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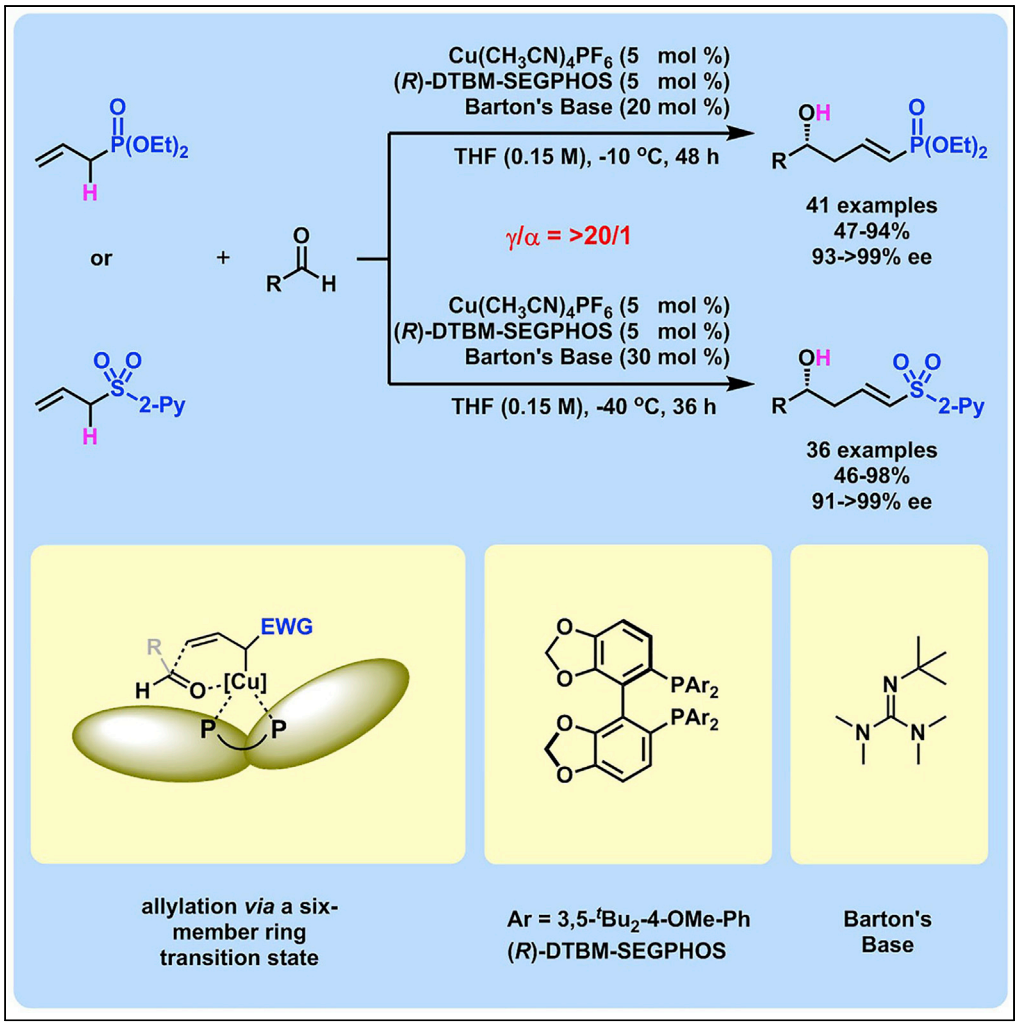

Wen-Jun Yue, Cheng-Yuan Zhang, Liang Yin

liangyin@sioc.ac.cn

HIGHLIGHTS

Asymmetric vinylogous aldol

Excellent regioselectivity

HWE and Julia olefinations

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Asymmetric Vinylogous Aldol-type Reactions of Aldehydes with Allyl Phosphonate and Sulfone

Wen-Jun Yue,[1] Cheng-Yuan Zhang,[1] and Liang Yin[1,2,*]

SUMMARY

Two catalytic asymmetric vinylogous aldol-type reactions of aldehydes with allyl phosphonate and allyl sulfone have been uncovered in good to high yields for the first time. The bulky ligand—(*R*)-DTBM-SEGPHOS—was found to be the key to perfectly control both regio- and enantioselectivities. Transformations of the vinylogous products (including Horner-Wadsworth-Emmons and Julia olefinations) were successfully realized by virtue of the phosphonate and sulfone moieties. Moreover, the present methodology was successfully applied in the asymmetric synthesis of natural products.

INTRODUCTION

Asymmetric vinylogous aldol reaction (VAR) has been one of the most important reactions in the synthesis of complex natural products, especially in the synthesis of polyketides. In the past decades, catalytic asymmetric VAR of aldehydes or ketones has evolved from classical Mukaiyama vinylogous aldol reaction (Denmark et al., 2005; Casiraghi et al., 2011; Pansare and Paul, 2011; Bisai, 2012; Kalesse et al., 2014; Hosokawa, 2018a, 2018b) to direct vinylogous aldol reaction (DVAR) (Li and Yin, 2018; Otsuka et al., 2013; Zhu et al., 2013; Li et al., 2014; Han and Chang, 2016; Jing et al., 2016; Ray and Mukherjee, 2018), which enjoys the advantages of easy reaction protocol and high atom economy (Trost, 1991; Anastas and Crabtree, 2009; Newhouse et al., 2009). However, the nucleophiles in DVAR were mainly limited to unsaturated carbonyl compounds and their close derivatives (Bai et al., 2017). Unsaturated phosphonates or phosphine oxides, as well as unsaturated sulfones, have never been investigated as prenucleophiles in vinylogous aldol-type reactions.

In such reactions, synthetically versatile chiral vinylogous products containing α,β-unsaturated phosphonate or phosphine oxide moiety or α,β-unsaturated sulfone motif (Nishida et al., 2008; Xue et al., 2011; Konno et al., 2012; Lefevre et al., 2013; Hornillos et al., 2015; Lim and Hayashi, 2015, 2017; Wang and Hayashi, 2018; El-Awa et al., 2009; Alba et al., 2010; Nielsen et al., 2010; Zhu and Lu, 2010; Moteki et al., 2010; Quintard et al., 2011; Moure et al., 2011; Nishimura et al., 2012; Halskov et al., 2012; Zhou et al., 2012; Hernández-Toribio et al., 2012), would be produced. Furthermore, phosphonates and phosphine oxides had great applications in medicinal and agricultural chemistry (Mucha et al., 2011; Ordóñez et al., 2012; Corbridge, 2013; Horsman and Zechel, 2017). Sulfones, especially α,β-unsaturated sulfones, were widely distributed in biologically active compounds, even in the commercial pharmaceuticals (Meadows and Gervay-Hague, 2006; Dunny et al., 2013; Woo et al., 2014; Fang et al., 2016). Therefore it is highly desirable to achieve a vinylogous aldol-type reaction of unsaturated phosphonates or phosphine oxides, as well as unsaturated sulfones.

One inherent difficulty faced in the vinylogous aldol-type reaction of allyl phosphonate or allyl sulfone is the control of regioselectivity. The addition of allyl phosphonate to aldehyde was investigated by Yuan and co-workers in detail (Scheme 1A) (Yuan et al., 1990, 1991). Treating allyl phosphonate with ^{n}BuLi in tetrahydrofuran (THF) at −70°C afforded the corresponding delocalized allylic carbanion, which reacted with benzaldehyde to give a mixture of α- and γ-adducts. α-Addition was the natural tendency and thus dominated the addition pathways, which led to the vinylogous product (γ-adduct) in significantly low yield. Increasing the steric hindrance of the alkyl group in phosphonate only led to a slight improvement of the γ-selectivity.

Furthermore, the addition of allyl sulfone to benzaldehyde catalyzed by a phosphine-based strong base was studied by Verkade and co-workers, which delivered the α-adduct in 63% yield at −78°C (Scheme 1B) (Kisanga and Verkade, 2002). The same reaction promoted by stoichiometric ^{n}BuLi also afforded the

[1]CAS Key Laboratory of Synthetic Chemistry of Natural Substances, Centre for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

[2]Lead Contact

*Correspondence: liangyin@sioc.ac.cn

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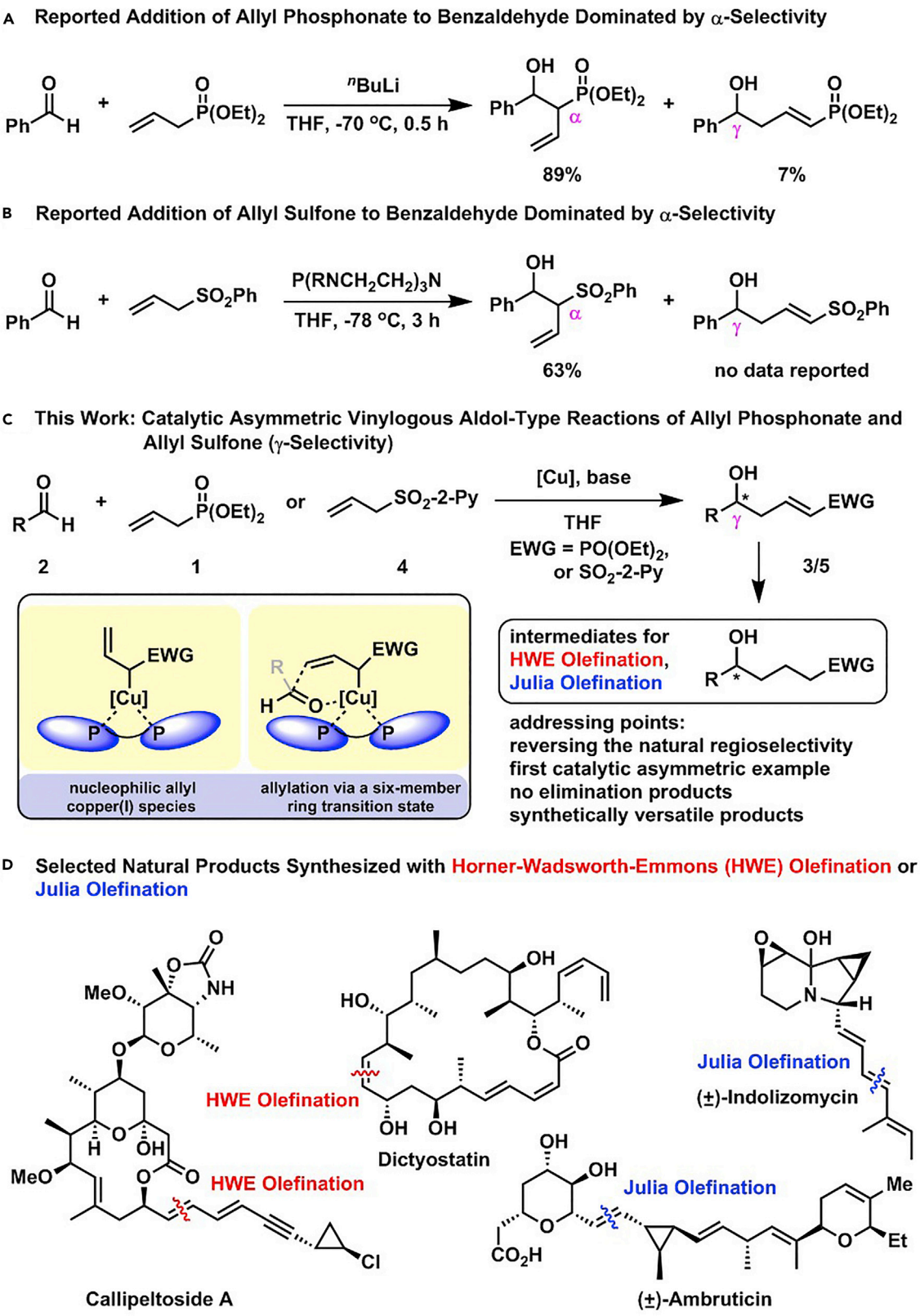


Scheme 1. Aldol-type Reactions of Aldehydes with Allyl Phosphonate and Sulfone and Selected Natural Products Synthesized with Horner-Wadsworth-Emmons and Julia Olefinations

α-adduct exclusively, which was employed to prepare acyclic 2-phenylsulfonyl 1,3-diene in 89% yield (Cuvigny et al., 1983, 1986; Chinkov et al., 2003). Obviously, it is challenging to overcome the inherent α-selectivity in the aldol-type reactions of allyl phosphonate and allyl sulfone. The other difficulty in the DVAR is the remote asymmetric induction as the functional group (aldehyde, ketone, ester, and amide generally, and phosphonate or sulfone here) is far from the reactive γ-position in form, which was viewed as a challenge in asymmetric catalysis (Shirokawa et al., 2004). To the best of our knowledge, there is no reported enantioselective method to carry out a vinylogous aldol-type reaction of allyl phosphonate or allyl sulfone (Scheme 1C).

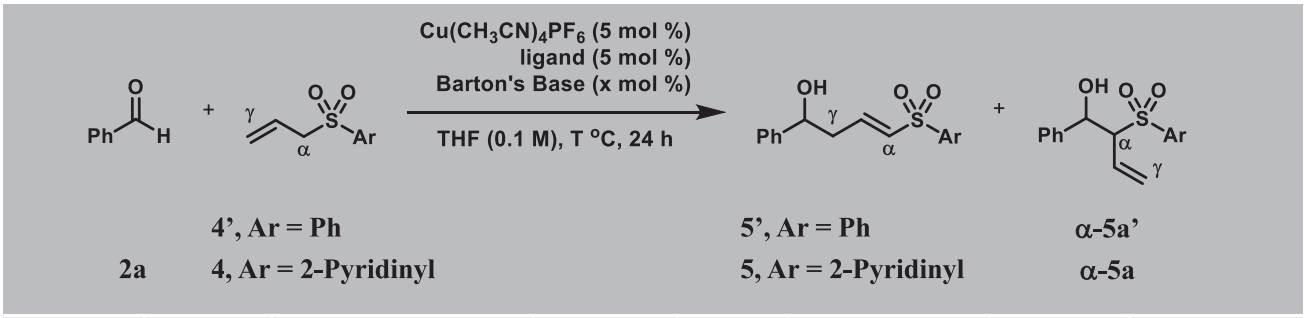
The α-carbanions of phosphonate and sulfone have been employed as nucleophiles in Horner-Wadsworth-Emmons (HWE) and Julia olefinations, which were identified as two prominent synthetic tools to assemble the carbon-carbon double bond in organic synthesis, especially in the total synthesis of complex natural products (Kobayashi et al., 2018; Ma et al., 2010) (such as callipeltoside A, dictyostatin, indolizomycin and ambruticin) (Scheme 1D) (Trost et al., 2002; Ho et al., 2013; Kim et al., 1993; Liu and Jacobson, 2001). The products from the saturation of vinylogous aldol-type products (**3**/**5**) would be suitable substrates for HWE and Julia olefinations for further structure elaboration. Herein, we report two asymmetric vinylogous aldol-type reactions of aldehydes with allyl phosphonate and allyl sulfone catalyzed by a bulky chiral copper(I) complex and an organic base. The deprotonation of allyl phosphonate or allyl sulfone would generate a nucleophilic allylcopper(I) species, which afforded the vinylogous product through an asymmetric allylation via a six-member ring transition state (Scheme 1C).

RESULTS AND DISCUSSION

The reaction of allyl sulfone **4′**/**4** and benzaldehyde (**2a**) was investigated as a model reaction in the presence of $Cu(CH_3CN)_4PF_6$, phosphine ligand, and Barton's base (Table 1). In all cases with **4′**, the vinylogous product **5a′** was obtained with unsatisfactory regio- and enantioselectivities (entries 1–9). (*R*)-DTBM-SEGPHOS, an effective bulky ligand, led to good control of the enantioselectivity in our previously reported catalytic asymmetric aldol reaction of unsaturated esters and aldehydes (Zhang and Yin, 2018) and gave excellent control of the regioselectivity. The enantioselectivity was improved from 43% to 76% by switching phenyl to 2-pyridinyl (entry 10). Lowering the temperature to −40°C resulted in 97% enantiomeric excess (ee) for **5a** (entry 11). The moderate yield was enhanced to 98% by changing the ratio of **2a**/**4**, increasing the amount of Barton's base to 30 mol %, and prolonging the reaction time to 36 h (entries 12–14). Finally, the catalyst loading was successfully decreased to 3 mol % without changing both regio- and enantioselectivities (entry 15).

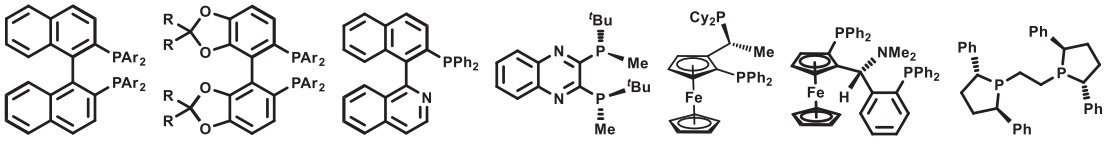
By modifying the optimized reaction conditions for **4** (3 equiv. **1**, 20 mol % Barton's base, and −10°C), the substrate scope of aldehydes **2** in the reaction with allyl phosphonate **1** was studied (Table 2). Aromatic aldehydes with electron-withdrawing groups or electron-donating groups were competent substrates to generate the corresponding vinylogous products uniformly in good yields with both excellent regioselectivity (>20/1) and excellent enantioselectivity (≥95% ee) (**3a**-**3o**). Moreover, the reaction was not sensitive to the position of a substituent on the phenyl ring of the aromatic aldehydes. Even the sterically congested *ortho*-CF_3-benzaldehyde afforded the product **3l** in 91% yield with 95% ee. 1-Naphthaldehyde was also an excellent substrate (**3p**). Moreover, the present reaction conditions were applicable to various heteroaromatic aldehydes (**3q**-**3x**). Although the yields were moderate in some cases, both regio- and enantioselectivities were excellent. Particularly noteworthy are the aldehydes containing a pyridine motif (**3t**) and a carbazole motif (**3x**) as these functional groups potentially can coordinate to the metal center and thus deactivate the catalyst.

α,β-Unsaturated aldehydes also served as suitable substrates (**3y**-**3ai**). Aryls, heteroaryls, alkyls, and vinyls with substituent were well tolerated at the β-position of the α,β-unsaturated aldehydes. Moreover, functional groups, such as alkyl chloride (**3af**), *tert*-butyldimethylsilyl (TBS)-ether (**3ag**), alkynyl (**3ah**), and prenyl (**3ai**), remained intact in the present reaction conditions. These functional groups offer the opportunity for further structure elaboration. It is noteworthy that acrolein (**2ab**), susceptible to conjugate addition, served as a suitable substrate to give the vinylogous product **3ab** in moderate yield with excellent enantioselectivity. The chiral aldehydes, including α,β-unsaturated aldehyde **2aj** derived from (−)-citronellal, (−)-perillaldehyde (**2ak**), and (−)-myrtenal (**2al**), were also investigated with both (*R*)-DTBM-SEGPHOS and (*S*)-DTBM-SEGPHOS. In both cases, the products (**3aj**, **3aj′**, **3ak**, **3ak′**, **3al**, and **3al′**) were obtained in good yields with excellent diastereoselectivity, which indicated that the asymmetric



Entry	Ar	Ligand	T (°C)	x	Total yield[b]	γ/α[b]	ee of 5a′/5a[c]
1	Ph	(*R*)-BINAP	rt	5	52%	1/1.5	45%
2	Ph	(*R*)-TOL-BINAP	rt	5	43%	1/1	33%
3	Ph	(*R*)-SEGPHOS	rt	5	42%	1/1.5	8%
4	Ph	(*R*)-QUINAP	rt	5	11%	1/1	40%
5	Ph	(*R*,*R*)-QUINOXP*	rt	5	48%	1.5/1	8%
6	Ph	(*R*)-(*S*)-JOSIPHOS	rt	5	51%	1/1	58%
7	Ph	(*R*,R_p)-TANIAPHOS	rt	5	47%	1/2	51%
8	Ph	(*R*,*R*)-Ph-BPE	rt	5	37%	1/1	14%
9	Ph	(*R*)-DTBM-SEGPHOS	rt	5	80%	>20/1	43%
10	2-Py	(*R*)-DTBM-SEGPHOS	rt	5	70%	>20/1	76%
11	2-Py	(*R*)-DTBM-SEGPHOS	−40	5	76%	>20/1	97%
12[d]	2-Py	(*R*)-DTBM-SEGPHOS	−40	5	79%	>20/1	97%
13[d]	2-Py	(*R*)-DTBM-SEGPHOS	−40	30	92%	>20/1	97%
14[d,e]	2-Py	(*R*)-DTBM-SEGPHOS	−40	30	98%	>20/1	97%
15[d,e,f]	2-Py	(*R*)-DTBM-SEGPHOS	−40	30	82%	>20/1	97%

Table 1. Optimization of the Reaction Conditions[a]



HPLC, high-performance liquid chromatography; NMR, nuclear magnetic resonance

[a] **4/4′**, 0.1 mmol; **2a**, 0.2 mmol.

[b] Determined by ^{1}H NMR analysis of reaction crude mixture using mesitylene as an internal standard.

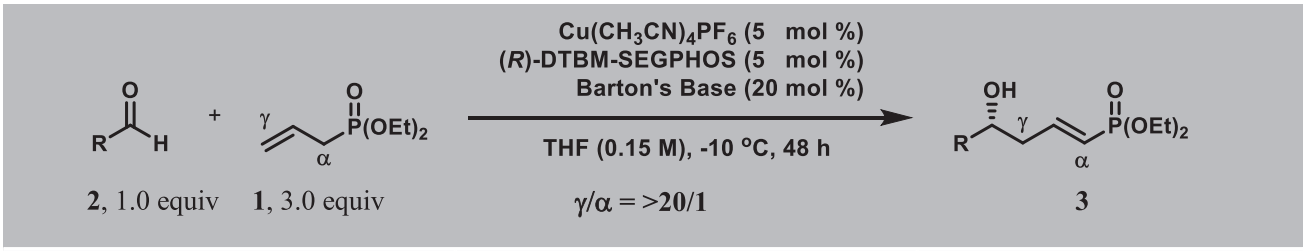
[c] Determined by chiral-stationary-phase HPLC analysis.

[d] **4**. 0.2 mmol; **2a**. 0.1 mmol.

[e] 36 h.

[f] $Cu(CH_3CN)_4PF_6$ and ligand, 3 mol %, Barton's base = 2-^{t}Bu-1,1,3,3-tetramethylguanidine.

introduction was dominated by the copper(I)-catalyst. The absolute configuration of **3a** was determined to be *R* by transforming it to a reported compound (for details, see Supplemental Information). The absolute configurations of other products were tentatively assigned by analogy.



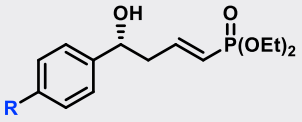
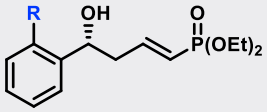
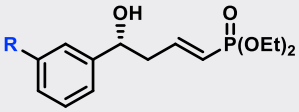
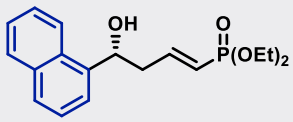
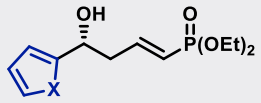
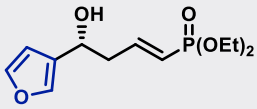
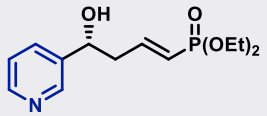
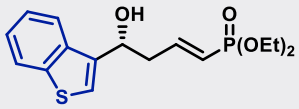
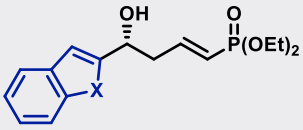
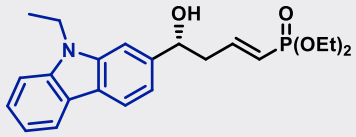
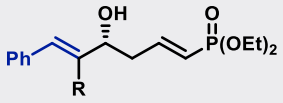
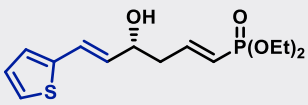
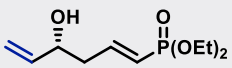
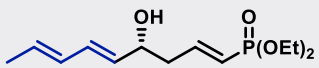
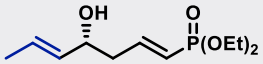
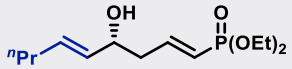
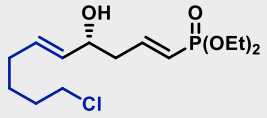
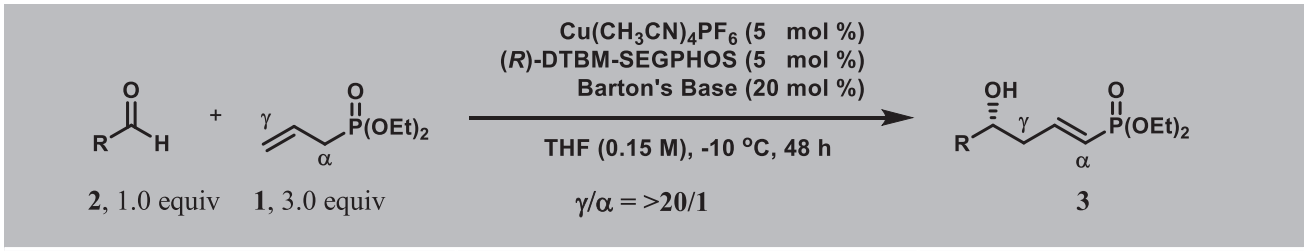
		
R = H, 3a, 85%, 99% ee;[b] R = F, 3b, 81%, 99% ee; R = Cl, 3c, 74%, 99% ee; R = Br, 3d, 77%, 98% ee; R = I, 3e, 92%, 99% ee; R = Me, 3f, 80%, 98% ee; R = ^{t}Bu, 3g, 90%, >99% ee; R = CH_3S, 3h, 85%, >99% ee; R = CH_3O, 3i, 81%, 97% ee; R = CF_3O, 3j, 83%, 99% ee;	R = F, 3k, 90%, 98% ee; R = CF_3, 3l, 91%, 95% ee; R = OCH_3, 3m, 91%, 98% ee;	R = Cl, 3n, 81%, 98% ee; R = Br, 3o, 88%, 97% ee;
		
	3p, 94%, 99% ee;	X = O, 3q, 85%, >99% ee; X = S, 3r, 91%, >99% ee;
		
3s, 76%, 98% ee;	3t, 55%, >99% ee;	3u, 85%, >99% ee;
		
X = O, 3v, 81%, 97% ee; X = S, 3w, 90%, >99% ee;	3x, 58%, >99% ee;	R = H, 3y, 76%, 97% ee; R = Me, 3z, 78%, 98% ee;
		
3aa, 85%, 98% ee;	3ab, 68%, 93% ee;	3ac, 58%, 97% ee;
		
3ad, 68%, 95% ee;	3ae, 71%, 93% ee;	3af, 71%, 97% ee;

Table 2. Substrate Scope of Aldehydes in the Reaction with 1[a]

(Continued on next page)



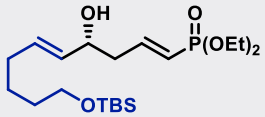
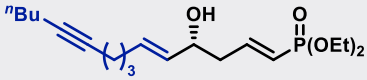
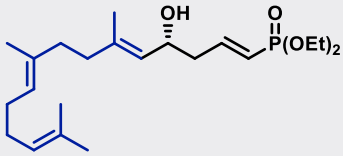
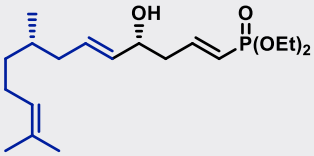
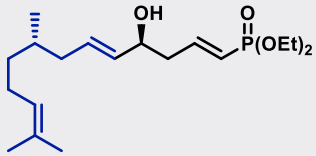
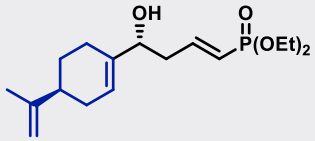
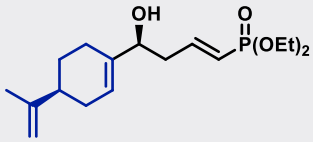
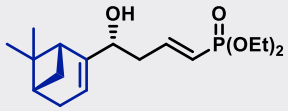
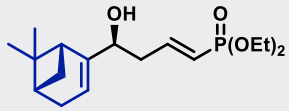
		
3ag, 47%, 98% ee;	3ah, 85%, 98% ee;	3ai, 68%, 99% ee;
		
3aj, 52%, 15/1 dr;	3aj′, 60%, >20/1 dr;[c]	3ak, 58%, >20/1 dr;
		
3ak′, 79%, >20/1 dr;[c]	3al, 88%, >20/1 dr;	3al′, 61%, >20/1 dr[c]

Table 2. Continued

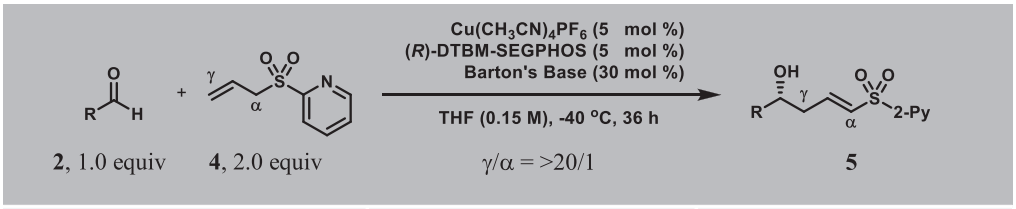
HPLC, high-performance liquid chromatography; NMR, nuclear magnetic resonance

[a]**2**, 0.3 mmol; **1**, 0.9 mmol. Isolated yield was reported. Regio- and diastereoselectivity were determined by ^{1}H NMR analysis of reaction crude mixture. Enantioselectivity was determined by chiral-stationary-phase HPLC analysis.

[b]Gram-scale synthesis.

[c](*S*)-DTBM-SEGPHOS was used.

Moreover, the substrate scope of aldehydes in the reaction with allyl sulfone **4** was evaluated (Table 3). Various aromatic aldehydes with a substituent at *ortho*-, *meta*-, or *para*-position were suitable substrates. Both 1-naphthyl and 2-naphthyl aldehydes were well applicable. The vinylogous products (**5a**-**5h**, **5k**, **5l**, **5n**, **5o**, **5p**, and **5am**-**5aq**) were isolated in moderate to excellent yields with excellent regio- and enantioselectivities. Heteroaromatic aldehydes also served as competent substrates without compromising enantioselectivity (**5q**, **5r**, **5u**, **5x**, **5ar** and **5as**). As for α,β-unsaturated aldehydes, aryls, heteroaryls, vinyls with substituent, and alkyls were accepted at β-position (**5y**, **5z**, **5aa**, **5ad**, **5ae**, **5at**, **5au**, and **5ah**). Moreover, the reaction conditions were successfully applied to chiral natural products bearing α,β-unsaturated aldehyde moiety, such as (−)-perillaldehyde (**2ak**) and (−)-myrtenal (**2al**). The corresponding vinylogous products (**5ak**, **5ak′**, **5al**, and **5al′**) were obtained in moderate yields with high diastereoselectivity. It is evident that in the case of (−)-myrtenal with (*S*)-DTBM-SEGPHOS, mismatch phenomenon was observed. The absolute configuration of **5a** was assigned to be *R* by its transformation to a known compound (for details, see Supplemental Information). Analogically, the stereochemistry of other products was dictated tentatively. It should be pointed out that the gram-scale syntheses of both **3a** and **5a** were successfully carried out with constant results. Moreover, it should be mentioned that aliphatic aldehydes afforded α-adducts mainly in low yields at the present reaction conditions, which is a limitation of the present reactions. However, the vinylogous products of aliphatic aldehydes could be potentially accessed by the transformations of vinylogous products of various α,β-unsaturated aldehydes by means of the carbon-carbon double bond.



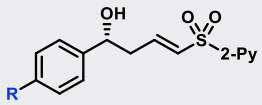
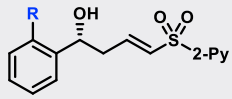
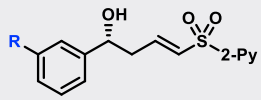
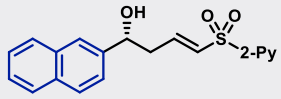
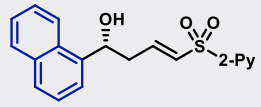
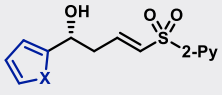
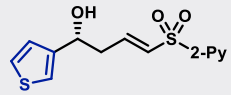
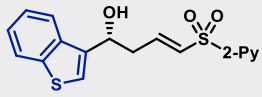
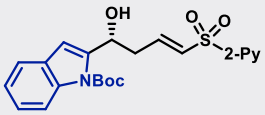
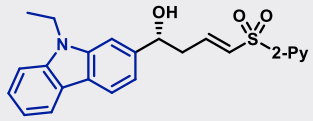
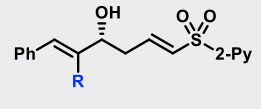
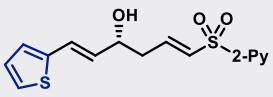
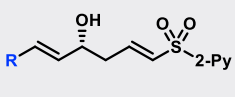
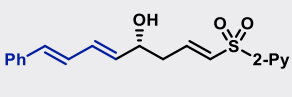
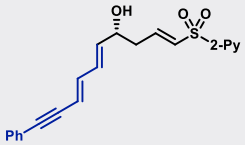
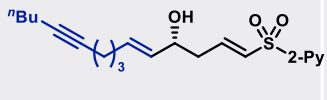
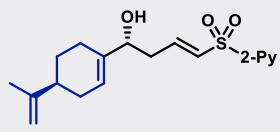
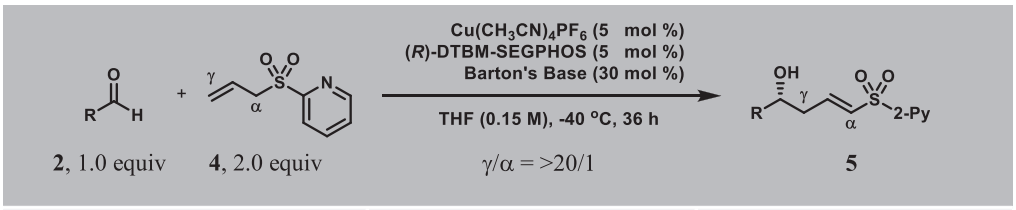
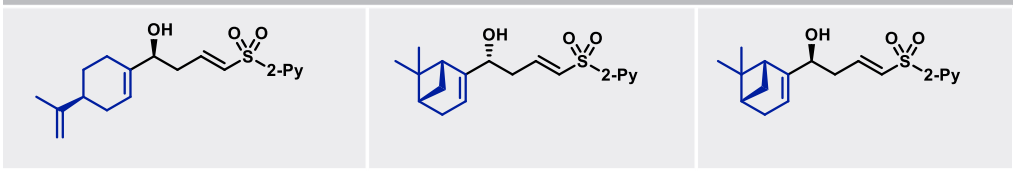
		
R = H, **5a**, 95%, 97% ee;[b] R = F, **5b**, 88%, 97% ee; R = Cl, **5c**, 93%, 97% ee; R = Br, **5d**, 85%, 92% ee; R = I, **5e**, 82%, 91% ee; R = Me, **5f**, 96%, 97% ee; R = ^{t}Bu, **5g**, 91%, 95% ee; R = CH_3S, **5h**, 90%, 97% ee; R = CO_2Me, **5am**, 76%, 98% ee;	R = F, **5K**, 95%, 98% ee; R = Br, **5an**, 85%, 92% ee; R = Me, **5ao**, 98%, 99% ee; R = CF_3, **5l**, 81%, 97% ee;	R = F, **5ap**, 80%, 97% ee; R = Cl, **5n**, 81%, 98% ee; R = Br, **5o**, 76%, 98% ee;
		
	5aq, 88%, 97% ee;	**5p**, 97%, 95% ee;
		
X = O, **5q**, 81%, 98% ee; X = S, **5r**, 84%, 98% ee;	**5ar**, 76%, >99% ee;	**5u**, 85%, 95% ee;
		
5as, 78%, 97% ee;	**5x**, 46%, 93% ee;	R = H, **5y**, 84%, 94% ee; R = Me, **5z**, 51%, 95% ee;
		
5aa, 80%, 92% ee;	R = Me, **5ad**, 50%, 93% ee; R = ^{n}Pr, **5ae**, 70%, 97% ee;	**5at**, 88%, 96% ee;
		
5au, 80%, 94% ee;	**5ah**, 70%, 95% ee;	**5ak**, 56%, >20/1 dr;

Table 3. Substrate Scope of Aldehydes in the Reaction with 4[a]

(Continued on next page)





5ak′, 60%, >20/1 dr;[c]	5al, 68%, >20/1 dr;	5al′, 53%, 10/1 dr[c]

Table 3. Continued

HPLC, high-performance liquid chromatography; NMR, nuclear magnetic resonance

[a]**2**, 0.3 mmol; **4**, 0.6 mmol. Isolated yield was reported. Regio- and diastereoselectivity were determined by ^{1}H NMR analysis of reaction crude mixture. Enantioselectivity was determined by chiral-stationary-phase HPLC analysis.

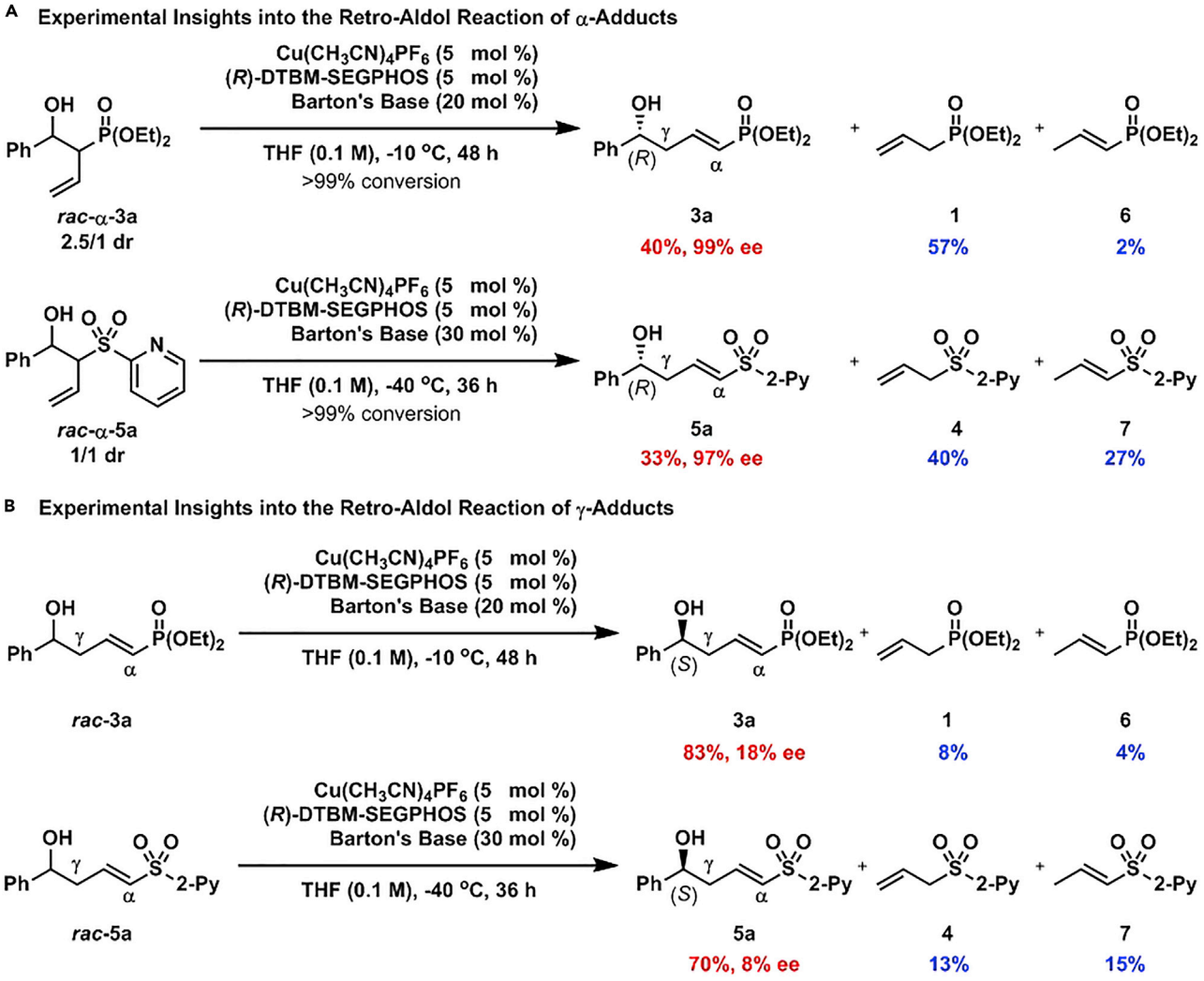
[b]Gram-scale synthesis.

[c](*S*)-DTBM-SEGPHOS was used.

To get insights into the mechanism, *rac*-**α-3a** and *rac*-**α-5a** (racemic α-adducts) prepared according to a reported and a modified reaction procedure (for details, see Supplemental Information) were subjected to the standard reaction conditions, respectively (Scheme 2A). It was found that *rac*-**α-3a** was completely consumed and **3a** was observed in 40% yield with 99% ee, together with benzaldehyde (**2a**), allyl phosphonate **1**, and α,β-unsaturated phosphonate **6**. These results clearly indicated that *retro*-aldol reaction of *rac*-**α-3a** proceeded to afford benzaldehyde (**2a**) and allyl phosphonate **1**. One portion of allyl phosphonate **1** reacted with benzaldehyde (**2a**) to give the vinylogous product **3a** in 40% yield with 99% ee in the presence of 5 mol % copper(I) catalyst and 20 mol % Barton's base. One portion of allyl phosphonate **1** isomerized to α,β-unsaturated phosphonate **6**, whereas the other portion of allyl phosphonate **1** remained. The same tendency was also observed in the *retro*-aldol reaction of *rac*-**α-5a**. This phenomenon indicated that significantly reversible α-addition led to the transformation of α-adducts to γ-adducts, which finally led to excellent control of the regioselectivity.

Rac-**3a** and *rac*-**5a** prepared by Cu(CH_3CN)$_4PF_6$-*rac*-DTBM-SEGPHOS-catalyzed reactions were also submitted to the standard reaction conditions, respectively (Scheme 2B). Thin-layer chromatography, ^{1}H nuclear magnetic resonance, and chiral high-performance liquid chromatographic analyses of the reaction crude mixtures indicated that slow and inefficient *retro*-vinylogous additions occurred, as **3a** was obtained in 83% yield with −18% ee, whereas **5a** was generated in 70% yield with −8% ee. It was obvious that the *retro*-vinylogous aldol reactions of both (*R*)-**3a** and (*R*)-**5a** proceeded selectively, which resulted in the slight enrichment of (*S*)-**3a** and (*S*)-**5a** in the reaction mixtures. However, these *retro*-vinylogous aldol reactions were very slow and inefficient, which would not have detrimental effect on the enantioselectivity in the catalytic asymmetric vinylogous aldol-type reactions of allyl phosphonate **1** and allyl sulfone **4**. Based on these important experimental observations and literatures (Bazán-Tejeda et al., 2006; Yamaguchi et al., 2007; Bouaouli et al., 2018), a possible reaction pathway was proposed in Supplemental Information.

The transformations of the vinylogous aldol products (**3a** and **5a**) were carried out as shown in Scheme 3. The cleavage of unsaturated double bond in **3a** was easily achieved through ozonolysis to deliver diol **8** in 67% yield after the reduction of generated aldehyde moiety with $NaBH_4$. After being protected as TBS-ether, **3a** was reduced to phosphonate **10** with H_2 in the presence of Pd/C. **10** Was easily transformed to α,β-unsaturated compounds **11** and **12** via α-functionalization and subsequent HWE olefination. The sulfone moiety in **5a** was successfully removed without touching the double bond to afford ester **13** in 52% yield after the protection of the alcohol motif. Sulfone **15** was easily accessed through the reduction of the unsaturated double bond and the protection of the hydroxyl group in **5a**, which was transformed to olefin **16** in 67% yield with >20/1 *E*/*Z* ratio through modified Julia olefination. Ketone **17** was prepared from **15** in 68% yield in two steps by α-functionalization and the following removal of the sulfone group. Moreover, chiral diol **18** was synthesized from **5a** in 74% yield with >20/1 diastereoisomeric ratio (dr) in two steps through intramolecular oxo-Michael addition and the



Scheme 2. Trials for *retro*-Aldol Reactions of α-Adducts and γ-Adducts

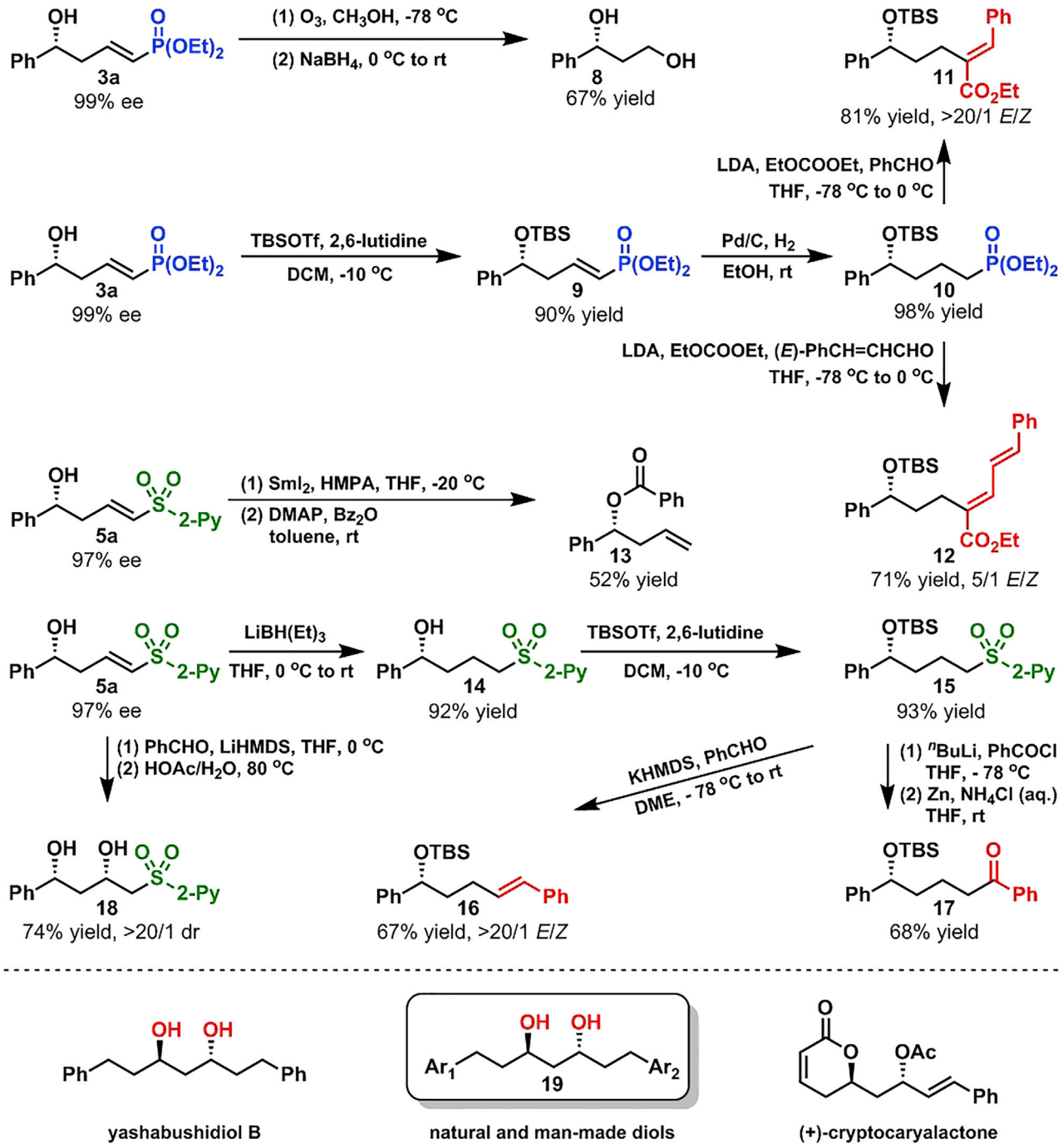
cleavage of the generated acetal motif. Furthermore, the synthetic utilities of the present methodology were showcased by its applications in the asymmetric synthesis of yashabushidiol B and the formal asymmetric synthesis of (+)-cryptocaryalactone (for the details, see Supplemental Information). Moreover, our synthetic route provided a straightforward method for the asymmetric synthesis of various chiral diols **19**. Some of the diols **19** (both natural and man-made) exhibited significant anti-proliferative activity on some human cancer cell lines (Narasimhulu et al., 2009; Yokosuka et al., 2002).

Limitations of Study

Aliphatic aldehydes were not applicable in the present reactions as α-adducts were obtained in low yields and no vinylogous products were generated. Fortunately, α,β-unsaturated aldehydes served as competent substrates and their vinylogous products could be potentially converted to the vinylogous products of aliphatic aldehydes through the transformations of carbon-carbon double bond.

Conclusion

In summary, two copper(I)-(*R*)-DBTM-SEGPHOS complex-catalyzed asymmetric vinylogous aldol-type reactions of aldehydes with allyl phosphonate and allyl sulfone were disclosed. These two reactions enjoyed advantages of 100% atomic economy, mild reaction conditions, easy reaction protocol, broad substrate scope, excellent regioselectivity, and excellent enantioselectivity. The mechanistic studies revealed a



Scheme 3. Transformations of the Vinylogous Products

significantly reversible α-addition process and a slightly reversible γ-addition process, which accounted for the perfect control of the regioselectivity in these two vinylogous aldol-type reactions. Finally, various transformations of the vinylogous products (including HWE and Julia olefinations) were successfully carried out by means of phosphonate and sulfone. Application of the present methodology in the asymmetric synthesis of complex natural products is currently on the way in our laboratory.

METHODS

All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.03.010.

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AUTHOR CONTRIBUTIONS

L.Y. conceived the project and designed the experiments. W.-J.Y. and C.-Y.Z. performed and analyzed the experiments. L.Y. wrote the manuscript. W.-J.Y. wrote the Supplemental Information and contributed other related materials. All the authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

Asymmetric Vinylogous Aldol-type Reactions of Aldehydes with Allyl Phosphonate and Sulfone

Wen-Jun Yue, Cheng-Yuan Zhang, and Liang Yin

Supplement Information

Asymmetric Vinylogous Aldol-Type Reactions of Aldehydes with Allyl Phosphonate and Sulfone

Wen-Jun Yue,[1] Cheng-Yuan Zhang,[1] and Liang Yin[1,2,*]

[1]CAS Key Laboratory of Synthetic Chemistry of Natural Substances, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

[2]Lead Contact

*Correspondence:liangyin@sioc.ac.cn

Copies of product NMR spectra

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2ah**, related to **Table 2**

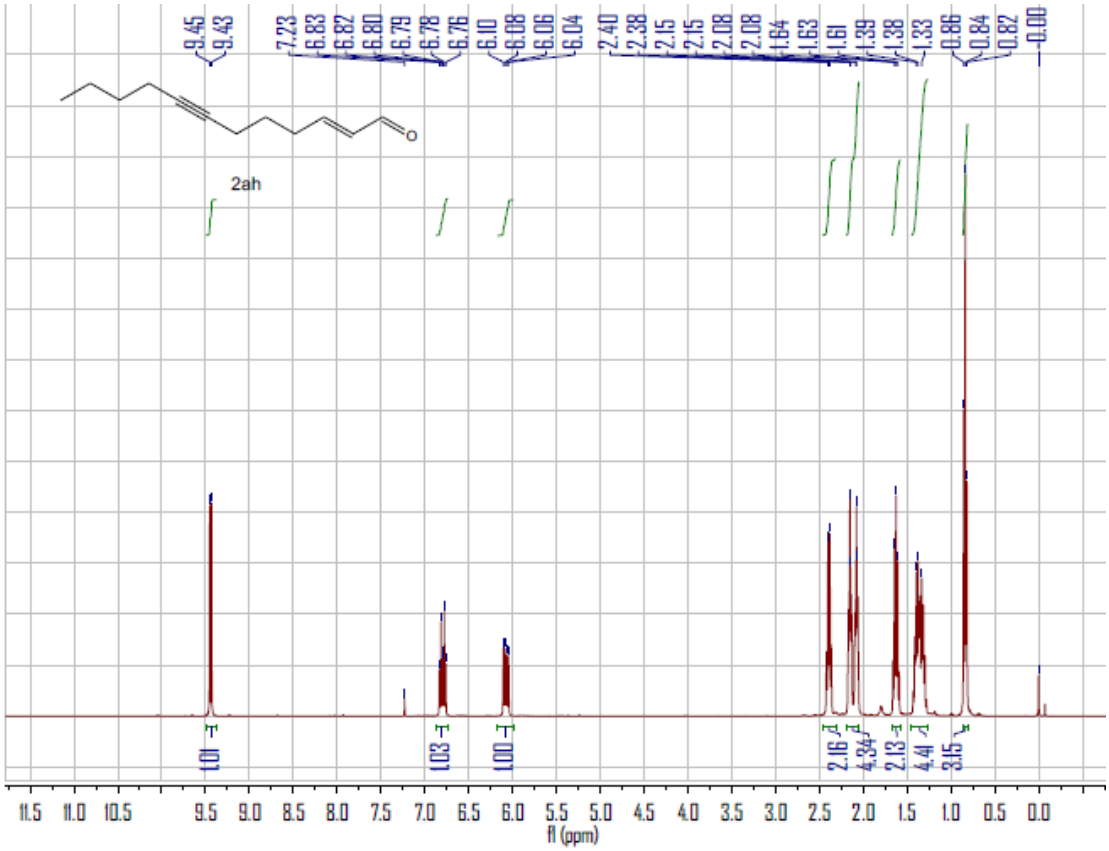


Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2ah**, related to **Table 2**

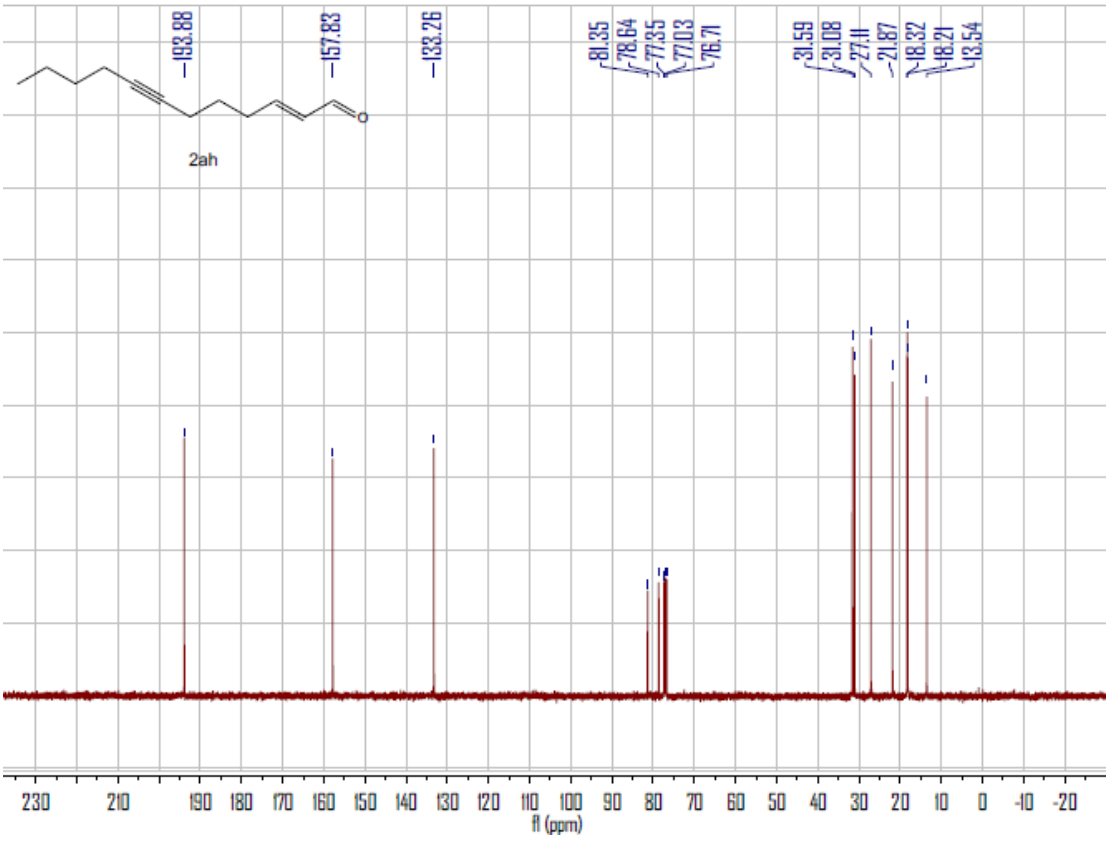


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3a**, related to **Table 2**

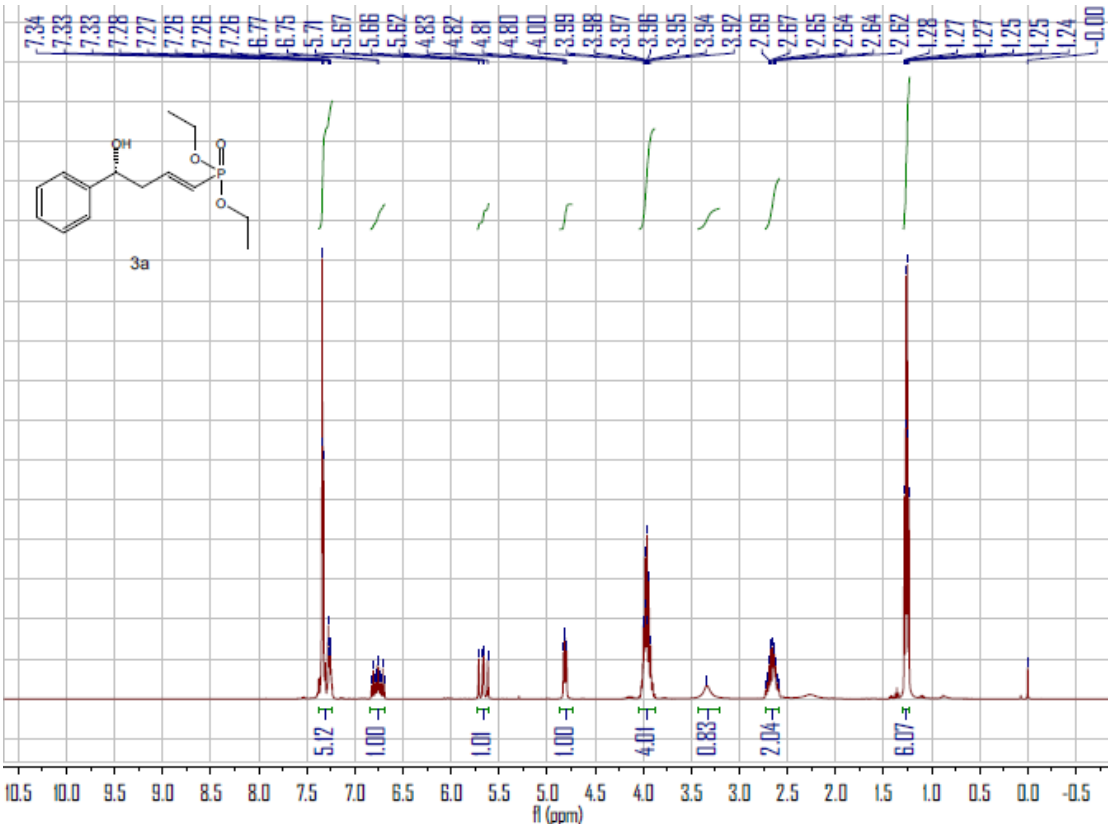


Figure S4. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3a**, related to **Table 2**

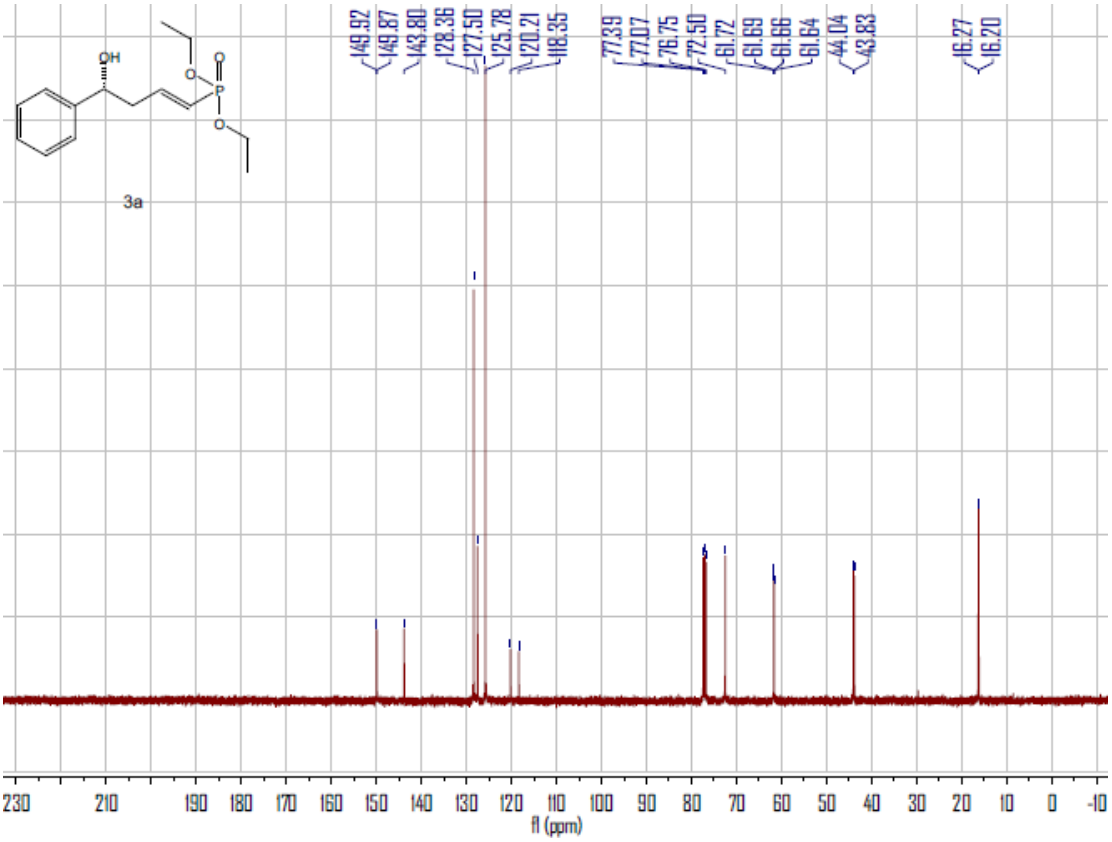


Figure S5. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3a**, related to **Table 2**

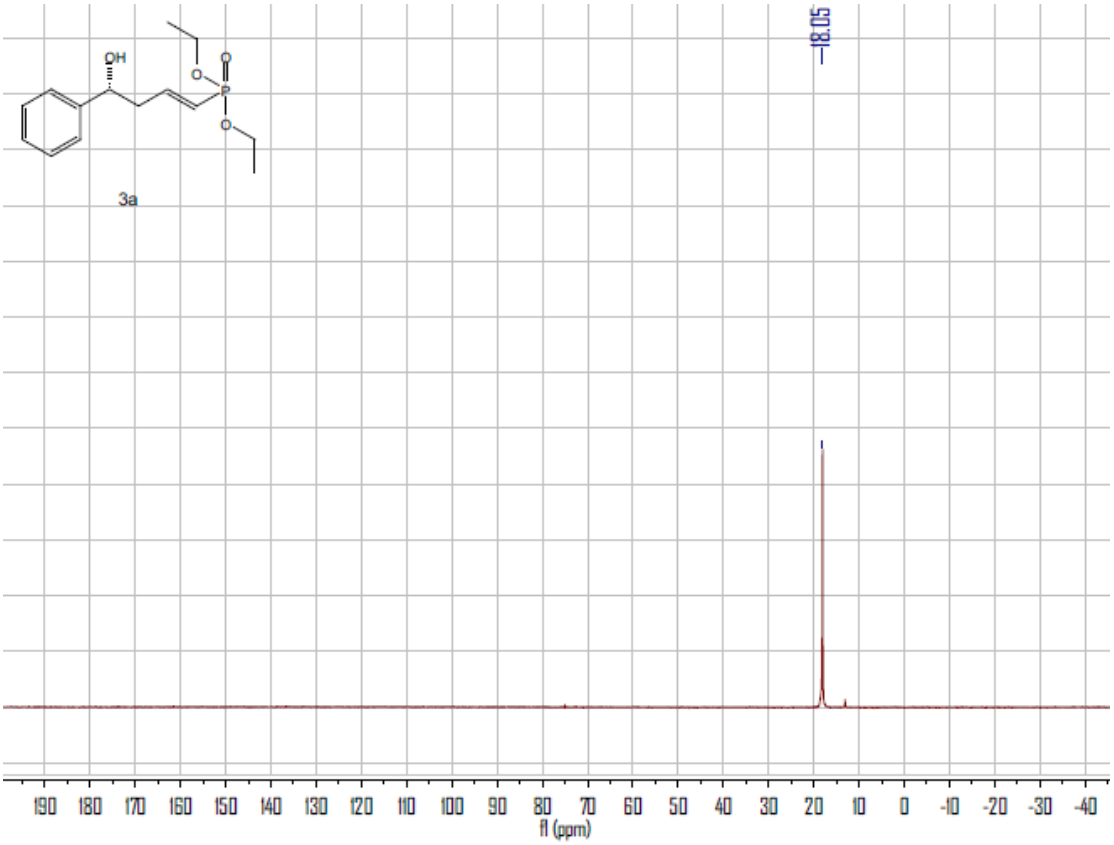


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3b**, related to **Table 2**

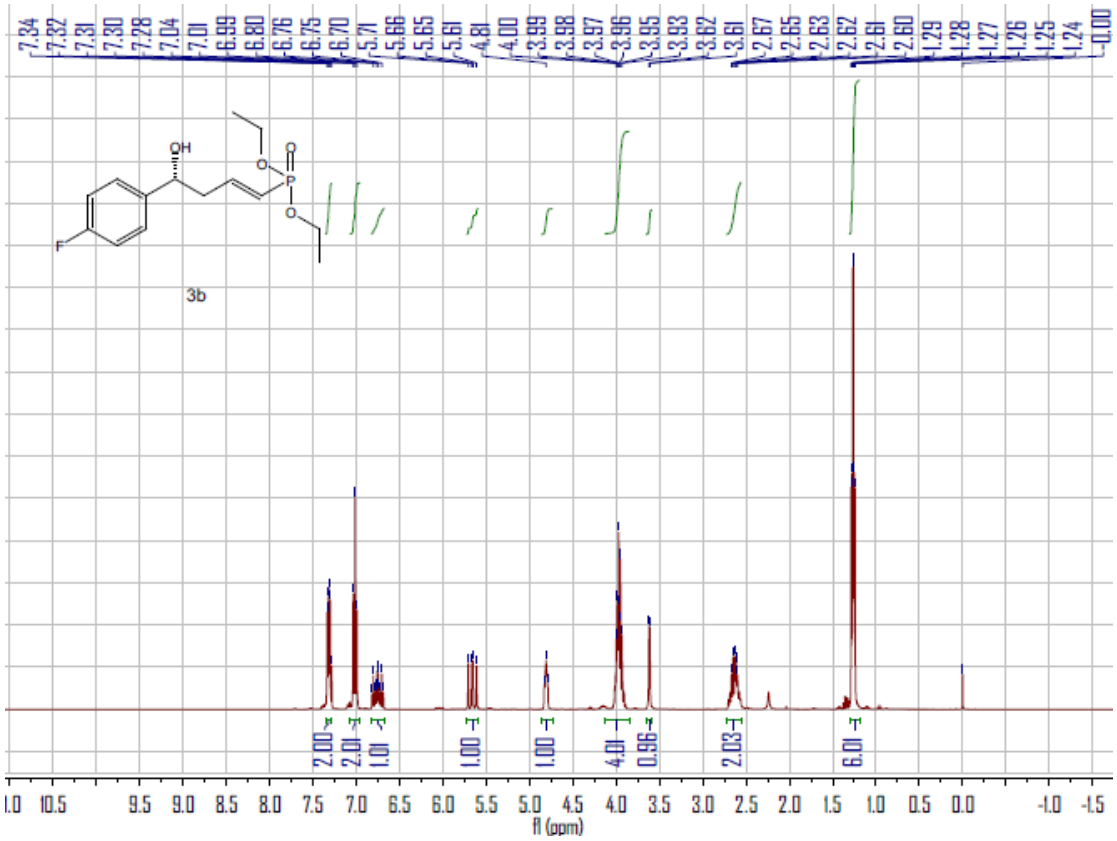


Figure S7. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3b**, related to **Table 2**

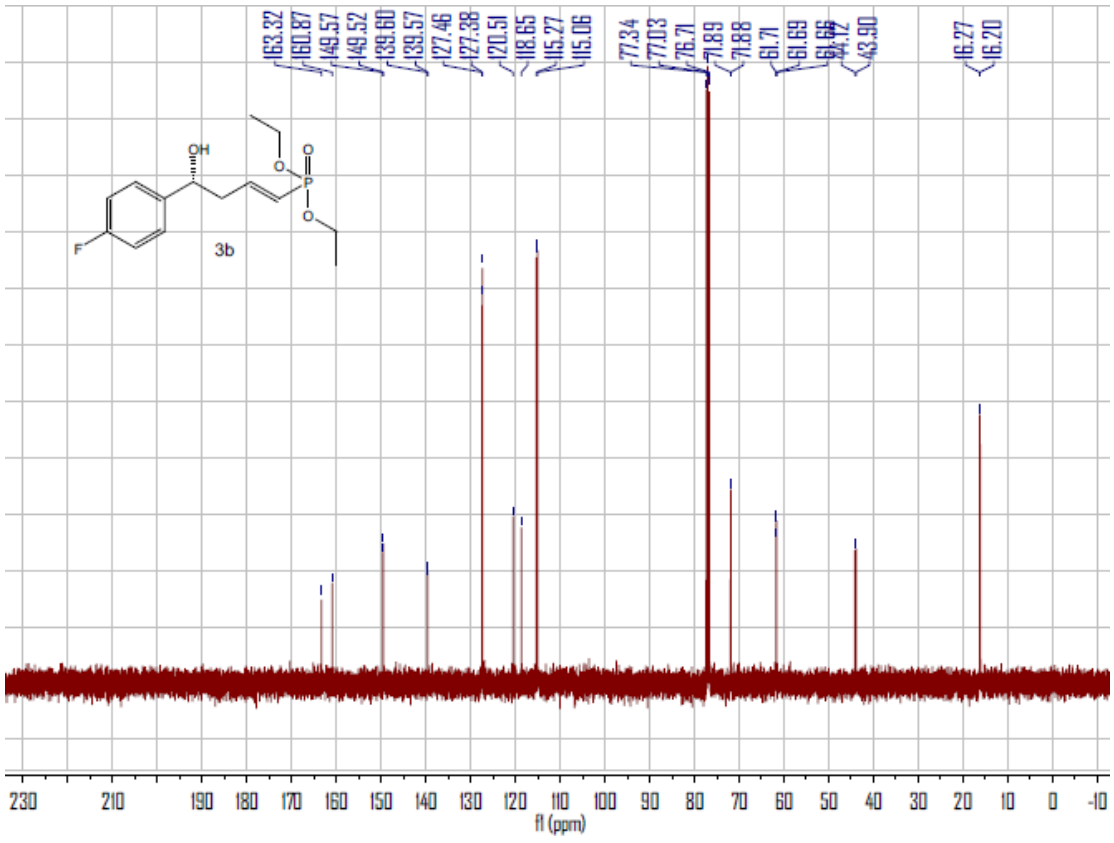


Figure S8. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3b**, related to **Table 2**

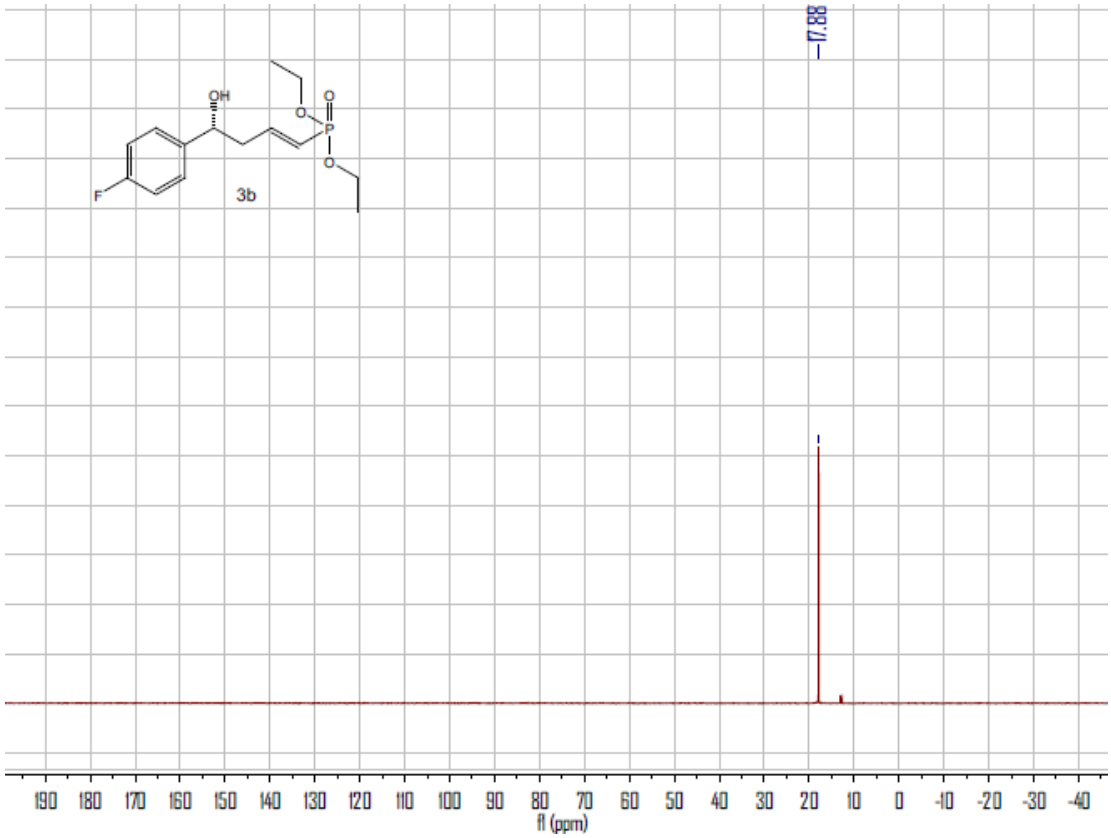


Figure S9. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3b**, related to **Table 2**

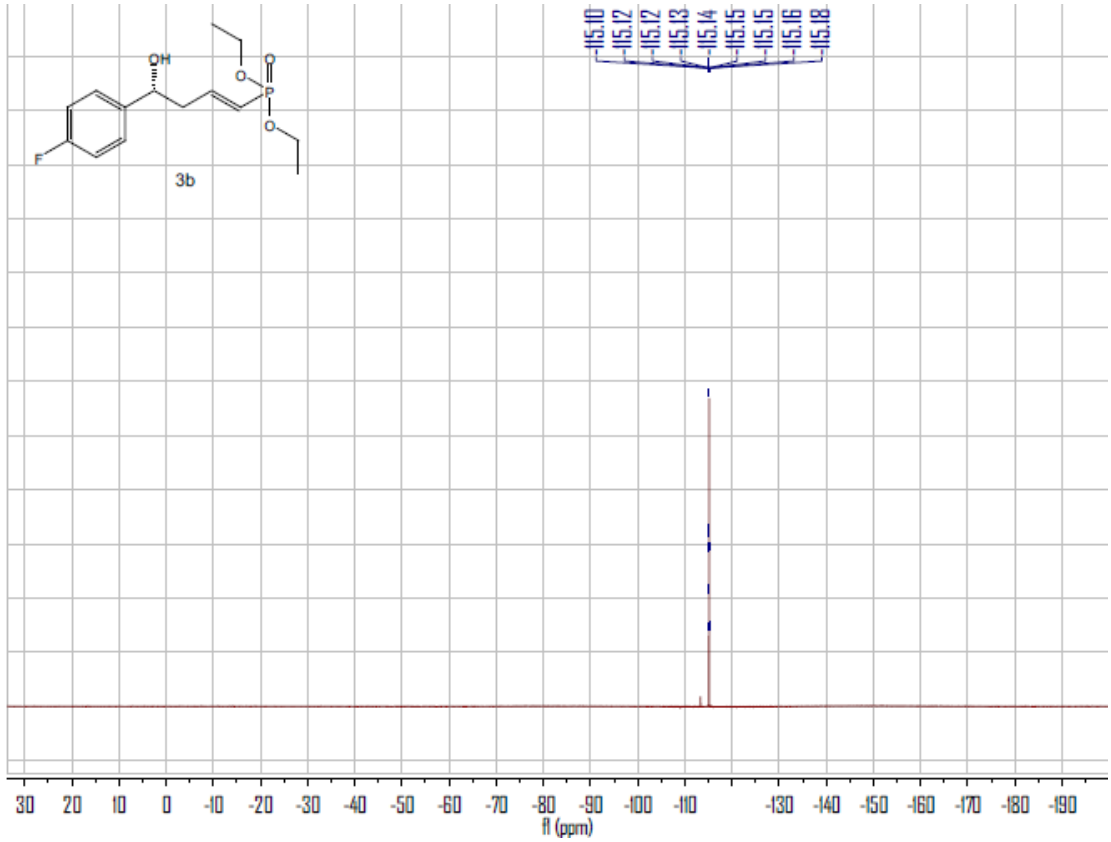


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3c**, related to **Table 2**

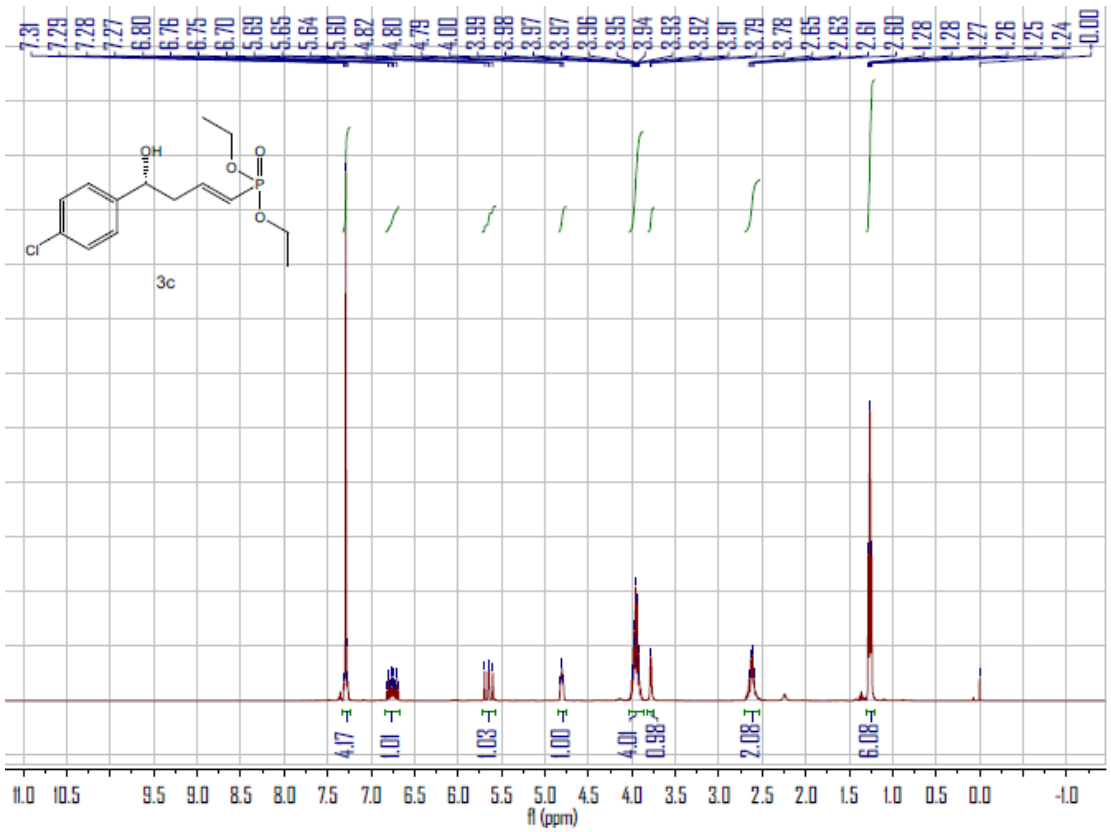


Figure S11. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3c**, related to **Table 2**

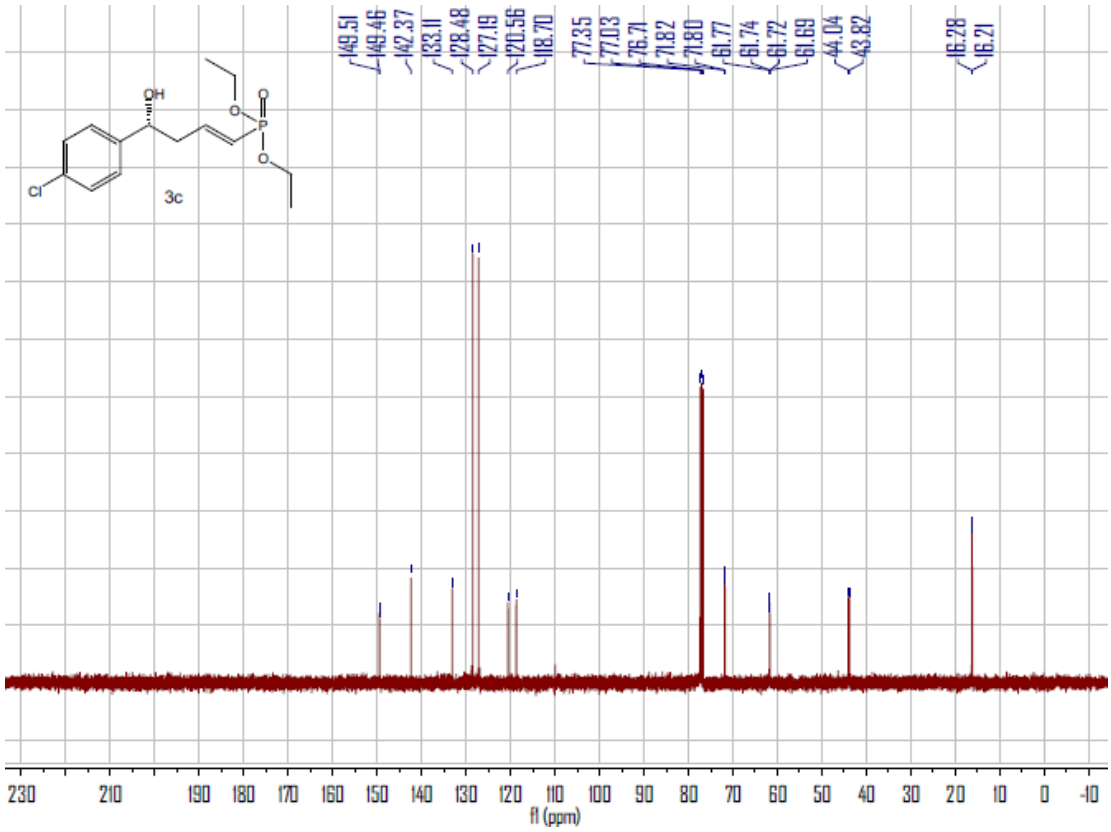


Figure S12. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3c**, related to **Table 2**

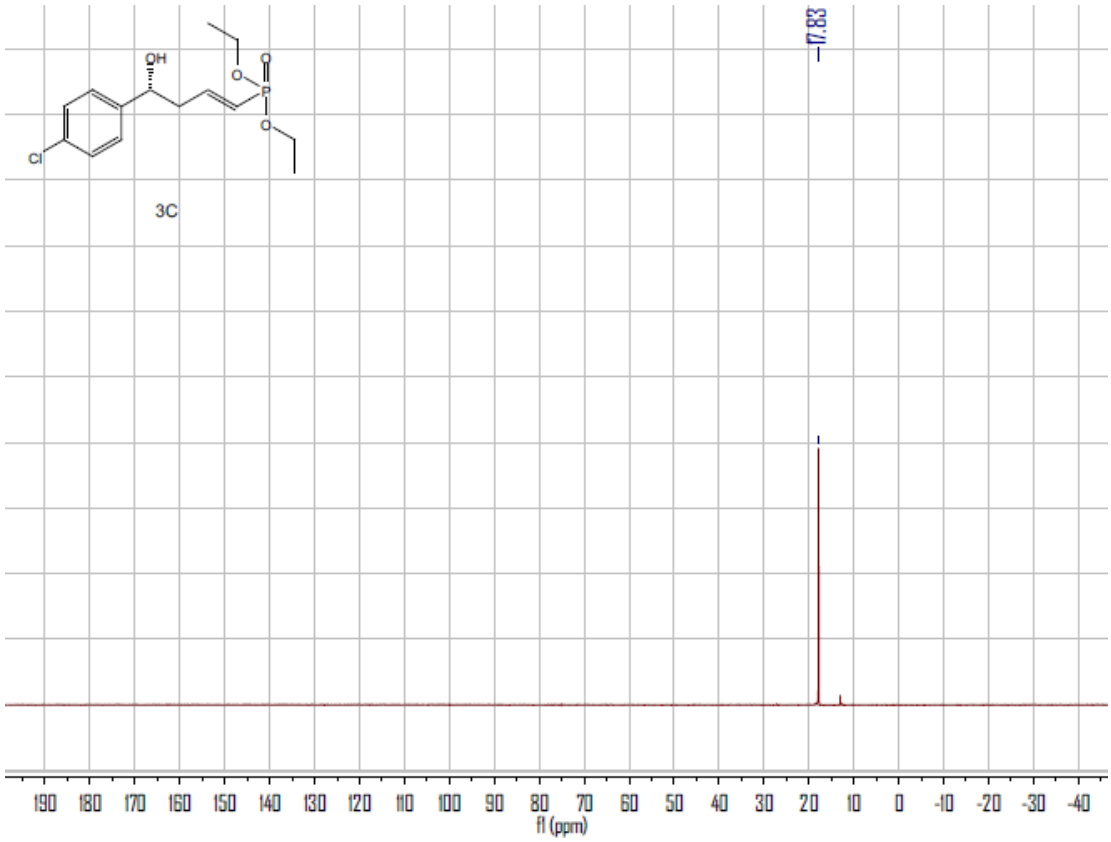


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3d**, related to **Table 2**

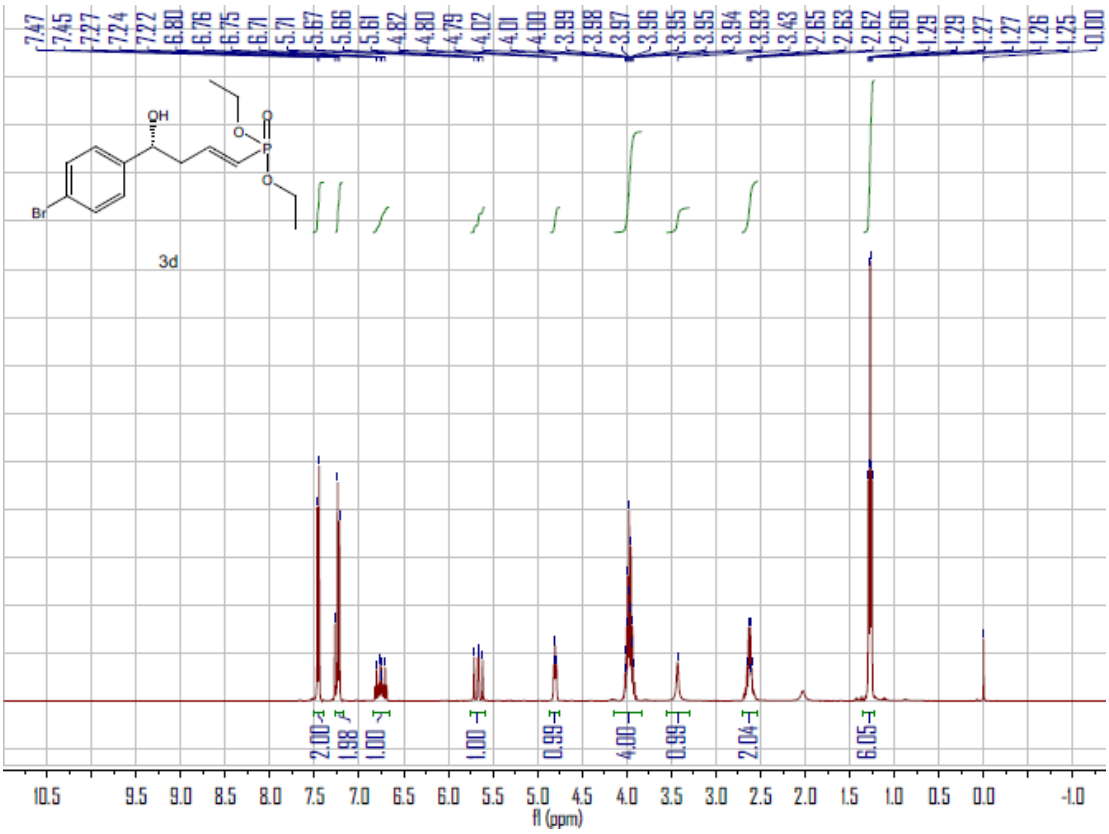


Figure S14. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3d**, related to **Table 2**

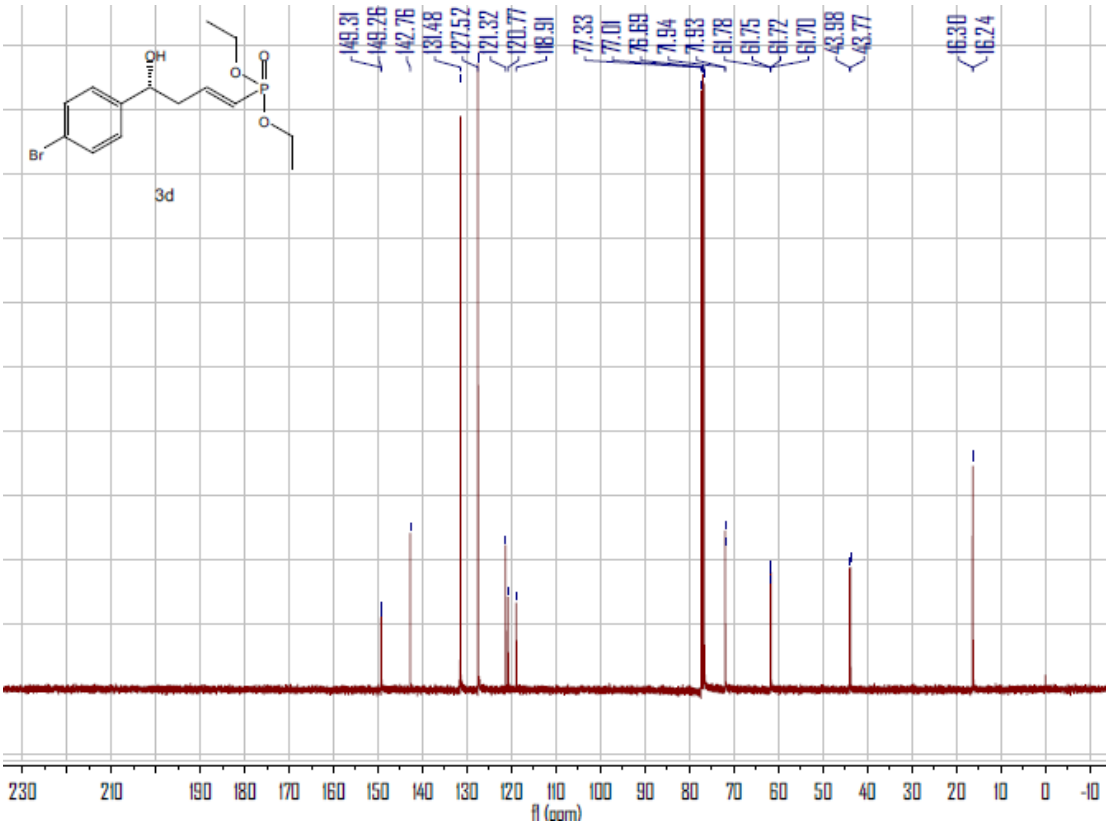


Figure S15. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3d**, related to **Table 2**

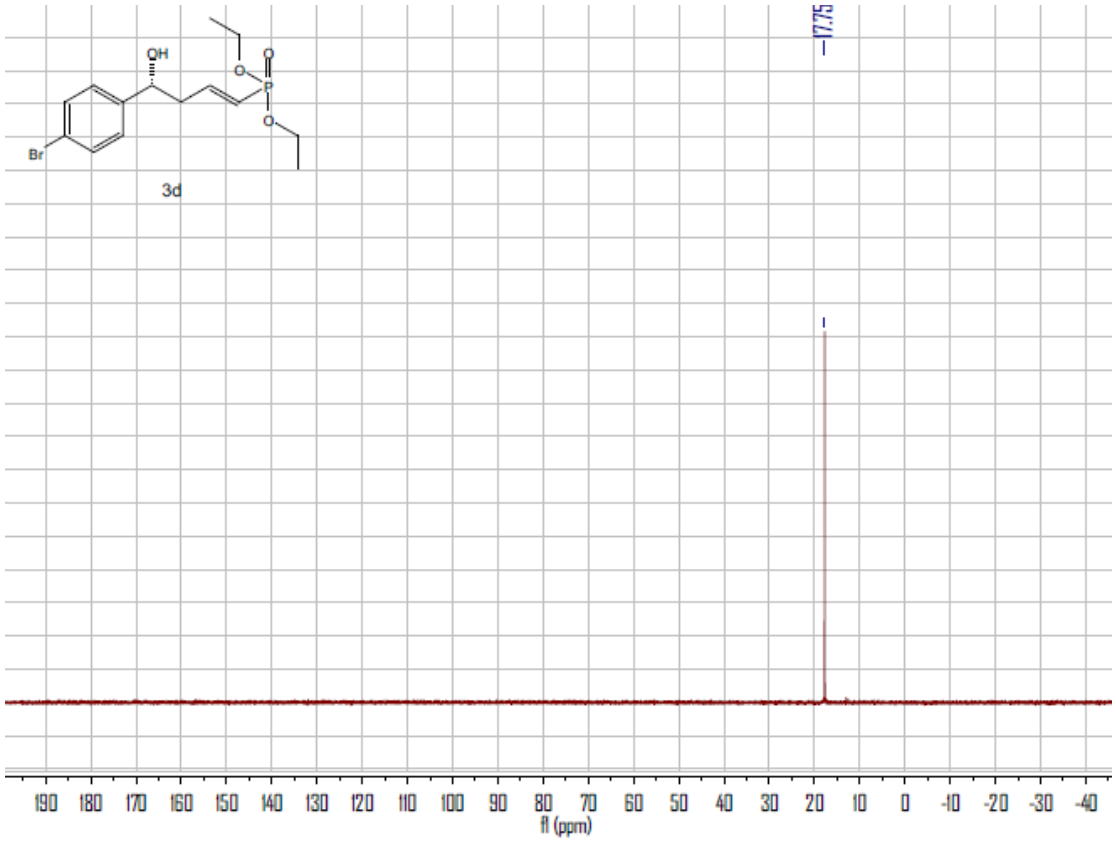


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3e**, related to **Table 2**

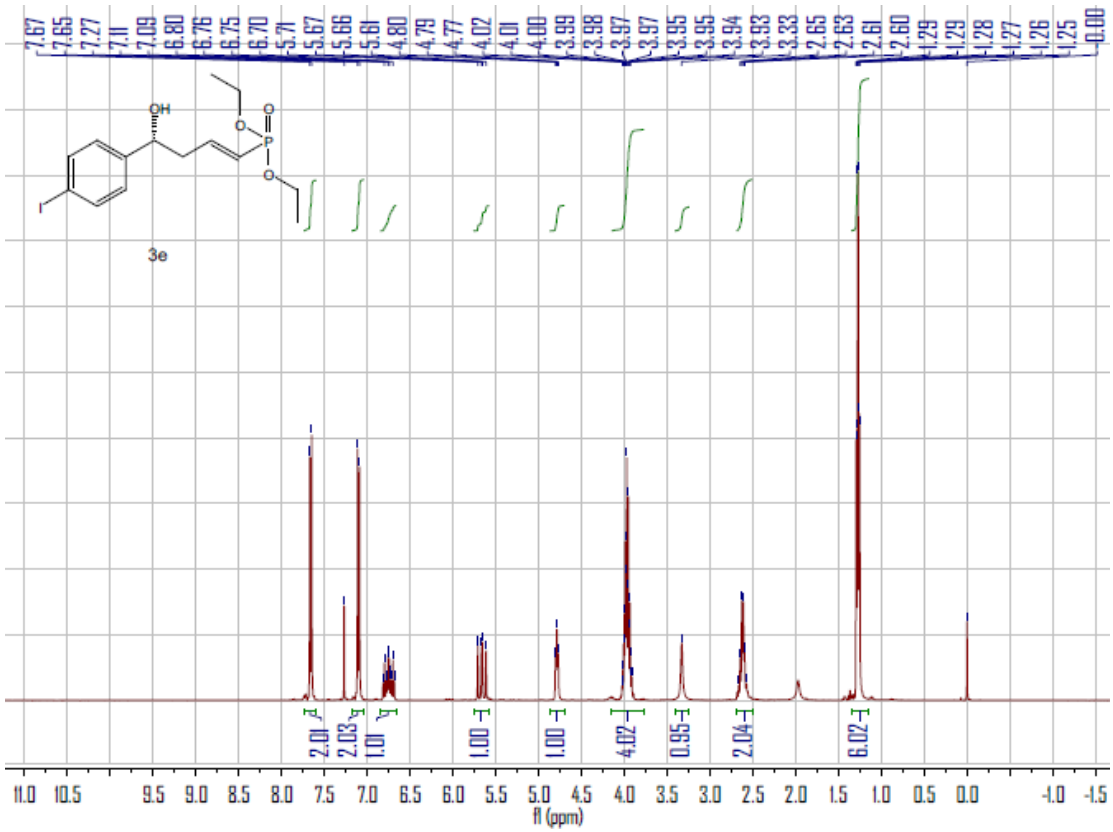


Figure S17. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3e**, related to **Table 2**

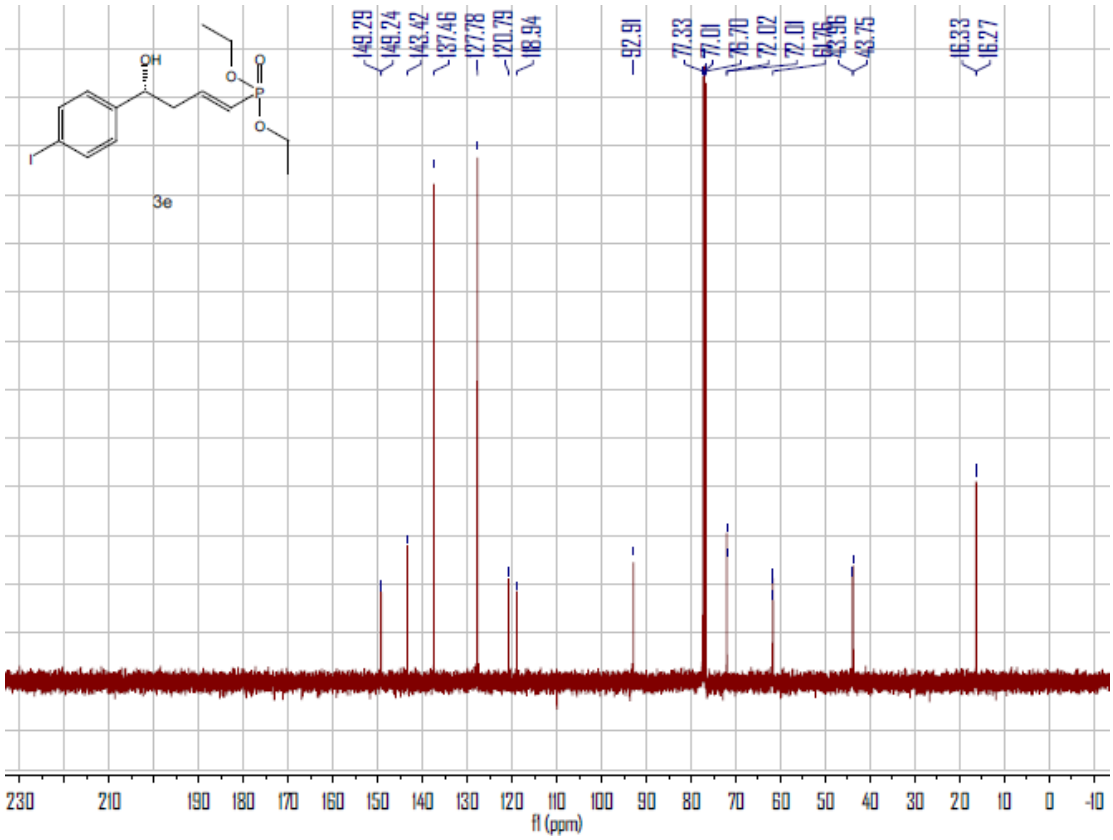


Figure S18. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3e**, related to **Table 2**

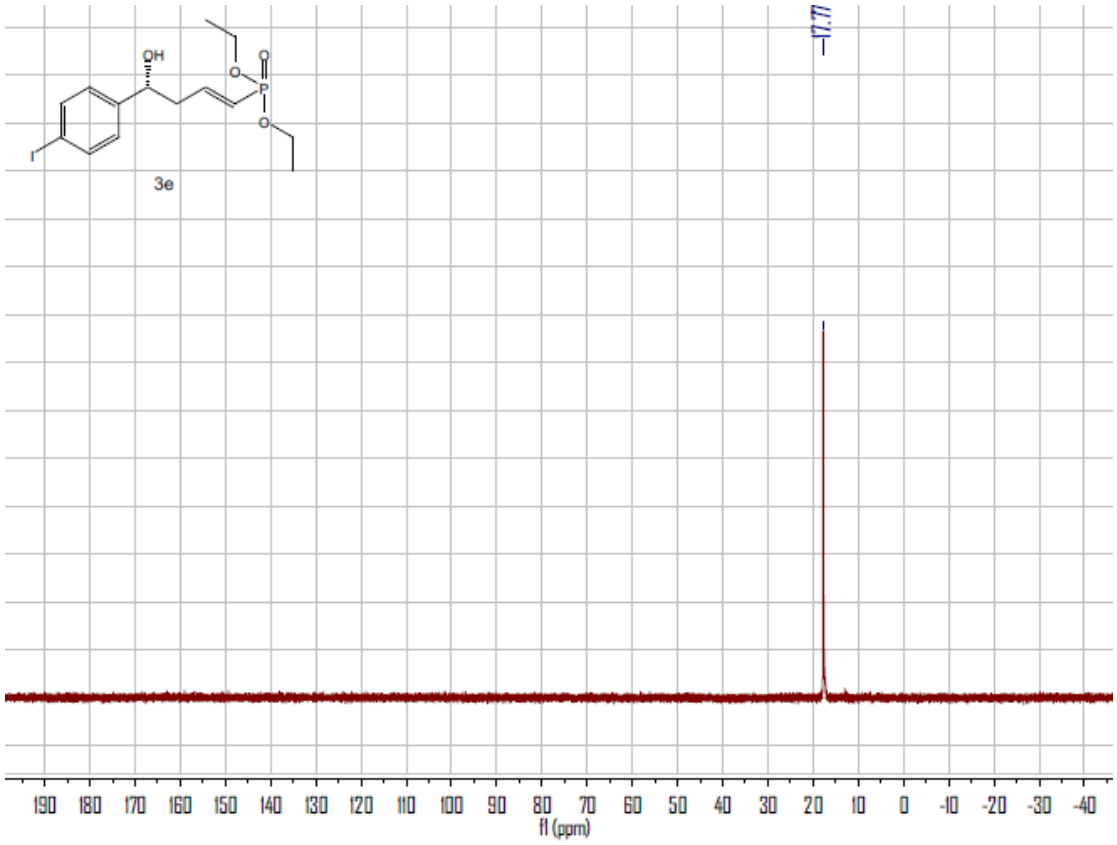


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3f**, related to **Table 2**

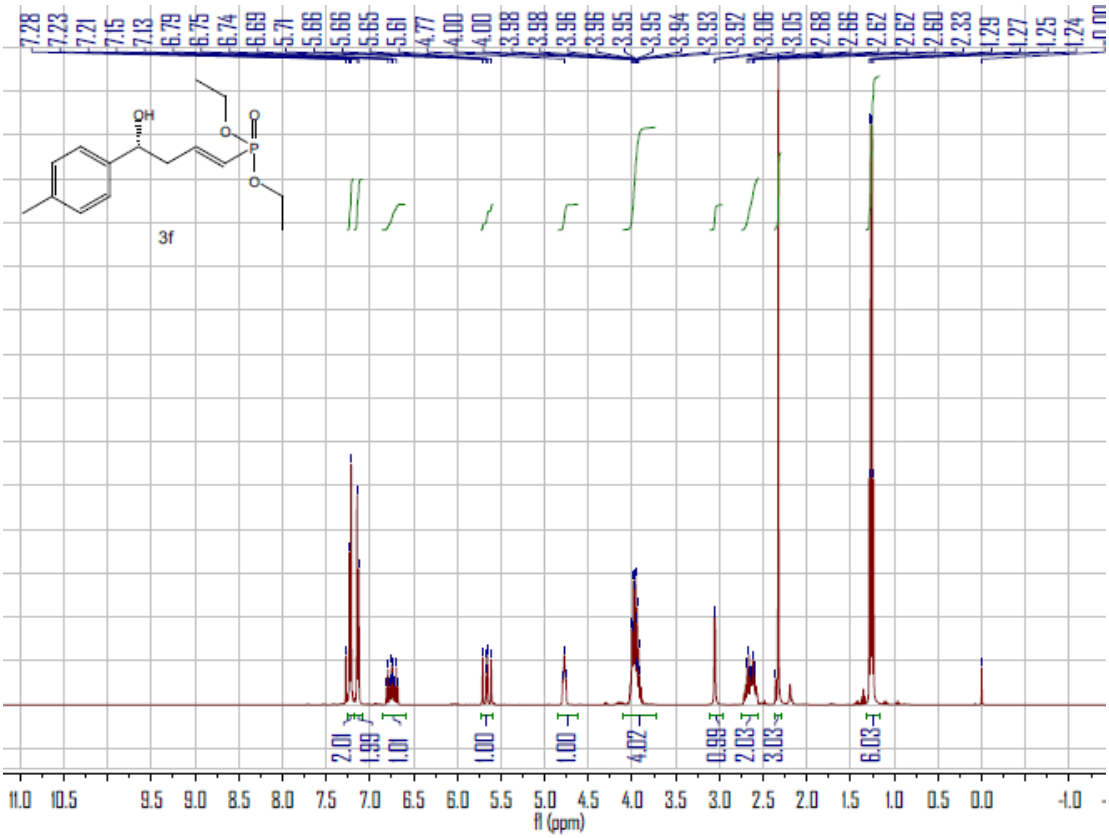


Figure S20. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3f**, related to **Table 2**

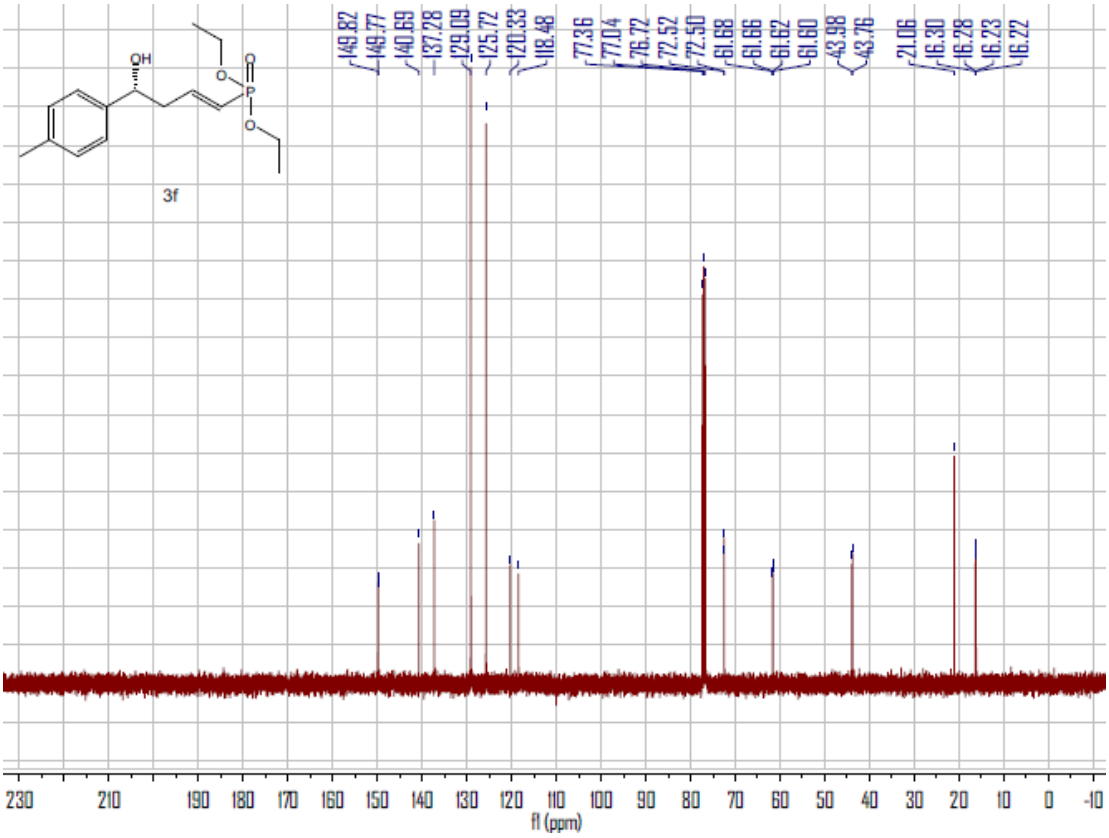


Figure S21. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3f**, related to **Table 2**

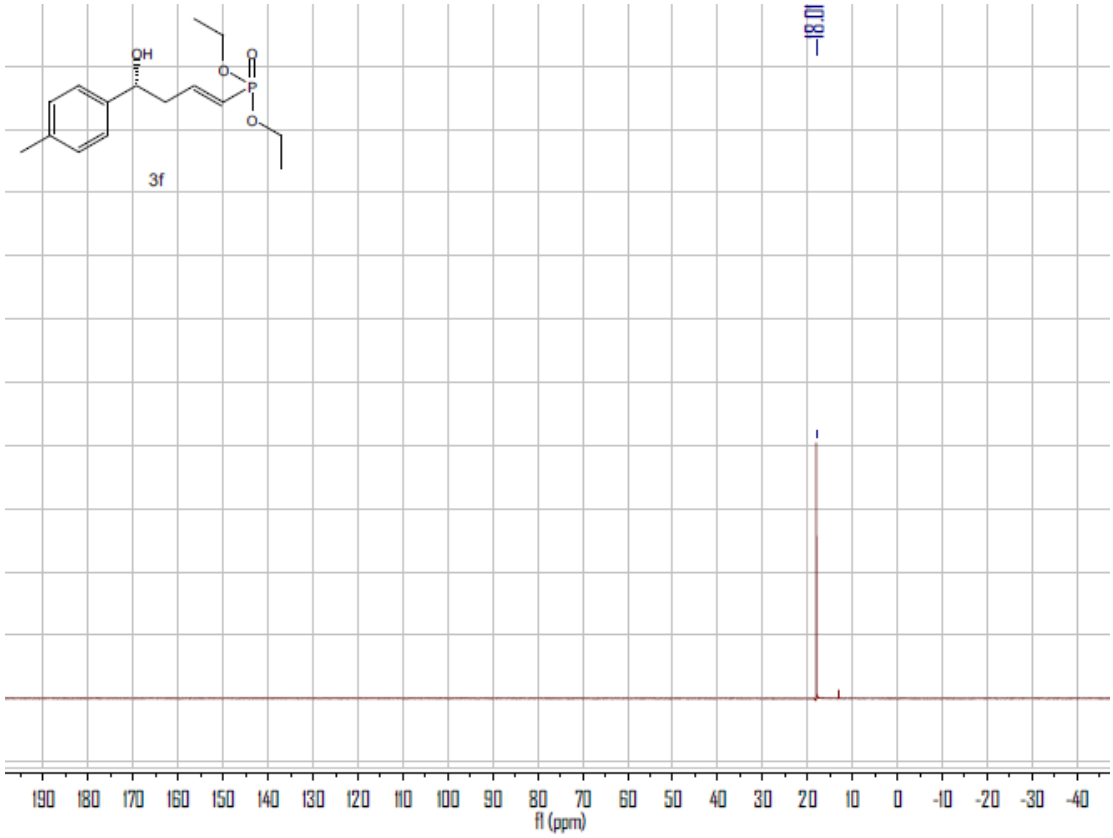


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3g**, related to **Table 2**

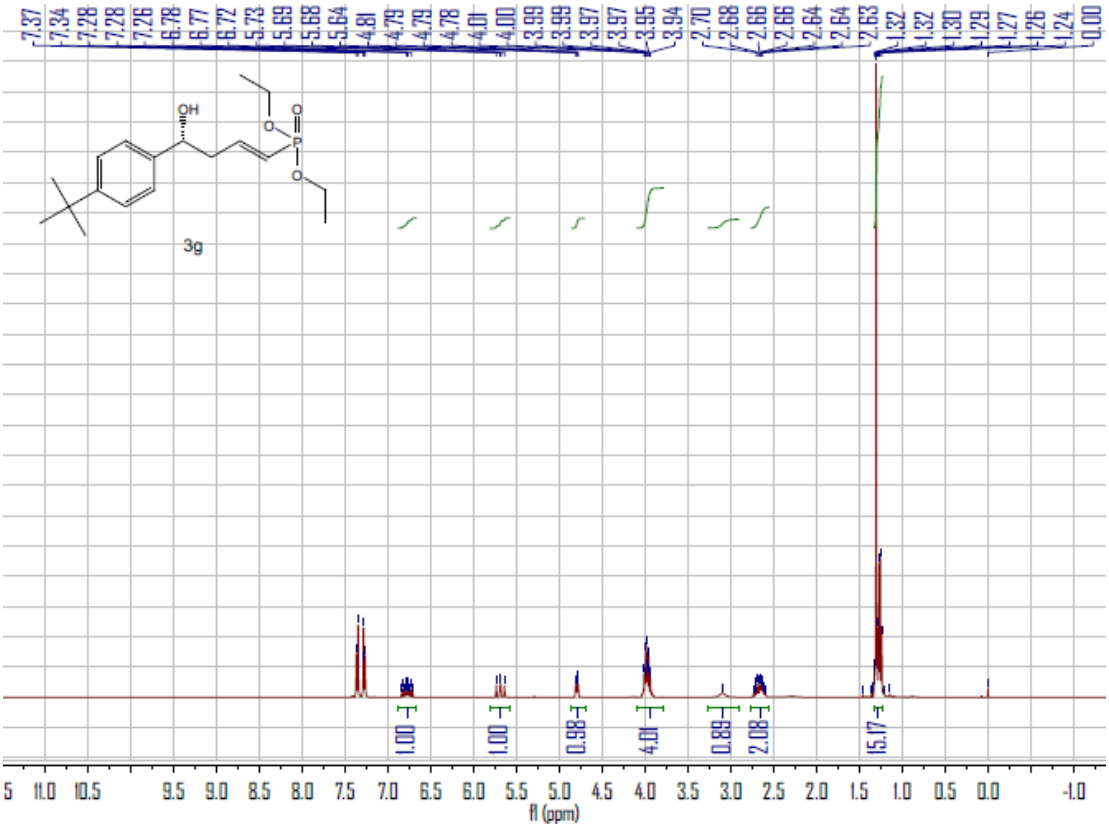


Figure S23. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3g**, related to **Table 2**

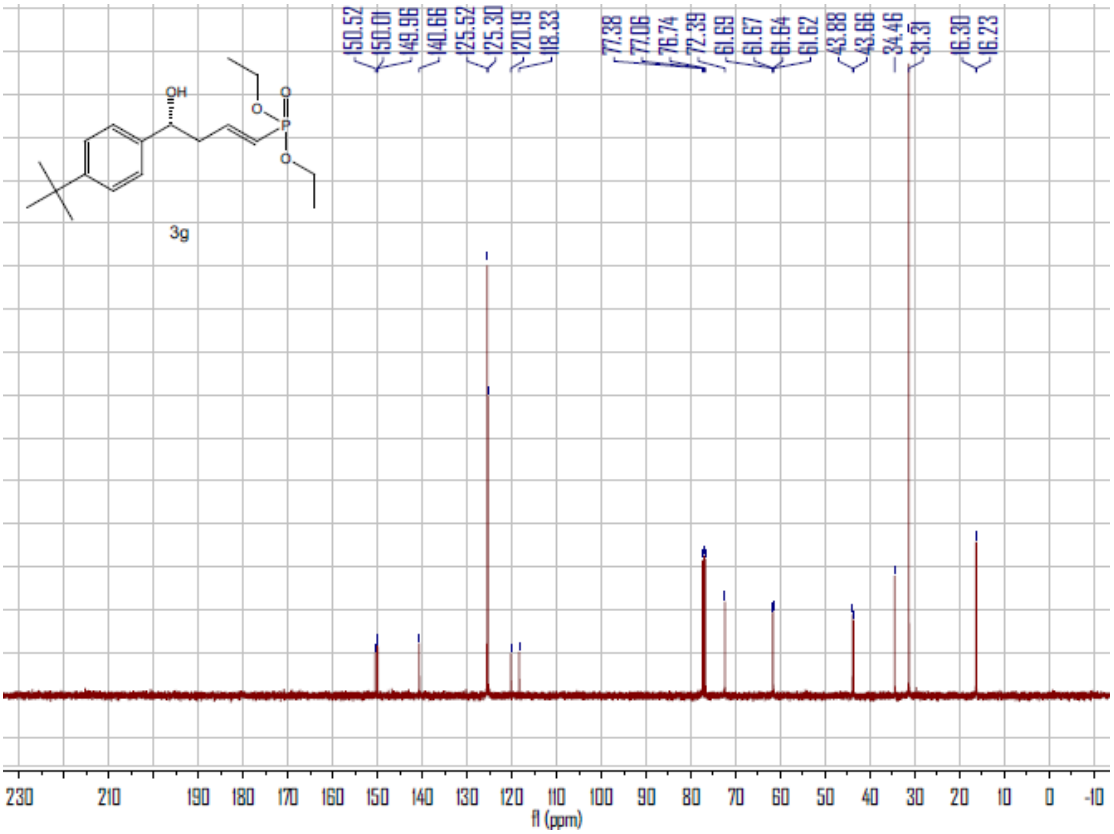


Figure S24. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3g**, related to **Table 2**

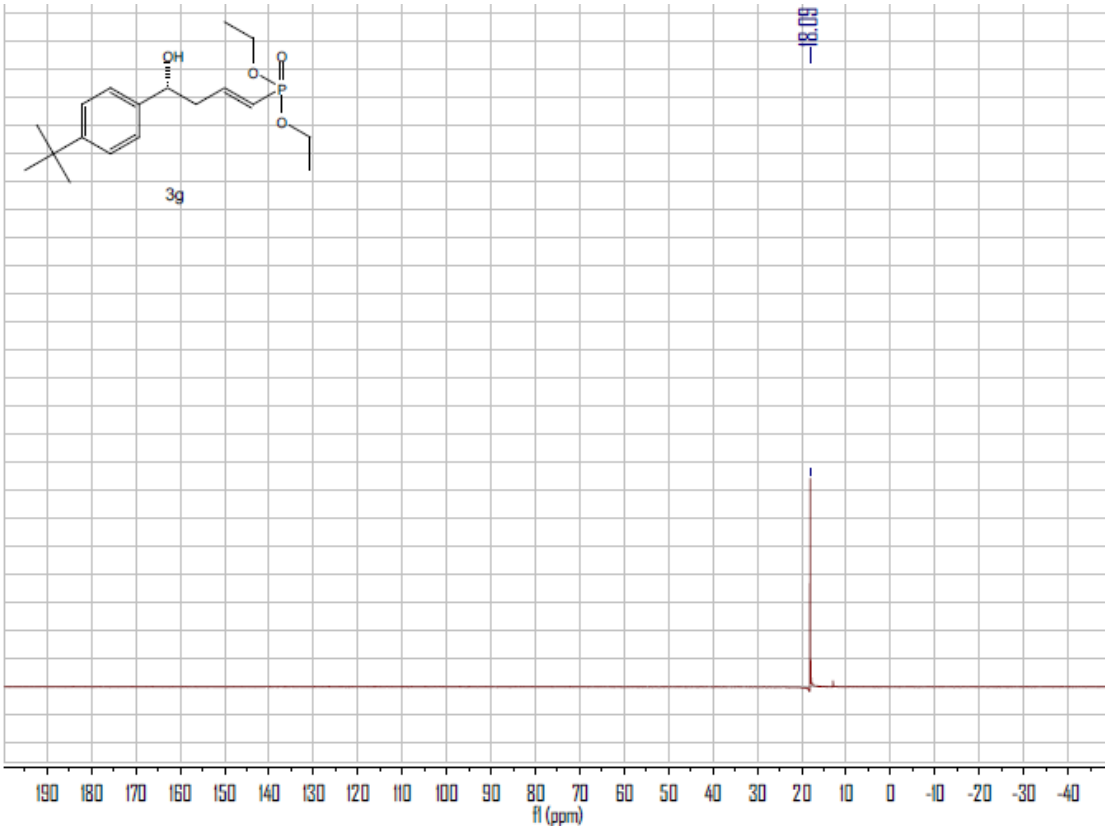


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3h**, related to **Table 2**

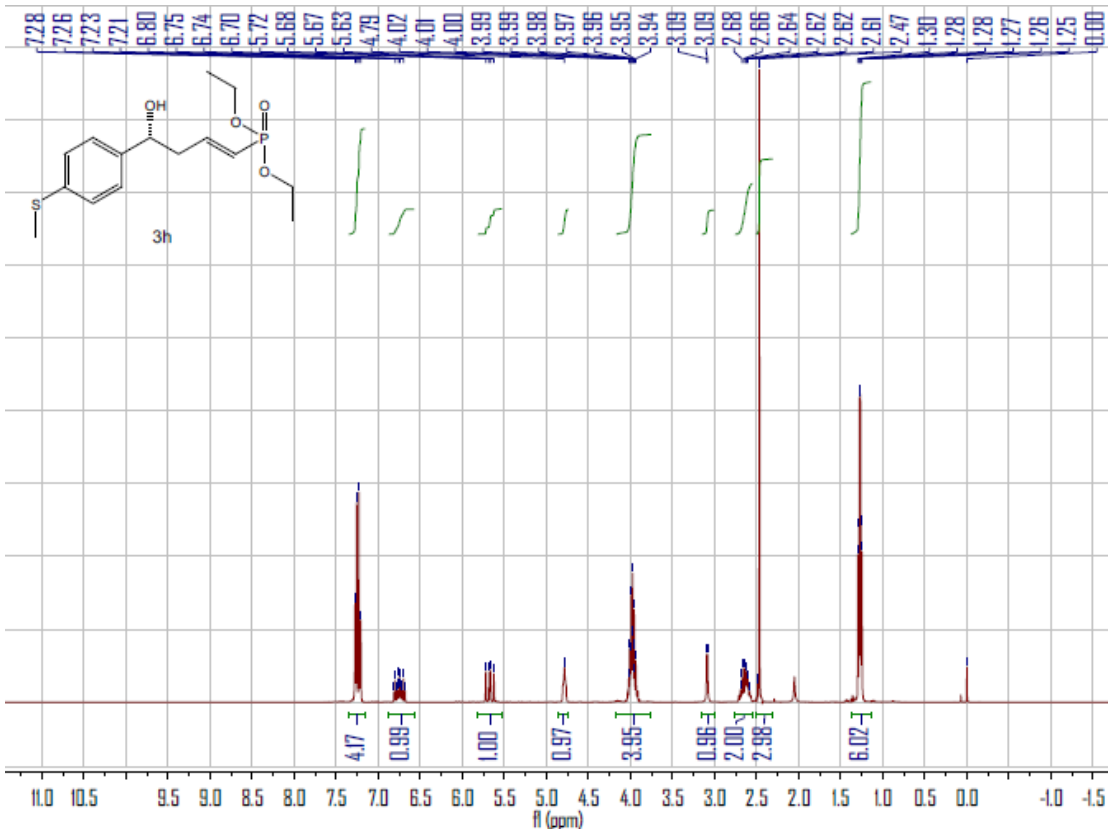


Figure S26. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3h**, related to **Table 2**

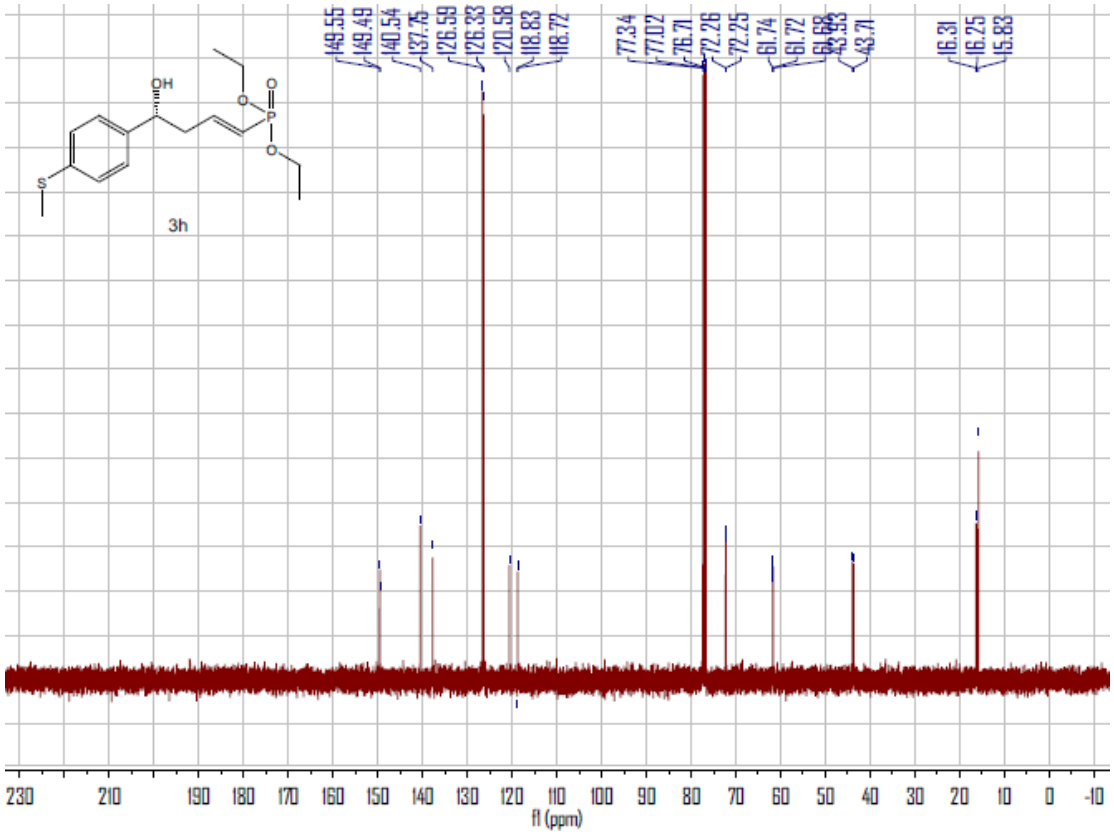


Figure S27. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3h**, related to **Table 2**

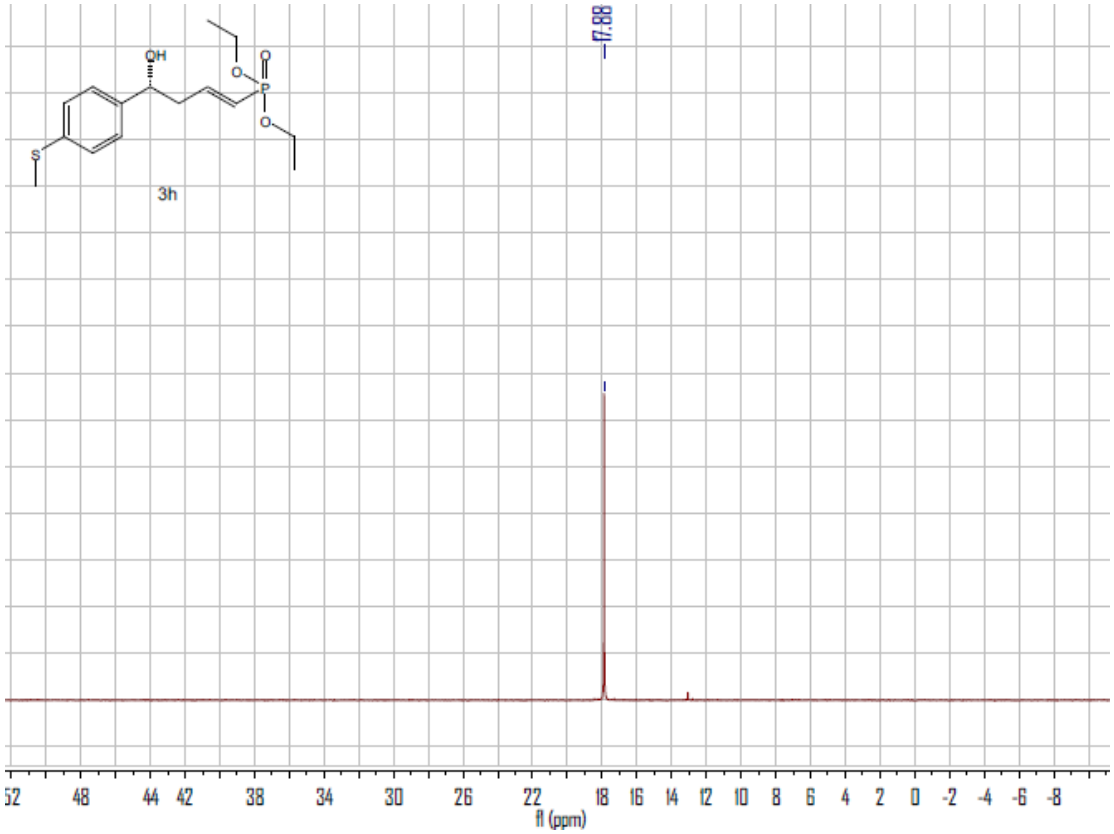


Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3i**, related to **Table 2**

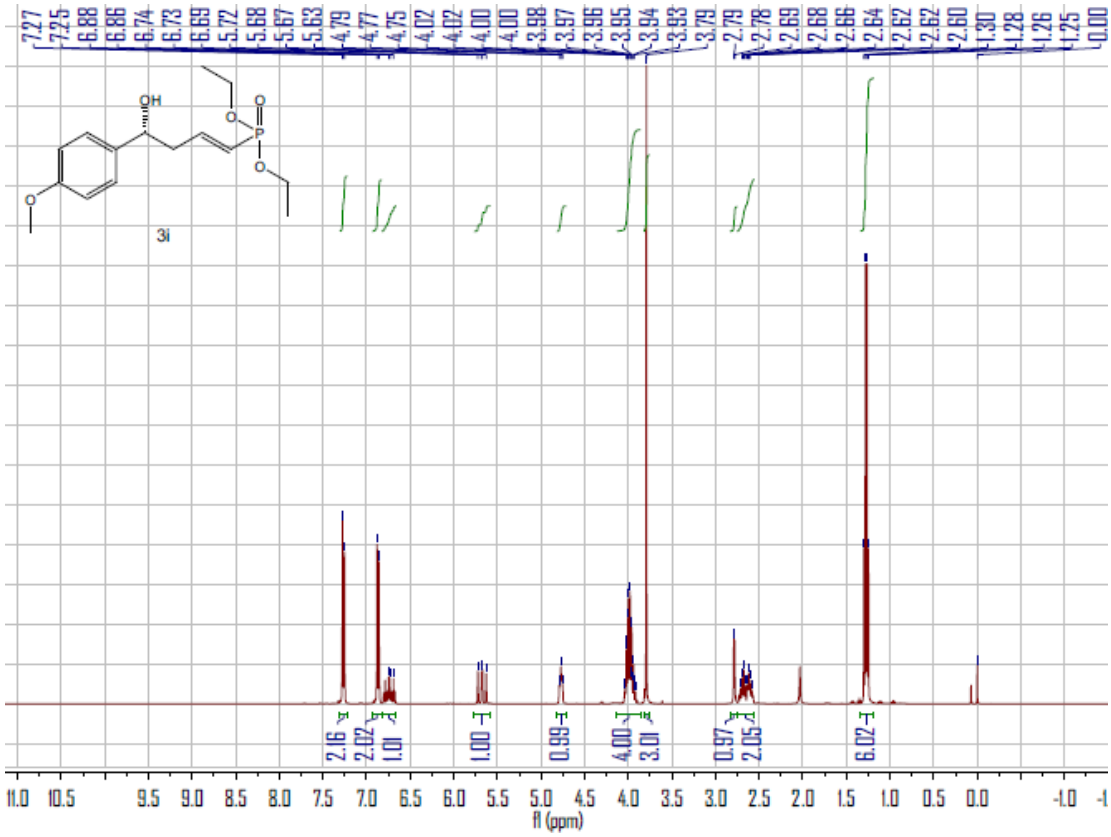


Figure S29. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3i**, related to **Table 2**

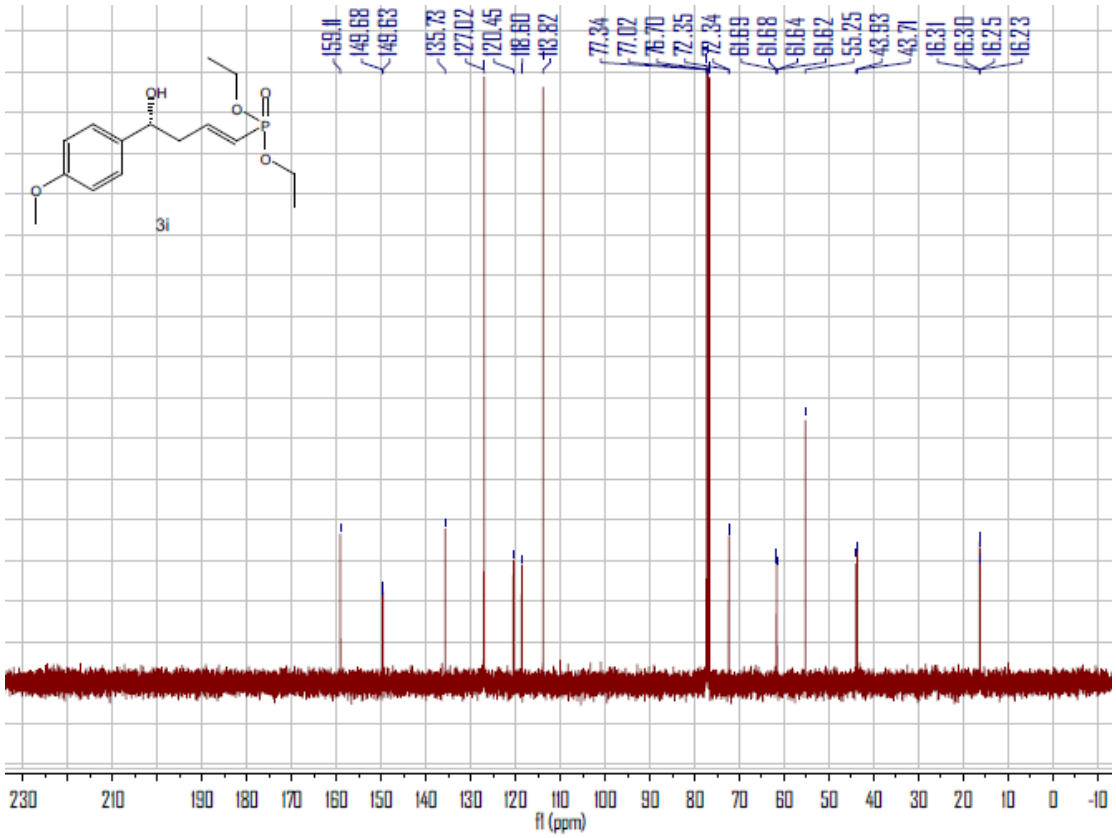


Figure S29. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3i**, related to **Table 2**

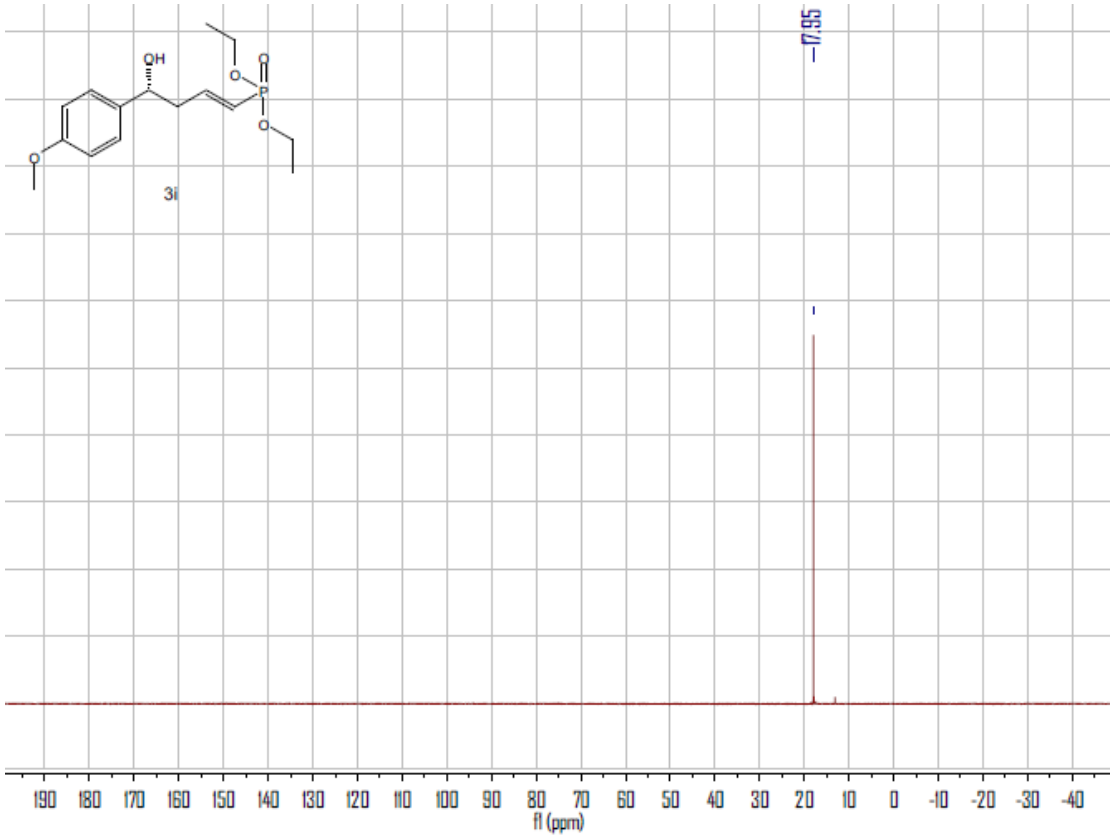


Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3j**, related to **Table 2**

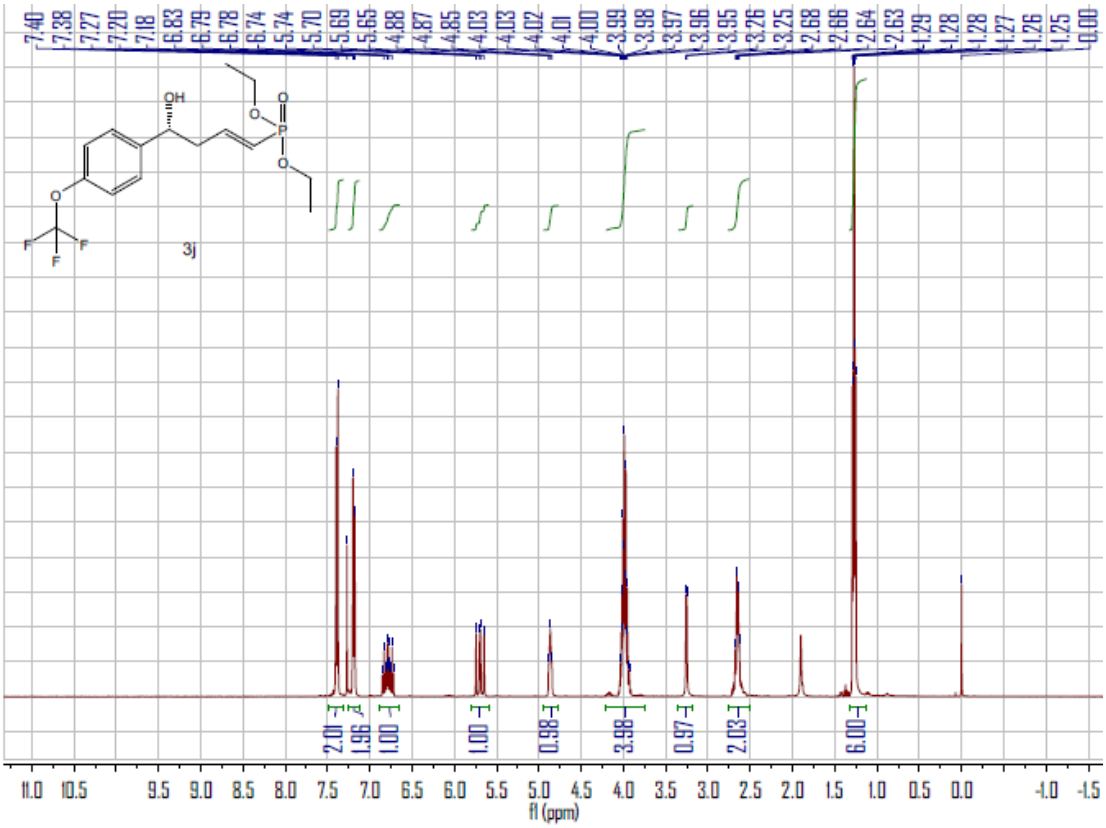


Figure S31. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3j**, related to **Table 2**

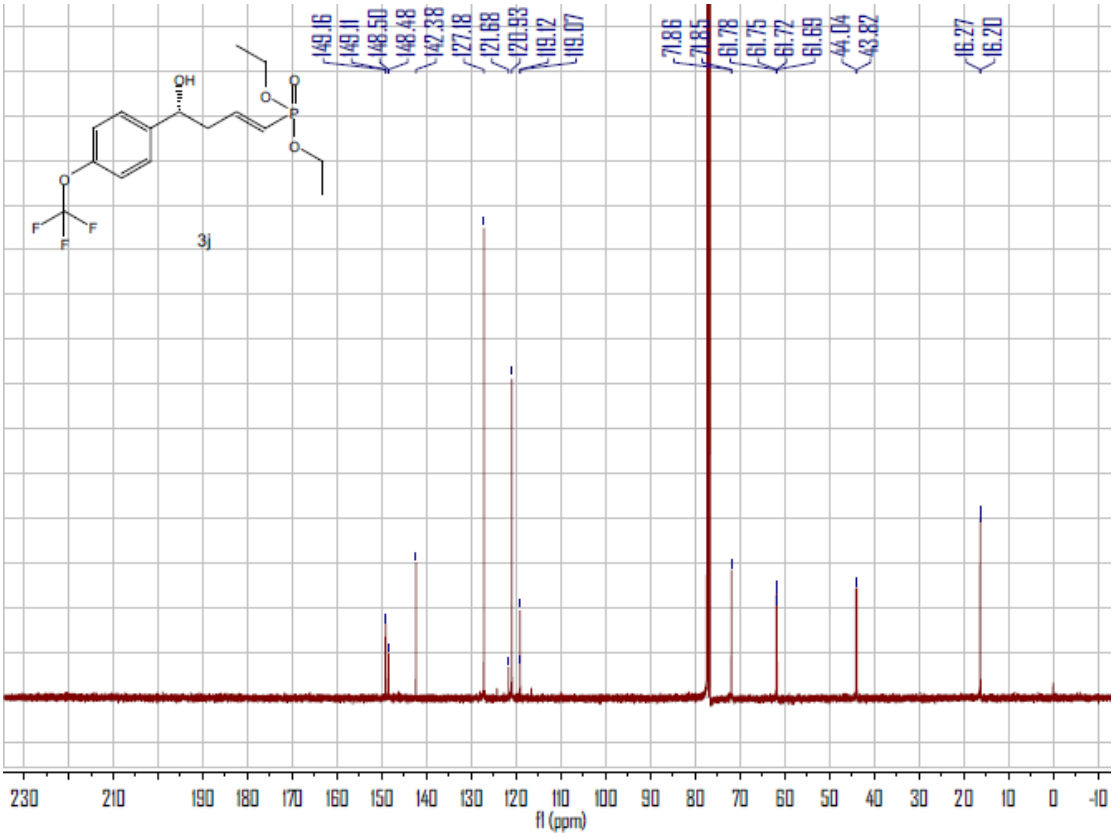


Figure S32. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3j**, related to **Table 2**

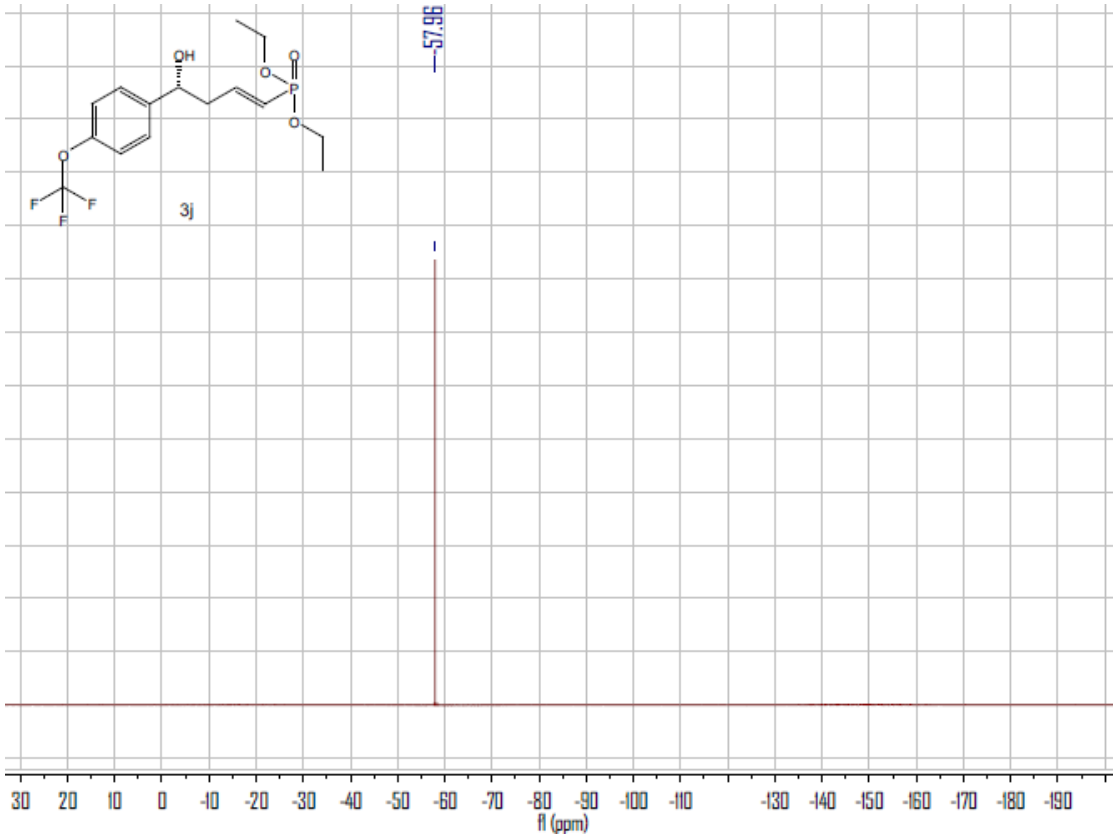


Figure S33. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3j**, related to **Table 2**

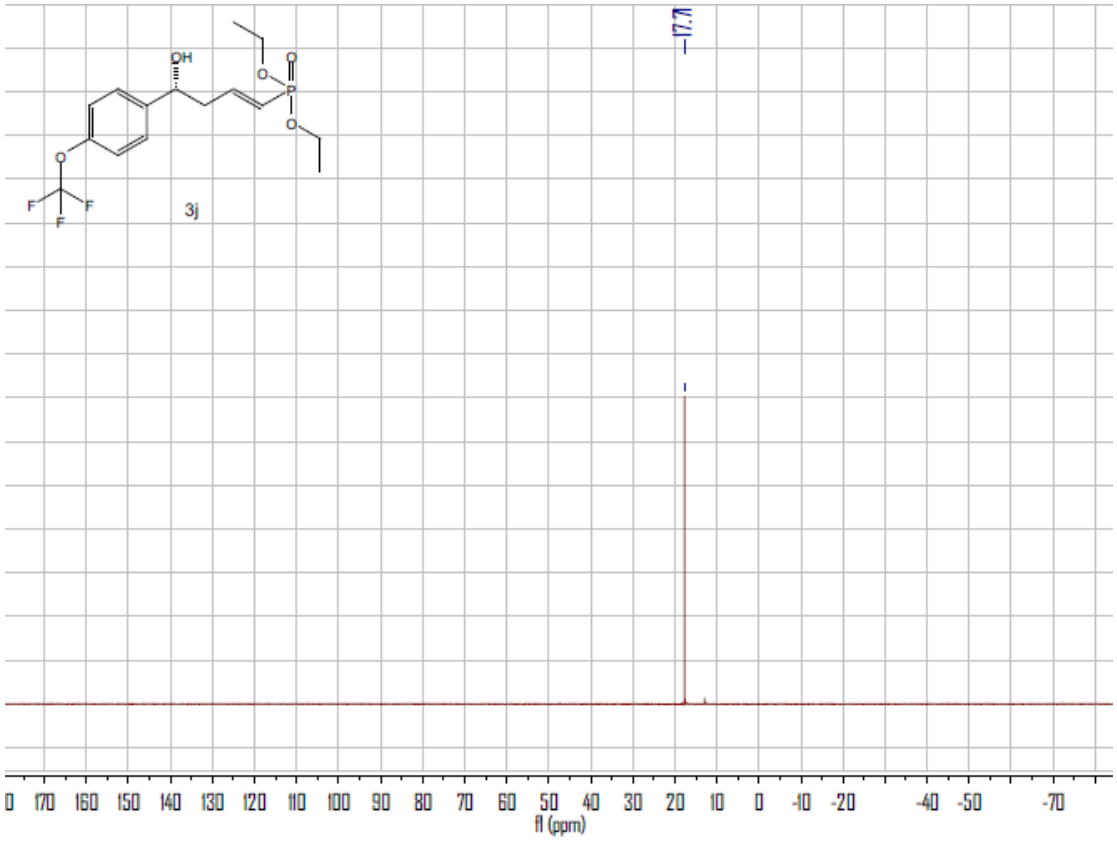


Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3k**, related to **Table 2**

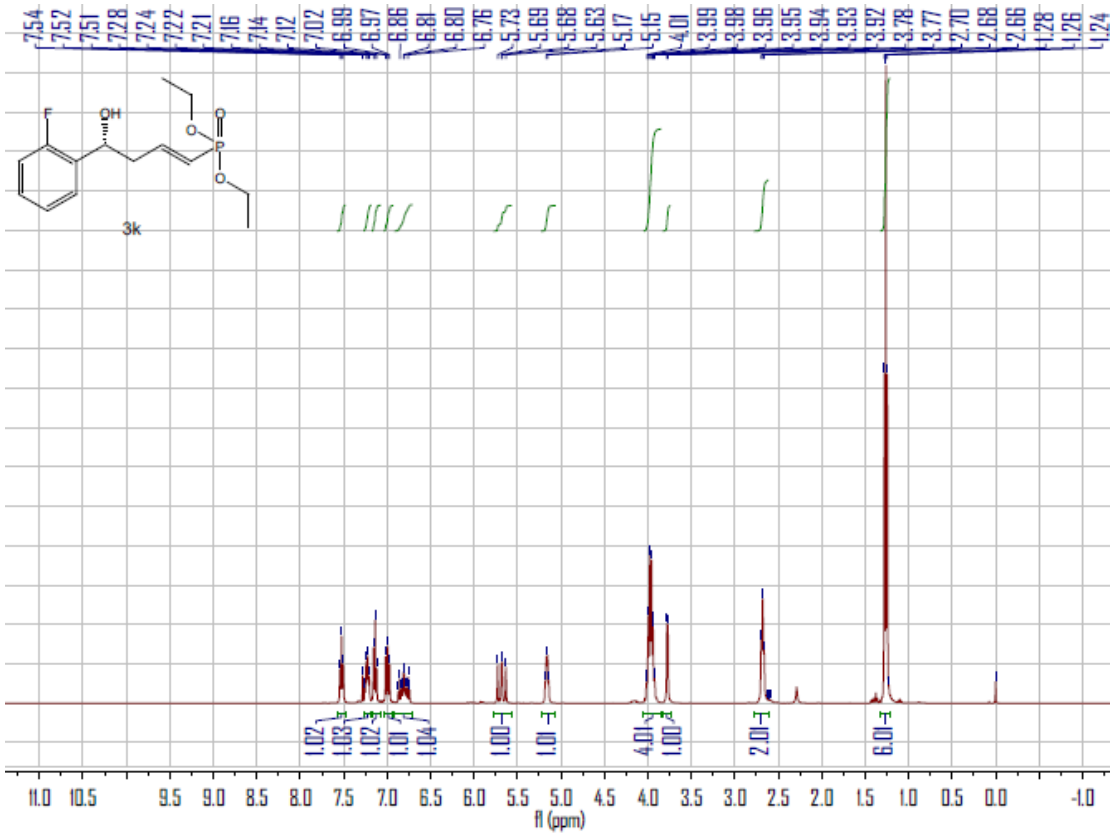


Figure S35. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3k**, related to **Table 2**

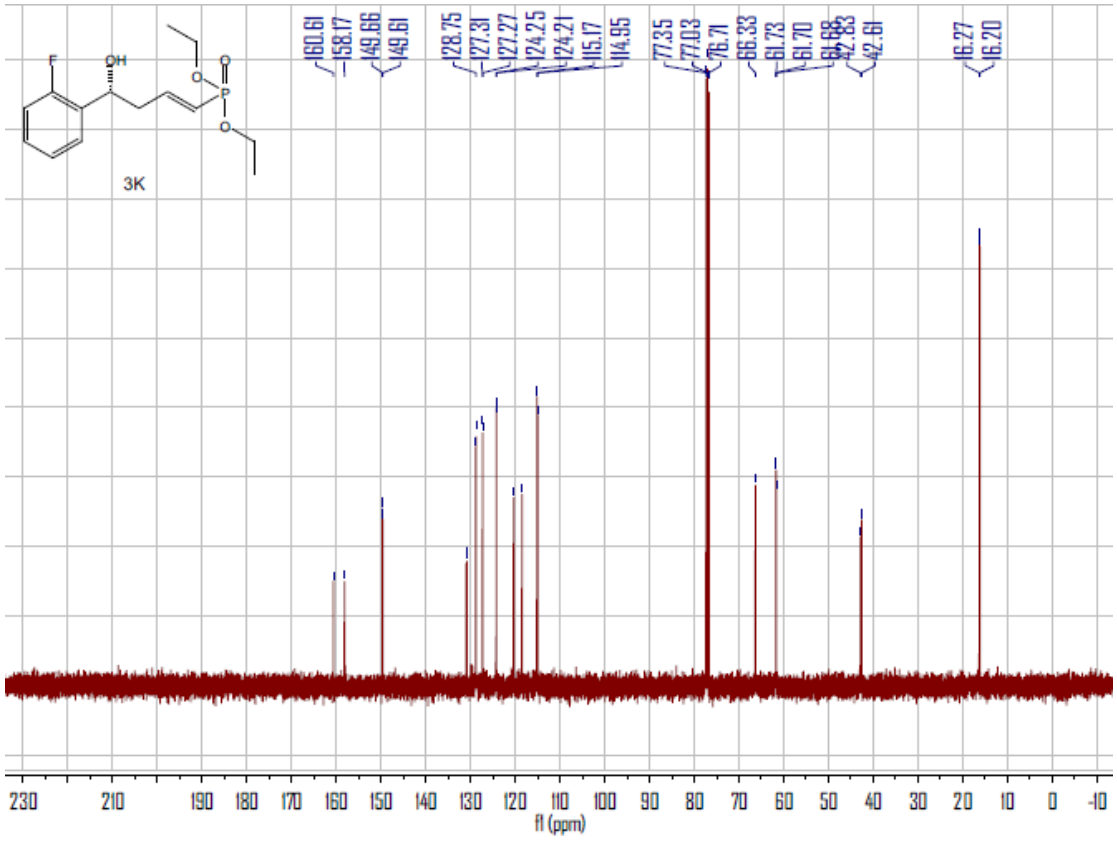


Figure S36. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3k**, related to **Table 2**

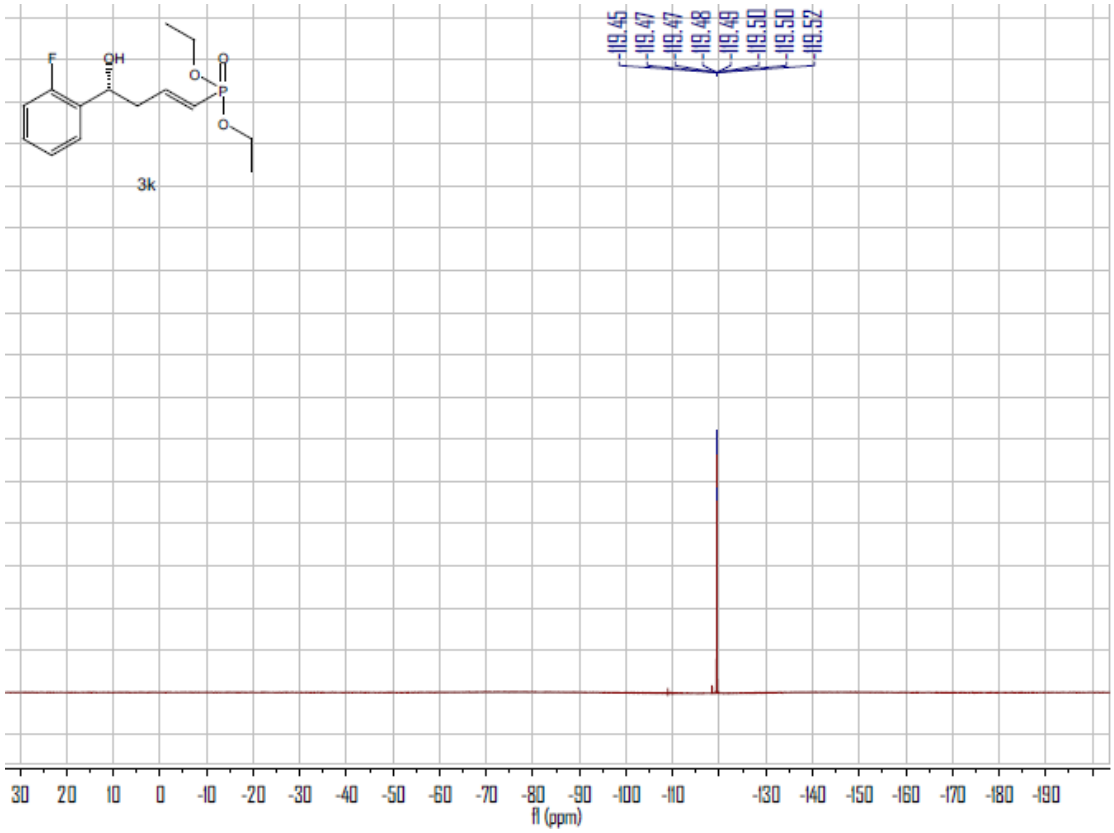


Figure S37. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3k**, related to **Table 2**

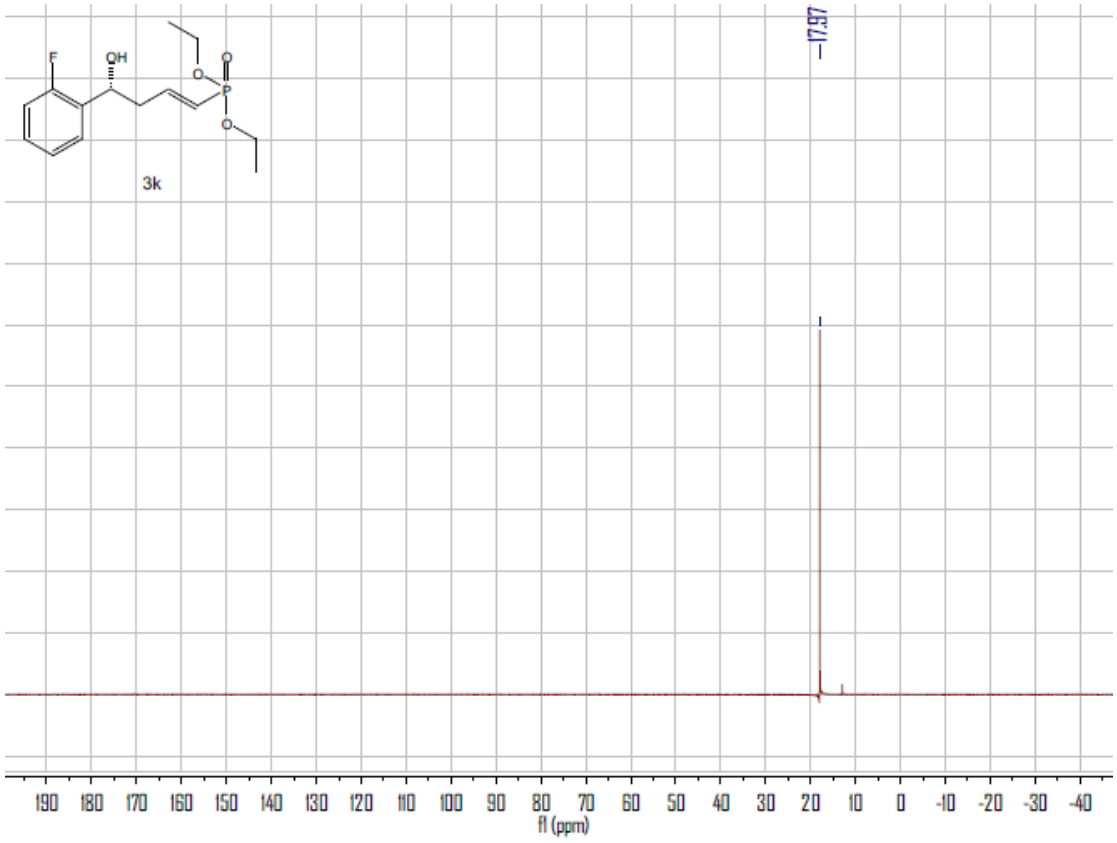


Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3l**, related to **Table 2**

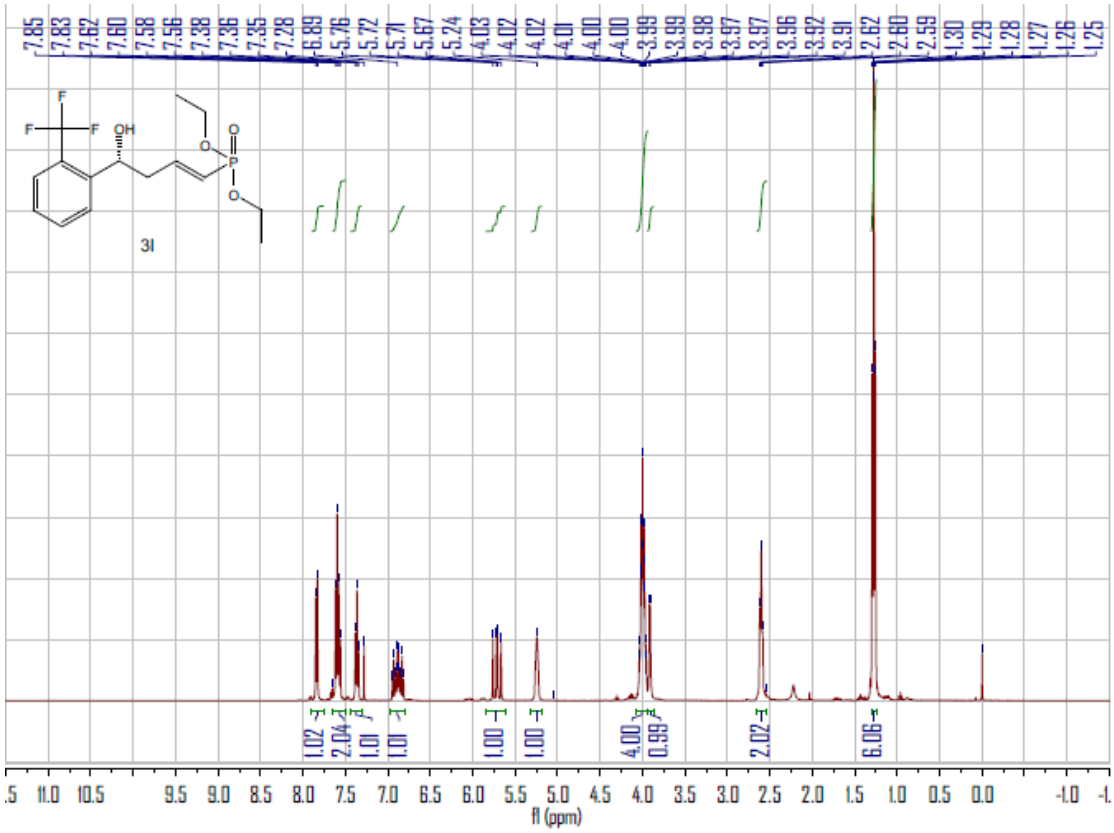


Figure S39. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3l**, related to **Table 2**

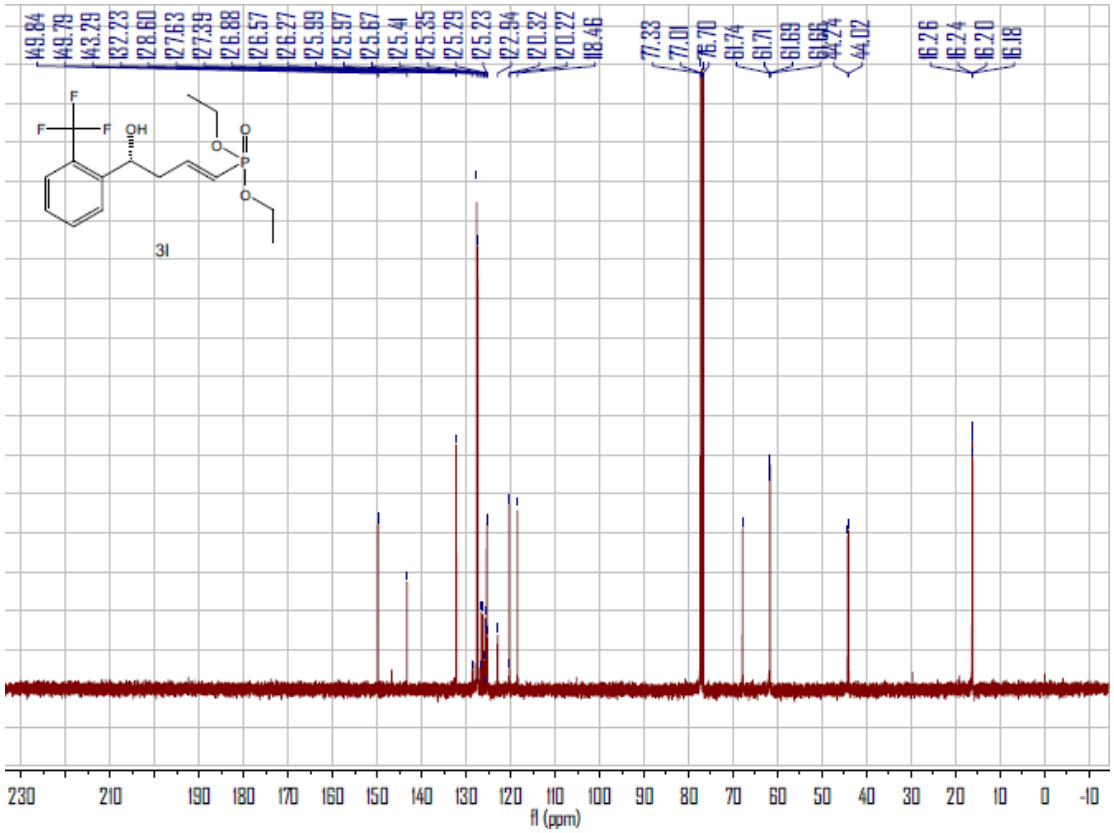


Figure S40. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3l**, related to **Table 2**

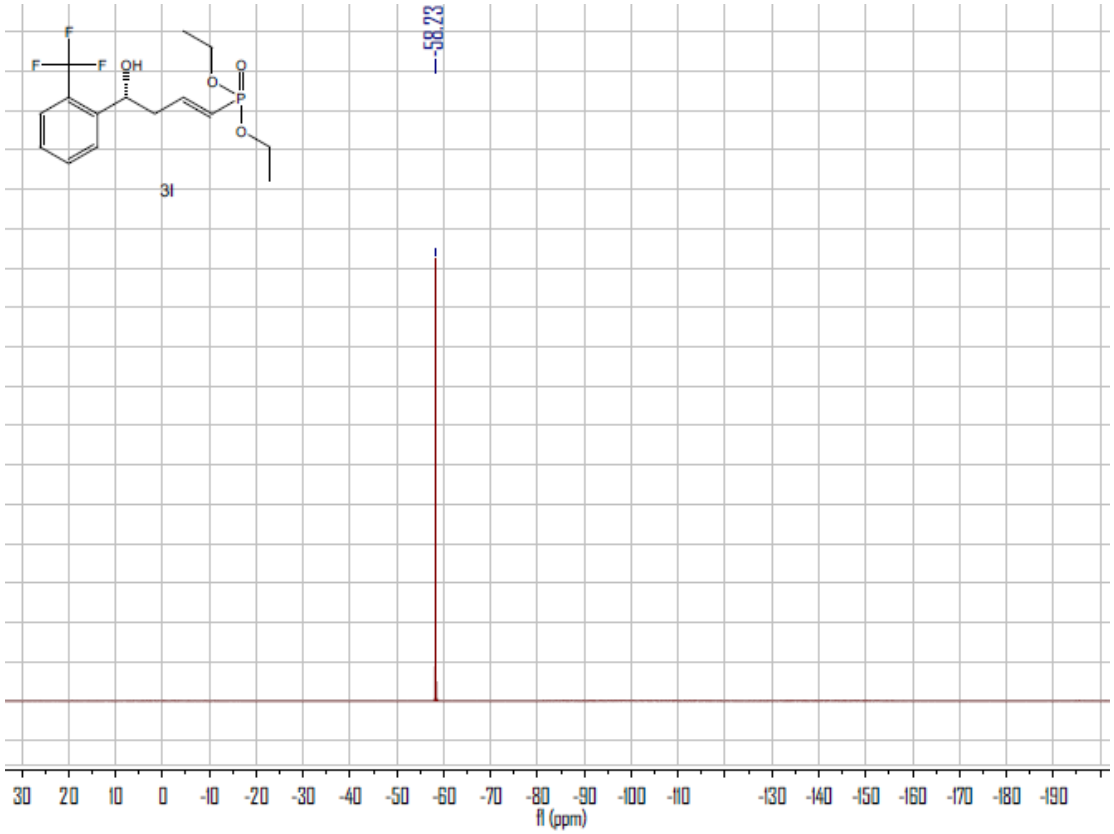


Figure S41. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3l**, related to **Table 2**

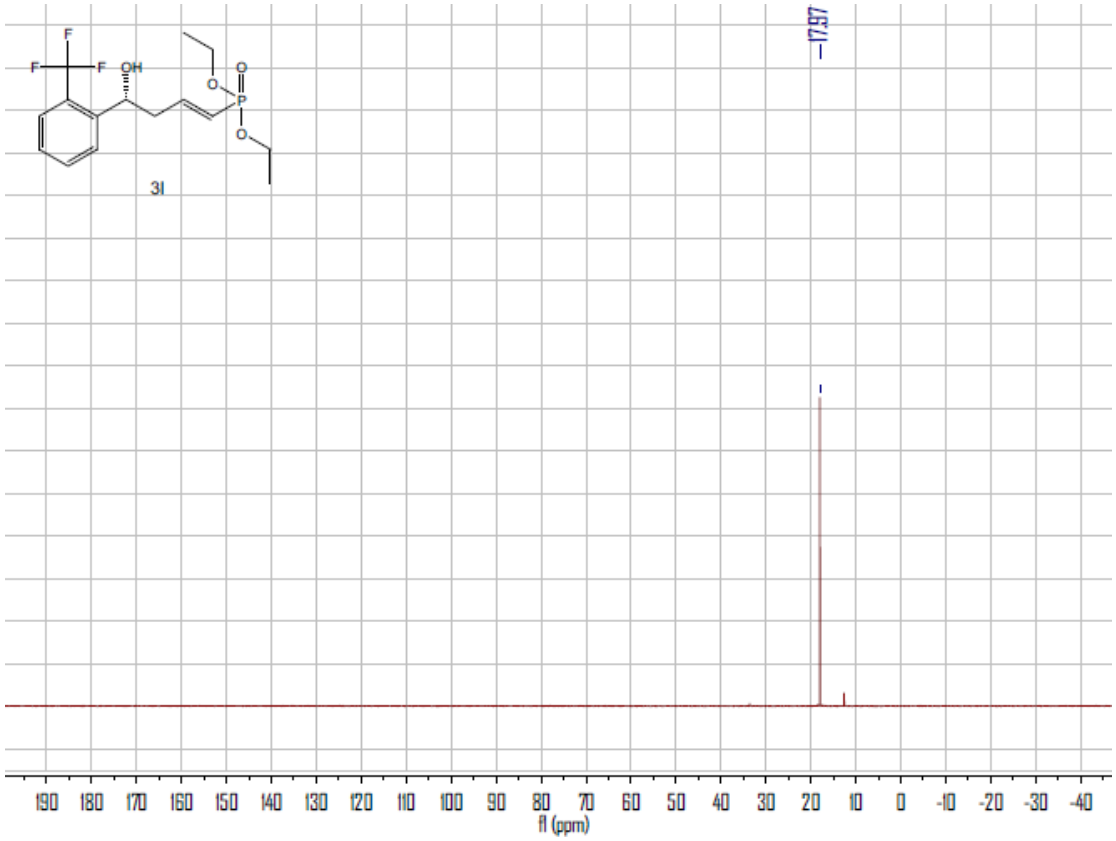


Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3m**, related to **Table 2**

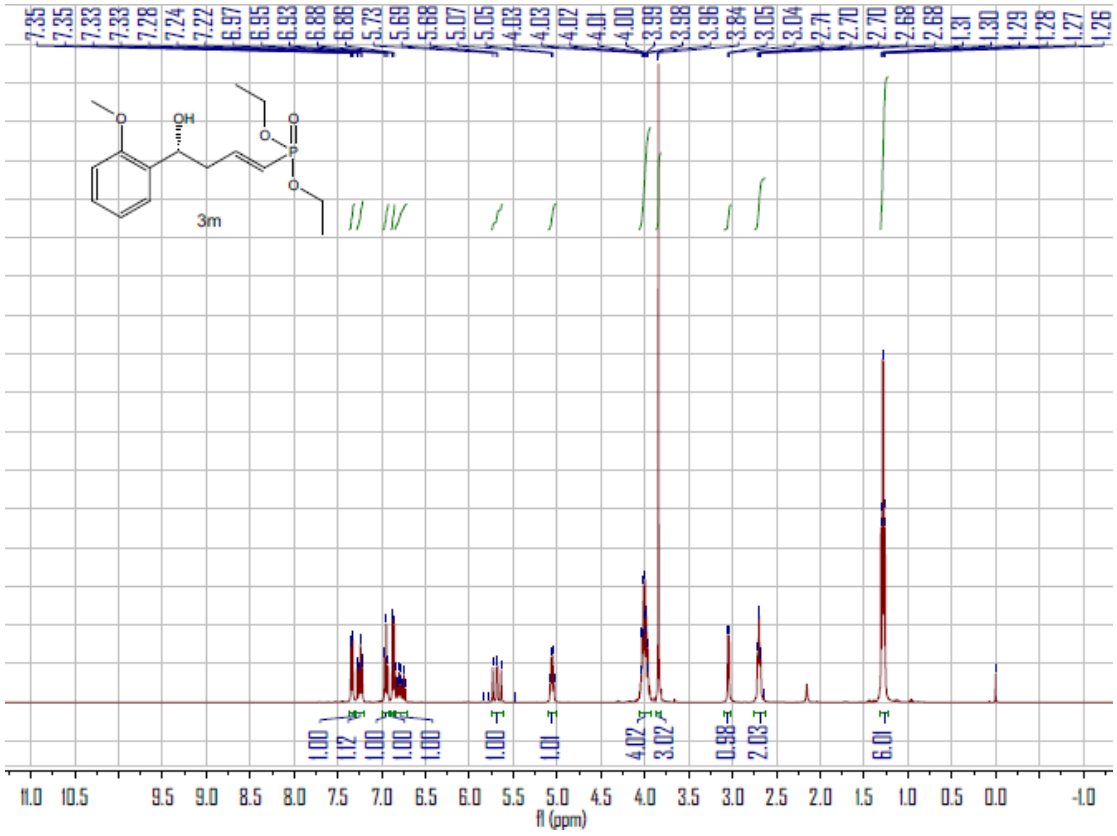


Figure S43. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3m**, related to **Table 2**

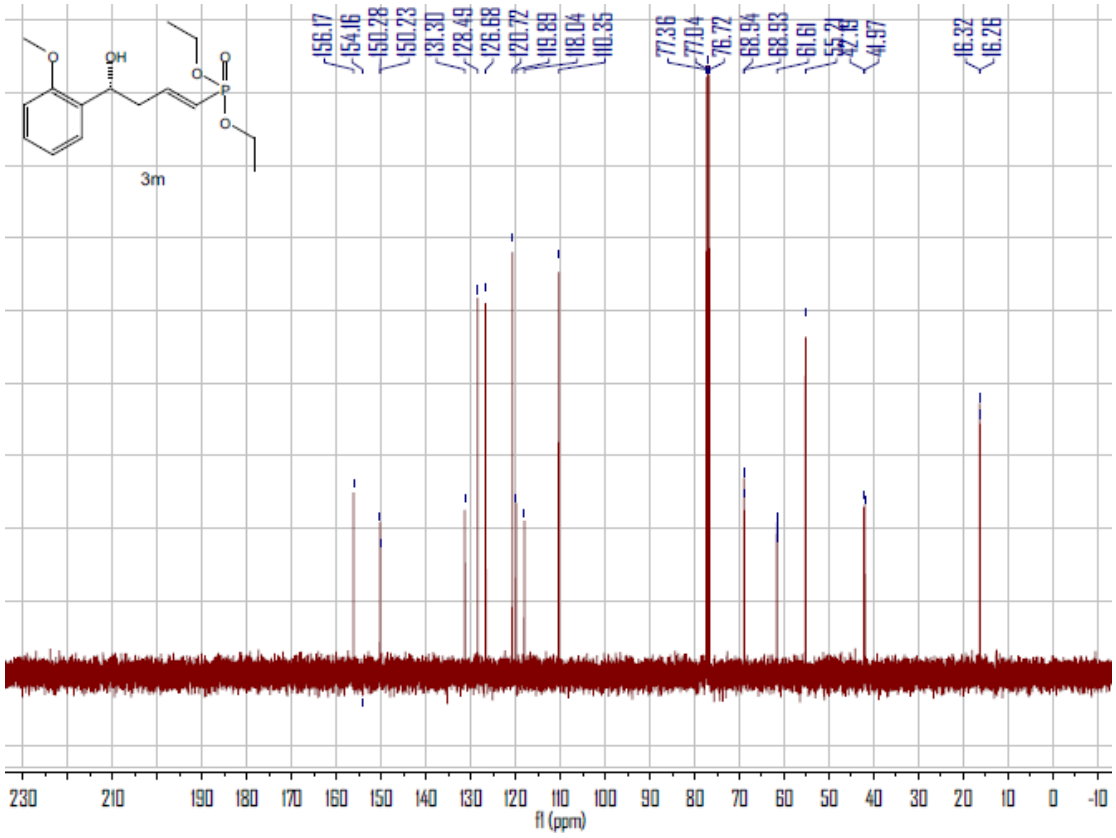


Figure S44. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3m**, related to **Table 2**

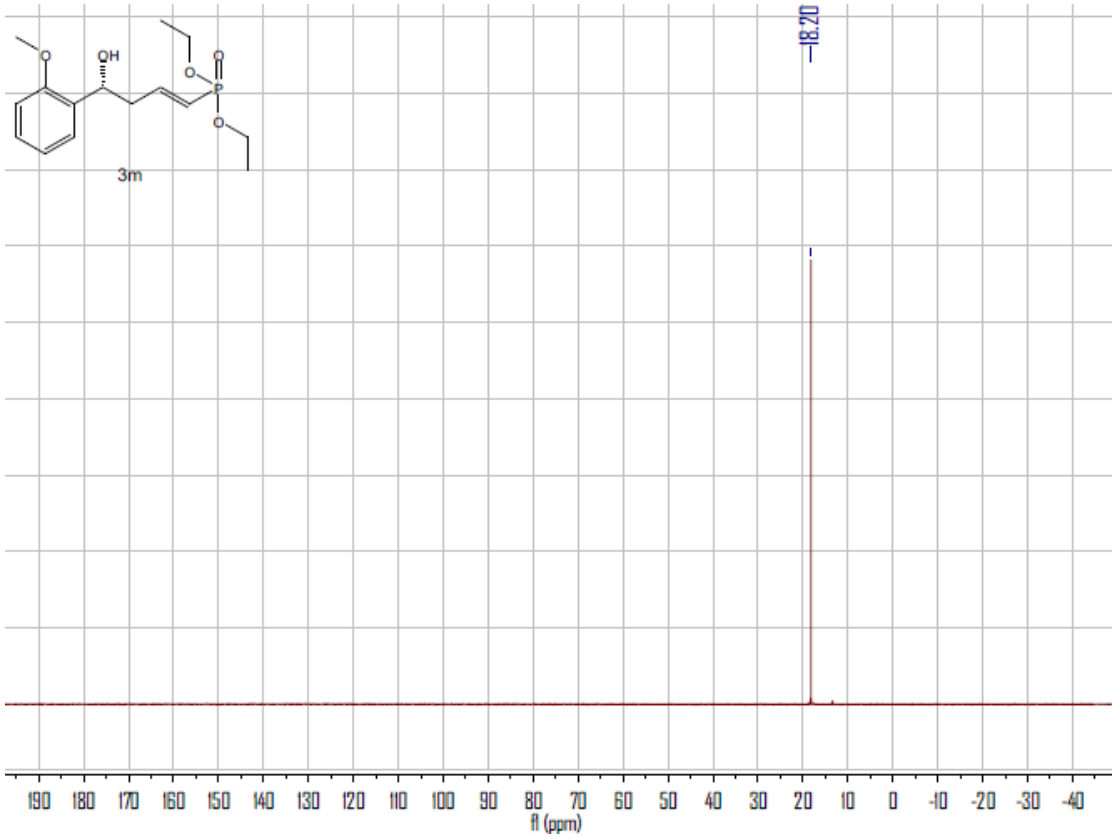


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3n**, related to **Table 2**

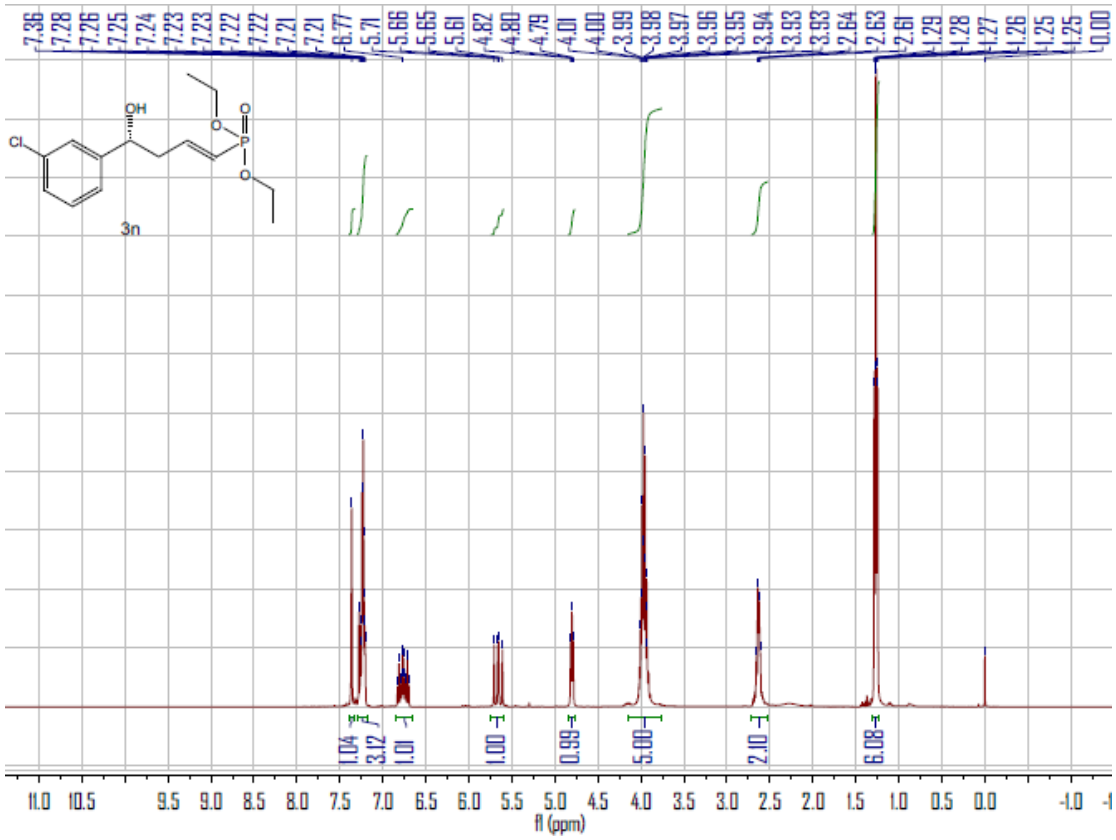


Figure S46. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3n**, related to **Table 2**

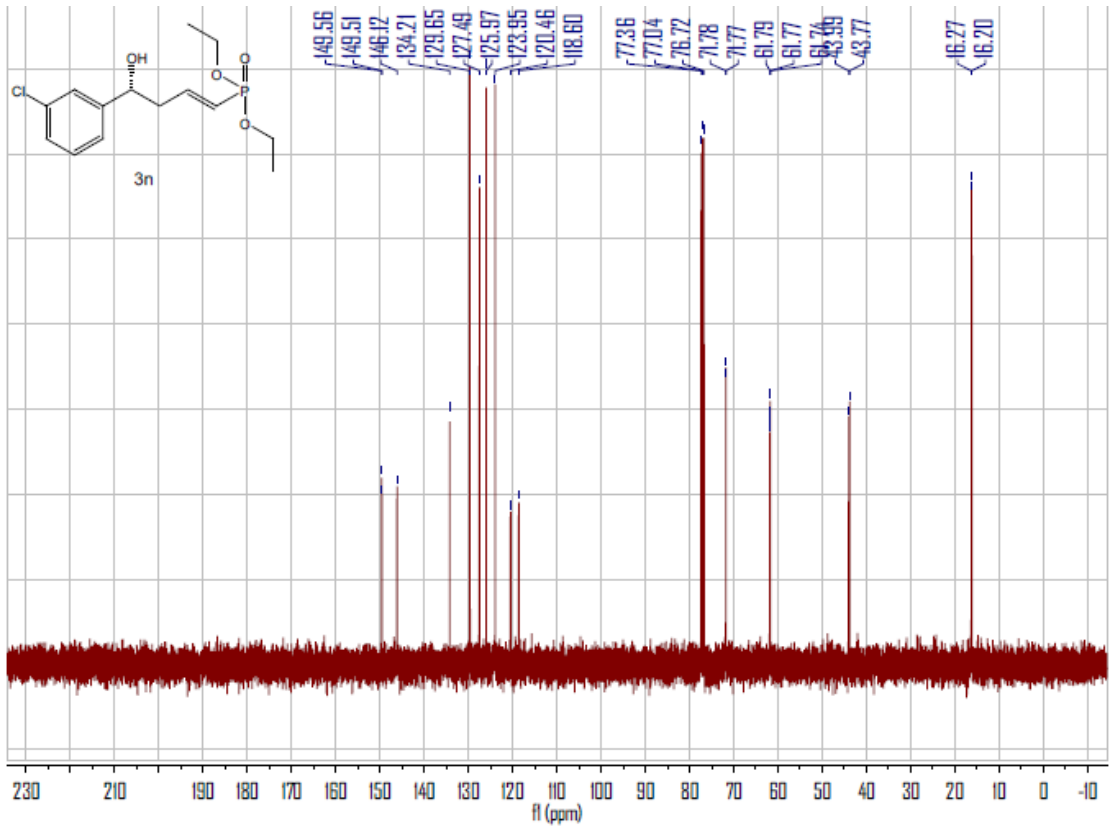


Figure S47. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3n**, related to **Table 2**

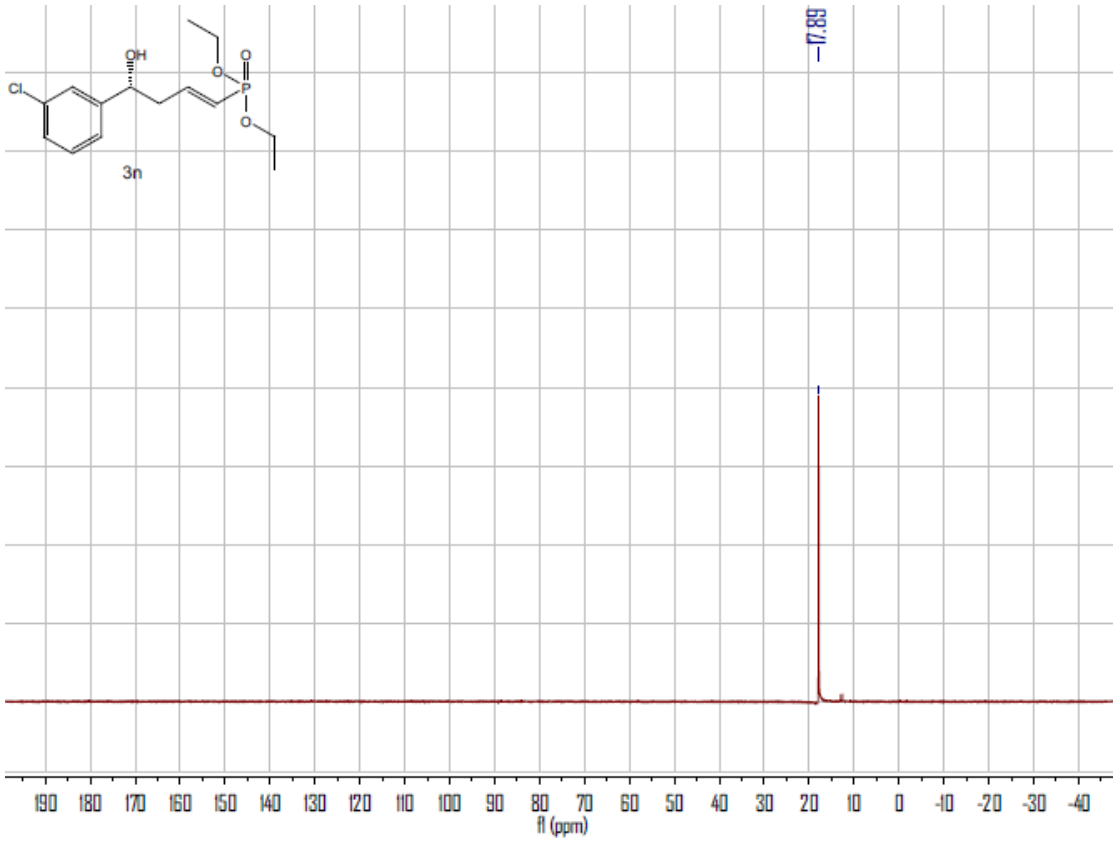


Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3o**, related to **Table 2**

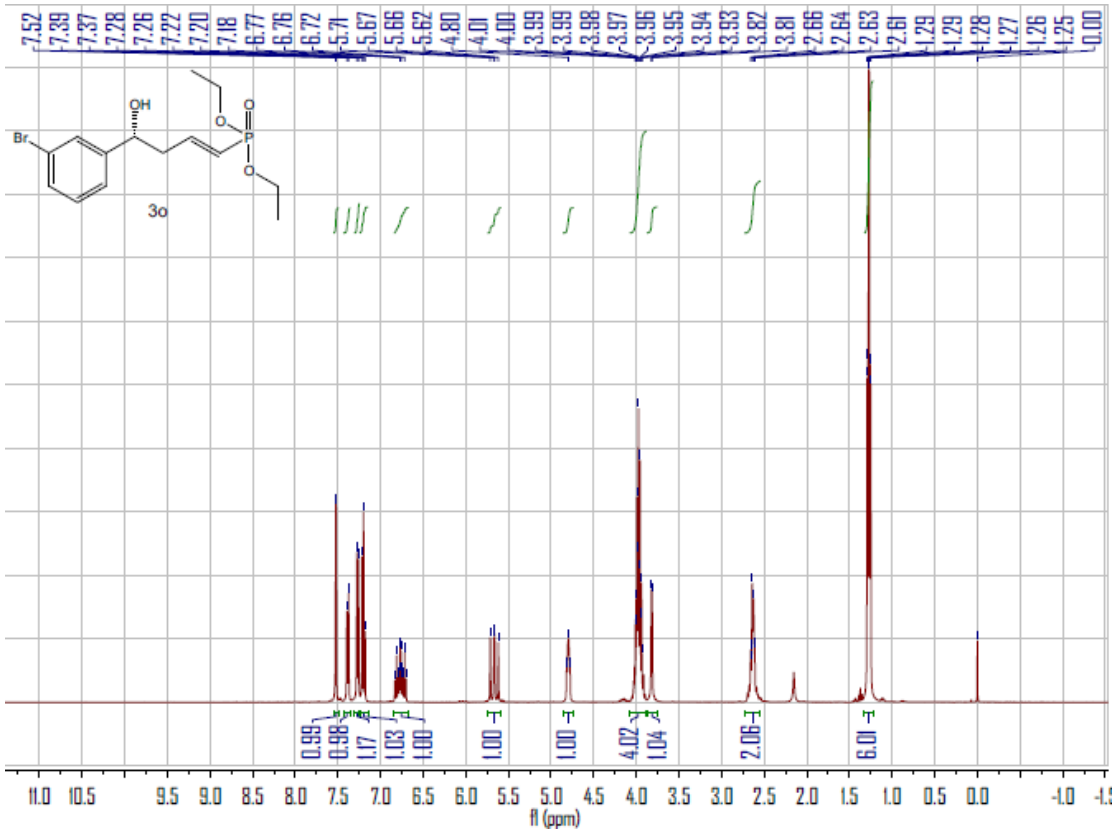


Figure S49. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3o**, related to **Table 2**

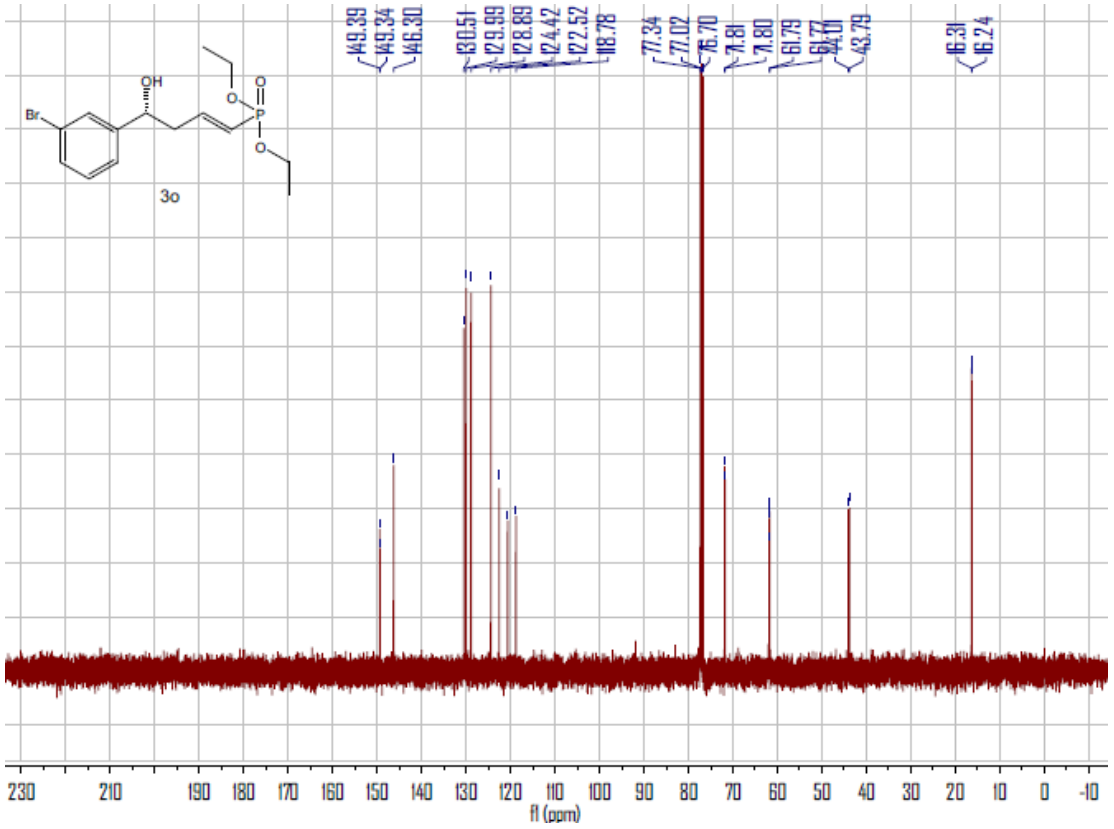


Figure S50. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3o**, related to **Table 2**

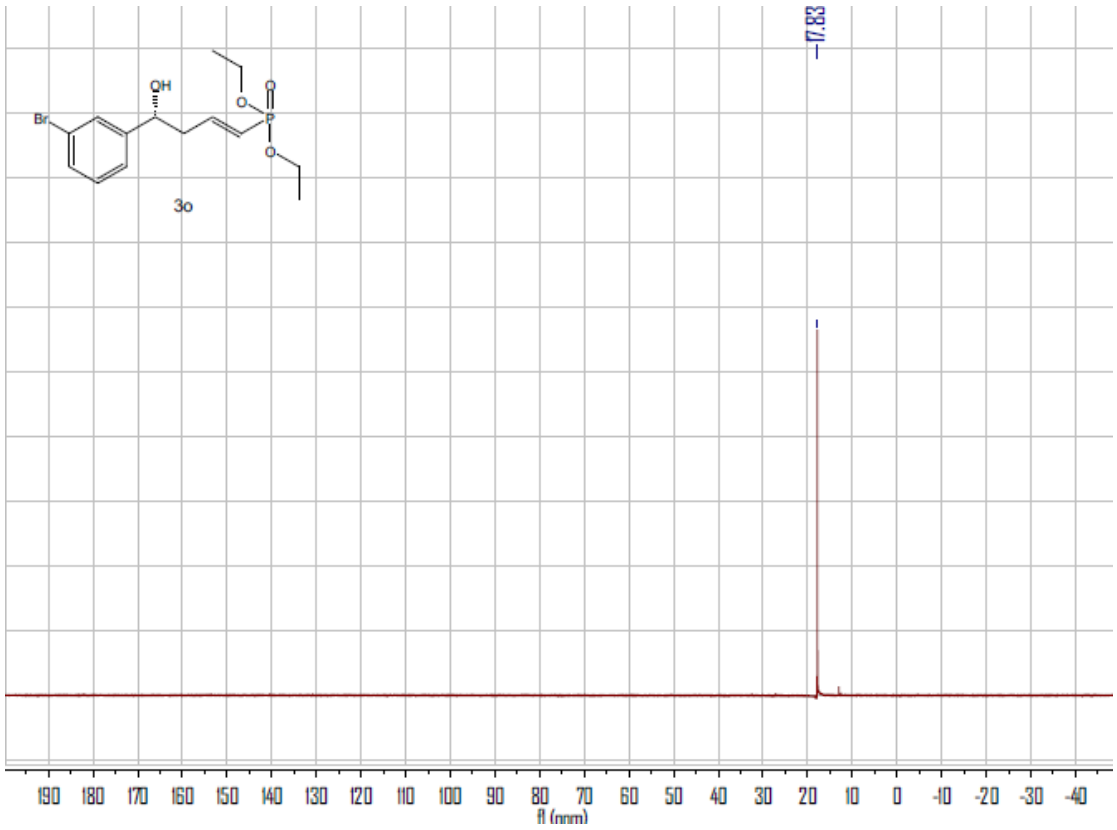


Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3p**, related to **Table 2**

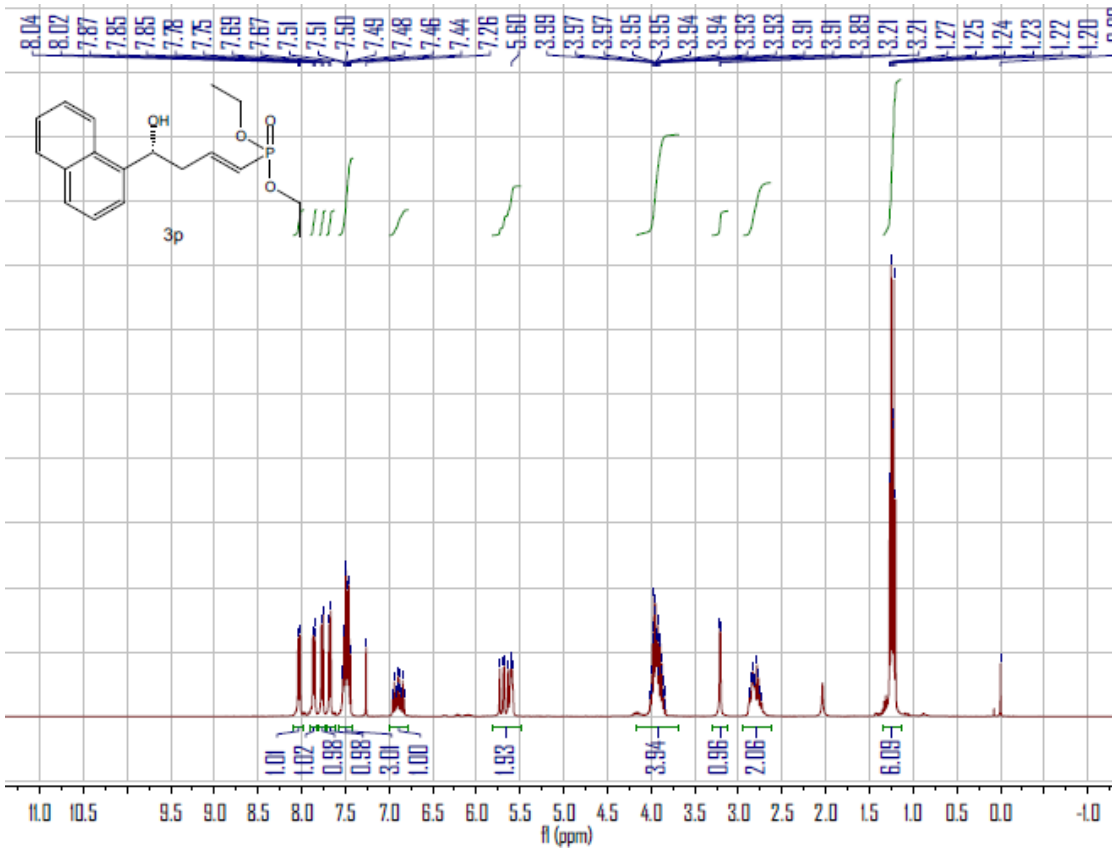


Figure S52. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3p**, related to **Table 2**

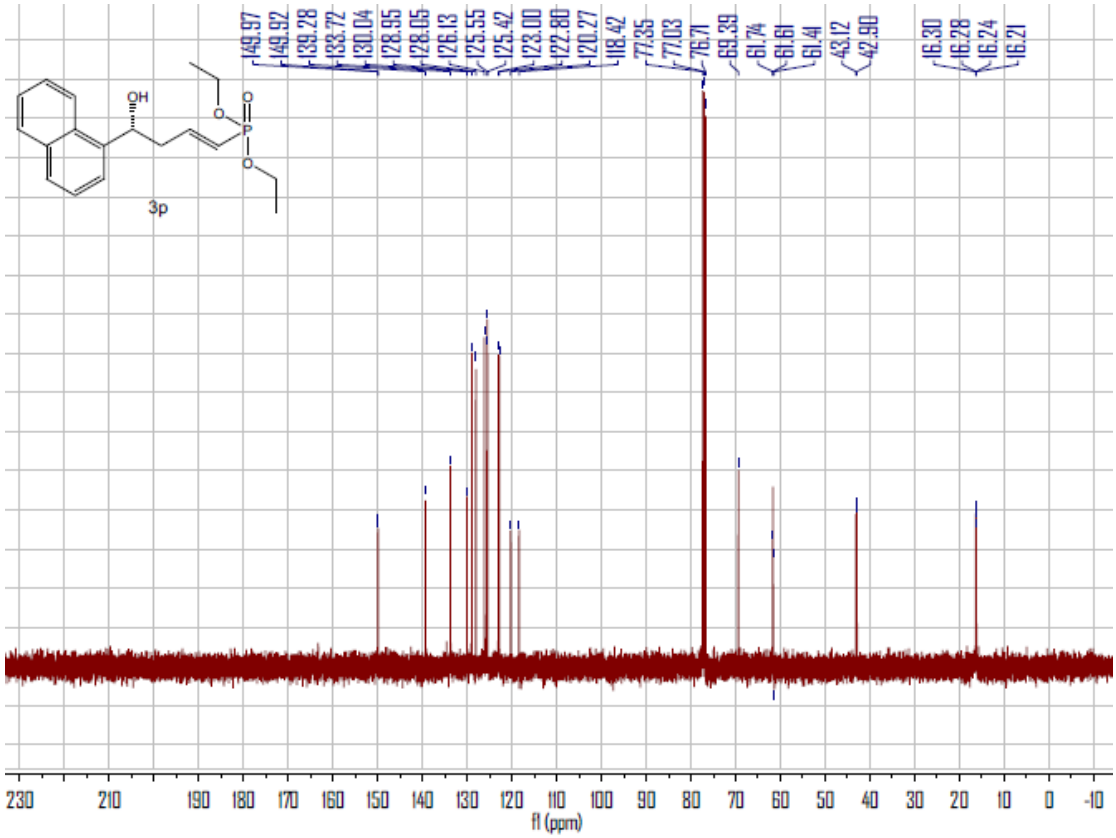


Figure S53. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3p**, related to **Table 2**

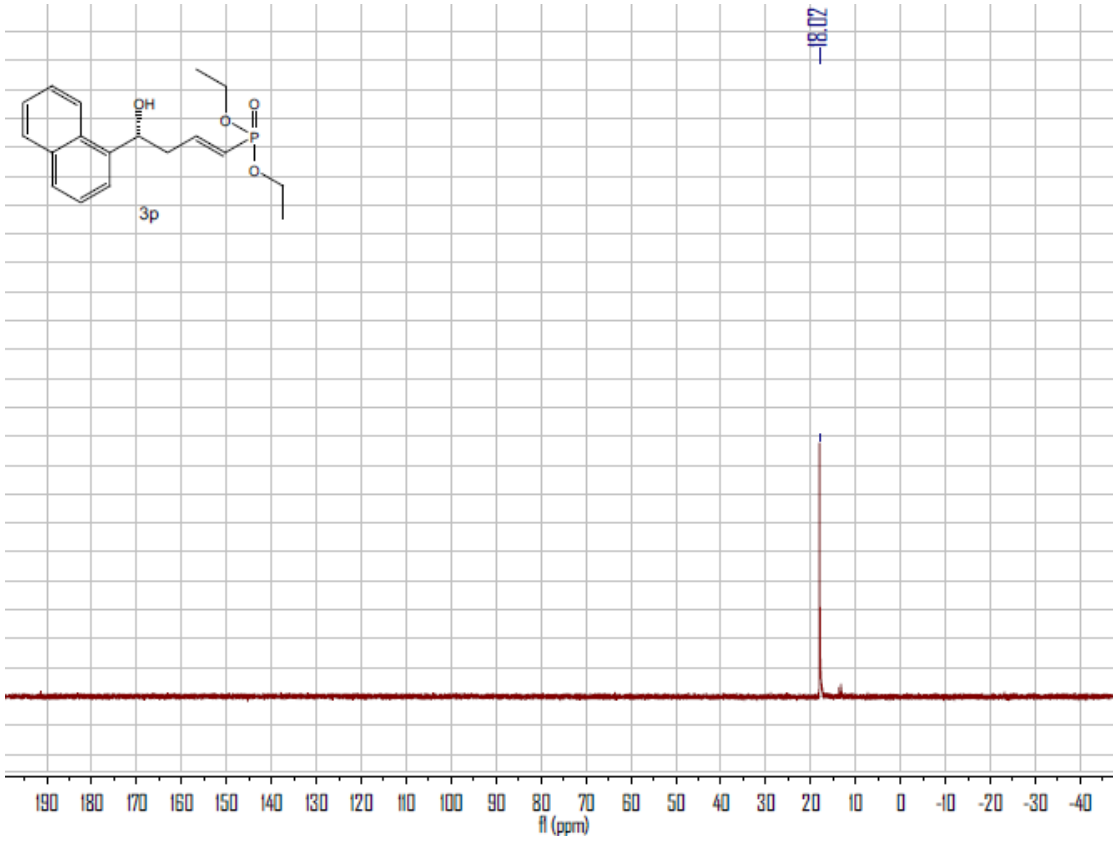


Figure S54. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3q**, related to **Table 2**

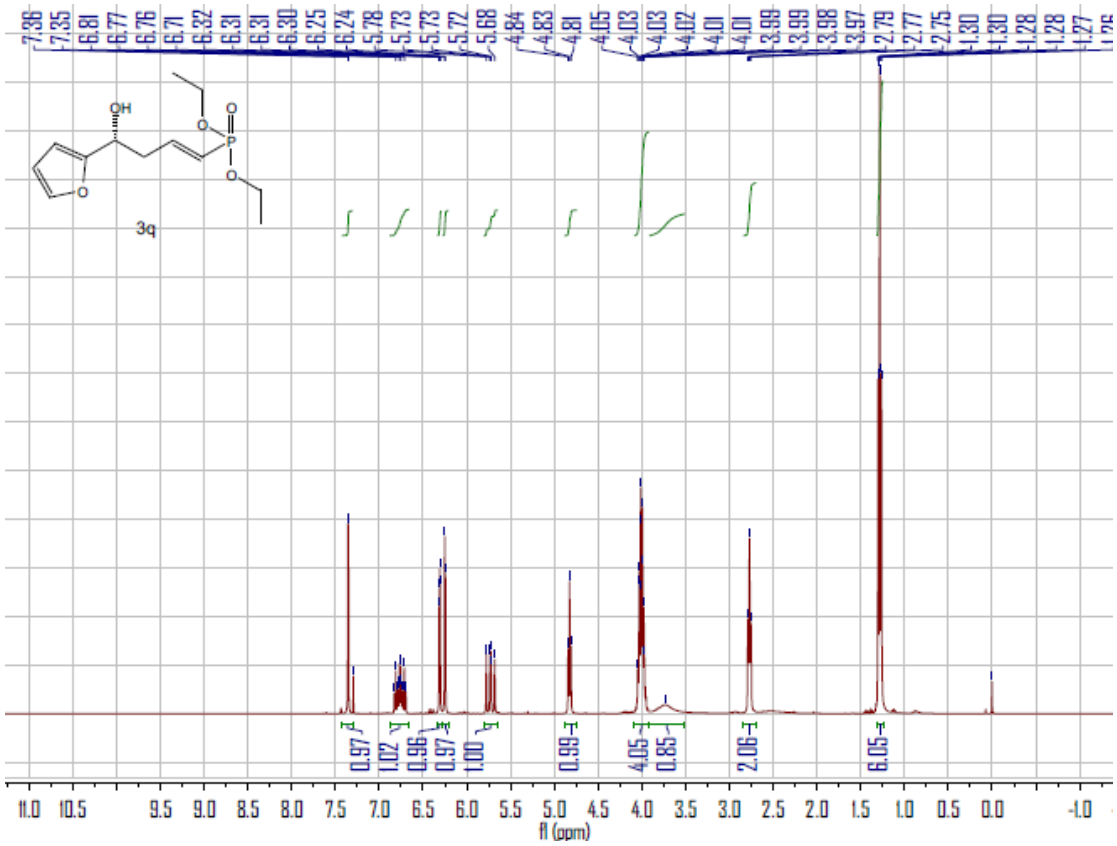


Figure S55. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3q**, related to **Table 2**

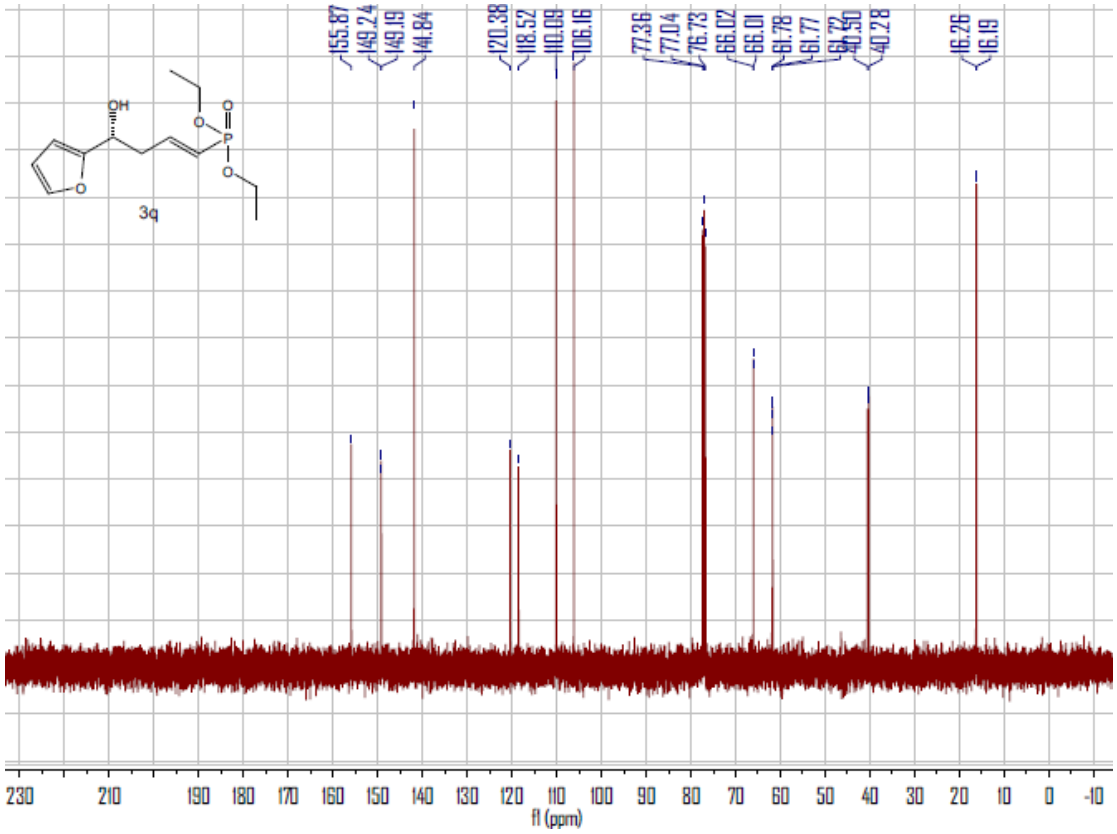


Figure S56. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3q**, related to **Table 2**

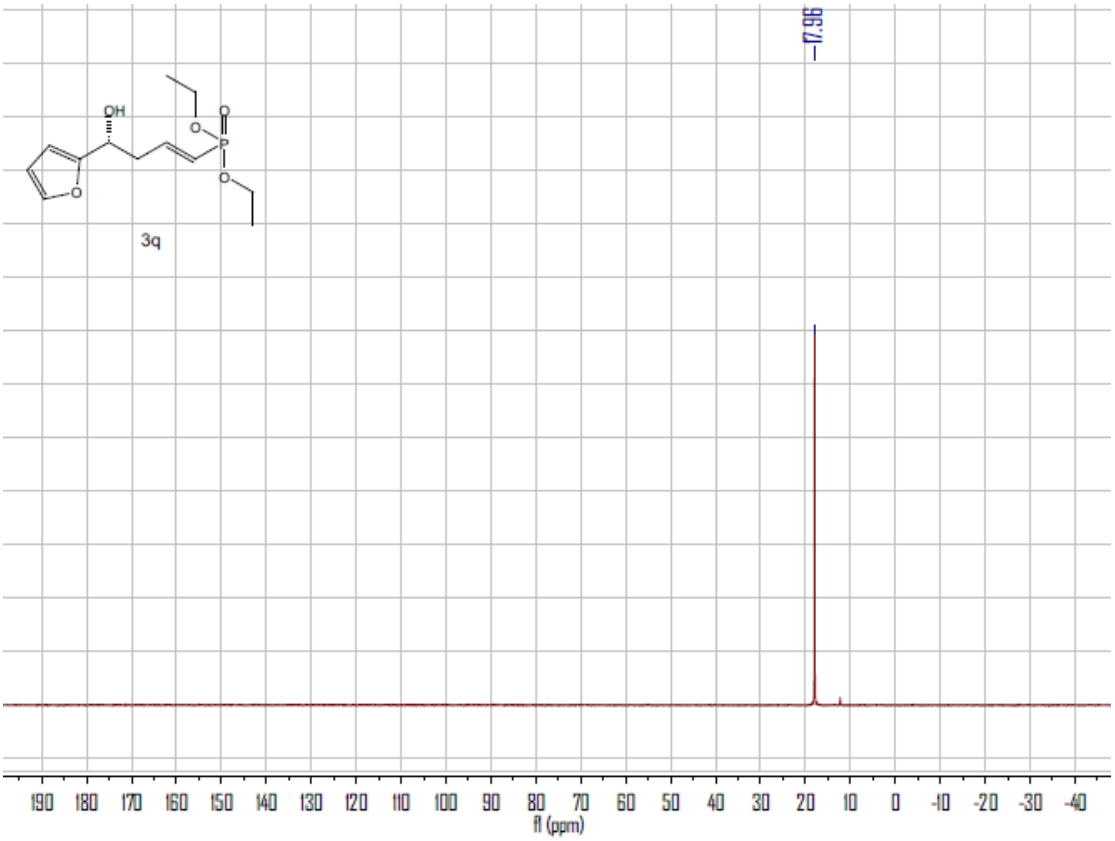


Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3r**, related to **Table 2**

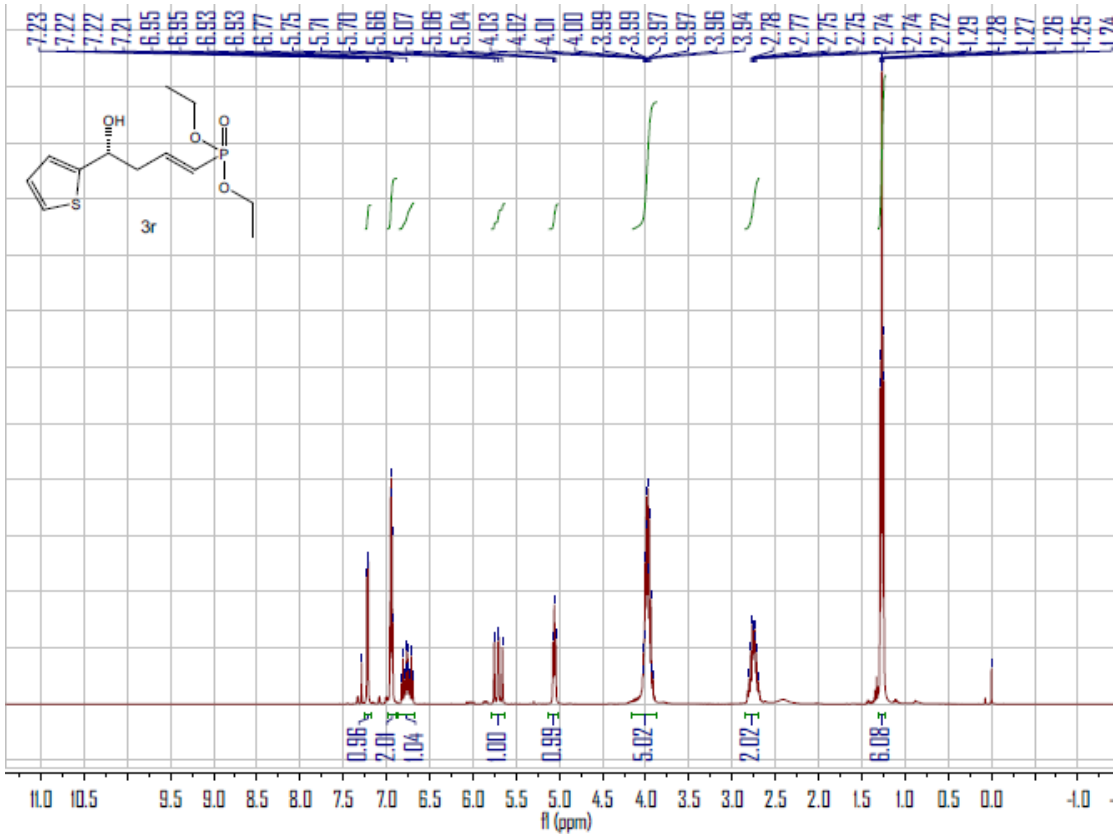


Figure S58. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3r**, related to **Table 2**

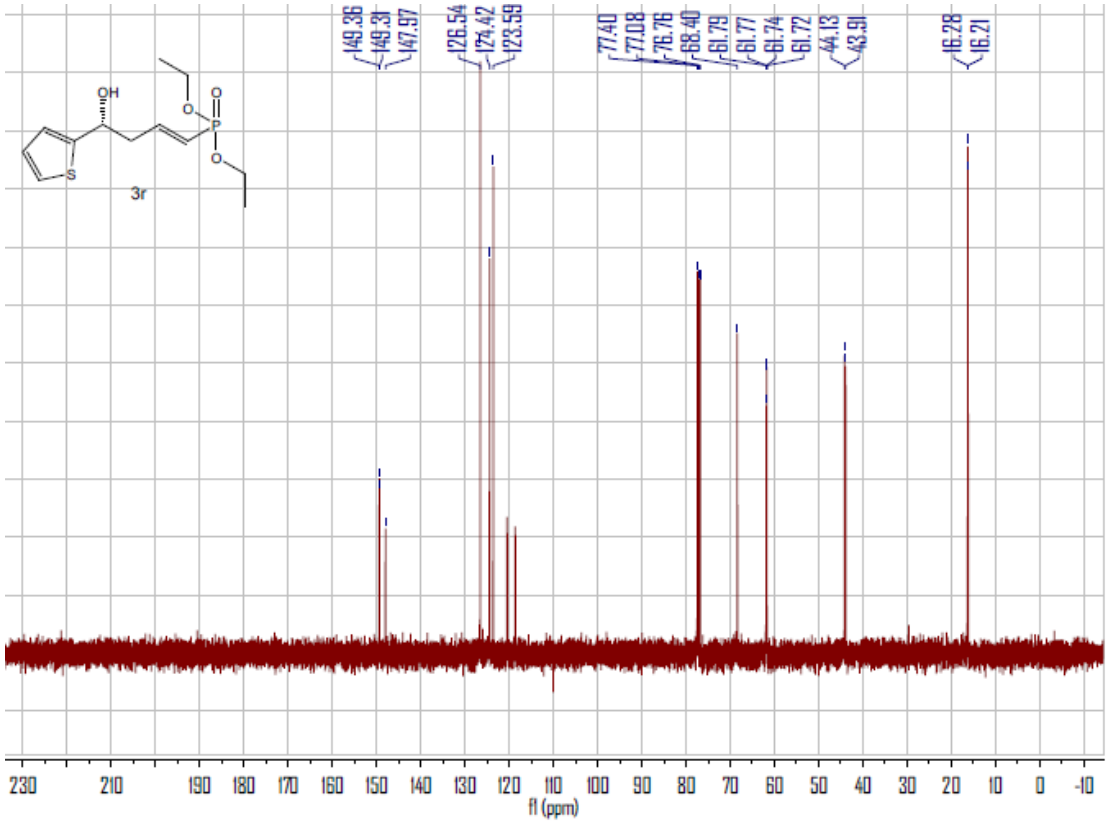


Figure S59. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3r**, related to **Table 2**

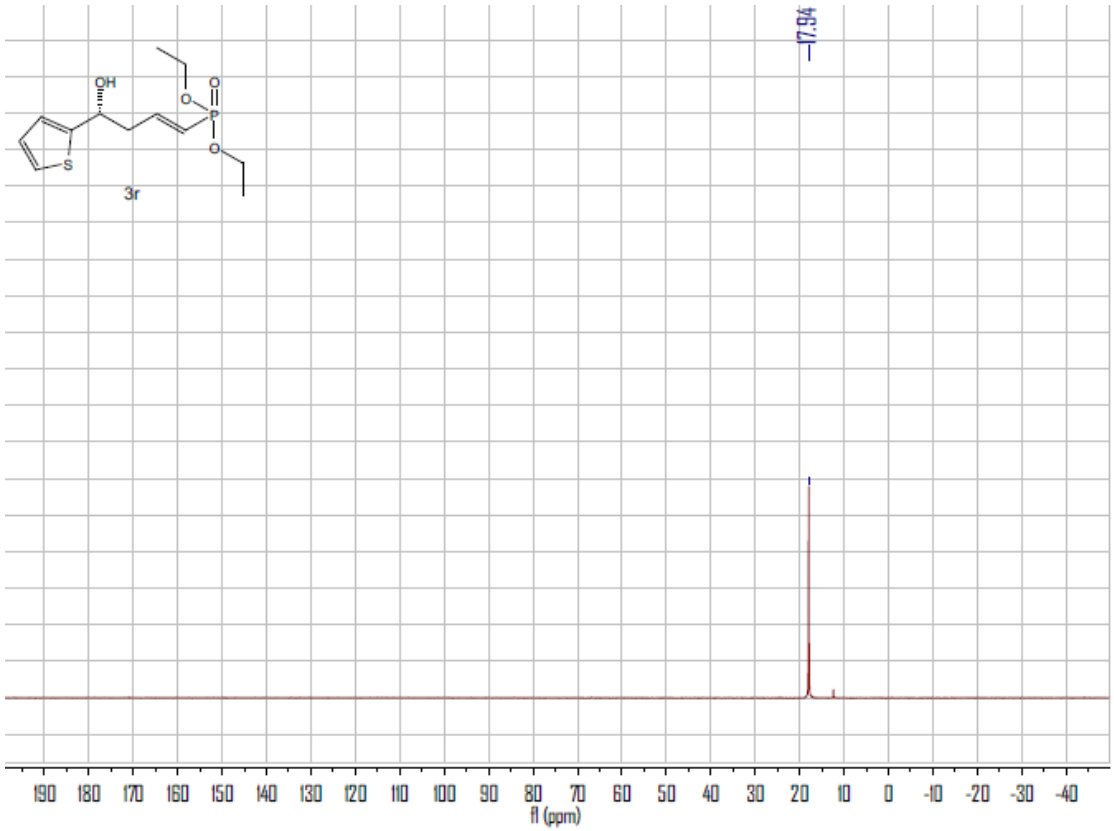


Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3s**, related to **Table 2**

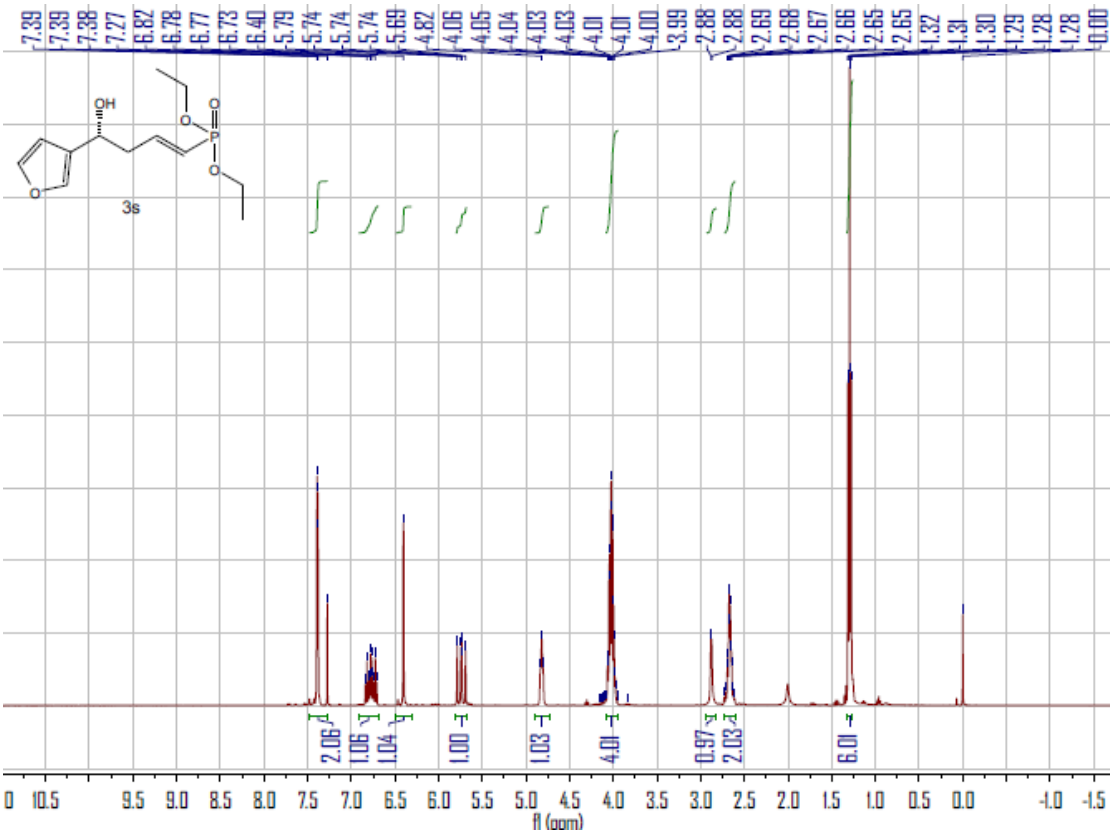


Figure S61. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3s**, related to **Table 2**

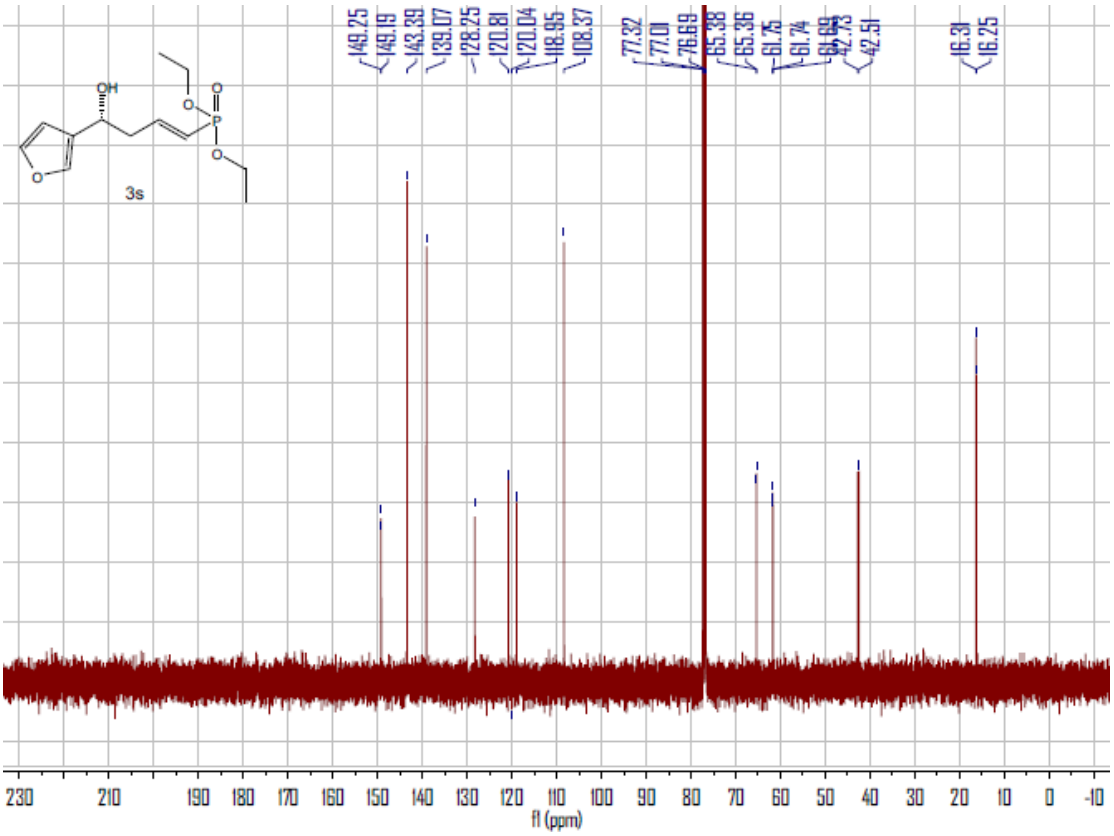


Figure S62. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3s**, related to **Table 2**

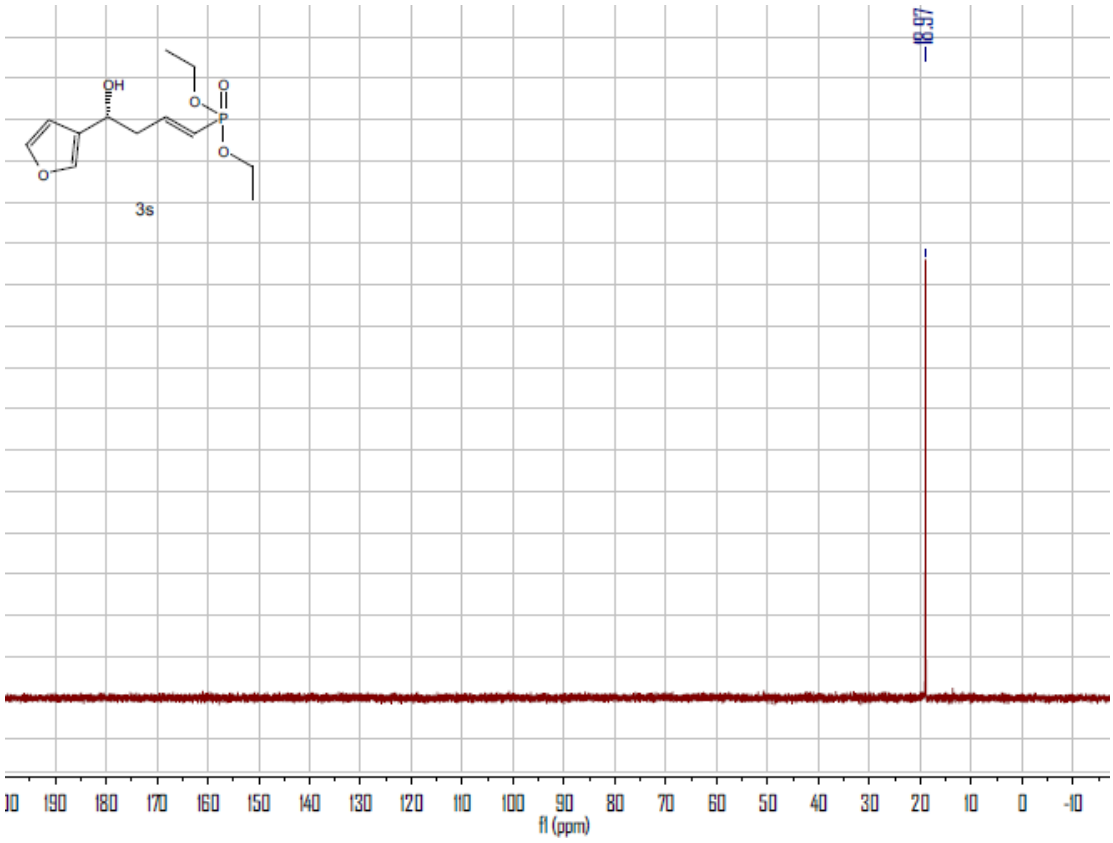


Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3t**, related to **Table 2**

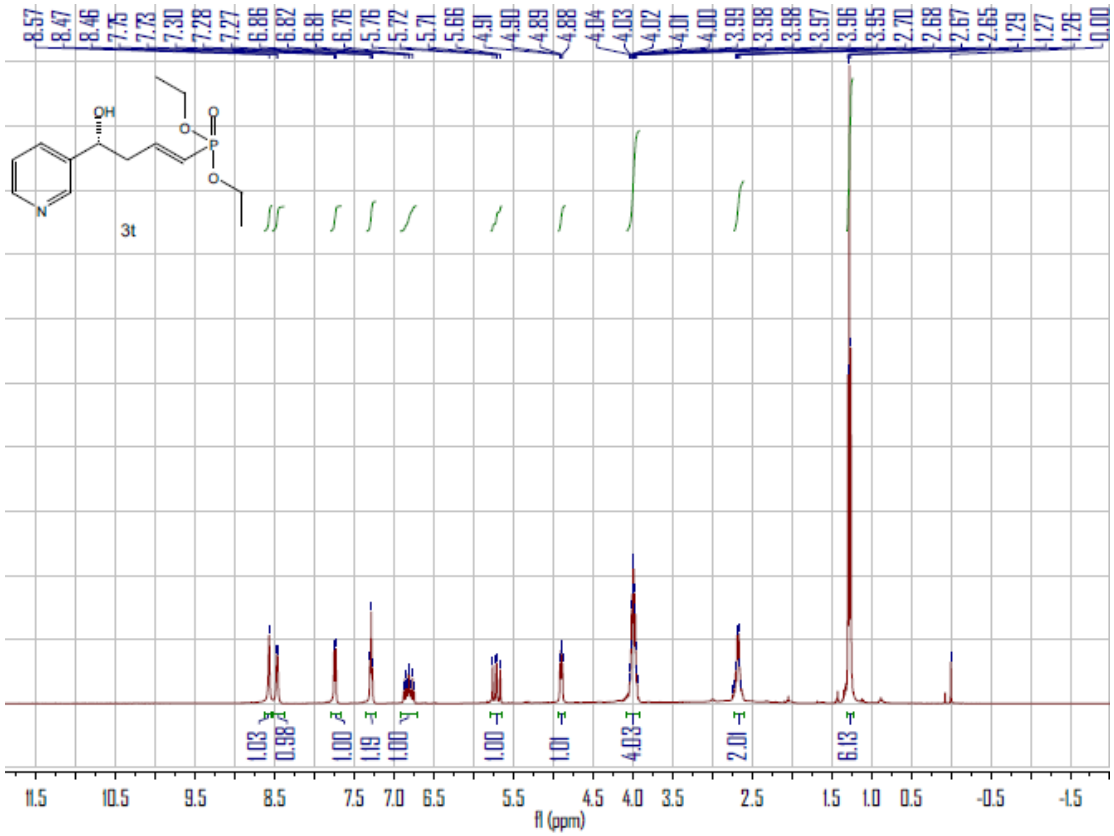


Figure S64. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3t**, related to **Table 2**

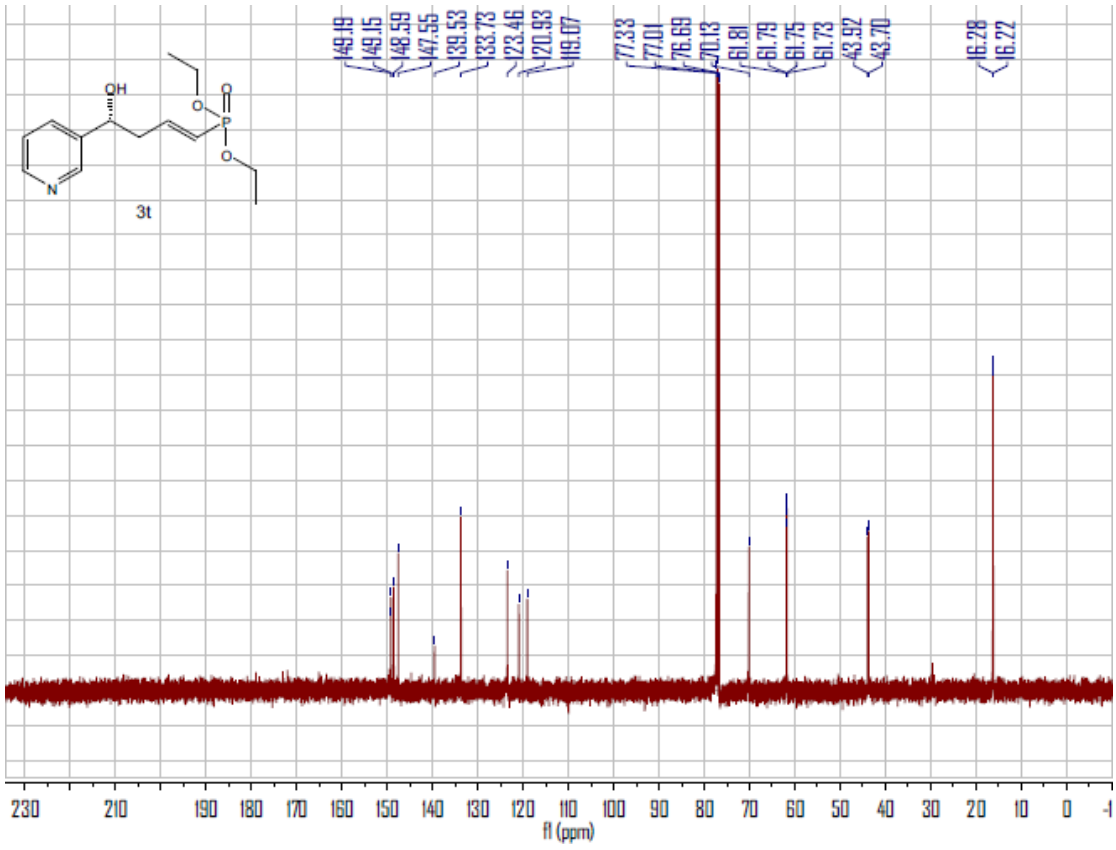


Figure S65. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3t**, related to **Table 2**

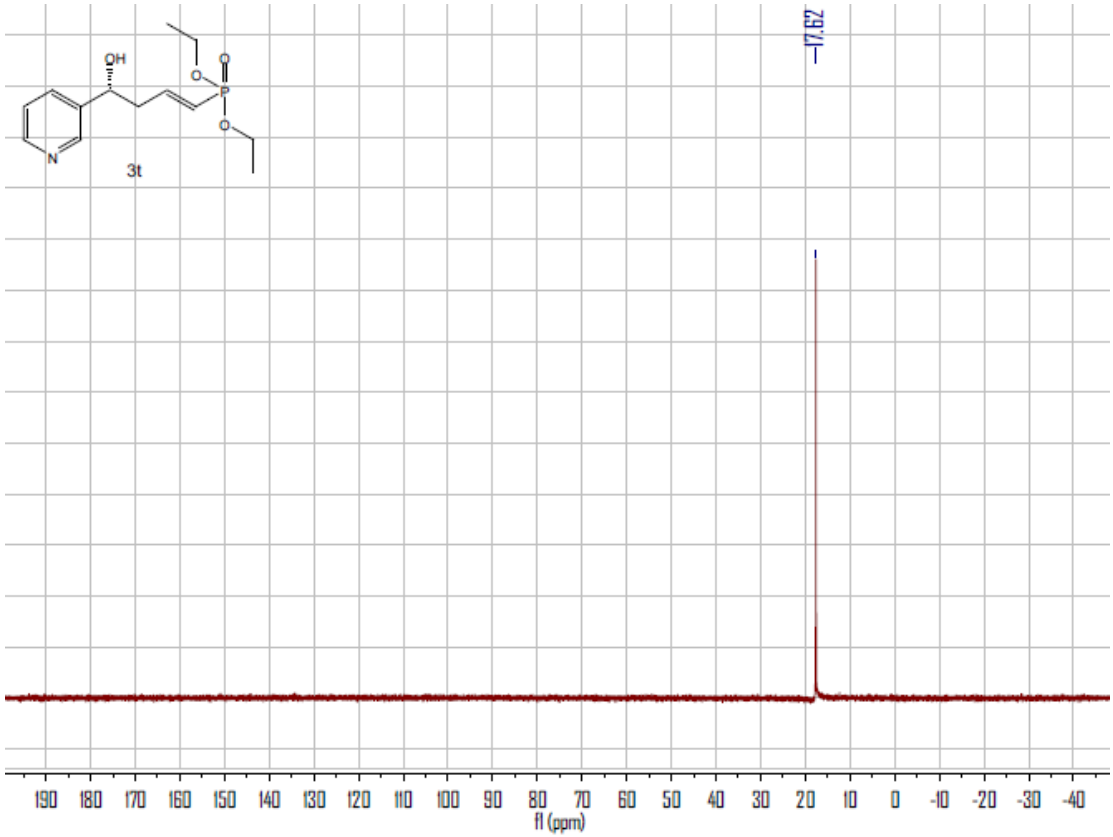


Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3u**, related to **Table 2**

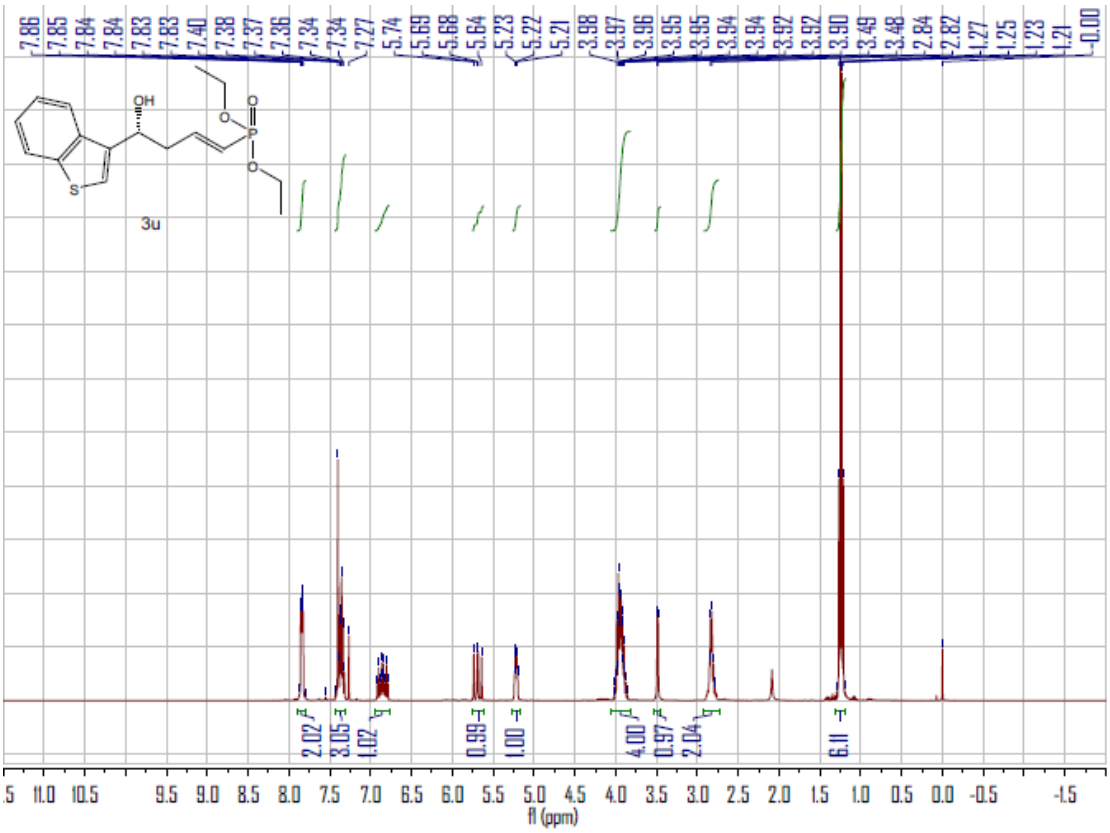


Figure S67. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3u**, related to **Table 2**

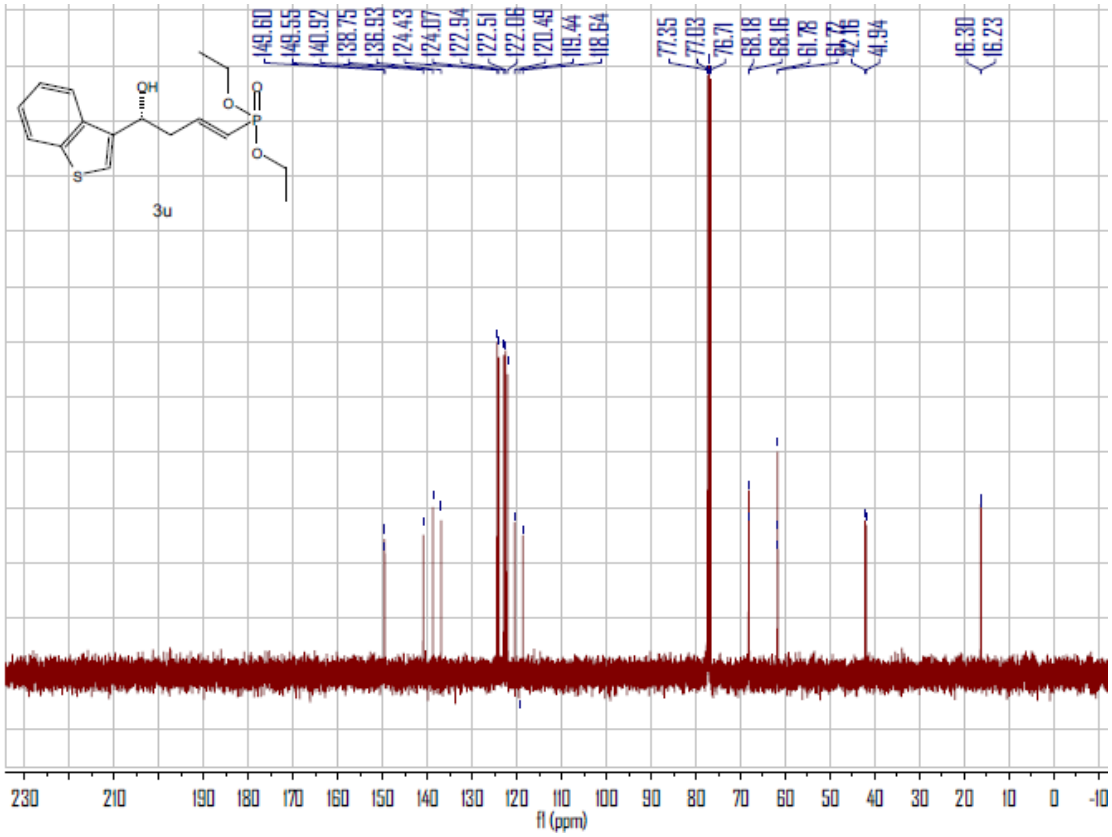


Figure S68. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3u**, related to **Table 2**

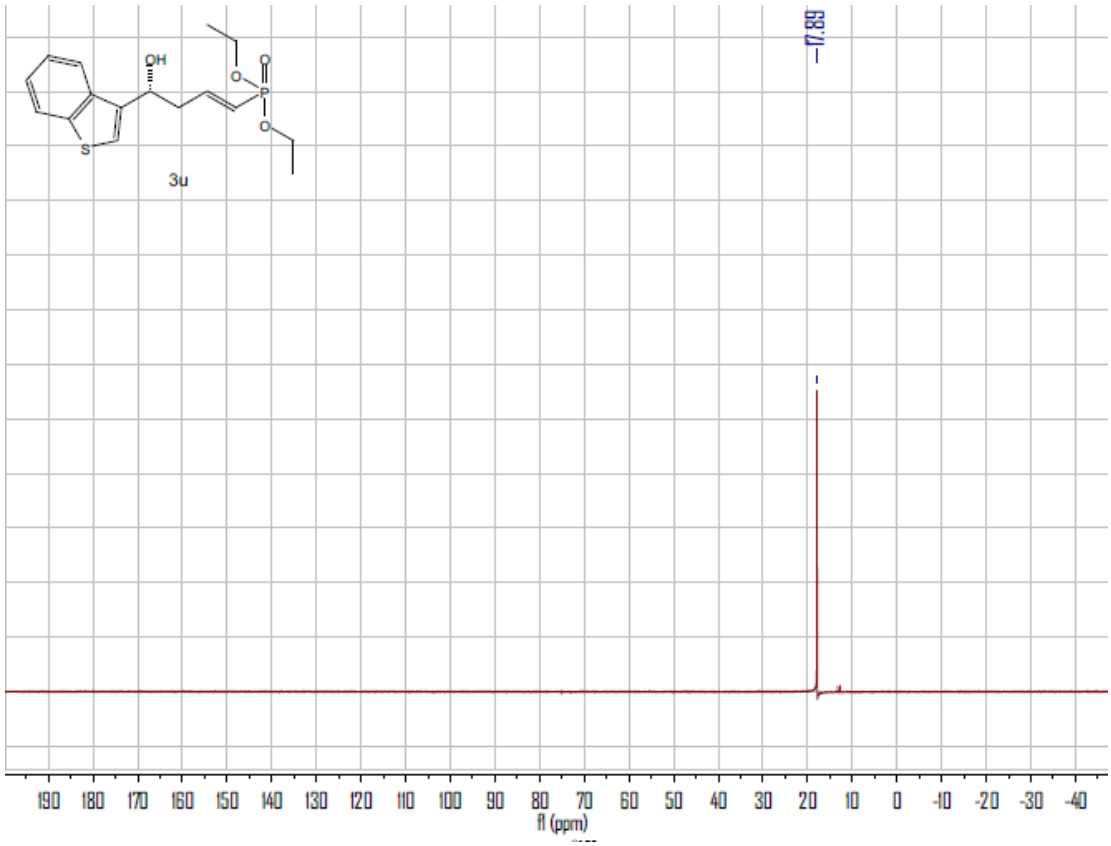


Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3v**, related to **Table 2**

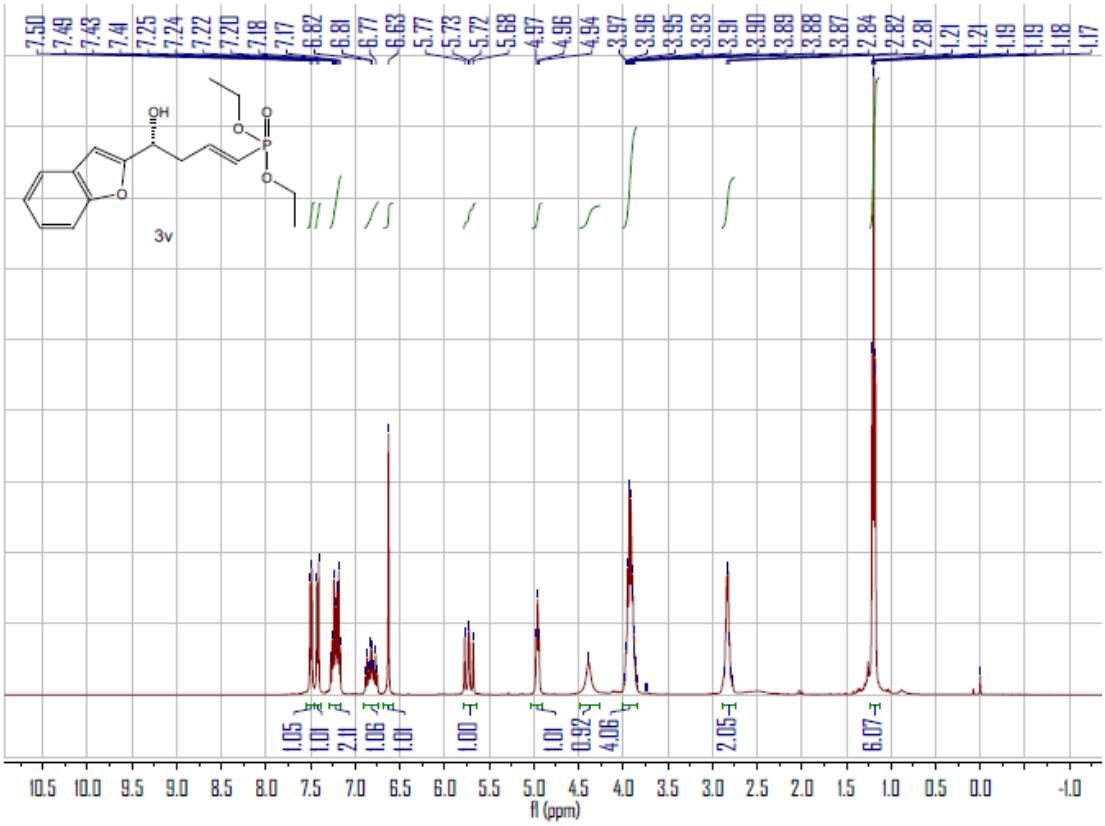


Figure S70. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3v**, related to **Table 2**

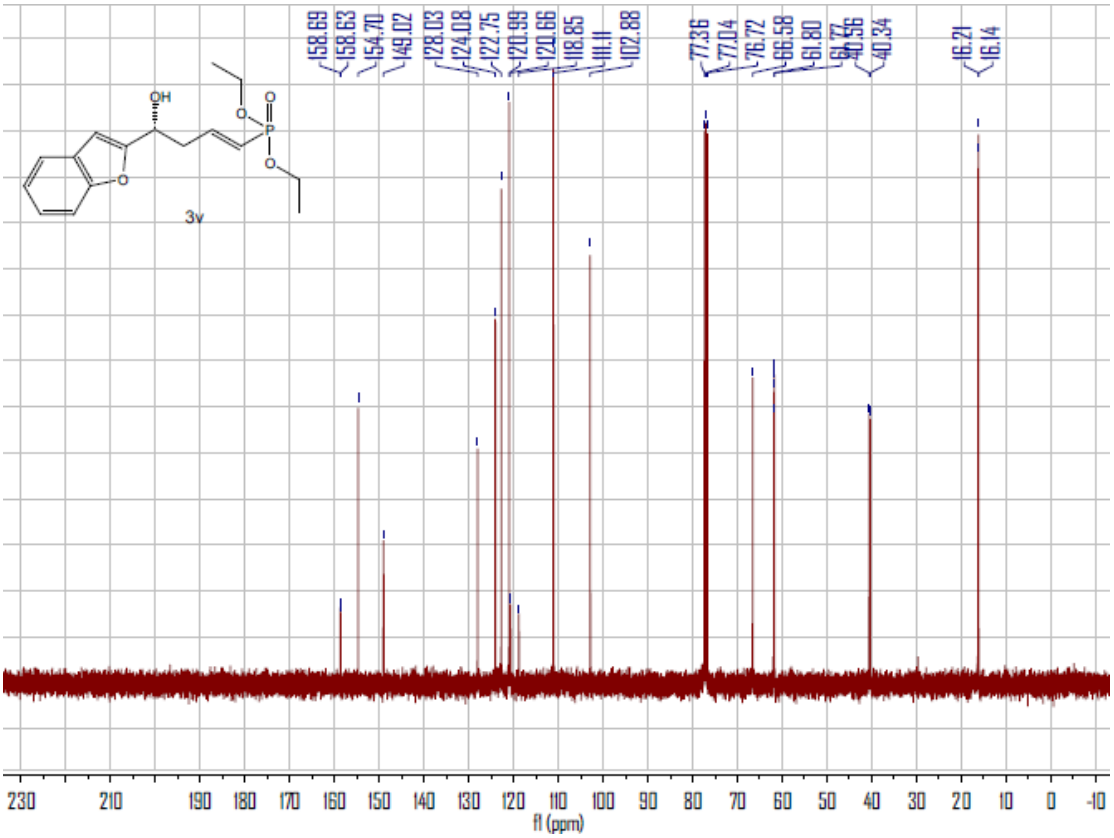


Figure S71. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3v**, related to **Table 2**

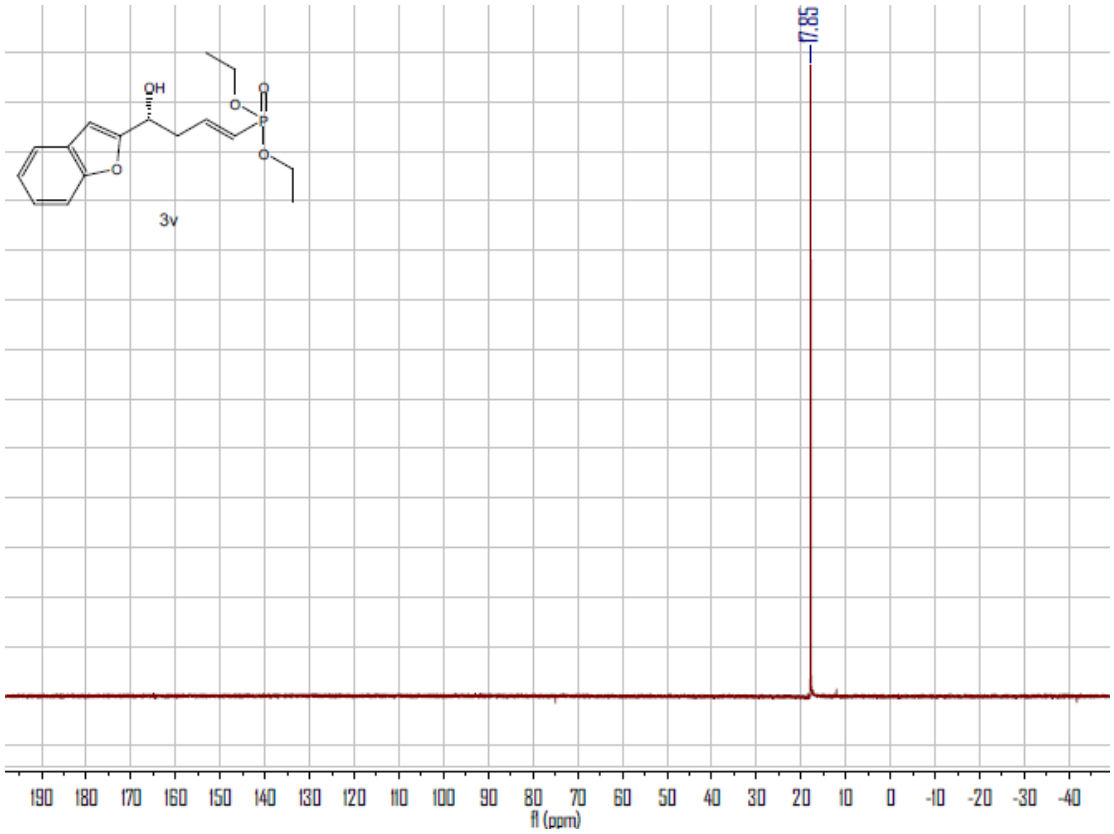


Figure S72. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3w**, related to **Table 2**

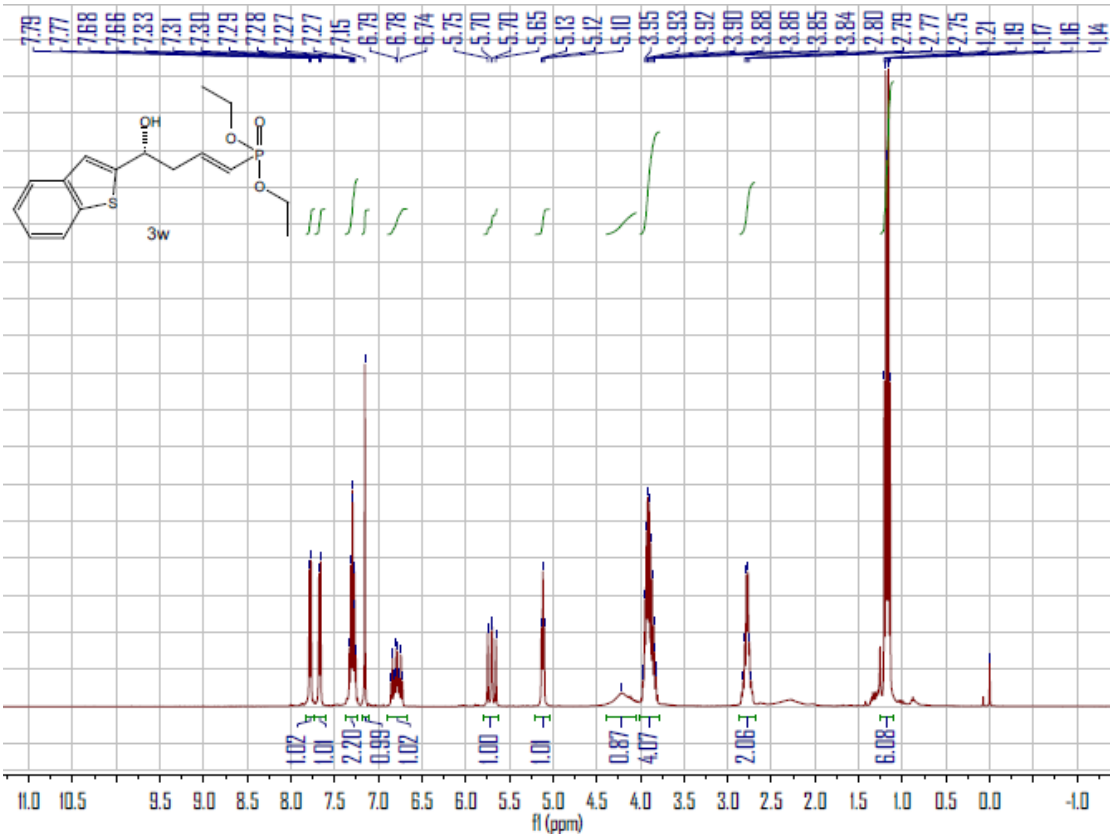


Figure S73. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3w**, related to **Table 2**

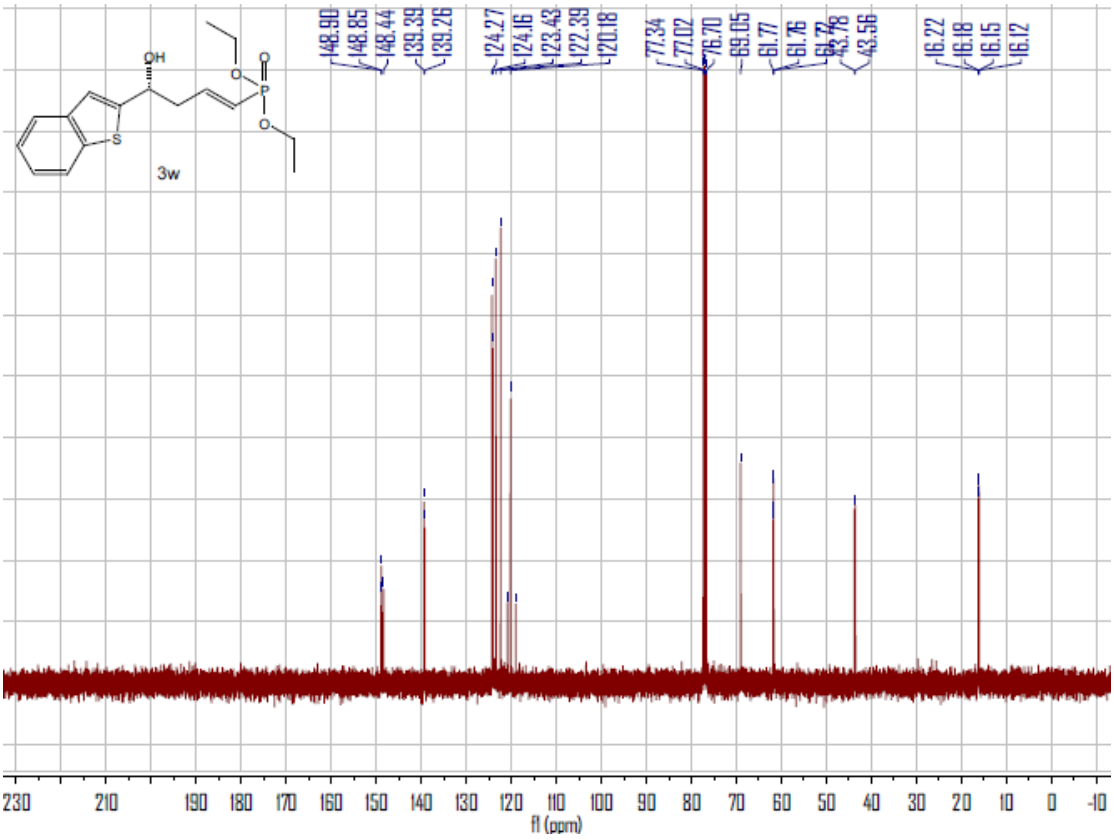


Figure S74. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3w**, related to **Table 2**

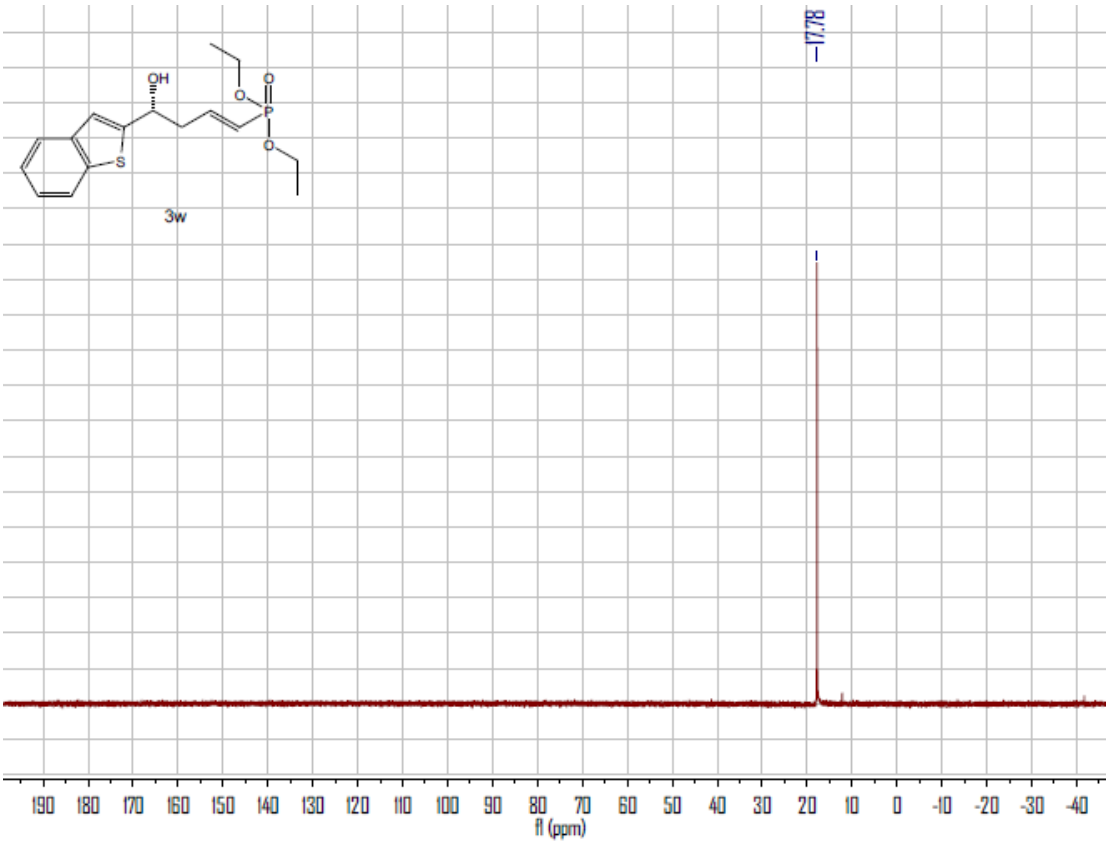


Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3x**, related to **Table 2**

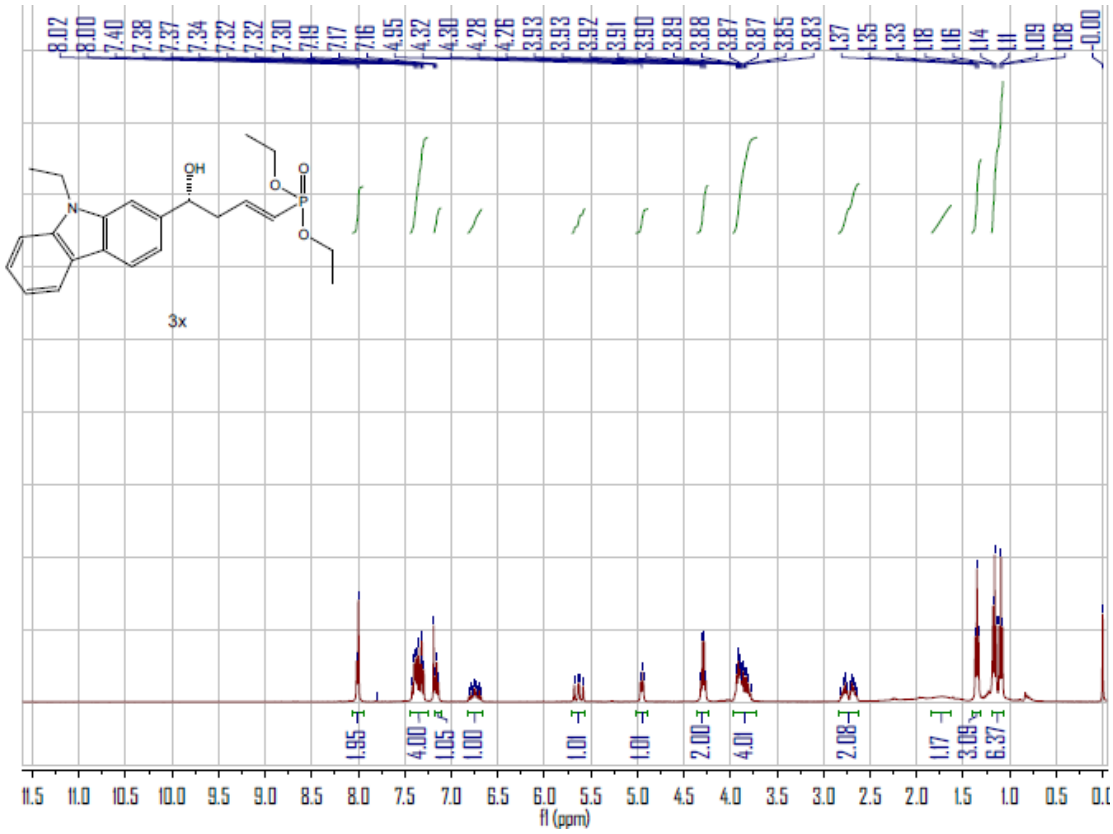


Figure S76. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3x**, related to **Table 2**

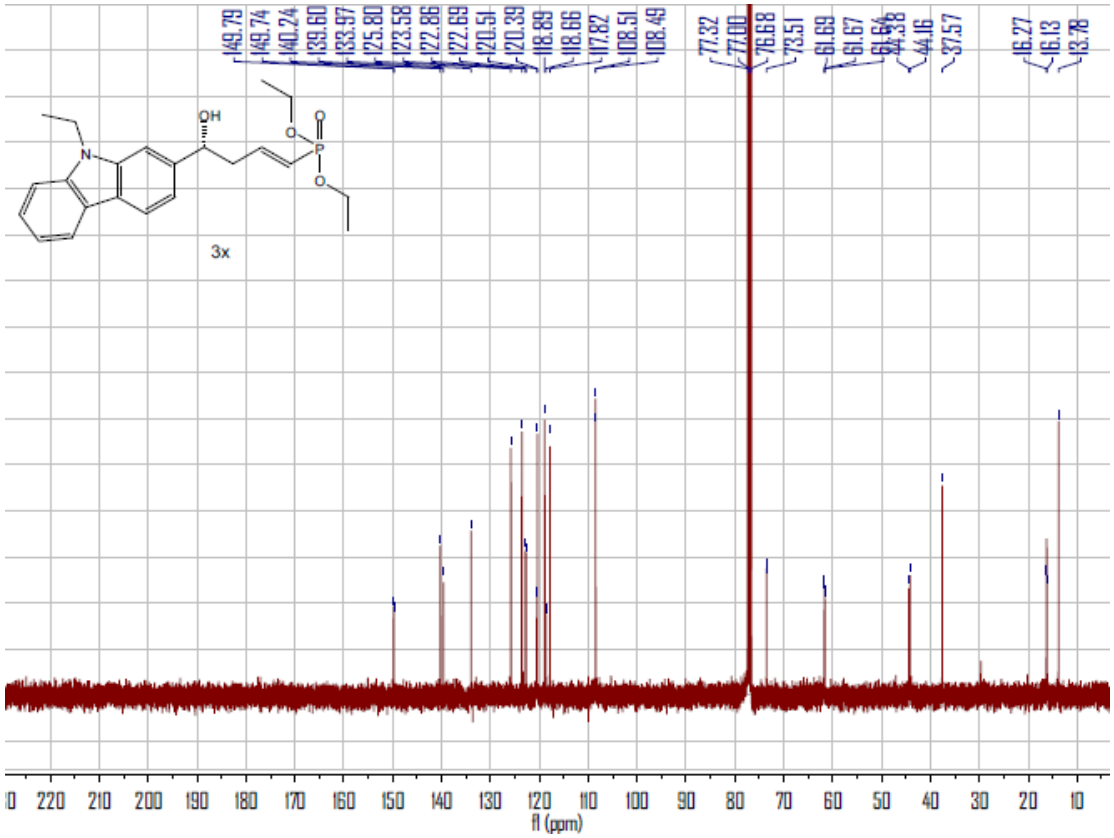


Figure S77. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3x**, related to **Table 2**

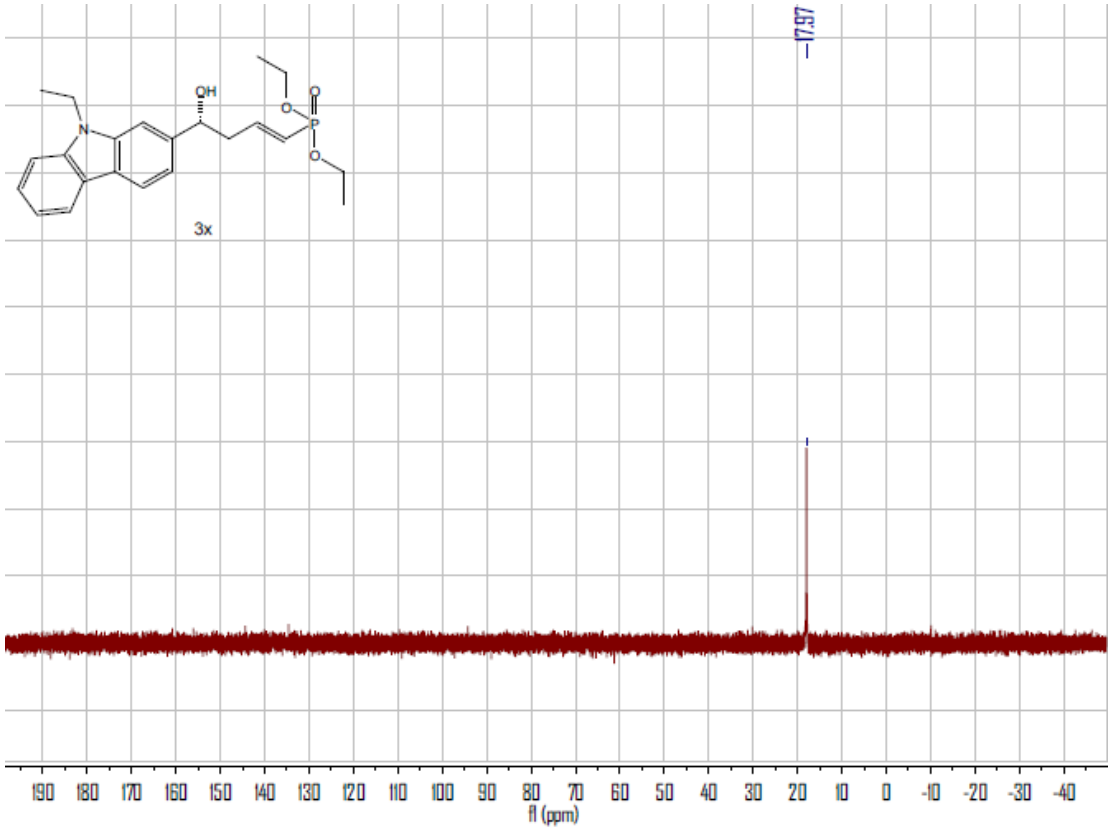


Figure S78. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3y**, related to **Table 2**

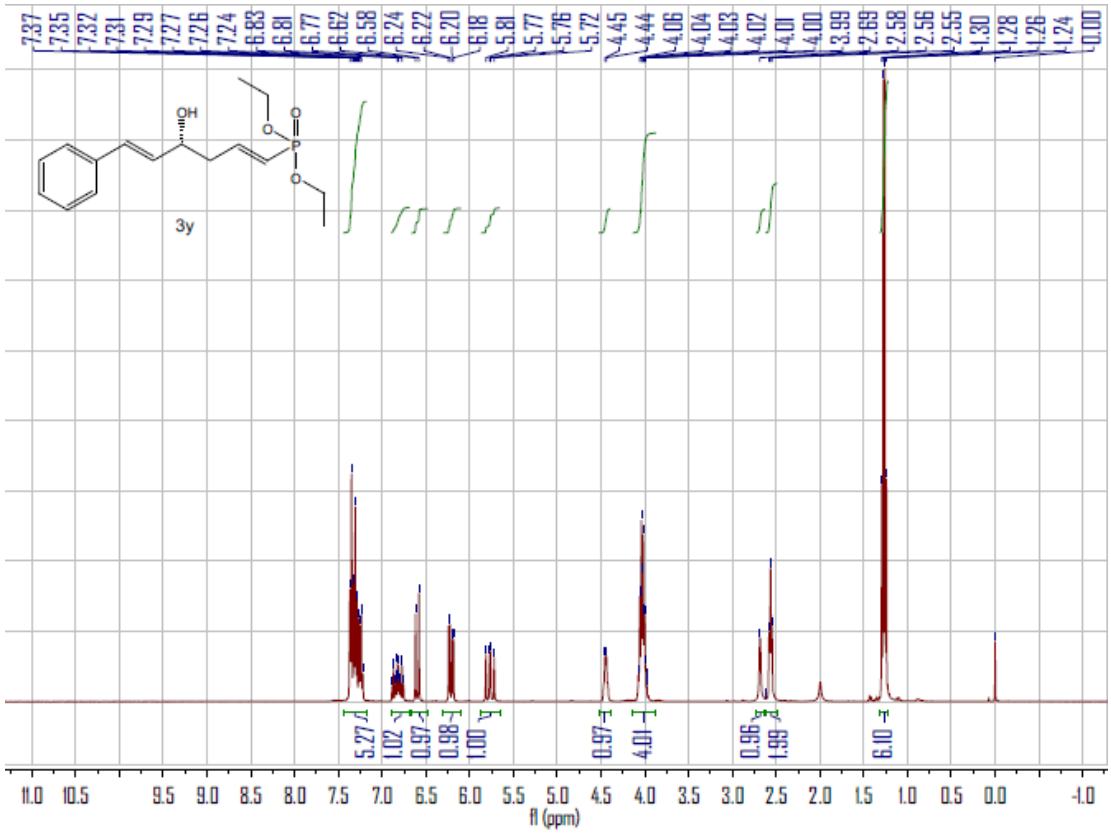


Figure S79. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3y**, related to **Table 2**

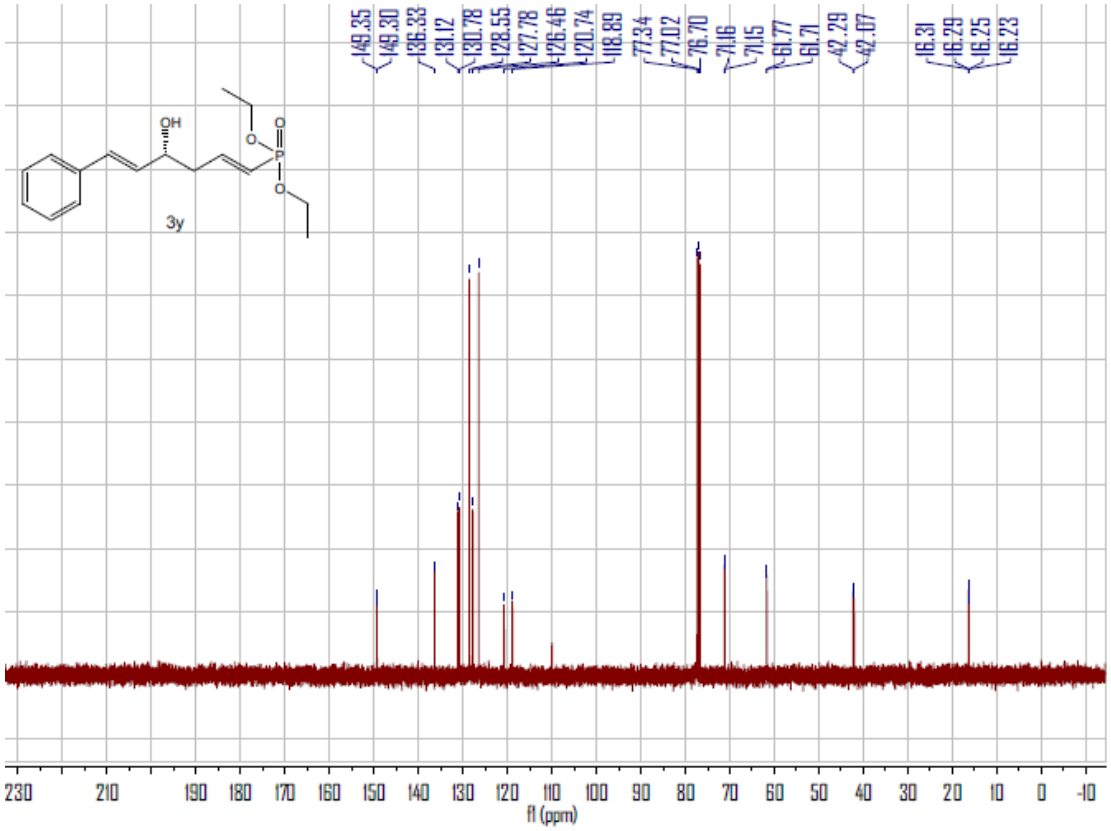


Figure S80. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3y**, related to **Table 2**

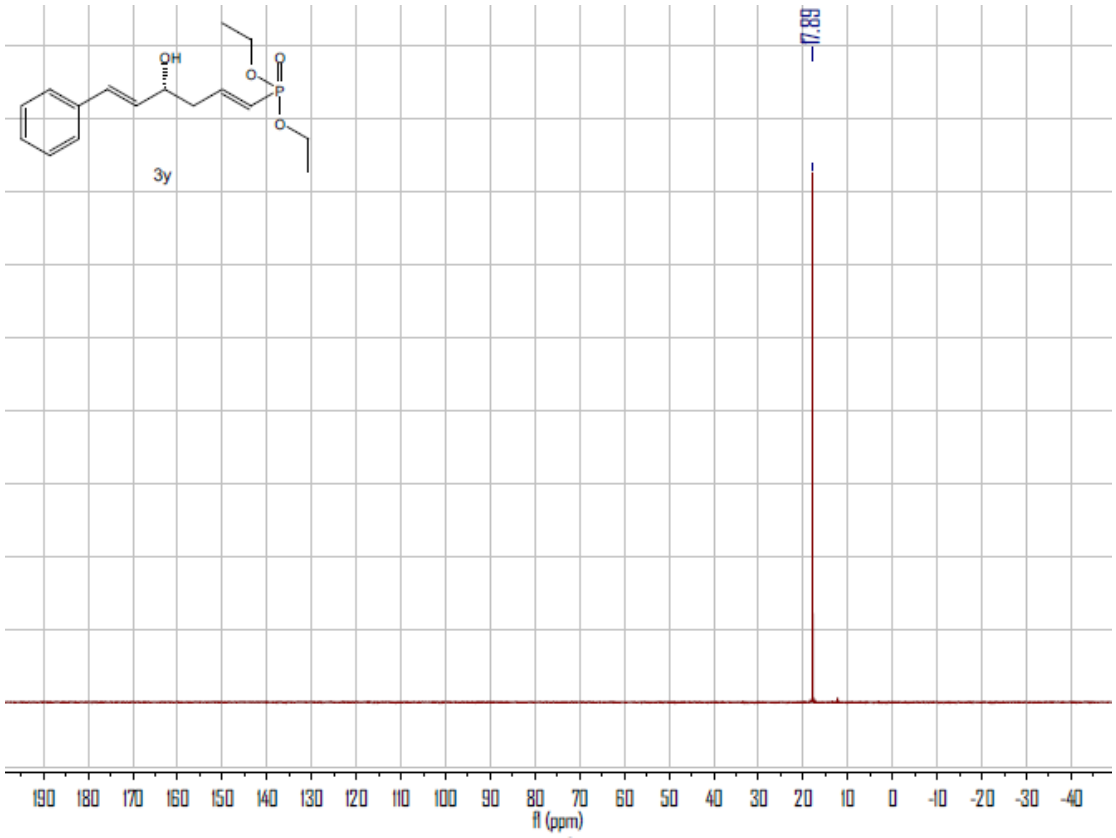


Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3z**, related to **Table 2**

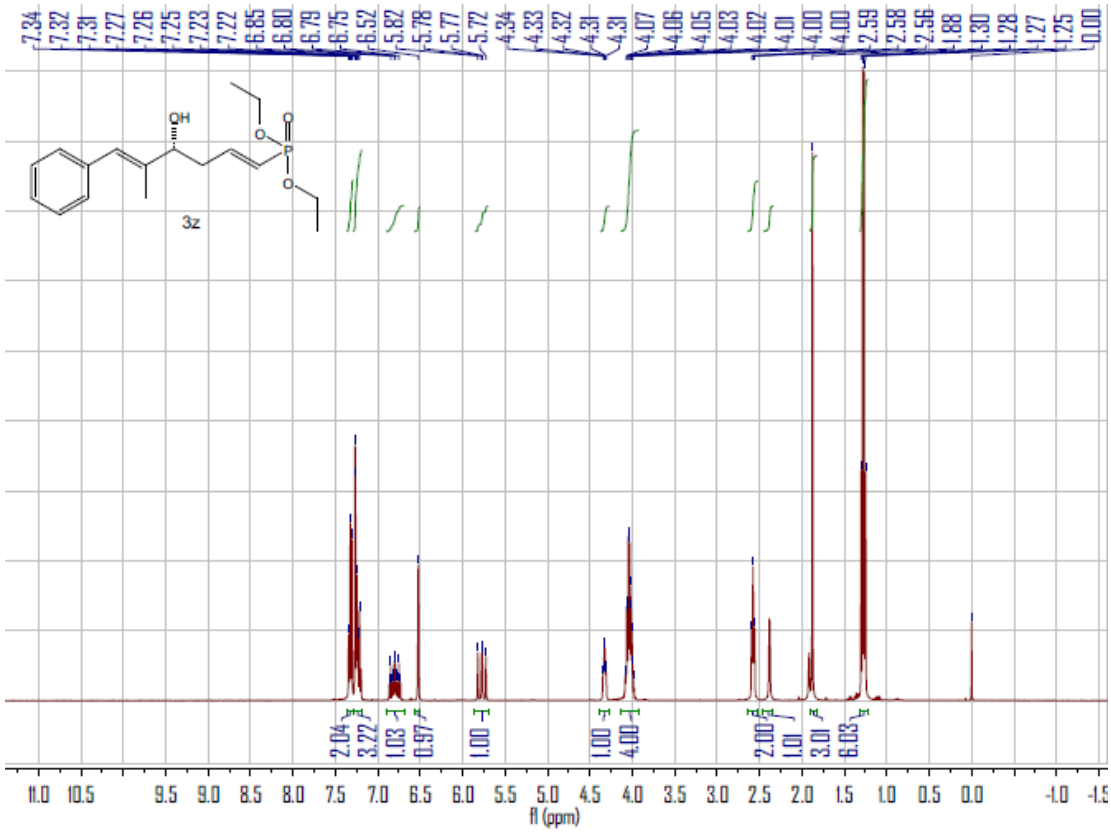


Figure S82. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3z**, related to **Table 2**

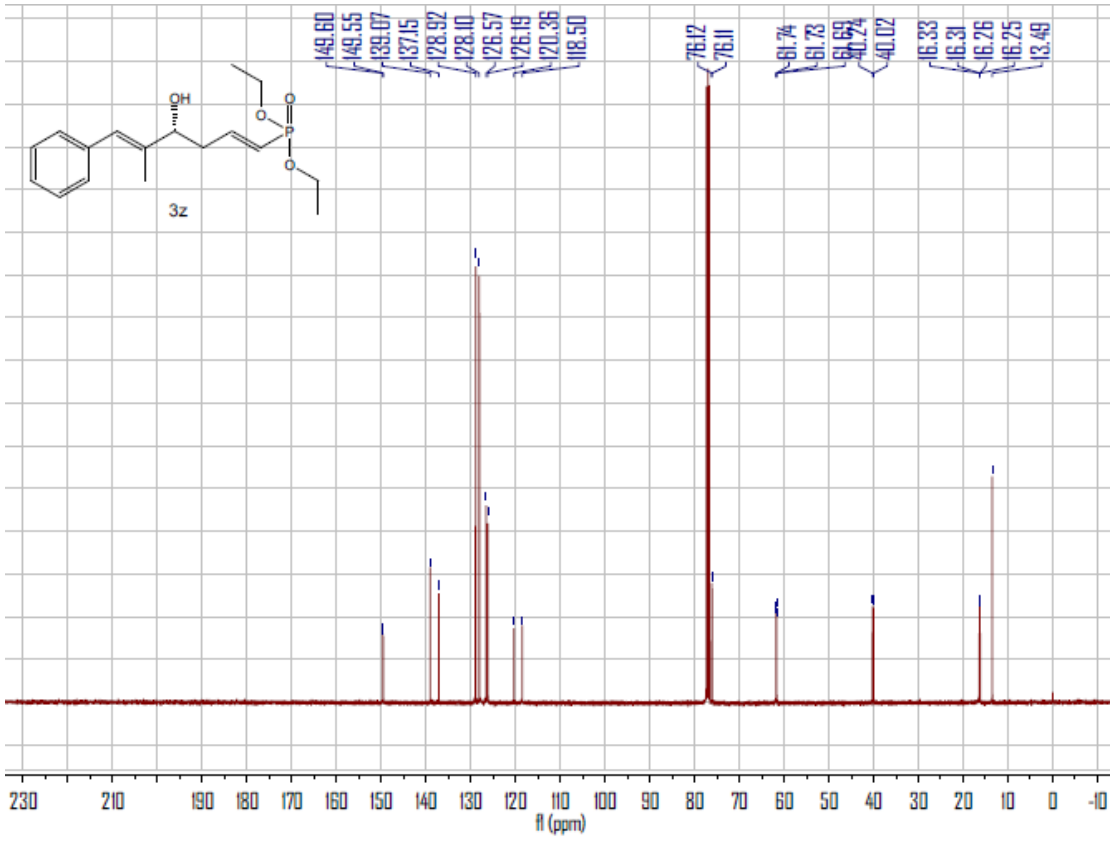


Figure S83. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3z**, related to **Table 2**

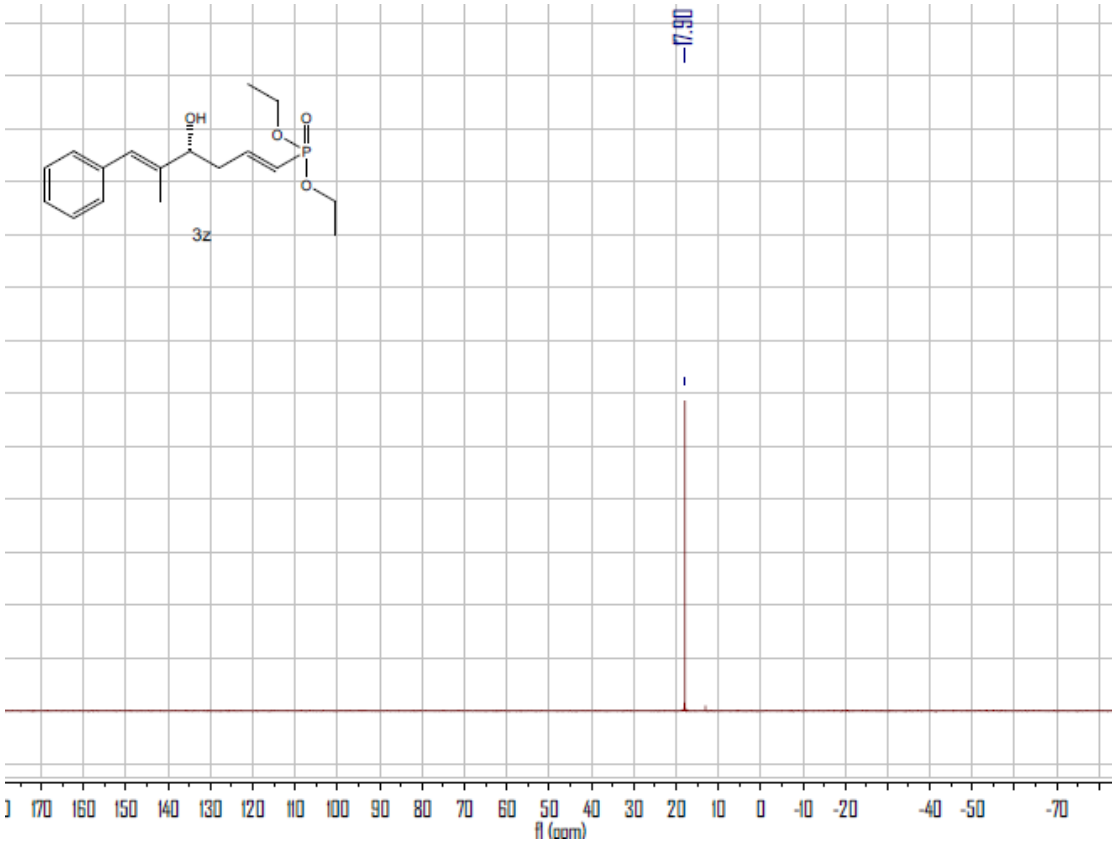


Figure S84. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3aa**, related to **Table 2**

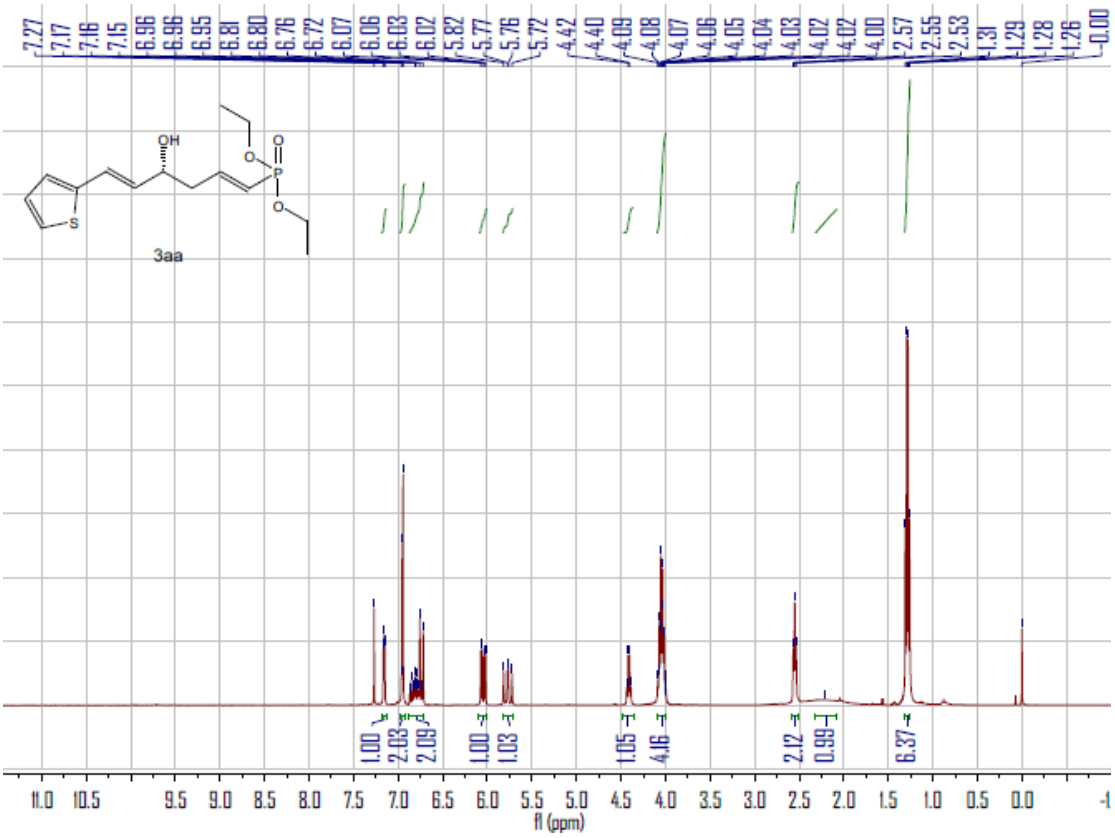


Figure S85. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3aa**, related to **Table 2**

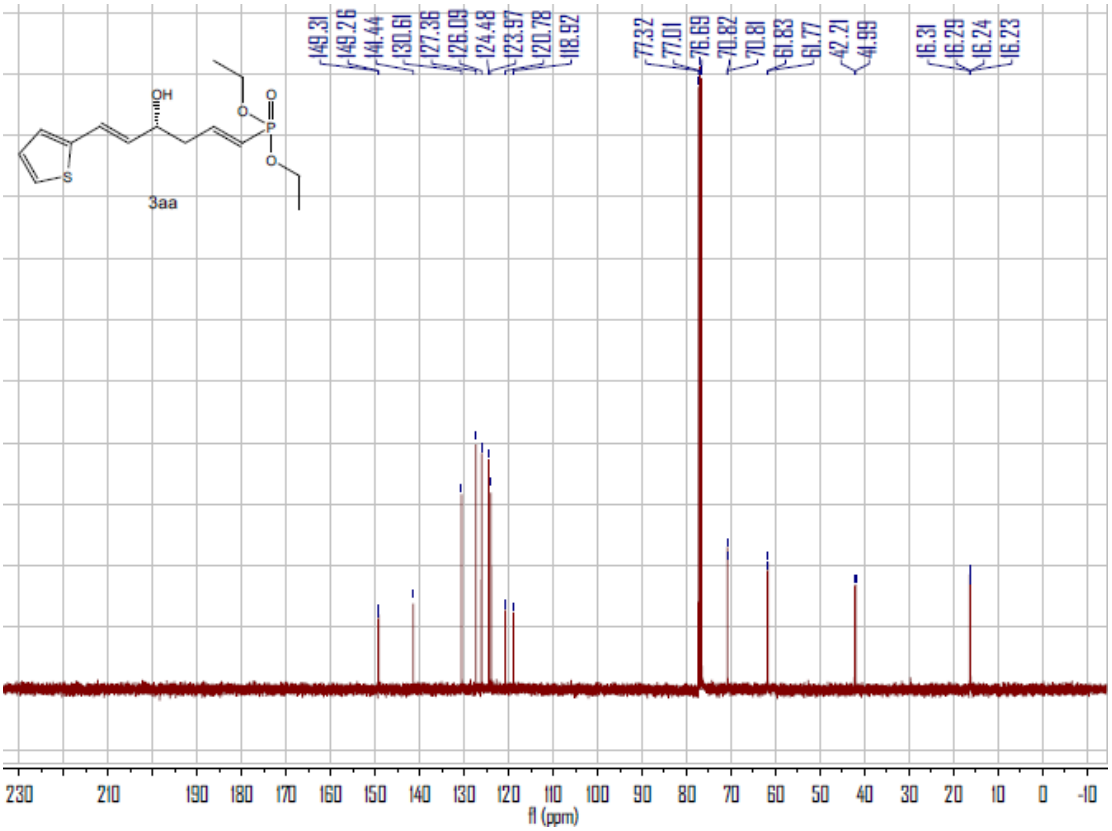


Figure S86. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3aa**, related to **Table 2**

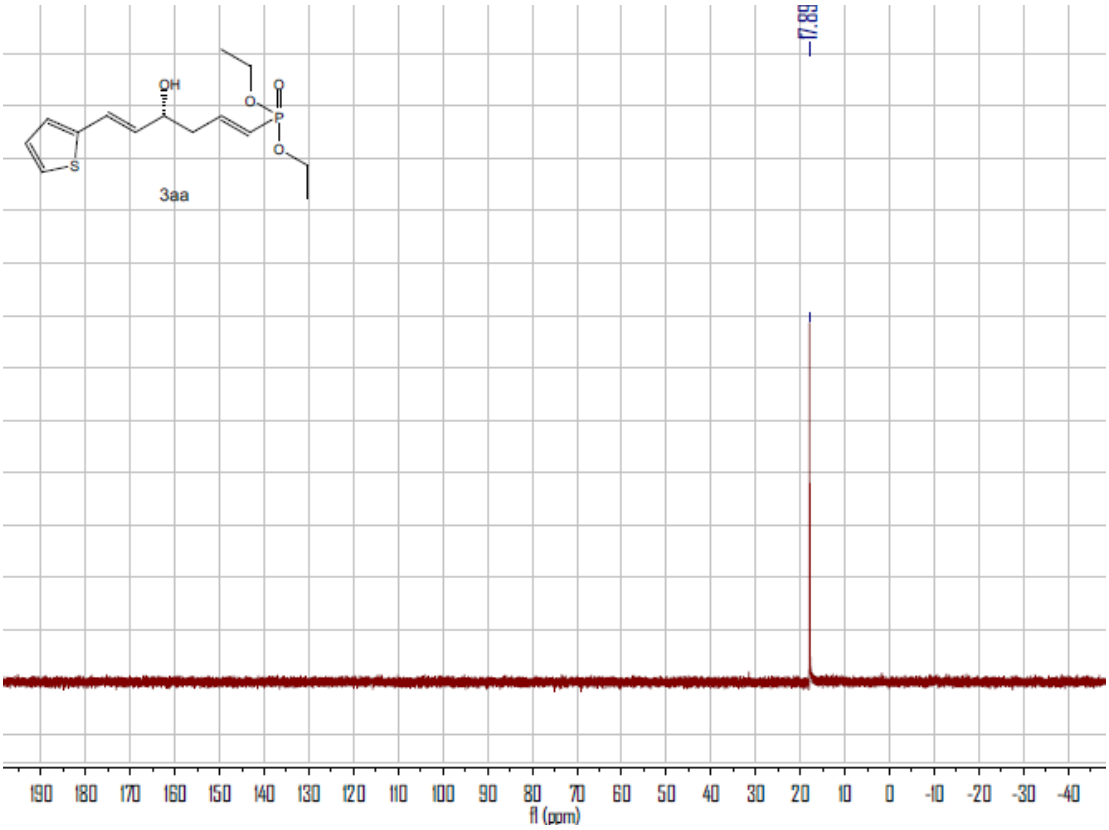


Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ab**, related to **Table 2**

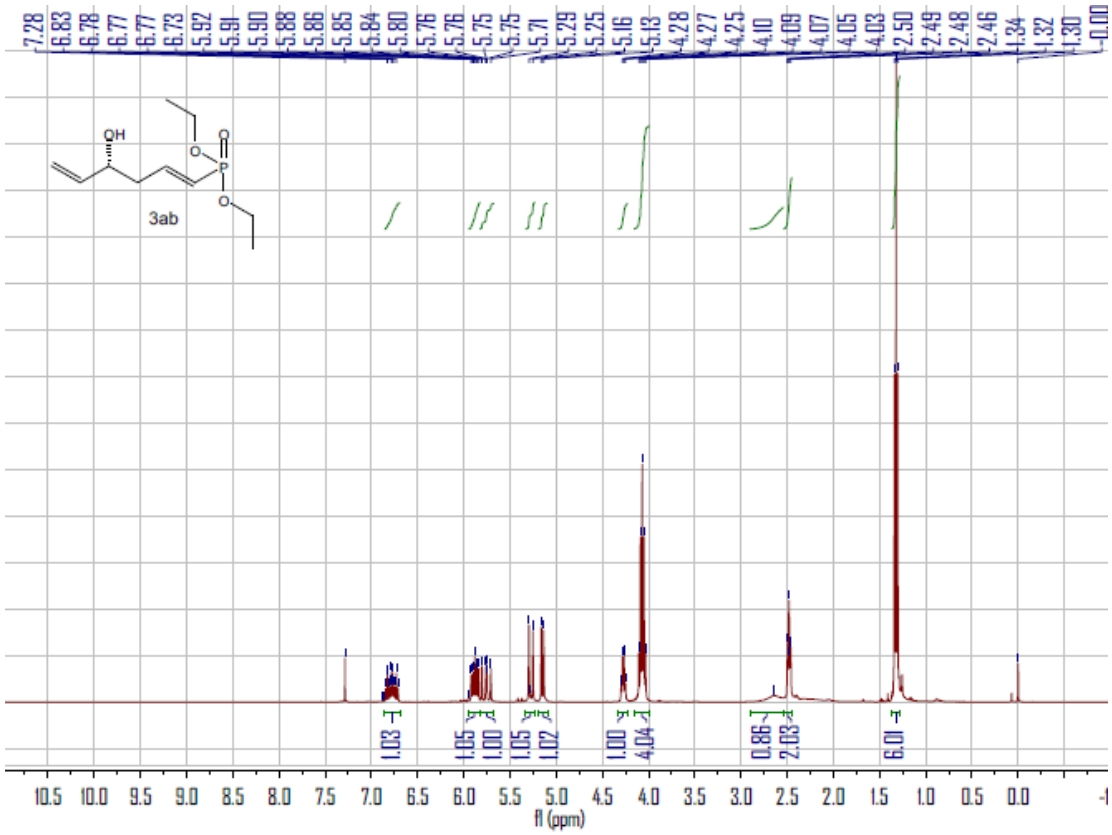


Figure S88. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3ab**, related to **Table 2**

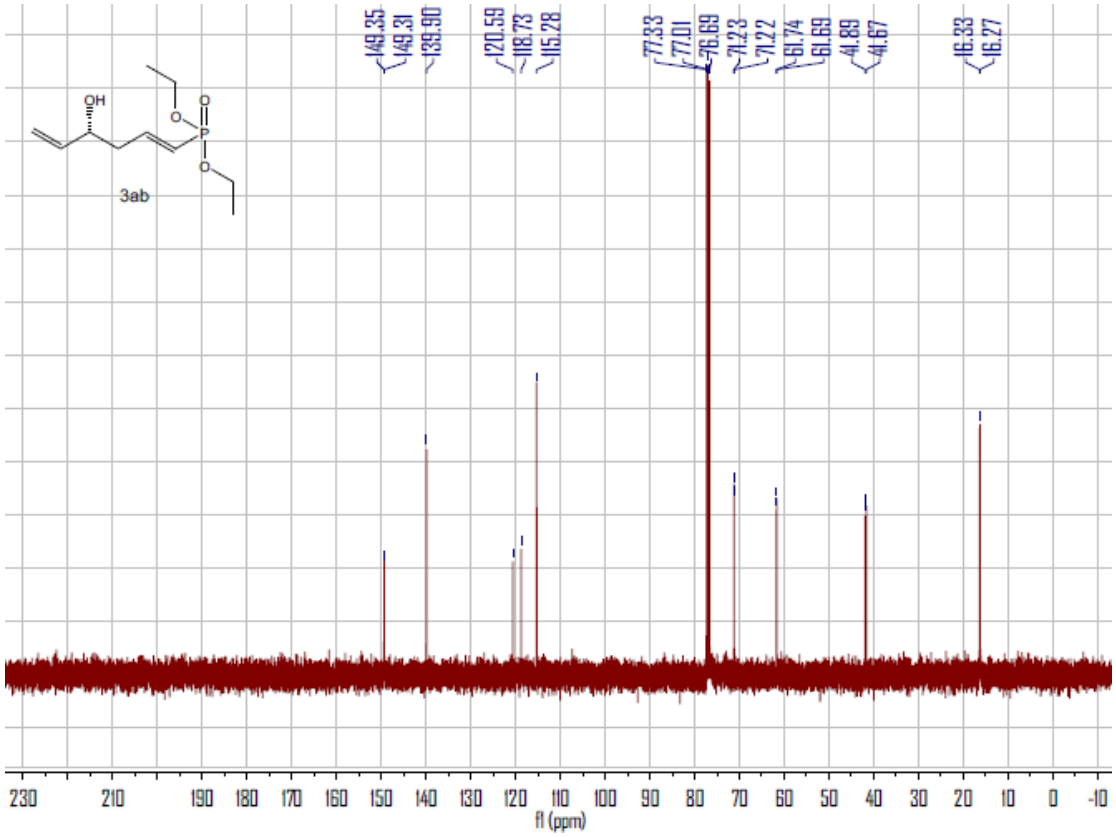


Figure S89. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3ab**, related to **Table 2**

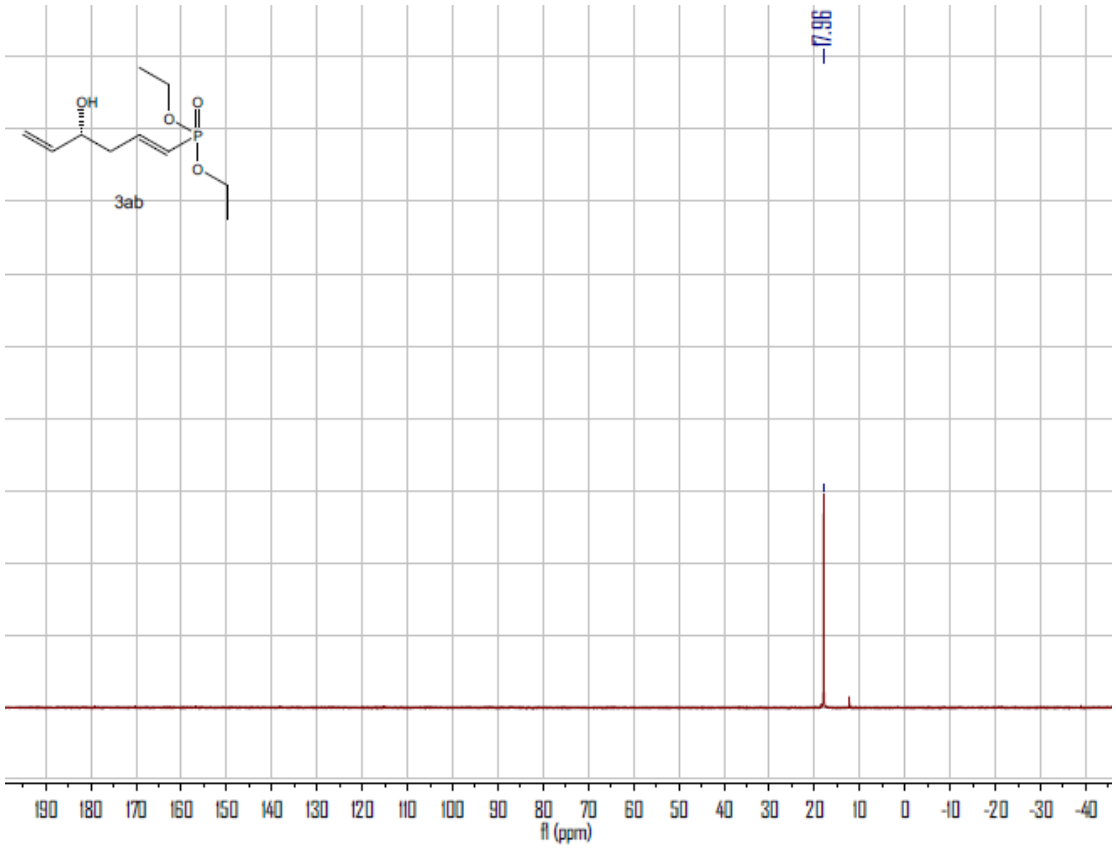


Figure S90. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ac**, related to **Table 2**

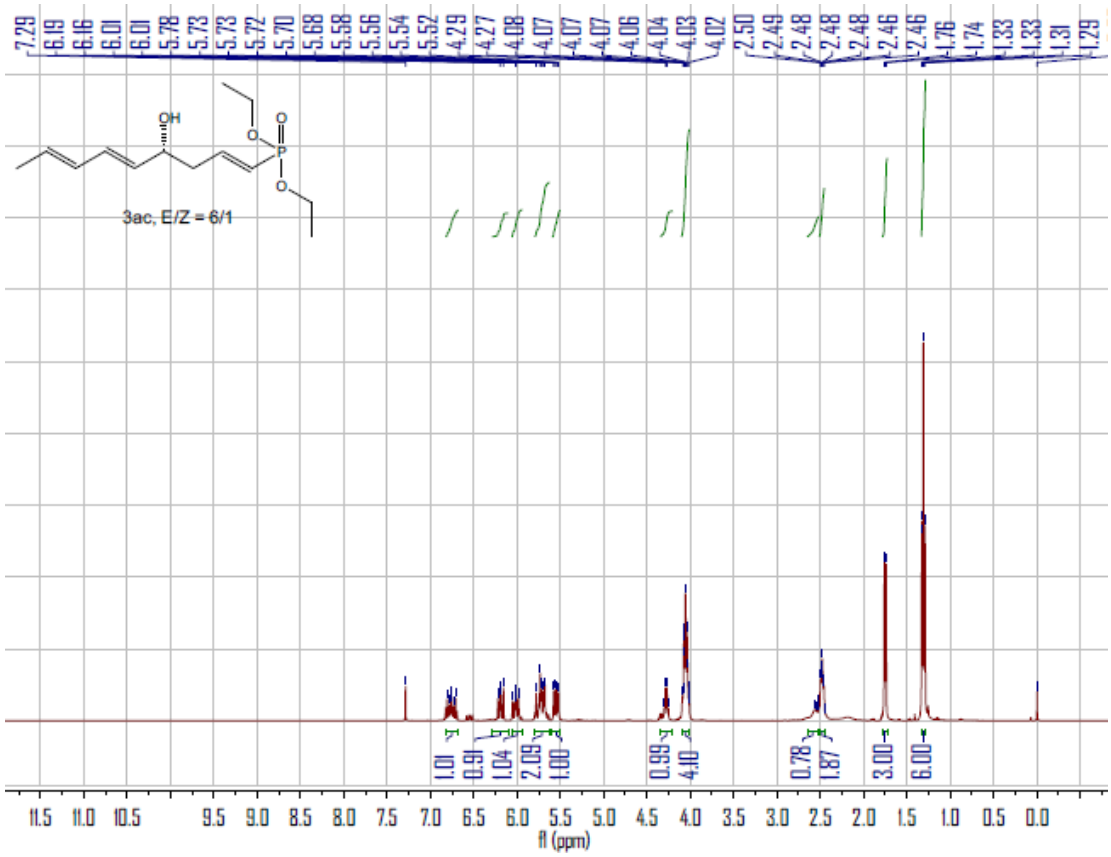


Figure S91. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3ac**, related to **Table 2**

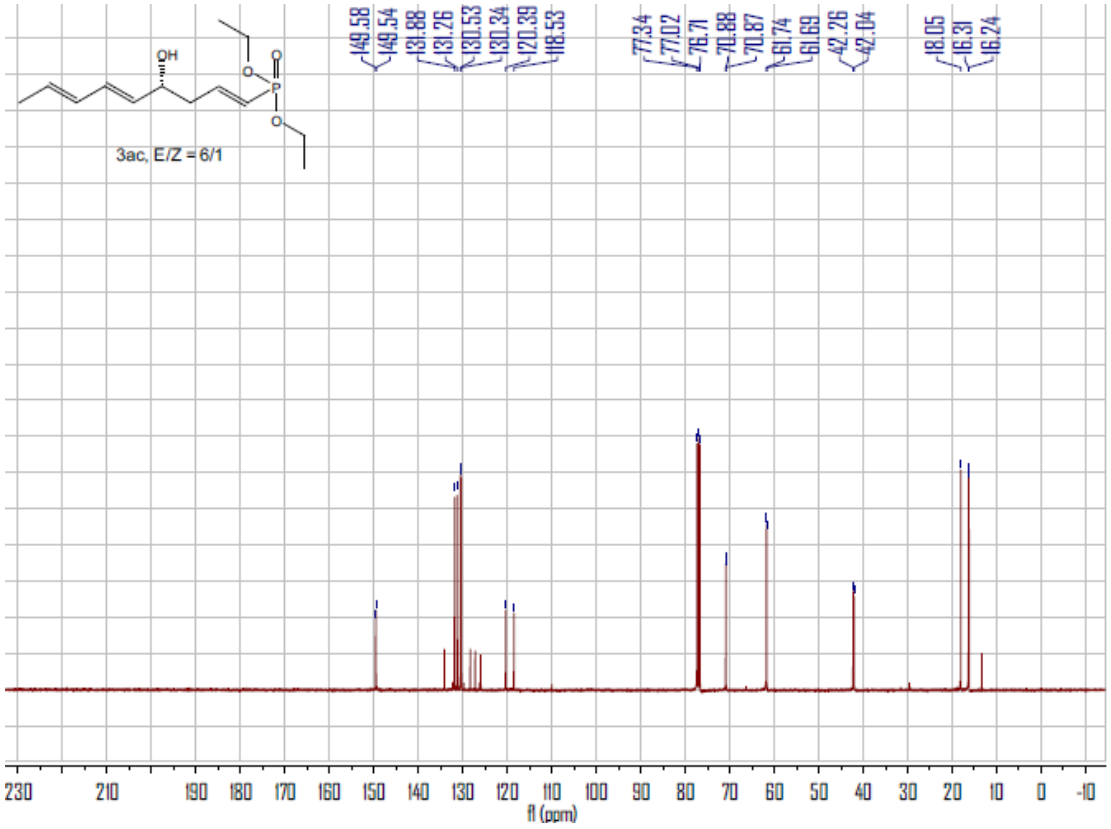


Figure S92. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3ac**, related to **Table 2**

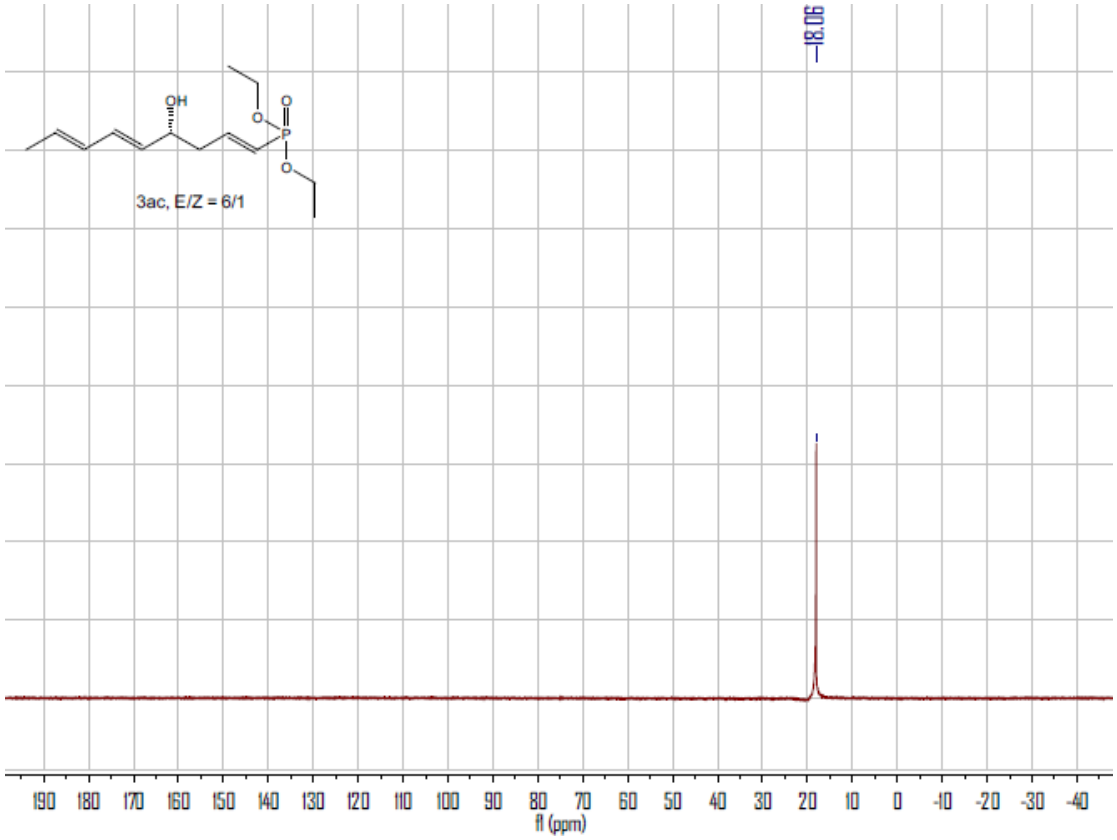


Figure S93. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ad**, related to **Table 2**

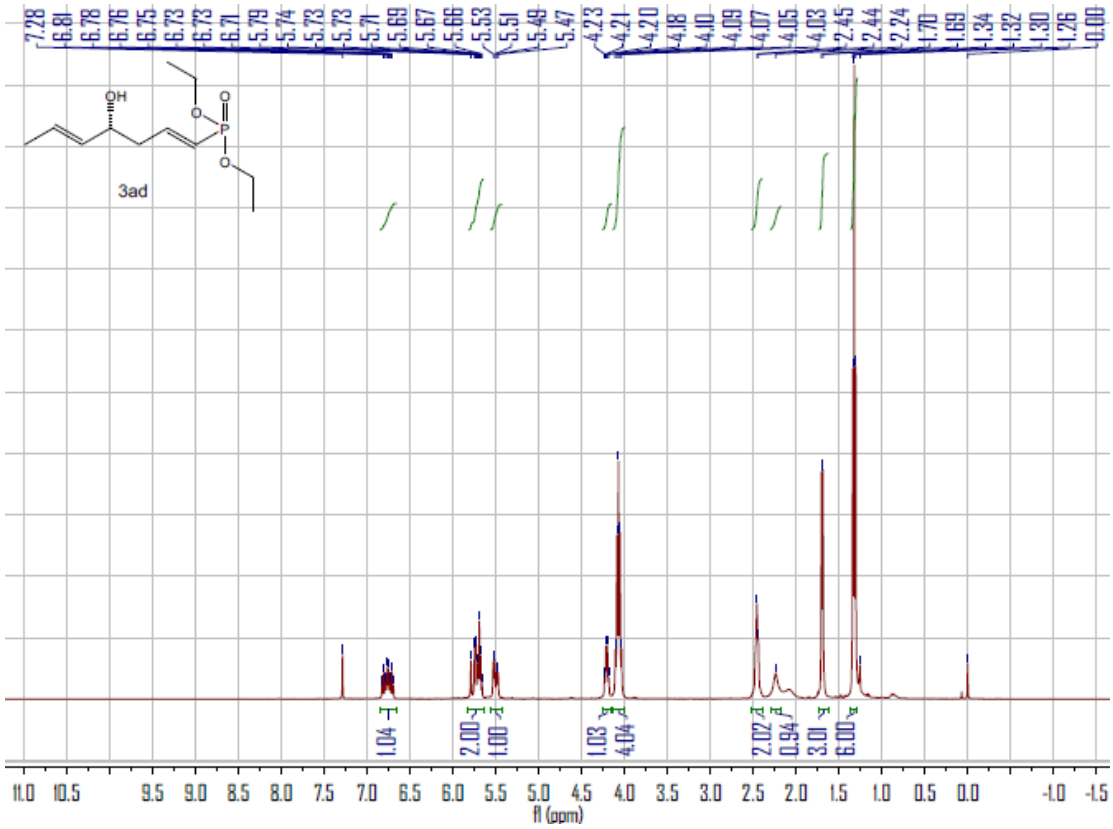


Figure S94. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3ad**, related to **Table 2**

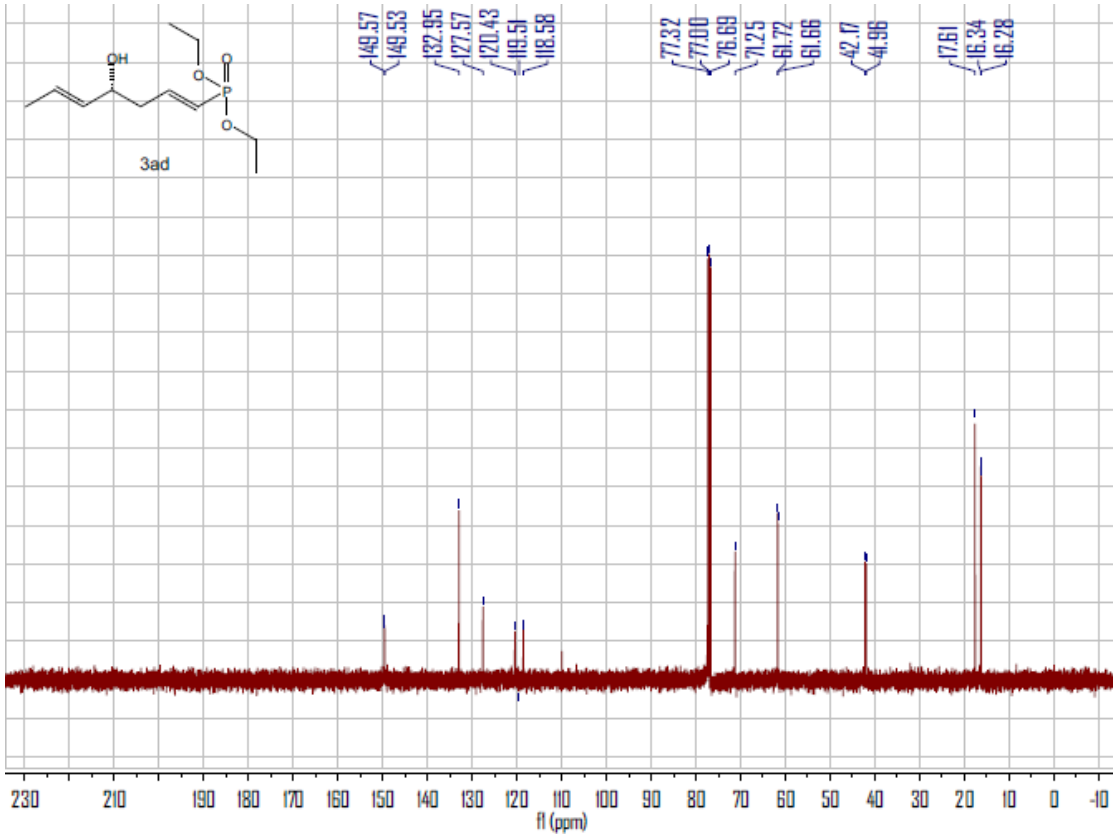


Figure S95. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3ad**, related to **Table 2**

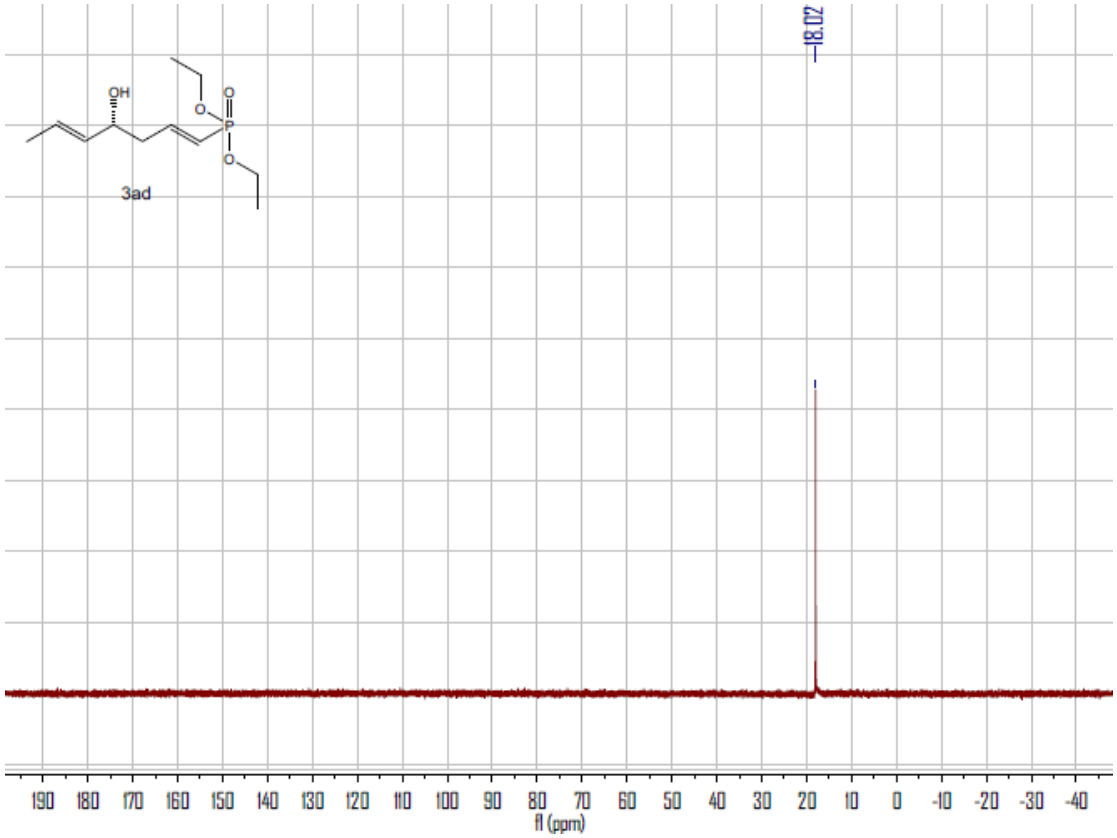


Figure S96. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ae**, related to **Table 2**

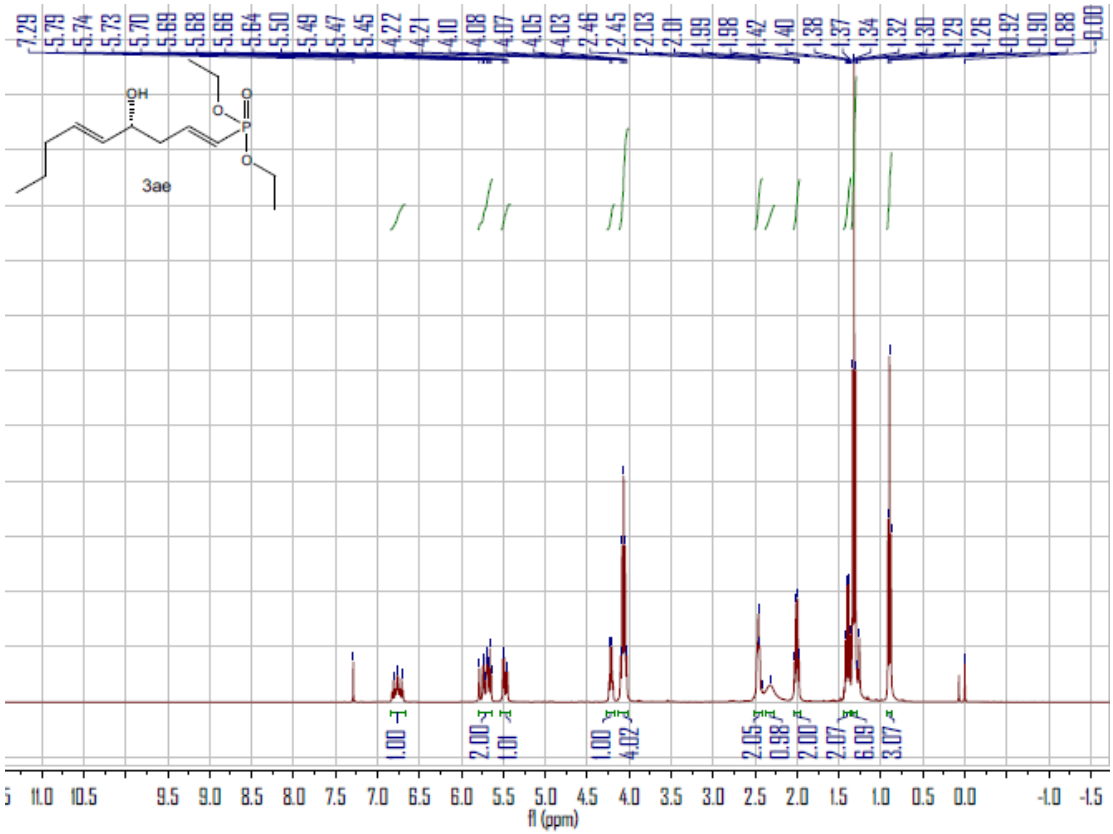


Figure S97. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3ae**, related to **Table 2**

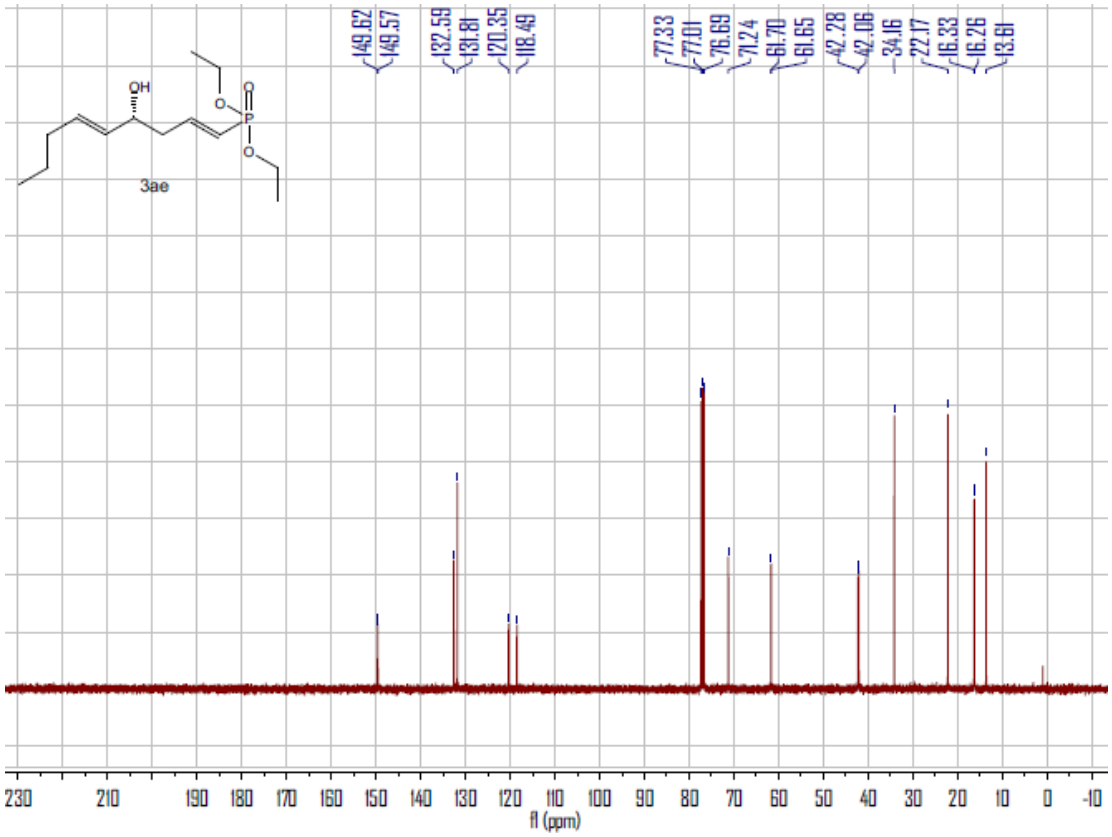


Figure S98. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3ae**, related to **Table 2**

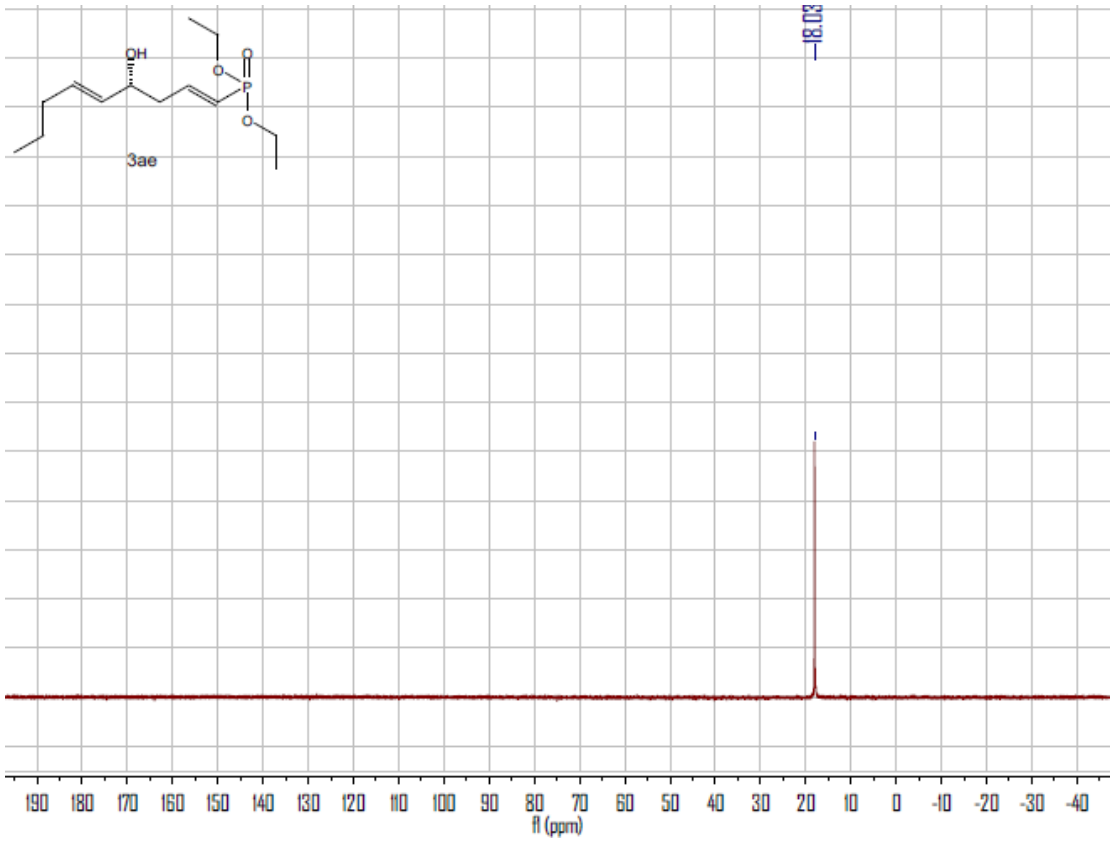


Figure S99. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3af**, related to **Table 2**

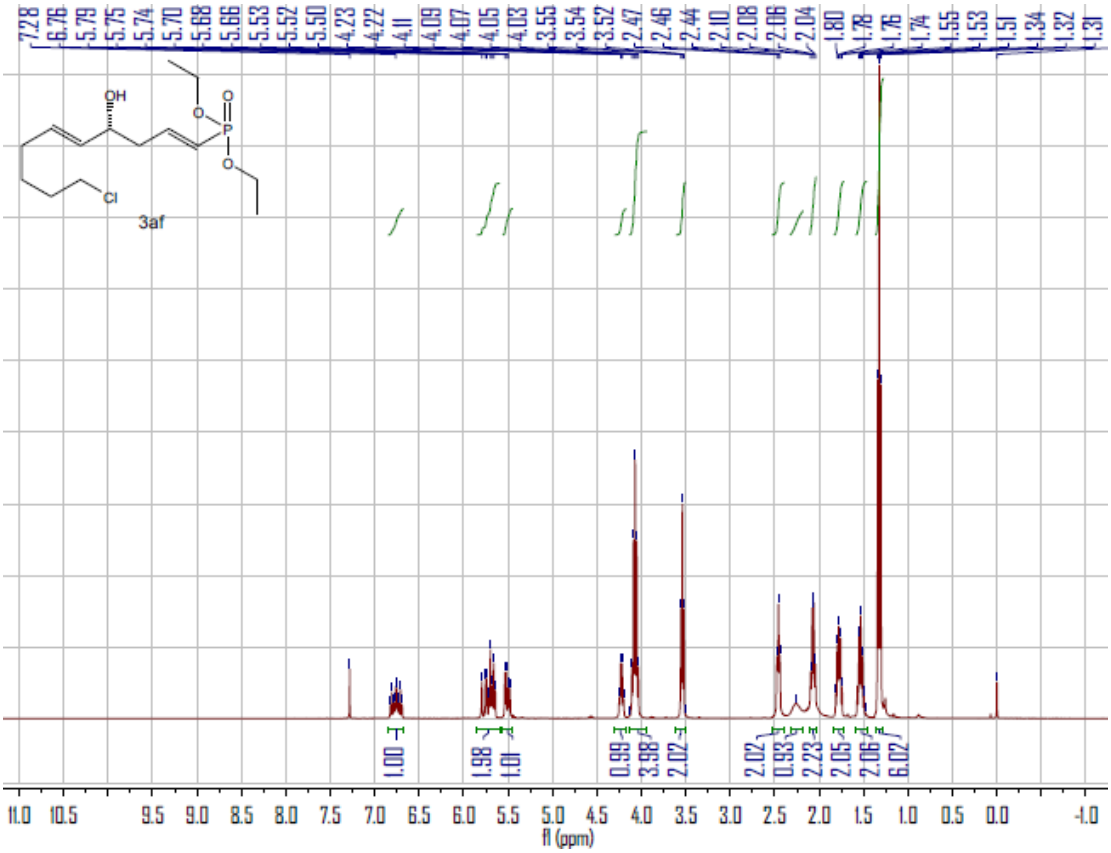


Figure S100. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3af**, related to **Table 2**

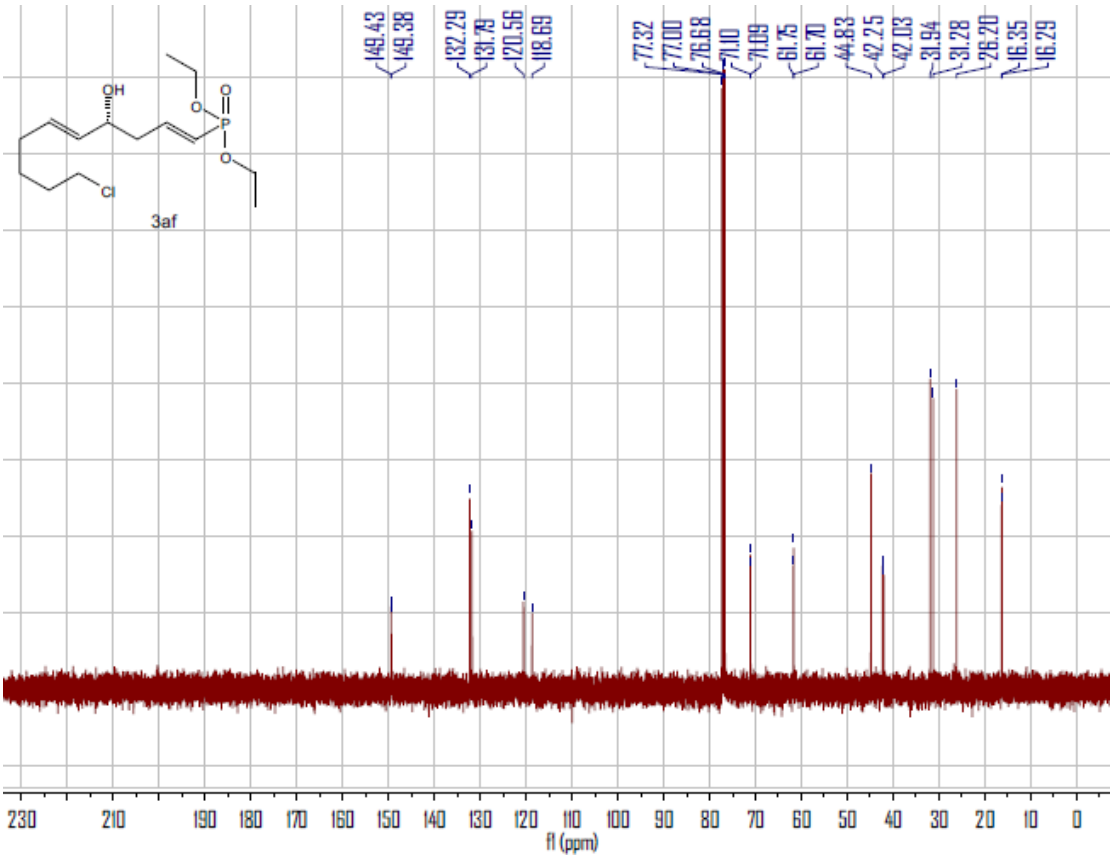


Figure S101. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3af**, related to **Table 2**

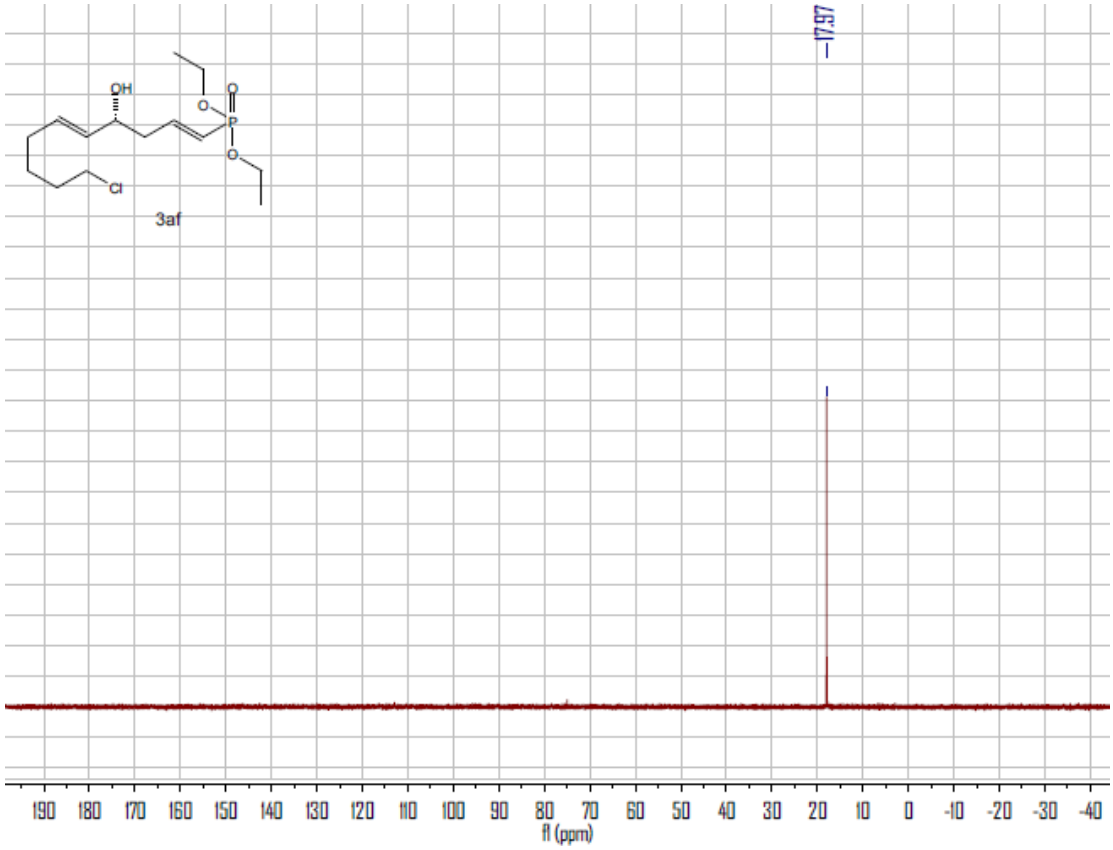


Figure S102. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ag**, related to **Table 2**

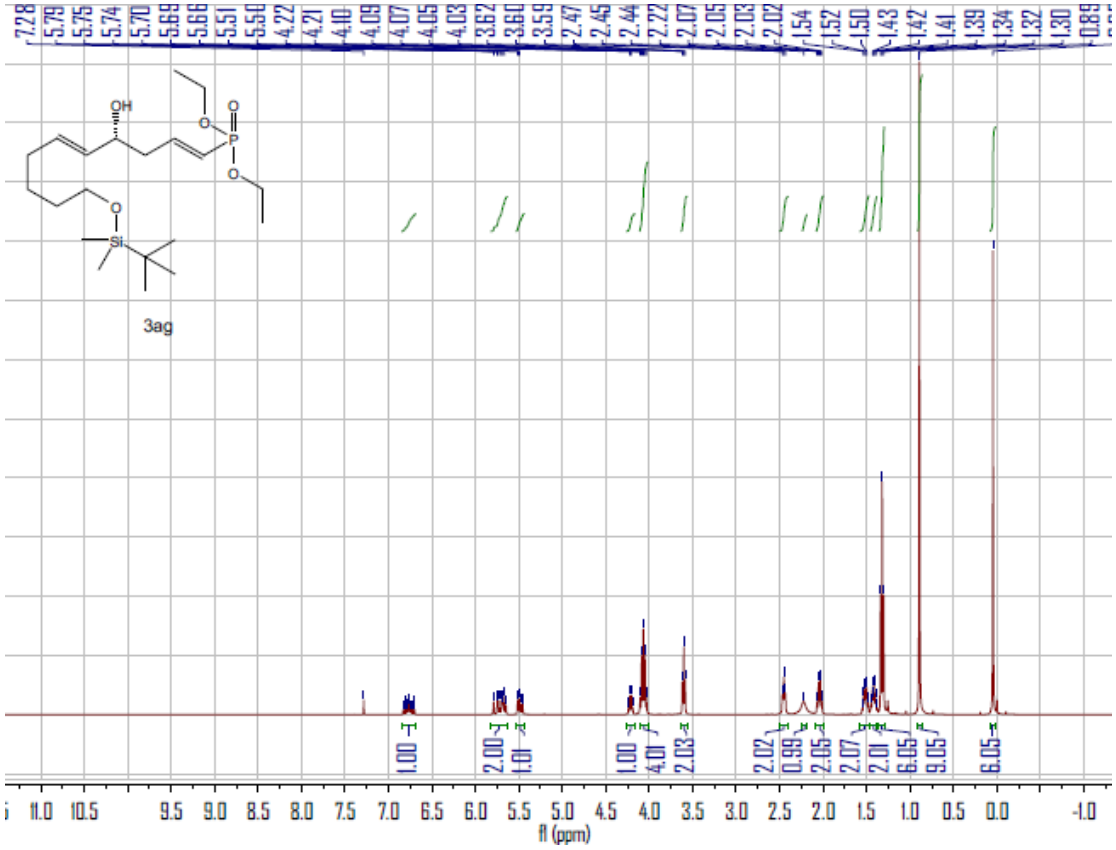


Figure S103. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3ag**, related to **Table 2**

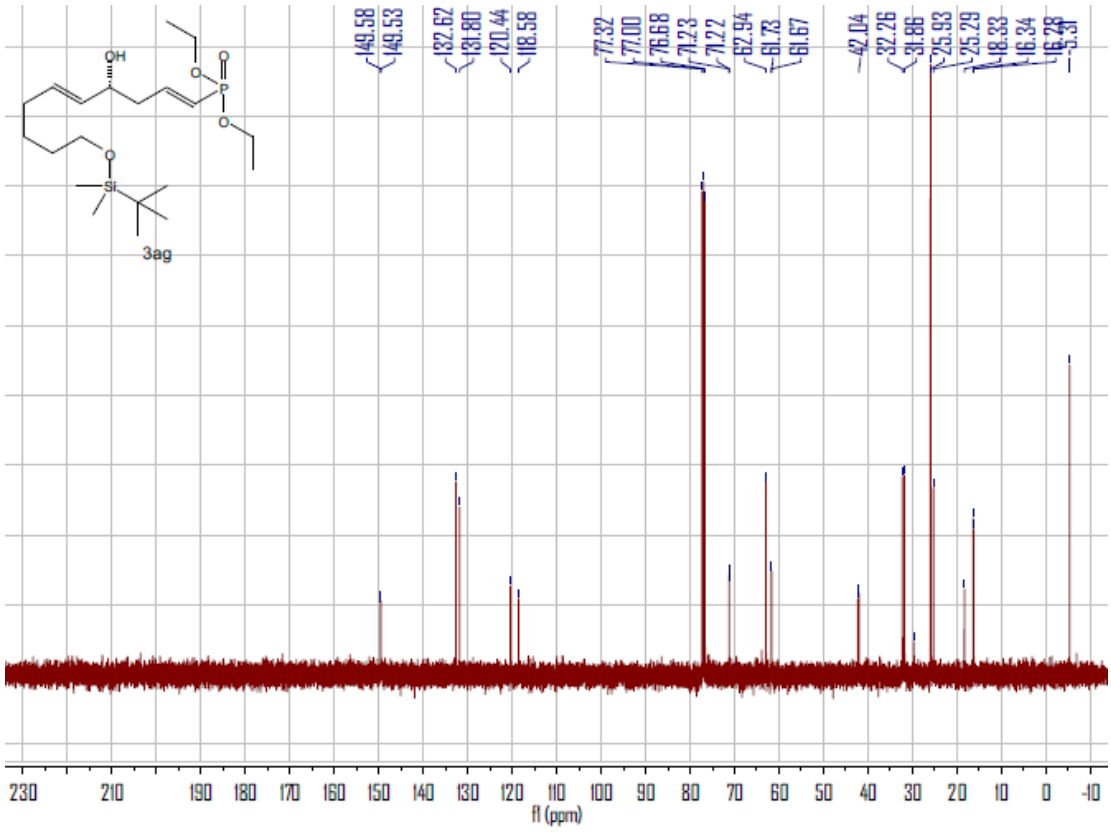


Figure S104. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3ag**, related to **Table 2**

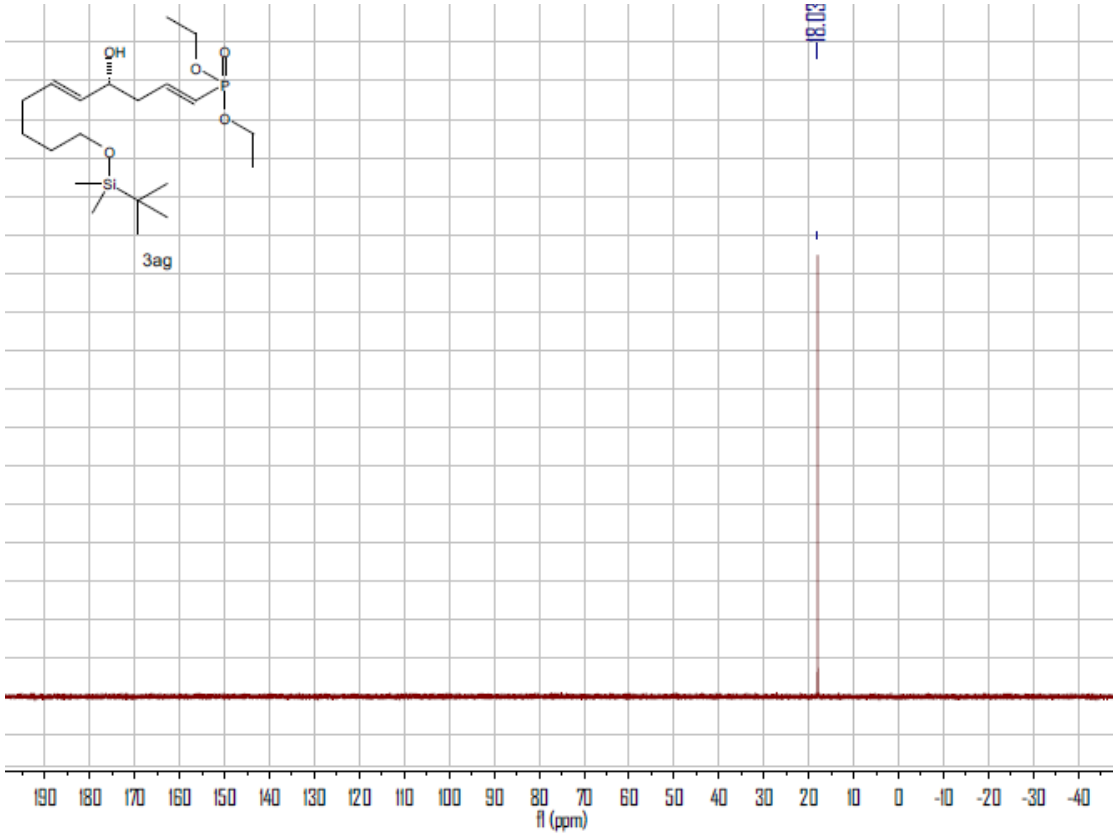


Figure S105. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ah**, related to **Table 2**

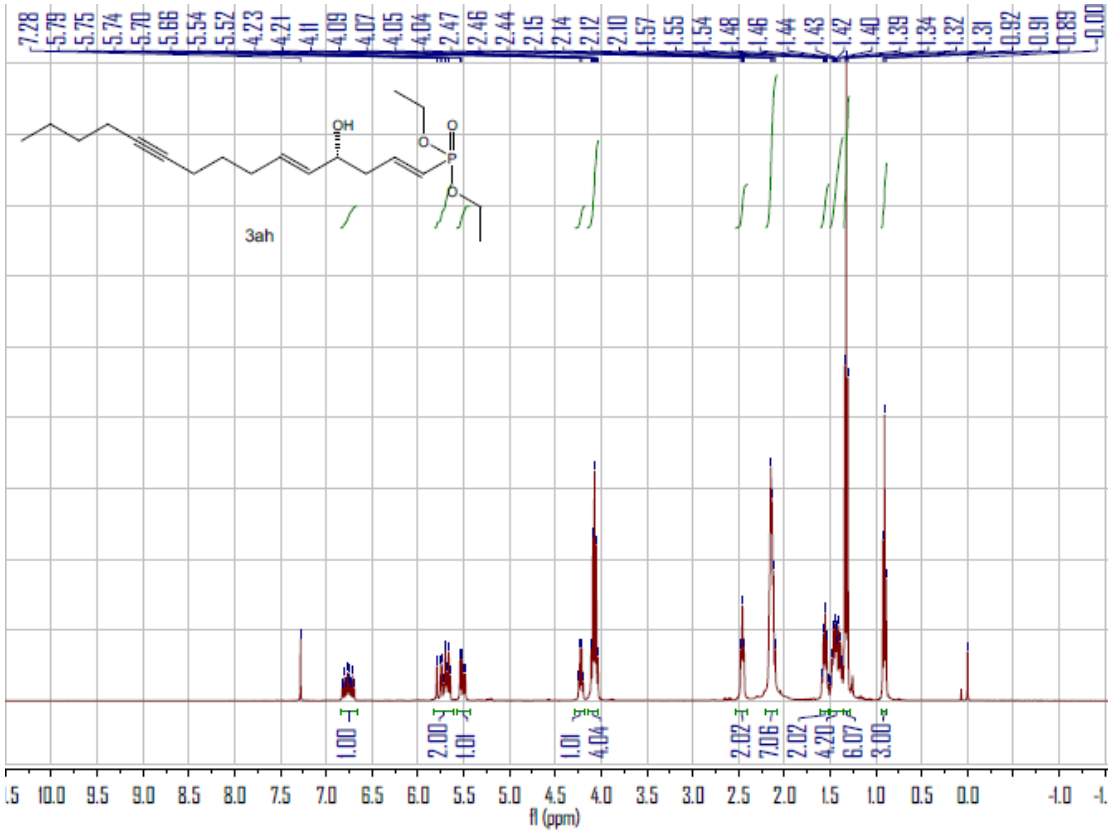


Figure S106. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3ah**, related to **Table 2**

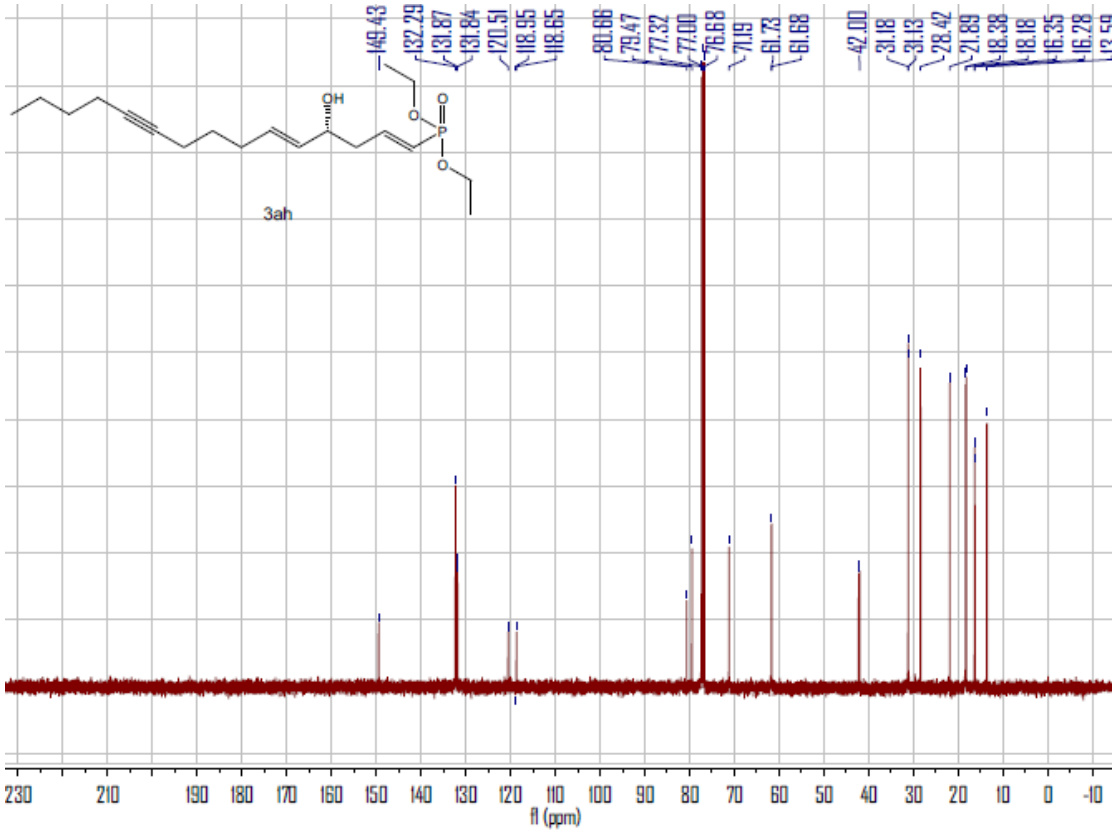


Figure S107. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3ah**, related to **Table 2**

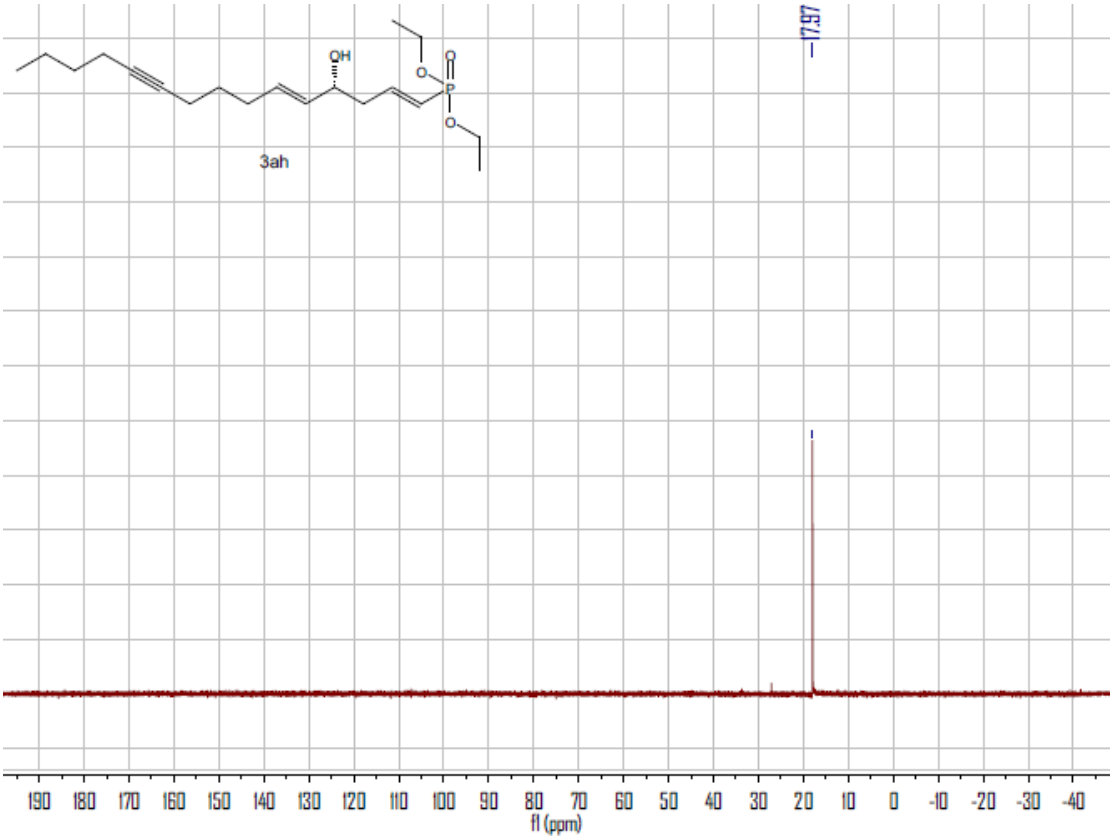


Figure S108. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ai**, related to **Table 2**

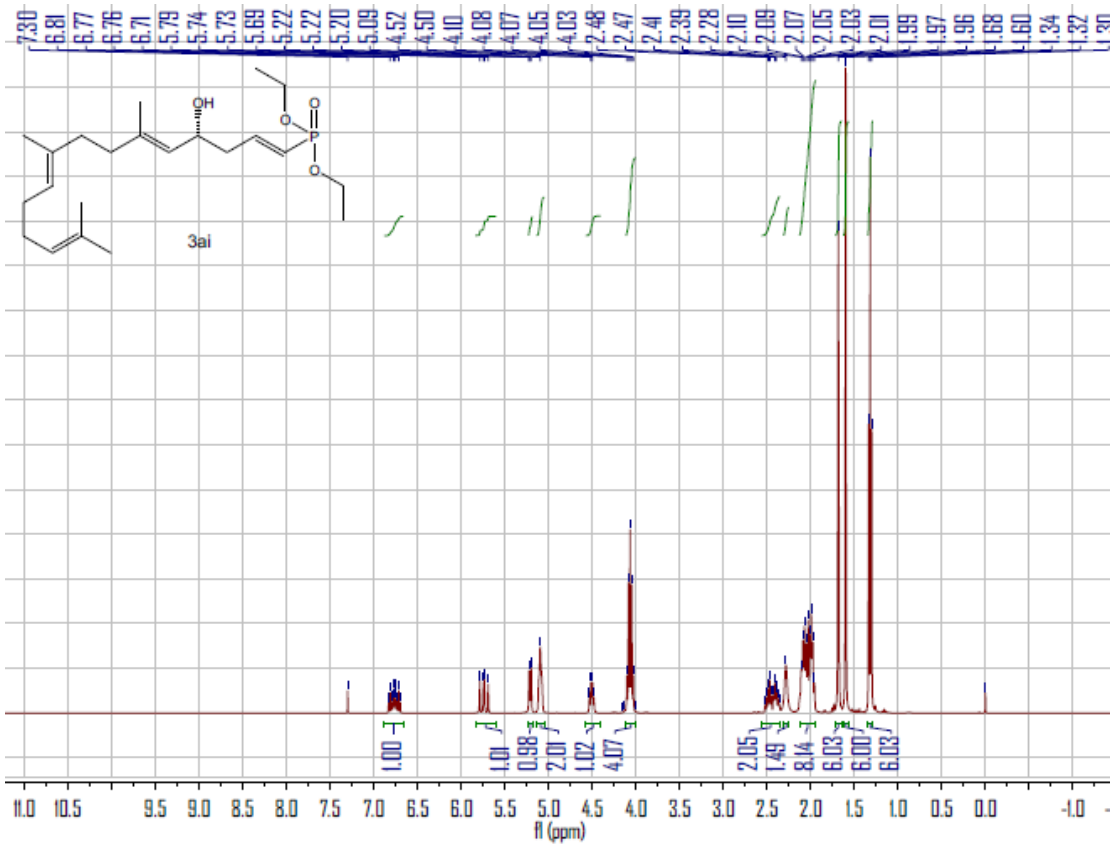


Figure S109. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3ai**, related to **Table 2**

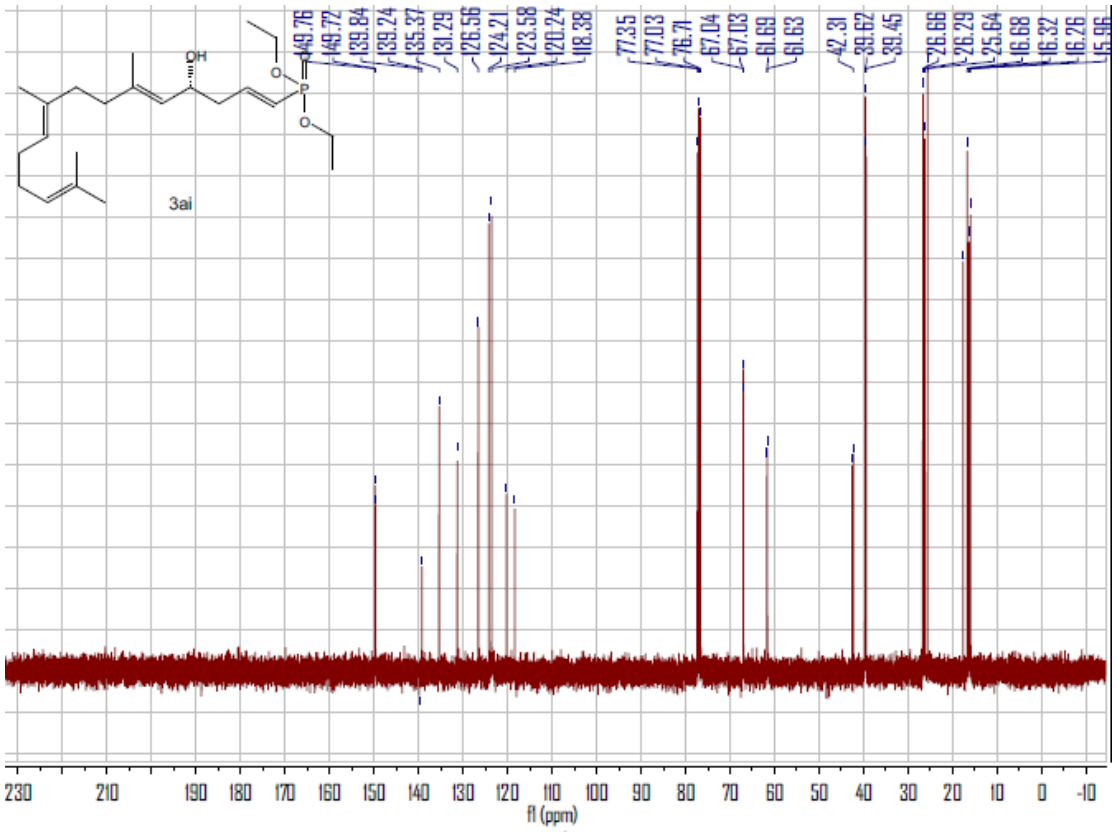


Figure S110. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3ai**, related to **Table 2**

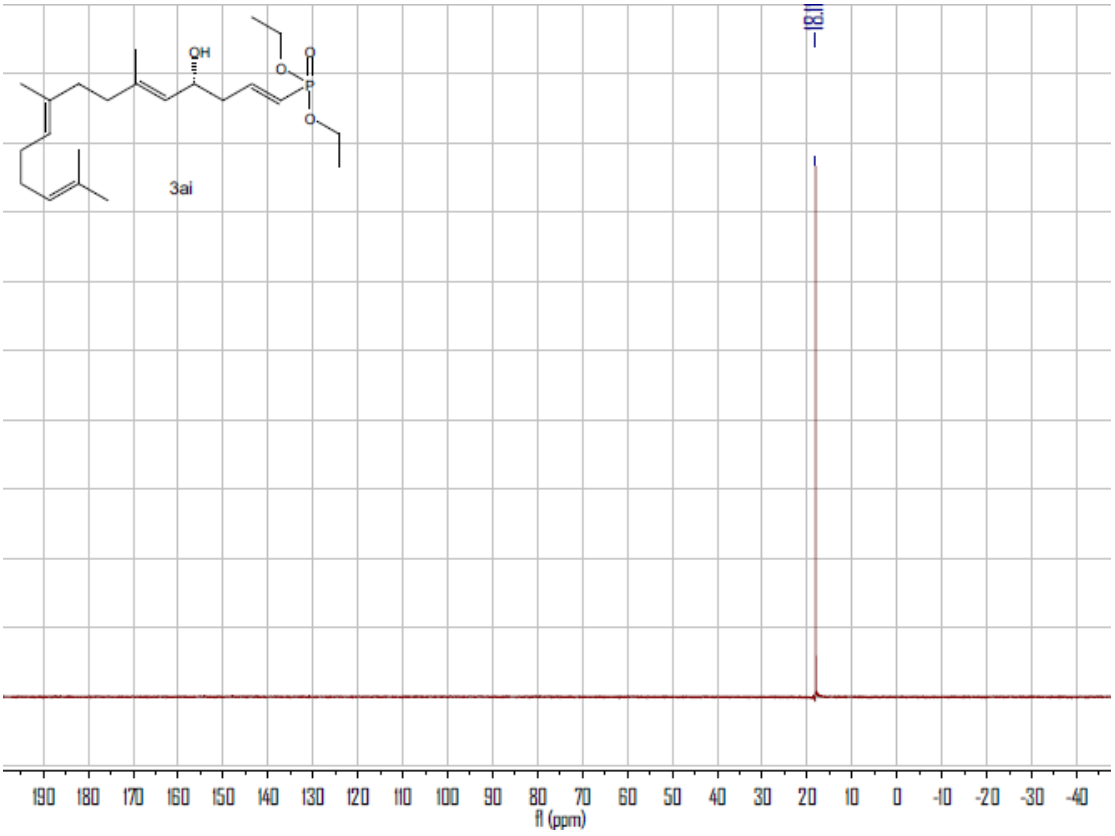


Figure S111. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3aj**, related to **Table 2**

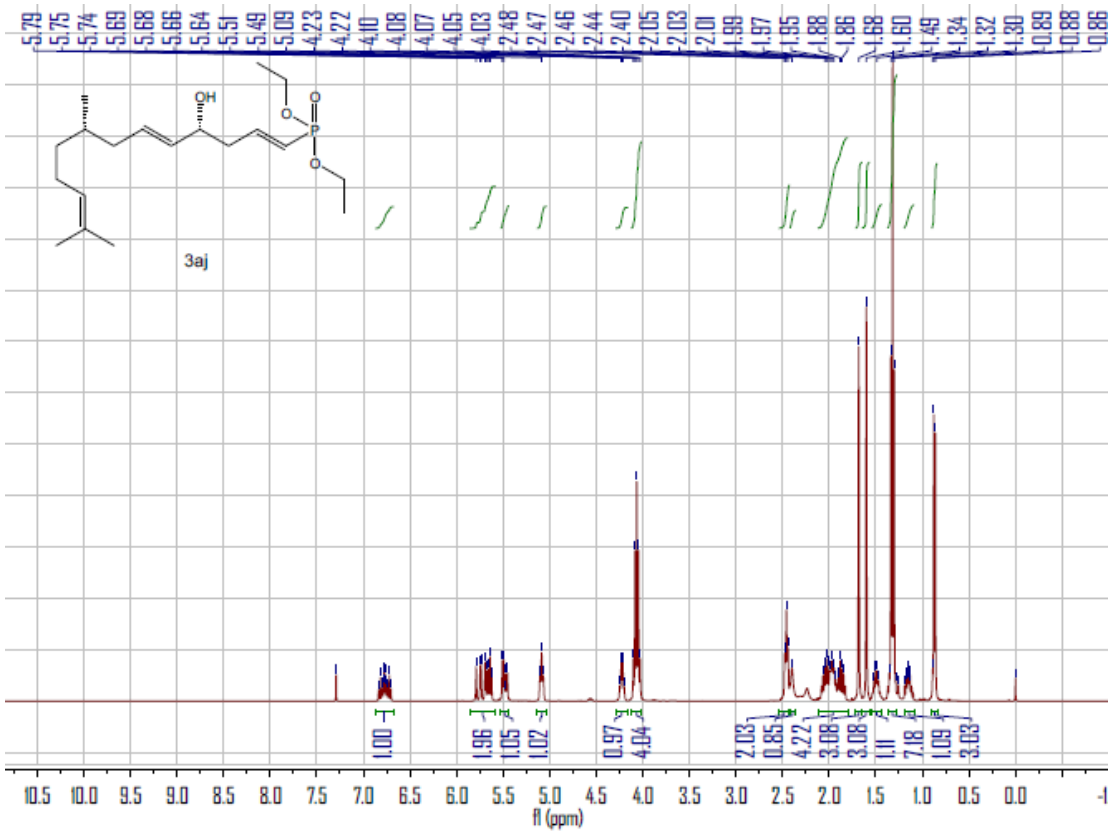


Figure S112. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3aj**, related to **Table 2**

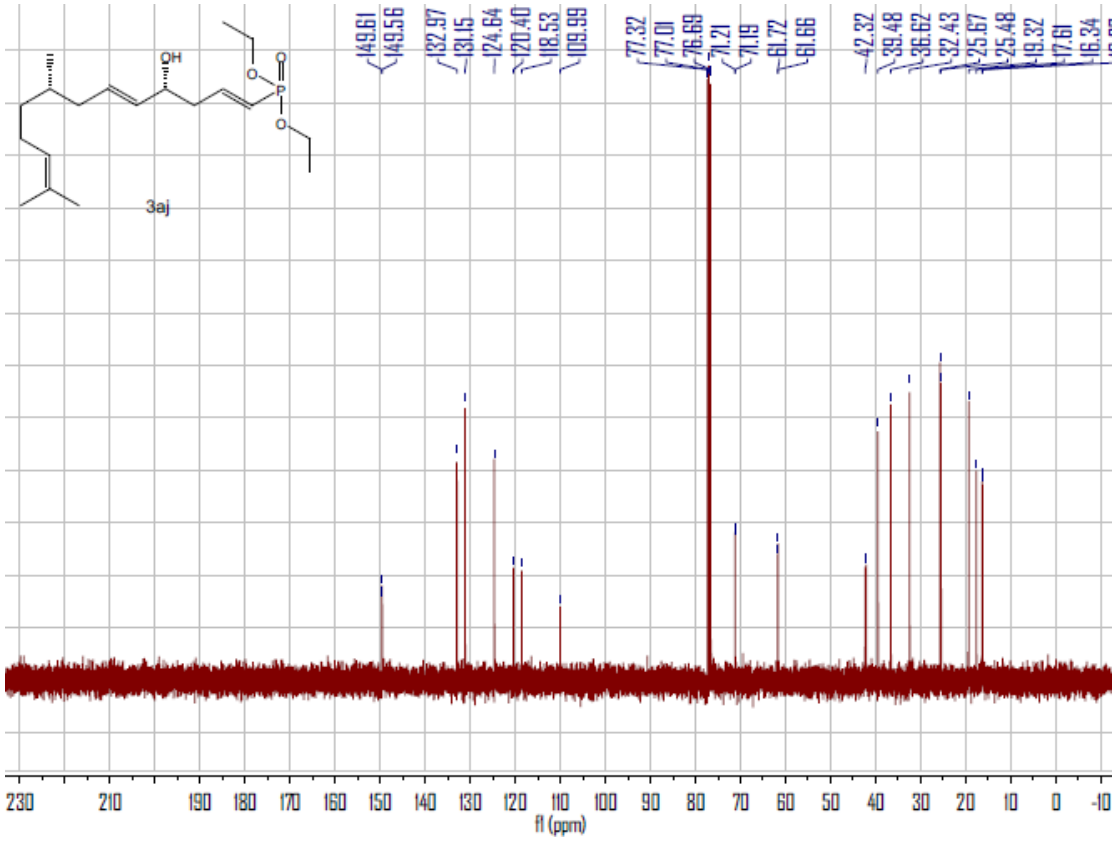


Figure S113. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3aj**, related to **Table 2**

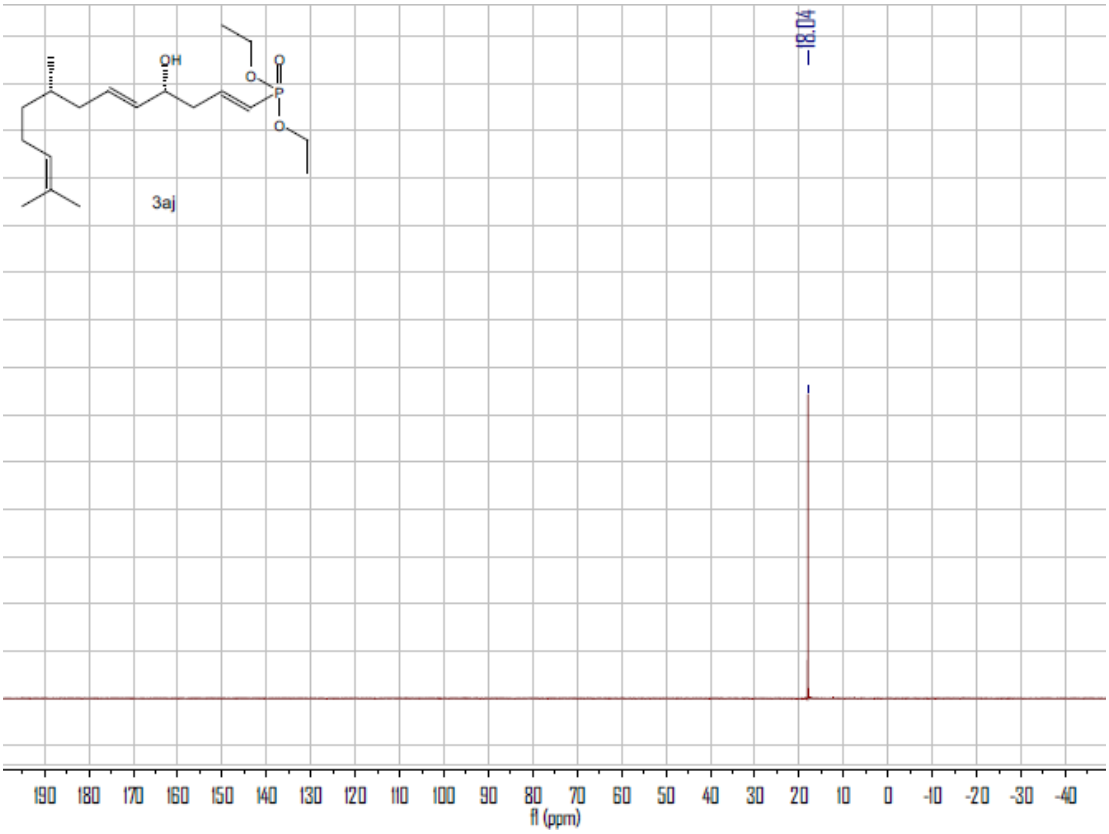


Figure S114. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3aj'**, related to **Table 2**

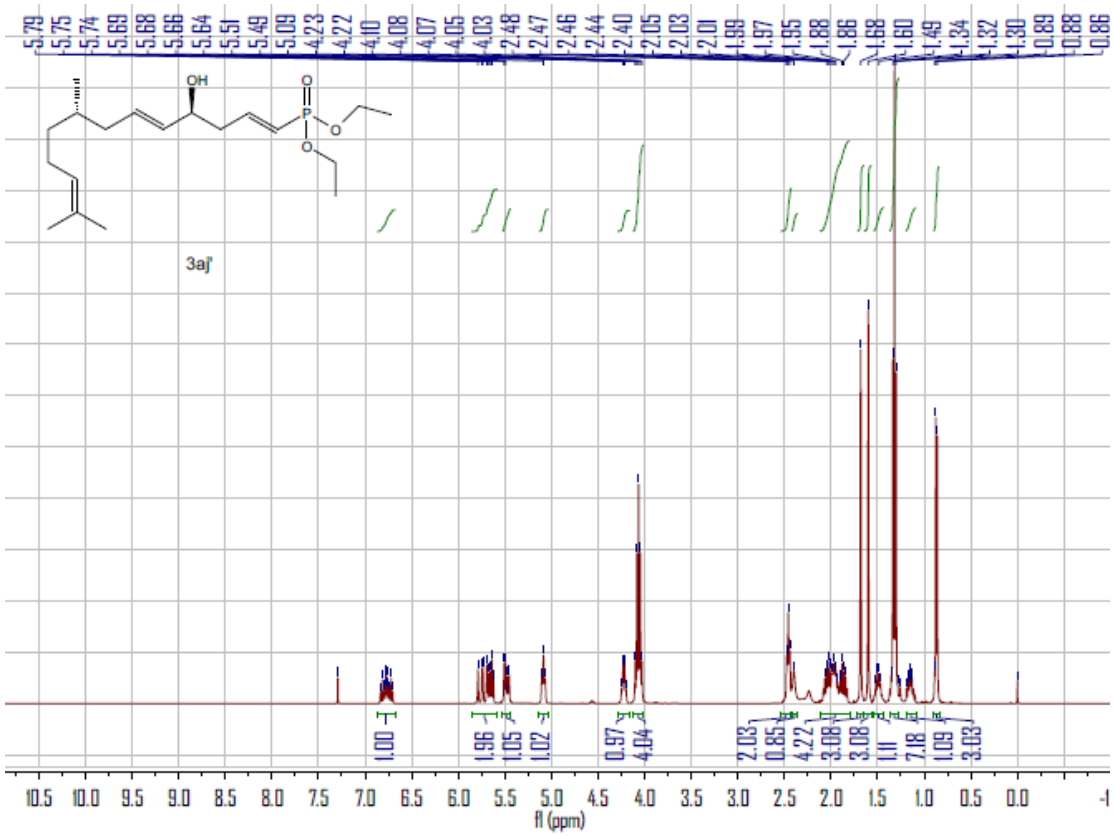


Figure S115. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3aj'**, related to **Table 2**

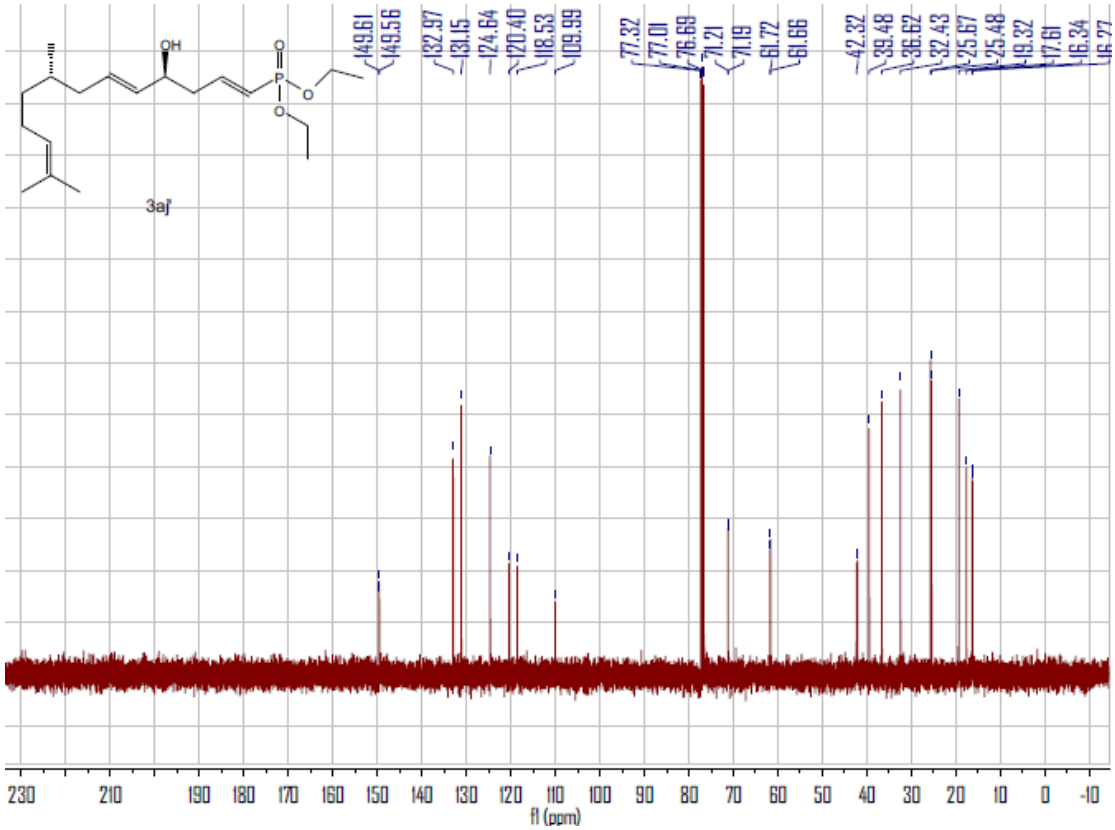


Figure S116. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3aj'**, related to **Table 2**

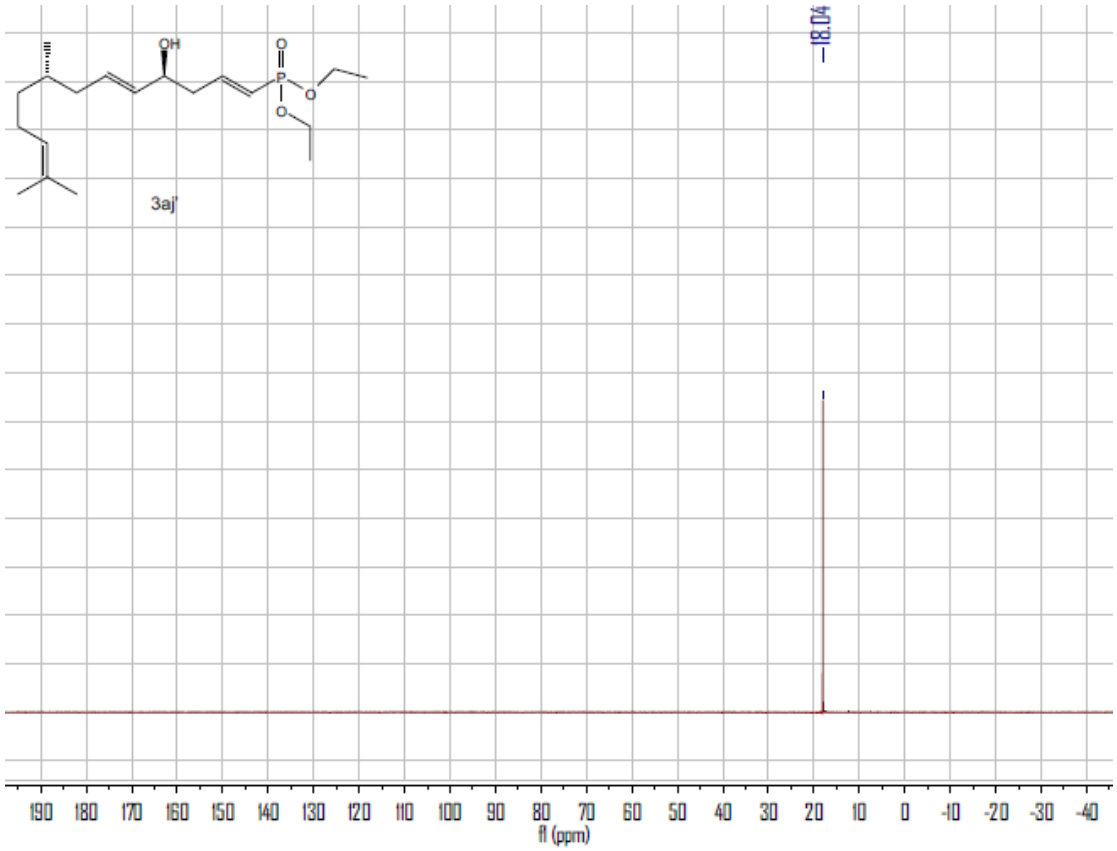


Figure S117. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ak**, related to **Table 2**

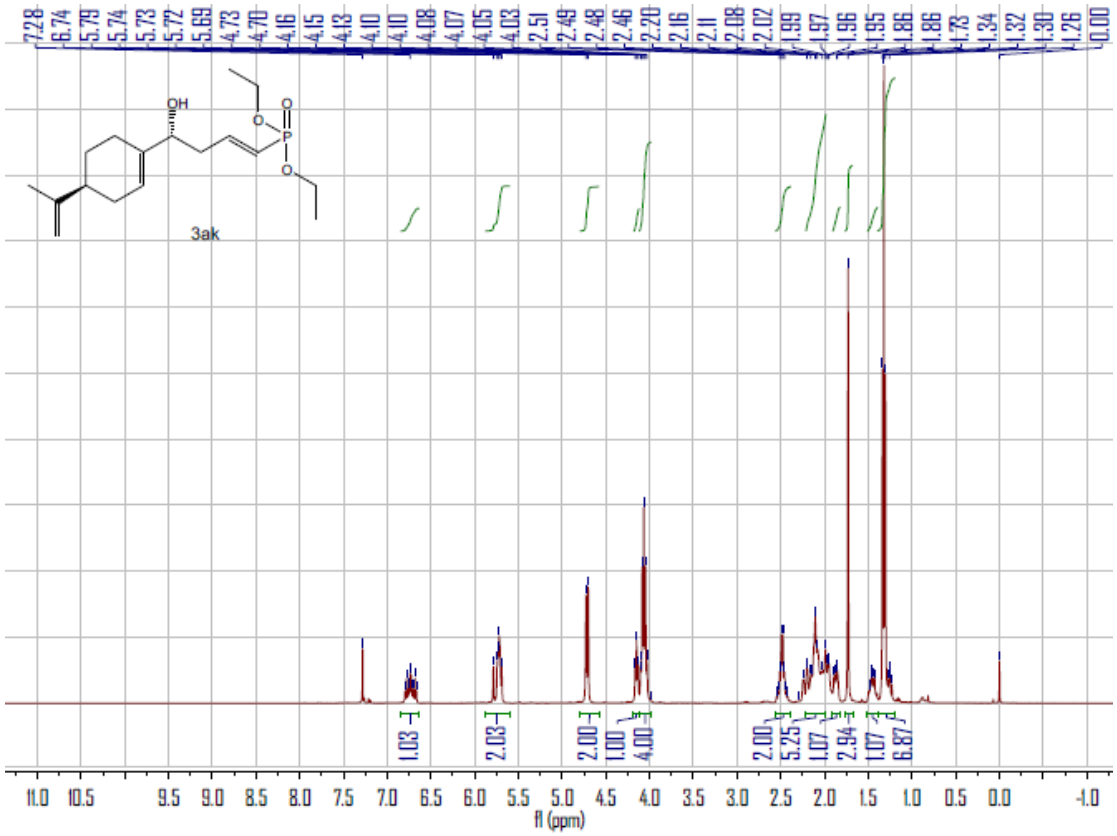


Figure S118. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3ak**, related to **Table 2**

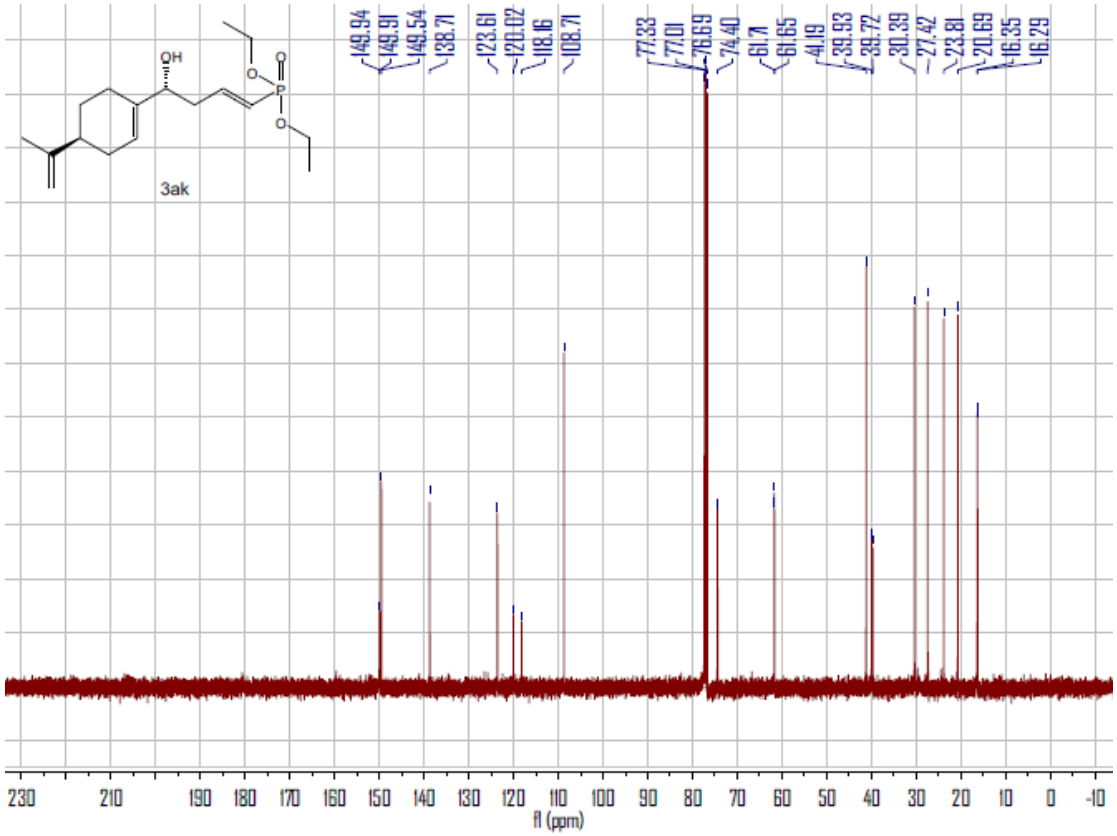


Figure S119. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3ak**, related to **Table 2**

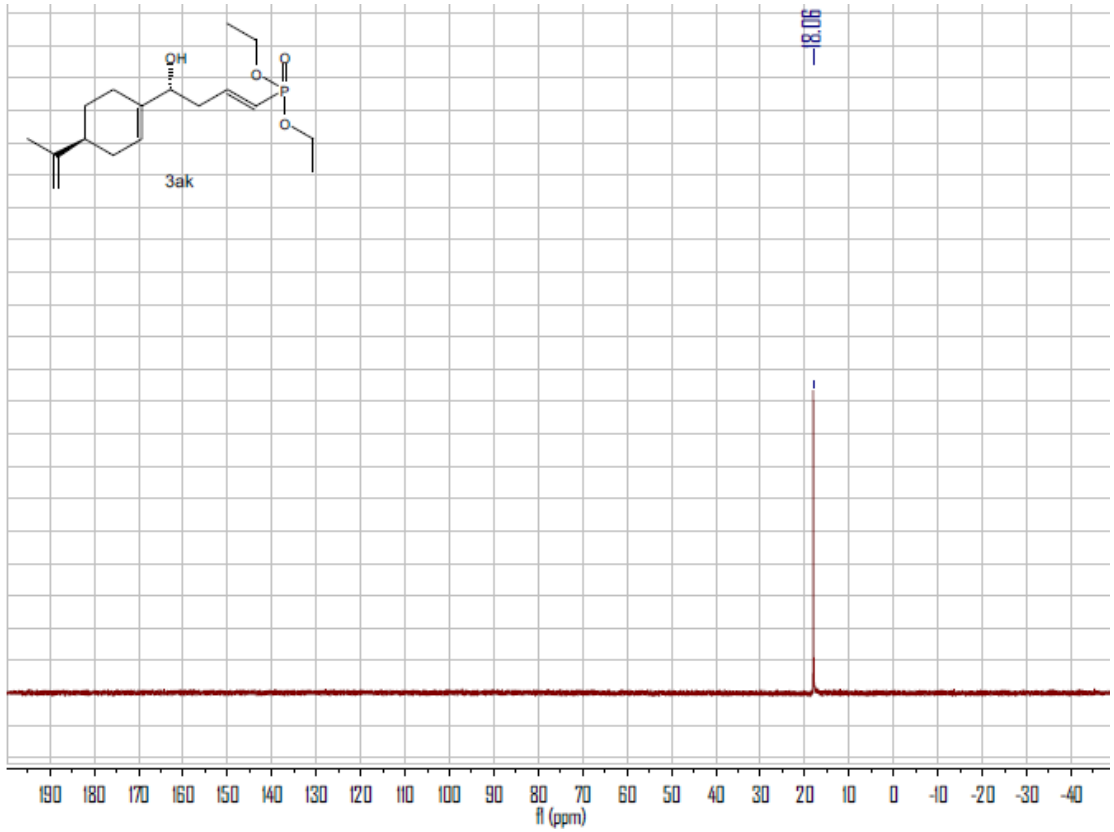


Figure S120. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ak'**, related to **Table 2**

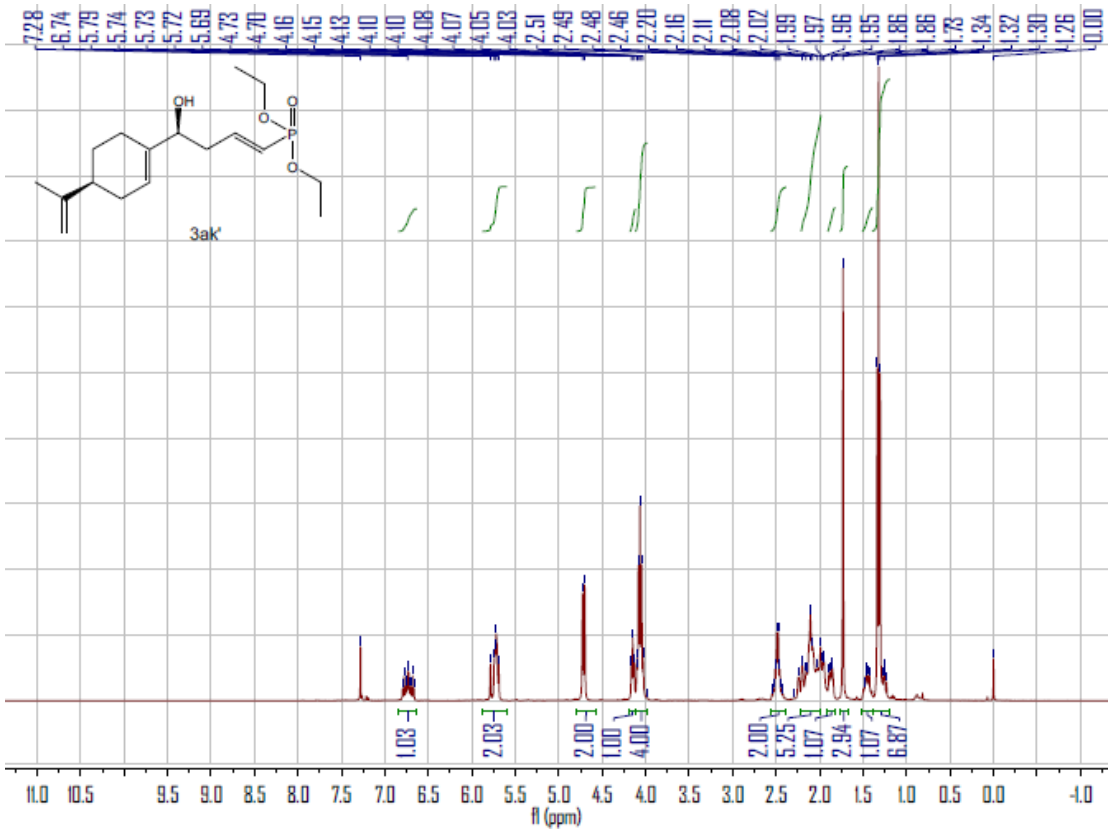


Figure S121. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3ak'**, related to **Table 2**

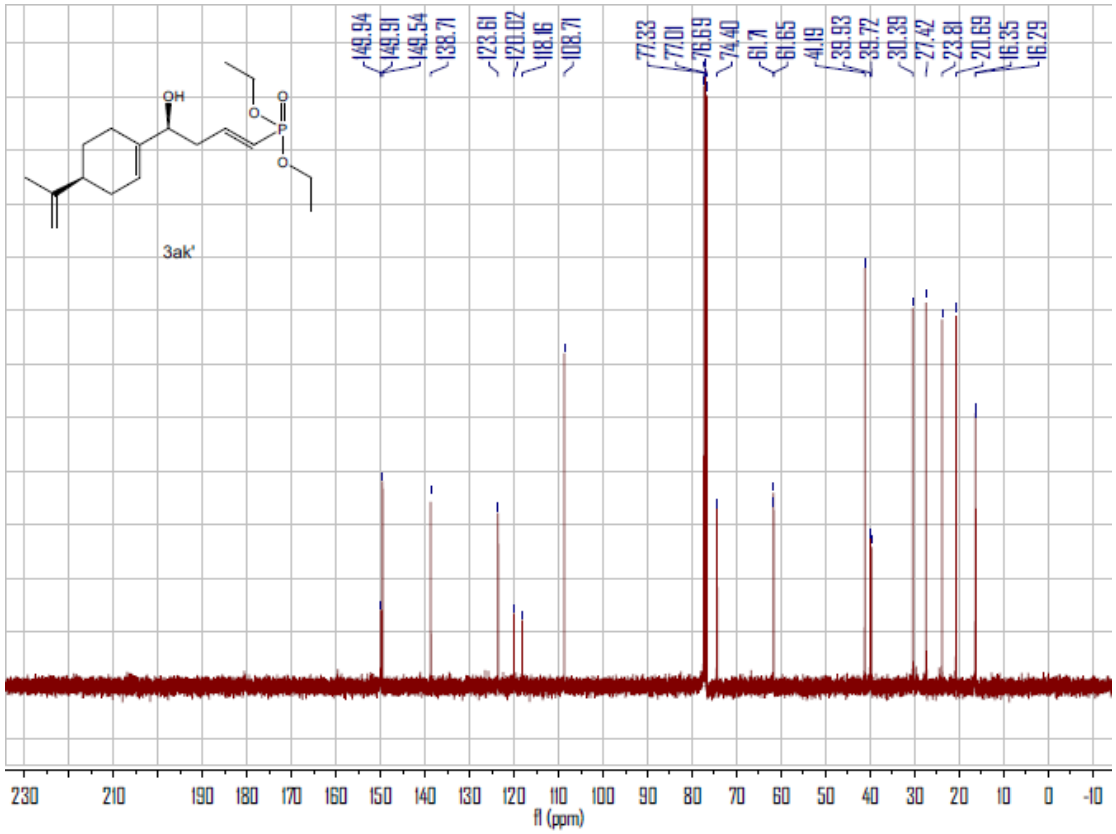


Figure S122. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3ak'**, related to **Table 2**

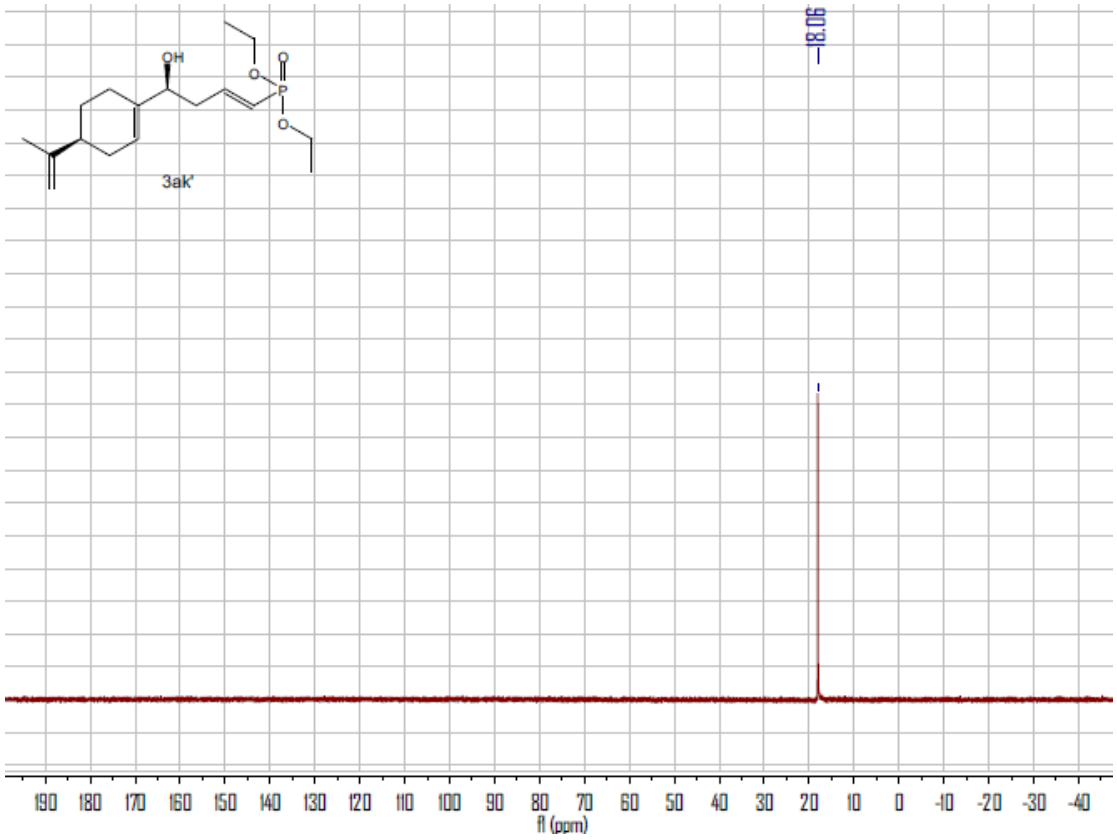


Figure S123. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3al**, related to **Table 2**

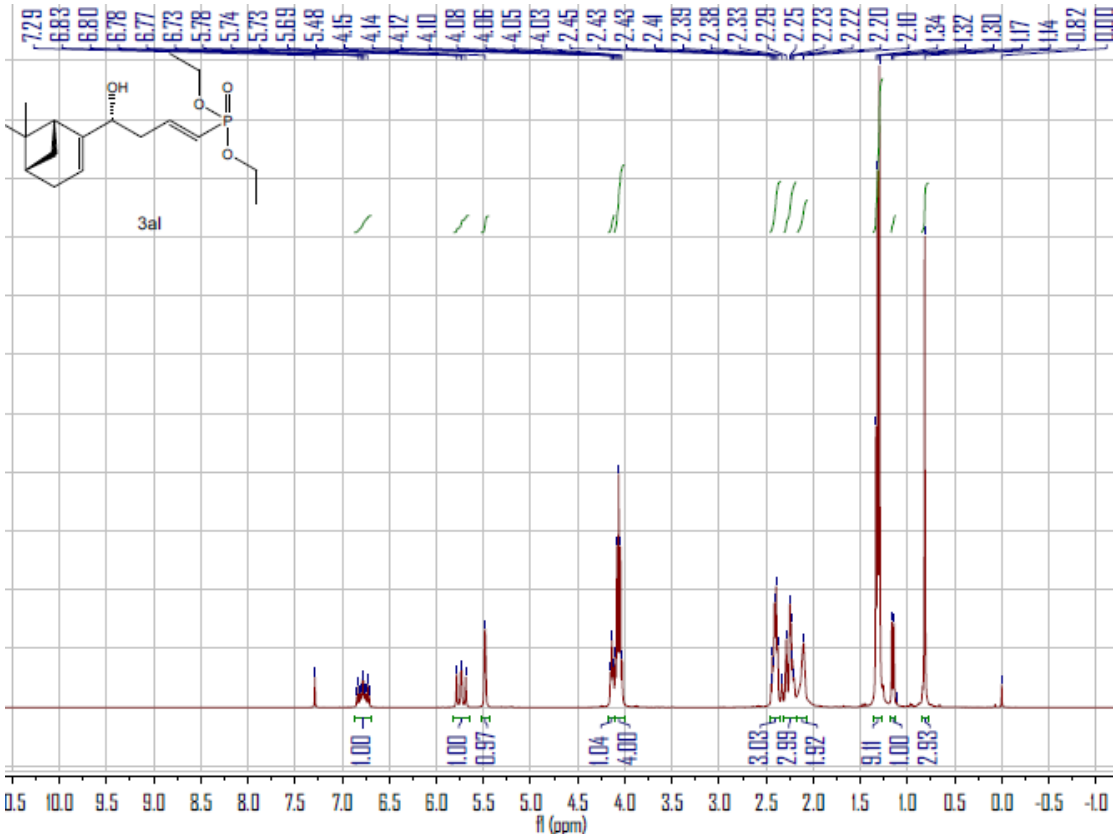


Figure S124. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3al**, related to **Table 2**

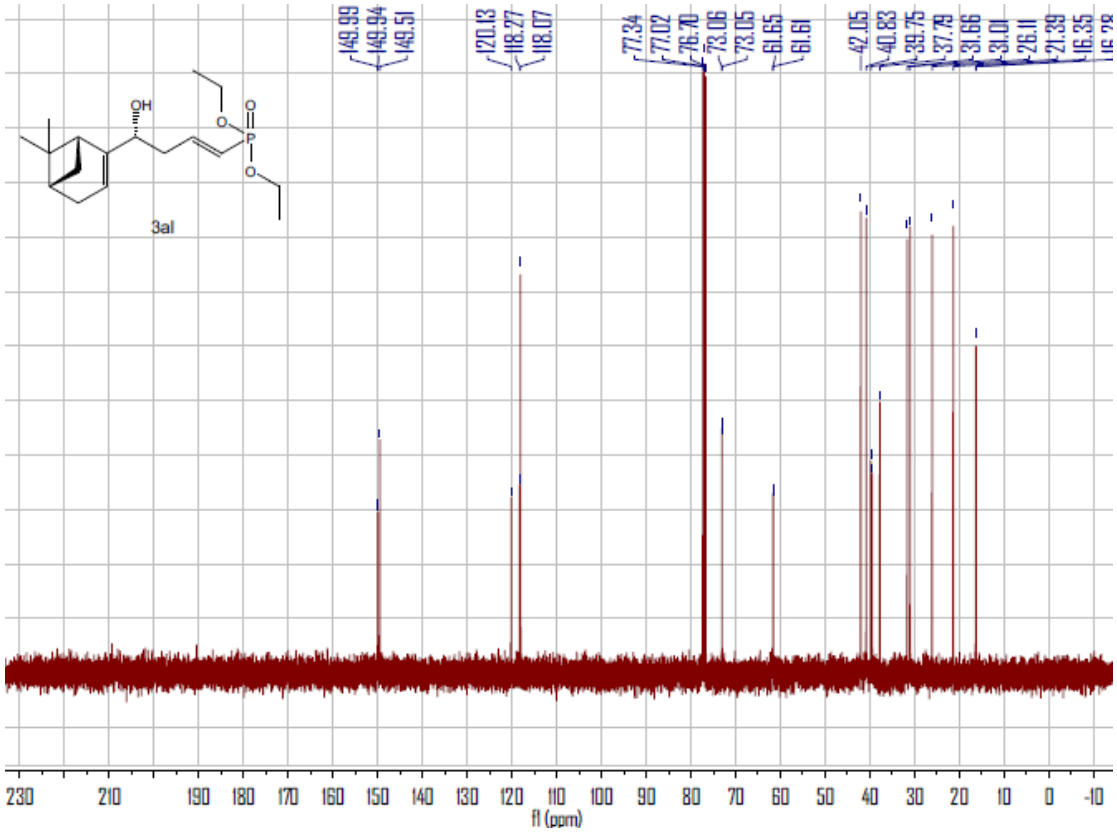


Figure S125. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3al**, related to **Table 2**

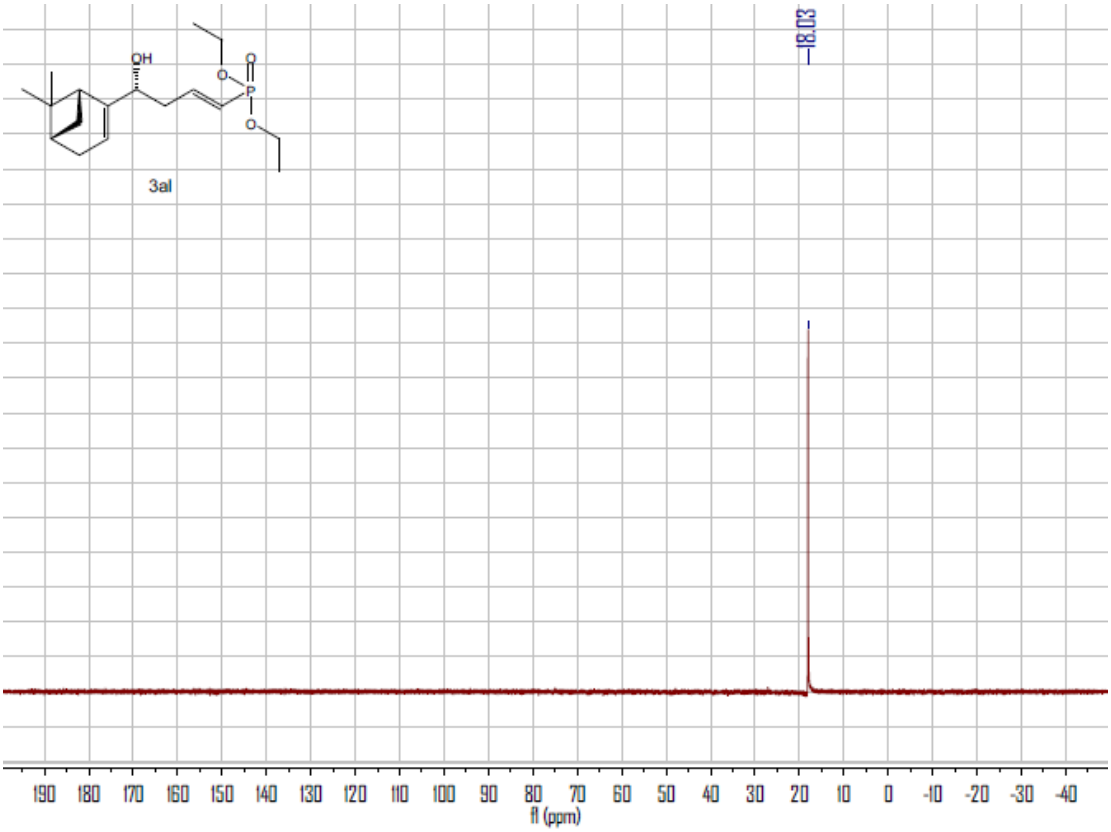


Figure S126. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3al'**, related to **Table 2**

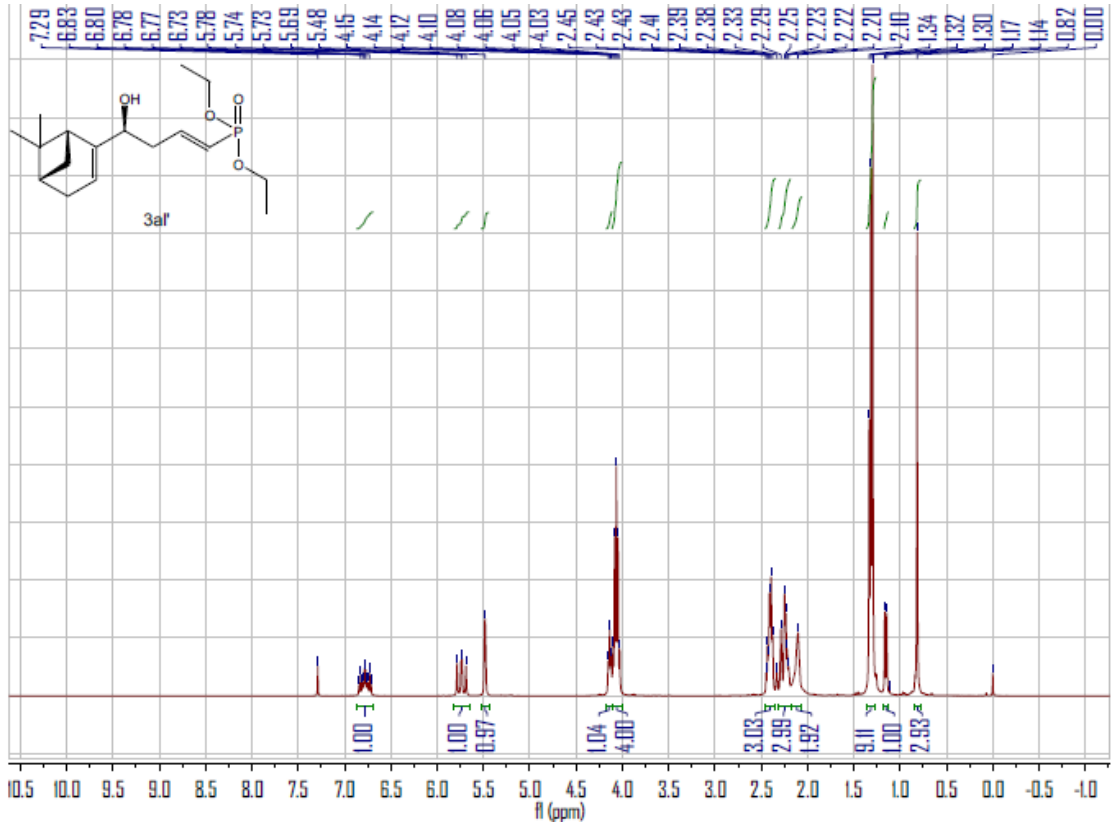


Figure S127. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3al'**, related to **Table 2**

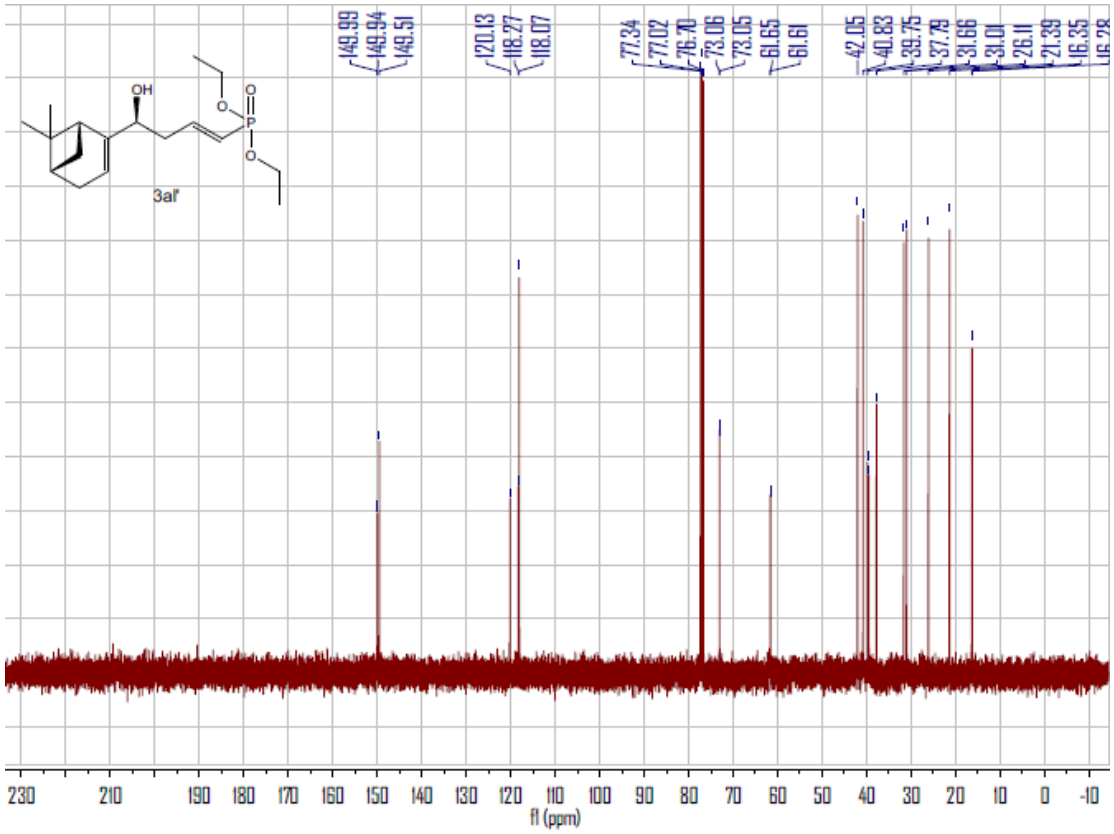


Figure S128. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3al'**, related to **Table 2**

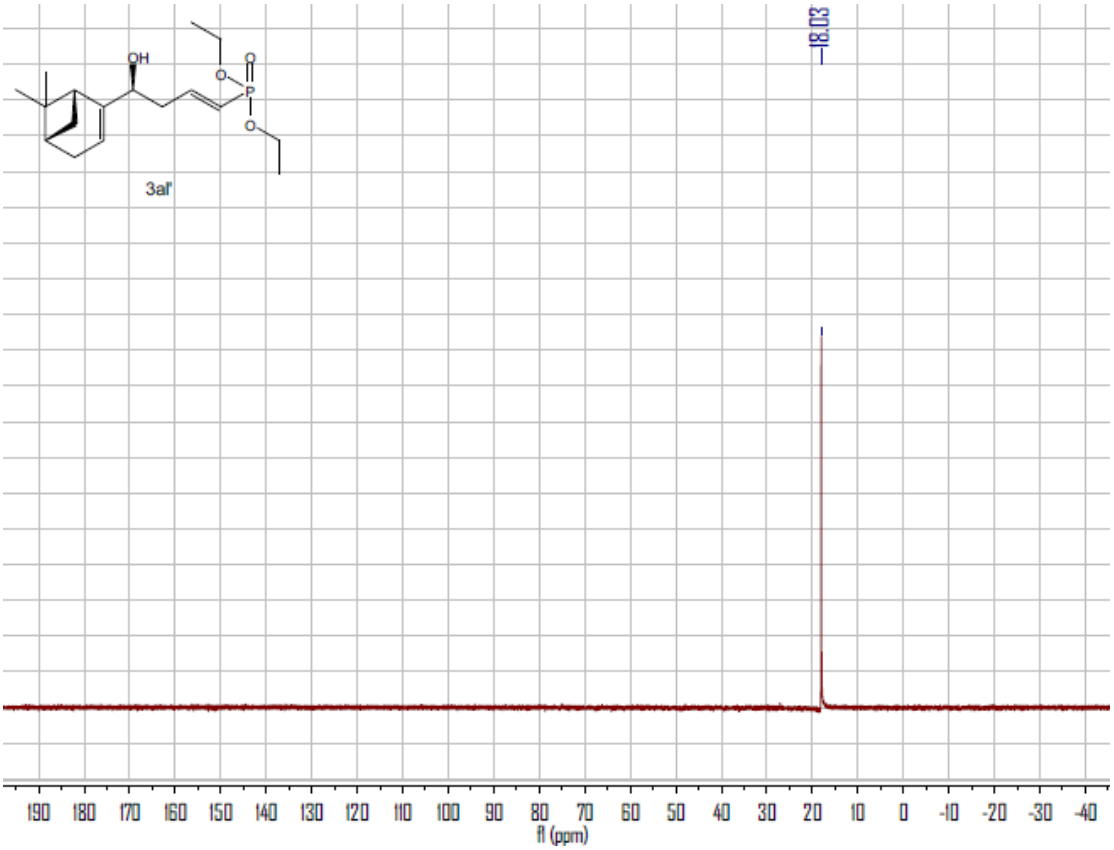


Figure S129. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5a**, related to **Table 3**

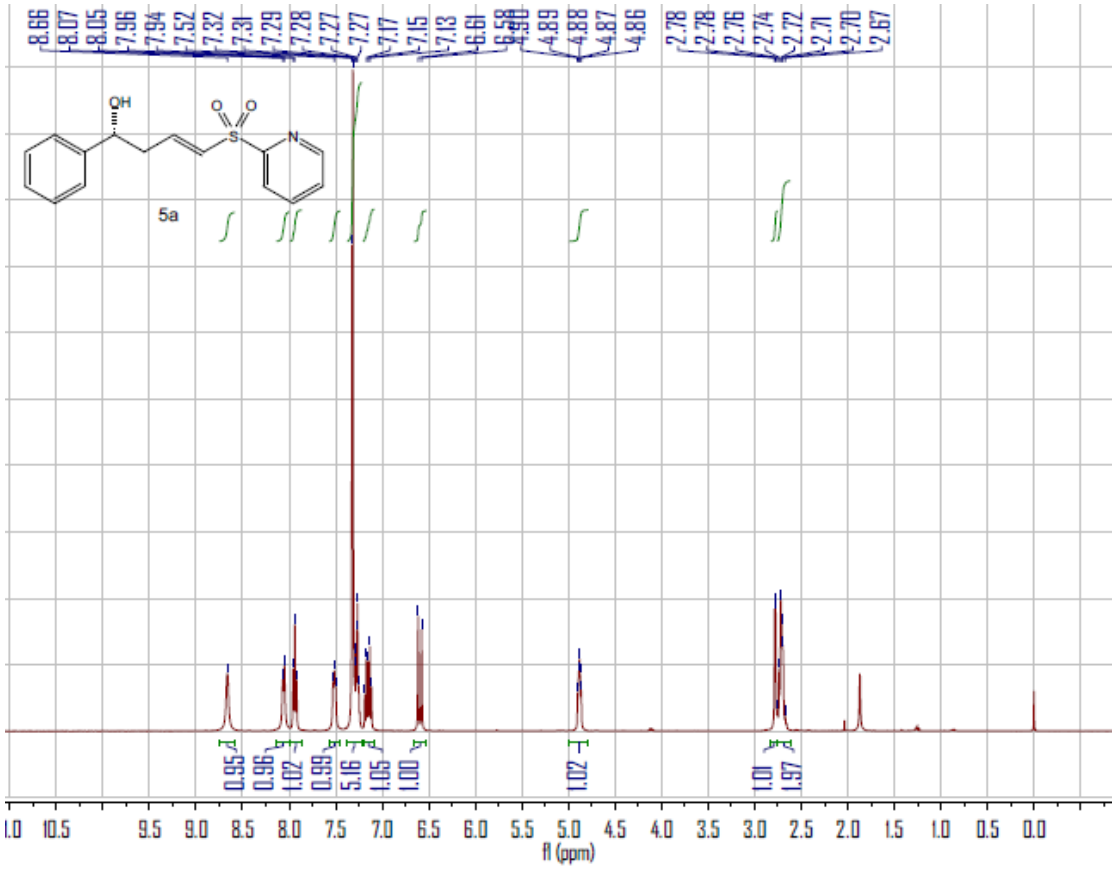


Figure S130. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5a**, related to **Table 3**

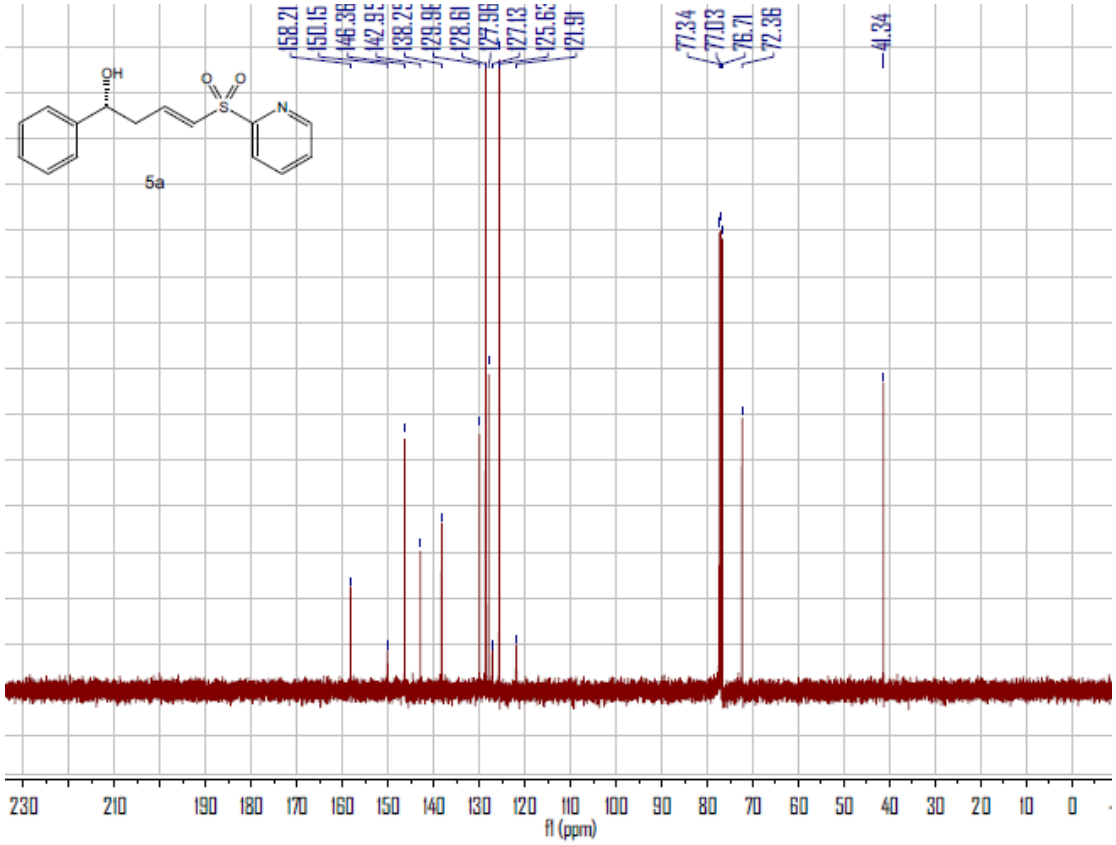


Figure S131. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5b**, related to **Table 3**

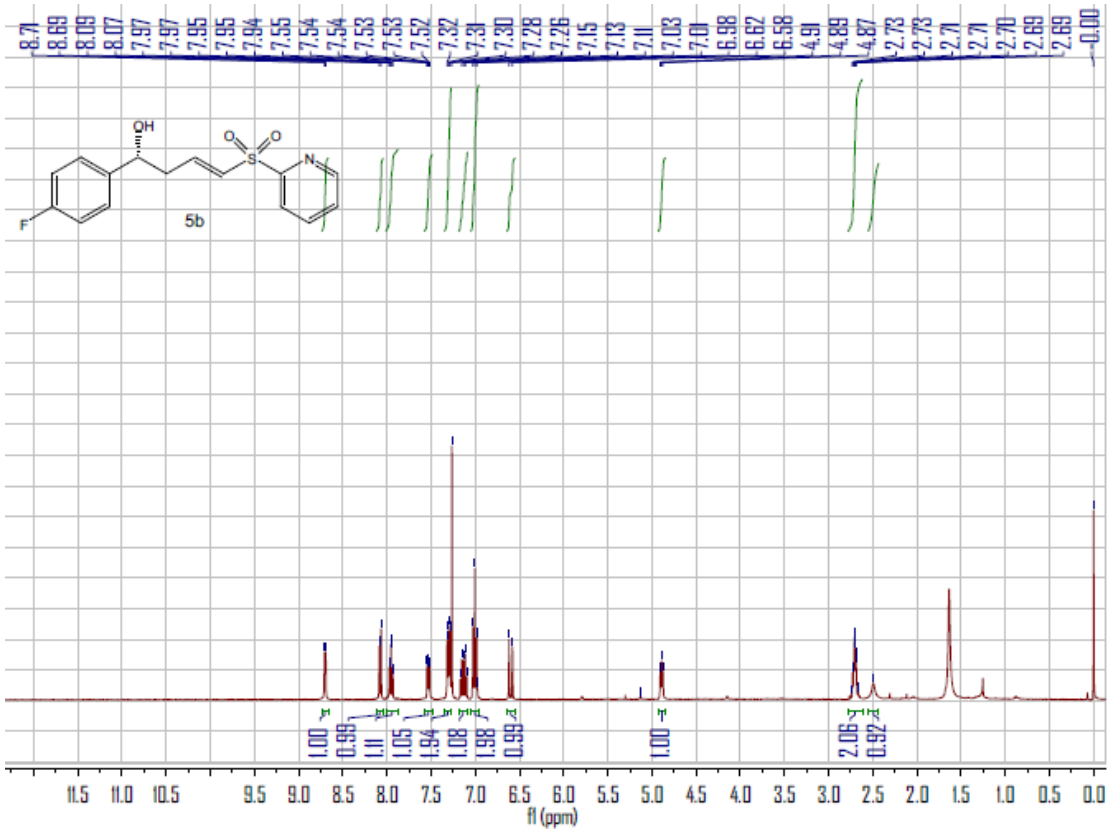


Figure S132. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5b**, related to **Table 3**

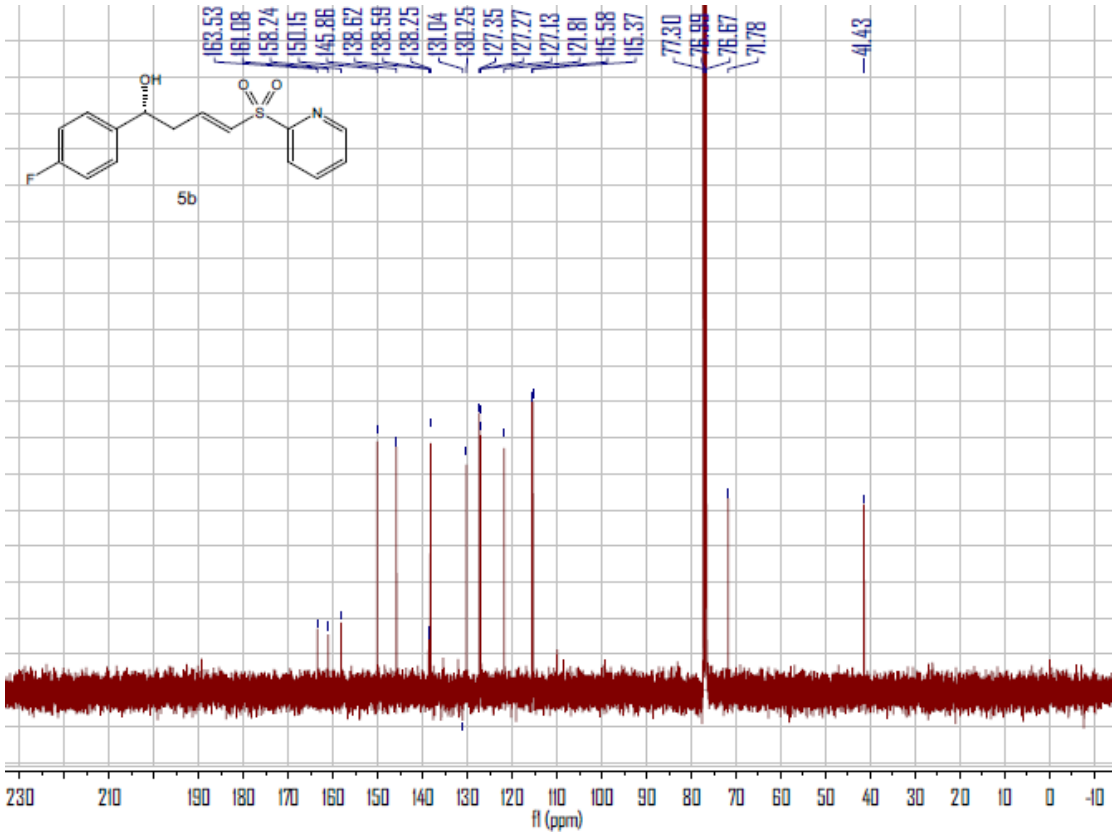


Figure S133. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5b**, related to **Table 3**

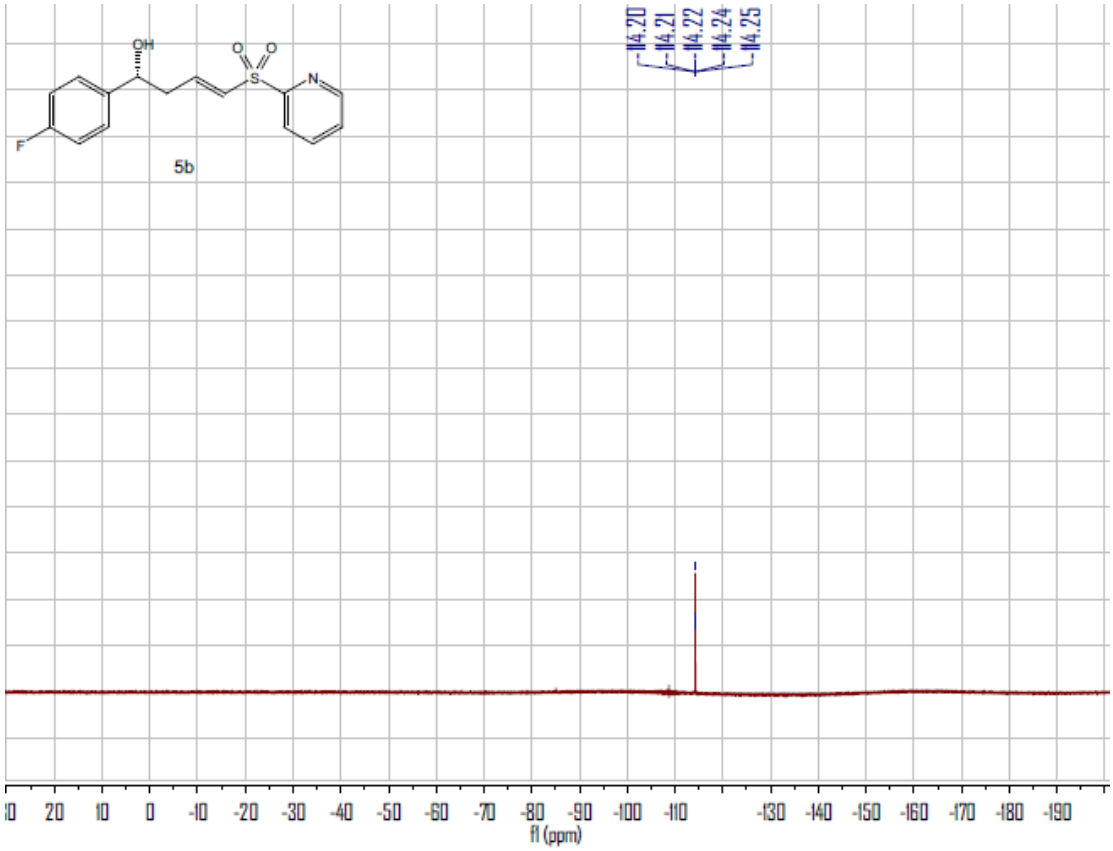


Figure S134. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5c**, related to **Table 3**

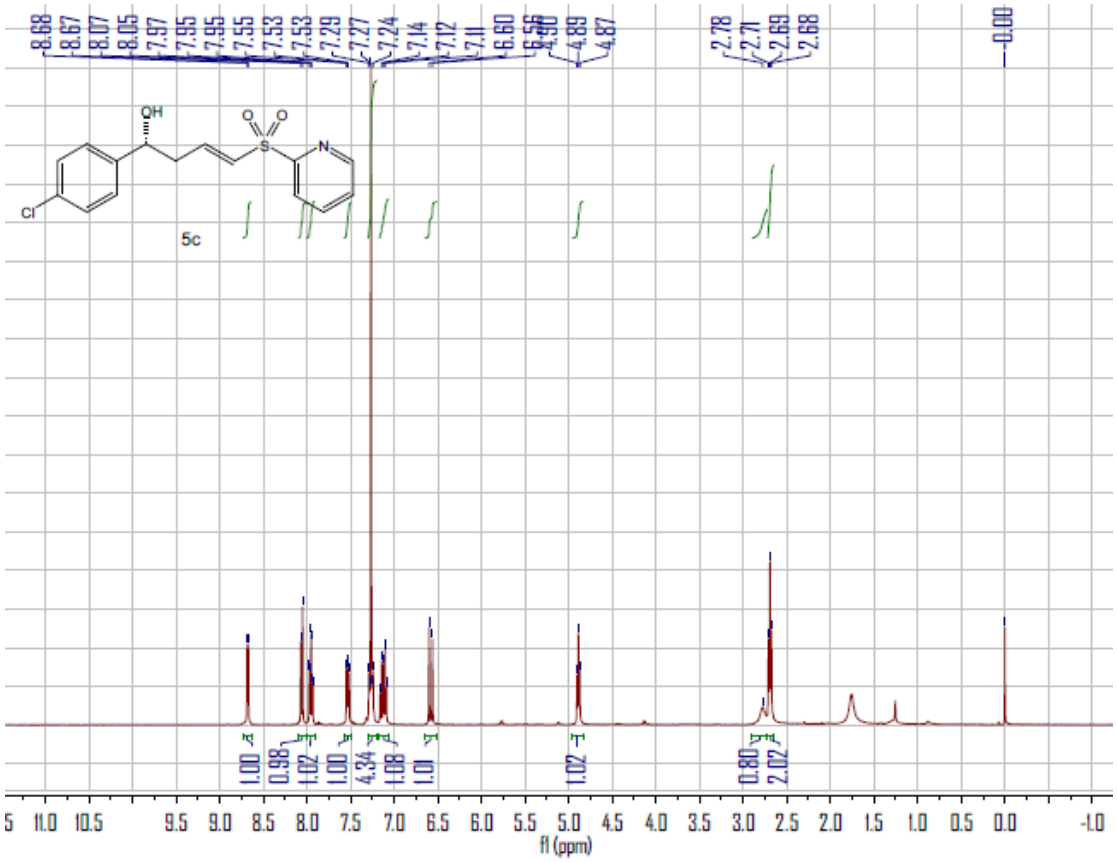


Figure S135. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5c**, related to **Table 3**

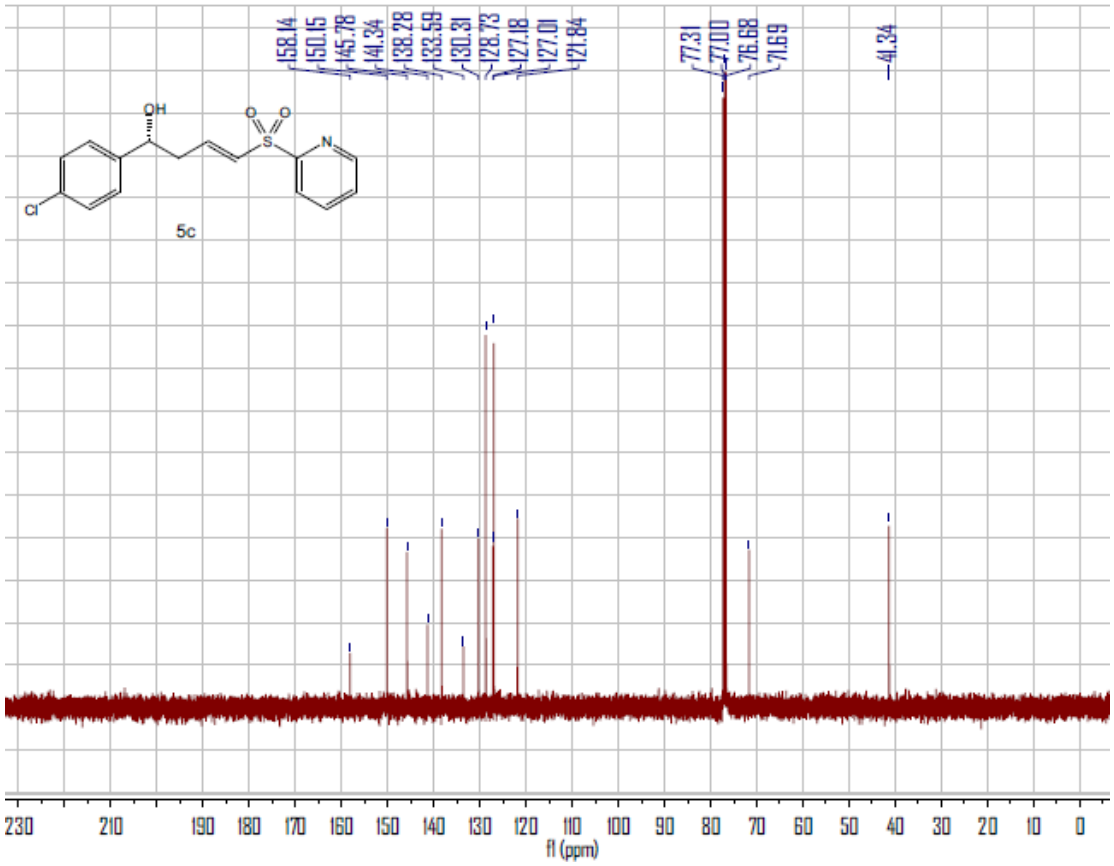


Figure S136. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5d**, related to **Table 3**

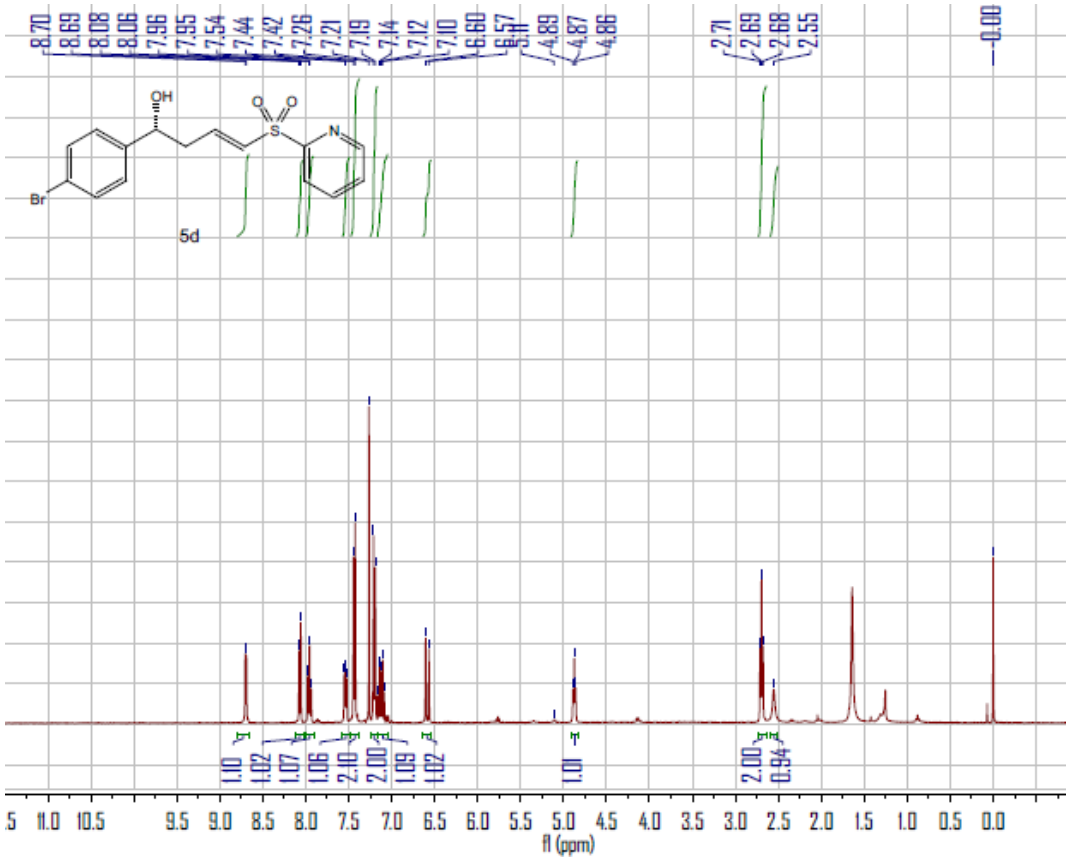


Figure S137. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5d**, related to **Table 3**

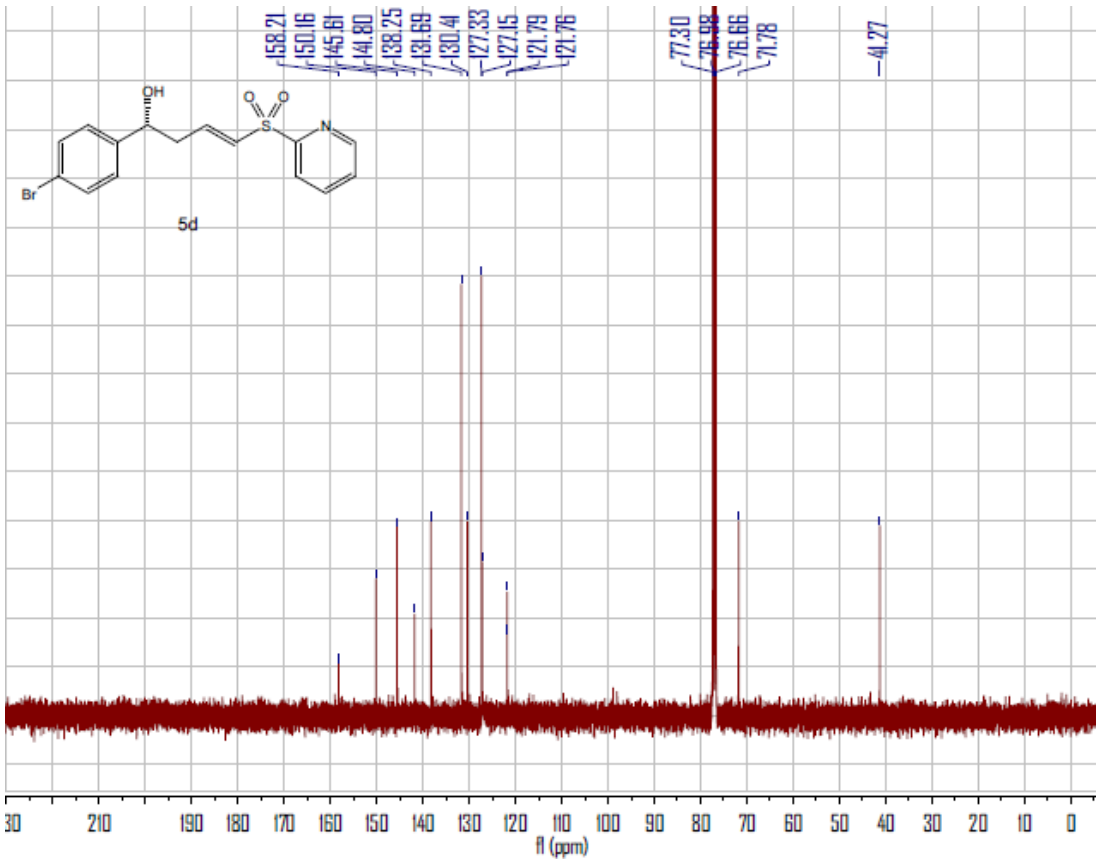


Figure S138. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5e**, related to **Table 3**

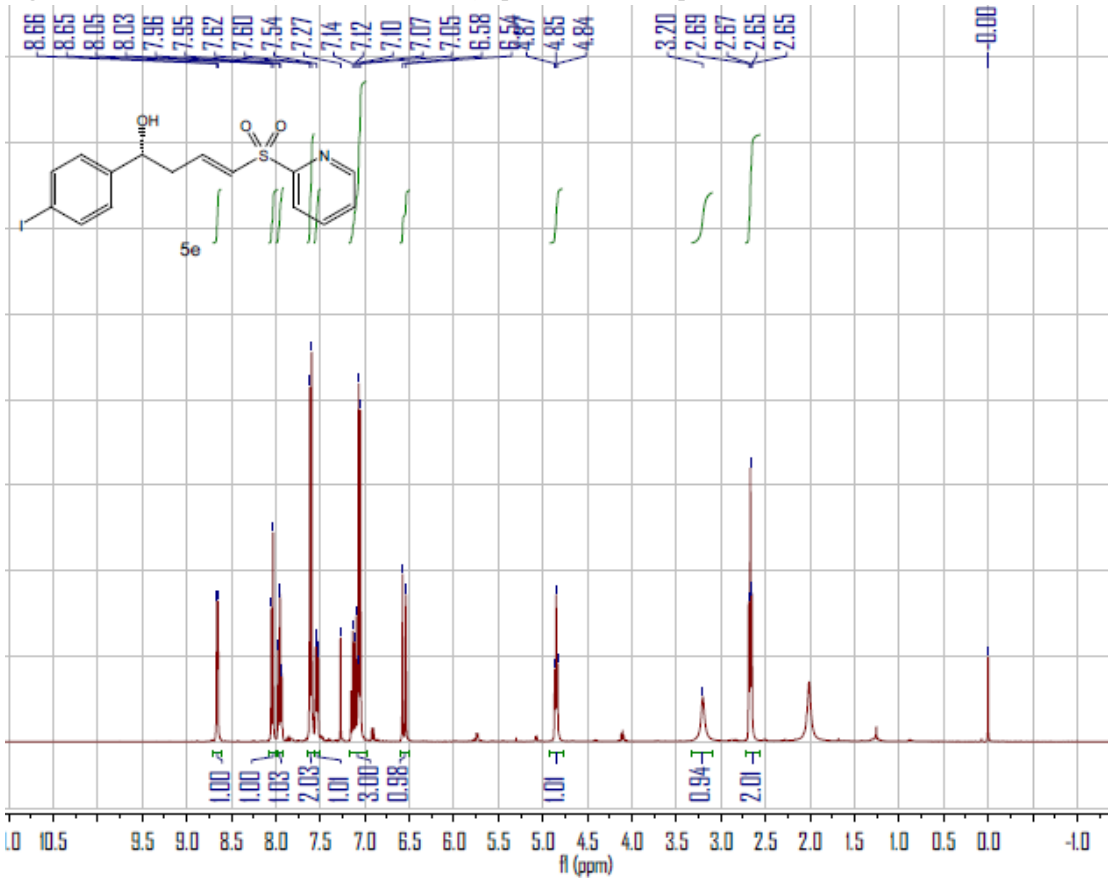


Figure S139. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5e**, related to **Table 3**

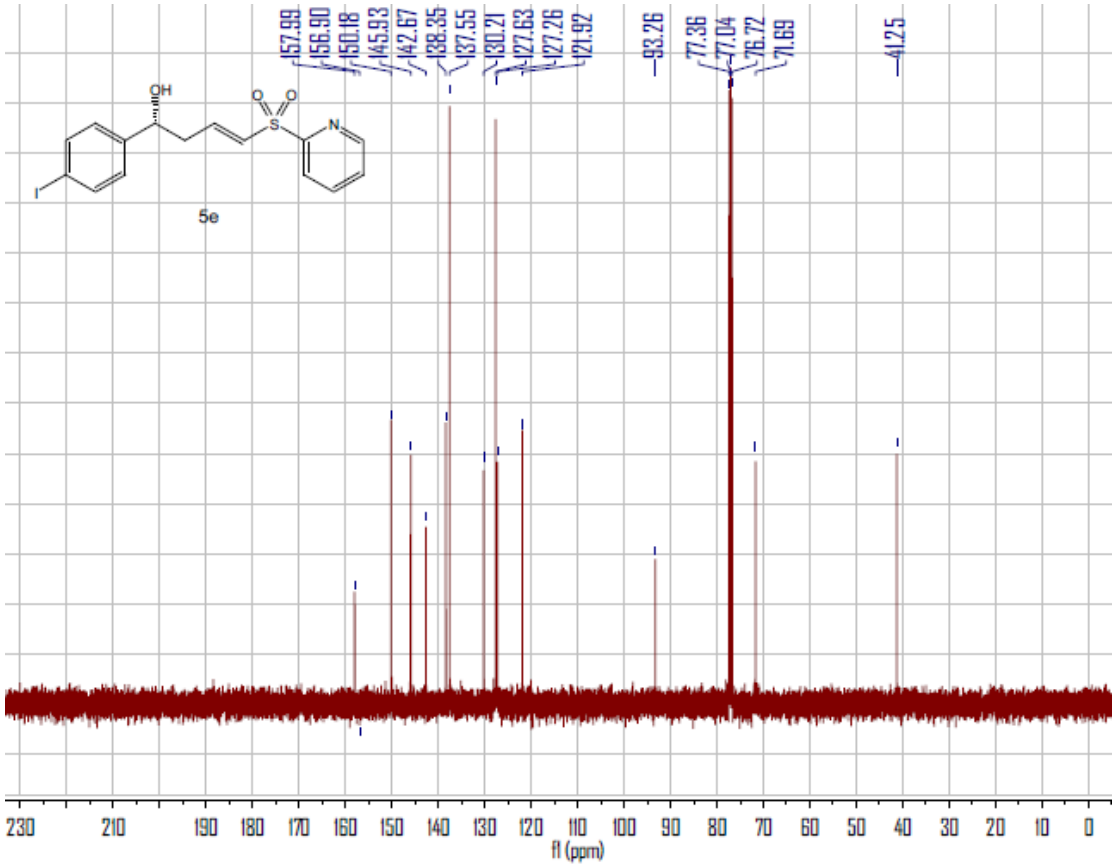


Figure S140. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5f**, related to **Table 3**

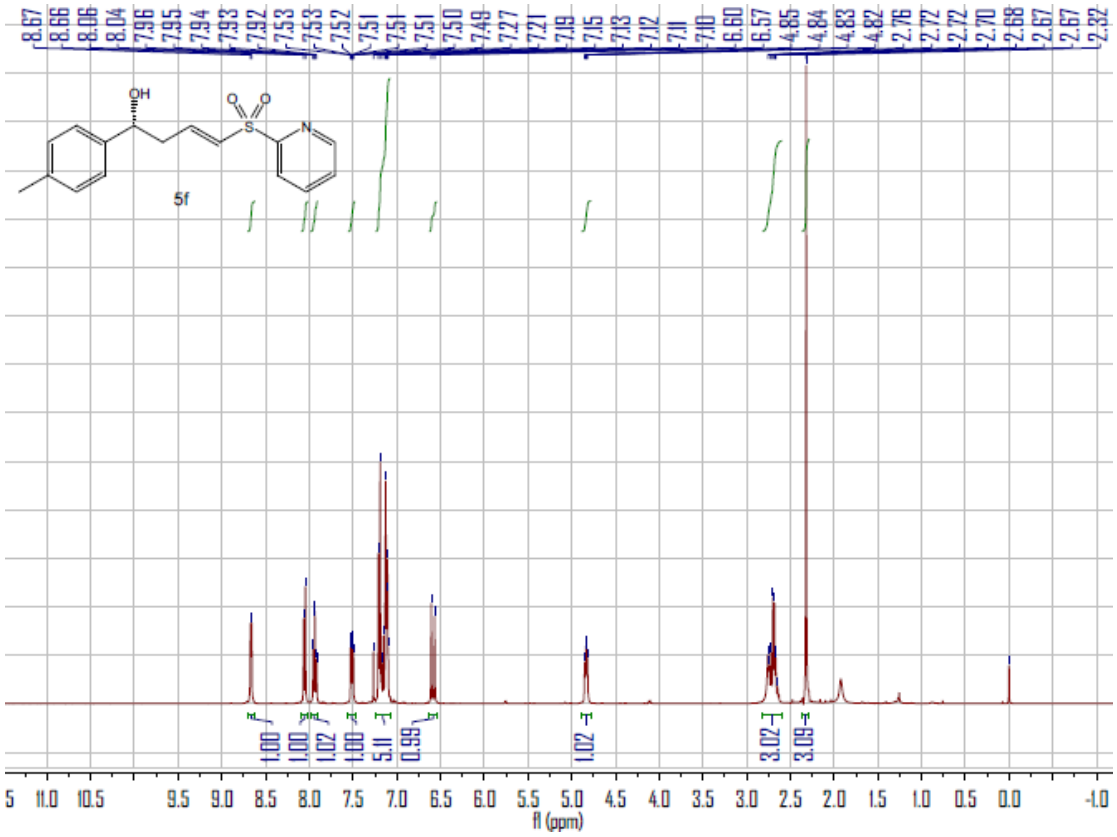


Figure S141. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5f**, related to **Table 3**

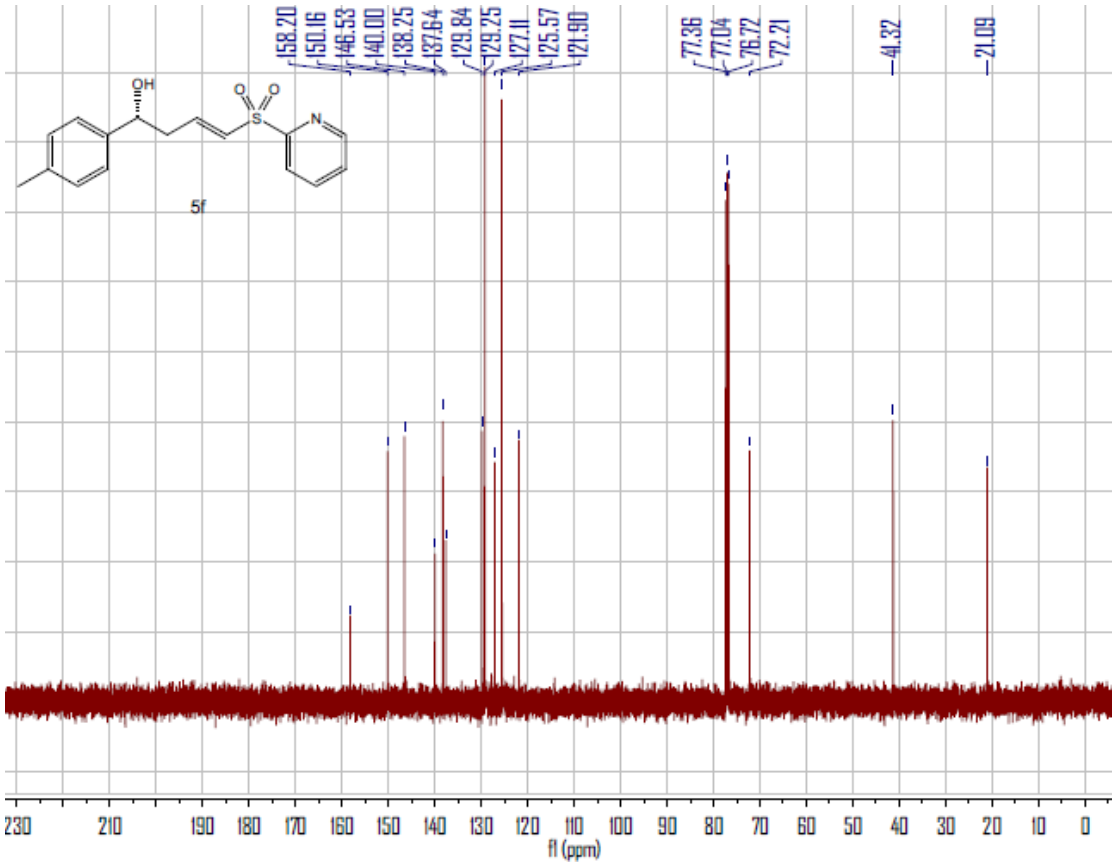


Figure S142. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5g**, related to **Table 3**

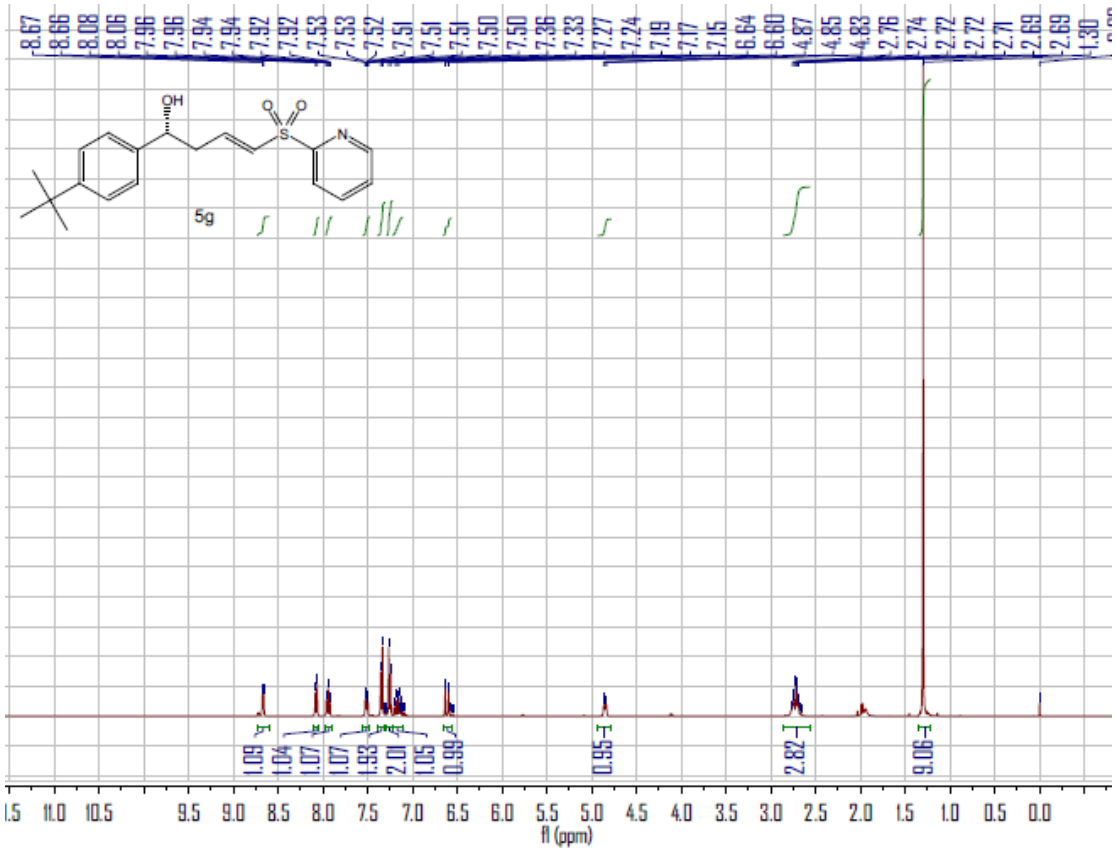


Figure S143. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5g**, related to **Table 3**

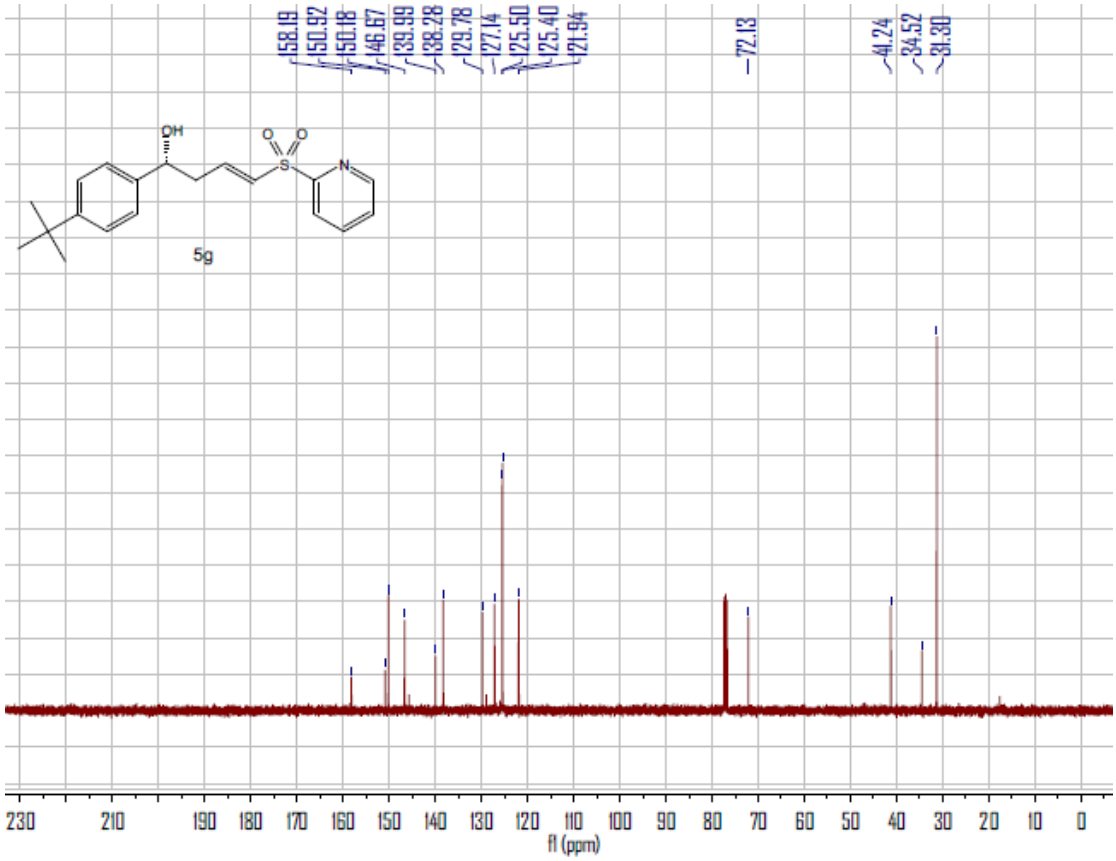


Figure S144. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5h**, related to **Table 3**

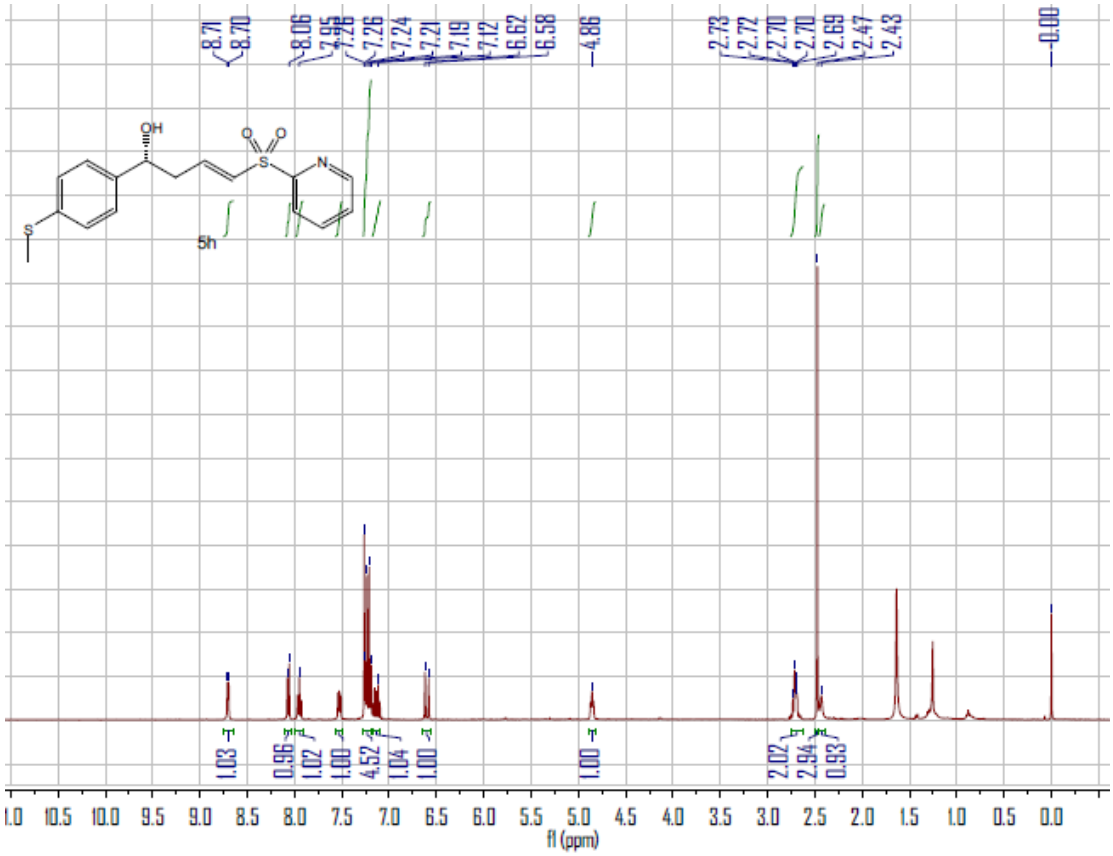


Figure S145. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5h**, related to **Table 3**

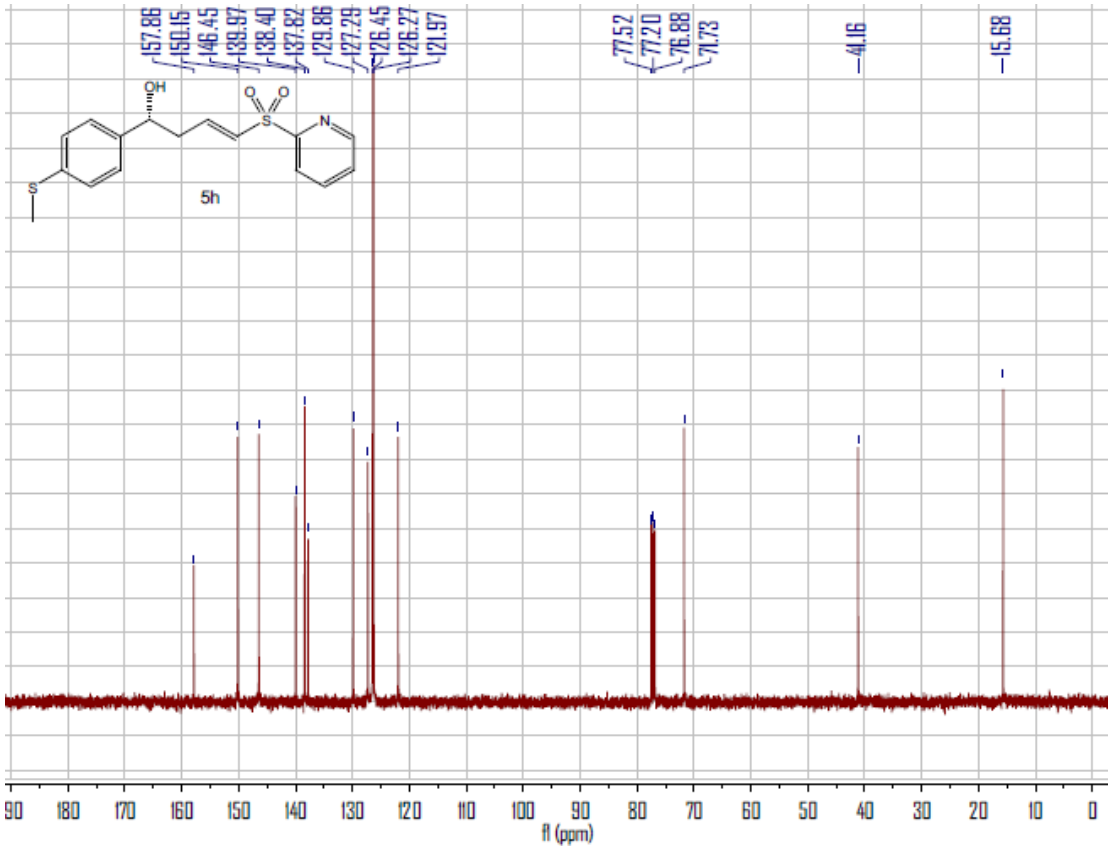


Figure S146. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5k**, related to **Table 3**

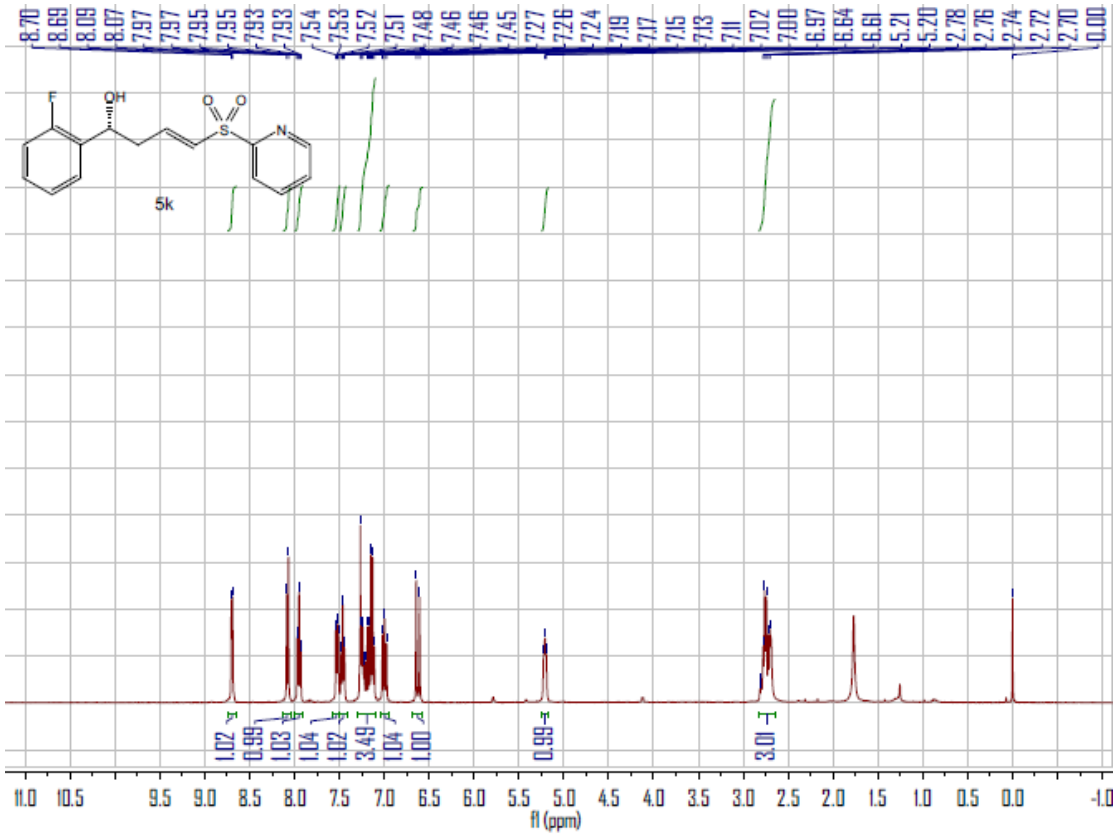


Figure S147. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5k**, related to **Table 3**

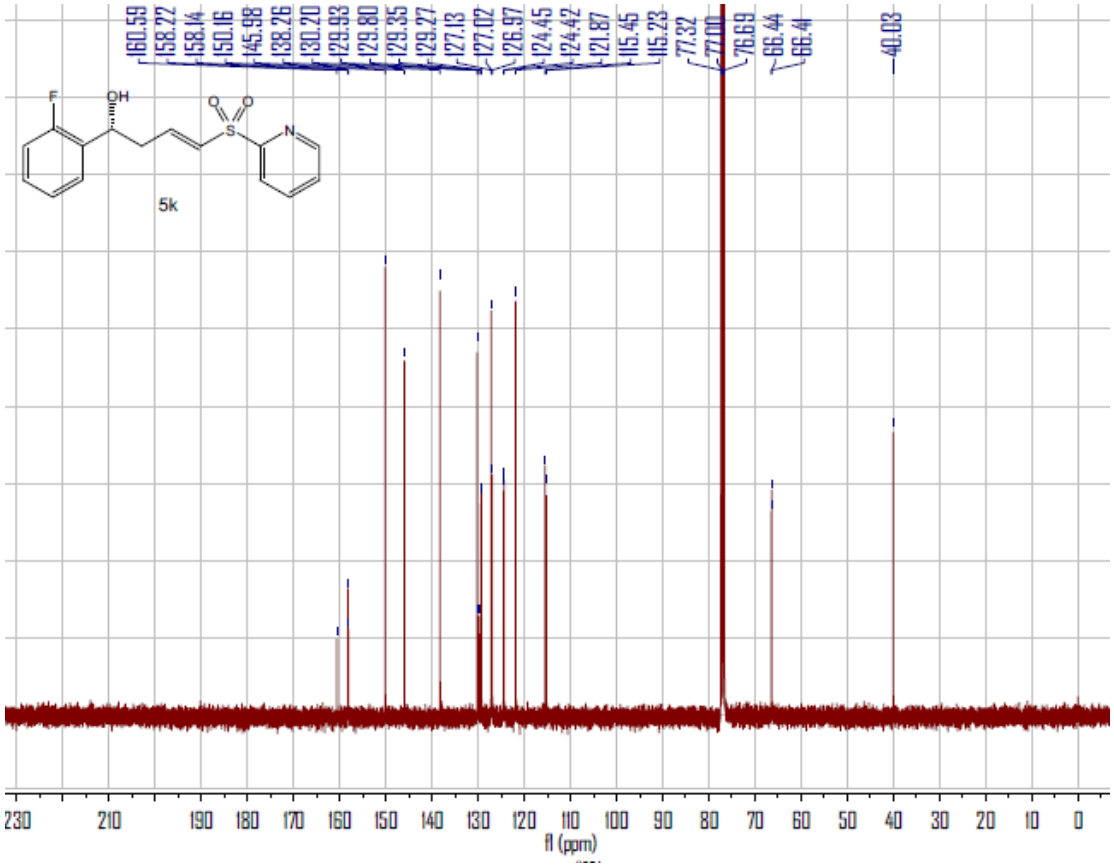


Figure S148. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5k**, related to **Table 3**

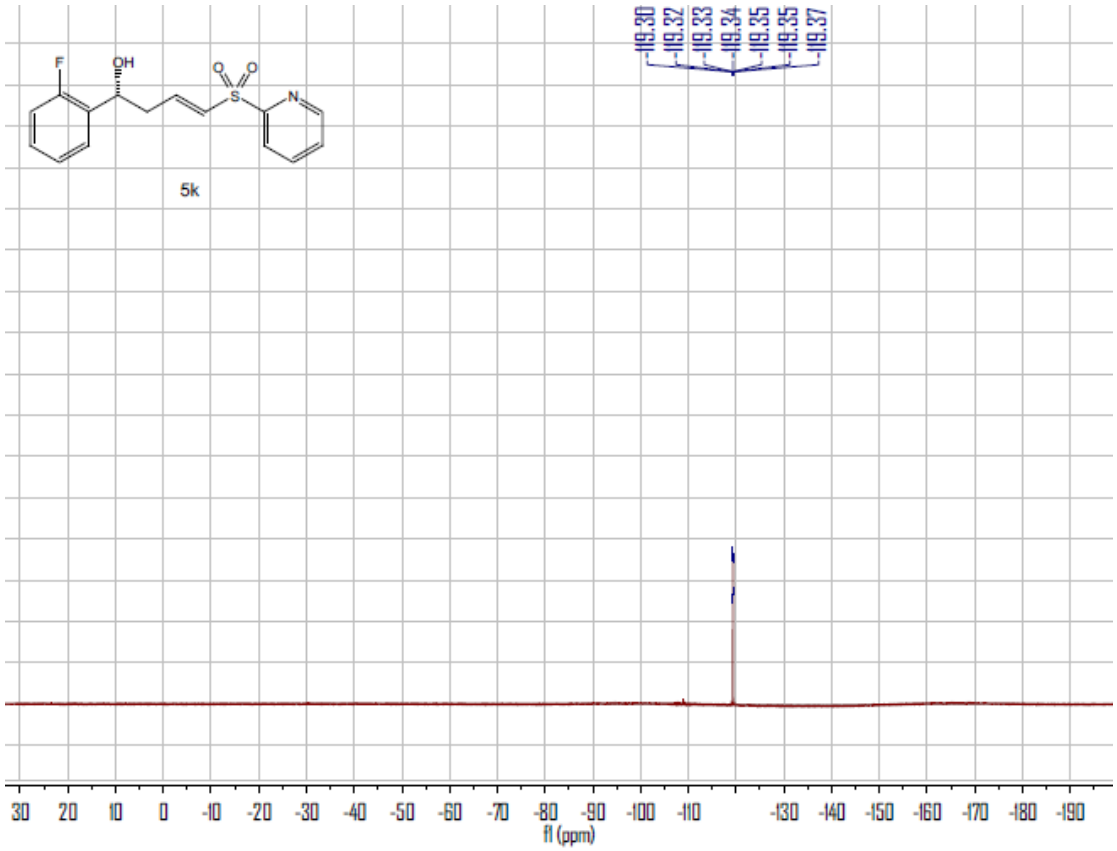


Figure S149. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5l**, related to **Table 3**

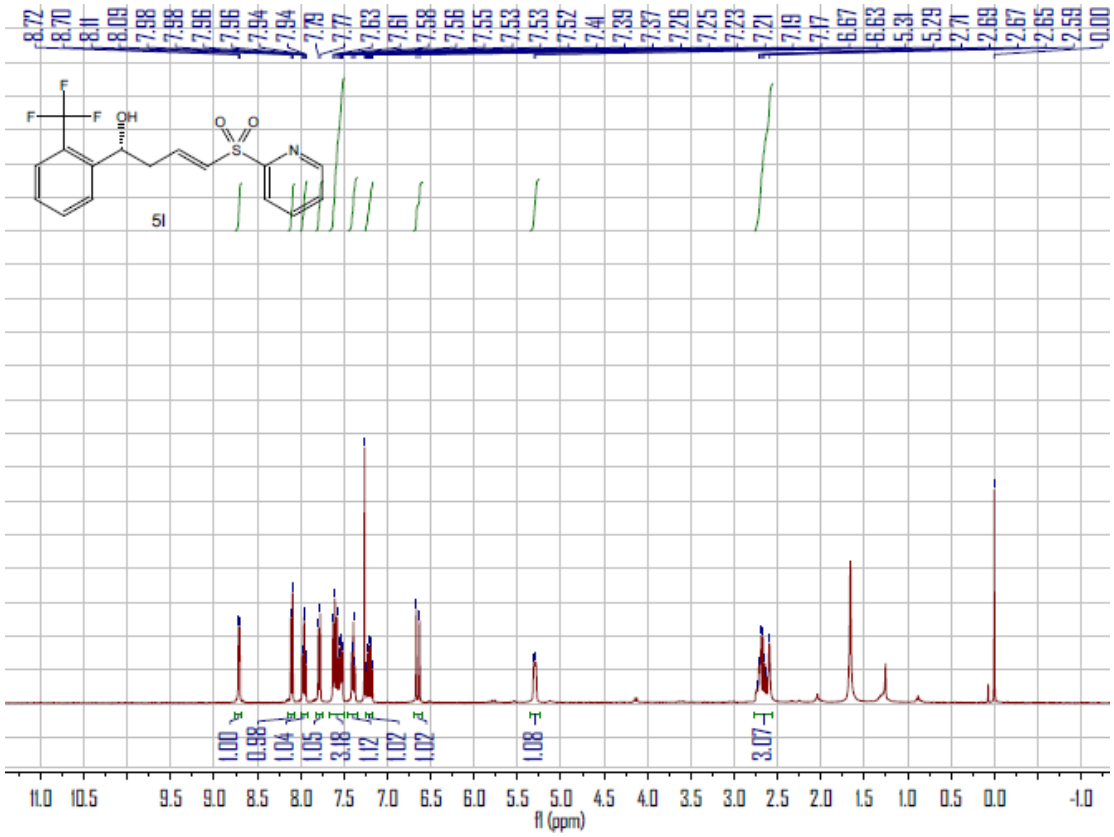


Figure S150. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5l**, related to **Table 3**

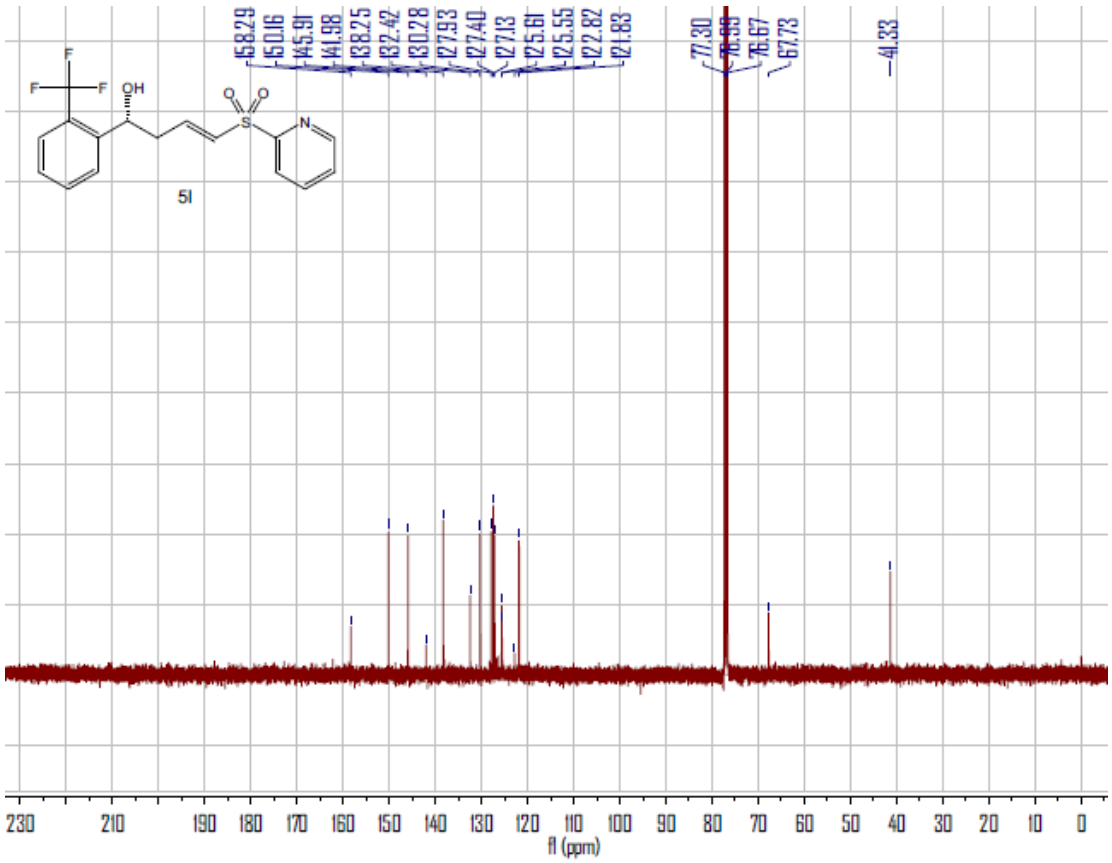


Figure S151. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5l**, related to **Table 3**

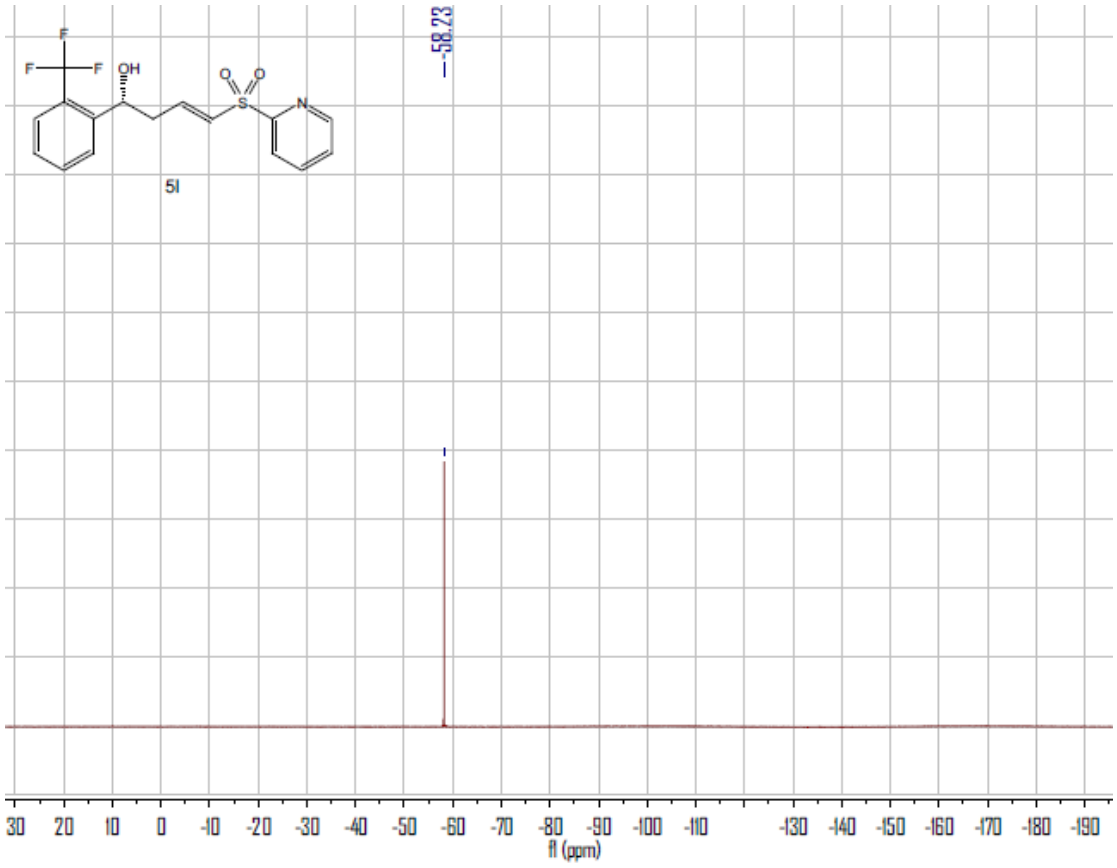


Figure S152. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5n**, related to **Table 3**

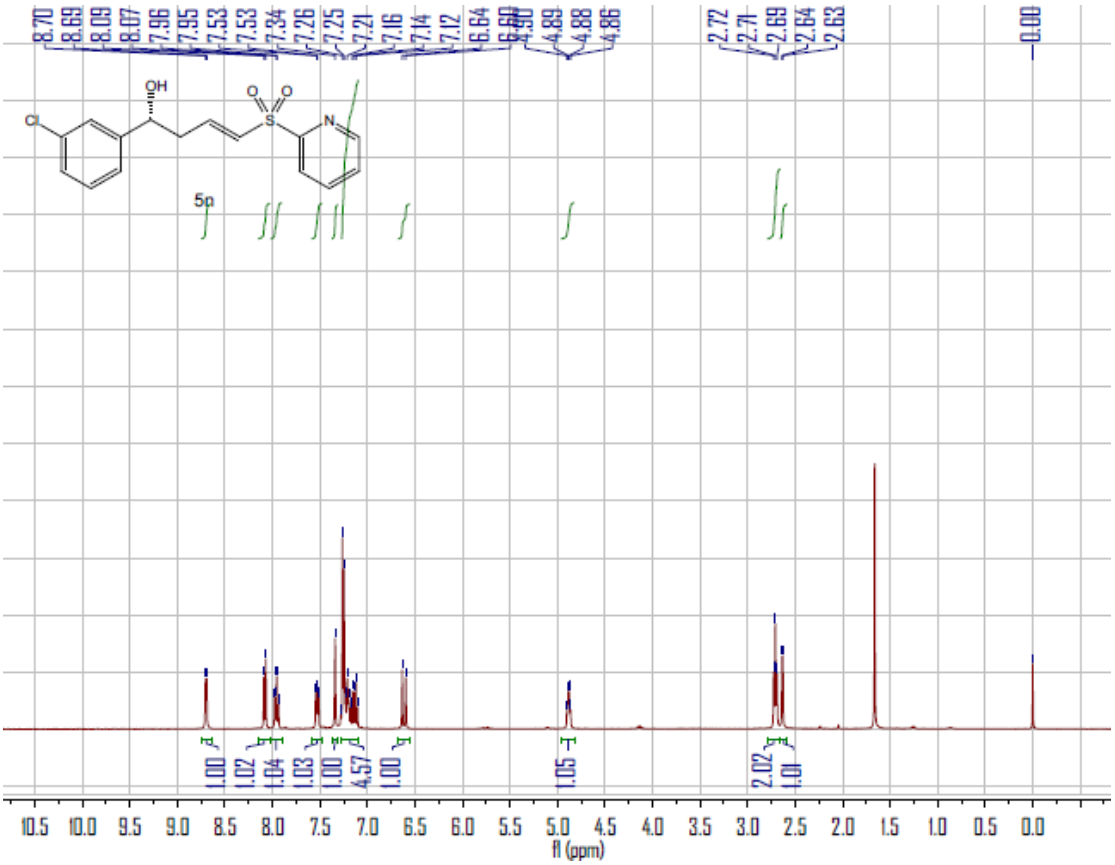


Figure S153. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5n**, related to **Table 3**

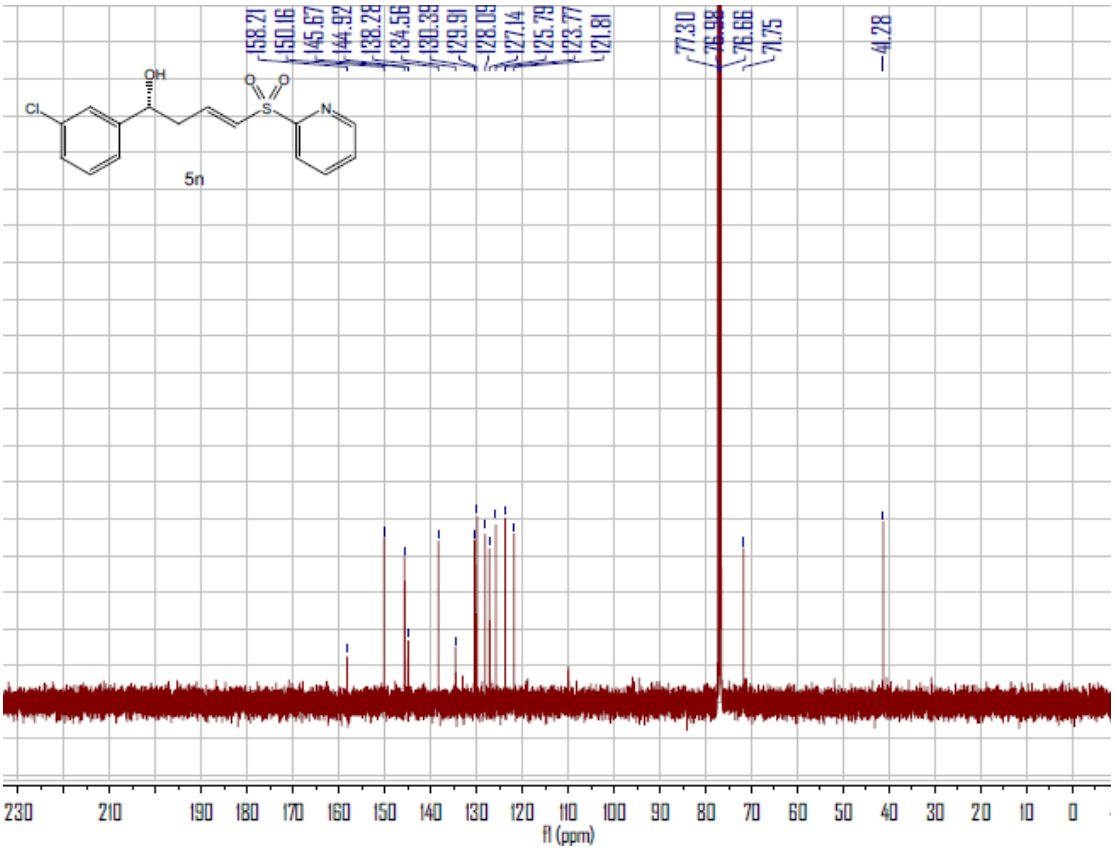


Figure S154. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5o**, related to **Table 3**

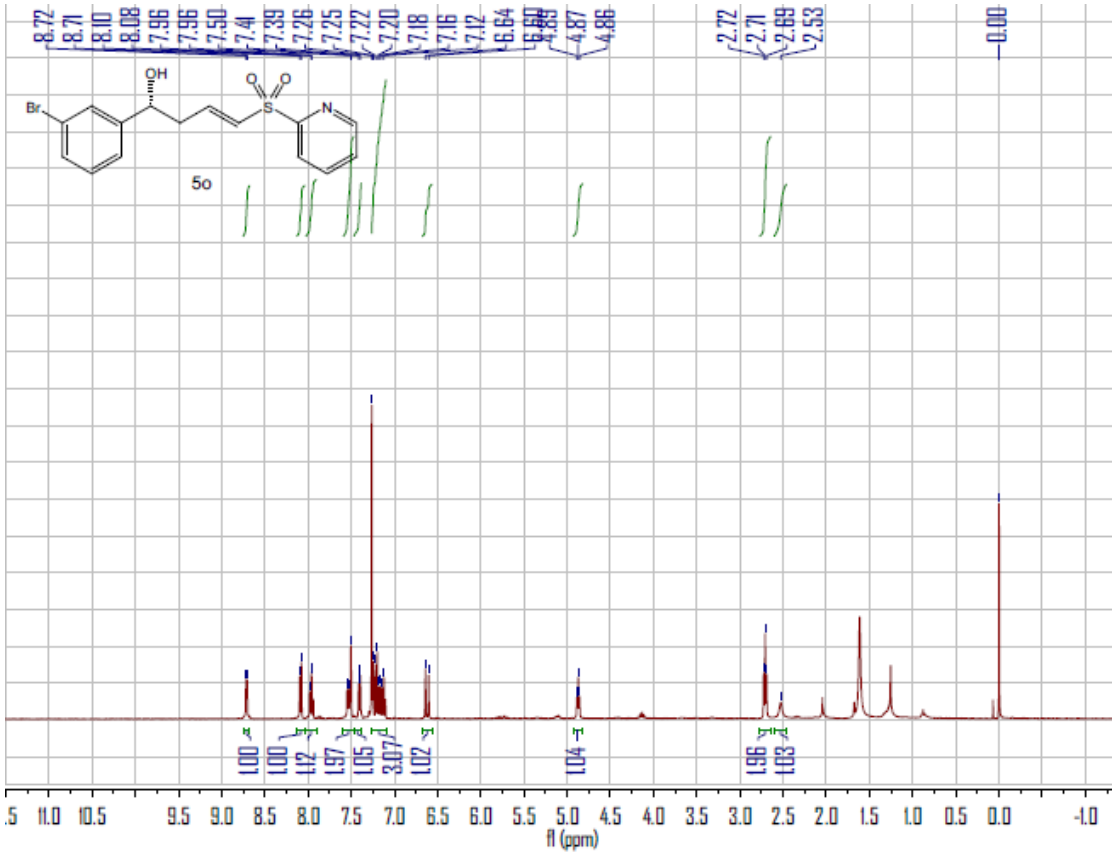


Figure S155. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5o**, related to **Table 3**

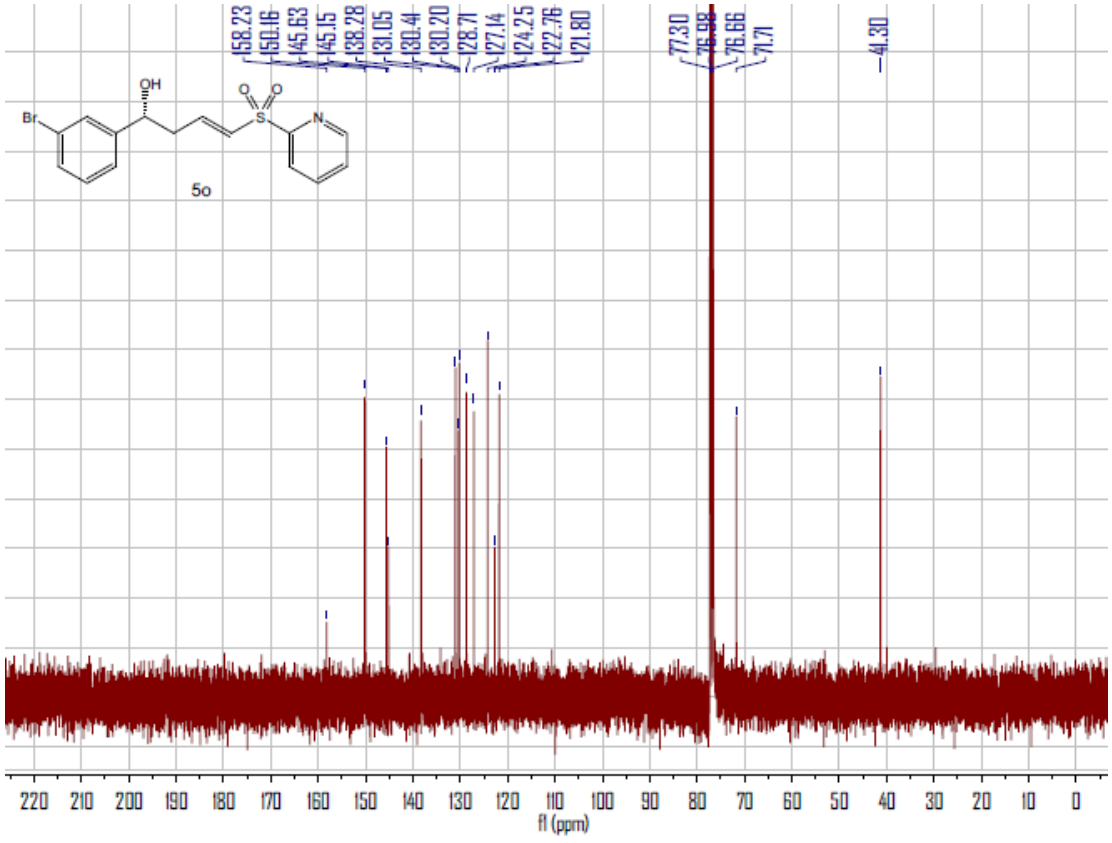


Figure S156. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5p**, related to **Table 3**

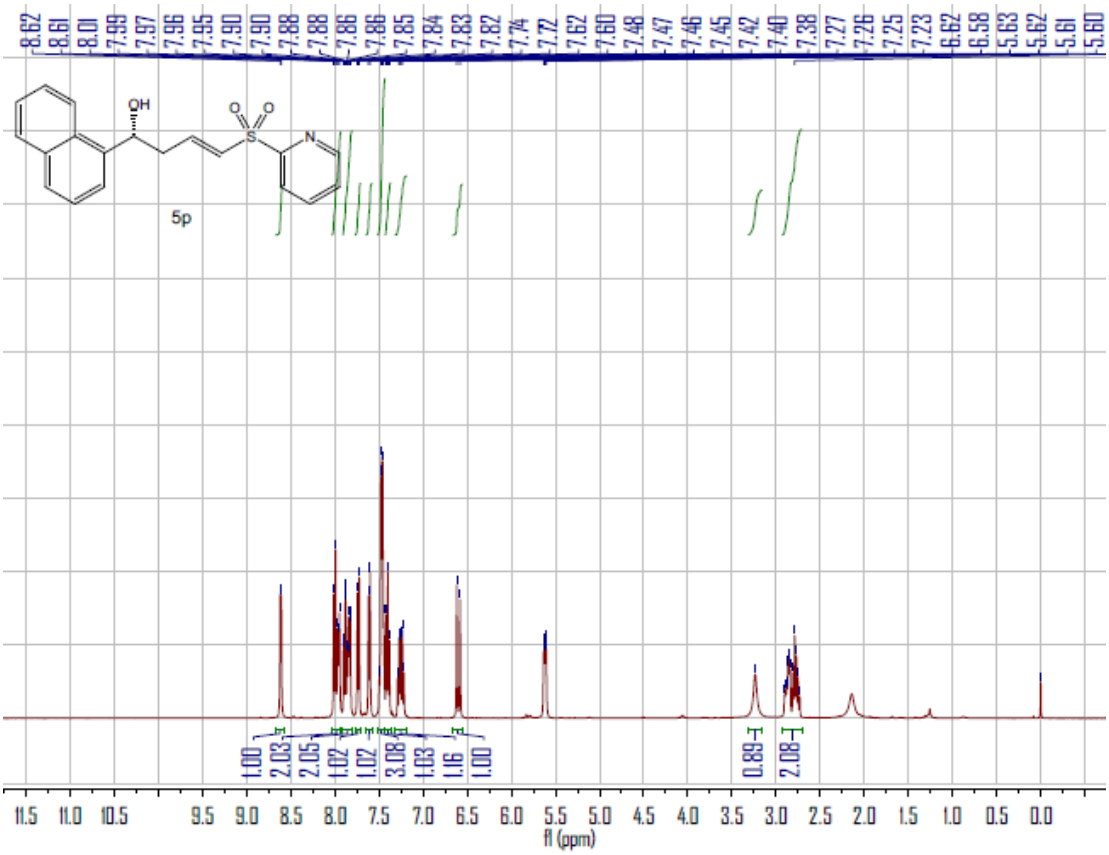


Figure S157. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5p**, related to **Table 3**

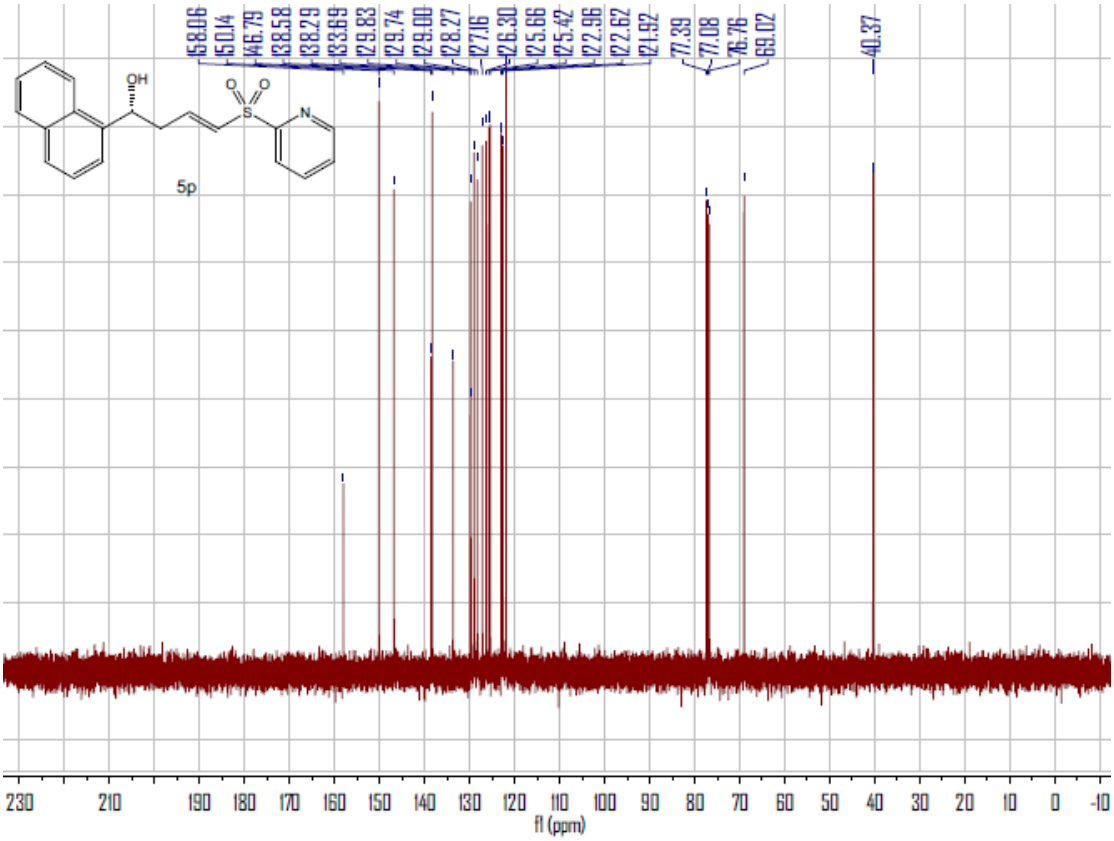


Figure S158. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5q**, related to **Table 3**

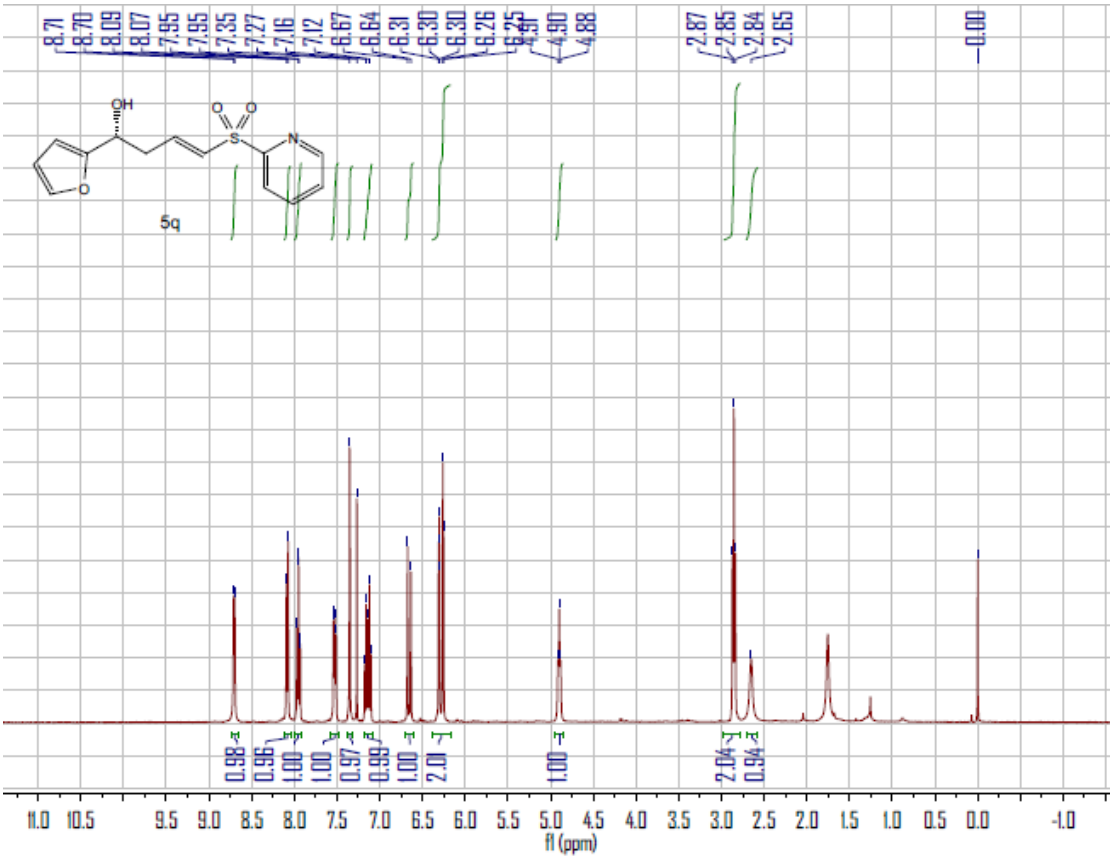


Figure S159. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5q**, related to **Table 3**

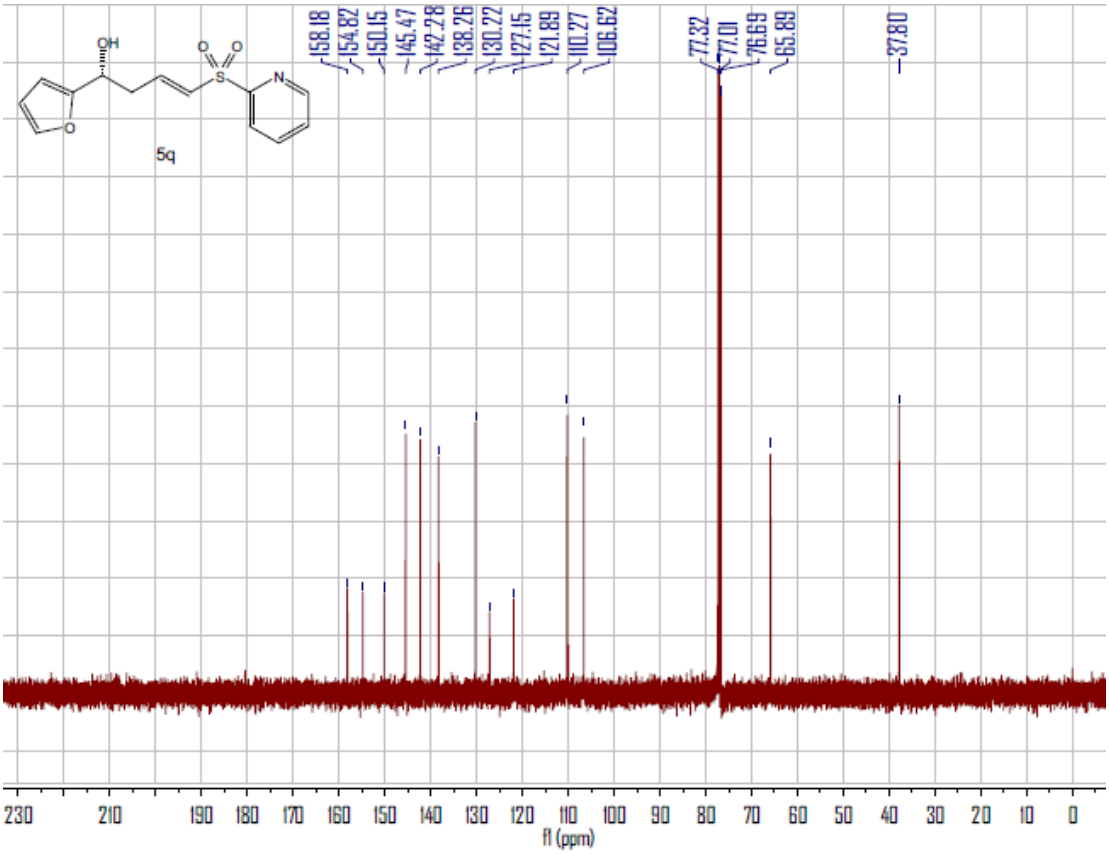


Figure S160. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5r**, related to **Table 3**

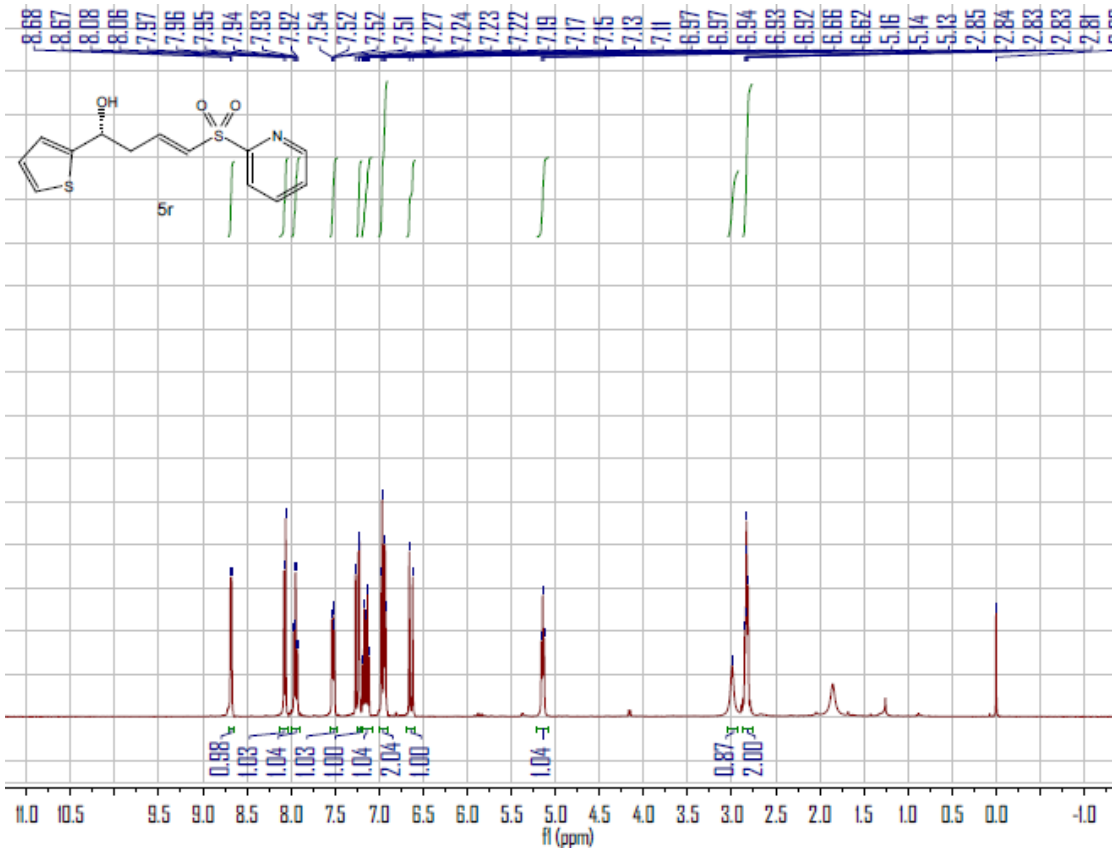


Figure S161. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5r**, related to **Table 3**

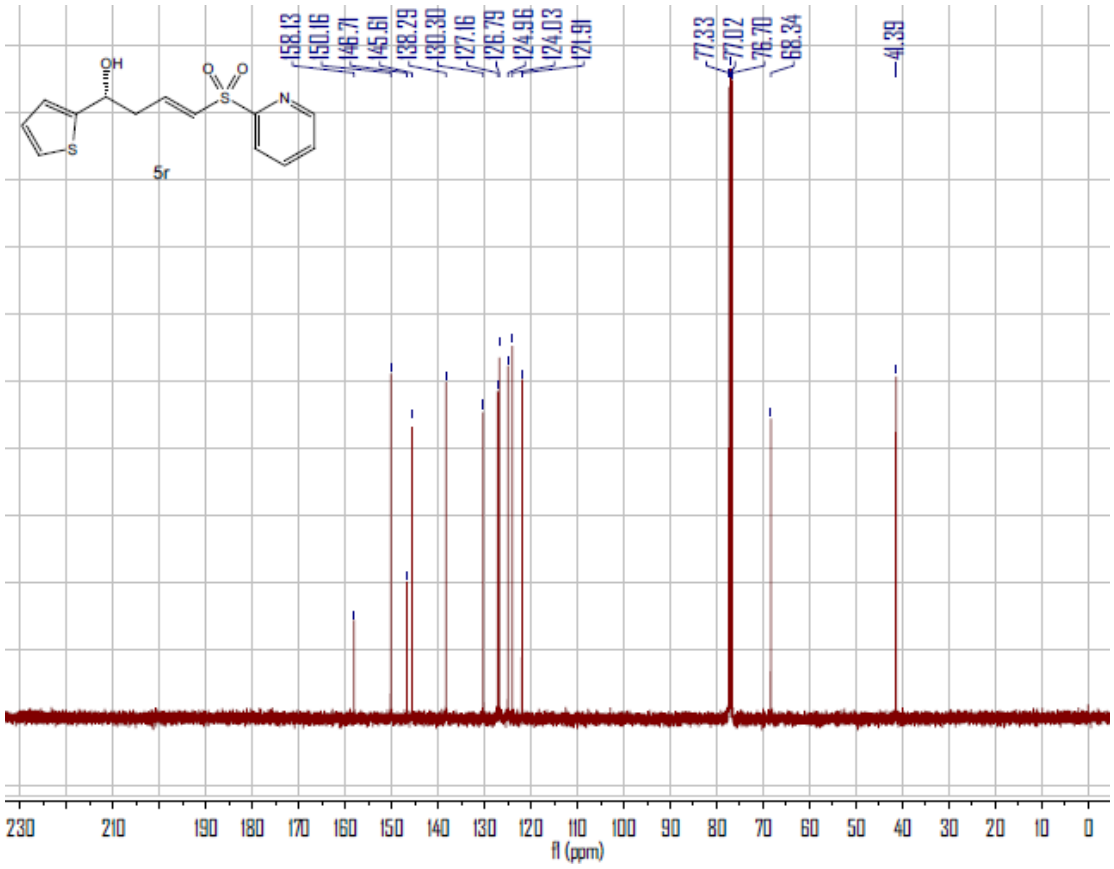


Figure S162. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5u**, related to **Table 3**

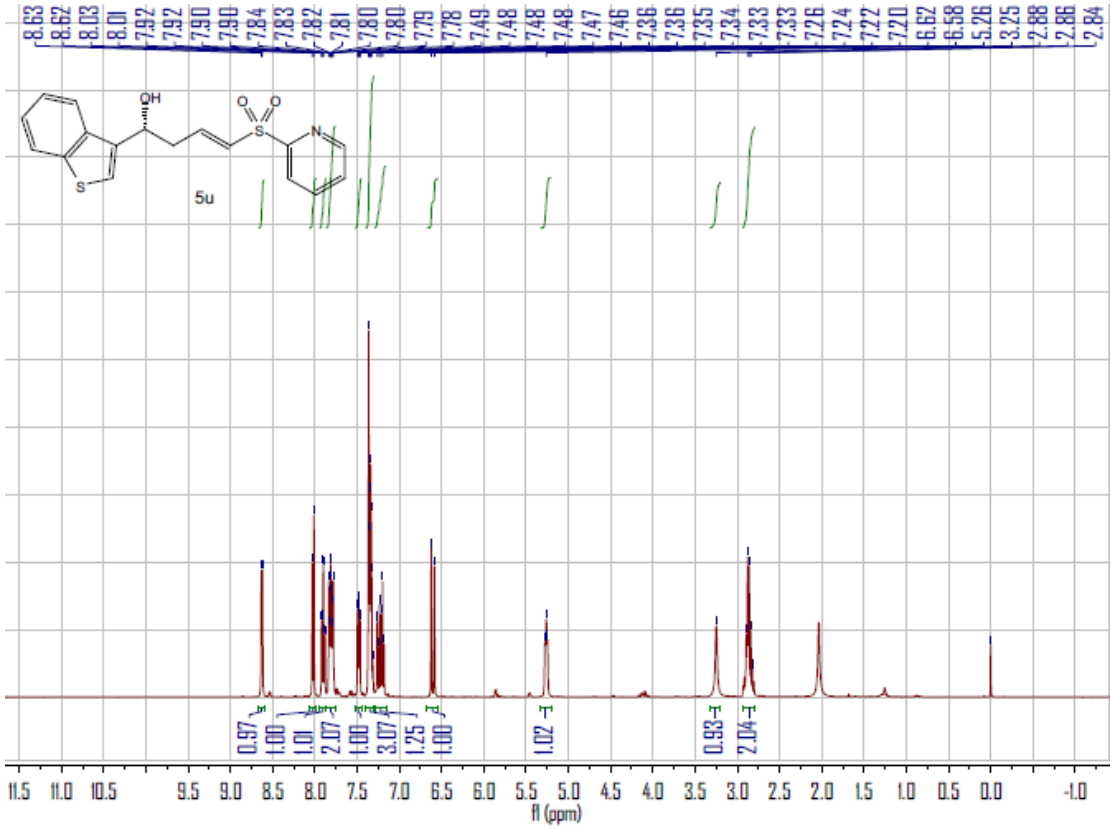


Figure S163. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5u**, related to **Table 3**

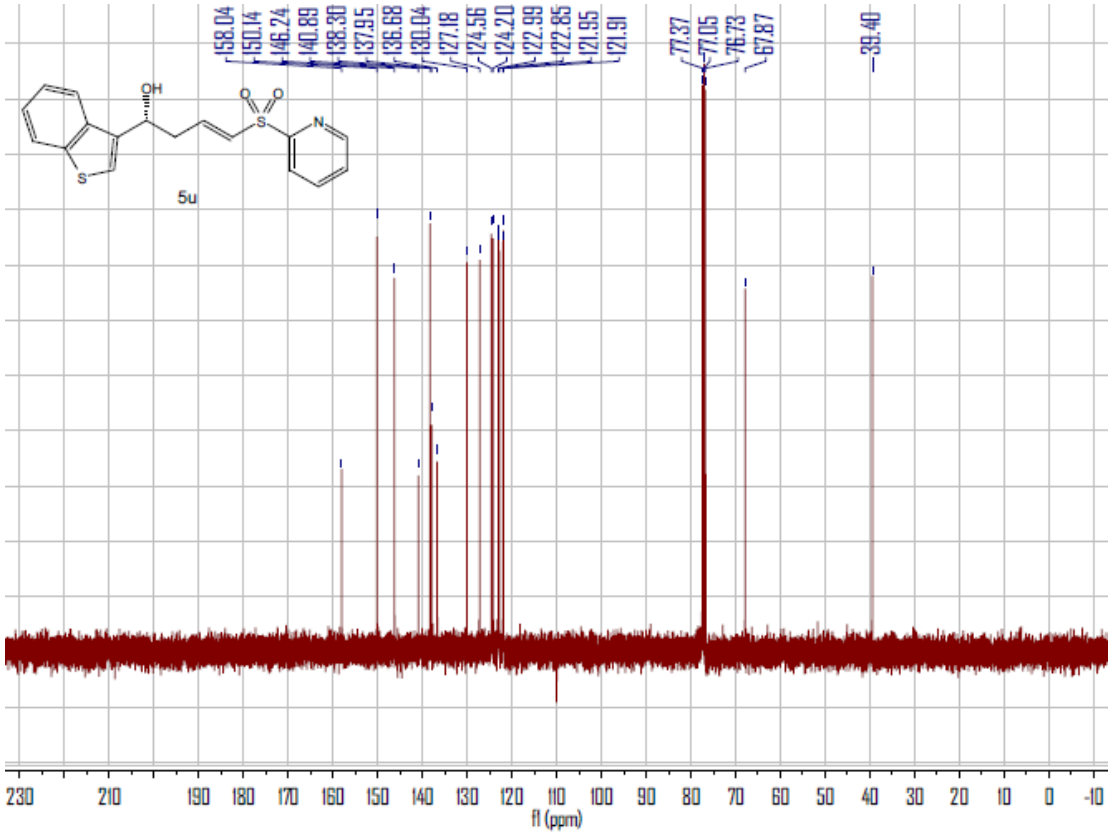


Figure S164. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5x**, related to **Table 3**

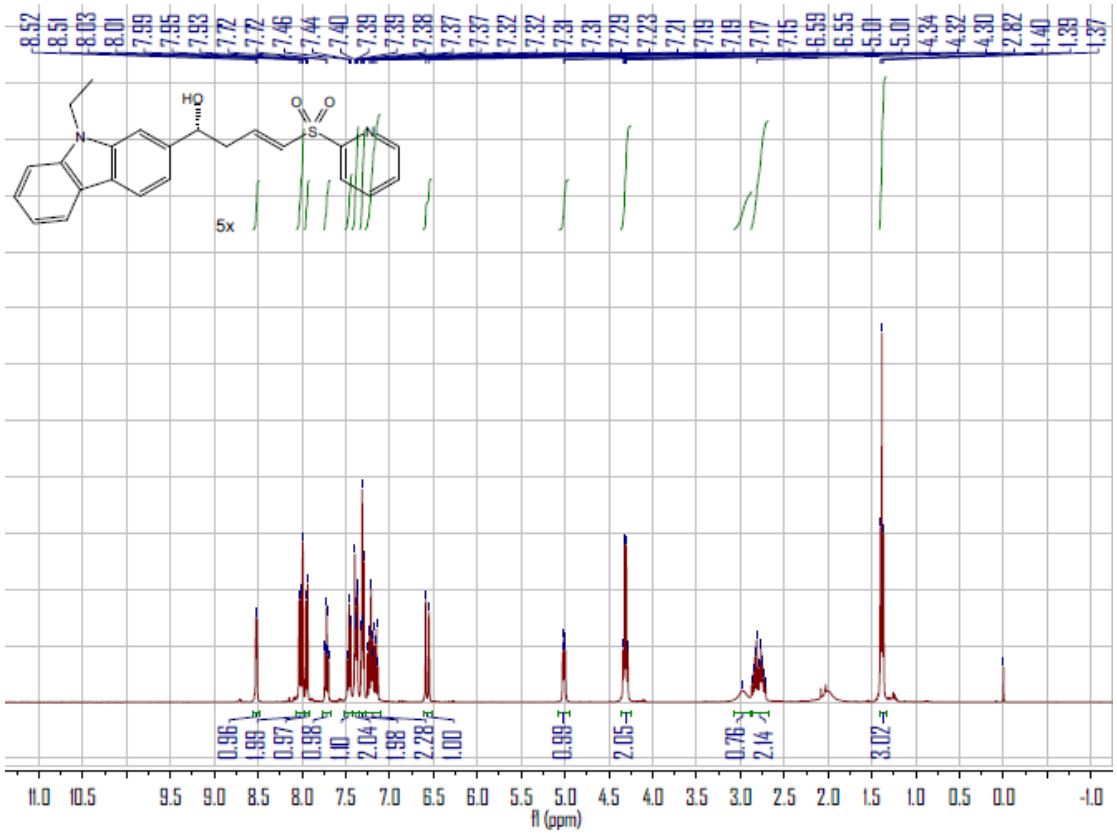


Figure S165. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5x**, related to **Table 3**

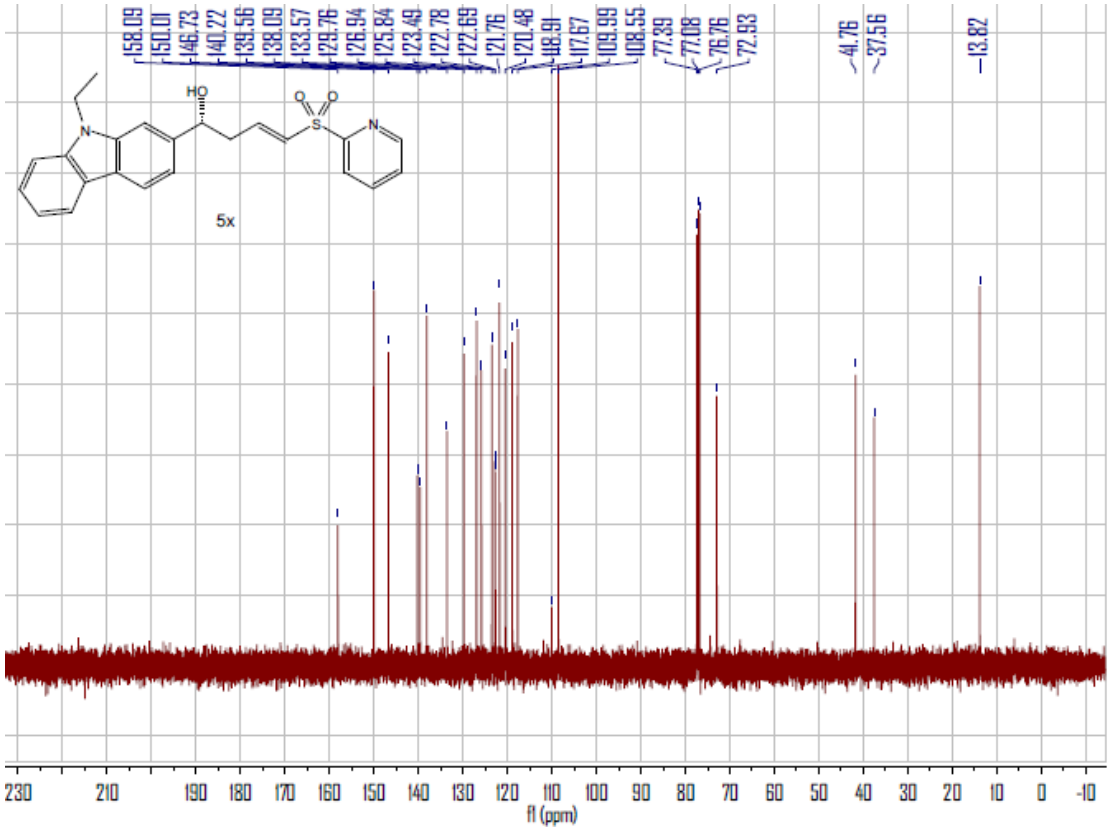


Figure S166. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5y**, related to **Table 3**

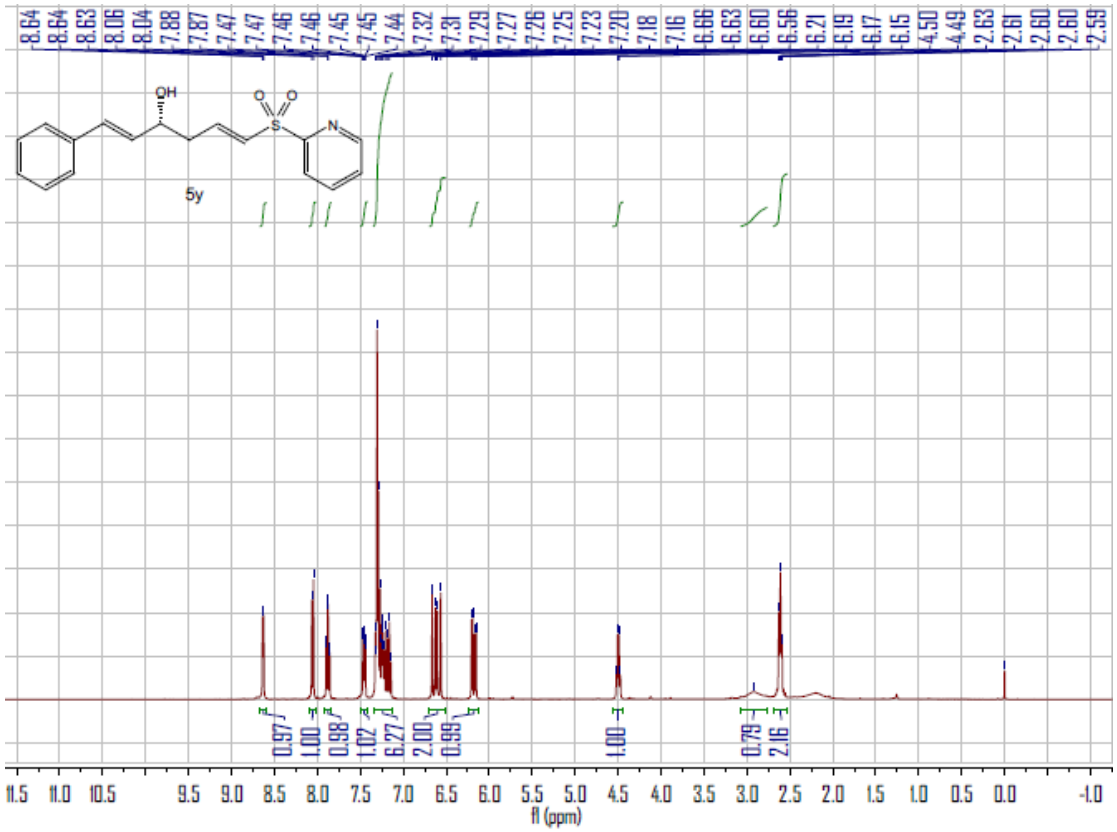


Figure S167. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5y**, related to **Table 3**

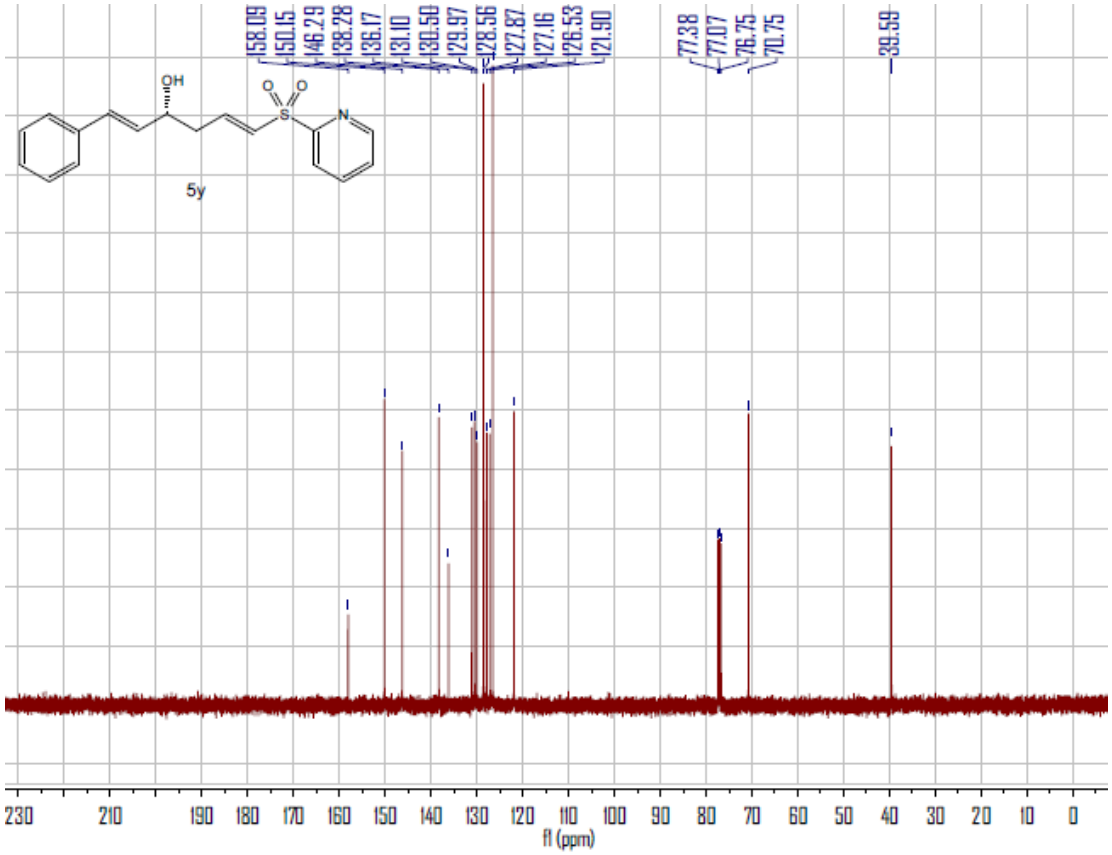


Figure S168. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5z**, related to **Table 3**

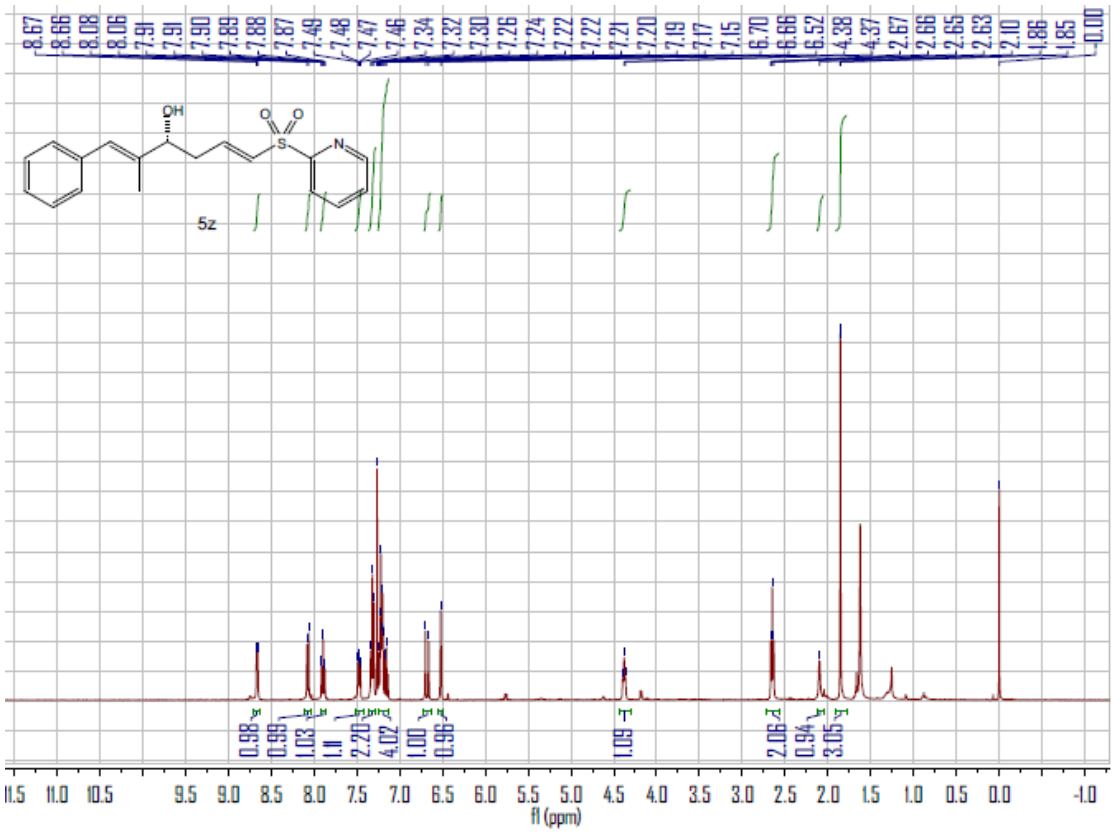


Figure S169. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5z**, related to **Table 3**

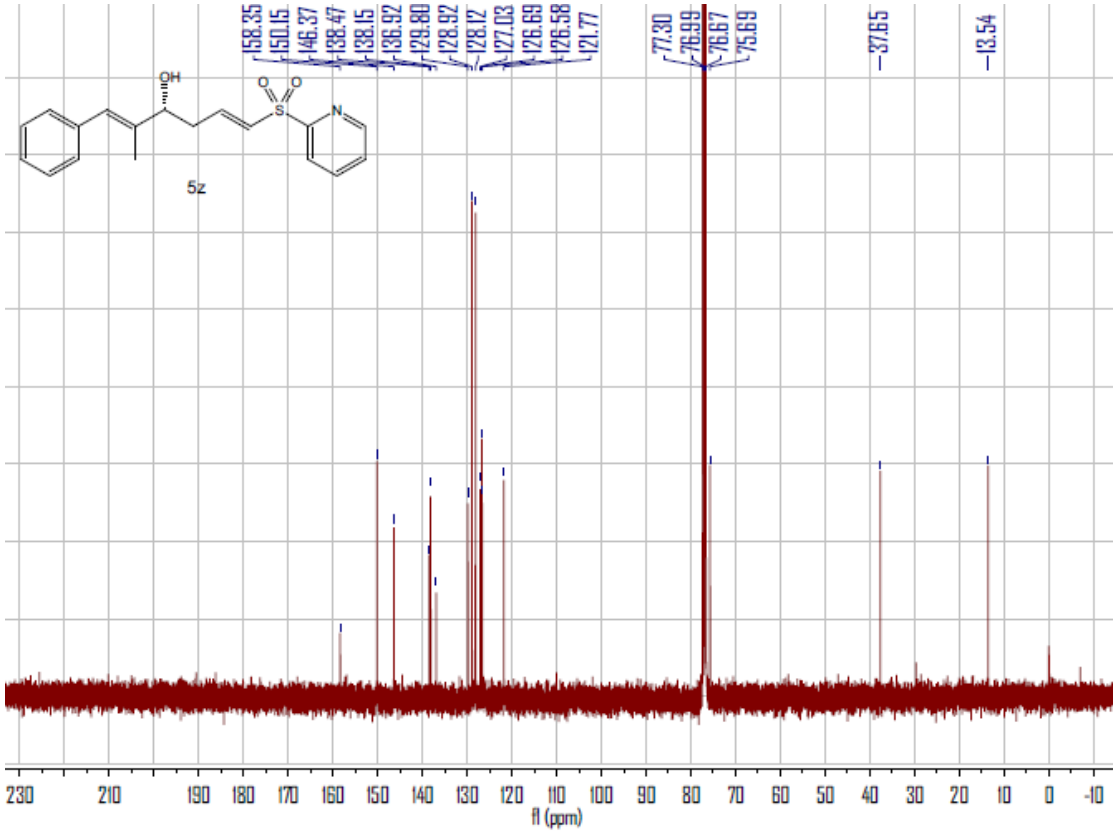


Figure S170. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5aa**, related to **Table 3**

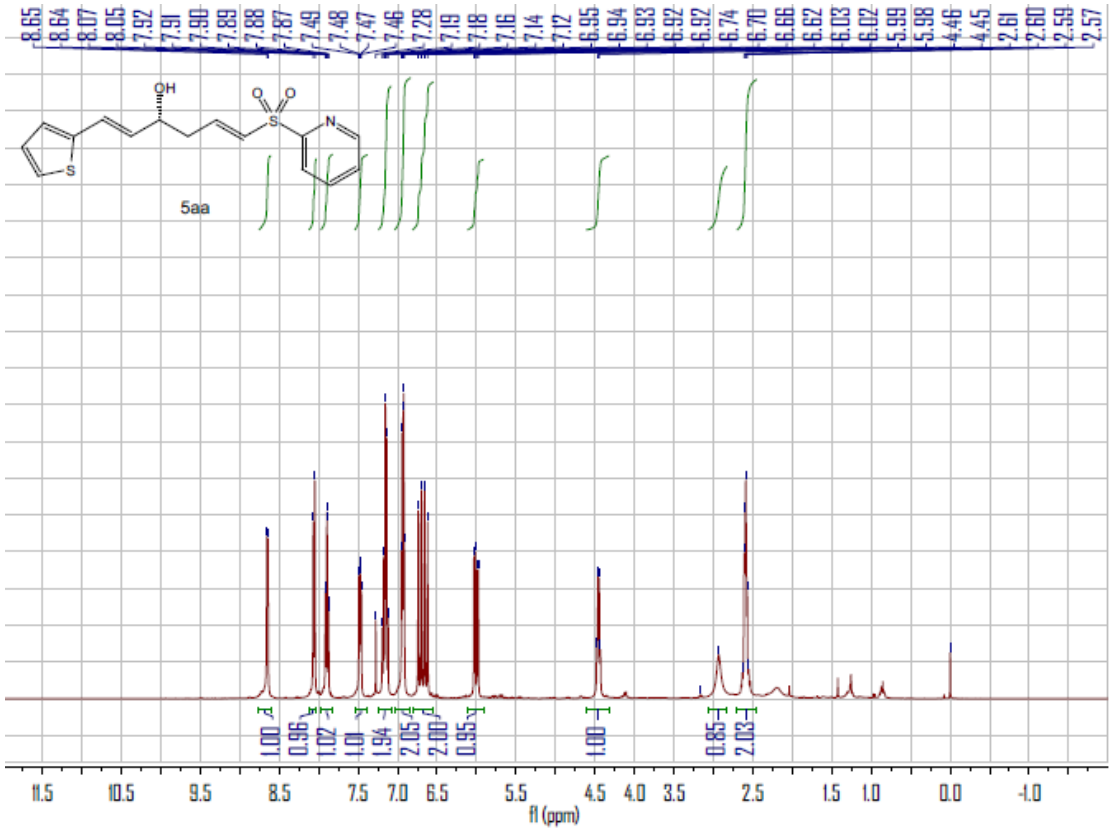


Figure S171. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5aa**, related to **Table 3**

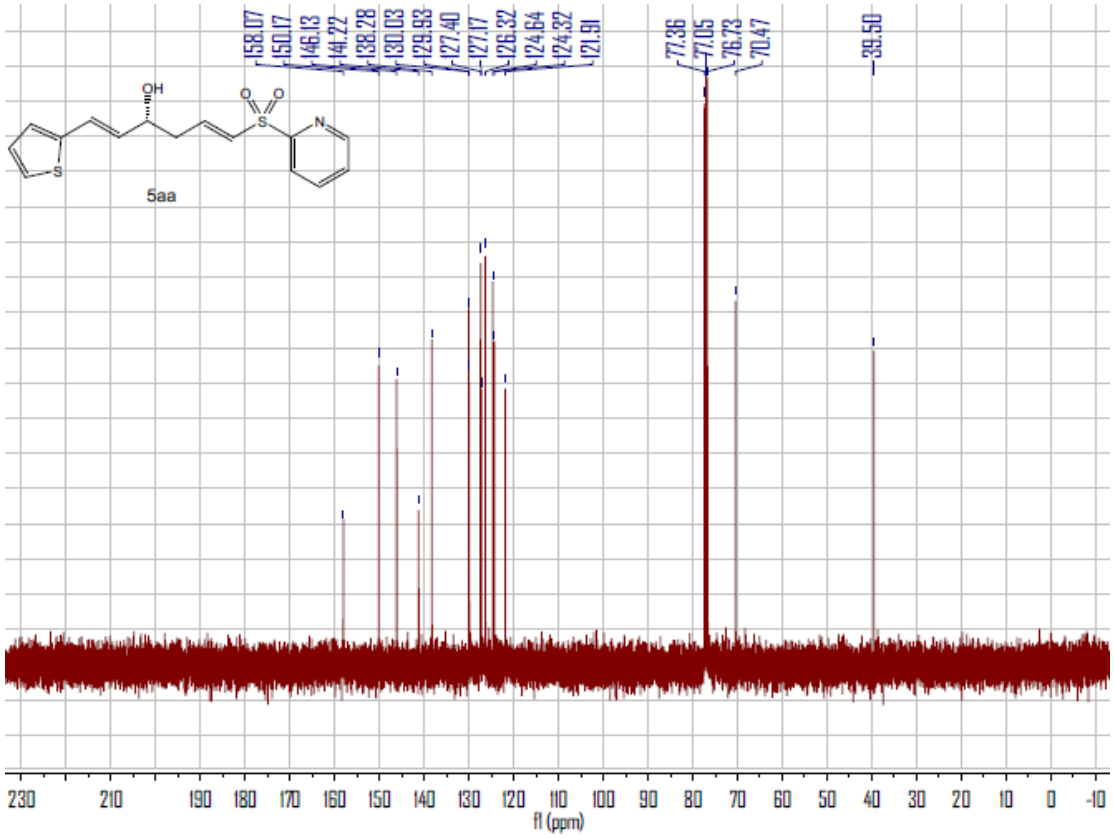


Figure S172. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ad**, related to **Table 3**

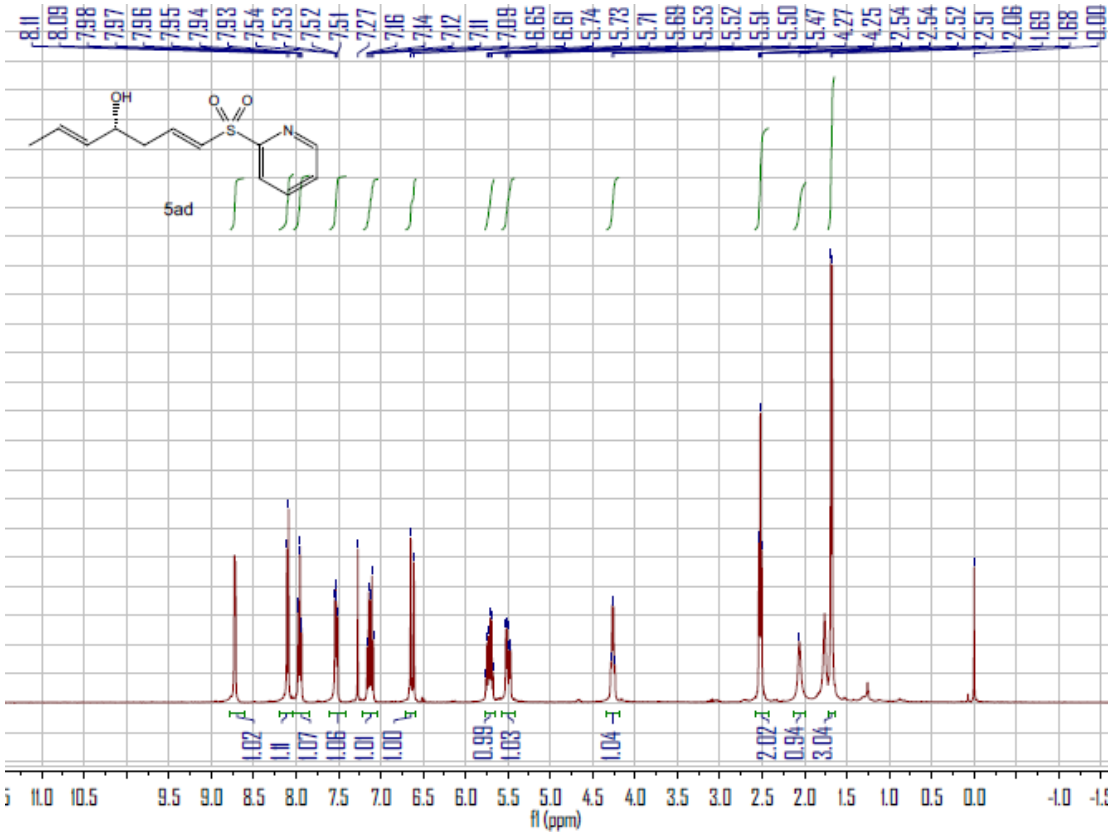


Figure S173. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5ad**, related to **Table 3**

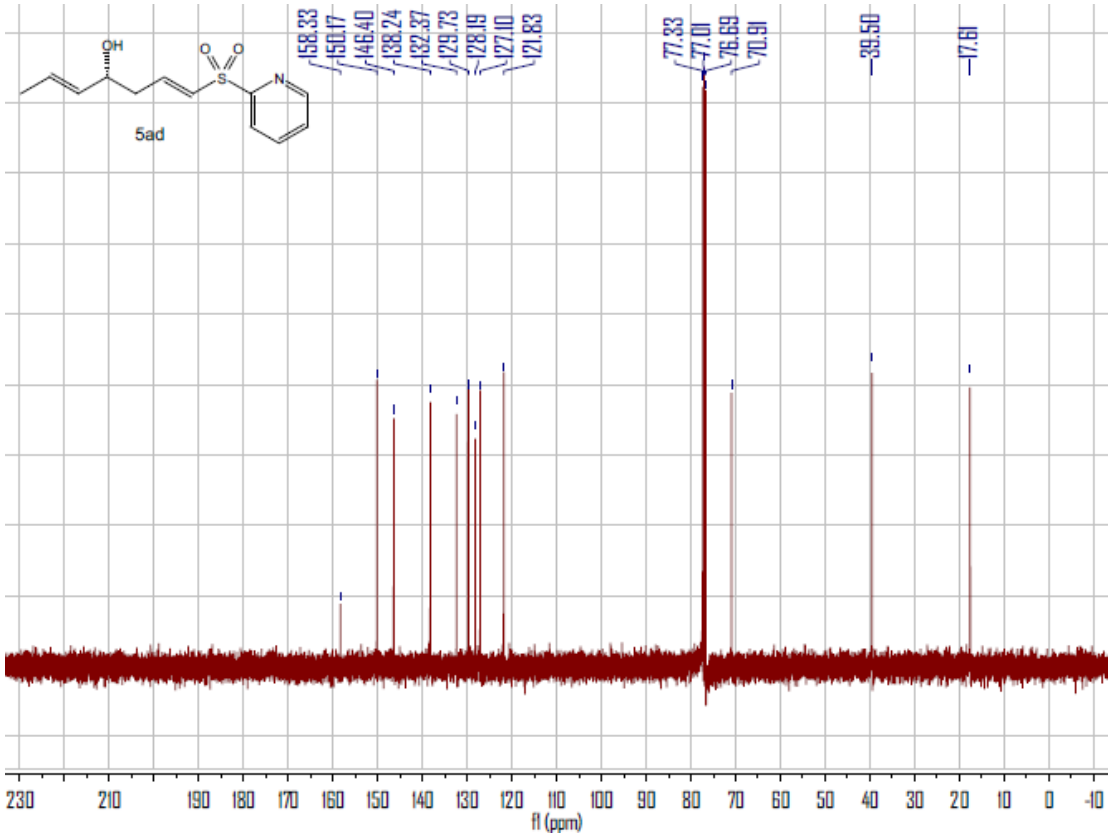


Figure S174. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ae**, related to **Table 3**

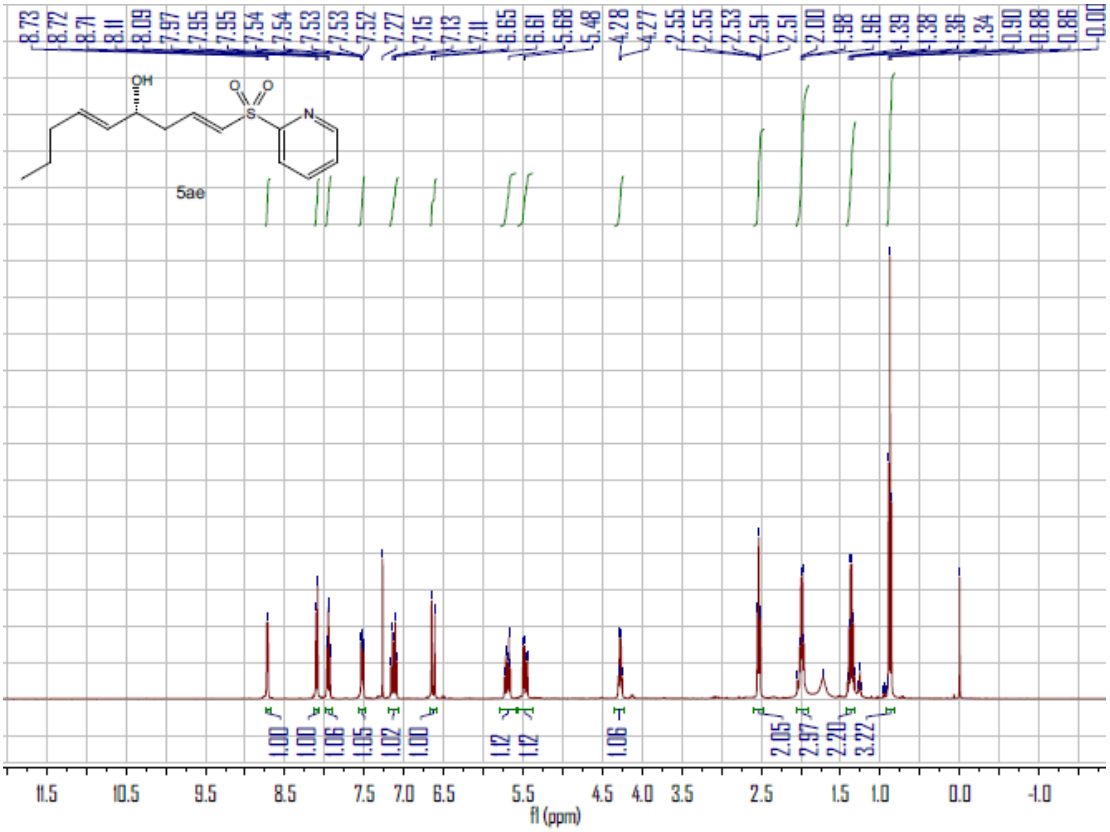


Figure S175. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5ae**, related to **Table 3**

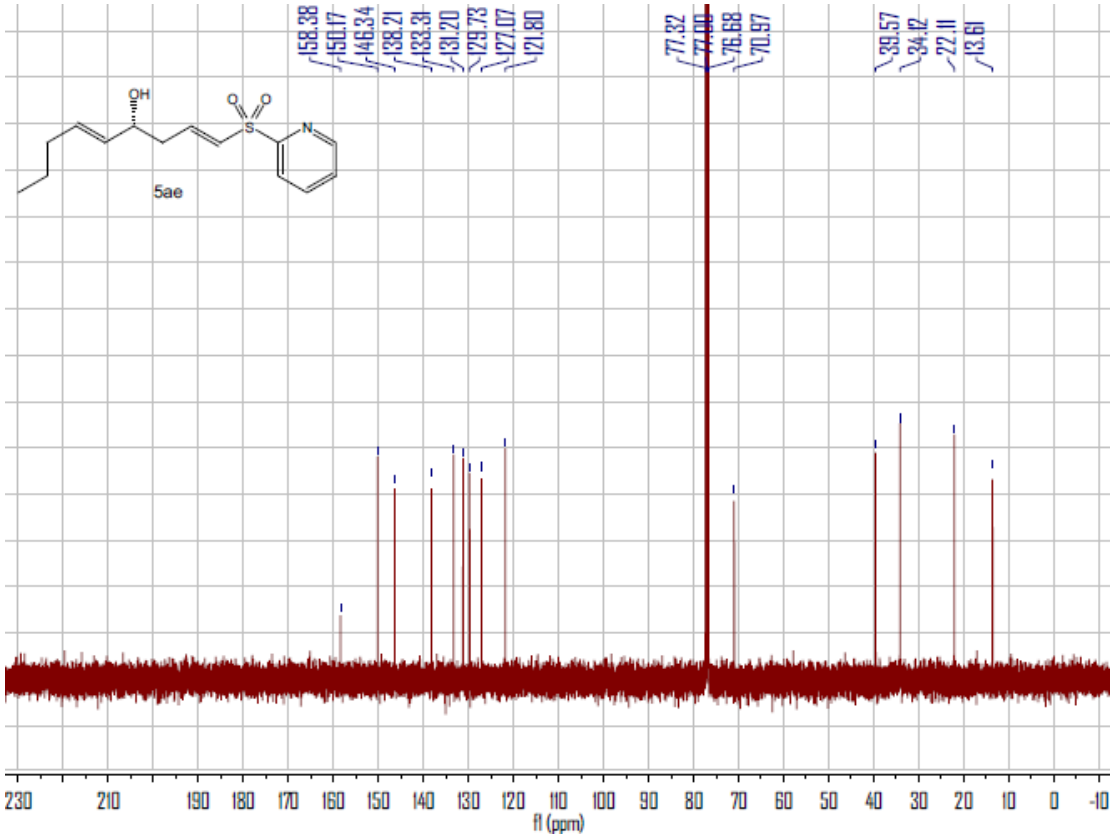


Figure S176. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ah**, related to **Table 3**

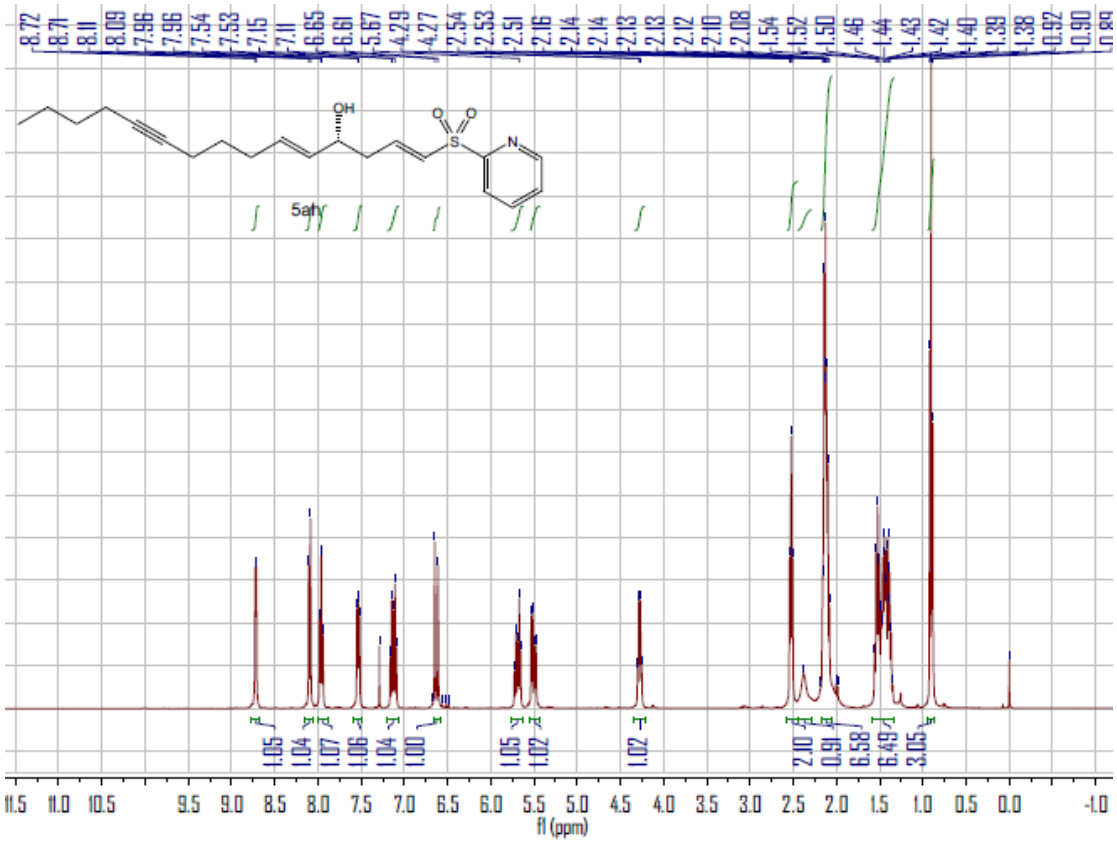


Figure S177. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5ah**, related to **Table 3**

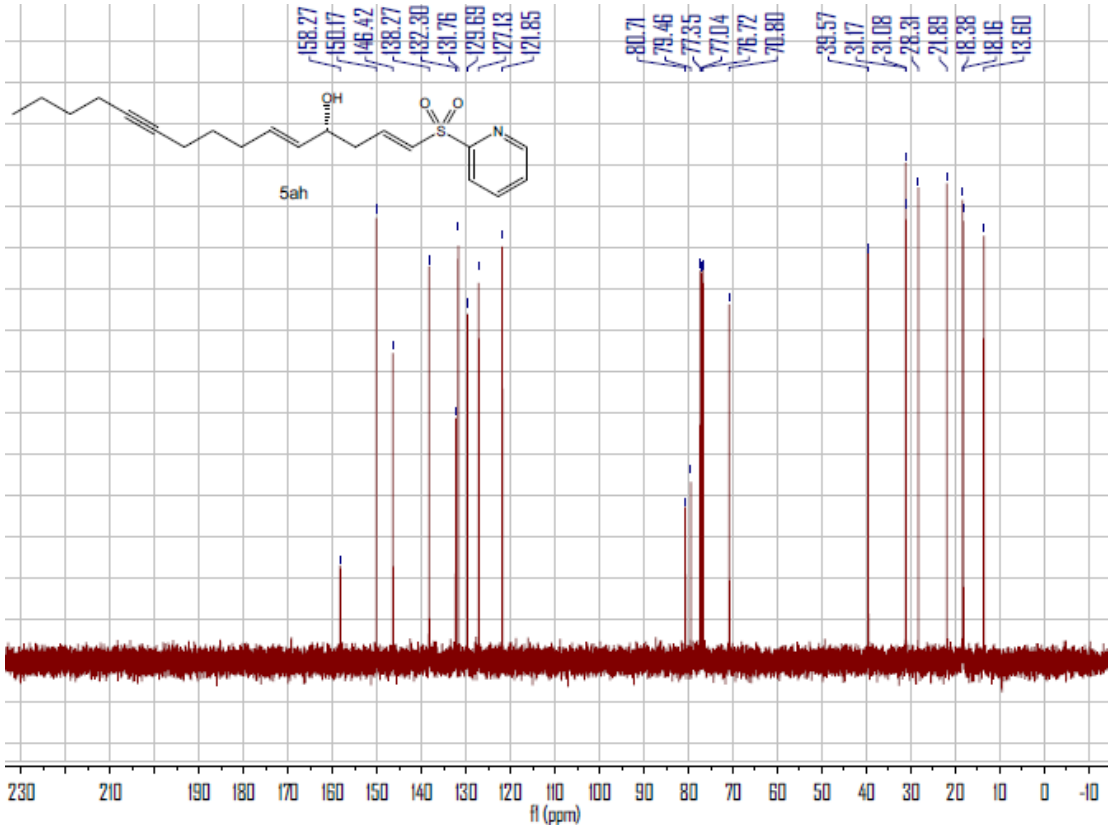


Figure S178. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ak**, related to **Table 3**

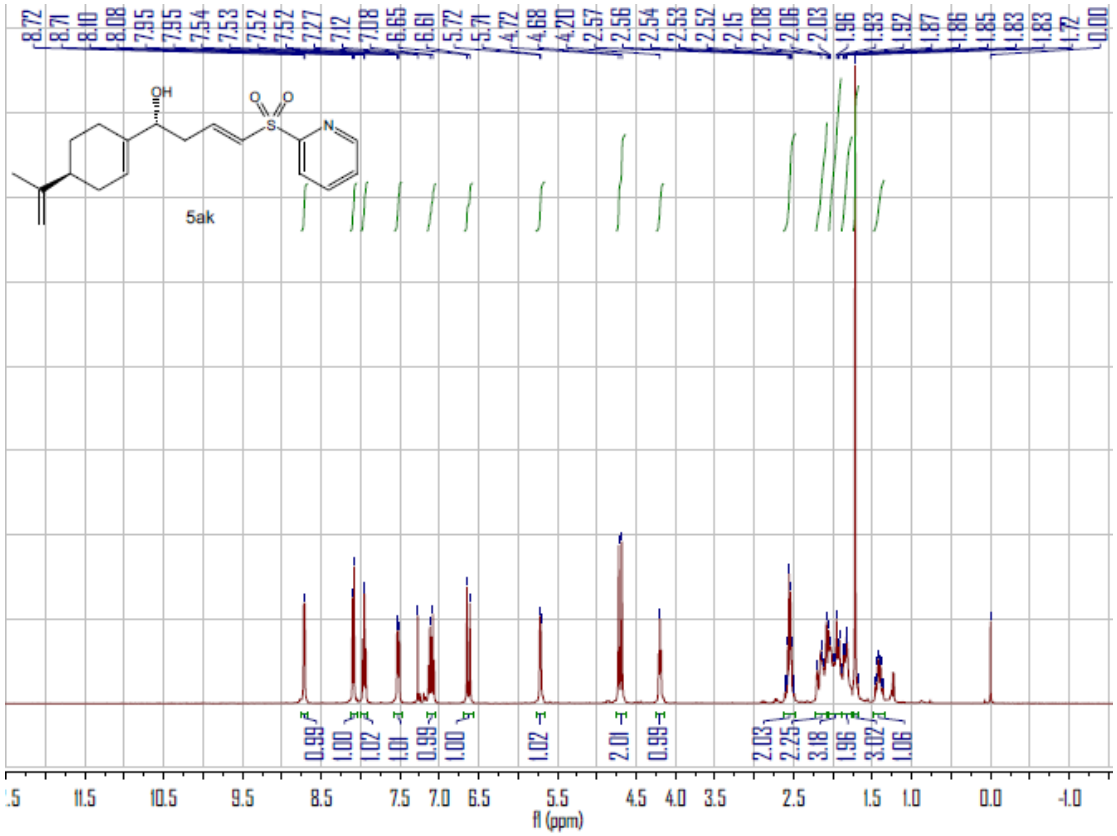


Figure S179. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5ak**, related to **Table 3**

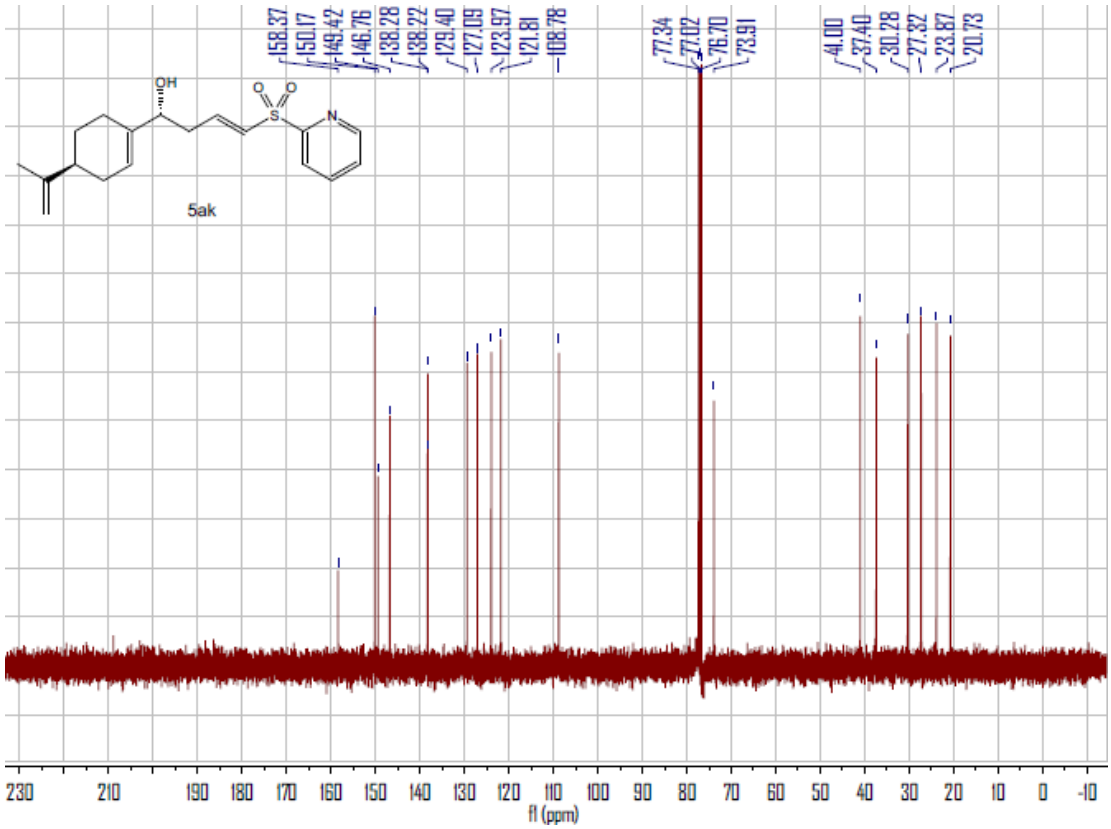


Figure S180. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ak'**, related to **Table 3**

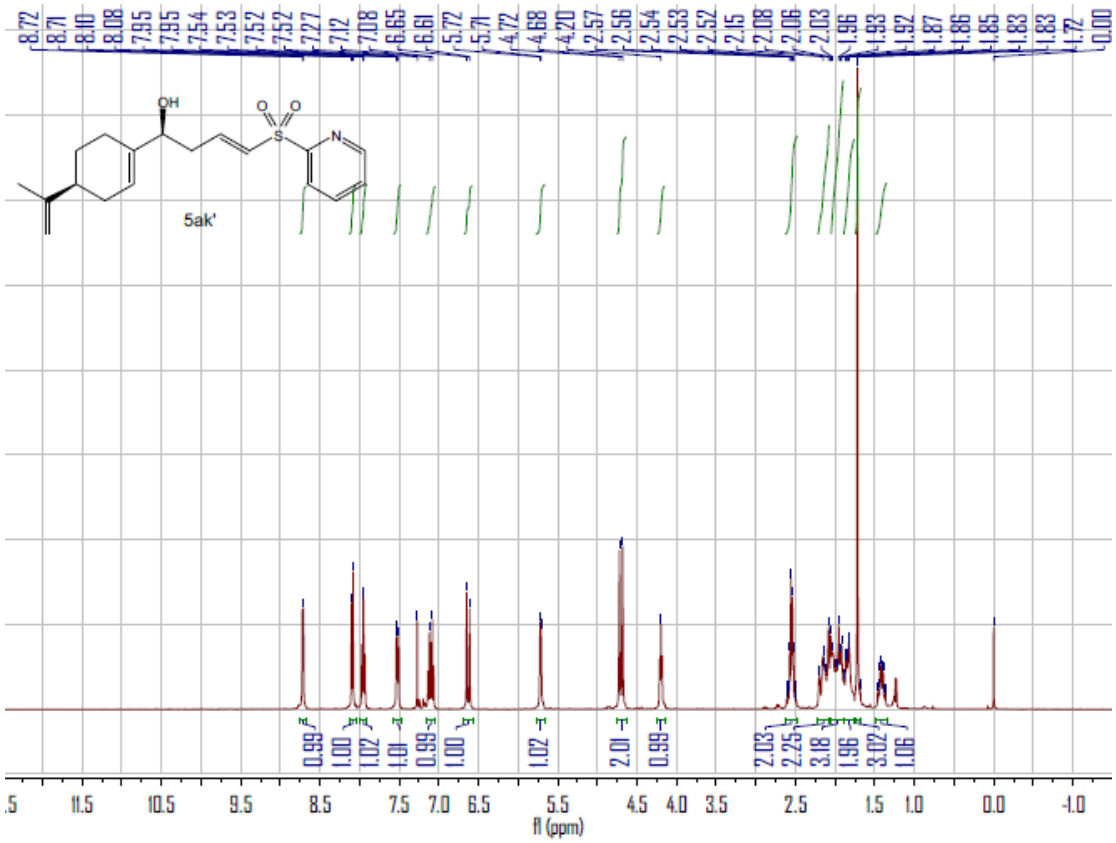


Figure S181. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5ak'**, related to **Table 3**

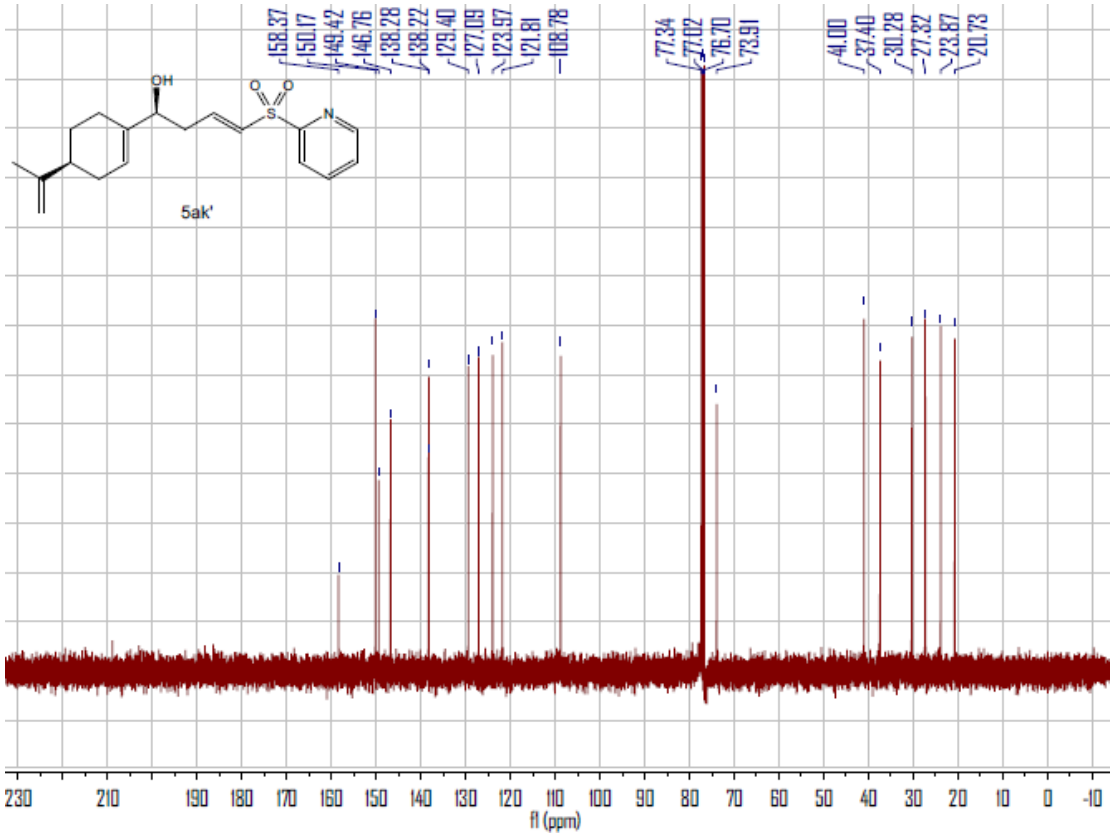


Figure S182. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5al**, related to **Table 3**

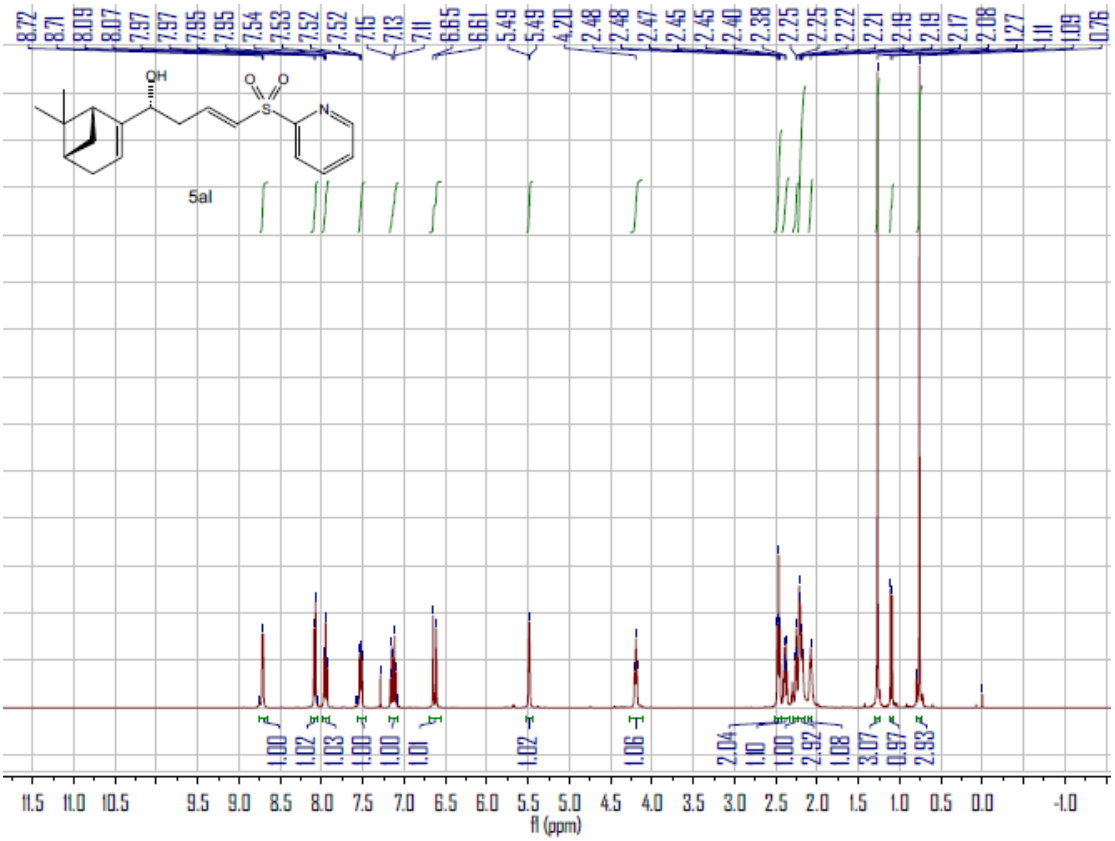


Figure S183. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5al**, related to **Table 3**

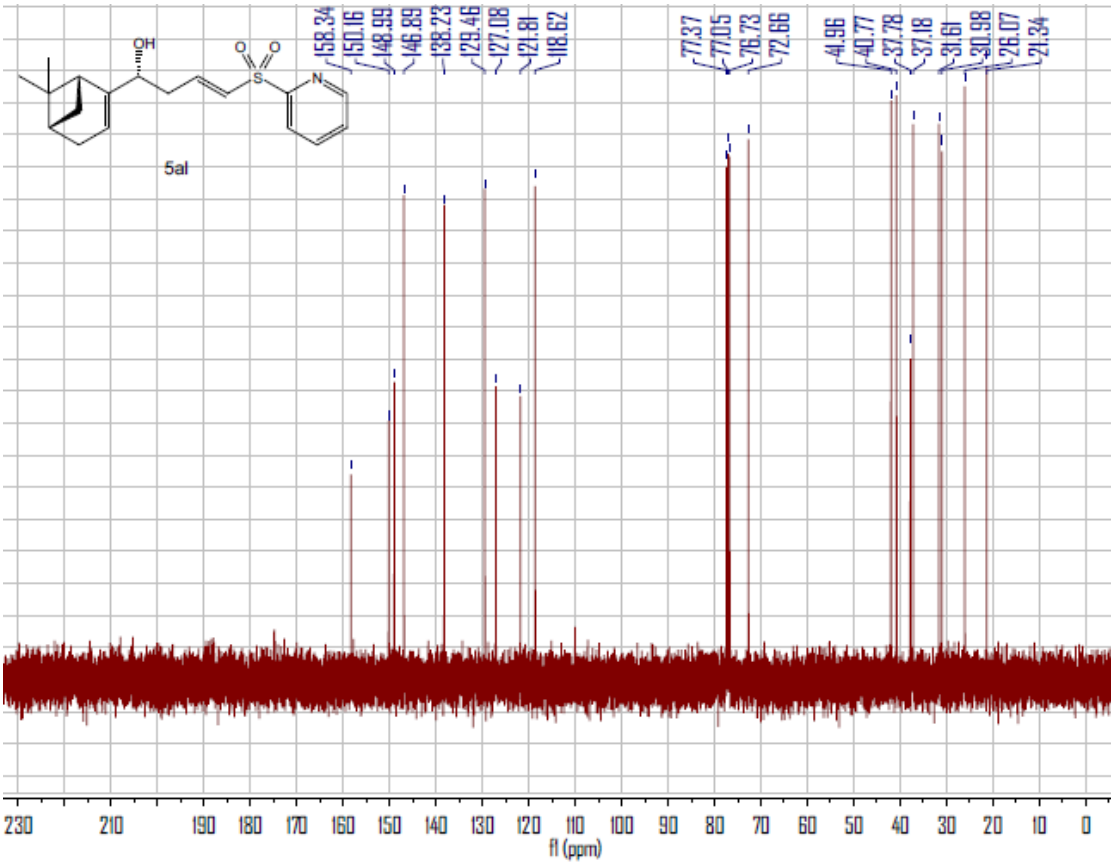


Figure S184. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5al'**, related to **Table 3**

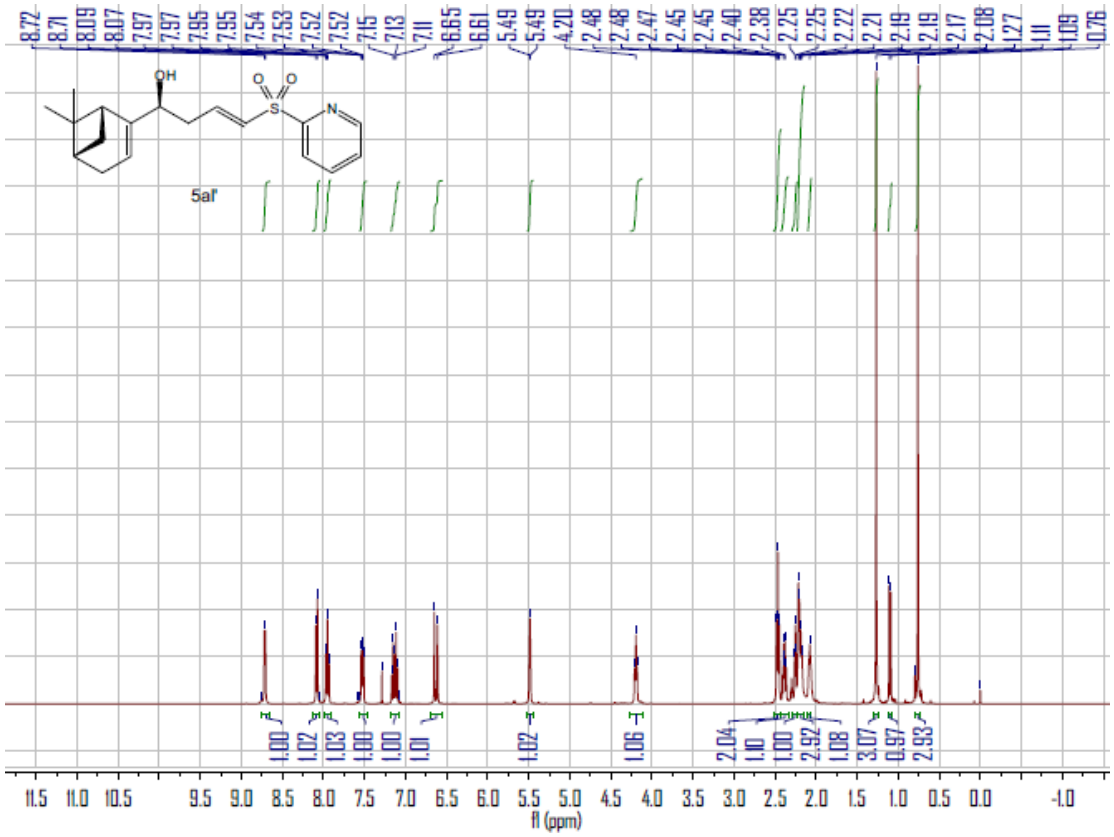


Figure S185. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5al'**, related to **Table 3**

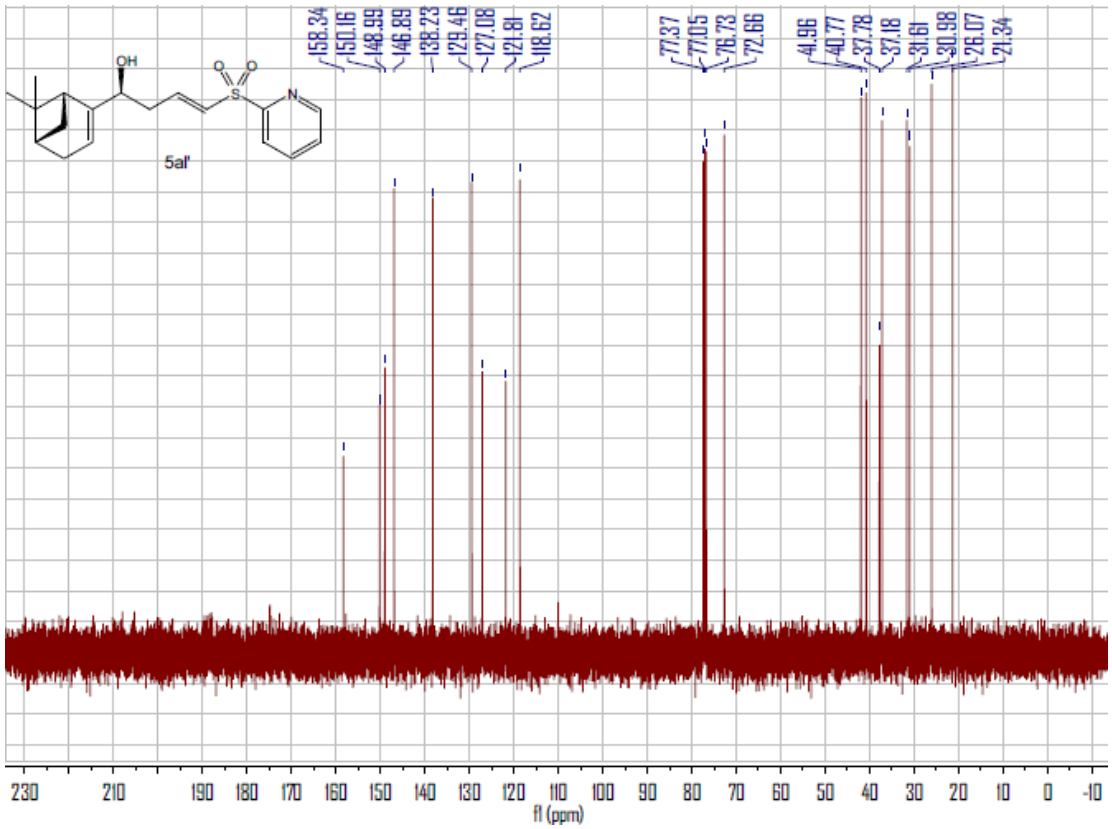


Figure S186. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5am**, related to **Table 3**

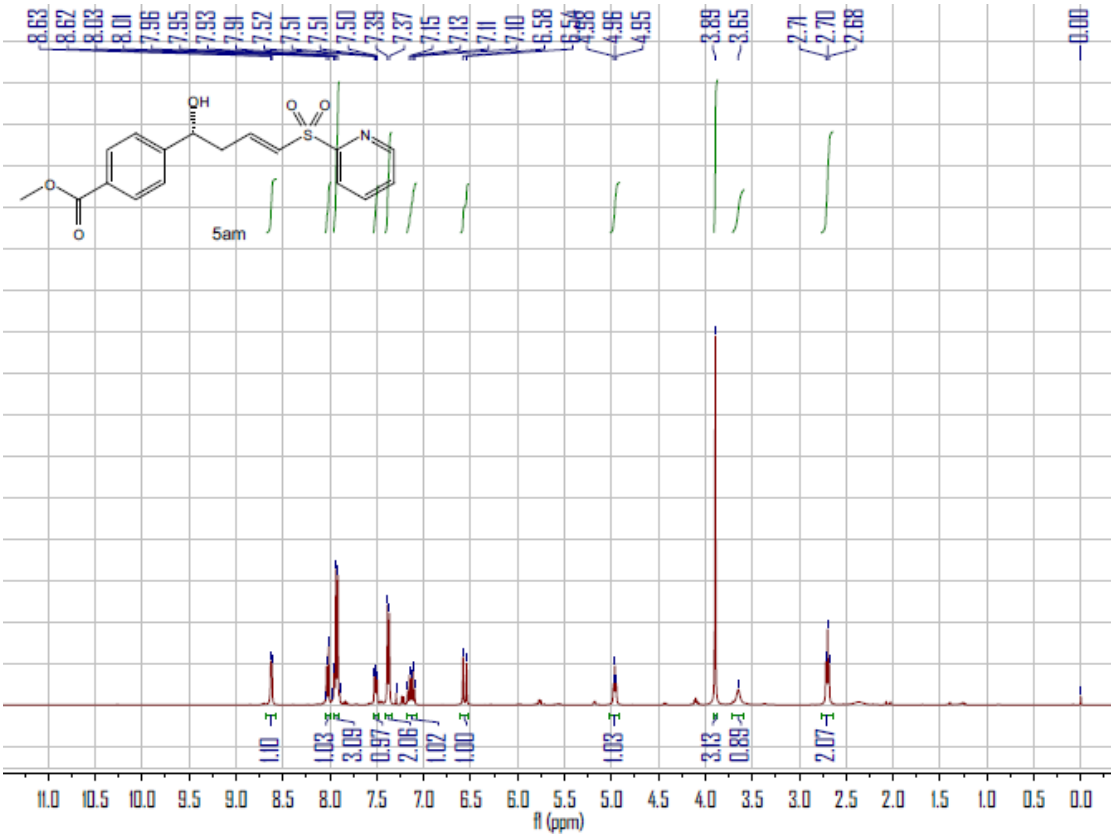


Figure S187. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5am**, related to **Table 3**

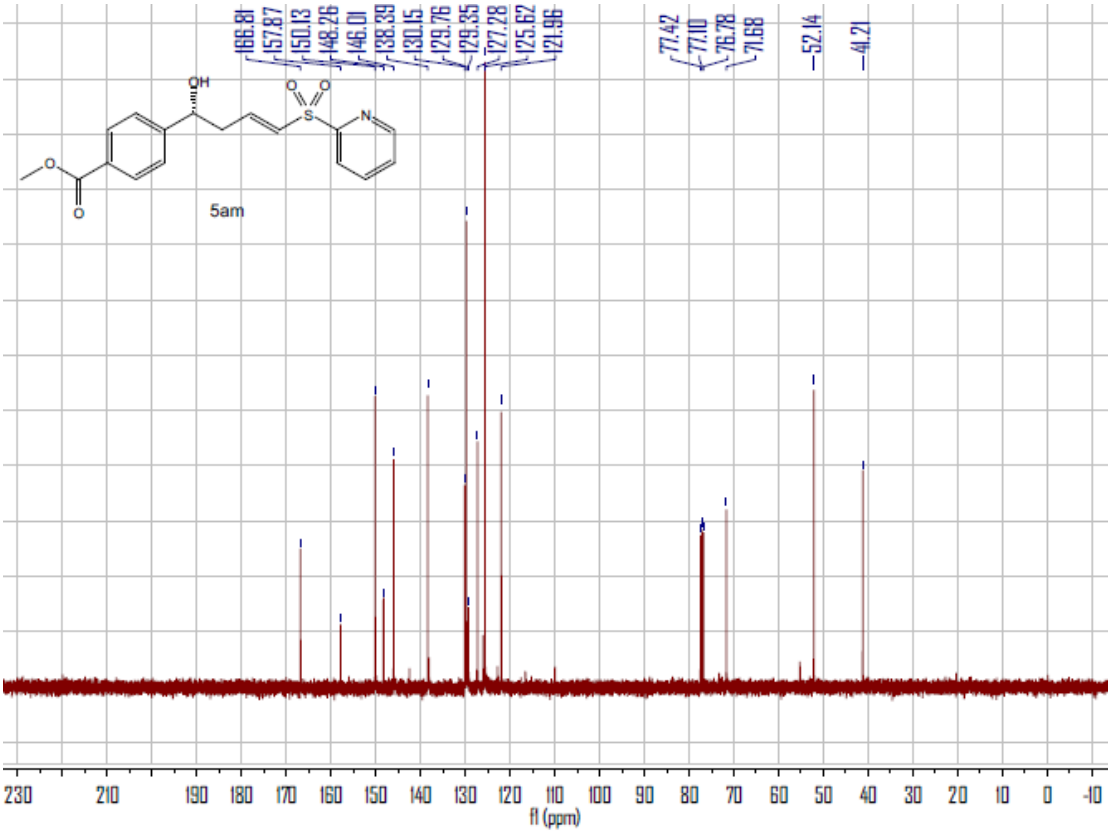


Figure S188. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5an**, related to **Table 3**

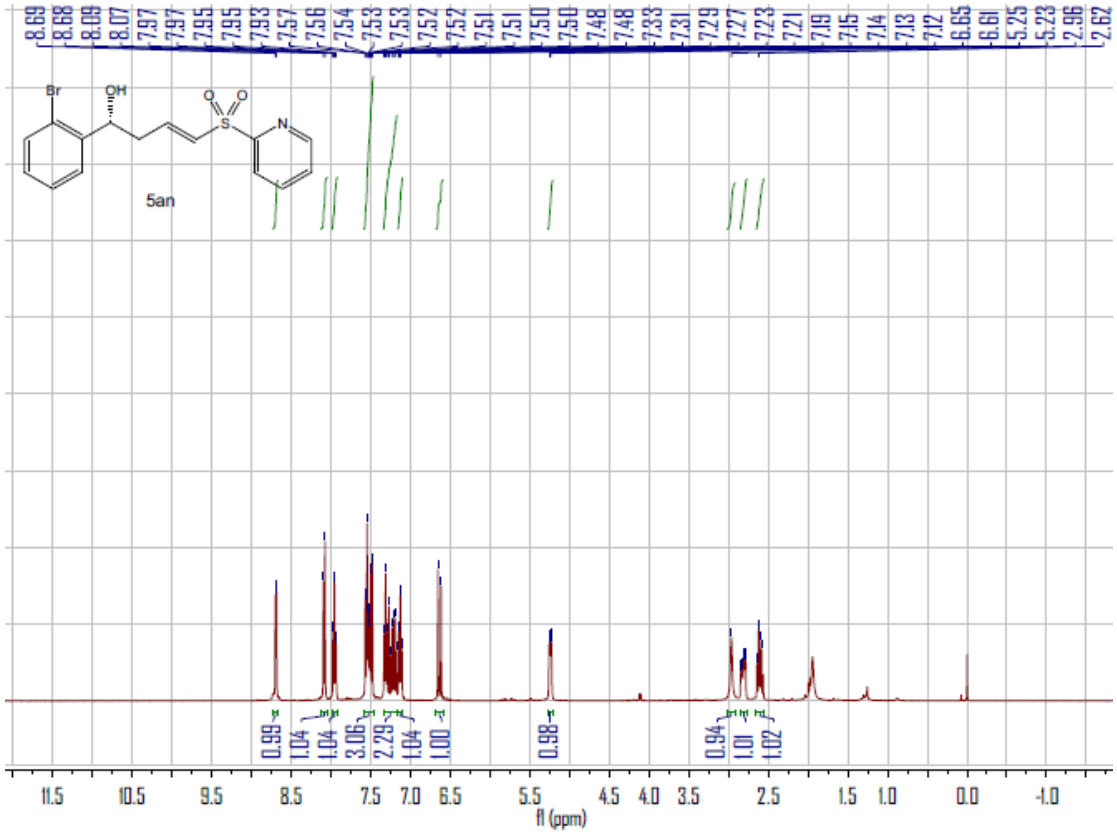


Figure S189. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5an**, related to **Table 3**

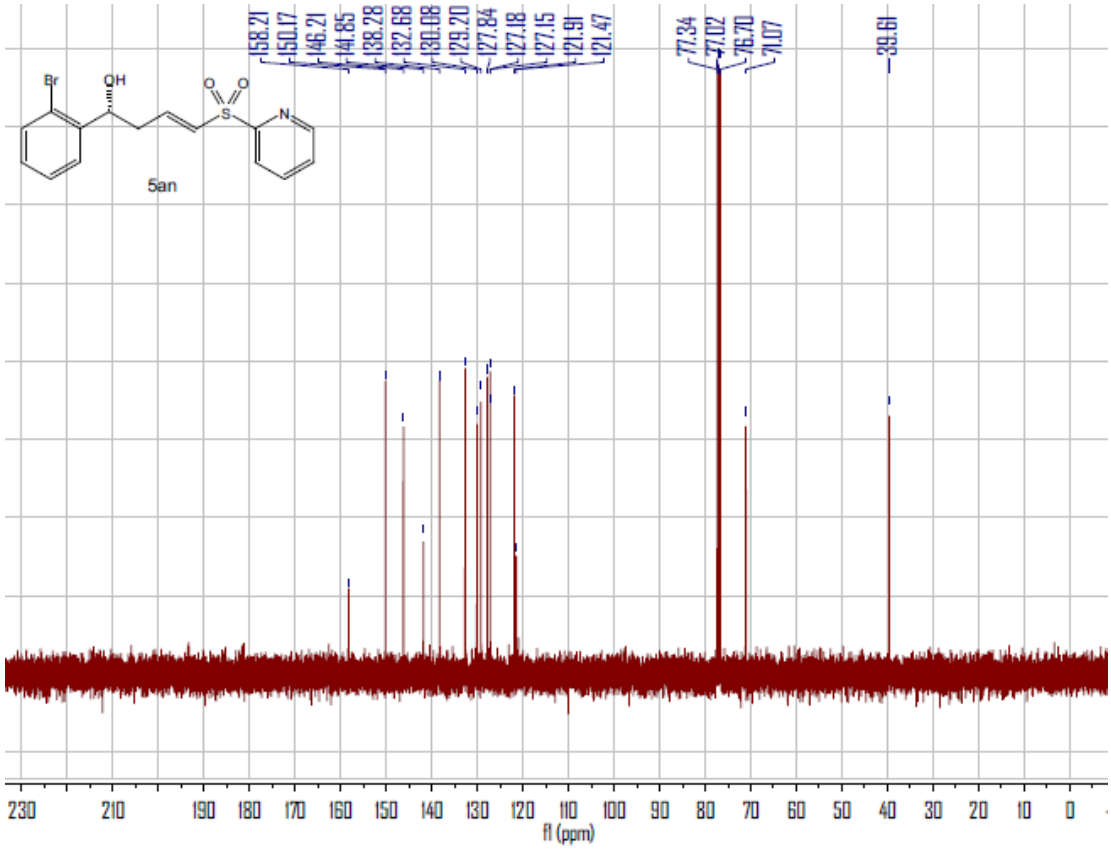


Figure S190. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ao**, related to **Table 3**

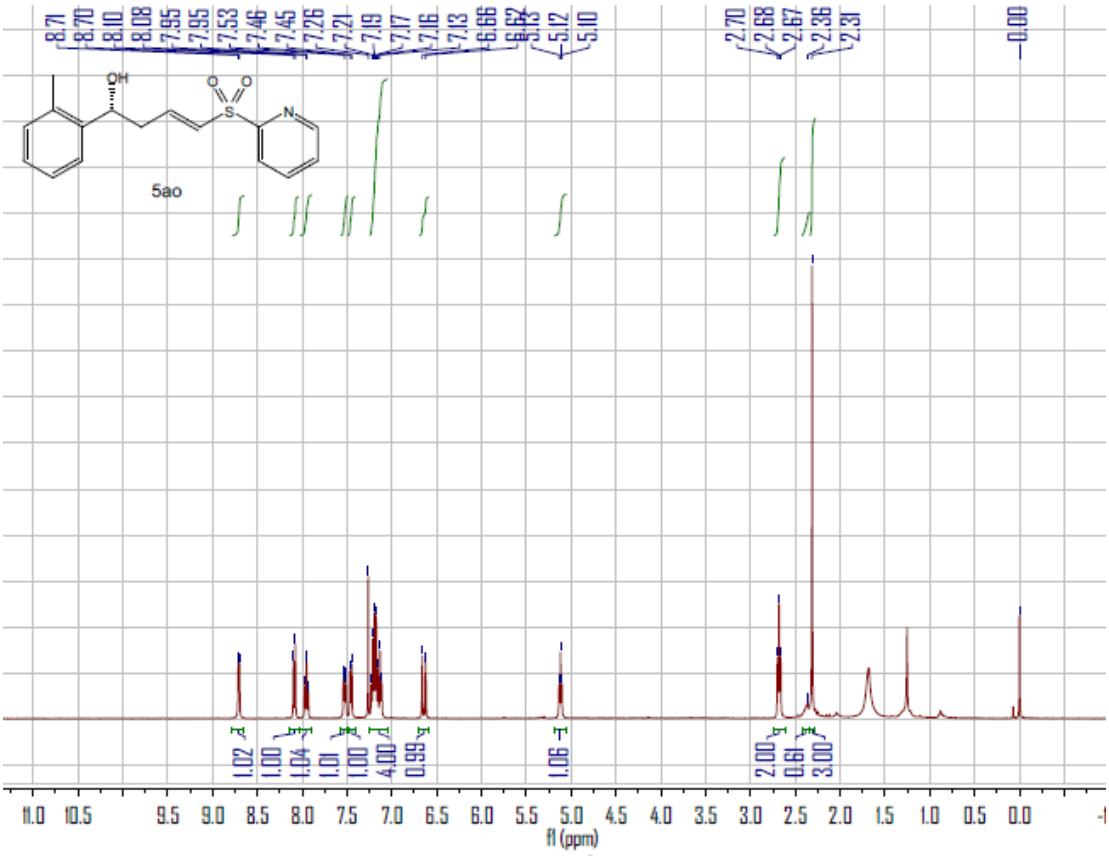


Figure S191. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5ao**, related to **Table 3**

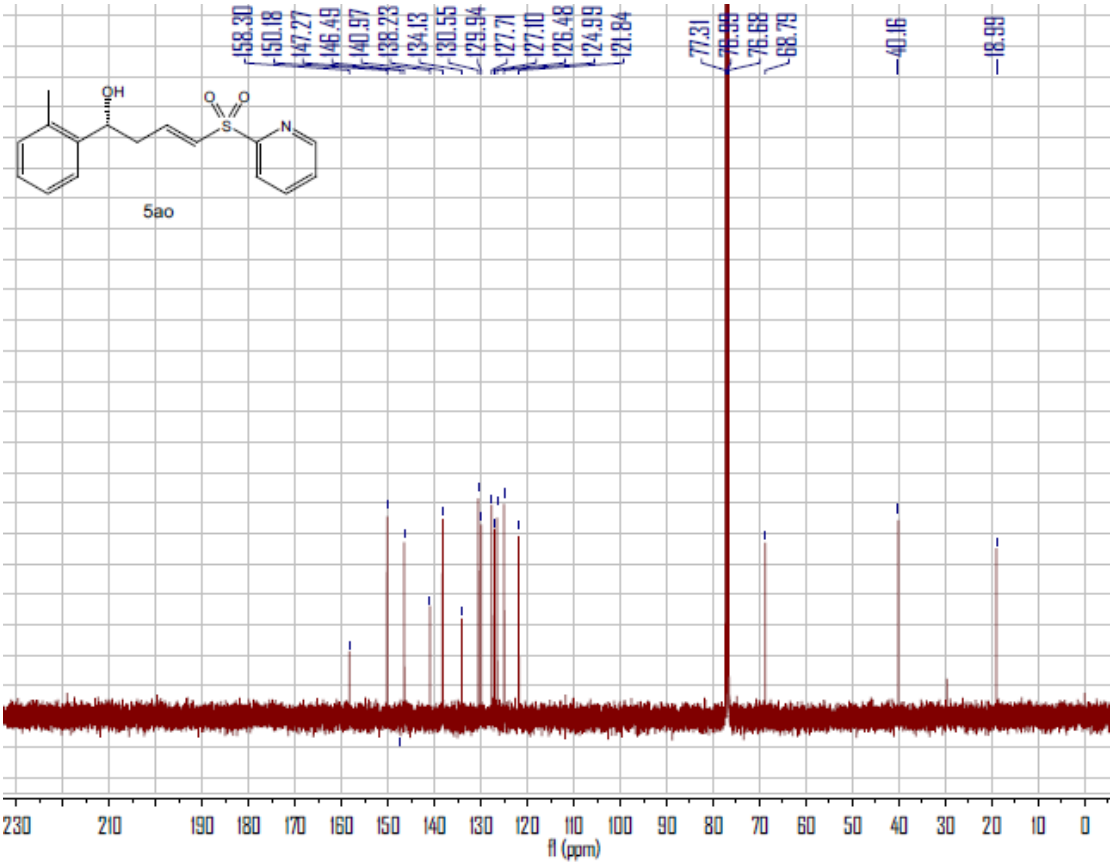


Figure S192. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ap**, related to **Table 3**

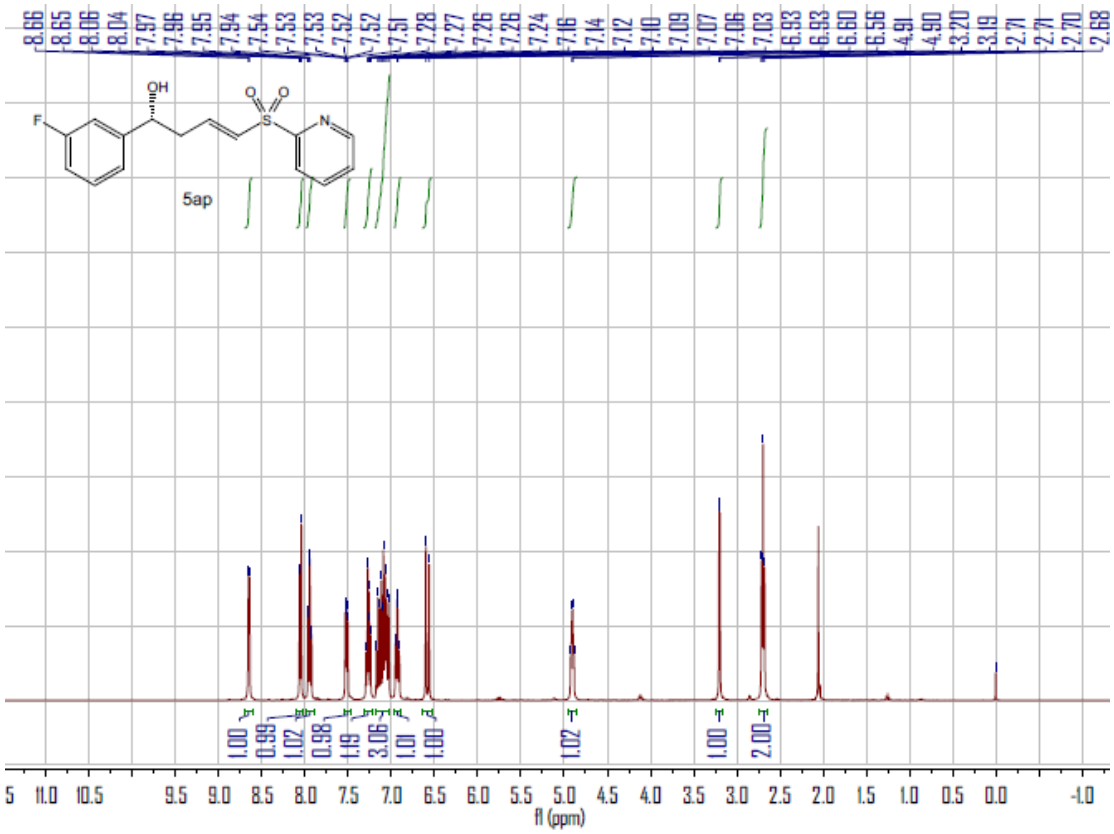


Figure S193. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5ap**, related to **Table 3**

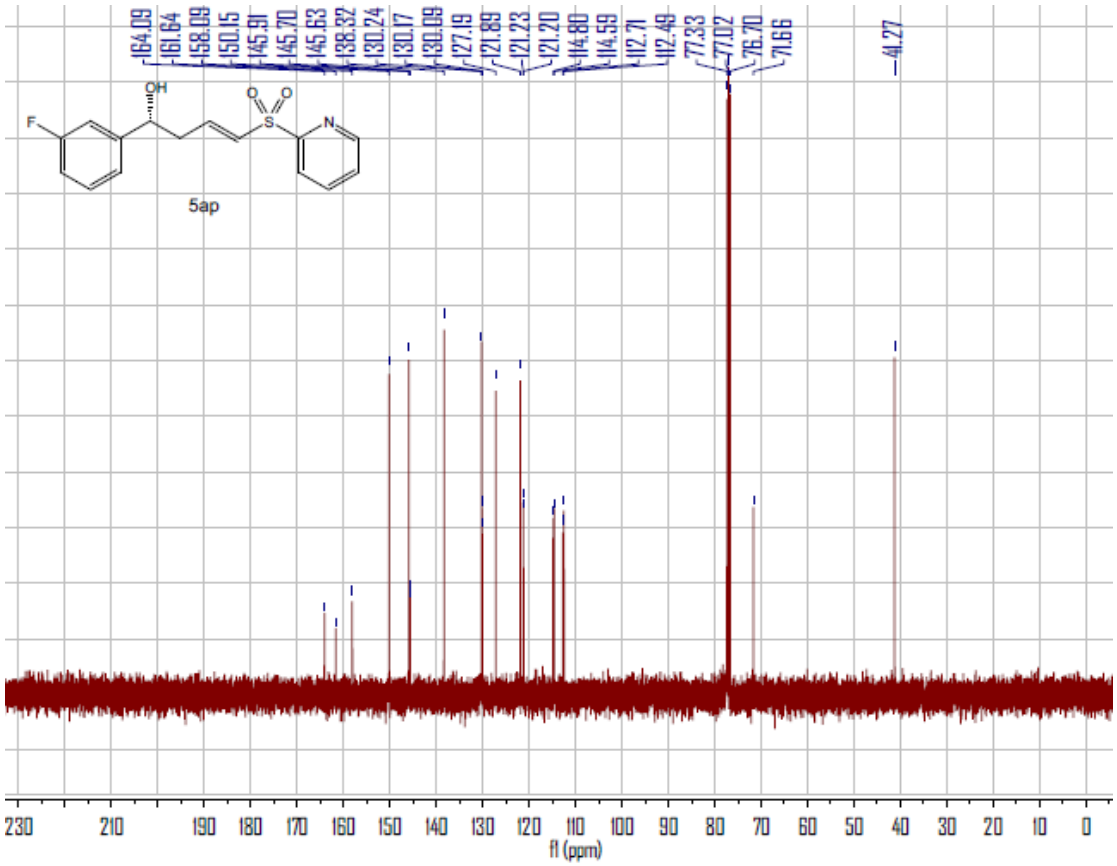


Figure S194. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5ap**, related to **Table 3**

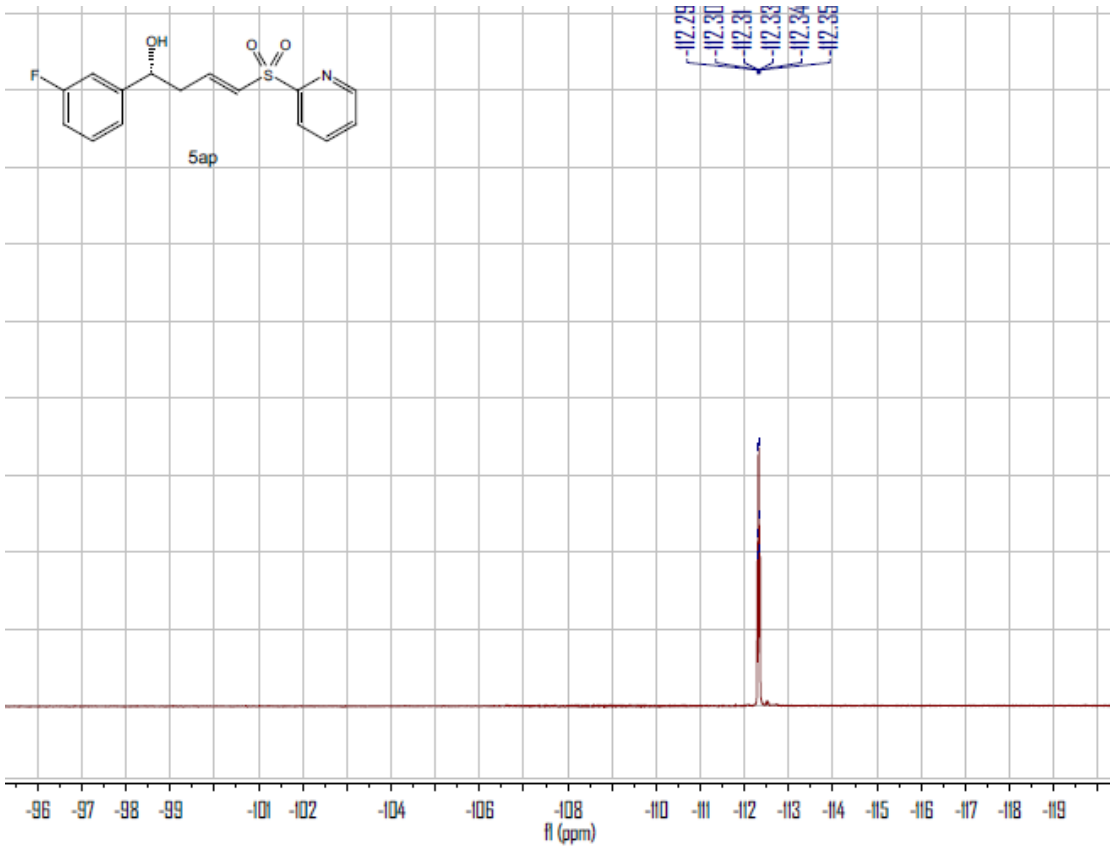


Figure S195. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5aq**, related to **Table 3**

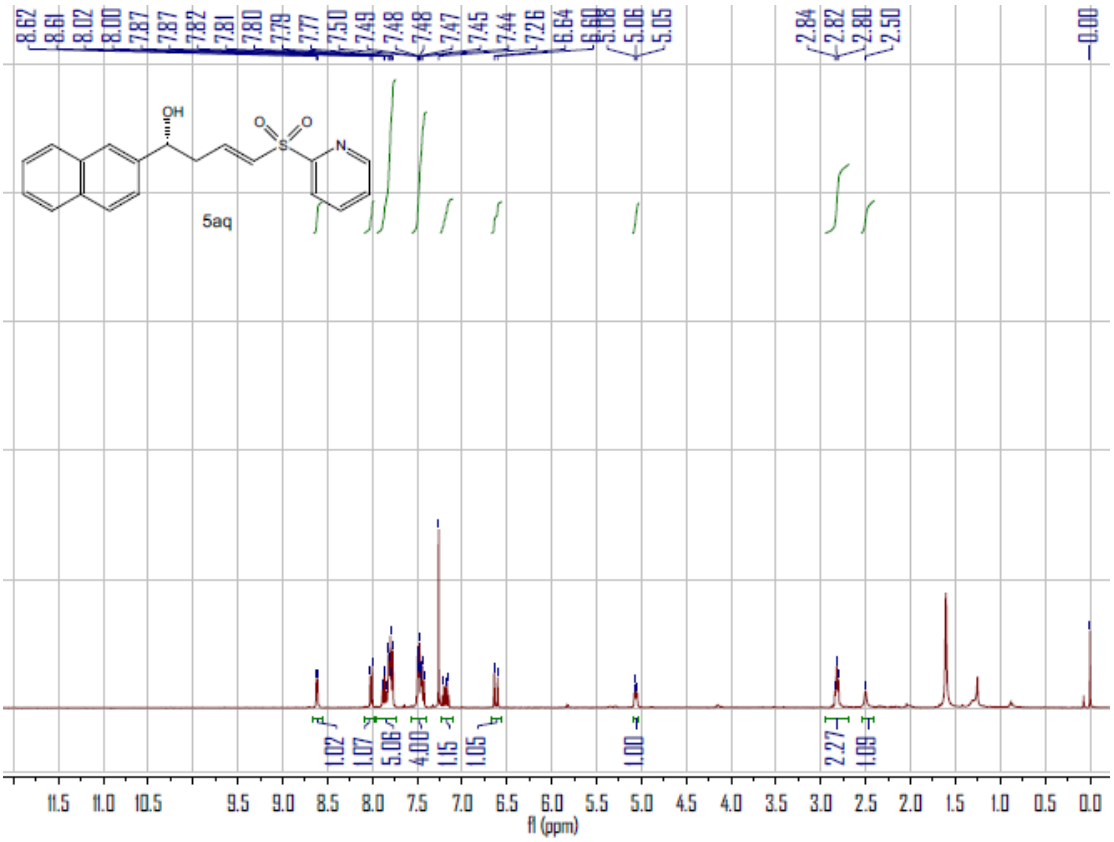


Figure S196. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5aq**, related to **Table 3**

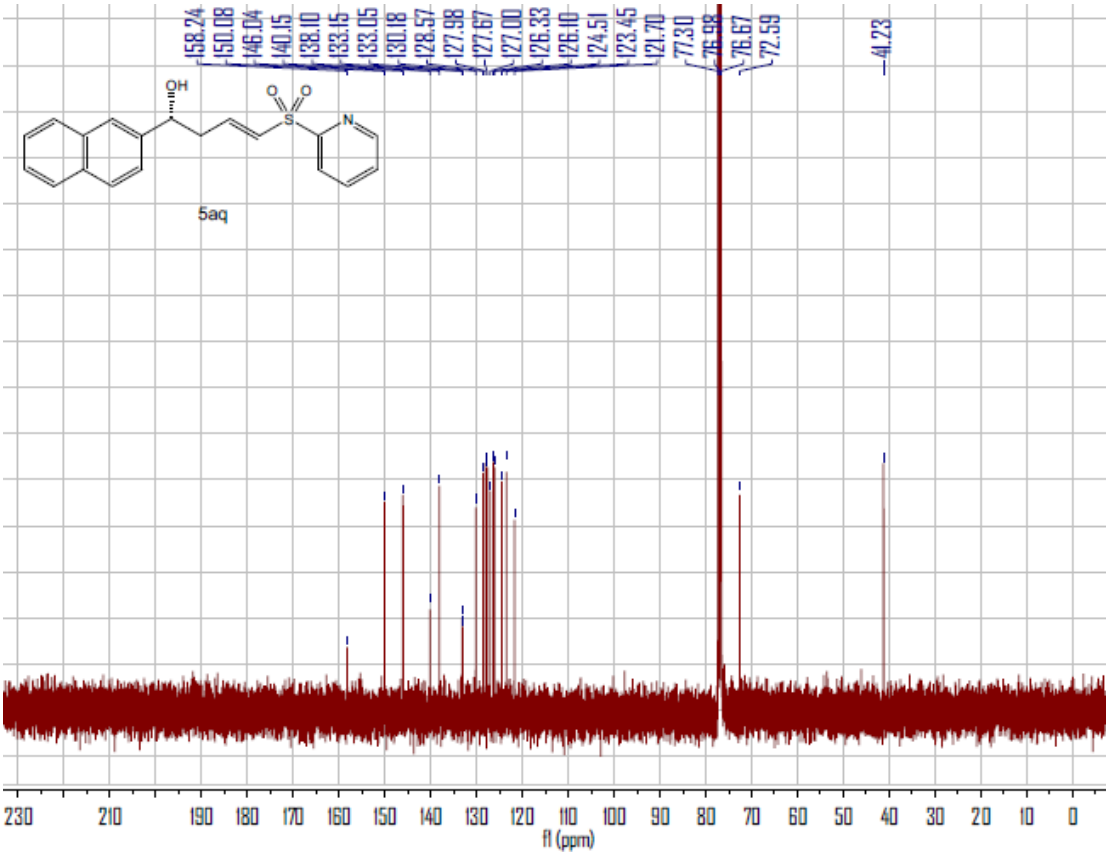


Figure S197. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ar**, related to **Table 3**

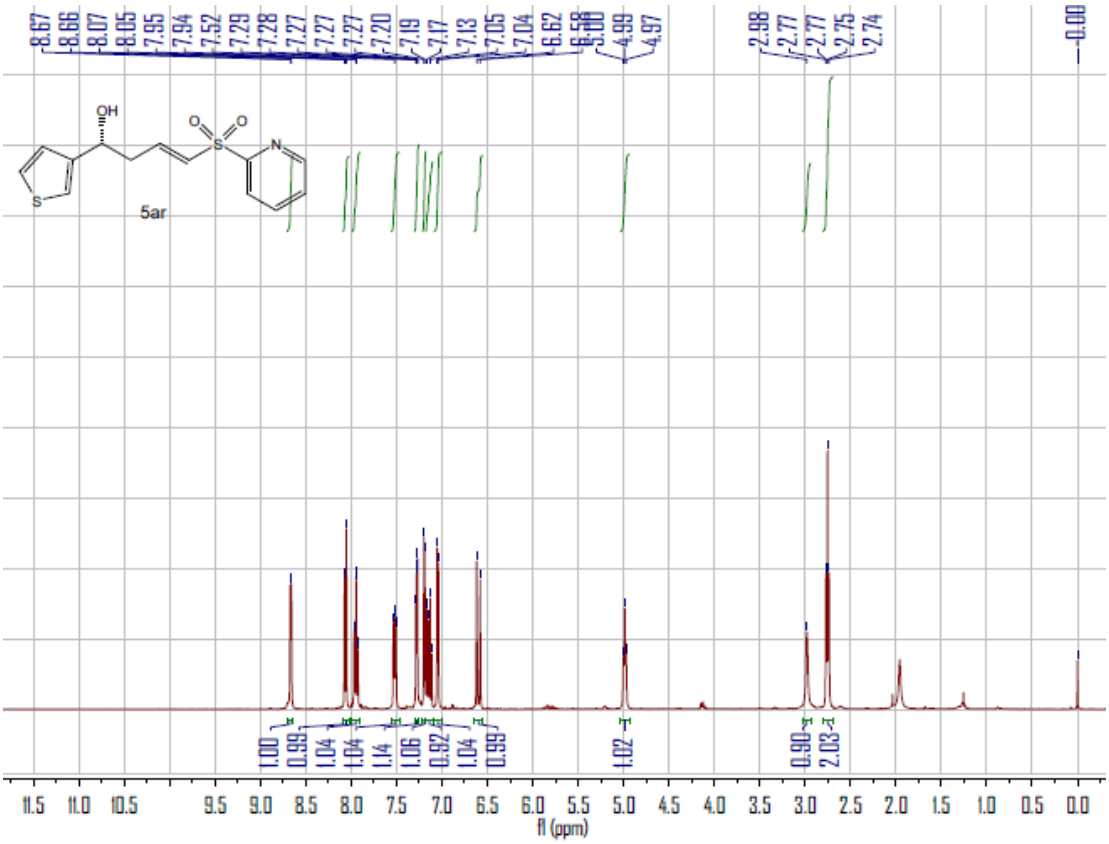


Figure S198. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5ar**, related to **Table 3**

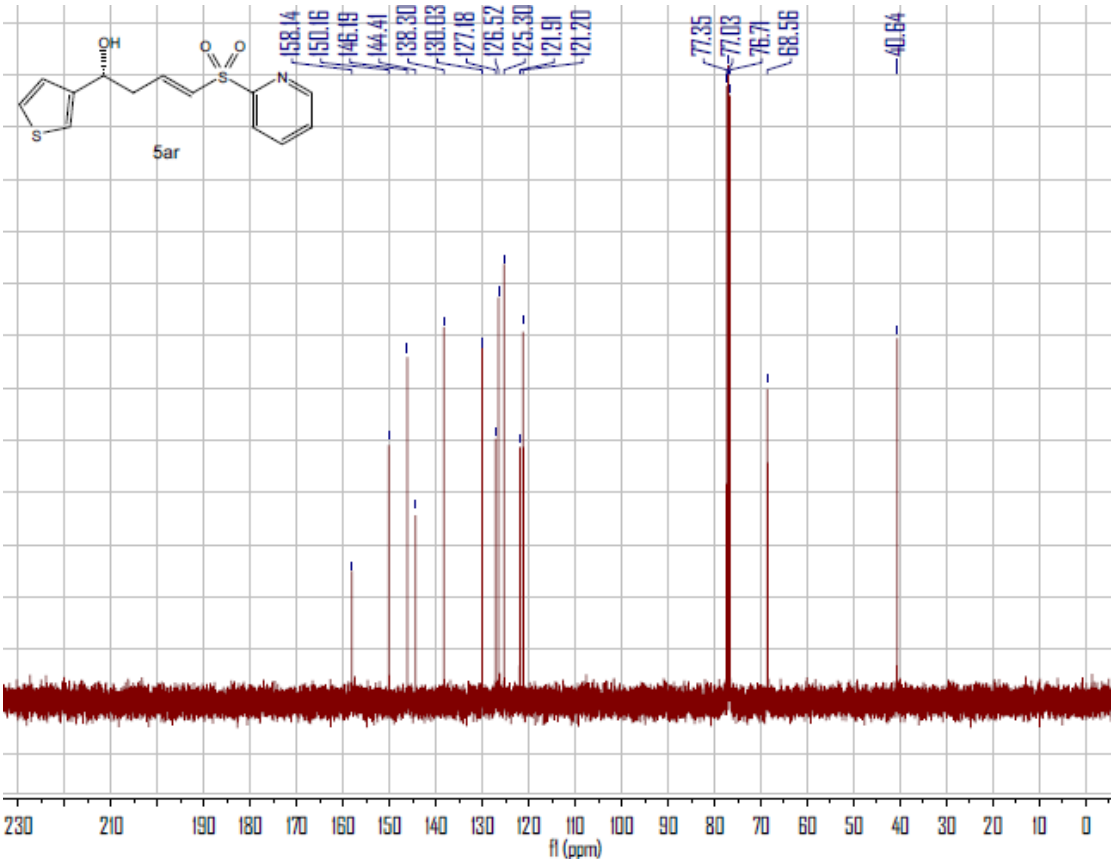


Figure S199. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5as**, related to **Table 3**

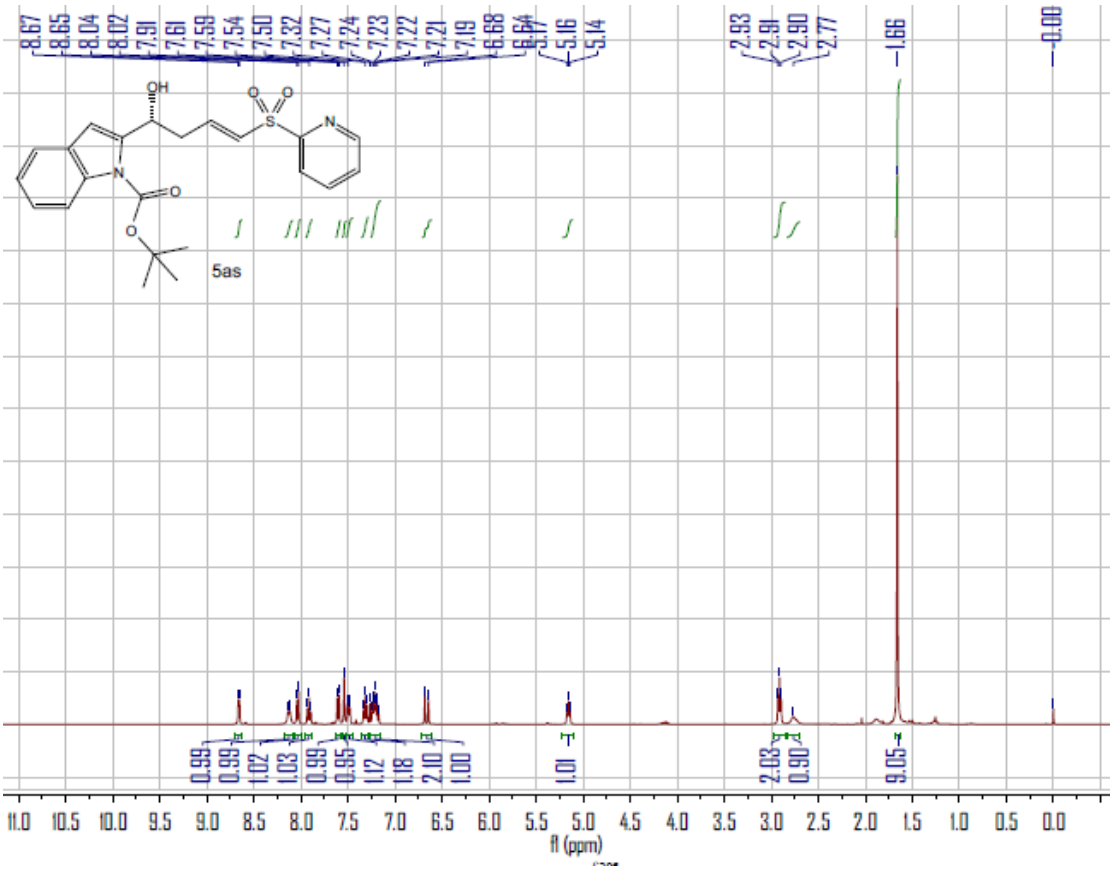


Figure S200. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5as**, related to **Table 3**

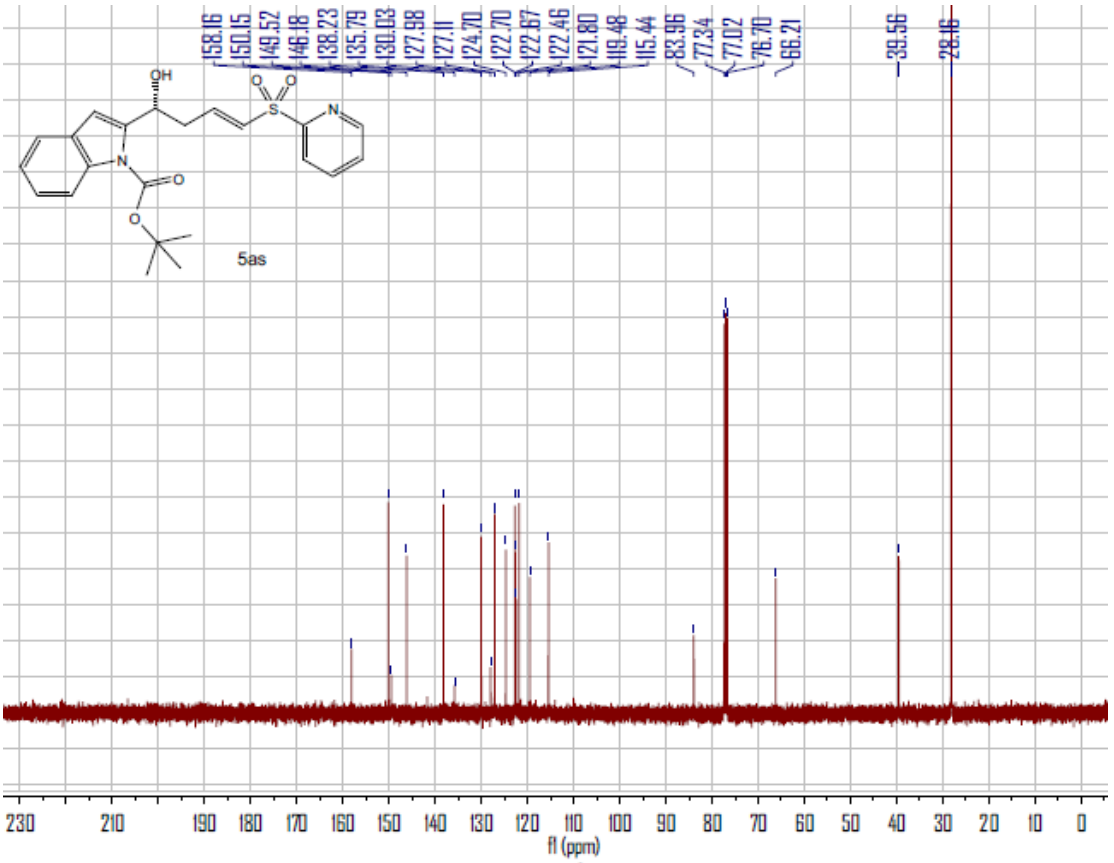


Figure S201. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5at**, related to **Table 3**

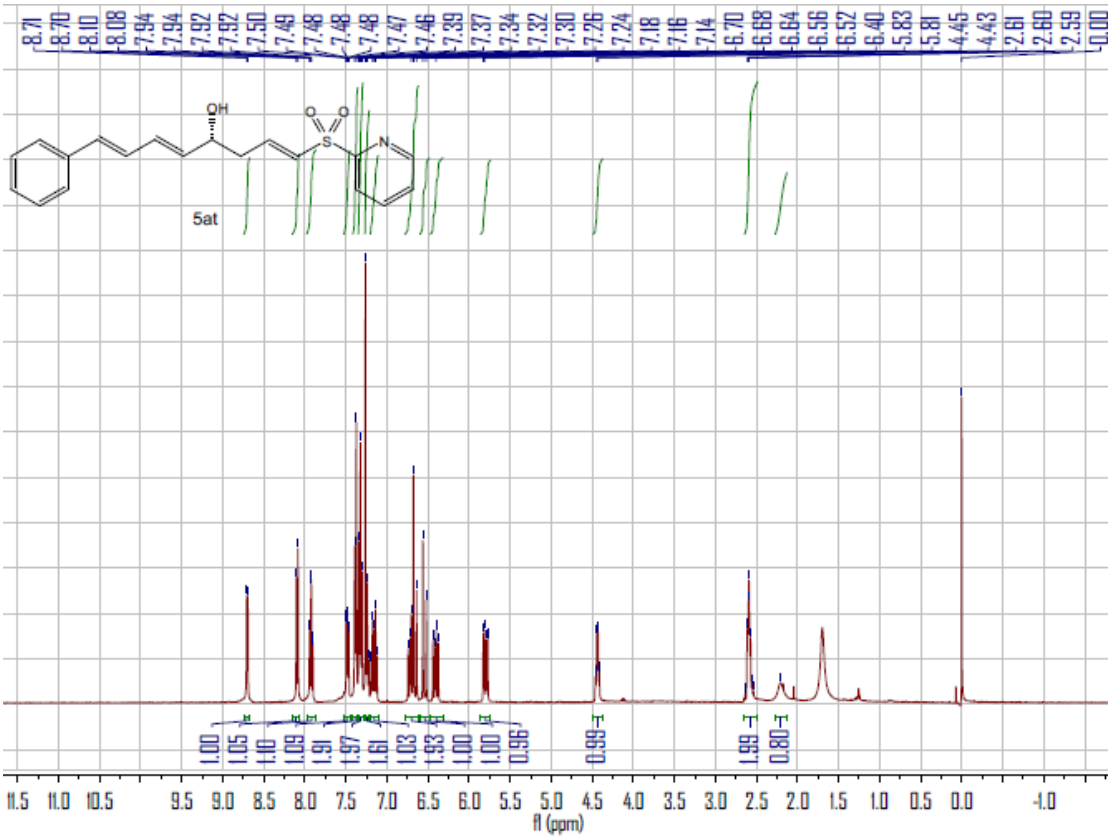


Figure S202. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5at**, related to **Table 3**

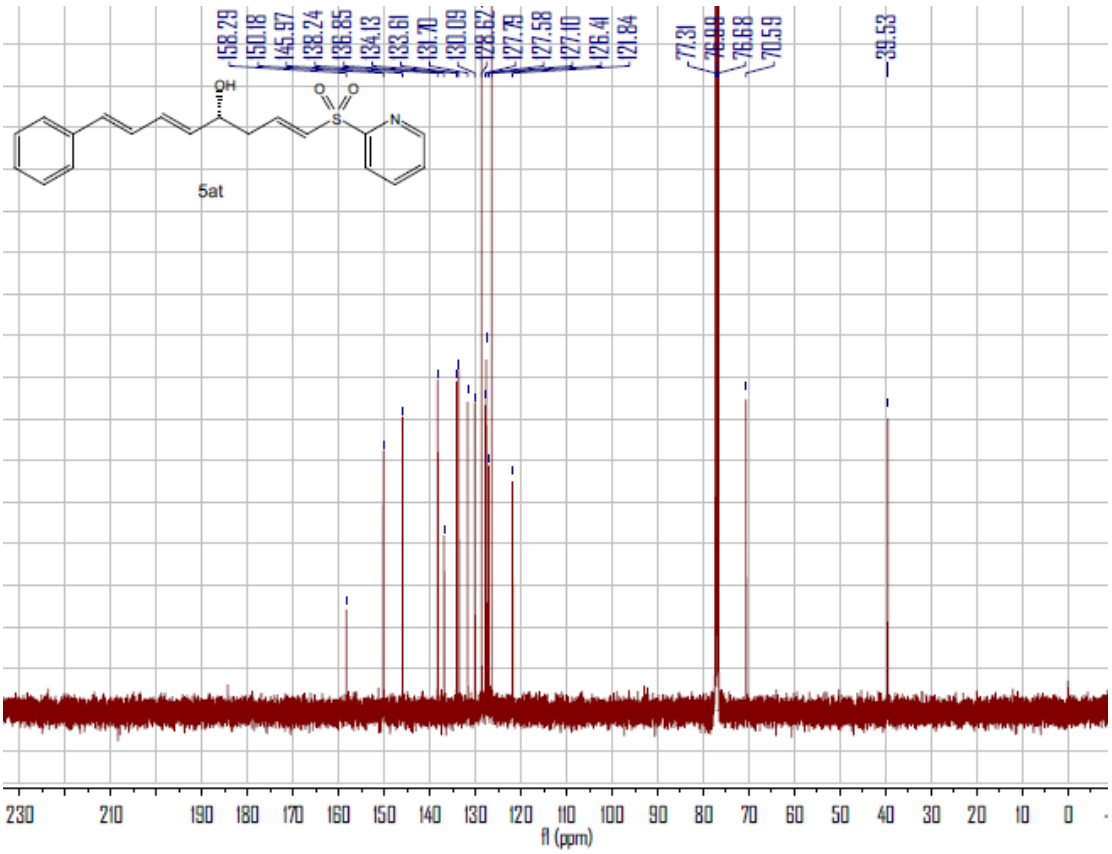


Figure S203. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5au**, related to **Table 3**

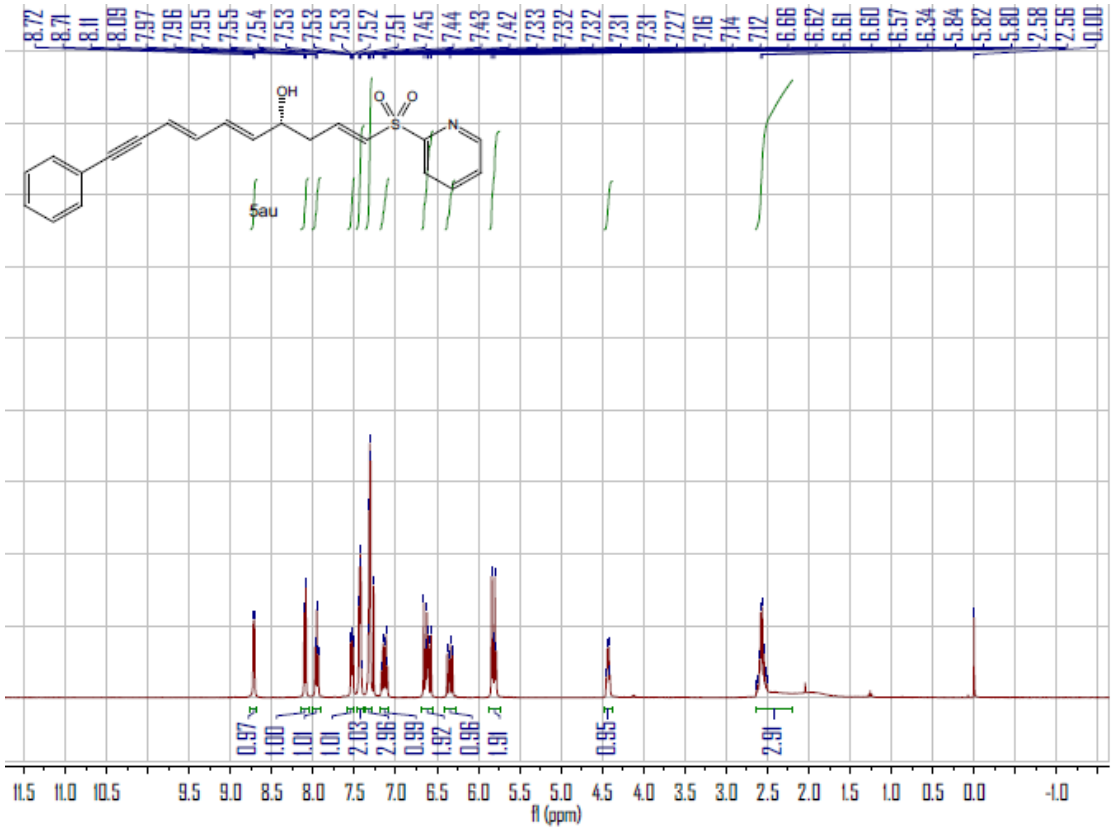


Figure S204. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5au**, related to **Table 3**

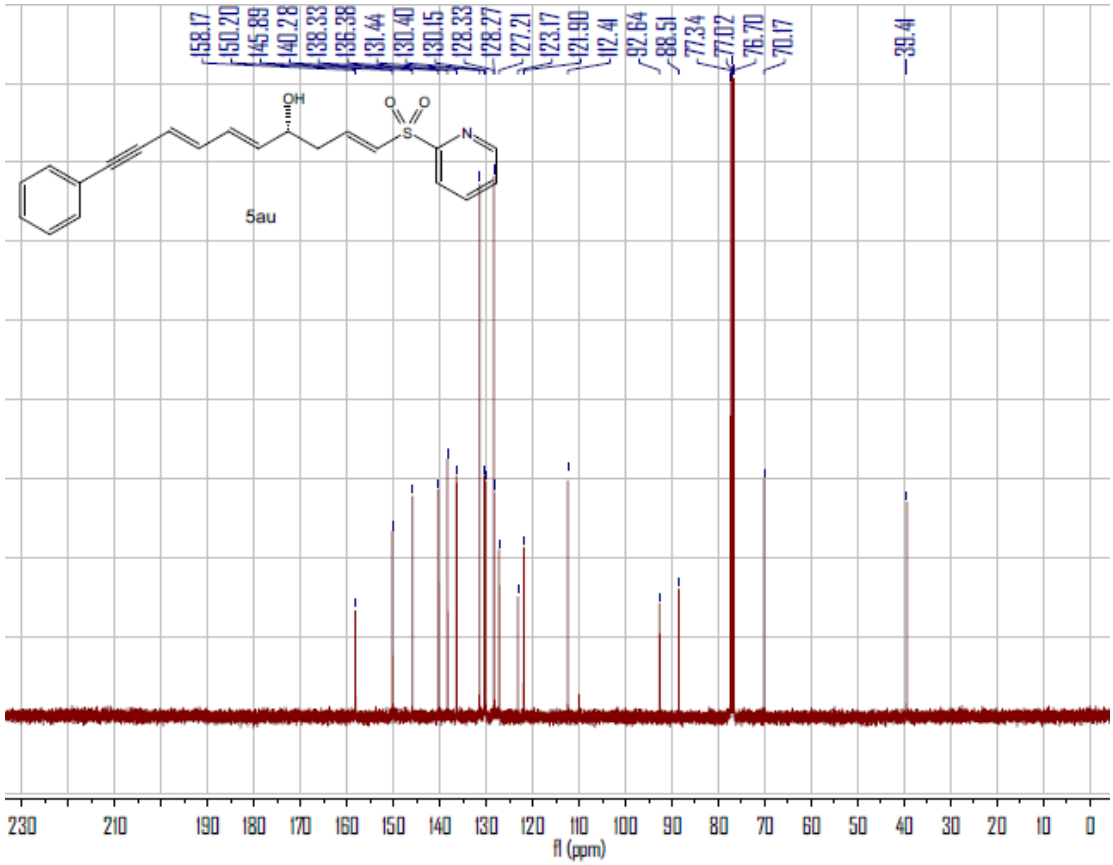


Figure S205. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **9**, related to **Scheme 3**

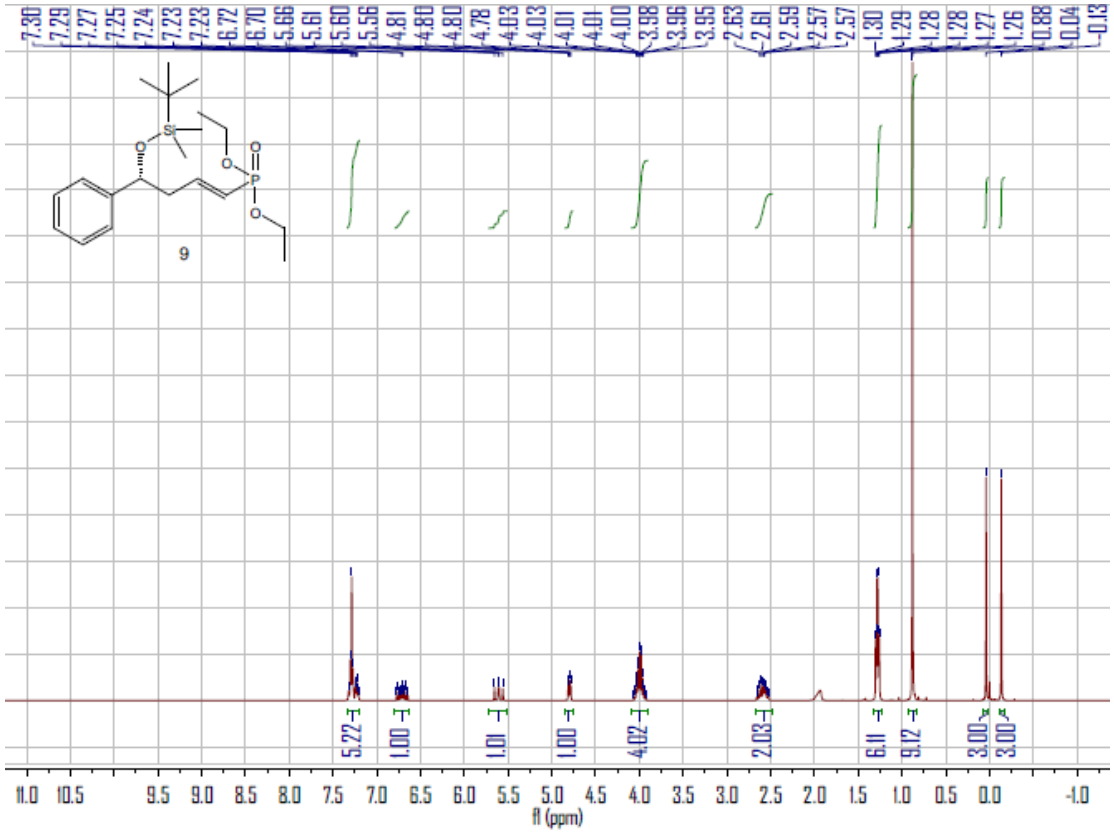


Figure S206. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **9**, related to **Scheme 3**

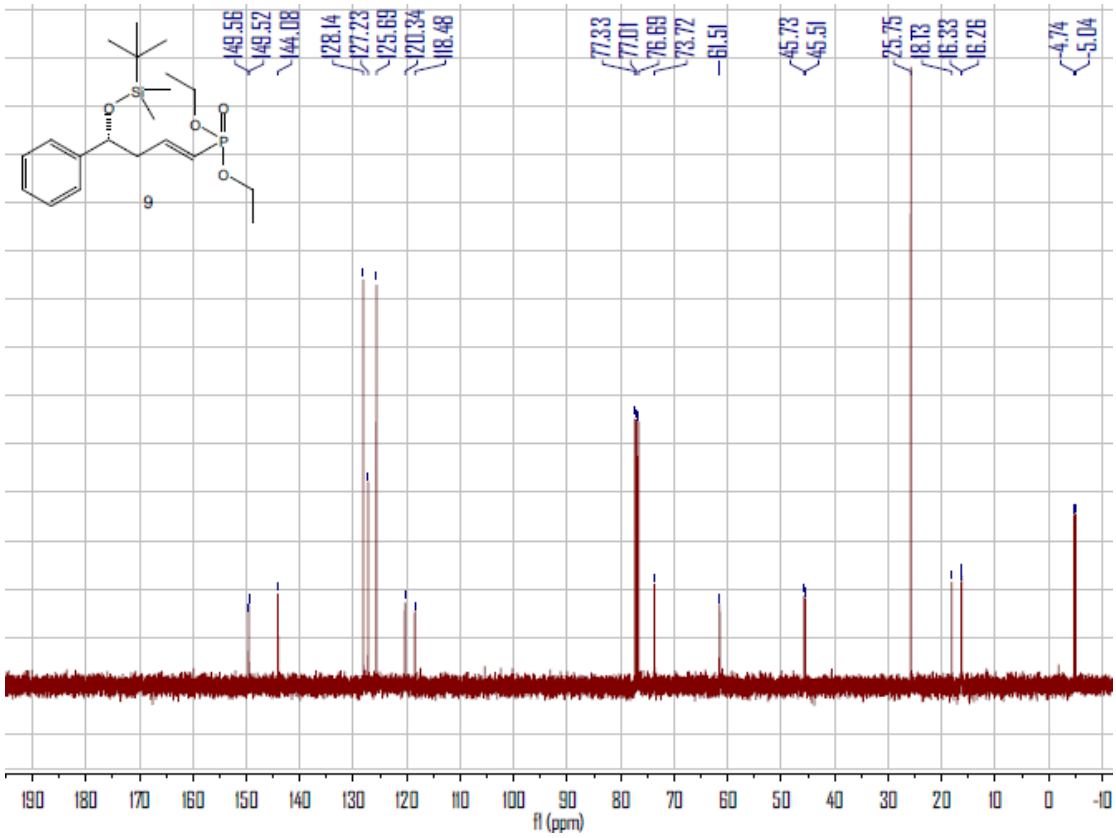


Figure S207. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **9**, related to **Scheme 3**

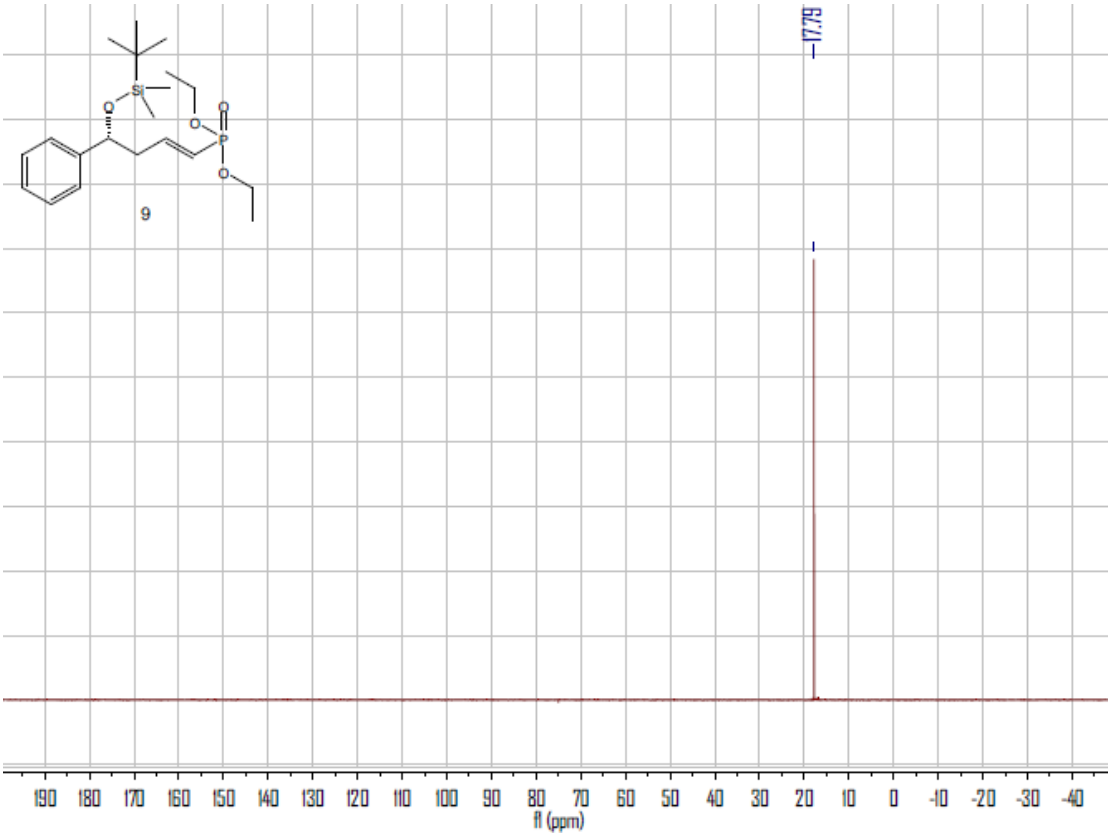


Figure S208. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **10**, related to **Scheme 3**

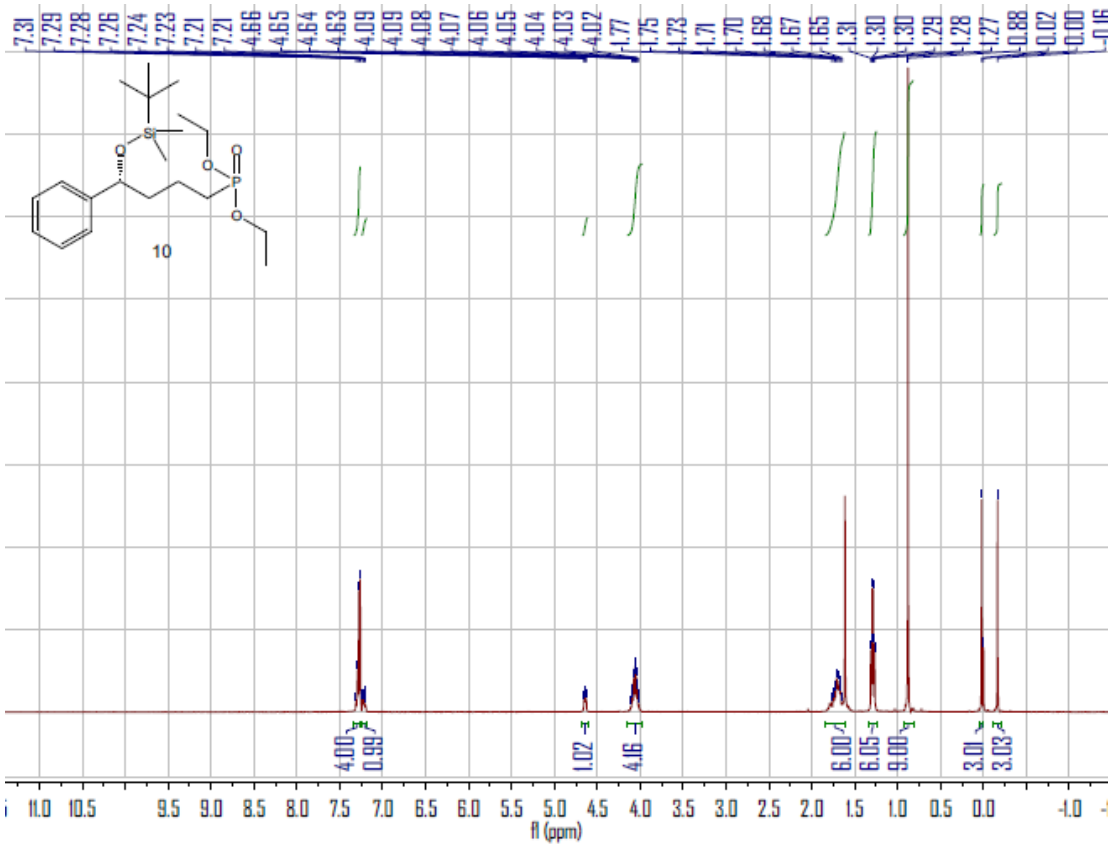


Figure S209. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **10**, related to **Scheme 3**

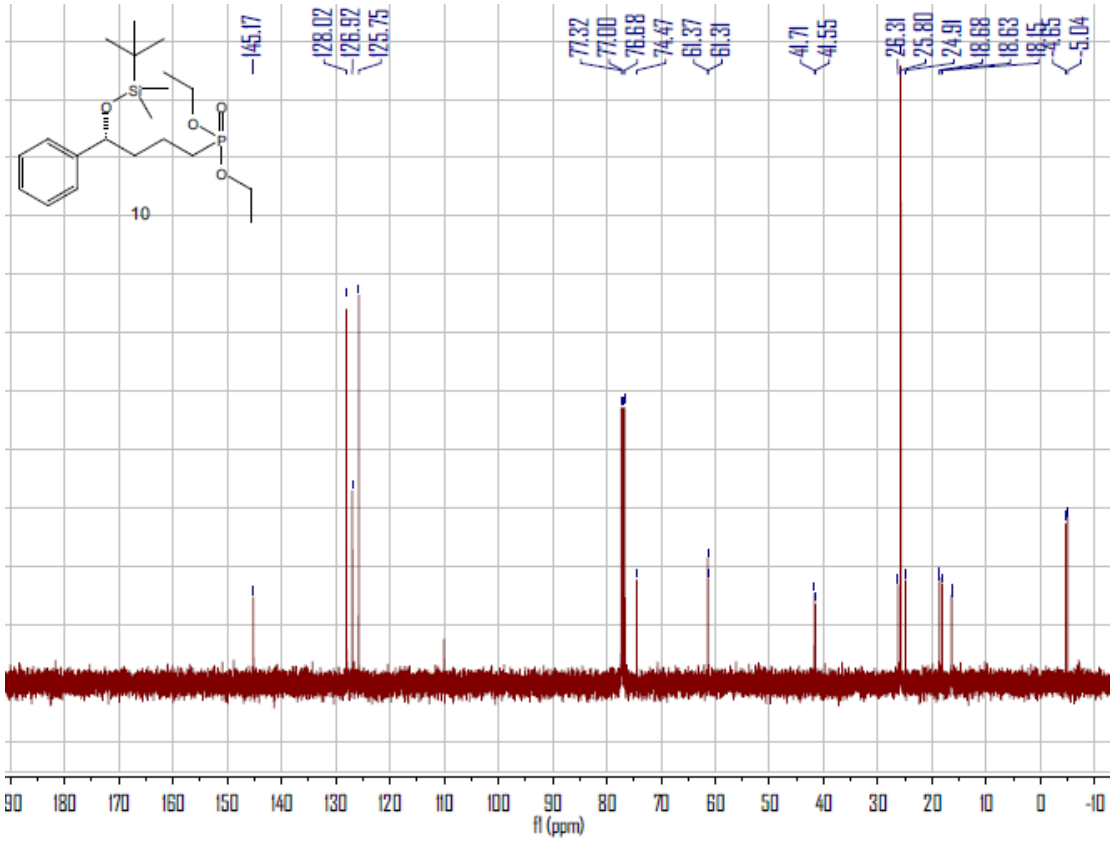


Figure S210. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **10**, related to **Scheme 3**

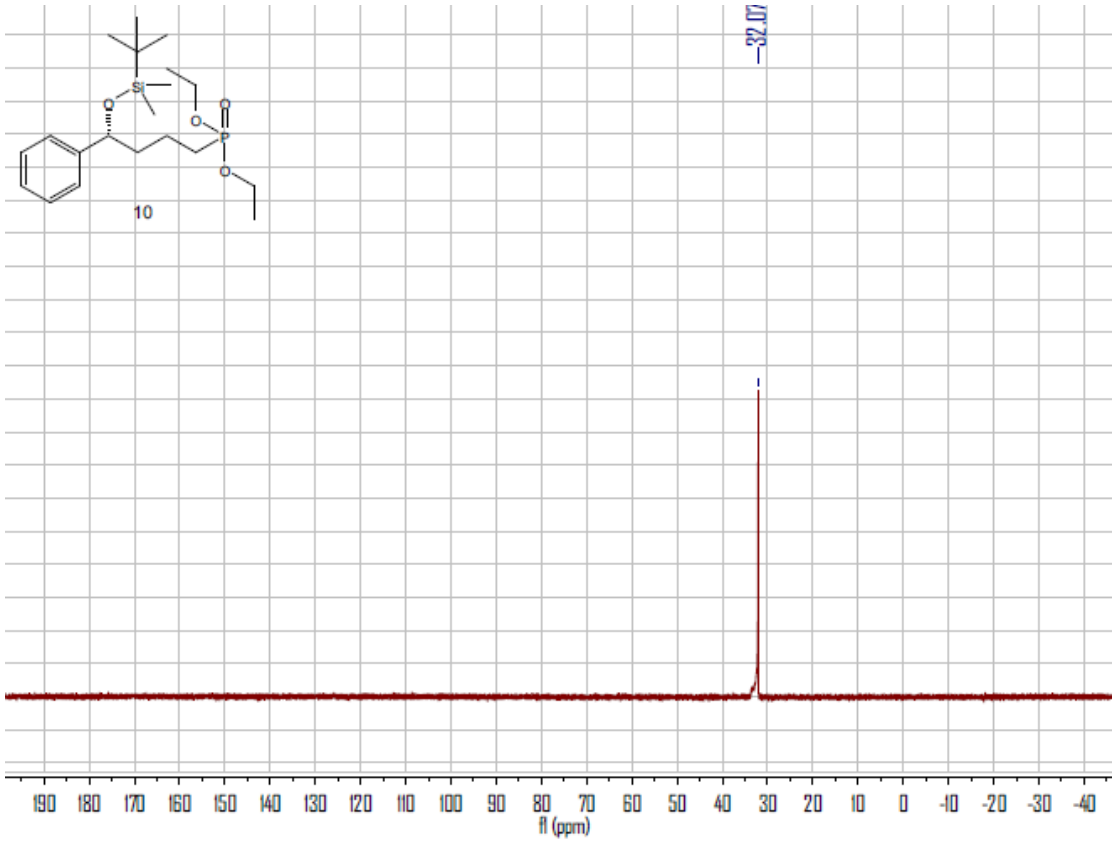


Figure S211. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11**, related to **Scheme 3**

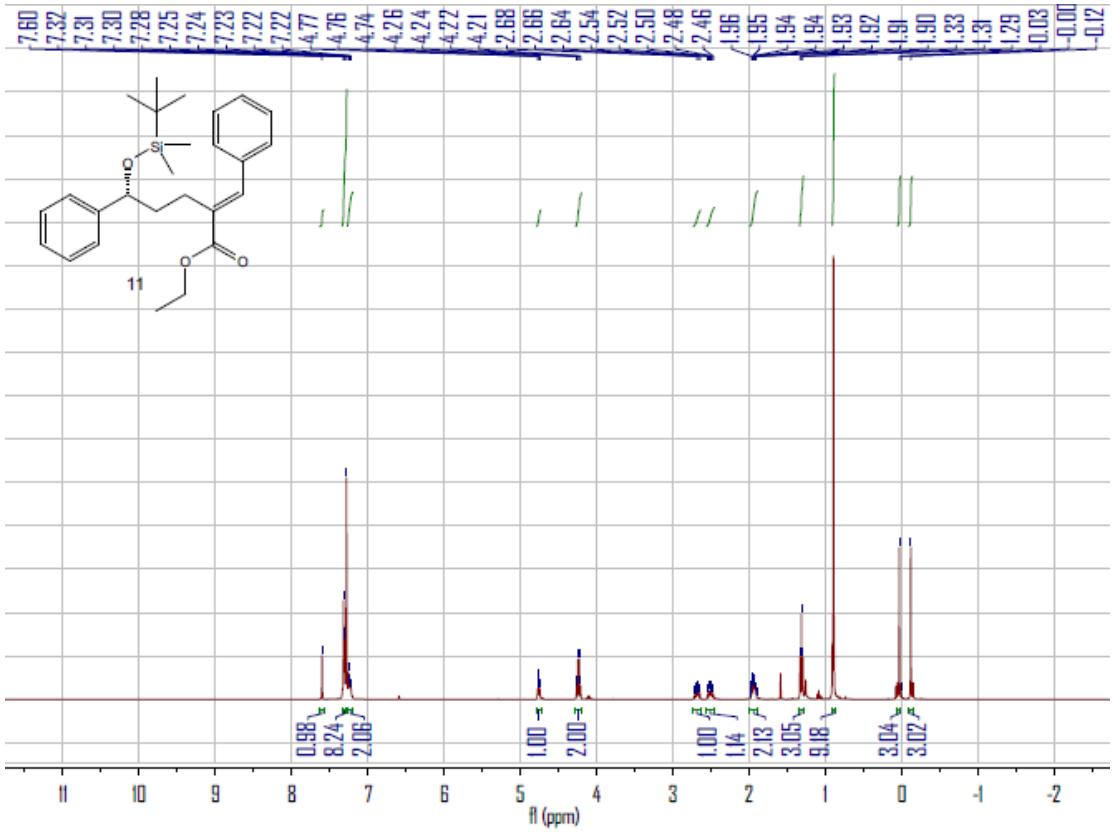


Figure S212. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **11**, related to **Scheme 3**

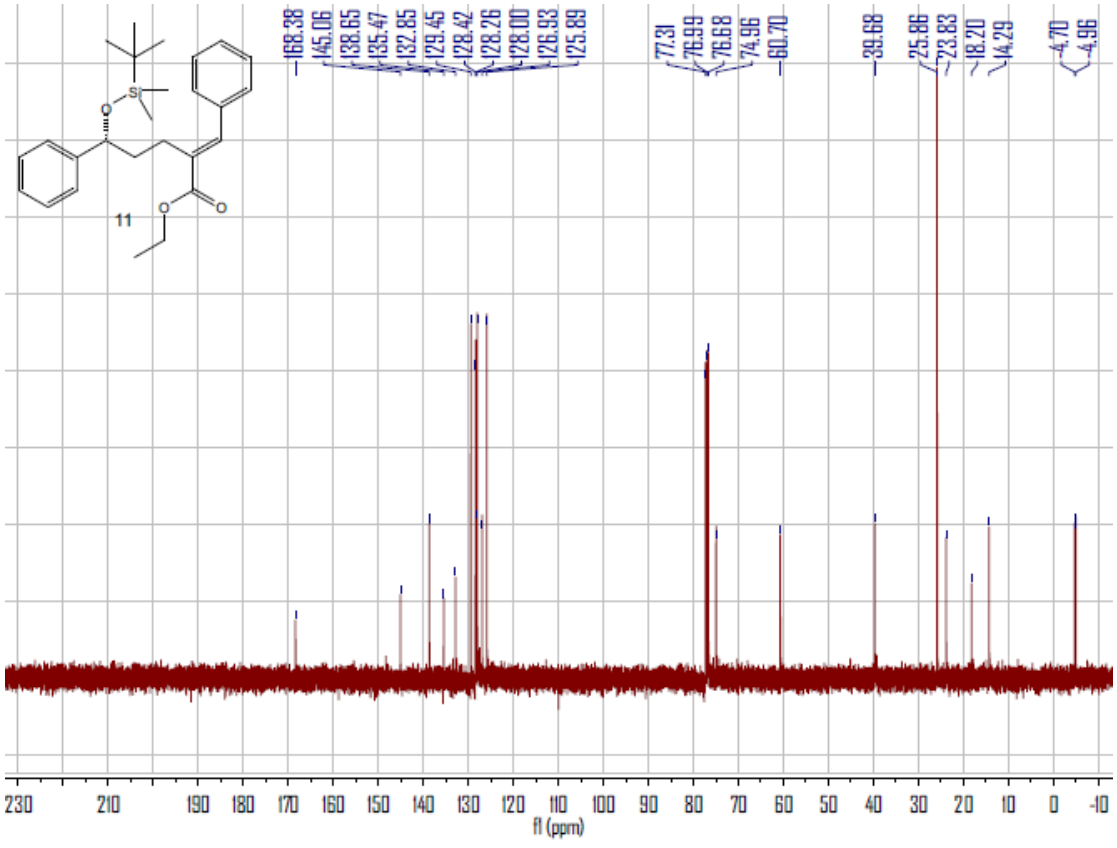


Figure S213. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **12**, related to **Scheme 3**

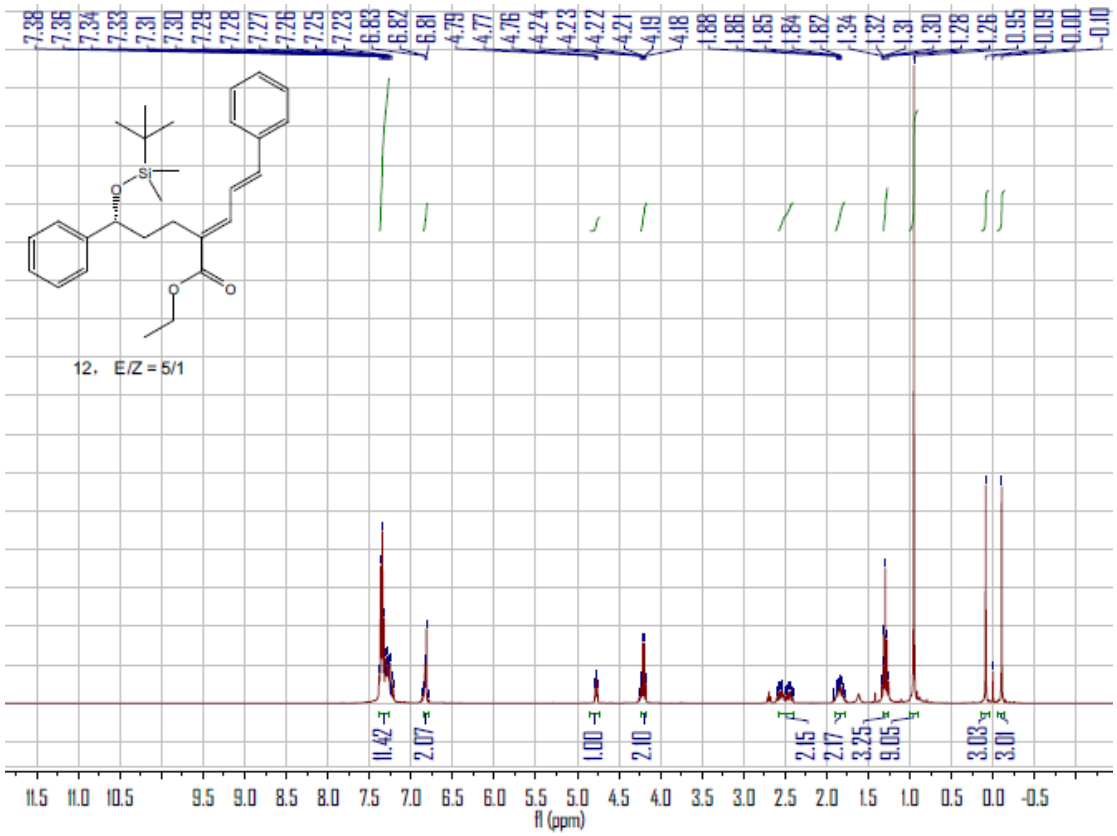


Figure S214. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **12**, related to **Scheme 3**

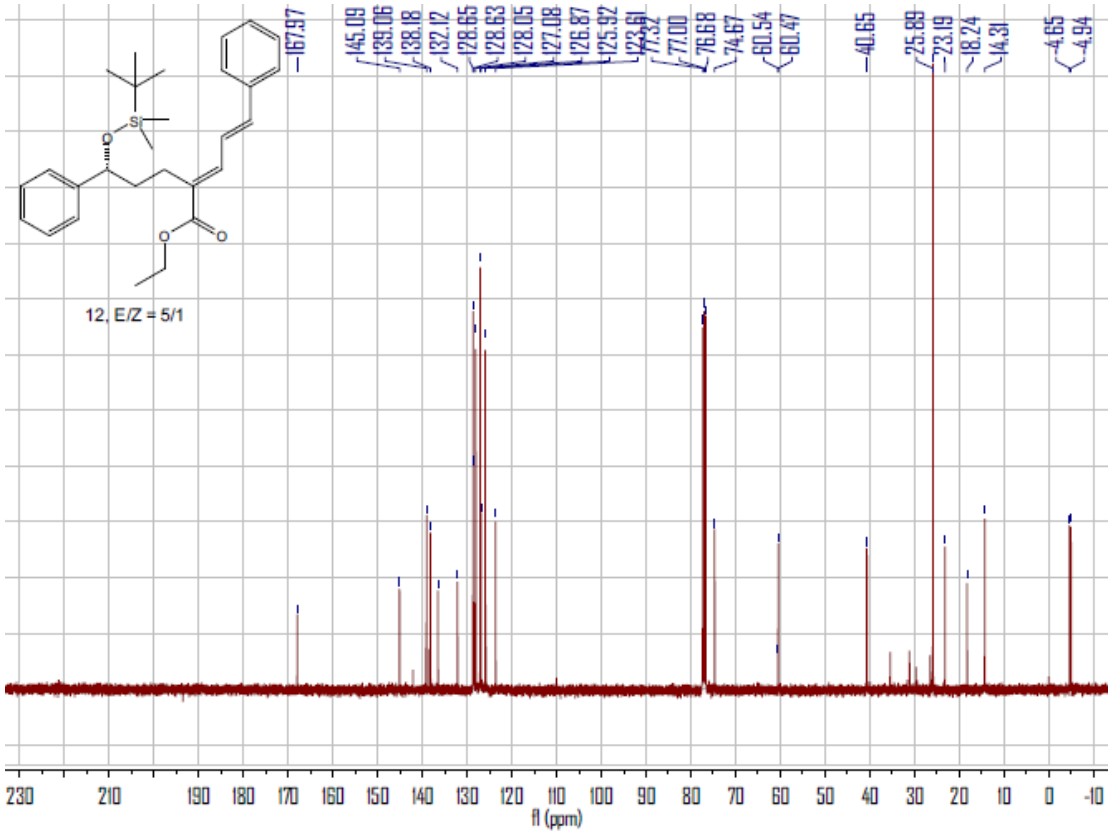


Figure S215. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **14**, related to **Scheme 3**

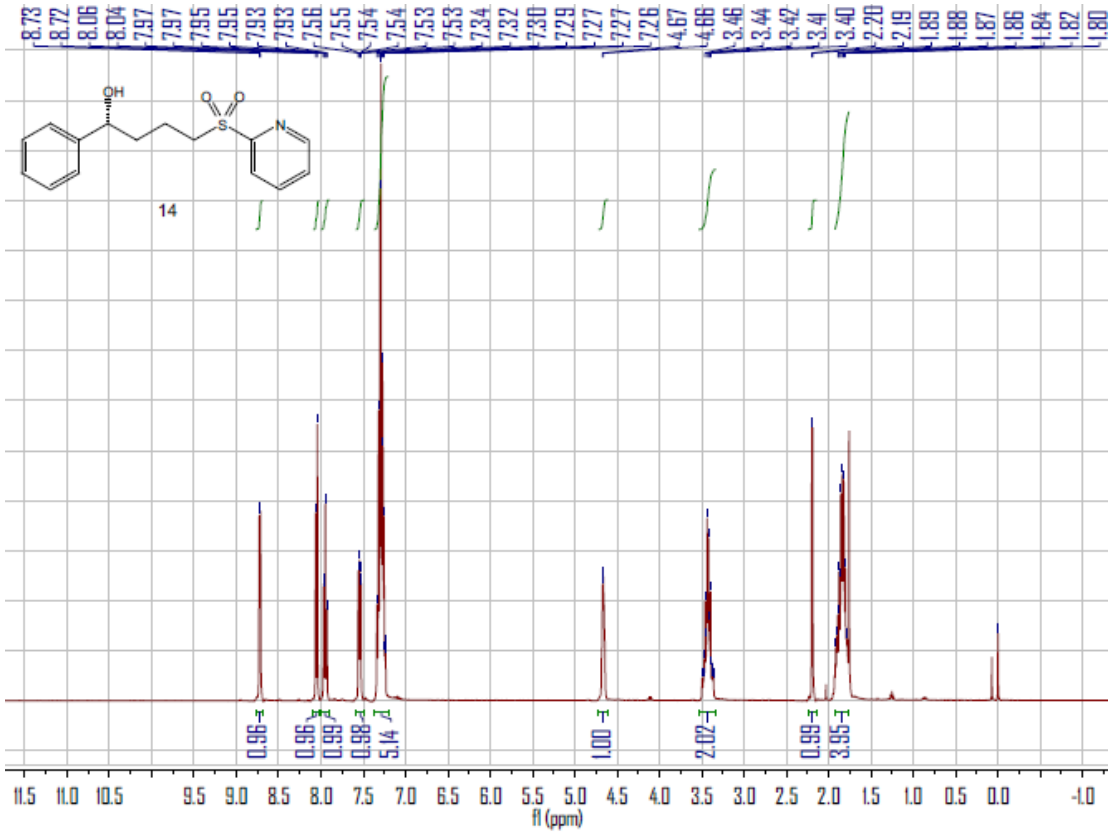


Figure S216. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **14**, related to **Scheme 3**

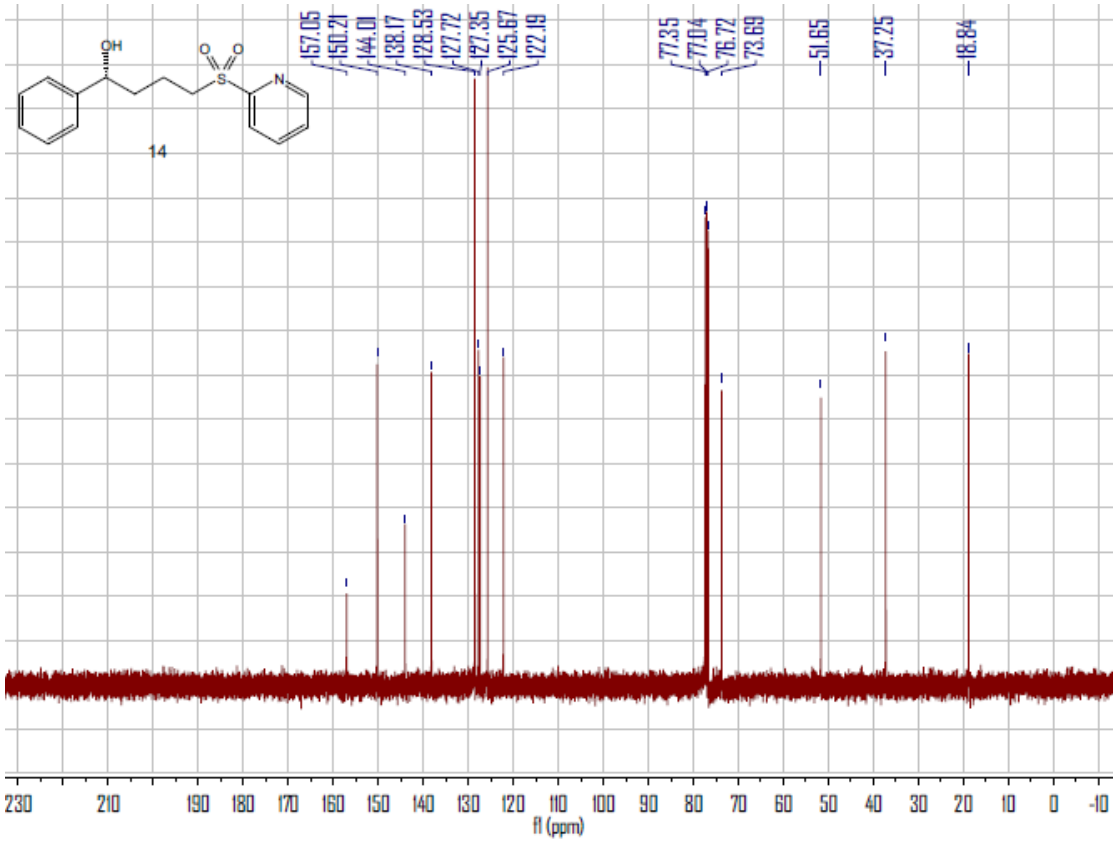


Figure S217. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **15**, related to **Scheme 3**

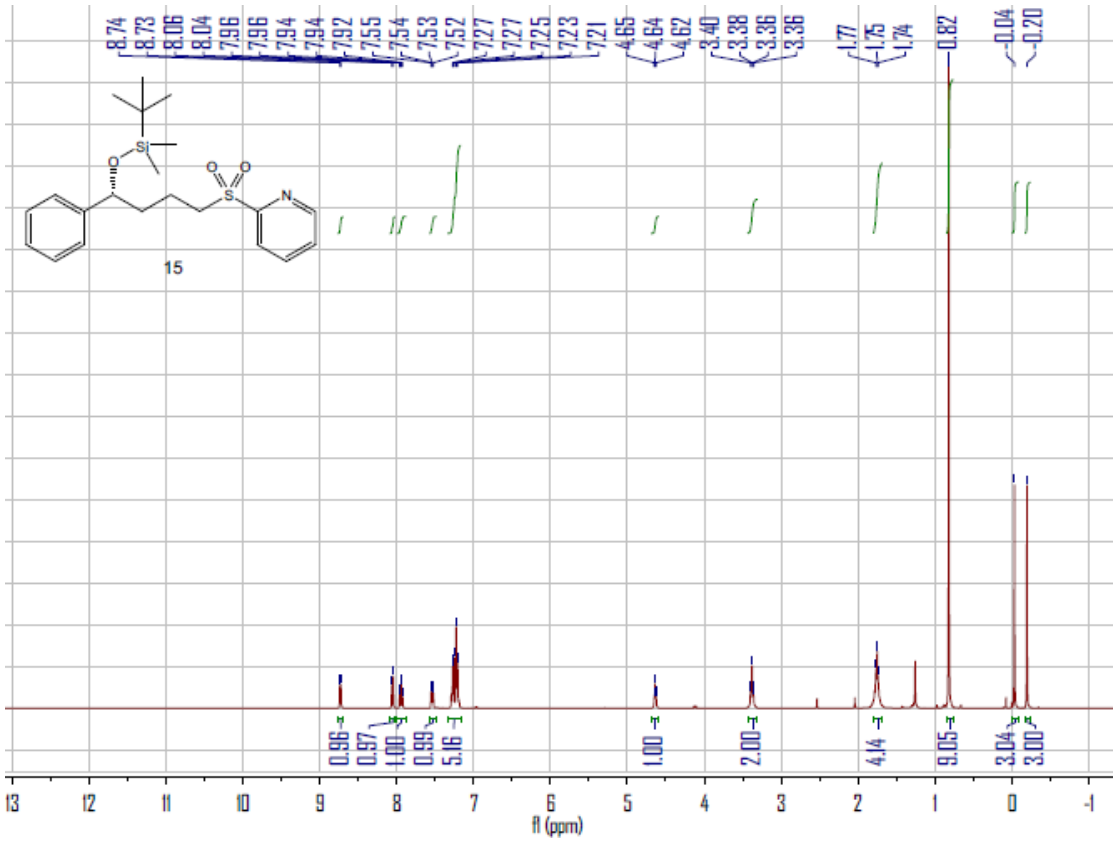


Figure S218. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **15**, related to **Scheme 3**

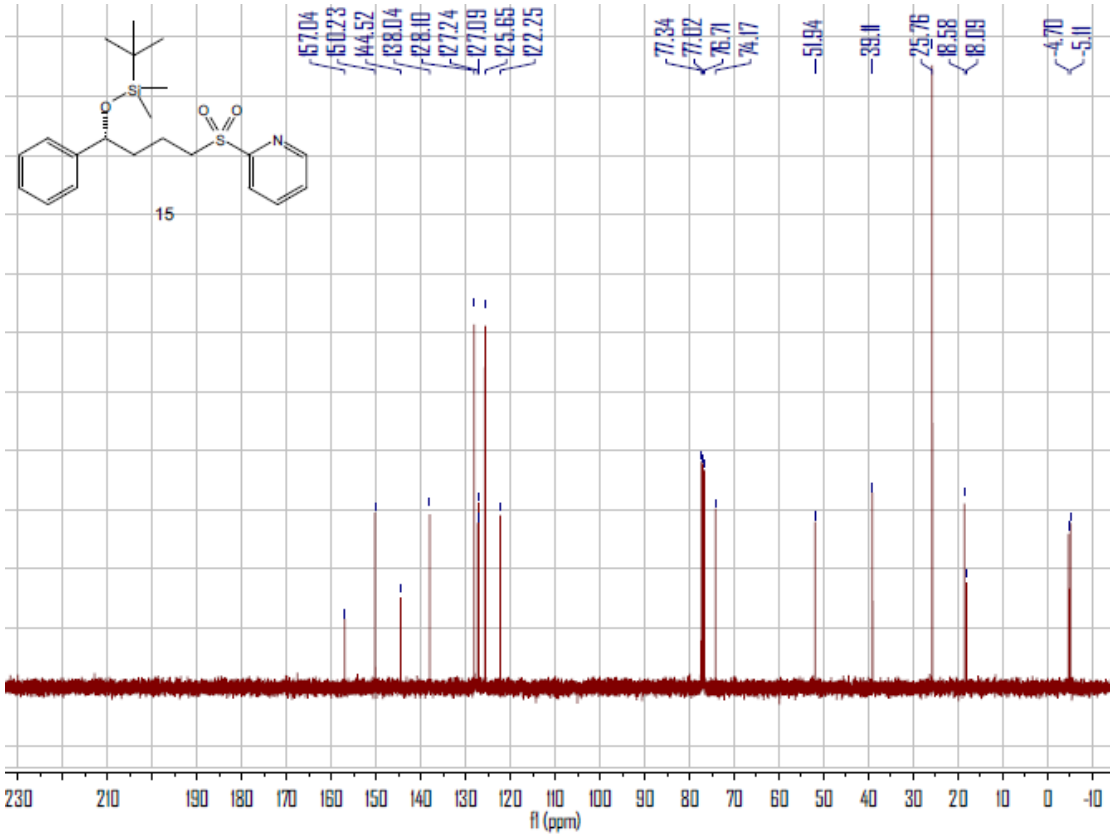


Figure S219. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **16**, related to **Scheme 3**

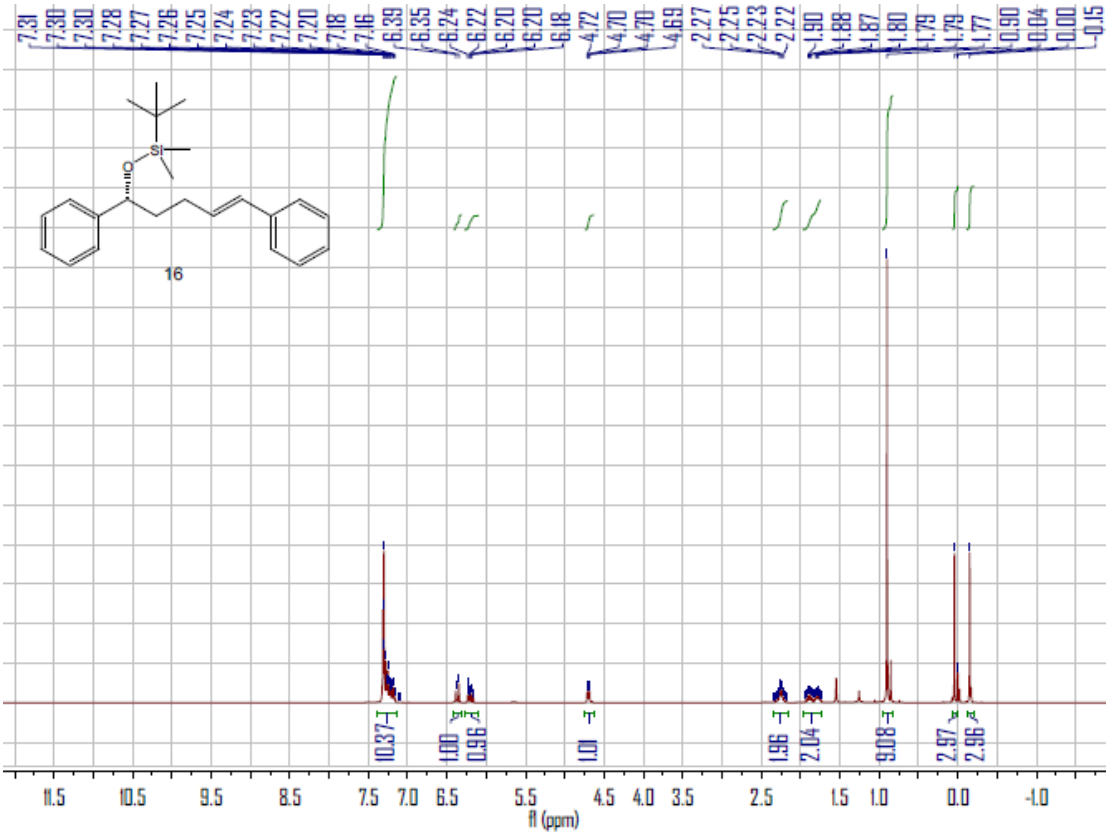


Figure S220. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **16**, related to **Scheme 3**

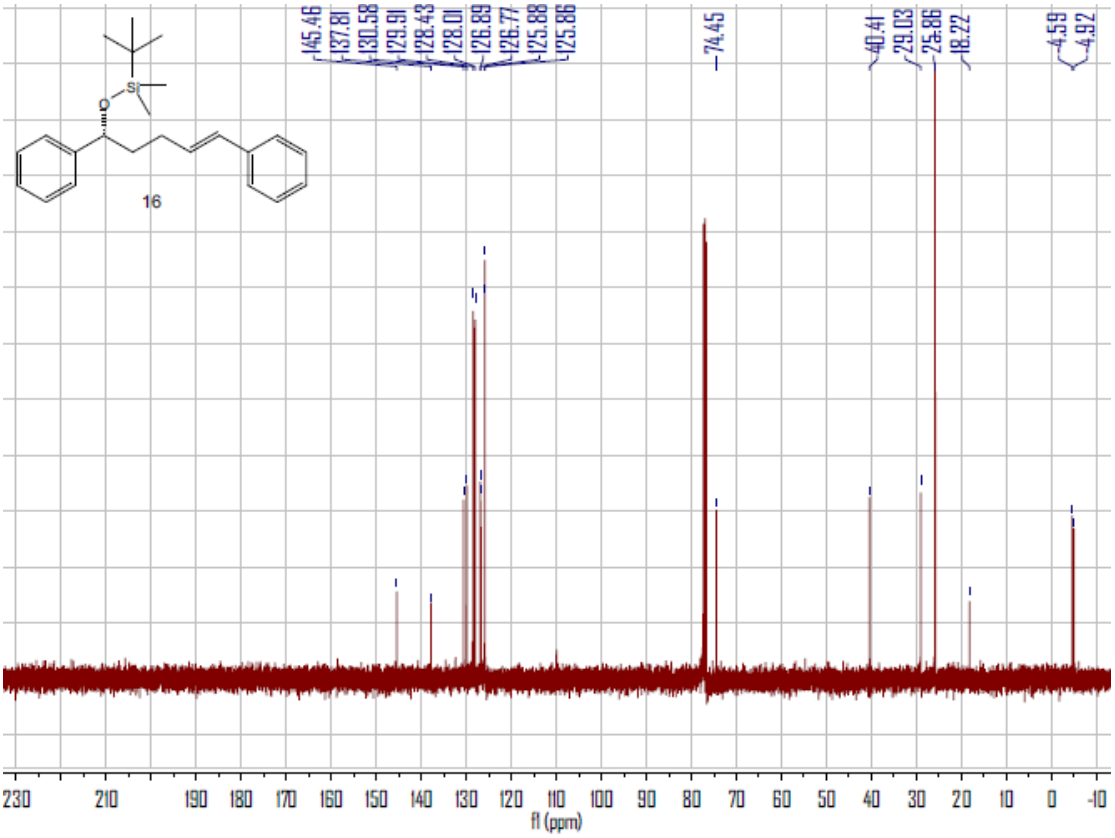


Figure S221. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **17**, related to **Scheme 3**

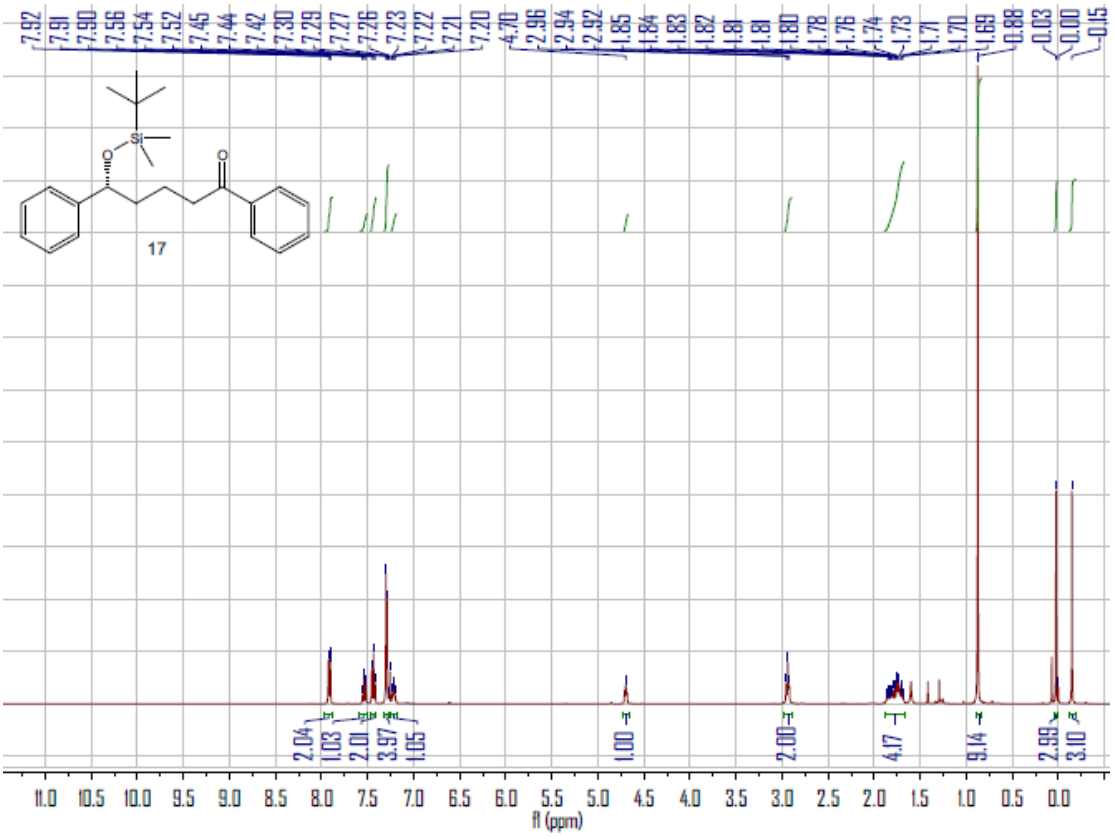


Figure S222. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **17**, related to **Scheme 3**

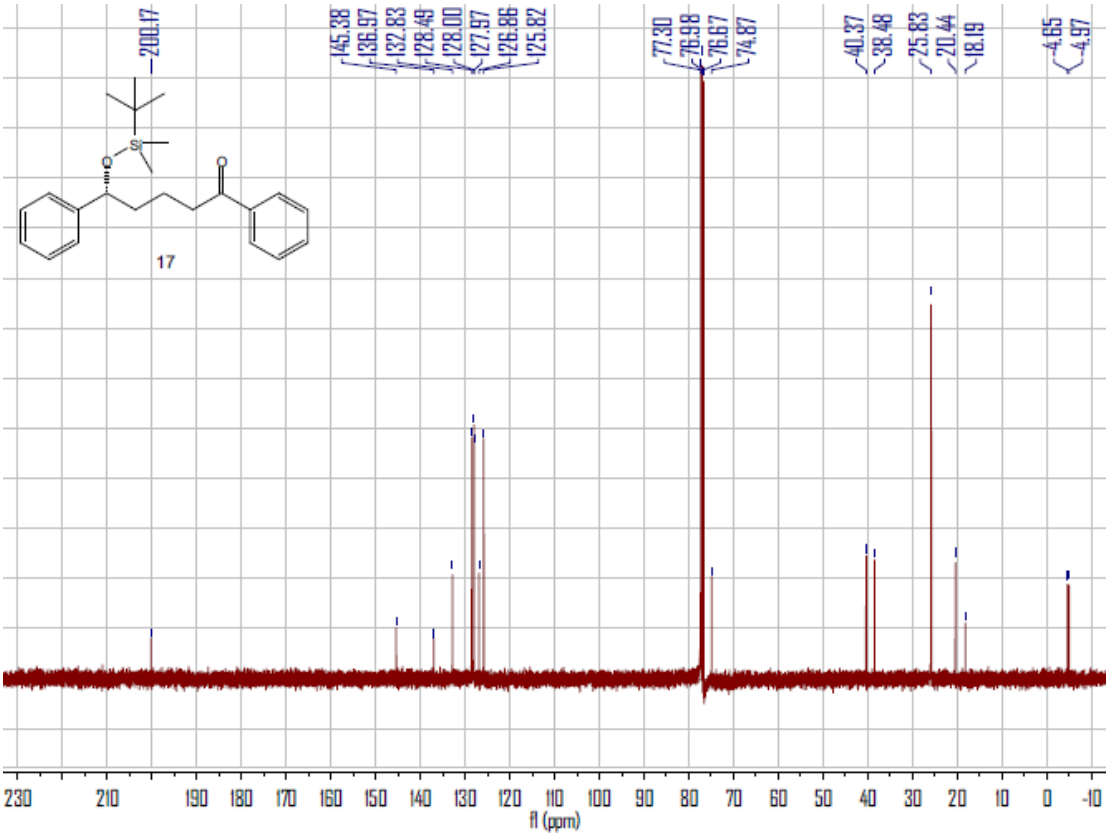


Figure S223. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **18**, related to **Scheme 3**

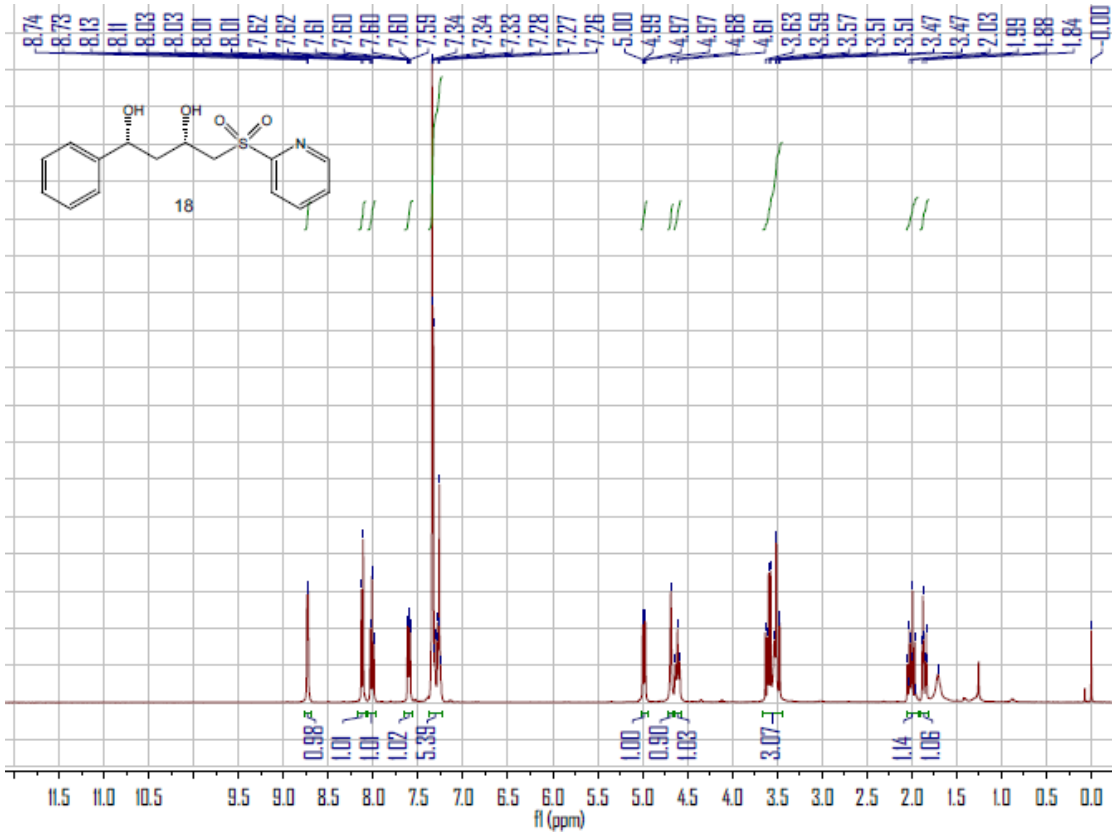


Figure S224. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **18**, related to **Scheme 3**

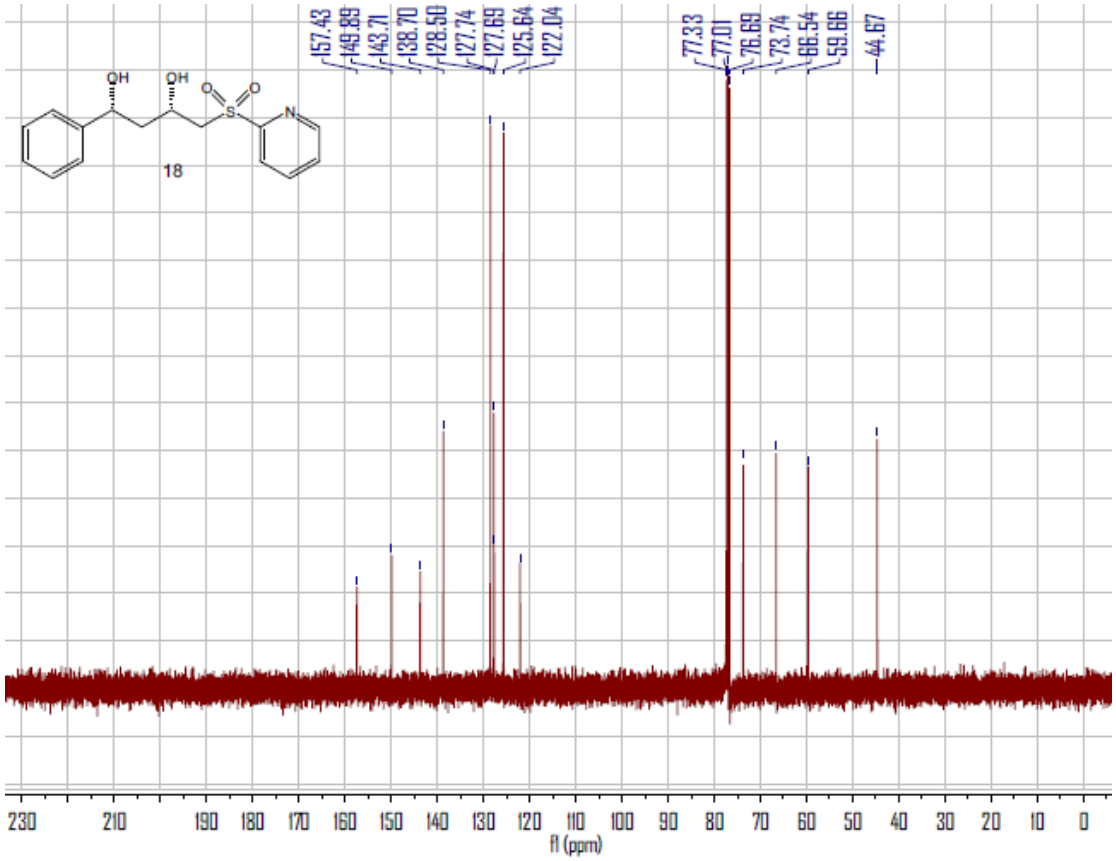


Figure S225. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **19**, related to **Scheme 3**

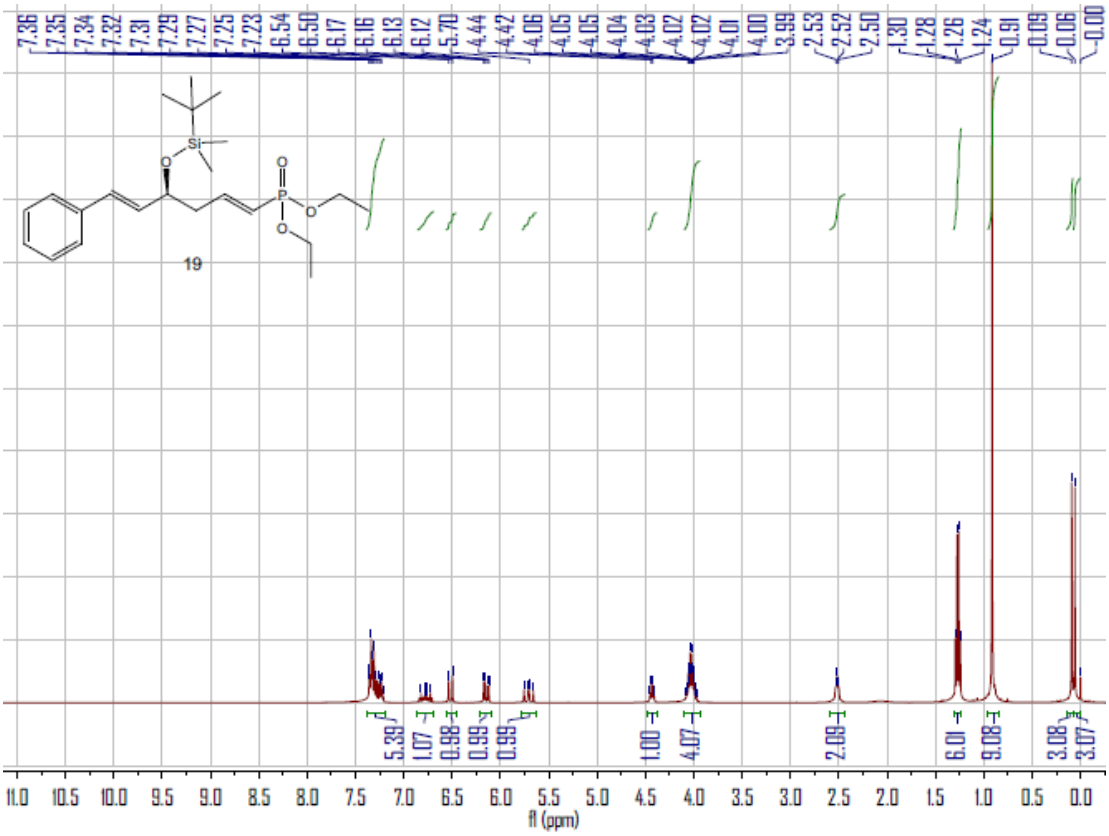


Figure S226. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **19**, related to **Scheme 3**

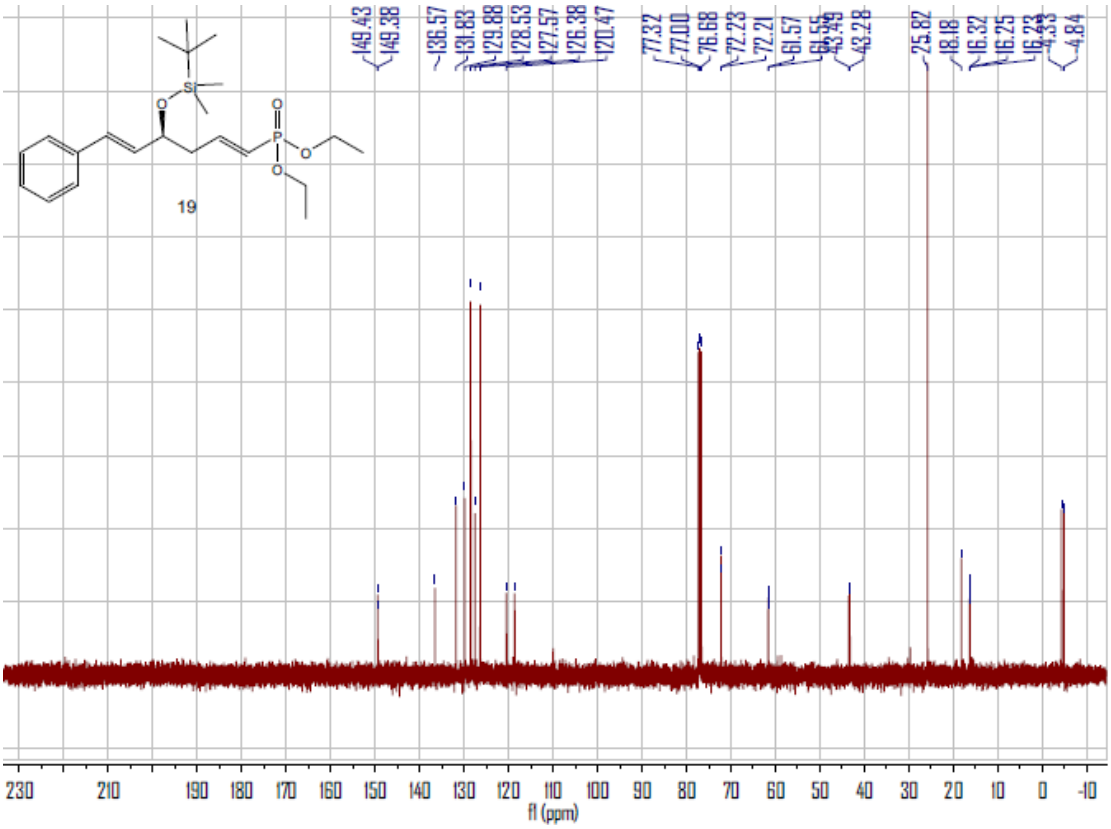


Figure S227. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **19**, related to **Scheme 3**

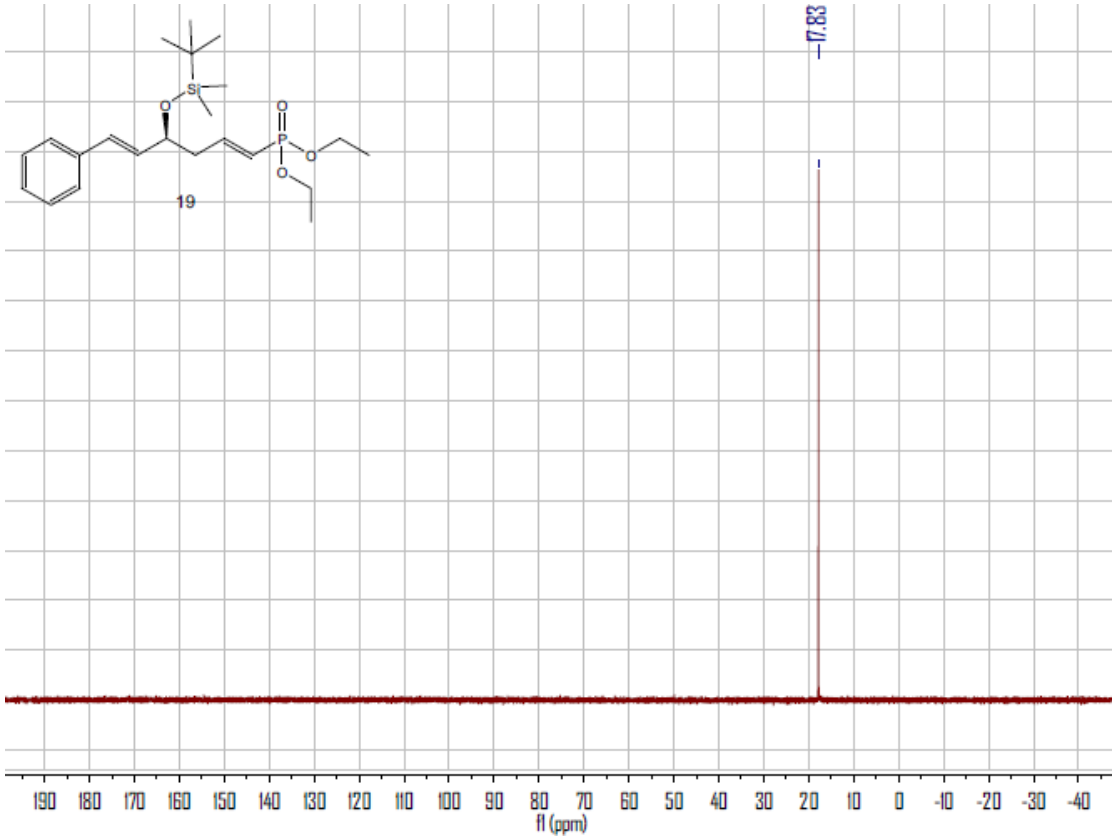


Figure S228. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **20**, related to **Scheme 3**

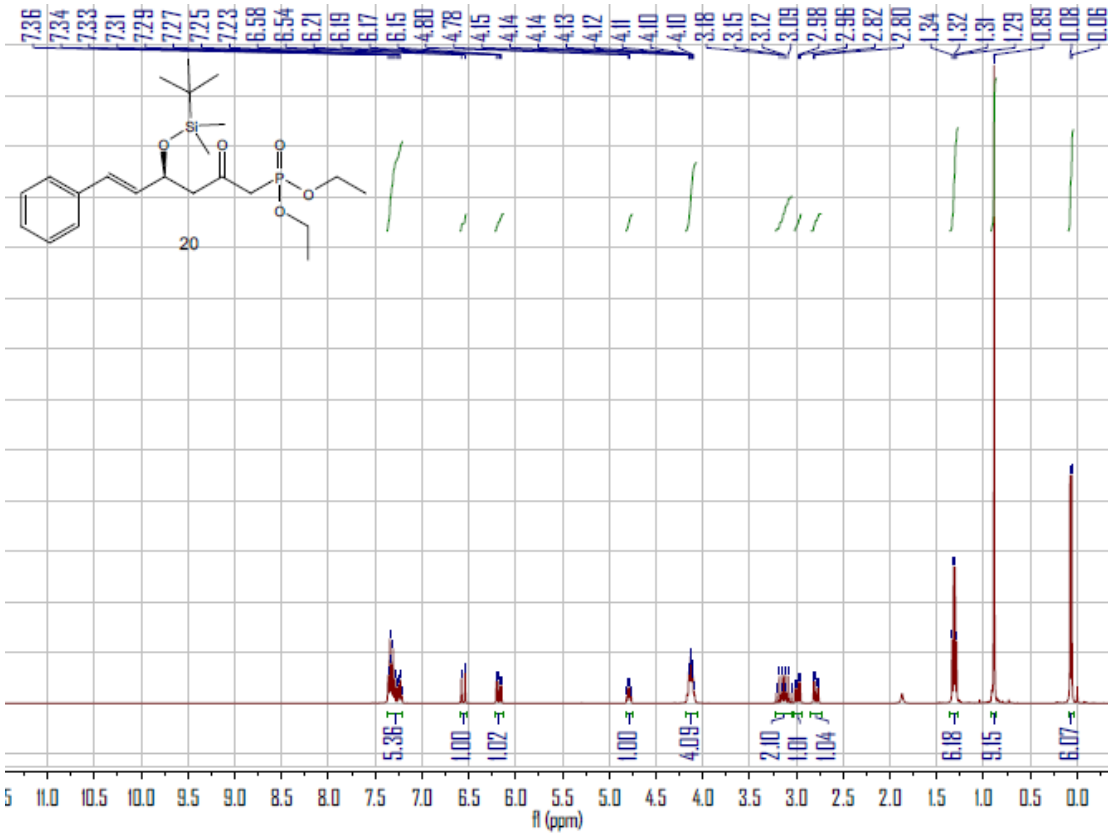


Figure S229. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **20**, related to **Scheme 3**

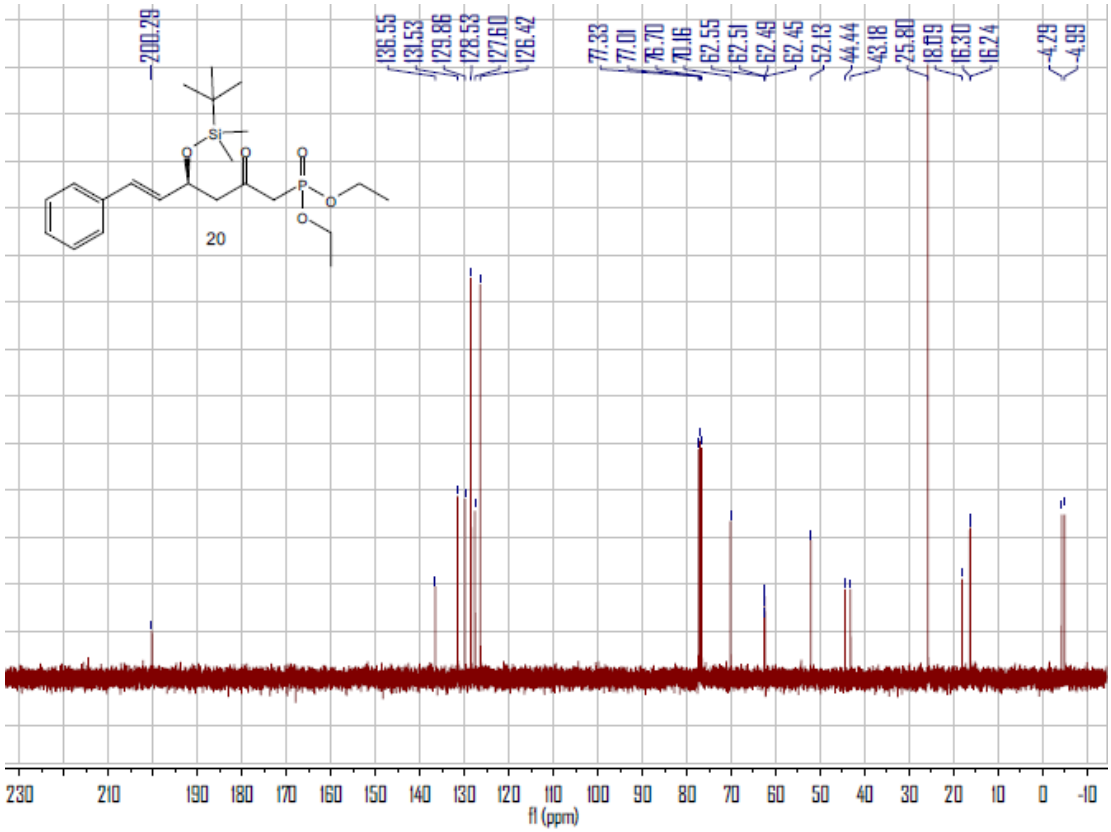


Figure S230. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **20**, related to **Scheme 3**

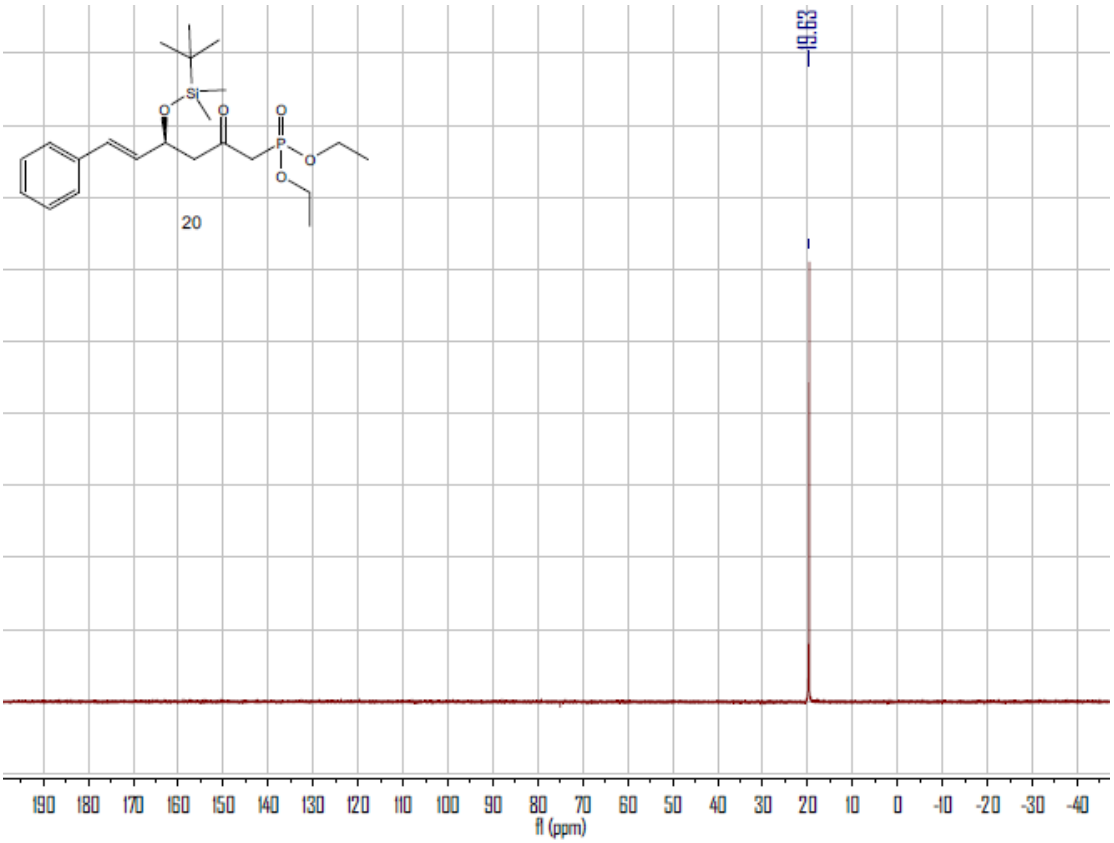


Figure S231. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **21**, related to **Scheme 3**

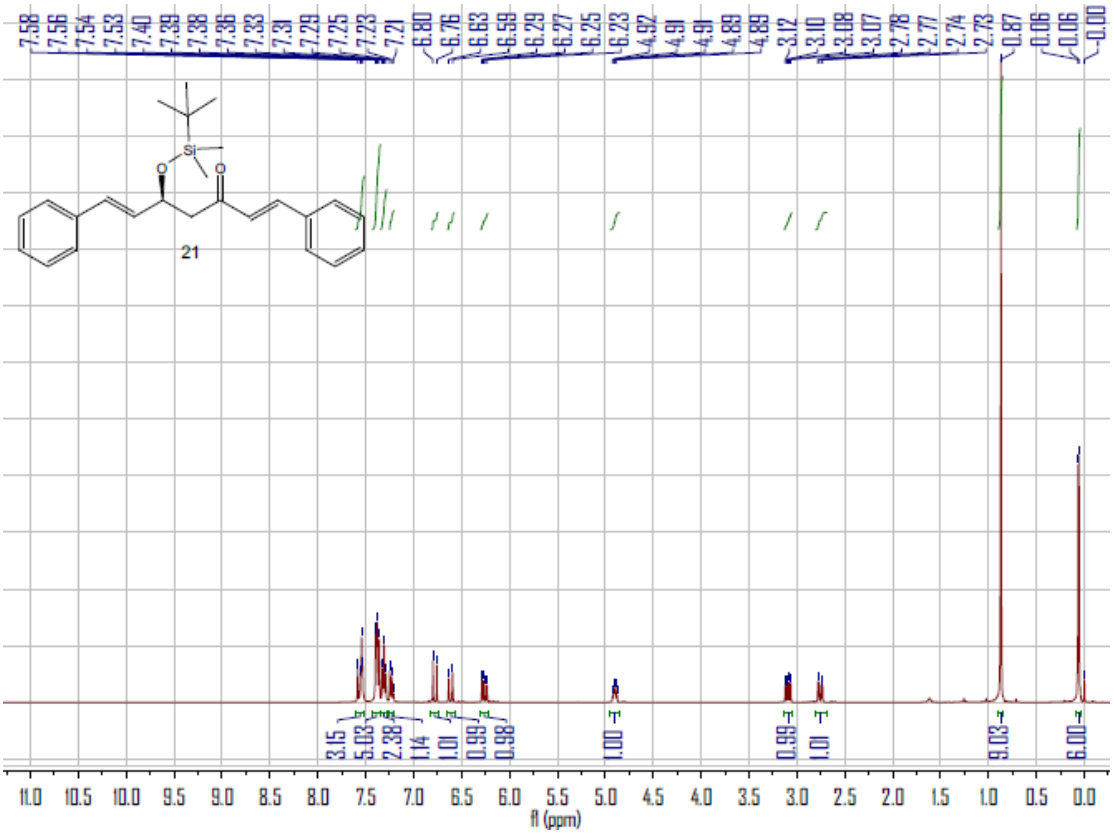


Figure S232. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **21**, related to **Scheme 3**

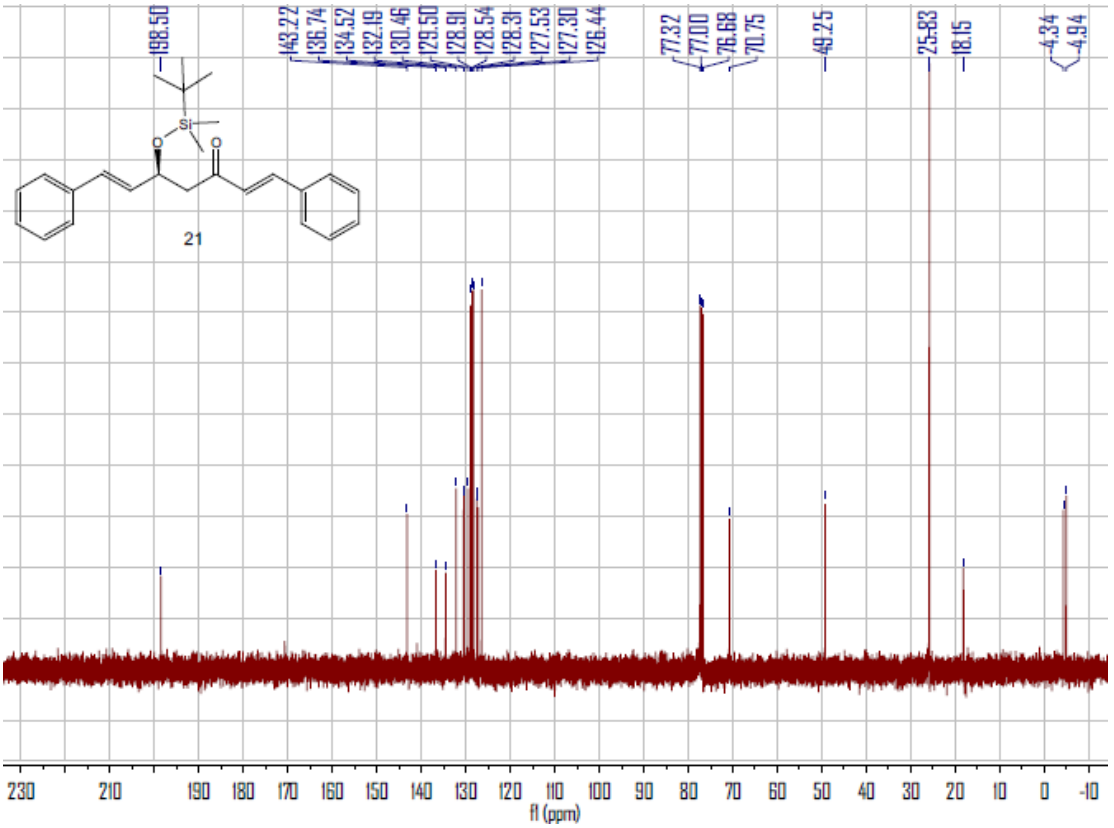


Figure S233. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **22**, related to **Scheme 3**

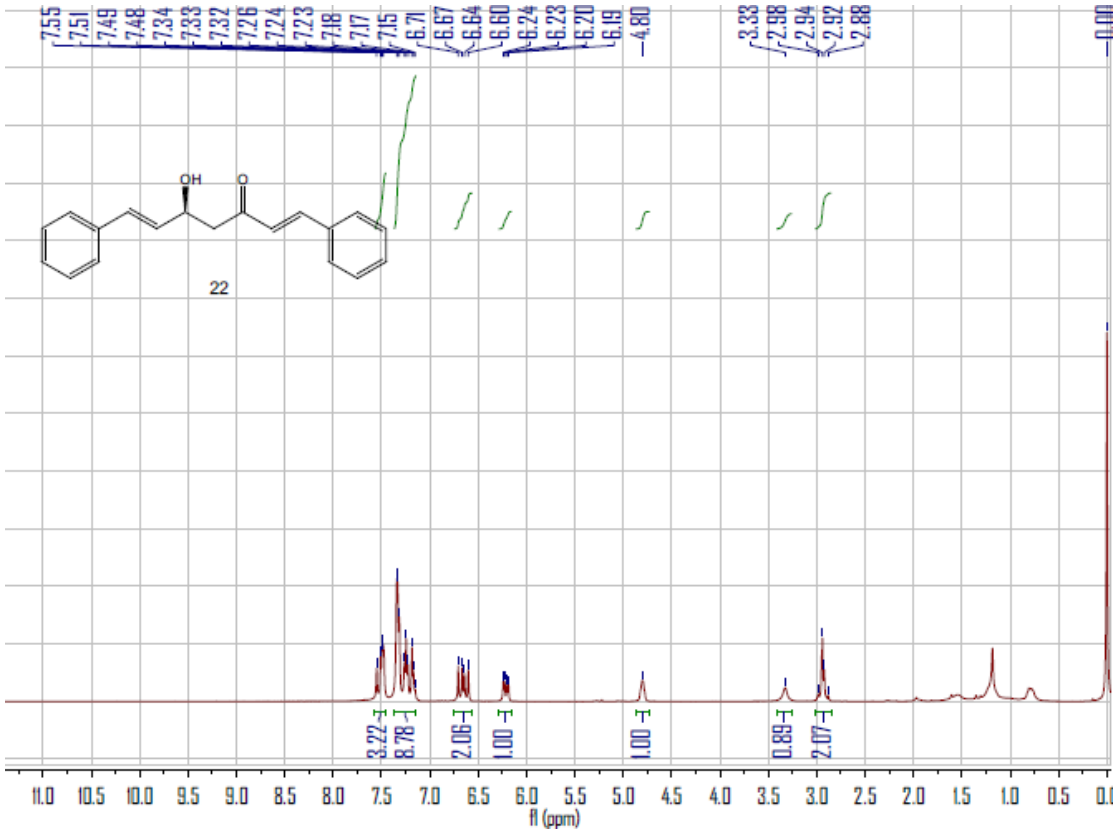


Figure S234. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **22**, related to **Scheme 3**

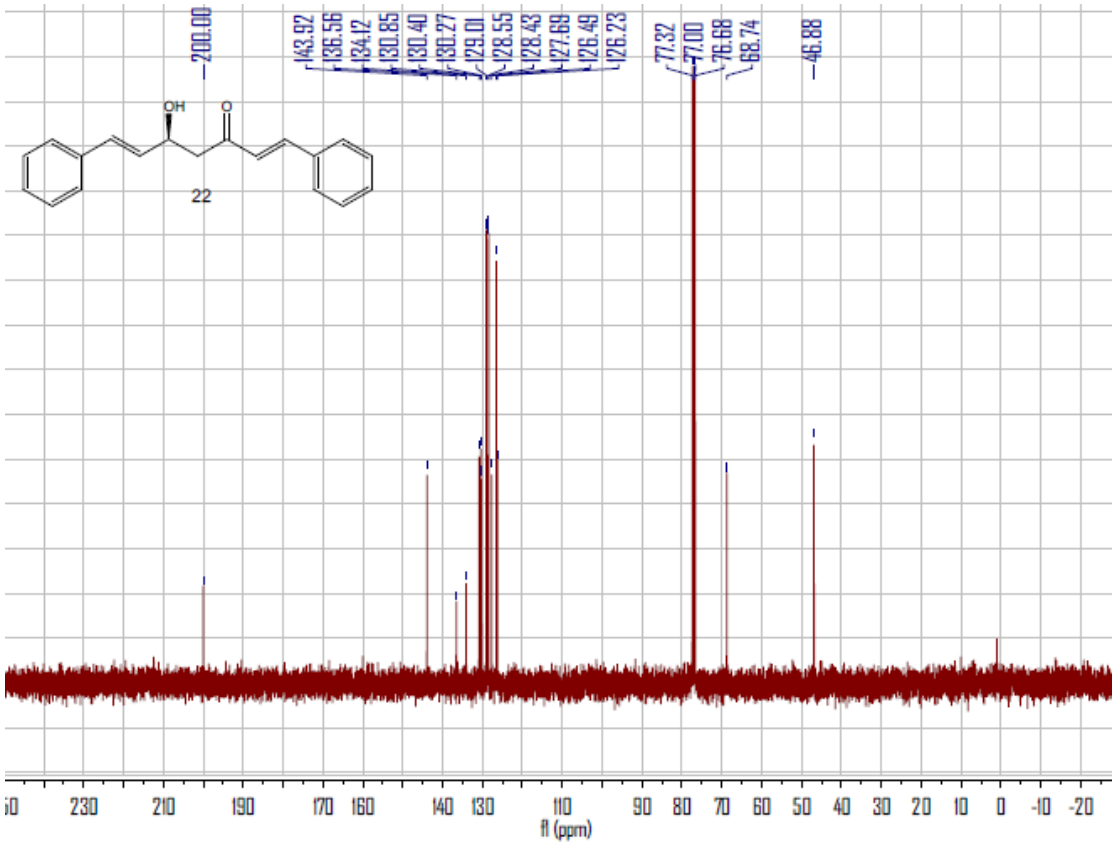


Figure S235. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **23**, related to **Scheme 3**

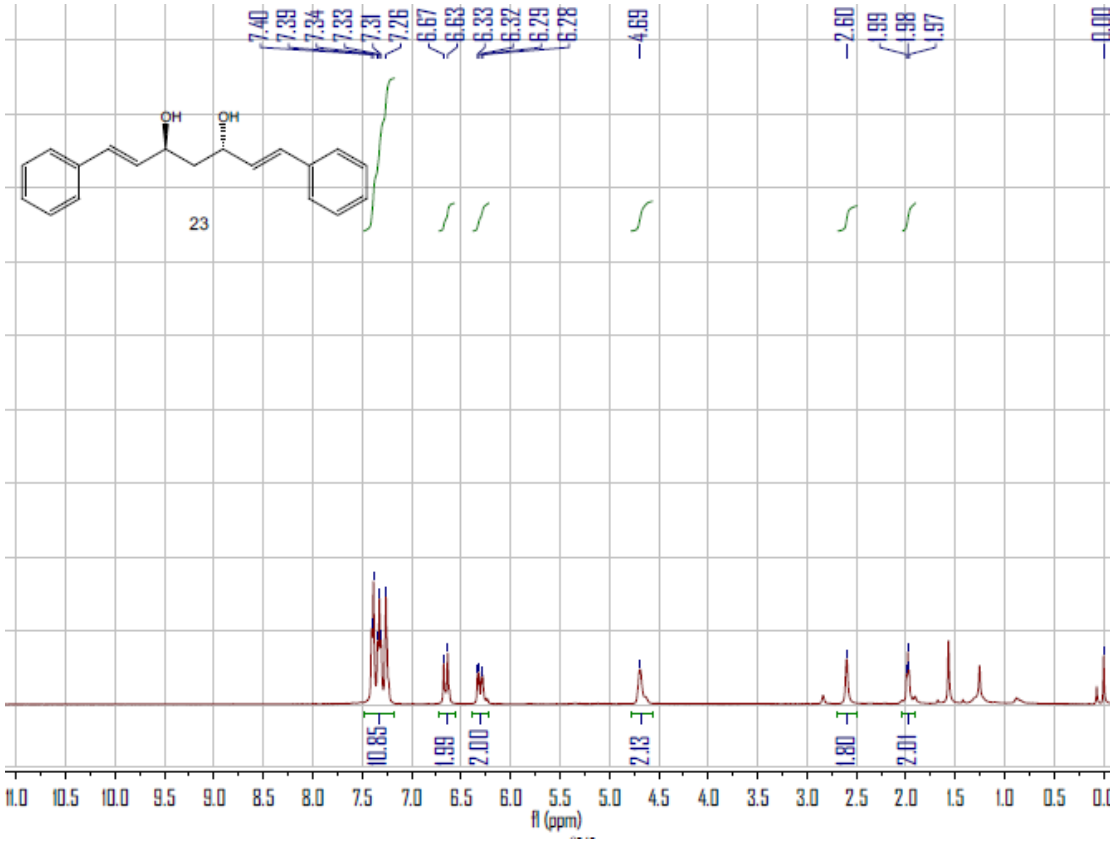


Figure S236. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **23**, related to **Scheme 3**

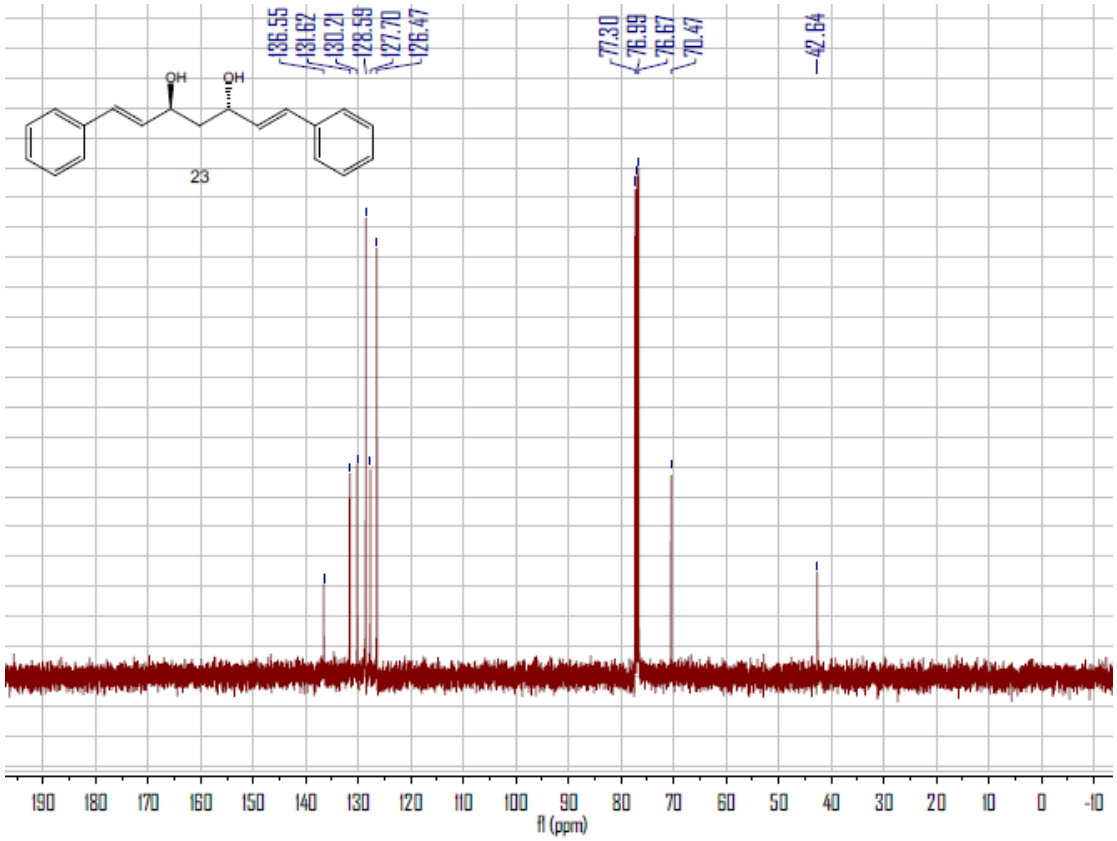


Figure S237. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **yashabushidiol B**, related to **Scheme 3**

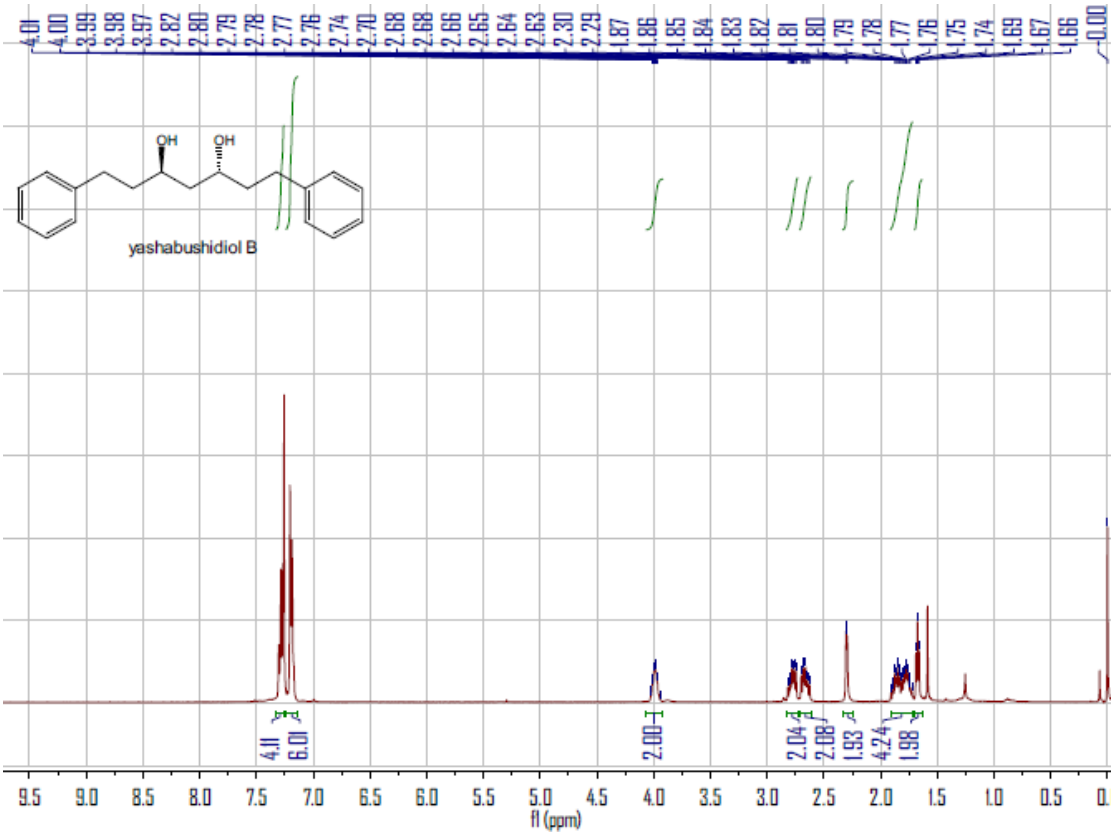
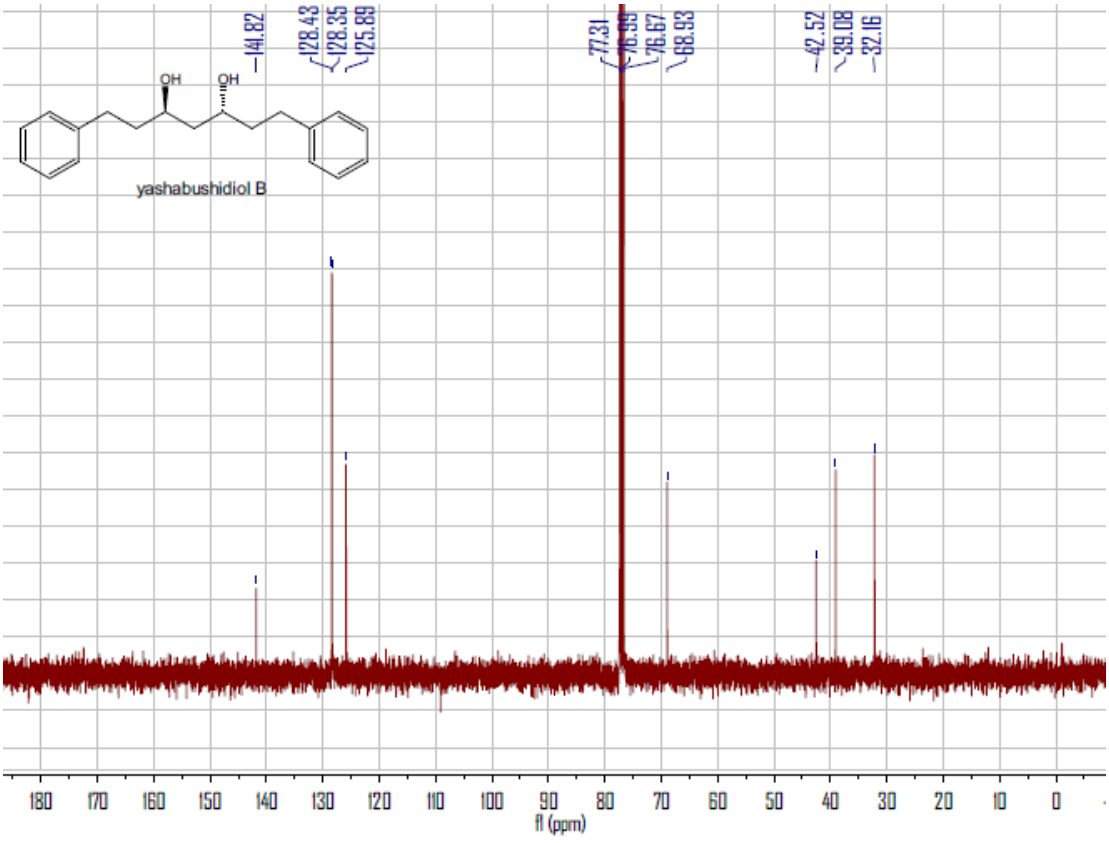


Figure S238. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **yashabushidiol B**, related to **Scheme 3**



Transparent Methods

All reagents were obtained commercially unless otherwise noted. Nuclear Magnetic Resonance (NMR) spectra were acquired on an Agilent 400 or Bruker 400 spectrometer. For ^{1}H NMR, chemical shifts were reported in δ ppm referenced to an internal $SiMe_4$ standard. For ^{19}F NMR, $CFCl_3$ was used as the reference with chemical shift at 0 ppm. For ^{13}C NMR, chemical shifts were reported in the scale relative to NMR solvent ($CDCl_3$: 77.0 ppm) as an internal reference. ^{31}P NMR spectra were referenced externally to phosphoric acid. Multiplicities are reported using the following abbreviations: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet. Mass spectra (EI) were measured on Agilent Technologies 5973N GC-MS. High-resolution mass spectra (EI) were measured on Waters Micromass GCT Premier spectrometer. Mass spectra (ESI) were measured on Agilent Technologies 1100 Series LC-MS. High-resolution mass spectra (ESI) were measured on Thermo Scientific LTQ FT Ultra FT-MS. Mass spectra (DART) and high-resolution mass spectra (DART) were measured on Thermo Fisher Scienticfic LTQ FTICR-MS. Infrared (IR) spectra were recorded on Thermo Scientific Nicolet iS5 FT-IR. Optical rotation was measured using a 1 mL cell with 1.0 dm path length on a JASCO P-1030 polarimeter. HPLC analysis was conducted on a Shimadzu HPLC system equipped with Daicel chiral-stationary-phase columns (4.6 mm×250 mm).

The procedure for preparation of 2ah: A solution of (triphenylphosphoranylidene)-acetaldehyde (3.04 g, 10 mmol, 1.0 equiv) and dec-5-ynal (1.52 g, 10 mmol, 1.0 equiv) in absolute chloroform (concentration of the aldehyde: 0.3 M) was refluxed until no further reaction progress was monitored by GC/MS. Then the reaction mixture was adsorbed on a small amount of silica gel and was purified by column chromatography (petroleum ether/ethyl acetate = 100/1 to 80/1) to afford the aldehyde **2ah** (0.54 g, 3 mmol, 30% yield) as a pale green oil.

General procedure for catalytic asymmetric direct vinylogous aldol-type reaction of aldehydes and allyl phosphonate:

Procedure A:

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with $[Cu(CH_3CN)_4]PF_6$ (5.6 mg, 0.15 mmol, 0.05 equiv) and (*R*)-DTBM-SEGPHOS (17.7 mg, 0.15 mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (2.0 mL, 0.15 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. Then allyl phosphonate **1** (160.4 mg, 0.9 mmol, 3.0 equiv) and aldehyde **2** (0.3 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -10 °C, Barton's Base (12 μL, 0.06 mmol, 0.20 equiv) was added. The resulting reaction mixture was stirred at -10 °C for 48 hours. Then, the reaction mixture was quenched by acetic acid (300 μL (0.4 M in THF), 0.12 mmol, 0.40 equiv) and was stirred for additional 20 minutes at -10 ^{o}C. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate/methanol) to give the desired product.

Procedure B:

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with $[Cu(CH_3CN)_4]PF_6$ (5.6 mg, 0.15 mmol, 0.05 equiv) and (*S*)-DTBM-SEGPHOS (17.7 mg, 0.15

mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (2.0 mL, 0.15 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. Then allyl phosphonate **1** (160.4 mg, 0.9 mmol, 3.0 equiv) and aldehyde **2** (0.3 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -10 °C, Barton's Base (12 μL, 0.06 mmol, 0.20 equiv) was added. The resulting reaction mixture was stirred at -10 °C for 48 hours. Then, the reaction mixture was quenched by acetic acid (300 μL (0.4 M in THF), 0.12 mmol, 0.40 equiv) and was stirred for additional 20 minutes at -10 ^{o}C. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate/methanol) to give the desired product.

General procedure for catalytic asymmetric direct vinylogous aldol-type reaction of aldehydes and allyl sulfone:

Procedure A:

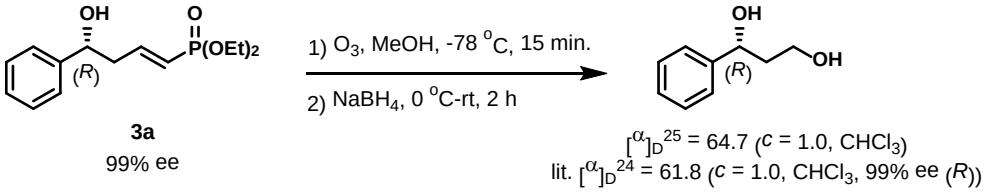
A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with $[Cu(CH_3CN)_4]PF_6$ (5.6 mg, 0.15 mmol, 0.05 equiv) and (*R*)-DTBM-SEGPHOS (17.7 mg, 0.15 mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (2.0 mL, 0.15 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. Then allyl sulfone **4** (109.9 mg, 0.6 mmol, 2.0 equiv) and aldehyde **2** (0.3 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -40 °C, Barton's Base (18 μL, 0.09 mmol, 0.30 equiv) was added. The resulting reaction mixture was stirred at -40 °C for 36 hours. Then, the reaction mixture was quenched by acetic acid (300 μL (0.4 M in THF), 0.12 mmol, 0.40 equiv) and was stirred for additional 20 minutes at -40 ^{o}C. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to give the desired product.

Procedure B:

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with $[Cu(CH_3CN)_4]PF_6$ (5.6 mg, 0.15 mmol, 0.05 equiv) and (*S*)-DTBM-SEGPHOS (17.7 mg, 0.15 mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (2.0 mL, 0.15 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. Then allyl sulfone **4** (109.9 mg, 0.6 mmol, 2.0 equiv) and aldehyde **2** (0.3 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -40 °C, Barton's Base (18 μL, 0.09 mmol, 0.30 equiv) was added. The resulting reaction mixture was stirred at -40 °C for 36 hours. Then, the reaction mixture was quenched by acetic acid (300 μL (0.4 M in THF), 0.12 mmol, 0.40 equiv) and was stirred for additional 20 minutes at -40 ^{o}C. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to give the desired product.

The procedure for determination of the absolute configuration of 3a

Absolute configuration of **3a** was determined by its transformation to (*R*)-1-phenylpropane-1,3-diol as shown below and the comparison of its optical rotation with the one reported in literature (Denmark et. al., 2004).



3a
99% ee

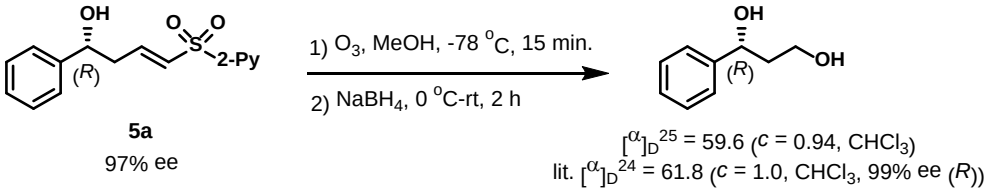
$[\alpha]_D^{25}$ = 64.7 (*c* = 1.0, $CHCl_3$)
lit. $[\alpha]_D^{24}$ = 61.8 (*c* = 1.0, $CHCl_3$, 99% ee (*R*))

Figure S239, related to **Table 2**

Ozone was bubbled into a solution of **3a** (110 mg, 0.39 mmol, 1.0 equiv) in MeOH (5.0 mL) at -78 °C until the appearance of a persistent blue color (about 30 min). The reaction solution was then allowed to warm up to 0 °C and the mixture was subsequently treated with $NaBH_4$ (73.8 mg, 1.95 mmol, 5 equiv.) at 0°C. The reaction mixture was allowed to warm up to room temperature and was stirred for additional 2 hours. Then, the reaction was quenched by H_2O (5 mL) and extracted with DCM (15 mL×3). The combined organic layers were dried over Na_2SO_4. After removal of solvent under reduced pressure, the crude was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to afford (*R*)-1-phenylpropane-1,3-diol (39 mg, colorless oil, 67% yield).

The procedure for determination of the absolute configuration of 5a

Absolute configuration of **5a** was determined by its transformation to (*R*)-1-phenylpropane-1,3-diol as shown below and the comparison of its optical rotation with the one reported in literature (Denmark et. al., 2004).



5a
97% ee

$[\alpha]_D^{25}$ = 59.6 (*c* = 0.94, $CHCl_3$)
lit. $[\alpha]_D^{24}$ = 61.8 (*c* = 1.0, $CHCl_3$, 99% ee (*R*))

Figure S240, related to **Table 3**

Ozone was bubbled into a solution of **5a** (94 mg, 0.33 mmol, 1.0 equiv) in MeOH (5.0 mL) at -78 °C until the appearance of a persistent blue color (about 30 min). The reaction solution was then allowed to warm up to 0 °C and the mixture was subsequently treated with $NaBH_4$ (62.4 mg, 1.65 mmol, 5 equiv.) at 0°C. The reaction mixture was allowed to warm up to room temperature and was stirred for additional 2 hours. Then, the reaction was quenched by H_2O (5 mL) and extracted with DCM (15 mL×3). The combined organic layers were dried over Na_2SO_4. After removal of solvent under reduced pressure, the crude was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to afford (*R*)-1-phenylpropane-1,3-diol (21 mg, colorless oil, 42% yield).

The procedure for preparation of *rac*-3a:

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with $[Cu(CH_3CN)_4]PF_6$ (9.3 mg, 0.025 mmol, 0.05 equiv) and *rac*-DTBM-SEGPHOS (29.5 mg, 0.025 mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (2.0 mL, 0.25 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. Then allyl phosphonate **1** (267.3 mg, 1.5 mmol, 3.0 equiv) and

aldehyde **2a** (53.1mg, 0.5 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -10 °C, Barton's Base (17.1mg, 0.10 mmol, 0.20 equiv) was added. The resulting reaction mixture was stirred at -10 °C for 48hours. Then, the reaction mixture was quenched by acetic acid (500 μL(0.4 M in THF), 0.20 mmol, 0.40 equiv) and was stirred for additional 20 minutes at -10 ^{o}C. Then the volatives wereremoved under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate/methanol = 30/15/1) to give ***rac*-3a**(128.0 mg, 90% yield) as a colorless oil.

The procedure for preparation of *rac*-5a:

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with $[Cu(CH_3CN)_4]PF_6$ (11.2 mg, 0.030 mmol, 0.05 equiv) and *rac*-DTBM-SEGPHOS (35.4 mg, 0.030 mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (2.0 mL, 0.30 M) was added via a syringe. The mixture was stirred for 15 minutes to give a colorless catalyst solution. Then allyl sulfone **4** (220.0 mg, 1.2 mmol, 2.0 equiv) and aldehyde **2a** (63.7mg, 0.6 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -40 °C, Barton's Base (30.8mg, 0.18 mmol, 0.30 equiv) was added. The resulting reaction mixture was stirred at -40 °C for 12 hours. Then, the reaction mixture was quenched by acetic acid (600 μL (0.4 M in THF), 0.20 mmol, 0.40 equiv), and was stirred for additional 20 minutes at -40 ^{o}C. Then the volatives were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/2) to give ***rac*-5a** (110.0 mg, 63% yield) as pale green powders.

The procedure for preparation of *rac*-α–3a:

***rac*-3a** was prepared according to a reported procedure (Yuan et. al., 1991). A dried 50 mL round bottom flask equipped with a magnetic stirring bar was charged with allyl phosphonate **1** (534.5 mg, 3.0 mmol, 1.0 equiv) under N_2 atmosphere. Anhydrous THF (10 mL) was added via a syringe. The mixture was cooled to -78 ^{o}C and was stirred for 10 minutes. Then ^{n}BuLi (1.3 mL (2.5 M solution in hexane), 3.15 mmol, 1.05 equiv) was added via a syringe. After 30 minutes, benzaldehyde **2a** (318.4 mg, 3 mmol, 1.0 equiv) was added via a syringe and the mixture was stirred for 30 minutes. The reaction was quenched by saturated aqueous NH_4Cl (5 mL) at -78 ^{o}C. The aqueous phase was extracted with ethyl acetate (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and the volatives were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate/methanol = 14/7/1) to give ***rac*-α-3a** (724.9 mg, 85% yield, dr = 2.5/1) as a colorless oil.

The procedure for preparation of *rac*-α-5a :

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with LDA (1.0 mL (2 M solution in hexane/THF), 2 mmol, 1.0 equiv) under N_2 atmosphere. Anhydrous THF (2 mL) was added via a syringe. The mixture was cooled to -78 ^{o}C and HMPA (358.4 mg, 2 mmol, 1.0 equiv) was added via a syringe. The resulting mixture was stirred at -78 ^{o}C for 30 minutes and then allyl sulfone **5** (439.8 mg, 2.4 mmol, 1.2 equiv) was added. After 30 minutes, benzaldehyde **2a** (318.4 mg, 3 mmol, 1.5 equiv) was added and the resulting mixture was stirred for 20 minutes. The reaction was quenched by saturated aqueous NH_4Cl (5 mL) at -78 ^{o}C. The aqueous phase was extracted with ethyl acetate (10 mL × 3). The combined organic extracts were dried over

anhydrous Na_2SO_4 and the volatives were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to give ***rac*-α-5a** (101.0 mg, 15% yield, dr = 1/1) as pale green powders.

Proposed Mechanism for the Copper(I)-Catalyzed Asymmetric Aldol-Type Reaction:

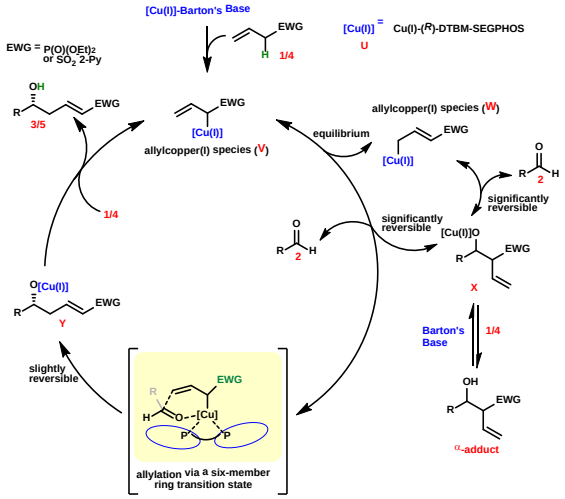


Figure S241, Proposed Mechanism, related to **Scheme 2**

Based on these experimental observations and literature proposals, a postulated reaction pathway was given as shown above. In the presence of copper(I) complex **U** and Barton's Base, the deprotonation of substrate **1**/**4** occurred smoothly to give allylcopper(I) species **V**, which might form an equilibrium with allylcopper(I) species **W**. The α-addition of **V** with aldehyde **2**produced copper(I) alkoxide complex **X**, which afforded α-adduct after protonation with substrate **1**/**4**. As demonstrated by the experiments, the α-addition was a significantl yreversible process. It waspossible that the γ-addition of **W** with aldehyde **2** also furnishedcopper(I) alkoxide complex**X**. The γ-addition ofallylcopper(I) species **V** generated copper(I) alkoxide complex**Y** through a six-memberring transition state, which was identifiedas a slightlyreversible process. The protonation of **Y** with additional substrate **1**/**4** led to γ-adduct.

The procedure for gram-scale preparation of vinylogous product 3a:

A dried 100 mL round bottom flaske quipped with a magnetic stirring bar was charged with $[Cu(CH_3CN)_4]PF_6$ (74.5 mg, 0.20 mmol, 0.05 equiv) and (*R*)-DTBM-SEGPHOS (235.9 mg, 0.20 mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (40 mL, 0.2 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. Then allyl phosphonate **1** (2.140 g, 12 mmol, 3.0 equiv) and benzaldehyde **2a** (424.5 mg, 4.0 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -10 °C, Barton's Base (137.0 mg, 0.80 mmol, 0.20 equiv) was added. The resulting reaction mixture was stirred at -10 °C for 48 hours. Then, the reaction mixture was quenched by acetic acid (4 mL (0.4 M in THF), 1.6 mmol, 0.40 equiv) and was stirred for additional 20 minutes at -10 ^{o}C. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate/methanol = 30/15/1) to give product **3a** (0.990 g, 85% yield, 99% ee) as a colorless oil.

The procedure for gram-scale preparation of vinylogous product 5a:

A dried 100 mL round bottom flaske quipped with a magnetic stirring bar was charged with $[Cu(CH_3CN)_4]PF_6$ (74.5 mg, 0.20 mmol, 0.05 equiv) and (*R*)-DTBM-SEGPHOS (235.9 mg, 0.20 mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (40 mL, 0.1 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. Then allyl sulfone **4** (1.466 g, 12 mmol, 3.0 equiv) and benzaldehyde **2a** (424.5 mg, 4.0 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -40 °C, Barton's Base (205.5 mg, 1.20 mmol, 0.30 equiv) was added. The resulting reaction mixture was stirred at -40 °C for 36 hours. Then, the reaction mixture was quenched by acetic acid (4 mL (0.4 M in THF), 1.6 mmol, 0.40 equiv) and was stirred for additional 20 minutes at -40 °C. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/2) to give product **5a** (1.100 g, 95% yield, 97% ee) as pale green powders.

Transformations of vinylogous product 3a:

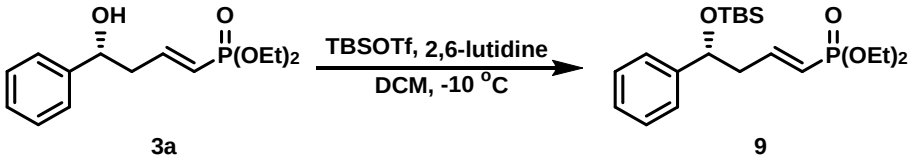


Figure S242, Transformations, related to **Scheme 3**

A dried 50 mL round bottom flask equipped with a magnetic stirring bar was charged with **3a** (250 mg, 0.88 mmol, 1.0 equiv) and 2,6-lutidine (189 mg, 1.76 mmol, 2.0 equiv) under N_2 atmosphere. After the mixture was cooled to -10 °C, TBSOTf (465 mg, 1.76 mmol, 2.0 equiv) was added via a syringe. The resulting mixture was stirred at -10 °C for 7 hours. After removing the volatiles under reduced pressure, the crude was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give product **9** (312 mg, 90% yield) as a colorless oil.

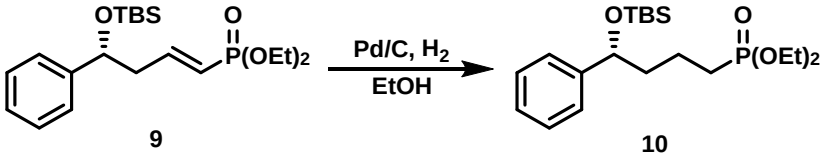


Figure S243, Transformations, related to **Scheme 3**

A dried 25 mL round bottom flask equipped with a magnetic stirring bar was charged with **9** (79.7 mg, 0.20 mmol, 1.0 equiv), Pd/C (16 mg, 5% *w*/*w*) and EtOH (4 mL). The resulting mixture was stirred at room temperature for 3 hours with a ballon filled with H_2. The black solids were filtered off and washed thoroughly with EtOH. The filtrate was concentrated under reduced pressure to give the crude, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give product **10** (78.5 mg, 98% yield) as a colorless oil.

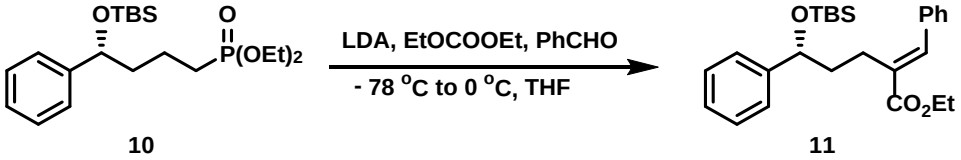


Figure S244, Transformations, related to **Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with LDA

(0.1 mL (2 M solution in hexane/THF), 2 mmol, 1.0 equiv) under N_2 atmosphere. Anhydrous THF (0.2 mL) was added via a syringe. The mixture was cooled to -78 ^oC and **10** (38.1 mg, 0.095 mmol, 1.0 equiv) in THF (0.5 mL) was added dropwise via a syringe. The resulting mixture was stirred at -78 °C for 5 minutes and then EtOCOOEt (11.8 mg, 0.10 mmol, 1.05 equiv) in THF (0.5 mL) was added dropwise via a syringe. The resulting mixture was stirred at -78 °C for 30 minutes and then was warmed to 0 °C. Benzaldehyde **2a** (11.1 mg, 0.105 mmol, 1.1 equiv) in THF (0.5 mL) was added dropwise via a syringe. The resulting mixture was stirred at room temperature overnight and then was quenched by saturated aqueous NH_4Cl (2 mL). The aqueous phase was extracted with diethyl ether (10 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and the volatives were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100/1) to give **11** (32.5 mg, 81% yield, E/Z > 20/1) as a colorless oil.

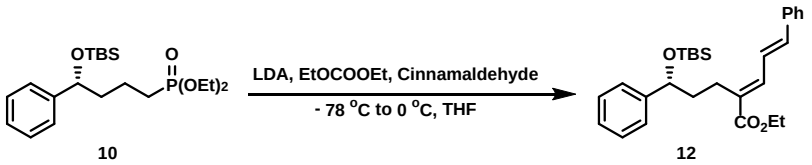


Figure S245, Transformations, related to **Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with LDA (0.105 mL (2 M solution in hexane/THF), 2 mmol, 1.0 equiv) under N_2 atmosphere. Anhydrous THF (0.2 mL) was added via a syringe. The mixture was cooled to -78 ^oC and **10** (40.1 mg, 0.10 mmol, 1.0 equiv) in THF (0.5 mL) was added dropwise via a syringe. The resulting mixture was stirred at -78 °C for 5 minutes and then EtOCOOEt (13.0 mg, 0.105 mmol, 1.05 equiv) in THF (0.5 mL) was added dropwise via a syringe. The resulting mixture was stirred at -78 °C for 30 minutes and then was warmed to 0 °C. Cinnamaldehyde **2y** (14.5 mg, 0.11 mmol, 1.1 equiv) in THF (0.5 mL) was added dropwise via a syringe. The resulting mixture was stirred at room temperature overnight and then was quenched by saturated aqueous NH_4Cl (2 mL). The aqueous phase was extracted with diethyl ether (10 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and the volatives were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100/1) to give **11** (32 mg, 71% yield, E/Z = 5/1) as a colorless oil.

Transformations of vinylogous product 5a:

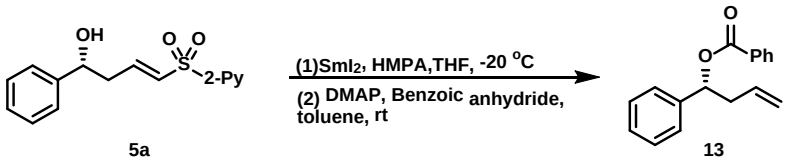


Figure S246, Transformations, related to **Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with **5a** (57.9 mg, 0.2 mmol, 1.0 equiv) under N_2 atmosphere. SmI_2 (10 mL (0.1 M solution in THF), 1 mmol, 5.0 equiv) was added via a syringe. The mixture was cooled to -20 ^oC and HMPA (0.8 mL) was added dropwise via a syringe. The resulting mixture was stirred at -20 °C for 2 hours, Then the reaction mixture was concentrated under reduced pressure to give the crude which was used in next step without further purification.

To the solution of above crude (0.2 mmol, 1.0 equiv) in toluene (2 mL) were added DMAP (4.8 mg, 0.04 mmol, 0.10 equiv) and benzoic anhydride (136 mg, 0.6 mmol, 1.5 equiv). The resulting mixture was stirred at room temperature for 10 hours. Then the reaction mixture was concentrated under reduced pressure to give the crude, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1) to give **13** (26 mg, 52% yield) as a pale yellow oil.

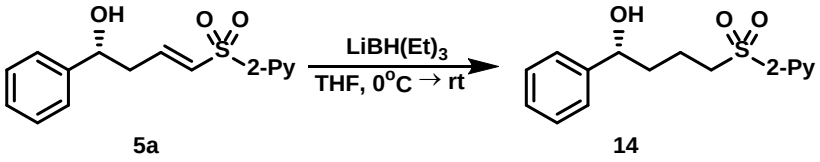


Figure S247, Transformations, related to **Scheme 3**

A dried 100 mL round bottom flask equipped with a magnetic stirring bar was charged with **5a** (1.00 g, 3.46 mmol, 1.0 equiv) under N_2 atmosphere. THF (40 mL) was added via a syringe. The mixture was cooled to 0 ^oC and $LiBH(Et)_3$ (4.5 mL (1 M solution in THF), 4.50 mmol, 1.3 equiv) was added dropwise via a syringe. The resulting mixture was stirred at room temperature for 4 hours. Then the reaction was quenched by saturated aqueous NH_4Cl (20 mL). The aqueous phase was extracted with ethyl acetate (50 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and the volatives were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give **14** (932 mg, 92% yield) as white powders.

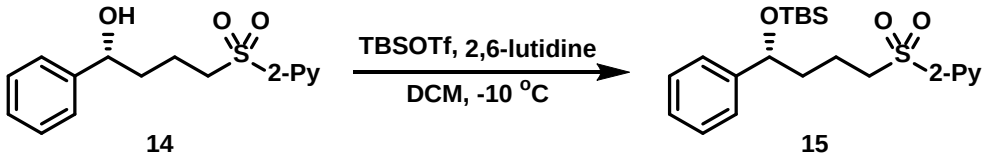


Figure S248, Transformations, related to **Scheme 3**

A dried 50 mL round bottom flask equipped with a magnetic stirring bar was charged with **14** (697 mg, 2.40 mmol, 1.0 equiv) and 2,6-lutidine (514 mg, 4.80 mmol, 2.0 equiv) under N_2 atmosphere. After cooling to -10 °C, TBSOTf (1.27 g, 4.80 mmol, 2.0 equiv) was added via a syringe. The resulting mixture was stirred at -10 °C for 12 hours. After removing the volatiles under reduced pressure, the crude was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to give product **15** (908 mg, 93% yield) as a colorless oil.

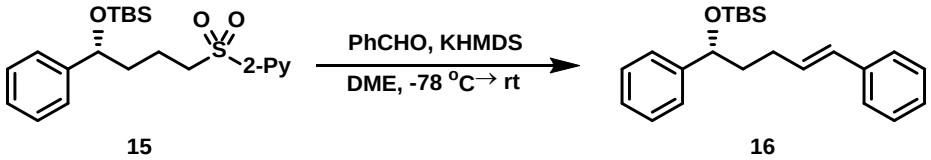


Figure S249, Transformations, related to **Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with **15** (81.2 mg, 0.20 mmol, 1.0 equiv) under N_2 atmosphere. Anhydrous DME (5 mL) was added via a syringe. The mixture was cooled to -78 ^oC and KHMDS (0.40 mL (1 M solution in THF), 0.40 mmol, 2.0 equiv) was added via a syringe. After 3 minutes, benzaldehyde **2a** (31.8 mg, 0.30 mmol, 1.5 equiv) was added via a syringe and the resulting mixture was stirred for 2 hours. Then the reaction mixture was warm to room temperature and stirred for 12 hours. The reaction was

quenched by saturated aqueous NH_4Cl (5 mL). The aqueous phase was extracted with ethyl acetate (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and the volatives were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100/1) to give **16** (47 mg, 67% yield) as a colorless oil.

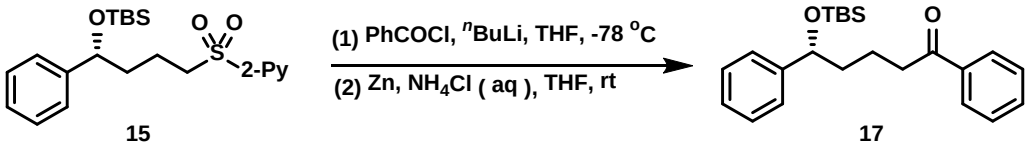


Figure S250, Transformations, related to **Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with **15** (40.6 mg, 0.10 mmol, 1.0 equiv) under N_2 atmosphere. Anhydrous THF (3 mL) was added via a syringe. The mixture was cooled to -78 °C and was stirred for 10 minutes. Then ^{n}BuLi (0.08 mL (1 M solution in THF), 0.20 mmol, 2.0 equiv) was added via a syringe. After 30 minutes, PhCOCl (21.1 mg, 0.15 mmol, 1.5 equiv) was added and the resulting mixture was stirred for 2 hours. Then the reaction was quenched by saturated aqueous NH_4Cl (5 mL). The aqueous phase was extracted with ethyl acetate (10 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and the volatives were removed under reduced pressure to give the crude which was used in next step without further purification.

The solution of above crude (0.1 mmol, 1.0 equiv) in THF (2 mL) was added to a mixture of activated Zn powder (180 mg) ,THF (4 mL) and H_2O(4 mL). The resulting mixture was stirred at room temperature for 4 hours. The solids were filtered off and washed thoroughly with DCM. The filtrate was dried over anhydrous Na_2SO_4 and the volatives were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to give **17** (25 mg, 68% yield) as a colorless oil.

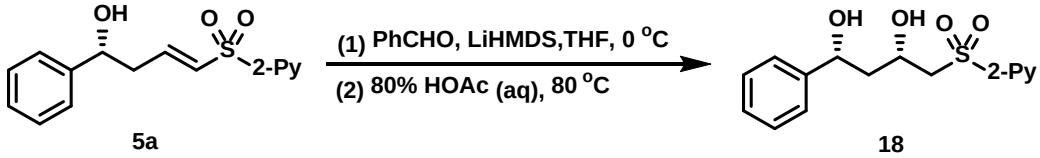


Figure S251, Transformations, related to **Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with **5a** (63.1 mg, 0.20 mmol, 1.0 equiv) under N_2 atmosphere. Anhydrous THF (2 mL) was added via a syringe. The mixture was cooled to 0 °C and was stirred for 10 minutes. Then benzaldehyde **2a** (23.4 mg, 0.22 mmol, 1.1 equiv) and LiHMDS (0.2 mL (1 M solution in THF), 0.20 mmol, 1.0 equiv) were added via a syringe. After 15 minutes, benzaldehyde **2a** (23.4 mg, 0.22 mmol, 1.1 equiv) and LiHMDS (0.2 mL (1 M solution in THF), 0.20 mmol, 1.0 equiv) was added again. This procedure was repeated twice. Then the resulting reaction mixture was quenched by saturated aqueous NH_4Cl (5 mL). The aqueous phase was extracted with ethyl acetate (10 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and the volatives were removed under reduced pressure to give the crude which was used in next step without further purification.

The above crude (0.2 mmol, 1.0 equiv) was added to HOAc (4 mL, 80% in water). The resulting reaction mixture was heating to 80 °C and stirred at this temperature overnight. Then the

resulting reaction mixture was quenched by saturated aqueous $NaHCO_3$ (20 mL). The aqueous phase was extracted with diethyl ether (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and the volatives were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/2) to give **18** (45.5 mg, 74% yield) as white powders.

Synthetic Application of the Methodology:

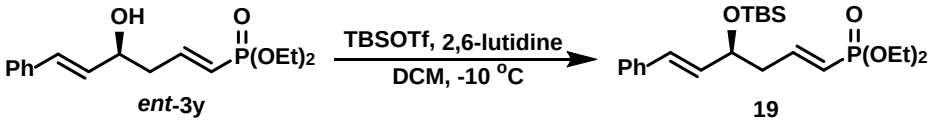


Figure S252, Synthetic application, related to **Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with ***ent*-3y** (93.1 mg, 0.30 mmol, 1.0 equiv) and 2,6-lutidine (64.3 mg, 0.60 mmol, 2.0 equiv) under N_2 atmosphere. After the mixture was cooled to -10 °C, TBSOTf (158.6 mg, 0.60 mmol, 2.0 equiv) was added. The resulting mixture was stirred at -10 °C for 4 hours. After removing the volatiles under reduced pressure, the crude was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give product **19** (105.7 mg, 83% yield) as a colorless oil.

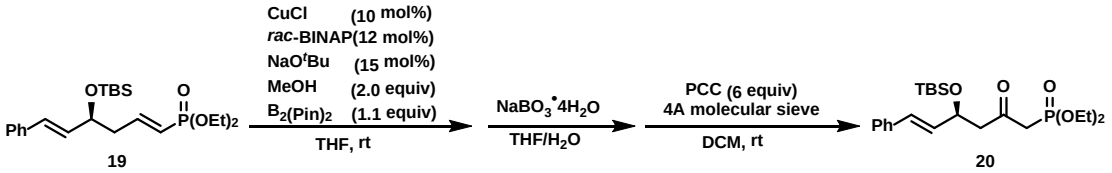


Figure S253, Synthetic application, related to **Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with CuCl (3.0 mg, 0.03 mmol, 0.10 equiv), *rac*-BINAP (22.5 mg, 0.036 mmol, 0.12 equiv) and NaO^tBu (4.3 mg, 0.045 mmol, 0.15 eqiv) in a glove box under Ar atmosphere. **19** (127.5 mg, 0.30 mmol, 1.0 equiv) and $B_2(Pin)_2$ (152.4 mg, 0.6 mmol, 2.0 equiv) were added under N_2 atmosphere. Anhydrous THF (3.0 mL) was added via a syringe. The mixture was stirred at room temperature for 15 minutes. Then MeOH (19.2 mg, 0.6 mmol, 2.0 equiv) was added. The resulting reaction mixture was stirred at room temperature for 24 hours. Then, water (3 ml) and $NaBO_3{\cdot}H_2O$ (138.6 mg, 0.90 mmol, 3.0 equiv) were added sequentially. The mixture was stirred at room temperature for additional 3 hours. Then the resulting reaction mixture was quenched by saturated aqueous NH_4Cl (5 mL). The aqueous phase was extracted with diethyl ether (10 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and the volatives were removed under reduced pressure to give the crude which was used in next step without further purification.

To the solution of above crude (0.30 mmol, 1.0 equiv) in DCM (18 mL) was added 4Å molecular sieves (350 mg) and PCC (516 mg, 2.40 mmol, 8.0 equiv). The resulting mixture was stirred at room temperature for 12 hours. The solids were filtered off and washed thoroughly with ethyl acetate. The filtrate was concentrated under reduced pressure to give the crude which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to give product **20** (97.8 mg, 74% yield) as a colorless oil.

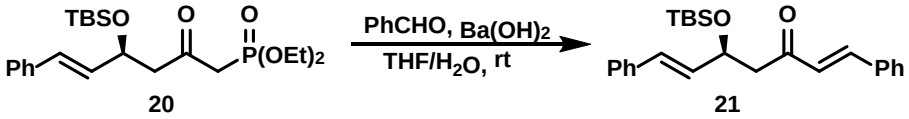


Figure S254, Synthetic application, related to **Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with **20** (61 mg, 0.14 mmol, 1.0 equiv) under N_2 atmosphere. THF (2.0 mL) was added via a syringe. Then $Ba(OH)_2$ (29.5 mg, 0.17 mmol, 1.25 equiv) was added. The resulting mixture was stirred for 30 minutes at room temperature and then benzaldehyde **2a** (15.3 mg, 0.15 mmol, 1.05 equiv) in THF/H_2O (2 mL, 40/1) was added dropwise via a syringe. The resulting mixture was stirred at room temperature for 2 hours. Then the reaction was quenched by saturated aqueous NH_4Cl (3 mL). The aqueous phase was extracted with diethyl ether (10 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and the volatives were removed under reduced pressure to give the crude, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100/1) to give product **21** (46.1 mg, 85% yield) as a colorless oil.

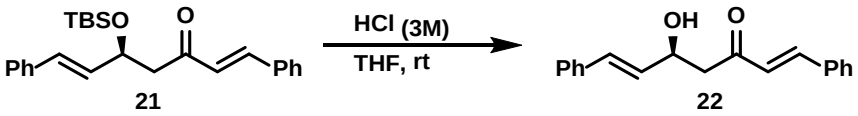


Figure S255, Synthetic application, related to **Scheme 3**

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with **21** (42 mg, 0.107 mmol, 1.0 equiv) and THF (2.0 mL). Then HCl (0.21 mL (3 M solution in water), 0.63 mmol, 6.0 equiv) was added. The resulting mixture was stirred at room temperature for 4 hours. Then the reaction was quenched by saturated aqueous $NaHCO_3$ (3 mL). The aqueous phase was extracted with diethyl ether (10 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and the volatives were removed under reduced pressure to give the crude, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to give product **22** (21.1 mg, 71% yield) as white powders.

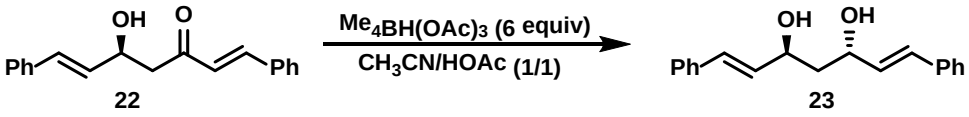
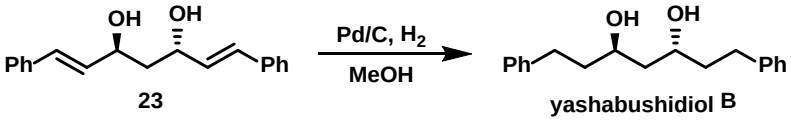


Figure S256, Synthetic application, related to **Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with $MeBH(OAc)_3$ (157.9 mg, 0.60 mmol, 6.0 equiv) under N_2 atmosphere. Anhydrous CH_3CN (0.5 mL) and HOAc (0.5 mL) were added via syringes. The resulting mixture was stirred at room temperature for 30 minutes. Then the resulting mixture was cooled to -20 °C. **22** (27.8 mg, 0.10 mmol, 1.0 equiv) in anhydrous CH_3CN (1 mL) was added dropwise via a syringe. The resulting mixture was stirred at -20 °C for 4 hours. Then the reaction was quenched by saturated aqueous sodium potassium tartarate and saturated aqueous $NaHCO_3$. The aqueous phase was extracted with diethyl ether (10 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and the volatives were removed under reduced pressure to give the crude, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give product **23** (25.2 mg, 90% yield, dr = 8/1) as white powders (Diastereoselectivity was determined by ^1H NMR

analysis of reaction crude mixture).

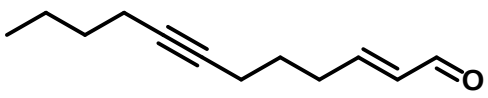


23 yashabushidiol B

Figure S257, Synthetic application, related to **Scheme 3**

A dried 25 mL round bottom flask equipped with a magnetic stirring bar was charged with **23** (25 mg, 0.09 mmol, 1.0 equiv), Pd/C (27.4 mg, 5% *w*/*w*) and EtOH (2 mL). The resulting mixture was stirred for 2 hours at room temperature with a ballon filled with H_2. The black solids were filtered off and washed thoroughly with EtOH. The filtrate was concentrated under reduced pressure to give the crude, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give product **yashabushidiol B** (23 mg, 88% yield) as white powders.

Characterization of all compounds:



2ah

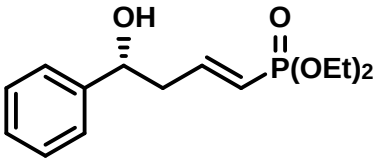
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (d, *J* = 7.9 Hz, 1H), 6.80 (dt, *J* = 15.6, 6.8 Hz, 1H), 6.07 (dd, *J* = 15.6, 7.9 Hz, 1H), 2.44–2.34 (m, 2H), 2.19–2.12 (m, 2H), 2.10–2.06 (m, 2H), 1.72–1.55 (m, 2H), 1.47–1.24 (m, 4H), 0.84 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.88, 157.83, 133.26, 81.35, 78.64, 31.59, 31.08, 27.11, 21.87, 18.32, 18.21, 13.54 ppm.

MS(EI) m/z $[M-H]^+$:177.00.

HRMS(EI) m/z $[M]^+$: calcd. 178.1358, found 178.1359.

IR (film):2933, 2320, 1698, 1652, 1286 cm^{-1}.



3a

3a: Procedure A, 78 mg, colorless liquid, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.12 (m, 5H), 6.76 (ddt, *J* = 22.0, 17.1, 7.0 Hz, 1H), 5.66 (dd, *J* = 21.2, 17.1 Hz, 1H), 4.81 (dd, *J* = 7.4, 5.5 Hz, 1H), 4.07–3.88 (m, 4H), 3.34 (s, 1H), 2.80–2.50 (m, 2H), 1.26 (td, *J* = 7.0, 5.4 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.89 (d, *J* = 4.9 Hz), 143.80, 128.36, 127.50, 125.78, 119.28 (d, *J* = 186.6 Hz), 72.50, 61.68 (d, *J* = 5.5 Hz), 43.94 (d, *J* = 22.0 Hz), 16.24 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.05 ppm.

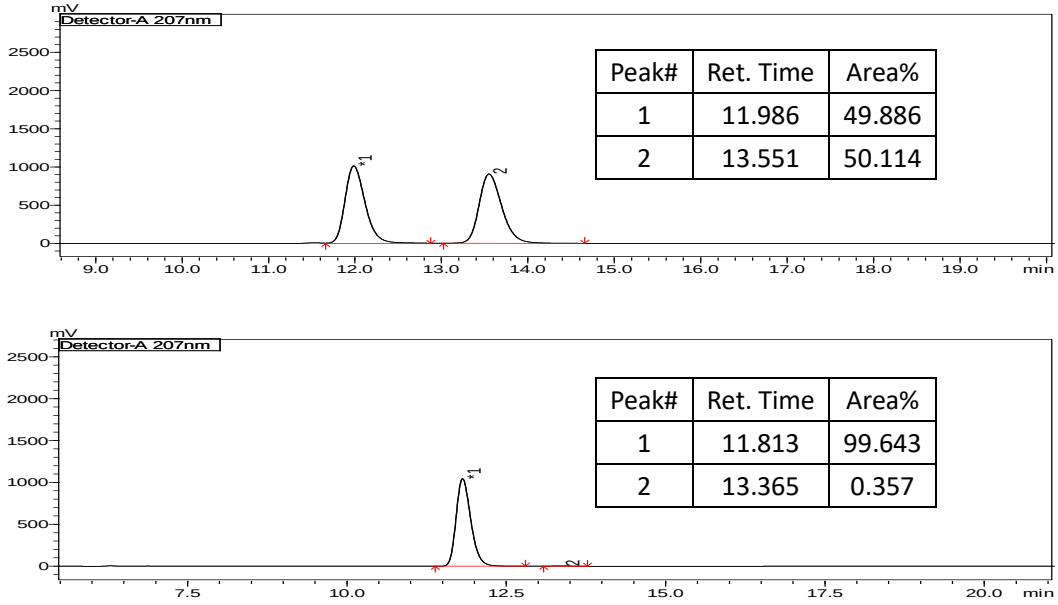
MS(ESI) m/z $[M+H]^+$: 285.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 285.1250, found 285.1250.

IR (film): 3361, 2984, 1632, 1259, 1020, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = +19.72 (*c* = 1.780, $CHCl_3$, 99% ee).

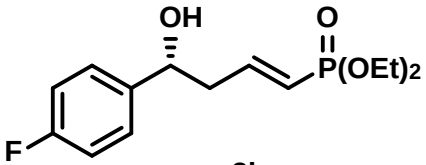
HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 13/3, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 11.8 min, t_R(minor) = 13.4 min, ee = 99%.



Peak#	Ret. Time	Area%
1	11.986	49.886
2	13.551	50.114

Peak#	Ret. Time	Area%
1	11.813	99.643
2	13.365	0.357

Figure S258, the HPLC spectrum of compound **3a,** related to **Table 2**



3b

3b: Procedure A, 73 mg, colorless liquid, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 6.75 (ddt, *J* = 22.0, 17.1, 7.0 Hz, 1H), 5.66 (dd, *J* = 21.1, 17.1 Hz, 1H), 4.81 (t, *J* = 7.9 Hz, 1H), 4.23–3.82 (m, 4H), 3.62 (d, *J* = 3.5 Hz, 1H), 2.77–2.52 (m, 2H), 1.26 (td, *J* = 7.1, 3.7 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.09 (d, *J* = 245.5 Hz), 149.55 (d, *J* = 5.0 Hz), 139.59 (d, *J* = 3.0 Hz), 127.42 (d, *J* = 8.1 Hz), 119.58 (d, *J* = 186.6 Hz), 115.17 (d, *J* = 21.3 Hz), 71.88 (d, *J* = 0.7 Hz), 61.70 (d, *J* = 5.4 Hz), 44.01 (d, *J* = 22.1 Hz), 16.24 (d, *J* = 6.5 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.10~-115.18 (m) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.88 ppm.

MS(ESI) m/z $[M+H]^+$: 303.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 303.1154, found 303.1155.

IR (film): 3354, 2984, 1633, 1510, 1260, 1026 cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = +20.98 (*c* = 2.070, $CHCl_3$, 99% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/*i*-PrOH = 15/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 18.5 min, t_R(minor) = 19.9 min, ee = 99%.

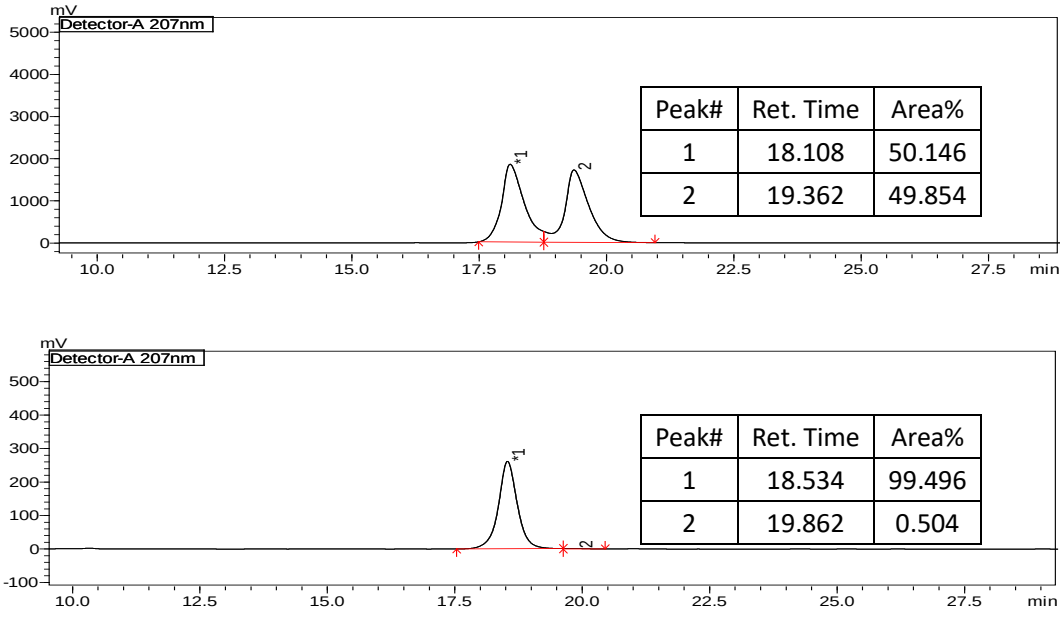
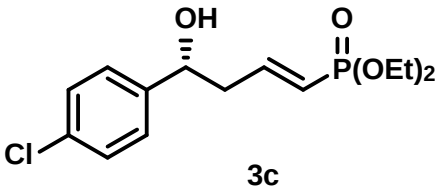


Figure S259, the HPLC spectrum of compound **3b,** related to **Table 2**



3c

3c: Procedure A, 71 mg, colorless liquid, 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.19 (m, 4H), 6.75 (ddt, *J* = 22.0, 17.1, 7.0 Hz, 1H), 5.65 (dd, *J* = 21.1, 17.1 Hz, 1H), 4.80 (t, *J* = 7.4 Hz, 1H), 4.06–3.89 (m, 4H), 3.78 (d, *J* = 3.2 Hz, 1H), 2.73–2.51 (m, 2H), 1.26 (td, *J* = 7.1, 2.7 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.49 (d, *J* = 5.0 Hz), 142.37, 133.11, 128.48, 127.19, 119.63 (d, *J* = 186.6 Hz), 71.81 (d, *J* = 1.3 Hz), 61.73 (d, *J* = 5.5 Hz), 43.93 (d, *J* = 22.1 Hz), 16.24 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.83 ppm.

MS(ESI) m/z $[M+H]^+$: 319.05.

HRMS(ESI) m/z $[M+H]^+$: calcd. 319.0860, found 319.0863.

IR (film): 3354, 2988, 1632, 1260, 1027, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +18.26 (*c* = 2.470, $CHCl_3$, 99% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/*i*-PrOH = 15/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 18.5 min, t_R(minor) = 19.9 min, ee = 99%.

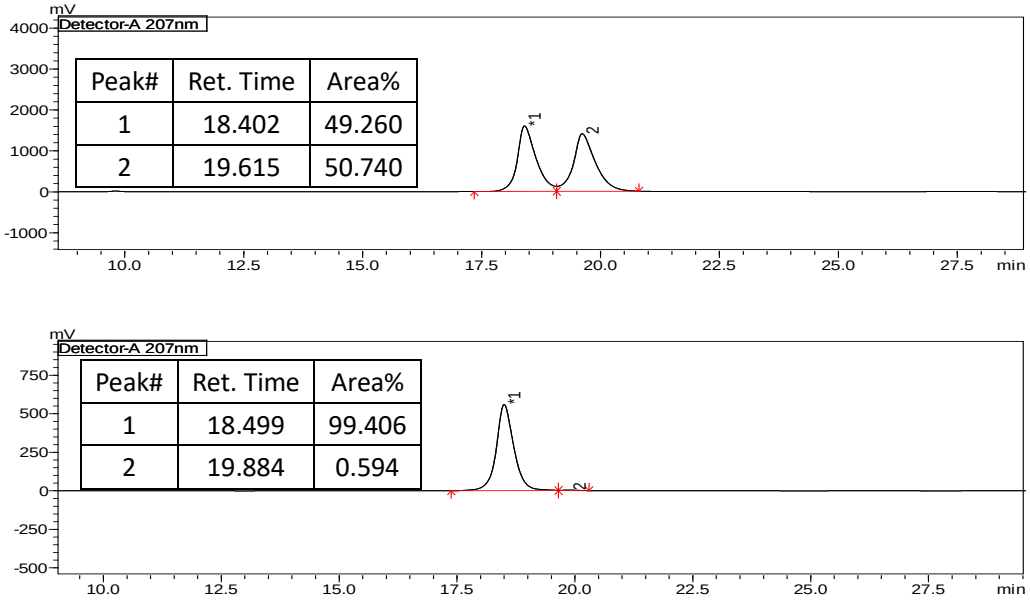
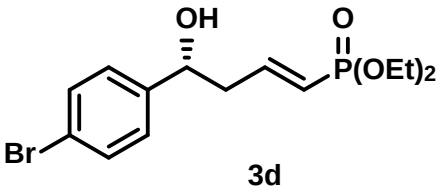


Figure S260, the HPLC spectrum of compound **3c,** related to **Table 2**



3d

3d: Procedure A, 84 mg, colorless liquid, 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.76 (ddt, *J* = 22.0, 17.1, 7.0 Hz, 1H), 5.66 (dd, *J* = 21.0, 17.1 Hz, 1H), 4.80 (t, *J* = 6.3 Hz, 1H), 4.03–3.84 (m, 4H), 3.43 (s, 1H), 2.72–2.54 (m, 2H), 1.27 (td, *J* = 7.1, 2.9 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.28 (d, *J* = 5.2 Hz), 142.76, 131.48 , 127.52, 121.32, 119.84 (d, *J* = 186.5 Hz), 71.93 (d, *J* = 1.2 Hz), 61.74 (d, *J* = 5.5 Hz), 43.87 (d, *J* = 22.0 Hz), 16.27 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.75 ppm.

MS(ESI) m/z $[M+H]^+$: 363.00.

HRMS(ESI) m/z $[M+H]^+$: calcd. 363.0353, found 363.0353.

IR (film): 3352, 2988, 1630, 1260, 1027, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +16.74 (*c* = 1.450, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/*i*-PrOH = 15/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 19.4 min, t_R(minor) = 20.8 min, ee = 98%.

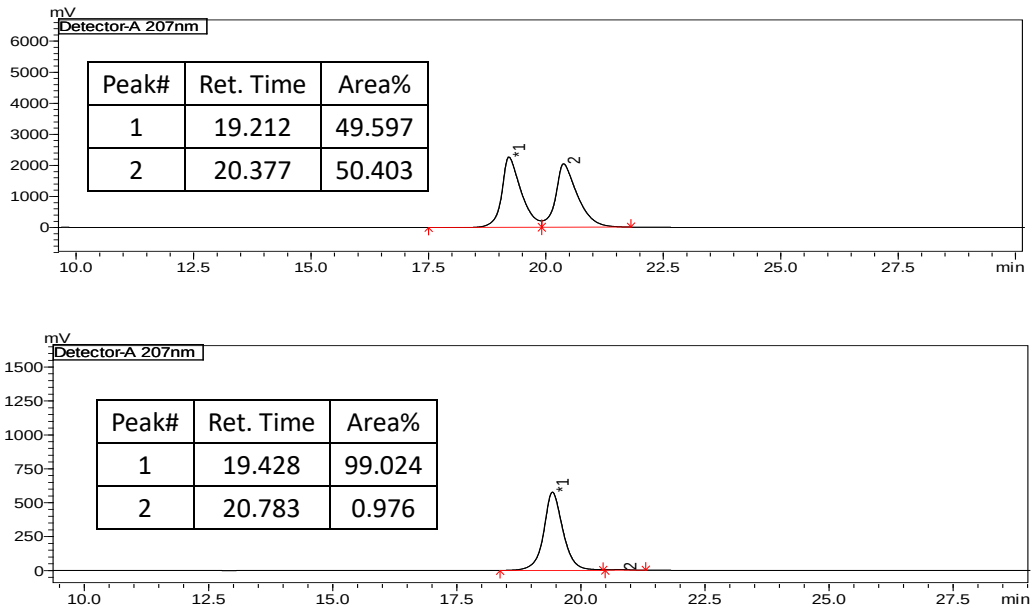
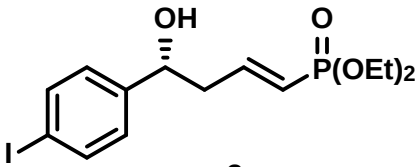


Figure S261, the HPLC spectrum of compound **3d,** related to **Table 2**



3e

3e: Procedure A, 113 mg, colorless liquid, 92% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.75 (ddt, *J* = 22.1, 17.1, 7.0 Hz, 1H), 5.66 (dd, *J* = 20.9, 17.1 Hz, 1H), 4.79 (t, *J* = 6.2 Hz, 1H), 4.05–3.86 (m, 4H), 3.33 (s, 1H), 2.79–2.21 (m, 2H), 1.27 (td, *J* = 7.1, 2.8 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.27 (d, *J* = 5.0 Hz), 143.42, 137.46, 127.78, 119.86 (d, *J* = 186.4 Hz), 92.91, 72.02 (d, *J* = 1.3 Hz), 61.75 (d, *J* = 5.4 Hz), 43.85 (d, *J* = 22.0 Hz), 16.30 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.77 ppm.

MS(ESI) m/z $[M+H]^+$: 411.00.

HRMS(ESI) m/z $[M+H]^+$: calcd. 411.0217, found 411.0215.

IR (film): 3354, 2986, 1634, 1260, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +16.00 (*c* = 2.60, $CHCl_3$, 99% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/*i*-PrOH = 39/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 64.7 min, t_R(minor) = 70.9 min, ee = 99%.

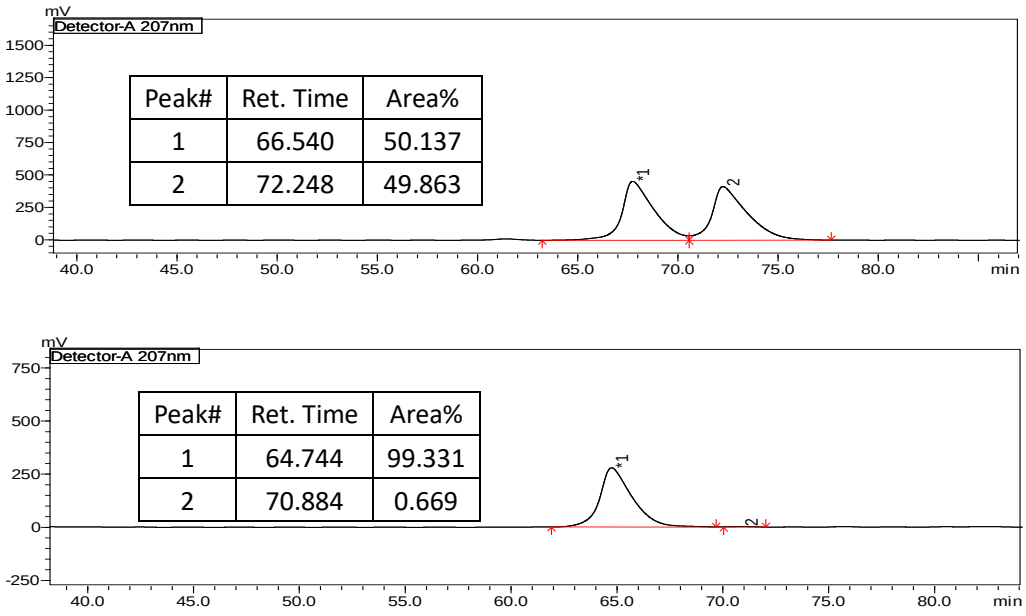
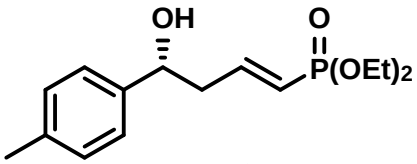


Figure S262, the HPLC spectrum of compound **3e,** related to **Table 2**



3f

3f: Procedure A, 72 mg, colorless liquid, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.74 (ddt, *J* = 22.0, 17.1, 7.0 Hz, 1H), 5.66 (dd, *J* = 21.2, 17.1 Hz, 1H), 4.77 (t, *J* = 7.9 Hz, 1H), 4.05–3.86 (m, 4H), 3.05 (d, *J* = 3.4 Hz, 1H), 2.80–2.51 (m, 2H), 2.33 (s, 3H), 1.26 (q, *J* = 6.9 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.79 (d, *J* = 4.9 Hz), 140.69, 137.28, 129.09, 125.72, 119.41 (d, *J* = 186.3 Hz), 72.51 (d, *J* = 1.2 Hz), 61.64 (d, *J* = 5.4 Hz), 43.87 (d, *J* = 21.9 Hz), 21.06, 16.26 (d, *J* = 6.6 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.01 ppm.

MS(ESI) m/z $[M+H]^+$: 341.15.

HRMS(ESI) m/z $[M+H]^+$: calcd. 341.1876, found 341.1879.

IR (film): 3371, 2985, 1635, 1260, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = +15.25 (*c* = 1.510, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/*i*-PrOH = 15/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 19.5 min, t_R(minor) = 23.9 min, ee = 98%.

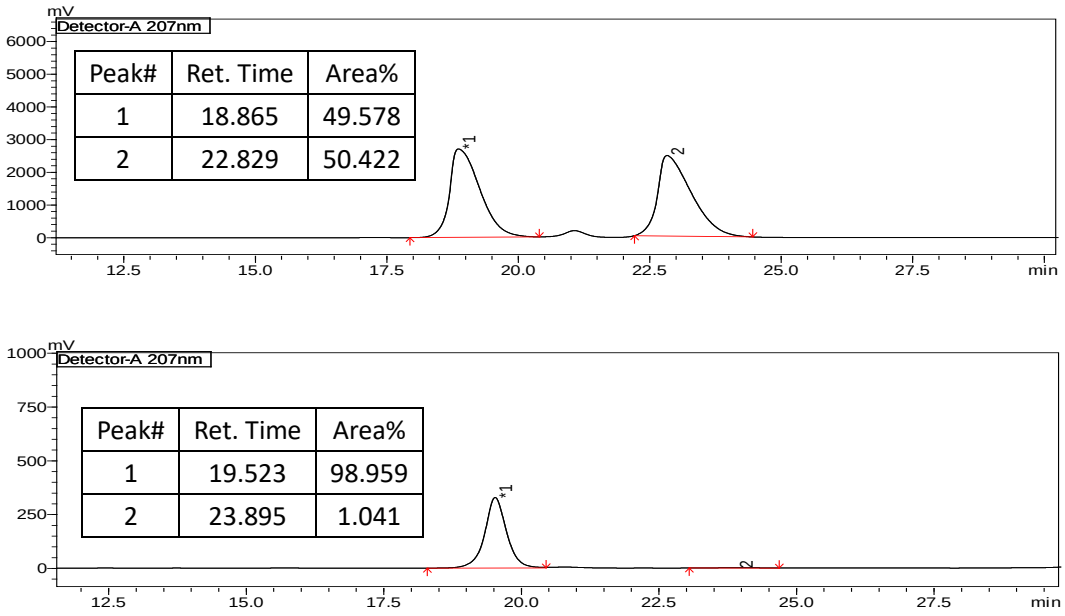
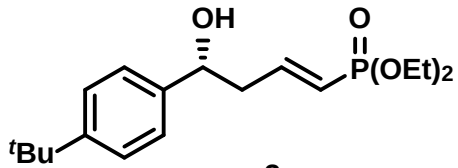


Figure S263, the HPLC spectrum of compound **3f,** related to **Table 2**



3g

3g: Procedure A, 92 mg, colorless liquid, 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 6.77 (ddt, *J* = 22.1, 17.1, 6.9 Hz, 1H), 5.69 (dd, *J* = 21.3, 17.1 Hz, 1H), 4.79 (dd, *J* = 7.3, 5.6 Hz, 1H), 4.08–3.89 (m, 4H), 3.10 (s, 1H), 2.83–2.53 (m, 2H), 1.40–1.15 (m, 15H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.52, 149.98 (d, *J* = 5.1 Hz), 140.66, 125.52 , 125.30, 119.26 (d, *J* = 186.3 Hz), 72.39, 61.65 (d, *J* = 5.5Hz), 43.77 (d, *J* = 22.0 Hz), 34.46 , 31.31, 16.27 (d, *J* = 6.5 Hz)ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.09 ppm.

MS(ESI) m/z $[M+H]^+$: 299.15.

HRMS(ESI) m/z $[M+H]^+$: calcd. 299.1407, found 299.1405.

IR (film): 3366, 2963, 1635, 1230, 1027, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = +16.03 (*c* = 3.325, $CHCl_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 37/3, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 23.6 min, t_R(minor) = 25.7 min, ee = > 99%.

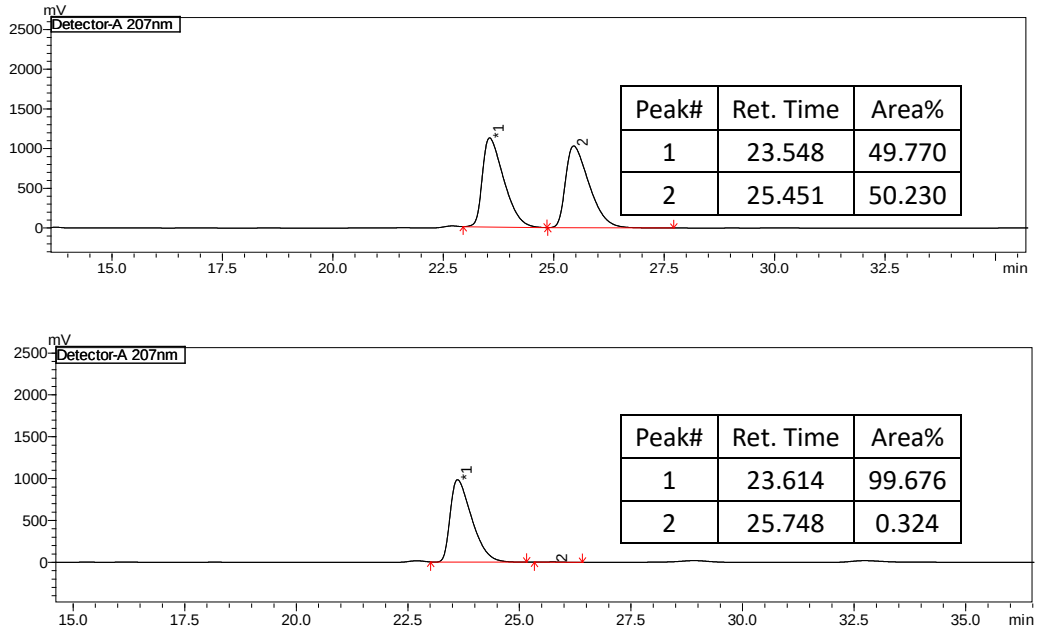
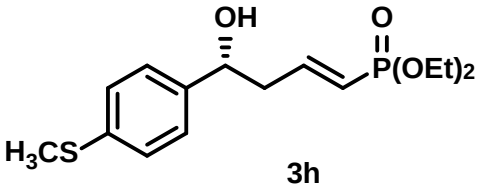


Figure S264, the HPLC spectrum of compound **3g,** related to **Table 2**



3h

3h: Procedure A, 84 mg, colorless liquid, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.75 (ddt, *J* = 22.0, 17.1, 7.0 Hz, 1H), 5.67 (dd, *J* = 21.1, 17.1 Hz, 1H), 4.79 (t, *J* = 7.4 Hz, 1H), 4.20–3.66 (m, 4H), 3.09 (d, *J* = 3.1 Hz, 1H), 2.74–2.54 (m, 2H), 2.47 (s, 3H), 1.27 (td, *J* = 7.0, 5.0 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.52 (d, *J* = 5.2 Hz), 140.54, 137.75, 126.59, 126.33, 119.65 (d, *J* = 186.3 Hz), 72.26 (d, *J* = 1.4 Hz), 61.70 (d, *J* = 5.5 Hz), 43.82 (d, *J* = 22.0 Hz), 16.28 (d, *J* = 6.0 Hz), 15.83 ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.88 ppm.

MS(ESI) m/z $[M+H]^+$: 331.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 331.1127, found 331.1126.

IR (film): 3366, 2988, 1635, 1260, 1025, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = +15.85 (*c* = 1.485, $CHCl_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/*i*-PrOH = 15/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 27.6 min, t_R(minor) = 30.4 min, ee = > 99%.

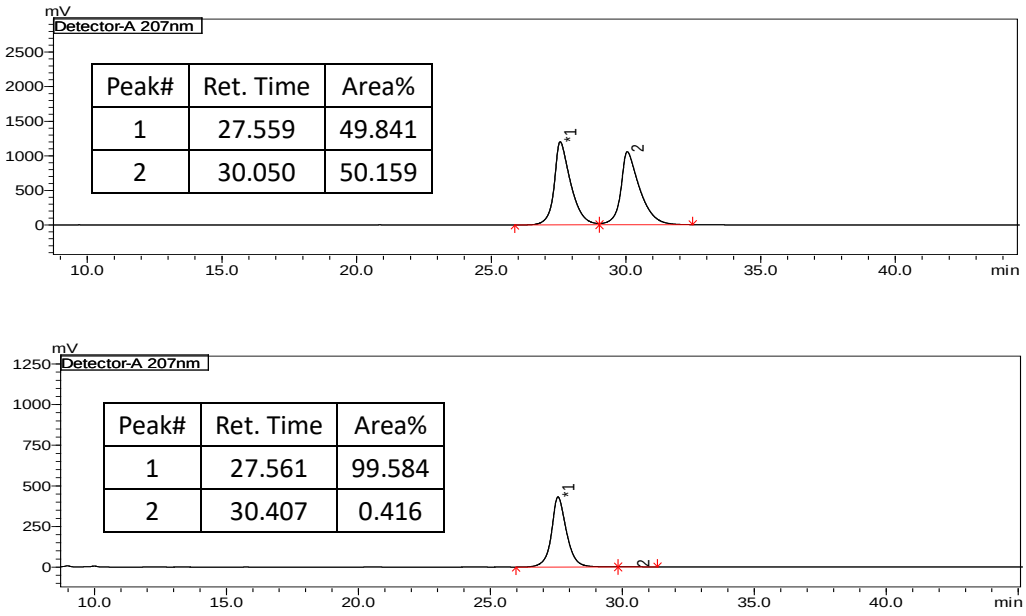
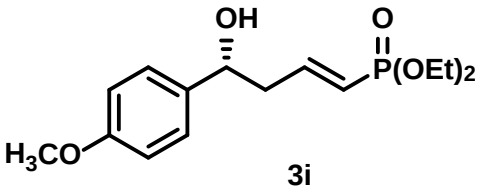


Figure S265, the HPLC spectrum of compound **3h,** related to **Table 2**



3i

3i: Procedure A, 76 mg, colorless liquid, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.74 (ddt, *J* = 22.0, 17.1, 7.0 Hz, 1H), 5.68 (dd, *J* = 21.1, 17.1 Hz, 1H), 4.77 (t, *J* = 7.9 Hz, 1H), 4.17–3.86 (m, 4H), 3.79 (s, 3H), 2.79 (d, *J* = 3.3 Hz, 1H), 2.75–2.53 (m, 2H), 1.27 (q, *J* = 7.0 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.11, 149.66 (d, *J* = 5.1 Hz), 135.73, 127.02, 119.53 (d, *J* = 186.5 Hz), 113.82, 72.34 (d, *J* = 1.2 Hz), 61.66 (d, *J* = 5.4 Hz), 55.25, 43.82 (d, *J* = 21.9 Hz), 16.27 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.95 ppm.

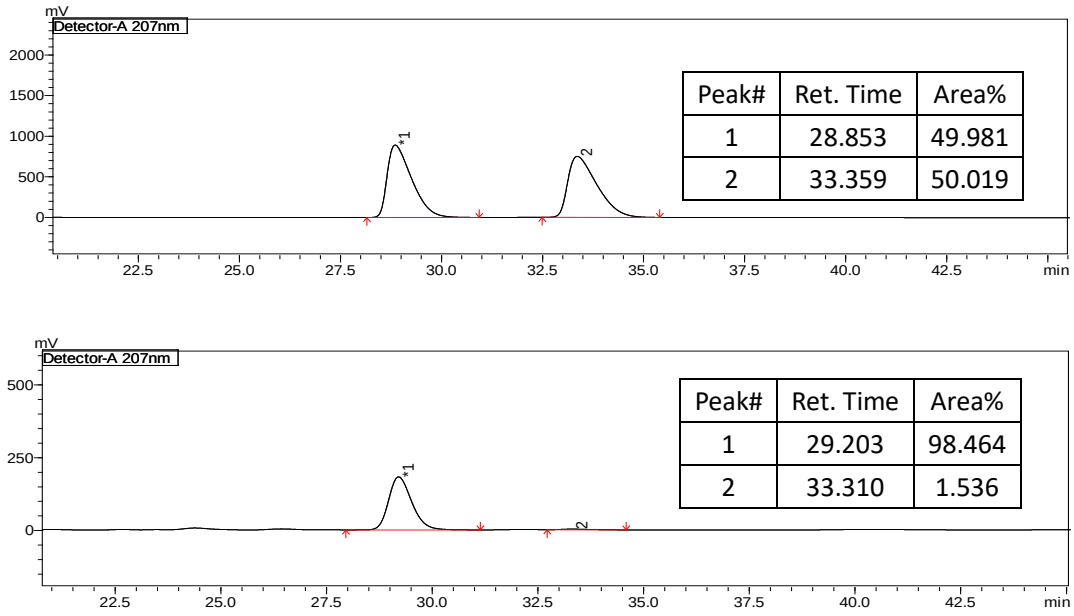
MS(ESI) m/z $[M+H]^+$: 315.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 315.1356, found 315.1355.

IR (film): 3368, 2988, 1612, 1260, 1028, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +16.00 (*c* = 1.600, $CHCl_3$, 97% ee).

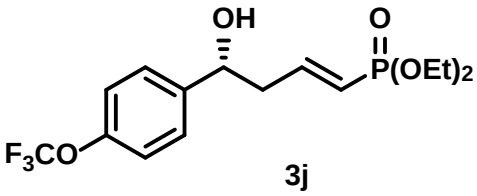
HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 29.2 min, t_R(minor) = 33.3 min, ee = 97%.



Peak#	Ret. Time	Area%
1	28.853	49.981
2	33.359	50.019

Peak#	Ret. Time	Area%
1	29.203	98.464
2	33.310	1.536

Figure S266, the HPLC spectrum of compound **3i,** related to **Table 2**



3j

3j: Procedure A, 88 mg, colorless liquid, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.79 (ddt, *J* = 22.0, 17.2, 7.0 Hz, 1H), 5.70 (dd, *J* = 20.9, 17.2 Hz, 1H), 4.87 (t, *J* = 7.6 Hz, 1H), 4.11–3.84 (m, 4H), 3.25 (d, *J* = 3.4 Hz, 1H), 2.74–2.56 (m, 2H), 1.27 (td, *J* = 7.1, 3.3 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.13 (d, *J* = 5.0 Hz), 148.49 (d, *J* = 1.8 Hz), 142.38, 127.18, 120.92, 120.40 (d, *J* = 257.0 Hz), 119.07, 71.85 (d, *J* = 1.3 Hz), 61.73 (d, *J* = 5.5 Hz), 43.93 (d, *J* = 22.1 Hz), 16.23 (d, *J* = 6.5 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.96 ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.71 ppm.

MS(ESI) m/z $[M+H]^+$: 369.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 369.1073, found 369.1071.

IR (film): 3361, 2989, 1636, 1260, 1028, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +14.54 (*c* = 1.100, $CHCl_3$, 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 19/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 20.9 min, t_R(minor) = 22.8 min, ee = 99%.

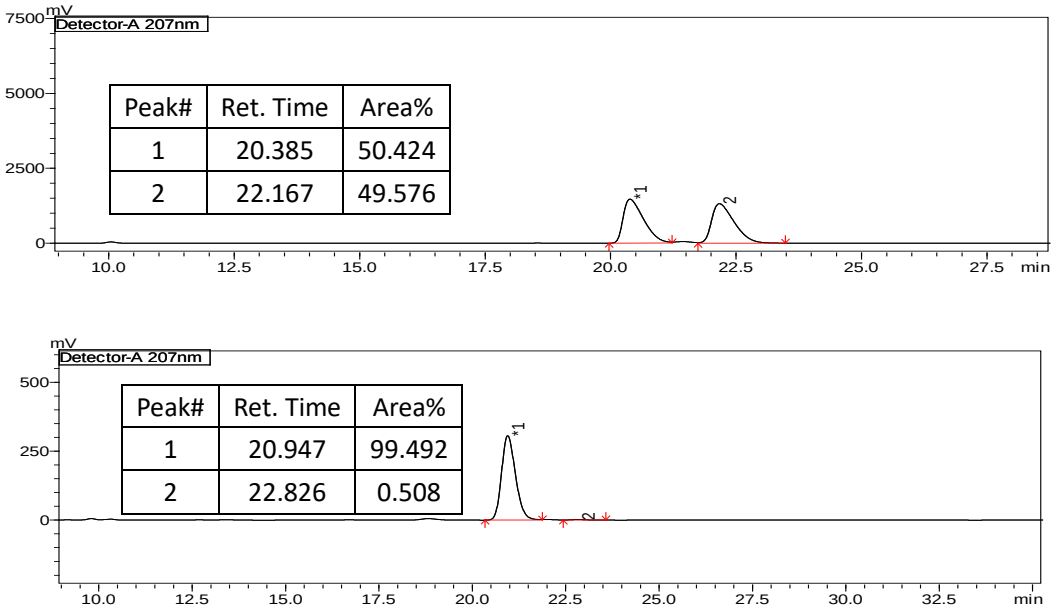
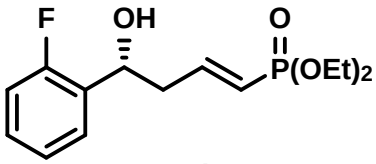


Figure S267, the HPLC spectrum of compound **3j,** related to **Table 2**



3k

3k: Procedure A, 82 mg, colorless liquid, 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (t, *J* = 6.9 Hz, 1H), 7.27–7.18 (m, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.05–6.95 (m, 1H), 6.81 (ddt, *J* = 24.0, 17.1, 6.9 Hz, 1H), 5.68 (dd, *J* = 21.2, 17.1 Hz, 1H), 5.16 (dd, *J* = 10.7, 5.6 Hz, 1H), 4.05–3.85 (m, 4H), 3.78 (d, *J* = 4.3 Hz, 1H), 2.78–2.58 (m, 2H), 1.25 (q, *J* = 7.0 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.39 (d, *J* = 245.2 Hz), 149.63 (d, *J* = 5.0 Hz), 130.88 (d, *J* = 13.4 Hz), 128.79 (d, *J* = 8.2 Hz), 127.29 (d, *J* = 4.4 Hz), 124.23 (d, *J* = 3.4 Hz), 119.43 (d, *J* = 186.4 Hz), 115.06 (d, *J* = 21.7 Hz), 66.33, 61.69 (d, *J* = 5.5Hz), 42.72 (d, *J* = 22.1 Hz), 16.23 (d, *J* = 6.5 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.42~-119.56 (m) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.97 ppm.

MS(ESI) m/z $[M+H]^+$: 303.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 303.1156, found 303.1155.

IR (film): 3353, 2986, 1634, 1260, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +23.86 (*c* = 2.480, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 12.7 min, t_R(minor) = 16.7 min, ee = 98%.

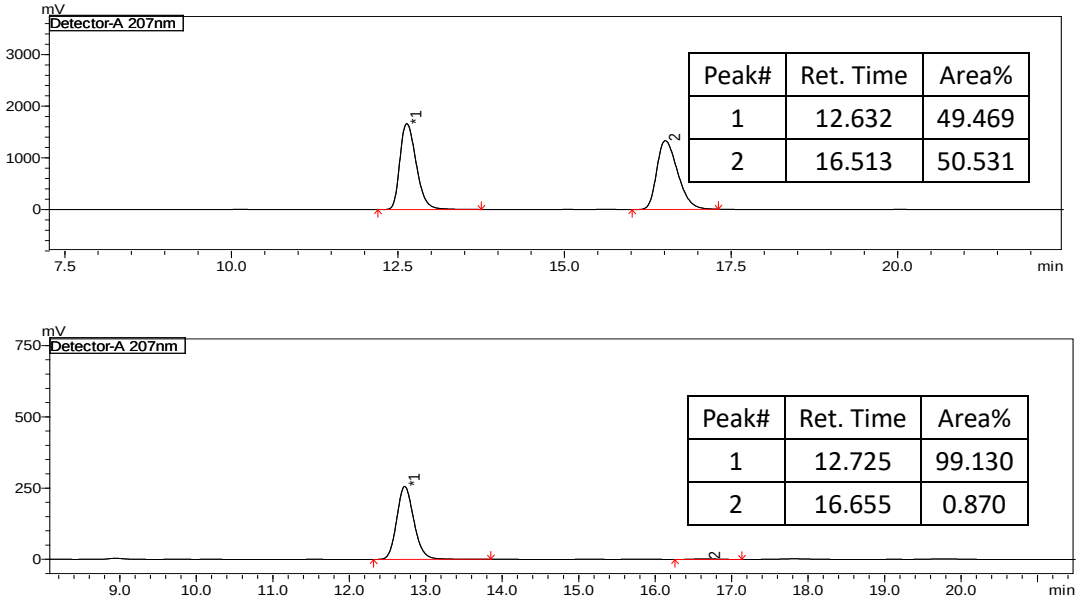
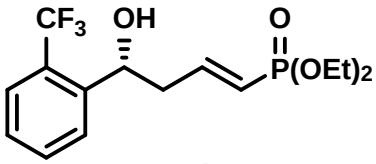


Figure S268, the HPLC spectrum of compound **3k,** related to **Table 2**



3l

3l: Procedure A, 96 mg, colorless liquid, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.59 (dd, *J* = 14.9, 7.7 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 6.88 (ddt, *J* = 22.0, 17.1, 6.9 Hz, 1H), 5.71 (dd, *J* = 21.1, 17.1 Hz, 1H), 5.34–5.14 (m, 1H), 4.05–3.94 (m, 4H), 3.91 (d, *J* = 3.3 Hz, 1H), 2.69–2.49 (m, 2H), 1.28 (td, *J* = 7.1, 2.3 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.81 (d, *J* = 5.0 Hz), 143.29, 132.23, 127.63, 127.39, 126.42 (q, *J* = 30.6 Hz), 125.32 (q, *J* = 5.9 Hz), 124.30 (q, *J* = 273.9 Hz), 119.39 (d, *J* = 186.8 Hz), 67.86, 61.70 (d, *J* = 5.5 Hz), 44.13 (d, *J* = 22.4 Hz), 16.22 (d, *J* = 6.5 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.23 ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 19.97 ppm.

MS(ESI) m/z $[M+Na]^+$: 375.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 353.1124, found 353.1122.

IR (film): 3342, 2985, 1632, 1259, 1056, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +28.63 (*c* = 2.655, $CHCl_3$, 95% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 9.5 min, t_R(minor) = 13.9 min, ee = 95%.

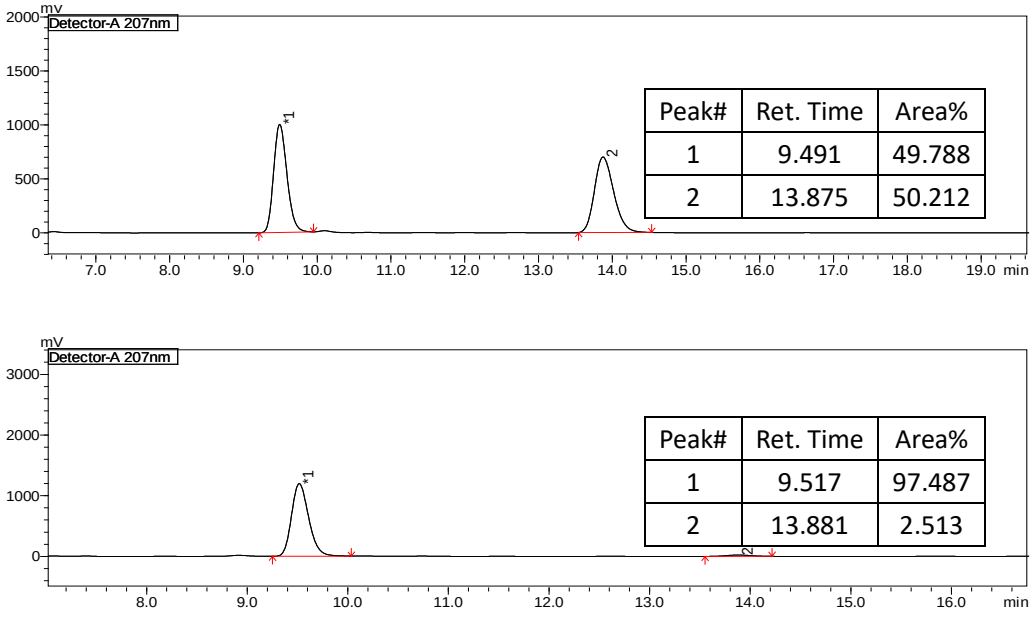
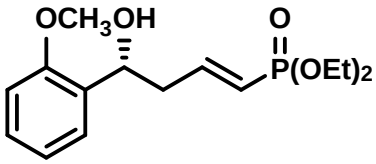


Figure S269, the HPLC spectrum of compound **3l,** related to **Table 2**



3m

3m: Procedure A, 86 mg, colorless liquid, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.29–7.21 (m, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.85–6.71 (m, 1H), 5.69 (dd, *J* = 21.4, 17.2 Hz, 1H), 5.06 (dd, *J* = 12.4, 6.0 Hz, 1H), 4.10–3.90 (m, 4H), 3.84 (s, 3H), 3.05 (d, *J* = 5.8 Hz, 1H), 2.72–2.67 (m, 2H), 1.28 (td, *J* = 7.1, 4.2 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.17, 150.25 (d, *J* = 4.8 Hz), 131.30, 128.49, 126.68, 120.72, 118.96 (d, *J* = 186.4 Hz), 110.35, 68.94 (d, *J* = 1.1 Hz), 61.59 (d, *J* = 5.4 Hz), 55.21, 42.08 (d, *J* = 21.9 Hz), 16.29 (d, *J* = 6.6 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.20 ppm.

MS(ESI) m/z $[M+Na]^+$: 337.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 315.1356, found 315.1354.

IR (film): 3365, 2982, 1632, 1239, 1026, 756 cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = +22.46 (*c* = 2.095, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 27.3 min, t_R(minor) = 34.0 min, ee = 98%.

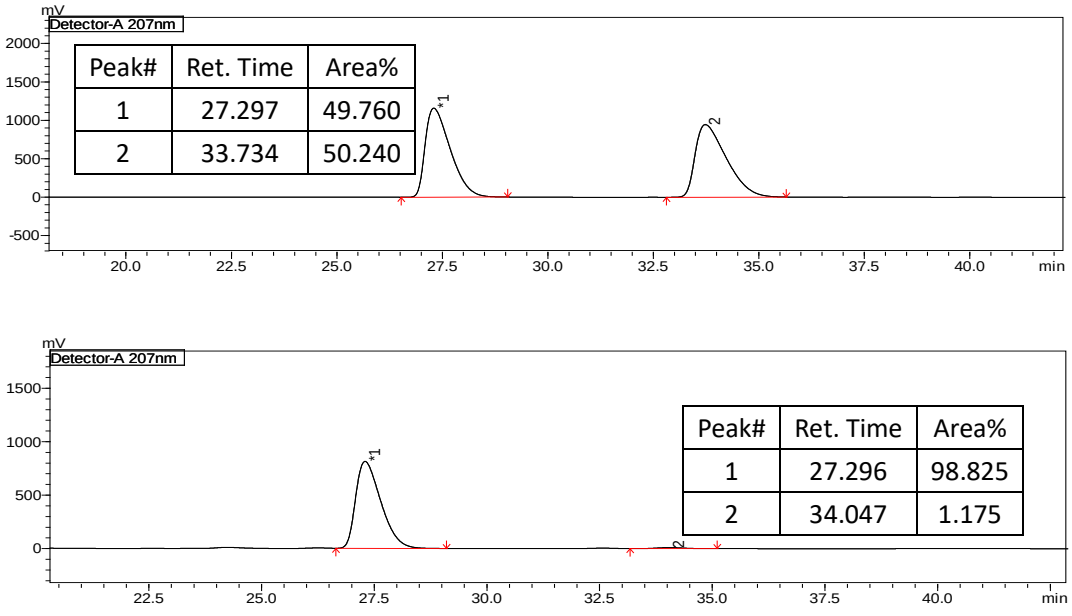
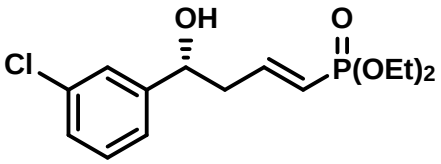


Figure S270, the HPLC spectrum of compound **3m,** related to **Table 2**



3n

3n: Procedure A, 77 mg, colorless liquid, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.29–7.18 (m, 3H), 6.76 (ddt, *J* = 22.0, 17.1, 7.0 Hz, 1H), 5.66 (dd, *J* = 21.1, 17.1 Hz, 1H), 4.87–4.69 (m, 1H), 4.07–3.90 (m, 5H), 2.73–2.53 (m, 2H), 1.27 (td, *J* = 7.1, 3.0 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.54 (d, *J* = 4.9 Hz), 146.12, 134.21, 129.65, 127.49, 125.97, 123.95, 119.53 (d, *J* = 186.6 Hz), 71.78 (d, *J* = 1.0 Hz), 61.78 (d, *J* = 5.4 Hz), 43.88 (d, *J* = 22.1 Hz), 16.23 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.89 ppm.

MS(ESI) m/z $[M+H]^+$: 319.05.

HRMS(ESI) m/z $[M+H]^+$: calcd. 319.0860, found 319.0863.

IR (film): 3346, 2984, 1635, 1259, 1027, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = +18.19 (*c* = 2.420, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 14.8 min, t_R(minor) = 18.4 min, ee = 98%.

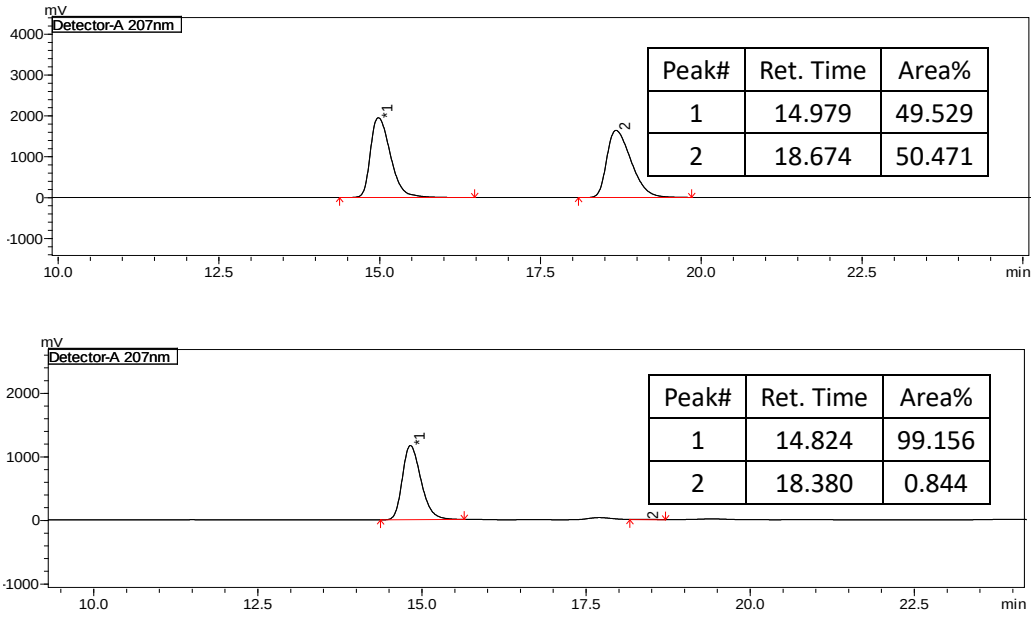
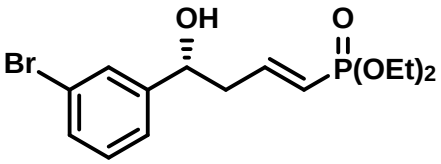


Figure S271, the HPLC spectrum of compound **3n,** related to **Table 2**



3o

3o: Procedure A, 96 mg, colorless liquid, 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.1 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 6.77 (ddt, *J* = 22.0, 17.1, 7.0 Hz, 1H), 5.67 (dd, *J* = 21.1, 17.1 Hz, 1H), 4.80 (t, *J* = 7.9 Hz, 1H), 4.07–3.90 (m, 4H), 3.82 (d, *J* = 3.7 Hz, 1H), 2.74–2.49 (m, 2H), 1.27 (td, *J* = 7.1, 3.1 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.37 (d, *J* = 5.1 Hz), 146.30, 130.51, 129.99, 128.89, 124.42, 122.52, 119.71 (d, *J* = 186.5 Hz), 71.81 (d, *J* = 1.3 Hz), 61.78 (d, *J* = 5.5 Hz), 43.90 (d, *J* = 22.1 Hz), 16.28 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.83 ppm.

MS(ESI) m/z $[M+H]^+$: 363.05.

HRMS(ESI) m/z $[M+H]^+$: calcd. 363.0355, found 363.0353.

IR (film): 3352, 2986, 1630, 1260, 1027, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +14.69 (*c* = 2.265, $CHCl_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 15.8 min, t_R(minor) = 20.3 min, ee = 97%.

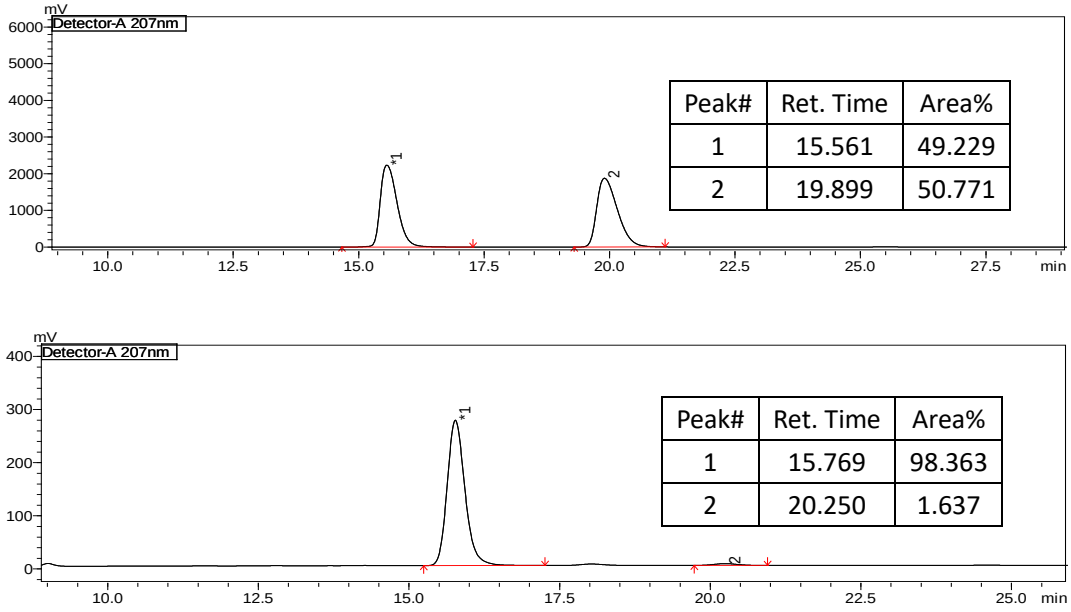
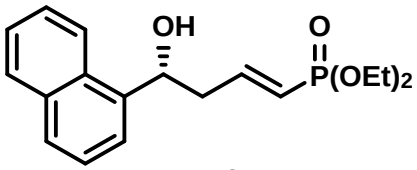


Figure S272, the HPLC spectrum of compound **3o,** related to **Table 2**



3p

3p: Procedure A, 94 mg, pale yellow liquid, 94% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 1H), 7.89–7.79 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 7.1 Hz, 1H), 7.56–7.42 (m, 3H), 6.89 (ddt, *J* = 22.0, 17.1, 6.9 Hz, 1H), 5.69 (dd, *J* = 21.1, 17.1 Hz, 1H), 5.62–5.56 (m, 1H), 4.05–3.77 (m, 4H), 3.21 (d, *J* = 3.4 Hz, 1H), 2.91–2.58 (m, 2H), 1.24 (dt, *J* = 12.9, 7.1 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.95 (d, *J* = 5.0 Hz), 139.28, 133.72, 130.04, 128.95, 128.05, 126.13, 125.55, 125.42, 123.00 , 122.80, 119.34 (d, *J* = 186.5 Hz), 69.39, 61.68 (d, *J* = 7.1 Hz), 43.01 (d, *J* = 22.0 Hz), 16.26 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.02 ppm.

MS(ESI) m/z $[M+H]^+$: 335.15.

HRMS(ESI) m/z $[M+H]^+$: calcd. 335.1407, found 335.1406.

IR (film): 3356, 2983, 1635, 1259, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = +38.34 (*c* = 1.620, $CHCl_3$, 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 22.2 min, t_R(minor) = 24.6 min, ee = 99%.

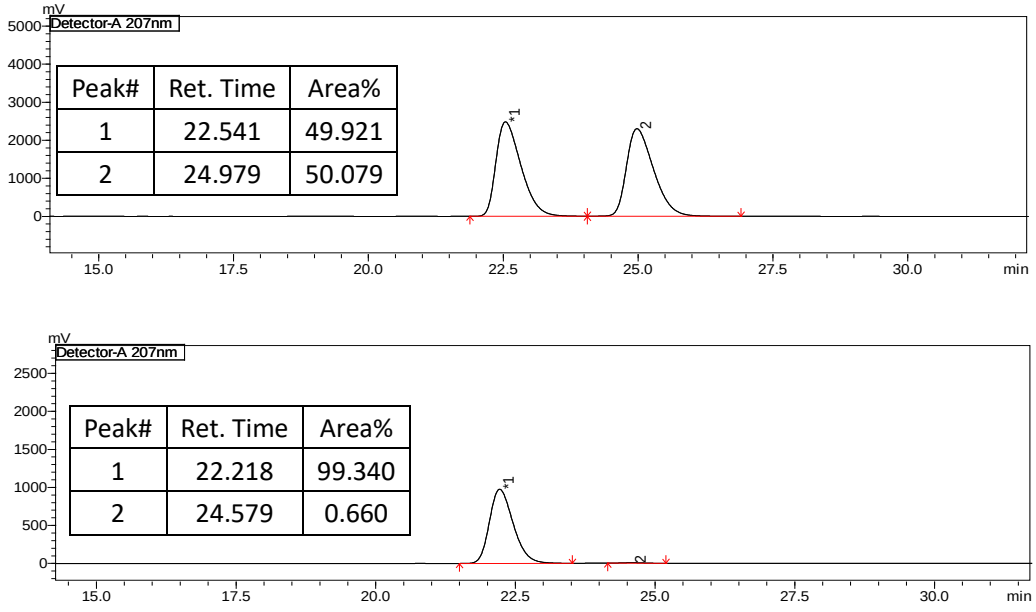
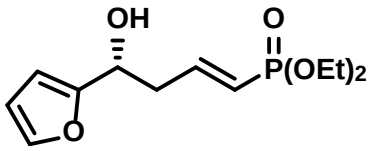


Figure S273, the HPLC spectrum of compound **3p,** related to **Table 2**



3q

3q: Procedure A, 70 mg, colorless liquid, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 1.0 Hz, 1H), 6.76 (ddt, *J* = 22.1, 17.2, 6.9 Hz, 1H), 6.31 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.25 (d, *J* = 3.2 Hz, 1H), 5.73 (dd, *J* = 21.0, 17.2 Hz, 1H), 4.83 (t, *J* = 6.6 Hz, 1H), 4.14–3.88 (m, 4H), 3.73 (s, 1H), 2.77 (t, *J* = 6.7 Hz, 2H), 1.28 (td, *J* = 7.1, 1.4 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.87, 149.22 (d, *J* = 5.1 Hz), 141.84, 119.45 (d, *J* = 186.7 Hz), 110.09, 106.16, 66.01 (d, *J* = 1.2 Hz), 61.75 (d, *J* = 5.6 Hz), 40.39 (d, *J* = 22.3 Hz), 16.23 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.96 ppm.

MS(ESI) m/z $[M+H]^+$: 275.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 275.1043, found 275.1045.

IR (film): 3361, 2985, 1635, 1226, 1020, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = +9.75 (*c* = 3.005, $CHCl_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 37/3, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 34.0 min, t_R(minor) = 39.4 min, ee = > 99%.

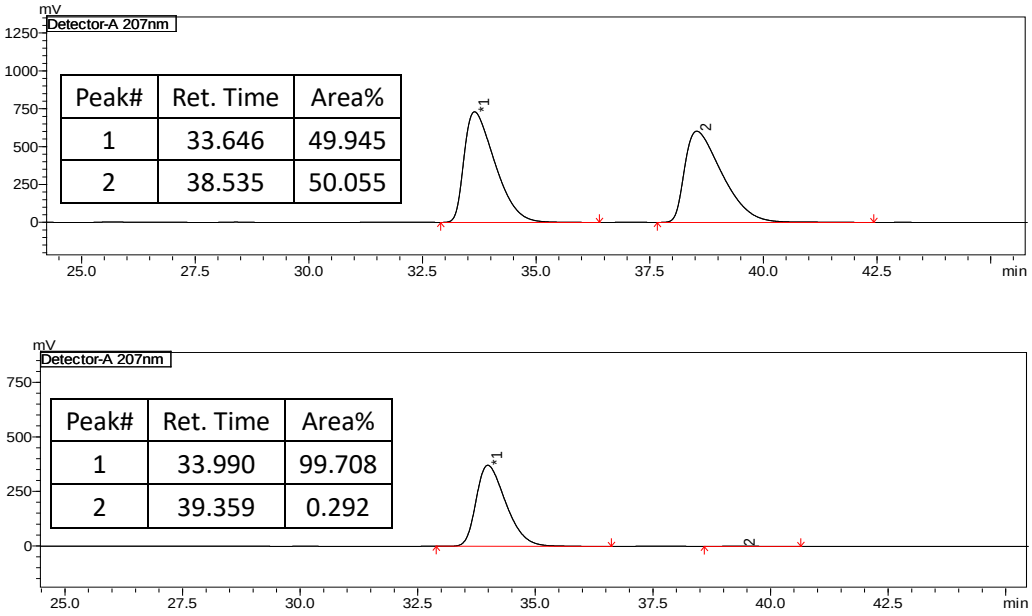
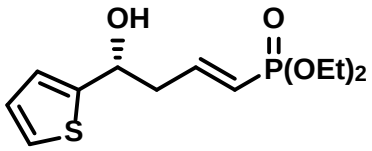


Figure S274, the HPLC spectrum of compound **3q,** related to **Table 2**



3r

3r: Procedure A, 79 mg, colorless liquid, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 4.8, 1.2 Hz, 1H), 6.94 (dd, *J* = 7.9, 3.0 Hz, 2H), 6.76 (ddt, *J* = 22.1, 17.1, 6.9 Hz, 1H), 5.71 (dd, *J* = 21.1, 17.1 Hz, 1H), 5.06 (t, *J* = 6.4 Hz, 1H), 4.22–3.70 (m, 5H), 2.91–2.59 (m, 2H), 1.27 (td, *J* = 7.1, 3.9 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.34 (d, *J* = 5.3 Hz), 147.97, 126.54, 124.42, 123.59, 119.53 (d, *J* = 186.4 Hz), 68.40, 61.75 (d, *J* = 5.4 Hz), 44.02 (d, *J* = 22.1 Hz), 16.24 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.94 ppm.

MS(ESI) m/z $[M+H]^+$: 291.05.

HRMS(ESI) m/z $[M+H]^+$: calcd. 291.0814, found 291.0813.

IR (film): 3342, 2984, 1634, 1259, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = +9.24 (*c* = 2.640, $CHCl_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 18.3 min, t_R(minor) = 20.3 min, ee = > 99%.

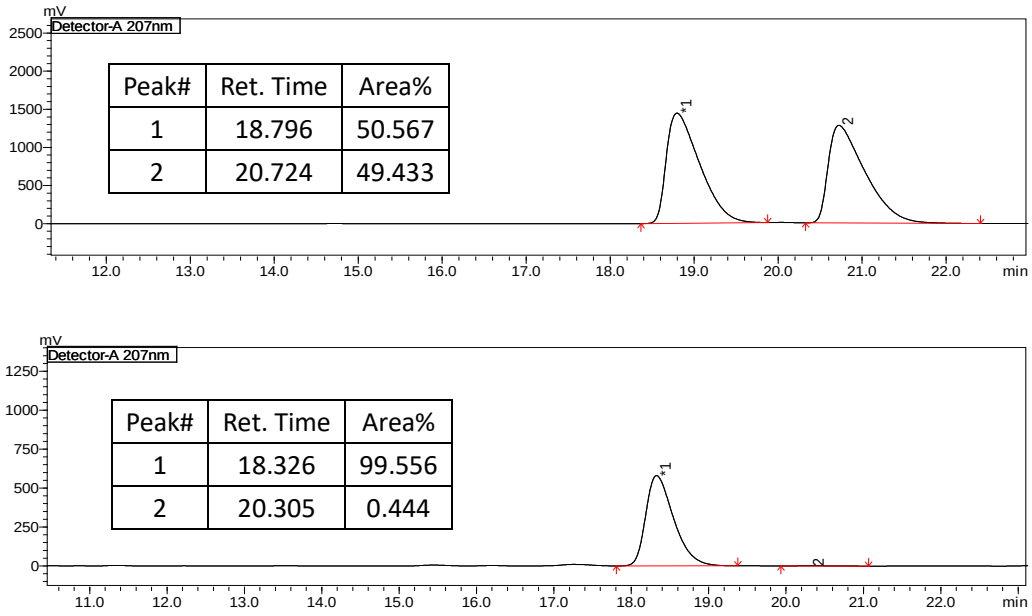
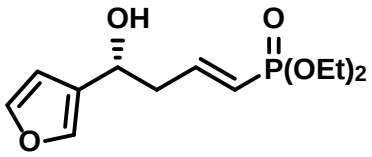


Figure S275, the HPLC spectrum of compound **3r,** related to **Table 2**



3s

3s: Procedure A, 63 mg, colorless liquid, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.34 (m, 2H), 6.77 (ddt, *J* = 22.0, 17.2, 6.9 Hz, 1H), 6.40 (s, 1H), 5.81–5.68 (m, 1H), 4.82 (t, *J* = 5.2 Hz, 1H), 4.17–3.89 (m, 4H), 2.88 (d, *J* = 2.5 Hz, 1H), 2.76–2.57 (m, 2H), 1.30 (td, *J* = 7.1, 1.6 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.22 (d, *J* = 5.2 Hz), 143.39, 139.07, 128.25, 119.88 (d, *J* = 186.6 Hz), 108.37, 65.37 (d, *J* = 1.4 Hz), 61.71 (d, *J* = 5.4 Hz), 42.62 (d, *J* = 22.1 Hz), 16.28 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.97 ppm.

MS(ESI) m/z $[M+H]^+$: 275.15.

HRMS(ESI) m/z $[M+H]^+$: calcd. 275.1043, found 275.1041.

IR (film): 3368, 2989, 1631, 1260, 1027, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = +10.84 (*c* = 1.070, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 15/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 21.1 min, t_R(minor) = 25.1 min, ee = 98%.

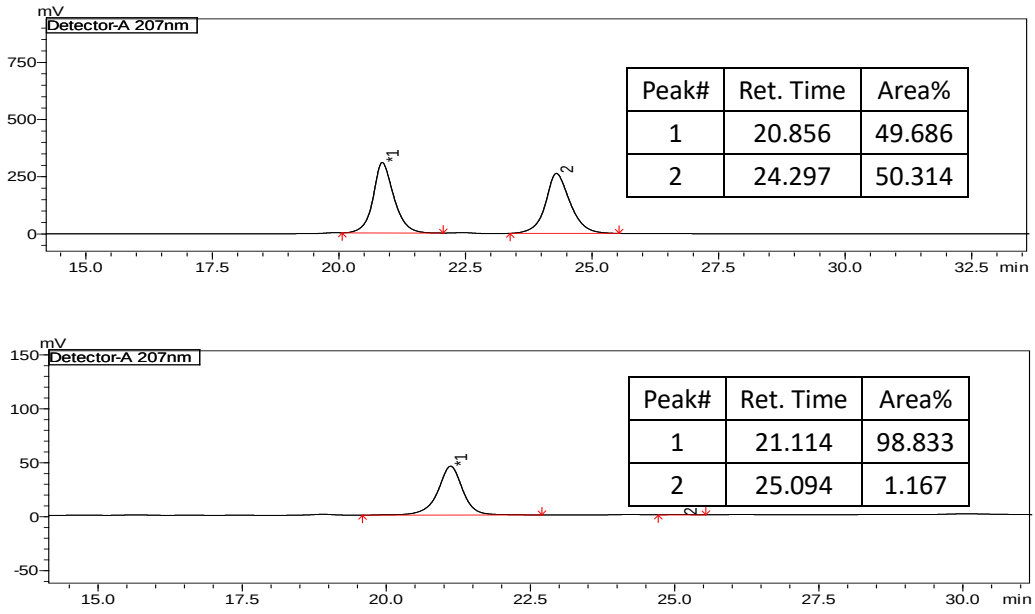
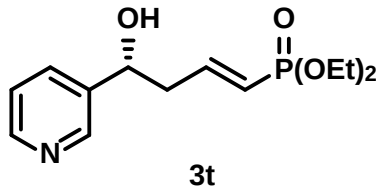


Figure S276, the HPLC spectrum of compound **3s,** related to **Table 2**



3t

3t: Procedure A, 47 mg, colorless liquid, 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.47 (d, *J* = 3.4 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 6.2 Hz, 1H), 6.81 (ddt, *J* = 24.1, 17.1, 6.9 Hz, 1H), 5.71 (dd, *J* = 20.9, 17.1 Hz, 1H), 4.90 (dd, *J* = 7.4, 5.3 Hz, 1H), 4.13–3.81 (m, 4H), 2.75–2.53 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.17 (d, *J* = 4.3 Hz), 148.59, 147.55, 139.53, 133.73, 123.46, 120.00 (d, *J* = 186.8 Hz), 70.13, 61.77 (d, *J* = 5.7 Hz), 43.81 (d, *J* = 22.1 Hz), 16.25 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.62 ppm.

MS(ESI) m/z $[M+Na]^+$: 308.05.

HRMS(ESI) m/z $[M+H]^+$: calcd. 286.1203, found 286.1203.

IR (film): 3355, 2983, 1634, 1229, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +34.45 (*c* = 4.000, $CHCl_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 49.9 min, t_R(minor) = 56.1 min, ee = > 99%.

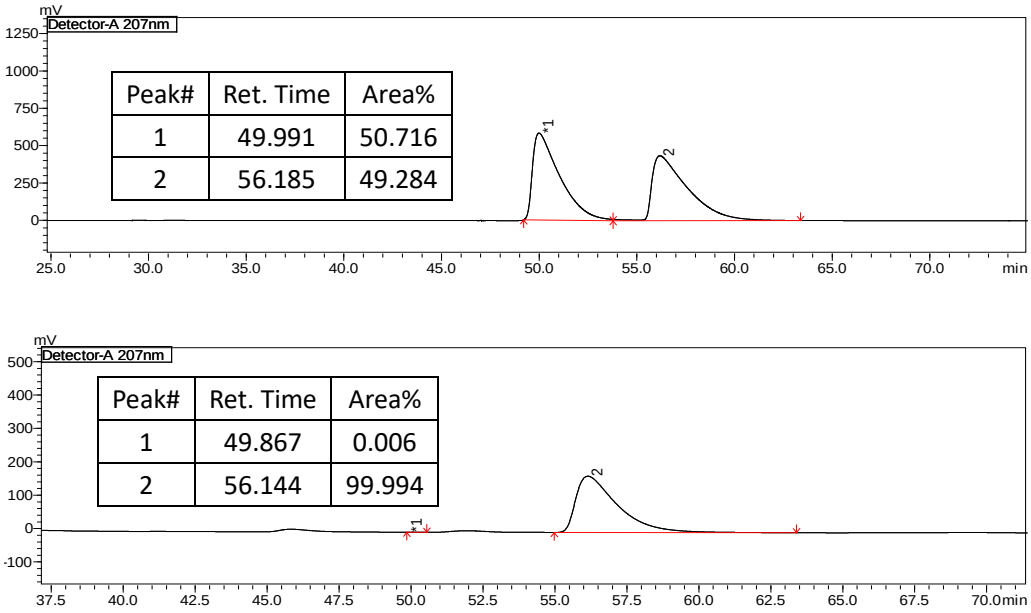
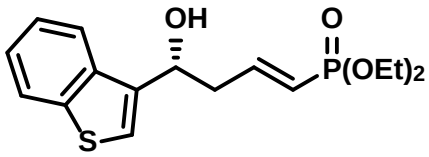


Figure S277, the HPLC spectrum of compound **3t,** related to **Table 2**



3u

3u: Procedure A, 87 mg, pale yellow liquid, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.78 (m, 2H), 7.48–7.28 (m, 3H), 6.85 (ddt, *J* = 22.0, 17.1, 6.9 Hz, 1H), 5.69 (dd, *J* = 21.0, 17.1 Hz, 1H), 5.32–5.07 (m, 1H), 4.03–3.85 (m, 4H), 3.49 (d, *J* = 3.9 Hz, 1H), 2.93–2.66 (m, 2H), 1.30–1.18 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.57 (d, *J* = 4.9 Hz), 140.92, 138.75, 136.93, 124.43, 124.07, 122.94, 122.51, 122.06, 119.56 (d, *J* = 186.5 Hz), 68.17 (d, *J* = 1.3 Hz), 61.72 (d, *J* = 6.1 Hz), 42.05 (d, *J* = 22.1 Hz), 16.27 (d, *J* = 6.6 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.89 ppm.

MS(ESI) m/z $[M+H]^+$: 341.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 341.0971, found 341.0972.

IR (film): 3351, 2988, 1630, 1260, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +32.45 (*c* = 1.465, $CHCl_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 21.2 min, t_R(minor) = 23.3 min, ee = > 99%.

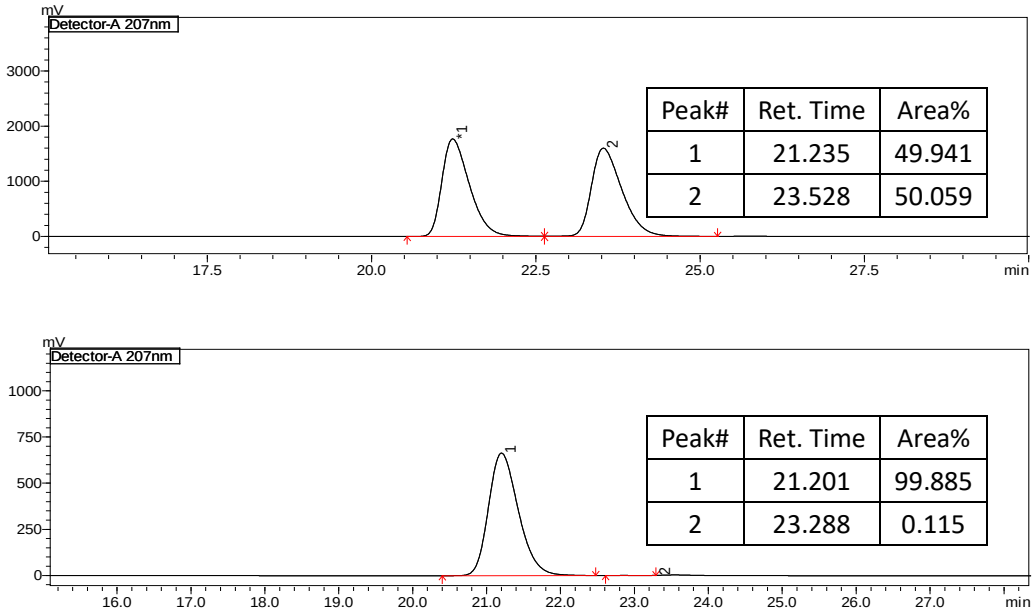
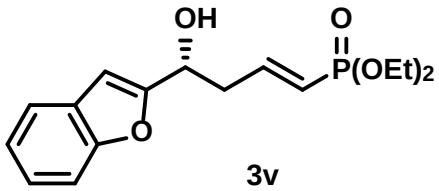


Figure S278, the HPLC spectrum of compound **3u,** related to **Table 2**



3v

3v: Procedure A, 79 mg, colorless liquid, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.31–7.09 (m, 2H), 6.82 (ddt, *J* = 24.0, 17.1, 6.9 Hz, 1H), 6.63 (s, 1H), 5.73 (dd, *J* = 20.9, 17.1 Hz, 1H), 4.96 (t, *J* = 6.2 Hz, 1H), 4.39 (s, 1H), 4.05–3.79 (m, 4H), 3.00–2.64 (m, 2H), 1.19 (td, *J* = 7.0, 1.2 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.66 (d, *J* = 5.4 Hz), 154.70, 149.02, 128.03, 124.08, 122.75, 120.99, 119.75 (d, *J* = 181.9 Hz), 111.11, 102.88, 66.58, 61.78 (d, *J* = 5.4 Hz), 40.45 (d, *J* = 22.4 Hz), 16.17 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.85 ppm.

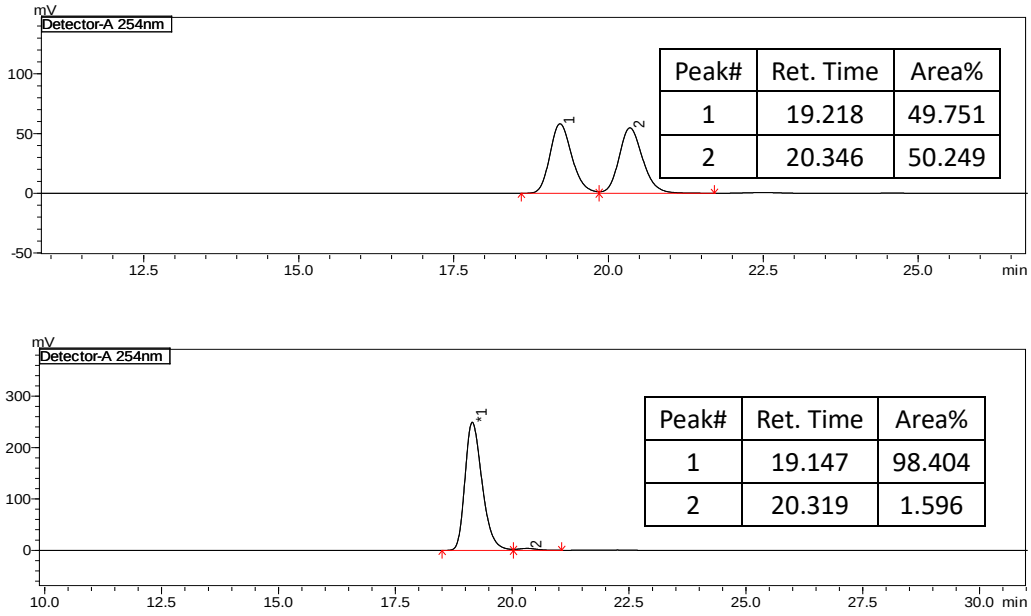
MS(ESI) m/z $[M+H]^+$: 325.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 325.1199, found 325.1200.

IR (film): 3341, 2988, 1632, 1260, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = +16.59 (*c* = 2.590, $CHCl_3$, 97% ee).

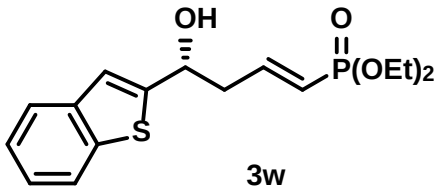
HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 19.1 min, t_R(minor) = 20.3 min, ee = 97%.



Peak#	Ret. Time	Area%
1	19.218	49.751
2	20.346	50.249

Peak#	Ret. Time	Area%
1	19.147	98.404
2	20.319	1.596

Figure S279, the HPLC spectrum of compound **3v,** related to **Table 2**



3w

3w: Procedure A, 92 mg, colorless liquid, 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.36–7.23 (m, 2H), 7.15 (s, 1H), 6.79 (ddt, *J* = 24.0, 17.1, 6.9 Hz, 1H), 5.70 (dd, *J* = 21.0, 17.1 Hz, 1H), 5.12 (t, *J* = 6.3 Hz, 1H), 4.21 (s, 1H), 4.01–3.75 (m, 4H), 2.87–2.67 (m, 2H), 1.23–1.11 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.87 (d, *J* = 4.9 Hz), 148.44, 139.39, 139.26, 124.27, 124.16, 123.43, 122.39, 120.18, 119.98 (d, *J* = 186.0 Hz), 69.05, 61.77 (d, *J* = 5.2 Hz), 43.67 (d, *J* = 22.3 Hz), 16.17 (dd, *J* = 6.5, 3.6 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.78 ppm.

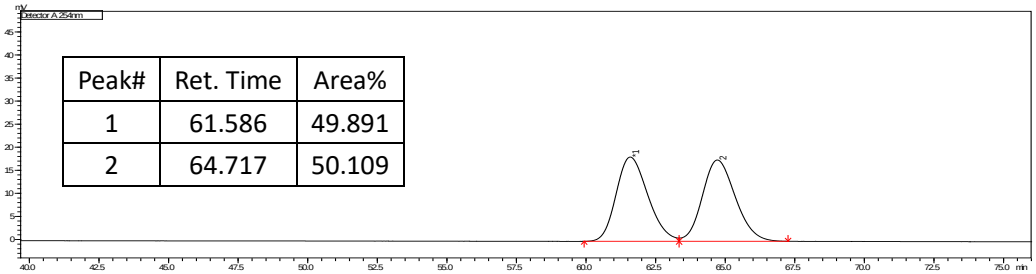
MS(ESI) m/z $[M+H]^+$: 341.05.

HRMS(ESI) m/z $[M+H]^+$: calcd. 341.0971, found 341.0972.

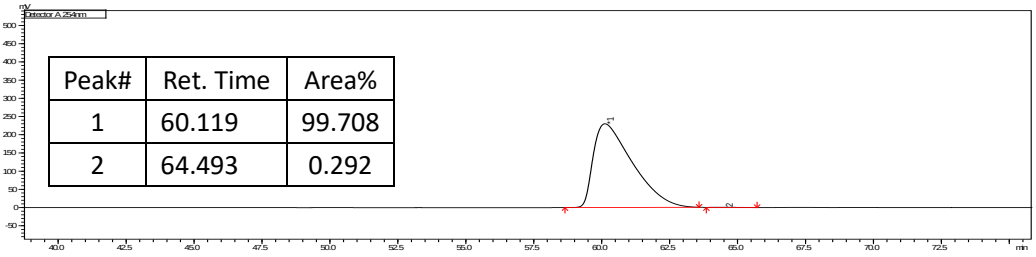
IR (film): 3336, 2988, 1635, 1260, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = +11.64 (*c* = 1.760, $CHCl_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 15/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 60.1 min, t_R(minor) = 64.5 min, ee = > 99%.

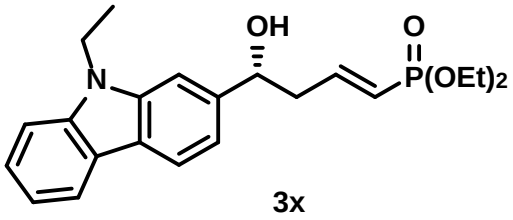


Peak#	Ret. Time	Area%
1	61.586	49.891
2	64.717	50.109



Peak#	Ret. Time	Area%
1	60.119	99.708
2	64.493	0.292

Figure S280, the HPLC spectrum of compound **3w,** related to **Table 2**



3x

3x: Procedure A, 70 mg, colorless liquid, 58% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.5 Hz, 2H), 7.53–7.33 (m, 4H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.96–6.65 (m, 1H), 5.70 (dd, *J* = 20.9, 17.3 Hz, 1H), 5.06–4.96 (m, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.03–3.80 (m, 4H), 2.91–2.69 (m, 2H), 1.90–1.70 (br, 1H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.30–1.10 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.76 (d, *J* = 4.9 Hz), 140.24, 139.60, 133.97, 125.80 , 123.58 , 122.86, 122.69, 120.39, 119.58 (d, *J* = 186.1 Hz), 118.89, 117.82, 108.51, 108.49, 73.50 (d, *J* = 1.1 Hz), 61.65 (d, *J* = 5.3 Hz), 44.27 (d, *J* = 21.8 Hz), 37.57, 16.77 (d, *J* = 6.5 Hz), 13.78 ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.97 ppm.

MS(ESI) m/z $[M+Na]^+$: 424.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 402.1829, found 402.1829.

IR (film): 3361, 2985, 1635, 1260, 1025, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = +14.31 (*c* = 0.460, $CHCl_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK IF-3, hexane/*i*-PrOH = 8/1, flow rate: 0.9 mL/min, λ = 207 nm, t_R(major) = 47.2 min, t_R(minor) = 53.7 min, ee = > 99%.

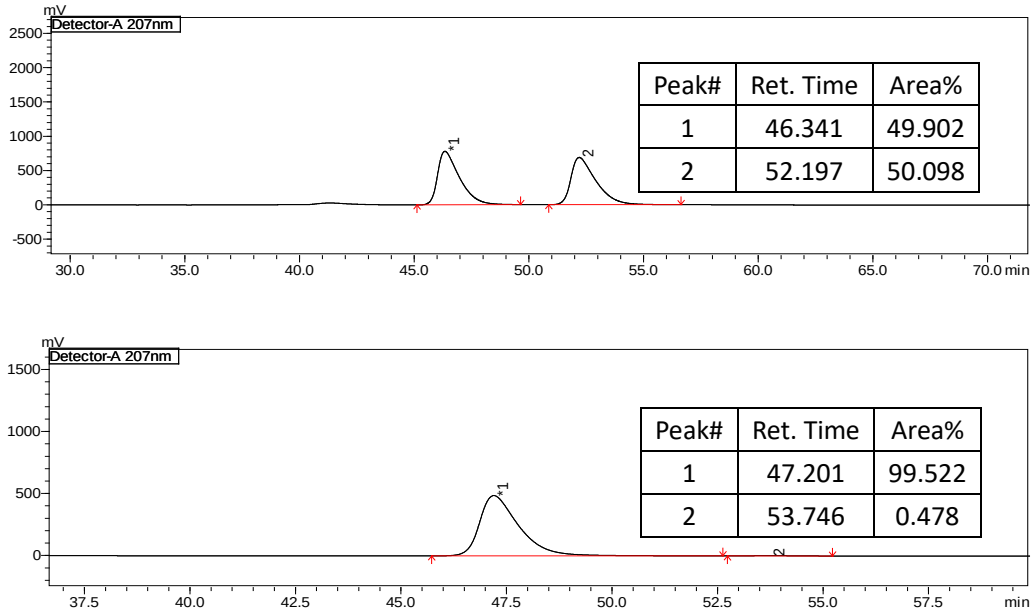
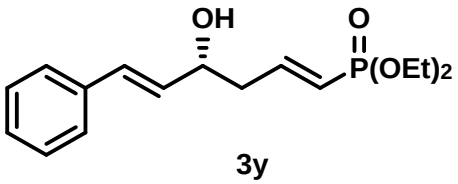


Figure S281, the HPLC spectrum of compound **3x,** related to **Table 2**



3y

3y: Procedure A, 71 mg, colorless liquid, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.17 (m, 5H), 6.82 (ddt, *J* = 22.0, 17.1, 7.0 Hz, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.9, 6.6 Hz, 1H), 5.77 (dd, *J* = 21.0, 17.1 Hz, 1H), 4.55–4.35 (m, 1H), 4.11–3.92 (m, 4H), 2.69 (s, 1H), 2.66–2.46 (m, 2H), 1.27 (q, *J* = 7.1 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.33 (d, *J* = 5.1 Hz), 136.33, 131.12, 130.78, 128.55, 127.78, 126.46, 119.82 (d, *J* = 186.4 Hz), 71.16 (d, *J* = 1.2 Hz), 61.74 (d, *J* = 5.3 Hz), 42.18 (d, *J* = 22.0 Hz), 16.27 (d, *J* = 6.6 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.89 ppm.

MS(ESI) m/z $[M+Na]^+$: 333.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 311.1407, found 311.1405.

IR (film): 3361, 2983, 1631, 1228, 1027, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +1.10 (*c* = 1.150, $CHCl_3$, 97% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/*i*-PrOH = 15/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 23.4 min, t_R(minor) = 25.6 min, ee = 97%.

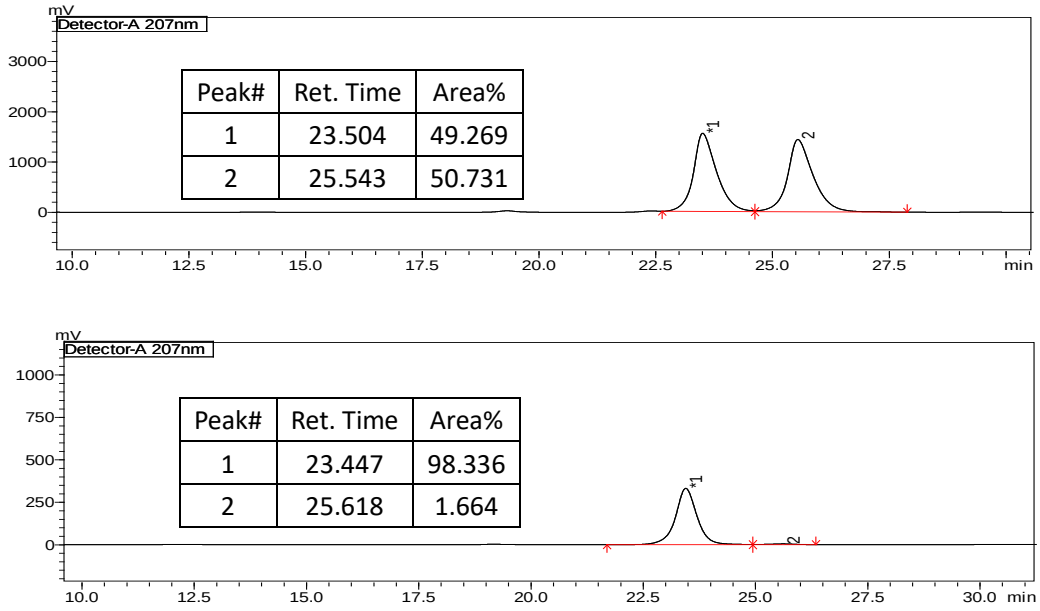
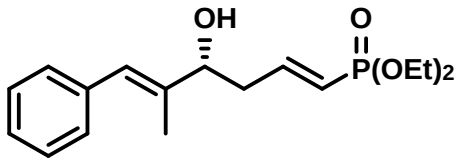


Figure S282, the HPLC spectrum of compound **3y,** related to **Table 2**



3z

3z: Procedure A, 76 mg, colorless liquid, 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.28–7.18 (m, 3H), 6.80 (ddt, *J* = 21.9, 17.1, 7.0 Hz, 1H), 6.52 (s, 1H), 5.77 (dd, *J* = 21.0, 17.1 Hz, 1H), 4.43–4.23 (m, 1H), 4.12–3.93 (m, 4H), 2.68–2.49 (m, 2H), 2.38 (d, *J* = 3.2 Hz, 1H), 1.88 (s, 3H), 1.28 (q, *J* = 7.2 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.58 (d, *J* = 4.9 Hz), 139.07, 137.15, 128.92, 128.10, 126.57, 126.19, 119.43 (d, *J* = 186.7 Hz), 76.11 (d, *J* = 1.2 Hz), 61.71 (d, *J* = 5.4 Hz), 40.13 (d, *J* = 22.0 Hz), 16.29 (d, *J* = 6.5 Hz), 13.49 ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.90 ppm.

MS(ESI) m/z $[M+Na]^+$: 347.15.

HRMS(ESI) m/z $[M+H]^+$: calcd. 325.1562, found 325.1562.

IR (film): 3366, 2985, 1634, 1260, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = -11.16 (*c* = 1.260, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/*i*-PrOH = 15/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 19.6 min, t_R(minor) = 22.4 min, ee = 98%.

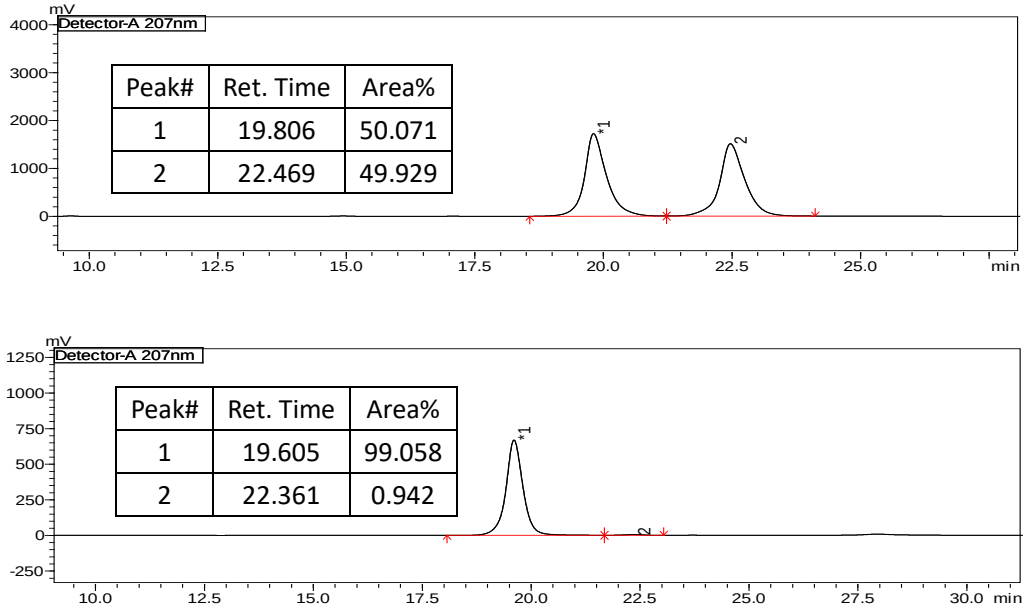
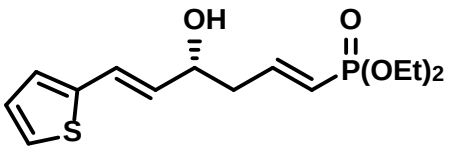


Figure S283, the HPLC spectrum of compound **3z,** related to **Table 2**



3aa

3aa: Procedure A, 81 mg, colorless liquid, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.13 (m, 1H), 6.98–6.93 (m, 2H), 6.89–6.68 (m, 2H), 6.05 (dd, *J* = 15.7, 6.4 Hz, 1H), 5.77 (dd, *J* = 21.0, 17.2 Hz, 1H), 4.51–4.31 (m, 1H), 4.10–3.98 (m, 4H), 2.65–2.45 (m, 2H), 2.34–2.10 (br, 1H), 1.29 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.28 (d, *J* = 4.8 Hz), 141.44, 130.61, 127.36, 126.09, 124.48, 123.97, 119.85 (d, *J* = 186.4 Hz), 70.81 (d, *J* = 1.2 Hz), 61.80 (d, *J* = 5.4 Hz), 42.10 (d, *J* = 22.0 Hz), 16.27 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.89 ppm.

MS(ESI) m/z $[M+H]^+$: 317.05.

HRMS(ESI) m/z $[M+H]^+$: calcd. 317.0971, found 317.0970.

IR (film): 3358, 2986, 1631, 1260, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = +3.05 (*c* = 0.680, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 22.6 min, t_R(minor) = 27.4 min, ee = 98%.

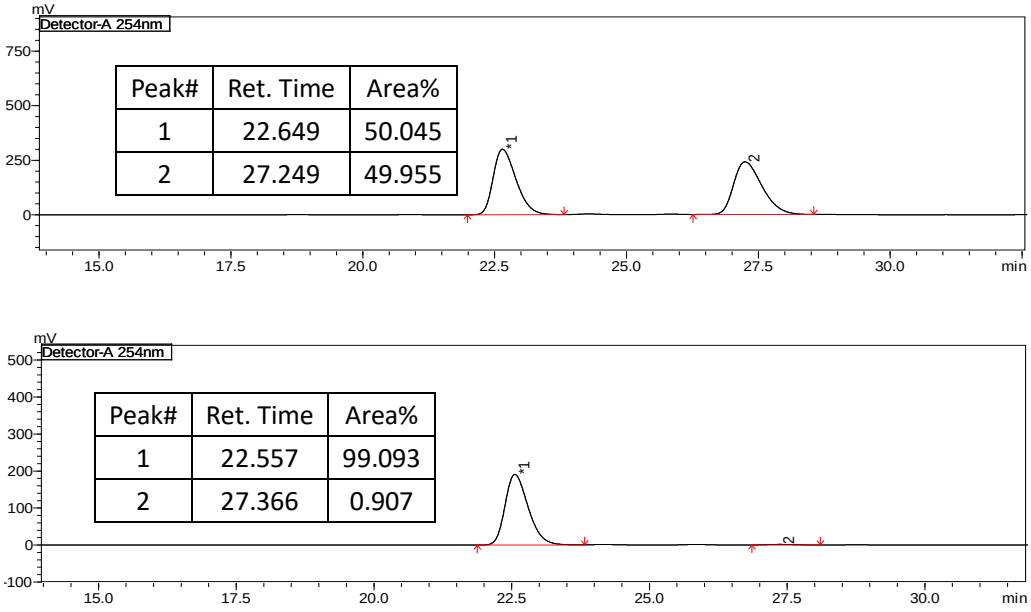
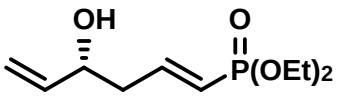


Figure S284, the HPLC spectrum of compound **3aa,** related to **Table 2**



3ab

3ab: Procedure A, 48 mg, colorless liquid, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (ddt, *J* = 22.0, 17.1, 7.0 Hz, 1H), 5.93–5.82 (m, 1H), 5.81–5.67 (m, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 5.15 (d, *J* = 10.4 Hz, 1H), 4.27 (q, *J* = 6.1 Hz, 1H), 4.17–3.97 (m, 4H), 2.64 (s, 1H), 2.58–2.38 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.33 (d, *J* = 5.0 Hz), 139.90, 119.66 (d, *J* = 186.9 Hz), 115.28, 71.22 (d, *J* = 1.2 Hz), 61.72 (d, *J* = 5.3 Hz), 41.78 (d, *J* = 22.0 Hz), 16.30 (d, *J* = 6.4 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.96 ppm.

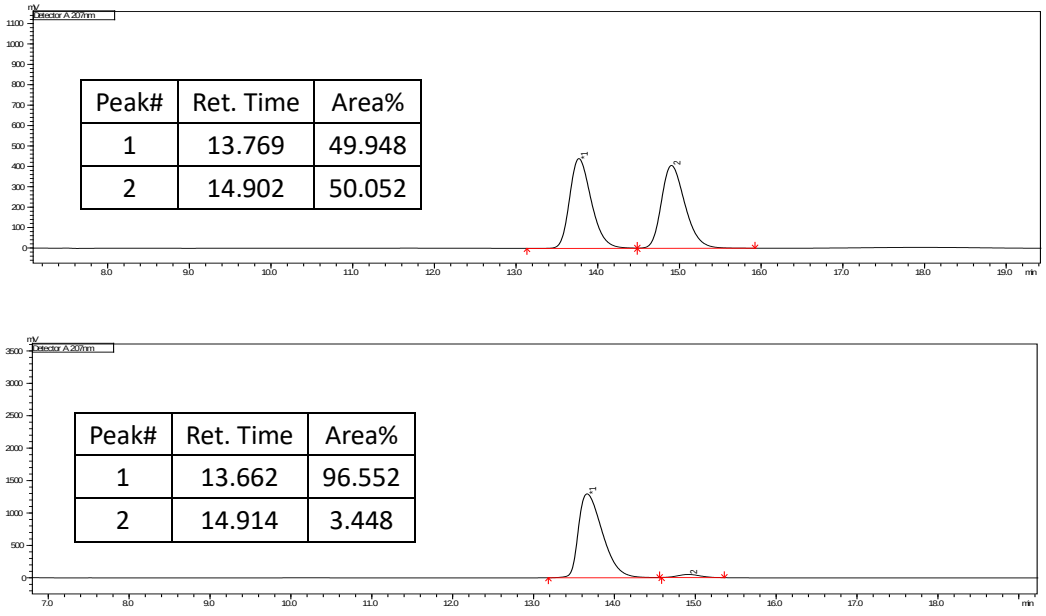
MS(ESI) m/z $[M+Na]^+$: 257.05.

HRMS(ESI) m/z $[M+H]^+$: calcd. 235.1094, found 235.1094.

IR (film): 3379, 2985, 1633, 1260, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +2.52 (*c* = 1.060, $CHCl_3$, 93% ee).

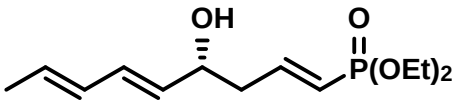
HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 13.7 min, t_R(minor) = 14.9 min, ee = 93%.



Peak#	Ret. Time	Area%
1	13.769	49.948
2	14.902	50.052

Peak#	Ret. Time	Area%
1	13.662	96.552
2	14.914	3.448

Figure S285, the HPLC spectrum of compound **3ab,** related to **Table 2**



3ac

3ac: Procedure A, 48 mg, colorless liquid, 58% yield, *E*/*Z* = 6/1 (**2ac** was used as a mixture (*E*/*Z* = 6/1)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (ddt, *J* = 21.9, 17.1, 7.0 Hz, 1H), 6.19 (dd, *J* = 15.2, 10.4 Hz, 1H), 6.07–5.90 (m, 1H), 5.82–5.62 (m, 2H), 5.55 (dd, *J* = 15.2, 6.8 Hz, 1H), 4.28 (q, *J* = 6.4 Hz, 1H), 4.11–3.98 (m, 4H), 2.56 (s, 1H), 2.51–2.43 (m, 2H), 1.75 (d, *J* = 7.0 Hz, 3H), 1.42–1.20 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.56 (d, *J* = 5.0 Hz), 131.88, 131.26, 130.53, 130.34, 119.46 (d, *J* = 186.6 Hz), 70.87 (d, *J* = 1.3 Hz), 61.71 (d, *J* = 5.5 Hz), 42.15 (d, *J* = 21.9 Hz), 18.05, 16.28 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.06 ppm.

MS(ESI) m/z $[M+Na]^+$: 297.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 275.1407, found 275.1407.

IR (film): 3363, 2962, 1634, 1260, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +8.32 (*c* = 0.510, $CHCl_3$, 97% ee, *E*/*Z* = 6/1).

HPLC: DAICEL CHIRALPAK IC, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 16.8 min, t_R(minor) = 19.6 min, ee = 97%.

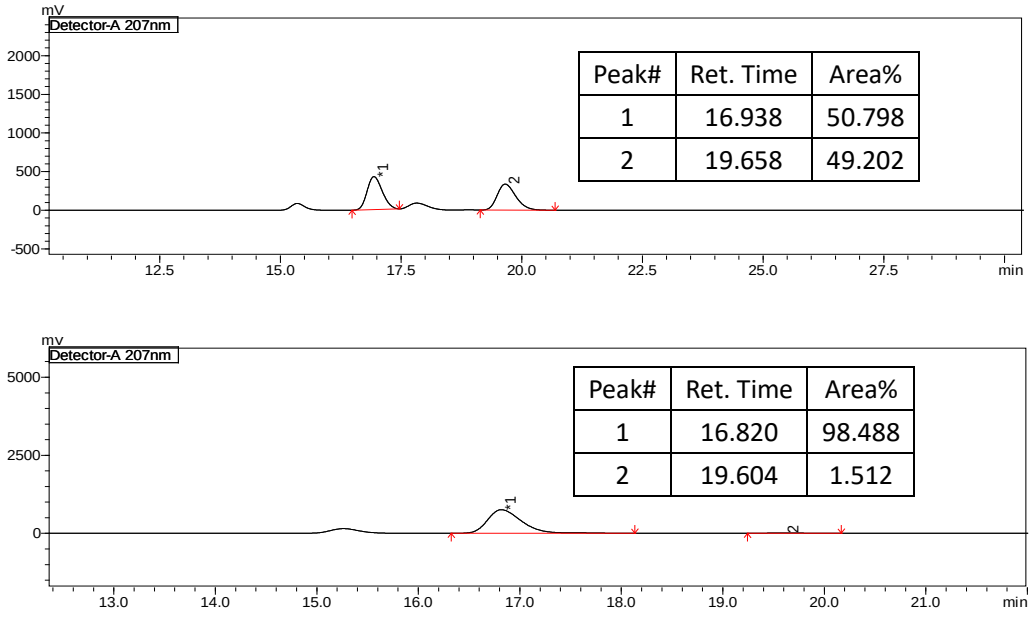
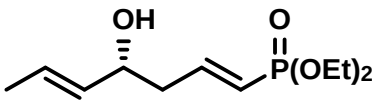


Figure S286, the HPLC spectrum of compound **3ac,** related to **Table 2**



3ad

3ad: Procedure A, 51 mg, colorless liquid, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (ddt, *J* = 24.1, 17.1, 7.0 Hz, 1H), 5.82–5.62 (m, 2H), 5.50 (dd, *J* = 15.3, 5.9 Hz, 1H), 4.21 (dd, *J* = 12.8, 6.4 Hz, 1H), 4.17–3.95 (m, 4H), 2.55–2.36 (m, 2H), 2.24 (s, 1H), 1.69 (d, *J* = 6.3 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.55 (d, *J* = 4.5 Hz), 132.95, 127.57, 119.50 (d, *J* = 185.8 Hz), 71.25, 61.69 (d, *J* = 5.5 Hz), 42.06 (d, *J* = 21.9 Hz), 17.61, 16.31 (d, *J* = 6.4 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.02 ppm.

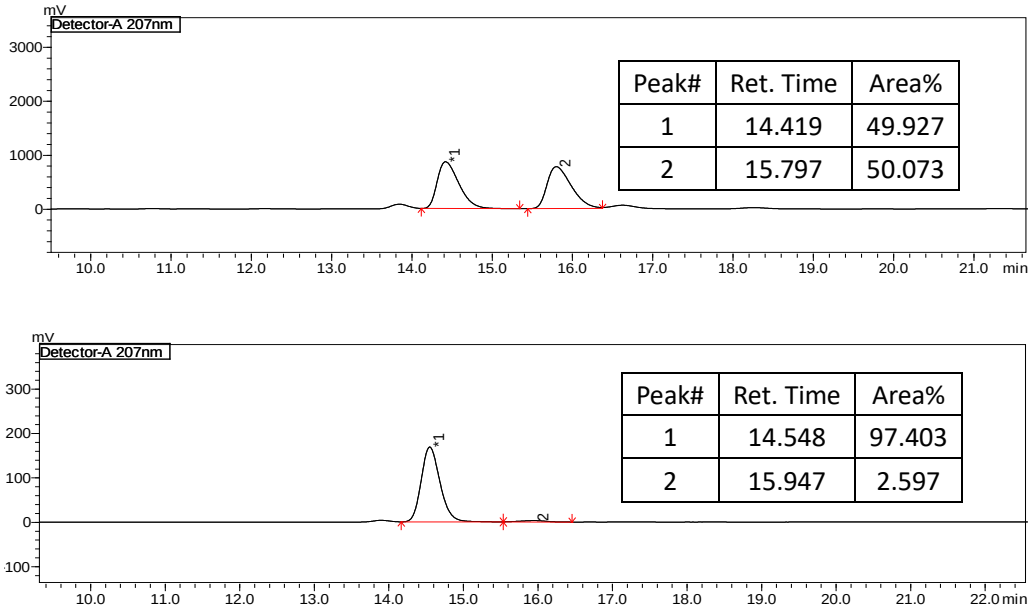
MS(ESI) m/z $[M+H]^+$: 249.10.

HRMS(ESI) m/z $[M+H]^+$: calcd. 249.1250, found 249.1251.

IR (film): 3386, 2985, 1633, 1259, 1020, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = +5.38 (*c* = 1.155, $CHCl_3$, 95% ee).

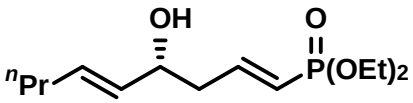
HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 14.5 min, t_R(minor) = 15.9 min, ee = 95%.



Peak#	Ret. Time	Area%
1	14.419	49.927
2	15.797	50.073

Peak#	Ret. Time	Area%
1	14.548	97.403
2	15.947	2.597

Figure S287, the HPLC spectrum of compound **3ad,** related to **Table 2**



3ae

3ae: Procedure A, 59 mg, colorless liquid, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (ddt, *J* = 24.1, 17.1, 7.0 Hz, 1H), 5.83–5.61 (m, 2H), 5.48 (dd, *J* = 15.4, 6.8 Hz, 1H), 4.22 (q, *J* = 6.4 Hz, 1H), 4.17–3.96 (m, 4H), 2.52–2.41 (m, 2H), 2.32 (s, 1H), 2.10–1.89 (m, 2H), 1.45–1.33 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 6H), 0.90 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.59 (d, *J* = 5.0 Hz), 132.59, 131.81, 119.42 (d, *J* = 187.0 Hz), 71.24, 61.67 (d, *J* = 5.2 Hz), 42.17 (d, *J* = 21.9 Hz), 34.16, 22.17, 16.29 (d, *J* = 6.5 Hz), 13.61 ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.03 ppm.

MS(ESI) m/z $[M+H]^+$: 277.15.

HRMS(ESI) m/z $[M+H]^+$: calcd. 277.1563, found 277.1563.

IR (film): 3384, 2960, 1635, 1230, 1098, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = +5.67 (*c* = 1.510, $CHCl_3$, 93% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 12.8 min, t_R(minor) = 13.8 min, ee = 93%.

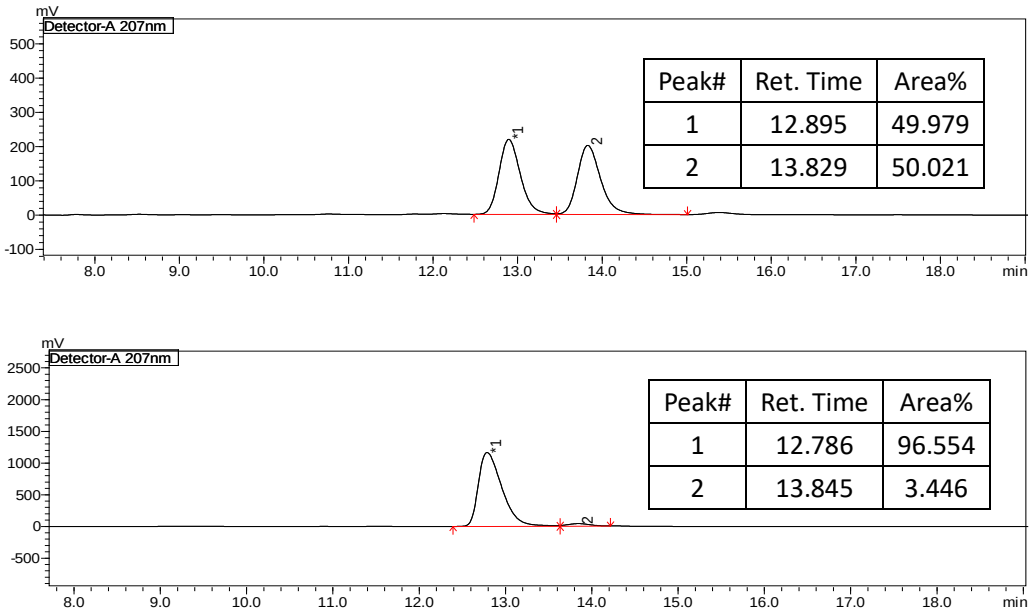
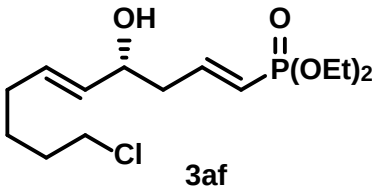


Figure S288, the HPLC spectrum of compound **3ae,** related to **Table 2**



3af

3af: Procedure A, 69 mg, colorless liquid, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (ddt, *J* = 24.1, 17.1, 7.0 Hz, 1H), 5.81–5.61 (m, 2H), 5.51 (dd, *J* = 15.4, 6.6 Hz, 1H), 4.22 (q, *J* = 6.3 Hz, 1H), 4.17–3.09 (m, 4H), 3.54 (t, *J* = 6.6 Hz, 2H), 2.46 (t, *J* = 6.5 Hz, 2H), 2.25 (s, 1H), 2.17–1.96 (m, 2H), 1.85–1.72 (m, 2H), 1.57–1.45 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.41 (d, *J* = 5.0 Hz), 132.29, 131.79, 119.62 (d, *J* = 187.1 Hz), 71.10 (d, *J* = 1.1 Hz), 61.73 (d, *J* = 5.4 Hz), 44.83, 42.14 (d, *J* = 22.0 Hz), 31.94, 31.28, 26.20, 16.32 (d, *J* = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.97 ppm.

MS(ESI) m/z $[M+Na]^+$: 347.05.

HRMS(ESI) m/z $[M+H]^+$: calcd. 325.1330, found 325.1332.

IR (film): 3379, 2987, 1635, 1260, 1028, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +5.66 (*c* = 0.940, $CHCl_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 18.1 min, t_R(minor) = 20.0 min, ee = 97%.

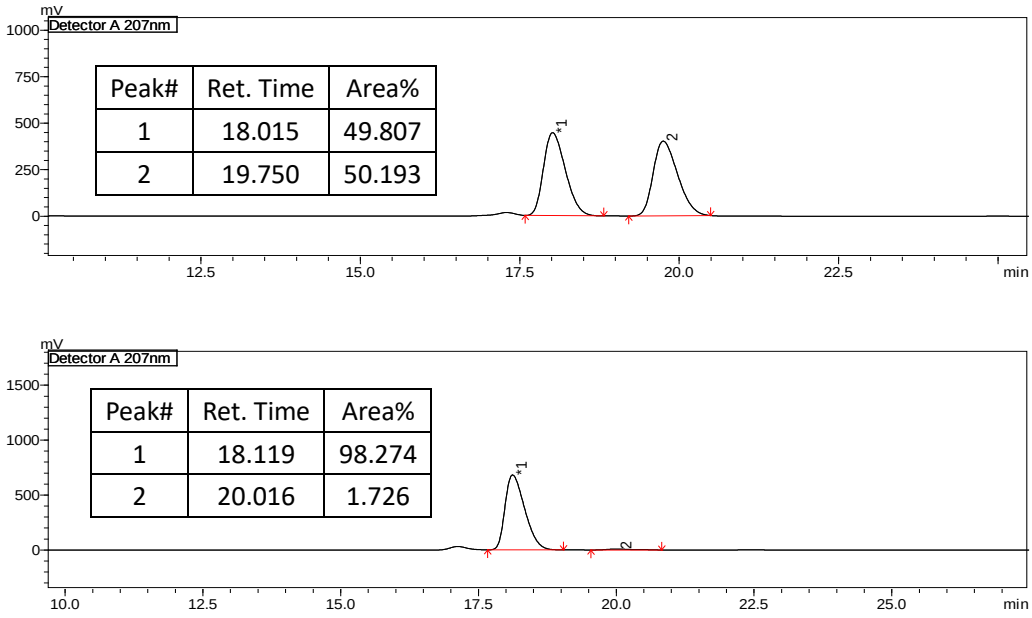
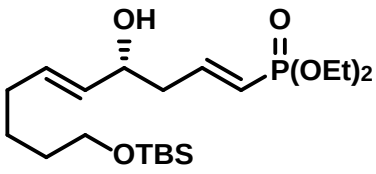


Figure S289, the HPLC spectrum of compound **3af,** related to **Table 2**



3ag

3ag: Procedure A, 59 mg, colorless liquid, 47% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (ddt, *J* = 24.1, 17.2, 7.0 Hz, 1H), 5.81–5.61 (m, 2H), 5.48 (dd, *J* = 15.4, 6.8 Hz, 1H), 4.21 (q, *J* = 6.4 Hz, 1H), 4.17–3.96 (m, 4H), 3.60 (t, *J* = 6.3 Hz, 2H), 2.45 (t, *J* = 6.4 Hz, 2H), 2.22 (s, 1H), 2.14–1.96 (m, 2H), 1.57–1.47 (m, 2H), 1.46–1.36 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 6H), 0.89 (s, 9H), 0.05 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.55 (d, *J* = 5.1 Hz), 132.62, 131.80, 119.51 (d, *J* = 186.9 Hz), 71.23 (d, *J* = 1.3 Hz), 62.94, 61.70 (d, *J* = 5.5 Hz), 42.15 (d, *J* = 21.9 Hz), 32.26, 31.86, 29.66, 25.93, 25.29, 18.33, 16.31 (d, *J* = 6.4 Hz), -5.31 ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.03 ppm.

MS(ESI) m/z $[M+Na]^+$: 443.15.

HRMS(ESI) m/z $[M+H]^+$: calcd. 421.2534, found 421.2534.

IR (film): 3381, 2930, 1633, 1255, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = +3.45 (*c* = 1.100, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 19.1 min, t_R(minor) = 20.9 min, ee = 98%.

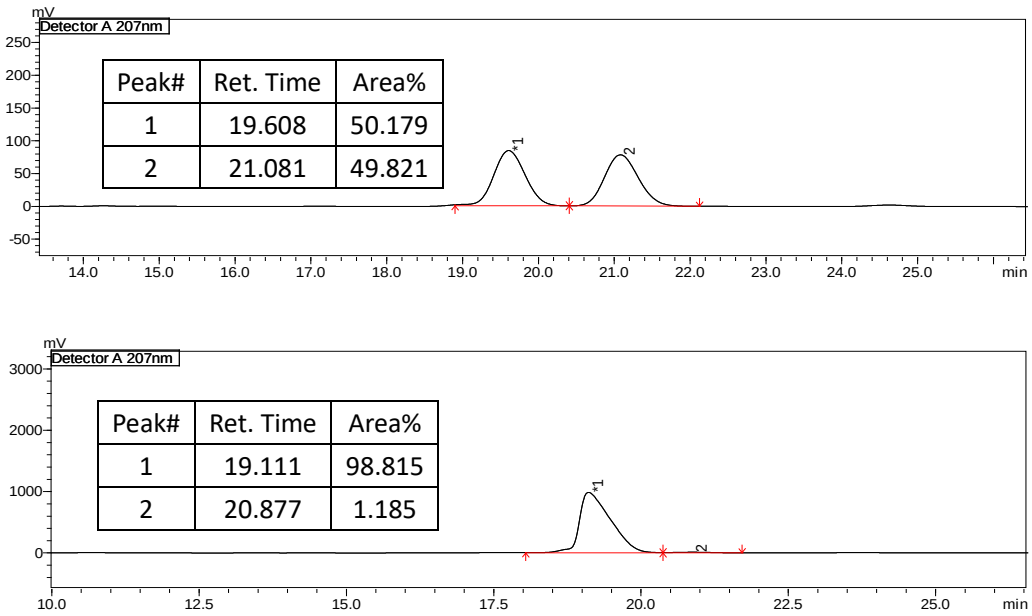
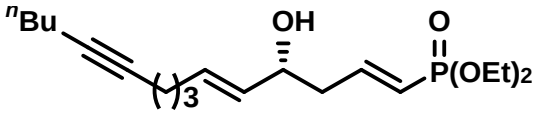


Figure S290, the HPLC spectrum of compound **3ag,** related to **Table 2**



3ah

3ah: Procedure A, 91 mg, colorless liquid, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (ddt, *J* = 22.1, 17.1, 7.0 Hz, 1H), 5.81–5.61 (m, 2H), 5.51 (dd, *J* = 15.4, 6.7 Hz, 1H), 4.22 (q, *J* = 6.4 Hz, 1H), 4.17–3.98 (m, 4H), 2.56–2.44 (m, 2H), 2.23–2.01 (m, 7H), 1.62–1.49 (m, 2H), 1.54–1.33 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 6H), 0.91 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.43, 132.29, 131.85 (d, *J* = 2.6 Hz), 119.58 (d, *J* = 187.0 Hz), 80.66, 79.47, 71.19, 61.71 (d, *J* = 5.6 Hz), 42.11 (d, *J* = 21.9 Hz), 31.18, 31.13, 28.42, 21.89, 18.38, 18.18, 16.32 (d, *J* = 6.4 Hz), 13.59 ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 17.97 ppm.

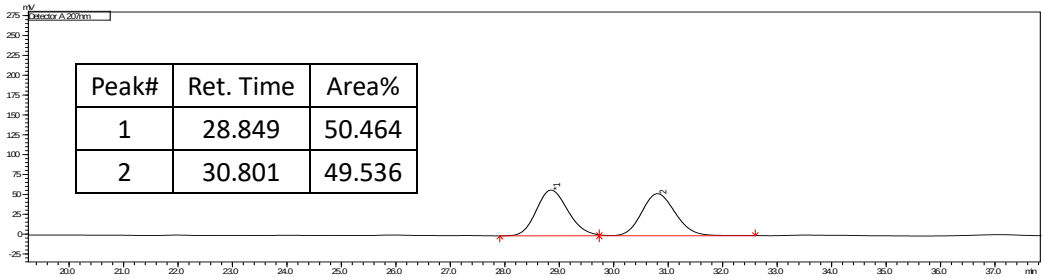
MS(ESI) m/z $[M+H]^+$: 357.15.

HRMS(ESI) m/z $[M+H]^+$: calcd. 357.2189, found 357.2191.

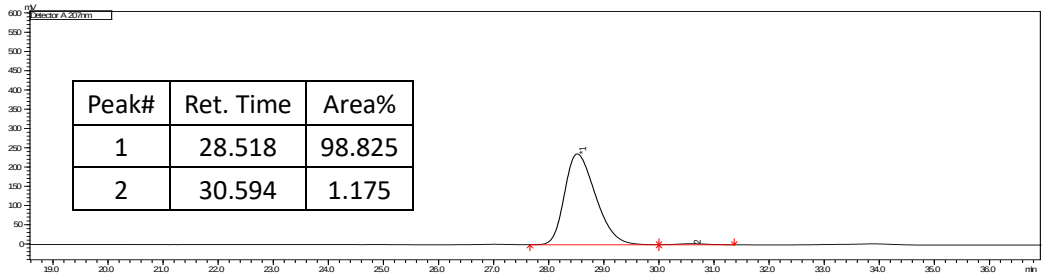
IR (film): 3379, 2932, 1634, 1275, 1027, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = +3.32 (*c* = 1.110, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 15/1, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 28.5 min, t_R(minor) = 30.6 min, ee = 98%.

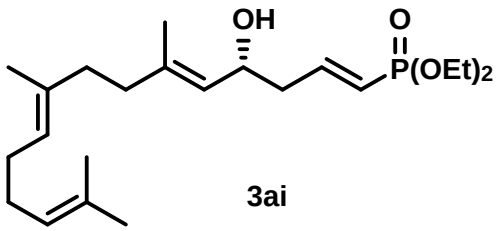


Peak#	Ret. Time	Area%
1	28.849	50.464
2	30.801	49.536



Peak#	Ret. Time	Area%
1	28.518	98.825
2	30.594	1.175

Figure S291, the HPLC spectrum of compound **3ah,** related to **Table 2**



3ai

3ai: Procedure A, 80 mg, colorless liquid, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (ddt, *J* = 22.0, 17.1, 7.0 Hz, 1H), 5.74 (dd, *J* = 21.3, 17.1 Hz, 1H), 5.21 (dd, *J* = 8.6, 0.7 Hz, 1H), 5.19–5.00 (m, 2H), 4.51 (dd, *J* = 14.4, 6.7 Hz, 1H), 4.17–4.00 (m, 4H), 2.55–2.33 (m, 2H), 2.28 (s, 1H), 2.13–1.93 (m, 8H), 1.68 (s, 6H), 1.60 (s, 6H), 1.32 (t, *J* = 7.1 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.74 (d, *J* = 4.7 Hz), 139.24, 135.37, 131.29, 126.56, 124.21, 123.58, 119.31 (d, *J* = 187.0 Hz), 67.04 (d, *J* = 1.0 Hz), 61.66 (d, *J* = 5.6 Hz), 42.42 (d, *J* = 21.7 Hz), 39.62, 39.45, 26.66, 26.29, 25.64, 17.63, 16.68, 16.29 (d, *J* = 6.5 Hz), 15.96 ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.11 ppm.

MS(ESI) m/z [M+Na]$^{+}$: 421.15.

HRMS(ESI) m/z [M+H]$^{+}$: calcd. 399.2659, found 399.2659.

IR (film): 3385, 2927, 1633, 1270, 1028, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = +2.53 (*c* = 2.675, $CHCl_3$, 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 37/3, flow rate: 0.8 mL/min, λ = 207 nm, t_R(major) = 19.3 min, t_R(minor) = 23.1 min, ee = 99%.

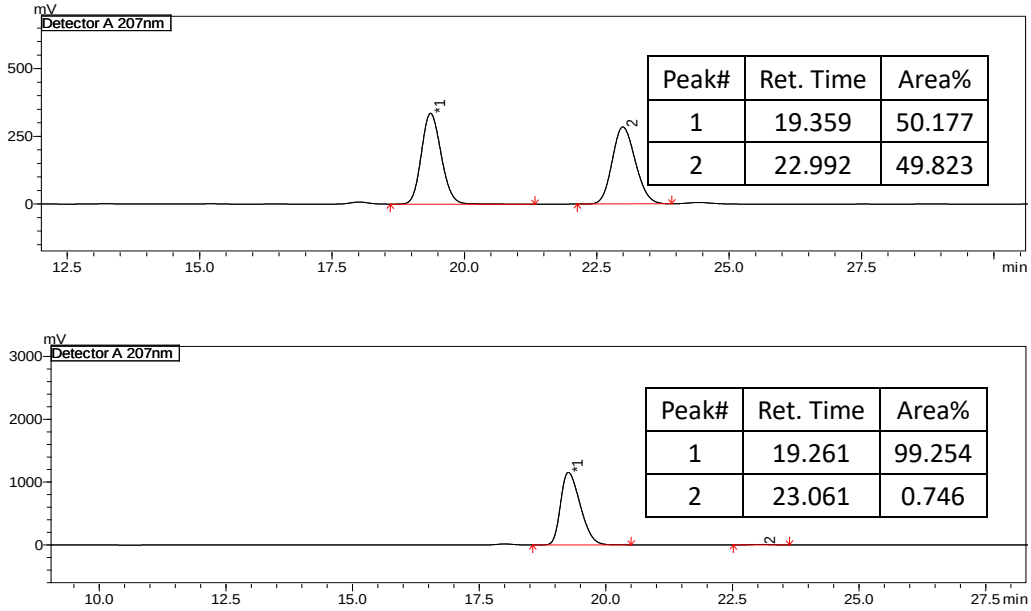
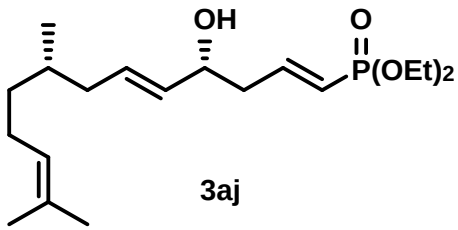


Figure S292, the HPLC spectrum of compound **3ai,** related to **Table 2**



3aj

3aj: Procedure A, 56 mg, colorless liquid, 52% yield, 15/1 dr (Diastereoselectivity was determined by ^{1}H NMR analysis of reaction crude mixture).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (ddt, *J* = 22.1, 17.1, 7.0 Hz, 1H), 5.80–5.60 (m, 2H), 5.48 (dd, *J* = 15.3, 6.7 Hz, 1H), 5.09 (t, *J* = 7.1 Hz, 1H), 4.32–4.16 (m, 1H), 4.17–3.95 (m, 4H), 2.56–2.40 (m, 2H), 2.40 (s, 1H), 2.11–1.81 (m, 4H), 1.68 (s, 3H), 1.60 (s, 3H), 1.55–1.45 (m, 1H), 1.40–1.23 (m, 7H), 1.22–1.07 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.58 (d, *J* = 4.8 Hz), 132.97, 131.15, 124.64, 119.47 (d, *J* = 187.1 Hz), 109.99, 71.20 (d, *J* = 1.2 Hz), 61.69 (d, *J* = 6.4 Hz), 42.21 (d, *J* = 21.9 Hz), 39.48, 36.62, 32.43, 25.67, 25.48, 19.32, 17.61, 16.31 (d, *J* = 6.4 Hz) ppm.

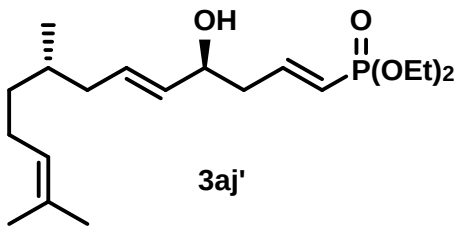
^{31}P NMR (162 MHz, $CDCl_3$) δ 18.04 ppm.

MS(ESI) m/z $[M+Na]^+$: 381.15.

HRMS(ESI) m/z $[M+H]^+$: calcd. 359.2346, found 359.2346.

IR (film): 3381, 2912, 1633, 1231, 1028, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +6.51 (*c* = 2.205, $CHCl_3$, 15/1 dr).



3aj'

3aj': Procedure B, 65 mg, colorless liquid, 60% yield, > 20/1 dr (Diastereoselectivity was determined by ^{1}H NMR analysis of reaction crude mixture).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (ddt, *J* = 22.1, 17.1, 7.0 Hz, 1H), 5.79–5.58 (m, 2H), 5.48 (dd, *J* = 15.3, 6.8 Hz, 1H), 5.09 (t, *J* = 7.1 Hz, 1H), 4.29–4.16 (m, 1H), 4.17–4.00 (m, 4H), 2.56–2.36 (m, 2H), 2.38 (s, 1H), 2.12–1.75 (m, 4H), 1.68 (s, 3H), 1.60 (s, 3H), 1.55–1.41 (m, 1H), 1.38–1.24 (m, 7H), 1.22–1.08 (m, 1H), 0.86 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.56 (d, *J* = 5.0 Hz), 132.96, 131.30, 131.18, 124.64, 119.46 (d, *J* = 187.1 Hz), 71.27 (d, *J* = 1.3 Hz), 61.69 (d, *J* = 5.2 Hz), 42.22 (d, *J* = 21.9 Hz), 39.53, 36.67, 32.40, 25.67, 25.48 , 19.30, 17.61, 16.31 (d, *J* = 6.4 Hz) ppm.

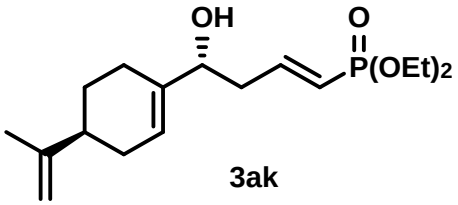
^{31}P NMR (162 MHz, $CDCl_3$) δ 18.03 ppm.

MS(ESI) m/z $[M+H]^+$: 381.15.

HRMS(ESI) m/z $[M+H]^+$: calcd. 359.2346, found 359.2347.

IR (film): 3380, 2964, 1633, 1231, 1028 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = -5.73 (*c* = 1.875, $CHCl_3$, > 20/1 dr).



3ak

3ak: Procedure A, 57 mg, colorless liquid, 58% yield, > 20/1 dr (Diastereoselectivity was determined by ^{1}H NMR analysis of reaction crude mixture).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (ddt, *J* = 24.1, 17.1, 6.9 Hz, 1H), 5.83–5.64 (m, 2H), 4.71 (d, *J* = 9.3 Hz, 2H), 4.15 (t, *J* = 6.6 Hz, 1H), 4.12–4.00 (m, 4H), 2.57–2.35 (m, 2H), 2.30–1.91 (m, 5H), 1.91–1.82 (m, 1H), 1.73 (s, 3H), 1.55–1.37 (m, 1H), 1.38–1.21 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.92 (d, *J* = 4.5 Hz), 149.54, 138.71, 123.61, 119.09 (d, *J* = 186.7 Hz), 108.71, 74.40, 61.68 (d, *J* = 5.4 Hz), 41.19, 39.82 (d, *J* = 21.9 Hz), 30.39, 27.42, 23.81, 20.69, 16.32 (d, *J* = 6.4 Hz) ppm.

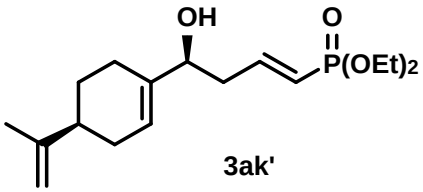
^{31}P NMR (162 MHz, $CDCl_3$) δ 18.06 ppm.

MS(ESI) m/z $[M+H]^+$: 329.15.

HRMS(ESI) m/z $[M+H]^+$: calcd. 329.1876, found 329.1877.

IR (film): 3379, 2988, 1636, 1260, 1028, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = -25.80 (*c* = 1.330, $CHCl_3$, > 20/1 dr).



3ak'

3ak': Procedure B, 78 mg, colorless liquid, 79% yield, > 20/1 dr (Diastereoselectivity was determined by ^{1}H NMR analysis of reaction crude mixture).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (ddt, *J* = 24.1, 17.2, 7.0 Hz, 1H), 5.82–5.65 (m, 2H), 4.71 (d, *J* = 12.2 Hz, 2H), 4.14 (t, *J* = 6.2 Hz, 1H), 4.16–4.00 (m, 4H), 2.59–2.39 (m, 3H), 2.21–2.05 (m, 3H), 2.02–1.90 (m, 1H), 1.89–1.75 (m, 1H), 1.73 (s, 3H), 1.56–1.49 (m, 1H), 1.36–1.20 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.03 (d, *J* = 4.9 Hz),149.5, 138.49, 122.37, 119.08 (d, *J* = 187.0 Hz), 108.68, 74.10 (d, *J* = 1.0 Hz), 61.68 (d, *J* = 5.4 Hz), 41.05, 40.12 (d, *J* = 22.0 Hz), 30.27, 27.30, 24.50, 20.73, 16.31 (d, *J* = 6.3 Hz) ppm.

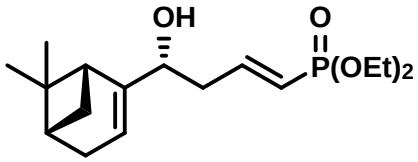
^{31}P NMR (162 MHz, $CDCl_3$) δ 18.10 ppm.

MS(ESI) m/z $[M+H]^+$: 329.15.

HRMS(ESI) m/z $[M+H]^+$: calcd. 329.1876, found 329.1876.

IR (film): 3379, 2985, 1642, 1260, 1028, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = -38.08 (*c* = 1.735, $CHCl_3$, > 20/1 dr).



3al

3al: Procedure A, 87 mg, colorless liquid, 88% yield, > 20/1 dr (Diastereoselectivity was determined by ^{1}H NMR analysis of reaction crude mixture).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (ddt, *J* = 23.9, 17.1, 6.8 Hz, 1H), 5.74 (dd, *J* = 21.1, 17.1 Hz, 1H), 5.48 (s, 1H), 4.14 (t, *J* = 6.0 Hz, 1H), 4.16–3.96 (m, 4H), 2.52–2.35 (m, 3H), 2.32–2.19 (m, 3H), 2.16–2.00 (m, 2H), 1.37–1.24 (m, 9H), 1.16 (d, *J* = 8.6 Hz, 1H), 0.82 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.97 (d, *J* = 4.9 Hz), 149.51, 119.20 (d, *J* = 187.0 Hz), 118.07, 73.05 (d, *J* = 1.1 Hz), 61.63 (d, *J* = 3.8 Hz), 42.05, 40.83, 39.64 (d, *J* = 22.0 Hz), 37.79, 31.66, 31.01, 26.11, 21.39, 16.31 (d, *J* = 6.5 Hz) ppm.

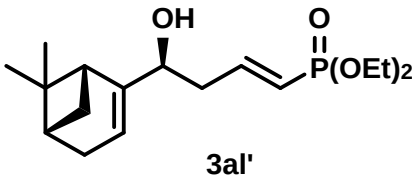
^{31}P NMR (162 MHz, $CDCl_3$) δ 18.03 ppm.

MS(ESI) m/z $[M+H]^+$: 329.15.

HRMS(ESI) m/z $[M+H]^+$: calcd. 329.1876, found 329.1876.

IR (film): 3384, 2914, 1635, 1260, 1027, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{29}$ = -9.99 (*c* = 1.540, $CHCl_3$, > 20/1 dr).



3al'

3al': Procedure B, 60 mg, colorless liquid, 61% yield, > 20/1 dr (Diastereoselectivity was determined by ^{1}H NMR analysis of reaction crude mixture).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (ddt, *J* = 24.0, 17.1, 6.9 Hz, 1H), 5.72 (dd, *J* = 21.2, 17.1 Hz, 1H), 5.48 (s, 1H), 4.14 (t, *J* = 6.5 Hz, 1H), 4.16–4.00 (m, 4H), 2.48–2.34 (m, 3H), 2.31–2.18 (m, 3H), 2.15–2.00 (m, 2H), 1.37–1.24 (m, 9H), 1.12 (d, *J* = 8.6 Hz, 1H), 0.84 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.00 (d, *J* = 4.8 Hz), 149.02, 119.10 (d, *J* = 187.0 Hz), 118.53, 72.99 (d, *J* = 0.9 Hz), 61.64 (d, *J* = 5.4 Hz), 41.82, 40.84, 39.57 (d, *J* = 22.0 Hz), 37.77, 31.60, 31.03, 26.04, 21.35, 16.30 (d, *J* = 6.5 Hz) ppm.

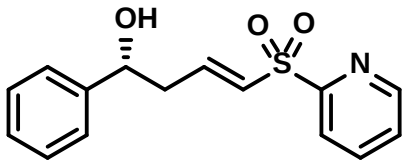
^{31}P NMR (162 MHz, $CDCl_3$) δ 18.11 ppm.

MS(ESI) m/z $[M+H]^+$: 329.15.

HRMS(ESI) m/z $[M+H]^+$:calcd. 329.1876, found 329.1875.

IR (film): 3379, 2988, 1631, 1260, 1028, 750 cm^{-1}.

Optical rotation:$[\alpha]_D^{29}$ = -24.74 (*c* = 1.870, $CHCl_3$, > 20/1 dr).



5a

5a: Procedure A, 83 mg, pale green solid, 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.94 (t, *J* = 7.7 Hz, 1H), 7.57–7.47 (m, 1H), 7.36–7.24 (m, 5H), 7.15 (dt, *J* = 15.2, 7.2 Hz, 1H), 6.60 (d, *J* = 15.2 Hz, 1H), 5.24–4.49 (m, 1H), 2.78 (d, *J* = 3.2 Hz, 1H), 2.76–2.66 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.21, 150.15, 146.36, 142.95, 138.25, 129.96, 128.61, 127.96, 127.13, 125.63, 121.91, 72.36, 41.34 ppm.

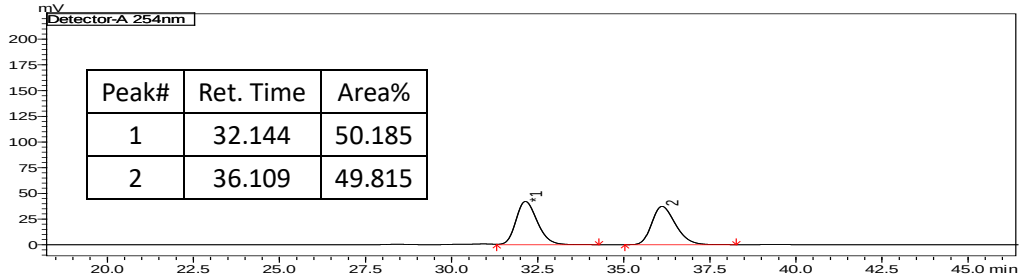
MS(ESI) m/z $[M+H]^+$: 290.00.

HRMS(ESI) m/z $[M+H]^+$: calcd. 290.0845, found 290.0846.

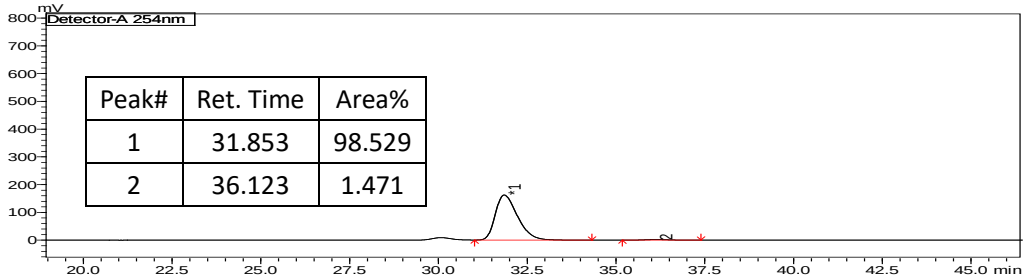
IR (film): 3502, 2914, 1630, 1428, 1170, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = +32.29 (*c* = 1.050, $CHCl_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 31.9 min, t_R(minor) = 36.1 min, ee = 97%.

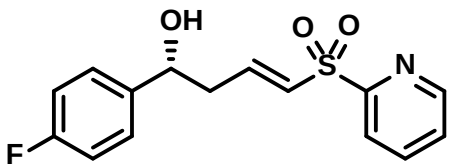


Peak#	Ret. Time	Area%
1	32.144	50.185
2	36.109	49.815



Peak#	Ret. Time	Area%
1	31.853	98.529
2	36.123	1.471

Figure S293, the HPLC spectrum of compound **5a,** related to **Table 3**



5b

5b: Procedure A, 81 mg, colorless crystal, 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.1 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.99–7.85 (m, 1H), 7.53 (dd, *J* = 7.1, 5.2 Hz, 1H), 7.30 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.13 (dt, *J* = 15.2, 7.3 Hz, 1H), 7.00 (t, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 15.2 Hz, 1H), 4.89 (t, *J* = 6.2 Hz, 1H), 2.81–2.62 (m, 2H), 2.49 (s, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.31 (d, *J* = 246.2 Hz), 158.24 , 150.15, 145.86, 138.61 (d, *J* = 3.2 Hz), 138.25, 130.25, 127.31 (d, *J* = 8.1 Hz), 127.13, 121.81, 115.48 (d, *J* = 21.4 Hz), 71.78, 41.43 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.86 ~ -117.88 (m) ppm.

MS(ESI) m/z $[M+Na]^+$: 329.95.

HRMS(ESI) m/z $[M+H]^+$: calcd. 308.0751, found 308.0752.

IR (film): 3405, 2921, 1428, 1276 cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = +21.10 (*c* = 0.250, $CHCl_3$, 97% ee).

HPLC: DAICEL CHIRALPAK IE, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 41.4 min, t_R(minor) = 47.7 min, ee = 97%.

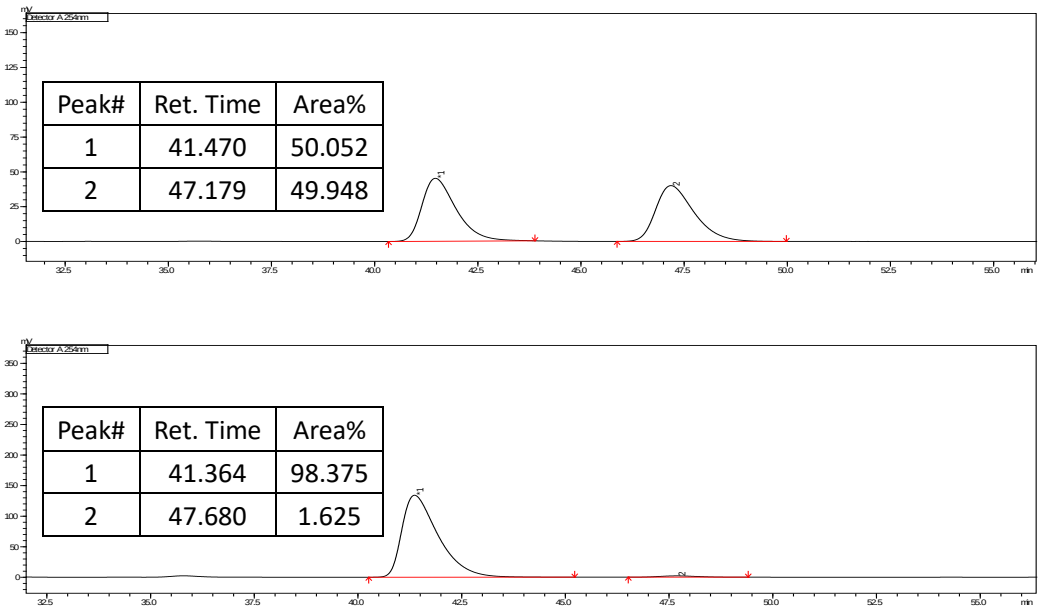
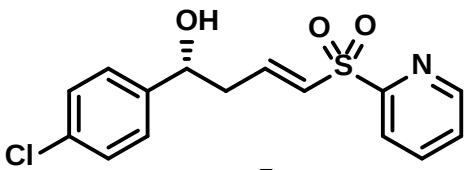


Figure S294, the HPLC spectrum of compound **5b,** related to **Table 3**



5c

5c: Procedure A, 90 mg, colorless crystal, 93% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.6 Hz, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.95 (td, *J* = 7.8, 1.6 Hz, 1H), 7.53 (dd, *J* = 7.1, 5.2 Hz, 1H), 7.31–7.21 (m, 4H), 7.12 (dt, *J* = 15.2, 7.3 Hz, 1H), 6.58 (d, *J* = 15.2 Hz, 1H), 4.89 (t, *J* = 6.3 Hz, 1H), 2.78 (s, 1H), 2.69 (t, *J* = 6.6 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.14, 150.15, 145.78, 141.34, 138.28, 133.59, 130.31, 128.73, 127.18, 127.01, 121.84, 71.69, 41.34 ppm.

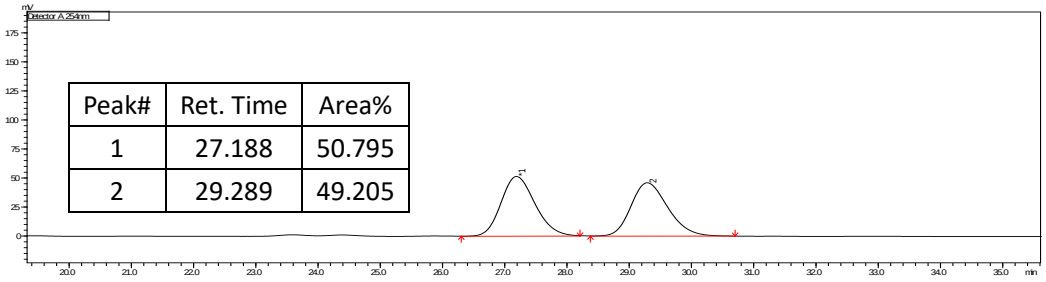
MS(ESI) m/z $[M+Na]^+$: 345.95.

HRMS(ESI) m/z $[M+H]^+$: calcd. 324.0456, found 324.0455.

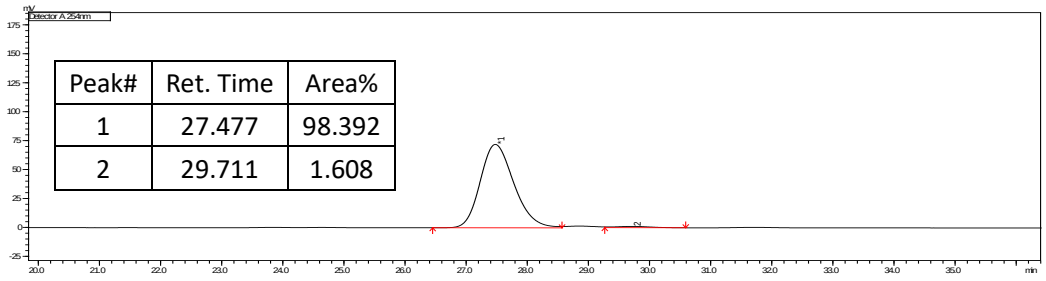
IR (film): 3494, 2919, 1630, 1453, 1163 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = +27.84 (*c* = 0.625, $CHCl_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 27.5 min, t_R(minor) = 29.7 min, ee = 97%.

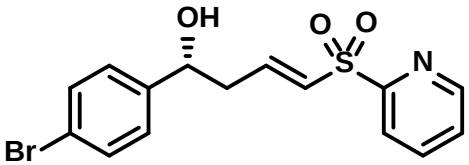


Peak#	Ret. Time	Area%
1	27.188	50.795
2	29.289	49.205



Peak#	Ret. Time	Area%
1	27.477	98.392
2	29.711	1.608

Figure S295, the HPLC spectrum of compound **5c,** related to **Table 3**



5d

5d: Procedure A, 94 mg, white powder, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.1 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.96 (td, *J* = 7.8, 1.6 Hz, 1H), 7.54 (dd, *J* = 6.6, 4.8 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.12 (dt, *J* = 15.2, 7.3 Hz, 1H), 6.59 (d, *J* = 15.2 Hz, 1H), 4.87 (t, *J* = 6.2 Hz, 1H), 2.69 (t, *J* = 7.0 Hz, 2H), 2.55 (s, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.21, 150.16, 145.61, 141.80, 138.25, 131.69, 130.41, 127.33, 127.15, 121.79, 121.76, 71.78, 41.27 ppm.

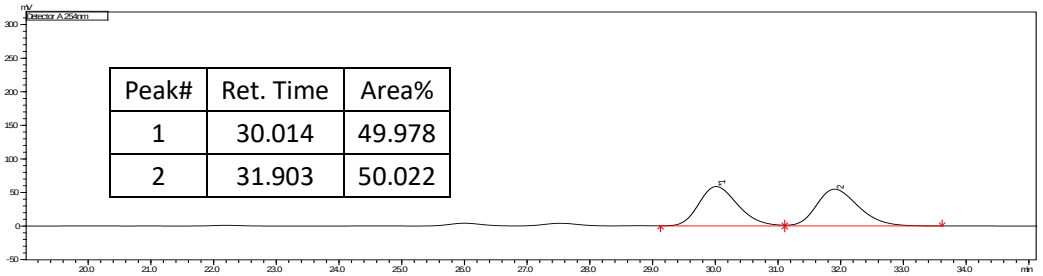
MS(ESI) m/z $[M+Na]^+$: 389.90.

HRMS(ESI) m/z $[M+H]^+$: calcd. 367.9951, found 367.9951.

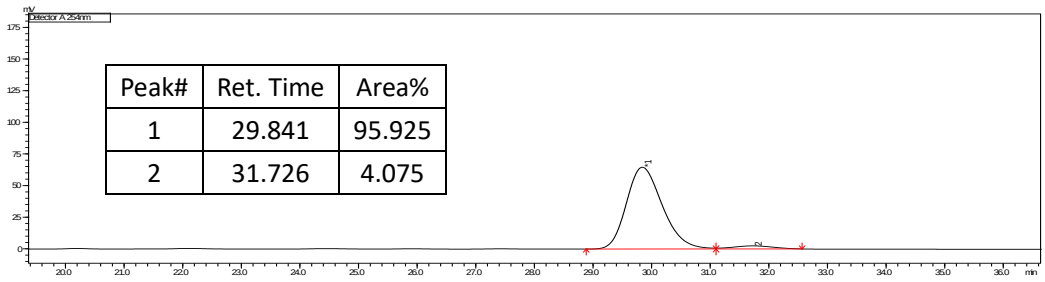
IR (film): 3490, 2924, 1428, 1262 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +30.84 (*c* = 0.335, $CHCl_3$, 92% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 29.8 min, t_R(minor) = 31.7 min, ee = 92%.

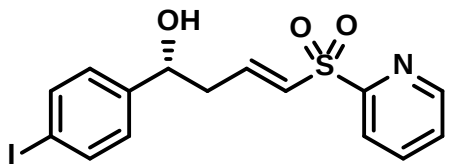


Peak#	Ret. Time	Area%
1	30.014	49.978
2	31.903	50.022



Peak#	Ret. Time	Area%
1	29.841	95.925
2	31.726	4.075

Figure S296, the HPLC spectrum of compound **5d,** related to **Table 3**



5e

5e: Procedure A, 102 mg, white powder, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.5 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.95 (td, *J* = 7.7, 1.6 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.54 (ddd, *J* = 7.5, 4.7, 0.9 Hz, 1H), 7.19–6.99 (m, 3H), 6.56 (d, *J* = 15.2 Hz, 1H), 4.85 (t, *J* = 6.2 Hz, 1H), 3.20 (s, 1H), 2.77–2.56 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.99, 150.18, 145.93, 142.67, 138.35, 137.55, 130.21, 127.63, 127.26, 121.92, 93.26, 71.69, 41.25 ppm.

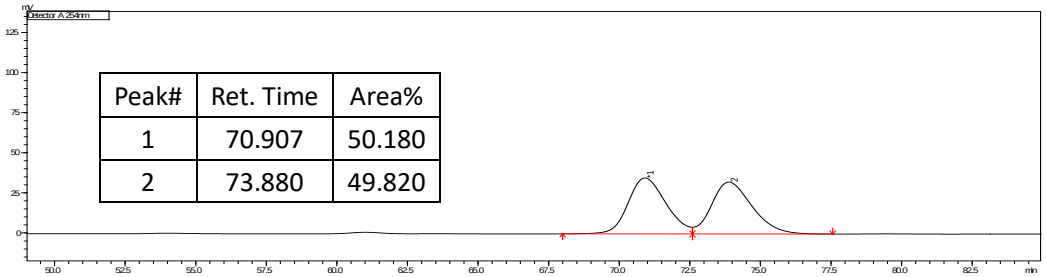
MS(ESI) m/z $[M+Na]^+$: 437.70.

HRMS(ESI) m/z $[M+H]^+$: calcd. 415.9812, found 415.9812.

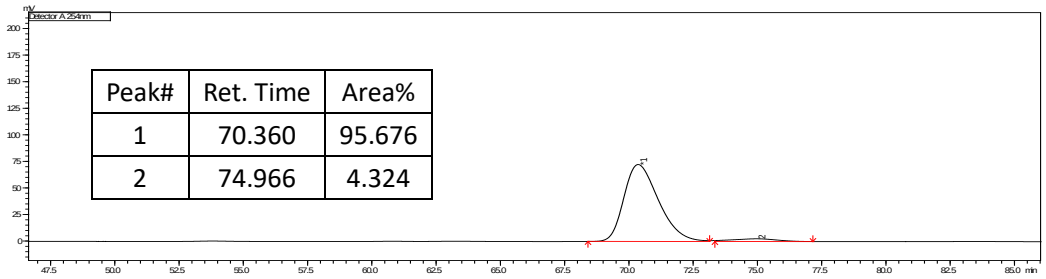
IR (film): 3493, 2919, 1630, 1427, 1163 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = +28.57 (*c* = 1.835, $CHCl_3$, 91% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 5/1, flow rate: 0.72 mL/min, λ = 254 nm, t_R(major) = 70.4 min, t_R(minor) = 75.0 min, ee = 91%.

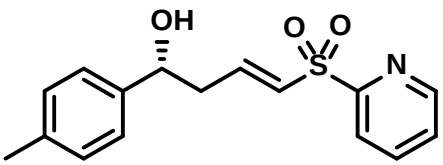


Peak#	Ret. Time	Area%
1	70.907	50.180
2	73.880	49.820



Peak#	Ret. Time	Area%
1	70.360	95.676
2	74.966	4.324

Figure S297, the HPLC spectrum of compound **5e,** related to **Table 3**



5f

5f: Procedure A, 87 mg, white powder, 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.2 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.93 (td, *J* = 7.8, 1.6 Hz, 1H), 7.51 (ddd, *J* = 7.5, 4.7, 0.9 Hz, 1H), 7.25–7.05 (m, 5H), 6.59 (d, *J* = 15.2 Hz, 1H), 4.93–4.75 (m, 1H), 2.84–2.58 (m, 3H), 2.32 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.20, 150.16, 146.53, 140.00, 138.25, 137.64, 129.84, 129.25, 127.11, 125.57, 121.90, 72.21, 41.32, 21.09 ppm.

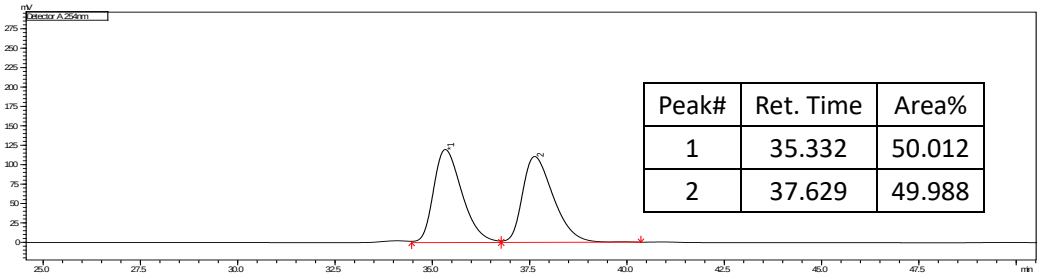
MS(ESI) m/z $[M+Na]^+$: 326.00.

HRMS(ESI) m/z $[M+H]^+$: calcd. 304.1002, found 304.1002.

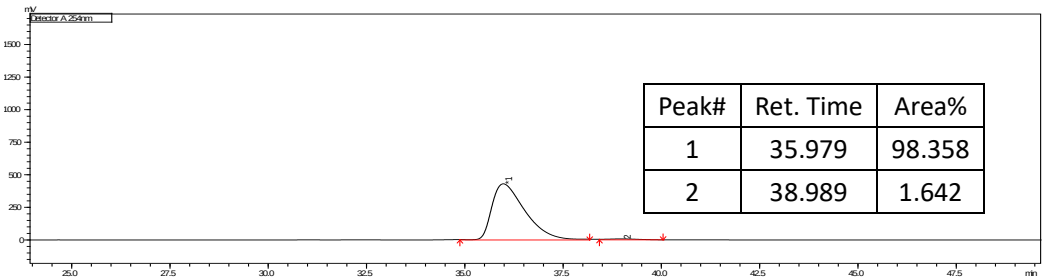
IR (film): 3514, 2921, 1630, 1428, 1270 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = +35.05 (*c* = 1.165, $CHCl_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 36.0 min, t_R(minor) = 39.0 min, ee = 97%.

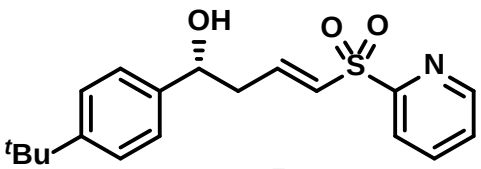


Peak#	Ret. Time	Area%
1	35.332	50.012
2	37.629	49.988



Peak#	Ret. Time	Area%
1	35.979	98.358
2	38.989	1.642

Figure S298, the HPLC spectrum of compound **5f,** related to **Table 3**



5g

5g: Procedure A, 94 mg, colorless liquid, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.6 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.94 (td, *J* = 7.8, 1.6 Hz, 1H), 7.51 (ddd, *J* = 7.6, 4.8, 0.9 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.22–7.06 (m, 1H), 6.62 (d, *J* = 15.2 Hz, 1H), 4.89–4.78 (m, 1H), 2.91–2.59 (m, 3H), 1.30 (s, 9H).ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.19, 150.92, 150.18, 146.67, 139.99, 138.28, 129.78, 127.14, 125.50, 125.40, 121.94, 72.13, 41.24, 34.52, 31.30 ppm.

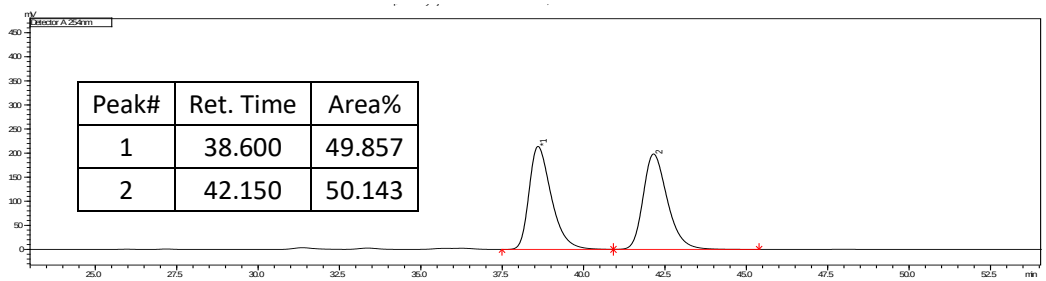
MS(ESI) m/z [M+Na]$^+$: 368.05.

HRMS(ESI) m/z [M+H]$^+$: calcd. 346.1471, found 346.1469.

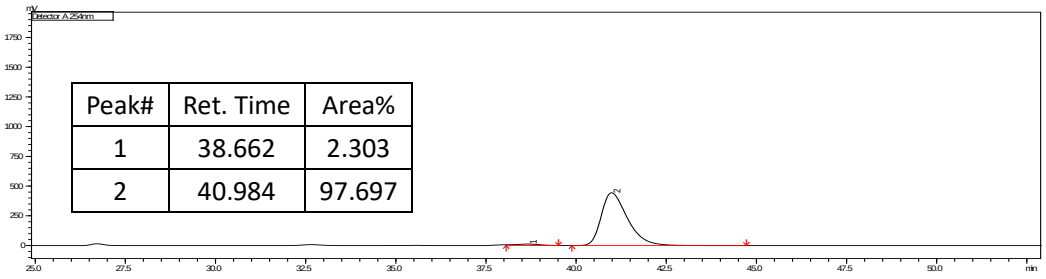
IR (film): 3507, 2989, 1461, 1260, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = +28.35 (*c* = 1.790, $CHCl_3$, 95% ee).

HPLC: DAICEL CHIRALPAK IG-3, hexane/*i*-PrOH = 3/1, flow rate: 0.6 mL/min, λ = 254 nm, t_R(major) = 41.0 min, t_R(minor) = 38.7 min, ee = 95%.

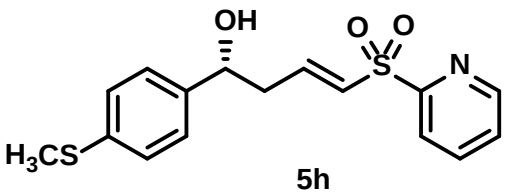


Peak#	Ret. Time	Area%
1	38.600	49.857
2	42.150	50.143



Peak#	Ret. Time	Area%
1	38.662	2.303
2	40.984	97.697

Figure S299, the HPLC spectrum of compound **5g,** related to **Table 3**



5h

5h: Procedure A, 91 mg, pale green liquid, 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.6 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.95 (td, *J* = 7.8, 1.6 Hz, 1H), 7.56–7.49 (m, 1H), 7.31–7.18 (m, 4H), 7.19–7.06 (m, 1H), 6.60 (d, *J* = 15.2 Hz, 1H), 4.86 (t, *J* = 6.2 Hz, 1H), 2.76–2.63 (m, 2H), 2.47 (s, 3H), 2.43 (s, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.86, 150.15, 146.45, 139.97, 138.40, 137.82, 129.86, 127.29, 126.45, 126.27, 121.97, 71.73, 41.16, 15.68 ppm.

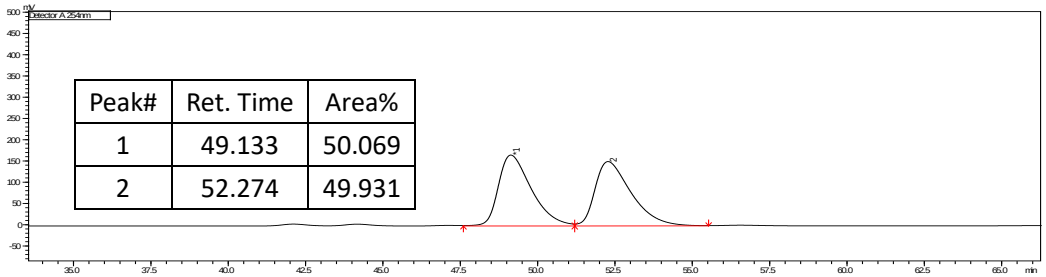
MS(ESI) m/z $[M+Na]^+$: 357.95.

HRMS(ESI) m/z $[M+H]^+$: calcd. 336.0723, found 336.0723.

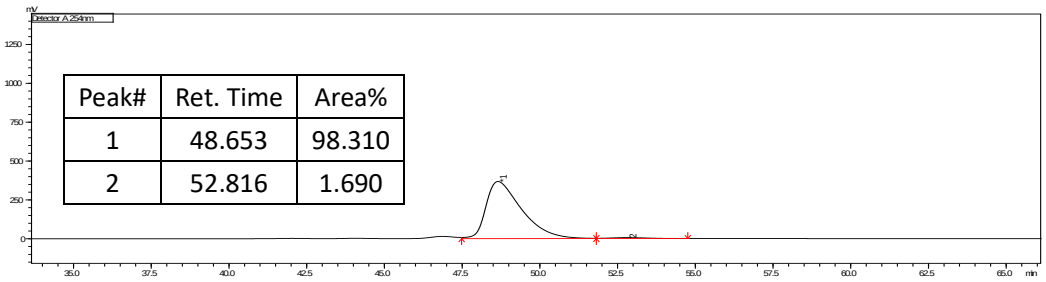
IR (film): 3393, 2921, 1428, 1270 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = +23.63 (*c* = 0.420, $CHCl_3$, 97% ee).

HPLC: DAICEL CHIRALPAK IE, hexane/*i*-PrOH = 11/5, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 48.7 min, t_R(minor) = 52.8 min, ee = 97%.

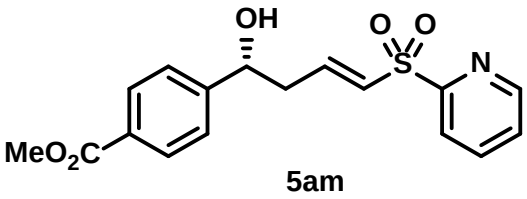


Peak#	Ret. Time	Area%
1	49.133	50.069
2	52.274	49.931



Peak#	Ret. Time	Area%
1	48.653	98.310
2	52.816	1.690

Figure S300, the HPLC spectrum of compound **5h,** related to **Table 3**



5am

5am: Procedure A, 79 mg, colorless liquid, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.3 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.97–7.87 (m, 3H), 7.51 (dd, *J* = 6.9, 4.9 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.13 (dt, *J* = 15.2, 7.2 Hz, 1H), 6.56 (d, *J* = 15.2 Hz, 1H), 4.96 (t, *J* = 6.1 Hz, 1H), 3.89 (s, 3H), 3.65 (s, 1H), 2.70 (t, *J* = 6.7 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.81, 157.87, 150.13, 148.20, 146.01, 138.39, 130.15, 129.76, 129.35, 127.28, 125.62, 121.96, 71.68, 52.14, 41.21 ppm.

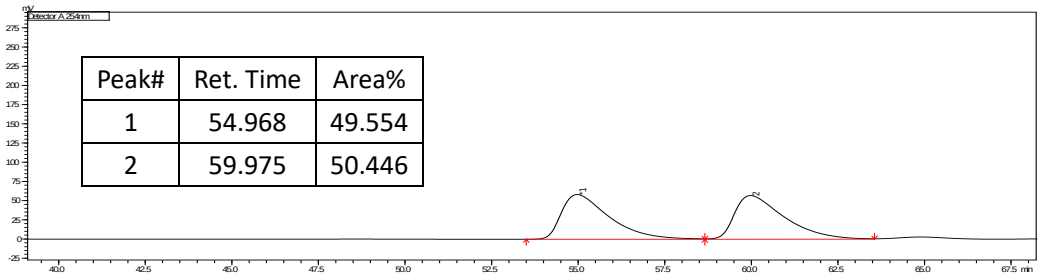
MS(ESI) m/z [M+Na]$^+$: 369.95.

HRMS(ESI) m/z [M+H]$^+$: calcd. 348.0900, found 348.0900.

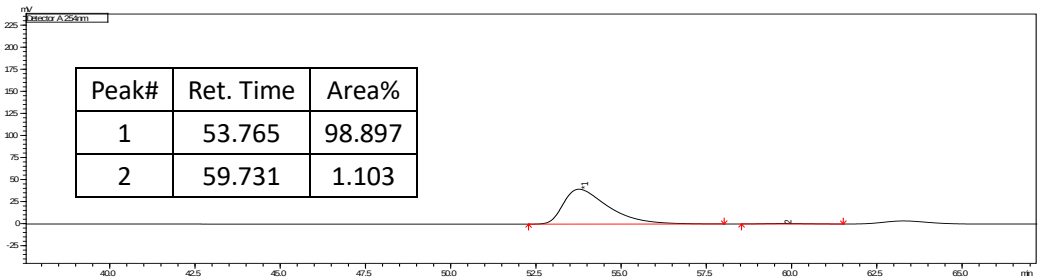
IR (film): 3493, 2952, 1717, 1429, 1026, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = +28.54 (*c* = 0.289, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 53.8 min, t_R(minor) = 59.7 min, ee = 98%.

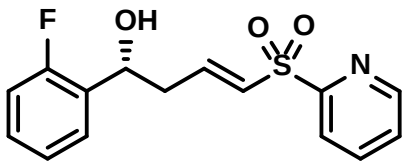


Peak#	Ret. Time	Area%
1	54.968	49.554
2	59.975	50.446



Peak#	Ret. Time	Area%
1	53.765	98.897
2	59.731	1.103

Figure S301, the HPLC spectrum of compound **5am,** related to **Table 3**



5k

5k: Procedure A, 88 mg, colorless liquid, 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.4 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.95 (td, *J* = 7.8, 1.5 Hz, 1H), 7.60–7.48 (m, 1H), 7.46 (td, *J* = 7.5, 1.2 Hz, 1H), 7.29–7.09 (m, 3H), 7.03–6.96 (m, 1H), 6.63 (d, *J* = 15.2 Hz, 1H), 5.24–5.18 (m, 1H), 2.86–2.66 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.59, 158.18 (d, *J* = 8.1 Hz), 150.16, 145.98, 138.26, 130.20, 129.87 (d, *J* = 13.2 Hz), 129.31 (d, *J* = 8.3 Hz), 127.13, 127.00 (d, *J* = 4.2 Hz), 124.43 (d, *J* = 3.5 Hz), 121.87, 115.34 (d, *J* = 21.6 Hz), 66.42 (d, *J* = 2.5 Hz), 40.03 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.29~-119.40 (m) ppm.

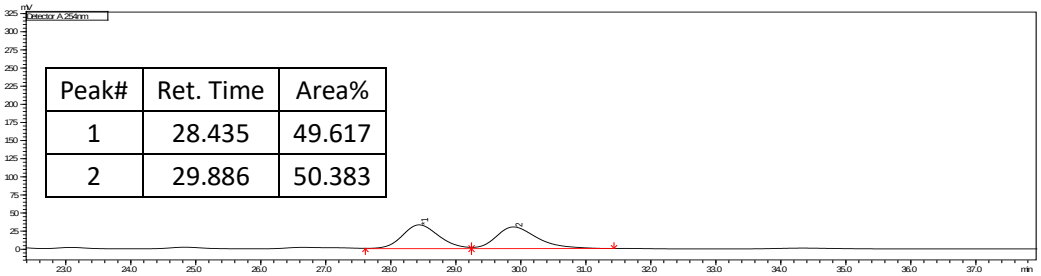
MS(ESI) m/z $[M+Na]^+$: 329.95.

HRMS(ESI) m/z $[M+H]^+$: calcd. 308.0751, found 308.0751.

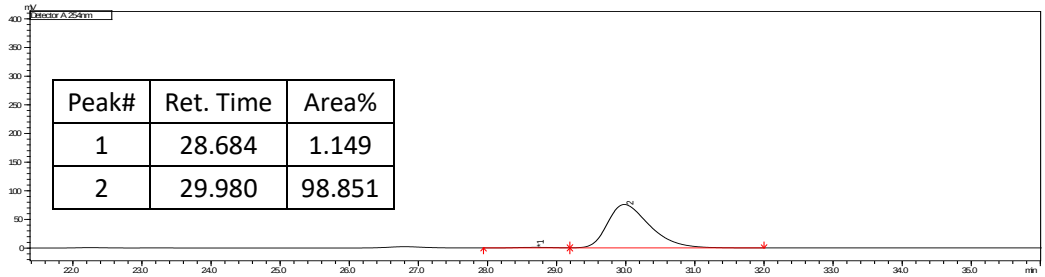
IR (film): 3490, 2989, 1456, 1275, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = +35.66 (*c* = 0.670, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK IE, hexane/*i*-PrOH = 11/5, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 30.0 min, t_R(minor) = 28.7 min, ee = 98%.

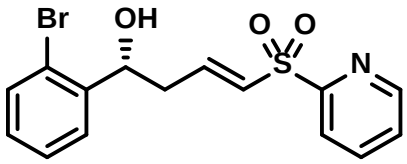


Peak#	Ret. Time	Area%
1	28.435	49.617
2	29.886	50.383



Peak#	Ret. Time	Area%
1	28.684	1.149
2	29.980	98.851

Figure S302, the HPLC spectrum of compound **5k,** related to **Table 3**



5an

5an: Procedure A, 94 mg, colorless liquid, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.1 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.95 (td, *J* = 7.8, 1.6 Hz, 1H), 7.58–7.43 (m, 3H), 7.36–7.16 (m, 2H), 7.13 (td, *J* = 7.8, 1.6 Hz, 1H), 6.63 (d, *J* = 15.2 Hz, 1H), 5.33–5.18 (m, 1H), 2.96 (s, 1H), 2.86–2.77 (m, 1H), 2.66–2.55 (m, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.21, 150.17, 146.21, 141.85, 138.28, 132.68, 130.08, 129.20, 127.84, 127.18, 127.15, 121.91, 121.47, 71.07, 39.61 ppm.

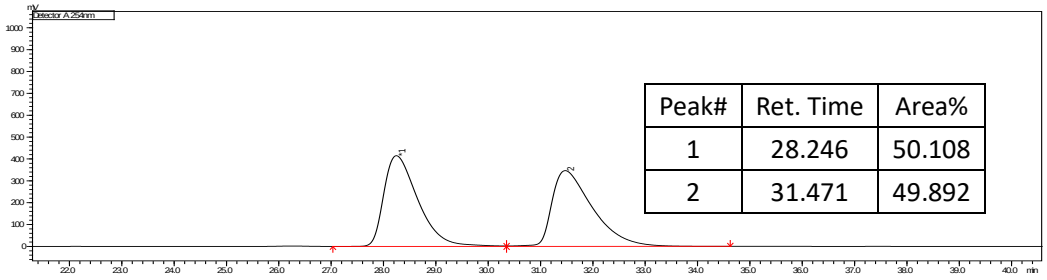
MS(ESI) m/z $[M+Na]^+$: 389.85.

HRMS(ESI) m/z $[M+H]^+$: calcd. 367.9951, found 367.9951.

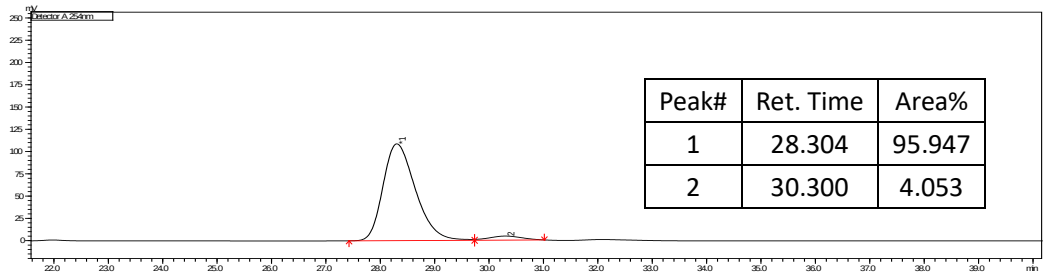
IR (film): 3493, 2960, 1632, 1428, 1198 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +69.81 (*c* = 1.070, $CHCl_3$, 92% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 28.3 min, t_R(minor) = 30.3 min, ee = 92%.

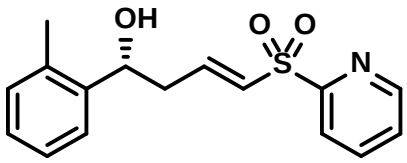


Peak#	Ret. Time	Area%
1	28.246	50.108
2	31.471	49.892



Peak#	Ret. Time	Area%
1	28.304	95.947
2	30.300	4.053

Figure S303, the HPLC spectrum of compound **5an,** related to **Table 3**



5ao

5ao: Procedure A, 89 mg, colorless liquid, 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.3 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.95 (td, *J* = 7.8, 1.4 Hz, 1H), 7.53 (dd, *J* = 7.0, 4.8 Hz, 1H), 7.46 (d, *J* = 6.9 Hz, 1H), 7.24–7.09 (m, 4H), 6.64 (d, *J* = 15.2 Hz, 1H), 5.12 (t, *J* = 6.2 Hz, 1H), 2.68 (t, *J* = 6.4 Hz, 2H), 2.36 (s, 1H), 2.31 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.30, 150.18, 146.49, 140.97, 138.23, 134.13, 130.55, 129.94, 127.71, 127.10, 126.48, 124.99, 121.84, 68.79, 40.16, 18.99 ppm.

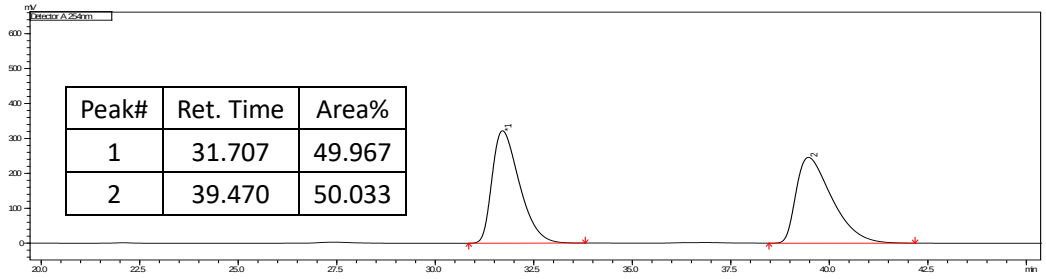
MS(ESI) m/z [M+Na]$^+$: 326.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 304.1002, found 304.1003.

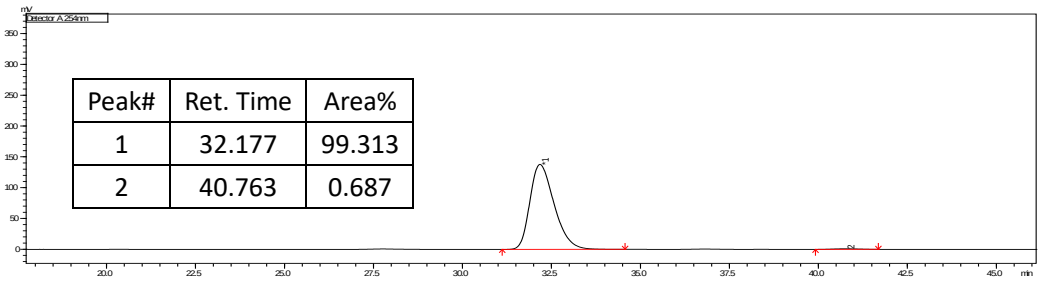
IR (film): 3405, 2918, 1462, 1276, cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = +40.80 (*c* = 0.345, $CHCl_3$, 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 32.2 min, t_R(minor) = 40.8 min, ee = 99%.

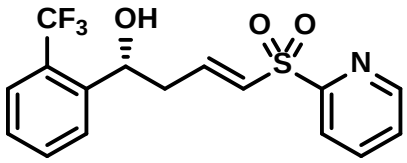


Peak#	Ret. Time	Area%
1	31.707	49.967
2	39.470	50.033



Peak#	Ret. Time	Area%
1	32.177	99.313
2	40.763	0.687

Figure S304, the HPLC spectrum of compound **5ao,** related to **Table 3**



5l

5l: Procedure A, 87 mg, colorless liquid, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.2 Hz, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 7.96 (td, *J* = 7.8, 1.6 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.67–7.49 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.21 (dt, *J* = 15.2, 7.4 Hz, 1H), 6.65 (d, *J* = 15.2 Hz, 1H), 5.35–5.25 (m, 1H), 2.77–2.56 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.29, 150.16, 145.91, 141.98, 138.25, 132.42, 130.28, 127.93, 127.40, 127.13, 125.61, 125.55, 122.82, 121.83, 67.73, 41.33 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.23 ppm.

MS(ESI) m/z $[M+Na]^+$: 379.95.

HRMS(ESI) m/z $[M+H]^+$: calcd. 358.0719, found 358.0718.

IR (film): 3494, 2925, 1132 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +54.75 (*c* = 2.750, $CHCl_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 19.9 min, t_R(minor) = 21.4 min, ee = 97%.

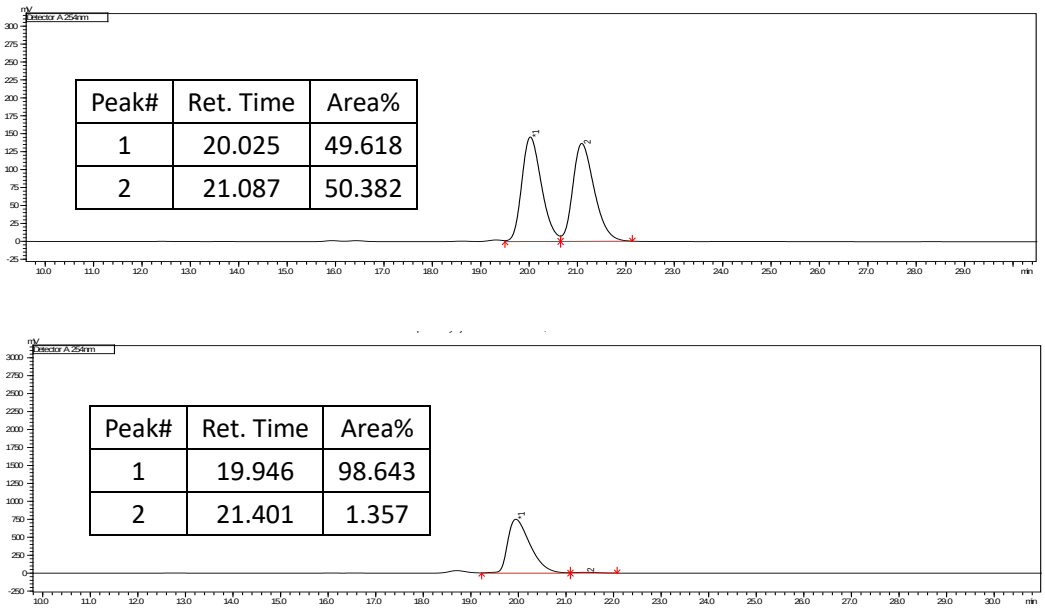
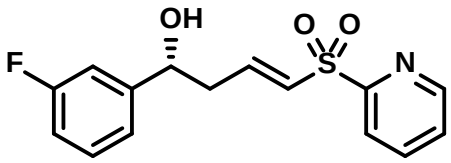


Figure S305, the HPLC spectrum of compound **5l,** related to **Table 3**



5ap

5ap: Procedure A, 74 mg, colorless liquid, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.2 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.95 (td, *J* = 7.8, 1.6 Hz, 1H), 7.57–7.47 (m, 1H), 7.32–7.22 (m, 1H), 7.19–7.01 (m, 3H), 6.93 (td, *J* = 8.3, 2.2 Hz, 1H), 6.58 (d, *J* = 15.2 Hz, 1H), 4.96–4.86 (m, 1H), 3.20 (d, *J* = 3.7 Hz, 1H), 2.80–2.62 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.87 (d, *J* = 246.5 Hz), 158.09, 150.15, 145.91, 145.66 (d, *J* = 6.8 Hz), 138.32, 130.24, 130.13 (d, *J* = 8.2 Hz), 127.19, 121.89, 121.22 (d, *J* = 2.9 Hz), 114.69 (d, *J* = 21.1 Hz), 112.60 (d, *J* = 22.0 Hz), 71.66, 41.27 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.27~-112.39 (m) ppm.

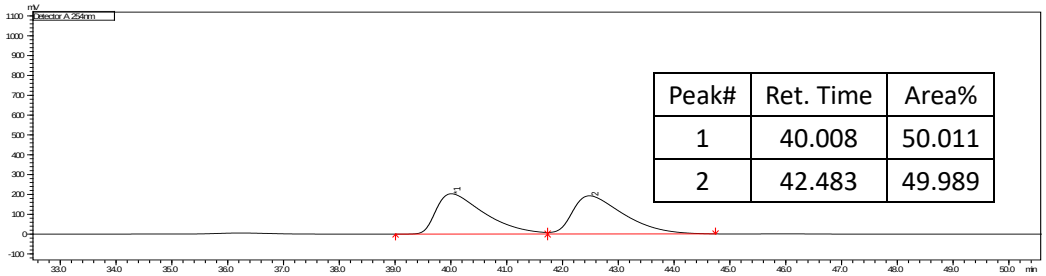
MS(ESI) m/z [M+Na]$^+$: 330.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 308.0751, found 308.0751.

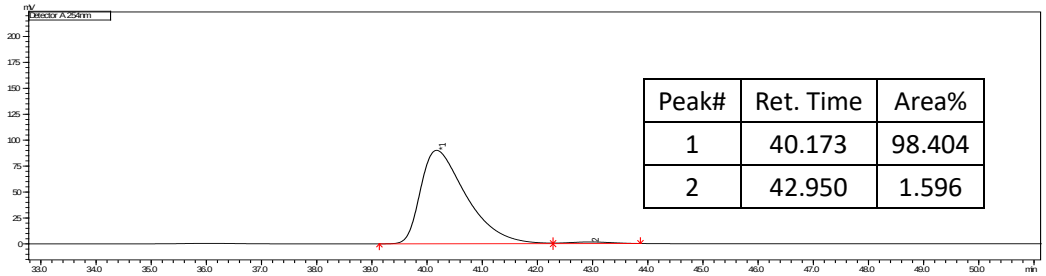
IR (film): 3316, 2915, 1428, 1232, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +36.50 (*c* = 1.355, $CHCl_3$, 97% ee).

HPLC: DAICEL CHIRALPAK IE, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 40.2 min, t_R(minor) = 43.0 min, ee = 97%.

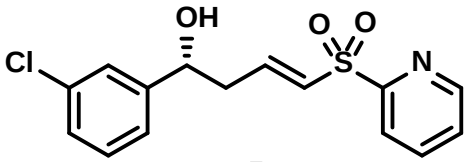


Peak#	Ret. Time	Area%
1	40.008	50.011
2	42.483	49.989



Peak#	Ret. Time	Area%
1	40.173	98.404
2	42.950	1.596

Figure S306, the HPLC spectrum of compound **5ap,** related to **Table 3**



5n

5n: Procedure A, 79 mg, colorless liquid, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.6 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.96 (td, *J* = 7.8, 1.5 Hz, 1H), 7.59–7.50 (m, 1H), 7.34 (s, 1H), 7.29–7.08 (m, 4H), 6.62 (d, *J* = 15.2 Hz, 1H), 4.96–4.85 (m, 1H), 2.71 (t, *J* = 6.7 Hz, 2H), 2.63 (d, *J* = 3.5 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.21, 150.16, 145.67, 144.92, 138.28, 134.56, 130.39, 129.91, 128.09, 127.14, 125.79, 123.77, 121.81, 71.75, 41.28 ppm.

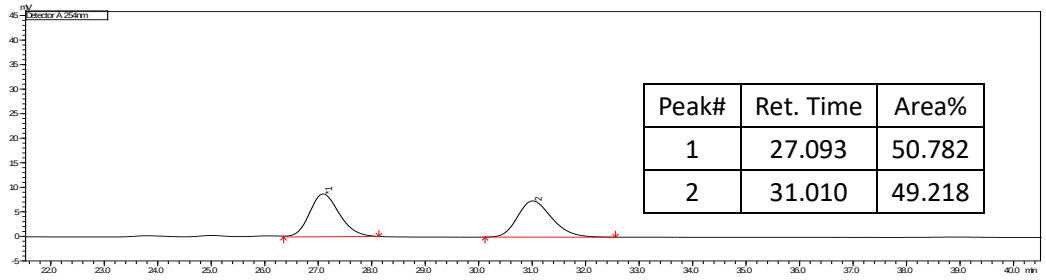
MS(ESI) m/z $[M+H]^+$: 323.95.

HRMS(ESI) m/z $[M+H]^+$: calcd. 324.0456, found 324.0457.

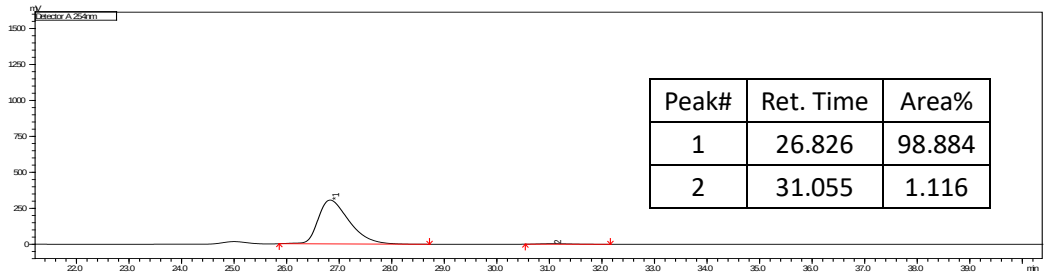
IR (film): 3396, 2924, 1428, 1270 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +37.10 (*c* = 0.300, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 26.8 min, t_R(minor) = 31.1 min, ee = 98%.

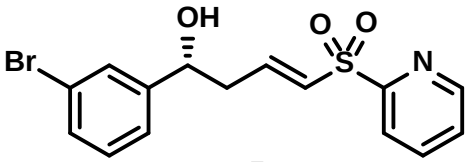


Peak#	Ret. Time	Area%
1	27.093	50.782
2	31.010	49.218



Peak#	Ret. Time	Area%
1	26.826	98.884
2	31.055	1.116

Figure S307, the HPLC spectrum of compound **5n,** related to **Table 3**



5o

5o: Procedure A, 84 mg, colorless liquid, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.6 Hz, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 7.96 (td, *J* = 7.8, 1.6 Hz, 1H), 7.59–7.46 (m, 2H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.27–7.05 (m, 3H), 6.62 (d, *J* = 15.3 Hz, 1H), 4.87 (t, *J* = 6.3 Hz, 1H), 2.71 (t, *J* = 6.8 Hz, 2H), 2.53 (s, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.23, 150.16, 145.63, 145.15, 138.28, 131.05, 130.41, 130.20, 128.71, 127.14, 124.25, 122.76, 121.80, 71.71, 41.30 ppm.

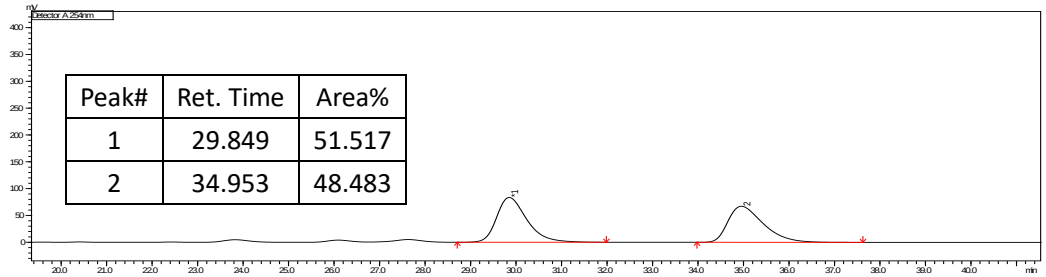
MS(ESI) m/z $[M+H]^+$: 367.90.

HRMS(ESI) m/z $[M+H]^+$: calcd. 367.9951, found 367.9951.

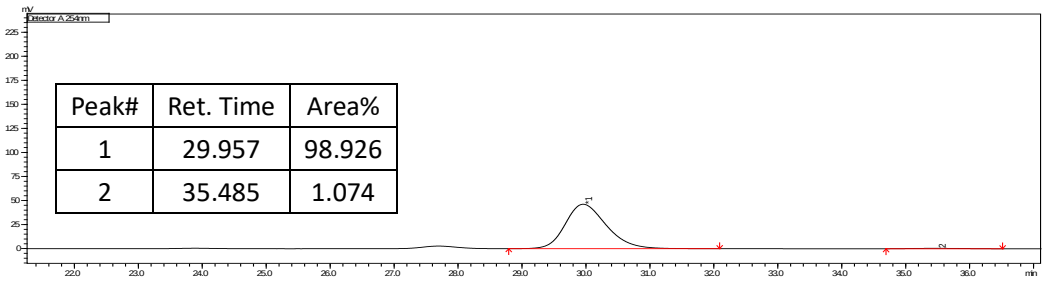
IR (film): 3485, 2961, 1428, 1261, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +33.07 (*c* = 1.850, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 30.0 min, t_R(minor) = 35.5 min, ee = 98%.

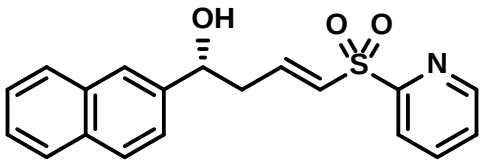


Peak#	Ret. Time	Area%
1	29.849	51.517
2	34.953	48.483



Peak#	Ret. Time	Area%
1	29.957	98.926
2	35.485	1.074

Figure S308, the HPLC spectrum of compound **5o,** related to **Table 3**



5aq

5aq: Procedure A, 90 mg, colorless liquid, 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.7 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.90–7.74 (m, 5H), 7.52–7.38 (m, 4H), 7.19 (dt, *J* = 15.2, 7.3 Hz, 1H), 6.61 (d, *J* = 15.2 Hz, 1H), 5.10–4.99 (m, 1H), 2.91–2.73 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.24, 150.08, 146.04, 140.15, 138.10, 133.15, 133.05, 130.18, 128.57, 127.98, 127.67, 127.00, 126.33, 126.10, 124.51, 123.45, 121.70, 72.59, 41.23 ppm.

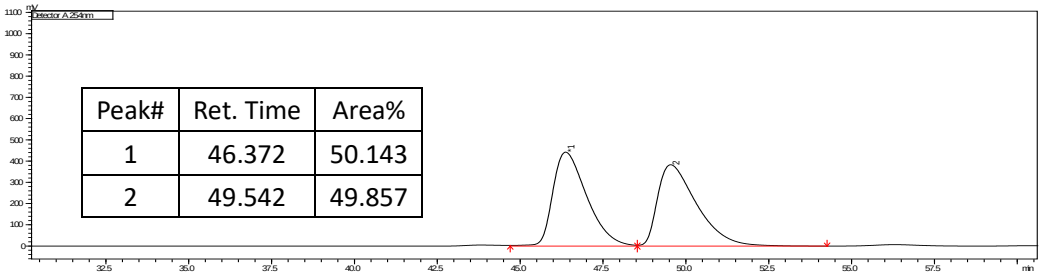
MS(ESI) m/z [M+Na]$^+$: 361.95.

HRMS(ESI) m/z [M+H]$^+$: calcd. 340.1002, found 340.1002.

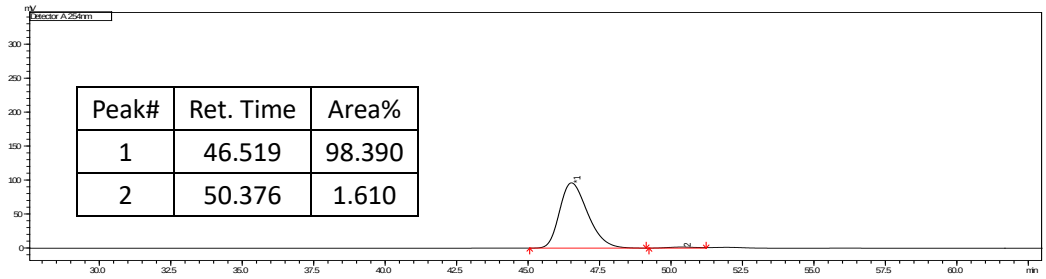
IR (film): 3494, 2925, 1427, 1162 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +30.68 (*c* = 2.200, $CHCl_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 46.5 min, t_R(minor) = 50.4 min, ee = 97%.

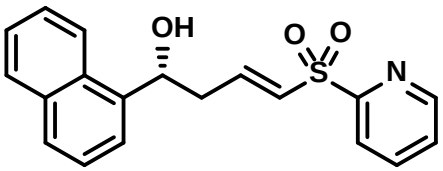


Peak#	Ret. Time	Area%
1	46.372	50.143
2	49.542	49.857



Peak#	Ret. Time	Area%
1	46.519	98.390
2	50.376	1.610

Figure S309, the HPLC spectrum of compound **5aq,** related to **Table 3**



5p

5p: Procedure A, 99 mg, colorless liquid, 97% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.6 Hz, 1H), 8.04–7.94 (m, 2H), 7.92–7.80 (m, 2H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 7.1 Hz, 1H), 7.50–7.43 (m, 3H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.25 (dt, *J* = 15.2, 7.2 Hz, 1H), 6.60 (d, *J* = 15.2 Hz, 1H), 5.69–5.58 (m, 1H), 3.24 (s, 1H), 2.93–2.67 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.06, 150.14, 146.79, 138.58, 138.29, 133.69, 129.83, 129.74, 129.00, 128.27, 127.16, 126.30, 125.66, 125.42, 122.96, 122.62, 121.92, 69.02, 40.37 ppm.

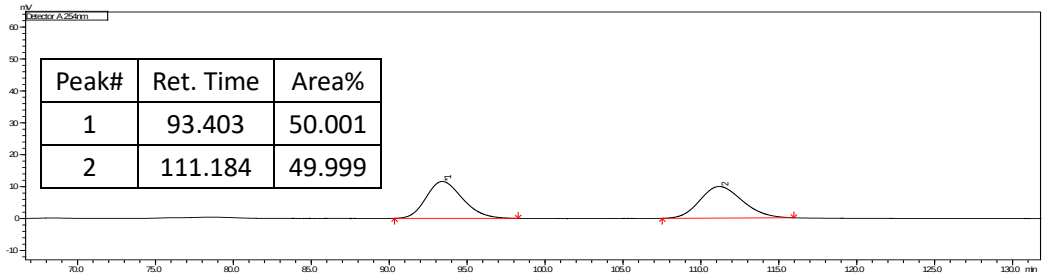
MS(ESI) m/z [M+Na]$^+$: 362.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 340.1002, found 340.1003.

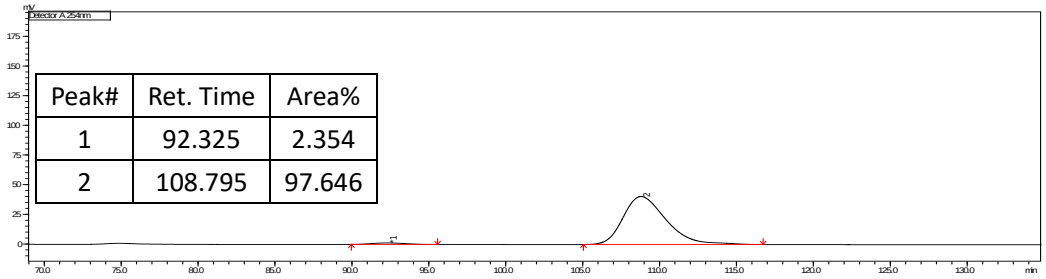
IR (film): 3493, 2989, 1427, 1275 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = +60.65 (*c* = 2.035, $CHCl_3$, 95% ee).

HPLC: DAICEL CHIRALPAK IG-3, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 108.8 min, t_R(minor) = 92.3 min, ee = 95%.

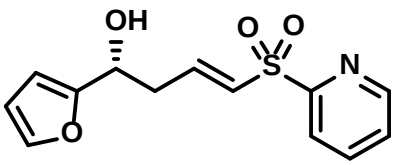


Peak#	Ret. Time	Area%
1	93.403	50.001
2	111.184	49.999



Peak#	Ret. Time	Area%
1	92.325	2.354
2	108.795	97.646

Figure S310, the HPLC spectrum of compound **5p,** related to **Table 3**



5q

5q: Procedure A, 70 mg, colorless liquid, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.2 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.95 (td, *J* = 7.8, 1.5 Hz, 1H), 7.53 (dd, *J* = 7.2, 5.0 Hz, 1H), 7.35 (s, 1H), 7.21–6.98 (m, 1H), 6.65 (d, *J* = 15.3 Hz, 1H), 6.39–6.00 (m, 2H), 4.90 (t, *J* = 6.0 Hz, 1H), 2.85 (t, *J* = 6.8 Hz, 2H), 2.65 (s, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.18, 154.82, 150.15, 145.47, 142.28, 138.26, 130.22, 127.15, 121.89, 110.27, 106.62, 65.89, 37.80 ppm.

MS(ESI) m/z $[M+Na]^+$: 301.95.

HRMS(ESI) m/z $[M+H]^+$: calcd. 280.0638, found 280.0639.

IR (film): 3349, 2924, 1631, 1429, 1163 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +21.31 (*c* = 0.535, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK IE, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 61.1 min, t_R(minor) = 67.4 min, ee = 98%.

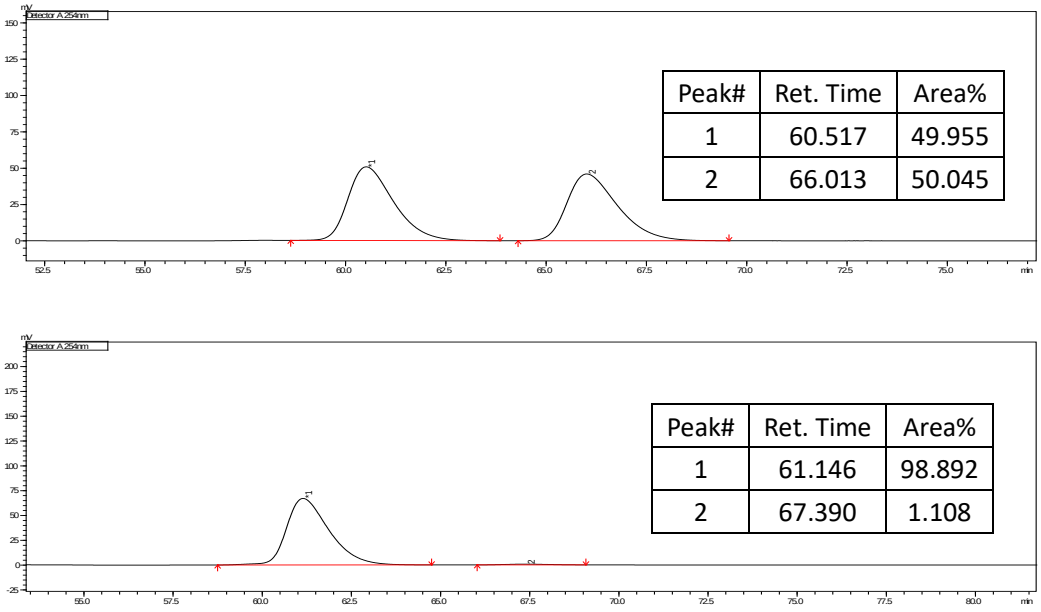
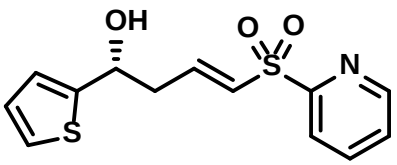


Figure S311, the HPLC spectrum of compound **5q,** related to **Table 3**



5r

5r: Procedure A, 74 mg, colorless liquid, 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.4 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.95 (td, *J* = 7.8, 1.5 Hz, 1H), 7.56–7.45 (m, 1H), 7.25–7.20 (m, 1H), 7.15 (dt, *J* = 15.2, 7.2 Hz, 1H), 7.00–6.88 (m, 2H), 6.64 (d, *J* = 15.2 Hz, 1H), 5.14 (t, *J* = 6.3 Hz, 1H), 2.99 (s, 1H), 2.89–2.71 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.13, 150.16, 146.71, 145.61, 138.29, 130.30, 127.16, 126.79, 124.96, 124.03, 121.91, 68.34, 41.39 ppm.

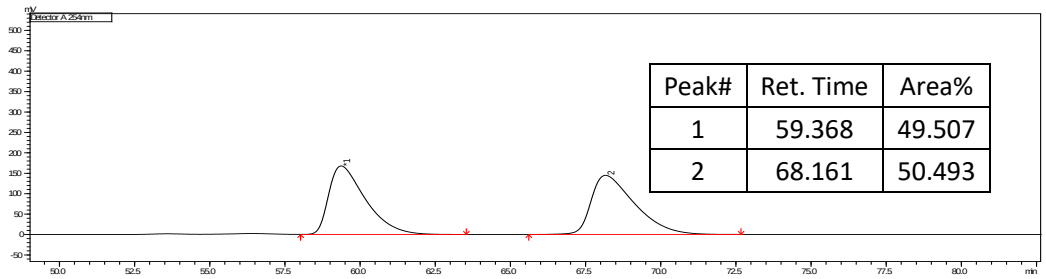
MS(ESI) m/z $[M+Na]^+$: 317.95.

HRMS(ESI) m/z $[M+H]^+$: calcd. 296.0410, found 296.0410.

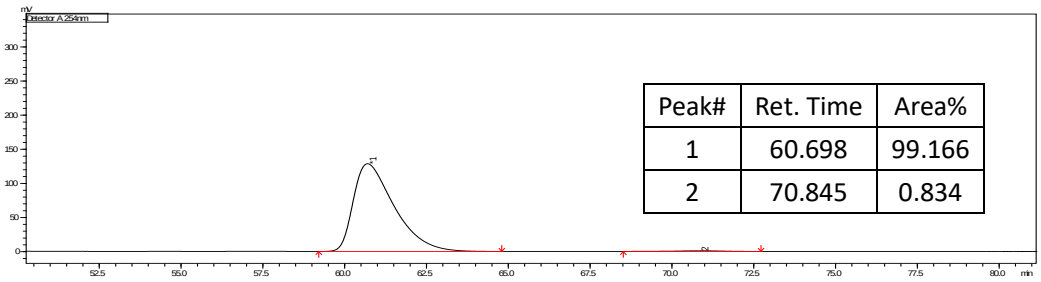
IR (film): 3392, 2922, 1630, 1428, 1238 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = +21.45 (*c* = 0.735, $CHCl_3$, 98% ee).

HPLC: DAICEL CHIRALPAK IE, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 60.7 min, t_R(minor) = 70.8 min, ee = 98%.

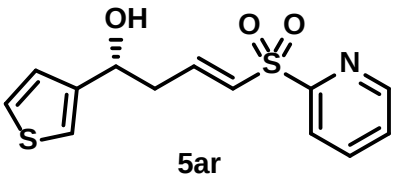


Peak#	Ret. Time	Area%
1	59.368	49.507
2	68.161	50.493



Peak#	Ret. Time	Area%
1	60.698	99.166
2	70.845	0.834

Figure S312, the HPLC spectrum of compound **5r,** related to **Table 3**



5ar

5ar: Procedure A, 67 mg, colorless liquid, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.4 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.94 (td, *J* = 7.8, 1.5 Hz, 1H), 7.60–7.44 (m, 1H), 7.38–7.18 (m, 1H), 7.23–7.10 (m, 2H), 7.05 (d, *J* = 4.9 Hz, 1H), 6.60 (d, *J* = 15.2 Hz, 1H), 4.98 (t, *J* = 6.0 Hz, 1H), 2.99 (s, 1H), 2.75 (t, *J* = 6.5 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.14, 150.16, 146.19, 144.41, 138.30, 130.03, 127.18, 126.52, 125.30, 121.91, 121.20, 68.56, 40.64 ppm.

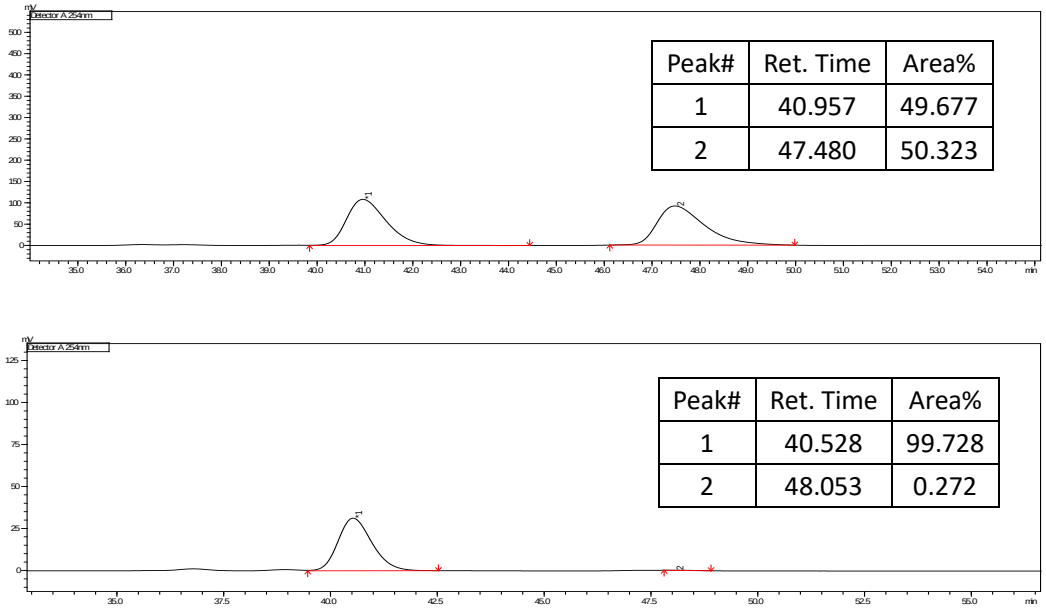
MS(ESI) m/z $[M+Na]^+$: 317.95.

HRMS(ESI) m/z $[M+H]^+$: calcd. 296.0410, found 296.0410.

IR (film): 3493, 3005, 1427, 1276 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = +30.34 (*c* = 1.115, $CHCl_3$, > 99% ee).

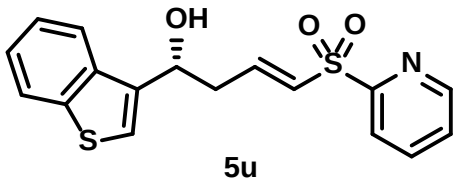
HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 40.5 min, t_R(minor) = 48.1 min, ee = > 99%.



Peak#	Ret. Time	Area%
1	40.957	49.677
2	47.480	50.323

Peak#	Ret. Time	Area%
1	40.528	99.728
2	48.053	0.272

Figure S313, the HPLC spectrum of compound **5ar,** related to **Table 3**



5u

5u: Procedure A, 88 mg, colorless liquid, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.6 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.90 (td, *J* = 7.8, 1.5 Hz, 1H), 7.86–7.76 (m, 2H), 7.50–7.45 (m, 1H), 7.39–7.30 (m, 3H), 7.28–7.16 (m, 1H), 6.60 (d, *J* = 15.2 Hz, 1H), 5.31–5.20 (m, 1H), 3.25 (s, 1H), 2.96–2.76 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.04, 150.14, 146.24, 140.89, 138.30, 137.95, 136.68, 130.04, 127.18, 124.56, 124.20, 122.99, 122.85, 121.95, 121.91, 67.87, 39.40 ppm.

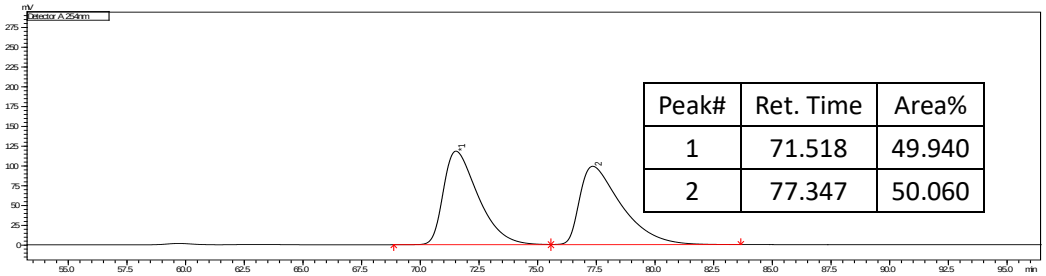
MS(ESI) m/z [M+Na]$^+$: 367.95.

HRMS(ESI) m/z [M+H]$^+$: calcd. 346.0566, found 346.0568.

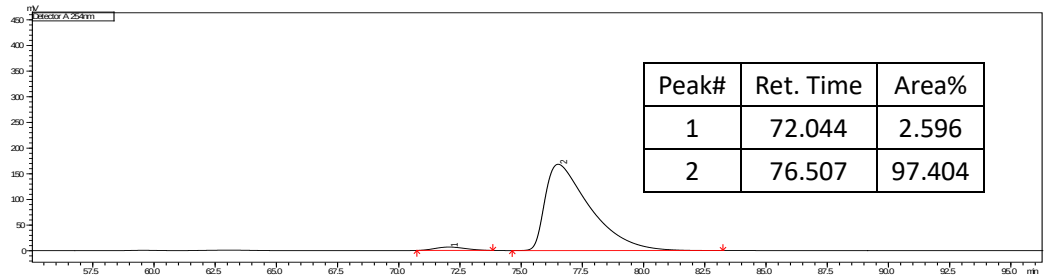
IR (film): 3493, 3054, 1428, 1276, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = +44.56 (*c* = 1.435, $CHCl_3$, 95% ee).

HPLC: DAICEL CHIRALPAK IE, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 76.5 min, t_R(minor) = 72.0 min, ee = 95%.

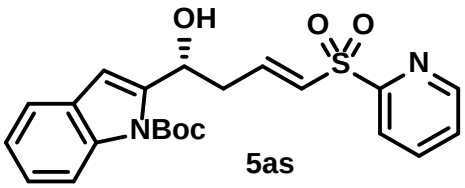


Peak#	Ret. Time	Area%
1	71.518	49.940
2	77.347	50.060



Peak#	Ret. Time	Area%
1	72.044	2.596
2	76.507	97.404

Figure S314, the HPLC spectrum of compound **5u,** related to **Table 3**



5as

5as: Procedure A, 100 mg, colorless liquid, 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.5 Hz, 1H), 8.13 (d, *J* = 7.7 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.91 (t, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.54 (s, 1H), 7.49 (dd, *J* = 7.5, 4.7 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.27–7.14 (m, 2H), 6.66 (d, *J* = 15.2 Hz, 1H), 5.16 (t, *J* = 6.2 Hz, 1H), 2.91 (t, *J* = 6.7 Hz, 2H), 2.77 (s, 1H), 1.66 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.16, 150.15, 149.52, 146.18, 138.23, 135.79, 130.03, 127.98, 127.11, 124.70, 122.70, 122.67, 122.46, 121.80, 119.48, 115.44, 83.96, 66.21, 39.56, 28.16 ppm.

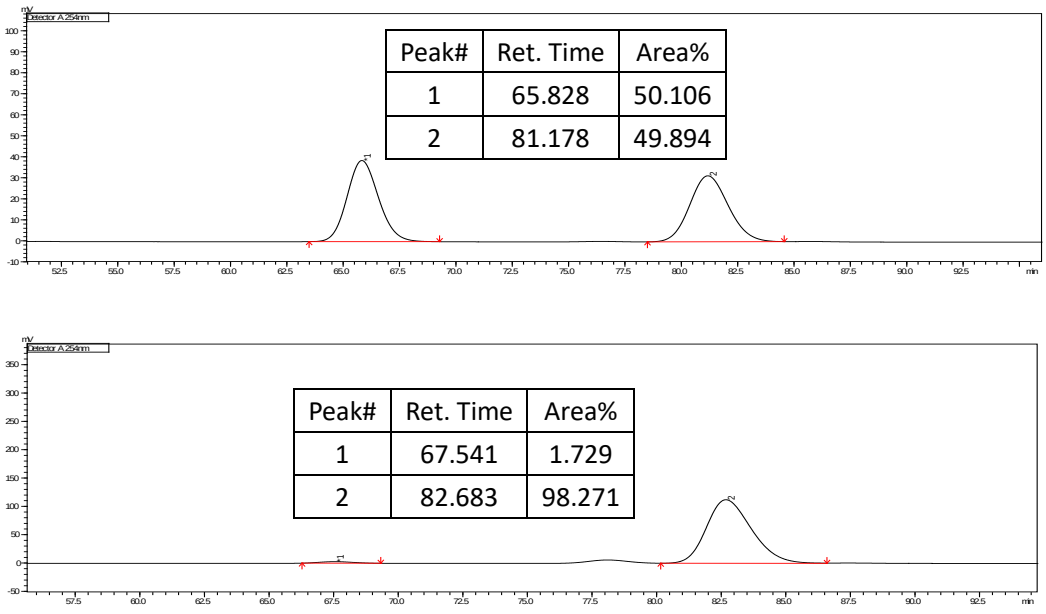
MS(ESI) m/z $[M+Na]^+$: 451.00.

HRMS(ESI) m/z $[M+H]^+$: calcd. 429.1479, found 429.1479.

IR (film): 3507, 2979, 1731, 1428, 1254 cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = +23.31 (*c* = 1.225, $CHCl_3$, 97% ee).

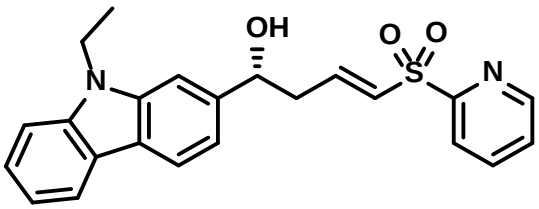
HPLC: DAICEL CHIRALPAK IG-3, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 82.7 min, t_R(minor) = 67.5 min, ee = 97%.



Peak#	Ret. Time	Area%
1	65.828	50.106
2	81.178	49.894

Peak#	Ret. Time	Area%
1	67.541	1.729
2	82.683	98.271

Figure S315, the HPLC spectrum of compound **5as,** related to **Table 3**



5x

5x: Procedure A, 56 mg, colorless liquid, 46% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.6 Hz, 1H), 8.06–7.97 (m, 2H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.72 (td, *J* = 7.8, 1.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.40–7.35 (m, 2H), 7.35–7.28 (m, 2H), 7.27–7.10 (m, 2H), 6.57 (d, *J* = 15.2 Hz, 1H), 5.11–4.92 (m, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 2.97 (s, 1H), 2.88–2.68 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.09, 150.01, 146.73, 140.22, 139.56, 138.09, 133.57, 129.76, 126.94, 125.84, 123.49, 122.78, 122.69, 121.76, 120.48, 118.91, 117.67, 109.99, 108.55, 72.93, 41.76, 37.56, 13.82 ppm.

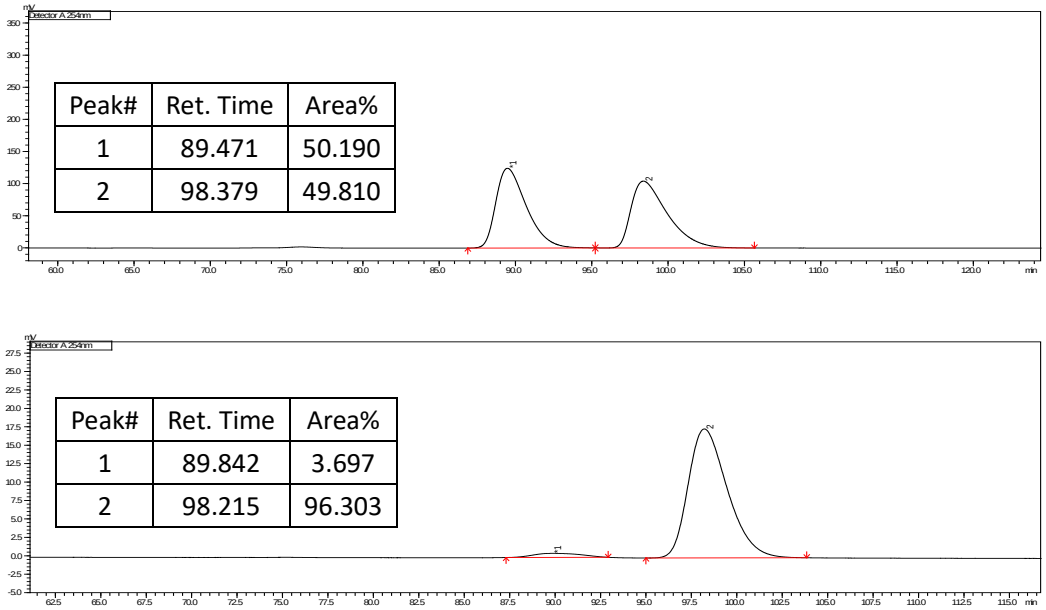
MS(ESI) m/z [M+Na]$^+$: 429.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 407.1351, found 407.1352.

IR (film): 3506, 2977, 1427, 1233, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = +29.12 (*c* = 2.140, $CHCl_3$, 93% ee).

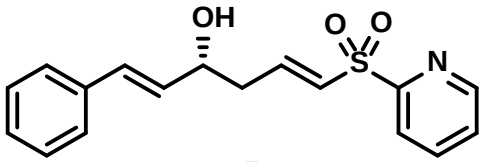
HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 98.2 min, t_R(minor) = 89.8 min, ee = 93%.



Peak#	Ret. Time	Area%
1	89.471	50.190
2	98.379	49.810

Peak#	Ret. Time	Area%
1	89.842	3.697
2	98.215	96.303

Figure S316, the HPLC spectrum of compound **5x,** related to **Table 3**



5y

5y: Procedure A, 79 mg, pale green solid, 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.1 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.88 (td, *J* = 7.8, 1.6 Hz, 1H), 7.45 (ddd, *J* = 7.6, 4.7, 0.9 Hz, 1H), 7.35–7.09 (m, 6H), 6.71–6.51 (m, 2H), 6.18 (dd, *J* = 15.9, 6.5 Hz, 1H), 4.55–4.45 (m, 1H), 2.92 (s, 1H), 2.68–2.52 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.09, 150.15, 146.29, 138.28, 136.17, 131.10, 130.50, 129.97, 128.56, 127.87, 127.16, 126.53, 121.90, 70.75, 39.59 ppm.

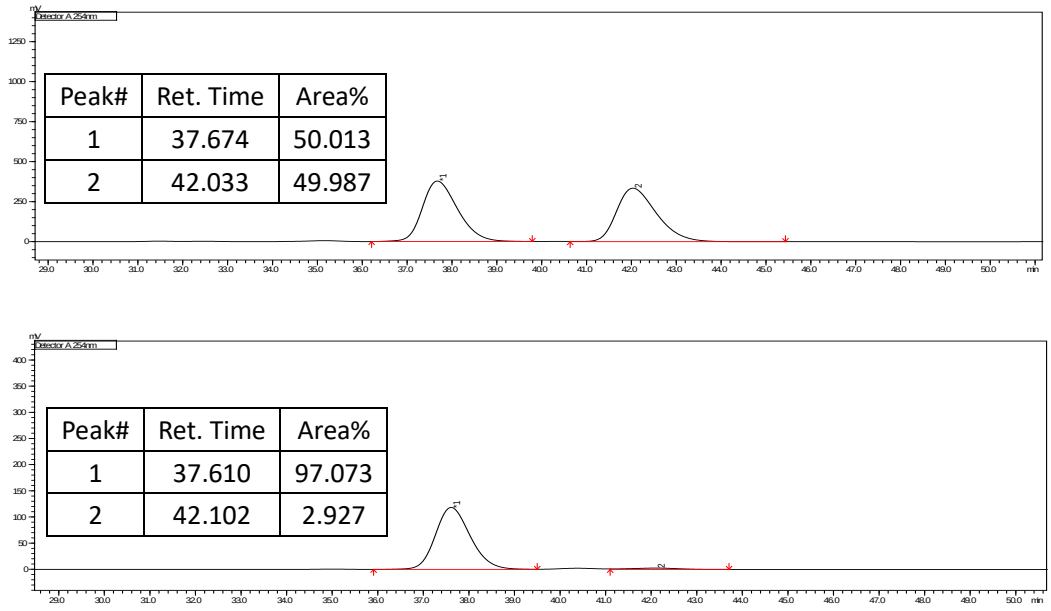
MS(ESI) m/z [M+Na]$^+$: 338.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 316.1002, found 316.1003.

IR (film): 3494, 2922, 1428, 1276 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = +14.38 (*c* = 1.910, $CHCl_3$, 94% ee).

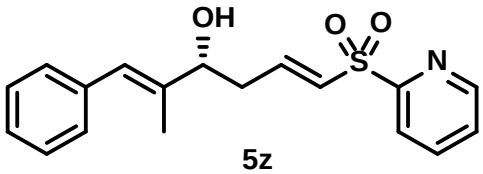
HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 37.6 min, t_R(minor) = 42.1 min, ee = 94%.



Peak#	Ret. Time	Area%
1	37.674	50.013
2	42.033	49.987

Peak#	Ret. Time	Area%
1	37.610	97.073
2	42.102	2.927

Figure S317, the HPLC spectrum of compound **5y,** related to **Table 3**



5z

5z: Procedure A, 50 mg, pale green solid, 51% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.4 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.89 (td, *J* = 7.8, 1.6 Hz, 1H), 7.47 (dd, *J* = 6.8, 4.8 Hz, 1H), 7.41–7.25 (m, 2H), 7.23–7.13 (m, 4H), 6.68 (d, *J* = 15.2 Hz, 1H), 6.52 (s, 1H), 4.38 (t, *J* = 6.0 Hz, 1H), 2.75–2.55 (m, 2H), 2.10 (s, 1H), 1.85 (d, *J* = 1.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.35, 150.15, 146.37, 138.47, 138.15, 136.92, 129.80, 128.92, 128.12, 127.03, 126.69, 126.58, 121.77, 75.69, 37.65, 13.54 ppm.

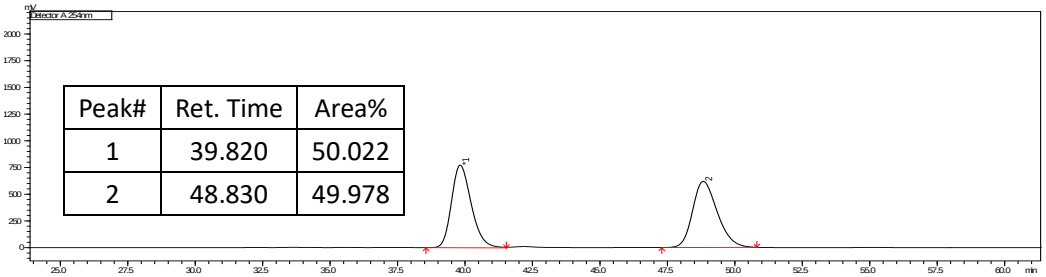
MS(ESI) m/z $[M+Na]^+$: 352.00.

HRMS(ESI) m/z $[M+H]^+$: calcd. 330.1158, found 330.1159.

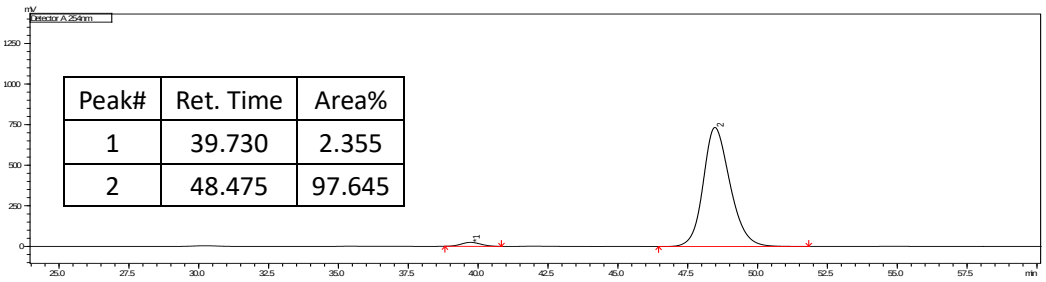
IR (film): 3305, 2921, 1427, 1163 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = -1.98 (*c* = 0.250, $CHCl_3$, 95% ee).

HPLC: DAICEL CHIRALPAK IG-3, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 48.5 min, t_R(minor) = 39.7 min, ee = 95%.

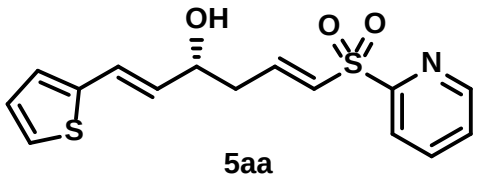


Peak#	Ret. Time	Area%
1	39.820	50.022
2	48.830	49.978



Peak#	Ret. Time	Area%
1	39.730	2.355
2	48.475	97.645

Figure S318, the HPLC spectrum of compound **5z,** related to **Table 3**



5aa

5aa: Procedure A, 77 mg, yellow liquid, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.3 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.89 (td, *J* = 7.8, 1.5 Hz, 1H), 7.47 (dd, *J* = 7.2, 5.0 Hz, 1H), 7.23–7.07 (m, 2H), 7.02–6.86 (m, 2H), 6.75–6.59 (m, 2H), 6.00 (dd, *J* = 15.7, 6.4 Hz, 1H), 4.55–4.35 (m, 1H), 2.93 (s, 1H), 2.66–2.47 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.07, 150.17, 146.13, 141.22, 138.28, 130.03, 129.93, 127.40, 127.17, 126.32, 124.64, 124.32, 121.91, 70.47, 39.50 ppm.

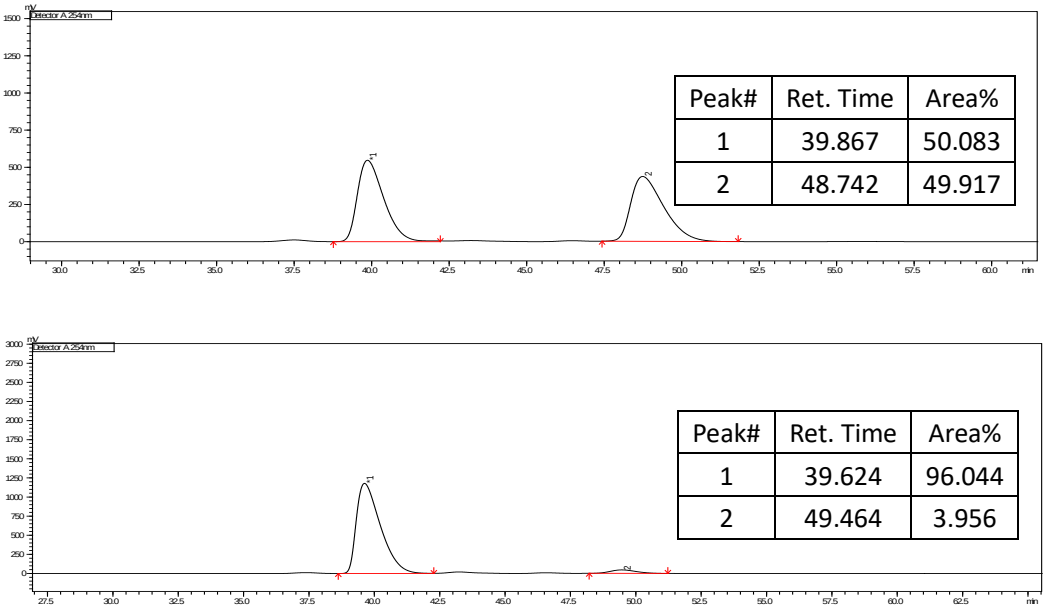
MS(ESI) m/z $[M+Na]^+$: 343.95.

HRMS(ESI) m/z $[M+H]^+$: calcd. 322.0566, found 322.0566.

IR (film): 3494, 2923, 1428, 1249 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +14.19 (*c* = 1.445, $CHCl_3$, 92% ee).

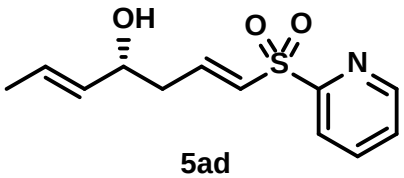
HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 39.6 min, t_R(minor) = 49.5 min, ee = 92%.



Peak#	Ret. Time	Area%
1	39.867	50.083
2	48.742	49.917

Peak#	Ret. Time	Area%
1	39.624	96.044
2	49.464	3.956

Figure S319, the HPLC spectrum of compound **5aa,** related to **Table 3**



5ad

5ad: Procedure A, 38 mg, colorless liquid, 50% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.0 Hz, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 7.95 (td, *J* = 7.8, 1.6 Hz, 1H), 7.53 (dd, *J* = 6.7, 4.8 Hz, 1H), 7.13 (dt, *J* = 15.2, 7.3 Hz, 1H), 6.63 (d, *J* = 15.2 Hz, 1H), 5.82–5.62 (m, 1H), 5.55–5.46 (m, 1H), 4.35–4.20 (m, 1H), 2.63–2.43 (m, 2H), 2.06 (s, 1H), 1.68 (d, *J* = 5.7 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.33, 150.17, 146.40, 138.24, 132.37, 129.73, 128.19, 127.10, 121.83, 70.91, 39.50, 17.61 ppm.

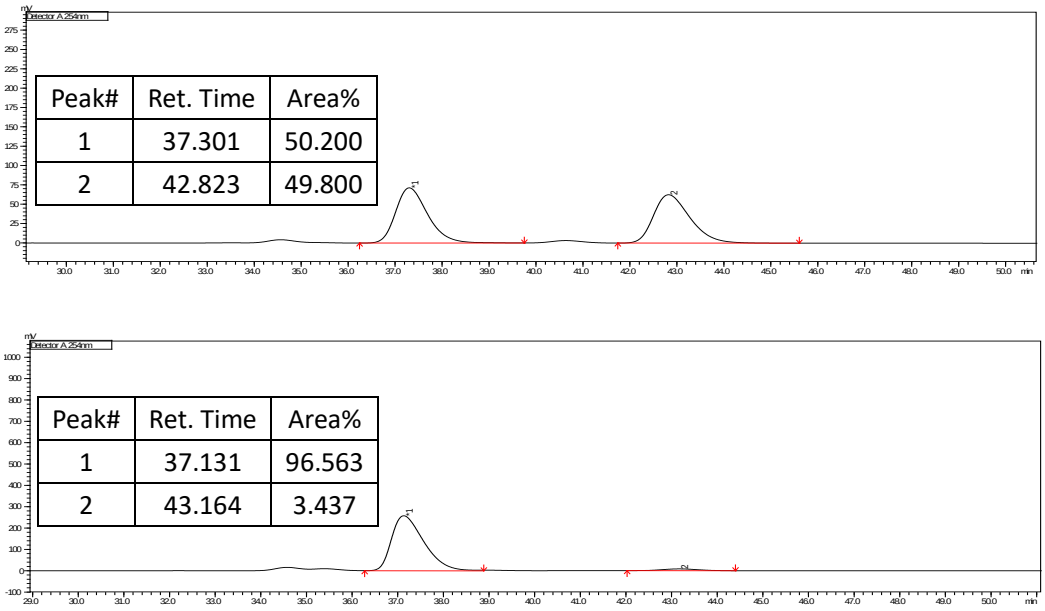
MS(ESI) m/z $[M+Na]^+$: 276.05.

HRMS(ESI) m/z $[M+H]^+$: calcd. 254.0845, found 254.0846.

IR (film): 3514, 2918, 1428, 1276, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = +10.63 (*c* = 0.600, $CHCl_3$, 93% ee).

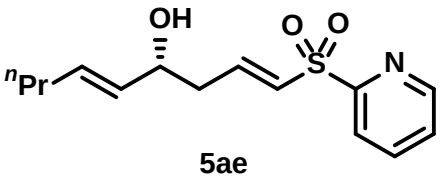
HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.6 mL/min, λ = 254 nm, t_R(major) = 37.1 min, t_R(minor) = 43.2 min, ee = 93%.



Peak#	Ret. Time	Area%
1	37.301	50.200
2	42.823	49.800

Peak#	Ret. Time	Area%
1	37.131	96.563
2	43.164	3.437

Figure S320, the HPLC spectrum of compound **5ad,** related to **Table 3**



5ae

5ae: Procedure A, 59 mg, colorless liquid, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.7 Hz, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 7.95 (td, *J* = 7.8, 1.7 Hz, 1H), 7.52 (ddd, *J* = 7.6, 4.7, 1.0 Hz, 1H), 7.13 (dt, *J* = 15.2, 7.3 Hz, 1H), 6.63 (d, *J* = 15.2 Hz, 1H), 5.78–5.62 (m, 1H), 5.47 (dd, *J* = 15.4, 6.9 Hz, 1H), 4.37–4.17 (m, 1H), 2.57–2.49 (m, 2H), 2.06–1.93 (m, 3H), 1.42–1.32 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.38, 150.17, 146.34, 138.21, 133.31, 131.20, 129.73, 127.07, 121.80, 70.97, 39.57, 34.12, 22.11, 13.61 ppm.

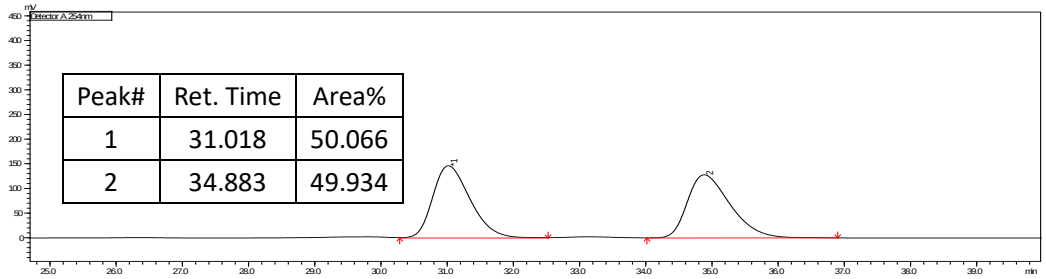
MS(ESI) m/z [M+Na]$^+$: 304.05.

HRMS(ESI) m/z [M+H]$^+$: calcd. 282.1158, found 282.1160.

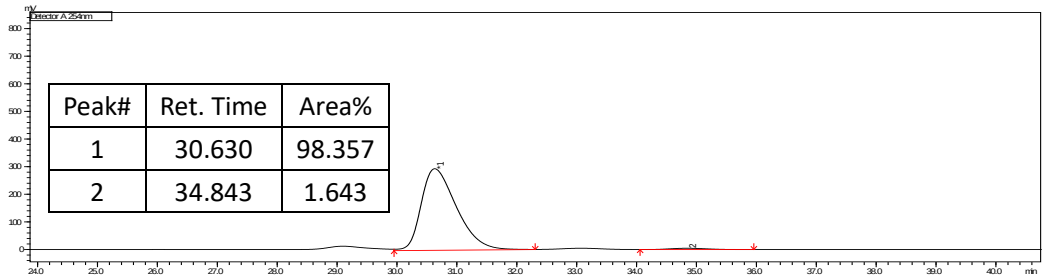
IR (film): 3405, 2957, 1428, 1170, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = +8.41 (*c* = 0.560, $CHCl_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.6 mL/min, λ = 254 nm, t_R(major) = 30.6 min, t_R(minor) = 34.8 min, ee = 97%.

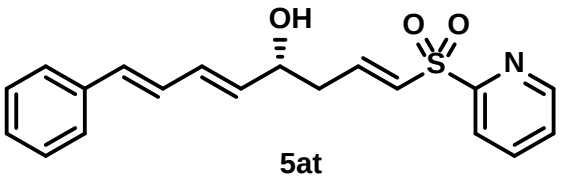


Peak#	Ret. Time	Area%
1	31.018	50.066
2	34.883	49.934



Peak#	Ret. Time	Area%
1	30.630	98.357
2	34.843	1.643

Figure S321, the HPLC spectrum of compound **5ae,** related to **Table 3**



5at

5at: Procedure A, 90 mg, colorless liquid, 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.1 Hz, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 7.92 (td, *J* = 7.8, 1.6 Hz, 1H), 7.51–7.45 (m, 1H), 7.42–7.36 (m, 2H), 7.34–7.30 (m, 2H), 7.28–7.21 (m, 1H), 7.16 (dt, *J* = 15.2, 7.3 Hz, 1H), 6.77–6.60 (m, 2H), 6.54 (d, *J* = 15.7 Hz, 1H), 6.41 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.80 (dd, *J* = 15.2, 6.6 Hz, 1H), 4.54–4.36 (m, 1H), 2.66–2.50 (m, 2H), 2.21 (s, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.29, 150.18, 145.97, 138.24, 136.85, 134.13, 133.61, 131.70, 130.09, 128.62, 127.79, 127.58, 127.10, 126.41, 121.84, 70.59, 39.53 ppm.

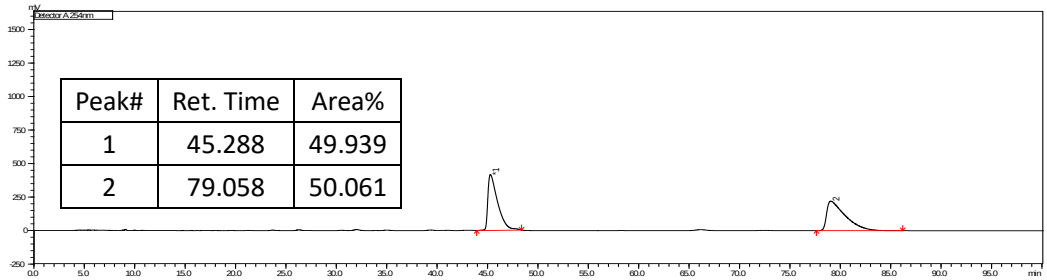
MS(ESI) m/z $[M+Na]^+$: 364.00.

HRMS(ESI) m/z $[M+H]^+$: calcd. 342.1158, found 342.1158.

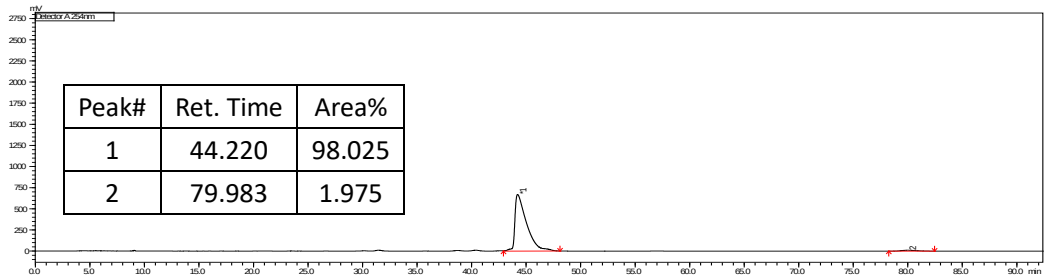
IR (film): 3492, 2924, 1630, 1450, 1162 cm^{-1}.

Optical rotation: $[\alpha]_D^{28}$ = +13.92 (*c* = 1.930, $CHCl_3$, 96% ee).

HPLC: DAICEL CHIRALPAK IBN-3, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 44.2 min, t_R(minor) = 80.0 min, ee = 96%.

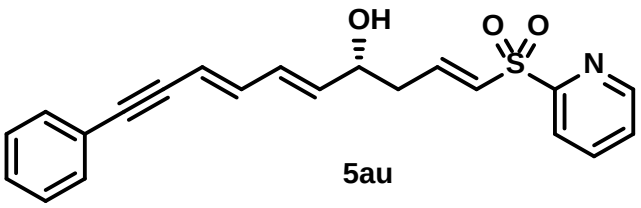


Peak#	Ret. Time	Area%
1	45.288	49.939
2	79.058	50.061



Peak#	Ret. Time	Area%
1	44.220	98.025
2	79.983	1.975

Figure S322, the HPLC spectrum of compound **5at,** related to **Table 3**



5au

5au: Procedure A, 88 mg, colorless liquid, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.1 Hz, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 7.95 (td, *J* = 7.8, 1.6 Hz, 1H), 7.53 (ddd, *J* = 7.6, 4.7, 1.0 Hz, 1H), 7.47–7.37 (m, 2H), 7.36–7.29 (m, 3H), 7.14 (dt, *J* = 15.2, 7.3 Hz, 1H), 6.71–6.53 (m, 2H), 6.34 (dd, *J* = 15.2, 10.9 Hz, 1H), 5.81 (dd, *J* = 15.3, 7.8 Hz, 2H), 4.53–4.36 (m, 1H), 2.66–2.20 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.17, 150.20, 145.89, 140.28, 138.33, 136.38, 131.44, 130.40, 130.15, 128.33, 128.27, 127.21, 123.17, 121.90, 112.41, 92.64, 88.51, 70.17, 39.41 ppm.

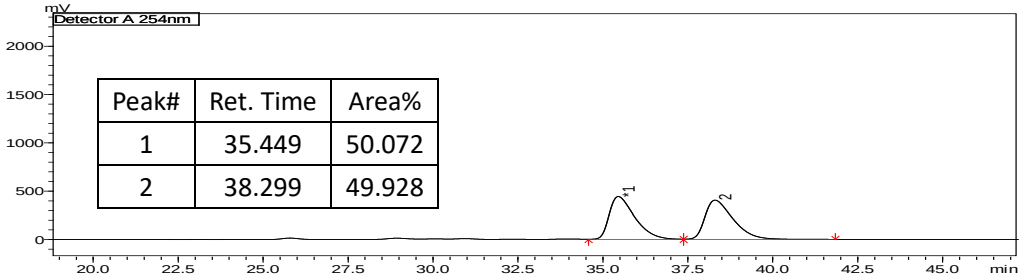
MS(ESI) m/z [M+Na]$^+$: 388.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 366.1158, found 366.1158.

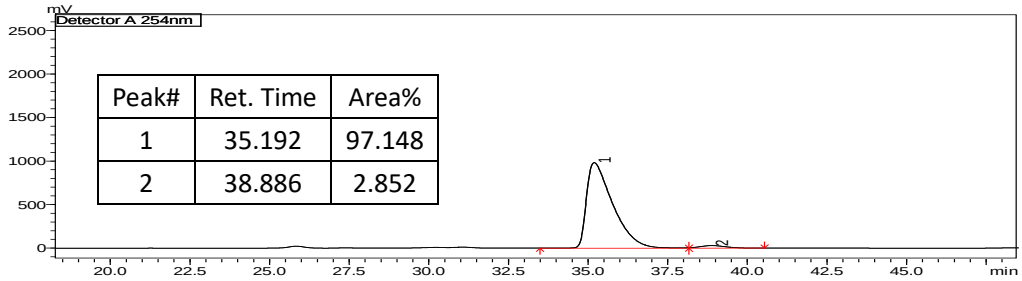
IR (film): 3493, 2989, 1428, 1275, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +33.73 (*c* = 0.900, $CHCl_3$, 94% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 35.2 min, t_R(minor) = 38.9 min, ee = 94%.

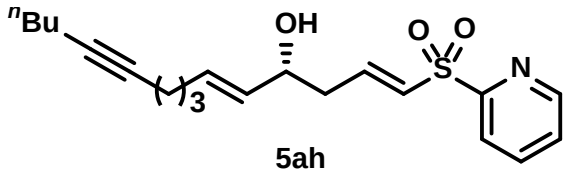


Peak#	Ret. Time	Area%
1	35.449	50.072
2	38.299	49.928



Peak#	Ret. Time	Area%
1	35.192	97.148
2	38.886	2.852

Figure S323, the HPLC spectrum of compound **5au,** related to **Table 3**



5ah

5ah: Procedure A, 76 mg, colorless liquid, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.5 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.96 (td, *J* = 7.8, 1.6 Hz, 1H), 7.53 (dd, *J* = 7.0, 4.8 Hz, 1H), 7.13 (dt, *J* = 15.2, 7.2 Hz, 1H), 6.63 (d, *J* = 15.2 Hz, 1H), 5.77–5.62 (m, 1H), 5.50 (dd, *J* = 15.4, 6.7 Hz, 1H), 4.36–4.28 (m, 1H), 2.52 (t, *J* = 6.5 Hz, 2H), 2.38 (s, 1H), 2.20–2.05 (m, 6H), 1.61–1.32 (m, 6H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.27, 150.17, 146.42, 138.27, 132.30, 131.76, 129.69, 127.13, 121.85, 80.71, 79.46, 70.80, 39.57, 31.17, 31.08, 28.31, 21.89, 18.38, 18.16, 13.60 ppm.

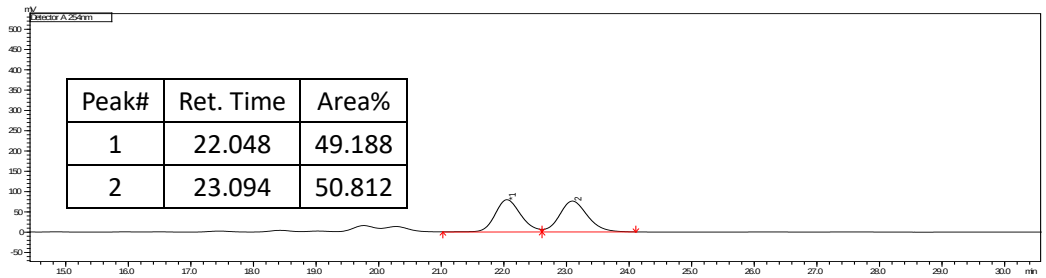
MS(ESI) m/z $[M+Na]^+$: 384.05.

HRMS(ESI) m/z $[M+H]^+$: calcd. 362.1784, found 362.1784.

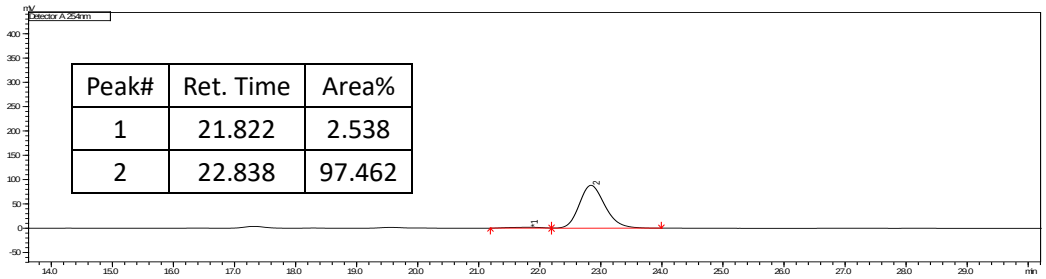
IR (film): 3514, 2931, 1428, 1276 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = +7.74 (*c* = 1.625, $CHCl_3$, 95% ee).

HPLC: DAICEL CHIRALPAK IG-3, hexane/*i*-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t_R(major) = 22.8 min, t_R(minor) = 21.8 min, ee = 95%.

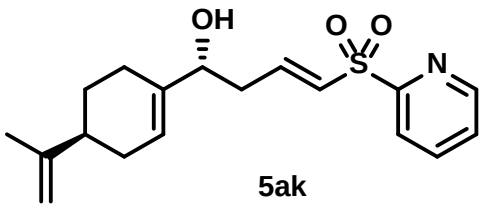


Peak#	Ret. Time	Area%
1	22.048	49.188
2	23.094	50.812



Peak#	Ret. Time	Area%
1	21.822	2.538
2	22.838	97.462

Figure S324, the HPLC spectrum of compound **5ah,** related to **Table 3**



5ak

5ak: Procedure A, 56 mg, colorless liquid, 56% yield, > 20/1 dr (Diastereoselectivity was determined by ^{1}H NMR analysis of reaction crude mixture).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.1 Hz, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 7.95 (td, *J* = 7.8, 1.6 Hz, 1H), 7.52 (ddd, *J* = 7.6, 4.7, 0.9 Hz, 1H), 7.10 (dt, *J* = 15.2, 7.2 Hz, 1H), 6.63 (d, *J* = 15.2 Hz, 1H), 5.72 (d, *J* = 4.0 Hz, 1H), 4.70 (d, *J* = 15.9 Hz, 2H), 4.20 (t, *J* = 6.4 Hz, 1H), 2.65–2.44 (m, 2H), 2.21–1.80 (m, 7H), 1.72 (s, 3H), 1.41 (m, 1H) ppm.

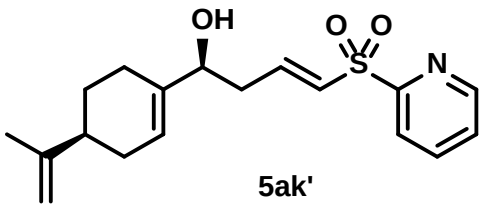
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.37, 150.17, 149.42, 146.76, 138.28, 138.22, 129.40, 127.09, 123.97, 121.81, 108.78, 73.91, 41.00, 37.40, 30.28, 27.32, 23.87, 20.73 ppm.

MS(ESI) m/z $[M+Na]^+$: 356.05.

HRMS(ESI) m/z $[M+H]^+$: calcd. 334.1471, found 334.1471.

IR (film): 3513, 2920, 1642, 1453, 1163 cm^{-1}.

Optical rotation: $[\alpha]_D^{26}$ = -25.34 (*c* = 1.025, $CHCl_3$, > 20/1 dr).



5ak'

5ak': Procedure B, 60 mg, colorless liquid, 60% yield, > 20/1 dr (Diastereoselectivity was determined by ^{1}H NMR analysis of reaction crude mixture).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.6 Hz, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 7.95 (td, *J* = 7.8, 1.6 Hz, 1H), 7.56–7.44 (m, 1H), 7.10 (dt, *J* = 14.9, 7.3 Hz, 1H), 6.63 (d, *J* = 15.2 Hz, 1H), 5.72 (s, 1H), 4.80–4.61 (m, 2H), 4.20 (t, *J* = 5.9 Hz, 1H), 2.59–2.49 (m, 2H), 2.21–1.79 (m, 7H), 1.72 (s, 3H), 1.50–1.35 (m, 1H) ppm.

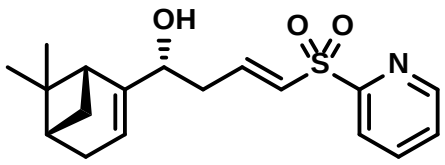
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.43, 150.17, 149.31, 146.67, 138.20, 137.98, 129.55, 127.06, 123.02, 121.78, 108.80, 73.84, 40.89, 37.64, 30.17, 27.17, 24.50, 20.79 ppm.

MS(ESI) m/z $[M+Na]^+$: 356.00.

HRMS(ESI) m/z $[M+H]^+$: calcd. 334.1471, found 334.1472.

IR (film): 3514, 2921, 1642, 1428, 1270 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = -33.51 (*c* = 0.480, $CHCl_3$, > 20/1 dr).



5al

5al: Procedure A, 68 mg, colorless liquid, 68% yield, > 20/1 dr (Diastereoselectivity was determined by ^{1}H NMR analysis of reaction crude mixture).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.4 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.95 (td, *J* = 7.8, 1.6 Hz, 1H), 7.55–7.50 (m, 1H), 7.18–7.09 (m, 1H), 6.63 (d, *J* = 15.3 Hz, 1H), 5.49 (d, *J* = 1.0 Hz, 1H), 4.20 (t, *J* = 6.0 Hz, 1H), 2.53–2.44 (m, 2H), 2.43–2.33 (m, 1H), 2.29–2.14 (m, 4H), 2.08 (s, 1H), 1.27 (s, 3H), 1.10 (d, *J* = 8.7 Hz, 1H), 0.76 (s, 3H) ppm.

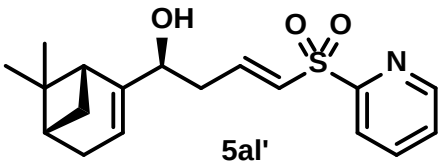
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.34, 150.16, 148.99, 146.89, 138.23, 129.46, 127.08, 121.81, 118.62, 72.66, 41.96, 40.77, 37.78, 37.18, 31.61, 30.98, 26.07, 21.34 ppm.

MS(ESI) m/z $[M+H]^+$: 334.05.

HRMS(ESI) m/z $[M+H]^+$: calcd. 334.1473, found 334.1473.

IR (film): 3508, 2984, 1630, 1428, 1204 cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = -9.72 (*c* = 1.995, $CHCl_3$, > 20/1 dr).



5al'

5al': Procedure B, 53 mg, colorless liquid, 53% yield, 10/1 dr (Diastereoselectivity was determined by ^{1}H NMR analysis of reaction crude mixture).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.5 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.95 (td, *J* = 7.8, 1.5 Hz, 1H), 7.52 (dd, *J* = 7.0, 4.9 Hz, 1H), 7.10 (dt, *J* = 14.7, 7.2 Hz, 1H), 6.62 (d, *J* = 15.3 Hz, 1H), 5.49 (s, 1H), 4.20 (t, *J* = 6.3 Hz, 1H), 2.58–2.42 (m, 2H), 2.39–2.30 (m, 1H), 2.27–2.21 (m, 2H), 2.18 (t, *J* = 5.1 Hz, 1H), 2.08 (s, 1H), 2.02–1.92 (m, 1H), 1.28 (s, 3H), 1.05 (d, *J* = 8.7 Hz, 1H), 0.80 (s, 3H) ppm.

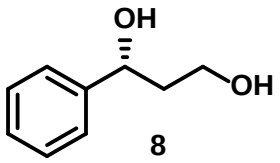
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.32, 150.18, 148.56, 146.72, 138.22, 129.47, 127.08, 121.83, 119.00, 72.56, 41.84, 40.77, 37.77, 37.08, 31.56, 31.00, 26.01, 21.35 ppm.

MS(ESI) m/z $[M+Na]^+$: 356.05.

HRMS(ESI) m/z $[M+H]^+$: calcd. 334.1471, found 334.1472.

IR (film): 3515, 2986, 1428, 1276 cm^{-1}.

Optical rotation: $[\alpha]_D^{27}$ = -31.50 (*c* = 1.470, $CHCl_3$, 10/1 dr).

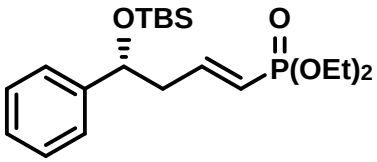


8

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.28 (m, 5H), 4.97 (dd, *J* = 8.8, 3.6 Hz, 1H), 3.87 (t, *J* = 5.6 Hz, 2H), 2.77 (s, 1H), 2.32 (s, 1H), 2.11–1.87 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 128.6, 127.7, 125.7, 74.6, 61.6, 40.5 ppm.

Optical rotation: $[\alpha]_D^{25}$ = +64.7 (c = 1.000, $CHCl_3$, 99% ee).



9

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.19 (m, 5H), 6.71 (ddt, *J* = 21.9, 17.1, 7.1 Hz, 1H), 5.61 (dd, *J* = 21.5, 17.1 Hz, 1H), 4.80 (dd, *J* = 6.5, 5.4 Hz, 1H), 4.07–3.91 (m, 4H), 2.71–2.45 (m, 2H), 1.28 (td, *J* = 7.1, 3.6 Hz, 6H), 0.88 (s, 9H), 0.04 (s, 3H), -0.13 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.54 (d, *J* = 4.7 Hz), 144.08, 128.14, 127.23, 125.69, 119.41 (d, *J* = 186.8 Hz), 73.72 (d, *J* = 1.4 Hz), 61.53 (d, *J* = 5.4 Hz), 45.62 (d, *J* = 21.9 Hz), 25.75, 18.13, 16.29 (d, *J* = 6.8 Hz), -4.74, -5.04 ppm.

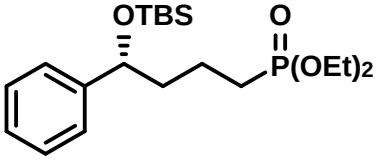
^{31}P NMR (162 MHz, $CDCl_3$) δ 17.79 ppm.

MS(ESI) m/z $[M+H]^+$: 399.20.

HRMS(ESI) m/z $[M+H]^+$: calcd. 399.2115, found 399.2116.

IR (film): 2982, 1634, 1259, 1029, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +28.54 (*c* = 1.580, $CHCl_3$).



10

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.27 (m, 4H), 7.25–7.17 (m, 1H), 4.64 (dd, *J* = 7.3, 3.6 Hz, 1H), 4.15–3.94 (m, 4H), 1.84–1.62 (m, 6H), 1.29 (td, *J* = 7.0, 4.4 Hz, 6H), 0.88 (s, 9H), 0.02 (s, 3H), -0.16 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.17, 128.02, 126.92, 125.75, 74.48 (d, *J* = 1.6 Hz), 61.34 (d, *J* = 6.5 Hz), 41.63 (d, *J* = 16.1 Hz), 25.80, 25.61 (d, *J* = 140.6 Hz), 18.65 (d, *J* = 5.0 Hz), 18.15, 16.41 (d, *J* = 6.1 Hz), -4.65, -5.04 ppm.

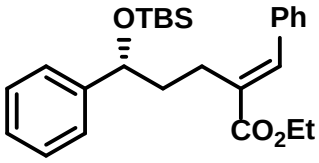
^{31}P NMR (162 MHz, $CDCl_3$) δ 32.07 ppm.

MS(ESI) m/z $[M+H]^+$: 401.20.

HRMS(ESI) m/z $[M+H]^+$: calcd. 401.2271, found 401.2271.

IR (film): 2929, 1454, 1270, 1030, 836 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +38.26 (*c* = 0.855, $CHCl_3$).



11

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.34–7.27 (m, 8H), 7.26–7.17 (m, 2H), 4.76 (t, *J* = 5.8 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.78–2.62 (m, 1H), 2.58–2.39 (m, 1H), 2.01–1.86 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.89 (s, 9H), 0.03 (s, 3H), -0.12 (s, 3H) ppm.

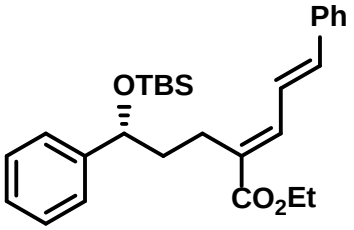
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.38, 145.06, 138.65, 135.47, 132.85, 129.45, 128.42, 128.26, 128.00, 126.93, 125.89, 74.96, 60.70, 39.68, 25.86, 23.83, 18.20, 14.29, -4.70, -4.96 ppm.

MS(ESI) m/z $[M+Na]^+$: 447.20.

HRMS(ESI) m/z $[M+Na]^+$: calcd. 447.2332, found 447.2332.

IR (film): 2956, 1709, 1630 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +106.96 (*c* = 0.915, $CHCl_3$).



12

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.17 (m, 11H), 6.90–6.75 (m, 2H), 4.77 (t, *J* = 5.7 Hz, 1H), 4.33–4.09 (m, 2H), 2.63–2.38 (m, 2H), 1.98–1.71 (m, 2H), 1.34–1.25 (m, 3H), 0.95 (s, 9H), 0.09 (s, 3H), -0.10 (s, 3H) ppm.

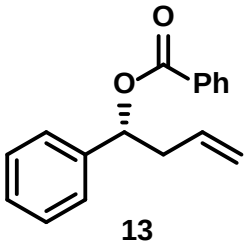
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.97, 145.09, 139.06, 138.18, 136.51, 132.12, 128.65, 128.63, 128.05, 127.08, 126.87, 125.92, 123.61, 74.67, 60.50, 40.65, 25.89, 23.19, 18.24, 14.31, -4.65, -4.94 ppm.

MS(ESI) m/z $[M+Na]^+$: 473.25.

HRMS(ESI) m/z $[M+Na]^+$: calcd. 473.2488, found 473.2488.

IR (film): 2927, 1704, 1621, 1452, 1228 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +102.52 (*c* = 0.890, $CHCl_3$).



13

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48–7.39 (m, 4H), 7.37–7.32 (m, 2H), 7.30–7.24 (m, 1H), 6.05 (dd, *J* = 7.5, 6.0 Hz, 1H), 5.79 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.12 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.07 (d, *J* = 10.7 Hz, 1H), 2.89–2.76 (m, 1H), 2.74–2.60 (m, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.42, 165.68, 133.21, 132.92, 129.61, 128.43, 128.32, 127.93, 126.43,

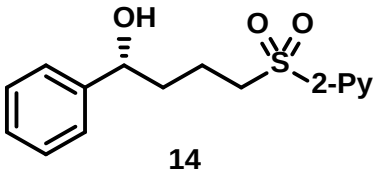
118.18 ppm.

MS(ESI) m/z [M+NH$_4$]$^+$: 270.10.

HRMS(ESI) m/z [M+NH$_4$]$^+$: calcd. 270.1489, found 270.1488.

IR (film): 2960, 1723, 1494, 1270, 1026 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = -2.676 (*c* = 0.275, $CHCl_3$).



14

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.2 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.95 (td, *J* = 7.7, 1.6 Hz, 1H), 7.58–7.48 (m, 1H), 7.35–7.22 (m, 5H), 4.77–4.58 (m, 1H), 3.55–3.31 (m, 2H), 2.20 (d, *J* = 3.4 Hz, 1H), 1.95–1.77 (m, 4H) ppm.

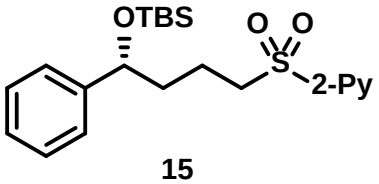
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.05, 150.21, 144.01, 138.17, 128.53, 127.72, 127.35, 125.67, 122.19, 73.69, 51.65, 37.25, 18.84 ppm.

MS(ESI) m/z [M+Na]$^+$: 314.00.

HRMS(ESI) m/z [M+Na]$^+$: calcd. 314.0821, found 314.0821.

IR (film): 3506, 2997, 1579, 1428, 1270, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +27.68 (*c* = 1.210, $CHCl_3$).



15

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.6 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.94 (td, *J* = 7.7, 1.2 Hz, 1H), 7.54 (dd, *J* = 7.6, 4.7 Hz, 1H), 7.35–7.03 (m, 5H), 4.64 (t, *J* = 5.0 Hz, 1H), 3.47–3.28 (m, 2H), 1.85–1.65 (m, 4H), 0.82 (s, 9H), -0.04 (s, 3H), -0.20 (s, 3H) ppm.

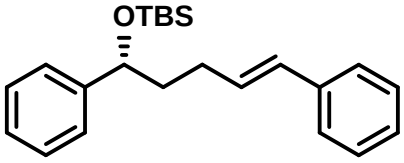
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.04, 150.23, 144.52, 138.04, 128.10, 127.24, 127.09, 125.65, 122.25, 74.17, 51.94, 39.11, 25.76, 18.58, 18.09, -4.70, -5.11 ppm.

MS(ESI) m/z [M+Na]$^+$: 428.15.

HRMS(ESI) m/z [M+Na]$^+$: calcd. 428.1686, found 428.1686.

IR (film): 2955, 1578, 1257, 1164, 777 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +52.64 (*c* = 1.520, $CHCl_3$).



16

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–6.89 (m, 10H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.20 (dt, *J* = 15.8, 6.7 Hz, 1H), 4.70 (dd, *J* = 7.4, 4.8 Hz, 1H), 2.41–2.07 (m, 2H), 1.98–1.65 (m, 2H), 0.90 (s, 9H), 0.04 (s, 3H), -0.15

(s, 3H) ppm.

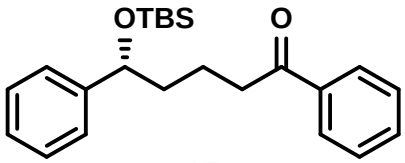
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.46, 137.81, 130.58, 129.91, 128.43, 128.01, 126.89, 126.77, 125.88, 125.86, 74.45, 40.41, 29.03, 25.86, 18.22, -4.59, -4.92 ppm.

MS(DART) m/z $[M+NH_4]^+$: 370.20.

HRMS(DART) m/z $[M+NH_4]^+$: calcd. 370.2561, found 370.2557.

IR (film): 2928, 1600, 1257, 1092, 777 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +27.29 (*c* = 0.920, $CHCl_3$).



17

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.86 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.49–7.35 (m, 2H), 7.32–7.23(m, 4H), 7.22–7.18 (m, 1H), 4.75–4.63 (m, 1H), 2.94 (t, *J* = 6.5 Hz, 2H), 1.88–1.65 (m, 4H), 0.88 (s, 9H), 0.03 (s, 3H), -0.15 (s, 3H) ppm.

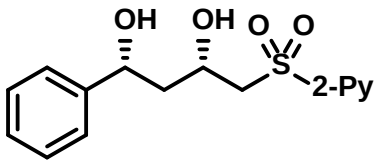
^{13}C NMR (100 MHz, $CDCl_3$) δ 200.17, 145.38, 136.97, 132.83, 128.49, 128.00, 127.97, 126.86, 125.82, 74.87, 40.37, 38.48, 25.83, 20.44, 18.19, -4.65, -4.97 ppm.

MS(ESI) m/z $[M+Na]^+$: 391.15.

HRMS(ESI) m/z $[M+Na]^+$: calcd. 391.2070, found 391.2072.

IR (film): 2927, 1690, 1450, 1270, 1097, 837 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +36.41 (*c* = 0.425, $CHCl_3$).



18

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.4 Hz, 1H), 8.12 (d, *J* = 7.9 Hz, 1H), 8.01 (td, *J* = 7.8, 1.6 Hz, 1H), 7.60 (ddd, *J* = 7.6, 4.7, 0.9 Hz, 1H), 7.39–7.22 (m, 5H), 4.98 (dd, *J* = 9.5, 3.0 Hz, 1H), 4.68 (s, 1H), 4.61 (t, *J* = 9.3 Hz, 1H), 3.60 (dd, *J* = 14.9, 9.0 Hz, 1H), 3.53 (s, 1H), 3.49 (dd, *J* = 14.9, 2.3 Hz, 1H), 2.08–1.95 (m, 1H), 1.86 (dt, *J* = 14.3, 3.0 Hz, 1H) ppm.

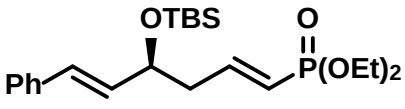
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.43, 149.89, 143.71, 138.70, 128.50, 127.74, 127.69, 125.64, 122.04, 73.74, 66.54, 59.66, 44.67 ppm.

MS(ESI) m/z $[M+H]^+$: 308.15.

HRMS(ESI) m/z $[M+H]^+$: calcd. 308.0951, found 308.0953.

IR (film): 3444, 2924, 1580, 1428, 1308, 793 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +27.58 (*c* = 0.710, $CHCl_3$).



19

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.18 (m, 5H), 6.77 (ddt, *J* = 21.8, 17.1, 7.1 Hz, 1H), 6.52 (d, *J* = 15.8

Hz, 1H), 6.15 (dd, *J* = 15.9, 6.4 Hz, 1H), 5.71 (dd, *J* = 21.3, 17.1 Hz, 1H), 4.43 (q, *J* = 5.9 Hz, 1H), 4.11–3.87 (m, 4H), 2.62–2.42 (m, 2H), 1.27 (q, *J* = 7.2 Hz, 6H), 0.91 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.41 (d, *J* = 4.9 Hz), 136.57, 131.83, 129.88, 128.53, 127.57, 126.38, 119.54 (d, *J* = 186.7 Hz), 72.22 (d, *J* = 1.3 Hz), 61.59 (d, *J* = 5.6 Hz), 43.39 (d, *J* = 21.8 Hz), 25.82, 18.18, 16.28 (d, *J* = 6.5 Hz), -4.33, -4.84 ppm.

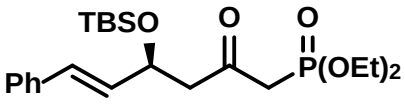
^{31}P NMR (162 MHz, $CDCl_3$) δ 17.83 ppm.

MS(ESI) m/z [M+Na]$^+$: 447.15.

HRMS(ESI) m/z [M+H]$^+$: calcd. 425.2271, found 425.2273.

IR (film): 2958, 1635, 1252, 1029 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = -19.61 (*c* = 1.145, $CHCl_3$).



20

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.18 (m, 5H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 15.9, 6.5 Hz, 1H), 4.79 (dd, *J* = 12.2, 6.4 Hz, 1H), 4.20–4.03 (m, 4H), 3.13 (dq, *J* = 22.6, 13.5 Hz, 2H), 2.99 (dd, *J* = 15.6, 7.5 Hz, 1H), 2.79 (dd, *J* = 15.6, 5.1 Hz, 1H), 1.41–1.23 (m, 6H), 0.89 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.29, 136.55, 131.53, 129.86, 128.53, 127.60, 126.42, 70.16, 62.50 (d, *J* = 6.4 Hz), 52.13, 43.81 (d, *J* = 126.7 Hz), 25.80, 18.09, 16.27 (d, *J* = 6.2 Hz), -4.29, -4.99 ppm.

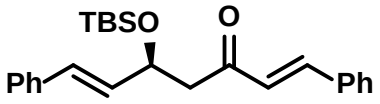
^{31}P NMR (162 MHz, $CDCl_3$) δ 19.63 ppm.

MS(ESI) m/z [M+Na]$^+$: 463.20.

HRMS(ESI) m/z [M+H]$^+$: calcd. 441.2221, found 441.2223.

IR (film): 2929, 1716, 1472, 1249, 1026, 780 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = -46.06 (*c* = 1.000, $CHCl_3$).



21

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.45 (m, 3H), 7.40–7.28 (m, 7H), 7.26–7.20 (m, 1H), 6.78 (d, *J* = 16.2 Hz, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.26 (dd, *J* = 15.9, 6.2 Hz, 1H), 4.90 (dt, *J* = 6.5, 5.5 Hz, 1H), 3.09 (dd, *J* = 14.7, 7.8 Hz, 1H), 2.76 (dd, *J* = 14.7, 4.9 Hz, 1H), 0.87 (s, 9H), 0.06 (s, 3H), 0.06 (s, 3H) ppm.

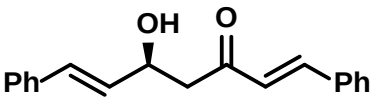
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.50, 143.22, 136.74, 134.52, 132.19, 130.46, 129.50, 128.91, 128.54, 128.31, 127.53, 127.30, 126.44, 70.75, 49.25, 25.83, 18.15, -4.34, -4.94 ppm.

MS(ESI) m/z [M+Na]$^+$: 415.15.

HRMS(ESI) m/z [M+Na]$^+$: calcd. 415.2064, found 415.2061.

IR (film): 2955, 1689, 1609, 1471, 1249, 836, 779 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = -104.50 (*c* = 1.000, $CHCl_3$).



22

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.41 (m, 3H), 7.38–7.04 (m, 8H), 6.70–6.50 (m, 2H), 6.21 (dd, *J* = 15.9, 5.9 Hz, 1H), 4.90–4.73 (m, 1H), 3.33 (s, 1H), 3.07–2.77 (m, 2H) ppm.

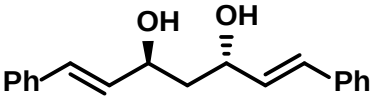
^{13}C NMR (100 MHz, $CDCl_3$) δ 200.00, 143.92, 136.56, 134.12, 130.85, 130.40, 130.27, 129.01, 128.55, 128.43, 127.69, 126.49, 126.23, 68.74, 46.88 ppm.

MS(ESI) m/z $[M+Li]^+$: 285.10.

HRMS(ESI) m/z $[M+Li]^+$: calcd. 285.1463, found 285.1462.

IR (film): 3385, 2924, 1458, 1275, 1260, 749 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = -10.78 (*c* = 0.615, $CHCl_3$).



23

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.20 (m, 10H), 6.65 (d, *J* = 15.8 Hz, 2H), 6.31 (dd, *J* = 15.8, 5.9 Hz, 2H), 4.79–4.58 (m, 2H), 2.60 (s, 2H), 1.98 (t, *J* = 5.3 Hz, 2H) ppm.

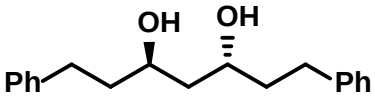
^{13}C NMR (100 MHz, $CDCl_3$) δ 136.55, 131.62, 130.21, 128.59, 127.70, 126.47, 70.47, 42.64 ppm.

MS(ESI) m/z $[M+Na]^+$: 303.10.

HRMS(ESI) m/z $[M+Na]^+$: calcd. 303.1356, found 303.1356.

IR (film): 3358, 2954, 2924, 1260, 963, 750 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +46.20 (*c* = 0.260, $CHCl_3$).



yashabushidiol B

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (m, 4H), 7.23–7.13 (m, 6H), 4.05–3.92 (m, 2H), 2.83–2.73 (m, 2H), 2.71–2.58 (m, 2H), 2.30 (d, *J* = 4.2 Hz, 2H), 1.92–1.71 (m, 4H), 1.67 (t, *J* = 5.6 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.82, 128.43, 128.35, 125.89, 68.93, 42.52, 39.08, 32.16 ppm.

MS(ESI) m/z $[M+Na]^+$: 307.10.

HRMS(ESI) m/z $[M+Na]^+$: calcd. 307.1674, found 307.1672.

IR (film): 3285, 2923, 1453, 1061, 919, 727 cm^{-1}.

Optical rotation: $[\alpha]_D^{25}$ = +5.66 (*c* = 0.250, $CHCl_3$). {literature (Hashimoto et. al., 1986), $[\alpha]_D$ = +7.2 ($CHCl_3$)}.

Supplemental References

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