d, $J = 4.3$ Hz), 120.1 (d, $J = 7.0$ Hz), 113.5 (d, $J = 10.7$ Hz), 55.8; ^{31}P NMR (162 MHz, CDCl_3) δ 6.5; ESI-MS: m/z 339.2 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{19}\text{H}_{15}\text{NaO}_4\text{P}]^+$: 361.0600; found: 361.0601.



2d: Colorless oil. 82% yield. 83% ee; Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 60/40, 254 nm, 12.0 min (*S*), 15.6 min (*R*); $[\alpha]_{\text{D}}^{27} = -17.4^\circ$ ($c = 0.58$, CHCl_3); The absolute configuration was assigned by analogy with compound **2f**. ^1H NMR (500 MHz, CDCl_3) δ 7.97 (ddd, $J = 14.7, 7.6, 1.0$ Hz, 1H), 7.94-7.90 (m, 1H), 7.71 (t, $J = 7.8$ Hz, 1H), 7.52-7.46 (m, 1H), 7.41 (d, $J = 3.0$ Hz, 1H), 7.14 (d, $J = 8.9$ Hz, 1H), 6.96-6.90 (m, 3H), 6.77-6.71 (m, 2H), 3.86 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.8 (d, $J = 1.3$ Hz), 156.5, 143.8 (d, $J = 8.2$ Hz), 143.2 (d, $J = 8.5$ Hz), 137.0 (d, $J = 6.9$ Hz), 133.8 (d, $J = 2.5$ Hz), 130.8 (d, $J = 9.2$ Hz), 128.4 (d, $J = 15.7$ Hz), 124.1 (d, $J = 12.3$ Hz), 123.2 (d, $J = 11.8$ Hz), 121.8 (d, $J = 181.2$ Hz), 121.5 (d, $J = 4.2$ Hz), 121.0 (d, $J = 6.9$ Hz), 116.0, 114.6 (d, $J = 1.2$ Hz), 110.0, 55.8, 55.5; ^{31}P NMR (162 MHz, CDCl_3) δ 7.1; ESI-MS: m/z 369.3 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{20}\text{H}_{17}\text{NaO}_5\text{P}]^+$: 391.0706; found: 391.07081.

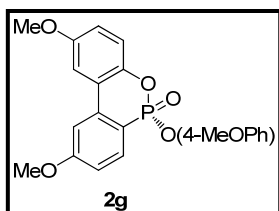


2e: White solid. 88% yield. 81% ee; Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 60/40, 254 nm, 8.3 min (*S*), 10.0 min (*R*); $[\alpha]_{\text{D}}^{27} = -34.5^\circ$ ($c = 0.3$, CHCl_3); The absolute configuration was assigned by analogy with compound **2f**. ^1H NMR (500 MHz, CDCl_3) δ 7.95 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.90 (dd, $J = 14.7, 7.7$ Hz, 1H), 7.81-7.77 (m, 1H), 7.40-7.35 (m, 1H), 7.32 (ddd, $J = 4.3, 3.7, 1.9$ Hz, 1H), 7.30-7.27 (m, 1H), 7.26-7.20 (m, 3H), 7.11 (td, $J = 7.6, 1.0$ Hz, 1H), 7.04 (dt, $J = 8.5, 1.2$ Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 150.1 (d, $J = 8.3$ Hz), 149.9 (d, $J = 8.5$ Hz), 144.6 (d, $J = 2.5$ Hz), 137.1 (d, $J = 7.4$ Hz), 130.7 (d, $J = 9.8$ Hz), 130.5, 129.6 (d, $J = 1.0$ Hz), 129.3 (d, $J = 16.2$ Hz), 128.6 (d, $J = 29.2$ Hz), 125.2, 124.8, 124.6 (d, $J = 12.8$ Hz), 122.6 (d, $J = 12.2$ Hz), 120.7 (d, $J = 4.4$ Hz), 120.2 (d, $J = 7.0$ Hz), 118.6 (d, $J = 184.5$ Hz), 22.2; ^{31}P NMR (162 MHz, CDCl_3) δ 7.3; ESI-MS: m/z 323.3 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{19}\text{H}_{15}\text{NaO}_3\text{P}]^+$: 345.0651; found: 345.0654.

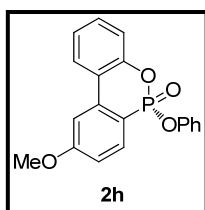


2f: White solid. 81% yield. 87% ee; Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 60/40, 254 nm, 10.3 min (*R*), 18.5 min (*S*); $[\alpha]_{\text{D}}^{27} = -227.2^\circ$ ($c = 0.61$, CHCl_3); The absolute configuration was determined by its X-ray structure. CCDC 1062715 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk). ^1H NMR (500 MHz, CDCl_3) δ 8.25 (d, $J = 7.9$ Hz, 1H), 8.14 (dd, $J = 14.9, 7.5$ Hz, 1H), 8.05 (t, $J = 7.3$ Hz, 1H), 7.97 (d, $J = 8.8$ Hz, 1H), 7.85-7.70 (m, 3H), 7.66 (d, $J = 8.2$ Hz, 1H), 7.59-7.40 (m, 6H), 7.30 (td, $J = 7.6, 2.9$ Hz, 2H), 7.11 (t, J

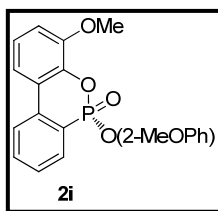
= 7.6 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 145.9 (d, $J = 8.9$ Hz), 145.7 (d, $J = 9.0$ Hz), 137.7 (d, $J = 6.9$ Hz), 134.6, 134.5, 134.0 (d, $J = 2.5$ Hz), 130.9 (d, $J = 9.5$ Hz), 128.3, 128.1, 127.7, 127.4 (d, $J = 2.7$ Hz), 127.0, 126.4 (d, $J = 4.9$ Hz), 126.3, 126.0, 125.8 (d, $J = 5.9$ Hz), 125.3 (d, $J = 1.6$ Hz), 125.2 (d, $J = 2.0$ Hz), 124.8, 124.6 (d, $J = 12.3$ Hz), 122.2, 121.6 (d, $J = 181.2$ Hz), 121.5 (d, $J = 1.3$ Hz), 121.2, 117.5 (d, $J = 12.3$ Hz), 116.2 (d, $J = 3.6$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 7.7; ESI-MS: m/z 409.4 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{26}\text{H}_{17}\text{NaO}_3\text{P}]^+$: 431.0808; found: 431.0811.



2g: Colorless oil. 85% yield. 87% ee; Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 60/40, 254 nm, 15.0 min (*S*), 20.2 min (*R*); $[\alpha]_{\text{D}}^{27} = -22.9^\circ$ ($c = 1.14$, CHCl_3); The absolute configuration was assigned by analogy with compound **2f**. ^1H NMR (500 MHz, CDCl_3) δ 7.91 (dd, $J = 14.3, 8.4$ Hz, 1H), 7.38 (dd, $J = 5.5, 2.3$ Hz, 1H), 7.36 (d, $J = 3.0$ Hz, 1H), 7.14 (d, $J = 8.9$ Hz, 1H), 7.04-6.99 (m, 1H), 6.93 (dd, $J = 9.1, 1.5$ Hz, 3H), 6.77-6.72 (m, 2H), 3.92 (s, 3H), 3.86 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.9 (d, $J = 3.0$ Hz), 156.8 (d, $J = 1.4$ Hz), 156.3, 144.1 (d, $J = 8.1$ Hz), 143.4 (d, $J = 8.5$ Hz), 139.1 (d, $J = 8.2$ Hz), 132.9 (d, $J = 10.7$ Hz), 128.6 (d, $J = 31.3$ Hz), 123.1 (d, $J = 11.5$ Hz), 121.6 (d, $J = 4.1$ Hz), 121.0 (d, $J = 7.1$ Hz), 116.0, 114.5 (d, $J = 1.2$ Hz), 113.9 (d, $J = 16.6$ Hz), 110.2, 109.9 (d, $J = 13.1$ Hz), 55.8, 55.6, 55.5; ^{31}P NMR (162 MHz, CDCl_3) δ 8.4; ESI-MS: m/z 399.2 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{21}\text{H}_{19}\text{NaO}_6\text{P}]^+$: 421.0811; found: 421.0814.

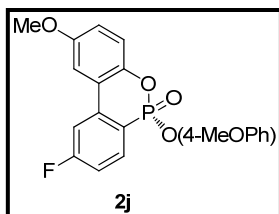


2h: Colorless oil. 85% yield. 88% ee; Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 60/40, 254 nm, 9.7 min, 12.4 min; $[\alpha]_{\text{D}}^{27} = -27.6^\circ$ ($c = 0.37$, CHCl_3); The absolute configuration was assigned by analogy with compound **2f**. ^1H NMR (500 MHz, CDCl_3) δ 7.94 (dd, $J = 14.4, 8.5$ Hz, 1H), 7.90 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.44 (dd, $J = 5.6, 2.3$ Hz, 1H), 7.41-7.36 (m, 1H), 7.32-7.27 (m, 1H), 7.23 (td, $J = 8.0, 1.5$ Hz, 3H), 7.11 (td, $J = 7.7, 1.0$ Hz, 1H), 7.03 (ddd, $J = 8.3, 3.9, 2.3$ Hz, 3H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.0 (d, $J = 3.2$ Hz), 150.2 (d, $J = 8.1$ Hz), 149.9 (d, $J = 8.5$ Hz), 139.2 (d, $J = 8.3$ Hz), 132.8 (d, $J = 10.7$ Hz), 130.7, 129.6 (d, $J = 1.1$ Hz), 128.6 (d, $J = 26.6$ Hz), 125.3, 125.2 (d, $J = 1.3$ Hz), 124.9, 122.4 (d, $J = 11.8$ Hz), 120.7 (d, $J = 4.3$ Hz), 120.3 (d, $J = 7.1$ Hz), 114.0 (d, $J = 16.6$ Hz), 109.7 (d, $J = 13.3$ Hz), 55.6; ^{31}P NMR (162 MHz, CDCl_3) δ 7.7; ESI-MS: m/z 339.2 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{19}\text{H}_{15}\text{NaO}_4\text{P}]^+$: 361.0600; found: 361.0603.

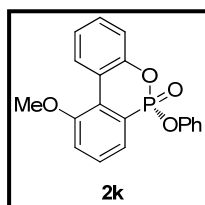


2i: Colorless oil. 17% yield. 78% ee; Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 70/30, 254 nm, 10.9 min (*R*), 14.1 min (*S*); $[\alpha]_{\text{D}}^{27} = -42.9^\circ$ ($c = 0.1$, CHCl_3); The absolute configuration was assigned by analogy with compound **2f**. ^1H NMR (500 MHz, CDCl_3) δ 8.06 (ddd, $J = 14.9, 7.6, 1.1$ Hz, 1H), 7.99-7.95 (m, 1H), 7.73 (t, $J = 7.8$ Hz, 1H), 7.55-7.51 (m, 2H), 7.30-7.27 (m, 1H), 7.21 (t, $J = 8.1$ Hz, 1H), 7.10-7.04 (m, 1H), 7.00 (d, $J = 8.1$ Hz, 1H), 6.85 (td, $J = 7.8, 1.3$ Hz, 1H), 6.79 (d, $J = 8.2$ Hz, 1H), 3.92 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ

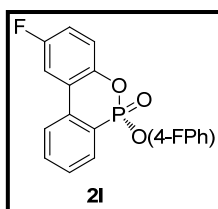
150.3 (d, $J = 6.0$ Hz), 137.5, 133.5, 130.9 (d, $J = 9.3$ Hz), 128.6, 128.1 (d, $J = 15.9$ Hz), 128.0, 126.0 (d, $J = 1.6$ Hz), 124.3, 124.2, 123.7 (d, $J = 12.1$ Hz), 123.0, 122.4 (d, $J = 3.3$ Hz), 121.5, 120.7, 116.6, 113.1, 112.3, 56.4, 55.5; ^{31}P NMR (162 MHz, CDCl_3) δ 6.9; ESI-MS: m/z 369.3 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{H}; \text{C}_{20}\text{H}_{18}\text{O}_5\text{P}]^+$: 369.0886; found: 369.0889.



2j: Colorless oil. 92% yield. 81% ee; Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 60/40, 254 nm, 12.0 min (*S*), 15.0 min (*R*); $[\alpha]_{\text{D}}^{27} = -13.3^\circ$ ($c = 1.12$, CHCl_3); The absolute configuration was assigned by analogy with compound **2f**. ^1H NMR (500 MHz, CDCl_3) δ 7.98 (ddd, $J = 14.3, 8.4, 5.9$ Hz, 1H), 7.59 (ddd, $J = 10.4, 5.2, 2.3$ Hz, 1H), 7.32 (d, $J = 3.0$ Hz, 1H), 7.22-7.17 (m, 1H), 7.16 (d, $J = 8.9$ Hz, 1H), 6.97 (ddd, $J = 8.9, 2.9, 1.1$ Hz, 1H), 6.94-6.90 (m, 2H), 6.77-6.72 (m, 2H), 3.87 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.2 (dd, $J = 254.1, 3.7$ Hz), 156.9 (d, $J = 1.4$ Hz), 156.5, 144.0 (d, $J = 8.1$ Hz), 143.1 (d, $J = 8.5$ Hz), 140.2 (t, $J = 8.7$ Hz), 133.7 (t, $J = 10.0$ Hz), 128.6 (d, $J = 28.3$ Hz), 122.4 (dd, $J = 11.5, 2.5$ Hz), 121.5 (d, $J = 4.1$ Hz), 121.2 (d, $J = 7.1$ Hz), 116.9, 116.0 (dd, $J = 22.0, 16.7$ Hz), 114.6 (d, $J = 1.2$ Hz), 111.4 (dd, $J = 23.4, 13.5$ Hz), 110.0, 55.8, 55.5; ^{31}P NMR (162 MHz, CDCl_3) δ 6.5; ESI-MS: m/z 387.2 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{20}\text{H}_{16}\text{FNaO}_5\text{P}]^+$: 409.0612; found: 409.0615.

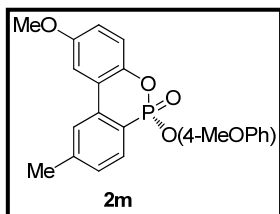


2k: Colorless oil. 49% yield. 58% ee; Enantiomeric excess was determined by chiral HPLC: Chiralcel OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 80/20, 254 nm, 19.3 min (*S*), 20.7 min (*R*); $[\alpha]_{\text{D}}^{27} = -43.9^\circ$ ($c = 0.12$, CHCl_3); The absolute configuration was assigned by analogy with compound **2f**. ^1H NMR (500 MHz, CDCl_3) δ 8.63 (dd, $J = 8.1, 1.6$ Hz, 1H), 7.67 (ddd, $J = 14.7, 7.4, 1.2$ Hz, 1H), 7.51 (ddd, $J = 8.2, 7.5, 5.0$ Hz, 1H), 7.39-7.34 (m, 1H), 7.32 (dd, $J = 8.3, 0.9$ Hz, 1H), 7.29-7.21 (m, 4H), 7.13 (dd, $J = 7.4, 0.7$ Hz, 1H), 7.04-7.00 (m, 2H), 4.00 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.6 (d, $J = 17.6$ Hz), 149.8 (d, $J = 8.5$ Hz), 149.1 (d, $J = 8.1$ Hz), 130.3 (d, $J = 1.4$ Hz), 129.8, 129.6 (d, $J = 1.1$ Hz), 129.5 (d, $J = 18.7$ Hz), 125.48 (d, $J = 8.0$ Hz), 125.19 (d, $J = 1.2$ Hz), 124.3, 124.2 (d, $J = 181.2$ Hz), 122.9 (d, $J = 8.6$ Hz), 122.0 (d, $J = 13.0$ Hz), 120.6 (d, $J = 4.4$ Hz), 119.9 (d, $J = 6.4$ Hz), 117.0 (d, $J = 3.0$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 7.5; ESI-MS: m/z 339.2 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{19}\text{H}_{15}\text{NaO}_4\text{P}]^+$: 361.0600; found: 361.0606.

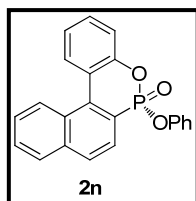


2l: Colorless oil. 84% yield. 75% ee; Enantiomeric excess was determined by chiral HPLC: Chiralcel OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 80/20, 254 nm, 8.8 min (*R*), 19.2 min (*S*); $[\alpha]_{\text{D}}^{27} = -24.0^\circ$ ($c = 0.42$, CHCl_3); The absolute configuration was assigned by analogy with compound **2f**. ^1H NMR (500 MHz, CDCl_3) δ 8.01 (ddd, $J = 14.8, 7.6, 1.0$ Hz, 1H), 7.95-7.89 (m, 1H), 7.82-7.75 (m, 1H), 7.64 (dd, $J = 9.4, 3.0$ Hz, 1H), 7.57 (tdd, $J = 7.5, 3.7, 0.8$ Hz, 1H), 7.21 (dd, $J = 9.0, 4.8$ Hz, 1H), 7.15-7.07 (m, 1H), 7.01 (ddd, $J = 9.1, 4.4, 1.4$ Hz, 2H), 6.98-6.92 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.7 (d, $J = 55.0$ Hz), 158.9 (d, $J = 1.6$ Hz), 158.5, 145.8 (dd, $J = 8.3, 2.5$ Hz), 145.5 (dd, $J = 8.5, 2.8$ Hz), 136.1 (dd, $J =$

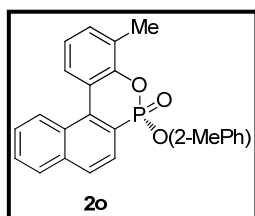
7.0, 2.2 Hz), 134.1 (d, $J = 2.5$ Hz), 130.9 (d, $J = 9.4$ Hz), 129.1 (d, $J = 15.7$ Hz), 124.3 (d, $J = 12.3$ Hz), 123.8 (dd, $J = 12.0, 8.0$ Hz), 122.0 (dd, $J = 8.4, 4.3$ Hz), 121.6 (dd, $J = 8.5, 7.1$ Hz), 117.5 (d, $J = 23.8$ Hz), 116.3 (dd, $J = 23.6, 1.2$ Hz), 111.7 (dd, $J = 25.2, 1.3$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 6.6; ESI-MS: m/z 345.2 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{18}\text{H}_{11}\text{F}_2\text{NaO}_3\text{P}]^+$: 367.0306; found: 367.0312.



2m: Colorless oil. 92% yield. 74% ee; Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 60/40, 254 nm, 11.5 min (*S*), 15.5 min (*R*); $[\alpha]_{\text{D}}^{27} = -24.0^\circ$ ($c = 0.84$, CHCl_3); The absolute configuration was assigned by analogy with compound **2f**. ^1H NMR (500 MHz, CDCl_3) δ 7.86 (dd, $J = 14.5, 7.7$ Hz, 1H), 7.72 (d, $J = 6.0$ Hz, 1H), 7.41 (d, $J = 3.0$ Hz, 1H), 7.31 (dd, $J = 7.8, 2.1$ Hz, 1H), 7.13 (d, $J = 8.9$ Hz, 1H), 6.95-6.88 (m, 3H), 6.77-6.69 (m, 2H), 3.87 (s, 3H), 3.73 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.8 (d, $J = 1.3$ Hz), 156.4, 144.4 (d, $J = 2.7$ Hz), 144.0 (d, $J = 8.2$ Hz), 143.3 (d, $J = 8.5$ Hz), 137.0 (d, $J = 7.4$ Hz), 130.8 (d, $J = 9.7$ Hz), 129.3 (d, $J = 16.1$ Hz), 128.6 (d, $J = 30.3$ Hz), 124.6 (d, $J = 12.7$ Hz), 123.2 (d, $J = 11.8$ Hz), 121.6 (d, $J = 4.1$ Hz), 121.0 (d, $J = 6.9$ Hz), 115.9, 114.5 (d, $J = 1.2$ Hz), 110.0, 55.8, 55.5, 22.1; ^{31}P NMR (162 MHz, CDCl_3) δ 7.9; ESI-MS: m/z 383.3 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{21}\text{H}_{19}\text{NaO}_5\text{P}]^+$: 405.0862; found: 405.0867.

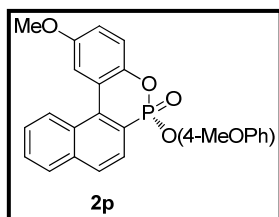


2n: Yellow solid. 87% yield. 88% ee; Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 80/20, 254 nm, 13.2 min (*S*), 15.1 min (*R*); $[\alpha]_{\text{D}}^{27} = -267.1^\circ$ ($c = 0.6$, CHCl_3); The absolute configuration was assigned by analogy with compound **2f**. ^1H NMR (500 MHz, CDCl_3) δ 8.57 (d, $J = 8.1$ Hz, 1H), 8.10 (dd, $J = 7.8, 1.5$ Hz, 1H), 8.01-7.92 (m, 3H), 7.69-7.59 (m, 2H), 7.48-7.42 (m, 1H), 7.36 (dd, $J = 15.1, 7.9$ Hz, 2H), 7.28-7.21 (m, 2H), 7.15-7.10 (m, 1H), 7.05-7.00 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 149.8 (d, $J = 8.7$ Hz), 149.4 (d, $J = 8.6$ Hz), 136.8 (d, $J = 2.5$ Hz), 136.6 (d, $J = 6.9$ Hz), 130.8 (d, $J = 1.7$ Hz), 130.1, 129.6, 129.1, 129.0, 128.3, 127.6 (d, $J = 1.6$ Hz), 126.5 (d, $J = 1.3$ Hz), 125.3 (d, $J = 1.3$ Hz), 124.7 (d, $J = 9.8$ Hz), 124.4 (d, $J = 1.0$ Hz), 123.6 (d, $J = 13.9$ Hz), 122.1, 120.7, 120.6, 120.5 (d, $J = 6.0$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 9.1; ESI-MS: m/z 359.3 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{22}\text{H}_{15}\text{NaO}_3\text{P}]^+$: 381.0651; found: 381.0656.

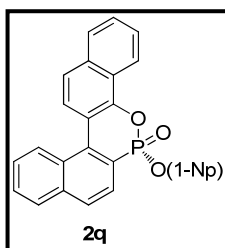


2o: Yellow oil. 88% yield. 87% ee; Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 95/5, 254 nm, 35.9 min (*R*), 38.2 min (*S*); $[\alpha]_{\text{D}}^{27} = -343.5^\circ$ ($c = 0.6$, CHCl_3); The absolute configuration was assigned by analogy with compound **2f**. ^1H NMR (500 MHz, CDCl_3) δ 8.57 (d, $J = 8.3$ Hz, 1H), 8.03-7.93 (m, 3H), 7.91 (dd, $J = 7.3, 1.8$ Hz, 1H), 7.69-7.58 (m, 2H), 7.47 (d, $J = 8.1$ Hz, 1H), 7.30-7.22 (m, 2H), 7.19-7.11 (m, 1H), 7.03 (t, $J = 6.3$ Hz, 2H), 2.21 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 148.7 (d, $J = 8.7$ Hz), 147.8 (d, $J = 8.8$ Hz), 137.0 (d, $J = 6.9$ Hz), 136.8 (d, $J = 2.5$ Hz), 131.6, 131.2, 129.9 (d, $J = 5.6$ Hz), 129.3 (d, $J = 6.1$ Hz), 129.1 (d, $J = 13.9$ Hz), 129.0, 128.9 (d, $J = 16.2$ Hz), 128.6 (d, $J = 1.6$ Hz), 128.2, 127.4, 127.0, 126.7, 125.0, 124.8 (d, $J = 9.9$ Hz), 123.8, 123.5 (d, $J = 13.6$ Hz), 121.6 (d, $J = 187.6$ Hz), 120.1 (d,

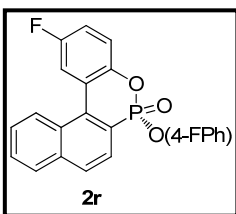
$J = 2.9$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 9.2; ESI-MS: m/z 387.3 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{24}\text{H}_{19}\text{NaO}_3\text{P}]^+$: 409.0964; found: 409.0969.



2p: Yellow solid. 62% yield. 75% ee; Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 70/30, 254 nm, 15.5 min (*S*), 19.1 min (*R*); $[\alpha]_{\text{D}}^{27} = -201.3^\circ$ ($c = 0.22$, CHCl_3); The absolute configuration was assigned by analogy with compound **2f**. ^1H NMR (500 MHz, CDCl_3) δ 8.67-8.60 (m, 1H), 8.02-7.89 (m, 3H), 7.65 (ddd, $J = 10.0, 6.8, 2.1$ Hz, 3H), 7.28 (d, $J = 8.9$ Hz, 1H), 6.99 (dd, $J = 8.9, 2.3$ Hz, 1H), 6.94 (dd, $J = 9.0, 1.3$ Hz, 2H), 6.79-6.71 (m, 2H), 3.89 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.8 (d, $J = 1.4$ Hz), 155.9 (d, $J = 0.9$ Hz), 143.3 (d, $J = 8.7$ Hz), 143.1 (d, $J = 8.6$ Hz), 136.8 (d, $J = 2.5$ Hz), 136.5 (d, $J = 6.8$ Hz), 129.2, 129.0, 128.9, 128.2, 127.6 (d, $J = 1.4$ Hz), 126.3, 124.8 (d, $J = 9.6$ Hz), 124.2 (d, $J = 13.7$ Hz), 122.5, 121.5 (d, $J = 4.2$ Hz), 121.2 (d, $J = 5.9$ Hz), 116.3 (d, $J = 1.7$ Hz), 115.1, 114.6 (d, $J = 1.0$ Hz), 55.9, 55.6; ^{31}P NMR (162 MHz, CDCl_3) δ 9.7; ESI-MS: m/z 419.3 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{24}\text{H}_{19}\text{NaO}_3\text{P}]^+$: 441.0862; found: 441.0866.



2q: White solid. 68% yield. 87% ee; Enantiomeric excess was determined by chiral HPLC: Chiralcel OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 70/30, 254 nm, 8.1 min (*R*), 16.8 min (*S*); $[\alpha]_{\text{D}}^{27} = -364.5^\circ$ ($c = 0.42$, CHCl_3); The absolute configuration was assigned by analogy with compound **2f**. ^1H NMR (500 MHz, CDCl_3) δ 8.66-8.56 (m, 1H), 8.24 (d, $J = 8.3$ Hz, 1H), 8.13 (d, $J = 8.7$ Hz, 1H), 8.08 (dd, $J = 12.9, 8.3$ Hz, 1H), 7.98 (dd, $J = 8.3, 3.6$ Hz, 2H), 7.83 (d, $J = 8.1$ Hz, 1H), 7.79 (d, $J = 8.8$ Hz, 1H), 7.71-7.63 (m, 2H), 7.60 (d, $J = 8.2$ Hz, 1H), 7.55-7.49 (m, 3H), 7.45 (ddd, $J = 8.1, 6.9, 1.1$ Hz, 1H), 7.30 (t, $J = 7.9$ Hz, 1H), 7.26-7.21 (m, 1H), 7.13 (d, $J = 8.4$ Hz, 1H), 6.98 (ddd, $J = 8.2, 6.9, 1.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 145.6 (d, $J = 8.8$ Hz), 137.4 (d, $J = 6.7$ Hz), 137.0 (d, $J = 2.5$ Hz), 134.5, 134.1, 129.1, 129.0, 128.3, 127.8, 127.5 (d, $J = 1.4$ Hz), 127.3 (d, $J = 2.2$ Hz), 127.0, 126.8 (d, $J = 0.9$ Hz), 126.7 (d, $J = 1.8$ Hz), 126.24, 126.18, 126.1 (d, $J = 4.9$ Hz), 125.8, 125.15, 125.13, 124.9 (d, $J = 10.1$ Hz), 123.7 (d, $J = 0.7$ Hz), 122.2, 122.1, 120.9, 120.6, 119.0 (d, $J = 14.4$ Hz), 116.0 (d, $J = 3.5$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 10.1; ESI-MS: m/z 459.4 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{H}; \text{C}_{30}\text{H}_{20}\text{O}_3\text{P}]^+$: 459.1145; found: 459.1142.

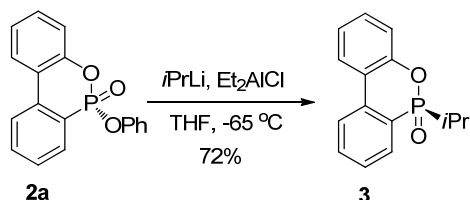


2r: White solid. 64% yield. 87% ee; Enantiomeric excess was determined by chiral HPLC: Chiralcel OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 80/20, 254 nm, 9.7 min (*S*), 12.5 min (*R*); $[\alpha]_{\text{D}}^{27} = -232.2^\circ$ ($c = 0.42$, CHCl_3); The absolute configuration was assigned by analogy with compound **2f**. ^1H NMR (500 MHz, CDCl_3) δ 8.61-8.51 (m, 1H), 8.06-7.91 (m, 3H), 7.85 (dd, $J = 9.6, 3.0$ Hz, 1H), 7.75-7.66 (m, 2H), 7.33 (dd, $J = 8.9, 4.9$ Hz, 1H), 7.22-7.14 (m, 1H), 7.00 (ddt, $J = 17.1, 14.6, 5.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.3 (d, $J = 133.1$ Hz), 158.4 (d, $J = 130.9$ Hz), 145.6 (dd, $J = 8.5, 2.7$ Hz), 145.2 (dd, $J = 8.8, 2.6$ Hz), 136.8 (d, $J = 2.4$ Hz), 135.5 (dd, $J = 6.8, 1.8$ Hz), 129.8 (d, $J = 16.1$ Hz), 129.3, 128.8 (d, $J = 13.6$ Hz), 128.6, 128.1, 125.9, 124.8 (dd, $J = 13.8, 8.3$ Hz), 124.6 (d, $J = 9.6$ Hz), 122.0 (dd, $J = 8.5, 4.4$ Hz), 121.8 (dd, $J = 8.6, 6.0$ Hz), 121.3 (d, $J = 175.0$ Hz), 117.2 (dd, $J = 25.7, 1.8$

Hz), 116.8 (d, $J = 23.6$ Hz), 116.3 (d, $J = 23.5$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 9.3; ESI-MS: m/z 395.3 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{22}\text{H}_{13}\text{F}_2\text{NaO}_3\text{P}]^+$: 417.0463; found: 417.0469.

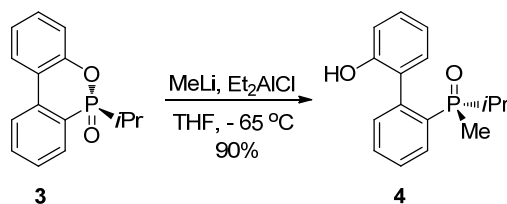
5. Experimental procedure for the reactions in Scheme 1

Synthesis of compound 3



Et_2AlCl (1.0 M in Hexane, 1.95 mL, 1.95 mmol) was added to a solution of compound **2a** (600 mg, 1.95 mmol) in THF (12 mL) at room temperature, the resulting mixture was cooled to $-65\text{ }^\circ\text{C}$ and stirred at the same temperature for 20 min, then $i\text{PrLi}$ (1.0 M in Hexane, 3.9 mL, 3.9 mmol) was dropped into the above solution and the resulting mixture was stirred for further 10 min. After quenched with saturated NH_4Cl aqueous solution, the mixture was extracted with ethyl acetate, dried over Na_2SO_4 , and concentrated under vacuum. The residue was purified by silica gel column chromatography (eluent: PE/EA, 1/1) to give the desired product **3** (362 mg, 72%) as yellow oil. **3**: Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, $25\text{ }^\circ\text{C}$, flow rate: 1 mL/min, hexanes/isopropanol: 80/20, 254 nm, 7.8 min, 9.5 min; $[\alpha]_{\text{D}}^{24} = 19.3^\circ$ ($c = 0.15$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.97 (dd, $J = 8.1, 4.6$ Hz, 1H), 7.93-7.85 (m, 2H), 7.72-7.66 (m, 1H), 7.51 (tdd, $J = 7.5, 2.9, 0.9$ Hz, 1H), 7.40-7.33 (m, 1H), 7.24 (dd, $J = 12.0, 4.5$ Hz, 2H), 2.28-2.11 (m, 1H), 1.19 (ddd, $J = 17.9, 16.4, 7.2$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 149.7 (d, $J = 8.7$ Hz), 136.0 (d, $J = 6.2$ Hz), 133.1 (d, $J = 2.5$ Hz), 130.8 (d, $J = 8.7$ Hz), 130.5, 128.2 (d, $J = 12.5$ Hz), 125.1, 124.3, 123.7 (d, $J = 8.7$ Hz), 123.5 (d, $J = 112.0$ Hz), 122.2 (d, $J = 10.0$ Hz), 120.2 (d, $J = 6.2$ Hz), 28.0 (d, $J = 97.5$ Hz), 15.2 (d, $J = 3.7$ Hz), 14.7 (d, $J = 2.5$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 42.8; ESI-MS: m/z 259.1 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{19}\text{H}_{15}\text{NaO}_4\text{P}]^+$: 258.0810; found: 259.0881.

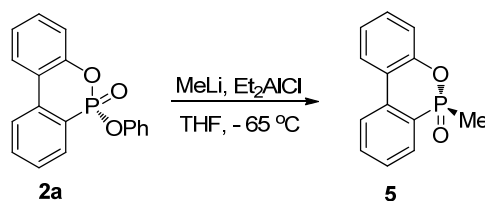
Synthesis of compound 4



Et_2AlCl (1.0 M in Hexane, 0.19 mL, 0.19 mmol) was added to a solution of compound **3** (50 mg, 0.19 mmol) in THF (2 mL) at room temperature, the resulting mixture was cooled to $-65\text{ }^\circ\text{C}$ and stirred at the same temperature for 20 min, then MeLi (1.6 M in ether, 0.24 mL, 0.39 mmol) was dropped into the above solution and the resulting mixture was stirred for further 10 min. After quenched with saturated NH_4Cl aqueous solution, the mixture was extracted with ethyl acetate, dried over Na_2SO_4 , and concentrated under vacuum. The residue was purified by silica gel column chromatography (eluent: PE/EA, 1/1) to give the desired product **4** (46 mg, 90%) as white solid. Compound **4** is a mixture of two atropisomers (2.2/1) at room temperature, however, the two

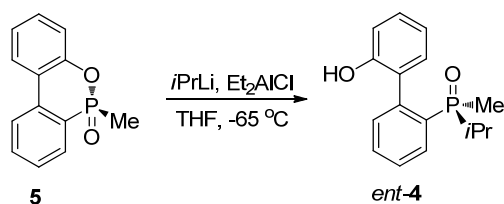
isomers could conversion to each other quickly at 100 °C and the ^1H NMR shows one compound at this temperature. Enantiomeric excess was determined by chiral HPLC: Chiralcel OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 230 nm, 7.6min, 9.3 min; $[\alpha]_{\text{D}}^{24} = 76.1^\circ$ ($c = 0.125$, CHCl_3); The ^1H NMR spectrum of **4** showed Mixtures at rt. However, the signals at 100 °C showed one isomer: ^1H NMR (500 MHz, d_6 -DMSO at 100 °C) δ 9.1 (br, 1H), 8.03-7.93 (m, 1H), 7.50 (dt, $J = 16.4, 8.5$ Hz, 2H), 7.22 (t, $J = 7.8$ Hz, 1H), 7.19-7.13 (m, 1H), 7.02 (d, $J = 7.3$ Hz, 1H), 6.91 (d, $J = 8.3$ Hz, 1H), 6.85 (t, $J = 7.5$ Hz, 1H), 1.68 (m, 1H), 1.25 (br, 3H), 0.90 (dd, $J = 15.8, 7.0$ Hz, 3H), 0.86 (dd, $J = 15.8, 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3 at rt) δ 154.3, 142.7, 142.6, 133.2, 133.1, 132.89, 132.87, 132.75, 132.68, 132.20, 132.18, 131.92, 131.90, 131.2, 131.1, 130.8, 130.5, 130.3, 130.3, 130.1, 130.0, 129.8, 127.7, 127.6, 127.44, 127.36, 122.1, 121.3, 120.8, 119.8, 27.0 (d, $J = 72.5$ Hz) (minor), 26.9 (d, $J = 70.0$ Hz) (major), 15.5 (d, $J = 102.5$ Hz) (minor), 15.4 (d, $J = 153.7$ Hz) (major), 12.0 (d, $J = 67.5$ Hz) (minor), 8.69 (d, $J = 70.0$ Hz) (major) (Due to C-P coupling and rotamers at rt, doublets in the aromatic region cannot be assigned and they are listed as singlets); ^{31}P NMR (162 MHz, CDCl_3 at rt) δ 53.2 (major), 47.2 (minor); ESI-MS: m/z 275.2 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{Na}; \text{C}_{16}\text{H}_{20}\text{O}_2\text{P}]^+$: 275.1201; found: 275.1197.

Synthesis of compound 5



Et_2AlCl (1.0 M in Hexane, 0.4 mL, 0.40 mmol) was added to a solution of compound **2a** (125 mg, 0.40 mmol) in THF (2 mL) at room temperature, the resulting mixture was cooled to -65°C and stirred at the same temperature for 20 min, then MeLi (1.6 M in ether, 0.38 mL, 0.6 mmol) was dropped into the above solution and the resulting mixture was stirred for further 10 min. After quenched with saturated NH_4Cl aqueous solution, the mixture was extracted with ethyl acetate, dried over Na_2SO_4 , and concentrated under vacuum. The residue was purified by silica gel column chromatography (eluent: PE/EA, 1/1) to give the desired product **5** (27 mg, 30%) as yellow oil. **5**: Enantiomeric excess was determined by chiral HPLC: Chiralpak AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 70/20, 230 nm, 7.0 min, 8.6 min; $[\alpha]_{\text{D}}^{24} = 5.8^\circ$ ($c = 0.125$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.98-7.80 (m, 3H), 7.68 (t, $J = 7.7$ Hz, 1H), 7.50 (td, $J = 7.3, 2.6$ Hz, 1H), 7.37 (t, $J = 7.7$ Hz, 1H), 7.26-7.21 (m, 2H), 1.82 (d, $J = 14.6$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 149.0 (d, $J = 8.1$ Hz), 135.2 (d, $J = 5.9$ Hz), 133.1, 130.5, 129.5 (d, $J = 11.5$ Hz), 128.4 (d, $J = 13.5$ Hz), 126.4, 125.1, 124.6, 123.9 (d, $J = 9.5$ Hz), 122.4 (d, $J = 11.4$ Hz), 120.5 (d, $J = 6.0$ Hz), 14.8 (d, $J = 100.4$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 35.3; ESI-MS: m/z 231.1 $[\text{M}+\text{H}]^+$; HRMS (ESI) calculated for $[\text{M}+\text{H}; \text{C}_{13}\text{H}_{11}\text{O}_2\text{P}]^+$: 230.0497; found: 231.0566.

Synthesis of compound ent-4



Et₂AlCl (1.0 M in Hexane, 22 μL, 0.022 mmol) was added to a solution of compound **5** (5 mg, 0.022 mmol) in THF (2 mL) at room temperature, the resulting mixture was cooled to -65 °C and stirred at the same temperature for 20 min, then *i*PrLi (1.0 M in Hexane, 44 μL, 0.044 mmol) was dropped into the above solution and the resulting mixture was stirred for further 10 min. After quenched with saturated NH₄Cl aqueous solution, the mixture was extracted with ethyl acetate, dried over Na₂SO₄, and concentrated under vacuum. The residue was purified by silica gel column chromatography (eluent: PE/EA, 1/1) to give the desired product *ent*-**4** (2.1 mg, 35%) as white solid. Enantiomeric excess was determined by chiral HPLC: Chiralcel OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 230 nm, 7.6 min, 9.3 min. Compound *ent*-**4** is a mixture of two atropisomers (2.2/1) at room temperature.

6. References

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7. X-ray of 2f

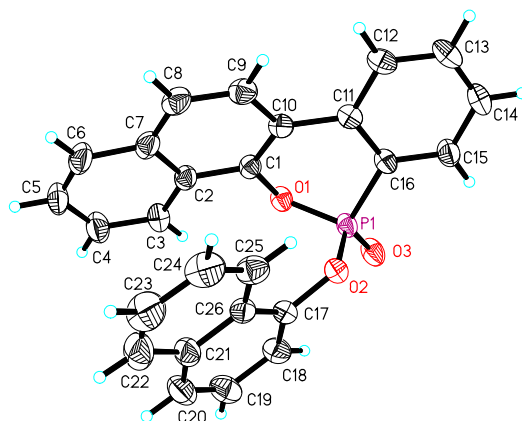
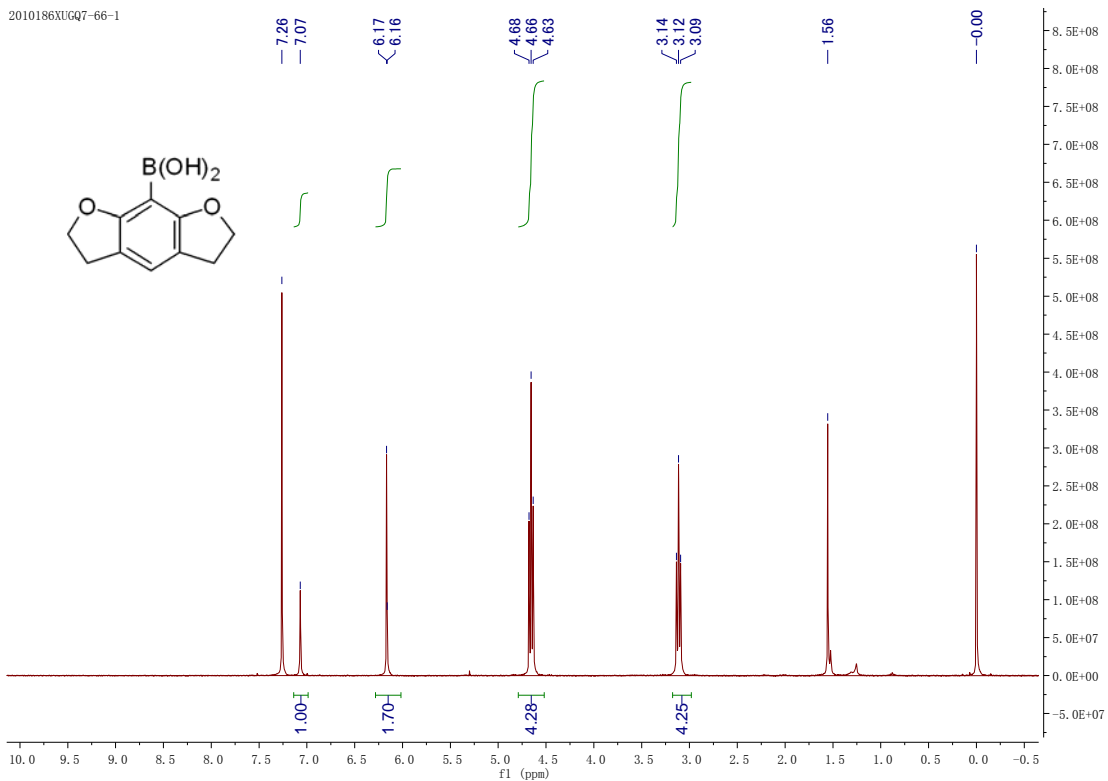


Table 1. Crystal data and structure refinement for 289.

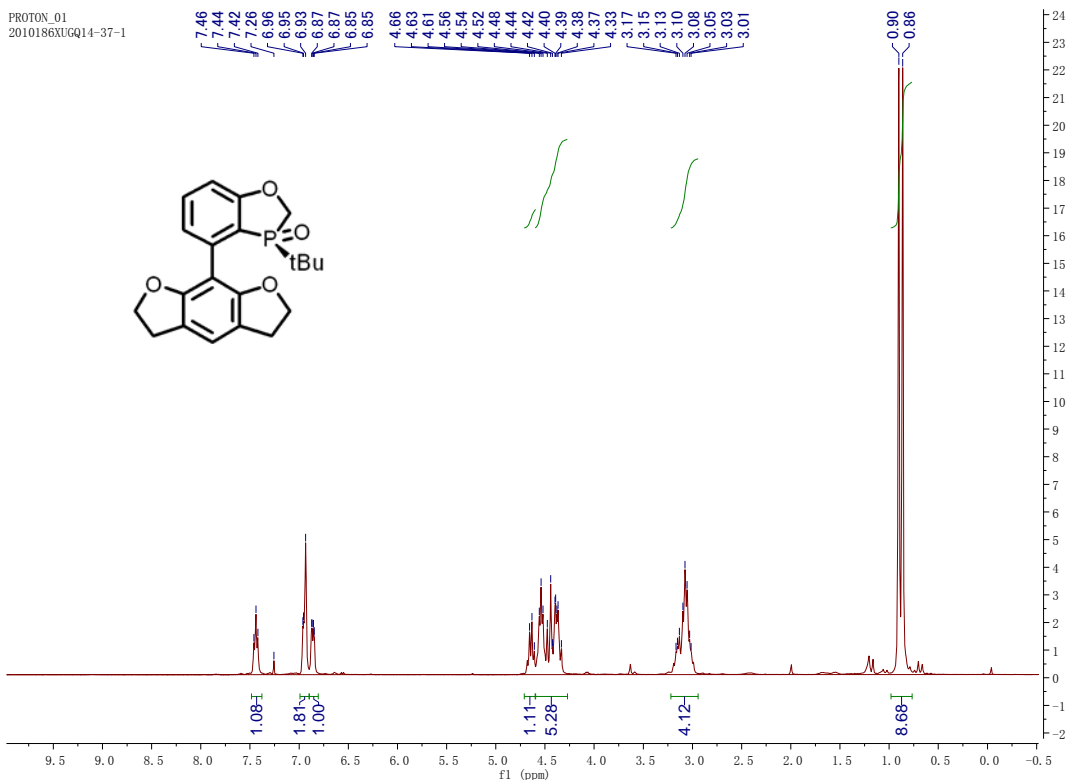
Identification code	289
Empirical formula	C ₂₆ H ₁₇ O ₃ P
Formula weight	408.37
Temperature	296(2) K
Wavelength	1.54178 Å
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 8.4926(17) Å alpha = 90 deg. b = 12.013(2) Å beta = 90 deg. c = 19.248(4) Å gamma = 90 deg.
Volume	1963.7(7) Å ³
Z, Calculated density	4, 1.381 Mg/m ³
Absorption coefficient	1.455 mm ⁻¹
F(000)	848
Crystal size	0.34 x 0.28 x 0.22 mm
Theta range for data collection	4.34 to 67.01 deg.
Limiting indices	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -22 ≤ l ≤ 22
Reflections collected / unique	8910 / 3380 [R(int) = 0.0281]
Completeness to theta = 67.01	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7529 and 0.5721
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3380 / 0 / 272
Goodness-of-fit on F ²	1.098
Final R indices [I > 2σ(I)]	R1 = 0.0394, wR2 = 0.1233
R indices (all data)	R1 = 0.0398, wR2 = 0.1239
Absolute structure parameter	0.08(2)
Extinction coefficient	0.0020(5)
Largest diff. peak and hole	0.344 and -0.264 e. Å ⁻³

8. NMR Spectra

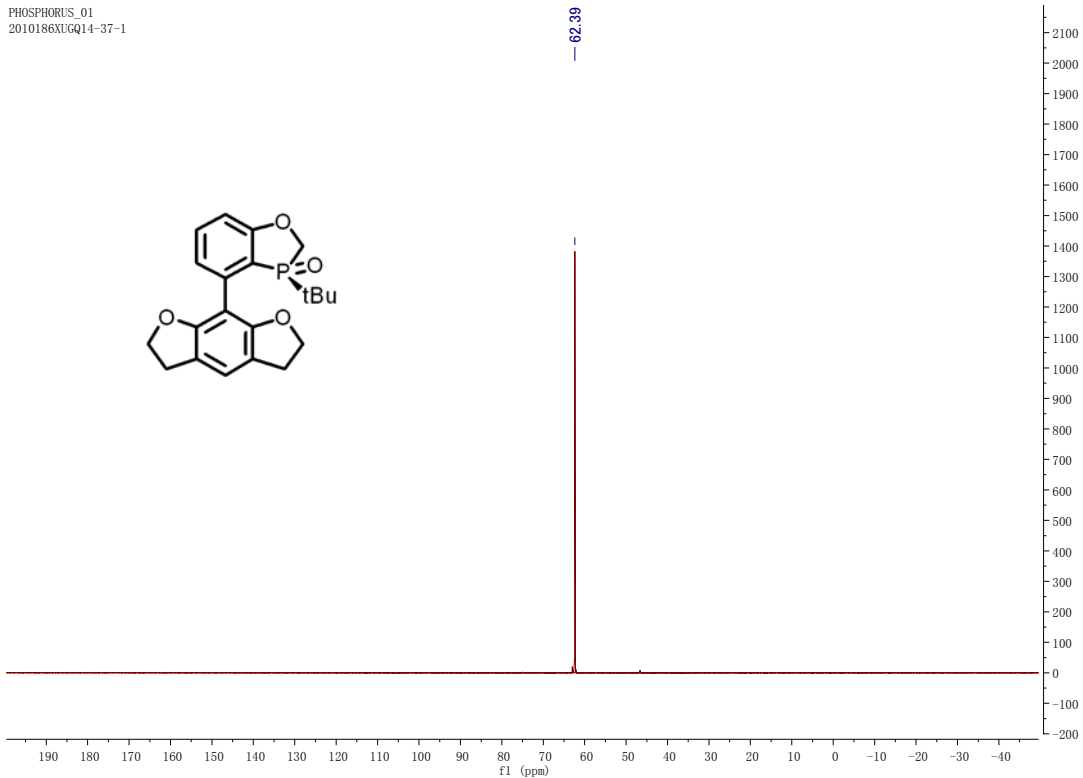
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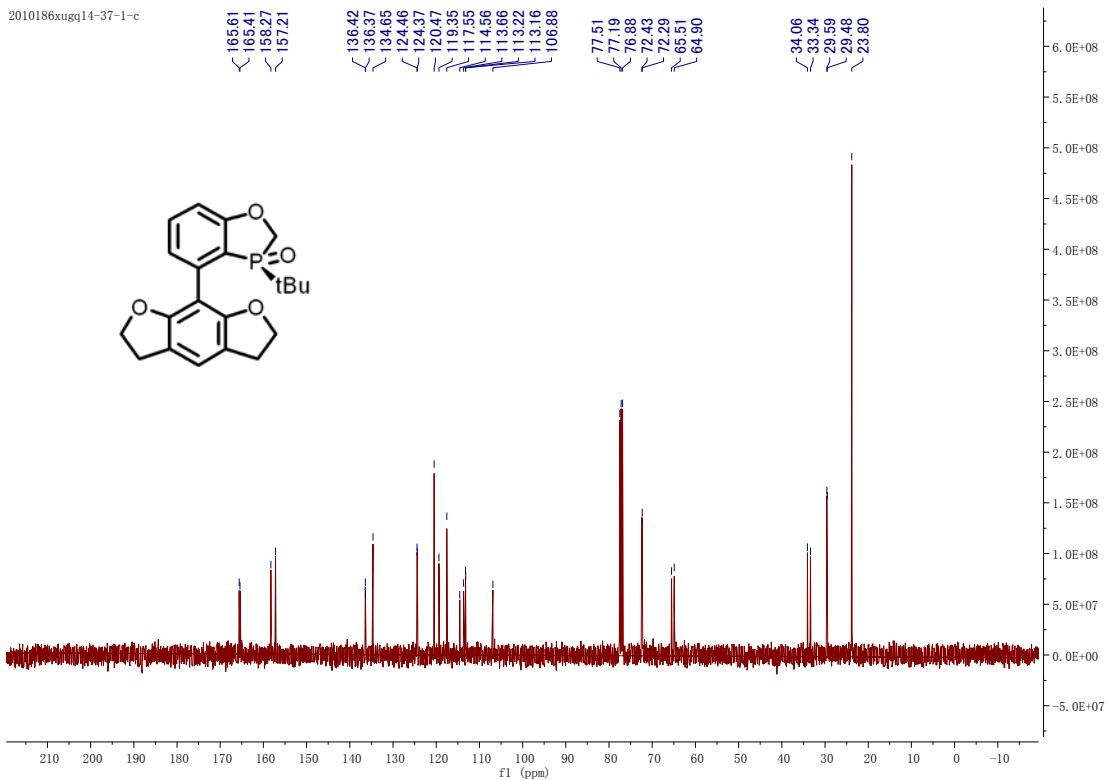
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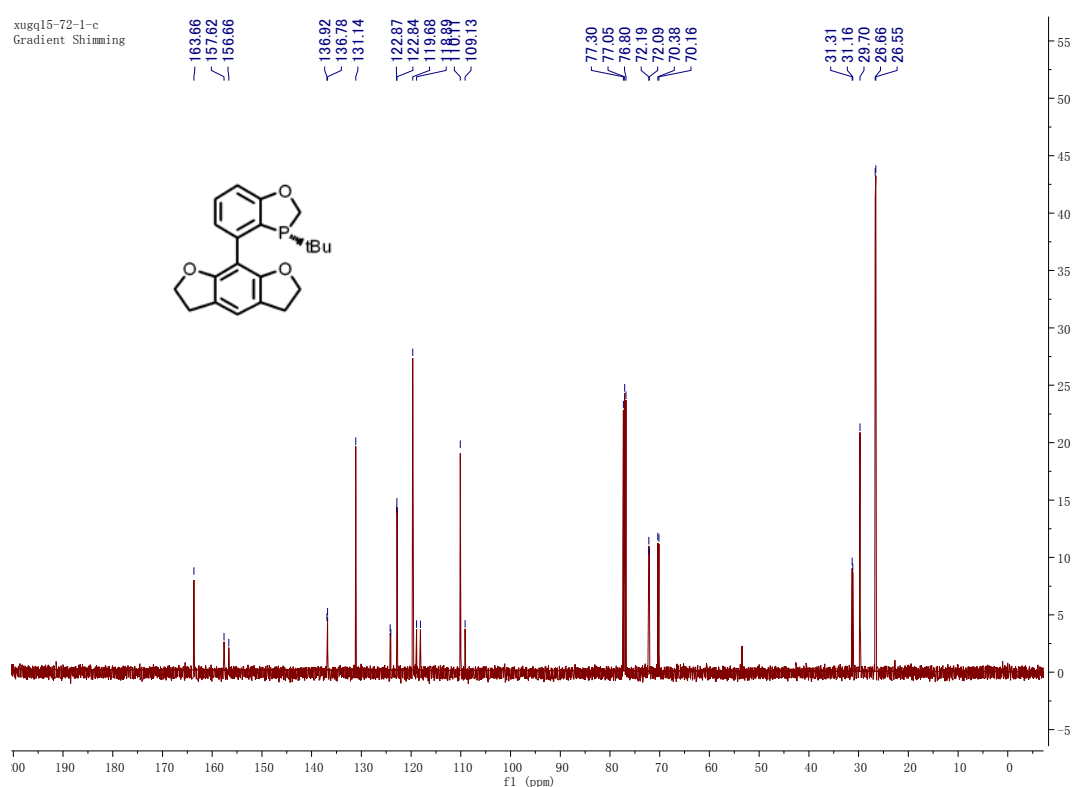
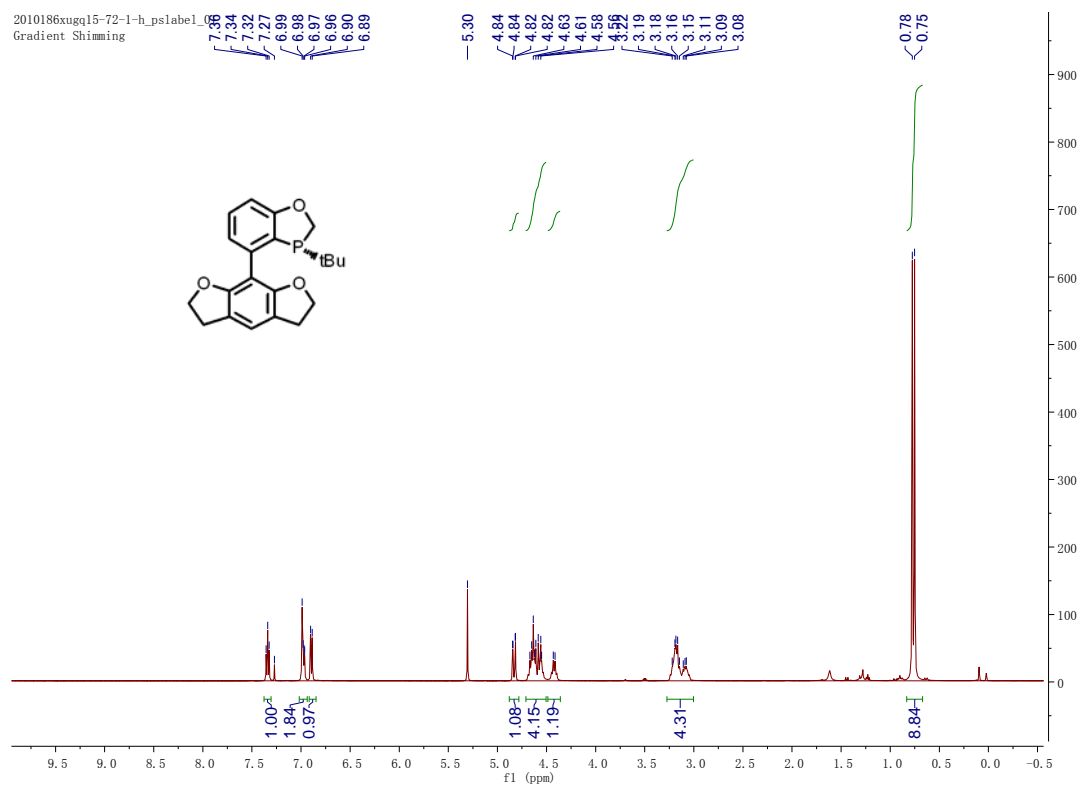


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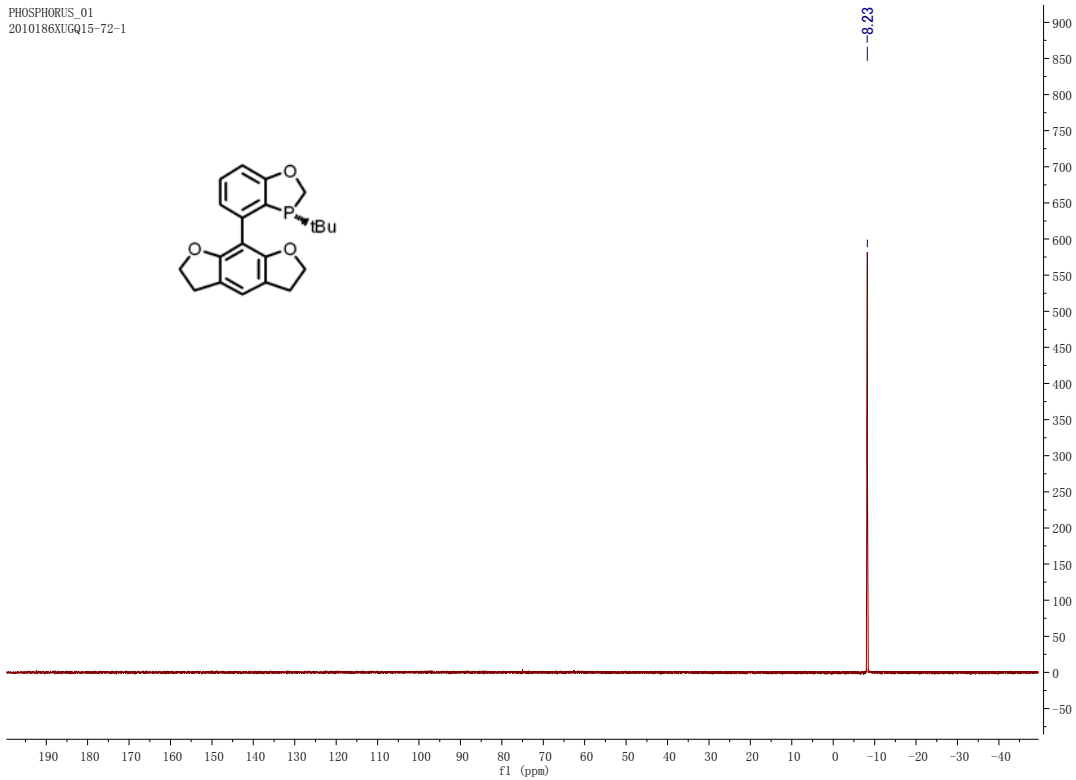


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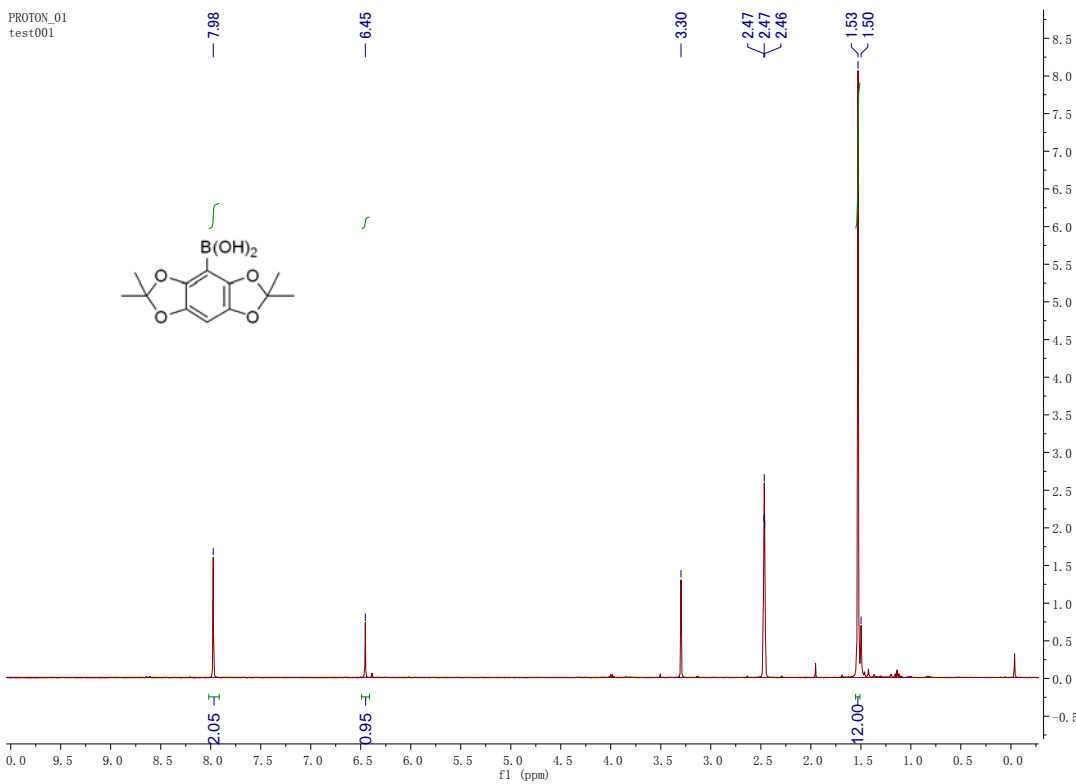


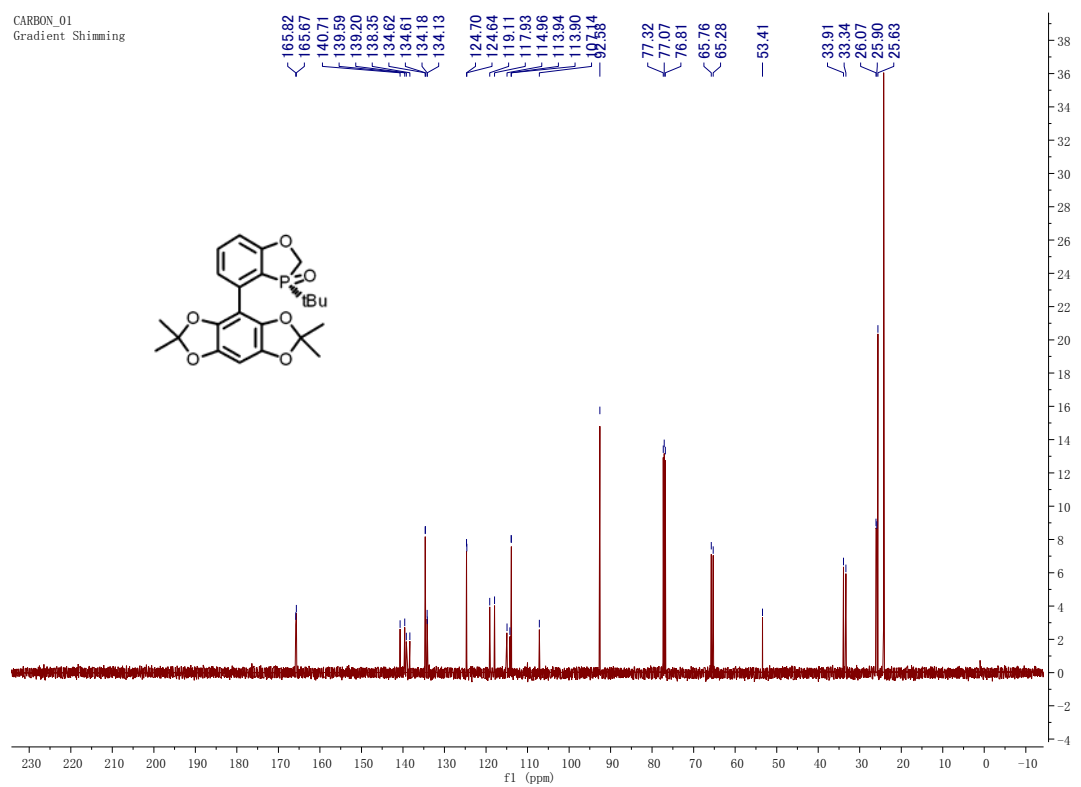
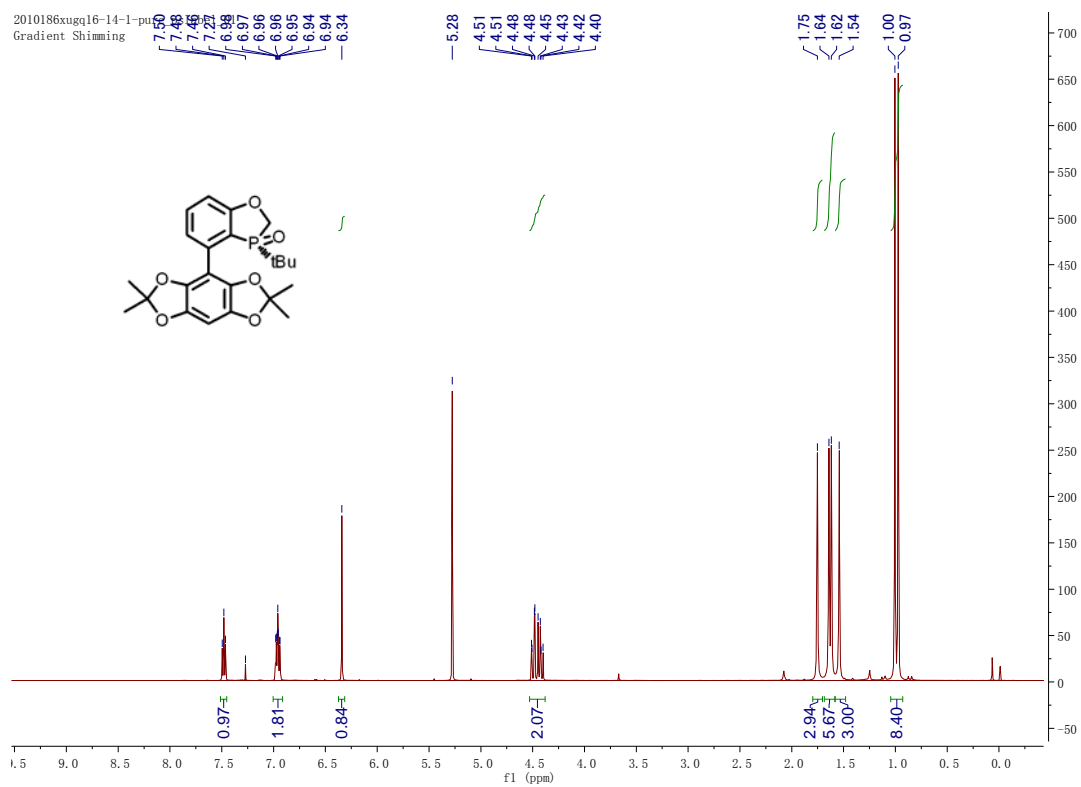


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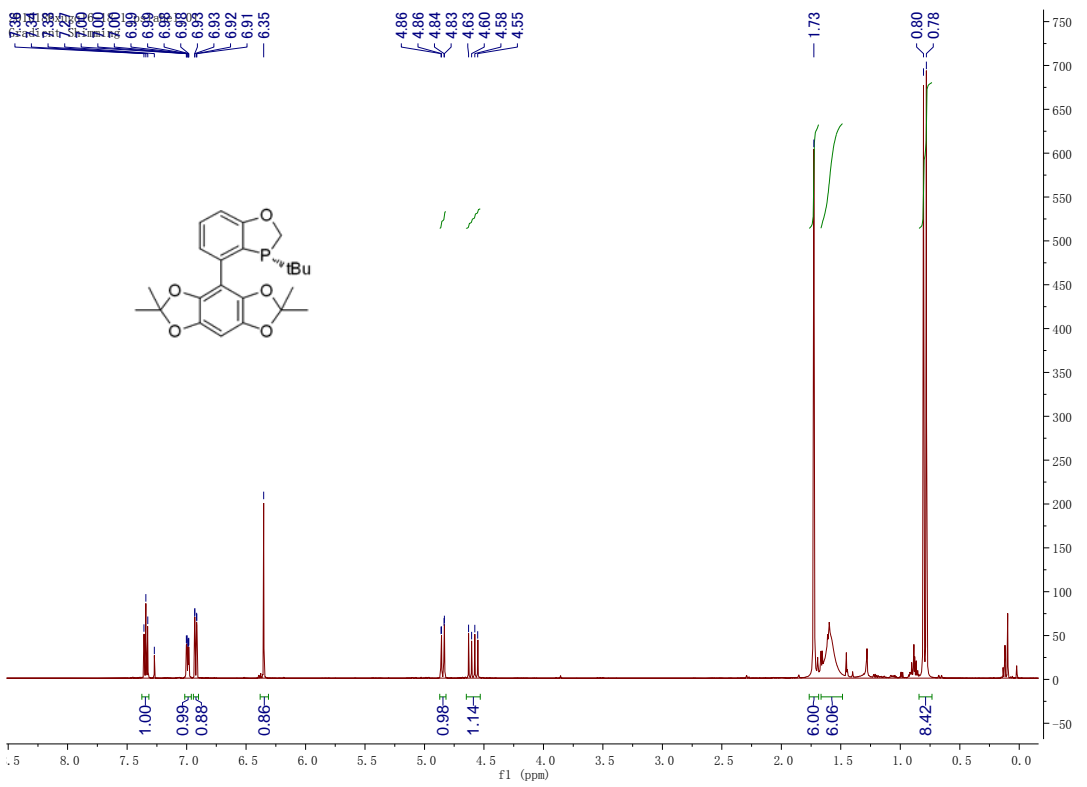
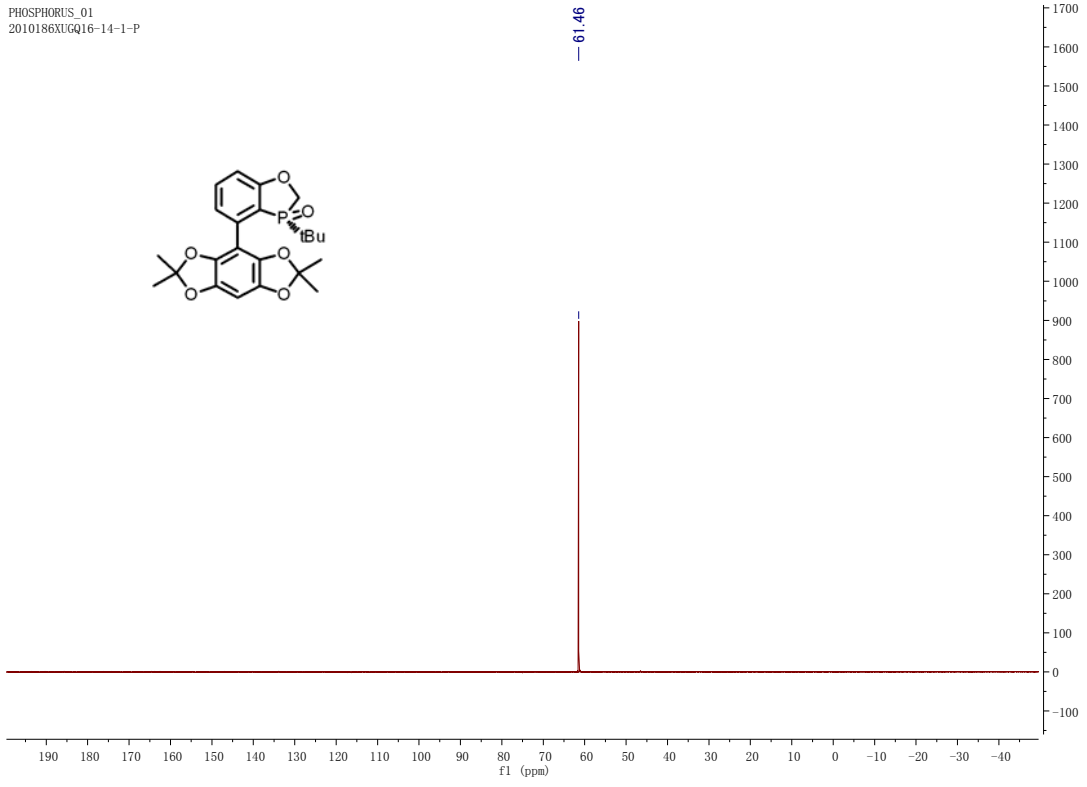


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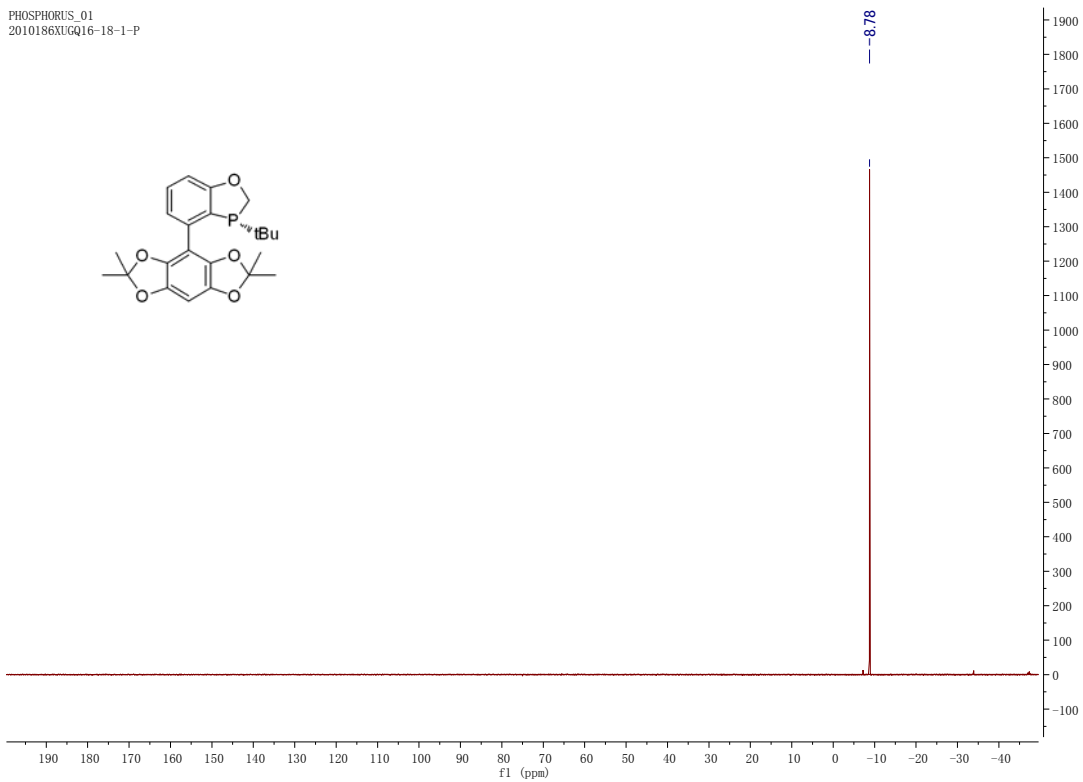
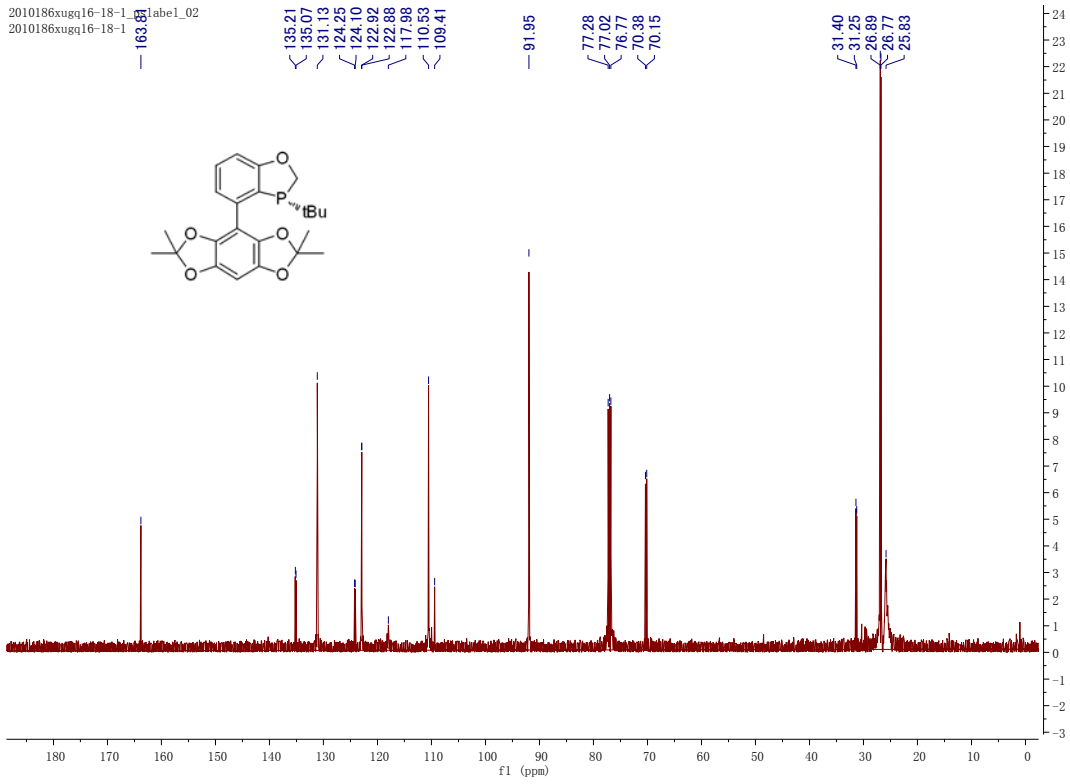


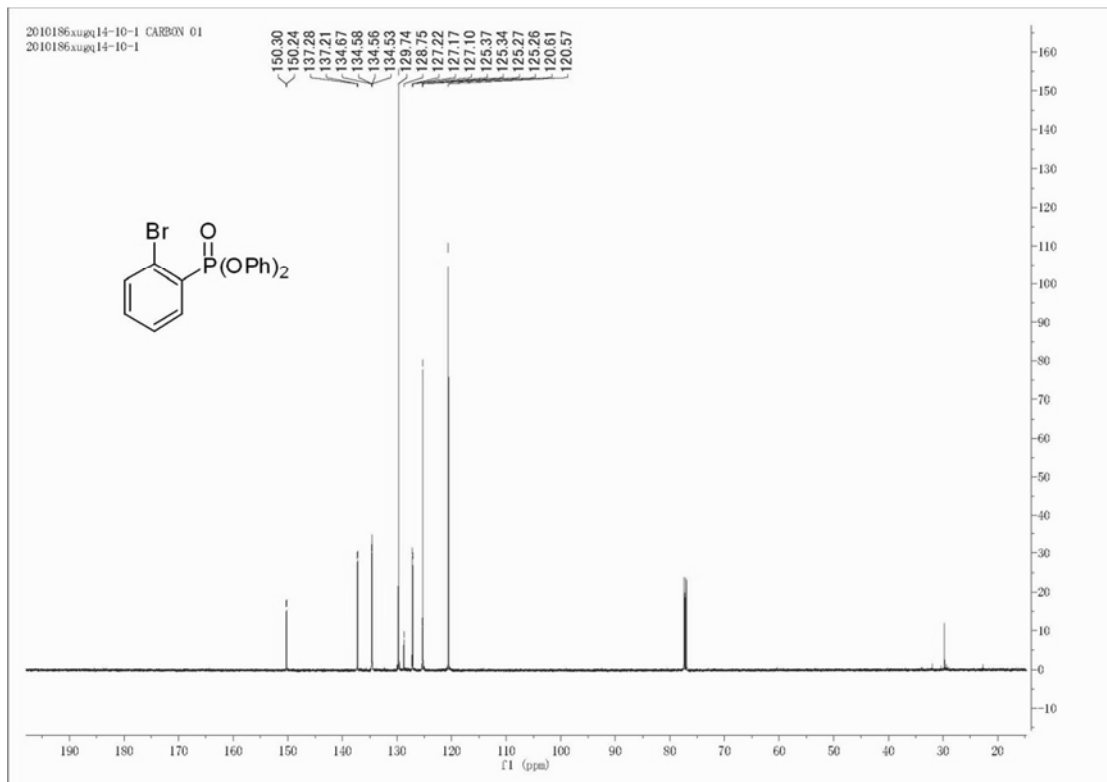
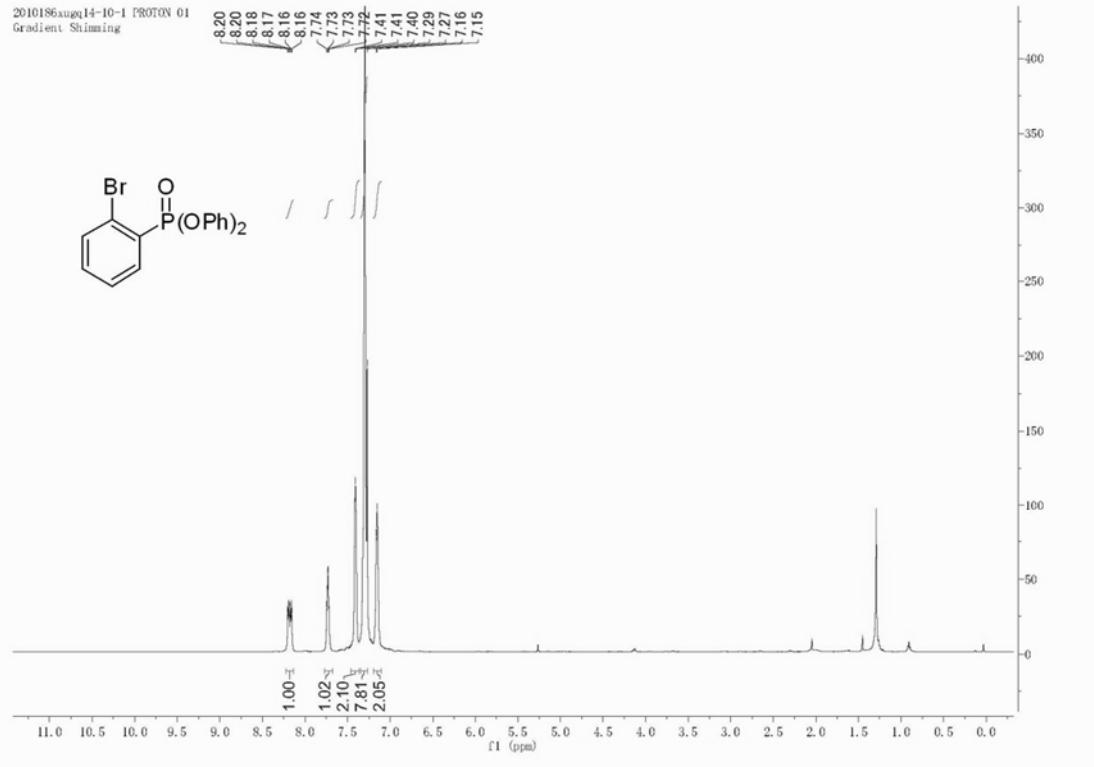


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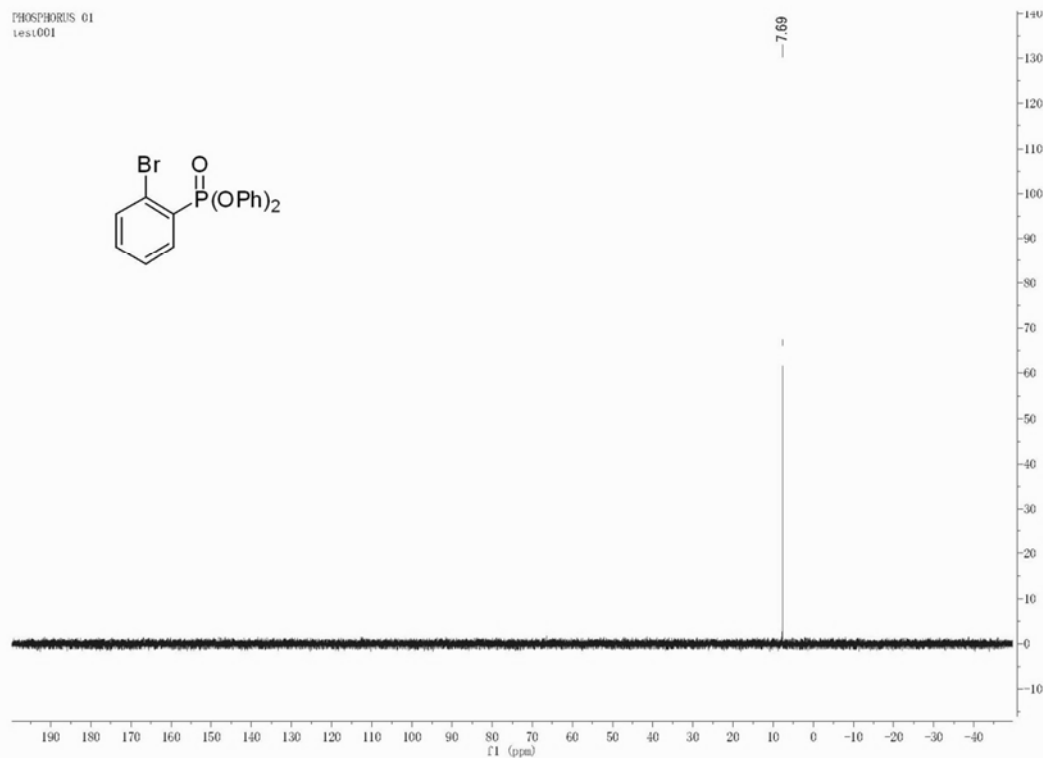
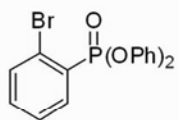


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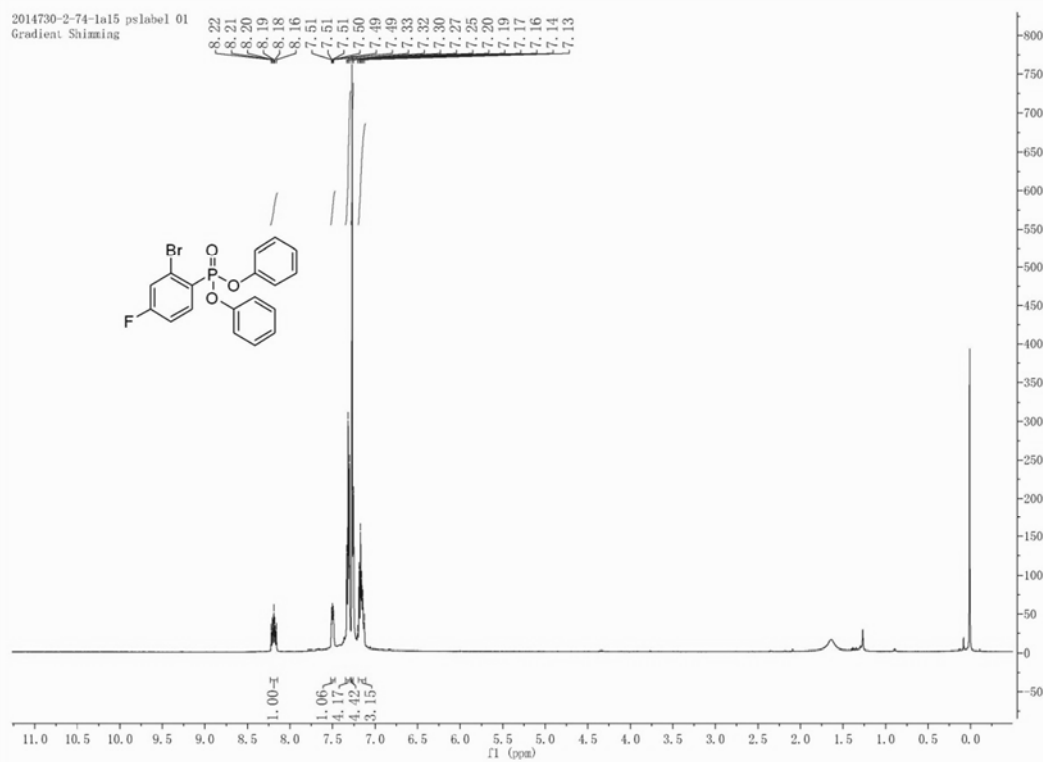
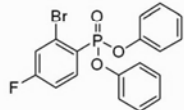


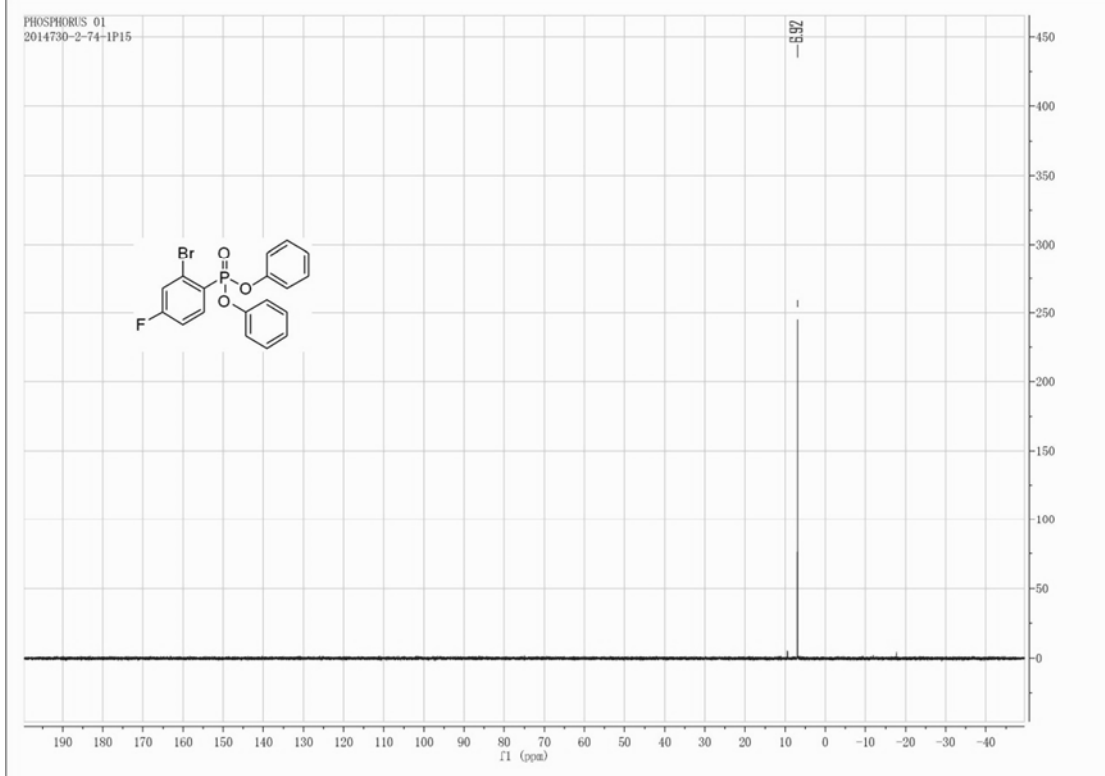
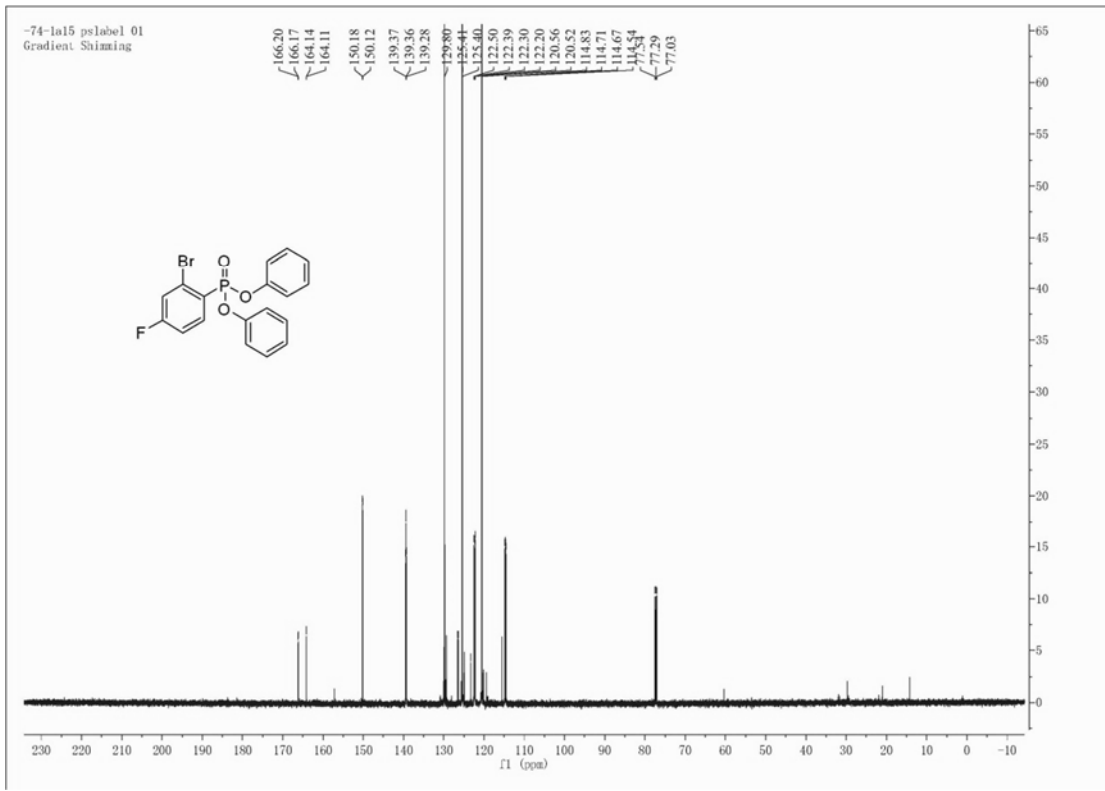


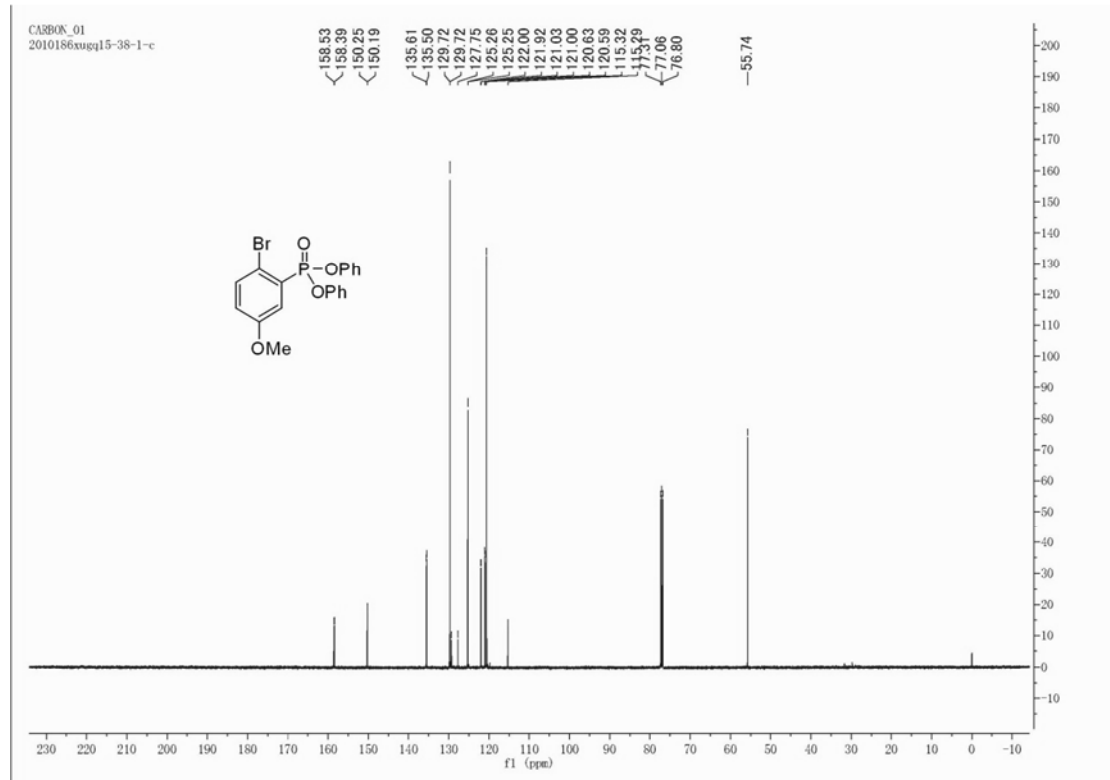
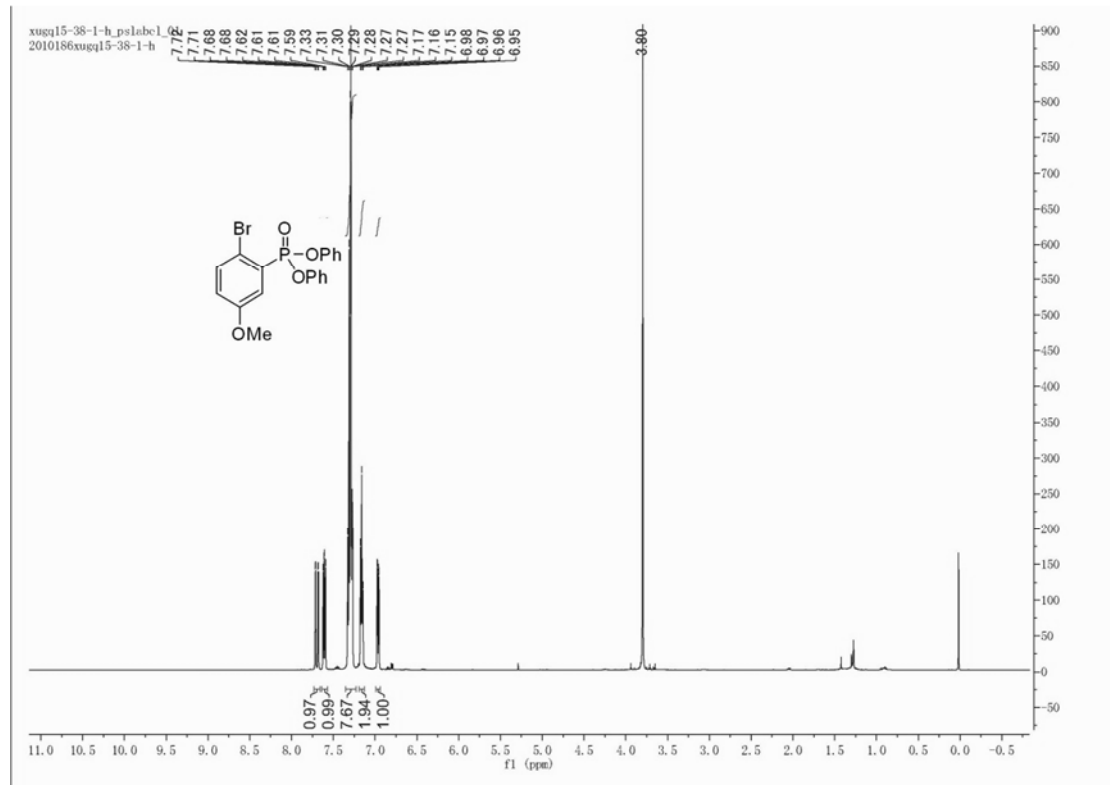
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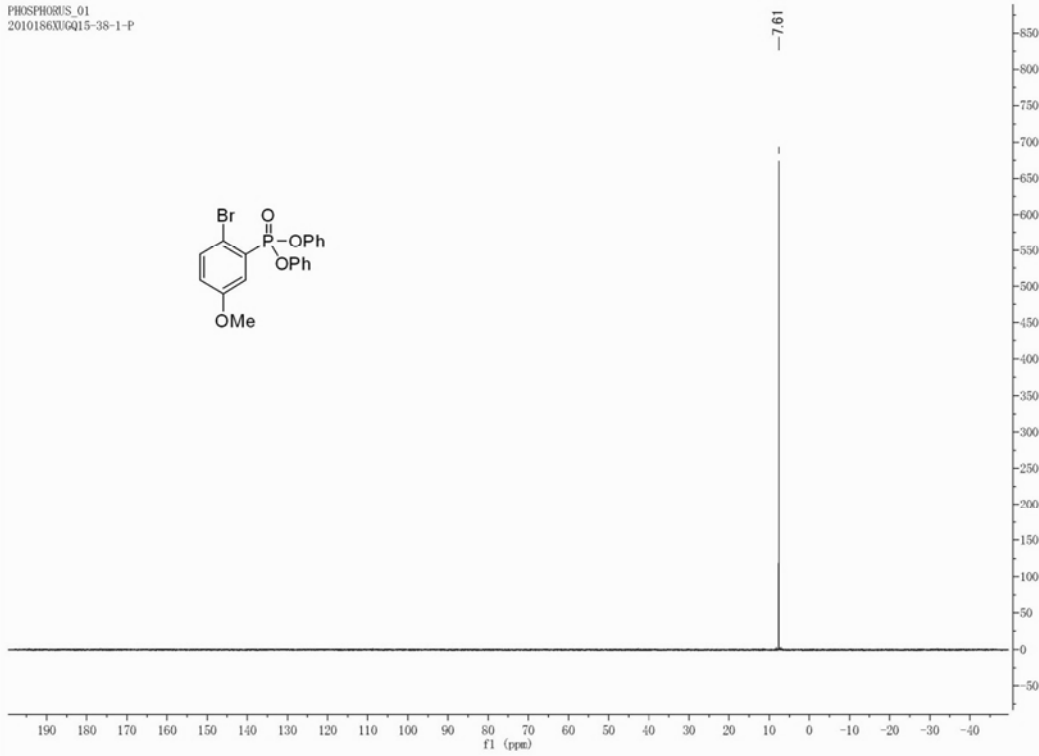
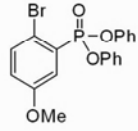
2014730-2-74-1a15 pslabel 01
Gradient Shimming



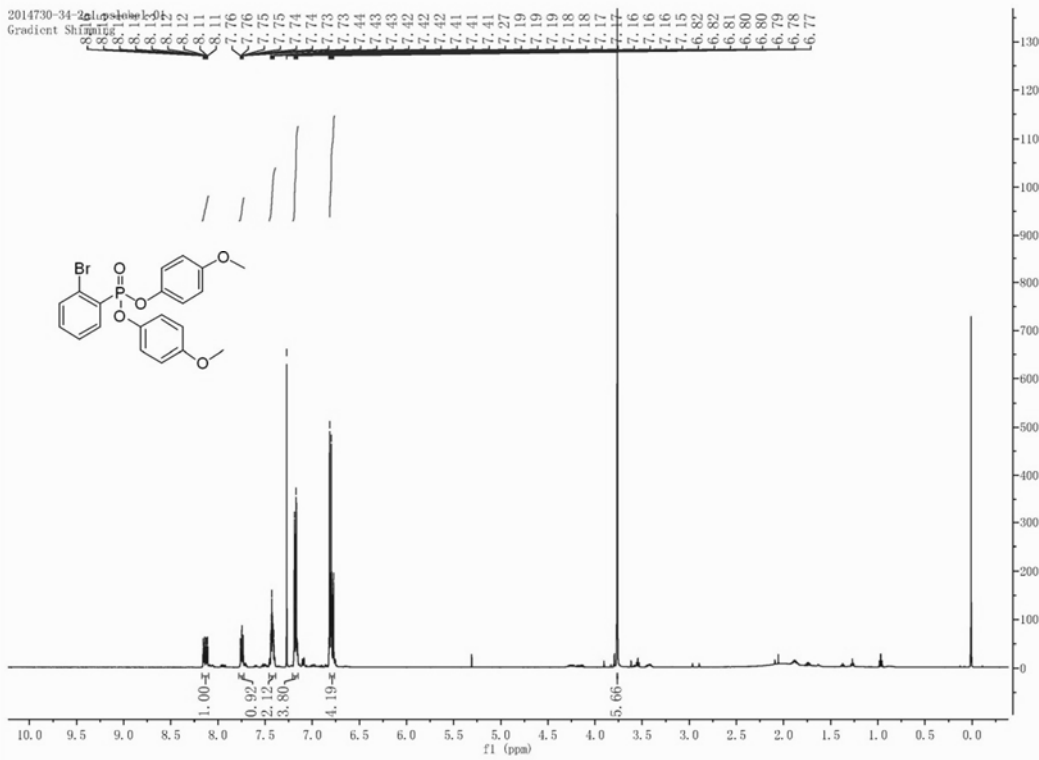
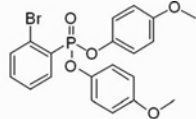




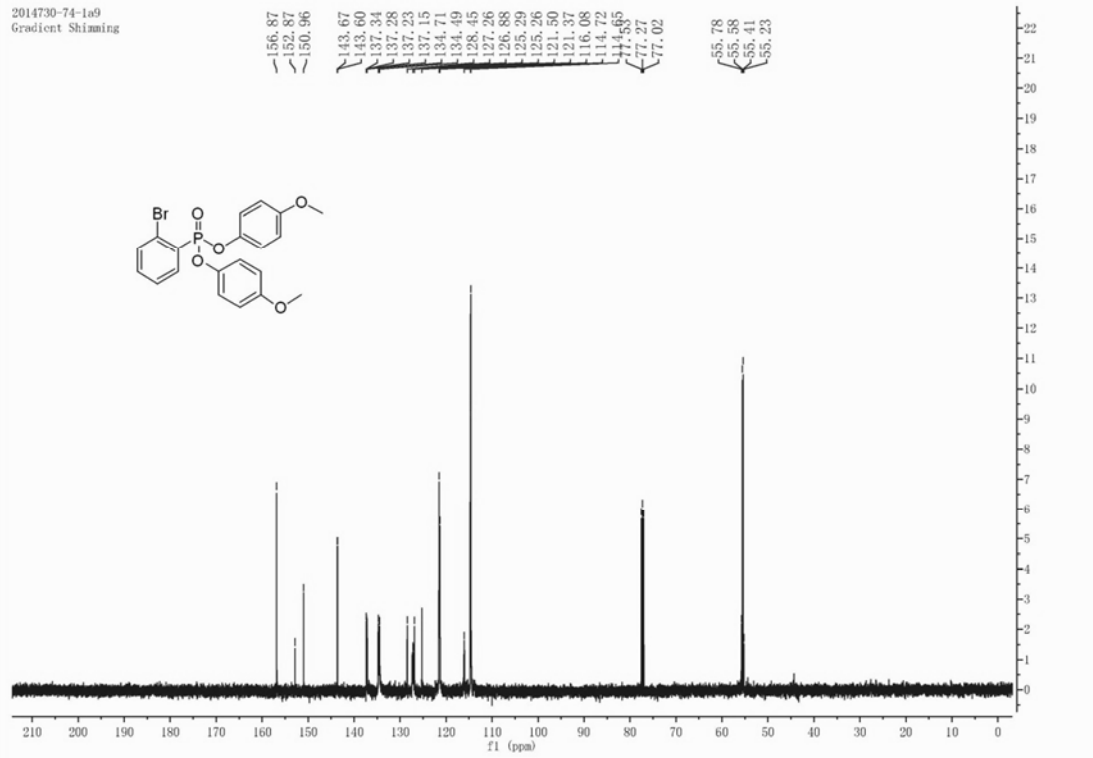
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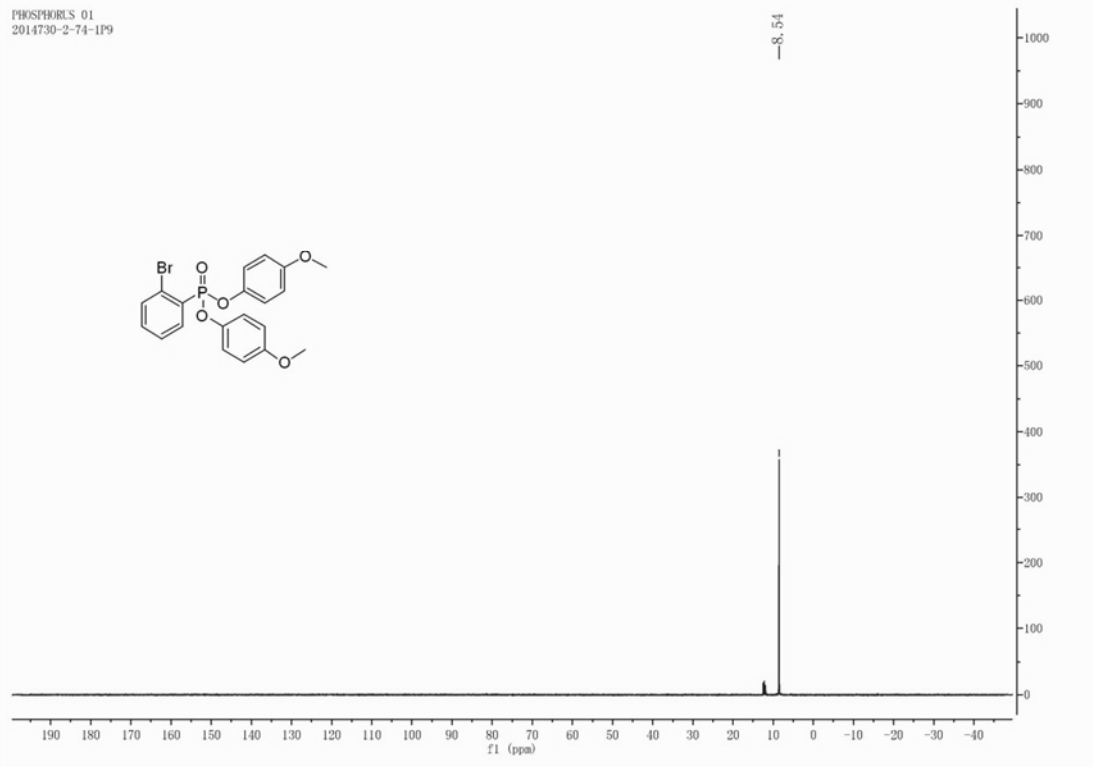
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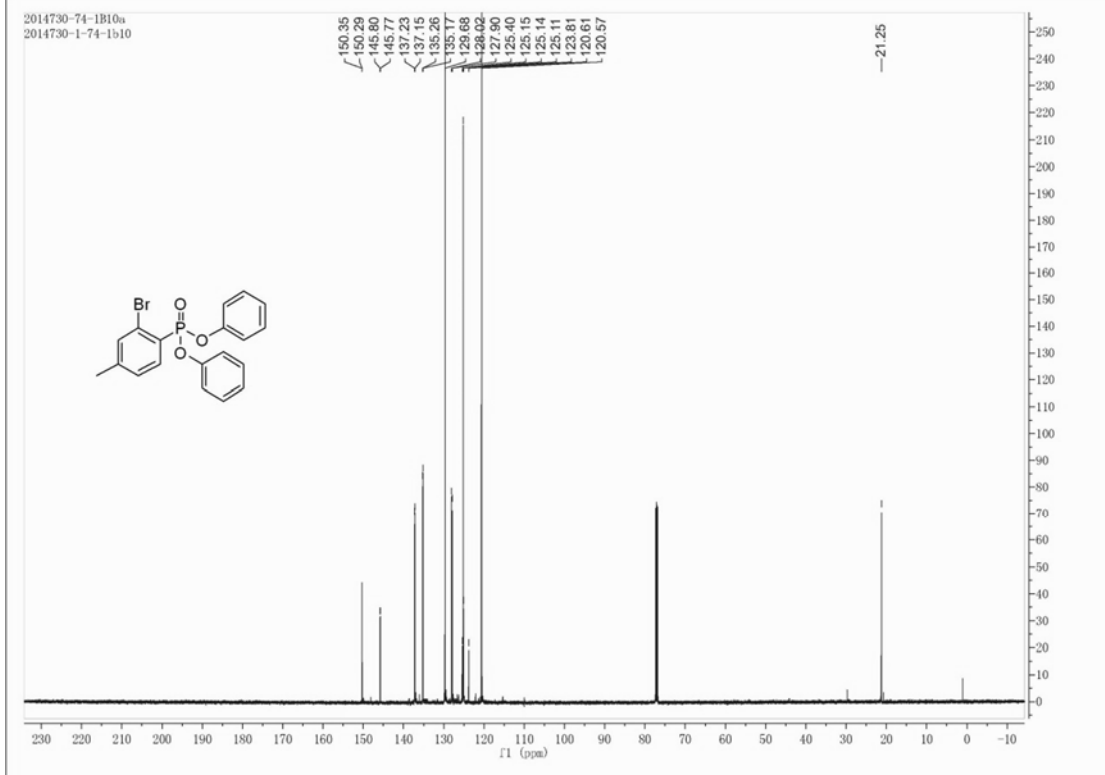
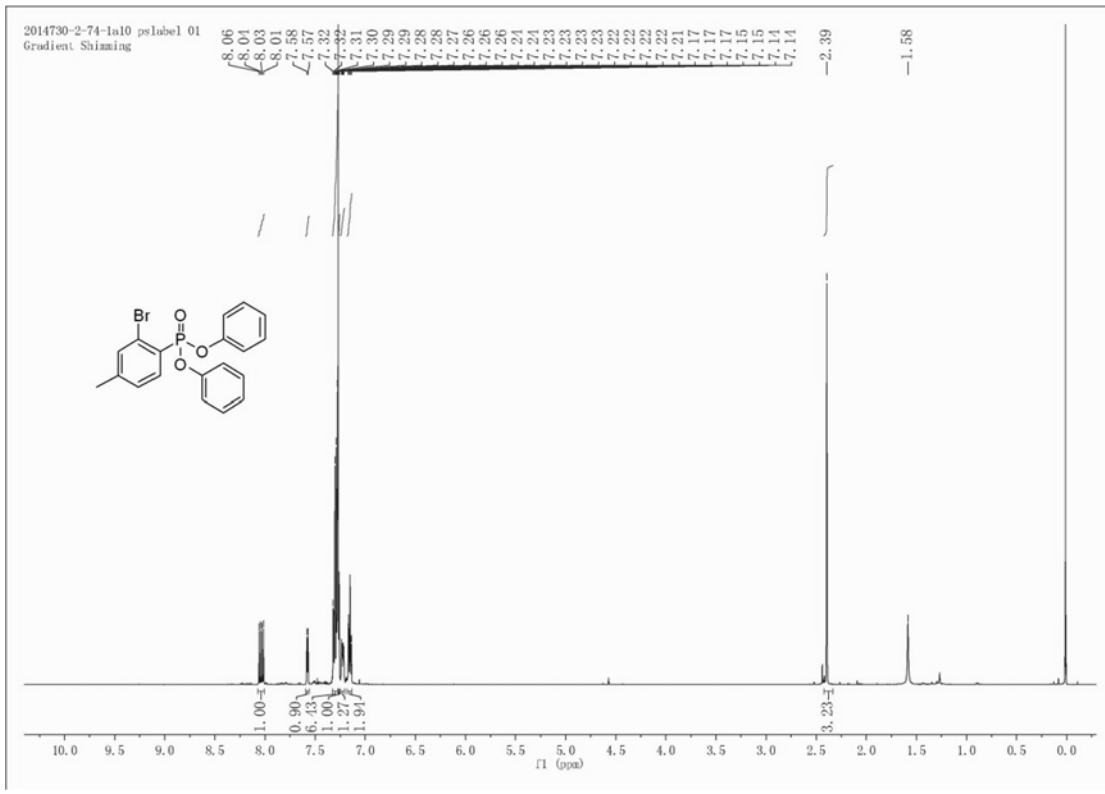


2014730-74-1a9
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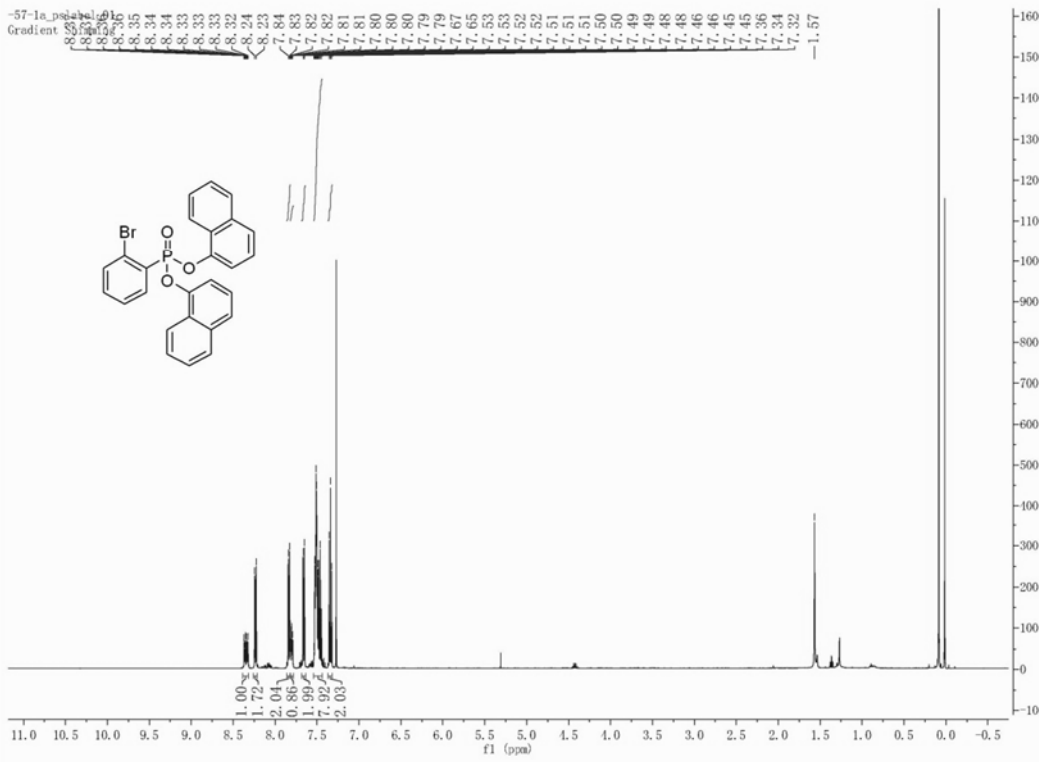
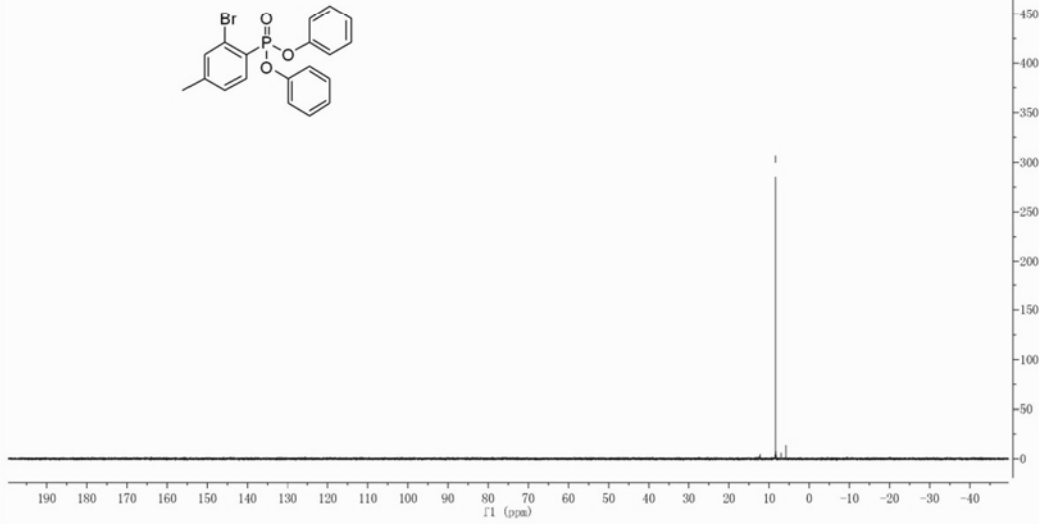


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2014730-2-74-1P9

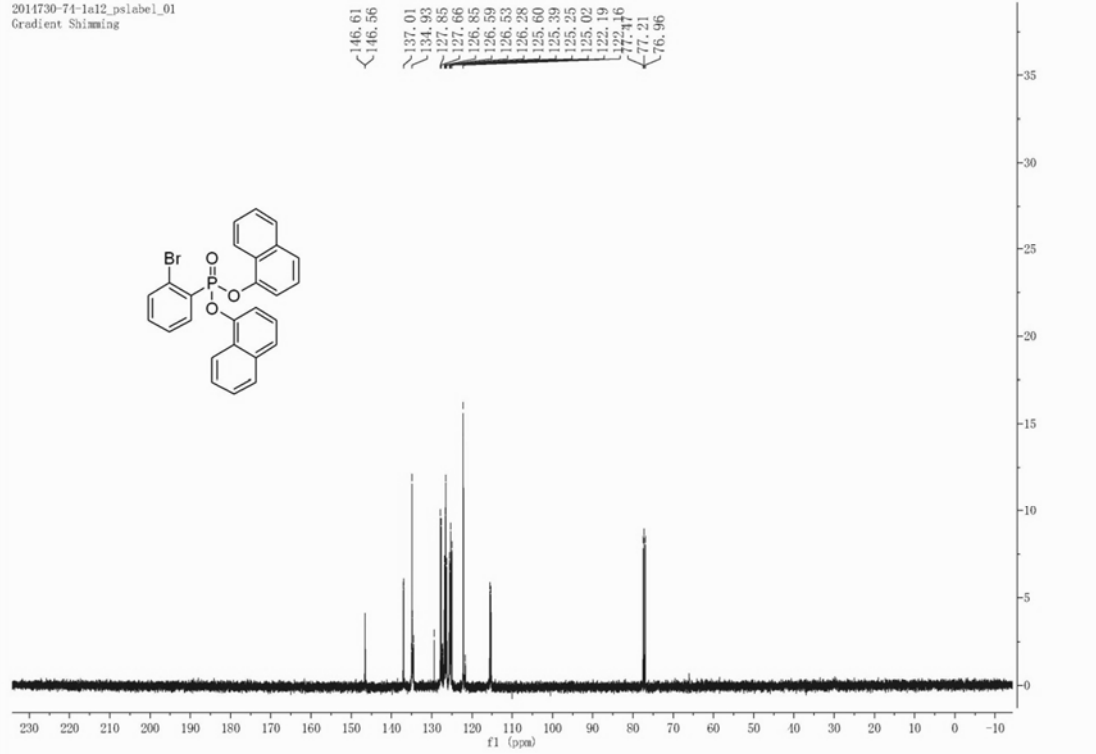




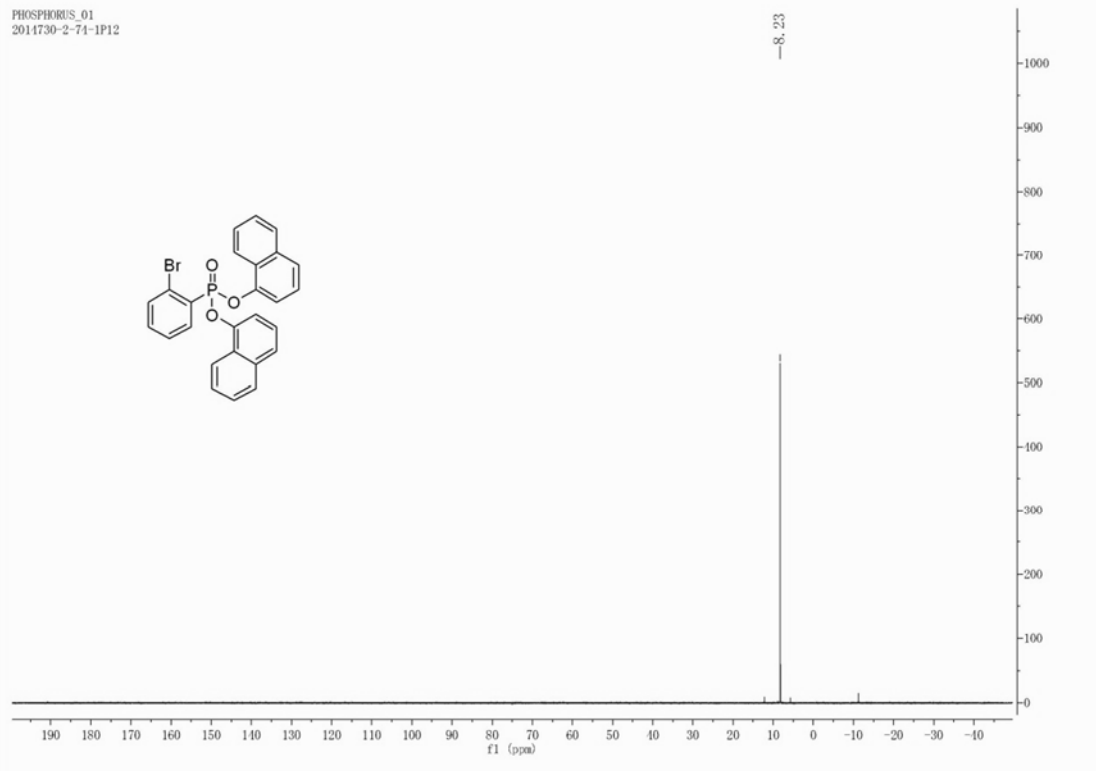
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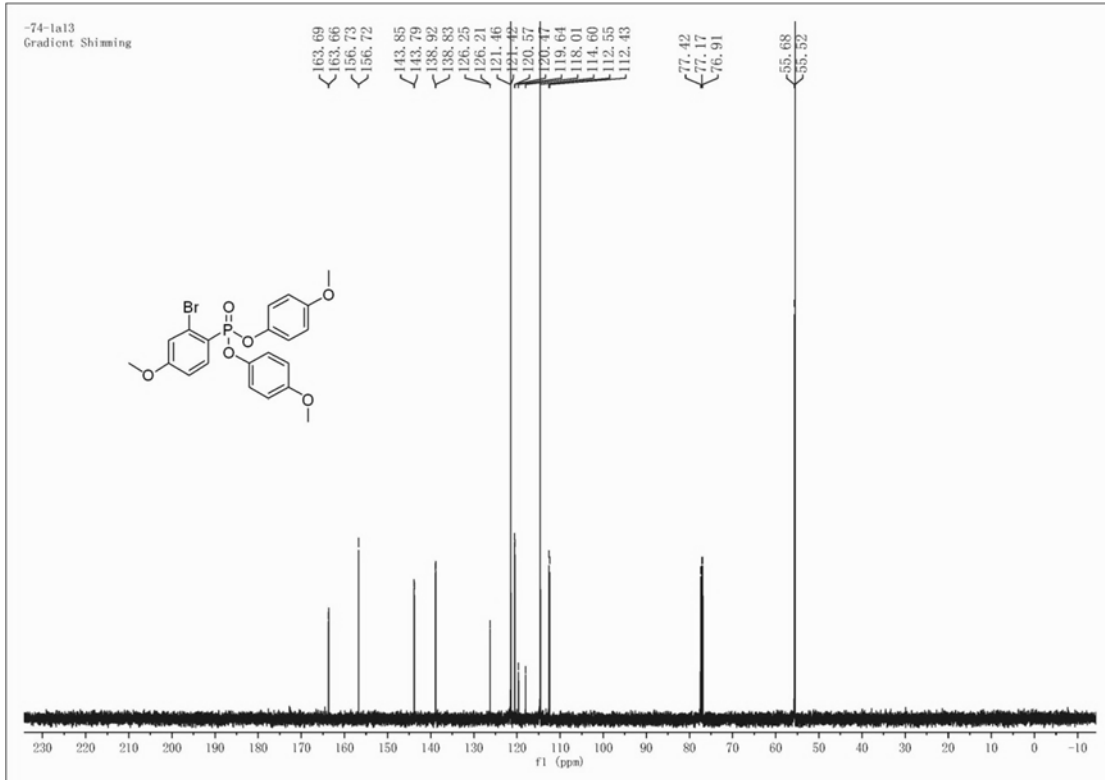
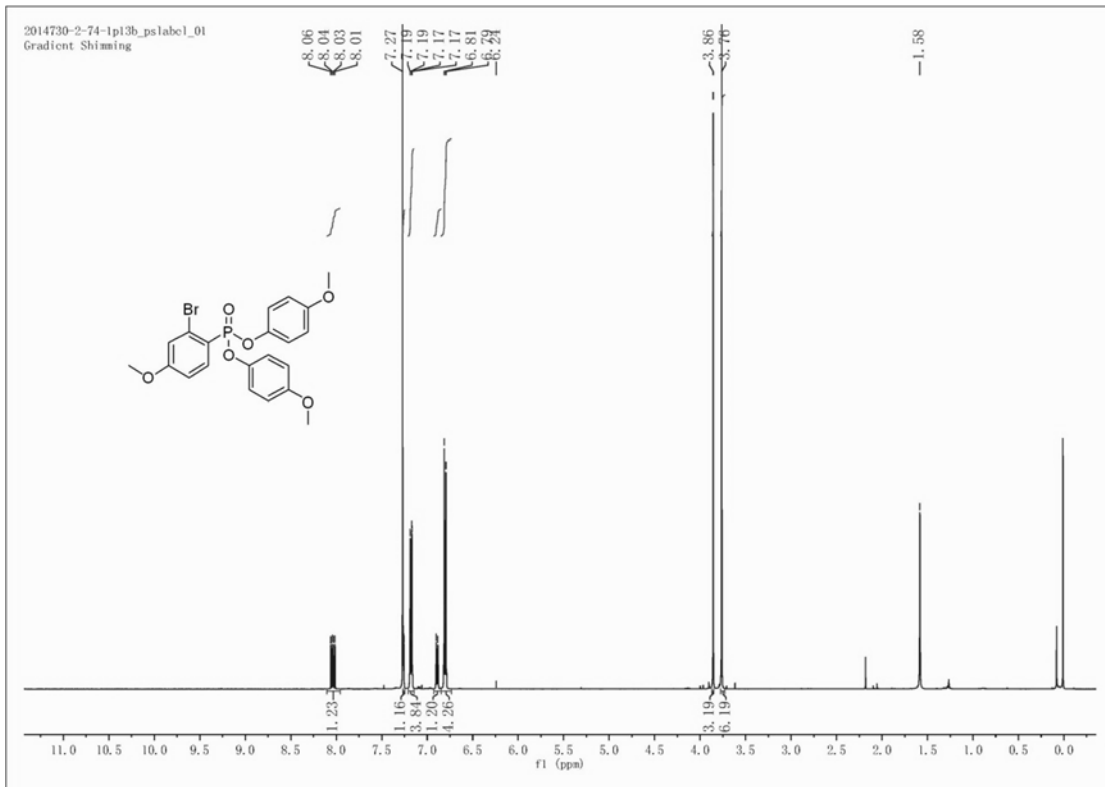


2014730-74-1a12_pslabel_01
Gradient Shimming

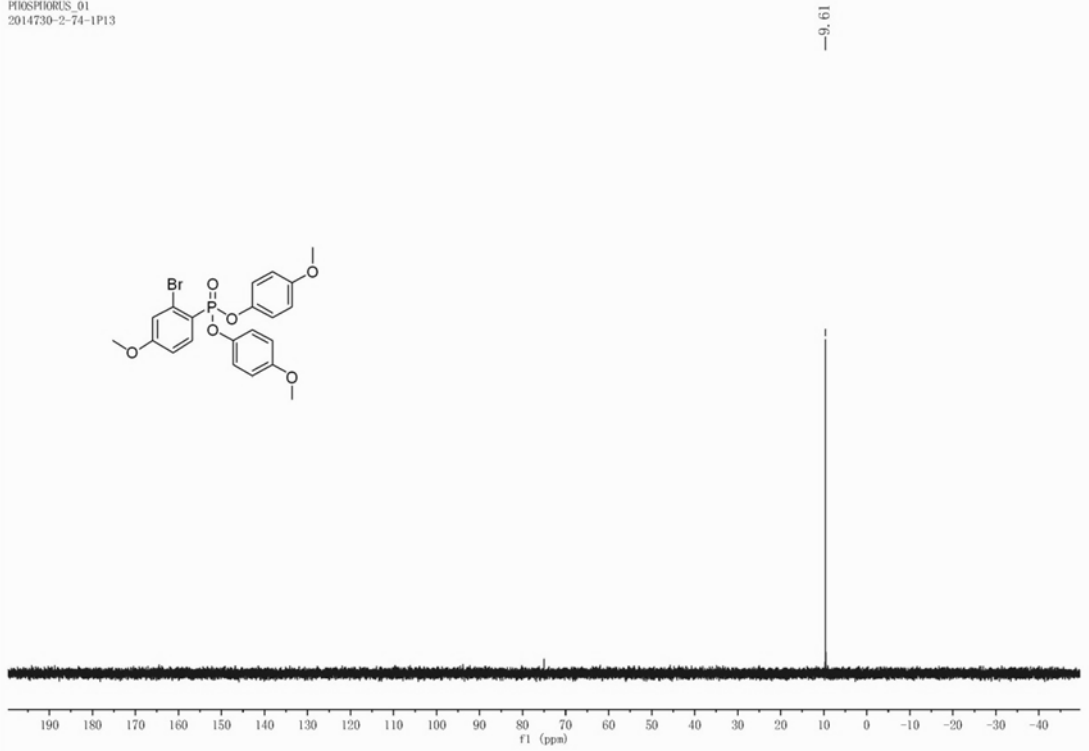
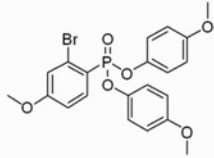


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2014730-2-74-1P12

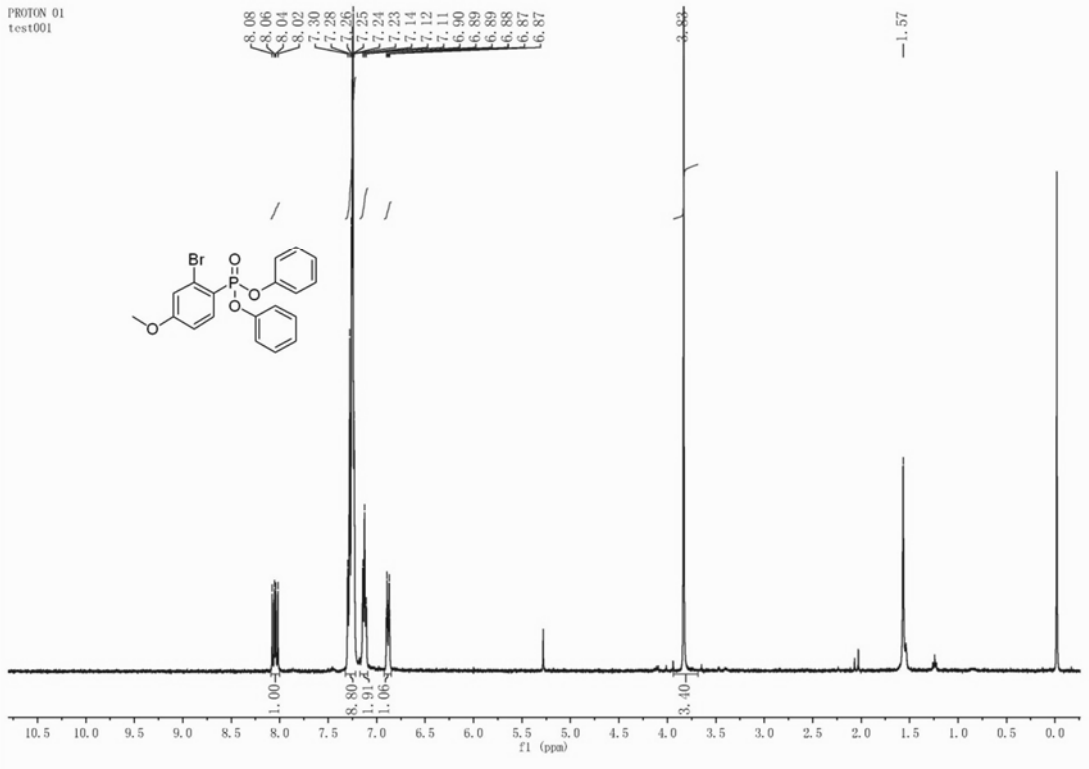
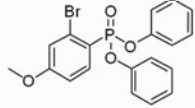


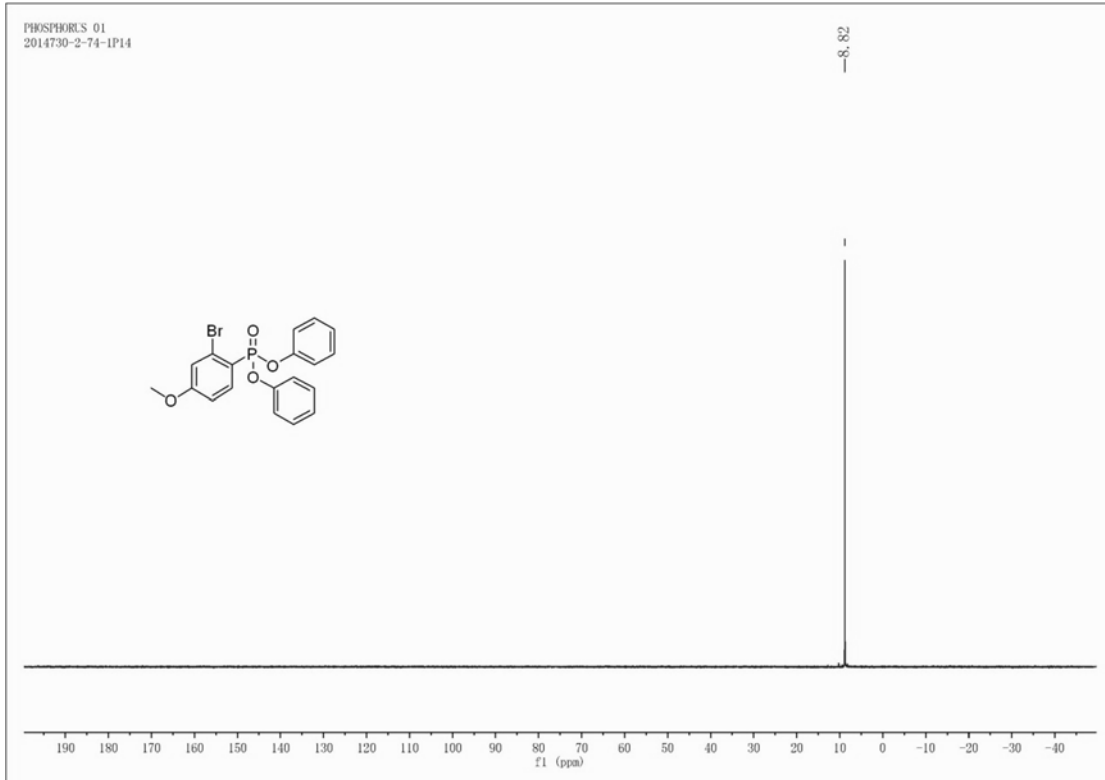
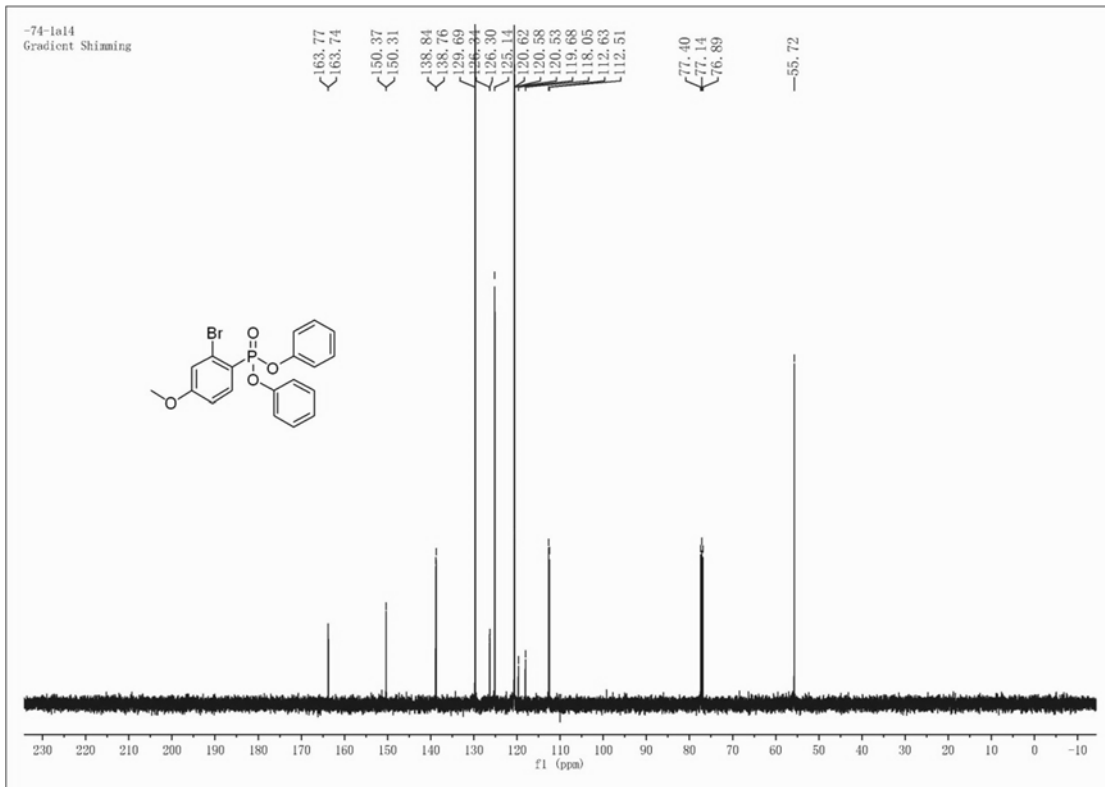


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2014730-2-74-1P13



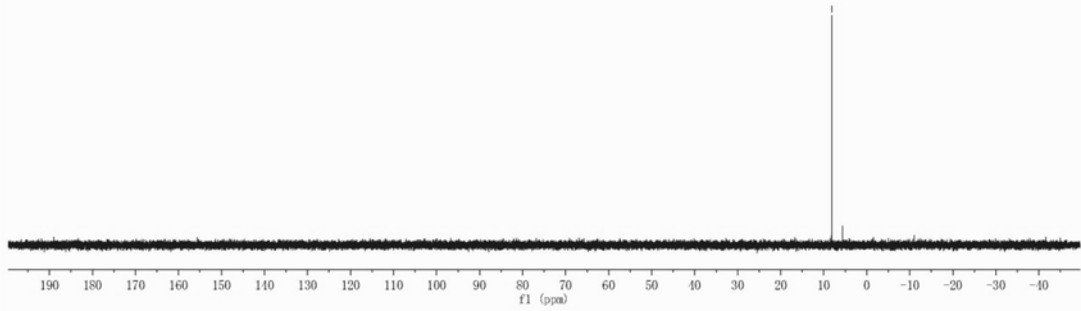
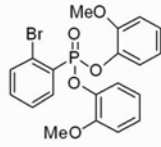
PROTON 01
test001



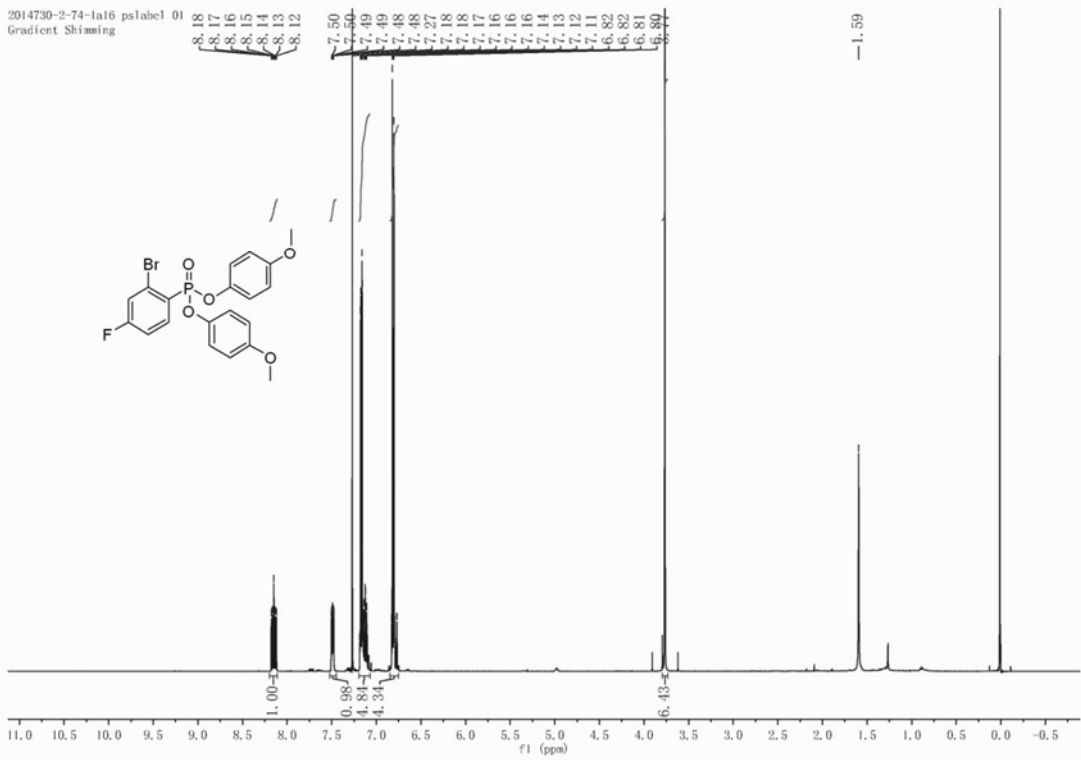
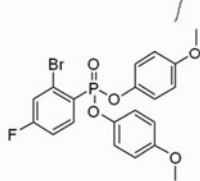


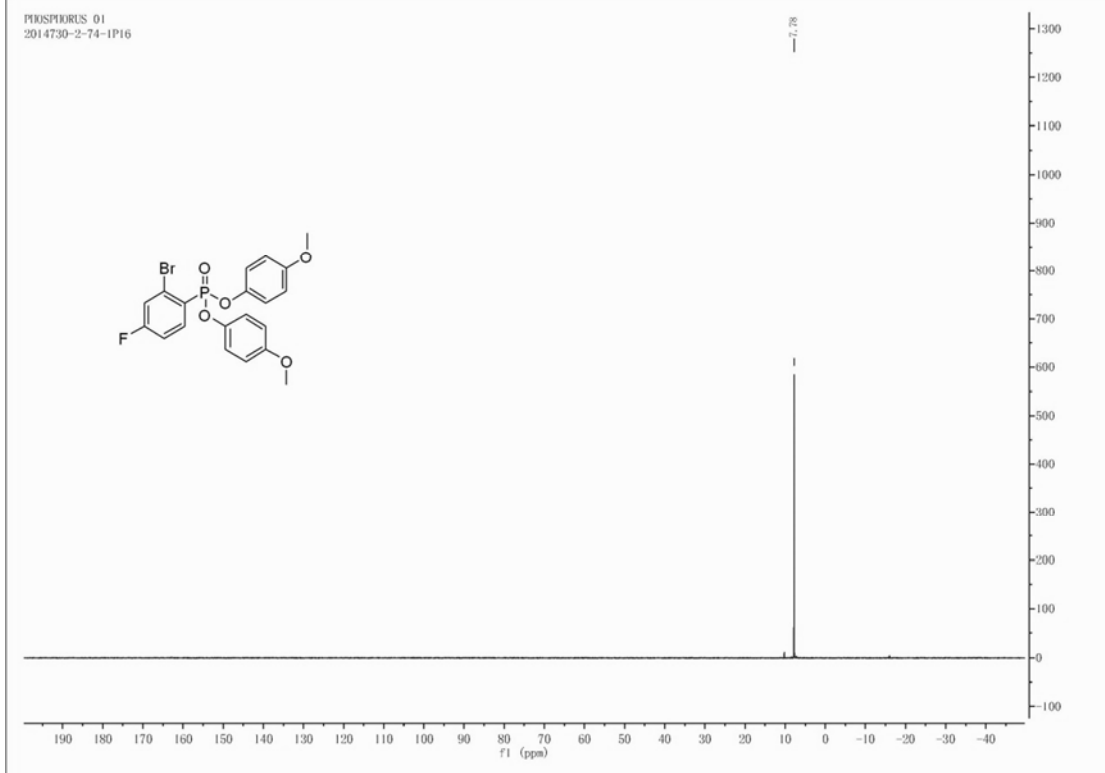
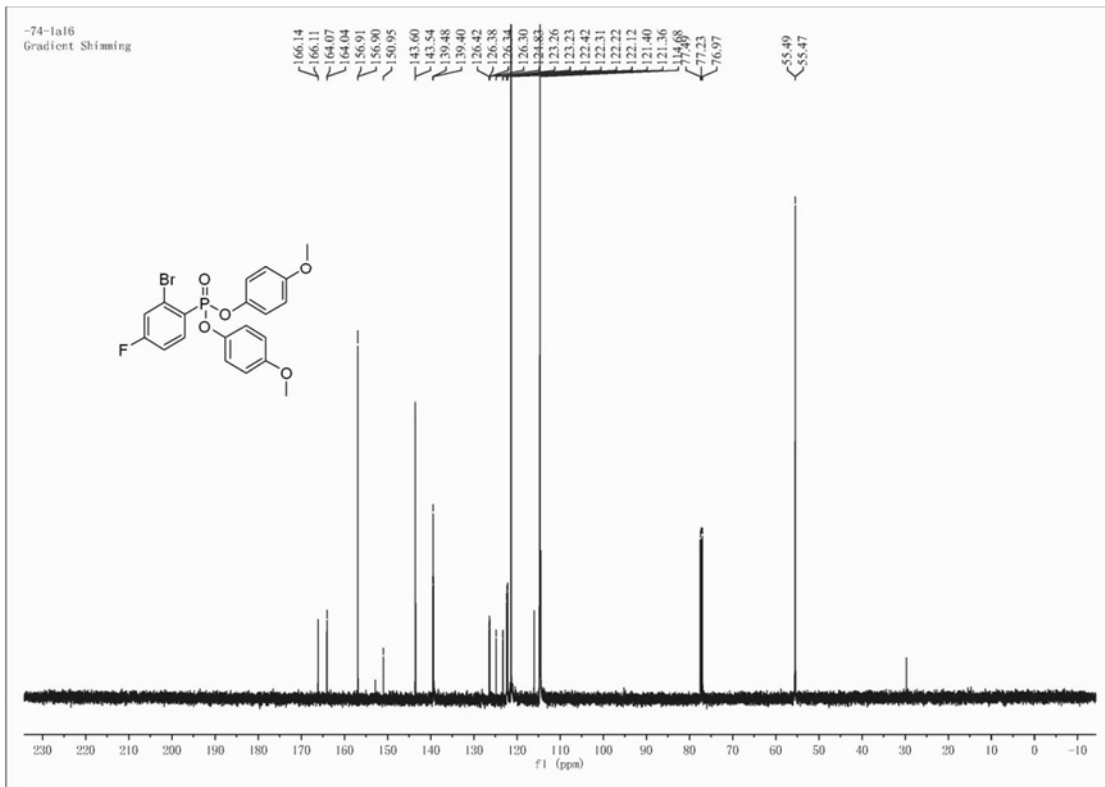
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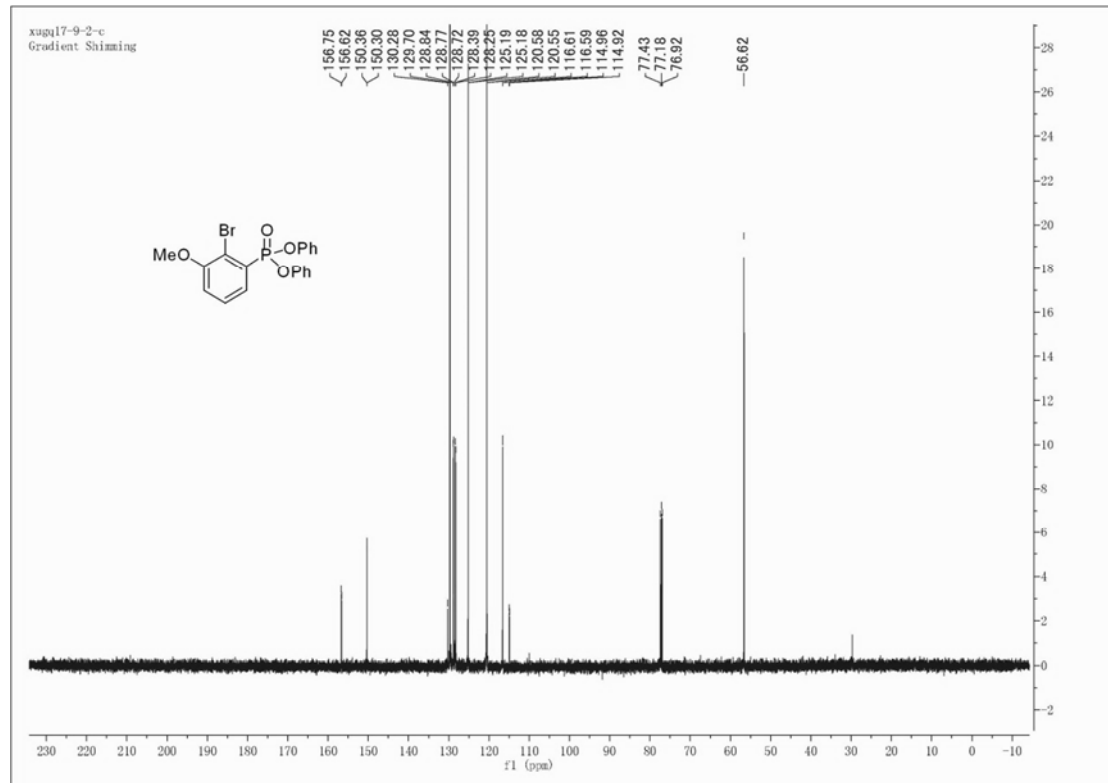
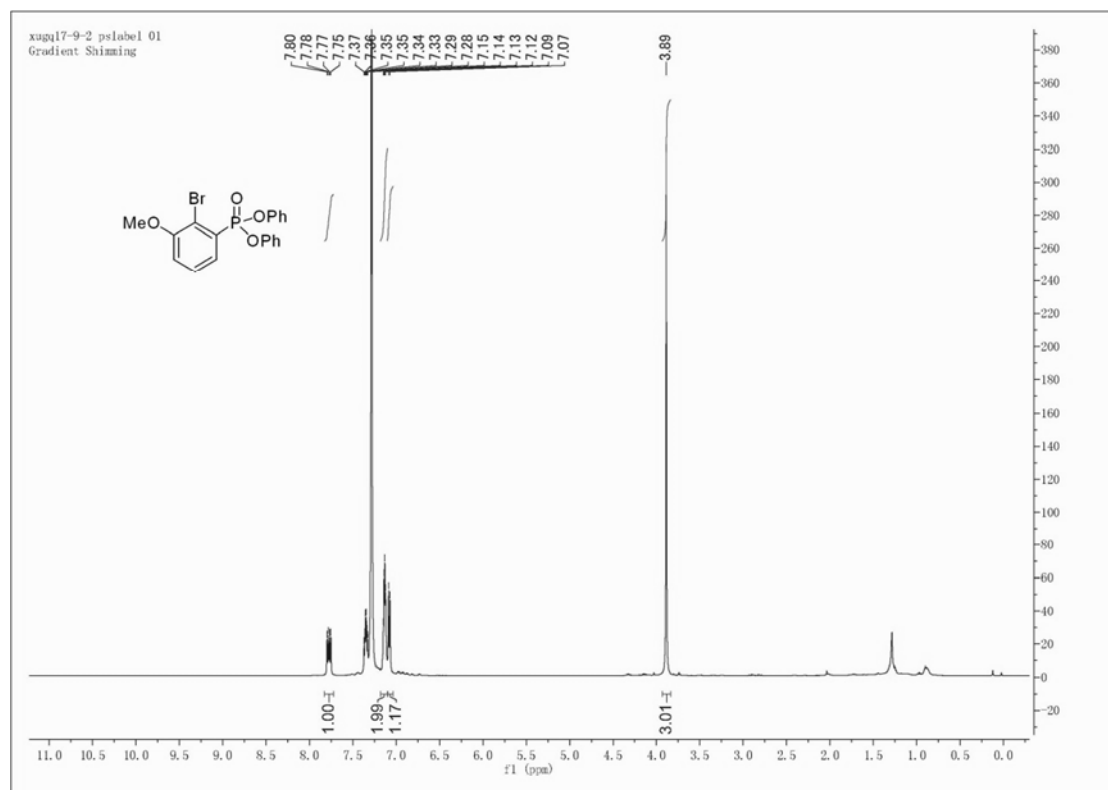
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2014730-2-74-1a16 pslabel 01
Gradient Shimming

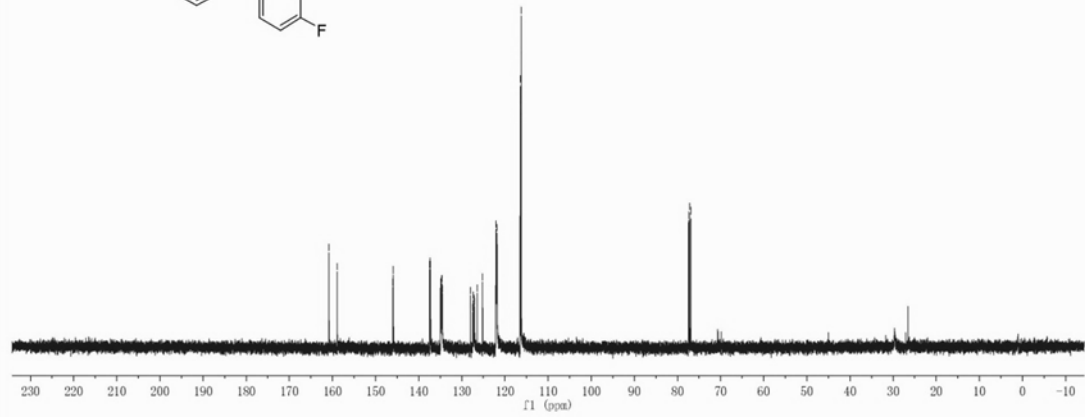
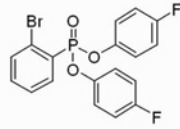






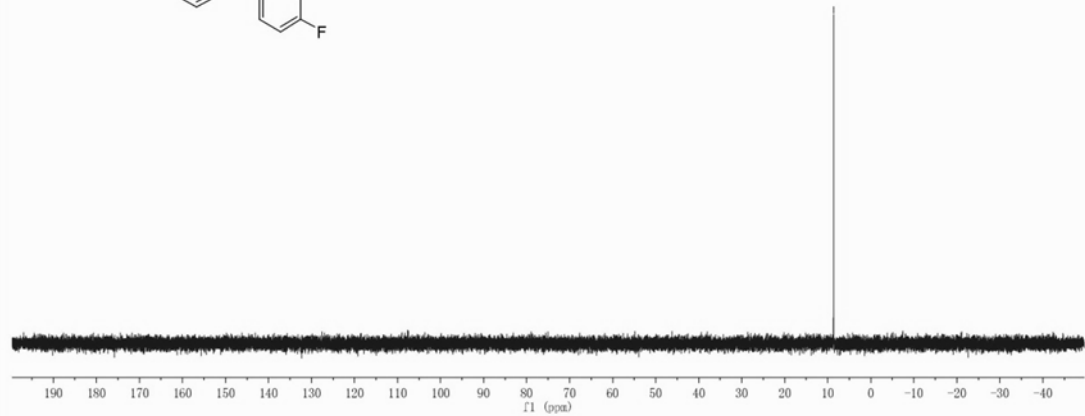
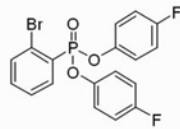
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Gradient Shimming

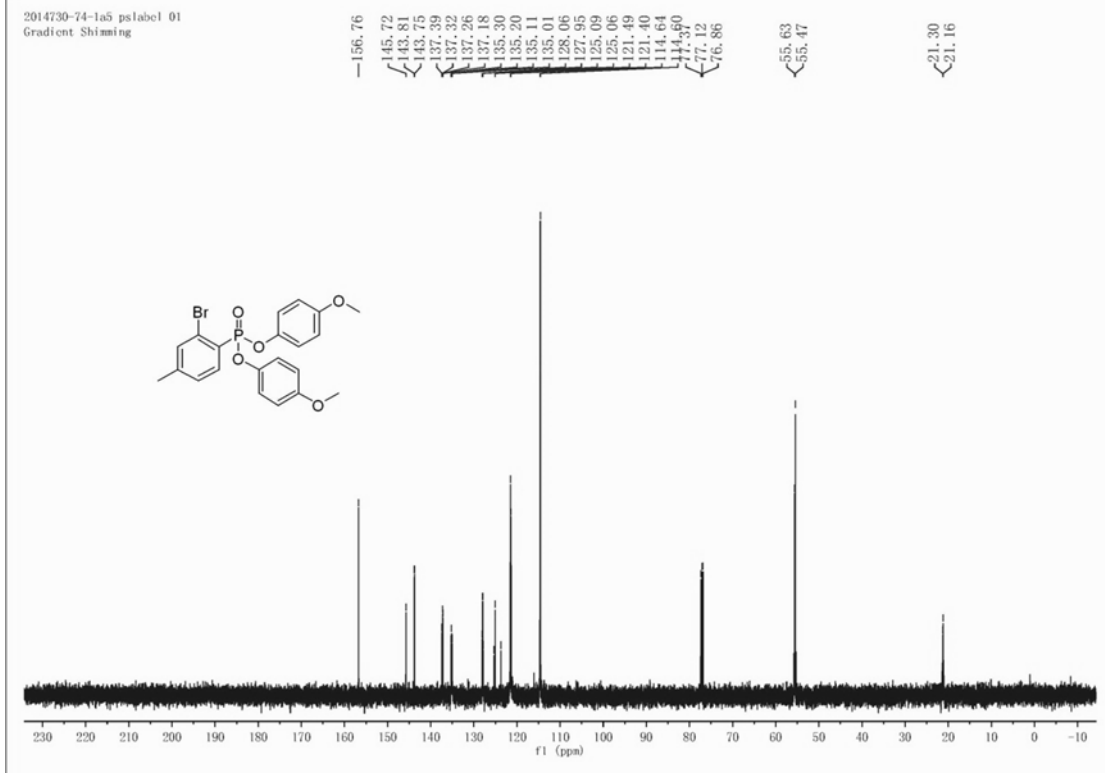
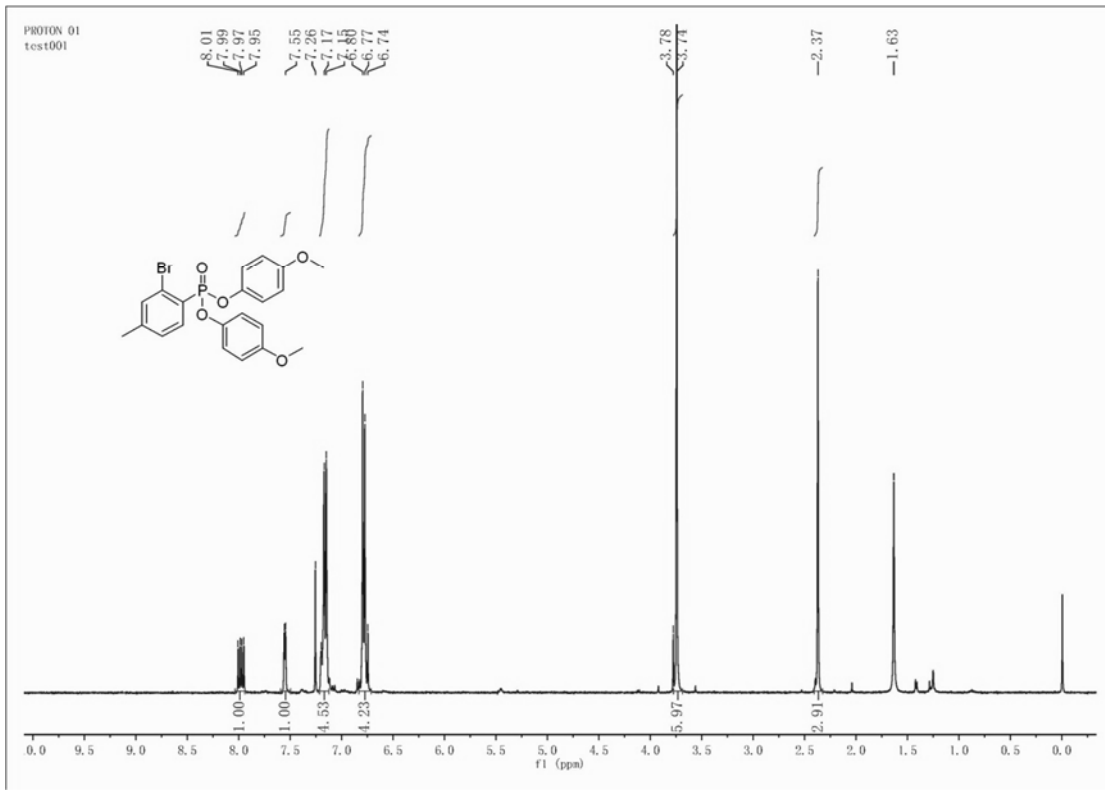
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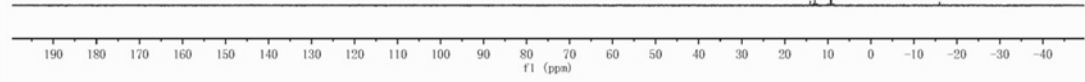
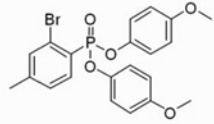
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77.15

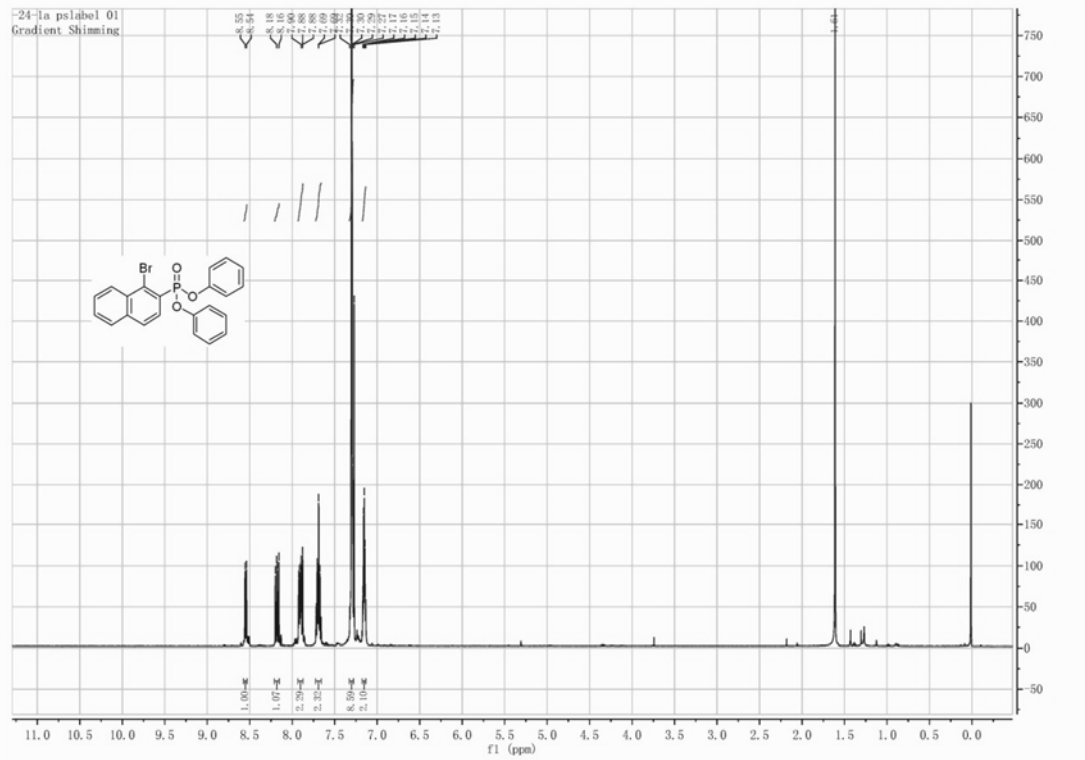
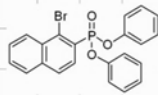




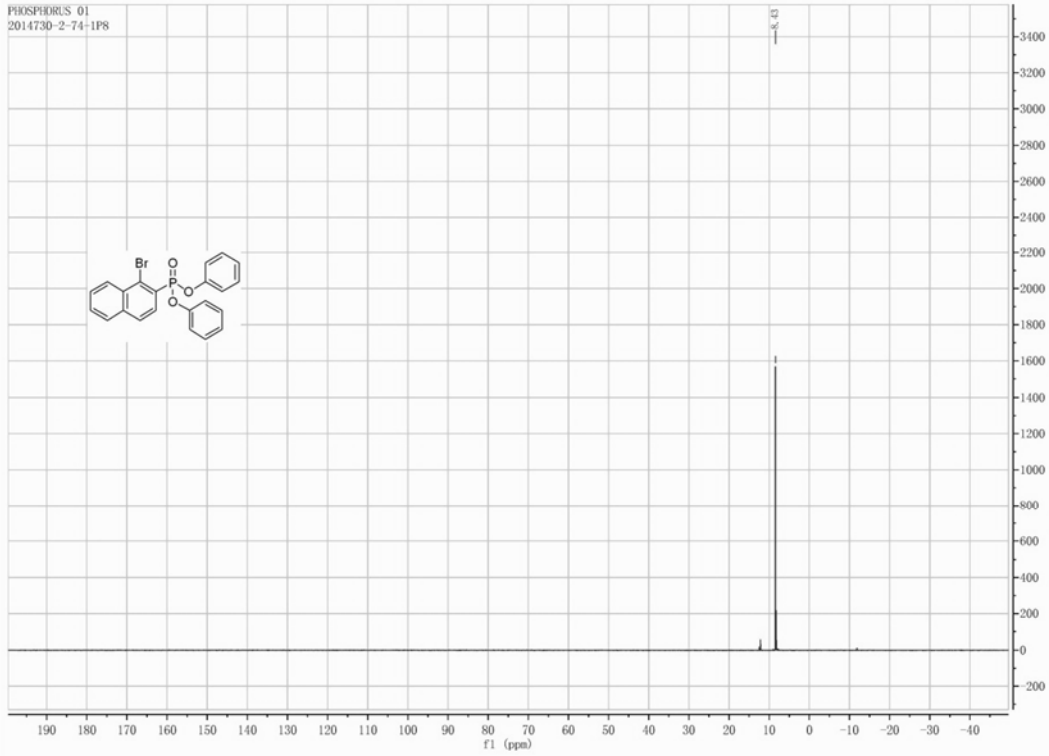
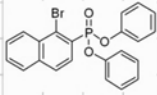
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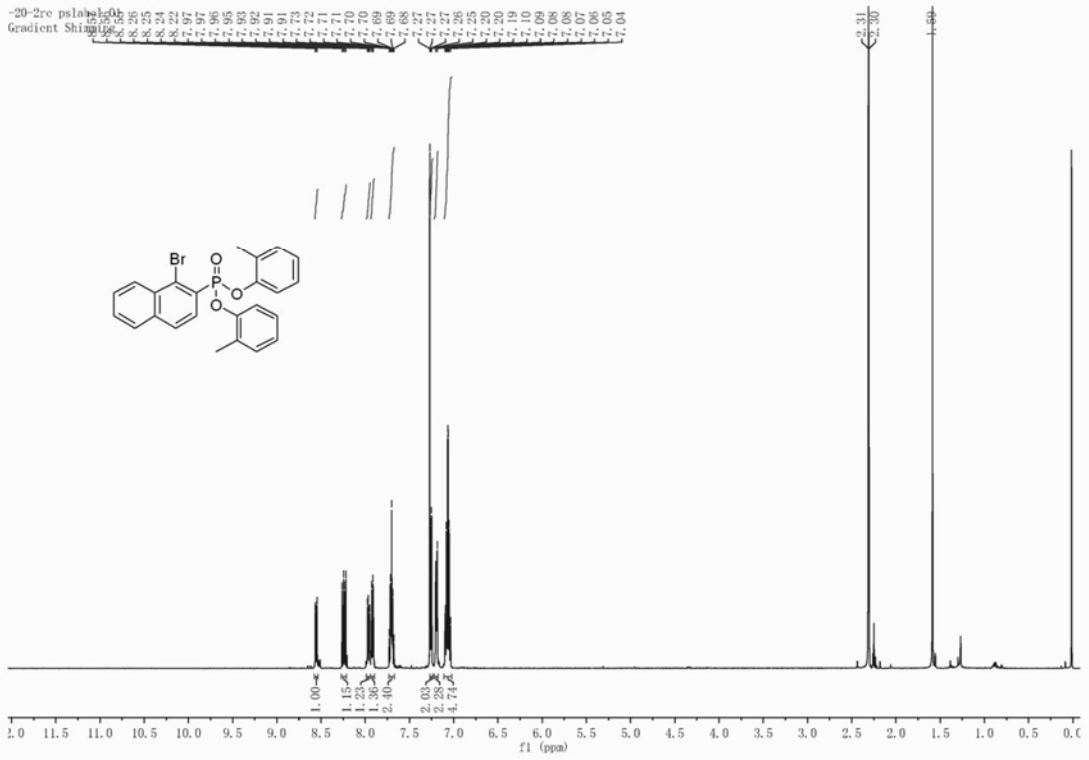
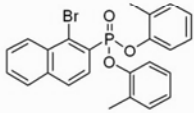
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Gradient Shimming



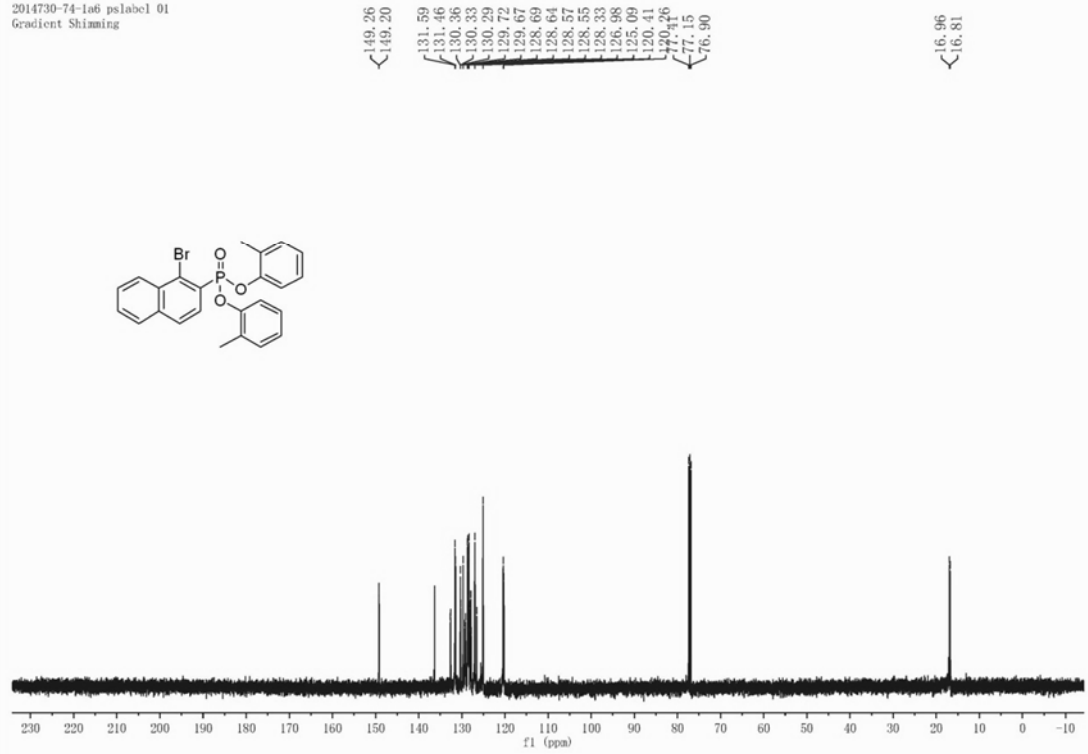
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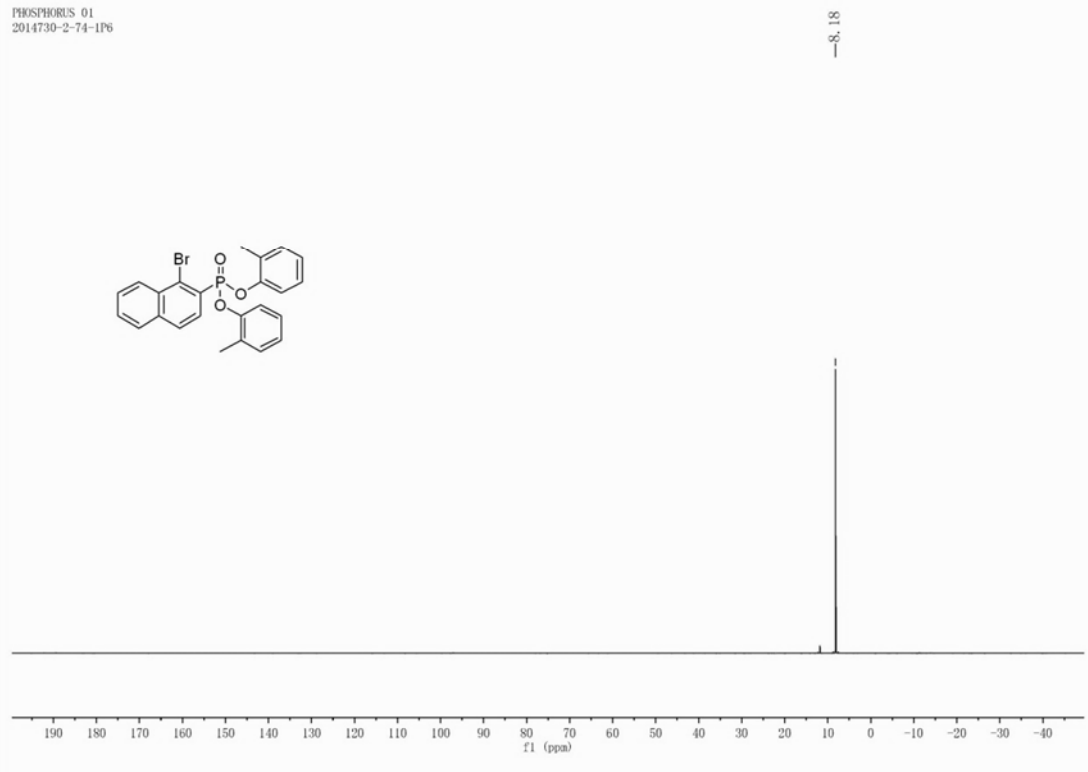
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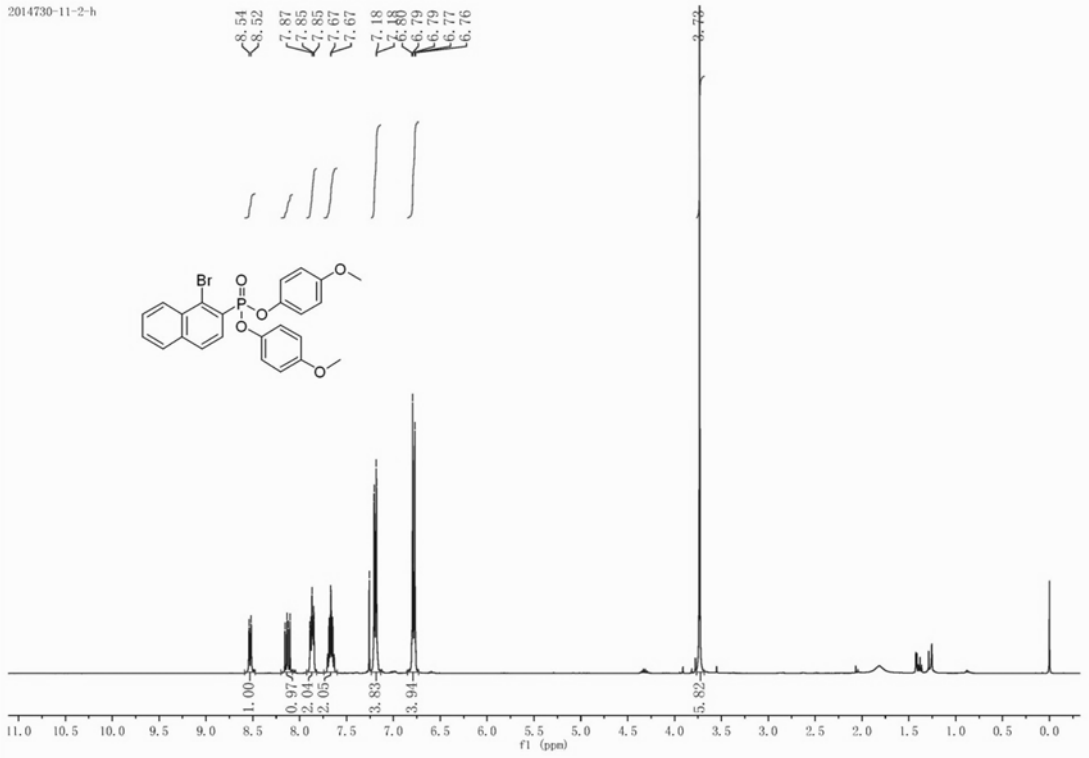
2014730-74-1a6 pslabel 01
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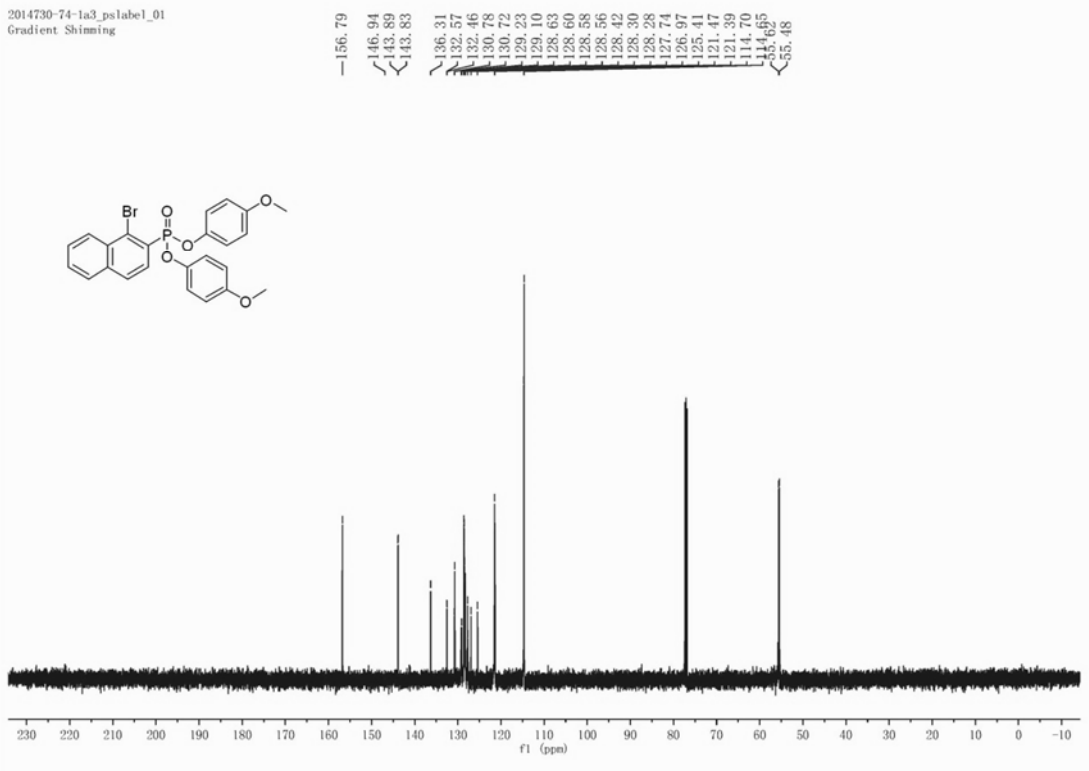
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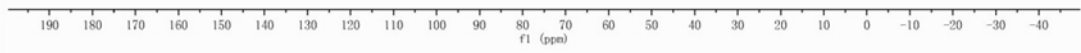
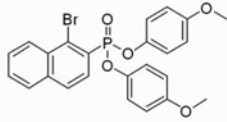
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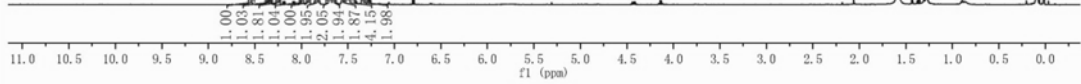
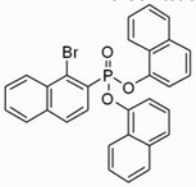
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Gradient Shimming

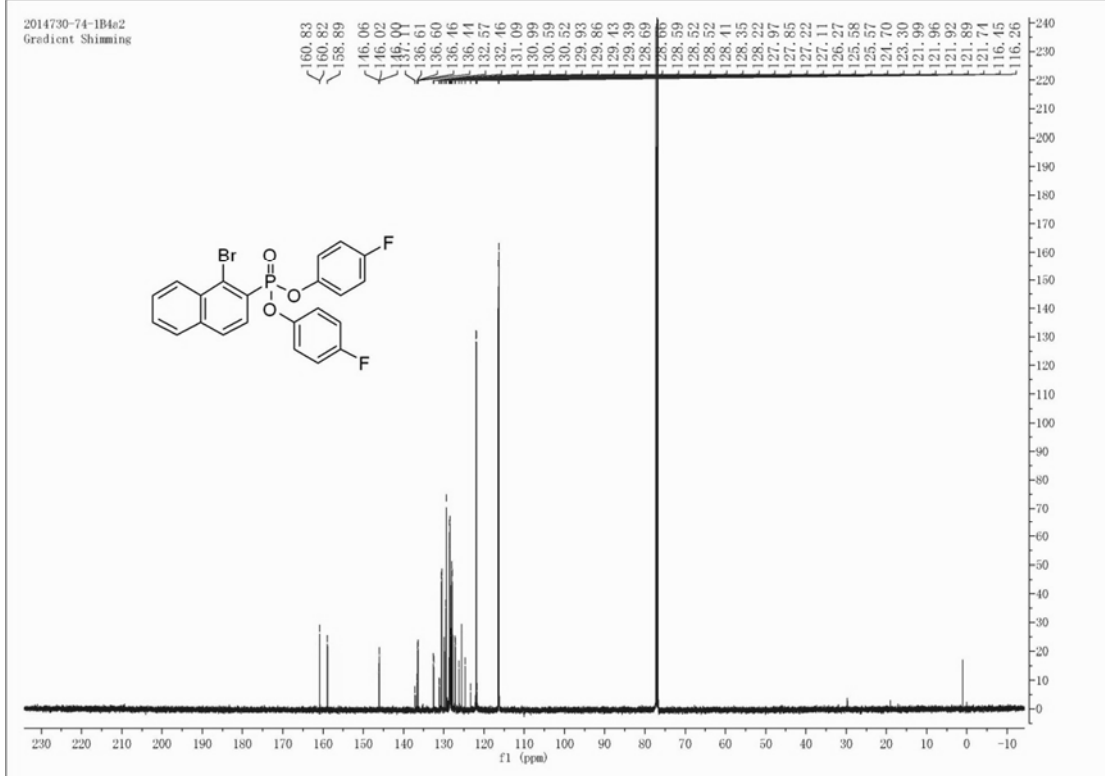
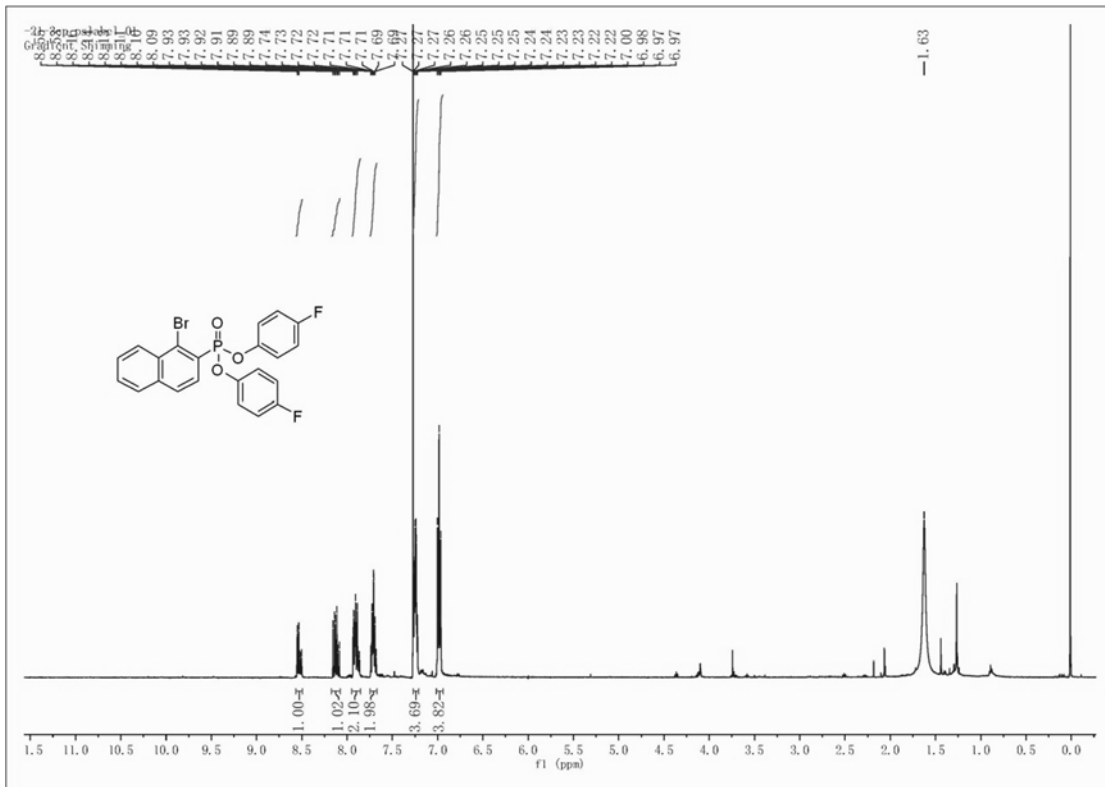


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2014730-2-74-1P3

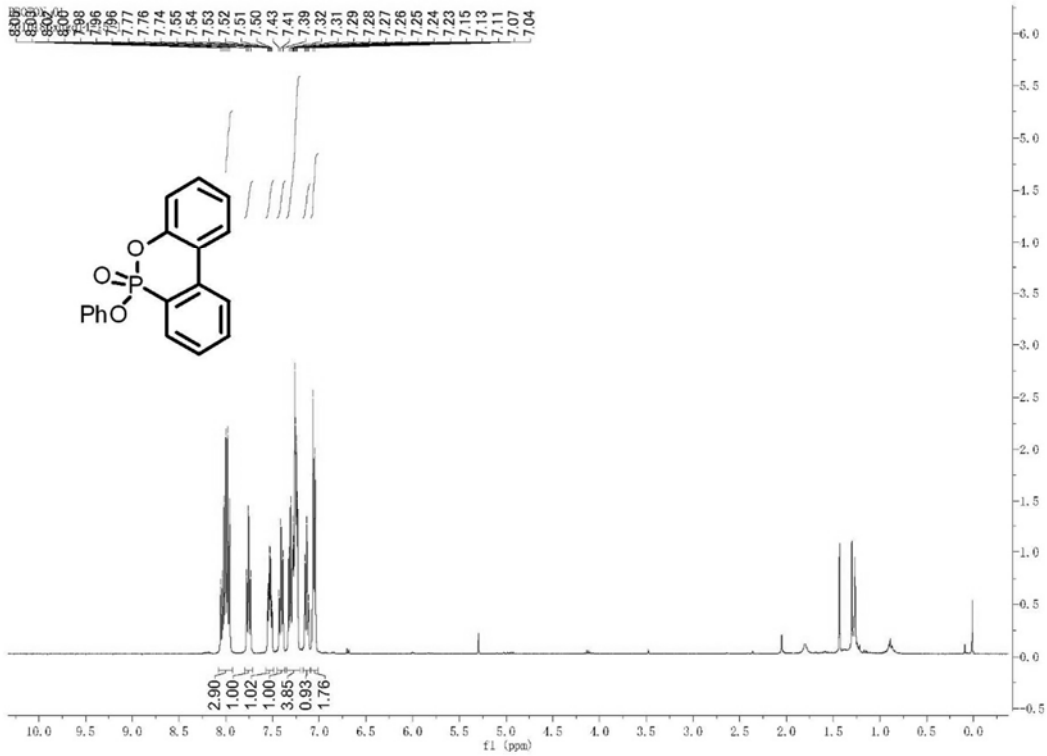
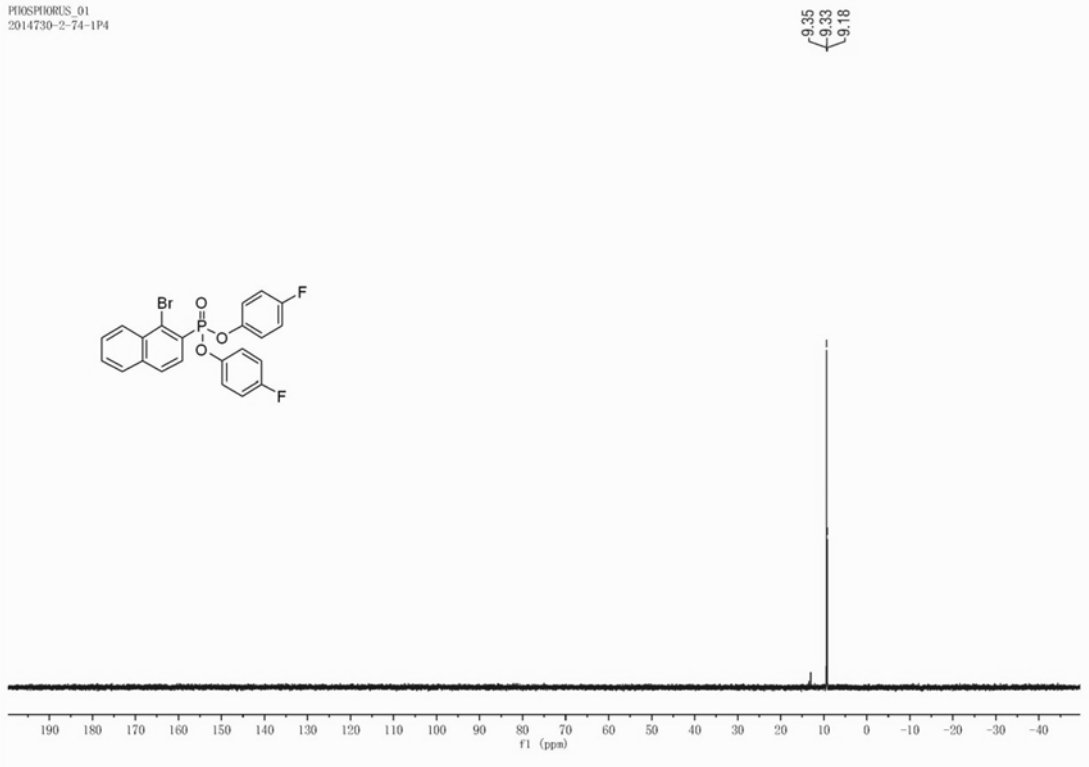


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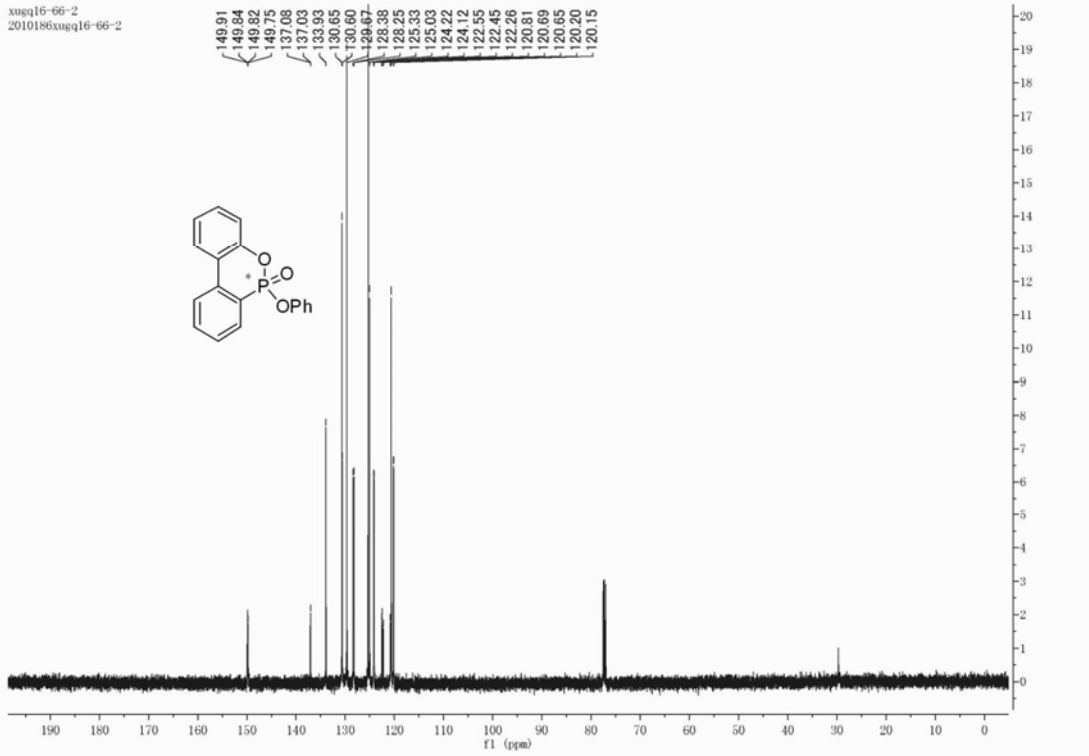




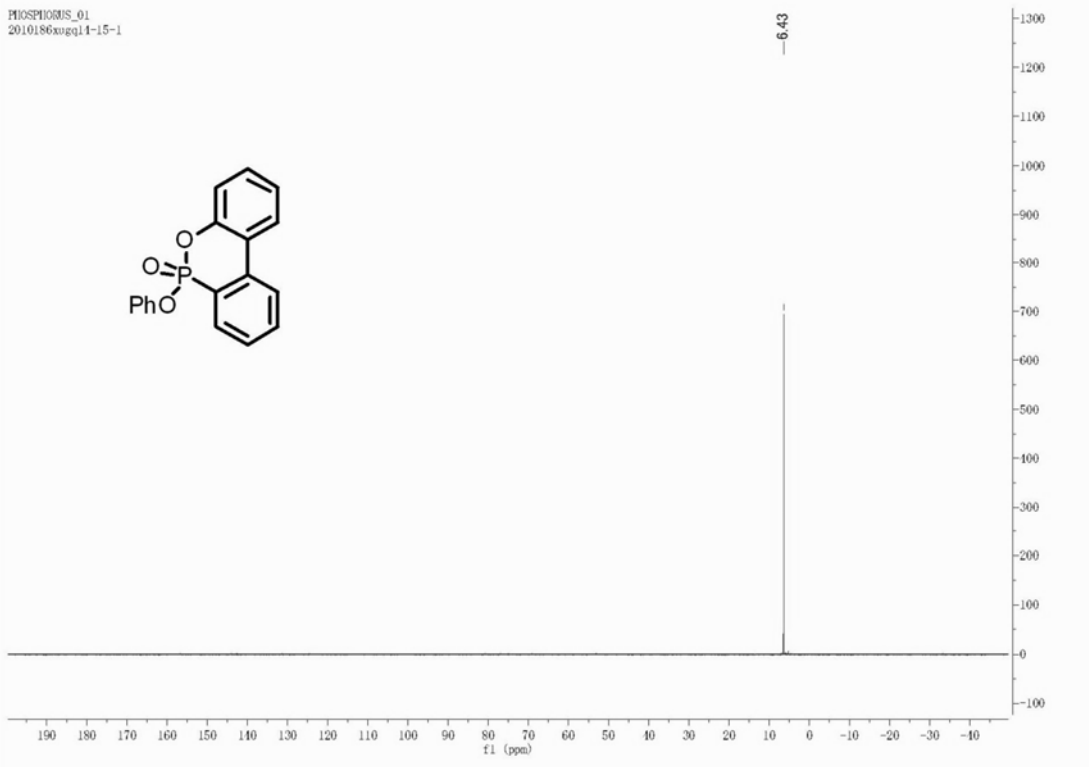
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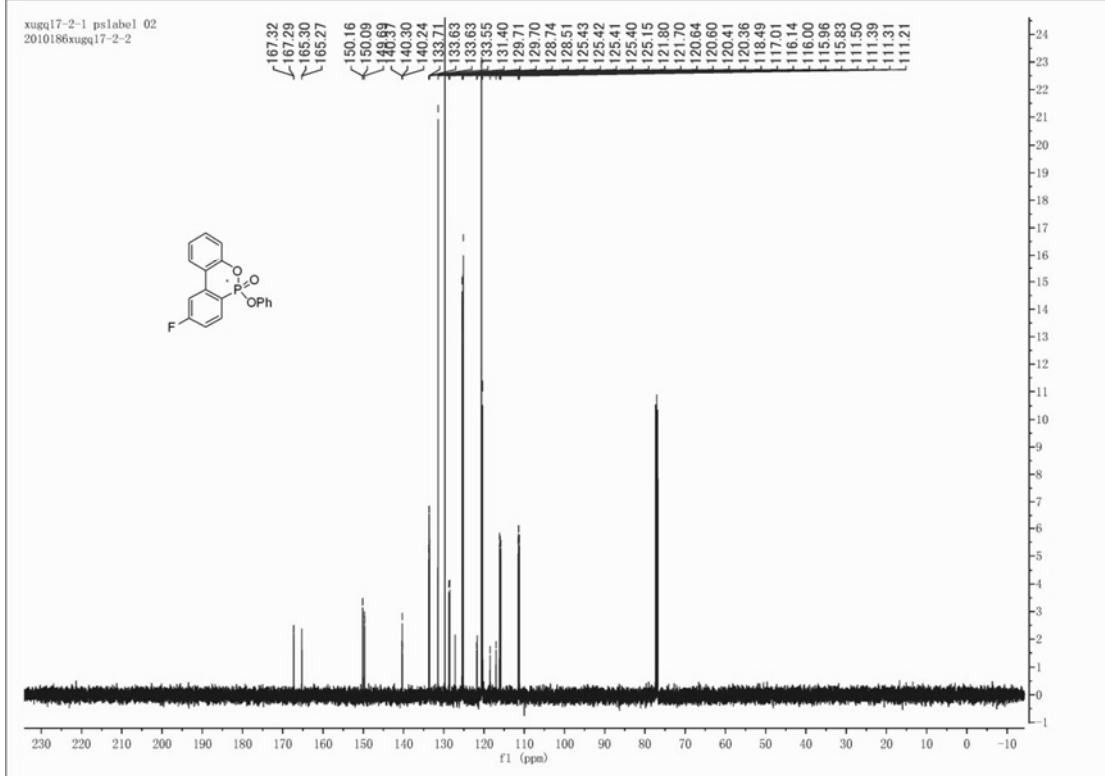
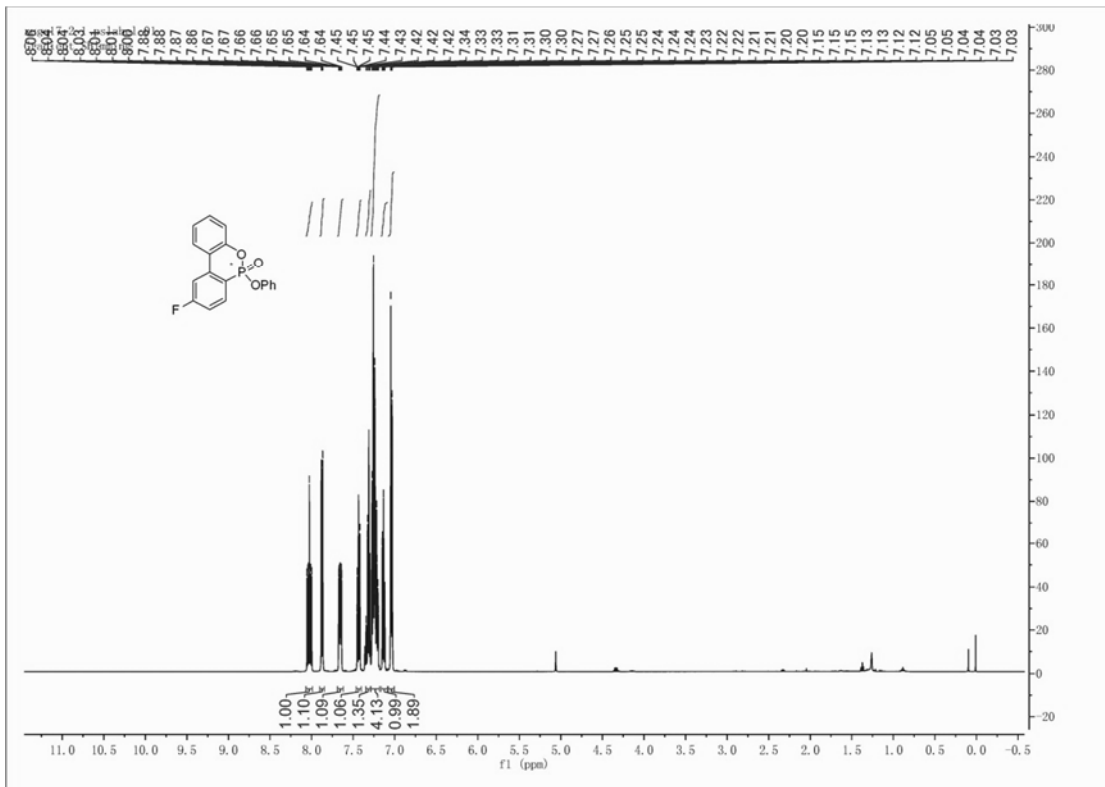


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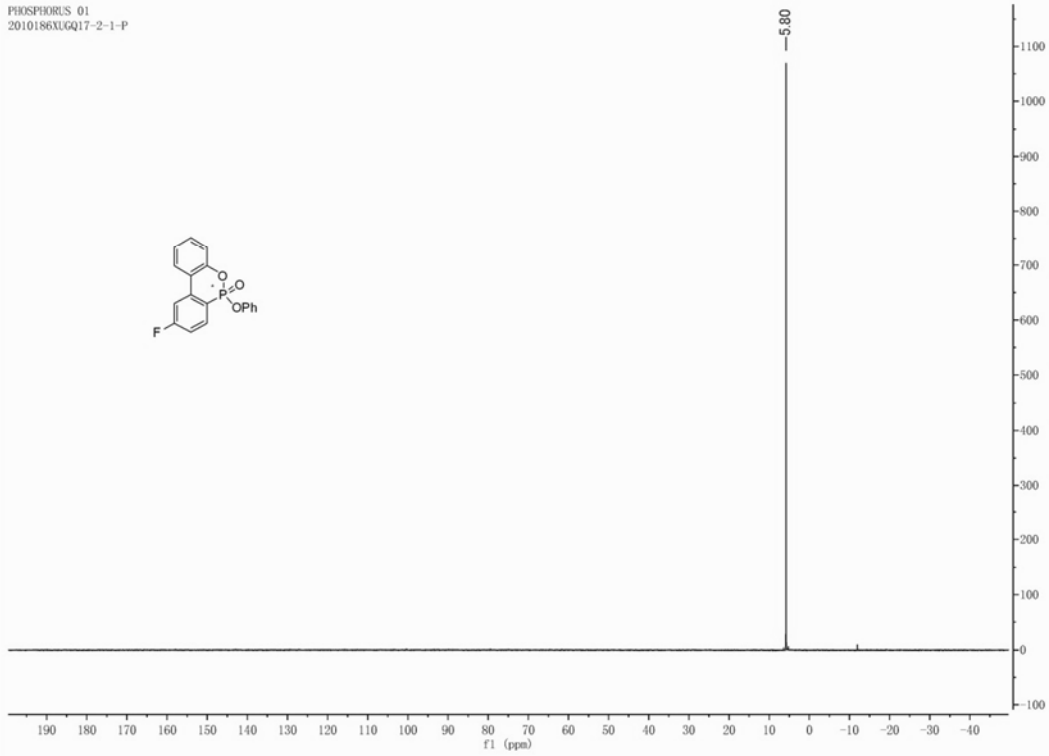
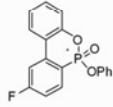


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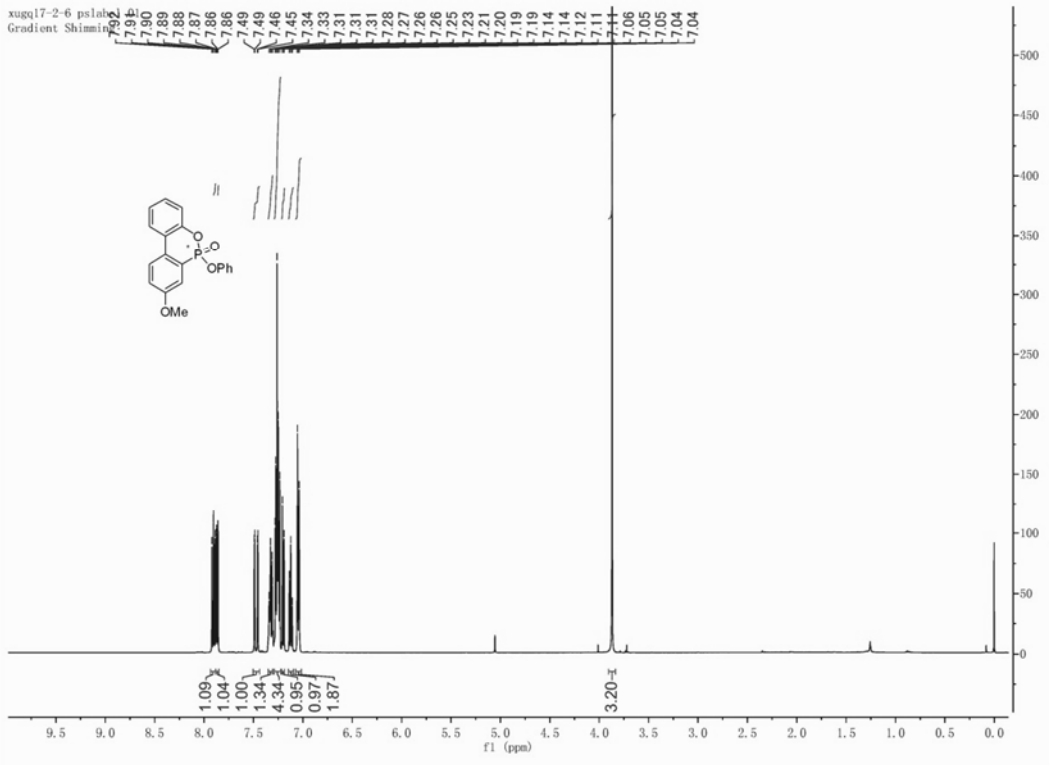
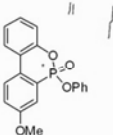




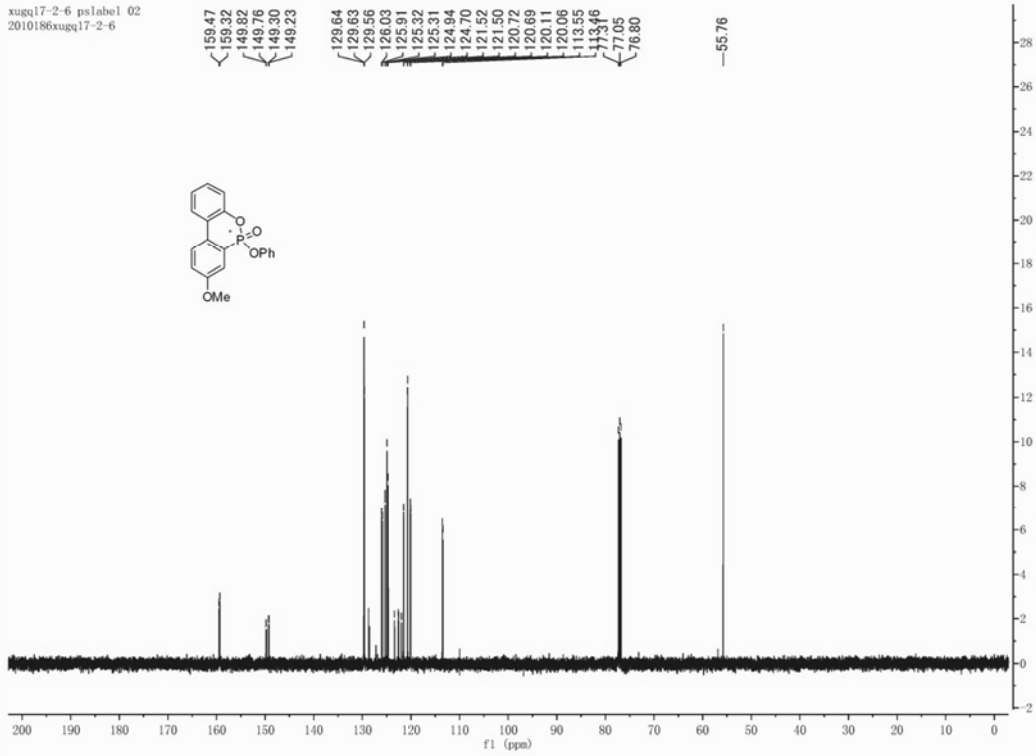
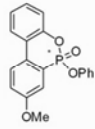
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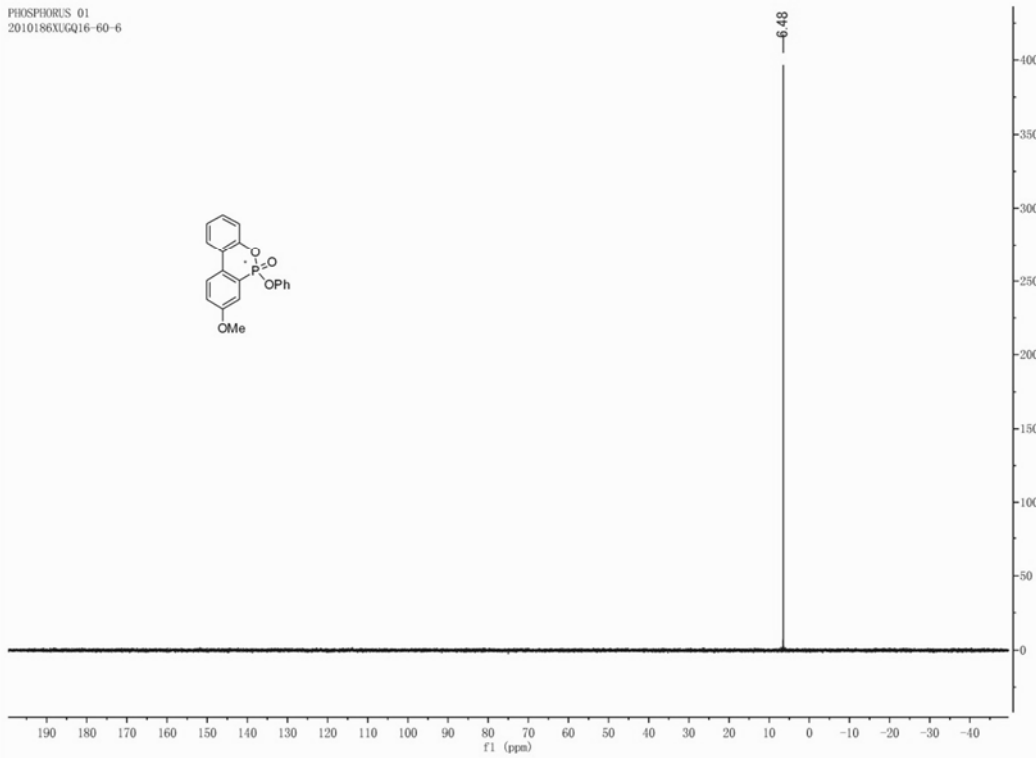
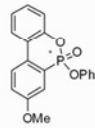
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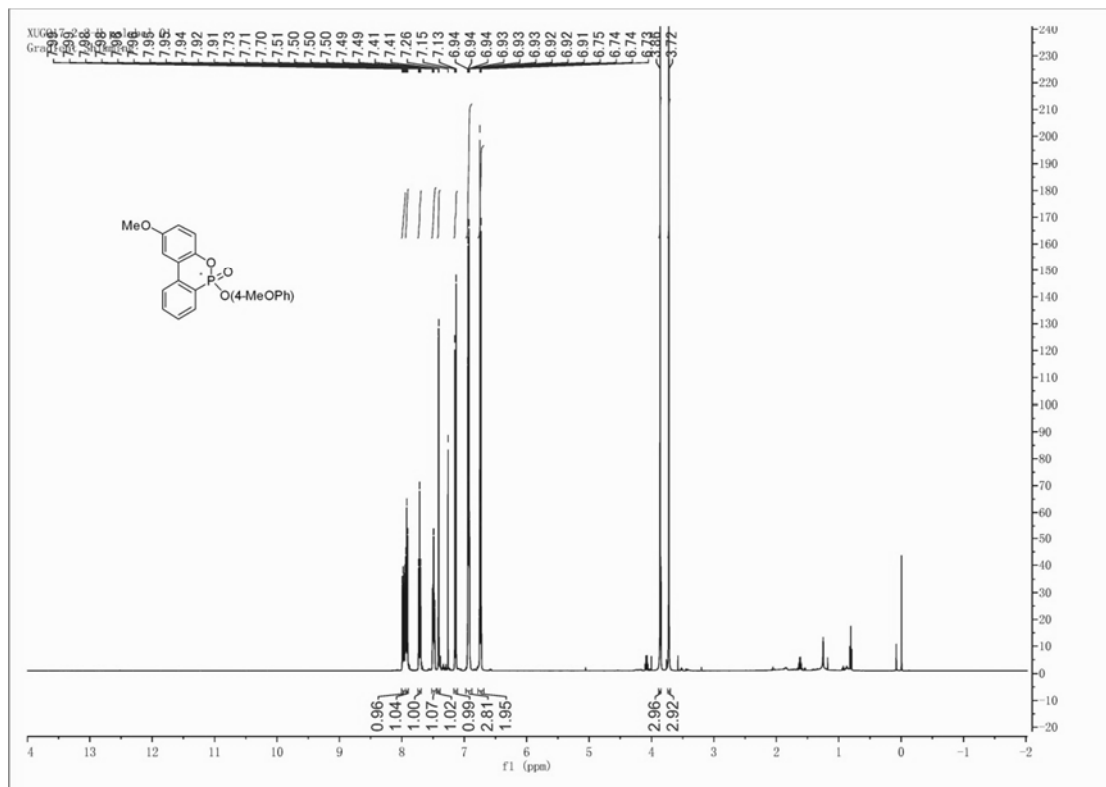


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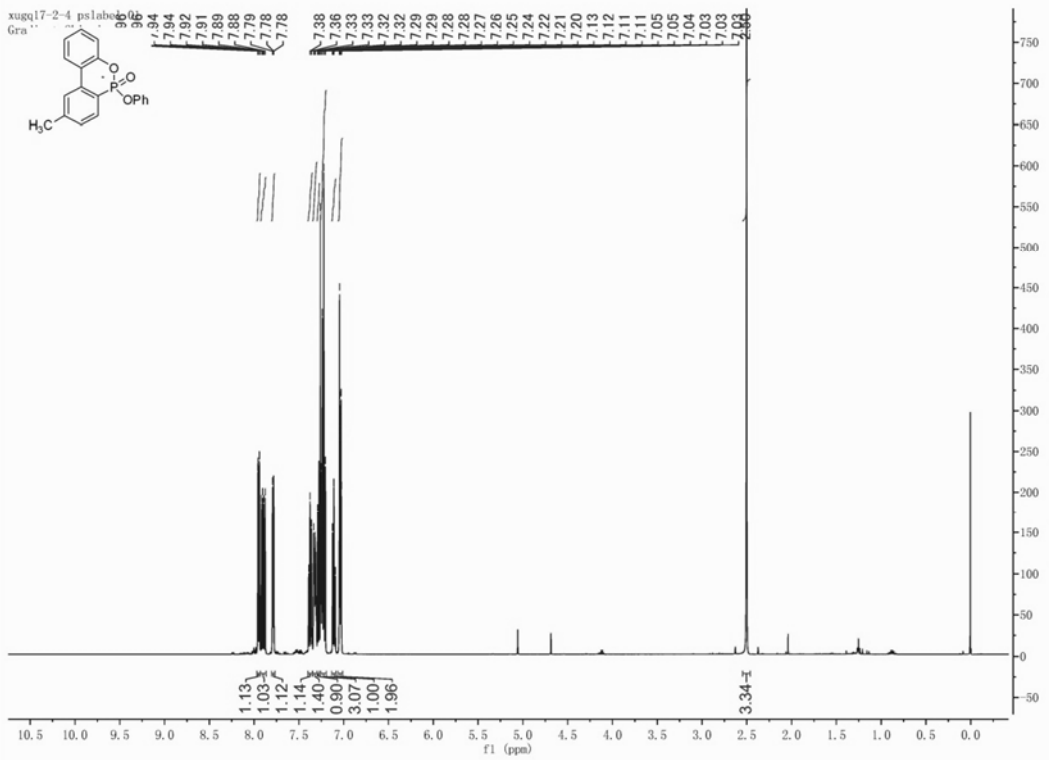
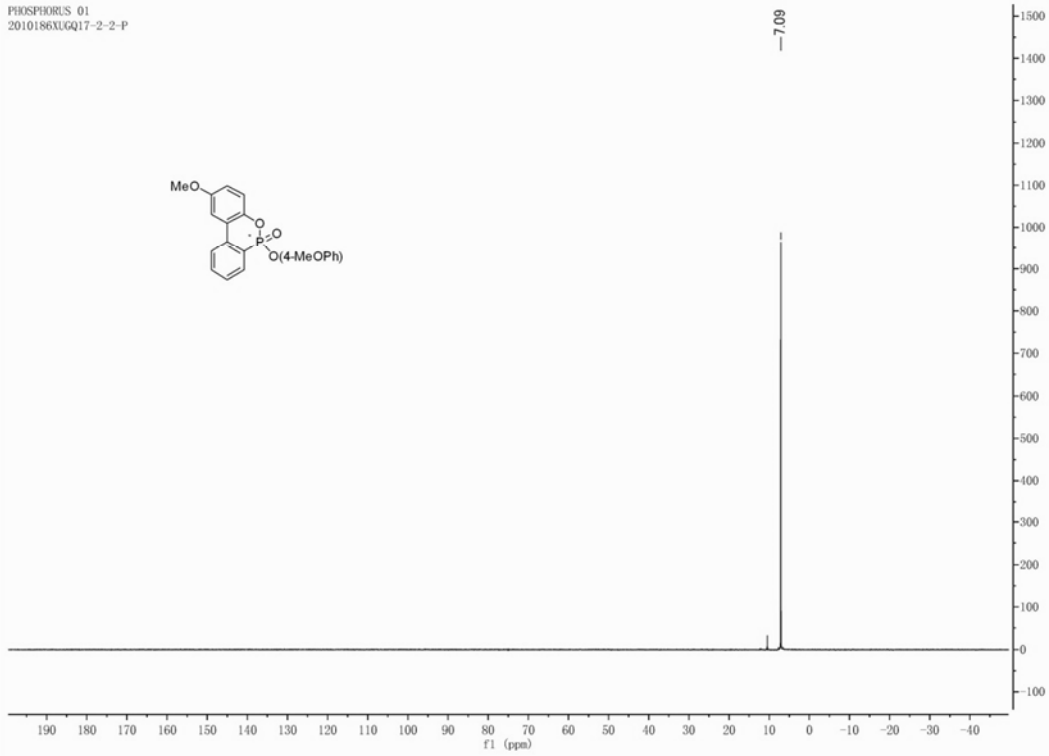
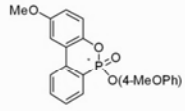


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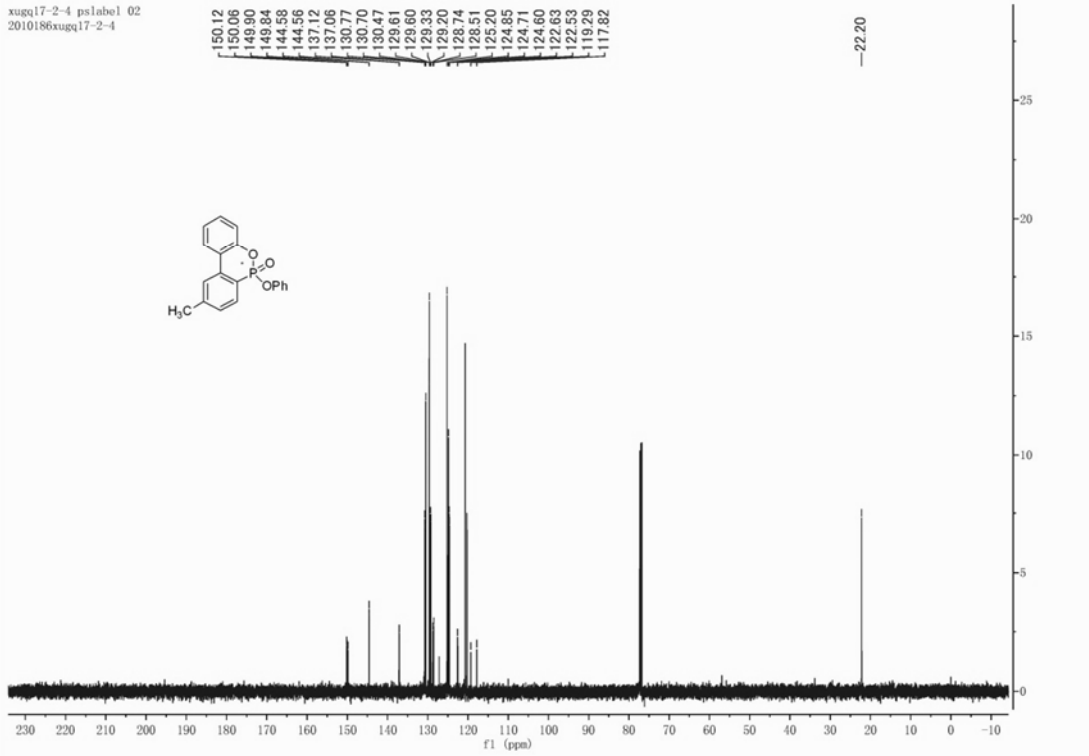




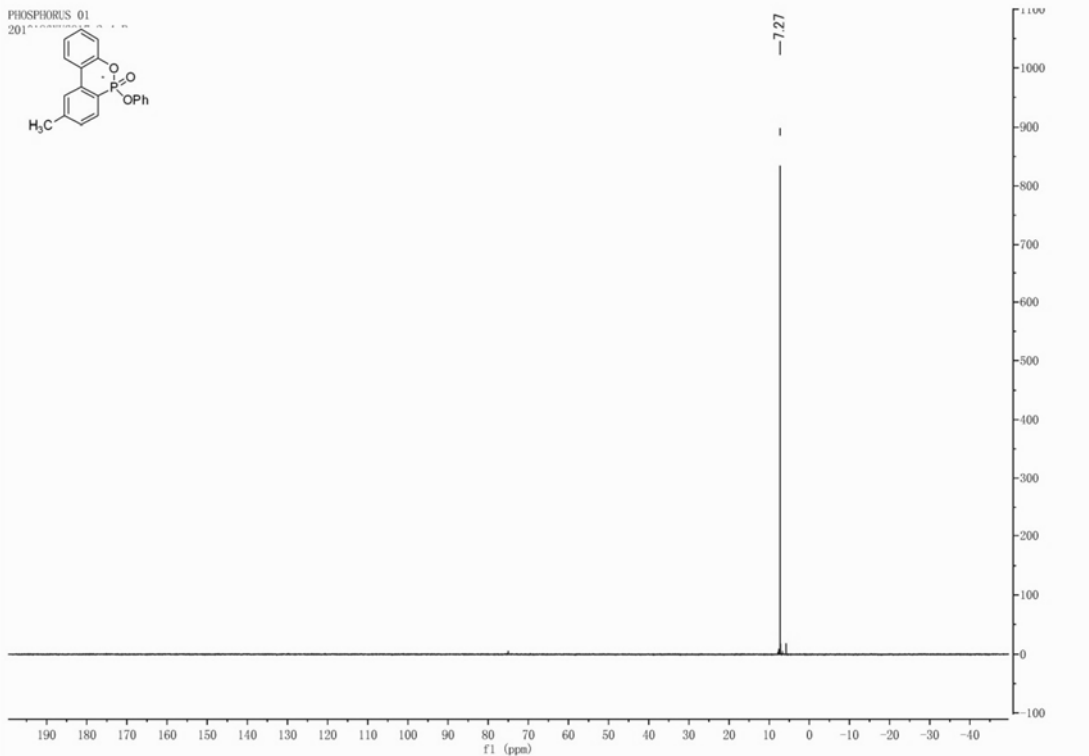
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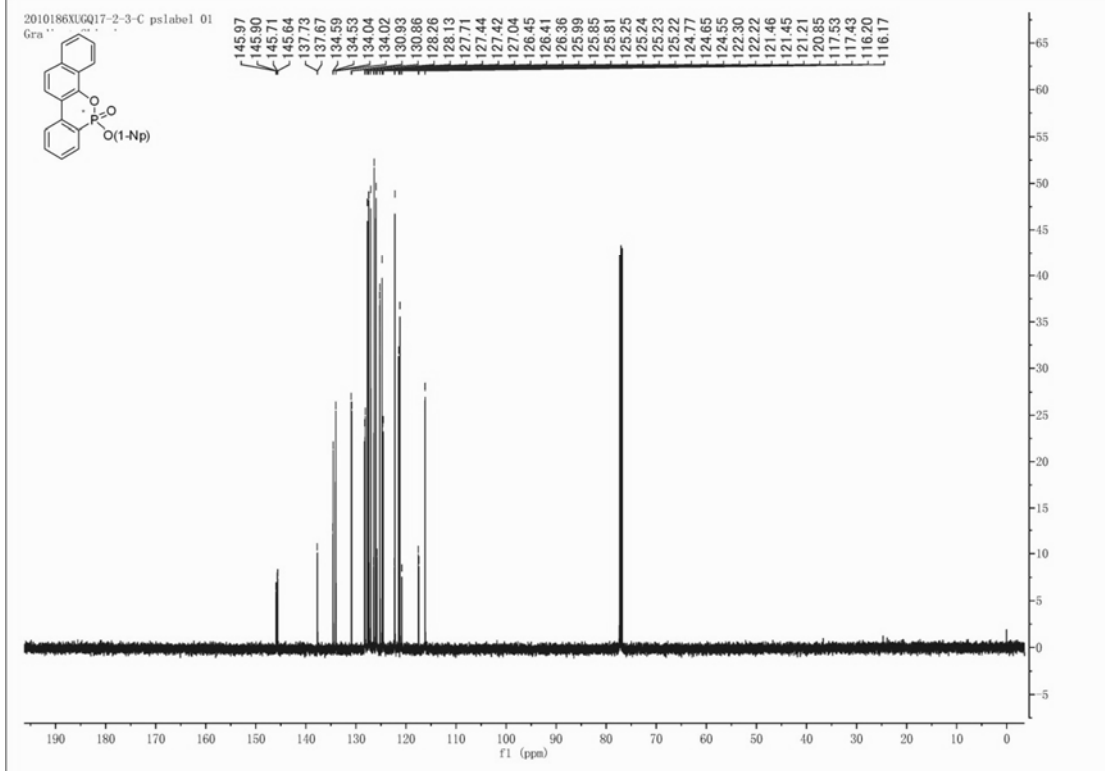
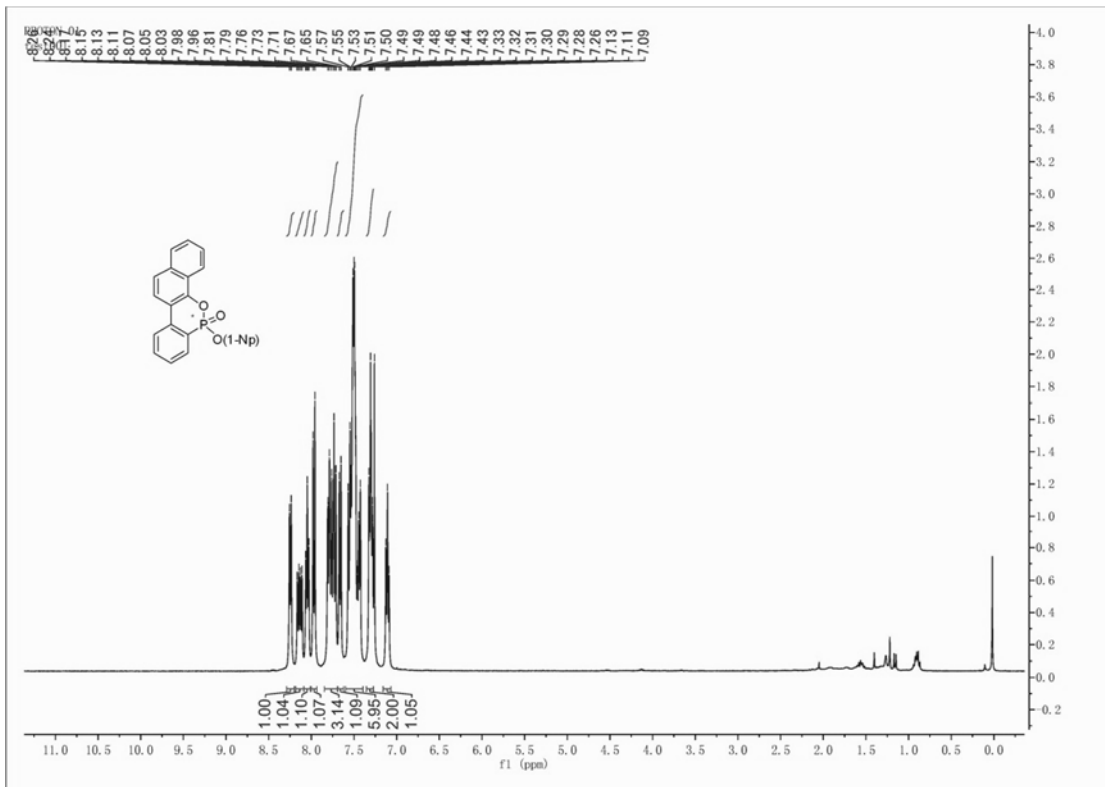


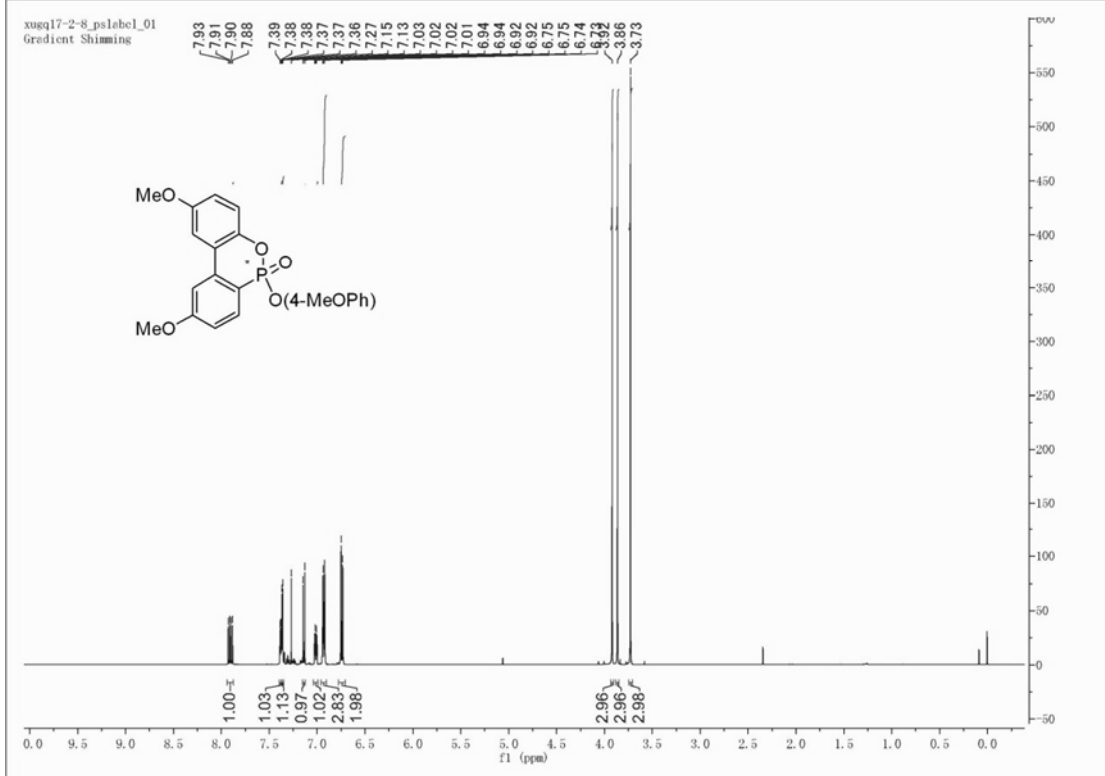
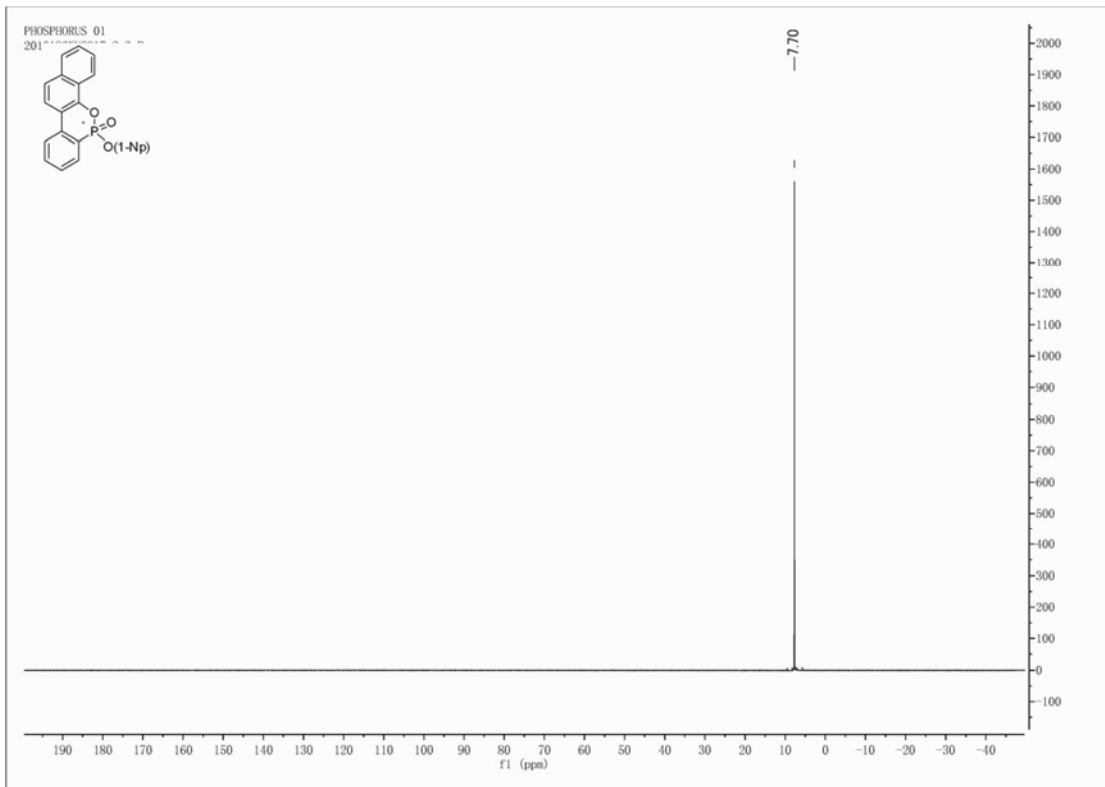
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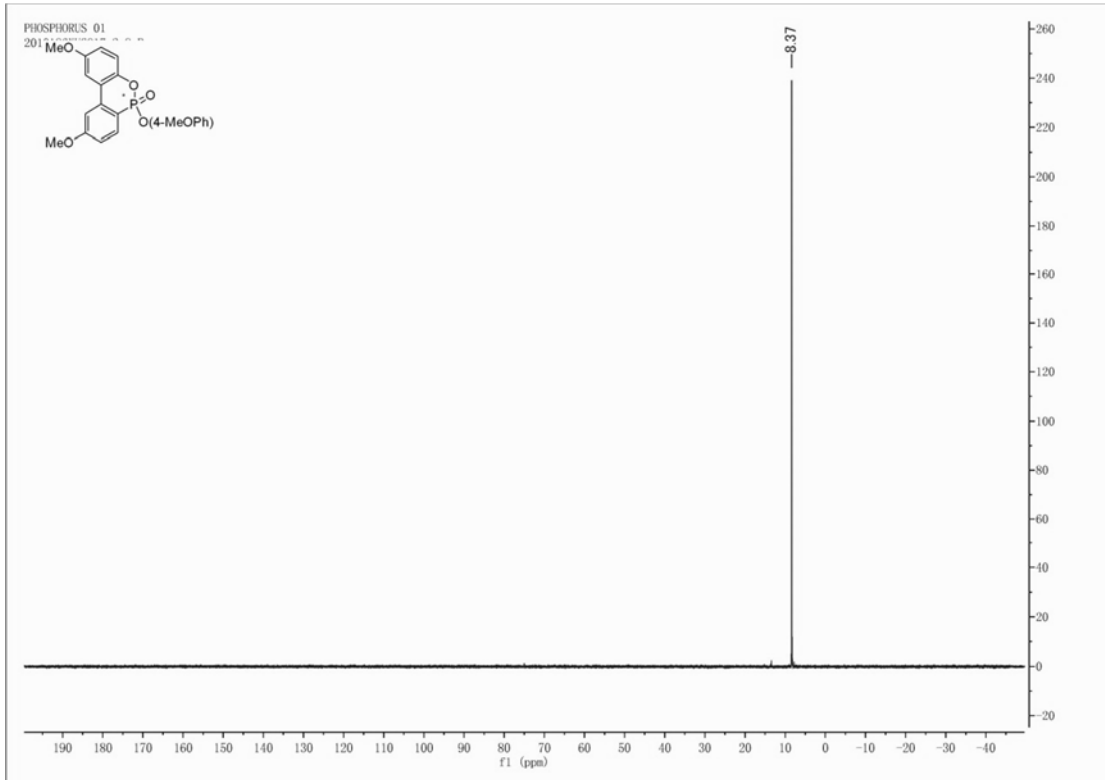
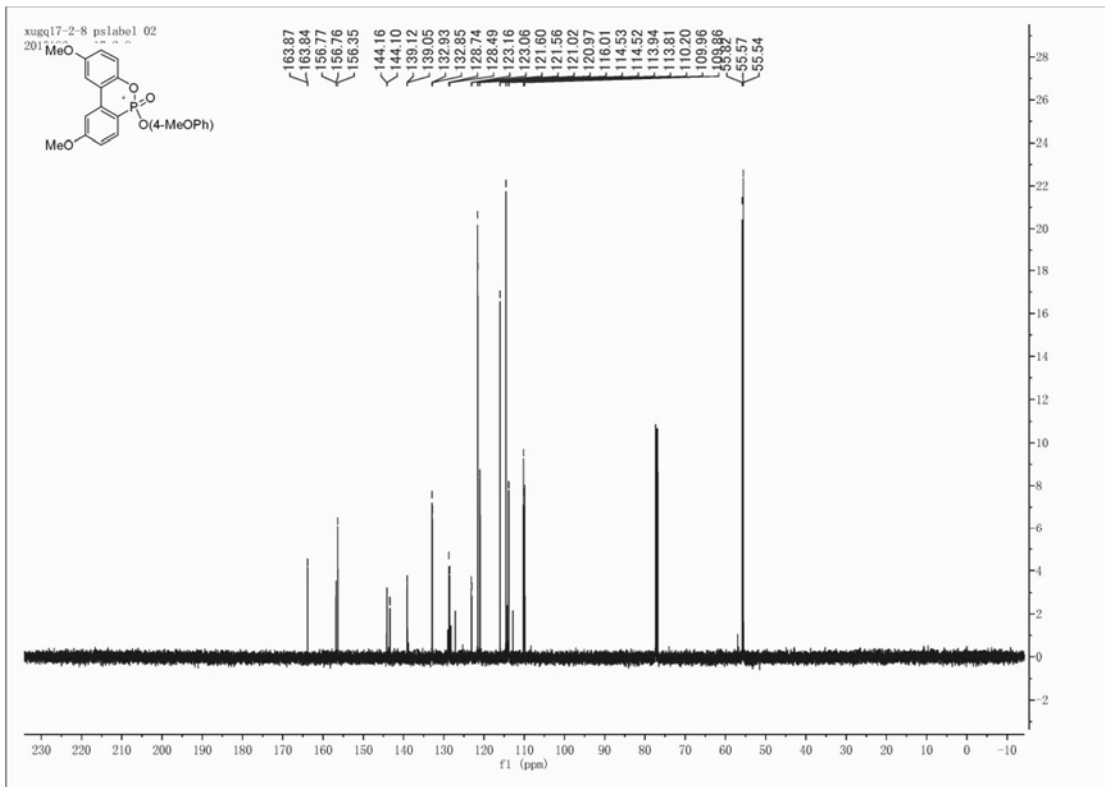


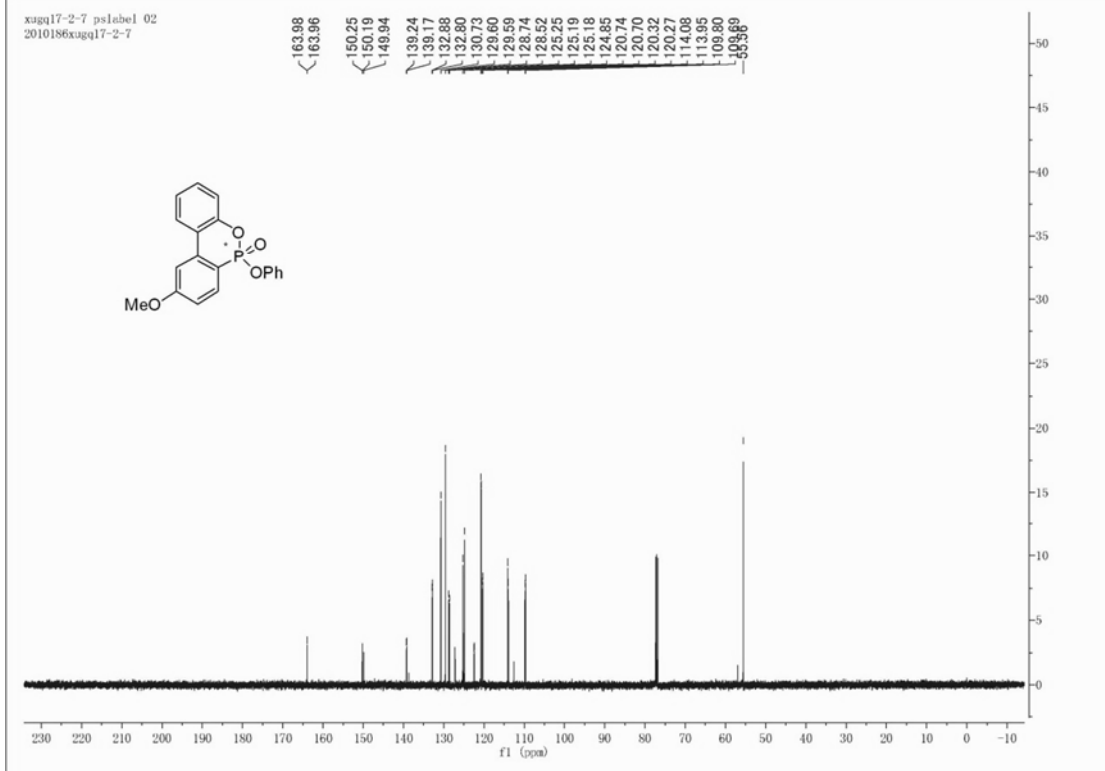
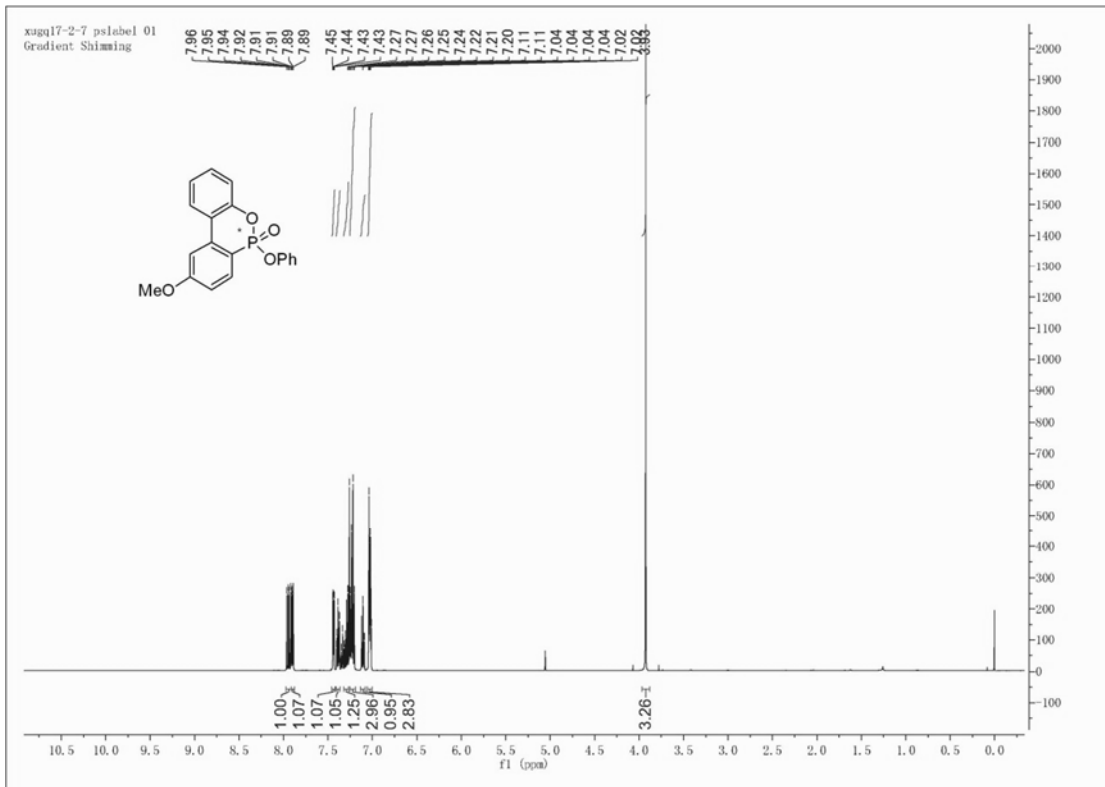
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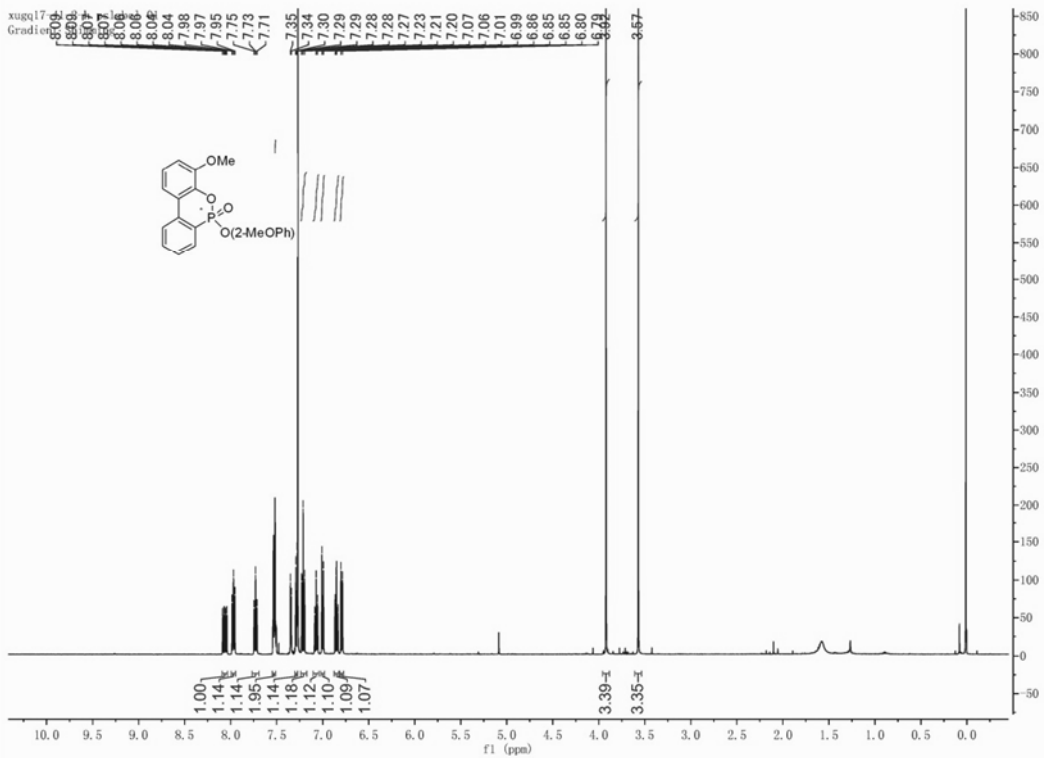
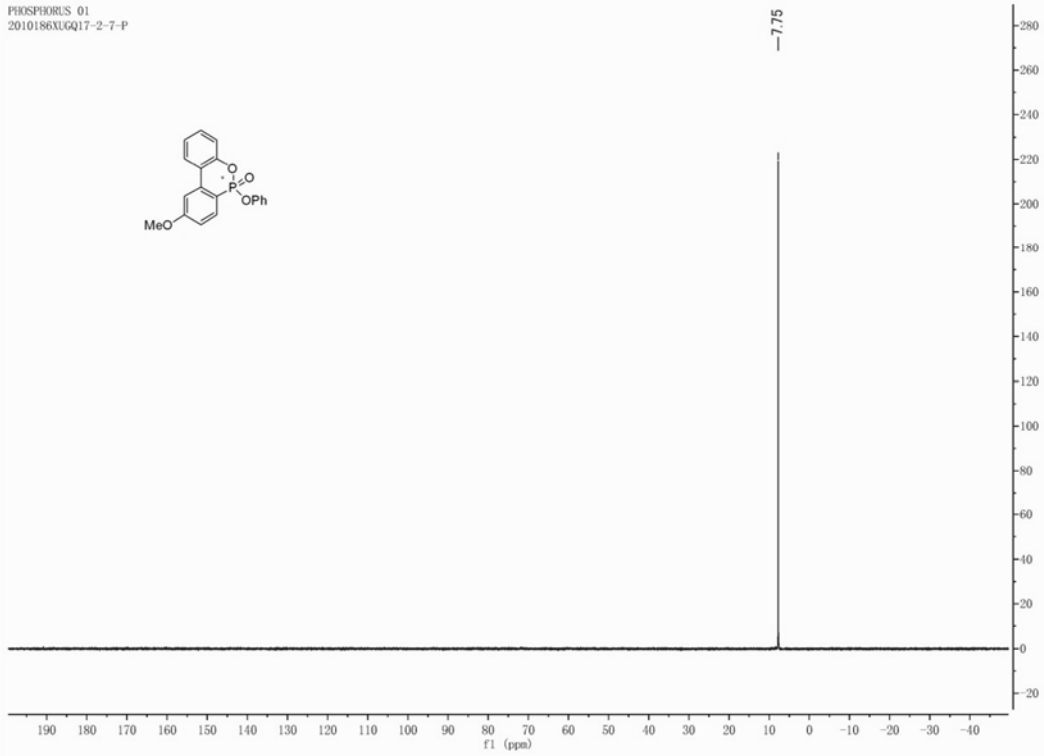
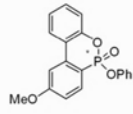




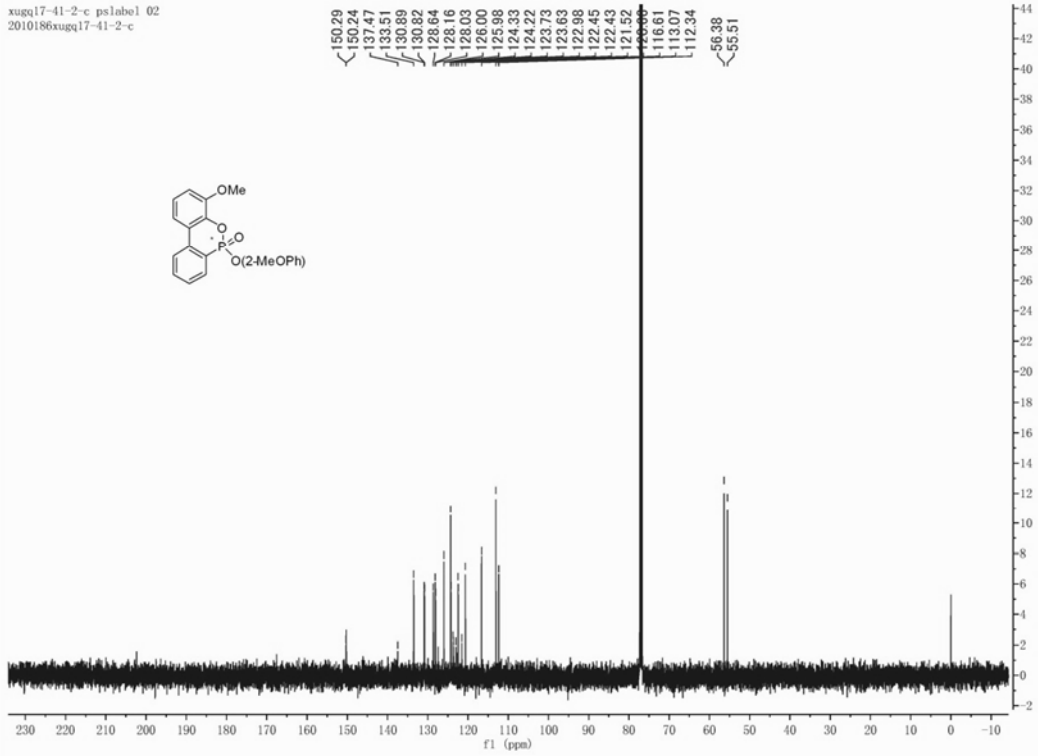




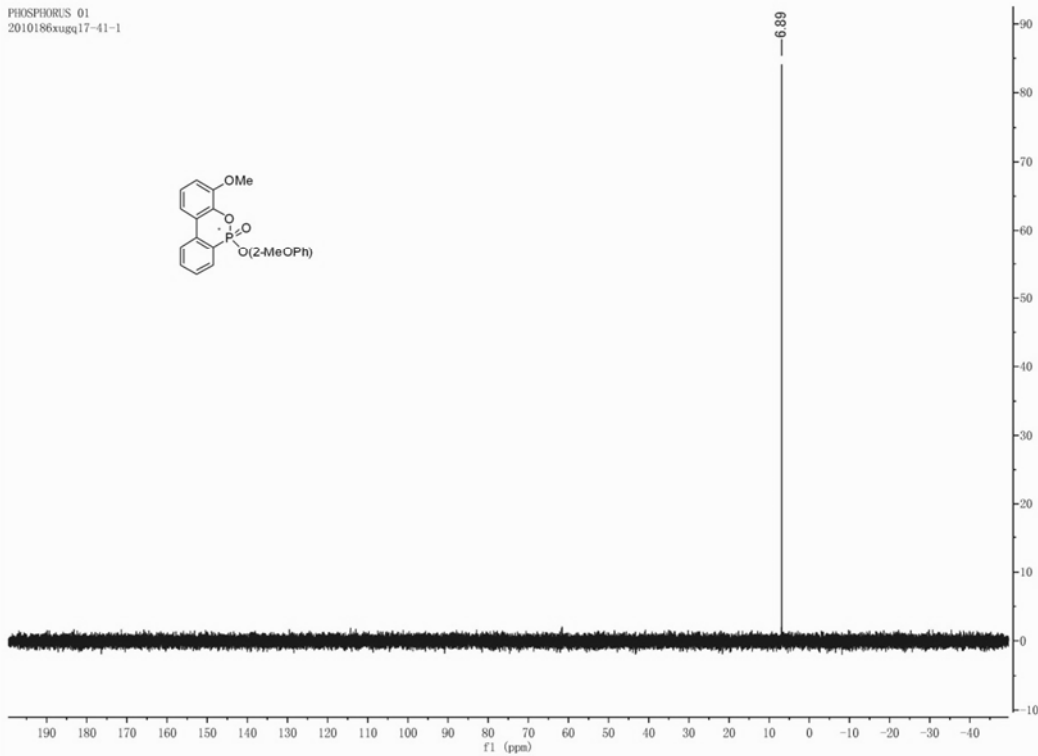
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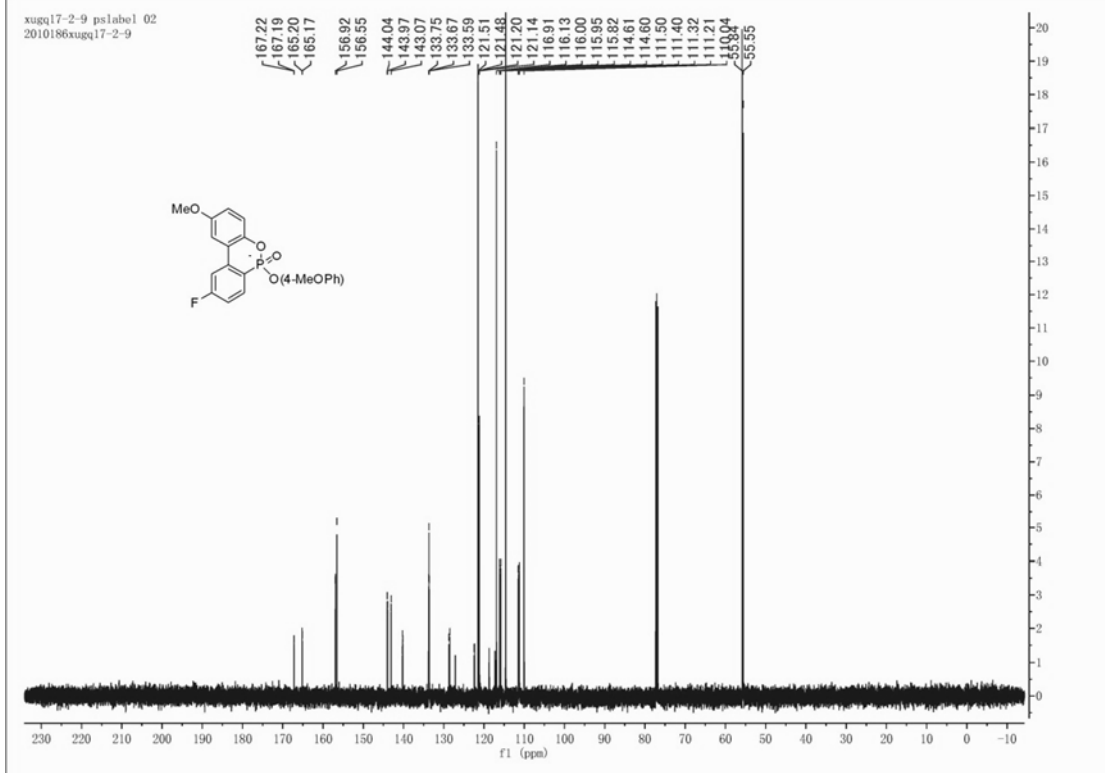
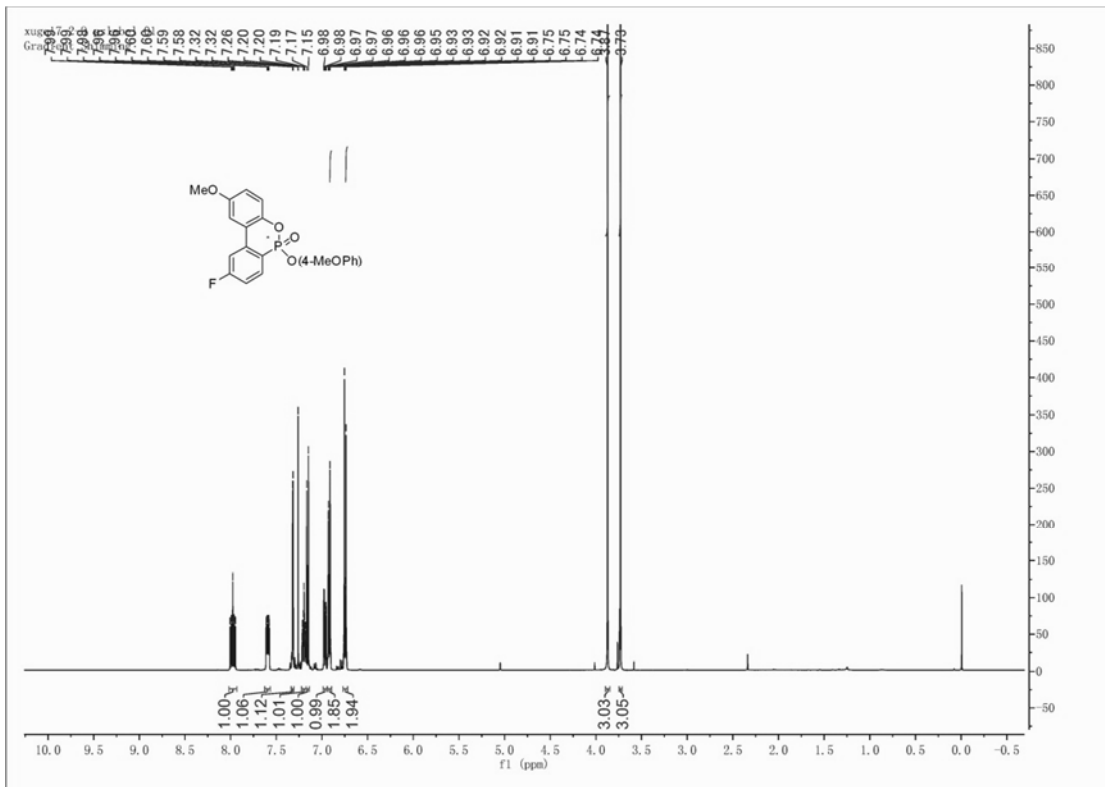


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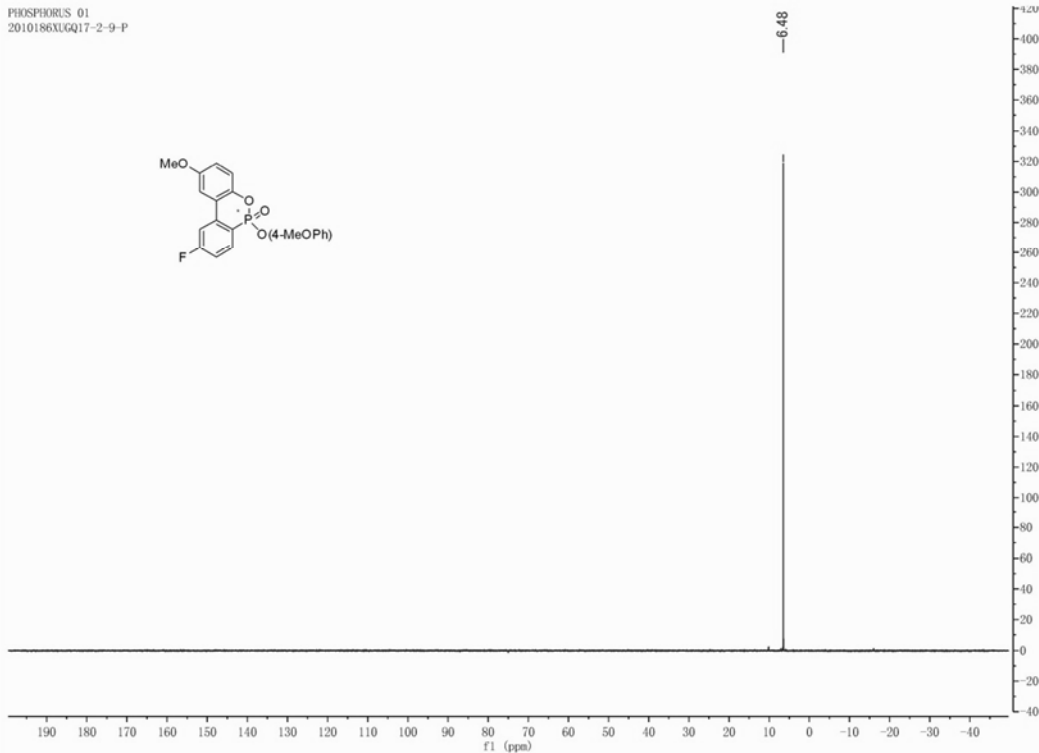
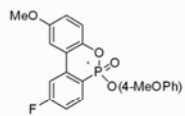


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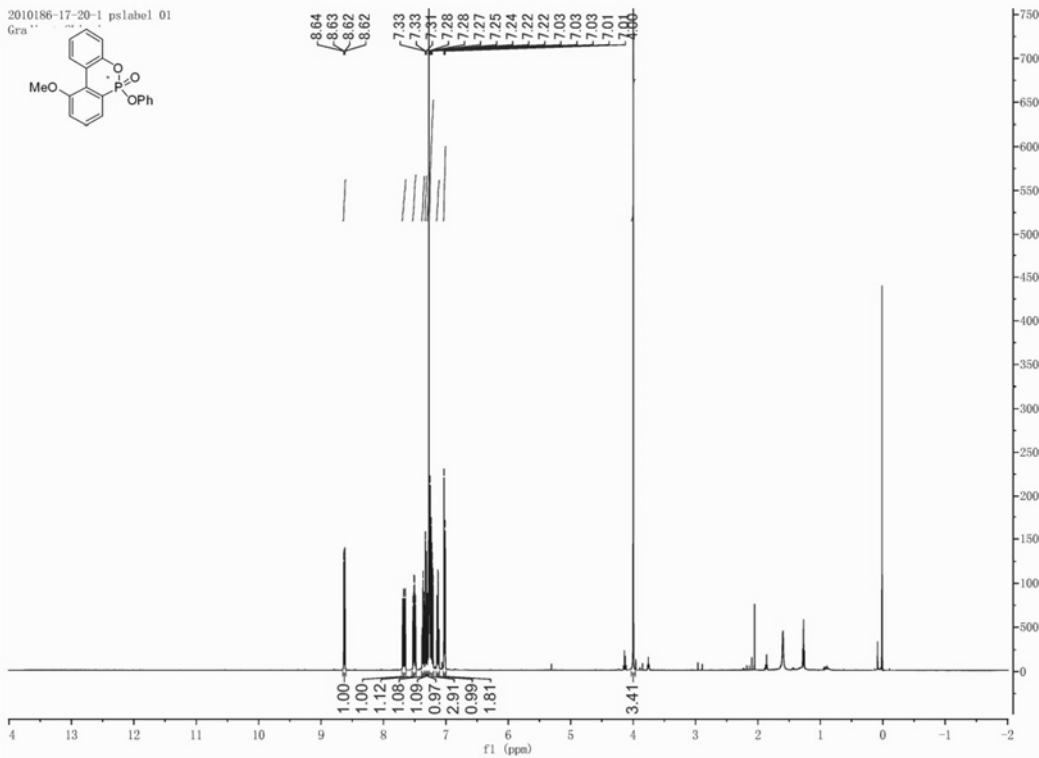
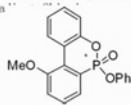


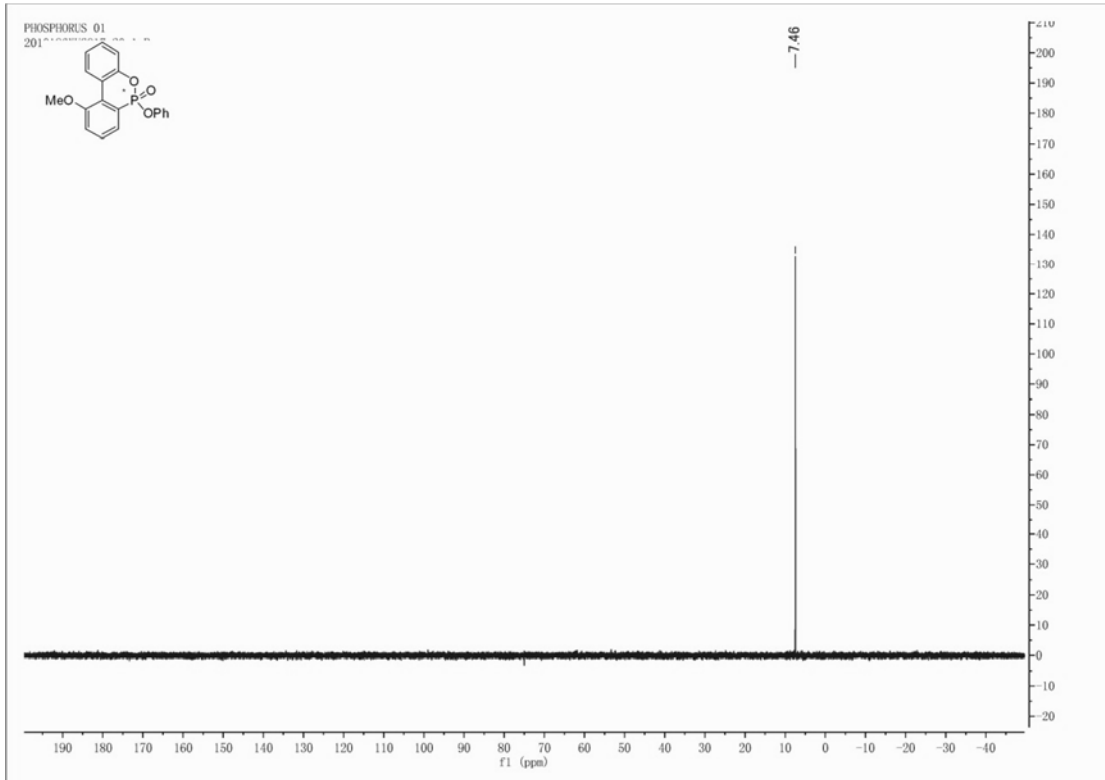
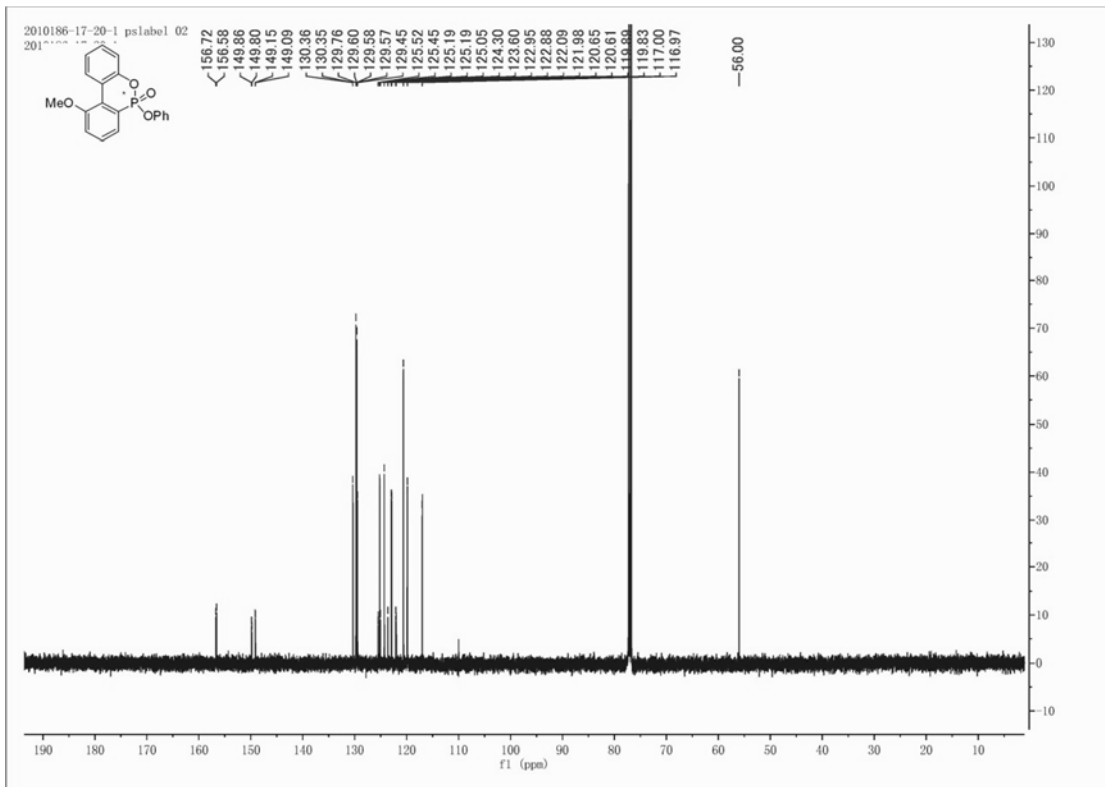


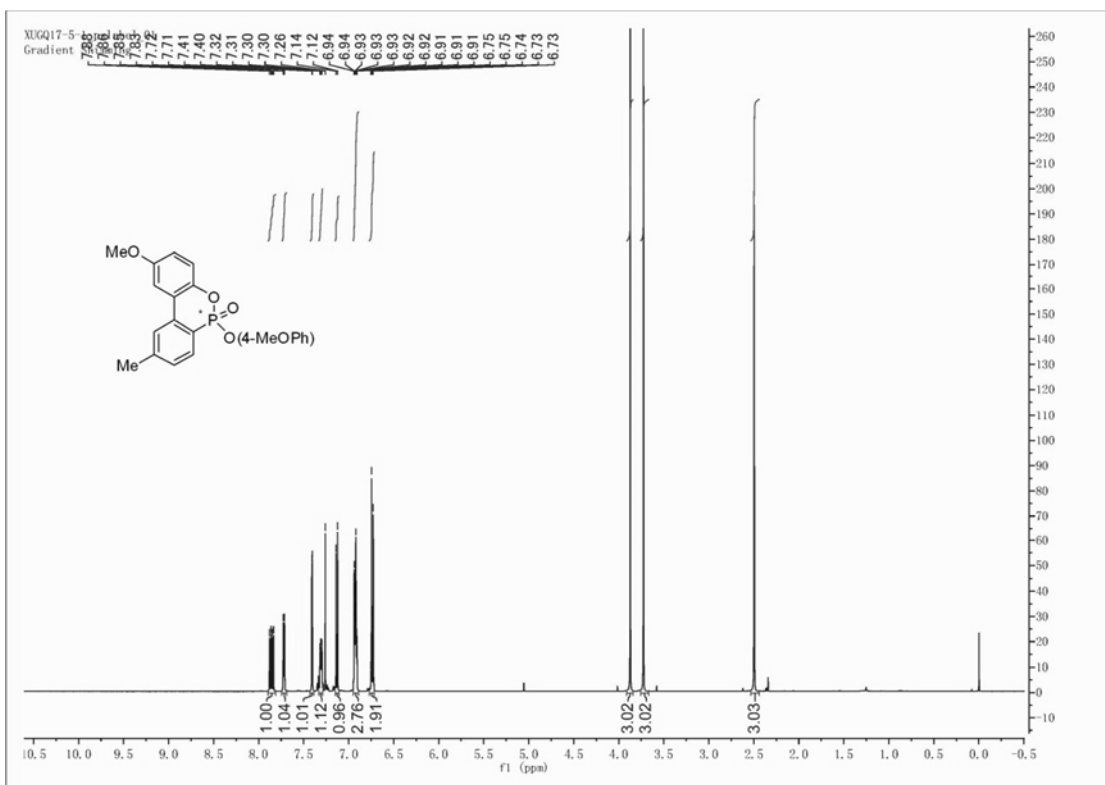
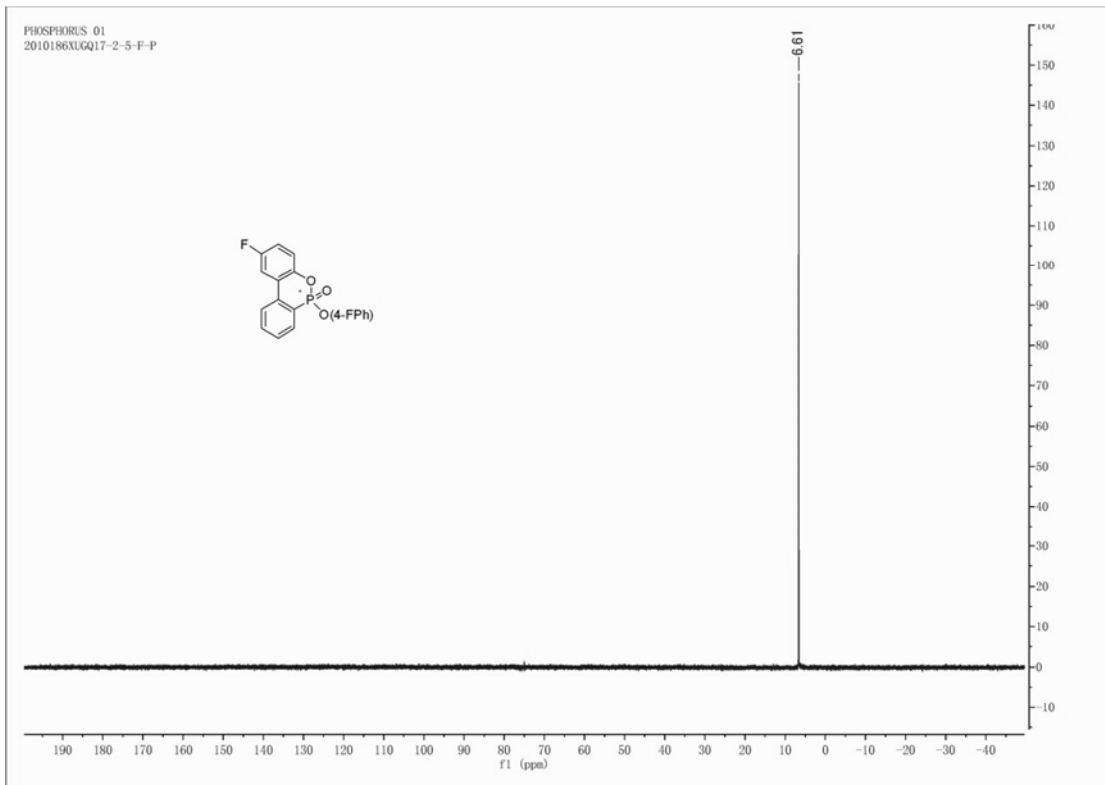
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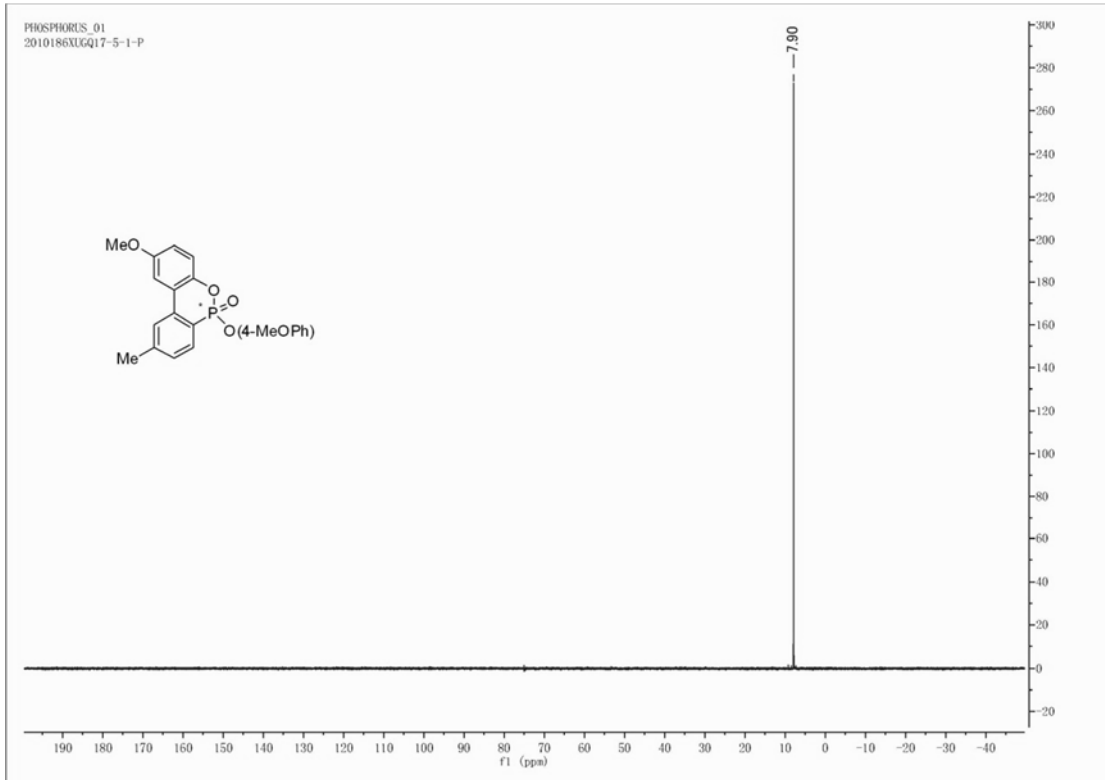
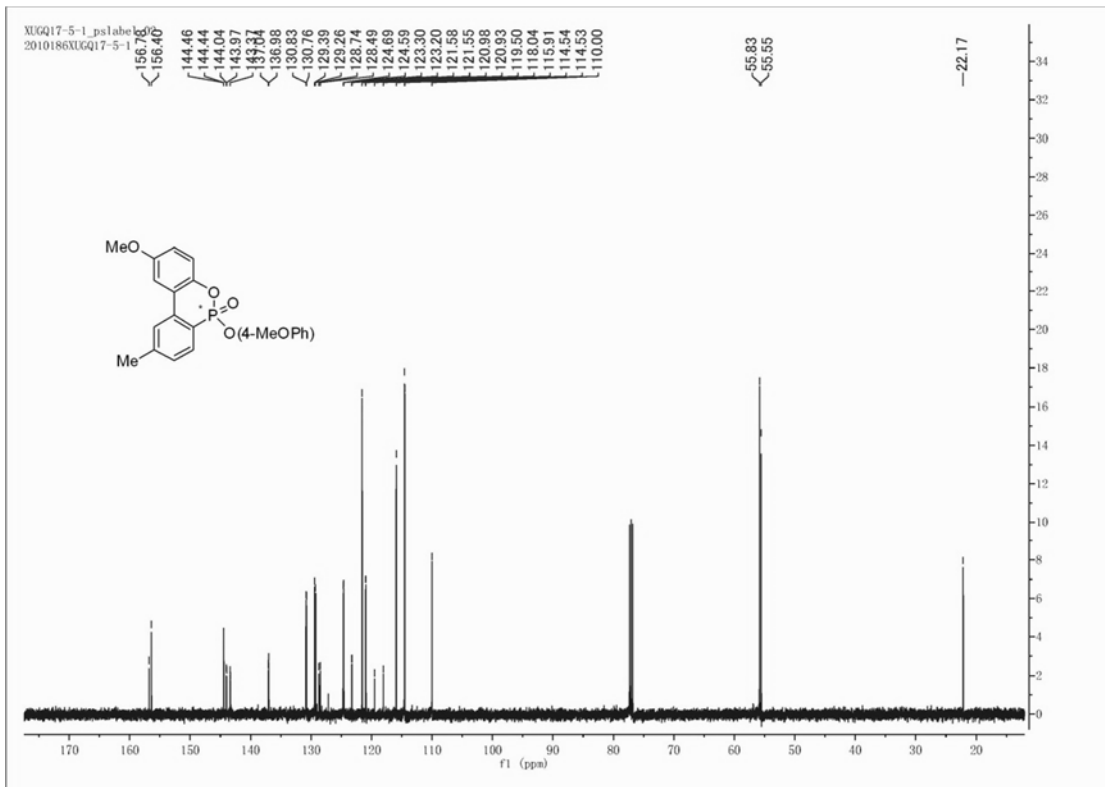


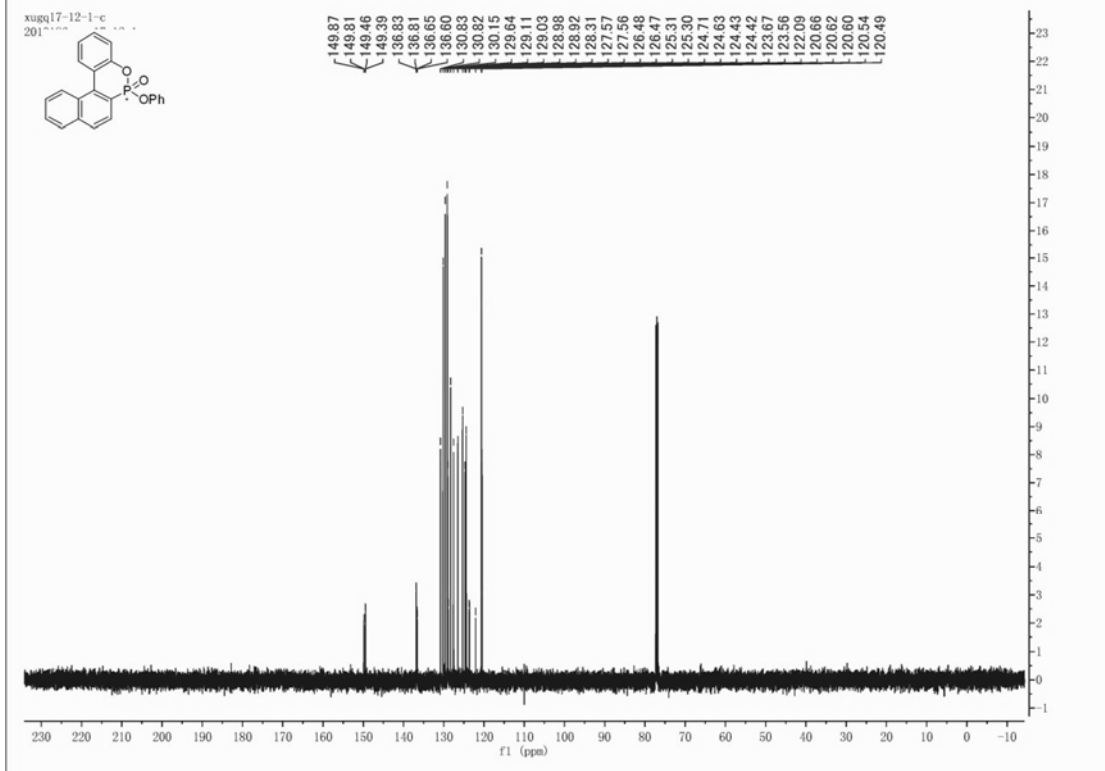
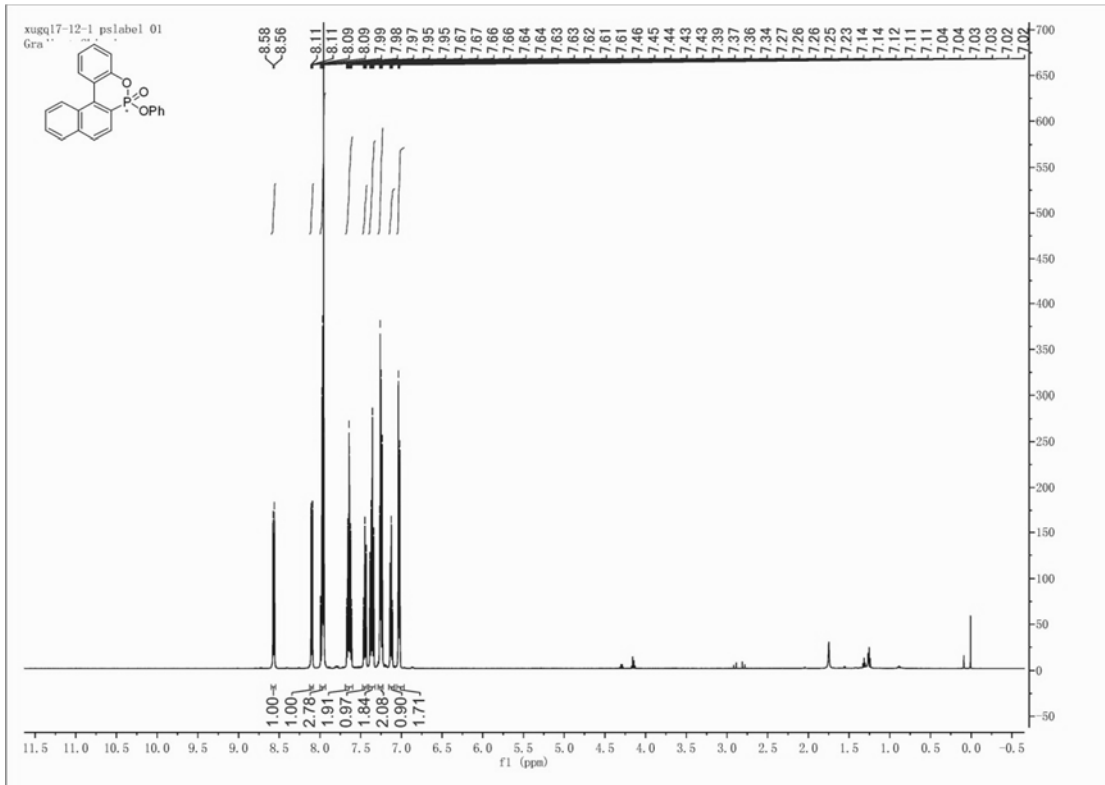
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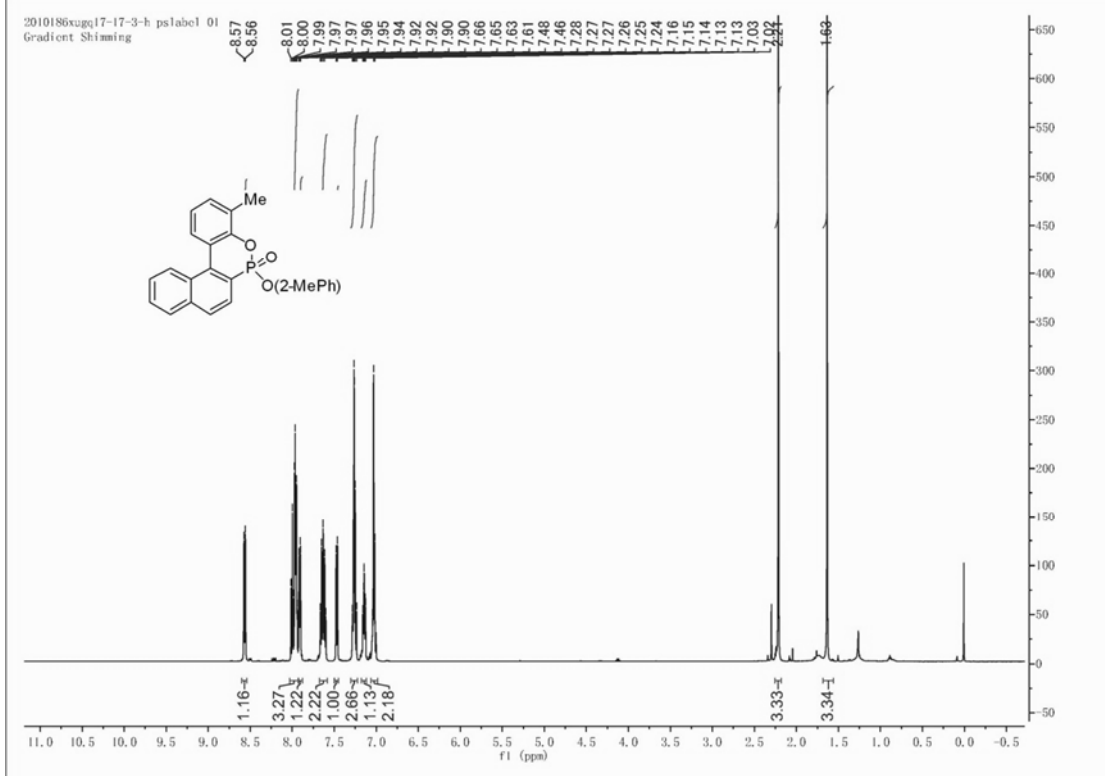
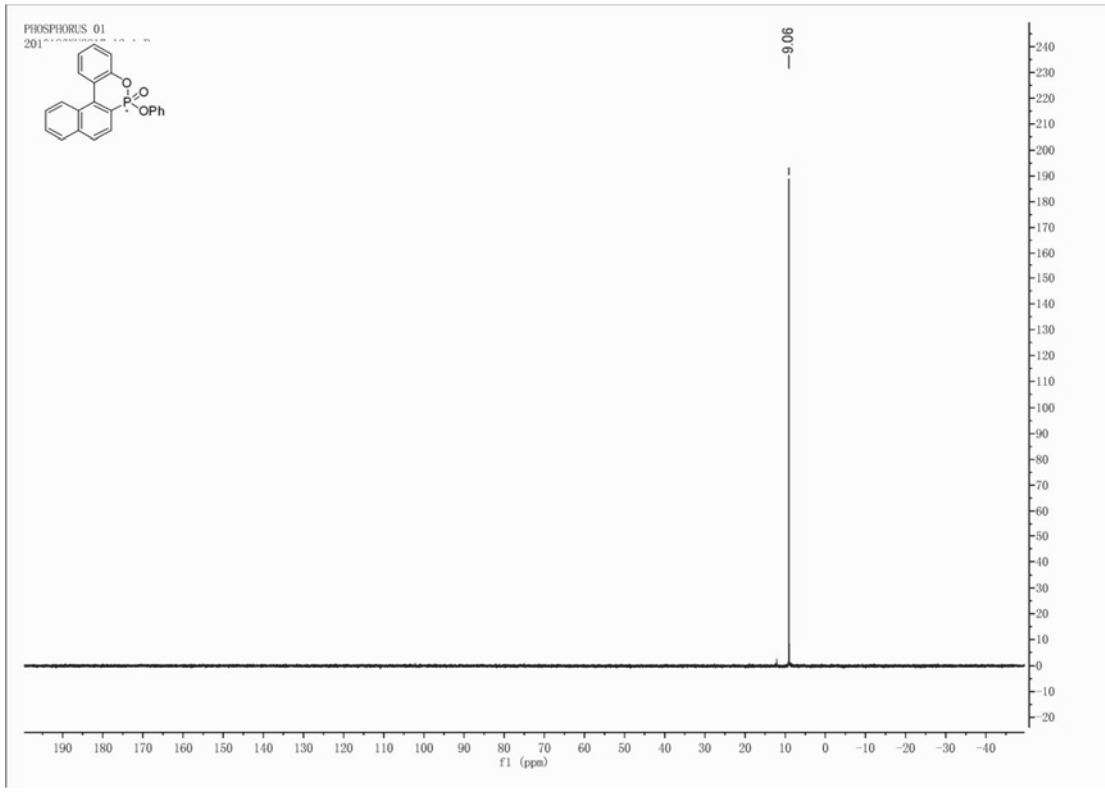




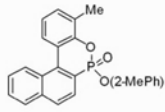






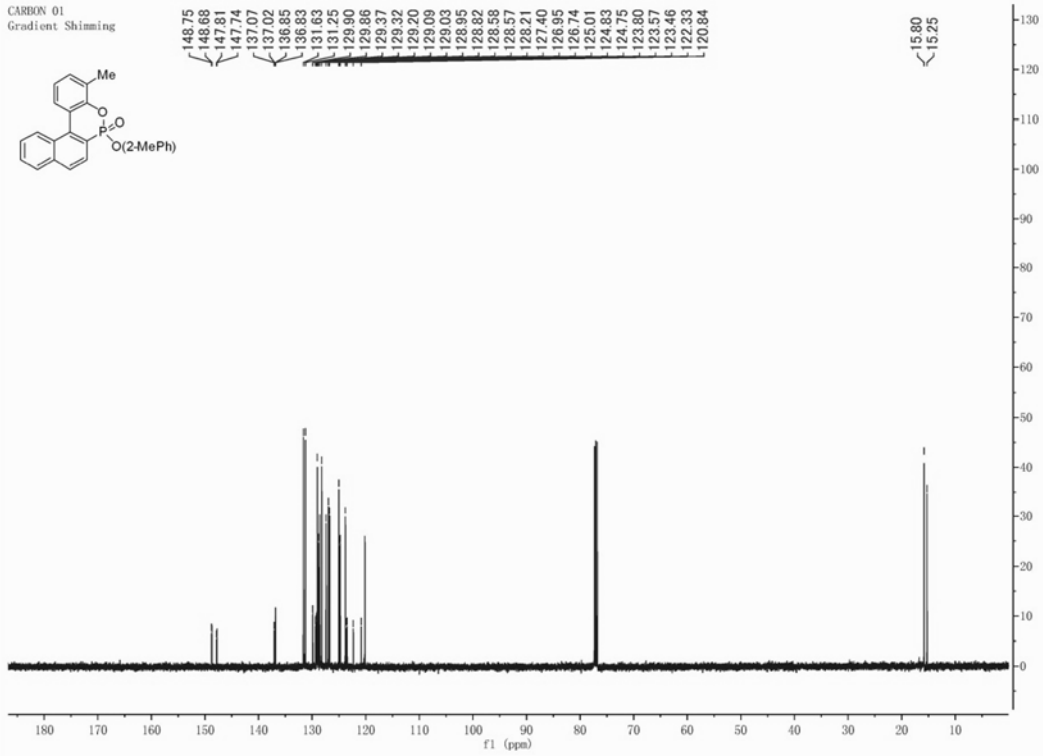


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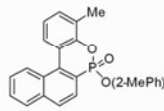


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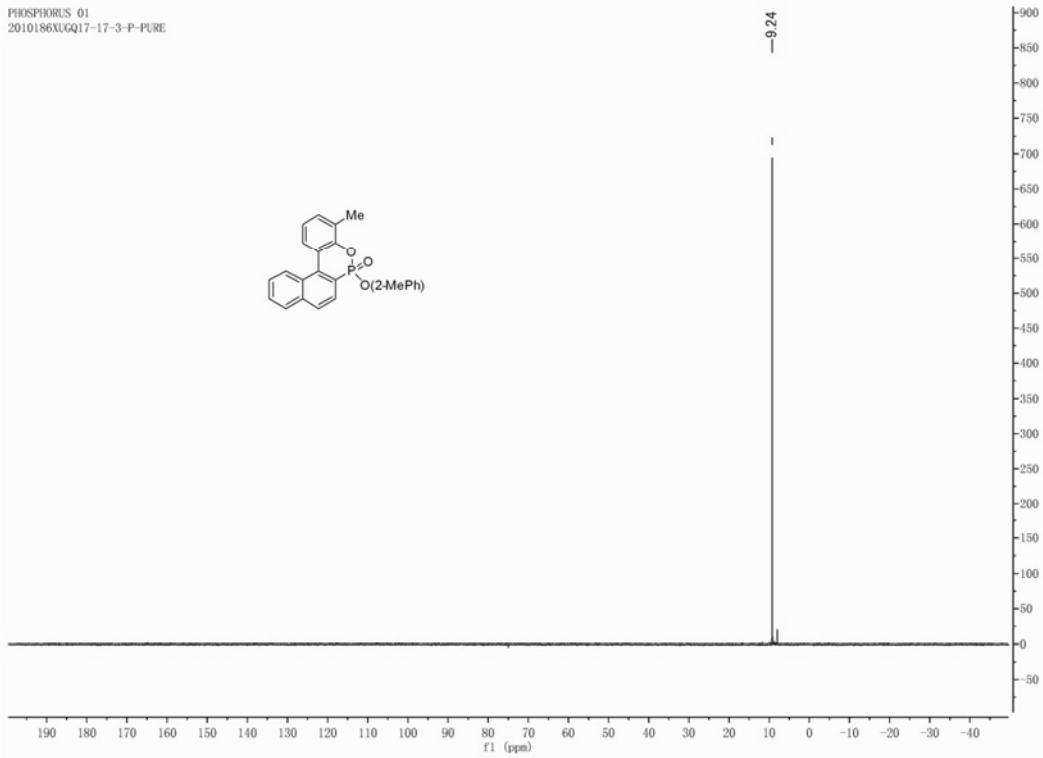
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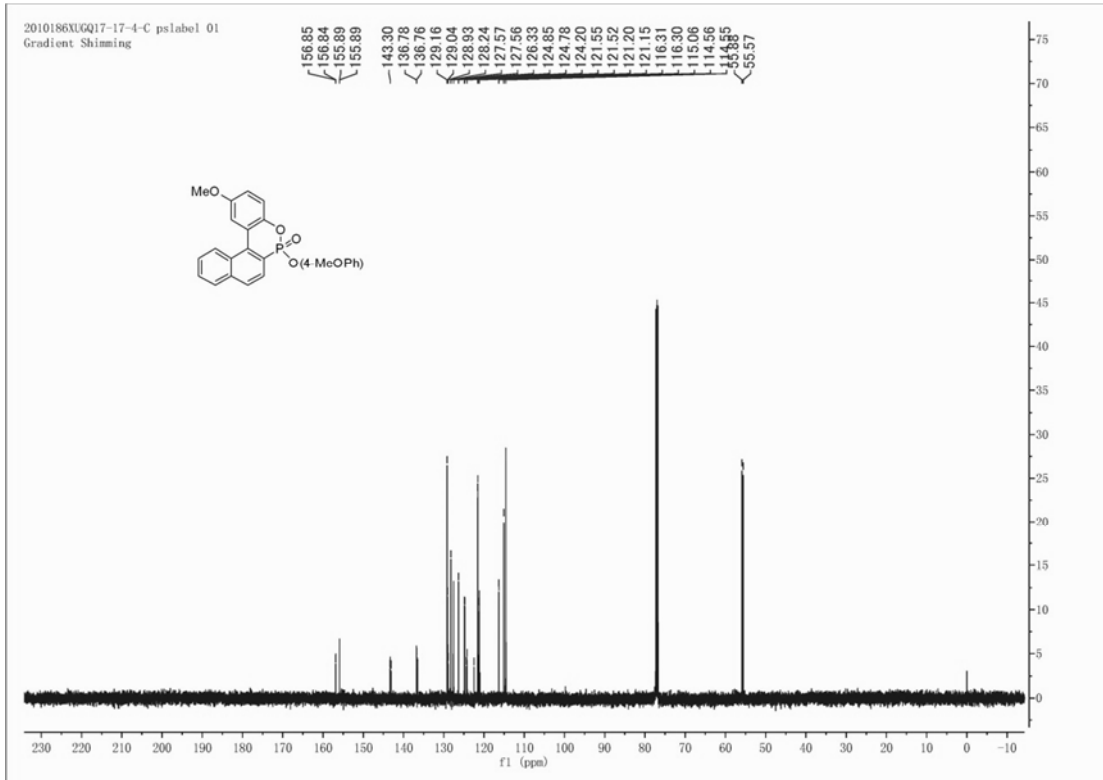
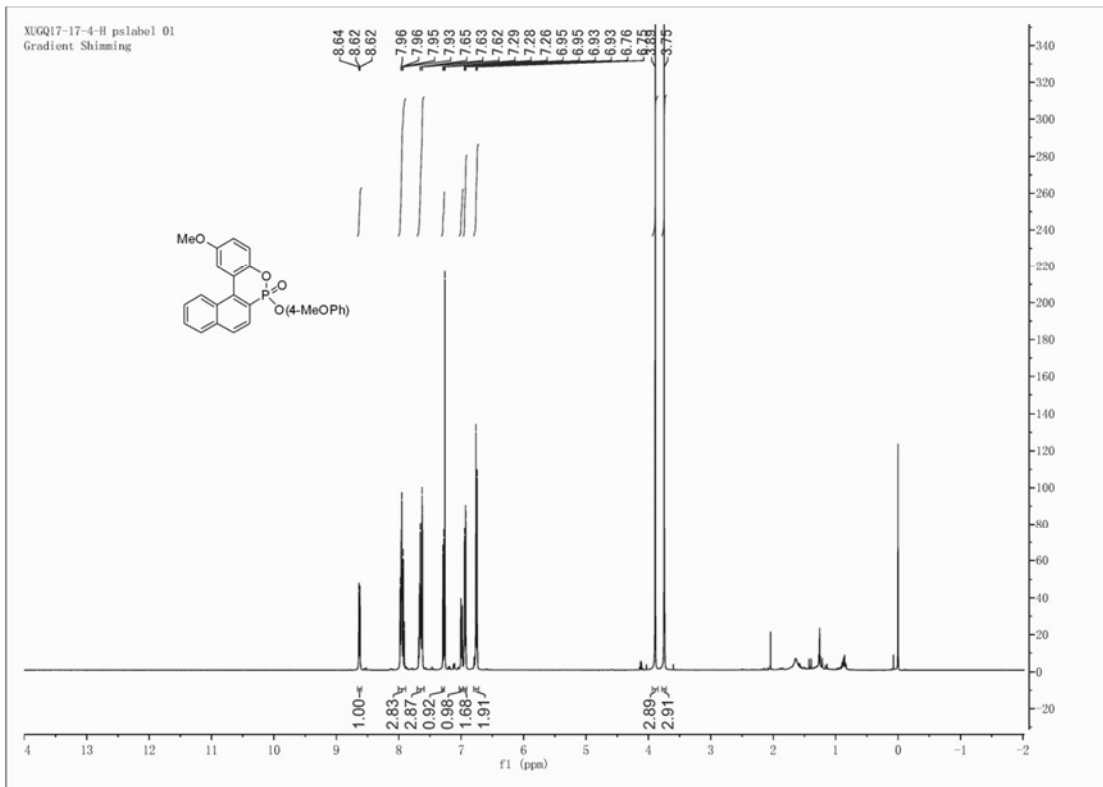


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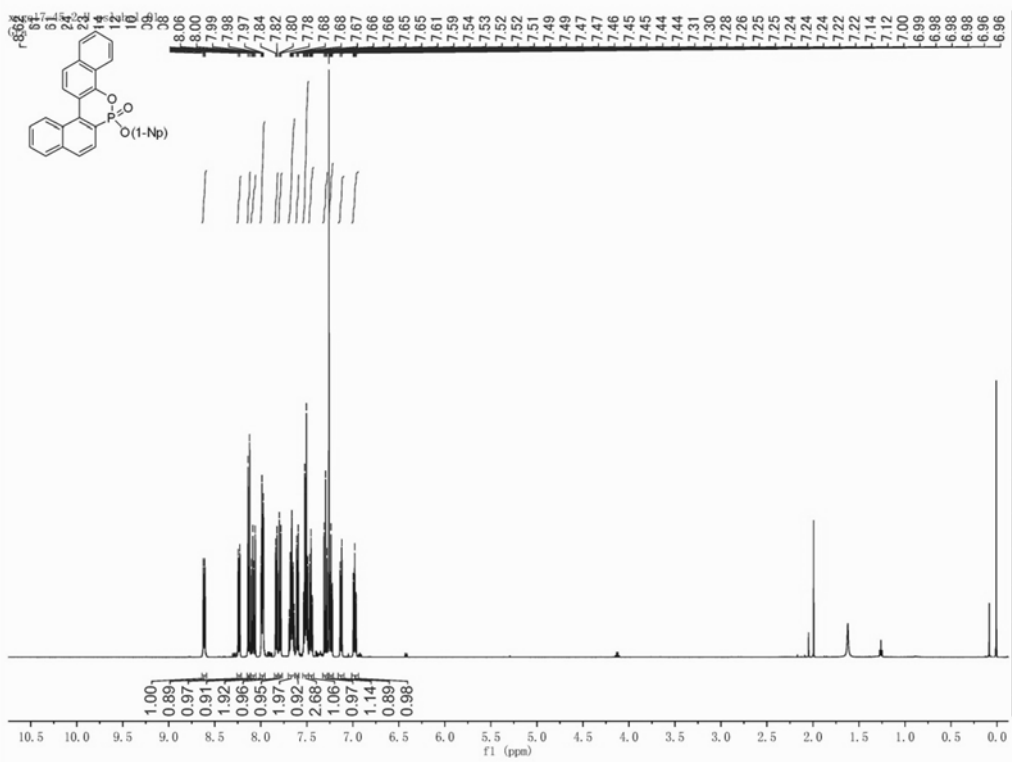
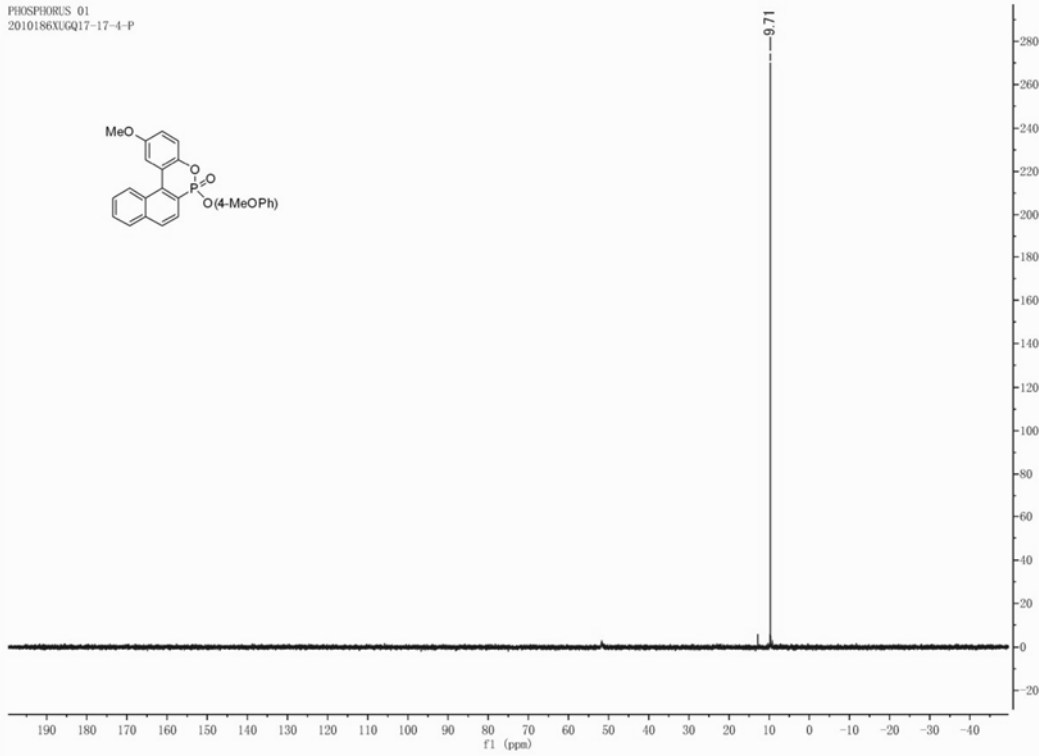
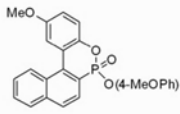


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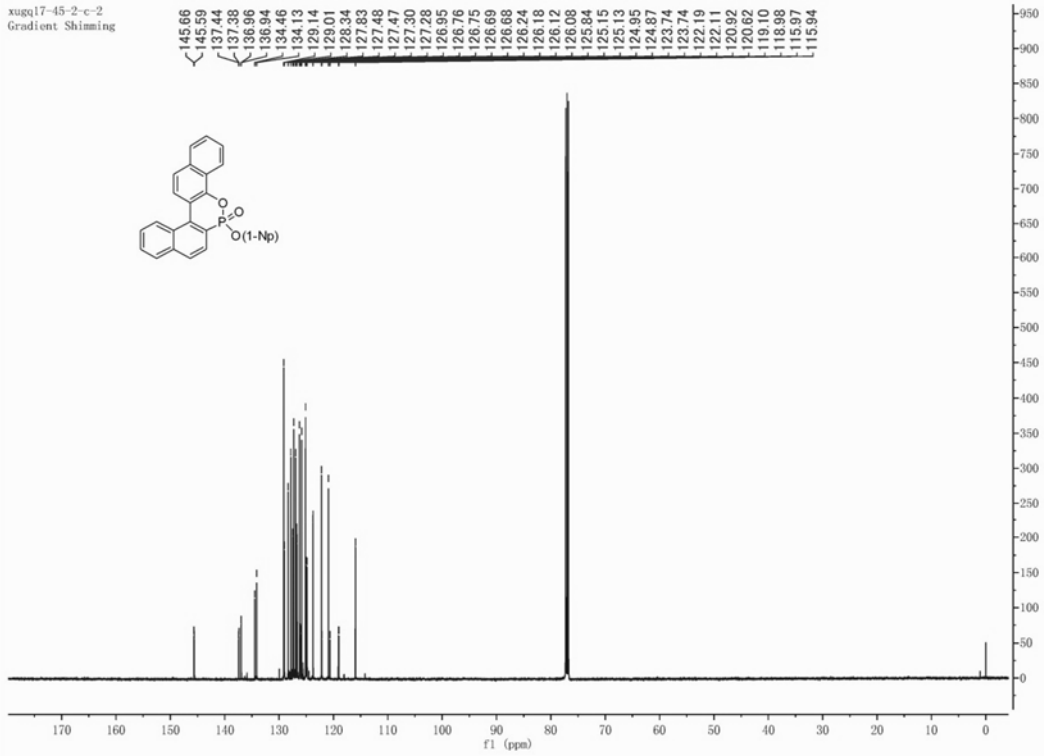




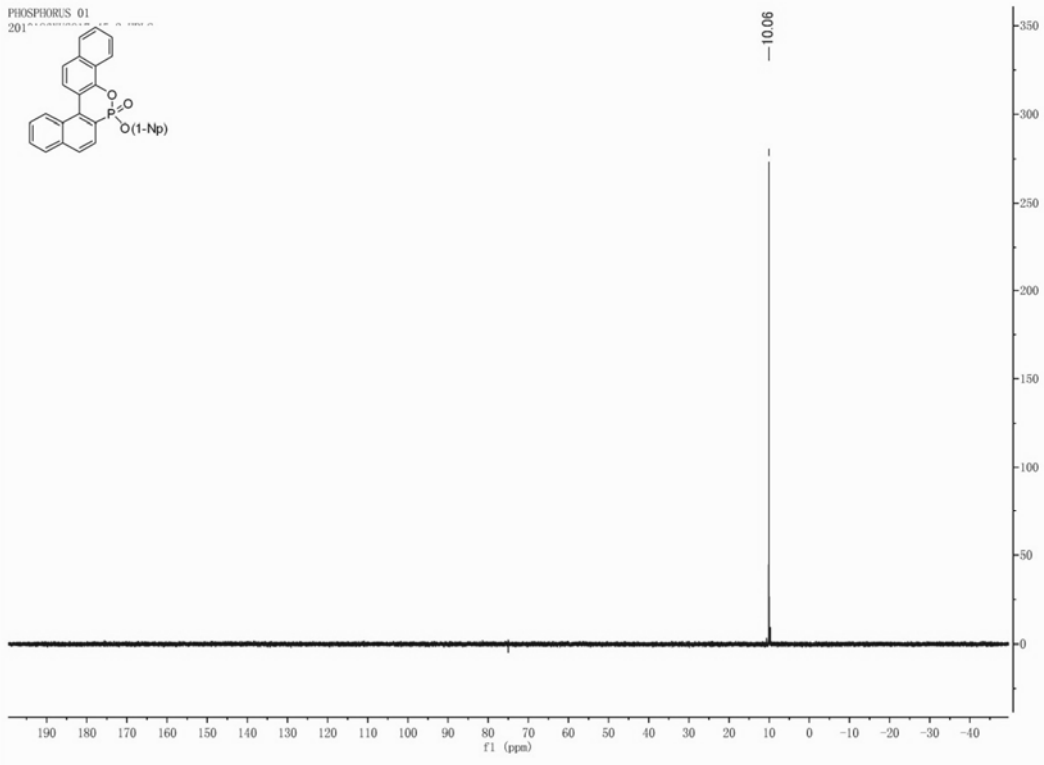
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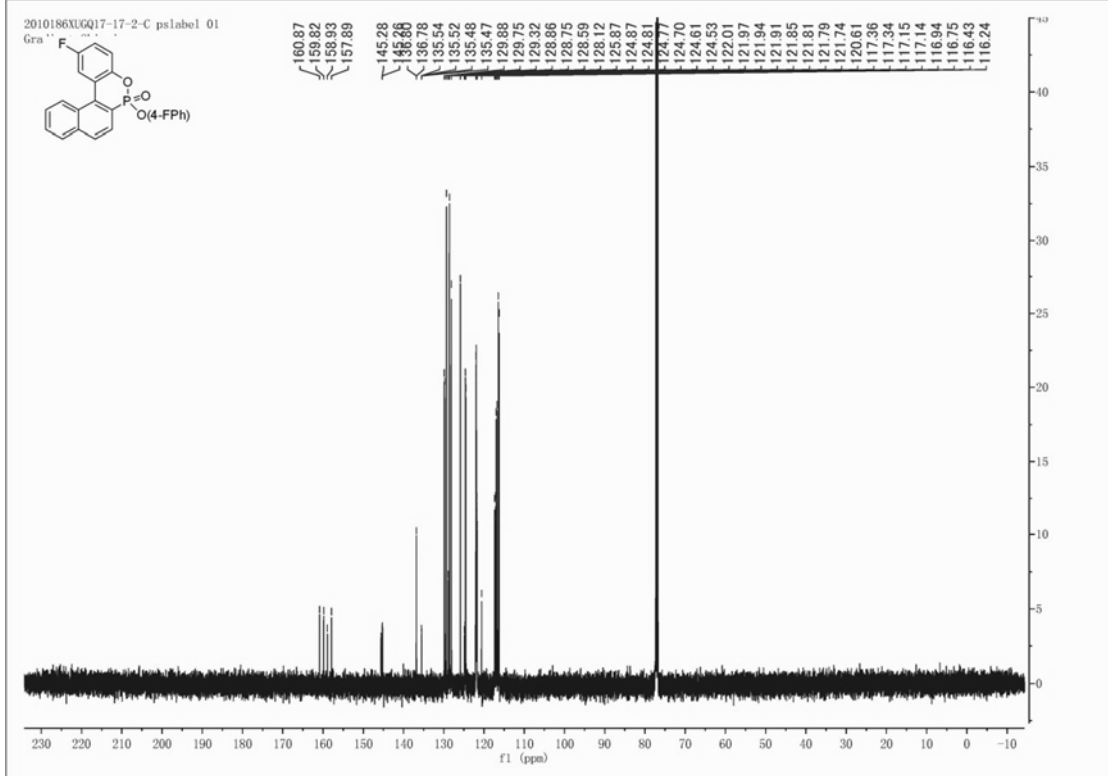
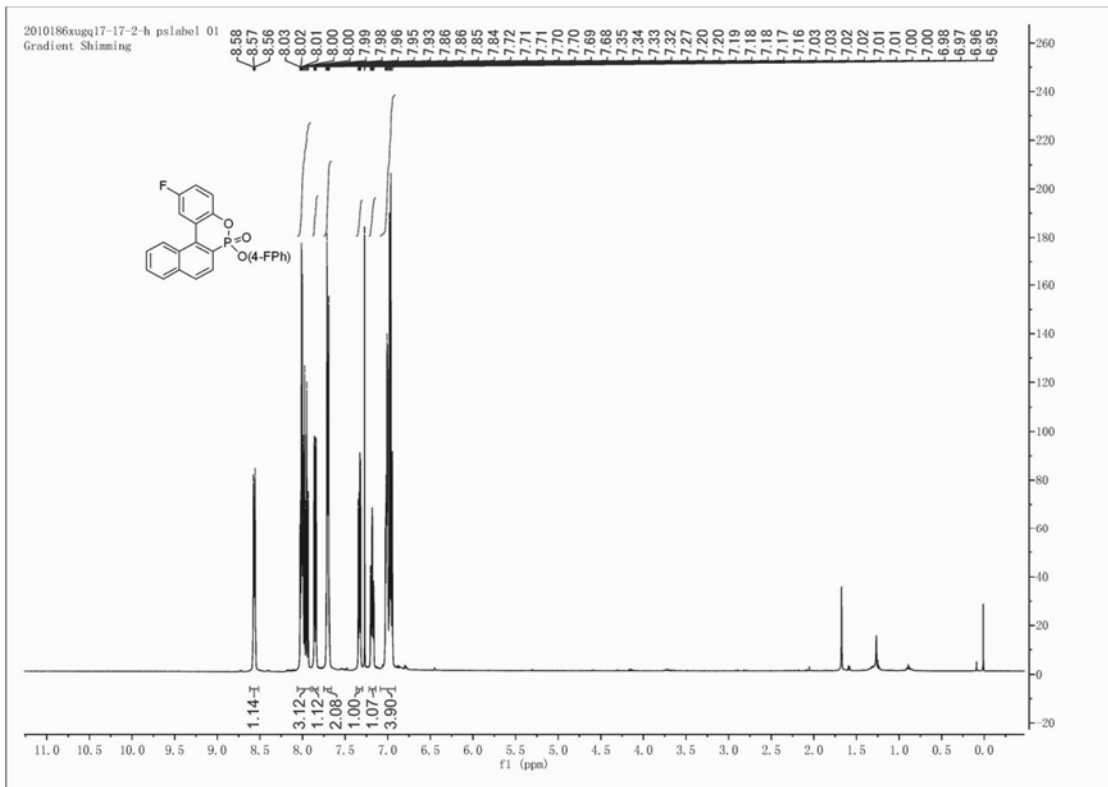


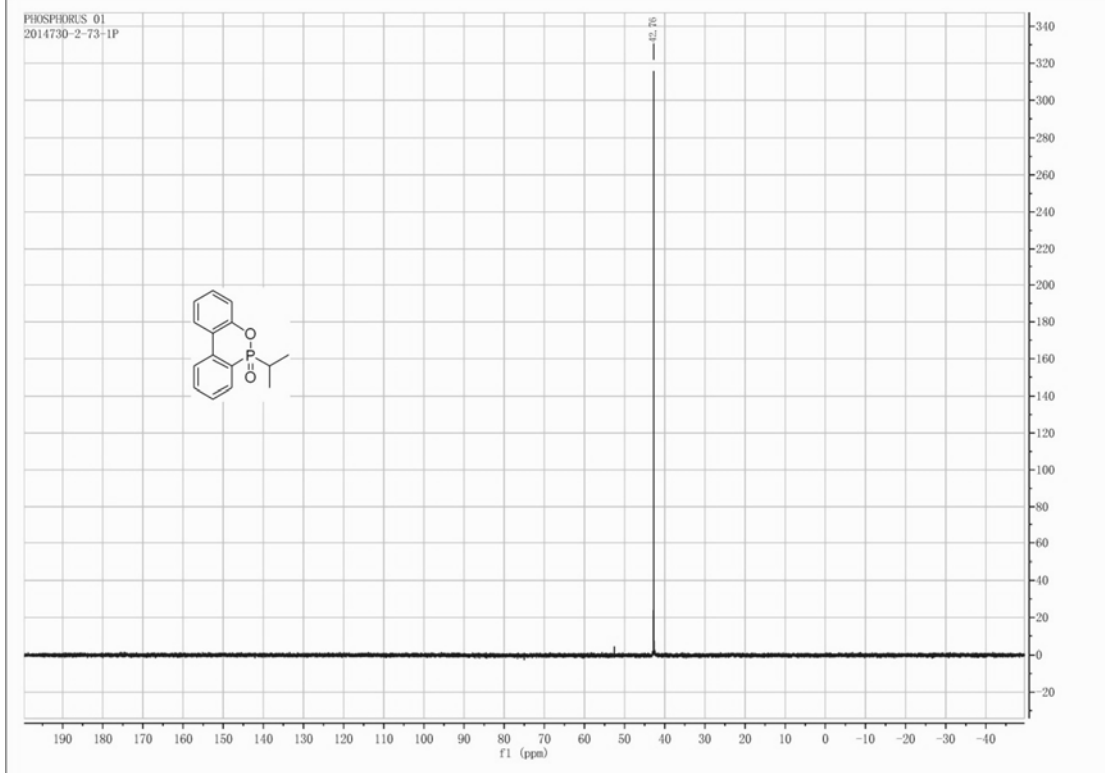
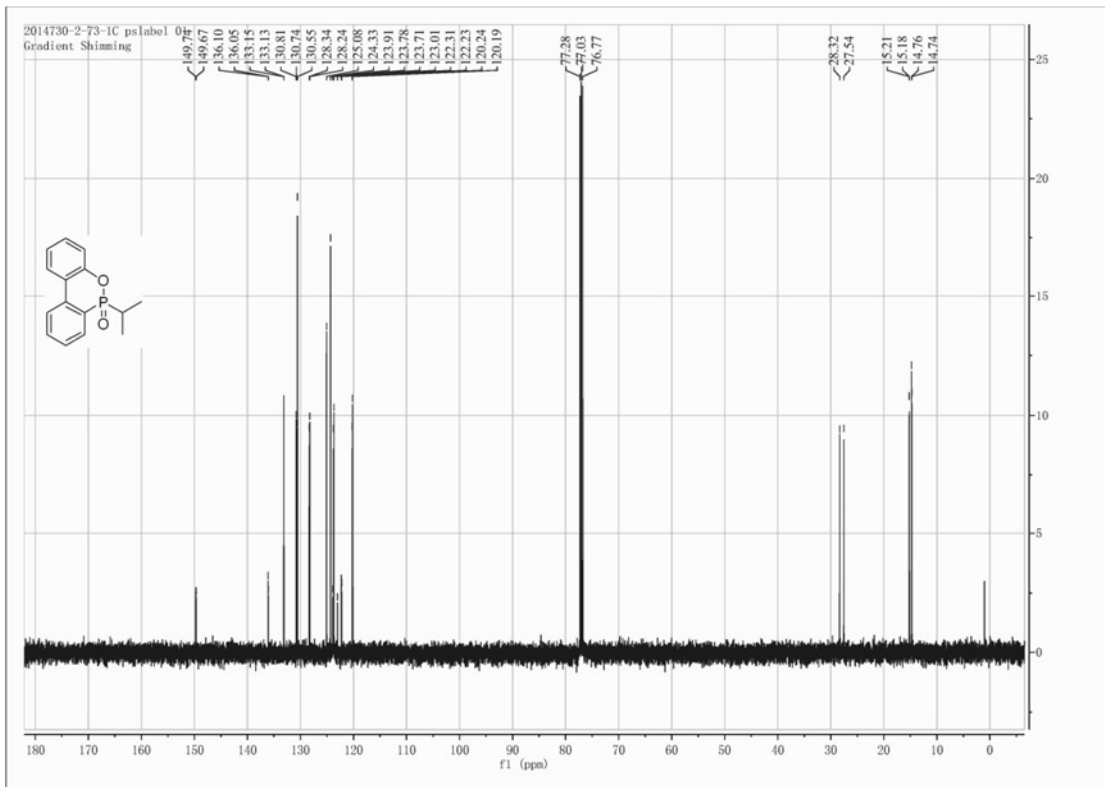
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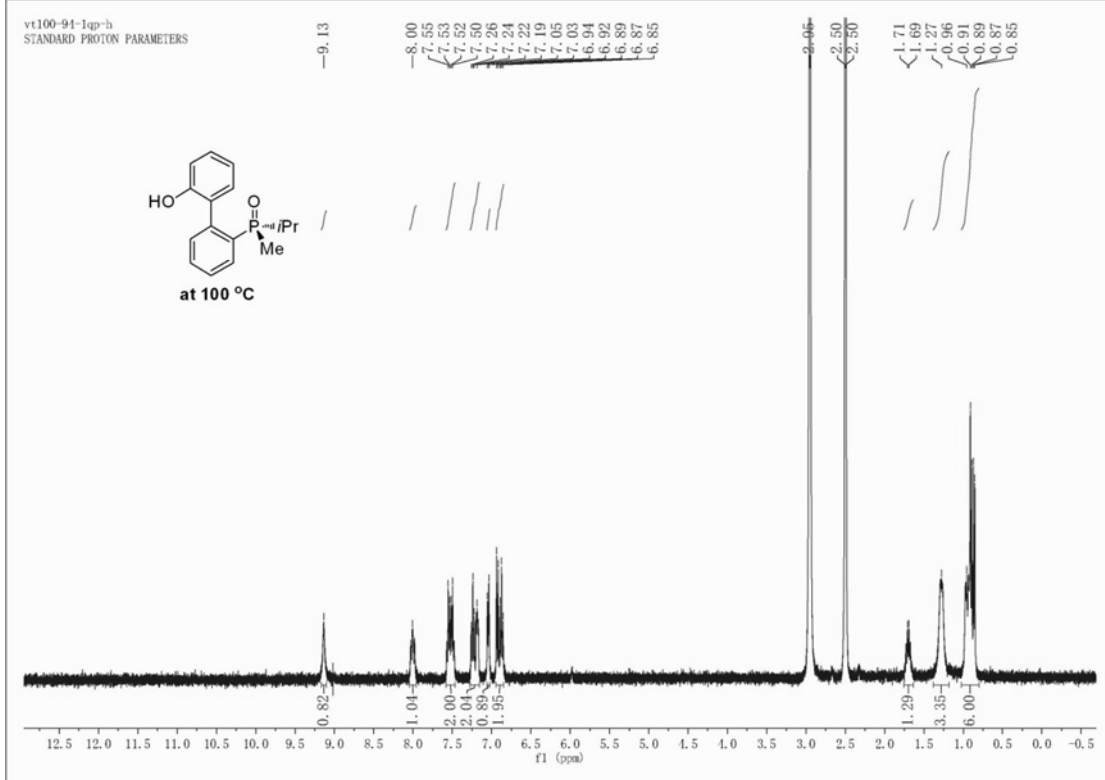
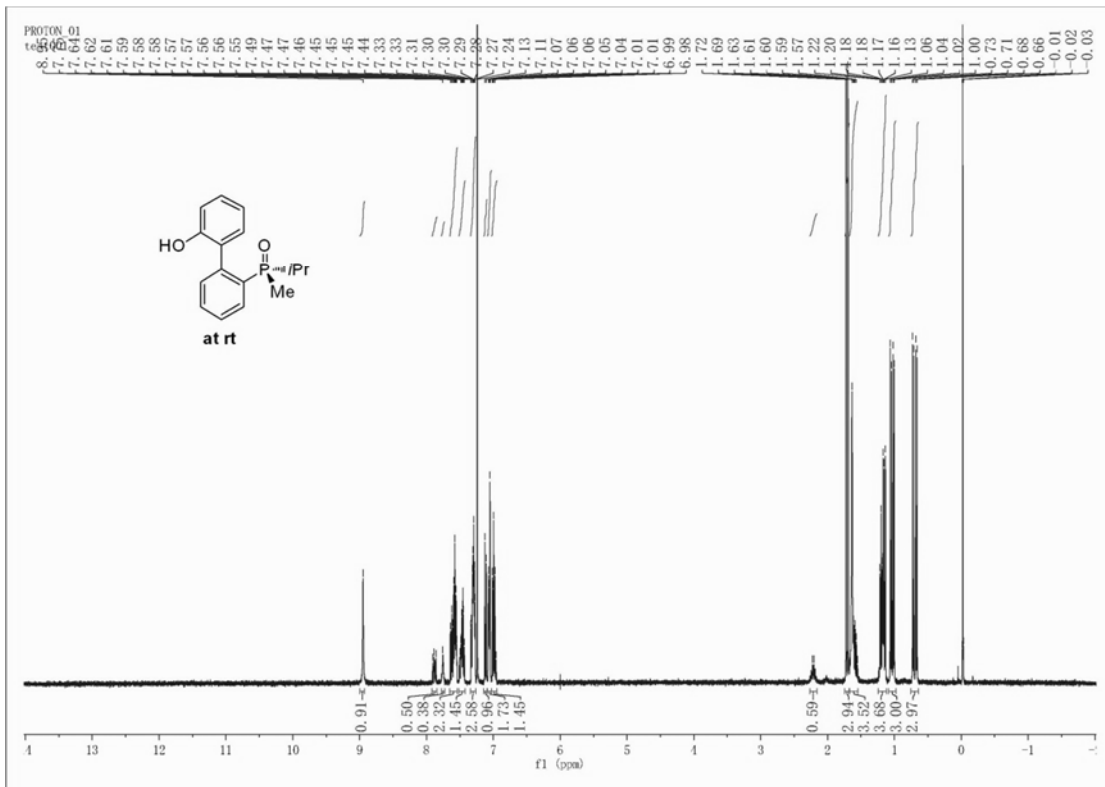


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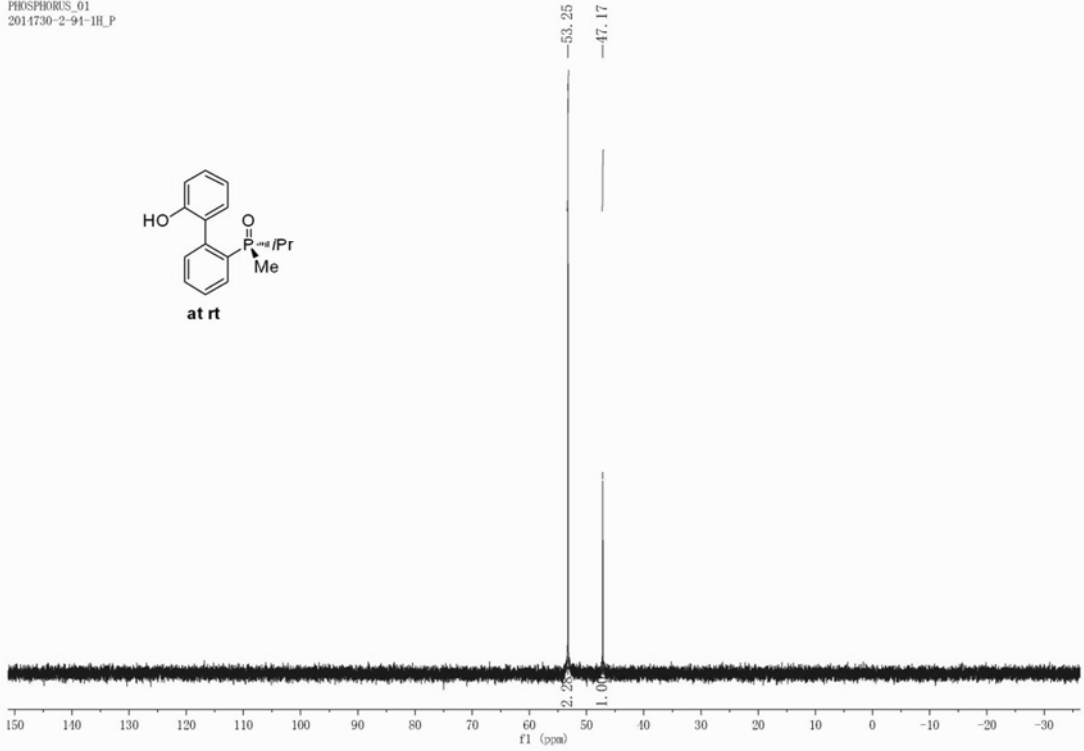
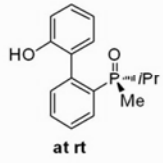




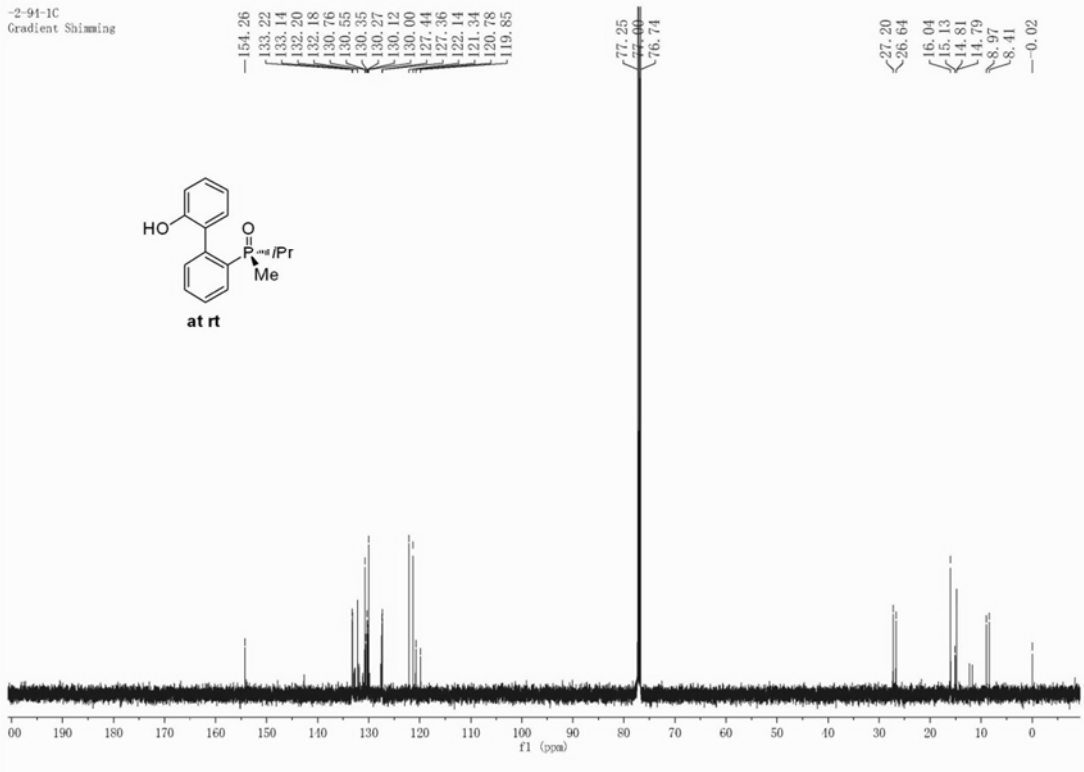
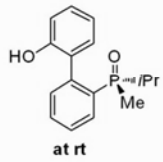


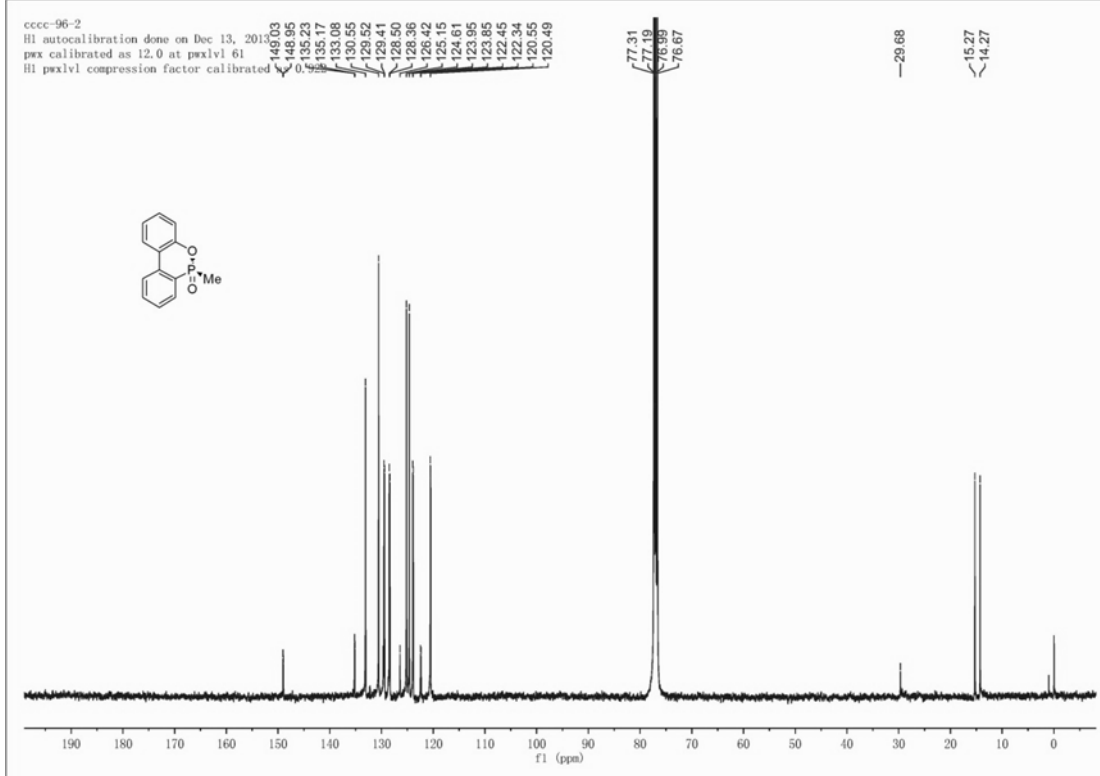
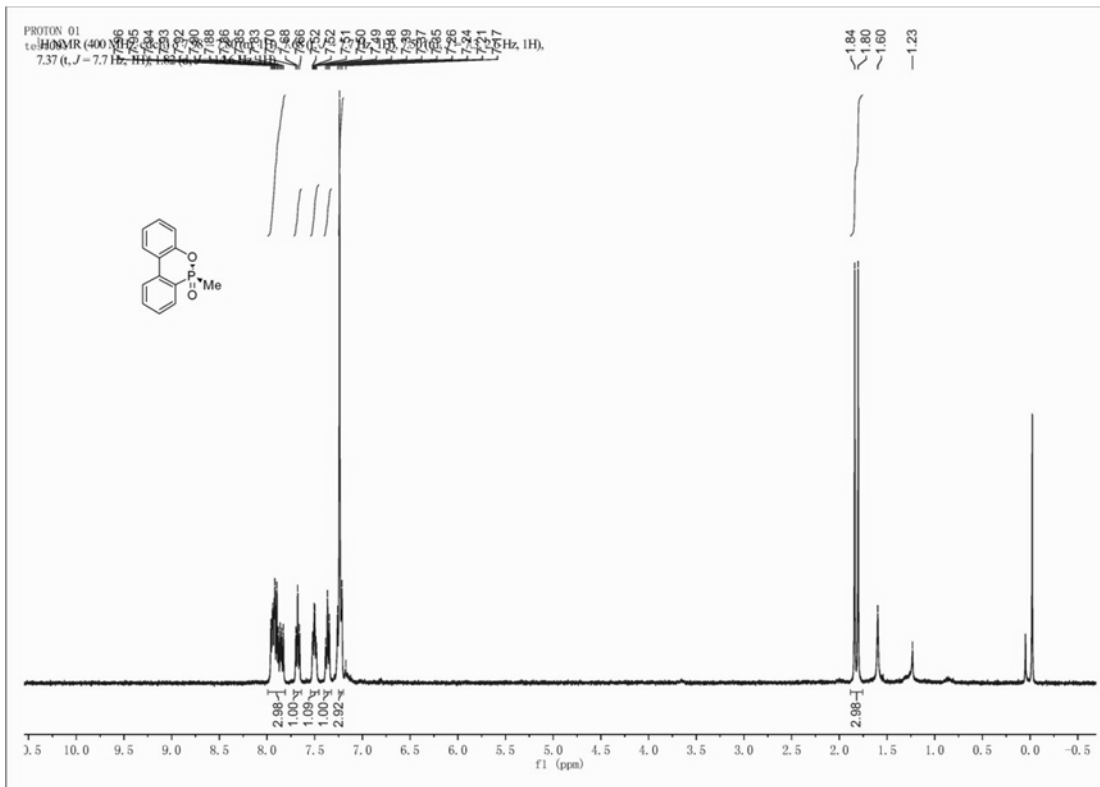


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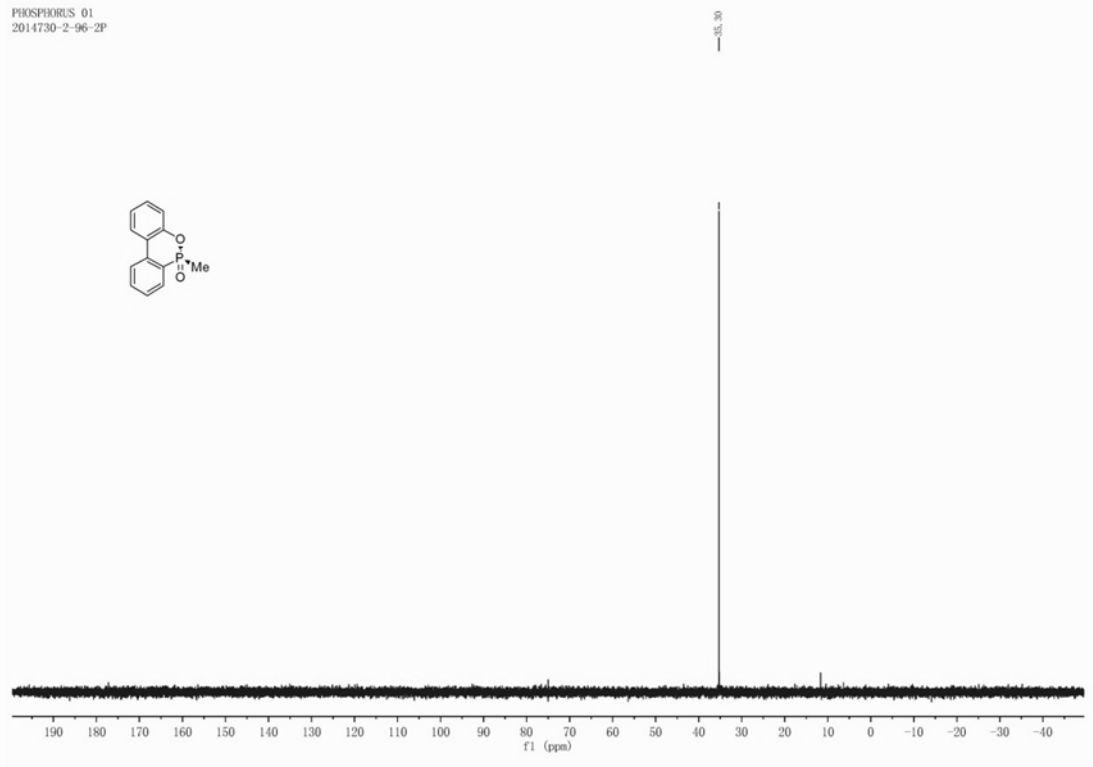
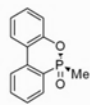


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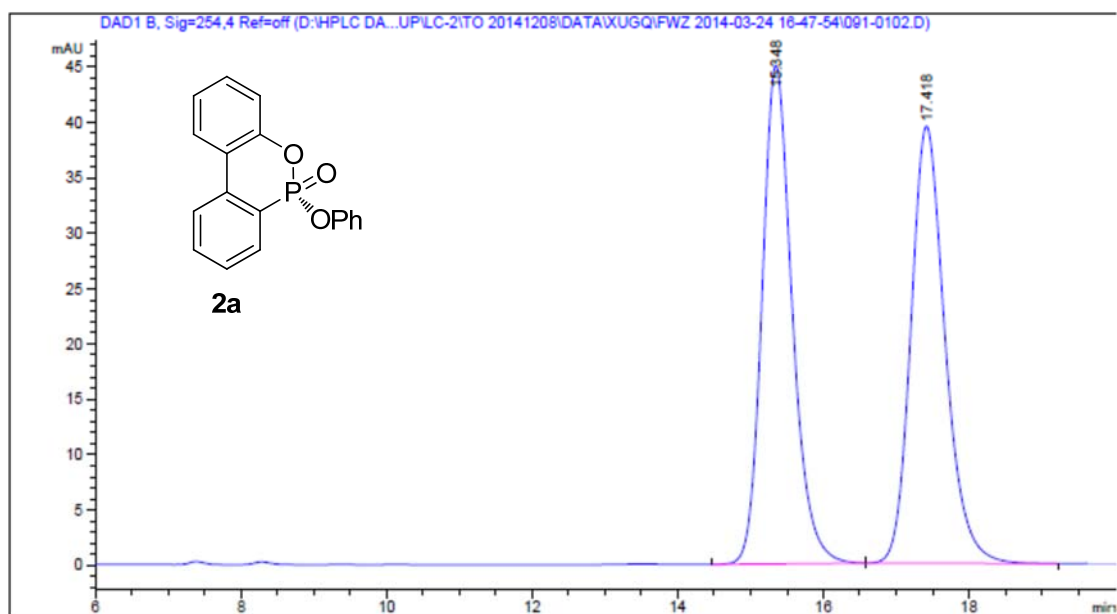




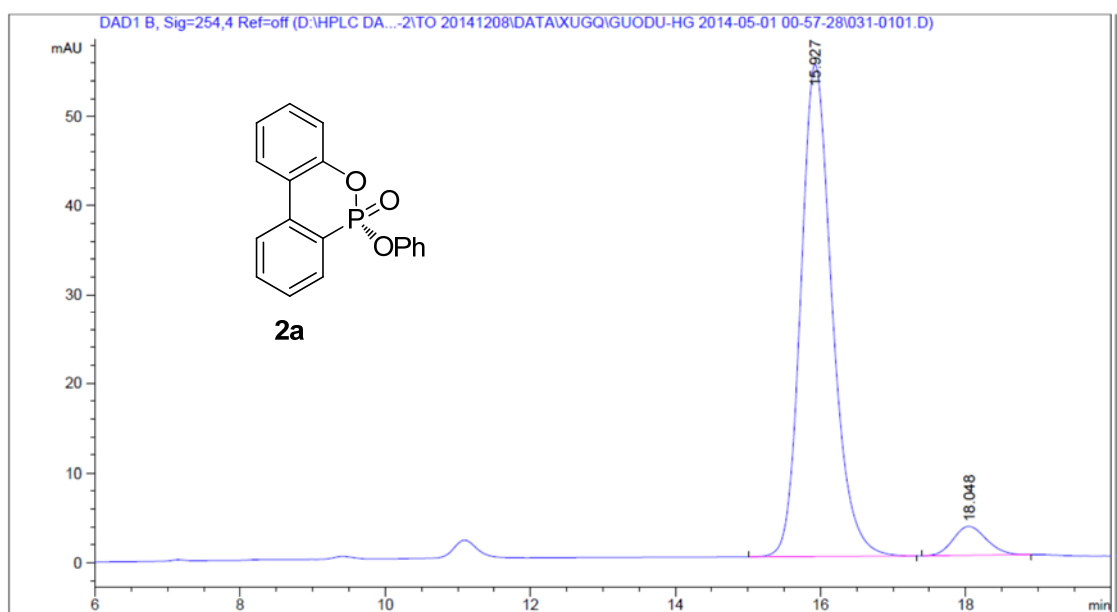
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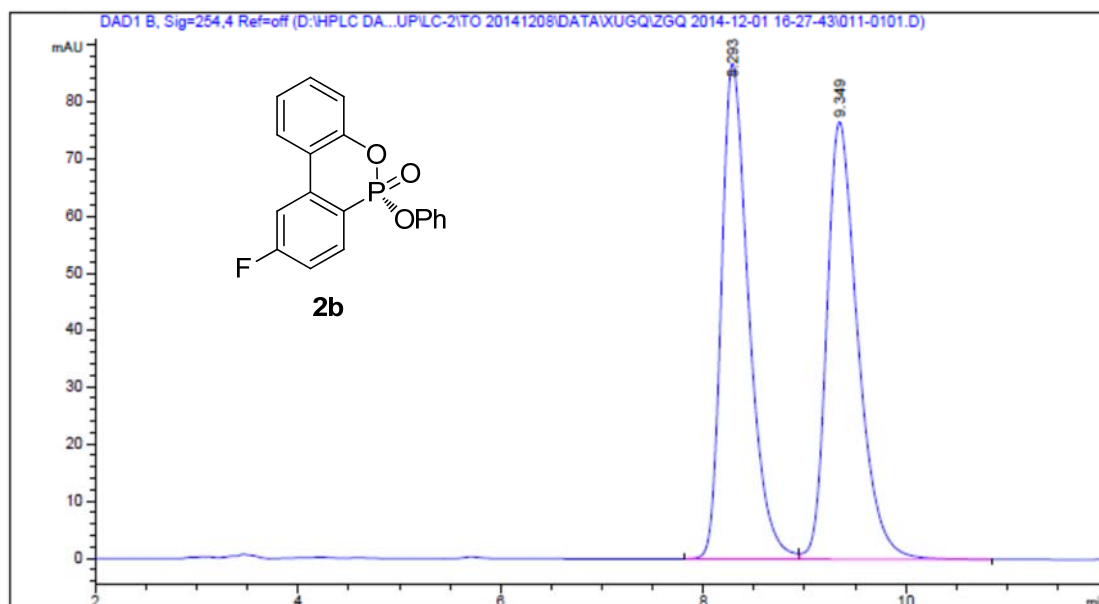
9. HPLC Charts



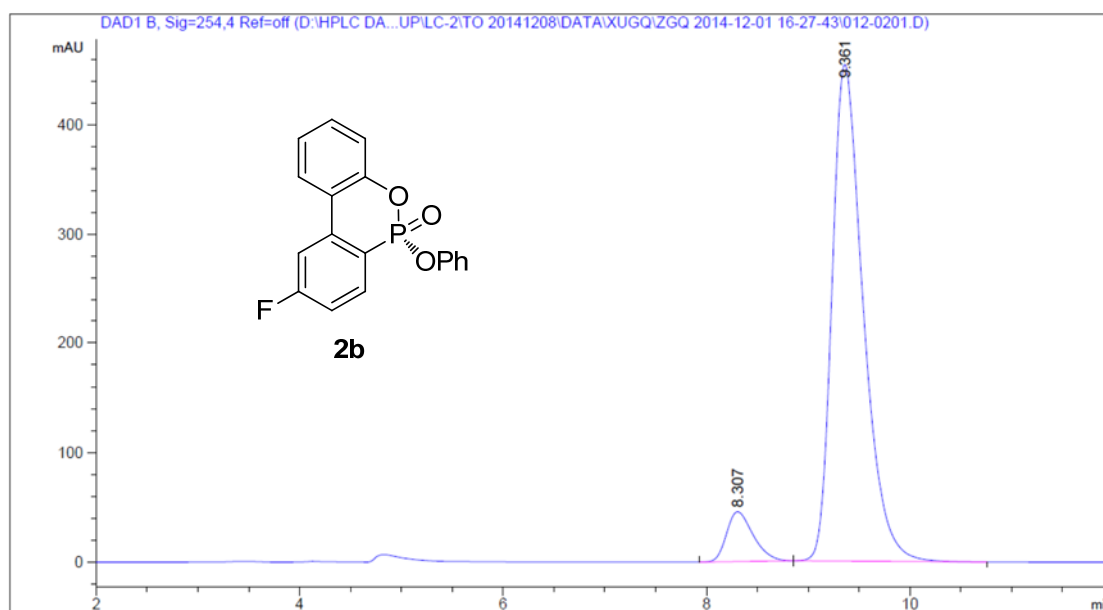
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2	17.417	BB	0.4968	614.75055	18.83336	50.0001



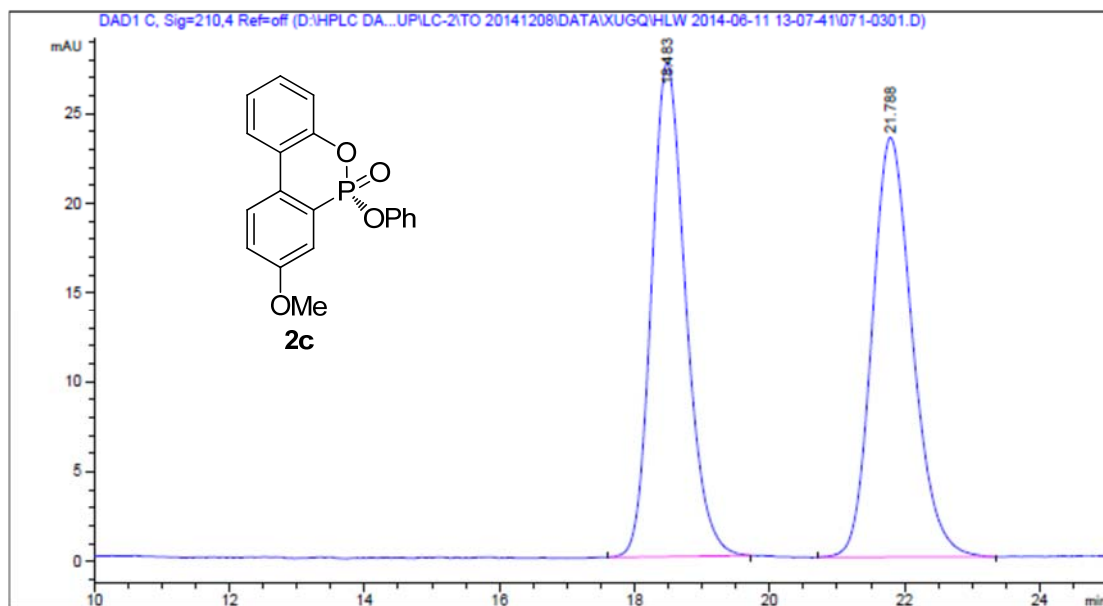
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.927	BB	0.4569	1649.40674	55.15456	94.1011
2	18.048	BB	0.4764	103.39570	3.23915	5.8989



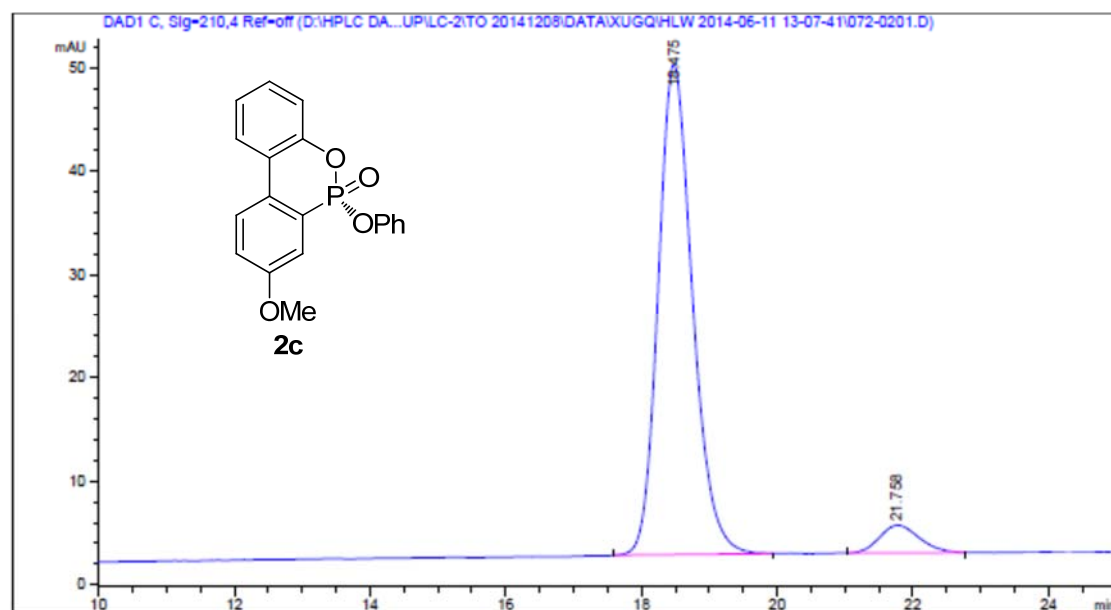
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1	8.293	BV	0.2844	1623.65710	86.75245	49.9039
2	9.349	VB	0.3224	1629.91235	76.56569	50.0961



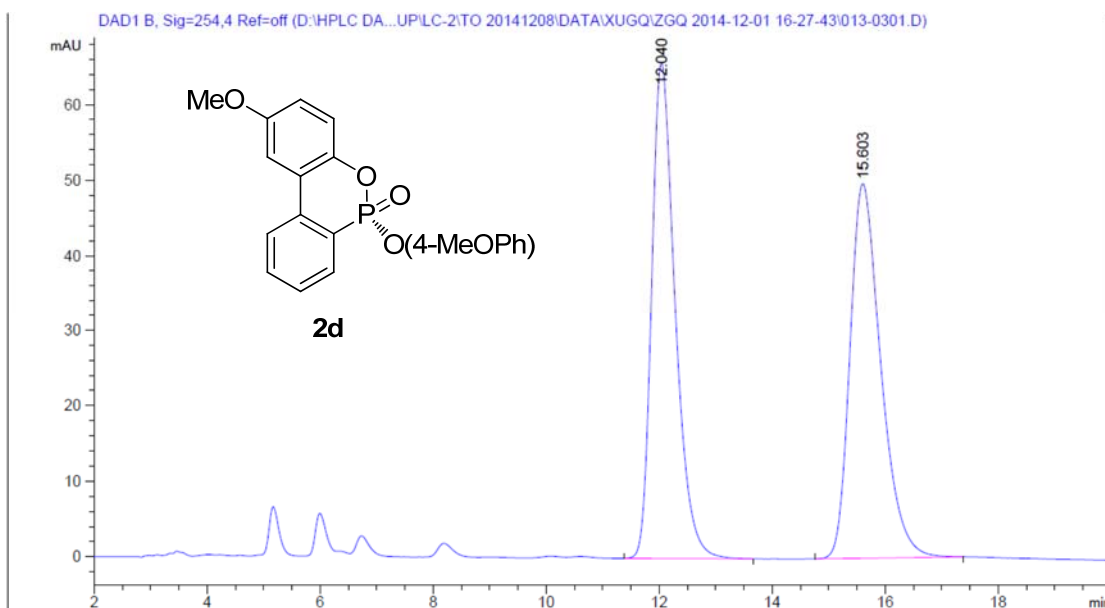
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2	9.361	BB	0.3219	9645.76953	454.00473	92.1328



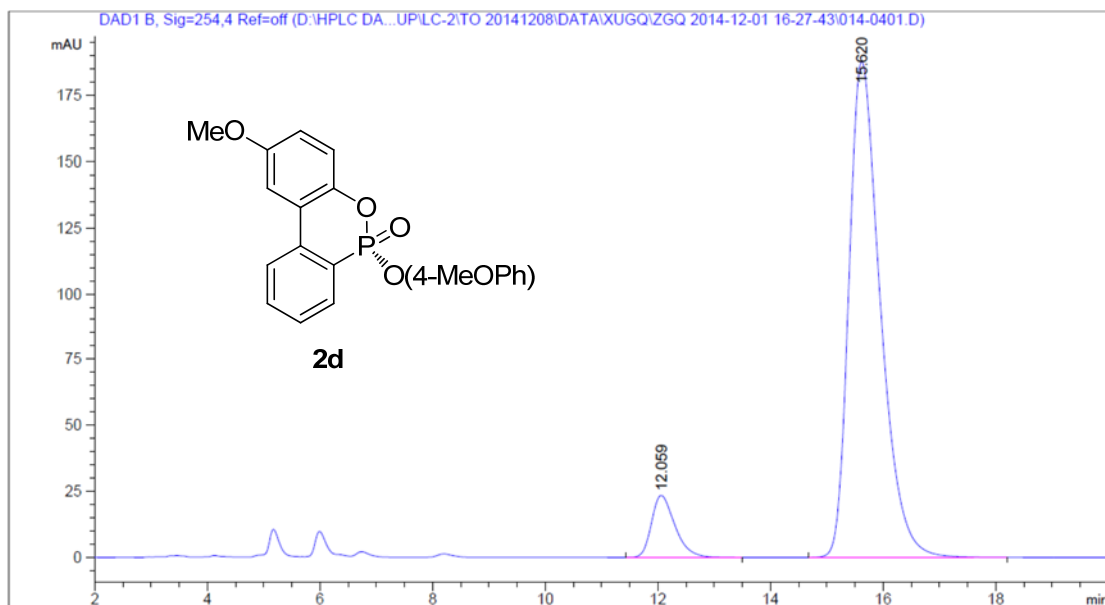
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1	18.483	BB	0.5431	966.84210	27.57523	49.8518
2	21.788	BB	0.6242	972.58972	23.43362	50.1482



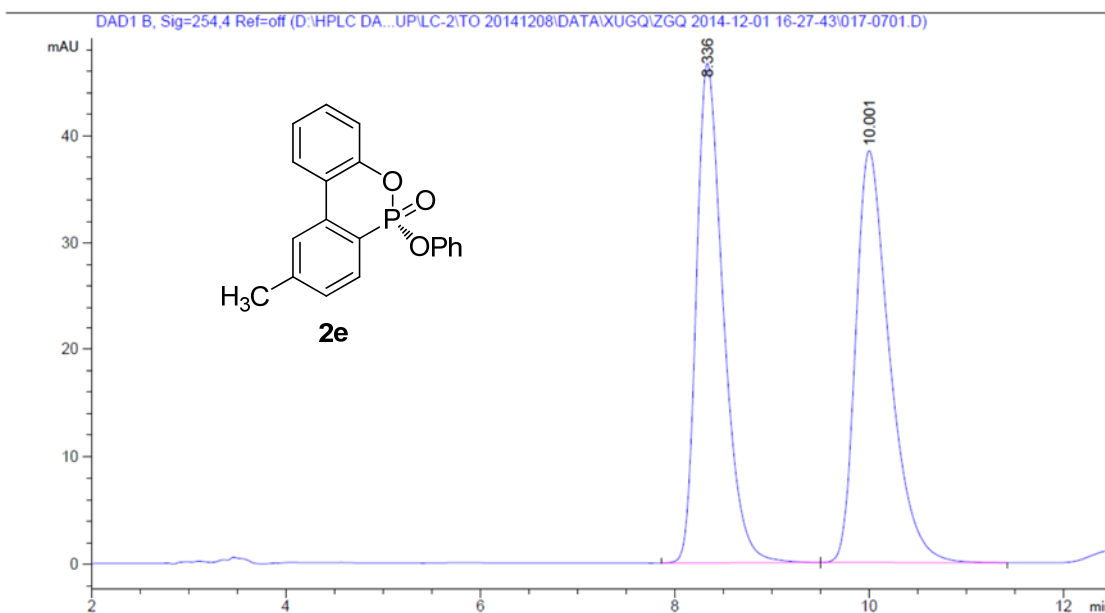
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2	21.758	BB	0.4871	108.86111	2.68463	6.1419



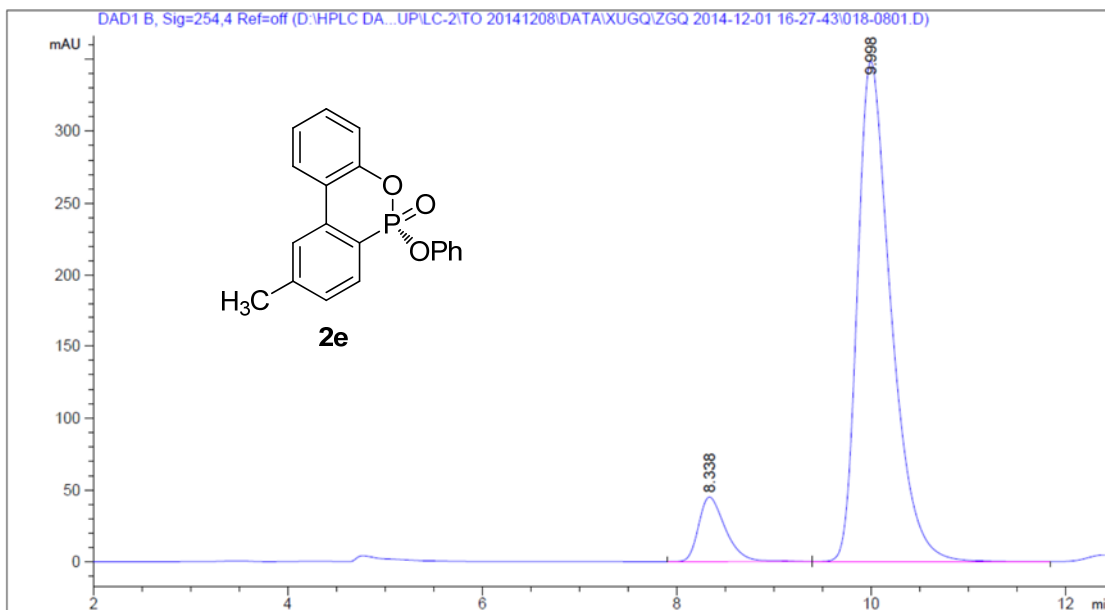
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1	12.040	BB	0.4352	1890.72644	65.81521	50.1169
2	15.603	BB	0.5752	1881.90857	49.76174	49.8831



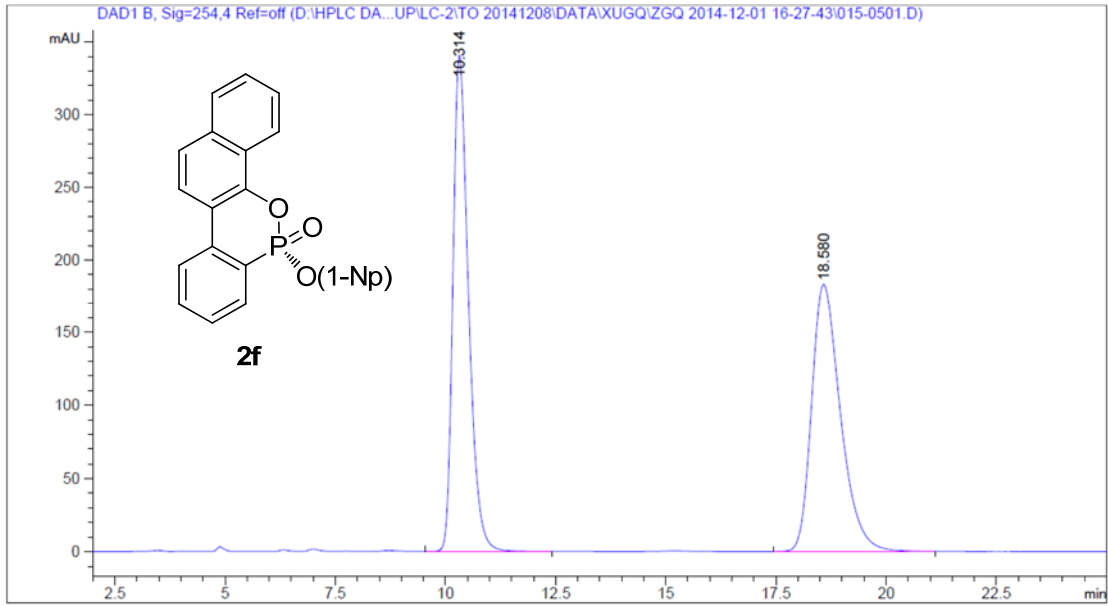
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.059	BB	0.4415	678.32086	23.44770	8.5399
2	15.620	BB	0.5874	7264.66113	187.77153	91.4601



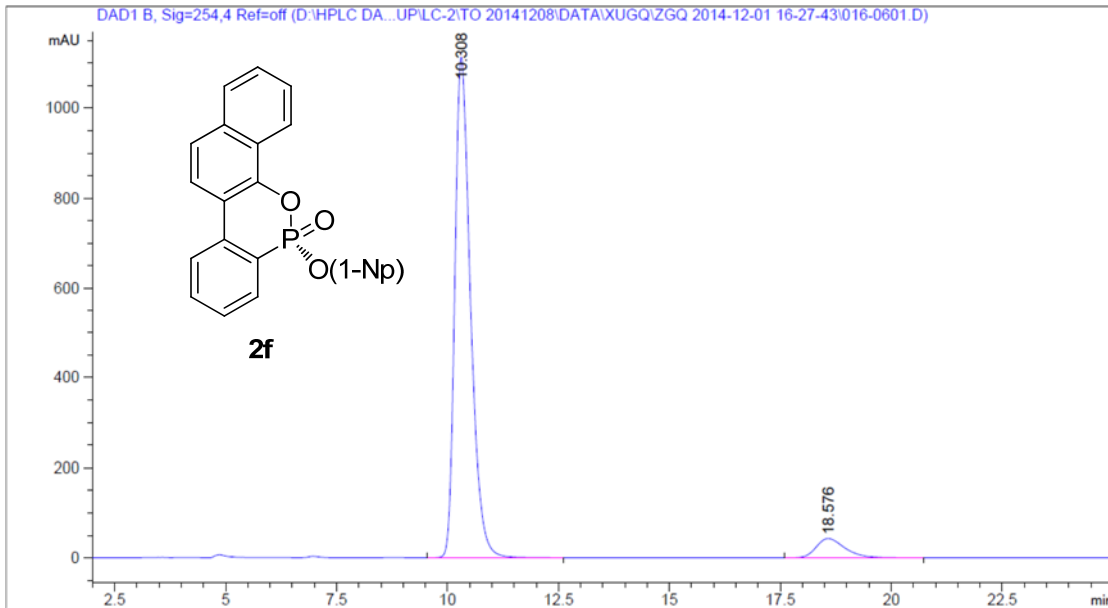
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.336	BB	0.2917	893.90137	46.61826	49.1007
2	10.001	BB	0.3612	926.64417	38.44072	50.8993



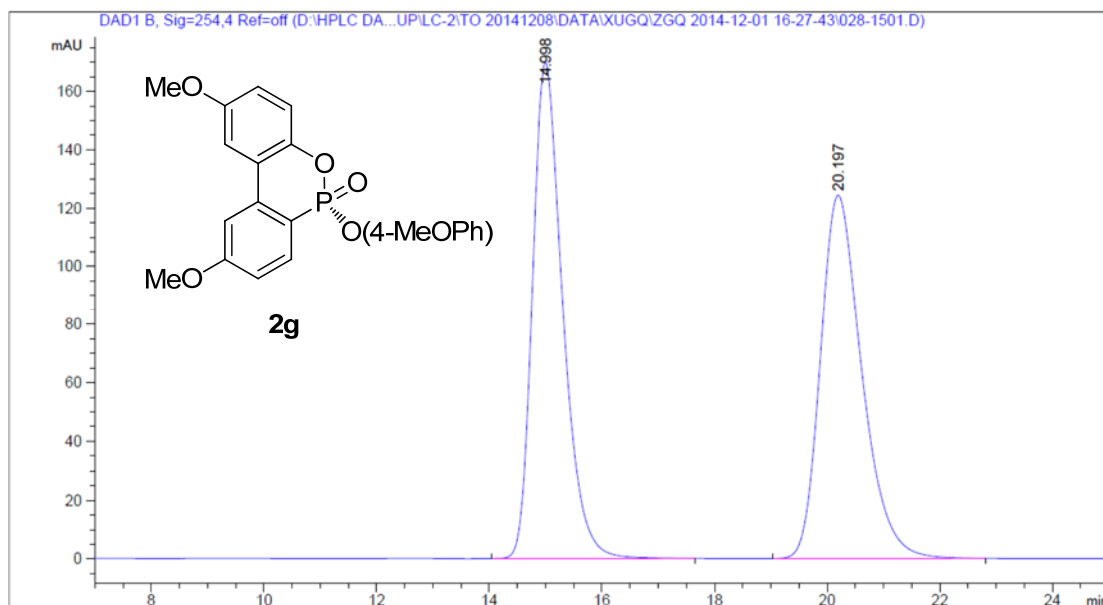
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.338	BB	0.2931	869.47882	45.06266	9.4446
2	9.998	BB	0.3592	8336.64648	348.40759	90.5554



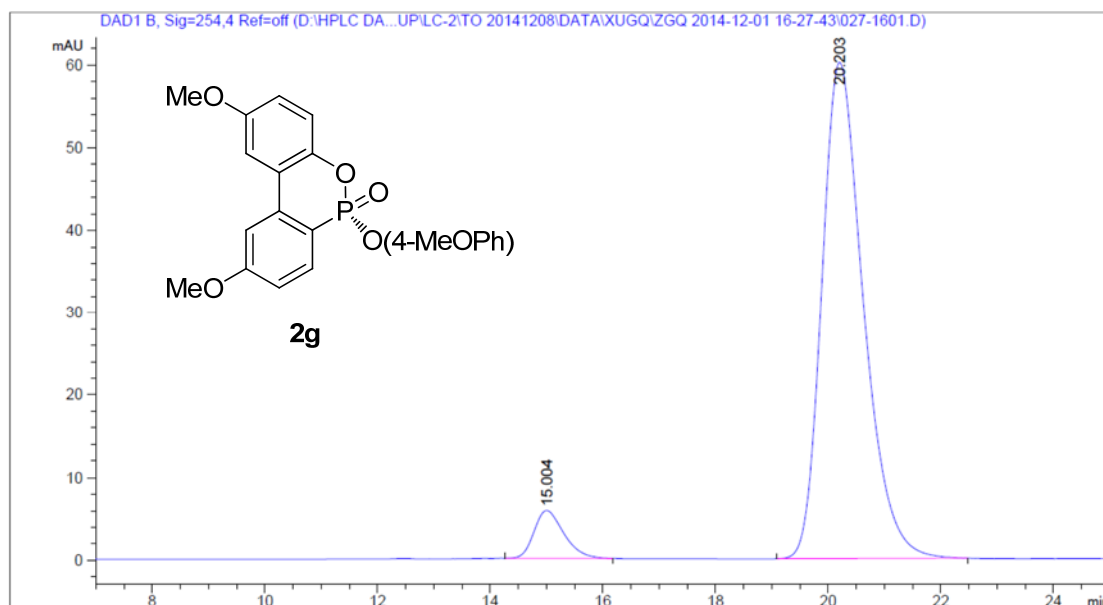
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.314	BB	0.3709	8321.04395	340.75812	50.0105
2	18.580	BB	0.6877	8317.56152	183.20532	49.9895



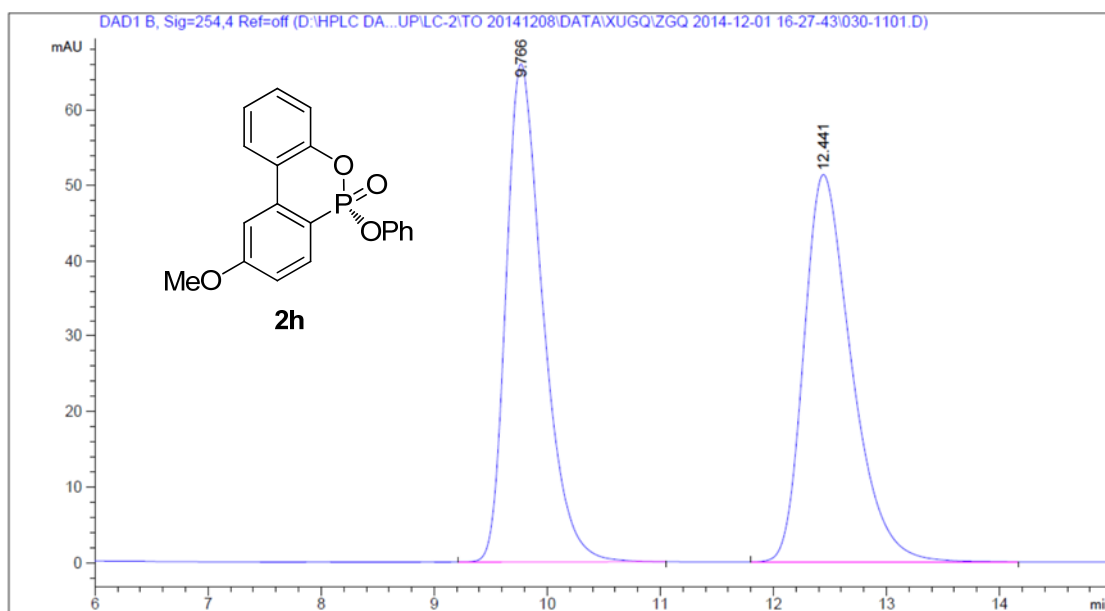
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.308	BB	0.3720	2.72778e4	1112.67944	93.3706
2	18.576	BB	0.6729	1936.74463	43.04469	6.6294



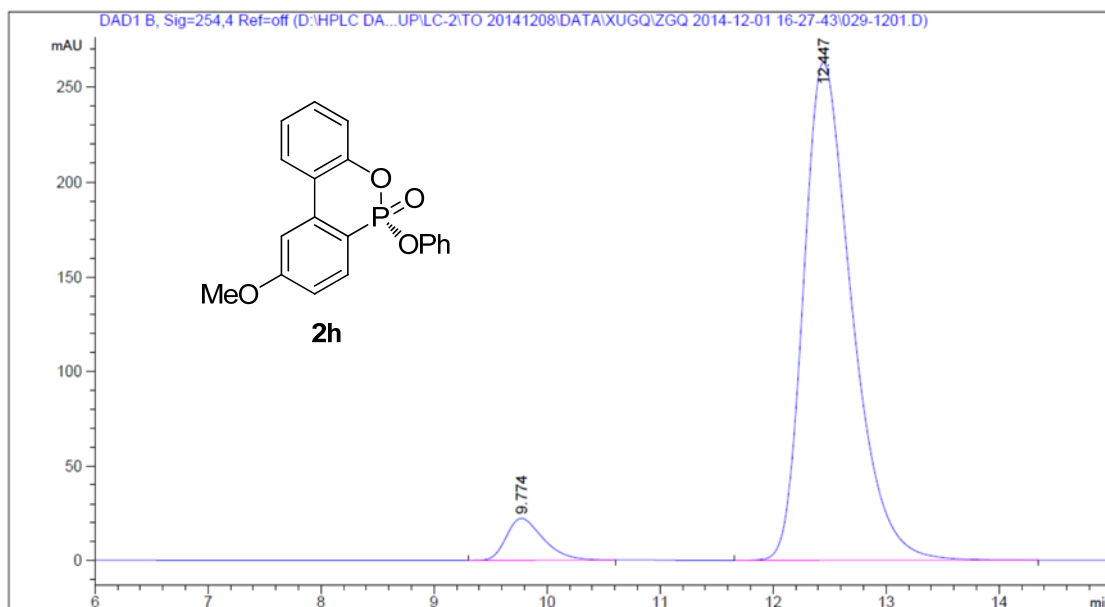
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.998	BB	0.5650	6303.42969	169.84343	49.9428
2	20.197	BB	0.7731	6317.86377	124.26816	50.0572



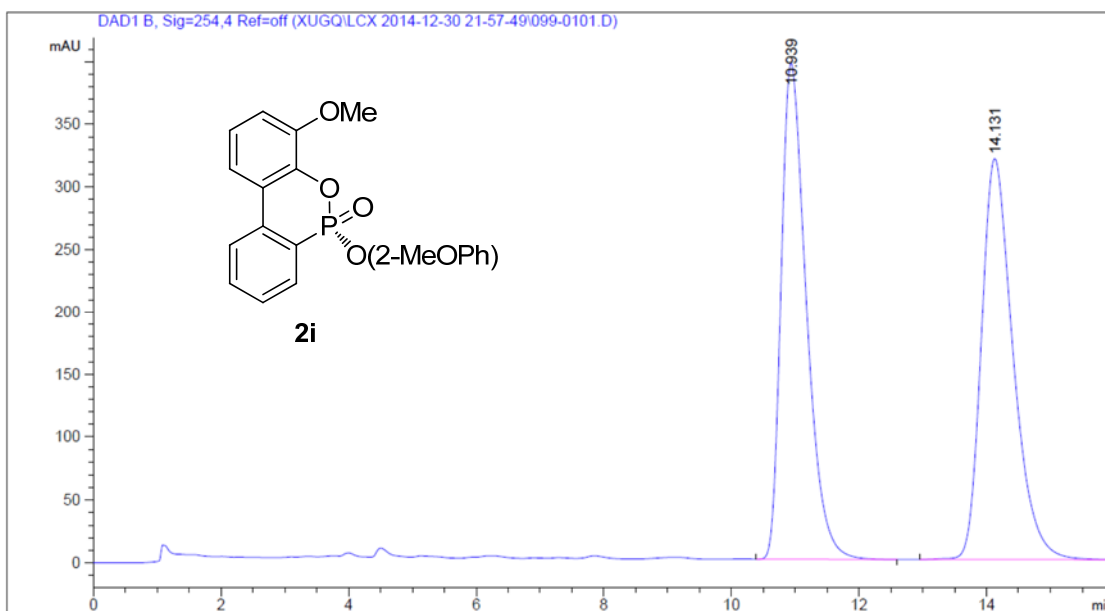
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.004	BB	0.5151	212.92143	5.78863	6.4893
2	20.203	BB	0.7797	3068.18213	60.09306	93.5107



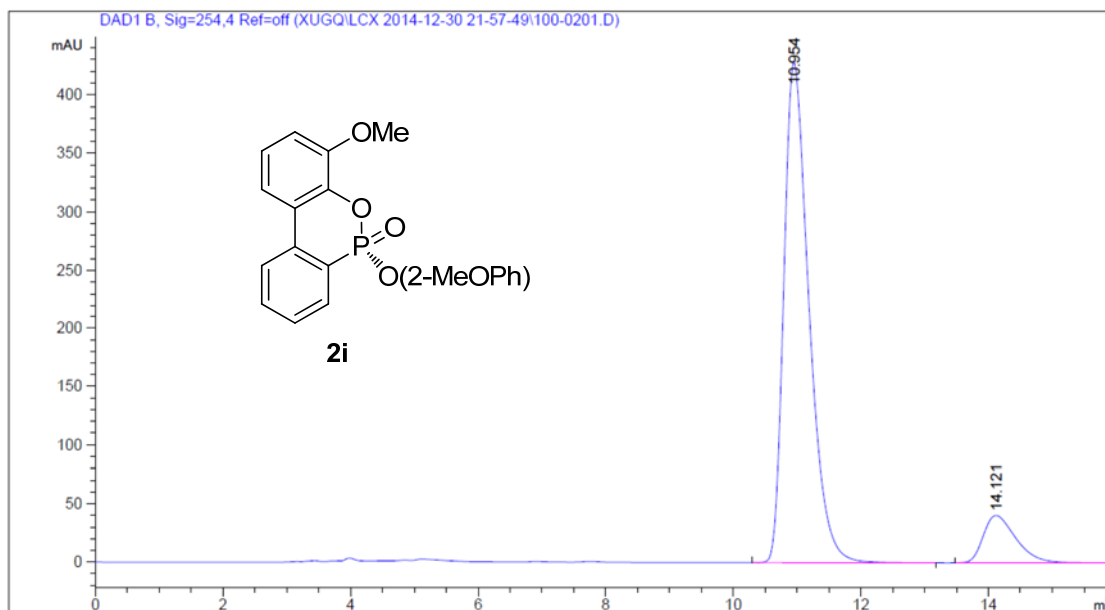
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.766	BB	0.3416	1491.37476	65.99689	49.8070
2	12.441	BB	0.4476	1502.93066	51.33106	50.1930



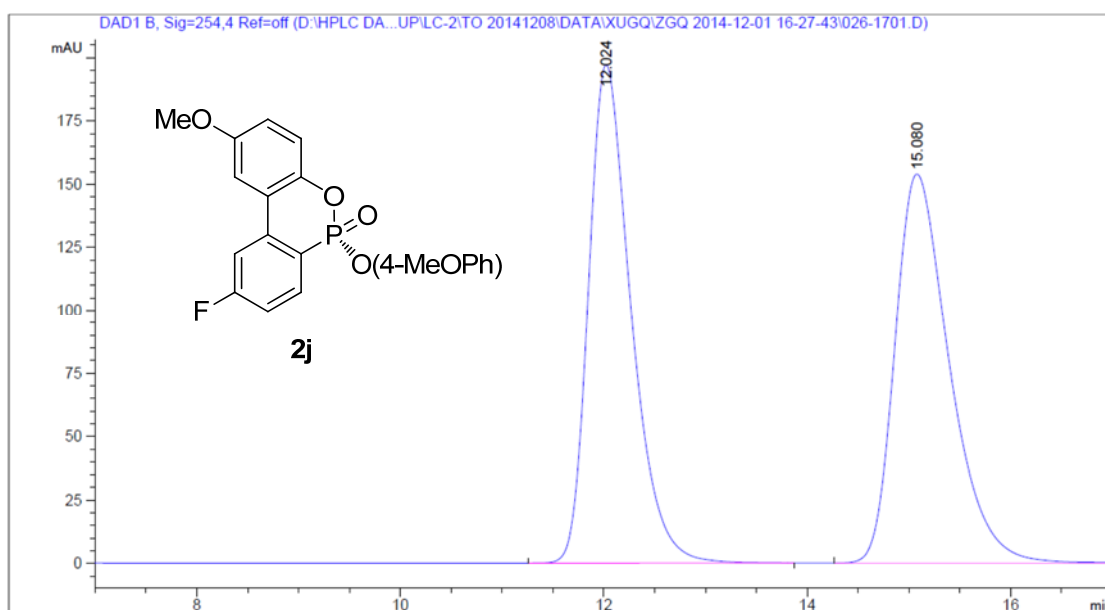
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.774	BB	0.3441	500.22464	22.09691	6.0326
2	12.447	BB	0.4518	7791.80273	262.88818	93.9674



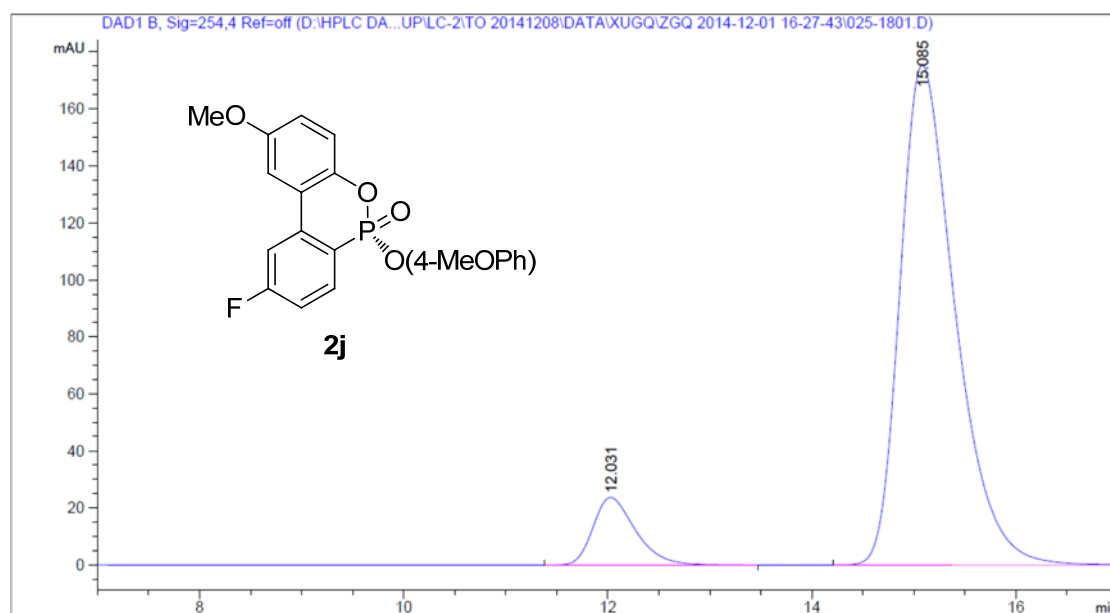
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.939	BB	0.4200	1.08641e4	396.10117	49.5540
2	14.131	BBA	0.5231	1.10597e4	320.09518	50.4460



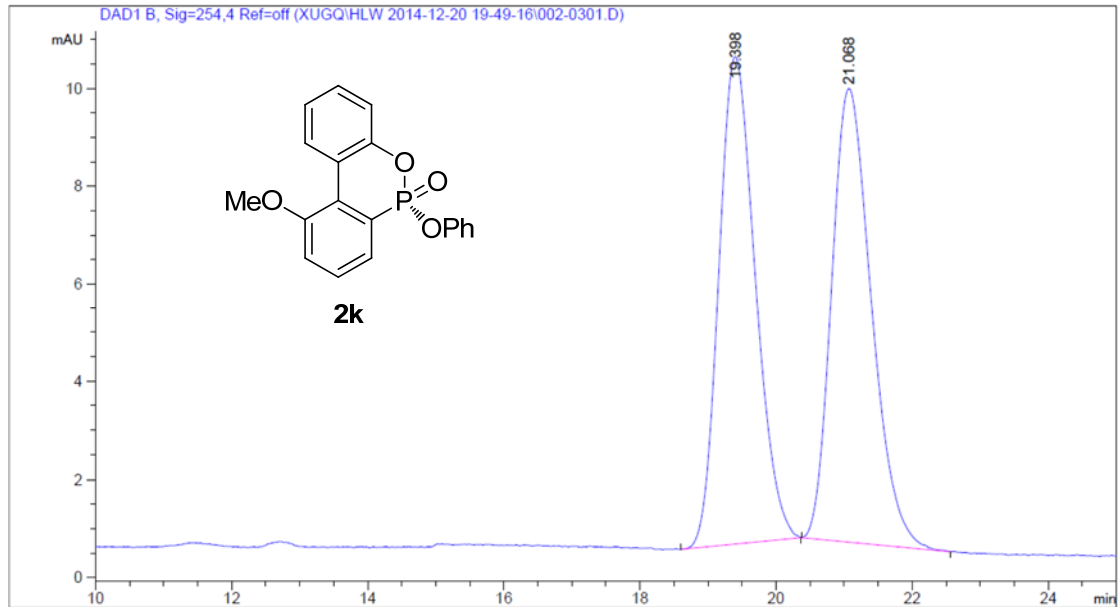
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.954	BB	0.4158	1.16673e4	428.31833	89.0327
2	14.121	BBA	0.5417	1437.20801	40.53434	10.9673



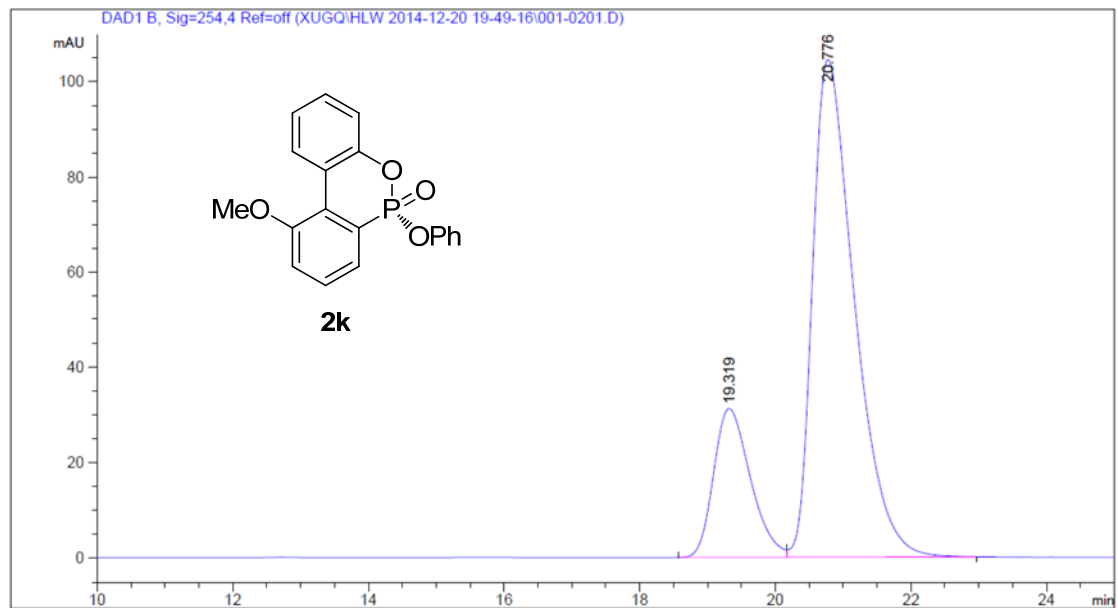
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.024	BB	0.4395	5699.89453	197.06105	50.0165
2	15.080	BB	0.5621	5696.13623	153.79773	49.9835



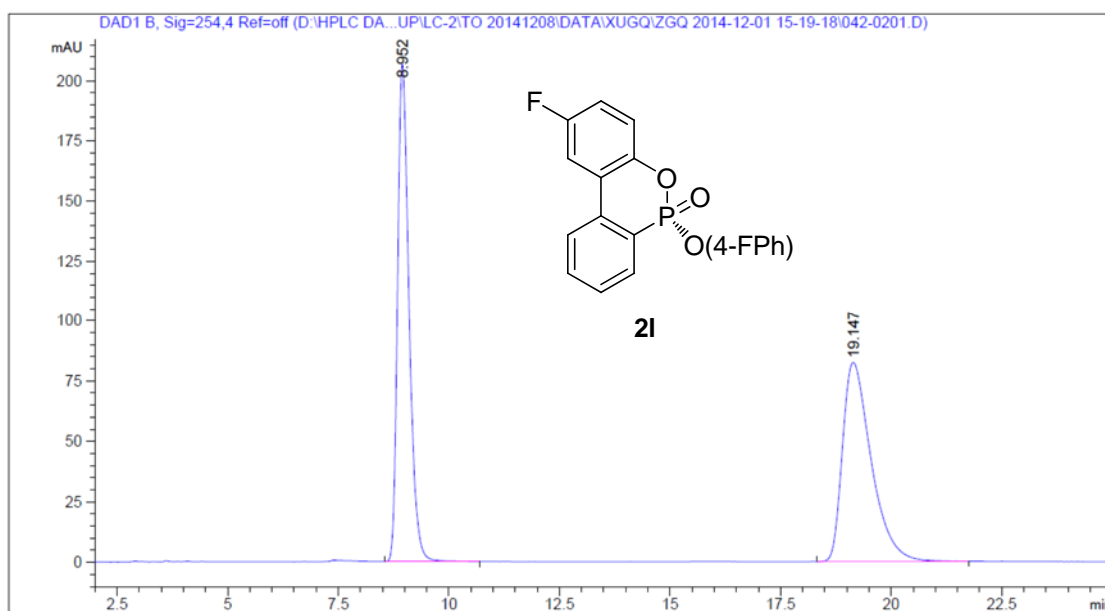
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.031	BB	0.4402	684.83386	23.62080	9.4646
2	15.085	BB	0.5700	6550.93311	175.29308	90.5354



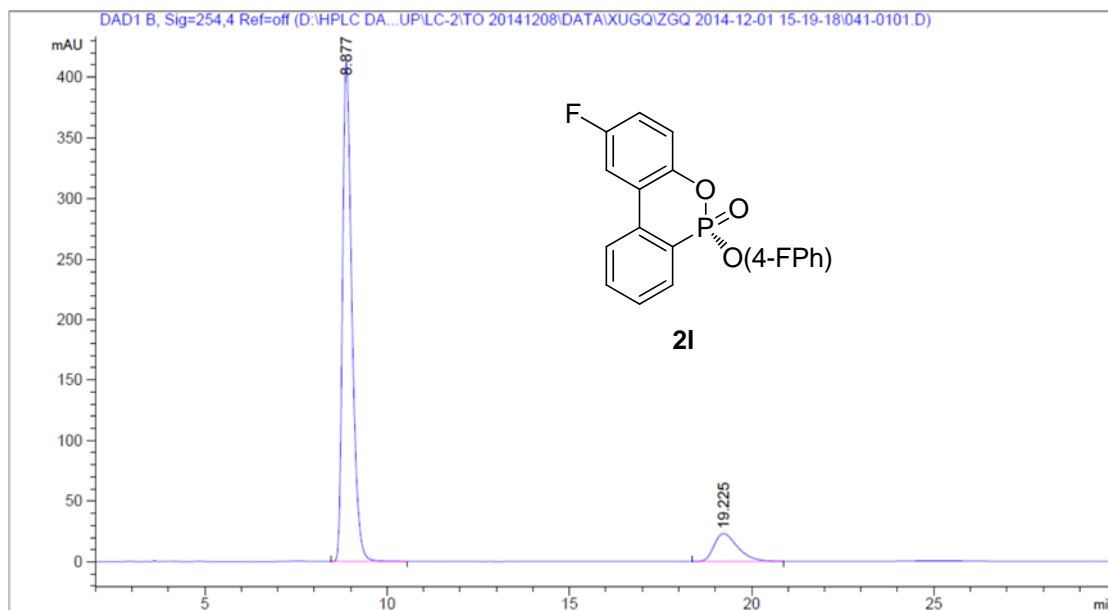
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.398	BB	0.5658	370.70523	9.96943	49.6680
2	21.068	BB	0.5925	375.66089	9.27501	50.3320



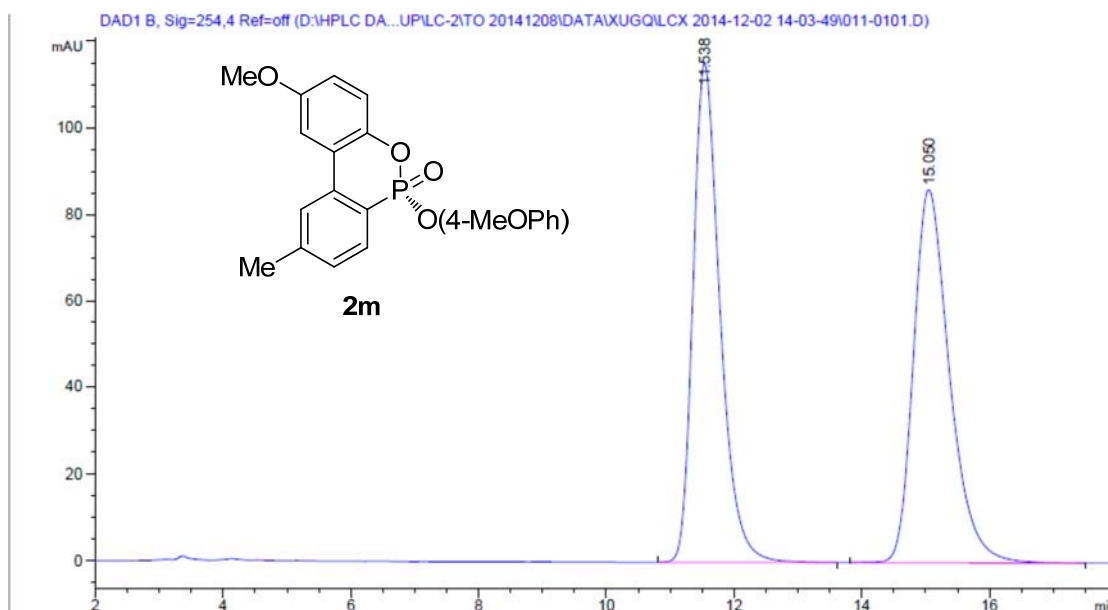
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.319	BV	0.5792	1170.59424	31.09806	20.7796
2	20.776	VB	0.6485	4462.78955	104.44370	79.2204



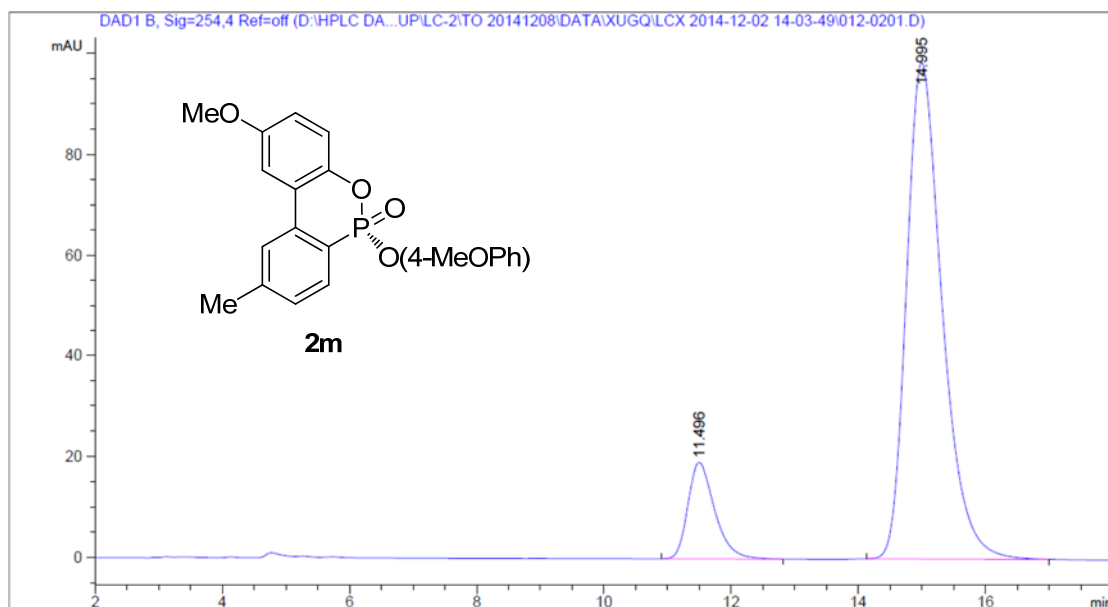
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.952	BB	0.2737	3714.48535	206.66362	50.0158
2	19.147	BB	0.6879	3712.14258	82.35204	49.9842



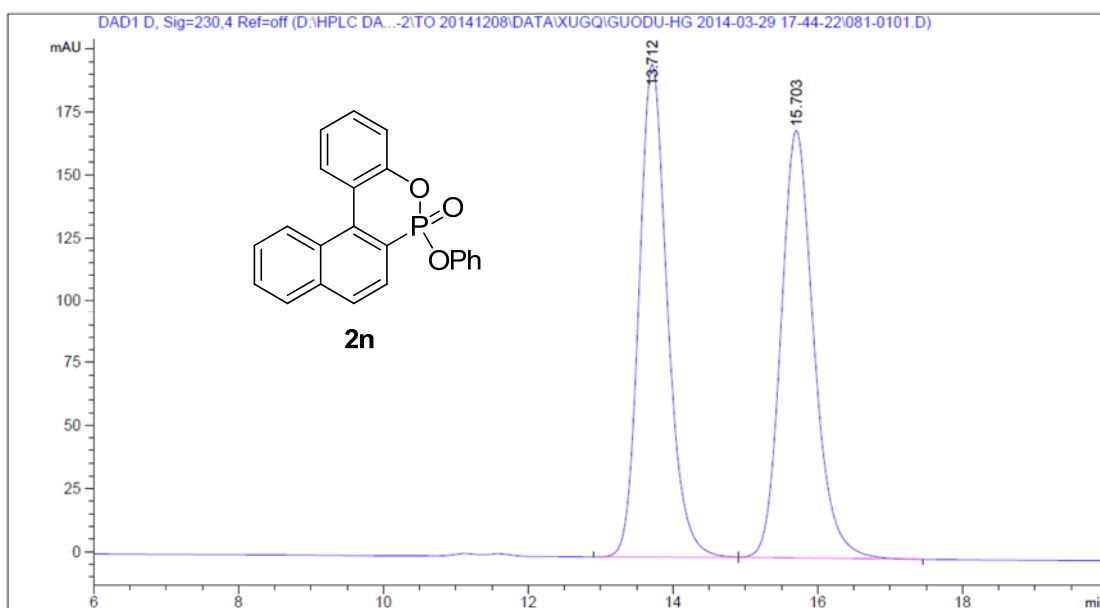
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.877	BB	0.2726	7373.39209	412.39771	87.7479
2	19.225	BB	0.6720	1029.53784	22.92013	12.2521



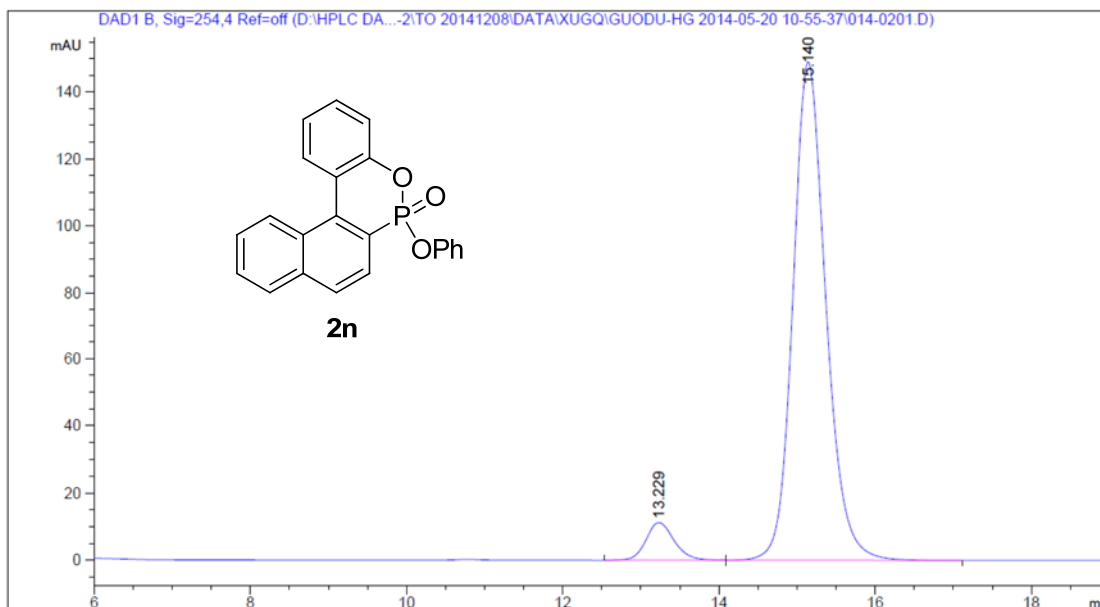
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.538	BB	0.4463	3384.24268	115.33861	50.0251
2	15.050	BB	0.5992	3380.84399	86.27750	49.9749



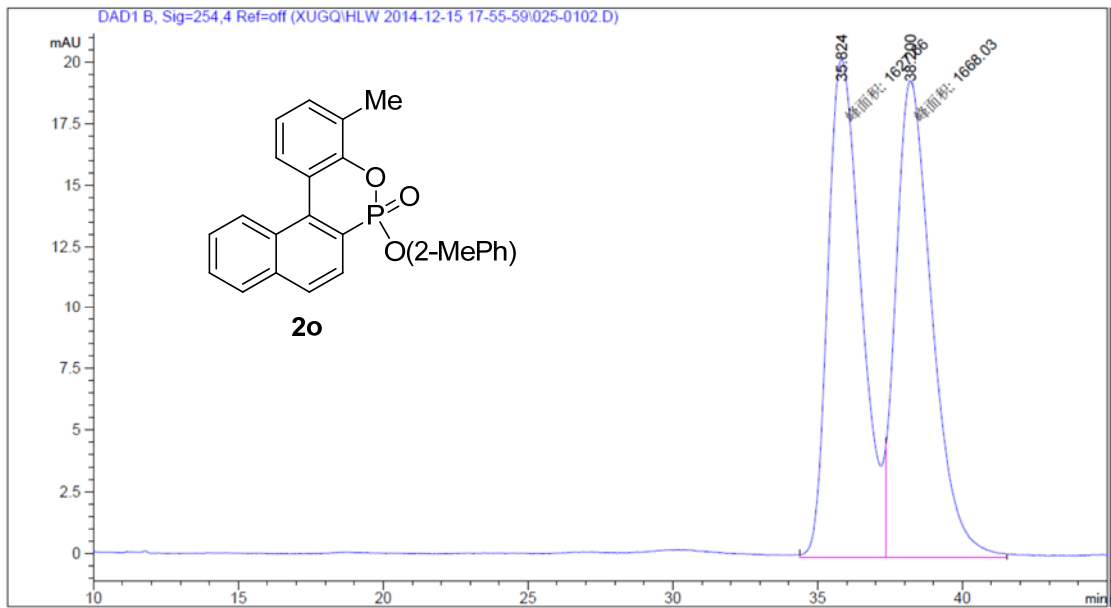
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.496	BB	0.4505	557.82233	19.00006	12.7091
2	14.995	BB	0.5941	3831.32715	98.44437	87.2909



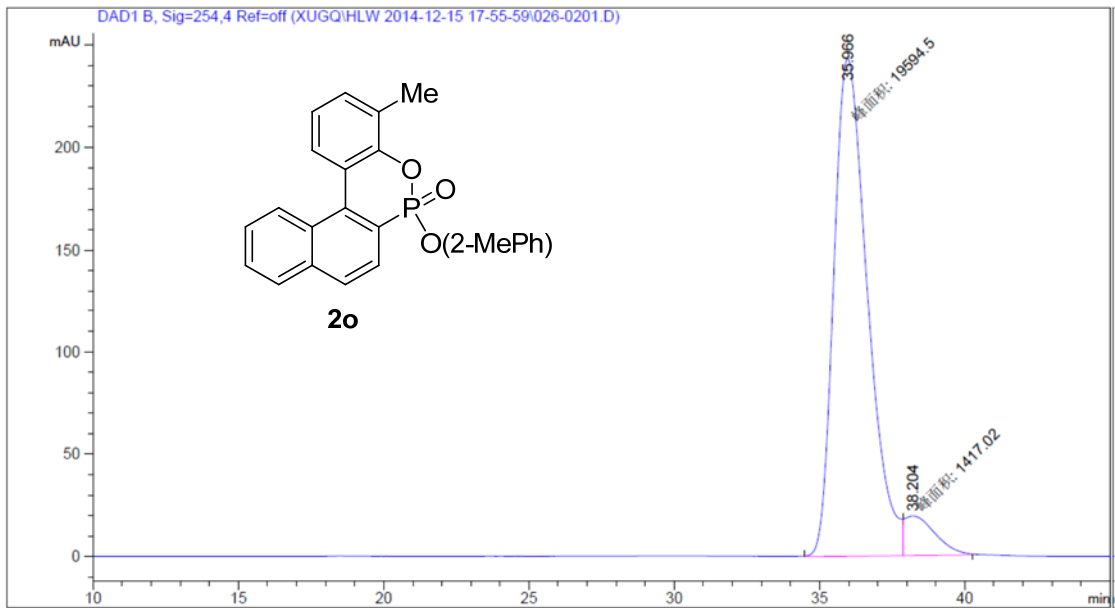
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.712	BB	0.4158	5312.53125	196.24107	49.8917
2	15.703	BB	0.4801	5335.60400	170.02783	50.1083



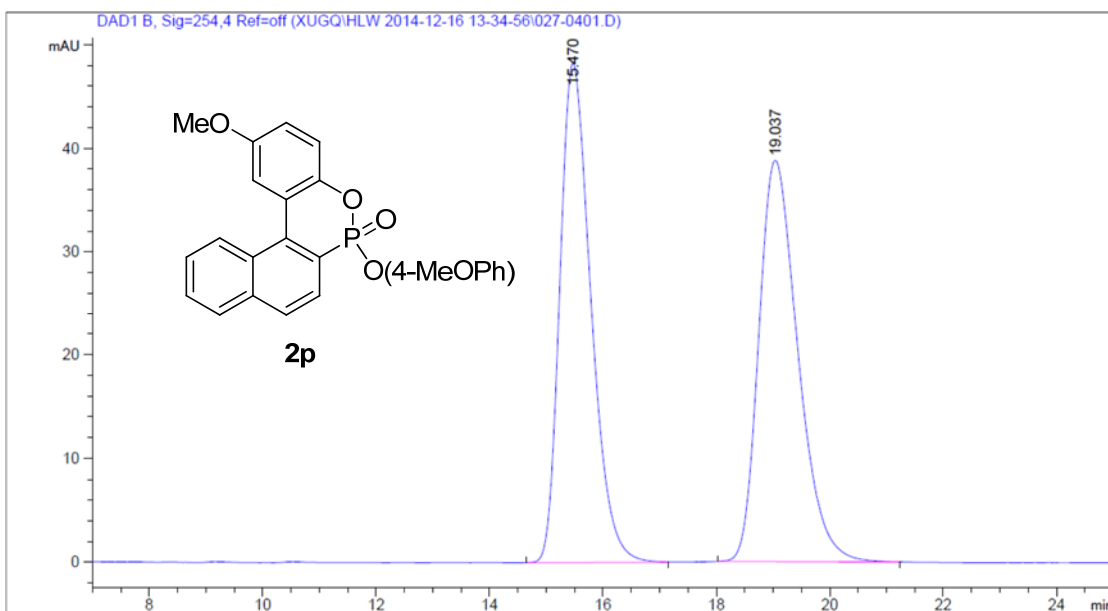
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.229	BB	0.3814	281.63165	11.27467	6.0725
2	15.140	BB	0.4470	4356.17383	149.03377	93.9275



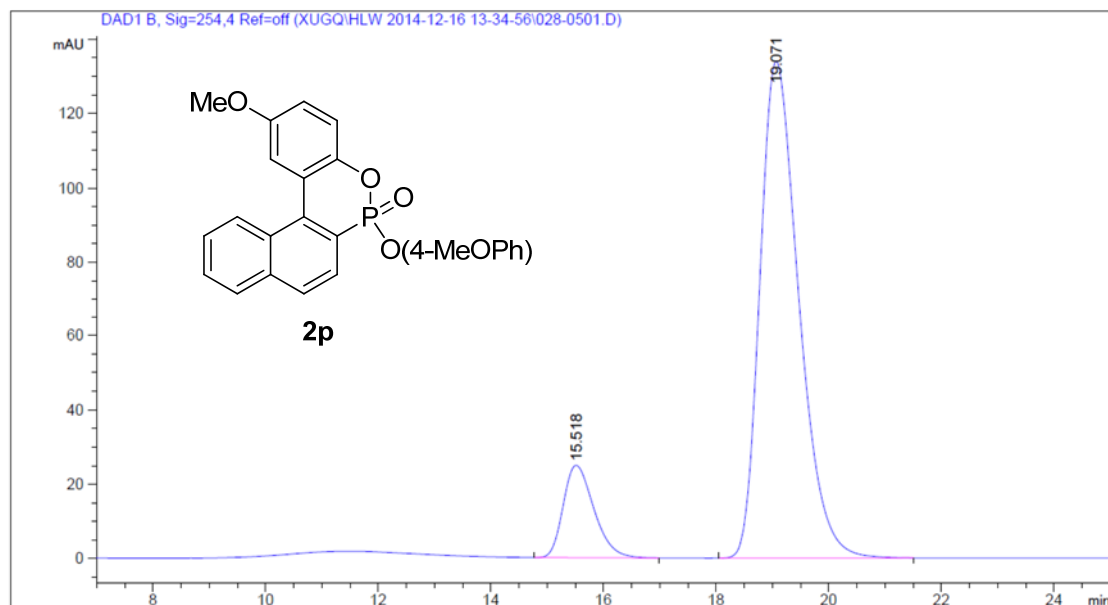
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	35.824	MF	1.3377	1627.66113	20.27981	49.3876
2	38.200	FM	1.4334	1668.02856	19.39507	50.6124



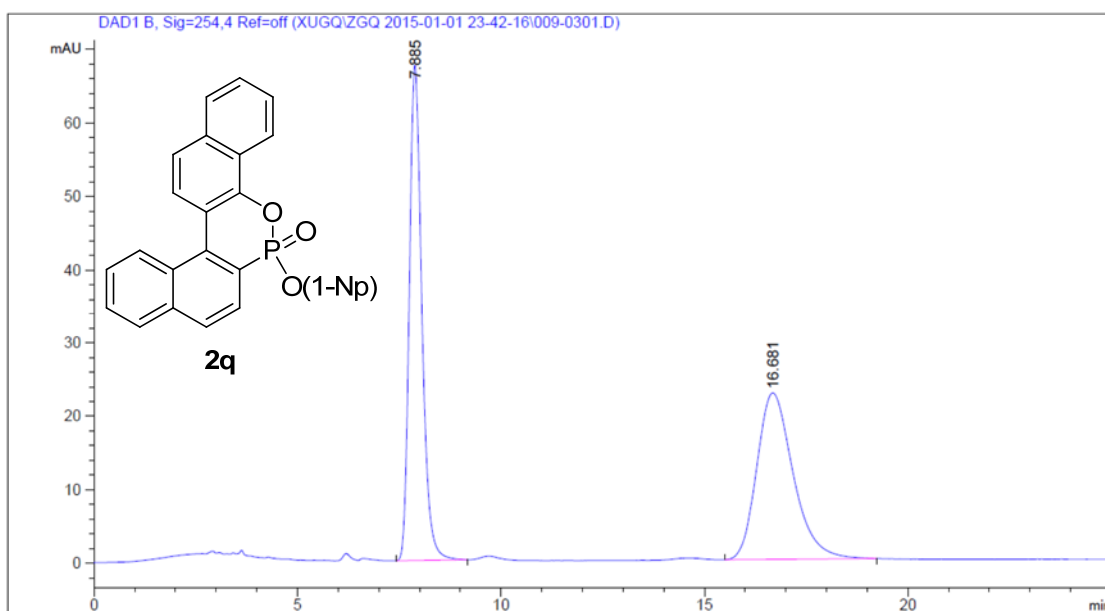
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	35.966	MF	1.3425	1.95945e4	243.26334	93.2560
2	38.204	FM	1.2215	1417.01563	19.33442	6.7440



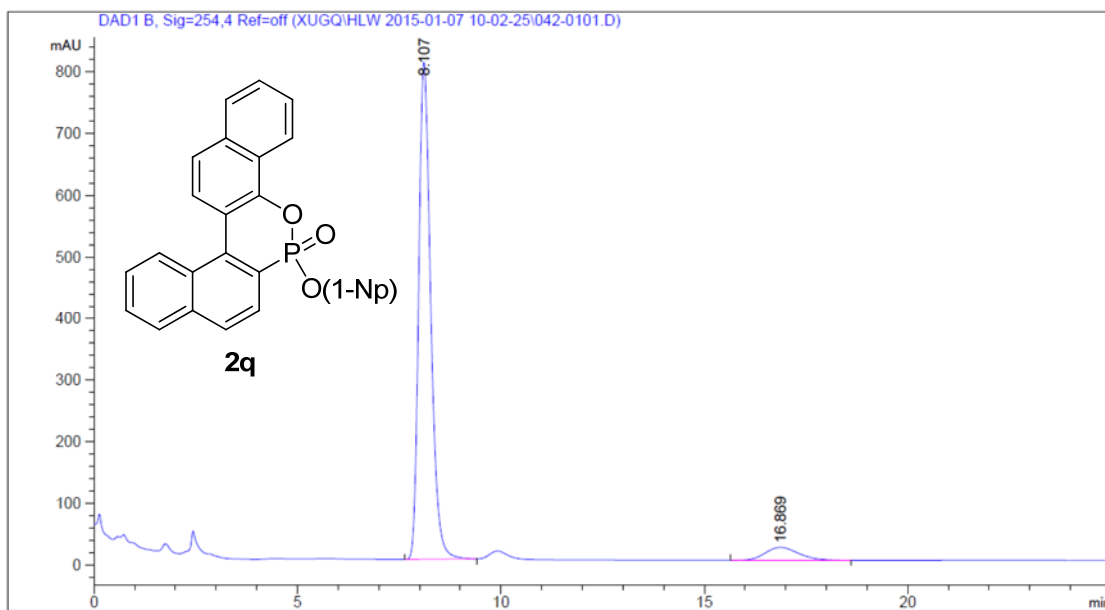
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.470	BB	0.5863	1829.17786	48.25369	49.7075
2	19.037	BB	0.7271	1850.70313	38.75734	50.2925



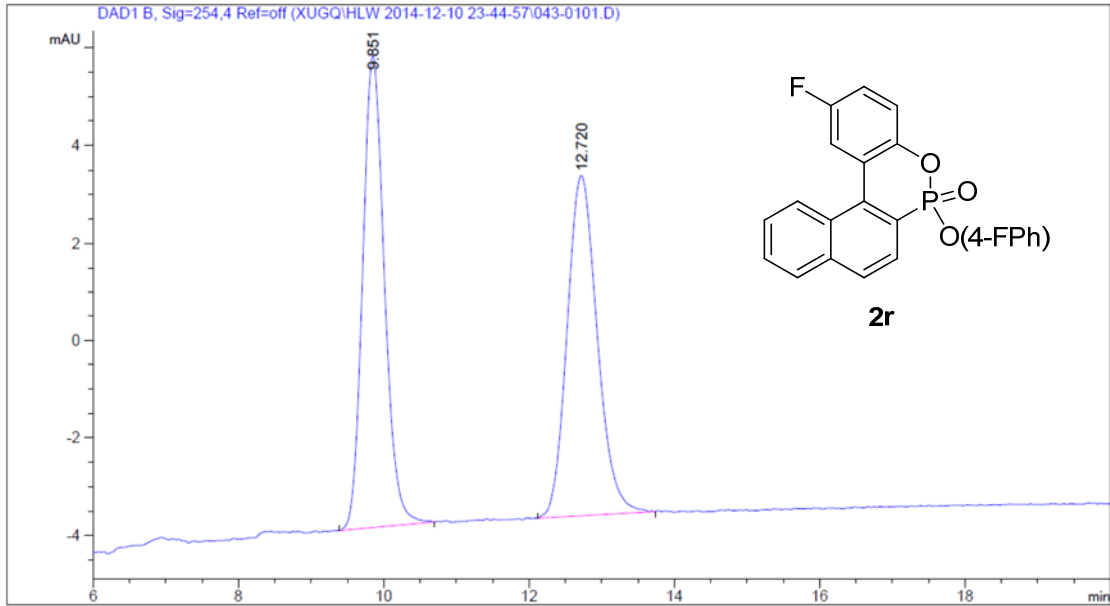
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.518	BB	0.5744	941.60693	24.83398	12.8393
2	19.071	BB	0.7332	6392.18896	133.84178	87.1607



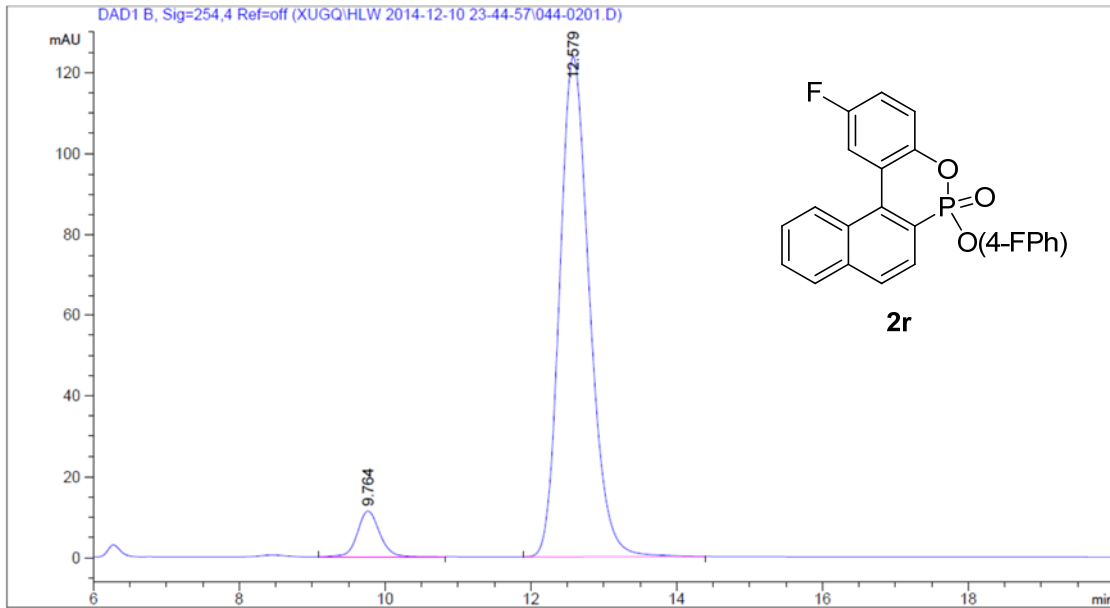
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.885	BB	0.3274	1443.62732	67.52410	50.6353
2	16.681	BB	0.9033	1407.40051	22.63987	49.3647



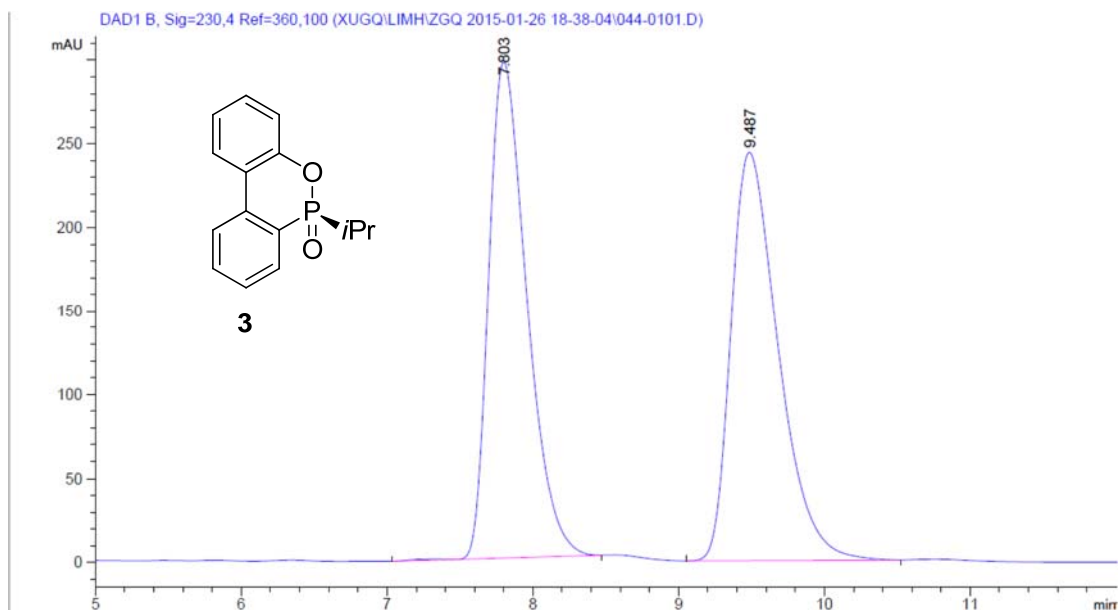
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.107	BB	0.3144	1.64460e4	804.81317	93.1566
2	16.869	BB	0.8599	1208.14343	20.97712	6.8434



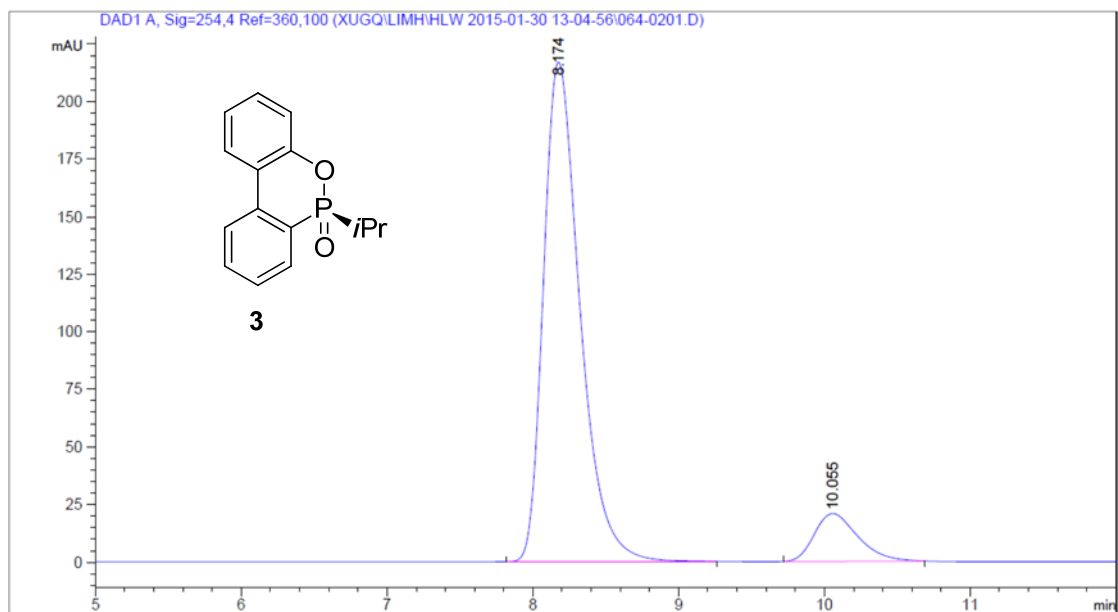
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
2	9.851	BB	0.3225	201.15520	9.67649	49.2637
3	12.720	BB	0.4359	201.28873	6.99166	49.2964



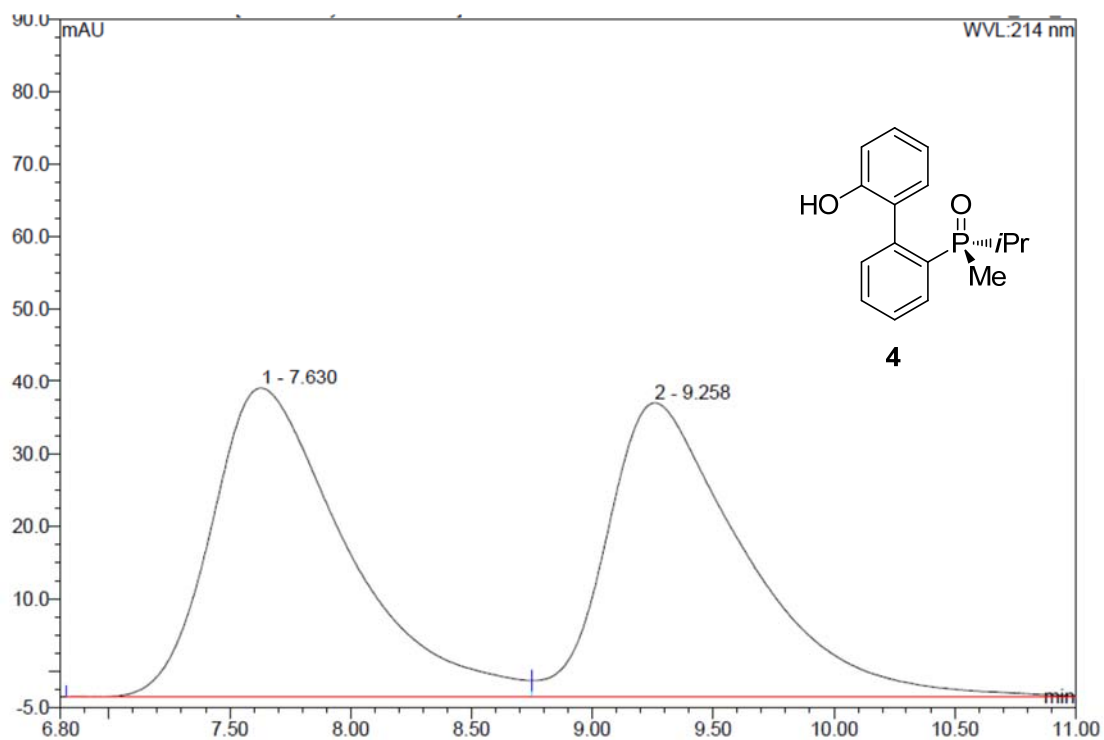
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.764	BB	0.3266	240.10005	11.36035	6.4200
2	12.579	BB	0.4360	3499.78052	123.73879	93.5800



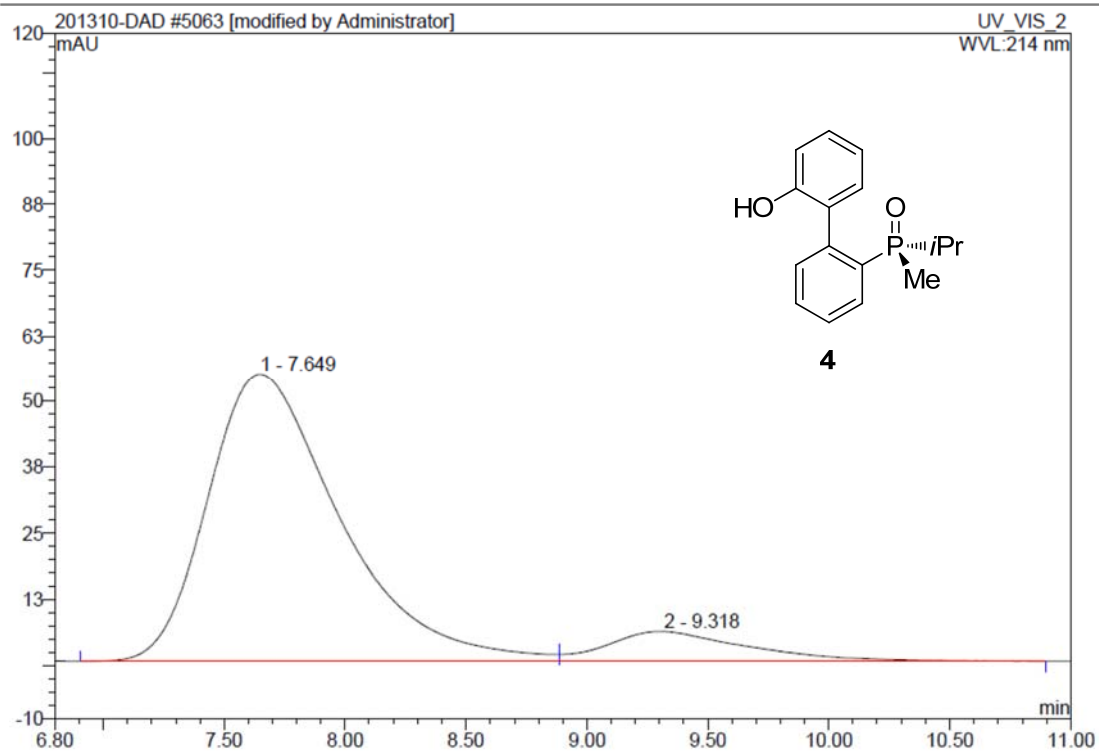
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.802	VV	0.2931	3.15191e4	1663.10193	49.6574
2	9.487	BV	0.3540	3.19540e4	1390.94507	50.3426



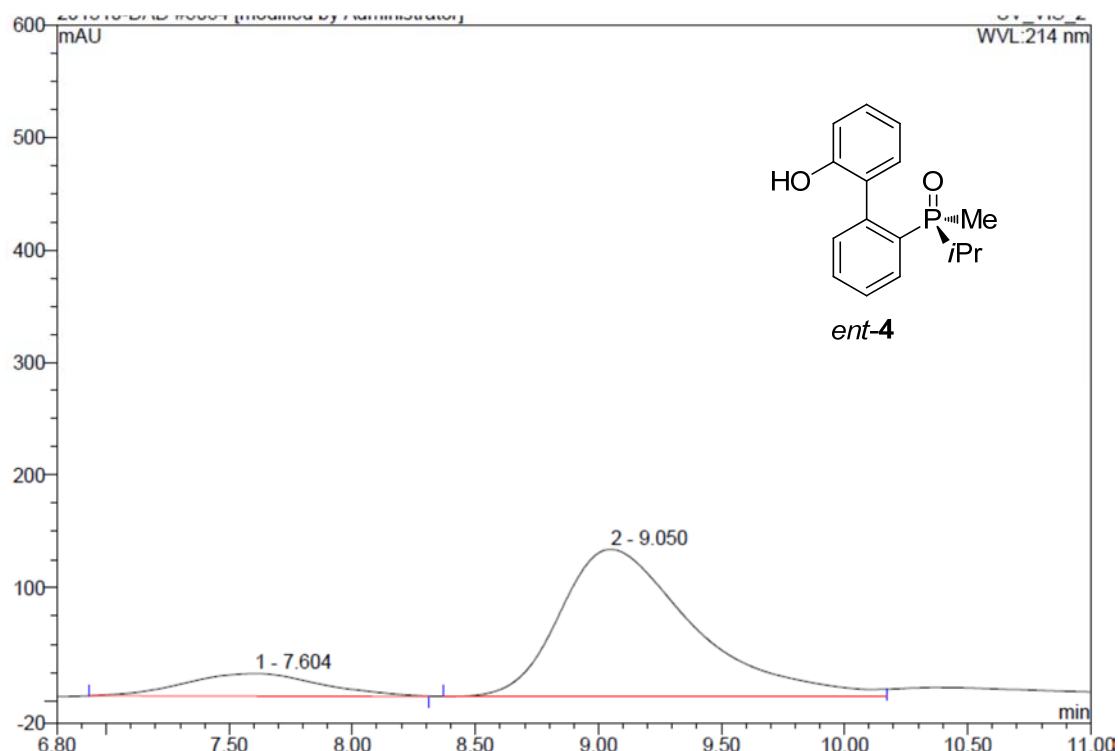
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.174	MM R	0.2896	3770.82056	217.02008	89.7536
2	10.055	MM R	0.3465	430.48071	20.70328	10.2464



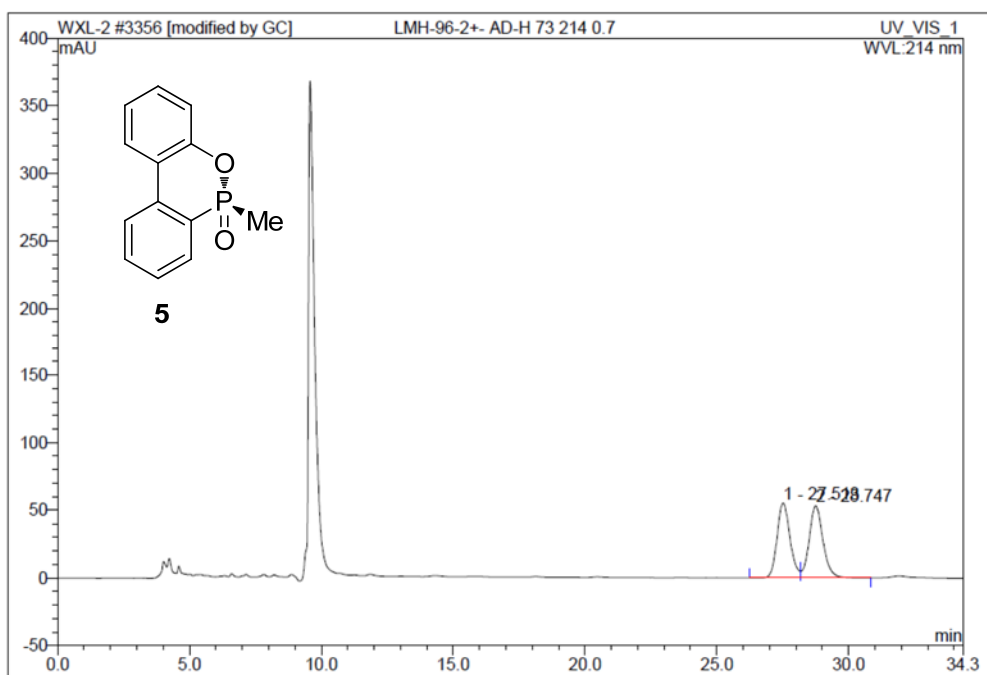
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.63	n.a.	42.502	27.440	50.67	n.a.	BM *
2	9.26	n.a.	40.455	26.717	49.33	n.a.	MB*



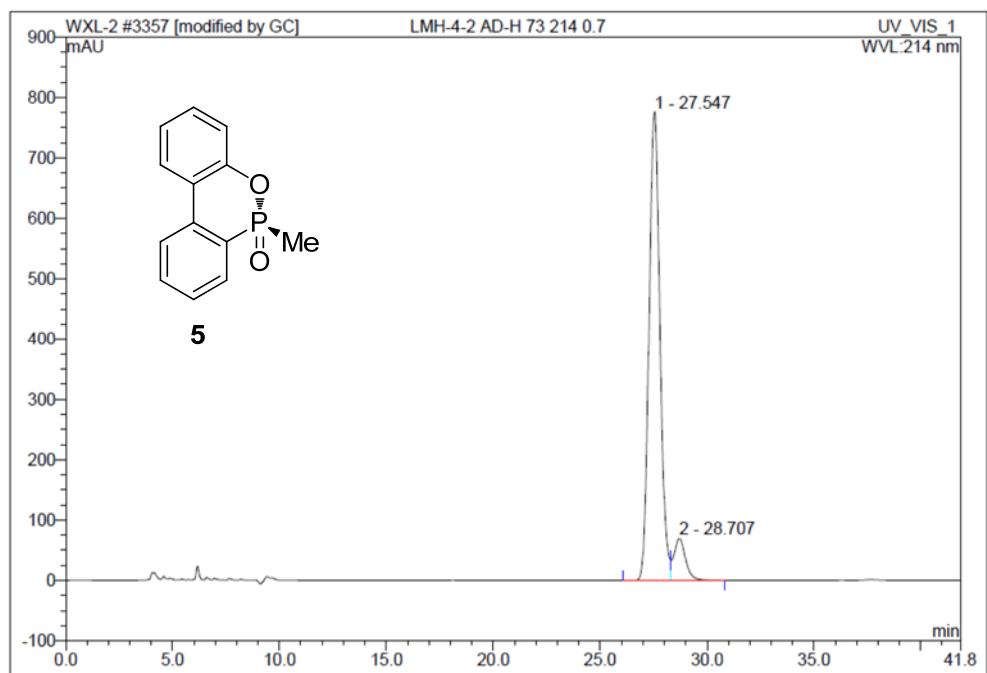
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.65	n.a.	54.344	34.386	90.06	n.a.	M *
2	9.32	n.a.	5.658	3.794	9.94	n.a.	MB*



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.60	n.a.	20.123	12.747	13.47	n.a.	BM *
2	9.05	n.a.	130.404	81.886	86.53	n.a.	BM *



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	27.51	n.a.	55.155	31.316	49.17	n.a.	BM *
2	28.75	n.a.	53.170	32.373	50.83	n.a.	MB*



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	27.55	n.a.	776.639	459.768	91.21	n.a.	BM*
2	28.71	n.a.	69.346	44.296	8.79	n.a.	MB*