

Supporting Information

Stereocontrolled 1,3-Phosphatylxy and 1,3-Halogen Migration Relay Toward Highly Functionalized 1,3-Dienes

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General Information	S2
Synthesis of Starting Materials:	
Preparation of α-halo Aldehydes and Ketones	S3
Preparation of Tetrahydro-2H-pyran-4-carbaldehyde	S7
Preparation of α-halo Propargylic Phosphates	S8
Copper-Catalyzed Synthesis of <i>Z</i>-dienes	S14
Gold-Catalyzed Synthesis of <i>E</i>-dienes	S17
Copper- and Gold-catalyzed Formation of α-fluoroallenes	S20
Crossover Experiments	S21
Functionalization of Compound 2	S22
Spectral Charts	S27

General Information:

NMR spectra were recorded on Bruker DPX-400 (400 MHz) and DRX-500 (500 MHz) instruments. GC/MS analyses were performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). HR EI MS analysis was performed on a JEOL GCmate II mass spectrometer. Column chromatography was carried out employing Merck (Kieselgel 60, 63-200 μm), ICN (ICN SiliTech, 63-200 μm), or SiliCycle (40-63 μm) silica gel. Precoated silica gel plates (0.2 mm, F-254) were used for thin-layer analytical chromatography.

All manipulations were conducted under an argon or nitrogen atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous dichloromethane, toluene, ether, and THF (BHT-free) was purchased from Aldrich, degassed with argon, and dried by passage through activated alumina on an Innovative Technology PureSolv system. Pentane, triethylamine, and dichloroethane were stored over calcium hydride and used without further purification. All other reagents were purchased from various commercial sources and used without additional purification.

Synthesis of Starting Materials

General Procedure for the Synthesis of α -Bromo Aldehydes and Ketones¹

Aldehyde (1.0 equiv), anhydrous diethyl ether, and dioxane (0.4 equiv) were added to a round bottom flask and cooled down to 0 °C. Br₂ (0.95 equiv) was carefully weighed in a graduated cylinder, transferred to an additional funnel and slowly added to the reaction mixture until the color changed. Once the reaction mixture turned colorless, Br₂ continued to be added dropwise. The reaction was quenched after 30 min with a saturated solution of Na₂S₂O₃ and it continued stirring for additional 30 min. It was then extracted three times with diethyl ether. Combined organic extracts were washed two more times with saturated solution of Na₂S₂O₃ and dried over anhydrous sodium sulfate. Solvents were removed under reduced pressure and the crude products were subjected to either fractional distillation or column chromatography.

Synthesis of 2-bromo-2-methylpropanal

Isobutyraldehyde (150 mmol, 10.81g), anhydrous diethylether (70 mL), dioxane (6.0 mmol, 0.51 mL), and Br₂ (148 mmol, 23.7 g, 7.6 mL) were used.

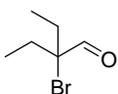


(55%), ¹H NMR (500 MHz, CDCl₃) δ ppm 1.77 (s, 6 H), 9.33 (s, 1 H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 26.5, 63.8, 192.7.

Synthesis of 2-bromo-2-ethylbutanal

2-ethylbutyraldehyde (20 mmol, 2.00 g), anhydrous diethylether (10 mL), dioxane (0.8 mmol, 0.068 mL), and Br₂ (19.5 mmol, 3.12 g, 1.00 mL) were used.



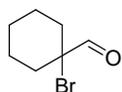
(60%), ¹H NMR (500 MHz, CDCl₃) δ ppm 0.99 (t, *J*=7.43 Hz, 6 H) 1.94 - 2.13 (m, 4 H) 9.39 (s, 1 H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 9.6, 28.7, 76.4, 194.1.

Synthesis of 1-bromocyclohexancarbaldehyde

Cyclohexancarbaldehyde (20 mmol, 2.24 g), anhydrous diethylether (10 mL), dioxane (0.8 mmol, 0.068 mL), and Br₂ (19.5 mmol, 3.12 g, 1.0 mL) were used.

¹ Napper, A. D. et al. *J. Med. Chem.* **2005**, *48*, 8045.

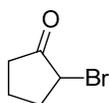


(58%), ^1H NMR (500 MHz, CDCl_3) δ ppm 1.53 - 1.65 (m, 4 H), 1.72 - 1.83 (m, 2 H), 1.94 - 2.12 (m, 4 H), 9.34 (s, 1 H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 23.2, 24.9, 34.44, 71.6, 192.8.

Synthesis of 2-bromocyclopentanone

Cyclopentanone (50 mmol, 4.2 g), anhydrous diethyl ether (20 mL), and dioxane (0.4 equiv, 0.17 mL) were added to a round bottom flask. The flask was placed in an acetone/dry ice bath and stirred for 5 min. Br_2 (0.95 equiv, 47.5 mmol, 7.59 g) was carefully weighed in a graduated cylinder, transferred to an additional funnel and slowly added to the reaction mixture at -78°C until the color changed. Once the reaction mixture turned colorless, Br_2 continued to be added dropwise. The ice bath was then removed and the reaction stirred overnight. Saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$ (15 mL) was added to reaction the mixture at room temperature and the reaction stirred for additional 0.5 h. After separation of phases, aqueous layer was extracted three times with diethyl ether. Combined organic extracts were dried over anhydrous sodium sulfate. Solvents were removed under reduced pressure and the crude product was subjected to column chromatography with Et_3N -treated silica gel (Hex/ EtOAc = 20/1) to afford the corresponding 2-bromocyclopentanone (3.58 g, 44%) as a brown liquid.

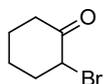


^1H NMR (500 MHz, CDCl_3) δ 1.89 - 2.06 (m, 1 H), 2.10 - 2.23 (m, 3 H), 2.28 - 2.41 (m, 2 H), 4.19 (dd, $J=6.42, 4.22$ Hz, 1 H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 20.2, 33.9, 34.9, 48.3, 211.2.

Synthesis of 2-bromocyclohexanone²

To a mixture of cyclohexanone (10 mmol, 0.982 g) and NBS (10.5 mmol, 1.87g) in dry Et_2O (10 mL) was added NH_4OAc (1 mmol, 0.08 g) and the solution stirred at room temperature. After completion (by GC/MS), the mixture was filtered and the filtrate was washed with water, dried and evaporated. The residue was subjected to column chromatography (Hex/ EtOAc = 20/1) to give the 2-bromocyclohexanone (1.27g, 73%).



(45%), ^1H NMR (500 MHz, CDCl_3) δ 1.69 - 1.76 (m, 1 H), 1.77 - 1.85 (m, 1 H), 1.91 - 2.07 (m, 2 H), 2.18 - 2.26 (m, 2 H), 2.28 - 2.37 (m, 2 H), 4.40 - 4.48 (m, 1 H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 23.9, 28.1, 32.4, 32.5, 34.0, 178.4.

² Tanemura, K. et al. *Chem. Commun.* **2004**, 470.

General Procedure for the Synthesis of α -Chloro Aldehydes and Ketones³

To the neat aldehyde (or 3.0 M solution in DCM) (1.0 equiv), in a flask equipped with an air cooler, was added sulfuryl chloride (1.05 equiv) at 0 °C. The reaction stirred at room temperature until deemed complete by GC/MS analysis. The resulting mixture was then poured into water and the phases were separated. The aqueous phase was extracted with DCM three times. The combined organic fractions were washed with brine and dried over sodium sulfate. Solvents were removed under reduced pressure and the crude products were subjected to either fractional distillation or column chromatography.

Synthesis of 2-chloro-2-methylpropanal

Isobutyraldehyde (5 mmol, 361 mg) and sulfuryl chloride (5.25 mmol, 708 mg) were used.

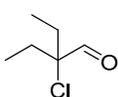


(61%), ¹H NMR (500 MHz, CDCl₃) δ ppm 1.63 (s, 6 H), 9.42 (s, 1 H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 25.8, 69.3, 194.9.

Synthesis of 2-chloro-2-ethylbutanal

2-ethylbutyraldehyde (5 mmol, 501 mg) and sulfuryl chloride (5.25 mmol, 708 mg) were used.

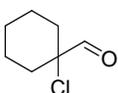


(68%), ¹H NMR (500 MHz, CDCl₃) δ ppm 0.96 (t, $J=7.34$ Hz, 6 H), 1.83 - 1.92 (m, 2 H), 1.93 - 2.03 (m, 2 H), 9.43 (s, 1 H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 8.4, 29.4, 79.2, 197.1.

Synthesis of 1-chlorocyclohexanecarbaldehyde

Cyclohexanecarbaldehyde (5 mmol, 561 mg), sulfuryl chloride (5.25 mmol, 708 mg), and DCM (1.5 mL) were used.



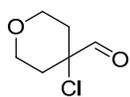
(71%), ¹H NMR (500 MHz, CDCl₃) δ ppm 0.84 - 0.90 (m, 2 H), 1.21 - 1.29 (m, 4 H), 1.54 - 1.64 (m, 2 H), 1.86 - 1.94 (m, 2 H), 9.38 (s, 1 H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 22.7, 24.8, 33.6, 73.7, 195.3.

Synthesis of 4-chlorotetrahydro-2H-pyran-4-carbaldehyde

Tetrahydro-2H-pyran-4-carbaldehyde (5 mmol, 571 mg), sulfuryl chloride (5.25 mmol, 708 mg) and DCM (1.5 mL) were used.

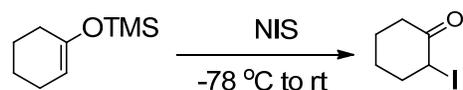
³ Sparling, B. A.; Moslin, R. M.; Timothy Jamison, T. F. *Org. Lett.*, **2008**, *10*, 1291.



(73%), ^1H NMR (500 MHz, CDCl_3) δ ppm 1.89 (d, $J=14.31$ Hz, 2 H), 2.07 - 2.20 (m, 2 H), 3.74 - 3.91 (m, 4 H), 9.41 (s, 1 H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 33.4, 63.2, 67.5, 193.7.

Synthesis of 2-iodocyclohexanone⁴



(Cyclohex-1-en-1-yl)trimethylsilane⁵ (10 mmol, 1.7 g) was dissolved in THF (30 mL) and cooled to -78 °C. A solution of *N*-iodosuccinimide (11.17 mmol, 2.62 g) in THF (15 mL) was added *via* cannula. After 30 minutes, the solution was warmed to room temperature and saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$ (25 mL) was added. After extraction with ethyl acetate and removing the solvents, hexane (15 mL) was added. The precipitate was filtered off. The organic layer was further washed with saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL), dried over Na_2SO_4 . Solvents were removed under reduced pressure and crude material was purified by column chromatography (Hex/EtOAc: 20/1) to yield the α -Iodo cyclohexanone (2.1 g, 92%) as a light yellow oil.



^1H NMR (500 MHz, CDCl_3) δ ppm 1.63 - 1.72 (m, 2 H), 1.81 - 1.97 (m, 2 H), 1.99 - 2.07 (m, 1 H), 2.07 - 2.17 (m, 1H), 2.21 - 2.31 (m, 2 H), 4.62 (t, $J=4.40$ Hz, 1 H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 22.6, 26.6, 32.8, 36.4, 37.4, 204.5.

General procedure for the synthesis of α -Fluoro ketones⁶

To a solution of ketone (11.0 equiv) in acetonitrile, Selectfluor® (4.25 g, 12 mmol) was added and the reaction mixture was heated under reflux. After consumption of starting materials, heating was stopped and solvent was removed under reduced pressure. Dichloromethane (20 mL) was further added and insoluble materials were filtered off. The solution was washed with saturated aqueous NaHCO_3 , dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude material was subjected to column chromatography to afford the α -fluoro ketones.

⁴ Carson, C. A.; Kerr, M. A. *Org. Lett.* **2009**, *11*, 777.

⁵ This compound was made according to the reported procedure: Hong, A. Y.; Krout, M. R.; Jensen, T.; Bennett, N. B.; Harned, A. H.; Stoltz, B. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 2756.

⁶ Stavber, S.; Zupan, M. *Tetrahedron Lett.* **1996**, *37*, 3591

Synthesis of 2-fluorocyclohexanone

Cyclohexanone (10 mmol, 0.98 g), MeCN (120 mL) and Selectfluor® (12 mmol, 4.25 g) were used.

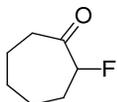


(85%) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.50 - 1.67 (m, 2 H), 1.69 - 1.78 (m, 1 H), 1.83 - 1.98 (m, 2 H), 2.19 - 2.29 (m, 1 H), 2.29 - 2.36 (m, 1 H), 2.37 - 2.46 (m, 1 H), 4.72 - 4.92 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 22.7, 26.9, 34.2, 40.2, 92.7 (d, $J_{\text{CF}}=190.50$ Hz), 205.6 (d, $J_{\text{CF}}=14.8$ Hz).

Synthesis of 2-fluorocycloheptanone:

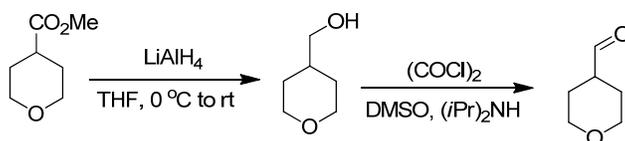
Cycloheptanone (10 mmol, 1.12 g), MeCN (120 mL) and Selectfluor® (12 mmol, 4.25 g) were used.



(37%), ^1H NMR (500 MHz, CDCl_3) δ ppm 1.44 - 1.55 (m, 1 H), 1.59 - 1.68 (m, 3 H), 1.72 - 1.86 (m, 2 H), 1.87 - 2.00 (m, 2 H), 2.42 - 2.55 (m, 2 H), 4.92 - 5.12 (m, 1 H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 23.0, 25.2, 28.2, 31.3, 39.9, 95.3 (d, $J_{\text{CF}}=246.85$ Hz), 208.6 (d, $J_{\text{CF}}=17.69$ Hz).

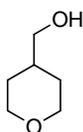
Preparation of tetrahydro-2H-pyran-4-carbaldehyde⁷



To a 250-mL Schlenk flask was added LiAlH_4 (1.5 equiv, 37.5 mmol, 1.42 g) and it was flushed with argon three times. THF (15 mL) was added at 0 °C and stirred for 5 min. The ester (25 mmol, 3.6 g) was added dropwise over 10 min through cannula. The suspension was stirred for an additional 20 min, when TLC analysis showed the complete formation of the alcohol. The reaction mixture is cooled with an ice-water bath while 10 mL of a 10% aqueous potassium hydroxide solution was added dropwise. The mixture was stirred overnight at room temperature, then the white precipitate was removed by filtration through a Celite pad. The solution was further extracted with diethyl ether and combined organic layers were washed with brine, dried with anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was

⁷ Dondoni, A.; Perrone, D. *Org. Synth.* **2004**, *10*, 320

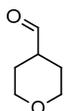
subjected to column chromatography (Hex/EtOAc= 5/1) to give the corresponding alcohol as a yellow oil (1.83g, 63%)



$^1\text{H NMR}$ (500 MHz, CDCl_3) δ ppm 1.14 - 1.35 (m, 2 H), 1.60 (d, $J=13.45$ Hz, 2 H), 1.63 - 1.74 (m, 1 H), 2.58 (br. s., 1 H), 3.25 - 3.46 (m, 4 H), 3.93 (dd, $J=11.11, 4.09$ Hz, 2 H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ ppm 29.5, 37.6, 67.5, 67.7.

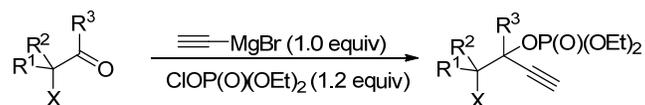
To an oven dried 250-mL Schlenk flask containing a solution of oxalyl chloride (1.5 equiv, 15 mmol, 1.9 g) in DCM (5 mL) was added, sequentially, dimethyl sulfoxide (3 equiv, 30 mmol, 2.34 g) and (tetrahydro-2H-pyran-4-yl) methanol (10 mmol, 781 mg) at -78°C . *N,N*-Diisopropylethylamine (5.5 equiv, 55 mmol, 5.56 g) was then added over 5 min and the reaction flask was removed from the bath and allowed to warm to 0°C over 10 min. The reaction solution was transferred to a 500-mL separatory funnel charged with 50 mL of ice-cold 1 M hydrochloric acid solution. The two phases were separated and aqueous layer was further extracted with DCM. Solvents were removed under reduced pressure and crude product was subjected to column chromatography (Hex/EtOAc= 20/1) to give the corresponding products in 89% yield.



$^1\text{H NMR}$ (500 MHz, CDCl_3) δ ppm 1.59 - 1.68 (m, 2 H), 1.80 (dd, $J=12.84, 1.83$ Hz, 2 H), 2.40 - 2.50 (m, 1 H), 3.43 (dt, $J=11.00, 2.20$ Hz, 2 H), 3.89 (td, $J=11.55, 3.67, 3.48$ Hz, 2 H), 9.59 (s, 1 H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ ppm 25.8, 46.9, 66.7, 202.8.

General procedure for the synthesis of 4-halo-propargylicdiethylphosphates⁸



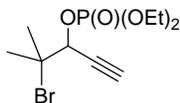
Neat α -halo carbonyl compound (or its solution in anhydrous THF) (1.0 equiv) was added dropwise to an ice cooled flask containing a solution of ethynylmagnesium bromide in THF (1.0 equiv) while stirring. After addition the reaction mixture was allowed to warm to room temperature and stirred for an additional 1 h. Reaction mixture was then placed in an ice-water bath and neat diethylchlorophosphate (1.2 equiv) was added dropwise. Reaction mixture was allowed to warm to room temperature and stirred until judged complete by TLC and GC/MS analyses. After completion, reaction mixture was poured into ammonium chloride solution and extracted three times with ethyl acetate. Combined organic extracts were dried over anhydrous

⁸ Dudnik, A. S.; Schwier, T.; Gevorgyan, V. *Tetrahedron*, **2009**, *65*, 1859.

Na₂SO₄. Solvents were removed under reduced pressure and the residue was purified by column chromatography (Hex/EtOAc= 1/2) to give the corresponding α -halo propargyl phosphate.

Synthesis of 4-bromo-4-methylpent-1-yn-3-yl diethyl phosphate (1a)

2-bromo-2-methylpropanal (30 mmol, 4.53 g), ethynylmagnesium bromide (30 mmol, 0.54 M, 55.5 mL) and neat diethylchlorophosphate (36 mmol, 6.2 g) were used.



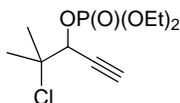
(55%) ¹H NMR (500 MHz, CDCl₃) δ ppm 1.27 - 1.31 (m, 6 H), 1.77 (s, 6 H), 2.62 - 2.65 (m, 1 H), 4.07 - 4.17 (m, 4 H), 4.93 - 4.98 (m, 1 H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 16.0 (t, J_{CP} =7.40 Hz), 29.3, 29.6, 62.8 (d, J_{CP} =7.40 Hz), 64.3 (dd, J_{CP} =11.10, 5.55 Hz), 74.9 (d, J_{CP} =5.55 Hz), 76.4, 78.2.

HRMS (EI) calcd. for C₁₀H₁₈BrO₄P: 313.0207, Found: 313.0212.

Synthesis of 4-chloro-4-methylpent-1-yn-3-yl diethyl phosphate (1b)

2-chloro-2-methylpropanal (5 mmol, 533 mg), ethynylmagnesium bromide (5 mmol, 0.54 M, 9.3 mL) and neat diethylchlorophosphate (6 mmol, 1.03g) were used.



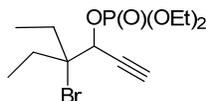
(59%) ¹H NMR (500 MHz, CDCl₃) δ ppm 1.30 (m, 6 H), 1.61 (s, 3 H), 1.62 (s, 3 H), 2.61 (d, J =2.20 Hz, 1 H), 4.06 - 4.18 (m, 4 H), 4.93 (dd, J =7.70, 2.20 Hz, 1 H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 16.0 (t, J_{CP} =5.55 Hz), 27.6, 28.1, 64.2 (dd, J_{CP} =9.25, 5.55 Hz), 68.5 (d, J_{CP} =7.4), 74.4 (d, J_{CP} =5.55 Hz), 76.3, 78.1.

HRMS (EI) calcd. for C₁₀H₁₈ClO₄P: 269.0710, Found: 269.0705.

Synthesis of 4-bromo-4-ethylhex-1-yn-3-yl diethyl phosphate (1c)

2-bromo-2-ethylbutanal (5 mmol, 895 mg), ethynylmagnesium bromide (5 mmol, 0.54 M, 9.3 mL) and neat diethylchlorophosphate (6 mmol, 1.03g) were used.



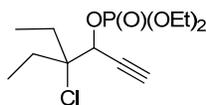
(63%) ¹H NMR (500 MHz, CDCl₃) δ ppm 1.02 (ddd, J =7.34, 3.67 Hz, 6 H), 1.29 - 1.36 (m, 6 H), 1.90 - 1.97 (m, 2 H), 1.98 - 2.07 (m, 2 H), 2.63 (d, J =2.20 Hz, 3 H), 4.11 - 4.19 (m, 4 H), 5.14 (dd, J =7.34, 2.20 Hz, 1 H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 9.50, 16.1 (t, J_{CP} =7.40 Hz), 30.5, 31.1, 64.2 (d, J_{CP} =7.40 Hz), 72.5 (d, J_{CP} =5.55 Hz), 75.5 (d, J_{CP} =7.41 Hz), 76.7, 78.3.

HRMS (EI) calcd. for C₁₂H₂₂BrO₄P: 341.0517, Found: 341.0514.

Synthesis of 4-chloro-4-ethylhex-1-yn-3-yl diethyl phosphate (1m)

2-chloro-2-ethylpentanal (5 mmol, 673 mg), ethynylmagnesium bromide (5 mmol, 0.54 M, 9.3 mL) and neat diethylchlorophosphate (6 mmol, 1.03g) were used.



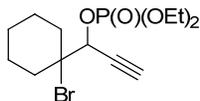
(65%) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.04 (dt, $J=7.43$, 1.65 Hz, 6 H), 1.32 - 1.39 (m, 6 H), 1.95 - 2.02 (m, 4 H) 2.63 (d, $J=2.20$ Hz, 1 H) 4.12 - 4.22 (m, 4 H) 5.15 (dd, $J=7.70$, 2.20 Hz, 1 H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 8.3, 16.1 (t, $J_{\text{CP}}=7.40$ Hz), 29.4, 30.0, 64.2 (d, $J_{\text{CP}}=7.40$ Hz), 72.3 (d, $J_{\text{CP}}=7.40$ Hz), 76.6, 78.2.

HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{22}\text{ClO}_4\text{P}$: 297.1023, Found: 297.1016.

Synthesis of 1-(1-bromocyclohexyl)prop-2-yn-1-yl diethyl phosphate (1n)

1-bromocyclohexanecarbaldehyde (5 mmol, 955 mg), ethynylmagnesium bromide (5 mmol, 0.54 M, 9.3 mL) and neat diethylchlorophosphate (6 mmol, 1.03g) were used.



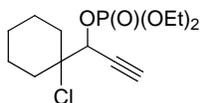
(67%) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.31 - 1.37 (m, 6 H), 1.60 - 1.83 (m, 8 H), 2.03 - 2.23 (m, 2 H), 2.64 (d, $J=2.20$ Hz, 1 H), 4.11 - 4.21 (m, 4 H), 5.02 (dd, $J=7.70$, 2.20 Hz, 1 H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.1 (t, $J_{\text{CP}}=7.40$ Hz), 22.3 (d, $J_{\text{CP}}=7.40$ Hz) 25.1, 35.8, 64.3 (d, $J_{\text{CP}}=5.55$ Hz), 75.0 (d, $J_{\text{CP}}=5.55$ Hz), 76.4, 78.5.

HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{22}\text{BrO}_4\text{P}$: 353.0517, Found: 353.0516.

Synthesis of 1-(1-chlorocyclohexyl)prop-2-yn-1-yl diethyl phosphate (1d)

1-chlorocyclohexanecarbaldehyde (5 mmol, 733 mg), ethynylmagnesium bromide (5 mmol, 0.54 M, 9.3 mL) and neat diethylchlorophosphate (6 mmol, 1.03g) were used.



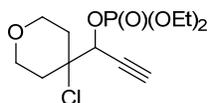
(63%) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.26 (t, $J=7.02$ Hz, 6 H), 1.50 - 1.73 (m, 8 H), 1.84 - 1.96 (m, 2 H), 2.60 (s, 1 H), 3.98 - 4.16 (m, 4 H), 4.91 (d, $J=8.18$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.0 (d, $J_{\text{CP}}=5.90$ Hz), 21.3 (d, $J_{\text{CP}}=5.90$ Hz), 25.0, 34.4, 34.6, 64.2 (t, $J_{\text{CP}}=5.90$ Hz), 74.0 (d, $J_{\text{CP}}=8.85$ Hz), 74.6 (d, $J_{\text{CP}}=5.90$ Hz), 76.8, 78.0.

HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{22}\text{ClO}_4\text{P}$: 309.1023, Found: 309.1011.

1-(4-chlorotetrahydro-2H-pyran-4-yl)prop-2-yn-1-yl diethyl phosphate (1e)

4-chlorotetrahydro-2H-pyran-4-carbaldehyde (5 mmol, 743 mg), ethynylmagnesium bromide (5 mmol, 0.54 M, 9.3 mL) and neat diethylchlorophosphate (6 mmol, 1.03g) were used.



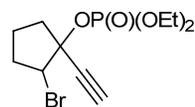
(69%) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.29 - 1.35 (m, 6 H), 1.82 (t, $J=15.13$ Hz, 2 H), 2.02 - 2.12 (m, 2 H), 2.66 (d, $J=2.02$ Hz, 1 H), 3.77 (t, $J=11.65$ Hz, 2 H), 3.84 - 3.91 (m, 2 H), 4.08 - 4.19 (m, 4 H), 4.98 (dd, $J=8.07$, 1.47 Hz, 1 H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.0 (t, $J_{\text{CP}}=7.40$ Hz), 34.4, 34.7, 63.1, 63.2, 64.3 (t, $J_{\text{CP}}=6.47$ Hz), 67.3 (d, $J_{\text{CP}}=8.32$ Hz), 70.9 (d, $J_{\text{CP}}=8.32$ Hz), 74.1 (d, $J_{\text{CP}}=4.62$ Hz).

HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{20}\text{ClO}_5\text{P}$: 311.08371, Found: 311.07961.

Synthesis of 2-bromo-1-ethynylcyclopentyl diethyl phosphate (1f)

2-bromocyclopentanone (5 mmol, 815 mg), ethynylmagnesium bromide (5 mmol, 0.54 M, 9.3 mL) and neat diethylchlorophosphate (6 mmol, 1.03g) were used.



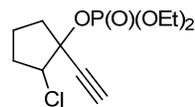
(53%) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.31 (dq, $J=6.97$, 1.10 Hz, 6 H), 1.70 - 1.83 (m, 1 H), 1.89 - 1.98 (m, 1 H), 2.05 - 2.17 (m, 2 H), 2.31 - 2.46 (m, 1 H), 2.61 - 2.75 (m, 2 H), 4.03 - 4.22 (m, 4 H), 4.25 (dt, $J=7.52$, 3.30 Hz, 1 H)

^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.0 (t, $J_{\text{CP}}=11.02$ Hz), 19.8, 32.9, 36.8, 64.2 (d, $J_{\text{CP}}=7.40$ Hz), 75.7, 80.5, 81.0 (d, $J_{\text{CP}}=7.40$ Hz).

HRMS (EI) calcd. for $\text{C}_{11}\text{H}_{18}\text{BrO}_4\text{P}$: 325.0204, Found: 325.0204.

Synthesis of 2-chloro-1-ethynylcyclopentyl diethyl phosphate (1g)

2-chlorocyclopentanone (5 mmol, 593 mg), ethynylmagnesium bromide (5 mmol, 0.54 M, 9.3 mL) and neat diethylchlorophosphate (6 mmol, 1.03g) were used to afford the product as a brown solid. (m.p= 41 °C)



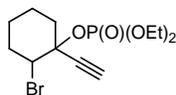
(51%), ^1H NMR (500 MHz, CDCl_3) δ ppm 1.32 - 1.37 (m, 6 H), 1.75 - 1.88 (m, 1 H), 1.93 - 2.09 (m, 2 H), 2.14 - 2.23 (m, 1 H), 2.31 - 2.41 (m, 1 H), 2.64 - 2.71 (m, 1 H), 2.72 (s, 1 H), 4.08 - 4.26 (m, 4 H), 4.30 (dt, $J=6.60$, 2.57 Hz, 5 H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.1 (d, $J_{\text{CP}}=3.70$ Hz), 19.1, 32.1, 36.7, 64.2 (d, $J_{\text{CP}}=7.36$ Hz), 66.5 (d, $J_{\text{CP}}=7.40$ Hz), 75.9, 81.1 (d, $J_{\text{CP}}=7.40$ Hz).

HRMS (EI) calcd. for C₁₁H₁₈ClO₄P: 281.0710, Found: 281.0707.

Synthesis of 2-bromo-1-ethynylcyclohexyl diethyl phosphate (1h)

2-bromocyclohexanone (5 mmol, 885 mg), ethynylmagnesium bromide (5 mmol, 0.54 M, 9.3 mL) and neat diethylchlorophosphate (6 mmol, 1.03g) were used.



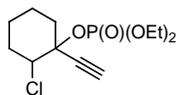
(62%) ¹H NMR (500 MHz, CDCl₃) δ ppm 1.30 (dt, *J*=7.15, 1.10 Hz, 6 H), 1.37 - 1.47 (m, 1 H), 1.56 - 1.76 (m, 4 H), 1.86 - 1.95 (m, 1 H), 1.98 - 2.08 (m, 1 H), 2.15 - 2.23 (m, 1 H), 2.78 (s, 1 H), 4.05 - 4.24 (m, 4 H), 4.50 (s, 1 H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 16.0 (d, *J*_{CP}=11.10 Hz), 21.5, 32.3, 35.5, 58.3 (d, *J*_{CP}=7.40 Hz), 63.9 (d, *J*_{CP}=7.35 Hz), 64.1 (d, *J*_{CP}=5.55 Hz), 76.5 (d, *J*_{CP}=7.36 Hz), 81.1.

HRMS (EI) calcd. for C₁₂H₂₀BrO₄P: 339.0361, Found: 339.0360.

Synthesis of 2-chloro-1-ethynylcyclohexyl diethyl phosphate (1i)

2-chlorocyclohexanone (5 mmol, 663 mg), ethynylmagnesium bromide (5 mmol, 0.54 M, 9.3 mL) and neat diethylchlorophosphate (6 mmol, 1.03g) were used.



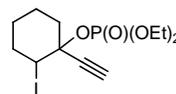
(67%) ¹H NMR (500 MHz, CDCl₃) δ ppm 1.31 - 1.39 (m, 6 H), 1.54 - 1.61 (m, 2 H), 1.61 - 1.70 (m, 2 H), 2.10 - 2.19 (m, 4 H), 4.09 - 4.25 (m, 4 H), 6.24 (s, 1 H) 6.90 (d, *J*=5.14 Hz, 1 H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 15.9 (d, *J*_{CP}=7.40 Hz) 21.5, 31.4, 34.7, 63.8 (dd, *J*_{CP}=18.50, 5.55 Hz), 64.4 (d, *J*_{CP}=7.40 Hz), 76.9 (d, *J*_{CP}=7.40 Hz), 77.3, 81.2.

HRMS (EI) calcd. for C₁₂H₂₀ClO₄P: 295.0866, Found: 295.0868.

Synthesis of diethyl (1-ethynyl-2-iodocyclohexyl) phosphate (1j)

2-iodocyclohexanone (5 mmol, 1.12 g), ethynylmagnesium bromide (5 mmol, 0.54 M, 9.3 mL) and neat diethylchlorophosphate (6 mmol, 1.03g) were used.



(69%) ¹H NMR (500 MHz, CDCl₃) δ ppm 1.25 (t, *J*=6.97 Hz, 6 H), 1.51 - 1.63 (m, 4 H), 1.64 - 1.74 (m, 1 H), 1.82 - 1.91 (m, 1 H), 1.99 - 2.16 (m, 2 H) 2.74 (s, 1 H), 3.93 - 4.02 (m, 1 H), 4.02 - 4.19 (m, 4 H).

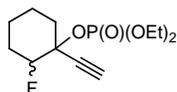
¹³C NMR (126 MHz, CDCl₃) δ ppm 16.1 (d, *J*_{CP}=6.47 Hz), 21.6, 30.9, 34.4 36.1, 39.9 (d, *J*_{CP}=5.55 Hz), 63.9 (d, *J*_{CP}=6.47 Hz), 64.2 (d, *J*_{CP}=5.55 Hz), 76.6 (d, *J*_{CP}=8.32 Hz), 81.1.

HRMS (EI) calcd. for $C_{12}H_{20}IO_4P$: 387.0211, Found: 387.0215.

Synthesis of diethyl (1-ethynyl-2-fluorocyclohexyl) phosphate

2-fluorocyclohexanone (5 mmol, 580 mg), ethynylmagnesium bromide (5 mmol, 0.54 M, 9.3 mL) and neat diethylchlorophosphate (6 mmol, 1.03g) were used.

(69%) (1:1.2 mixture) 1H NMR (500 MHz, $CDCl_3$) δ ppm 1.17 - 1.26 (m, 12 H), 1.30 - 1.66 (m, 8 H), 1.67 - 1.99 (m, 8 H), 2.71 (s, 2 H), 2.75 (s, 2 H), 3.95 - 4.10 (m, 8 H) 4.40 - 4.58 (m, 1 H) 4.80 (d, $J=49.15$ Hz, 1 H).



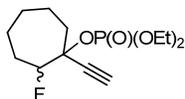
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 15.9 (t, $J=6.01$ Hz), 19.4, 21.4 - 22.2 (m), 27.9 (d, $J=20.35$ Hz), 28.7 (d, $J=17.57$ Hz), 33.9, 36.4, 63.7 (d, $J=5.55$ Hz), 63.9 (d, $J=6.47$ Hz), 77.8 (d, $J=24.97$ Hz), 78.7 (d, $J=8.32$ Hz), 78.9 (d, $J=9.25$ Hz), 79.1, 80.4 (d, $J=9.25$ Hz), 90.6, 92.2 (d, $J=35.14$ Hz), 93.8.

HRMS (EI) calcd. for $C_{12}H_{20}FO_4P$: 279.1150, Found: 279.1154.

Synthesis of diethyl (1-ethynyl-2-fluorocycloheptyl) phosphate

2-fluorocycloheptanone (5 mmol, 651 mg), ethynylmagnesium bromide (5 mmol, 0.54 M, 9.3 mL) and neat diethylchlorophosphate (6 mmol, 1.03g) were used.

(69%) 1H NMR (500 MHz, $CDCl_3$) δ ppm 1.31 (t, $J=7.15$ Hz, 12 H), 1.41 - 1.81 (m, 12 H), 1.83 - 2.35 (m, 10 H), 2.73, 2.78, 4.04 - 4.19 (m, 8 H), 4.61 (ddd, $J=47.04, 9.81, 3.30$ Hz, 1 H), 5.00 (dd, $J=47.13, 6.42$ Hz, 1 H).



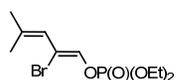
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 16.0 (t, $J=6.47$ Hz), 20.3, 21.0 (d, $J=12.02$ Hz), 21.3, 25.6 (d, $J=36.07$ Hz) 28.2 (d, $J=21.27$ Hz), 28.8 (d, $J=20.35$ Hz), 34.7, 36.1, 63.2 - 65.1 (m), 77.5 (d, $J=101.73$ Hz), 79.3, 80.2, 80.6 (d, $J=8.32$ Hz), 80.8 (d, $J=9.25$ Hz), 82.1 (dd, $J=19.42, 7.40$ Hz), 95.1 (dd, $J=185.42, 5.09$ Hz), 96.9 (dd, $J=185.42, 6.01$ Hz).

HRMS (EI) calcd. for $C_{13}H_{22}FO_4P$: 293.1318, Found: 293.1314.

Copper-Catalyzed Synthesis of Z- Dienes

To an oven dried 10 mL Schlenk flask loaded with commercially available copper (I) trifluoromethanesulfonate benzene complex (10 mol%, 0.05 mmol, 25 mg) equipped with magnetic stir bar was added 10 mL 1,2-dichloroethane (0.05M) via cannula and desired 4-halo-propargylicdiethylphosphate (0.5 mmol) under argon atmosphere. The reaction was then heated to 80°C in an oil bath until deemed complete by GC/MS analysis. Once completed, the reaction mixture was allowed to cool to rt, then filtered through a small plug of Celite. The crude mixture was then concentrated by column chromatography (Hex/EtOAc=2/1)

(Z)-2-bromo-4-methylpenta-1,3-dien-1-yl diethyl phosphate (2a)

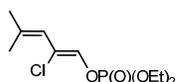


(86%) (Z only) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.38 (dt, $J=7.15$, 1.10 Hz, 6 H), 1.80 (d, $J=1.28$ Hz, 3 H), 1.81 (d, $J=1.47$ Hz, 3 H), 4.17 - 4.26 (m, 4 H), 5.63 - 5.68 (m, 1 H), 6.75 (dd, $J=4.95$, 1.65 Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.1 (d, $J_{\text{CP}}=5.55$ Hz), 19.4, 25.6, 64.8 (d, $J_{\text{CP}}=5.55$ Hz), 107.4, 120.1, 135.1 (d, $J_{\text{CP}}=3.70$ Hz), 140.8.

HRMS (EI) calcd. for $\text{C}_{10}\text{H}_{18}\text{BrO}_4\text{P}$: 312.01260, Found: 312.01098.

(Z)-2-chloro-4-methylpenta-1,3-dien-1-yl diethyl phosphate (2b)

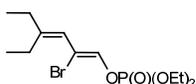


(95%) (Z only) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.37 (dt, $J=7.06$, 0.92 Hz, 6 H), 1.80 (d, $J=1.10$ Hz, 3 H), 1.82 (d, $J=1.47$ Hz, 3 H), 4.16 - 4.24 (m, 4 H), 5.55 - 5.59 (m, 1 H), 6.66 (dd, $J=5.14$, 1.47 Hz, 1 H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.1 (d, $J_{\text{CP}}=5.55$ Hz), 19.6, 26.0, 64.8 (d, $J_{\text{CP}}=5.55$ Hz), 117.6, 118.6, 133.6 (d, $J_{\text{CP}}=3.7$ Hz), 140.5.

HRMS (EI) calcd. for $\text{C}_{10}\text{H}_{18}\text{ClO}_4\text{P}$: 268.06312, Found: 268.06389.

(Z)-2-bromo-4-ethylhexa-1,3-dien-1-yl diethyl phosphate (2c)



(69%) (Z:E = 19:1, mixture) ^1H NMR (500 MHz, CDCl_3) δ ppm 0.99 - 1.06 (m, 6 H), 1.38 (dt, $J=7.06$, 0.92 Hz, 6 H), 2.12 (dq, $J=7.40$, 1.28 Hz, 2 H), 2.22 (q, $J=7.70$ Hz, 2 H), 4.17 - 4.26 (m, 4 H), 5.62 (s, 1 H), 6.76 (dd, $J=4.95$, 1.65 Hz, 1 H).

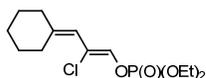
^{13}C NMR (126 MHz, CDCl_3) δ ppm 12.3, 13.2, 16.0, 24.3, 28.6, 64.8 (d,

$J_{CP}=5.55$ Hz), 107.3 (d, $J_{CP}=11.10$ Hz), 117.9, 134.2 (d, $J_{CP}=10.45$ Hz) 151.99.

HRMS (EI) calcd. for $C_{12}H_{22}BrO_4P$: 340.04390, Found: 340.04262.

(Z)-2-chloro-3-cyclohexylideneprop-1-en-1-yl diethyl phosphate (2d)

(75%) (*Z:E*= 10:1, mixture) 1H NMR (500 MHz, $CDCl_3$) δ ppm 1.37 (dt, $J=6.97, 1.10$ Hz, 6 H), 1.52 - 1.58 (m, 2 H), 1.58 - 1.64 (m, 2 H), 1.84 - 1.90 (m, 2 H), 1.98 - 2.05 (m, 2 H), 4.14 - 4.26 (m, 4 H), 5.56 (m, 1 H) 6.68 (td, $J=4.77, 1.10$ Hz, 1 H).

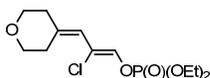


^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 16.0 (d, $J_{CP}=5.55$ Hz), 22.2, 22.7, 25.3, 27.3, 42.6, 64.8 (d, $J_{CP}=5.55$ Hz), 120.3 (d, $J_{CP}=11.10$ Hz), 125.5, 131.8 (d, $J_{CP}=5.55$ Hz), 132.4.

HRMS (EI) calcd. for $C_{13}H_{22}ClO_4P$: 309.1023, Found: 309.1024.

(Z)-2-chloro-3-(dihydro-2H-pyran-4(3H)-ylidene)prop-1-en-1-yl diethyl phosphate (2e)

(77%) (*Z* only) 1H NMR (500 MHz, $CDCl_3$) δ ppm 1.31 (dt, $J=7.06, 0.92$ Hz, 6 H), 2.23 (t, $J=5.50$ Hz, 2 H), 2.45 (t, $J=5.50$ Hz, 2 H), 3.61 (t, $J=5.50$ Hz, 2 H), 3.66 (t, $J=5.50$ Hz, 2 H), 4.11 - 4.18 (m, 4 H), 5.55 - 5.61 (m, 1 H), 6.63 (dd, $J=5.14, 1.47$ Hz, 1 H).

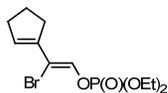


^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 16.0 (d, $J_{CP}=6.47$ Hz), 31.0, 36.8, 64.8 (d, $J_{CP}=6.47$ Hz), 68.3, 68.9, 116.2 (d, $J_{CP}=11.10$ Hz), 116.9, 133.8 (d, $J_{CP}=3.70$ Hz), 142.4.

HRMS (EI) calcd. for $C_{12}H_{20}ClO_5P$: 310.07368, Found: 310.07386.

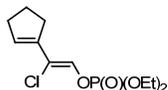
(Z)-2-bromo-2-(cyclopent-1-en-1-yl)vinyl diethyl phosphate (2f)

(91%) (*Z* only) 1H NMR (500 MHz, $CDCl_3$) δ ppm 1.32 (t, $J=7.15$ Hz, 6 H), 1.90 - 2.04 (m, 2 H), 2.35 - 2.46 (m, 4 H), 4.10 - 4.20 (m, 4 H), 6.06 (s, 1 H), 6.93 (d, $J=5.50$ Hz, 1 H).



^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 16.0 (d, $J_{CP}=6.47$ Hz), 24.1, 32.3, 32.5, 64.9 (d, $J_{CP}=6.47$ Hz), 109.1 (d, $J_{CP}=12.02$ Hz), 133.9, 134.6, 137.3.

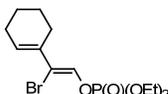
HRMS (EI) calcd for $C_{11}H_{18}BrO_4P$: 325.0207, Found: 325.0209.

(Z)-2-chloro-2-(cyclopent-1-en-1-yl)vinyl diethyl phosphate (2g)

(95%) (*Z* only) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.37 (dt, $J=7.06$, 0.92 Hz, 6 H), 1.96 - 2.05 (m, 2 H), 2.44 (t, $J=7.52$ Hz, 4 H), 4.16 - 4.25 (m, 4 H), 6.13 (s, 1 H), 6.86 (d, $J=5.14$ Hz, 1 H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.0 (d, $J=7.40$ Hz), 23.9, 32.2, 32.5, 64.9 (d, $J_{\text{CP}}=5.55$ Hz), 118.8 (d, $J_{\text{CP}}=11.10$ Hz), 132.0, 132.8 (d, $J_{\text{CP}}=3.70$ Hz), 136.7.

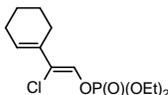
HRMS (EI) calcd. for $\text{C}_{11}\text{H}_{18}\text{ClO}_4\text{P}$: 280.06312, Found: 280.06440.

(Z)-2-bromo-2-(cyclohex-1-en-1-yl)vinyl diethyl phosphate (2h)

(86%) (*Z* only) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.38 (dt, $J=7.06$, 0.92 Hz, 6 H), 1.55 - 1.63 (m, 2 H), 1.63 - 1.71 (m, 2 H), 2.13 - 2.22 (m, 4 H), 4.16 - 4.26 (m, 4 H), 6.21 (t, $J=3.85$ Hz, 1 H), 7.02 (d, $J=5.14$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 6.1 (d, $J_{\text{CP}}=6.47$ Hz), 22.0, 22.5, 25.8, 26.6, 29.7, 64.8 (d, $J_{\text{CP}}=6.47$ Hz), 115.3, 130.5, 130.9, 132.7 (d, $J_{\text{CP}}=3.70$ Hz).

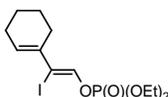
HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{20}\text{BrO}_4\text{P}$: 338.02825, Found: 338.02681.

(Z)-2-chloro-2-(cyclohex-1-en-1-yl)vinyl diethyl phosphate (2i)

(75%) (*Z* only) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.35 (dt, $J=7.06$, 0.92 Hz, 6 H), 1.54 - 1.62 (m, 2 H), 1.62 - 1.71 (m, 2 H), 2.07 - 2.21 (m, 4 H), 4.12 - 4.23 (m, 4 H), 6.24 (s, 1 H), 6.90 (d, $J=5.14$ Hz, 1 H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.0 (d, $J_{\text{CP}}=6.47$ Hz), 21.9, 22.3, 25.6 (d, $J_{\text{CP}}=6.47$ Hz), 64.8 (d, $J_{\text{CP}}=6.47$ Hz), 123.3 (d, $J_{\text{CP}}=11.10$ Hz), 128.4, 129.8, 130.9 (d, $J_{\text{CP}}=2.78$ Hz).

HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{20}\text{ClO}_4\text{P}$: 338.02825, Found: 338.02861.

(Z)-2-(cyclohex-1-en-1-yl)-2-iodovinyl diethyl phosphate (2j)

(64%) (*Z* only) ^1H NMR (500 MHz, CDCl_3) 1.33 (t, $J=7.15$ Hz, 6 H), 1.49 - 1.55 (m, 2 H), 1.57 - 1.63 (m, 2 H), 2.05 - 2.11 (m, 2 H), 2.15 - 2.22 (m, 2 H), 4.11 - 4.20 (m, 4 H), 6.03 (t, $J=4.03$ Hz, 1 H), 6.77 (d, $J=5.14$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.1 (d, $J_{\text{CP}}=5.55$ Hz), 22.1, 22.7, 26.1, 27.7, 64.8 (d, $J_{\text{CP}}=5.55$ Hz), 94.6 (d, $J_{\text{CP}}=12.95$ Hz), 132.4, 132.9, 136.8.

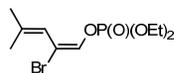
HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{20}\text{IO}_4\text{P}$: 387.0211, Found: 387.0216.

Gold-Catalyzed Synthesis of *E*- Dienes

To an oven dried 10 mL Schlenk flask loaded with commercially available [tris(*para*-trifluoromethylphenyl)phosphine]gold(I) chloride (5 mol%, 0.025 mmol, 175 mg) equipped with magnetic stir bar was added 10 mL toluene (0.05M) via cannula and desired 4-halo-propargylicdiethylphosphate (0.5 mmol) under argon atmosphere. The reaction was then heated to 100°C in an oil bath until judged complete by GC/MS analysis. Once completed, the reaction mixture was allowed to cool to rt and then filtered through a small plug of Celite. The crude mixture was then concentrated by column chromatography (Hex/EtOAc=2/1).

(*E*)-2-bromo-4-methylpenta-1,3-dien-1-yl diethyl phosphate (**3a**)

(96%) (*E*:*Z* = 9:1, mixture) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.33 (dt, $J=7.06, 0.92$ Hz, 6 H), 1.72 (d, $J=1.10$ Hz, 3 H), 1.77 - 1.81 (d, $J=1.10$ Hz, 3 H), 4.09 - 4.19 (m, 4 H, **3a**+**2a**), 5.55 - 5.68 (m, 1 H, **3a**+**2a**), 6.73 (dd, $J=5.14, 1.10$ Hz, 1 H).

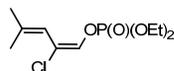


^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.0 (d, $J_{\text{CP}}=7.40$ Hz, **3a**), 19.4 (**2a**), 20.2 (**3a**), 25.6 (**3a**), 64.6 (d, $J_{\text{CP}}=5.55$ Hz, **3a**) 64.8 (d, $J_{\text{CP}}=5.55$ Hz, **2a**), 107.4 (d, $J_{\text{CP}}=12.95$ Hz, **2a**), 109.5 (d, $J_{\text{CP}}=12.95$ Hz, **3a**), 118.1 (**3a**), 120.1 (**2a**), 132.5 (d, $J_{\text{CP}}=11.10$ Hz, **2a**), 133.7 (d, $J_{\text{CP}}=5.55$ Hz, **3a**), 141.9 (**3a**), 140.7 (**2a**).

HRMS (EI) calcd. for $\text{C}_{10}\text{H}_{18}\text{BrO}_4\text{P}$: 312.01260, Found: 312.01178.

(*E*)-2-chloro-4-methylpenta-1,3-dien-1-yl diethyl phosphate (**3b**)

(95%) (*E*:*Z* = 6:1, mixture) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.31 - 1.39 (m, 6 H, **3b**+**2b**), 1.78 (d, $J=1.10$ Hz, 3 H, **3b**), 1.79 (d, $J=1.47$ Hz, **2b**), 1.81 - 1.83 (m, 3H, **3b**+**2b**), 4.10 - 4.24 (m, 4 H, **3b**+**2b**), 5.53 - 5.58 (m, **2b**), 5.62 - 5.68 (m, 1 H, **3b**), 6.66 (dd, $J=5.14, 1.10$ Hz, 1 H, **3b**+**2b**).

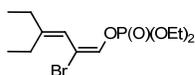


^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.0 (d, $J_{\text{CP}}=7.40$ Hz, **3b**+**2b**), 19.6 (**2b**), 20.3 (**3b**), 26.0 (**2b**), 26.1 (**3b**), 64.6 (d, $J_{\text{CP}}=5.55$ Hz, **3b**), 64.8 (d, $J_{\text{CP}}=5.55$ Hz, **2b**), 116.4 (**3b**+**2b**), 118.6 (**2b**), 120.5 (d, $J_{\text{CP}}=12.95$ Hz, **3b**), 132.5 (**3b**), 133.6 (d, $J_{\text{CP}}=3.70$ Hz, **2b**), 141.8 (**3c**).

HRMS (EI) calcd. for C₁₀H₁₈ClO₄P: 269.0731, Found: 269.0721.

(E)-2-bromo-4-ethylhexa-1,3-dien-1-yl diethyl phosphate (3c)

(97%) (*E:Z* = 8:1, mixture) ¹H NMR (500 MHz, CDCl₃) δ ppm 0.94 - 1.07 (m, 6 H), 1.27 - 1.40 (dt, *J*=7.06, 0.92 Hz, 6 H), 2.09 - 2.25 (m, 4 H), 4.10 - 4.19 (m, 4 H), 5.61 (s, 1H), 6.75 (dd, *J*=4.77, 1.47 Hz, 1H).

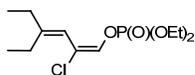


¹³C NMR (126 MHz, CDCl₃) δ ppm 12.1 (**3c**), 12.2 (**2c**), 12.3 (**3c**), 13.1 (**2c**), 16.0 (d, *J*_{CP}=6.47 Hz, **3c**), 24.2 (**2c**), 24.9 (**3c**), 28.5 (**3c**), 64.6 (d, *J*_{CP}=6.5 Hz, **3c**), 64.8 (d, *J*_{CP}=5.55 Hz, **2c**), 107.3 (d, *J*_{CP}=12.02 Hz, **2c**), 109.4 (d, *J*_{CP}=12.95 Hz, **3c**), 115.8 (**3c**), 117.9 (**2c**), 133.7 (d, *J*_{CP}=4.63 Hz, **3c**), 134.1 (d, *J*_{CP}=3.70 Hz, **2c**), 151.9 (**2c**), 152.6 (**3c**).

HRMS (EI) calcd. for C₁₂H₂₂BrO₄P: 340.04390, Found: 340.04281.

(E)-2-chloro-4-ethylhexa-1,3-dien-1-yl diethyl phosphate (3m)

(98%) (*E:Z* = 13:1, mixture) ¹H NMR (500 MHz, CDCl₃) δ ppm 1.00 - 1.07 (m, 6 H), 1.35 (dt, *J*=7.06, 1.10 Hz, 6H), 1.37 - 1.42 (m, **Z**), 2.10 - 2.18 (m, 2 H, **3m+Z**), 2.19 - 2.29 (m, 2 H, **3m+Z**), 4.10 - 4.25 (m, 4 H, **3m+Z**), 5.54 (s, **Z**), 5.65 (s, 1 H, **3m**), 6.63 - 6.72 (m, 1 H, **3m+Z**).

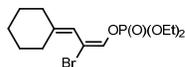


¹³C NMR (126 MHz, CDCl₃) δ ppm 12.3 (**Z**), 12.5 (d, *J*_{CP}=14.80 Hz), 16.0, 16.1, 24.4(**Z**), 25.0, 28.92 (**Z**), 29.1, 64.6 (d, *J*_{CP}=5.55 Hz), 114.1, 116.4, 120.6 (**Z**), 132.6 (d, *J*_{CP}=5.55 Hz), 152.6.

HRMS (EI) calcd. for C₁₂H₂₂ClO₄P:296.09442, Found: 292.09556.

(E)-2-bromo-3-cyclohexylideneprop-1-en-1-yl diethyl phosphate (3n)

(91%) (*E:Z* = 9:1, mixture) ¹H NMR (500 MHz, CDCl₃) δ ppm 1.34 (dt, *J*=7.11, 0.83 Hz, 6 H), 1.51 - 1.61 (m, 6 H), 2.12 - 2.21 (m, 4 H), 2.28 (t, *J*=5.50 Hz, **Z**), 4.05 - 4.24 (m, 4 H), 5.55 (s, 0.78 H, **3n**), 5.60 (s, 0.08 H, **Z**), 6.74 (dd, *J*=5.04, 1.19 Hz, 1 H).

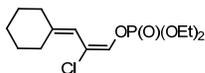


¹³C NMR (126 MHz, CDCl₃) δ ppm 16.0 (d, *J*_{CP}=6.47 Hz, **3n**), 26.3 (**3n**), 26.4 (**Z**), 27.2 (**3n**), 27.8 (**Z**), 28.3 (**3n**), 29.8 (**Z**), 30.8 (**3n**), 36.6 (**3n**), 36.7 (**Z**), 64.6 (d, *J*_{CP}=5.55 Hz, **3n**), 64.8 (d, *J*=6.47 Hz, **Z**), 109.2 (d, *J*_{CP}=12.95 Hz, **3n**), 114.7 (**3n**), 116.6 (**Z**), 133.7 (d, *J*_{CP}=4.62 Hz, **3n**), 134.5 (**Z**), 148.6 (**Z**), 149.4 (**3n**).

HRMS (EI) calcd. for C₁₃H₂₂BrO₄P: 352.04390, Found: 352.04201.

(E)-2-chloro-3-cyclohexylideneprop-1-en-1-yl diethyl phosphate (3d)

(90%) (*E:Z* = 19:1, mixture) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.31 (dt, $J=7.06, 0.92$ Hz, 6 H), 1.48 - 1.61 (m, 6 H), 1.99 (**2d**), 2.09 - 2.16 (m, 2 H), 2.20 (t, $J=5.50$ Hz, 2 H), 2.28 (t, $J=5.50$ Hz, **2d**), 4.04 - 4.20 (m, 4 H), 5.47 (s, **2d**), 5.51 (s, 1 H) 6.50 - 6.70 (m, 1 H, **3d+2d**).

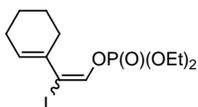


^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.0 (d, $J_{\text{CP}}=6.47$ Hz, **3d**), 26.3 (**3d**), 26.4 (**2d**), 27.4 (**3d**), 27.8 (**2d**), 28.3 (**2d**), 28.4 (**3d**), 29.9 (**2d**), 30.9 (**3d**), 37.0 (**3d**), 64.6 (d, $J_{\text{CP}}=5.55$ Hz, **3d**), 64.8 (d, $J_{\text{CP}}=5.55$ Hz, **2d**), 113.2 (**3d**), 115.2 (**2d**), 120.2 (d, $J_{\text{CP}}=12.95$ Hz, **3d**), 132.6 (d, $J_{\text{CP}}=4.62$ Hz, **3d**), 133.1 (d, $J_{\text{CP}}=3.70$ Hz, **2d**), 148.4 (**2d**) 149.4 (**3d**).

HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{22}\text{ClO}_4\text{P}$: 309.1023, Found: 309.1015.

(E)-2-(cyclohex-1-en-1-yl)-2-iodovinyl diethyl phosphate (3j), (Z)-2-(cyclohex-1-en-1-yl)-2-iodovinyl diethyl phosphate (2j)

(89%) (*E:Z* = 1.5:1, mixture) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.29 - 1.36 (m, 10 H, **3j+2j**), 1.50 - 1.57 (m, 3 H, **3j+2j**), 1.58 - 1.65 (m, 3 H, **3j+2j**), 2.00 - 2.11 (m, 3 H, **3j+2j**), 2.17 - 2.23 (m, 3 H, **3j+2j**), 4.02 - 4.26 (m, 6 H, **3j+2j**), 5.95 - 6.00 (m, 0.9 H, **3j**), 6.02 - 6.07 (m, 0.58 H, **2j**), 6.75 (d, $J=4.77$ Hz, 0.76 H, **3j**), 6.78 (d, $J=4.95$ Hz, 1 H, **2j**).

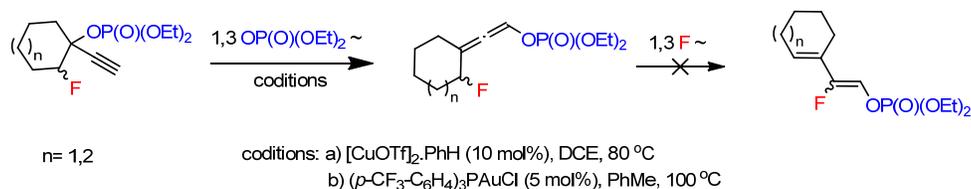


^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.0 (d, $J_{\text{CP}}=6.47$ Hz, **3j+2j**), 21.7 (**3j**), 22.1 (**2j**), 22.6 (**2j**), 22.7 (**3j**), 25.7 (**3j**), 26.0 (**2j**), 27.7 (**2j**), 28.3 (**3j**), 64.6 (d, $J_{\text{CP}}=5.55$ Hz, **3j**), 64.9 (d, $J_{\text{CP}}=6.47$ Hz, **2j**), 90.9 (d, $J_{\text{CP}}=11.1$ Hz, **3j**), 94.7 (d, $J_{\text{CP}}=12.02$ Hz, **2j**), 131.6 (**3j**), 132.4 (**2j**), 132.9 (**2j**), 133.8 (**3j**), 136.1 (d, $J_{\text{CP}}=4.63$ Hz, **3j**), 136.8 (d, $J_{\text{CP}}=2.78$ Hz, **2j**).

HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{20}\text{IO}_4\text{P}$: 387.0211, Found: 387.0216.

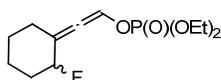
Copper- and Gold-Catalyzed Formation of α -fluorollenes

Attempt to isomerize α -fluoro propargylic phosphates only led to the formation of the corresponding α -fluoroallenes via 1,3-phosphatylxy group migration.



Diethyl (2-(2-fluorocyclohexylidene)vinyl) phosphate

(89%) (1.1:1, mixture) ^1H NMR (500 MHz, CDCl_3) 1.25 - 1.31 (m, 21 H), 1.40 - 1.51 (m, 2 H), 1.52 - 1.63 (m, 4 H), 1.69 - 1.93 (m, 6 H), 2.06 - 2.19 (m, 2 H), 2.33 - 2.44 (m, 2 H), 4.03 - 4.14 (m, 17 H), 6.60 - 6.71 (m, 2 H).

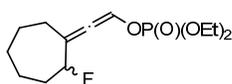


^{13}C NMR (126 MHz, CDCl_3) δ ppm 15.2 - 17.1 (m), 21.4 (dd, $J=24.97$, 5.55 Hz), 26.0 (d, $J=5.55$ Hz), 29.7 (d, $J=16.65$ Hz), 33.0 (dd, $J=20.35$, 8.32 Hz), 64.2 (d, $J=5.55$ Hz), 87.3 - 90.7 (m), 112.4 (d, $J=6.47$ Hz), 117.3, 189.2.

LRMS for $\text{C}_{12}\text{H}_{20}\text{FO}_4\text{P}$: 279.1.

Diethyl (2-(2-fluorocycloheptylidene)vinyl) phosphate

(89%) (1:1, mixture) ^1H NMR (500 MHz, CDCl_3) δ ppm 1.31 (t, $J=7.06$ Hz, 12 H), 1.49 - 1.79 (m, 12 H), 1.86 - 2.03 (m, 4 H), 2.20 - 2.29 (m, 2 H), 2.31 - 2.44 (m, 2 H), 4.07 - 4.20 (m, 8 H), 5.06 (dt, $J=22.28$, 5.73 Hz, 1 H), 5.15 (dt, $J=22.47$, 5.55 Hz, 1 H), 6.64 - 6.78 (m, 2 H).

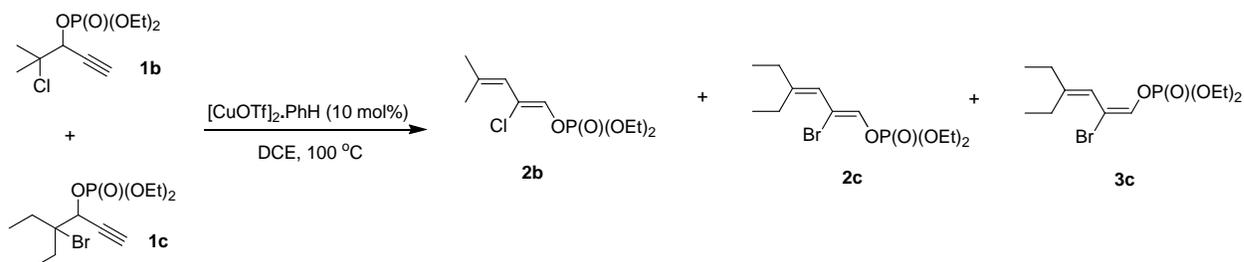


^{13}C NMR (126 MHz, CDCl_3) δ ppm 16.0 (d, $J=6.47$ Hz), 22.8 (d, $J=6.47$ Hz), 23.0 (d, $J=6.47$ Hz), 28.1 (d, $J=24.04$ Hz), 28.6 (d, $J=25.89$ Hz), 29.6 (d, $J=23.12$ Hz), 34.1 (d, $J=14.80$ Hz), 34.2 (d, $J=14.80$ Hz), 64.2 (d, $J=4.62$ Hz), 91.5 (d, $J=8.32$ Hz), 92.9 (d, $J=9.25$ Hz), 112.3 (t, $J=7.40$ Hz), 119.8 (d, $J=7.40$ Hz), 119.9 (d, $J=7.40$ Hz), 192.4 - 194.1 (m).

LRMS for $\text{C}_{13}\text{H}_{22}\text{FO}_4\text{P}$: 293.1

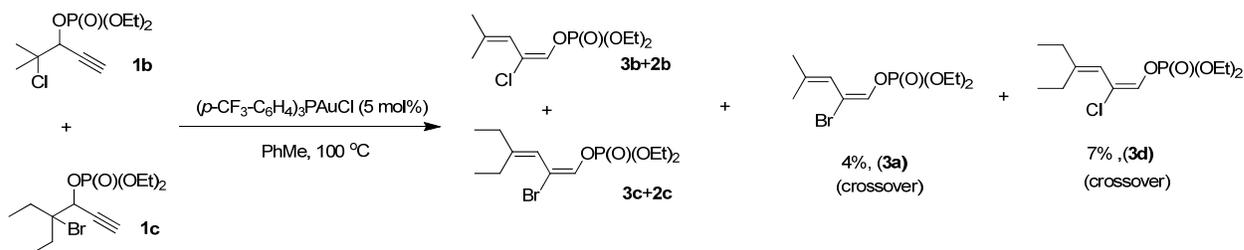
Crossover experiments

a) Copper-catalyzed reaction



To a 3 mL Wheaton V-vial equipped with spin bar was added copper (I) trifluoromethanesulfonate benzene complex (10 mol%, 0.01 mmol, 5 mg) and pentadecane (10 μL , as an internal standard) under nitrogen atmosphere. A solution of **1b** (0.05 mmol, 13 mg) and **1c** (0.05 mmol, 17 mg) in dry DCE (2 mL) was transferred through cannula. The reaction was heated to 100 °C and frequently checked with GC/MS until judged completed. Expected products **2b** and **2c** were observed with no crossover products detected by GC/MS analysis.

b) Gold-catalyzed reaction

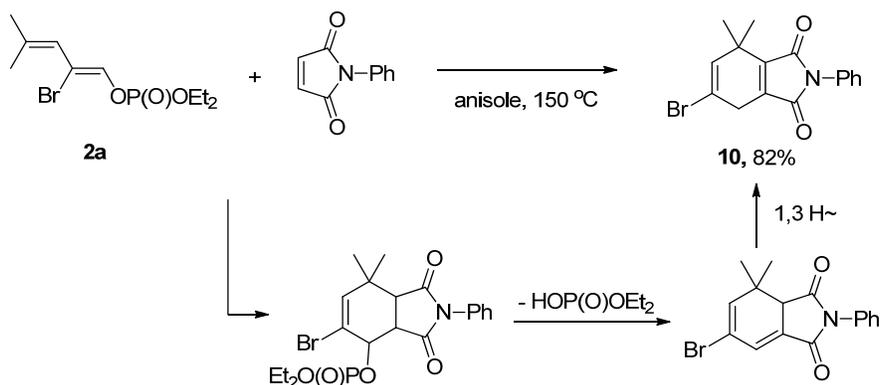


To a 3 mL Wheaton V-vial equipped with spin bar was added [tris(*para*-trifluoromethylphenyl)phosphine]gold(I) chloride (5 mol%, 0.005 mmol, 3.5 mg) and pentadecane (10 μL , as an internal standard) under nitrogen atmosphere. A solution of **1b** (0.05 mmol, 13 mg) and **1c** (0.05 mmol, 17 mg) in dry toluene (2 mL) was transferred through cannula. The reaction was heated to 100 °C and was checked with GC/MS until judged completed. In addition to the expected products (**3b**, **2b**, **3c**, **2c**), the crossover products **3a** (4%) and **3d** (7%) were also detected by GC/MS analysis.

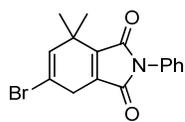
Functionalization of compound 2

1) Diels-Alder reaction⁹

A) Synthesis of 6-bromo-4,4-dimethyl-2-phenyl-4,7-dihydro-1H-isindole-1,3(2H)-dione (10)



An oven-dried Wheaton V-vial was charged with diene **2a** (0.2 mmol, 63 mg), N-phenylmaleimide (1.5 equiv, 0.3 mmol, 52 mg) and anisole (0.5 mL). The reaction mixture was stirred overnight at 150 °C and then cooled to rt. After removing solvent under vacuum, the residue was subjected to column chromatography on silica gel to give product **10** in 82% yield as a white solid (mp=120 °C).

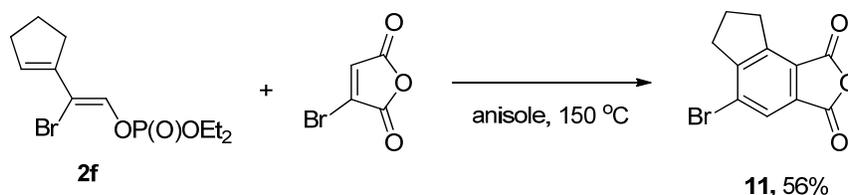


¹H NMR (500 MHz, CDCl₃) 1.46 (s, 6 H), 3.44 (d, *J*=0.92 Hz, 2 H), 5.91 - 6.19 (m, 1 H), 7.30 - 7.40 (m, 3 H), 7.41 - 7.68 (m, 2 H).

¹³C NMR (126 MHz, CDCl₃) δ ppm 27.6, 31.6, 37.5, 115.0, 126.0, 127.7, 129.1, 131.4, 136.3, 137.3, 144.2, 168.1.

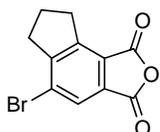
HRMS (EI) calcd. for C₁₆H₁₄BrNO₂: 332.0286, Found: 332.0282.

B) Synthesis of 5-bromo-7,8-dihydro-1H-indeno[4,5-c]furan-1,3(6H)-dione (11)



⁹ Wang, Y. L.; Lu, B. A.; Zhang, L. *Chem. Commun.* **2010**, 46, 9179.

An oven-dried Wheaton V-vial was charged with diene **2f** (0.2 mmol, 62 mg), bromomaleic anhydride (1.5 equiv, 0.3 mmol, 53 mg) and anisole (1 mL). The reaction mixture was stirred overnight at 150 °C and then cooled to rt. After removing solvent under vacuum, the residue was subjected to column chromatography on silica gel to give product **11** in 56% yield as a white solid (mp= 98 °C).

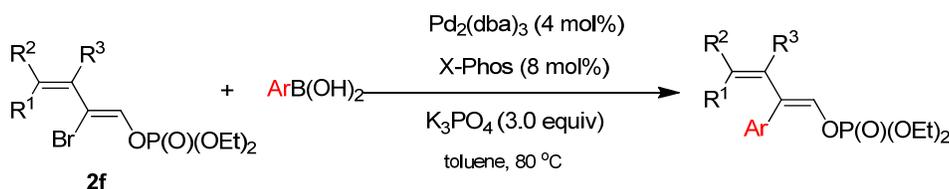


$^1\text{H NMR}$ (500 MHz, CDCl_3) δ ppm 2.12 - 2.49 (m, 2 H), 3.10 (t, $J=7.52$ Hz, 2 H), 3.39 (t, $J=7.43$ Hz, 2 H), 7.96 (s, 1 H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ ppm 24.3, 32.2, 35.2, 125.6, 127.5, 128.3, 131.4, 146.4, 155.6, 162.2, 162.63.

HRMS (EI) calcd. for $\text{C}_{11}\text{H}_7\text{BrO}_3$: 265.95786, Found: 265.95874.

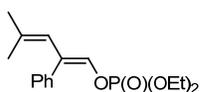
2) Suzuki cross-coupling on vinyl bromide¹⁰



An oven-dried 5 mL Wheaton V-vial was charged with XPhos (8 mol %), $\text{Pd}_2(\text{dba})_3$ (4 mol %), arylboronic acid (2 equiv), 0.8 mmol, 97.4 mg) and anhydrous K_3PO_4 (3equiv, 1.2 mmol, 260 mg) in the glove box. A solution of diene (1.0 equiv) in toluene (4 mL) was added through cannula. The reaction stirred at 80 °C overnight and then cooled to room temperature. After filtration through a small pad of Celite, solvents were removed under vacuum and the residue was subjected to column chromatography (Hex/EtOAc=2/1) to give the phenylated products.

Synthesis of (Z)-diethyl (4-methyl-2-phenylpenta-1,3-dien-1-yl) phosphate (**12**)

XPhos (8 mol %, 7.5 mg), $\text{Pd}_2(\text{dba})_3$ (4 mol %, 7.5 mg), phenylboronic acid (2 equiv, 0.4 mmol, 49 mg), anhydrous K_3PO_4 (3equiv, 0.6 mmol, 130 mg), diene **2a** (0.2 mmol, 63 mg) and toluene (2 mL) were used to afford the diene **12** in 78% yield (49 mg) as a yellowish oil.



$^1\text{H NMR}$ (500 MHz, CDCl_3) 1.29 (dt, $J=7.06$, 0.92 Hz, 6 H), 1.67 (s, 3 H), 1.83 (s, 3 H), 4.04 - 4.16 (m, 4 H), 5.72 (s, 1 H), 6.56 (d, $J=4.59$ Hz, 1 H), 7.21 - 7.28 (m, 1 H), 7.32 (t, $J=7.24$ Hz, 2 H), 7.42 (d, $J=7.34$ Hz, 2 H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ ppm 16.0 (d, $J_{\text{CP}}=6.47$ Hz), 19.4, 26.2,

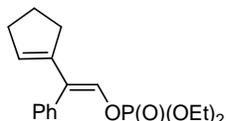
¹⁰ Billingsley, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3358.

64.4 (d, $J_{CP}=5.55$ Hz), 121.3, 124.3 (d, $J_{CP}=10.17$ Hz), 127.2, 128.0, 128.8, 134.0 (d, $J_{CP}=5.55$ Hz), 136.1, 137.40.

HRMS (EI) calcd. for $C_{16}H_{23}O_4P$: 311.1412, Found: 311.1400.

Synthesis of (Z)-2-(cyclopent-1-en-1-yl)-2-phenylvinyl diethyl phosphate (**13**)

XPhos (8 mol %, 15.2 mg), $Pd_2(dba)_3$ (4 mol %, 14.6 mg), phenylboronic acid (2 equiv, 0.8 mmol, 97.4 mg), anhydrous K_3PO_4 (3equiv, 1.2 mmol, 260 mg), diene **2f** (0.4 mmol, 130 mg) and toluene (4 mL) were used to afford the diene **13** in 91% yield (116 mg) as a brownish oil.



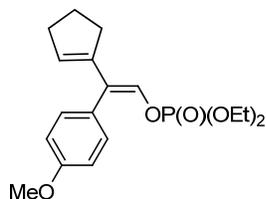
1H NMR (500 MHz, $CDCl_3$) δ ppm 1.52 (dt, $J=7.15, 0.73$ Hz, 6 H), 2.18 - 2.31 (m, 2 H), 2.53 - 2.68 (m, 2 H), 2.71 - 2.83 (m, 2 H), 4.10 - 4.43 (m, 4 H), 5.68 (br. s., 1 H), 6.98 (d, $J=4.58$ Hz, 1 H), 7.49 - 7.57 (m, 3 H), 7.59 - 7.67 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 15.9 (d, $J_{CP}=6.47$ Hz), 23.3, 32.1, 32.7, 64.3 (d, $J_{CP}=6.48$ Hz), 127.1, 127.8, 129.49, 131, 132.9 (d, $J_{CP}=4.63$ Hz), 134.1, 135.7, 140.5.

HRMS (EI) calcd. for $C_{17}H_{23}O_4P$: 322.13340, Found: 322.13264.

Synthesis of (Z)-2-(cyclopent-1-en-1-yl)-2-(4-methoxyphenyl)vinyl diethyl phosphate

XPhos (8 mol %, 11.4 mg), $Pd_2(dba)_3$ (4 mol %, 11 mg), 4-methoxyphenylboronic acid (2 equiv, 0.6 mmol, 91 mg), anhydrous K_3PO_4 (3 equiv, 0.9 mmol, 195 mg), **2f** (0.3 mmol, 98 mg) and toluene (3 mL) were used to give the desired product in 85% yield (92 mg) as a yellow oil.

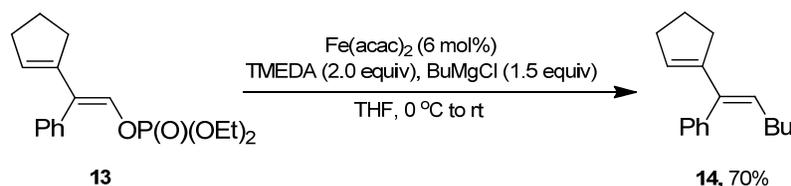


1H NMR (500 MHz, $CDCl_3$) δ ppm 1.25 (dt, $J=7.06, 0.92$ Hz, 6 H), 1.90 - 2.01 (m, 2 H), 2.31 - 2.38 (m, 2 H), 2.45 - 2.52 (m, 2 H), 3.81 (s, 3 H), 3.98 - 4.06 (m, 4 H), 5.44 (br. s., 1 H), 6.68 (d, $J=4.40$ Hz, 1 H), 6.84 - 6.92 (m, 2 H), 7.08 - 7.21 (m, 2 H).

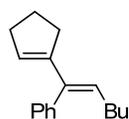
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 16.4, 23.8, 32.6, 33.1, 55.57, 64.7 (d, $J=5.55$ Hz), 113.6, 127.14 (d, $J=11.10$ Hz), 128.3, 131.0, 131.2, 133.2, 141.2, 159.1.

HRMS (EI) calcd. for $C_{18}H_{25}O_5P$: 352.14396, Found: 352.14321.

Kumada cross-coupling on vinyl phosphate¹¹



An oven-dried 3 mL Wheaton V-vial was charged with Fe(acac)_3 (6 mol %, 4.2 mg) and THF (2 mL). TMEDA (2 equiv, 0.4 mmol, 51 mg) and **13** (0.2 mmol, 64 mg) were added to the solution and the vial was then placed in an ice-water bath. A solution of n-butyilmagnesium chloride in tetrahydrofuran (1.5 equiv, 0.3 mmol) was added to the reaction mixture dropwise. The reaction stirred at 0 °C for half an hour and then warmed to room temperature. The mixture was then passed through a pad of Celite and the residue was subjected to column chromatography (pure Hexanes) to give product **14** in 70% yield (31 mg) as a yellowish oil.

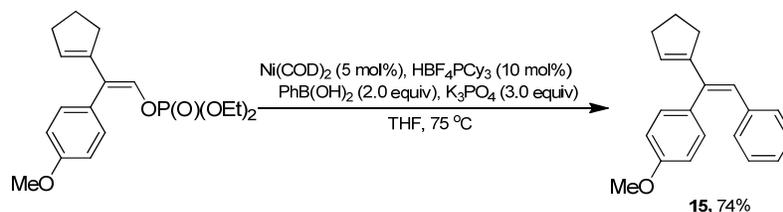


¹H NMR (500 MHz, CDCl_3) δ ppm 0.84 (t, $J=7.34$ Hz, 3 H), 1.24 - 1.32 (m, 4 H), 1.89 - 2.01 (m, 2 H), 2.31 - 2.43 (m, 2H), 2.55 - 2.64 (m, 2 H) 5.14 (br. s., 1 H), 5.63 (t, $J=7.70$ Hz, 1 H), 7.14 (d, $J=7.34$ Hz, 2 H), 7.26 - 7.31 (m, 1H), 7.36 (t, $J=7.34$ Hz, 2 H).

¹³C NMR (126 MHz, CDCl_3) δ ppm 14.3, 22.7, 23.6, 29.3, 32.6, 32.9, 33.5, 126.7, 127.2, 127.5, 128.2, 129.2, 129.4, 129.8, 145.9.

HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{22}$: 226.17147, Found: 226.17132

Suzuki cross-coupling on vinyl phosphate¹²

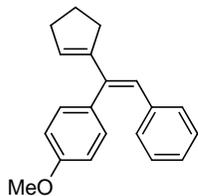


An oven-dried 3 mL Wheaton V-vial was charged with Ni(COD)_2 (5 mol %, 1.4 mg), $\text{HBF}_4\cdot\text{PCy}_3$ (10 mol %, 3.7 mg), phenylboronic acid (2 equiv, 0.2 mmol, 24.5 mg) and anhydrous K_3PO_4 (3equiv, 0.3 mmol, 75 mg) in the glove box. A solution of (Z)-2-(cyclopent-1-en-1-yl)-2-(4-methoxyphenyl)vinyl diethyl phosphate (0.1 mmol, 35 mg) in THF (1 mL) was added through cannula. The reaction stirred at 75 °C overnight and then cooled to room temperature. After

¹¹ Begtrup et al. *Tetrahedron Lett.* **2007**, 46, 4261

¹² Skrydstrup et al. *J. Org. Chem.* **2007**, 72, 6464

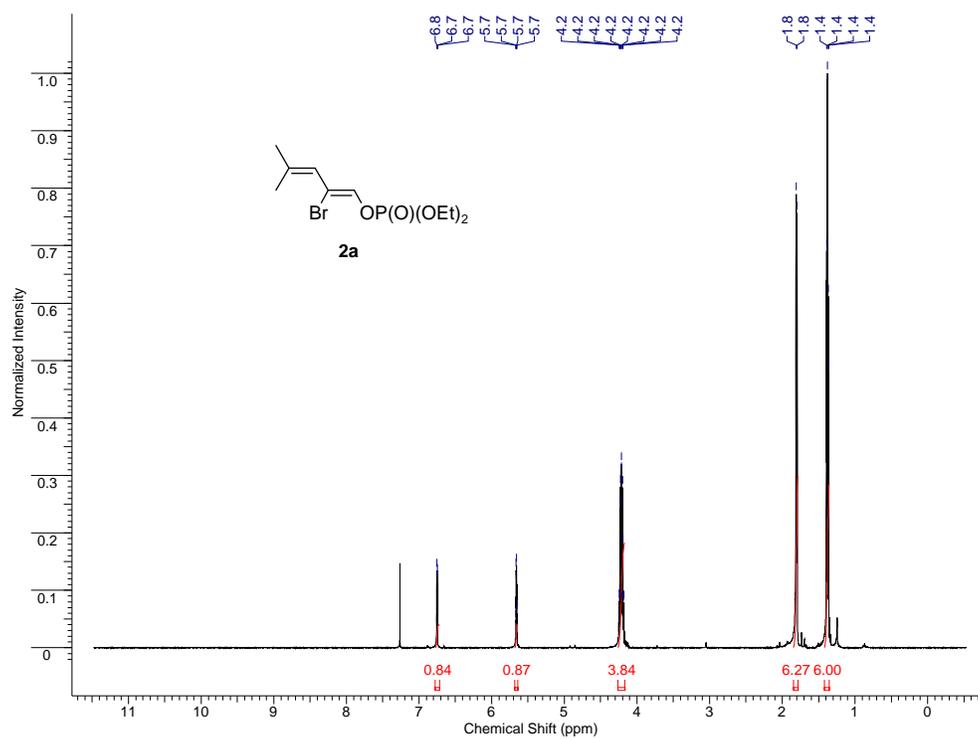
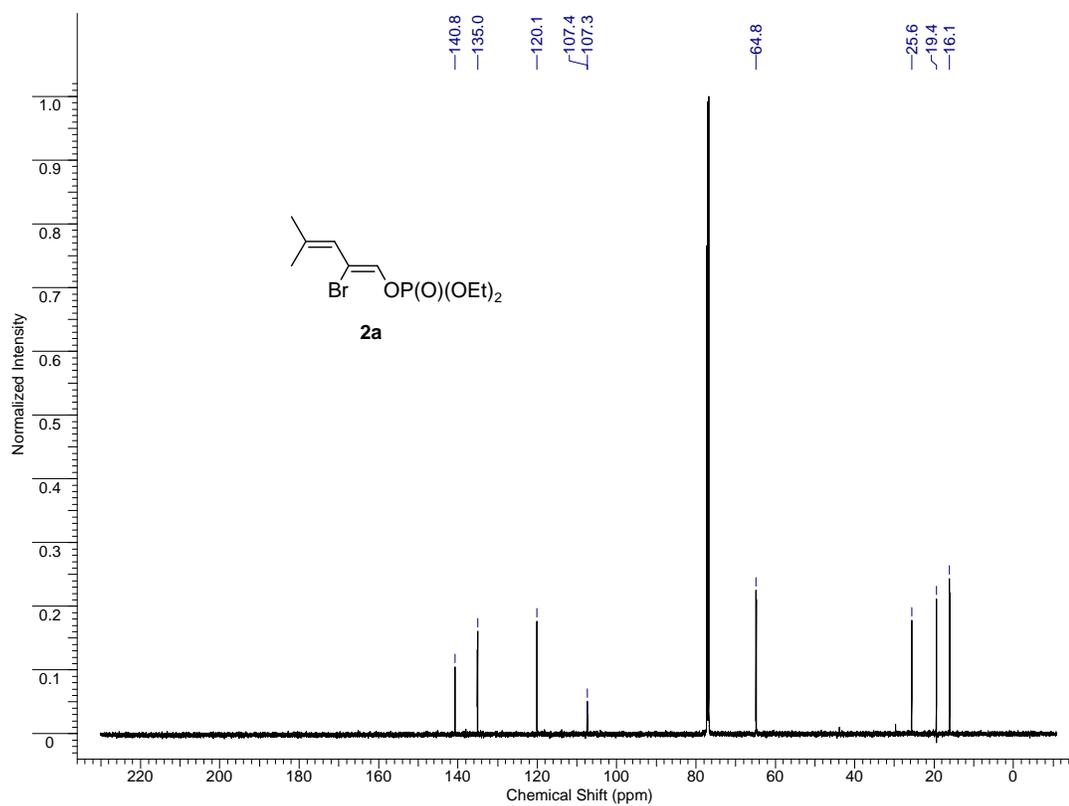
filtration through a small pad of Celite, solvents were removed under vacuum and the residue was subjected to column chromatography (pure Hexane) to give the product **15** in 74% yield (20 mg) as a yellowish oil.

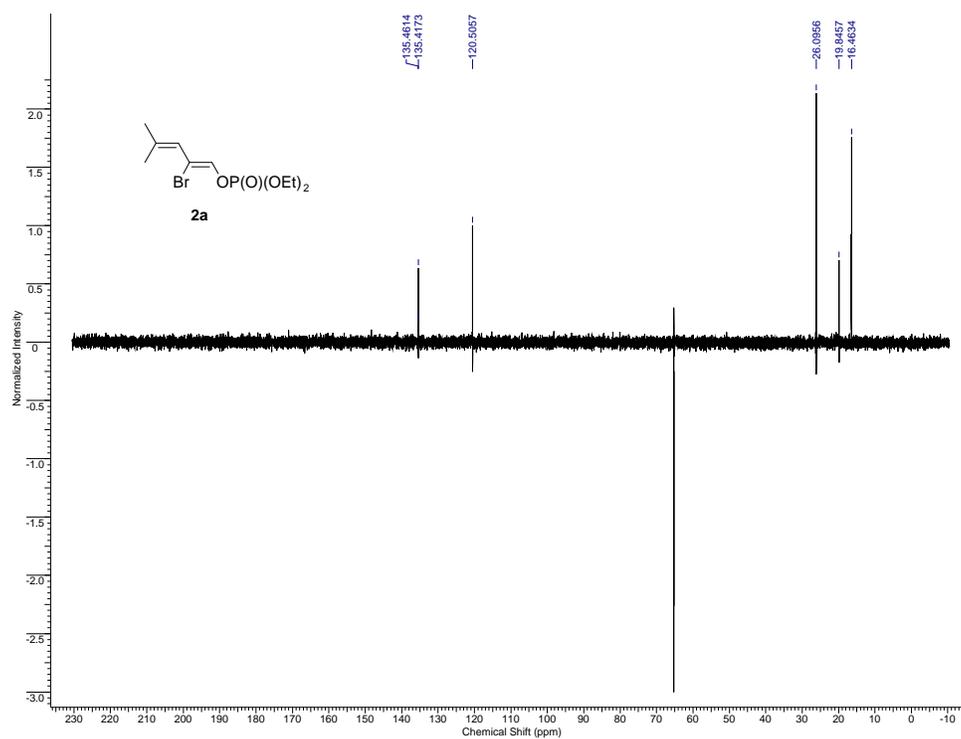
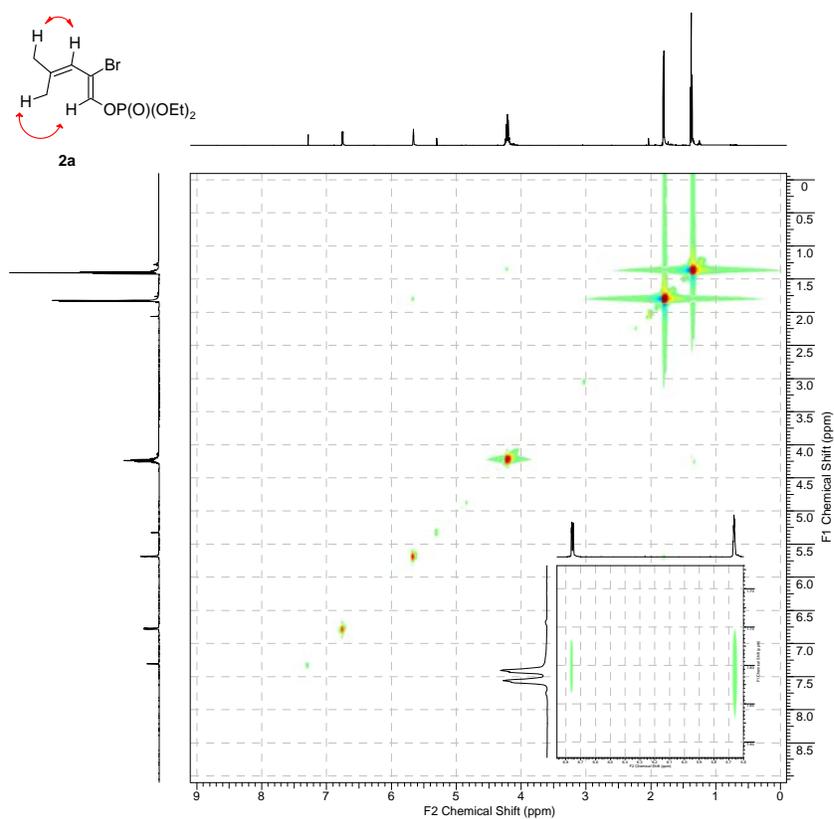


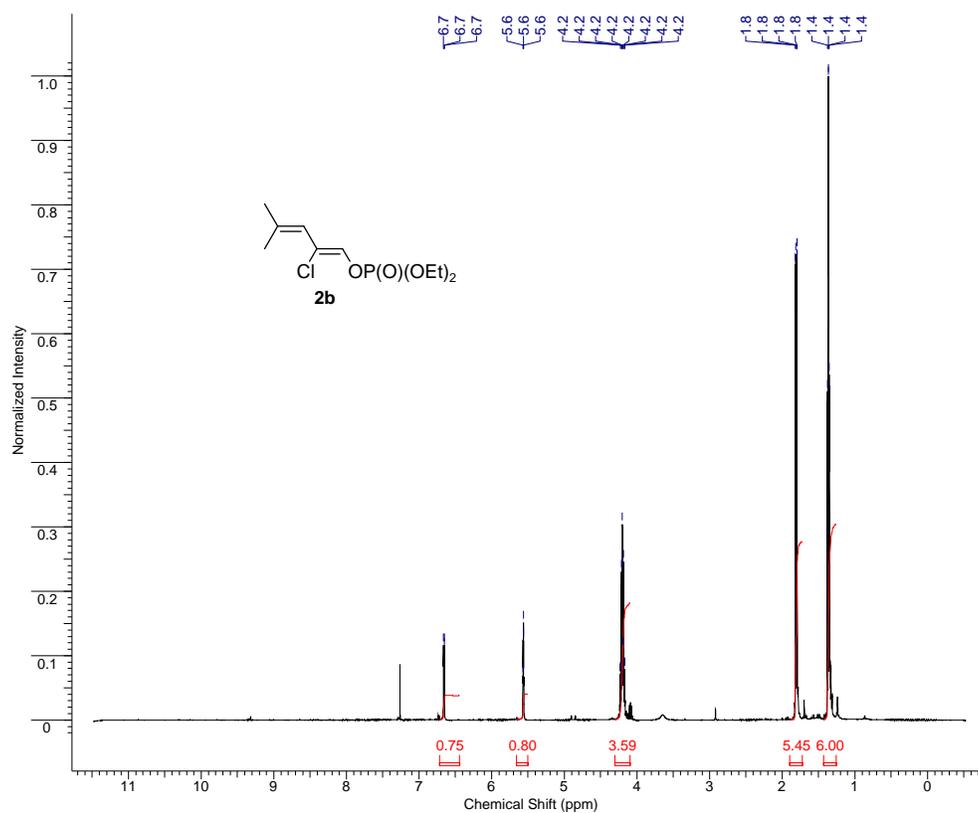
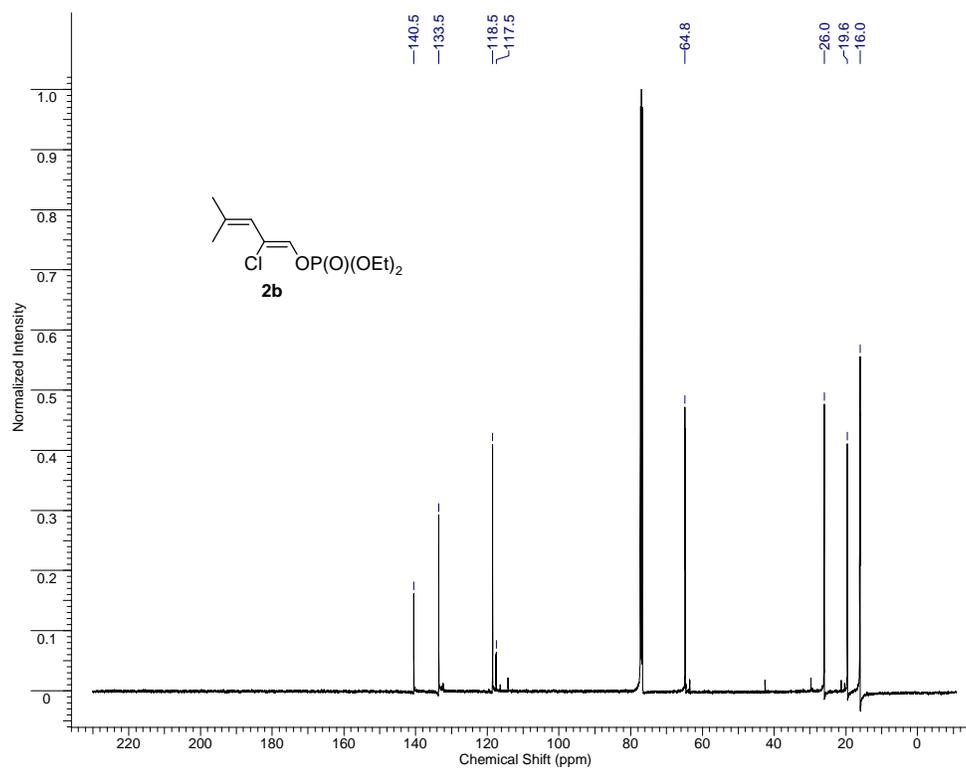
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ ppm 1.96 - 2.10 (m, 2 H), 2.39 - 2.50 (m, 2 H), 2.68 - 2.81 (m, 2 H), 3.87 (s, 3 H), 5.42 (br. s., 1 H), 6.52 (s, 1 H), 6.87 - 6.97 (m, 3 H) 7.05 - 7.15 (m, 4 H) 7.25 - 7.32 (m, 1 H) 7.36 - 7.44 (m, 1H).

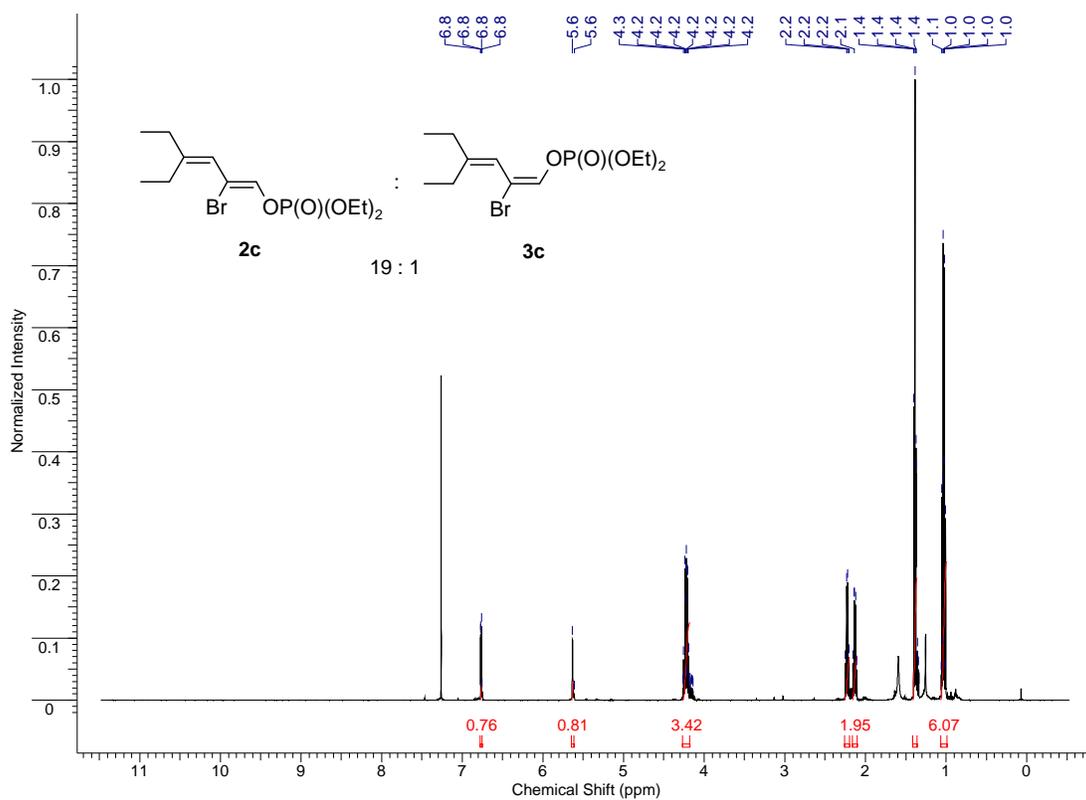
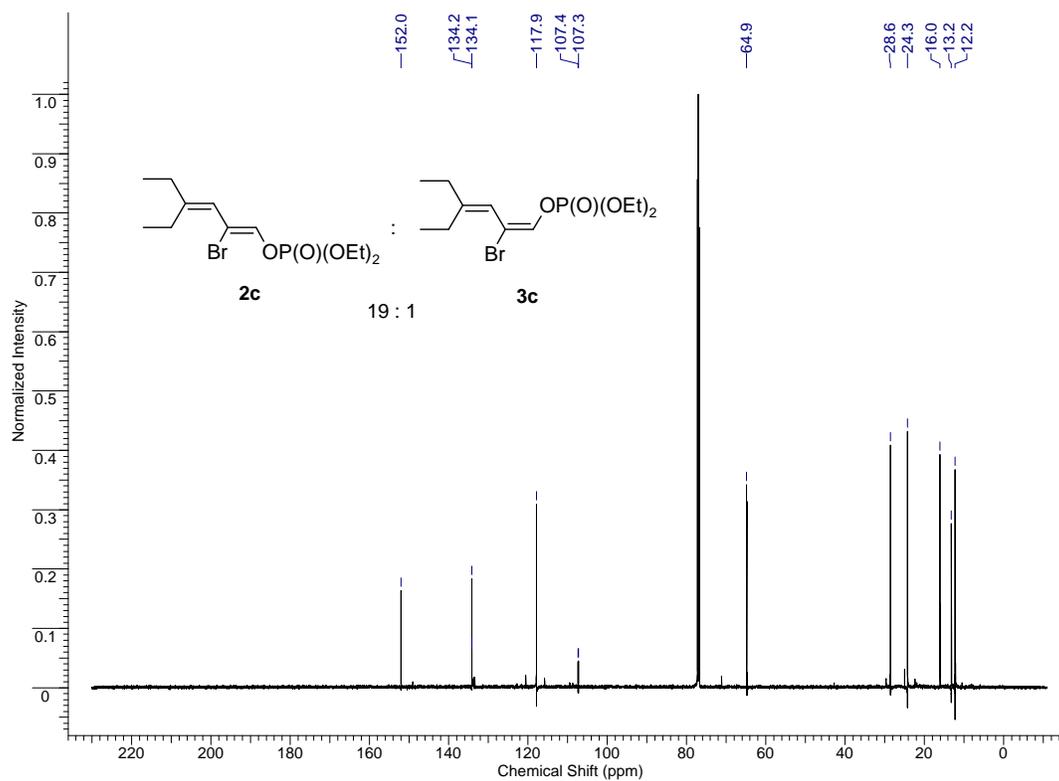
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ ppm 23.8, 33.1, 33.7, 55.6, 114.3, 126.6, 127.1, 128.2, 129.7, 131.1, 132.4, 132.9, 137.92, 139.7, 147.16, 158.9.

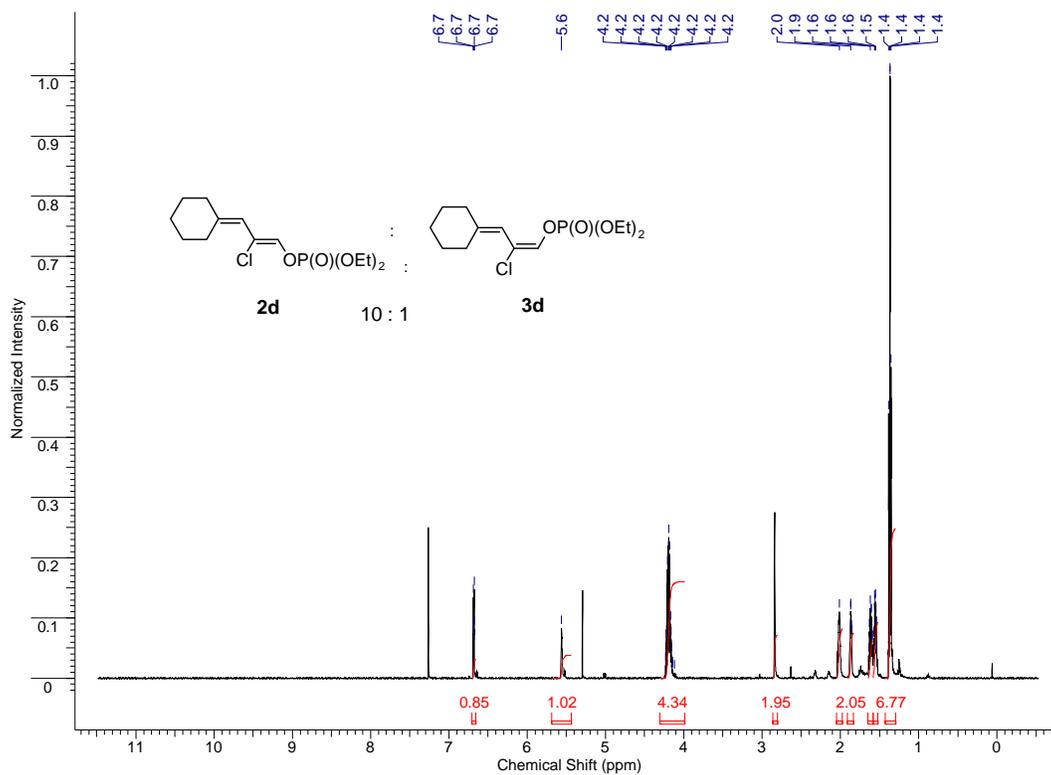
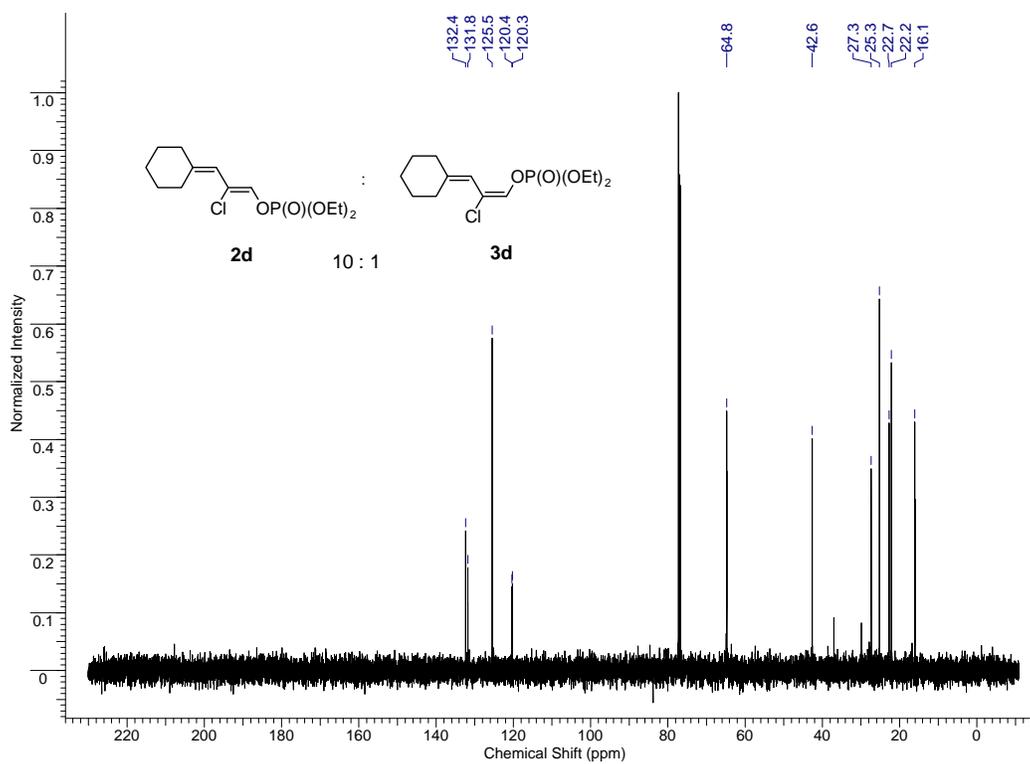
HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{20}\text{O}$: 276.15142, Found: 276.15067.

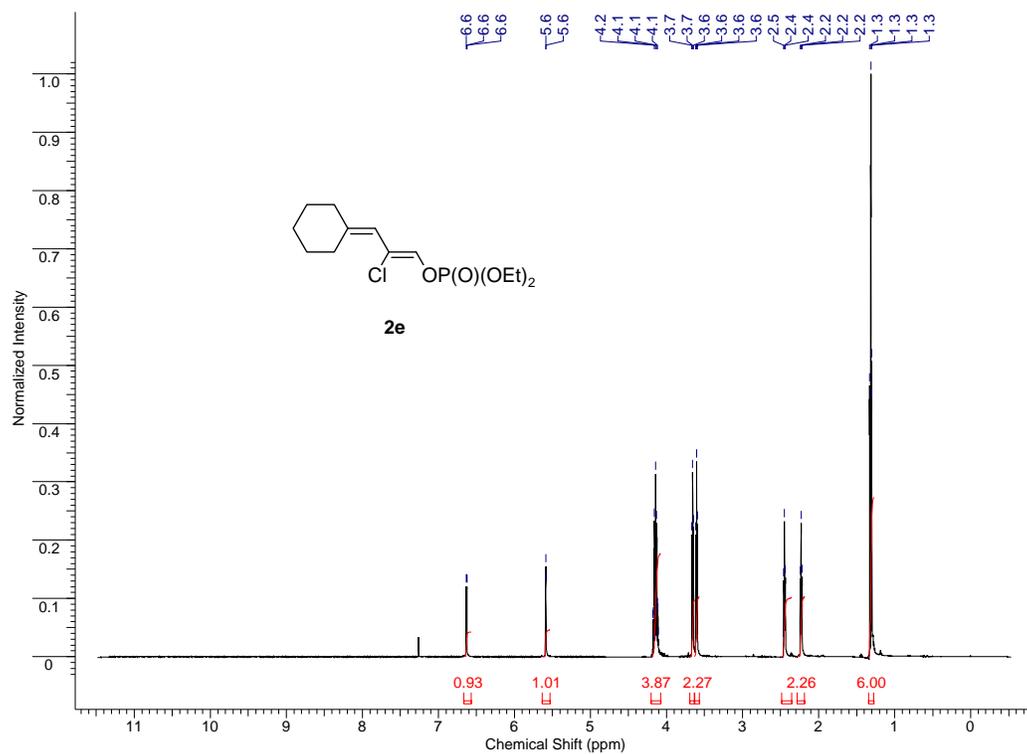
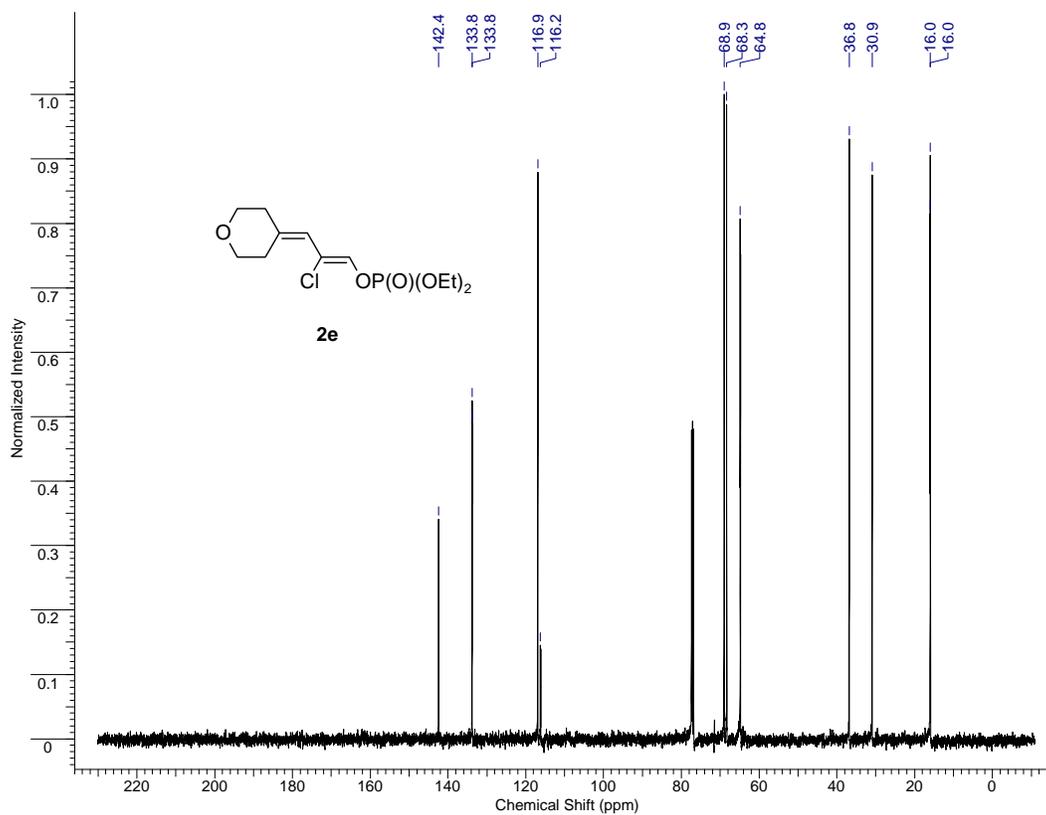
¹H Spectrum of **2a**¹³C Spectrum of **2a**

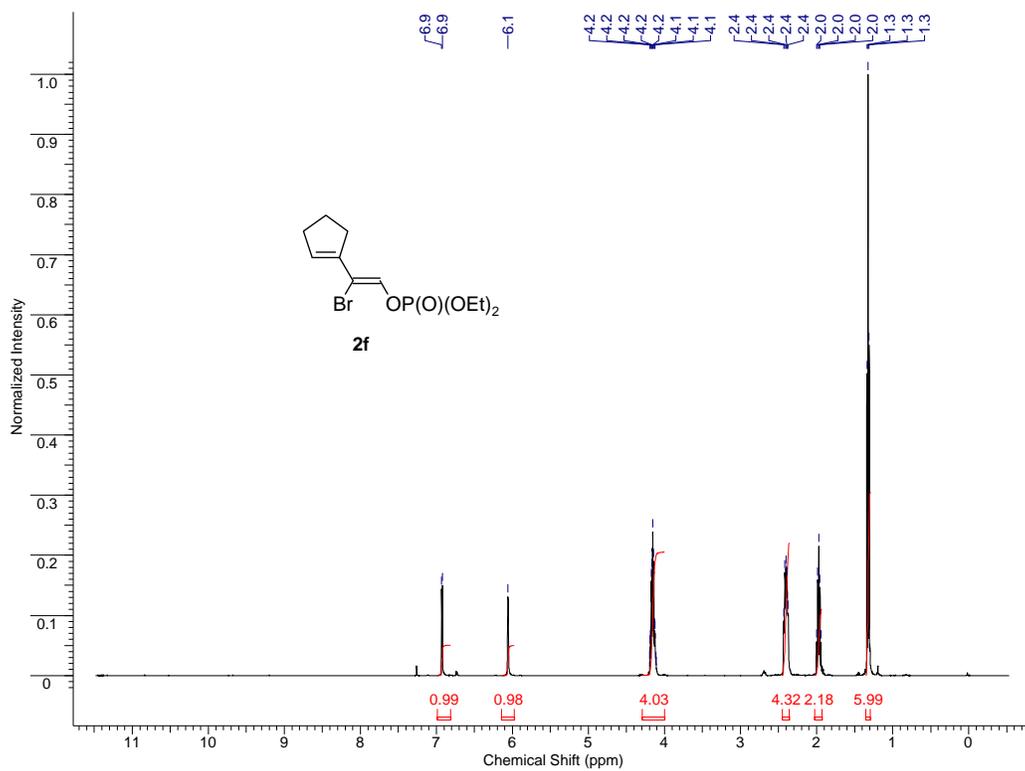
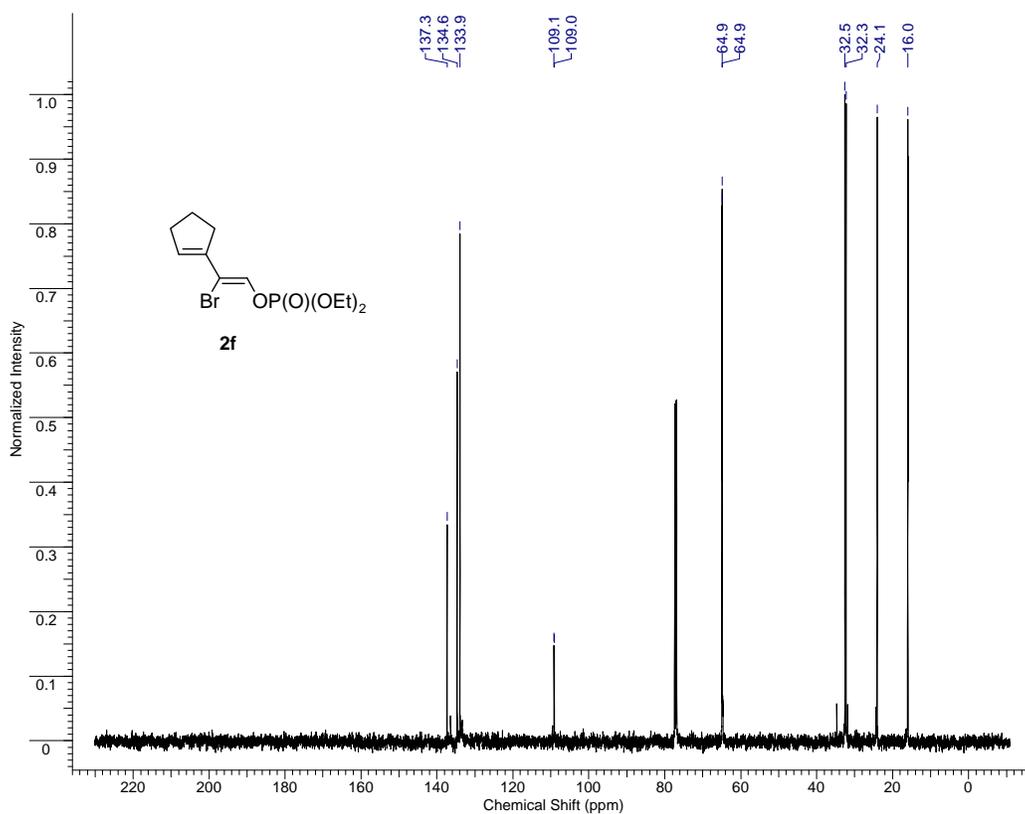
¹³CDEPT Spectrum of **2a**NOESY Spectrum of **2a**

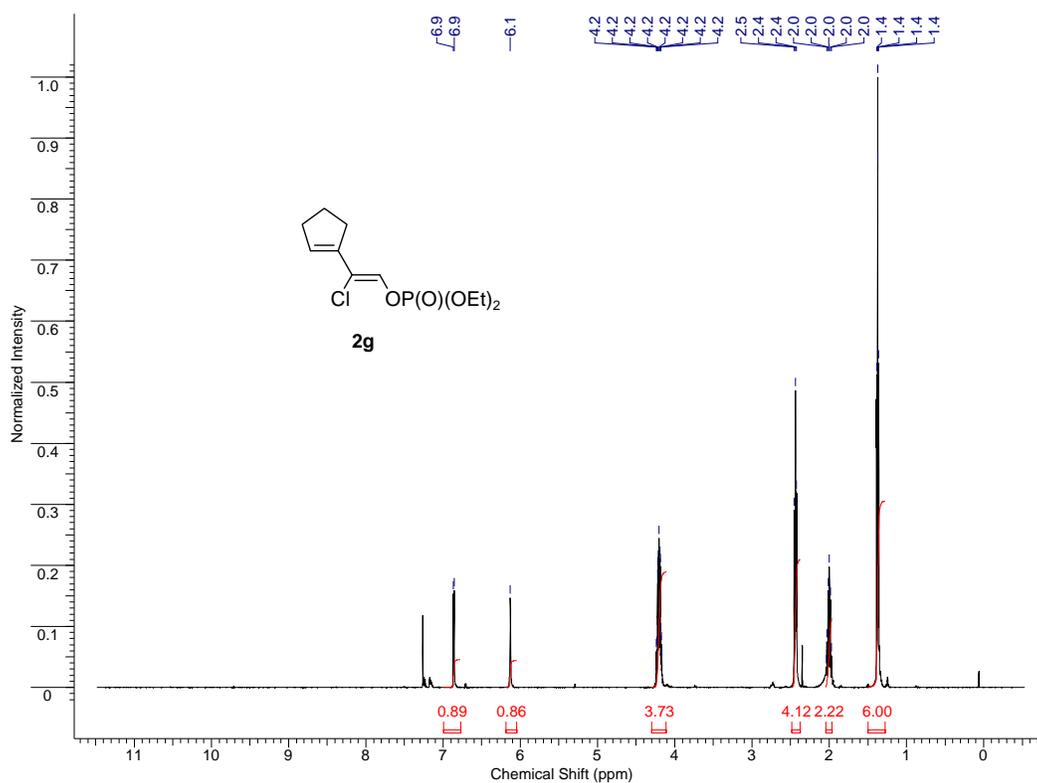
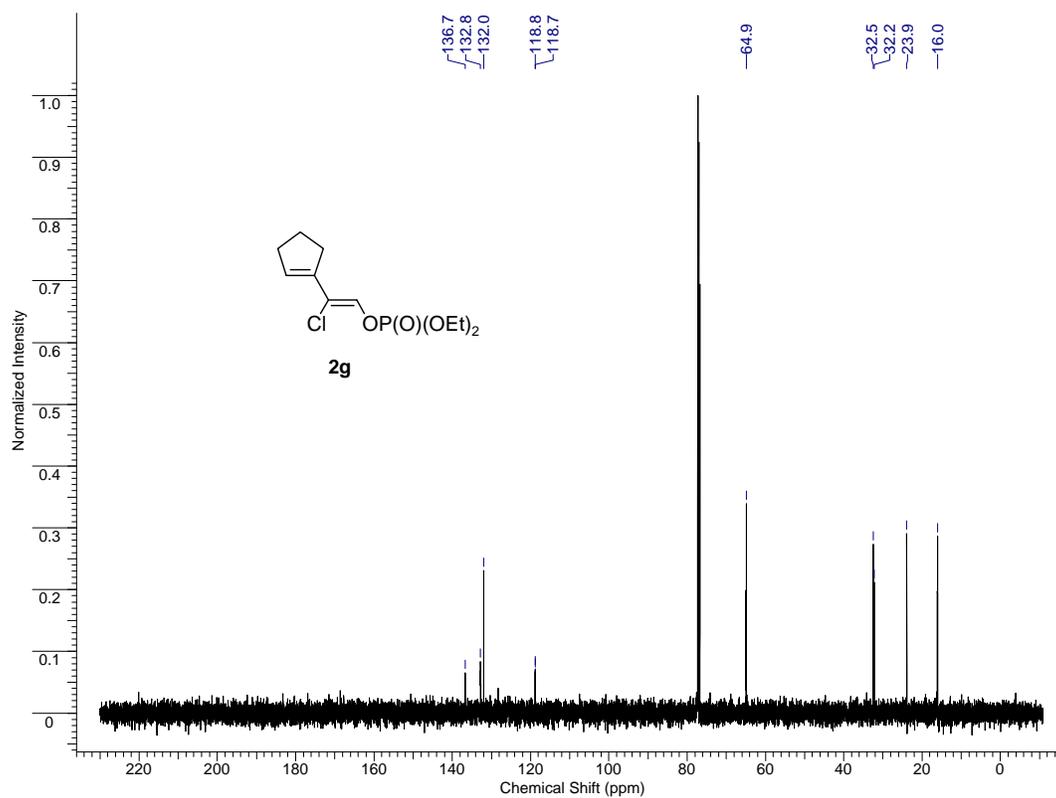
¹H Spectrum of **2b**¹³C Spectrum of **2b**

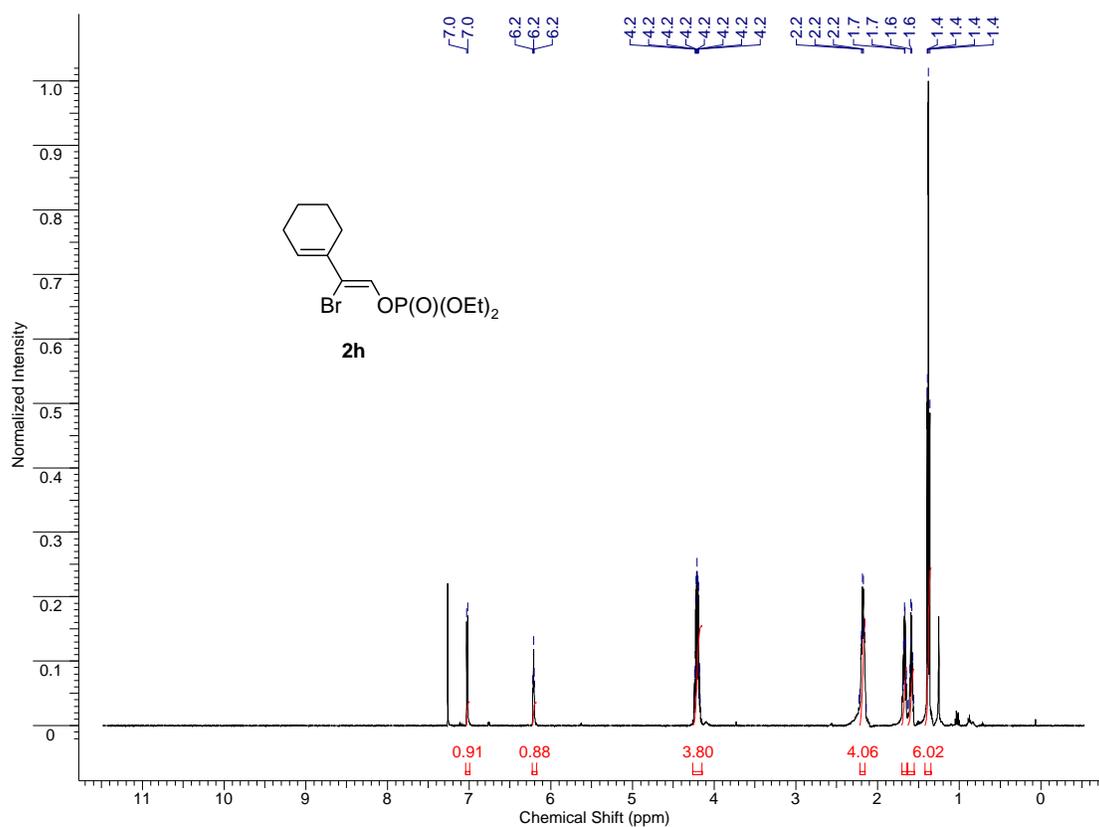
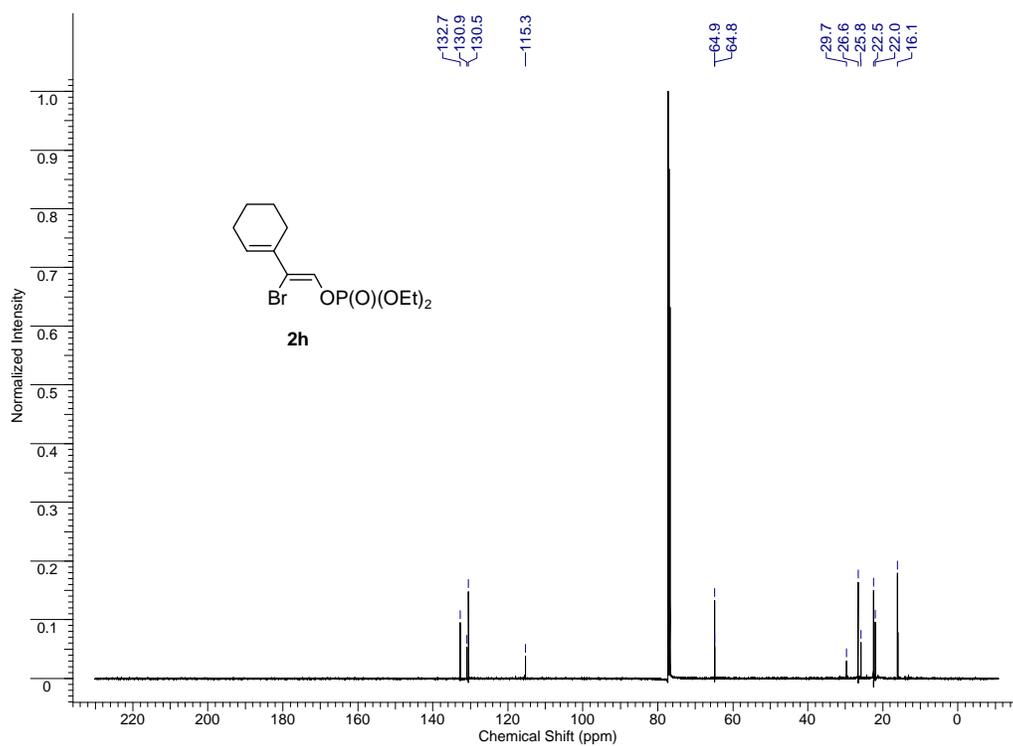
¹H Spectrum of **2c** + **3c**¹³C Spectrum of **2c** + **3c**

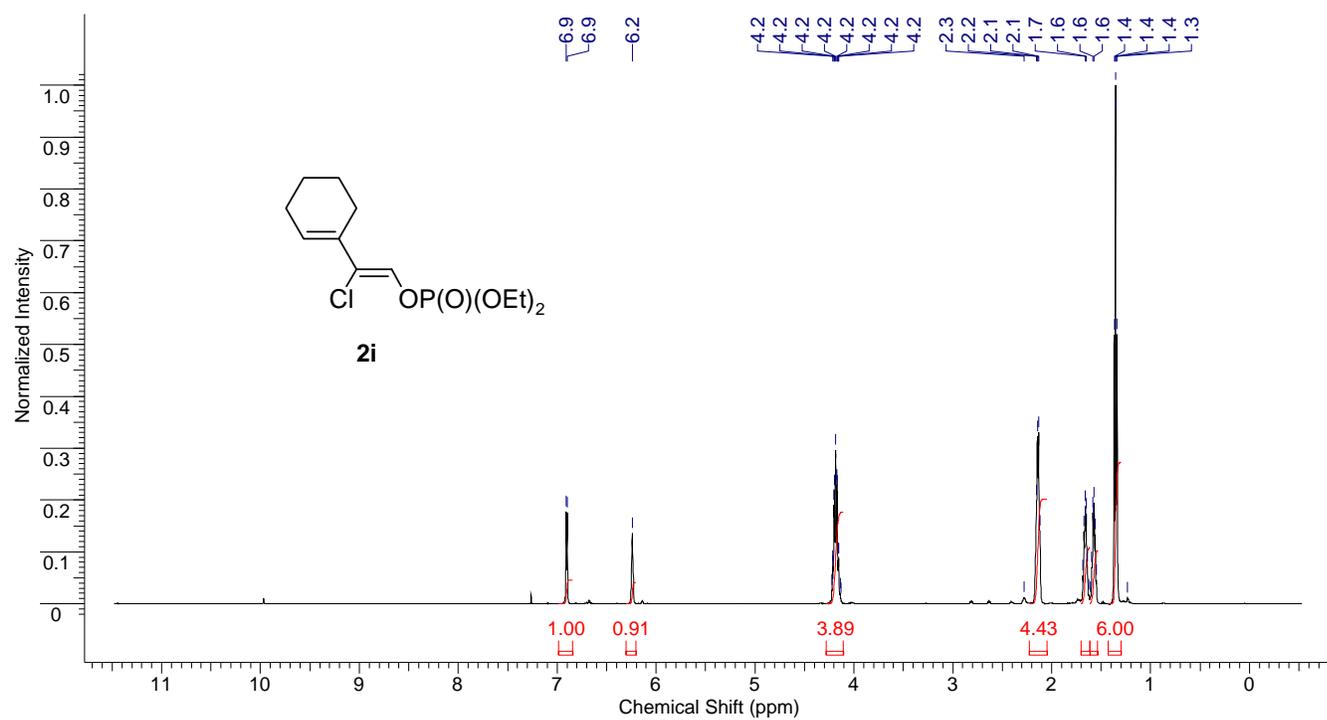
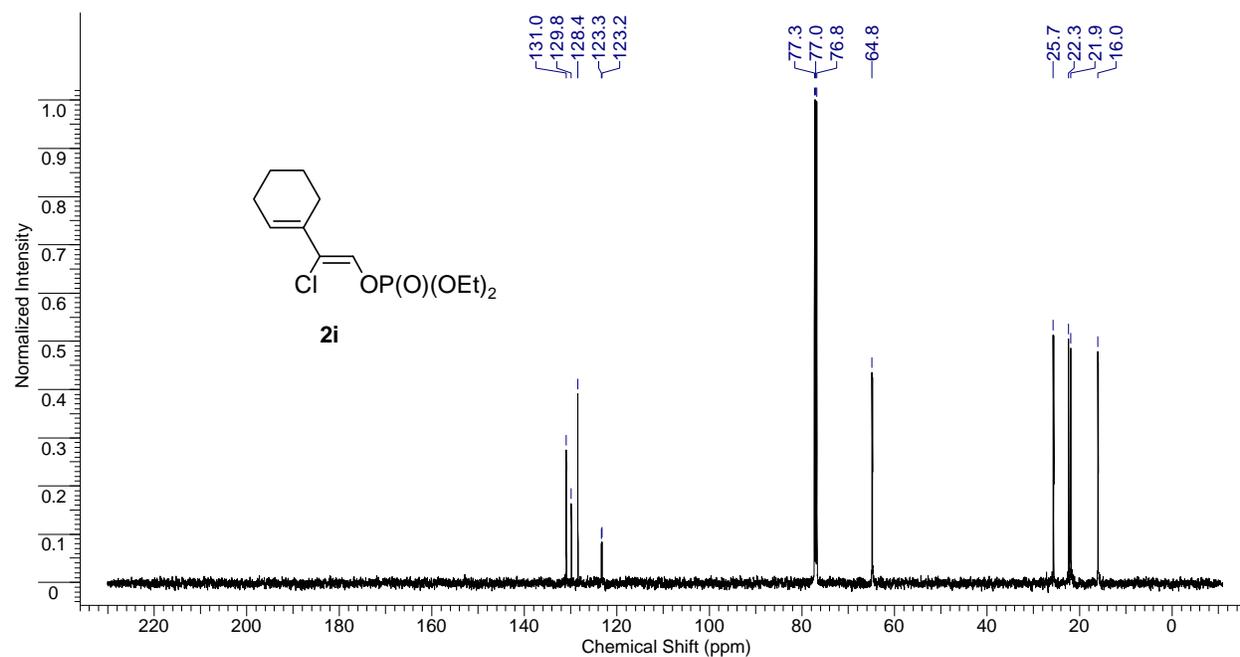
¹H Spectrum of **2d** + **3d**¹³C Spectrum of **2d** + **3d**

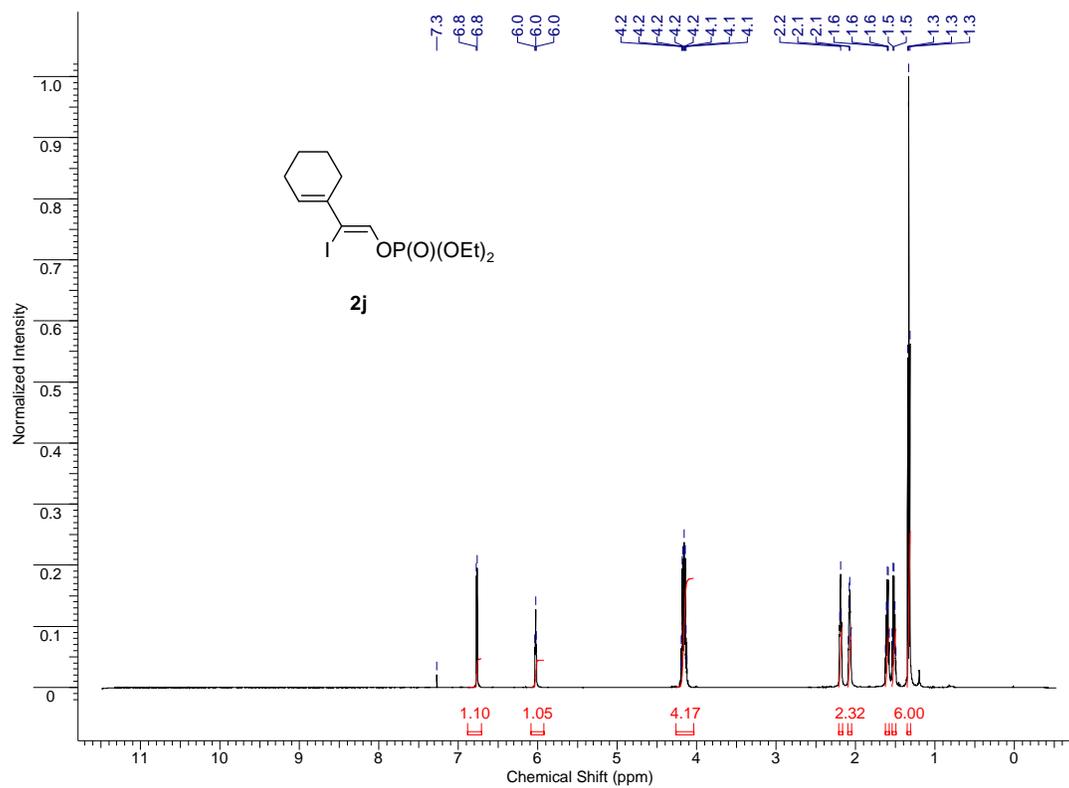
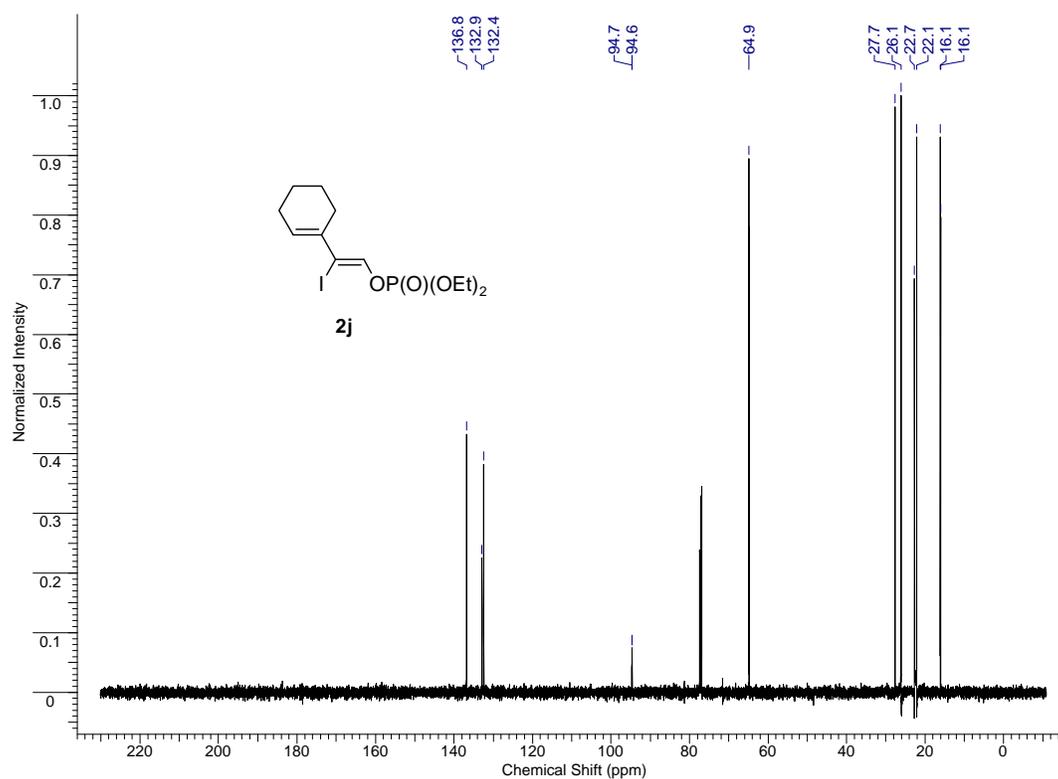
¹H Spectrum of **2e**¹³C Spectrum of **2e**

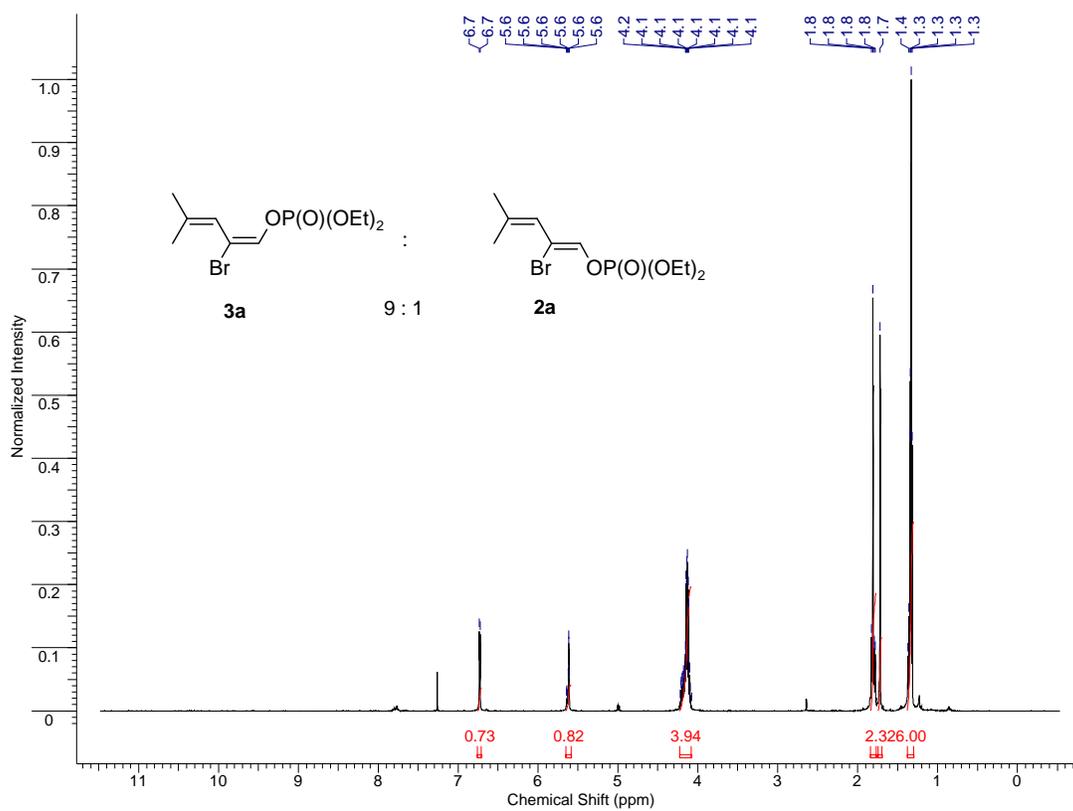
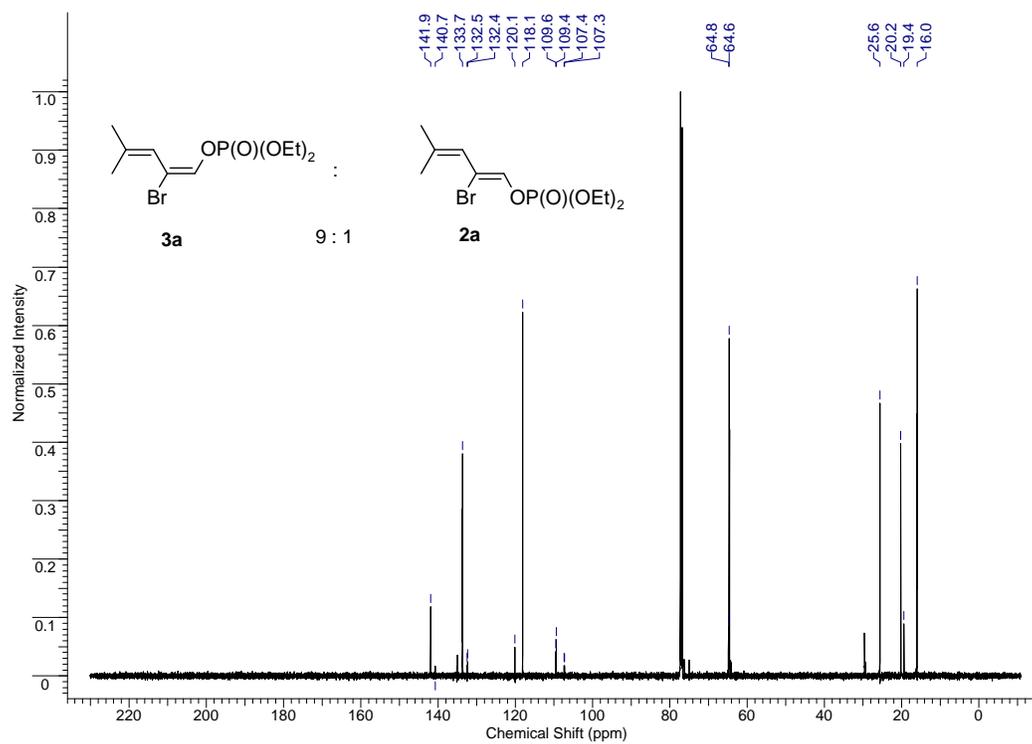
¹H Spectrum of **2f**¹³C Spectrum of **2f**

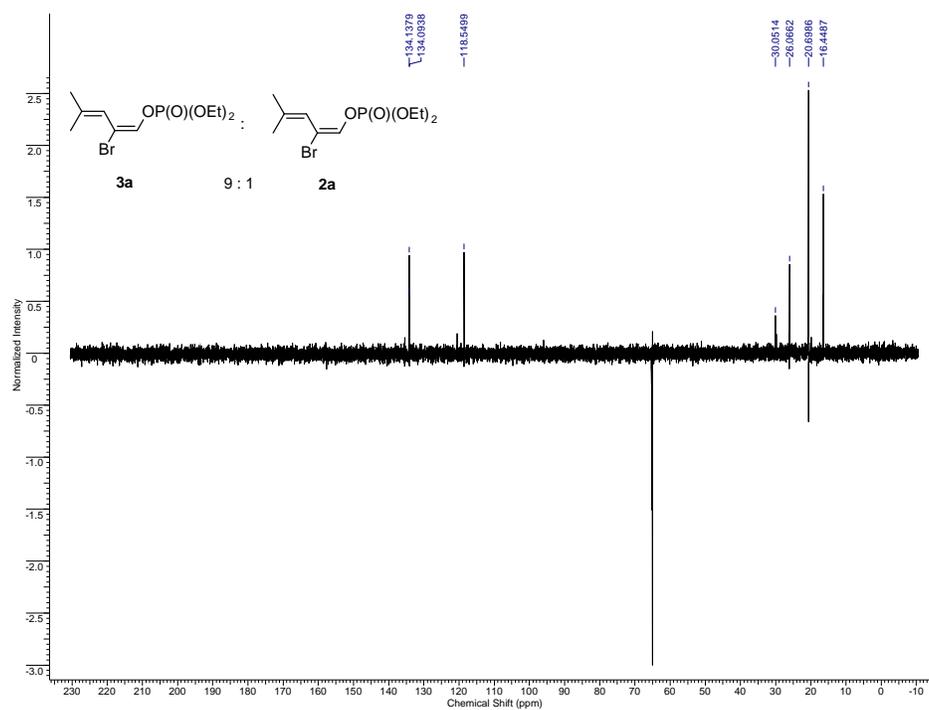
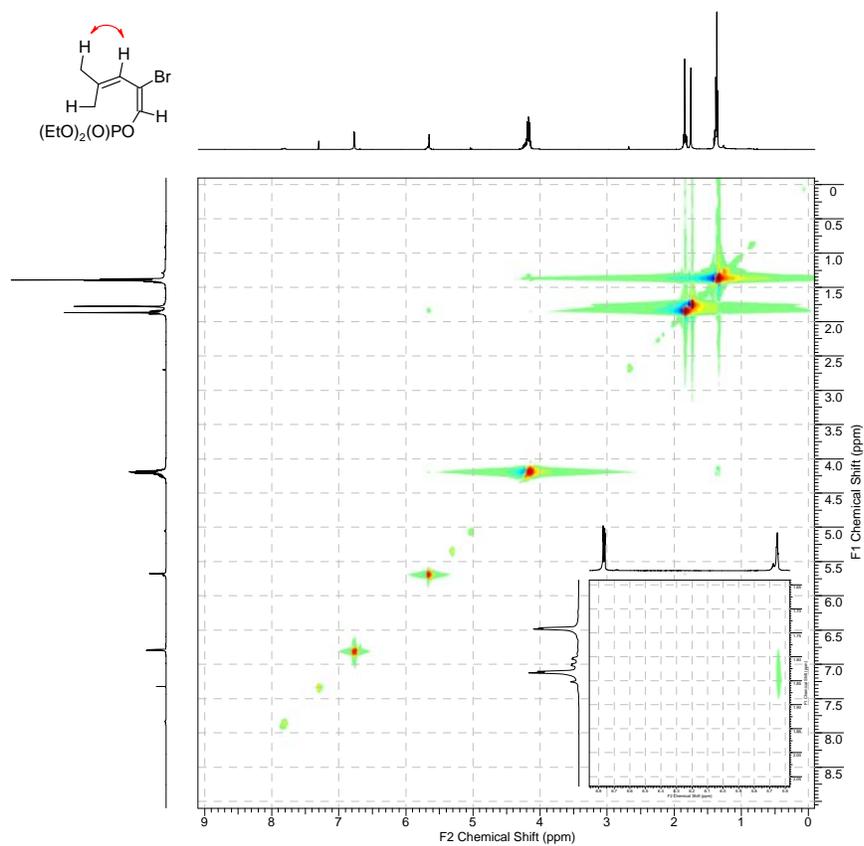
¹H Spectrum of **2g**¹³C Spectrum of **2g**

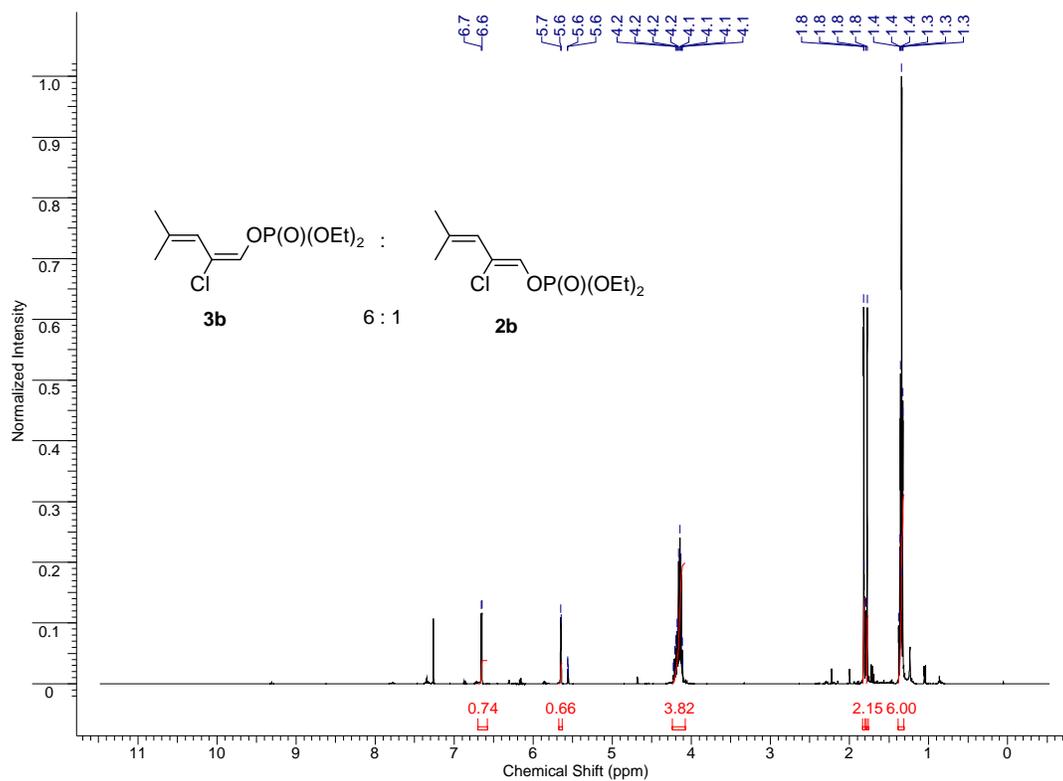
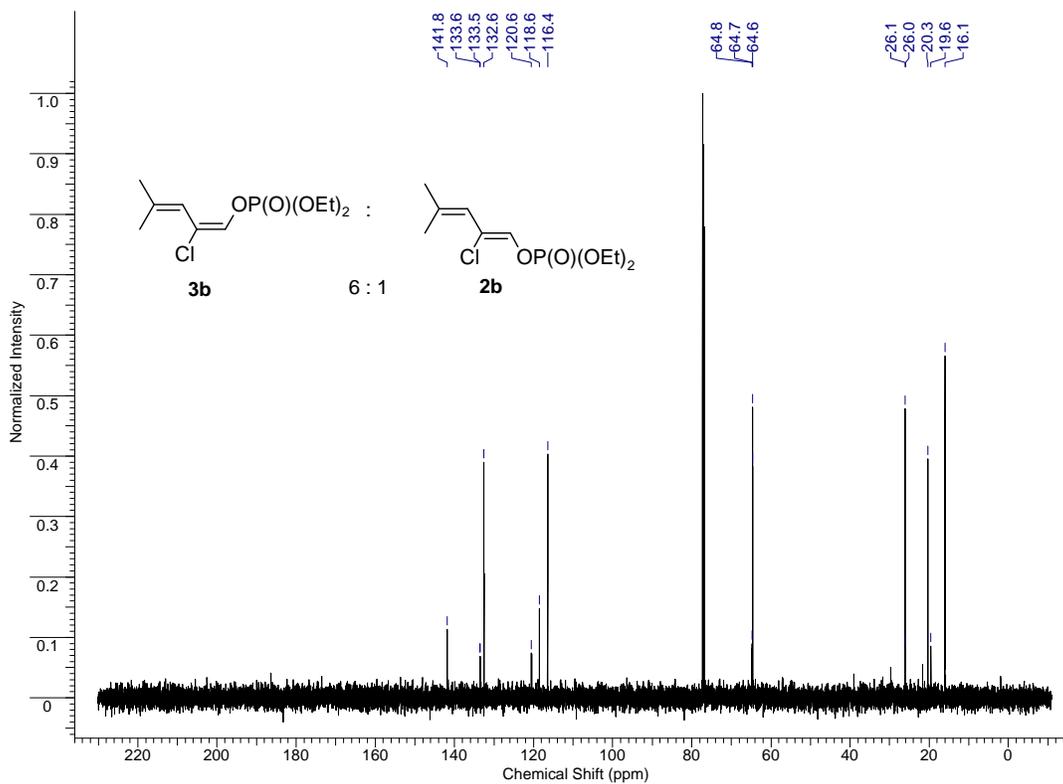
¹H Spectrum of **2h**¹³C Spectrum of **2h**

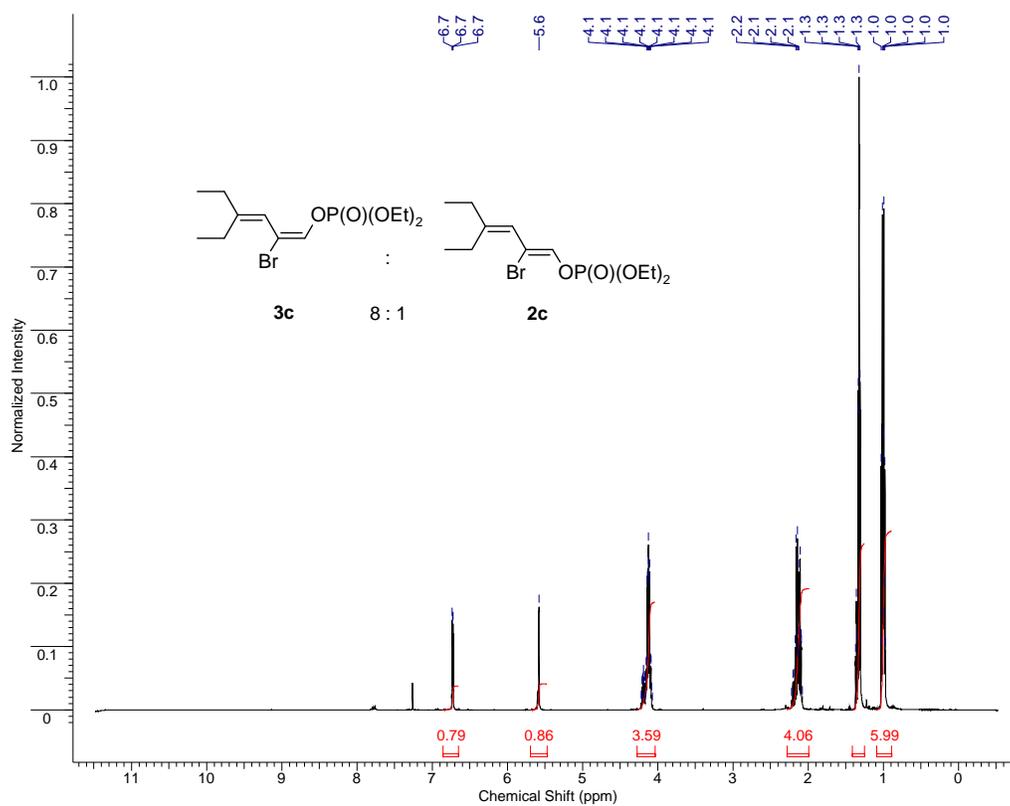
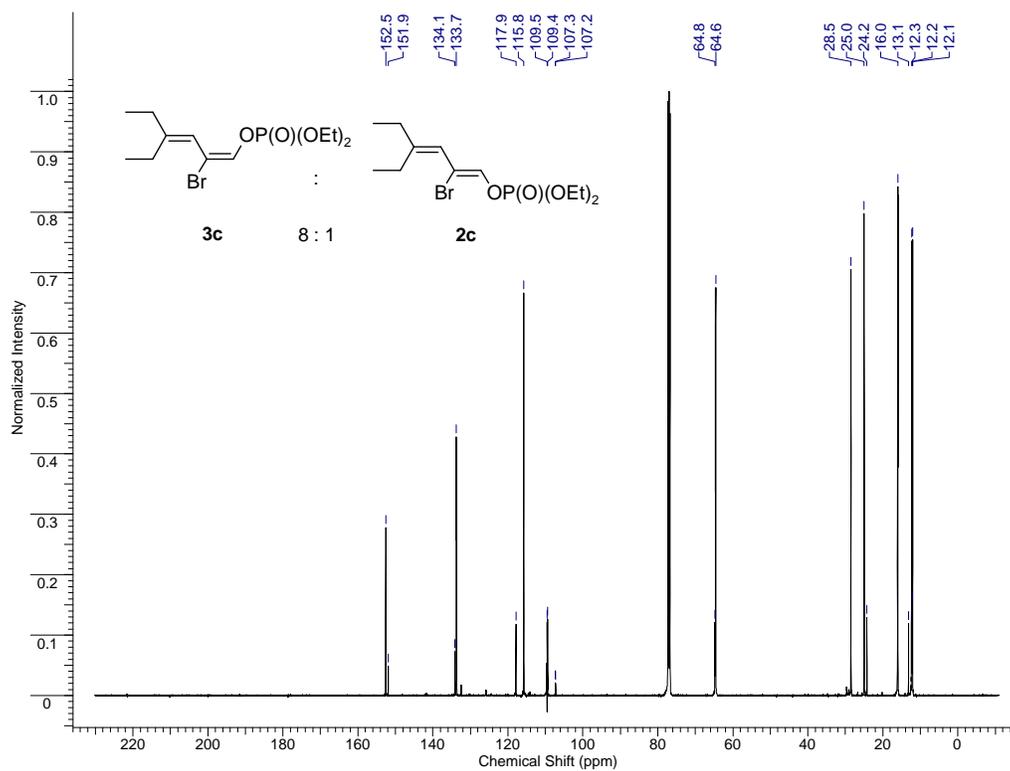
¹H Spectrum of **2i**¹³C Spectrum of **2i**

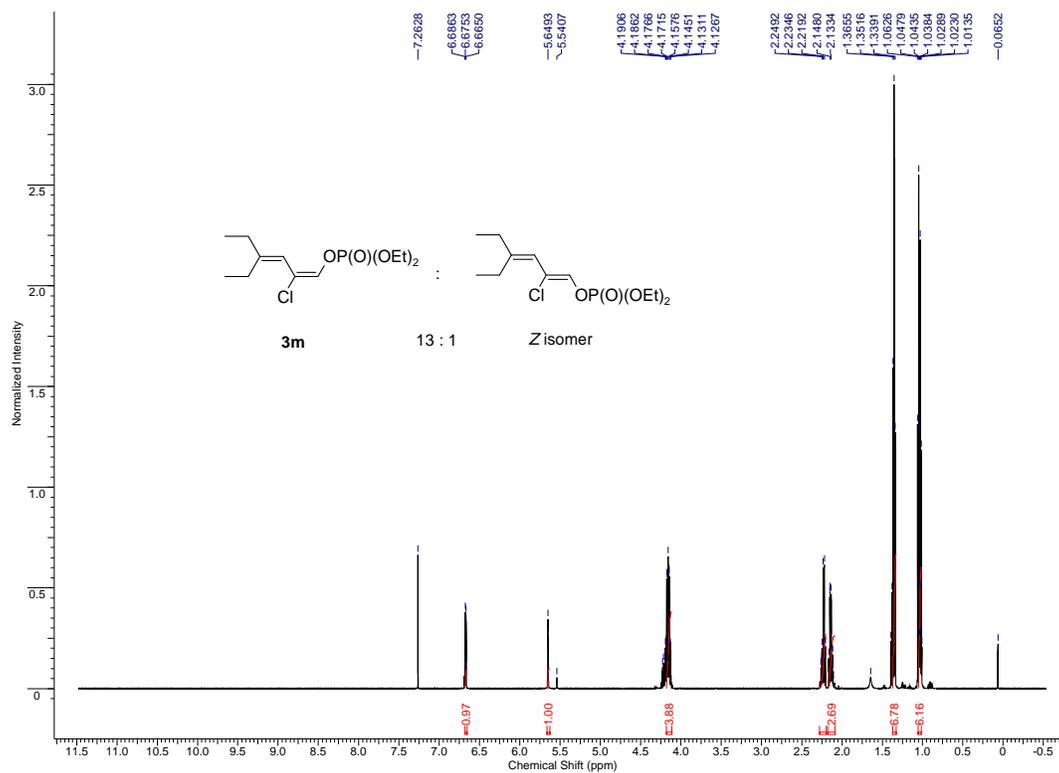
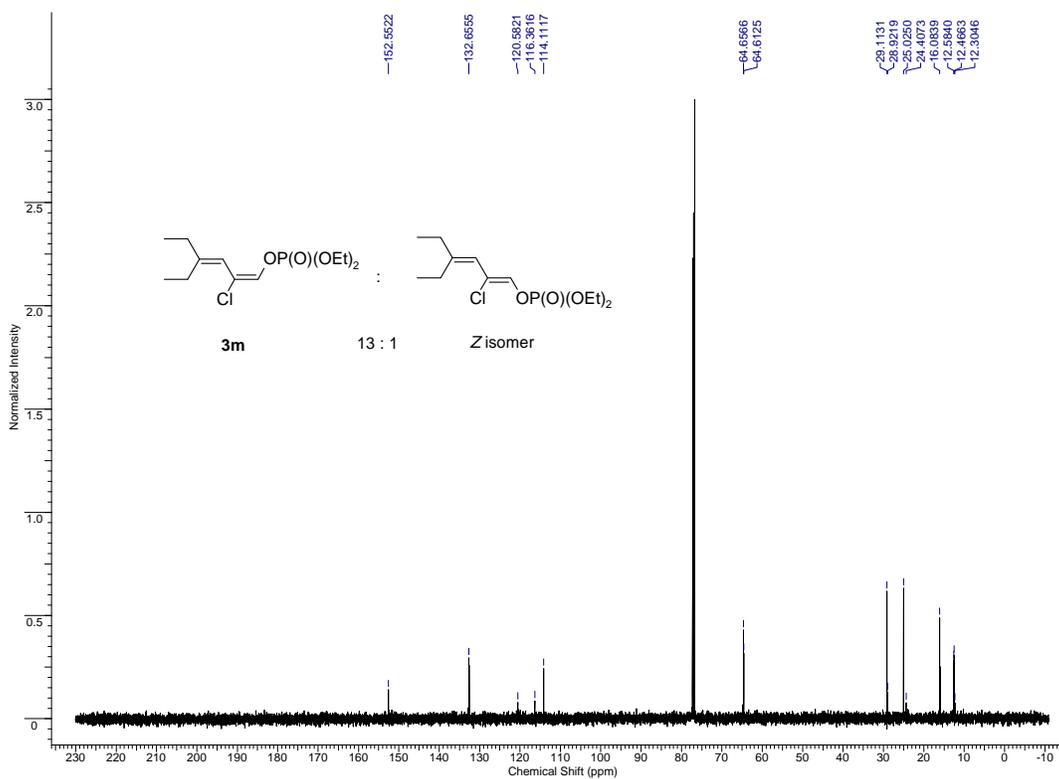
¹H Spectrum of **2j**¹³C Spectrum of **2i**

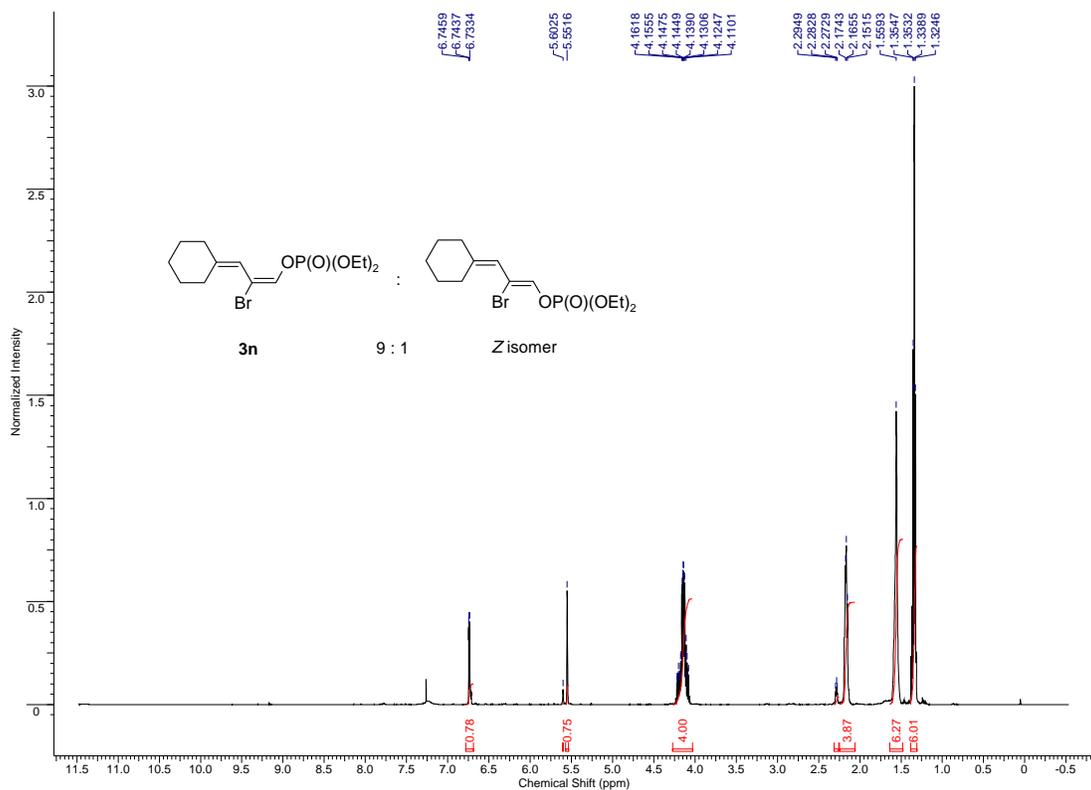
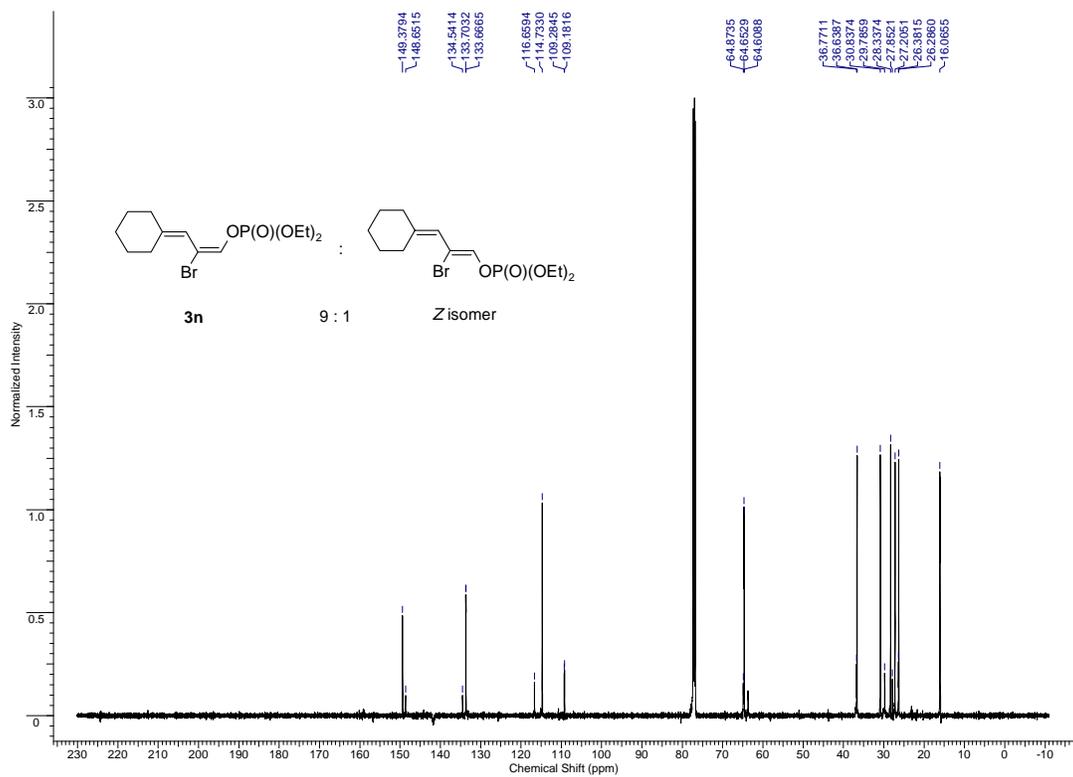
¹H Spectrum of **3a** + **2a**¹³C Spectrum of **3a** + **2a**

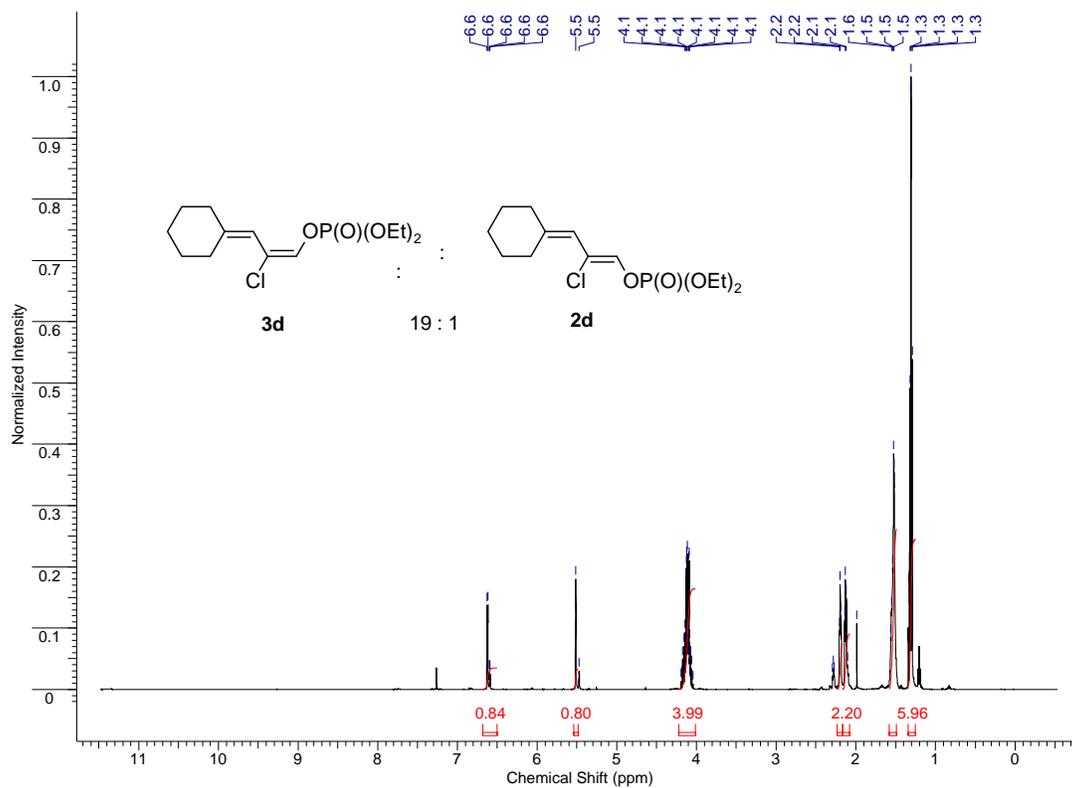
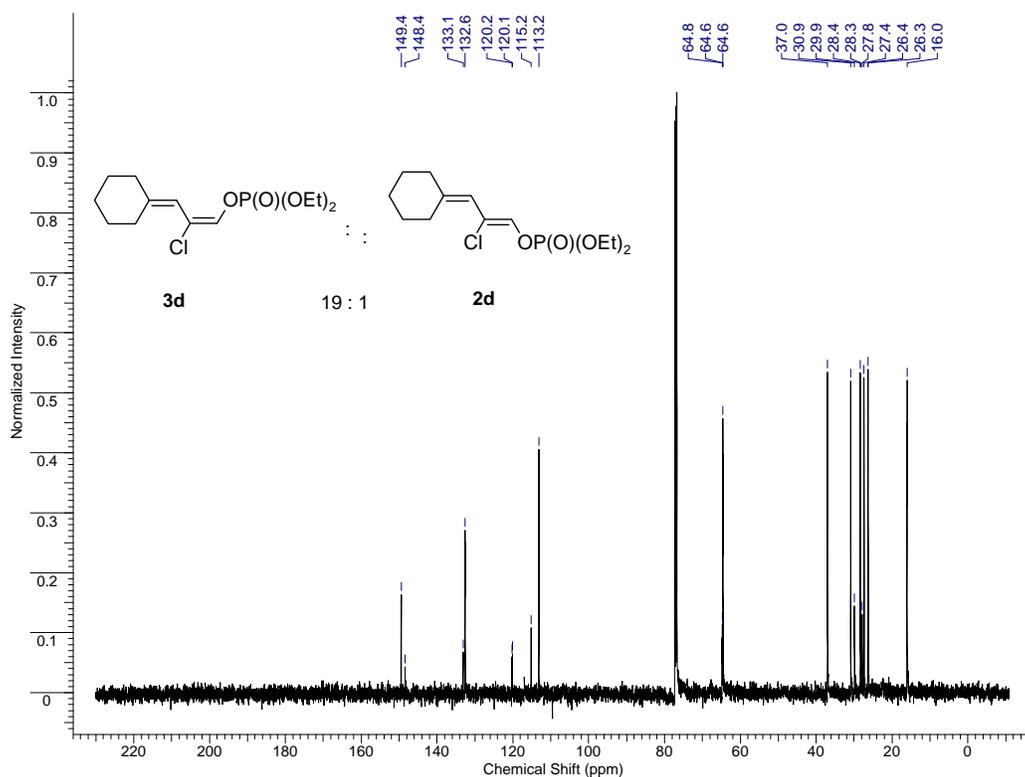
¹³CDEPT Spectrum of **3b** + **2b**NOESY Spectrum of **3a** + **2b** (9:1)

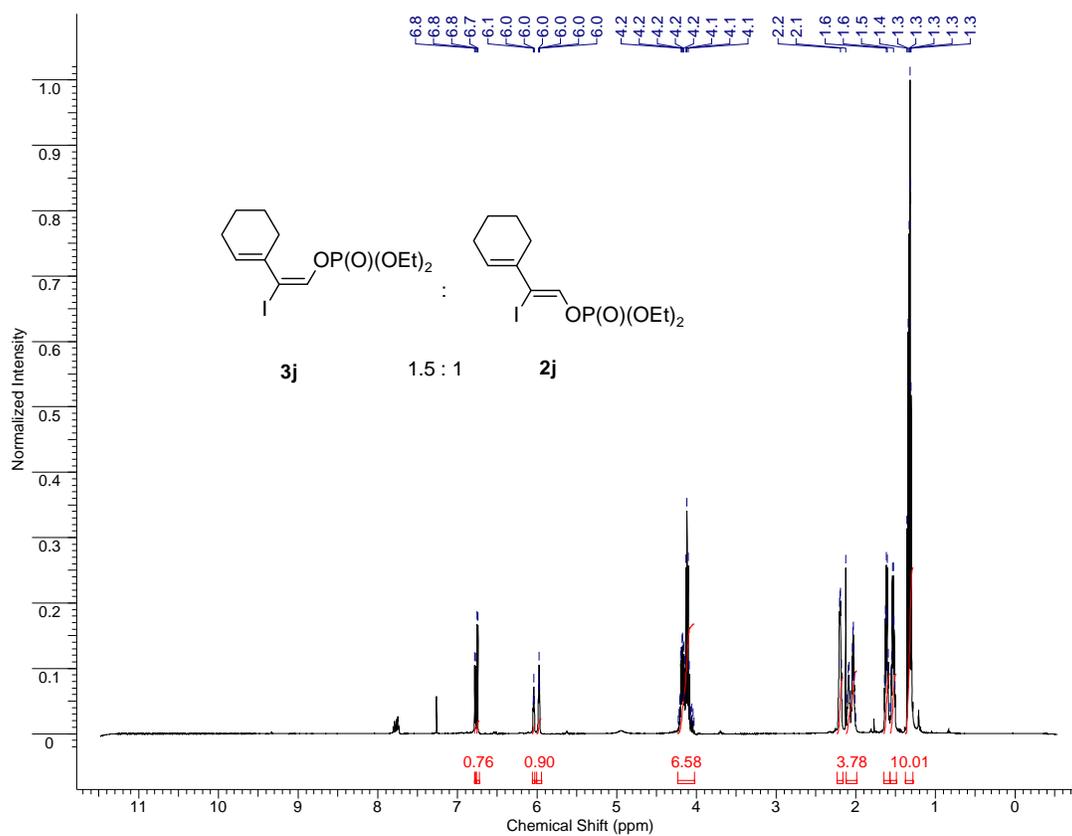
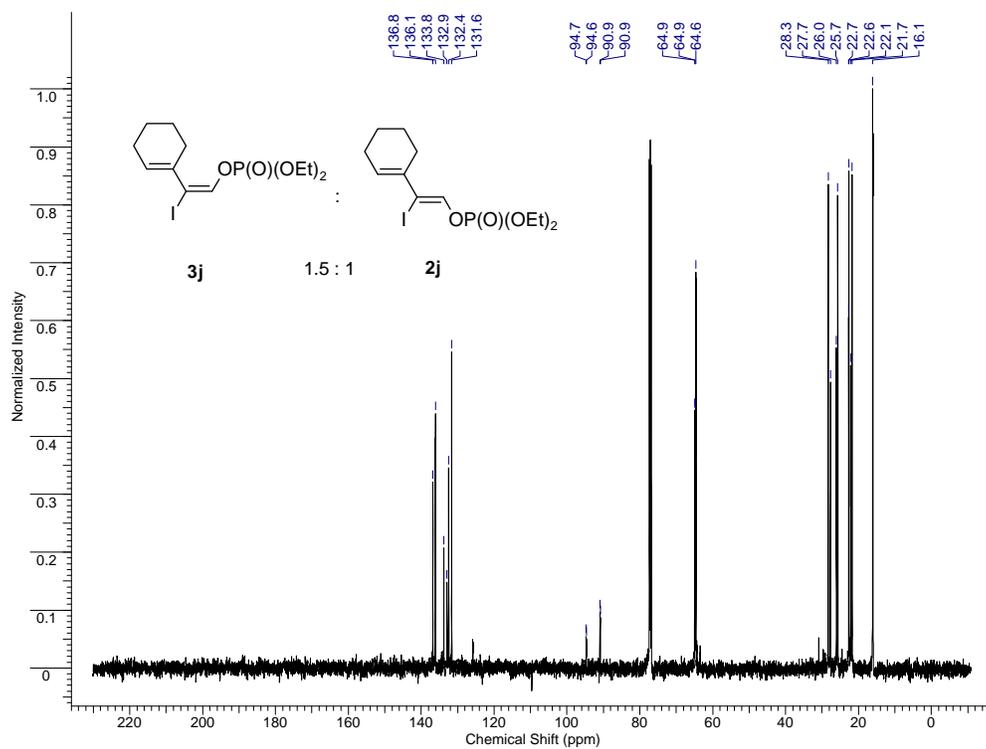
¹H Spectrum of **3b** + **2b**¹³C Spectrum of **3b** + **2b**

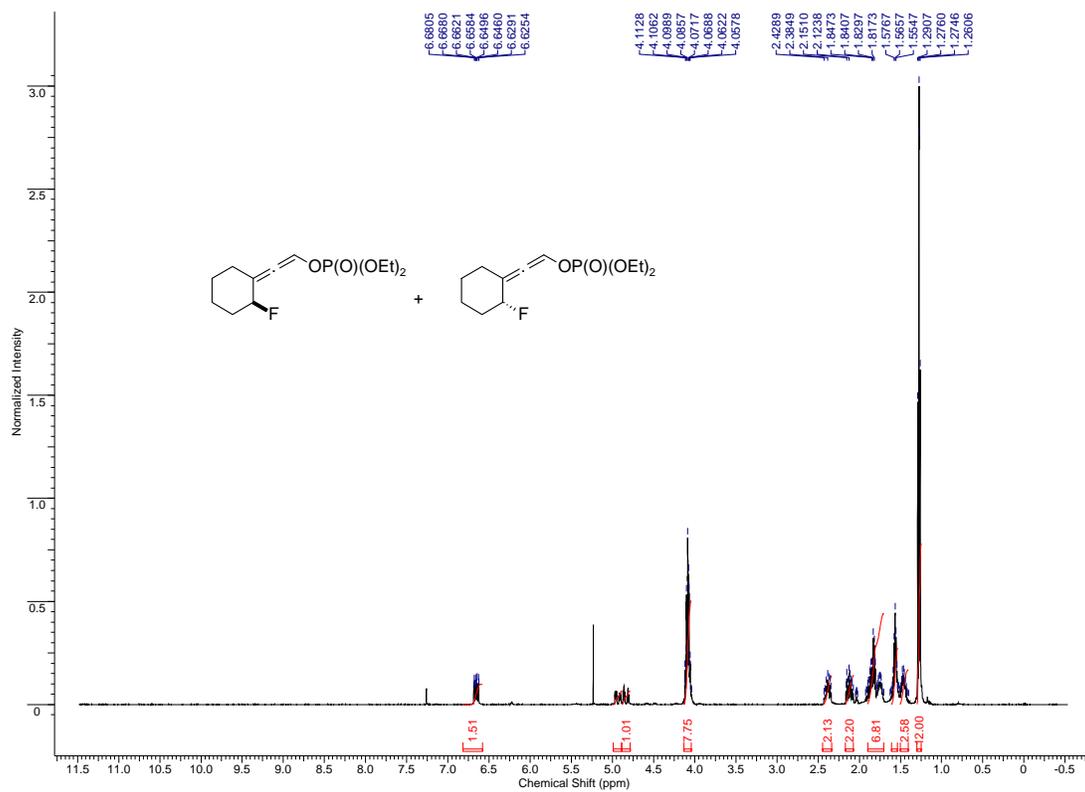
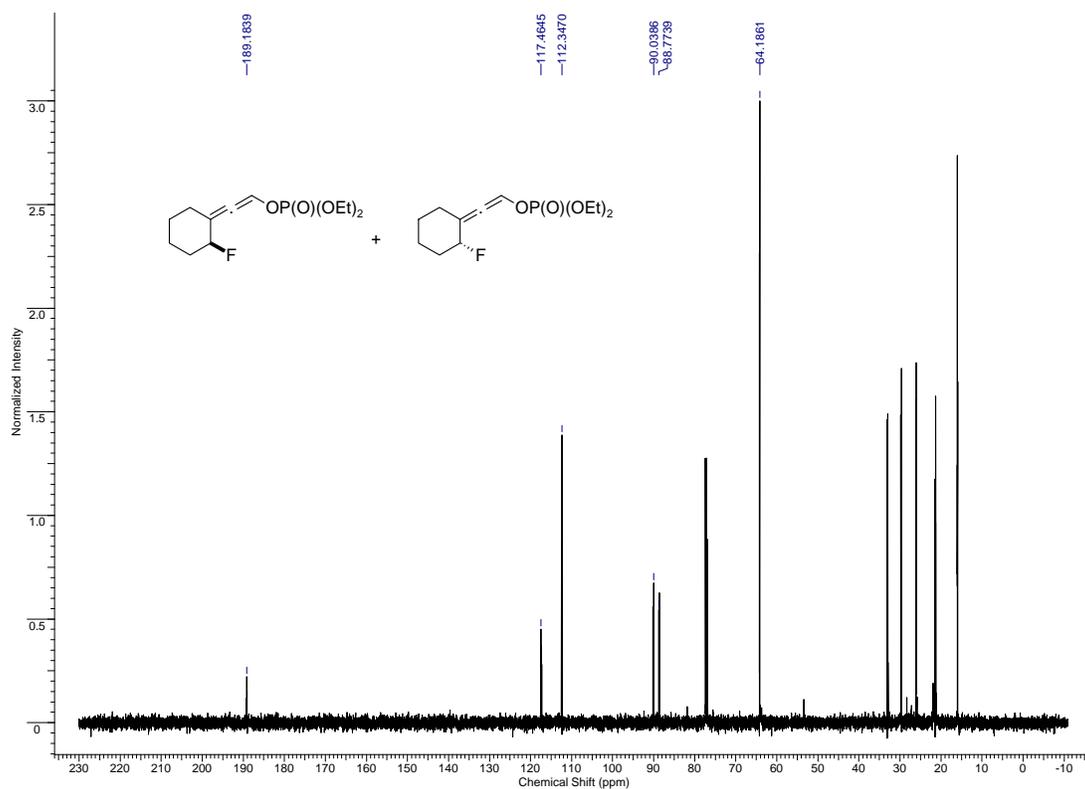
¹H Spectrum of **3c** + **2c**¹³C Spectrum of **3c** + **2c**

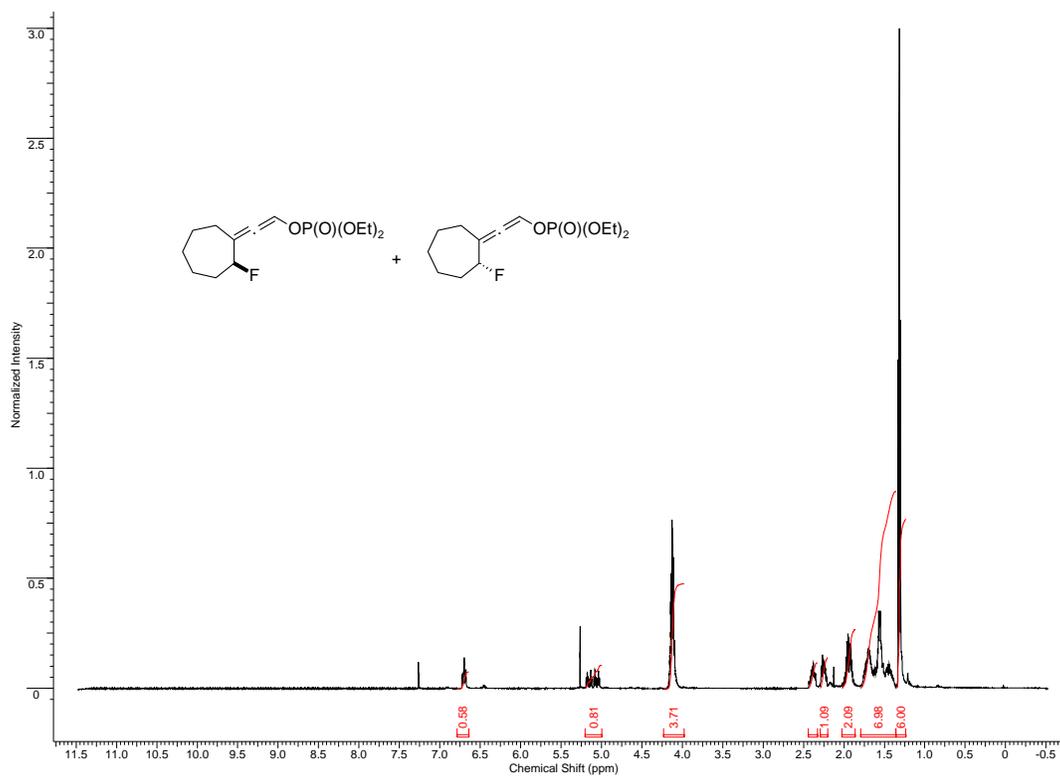
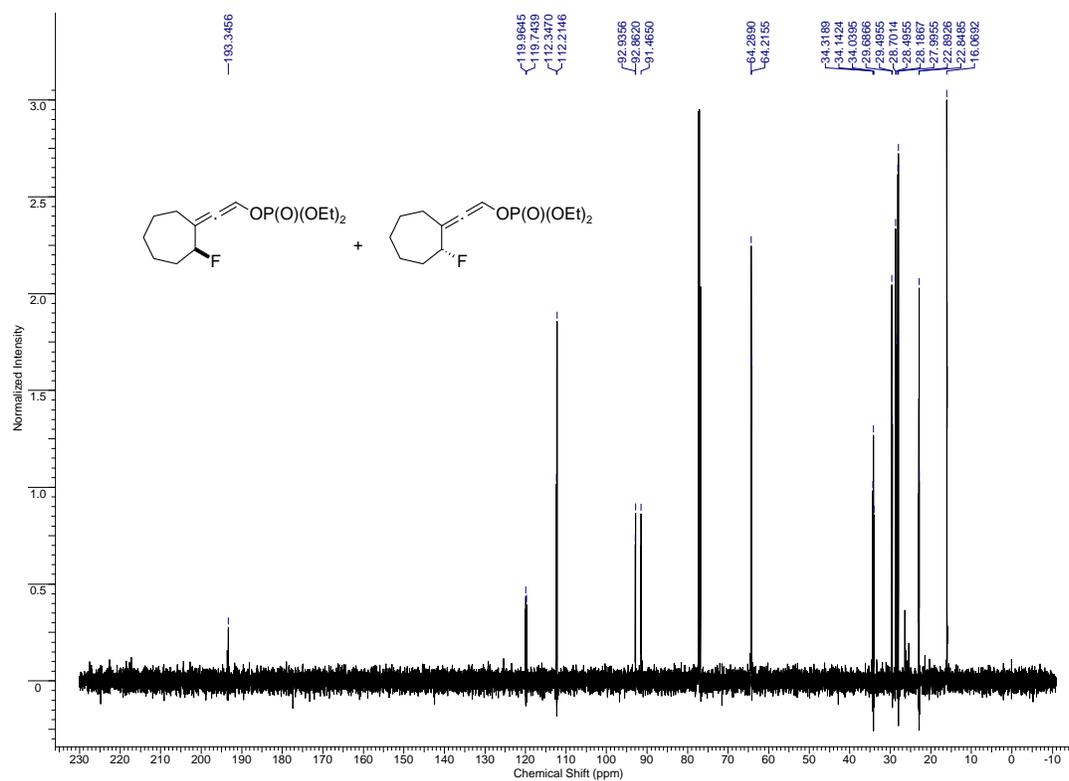
¹H Spectrum of **3m** + **Z** isomer¹³C Spectrum of **3m** + **Z** isomer

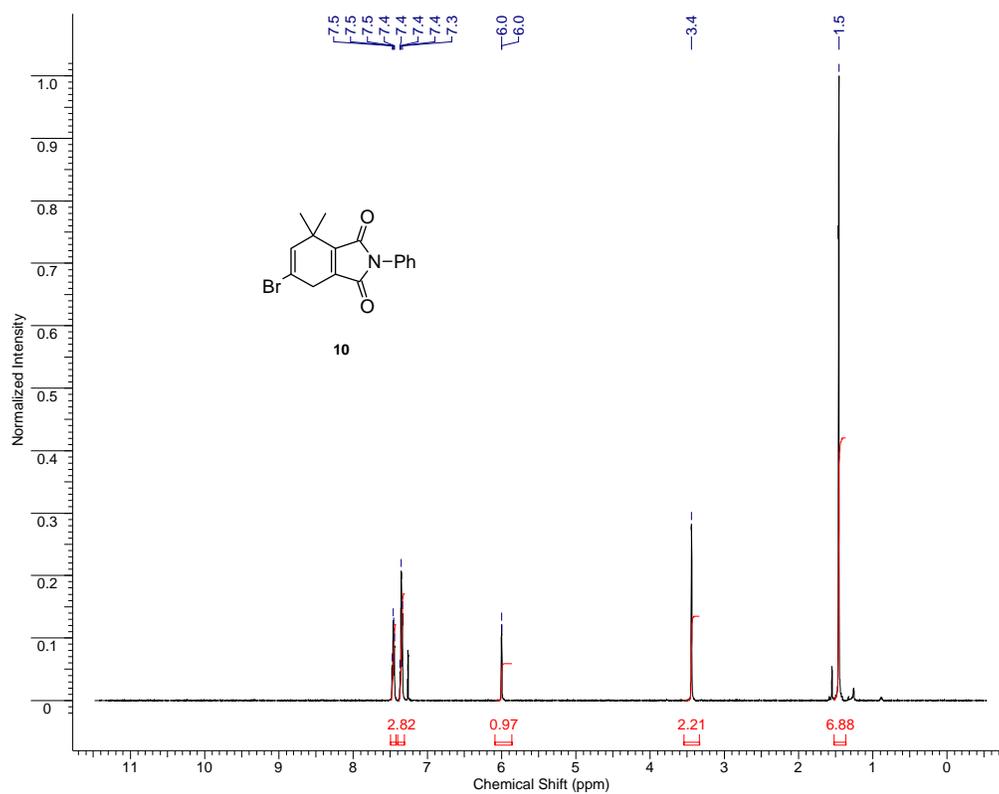
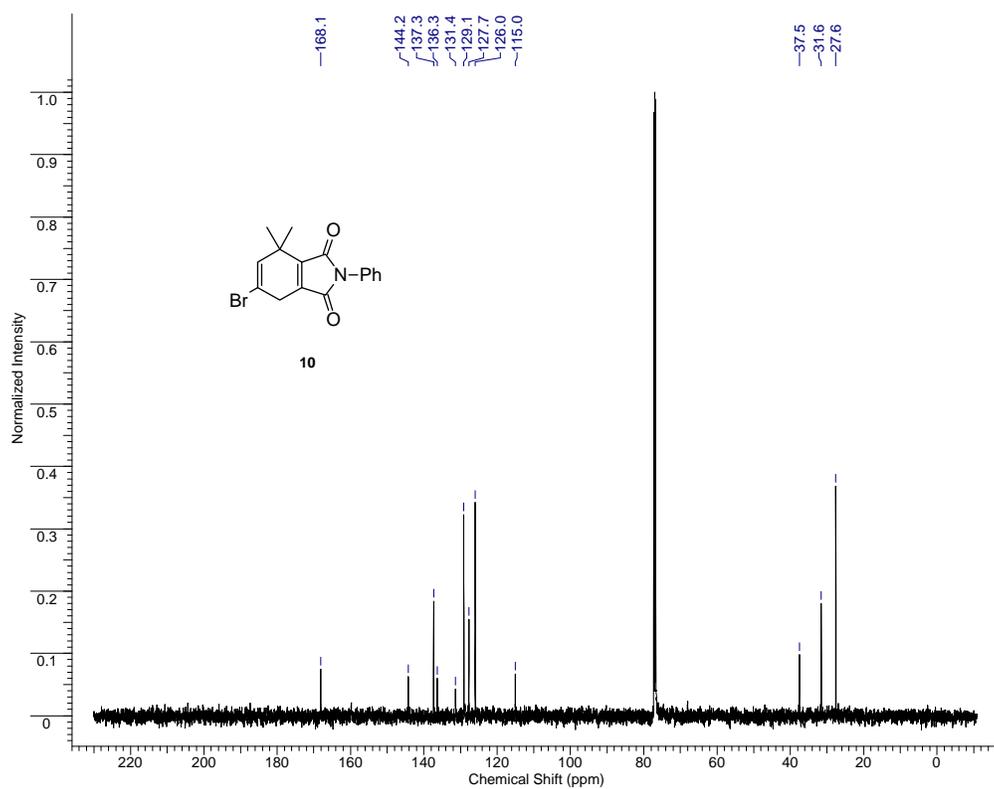
¹H Spectrum of **3n** + **Z** isomer¹³C Spectrum of **3n** + **Z** isomer

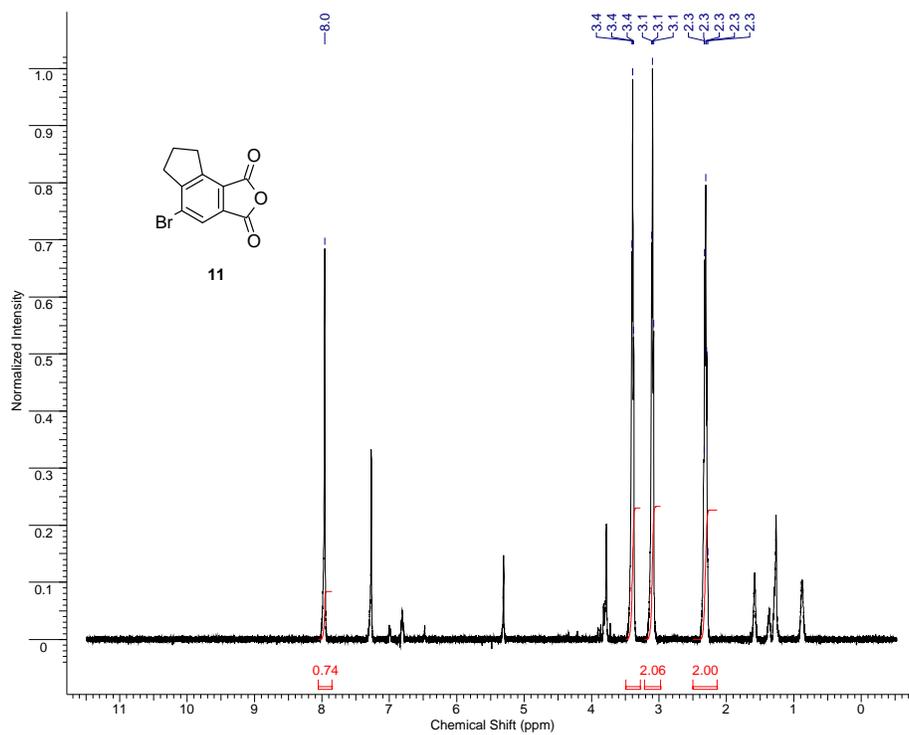
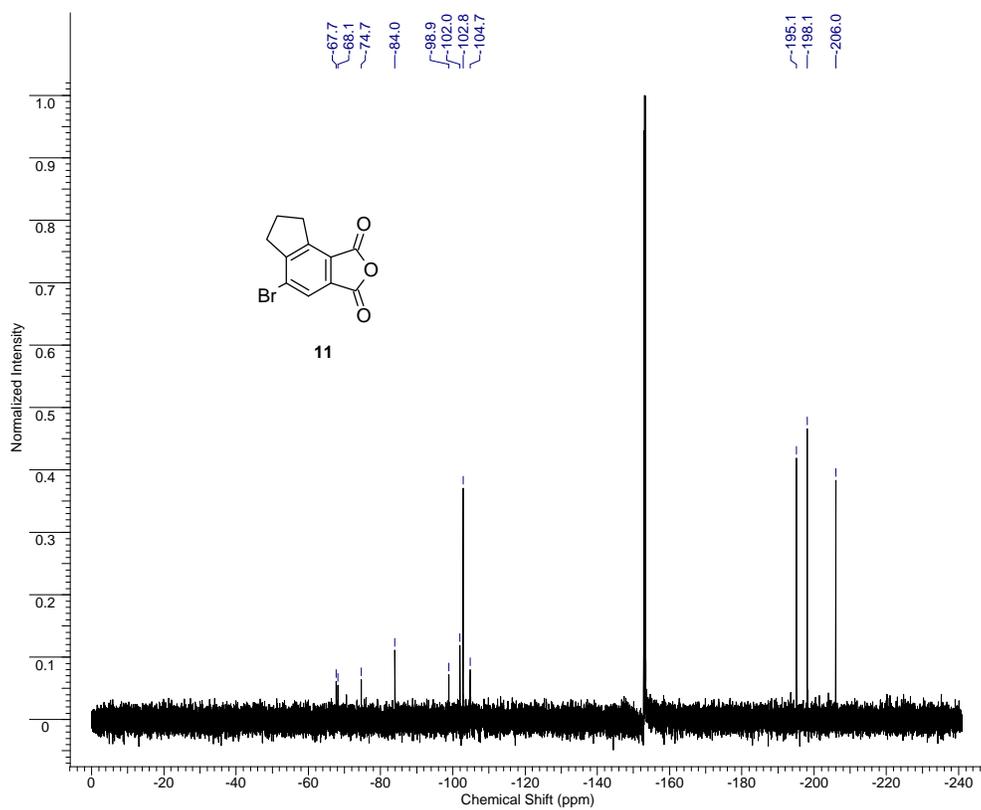
¹H Spectrum of **3d** + **2d**¹³C Spectrum of **3d** + **2d**

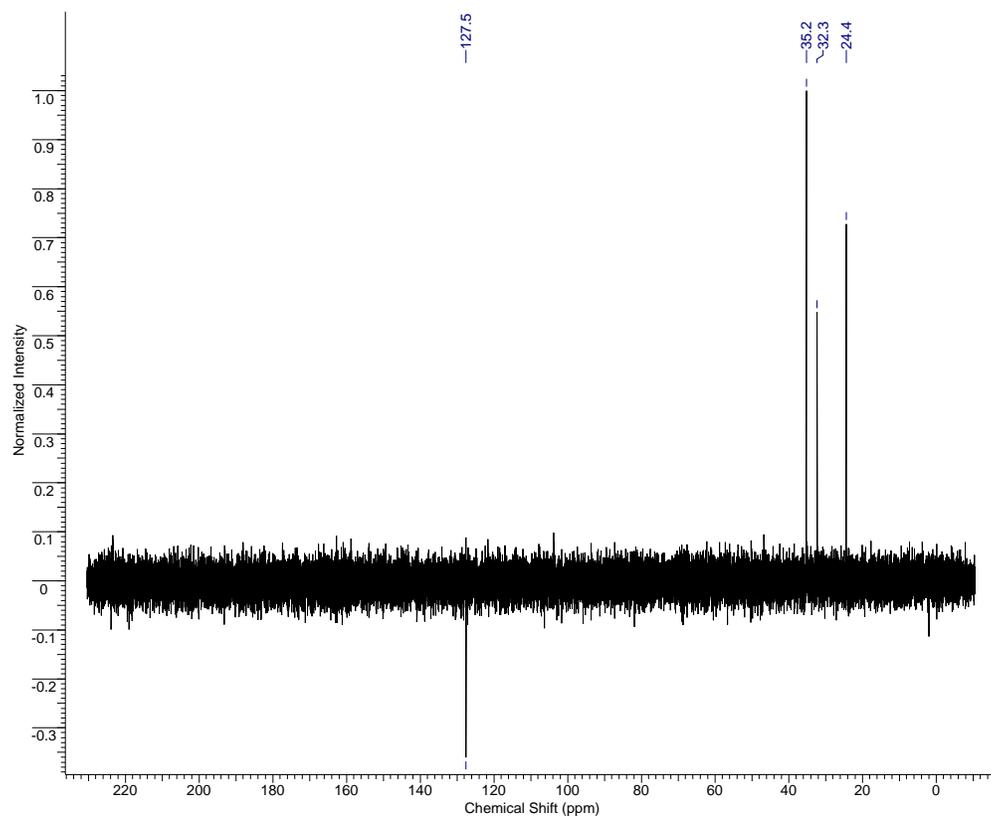
¹H Spectrum of **3j** + **2j**¹³C Spectrum of **3j** + **2j**

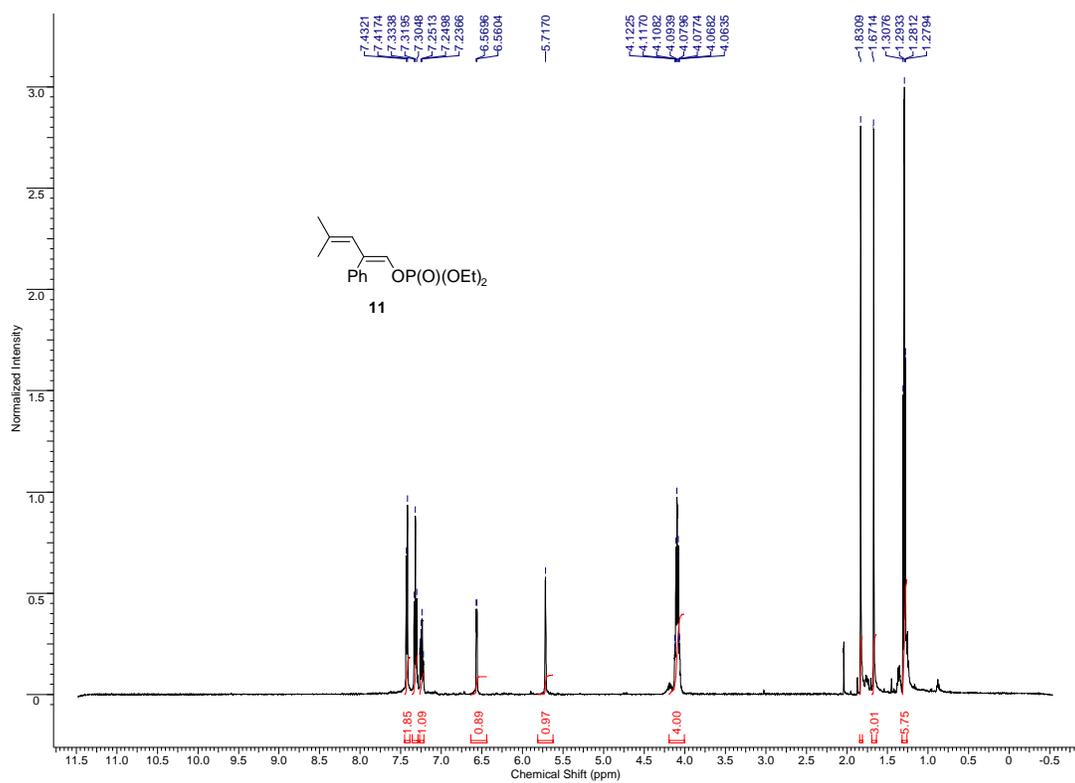
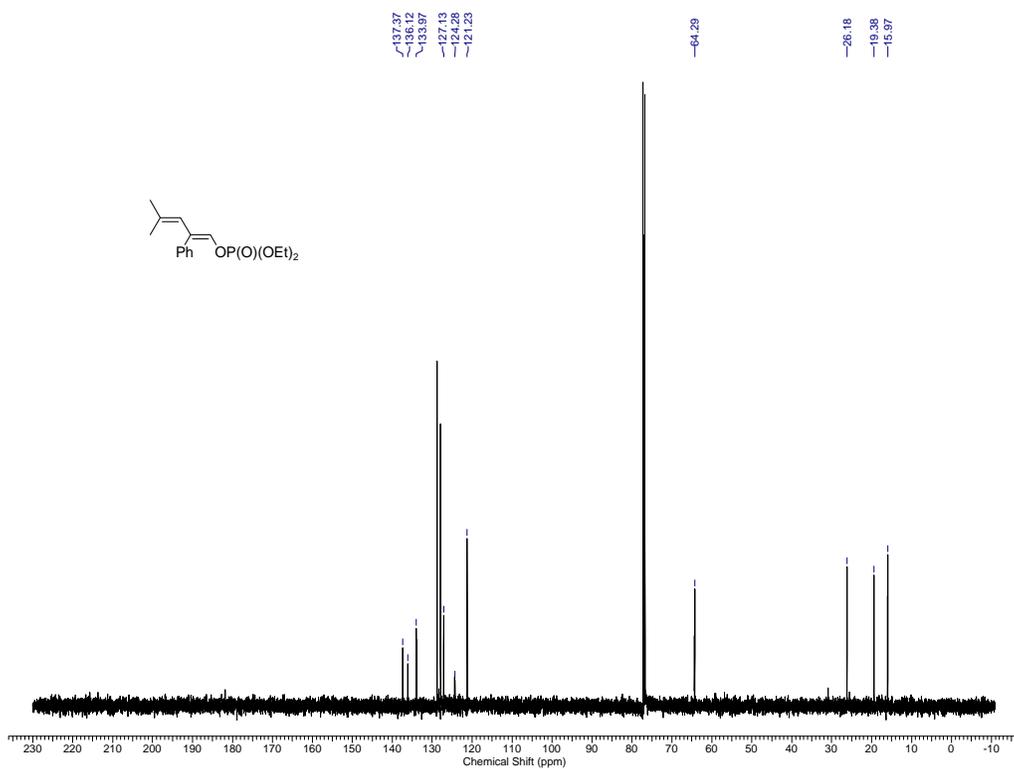
¹H Spectrum of Diethyl (2-(2-fluorocyclohexylidene)vinyl) phosphate¹³C Spectrum of Diethyl (2-(2-fluorocyclohexylidene)vinyl) phosphate

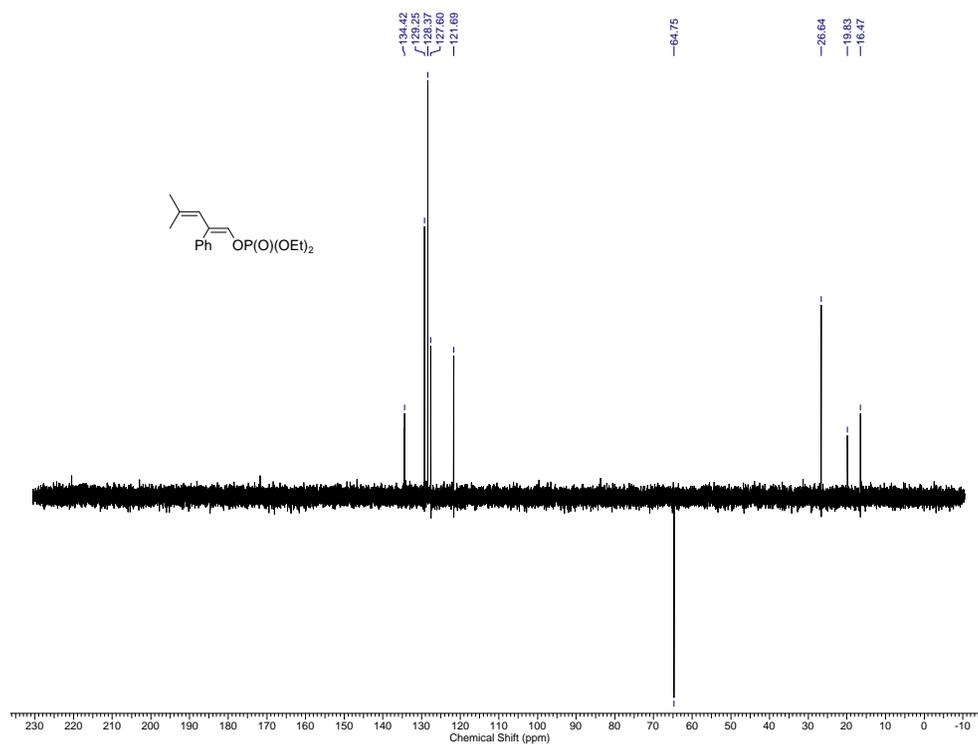
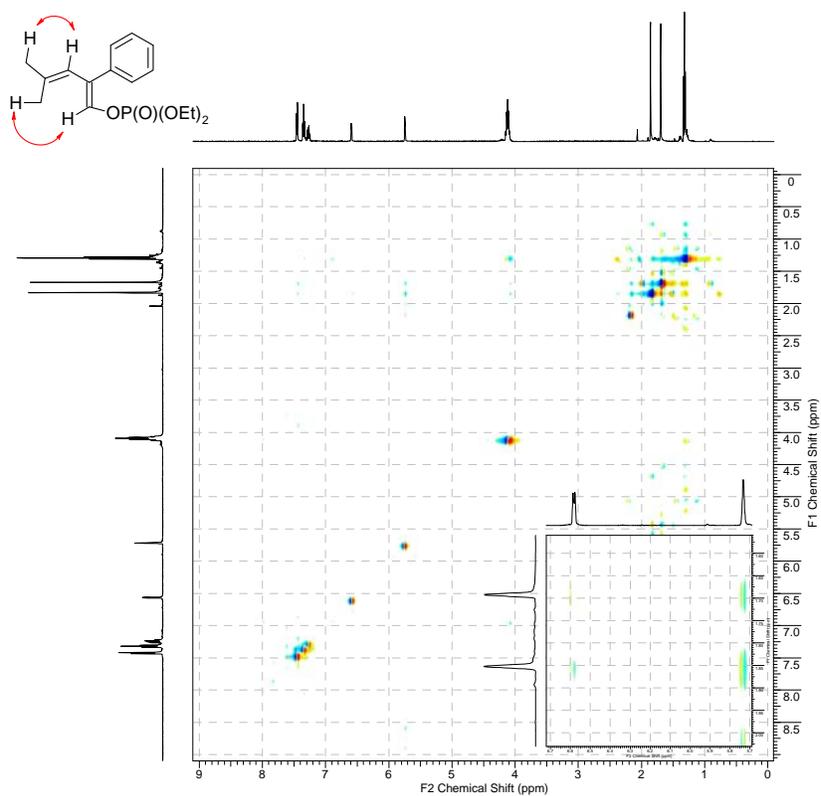
¹H Spectra of Diethyl (2-(2-fluorocycloheptylidene)vinyl) phosphate¹³C Spectra of Diethyl (2-(2-fluorocycloheptylidene)vinyl) phosphate

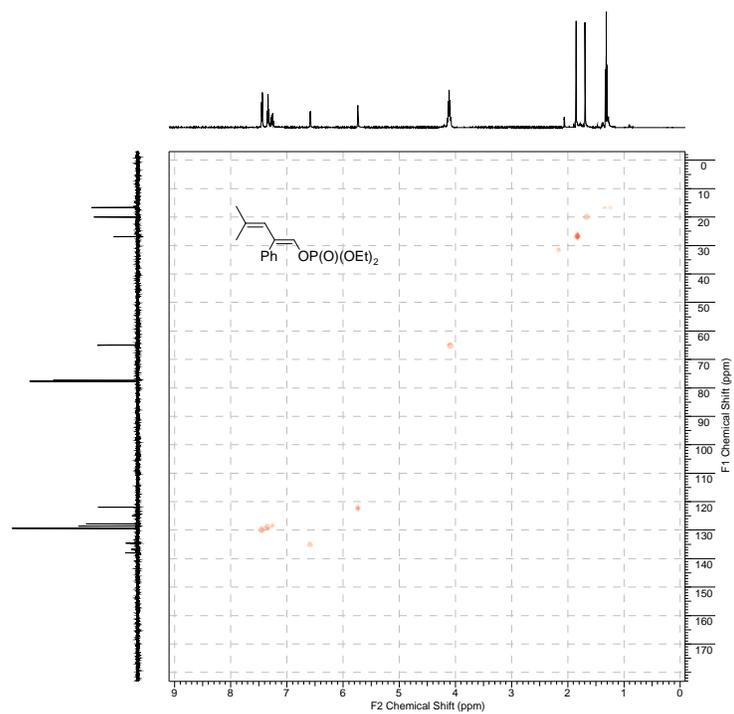
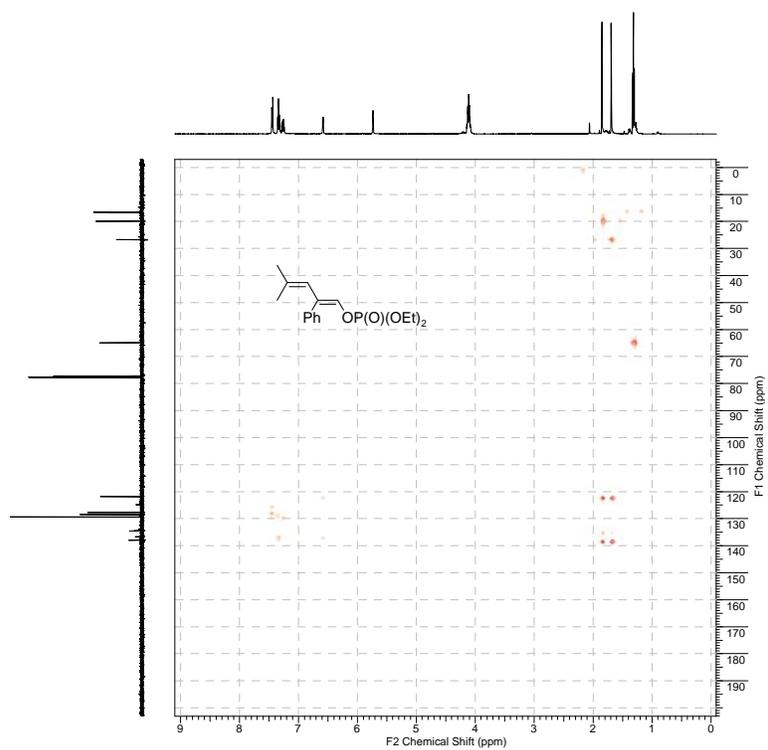
¹H Spectrum of **10**¹³C Spectrum of **10**

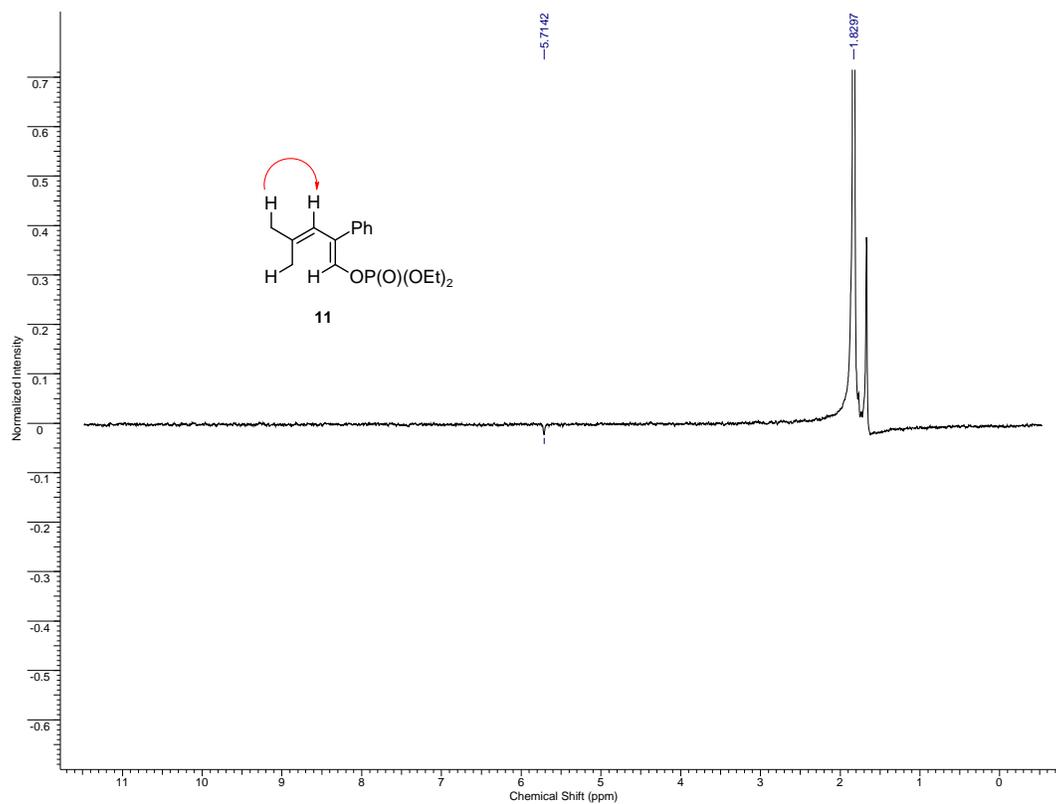
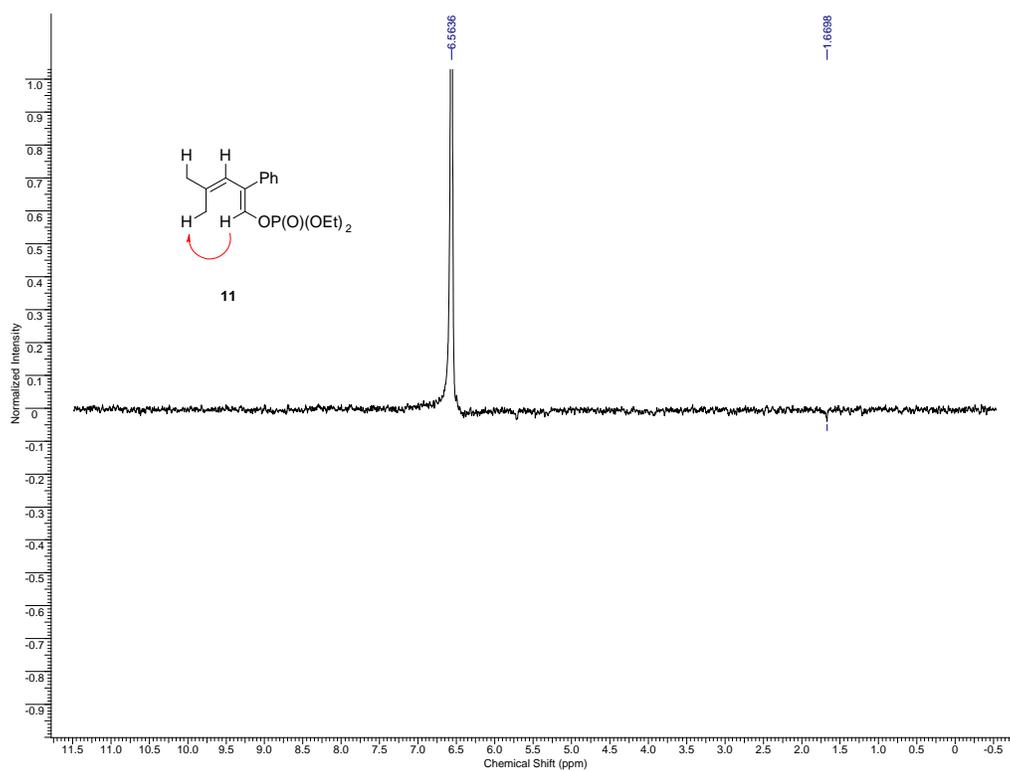
¹H Spectrum of **11**¹³C Spectra of **11**

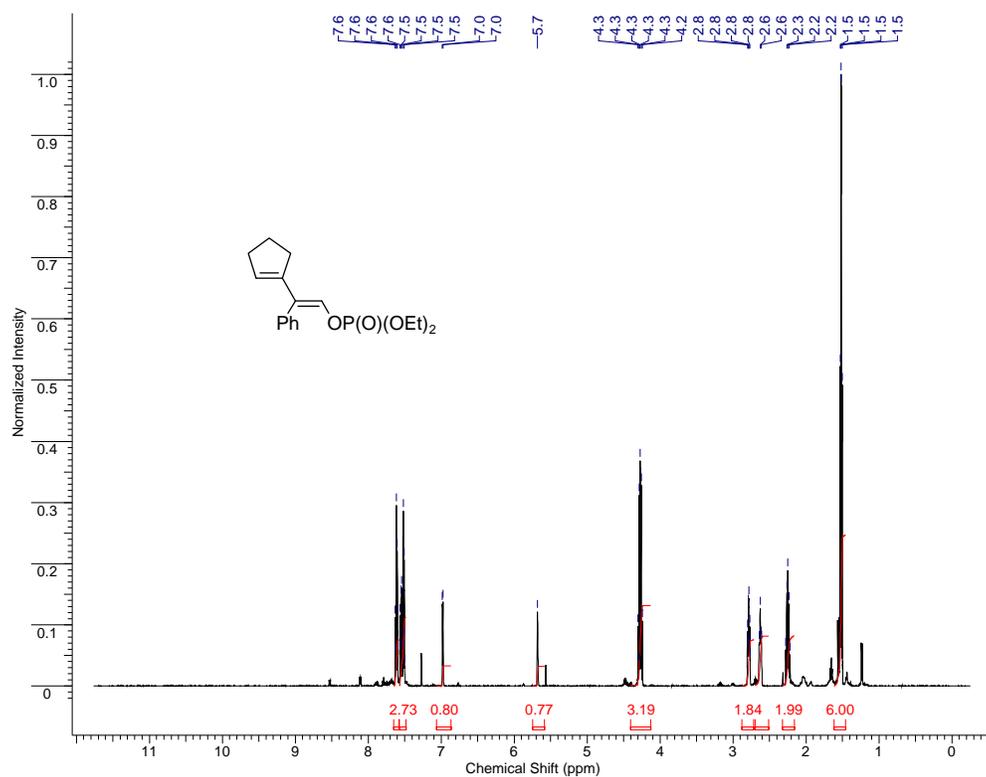
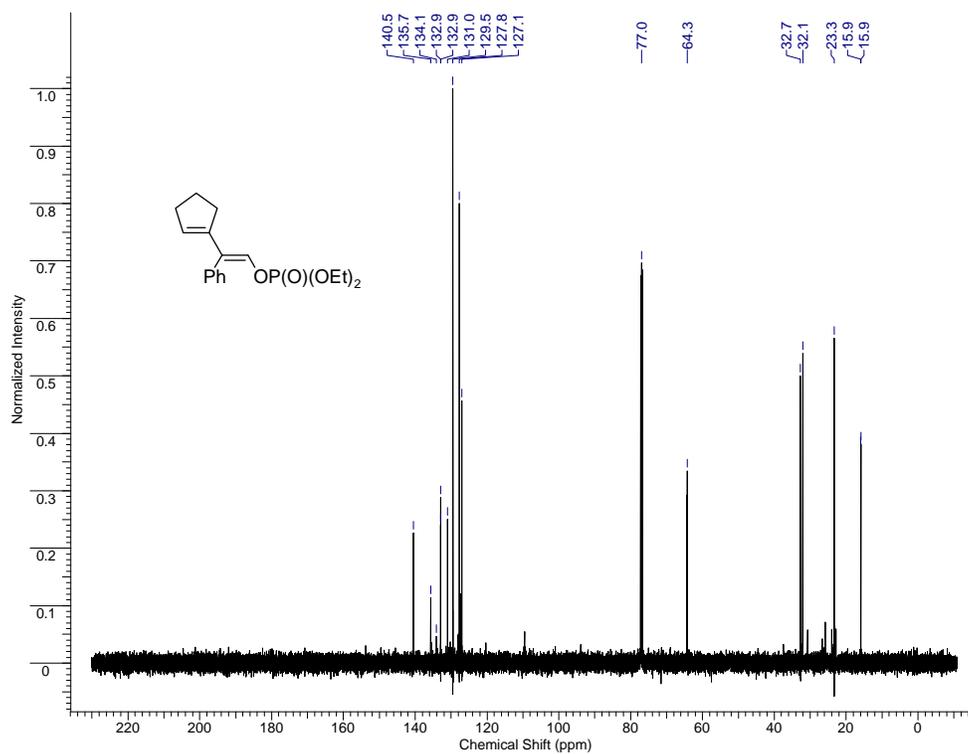
^{13}C -DEPT Spectra of **11**

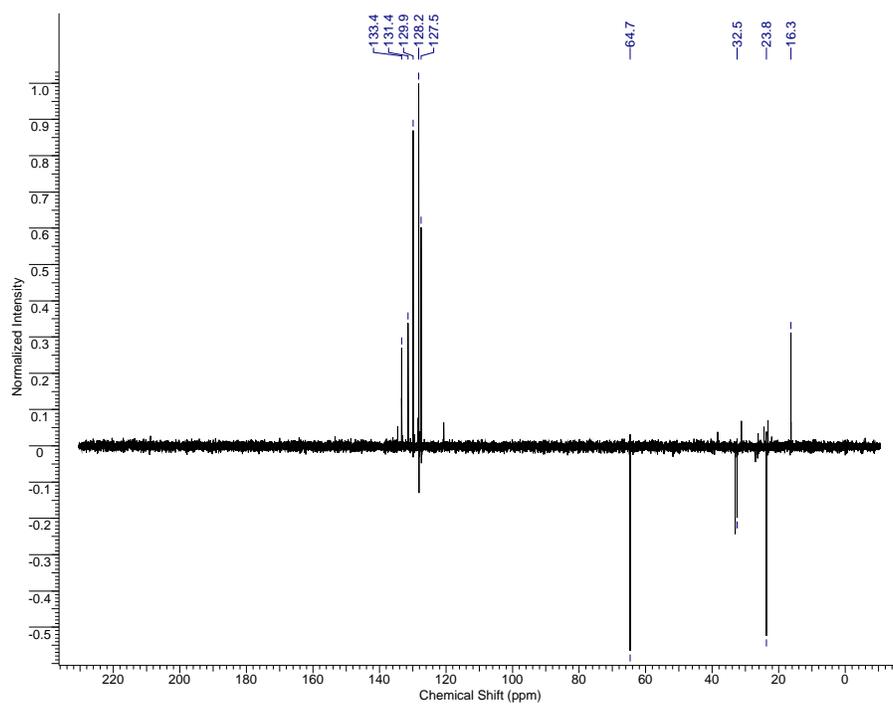
¹H Spectra of 12¹³C Spectra of 12

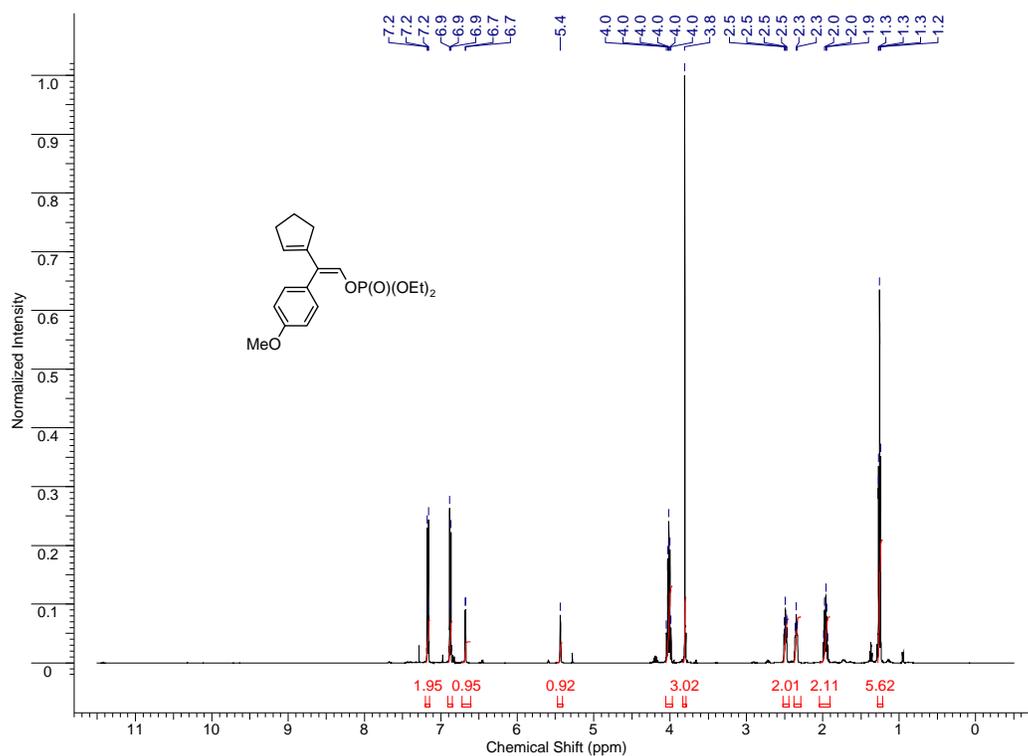
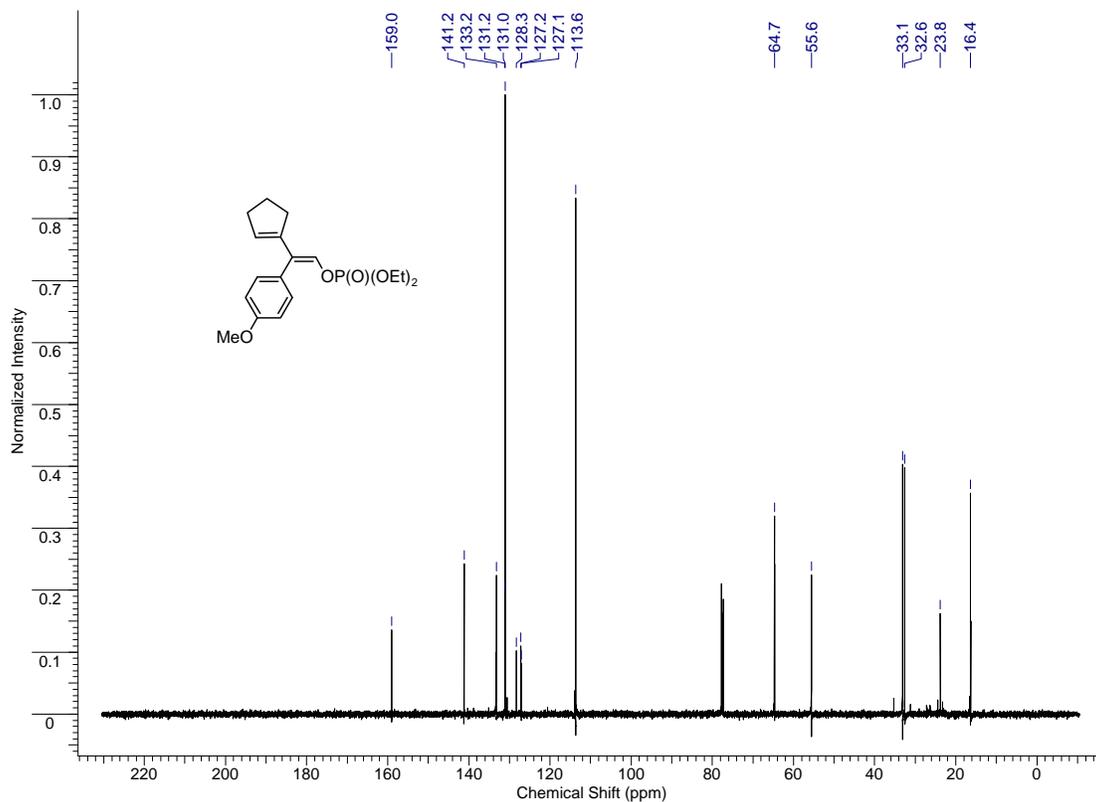
¹³C-DEPT Spectra of **12**NOESY Spectra of **12**

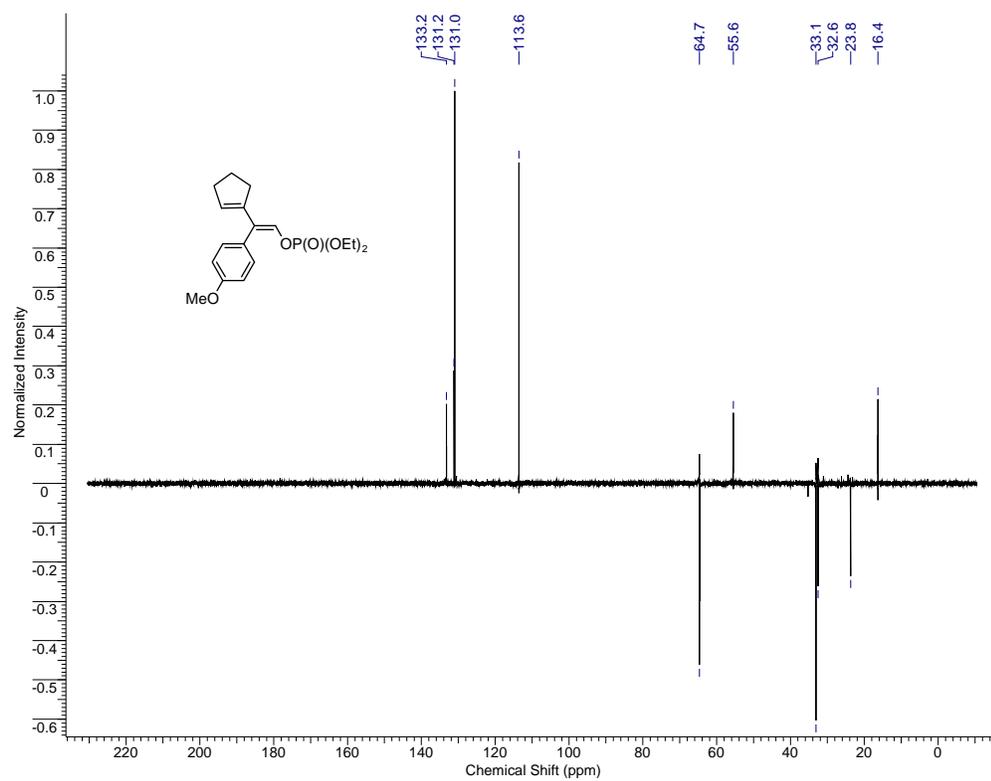
HMQC Spectra of **12**HMBC Spectra of **12**

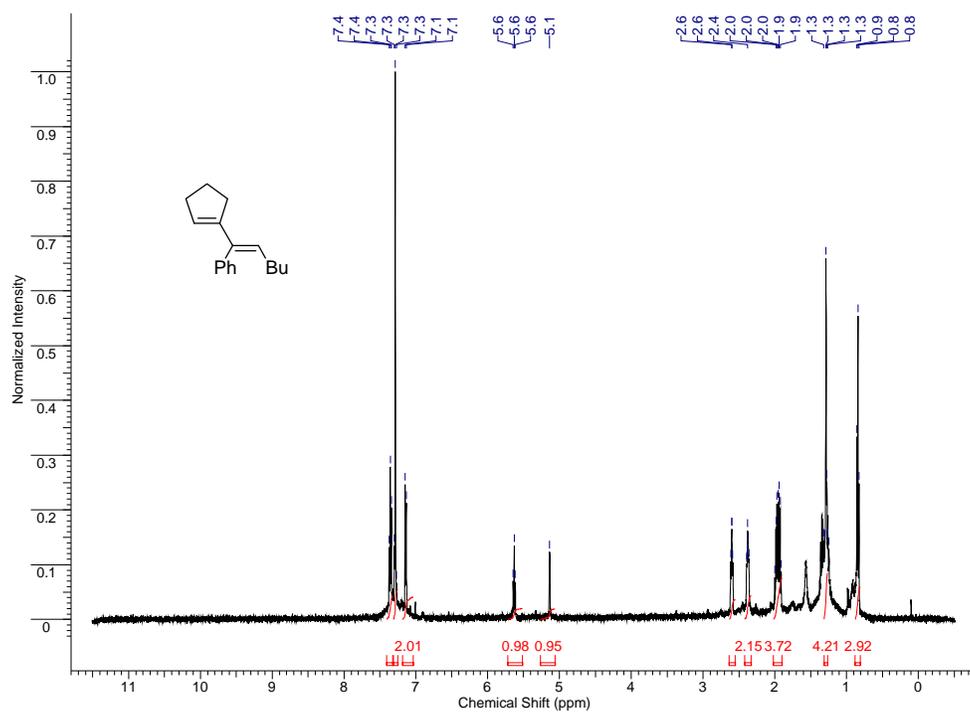
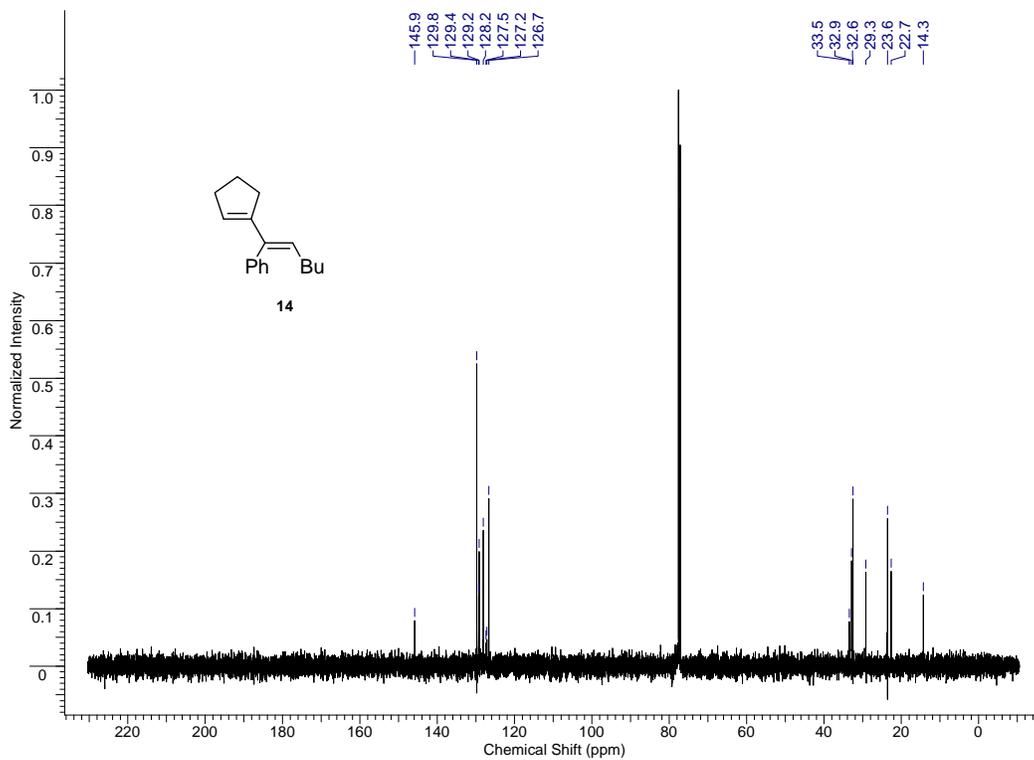
Selective NOESY Spectra of **12**Selective NOESY Spectra of **12**

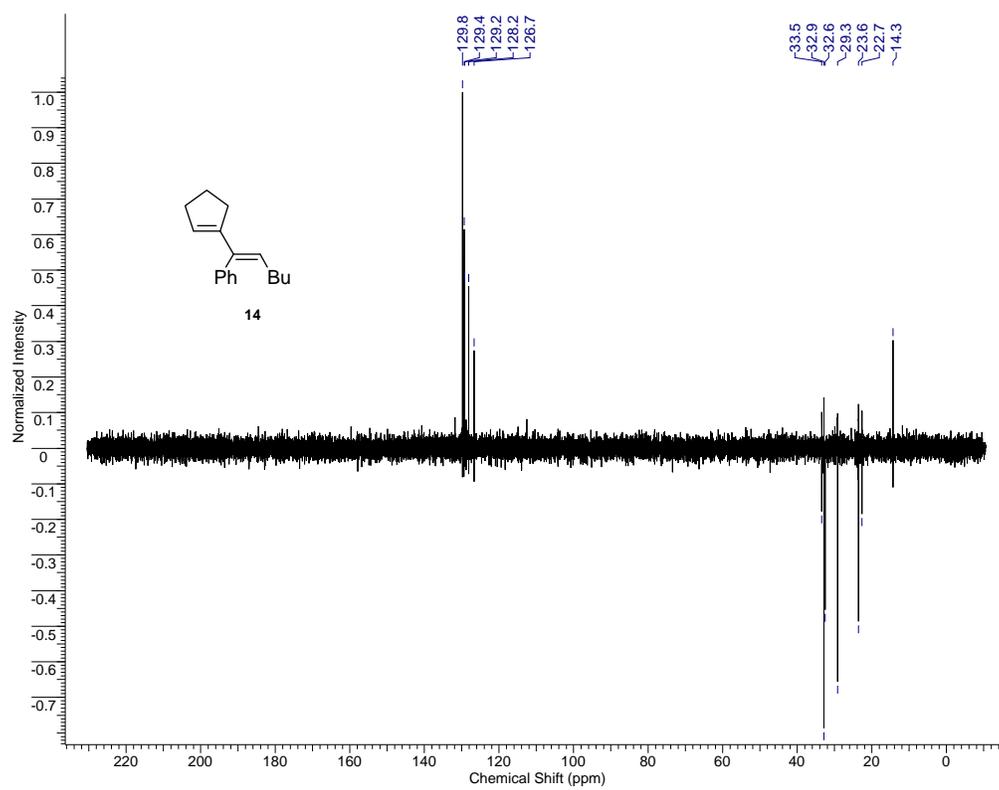
¹H Spectra of 13¹³C Spectrum of 13

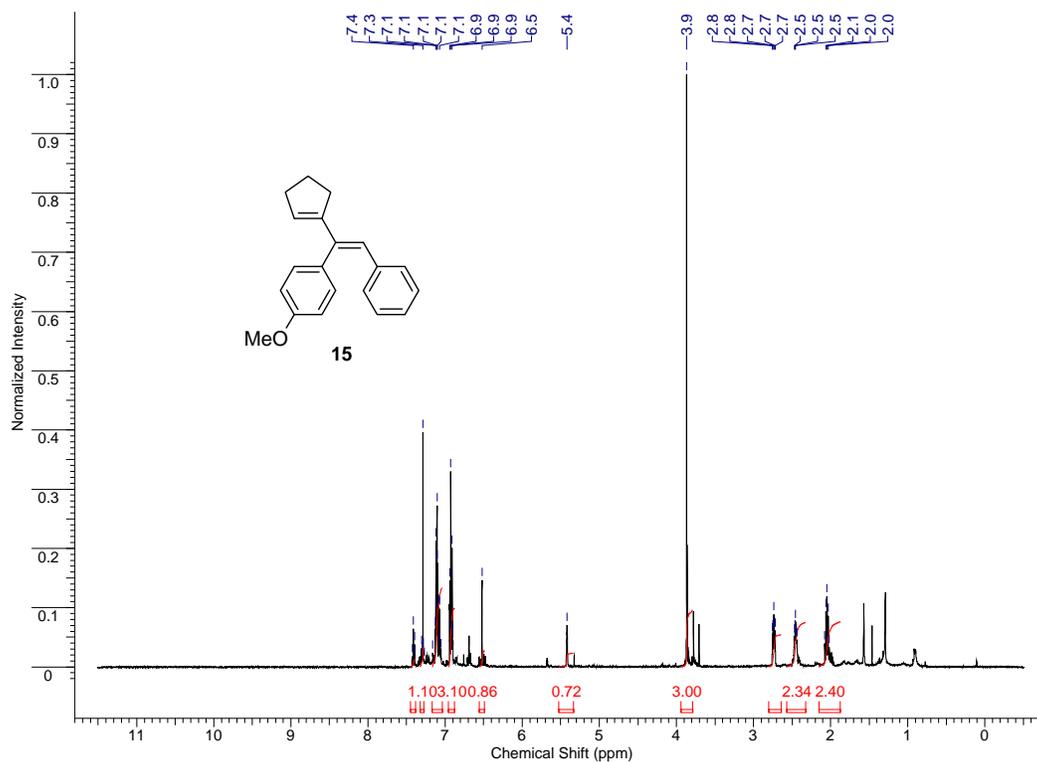
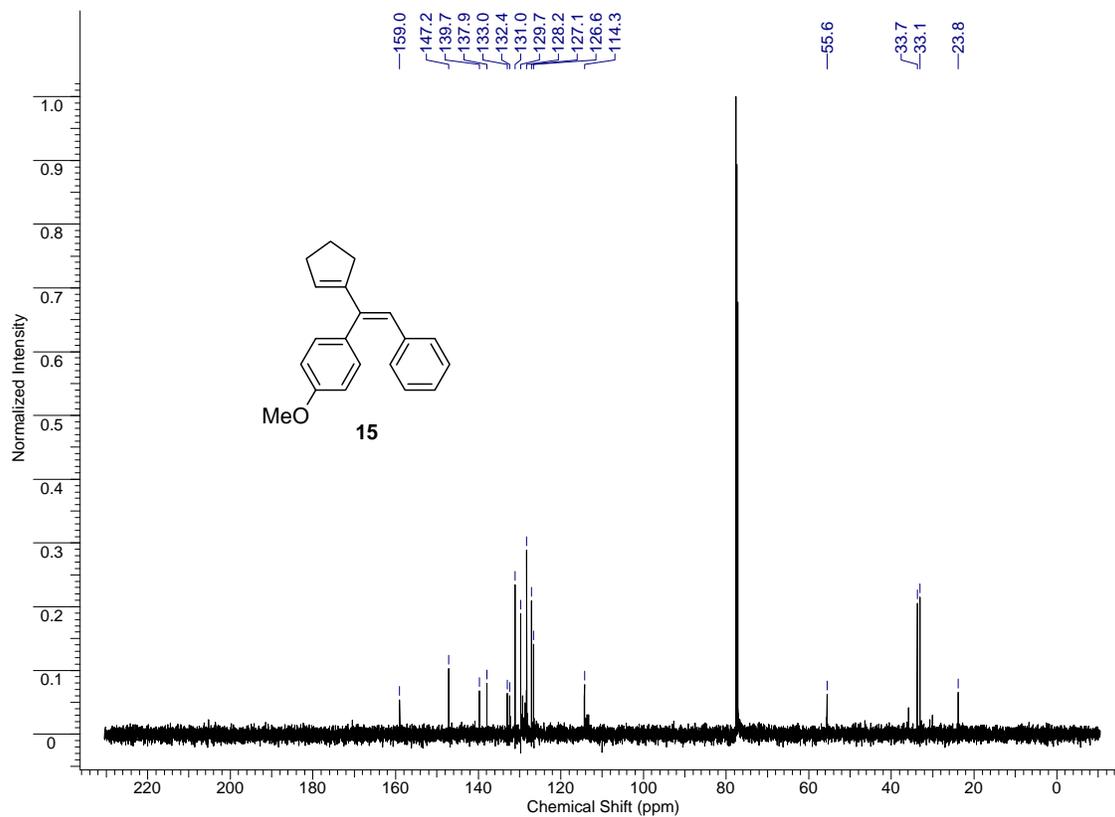
^{13}C -DEPT Spectra of 13

¹H Spectra of (Z)-2-(cyclopent-1-en-1-yl)-2-(4-methoxyphenyl)vinyl diethyl phosphate¹³C Spectra of (Z)-2-(cyclopent-1-en-1-yl)-2-(4-methoxyphenyl)vinyl diethyl phosphate

¹³C-DEPT Spectra of (Z)-2-(cyclopent-1-en-1-yl)-2-(4-methoxyphenyl)vinyl diethyl phosphate

¹H Spectra of **14**¹³C Spectra of **14**

^{13}C -DEPT spectra of **14**

¹H Spectrum of **15**¹³C Spectrum of **15**

¹³C-Dept Spectra of **15**