Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for:

Transition-Metal-Free Radical Cleavage of Hydrazonyl N-S Bond: Tosyl Radical Initiated Cascade C(sp^3)-OAr Cleavage, Sulfonyl Rearrangement and Atropisomeric Cyclopropanation

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Table of Contents for Supporting Information

1. General Information:

Solvents and reagents were reagent grade and used without purification unless otherwise noted. Anhydrous solvents were obtained as follow: THF, toluene, and 1,4-dioxane were dried by distillation from sodium and benzophenone; All reactions were carried out in oven dried glassware unless otherwise specified. All ^{1}H-NMR (400 MHz) spectra were recorded on a Bruker-DMX 400 using $CDCl_3$ solution in the presence of tetramethylsilane (TMS) as an internal standard and are reported in ppm (δ). Coupling constants are reported in Hertz (Hz). Spectral splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; and br, broad. High resolution mass spectroscopic data of the products were collected on a Waters Micromass GCT instrument using EI (70 eV) or an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS using ESI. The evolution of hydrogen was analyzed by gas chromatography (GC-2014, Shimadzu, Japan, TCD, nitrogen as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector). The Gaussian 03 program was used for the ab initio molecular orbital calculations with the basis sets implemented in the Gaussian program.[1]

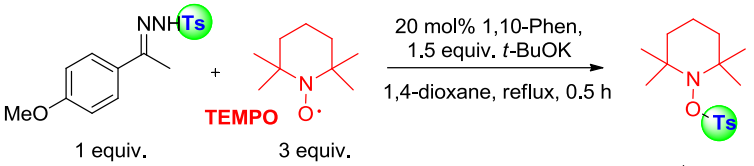
Reference:

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2004.

2. Studies on Generation of Tosyl Radical and Molecular Hydrogen

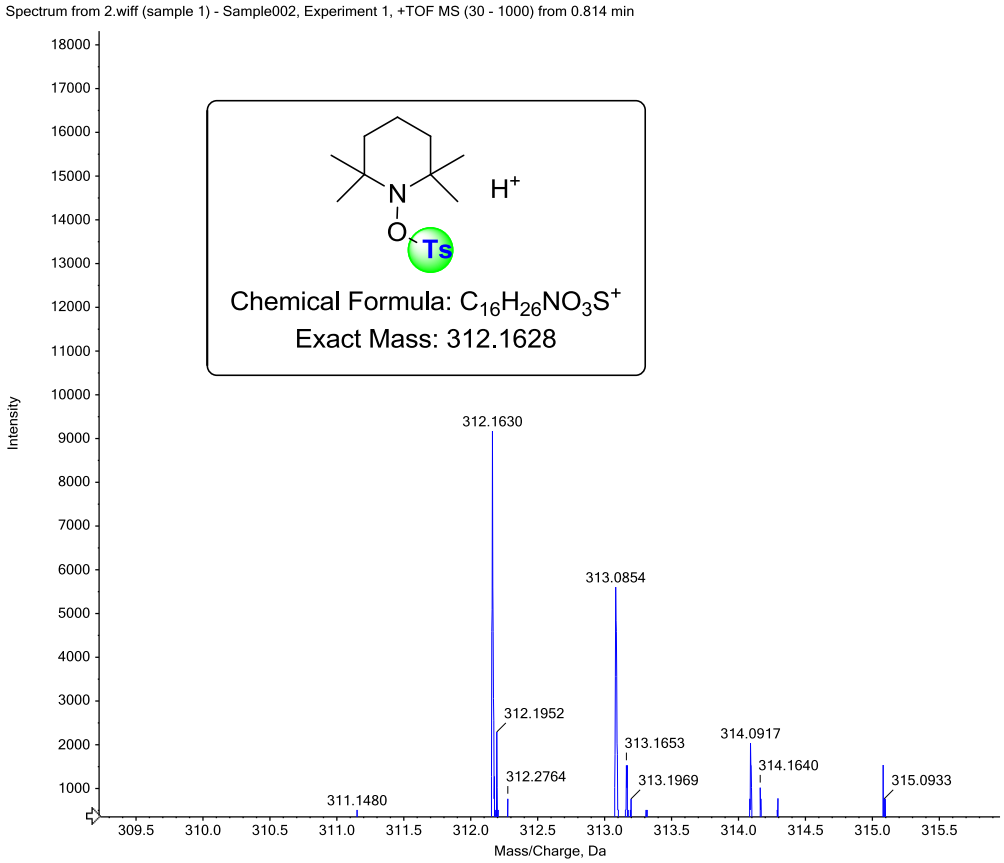
2.1 Evidences of Tosyl Radical Generated from *N*-Tosylhydrazones

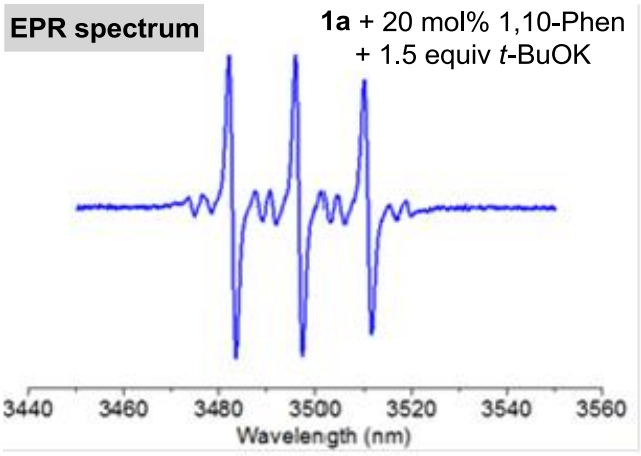
2.1.1 TEMPO as Radical Scavenger and EPR Study:



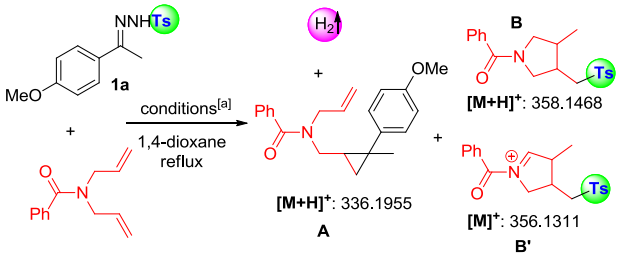
1 equiv. 3 equiv.

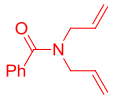
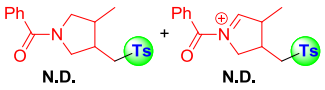
HRMS (ESI): ([M+H]$^+$) Calcd for $C_{16}H_{26}NO_3S^+$: 312.1628, Found: 312.1630.





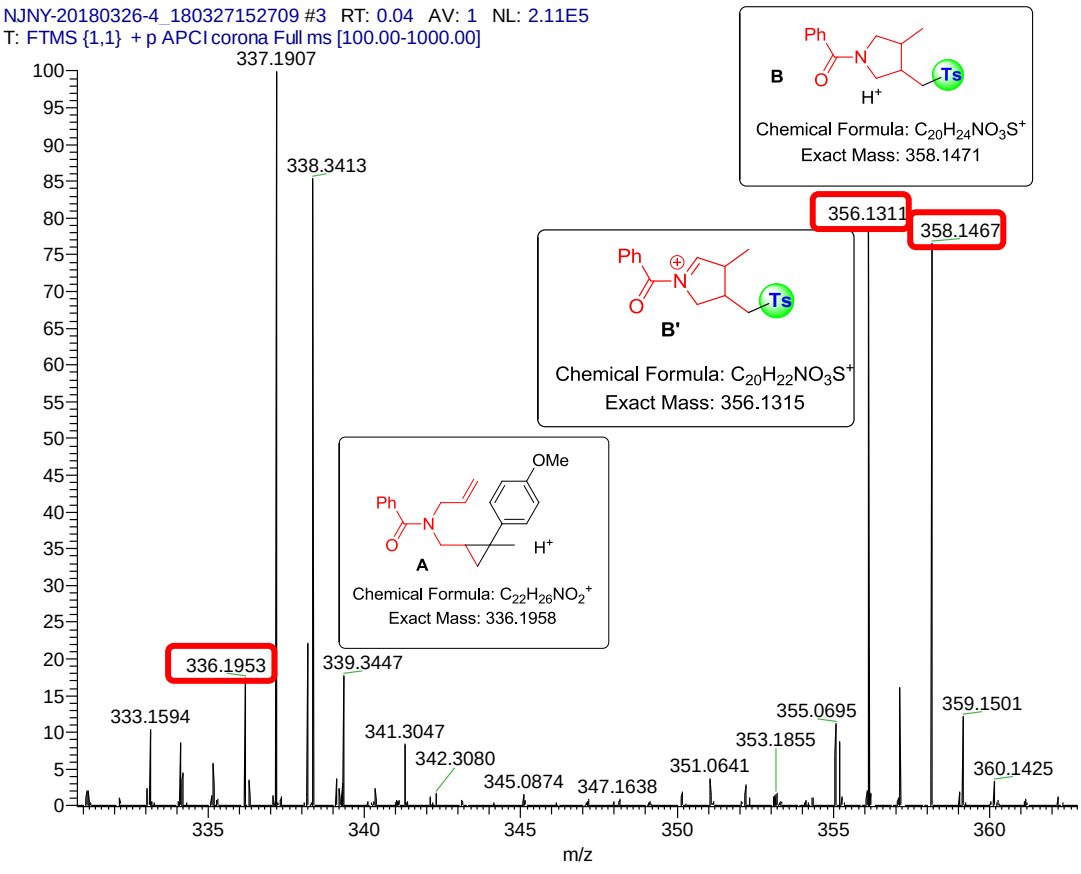
2.1.2 *N,N*-diallylbenzamide as Trapping Reagent:



Entry	Radical Initiator	HR-MS Result	H_2 Evolution
1	20 mol% 1,10-phen/*t*-BuOK (1.5 eq.)	**A** + **B** + **B'**	Yes
2	20 mol% 1,10-phen/K_2CO_3 (1.5 eq.)	**A** + **B** + **B'**	Yes
3	20 mol% 1,10-phen/K_2CO_3 (15 mol%)	**A** + **B** + **B'**	Yes
4[b]	20 mol% 1,10-phen/K_2CO_3 (15 mol%)	**A** + **B** + **B'**	Yes
5	K_2CO_3 (1.5 eq.)	Only **A**	No
6	TBAI (0.2 eq.)/TBHP (2 eq.)	**B** + **B'**	No
7	5 mol% $Pd(OAc)_2$ + 20 mol% 1,10-phen + K_2CO_3 (15 mol%)	**A** + **B** + **B'**	Yes
8	5 mol% $Pd(PPh_3)_2Cl_2$ + K_2CO_3 (15 mol%)	Only **A**	No
g[c]	TsNa + 		N.D.

[a] *N*-tosylhydrazone (**1a**, 0.1 mmol), *N,N*-diallylbenzamide (0.12 mmol), catalyst or oxidant in 3 mL refluxing 1,4-dioxane for 2 hours. [b] High purity reagents: 1,10-phen (anhydrous, purity>99+%), K_2CO_3 (purity: 99.997%). [c] N.D.= Not Detected.

Entry 1: (20 mol% 1,10-phen + 1.5 equiv *t*-BuOK)



Entry 2: (20 mol% 1,10-phen + 1.5 equiv K_2CO_3)

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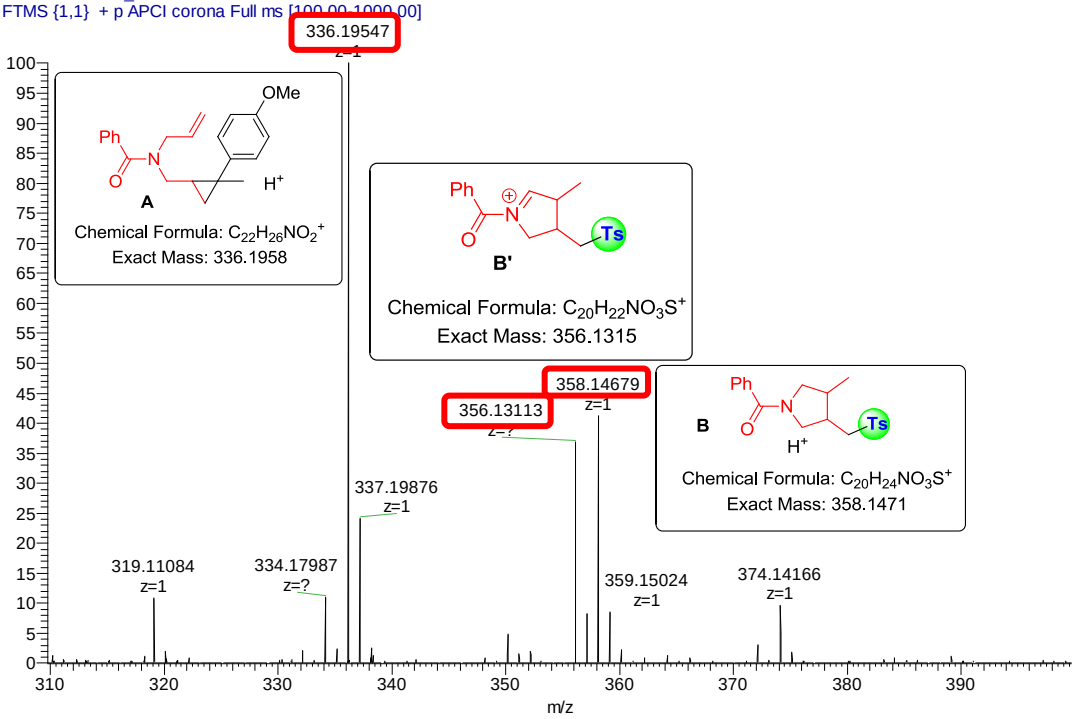
T: FTMS {1,1} + p APCI corona Full ms [100.00-1000.00]



Entry 3: (20 mol% 1,10-phen + 15 mol% K_2CO_3)

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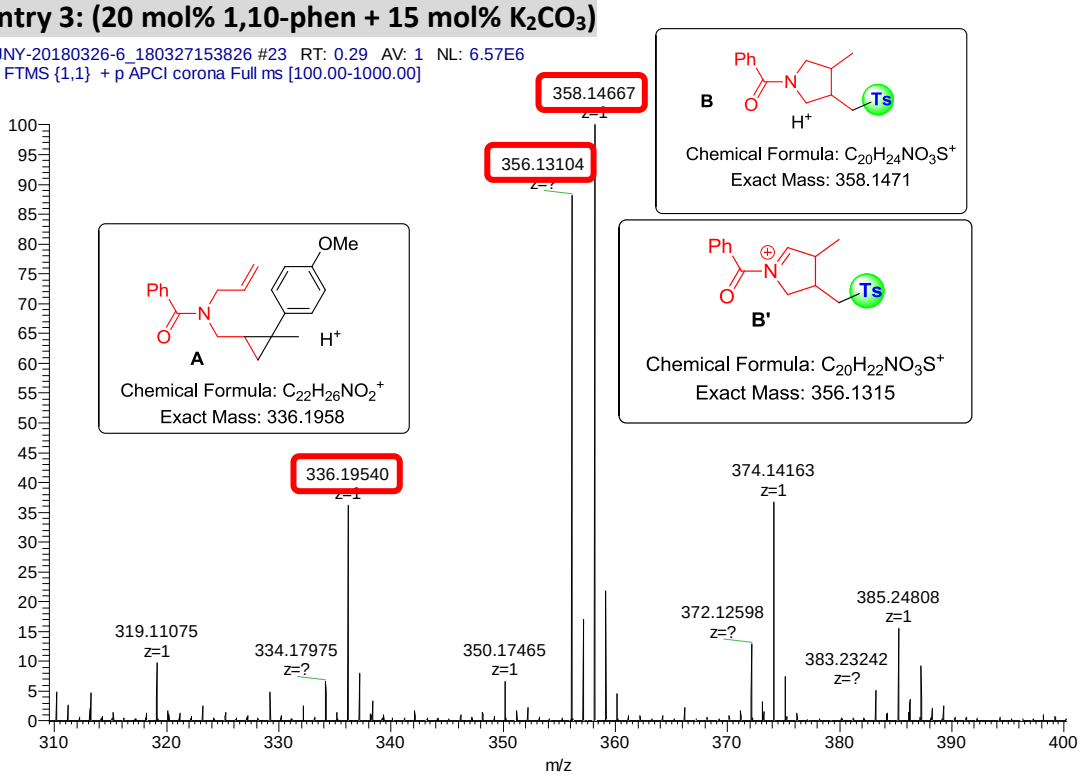
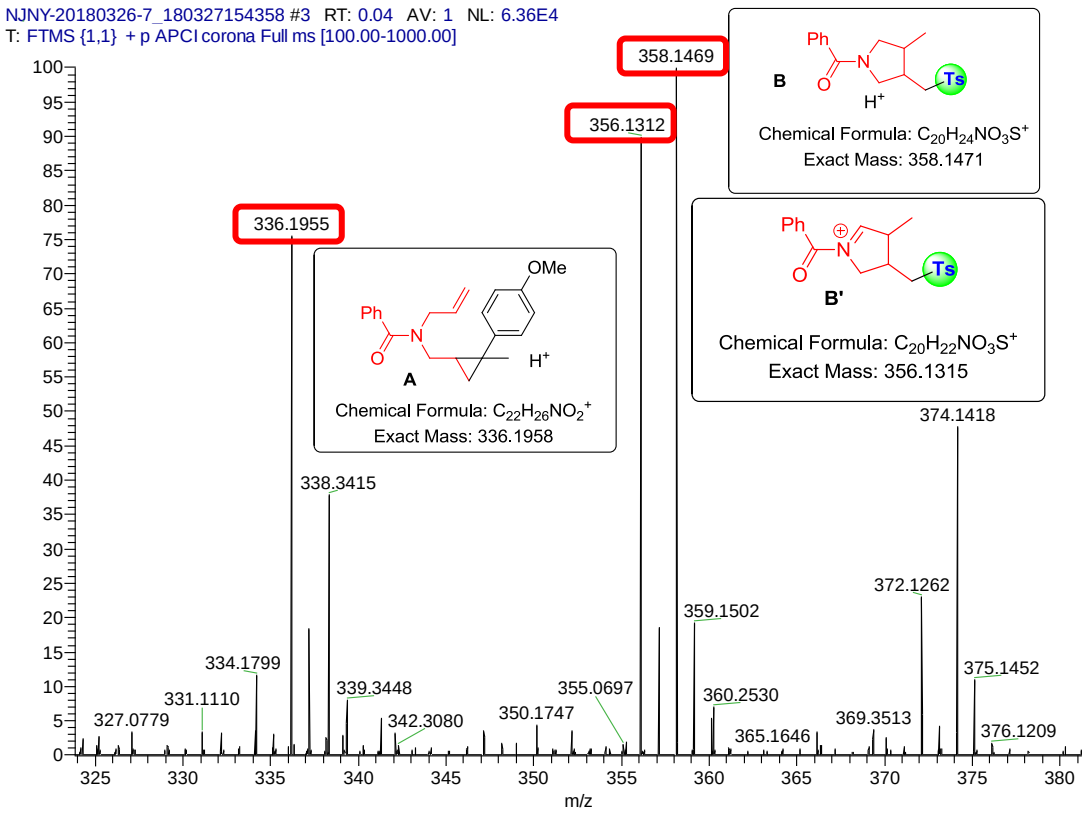
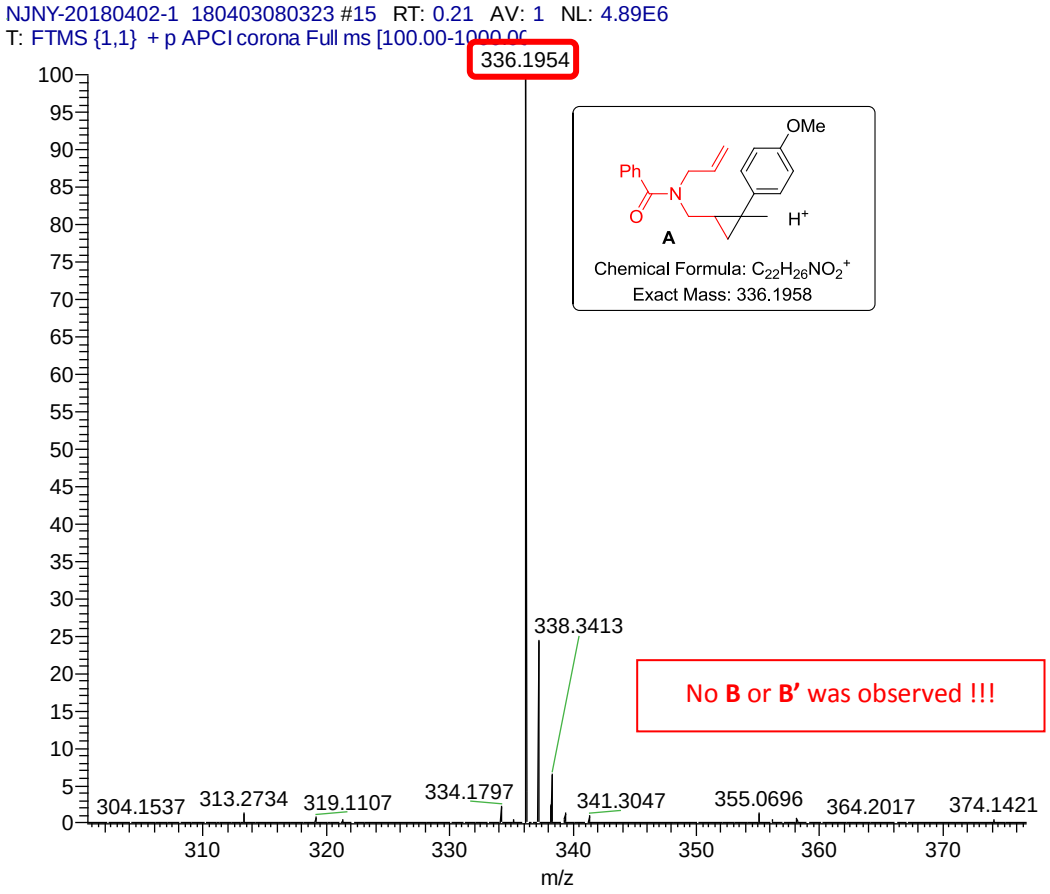
T: FTMS {1,1} + p APCI corona Full ms [100.00-1000.00]



Entry 4: [20 mol% 1,10-phen (high purity) + 15 mol% K_2CO_3(high purity)]

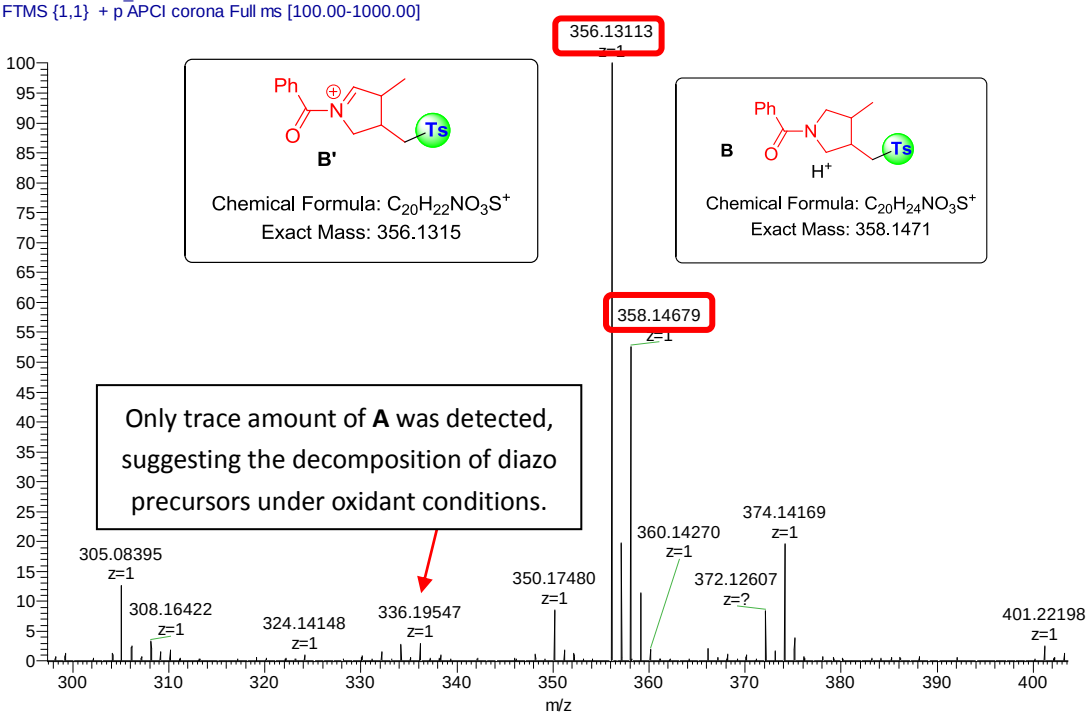


Entry 5: (1.5 equiv K_2CO_3)



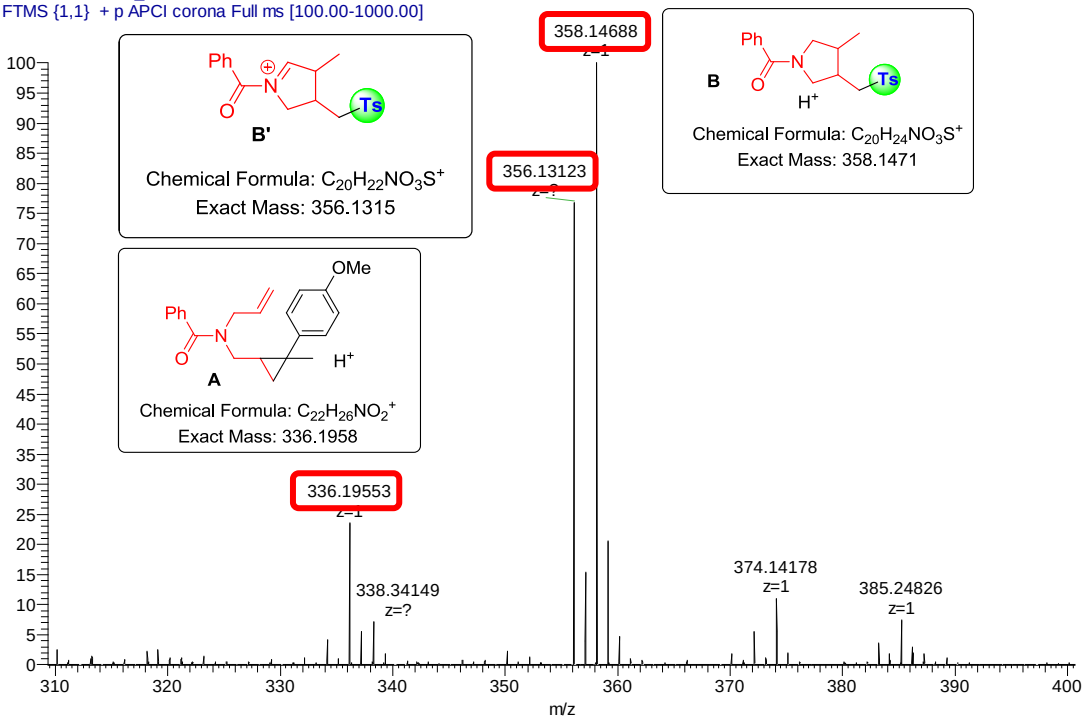
Entry 6: (0.2 equiv TBAI + 2 equiv TBHP)

NJNY-20180326-9_180327155508 #23 RT: 0.27 AV: 1 NL: 1.26E7
T: FTMS {1,1} + p APCI corona Full ms [100.00-1000.00]

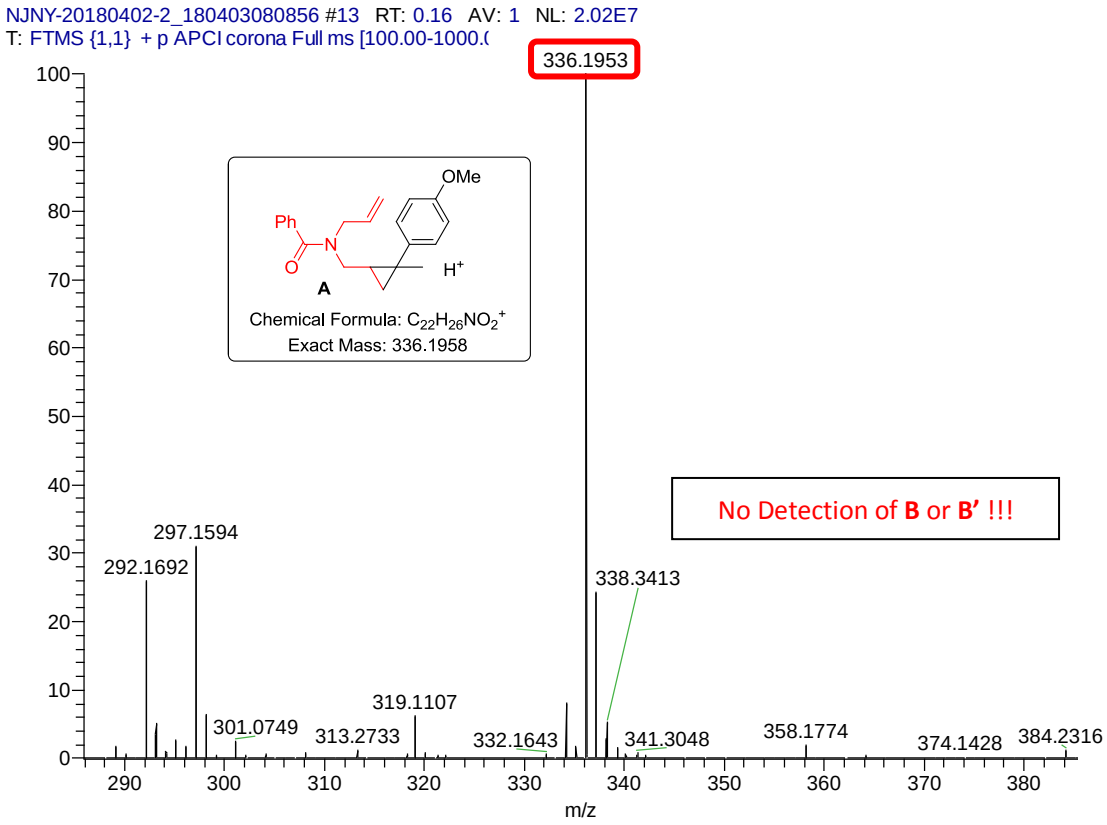


Entry 7: (5 mol% $Pd(OAc)_2$ + 20 mol% 1,10-phen + 15 mol% K_2CO_3)

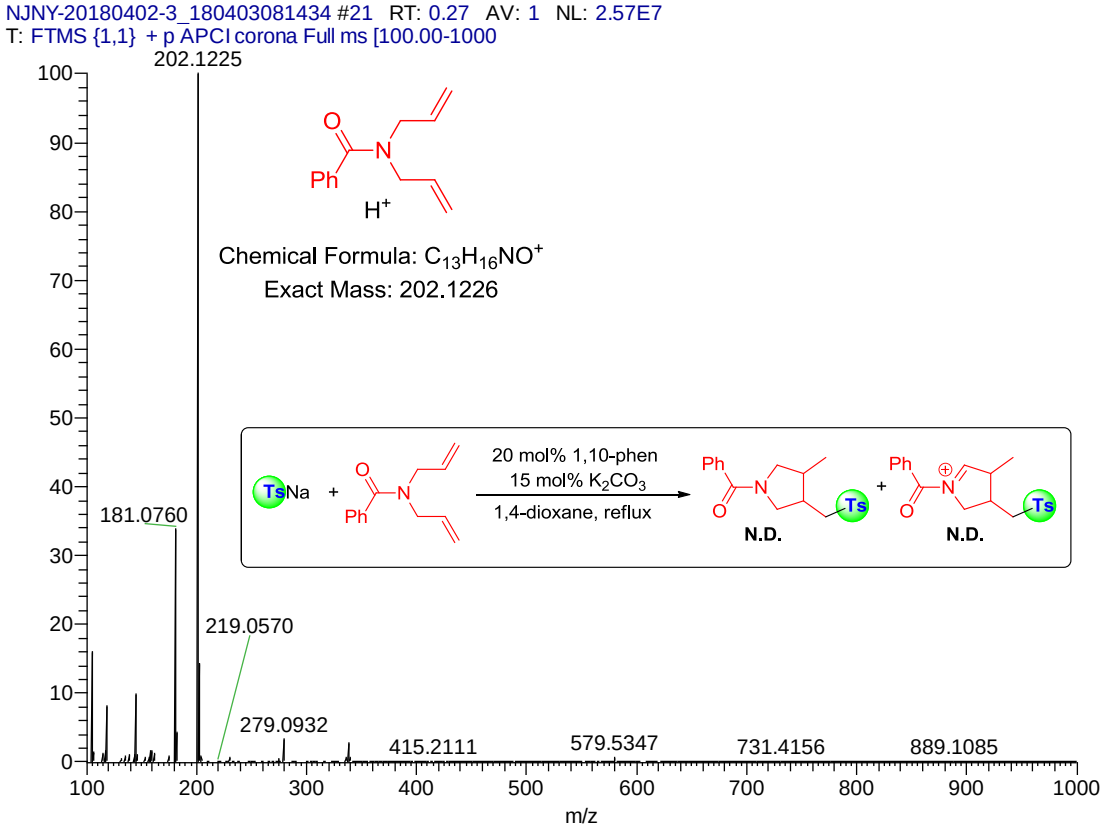
NJNY-20180326-11_180327160620 #23 RT: 0.29 AV: 1 NL: 3.72E6
T: FTMS {1,1} + p APCI corona Full ms [100.00-1000.00]



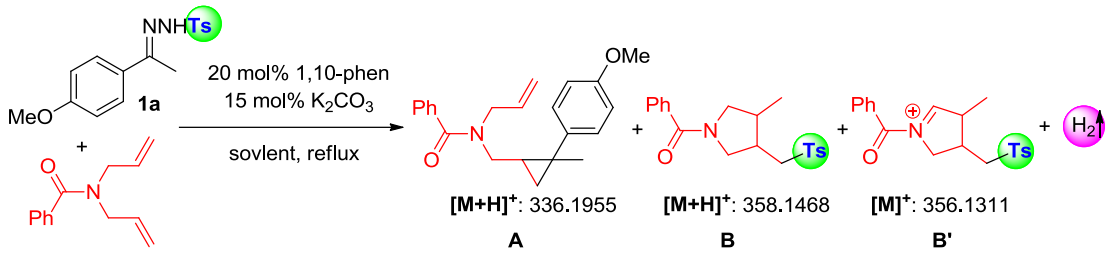
Entry 8: (5 mol% $Pd(PPh_3)_2Cl_2$ + 15 mol% K_2CO_3)



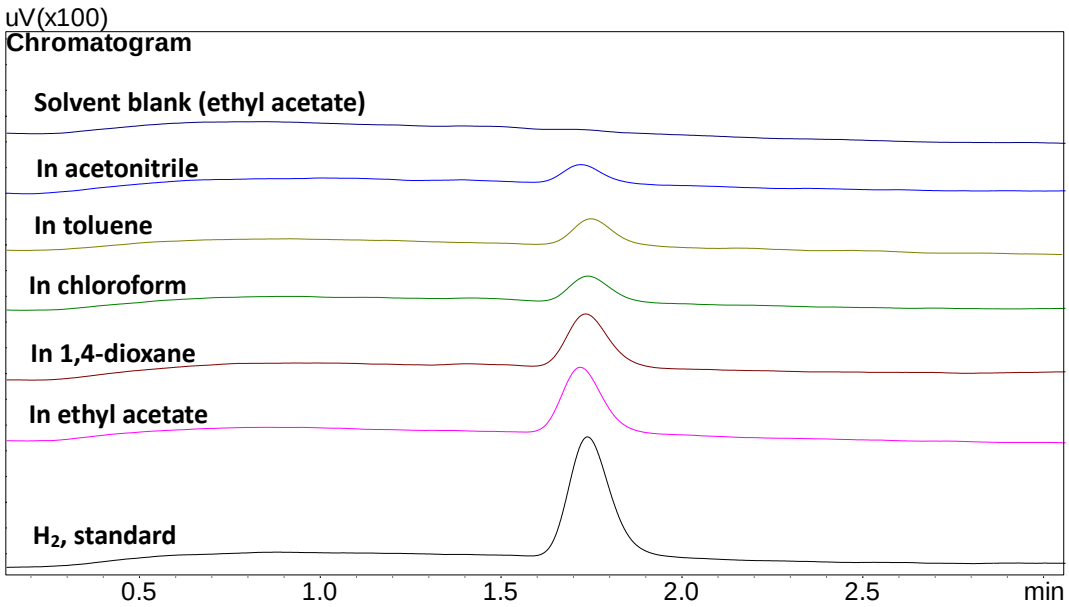
Entry 9: Ts anion cannot be converted into Ts radical by 1,10-phen/K_2CO_3



2.2 Evidences of Hydrogen Evolution Generated from *N*-Tosylhydrazones



Gas Chromatography Results for the Above Equation in Various Sovlents:

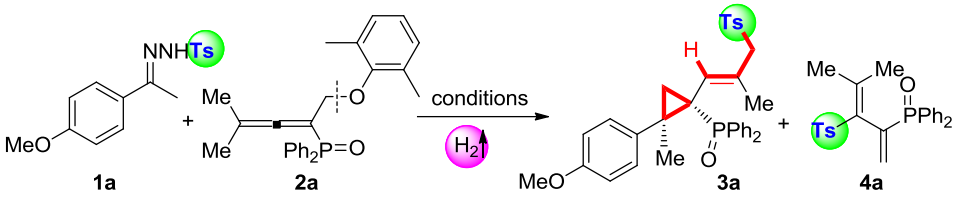


3. General Procedures for the Metal-Free Cascade Reaction of *N*-Tosyl-hydrazones with Phosphinyl Allenes

To a 15 mL sealed reaction tube was added *N*-tosylhydrazones (**1a**, 286 mg, 0.9 mmol), phosphinyl allenes (**2a**, 120 mg, 0.3 mmol), 1,10-phen (12 mg, 20 mol%), K_2CO_3 (103.5 mg, 0.75 mmol), and 3 mL degassed 1,4-dioxane. The reaction mixture was then heated to reflux for 8 hours until the complete consuming of **2a** monitored by TLC. After all of the volatiles were removed under vacuum, the crude product was purified on flash chromatography (eluent: 1:2 (v/v) of ethyl acetate/petroleum ether) to afford product **3a** as a white solid.

4. Optimization of the Cascade Reaction Conditions

4.1 Screenings on Bases and Catalysts[a]

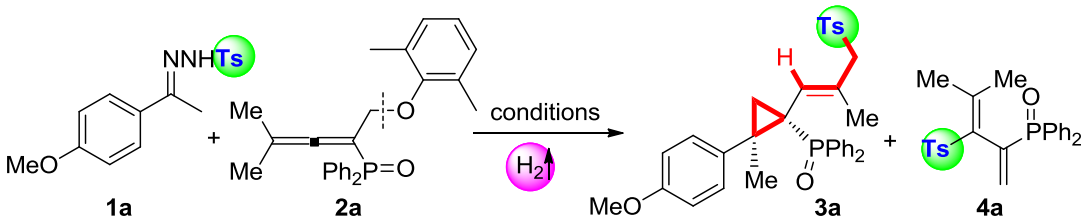


1a 2a 3a 4a

entry	catalyst	base	solvent	yield(%, **3a**/**4a**)[b]
1	1,10-phen	*t*-BuOK (15mol%)	1,4-dioxane	0/14
2	1,10-phen	K_2CO_3 (15mol%)	1,4-dioxane	<5/85
3	1,10-phen	K_2CO_3 (1.5 eq.)	1,4-dioxane	35/30
4	1,10-Phen	K_2CO_3 (2.5 eq.)	1,4-dioxane	74/0
5	2,2'-bipyridine	K_2CO_3 (2.5 eq.)	1,4-dioxane	38/13
6	2,9-dimetheyl-1,10-phenanthroline	K_2CO_3 (2.5 eq.)	1,4-dioxane	36/11
7	2,2':6',2''-terpyridine	K_2CO_3 (2.5 eq.)	1,4-dioxane	42/9
8	4,7-dimethoxy-1,10-phenanthroline	K_2CO_3 (2.5 eq.)	1,4-dioxane	50/0
9[c,d]	$Pd(PPh_3)_2Cl_2$	K_2CO_3 (2.5 eq.)	1,4-dioxane	0/0
10[c]	$Pd(OAc)_2$/1,10-phen	K_2CO_3 (2.5 eq.)	1,4-dioxane	40/0
11[c]	$CoCl_2$/1,10-phen	K_2CO_3 (2.5 eq.)	1,4-dioxane	21/0
12[c]	$NiCl_2$/1,10-phen	K_2CO_3 (2.5 eq.)	1,4-dioxane	54/0
13[c]	$Rh(OAc)_2$/1,10-phen	K_2CO_3 (2.5 eq.)	1,4-dioxane	47/0
14[c]	$Cu(OAc)_2$/1,10-phen	K_2CO_3 (2.5 eq.)	1,4-dioxane	0/0
15[c]	$Zn(OAc)_2$/1,10-phen	K_2CO_3 (2.5 eq.)	1,4-dioxane	19/0
16[c]	$Mn(OAc)_3$/1,10-phen	K_2CO_3 (2.5 eq.)	1,4-dioxane	14/5
17[c]	$IrCl_3 \cdot H_2O$/1,10-phen	K_2CO_3 (2.5 eq.)	1,4-dioxane	20/7
18[c]	$Fe(acac)_3$/1,10-phen	K_2CO_3 (2.5 eq.)	1,4-dioxane	38/0
19[c]	$Fe(OAc)_2$/1,10-phen	K_2CO_3 (2.5 eq.)	1,4-dioxane	27/0
20[e]	1,10-phen	K_2CO_3 (2.5 eq.)	1,4-dioxane	75/0
21	1,10-phen	DMAP (2.5 eq.)	1,4-dioxane	0/0
22	1,10-phen	t-BuOK (2.5 eq.)	1,4-dioxane	6/10
23	1,10-phen	Cs_2CO_3 (2.5 eq.)	1,4-dioxane	17/4
24	1,10-phen	t-BuOLi (2.5 eq.)	1,4-dioxane	0/0
25	1,10-phen	$(i\text{-}Pr)_2NEt$ (2.5 eq.)	1,4-dioxane	N.R.
26	1,10-phen	DBN (2.5 eq.)	1,4-dioxane	0/0
27	1,10-phen	DBU (2.5 eq.)	1,4-dioxane	0/0
28	1,10-phen	NaH (2.5 eq.)	1,4-dioxane	0/0
29	1,10-phen	Na_2CO_3 (2.5 eq.)	1,4-dioxane	26/12
30	1,10-phen	PivONa (2.5 eq.)	1,4-dioxane	57/0
31	1,10-phen	CsF (2.5 eq.)	1,4-dioxane	53/0
32	1,10-phen	K_3PO_4 (2.5 eq.)	1,4-dioxane	0/0
33	1,10-phen	NH_4HCO_3 (2.5 eq.)	1,4-dioxane	N.R.
34	1,10-phen	$NaHCO_3$ (2.5 eq.)	1,4-dioxane	56/0

[a] Reaction conditions: *N*-tosylhydrazone (**1a**, 0.9 mmol), phosphinyl allenes (**2a**, 0.3 mmol), 1,10-phen (20 mol%), base, in 3 mL solvent at the indicated temperature for 8 hours. [b] Isolated yield by column chromatography. [c] 5 mol% metal catalyst. [d] The major product was phosphinyl [3]dendralenes. [e] High purity reagents: 1,10-phen (anhydrous, purity>99+%), K_2CO_3 (purity: 99.997%).

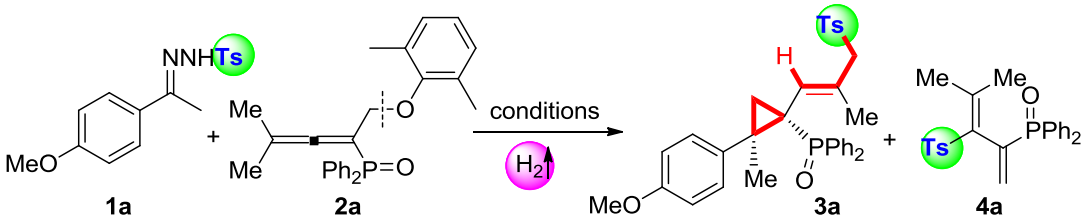
4.2 Screenings on Solvents[a]



entry	catalyst (20 mol%)	base (2.5 eq.)	solvent	yield of **3a** (%)[b]
1	1,10-Phen	K_2CO_3	THF	trace
2	1,10-Phen	K_2CO_3	Ethyl Acetate	45
3	1,10-Phen	K_2CO_3	DMF	9
4	1,10-Phen	K_2CO_3	Toluene	17
5	1,10-Phen	K_2CO_3	CH_3NO_2	trace
6	1,10-Phen	K_2CO_3	1,2-Dimethoxyethane	13
7	1,10-Phen	K_2CO_3	1,4-dioxane	74

[a] Reaction conditions: *N*-tosylhydrazone (**1a**, 0.9 mmol), phosphinyl allenes (**2a**, 0.3 mmol), 1,10-phen (20 mol%), K_2CO_3 (0.75 mmol) in 3 mL solvent at the indicated temperature for 8 hours. [b] Isolated yield by column chromatography.

4.3 Screenings on Loading of Catalyst[a]

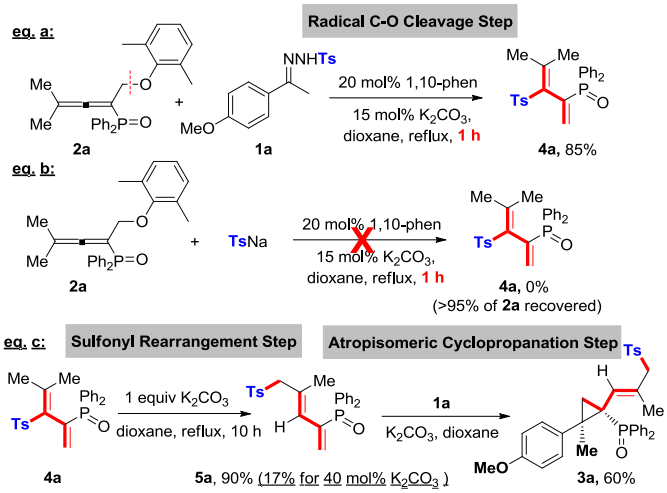


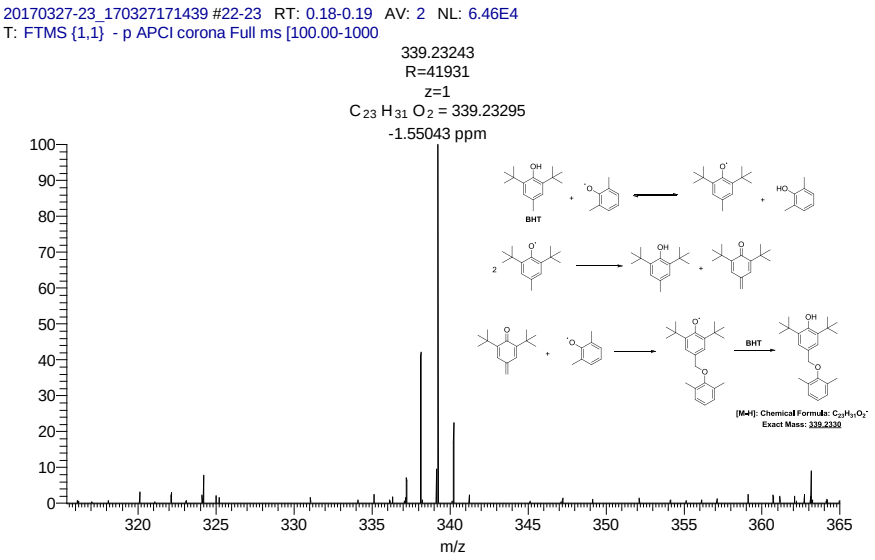
entry	catalyst	loading (mol%)	yield of **3a** (%)[b]
1	1,10-phen	5	61
2	1,10-phen	10	63
3	1,10-phen	20	74
4	1,10-phen	50	68
5	1,10-phen	100	69
6	1,10-phen	200	67

[a] Reaction conditions: *N*-tosylhydrazone (**1a**, 0.9 mmol), phosphinyl allenes (**2a**, 0.3 mmol), 1,10-phen, K_2CO_3 (0.75 mmol) in 3 mL 1,4-dioxane at 101℃ for 8 hours. [b] Isolated yield by column chromatography.

5. Mechanistic Studies on Cascade Reactions

5.1 Capture of Reaction intermediates and Kinetic Studies





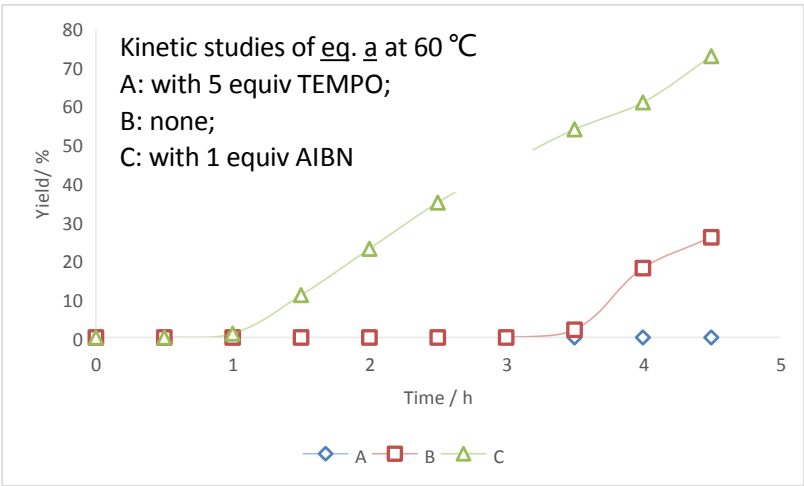
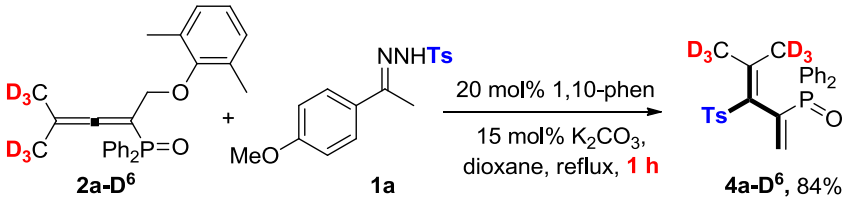
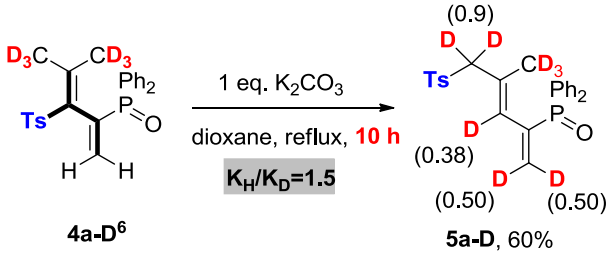
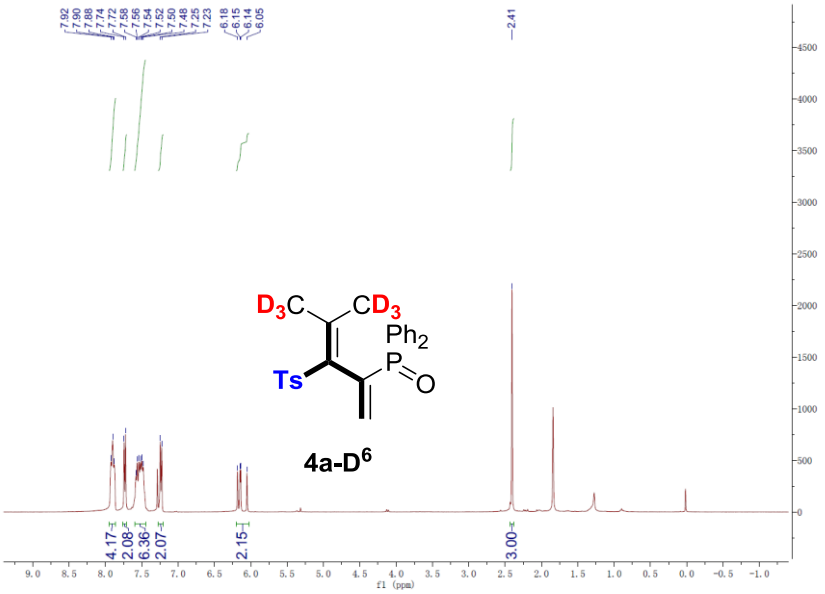


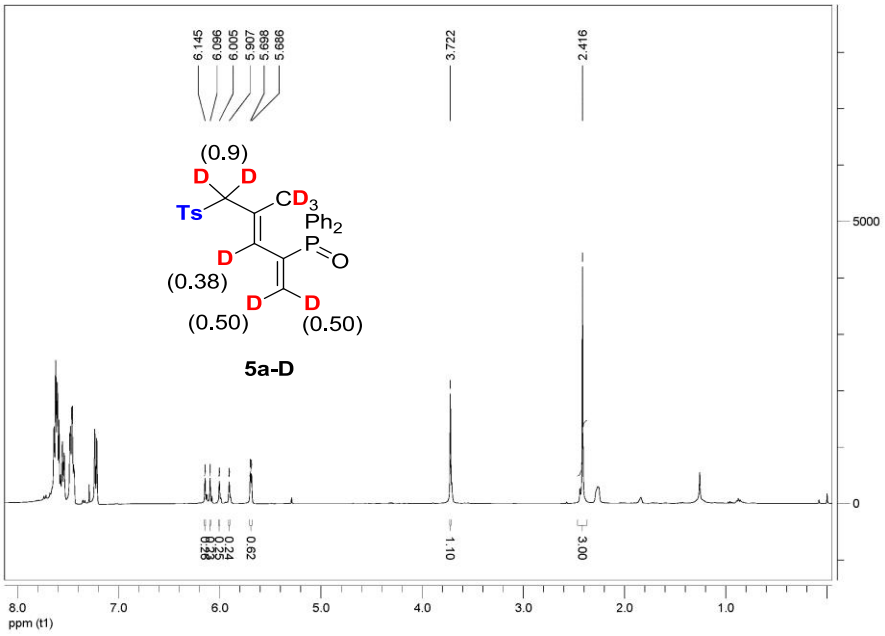
Figure S1. Kinetic Studies on "Radical C-O Cleavage Step" (eq. a) at 60°C

5.2 Deuterium Experiments



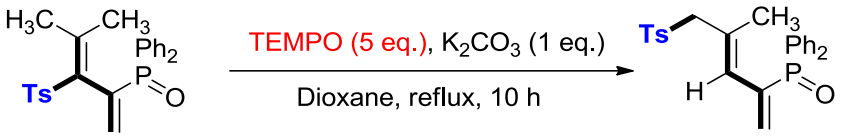






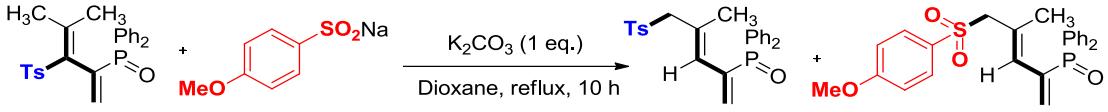
5.3 Studies on Sulfonyl Rearrangement Step

1) The sulfonyl rearrangement should not undergo a radical pathway:



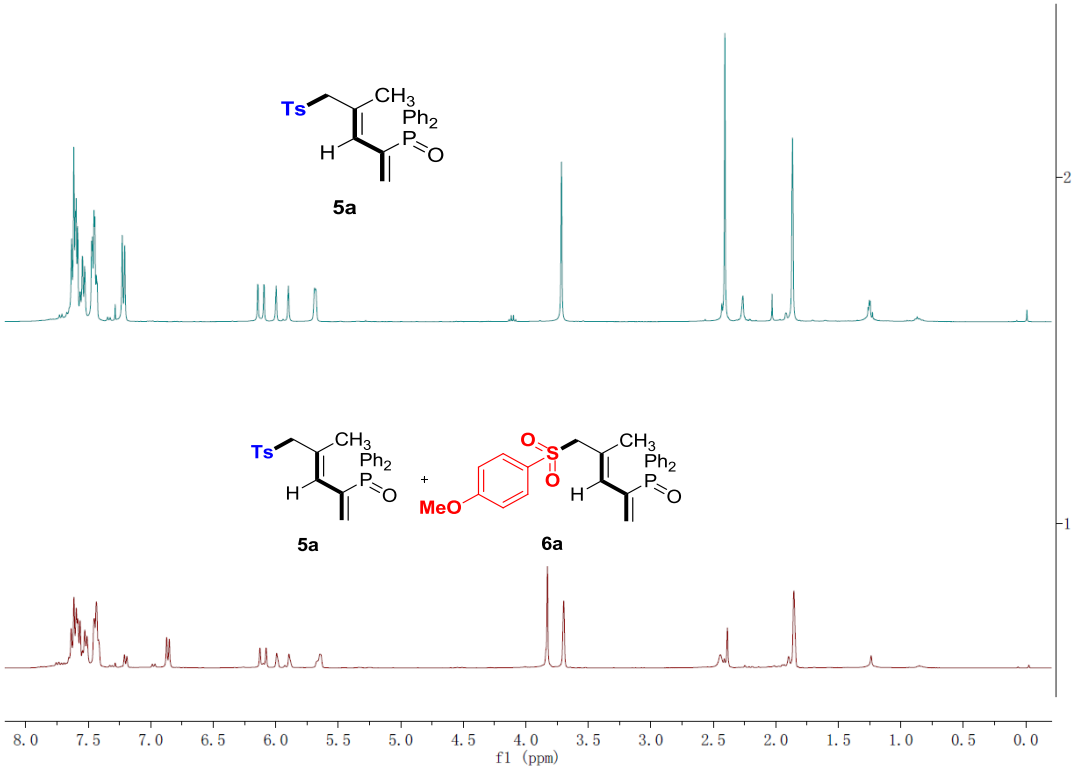
4a **5a, 90%**

2) Competitive sulfonyl source indicates an intramolecular process:

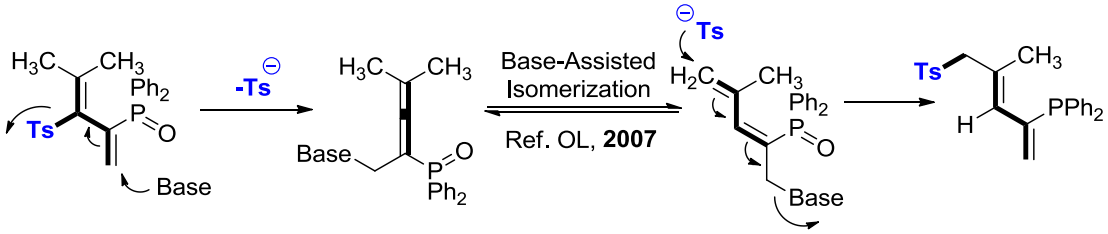


4a (3 eq.) **5a** **6a**

(5a : 6a = 1:3, ^{1}HNMR result)



Possible Mechanism for the Sulfonyl Rearrangement Step:



Stoichiometric Base-Assisted Isomerization of Allenes, see: M. Shi, *et al. Org. Lett.* **2007**, *9*, 117.

5.4 Electron Paramagnetic Resonance (EPR) Experiments for Cascade Reaction

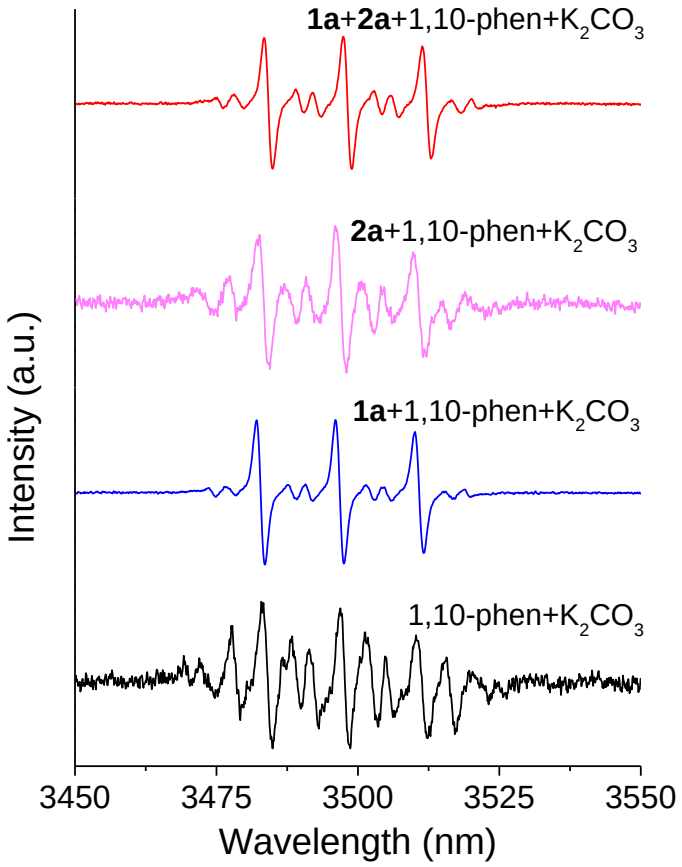
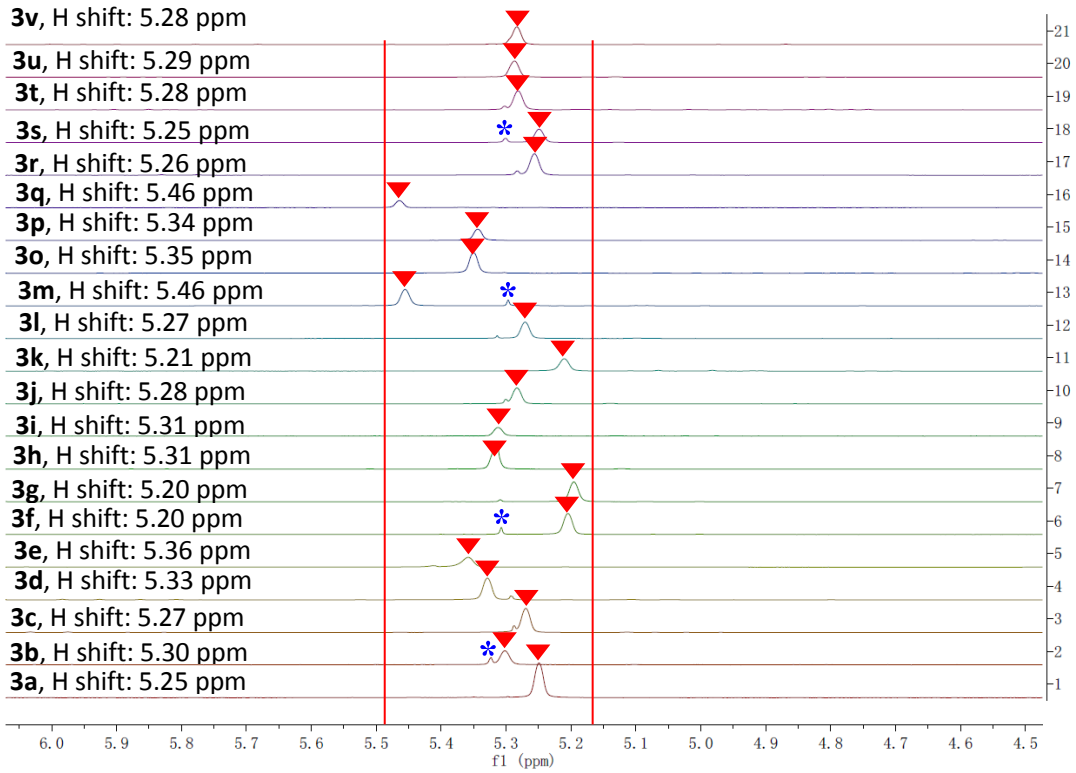


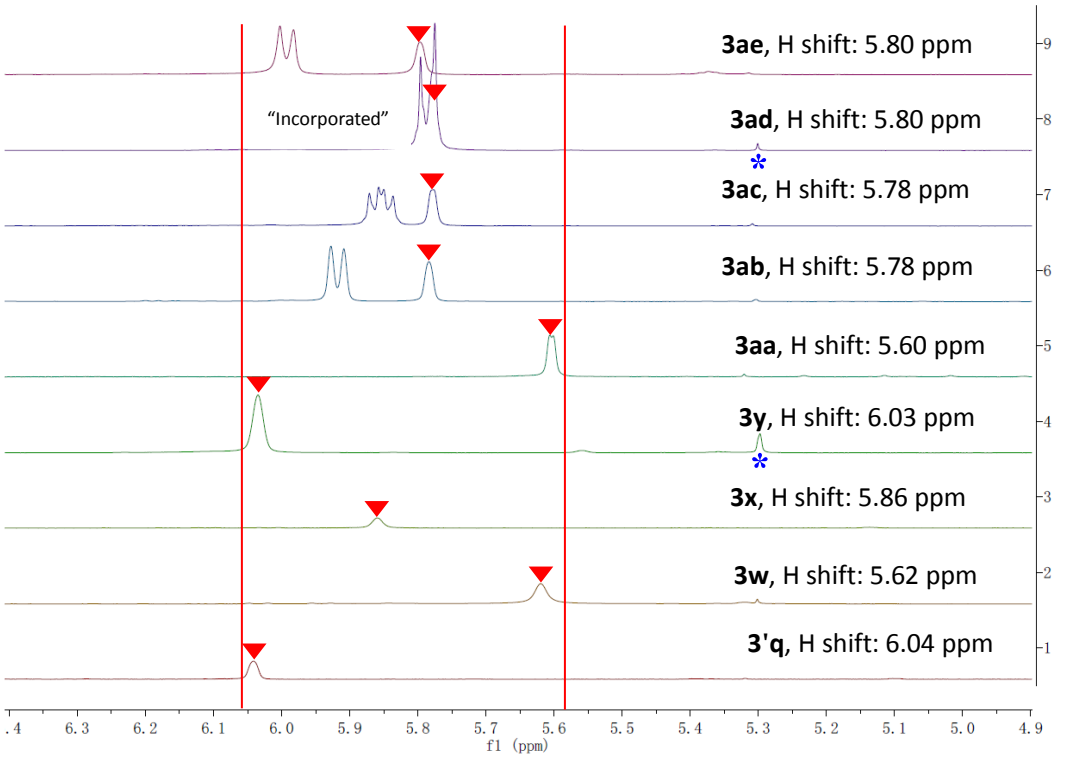
Figure S2: (a) 1,10-phenanthroline (0.02 mmol) and K_2CO_3 (0.25 mmol) with DMPO in 1,4-dioxane (1 mL) at 110℃ for 0.5 h, the black line; (b) **1a** (0.1 mmol), 1,10-phenanthroline (0.02 mmol) and K_2CO_3 (0.25 mmol) with DMPO in 1,4-dioxane (1 mL) at 110℃ for 0.5 h, the blue line; (c) **2a** (0.1 mmol), 1,10-Phenanthroline (0.02 mmol) and K_2CO_3 (0.25 mmol) with DMPO in 1,4-dioxane (1 mL) at 110℃ for 0.5 h, the pink line; (d) **1a** (0.3 mmol), **2a** (0.1 mmol), 1,10-phenanthroline (0.02 mmol) and K_2CO_3 (0.25 mmol) with DMPO in 1,4-dioxane (1 mL) at 110℃ for 0.5 h, the orange line.

5.5 Alkenyl-H Chemical Shifts of All Atropisomers

Products in Table 2 (5.20-5.46 ppm)

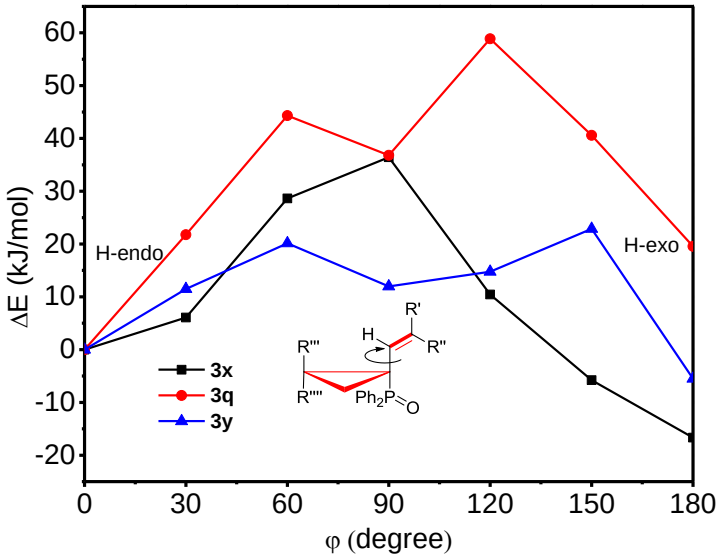


Products in Table 3 (5.60-6.04 ppm)



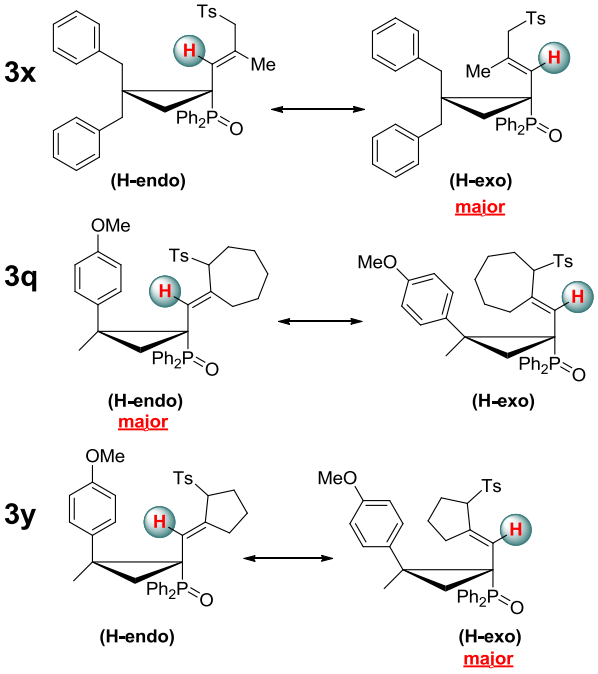
▼: Alkenyl-H; ✲: trace CH_2Cl_2

5.6 DFT Calculations of Torsion Energy profile Associated with Dihedral Angle for Compounds 3x, 3q and 3y



The geometries of complexes were fully optimized at the HF/6-311G level after which torsional potentials for each molecule were calculated at B3LYP/6-311G level.

Dihedral Angle *（KJ/mol）*	*30 º*	*60 º*	*90 º*	*120 º*	*150 º*	*180 º*
3x (endo→exo)	6.0649	28.6442	36.4419	10.4495	-5.7761	-16.6749
3q (endo→exo)	21.7658	44.3130	36.8083	58.8690	40.5882	19.5542
3y (endo→exo)	11.4849	20.1451	11.9734	14.7504	22.8731	-5.4982



6. X-Ray Crystallography Data

6.1 X-Ray Crystallography Data of 3h

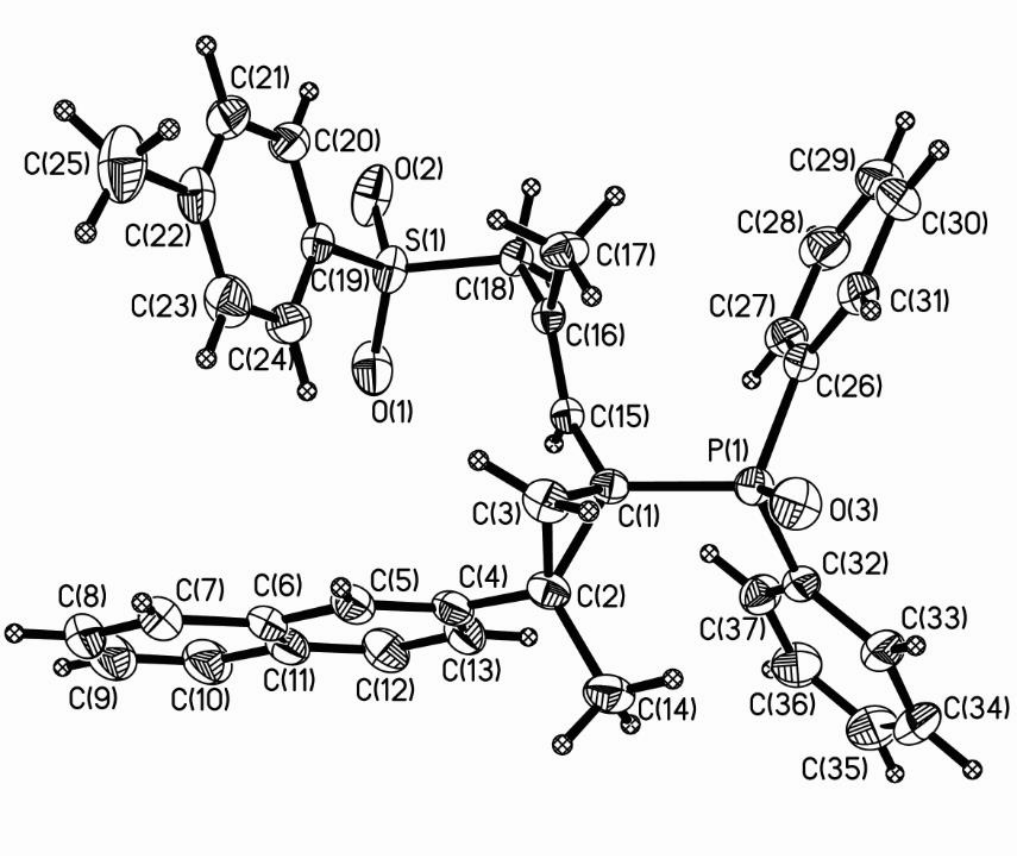


Table S1. Crystal data and structure refinement for 3h.

Identification code	3h	
Empirical formula	C37 H35 O3 P S	
Formula weight	590.68	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.3705(6) Å	α= 90°.
	b = 13.8788(8) Å	β= 106.7020(10)°.
	c = 19.1238(10) Å	γ = 90°.
Volume	3144.8(3) $Å^3$	
Z	4	
Density (calculated)	1.248 Mg/m^3	
Absorption coefficient	0.189 mm^{-1}	
F(000)	1248	
Crystal size	0.350 x 0.320 x 0.280 mm^3	

Theta range for data collection	2.260 to 27.509°.
Index ranges	-15<=h<=16, -17<=k<=18, -24<=l<=24
Reflections collected	30918
Independent reflections	7092 [R(int) = 0.0423]
Completeness to theta = 25.242°	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.955 and 0.930
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7092 / 0 / 370
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0464, wR2 = 0.1122
R indices (all data)	R1 = 0.0729, wR2 = 0.1237
Extinction coefficient	n/a
Largest diff. peak and hole	0.238 and -0.321 e.Å^{-3}

Table S2. Bond lengths [Å] and angles [°] for 3h.

C(1)-C(15)	1.491(2)
C(1)-C(3)	1.527(2)
C(1)-C(2)	1.547(2)
C(1)-P(1)	1.8243(17)
C(2)-C(3)	1.495(3)
C(2)-C(4)	1.501(3)
C(2)-C(14)	1.516(3)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.364(3)
C(4)-C(13)	1.408(3)
C(5)-C(6)	1.413(3)
C(5)-H(5)	0.9300
C(6)-C(11)	1.413(3)
C(6)-C(7)	1.420(3)
C(7)-C(8)	1.361(4)
C(7)-H(7)	0.9300
C(8)-C(9)	1.387(5)
C(8)-H(8)	0.9300
C(9)-C(10)	1.354(4)
C(9)-H(9)	0.9300

C(10)-C(11)	1.423(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.405(3)
C(12)-C(13)	1.364(3)
C(12)-H(12)	0.9300
C(13)-H(13)	0.9300
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(16)	1.326(2)
C(15)-H(15)	0.9300
C(16)-C(17)	1.504(2)
C(16)-C(18)	1.509(2)
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-S(1)	1.7733(17)
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(19)-C(24)	1.375(3)
C(19)-C(20)	1.376(3)
C(19)-S(1)	1.7564(17)
C(20)-C(21)	1.378(3)
C(20)-H(20)	0.9300
C(21)-C(22)	1.361(3)
C(21)-H(21)	0.9300
C(22)-C(23)	1.374(3)
C(22)-C(25)	1.507(3)
C(23)-C(24)	1.380(3)
C(23)-H(23)	0.9300
C(24)-H(24)	0.9300
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(26)-C(27)	1.3900
C(26)-C(31)	1.3900
C(26)-P(1)	1.8143(10)
C(27)-C(28)	1.3900

C(27)-H(27)	0.9300
C(28)-C(29)	1.3900
C(28)-H(28)	0.9300
C(29)-C(30)	1.3900
C(29)-H(29)	0.9300
C(30)-C(31)	1.3900
C(30)-H(30)	0.9300
C(31)-H(31)	0.9300
C(32)-C(37)	1.384(3)
C(32)-C(33)	1.389(3)
C(32)-P(1)	1.8054(19)
C(33)-C(34)	1.377(3)
C(33)-H(33)	0.9300
C(34)-C(35)	1.371(4)
C(34)-H(34)	0.9300
C(35)-C(36)	1.366(4)
C(35)-H(35)	0.9300
C(36)-C(37)	1.378(3)
C(36)-H(36)	0.9300
C(37)-H(37)	0.9300
O(1)-S(1)	1.4333(16)
O(2)-S(1)	1.4346(16)
O(3)-P(1)	1.4783(13)

C(15)-C(1)-C(3)	118.69(15)
C(15)-C(1)-C(2)	119.08(14)
C(3)-C(1)-C(2)	58.19(11)
C(15)-C(1)-P(1)	116.28(11)
C(3)-C(1)-P(1)	113.86(12)
C(2)-C(1)-P(1)	117.99(12)
C(3)-C(2)-C(4)	118.32(16)
C(3)-C(2)-C(14)	118.37(16)
C(4)-C(2)-C(14)	113.08(15)
C(3)-C(2)-C(1)	60.23(11)
C(4)-C(2)-C(1)	116.76(15)
C(14)-C(2)-C(1)	120.50(16)
C(2)-C(3)-C(1)	61.58(11)

C(2)-C(3)-H(3A)	117.6
C(1)-C(3)-H(3A)	117.6
C(2)-C(3)-H(3B)	117.6
C(1)-C(3)-H(3B)	117.6
H(3A)-C(3)-H(3B)	114.7
C(5)-C(4)-C(13)	118.44(19)
C(5)-C(4)-C(2)	121.44(18)
C(13)-C(4)-C(2)	120.06(17)
C(4)-C(5)-C(6)	122.0(2)
C(4)-C(5)-H(5)	119.0
C(6)-C(5)-H(5)	119.0
C(11)-C(6)-C(5)	118.8(2)
C(11)-C(6)-C(7)	118.7(2)
C(5)-C(6)-C(7)	122.5(2)
C(8)-C(7)-C(6)	120.6(3)
C(8)-C(7)-H(7)	119.7
C(6)-C(7)-H(7)	119.7
C(7)-C(8)-C(9)	120.6(3)
C(7)-C(8)-H(8)	119.7
C(9)-C(8)-H(8)	119.7
C(10)-C(9)-C(8)	120.9(3)
C(10)-C(9)-H(9)	119.6
C(8)-C(9)-H(9)	119.6
C(9)-C(10)-C(11)	120.7(3)
C(9)-C(10)-H(10)	119.6
C(11)-C(10)-H(10)	119.6
C(12)-C(11)-C(6)	118.6(2)
C(12)-C(11)-C(10)	122.9(3)
C(6)-C(11)-C(10)	118.5(2)
C(13)-C(12)-C(11)	121.0(2)
C(13)-C(12)-H(12)	119.5
C(11)-C(12)-H(12)	119.5
C(12)-C(13)-C(4)	121.2(2)
C(12)-C(13)-H(13)	119.4
C(4)-C(13)-H(13)	119.4
C(2)-C(14)-H(14A)	109.5
C(2)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5

C(2)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-C(1)	124.99(15)
C(16)-C(15)-H(15)	117.5
C(1)-C(15)-H(15)	117.5
C(15)-C(16)-C(17)	124.50(15)
C(15)-C(16)-C(18)	120.17(14)
C(17)-C(16)-C(18)	115.25(14)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-S(1)	114.75(12)
C(16)-C(18)-H(18A)	108.6
S(1)-C(18)-H(18A)	108.6
C(16)-C(18)-H(18B)	108.6
S(1)-C(18)-H(18B)	108.6
H(18A)-C(18)-H(18B)	107.6
C(24)-C(19)-C(20)	120.57(17)
C(24)-C(19)-S(1)	119.75(14)
C(20)-C(19)-S(1)	119.66(15)
C(19)-C(20)-C(21)	118.88(19)
C(19)-C(20)-H(20)	120.6
C(21)-C(20)-H(20)	120.6
C(22)-C(21)-C(20)	121.78(19)
C(22)-C(21)-H(21)	119.1
C(20)-C(21)-H(21)	119.1
C(21)-C(22)-C(23)	118.49(19)
C(21)-C(22)-C(25)	120.1(2)
C(23)-C(22)-C(25)	121.4(2)
C(22)-C(23)-C(24)	121.3(2)
C(22)-C(23)-H(23)	119.3
C(24)-C(23)-H(23)	119.3
C(19)-C(24)-C(23)	118.94(19)
C(19)-C(24)-H(24)	120.5

C(23)-C(24)-H(24)	120.5
C(22)-C(25)-H(25A)	109.5
C(22)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(22)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(27)-C(26)-C(31)	120.0
C(27)-C(26)-P(1)	123.43(7)
C(31)-C(26)-P(1)	116.55(7)
C(26)-C(27)-C(28)	120.0
C(26)-C(27)-H(27)	120.0
C(28)-C(27)-H(27)	120.0
C(27)-C(28)-C(29)	120.0
C(27)-C(28)-H(28)	120.0
C(29)-C(28)-H(28)	120.0
C(30)-C(29)-C(28)	120.0
C(30)-C(29)-H(29)	120.0
C(28)-C(29)-H(29)	120.0
C(31)-C(30)-C(29)	120.0
C(31)-C(30)-H(30)	120.0
C(29)-C(30)-H(30)	120.0
C(30)-C(31)-C(26)	120.0
C(30)-C(31)-H(31)	120.0
C(26)-C(31)-H(31)	120.0
C(37)-C(32)-C(33)	118.96(19)
C(37)-C(32)-P(1)	123.06(14)
C(33)-C(32)-P(1)	117.96(15)
C(34)-C(33)-C(32)	120.1(2)
C(34)-C(33)-H(33)	120.0
C(32)-C(33)-H(33)	120.0
C(35)-C(34)-C(33)	120.1(2)
C(35)-C(34)-H(34)	120.0
C(33)-C(34)-H(34)	120.0
C(36)-C(35)-C(34)	120.5(2)
C(36)-C(35)-H(35)	119.8
C(34)-C(35)-H(35)	119.8
C(35)-C(36)-C(37)	119.9(2)

C(35)-C(36)-H(36)	120.0
C(37)-C(36)-H(36)	120.0
C(36)-C(37)-C(32)	120.4(2)
C(36)-C(37)-H(37)	119.8
C(32)-C(37)-H(37)	119.8
O(3)-P(1)-C(32)	111.76(9)
O(3)-P(1)-C(26)	110.27(7)
C(32)-P(1)-C(26)	105.90(7)
O(3)-P(1)-C(1)	112.94(8)
C(32)-P(1)-C(1)	107.38(8)
C(26)-P(1)-C(1)	108.27(7)
O(1)-S(1)-O(2)	118.50(10)
O(1)-S(1)-C(19)	107.87(9)
O(2)-S(1)-C(19)	108.24(9)
O(1)-S(1)-C(18)	109.05(9)
O(2)-S(1)-C(18)	107.02(9)
C(19)-S(1)-C(18)	105.43(8)

Symmetry transformations used to generate equivalent atoms:

Table S3. Hydrogen bonds for 3h [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(3)-H(3A)...O(3)	0.97	2.54	3.018(2)	110
C(18)-H(18A)...O(1)#1	0.97	2.42	3.350(2)	161
C(18)-H(18B)...O(3)#2	0.97	2.33	3.242(2)	157
C(37)-H(37)...O(2)#1	0.93	2.42	3.195(2)	141

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,y+1/2,-z+3/2

6.2 X-Ray Crystallography Data of 3x

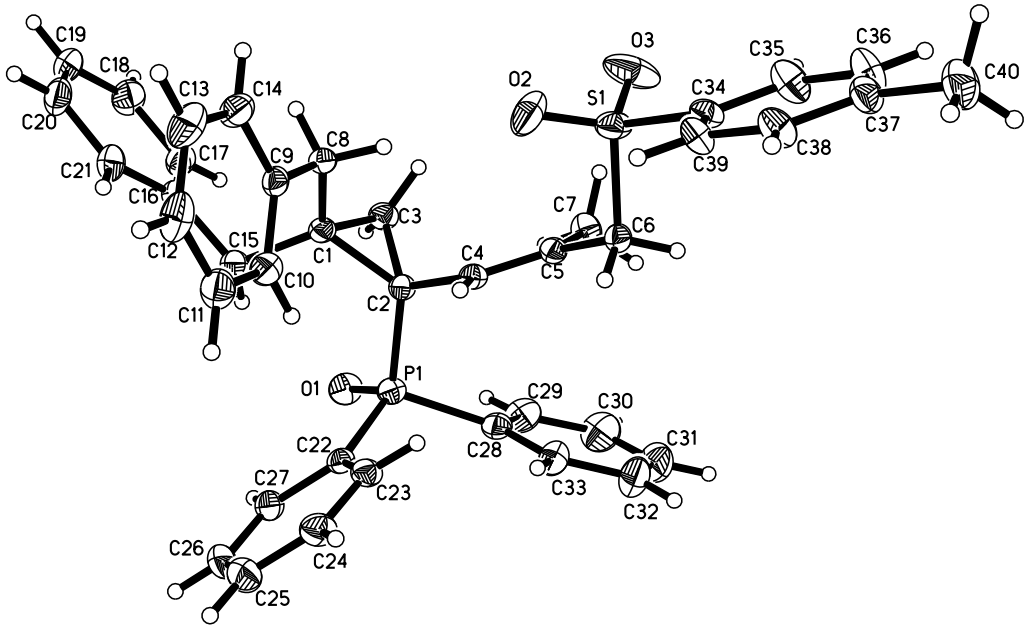


Table S4. Crystal data and structure refinement for 3x.

Identification code	3x	
Empirical formula	C40 H39 O3 P S	
Formula weight	630.74	
Temperature	296(2) K	
Wavelength	0.71073 ?	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 10.9576(5) ?	a= 90?
	b = 24.0001(11) ?	b= 94.036(2)?
	c = 13.0509(6) ?	g = 90?
Volume	3423.7(3) ?3	
Z	4	
Density (calculated)	1.224 Mg/m3	
Absorption coefficient	0.178 mm-1	
F(000)	1336	
Crystal size	0.100 x 0.080 x 0.030 mm3	
Theta range for data collection	2.521 to 27.526?	
Index ranges	-13<=h<=14, -31<=k<=30, -15<=l<=16	
Reflections collected	39323	
Independent reflections	7858 [R(int) = 0.0424]	
Completeness to theta = 25.242?	99.7 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7456 and 0.6804
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	7858 / 0 / 408
Goodness-of-fit on F2	1.018
Final R indices [I>2sigma(I)]	R1 = 0.0501, wR2 = 0.1136
R indices (all data)	R1 = 0.0969, wR2 = 0.1315
Extinction coefficient	n/a
Largest diff. peak and hole	0.194 and -0.283 e.?-3

Table S5. Bond lengths [Å] and angles [°] for 3x.

C(1)-C(3)	1.494(3)
C(1)-C(8)	1.523(2)
C(1)-C(15)	1.527(3)
C(1)-C(2)	1.549(2)
C(2)-C(4)	1.498(2)
C(2)-C(3)	1.522(2)
C(2)-P(1)	1.8212(17)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.327(2)
C(4)-H(4)	0.9300
C(5)-C(7)	1.499(3)
C(5)-C(6)	1.505(2)
C(6)-S(1)	1.7780(18)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-C(9)	1.503(3)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.376(3)
C(9)-C(14)	1.382(3)
C(10)-C(11)	1.380(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.367(3)

C(11)-H(11)	0.9300
C(12)-C(13)	1.365(4)
C(12)-H(12)	0.9300
C(13)-C(14)	1.377(3)
C(13)-H(13)	0.9300
C(14)-H(14)	0.9300
C(15)-C(16)	1.509(3)
C(16)-C(17)	1.376(3)
C(16)-C(21)	1.386(3)
C(17)-C(18)	1.393(3)
C(17)-H(17)	0.9300
C(18)-C(19)	1.374(3)
C(18)-H(18)	0.9300
C(19)-C(20)	1.354(3)
C(19)-H(19)	0.9300
C(20)-C(21)	1.379(3)
C(20)-H(20)	0.9300
C(21)-H(21)	0.9300
C(22)-C(27)	1.396(3)
C(22)-C(23)	1.398(2)
C(22)-P(1)	1.8000(19)
C(23)-C(24)	1.371(3)
C(23)-H(23)	0.9300
C(24)-C(25)	1.378(3)
C(24)-H(24)	0.9300
C(25)-C(26)	1.368(3)
C(25)-H(25)	0.9300
C(26)-C(27)	1.374(3)
C(26)-H(26)	0.9300
C(27)-H(27)	0.9300
C(28)-C(29)	1.378(3)
C(28)-C(33)	1.383(3)
C(28)-P(1)	1.812(2)
C(29)-C(30)	1.388(4)
C(29)-H(29)	0.9300
C(30)-C(31)	1.365(4)
C(30)-H(30)	0.9300
C(31)-C(32)	1.366(4)

C(31)-H(31)	0.9300
C(32)-C(33)	1.376(3)
C(32)-H(32)	0.9300
(33)-H(33)	0.9300
C(34)-C(39)	1.374(3)
C(34)-C(35)	1.378(3)
C(34)-S(1)	1.761(2)
C(35)-C(36)	1.370(3)
C(35)-H(35)	0.9300
C(36)-C(37)	1.375(3)
C(36)-H(36)	0.9300
C(37)-C(38)	1.375(3)
C(37)-C(40)	1.503(3)
C(38)-C(39)	1.373(3)
C(38)-H(38)	0.9300
C(39)-H(39)	0.9300
C(40)-H(40A)	0.9600
C(40)-H(40B)	0.9600
C(40)-H(40C)	0.9600
O(1)-P(1)	1.4839(13)
O(2)-S(1)	1.4359(18)
O(3)-S(1)	1.4176(18)

C(3)-C(1)-C(8)	115.12(15)
C(3)-C(1)-C(15)	117.80(16)
C(8)-C(1)-C(15)	115.25(16)
C(3)-C(1)-C(2)	60.00(12)
C(8)-C(1)-C(2)	116.90(15)
C(15)-C(1)-C(2)	120.44(15)
C(4)-C(2)-C(3)	118.96(15)
C(4)-C(2)-C(1)	116.75(14)
C(3)-C(2)-C(1)	58.21(11)
C(4)-C(2)-P(1)	115.94(12)
C(3)-C(2)-P(1)	114.75(12)
C(1)-C(2)-P(1)	119.92(12)
C(1)-C(3)-C(2)	61.79(12)
C(1)-C(3)-H(3A)	117.6
C(2)-C(3)-H(3A)	117.6

C(1)-C(3)-H(3B)	117.6
C(2)-C(3)-H(3B)	117.6
H(3A)-C(3)-H(3B)	114.7
C(5)-C(4)-C(2)	127.55(16)
C(5)-C(4)-H(4)	116.2
C(2)-C(4)-H(4)	116.2
C(4)-C(5)-C(7)	125.94(17)
C(4)-C(5)-C(6)	118.22(16)
C(7)-C(5)-C(6)	115.83(16)
C(5)-C(6)-S(1)	110.19(13)
C(5)-C(6)-H(6A)	109.6
S(1)-C(6)-H(6A)	109.6
C(5)-C(6)-H(6B)	109.6
S(1)-C(6)-H(6B)	109.6
H(6A)-C(6)-H(6B)	108.1
C(5)-C(7)-H(7A)	109.5
C(5)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(5)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-C(1)	117.38(15)
C(9)-C(8)-H(8A)	108.0
C(1)-C(8)-H(8A)	108.0
C(9)-C(8)-H(8B)	108.0
C(1)-C(8)-H(8B)	108.0
H(8A)-C(8)-H(8B)	107.2
C(10)-C(9)-C(14)	117.29(19)
C(10)-C(9)-C(8)	123.28(17)
C(14)-C(9)-C(8)	119.43(18)
C(9)-C(10)-C(11)	121.4(2)
C(9)-C(10)-H(10)	119.3
C(11)-C(10)-H(10)	119.3
C(12)-C(11)-C(10)	120.3(2)
C(12)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9
C(13)-C(12)-C(11)	119.3(2)
C(13)-C(12)-H(12)	120.3

C(11)-C(12)-H(12)	120.3
C(12)-C(13)-C(14)	120.3(2)
C(12)-C(13)-H(13)	119.9
C(14)-C(13)-H(13)	119.9
C(13)-C(14)-C(9)	121.4(2)
C(13)-C(14)-H(14)	119.3
C(9)-C(14)-H(14)	119.3
C(16)-C(15)-C(1)	112.30(15)
C(16)-C(15)-H(15A)	109.1
C(1)-C(15)-H(15A)	109.1
C(16)-C(15)-H(15B)	109.1
C(1)-C(15)-H(15B)	109.1
H(15A)-C(15)-H(15B)	107.9
C(17)-C(16)-C(21)	117.65(19)
C(17)-C(16)-C(15)	121.44(18)
C(21)-C(16)-C(15)	120.90(19)
C(16)-C(17)-C(18)	120.6(2)
C(16)-C(17)-H(17)	119.7
C(18)-C(17)-H(17)	119.7
C(19)-C(18)-C(17)	120.1(2)
C(19)-C(18)-H(18)	119.9
C(17)-C(18)-H(18)	119.9
C(20)-C(19)-C(18)	119.9(2)
C(20)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0
C(19)-C(20)-C(21)	120.0(2)
C(19)-C(20)-H(20)	120.0
C(21)-C(20)-H(20)	120.0
C(20)-C(21)-C(16)	121.7(2)
C(20)-C(21)-H(21)	119.2
C(16)-C(21)-H(21)	119.2
C(27)-C(22)-C(23)	118.27(18)
C(27)-C(22)-P(1)	117.19(15)
C(23)-C(22)-P(1)	124.50(14)
C(24)-C(23)-C(22)	120.11(18)
C(24)-C(23)-H(23)	119.9
C(22)-C(23)-H(23)	119.9
C(23)-C(24)-C(25)	120.7(2)

C(23)-C(24)-H(24)	119.6
C(25)-C(24)-H(24)	119.6
C(26)-C(25)-C(24)	119.9(2)
C(26)-C(25)-H(25)	120.1
C(24)-C(25)-H(25)	120.1
C(25)-C(26)-C(27)	120.3(2)
C(25)-C(26)-H(26)	119.8
C(27)-C(26)-H(26)	119.8
C(26)-C(27)-C(22)	120.7(2)
C(26)-C(27)-H(27)	119.7
C(22)-C(27)-H(27)	119.7
C(29)-C(28)-C(33)	118.3(2)
C(29)-C(28)-P(1)	115.89(17)
C(33)-C(28)-P(1)	125.68(16)
C(28)-C(29)-C(30)	120.7(3)
C(28)-C(29)-H(29)	119.7
C(30)-C(29)-H(29)	119.7
C(31)-C(30)-C(29)	120.1(3)
C(31)-C(30)-H(30)	120.0
C(29)-C(30)-H(30)	120.0
C(30)-C(31)-C(32)	119.8(3)
C(30)-C(31)-H(31)	120.1
C(32)-C(31)-H(31)	120.1
C(31)-C(32)-C(33)	120.5(3)
C(31)-C(32)-H(32)	119.7
C(33)-C(32)-H(32)	119.7
C(32)-C(33)-C(28)	120.6(2)
C(32)-C(33)-H(33)	119.7
C(28)-C(33)-H(33)	119.7
C(39)-C(34)-C(35)	119.70(19)
C(39)-C(34)-S(1)	120.30(16)
C(35)-C(34)-S(1)	120.00(16)
C(36)-C(35)-C(34)	119.2(2)
C(36)-C(35)-H(35)	120.4
C(34)-C(35)-H(35)	120.4
C(35)-C(36)-C(37)	122.2(2)
C(35)-C(36)-H(36)	118.9
C(37)-C(36)-H(36)	118.9

C(36)-C(37)-C(38)	117.7(2)
C(36)-C(37)-C(40)	120.9(2)
C(38)-C(37)-C(40)	121.5(2)
C(39)-C(38)-C(37)	121.26(19)
C(39)-C(38)-H(38)	119.4
C(37)-C(38)-H(38)	119.4
C(38)-C(39)-C(34)	120.01(19)
C(38)-C(39)-H(39)	120.0
C(34)-C(39)-H(39)	120.0
C(37)-C(40)-H(40A)	109.5
C(37)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(37)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
O(1)-P(1)-C(22)	111.32(8)
O(1)-P(1)-C(28)	110.23(9)
C(22)-P(1)-C(28)	109.10(9)
O(1)-P(1)-C(2)	113.50(8)
C(22)-P(1)-C(2)	107.00(8)
C(28)-P(1)-C(2)	105.43(8)
O(3)-S(1)-O(2)	119.42(14)
O(3)-S(1)-C(34)	108.07(11)
O(2)-S(1)-C(34)	108.54(10)
O(3)-S(1)-C(6)	107.72(11)
O(2)-S(1)-C(6)	107.39(10)
C(34)-S(1)-C(6)	104.76(9)

Symmetry transformations used to generate equivalent atoms:

6.3 X-Ray Crystallography Data of 3aa

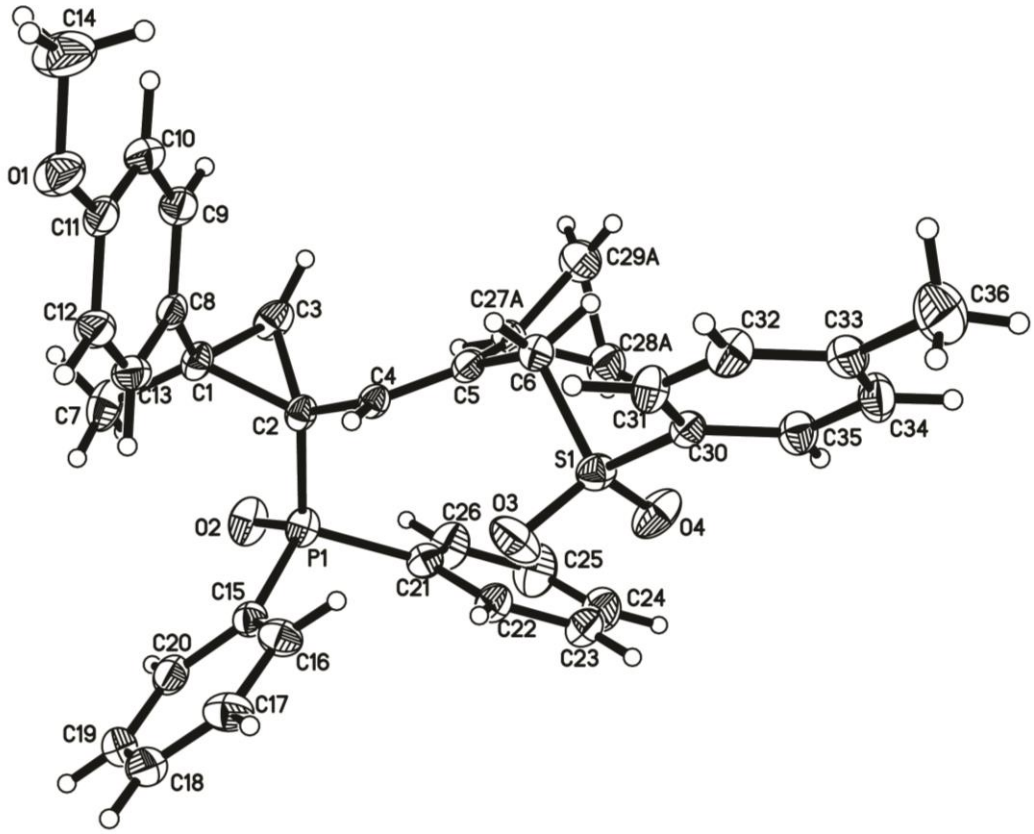


Table S6. Crystal data and structure refinement for 3aa.

Identification code	3aa	
Empirical formula	C36 H37 O4 P S	
Formula weight	596.68	
Temperature	296(2) K	
Wavelength	0.71073 ?	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 8.7333(10) ?	a= 90?
	b = 32.515(5) ?	b= 92.555(4)?
	c = 11.3552(17) ?	g = 90?
Volume	3221.2(8) ?3	
Z	4	
Density (calculated)	1.230 Mg/m3	
Absorption coefficient	0.187 mm-1	
F(000)	1264	
Crystal size	0.080 x 0.060 x 0.020 mm3	
Theta range for data collection	2.334 to 27.594?	
Index ranges	-10<=h<=11, -42<=k<=30, -14<=l<=14	

Reflections collected	32918
Independent reflections	7225 [R(int) = 0.0522]
Completeness to theta = 25.242?	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6984
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	7225 / 90 / 409
Goodness-of-fit on F2	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0566, wR2 = 0.1176
R indices (all data)	R1 = 0.1292, wR2 = 0.1417
Extinction coefficient	n/a
Largest diff. peak and hole	0.286 and -0.270 e.?-3

Table S7. Bond lengths [Å] and angles [°] for 3aa.

C(1)-C(3)	1.486(3)
C(1)-C(8)	1.500(3)
C(1)-C(7)	1.529(3)
C(1)-C(2)	1.559(3)
C(2)-C(4)	1.499(3)
C(2)-C(3)	1.524(3)
C(2)-P(1)	1.815(2)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.324(3)
C(4)-H(4)	0.9300
C(5)-C(27A)	1.46(3)
C(5)-C(6)	1.514(3)
C(5)-C(27B)	1.52(4)
C(6)-S(1)	1.779(2)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-C(9)	1.371(3)
C(8)-C(13)	1.391(3)
C(9)-C(10)	1.390(3)
C(9)-H(9)	0.9300

C(10)-C(11)	1.369(3)
C(10)-H(10)	0.9300
C(11)-O(1)	1.371(3)
C(11)-C(12)	1.380(3)
C(12)-C(13)	1.361(3)
C(12)-H(12)	0.9300
C(13)-H(13)	0.9300
C(14)-O(1)	1.401(3)
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(20)	1.395(3)
C(15)-C(16)	1.398(3)
C(15)-P(1)	1.807(2)
C(16)-C(17)	1.385(3)
C(16)-H(16)	0.9300
C(17)-C(18)	1.364(4)
C(17)-H(17)	0.9300
C(18)-C(19)	1.366(4)
C(18)-H(18)	0.9300
C(19)-C(20)	1.387(4)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300
C(21)-C(22)	1.381(3)
C(21)-C(26)	1.387(3)
C(21)-P(1)	1.805(2)
C(22)-C(23)	1.394(4)
C(22)-H(22)	0.9300
C(23)-C(24)	1.367(4)
C(23)-H(23)	0.9300
C(24)-C(25)	1.358(5)
C(24)-H(24)	0.9300
C(25)-C(26)	1.378(4)
C(25)-H(25)	0.9300
C(26)-H(26)	0.9300
C(27A)-C(28A)	1.48(3)
C(27A)-C(29A)	1.51(2)
C(27A)-H(27A)	0.9800

C(28A)-C(29A)	1.483(8)
C(28A)-H(28A)	0.9700
C(28A)-H(28B)	0.9700
C(29A)-H(29A)	0.9700
C(29A)-H(29B)	0.9700
C(27B)-C(29B)	1.46(3)
C(27B)-C(28B)	1.53(4)
C(27B)-H(27B)	0.9800
C(28B)-C(29B)	1.451(14)
C(28B)-H(28C)	0.8557
C(28B)-H(28D)	0.8553
C(29B)-H(29C)	0.9700
C(29B)-H(29D)	0.9700
C(30)-C(35)	1.374(3)
C(30)-C(31)	1.384(3)
C(30)-S(1)	1.758(2)
C(31)-C(32)	1.376(3)
C(31)-H(31)	0.9300
C(32)-C(33)	1.376(3)
C(32)-H(32)	0.9300
C(33)-C(34)	1.369(4)
C(33)-C(36)	1.507(4)
C(34)-C(35)	1.377(3)
C(34)-H(34)	0.9300
C(35)-H(35)	0.9300
C(36)-H(36A)	0.9600
C(36)-H(36B)	0.9600
C(36)-H(36C)	0.9600
O(2)-P(1)	1.4766(17)
O(3)-S(1)	1.4293(18)
O(4)-S(1)	1.4338(18)

C(3)-C(1)-C(8)	121.5(2)
C(3)-C(1)-C(7)	117.8(2)
C(8)-C(1)-C(7)	111.2(2)
C(3)-C(1)-C(2)	59.99(15)
C(8)-C(1)-C(2)	116.54(18)
C(7)-C(1)-C(2)	121.3(2)

C(4)-C(2)-C(3)	116.6(2)
C(4)-C(2)-C(1)	115.88(18)
C(3)-C(2)-C(1)	57.61(15)
C(4)-C(2)-P(1)	117.55(15)
C(3)-C(2)-P(1)	118.60(16)
C(1)-C(2)-P(1)	116.87(16)
C(1)-C(3)-C(2)	62.40(15)
C(1)-C(3)-H(3A)	117.5
C(2)-C(3)-H(3A)	117.5
C(1)-C(3)-H(3B)	117.5
C(2)-C(3)-H(3B)	117.5
H(3A)-C(3)-H(3B)	114.6
C(5)-C(4)-C(2)	126.4(2)
C(5)-C(4)-H(4)	116.8
C(2)-C(4)-H(4)	116.8
C(4)-C(5)-C(27A)	122.0(11)
C(4)-C(5)-C(6)	119.0(2)
C(27A)-C(5)-C(6)	119.0(11)
C(4)-C(5)-C(27B)	124.8(16)
C(6)-C(5)-C(27B)	115.9(16)
C(5)-C(6)-S(1)	114.70(15)
C(5)-C(6)-H(6A)	108.6
S(1)-C(6)-H(6A)	108.6
C(5)-C(6)-H(6B)	108.6
S(1)-C(6)-H(6B)	108.6
H(6A)-C(6)-H(6B)	107.6
C(1)-C(7)-H(7A)	109.5
C(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-C(13)	117.1(2)
C(9)-C(8)-C(1)	123.8(2)
C(13)-C(8)-C(1)	119.0(2)
C(8)-C(9)-C(10)	122.1(2)
C(8)-C(9)-H(9)	118.9
C(10)-C(9)-H(9)	118.9

C(11)-C(10)-C(9)	119.4(2)
C(11)-C(10)-H(10)	120.3
C(9)-C(10)-H(10)	120.3
C(10)-C(11)-O(1)	125.0(2)
C(10)-C(11)-C(12)	119.2(2)
O(1)-C(11)-C(12)	115.8(2)
C(13)-C(12)-C(11)	120.8(2)
C(13)-C(12)-H(12)	119.6
C(11)-C(12)-H(12)	119.6
C(12)-C(13)-C(8)	121.4(2)
C(12)-C(13)-H(13)	119.3
C(8)-C(13)-H(13)	119.3
O(1)-C(14)-H(14A)	109.5
O(1)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
O(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(20)-C(15)-C(16)	117.6(2)
C(20)-C(15)-P(1)	117.4(2)
C(16)-C(15)-P(1)	124.99(18)
C(17)-C(16)-C(15)	121.0(2)
C(17)-C(16)-H(16)	119.5
C(15)-C(16)-H(16)	119.5
C(18)-C(17)-C(16)	120.2(3)
C(18)-C(17)-H(17)	119.9
C(16)-C(17)-H(17)	119.9
C(17)-C(18)-C(19)	120.2(3)
C(17)-C(18)-H(18)	119.9
C(19)-C(18)-H(18)	119.9
C(18)-C(19)-C(20)	120.5(3)
C(18)-C(19)-H(19)	119.7
C(20)-C(19)-H(19)	119.7
C(19)-C(20)-C(15)	120.5(3)
C(19)-C(20)-H(20)	119.7
C(15)-C(20)-H(20)	119.7
C(22)-C(21)-C(26)	118.2(2)
C(22)-C(21)-P(1)	125.71(19)

C(26)-C(21)-P(1)	116.0(2)
C(21)-C(22)-C(23)	120.5(3)
C(21)-C(22)-H(22)	119.7
C(23)-C(22)-H(22)	119.7
C(24)-C(23)-C(22)	119.8(3)
C(24)-C(23)-H(23)	120.1
C(22)-C(23)-H(23)	120.1
C(25)-C(24)-C(23)	120.3(3)
C(25)-C(24)-H(24)	119.8
C(23)-C(24)-H(24)	119.8
C(24)-C(25)-C(26)	120.4(3)
C(24)-C(25)-H(25)	119.8
C(26)-C(25)-H(25)	119.8
C(25)-C(26)-C(21)	120.7(3)
C(25)-C(26)-H(26)	119.6
C(21)-C(26)-H(26)	119.6
C(5)-C(27A)-C(28A)	127.5(19)
C(5)-C(27A)-C(29A)	127.8(18)
C(28A)-C(27A)-C(29A)	59.5(10)
C(5)-C(27A)-H(27A)	110.9
C(28A)-C(27A)-H(27A)	110.9
C(29A)-C(27A)-H(27A)	110.9
C(27A)-C(28A)-C(29A)	61.2(8)
C(27A)-C(28A)-H(28A)	117.7
C(29A)-C(28A)-H(28A)	117.7
C(27A)-C(28A)-H(28B)	117.6
C(29A)-C(28A)-H(28B)	117.7
H(28A)-C(28A)-H(28B)	114.8
C(28A)-C(29A)-C(27A)	59.3(10)
C(28A)-C(29A)-H(29A)	117.8
C(27A)-C(29A)-H(29A)	117.8
C(28A)-C(29A)-H(29B)	117.8
C(27A)-C(29A)-H(29B)	117.8
H(29A)-C(29A)-H(29B)	115.0
C(29B)-C(27B)-C(5)	114(3)
C(29B)-C(27B)-C(28B)	57.8(14)
C(5)-C(27B)-C(28B)	117(3)
C(29B)-C(27B)-H(27B)	118.2

C(5)-C(27B)-H(27B)	118.2
C(28B)-C(27B)-H(27B)	118.2
C(29B)-C(28B)-C(27B)	58.7(14)
C(29B)-C(28B)-H(28C)	119.8
C(27B)-C(28B)-H(28C)	111.5
C(29B)-C(28B)-H(28D)	117.8
C(27B)-C(28B)-H(28D)	119.6
H(28C)-C(28B)-H(28D)	116.6
C(28B)-C(29B)-C(27B)	63.5(17)
C(28B)-C(29B)-H(29C)	117.4
C(27B)-C(29B)-H(29C)	117.4
C(28B)-C(29B)-H(29D)	117.4
C(27B)-C(29B)-H(29D)	117.4
H(29C)-C(29B)-H(29D)	114.5
C(35)-C(30)-C(31)	119.9(2)
C(35)-C(30)-S(1)	119.47(17)
C(31)-C(30)-S(1)	120.68(18)
C(32)-C(31)-C(30)	119.5(2)
C(32)-C(31)-H(31)	120.2
C(30)-C(31)-H(31)	120.2
C(31)-C(32)-C(33)	121.3(2)
C(31)-C(32)-H(32)	119.3
C(33)-C(32)-H(32)	119.3
C(34)-C(33)-C(32)	118.1(2)
C(34)-C(33)-C(36)	122.1(3)
C(32)-C(33)-C(36)	119.8(3)
C(33)-C(34)-C(35)	122.0(2)
C(33)-C(34)-H(34)	119.0
C(35)-C(34)-H(34)	119.0
C(30)-C(35)-C(34)	119.2(2)
C(30)-C(35)-H(35)	120.4
C(34)-C(35)-H(35)	120.4
C(33)-C(36)-H(36A)	109.5
C(33)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(33)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5

C(11)-O(1)-C(14)	119.3(2)
O(2)-P(1)-C(21)	108.76(10)
O(2)-P(1)-C(15)	111.70(11)
C(21)-P(1)-C(15)	108.86(11)
O(2)-P(1)-C(2)	113.42(11)
C(21)-P(1)-C(2)	110.24(10)
C(15)-P(1)-C(2)	103.73(10)
O(3)-S(1)-O(4)	117.91(13)
O(3)-S(1)-C(30)	109.27(10)
O(4)-S(1)-C(30)	107.71(11)
O(3)-S(1)-C(6)	108.15(12)
O(4)-S(1)-C(6)	109.71(12)
C(30)-S(1)-C(6)	103.09(10)

Symmetry transformations used to generate equivalent atoms:

6.4 X-Ray Crystallography Data of 3ae

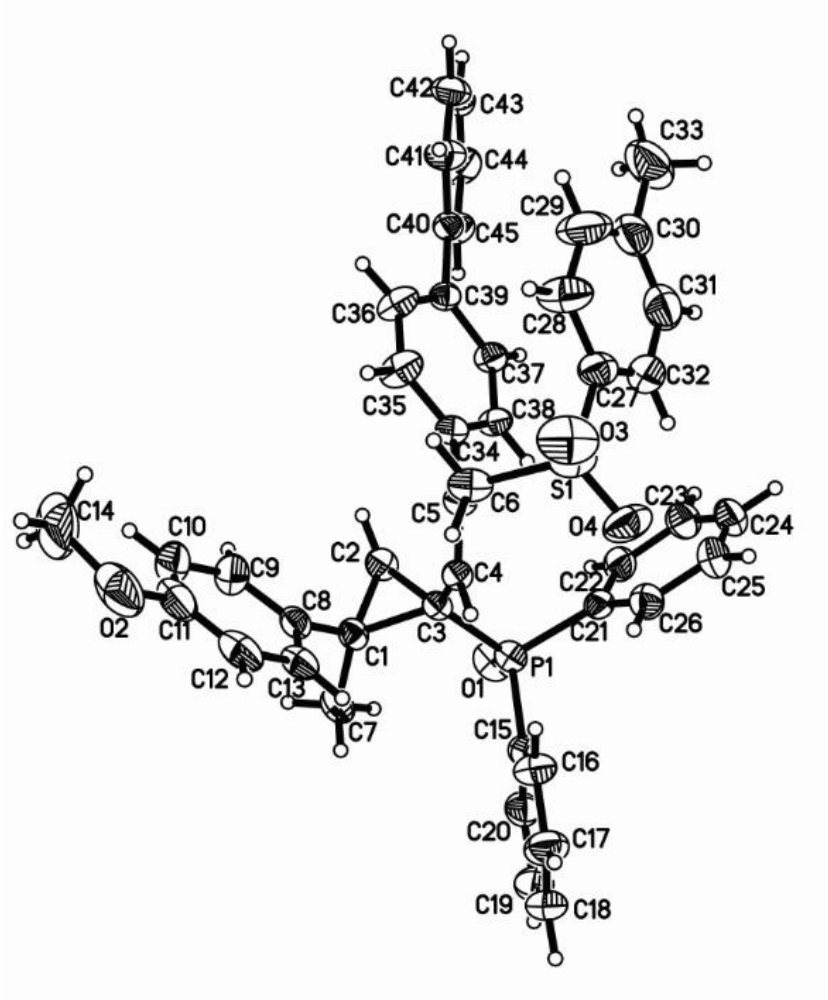


Table S8. Crystal data and structure refinement for 3ae.

Identification code	3ae	
Empirical formula	C45 H41 O4 P S	
Formula weight	708.81	
Temperature	296(2) K	
Wavelength	0.71073 ?	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.2440(3) ?	a= 85.2160(10)?
	b = 13.1272(5) ?	b= 77.3190(10)?
	c = 15.4443(5) ?	g = 69.9810(10)?
Volume	1903.71(11) ?3	
Z	2	
Density (calculated)	1.237 Mg/m3	
Absorption coefficient	0.170 mm-1	
F(000)	748	
Crystal size	0.250 x 0.220 x 0.180 mm3	
Theta range for data collection	2.143 to 27.518?	
Index ranges	-13<=h<=13, -17<=k<=17, -19<=l<=20	
Reflections collected	29840	
Independent reflections	8679 [R(int) = 0.0343]	
Completeness to theta = 25.242?	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.6811	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	8679 / 0 / 463	
Goodness-of-fit on F2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0539, wR2 = 0.1232	
R indices (all data)	R1 = 0.0945, wR2 = 0.1402	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.179 and -0.271 e.?-3	

Table S9. Bond lengths [Å] and angles [°] for 3ae.

C(1)-C(2)	1.497(2)
C(1)-C(8)	1.501(3)
C(1)-C(7)	1.521(3)
C(1)-C(3)	1.557(2)

C(2)-C(3)	1.521(2)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.487(2)
C(3)-P(1)	1.8190(18)
C(4)-C(5)	1.331(2)
C(4)-H(4)	0.9300
C(5)-C(34)	1.489(2)
C(5)-C(6)	1.512(2)
C(6)-S(1)	1.781(2)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-C(9)	1.380(3)
C(8)-C(13)	1.385(3)
C(9)-C(10)	1.389(4)
C(9)-H(9)	0.9300
C(10)-C(11)	1.359(4)
C(10)-H(10)	0.9300
C(11)-C(12)	1.357(4)
C(11)-O(2)	1.386(3)
C(12)-C(13)	1.385(3)
C(12)-H(12)	0.9300
C(13)-H(13)	0.9300
C(14)-O(2)	1.438(5)
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(16)	1.386(3)
C(15)-P(1)	1.804(2)
C(16)-C(17)	1.381(3)
C(16)-H(16)	0.9300
C(17)-C(18)	1.365(4)
C(17)-H(17)	0.9300
C(18)-C(19)	1.369(4)
C(18)-H(18)	0.9300

C(19)-C(20)	1.370(3)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300
C(21)-C(26)	1.380(3)
C(21)-C(22)	1.390(3)
C(21)-P(1)	1.8123(19)
C(22)-C(23)	1.380(3)
C(22)-H(22)	0.9300
C(23)-C(24)	1.361(4)
C(23)-H(23)	0.9300
C(24)-C(25)	1.365(3)
C(24)-H(24)	0.9300
C(25)-C(26)	1.380(3)
C(25)-H(25)	0.9300
C(26)-H(26)	0.9300
C(27)-C(32)	1.364(3)
C(27)-C(28)	1.372(3)
C(27)-S(1)	1.759(2)
C(28)-C(29)	1.383(4)
C(28)-H(28)	0.9300
C(29)-C(30)	1.362(4)
C(29)-H(29)	0.9300
C(30)-C(31)	1.351(4)
C(30)-C(33)	1.512(4)
C(31)-C(32)	1.383(4)
C(31)-H(31)	0.9300
C(32)-H(32)	0.9300
C(33)-H(33A)	0.9600
C(33)-H(33B)	0.9600
C(33)-H(33C)	0.9600
C(34)-C(38)	1.375(2)
C(34)-C(35)	1.382(3)
C(35)-C(36)	1.376(3)
C(35)-H(35)	0.9300
C(36)-C(39)	1.379(3)
C(36)-H(36)	0.9300
C(37)-C(38)	1.377(2)
C(37)-C(39)	1.387(2)

C(37)-H(37)	0.9300
C(38)-H(38)	0.9300
C(39)-C(40)	1.481(2)
C(40)-C(45)	1.379(3)
C(40)-C(41)	1.384(3)
C(41)-C(42)	1.389(3)
C(41)-H(41)	0.9300
C(42)-C(43)	1.358(3)
C(42)-H(42)	0.9300
C(43)-C(44)	1.356(4)
C(43)-H(43)	0.9300
C(44)-C(45)	1.381(3)
C(44)-H(44)	0.9300
C(45)-H(45)	0.9300
O(1)-P(1)	1.4812(13)
O(3)-S(1)	1.4362(16)
O(4)-S(1)	1.4318(17)

C(2)-C(1)-C(8)	116.71(16)
C(2)-C(1)-C(7)	120.27(16)
C(8)-C(1)-C(7)	112.49(15)
C(2)-C(1)-C(3)	59.68(11)
C(8)-C(1)-C(3)	117.18(14)
C(7)-C(1)-C(3)	121.05(16)
C(1)-C(2)-C(3)	62.12(11)
C(1)-C(2)-H(2A)	117.5
C(3)-C(2)-H(2A)	117.5
C(1)-C(2)-H(2B)	117.5
C(3)-C(2)-H(2B)	117.5
H(2A)-C(2)-H(2B)	114.6
C(4)-C(3)-C(2)	121.23(15)
C(4)-C(3)-C(1)	115.98(14)
C(2)-C(3)-C(1)	58.20(11)
C(4)-C(3)-P(1)	117.86(12)
C(2)-C(3)-P(1)	113.41(12)
C(1)-C(3)-P(1)	116.60(12)
C(5)-C(4)-C(3)	130.24(15)
C(5)-C(4)-H(4)	114.9

C(3)-C(4)-H(4)	114.9
C(4)-C(5)-C(34)	125.87(15)
C(4)-C(5)-C(6)	117.83(15)
C(34)-C(5)-C(6)	116.27(15)
C(5)-C(6)-S(1)	117.03(15)
C(5)-C(6)-H(6A)	108.0
S(1)-C(6)-H(6A)	108.0
C(5)-C(6)-H(6B)	108.0
S(1)-C(6)-H(6B)	108.0
H(6A)-C(6)-H(6B)	107.3
C(1)-C(7)-H(7A)	109.5
C(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-C(13)	116.9(2)
C(9)-C(8)-C(1)	120.25(19)
C(13)-C(8)-C(1)	122.76(19)
C(8)-C(9)-C(10)	121.9(3)
C(8)-C(9)-H(9)	119.1
C(10)-C(9)-H(9)	119.1
C(11)-C(10)-C(9)	119.7(3)
C(11)-C(10)-H(10)	120.1
C(9)-C(10)-H(10)	120.1
C(12)-C(11)-C(10)	119.7(3)
C(12)-C(11)-O(2)	116.0(3)
C(10)-C(11)-O(2)	124.4(3)
C(11)-C(12)-C(13)	121.0(3)
C(11)-C(12)-H(12)	119.5
C(13)-C(12)-H(12)	119.5
C(8)-C(13)-C(12)	120.8(2)
C(8)-C(13)-H(13)	119.6
C(12)-C(13)-H(13)	119.6
O(2)-C(14)-H(14A)	109.5
O(2)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
O(2)-C(14)-H(14C)	109.5

H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(20)-C(15)-C(16)	118.18(19)
C(20)-C(15)-P(1)	115.80(16)
C(16)-C(15)-P(1)	126.02(15)
C(17)-C(16)-C(15)	120.7(2)
C(17)-C(16)-H(16)	119.7
C(15)-C(16)-H(16)	119.7
C(18)-C(17)-C(16)	120.0(3)
C(18)-C(17)-H(17)	120.0
C(16)-C(17)-H(17)	120.0
C(17)-C(18)-C(19)	119.9(2)
C(17)-C(18)-H(18)	120.1
C(19)-C(18)-H(18)	120.1
C(18)-C(19)-C(20)	120.5(2)
C(18)-C(19)-H(19)	119.8
C(20)-C(19)-H(19)	119.8
C(19)-C(20)-C(15)	120.7(2)
C(19)-C(20)-H(20)	119.6
C(15)-C(20)-H(20)	119.6
C(26)-C(21)-C(22)	118.44(19)
C(26)-C(21)-P(1)	125.79(15)
C(22)-C(21)-P(1)	115.77(15)
C(23)-C(22)-C(21)	120.5(2)
C(23)-C(22)-H(22)	119.8
C(21)-C(22)-H(22)	119.8
C(24)-C(23)-C(22)	120.2(2)
C(24)-C(23)-H(23)	119.9
C(22)-C(23)-H(23)	119.9
C(23)-C(24)-C(25)	120.0(2)
C(23)-C(24)-H(24)	120.0
C(25)-C(24)-H(24)	120.0
C(24)-C(25)-C(26)	120.6(2)
C(24)-C(25)-H(25)	119.7
C(26)-C(25)-H(25)	119.7
C(21)-C(26)-C(25)	120.3(2)
C(21)-C(26)-H(26)	119.9
C(25)-C(26)-H(26)	119.9

C(32)-C(27)-C(28)	118.8(2)
C(32)-C(27)-S(1)	120.41(18)
C(28)-C(27)-S(1)	120.7(2)
C(27)-C(28)-C(29)	119.0(3)
C(27)-C(28)-H(28)	120.5
C(29)-C(28)-H(28)	120.5
C(30)-C(29)-C(28)	122.7(3)
C(30)-C(29)-H(29)	118.6
C(28)-C(29)-H(29)	118.6
C(31)-C(30)-C(29)	117.2(3)
C(31)-C(30)-C(33)	122.3(4)
C(29)-C(30)-C(33)	120.5(3)
C(30)-C(31)-C(32)	121.7(3)
C(30)-C(31)-H(31)	119.1
C(32)-C(31)-H(31)	119.1
C(27)-C(32)-C(31)	120.5(3)
C(27)-C(32)-H(32)	119.7
C(31)-C(32)-H(32)	119.7
C(30)-C(33)-H(33A)	109.5
C(30)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
C(30)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
C(38)-C(34)-C(35)	116.97(16)
C(38)-C(34)-C(5)	121.82(16)
C(35)-C(34)-C(5)	121.16(16)
C(36)-C(35)-C(34)	121.79(18)
C(36)-C(35)-H(35)	119.1
C(34)-C(35)-H(35)	119.1
C(35)-C(36)-C(39)	121.23(18)
C(35)-C(36)-H(36)	119.4
C(39)-C(36)-H(36)	119.4
C(38)-C(37)-C(39)	121.55(17)
C(38)-C(37)-H(37)	119.2
C(39)-C(37)-H(37)	119.2
C(34)-C(38)-C(37)	121.42(17)
C(34)-C(38)-H(38)	119.3

C(37)-C(38)-H(38)	119.3
C(36)-C(39)-C(37)	116.87(16)
C(36)-C(39)-C(40)	122.03(16)
C(37)-C(39)-C(40)	121.04(16)
C(45)-C(40)-C(41)	117.13(17)
C(45)-C(40)-C(39)	122.17(16)
C(41)-C(40)-C(39)	120.66(17)
C(40)-C(41)-C(42)	120.8(2)
C(40)-C(41)-H(41)	119.6
C(42)-C(41)-H(41)	119.6
C(43)-C(42)-C(41)	120.4(2)
C(43)-C(42)-H(42)	119.8
C(41)-C(42)-H(42)	119.8
C(44)-C(43)-C(42)	119.9(2)
C(44)-C(43)-H(43)	120.1
C(42)-C(43)-H(43)	120.1
C(43)-C(44)-C(45)	120.1(2)
C(43)-C(44)-H(44)	120.0
C(45)-C(44)-H(44)	120.0
C(40)-C(45)-C(44)	121.7(2)
C(40)-C(45)-H(45)	119.1
C(44)-C(45)-H(45)	119.1
C(11)-O(2)-C(14)	117.2(3)
O(1)-P(1)-C(15)	111.04(9)
O(1)-P(1)-C(21)	109.49(8)
C(15)-P(1)-C(21)	108.00(9)
O(1)-P(1)-C(3)	112.71(8)
C(15)-P(1)-C(3)	108.13(8)
C(21)-P(1)-C(3)	107.29(8)
O(4)-S(1)-O(3)	118.01(11)
O(4)-S(1)-C(27)	108.54(12)
O(3)-S(1)-C(27)	108.29(11)
O(4)-S(1)-C(6)	108.93(10)
O(3)-S(1)-C(6)	106.29(11)
C(27)-S(1)-C(6)	106.18(9)

Symmetry transformations used to generate equivalent atoms:

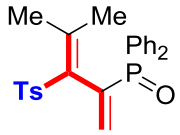
7. Characterizations of Substrates, Intermediates and Coupling Products

7.1 Substrates

All of the phosphonyl allene substrates were known and had been used for other cross-coupling reactions, please see our previous works for details: L. Wu *et. al.*, *J. Org. Chem*. **2015**, *80*, 673-680; L. Wu *et al.*, *ACS. Catal.* **2017**, *7*, 181-185; L. Wu *et. al.*, Org. *Lett.* **2017**, *19*, 1946-1949.

7.2 Isolated Intermediates

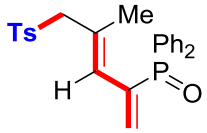
(4-methyl-3-tosylpenta-1,3-dien-2-yl)diphenylphosphine oxide (4a)



4a

White solids, *m.p.*: 153.8-155.3℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (t, *J* = 8.3 Hz, 4H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.60-7.44 (m, 6H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.12 (dd, *J* = 28.2, 23.8 Hz, 2H), 2.39 (s, 3H), 1.99 (d, *J* = 2.6 Hz, 3H), 1.80 (d, *J* = 1.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.8 (d, *J* = 4.8 Hz), 1437, 141.5, 140.5, 139.4, 137.3 (d, *J* = 9.9 Hz), 135.0 (d, *J* = 7.0 Hz), 133.0, 132.6 (d, *J* = 9.9 Hz), 132.1 (d, *J* = 9.7 Hz), 132.0, 131.6, 130.6. 129.5, 128.5 (d, *J* = 11.9 Hz), 128.2 (d, *J* = 12.4 Hz), 127.7, 26.2 (d, *J* = 1.1 Hz), 22.0, 21.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.4 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{25}H_{26}O_3PS$: 437.1335, Found: 437.1327. **IR** (film) ν 3054, 2953, 2922, 1619, 1588, 1435, 1289, 1248, 1195, 1180, 1140, 1116, 1086, 974, 820, 727,692 cm^{-1}.

(*E*)-(4-methyl-5-tosylpenta-1,3-dien-2-yl)diphenylphosphine oxide (5a)

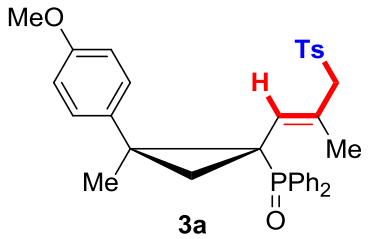


5a

White solids, *m.p.*: 142.9-143.9℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65-7.58 (m, 6H), 7.58-7.52 (m, 2H), 7.47-7.43 (m, 4H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.03 (dd, *J* = 68.8, 29.4 Hz, 2H), 5.68 (d, *J* = 3.6 Hz, 1H), 3.71 (s, 2H), 2.41 (s, 3H), 1.87 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.7, 140.4, 139.5, 135.5, 132.9 (d, *J* = 6.7 Hz), 132.1 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 9.8 Hz), 131.3, 130.3 (d, *J* = 3.1 Hz), 130.2, 129.9 (d, *J* = 10.9 Hz), 129.7, 128.6(d, *J* = 12.1 Hz), 128.2, 66.2, 21.7, 18.8 (d, *J* = 1.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ27.6 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{25}H_{25}NaO_3PS$: 459.1154, Found: 459.1153. **IR** (film) ν 3045, 2918, 2848, 1600, 1584, 1430, 1315, 1295, 1177, 1143, 1116, 1082, 967, 825, 723, 696 cm^{-1}.

7.3 Coupling Products

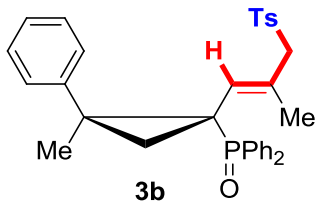
(*E*)-(2-(4-methoxyphenyl)-2-methyl-1-(2-methyl-3-tosylprop-1-en-1-yl)cyclopropyl)diphenylphosphine oxide (3a)



3a

White solids, *m.p.*: 196.4-17.6℃ (127 mg, 74% yield). TLC (R_f = 0.20, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00-7.95 (m, 2H), 7.77-7.70 (m, 2H), 7.63-7.54 (m, 3H), 7.50-7.42 (m, 3H), 7.38 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.25 (s, 1H), 3.79 (s, 3H), 3.23 (d, *J* = 13.4 Hz, 1H), 3.07 (dd, *J* = 13.3, 2.5 Hz, 1H), 2.41 (s, 3H), 2.27 (dd, *J* = 13.7, 4.8 Hz, 1H), 1.73 (s, 3H), 1.59 (dd, *J* = 6.8, 5.1 Hz, 1H), 0.90 (d, *J* = 2.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 144.5, 137.3, 134.4, 134.3 (d, *J* = 1.2 Hz), 133.3 (d, *J* = 13.1 Hz), 132.8 (d, *J* = 4.1 Hz), 132.7 (d, *J* = 9.1 Hz), 132.0 (d, *J* = 49.5 Hz), 131.8 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 9.5 Hz), 131.1 (d, *J* = 3.0 Hz), 129.7, 129.0, 128.7 (d, *J* = 11.7 Hz),127.9 (d, *J* = 11.7 Hz), 127.8, 113.7, 65.3, 55.3, 33.2 (d, *J* = 1.8 Hz), 29.9 (d, *J* =93.9 Hz), 24.2 (d, *J* = 2.3 Hz), 22.2 (d, *J* = 4.0 Hz), 21.6, 18.2 (d, *J* = 2.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.3 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{34}H_{36}O_4PS$: 571.2066, Found: 571.2062. **IR** (film) ν 3034, 2963, 2918, 1622, 1543, 1434, 1361, 1261, 1221, 1088, 910, 804, 729 cm^{-1}.

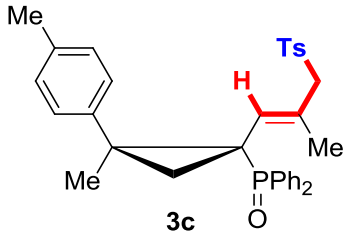
(*E*)-(2-methyl-1-(2-methyl-3-tosylprop-1-en-1-yl)-2-phenylcyclopropyl)diphenylphosphine oxide (3b)



3b

White solids, *m.p.*: 202.3-203.4℃ (97 mg, 60% yield). TLC (R_f = 0.21, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 10.4, 7.6 Hz, 2H), 7.75 (dd, *J* = 10.9, 7.9 Hz, 2H), 7.63-7.59 (m, 3H), 7.46 (d, *J* = 7.9 Hz, 3H), 7.41-7.37 (m, 2H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.25-7.23 (m, 5H), 5.30 (s, 1H), 3.25 (d, *J* = 13.4 Hz, 1H), 3.07-3.03 (m, 1H), 2.43 (s, 3H), 2.32 (dd, *J* = 13.8, 4.6 Hz, 1H), 1.67-1.63 (m, 4H), 0.89 (d, *J* = 2.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.5, 142.3, 137.1, 134.3, 133.3 (d, *J* = 8.8 Hz), 132.7 (d, *J* = 8.8 Hz), 132.2, 131.9, 131.8 (d, *J* = 2.9 Hz), 131.3 (d, *J* = 9.5 Hz), 131.2 (d, *J* = 2.7 Hz), 129.7, 128.7 (d, *J* = 11.7 Hz), 128.4, 128.0, 127.9, 127.8, 126.6, 65.2 (d, *J* = 1.6 Hz), 33.8 (d, *J* = 1.8 Hz), 30.0 (d, *J* = 93.9 Hz), 24.0 (d, *J* = 2.3 Hz), 22.1 (d, *J* = 4.2 Hz), 21.6, 18.2 (d, *J* = 2.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.2 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{33}H_{34}O_3PS$: 541.1961, Found: 541.1953. **IR** (film) ν 3027, 2944, 2918, 1621, 1596, 1435, 1312, 1246, 1189, 1133, 1085, 894, 819 cm^{-1}.

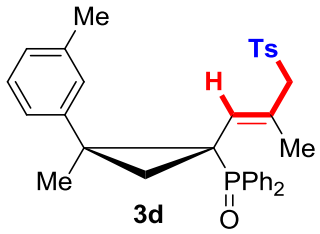
(*E*)-(2-methyl-1-(2-methyl-3-tosylprop-1-en-1-yl)-2-(p-tolyl)cyclopropyl)diphenylphosphine oxide (3c)



3c

White solids, *m.p.*: 183.7-185.6℃ (100 mg, 60% yield). TLC (R_f = 0.27, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02-7.97 (m, 2H), 7.77-7.73 (m, 2H), 7.61-7.55 (m, 3H), 7.48 (d, *J* = 8.2 Hz, 3H), 7.41-7.37 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.12 (q, *J* = 8.3 Hz, 4H), 5.27 (s, 1H), 3.25 (d, *J* = 13.4 Hz, 1H), 3.08 (dd, *J* = 13.4, 2.4 Hz, 1H), 2.40 (s, 3H), 2.32- 2.26 (m, 4H), 1.76 (s, 3H), 1.63 (dd, *J* = 6.7, 5.1 Hz, 1H), 0.90 (d, *J* = 2.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.5, 139.1, 137.3, 136.1, 134.3, 133.3 (d, *J* = 7.7 Hz), 132.7 (d, *J* = 8.9 Hz), 132.3 (d, *J* =99.0 Hz), 132.2, 131.8, 131.7, 131.4 (d, *J* = 9.5 Hz), 131.2 (d, *J* = 2.7 Hz), 129.7, 129.1, 128.7 (d, *J* = 11.7 Hz), 127.9 (d, *J* = 11.7 Hz), 127.8, 65.3 (d, *J* = 1.0 Hz), 33.5 (d, *J* = 1.8 Hz), 29.9 (d, *J* = 93.9 Hz), 24.0 (d, *J* = 2.4 Hz), 22.1 (d, *J* = 4.1 Hz), 21.6, 21.1, 18.1 (d, *J* = 2.3 Hz) . **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.5 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{34}H_{36}O_3PS$: 555.2117, Found: 555.2108. **IR** (film) ν 3051, 2959, 2915, 1593, 1435, 1296, 1189, 1134, 1087, 818, 724 cm^{-1}.

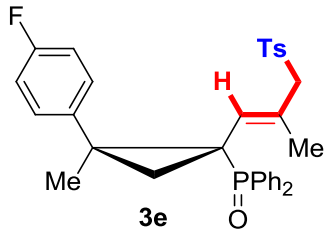
(*E*)-(2-methyl-1-(2-methyl-3-tosylprop-1-en-1-yl)-2-(m-tolyl)cyclopropyl)diphenylphosphine oxide (3d)



3d

White solids, *m.p.*: 169.7-171.5℃ (75 mg, 45% yield). TLC (R_f = 0.24, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04-7.99 (m, 2H), 7.76-7.72 (m, 2H), 7.64-7.57 (m, 3H), 7.47-7.42 (m, 3H), 7.40-7.36 (m, 2H), 7.26-7.21 (m, 3H), 7.06-7.04 (m, 3H), 5.33 (s, 1H), 3.27 (d, *J* = 13.4 Hz, 1H), 3.05 (dd, *J* = 13.4, 2.5 Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H), 2.29 (dd, *J* = 13.6, 4.8 Hz, 1H), 1.75 (s, 3H), 1.63 (dd, *J* = 6.7, 5.1 Hz, 1H), 0.85 (d, *J* = 2.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.5, 142.2, 138.0, 137.2, 134.4, 133.3 (d, *J* = 10.6 Hz), 132.7 (d, *J* = 8.6 Hz), 132.3, 132.2 (d, *J* =72.7 Hz), 131.8 (d, *J* = 2.7 Hz), 131.3 (d, *J* = 9.5 Hz), 131.1 (d, *J* = 2.6 Hz), 129.7, 128.7 (d, *J* = 11.8 Hz), 128.1 (d, *J* =38.4 Hz), 127.8, 127.4, 125.2, 65.2 (d, *J* = 1.2 Hz), 33.8 (d, *J* = 1.8 Hz), 31.0, 29.9 (d, *J* = 92.9 Hz), 24.1 (d, *J* = 2.3 Hz), 22.3 (d, *J* = 4.2 Hz), 21.7, 21.6, 18.2 (d, *J* = 2.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.4 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{34}H_{36}O_3PS$: 555.2117, Found: 555.2114. **IR** (film) ν 3039, 2951, 2915, 1593, 1436, 1301, 1185, 1134, 1089, 818, 723 cm^{-1}.

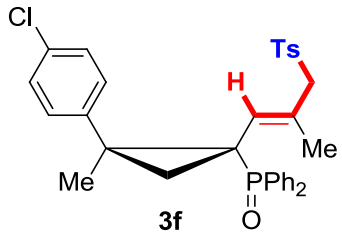
(*E*)-(2-(4-fluorophenyl)-2-methyl-1-(2-methyl-3-tosylprop-1-en-1-yl)cyclopropyl)diphenylphosphine oxide (3e)



3e

White solids, *m.p.*: 211.2-213.1℃ (82 mg, 49% yield). TLC (R_f = 0.17, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14-8.06 (m, 2H), 7.89-7.84 (m, 2H), 7.78-7.66 (m, 3H), 7.63-7.57 (m, 3H), 7.51 (d, *J* = 5.8 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.31-7.25 (m, 2H), 7.14-7.10 (m, 2H), 5.36 (s, 1H), 3.37 (d, *J* = 13.3 Hz, 1H), 3.20 (d, *J* = 13.3 Hz, 1H), 2.53 (s, 3H), 2.43 (dd, *J* = 13.6, 4.2 Hz, 1H), 1.85 (s, 3H), 1.77-1.69 (m, 1H), 1.05 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4 (d, *J* = 245.43 Hz), 138.0 (d, *J* = 2.0 Hz), 137.2, 134.3, 133.2 (d, *J* = 16.5 Hz), 132.6 (d, *J* = 8.8 Hz), 132.4 (d, *J* = 3.8 Hz), 132.2 (d, *J* = 7.7 Hz), 132.1, 131.9 (d, *J* = 2.6 Hz), 131.3 (d, *J* = 2.8 Hz), 131.2 (d, *J* = 9.4 Hz), 129.8, 129.5 (d, *J* = 8.0 Hz), 128.8 (d, *J* = 11.7 Hz), 127.9 (d, *J* = 11.8 Hz), 127.7, 115.2 (d, *J* = 22.22 Hz), 65.2 (d, *J* = 1.6 Hz), 33.1 (d, *J* = 1.4 Hz), 30.1 (d, *J* = 92.9 Hz), 24.3 (d, *J* = 2.5 Hz), 22.2 (d, *J* = 4.0 Hz), 21.6, 18.2 (d, *J* = 2.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.8 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{33}H_{33}FO_3PS$: 559.1867, Found: 559.1862. **IR** (film) ν 3051, 2959, 2915, 1593, 1509, 1435, 1300, 1188, 1135, 1086, 838, 723 cm^{-1}.

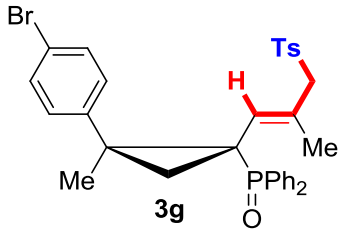
(*E*)-(2-(4-chlorophenyl)-2-methyl-1-(2-methyl-3-tosylprop-1-en-1-yl)cyclopropyl)diphenylphosphine oxide (3f)



3f

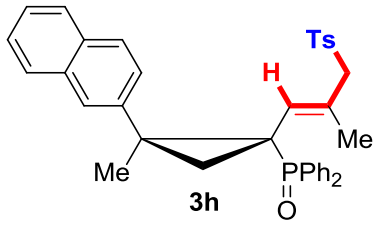
White solids, *m.p.*: 229.2-231.1℃ (62 mg, 36% yield). TLC (R_f = 0.20, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01-7.95 (m, 2H), 7.78-7.73 (m, 2H), 7.62- 7.57 (m, 3H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.49-7.45 (m, 1H), 7.42-7.38 (m, 2H), 7.30-7.26 (m, 4H), 7.13 (d, *J* = 8.5 Hz, 2H), 5.20 (s, 1H), 3.25 (d, *J* = 13.3 Hz, 1H), 3.11 (dd, *J* = 13.3, 2.7 Hz, 1H), 2.43 (s, 3H), 2.32 (dd, *J* = 13.6, 4.9 Hz, 1H), 1.74 (s, 3H), 1.63 (dd, *J* = 6.4, 5.5 Hz, 1H), 0.97 (d, *J* = 2.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 140.7, 137.3, 134.2, 133.1 (d, *J* = 17.7 Hz), 132.6 (d, *J* = 8.8 Hz), 132.5 (d, *J* = 7.7 Hz), 132.3, 132.2, 131.9 (d, *J* = 2.7 Hz), 131.3, 131.2, 129.8, 129.3, 128.8 (d, *J* = 11.7 Hz), 128.5, 127.9 (d, *J* = 11.8 Hz), 127.7, 65.3 (d, *J* = 1.5 Hz), 33.1 (d, *J* = 1.7 Hz), 30.2 (d, *J* = 92.9 Hz), 24.1 (d, *J* = 2.4 Hz), 21.8 (d, *J* = 4.1 Hz), 21.6, 18.2 (d, *J* = 2.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.7 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{33}H_{33}ClO_3PS$: 575.1571, Found: 575.1560. **IR** (film) ν 3055, 2959, 2923, 1593, 1509, 1436, 1297, 1189, 1133, 1086, 834, 697 cm^{-1}.

(*E*)-(2-(4-bromophenyl)-2-methyl-1-(2-methyl-3-tosylprop-1-en-1-yl)cyclopropyl)diphenylphosphine oxide (3g)



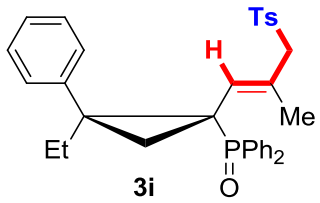
White solids, *m.p.*: 220.9-222.9℃ (56 mg, 30% yield). TLC (R_f = 0.15, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00-7.95 (m, 2H), 7.78-7.73 (m, 2H), 7.64-7.56 (m, 3H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.50-7.44 (m, 2H), 7.44-7.37 (m, 3H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 5.20 (s, 1H), 3.24 (d, *J* = 13.3 Hz, 1H), 3.12 (dd, *J* = 13.3, 2.6 Hz, 1H), 2.43 (s, 3H), 2.32 (dd, *J* = 13.6, 4.9 Hz, 1H), 1.74 (s, 3H), 1.65-1.59 (m, 1H), 0.98 (d, *J* = 2.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 141.2, 137.4, 134.2, 133.1 (d, *J* = 18.4 Hz), 132.6 (d, *J* = 8.9 Hz), 132.5, 132.2 (d, *J* = 3.8 Hz), 131.9 (d, *J* = 2.6 Hz), 131.5, 131.3, 131.2, 129.8, 129.7, 128.8 (d, *J* = 11.7 Hz), 128.0 (d, *J* = 11.8 Hz), 127.7, 120.4, 65.3 (d, *J* = 1.1 Hz), 33.1 (d, *J* = 1.7 Hz), 30.2 (d, *J* = 92.9 Hz), 24.1 (d, *J* = 1.9 Hz), 21.7 (d, *J* = 4.1 Hz), 21.6, 18.2 (d, *J* = 2.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.7 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{33}H_{33}BrO_3PS$: 619.1066, Found: 619.1057. **IR** (film) ν 3051, 2963, 2915, 1593, 1509, 1435, 1294, 1189, 1134, 1086, 819, 723, 544 cm^{-1}.

(*E*)-(2-methyl-1-(2-methyl-3-tosylprop-1-en-1-yl)-2-(naphthalen-2-yl)cyclopropyl)diphenylphosphine oxide (3h)



White solids, *m.p.*: 232.0-234.0℃ (99 mg, 56% yield). TLC (R_f = 0.22, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11-8.06 (m, 2H), 7.83-7.78 (m, 5H), 7.65-7.61 (m, 4H), 7.50-7.47 (m, 3H), 7.44-7.41 (m, 2H), 7.37-7.33 (m, 3H), 7.10 (d, *J* = 8.1 Hz, 2H), 5.31 (s, 1H), 3.14 (d, *J* = 13.5 Hz, 1H), 2.99 (dd, *J* = 13.4, 2.5 Hz, 1H), 2.42 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.36 (s, 3H), 1.85 (s, 3H), 1.81 (dd, *J* = 6.7, 5.1 Hz, 1H), 0.97 (d, *J* = 2.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 140.0, 137.2, 134.4, 133.4, 133.3 (d, *J* = 25.25 Hz), 132.7 (d, *J* = 8.8 Hz), 132.5 (d, *J* = 4.04 Hz), 132.21 (d, *J* = 8.08 Hz), 132.20, 132.1, 131.9 (d, *J* = 2.02 Hz), 131.4 (d, *J* = 9.4 Hz), 131.2 (d, *J* = 3.03 Hz), 130.0, 129.6, 128.8 (d, *J* = 11.7 Hz), 128.0 (d, *J* =5.05 Hz), 127.9, 127.6, 126.5, 126.4, 126.1, 125.8, 65.3 (d, *J* = 1.4 Hz), 34.0 (d, *J* = 1.9 Hz), 30.2 (d, *J* = 92.9 Hz), 24.3 (d, *J* = 2.1 Hz), 22.1 (d, *J* = 4.1 Hz), 21.6, 18.2 (d, *J* = 2.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.8 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{37}H_{36}O_3PS$: 591.2117, Found: 591.2108. **IR** (film) ν 3051, 2963, 2915, 1593, 1429, 1293, 1185, 1133, 1081, 901, 749 cm^{-1}.

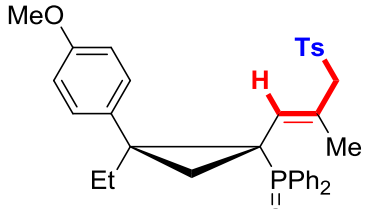
(*E*)-(2-ethyl-1-(2-methyl-3-tosylprop-1-en-1-yl)-2-phenylcyclopropyl)diphenylphosphine oxide (3i)



3i

White solids, *m.p.*: 163.4-164.4℃ (67 mg, 40% yield). TLC (R_f = 0.35, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 11.5, 7.7 Hz, 2H), 7.75 (dd, *J* = 10.6, 7.7 Hz, 2H), 7.63-7.61 (m, 3H), 7.48-7.44 (m, 3H), 7.41-7.36 (m, 2H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.25-7.20 (m, 5H), 5.31 (s, 1H), 3.22 (d, *J* = 13.4 Hz, 1H), 3.01 (dd, *J* = 13.5, 2.4 Hz, 1H), 2.58-2.49 (m, 1H), 2.43 (s, 3H), 2.26 (dd, *J* = 13.7, 4.7 Hz, 1H), 1.79-1.70 (m, 1H), 1.60-1.55 (m, 1H), 0.87 (d, *J* = 2.7 Hz, 3H), 0.70 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.5, 139.8, 137.2, 134.5, 133.4 (d, *J* = 16.5 Hz), 132.8 (d, *J* = 3.4 Hz), 132.7 (d, *J* = 8.9 Hz), 131.9 (d, *J* = 82.8 Hz), 131.8 (d, *J* = 1.8 Hz), 131.3 (d, *J* = 9.5 Hz), 131.1, 129.7, 128.9, 128.7 (d, *J* = 12.1 Hz), 128.3, 127.9, 127.8, 126.7, 65.2, 40.2, 30.8 (d, *J* = 91.9 Hz), 27.0 (d, *J* = 3.0 Hz), 22.7, 21.6, 18.2, 11.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.2 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{34}H_{36}O_3PS$: 555.2117, Found: 555.2114. **IR** (film) ν 3051, 2955, 2859, 1597, 1435, 1316, 1190, 1146, 1117, 817, 724 cm^{-1}.

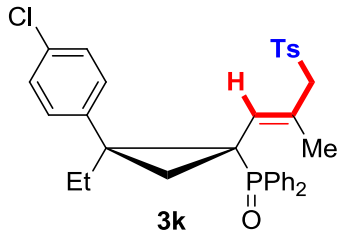
(*E*)-(2-ethyl-2-(4-methoxyphenyl)-1-(2-methyl-3-tosylprop-1-en-1-yl)cyclopropyl)diphenylphosphine oxide (3j)



3j

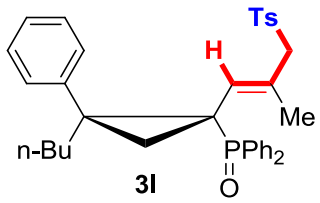
White solids, *m.p.*: 160.5-162.5℃ (70 mg, 40% yield). TLC (R_f = 0.21, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04-7.99 (m, 2H), 7.74 (dd, *J* = 11.0, 7.5 Hz, 2H), 7.61-7.57 (m, 3H), 7.48-7.43 (m, 3H), 7.40-7.37 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.28 (s, 1H), 3.79 (s, 3H), 3.22 (d, *J* = 13.4 Hz, 1H), 3.05 (dd, *J* = 13.4, 2.3 Hz, 1H), 2.57-2.46 (m, 1H), 2.41 (s, 3H), 2.23 (dd, *J* = 13.8, 4.7 Hz, 1H), 1.71 (td, *J* = 14.0, 7.0 Hz, 1H), 1.55-1.52 (m, 1H), 0.90 (d, *J* = 3.1 Hz, 3H), 0.70 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 144.5, 137.3, 134.6, 133.5 (d, *J* = 20.2 Hz), 132.9 (d, *J* = 4.1 Hz), 132.7 (d, *J* = 8.8 Hz), 132.3, 131.8 (d, *J* = 2.7 Hz), 131.4 (d, *J* = 7.7 Hz), 131.2 (d, *J* = 9.5 Hz), 131.1 (d, *J* = 2.7 Hz), 129.9, 129.7, 128.7 (d, *J* = 11.7 Hz), 127.9 (d, *J* = 11.7 Hz), 127.8, 113.7, 65.3 (d, *J* = 1.2 Hz), 55.3, 39.6 (d, *J* = 1.6 Hz), 30.7 (d, *J* = 93.9 Hz), 27.1 (d, *J* = 4.0 Hz), 22.9 (d, *J* = 2.4 Hz), 21.6, 18.2 (d, *J* = 2.3 Hz), 11.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.5 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{35}H_{38}O_4PS$: 585.2223, Found: 585.2220. **IR** (film) ν 3047, 2955, 2915, 1597, 1512, 1433, 1322, 1243, 1187, 1146, 1087, 1028, 828, 724 cm^{-1}.

(*E*)-(2-(4-chlorophenyl)-2-ethyl-1-(2-methyl-3-tosylprop-1-en-1-yl)cyclopropyl)diphenylphosphine oxide (3k)



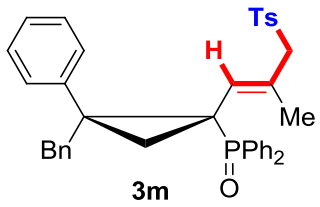
White solids, *m.p.*: 166.3-167.5℃ (76 mg, 43% yield). TLC (R_f = 0.17, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 10.0, 7.7 Hz, 2H), 7.75 (dd, *J* = 11.0, 7.5 Hz, 2H), 7.63-7.58 (m, 3H), 7.51-7.44 (m, 3H), 7.41-7.37 (m, 2H), 7.29-7.25 (m, 4H), 7.10 (d, *J* = 8.3 Hz, 2H), 5.21 (s, 1H), 3.21 (d, *J* = 13.3 Hz, 1H), 3.07 (dd, *J* = 13.4, 2.4 Hz, 1H), 2.58-2.48 (m, 1H), 2.43 (s, 3H), 2.26 (dd, *J* = 13.6, 4.8 Hz, 1H), 1.74-1.64 (m, 1H), 1.57-1.54 (m, 1H), 0.96 (d, *J* = 2.4 Hz, 3H), 0.68 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 138.4, 137.3, 134.4, 133.2 (d, *J* = 29.29 Hz), 132.6 (d, *J* = 8.8 Hz), 132.4, 132.3 (d, *J* = 2.5 Hz), 132.1 (d, *J* = 7.3 Hz), 131.9, 131.2, 131.1, 130.2, 129.8, 128.7 (d, *J* = 11.7 Hz), 128.5, 127.9 (d, *J* = 11.7 Hz), 127.7, 65.3, 39.5, 31.0 (d, *J* = 92.9 Hz), 26.7 (d, *J* = 4.1 Hz), 22.8 (d, *J* = 2.2 Hz), 21.6, 18.2 (d, *J* = 1.9 Hz), 11.8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.8 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{34}H_{35}ClO_3PS$: 589.1728, Found: 589.1721. **IR** (film) ν 3055, 2963, 2923, 2875, 1597, 1435, 1316, 1184, 1148, 1086, 1009, 836, 722 cm^{-1}.

(*E*)-(2-butyl-1-(2-methyl-3-tosylprop-1-en-1-yl)-2-phenylcyclopropyl)diphenylphosphine oxide (3l)



White solids, *m.p.*: 161.2-163.2℃ (113 mg, 65% yield). TLC (R_f = 0.29, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06-8.01 (m, 2H), 7.77-7.73 (m, 2H), 7.62-7.59 (m, 3H), 7.45 (d, *J* = 8.2 Hz, 3H), 7.41-7.35 (m, 2H), 7.33 (d, *J* = 2.02 Hz, 2H), 7.25-7.19 (m, 5H), 5.27 (s, 1H), 3.20 (d, *J* = 13.4 Hz, 1H), 3.00 (dd, *J* = 13.4, 2.4 Hz, 1H), 2.58-2.48 (m, 1H), 2.42 (s, 3H), 2.29 (dd, *J* = 13.7, 4.8 Hz, 1H), 1.82-1.71 (m, 1H), 1.61 (t, *J* = 5.5 Hz, 1H), 1.26-1.09 (m, 3H), 1.01- 0.91 (m, 1H), 0.87 (d, *J* = 2.5 Hz, 3H), 0.73 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.5, 140.3, 137.2, 134.5, 133.4 (d, *J* = 12.1 Hz), 132.8, 132.7 (d, *J* = 8.7 Hz), 131.9 (d, *J* = 88.9 Hz), 131.8 (d, *J* = 2.6 Hz), 131.3 (d, *J* = 9.5 Hz), 131.1 (d, *J* = 2.6 Hz), 129.7, 128.8, 128.7, 128.3, 127.9 (d, *J* = 72.7 Hz), 127.8, 126.6, 65.2 (d, *J* = 1.3 Hz), 39.1 (d, *J* = 1.7 Hz), 33.4 (d, *J* = 3.9 Hz), 30.1(d, *J* = 92.9 Hz), 30.0, 22.9, 22.5, 21.6, 18.2 (d, *J* = 2.4 Hz), 14.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.1 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{36}H_{40}O_3PS$: 583.2430, Found: 583.2428. **IR** (film) ν 3055, 2956, 2919, 1597, 1434, 1314, 1192, 1145, 1087, 813, 722 cm^{-1}.

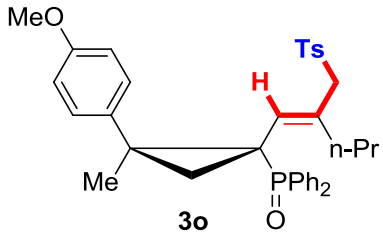
(*E*)-(2-benzyl-1-(2-methyl-3-tosylprop-1-en-1-yl)-2-phenylcyclopropyl)diphenylphosphine oxide (3m)



3m

White solids, *m.p.*: 215.6-216.9℃ (74 mg, 40% yield). TLC (R_f = 0.27, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18-8.13 (m, 2H), 7.84 (dd, *J* = 11.1, 7.2 Hz, 2H), 7.70-7.64 (m, 3H), 7.49-7.47 (m, 1H), 7.45-7.40 (m, 4H), 7.27-7.17 (m, 5H), 7.09-7.00 (m, 5H), 6.85-6.83 (m, 2H), 5.46 (s, 1H), 4.01 (d, *J* = 13.7 Hz, 1H), 3.24 (d, *J* = 13.4 Hz, 1H), 3.02 (dd, *J* = 13.4, 2.1 Hz, 1H), 2.91 (d, *J* = 13.6 Hz, 1H), 2.63 (dd, *J* = 13.7, 4.8 Hz, 1H), 2.40 (s, 3H), 1.56-1.53 (m, 1H), 0.83 (d, *J* = 2.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.5, 139.9, 139.8, 137.0, 134.4, 133.2 (d, *J* = 30.3 Hz), 132.7 (d, *J* = 8.8 Hz), 132.6, 132.5 (d, *J* = 3.8 Hz), 132.0 (d, *J* = 2.5 Hz), 131.6 (d, *J* = 7.8 Hz), 131.29 (d, *J* = 9.4 Hz), 131.28 (d, *J* = 2.9 Hz), 129.6 (d, *J* = 18.4 Hz), 129.4, 128.9 (d, *J* = 11.7 Hz), 128.2, 128.0 (d, *J* = 11.8 Hz), 127.8, 127.6, 126.7, 125.7, 65.1, 40.2 (d, *J* = 1.8 Hz), 39.9 (d, *J* = 4.1 Hz), 30.3 (d, *J* = 92.9 Hz), 23.0 (d, *J* = 1.8 Hz), 21.6, 18.2 (d, *J* = 2.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.9 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{39}H_{38}O_3PS$: 617.2274, Found: 617.2271. **IR** (film) ν 3055, 3019, 2927, 1597, 1437, 1311, 1189, 1145, 1081, 814, 724 cm^{-1}.

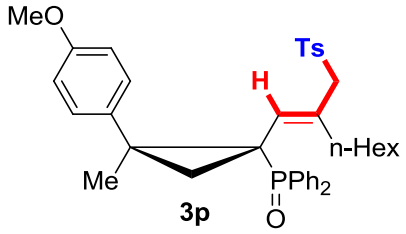
(*E*)-(2-(4-methoxyphenyl)-2-methyl-1-(2-(tosylmethyl)pent-1-en-1-yl)cyclopropyl)diphenylphosphine oxide (3o)



3o

White solids, *m.p.*: 170.2-172.1℃ (72 mg, 40% yield). TLC (R_f = 0.16, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09-8.01 (m, 2H), 7.83 (dd, *J* = 11.0, 7.7 Hz, 2H), 7.65-7.58 (m, 3H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.50-7.40 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 5.35 (s, 1H), 3.78 (s, 3H), 3.32 (d, *J* = 13.5 Hz, 1H), 3.02 (d, *J* = 13.6 Hz, 1H), 2.41 (s, 3H), 2.31 (dd, *J* = 13.7, 4.7 Hz, 1H), 1.74 (s, 3H), 1.63-1.57 (m, 1H), 1.05-0.98 (m, 1H), 0.94-0.70 (m, 3H), 0.64 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 144.5, 137.6, 134.9 (d, *J* = 7.8 Hz), 134.5 (d, *J* = 5.1 Hz), 133.33 (d, *J* = 4.0 Hz), 133.32 (d, *J* = 26.3 Hz), 132.7 (d, *J* = 8.8 Hz), 132.2, 131.7 (d, *J* = 2.6 Hz), 131.4 (d, *J* = 9.4 Hz), 131.1 (d, *J* = 2.7 Hz), 129.7, 129.1, 128.7 (d, *J* = 11.7 Hz), 128.1 (d, *J* = 11.8 Hz), 127.7, 113.7, 61.3, 55.2, 33.1 (d, *J* = 1.8 Hz), 32.2 (d, *J* = 1.4 Hz), 29.7 (d, *J* = 92. Hz), 24.1 (d, *J* = 1.6 Hz), 22.2 (d, *J* = 3.9 Hz), 21.6, 19.6 (d, *J* = 1.6 Hz), 14.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.9 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{36}H_{39}NaO_4PS$: 621.2199, Found: 621.2189. **IR** (film) ν 3055, 2947, 2919, 1609, 1513, 1433, 1311, 1248, 1190, 1147, 1081, 1029, 839, 703 cm^{-1}.

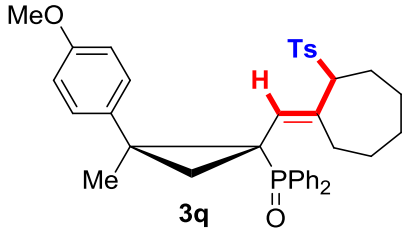
(*E*)-(2-(4-methoxyphenyl)-2-methyl-1-(2-(tosylmethyl)oct-1-en-1-yl)cyclopropyl)diphenylphosphine oxide (3p)



3p

White solids, *m.p.*: 167.3-169.1℃ (60 mg, 31% yield). TLC (R_f = 0.33, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08-8.01 (m, 2H), 7.81 (dd, *J* = 11.0, 7.2 Hz, 2H), 7.67-7.59 (m, 3H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.48-7.41 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.34 (s, 1H), 3.79 (s, 3H), 3.32 (d, *J* = 13.6 Hz, 1H), 3.01 (d, *J* = 13.5 Hz, 1H), 2.42 (s, 3H), 2.30 (dd, *J* = 13.7, 4.6 Hz, 1H), 1.74 (s, 3H), 1.60-1.55 (m, 1H), 1.27-1.18 (m, 4H), 1.13-0.93 (m, 6H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 144.5, 137.6, 135.0 (d, *J* = 7.9 Hz), 134.6, 133.3 (d, *J* = 14.3 Hz), 133.0 (d, *J* = 4.1 Hz), 132.67 (d, *J* = 8.9 Hz), 131.7 (d, *J* = 2.4 Hz), 131.4 (d, *J* = 9.4 Hz), 131.1 (d, *J* = 2.7 Hz), 129.7, 129.1, 128.7 (d, *J* = 11.7 Hz), 128.1 (d, *J* = 11.8 Hz), 127.8, 113.7, 61.3, 55.3, 33.2 (d, *J* = 2.0 Hz), 31.5, 30.3, 29.7 (d, *J* = 92.9 Hz), 29.3, 26.2 (d, *J* = 1.7 Hz), 24.1, 22.6, 22.2 (d, *J* = 4.0 Hz), 21.6, 14.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.0 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{39}H_{46}O_4PS$: 641.2849, Found: 641.2846. **IR** (film) ν 3040, 2948, 2926, 1598, 1513, 1436, 1314, 1244, 1179, 1145, 1085,1032, 831, 722 cm^{-1}.

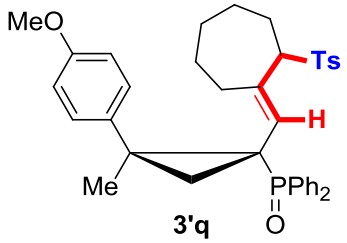
(*E*)-(2-(4-methoxyphenyl)-2-methyl-1-((2-tosylcycloheptylidene)methyl)cyclopropyl)diphenylphosphine oxide (3q)



3q

White solides, *m.p.*: 187.9-188.6℃ (80 mg, 42% yield). TLC (R_f = 0.15, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27-8.18 (m, 2H), 8.05-7.98 (m, 2H), 7.63 (s, 3H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.49-7.45 (m, 3H), 7.28-7.26 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.46 (s, 1H), 3.79 (s, 3H), 3.00-2.95 (m, 1H), 2.43 (s, 3H), 2.31 (dd, *J* = 13.9, 4.9 Hz, 1H), 1.94 (dd, *J* = 12.7, 5.5 Hz, 1H), 1.89 (t, *J* = 5.8 Hz, 1H), 1.83 (s, 3H), 1.57-1.41 (m, 3H), 1.37-1.31 (m, 1H), 1.13-0.98 (m, 3H), 0.92-0.88 (m, 1H), 0.43-0.34 (m, 1H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.6 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{38}H_{42}O_4PS$: 625.2536, Found: 625.2523. **IR** (film) ν 3052, 2920, 2848, 2229, 1606, 1513, 1436, 1307, 1246, 1182, 1141, 1083, 1031, 829, 808, 724, 702 cm^{-1}.

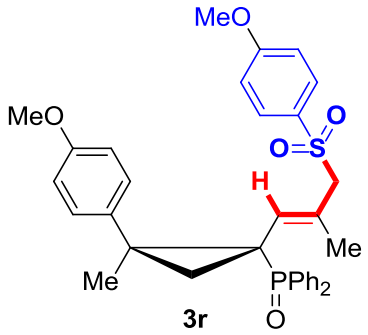
(*E*)-(2-(4-methoxyphenyl)-2-methyl-1-((2-tosylcycloheptylidene)methyl)cyclopropyl)diphenyl phosphine oxide (3'q)



3'q

White solides, *m.p.*: 199.4-201.4℃ (17 mg, 9% yield). TLC (R_f = 0.20, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19-8.08 (m, 2H), 7.72-7.67 (m, 5H), 7.45-7.40 (m, 3H), 7.32 (dd, *J* = 7.5, 2.3 Hz, 2H), 7.20 (dd, *J* = 7.7, 5.5 Hz, 4H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.04 (s, 1H), 3.81 (s, 3H), 3.05 (d, *J* = 10.2 Hz, 1H), 2.42 (s, 3H), 2.30 (dd, *J* = 13.8, 4.7 Hz, 1H), 1.79 (s, 3H), 1.70-1.59 (m, 3H), 1.36-1.30 (m, 1H), 1.22-1.11 (m, 2H), 0.97-0.83 (m, 3H), 0.63- 0.50 (m, 2H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.5 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{38}H_{42}O_4PS$: 625.2536, Found: 625.2516. **IR** (film) ν 3053, 2960, 2925, 2848, 2157, 1598, 1513, 1436, 1316, 1244, 1179, 1146, 1085, 1031, 831, 811, 724, 693 cm^{-1}.

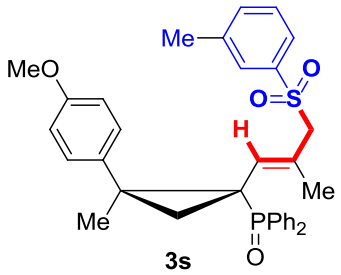
(*E*)-(2-(4-methoxyphenyl)-1-(3-((4-methoxyphenyl)sulfonyl)-2-methylprop-1-en-1-yl)-2-methylcyclopropyl)diphenylphosphine oxide (3r)



3r

White solids, *m.p.*: 169.7-170.5℃ (108 mg, 61% yield). TLC (R_f = 0.10, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00-7.96 (m, 2H), 7.76-7.72 (m, 2H), 7.59-7.55 (m, 3H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.47-7.43 (m, 1H), 7.40-7.37 (m, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.87 (dd, *J* = 12.1, 8.5 Hz, 4H), 5.26 (s, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.25 (d, *J* = 13.4 Hz, 1H), 3.09-3.06 (m, 1H), 2.27 (dd, *J* = 13.8, 4.6 Hz, 1H), 1.73 (s, 3H), 1.62-1.56 (m, 1H), 0.91 (d, *J* = 2.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.5, 158.1, 134.4, 134.3, 133.3 (d, *J* = 11.6 Hz), 132.7 (d, *J* = 9.0 Hz), 132.2, 132.1 (d, *J* = 84.8 Hz), 132.0 (d, *J* = 7.7 Hz), 131.8 (d, *J* = 2.6 Hz), 131.3 (d, *J* = 9.5 Hz), 131.1 (d, *J* = 2.4 Hz), 129.9, 129.0, 128.7 (d, *J* = 11.7 Hz), 127.9 (d, *J* = 11.7 Hz), 114.2, 113.8, 65.5, 55.7, 55.3, 33.2 (d, *J* = 1.8 Hz), 29.9 (d, *J* = 93.9 Hz), 24.2 (d, *J* = 2.5 Hz), 22.3 (d, *J* = 4.1 Hz), 18.1 (d, *J* = 2.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.2 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{34}H_{35}NaO_5PS$: 609.1835, Found: 609.1851. **IR** (film) ν 3063, 2957, 2927, 1597, 1436, 1311, 1180, 1146, 1087, 1021, 833, 702 cm^{-1}.

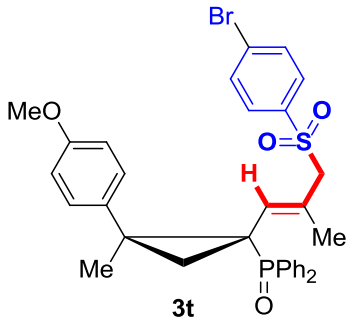
(*E*)-(2-(4-methoxyphenyl)-2-methyl-1-(2-methyl-3-(m-tolylsulfonyl)prop-1-en-1-yl)cycloprop yl)diphenylphosphine oxide (3s)



3s

White solids, *m.p.*: 163.4-165.3℃ (55 mg, 32% yield). TLC (R_f = 0.20, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 11.3, 7.6 Hz, 2H), 7.77 (dd, *J* = 10.8, 8.0 Hz, 2H), 7.60-7.57 (m, 3H), 7.52 (s, 1H), 7.50-7.43 (m, 2H), 7.42-7.34 (m, 4H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 5.25 (s, 1H), 3.79 (s, 3H), 3.24 (d, *J* = 13.3 Hz, 1H), 3.14-3.06 (m, 1H), 2.39 (s, 3H), 2.29 (dd, *J* = 13.7, 4.7 Hz, 1H), 1.76 (s, 3H), 1.66-1.58 (m, 1H), 0.96 (d, *J* = 2.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 140.1, 139.4, 134.4, 134.3, 134.2, 133.0 (d, *J* = 4.1 Hz), 132.69 (d, *J* = 24.2 Hz), 132.68 (d, *J* = 8.9 Hz), 132.2, 131.8 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 7.7 Hz), 131.6, 131.3 (d, *J* = 9.5 Hz), 131.1 (d, *J* = 2.8 Hz), 129.0, 128.9, 128.7 (d, *J* = 11.7 Hz), 127.91 (d, *J* = 11.7 Hz), 127.90, 124.8, 113.7, 65.2, 55.3, 33.2 (d, *J* = 1.7 Hz), 30.0 (d, *J* = 92.9 Hz), 24.2 (d, *J* = 2.5 Hz), 22.2 (d, *J* = 4.0 Hz), 21.3, 18.2 (d, *J* = 2.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.2 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{34}H_{35}NaO_4PS$: 593.1886, Found: 593.1895. **IR** (film) ν 3051, 2959, 2915, 1593, 1435, 1296, 1189, 1134, 1087, 818, 724 cm^{-1}.

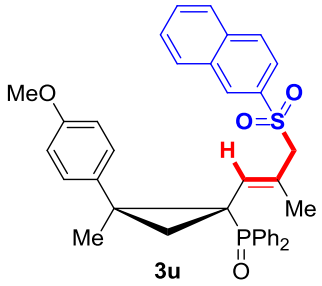
(*E*)-(1-(3-((4-bromophenyl)sulfonyl)-2-methylprop-1-en-1-yl)-2-(4-methoxyphenyl)-2-methyl cyclopropyl)diphenylphosphine oxide (3t)



3t

White solids, *m.p.*: 177.5-178.9℃ (78 mg, 41% yield). TLC (R_f = 0.22, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 11.4, 7.5 Hz, 2H), 7.73 (dd, *J* = 10.8, 8.0 Hz, 2H), 7.61-7.57 (m, 4H), 7.49-7.37 (m, 6H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 5.28 (s, 1H), 3.80 (s, 3H), 3.27 (d, *J* = 13.4 Hz, 1H), 3.09 (dd, *J* = 13.4, 1.6 Hz, 1H), 2.30 (dd, *J* = 13.7, 4.7 Hz, 1H), 1.74 (s, 3H), 1.62-1.57 (m, 1H), 0.93 (d, *J* = 2.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 139.1, 134.3, 133.3, 133.2, 132.6 (d, *J* = 8.7 Hz), 132.4, 131.9 (d, *J* = 2.6 Hz), 131.34, 131.28, 131.25, 131.2 (d, *J* = 2.9 Hz), 129.3, 129.0, 128.9, 128.8 (d, *J* = 11.7 Hz), 127.9 (d, *J* = 11.7 Hz), 113.8, 65.3 (d, *J* = 1.3 Hz), 55.3, 33.3 (d, *J* = 1.5 Hz), 29.9 (d, *J* = 93.9 Hz), 24.2 (d, *J* = 2.0 Hz), 22.3 (d, *J* = 4.0 Hz), 18.2 (d, *J* = 2.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.3 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{33}H_{32}BrNaO_4PS$: 657.0835, Found: 657.0844. **IR** (film) ν 3055, 2959, 2911, 1593, 1436, 1311, 1190, 1146, 1085, 835, 701, 658 cm^{-1}.

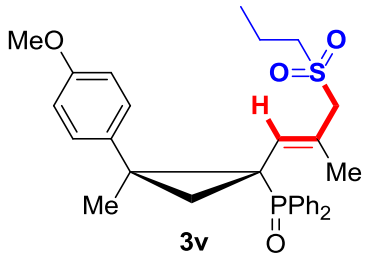
(*E*)-(2-(4-methoxyphenyl)-2-methyl-1-(2-methyl-3-(naphthalen-2-ylsulfonyl)prop-1-en-1-yl)cyclopropyl)diphenylphosphine oxide (3u)



3u

White solids, *m.p.*: 177.2-179.1℃ (73 mg, 41% yield). TLC (R_f = 0.19, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.02-7.88 (m, 5H), 7.77 (dd, *J* = 10.8, 8.0 Hz, 2H), 7.69-7.60 (m, 3H), 7.60-7.55 (m, 2H), 7.49-7.39 (m, 4H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 5.29 (s, 1H), 3.78 (s, 3H), 3.34 (d, *J* = 13.3 Hz, 1H), 3.20 (d, *J* = 13.4 Hz, 1H), 2.30 (dd, *J* = 13.7, 4.7 Hz, 1H), 1.77 (s, 3H), 1.67-1.60 (m, 1H), 0.98 (d, *J* = 2.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 137.2, 135.2, 134.4, 134.2, 133.3 (d, *J* = 15.7 Hz), 133.1 (d, *J* = 4.0 Hz), 132.8, 132.7 (d, *J* = 8.8 Hz), 132.2, 132.1, 131.8 (d, *J* = 2.5 Hz), 131.7 (d, *J* = 7.3 Hz), 131.3 (d, *J* = 9.6 Hz), 131.2 (d, *J* = 2.5 Hz), 129.4 (d, *J* = 12.3 Hz), 129.3, 128.9, 128.7 (d, *J* = 11.6 Hz), 128.0, 127.9, 127.8 (d, *J* = 10.9 Hz), 122.5, 113.8, 65.3, 55.3, 33.2, 30.0 (d, *J* = 93.9 Hz), 24.2 (d, *J* = 2.5 Hz), 22.2 (d, *J* = 4.0 Hz), 18.2 (d, *J* = 2.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.2(s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{37}H_{35}NaO_4PS$: 629.1886, Found: 629.1891. **IR** (film) ν 3051, 2959, 2915, 1609, 1436, 1311, 1178, 1147, 1069, 832, 704 cm^{-1}.

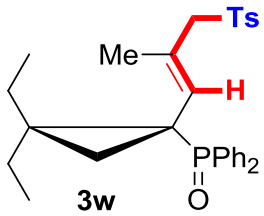
(*E*)-(2-(4-methoxyphenyl)-2-methyl-1-(2-methyl-3-(propylsulfonyl)prop-1-en-1-yl)cyclopropyl)diphenylphosphine oxide (3v)



3v

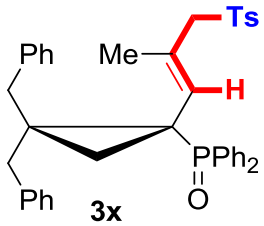
White solids, *m.p.*: 177.9-179.3℃ (74 mg, 47% yield). TLC (R_f = 0.16, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 10.8, 7.8 Hz, 2H), 7.67 (dd, *J* = 10.7, 8.0 Hz, 2H), 7.63-7.56 (m, 3H), 7.46-7.43 (m, 1H), 7.40-7.32 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 5.28 (s, 1H), 3.78 (s, 3H), 3.25 (d, *J* = 14.1 Hz, 1H), 2.94 (dd, *J* = 14.1, 3.7 Hz, 1H), 2.32 (dd, *J* = 13.7, 4.7 Hz, 1H), 2.05 (t, *J* = 7.3 Hz, 2H), 1.66-1.64 (m, 4H), 1.60-1.50 (m, 2H), 1.03 (d, *J* = 2.7 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.2, 134.5 (d, *J* = 34.3 Hz), 133.4, 133.3 (d, *J* = 1.4 Hz), 132.5 (d, *J* = 8.7 Hz), 132.3, 132.0 (d, *J* = 2.6 Hz), 131.8 (d, *J* = 4.1 Hz), 131.3 (d, *J* = 2.6 Hz), 131.2 (d, *J* = 9.5 Hz), 129.1, 128.8 (d, *J* = 11.7 Hz), 127.7 (d, *J* = 11.7 Hz), 113.9, 62.4 (d, *J* = 1.8 Hz), 55.2, 51.9, 33.2 (d, *J* = 1.7 Hz), 29.9 (d, *J* = 93.9 Hz), 24.3 (d, *J* = 2.4 Hz), 22.6 (d, *J* = 4.1 Hz), 17.8 (d, *J* = 2.2 Hz), 15.11, 13.01. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.2 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{30}H_{35}NaO_4PS$: 545.1886, Found: 545.1892. **IR** (film) ν 3063, 2955, 2903, 1614, 1515, 1312, 1252, 1175, 1146, 1027, 837, 725 cm^{-1}.

(*E*)-(2,2-diethyl-1-(2-methyl-3-tosylprop-1-en-1-yl)cyclopropyl)diphenylphosphine oxide (3w)



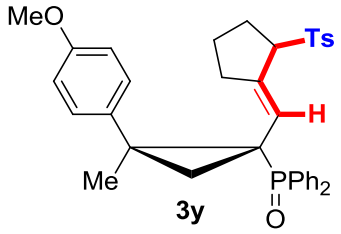
White solids, *m.p.*: 189.8-190.4℃ (84 mg, 55% yield). TLC (R_f = 0.21, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.81 (m, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.58-7.52 (m, 4H), 7.51-7.46 (m, 2H), 7.45-7.38 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.62 (s, 1H), 3.60 (d, *J* = 13.5 Hz, 1H), 3.35 (dd, *J* = 13.5, 3.3 Hz, 1H), 2.43 (s, 3H), 2.00-1.91 (m, 2H), 1.64-1.59 (m, 2H), 0.94-0.86 (m, 7H), 0.85-0.81 (m, 3H), 0.69-0.63 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.7, 136.3, 133.5 (d, *J* = 8.5 Hz), 132.7 (d, *J* = 7.8 Hz), 131.8 (d, *J* = 3.6 Hz), 131.7 (d, *J* = 1.7 Hz), 131.5 (d, *J* = 2.2 Hz), 131.4, 131.1 (d, *J* = 2.2 Hz), 129.9, 129.7, 128.5 (d, *J* = 11.7 Hz), 128.0, 127.4 (d, *J* = 11.8 Hz), 65.9 (d, *J* = 1.3 Hz), 34.2 (d, *J* = 1.3 Hz), 29.7 (d, *J* = 1.1 Hz), 25.7, 25.0 (d, *J* = 1.8 Hz), 22.1 (d, *J* = 4.4 Hz), 21.6, 17.5, 11.0, 10.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.3 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{30}H_{36}O_3PS$: 507.2117, Found: 507.2114. **IR** (film) ν 3055, 2959, 2907, 2871, 1589, 1434, 1317, 1245, 1175, 1154, 1086, 849, 726 cm^{-1}.

(*E*)-(2,2-dibenzyl-1-(2-methyl-3-tosylprop-1-en-1-yl)cyclopropyl)diphenylphosphine oxide (3x)



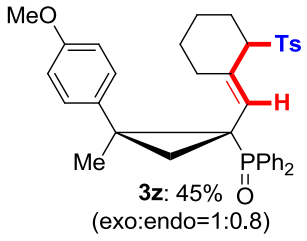
White solids, *m.p.*: 202.2-203.6℃ (112 mg, 59% yield). TLC (R_f = 0.36, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85-7.77 (m, 3H), 7.75-7.73 (m, 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.59-7.47 (m, 3H), 7.43-7.39 (m, 4H), 7.22-7.17 (m, 6H), 7.10 (d, *J* = 7.2 Hz, 2H), 6.90 (d, *J* = 7.2 Hz, 2H), 5.86 (s, 1H), 3.70 (d, *J* = 15.0 Hz, 1H), 3.63 (d, *J* = 13.4 Hz, 1H), 3.46 (dd, *J* = 13.4, 2.9 Hz, 1H), 2.84 (dd, *J* = 21.9, 15.4 Hz, 2H), 2.48 (dd, *J* = 15.5, 4.5 Hz, 2H), 2.25 (s, 3H), 2.18 (d, *J* = 15.6 Hz, 1H), 1.13-1.02 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.0 (d, *J* = 2.5 Hz), 140.0 (d, *J* = 1.7 Hz), 138.6 (d, *J* = 1.9 Hz), 136.4 (d, *J* = 2.1 Hz), 134.2 (dd, *J* = 8.9, 2.3 Hz), 133.3 (d, *J* = 28.5 Hz), 132.7 (d, *J* = 7.8 Hz), 132.3 (d, *J* = 22.7 Hz), 131.9, 131.8, 131.4, 130.0 (d, *J* = 2.0 Hz), 129.7 (d, *J* = 2.2 Hz), 129.5, 128.7 (dd, *J* = 11.6, 1.7 Hz), 128.3, 128.1 (d, *J* = 2.4 Hz), 128.0 (d, *J* = 2.4 Hz), 127.9 (d, *J* = 2.0 Hz), 127.8 (d, *J* = 11.11 Hz), 126.2, 125.8 (d, *J* = 1.3 Hz), 66.2, 39.0, 35.2, 33.0, 29.5 (d, *J* = 90.9 Hz), 25.3, 21.5 (d, *J* = 2.7 Hz), 17.8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.6 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{40}H_{40}O_3PS$: 631.2430, Found: 631.2422. **IR** (film) ν 3063, 2959, 2907, 1597, 1435, 1317, 1175, 1147, 1087, 812, 726 cm^{-1}.

(*E*)-(2-(4-methoxyphenyl)-2-methyl-1-((2-tosylcyclopentylidene)methyl)cyclopropyl)diphenyl phosphine oxide (3y)



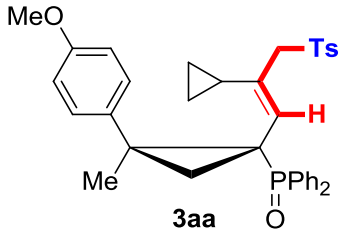
White solids, *m.p.*: 224.5-226.3℃ (56 mg, 31% yield). TLC (R_f = 0.18, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 10.3, 8.0 Hz, 2H), 7.66-7.61 (m, 5H), 7.38-7.36 (m, 3H), 7.33-7.28 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.03 (s, 1H), 3.75 (s, 3H), 3.52-3.42 (m, 1H), 2.38 (s, 3H), 2.22 (dd, *J* = 14.4, 4.4 Hz, 1H), 1.61 (s, 3H), 1.56-1.38 (m, 4H), 1.07-0.97 (m, 1H), 0.92-0.83 (m, 1H), 0.22-0.09 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 144.2, 142.6 (d, *J* = 9.2 Hz), 135.3 (d, *J* = 1.3 Hz), 134.6 (d, *J* = 6.4 Hz), 134.4, 133.6 (d, *J* = 2.0 Hz), 132.3 (d, *J* = 8.6 Hz), 131.9 (d, *J* = 2.6 Hz), 131.2 (d, *J* = 9.5 Hz), 131.0 (d, *J* = 2.7 Hz), 129.5, 129.3, 129.1, 128.8 (d, *J* = 11.7 Hz), 127.4 (d, *J* = 11.7 Hz), 127.2 (d, *J* = 4.3 Hz), 114.3, 69.0 (d, *J* = 1.8 Hz), 55.4, 33.2 (d, *J* = 1.1 Hz), 31.8 (d, *J* =92.9 Hz), 30.7 (d, *J* = 2.4 Hz), 27.7, 23.8 (d, *J* = 2.1 Hz), 23.6 (d, *J* = 4.5 Hz), 22.9, 21.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.1 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{36}H_{37}NaO_4PS$: 619.2042, Found: 619.2032. **IR** (film) ν 3055, 2947, 2915, 1598, 1513, 1435, 1296, 1246, 1177, 1135, 1085, 835, 705 cm^{-1}.

(*E*)-(2-(4-methoxyphenyl)-2-methyl-1-((2-tosylcyclohexylidene)methyl)cyclopropyl)diphenyl phosphine oxide (3z)



(82 mg, 45% for *exo*- and *endo*- isomers in total), **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{37}H_{39}NaO_4PS$: 633.2199, Found: 633.2206. The H-*exo* and H-*endo* isomers cannot be isolated by flash column, even for preparative HPLC. However, the ratio of these two compounds can be determined by ^{1}HNMR, see Page 124.

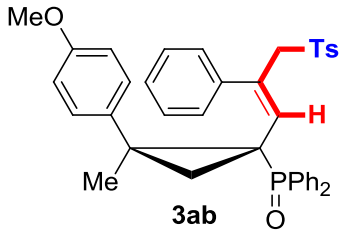
(*E*)-(1-(2-cyclopropyl-3-tosylprop-1-en-1-yl)-2-(4-methoxyphenyl)-2-methylcyclopropyl)diphenylphosphine oxide (3aa)



White solids, *m.p.*: 187.6-189.5℃ (117 mg, 65% yield). TLC (R_f = 0.15, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11-8.06 (m, 2H), 7.89-7.80 (m, 2H), 7.63-7.61 (m, 3H), 7.45-7.37 (m, 5H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.60 (d,

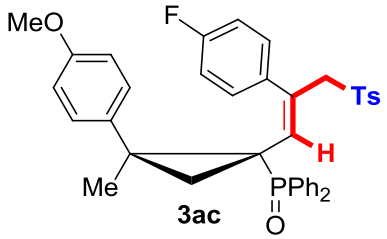
J = 2.0 Hz, 1H), 3.79 (s, 3H), 2.76 (d, *J* = 14.0 Hz, 1H), 2.64 (dd, *J* = 14.0, 2.2 Hz, 1H), 2.42 (s, 3H), 2.30 (dd, *J* = 13.8, 4.7 Hz, 1H), 1.90-1.84 (m, 1H), 1.72 (s, 3H), 1.20-1.08 (m, 1H), 0.48-0.35 (m, 1H), 0.00-(-0.12) (m, 2H), (-0.19)-(-0.26) (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 144.5, 137.3, 134.71 (d, *J* = 0.8 Hz), 134.66, 133.8 (d, *J* = 8.0 Hz), 133.6 (d, *J* = 17.7 Hz), 132.54 (d, *J* = 8.8 Hz), 132.45 (d, *J* = 3.7 Hz), 131.7 (d, *J* = 2.4 Hz), 131.2 (d, *J* = 9.4 Hz), 131.1 (d, *J* = 2.6 Hz), 129.7, 129.1, 128.7 (d, *J* = 11.7 Hz), 127.82 (d, *J* = 11.6 Hz), 127.79, 113.8, 56.4, 55.3, 33.7 (d, *J* = 1.3 Hz), 29.9 (d, *J* = 92.9 Hz), 24.3 (d, *J* = 2.1 Hz), 22.5(d, *J* = 4.0 Hz), 21.6, 12.4 (d, *J* = 1.9 Hz), 4.7, 4.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.4 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{36}H_{37}NaO_4PS$: 619.2042, Found: 619.2035. **IR** (film) ν 3051, 2959, 2915, 1589, 1433, 1312, 1246, 1181, 1146, 1086, 1030, 831, 722 cm^{-1}.

(*E*)-(2-(4-methoxyphenyl)-2-methyl-1-(2-phenyl-3-tosylprop-1-en-1-yl)cyclopropyl)diphenylphosphine oxide (3ab)



White solids, *m.p.*: 178.9-180.3℃ (78 mg, 41% yield). TLC (R_f = 0.16, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10-8.04 (m, 4H), 7.70-7.61 (m, 6H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.05-7.01 (m, 1H), 6.96-6.87 (m, 6H), 6.82 (d, *J* = 8.3 Hz, 2H), 5.92 (d, *J* = 7.6 Hz, 2H), 5.78 (s, 1H), 3.82 (s, 3H), 3.63 (d, *J* = 13.9 Hz, 1H), 3.40 (d, *J* = 14.0 Hz, 1H), 2.26 (s, 3H), 1.78 (s, 3H), 1.70 (dd, *J* = 13.9, 5.8 Hz, 1H), 0.86-0.83 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 144.0, 137.0 (d, *J* = 1.8 Hz), 136.4, 134.7 (d, *J* = 0.8 Hz), 134.1, 133.6 (d, *J* = 6.6 Hz), 133.3, 133.0 (d, *J* = 8.7 Hz), 132.2, 132.1, 132.0 (d, *J* = 2.8 Hz), 131.58 (d, *J* = 10.1 Hz), 131.57 (d, *J* = 3.03 Hz), 129.3, 129.2, 129.0 (d, *J* = 11.7 Hz), 128.6 (d, *J* = 11.7 Hz), 127.9, 127.6, 127.3, 113.3, 65.4, 55.3, 38.2 (d, *J* = 2.6 Hz), 30.6 (d, *J* = 94.9 Hz), 22.9 (d, *J* = 3.4 Hz), 21.4, 21.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.2 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{39}H_{37}NaO_4PS$: 655.2042, Found: 655.2052. **IR** (film) ν 3055, 2947, 2907, 1601, 1513, 1436, 1311, 1176, 1156, 1027, 830, 712 cm^{-1}.

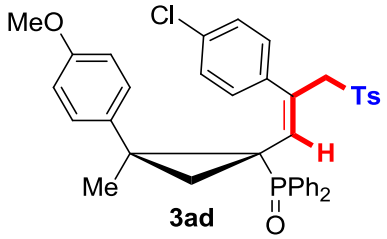
(*E*)-(1-(2-(4-fluorophenyl)-3-tosylprop-1-en-1-yl)-2-(4-methoxyphenyl)-2-methylcyclopropyl) diphenylphosphine oxide (3ac)



White solids, *m.p.*: 189.8-191.7℃ (74 mg, 38% yield). TLC (R_f = 0.27, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13-8.01 (m, 4H), 7.67-7.65 (m, 6H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.98-6.93 (m, 4H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.61-6.57 (m, 2H), 5.87-5.84 (m, 2H), 5.78 (s, 1H), 3.81 (s, 3H), 3.57 (d, *J* = 14.0 Hz, 1H), 3.39 (d, *J* = 13.9 Hz, 1H), 2.29 (s, 3H), 1.80 (s, 3H), 1.73 (dd, *J* = 13.9, 5.8 Hz, 1H), 0.85-0.80 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.9 (d, *J* = 249.47 Hz), 158.1,

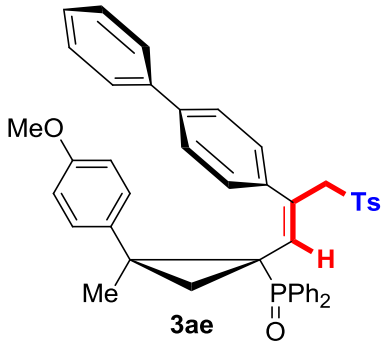
144.3, 136.4, 134.7 (d, *J* = 0.7 Hz), 134.7, 134.0 (d, *J* = 6.5 Hz), 133.9, 133.0 (d, *J* = 8.7 Hz), 132.9 (d, *J* = 26.3 Hz), 132.1, 131.9 (d, *J* = 37.4 Hz), 131.6 (d, *J* = 10.1 Hz), 130.9 (d, *J* = 10.1 Hz), 129.6 (d, *J* = 7.8 Hz), 129.3, 129.2, 129.0 (d, *J* = 11.8 Hz), 128.6 (d, *J* = 11.7 Hz), 127.9, 114.6 (d, *J* = 21.2 Hz), 113.4, 65.5, 55.3, 38.4 (d, *J* = 2.7 Hz), 31.5 (d, *J* = 94.9 Hz), 22.9 (d, *J* = 3.3 Hz), 21.4, 21.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.3 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{39}H_{37}FO_4PS$: 651.2129, Found: 651.2124. **IR** (film) ν 3055, 2959, 2927, 1597, 1511, 1433, 1313, 1248, 1181, 1148, 1081, 844, 704 cm^{-1}.

(*E*)-(1-(2-(4-chlorophenyl)-3-tosylprop-1-en-1-yl)-2-(4-methoxyphenyl)-2-methylcyclopropyl) diphenylphosphine oxide (3ad)



White solids, *m.p.*: 199.6-200.5℃ (80 mg, 40% yield). TLC (R_f = 0.21, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11-8.02 (m, 4H), 7.67-7.64 (m, 6H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.98-6.91 (m, 4H), 6.86-6.80 (m, 4H), 5.80(s, 1H), 5.78 (s, 2H), 3.80 (s, 3H), 3.57 (d, *J* = 14.1 Hz, 1H), 3.38 (d, *J* = 14.0 Hz, 1H), 2.30 (s, 3H), 1.81 (s, 3H), 1.74 (dd, *J* = 13.8, 5.8 Hz, 1H), 0.88-0.83 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.2, 144.4, 136.3, 135.28 (d, *J* = 1.8 Hz), 134.7, 134.3 (d, *J* = 6.4 Hz), 133.8, 133.4, 133.0 (d, *J* = 8.8 Hz), 132.8, 132.1 (d, *J* = 2.5 Hz), 132.0, 131.7 (d, *J* = 2.4 Hz), 131.6 (d, *J* = 9.8 Hz), 130.8 (d, *J* = 10.2 Hz), 129.3, 129.2, 129.0 (d, *J* = 11.7 Hz), 128.7 (d, *J* = 11.8 Hz), 127.9, 127.8, 113.4, 65.3, 55.3, 38.6 (d, *J* = 2.7 Hz), 31.5 (d, *J* = 94.9 Hz), 22.9 (d, *J* = 3.2 Hz), 21.5, 21.3 (d, *J* = 1.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.2 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{39}H_{37}ClO_4PS$: 667.1833, Found: 667.1832. **IR** (film) ν 3051, 2959, 2927, 1609, 1433, 1303, 1248, 1181, 1148, 1087, 839, 708, 669 cm^{-1}.

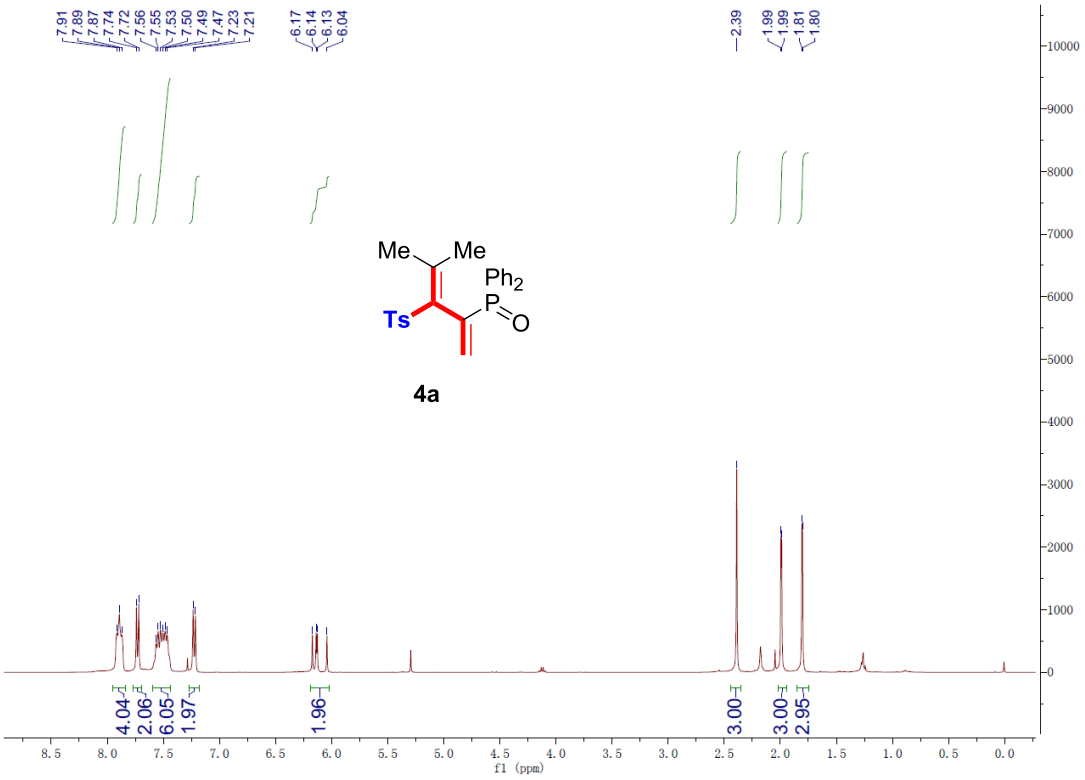
(*E*)-(1-(2-([1,1'-biphenyl]-4-yl)-3-tosylprop-1-en-1-yl)-2-(4-methoxyphenyl)-2-methylcyclopropyl)diphenylphosphine oxide (3ae)

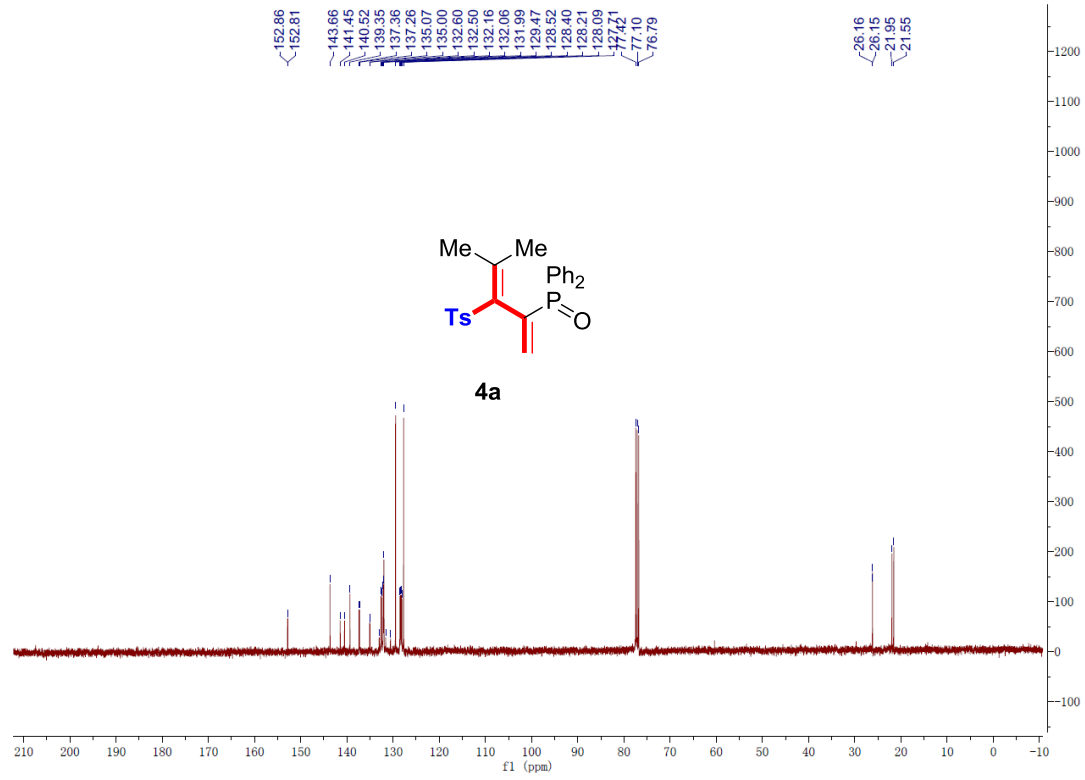


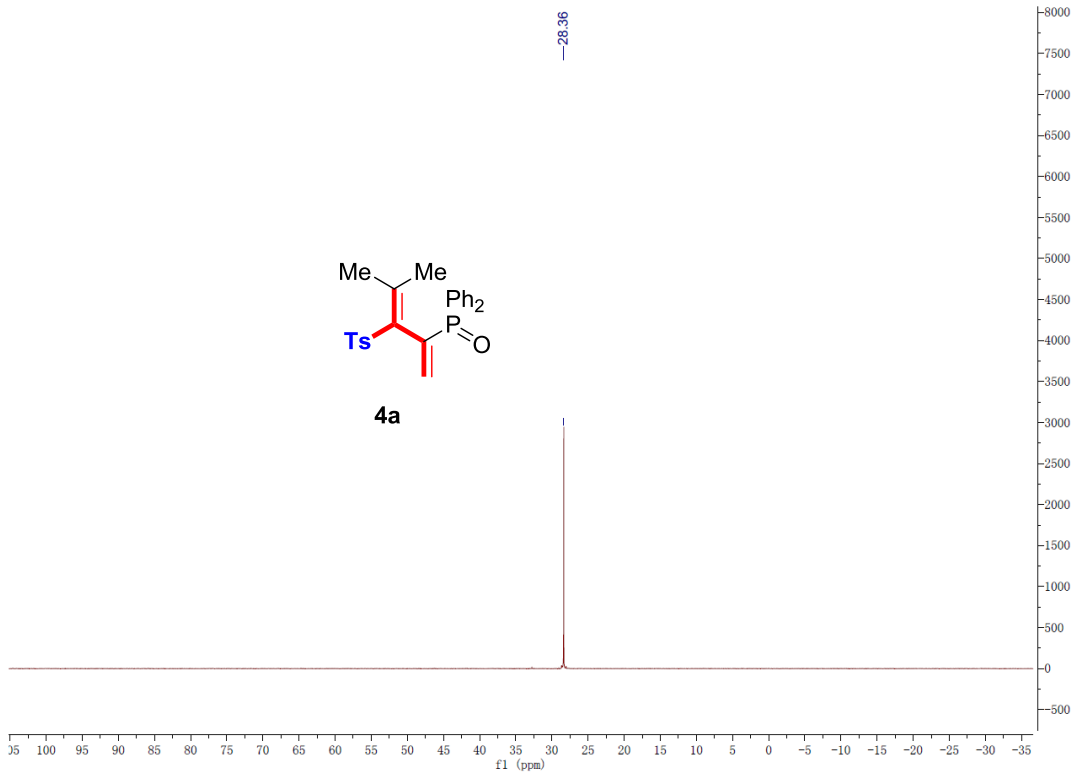
White solids, *m.p.*: 172.8-174.1℃ (70 mg, 33% yield). TLC (R_f = 0.26, petroleum ether/ethyl acetate=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12-8.08 (m, 4H), 7.73-7.63 (m, 6H), 7.50-7.44 (m, 4H), 7.39-7.34 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 5.99 (d, *J* = 8.0 Hz, 2H), 5.80 (s, 1H), 3.84 (s, 3H), 3.70 (d, *J* = 14.1 Hz, 1H), 3.44 (d, *J* = 14.1 Hz, 1H), 2.17 (s, 3H), 1.82 (s, 3H), 1.77 (dd, *J* = 14.1, 5.9 Hz, 1H),

1.01-0.97 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 144.0, 140.2 (d, *J* = 11.0 Hz), 136.4, 135.6 (d, *J* = 1.8 Hz), 134.7, 134.1 (d, *J* = 2.7 Hz), 133.6 (d, *J* = 6.5 Hz), 133.2 (d, *J* = 16.7 Hz), 133.1 (d, *J* = 8.8 Hz), 132.2, 132.0 (d, *J* = 2.3 Hz), 131.8 (d, *J* = 10.2 Hz), 131.60 (d, *J* = 2.6 Hz), 131.59 (d, *J* = 9.7 Hz), 129.3, 129.2, 129.0 (d, *J* = 11.7 Hz), 128.8, 128.6 (d, *J* = 11.9 Hz), 128.4, 128.0, 127.5, 126.9, 126.2, 113.3, 65.4, 55.3, 38.5 (d, *J* = 2.5 Hz), 31.7 (d, *J* = 95.9 Hz), 29.7, 22.9 (d, *J* = 3.4 Hz), 21.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.3 (d, *J* = 4.4 Hz). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{45}H_{42}O_4PS$: 709.2536, Found: 709.2537. **IR** (film) ν 3056, 2952, 2919, 1602, 1513, 1436, 1246, 1186, 1116, 1030, 833, 722 cm^{-1}.

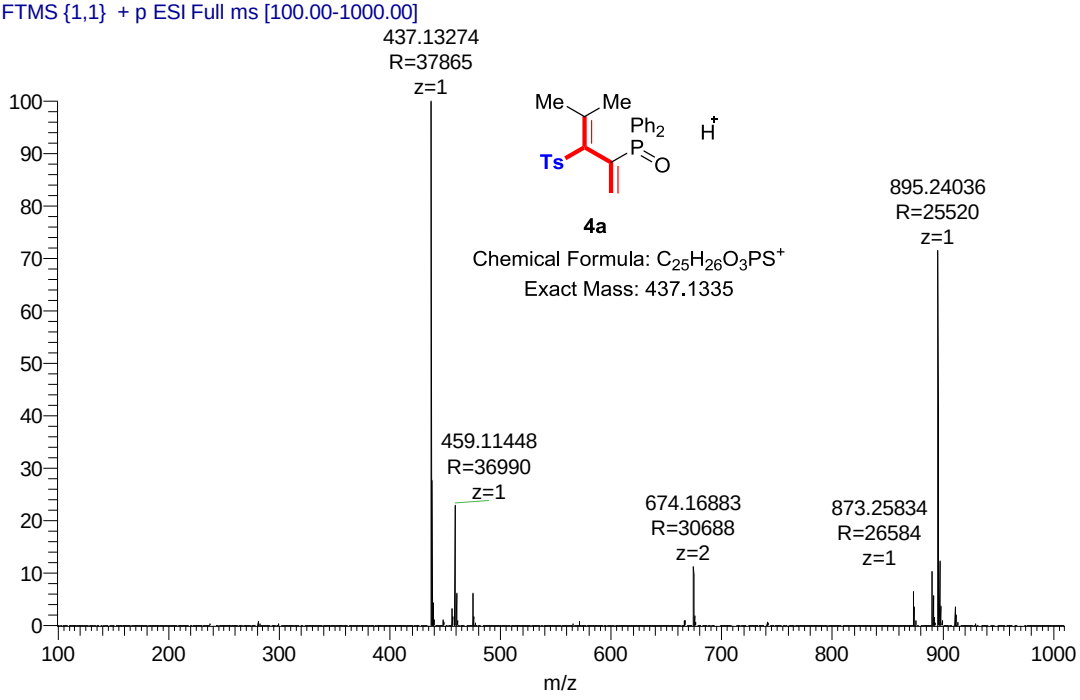
8. ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR and HRMS Spectra

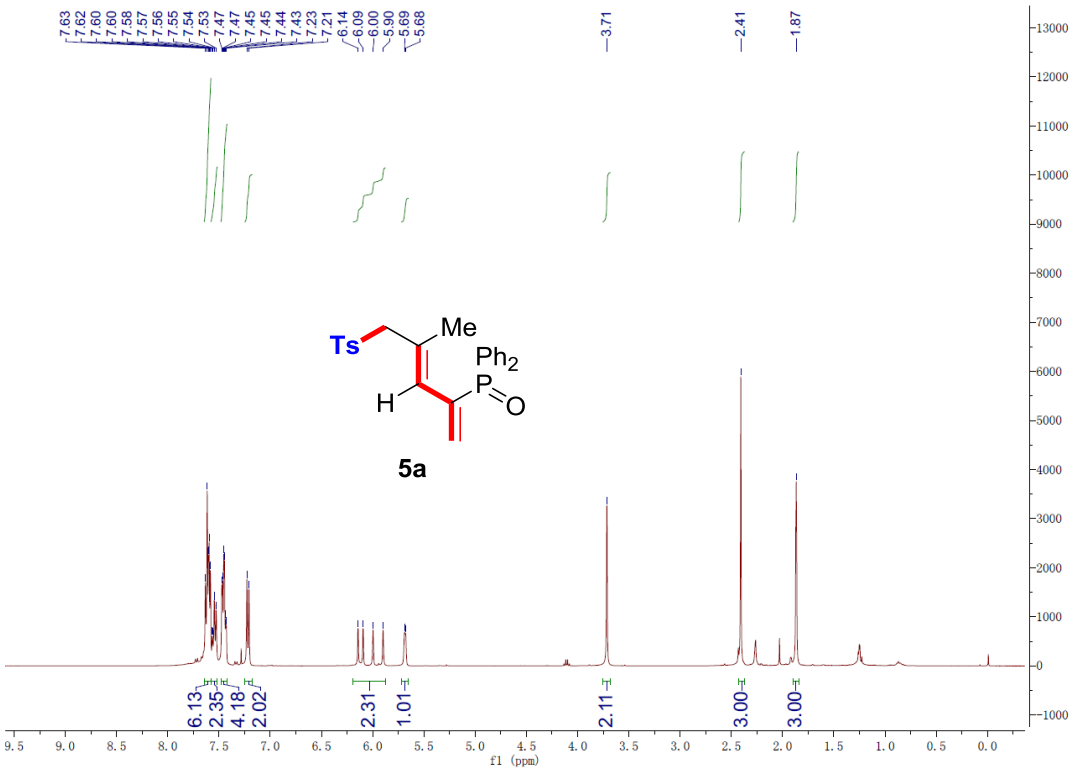


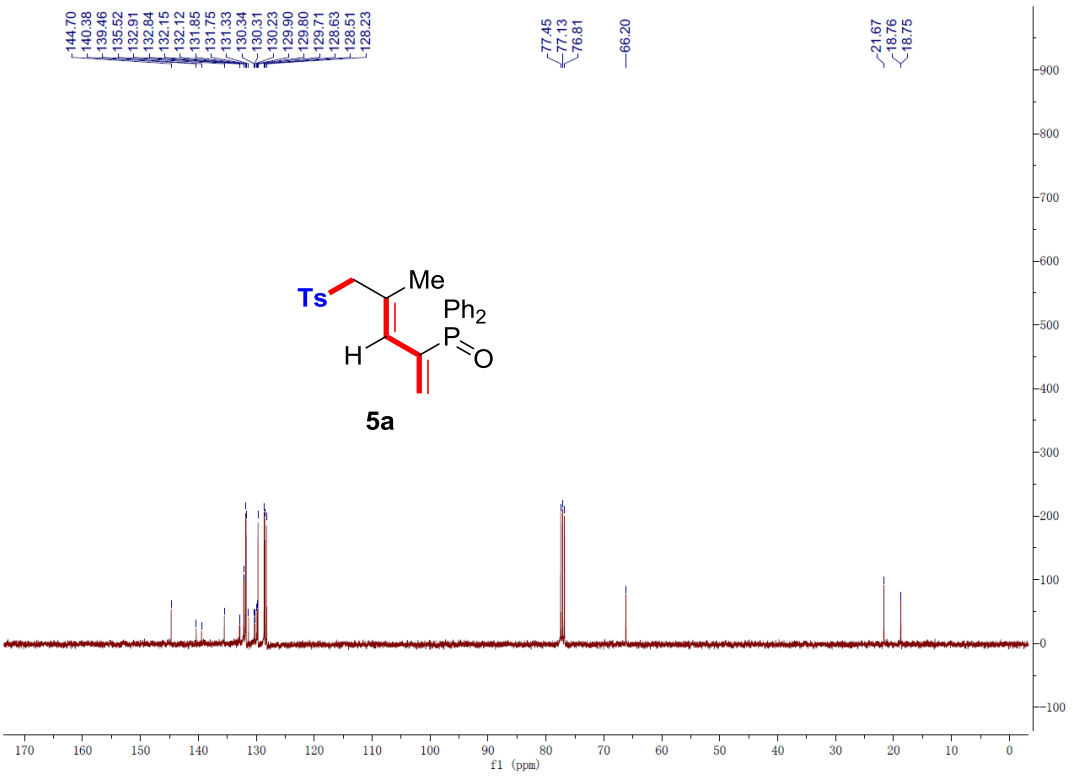


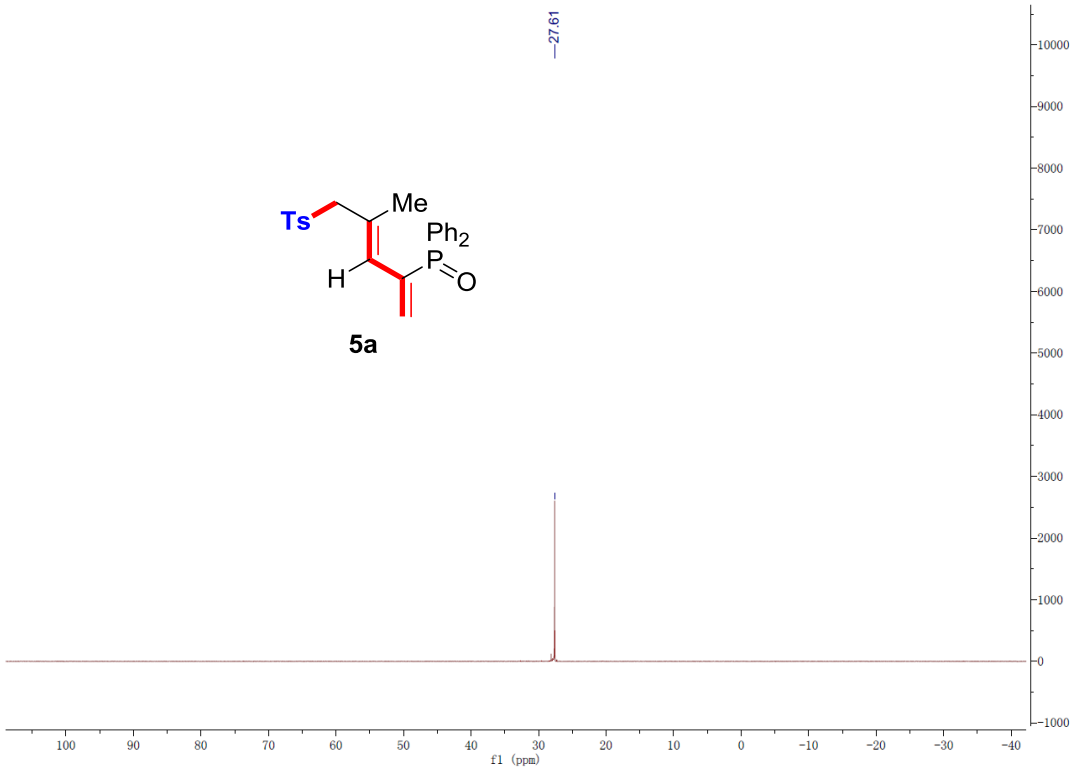


20170505-42_170506141734 #29-34 RT: 0.29-0.33 AV: 6 NL: 1.94E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

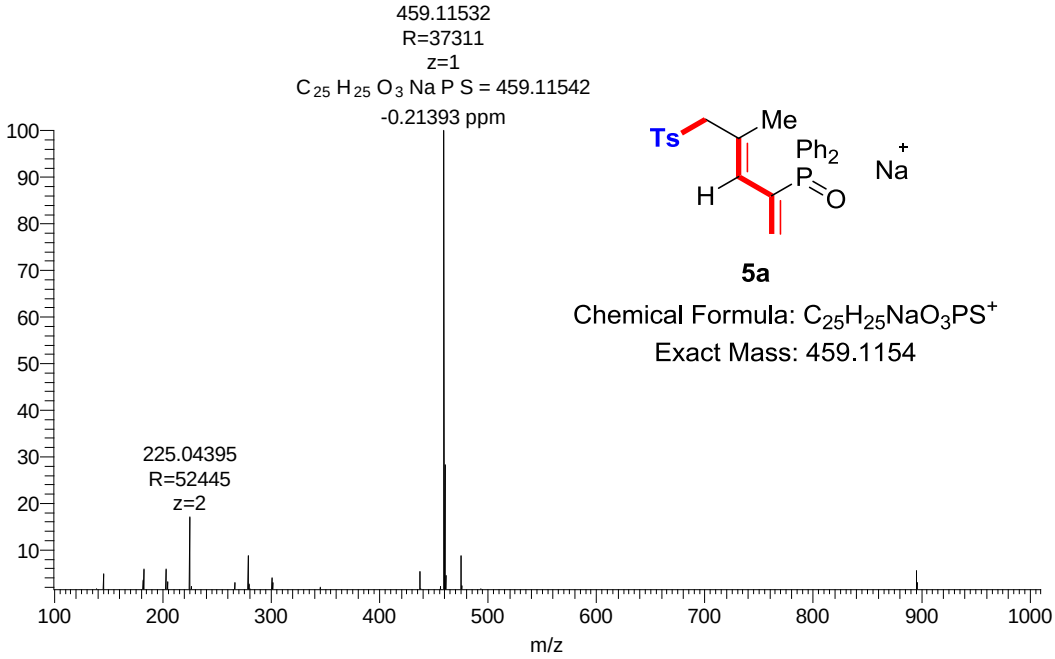


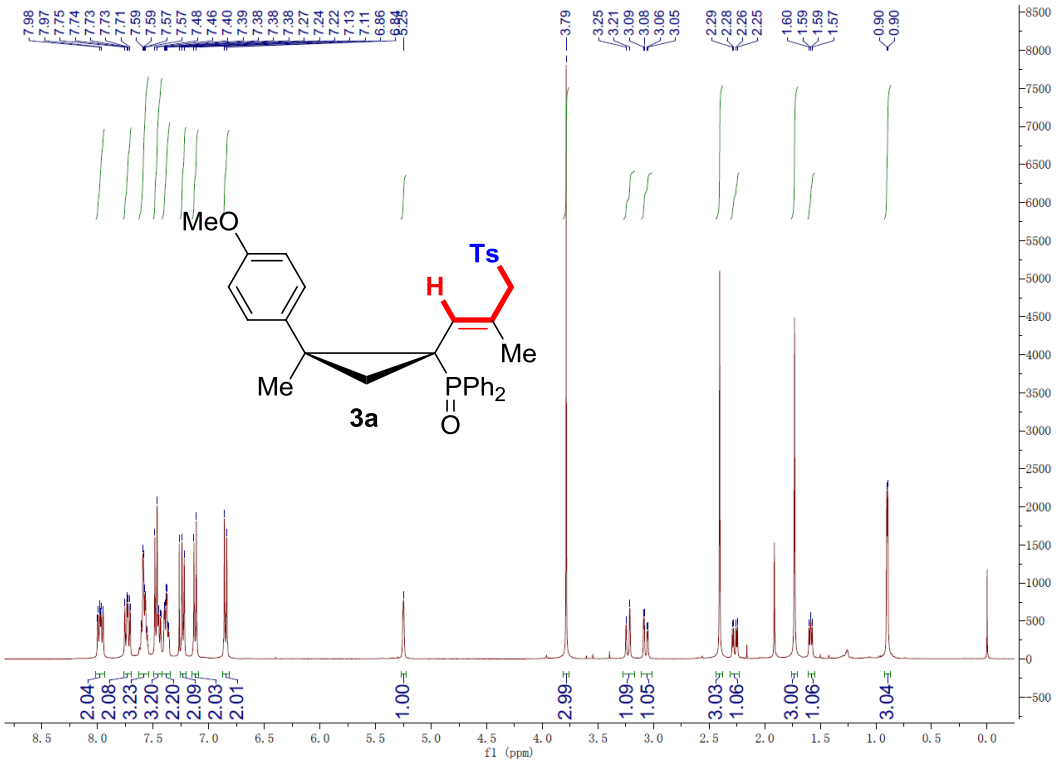

7.63
7.62
7.60
7.60
7.58
7.57
7.56
7.55
7.54
7.53
7.47
7.47
7.45
7.45
7.44
7.43
7.23
7.21
6.14
6.09
6.00
5.90
5.69
5.68
3.71
2.41
1.87
Ts
Me
Ph2
P
O
H
5a
6.13
2.35
4.18
2.02
2.31
1.01
2.11
3.00
3.00
f1 (ppm)

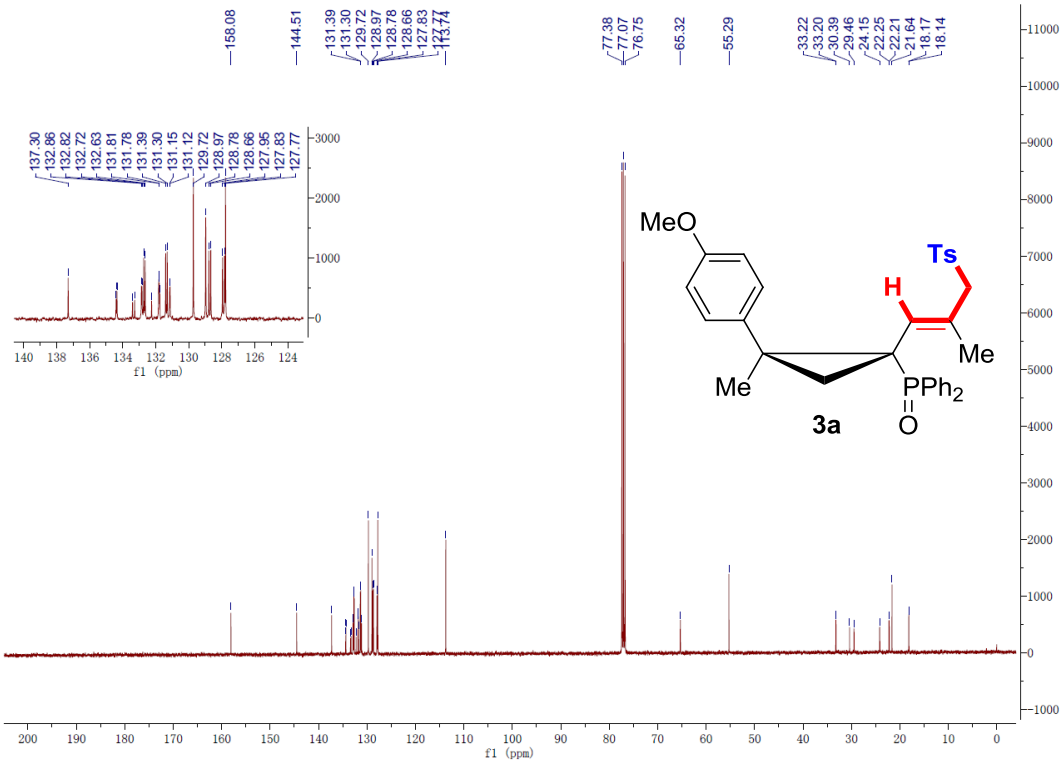

144.70
140.38
139.46
135.52
132.91
132.84
132.15
132.12
131.85
131.75
131.33
130.34
130.31
130.23
129.90
129.80
129.71
128.63
128.51
128.23
77.45
77.13
76.81
66.20
21.67
18.76
18.75
Ts
Me
Ph2
P
O
H
5a
f1 (ppm)

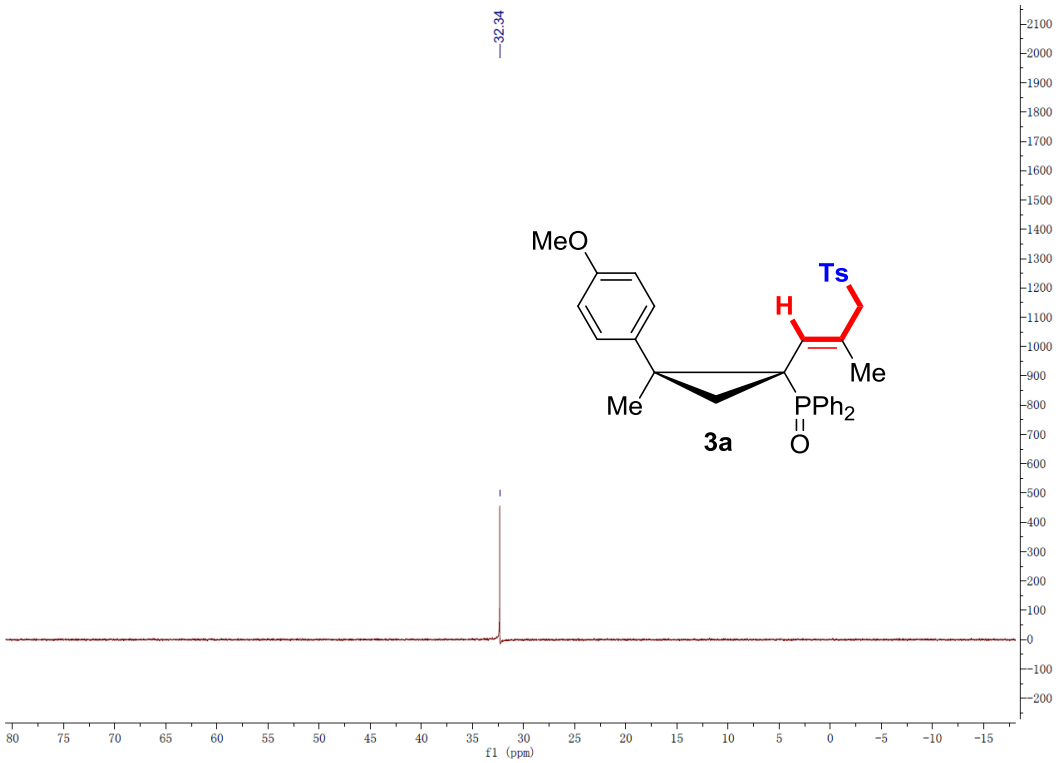


njny-20170904-11 #60-61 RT: 0.49-0.50 AV: 2 NL: 1.38E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

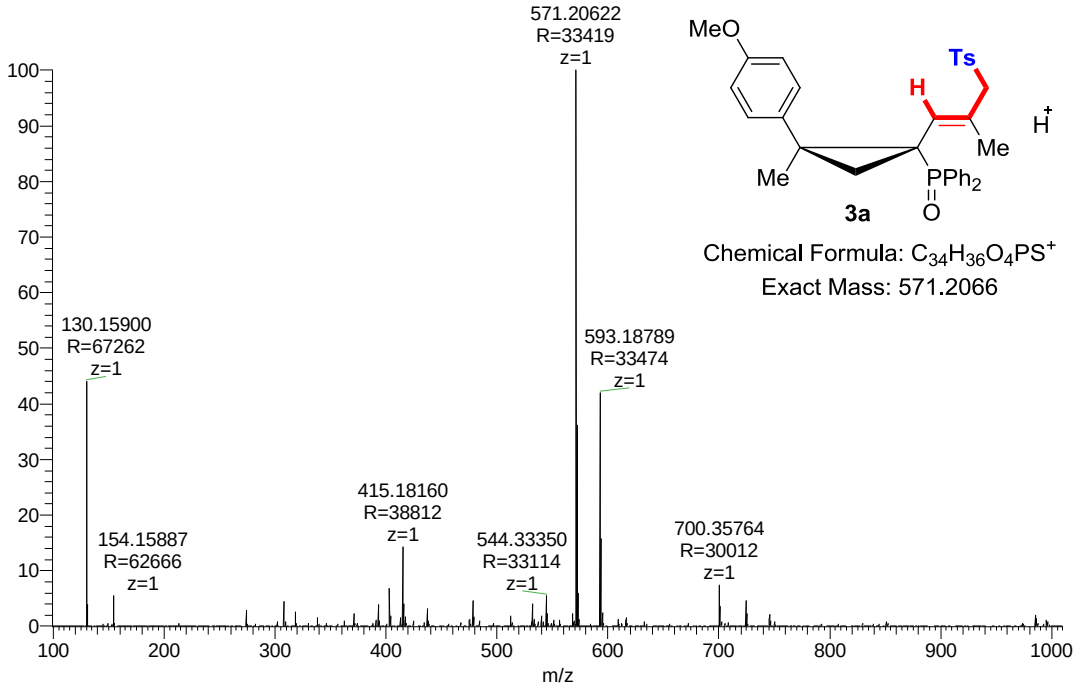


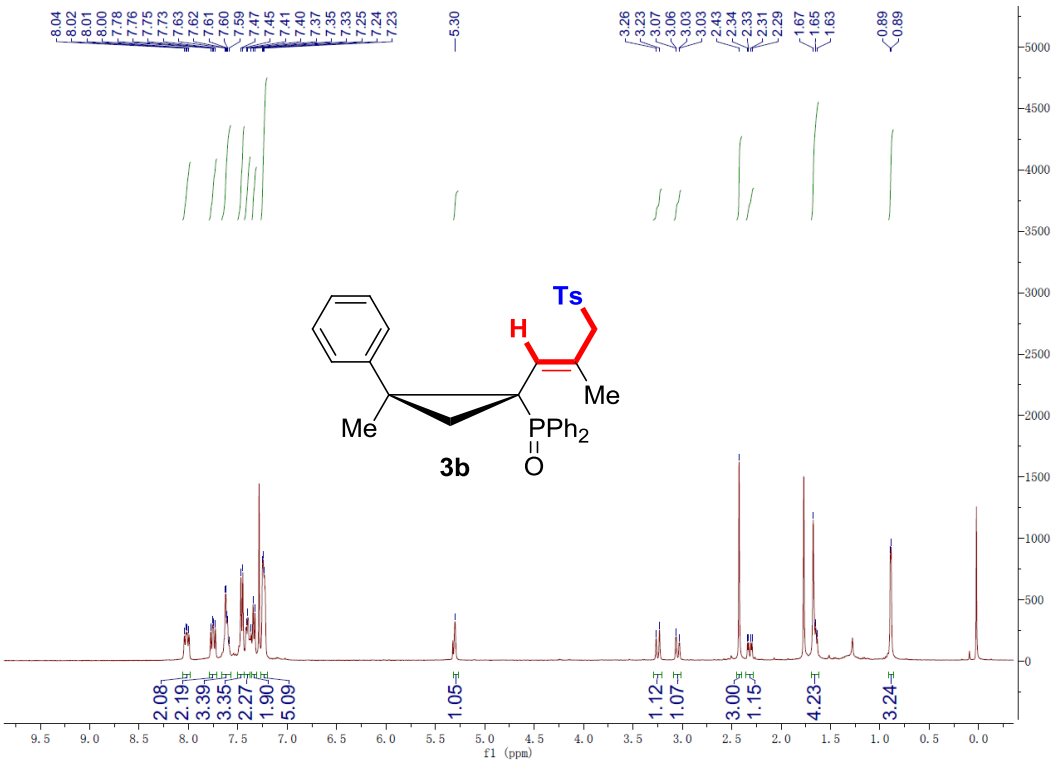

MeO
Ts
H
Me
Me
PPh2
O
3a
f1 (ppm)

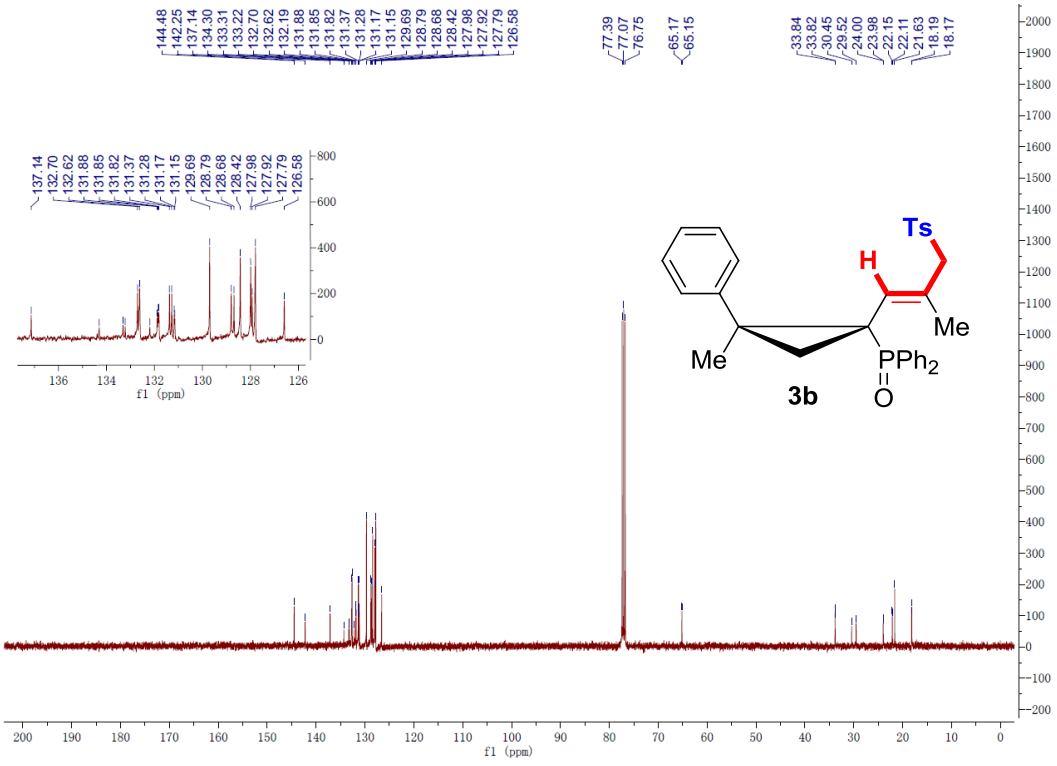

MeO
Ts
H
Me
Me
PPh2
O
3a
f1 (ppm)

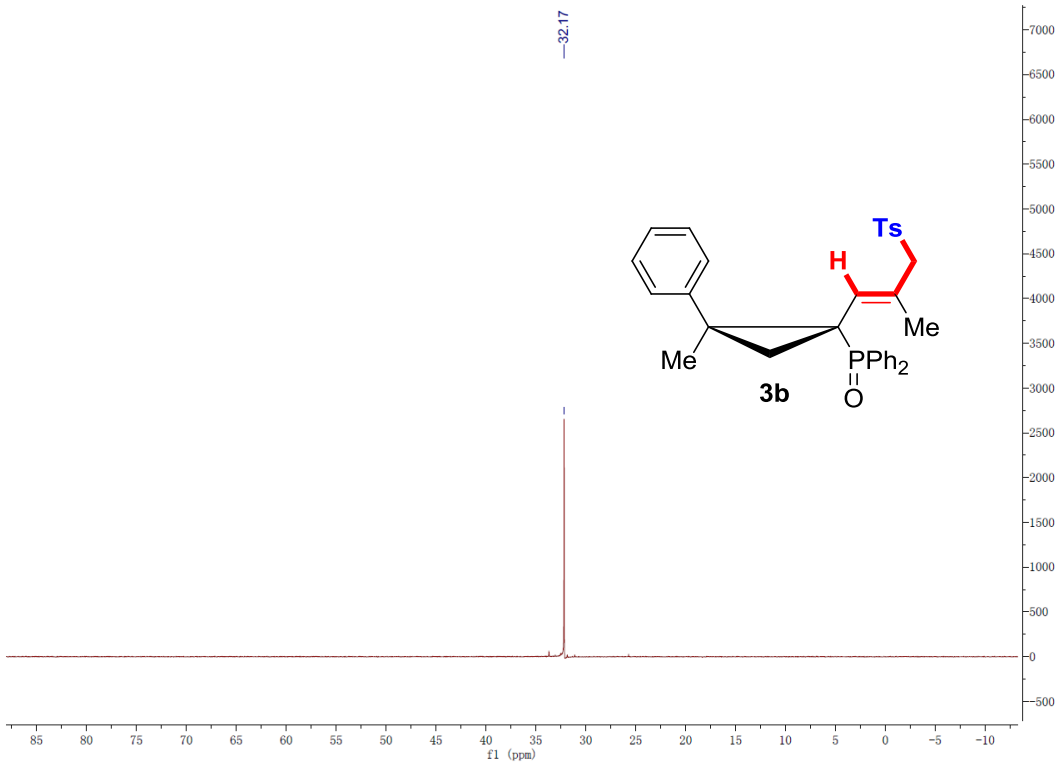


NJNY-20160115-1 #15-16 RT: 0.15-0.16 AV: 2 NL: 1.03E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

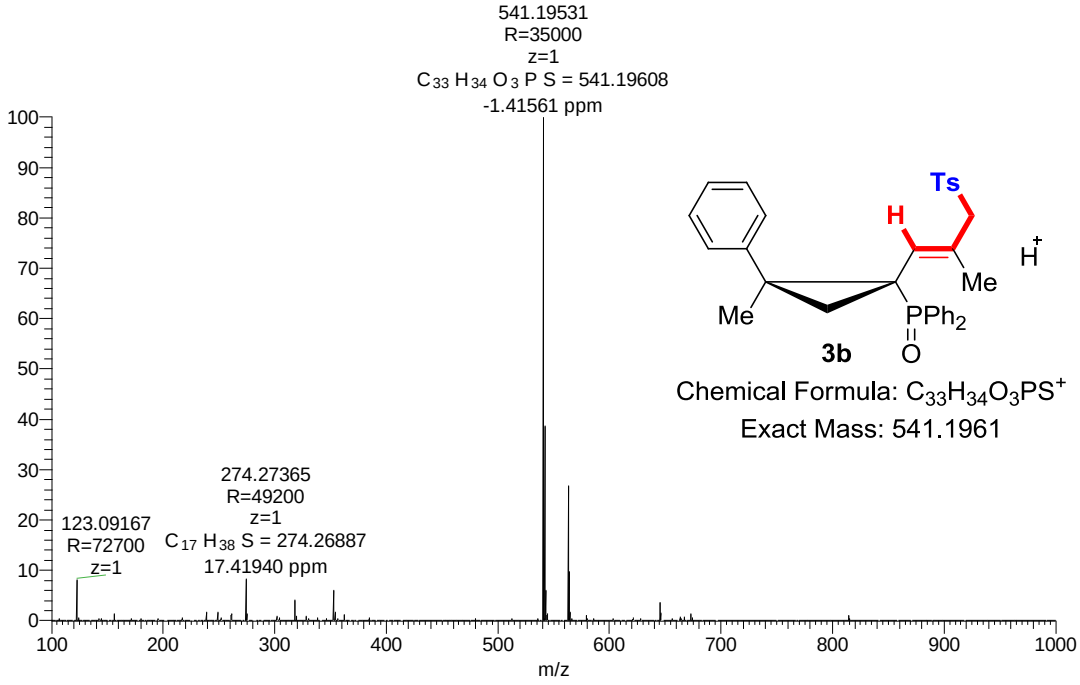


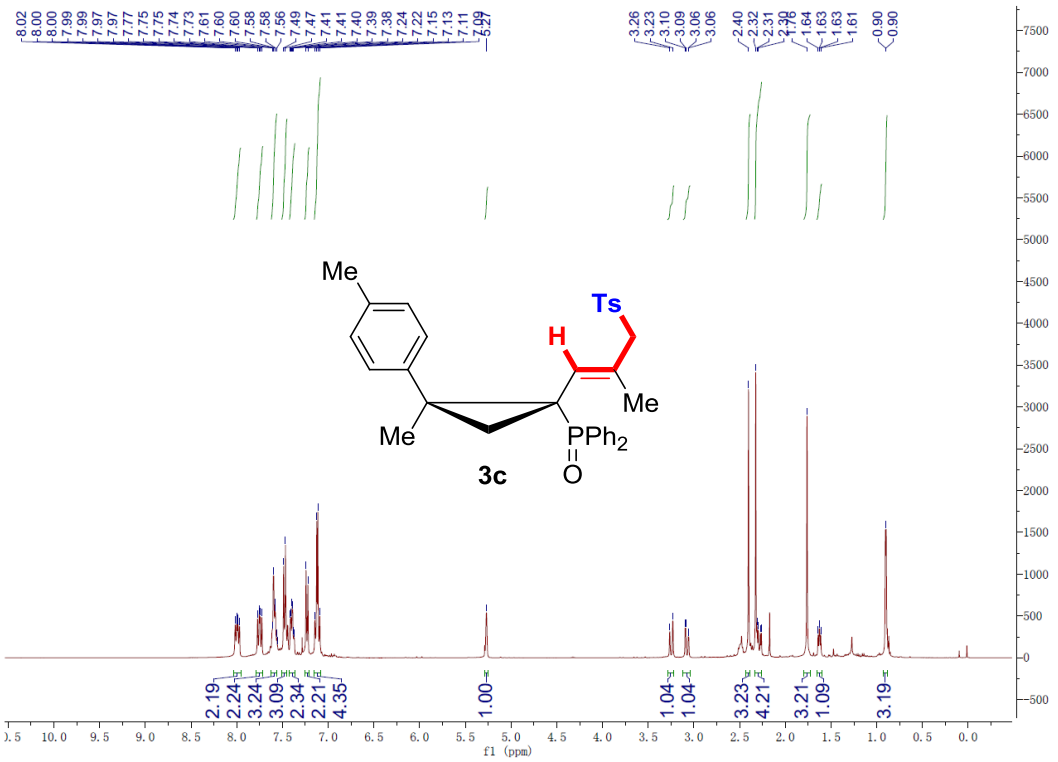

Ts
H
Me
Me
PPh2
O
3b
f1 (ppm)

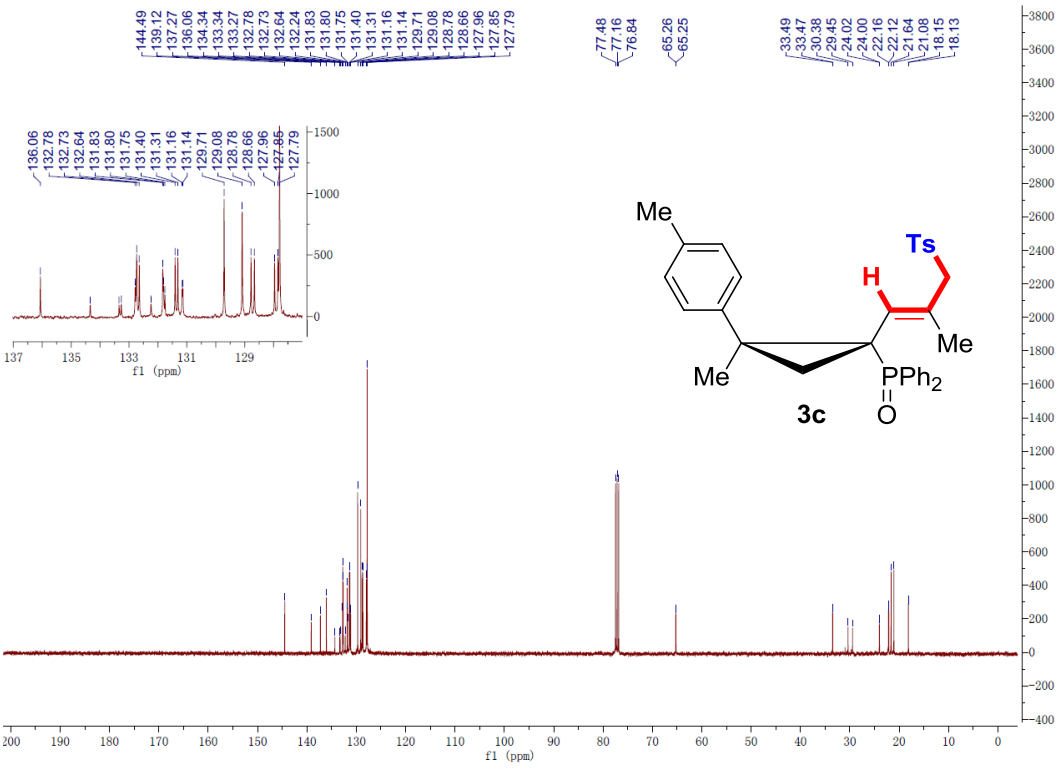

Ts
H
Me
Me
PPh2
O
3b
f1 (ppm)

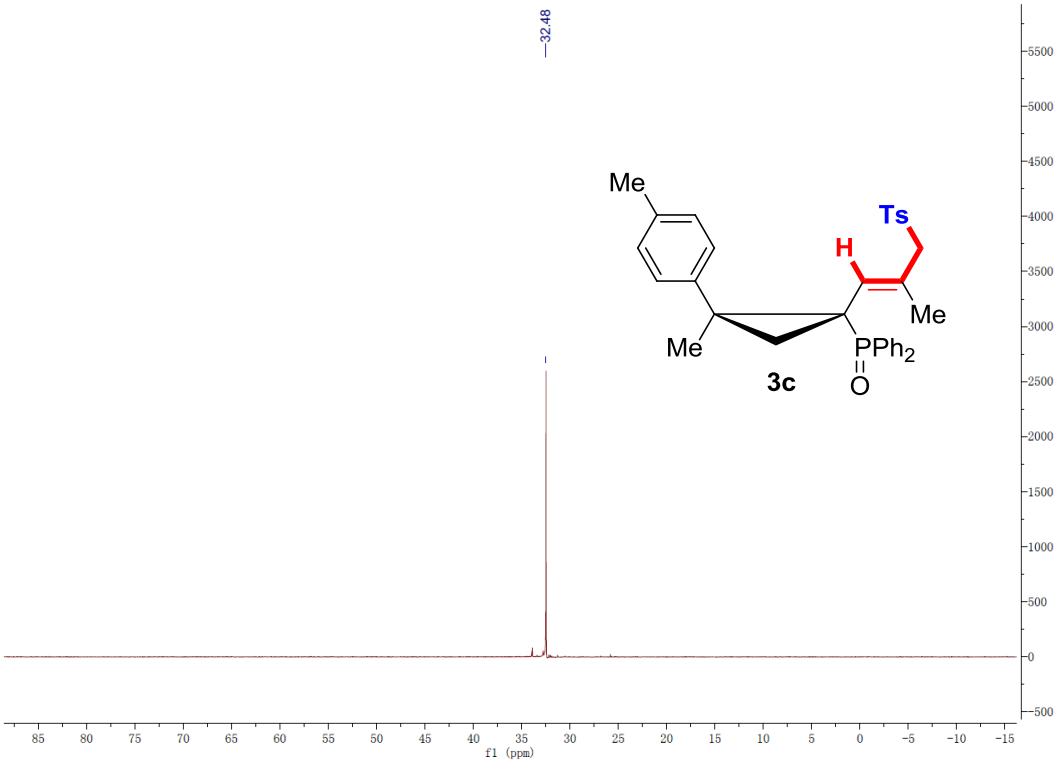


25 #36 RT: 0.39 AV: 1 NL: 4.76E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

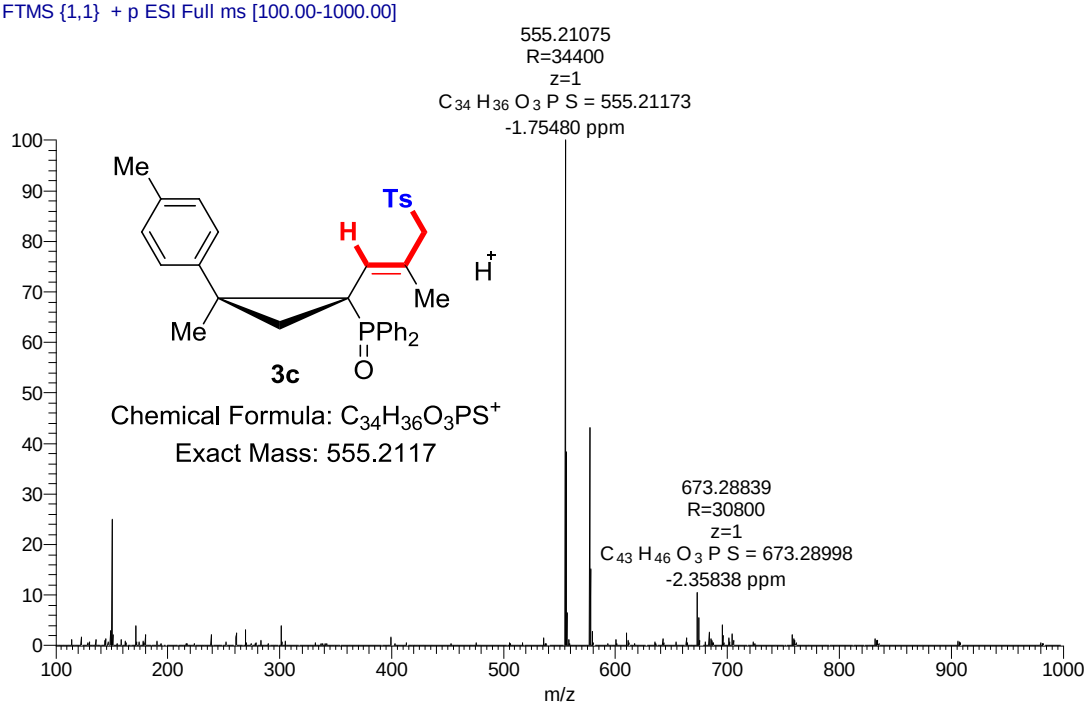


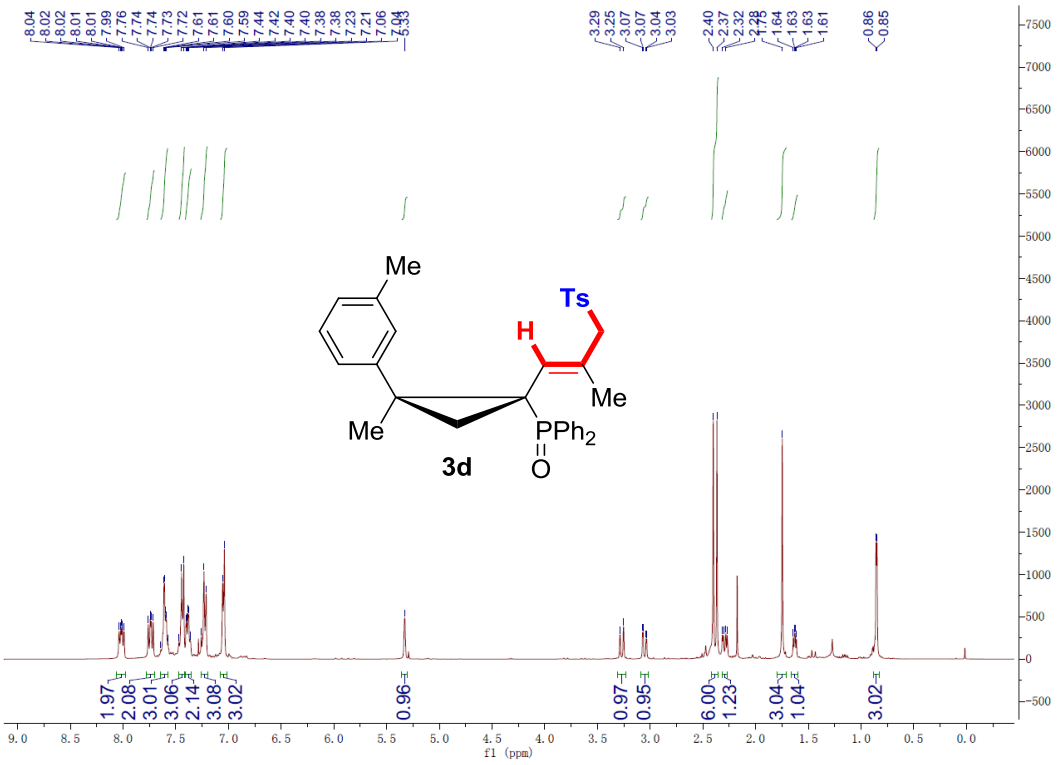

Me
Ts
H
Me
Me
PPh2
O
3c
f1 (ppm)

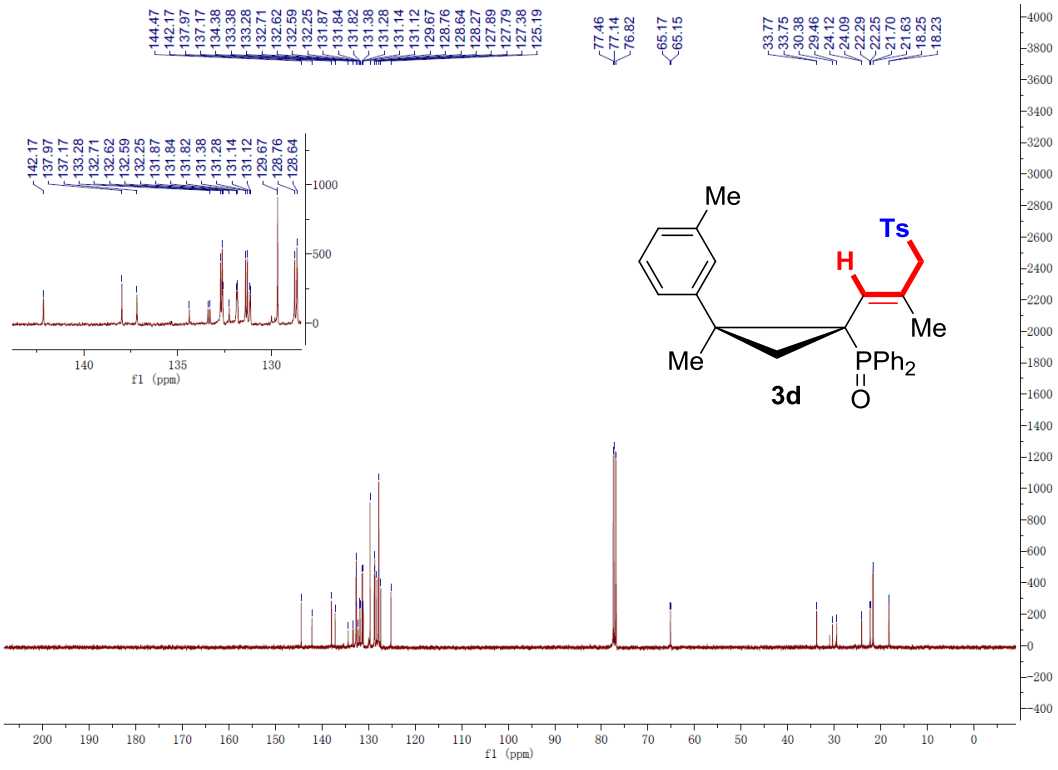

Me
Ts
H
Me
Me
PPh2
O
3c
f1 (ppm)

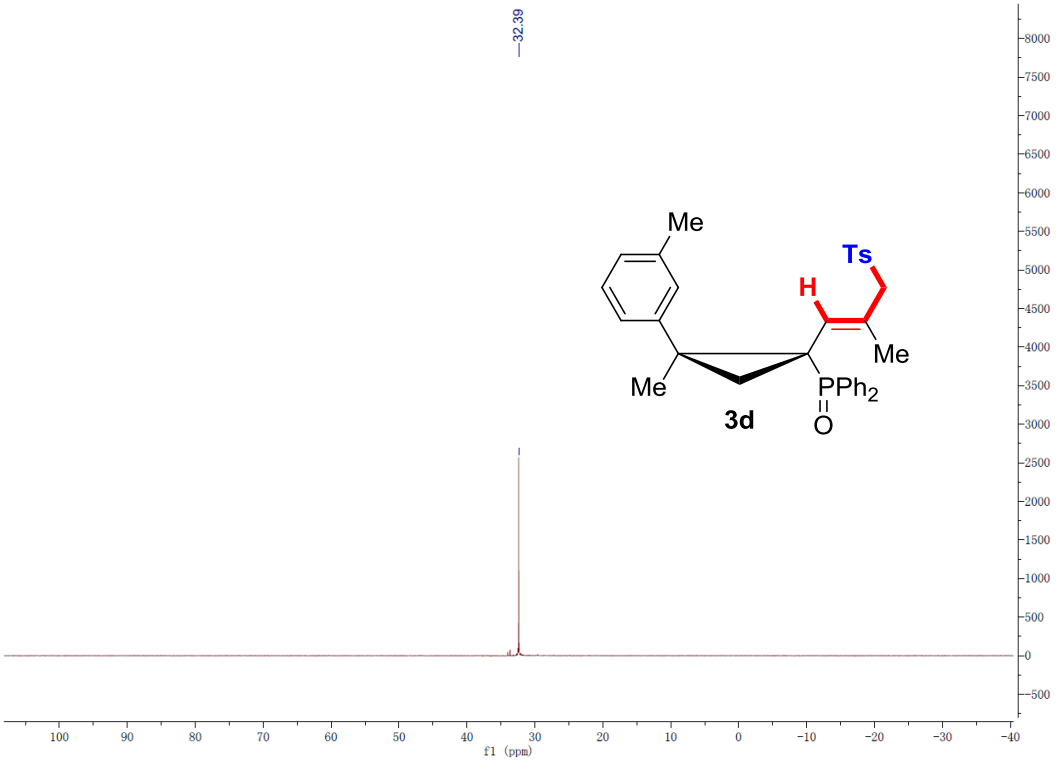


20160408-2 #47 RT: 0.51 AV: 1 NL: 1.31E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

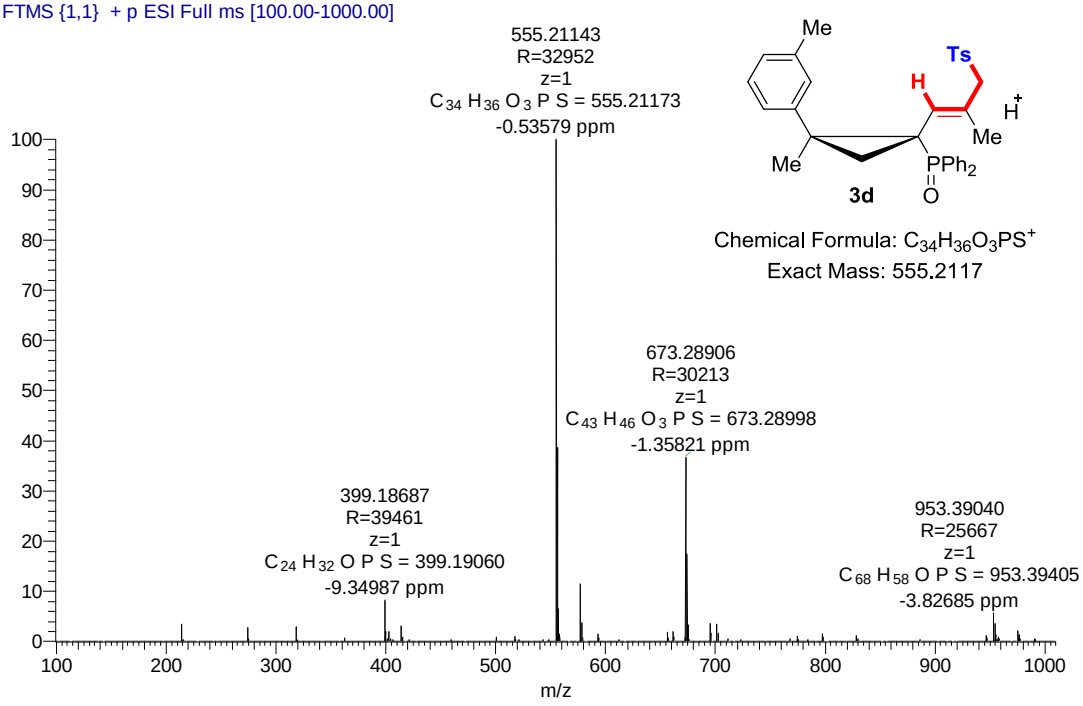



Me
Ts
H
Me
Me
PPh2
O
3d
f1 (ppm)

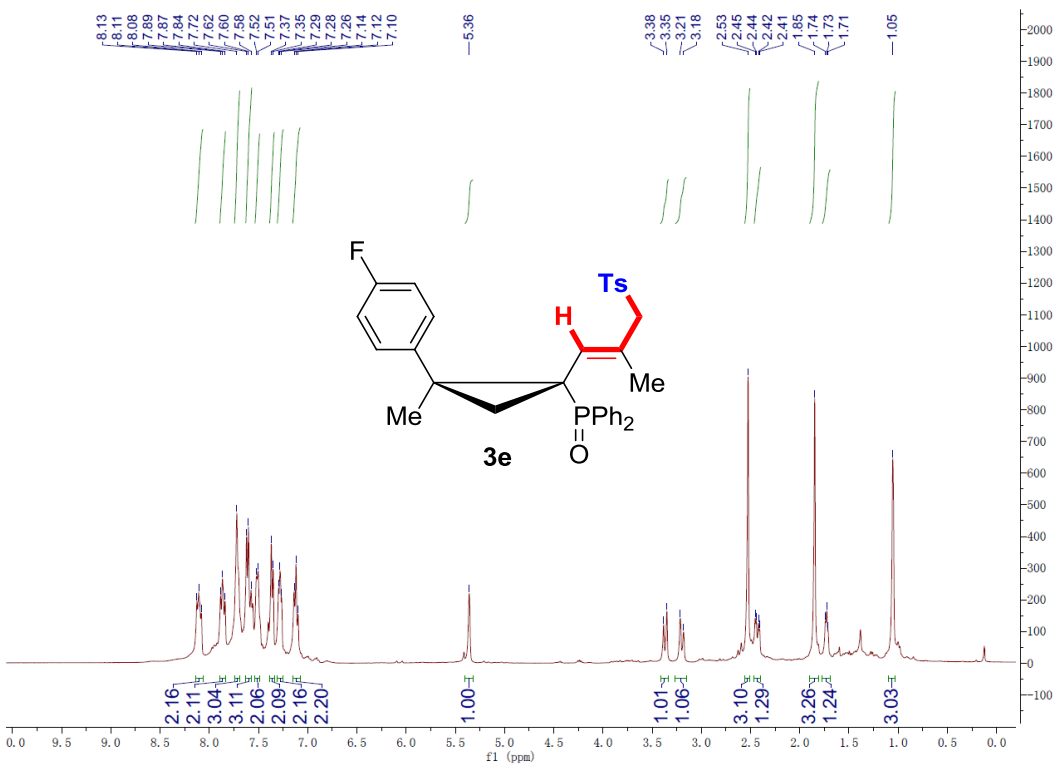

Me
Ts
H
Me
Me
PPh2
O
3d
f1 (ppm)

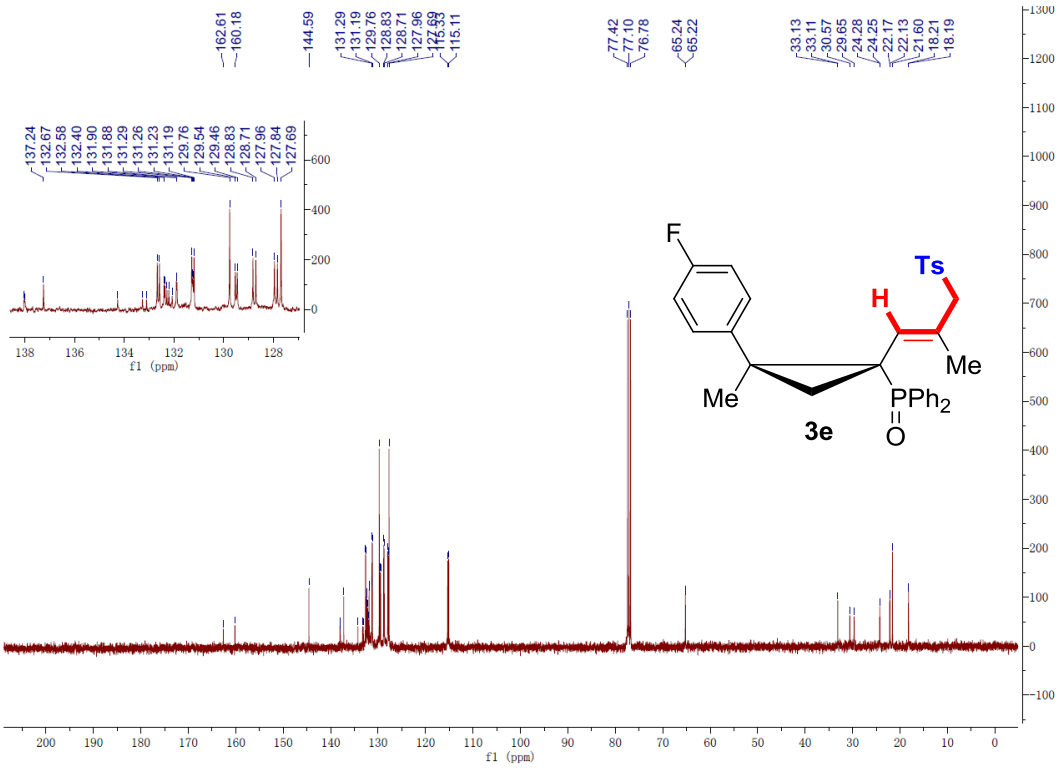


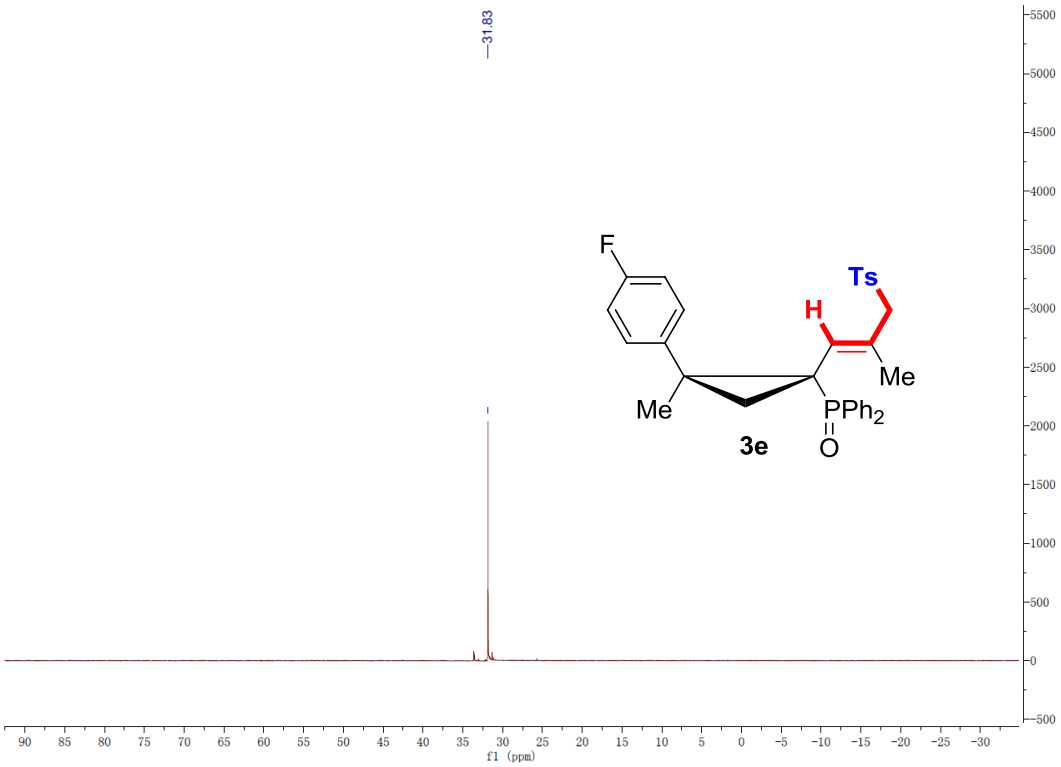
6 #19-20 RT: 0.21-0.22 AV: 2 NL: 1.82E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]



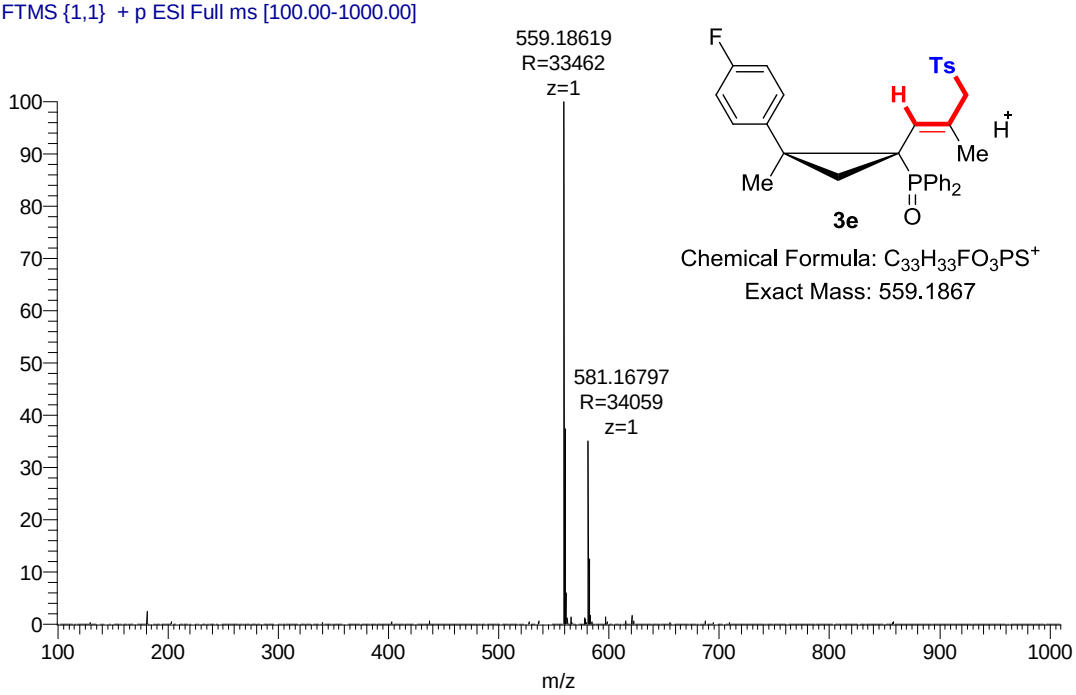
Chemical Formula: $C_{34}H_{36}O_3PS^+$
Exact Mass: 555.2117

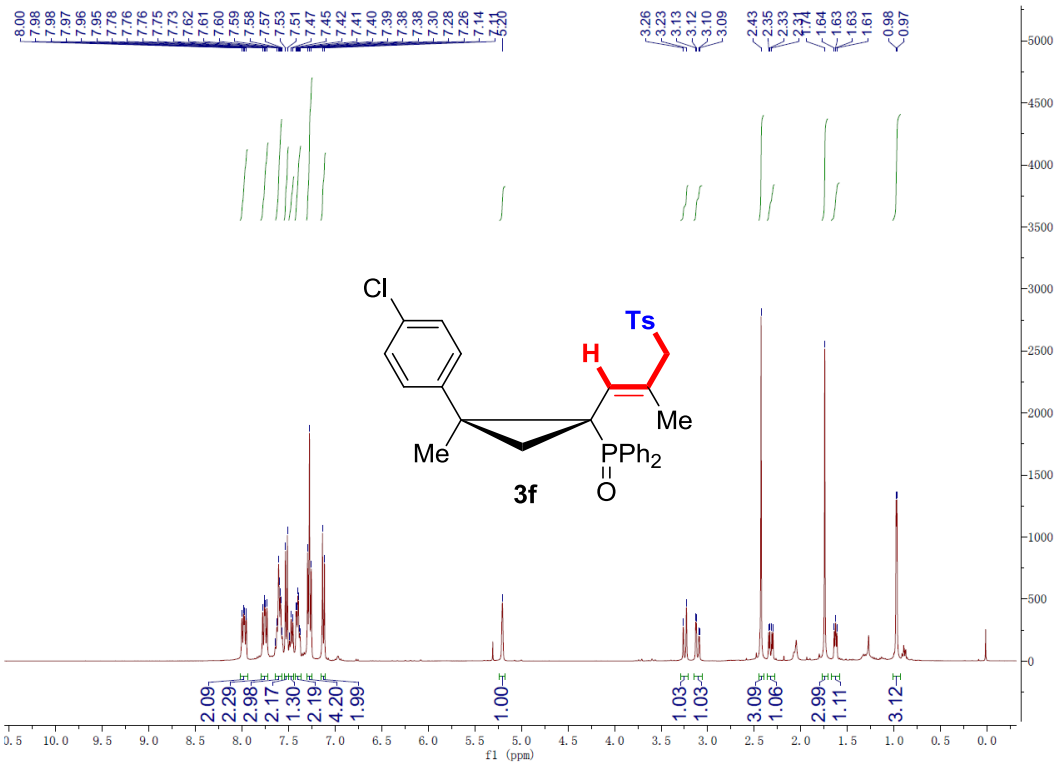

F
Ts
H
Me
Me
PPh2
O
3e
f1 (ppm)

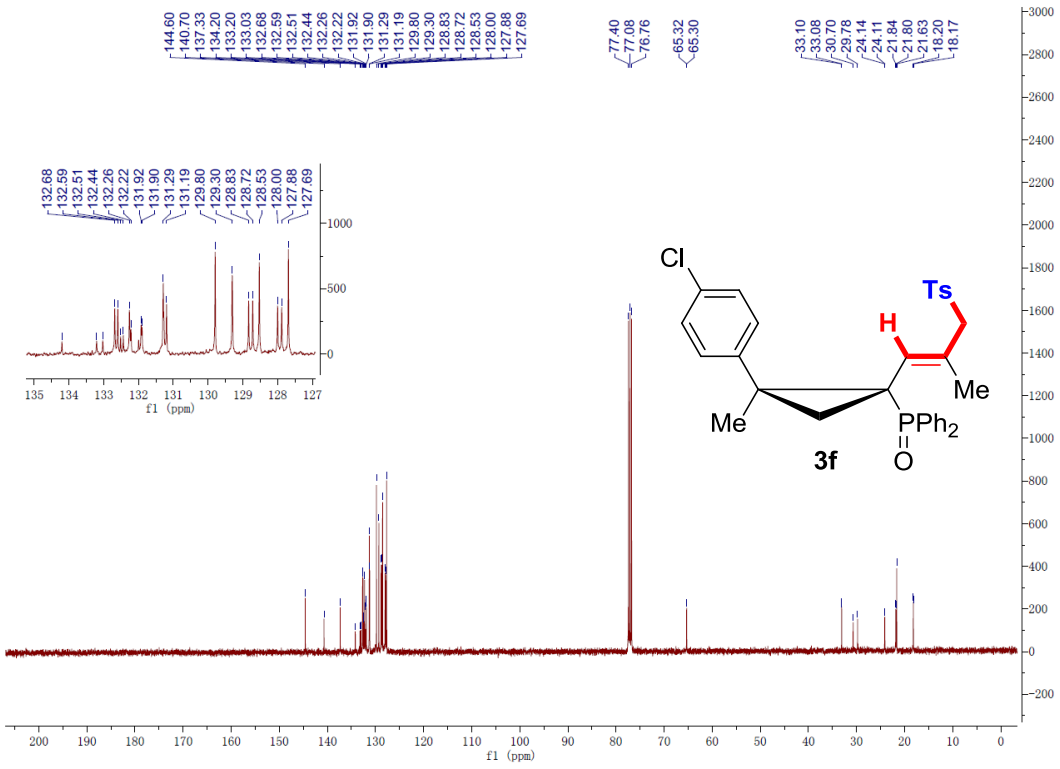

F
Ts
H
Me
Me
PPh2
O
3e
f1 (ppm)

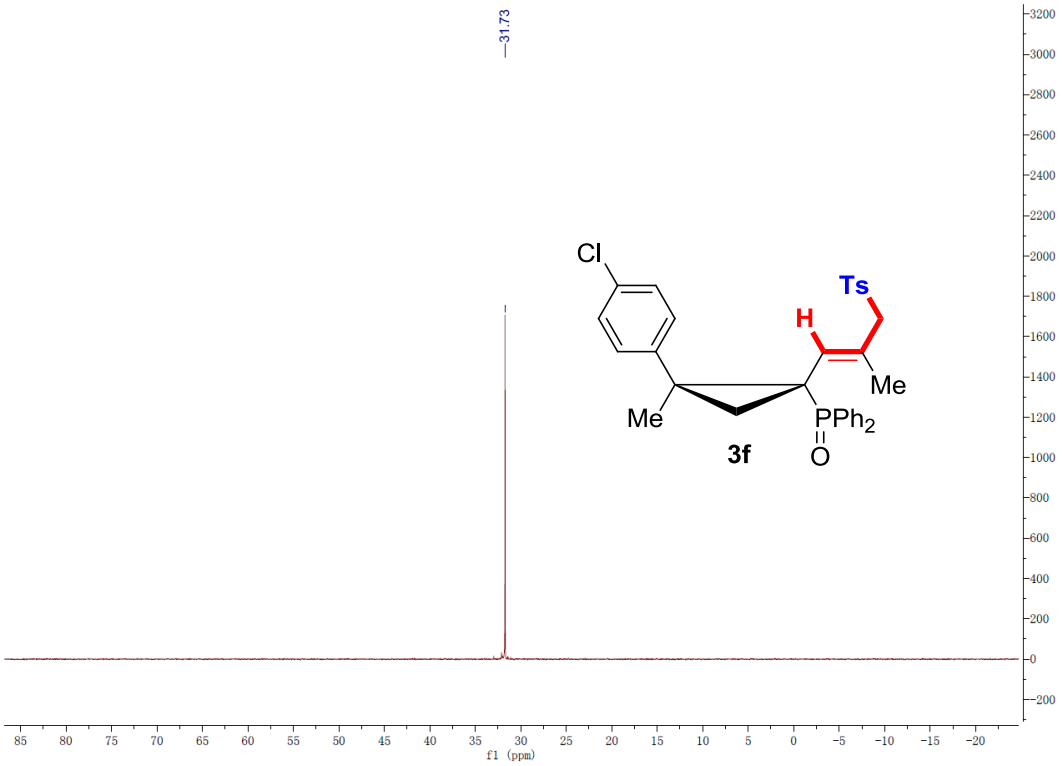


20170505-43_170506143308 #33-36 RT: 0.32-0.35 AV: 4 NL: 1.09E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

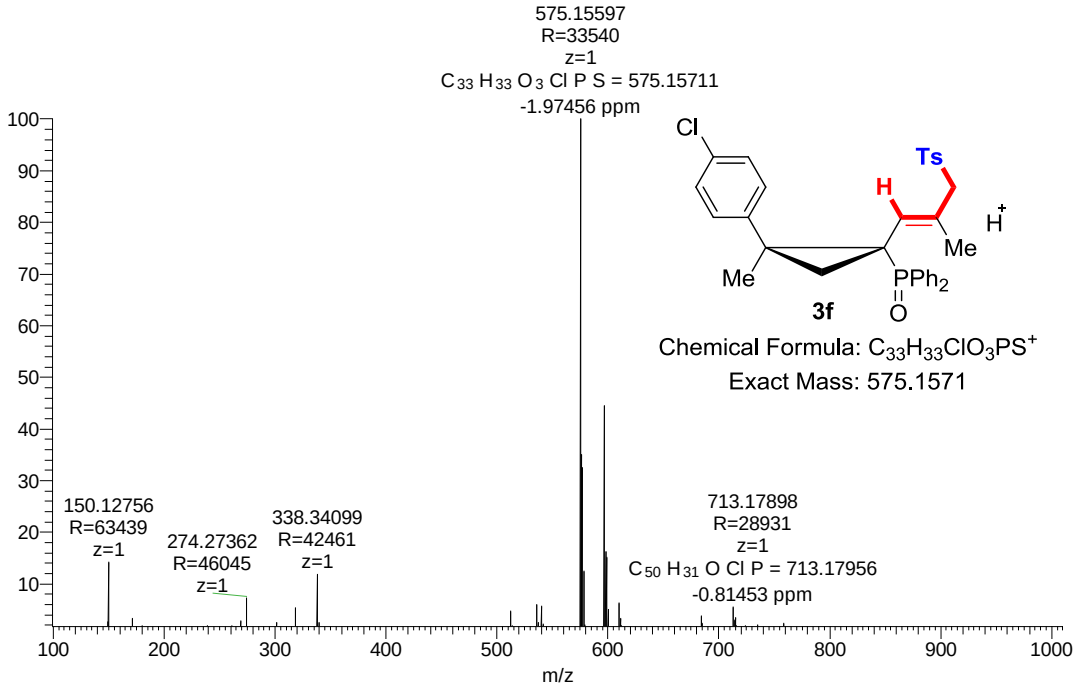


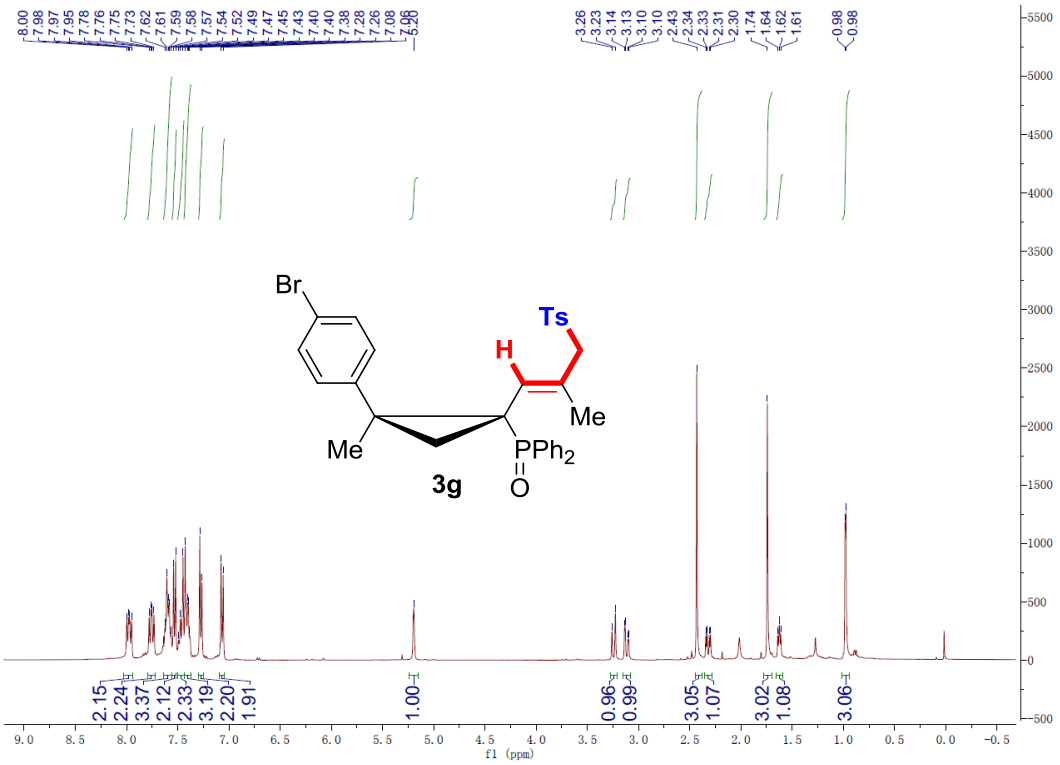

Cl
Ts
H
Me
Me
PPh2
O
3f
f1 (ppm)

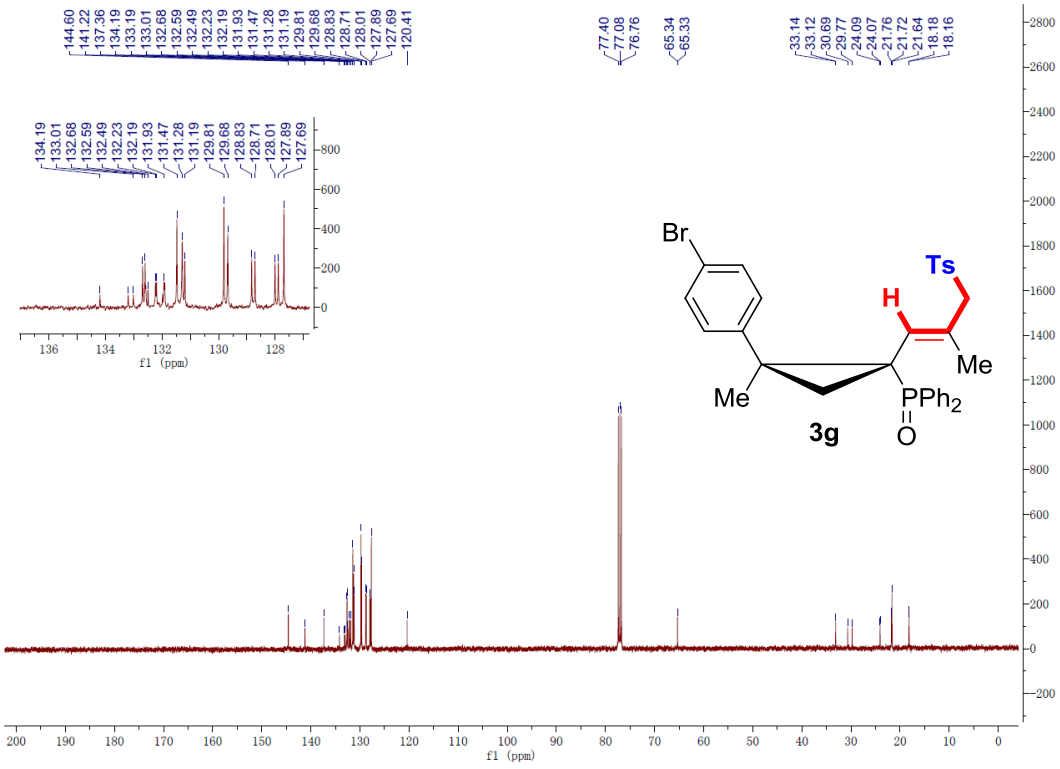

Cl
Ts
H
Me
Me
PPh2
O
3f
f1 (ppm)

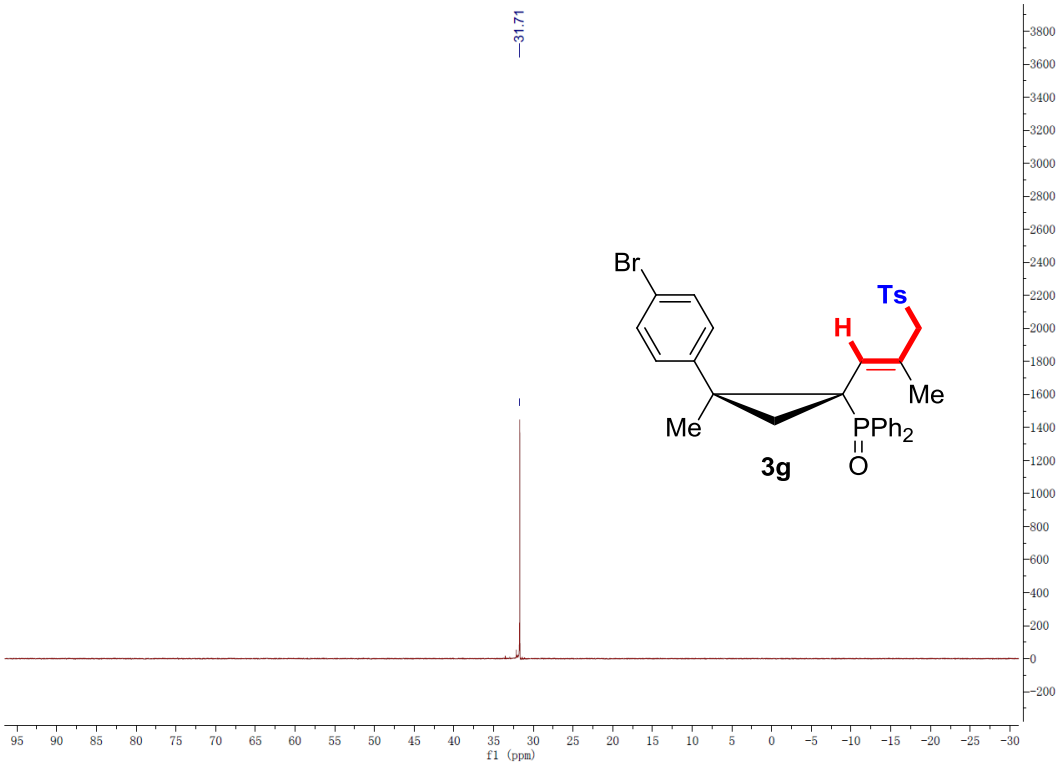


20160408-3 #38-39 RT: 0.41-0.43 AV: 2 NL: 1.24E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

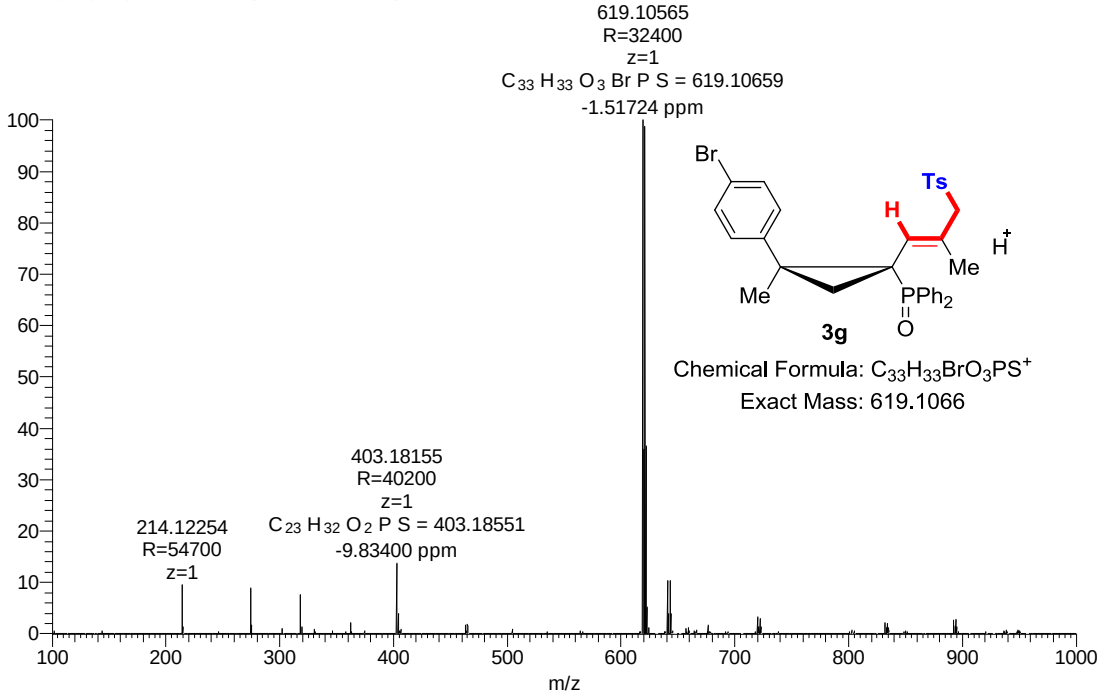


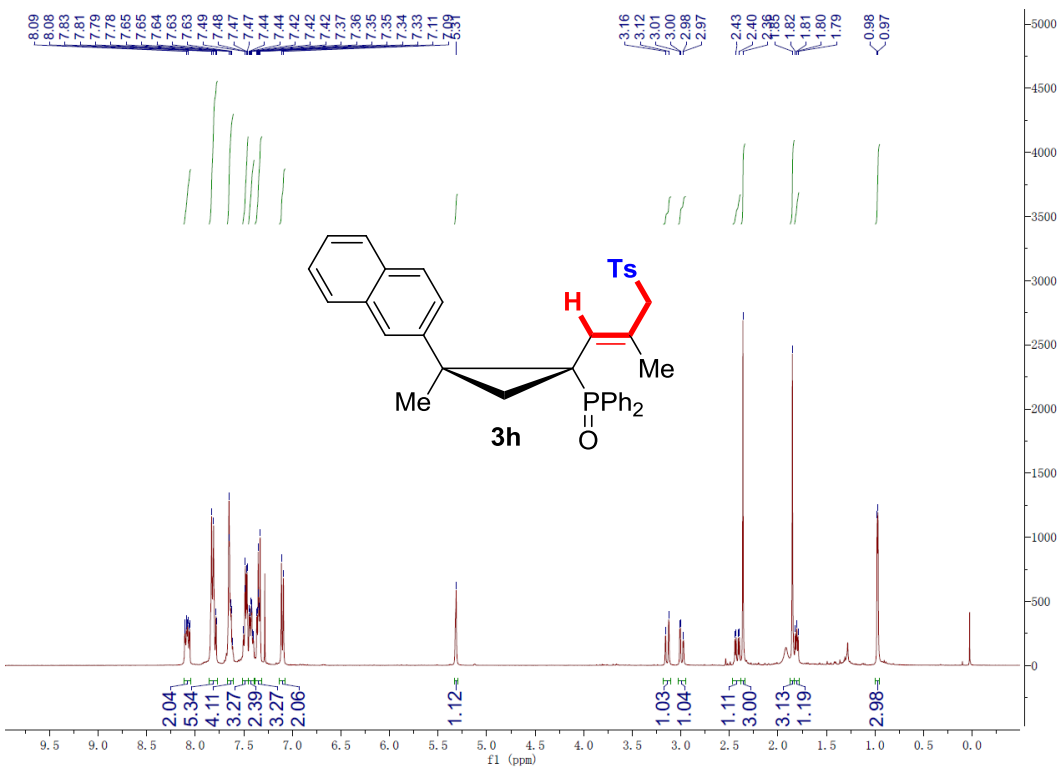

Br
Ts
H
Me
Me
PPh2
O
3g
f1 (ppm)

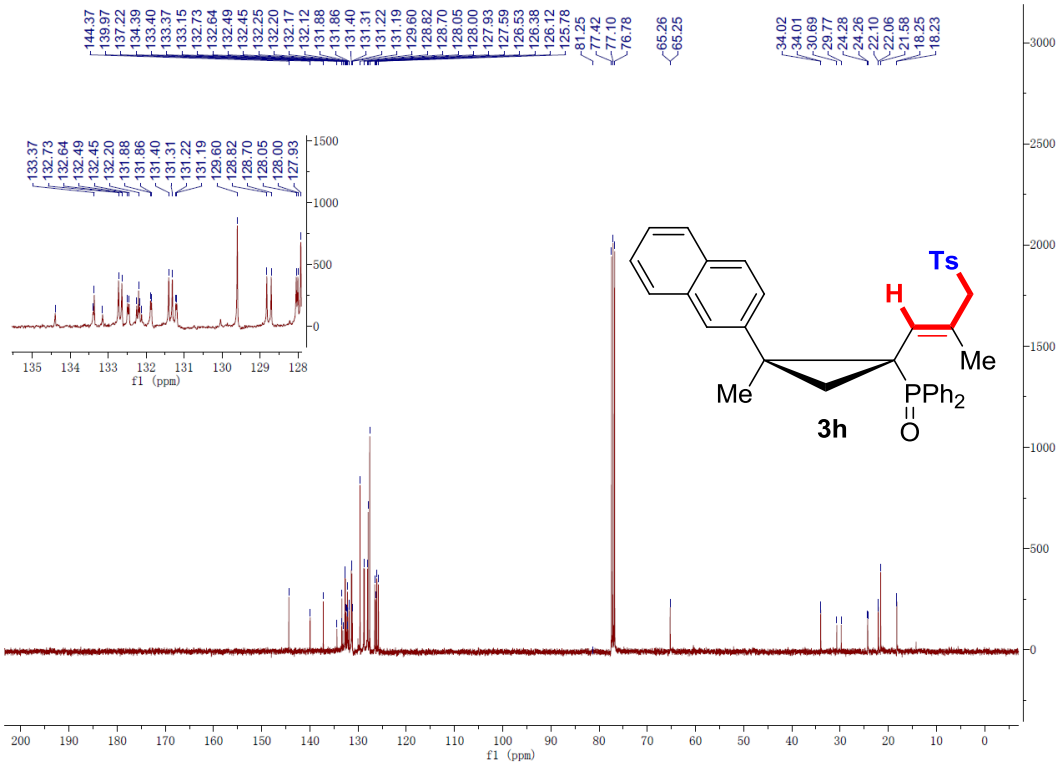

Br
Ts
H
Me
Me
PPh2
O
3g
f1 (ppm)

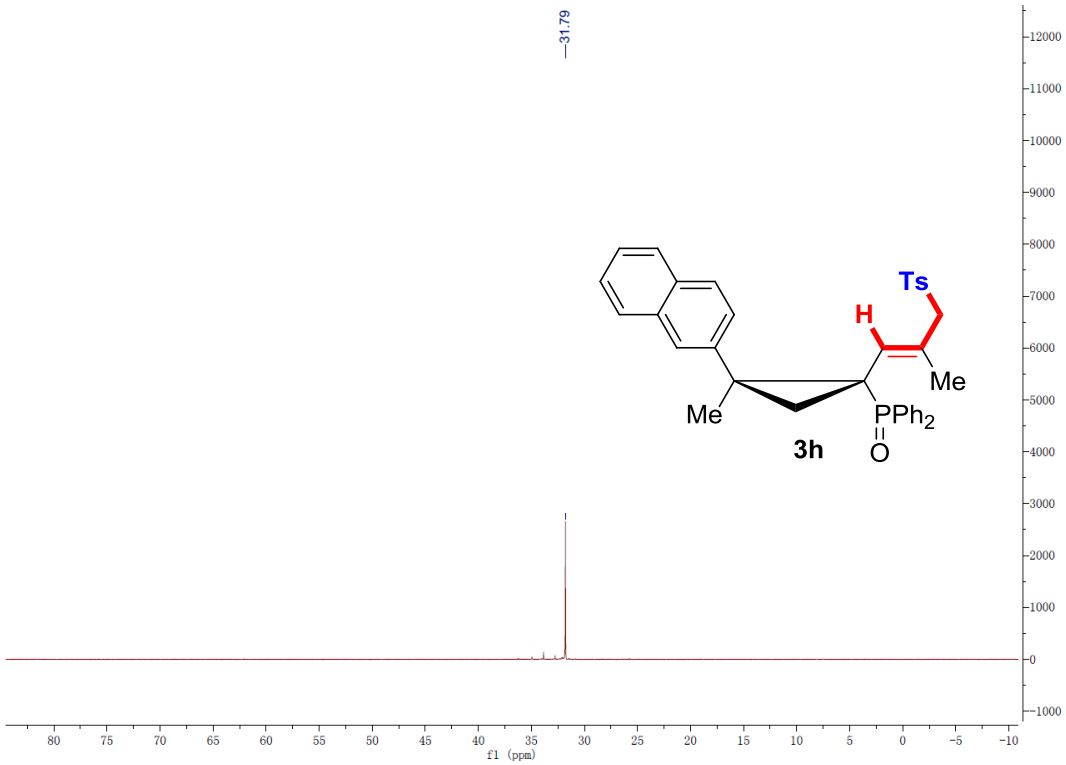


5 #20 RT: 0.22 AV: 1 NL: 1.76E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

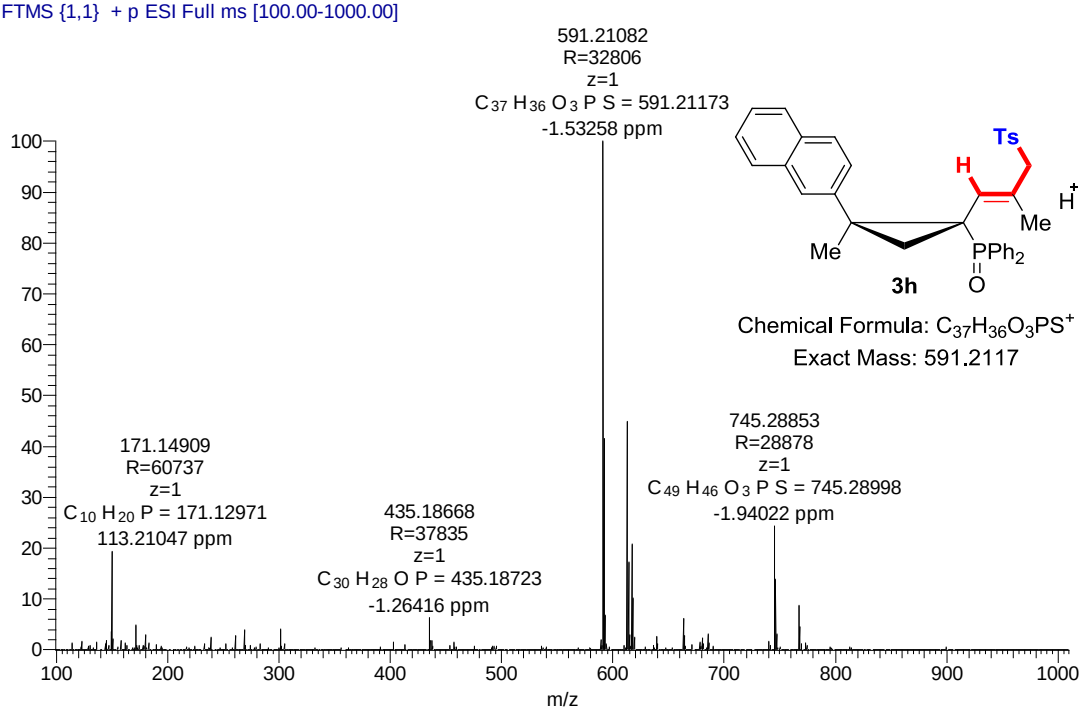


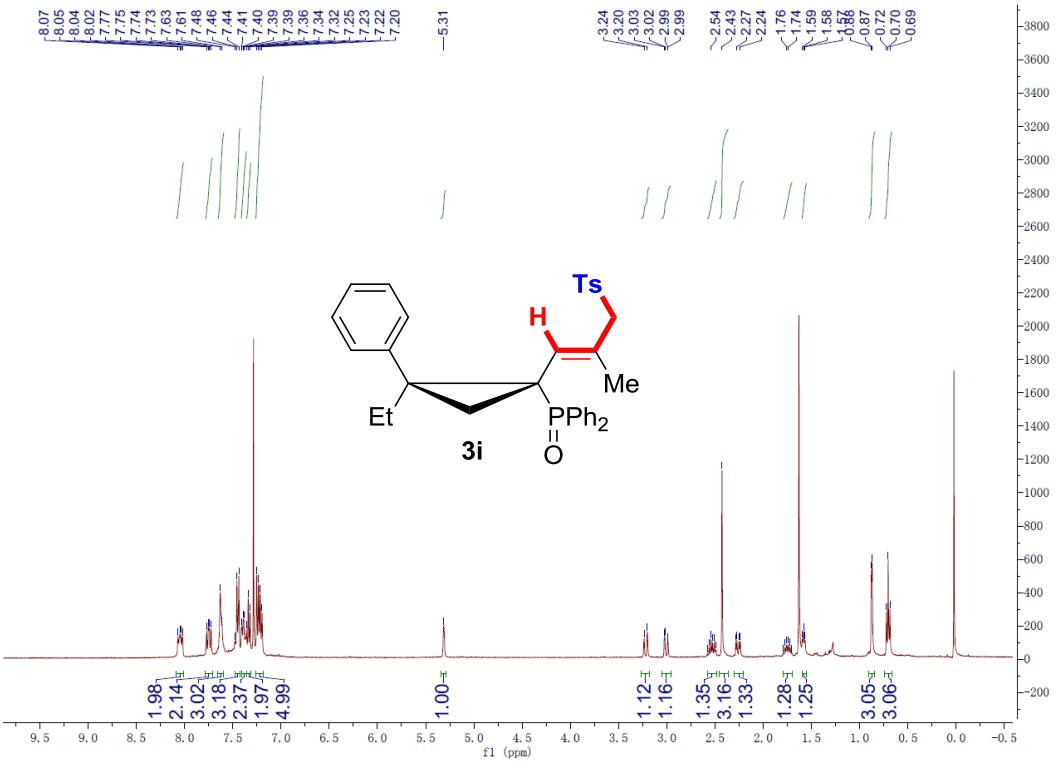

Ts
H
Me
Me
PPh2
O
3h
f1 (ppm)

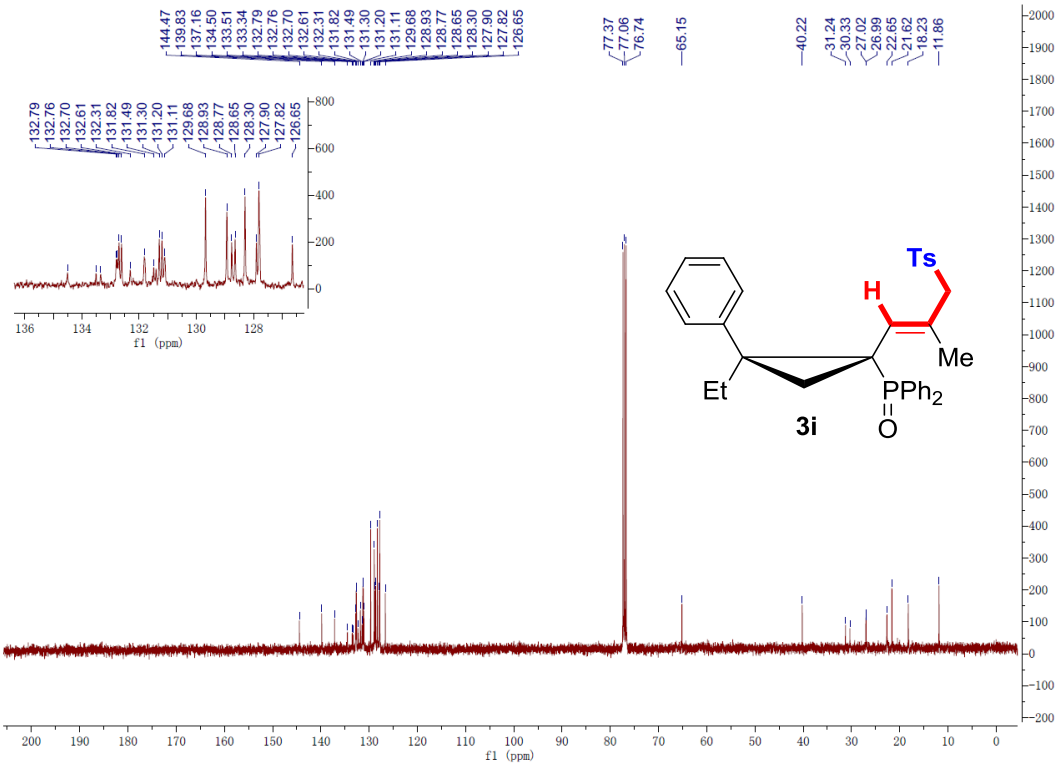

Ts
H
Me
Me
PPh2
O
3h
f1 (ppm)

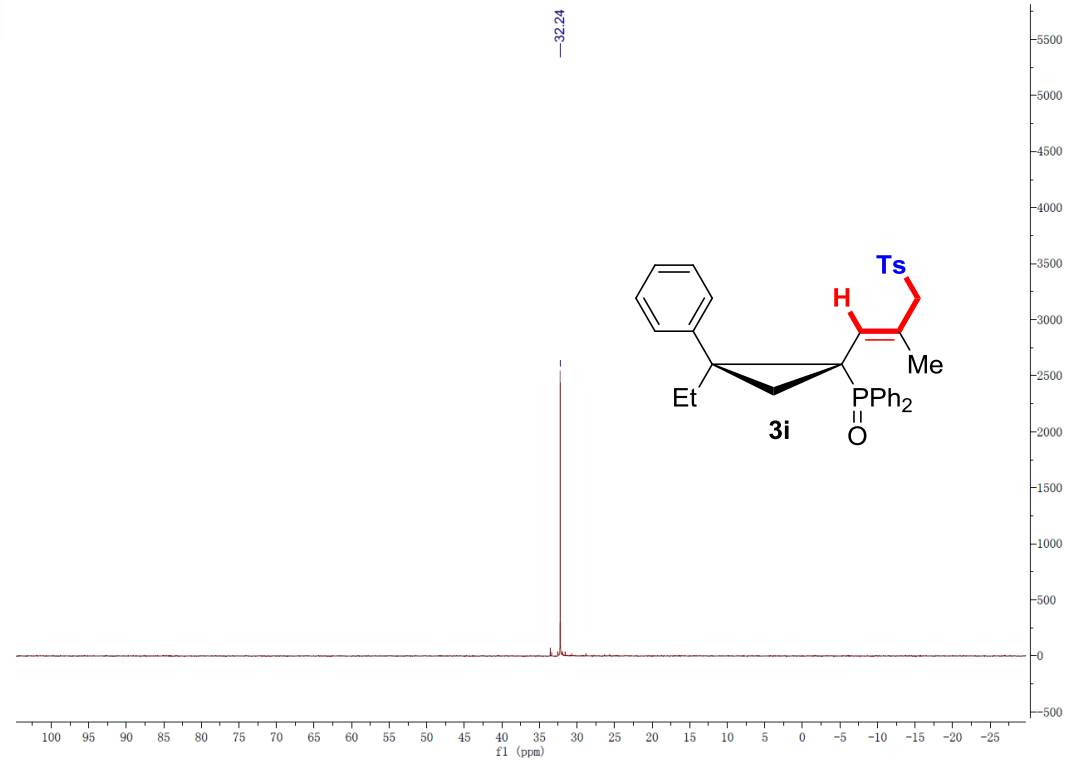


20160408-4 #50-51 RT: 0.56-0.57 AV: 2 NL: 9.04E4
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

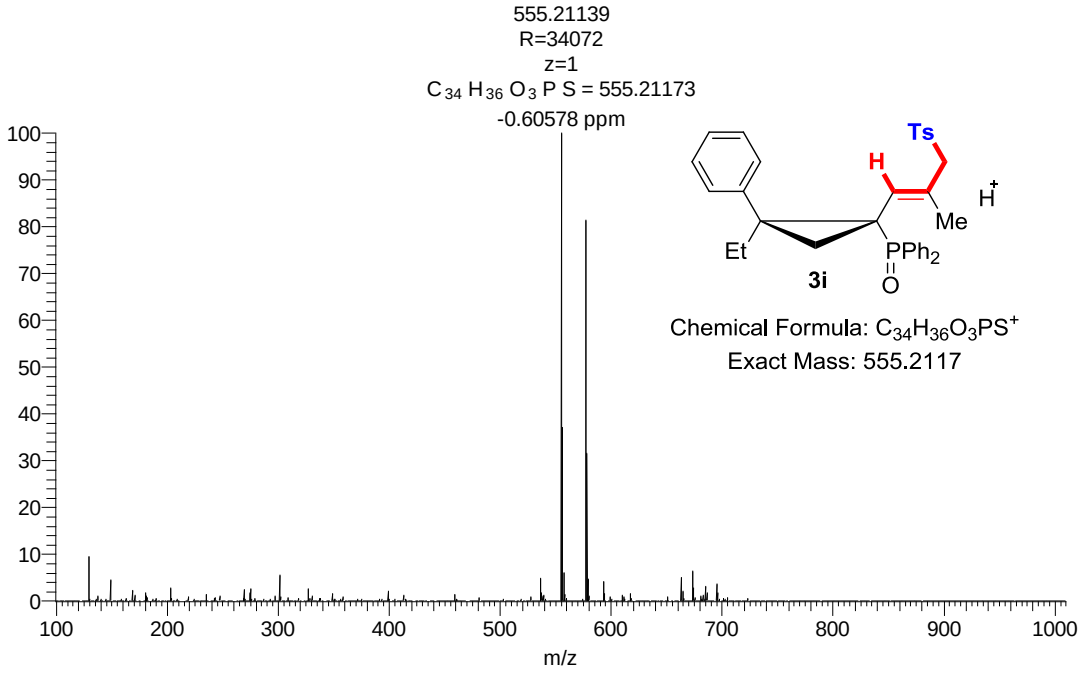


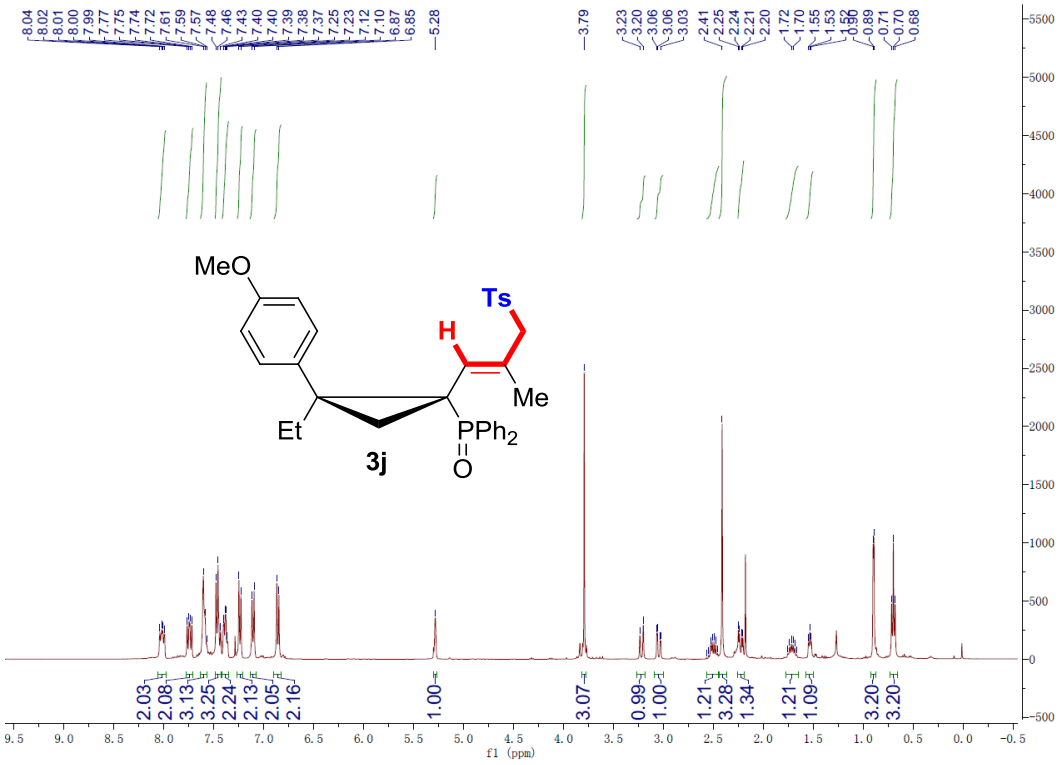

Ts
H
Me
Et
PPh2
O
3i
f1 (ppm)

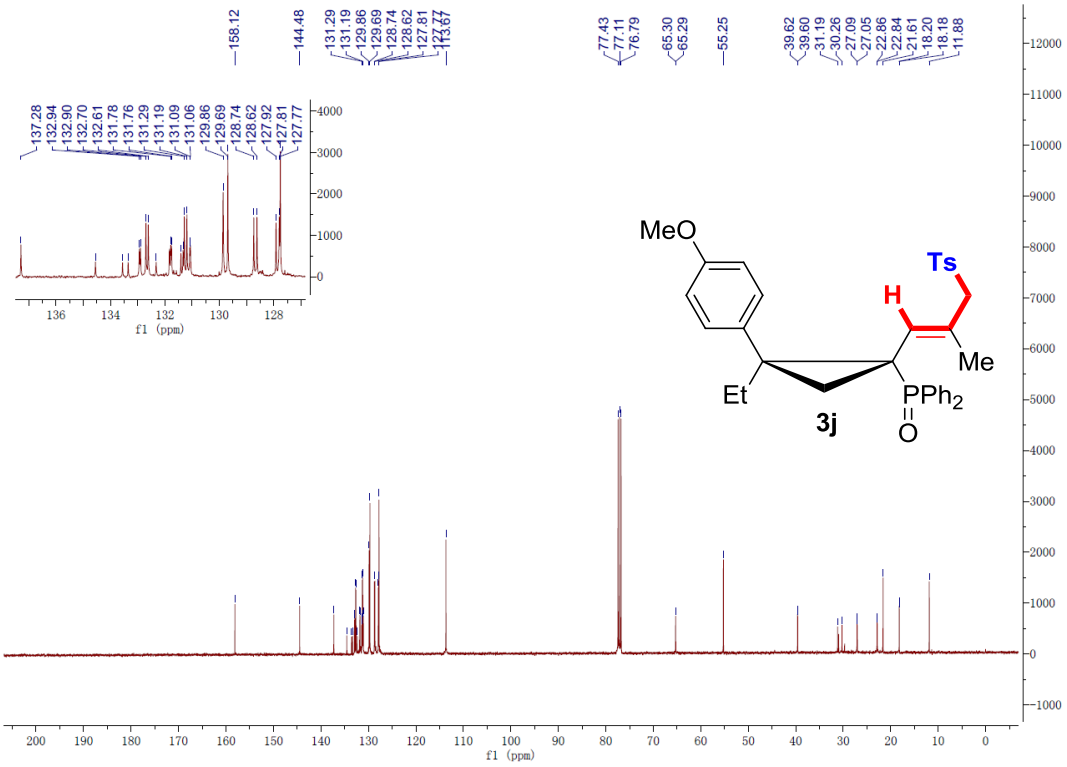

Ts
H
Me
Et
PPh2
O
3i
f1 (ppm)

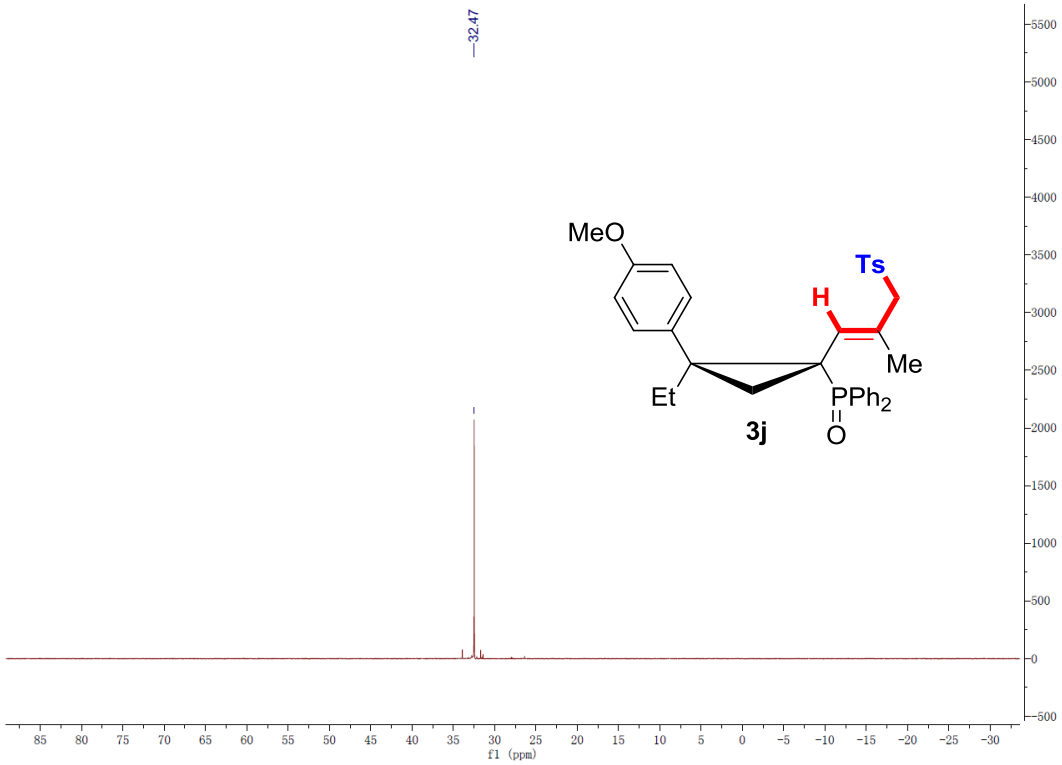


20170505-26_170506092801 #45-46 RT: 0.45-0.46 AV: 2 NL: 1.62E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]



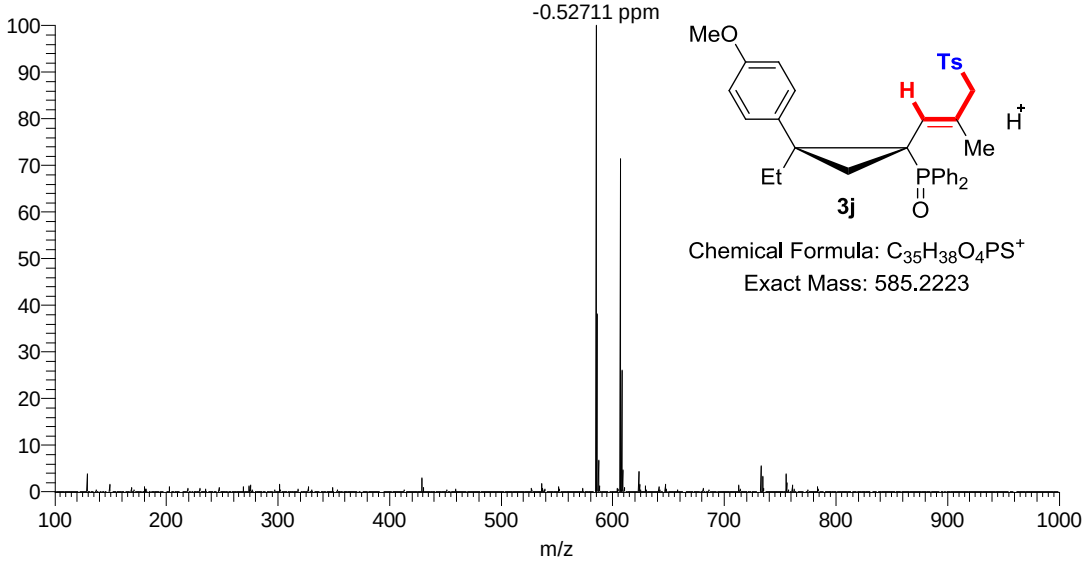

MeO
Ts
H
Me
Et
PPh2
O
3j
f1 (ppm)


MeO
Ts
H
Me
Et
PPh2
O
3j
f1 (ppm)

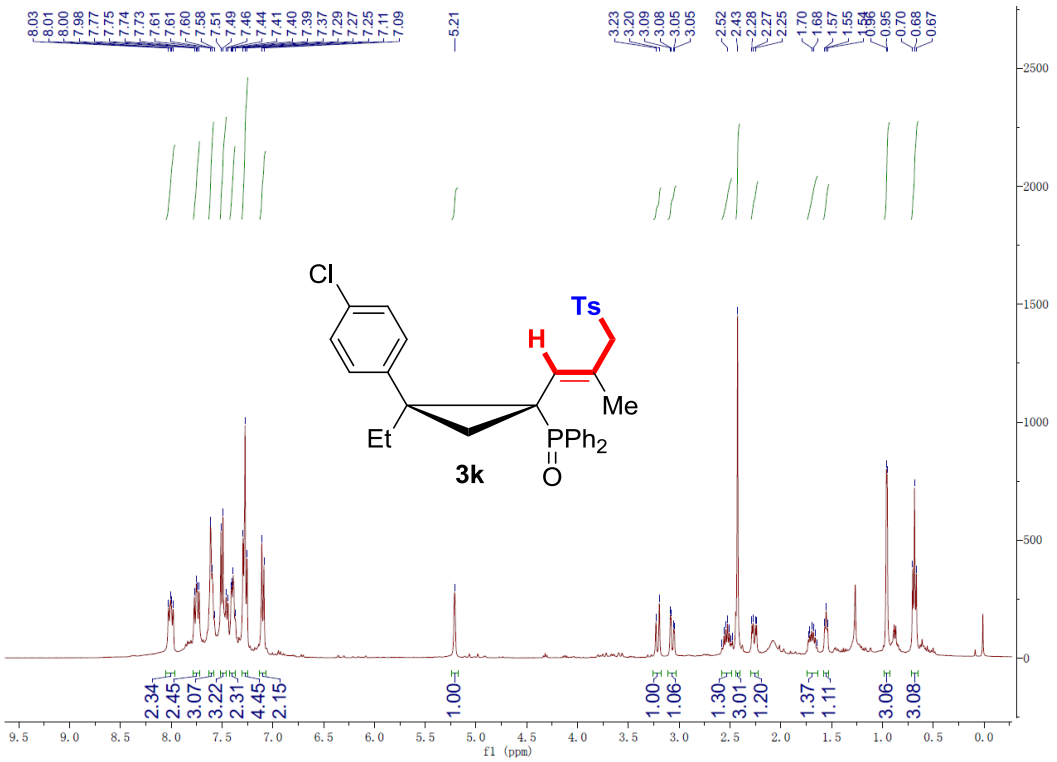


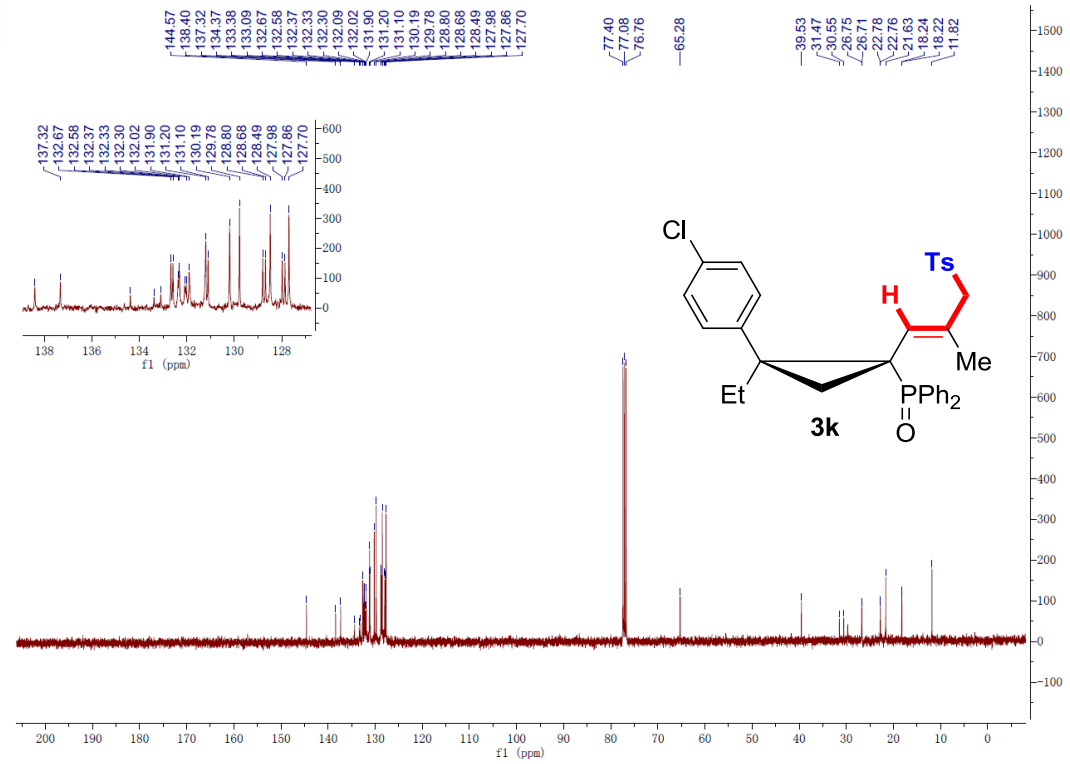
20170505-27_170506093837 #43 RT: 0.42 AV: 1 NL: 3.20E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

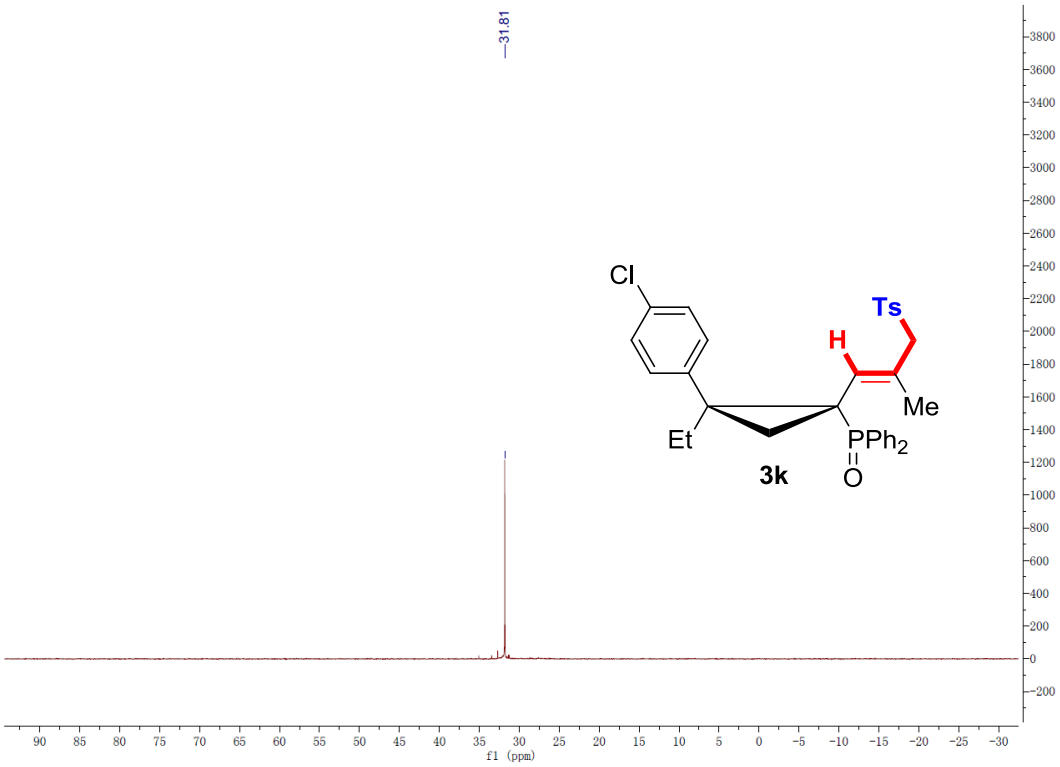
585.22198
R=33800
z=1
$C_{35}H_{38}O_4PS$ = 585.22229
-0.52711 ppm



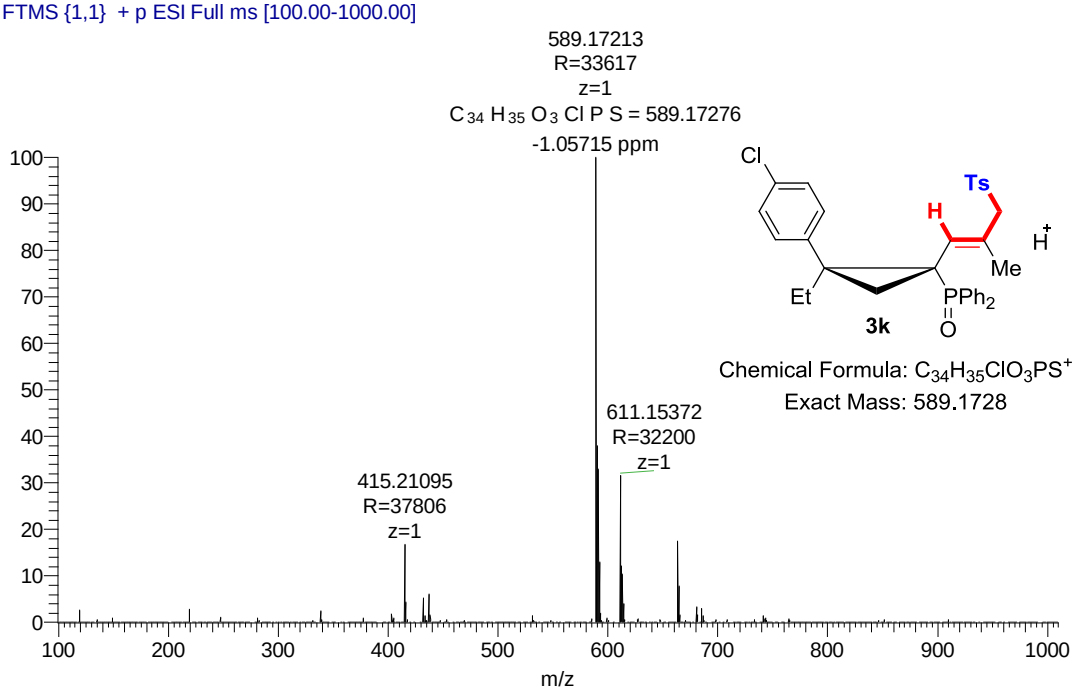
Chemical Formula: $C_{35}H_{38}O_4PS^+$
Exact Mass: 585.2223

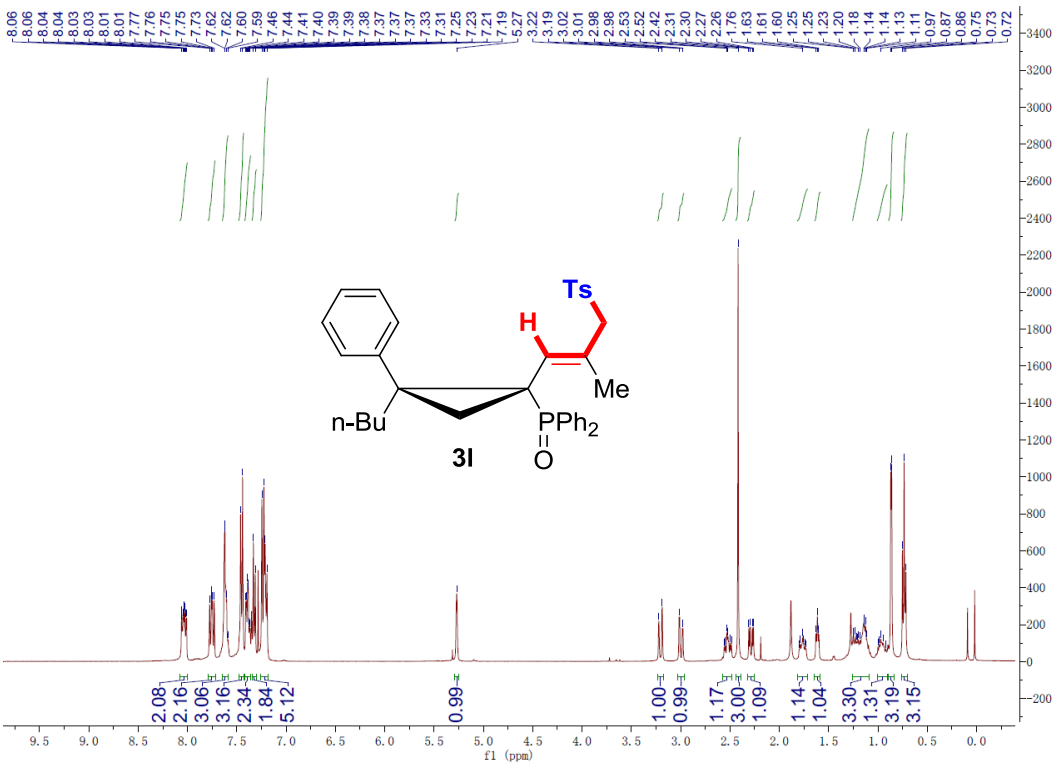

Cl
Ts
H
Me
Et
PPh2
O
3k
f1 (ppm)

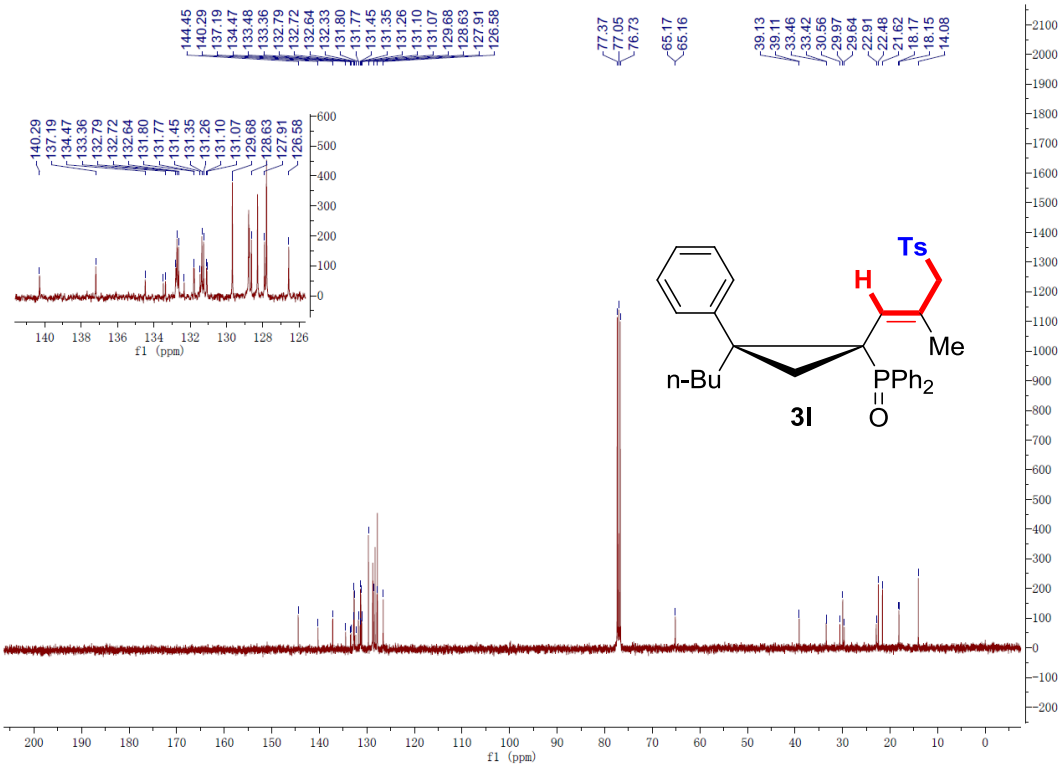

Cl
Ts
H
Me
Et
PPh2
O
3k
f1 (ppm)

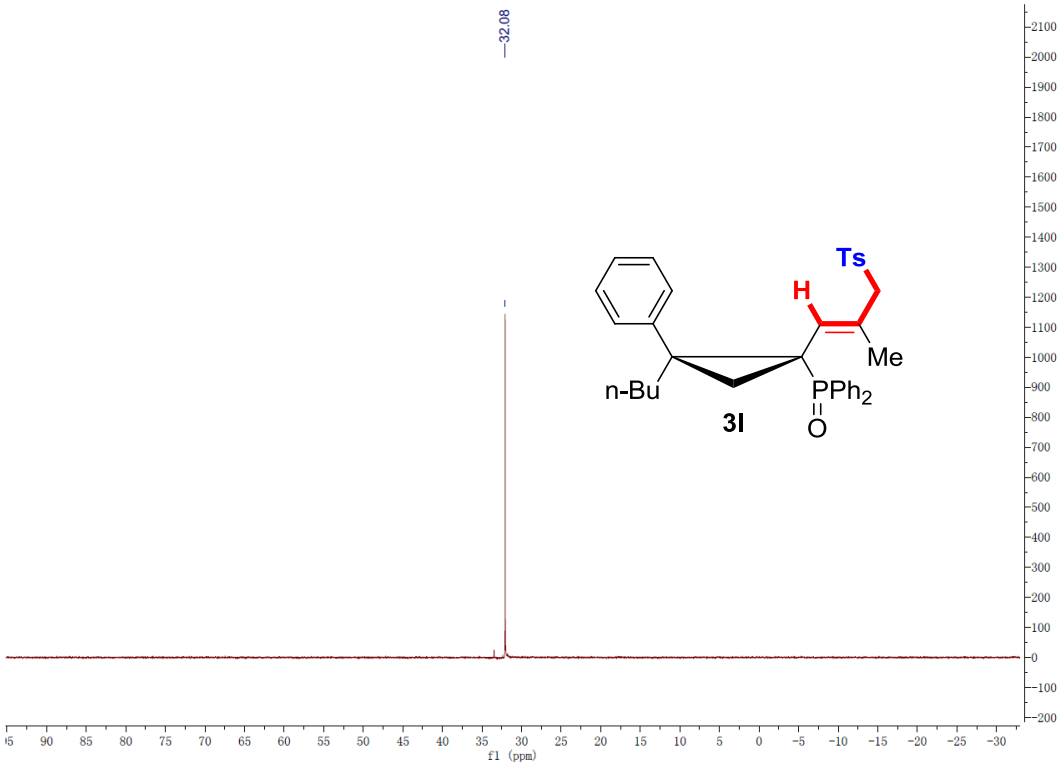


20170505-28_170506103913 #8-9 RT: 0.09-0.10 AV: 2 NL: 6.41E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

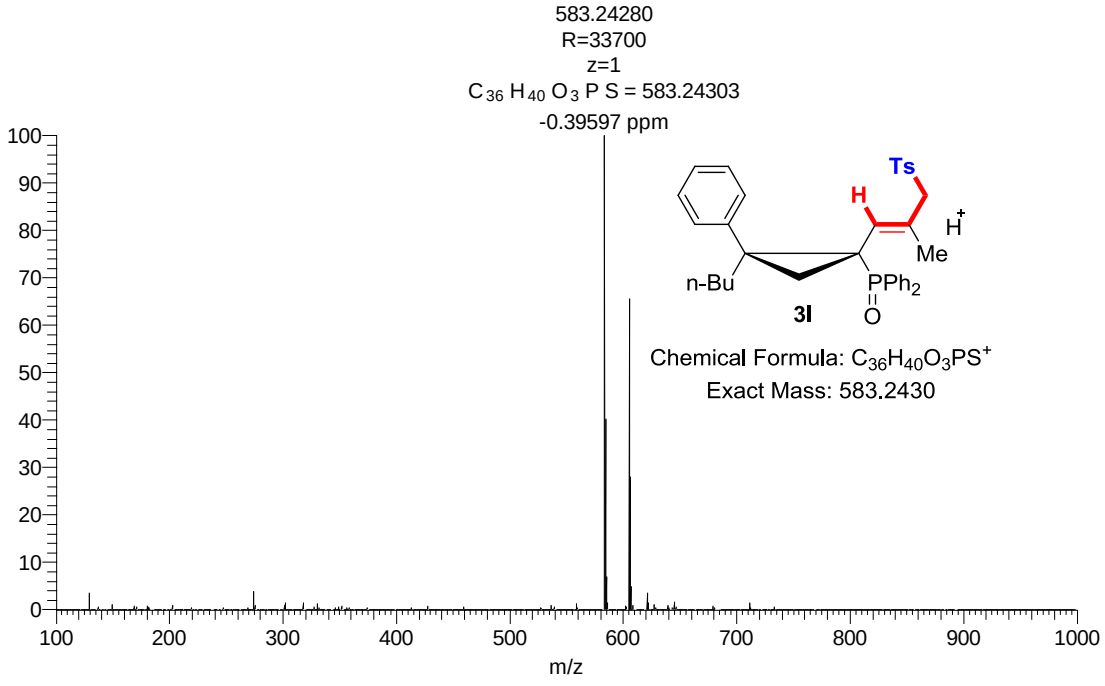


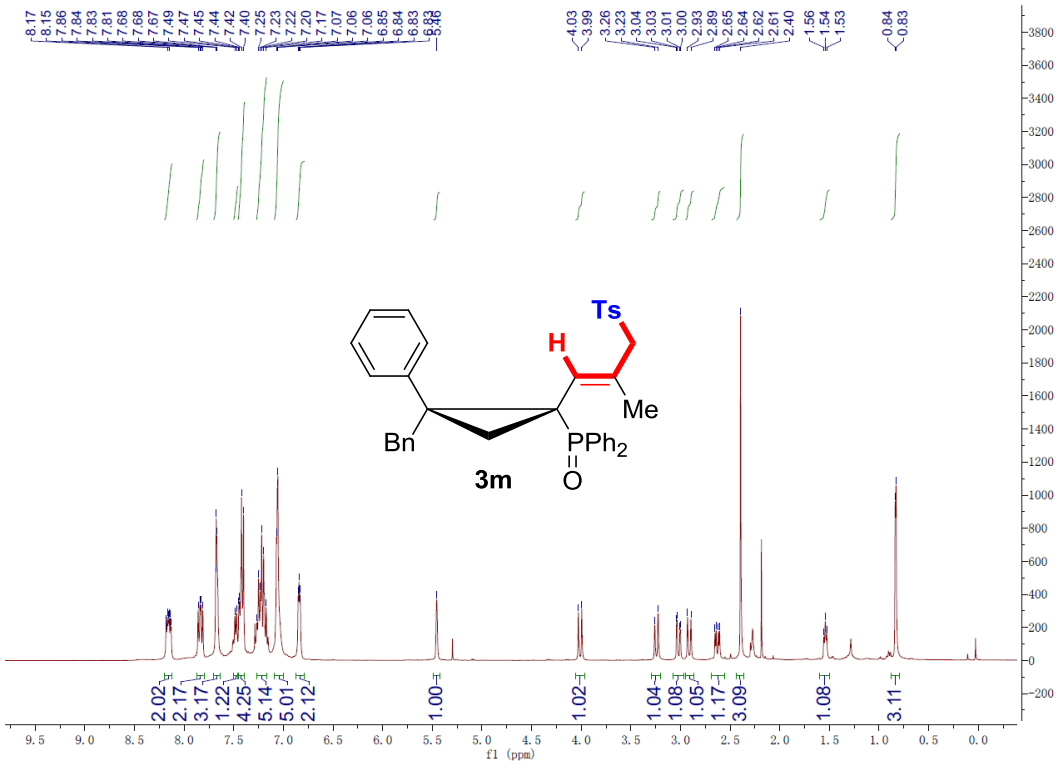

Ts
H
Me
n-Bu
PPh2
O
3l
f1 (ppm)

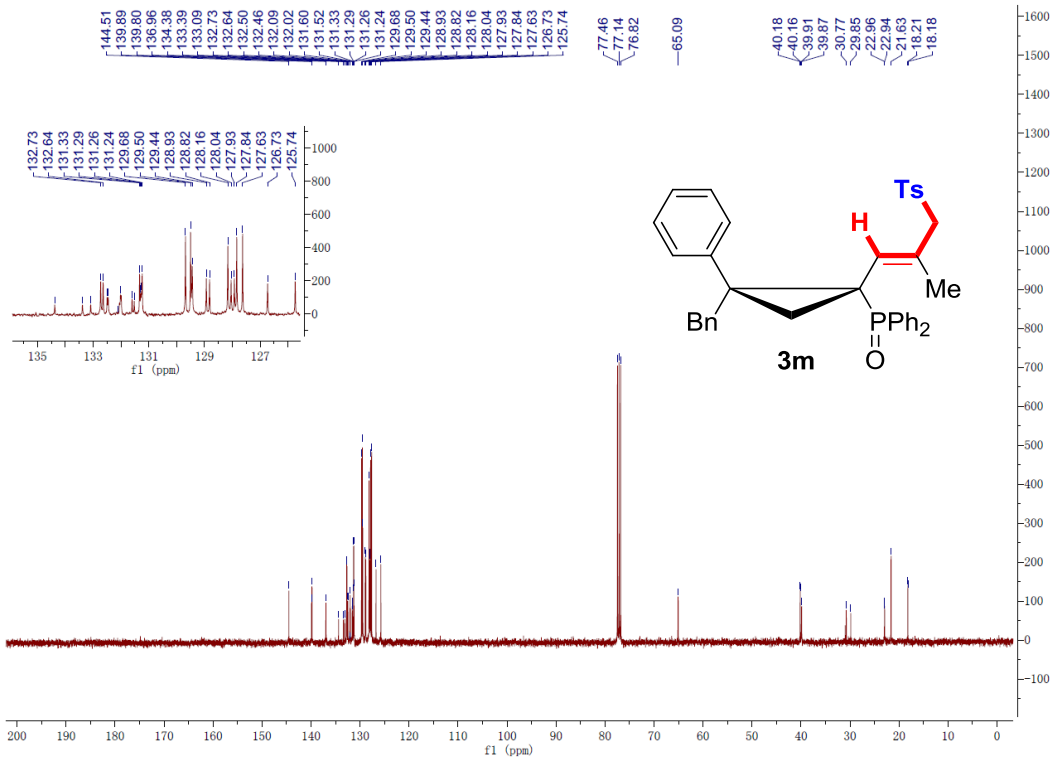

Ts
H
Me
n-Bu
PPh2
O
3l
f1 (ppm)

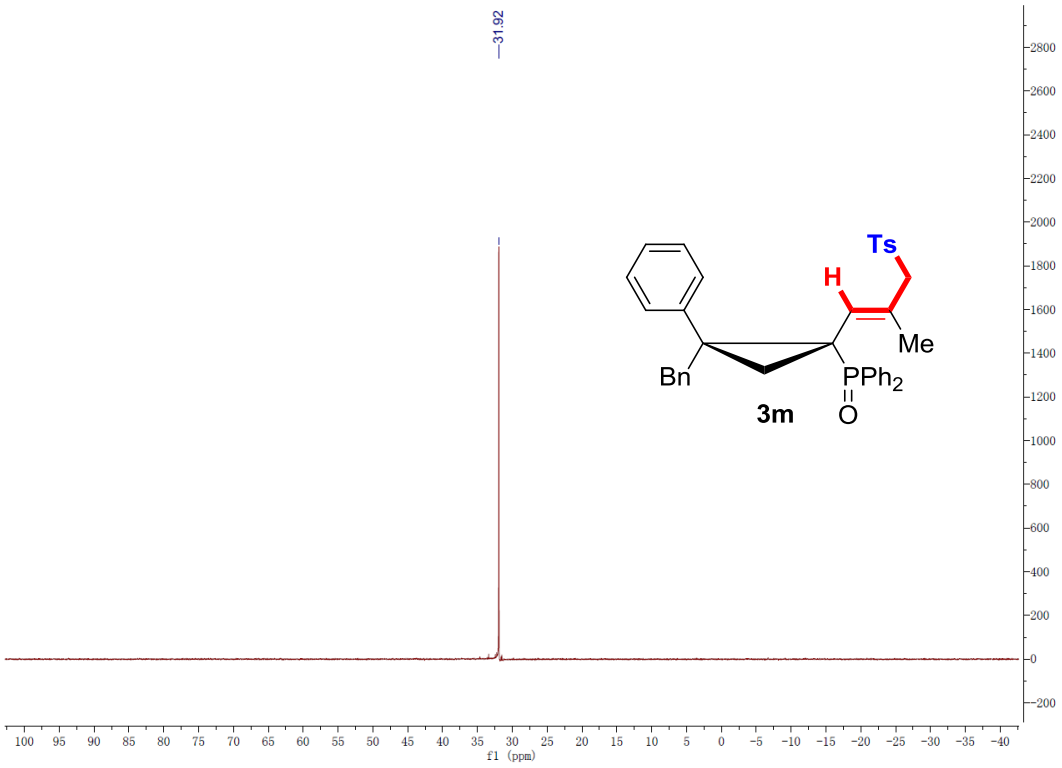


20170505-30_170506111031 #48 RT: 0.47 AV: 1 NL: 3.50E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

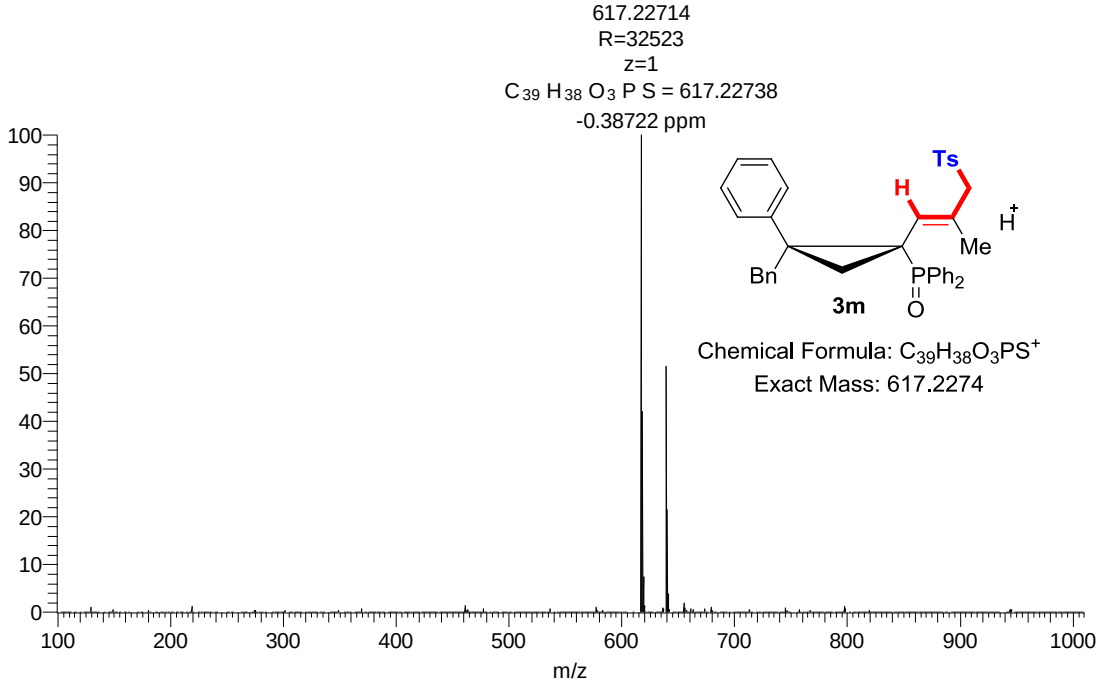


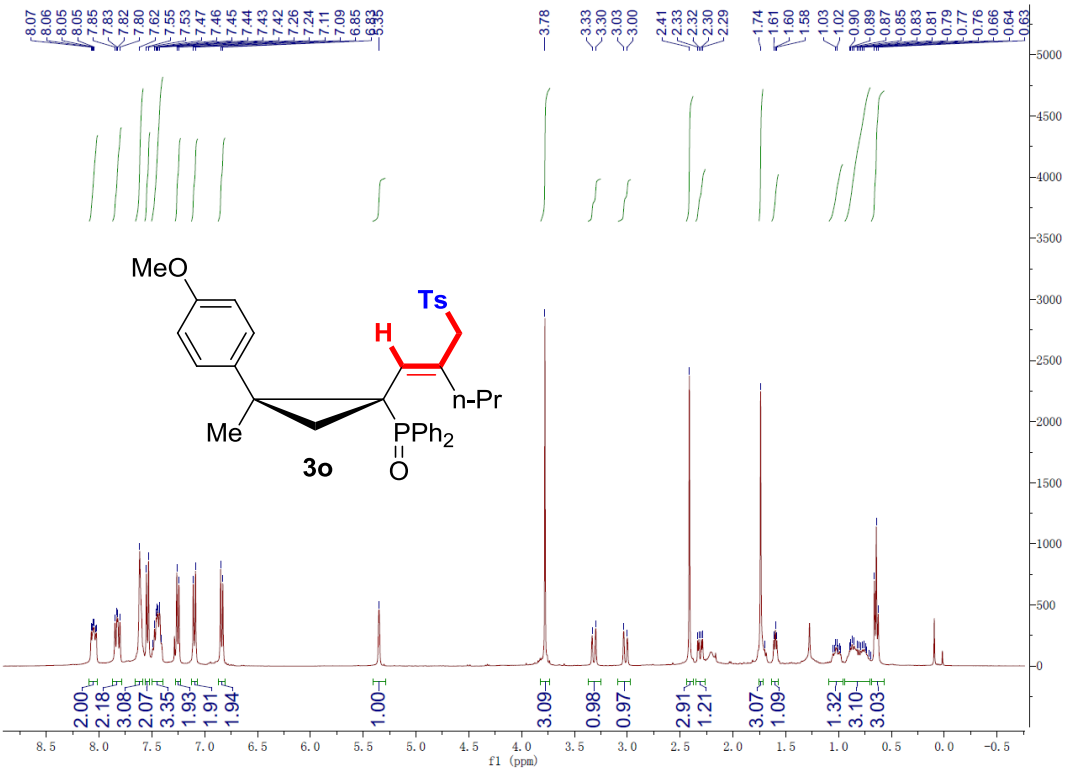

Ts
H
Me
Bn
PPh2
O
3m
f1 (ppm)

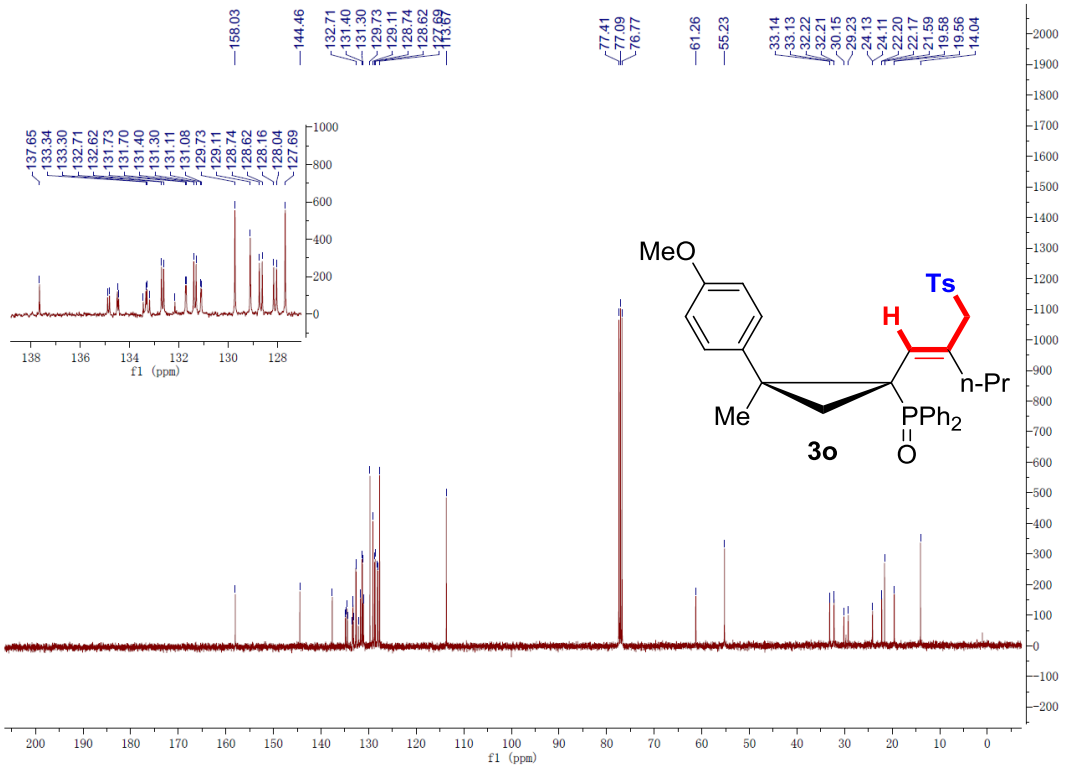

Ts
H
Me
Bn
PPh2
O
3m
f1 (ppm)

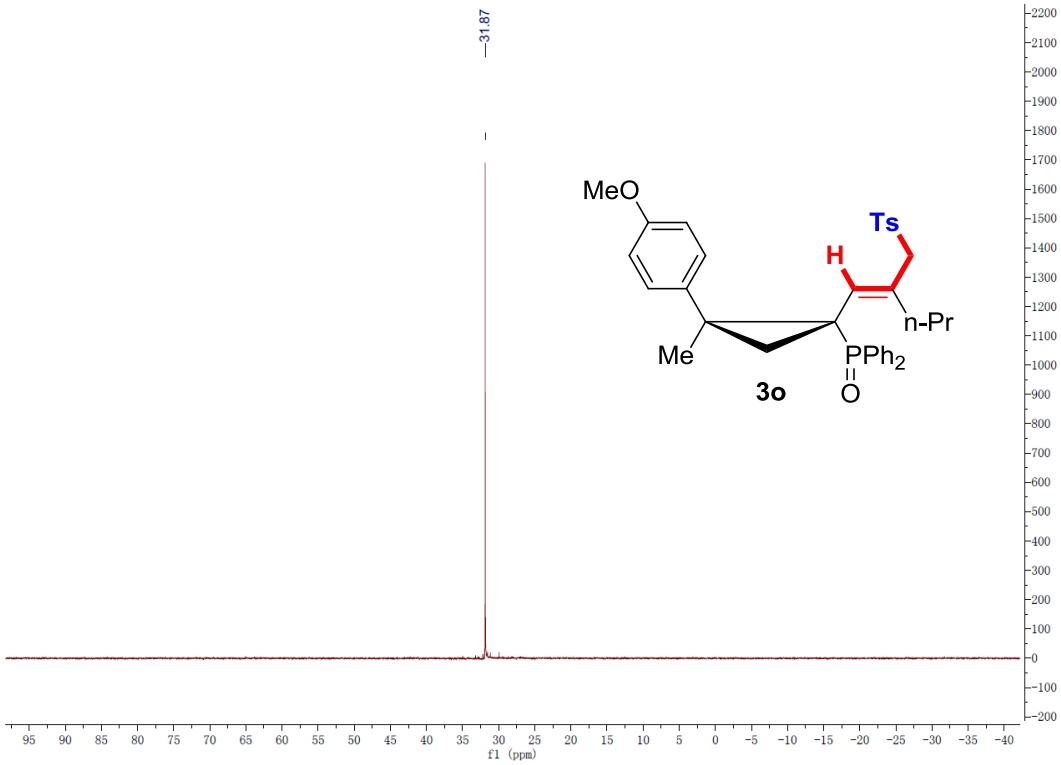


20170505-29_170506105455 #39-44 RT: 0.39-0.45 AV: 6 NL: 6.97E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

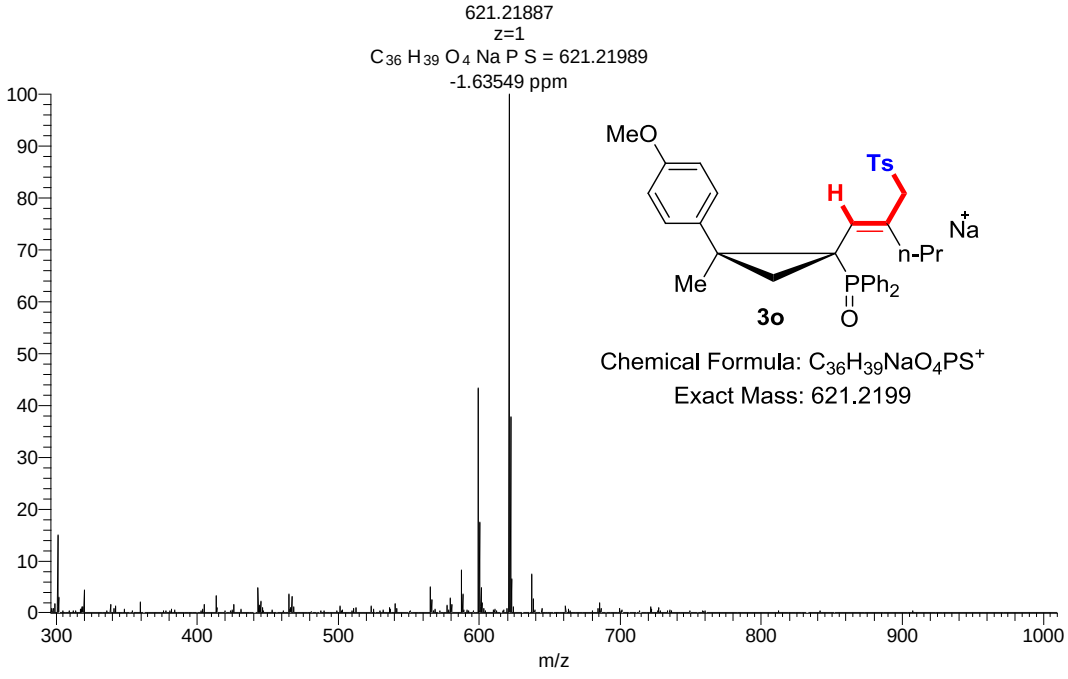


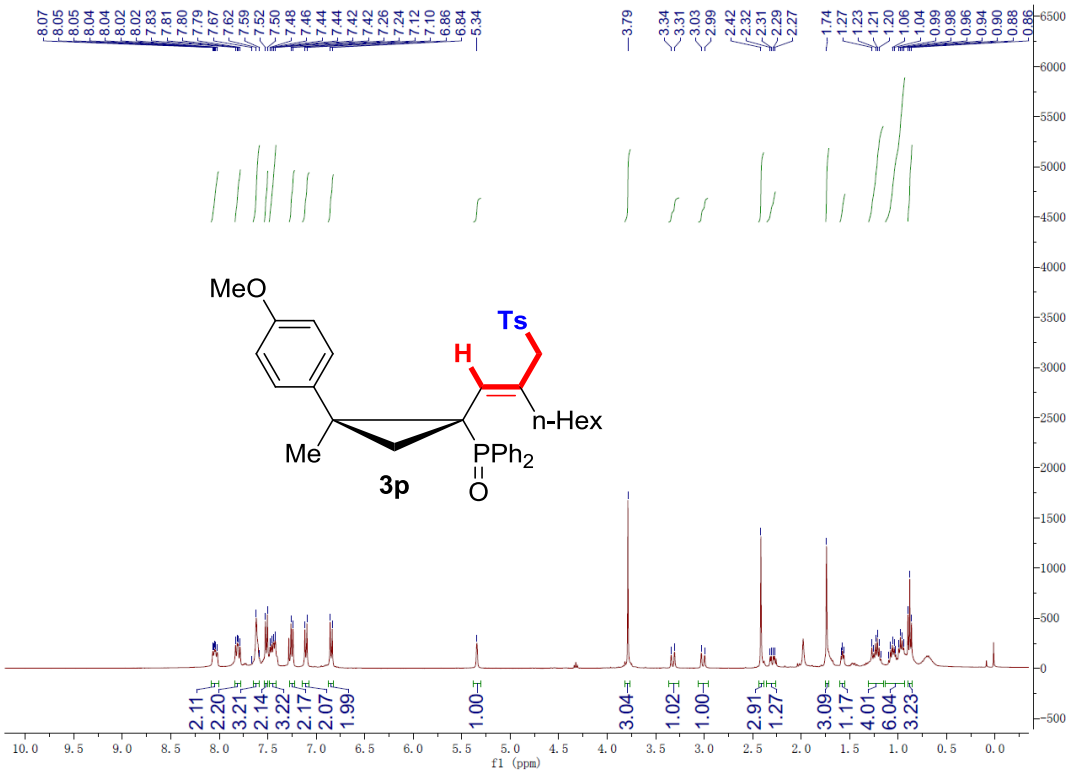

MeO
Ts
H
n-Pr
Me
PPh2
O
3o
f1 (ppm)

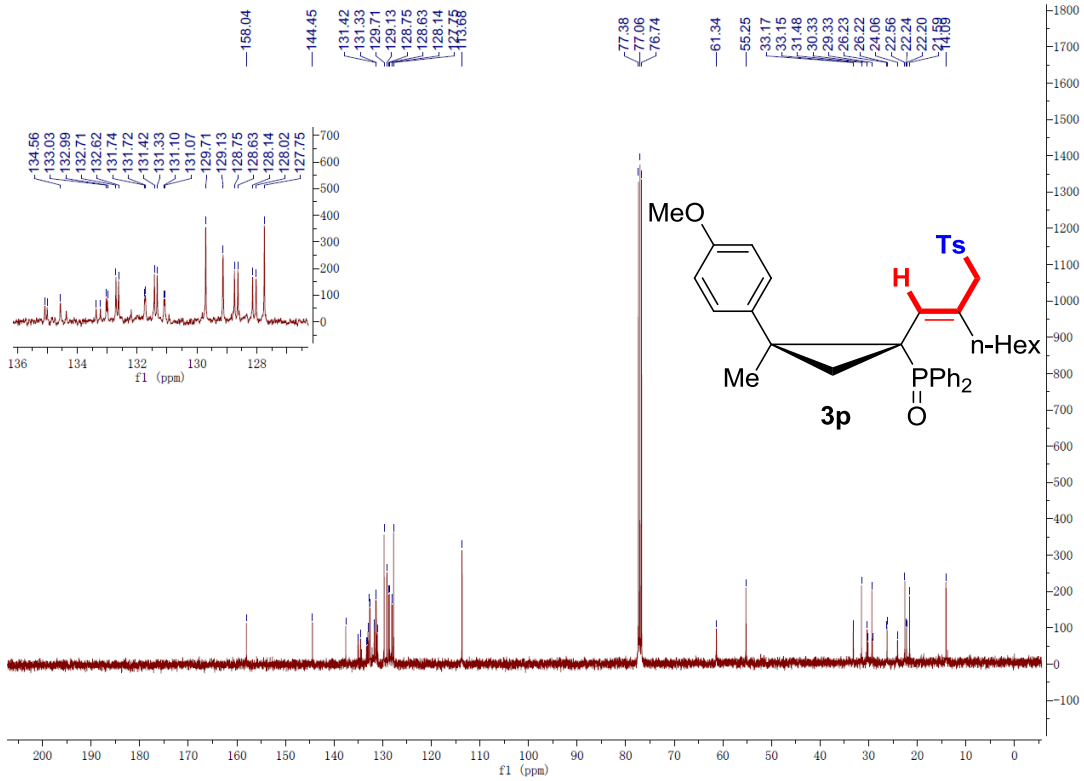

MeO
Ts
H
n-Pr
Me
PPh2
O
3o
f1 (ppm)

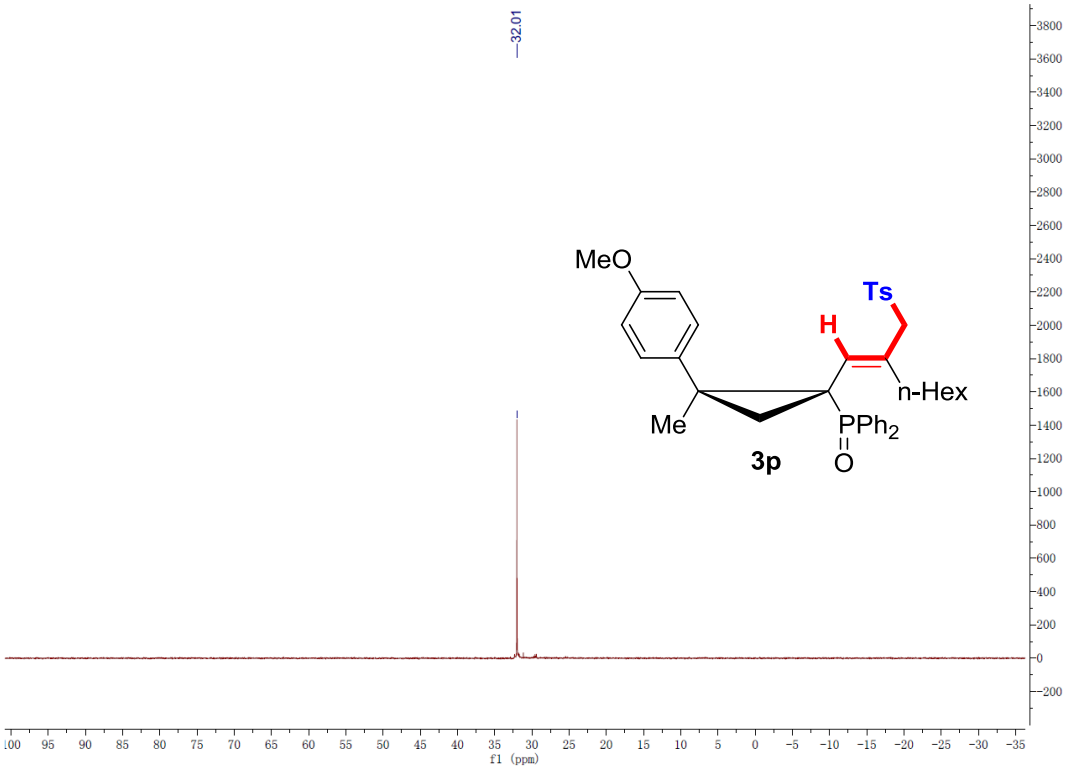


20160930-3 #94 RT: 1.03 AV: 1 NL: 7.72E4
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

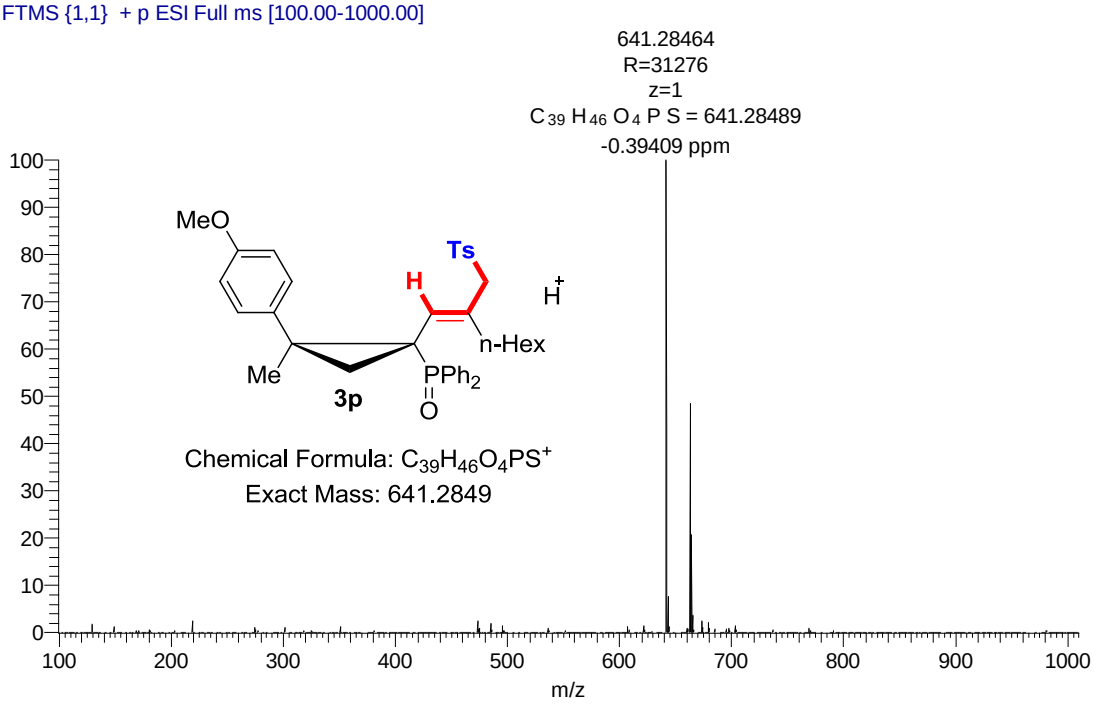


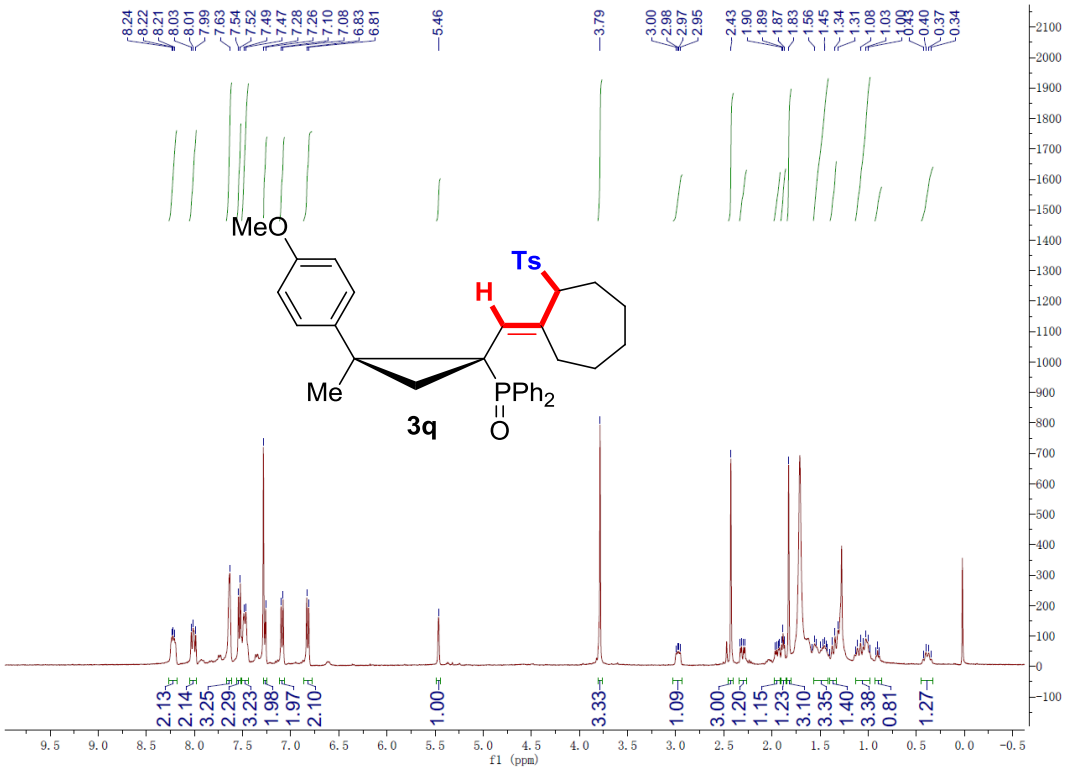

MeO
Ts
H
n-Hex
Me
PPh2
O
3p
f1 (ppm)

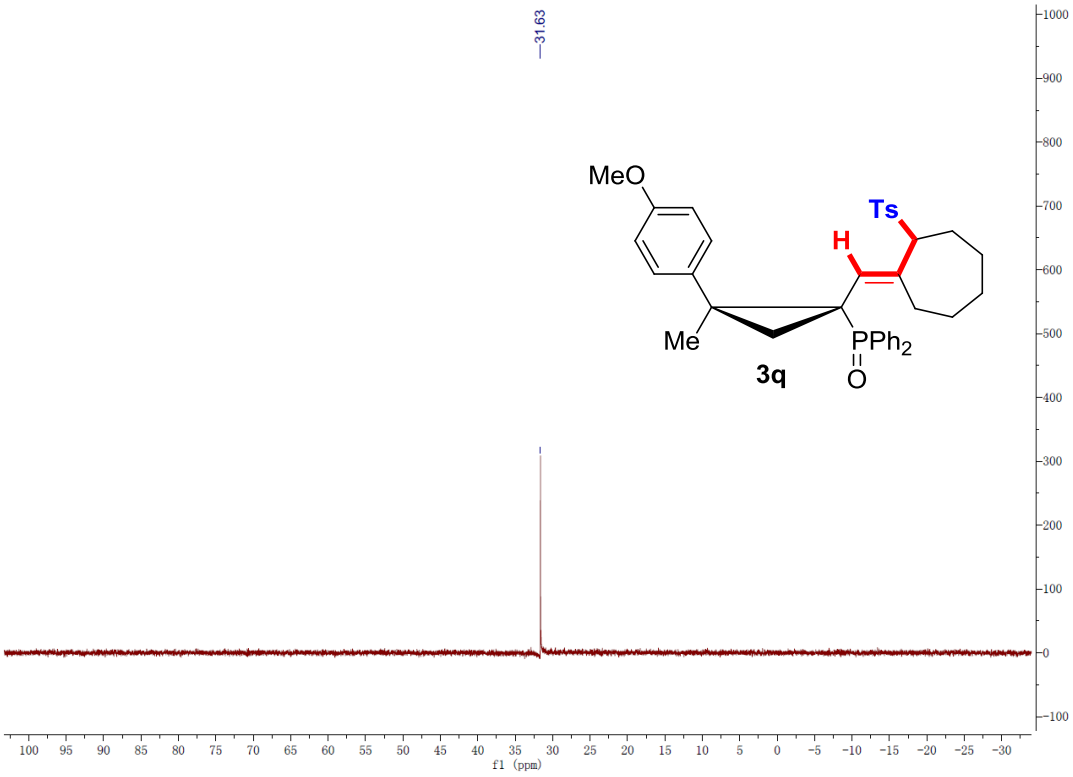

MeO
Ts
H
n-Hex
Me
PPh2
O
3p
f1 (ppm)

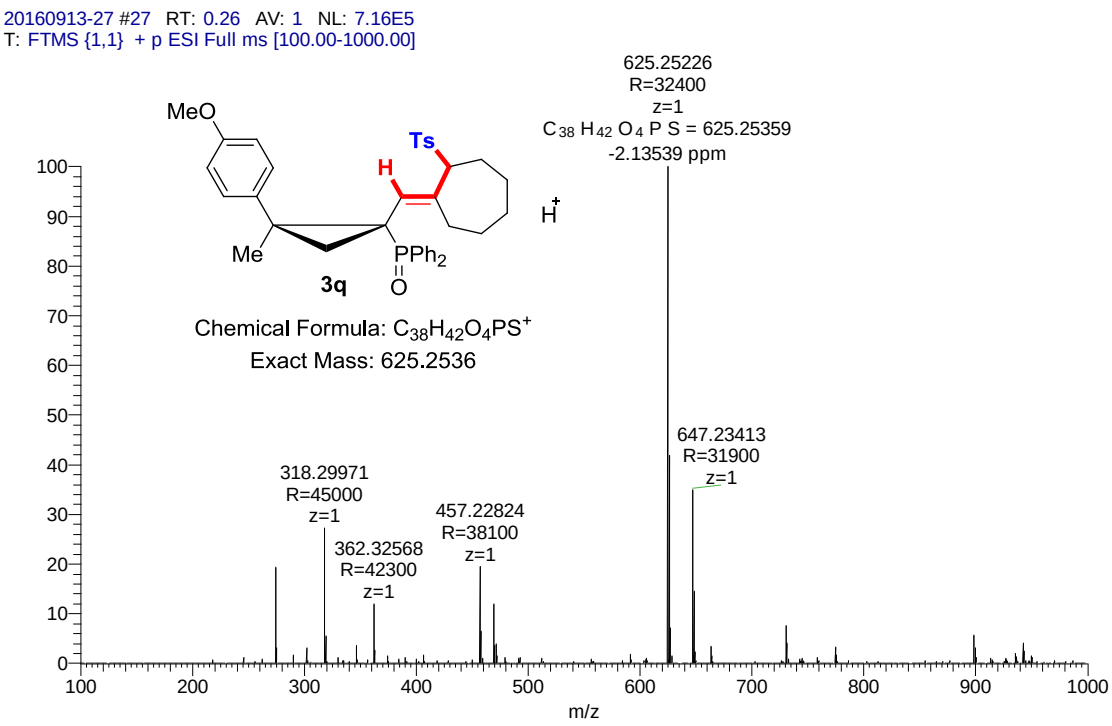


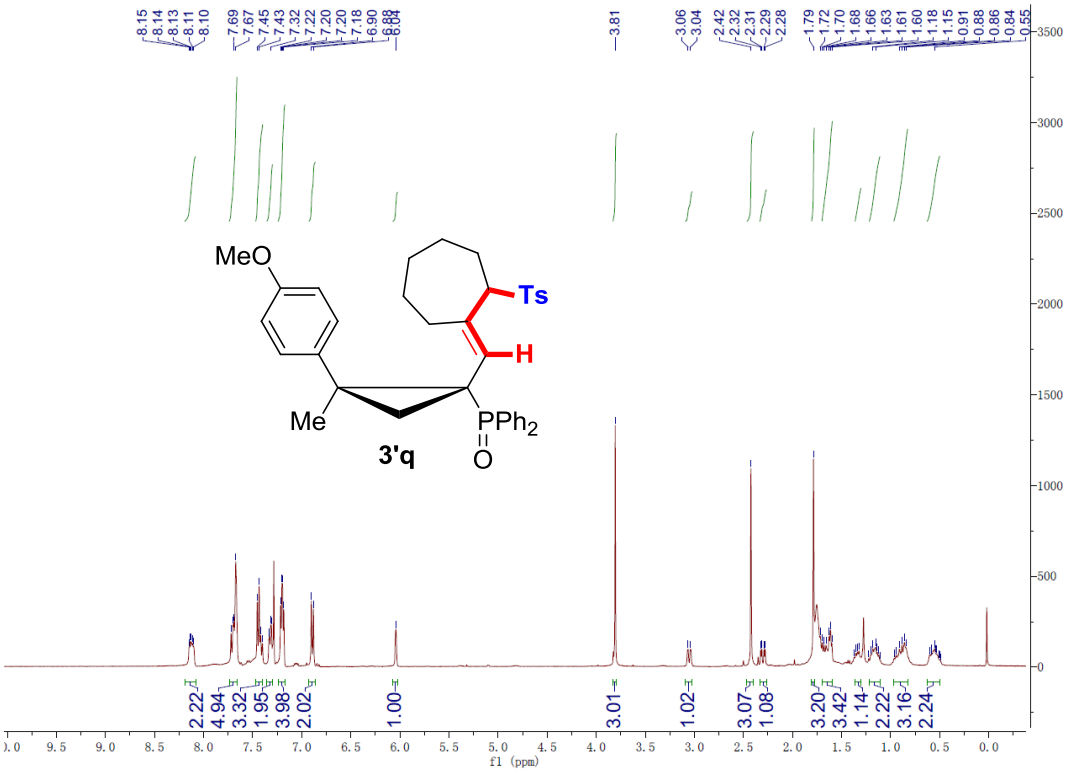
20170505-35_170506122826 #41-46 RT: 0.41-0.47 AV: 6 NL: 4.69E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

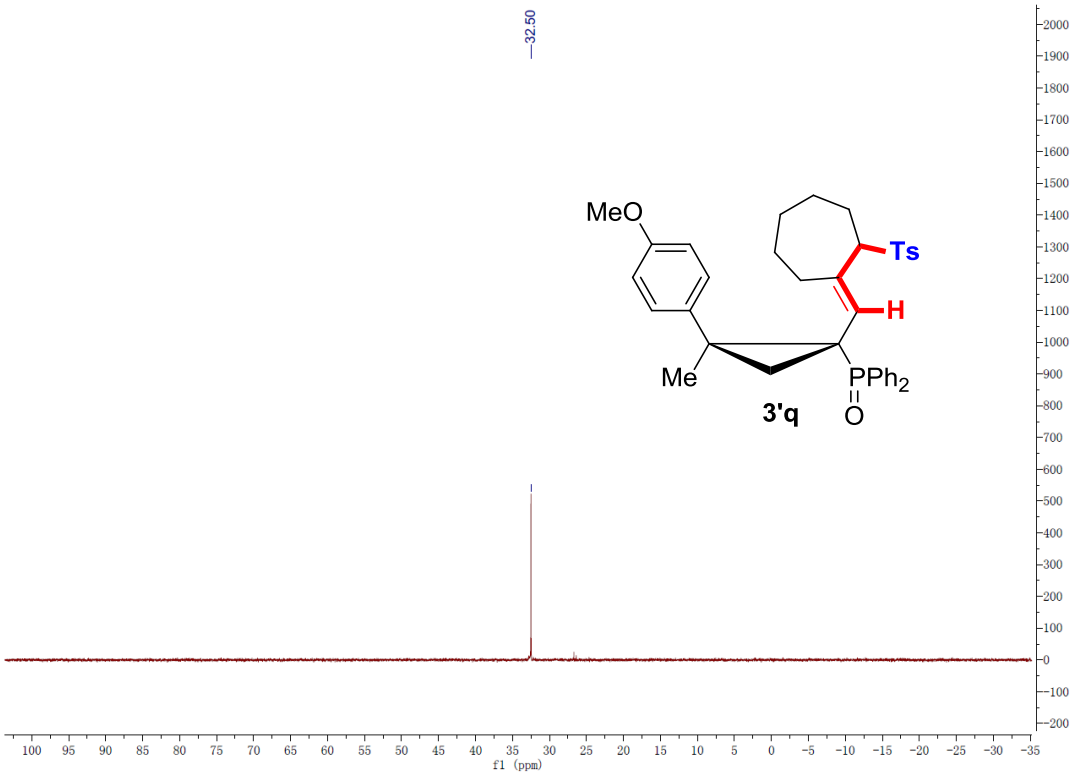



MeO
Ts
H
Me
PPh2
O
3q

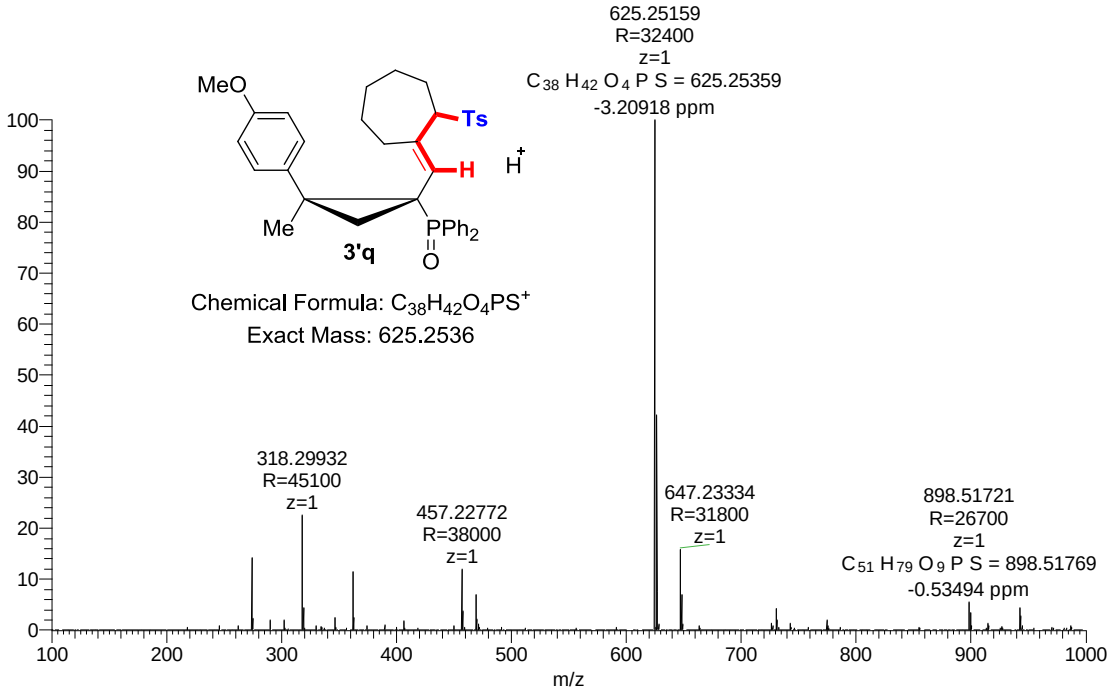

MeO
Ts
H
Me
PPh2
O
3q

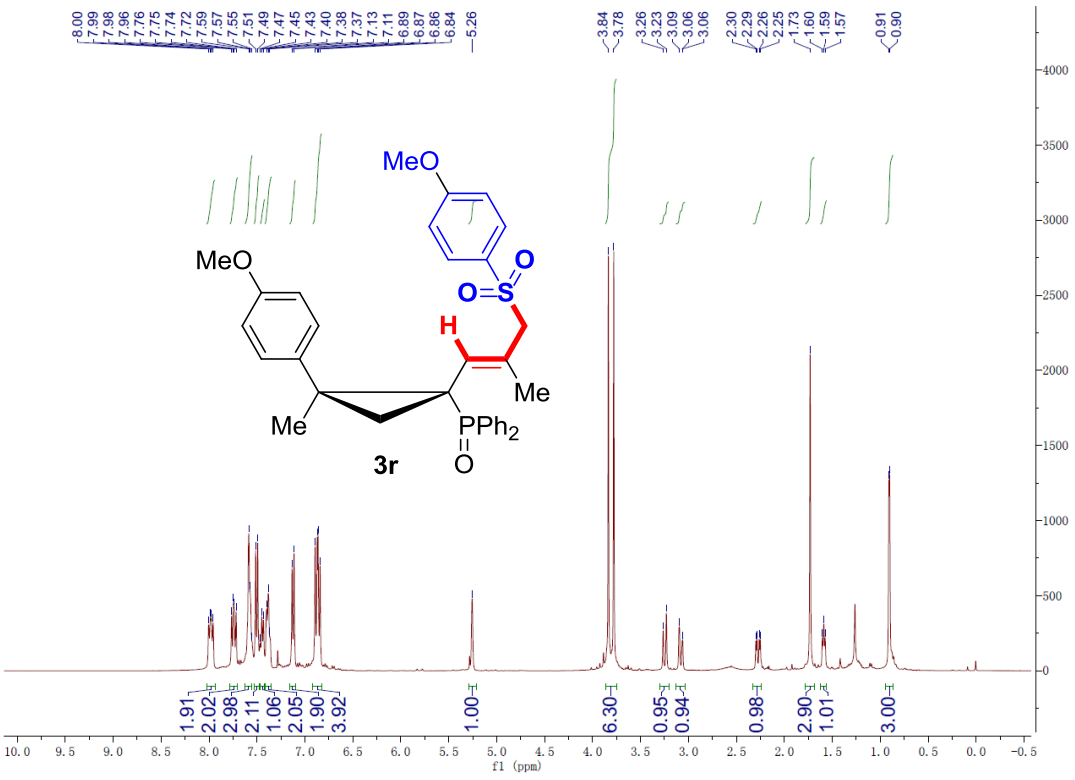

20160913-27 #27 RT: 0.26 AV: 1 NL: 7.16E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]
625.25226
R=32400
z=1
C 38 H 42 O 4 P S = 625.25359
-2.13539 ppm
MeO
Ts
H
Me
PPh2
O
3q
H+
Chemical Formula: C38H42O4PS+
Exact Mass: 625.2536
647.23413
R=31900
z=1
318.29971
R=45000
z=1
457.22824
R=38100
z=1
362.32568
R=42300
z=1
m/z

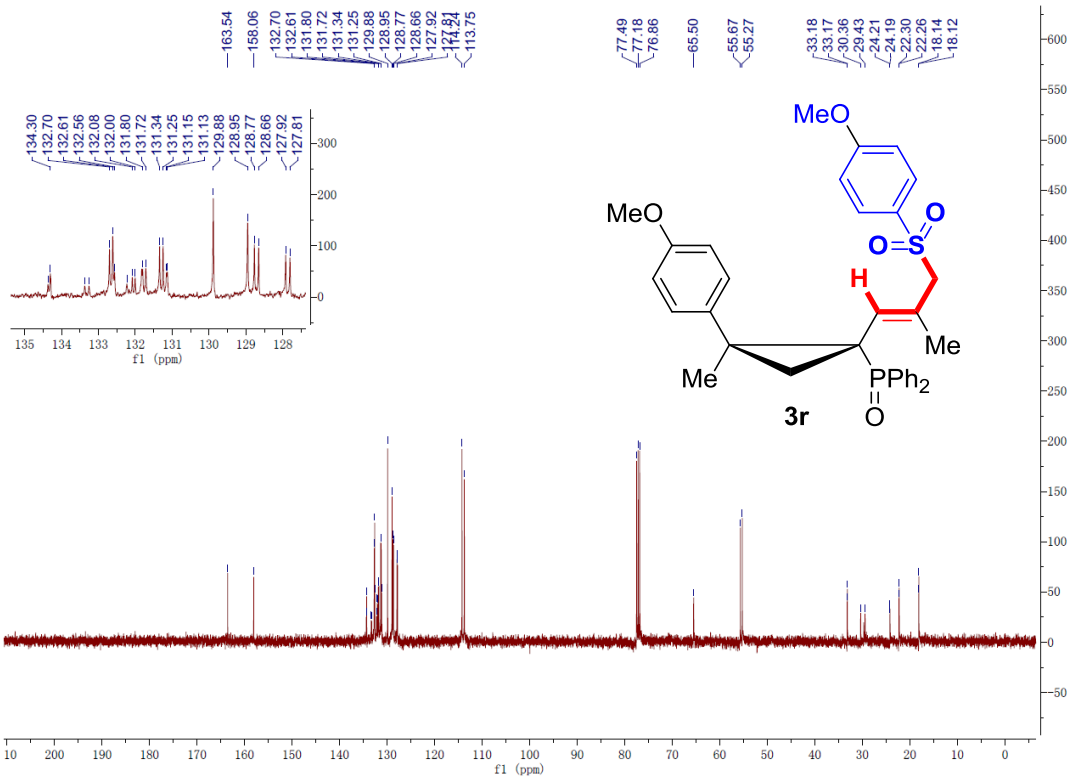

MeO
Ts
H
Me
PPh2
O
3'q
f1 (ppm)

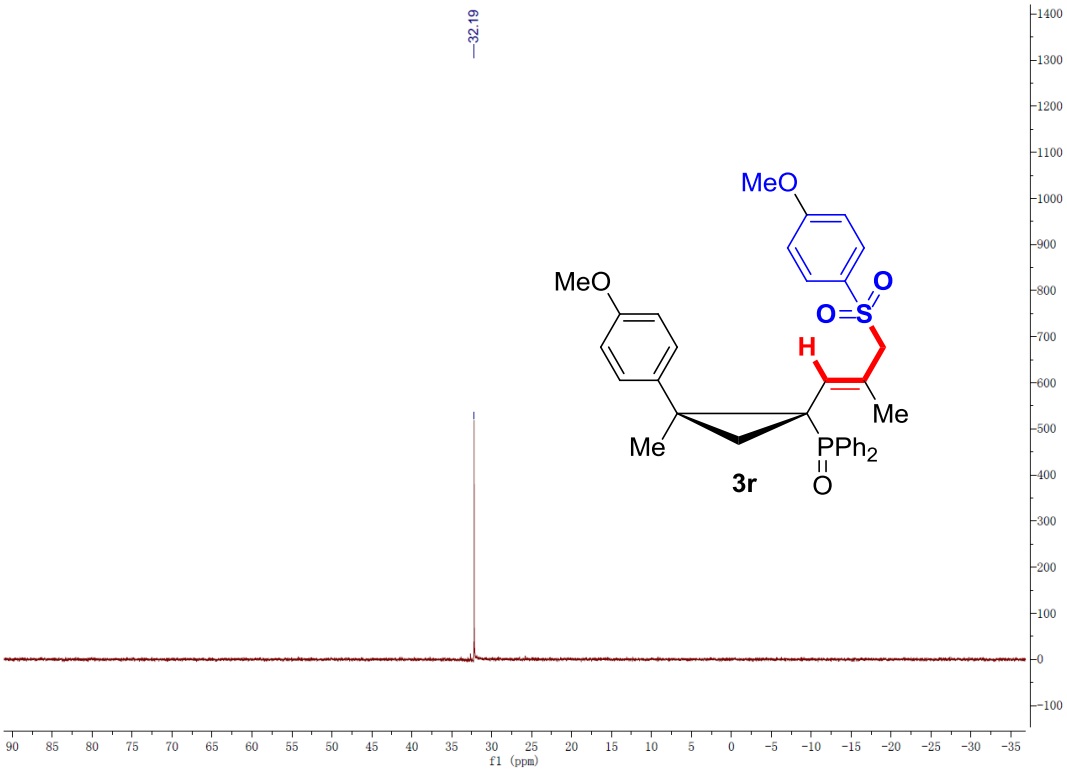


20160913-28 #18 RT: 0.19 AV: 1 NL: 1.50E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

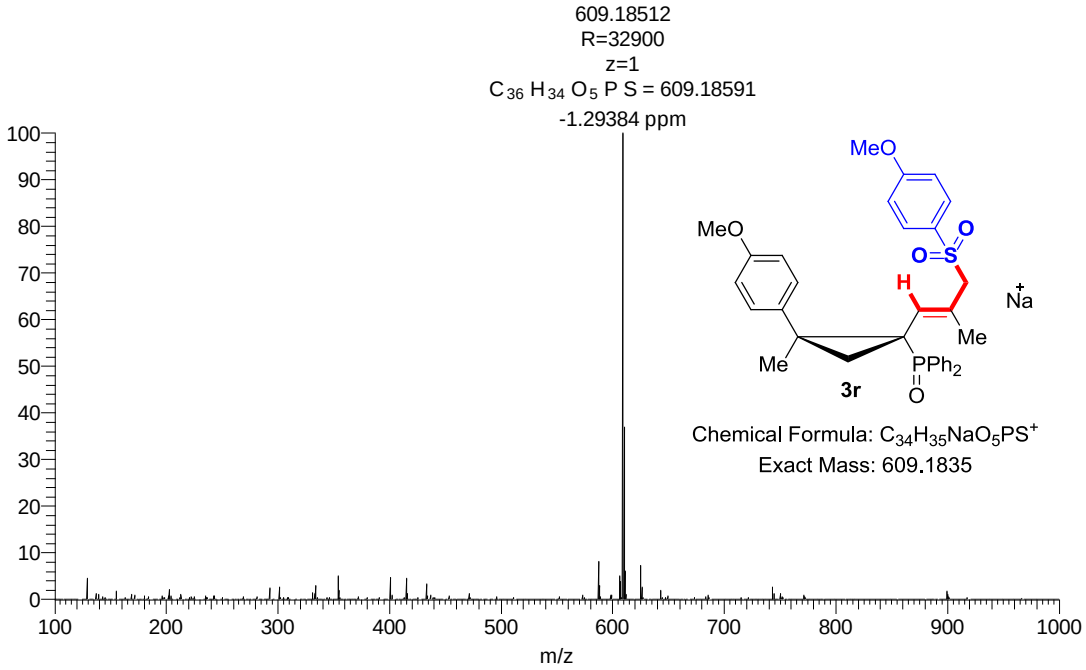


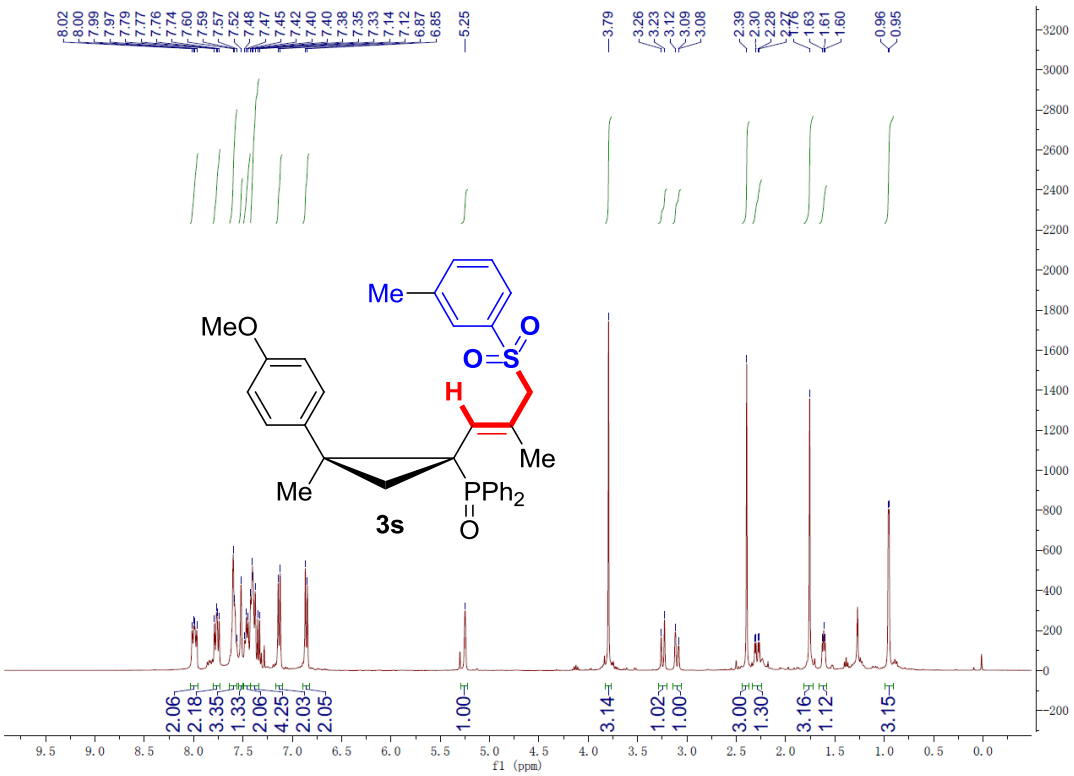

MeO
MeO
O
O=S
H
Me
Me
PPh2
O
3r
f1 (ppm)

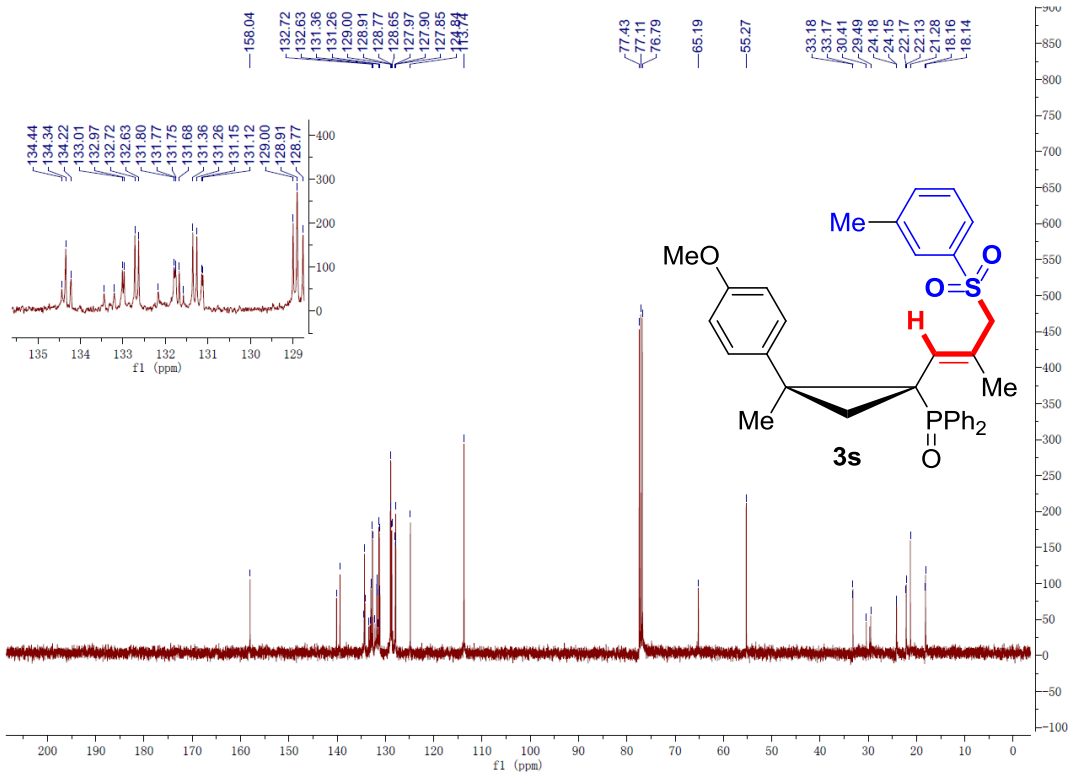

MeO
MeO
O
O=S
H
Me
Me
PPh2
O
3r
f1 (ppm)

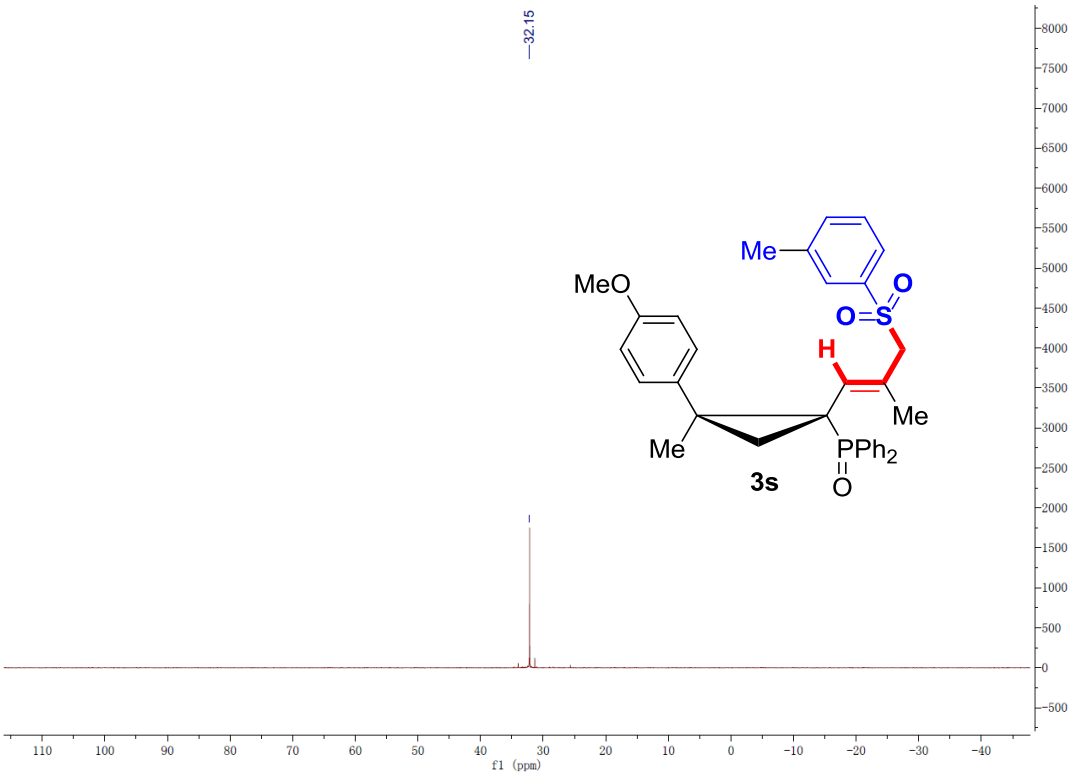


20 #42 RT: 0.43 AV: 1 NL: 2.99E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

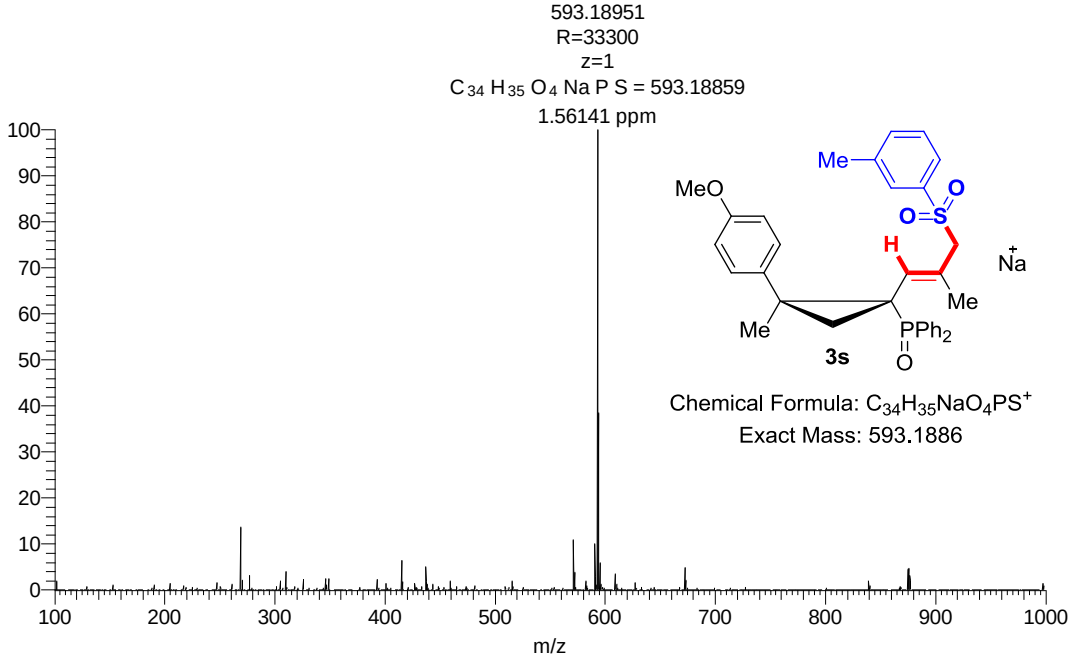


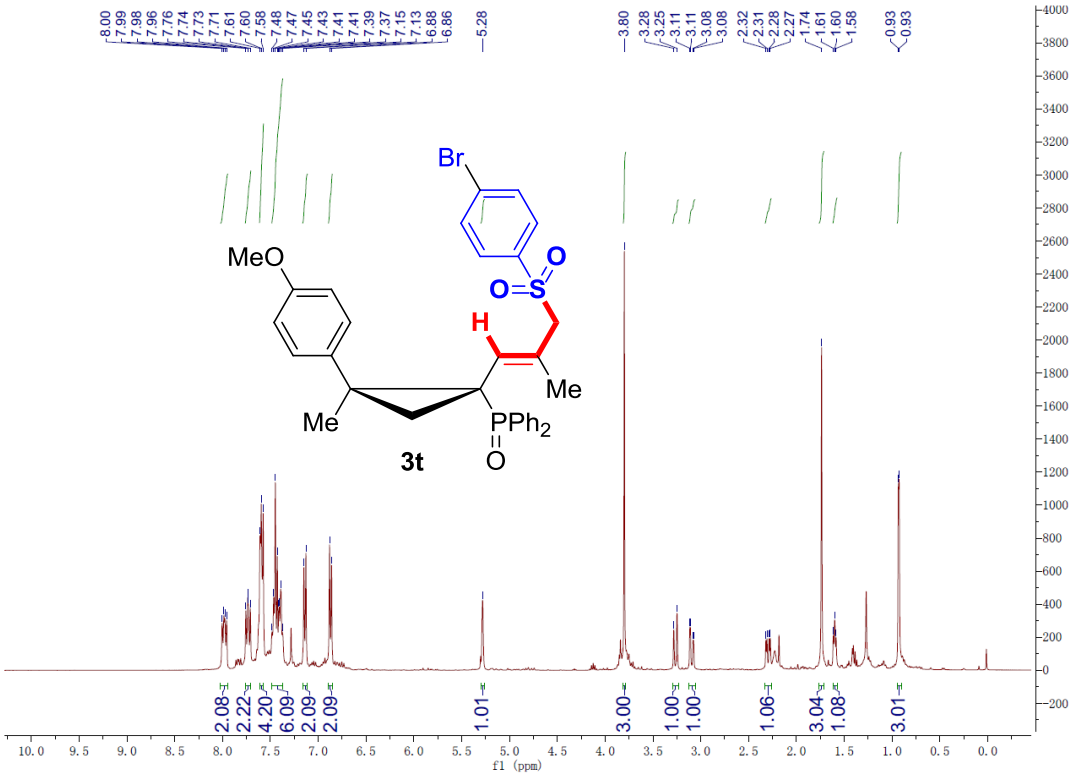

Me
MeO
O
O=S
H
Me
Me
PPh2
O
3s
f1 (ppm)

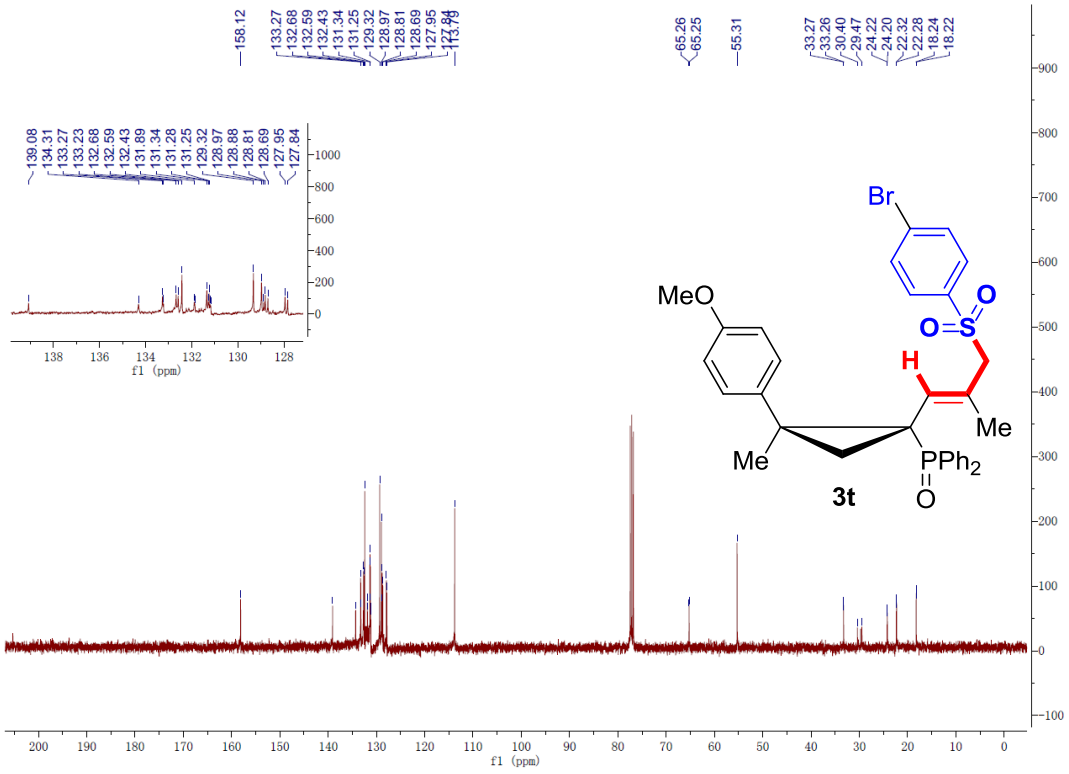

Me
MeO
O
O=S
H
Me
Me
PPh2
O
3s
f1 (ppm)

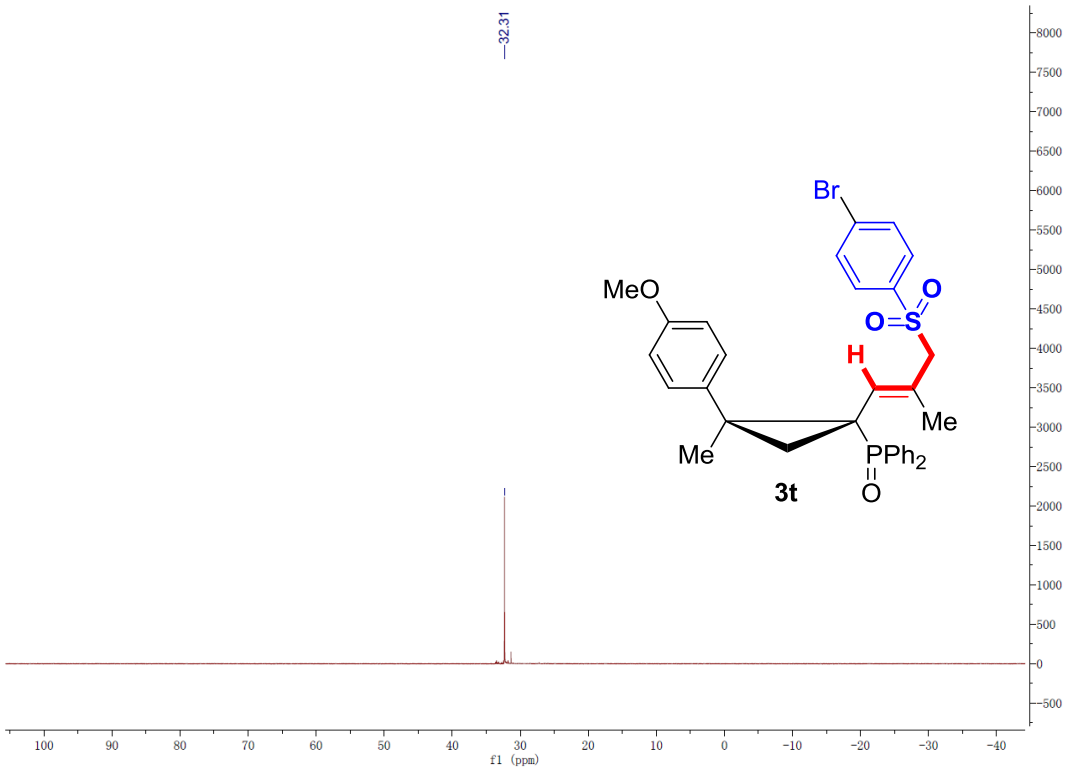


25 #23 RT: 0.24 AV: 1 NL: 8.21E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

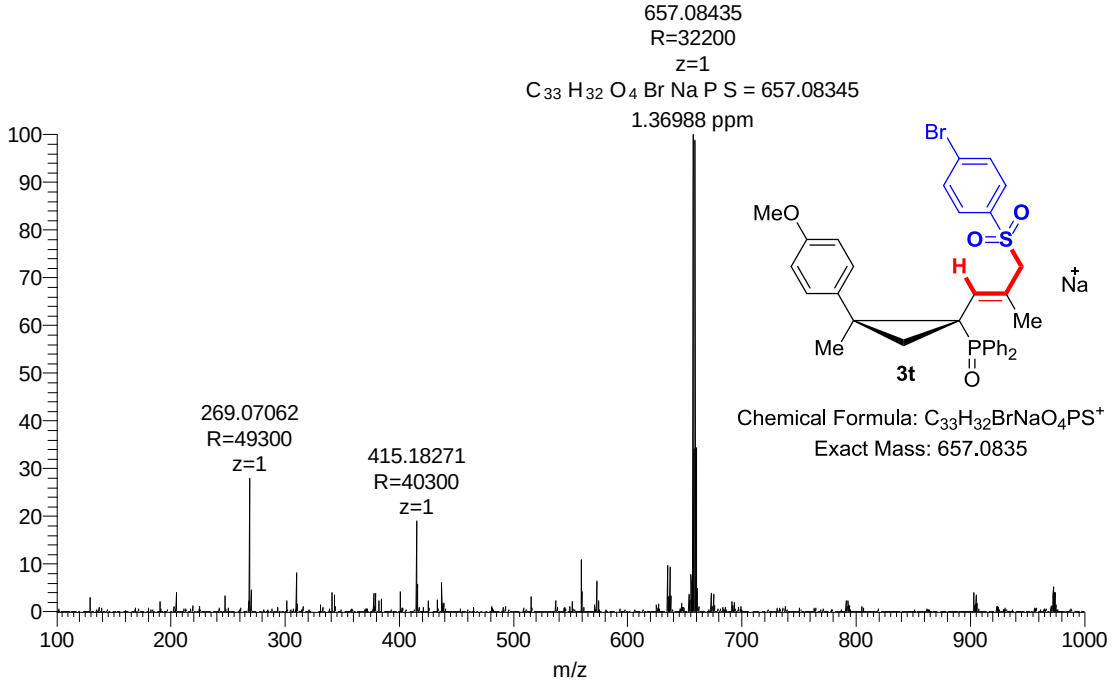


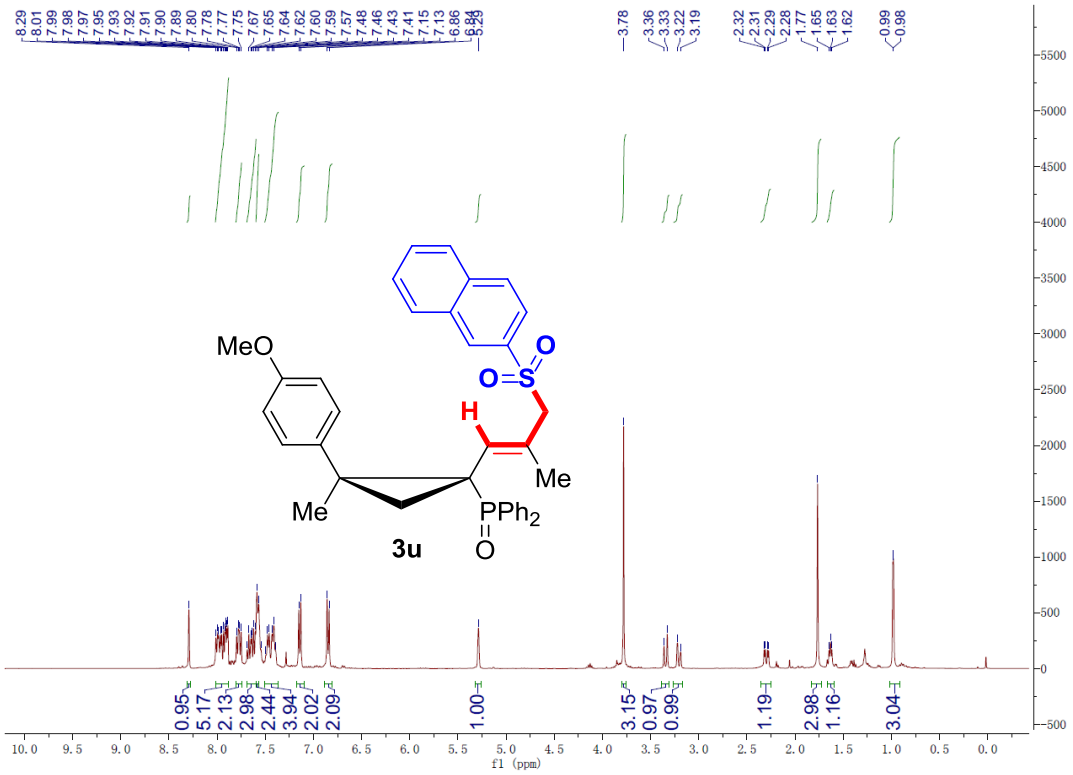

Br
MeO
O
O=S
H
Me
Me
PPh2
O
3t
f1 (ppm)

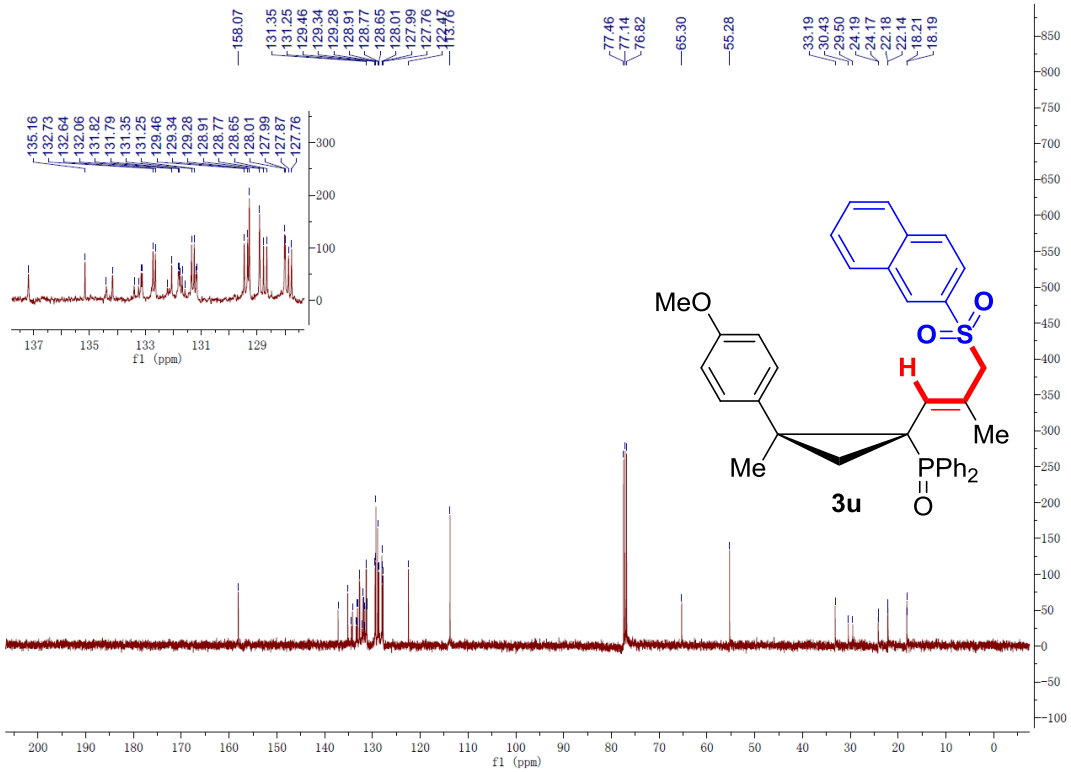

Br
MeO
O
O=S
H
Me
Me
PPh2
O
3t
f1 (ppm)

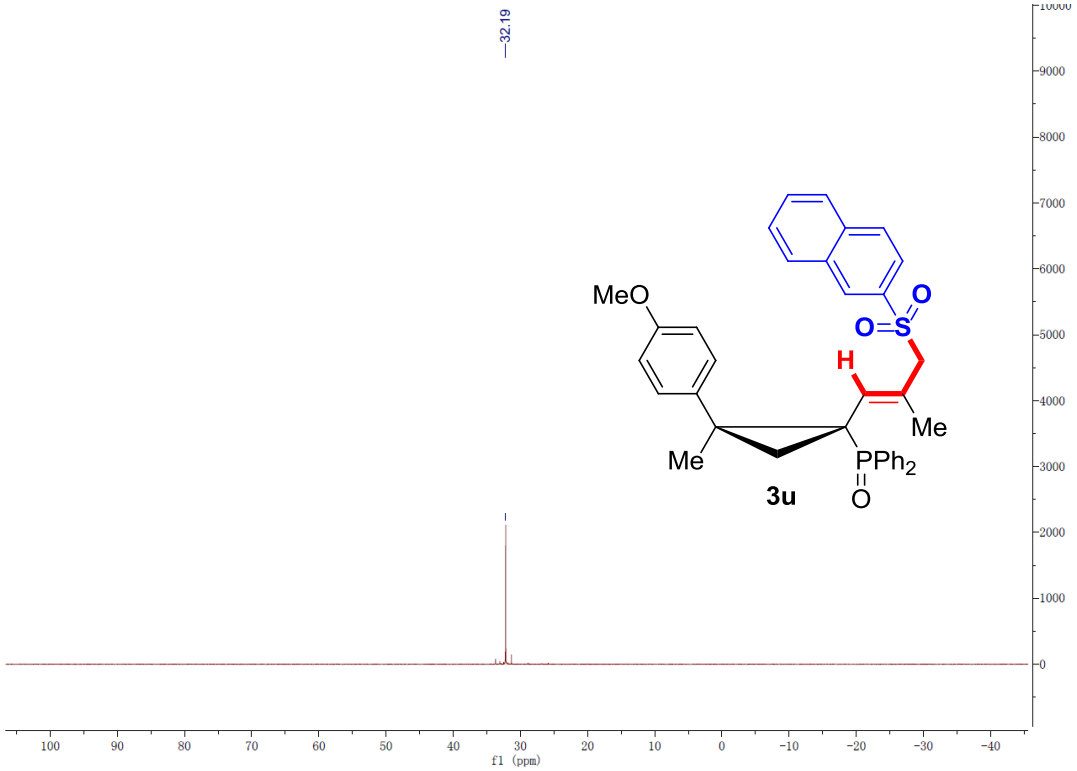


23 #31 RT: 0.32 AV: 1 NL: 2.70E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

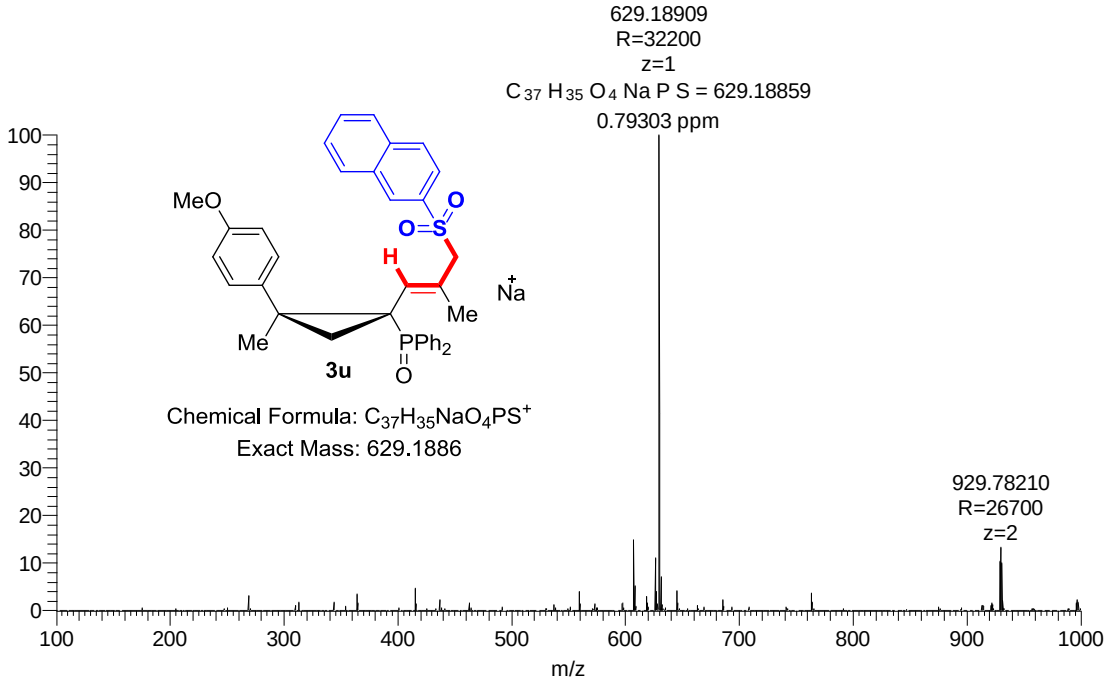


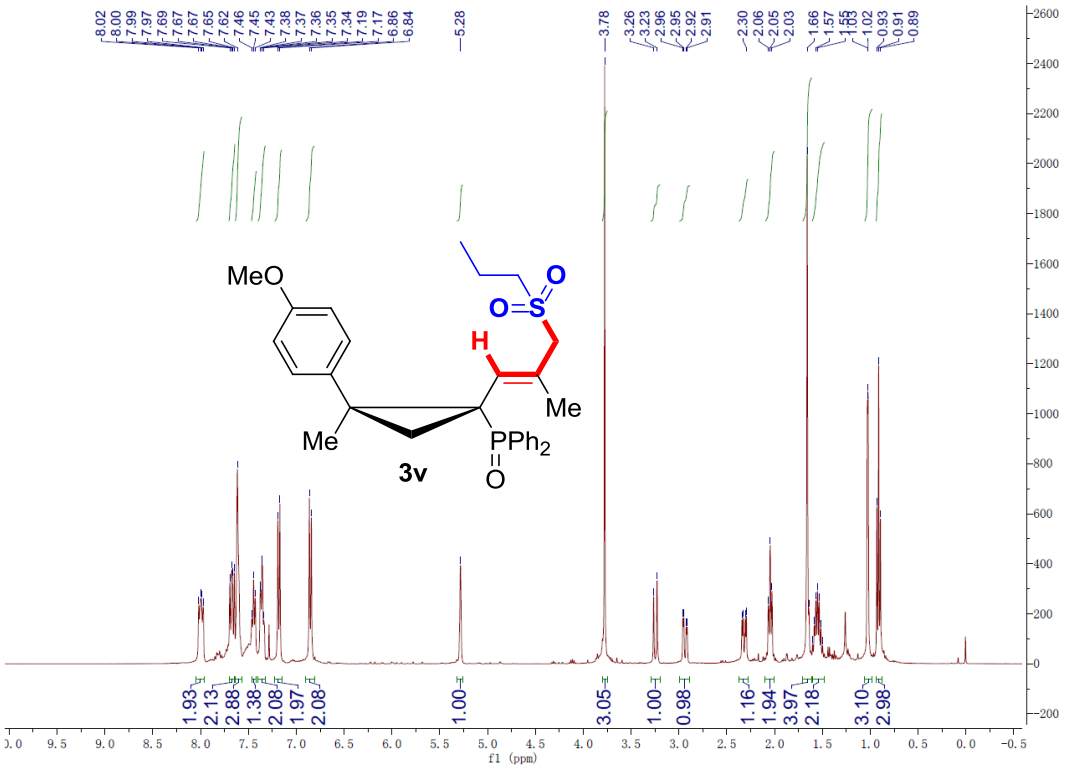

MeO
O
O=S
H
Me
Me
PPh2
O
3u
f1 (ppm)

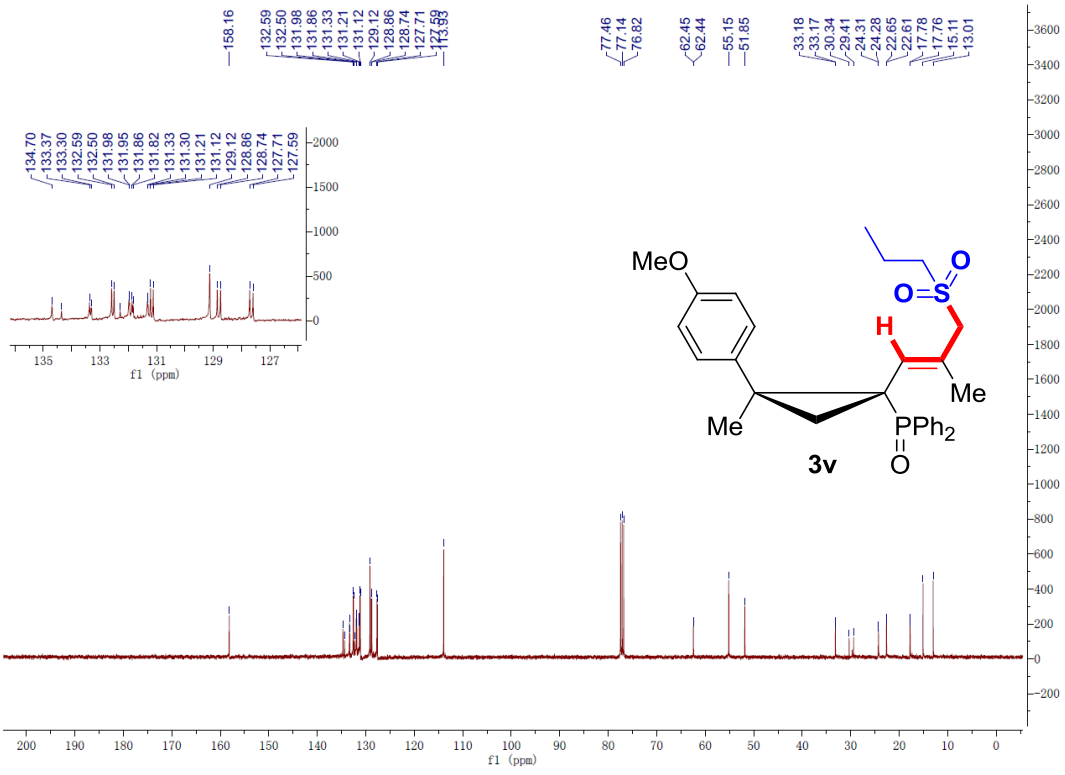

MeO
O
O=S
H
Me
Me
PPh2
O
3u
f1 (ppm)

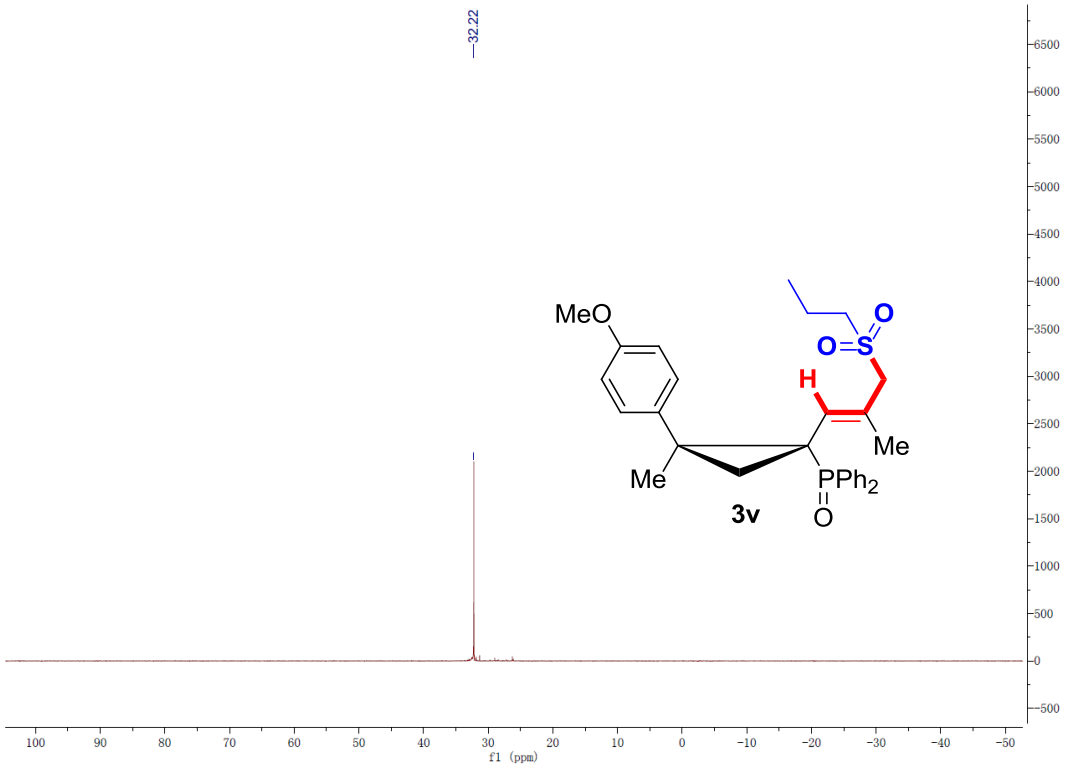


24 #32 RT: 0.34 AV: 1 NL: 1.02E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

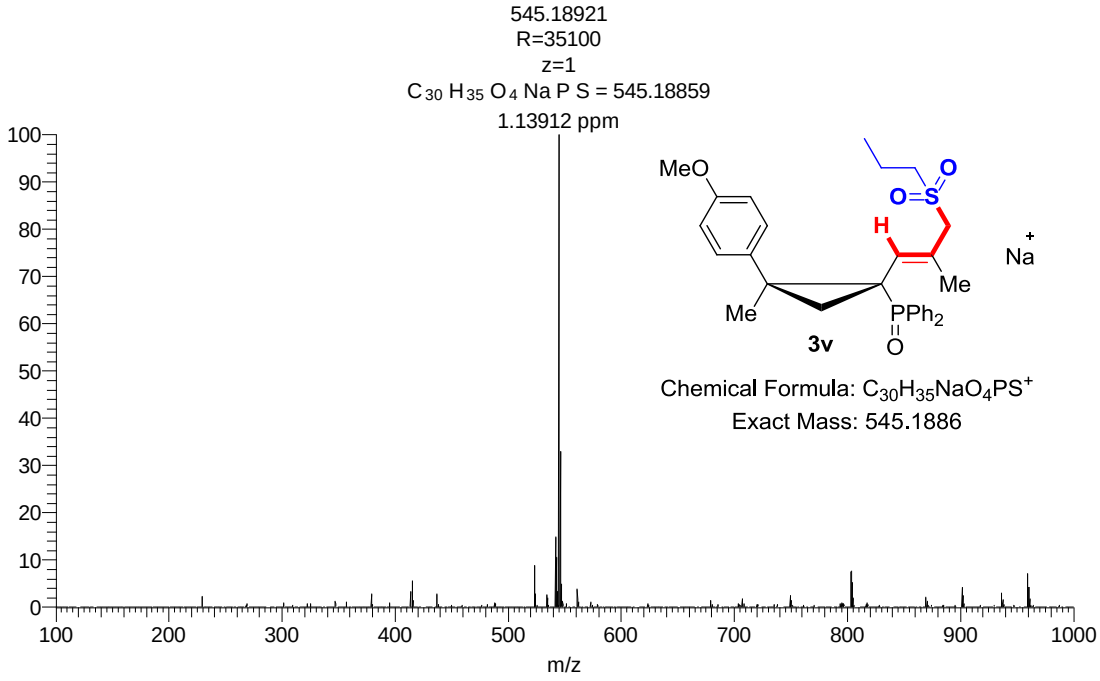


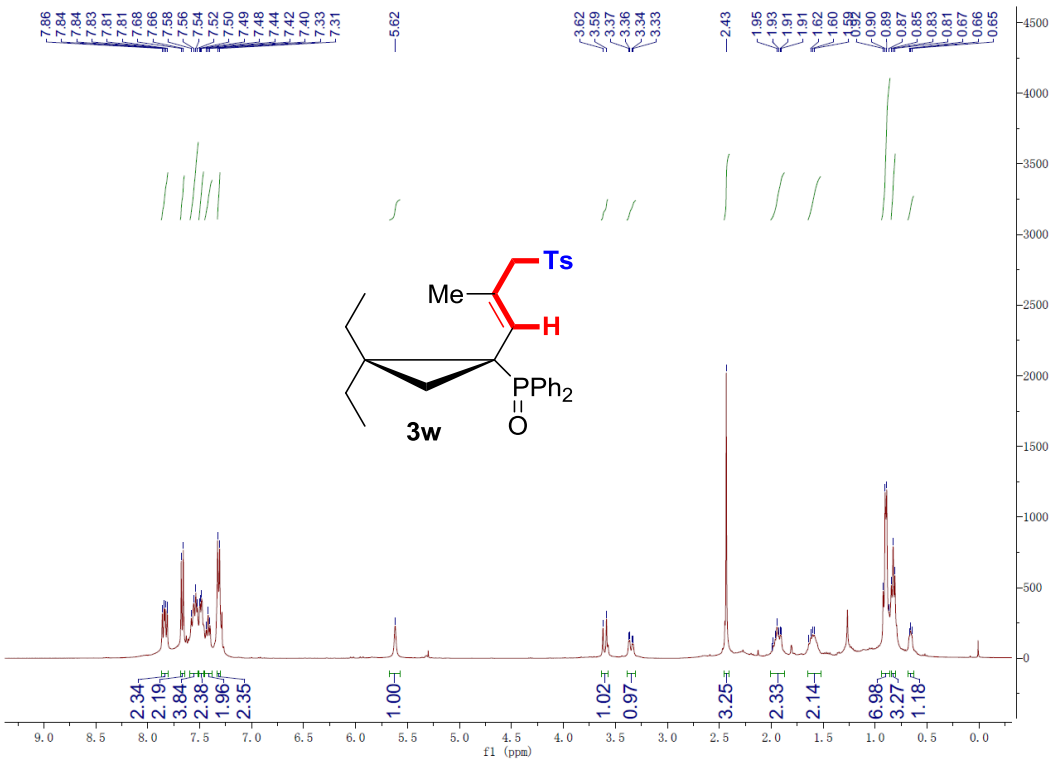

MeO
O
O=S
H
Me
Me
PPh2
O
3v
f1 (ppm)

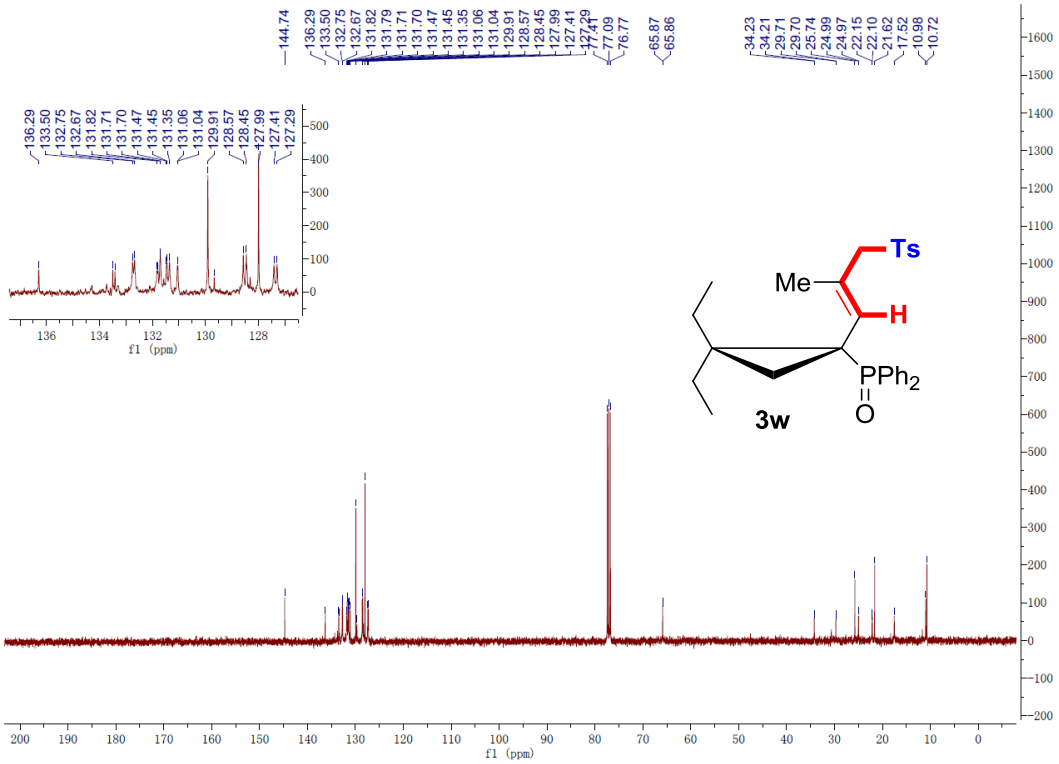

MeO
O
O=S
H
Me
Me
PPh2
O
3v
f1 (ppm)

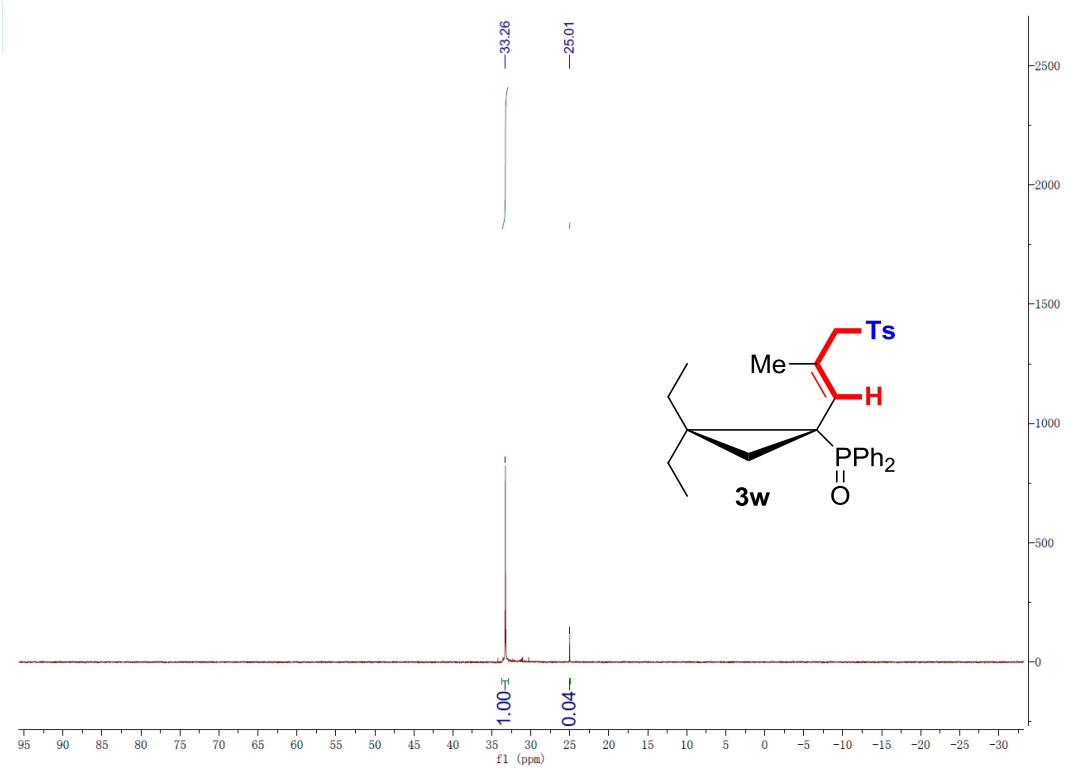


26 #30 RT: 0.31 AV: 1 NL: 1.37E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

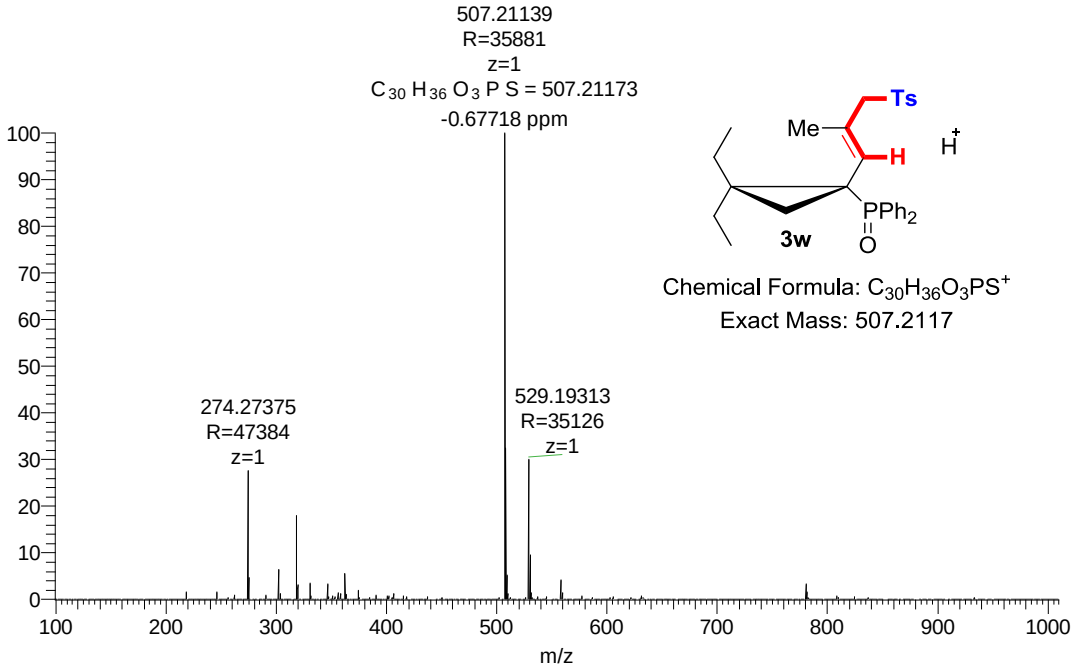



Ts
Me
H
PPh2
O
3w
f1 (ppm)

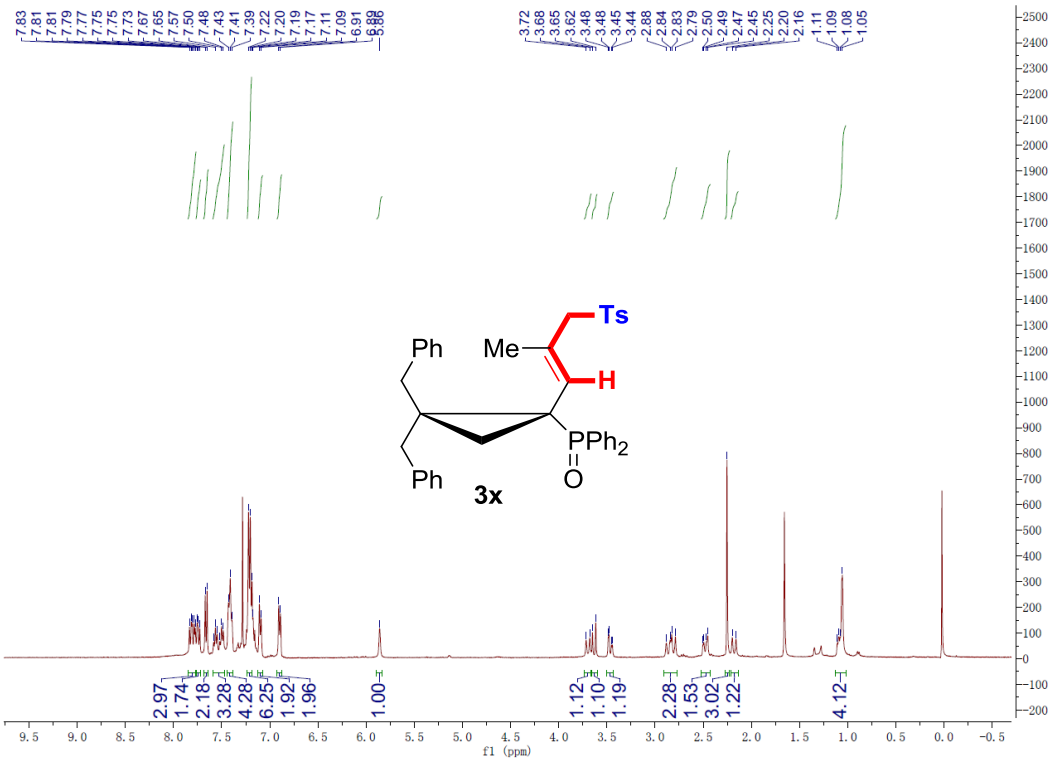

Ts
Me
H
PPh2
O
3w
f1 (ppm)

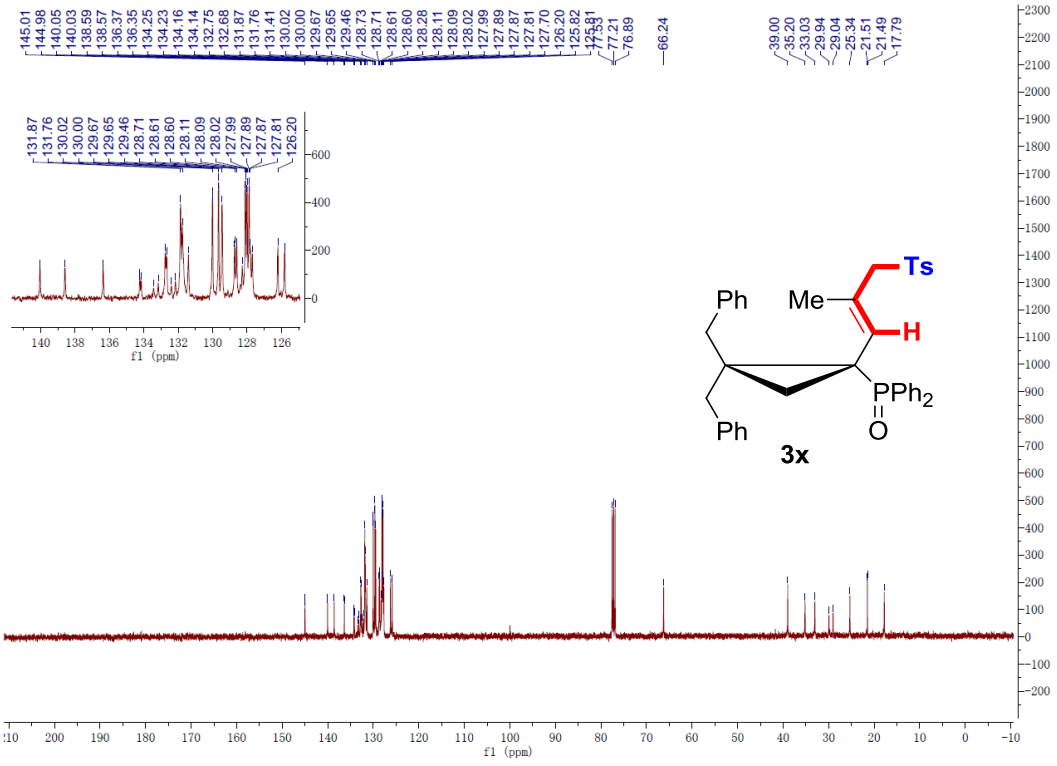


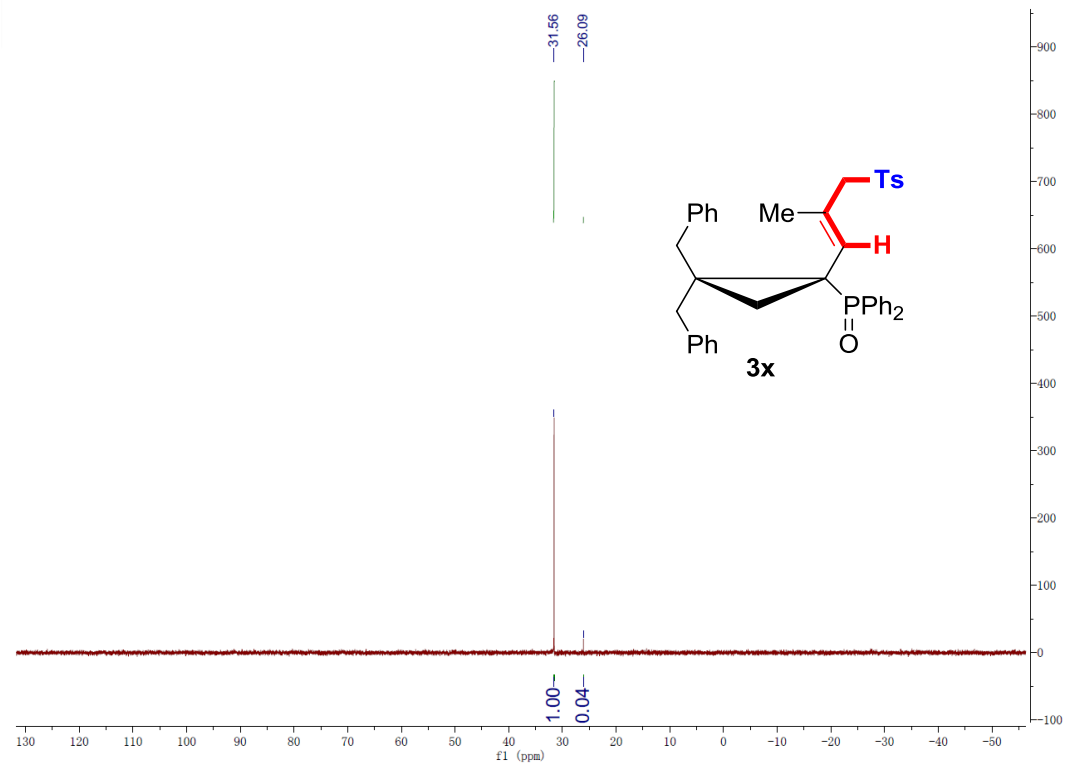
20170505-32_170506114140 #37-39 RT: 0.33-0.35 AV: 3 NL: 2.04E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]



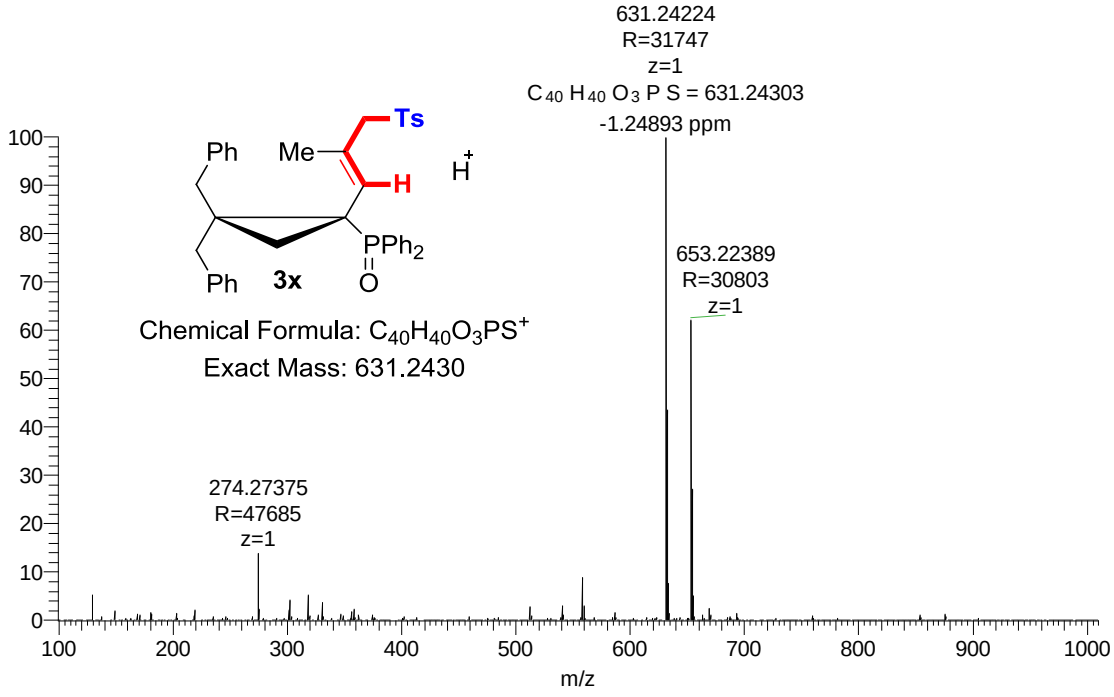
Chemical Formula: $C_{30}H_{36}O_3PS^+$
Exact Mass: 507.2117

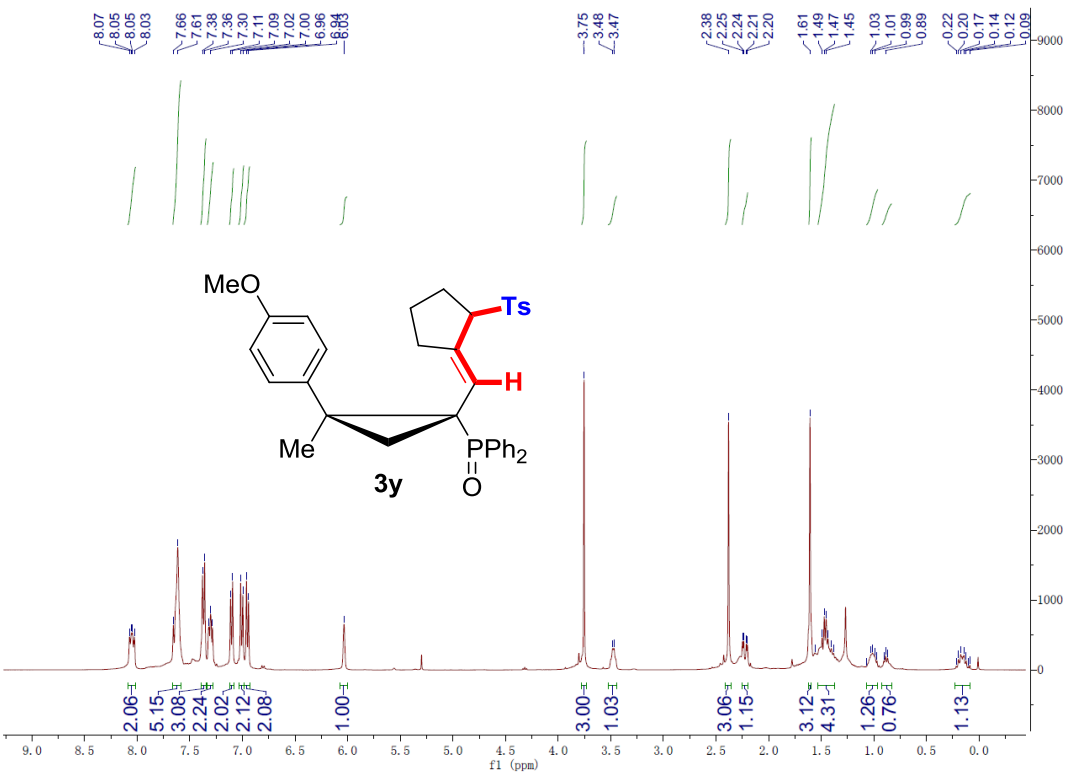

Ts
Ph
Me
H
PPh2
O
Ph
3x
2.97
1.74
2.18
3.28
4.28
6.25
1.92
1.96
1.00
1.12
1.10
1.19
2.28
1.53
3.02
1.22
4.12
f1 (ppm)

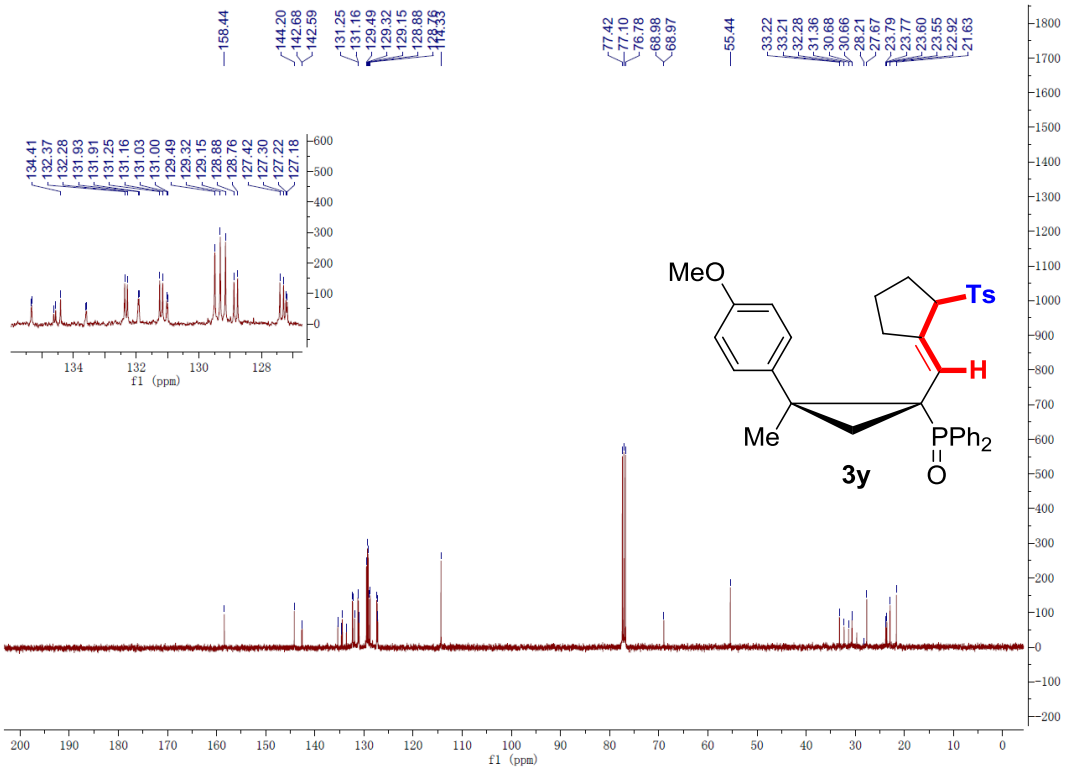

Ts
Ph
Me
H
PPh2
O
Ph
3x
f1 (ppm)

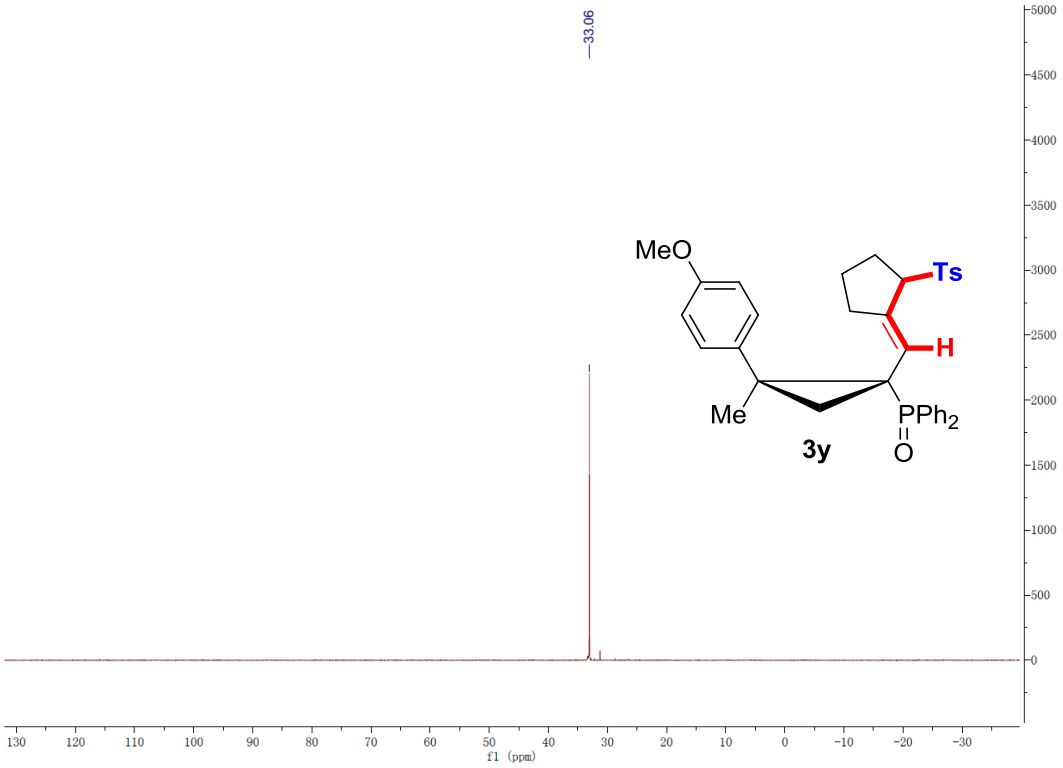


20170505-31 #67-71 RT: 0.71-0.76 AV: 5 NL: 2.23E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

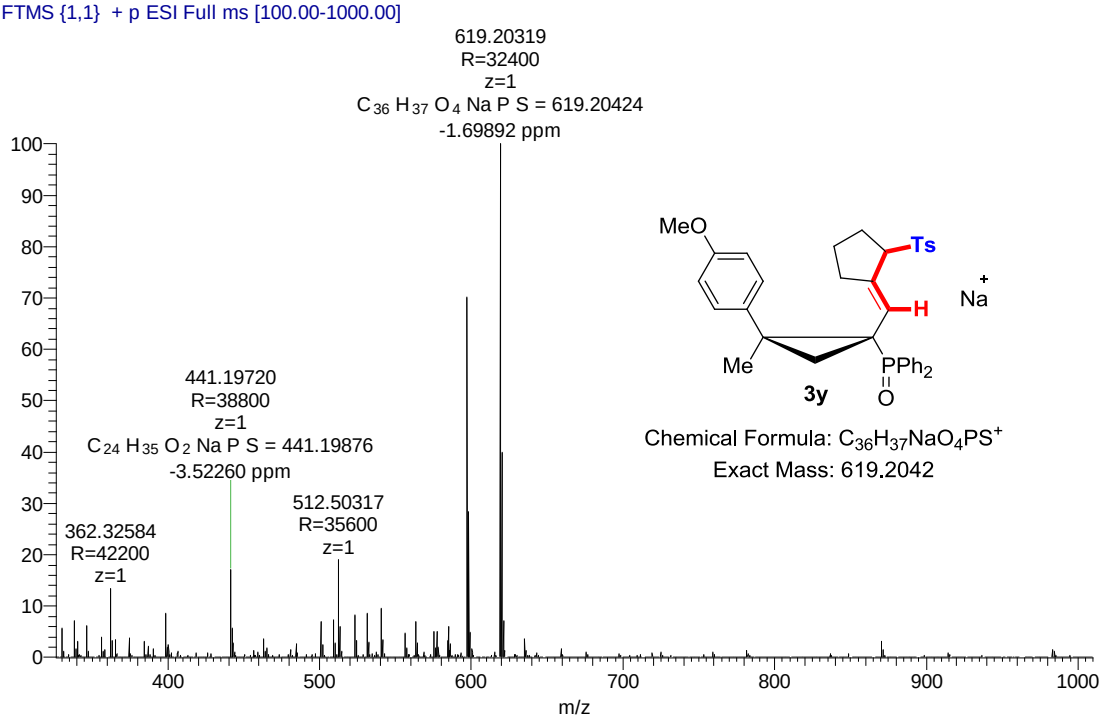


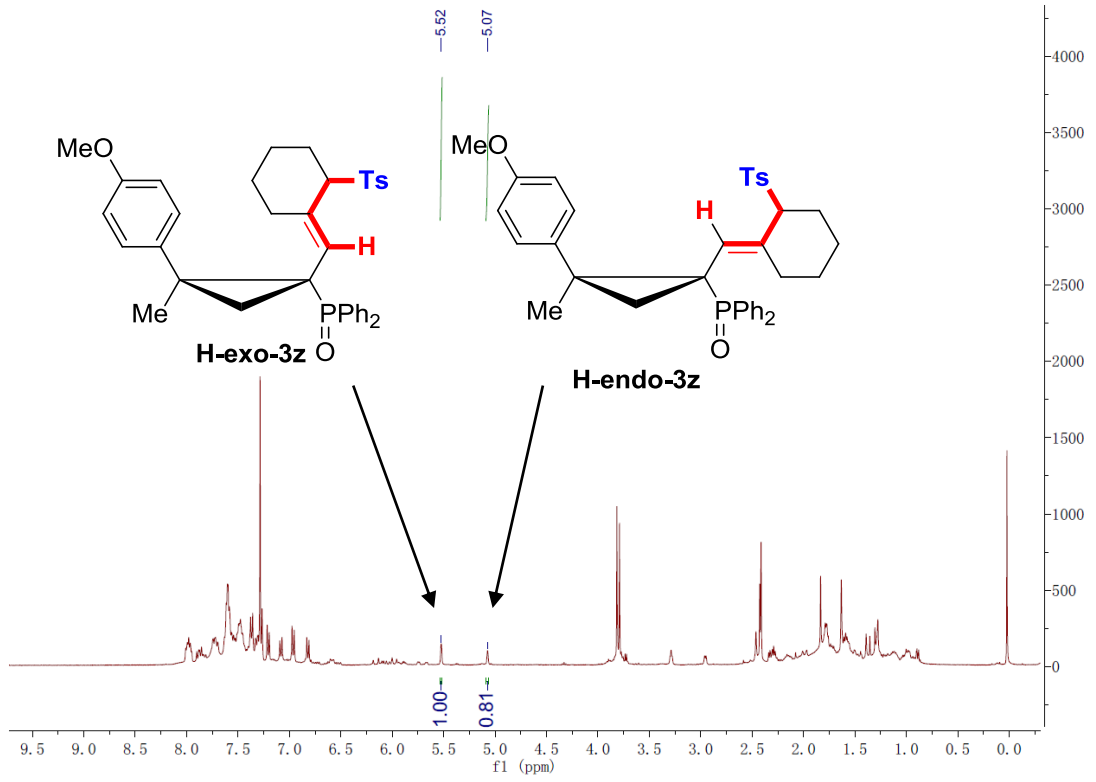

MeO
Ts
H
Me
PPh2
O
3y
f1 (ppm)


MeO
Ts
H
Me
PPh2
O
3y
f1 (ppm)

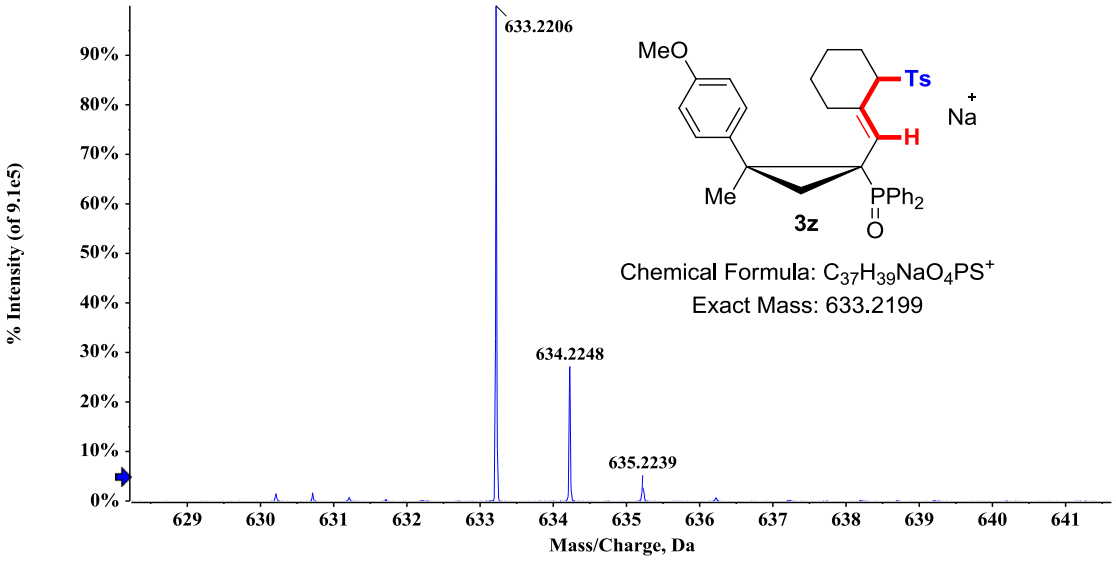


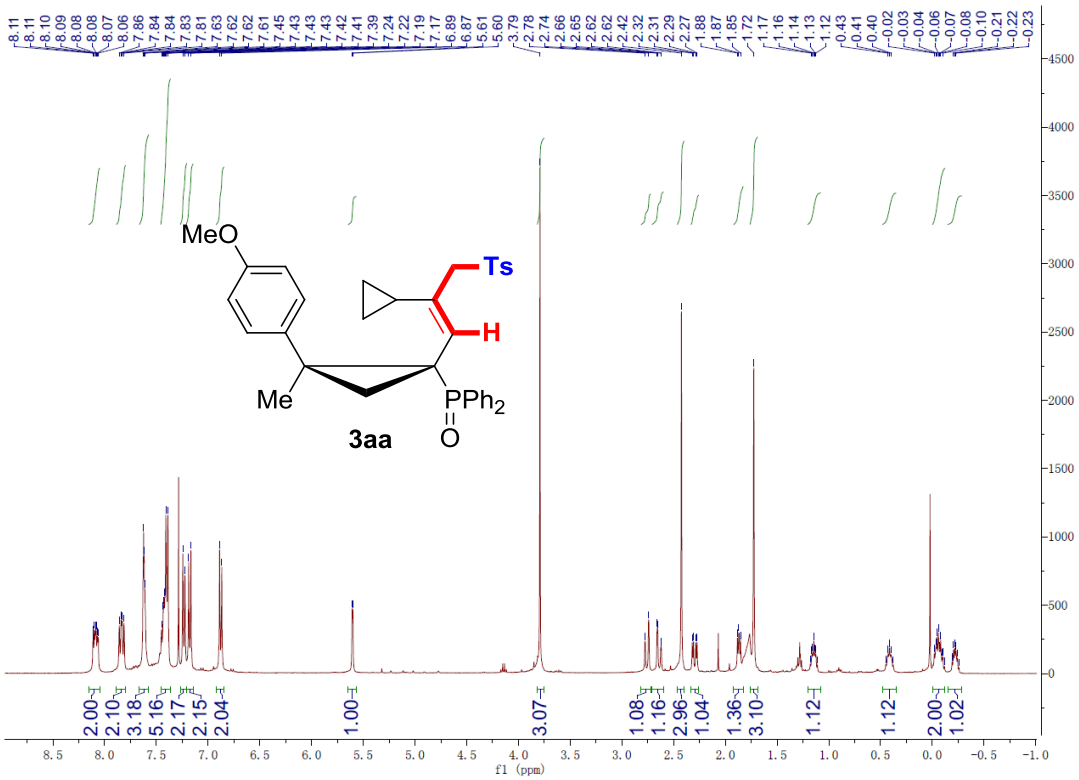
20160913-25 #35 RT: 0.35 AV: 1 NL: 3.65E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

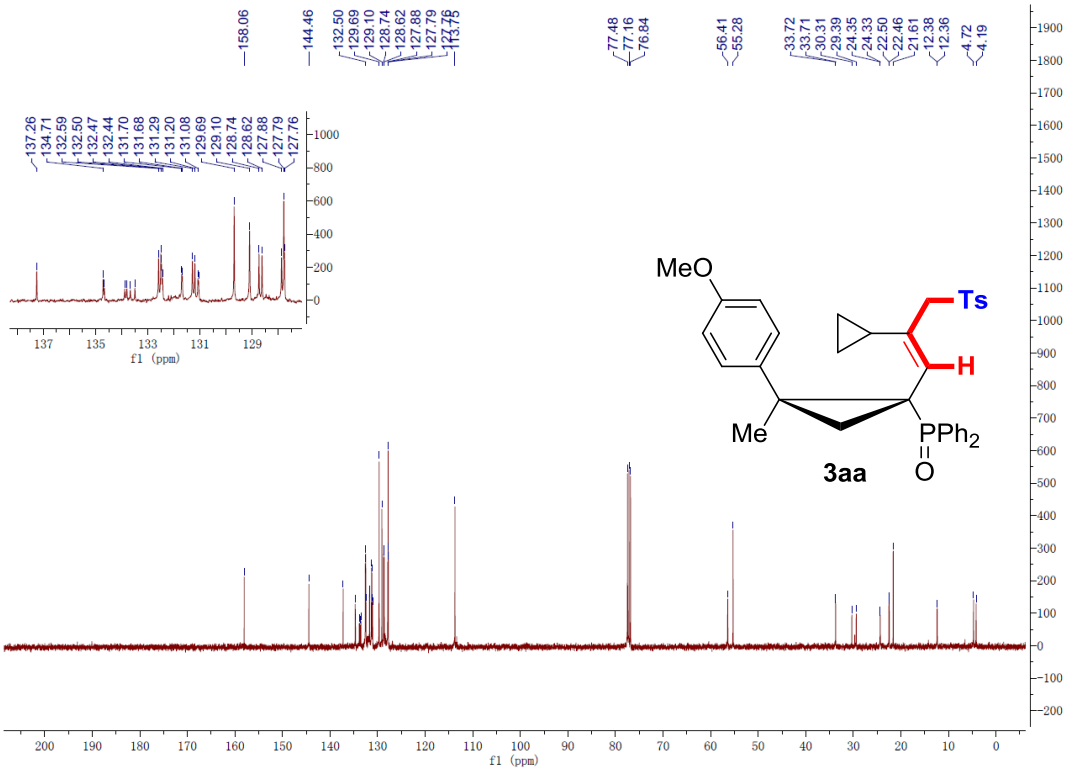


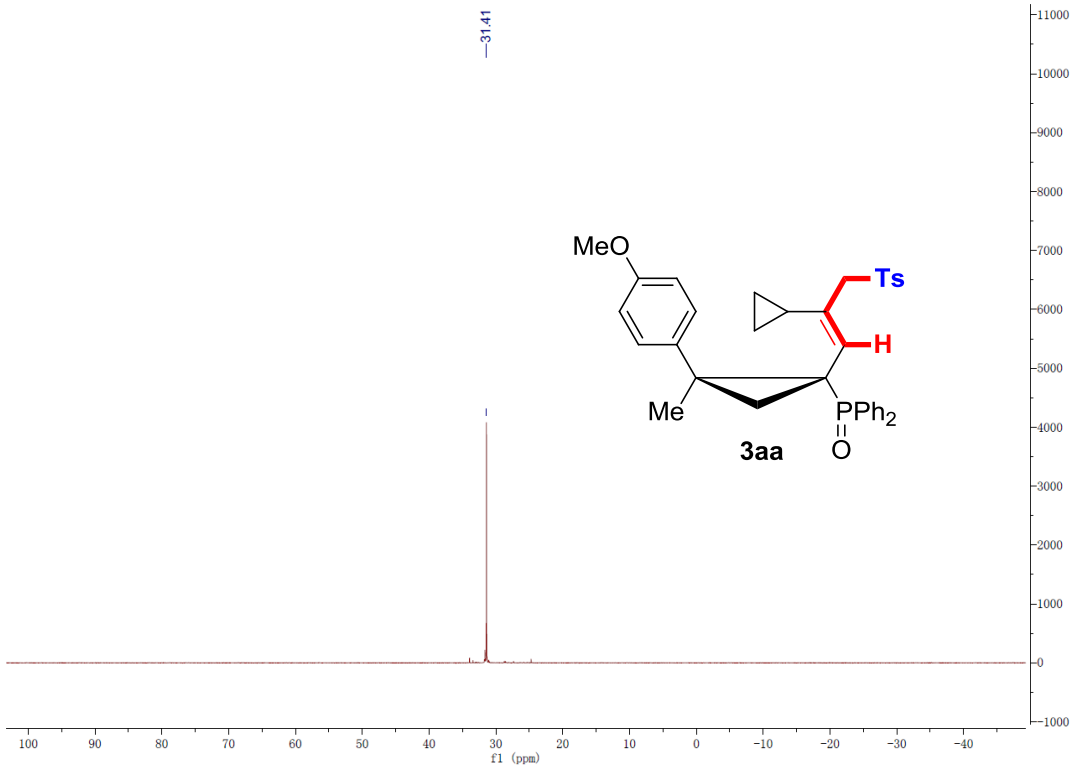


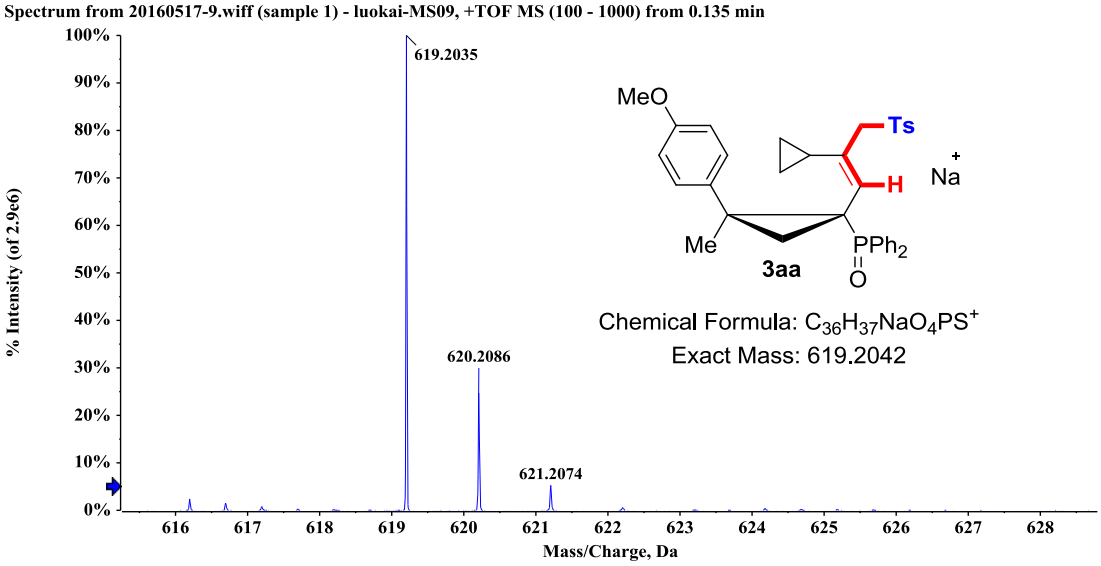
Spectrum from 20160517-8.wiff (sample 1) - luokai-MS08, +TOF MS (100 - 1000) from 0.149 min

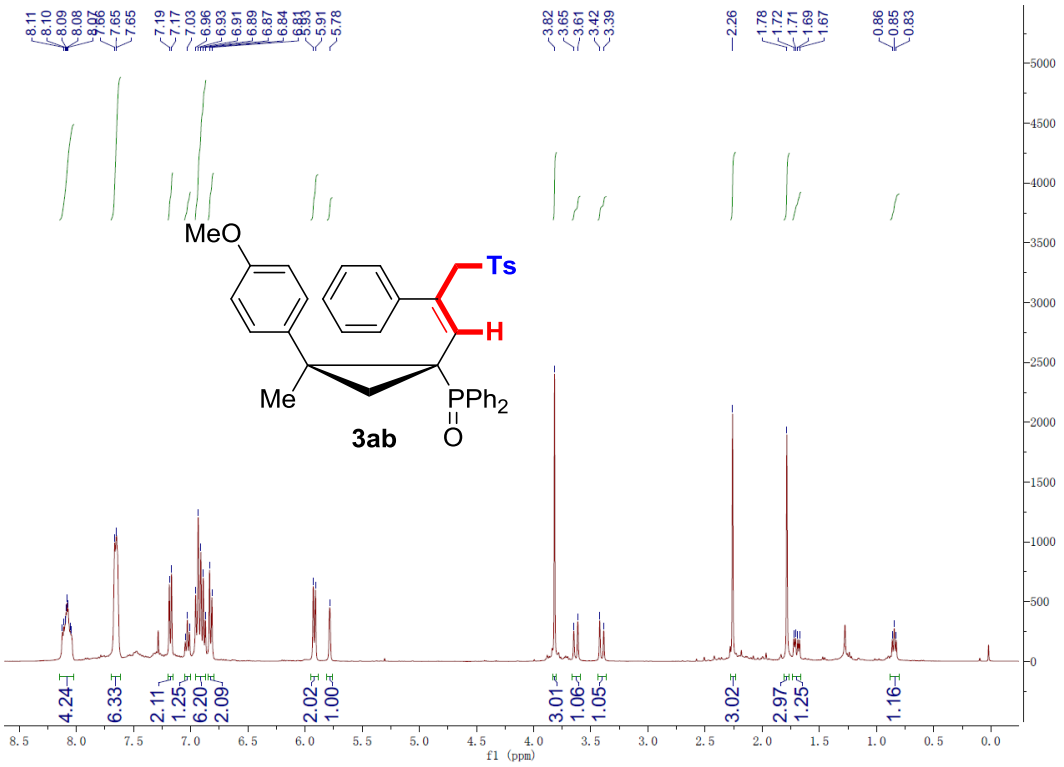


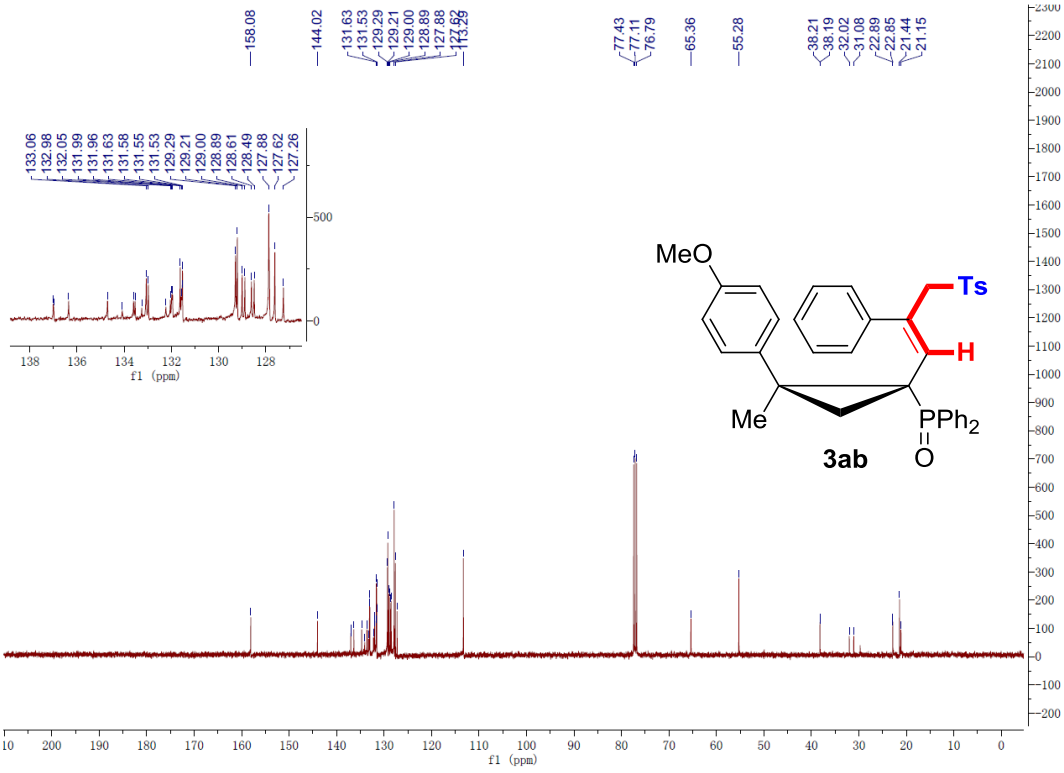

MeO
Ts
H
Me
PPh2
O
3aa
f1 (ppm)

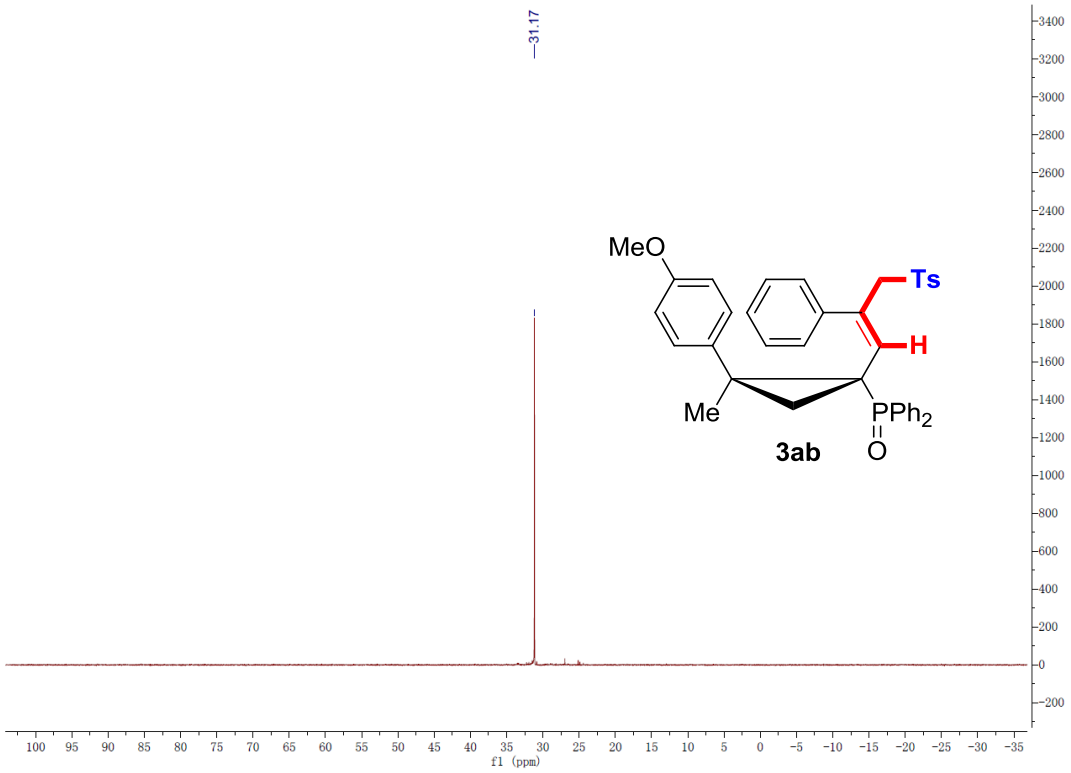

MeO
Ts
H
Me
PPh2
O
3aa
f1 (ppm)


31.41
MeO
Ts
H
Me
PPh2
O
3aa
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

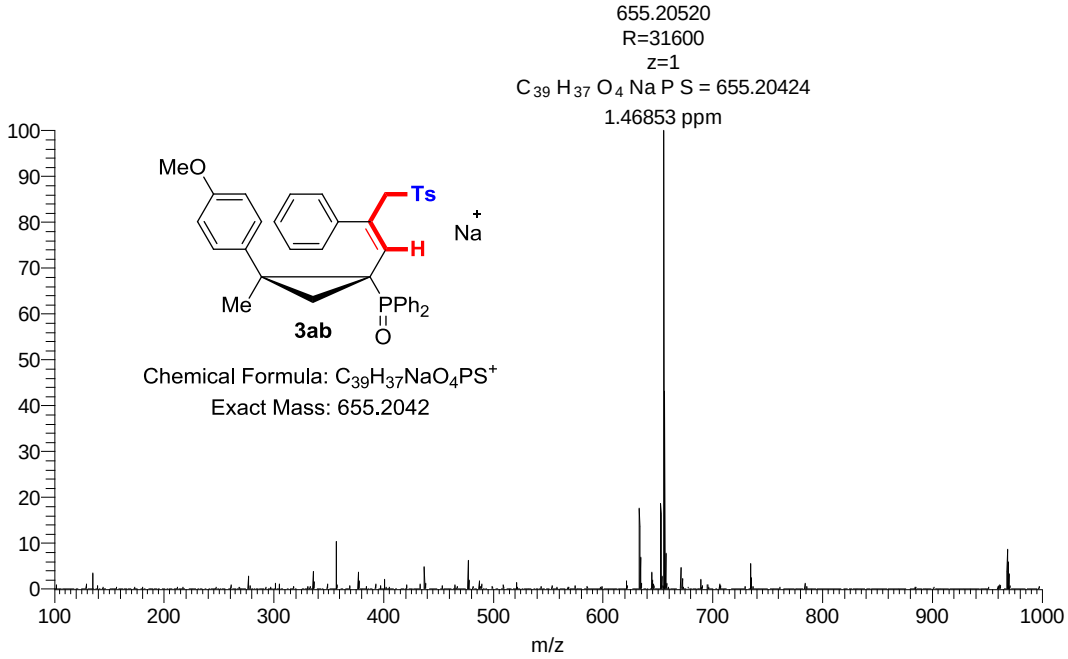

Spectrum from 20160517-9.wiff (sample 1) - luokai-MS09, +TOF MS (100 - 1000) from 0.135 min
% Intensity (of 2.9e6)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
619.2035
620.2086
621.2074
MeO
Ts
H
Na+
Me
PPh2
O
3aa
Chemical Formula: C36H37NaO4PS+
Exact Mass: 619.2042
616
617
618
619
620
621
622
623
624
625
626
627
628
Mass/Charge, Da

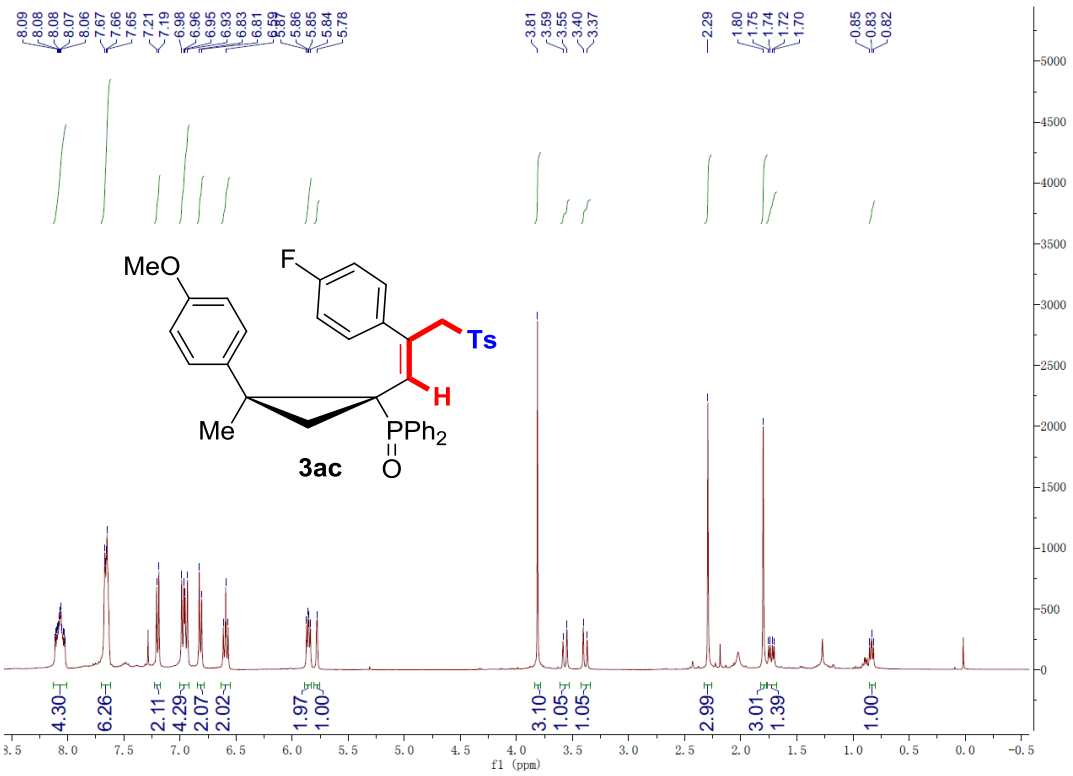

MeO
Ts
H
Me
PPh2
O
3ab
f1 (ppm)

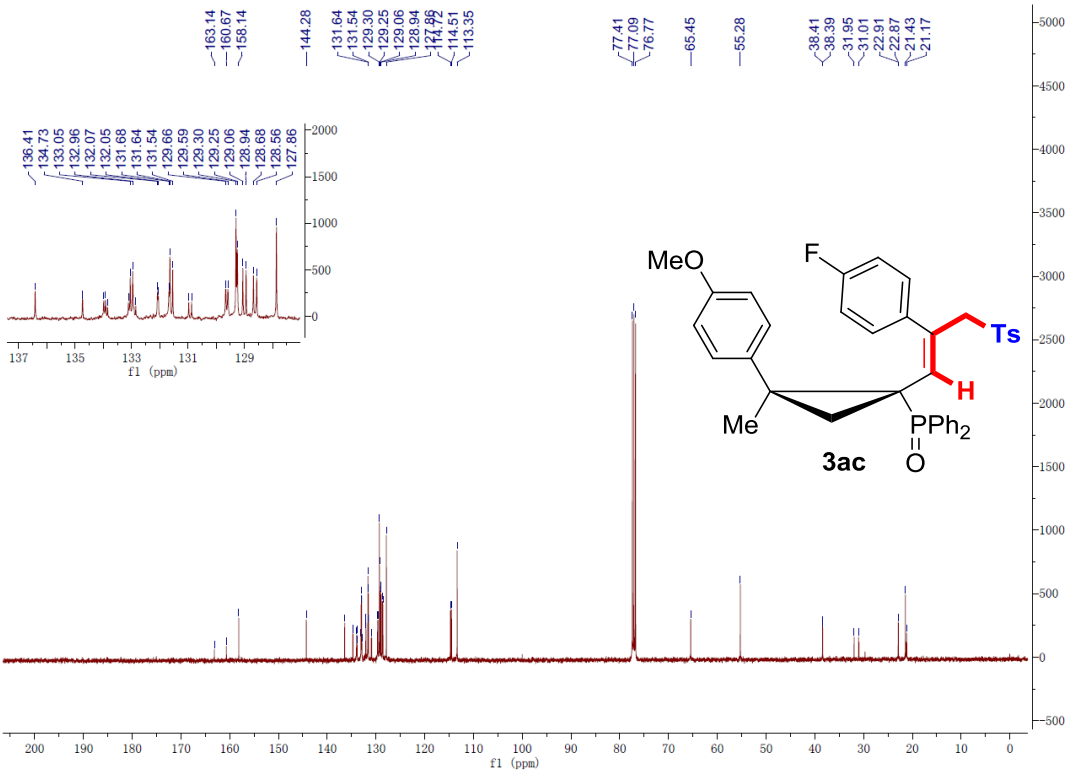

MeO
Ts
H
Me
PPh2
O
3ab
f1 (ppm)

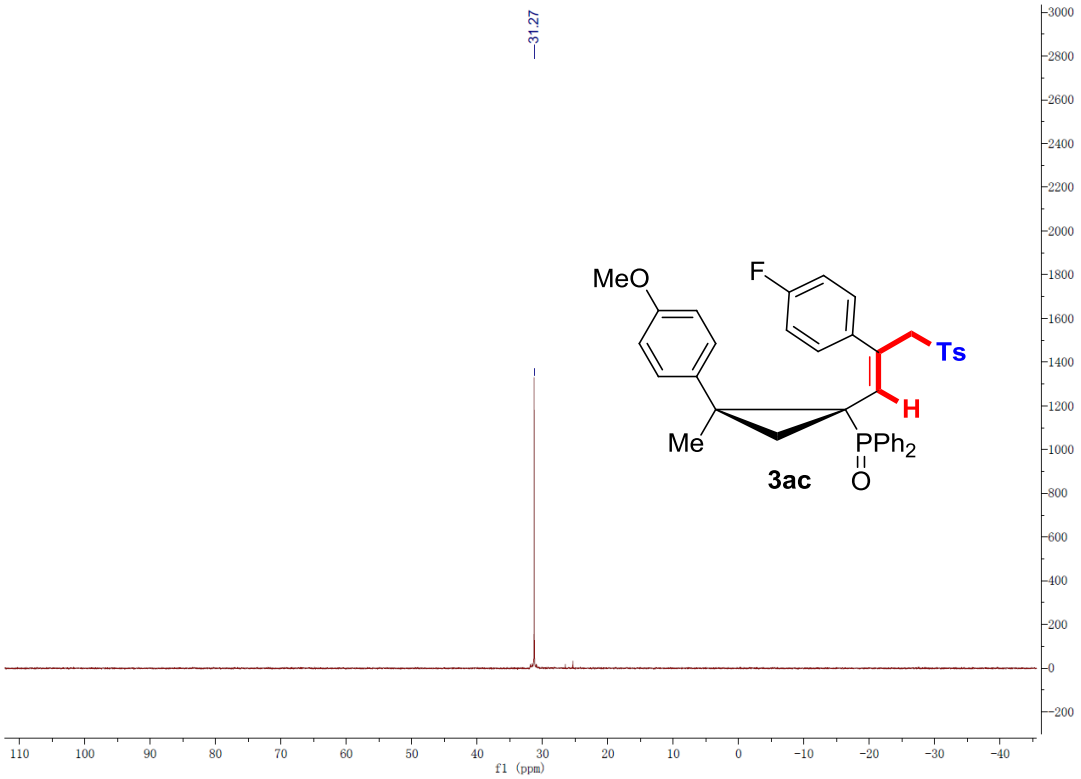


21 #25 RT: 0.26 AV: 1 NL: 4.77E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

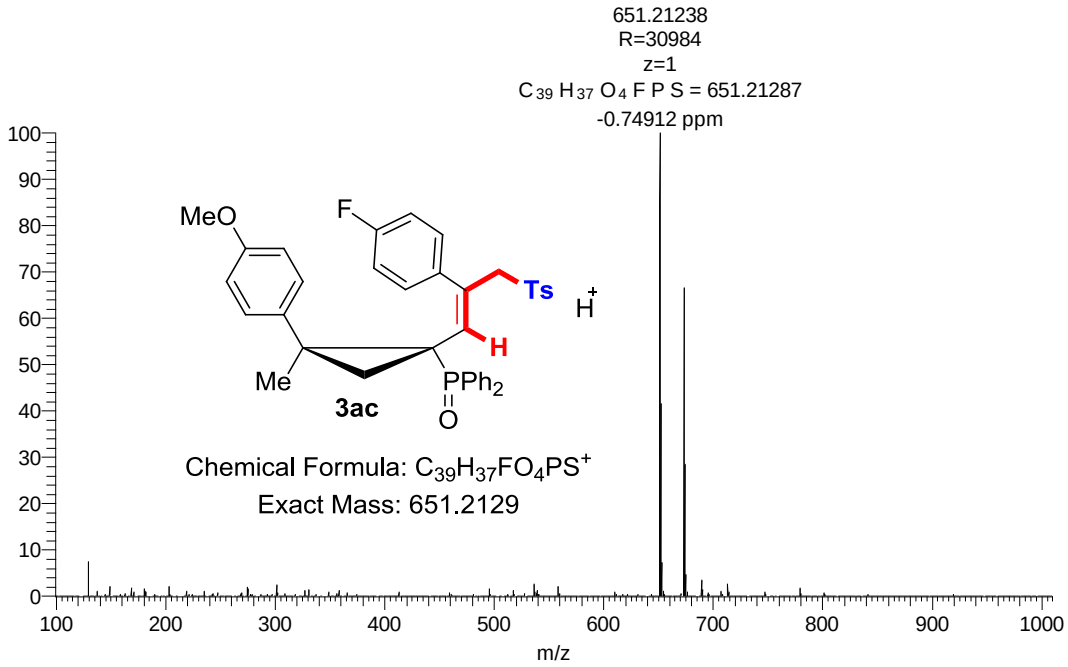


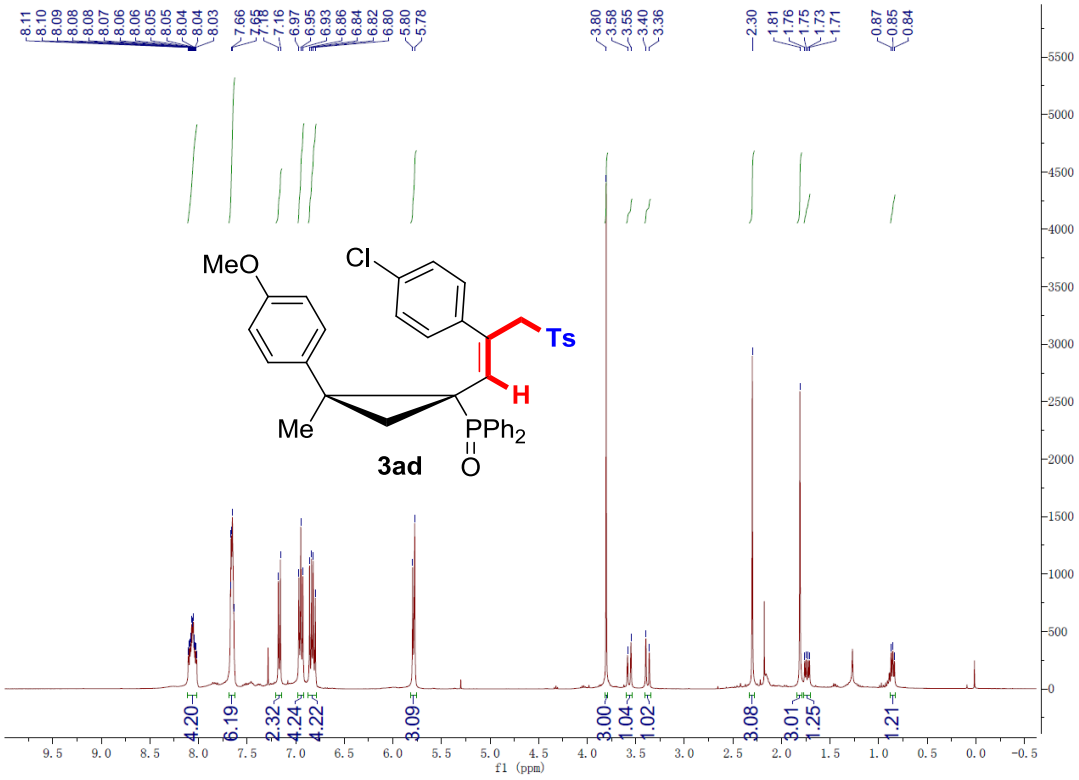

MeO
F
Ts
H
Me
PPh2
O
3ac
f1 (ppm)

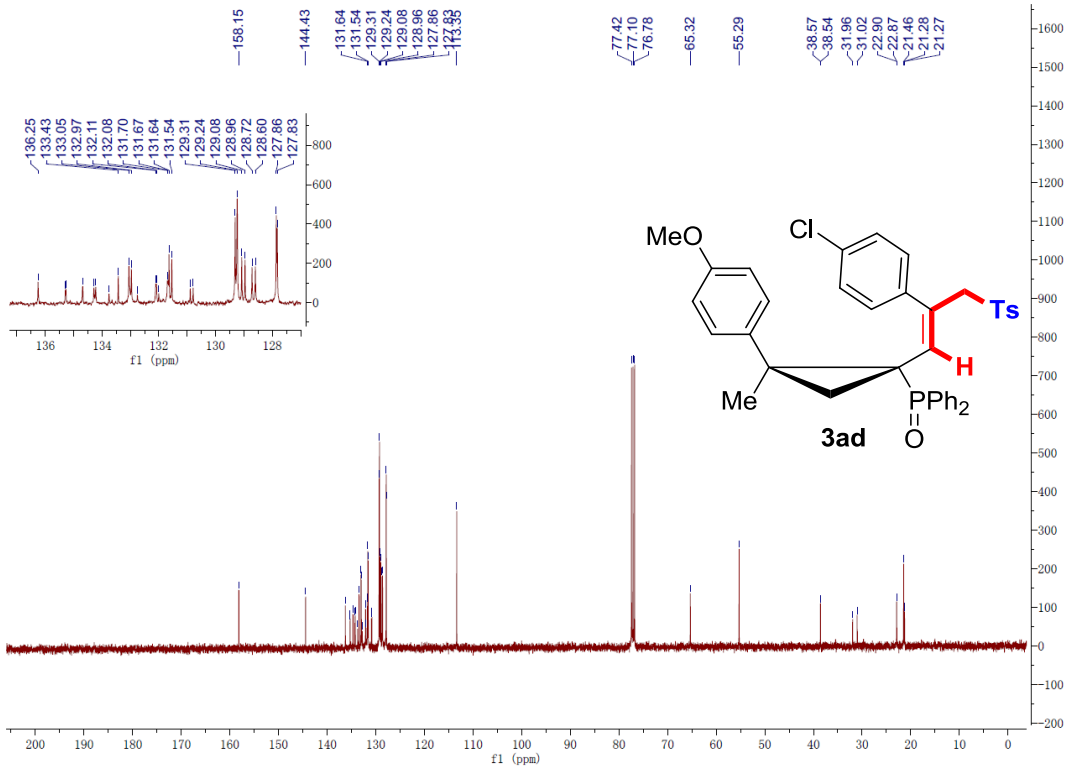

MeO
F
Ts
H
Me
PPh2
O
3ac
f1 (ppm)

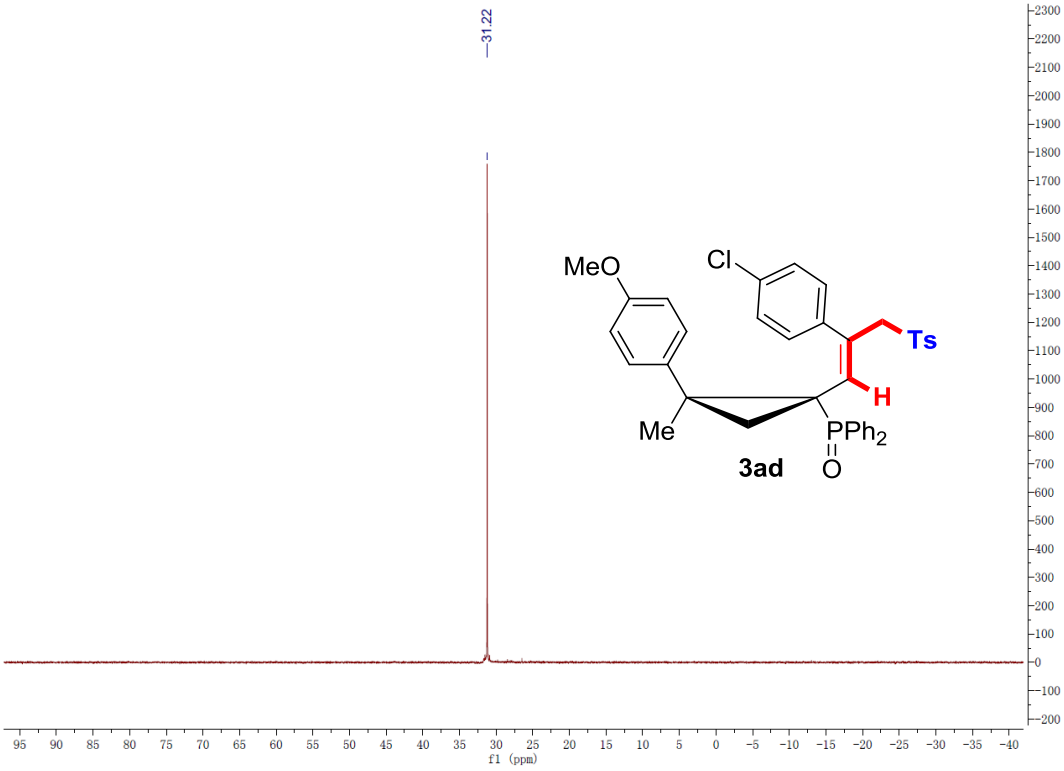


20170505-33_170506115714 #41-42 RT: 0.42-0.43 AV: 2 NL: 1.68E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

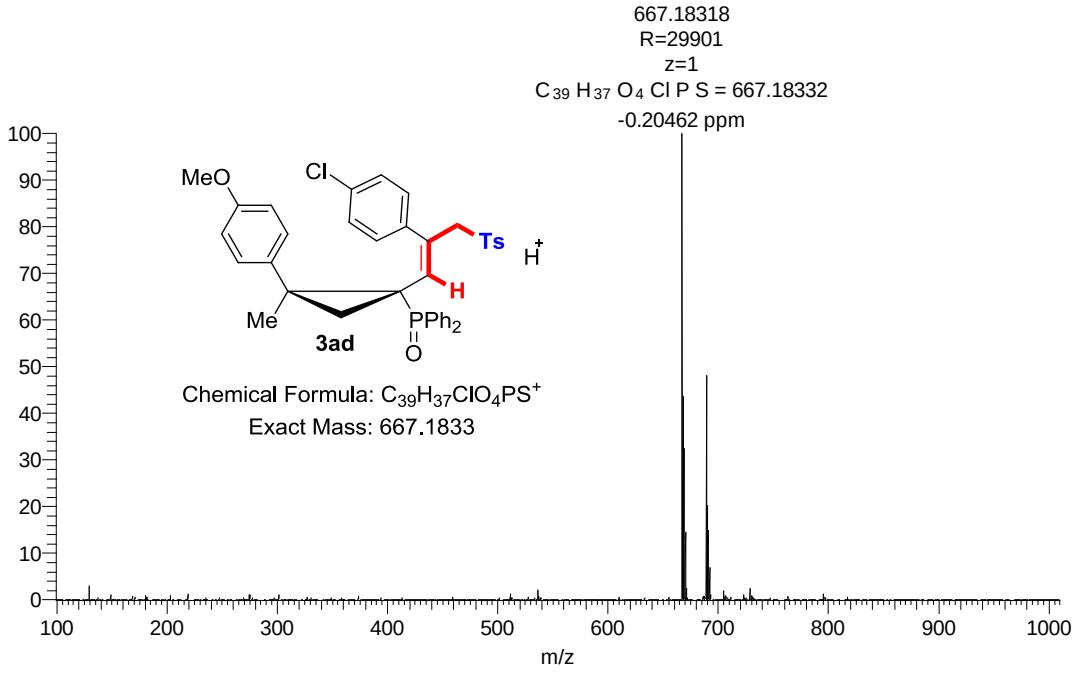


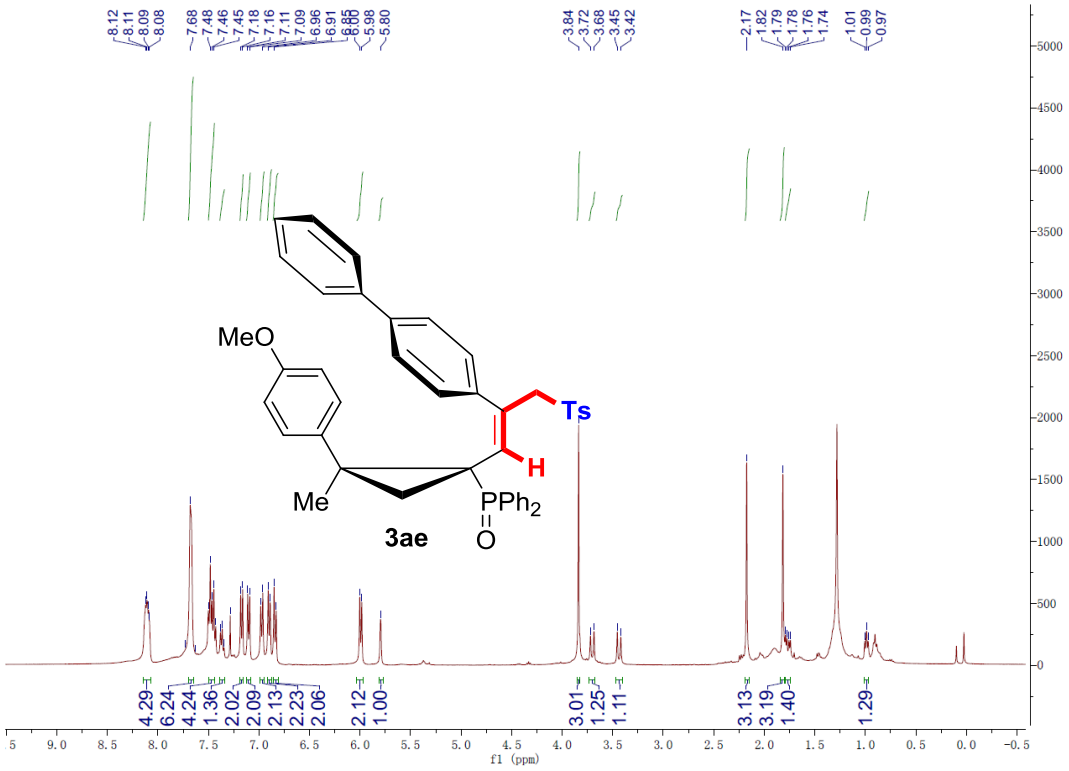

MeO
Cl
Ts
H
Me
PPh2
O
3ad
f1 (ppm)

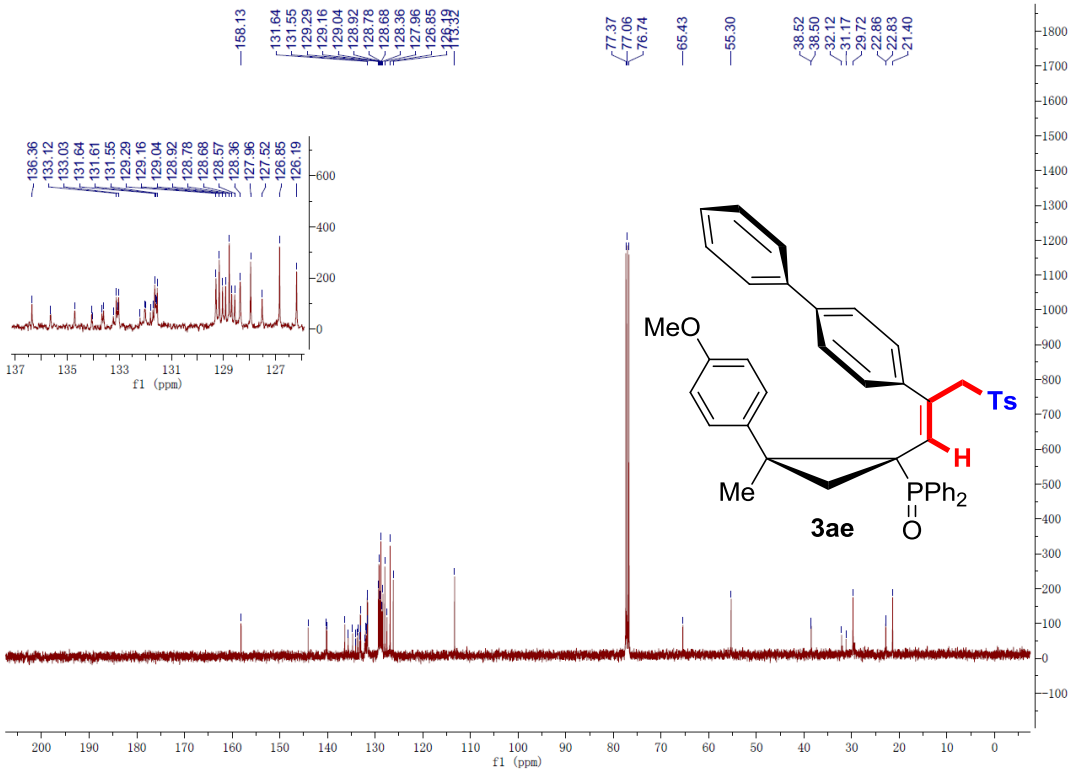

MeO
Cl
Ts
H
Me
PPh2
O
3ad
f1 (ppm)

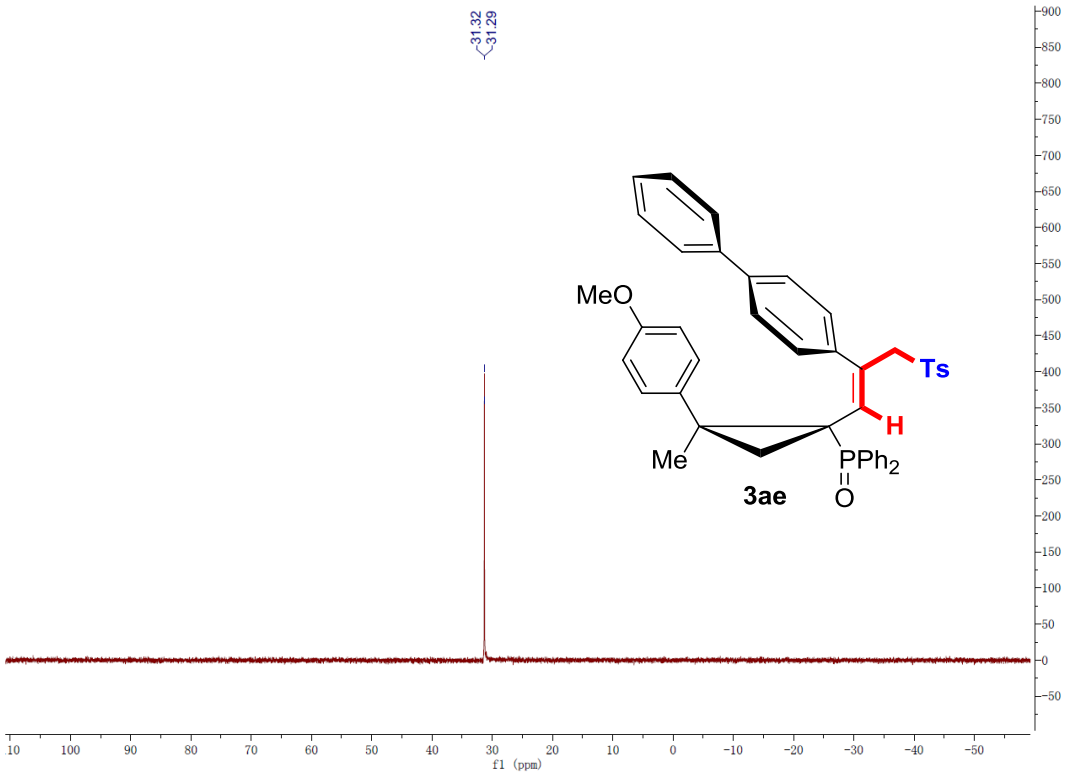


20170505-34_170506121250 #39-41 RT: 0.40-0.43 AV: 3 NL: 3.02E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

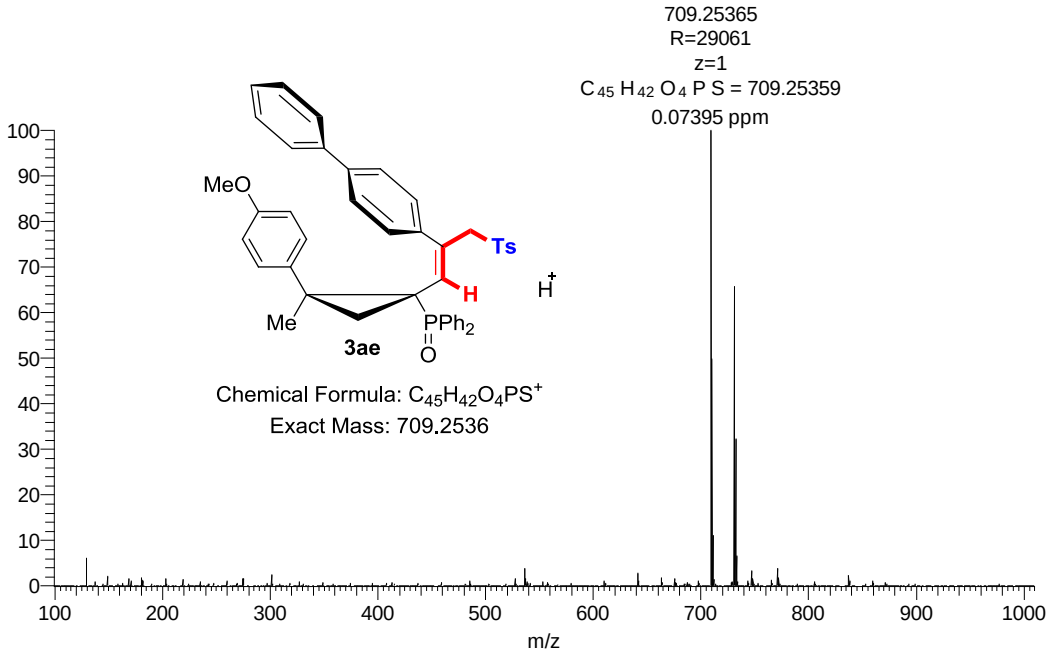


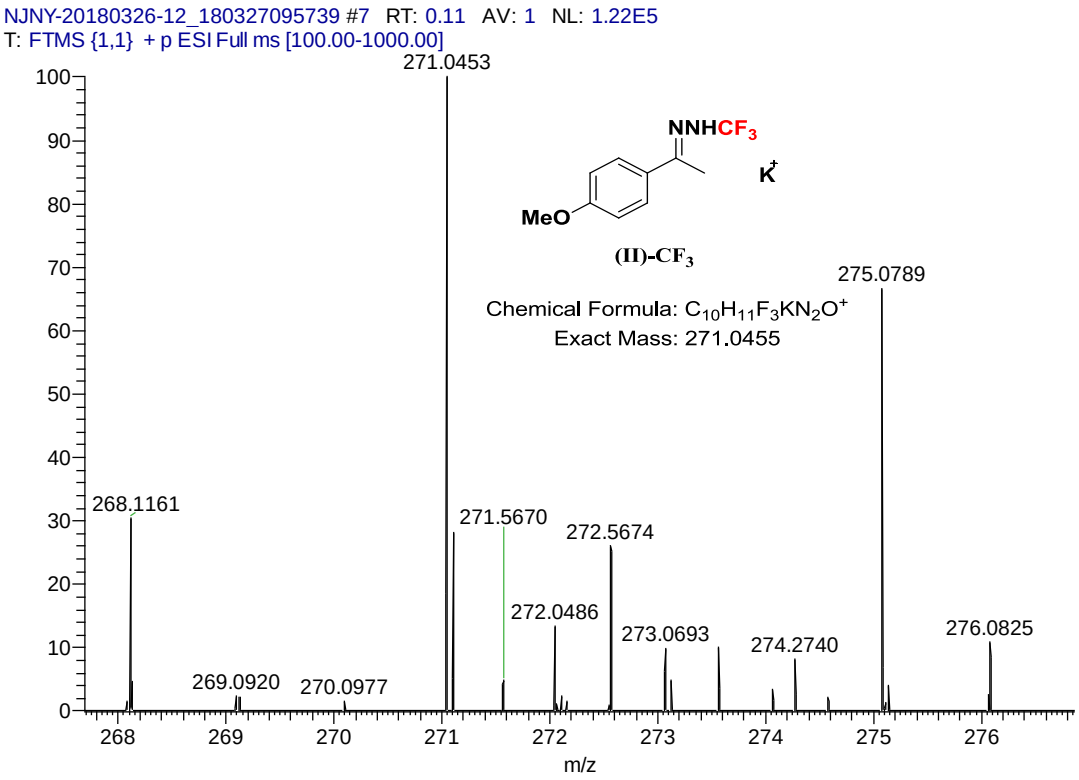

MeO
Ts
H
Me
PPh2
O
3ae
f1 (ppm)


MeO
Ts
H
Me
PPh2
O
3ae
f1 (ppm)



20170505-36_170506124401 #35-38 RT: 0.38-0.41 AV: 4 NL: 1.64E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]




NJNY-20180326-12_180327095739 #7 RT: 0.11 AV: 1 NL: 1.22E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]
271.0453
NNHCF3
K+
MeO
(II)-CF3
275.0789
Chemical Formula: C10H11F3KN2O+
Exact Mass: 271.0455
268.1161
271.5670
272.5674
272.0486
273.0693
274.2740
276.0825
269.0920
270.0977
100
90
80
70
60
50
40
30
20
10
0
268
269
270
271
272
273
274
275
276
m/z