

Supporting Information

Lewis acid-catalyzed phosphinoylation and halogenation of α,β -unsaturated ketones: Access to γ -halo allylic phosphonates

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General Information

All chemicals were purchased from Aldrich, TCI and J&K Chemical and used without further purification. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Silica gel 60 (230-400 mesh) was used for column chromatography. ^1H and ^{13}C NMR spectra were recorded using CDCl_3 solvent on a Bruker advance III 400 spectrometer (400 MHz for ^1H , 162 MHz for ^{31}P and 101 MHz for ^{13}C). The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^1H and ^{13}C NMR spectroscopy. High-resolution mass spectra (HRMS) were measured with Thermo Scientific DSQ II mass spectrometer. X-ray diffraction experiments were performed on a SuperNova, Dual, Cu at zero, Eos diffractometer.

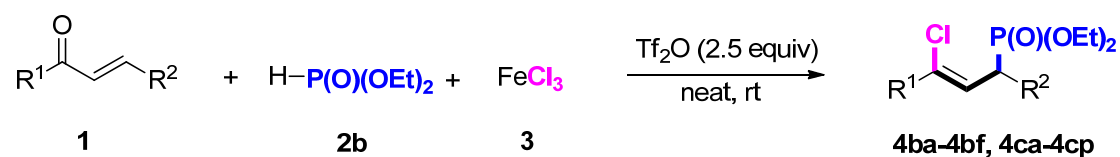
Experimental Section

1. General procedure for synthesis of product 4aa-4az, 4aaa-4aab



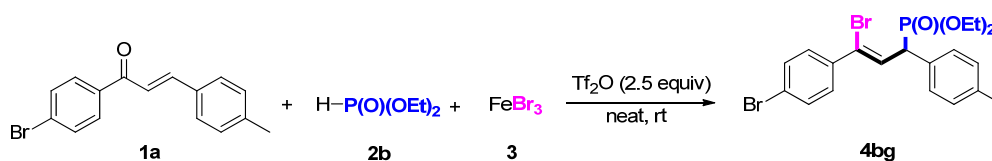
An oven-dried 10 mL screw-capped vial containing **1** (0.1 mmol, 1.0 equiv), FeCl_3 (0.08 mmol, 8 mol%) and PCl_5 (0.8 mmol, 0.8 equiv), bis(2,2,2-trifluoroethyl) phosphonate **2a** (0.2 mmol, 2.0 equiv), Tf_2O (0.2 mmol, 2 equiv), and DCE (2 mL) was added via syringe, and then heated to 25 $^\circ\text{C}$ for 8 h under air condition. And then the solvent was removed in vacuo and residue was purified by column chromatography on a silica gel column using petroleum ether/ethyl acetate as eluent to afford the desired product **4**.

2. General procedure for synthesis of product 4ba-4bf, 4ca-4cp



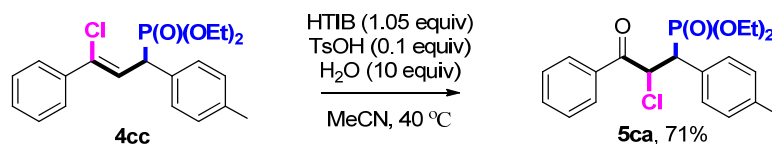
An oven-dried 10 mL screw-capped vial containing **1** (0.1 mmol, 1.0 equiv) and FeCl₃ (0.1 mmol, 1.0 equiv), **2b** (0.2 mmol, 2.0 equiv) and Tf₂O (0.25 mmol, 2.5 equiv) was added via syringe, and then heated to 25 °C for 8 h under air condition. And then the solvent was removed in vacuo and residue was purified by column chromatography on a silica gel column using petroleum ether/ethyl acetate as eluent to afford the desired product **4**.

3. General procedure for synthesis of product **4bg**



An oven-dried 10 mL screw-capped vial containing **1a** (0.1 mmol, 1.0 equiv) and FeBr₃ (0.07 mmol, 0.7 equiv), **2b** (0.2 mmol, 2.0 equiv) and Tf₂O (0.25 mmol, 2.5 equiv) was added via syringe, and then heated to -10 °C for 8 h under air condition. And then the solvent was removed in vacuo and residue was purified by column chromatography on a silica gel column using petroleum ether/ethyl acetate as eluent to afford the desired product 43.8 mg **4bg** (75%).

4. Synthesis of **5ca**¹

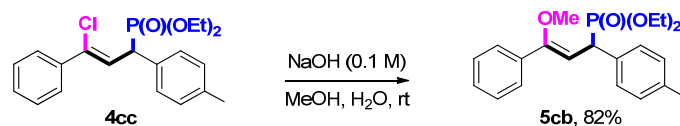


To a vial were added **4cc** (0.2 mmol, 1 equiv), *p*-TsOH·H₂O (0.02 mmol, 0.1 equiv), MeCN 1 mL, H₂O 1 mL and HTIB (0.22 mmol, 1.1 equiv). The suspension was vigorously stirred at 40 °C until a homogenous solution was obtained and let to stir at least an additional 30 minutes afterward.

The solution was diluted with water (1:1) and extracted with Et₂O. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated by rotatory evaporation. The crude product was purified by column chromatography on a short silica gel column (petroleum ether/ethyl acetate = 20/1) to afford 55.9 mg (71%) of **5ca**.

1 .Wu S-W, Liu J-L, Liu F. Metal-Free Microwave-Assisted Decarboxylative Elimination for the Synthesis of Olefins, *Org. Lett.*, **2016**, *18*, 1-3.

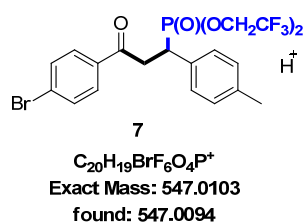
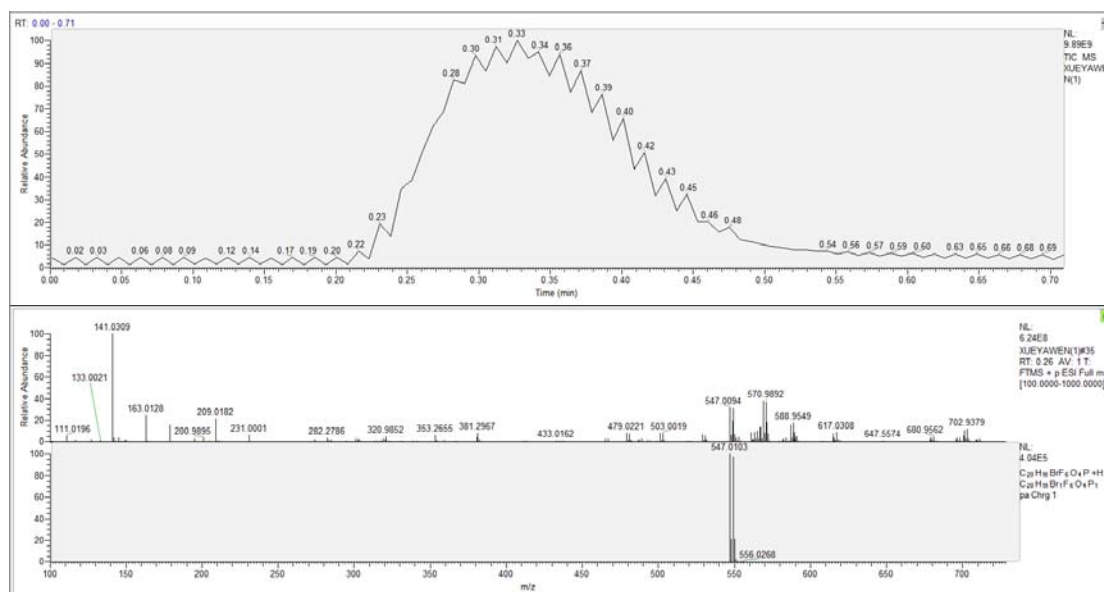
5. Synthesis of 5cb²



An oven-dried 10 mL screw-capped vial containing **4cc** (0.1 mmol), methanol (2 mL) and 10% NaOH (0.2 mL) was added via syringe, and then heated to 25 °C for 8 h under air condition.

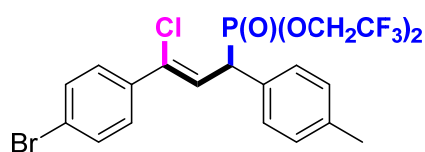
Resulting reaction mixture was stirred a room temperature for 20 min. Reaction progress was monitored by TLC. After complete consumption of reactant, the reaction mixture was poured into water. Solid product was filtered dried and recrystallized with ethanol to attainment 61mg **5cb** (82%).

6. In situ HRMS Spectra of 7



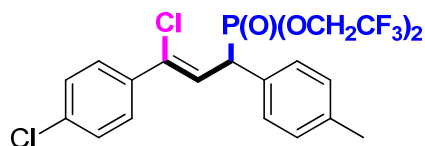
2.Sharma P K, Kumar R, Ram S, et al. Deadly KCN and pricey metal free track for accessing β -ketonitriles employing mild reaction conditions, *Synthetic Commun.*, **2021**, 1847-1856

Analytical Data of Products



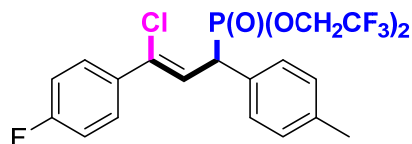
4aa

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 52 mg (92%) of **4aa**. **Bis(2,2,2-trifluoroethyl) (Z)-(3-(4-bromophenyl)-3-chloro-1-(p-tolyl)allyl)phosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 – 7.41 (m, 4H), 7.34 (dd, $J = 8.2, 2.4$ Hz, 2H), 7.20 (d, $J = 7.9$ Hz, 2H), 6.47 (dd, $J = 10.3, 8.1$ Hz, 1H), 4.71 (dd, $J = 24.7, 10.3$ Hz, 1H), 4.45 – 4.14 (m, 3H), 3.97 – 3.75 (m, 1H), 2.35 (d, $J = 2.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.28 (d, $J = 3.5$ Hz), 136.18 (d, $J = 17.2$ Hz), 136.02 (d, $J = 3.0$ Hz), 131.60, 129.93 (d, $J = 2.6$ Hz), 129.45 (d, $J = 8.5$ Hz), 128.75 (d, $J = 7.2$ Hz), 128.24 (d, $J = 2.1$ Hz), 123.61 (d, $J = 8.7$ Hz), 122.33 (qd, $J_{\text{F-C}} = 277.7$ Hz, $J_{\text{P-C}} = 8.3$ Hz), 122.27 (qd, $J_{\text{F-C}} = 267.1$ Hz, $J_{\text{P-C}} = 7.8$ Hz), 120.23 (d, $J = 8.7$ Hz), 62.89 (qd, $J_{\text{F-C}} = 37.9$, $J_{\text{P-C}} = 6.4$ Hz), 62.29 (qd, $J_{\text{F-C}} = 38.1$, $J_{\text{P-C}} = 6.9$ Hz), 45.59 (d, $J = 140.9$ Hz), 21.06. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 26.93. **HRMS (ESI)** Calcd. For $\text{C}_{20}\text{H}_{17}\text{BrClF}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 586.9584, found. 586.9581.



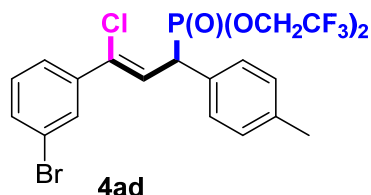
4ab

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 43 mg (85%) of **4ab**. **Bis(2,2,2-trifluoroethyl) (Z)-(3-chloro-3-(4-chlorophenyl)-1-(p-tolyl)allyl)phosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 (d, $J = 8.6$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 4H), 7.20 (d, $J = 7.9$ Hz, 2H), 6.46 (dd, $J = 10.3, 8.1$ Hz, 1H), 4.71 (dd, $J = 24.7, 10.3$ Hz, 1H), 4.41 – 4.18 (m, 3H), 3.84 (dt, $J = 12.2, 8.2$ Hz, 1H), 2.35 (d, $J = 2.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.29 (d, $J = 3.6$ Hz), 136.12 (d, $J = 17.2$ Hz), 135.57 (d, $J = 2.9$ Hz), 135.37, 129.93 (d, $J = 2.8$ Hz), 129.49 (d, $J = 8.4$ Hz), 128.76 (d, $J = 7.1$ Hz), 128.64, 128.00 (d, $J = 2.1$ Hz), 122.34 (qd, $J_{\text{F-C}} = 261.6$ Hz, $J_{\text{P-C}} = 8.0$ Hz), 122.33 (qd, $J_{\text{F-C}} = 277.7$ Hz, $J_{\text{P-C}} = 8.2$ Hz), 120.16 (d, $J = 8.7$ Hz), 62.90 (qd, $J_{\text{F-C}} = 37.9$, $J_{\text{P-C}} = 6.3$ Hz), 62.30 (qd, $J_{\text{F-C}} = 37.9$, $J_{\text{P-C}} = 6.7$ Hz), 45.59 (d, $J = 140.9$ Hz), 21.09. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 26.98. **HRMS (ESI)** Calcd. For $\text{C}_{20}\text{H}_{17}\text{Cl}_2\text{F}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 543.0089, found 543.0086.



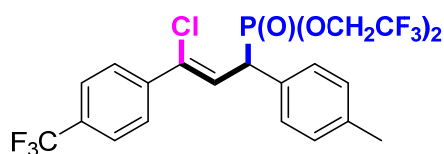
4ac

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 48 mg (96%) of **4ac**. **Bis(2,2,2-trifluoroethyl) (1-(4-bromophenyl)vinyl)phosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.55 (dd, $J = 8.6, 5.4$ Hz, 2H), 7.34 (dd, $J = 8.2, 2.5$ Hz, 2H), 7.20 (d, $J = 7.9$ Hz, 2H), 7.05 (t, $J = 8.6$ Hz, 2H), 6.41 (dd, $J = 10.3, 8.0$ Hz, 1H), 4.71 (dd, $J = 24.7, 10.3$ Hz, 1H), 4.44 – 4.18 (m, 3H), 3.94 – 3.74 (m, 1H), 2.35 (d, $J = 2.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.28 (d, $J = 249.7$ Hz), 138.24 (d, $J = 3.4$ Hz), 136.20 (d, $J = 17.3$ Hz), 133.36, 129.91 (d, $J = 2.7$ Hz), 129.63 (d, $J = 8.4$ Hz), 128.77 (d, $J = 7.1$ Hz), 128.62 (d, $J = 2.0$ Hz), 123.78 (qd, $J_{\text{F-C}} = 277.7$ Hz, $J_{\text{P-C}} = 8.2$ Hz), 122.36 (qd, $J_{\text{F-C}} = 261.4$ Hz, $J_{\text{P-C}} = 8.3$ Hz), 119.63 (d, $J = 8.6$ Hz), 115.44 (d, $J = 22.0$ Hz), 62.89 (qd, $J_{\text{F-C}} = 37.9$, $J_{\text{P-C}} = 6.2$ Hz), 62.32 (qd, $J_{\text{F-C}} = 37.9$, $J_{\text{P-C}} = 6.8$ Hz), 45.58 (d, $J = 140.9$ Hz), 21.06. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 27.11. **HRMS (ESI)** Calcd. For $\text{C}_{20}\text{H}_{17}\text{ClF}_7\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 527.0384, found 527.0385.



4ad

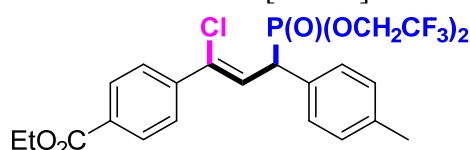
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 48 mg (85%) of **4ad**. **Bis(2,2,2-trifluoroethyl) (Z)-(3-(3-bromophenyl)-3-chloro-1-(p-tolyl)allyl)phosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.71 (d, $J = 1.8$ Hz, 1H), 7.54 – 7.46 (m, 2H), 7.34 (dd, $J = 8.2, 2.4$ Hz, 2H), 7.22 (t, $J = 8.3$ Hz, 3H), 6.48 (dd, $J = 10.2, 8.1$ Hz, 1H), 4.71 (dd, $J = 24.6, 10.3$ Hz, 1H), 4.47 – 4.12 (m, 3H), 3.95 – 3.74 (m, 1H), 2.36 (d, $J = 2.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 139.05 (d, $J = 3.0$ Hz), 138.33 (d, $J = 3.5$ Hz), 135.64 (d, $J = 17.2$ Hz), 132.33, 129.98, 129.95, 129.72 (d, $J = 2.1$ Hz), 129.40 (d, $J = 8.5$ Hz), 128.77 (d, $J = 7.2$ Hz), 125.37 (d, $J = 2.0$ Hz), 122.56 (d, $J = 8.5$ Hz), 122.00 (qd, $J_{\text{F-C}} = 139.7$ Hz, $J_{\text{P-C}} = 6.9$ Hz), 121.87 (qd, $J_{\text{F-C}} = 133.4$ Hz, $J_{\text{P-C}} = 4.1$ Hz), 120.99 (d, $J = 8.5$ Hz), 62.97 (qd, $J_{\text{F-C}} = 37.9$ Hz, $J_{\text{P-C}} = 6.5$ Hz), 62.48 (qd, $J_{\text{F-C}} = 61.0$ Hz, $J_{\text{P-C}} = 6.6$ Hz), 45.59 (d, $J = 141.0$ Hz), 21.11. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 26.91. **HRMS (ESI)** Calcd. For $\text{C}_{20}\text{H}_{17}\text{BrClF}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 586.9584, found 586.9585.



4ae

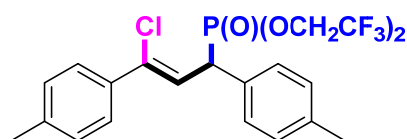
Purification was performed by column chromatography (petroleum ether/ethyl acetate

= 4/1) to afford 45 mg (82%) of **4ae**. **Dibenzyl(1-(4-methoxyphenyl)vinyl)phosphine oxide**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 – 7.59 (m, 4H), 7.35 (dd, J = 8.2, 2.4 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 6.56 (dd, J = 10.3, 8.0 Hz, 1H), 4.74 (dd, J = 24.6, 10.3 Hz, 1H), 4.45 – 4.16 (m, 3H), 4.02 – 3.68 (m, 1H), 2.36 (d, J = 2.2 Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 140.44, 138.42 (d, J = 3.6 Hz), 135.90, 135.72, 131.23 (d, J = 32.5 Hz), 130.00 (d, J = 2.7 Hz), 129.28 (d, J = 8.5 Hz), 128.77 (d, J = 7.2 Hz), 127.10 (d, J = 2.0 Hz), 125.49 (d, J = 3.9 Hz), 122.33 (qd, $J_{\text{F-C}}$ = 277.5 Hz, $J_{\text{P-C}}$ = 8.4 Hz), 121.86 (d, J = 8.6 Hz), 120.91 (qd, $J_{\text{F-C}}$ = 261.3 Hz, $J_{\text{P-C}}$ = 8.1 Hz), 62.87 (qd, $J_{\text{F-C}}$ = 66.9 Hz, $J_{\text{P-C}}$ = 6.3 Hz), 62.49 (qd, $J_{\text{F-C}}$ = 67.0 Hz, $J_{\text{P-C}}$ = 6.9 Hz), 45.65 (d, J = 141.0 Hz), 21.11. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 26.77. **HRMS (ESI)** Calcd. For $\text{C}_{21}\text{H}_{17}\text{ClF}_9 \text{Na O}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 577.0352, found 577.0353.



4af

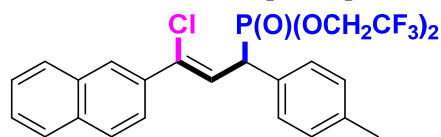
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 37 mg (66%) of **4af**. **Ethyl (Z)-4-(3-(bis(2,2,2-trifluoroethoxy)phosphoryl)-1-chloro-3-(p-tolyl)prop-1-en-1-yl)benzoate**. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.04 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.36 (dd, J = 8.2, 2.4 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 6.57 (dd, J = 10.3, 8.1 Hz, 1H), 4.75 (dd, J = 24.6, 10.3 Hz, 1H), 4.48 – 4.20 (m, 5H), 3.95 – 3.76 (m, 1H), 2.36 (d, J = 2.2 Hz, 3H), 1.40 (t, J = 7.1 Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.89, 139.68 (d, 3.2 Hz), 136.33 (d, J = 17.3 Hz), 131.11, 129.97 (d, J = 2.7 Hz), 129.67, 129.37 (d, J = 8.4 Hz), 128.78 (d, J = 7.1 Hz), 126.64 (d, J = 2.0 Hz), 122.40 (qd, $J_{\text{F-C}}$ = 277.6 Hz, $J_{\text{P-C}}$ = 7.8 Hz), 122.32 (qd, $J_{\text{F-C}}$ = 277.5 Hz, $J_{\text{P-C}}$ = 8.2 Hz), 121.53 (d, J = 8.7 Hz), 62.83 (qd, $J_{\text{F-C}}$ = 61.7, $J_{\text{P-C}}$ = 6.6 Hz), 62.45 (qd, $J_{\text{F-C}}$ = 61.7, $J_{\text{P-C}}$ = 6.8 Hz), 61.19, 45.66 (d, J = 141.2 Hz), 29.68, 21.10, 14.27. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 26.86. **HRMS (ESI)** Calcd. For $\text{C}_{23}\text{H}_{22}\text{ClF}_6\text{NaO}_5\text{P}$ $[\text{M}+\text{Na}]^+$: 581.0690, found 581.0691.



4ag

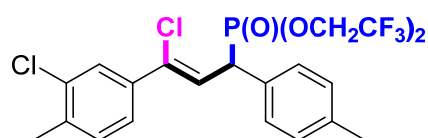
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 41 mg (81%) of **4ag**. **Dibutyl (1-(4-methoxyphenyl)vinyl)phosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46 (d, J = 8.1 Hz, 2H), 7.34 (dd, J = 8.2, 2.5 Hz, 2H), 7.22 – 7.15 (m, 4H), 6.43 (dd, J = 10.3, 8.1 Hz, 1H), 4.73 (dd, J = 24.7, 10.3 Hz, 1H), 4.46 – 4.10 (m, 3H), 3.86 (dt, J = 12.1, 8.2 Hz, 1H), 2.40 – 2.28 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 139.54, 138.09 (d, J = 3.5 Hz), 137.37 (d, J = 17.3 Hz), 134.32 (d, J = 2.9 Hz), 129.85, 129.82, 129.10, 128.77 (d, J = 7.2 Hz), 126.62 (d, J = 1.9 Hz), 122.44 (qd, $J_{\text{F-C}}$ = 277.7 Hz, $J_{\text{P-C}}$ = 8.4 Hz), 122.36 (qd, $J_{\text{F-C}}$ = 277.7 Hz, $J_{\text{P-C}}$ = 8.2 Hz), 118.59 (d, J = 8.8 Hz), 62.79

(qd, J_{F-C} 44.4 Hz, J_{P-C} = 6.5 Hz), 62.37 (qd, J_{F-C} = 45.0 Hz, J_{P-C} = 7.0 Hz), 53.40, 45.51 (d, J = 140.5 Hz), 21.14. ^{31}P NMR (162 MHz, CDCl_3) δ 27.31. HRMS (ESI) Calcd. For $\text{C}_{21}\text{H}_{20}\text{ClF}_6\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 523.0635, found 523.0635.



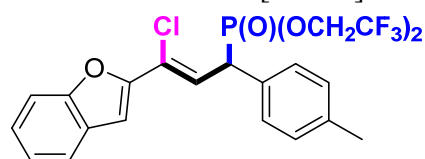
4ah

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 25 mg (46%) of **4ah**. **Bis(2,2,2-trifluoroethyl) (1-phenylvinyl)phosphonate**. Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 1.9 Hz, 1H), 7.93 – 7.75 (m, 3H), 7.67 (dd, J = 8.7, 1.9 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.39 (dd, J = 8.2, 2.4 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 6.62 (dd, J = 10.2, 8.1 Hz, 1H), 4.80 (dd, J = 24.7, 10.3 Hz, 1H), 4.52 – 4.13 (m, 3H), 3.87 (dt, J = 12.2, 8.2 Hz, 1H), 2.36 (d, J = 2.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.33 (d, J = 15.3 Hz), 144.35 (d, J = 3.6 Hz), 134.87 (d, J = 1.5 Hz), 132.07, 130.49 (d, J = 7.7 Hz), 129.56, 129.02 (d, J = 7.0 Hz), 128.88, 128.51 (d, J = 2.9 Hz), 122.41 (qd, J_{F-C} = 285.9 Hz, J_{P-C} = 8.4 Hz), 122.30 (qd, J_{F-C} = 275.5 Hz, J_{P-C} = 9.2 Hz), 62.58 (qd, J_{F-C} = 92.4 Hz, J_{P-C} = 7.4 Hz), 62.28 (qd, J_{F-C} = 92.0 Hz, J_{P-C} = 6.7 Hz), 38.45 (d, J = 141.2 Hz), 28.40, 15.28. ^{31}P NMR (162 MHz, CDCl_3) δ 27.20. HRMS (ESI) Calcd. For $\text{C}_{24}\text{H}_{20}\text{ClF}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 559.0635, found 559.0625.



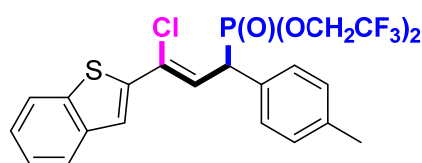
4ai

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 42 mg (78%) of **4ai**. **Bis(2,2,2-trifluoroethyl) (Z)-(3-chloro-3-(3-chloro-4-methylphenyl)-1-phenylallyl)phosphonate**. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, J = 2.0 Hz, 1H), 7.38 – 7.30 (m, 5H), 7.20 (d, J = 7.9 Hz, 2H), 6.45 (dd, J = 10.1, 8.1 Hz, 1H), 4.71 (dd, J = 24.7, 10.3 Hz, 1H), 4.40 – 4.17 (m, 3H), 3.92 – 3.74 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.23 (d, J = 3.6 Hz), 136.39, 136.23, 135.78 – 135.35 (m), 129.91 (d, J = 2.6 Hz), 129.56 (d, J = 8.4 Hz), 129.04, 128.76 (d, J = 7.1 Hz), 125.38 (d, J = 2.0 Hz), 122.38 (qd, J_{F-C} = 285.9 Hz, J_{P-C} = 8.1 Hz), 122.30 (qd, J_{F-C} = 285.8 Hz, J_{P-C} = 8.1 Hz), 119.83 (d, J = 8.7 Hz), 62.78 (qd, J_{F-C} = 57.2, J_{P-C} = 6.7 Hz), 62.40 (qd, J_{F-C} = 57.3, J_{P-C} = 6.7 Hz), 45.56 (d, J = 140.8 Hz), 21.06, 20.04. ^{31}P NMR (162 MHz, CDCl_3) δ 27.08. HRMS (ESI) Calcd. For $\text{C}_{21}\text{H}_{19}\text{Cl}_2\text{F}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 557.0245, found 557.0246.



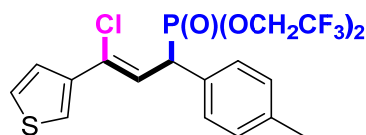
4aj

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 20 mg (37%) of **4aj**. **Bis(2,2,2-trifluoroethyl) (Z)-(3-(benzofuran-2-yl)-3-chloro-1-(p-tolyl)allyl)phosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.56 (d, $J = 7.7$ Hz, 1H), 7.46 (d, $J = 8.3$ Hz, 1H), 7.39 (dd, $J = 8.1, 2.4$ Hz, 2H), 7.33 (t, $J = 7.8$ Hz, 1H), 7.23 (t, $J = 9.5$ Hz, 3H), 7.00 – 6.88 (m, 2H), 4.71 (dd, $J = 24.8, 10.6$ Hz, 1H), 4.45 – 4.18 (m, 3H), 3.95 – 3.80 (m, 1H), 2.35 (d, $J = 2.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.31, 151.41 (d, $J = 4.3$ Hz), 138.30 (d, $J = 3.5$ Hz), 129.94 (d, $J = 2.7$ Hz), 129.37 (d, $J = 8.6$ Hz), 128.85, 128.78, 128.06, 125.96 (d, $J = 17.6$ Hz), 124.54 (d, $J = 249.7$ Hz), 122.36 (qd, $J_{\text{F-C}} = 285.8$ Hz, $J_{\text{P-C}} = 7.8$ Hz), 122.28 (qd, $J_{\text{F-C}} = 285.4$ Hz, $J_{\text{P-C}} = 7.9$ Hz), 121.63, 119.41 (d, $J = 9.2$ Hz), 111.22, 107.03 (d, $J = 2.9$ Hz), 62.94 (qd, $J_{\text{F-C}} = 37.9$ Hz, $J_{\text{P-C}} = 6.5$ Hz), 62.53 (qd, $J_{\text{F-C}} = 38.1$ Hz, $J_{\text{P-C}} = 6.9$ Hz), 44.86 (d, $J = 141.6$ Hz), 21.10. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 26.63. **HRMS (ESI)** Calcd. For $\text{C}_{22}\text{H}_{18}\text{ClF}_6\text{NaO}_4\text{P}$ $[\text{M}+\text{Na}]^+$: 549.0428, found 549.0426.



4ak

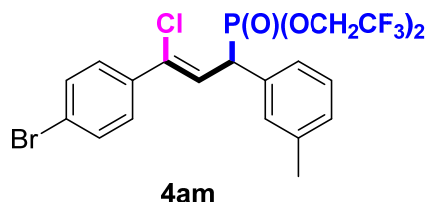
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 18 mg (33%) of **4ak**. **Bis(2,2,2-trifluoroethyl) (R,Z)-(3-(benzo[b]thiophen-2-yl)-3-chloro-1-(p-tolyl)allyl)phosphonate**. Colorless oil, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 – 7.71 (m, 2H), 7.57 (s, 1H), 7.39 – 7.31 (m, 4H), 7.21 (d, $J = 7.9$ Hz, 2H), 6.56 (dd, $J = 10.2, 8.3$ Hz, 1H), 4.72 (dd, $J = 24.9, 10.2$ Hz, 1H), 4.50 – 4.19 (m, 3H), 3.99 – 3.80 (m, 1H), 2.36 (d, $J = 2.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 139.68 (d, $J = 3.9$ Hz), 139.44, 139.18 (d, $J = 1.0$ Hz), 138.32 (d, $J = 3.4$ Hz), 130.75 (d, $J = 17.7$ Hz), 129.96 (d, $J = 2.7$ Hz), 129.35 (d, $J = 8.6$ Hz), 128.78 (d, $J = 7.2$ Hz), 125.73, 124.85, 124.43 (d, $J = 2.9$ Hz), 124.33 (d, $J = 9.1$ Hz), 122.36 (qd, $J_{\text{F-C}} = 270.0$ Hz, $J_{\text{P-C}} = 7.8$ Hz), 122.28 (qd, $J_{\text{F-C}} = 269.9$ Hz, $J_{\text{P-C}} = 7.5$ Hz), 122.09, 120.03 (d, $J = 9.1$ Hz), 62.90 (qd, $J_{\text{F-C}} = 44.5$ Hz, $J_{\text{P-C}} = 6.3$ Hz), 62.54 (qd, $J_{\text{F-C}} = 41.4$ Hz, $J_{\text{P-C}} = 6.9$ Hz), 45.45 (d, $J = 141.6$ Hz), 21.11. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 26.58. **HRMS (ESI)** Calcd. For $\text{C}_{22}\text{H}_{18}\text{ClF}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 565.0199, found 565.0207.



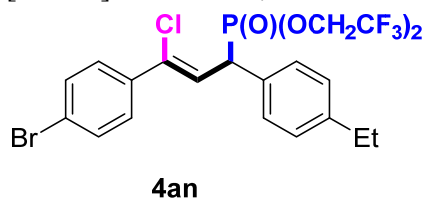
4al

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 21 mg (42%) of **4al**. **Dimethyl (1-(4-methoxyphenyl)vinyl)phosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.59 – 7.43 (m, 1H), 7.33 (td, $J = 8.0, 2.7$ Hz, 3H), 7.28 (dd, $J = 5.2, 1.4$ Hz, 1H), 7.20 (d, $J = 7.8$ Hz, 2H), 6.46 (dd, $J = 10.2, 8.2$ Hz, 1H), 4.69 (dd, $J = 24.7, 10.3$ Hz, 1H), 4.46 – 4.18 (m, 3H), 3.84 (dt, $J = 12.1, 8.2$ Hz, 1H), 2.35 (d, $J = 2.2$ Hz, 3H). $^{13}\text{C NMR}$

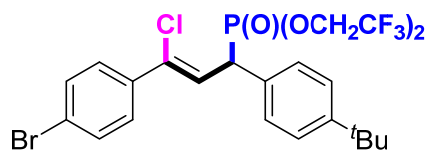
(101 MHz, CDCl₃) δ 138.60, 138.16 (d, $J = 3.4$ Hz), 132.06 (d, $J = 17.4$ Hz), 129.88 (d, $J = 2.6$ Hz), 129.76 (d, $J = 8.4$ Hz), 128.76 (d, $J = 7.3$ Hz), 126.55, 124.95, 124.51 (d, $J = 2.7$ Hz), 122.38 (qd, $J_{F-C} = 286.0$ Hz, $J_{P-C} = 8.7$ Hz), 122.32 (qd, $J_{F-C} = 282.2$ Hz, $J_{P-C} = 7.9$ Hz), 118.10 (d, $J = 8.7$ Hz), 62.80 (qd, $J_{F-C} = 52.5$ Hz, $J_{P-C} = 6.5$ Hz), 62.46 (qd, $J_{F-C} = 45.1$ Hz, $J_{P-C} = 7.4$ Hz), 45.13 (d, $J = 141.1$ Hz), 21.09. ³¹P NMR (162 MHz, CDCl₃) δ 27.18. HRMS (ESI) Calcd. For C₁₈H₁₆ClF₆NaO₃P [M+Na]⁺: 515.0043, found 515.0043.



Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 46 mg (82%) of **4am**. **Bis(2,2,2-trifluoroethyl) (Z)-(3-(4-bromophenyl)-3-chloro-1-(m-tolyl)allyl)phosphonate**. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.43 (m, 4H), 7.33 – 7.24 (m, 3H), 7.16 (dd, $J = 7.0, 2.0$ Hz, 1H), 6.48 (dd, $J = 10.3, 8.0$ Hz, 1H), 4.71 (dd, $J = 24.8, 10.3$ Hz, 1H), 4.41 – 4.14 (m, 3H), 3.83 (dt, $J = 12.1, 8.2$ Hz, 1H), 2.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 139.13 (d, $J = 2.7$ Hz), 136.25 (d, $J = 17.2$ Hz), 136.02 (d, $J = 3.0$ Hz), 132.44 (d, $J = 8.3$ Hz), 131.63, 129.62 (d, $J = 7.2$ Hz), 129.13 (dd, $J = 7.8, 3.1$ Hz), 128.27 (d, $J = 2.1$ Hz), 125.90 (d, $J = 7.2$ Hz), 123.65, 120.15 (d, $J = 8.9$ Hz), 122.41 (qd, $J_{F-C} = 277.9$ Hz, $J_{P-C} = 9.2$ Hz), 122.41 (qd, $J_{F-C} = 277.9$ Hz, $J_{P-C} = 8.6$ Hz), 62.77 (qd, $J_{F-C} = 60.9$ Hz, $J_{P-C} = 6.3$ Hz), 62.46 (qd, $J_{F-C} = 60.4$ Hz, $J_{P-C} = 6.9$ Hz), 45.99 (d, $J = 140.6$ Hz), 21.38. ³¹P NMR (162 MHz, CDCl₃) δ 26.79. HRMS (ESI) Calcd. For C₂₀H₁₇ClF₆NaO₃P [M+Na]⁺: 586.9584, found 586.9594.

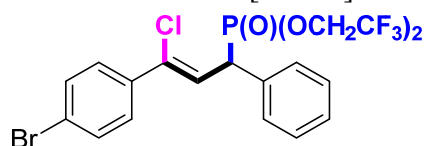


Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 50 mg (86%) of **4an**. **Bis(2,2,2-trifluoroethyl) (Z)-(3-(4-bromophenyl)-3-chloro-1-(4-ethylphenyl)allyl)phosphonate**. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.54 – 7.41 (m, 4H), 7.36 (dd, $J = 8.2, 2.4$ Hz, 2H), 7.23 (d, $J = 7.9$ Hz, 2H), 6.47 (dd, $J = 10.3, 8.0$ Hz, 1H), 4.72 (dd, $J = 24.7, 10.3$ Hz, 4H), 4.41 – 4.19 (m, 1H), 3.94 – 3.74 (m, 1H), 2.65 (q, $J = 7.4$ Hz, 2H), 1.28 – 1.21 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 194.33 (d, $J = 15.3$ Hz), 144.35 (d, $J = 3.6$ Hz), 134.87 (d, $J = 1.5$ Hz), 132.07, 130.49 (d, $J = 7.7$ Hz), 129.56, 129.02 (d, $J = 7.0$ Hz), 128.88, 128.51 (d, $J = 2.9$ Hz), 62.89 (d, $J = 43.7$ Hz), 61.97 (d, $J = 30.6$ Hz), 38.45 (d, $J = 141.2$ Hz), 28.40, 15.28. ³¹P NMR (162 MHz, CDCl₃) δ 26.88. HRMS (ESI) Calcd. For C₂₁H₁₉ClF₆NaO₃P [M+Na]⁺: 600.9740, found 600.9749.



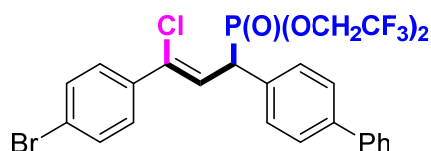
4ao

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 53 mg (88%) of **4ao**. **Bis(2,2,2-trifluoroethyl) (Z)-(3-(4-bromophenyl)-1-(4-(tert-butyl)phenyl)-3-chloroallyl)phosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 – 7.31 (m, 8H), 6.48 (dd, $J = 10.3, 7.8$ Hz, 1H), 4.73 (dd, $J = 24.7, 10.4$ Hz, 1H), 4.41 – 4.19 (m, 3H), 3.90 – 3.70 (m, 1H), 1.31 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.52 (d, $J = 3.5$ Hz), 136.14 (d, $J = 14.3$ Hz), 136.04, 131.61, 129.37 (d, $J = 8.4$ Hz), 128.55 (d, $J = 7.2$ Hz), 128.26 (d, $J = 2.1$ Hz), 126.19 (d, $J_{\text{F-C}} = 2.6$ Hz), 123.61 (d, $J = 8.9$ Hz), 122.42 (qd, $J_{\text{F-C}} = 277.6$ Hz, $J_{\text{P-C}} = 8.1$ Hz), 122.34 (qd, $J = 277.9$ Hz, $J_{\text{P-C}} = 7.8$ Hz), 120.23 (d, $J = 8.9$ Hz), 62.80 (qd, $J_{\text{F-C}} = 53.5$ Hz, $J_{\text{P-C}} = 6.5$ Hz), 62.43 (qd, $J_{\text{F-C}} = 53.7$ Hz, $J_{\text{P-C}} = 7.0$ Hz), 45.58 (d, $J = 140.7$ Hz), 34.58, 31.19. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 26.86. **HRMS (ESI)** Calcd. For $\text{C}_{23}\text{H}_{23}\text{ClF}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 629.0053, found 629.0048.



4ap

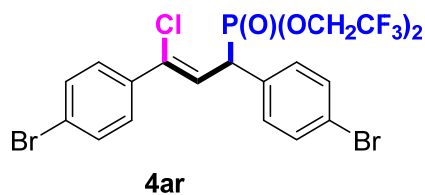
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 47 mg (85%) of **4ap**. **Ethyl (1-(4-bromophenyl)vinyl)(phenyl)phosphinate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53 – 7.44 (m, 4H), 7.41 (dd, $J = 13.8, 6.5$ Hz, 3H), 7.36 (dd, $J = 7.0, 1.9$ Hz, 1H), 6.49 (dd, $J = 10.3, 8.1$ Hz, 1H), 4.75 (dd, $J = 24.8, 10.3$ Hz, 1H), 4.42 – 4.18 (m, 3H), 3.95 – 3.72 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 136.42 (d, $J = 17.2$ Hz), 135.98 (d, $J = 3.0$ Hz), 132.64 (d, $J = 8.3$ Hz), 131.63, 129.24 (d, $J = 2.7$ Hz), 128.92 (d, $J = 7.3$ Hz), 128.39 (d, $J = 3.4$ Hz), 128.25 (d, $J = 2.0$ Hz), 123.68 (d, $J = 9.0$ Hz), 122.35 (qd, $J_{\text{F-C}} = 268.6$ Hz, $J_{\text{P-C}} = 9.2$ Hz), 122.25 (qd, $J_{\text{F-C}} = 269.8$ Hz, $J_{\text{P-C}} = 7.7$ Hz), 120.03 (d, $J = 9.0$ Hz), 62.91 (qd, $J_{\text{F-C}} = 37.9$ Hz, $J_{\text{P-C}} = 6.4$ Hz), 62.37 (qd, $J_{\text{F-C}} = 38.2$ Hz, $J_{\text{P-C}} = 6.9$ Hz), 46.02 (d, $J = 140.8$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 26.74. **HRMS (ESI)** Calcd. For $\text{C}_{19}\text{H}_{15}\text{ClF}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 572.9427, found 572.9428.



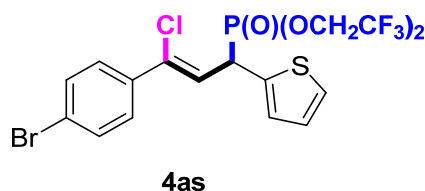
4aq

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 46 mg (74%) of **4aq**. **Bis(2,2,2-trifluoroethyl) (Z)-(1-([1,1'-biphenyl]-4-yl)-3-(4-bromophenyl)-3-chloroallyl)phosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.61 (dd, $J = 18.9, 7.8$ Hz, 4H), 7.56 – 7.42 (m, 8H), 7.36 (t, $J = 7.2$

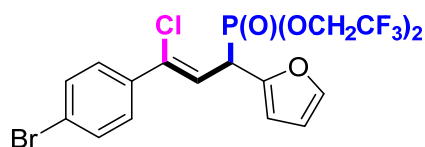
Hz, 1H), 6.52 (dd, $J = 10.3, 8.0$ Hz, 1H), 4.80 (dd, $J = 24.8, 10.3$ Hz, 1H), 4.48 – 4.20 (m, 3H), 4.03 – 3.83 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.28 (d, $J = 3.5$ Hz), 140.04, 136.53 (d, $J = 17.2$ Hz), 135.94 (d, $J = 3.0$ Hz), 131.65, 131.51 (d, $J = 8.4$ Hz), 129.30 (d, $J = 7.3$ Hz), 128.86, 128.26 (d, $J = 2.0$ Hz), 127.87 (d, $J = 2.8$ Hz), 127.67, 127.02 (d, $J = 8.9$ Hz), 123.71, 122.40 (qd, $J_{\text{F-C}} = 277.4$ Hz, $J_{\text{P-C}} = 5.7$ Hz), 122.23 (qd, $J_{\text{F-C}} = 278.0$ Hz, $J_{\text{P-C}} = 8.9$ Hz), 119.90 (d, $J = 8.9$ Hz), 62.87 (qd, $J_{\text{F-C}} = 51.7$ Hz, $J_{\text{P-C}} = 6.5$ Hz), 62.49 (qd, $J_{\text{F-C}} = 51.9$ Hz, $J_{\text{P-C}} = 6.8$ Hz), 45.67 (d, $J = 141.0$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 26.67. HRMS (ESI) Calcd. For $\text{C}_{25}\text{H}_{19}\text{ClF}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 648.9740, found 648.9731.



Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 52 mg (82%) of **4ar**. **Bis(2,2,2-trifluoroethyl) (Z)-(1,3-bis(4-bromophenyl)-3-chloroallyl)phosphonate**. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.52 (t, $J = 8.1$ Hz, 4H), 7.43 (d, $J = 8.7$ Hz, 2H), 7.33 (dd, $J = 8.6, 2.4$ Hz, 2H), 6.42 (dd, $J = 10.2, 8.2$ Hz, 1H), 4.70 (dd, $J = 24.8, 10.2$ Hz, 1H), 4.47 – 4.17 (m, 3H), 4.09 – 3.86 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.60, 138.16 (d, $J = 3.4$ Hz), 132.06 (d, $J = 17.4$ Hz), 129.88 (d, $J = 2.6$ Hz), 129.76 (d, $J = 8.4$ Hz), 128.76 (d, $J = 7.3$ Hz), 126.55, 124.95, 124.51 (d, $J = 2.7$ Hz), 122.34 (qd, $J_{\text{F-C}} = 277.1$ Hz, $J_{\text{P-C}} = 7.3$ Hz), 122.25 (qd, $J_{\text{F-C}} = 277.7$ Hz, $J_{\text{P-C}} = 7.1$ Hz), 118.10 (d, $J = 8.7$ Hz), 62.88 (qd, $J_{\text{F-C}} = 44.7$ Hz, $J_{\text{P-C}} = 5.2$ Hz), 62.46 (qd, $J_{\text{F-C}} = 38.1$ Hz, $J_{\text{P-C}} = 5.4$ Hz), 45.13 (d, $J = 141.1$ Hz), 21.09. ^{31}P NMR (162 MHz, CDCl_3) δ 26.08. HRMS (ESI) Calcd. For $\text{C}_{19}\text{H}_{14}\text{Br}_2\text{ClF}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 650.8532, found 650.8539.

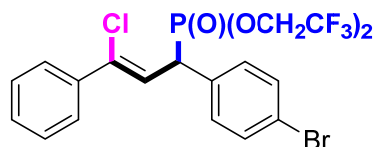


Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 23 mg (41%) of **4as**. **Bis(2,2,2-trifluoroethyl) (Z)-(3-(4-bromophenyl)-3-chloro-1-(thiophen-2-yl)allyl)phosphonate**. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 8.7$ Hz, 2H), 7.45 (d, $J = 8.7$ Hz, 2H), 7.43 – 7.34 (m, 2H), 7.20 (d, $J = 5.0$ Hz, 1H), 6.39 (dd, $J = 10.3, 7.3$ Hz, 1H), 4.92 (dd, $J = 24.6, 10.3$ Hz, 1H), 4.42 – 4.22 (m, 3H), 4.04 – 3.89 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.40 (d, $J = 16.6$ Hz), 135.88 (d, $J = 3.1$ Hz), 131.79 (d, $J = 8.8$ Hz), 131.66, 128.25 (d, $J = 2.1$ Hz), 127.46 (d, $J = 5.2$ Hz), 126.93 (d, $J = 1.7$ Hz), 123.92 (d, $J = 9.9$ Hz), 123.74 (d, $J = 9.3$ Hz), 122.30 (qd, $J_{\text{F-C}} = 274.0$ Hz, $J_{\text{P-C}} = 3.7$ Hz), 122.26 (qd, $J_{\text{F-C}} = 273.8$ Hz, $J_{\text{P-C}} = 4.3$ Hz), 119.68 (d, $J = 9.3$ Hz), 62.84 (qd, $J_{\text{F-C}} = 44.2$ Hz, $J_{\text{P-C}} = 6.2$ Hz), 62.47 (qd, $J_{\text{F-C}} = 41.7$ Hz, $J_{\text{P-C}} = 6.8$ Hz), 41.56 (d, $J = 143.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 25.79. HRMS (ESI) Calcd. For $\text{C}_{17}\text{H}_{13}\text{BrClF}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 578.8991, found 578.9001.



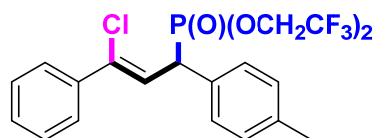
4at

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 19 mg (35%) of **4at**. **Bis(2,2,2-trifluoroethyl) (Z)-(3-(4-bromophenyl)-3-chloro-1-(furan-2-yl)allyl)phosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.58 (dd, $J = 7.5, 2.2$ Hz, 3H), 7.41 – 7.36 (m, 3H), 6.07 (dd, $J = 10.9, 6.8$ Hz, 1H), 4.46 – 4.18 (m, 5H), 3.54 – 3.18 (m, $J = 22.9, 10.9, 5.2$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.38, 138.21, 137.30, 129.30, 128.50, 126.64 (d, $J = 2.4$ Hz), 122.60 (d, $J_{\text{F-C}} = 277.4$ Hz, $J_{\text{P-C}} = 4.2$ Hz), 122.53 (d, $J_{\text{F-C}} = 273.0$ Hz, $J_{\text{P-C}} = 3.3$ Hz), 118.73 (d, $J = 10.0$ Hz), 45.31 (d, $J = 137.1$ Hz), 62.10 (d, $J_{\text{F-C}} = 37.7$ Hz, $J_{\text{P-C}} = 6.7$ Hz), 61.93 (d, $J_{\text{F-C}} = 37.5$ Hz, $J_{\text{P-C}} = 6.1$ Hz), 38.48 (d, $J = 3.7$ Hz), 32.16 (d, $J = 7.17$ Hz), 29.97 (d, $J = 7.17$ Hz), 25.78. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 30.27. **HRMS (ESI)** Calcd. For $\text{C}_{17}\text{H}_{13}\text{BrClF}_6\text{NaO}_4\text{P}$ $[\text{M}+\text{Na}]^+$: 562.9220, found 562.9229.



4au

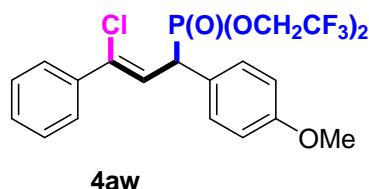
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 48 mg (88%) of **4au**. **Bis(2,2,2-trifluoroethyl) (1-(4-chlorophenyl)vinyl)phosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 (dd, $J = 6.8, 2.8$ Hz, 2H), 7.53 (d, $J = 8.2$ Hz, 2H), 7.41 – 7.37 (m, 3H), 7.35 (d, $J = 2.5$ Hz, 1H), 7.33 (d, $J = 2.4$ Hz, 1H), 6.43 (dd, $J = 10.2, 8.2$ Hz, 1H), 4.73 (dd, $J = 24.8, 10.2$ Hz, 1H), 4.50 – 4.23 (m, 3H), 4.06 – 3.94 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.13 (d, $J = 17.1$ Hz), 136.86 (d, $J = 2.9$ Hz), 132.31 (d, $J = 2.7$ Hz), 132.07 (d, $J = 8.2$ Hz), 130.53 (d, $J = 7.2$ Hz), 129.60, 128.53, 126.74 (d, $J = 1.8$ Hz), 122.42 (d, $J = 4.2$ Hz), 122.37 (qd, $J_{\text{F-C}} = 277.9$ Hz, $J_{\text{P-C}} = 8.6$ Hz), 122.28 (qd, $J_{\text{F-C}} = 277.8$ Hz, $J_{\text{P-C}} = 8.6$ Hz), 118.73 (d, $J = 8.8$ Hz), 62.84 (qd, $J_{\text{F-C}} = 38.1$ Hz, $J_{\text{P-C}} = 6.6$ Hz), 62.58 (qd, $J_{\text{F-C}} = 38.2$ Hz, $J_{\text{P-C}} = 6.7$ Hz), 45.35 (d, $J = 141.6$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 26.34. **HRMS (ESI)** Calcd. For $\text{C}_{19}\text{H}_{15}\text{BrClF}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 572.9427, found 572.9428.



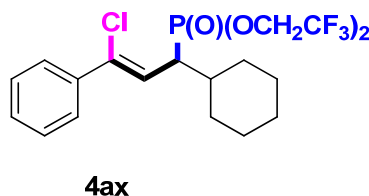
4av

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 44 mg (90%) of **4av**. **Bis(2,2,2-trifluoroethyl) (1-(4-methoxyphenyl)vinyl)phosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 (dd, $J = 6.5, 3.2$ Hz, 2H), 7.35 (td, $J = 6.6, 5.8, 2.3$ Hz, 5H), 7.20 (d, $J = 7.7$ Hz, 2H), 6.48 (dd, $J = 10.3, 8.1$ Hz, 1H), 4.74 (dd, $J = 24.7, 10.3$ Hz, 1H), 4.44 – 4.12 (m,

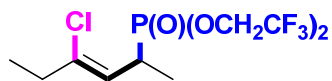
3H), 3.86 (dt, $J = 12.1, 8.2$ Hz, 1H), 2.35 (d, $J = 2.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.15 (d, $J = 3.5$ Hz), 137.30 (d, $J = 17.2$ Hz), 137.13 (d, $J = 2.9$ Hz), 129.87 (d, $J = 2.6$ Hz), 129.71 (d, $J = 8.4$ Hz), 129.36, 128.78 (d, $J = 7.2$ Hz), 128.44, 126.74 (d, $J = 2.0$ Hz), 122.44 (qd, $J_{\text{F-C}} = 277.7$ Hz, $J_{\text{P-C}} = 8.4$ Hz), 122.36 (qd, $J_{\text{F-C}} = 277.6$ Hz, $J_{\text{P-C}} = 8.1$ Hz), 119.61 (d, $J = 8.7$ Hz), 62.81 (qd, $J_{\text{F-C}} = 46.8$ Hz, $J_{\text{P-C}} = 6.5$ Hz), 62.44 (qd, $J_{\text{F-C}} = 47.0$ Hz, $J_{\text{P-C}} = 7.0$ Hz), 45.55 (d, $J = 140.8$ Hz), 21.07. ^{31}P NMR (162 MHz, CDCl_3) δ 27.21. HRMS (ESI) Calcd. For $\text{C}_{20}\text{H}_{18}\text{ClF}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 509.0478, found 509.0469.



Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 36 mg (72%) of **4aw**. **Bis(2,2,2-trifluoroethyl) (1-(4-fluorophenyl)vinyl)phosphonate**. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.58 (dd, $J = 6.5, 3.2$ Hz, 2H), 7.45 – 7.30 (m, 5H), 6.92 (d, $J = 8.6$ Hz, 2H), 6.46 (dd, $J = 10.2, 8.0$ Hz, 1H), 4.72 (dd, $J = 24.6, 10.3$ Hz, 1H), 4.45 – 4.16 (m, 3H), 3.88 (dt, $J = 12.1, 8.2$ Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.47 (d, $J = 3.2$ Hz), 137.27 (d, $J = 17.3$ Hz), 137.12 (d, $J = 2.9$ Hz), 130.03 (d, $J = 7.2$ Hz), 129.37, 128.45, 126.74 (d, $J = 2.1$ Hz), 124.59 (d, $J = 8.5$ Hz), 122.44 (qd, $J_{\text{F-C}} = 277.4$ Hz, $J_{\text{P-C}} = 8.2$ Hz), 122.36 (qd, $J_{\text{F-C}} = 277.7$ Hz, $J_{\text{P-C}} = 7.8$ Hz), 119.65 (d, $J = 8.4$ Hz), 114.58 (d, $J = 2.5$ Hz), 62.81 (qd, $J_{\text{F-C}} = 46.6$ Hz, $J_{\text{P-C}} = 6.4$ Hz), 62.43 (qd, $J_{\text{F-C}} = 46.7$ Hz, $J_{\text{P-C}} = 7.1$ Hz), 55.28, 45.05 (d, $J = 141.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 27.25. HRMS (ESI) Calcd. For $\text{C}_{20}\text{H}_{18}\text{ClF}_6\text{NaO}_4\text{P}$ $[\text{M}+\text{Na}]^+$: 525.0425, found 525.0428.

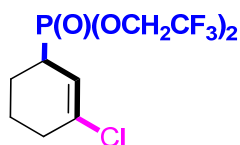


Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 23 mg (48%) of **4bx**. **Bis(2,2,2-trifluoroethyl) (Z)-(3-chloro-1-cyclohexyl-3-phenylallyl)phosphonate**. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.58 (dd, $J = 7.5, 2.2$ Hz, 2H), 7.38 (dd, $J = 5.2, 2.2$ Hz, 2H), 6.07 (dd, $J = 10.9, 6.8$ Hz, 1H), 4.47 – 4.22 (m, 3H), 3.49 (ddd, $J = 22.9, 10.9, 5.2$ Hz, 1H), 2.00 – 1.62 (m, 5H), 1.37 – 1.06 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.29 (d, $J = 17.5$ Hz), 137.28 (d, $J = 3.5$ Hz), 129.30, 128.50, 126.64 (d, $J = 2.4$ Hz), 122.58 (qd, $J_{\text{F-C}} = 273.2$ Hz, $J_{\text{P-C}} = 4.2$ Hz), 122.53 (qd, $J_{\text{F-C}} = 273.0$ Hz, $J_{\text{P-C}} = 4.5$ Hz), 118.73 (d, $J = 10.0$ Hz), 62.10 (qd, $J_{\text{F-C}} = 37.6$ Hz, $J_{\text{P-C}} = 6.7$ Hz), 61.99 (qd, $J_{\text{F-C}} = 37.9$ Hz, $J_{\text{P-C}} = 6.0$ Hz), 45.31 (d, $J = 137.1$ Hz), 38.48 (d, $J = 3.7$ Hz), 32.16 (d, $J = 12.3$ Hz), 29.97 (d, $J = 7.2$ Hz), 25.95 (d, $J = 33.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 30.27. HRMS (ESI) Calcd. For $\text{C}_{19}\text{H}_{22}\text{ClF}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 501.0791, found 501.0798.



4ay
Z:E = 3:1

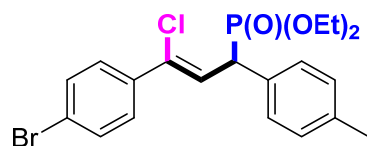
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 16 mg (43%) of **4by**. **Bis(2,2,2-trifluoroethyl) (Z)-(4-chlorohex-3-en-2-yl)phosphonate**. Colorless oil. **Select the major product:** $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.65 (q, $J = 6.5$ Hz, 1H), 4.57 – 4.27 (m, 4H), 2.91 – 2.69 (m, 1H), 2.59 – 2.24 (m, 2H), 1.75 (dd, $J = 6.6, 1.6$ Hz, 3H), 1.18 (dd, $J = 19.8, 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.22, 131.14, 123.87, 122.57 (qd, $J_{\text{F-C}} = 285.1$ Hz, $J_{\text{P-C}} = 4.9$ Hz), 122.51 (qd, $J_{\text{F-C}} = 282.4$ Hz, $J_{\text{P-C}} = 7.7$ Hz), 62.20 (qd, $J_{\text{F-C}} = 63.2$ Hz, $J_{\text{P-C}} = 25.3$ Hz), 61.98 (qd, $J_{\text{F-C}} = 44.3$ Hz, $J_{\text{P-C}} = 24.7$ Hz), 39.53 (d, $J = 1.6$ Hz), 29.05 (d, $J = 142.4$ Hz), 14.02. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 36.96. **Select the minor product:** $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.38 (dd, $J = 10.0, 6.2$ Hz, 1H), 4.57 – 4.27 (m, 4H), 2.91 – 2.69 (m, 1H), 2.59 – 2.24 (m, 2H), 1.75 (dd, $J = 6.6, 1.6$ Hz, 3H), 1.18 (dd, $J = 19.8, 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.22, 130.95, 123.95 (d, $J = 7.7$ Hz), 123.87, 122.57 (qd, $J_{\text{F-C}} = 285.1$ Hz, $J_{\text{P-C}} = 4.9$ Hz), 122.51 (qd, $J_{\text{F-C}} = 282.4$ Hz, $J_{\text{P-C}} = 7.7$ Hz), 62.20 (qd, $J_{\text{F-C}} = 63.2$ Hz, $J_{\text{P-C}} = 25.3$ Hz), 61.98 (qd, $J_{\text{F-C}} = 44.3$ Hz, $J_{\text{P-C}} = 24.7$ Hz), 39.53 (d, $J = 1.6$ Hz), 29.05 (d, $J = 142.4$ Hz), 11.85 (d, $J = 4.9$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 32.64. **HRMS (ESI)** Calcd. For $\text{C}_{10}\text{H}_{14}\text{ClF}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 385.0165, found 385.0169.



4az
Z:E = 1.2:1

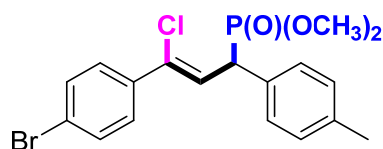
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 16 mg (44%) of **4bz**. **Bis(2,2,2-trifluoroethyl) (R)-(3-chlorocyclohex-2-en-1-yl)phosphonate**. Colorless oil. **Select the major product:** $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.88 (s, 1H), 4.46 – 4.36 (m, 4H), 3.00 – 2.54 (m, 1H), 2.53 – 1.67 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.56 (d, $J = 17.1$ Hz), 129.09 (d, $J = 22.3$ Hz), 124.29, 116.42 (d, $J = 9.3$ Hz), 122.48 (qd, $J_{\text{F-C}} = 284.9$ Hz, $J_{\text{P-C}} = 7.5$ Hz), 122.42 (qd, $J_{\text{F-C}} = 282.5$ Hz, $J_{\text{P-C}} = 7.4$ Hz), 62.49 (qd, $J_{\text{F-C}} = 32.3$, $J_{\text{P-C}} = 6.4$ Hz), 62.08 (qd, $J_{\text{F-C}} = 37.8$, $J_{\text{P-C}} = 5.3$ Hz), 33.08 (d, $J = 146.7$ Hz), 31.15 (d, $J = 3.2$ Hz), 25.31 (d, $J = 17.9$ Hz), 20.52 (d, $J = 4.6$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 33.65. **Select the minor product:** $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.84 – 5.77 (m, 1H), 4.46 – 4.36 (m, 4H), 3.00 – 2.54 (m, 1H), 2.53 – 1.67 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.56 (d, $J = 17.1$ Hz), 129.09 (d, $J = 22.3$ Hz), 124.30 (d, $J = 1.7$ Hz), 122.48 (qd, $J_{\text{F-C}} = 284.9$ Hz, $J_{\text{P-C}} = 7.5$ Hz), 122.42 (qd, $J_{\text{F-C}} = 282.5$ Hz, $J_{\text{P-C}} = 7.4$ Hz), 116.42 (d, $J = 9.3$ Hz), 62.49 (qd, $J_{\text{F-C}} = 32.3$, $J_{\text{P-C}} = 6.4$ Hz), 62.08 (qd, $J_{\text{F-C}} = 37.8$, $J_{\text{P-C}} = 5.3$ Hz), 35.70 (d, $J = 143.9$ Hz), 32.15 (d, $J = 3.2$ Hz), 21.53 (d, $J = 10.2$ Hz), 20.94 (d, $J = 5.0$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 31.10. **HRMS (ESI)** Calcd. For $\text{C}_{10}\text{H}_{12}\text{ClF}_6\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$:

383.0009, found 383.0006.



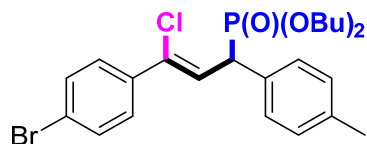
4ba

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 40 mg (85%) of **4ba**. **(Z)-3-(4-bromophenyl)-3-chloro-1-(p-tolyl)allyl(oxo)phosphane--ethoxyethane (1/1)**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.24 (s, 4H), 7.19 – 7.15 (m, 2H), 6.95 (d, $J = 7.8$ Hz, 2H), 6.37 (dd, $J = 10.4$, 7.9 Hz, 1H), 4.34 (dd, $J = 23.1$, 10.4 Hz, 1H), 3.96 – 3.86 (m, 2H), 3.83 – 3.73 (m, 1H), 3.68 – 3.55 (m, 1H), 2.21 – 2.01 (m, 3H), 1.08 (t, $J = 7.2$ Hz, 3H), 0.93 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 136.51 (dd, $J = 82.3$, 2.6 Hz), 133.91 (d, $J = 16.0$ Hz), 131.41 (d, $J = 8.0$ Hz), 131.18, 129.25 (d, $J = 2.2$ Hz), 128.53 (d, $J = 6.6$ Hz), 127.91 (d, $J = 1.6$ Hz), 122.83, 122.75 (d, $J = 8.1$ Hz), 62.74 (d, $J = 6.9$ Hz), 62.41 (d, $J = 7.2$ Hz), 45.60 (d, $J = 138.9$ Hz), 20.83, 16.12 (dd, $J = 22.1$, 5.6 Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 24.03. **HRMS (ESI)** Calcd. For $\text{C}_{20}\text{H}_{23}\text{BrClNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 479.0149, found 479.0149.



4bb

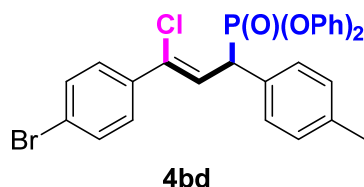
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 30 mg (71%) of **4bb**. **Dimethyl (Z)-3-(4-bromophenyl)-3-chloro-1-(p-tolyl)propylphosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46 (s, 4H), 7.35 (dd, $J = 8.1$, 2.2 Hz, 2H), 7.17 (d, $J = 7.8$ Hz, 2H), 6.54 (dd, $J = 10.4$, 8.0 Hz, 1H), 4.55 (dd, $J = 23.1$, 10.4 Hz, 1H), 3.75 (d, $J = 10.7$ Hz, 3H), 3.56 (d, $J = 10.7$ Hz, 3H), 2.33 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.40 (d, $J = 3.0$ Hz), 136.26 (d, $J = 2.4$ Hz), 134.40 (d, $J = 16.2$ Hz), 131.46, 129.63 (d, $J = 2.4$ Hz), 128.72 (d, $J = 6.9$ Hz), 128.21 (d, $J = 1.7$ Hz), 123.19, 122.60 (d, $J = 8.1$ Hz), 53.66 (d, $J = 7.0$ Hz), 53.35 (d, $J = 7.3$ Hz), 45.35 (d, $J = 139.2$ Hz), 21.07. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 26.42. **HRMS (ESI)** Calcd. For $\text{C}_{18}\text{H}_{19}\text{BrClNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 450.9836, found 450.9837.



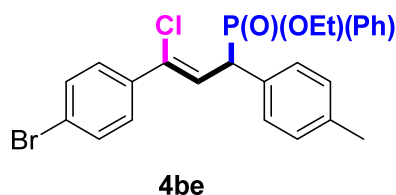
4bc

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 36 mg (70%) of **4bc**. **Dibutyl (Z)-3-(4-bromophenyl)-3-chloro-1-(p-tolyl)allylphosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.23 (d, $J = 5.1$ Hz, 3H), 7.13 (d, $J = 7.7$ Hz, 2H), 6.93 (d, $J = 7.5$ Hz, 2H), 6.31 (t, $J = 8.7$ Hz, 1H), 4.31 (dd, $J = 23.4$, 10.2 Hz, 1H), 3.79 (d, $J = 6.7$ Hz, 2H), 3.67 (d, $J = 6.7$ Hz, 1H), 3.52 (d, $J = 7.9$ Hz, 1H), 2.10 (s, 3H), 1.37 (q, $J = 6.7$ Hz, 2H), 1.21 (q, $J = 7.3$ Hz, 2H), 1.13

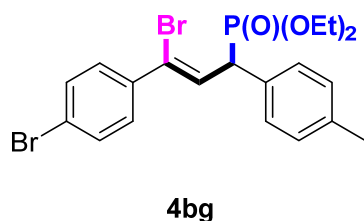
(q, $J = 7.3$ Hz, 2H), 1.06 – 0.97 (m, 2H), 0.63 (dt, $J = 23.1, 7.4$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.21, 136.46, 131.72, 131.43, 129.48, 128.80, 128.21, 123.13, 123.06, 66.69, 66.26, 32.54, 32.36, 21.06, 13.58, 13.52. ^{31}P NMR (162 MHz, CDCl_3) δ 23.98. HRMS (ESI) Calcd. For $\text{C}_{24}\text{H}_{31}\text{BrClNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 535.0775, found 535.0786.



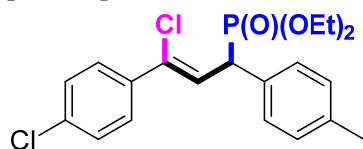
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 24 mg (43%) of **4bd**. **Diphenyl (Z)-3-(4-bromophenyl)-3-chloro-1-(p-tolyl)allylphosphonate**. Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.44 (m, 2H), 7.43 (dd, $J = 8.2, 2.3$ Hz, 2H), 7.39 – 7.27 (m, 3H), 7.27 – 7.07 (m, 9H), 6.93 – 6.86 (m, 2H), 6.62 (dd, $J = 10.4, 8.5$ Hz, 1H), 4.91 (dd, $J = 23.5, 10.4$ Hz, 1H), 2.34 (d, $J = 2.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.41 (dd, $J = 23.2, 9.9$ Hz), 137.74 (d, $J = 3.3$ Hz), 131.47, 130.64 (d, $J = 8.2$ Hz), 129.84, 129.72 (d, $J = 2.5$ Hz), 129.60 (d, $J = 10.1$ Hz), 129.04 (d, $J = 7.3$ Hz), 128.29 (d, $J = 1.9$ Hz), 125.59, 125.10 (d, $J = 7.0$ Hz), 123.37, 121.63 (d, $J = 8.0$ Hz), 120.44 (dd, $J = 4.2, 3.3$ Hz), 46.09 (d, $J = 140.9$ Hz), 21.11. ^{31}P NMR (162 MHz, CDCl_3) δ 16.65. HRMS (ESI) Calcd. For $\text{C}_{28}\text{H}_{23}\text{BrClNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 575.0149, found 575.0160.



Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 33 mg (68%) of **4be**. **Ethyl (Z)-3-(4-bromophenyl)-3-chloro-1-(p-tolyl)allyl(phenyl)phosphinate**. Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 7.80 – 7.71 (m, 1H), 7.66 – 7.56 (m, 1H), 7.55 – 7.24 (m, 8H), 7.15 (d, $J = 7.9$ Hz, 2H), 7.03 (d, $J = 7.9$ Hz, 1H), 6.46 (dd, $J = 10.8, 7.5$ Hz, 1H), 4.64 – 4.50 (m, 1H), 4.03 – 3.85 (m, 2H), 2.36 – 2.24 (m, 3H), 1.23 (dt, $J = 54.1, 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.07 (d, $J = 2.7$ Hz), 136.77 (dd, $J = 32.0, 2.8$ Hz), 136.46 (d, $J = 2.6$ Hz), 134.54 (d, $J = 14.8$ Hz), 132.35 (d, $J = 2.9$ Hz), 132.01 (d, $J = 9.5$ Hz), 131.33, 129.35 (d, $J = 2.1$ Hz), 129.03 (d, $J = 5.7$ Hz), 128.25 (d, $J = 12.5$ Hz), 128.10, 122.98, 122.78 (d, $J = 8.4$ Hz), 122.63 (d, $J = 4.4$ Hz), 61.51 (t, $J = 7.6$ Hz), 49.10 (d, $J = 94.1$ Hz), 16.54 (d, $J = 6.0$ Hz), 16.33 (d, $J = 6.0$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 37.72. HRMS (ESI) Calcd. For $\text{C}_{24}\text{H}_{23}\text{BrClNaO}_2\text{P}$ $[\text{M}+\text{Na}]^+$: 511.0200, found 511.0200.

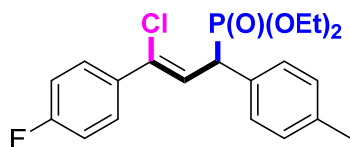


Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 38 mg (75%) of **4bg**. **Diethyl (Z)-(3-bromo-3-(4-bromophenyl)-1-(p-tolyl)allyl)phosphonate**. Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.48 – 7.38 (m, 4H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.16 (d, $J = 7.7$ Hz, 2H), 6.66 – 6.57 (m, 1H), 4.48 (dd, $J = 22.9, 10.3$ Hz, 1H), 4.10 (td, $J = 8.3, 7.7, 2.7$ Hz, 2H), 4.04 – 3.93 (m, 1H), 3.82 (dd, $J = 16.3, 8.1$ Hz, 1H), 2.33 (s, 0H), 1.31-1.12 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.25 (d, $J = 1.9$ Hz), 137.24 (d, $J = 2.5$ Hz), 131.39, 129.51 (d, $J = 2.2$ Hz), 129.28, 128.81 (d, $J = 6.7$ Hz), 126.91 (d, $J = 7.5$ Hz), 123.06, 62.99 (d, $J = 7.0$ Hz), 62.67 (d, $J = 7.1$ Hz), 48.77 (d, $J = 137.5$ Hz), 21.08, 16.48 (d, $J = 5.7$ Hz), 16.24 (d, $J = 5.9$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 23.76. **HRMS (ESI)** Calcd. For $\text{C}_{20}\text{H}_{23}\text{Br}_2\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 522.9644, found 522.9644.



4ca

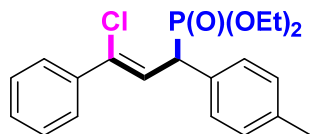
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 33 mg (81%) of **4ca**. **Diethyl (R,Z)-(3-chloro-3-(4-chlorophenyl)-1-(p-tolyl)allyl)phosphonate**. Colorless oil, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 (d, $J = 8.7$ Hz, 2H), 7.39 – 7.28 (m, 4H), 7.16 (d, $J = 7.8$ Hz, 2H), 6.56 – 6.50 (m, 1H), 4.53 (dd, $J = 23.0, 10.4$ Hz, 1H), 4.17 – 3.89 (m, 3H), 3.81 (ddt, $J = 15.3, 10.1, 7.0$ Hz, 1H), 2.33 (d, $J = 1.8$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.14 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.21 (d, $J = 3.1$ Hz), 135.96 (d, $J = 2.6$ Hz), 134.85, 134.10 (d, $J = 15.9$ Hz), 131.74 (d, $J = 7.9$ Hz), 129.49 (d, $J = 2.3$ Hz), 128.77 (d, $J = 6.8$ Hz), 128.48, 127.92 (d, $J = 1.8$ Hz), 122.95 (d, $J = 8.1$ Hz), 62.81 (dd, $J = 31.8, 7.1$ Hz), 45.82 (d, $J = 139.0$ Hz), 21.07, 16.34 (dd, $J = 21.9, 5.9$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 24.11. **HRMS (ESI)** Calcd. For $\text{C}_{20}\text{H}_{13}\text{Cl}_2\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 435.0654, found. 435.0652.



4cb

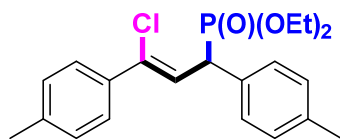
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 35 mg (88%) of **4cb**. **Diethyl (R,Z)-(3-chloro-3-(4-fluorophenyl)-1-(p-tolyl)allyl)phosphonate**. Colorless oil, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.60 – 7.53 (m, 2H), 7.39 – 7.33 (m, 2H), 7.16 (d, $J = 7.8$ Hz, 2H), 7.03 (t, $J = 8.6$ Hz, 2H), 6.54 – 6.44 (m, 1H), 4.52 (dd, $J = 23.1, 10.4$ Hz, 1H), 4.18 – 3.92 (m, 3H), 3.88 – 3.75 (m, 1H), 2.33 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.14 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.00 (d, $J = 249.3$ Hz), 137.16 (d, $J = 3.1$ Hz), 134.17 (d, $J = 16.1$ Hz), 133.73, 131.86 (d, $J = 7.8$ Hz), 129.47 (d, $J = 2.3$ Hz), 128.77 (d, $J = 6.7$ Hz), 128.53 (dd, $J = 8.4, 1.7$ Hz), 122.37 (d, $J = 7.8$ Hz), 115.26 (d, $J = 21.8$ Hz), 62.78 (d

d, $J = 29.7, 7.1$ Hz), 45.79 (d, $J = 139.0$ Hz), 21.06, 16.34 (dd, $J = 21.9, 5.9$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 24.25. HRMS (ESI) Calcd. For $\text{C}_{20}\text{H}_{23}\text{ClNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 419.0950, found. 419.0946.



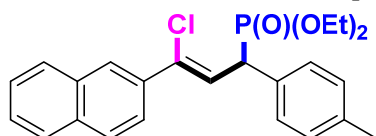
4cc

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 31 mg (83%) of **4cc**. Diethyl (*R,Z*)-(3-chloro-3-phenyl-1-(*p*-tolyl)allyl)phosphonate. Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.56 (m, 2H), 7.39 – 7.32 (m, 5H), 7.16 (d, $J = 7.7$ Hz, 2H), 6.59 – 6.49 (m, 1H), 4.56 (dd, $J = 23.1, 10.4$ Hz, 1H), 4.17 – 3.94 (m, 3H), 3.83 (dt, $J = 10.0, 7.4$ Hz, 1H), 2.33 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.15 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.53 (d, $J = 2.5$ Hz), 137.07 (d, $J = 3.1$ Hz), 135.28 (d, $J = 16.1$ Hz), 131.95 (d, $J = 8.0$ Hz), 129.44 (d, $J = 2.4$ Hz), 128.91, 128.80 (d, $J = 6.9$ Hz), 128.30, 126.67 (d, $J = 1.8$ Hz), 12.237 (d, $J = 8.1$ Hz), 62.76 (dd, $J = 20.0, 7.1$ Hz), 45.75 (d, $J = 138.7$ Hz), 21.07, 16.35 (dd, $J = 21.8, 6.0$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 24.33. HRMS (ESI) Calcd. For $\text{C}_{20}\text{H}_{24}\text{ClNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 401.1044, found. 401.1045.



4cd

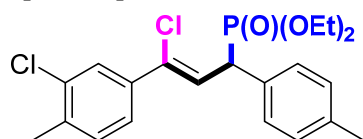
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 33 mg (84%) of **4cd**. Diethyl (*R,Z*)-(3-chloro-1,3-di-*p*-tolylallyl)phosphonate. Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.2$ Hz, 2H), 7.39 – 7.32 (m, 2H), 7.15 (d, $J = 7.9$ Hz, 4H), 6.54 – 6.46 (m, 1H), 4.54 (dd, $J = 23.1, 10.4$ Hz, 1H), 4.15 – 3.93 (m, 3H), 3.90 – 3.76 (m, 1H), 2.38 – 2.27 (m, 6H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.14 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.97, 136.99 (d, $J = 3.0$ Hz), 135.43, 135.27, 134.77 (d, $J = 2.5$ Hz), 132.10 (d, $J = 7.9$ Hz), 129.39 (d, $J = 2.4$ Hz), 128.95, 128.80 (d, $J = 6.8$ Hz), 126.55 (d, $J = 1.8$ Hz), 121.40 (d, $J = 8.2$ Hz), 62.71 (dd, $J = 14.6, 7.1$ Hz), 45.72 (d, $J = 138.7$ Hz), 21.10, 16.33 (dd, $J = 22.0, 5.9$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 24.45. HRMS (ESI) Calcd. For $\text{C}_{21}\text{H}_{26}\text{ClNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 415.1200, found. 415.1197.



4ce

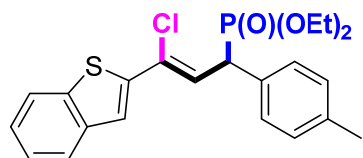
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 20 mg (47%) of **4ce**. Diethyl (*R,Z*)-(3-chloro-3-(naphthalen-1-yl)-1-(*p*-tolyl)allyl)phosphonate.

len-2-yl)-1-(p-tolyl)allyl)phosphonate. Colorless oil, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.08 (s, 1H), 7.91 – 7.77 (m, 3H), 7.74 – 7.64 (m, 1H), 7.53 – 7.47 (m, 2H), 7.44 – 7.38 (m, 2H), 7.18 (d, $J = 7.9$ Hz, 2H), 6.73 – 6.65 (m, 1H), 4.63 (dd, $J = 23.1, 10.4$ Hz, 1H), 4.20 – 3.95 (m, 3H), 3.90 – 3.78 (m, 1H), 2.34 (s, 3H), 1.30 (t, $J = 7.0$ Hz, 3H), 1.16 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.13 (d, $J = 3.0$ Hz), 135.37 (d, $J = 16.0$ Hz), 134.61 (d, $J = 2.6$ Hz), 133.10 (d, $J = 40.6$ Hz), 131.98 (d, $J = 8.0$ Hz), 129.48 (d, $J = 2.4$ Hz), 128.85 (d, $J = 6.8$ Hz), 128.45, 127.97, 127.51, 126.72, 126.56, 126.35 (d, $J = 2.2$ Hz), 123.91 (d, $J = 1.4$ Hz), 122.72 (d, $J = 8.1$ Hz), 62.83 (dd, $J = 20.4, 7.1$ Hz), 46.60, 45.22, 21.09, 16.37 (dd, $J = 22.5, 5.9$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 24.34. **HRMS (ESI)** Calcd. For $\text{C}_{24}\text{H}_{26}\text{ClNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 451.1200, found. 415.1201.



4cf

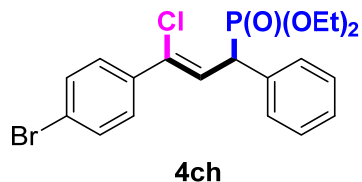
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 34 mg (80%) of **4cf**. **Diethyl (R,Z)-(3-chloro-3-(3-chloro-4-methylphenyl)-1-(p-tolyl)allyl)phosphonate**. Colorless oil, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.44 (d, $J = 1.8$ Hz, 1H), 7.38 – 7.33 (m, 3H), 7.30 (d, $J = 8.4$ Hz, 1H), 7.16 (d, $J = 8.0$ Hz, 2H), 6.56 – 6.48 (m, 1H), 4.52 (dd, $J = 23.0, 10.4$ Hz, 1H), 4.16 – 3.92 (m, 3H), 3.87 – 3.75 (m, 1H), 2.39 – 2.32 (m, 6H), 1.29 (t, $J = 7.0$ Hz, 3H), 1.14 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.16 (d, $J = 3.1$ Hz), 136.04, 136.00 (d, $J = 2.5$ Hz), 135.03, 134.29 (d, $J = 16.1$ Hz), 131.87 (d, $J = 8.0$ Hz), 129.47 (d, $J = 2.3$ Hz), 128.98 (d, $J = 1.8$ Hz), 128.88 (d, $J = 7.9$ Hz), 128.77, 125.34 (d, $J = 1.8$ Hz), 122.68 (d, $J = 8.0$ Hz), 62.79 (dd, $J = 28.9, 7.2$ Hz), 45.82 (d, $J = 138.9$ Hz), 21.06, 20.03, 16.34 (dd, $J = 22.8, 5.9$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 24.16. **HRMS (ESI)** Calcd. For $\text{C}_{21}\text{H}_{25}\text{Cl}_2\text{NaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 449.0811, found. 449.0813.



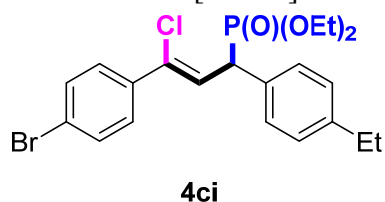
4cg

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 13 mg (29%) of **4cg**. **Diethyl (R,Z)-(3-(benzo[b]thiophen-2-yl)-3-chloro-1-(p-tolyl)allyl)phosphonate**. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 – 7.68 (m, 2H), 7.52 (s, 1H), 7.41 – 7.29 (m, 4H), 7.17 (d, $J = 7.9$ Hz, 2H), 6.63 (dd, $J = 10.4, 8.2$ Hz, 1H), 4.54 (dd, $J = 23.3, 10.4$ Hz, 1H), 4.16 – 3.95 (m, 3H), 3.92 – 3.79 (m, 1H), 2.33 (d, $J = 1.9$ Hz, 3H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.16 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 140.45 (d, $J = 3.3$ Hz), 139.32 (d, $J = 4.3$ Hz), 137.24 (d, $J = 3.0$ Hz), 131.63 (d,

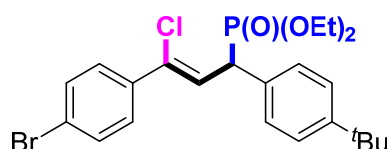
$J = 7.9$ Hz), 129.52 (d, $J = 2.2$ Hz), 129.00, 128.83 (d, $J = 6.8$ Hz), 125.41, 124.71, 124.13, 123.63 (d, $J = 2.3$ Hz), 123.21 (d, $J = 8.4$ Hz), 122.04, 62.89 (dd, $J = 15.6, 7.1$ Hz), 45.77 (d, $J = 139.3$ Hz), 21.08, 16.37 (dd, $J = 20.0, 5.8$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 23.66. HRMS (ESI) Calcd. For $\text{C}_{22}\text{H}_{24}\text{ClNaO}_3\text{PS}$ $[\text{M}+\text{Na}]^+$: 457.0765, found. 457.0770.



Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 39 mg (88%) of **4ch**. Diethyl (*R,Z*)-(3-(4-bromophenyl)-3-chloro-1-phenylallyl)phosphonate. Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.44 (m, 6H), 7.38 – 7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 6.60 – 6.52 (m, 1H), 4.56 (dd, $J = 23.2, 10.4$ Hz, 1H), 4.17 – 3.91 (m, 3H), 3.86 – 3.74 (m, 1H), 1.29 (t, $J = 7.0$ Hz, 3H), 1.12 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.40 (d, $J = 2.6$ Hz), 134.87 (d, $J = 7.8$ Hz), 134.38 (d, $J = 16.2$ Hz), 131.48, 128.97 (d, $J = 6.7$ Hz), 128.79 (d, $J = 2.2$ Hz), 128.20 (d, $J = 1.7$ Hz), 127.50 (d, $J = 2.9$ Hz), 123.15, 122.86 (d, $J = 8.2$ Hz), 62.85 (dd, $J = 31.3, 7.1$ Hz), 46.31 (d, $J = 138.6$ Hz), 16.31 (dd, $J = 25.1, 5.9$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 23.83. HRMS (ESI) Calcd. For $\text{C}_{19}\text{H}_{21}\text{BrClNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 464.9992, found. 464.9992.

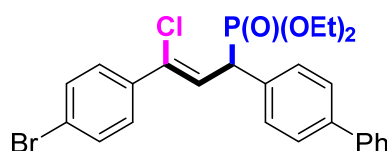


Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 39 mg (82%) of **4ci**. Diethyl (*R,Z*)-(3-(4-bromophenyl)-3-chloro-1-(4-ethylphenyl)allyl)phosphonate. Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.42 (m, 4H), 7.40 – 7.36 (m, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 6.58 – 6.51 (m, 1H), 4.53 (dd, $J = 23.1, 10.4$ Hz, 1H), 4.16 – 3.92 (m, 3H), 3.87 – 3.75 (m, 1H), 2.63 (q, $J = 7.6$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.22 (t, $J = 7.6$ Hz, 3H), 1.13 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.55 (d, $J = 3.0$ Hz), 136.45 (d, $J = 2.7$ Hz), 134.11 (d, $J = 16.1$ Hz), 131.90 (d, $J = 7.9$ Hz), 131.44, 128.83 (d, $J = 6.7$ Hz), 128.29 (d, $J = 2.4$ Hz), 128.19 (d, $J = 1.8$ Hz), 123.09 (d, $J = 3.7$ Hz), 123.03, 62.79 (dd, $J = 32.0, 7.2$ Hz), 45.90 (d, $J = 138.8$ Hz), 28.44, 16.32 (dd, $J = 24.6, 5.9$ Hz), 15.47. ^{31}P NMR (162 MHz, CDCl_3) δ 24.02. HRMS (ESI) Calcd. For $\text{C}_{20}\text{H}_{23}\text{ClNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 493.0305, found. 493.0308.



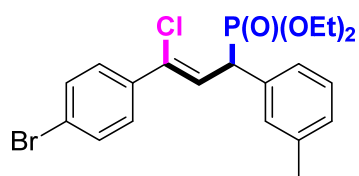
4cj

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 42 mg (84%) of **4cj**. **Diethyl (R,Z)-3-(4-bromophenyl)-1-(4-(tert-butyl)phenyl)-3-chloroallylphosphonate**. Colorless oil, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.47 (s, 4H), 7.37 (s, 4H), 6.59 – 6.50 (m, 1H), 4.55 (dd, $J = 23.2, 10.5$ Hz, 1H), 4.16 – 3.91 (m, 3H), 3.88 – 3.76 (m, 1H), 1.32 – 1.25 (m, 12H), 1.11 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 150.43 (d, $J = 3.1$ Hz), 136.45 (d, $J = 2.7$ Hz), 134.09 (d, $J = 16.0$ Hz), 131.56 (d, $J = 8.2$ Hz), 131.45, 128.52 (d, $J = 6.7$ Hz), 128.20 (d, $J = 1.8$ Hz), 125.74 (d, $J = 2.4$ Hz), 123.08, 123.00 (d, $J = 8.4$ Hz), 62.82 (dd, $J = 30.3, 7.1$ Hz), 45.81 (d, $J = 138.6$ Hz), 34.47, 31.27, 16.30 (dd, $J = 29.3, 5.9$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 24.04. **HRMS (ESI)** Calcd. For $\text{C}_{23}\text{H}_{29}\text{BrClNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 521.0618, found. 521.0614.



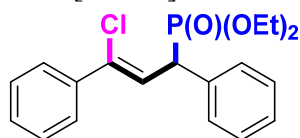
4ck

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 46 mg (89%) of **4ck**. **Diethyl (R,Z)-1-([1,1'-biphenyl]-4-yl)-3-(4-bromophenyl)-3-chloroallylphosphonate**. Colorless oil, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 – 7.52 (m, 6H), 7.51 – 7.41 (m, 6H), 7.38 – 7.31 (m, 1H), 6.67 – 6.51 (m, 1H), 4.61 (dd, $J = 23.1, 10.4$ Hz, 1H), 4.19 – 3.95 (m, 3H), 3.94 – 3.80 (m, 1H), 1.30 (t, $J = 7.0$ Hz, 3H), 1.16 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 140.48, 140.37 (d, $J = 3.2$ Hz), 136.35 (d, $J = 2.6$ Hz), 134.52 (d, $J = 16.1$ Hz), 133.83 (d, $J = 8.1$ Hz), 131.50, 129.33 (d, $J = 6.8$ Hz), 128.77, 128.22 (d, $J = 1.7$ Hz), 127.49 (d, $J = 2.5$ Hz), 127.37, 127.00, 123.20, 122.67 (d, $J = 8.2$ Hz), 62.93 (dd, $J = 27.1, 7.2$ Hz), 45.94 (d, $J = 138.8$ Hz), 16.36 (dd, $J = 22.6, 5.9$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 23.75. **HRMS (ESI)** Calcd. For $\text{C}_{25}\text{H}_{25}\text{BrClNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 541.0305, found. 541.0310.



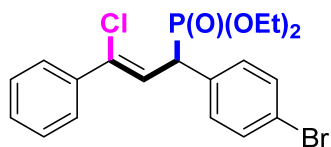
4cl

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 25 mg (54%) of **4cl**. **Diethyl (*R,Z*)-(3-(4-bromophenyl)-3-chloro-1-(*m*-tolyl)allyl)phosphonate**. Colorless oil, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46 (s, 4H), 7.29 – 7.20 (m, 3H), 7.08 (d, $J = 7.1$ Hz, 1H), 6.60 – 6.51 (m, 1H), 4.52 (dd, $J = 23.2, 10.4$ Hz, 1H), 4.17 – 3.90 (m, 3H), 3.86 – 3.74 (m, 1H), 2.35 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.12 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.42 (d, $J = 2.4$ Hz), 136.36 (d, $J = 2.6$ Hz), 134.59 (d, $J = 7.8$ Hz), 134.19 (d, $J = 16.1$ Hz), 131.42, 129.61 (d, $J = 6.8$ Hz), 128.62 (d, $J = 2.4$ Hz), 128.25 (d, $J = 2.9$ Hz), 128.16 (d, $J = 1.8$ Hz), 125.92 (d, $J = 6.6$ Hz), 123.07, 122.89 (d, $J = 8.3$ Hz), 62.83 (dd, $J = 33.7, 7.1$ Hz), 46.19 (d, $J = 138.7$ Hz), 21.37, 16.26 (dd, $J = 25.2, 5.9$ Hz). $^3\text{P NMR}$ (162 MHz, CDCl_3) δ 23.80. **HRMS (ESI)** Calcd. For $\text{C}_{20}\text{H}_{23}\text{BrClNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 479.0149, found. 479.0153.



4cm

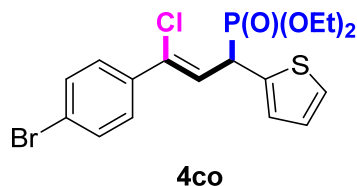
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 31 mg (86%) of **4cm**. **Diethyl (*R,Z*)-(3-chloro-1,3-diphenylallyl)phosphonate**. Colorless oil, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 – 7.57 (m, 2H), 7.50 – 7.47 (m, 2H), 7.39 – 7.32 (m, 5H), 7.31 – 7.25 (m, 1H), 6.64 – 6.45 (m, 1H), 4.59 (dd, $J = 23.2, 10.4$ Hz, 1H), 4.17 – 3.92 (m, 3H), 3.89 – 3.76 (m, 1H), 1.29 (t, $J = 7.0$ Hz, 3H), 1.13 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.50 (d, $J = 2.6$ Hz), 135.49 (d, $J = 16.1$ Hz), 135.13 (d, $J = 7.8$ Hz), 129.02, 128.96, 128.72 (d, $J = 2.3$ Hz), 128.32, 127.38 (d, $J = 2.9$ Hz), 126.68 (d, $J = 1.8$ Hz), 122.21 (d, $J = 8.3$ Hz), 62.79 (dd, $J = 19.2, 7.1$ Hz), 46.23 (d, $J = 138.4$ Hz), 16.31 (dd, $J = 25.0, 6.0$ Hz). $^3\text{P NMR}$ (162 MHz, CDCl_3) δ 24.09. **HRMS (ESI)** Calcd. For $\text{C}_{19}\text{H}_{22}\text{ClNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$: 387.0887, found. 387.0885.



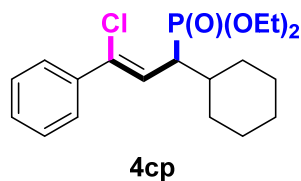
4cn

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 37 mg (83%) of **4cn**. **Diethyl (*R,Z*)-(1-(4-bromophenyl)-3-chloro-3-phenylallyl)phosphonate**. Colorless oil, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.61 – 7.56 (m, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.38 – 7.34 (m, 5H), 6.53 – 6.46 (m, 1H), 4.54 (dd, $J = 23.2, 10.3$ Hz, 1H), 4.18 – 3.95 (m, 3H), 3.94 – 3.82 (m, 1H), 1.29 (t, $J = 7.0$ Hz, 3H), 1.17 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.27 (d, $J = 2.3$ Hz), 136.06 (d, $J = 15.8$ Hz), 134.29 (d, $J = 7.9$ Hz), 131.80 (d, $J = 2.3$ Hz), 130.61 (d, $J = 6.8$ Hz), 129.11, 128.37, 126.65 (d, $J = 1.7$ Hz), 121.49 (d, $J = 8.3$ Hz), 121.41 (d, $J = 3.$

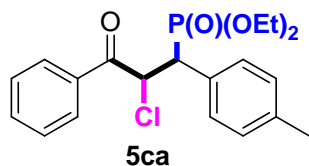
9 Hz), 62.88, 45.56 (d, $J = 139.1$ Hz), 16.33 (dd, $J = 19.5, 5.9$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 23.40. HRMS (ESI) Calcd. For $\text{C}_{19}\text{H}_{21}\text{BrClNaO}_3\text{P}$ [$\text{M}+\text{Na}$] $^+$: 464.9992, found. 464.9996.



Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 22 mg (49%) of **4co**. Diethyl (*R,Z*)-(3-(4-bromophenyl)-3-chloro-1-(thiophen-2-yl)allyl)phosphonate. Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 7.48 (s, 4H), 7.33 – 7.29 (m, 2H), 7.23 – 7.18 (m, 1H), 6.50 – 6.42 (m, 1H), 4.72 (dd, $J = 23.0, 10.4$ Hz, 1H), 4.16 – 3.97 (m, 3H), 3.95 – 3.83 (m, 1H), 1.26 (t, $J = 7.0$ Hz, 3H), 1.18 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.28 (d, $J = 2.6$ Hz), 134.38 (d, $J = 15.5$ Hz), 133.98 (d, $J = 8.0$ Hz), 131.51, 128.19 (d, $J = 1.8$ Hz), 127.90 (d, $J = 5.1$ Hz), 125.94 (d, $J = 1.5$ Hz), 123.22, 122.97 (d, $J = 9.2$ Hz), 122.36 (d, $J = 8.4$ Hz), 62.96 (dd, $J = 19.6, 7.1$ Hz), 41.79 (d, $J = 141.0$ Hz), 16.33 (dd, $J = 16.6, 5.8$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 22.97. HRMS (ESI) Calcd. For $\text{C}_{17}\text{H}_{19}\text{BrClNaO}_3\text{PS}$ [$\text{M}+\text{Na}$] $^+$: 470.9557, found. 470.9555.

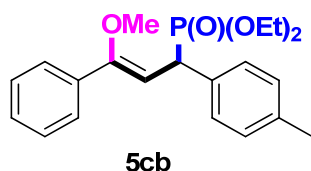


Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 34 mg (92%) of **4cp**. Diethyl (*S,Z*)-(3-chloro-1-cyclohexyl-3-phenylallyl)phosphonate. Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 6.5$ Hz, 2H), 7.41 – 7.32 (m, 2H), 6.22 – 6.10 (m, 1H), 4.18 – 4.04 (m, 4H), 3.37 – 3.24 (m, 1H), 2.06 – 1.84 (m, 3H), 1.79 – 1.59 (m, 3H), 1.39 – 1.06 (m, 11H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.78 (d, $J = 3.1$ Hz), 136.08 (d, $J = 16.3$ Hz), 128.77, 128.33, 126.56 (d, $J = 2.1$ Hz), 121.52 (d, $J = 9.0$ Hz), 61.89 (dd, $J = 13.3, 7.0$ Hz), 45.11 (d, $J = 136.8$ Hz), 38.71 (d, $J = 3.8$ Hz), 31.23 (dd), 26.34 (d, $J = 1.5$ Hz), 26.14 (d, $J = 31.0$ Hz), 16.42. ^{31}P NMR (162 MHz, CDCl_3) δ 27.56. HRMS (ESI) Calcd. For $\text{C}_{19}\text{H}_{28}\text{ClNaO}_3\text{P}$ [$\text{M}+\text{Na}$] $^+$: 393.1357, found. 393.1356.



Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 56 mg (71%) of **5ca**. Diethyl (2-chloro-3-oxo-3-phenyl-1-(p-tolyl)propyl)phosphonate. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J =$

7.9 Hz, 2H), 7.64 (t, $J = 6.9$ Hz, 1H), 7.54 (t, $J = 7.0$ Hz, 2H), 7.36 (d, $J = 7.9$ Hz, 2H), 7.21 (d, $J = 7.1$ Hz, 2H), 5.91 – 5.76 (m, 1H), 4.16 (dd, $J = 21.3, 11.6$ Hz, 1H), 3.94 – 3.75 (m, 3H), 3.67 – 3.54 (m, 1H), 2.37 (d, $J = 2.2$ Hz, 3H), 1.06 (t, $J = 7.0$ Hz, 3H), 0.99 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.14, 136.41, 134.69, 133.83, 130.87, 130.17 (d, $J = 6.0$ Hz), 129.77 (d, $J = 7.5$ Hz), 129.21, 128.87 (d, $J = 7.4$ Hz), 63.26, 62.28, 55.17 (d, $J = 8.9$ Hz), 21.15, 15.92 (d, $J = 1.9$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 22.66. HRMS (ESI) Calcd. For $\text{C}_{20}\text{H}_{24}\text{ClNaO}_4\text{P}$ $[\text{M}+\text{Na}]^+$: 417.0993, found 417.0990.



Purification was performed by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 61 mg (82%) of **5cb**. Diethyl (*Z*)-(3-methoxy-3-phenyl-1-(*p*-tolyl)allyl)phosphonate. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.25 (m, 3H), 7.25 – 7.17 (m, 4H), 7.11 (dd, $J = 8.1, 1.8$ Hz, 2H), 6.85 (dd, $J = 22.6, 9.2$ Hz, 1H), 4.65 (dd, $J = 9.2, 2.5$ Hz, 1H), 4.11 – 3.92 (m, 4H), 3.22 (s, 3H), 2.39 (s, 3H), 1.23 (dt, $J = 23.5, 7.1$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.83 (d, $J = 8.9$ Hz), 139.84, 137.74, 134.59, 132.83, 131.33 (d, $J = 9.1$ Hz), 129.11 (d, $J = 2.6$ Hz), 129.07, 128.61, 128.03, 126.96, 62.20 (d, $J = 5.9$ Hz), 56.18, 21.25, 16.24 (t, $J = 6.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 16.32. HRMS (ESI) Calcd. For $\text{C}_{21}\text{H}_{27}\text{NaO}_4\text{P}$ $[\text{M}+\text{Na}]^+$: 397.1539, found 397.1550.

Crystal Structure for 5ca

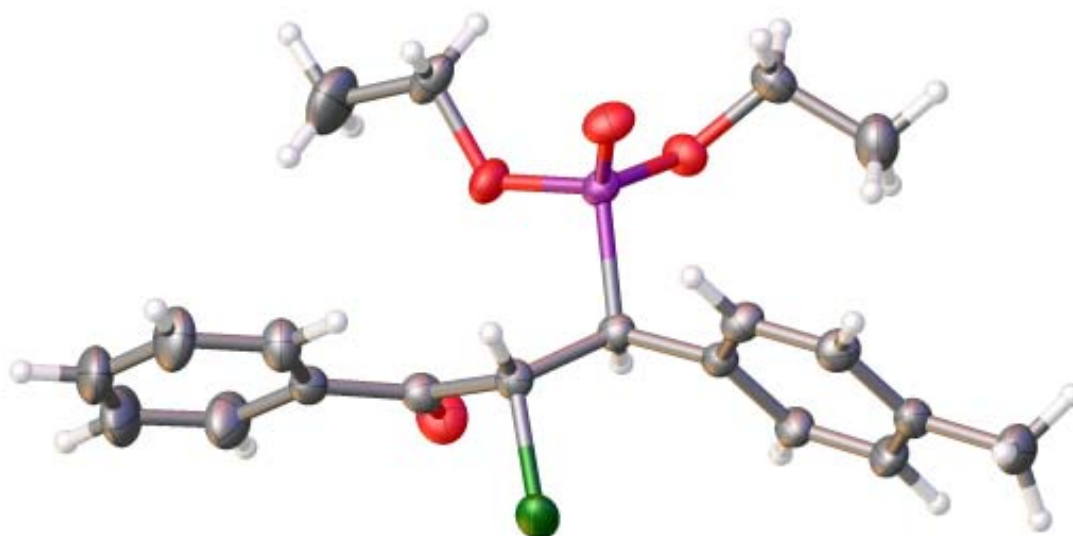


Figure 1. The structure of **5ca**.

Table 1. Crystal data and structure refinement for **5ca**.

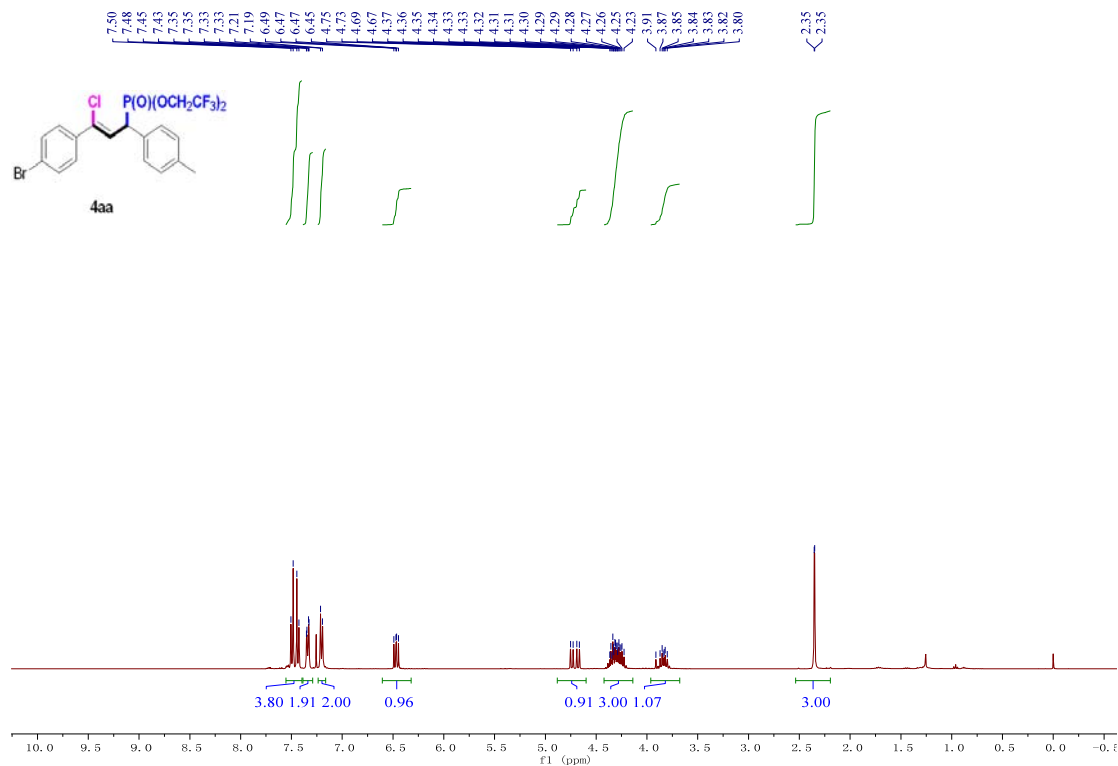
Identification code	wumingy_0615_auto
Empirical formula	C ₂₀ H ₂₄ ClO ₄ P
Formula weight	394.81
Temperature/K	149.99(13)
Crystal system	monoclinic
Space group	C2/c
a/Å	25.4378(10)
b/Å	8.1475(2)
c/Å	21.1676(8)
α/°	90
β/°	114.232(5)
γ/°	90
Volume/Å ³	4000.5(3)
Z	8
ρ _{calc} /cm ³	1.311
μ/mm ⁻¹	0.293
F(000)	1664.0
Crystal size/mm ³	0.08 × 0.07 × 0.06
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.512 to 61.626
Index ranges	-35 ≤ h ≤ 32, -10 ≤ k ≤ 11, -26 ≤ l ≤ 28
Reflections collected	20883
Independent reflections	5081 [R _{int} = 0.0306, R _{sigma} = 0.0276]
Data/restraints/parameters	5081/0/238
Goodness-of-fit on F ²	1.042
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0396, wR ₂ = 0.1000
Final R indexes [all data]	R ₁ = 0.0589, wR ₂ = 0.1127
Largest diff. peak/hole / e Å ⁻³	0.32/-0.35
Crystallization: Crystals of compound 5ca suitable for X-ray analysis were grown from the solvent of dichloromethane by slow evaporation method.	

Single crystals of C₂₀H₂₄ClO₄P [wumingy_0615_auto] were collected. A suitable crystal was selected and collected on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 149.99(13) K during data collection. Using Olex2, the structure was solved with the Unknown structure solution

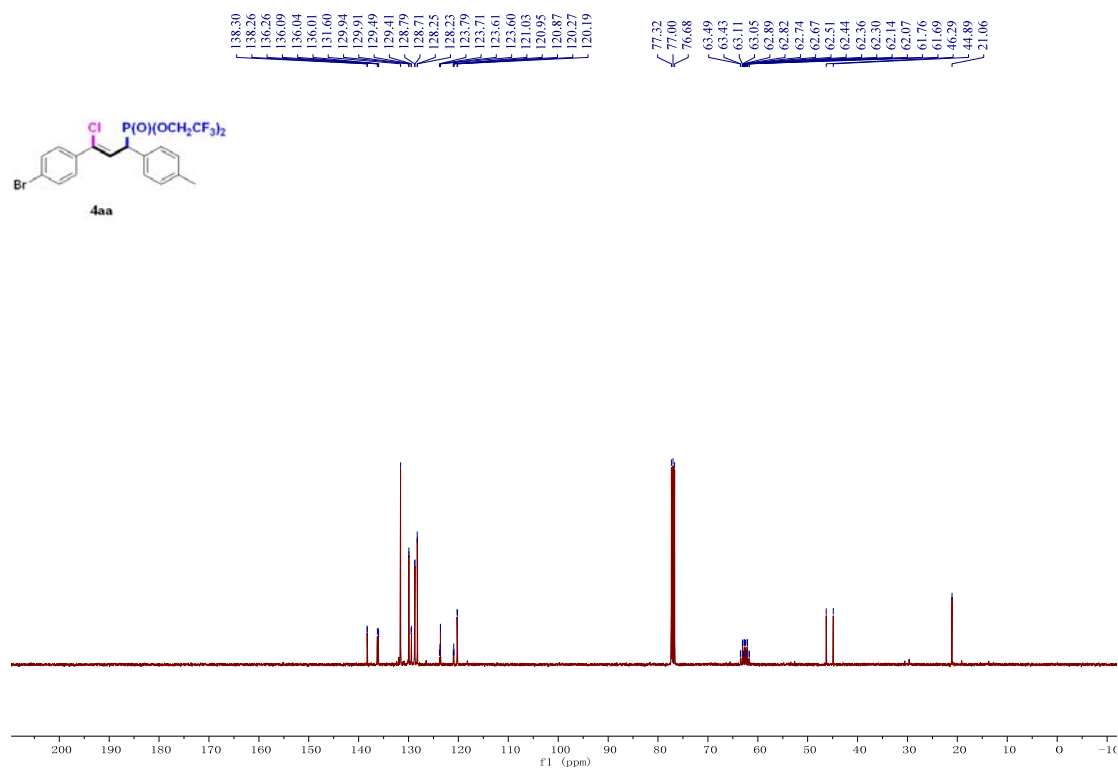
program using Unknown and refined with the Unknown refinement package using Unknown minimisation. Refined structure and crystallographic parameters are summarized in Figure 1 and Table 1. CCDC 2279951 contains the supplementary crystallographic data for wumingy_0615_auto. The crystallographic data of the compound can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

^1H , ^{13}C and ^{31}P NMR Spectra of Products

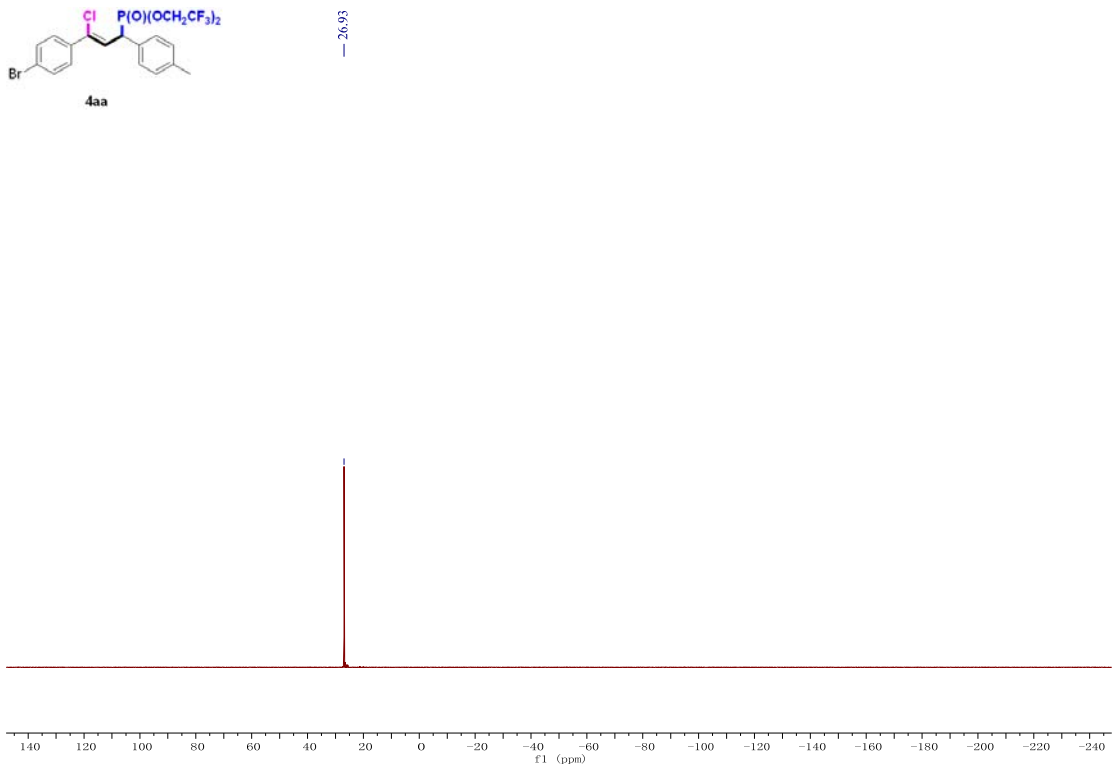
^1H NMR (400 MHz, CDCl_3)



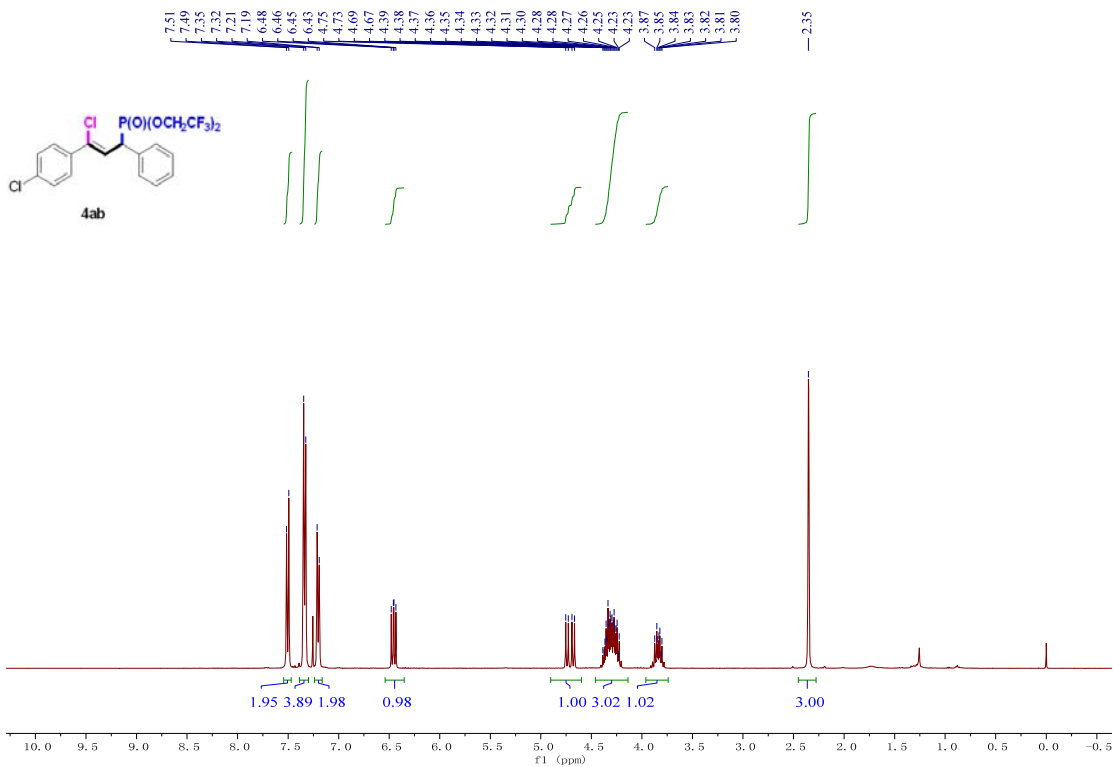
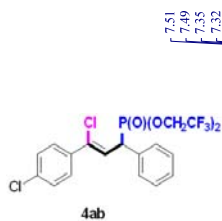
^{13}C NMR (101 MHz, CDCl_3)



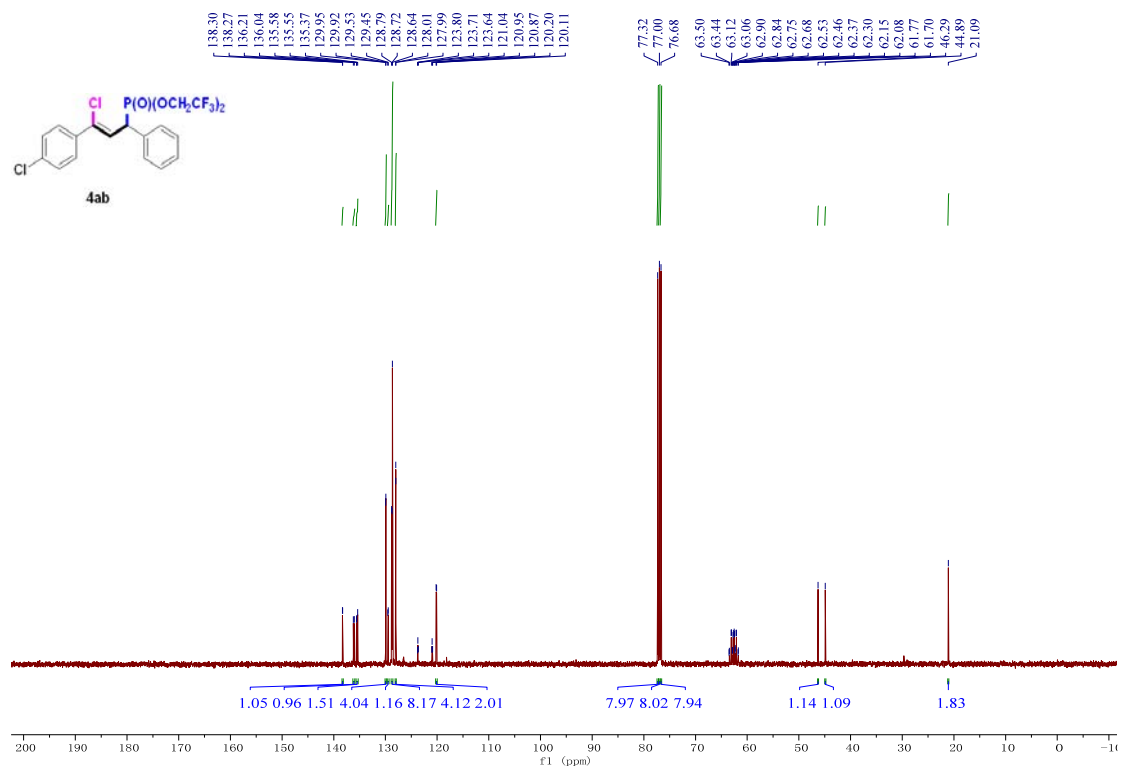
^{31}P NMR (162 MHz, CDCl_3)



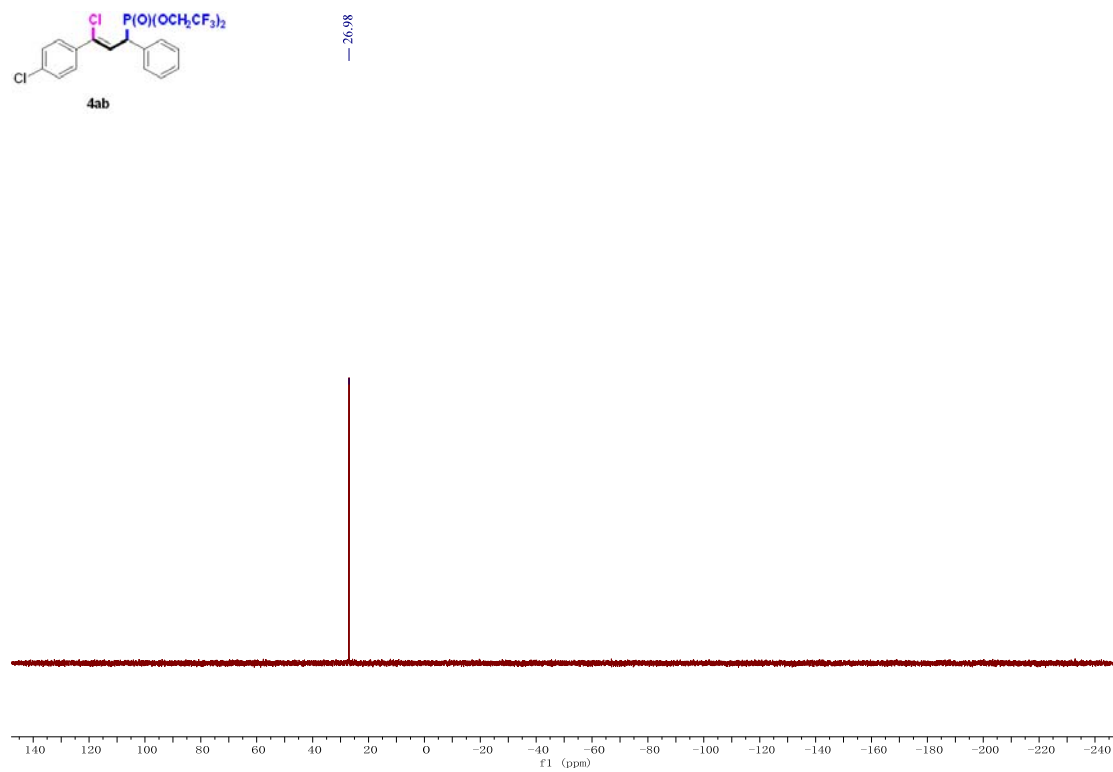
^1H NMR (400 MHz, CDCl_3)



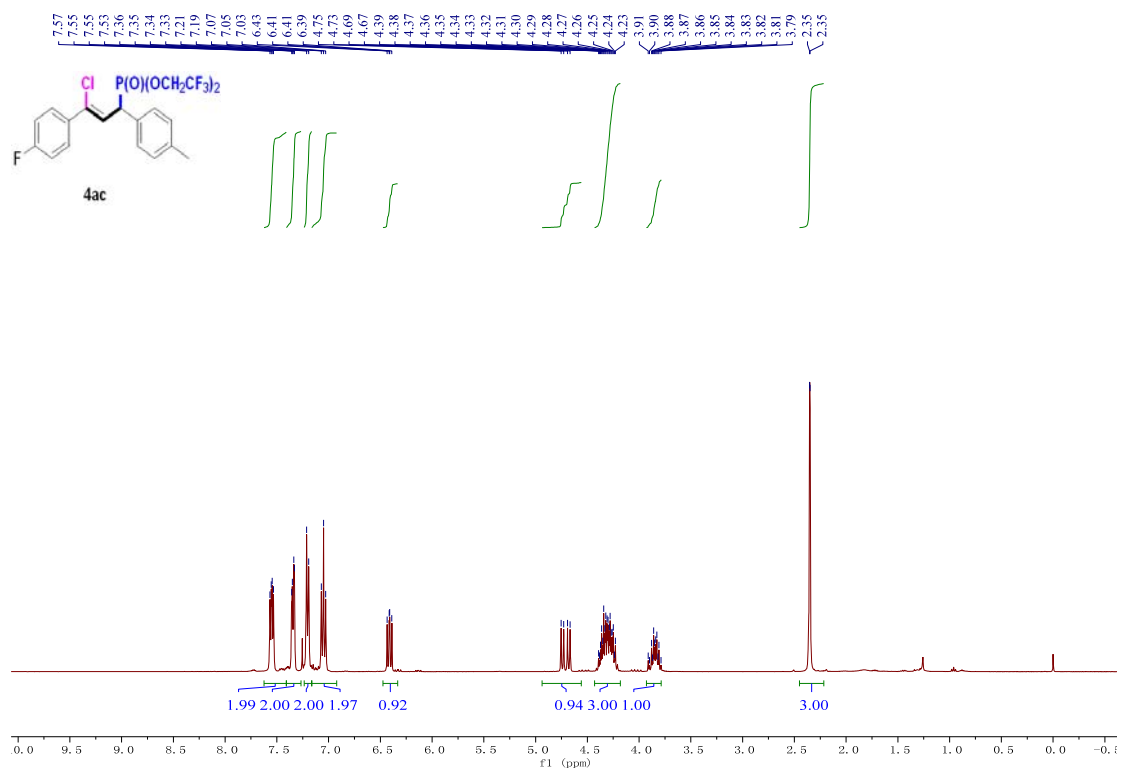
^{13}C NMR (101 MHz, CDCl_3)



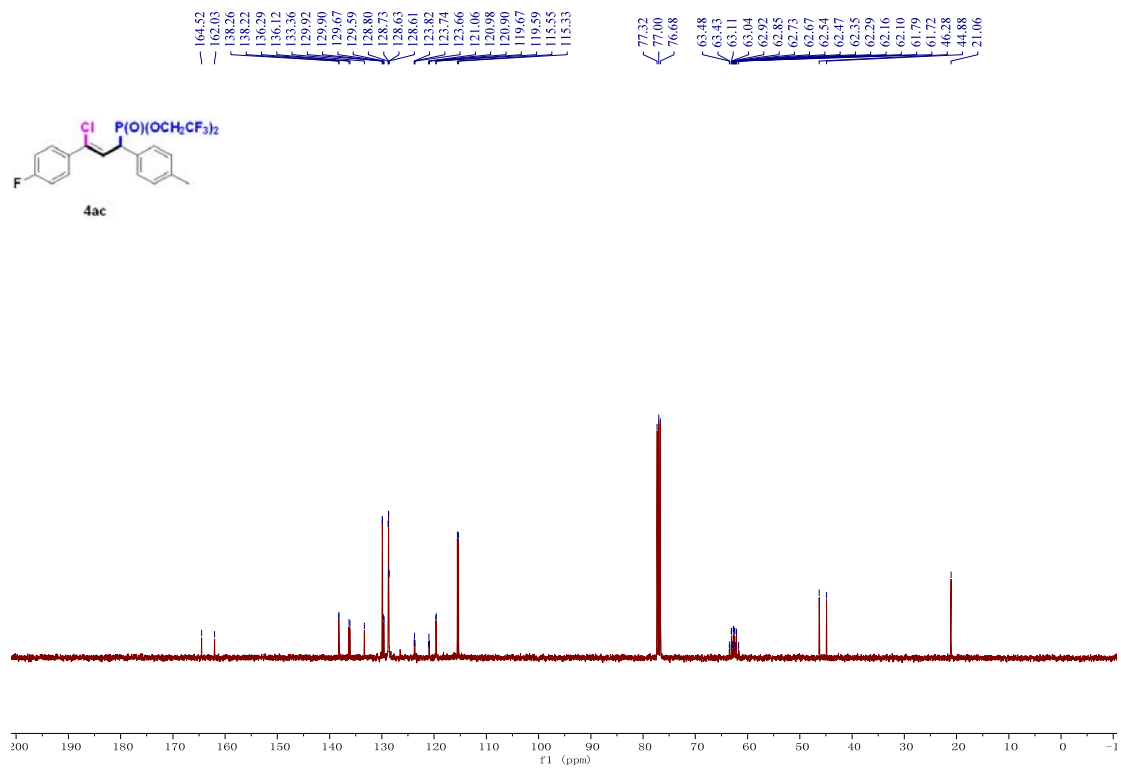
^{31}P NMR (162 MHz, CDCl_3)



¹H NMR (400 MHz, CDCl₃)



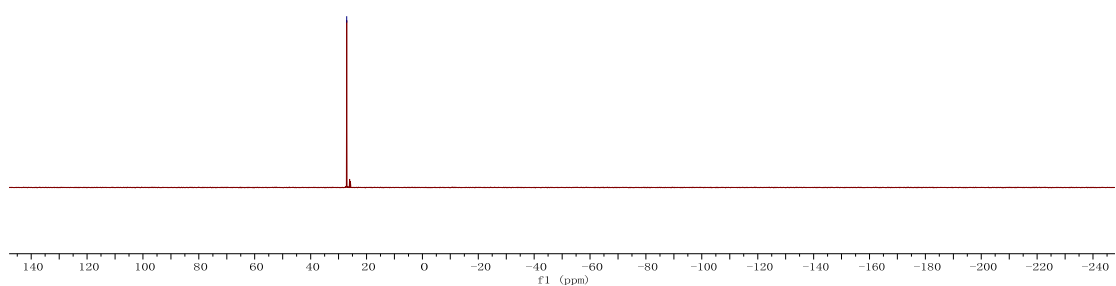
¹³C NMR (101 MHz, CDCl₃)



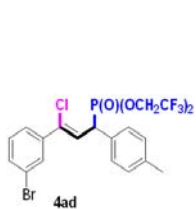
^{31}P NMR (162 MHz, CDCl_3)



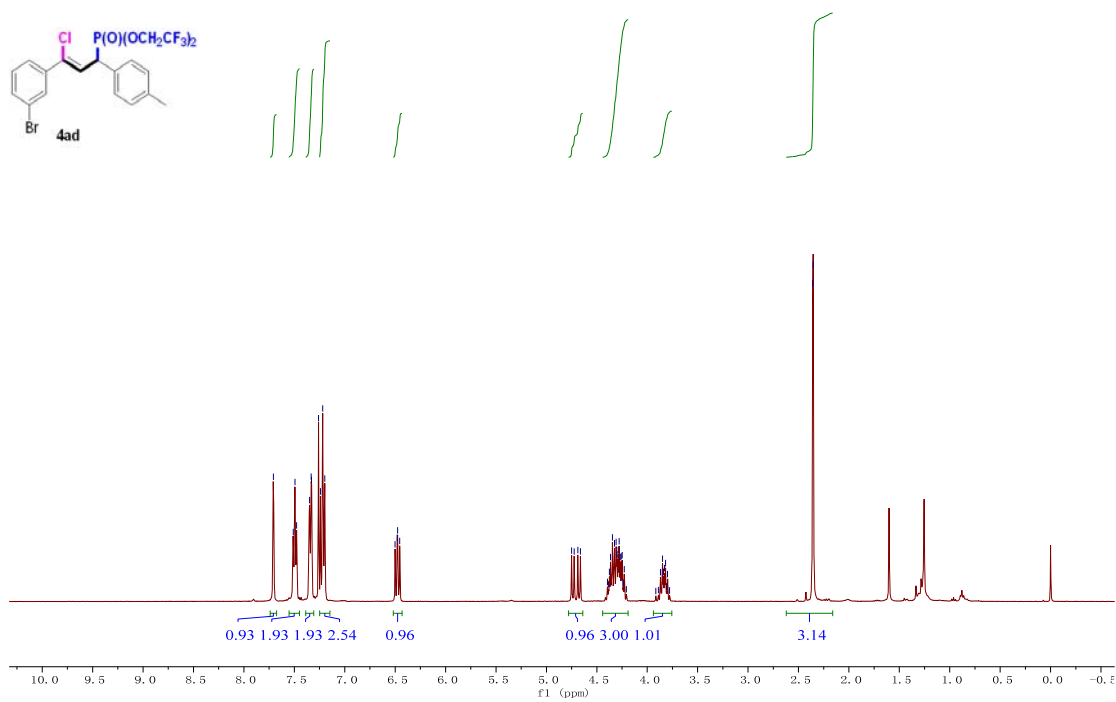
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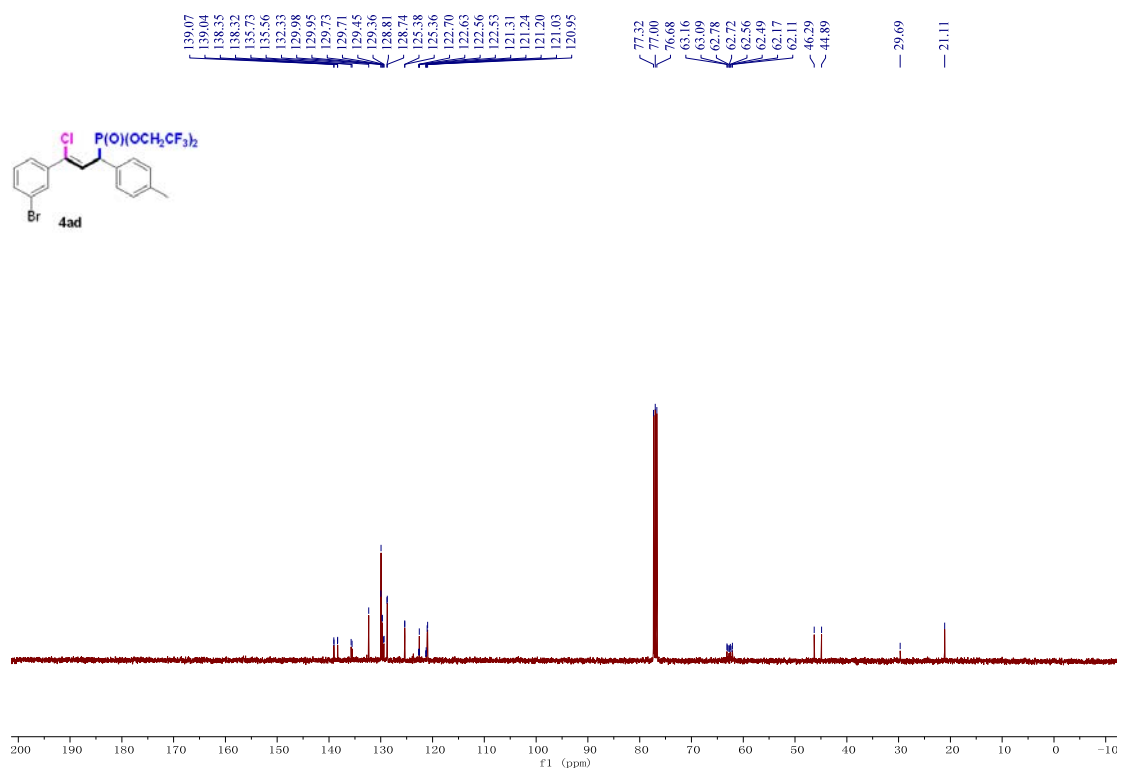
^1H NMR (400 MHz, CDCl_3)



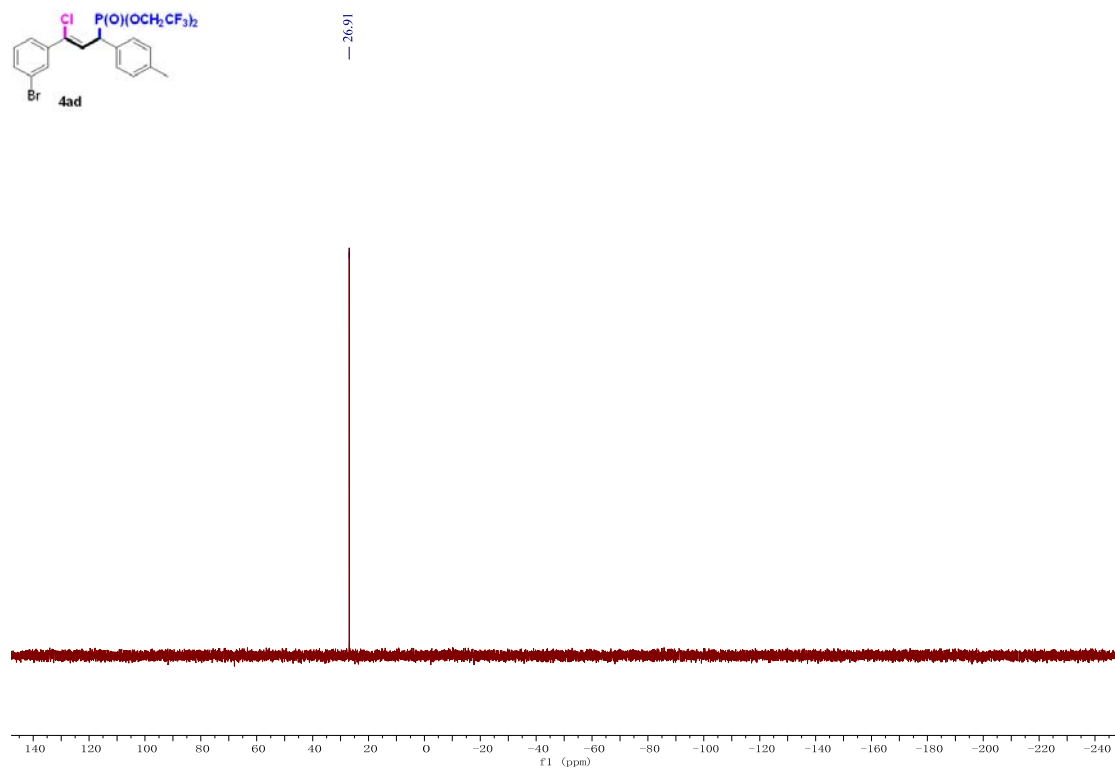
7.71 7.51 7.49 7.48 7.35 7.33 7.33 7.26 7.24 7.22 7.20 6.50 6.48 6.48 6.45 4.75 4.72 4.69 4.66 4.66 4.39 4.37 4.36 4.34 4.32 4.31 4.30 4.29 4.28 4.28 4.27 4.26 4.25 4.24 4.24 4.23 4.21 4.21 3.92 3.89 3.87 3.85 3.85 3.84 3.83 3.82 3.81 3.80 3.78 3.76 2.35



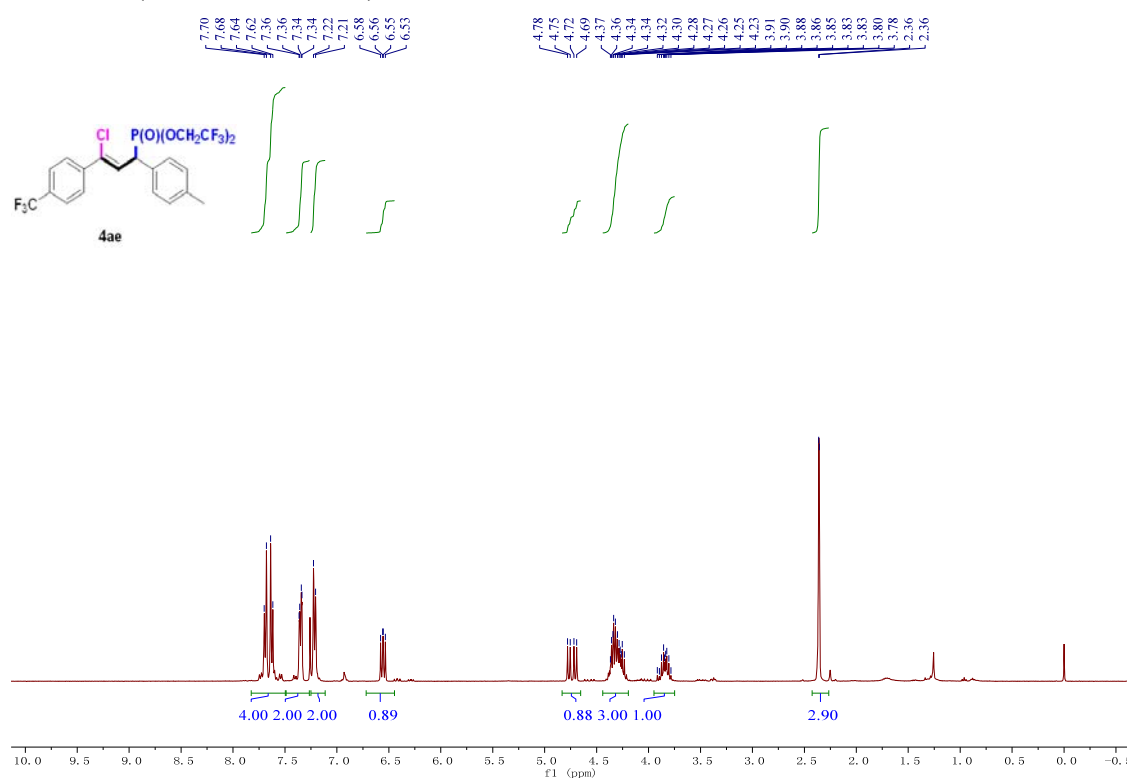
^{13}C NMR (101 MHz, CDCl_3)



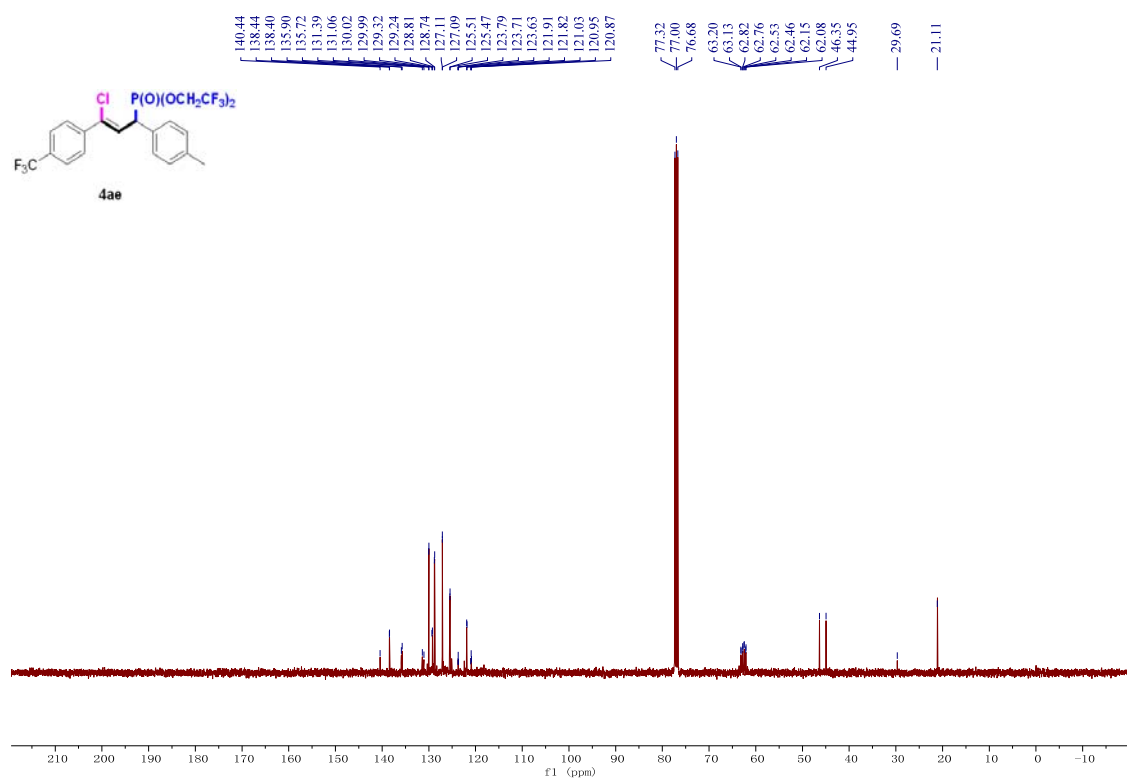
^{31}P NMR (162 MHz, CDCl_3)



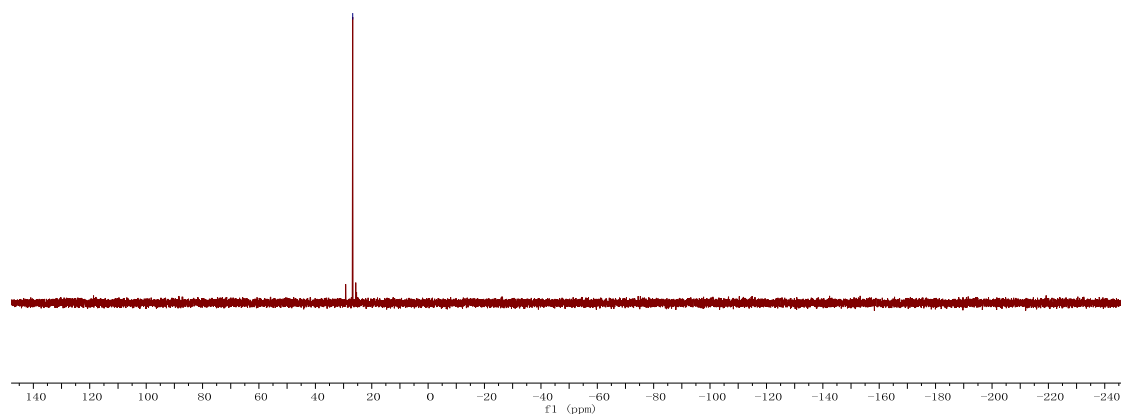
¹H NMR (400 MHz, CDCl₃)



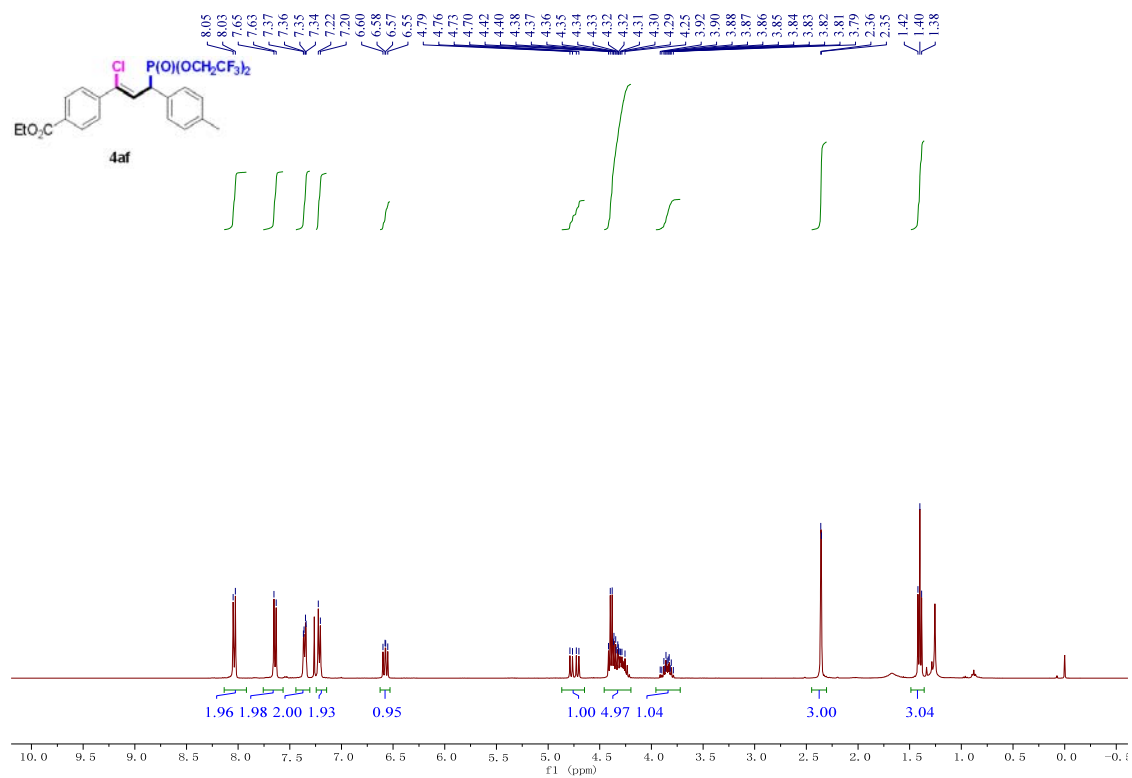
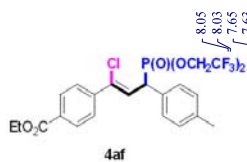
¹³C NMR (101 MHz, CDCl₃)



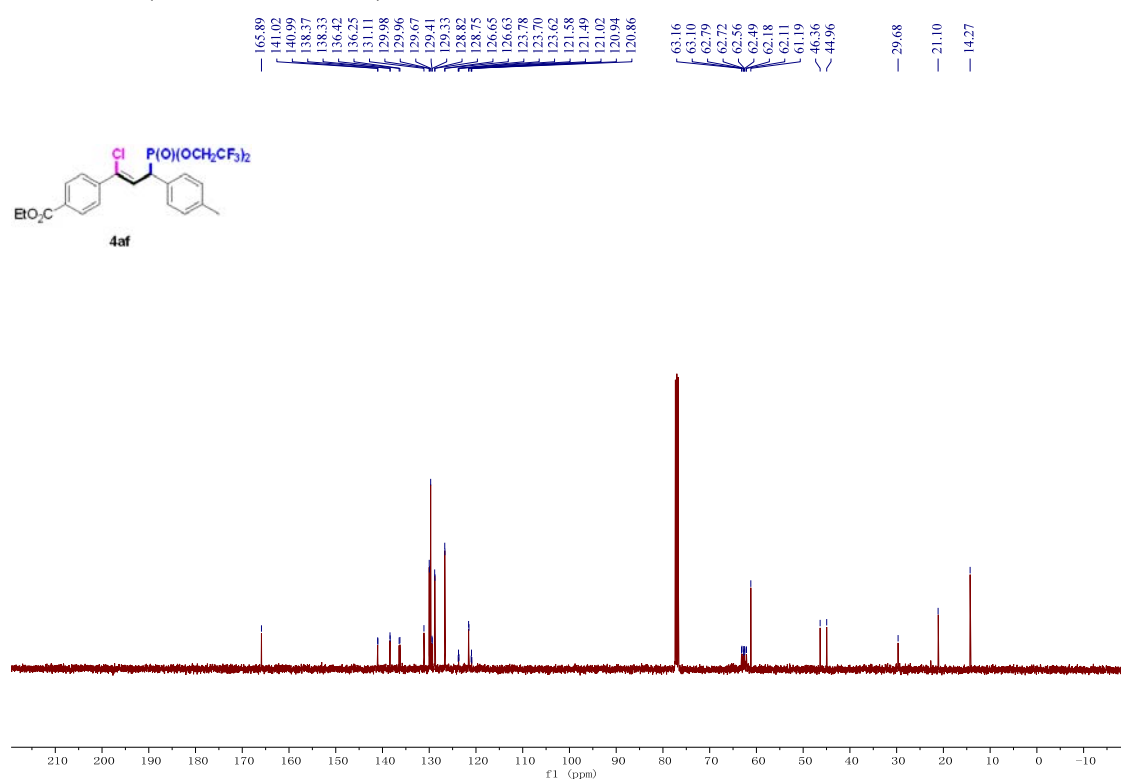
^{31}P NMR (162 MHz, CDCl_3)



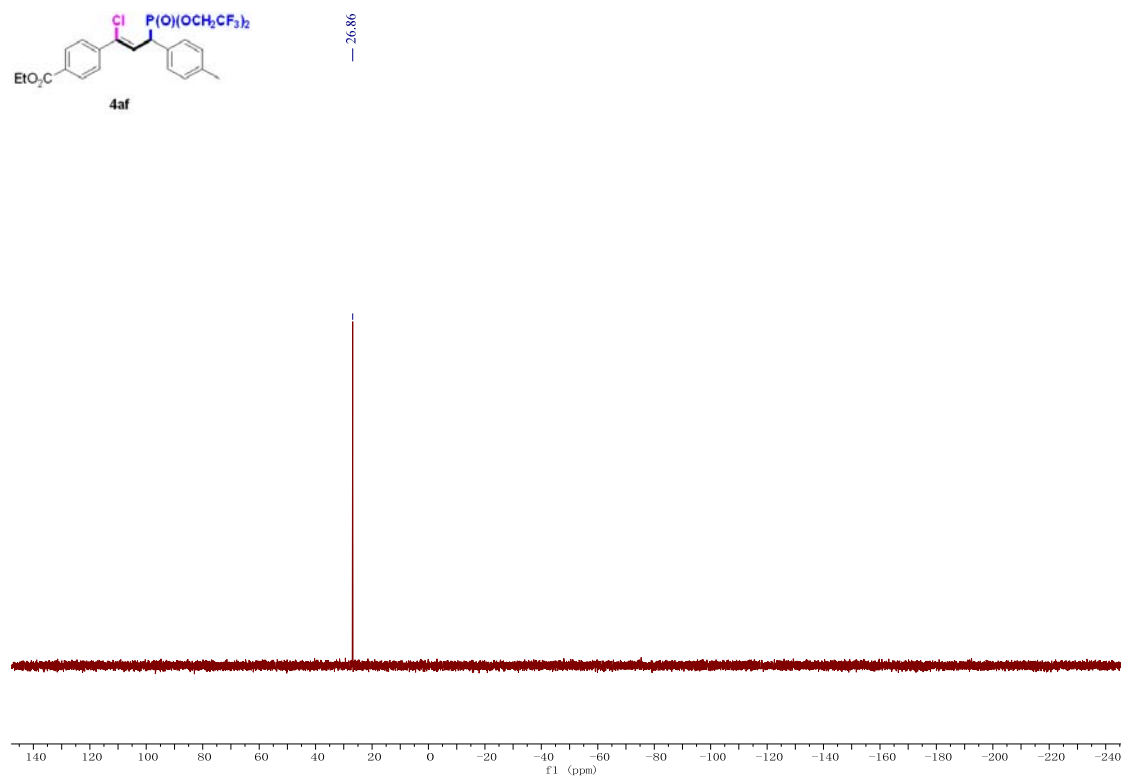
^1H NMR (400 MHz, CDCl_3)



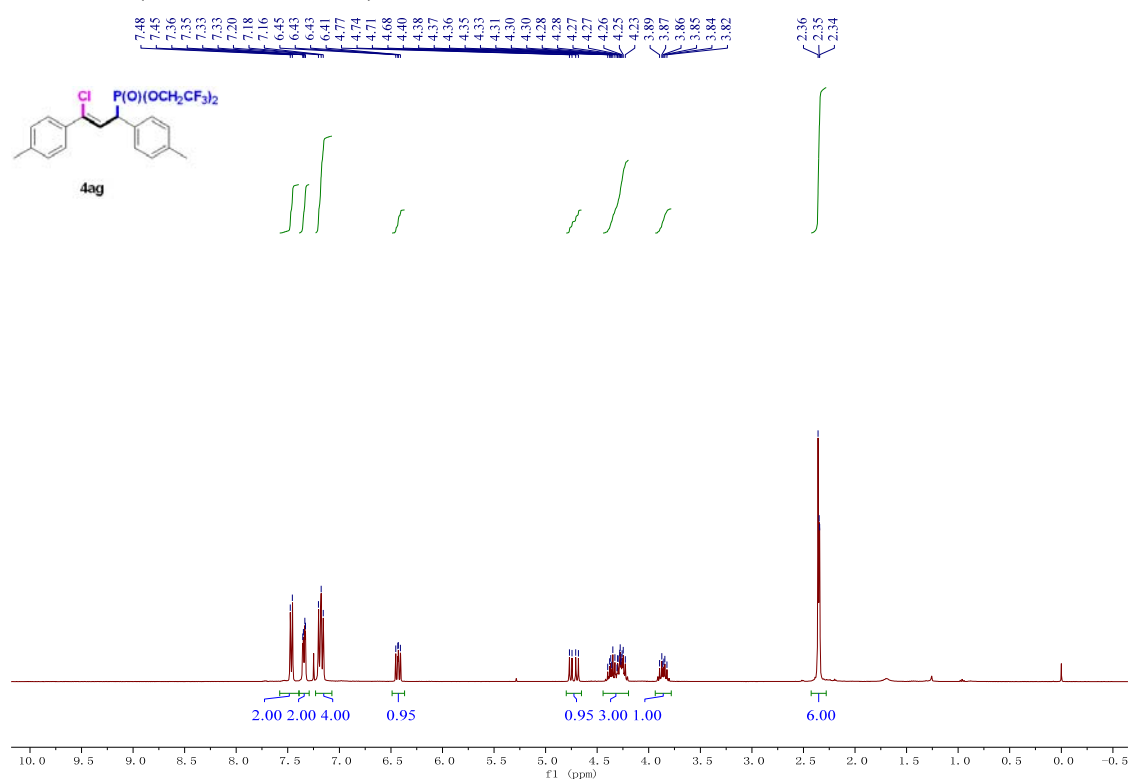
^{13}C NMR (101 MHz, CDCl_3)



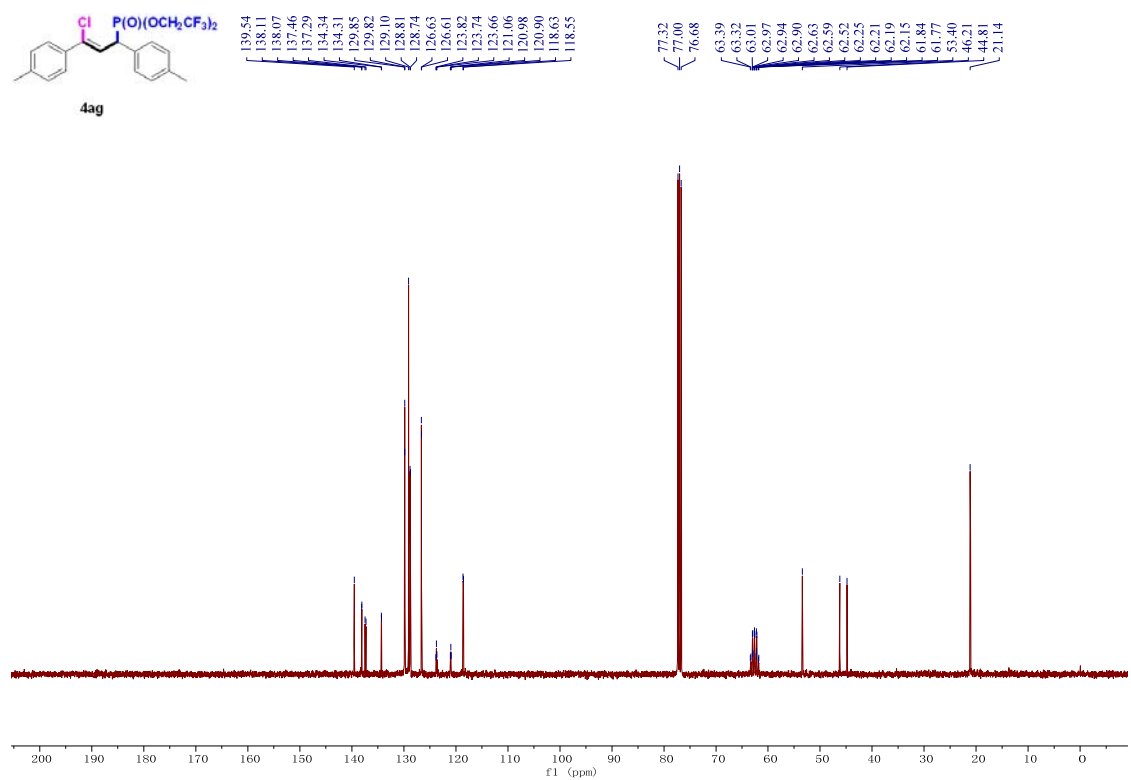
^{31}P NMR (162 MHz, CDCl_3)



¹H NMR (400 MHz, CDCl₃)



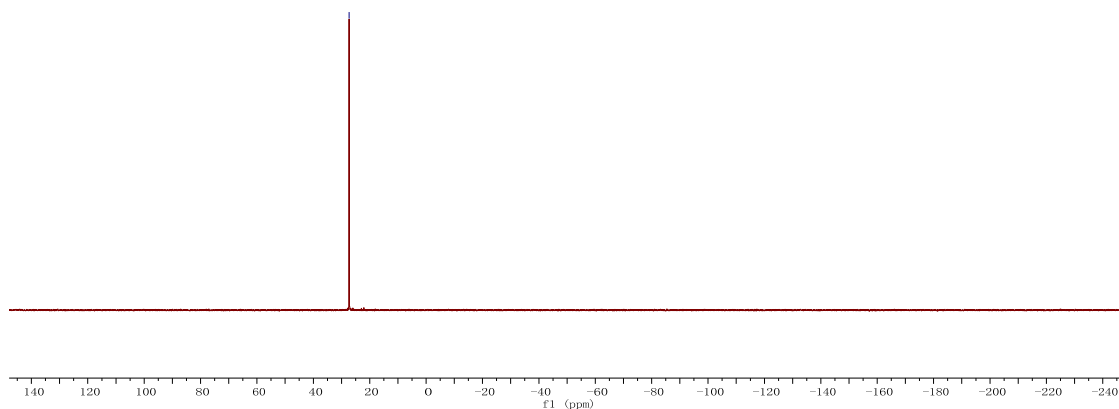
¹³C NMR (101 MHz, CDCl₃)



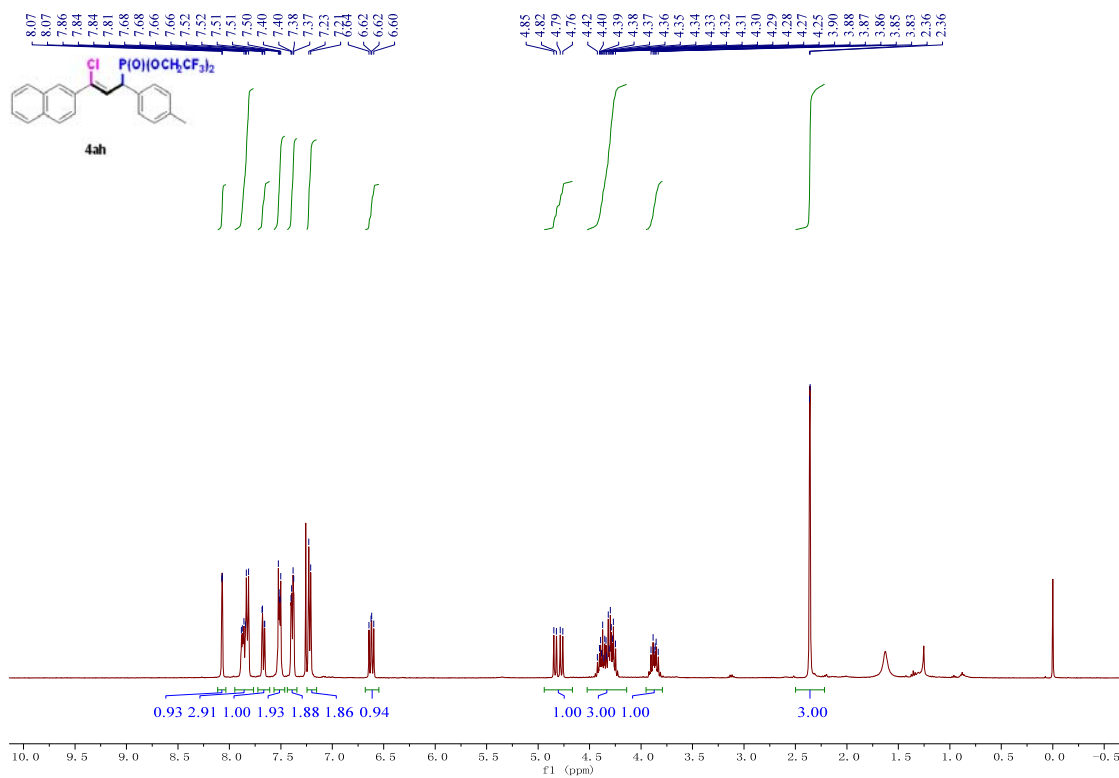
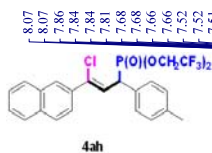
^{31}P NMR (162 MHz, CDCl_3)



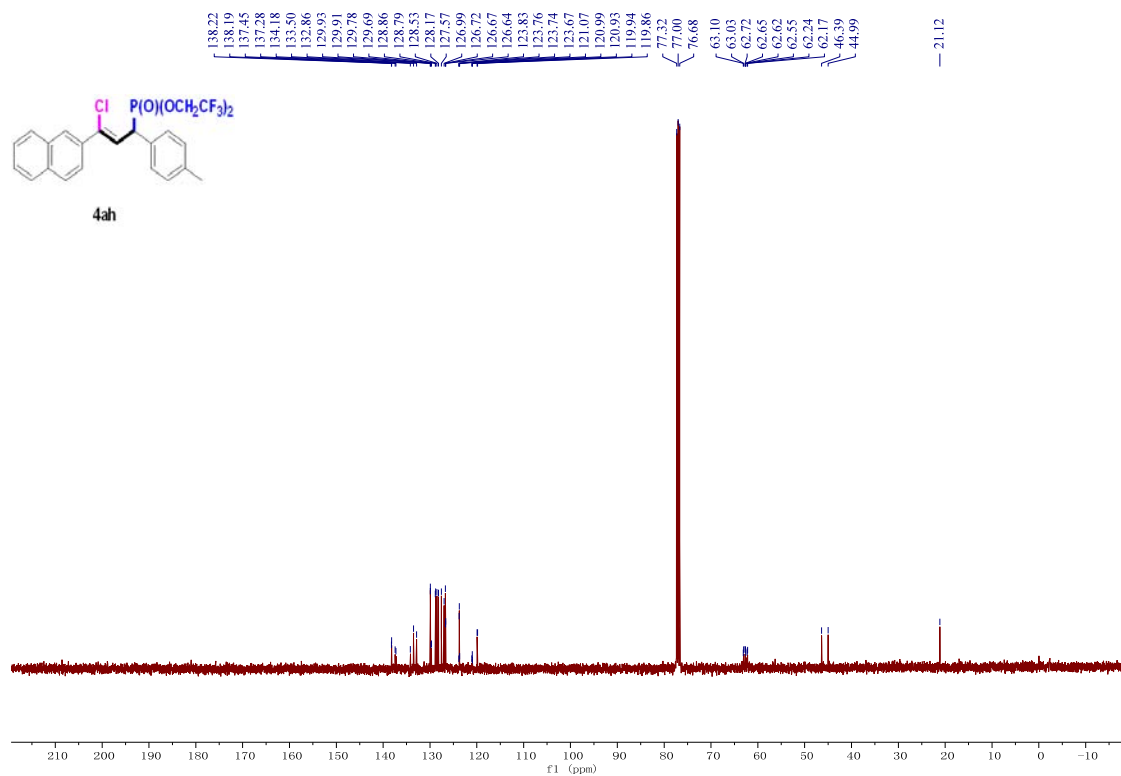
-27.31



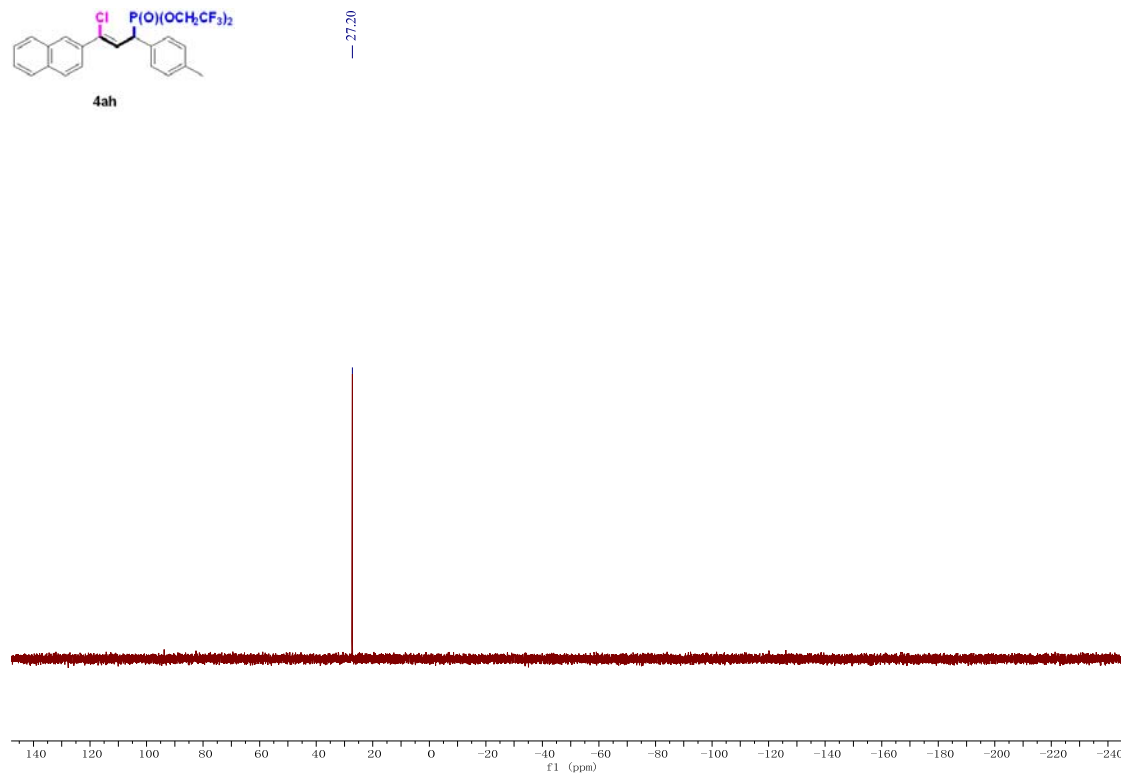
^1H NMR (400 MHz, CDCl_3)



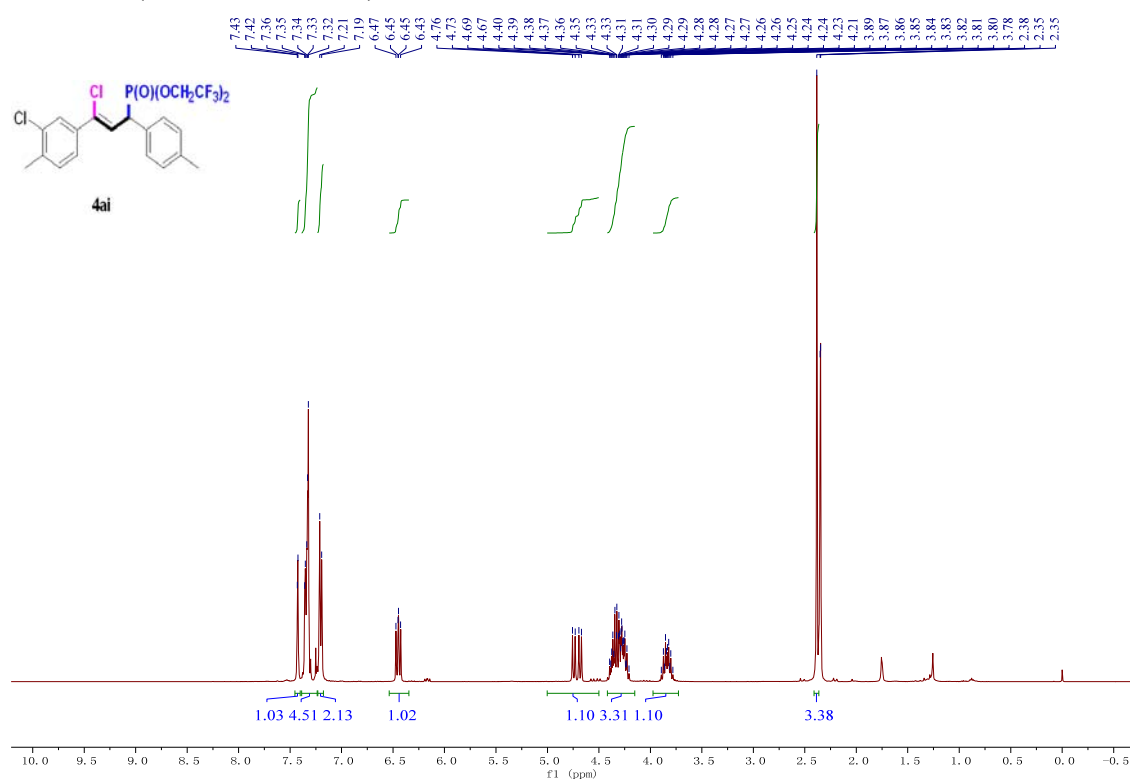
^{13}C NMR (101 MHz, CDCl_3)



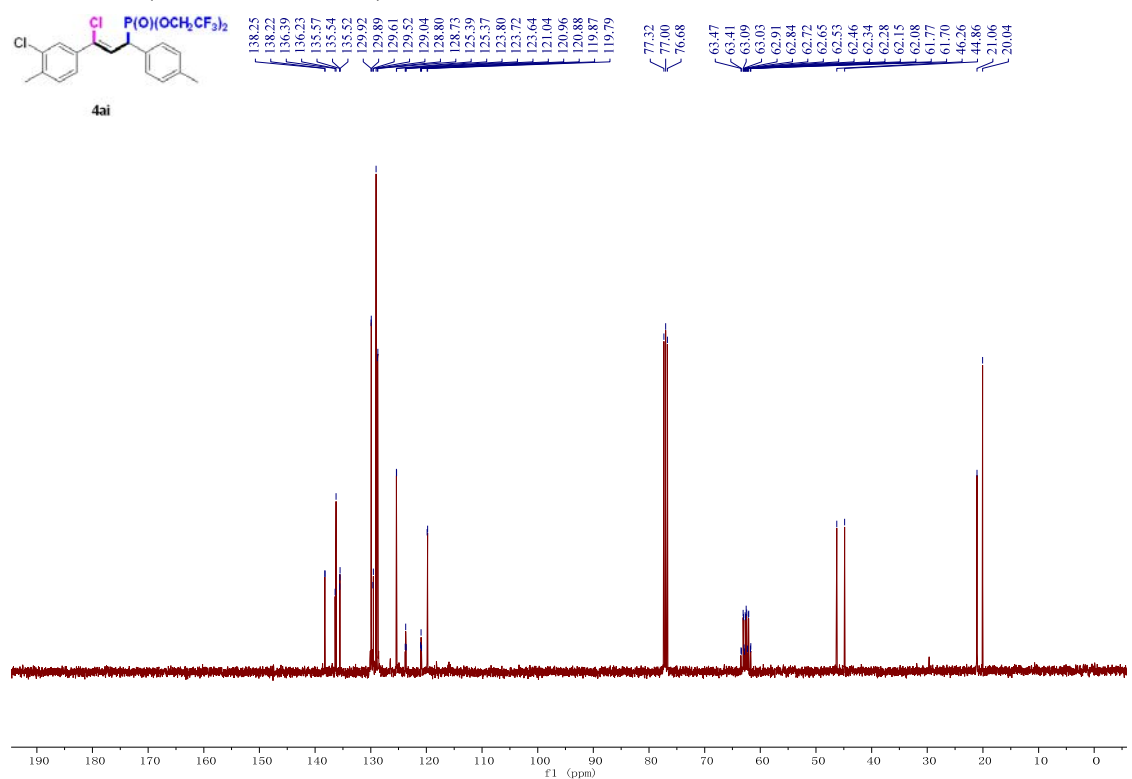
^{31}P NMR (162 MHz, CDCl_3)



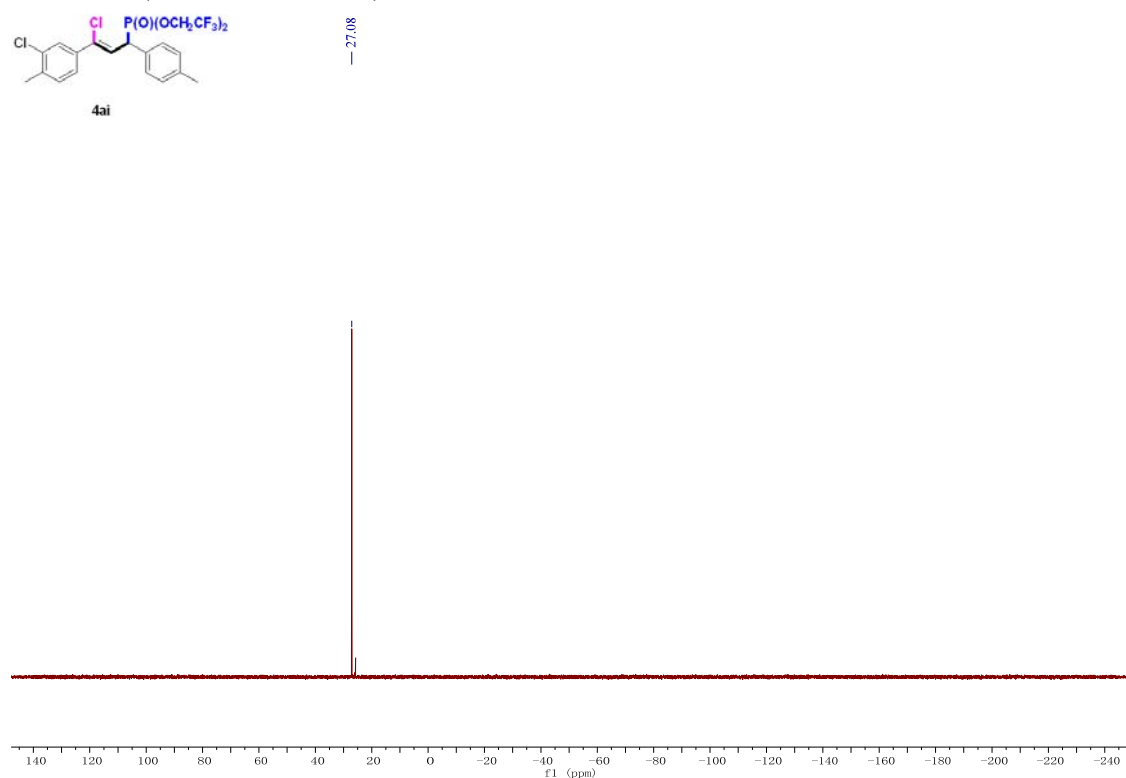
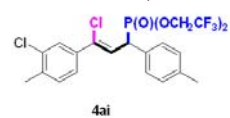
¹H NMR (400 MHz, CDCl₃)



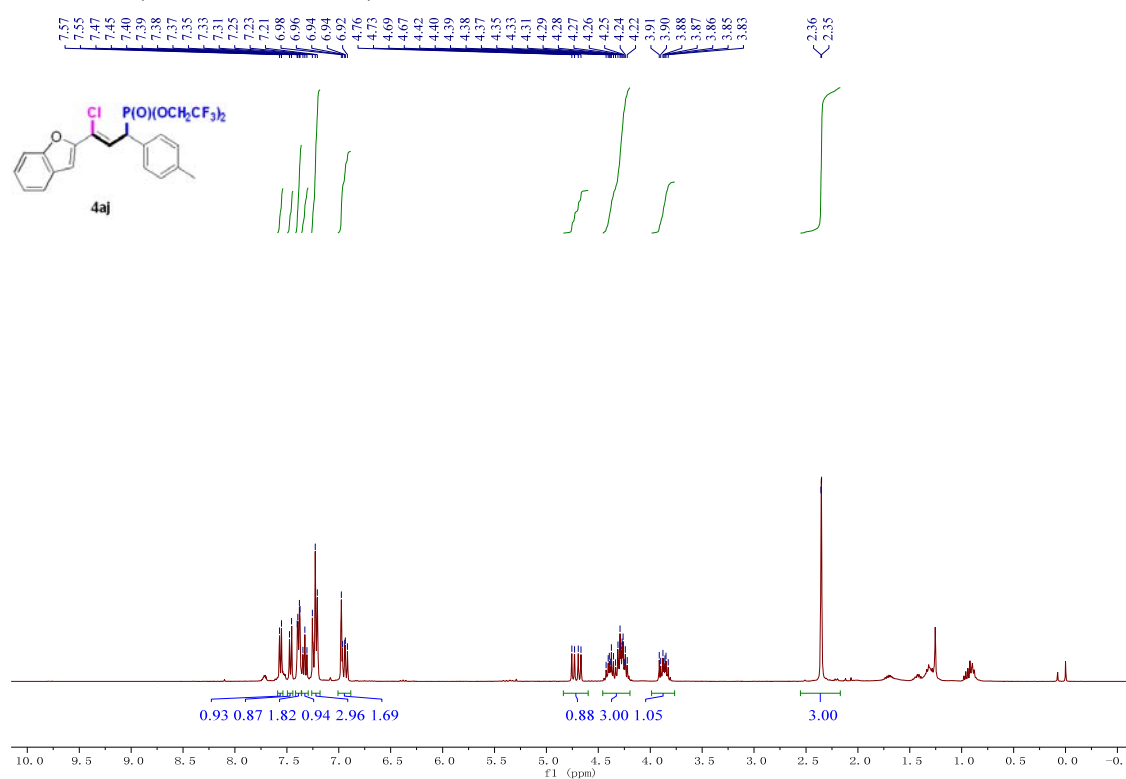
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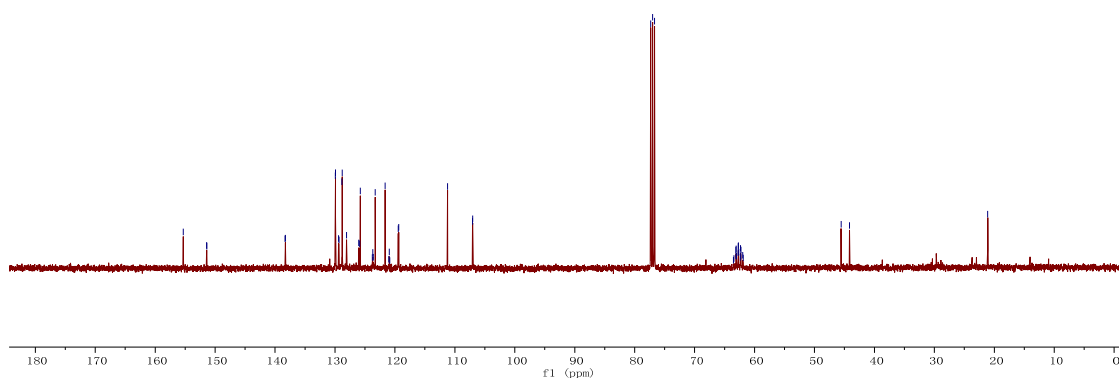
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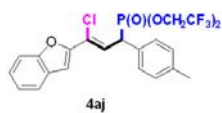
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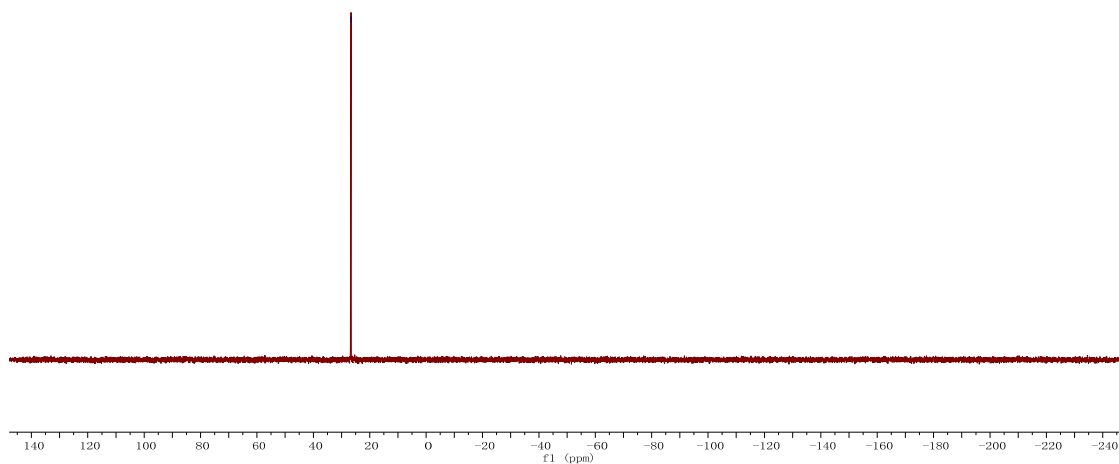
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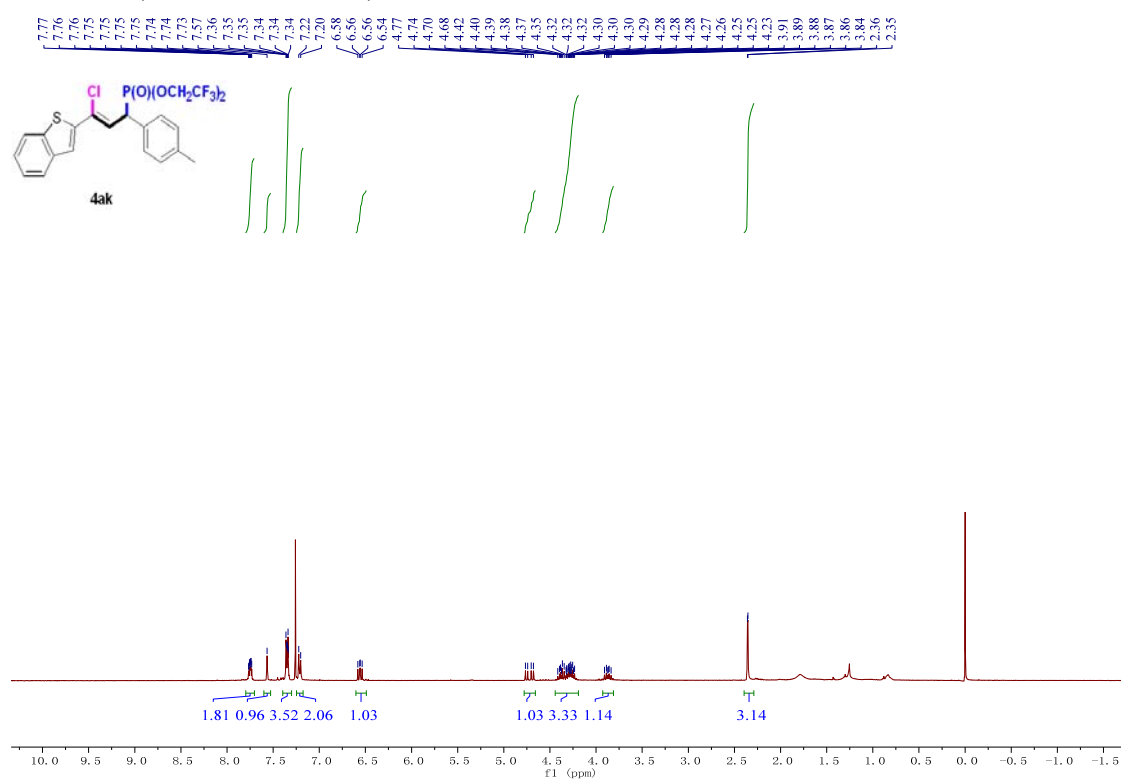
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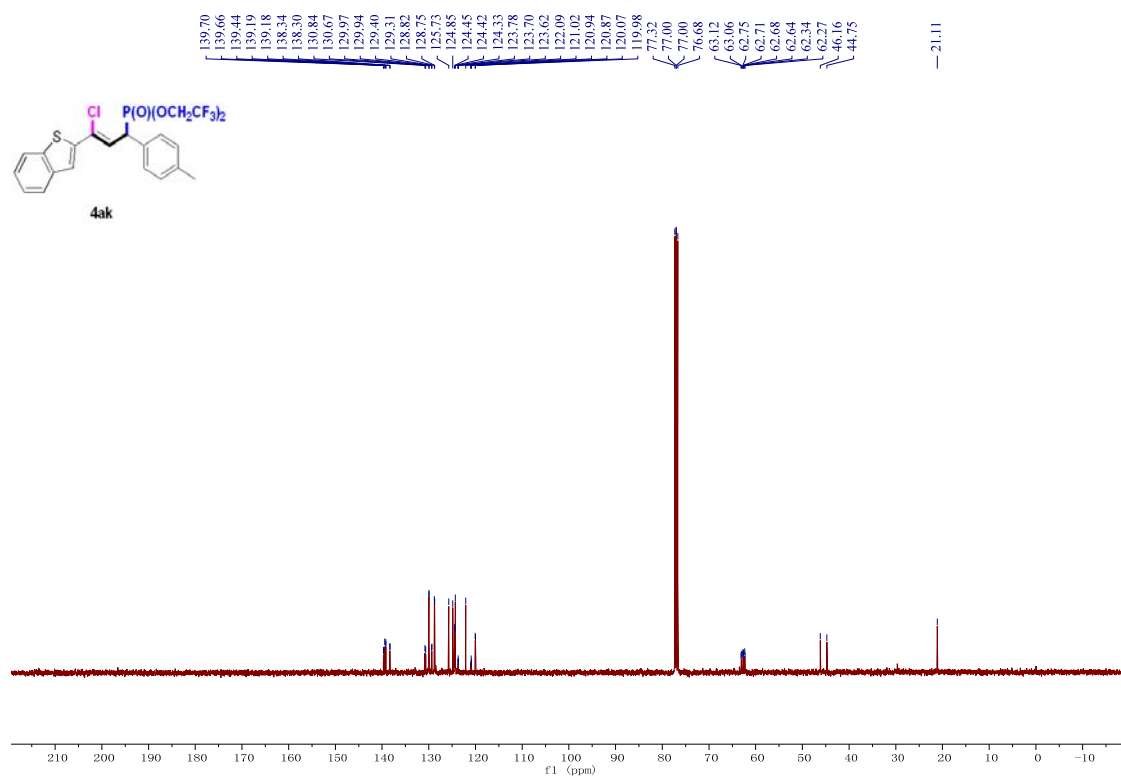
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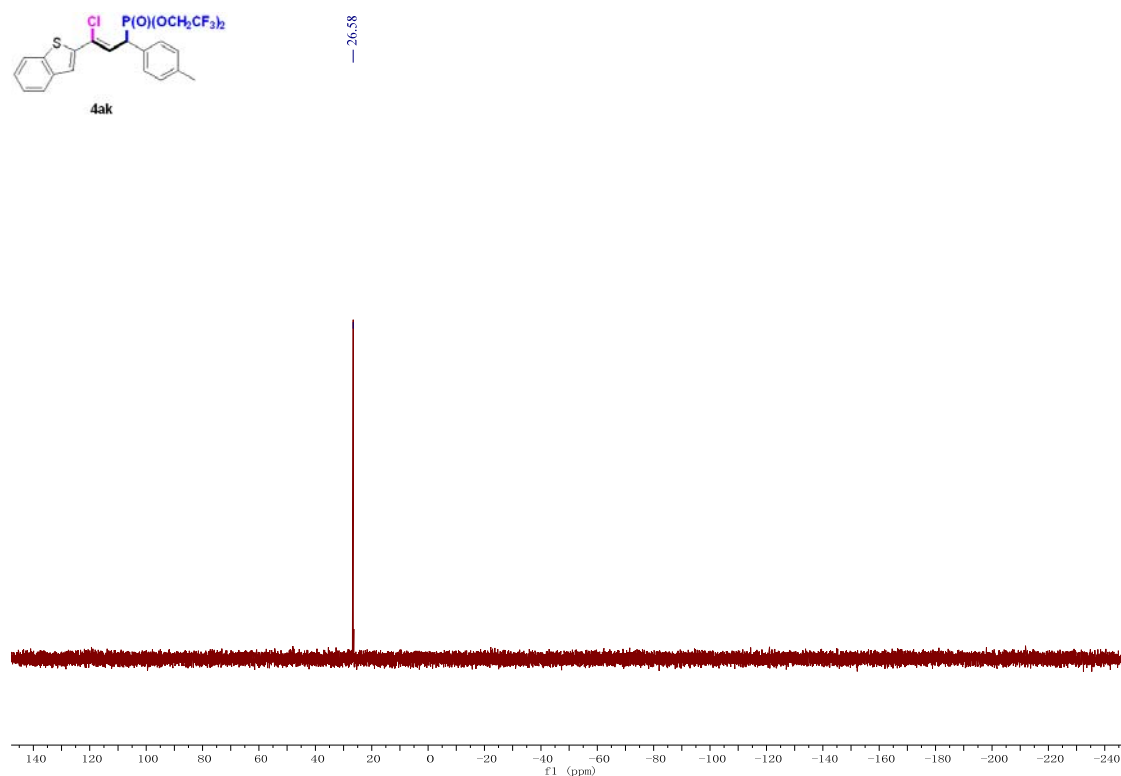
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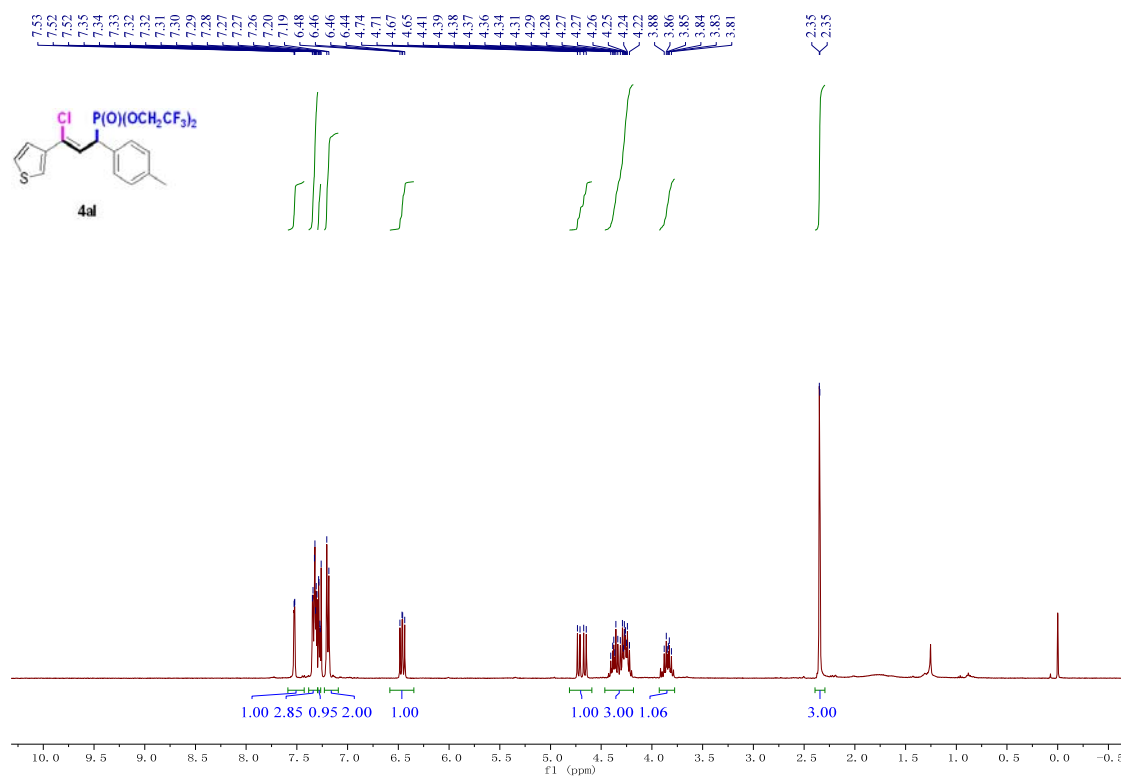
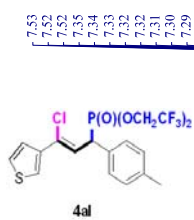
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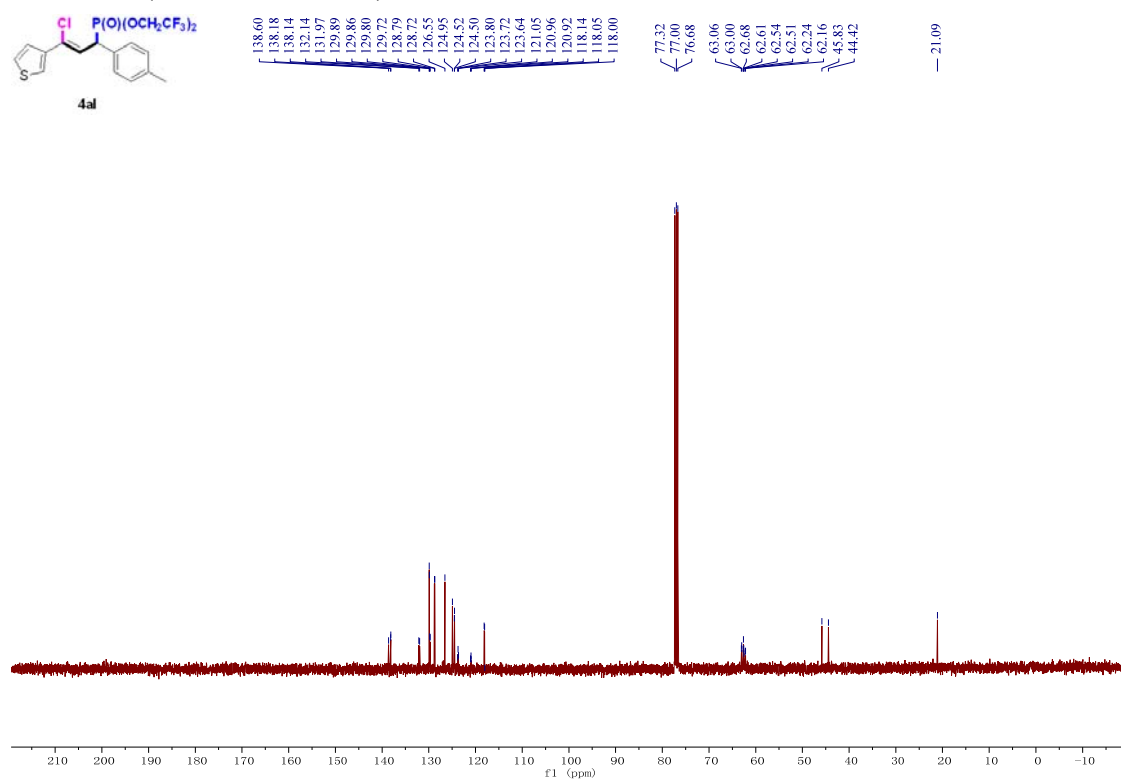
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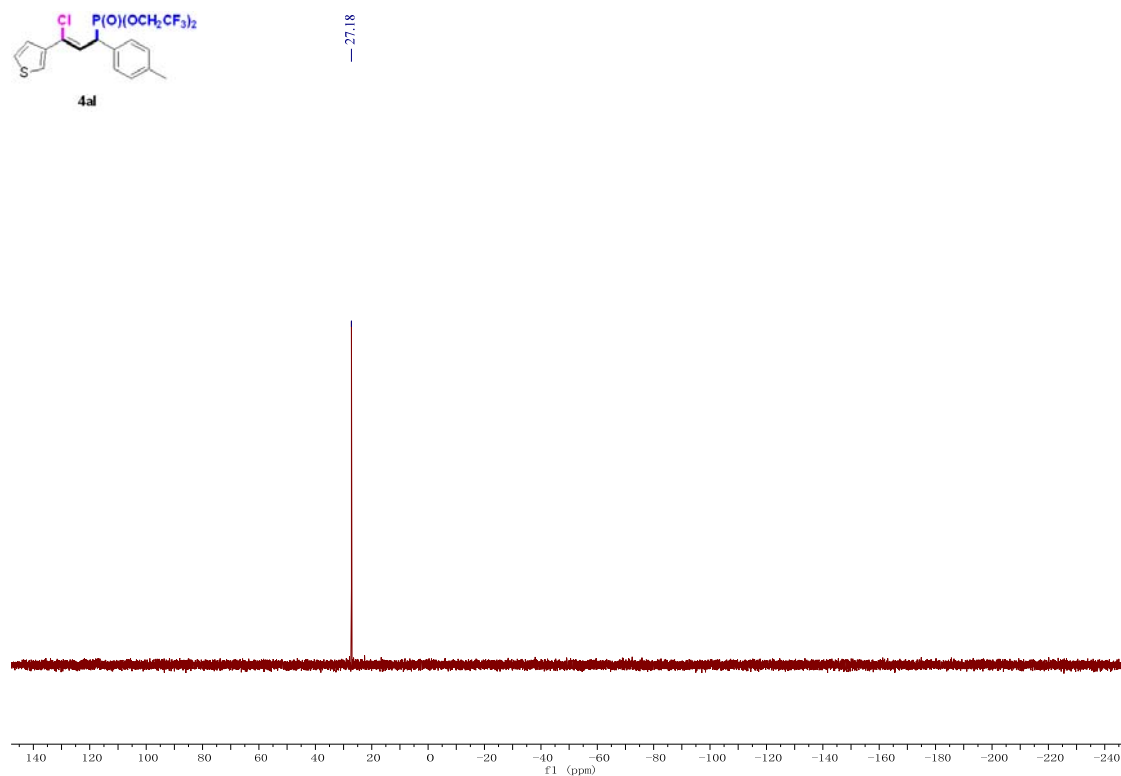
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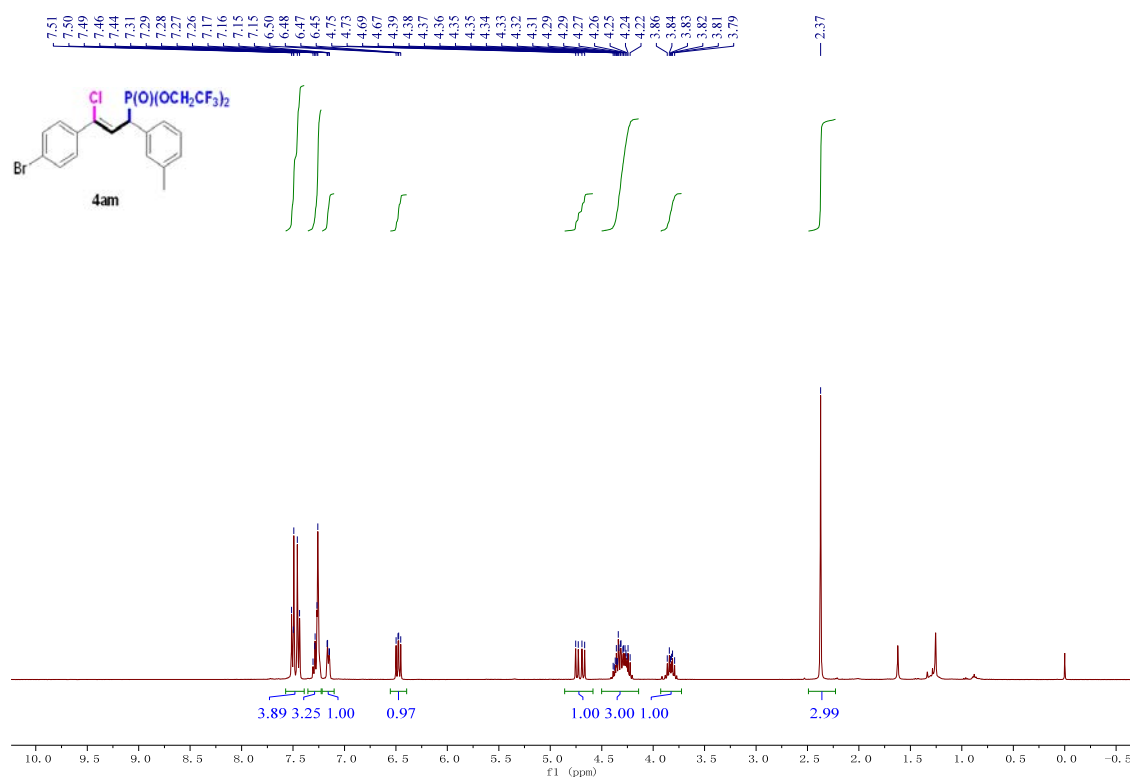
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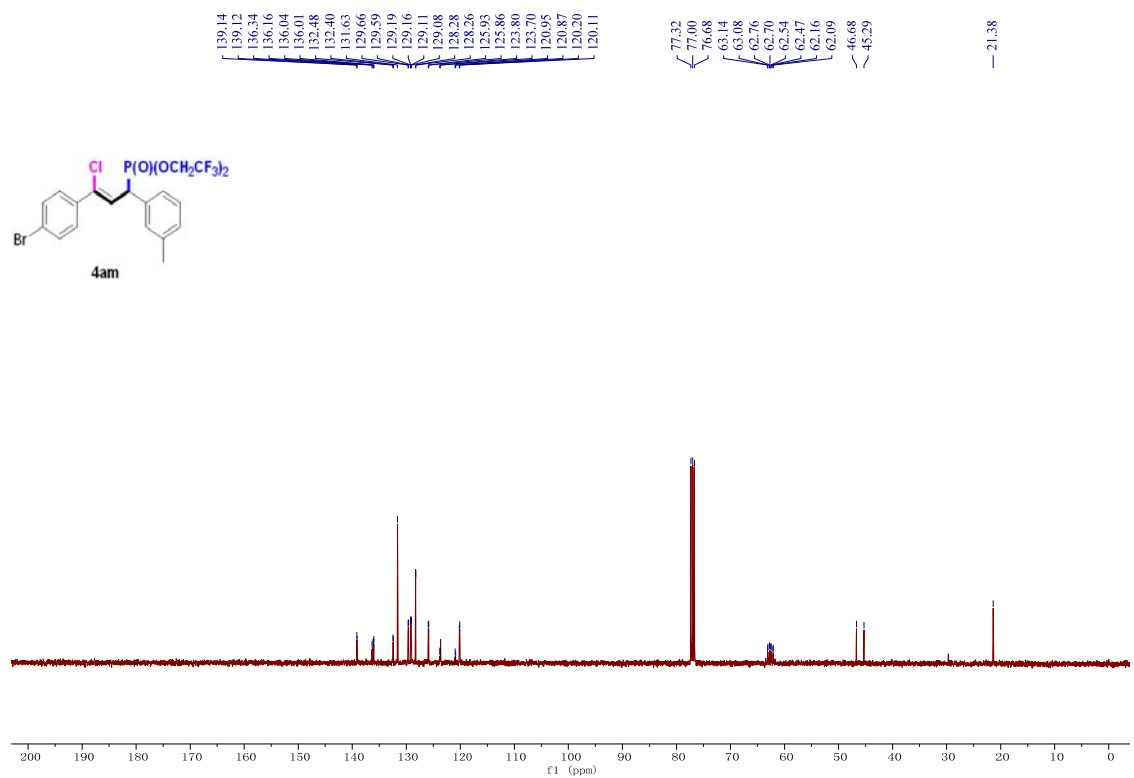
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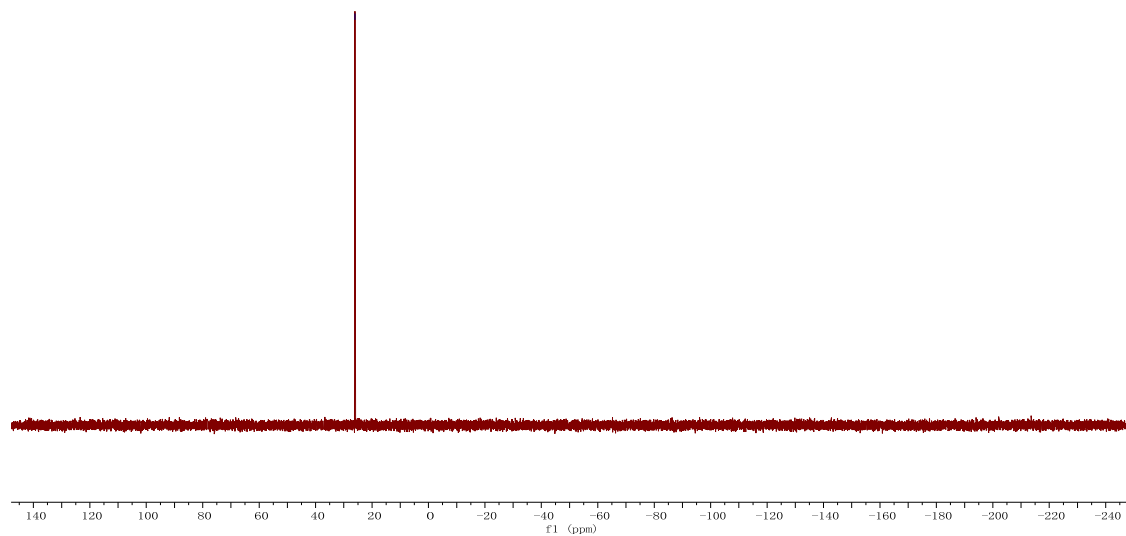
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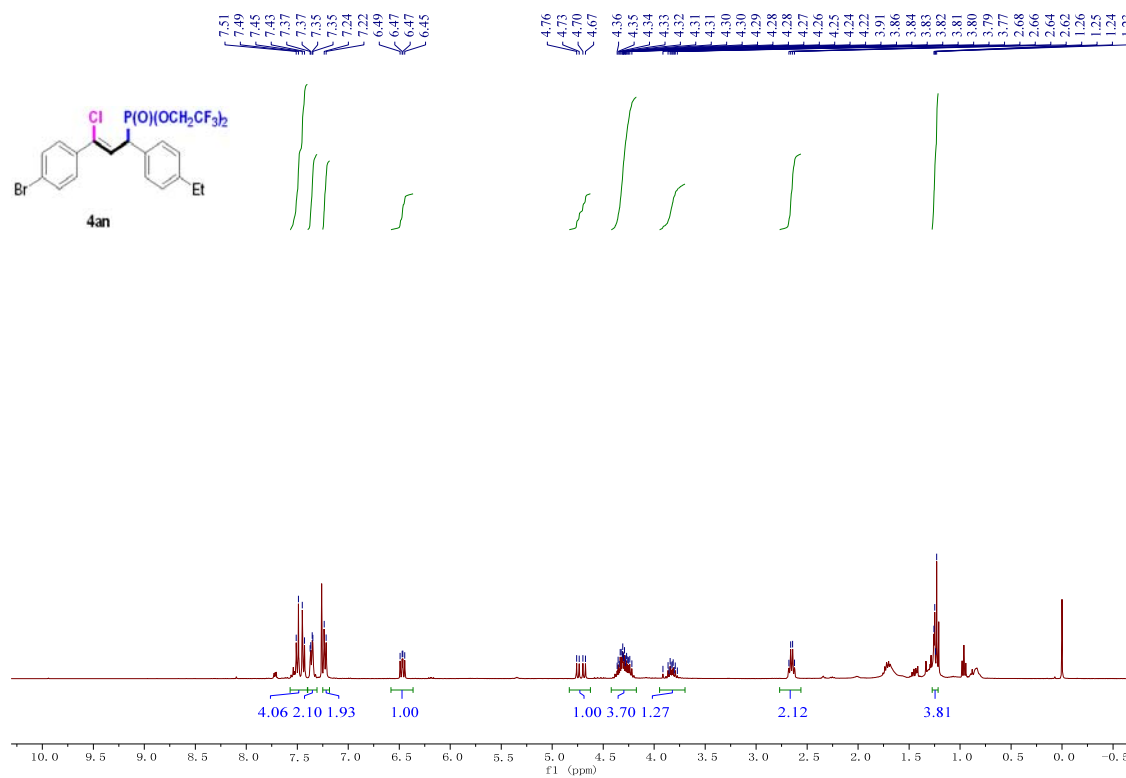
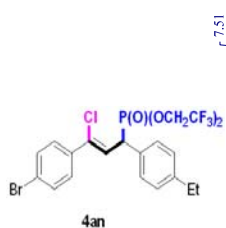
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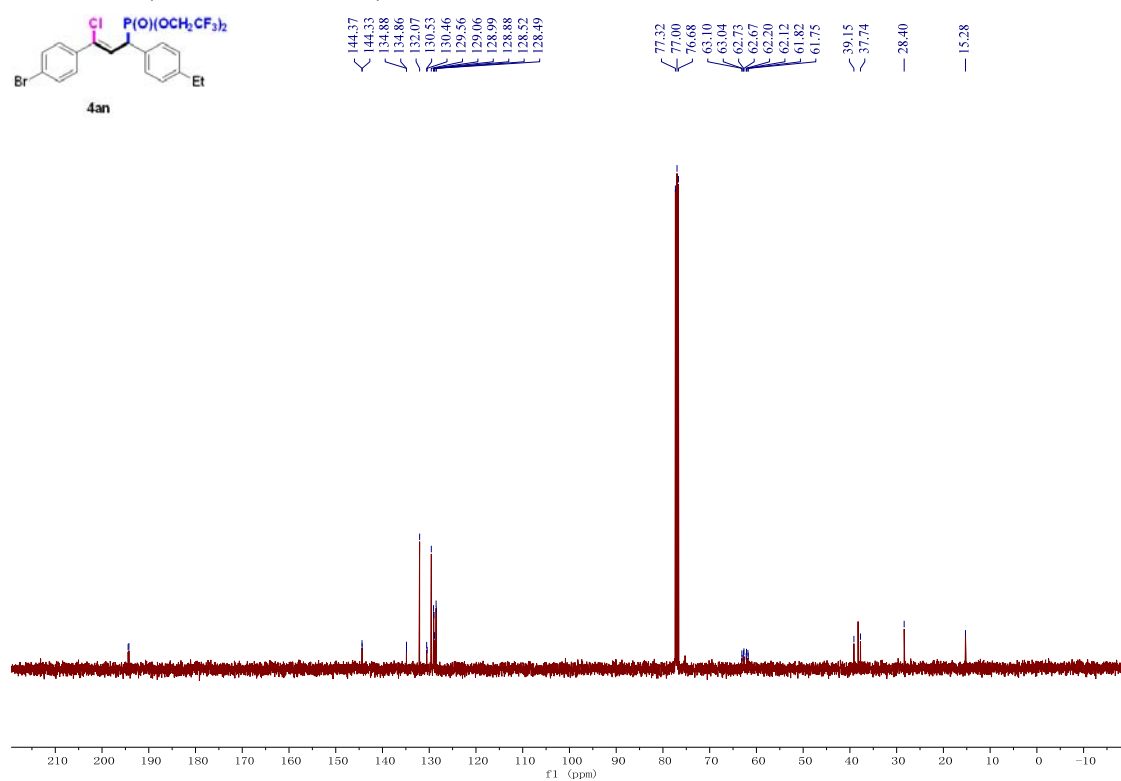
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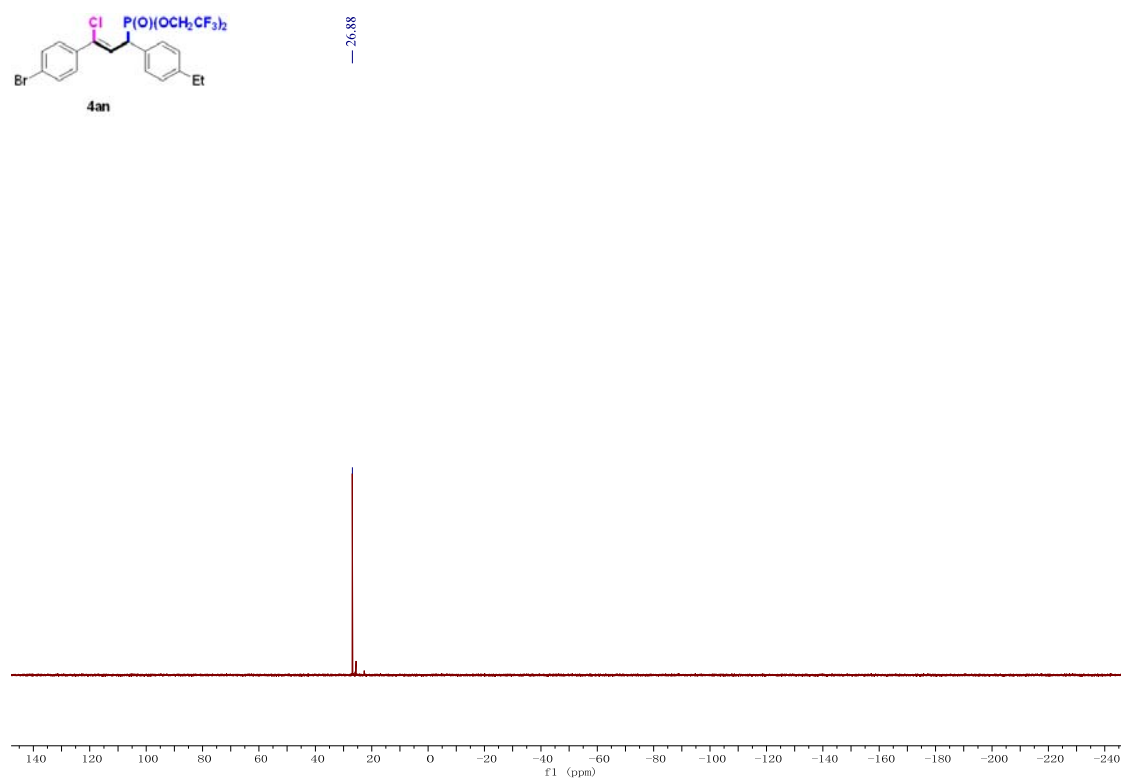
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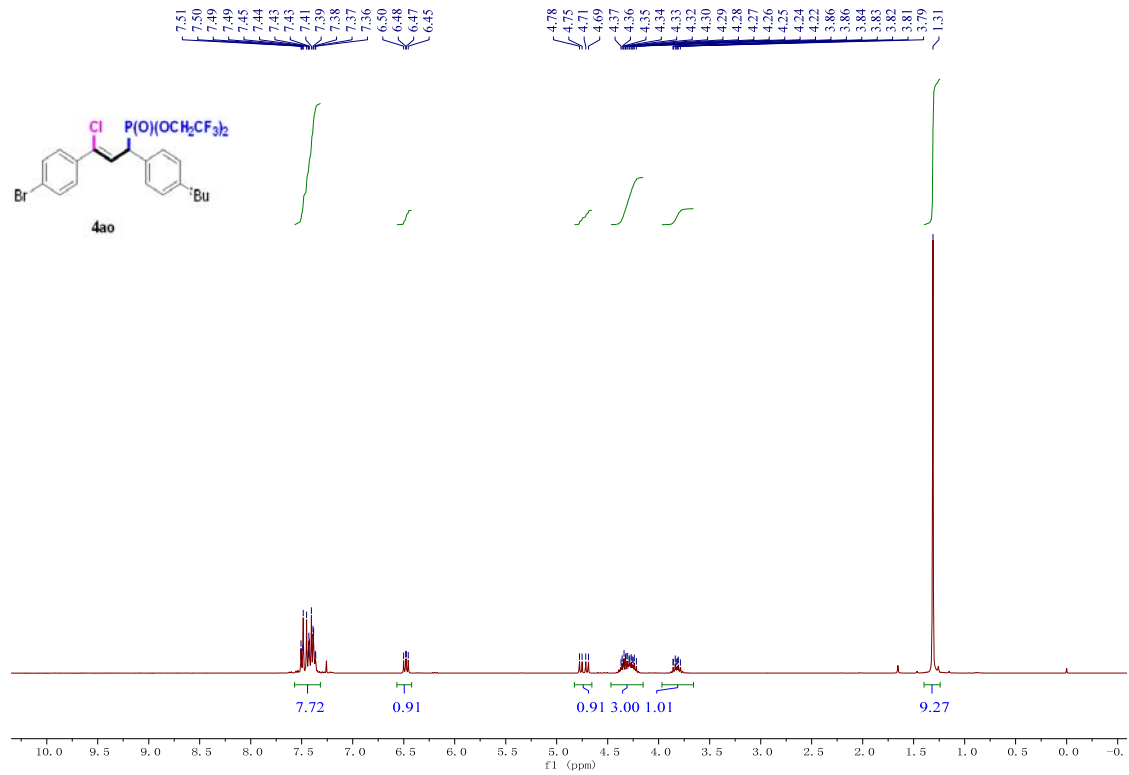
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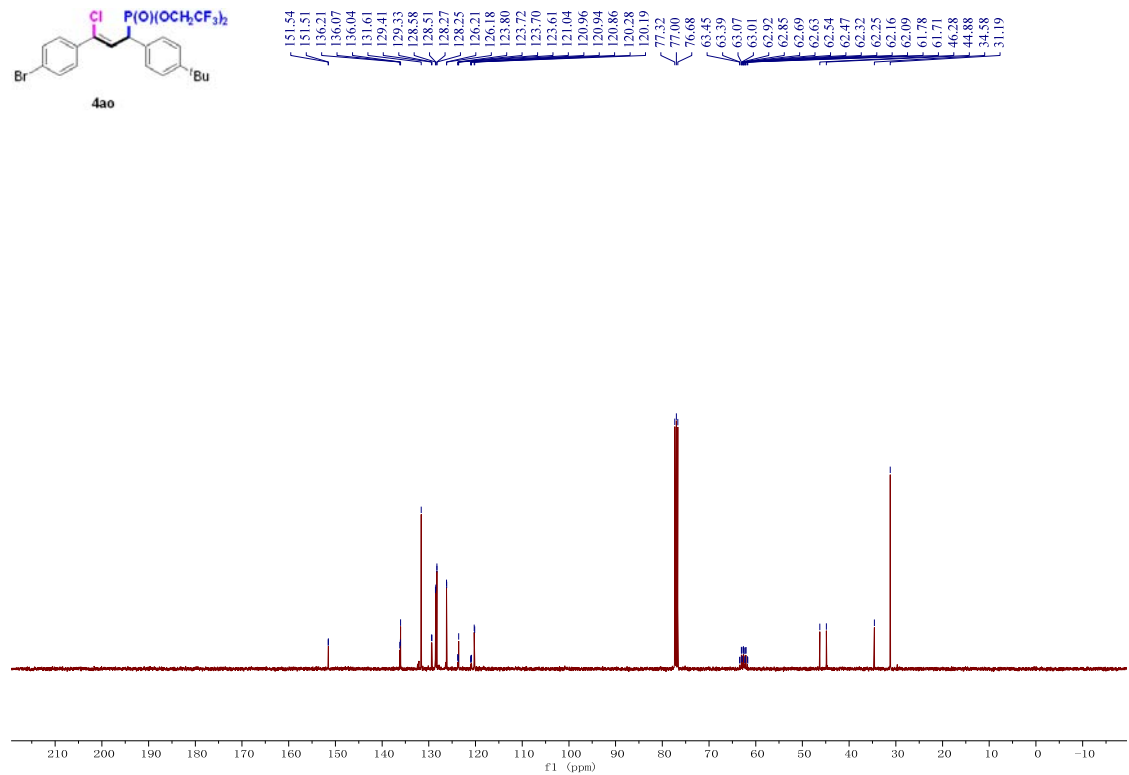
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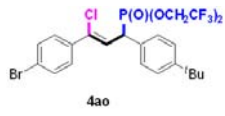
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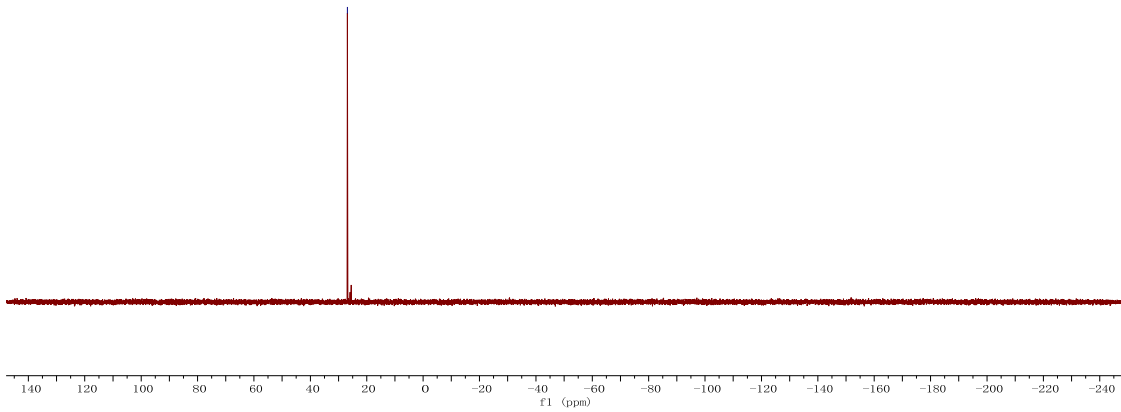
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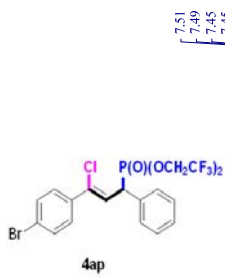
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26.86

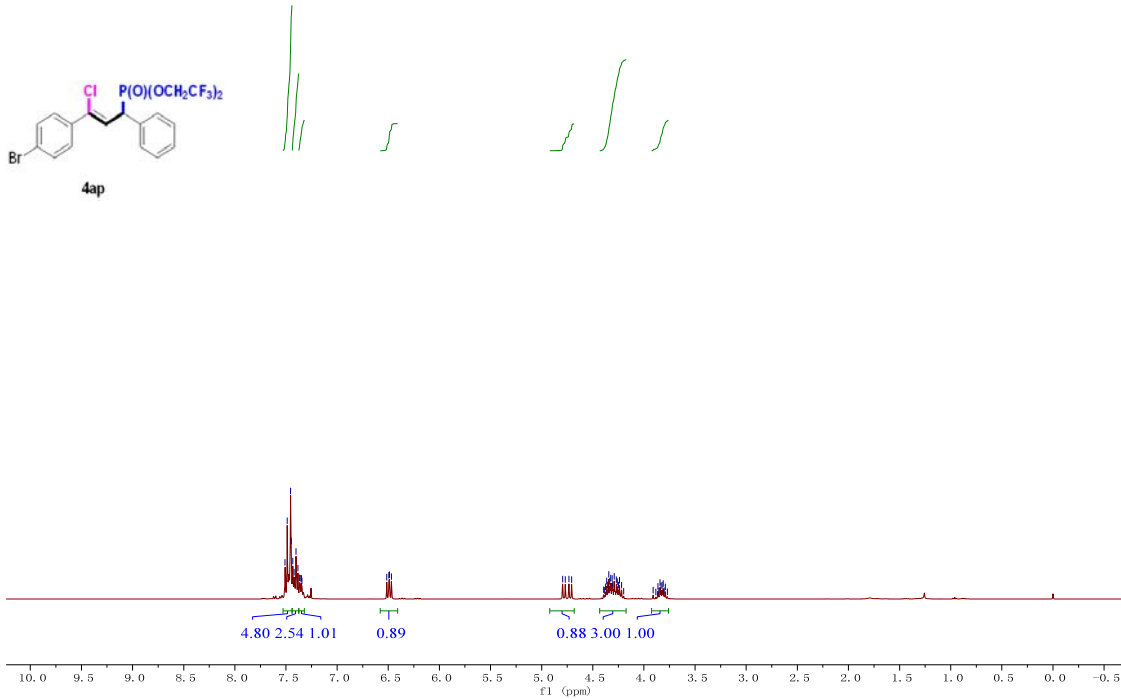


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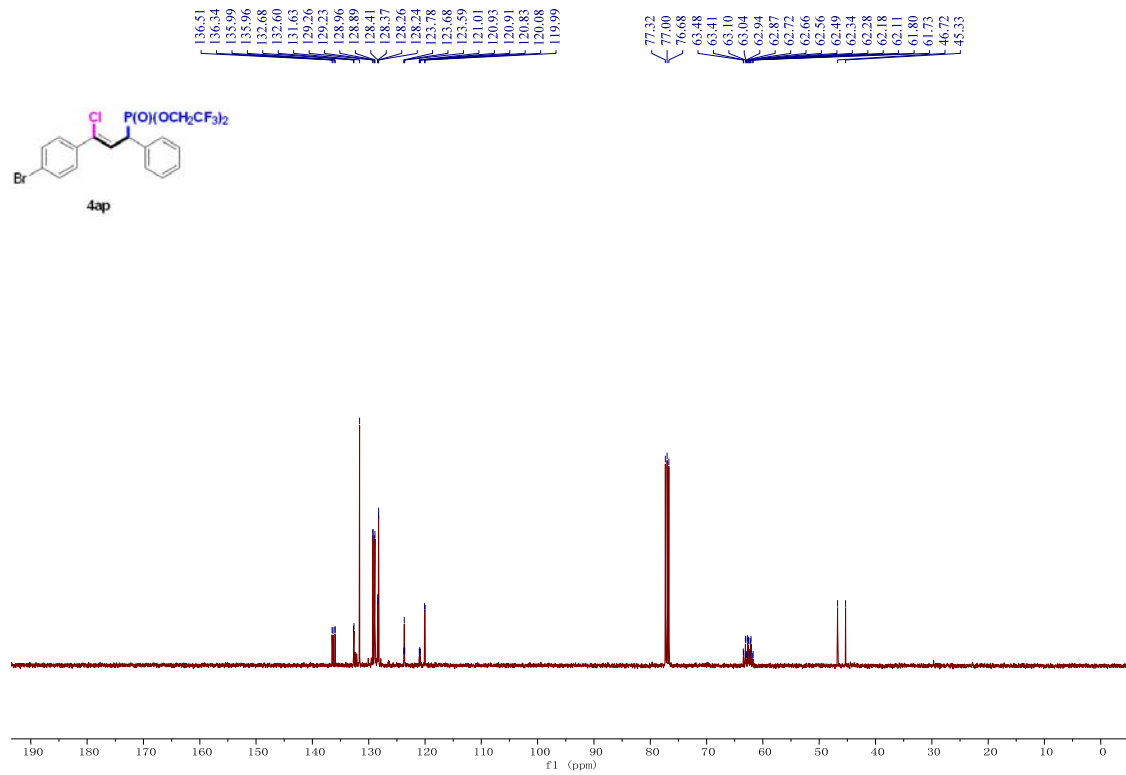


7.51
7.49
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7.35
7.34
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6.49
6.47

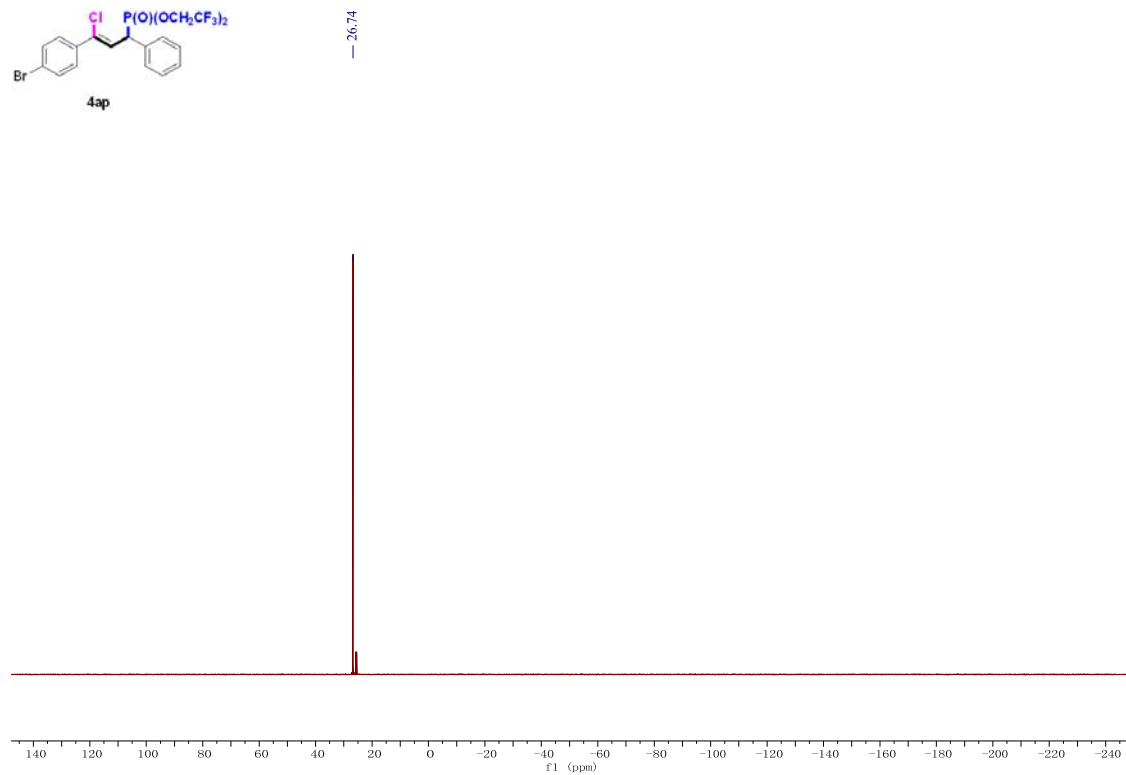
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4.25
4.22
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3.77



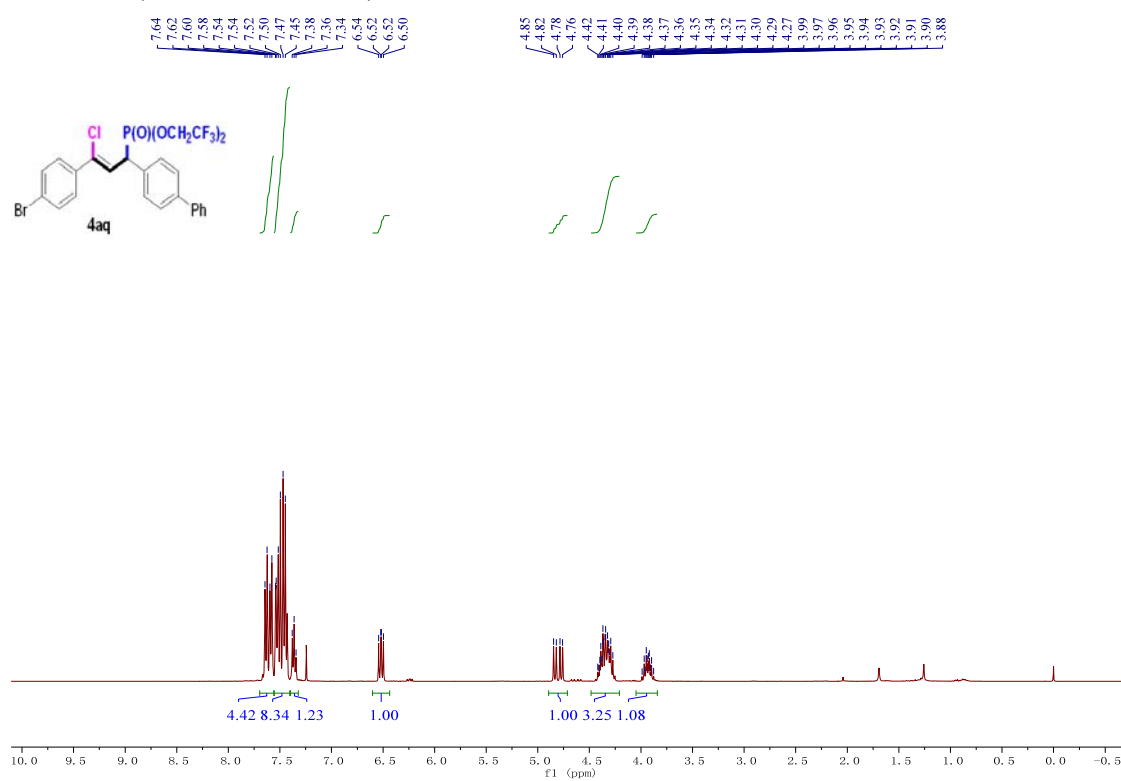
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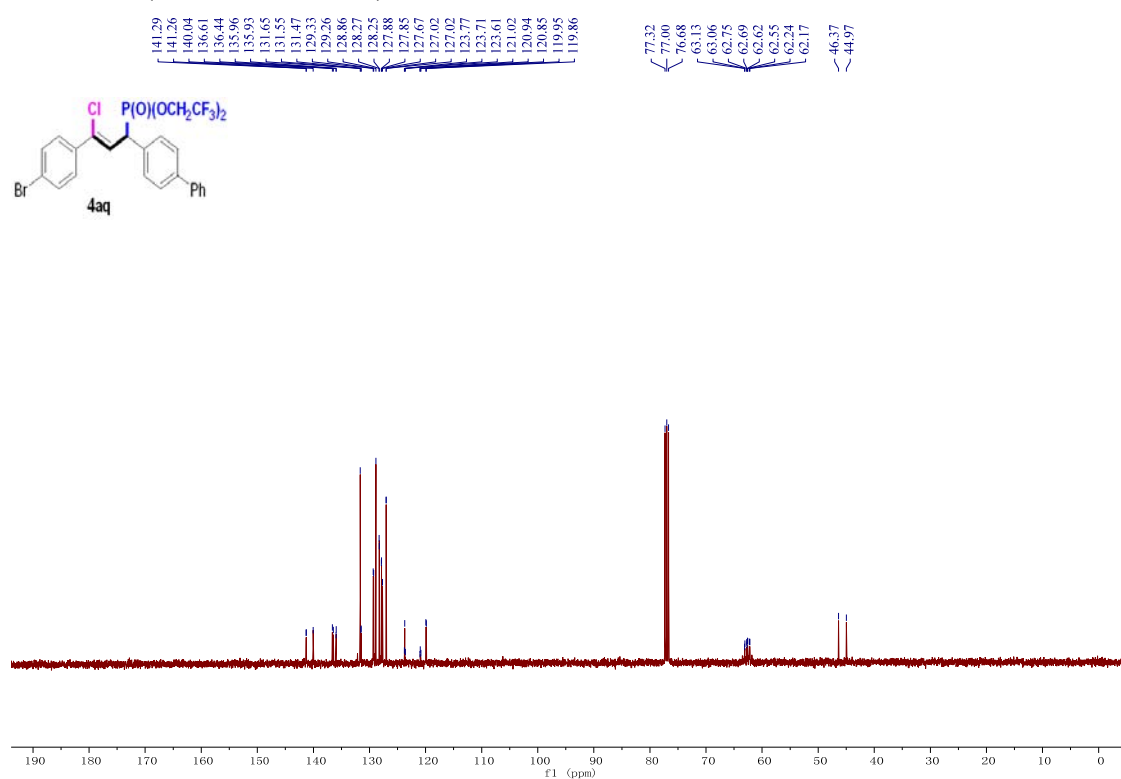
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^1H NMR (400 MHz, CDCl_3)



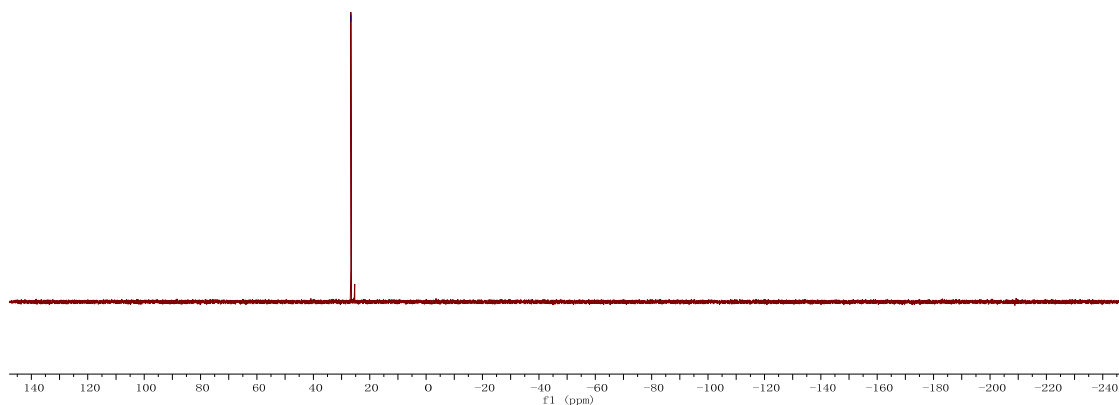
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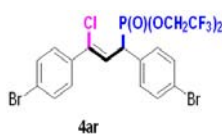
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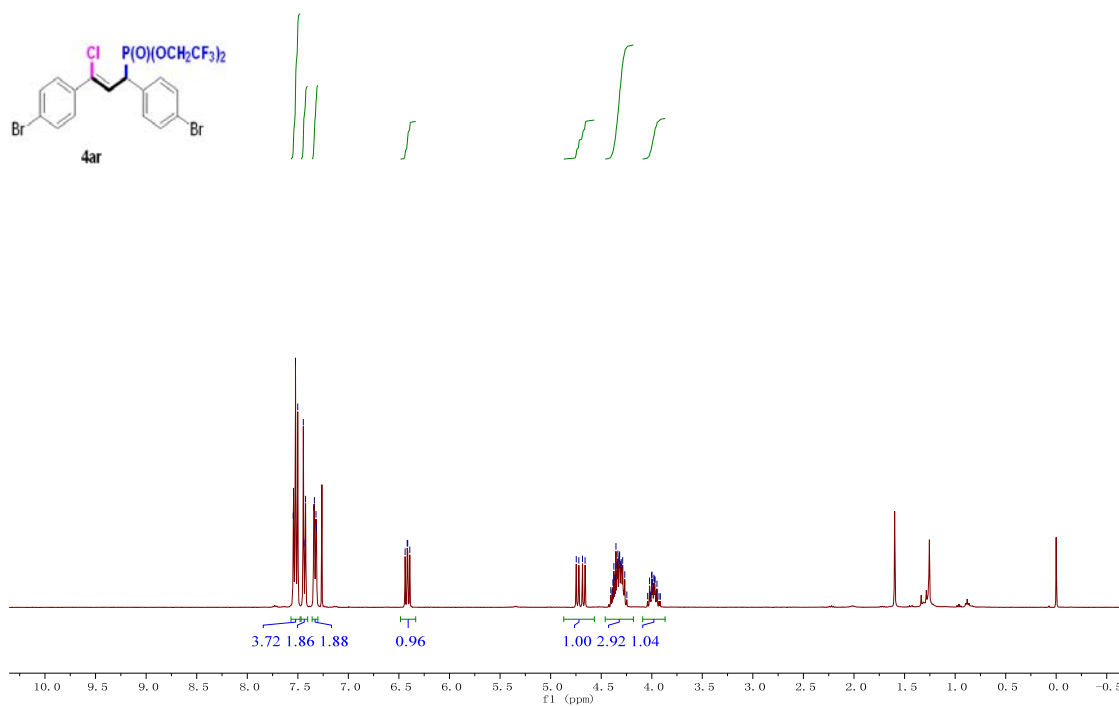
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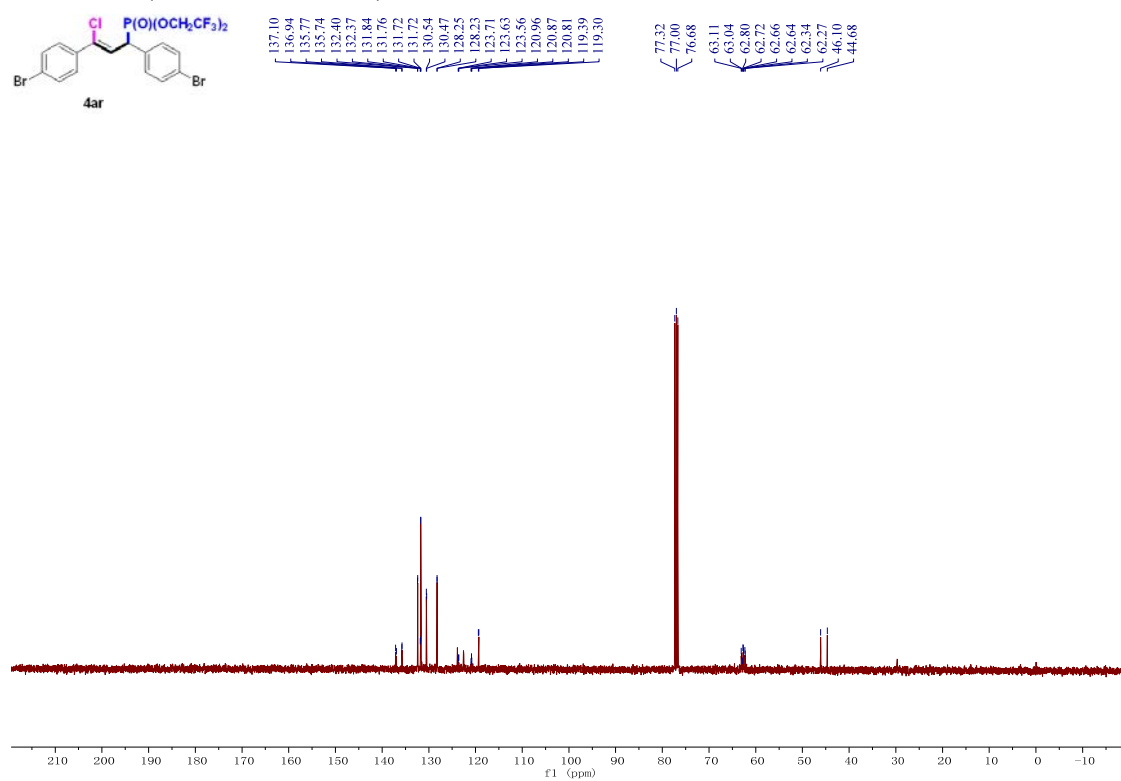
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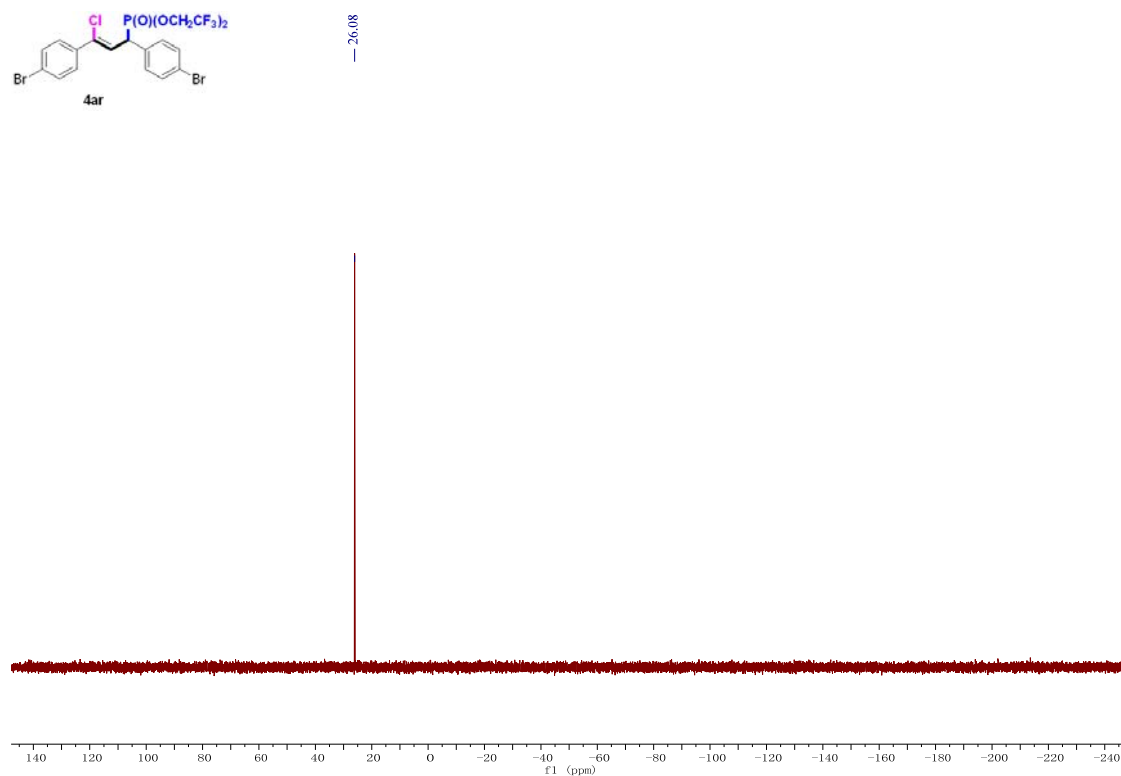
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3.93
3.92



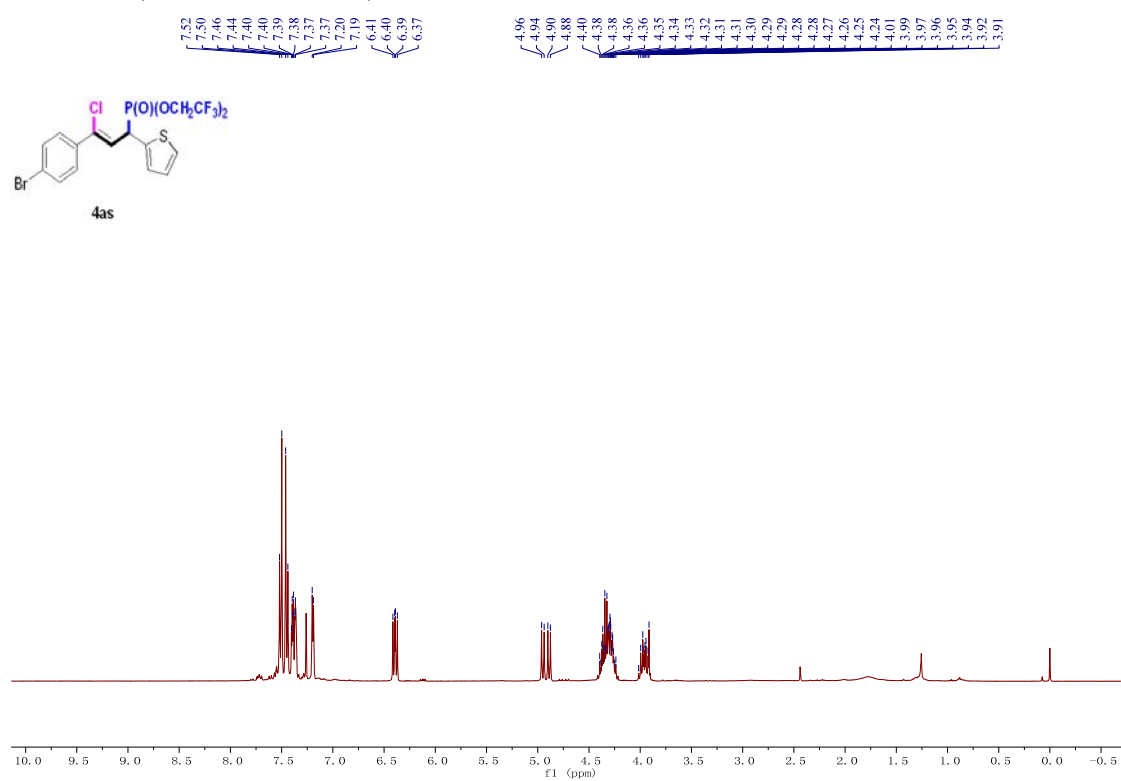
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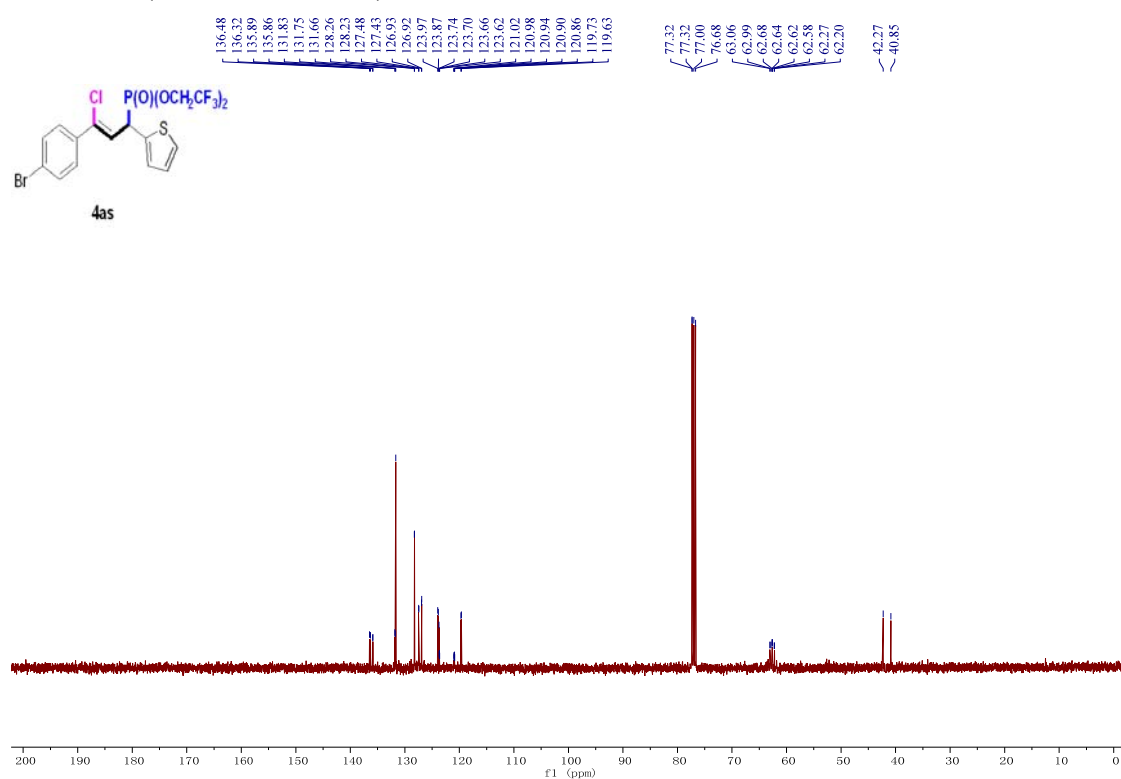
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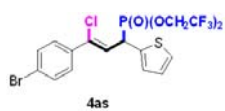
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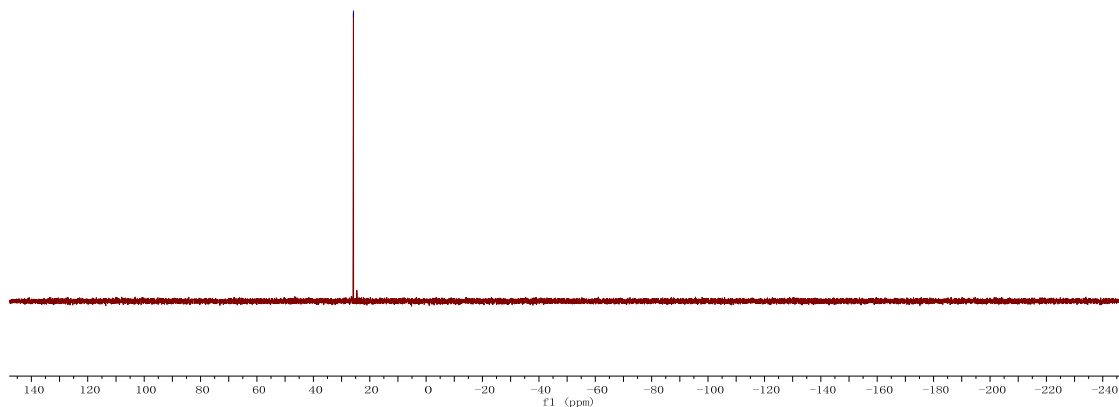
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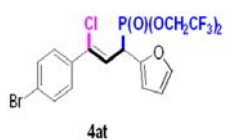
^{31}P NMR (162 MHz, CDCl_3)



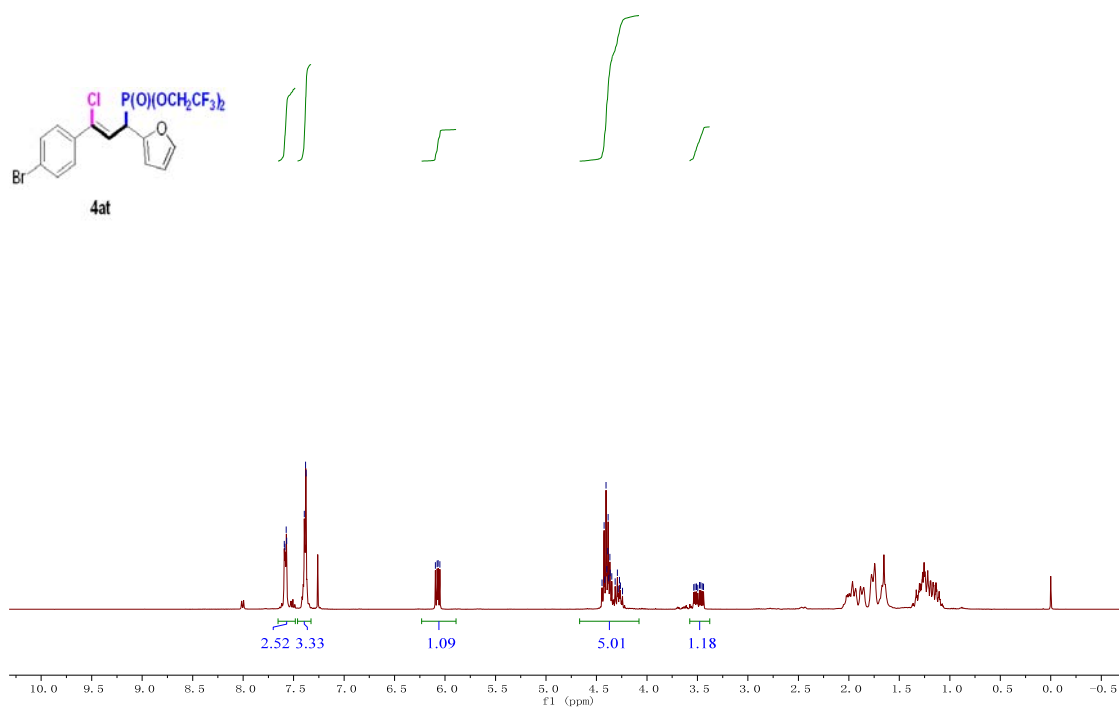
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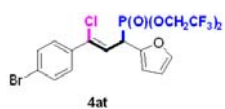
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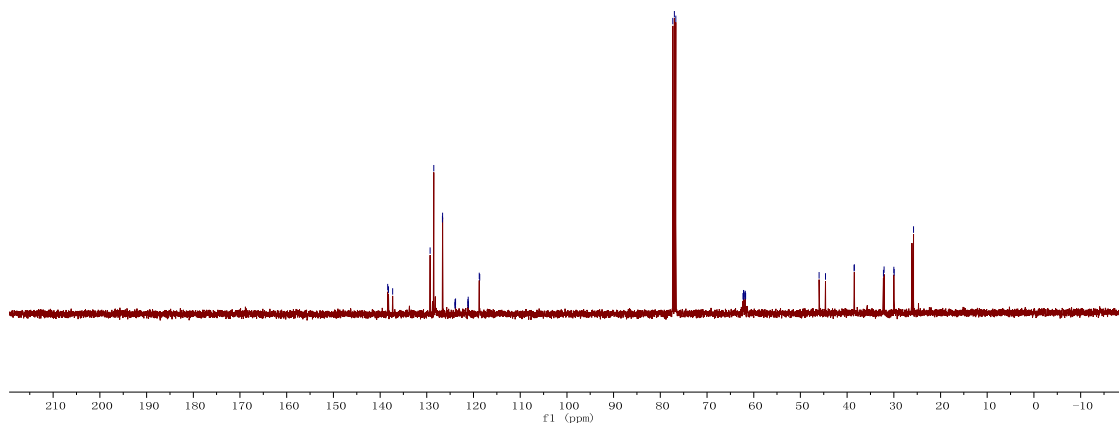
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3.44



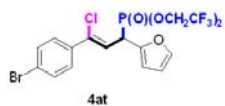
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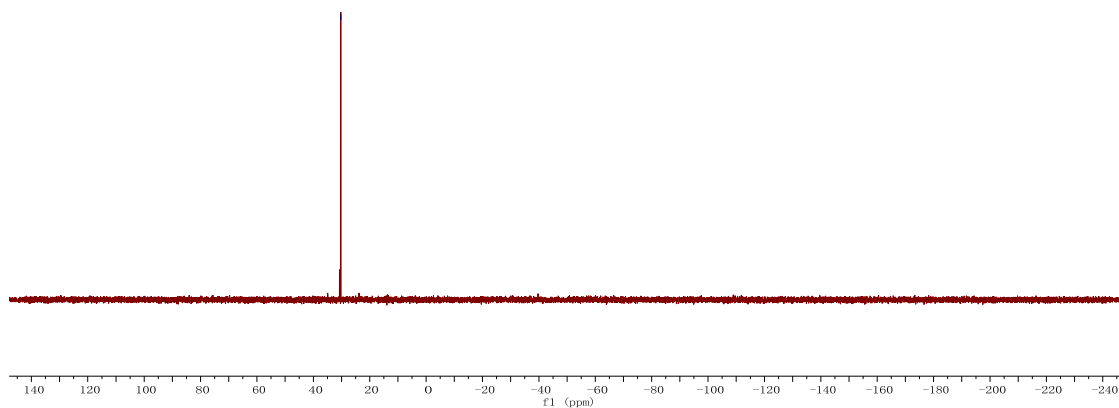
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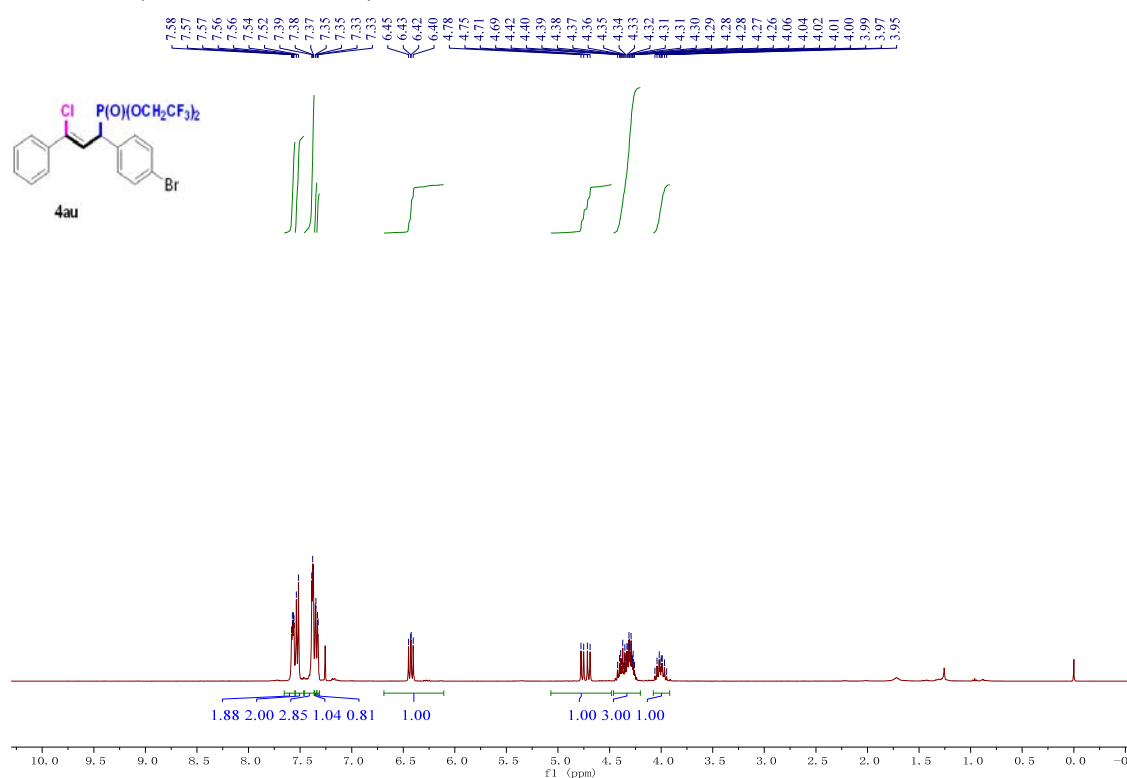
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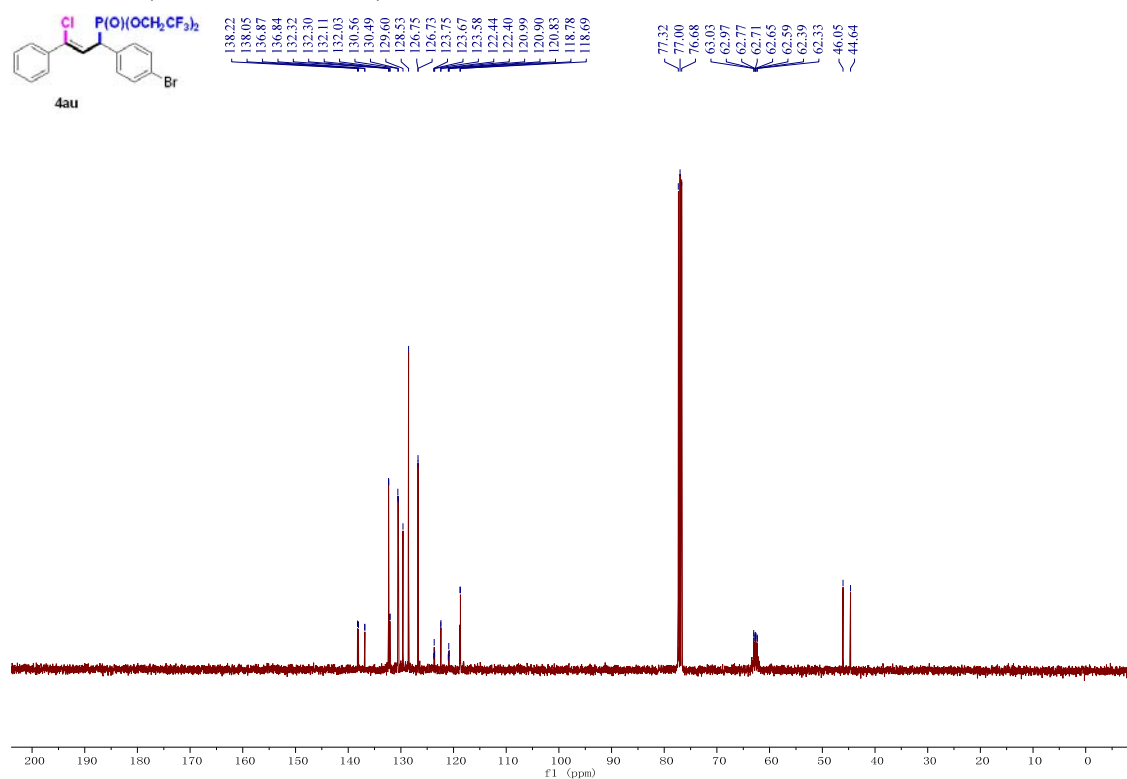
30.27



¹H NMR (400 MHz, CDCl₃)



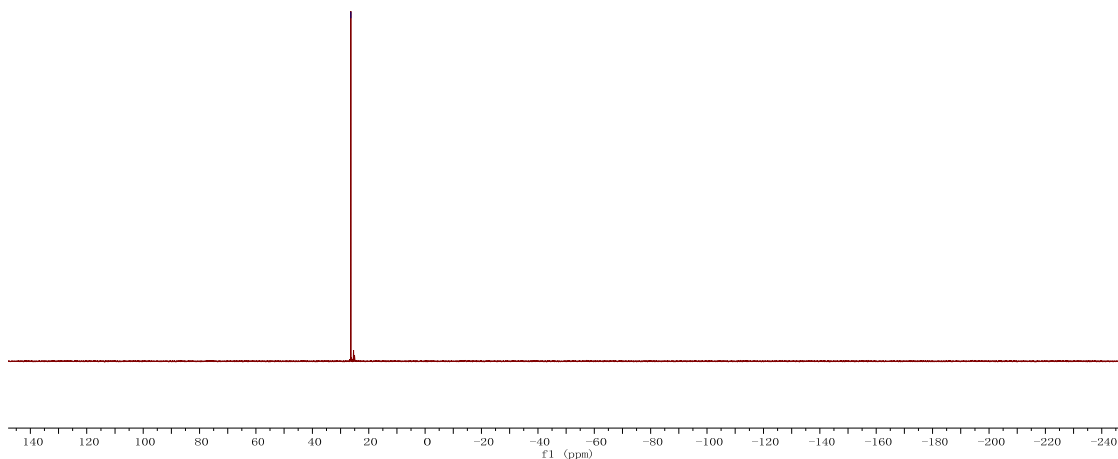
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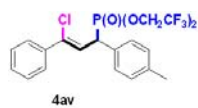
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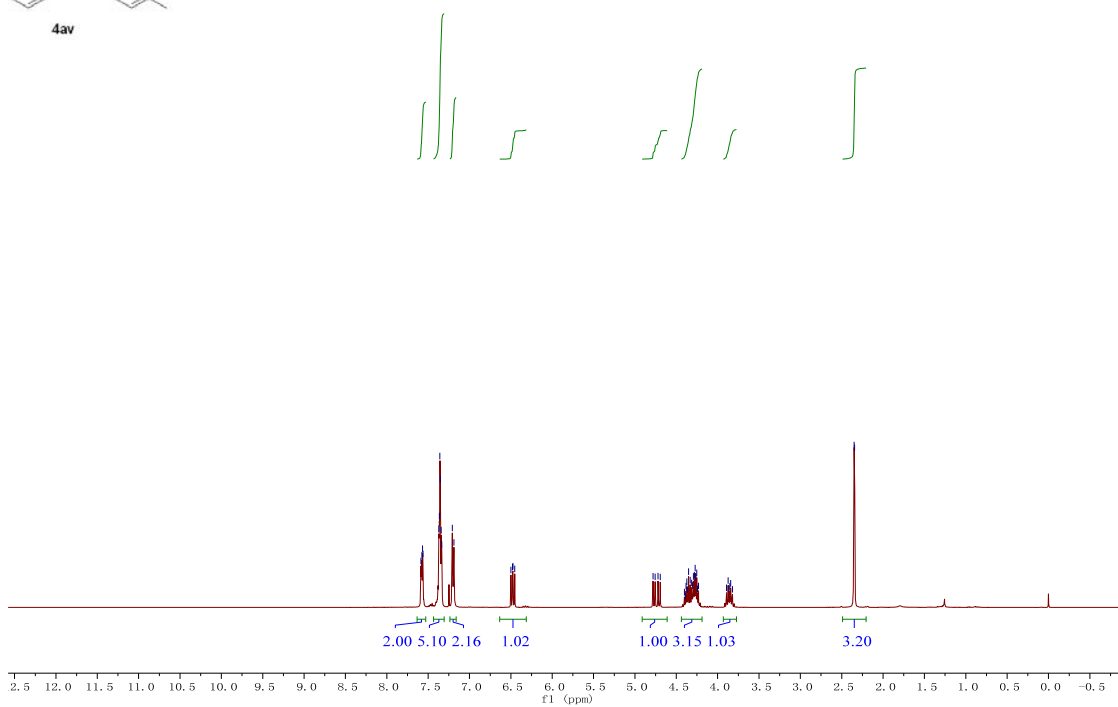
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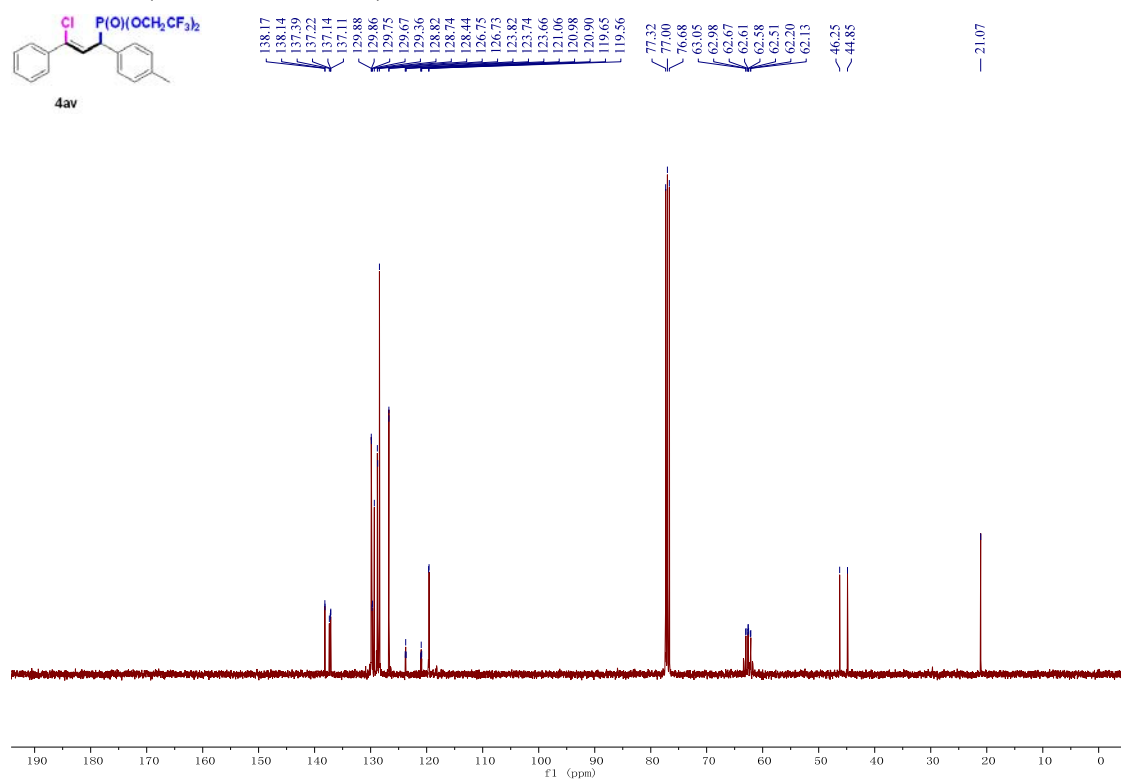
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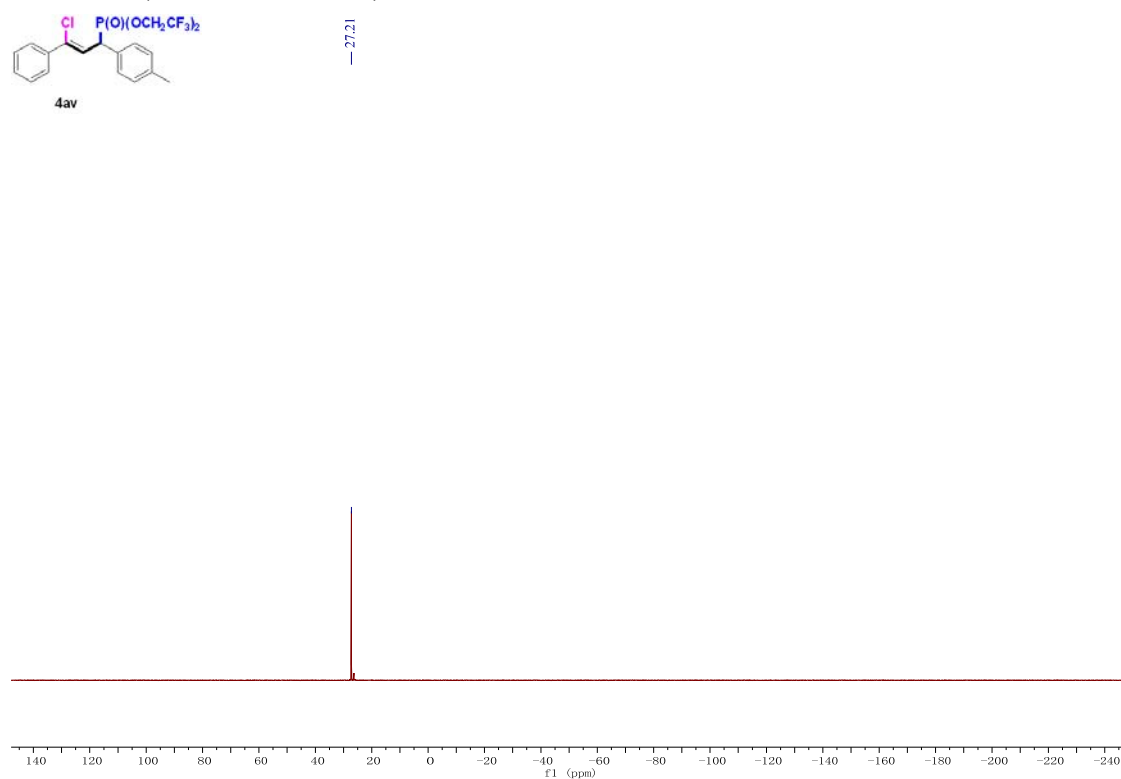
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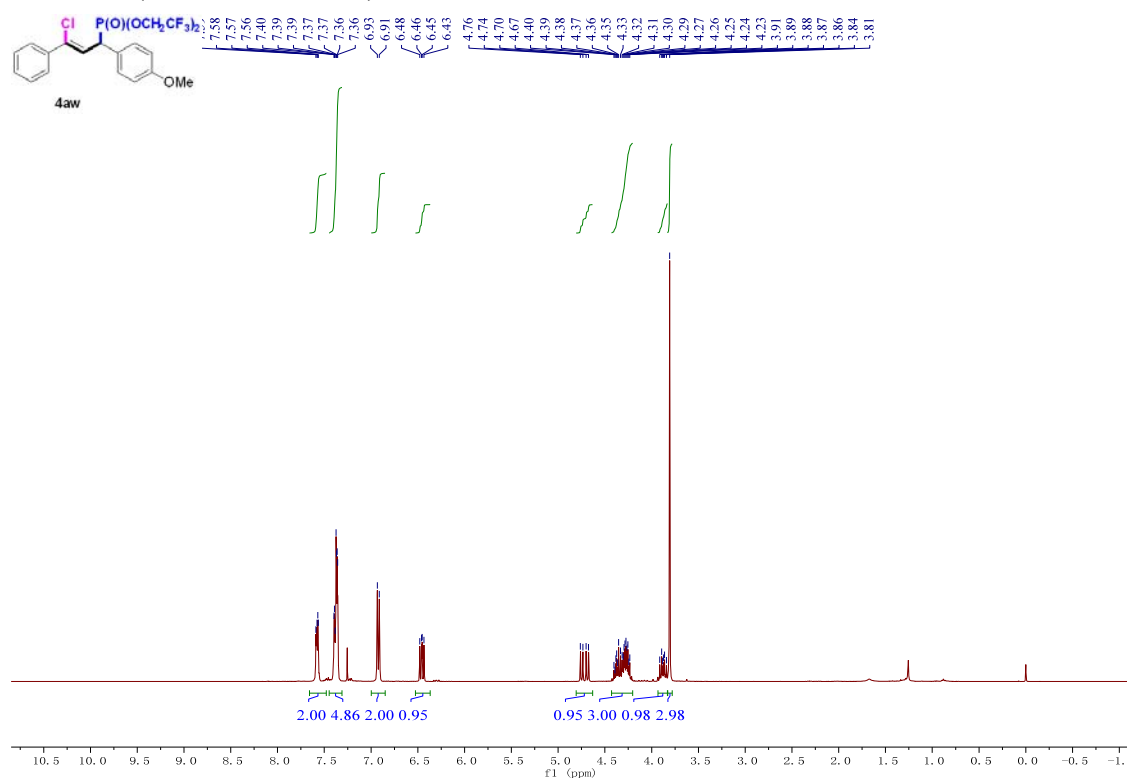
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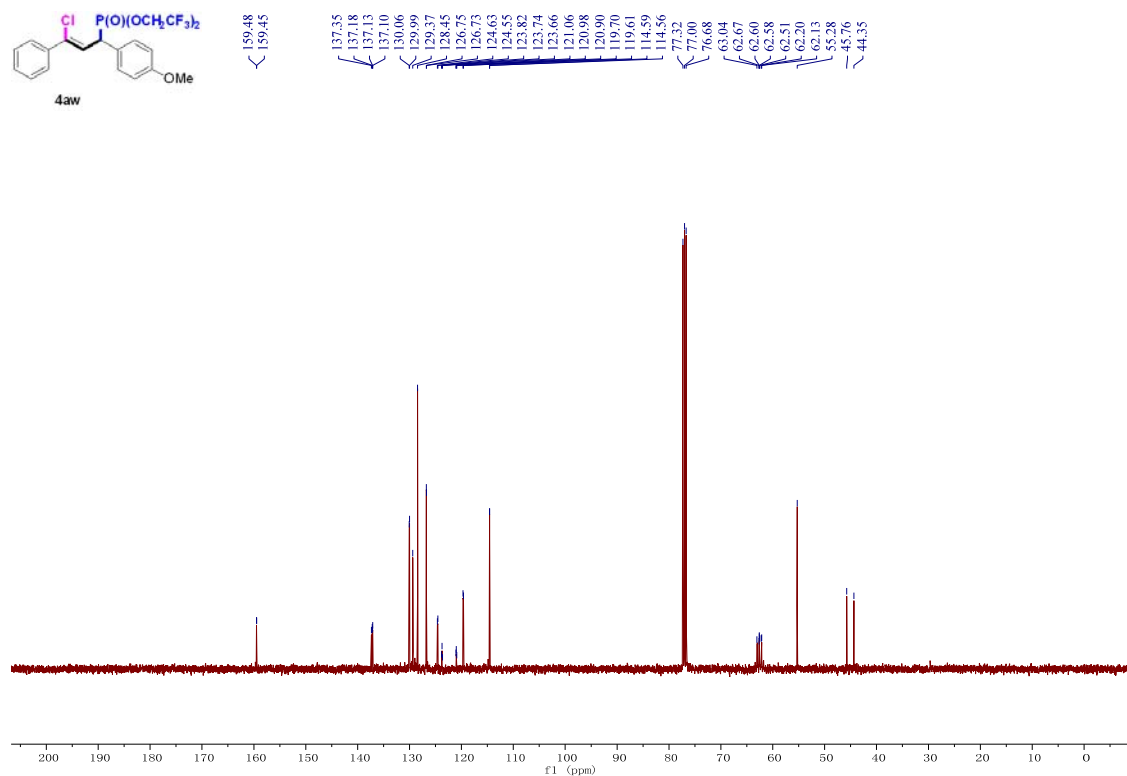
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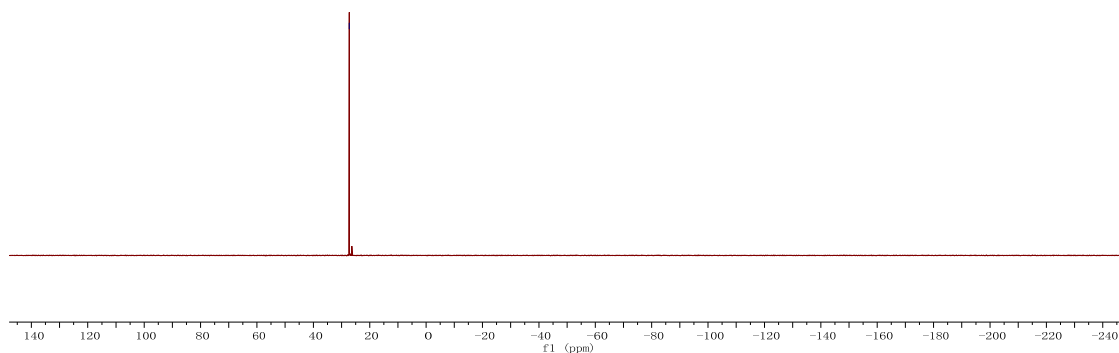
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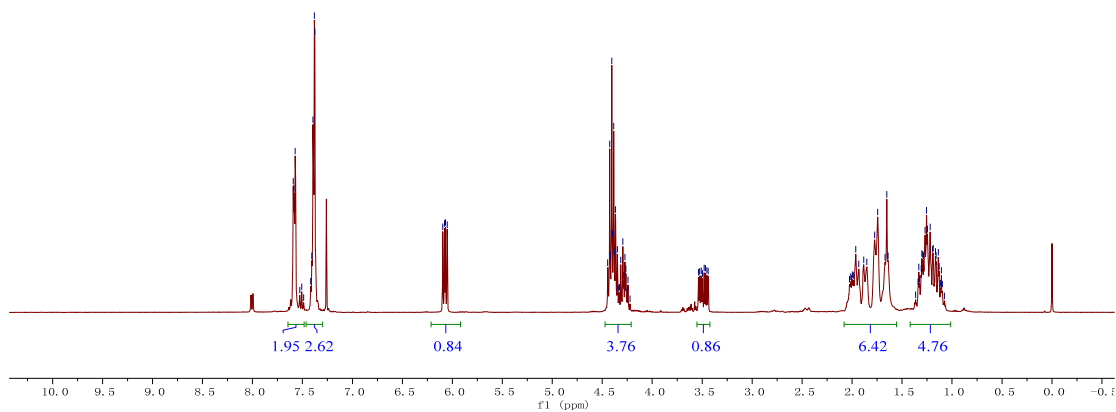
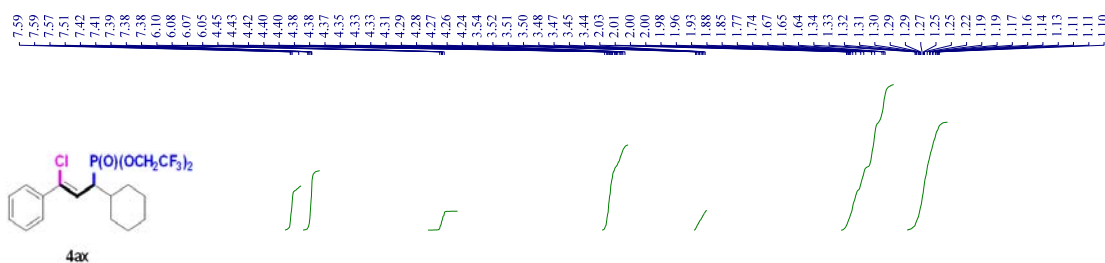
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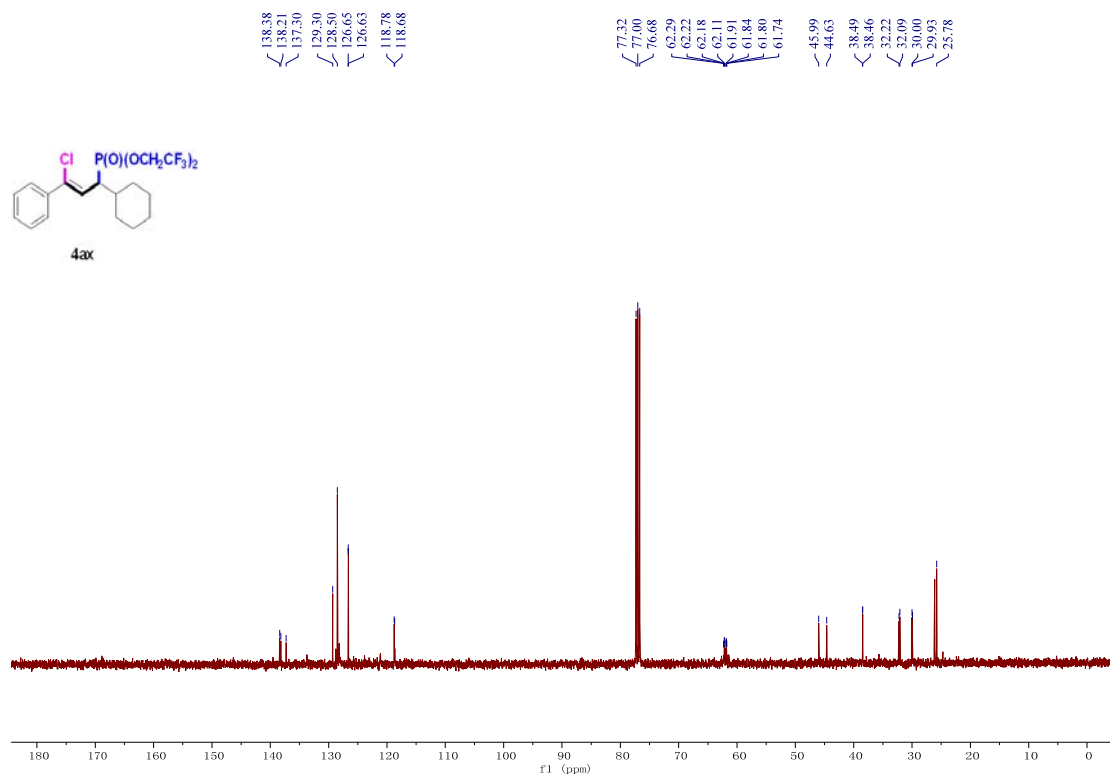
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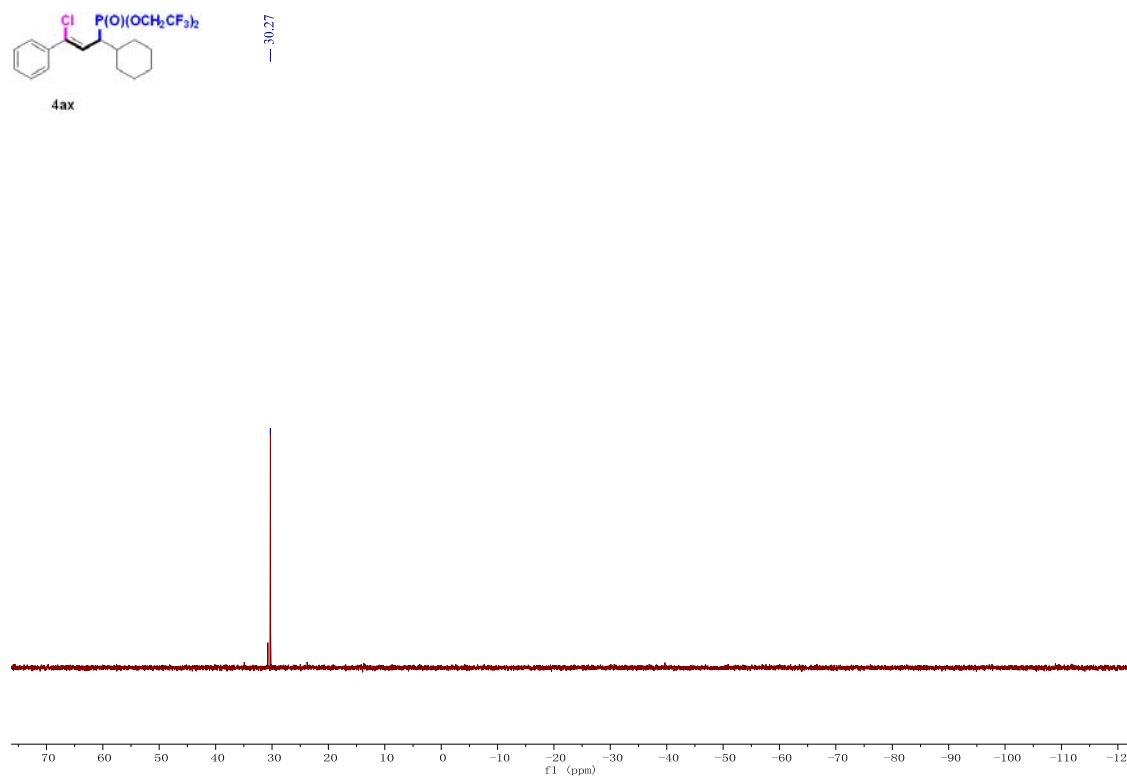
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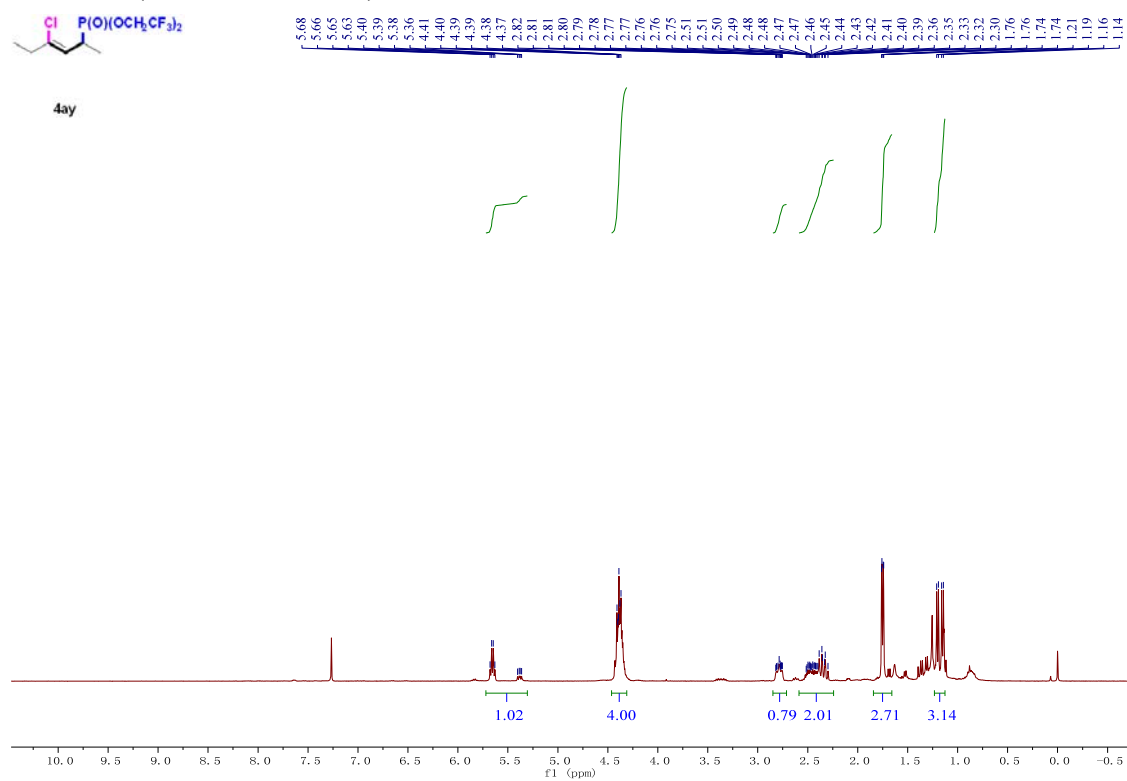
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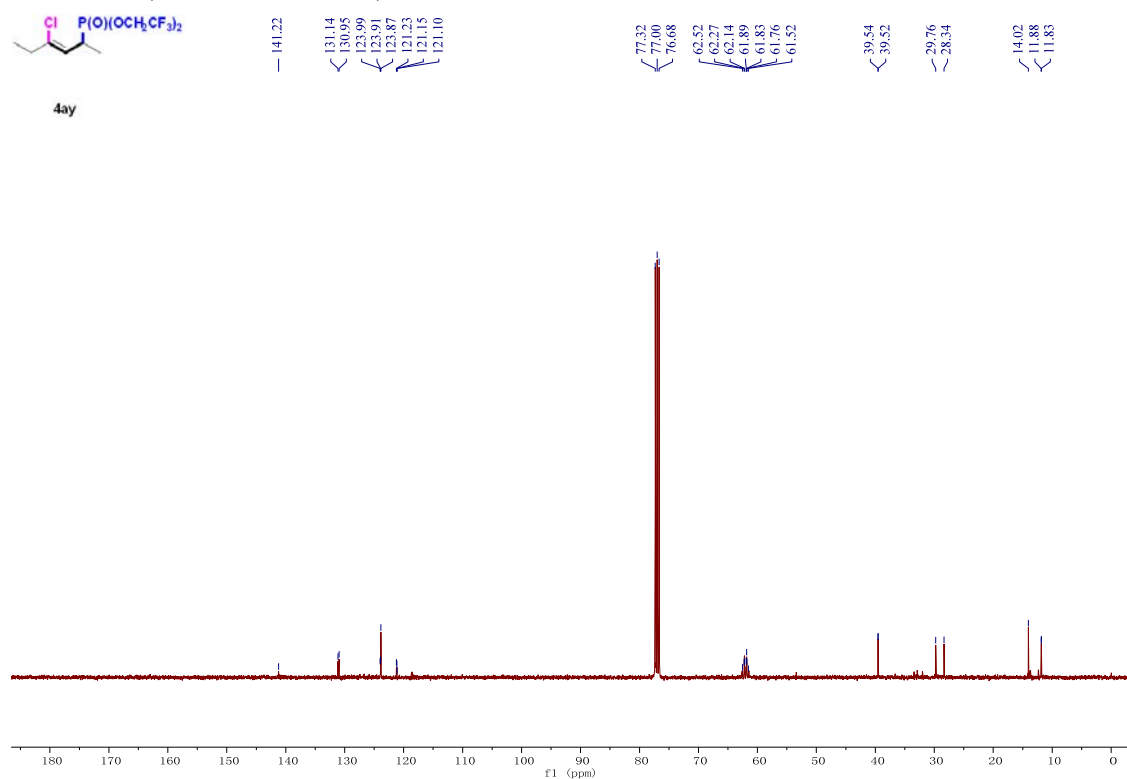
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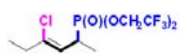
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¹³C NMR (101 MHz, CDCl₃)

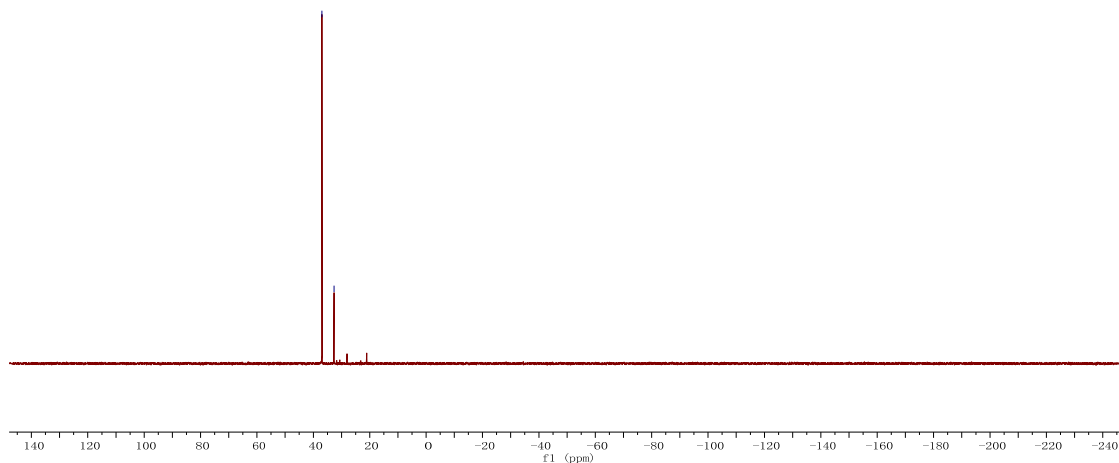


^{31}P NMR (162 MHz, CDCl_3)



36.96
32.64

4ay

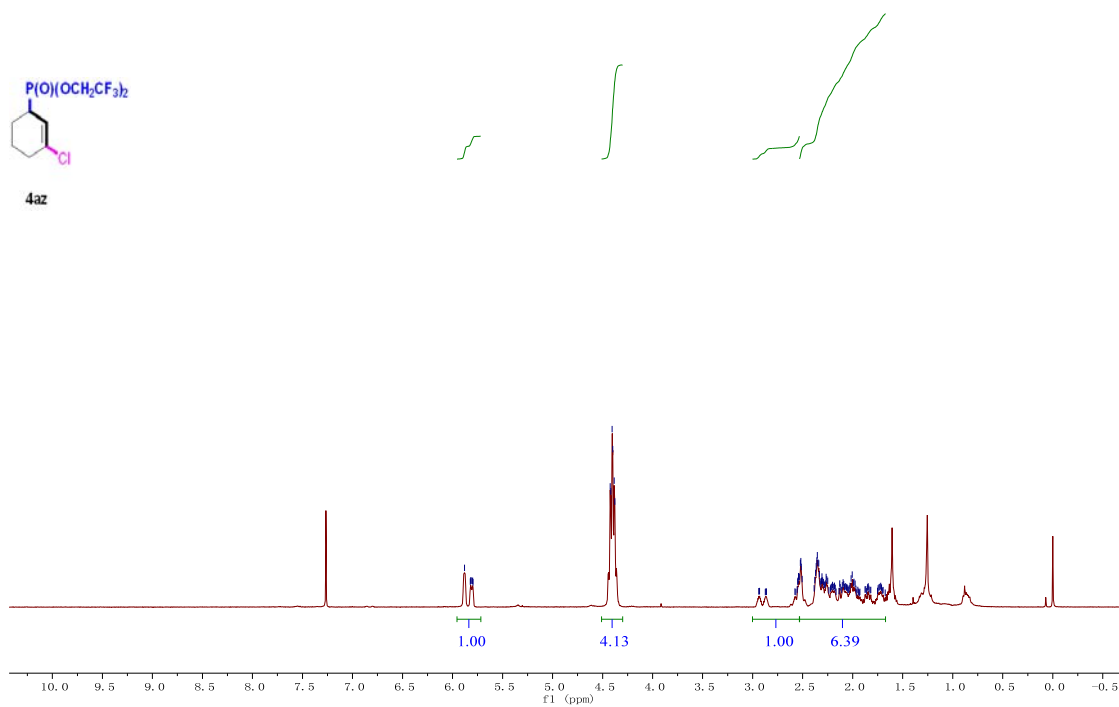


^1H NMR (400 MHz, CDCl_3)

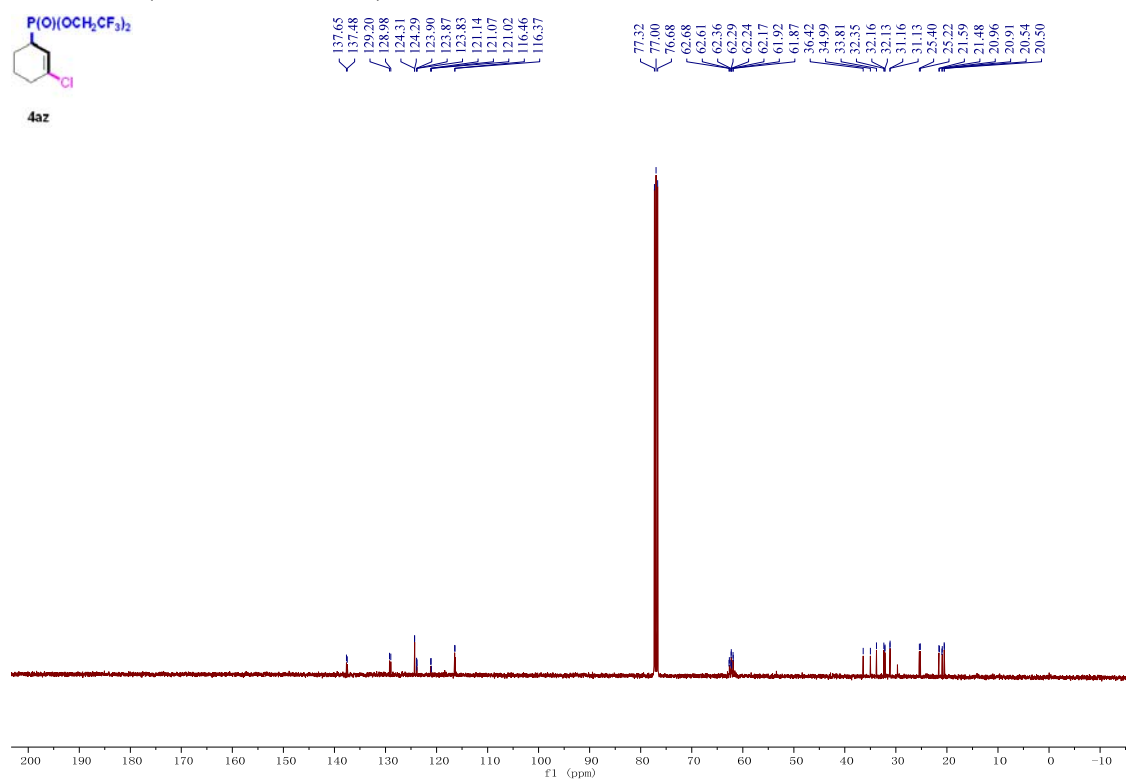
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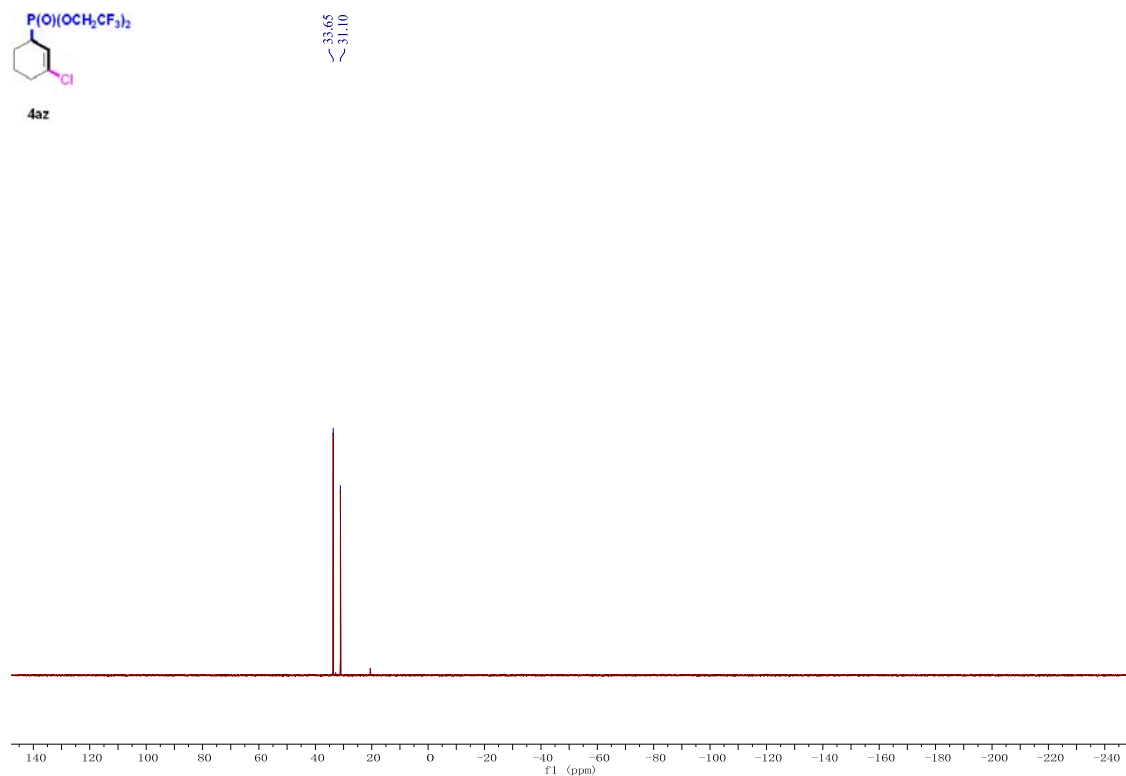
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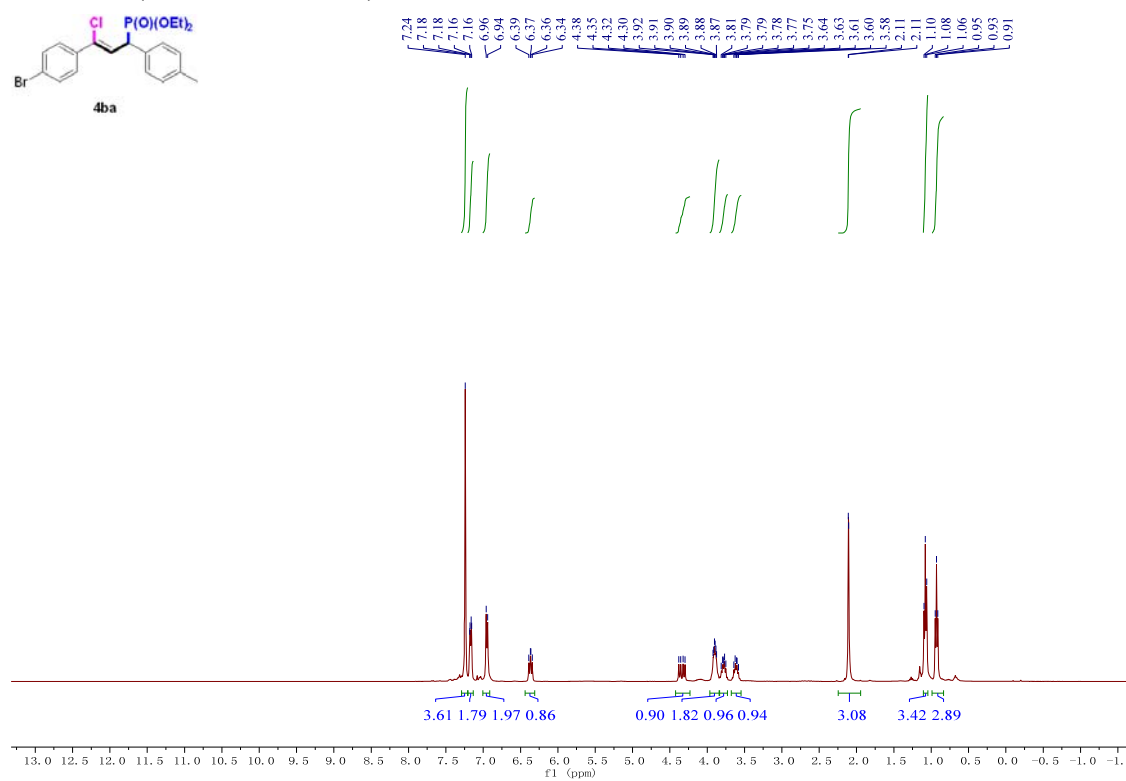
¹³C NMR (101 MHz, CDCl₃)



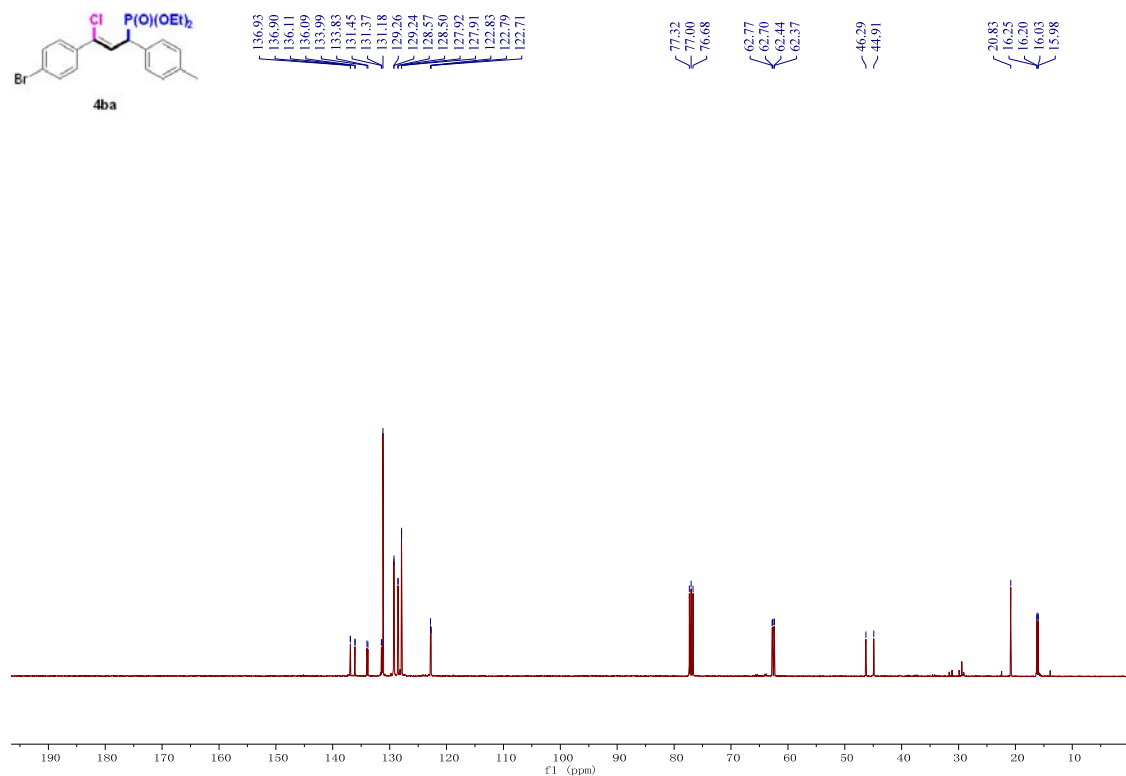
³¹P NMR (162 MHz, CDCl₃)



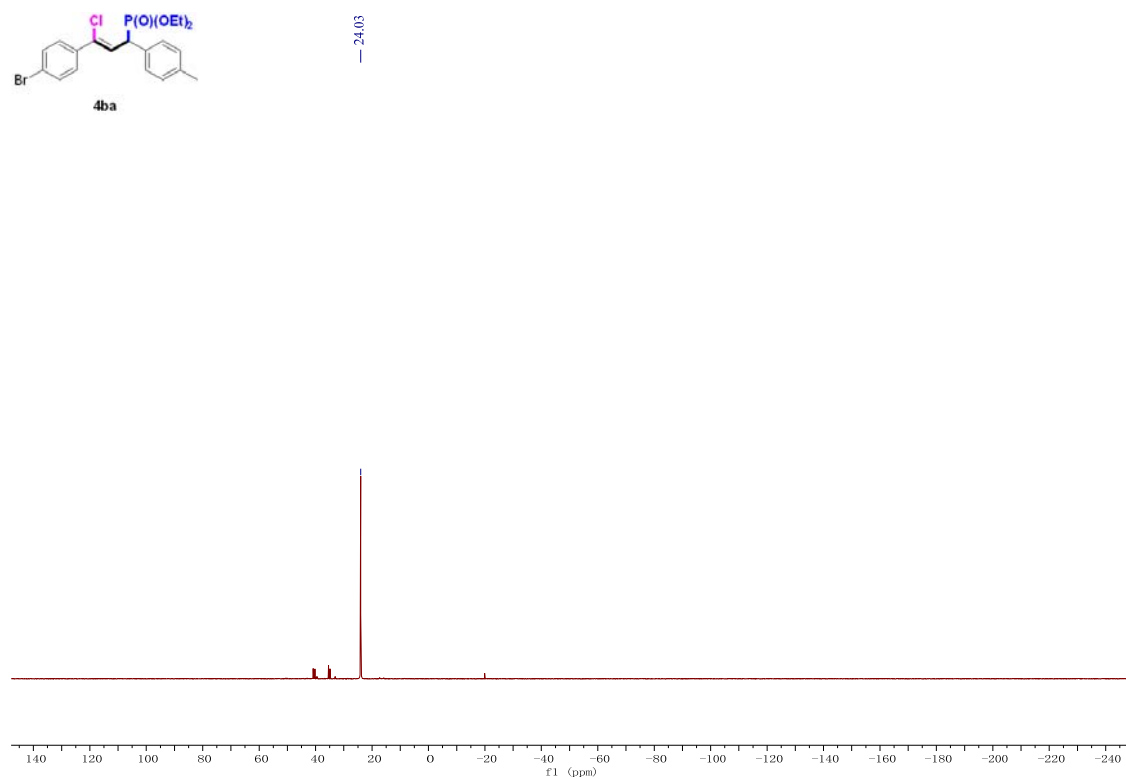
¹H NMR (400 MHz, CDCl₃)



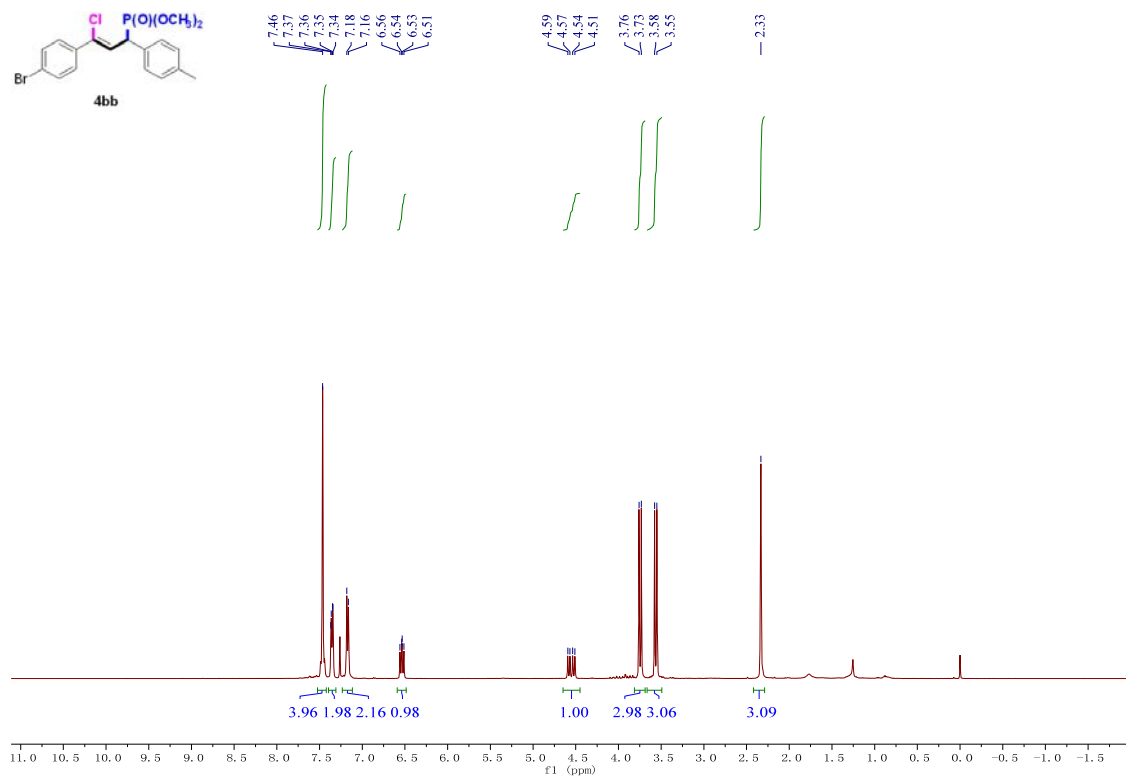
¹³C NMR (101 MHz, CDCl₃)



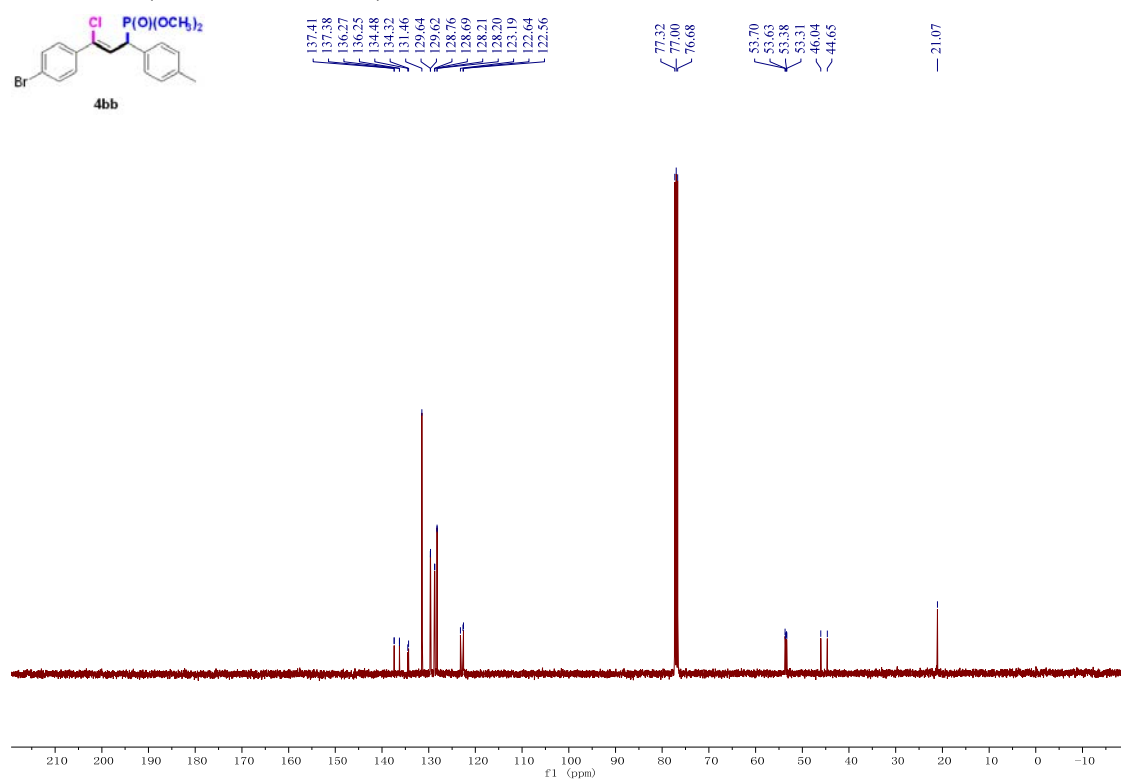
^{31}P NMR (162 MHz, CDCl_3)



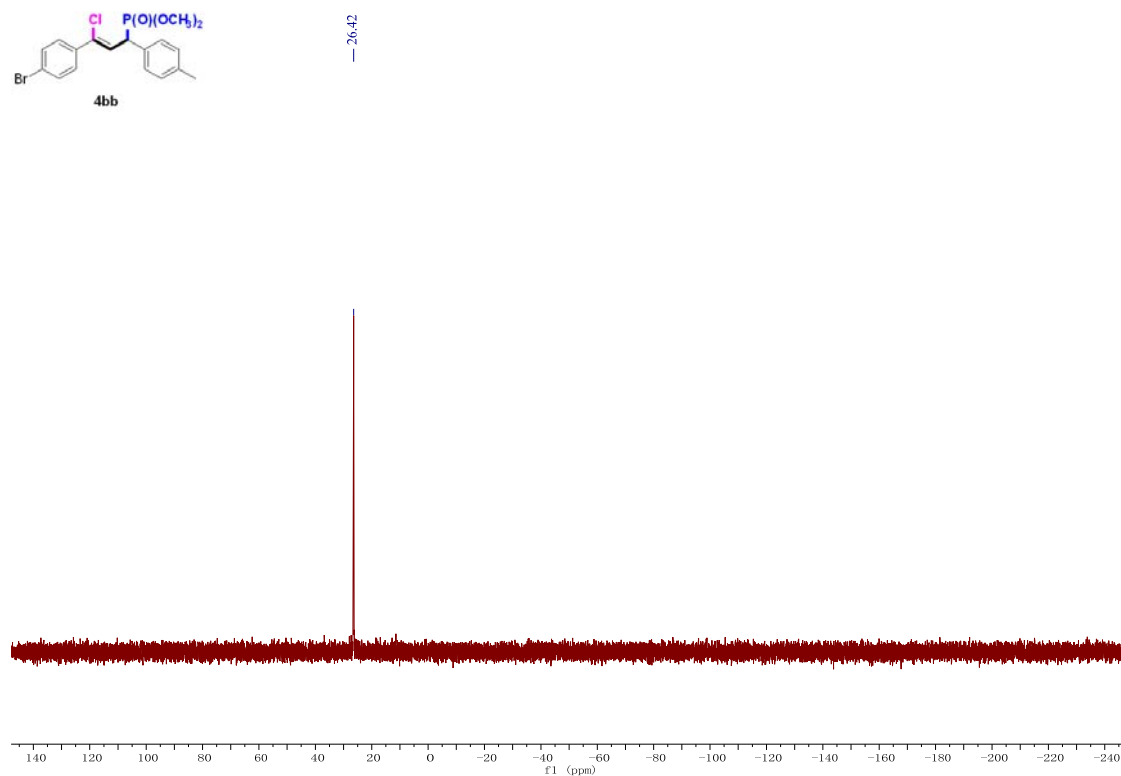
^1H NMR (400 MHz, CDCl_3)



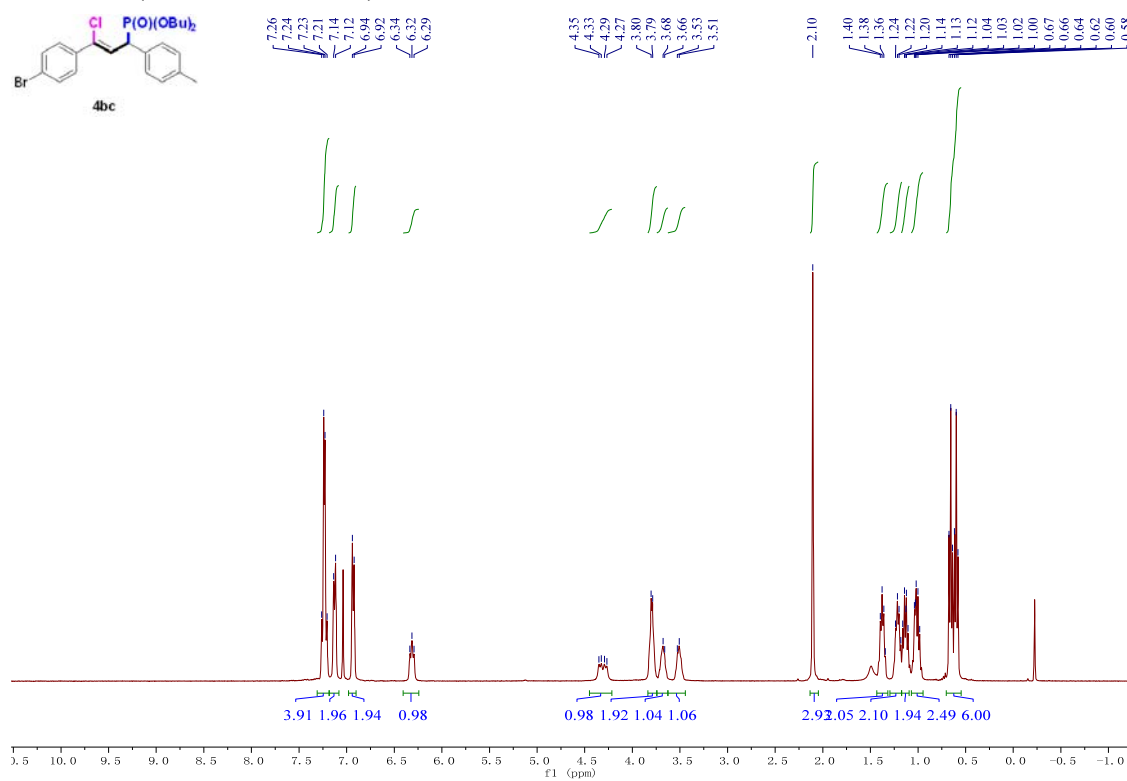
¹³C NMR (101 MHz, CDCl₃)



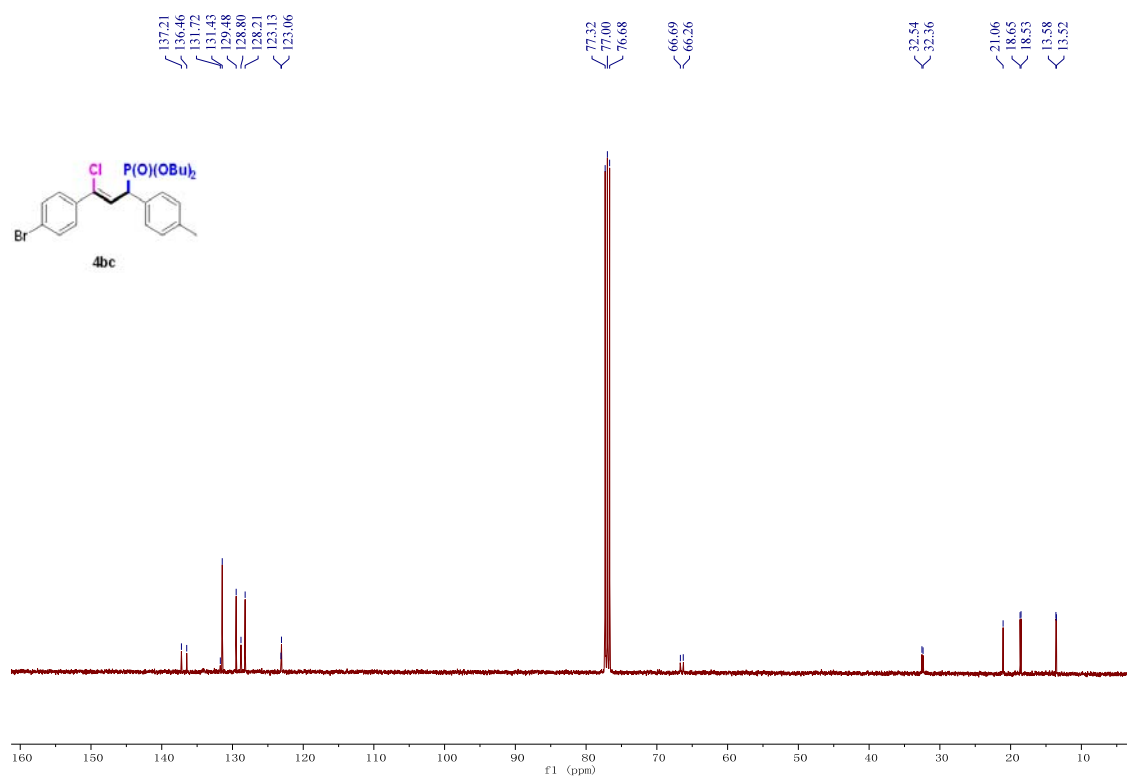
³¹P NMR (162 MHz, CDCl₃)



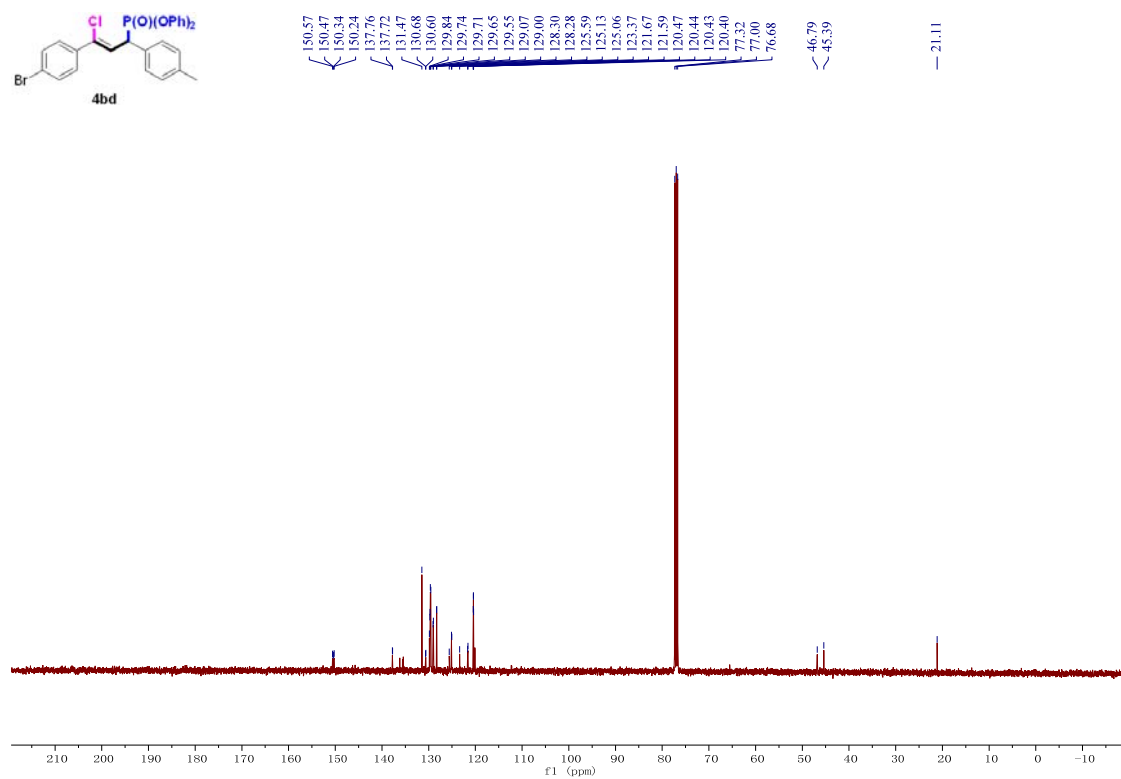
^1H NMR (400 MHz, CDCl_3)



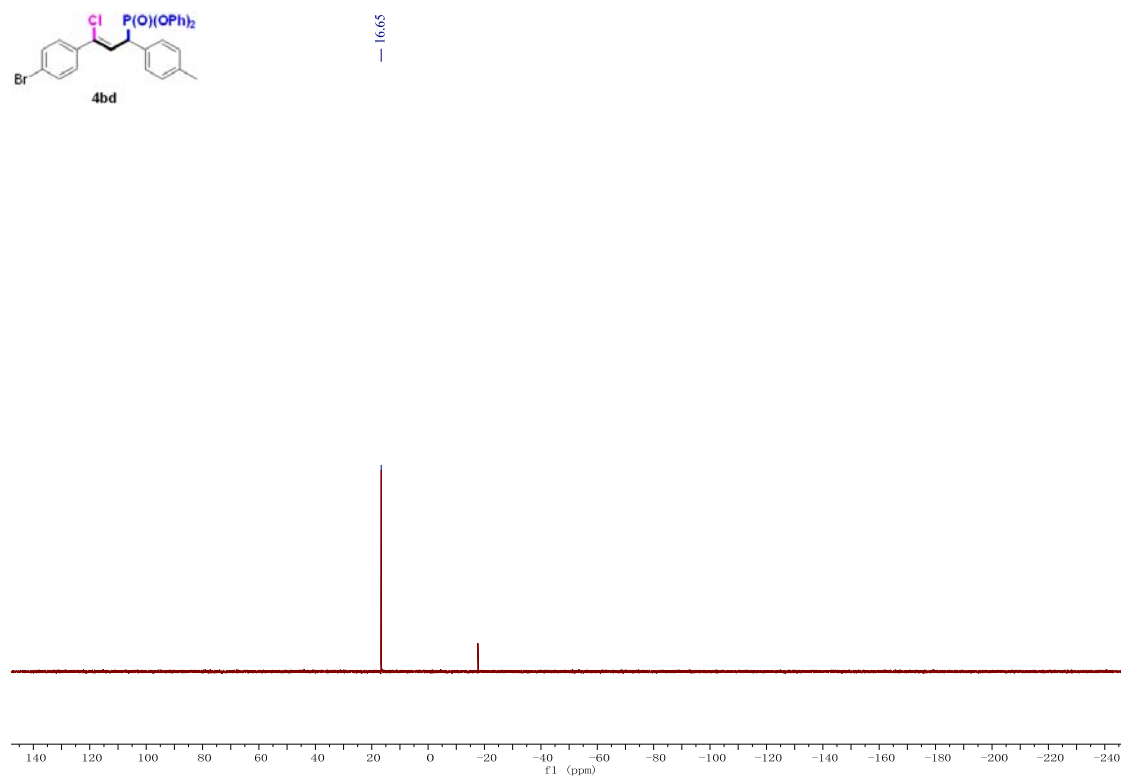
^{13}C NMR (101 MHz, CDCl_3)



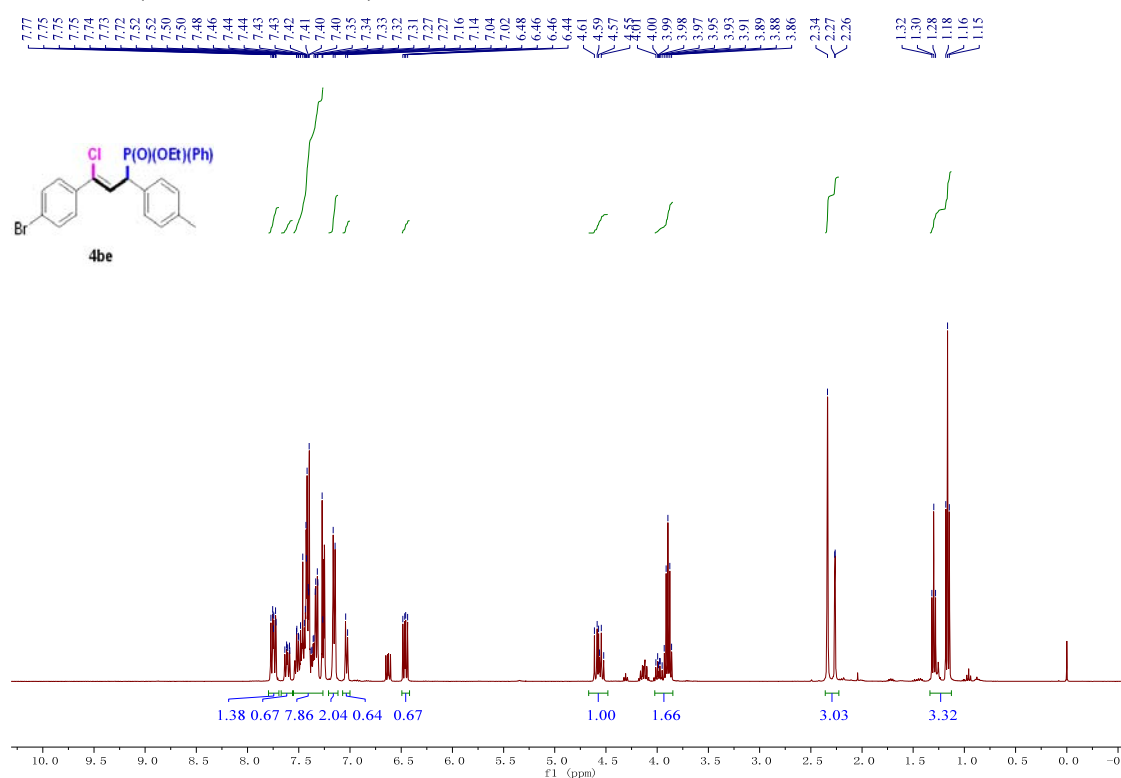
^{13}C NMR (101 MHz, CDCl_3)



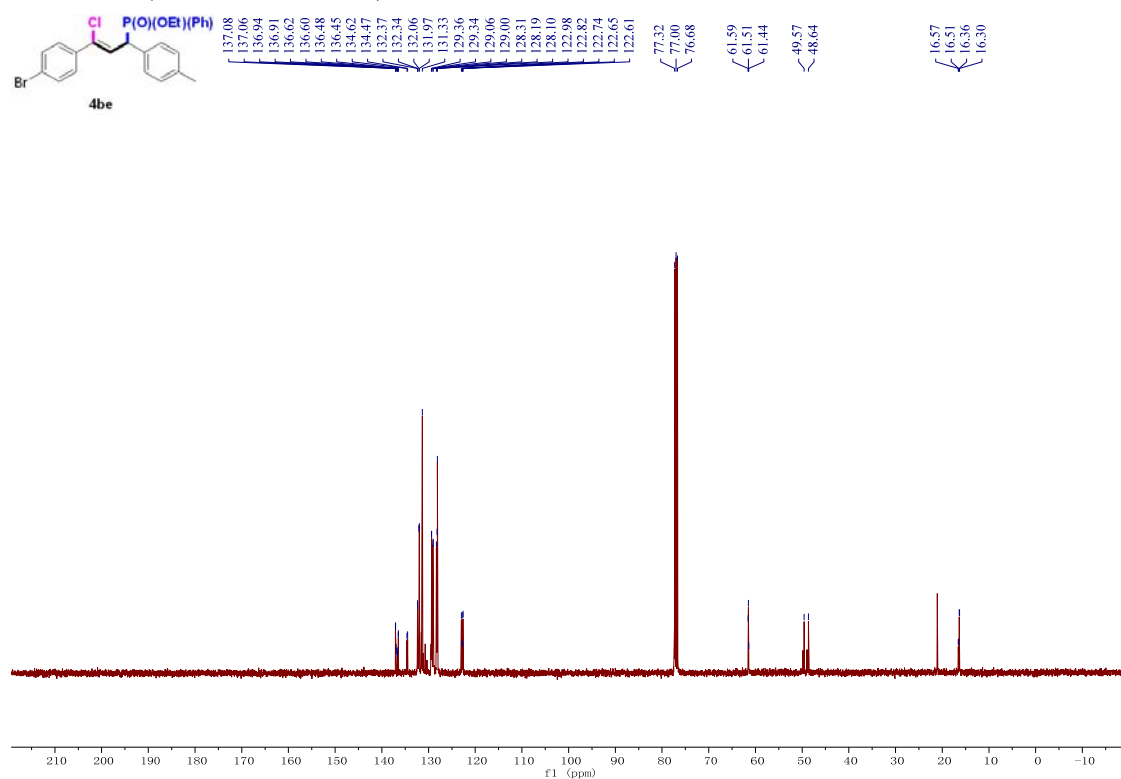
^{31}P NMR (162 MHz, CDCl_3)



¹H NMR (400 MHz, CDCl₃)



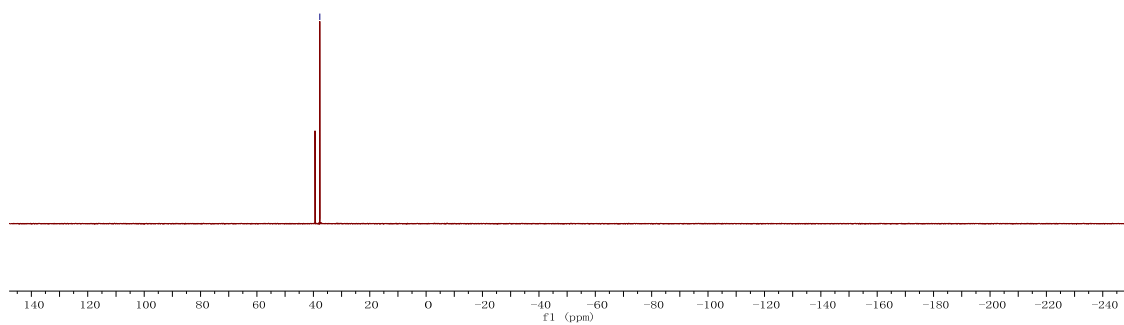
¹³C NMR (101 MHz, CDCl₃)



^{31}P NMR (162 MHz, CDCl_3)



37.72

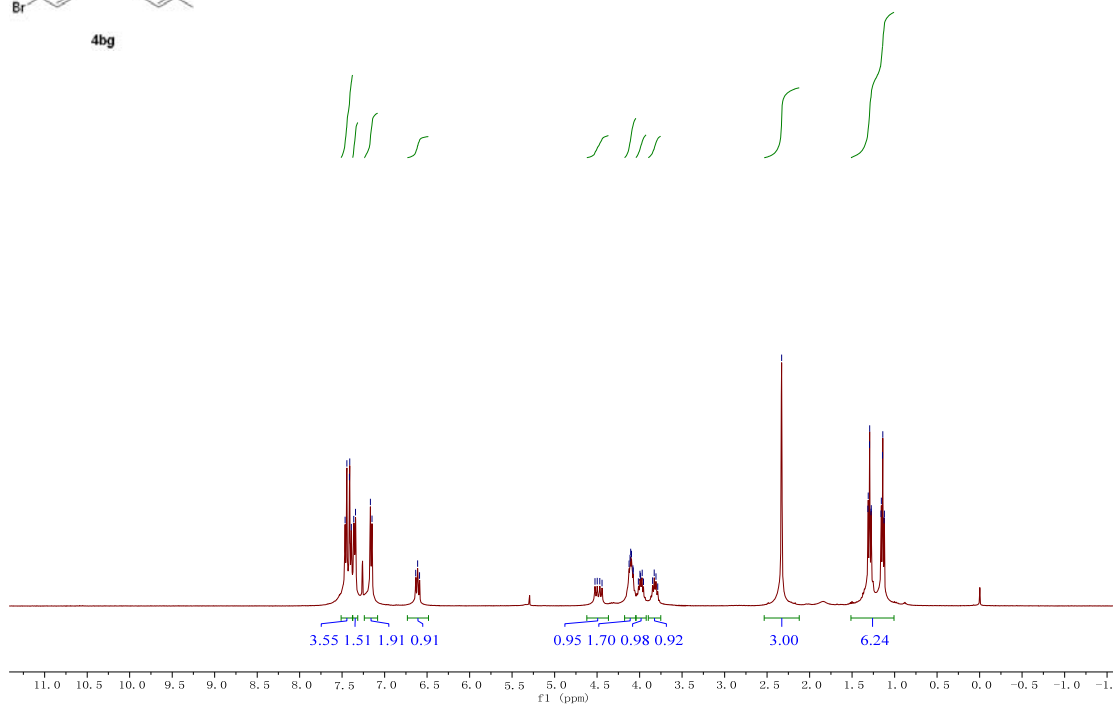


^1H NMR (400 MHz, CDCl_3)



7.47
7.44
7.41
7.39
7.36
7.34
7.17
7.15
6.63
6.59

4.53
4.50
4.47
4.44
4.12
4.11
4.10
4.08
4.07
4.01
4.00
3.99
3.97
3.95
3.85
3.83
3.81
3.79
2.33
1.31
1.30
1.29
1.28
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1.16
1.16
1.14
1.14
1.12
1.12



^{13}C NMR (101 MHz, CDCl_3)



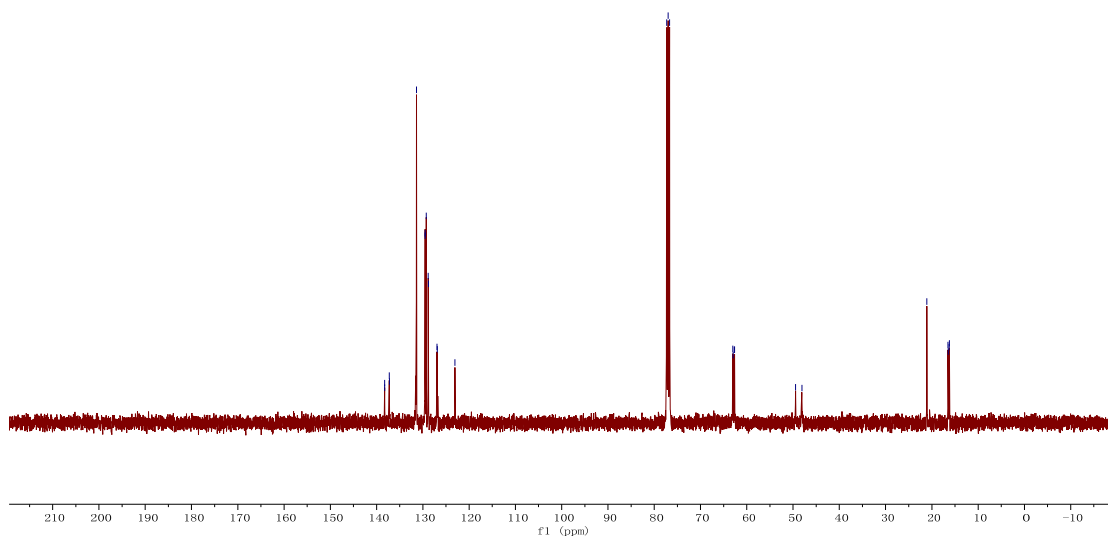
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137.25
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129.52
129.50
129.28
128.84
128.78
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126.88
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76.68

63.03
62.96
62.71
62.64

49.46
48.09

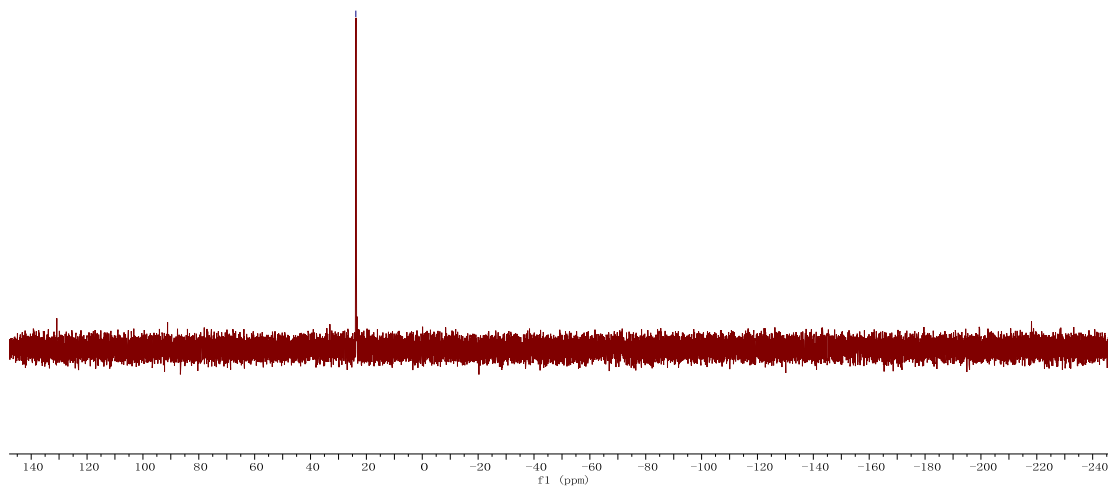
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16.51
16.45
16.27
16.22



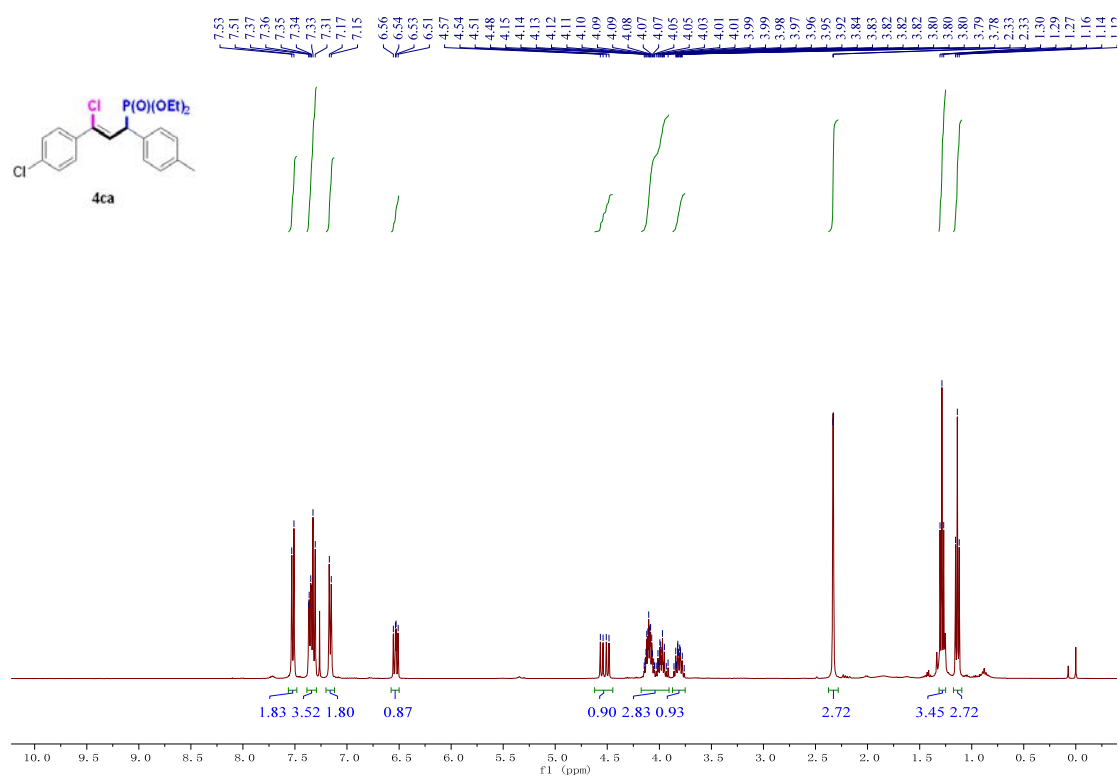
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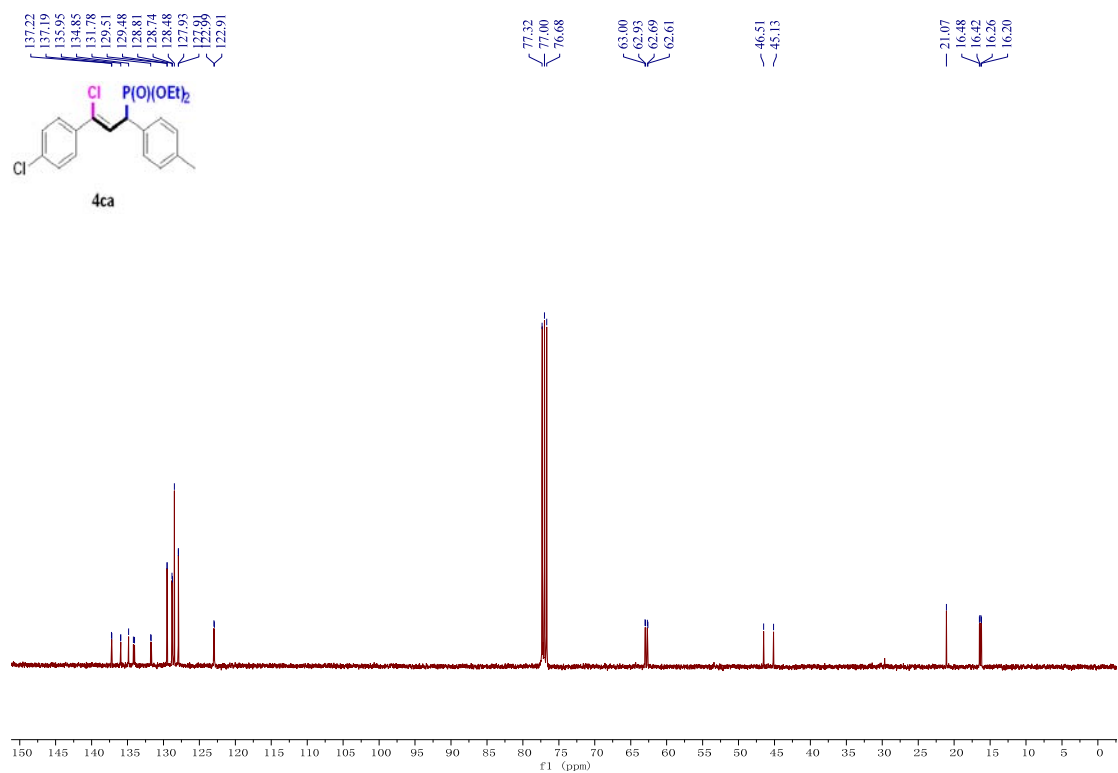
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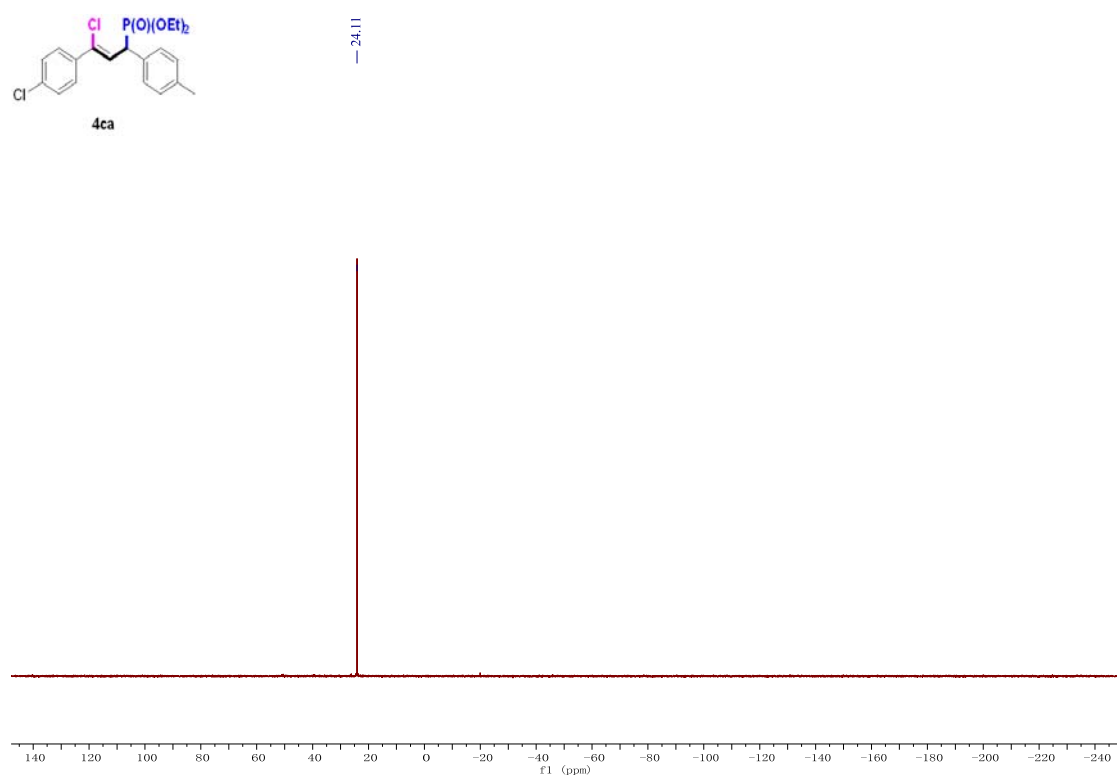
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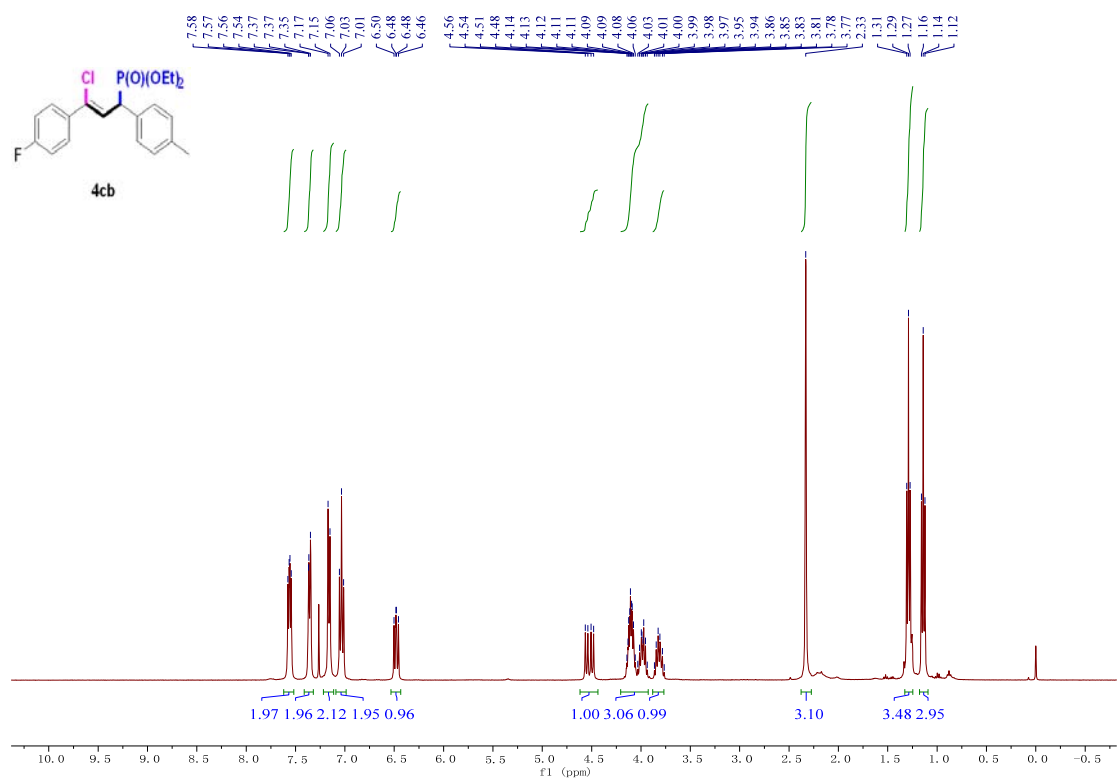
^{13}C NMR (101 MHz, CDCl_3)



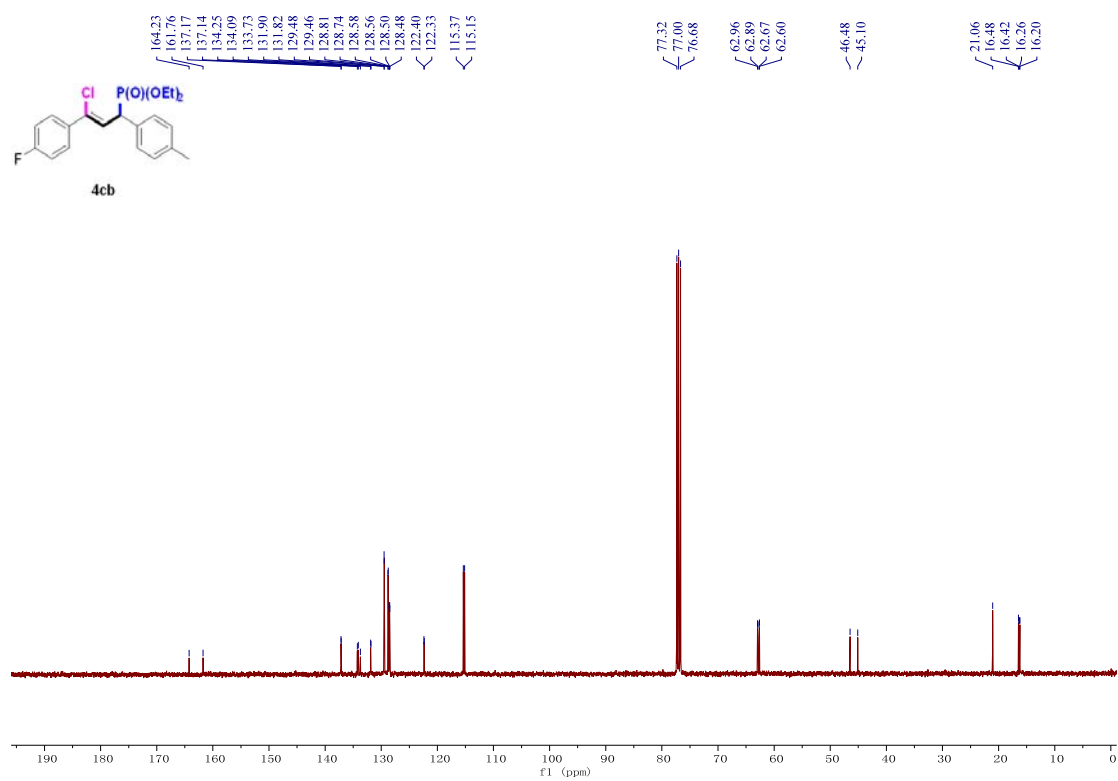
^{31}P NMR (162 MHz, CDCl_3)



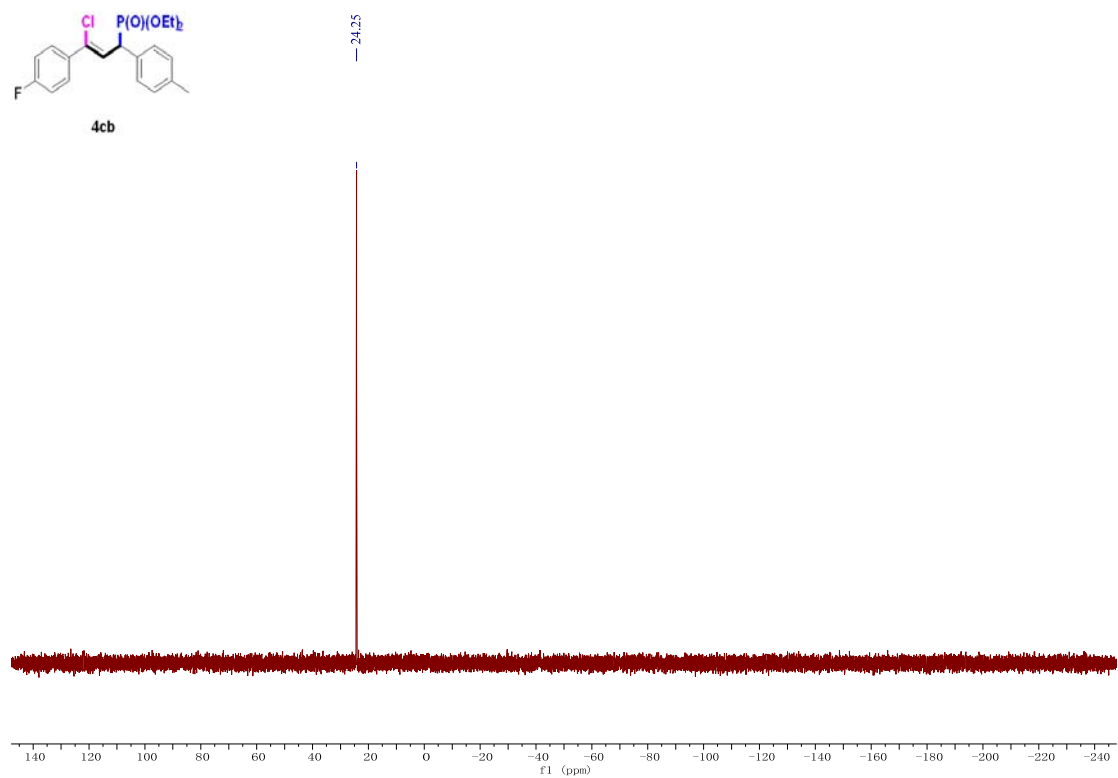
^1H NMR (400 MHz, CDCl_3)



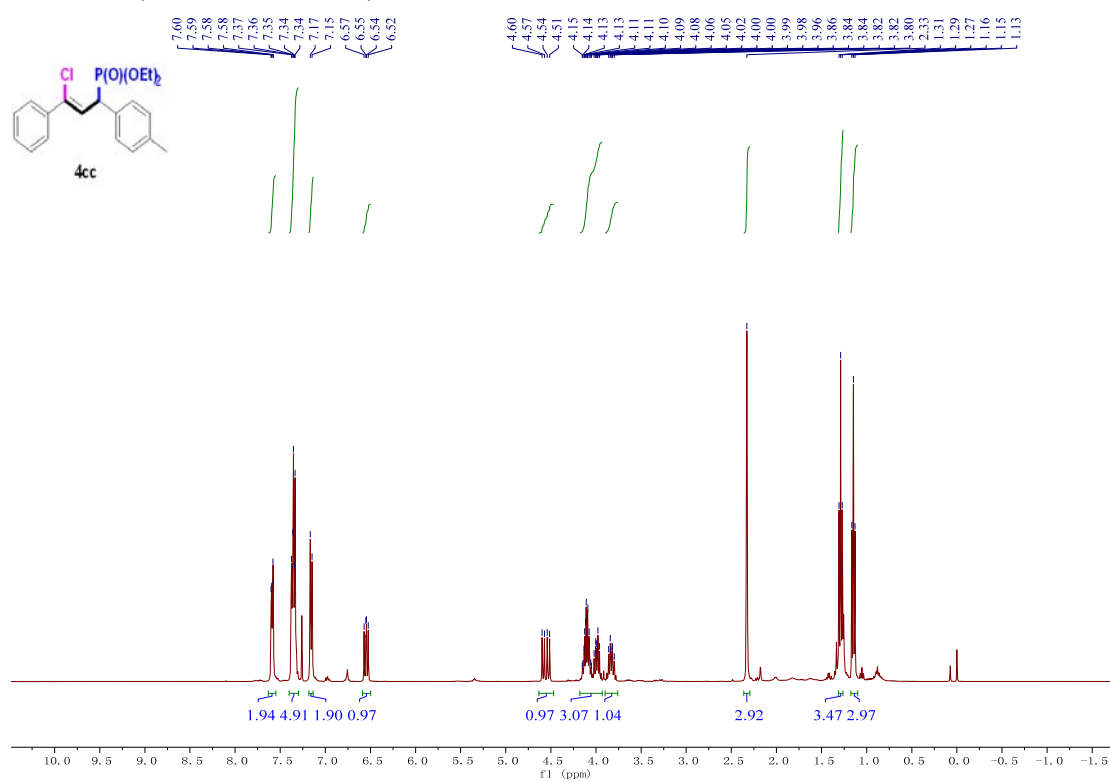
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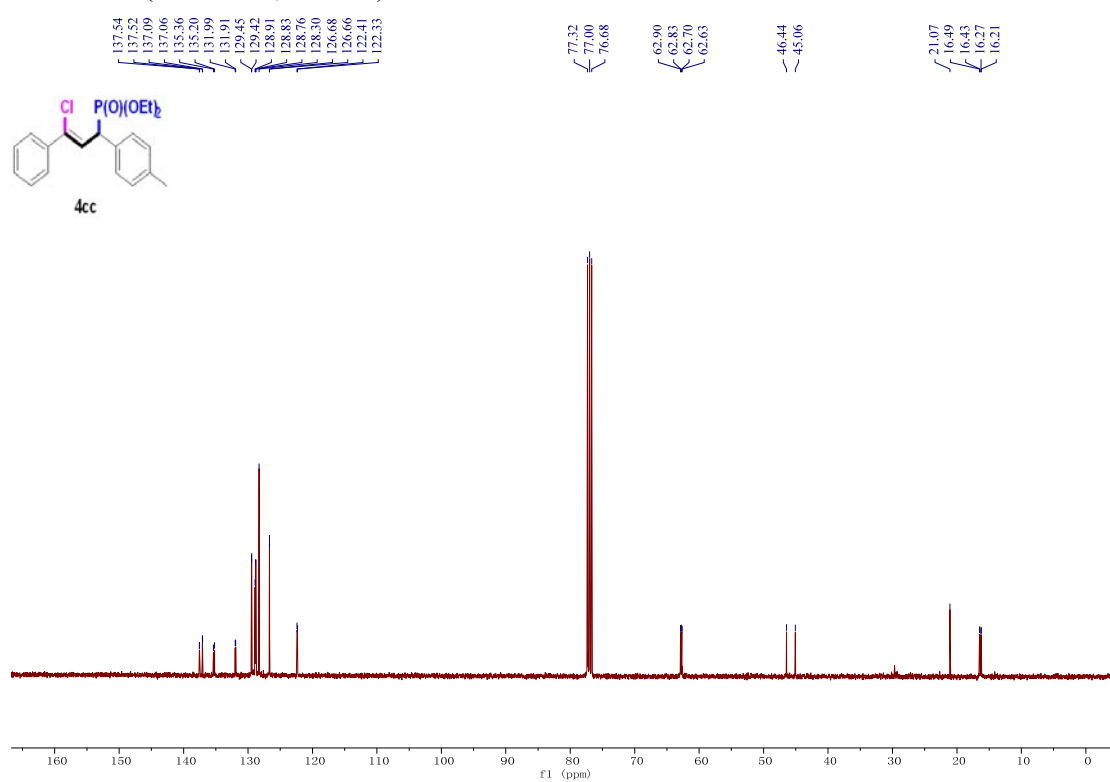
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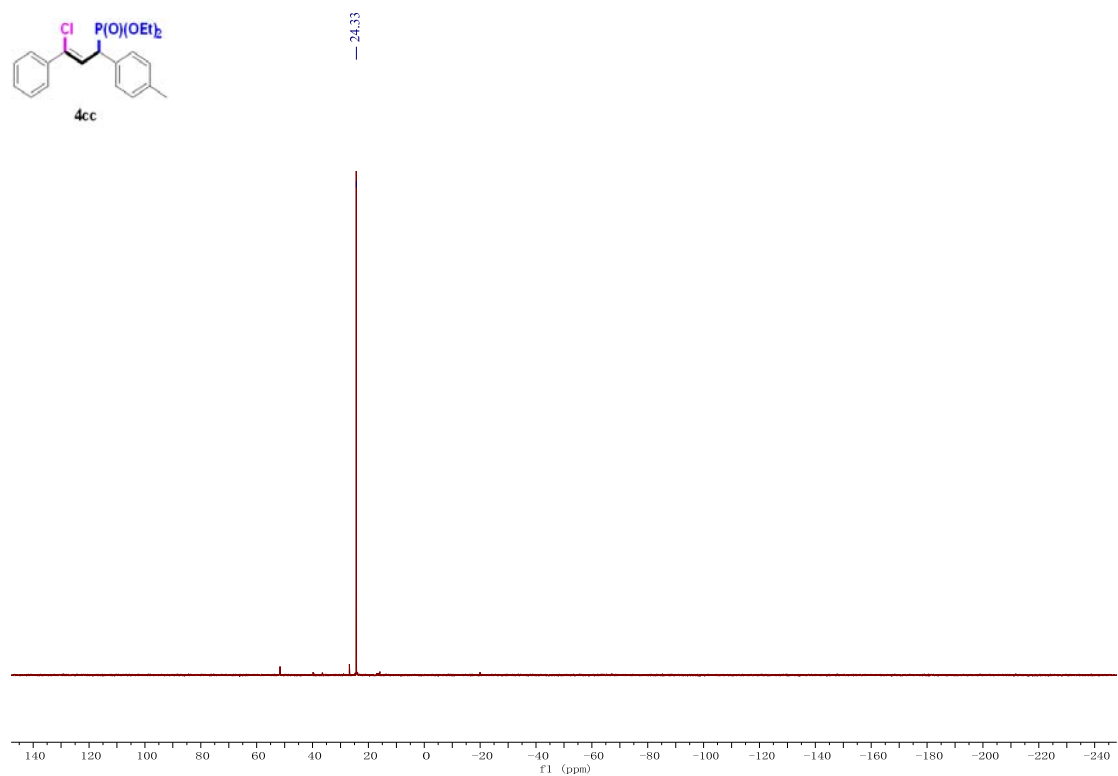
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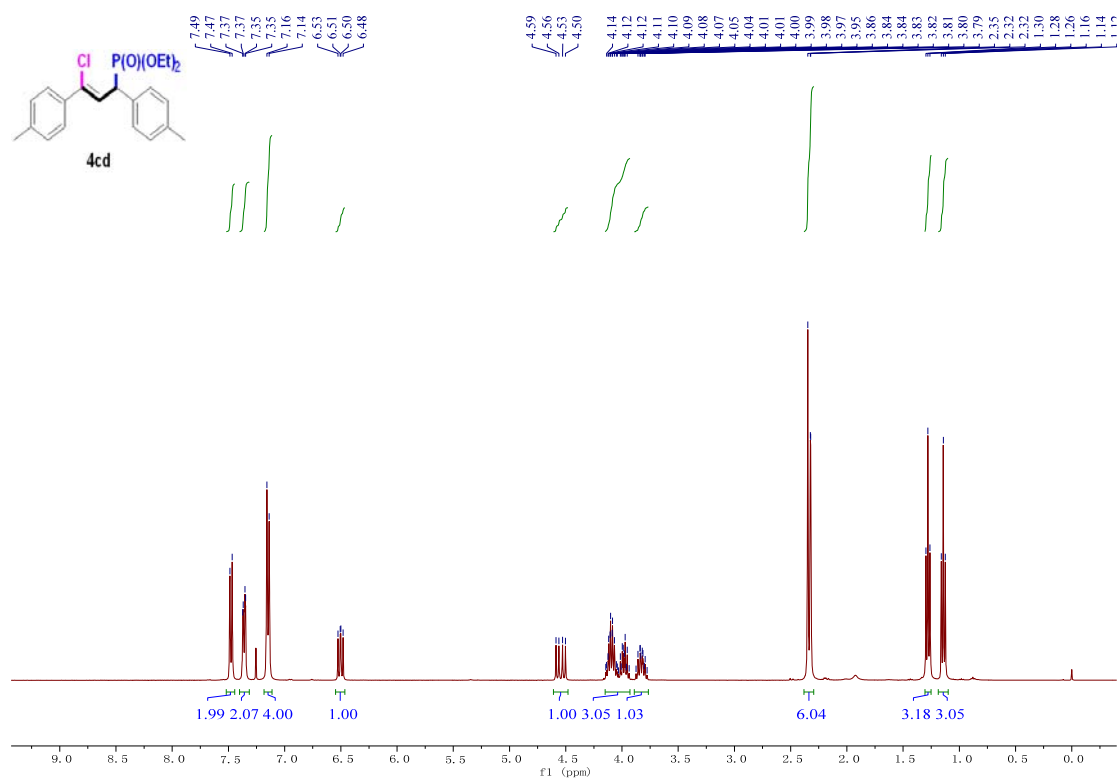
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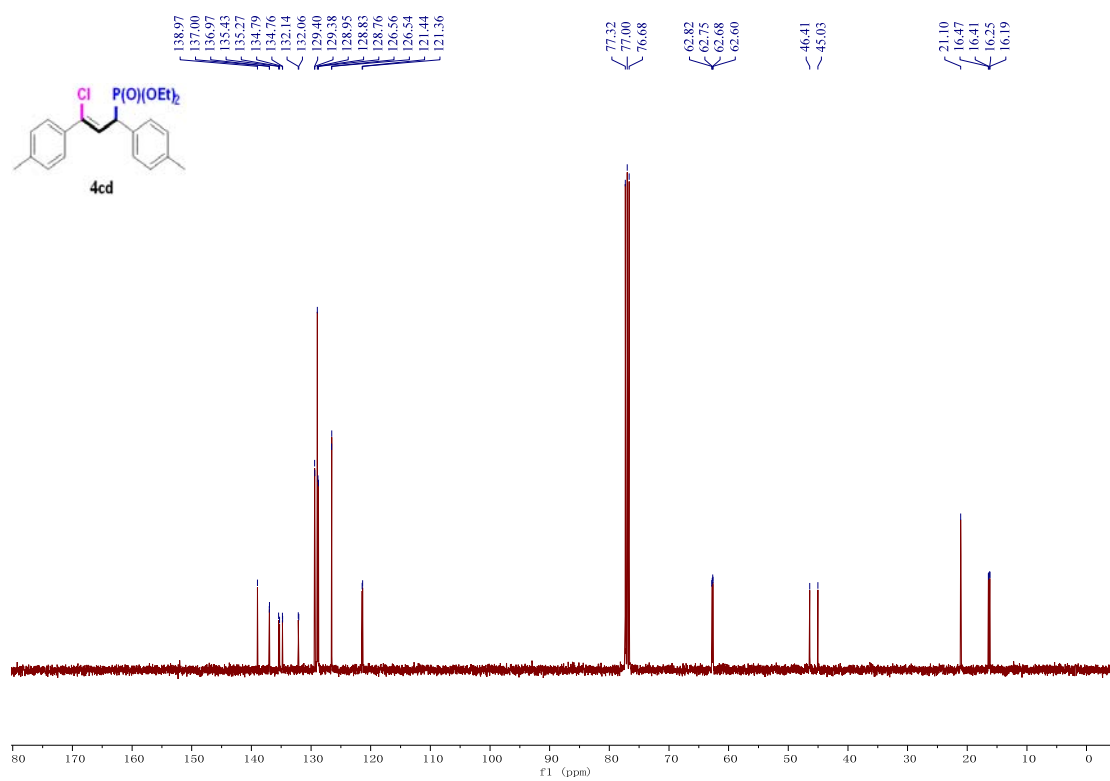
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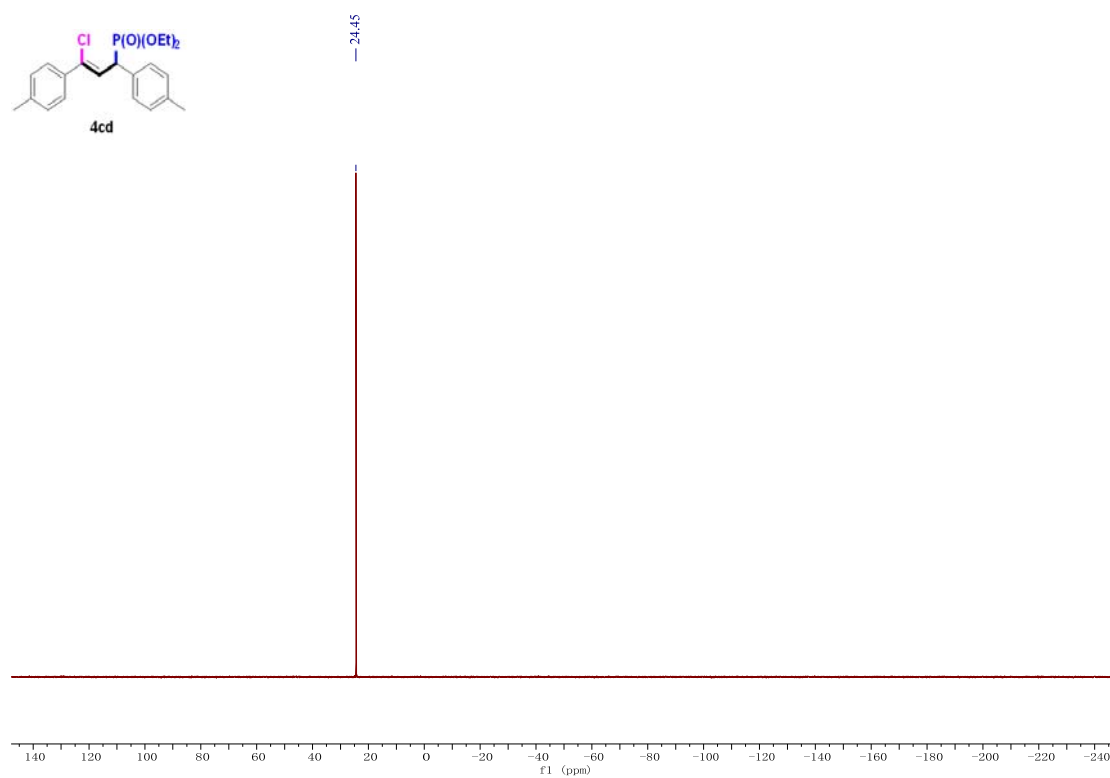
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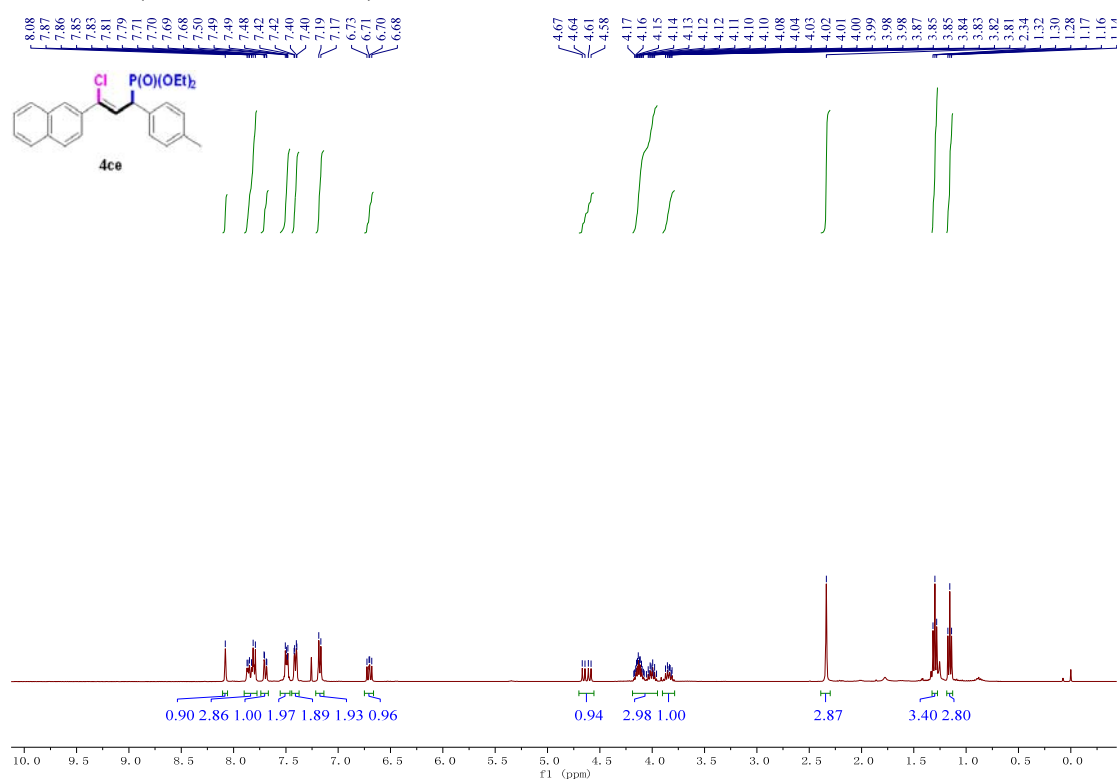
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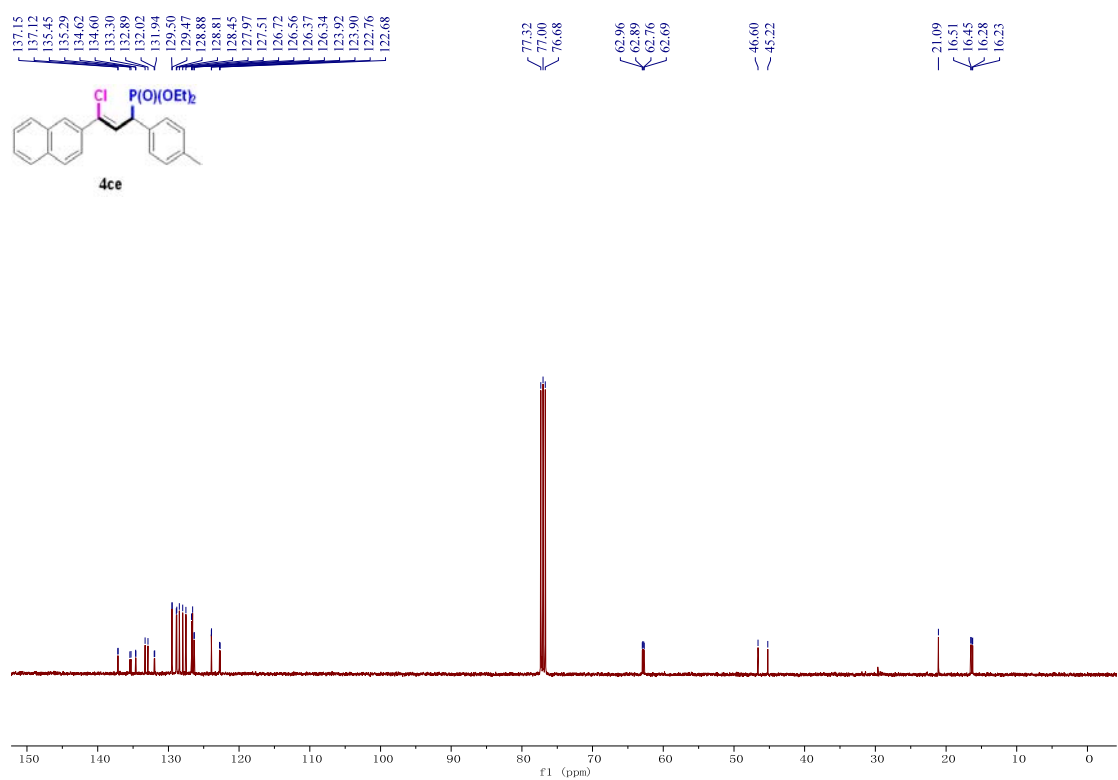
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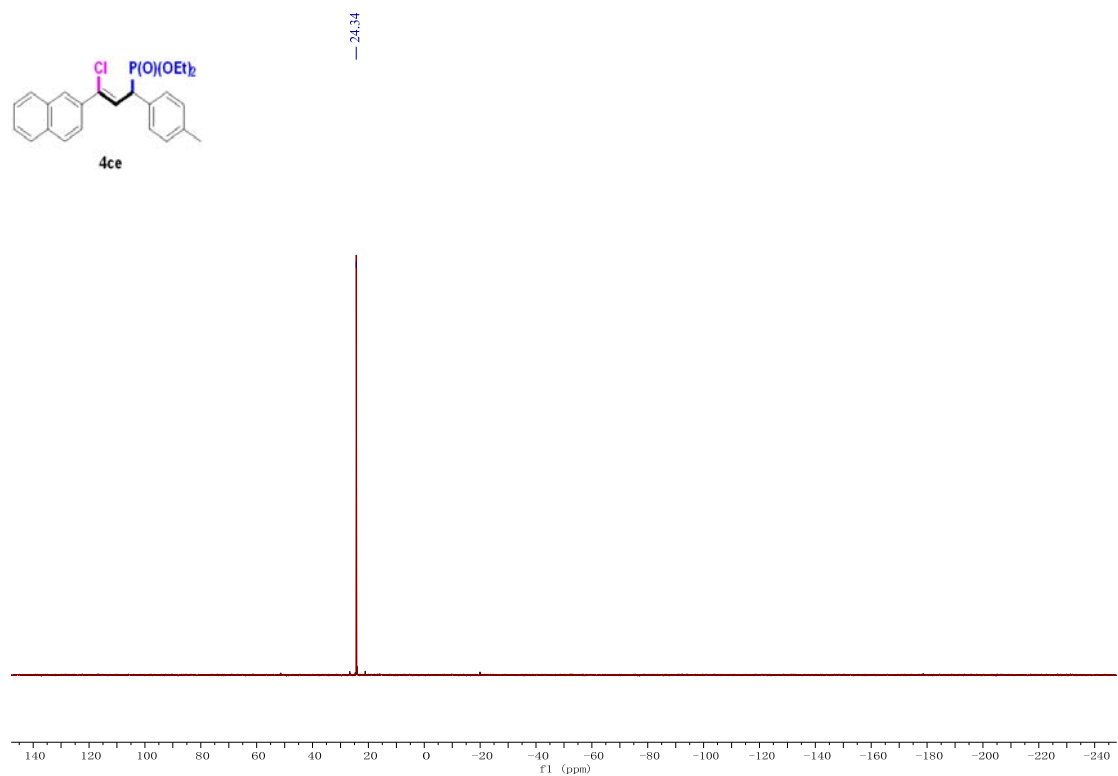
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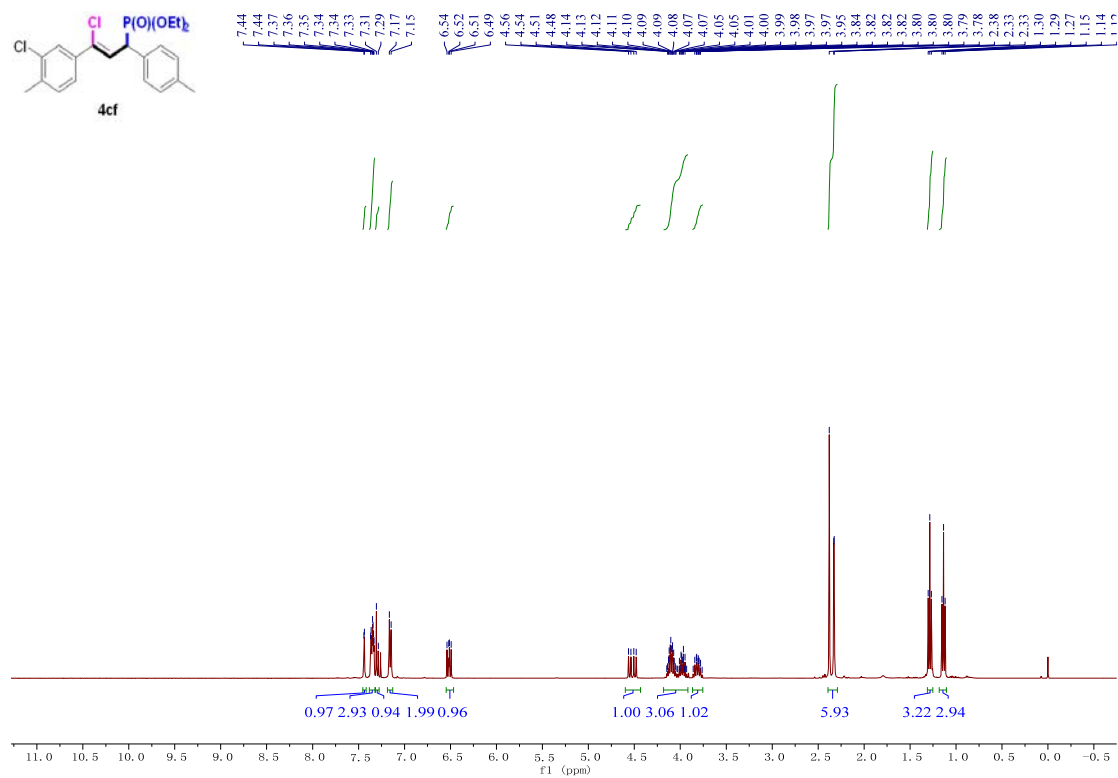
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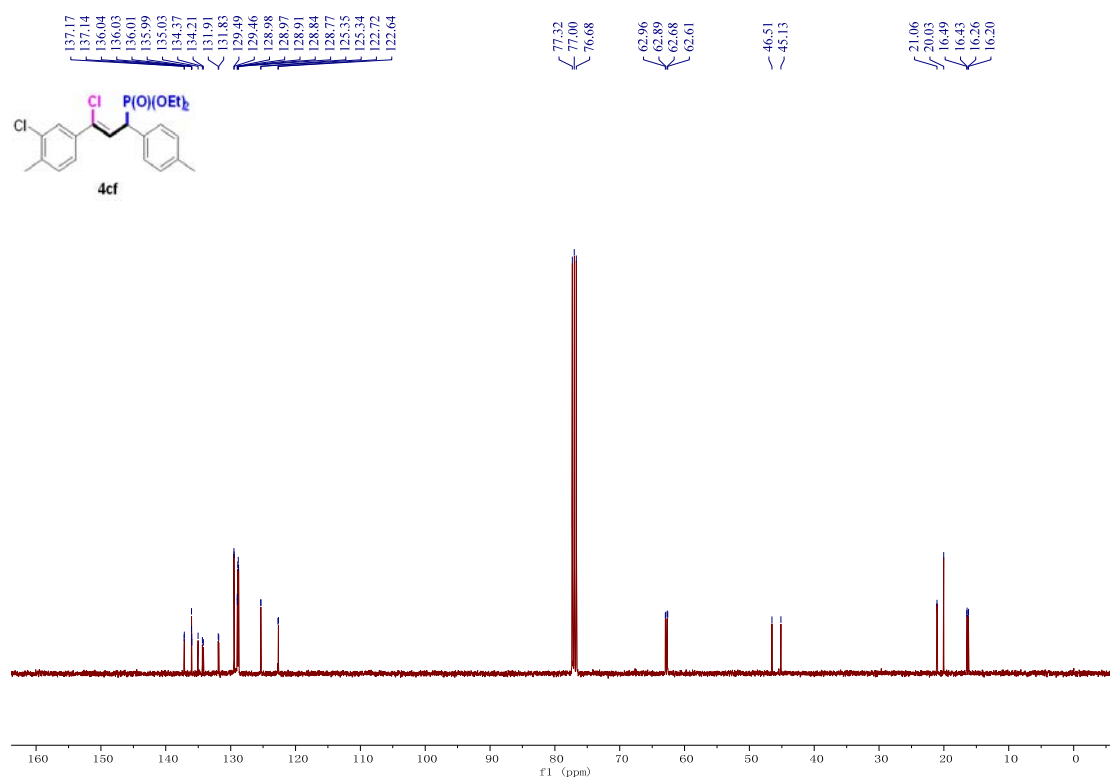
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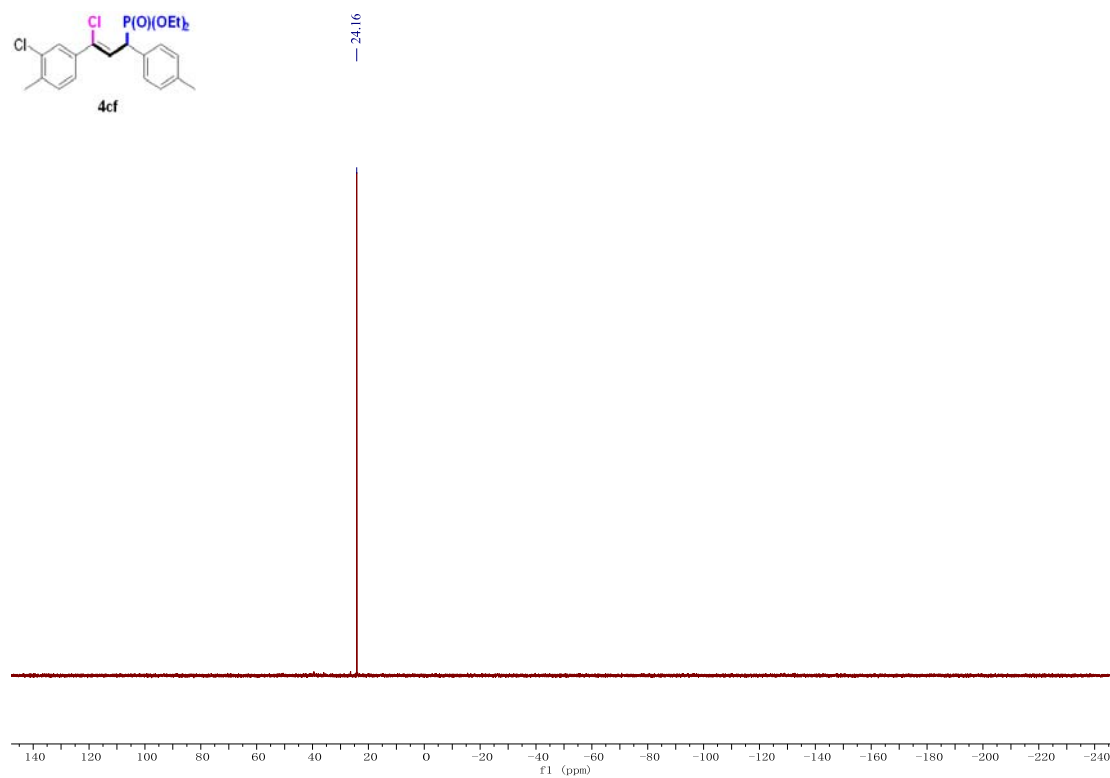
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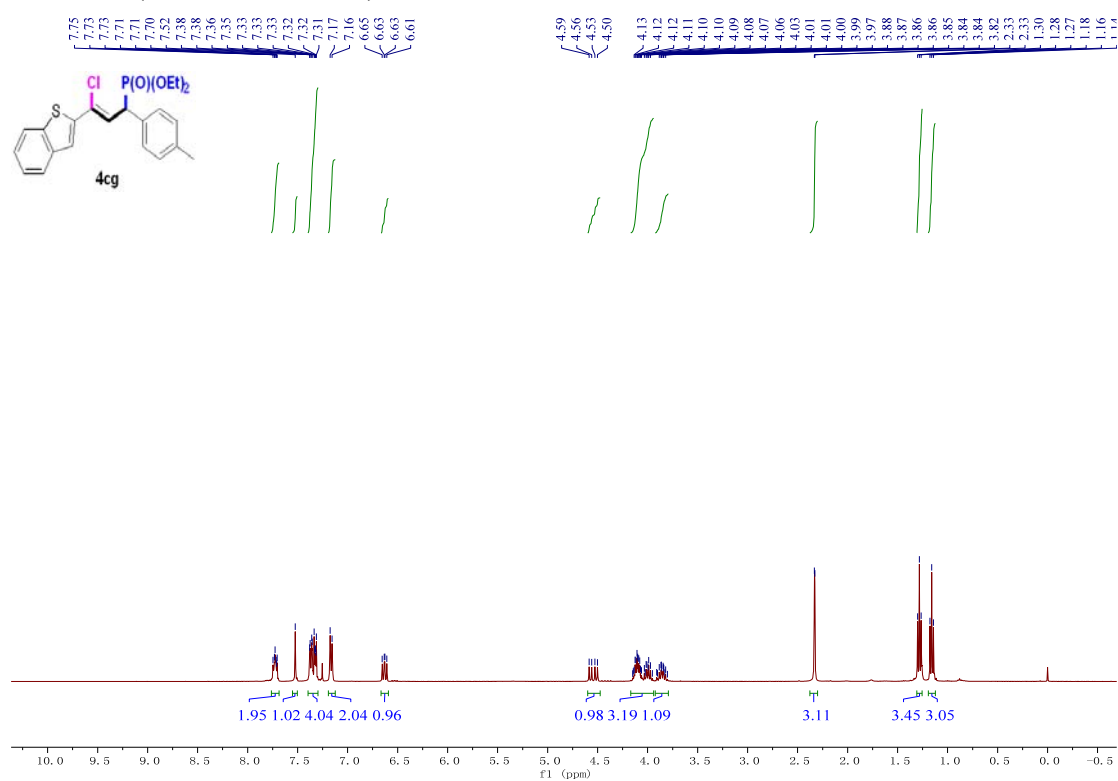
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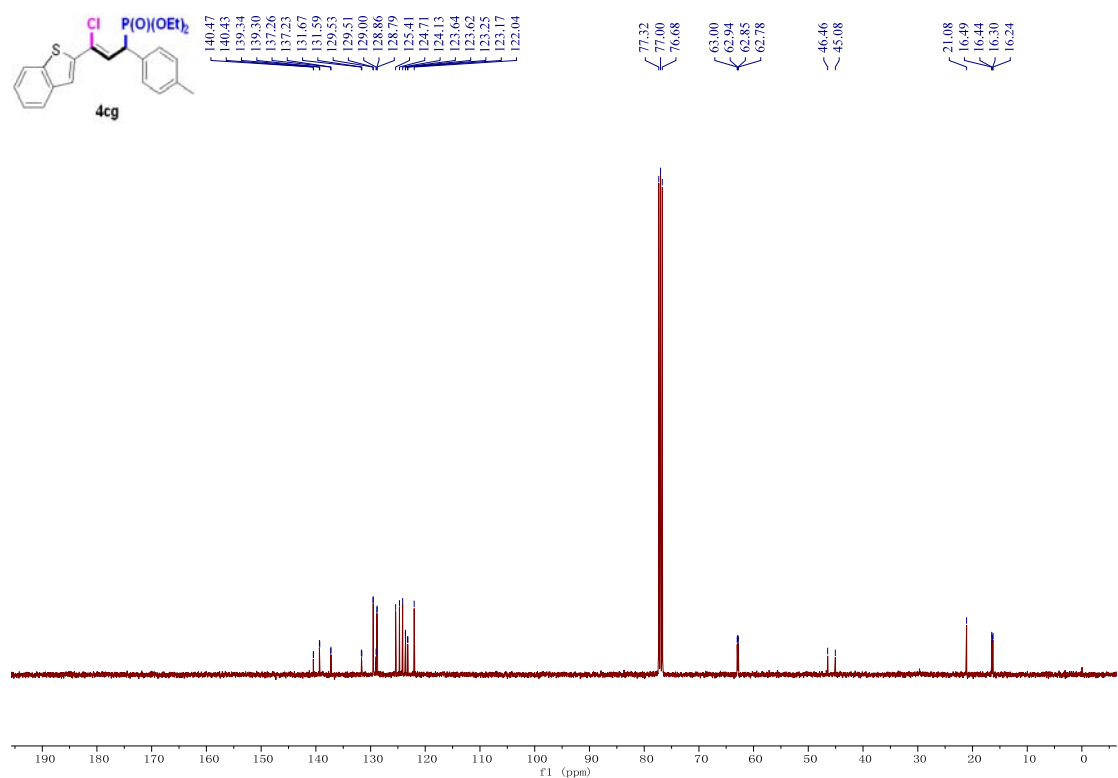
^{31}P NMR (162 MHz, CDCl_3)



¹H NMR (400 MHz, CDCl₃)



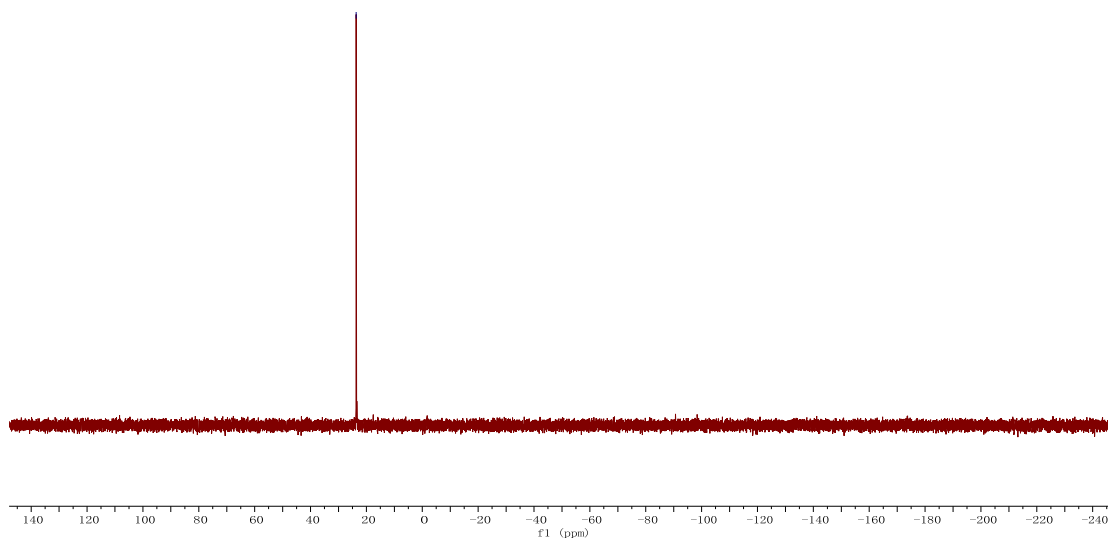
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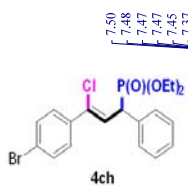
^{31}P NMR (162 MHz, CDCl_3)



- 23.66

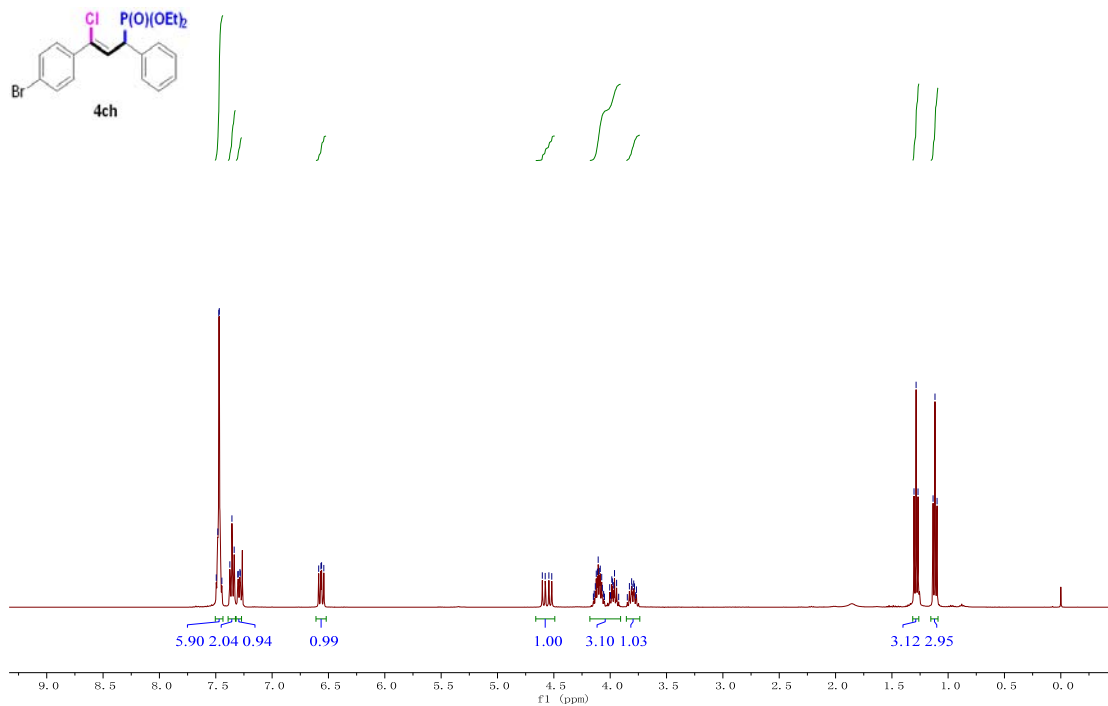


^1H NMR (400 MHz, CDCl_3)

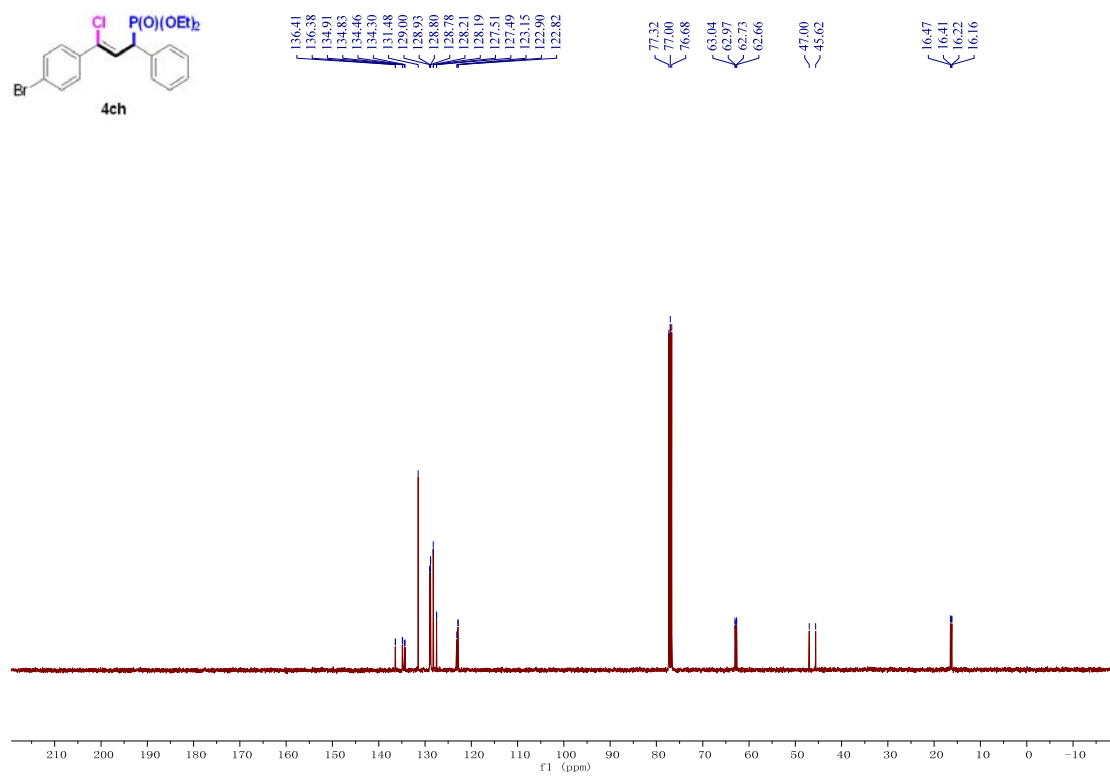


7.50
7.48
7.47
7.47
7.45
7.37
7.36
7.34
7.30
7.30
7.29
7.28
6.59
6.57
6.56
6.54

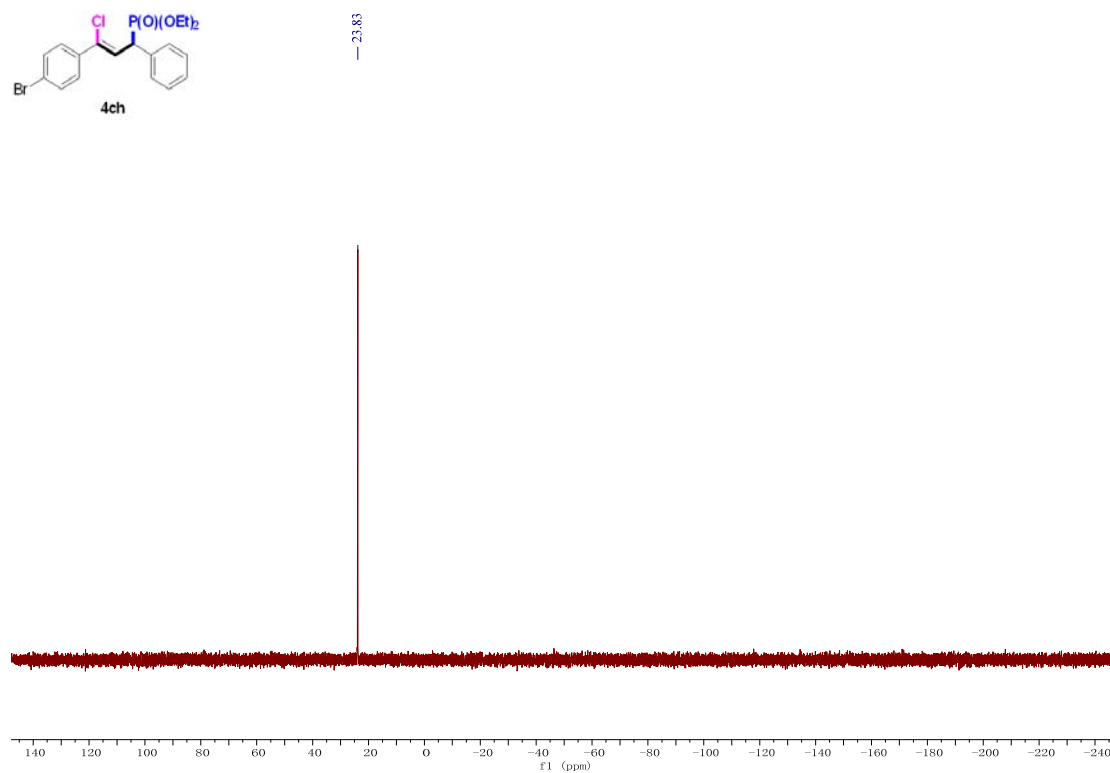
4.60
4.58
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4.12
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4.10
4.09
4.08
4.07
4.06
4.05
4.00
4.00
3.99
3.98
3.97
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3.29
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1.13
1.12
1.10



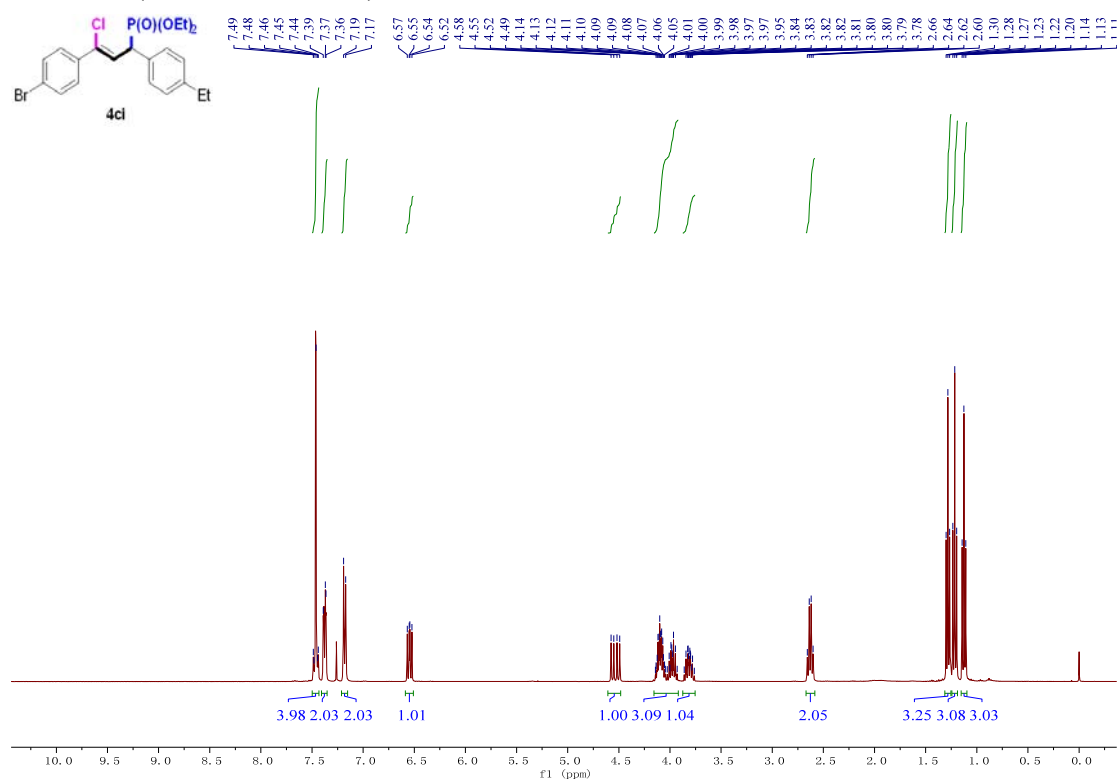
^{13}C NMR (101 MHz, CDCl_3)



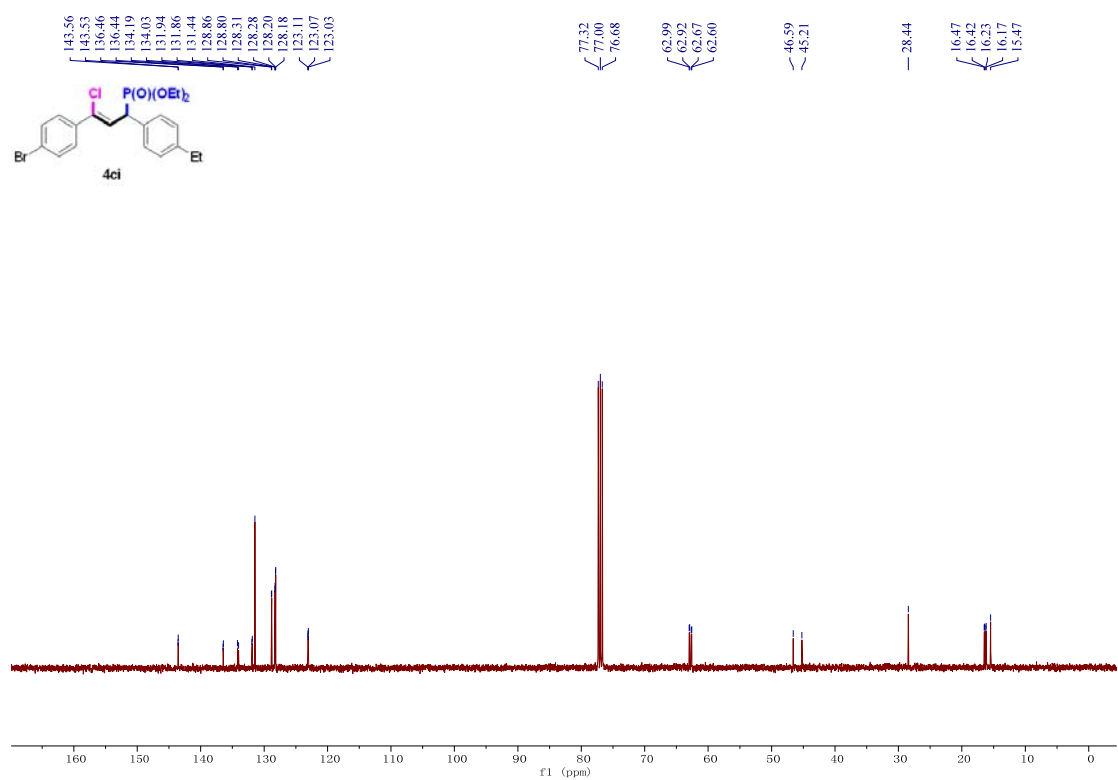
^{31}P NMR (162 MHz, CDCl_3)



¹H NMR (400 MHz, CDCl₃)



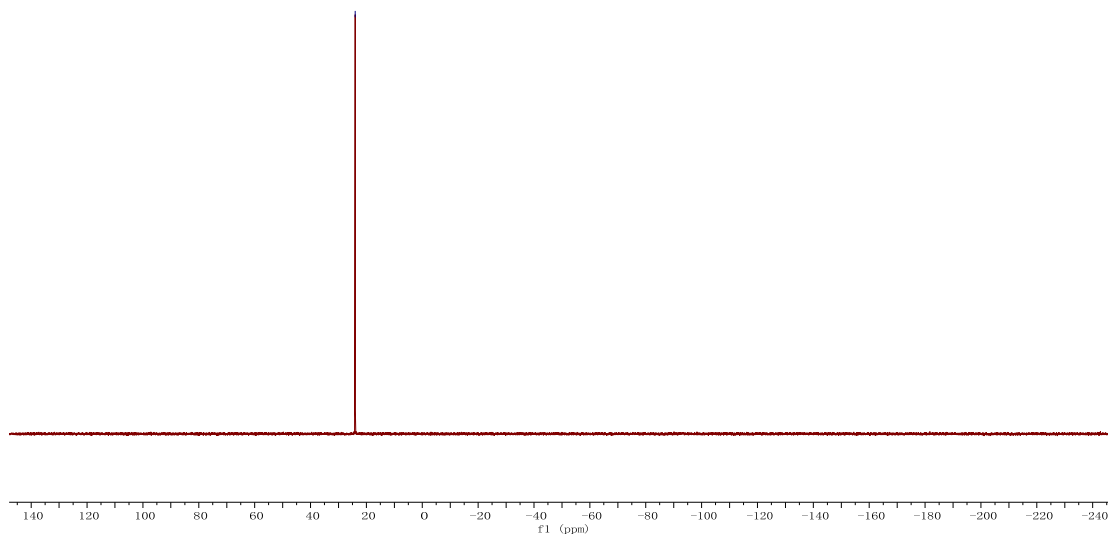
¹³C NMR (101 MHz, CDCl₃)



^{31}P NMR (162 MHz, CDCl_3)



24.02



^1H NMR (400 MHz, CDCl_3)

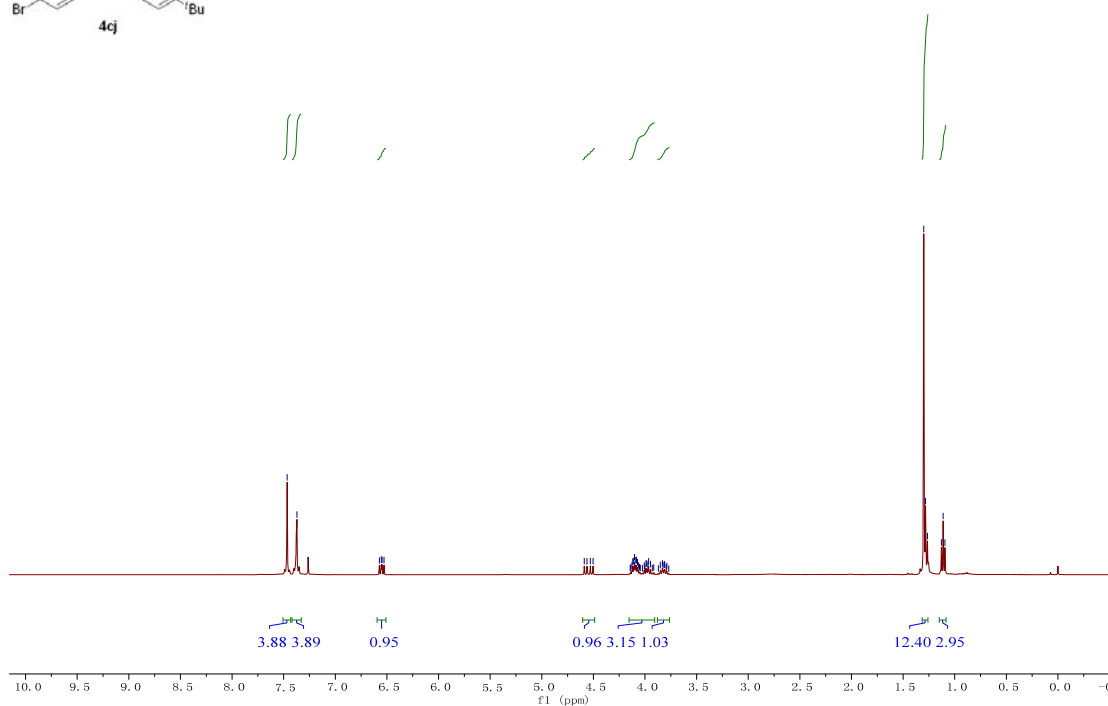


7.47
7.37

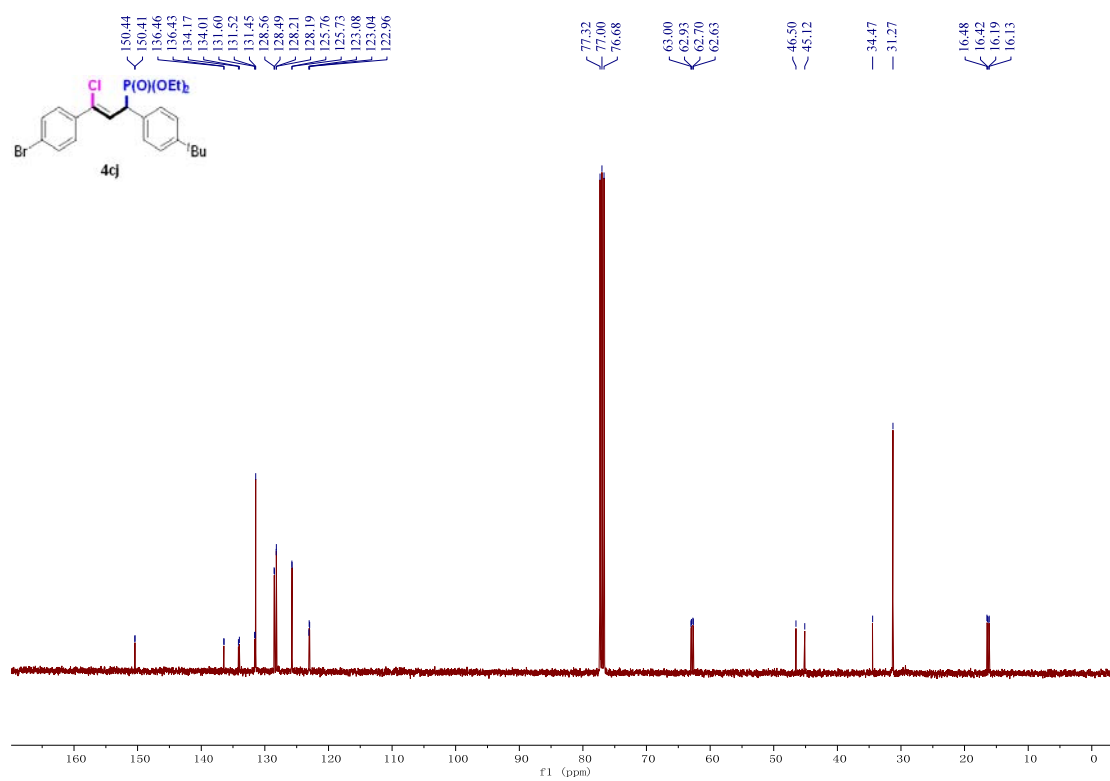
6.57
6.55
6.53
6.55

4.59
4.56
4.55
4.50

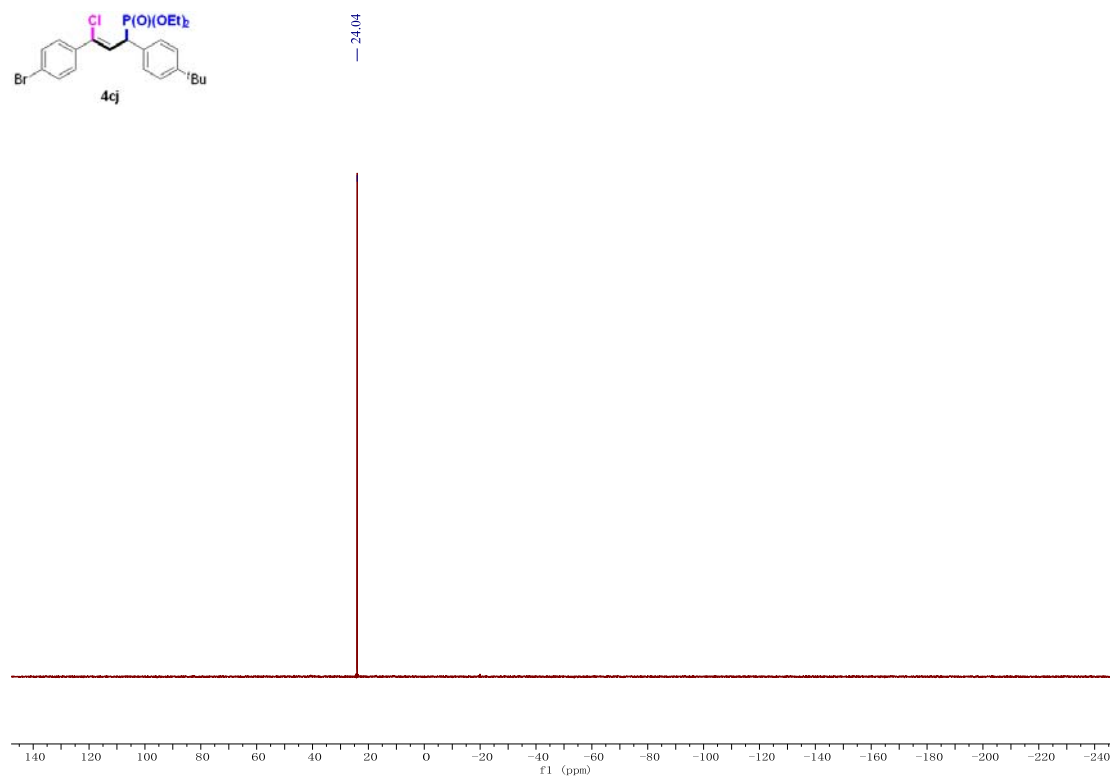
4.14
4.13
4.12
4.11
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4.07
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4.05
4.05
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3.99
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1.00



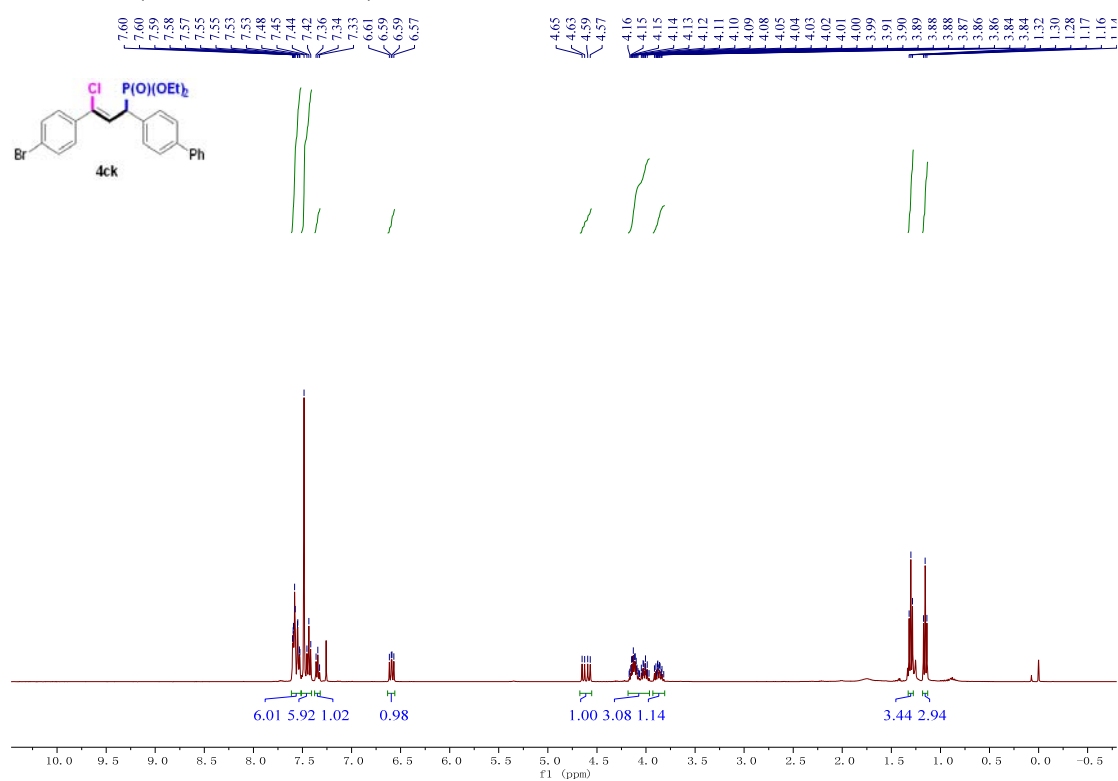
^{13}C NMR (101 MHz, CDCl_3)



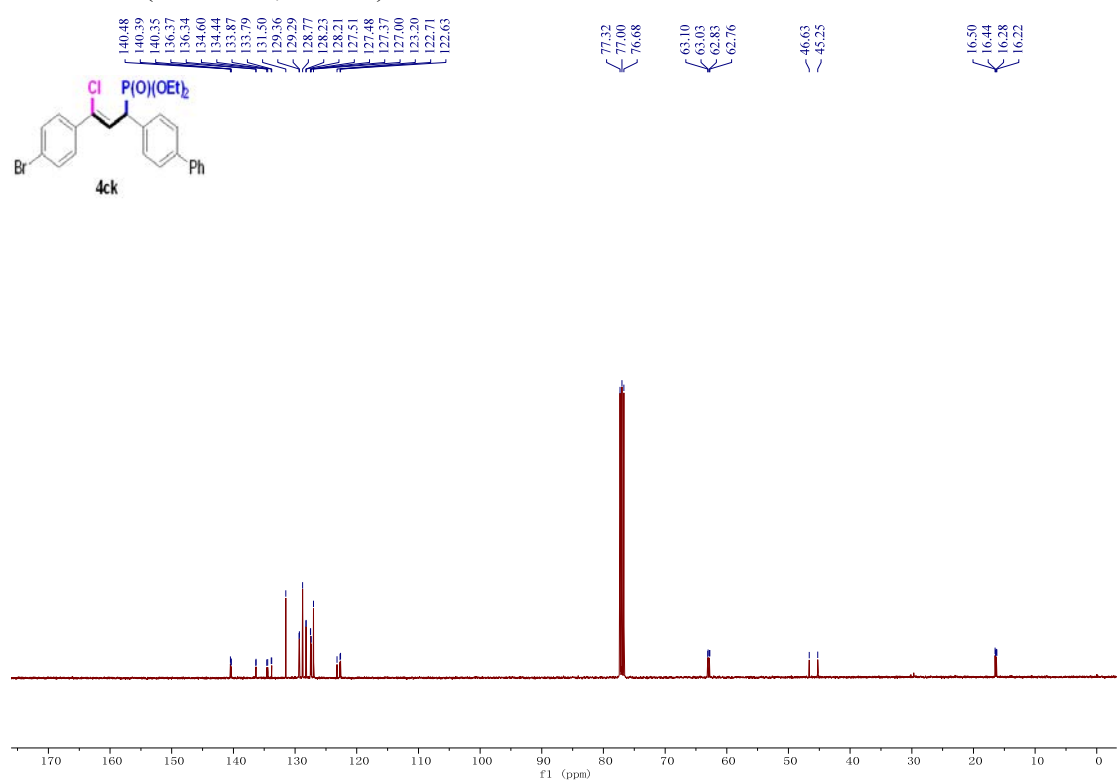
^{31}P NMR (162 MHz, CDCl_3)



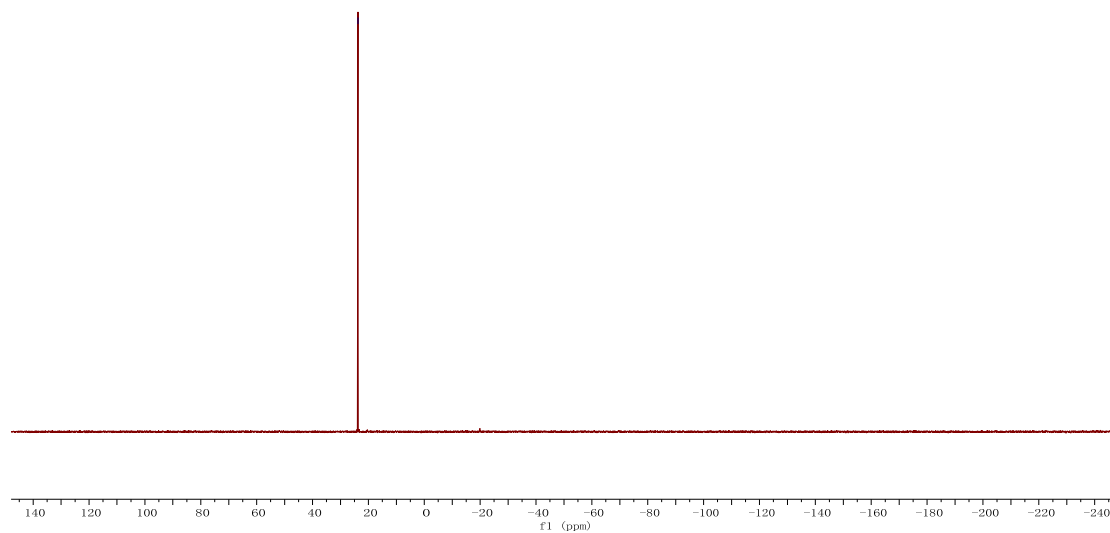
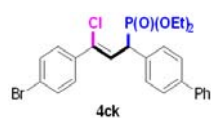
¹H NMR (400 MHz, CDCl₃)



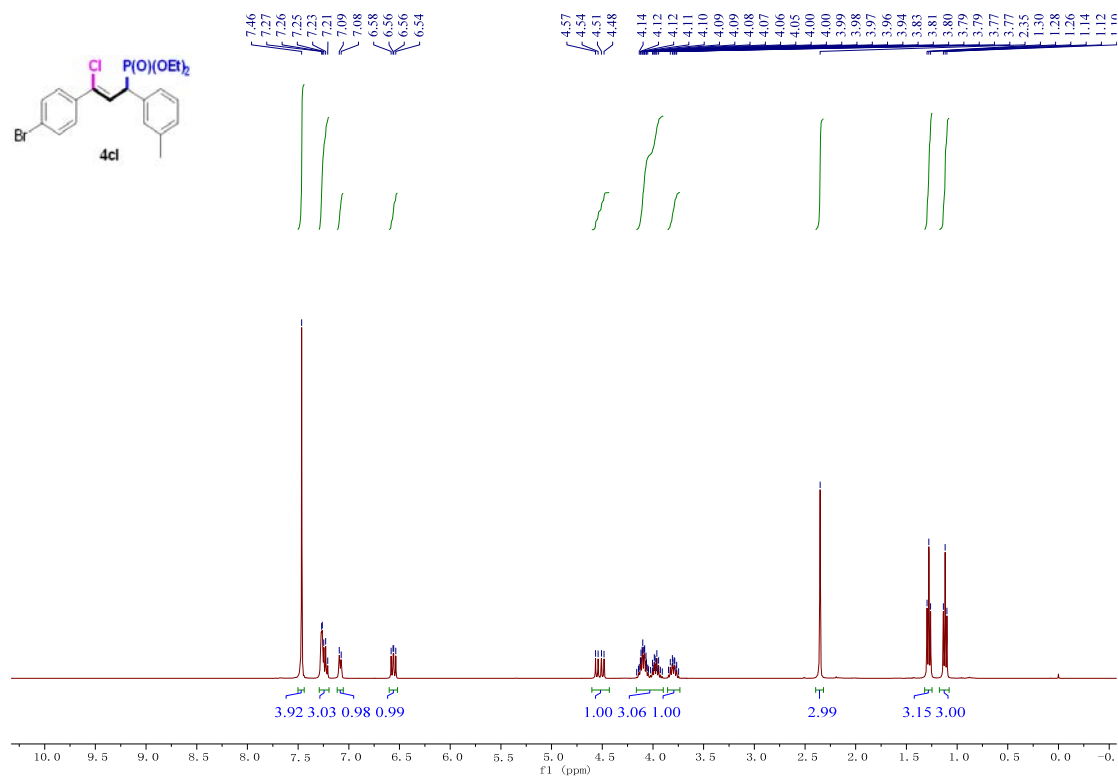
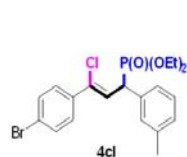
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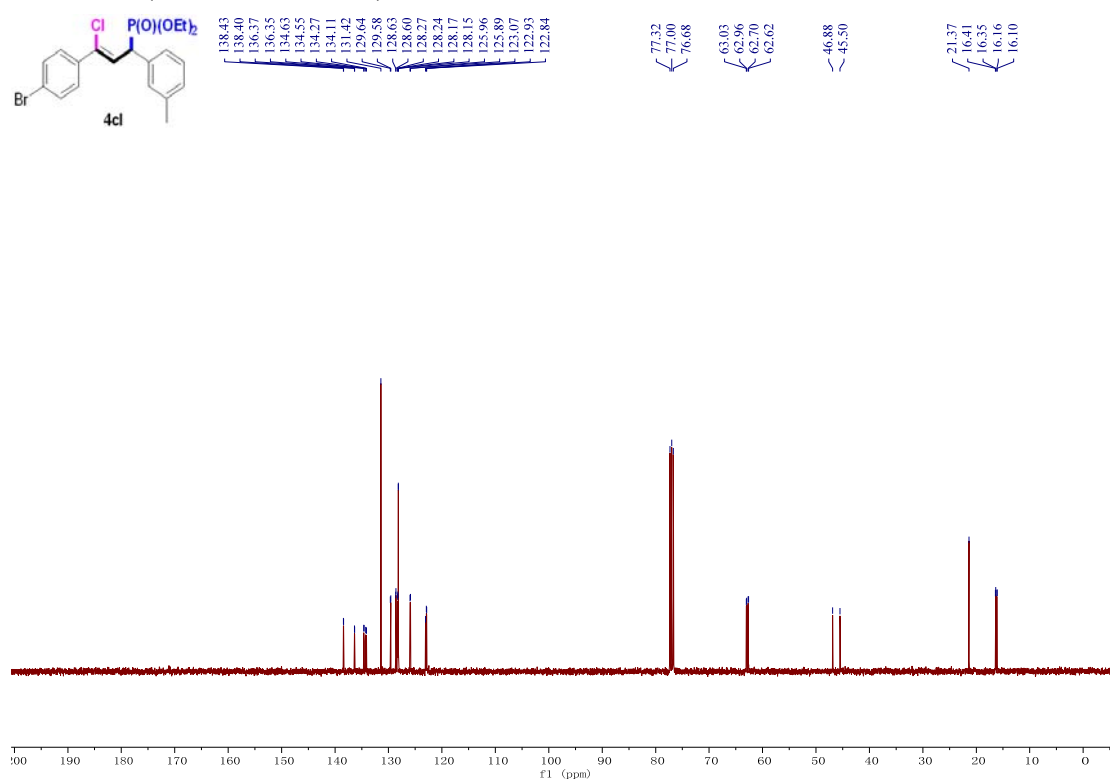
^{31}P NMR (162 MHz, CDCl_3)



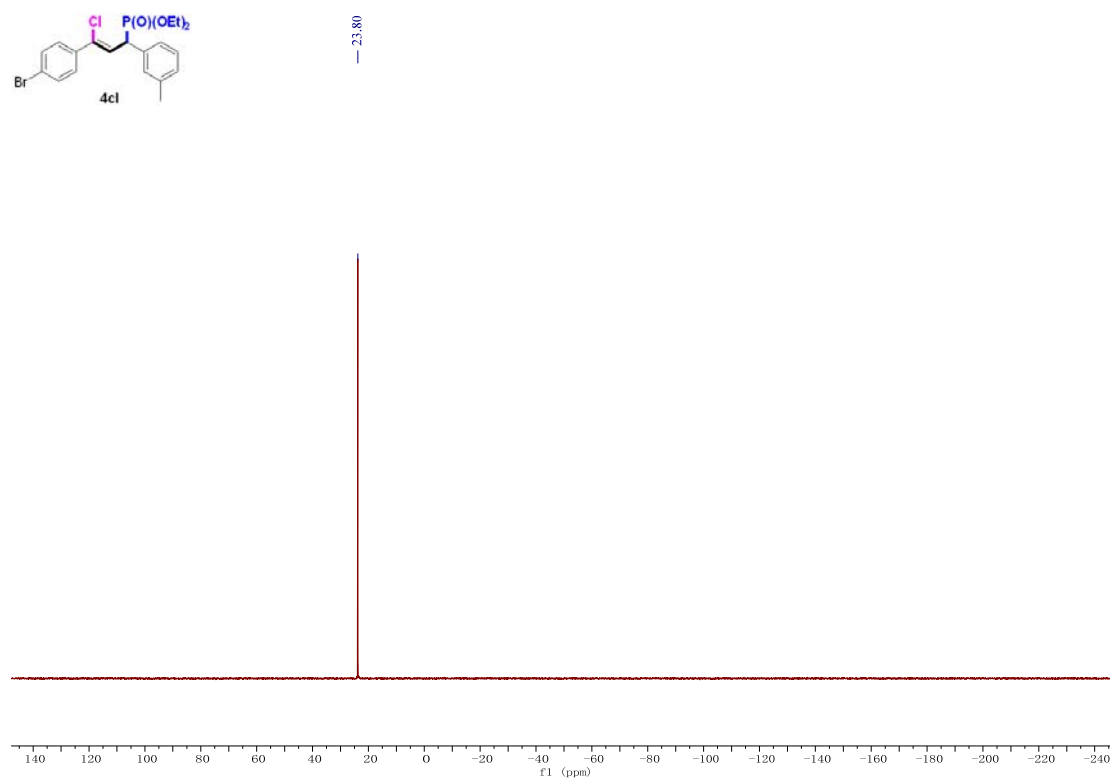
^1H NMR (400 MHz, CDCl_3)



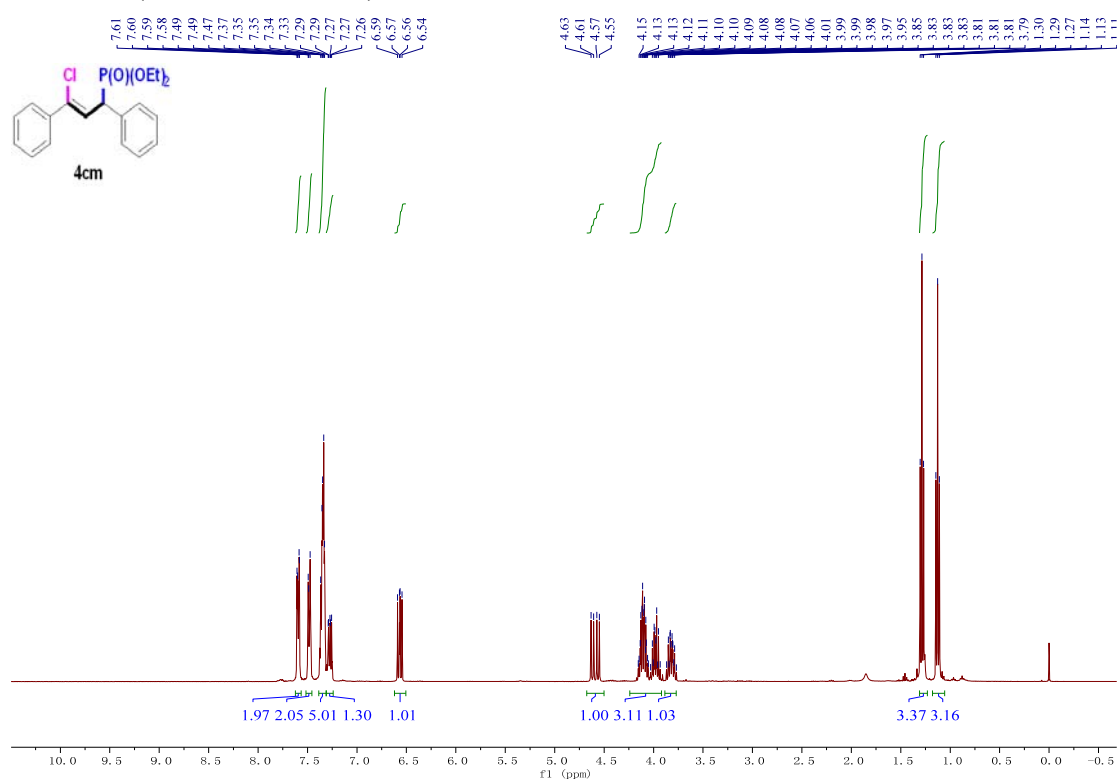
^{13}C NMR (101 MHz, CDCl_3)



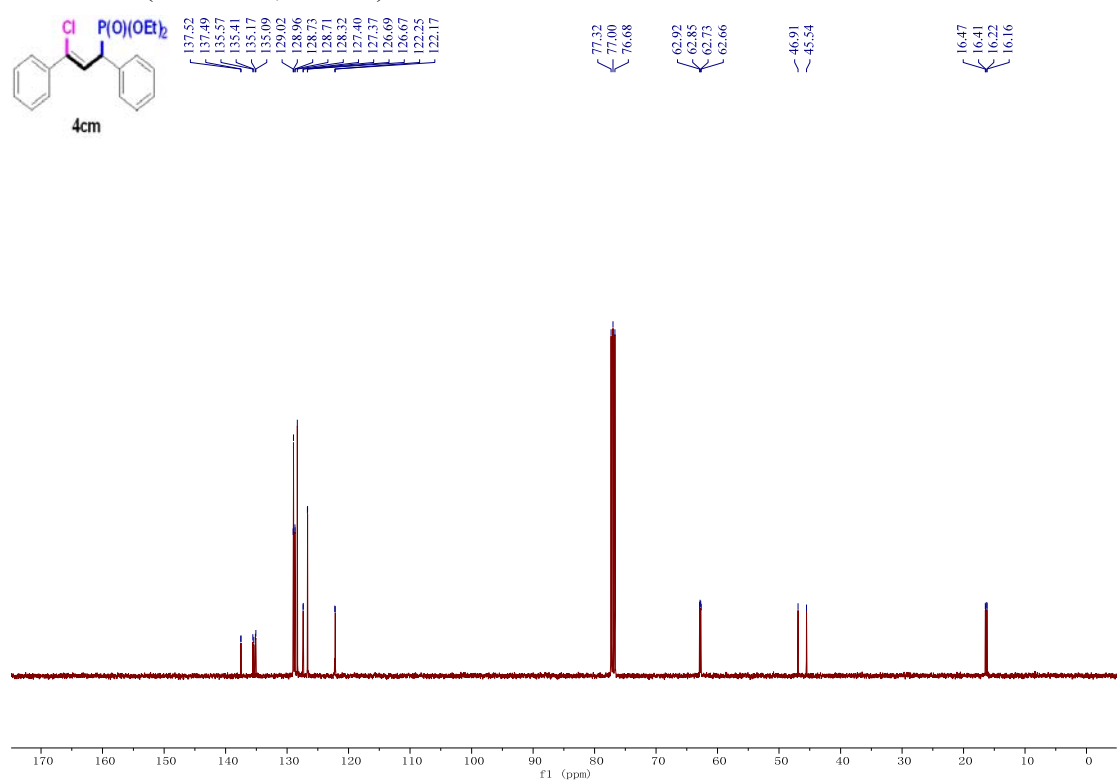
^{31}P NMR (162 MHz, CDCl_3)



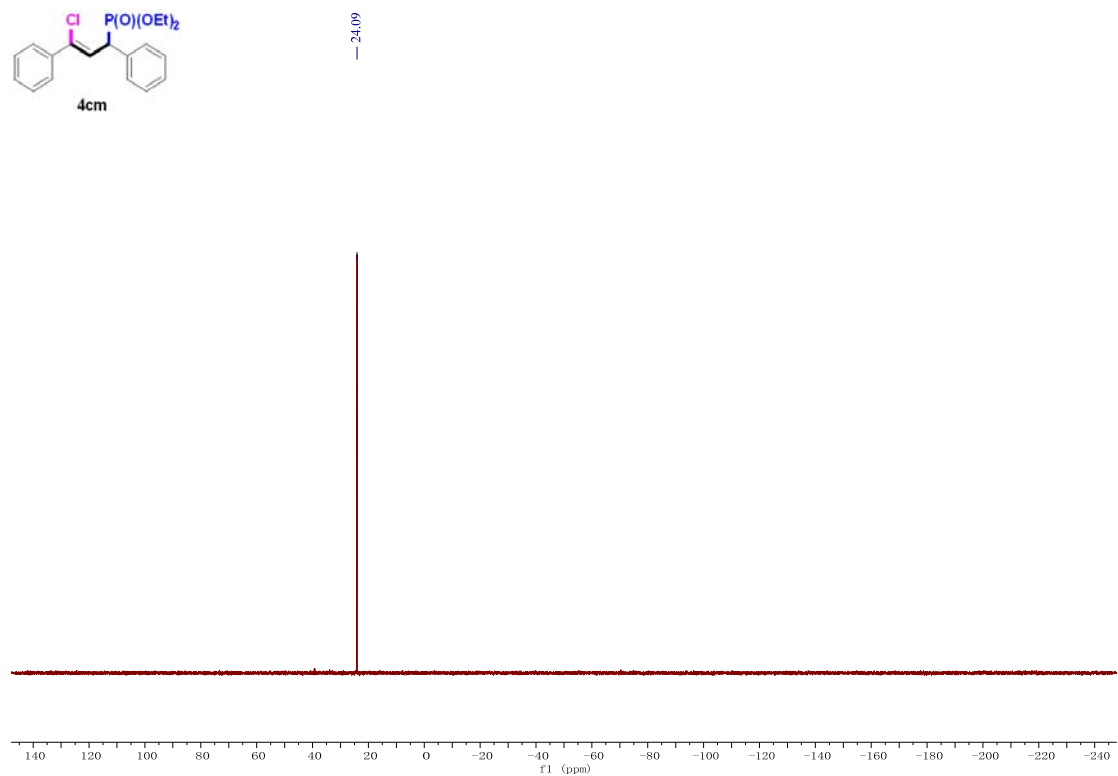
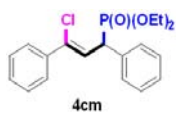
¹H NMR (400 MHz, CDCl₃)



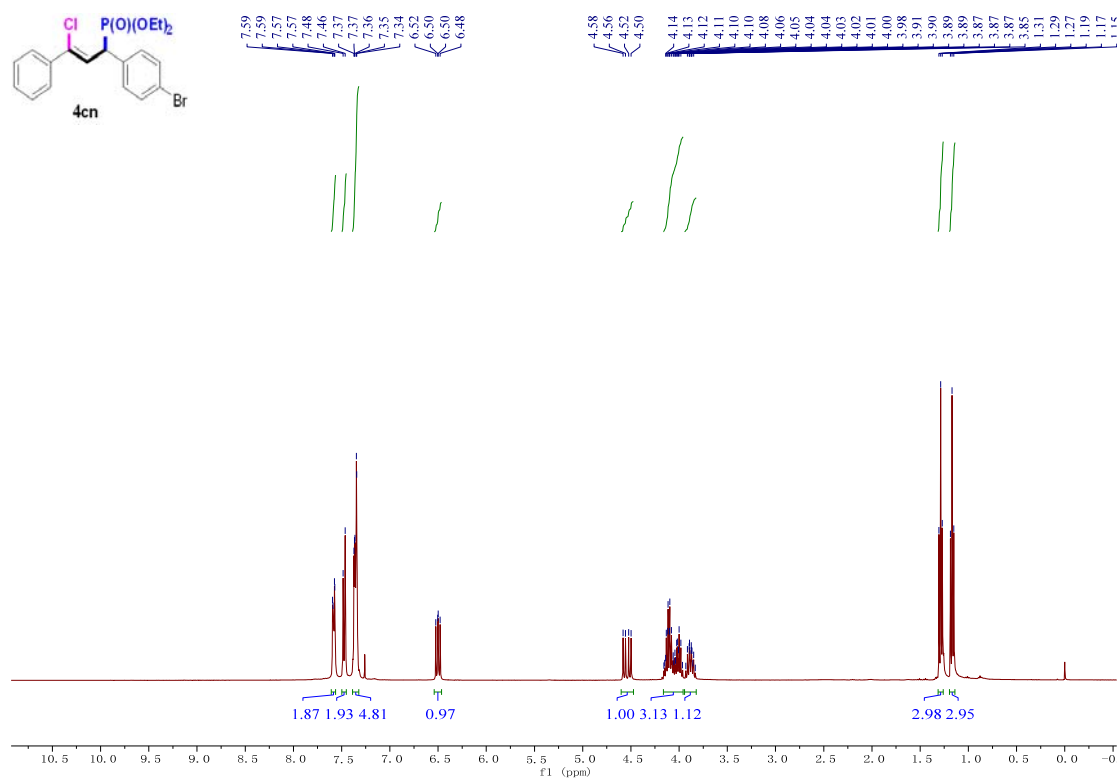
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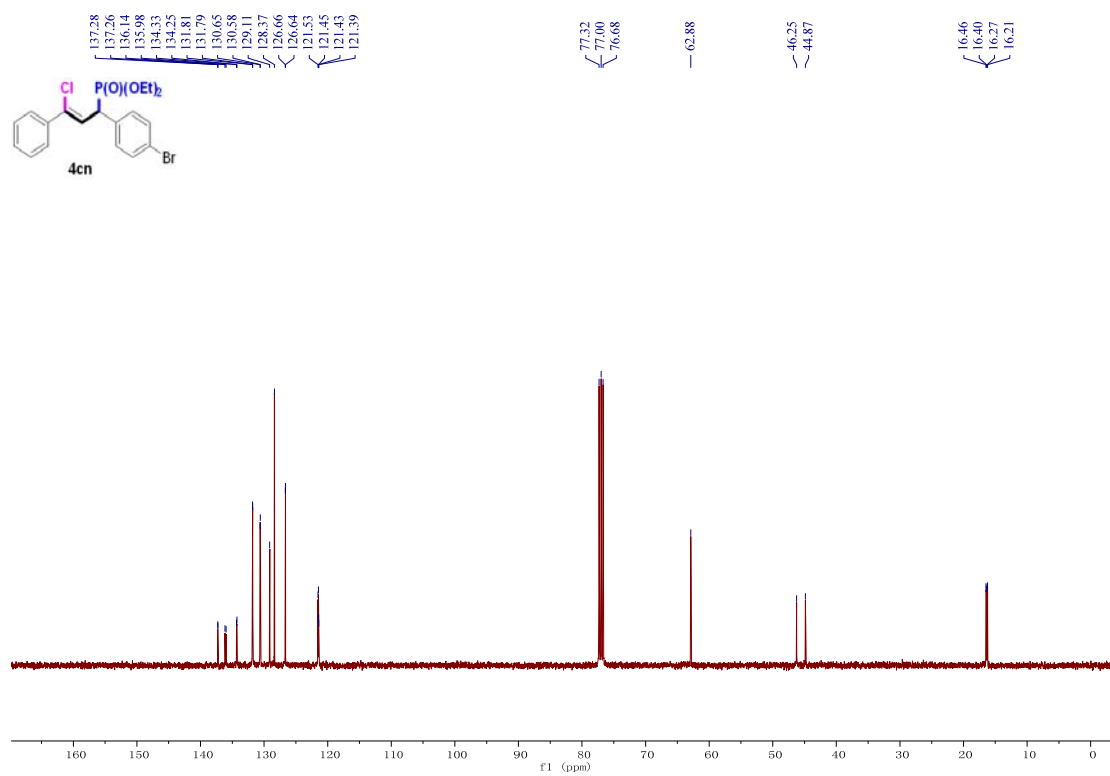
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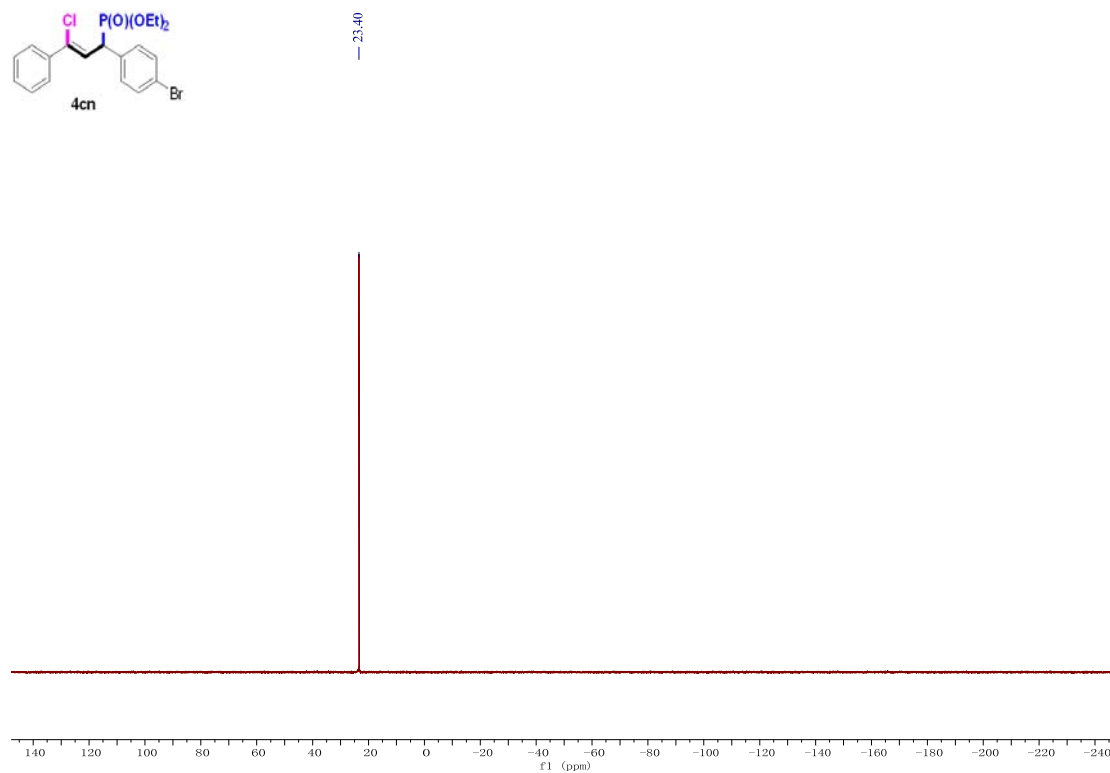
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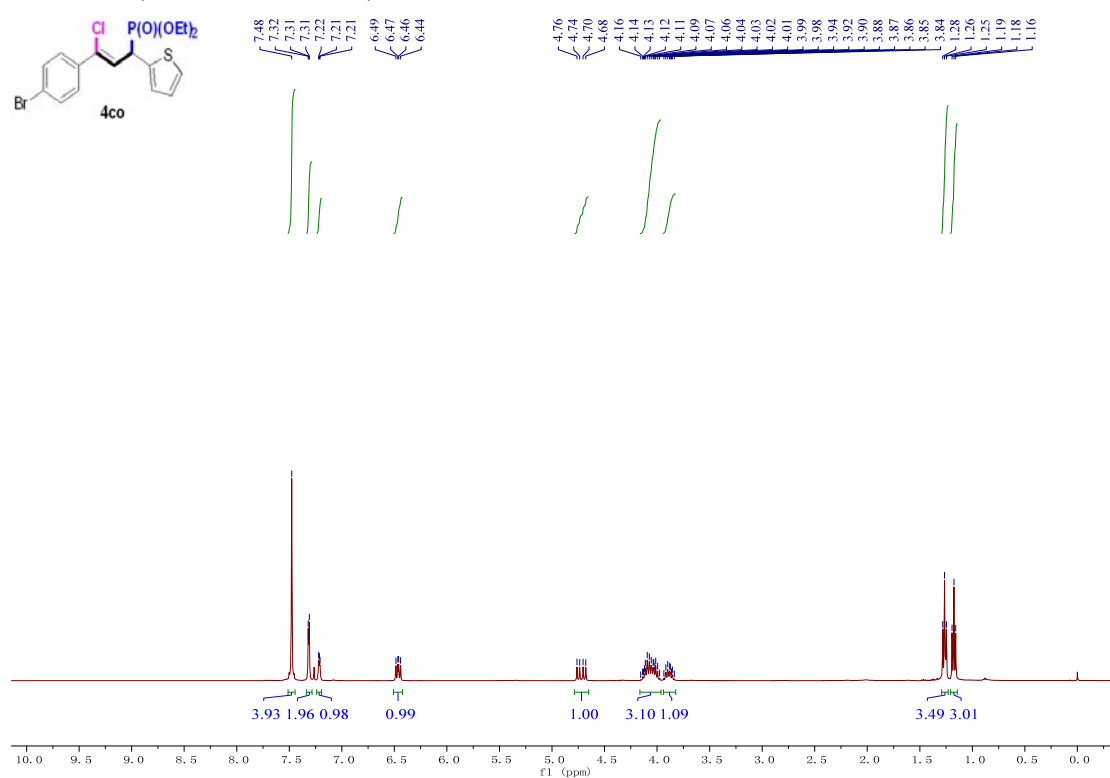
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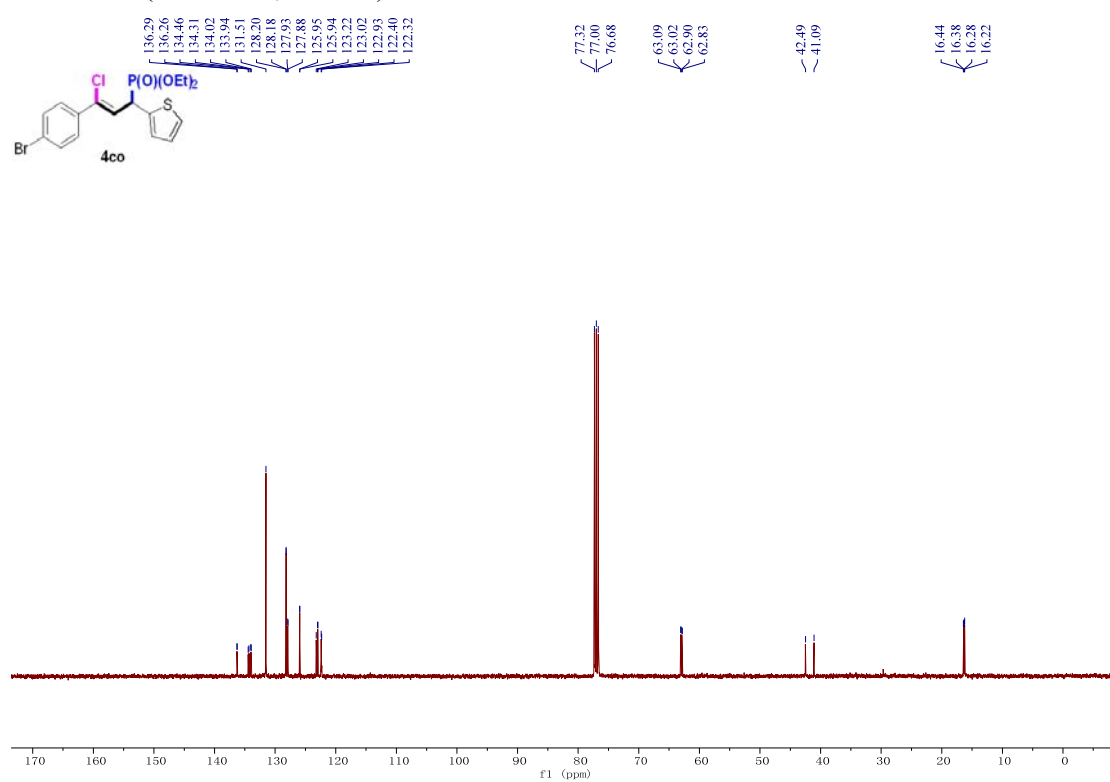
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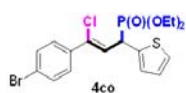
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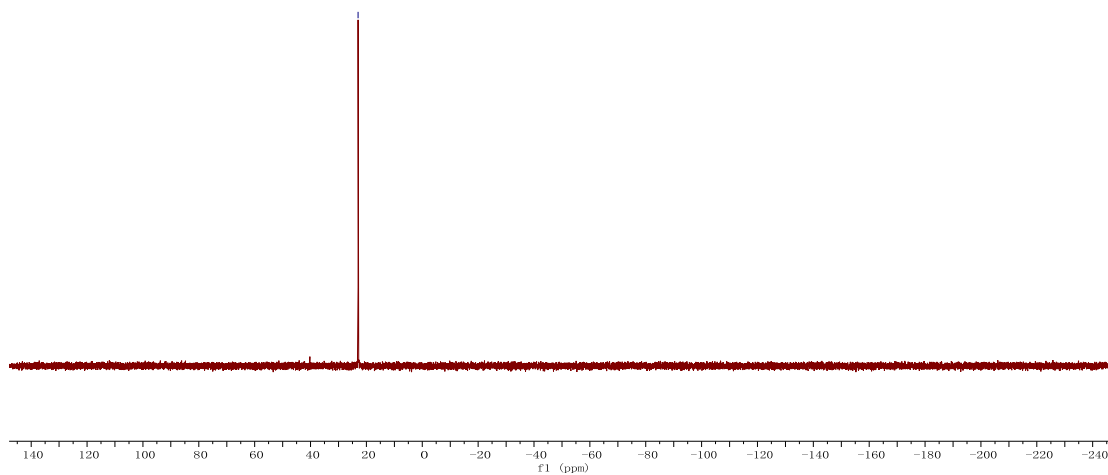
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^{31}P NMR (162 MHz, CDCl_3)



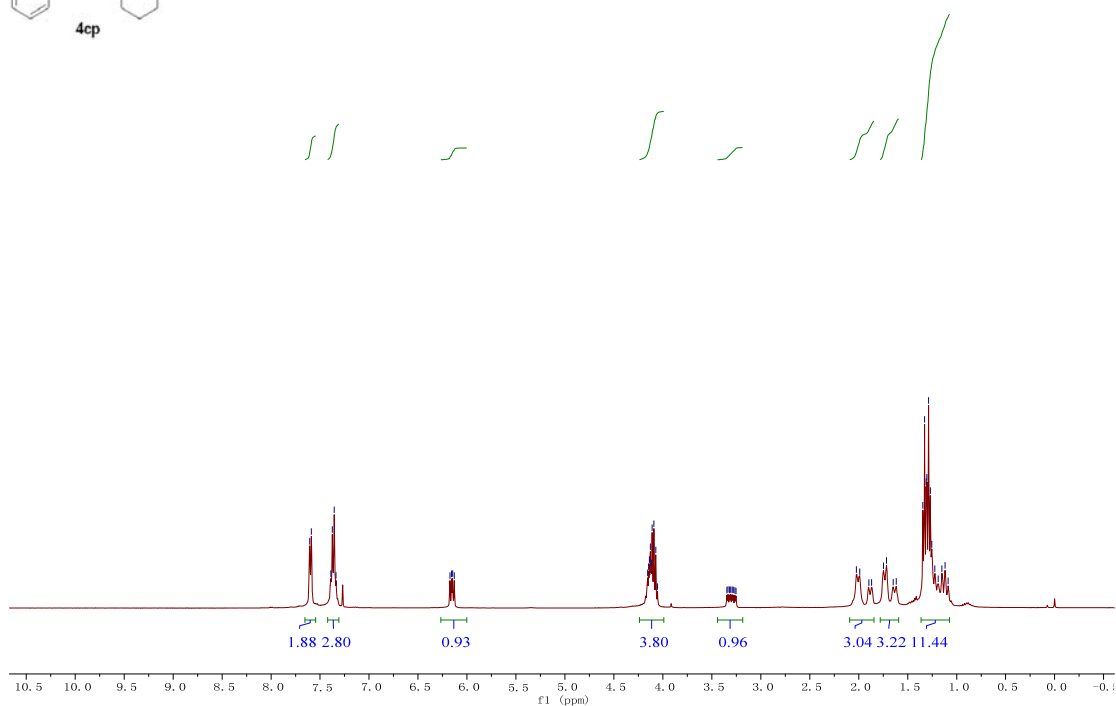
-22.97



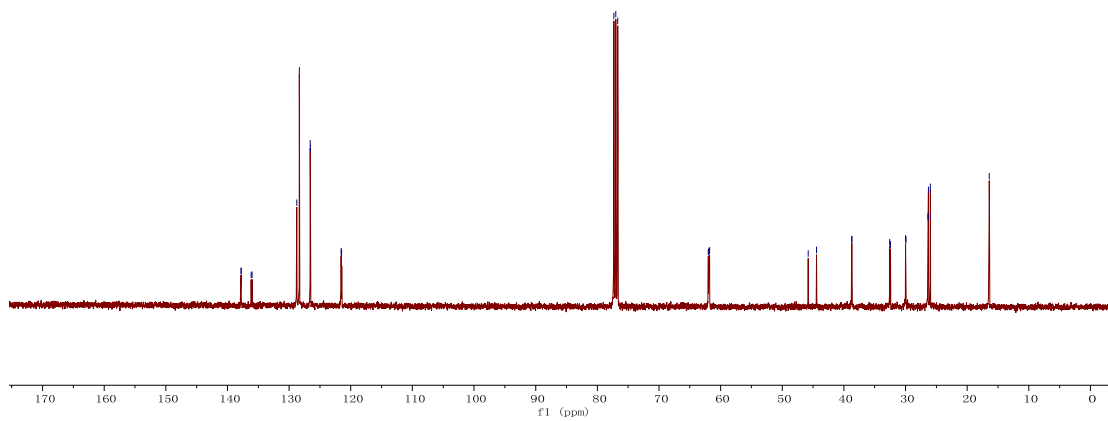
^1H NMR (400 MHz, CDCl_3)



7.61, 7.59, 7.39, 7.37, 7.36, 7.34, 6.17, 6.16, 6.15, 6.13, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.09, 4.07, 4.05, 3.35, 3.33, 3.32, 3.31, 3.29, 3.28, 3.26, 2.02, 1.99, 1.90, 1.87, 1.75, 1.72, 1.66, 1.62, 1.35, 1.33, 1.31, 1.30, 1.29, 1.27, 1.25, 1.22, 1.19, 1.15, 1.12, 1.00



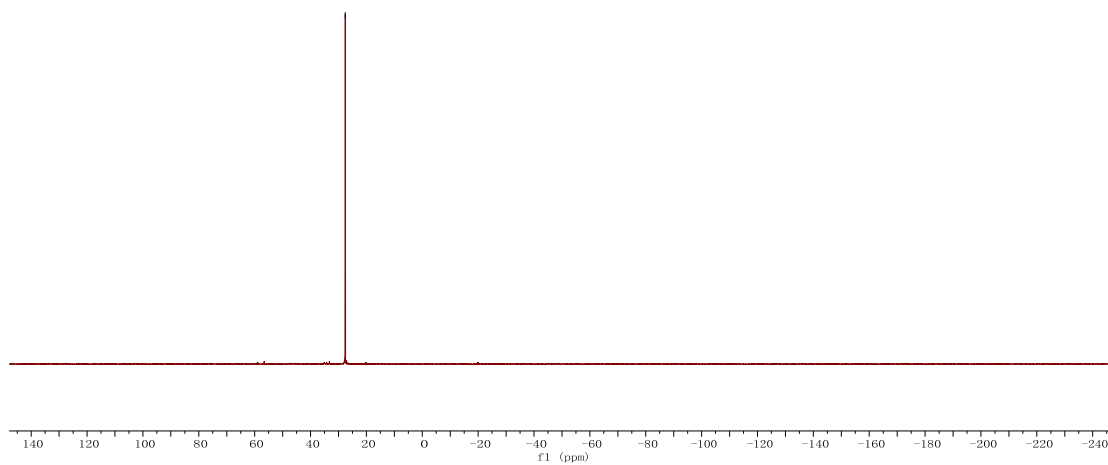
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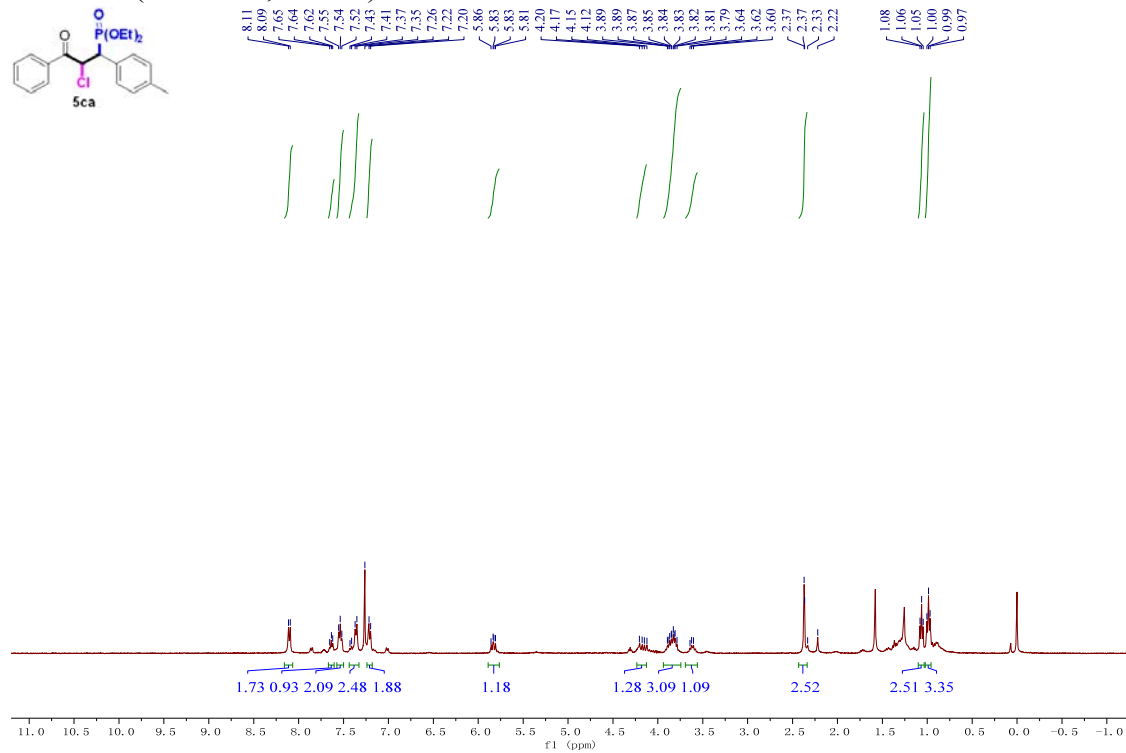
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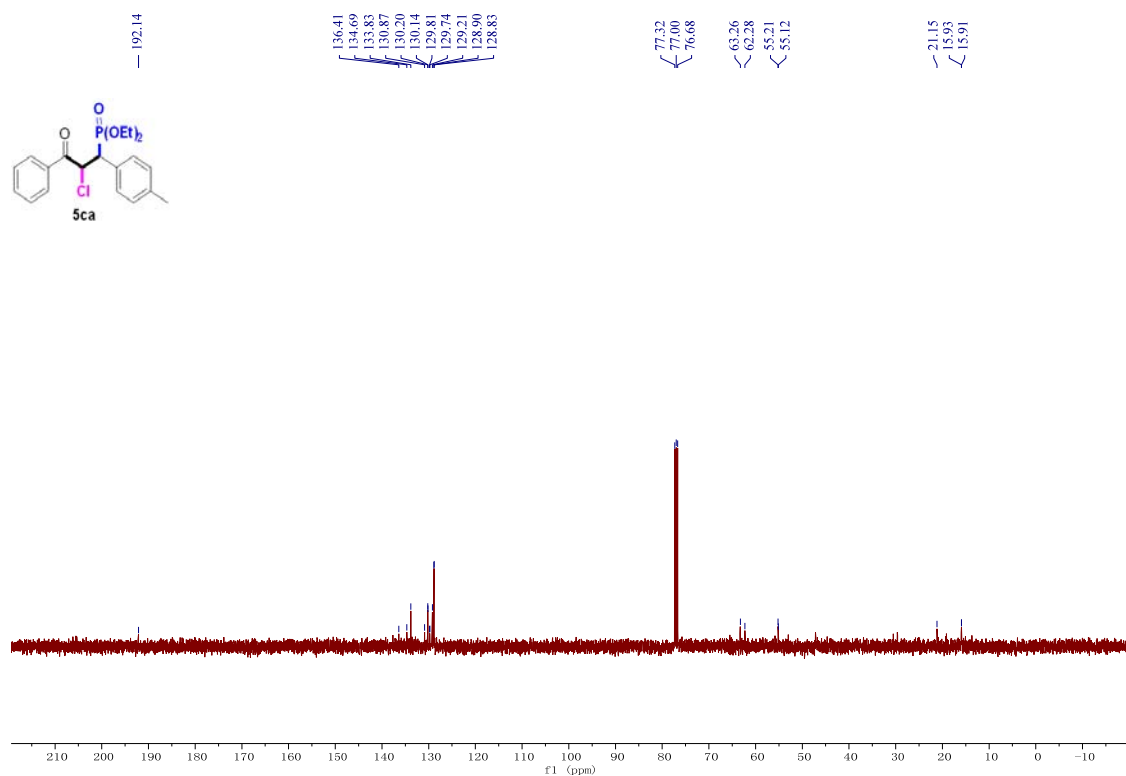
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¹H NMR (400 MHz, CDCl₃)



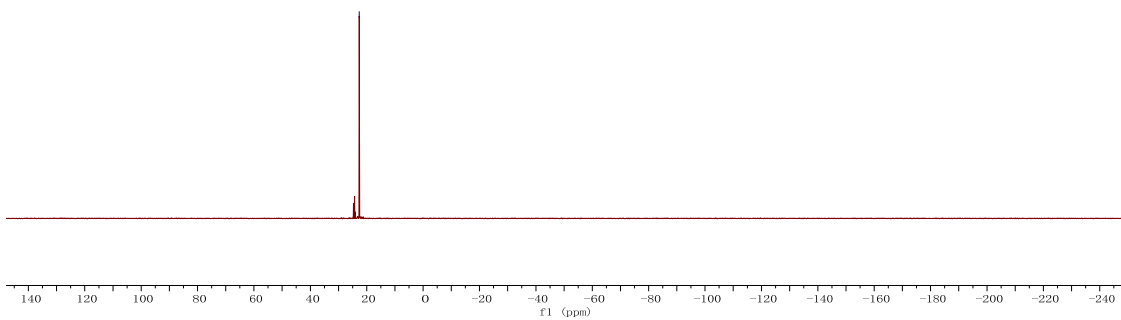
¹³C NMR (101 MHz, CDCl₃)



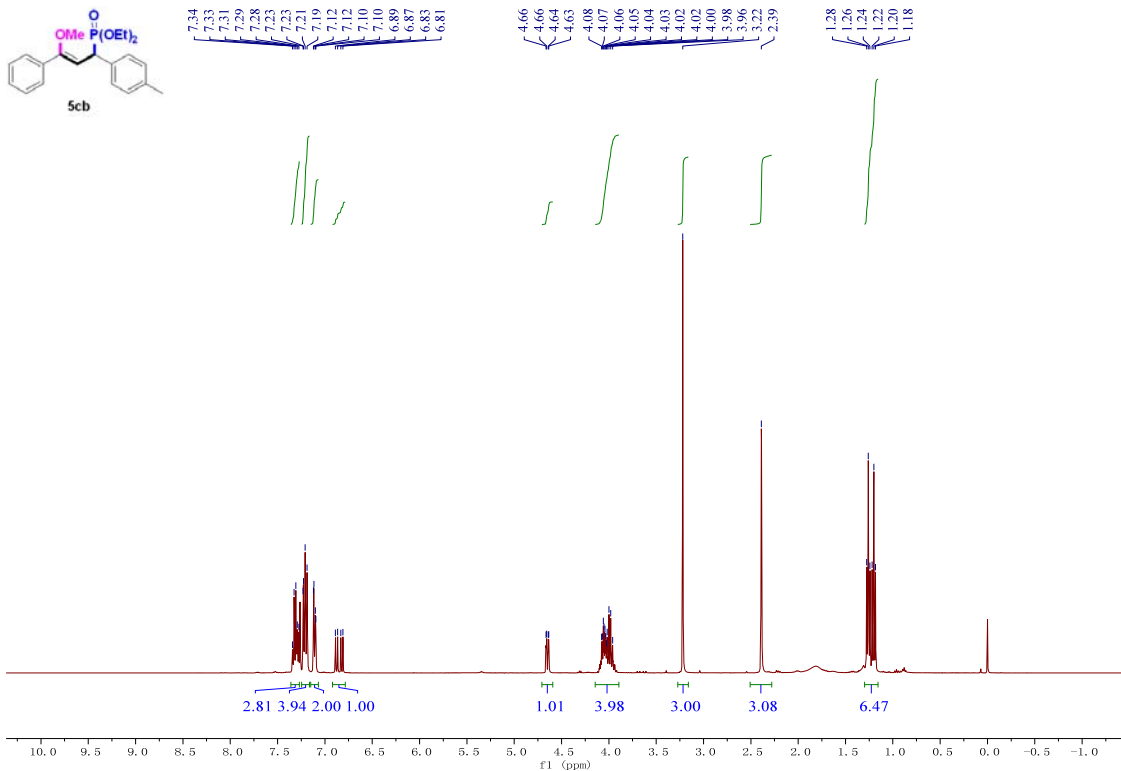
³¹P NMR (162 MHz, CDCl₃)



— 22.66



¹H NMR (400 MHz, CDCl₃)



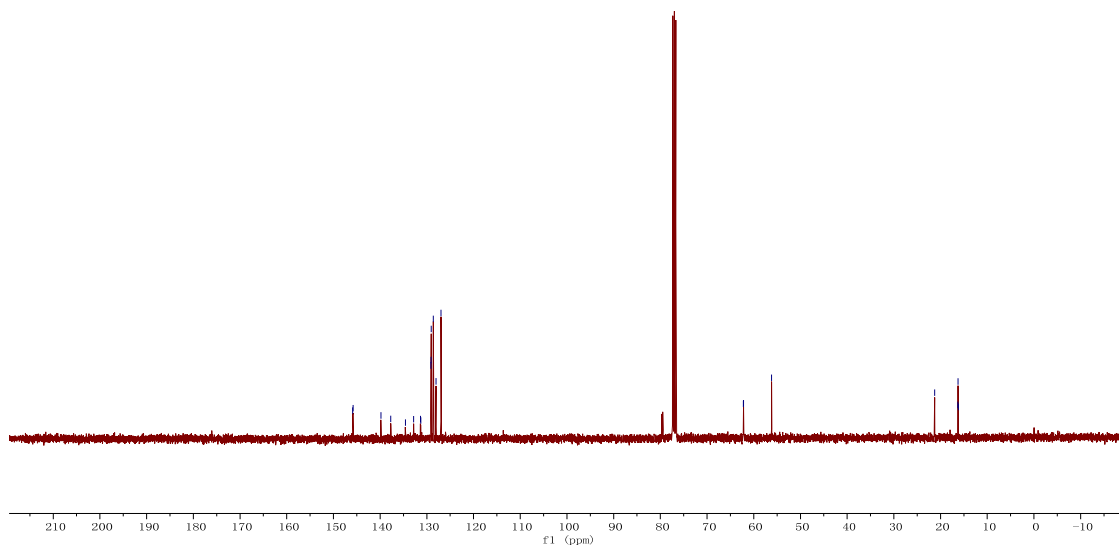
¹³C NMR (101 MHz, CDCl₃)



145.87
 145.78
 139.84
 137.64
 137.49
 133.89
 131.37
 131.28
 129.12
 129.09
 129.07
 128.61
 128.03
 126.96

62.23
 62.17
 56.18

21.25
 16.31
 16.24
 16.18



^{31}P NMR (162 MHz, CDCl_3)



16.32

