

Supporting Information for:

**Visible-Light-Driven α -Allenlylic C-O Bond Cleavage and
Alkenyl C-S formation: Metal-Free and Oxidant-Free
Thiolation of Allenyl Phosphine Oxides**

Ling Zhang,[†] Jie Zhu,[†] Jing Ma,[†] Lei Wu^{*,†,‡} and Wei-Hua Zhang^{*,†}

[†] Jiangsu Key Laboratory of Pesticide Science and Department of Chemistry, College of Sciences, Nanjing Agricultural University, Nanjing 210095, P. R. China. [Tel/Fax: +86-25-84396716; E-mail: rickywu@njau.edu.cn]

[‡] Beijing National Laboratory for Molecular Sciences and Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

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1. General Information

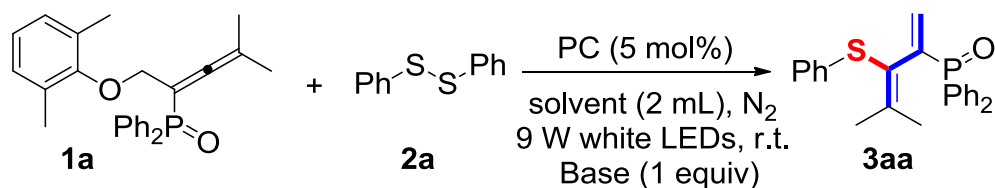
Solvents and reagents were reagent grade and used without purification unless otherwise noted. All reactions were carried out in oven dried glassware under nitrogen. All ^1H -NMR (400 MHz) spectra were recorded on a Bruker-DMX 400 using CDCl_3 solution in the presence of tetramethylsilane (TMS) as an 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.

2. General Procedures for Photoredox Thiolation of Allenylphosphine Oxides with Diaryl Sulfides

To a 5 mL two-necked flask equipped with condenser under nitrogen was added allenylphosphine oxide (**1a**, 80 mg, 0.2 mmol), disulfides (**2a**, 44 mg, 0.2 mmol), eosin Y (7 mg, 5 mol%), DBU (15 mg, 0.1 mmol) and 2 mL DMSO. The reaction mixture was then stirred for 8 hours irradiated by 9 W White LEDs at room temperature. The resulting mixture was diluted with ethyl acetate and washed with saturated NaHCO_3 solution and brine. After evaporating the volatiles, the residue was purified by column chromatography (eluent: 1:1 (v/v) of ethyl acetate/petroleum ether) to afford product **3aa** as a yellow liquid.

3. Reaction Conditions Optimization

Table S1. Condition Screenings on Catalyst, Solvent and Base

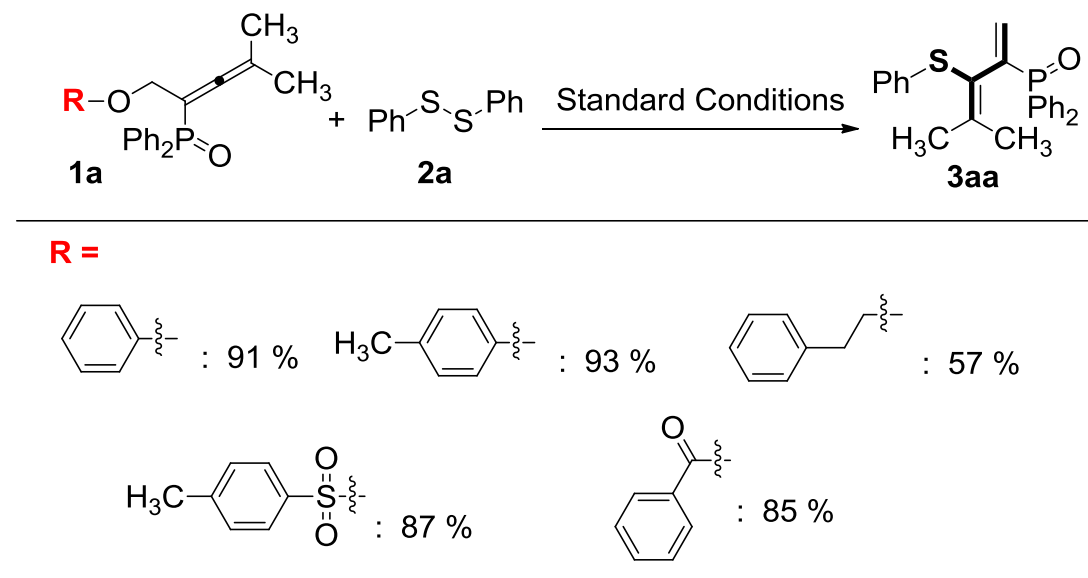


entry	photocatalyst (PC)	solvent	base	yield (%) ^a
1	Eosin Y	THF	PivONa	63
2	Eosin Y	CH ₃ CN	PivONa	45
3	Eosin Y	dichloroethane	PivONa	10
4	Eosin Y	H ₂ O	PivONa	17
5	Eosin Y	DMSO	PivONa	93(86)
6	Eosin Y	DMF	PivONa	92(82)
7	Eosin Y	toluene	PivONa	trace
8	Eosin Y	CHCl ₃	PivONa	46
9	Eosin Y	EtOH	PivONa	33
10	Eosin Y	dioxane	PivONa	88(79)
11	Eosin Y	NMP	PivONa	72
12	Eosin Y	Chlorobenzene	PivONa	30
13	Eosin Y	CH ₃ NO ₂	PivONa	35
14	Eosin B	DMSO	PivONa	83(75)
15	Rhodamine B	DMSO	PivONa	67
16	Eosin Y disodium	DMSO	PivONa	90(82)
17	fluorecein	DMSO	PivONa	63
18	Alizarin Red S	DMSO	PivONa	91(80)
20	Riboflavine	DMSO	PivONa	78
21	Eosin Y	DMSO	K ₂ CO ₃	97(90)
22	Eosin Y	DMSO	<i>t</i> -BuOK	97(89)
23	Eosin Y	DMSO	NaHCO ₃	50
24	Eosin Y	DMSO	CsCO ₃	97(91)
25	Eosin Y	DMSO	DBU	97(92)
26	Eosin Y	DMSO	DABCO	89(81)
27	Eosin Y	DMSO	PPh ₃	77
28 ^b	Eosin Y	DMSO	DBU	98(92)

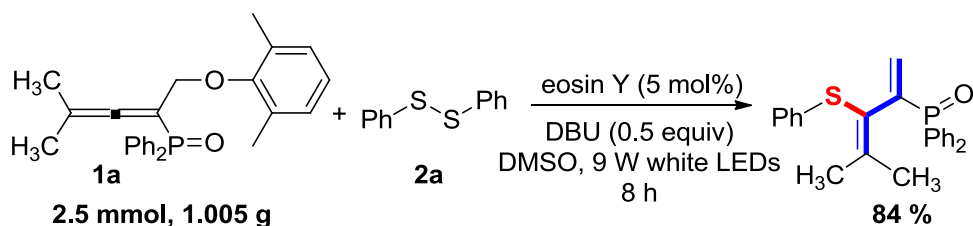
Reaction conditions: allenylphosphine oxide (**1a**, 0.2 mmol), diphenyl disulfides (**2a**, 0.2 mmol), photocatalyst (PC, 5 mol%), base (1 equiv), N₂, 8 h;

^a yield based on ³¹P NMR, the number in brackets refer to isolated yields; ^b 0.5 equiv DBU.

4. The Additional Substrate Scope on Ether Moiety

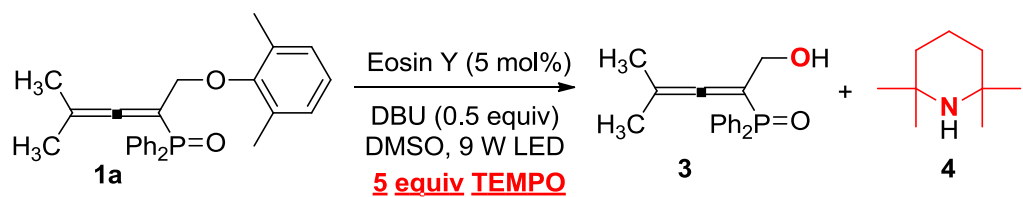


5. Gram-Scale Synthesis



To a 100 mL two-necked flask equipped with condenser under nitrogen was added allenylphosphine oxide (**1a**, 1.005 g, 2.5 mmol), disulfides (**2a**, 546 mg, 2.5 mmol), eosin Y (81 mg, 5 mol%, 0.125 mmol), DBU (190 mg, 1.25 mmol) and 25 mL DMSO. The reaction mixture was stirred for 8 hours irradiated by 9 W White LEDs at room temperature. The resulting mixture was diluted with ethyl acetate and washed with saturated NaHCO₃ solution and brine. After evaporating the volatiles, the residue was further purified by column chromatography (eluent: 1:1 (v/v) of ethyl acetate/petroleum ether) to afford product **3aa** in 84% yield (820 mg).

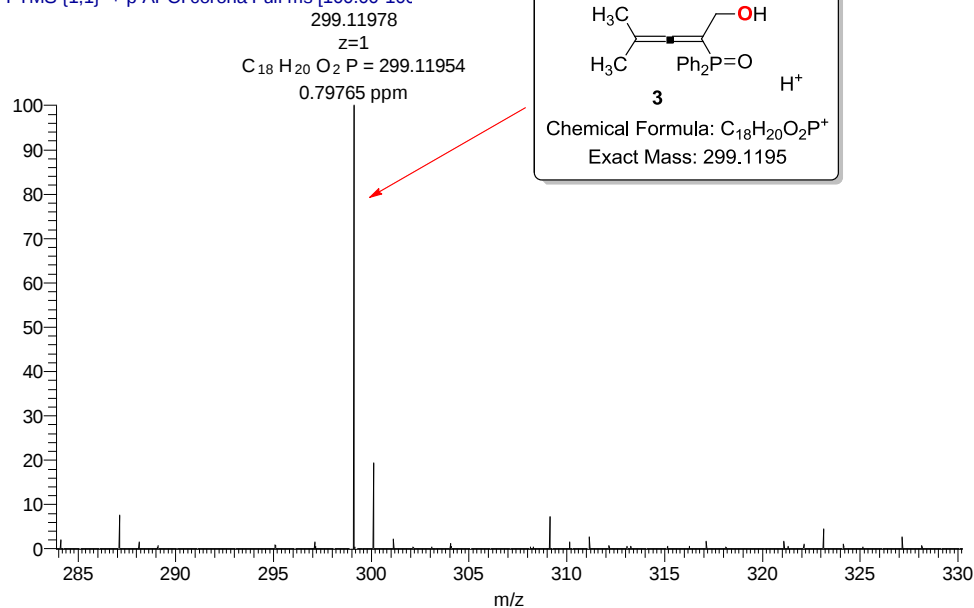
6. HR-MS Spectra for Mechanistic Study



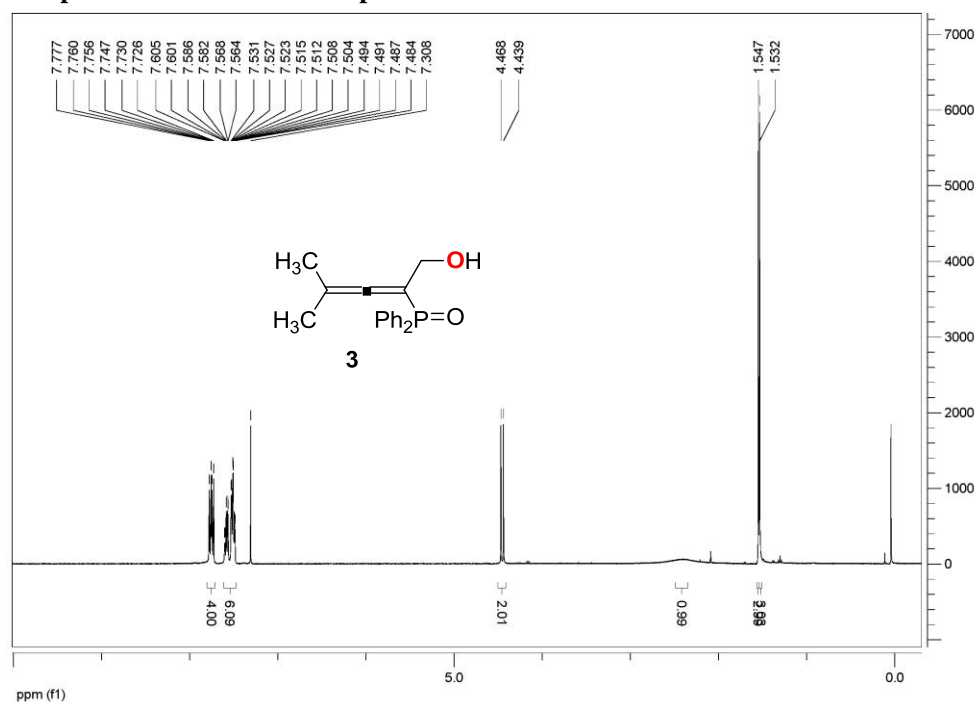
Detected by APCI-MS/¹HNMR

Detected by ESI-MS

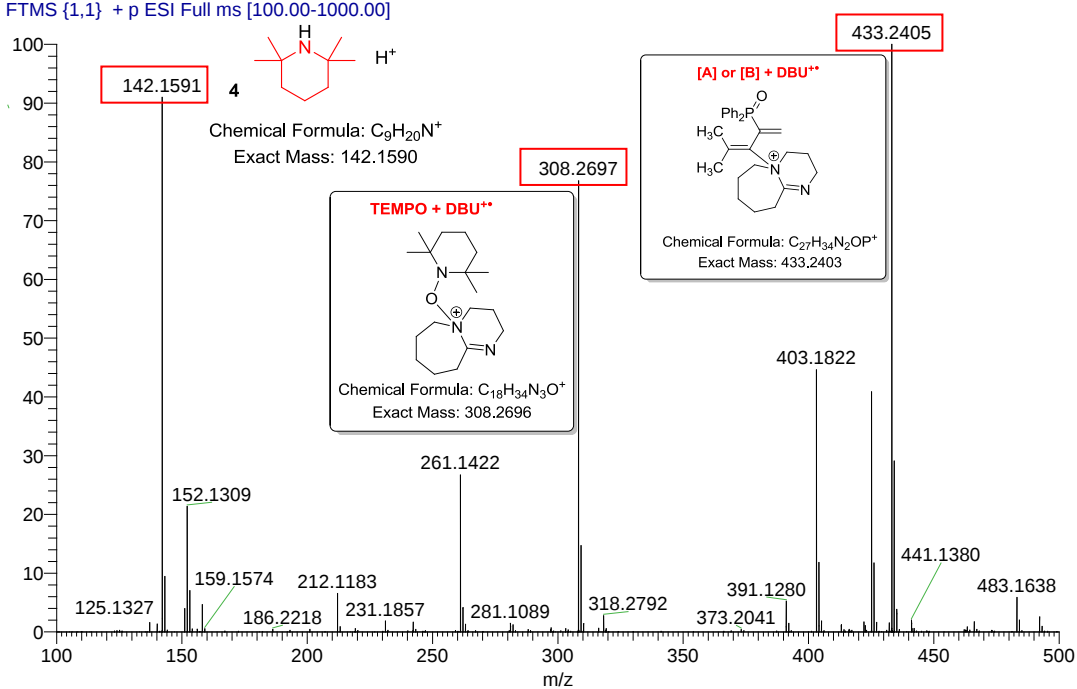
30_170314152421 #28 RT: 0.20 AV: 1 NL: 1.39E7
T: FTMS [1,1] + p APCI corona Full ms [100.00-100



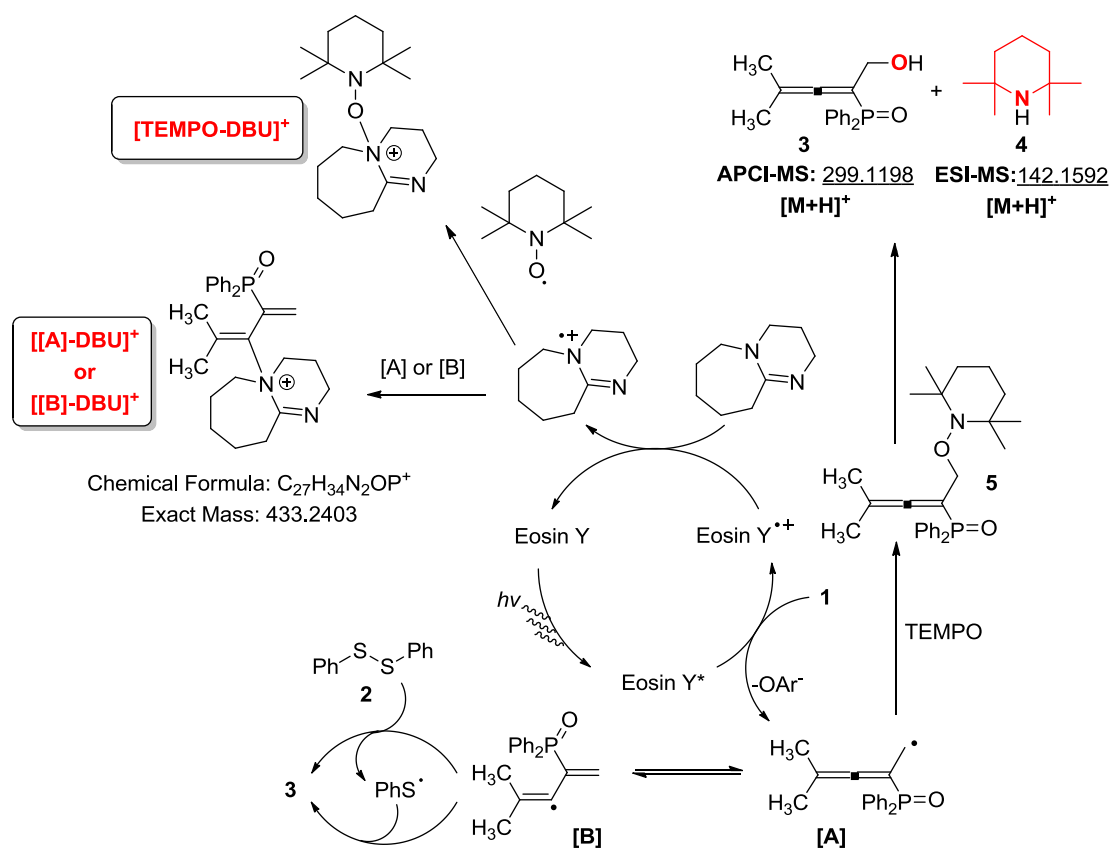
¹HNMR spectrum for isolated compound 3:



30 #12 RT: 0.12 AV: 1 NL: 7.41E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

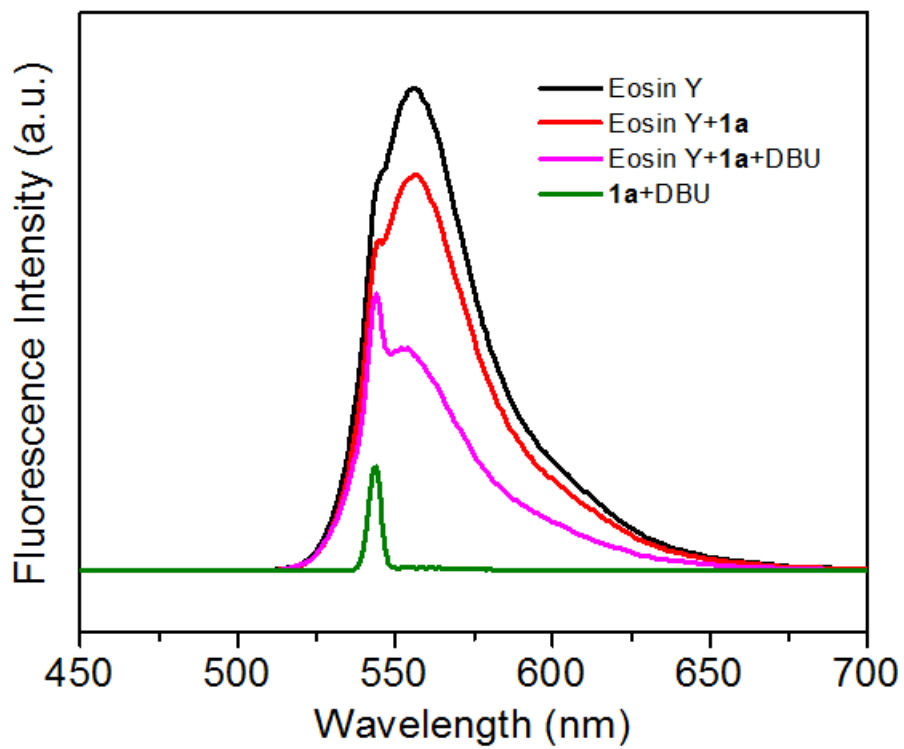


Chemical Formula: $C_{18}H_{34}N_3O^+$
Exact Mass: 308.2696

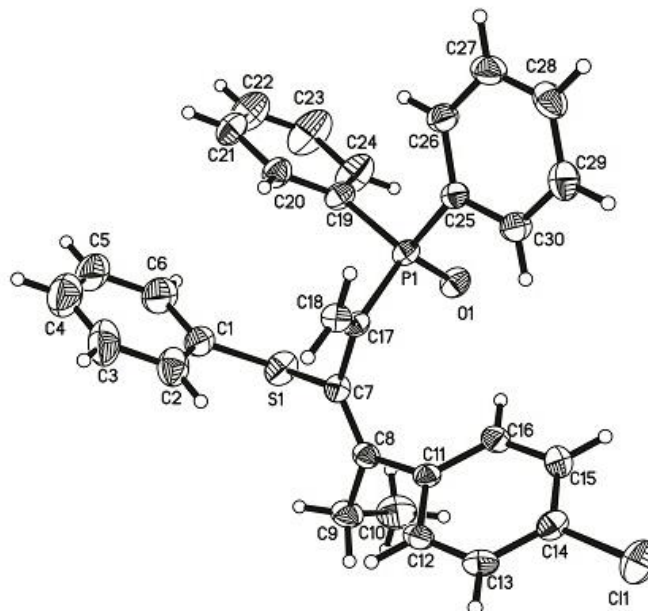


7. Quenching Experiment of eosin Y

Concentration: [eosin Y] = 0.5 $\mu\text{mol/L}$; [**1a**] = 10 $\mu\text{mol/L}$; [DBU] = 5 $\mu\text{mol/L}$



(The ellipsoid contour percent probability level is 30%)



Empirical formula	C30 H26 Cl O P S		
Formula weight	500.99		
Temperature	296(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P2 ₁ /c		
Unit cell dimensions	a = 9.3715(5) Å	b = 10.7636(6) Å	c = 26.6835(16) Å
			= 90°.
			= 98.342(2)°.
			= 90°.
Volume	2663.1(3) Å ³		
Z	4		
Density (calculated)	1.250 Mg/m ³		
Absorption coefficient	0.302 mm ⁻¹		
F(000)	1048		
Crystal size	0.100 x 0.090 x 0.030 mm ³		
Theta range for data collection	2.442 to 27.581 °		
Index ranges	-12<=h<=12, -14<=k<=11, -34<=l<=24		
Reflections collected	23765		

Independent reflections	6119 [R(int) = 0.0341]
Completeness to theta = 25.242 °	99.5 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6119 / 0 / 308
Goodness-of-fit on F ²	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0514, wR2 = 0.1358
R indices (all data)	R1 = 0.0841, wR2 = 0.1537
Extinction coefficient	n/a
Largest diff. peak and hole	0.352 and -0.287 e.Å ⁻³

Table S3. Bond lengths [Å] and angles [°]

C(1)-C(6)	1.382(4)
C(1)-C(2)	1.386(4)
C(1)-S(1)	1.785(3)
C(2)-C(3)	1.382(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.351(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.361(6)
C(4)-H(4)	0.9300
C(5)-C(6)	1.418(5)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-C(8)	1.340(3)
C(7)-C(17)	1.485(3)
C(7)-S(1)	1.780(2)
C(8)-C(11)	1.494(3)
C(8)-C(9)	1.515(3)
C(9)-C(10)	1.521(4)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(16)	1.390(3)
C(11)-C(12)	1.397(3)
C(12)-C(13)	1.375(3)

C(12)-H(12)	0.9300
C(13)-C(14)	1.376(3)
C(13)-H(13)	0.9300
C(14)-C(15)	1.384(3)
C(14)-Cl(1)	1.741(2)
C(15)-C(16)	1.381(3)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(17)-C(18)	1.324(3)
C(17)-P(1)	1.821(2)
C(18)-H(18A)	0.9300
C(18)-H(18B)	0.9300
C(19)-C(20)	1.381(3)
C(19)-C(24)	1.382(3)
C(19)-P(1)	1.800(2)
C(20)-C(21)	1.381(3)
C(20)-H(20)	0.9300
C(21)-C(22)	1.373(4)
C(21)-H(21)	0.9300
C(22)-C(23)	1.353(5)
C(22)-H(22)	0.9300
C(23)-C(24)	1.380(4)
C(23)-H(23)	0.9300
C(24)-H(24)	0.9300
C(25)-C(30)	1.393(3)
C(25)-C(26)	1.394(3)
C(25)-P(1)	1.811(2)
C(26)-C(27)	1.380(3)
C(26)-H(26)	0.9300
C(27)-C(28)	1.365(4)
C(27)-H(27)	0.9300
C(28)-C(29)	1.382(4)
C(28)-H(28)	0.9300
C(29)-C(30)	1.377(3)
C(29)-H(29)	0.9300
C(30)-H(30)	0.9300
O(1)-P(1)	1.4793(15)

C(6)-C(1)-C(2)	119.8(3)
C(6)-C(1)-S(1)	117.4(3)
C(2)-C(1)-S(1)	122.8(2)
C(3)-C(2)-C(1)	120.0(3)
C(3)-C(2)-H(2)	120.0
C(1)-C(2)-H(2)	120.0
C(4)-C(3)-C(2)	120.6(4)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	120.8(4)
C(3)-C(4)-H(4)	119.6
C(5)-C(4)-H(4)	119.6
C(4)-C(5)-C(6)	120.2(3)
C(4)-C(5)-H(5)	119.9
C(6)-C(5)-H(5)	119.9
C(1)-C(6)-C(5)	118.6(4)
C(1)-C(6)-H(6)	120.7
C(5)-C(6)-H(6)	120.7
C(8)-C(7)-C(17)	125.49(18)
C(8)-C(7)-S(1)	119.38(16)
C(17)-C(7)-S(1)	114.80(15)
C(7)-C(8)-C(11)	121.93(18)
C(7)-C(8)-C(9)	123.4(2)
C(11)-C(8)-C(9)	114.45(19)
C(8)-C(9)-C(10)	111.0(2)
C(8)-C(9)-H(9A)	109.4
C(10)-C(9)-H(9A)	109.4
C(8)-C(9)-H(9B)	109.4
C(10)-C(9)-H(9B)	109.4
H(9A)-C(9)-H(9B)	108.0
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(16)-C(11)-C(12)	118.2(2)
C(16)-C(11)-C(8)	121.42(19)

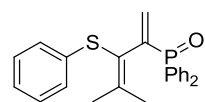
C(12)-C(11)-C(8)	120.32(19)
C(13)-C(12)-C(11)	121.1(2)
C(13)-C(12)-H(12)	119.5
C(11)-C(12)-H(12)	119.5
C(12)-C(13)-C(14)	119.5(2)
C(12)-C(13)-H(13)	120.2
C(14)-C(13)-H(13)	120.2
C(13)-C(14)-C(15)	120.9(2)
C(13)-C(14)-Cl(1)	119.29(18)
C(15)-C(14)-Cl(1)	119.85(18)
C(16)-C(15)-C(14)	119.2(2)
C(16)-C(15)-H(15)	120.4
C(14)-C(15)-H(15)	120.4
C(15)-C(16)-C(11)	121.1(2)
C(15)-C(16)-H(16)	119.4
C(11)-C(16)-H(16)	119.4
C(18)-C(17)-C(7)	122.44(19)
C(18)-C(17)-P(1)	121.72(16)
C(7)-C(17)-P(1)	115.83(14)
C(17)-C(18)-H(18A)	120.0
C(17)-C(18)-H(18B)	120.0
H(18A)-C(18)-H(18B)	120.0
C(20)-C(19)-C(24)	119.0(2)
C(20)-C(19)-P(1)	123.95(17)
C(24)-C(19)-P(1)	117.06(19)
C(19)-C(20)-C(21)	120.6(2)
C(19)-C(20)-H(20)	119.7
C(21)-C(20)-H(20)	119.7
C(22)-C(21)-C(20)	119.5(3)
C(22)-C(21)-H(21)	120.2
C(20)-C(21)-H(21)	120.2
C(23)-C(22)-C(21)	120.2(3)
C(23)-C(22)-H(22)	119.9
C(21)-C(22)-H(22)	119.9
C(22)-C(23)-C(24)	120.9(3)
C(22)-C(23)-H(23)	119.5
C(24)-C(23)-H(23)	119.5
C(23)-C(24)-C(19)	119.7(3)

C(23)-C(24)-H(24)	120.1
C(19)-C(24)-H(24)	120.1
C(30)-C(25)-C(26)	118.1(2)
C(30)-C(25)-P(1)	118.86(16)
C(26)-C(25)-P(1)	122.60(17)
C(27)-C(26)-C(25)	120.6(2)
C(27)-C(26)-H(26)	119.7
C(25)-C(26)-H(26)	119.7
C(28)-C(27)-C(26)	120.4(2)
C(28)-C(27)-H(27)	119.8
C(26)-C(27)-H(27)	119.8
C(27)-C(28)-C(29)	120.1(2)
C(27)-C(28)-H(28)	120.0
C(29)-C(28)-H(28)	120.0
C(30)-C(29)-C(28)	120.0(2)
C(30)-C(29)-H(29)	120.0
C(28)-C(29)-H(29)	120.0
C(29)-C(30)-C(25)	120.8(2)
C(29)-C(30)-H(30)	119.6
C(25)-C(30)-H(30)	119.6
O(1)-P(1)-C(19)	112.78(10)
O(1)-P(1)-C(25)	111.66(9)
C(19)-P(1)-C(25)	105.84(11)
O(1)-P(1)-C(17)	112.44(9)
C(19)-P(1)-C(17)	106.90(10)
C(25)-P(1)-C(17)	106.78(9)
C(7)-S(1)-C(1)	103.03(11)

Symmetry transformations used to generate equivalent atoms:

9. Characterization Data of Coupling Products

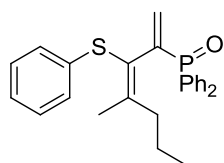
(4-methyl-3-(phenylthio)penta-1,3-dien-2-yl)diphenylphosphine oxide (3aa)



Yellow liquid (72 mg, 92% yield). TLC (R_f = 0.26, PET/EA = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.66-7.60 (m, 4H), 7.47 (t, J = 7.4 Hz, 2H), 7.38-7.34 (m, 4H), 7.19 (t, J =

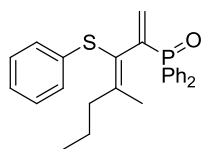
7.5 Hz, 2H), 7.11 (t, $J = 7.2$ Hz, 1H), 6.94 (d, $J = 7.7$ Hz, 2H), 5.80 (s, 1H), 5.73 (d, $J = 22.5$ Hz, 1H), 2.01 (d, $J = 2.9$ Hz, 3H), 1.78 (d, $J = 2.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.9 (d, $J = 6.6$ Hz), 142.7 (d, $J = 92.6$ Hz), 135.6, 132.6 (d, $J = 1.7$ Hz), 132.5, 131.9 (d, $J = 9.8$ Hz), 131.7 (d, $J = 2.6$ Hz), 131.5, 128.8 (d, $J = 30.4$ Hz), 128.1 (d, $J = 12.1$ Hz), 125.8, 122.3 (d, $J = 7.8$ Hz), 23.0, 22.5. ^{31}P NMR (162 MHz, CDCl_3) δ 28.4 (s). HRMS (ESI): $([\text{M}+\text{Na}]^+)$ Calcd for $\text{C}_{24}\text{H}_{23}\text{ONaPS}$: 413.1099, Found: 413.1096. IR (film) ν 3055, 2911, 2849, 1713, 1581, 1477, 1437, 1174, 1166, 728, 691 cm^{-1} .

(E)-(4-methyl-3-(phenylthio)hepta-1,3-dien-2-yl)diphenylphosphine oxide (3ba-E)



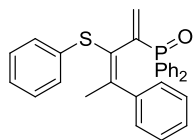
Yellow liquid (19 mg, 23% yield). TLC ($R_f = 0.25$, PET/EA = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.65 (dd, $J = 11.9, 7.3$ Hz, 4H), 7.53 (dd, $J = 7.5, 6.3$ Hz, 2H), 7.43-7.39 (m, 4H), 7.24 (t, $J = 7.5$ Hz, 2H), 7.17 (t, $J = 7.3$ Hz, 1H), 6.97 (d, $J = 7.4$ Hz, 2H), 5.83 (d, $J = 9.9$ Hz, 1H), 5.76 (d, $J = 30.5$ Hz, 1H), 2.10 (dd, $J = 8.6, 7.0$ Hz, 2H), 2.00 (d, $J = 3.1$ Hz, 3H), 1.43-1.33 (m, 2H), 0.88 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.9 (d, $J = 6.3$ Hz), 142.5 (d, $J = 92.2$ Hz), 135.6, 132.7, 132.0 (d, $J = 9.8$ Hz), 131.9, 131.6 (d, $J = 2.8$ Hz), 129.0, 128.6, 128.0 (d, $J = 12.1$ Hz), 125.8, 122.5 (d, $J = 7.9$ Hz), 38.3, 21.8, 19.9, 14.2. ^{31}P NMR (162 MHz, CDCl_3) δ 28.1 (s). HRMS (ESI): $([\text{M}+\text{H}]^+)$ Calcd for $\text{C}_{26}\text{H}_{28}\text{OPS}$: 419.1593, Found: 419.1589. IR (film) ν 3051, 2961, 2928, 1686, 1477, 1375, 1231, 1189, 1126, 1089, 1024, 973, 886, 745, 758 cm^{-1} .

(Z)-(4-methyl-3-(phenylthio)hepta-1,3-dien-2-yl)diphenylphosphine oxide (3ba-Z)



Yellow liquid (13 mg, 15% yield). TLC ($R_f = 0.32$, PET/EA = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.65 (dd, $J = 11.8, 7.7$ Hz, 4H), 7.52 (t, $J = 7.3$ Hz, 2H), 7.42-7.37 (m, 4H), 7.28-7.24 (m, 2H), 7.18 (t, $J = 7.2$ Hz, 1H), 7.00 (d, $J = 7.6$ Hz, 2H), 5.97 (d, $J = 18.0$ Hz, 1H), 5.81 (d, $J = 38.0$ Hz, 1H), 2.43-2.39 (m, 2H), 1.77 (d, $J = 2.0$ Hz, 3H), 1.29 (d, $J = 9.4$ Hz, 2H), 0.85 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.6 (d, $J = 6.7$ Hz), 142.3 (d, $J = 92.2$ Hz), 135.6, 132.9 (d, $J = 8.9$ Hz), 132.7, 132.1 (d, $J = 9.8$ Hz), 131.6 (d, $J = 2.6$ Hz), 129.0, 128.6, 128.0 (d, $J = 12.1$ Hz), 125.9, 122.6 (d, $J = 8.4$ Hz), 38.0, 21.6, 20.9, 14.2. ^{31}P NMR (162 MHz, CDCl_3) δ 28.4 (s). IR (film) ν 2956, 2928, 2868, 2841, 1611, 1453, 1322, 1207, 1166, 1126, 1108, 1061, 973, 951, 901, 865, 721 cm^{-1} .

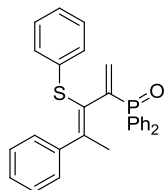
(E)-diphenyl(4-phenyl-3-(phenylthio)penta-1,3-dien-2-yl)phosphine oxide (3ca-E)



Yellow liquid (49 mg, 54% yield). TLC ($R_f = 0.25$, PET/EA = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.28 (m, 15H), 7.20-7.11 (m, 3H), 6.87 (d, $J = 7.5$ Hz, 2H), 5.50 (d, $J = 40.8$ Hz, 1H), 5.16 (d, $J = 18.4$ Hz, 1H), 2.48 (d, $J = 2.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ

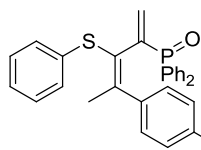
151.1 (d, $J = 6.6$ Hz), 142.6, 141.7, 135.1, 134.0 (d, $J = 11.0$ Hz), 132.9, 131.9, 131.7 (d, $J = 9.8$ Hz), 131.4 (d, $J = 2.6$ Hz), 129.0, 128.5, 128.1 (d, $J = 5.4$ Hz), 128.0, 127.1, 126.5 (d, $J = 6.9$ Hz), 125.7, 24.4. **^{31}P NMR** (162 MHz, CDCl_3) δ 28.4 (s). **HRMS (ESI):** ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{29}\text{H}_{26}\text{OPS}$: 453.1436, Found: 453.1432. **IR** (film) ν 2976, 2953, 2838, 1978, 1589, 1532, 1396, 1297, 1188, 1119, 1078, 1035, 997, 968, 908, 790 cm^{-1} .

(Z)-diphenyl(4-phenyl-3-(phenylthio)penta-1,3-dien-2-yl)phosphine oxide (3ca-Z)



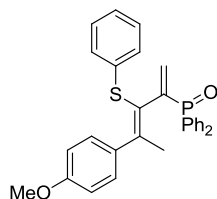
Yellow liquid (14 mg, 16% yield). TLC ($R_f = 0.25$, PET/EA = 1:1). **^1H NMR** (400 MHz, CDCl_3) δ 7.75-7.70 (m, 4H), 7.57 (s, 2H), 7.44 (s, 4H), 7.28-7.19 (m, 6H), 7.02 (s, 4H), 6.17 (d, $J = 17.9$ Hz, 1H), 6.00 (d, $J = 37.2$ Hz, 1H), 2.01 (s, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 149.9 (d, $J = 6.9$ Hz), 142.2, 141.3, 135.33, 133.6 (d, $J = 7.7$ Hz), 132.1 (d, $J = 9.9$ Hz), 131.9 (d, $J = 103.5$ Hz), 131.8 (d, $J = 2.6$ Hz), 129.7, 128.6, 128.09 (d, $J = 18.0$ Hz), 128.06, 127.4, 127.3, 126.2, 125.2 (d, $J = 8.3$ Hz), 24.0. **^{31}P NMR** (162 MHz, CDCl_3) δ 28.5 (s). **IR** (film) ν 3051, 2983, 2033, 1582, 1487, 1422, 1298, 1187, 1119, 1092, 1022, 909, 730, 703 cm^{-1} .

(E)-(4-(4-methoxyphenyl)-3-(phenylthio)penta-1,3-dien-2-yl)diphenylphosphine oxide (3da-E)



Yellow liquid (36 mg, 37% yield). TLC ($R_f = 0.34$, PET/EA = 1:1). **^1H NMR** (400 MHz, CDCl_3) δ 7.46-7.39 (m, 8H), 7.30 (td, $J = 7.6, 2.8$ Hz, 4H), 7.19-7.10 (m, 3H), 6.87-6.85 (m, 4H), 5.51 (d, $J = 40.9$ Hz, 1H), 5.20 (d, $J = 18.4$ Hz, 1H), 3.82 (s, 3H), 2.45 (d, $J = 2.6$ Hz, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 158.7, 150.9 (d, $J = 6.5$ Hz), 142.4 (d, $J = 95.8$ Hz), 135.2, 134.9, 133.8 (d, $J = 10.9$ Hz), 132.5 (d, $J = 102.9$ Hz), 131.7 (d, $J = 9.7$ Hz), 131.4 (d, $J = 2.7$ Hz), 129.8, 128.8, 128.3 (d, $J = 41.0$ Hz), 128.0, 125.8 (d, $J = 6.8$ Hz), 125.7, 113.4, 55.3, 24.4. **^{31}P NMR** (162 MHz, CDCl_3) δ 28.3 (s). **HRMS (ESI):** ($[\text{M}+\text{Na}]^+$) Calcd for $\text{C}_{30}\text{H}_{27}\text{O}_2\text{NaPS}$: 505.1367, Found: 505.1367. **IR** (film) ν 3056, 2971, 2933, 2829, 2029, 1607, 1508, 1450, 1400, 1371, 1300, 1245, 1189, 1114, 1100, 1036, 958, 835, 723 cm^{-1} .

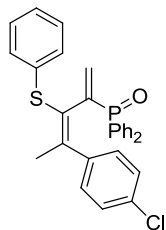
(Z)-(4-(4-methoxyphenyl)-3-(phenylthio)penta-1,3-dien-2-yl)diphenylphosphine oxide (3da-Z)



Yellow liquid (19 mg, 20% yield). TLC ($R_f = 0.25$, PET/EA = 1:1). **^1H NMR** (400 MHz, CDCl_3) δ 7.71 (dd, $J = 11.9, 7.6$ Hz, 4H), 7.56 (t, $J = 7.3$ Hz, 2H), 7.43 (td, $J = 7.7, 2.6$ Hz, 4H), 7.26 (t, $J = 7.6$ Hz, 2H), 7.19 (t, $J = 7.2$ Hz, 1H), 6.99 (dd, $J = 12.5, 8.1$ Hz, 4H), 6.81 (d,

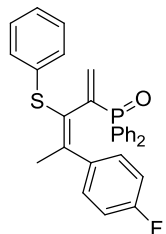
$J = 8.6$ Hz, 2H), 6.14 (d, $J = 18.0$ Hz, 1H), 5.98 (d, $J = 37.4$ Hz, 1H), 3.78 (s, 3H), 2.00 (d, $J = 2.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.8, 149.5 (d, $J = 6.9$ Hz), 141.9 (d, $J = 91.2$ Hz), 135.5, 134.4, 133.5 (d, $J = 7.9$ Hz), 132.1 (d, $J = 9.9$ Hz), 132.0 (d, $J = 103.4$ Hz), 131.8 (d, $J = 2.6$ Hz), 129.5, 128.8, 128.6, 128.1 (d, $J = 12.1$ Hz), 126.1, 124.6 (d, $J = 8.2$ Hz), 113.3, 55.2, 24.0. ^{31}P NMR (162 MHz, CDCl_3) δ 28.5 (s). IR (film) ν 2974, 2936, 2833, 2159, 1606, 1508, 1436, 1297, 1243, 1167, 1115, 1032, 953, 831, 756, 720 cm^{-1} .

(E)-4-(4-chlorophenyl)-3-(phenylthio)penta-1,3-dien-2-yl)diphenylphosphine oxide (3ea)



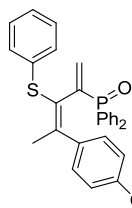
Yellow solids, *m.p.*: 83.6-85.1°C (recrystallized from $\text{CH}_2\text{Cl}_2/\text{PET}/\text{EA} = 1:1:1$) (52 mg, 53% yield). TLC ($R_f = 0.25$, $\text{PET}/\text{EA} = 1:1$). ^1H NMR (400 MHz, CDCl_3) δ 7.47 (t, $J = 7.3$ Hz, 2H), 7.43-7.38 (m, 6H), 7.35-7.28 (m, 6H), 7.21-7.13 (m, 3H), 6.89 (d, $J = 7.4$ Hz, 2H), 5.51 (d, $J = 40.6$ Hz, 1H), 5.20 (d, $J = 18.4$ Hz, 1H), 2.45 (d, $J = 2.7$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.4 (d, $J = 6.4$ Hz), 142.2 (d, $J = 95.2$ Hz), 141.0, 134.8, 134.1 (d, $J = 10.8$ Hz), 132.9 (d, $J = 34.2$ Hz), 131.6 (d, $J = 9.7$ Hz), 131.5 (d, $J = 2.6$ Hz), 130.0, 129.2, 128.6, 128.2 (d, $J = 2.4$ Hz), 128.1, 127.3 (d, $J = 6.7$ Hz), 125.9, 24.2. ^{31}P NMR (162 MHz, CDCl_3) δ 28.0 (s). HRMS (ESI): ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{29}\text{H}_{25}\text{OClPS}$: 487.1047, Found: 487.1042. IR (film) ν 3053, 2912, 2849, 1581, 1478, 1438, 1277, 1176, 1116, 1022, 925, 856, 826, 722, 688 cm^{-1} .

(E)-4-(4-fluorophenyl)-3-(phenylthio)penta-1,3-dien-2-yl)diphenylphosphine oxide (3fa)



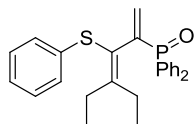
Yellow solids, *m.p.*: 112.7-113.9°C (recrystallized from $\text{CH}_2\text{Cl}_2/\text{PET}/\text{EA} = 1:1:1$) (48 mg, 51% yield). TLC ($R_f = 0.24$, $\text{PET}/\text{EA} = 1:1$). ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.38 (m, 8H), 7.31 (dd, $J = 13.0, 7.4$ Hz, 4H), 7.20-7.12 (m, 3H), 7.02 (t, $J = 8.5$ Hz, 2H), 6.87 (d, $J = 7.5$ Hz, 2H), 5.50 (d, $J = 40.8$ Hz, 1H), 5.18 (d, $J = 18.4$ Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.0 (d, $J = 246.2$ Hz), 149.9 (d, $J = 6.5$ Hz), 142.2 (d, $J = 95.3$ Hz), 138.5, 134.9, 134.0 (d, $J = 11.1$ Hz), 132.7, 131.6 (d, $J = 9.8$ Hz), 131.5 (d, $J = 2.7$ Hz), 130.3 (d, $J = 7.9$ Hz), 129.1, 128.6, 128.2 (d, $J = 12.2$ Hz), 127.0 (d, $J = 6.8$ Hz), 125.9, 115.0 (d, $J = 21.3$ Hz), 24.4. ^{31}P NMR (162 MHz, CDCl_3) δ 28.2 (s). HRMS (ESI): ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{29}\text{H}_{25}\text{OFPS}$: 471.1342, Found: 471.1334. IR (film) ν 3049, 2957, 2917, 2848, 1581, 1506, 1436, 1235, 1219, 1175, 1151, 1110, 1071, 1024, 943, 842, 745, 692 cm^{-1} .

(E)-diphenyl(3-(phenylthio)-4-(4-(trifluoromethyl)phenyl)penta-1,3-dien-2-yl)phosphine oxide (3ga)



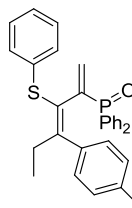
Yellow solids, *m.p.*: 133.9-135.3°C (recrystallized from CH₂Cl₂/PET/EA = 1:1:1) (51 mg, 49% yield). TLC (*R_f* = 0.13, PET/EA = 1:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.60-7.56 (m, 4H), 7.47 (t, *J* = 7.1 Hz, 2H), 7.38-7.28 (m, 8H), 7.22-7.14 (m, 3H), 6.91 (d, *J* = 7.4 Hz, 2H), 5.51 (d, *J* = 40.4 Hz, 1H), 5.16 (d, *J* = 18.3 Hz, 1H), 2.47 (d, *J* = 2.7 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 148.7 (d, *J* = 6.7 Hz), 146.4, 142.0 (d, *J* = 94.8 Hz), 134.5, 134.2 (d, *J* = 10.6 Hz), 132.6, 131.7, 131.6, 129.5, 129.1, 128.6, 128.2, 128.1, 126.2, 125.0 (d, *J* = 3.7 Hz), 24.1. **³¹P NMR** (162 MHz, CDCl₃) δ 27.9 (s). **HRMS (ESI):** ([*M*+*H*]⁺) Calcd for C₃₀H₂₅OF₃PS: 521.1310, Found: 521.1304. **IR** (film) ν 2929, 2867, 2839, 1686, 1612, 1476, 1406, 1322, 1182, 1152, 1110, 1062, 1018, 984, 946, 865, 842, 773, 723 cm⁻¹.

(4-ethyl-3-(phenylthio)hexa-1,3-dien-2-yl)diphenylphosphine oxide (3ha)



Yellow liquid (43 mg, 52% yield). TLC (*R_f* = 0.33, PET/EA = 1:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.66 (dd, *J* = 11.7, 7.8 Hz, 4H), 7.52 (t, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 6.6 Hz, 4H), 7.27 (t, *J* = 6.9 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 2H), 5.98 (d, *J* = 17.9 Hz, 1H), 5.82 (d, *J* = 37.4 Hz, 1H), 2.42 (q, *J* = 7.3 Hz, 2H), 2.09 (q, *J* = 7.3 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.80 (t, *J* = 7.5 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 158.5 (d, *J* = 6.8 Hz), 141.9 (d, *J* = 91.2 Hz), 135.4, 132.2, 132.1, 131.7 (d, *J* = 2.7 Hz), 129.1, 128.7, 128.0 (d, *J* = 12.2 Hz), 126.0, 122.1 (d, *J* = 8.3 Hz), 26.7, 25.7, 13.8, 13.2 (d, *J* = 2.8 Hz). **³¹P NMR** (162 MHz, CDCl₃) δ 28.6 (s). **HRMS (ESI):** ([*M*+*Na*]⁺) Calcd for C₂₆H₂₇ONaPS: 441.1412, Found: 441.1419. **IR** (film) ν 3053, 2986, 1568, 1462, 1422, 1289, 1178, 1124, 1118, 1035, 909, 725, 693 cm⁻¹.

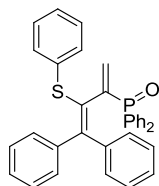
(*E*)-(4-(4-chlorophenyl)-3-(phenylthio)hexa-1,3-dien-2-yl)diphenylphosphine oxide (3ia)



Yellow solids, *m.p.*: 158.7-160.1°C (recrystallized from CH₂Cl₂/PET/EA = 1:1:1) (53 mg, 55% yield). TLC (*R_f* = 0.28, PET/EA = 1:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.47 (t, *J* = 7.2 Hz, 2H), 7.40-7.26 (m, 12H), 7.21-7.15 (m, 3H), 6.88 (d, *J* = 7.2 Hz, 2H), 5.52 (d, *J* = 40.3 Hz, 1H), 5.23 (d, *J* = 18.3 Hz, 1H), 2.90 (q, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 155.3 (d, *J* = 6.2 Hz), 141.8 (d, *J* = 94.8 Hz), 139.6, 134.8, 134.2 (d, *J* = 10.4 Hz), 133.0, 132.8, 131.6 (d, *J* = 9.8 Hz), 131.5 (d, *J* = 2.6 Hz), 130.5, 129.2, 128.6, 128.2 (d, *J* = 5.5 Hz), 128.1, 126.7 (d, *J* = 6.7 Hz), 126.0, 30.4, 12.8. **³¹P NMR** (162 MHz, CDCl₃) δ 27.0 (s). **HRMS (ESI):** ([*M*+*H*]⁺) Calcd for C₃₀H₂₇OClPS: 501.1203, Found: 501.1197. **IR** (film) ν 3058,

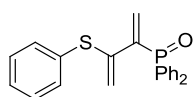
2965, 2930, 2872, 1583, 1479, 1435, 1207, 1191, 1177, 1104, 1084, 1013, 951, 853, 816, 737, 718 cm^{-1} .

(4,4-diphenyl-3-(phenylthio)buta-1,3-dien-2-yl)diphenylphosphine oxide (3ja)



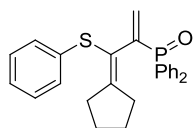
Yellow solids, *m.p.*: 168.7-169.9°C (recrystallized from $\text{CH}_2\text{Cl}_2/\text{PET}/\text{EA} = 1:1:1$) (73 mg, 71% yield). TLC ($R_f = 0.27$, $\text{PET}/\text{EA} = 1:1$). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49-7.45 (m, 8H), 7.35-7.23 (m, 12H), 7.18-7.15 (m, 3H), 6.91 (d, $J = 7.0$ Hz, 2H), 5.79 (d, $J = 40.0$ Hz, 1H), 5.40 (d, $J = 18.3$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.4 (d, $J = 6.7$ Hz), 142.0 (d, $J = 95.4$ Hz), 141.8, 135.7, 135.1 (d, $J = 10.3$ Hz), 132.8, 131.7 (d, $J = 9.8$ Hz), 131.4 (d, $J = 2.4$ Hz), 130.3, 129.2 (d, $J = 7.9$ Hz), 128.7 (d, $J = 7.2$ Hz), 128.5, 128.03 (d, $J = 3.4$ Hz), 128.02 (d, $J = 30.9$ Hz), 127.6 (d, $J = 25.8$ Hz), 125.7. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 28.3 (s). **HRMS (ESI):** ($[\text{M}+\text{Na}]^+$) Calcd for $\text{C}_{34}\text{H}_{27}\text{ONaPS}$: 537.1412, Found: 537.1419. **IR** (film) ν 2929, 2878, 2839, 1489, 1444, 1395, 1260, 1207, 1187, 1127, 1107, 1079, 1027, 976, 952, 905, 794, 771, 755, 725 cm^{-1} .

diphenyl(3-(phenylthio)buta-1,3-dien-2-yl)phosphine oxide (3ka)



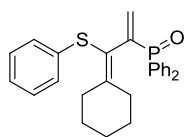
Yellow liquid (24 mg, 33% yield). TLC ($R_f = 0.34$, $\text{PET}/\text{EA} = 1:1$). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 (dd, $J = 11.9, 7.7$ Hz, 4H), 7.59-7.55 (m, 2H), 7.51-7.46 (m, 4H), 7.31-7.29 (m, 5H), 6.56 (d, $J = 39.9$ Hz, 1H), 6.11 (s, 1H), 5.63 (d, $J = 19.7$ Hz, 1H), 5.38 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 140.9 (d, $J = 91.0$ Hz), 139.1 (d, $J = 11.7$ Hz), 134.0 (d, $J = 9.7$ Hz), 133.0, 132.2, 132.0 (d, $J = 2.6$ Hz), 131.9 (d, $J = 9.7$ Hz), 131.4 (d, $J = 104.5$ Hz), 129.2, 128.5 (d, $J = 12.3$ Hz), 127.8, 123.4 (d, $J = 3.7$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 30.8 (s). **HRMS (ESI):** ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{22}\text{H}_{20}\text{OPS}$: 363.0967, Found: 363.0962. **IR** (film) ν 3056, 2952, 2923, 2848, 1715, 1581, 1476, 1437, 1240, 1174, 1117, 1094, 1024, 907, 724, 690 cm^{-1} .

(4-methyl-3-(phenylsulfonyl)penta-1,3-dien-2-yl)diphenylphosphine oxide (3la)



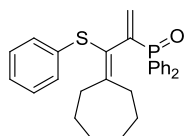
Yellow liquid (53 mg, 64% yield). TLC ($R_f = 0.27$, $\text{PET}/\text{EA} = 1:1$). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 (dd, $J = 11.9, 7.7$ Hz, 4H), 7.51 (t, $J = 7.4$ Hz, 2H), 7.41-7.36 (m, 4H), 7.22 (t, $J = 7.5$ Hz, 2H), 7.15 (t, $J = 7.2$ Hz, 1H), 7.00 (d, $J = 7.7$ Hz, 2H), 5.95 (d, $J = 13.4$ Hz, 1H), 5.88 (d, $J = 6.8$ Hz, 1H), 2.49-2.46 (m, 2H), 2.28 (s, 2H), 1.67-1.53 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.6 (d, $J = 7.0$ Hz), 143.3 (d, $J = 92.0$ Hz), 135.6, 133.1 (d, $J = 9.4$ Hz), 132.1 (d, $J = 102.9$ Hz), 132.0 (d, $J = 9.8$ Hz), 131.6 (d, $J = 2.7$ Hz), 128.7, 128.6, 128.0 (d, $J = 12.2$ Hz), 125.7, 118.2 (d, $J = 8.5$ Hz), 33.8, 33.6, 26.9, 26.0. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 28.2 (s). **HRMS (ESI):** ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{26}\text{H}_{26}\text{OPS}$: 417.1436, Found: 417.1430. **IR** (film) ν 3057, 2956, 2920, 2846, 1639, 1582, 1477, 1437, 1181, 1117, 1098, 907, 726, 691 cm^{-1} .

(3-cyclohexylidene-3-(phenylthio)prop-1-en-2-yl)diphenylphosphine oxide (3ma)



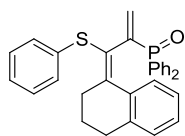
Yellow liquid (52 mg, 61% yield). TLC (R_f = 0.28, PET/EA = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.66 (dd, J = 11.9, 7.8 Hz, 4H), 7.52 (t, J = 7.4 Hz, 2H), 7.43-7.38 (m, 4H), 7.26 (dd, J = 14.2, 6.6 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 6.99 (d, J = 7.8 Hz, 2H), 5.90 (d, J = 17.9 Hz, 1H), 5.76 (d, J = 38.1 Hz, 1H), 2.58 (s, 2H), 2.25-2.22 (m, 2H), 1.53 (s, 4H), 1.35 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.5 (d, J = 6.5 Hz), 142.1 (d, J = 92.3 Hz), 135.7, 132.6, 132.2, 132.1 (d, J = 9.8 Hz), 131.7 (d, J = 2.6 Hz), 129.0, 128.6, 128.0 (d, J = 12.1 Hz), 125.8, 119.4 (d, J = 8.2 Hz), 33.2, 32.5, 28.2, 28.1, 26.3. ^{31}P NMR (162 MHz, CDCl_3) δ 28.2 (s). HRMS (ESI): $([\text{M}+\text{H}]^+)$ Calcd for $\text{C}_{27}\text{H}_{28}\text{OPS}$: 431.1593, Found: 431.1586. IR (film) ν 3057, 2923, 2849, 1644, 1581, 1477, 1437, 1193, 1169, 1117, 1098, 925, 908, 726, 691 cm^{-1} .

(3-cycloheptylidene-3-(phenylthio)prop-1-en-2-yl)diphenylphosphine oxide (3na)



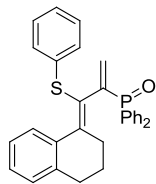
Yellow liquid (52 mg, 59% yield). TLC (R_f = 0.25, PET/EA = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 7.64 (dd, J = 11.8, 7.8 Hz, 4H), 7.50 (t, J = 7.4 Hz, 2H), 7.40-7.36 (m, 4H), 7.24 (t, J = 7.4 Hz, 2H), 7.16 (t, J = 7.2 Hz, 1H), 6.96 (d, J = 7.7 Hz, 2H), 5.86 (dd, J = 34.7, 28.2 Hz, 2H), 2.62 (d, J = 4.0 Hz, 2H), 2.36 (t, J = 5.8 Hz, 2H), 1.53-1.48 (m, 6H), 1.36 (d, J = 4.4 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.0 (d, J = 6.8 Hz), 142.0 (d, J = 92.0 Hz), 135.7, 132.64, 132.55, 132.0 (d, J = 9.8 Hz), 131.6 (d, J = 2.5 Hz), 128.9, 128.6, 128.0 (d, J = 12.1 Hz), 125.8, 122.0 (d, J = 7.8 Hz), 34.3, 33.6, 29.3, 28.5, 28.1, 27.4. ^{31}P NMR (162 MHz, CDCl_3) δ 28.6 (s). HRMS (ESI): $([\text{M}+\text{H}]^+)$ Calcd for $\text{C}_{28}\text{H}_{30}\text{OPS}$: 445.1749, Found: 445.1742. IR (film) ν 3050, 2921, 2850, 1581, 1506, 1477, 1436, 1194, 1175, 1163, 1112, 1098, 124, 942, 842, 736, 724, 691 cm^{-1} .

(E)-(3-(3,4-dihydronaphthalen-1(2H)-ylidene)-3-(phenylthio)prop-1-en-2-yl)diphenylphosphine oxide (30a-E)



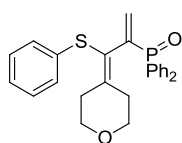
Yellow solids, $m.p.$: 145.3-146.6 $^{\circ}\text{C}$ (recrystallized from $\text{CH}_2\text{Cl}_2/\text{PET/EA}$ = 1:1:1) (28 mg, 29% yield). TLC (R_f = 0.23, PET/EA = 1:1). ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, J = 7.5 Hz, 1H), 7.58 (dd, J = 11.8, 7.8 Hz, 4H), 7.48 (t, J = 7.4 Hz, 2H), 7.37-7.33 (m, 4H), 7.24-7.11 (m, 6H), 6.88 (d, J = 7.6 Hz, 2H), 5.66 (d, J = 40.3 Hz, 1H), 5.40 (d, J = 18.1 Hz, 1H), 2.92 (s, 2H), 2.73 (t, J = 6.4 Hz, 2H), 1.90-1.83 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.4 (d, J = 6.1 Hz), 142.9 (d, J = 95.4 Hz), 140.1, 136.0, 135.3, 133.7 (d, J = 10.9 Hz), 131.7 (d, J = 9.7 Hz), 131.4 (d, J = 2.5 Hz), 130.3, 128.5 (d, J = 17.3 Hz), 128.2, 128.1, 127.5, 125.4 (d, J = 38.2 Hz), 124.7 (d, J = 7.5 Hz), 31.0 (d, J = 10.9 Hz), 29.7, 23.5. ^{31}P NMR (162 MHz, CDCl_3) δ 28.3 (s). HRMS (ESI): $([\text{M}+\text{H}]^+)$ Calcd for $\text{C}_{31}\text{H}_{28}\text{OPS}$: 479.1593, Found: 479.1582. IR (film) ν 2929, 2865, 1478, 1452, 1260, 1206, 1187, 1128, 1111, 1094, 1026, 974, 947, 922, 758, 735, 721 cm^{-1} .

(Z)-(3-(3,4-dihydronaphthalen-1(2H)-ylidene)-3-(phenylthio)prop-1-en-2-yl)diphenylphosphine oxide (30a-Z)



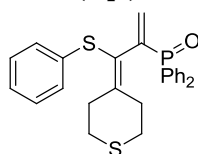
Yellow solids, *m.p.*: 130.7-131.6°C (recrystallized from CH₂Cl₂/PET/EA = 1:1:1) (24 mg, 25% yield). TLC (*R_f* = 0.30, PET/EA = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.70-7.6 (m, 5H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.1 Hz, 4H), 7.28 (d, *J* = 6.7 Hz, 2H), 7.20 (dd, *J* = 17.0, 7.5 Hz, 2H), 7.09-7.01 (m, 4H), 6.13 (d, *J* = 17.7 Hz, 1H), 6.01 (d, *J* = 37.3 Hz, 1H), 2.58-2.50 (m, 4H), 1.64 (p, *J* = 6.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 149.6 (d, *J* = 7.1 Hz), 142.1 (d, *J* = 91.6 Hz), 140.1, 136.1, 135.5, 133.9 (d, *J* = 8.4 Hz), 132.0 (d, *J* = 9.8 Hz), 131.7 (d, *J* = 2.4 Hz), 128.8 (d, *J* = 10.6 Hz), 128.5, 128.2, 128.1, 127.8, 125.9, 124.6, 122.0 (d, *J* = 8.5 Hz), 31.1, 29.0, 22.7. ³¹P NMR (162 MHz, CDCl₃) δ 28.2 (s). IR (film) ν 3050, 2928, 2861, 2839, 1583, 1475, 1451, 1435, 1259, 1178, 1168, 1128, 1110, 1085, 1023, 955, 901, 790, 760, 734, 719 cm⁻¹.

(3-(dihydro-2H-pyran-4(3H)-ylidene)-3-(phenylthio)prop-1-en-2-yl)diphenylphosphine oxide (3pa)



Yellow solids, *m.p.*: 86.6-87.8°C (recrystallized from CH₂Cl₂/PET/EA = 1:1:1) (48 mg, 56% yield). TLC (*R_f* = 0.26, PET/EA = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.66 (dd, *J* = 11.8, 7.7 Hz, 4H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.44-7.40 (m, 4H), 7.29-7.25 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 2H), 5.94 (d, *J* = 17.8 Hz, 1H), 5.76 (d, *J* = 37.6 Hz, 1H), 3.61 (t, *J* = 5.3 Hz, 2H), 3.41 (t, *J* = 5.3 Hz, 2H), 2.72 (d, *J* = 4.1 Hz, 2H), 2.36 (t, *J* = 5.1 Hz, 2H). ¹³C NMR δ 149.3 (d, *J* = 6.5 Hz), 141.7 (d, *J* = 91.6 Hz), 135.0, 132.9 (d, *J* = 8.7 Hz), 132.1 (d, *J* = 9.8 Hz), 131.9 (d, *J* = 2.6 Hz), 131.8 (d, *J* = 103.2 Hz), 129.3, 128.8, 128.1 (d, *J* = 12.2 Hz), 126.2, 121.9 (d, *J* = 8.2 Hz), 68.6, 68.4, 33.9, 32.9. ³¹P NMR (162 MHz, CDCl₃) δ 27.8 (s). HRMS (ESI): ([M+Na]⁺) Calcd for C₂₆H₂₅O₂NaPS: 455.1205, Found: 455.1211. IR (film) ν 3050, 2954, 2850, 2834, 1581, 1472, 1435, 1377, 1287, 1238, 1193, 1166, 1116, 1092, 992, 960, 828, 744, 691 cm⁻¹.

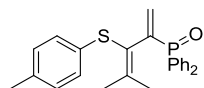
(3-(dihydro-2H-thiopyran-4(3H)-ylidene)-3-(phenylthio)prop-1-en-2-yl)diphenylphosphine oxide (3qa)



Dark brown solids, *m.p.*: 138.9-140.7°C (recrystallized from CH₂Cl₂/PET/EA = 1:1:1) (76 mg, 85% yield). TLC (*R_f* = 0.24, PET/EA = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.66 (dd, *J* = 11.9, 7.8 Hz, 4H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.45-7.41 (m, 4H), 7.29-7.25 (m, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 2H), 5.88 (d, *J* = 17.9 Hz, 1H), 5.72 (d, *J* = 37.8 Hz, 1H), 3.00-2.98 (m, 2H), 2.66-2.59 (m, 4H), 2.43 (dd, *J* = 7.0, 4.1 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 151.2 (d, *J* = 6.4 Hz), 141.8 (d, *J* = 91.5 Hz), 134.8, 132.4 (d, *J* = 8.9 Hz), 132.1 (d, *J* = 9.8 Hz),

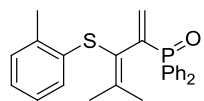
131.9 (d, $J = 2.7$ Hz), 131.3, 129.4, 128.8, 128.2 (d, $J = 12.2$ Hz), 126.3, 123.1 (d, $J = 8.0$ Hz), 34.9, 34.1, 30.5, 30.4. **^{31}P NMR** (162 MHz, CDCl_3) δ 27.6 (s). **HRMS (ESI):** ($[\text{M}+\text{Na}]^+$) Calcd for $\text{C}_{26}\text{H}_{25}\text{ONaPS}_2$: 471.0977, Found: 471.0982. **IR** (film) ν 2916, 2851, 2159, 2029, 1977, 1719, 1592, 1474, 1437, 1223, 1174, 1117, 1078, 940, 742, 728, 690 cm^{-1} .

(4-methyl-3-(p-tolylthio)penta-1,3-dien-2-yl)diphenylphosphine oxide (3ab)



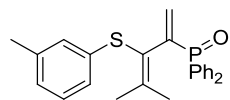
Yellow solids, *m.p.*: 124.7-125.8°C (recrystallized from $\text{CH}_2\text{Cl}_2/\text{PET}/\text{EA} = 1:1:1$) (50 mg, 62% yield). TLC ($R_f = 0.27$, $\text{PET}/\text{EA} = 1:1$). **^1H NMR** (400 MHz, CDCl_3) δ 7.65 (dd, $J = 11.8, 7.7$ Hz, 4H), 7.52 (t, $J = 7.4$ Hz, 2H), 7.42-7.38 (m, 4H), 7.05 (d, $J = 7.9$ Hz, 2H), 6.88 (d, $J = 8.0$ Hz, 2H), 5.82 (d, $J = 18.1$ Hz, 1H), 5.72 (d, $J = 38.8$ Hz, 1H), 2.32 (s, 3H), 2.02 (d, $J = 3.1$ Hz, 3H), 1.75 (d, $J = 2.2$ Hz, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 147.1 (d, $J = 6.7$ Hz), 142.6 (d, $J = 92.4$ Hz), 135.8, 132.6, 132.4 (d, $J = 9.5$ Hz), 132.0 (d, $J = 9.8$ Hz), 131.9, 131.64 (d, $J = 2.6$ Hz), 131.57, 129.4, 128.0 (d, $J = 12.1$ Hz), 122.7 (d, $J = 7.8$ Hz), 22.9, 22.5, 21.1. **^{31}P NMR** (162 MHz, CDCl_3) δ 28.3 (s). **HRMS (ESI):** ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{25}\text{H}_{26}\text{OPS}$: 405.1436, Found: 405.1430. **IR** (film) ν 3076, 3053, 2922, 2851, 1490, 1436, 1200, 1173, 1116, 1100, 908, 807, 725, 692 cm^{-1} .

(4-methyl-3-(o-tolylthio)penta-1,3-dien-2-yl)diphenylphosphine oxide (3ac)



Yellow solids, *m.p.*: 88.6-89.7°C (recrystallized from $\text{CH}_2\text{Cl}_2/\text{PET}/\text{EA} = 1:1:1$) (46 mg, 57% yield). TLC ($R_f = 0.30$, $\text{PET}/\text{EA} = 1:1$). **^1H NMR** (400 MHz, CDCl_3) δ 7.59 (dd, $J = 11.8, 7.8$ Hz, 4H), 7.49 (t, $J = 7.4$ Hz, 2H), 7.38-7.34 (m, 4H), 7.14-7.05 (m, 3H), 6.98 (d, $J = 7.6$ Hz, 1H), 5.87 (t, $J = 28.8$ Hz, 2H), 2.03 (d, $J = 2.7$ Hz, 3H), 1.87 (s, 3H), 1.81 (s, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 148.9 (d, $J = 6.8$ Hz), 142.4 (d, $J = 93.1$ Hz), 136.5, 134.8, 133.0 (d, $J = 9.7$ Hz), 132.7, 131.7 (d, $J = 9.7$ Hz), 131.6 (d, $J = 2.7$ Hz), 130.1, 128.1 (d, $J = 12.1$ Hz), 127.4, 125.6 (d, $J = 61.0$ Hz), 121.3 (d, $J = 7.4$ Hz), 23.1, 22.6, 19.7. **^{31}P NMR** (162 MHz, CDCl_3) δ 28.7 (s). **HRMS (ESI):** ($[\text{M}+\text{Na}]^+$) Calcd for $\text{C}_{25}\text{H}_{25}\text{ONaPS}$: 427.1256, Found: 427.1261. **IR** (film) ν 2984, 2932, 1587, 1465, 1433, 1206, 1187, 1130, 1113, 940, 745, 715 cm^{-1} .

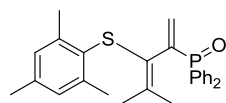
(4-methyl-3-(m-tolylthio)penta-1,3-dien-2-yl)diphenylphosphine oxide (3ad)



Yellow solids, *m.p.*: 92.2-92.7°C (recrystallized from $\text{CH}_2\text{Cl}_2/\text{PET}/\text{EA} = 1:1:1$) (29 mg, 36% yield). TLC ($R_f = 0.31$, $\text{PET}/\text{EA} = 1:1$). **^1H NMR** (400 MHz, CDCl_3) δ 7.65 (dd, $J = 11.8, 7.7$ Hz, 4H), 7.52 (t, $J = 7.4$ Hz, 2H), 7.40 (dd, $J = 7.4, 5.4$ Hz, 4H), 7.13 (t, $J = 7.6$ Hz, 1H), 6.97 (d, $J = 7.5$ Hz, 1H), 6.79 (d, $J = 7.7$ Hz, 1H), 6.72 (s, 1H), 5.80 (t, $J = 28.0$ Hz, 2H), 2.30 (s, 3H), 2.03 (d, $J = 3.0$ Hz, 3H), 1.78 (s, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 147.6 (d, $J = 6.5$ Hz), 142.7 (d, $J = 92.5$ Hz), 138.3, 135.3, 132.6, 132.5 (d, $J = 9.6$ Hz), 132.0 (d, $J = 9.8$ Hz), 131.6 (d, $J = 2.4$ Hz), 129.6, 128.4, 128.0 (d, $J = 12.1$ Hz), 126.7, 126.0, 122.4 (d, $J = 7.9$ Hz), 22.9, 22.5, 21.4. **^{31}P NMR** (162 MHz, CDCl_3) δ 28.3 (s). **HRMS (ESI):** ($[\text{M}+\text{Na}]^+$) Calcd for $\text{C}_{25}\text{H}_{25}\text{ONaPS}$:

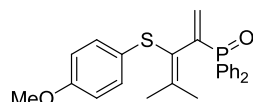
427.1256, Found: 427.1262. **IR**(film) ν 3030, 2984, 2937, 2881, 1590, 1476, 1438, 1366, 1204, 1185, 1170, 1112, 1079, 994, 940, 835, 754, 739 cm^{-1} .

(3-(mesitylthio)-4-methylpenta-1,3-dien-2-yl)diphenylphosphine oxide (3ae)



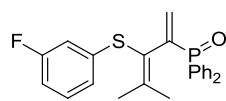
Yellow solids, *m.p.*: 69.8-70.7°C (recrystallized from $\text{CH}_2\text{Cl}_2/\text{PET}/\text{EA} = 1:1:1$) (56 mg, 65% yield). TLC ($R_f = 0.28$, $\text{PET}/\text{EA} = 1:1$). **^1H NMR** (400 MHz, CDCl_3) δ 7.65 (dd, $J = 11.5, 7.7$ Hz, 4H), 7.51 (t, $J = 7.4$ Hz, 2H), 7.42-7.38 (m, 4H), 6.84 (s, 2H), 5.68 (d, $J = 18.3$ Hz, 1H), 5.37 (d, $J = 39.8$ Hz, 1H), 2.27 (s, 3H), 2.22 (s, 6H), 2.03 (d, $J = 3.3$ Hz, 3H), 1.57 (d, $J = 2.4$ Hz, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 142.7 (d, $J = 90.9$ Hz), 142.5, 140.2 (d, $J = 6.5$ Hz), 137.5, 132.4 (d, $J = 56.2$ Hz), 132.1, 132.0, 131.7, 131.6 (d, $J = 2.7$ Hz), 129.1, 128.1 (d, $J = 11.9$ Hz), 123.0 (d, $J = 7.0$ Hz), 23.2, 22.0, 21.7, 21.0. **^{31}P NMR** (162 MHz, CDCl_3) δ 26.5 (s). **HRMS (ESI):** ($[\text{M}+\text{Na}]^+$) Calcd for $\text{C}_{27}\text{H}_{29}\text{ONaPS}$: 455.1569, Found: 455.1576. **IR** (film) ν 2978, 2933, 2864, 1600, 1488, 1435, 1366, 1205, 1180, 1130, 1029, 996, 972, 952, 747, 724 cm^{-1} .

(3-((4-methoxyphenyl)thio)-4-methylpenta-1,3-dien-2-yl)diphenylphosphine oxide (3af)



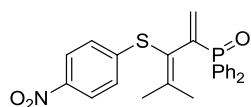
Yellow solids, *m.p.*: 155.4-156.3°C (recrystallized from $\text{CH}_2\text{Cl}_2/\text{PET}/\text{EA} = 1:1:1$) (62 mg, 74% yield). TLC ($R_f = 0.23$, $\text{PET}/\text{EA} = 1:1$). **^1H NMR** (400 MHz, CDCl_3) δ 7.68 (dd, $J = 11.7, 7.6$ Hz, 4H), 7.53 (t, $J = 7.3$ Hz, 2H), 7.44-7.39 (m, 4H), 6.94 (d, $J = 8.6$ Hz, 2H), 6.79 (d, $J = 8.6$ Hz, 2H), 5.80 (d, $J = 18.1$ Hz, 1H), 5.61 (d, $J = 38.9$ Hz, 1H), 3.80 (s, 3H), 2.03 (d, $J = 3.1$ Hz, 3H), 1.72 (d, $J = 2.1$ Hz, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 158.4, 145.8 (d, $J = 6.7$ Hz), 142.6 (d, $J = 92.4$ Hz), 132.6, 132.3 (d, $J = 9.3$ Hz), 132.0 (d, $J = 9.7$ Hz), 131.7, 131.6 (d, $J = 2.7$ Hz), 128.0 (d, $J = 12.0$ Hz), 126.1, 123.7 (d, $J = 7.8$ Hz), 114.3, 55.3, 22.9, 22.4. **^{31}P NMR** (162 MHz, CDCl_3) δ 27.8 (s). **HRMS (ESI):** ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{25}\text{H}_{26}\text{O}_2\text{PS}$: 421.1386, Found: 421.1379. **IR** (film) ν 2954, 2913, 2849, 1714, 1591, 1493, 1437, 1247, 1180, 1117, 1028, 907, 829, 730, 694 cm^{-1} .

(3-((3-fluorophenyl)thio)-4-methylpenta-1,3-dien-2-yl)diphenylphosphine oxide (3ag)



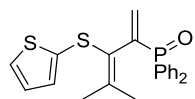
Yellow solids, *m.p.*: 81.7-82.6°C (recrystallized from $\text{CH}_2\text{Cl}_2/\text{PET}/\text{EA} = 1:1:1$) (59 mg, 72% yield). TLC ($R_f = 0.27$, $\text{PET}/\text{EA} = 1:1$). **^1H NMR** (400 MHz, CDCl_3) δ 7.63 (dd, $J = 11.9, 7.7$ Hz, 4H), 7.52 (t, $J = 7.4$ Hz, 2H), 7.42-7.37 (m, 4H), 7.16 (dd, $J = 14.0, 8.0$ Hz, 1H), 6.85-6.80 (m, 1H), 6.70 (d, $J = 7.8$ Hz, 1H), 6.59 (d, $J = 9.4$ Hz, 1H), 5.84 (d, $J = 21.0$ Hz, 1H), 5.77 (s, 1H), 2.04 (d, $J = 2.9$ Hz, 3H), 1.86 (d, $J = 2.1$ Hz, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 162.7 (d, $J = 247.7$ Hz), 149.1 (d, $J = 6.6$ Hz), 142.8 (d, $J = 92.7$ Hz), 138.2 (d, $J = 7.6$ Hz), 132.8 (d, $J = 9.8$ Hz), 131.91 (d, $J = 102.9$ Hz), 131.88 (d, $J = 9.8$ Hz), 131.7 (d, $J = 2.7$ Hz), 129.8 (d, $J = 8.4$ Hz), 128.1 (d, $J = 12.1$ Hz), 124.1 (d, $J = 2.8$ Hz), 121.7 (d, $J = 7.8$ Hz), 115.2 (d, $J = 23.2$ Hz), 112.6 (d, $J = 21.4$ Hz), 23.0, 22.7. **^{31}P NMR** (162 MHz, CDCl_3) δ 28.3 (s). **HRMS (ESI):** ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{24}\text{H}_{23}\text{OFPS}$: 409.1186, Found: 409.1181. **IR** (film) ν 2981, 2935, 1661, 1598, 1577, 1473, 1437, 1264, 1211, 1183, 1165, 1112, 1078, 1061, 996, 949, 876, 751, 724 cm^{-1} .

(4-methyl-3-((4-nitrophenyl)thio)penta-1,3-dien-2-yl)diphenylphosphine oxide (3ah)



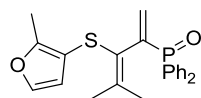
Yellow solids, *m.p.*: 184.8-186.1 °C (recrystallized from CH₂Cl₂/PET/EA = 1:1:1) (52 mg, 60% yield). TLC (*R_f* = 0.25, PET/EA = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.7 Hz, 2H), 7.60 (dd, *J* = 11.9, 7.7 Hz, 4H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.38-7.34 (m, 4H), 6.98 (d, *J* = 8.7 Hz, 2H), 5.93 (d, *J* = 39.6 Hz, 1H), 5.72 (d, *J* = 18.2 Hz, 1H), 2.04 (d, *J* = 2.7 Hz, 3H), 1.99 (d, *J* = 1.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 151.6 (d, *J* = 6.3 Hz), 146.2, 145.1, 143.2 (d, *J* = 93.0 Hz), 133.1 (d, *J* = 10.7 Hz), 131.84 (d, *J* = 2.7 Hz), 131.75 (d, *J* = 9.8 Hz), 131.7 (d, *J* = 102.9 Hz), 128.2 (d, *J* = 12.1 Hz), 127.0, 123.7, 120.1 (d, *J* = 7.3 Hz), 23.3, 23.0. ³¹P NMR (162 MHz, CDCl₃) δ 28.2 (s). HRMS (ESI): ([M+H]⁺) Calcd for C₂₄H₂₃O₃NPS: 436.1131, Found: 436.1126. IR (film) ν 3049, 2953, 2913, 2849, 1592, 1575, 1506, 1431, 1335, 1188, 1178, 1113, 1088, 975, 853, 845, 768, 694 cm⁻¹.

(4-methyl-3-(thiophen-2-ylthio)penta-1,3-dien-2-yl)diphenylphosphine oxide (3ai)



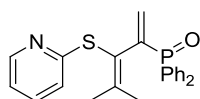
Dark brown liquid (74 mg, 93% yield). TLC (*R_f* = 0.32, PET/EA = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (dd, *J* = 11.7, 7.7 Hz, 4H), 7.54 (t, *J* = 7.3 Hz, 2H), 7.47-7.44 (m, 4H), 7.28 (d, *J* = 5.5 Hz, 1H), 6.92-6.89 (m, 1H), 6.78 (d, *J* = 3.4 Hz, 1H), 5.81 (d, *J* = 18.1 Hz, 1H), 5.55 (d, *J* = 39.0 Hz, 1H), 2.07 (d, *J* = 3.1 Hz, 3H), 1.67 (d, *J* = 2.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 145.4 (d, *J* = 6.4 Hz), 142.5 (d, *J* = 92.2 Hz), 134.6, 132.6 (d, *J* = 9.2 Hz), 132.2, 132.1 (d, *J* = 9.7 Hz), 131.9 (d, *J* = 102.4 Hz), 131.8 (d, *J* = 2.6 Hz), 128.1 (d, *J* = 12.1 Hz), 127.9 (d, *J* = 133.8 Hz), 124.8 (d, *J* = 7.6 Hz), 23.1, 22.4. ³¹P NMR (162 MHz, CDCl₃) δ 27.3 (s). HRMS (ESI): ([M+H]⁺) Calcd for C₂₂H₂₂O₂PS₂: 397.0844, Found: 397.0842. IR (film) ν 3058, 2910, 2846, 1436, 1367, 1200, 1174, 1116, 1099, 907, 725, 692 cm⁻¹.

(4-methyl-3-((2-methylfuran-3-yl)thio)penta-1,3-dien-2-yl)diphenylphosphine oxide (3aj)



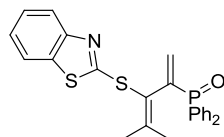
Brown liquid (55 mg, 70% yield). TLC (*R_f* = 0.31, PET/EA = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (dd, *J* = 11.3, 8.0 Hz, 4H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.1 Hz, 4H), 7.23 (s, 1H), 6.13 (s, 1H), 5.85 (d, *J* = 18.1 Hz, 1H), 5.52 (d, *J* = 39.1 Hz, 1H), 2.10 (s, 3H), 2.03 (d, *J* = 2.1 Hz, 3H), 1.65 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 153.5, 143.4 (d, *J* = 23.4 Hz), 142.9 (d, *J* = 61.7 Hz), 140.3, 132.3 (d, *J* = 9.4 Hz), 132.1 (d, *J* = 102.2 Hz), 132.0 (d, *J* = 9.6 Hz), 131.7 (d, *J* = 2.8 Hz), 128.1 (d, *J* = 12.0 Hz), 123.4, 114.4, 110.4, 23.1 (d, *J* = 1.8 Hz), 22.2, 11.9. ³¹P NMR (162 MHz, CDCl₃) δ 26.9 (s). HRMS (ESI): ([M+H]⁺) Calcd for C₂₃H₂₄O₂PS: 395.1229, Found: 395.1223. IR (film) ν 3051, 2954, 2922, 2850, 1747, 1723, 1437, 1377, 1160, 1116, 909, 726, 693 cm⁻¹.

(4-methyl-3-(pyridin-2-ylthio)penta-1,3-dien-2-yl)diphenylphosphine oxide (3ak)



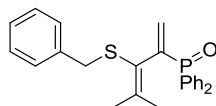
Brown solids, *m.p.*: 86.1-86.9°C (recrystallized from CH₂Cl₂/PET/EA = 1:1:1) (43 mg, 55% yield). TLC (*R_f* = 0.23, PET/EA = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, *J* = 4.4 Hz, 1H), 7.65 (dd, *J* = 11.6, 7.8 Hz, 4H), 7.49-7.34 (m, 7H), 6.95 (t, *J* = 7.5 Hz, 2H), 6.12 (d, *J* = 39.1 Hz, 1H), 5.90 (d, *J* = 18.3 Hz, 1H), 1.98 (s, 3H), 1.87 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.1, 149.8 (d, *J* = 6.4 Hz), 149.5, 143.5 (d, *J* = 92.4 Hz), 136.1, 133.7 (d, *J* = 9.7 Hz), 132.0 (d, *J* = 9.8 Hz), 131.8 (d, *J* = 102.7 Hz), 131.7 (d, *J* = 2.7 Hz), 128.0 (d, *J* = 12.1 Hz), 122.2, 120.1 (d, *J* = 7.9 Hz), 119.6, 23.2, 22.8. ³¹P NMR (162 MHz, CDCl₃) δ 28.6 (s). HRMS (ESI): ([M+H]⁺) Calcd for C₂₃H₂₃ONPS: 392.1232, Found: 392.1228. IR (film) ν 3056, 2910, 1574, 1437, 1417, 1173, 1118, 1100, 908, 725, 693 cm⁻¹.

(3-(benzo[d]thiazol-2-ylthio)-4-methylpenta-1,3-dien-2-yl)diphenylphosphine oxide (3al)



Yellow solids, *m.p.*: 131.6-132.9°C (recrystallized from CH₂Cl₂/PET/EA = 1:1:1) (61 mg, 68% yield). TLC (*R_f* = 0.26, PET/EA = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.71 (dd, *J* = 11.9, 7.7 Hz, 5H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.42-7.36 (m, 5H), 7.29 (t, *J* = 7.6 Hz, 1H), 6.32 (d, *J* = 38.8 Hz, 1H), 5.94 (d, *J* = 18.2 Hz, 1H), 2.09 (d, *J* = 2.8 Hz, 3H), 1.91 (d, *J* = 1.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.4, 154.0, 153.1 (d, *J* = 6.3 Hz), 143.4 (d, *J* = 92.9 Hz), 135.4, 134.1 (d, *J* = 9.7 Hz), 132.1, 132.0, 131.9, 130.9, 128.3 (d, *J* = 12.1 Hz), 126.0, 124.2, 121.3 (d, *J* = 92.8 Hz), 119.8 (d, *J* = 8.0 Hz), 23.4, 23.3. ³¹P NMR (162 MHz, CDCl₃) δ 28.4 (s). HRMS (ESI): ([M+H]⁺) Calcd for C₂₅H₂₃ONPS₂: 448.0953, Found: 448.0950. IR (film) ν 3054, 2954, 2915, 2849, 1454, 1424, 1183, 1114, 995, 751, 725, 691 cm⁻¹.

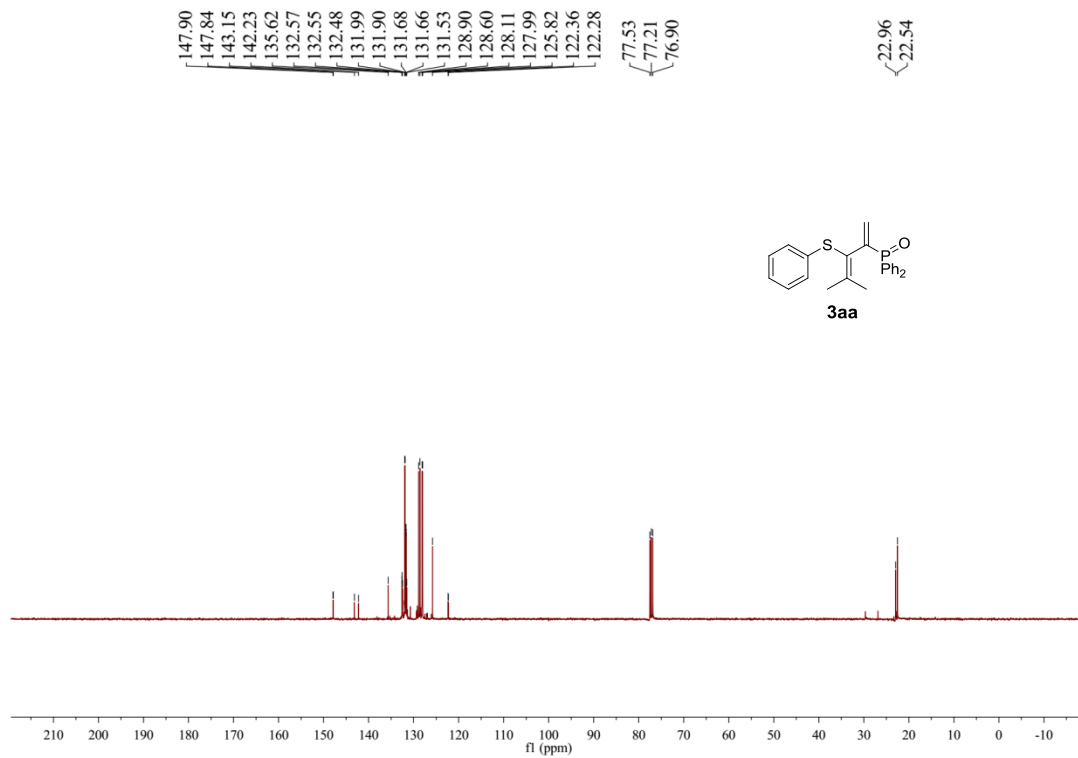
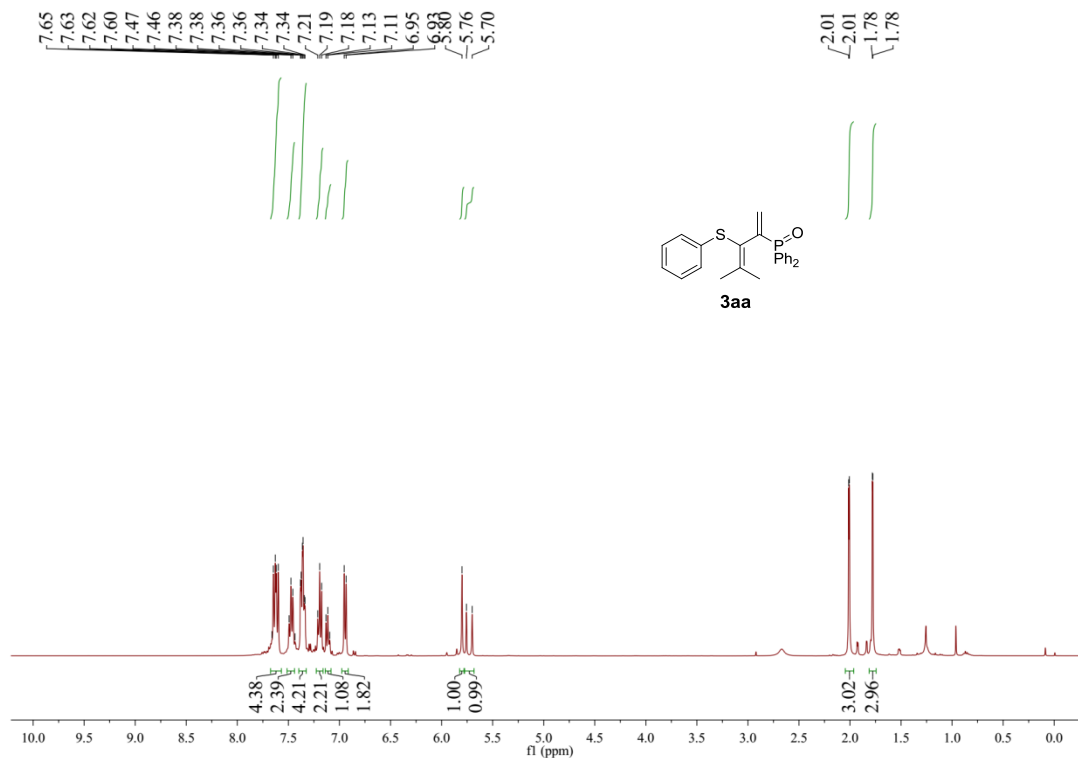
(3-(benzylthio)-4-methylpenta-1,3-dien-2-yl)diphenylphosphine oxide (3am)

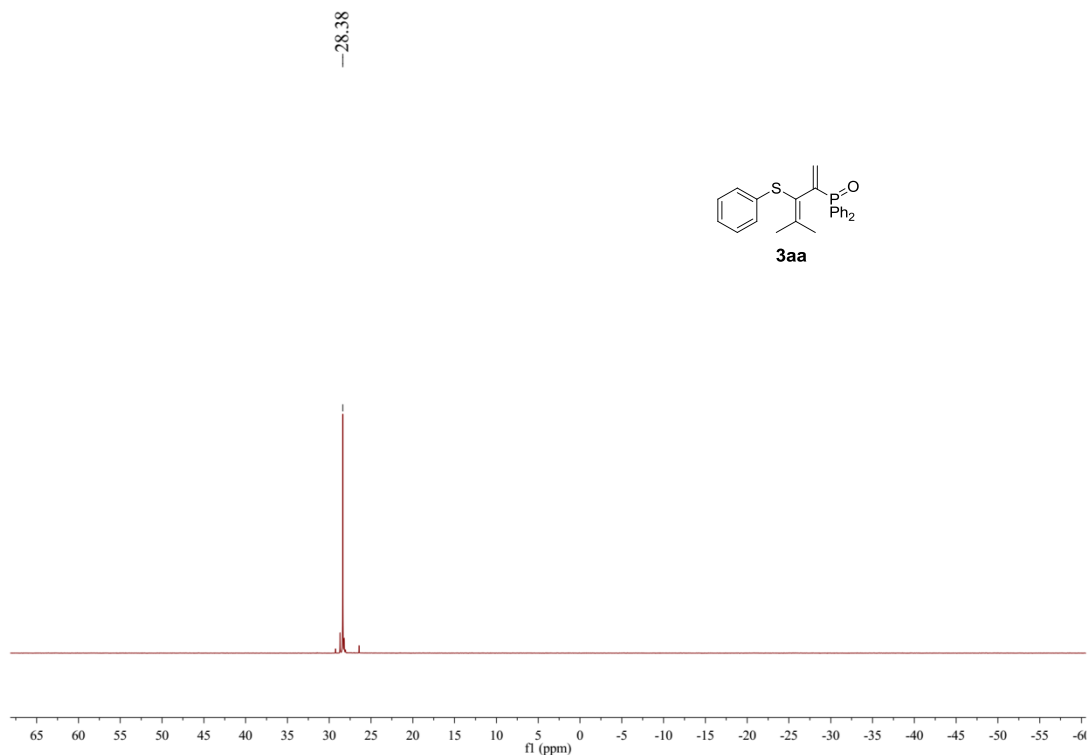


Yellow liquid (42 mg, 52% yield). TLC (*R_f* = 0.29, PET/EA = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.86 (dd, *J* = 11.6, 7.5 Hz, 4H), 7.54 (d, *J* = 6.8 Hz, 2H), 7.47 (td, *J* = 7.6, 2.6 Hz, 4H), 7.28-7.18 (m, 4H), 7.13 (d, *J* = 7.0 Hz, 2H), 6.19 (d, *J* = 18.0 Hz, 1H), 5.74 (d, *J* = 38.6 Hz, 1H), 3.58 (s, 2H), 1.76 (d, *J* = 3.1 Hz, 3H), 1.60 (d, *J* = 2.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.0 (d, *J* = 41.0 Hz), 143.9, 143.3, 138.1, 132.3 (d, *J* = 9.3 Hz), 132.1 (d, *J* = 102.7 Hz), 131.9 (d, *J* = 9.5 Hz), 131.7 (d, *J* = 2.7 Hz), 128.9, 128.3, 128.1 (d, *J* = 12.0 Hz), 126.8, 123.8 (d, *J* = 7.7 Hz), 37.9, 22.8, 22.0. ³¹P NMR (162 MHz, CDCl₃) δ 26.3 (s). HRMS (ESI): ([M+H]⁺) Calcd for C₂₅H₂₆OPS: 405.1442, Found: 405.1427. IR (film) ν 3059, 2932, 2851, 1484, 1453, 1436, 1200, 1173, 1116, 909, 725, 693 cm⁻¹.

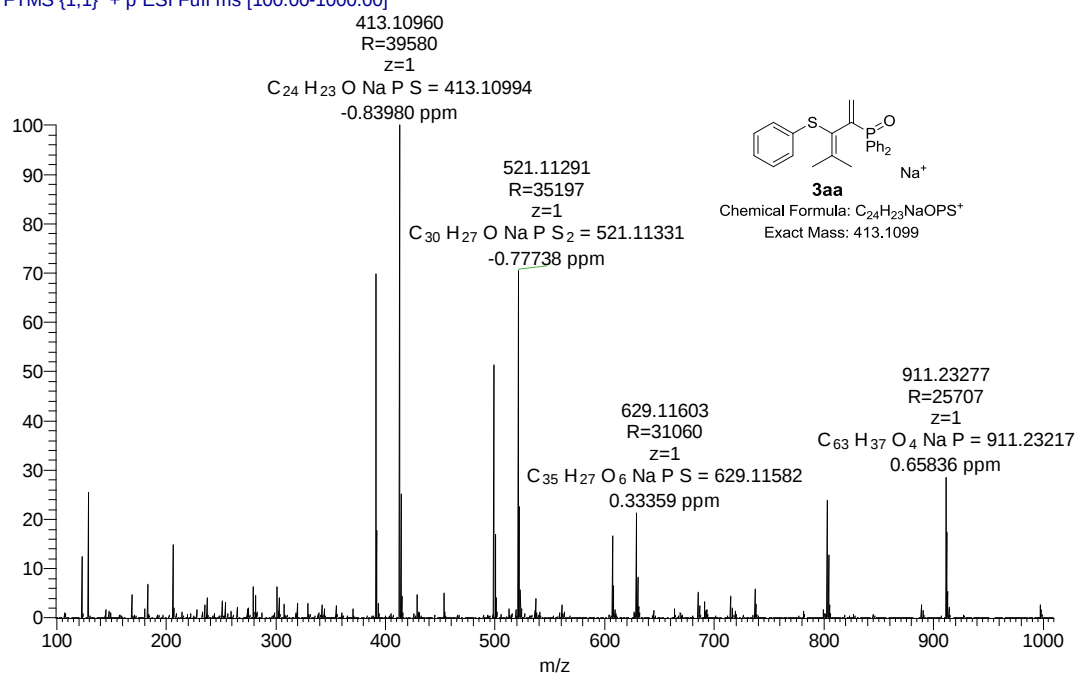
10. ^1H -NMR, ^{13}C -NMR, ^{31}P -NMR and HRMS spectra

3aa

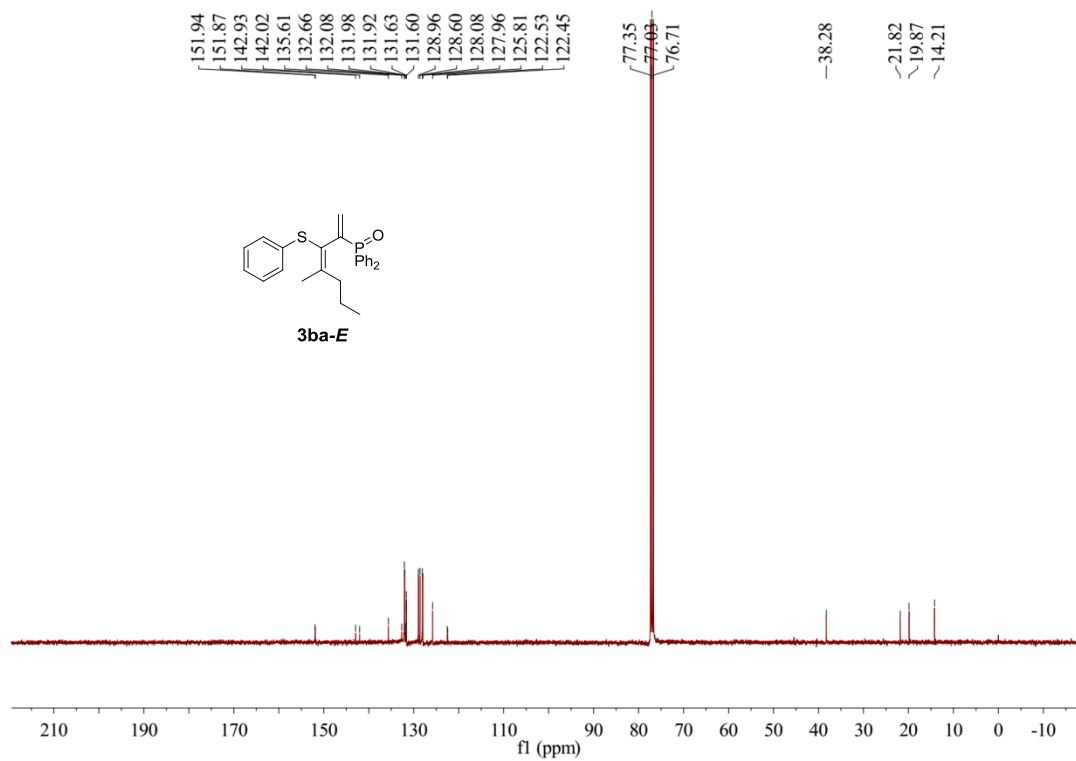
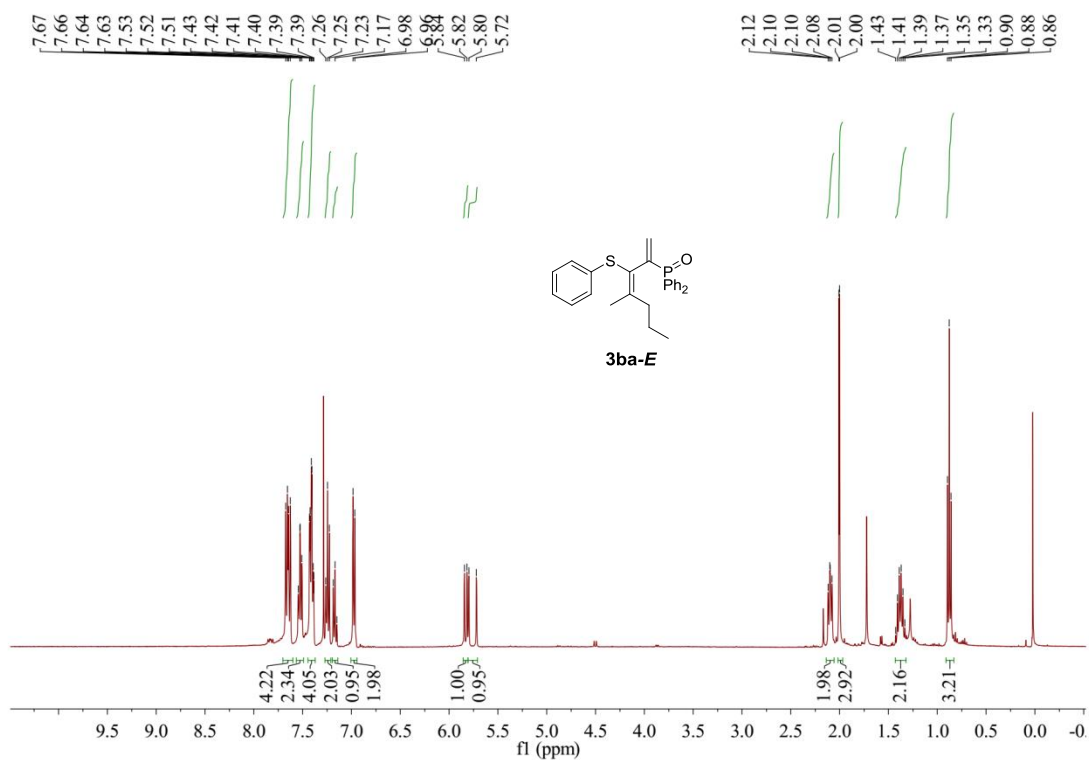


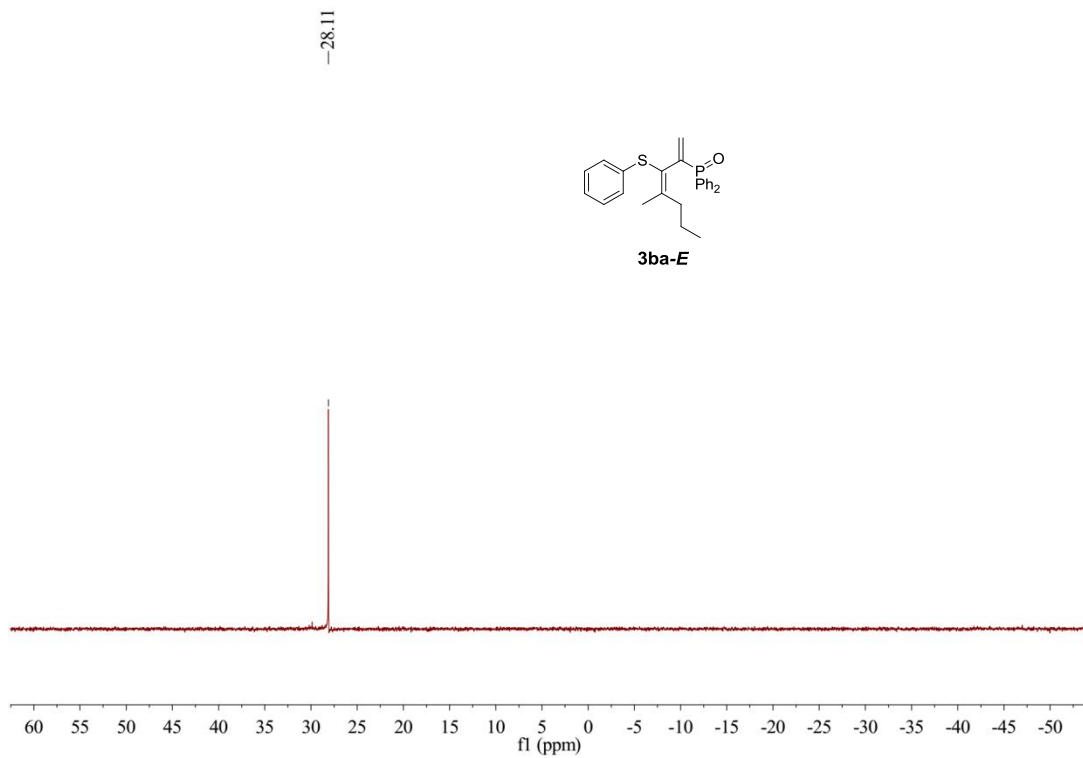


20160826-23 #55-59 RT: 0.58-0.62 AV: 5 NL: 7.26E4
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

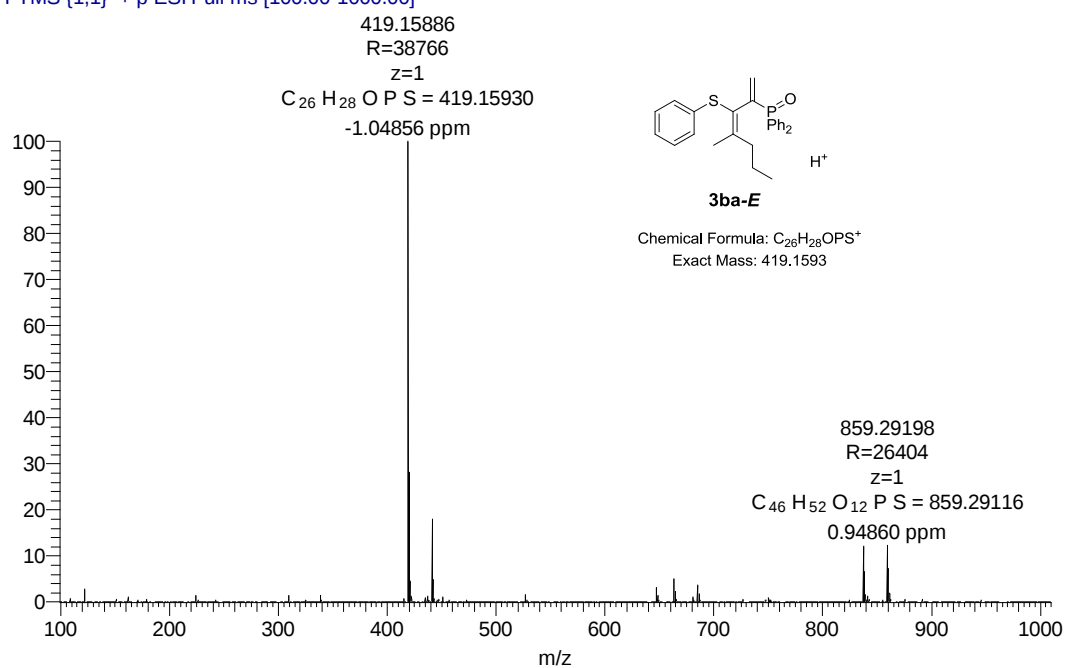


3ba-E

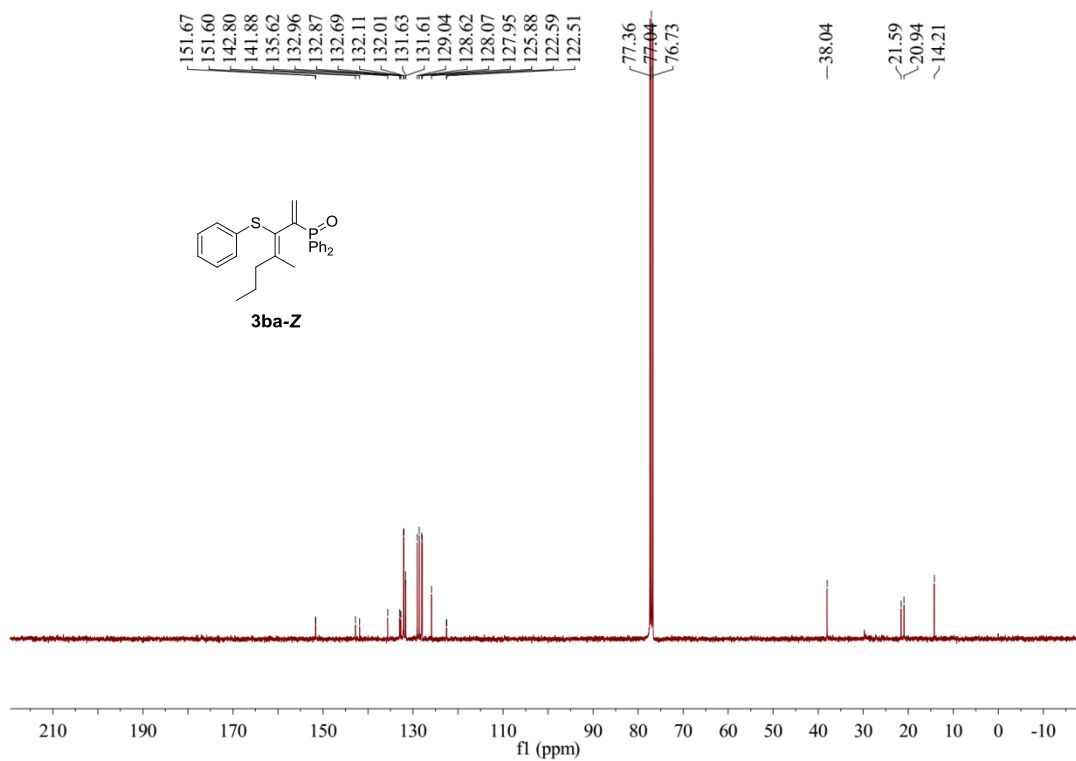
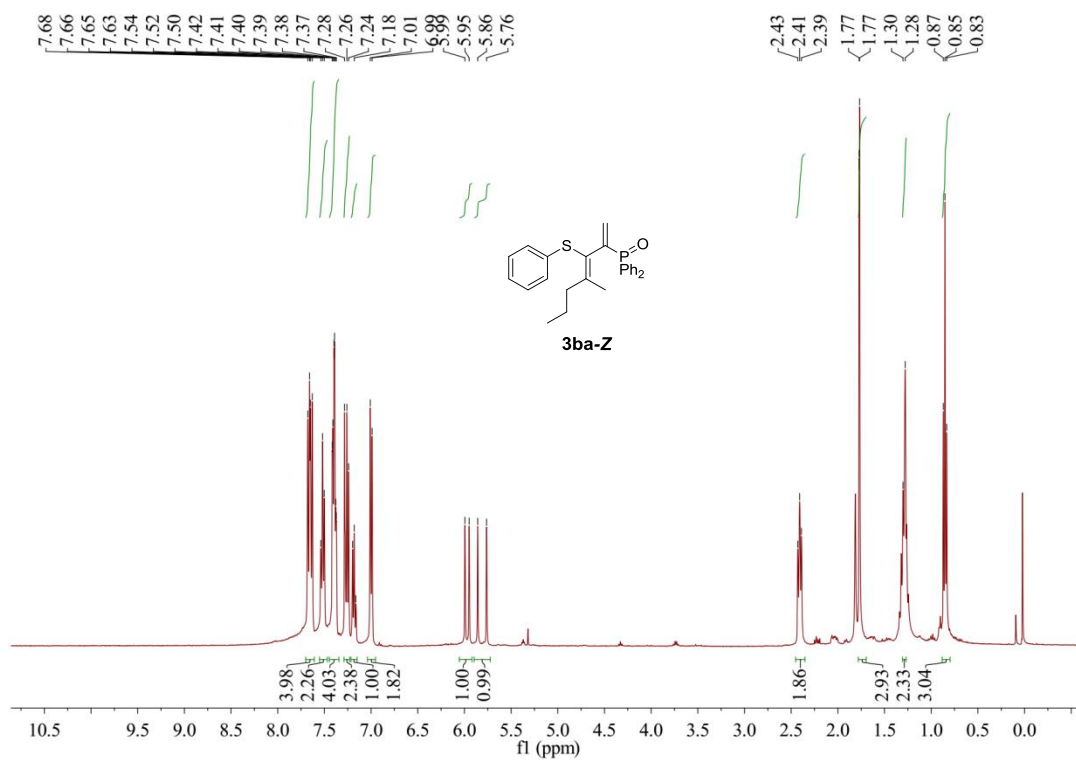


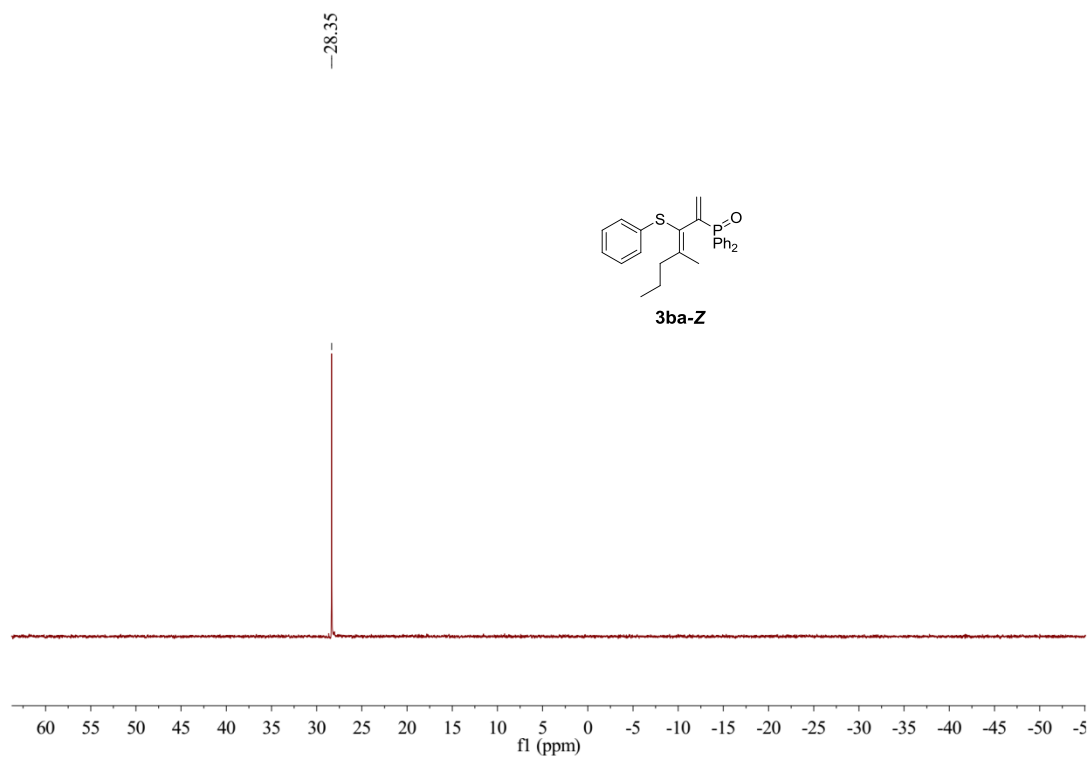


20170117-7 #39-41 RT: 0.40-0.43 AV: 3 NL: 5.72E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

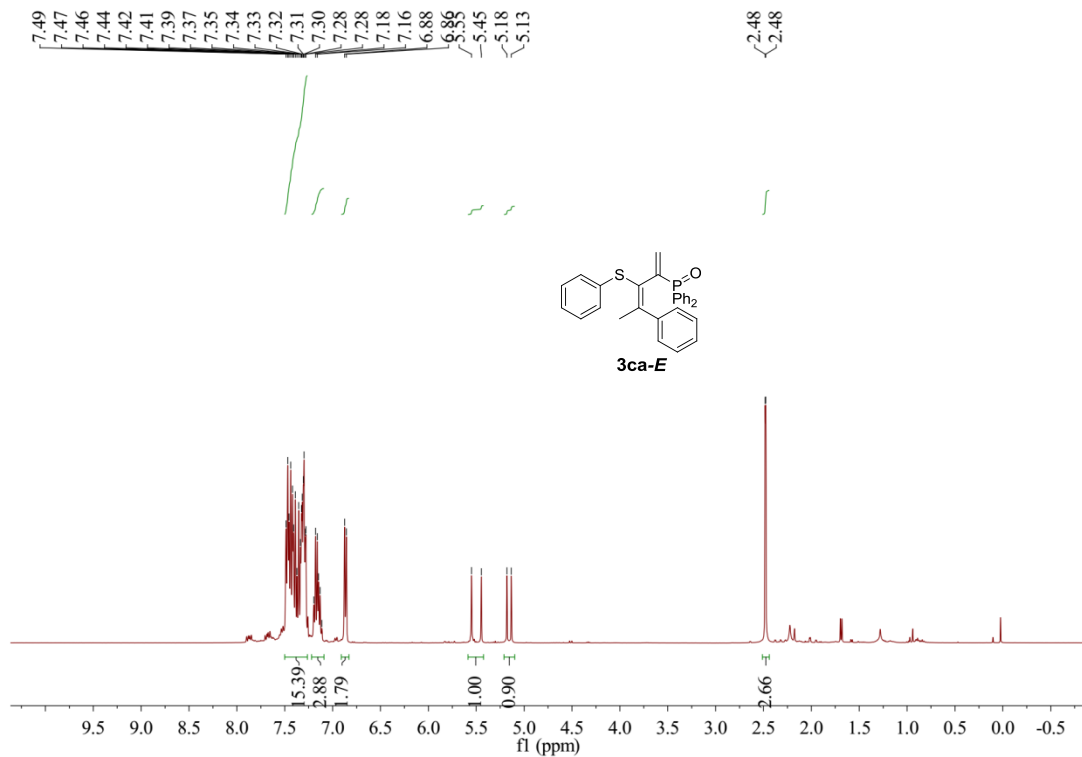


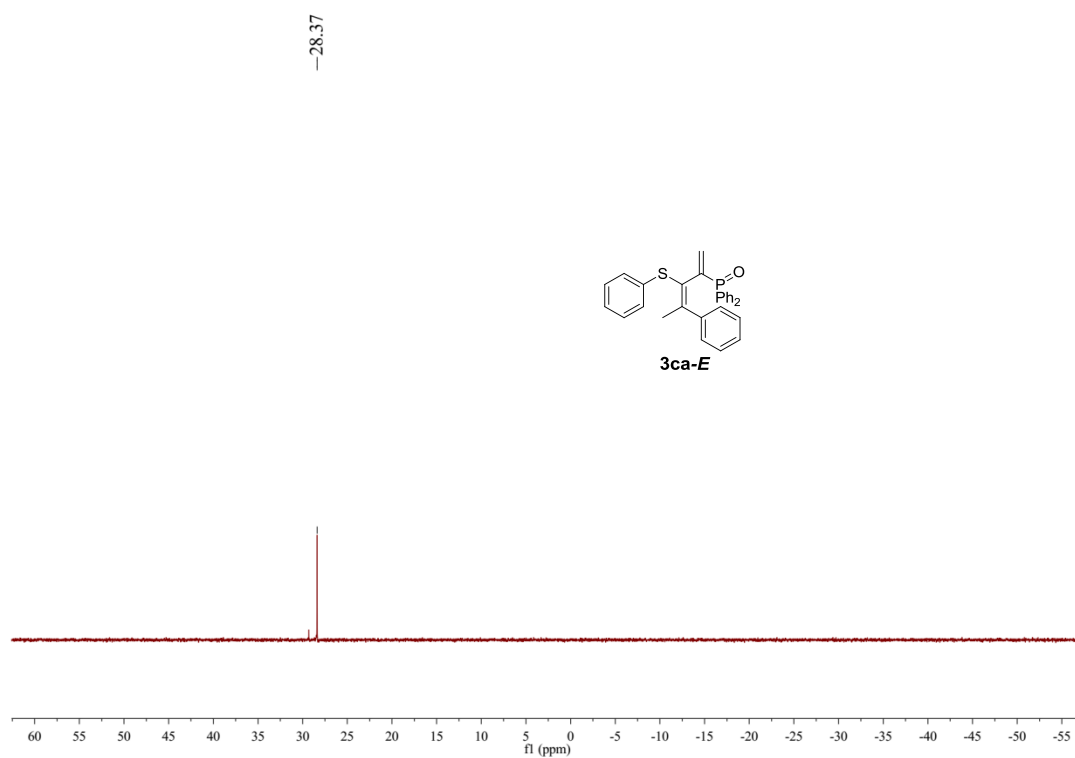
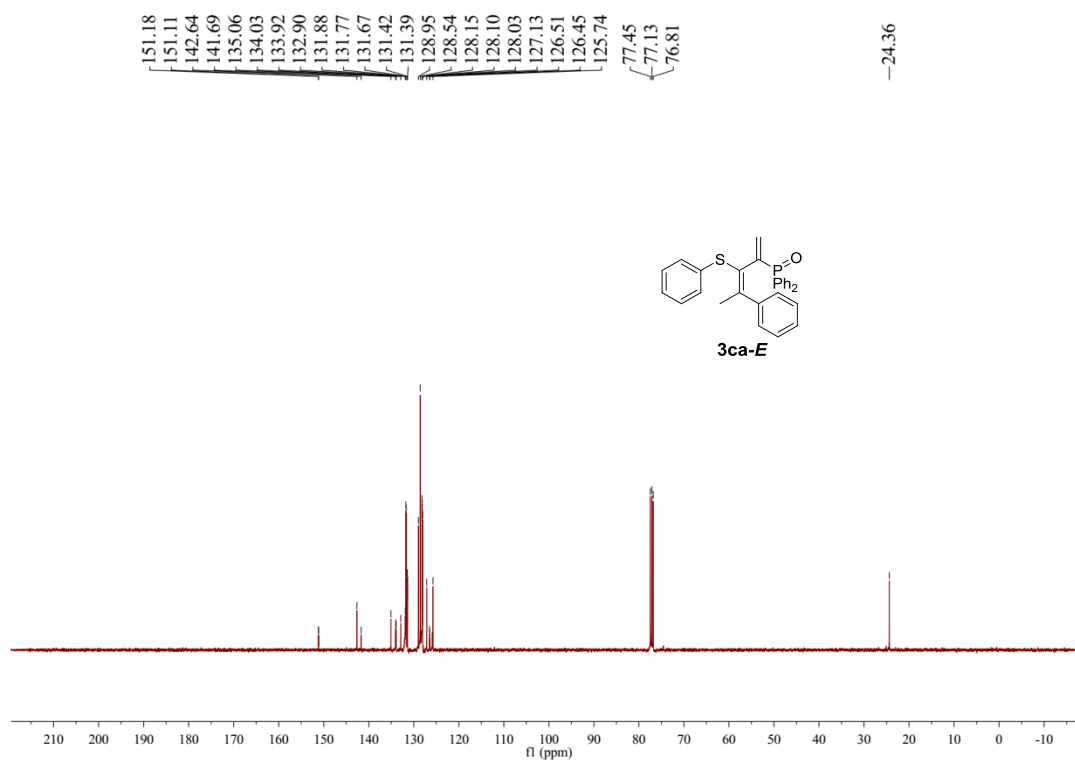
3ba-Z



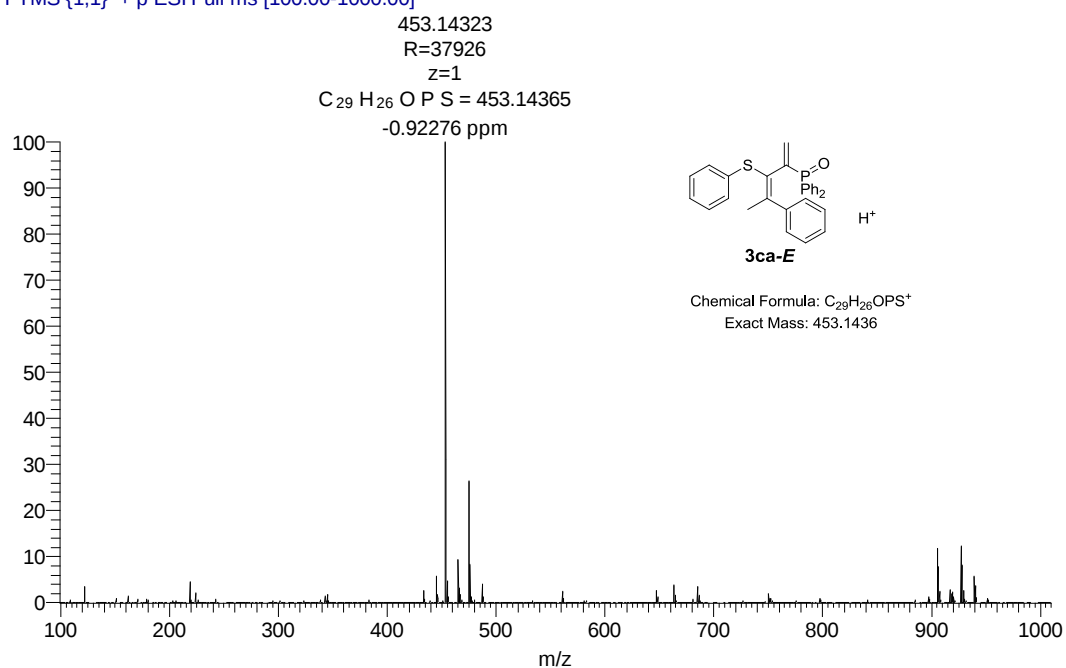


3ca-E

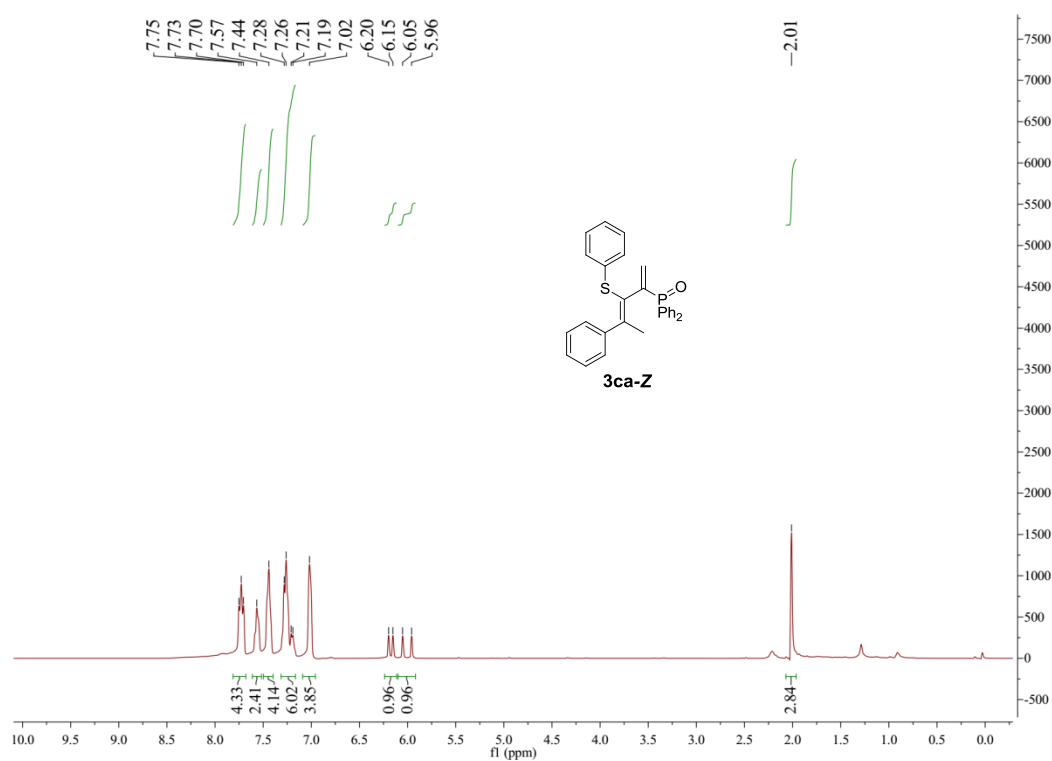


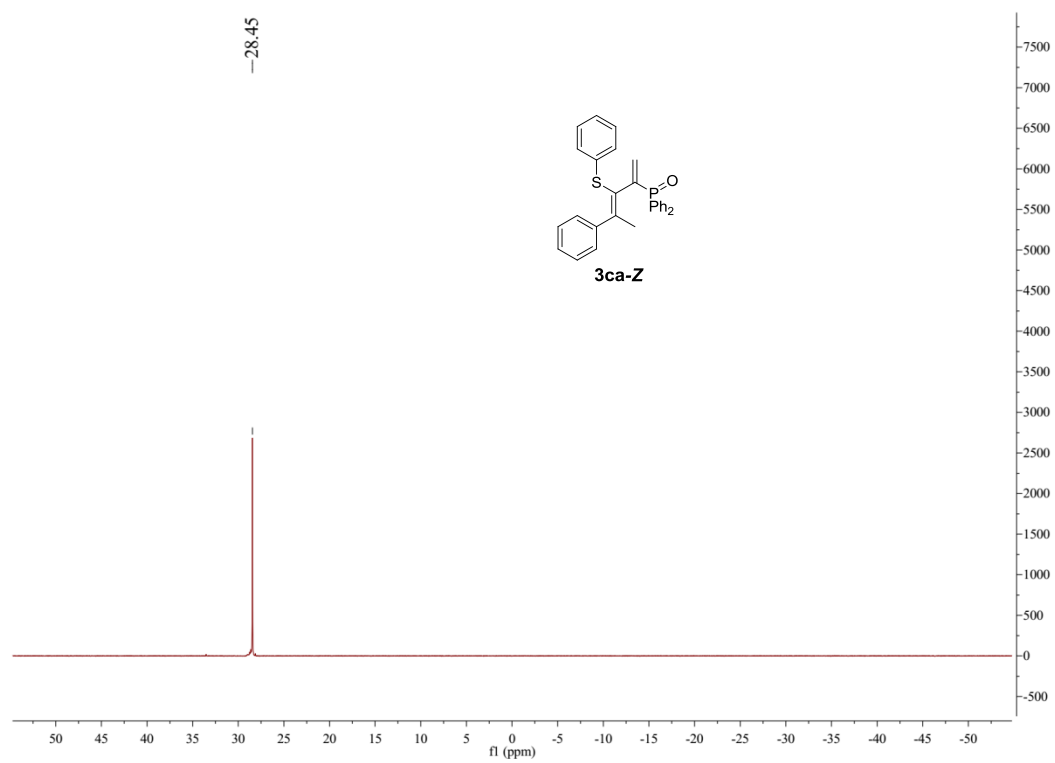
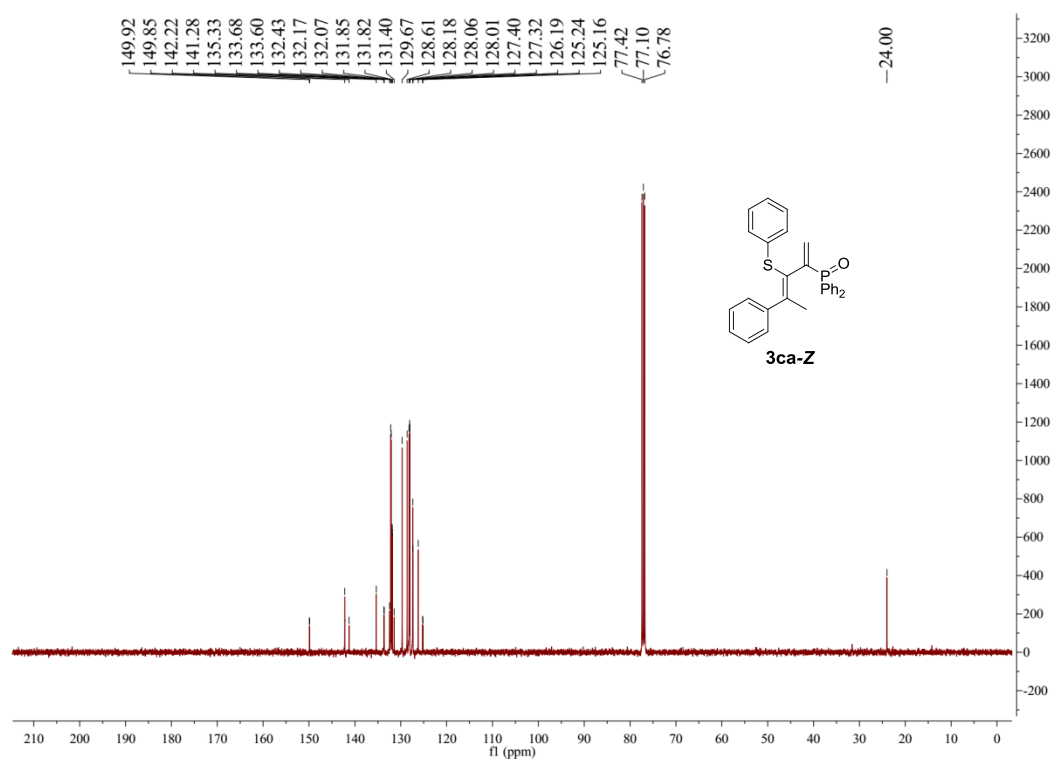


20170117-26 #54-55 RT: 0.58-0.59 AV: 2 NL: 3.33E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

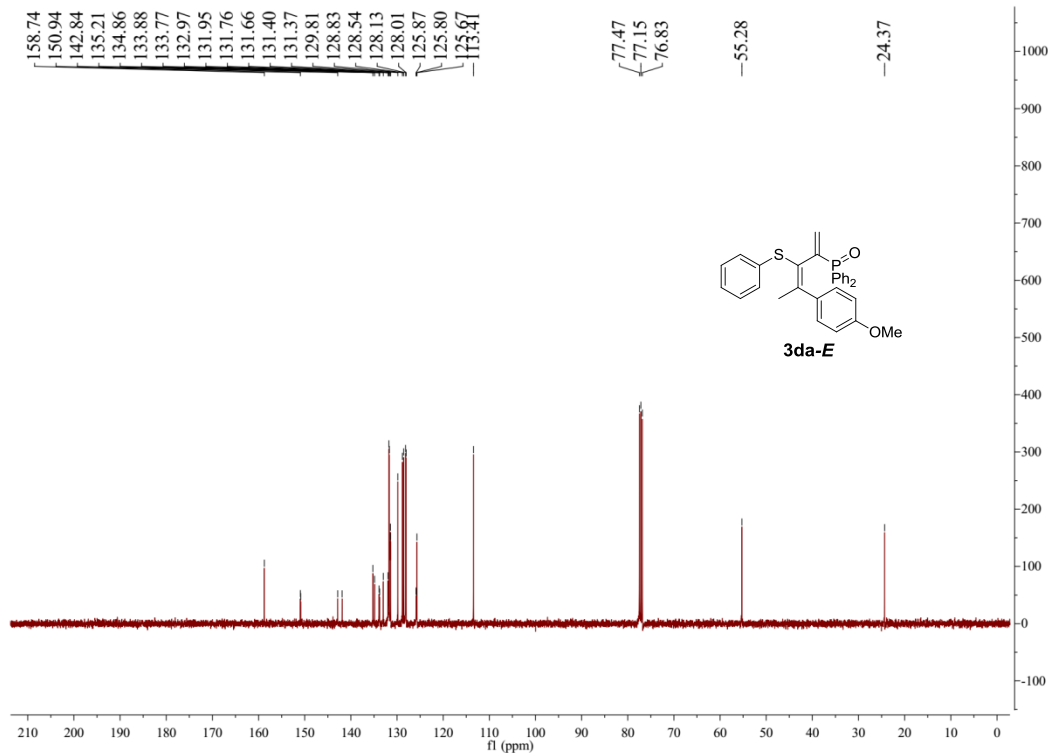
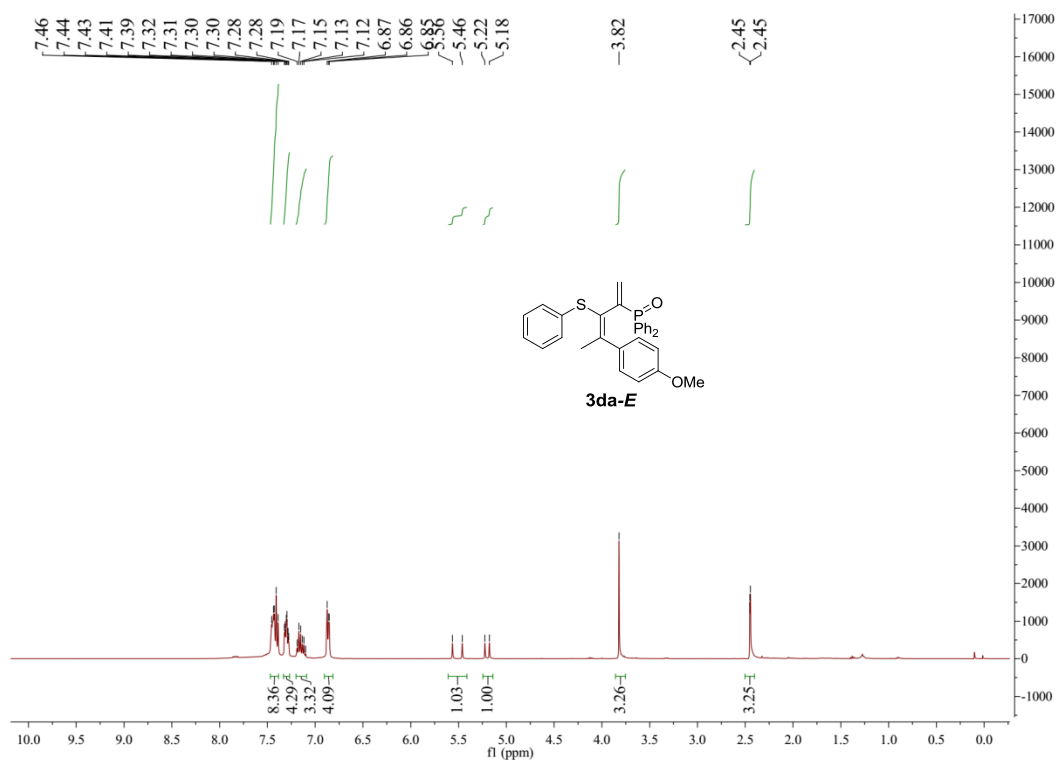


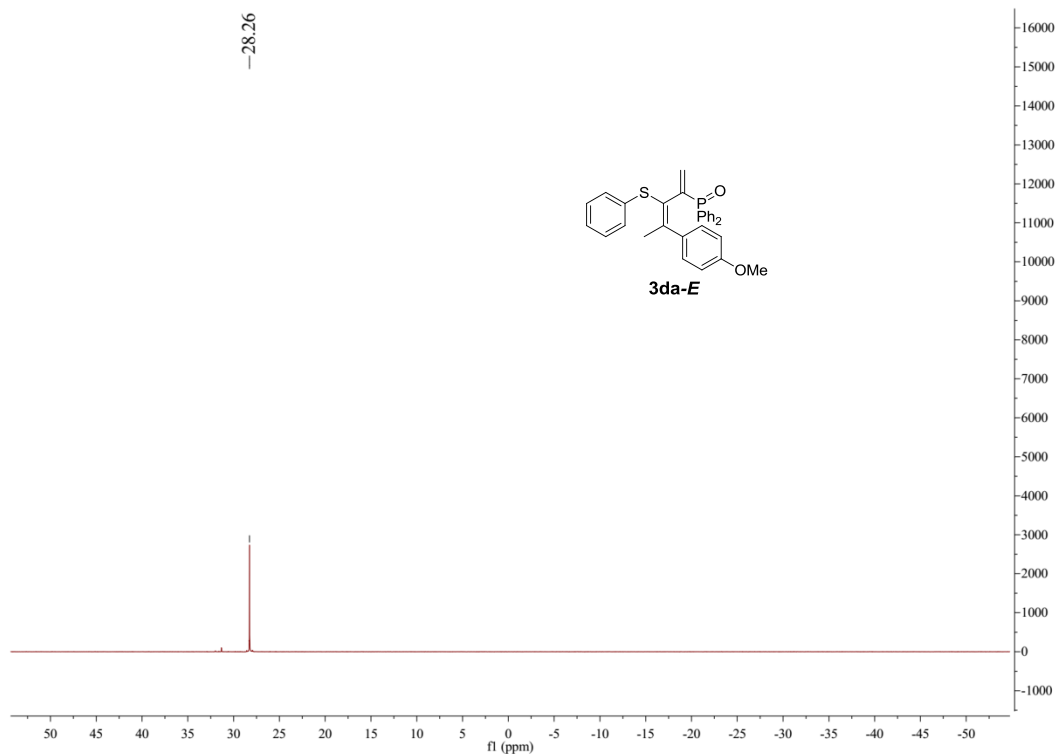
3ca-Z



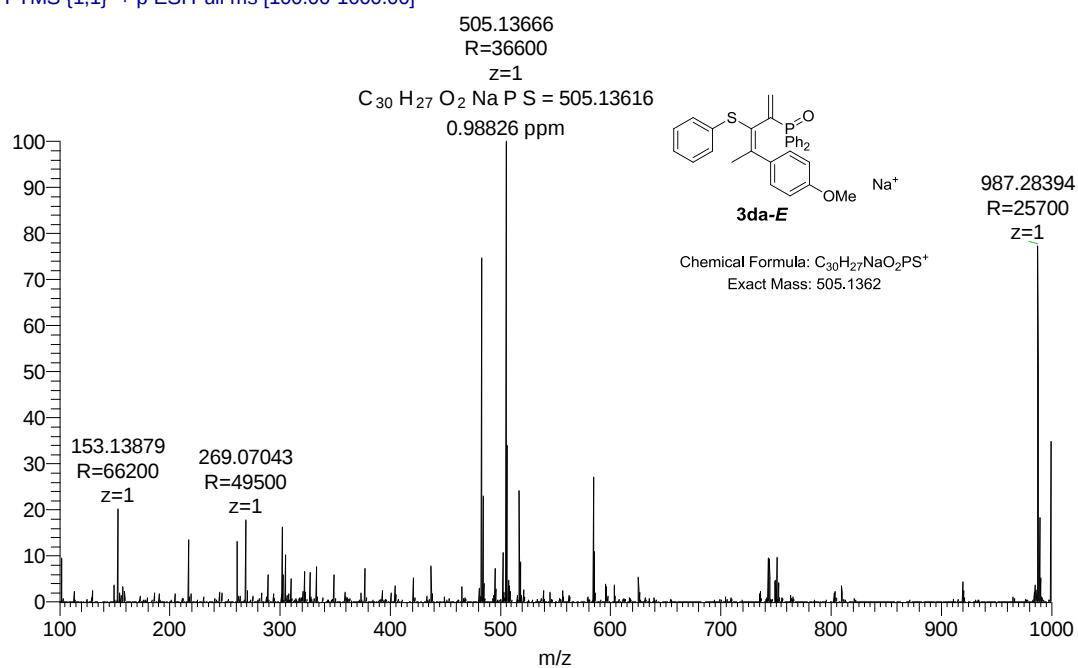


3da-E

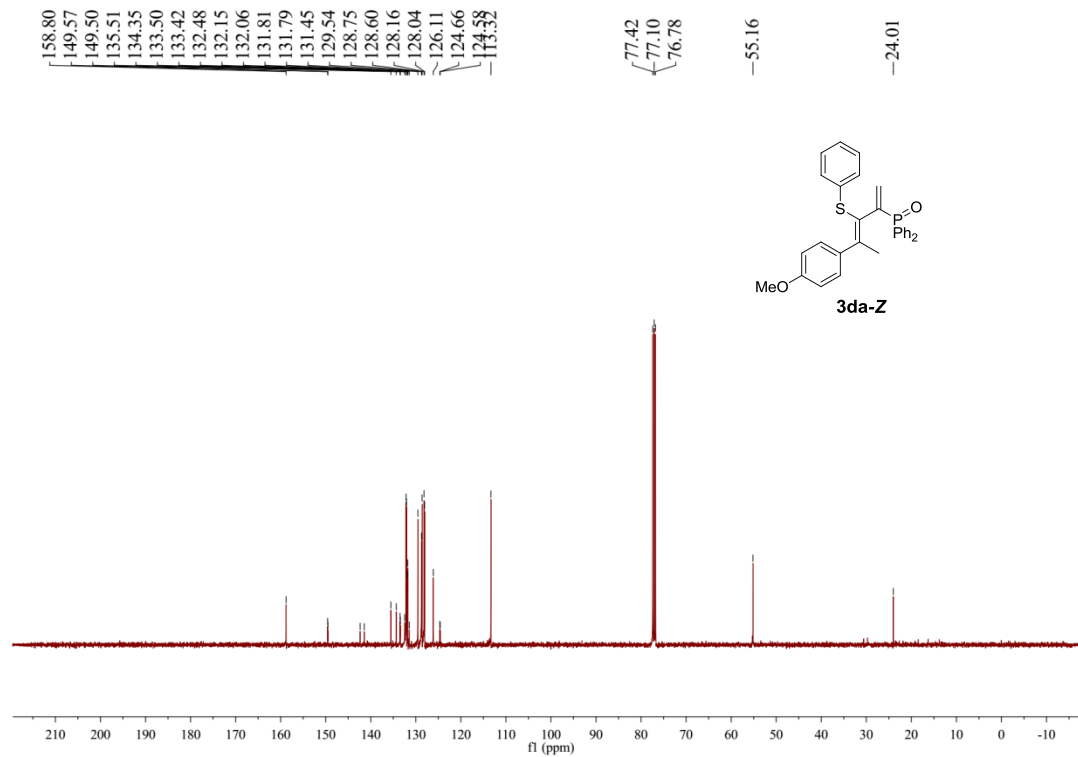
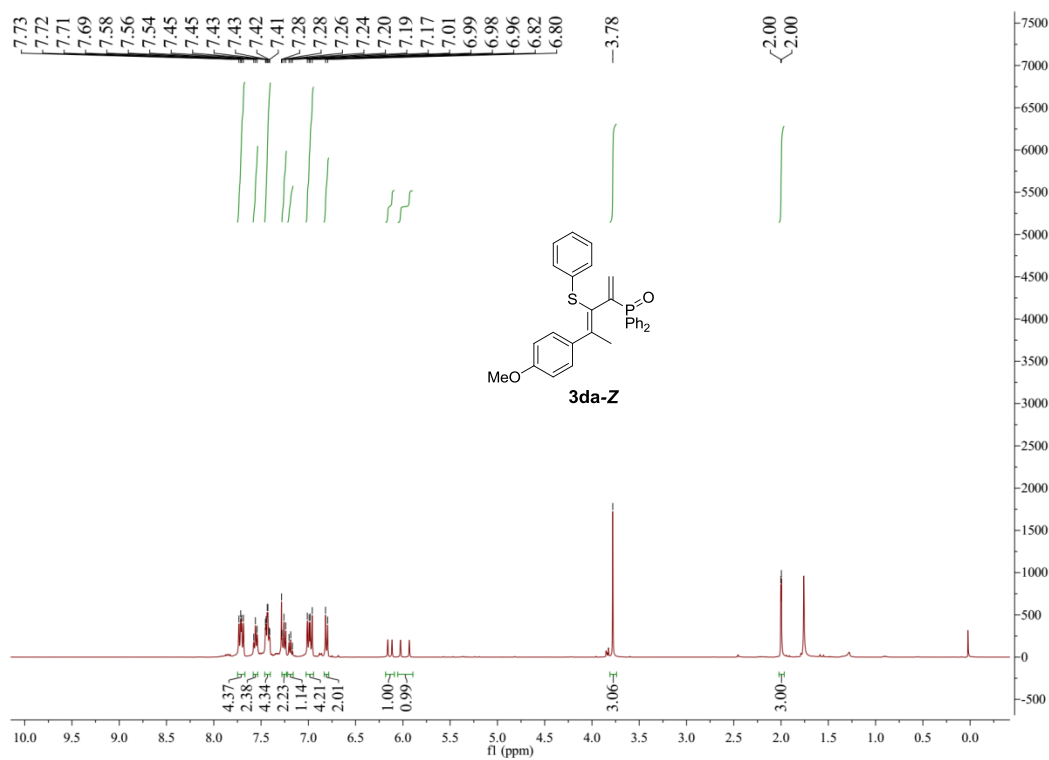


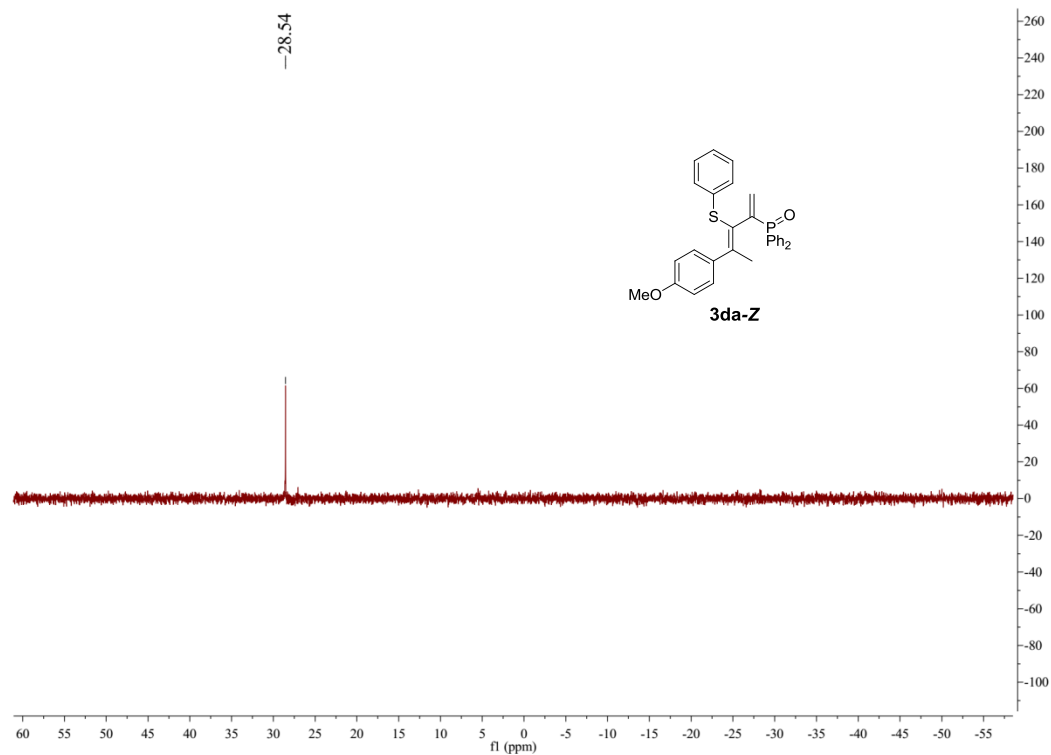


16 #20 RT: 0.21 AV: 1 NL: 4.56E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

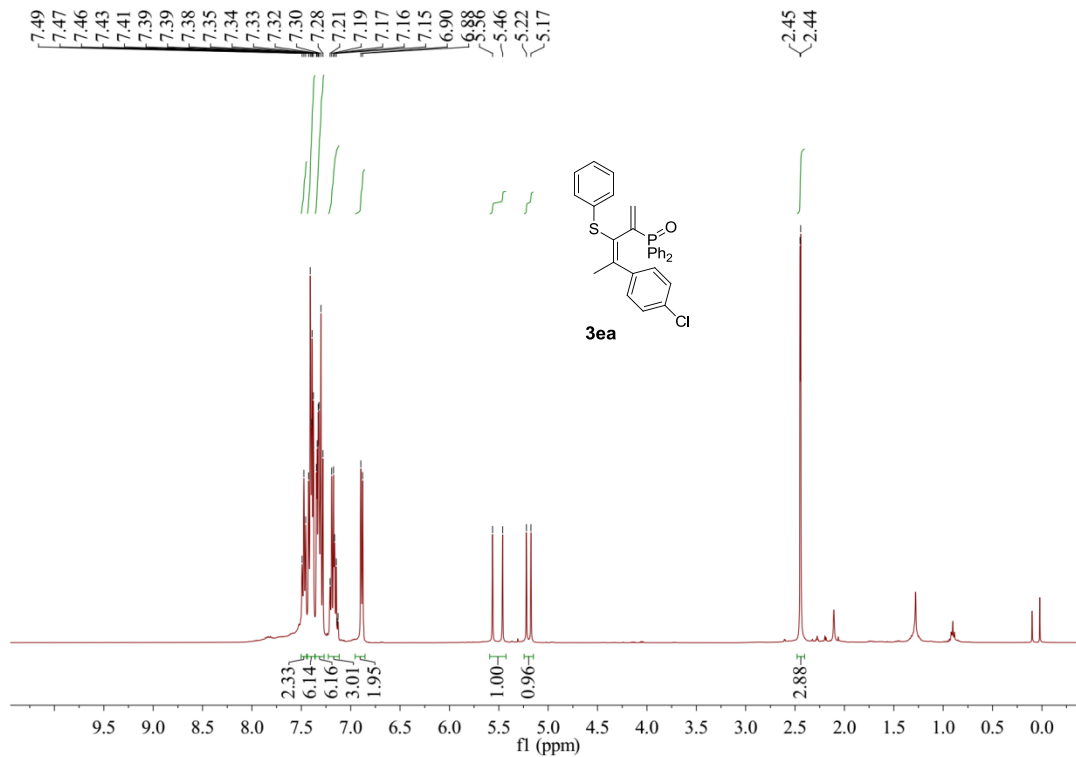


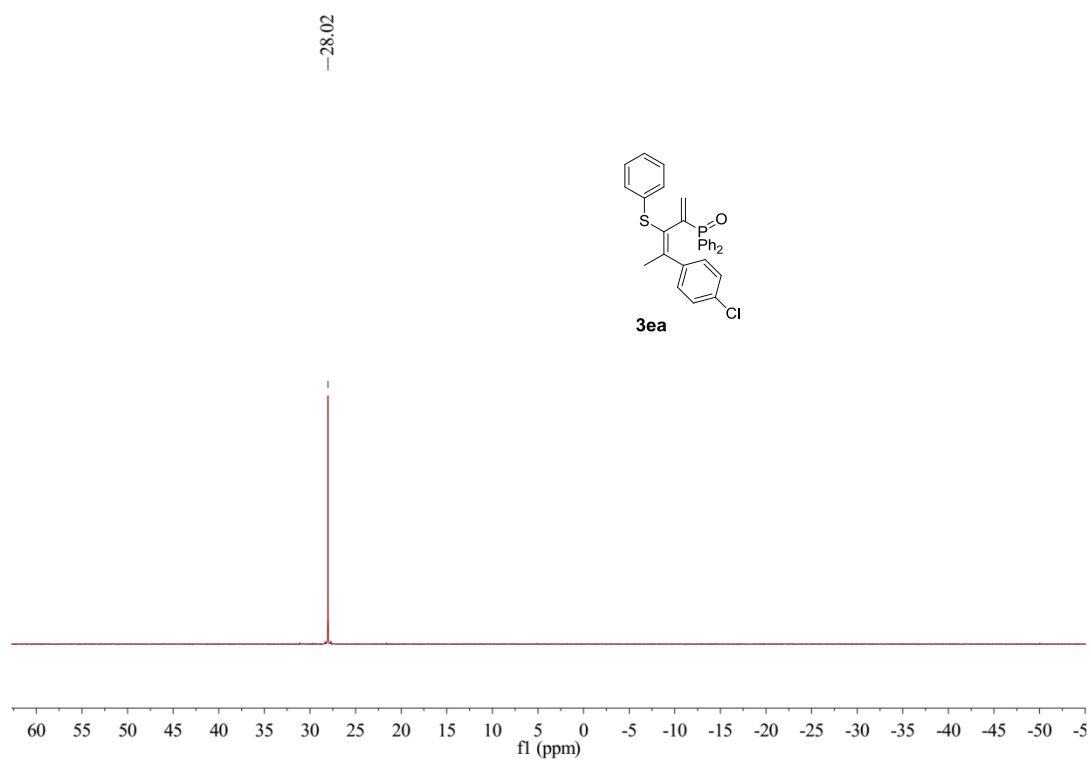
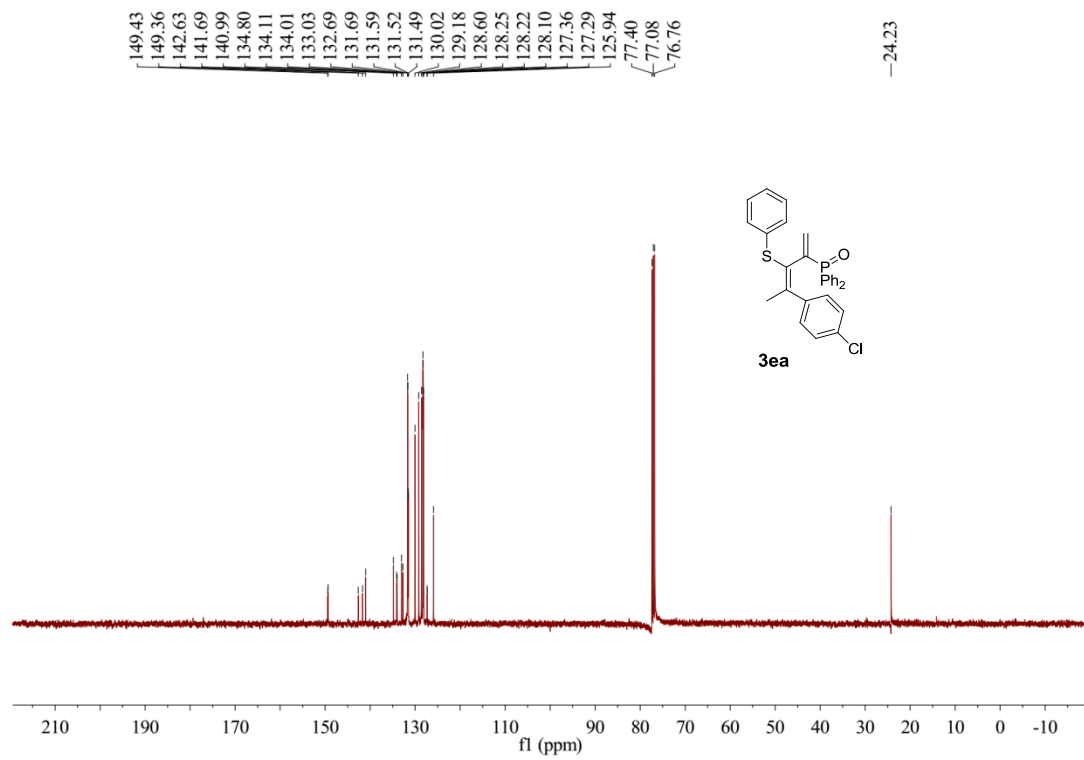
3da-Z



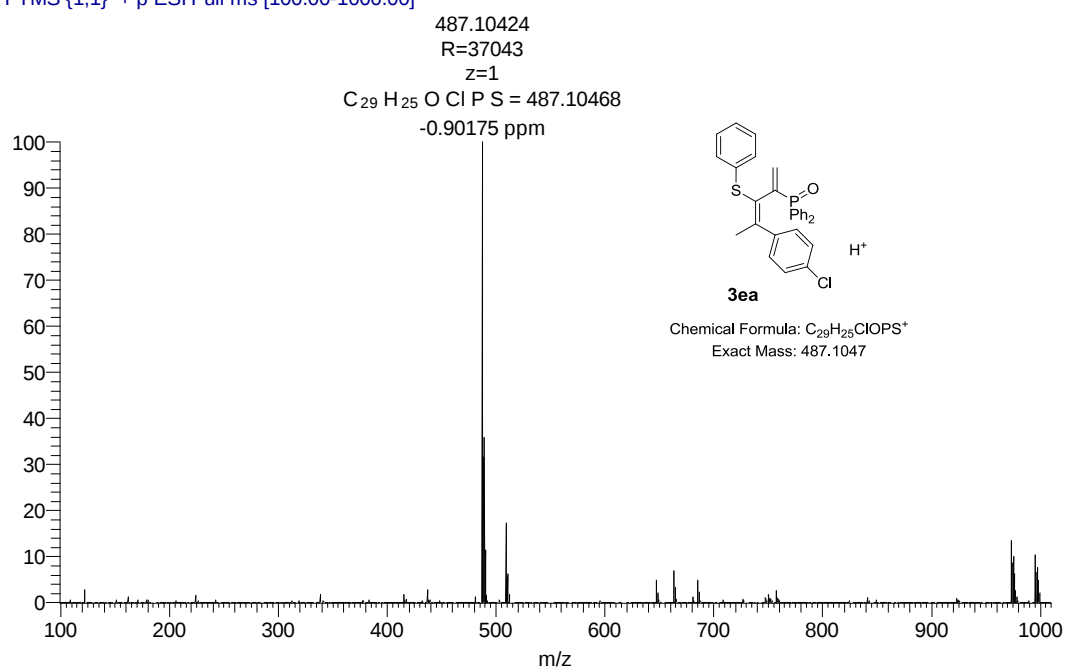


3ea (only E-)

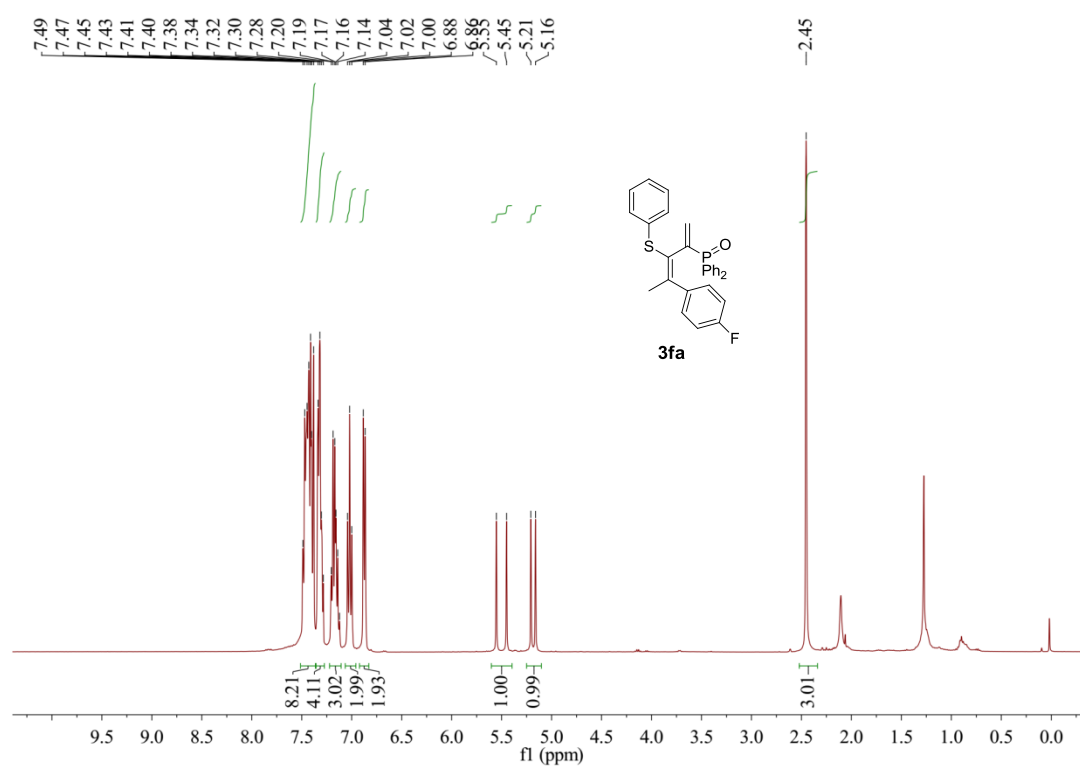


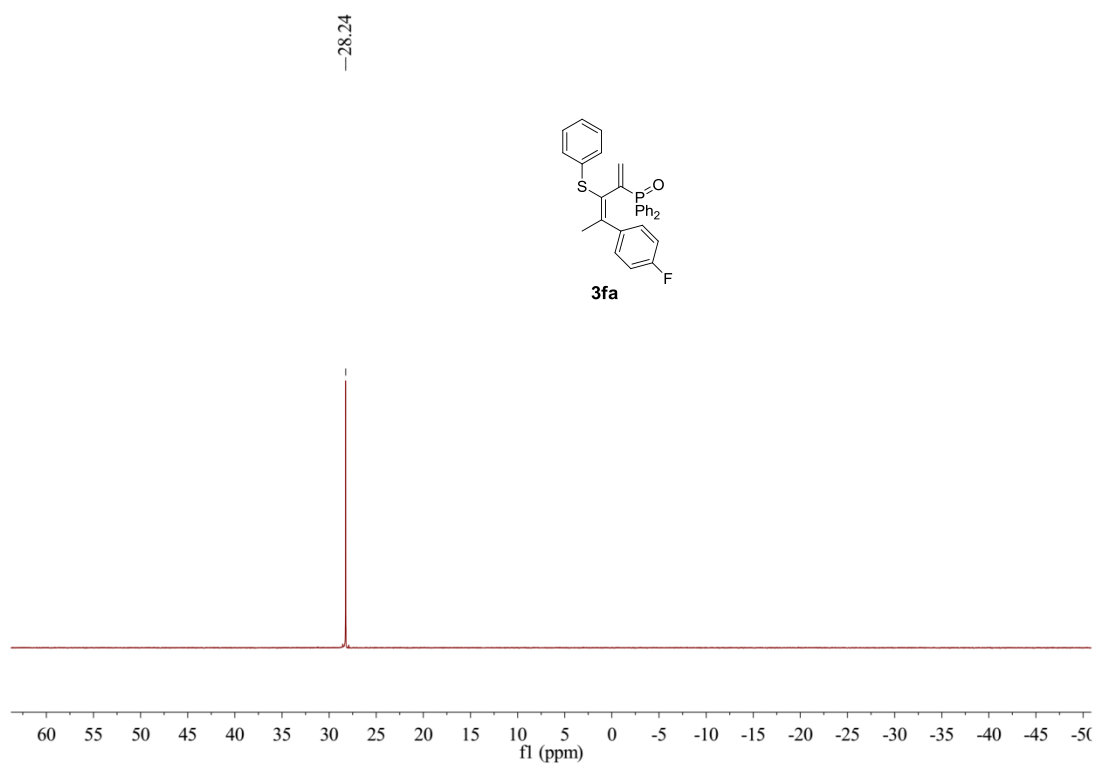
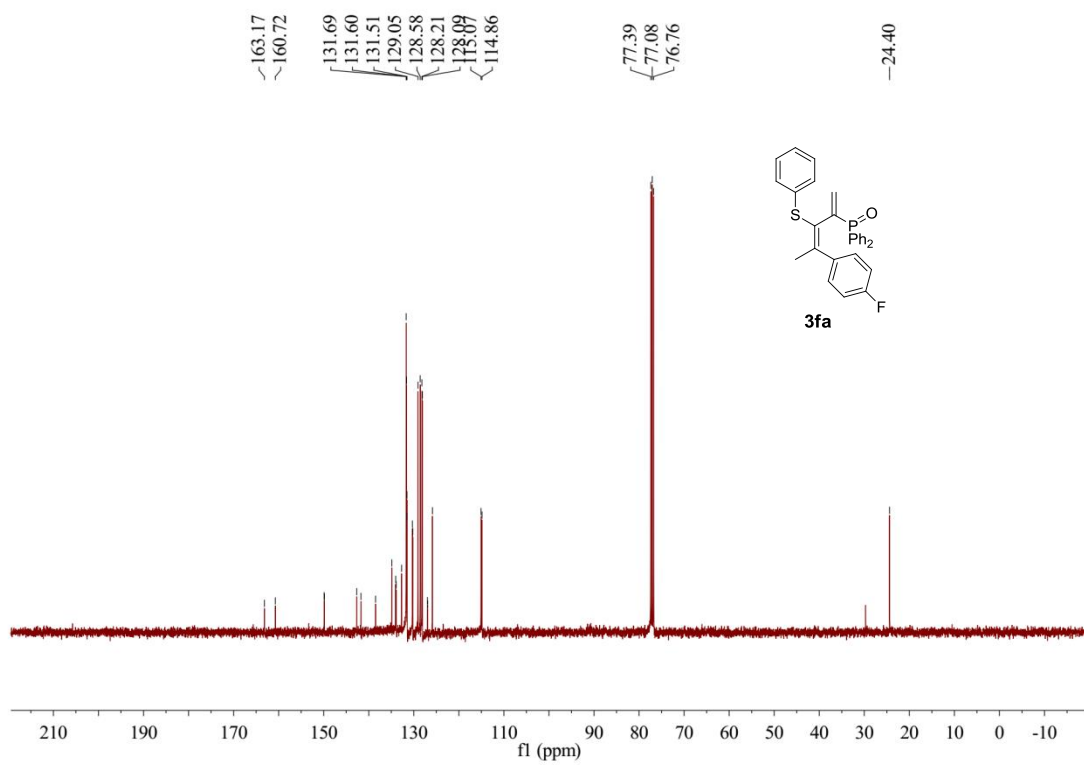


20170117-25 #35-36 RT: 0.38-0.39 AV: 2 NL: 3.84E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

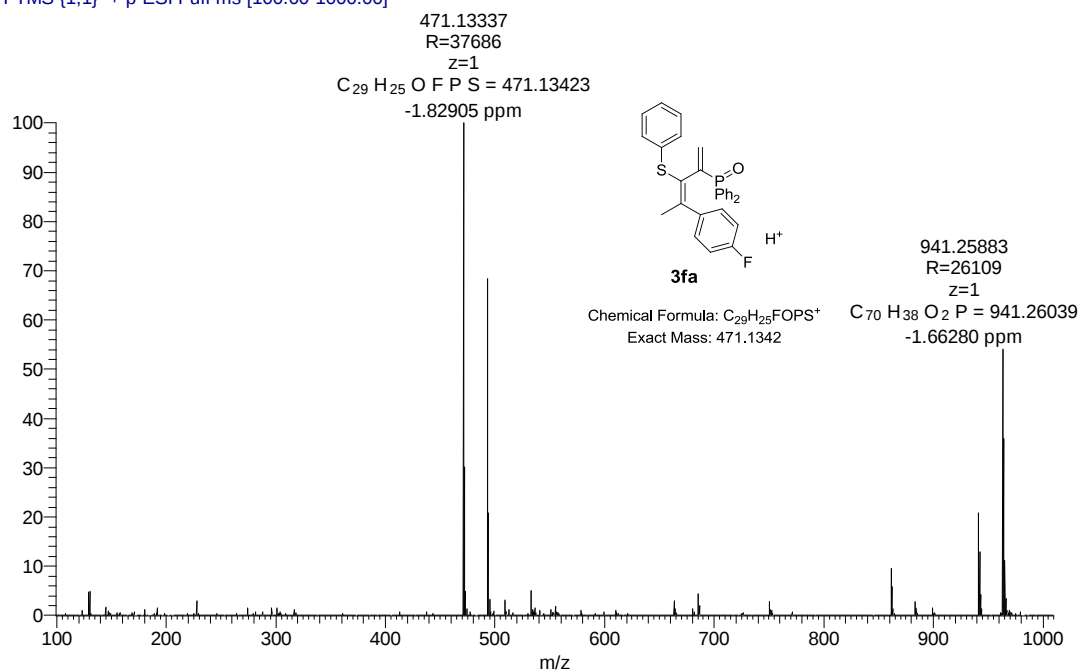


3fa (only E-)

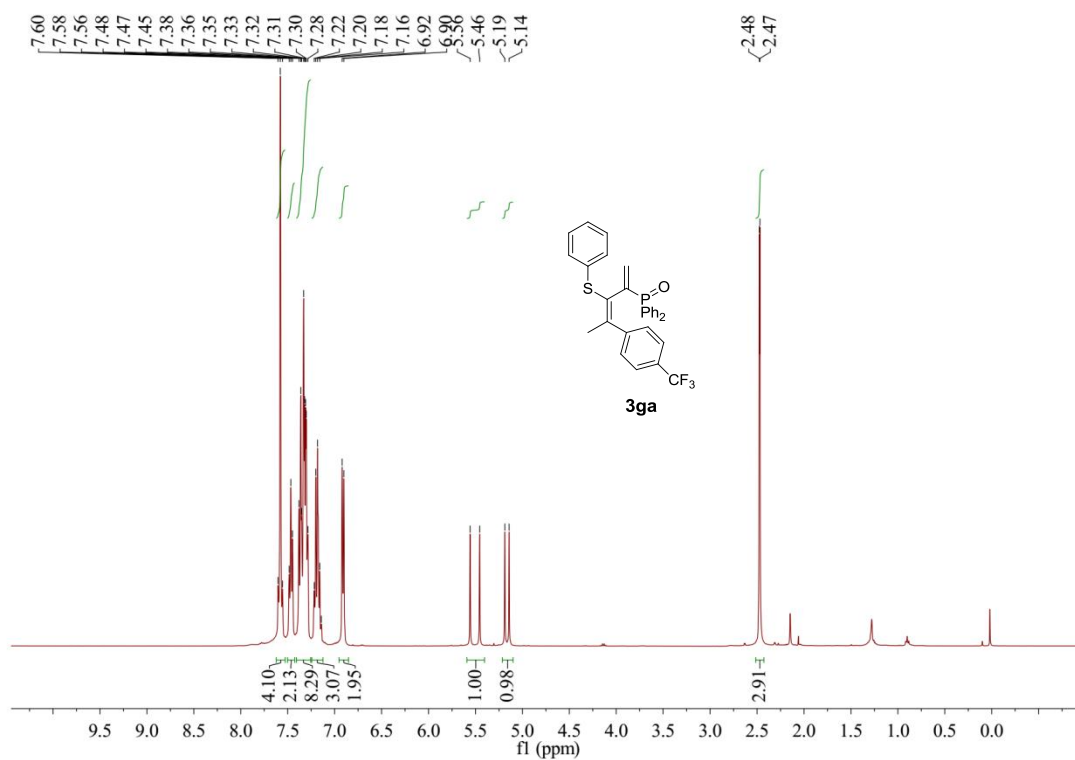


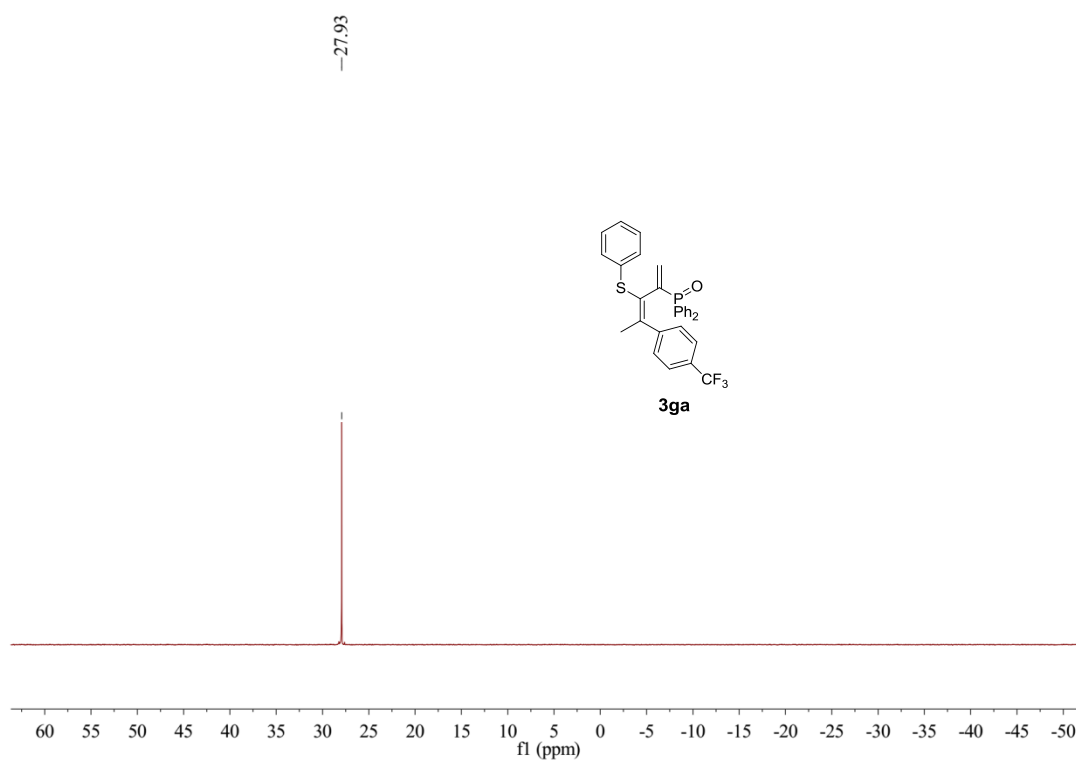
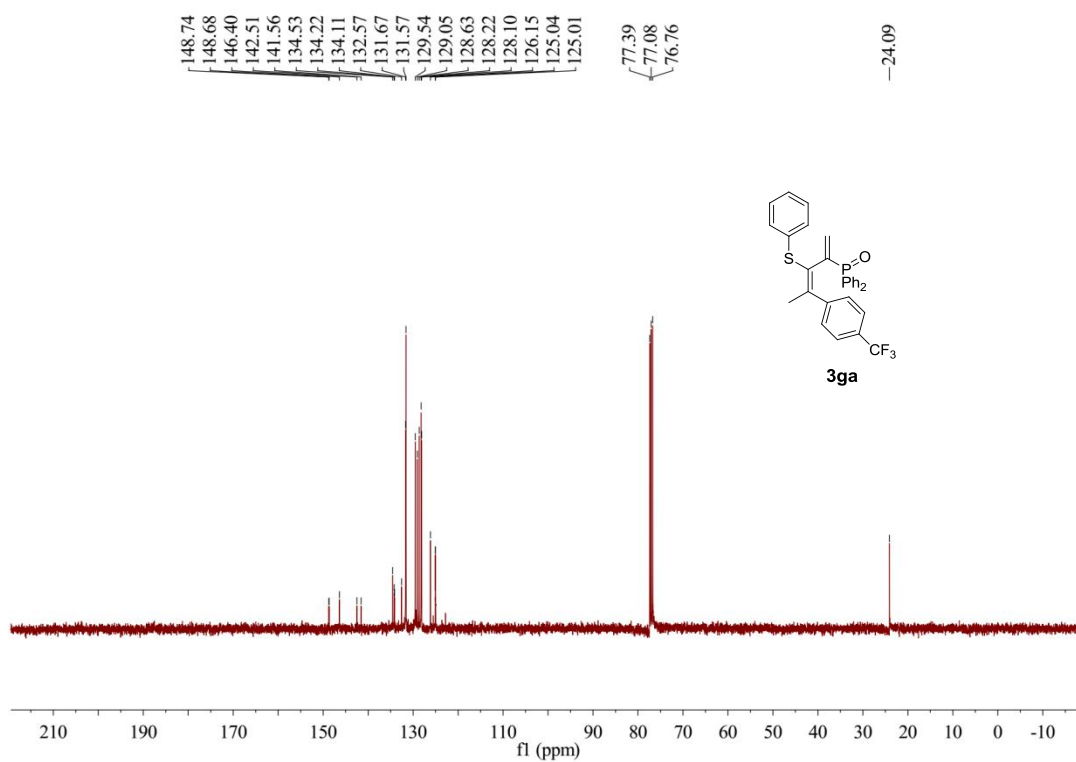


20161109-18 #29-30 RT: 0.33-0.34 AV: 2 NL: 5.71E4
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

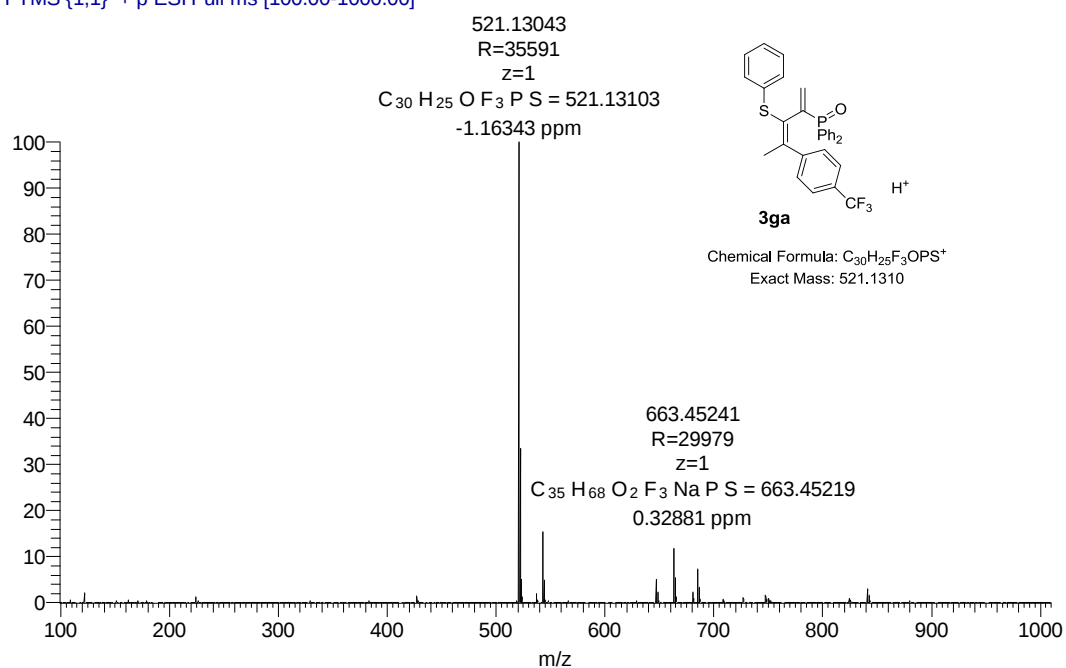


3ga (only E-)

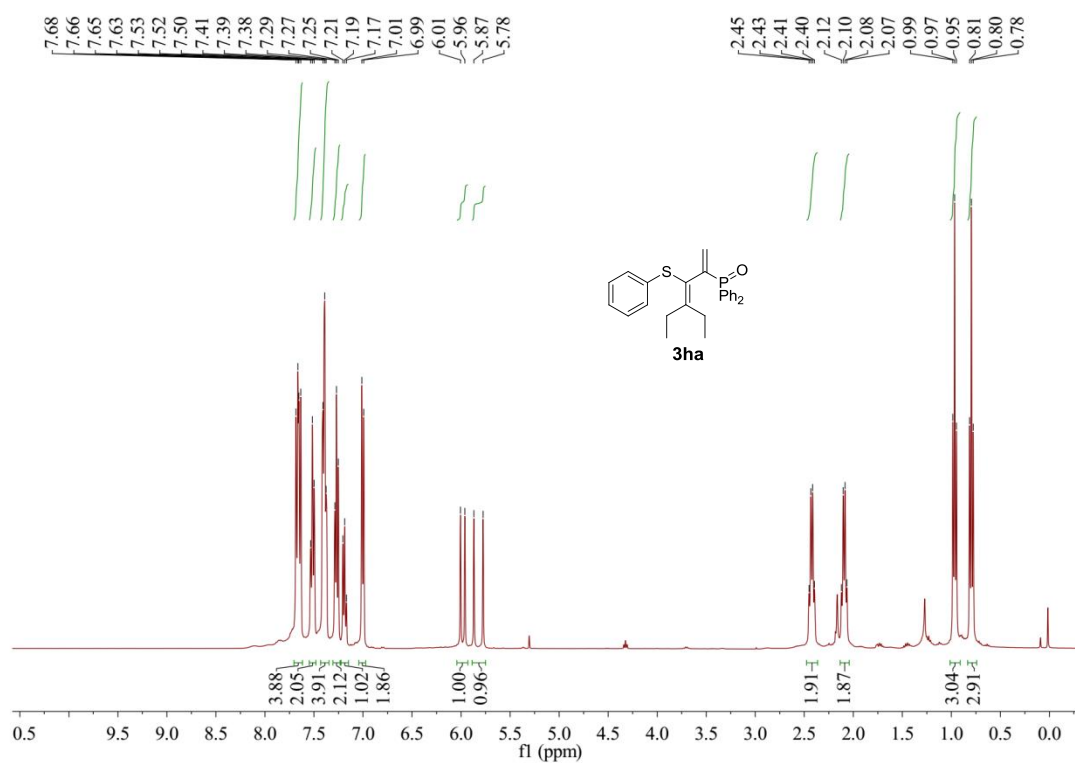


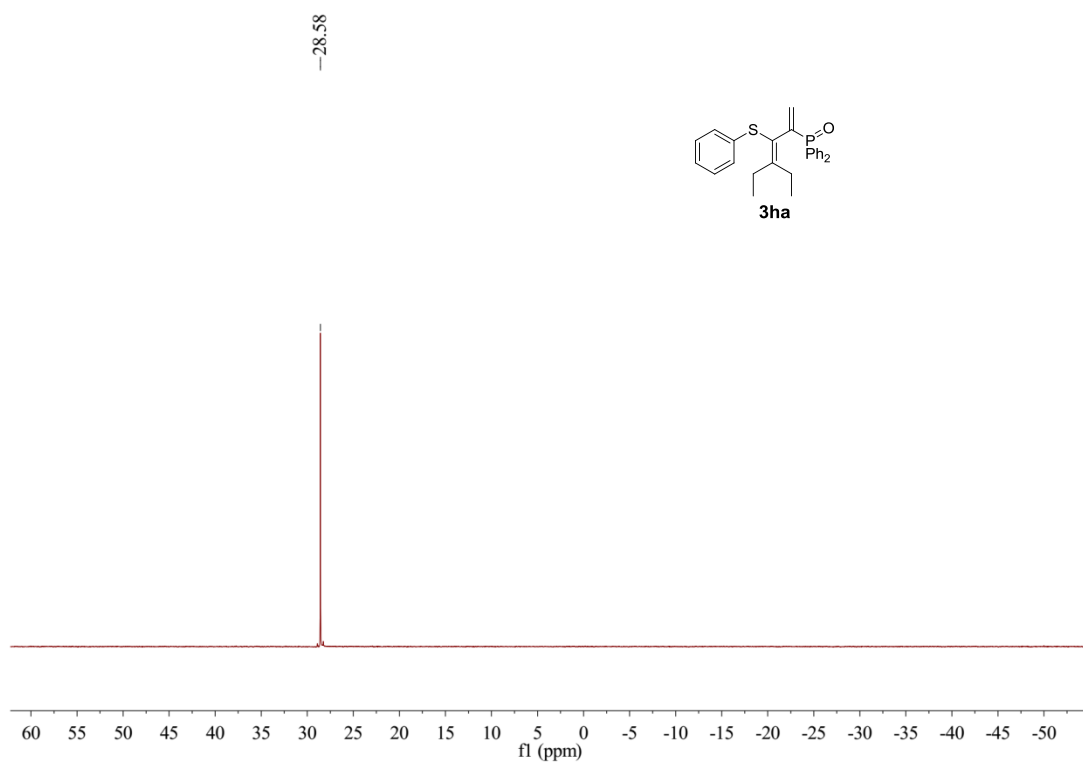
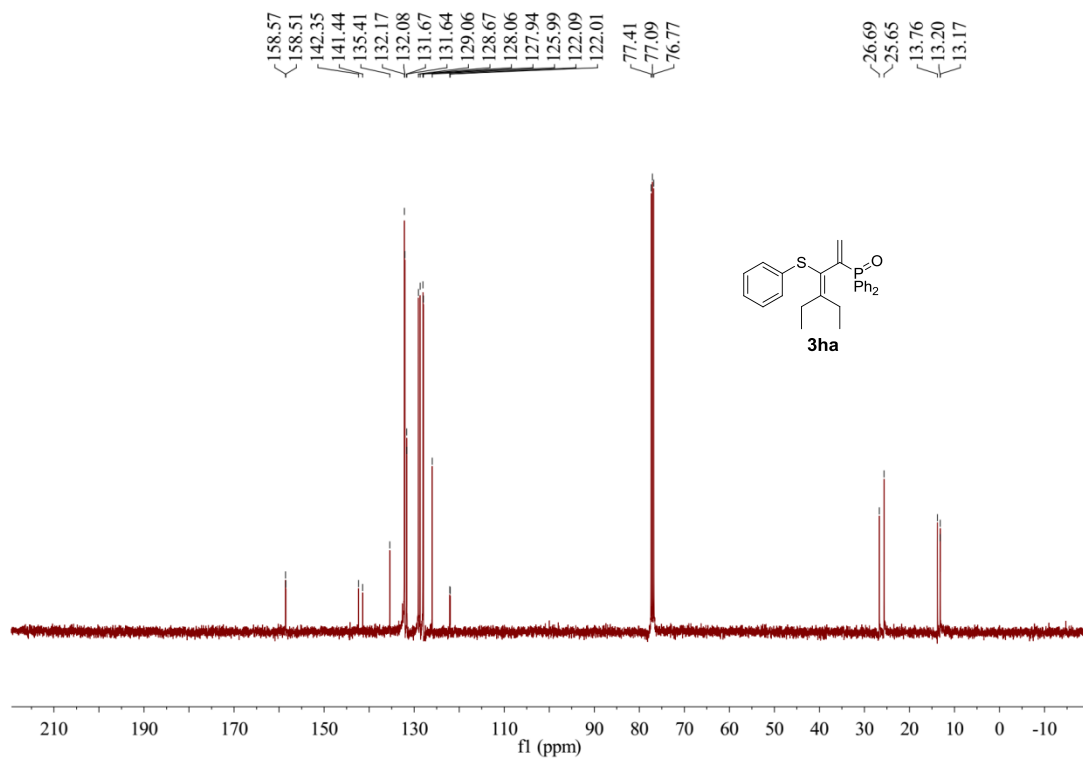


20170117-10 #49-50 RT: 0.53-0.54 AV: 2 NL: 5.77E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

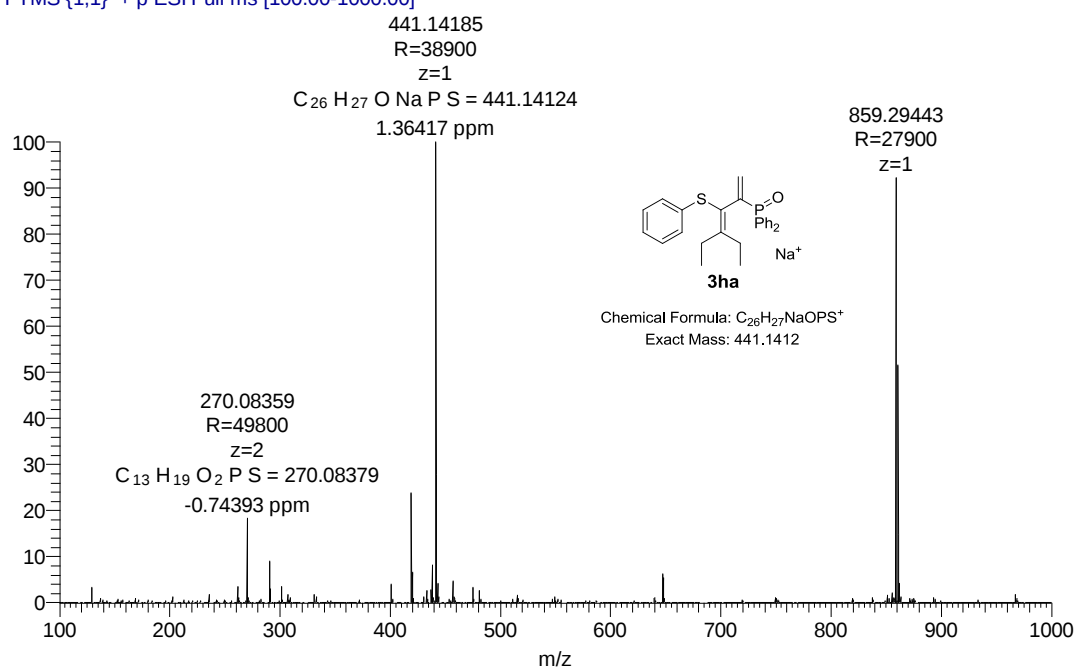


3ha

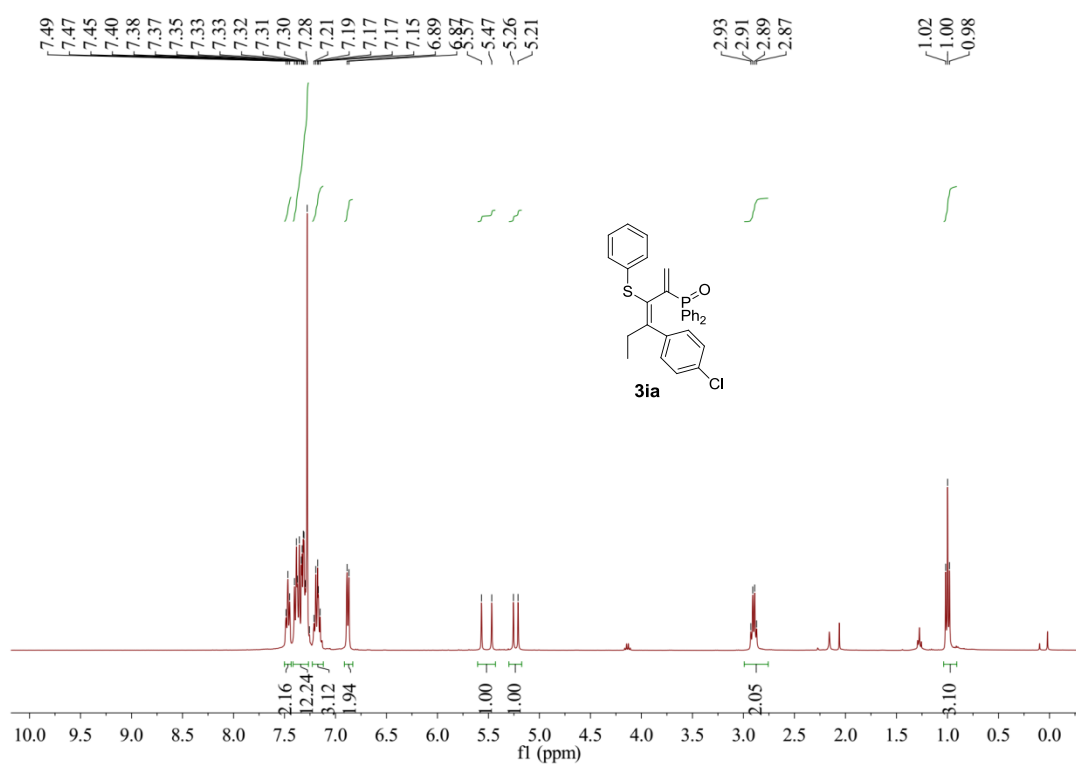


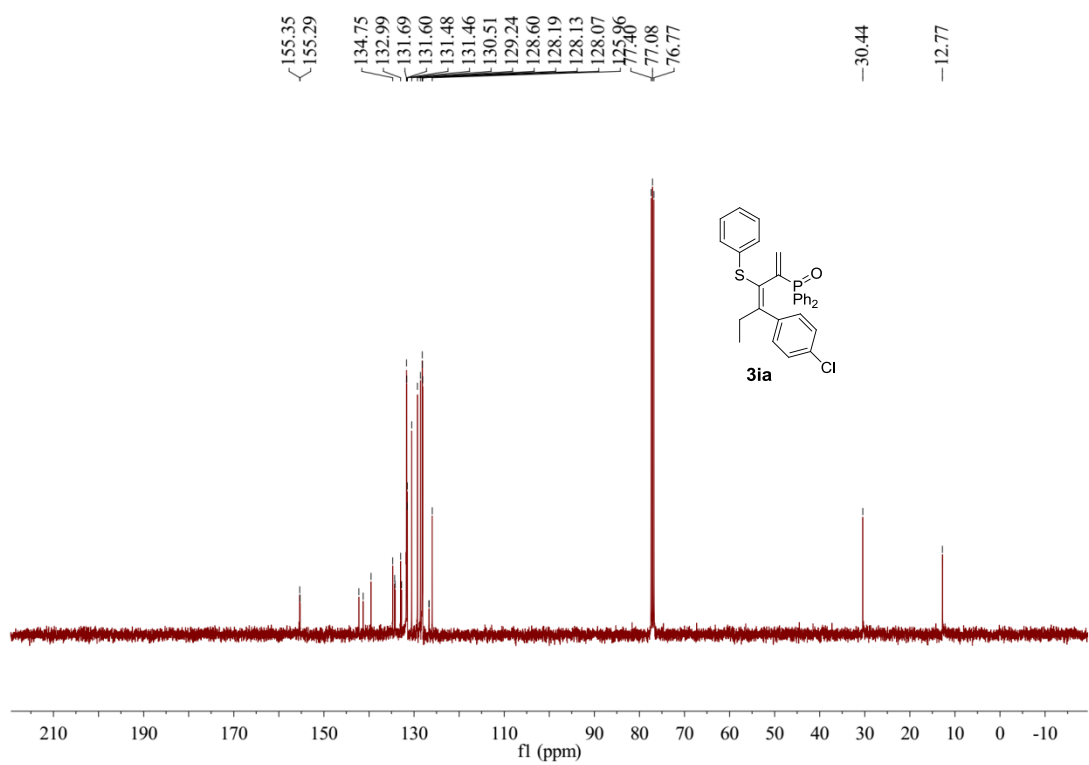


15 #32 RT: 0.33 AV: 1 NL: 4.08E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]



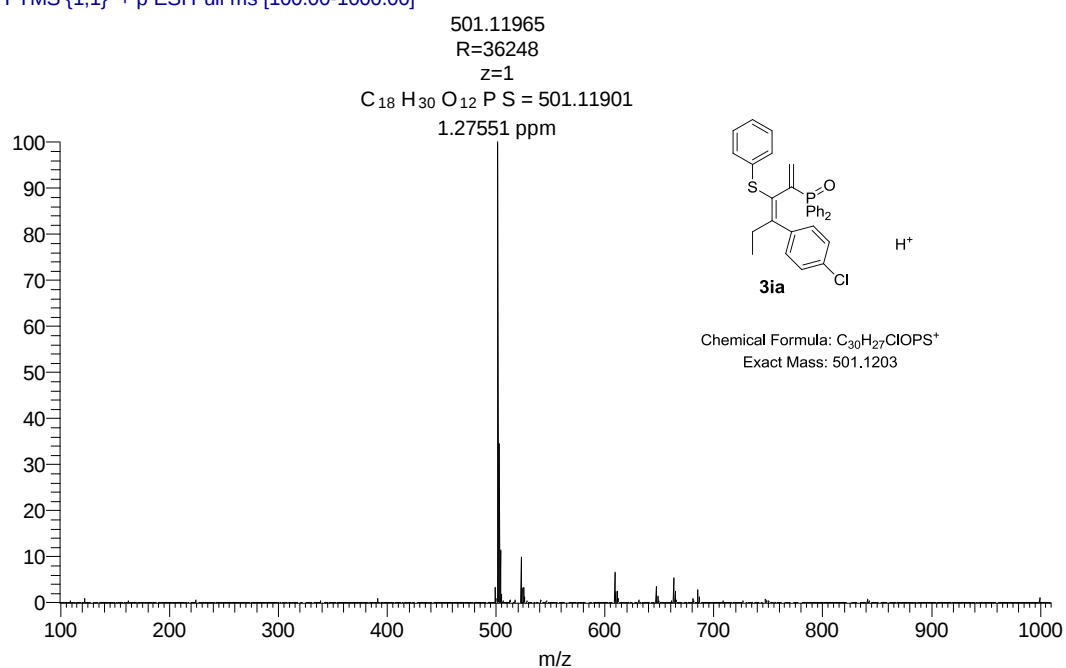
3ia (only E-)



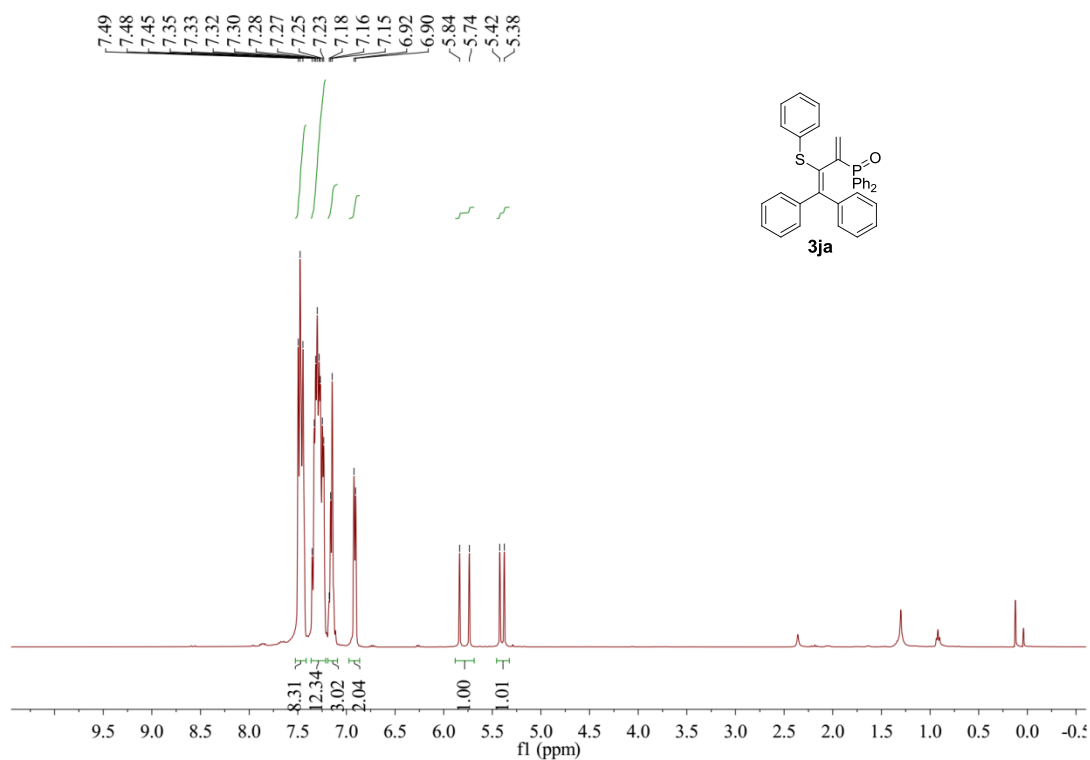


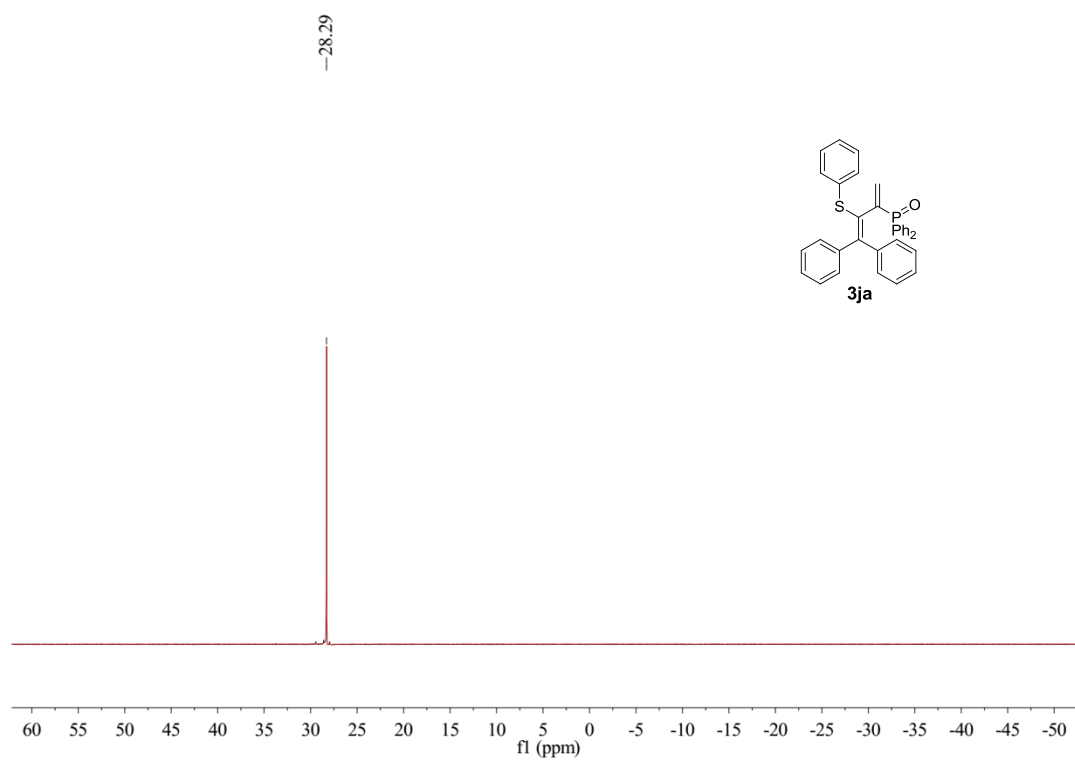
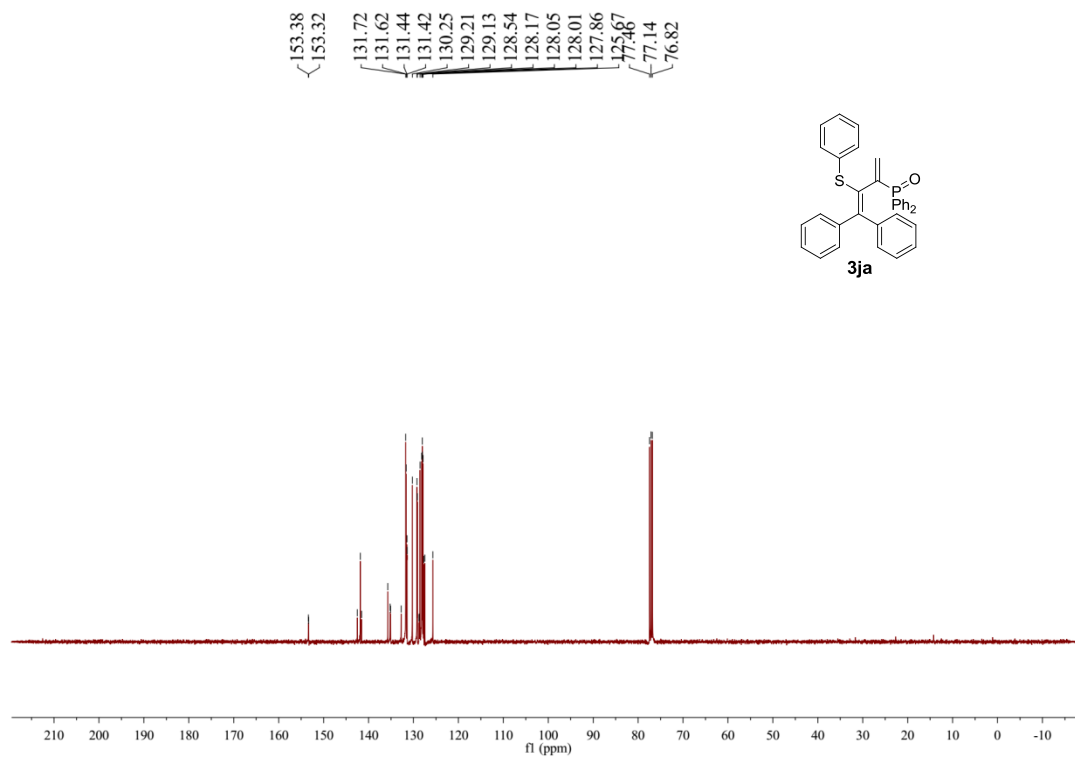
20170117-8 #43-44 RT: 0.47-0.48 AV: 2 NL: 6.14E5

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

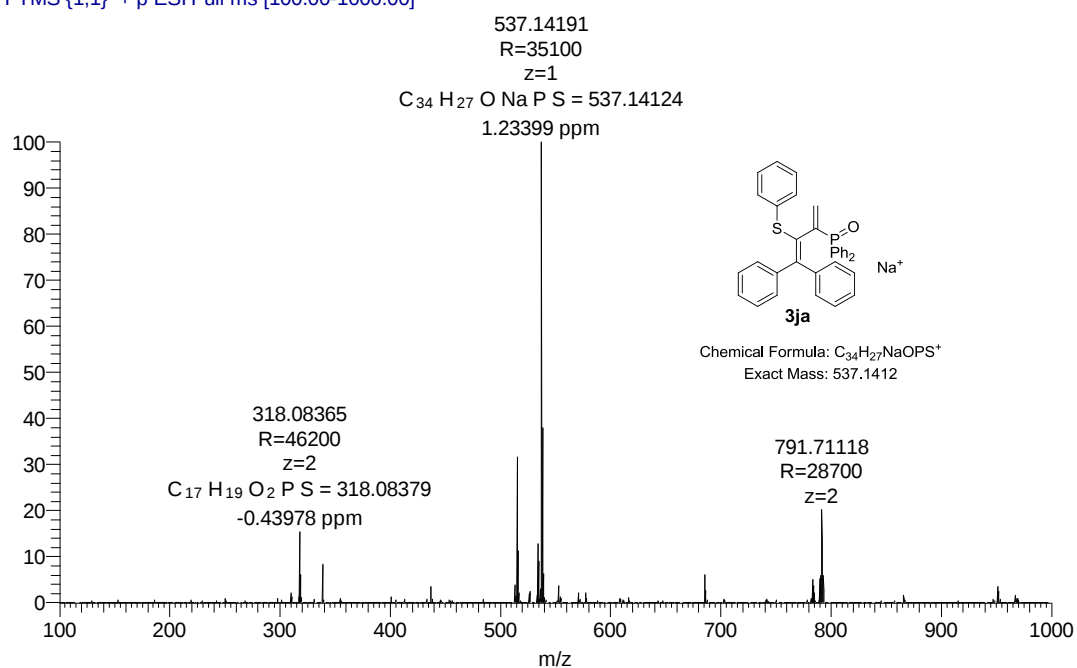


3ja

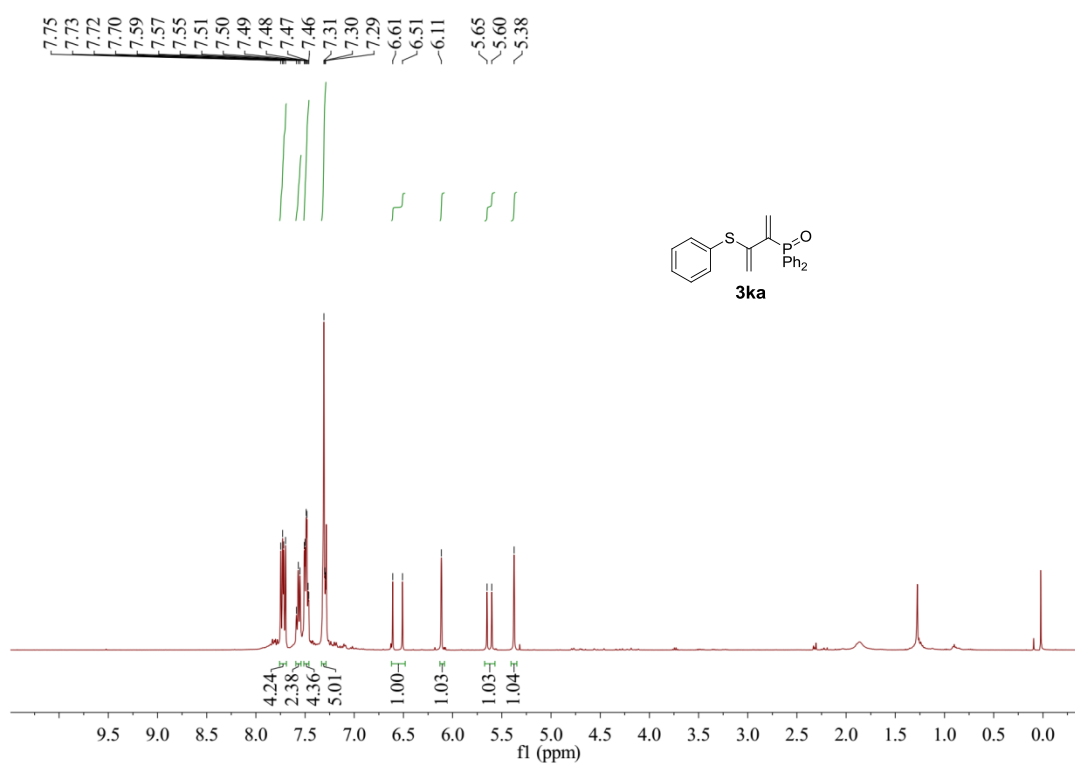


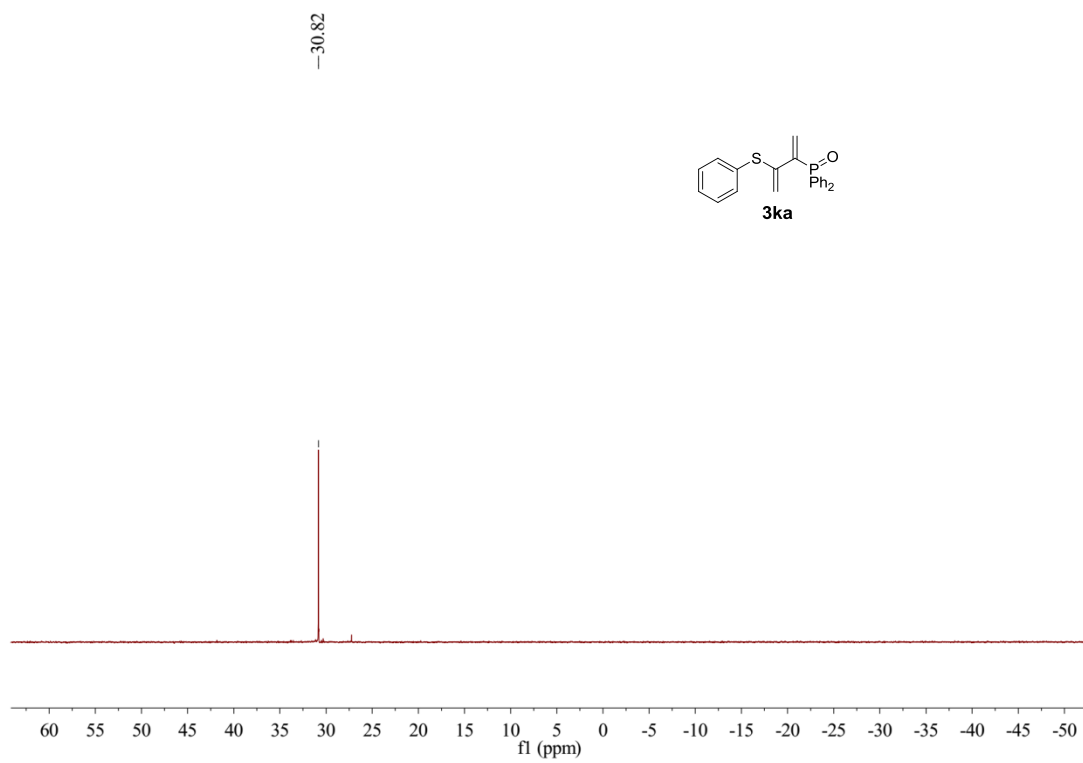
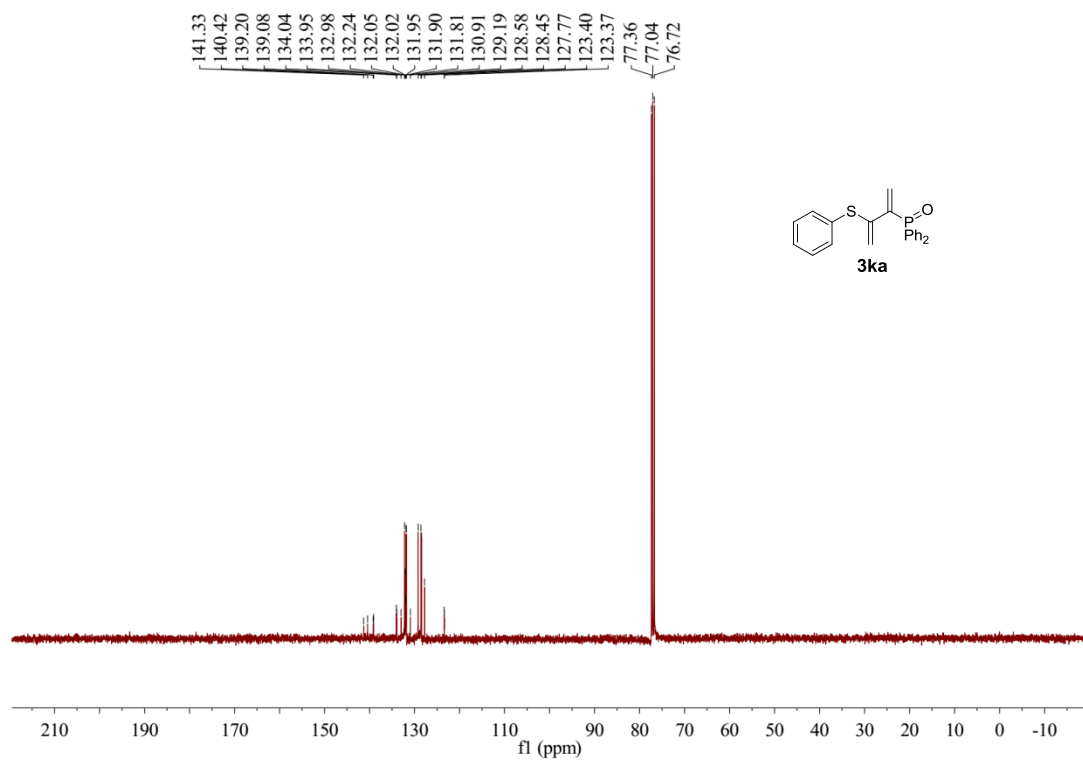


19 #35 RT: 0.35 AV: 1 NL: 5.56E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]



3ka





20170117-9 #41 RT: 0.42 AV: 1 NL: 6.78E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

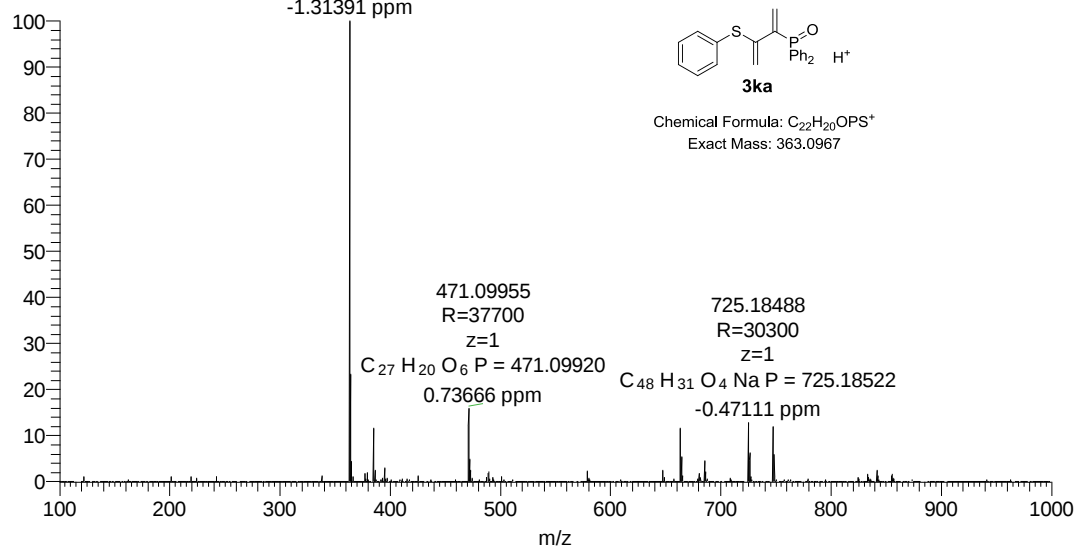
363.09622

R=43000

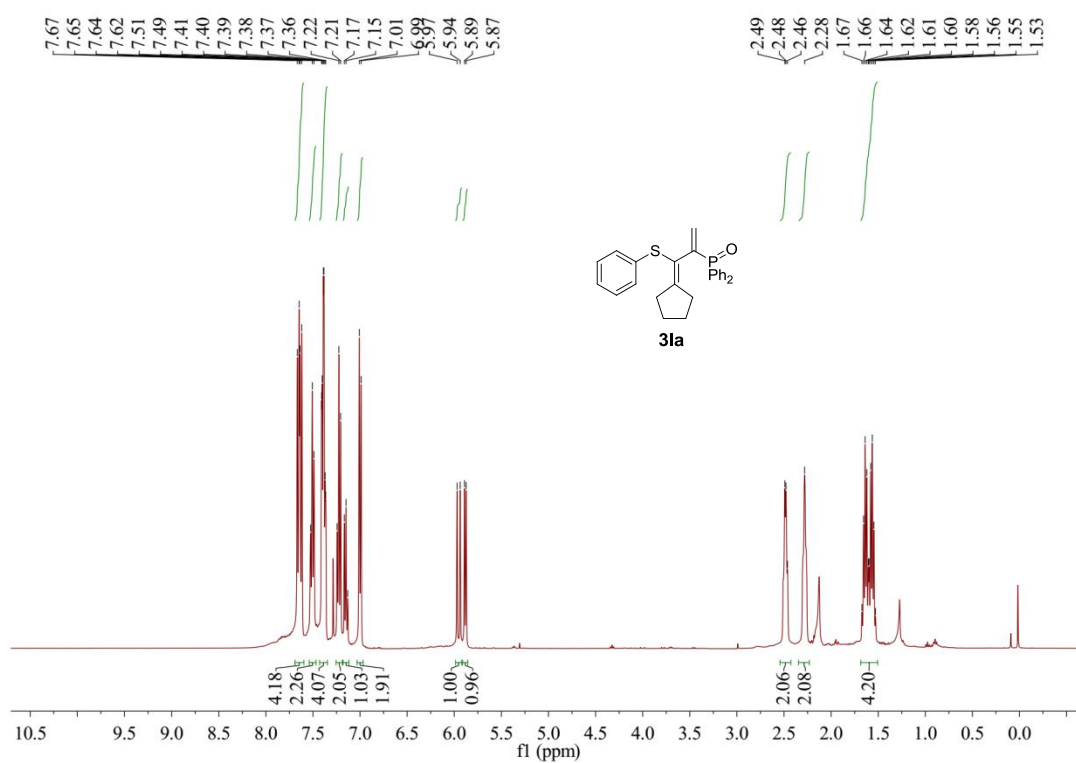
z=1

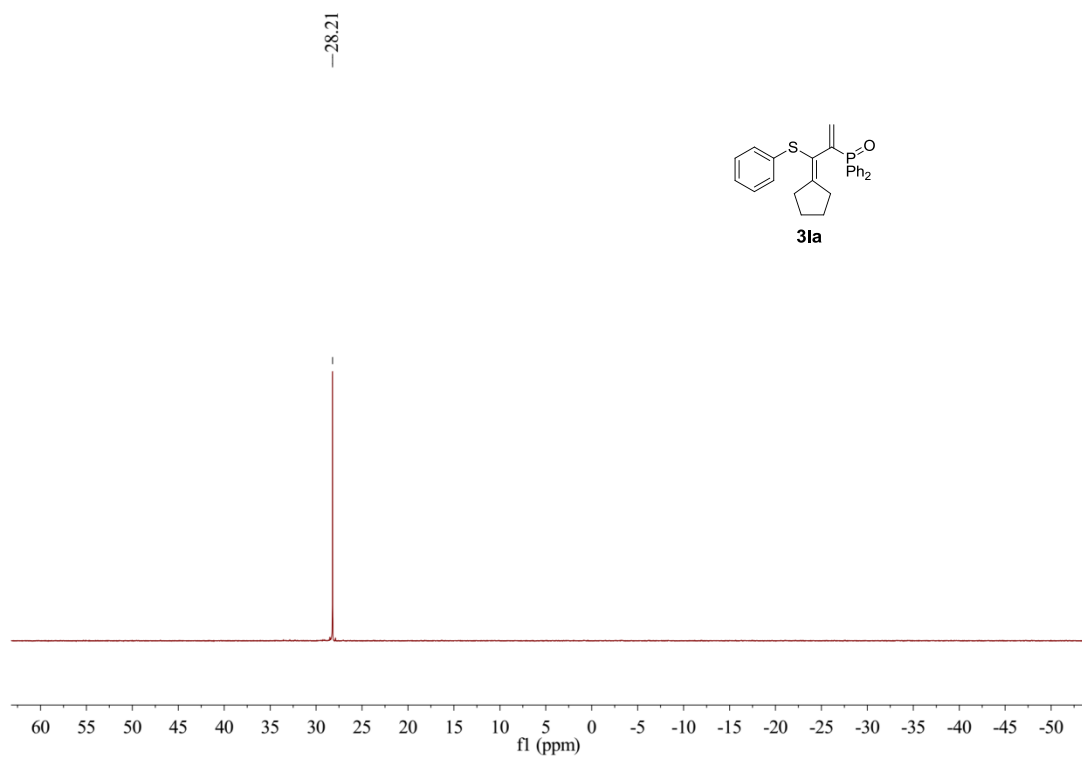
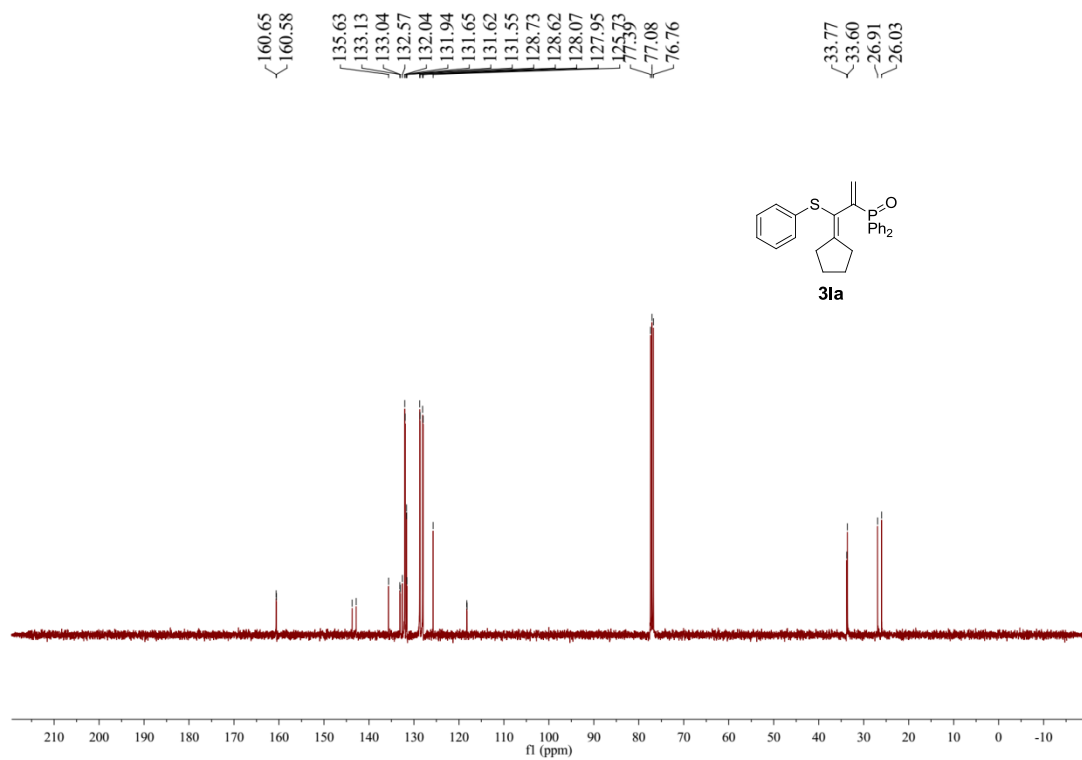
C₂₂H₂₀O P S = 363.09670

-1.31391 ppm

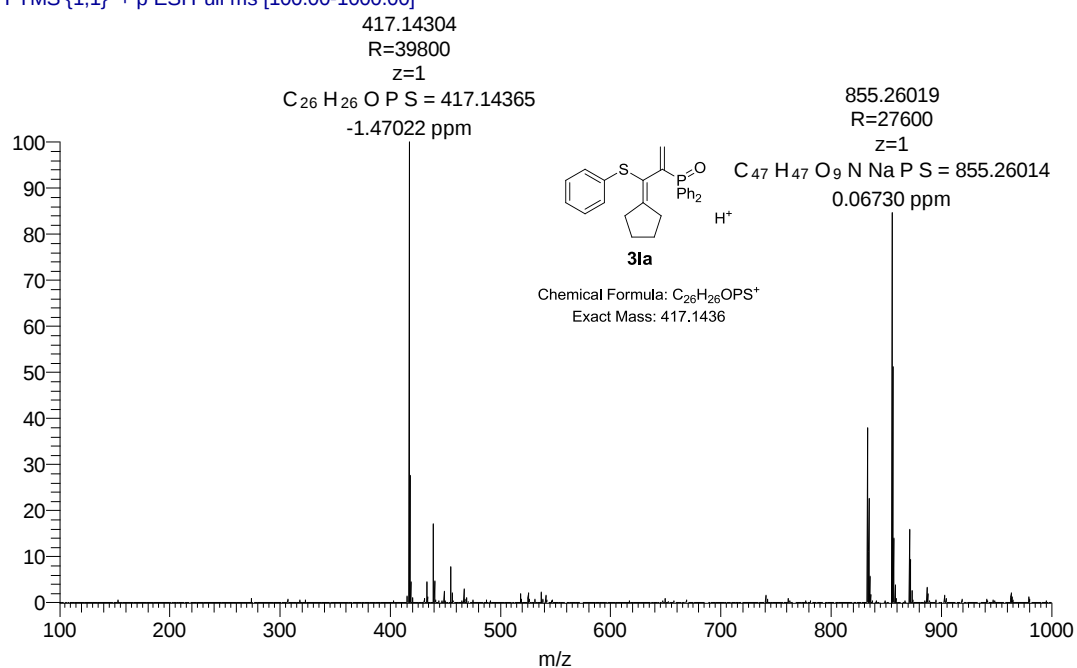


3la

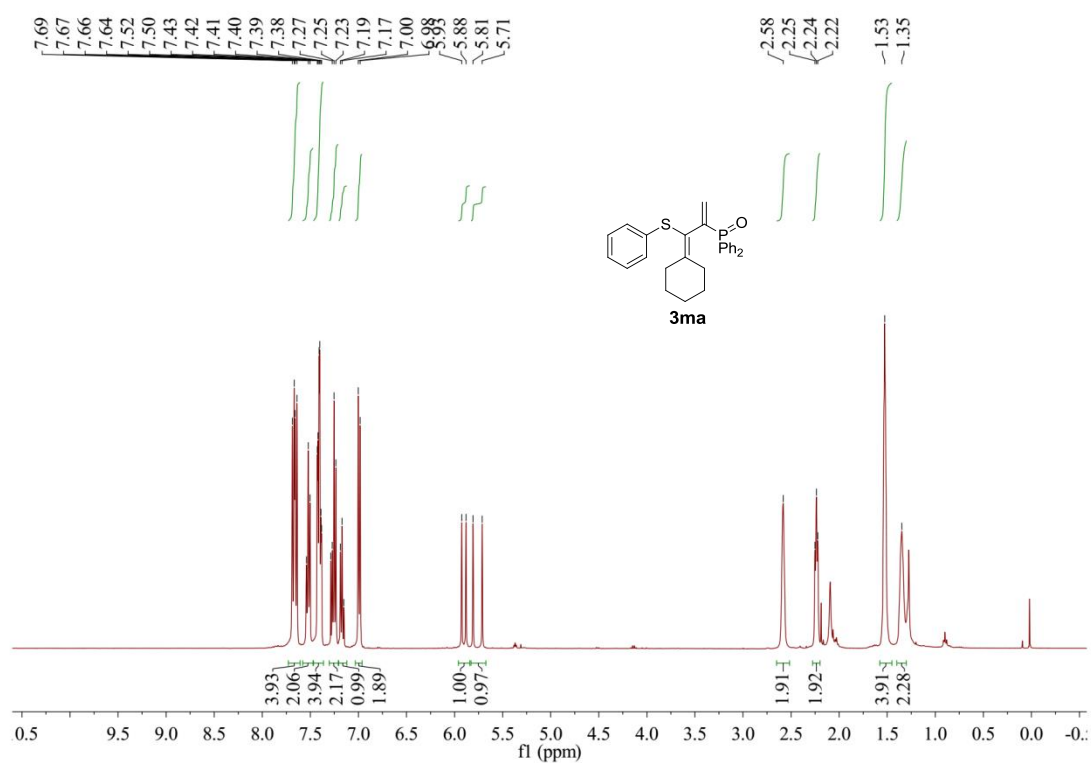


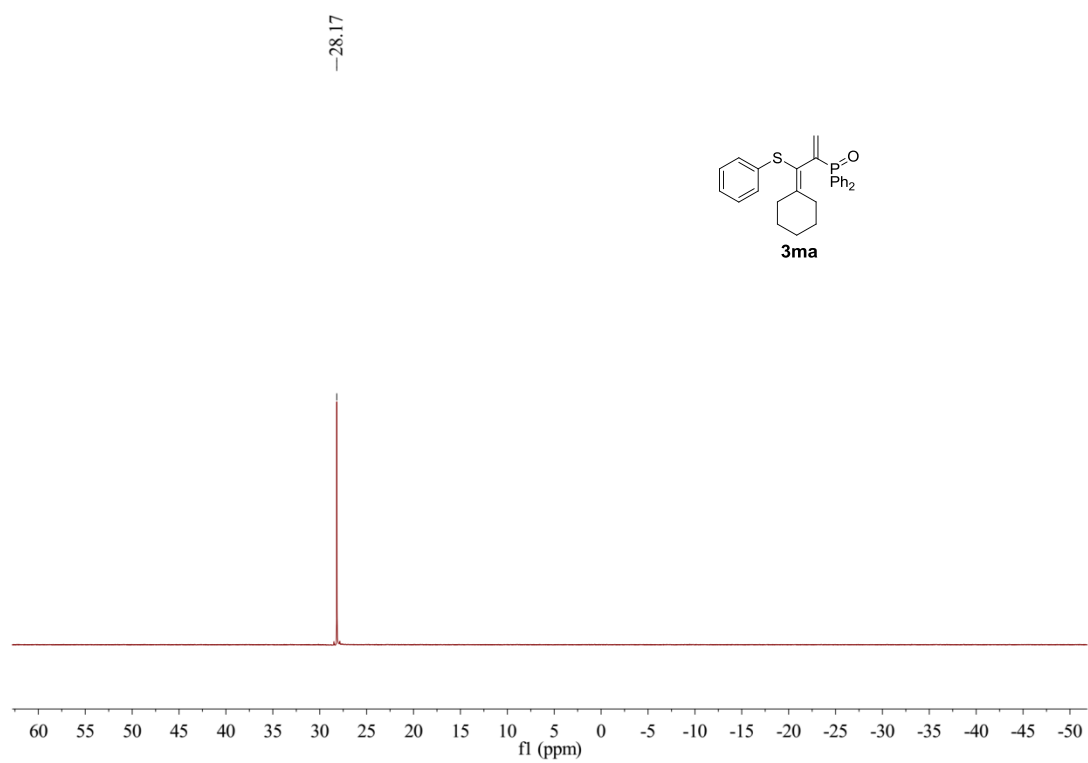
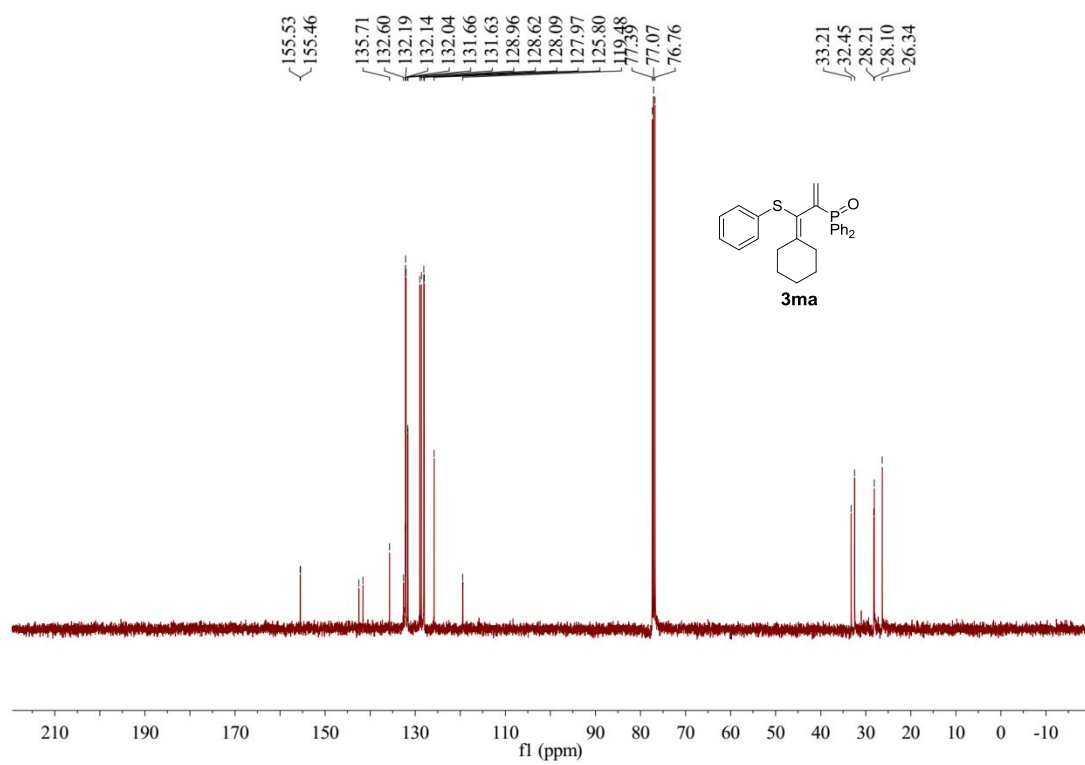


20170117-24 #20 RT: 0.21 AV: 1 NL: 3.55E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

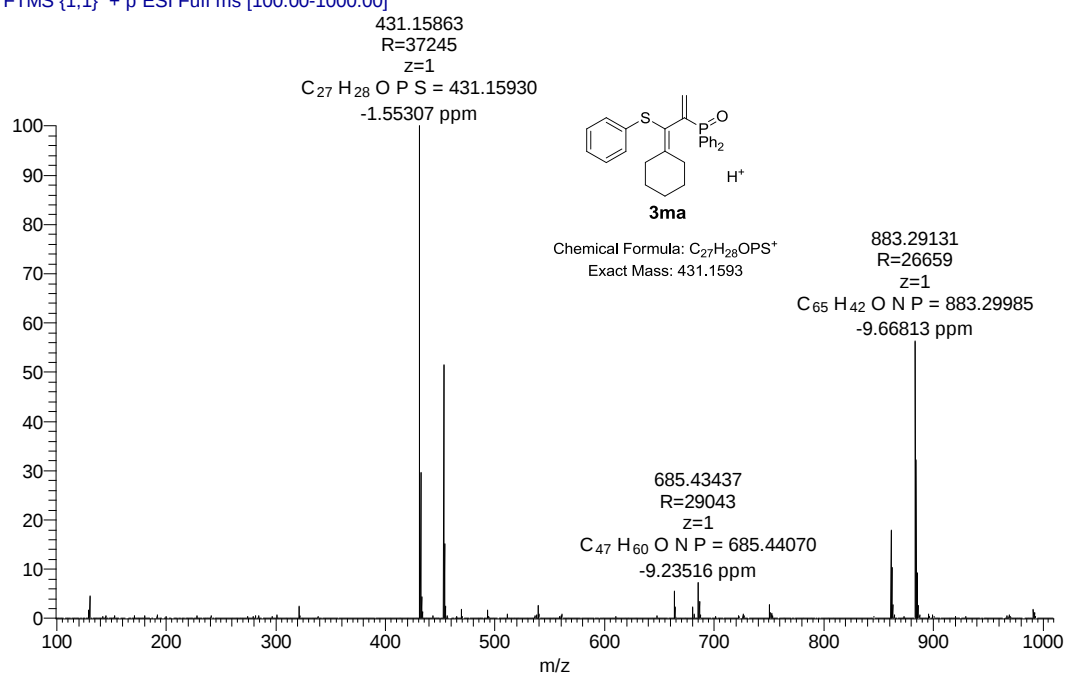


3ma

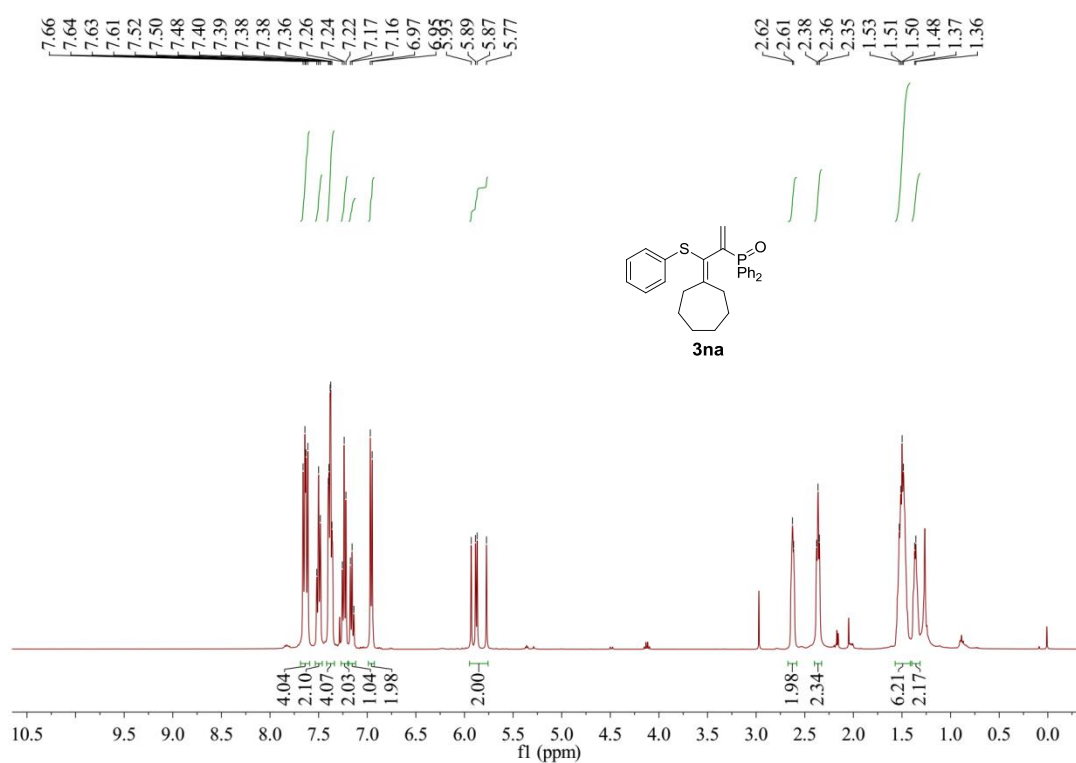


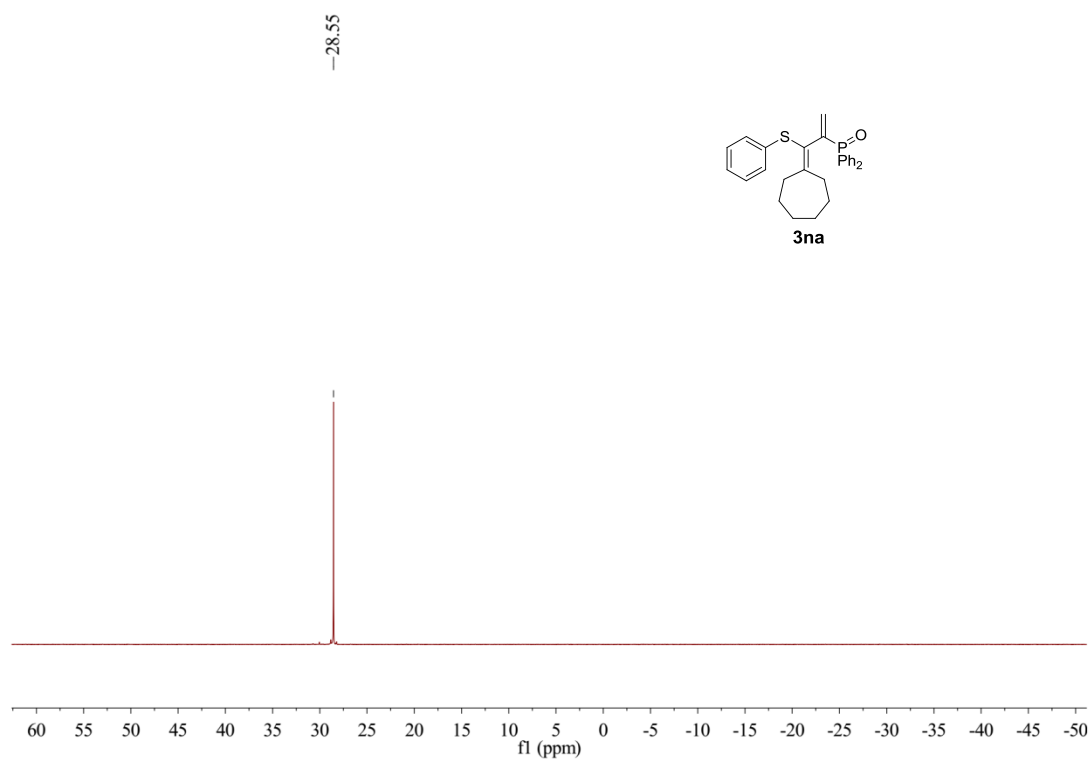
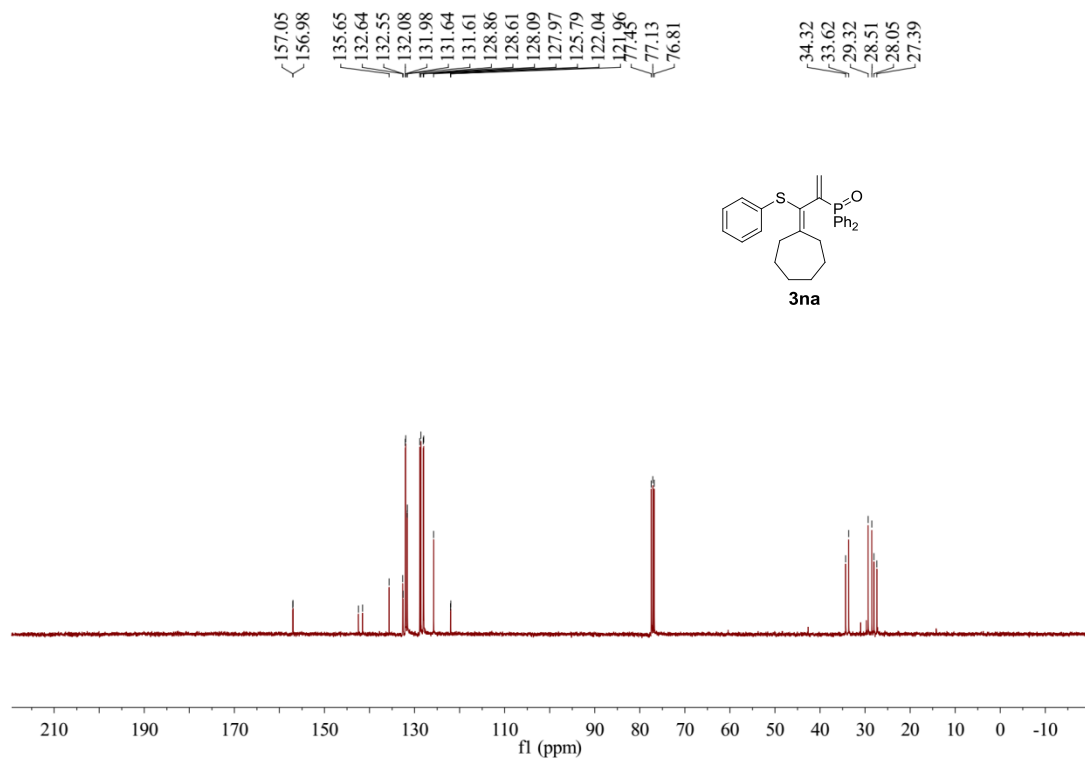


20161109-13 #36-37 RT: 0.41-0.42 AV: 2 NL: 9.06E4
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

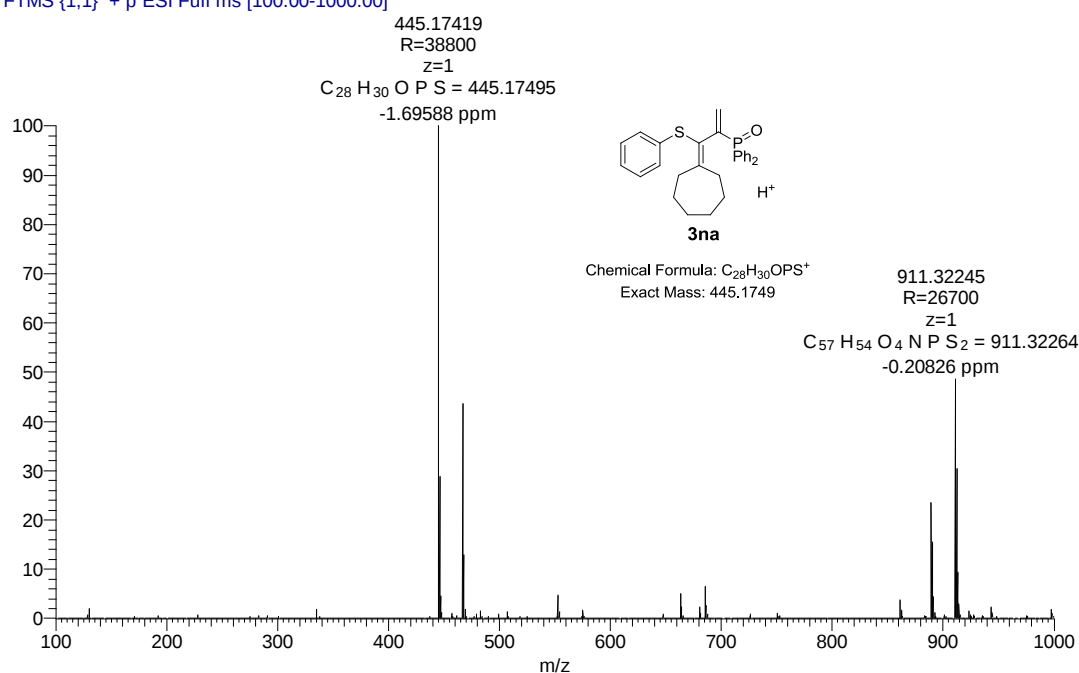


3na

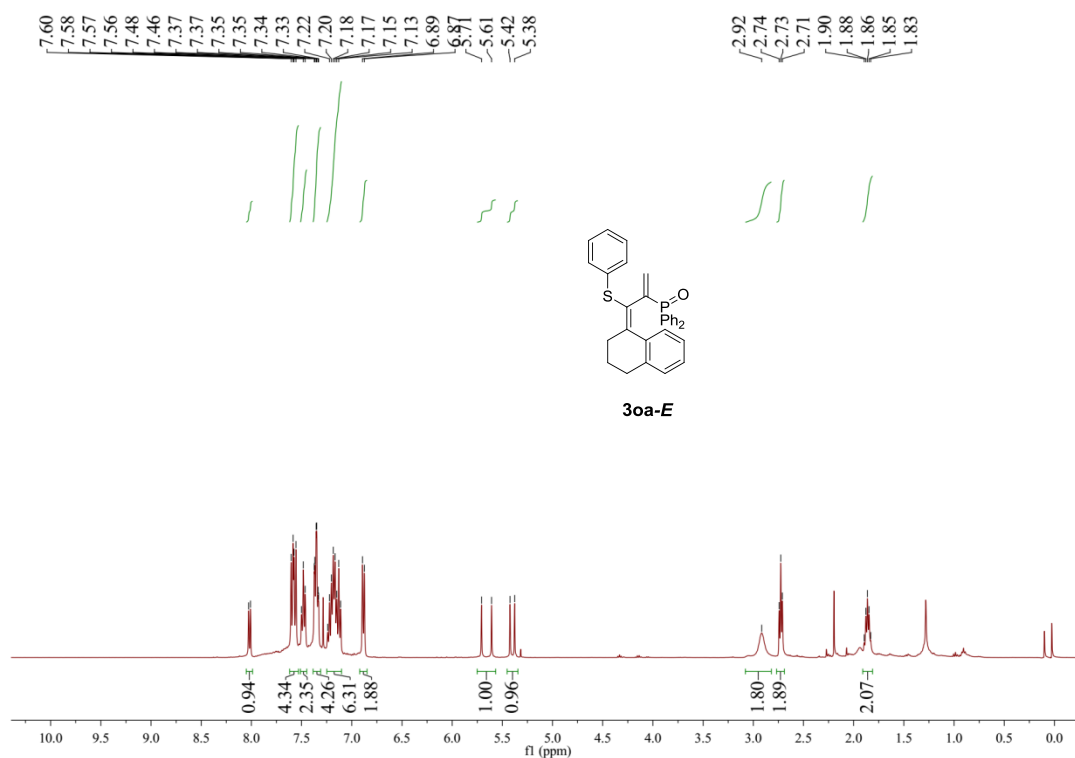


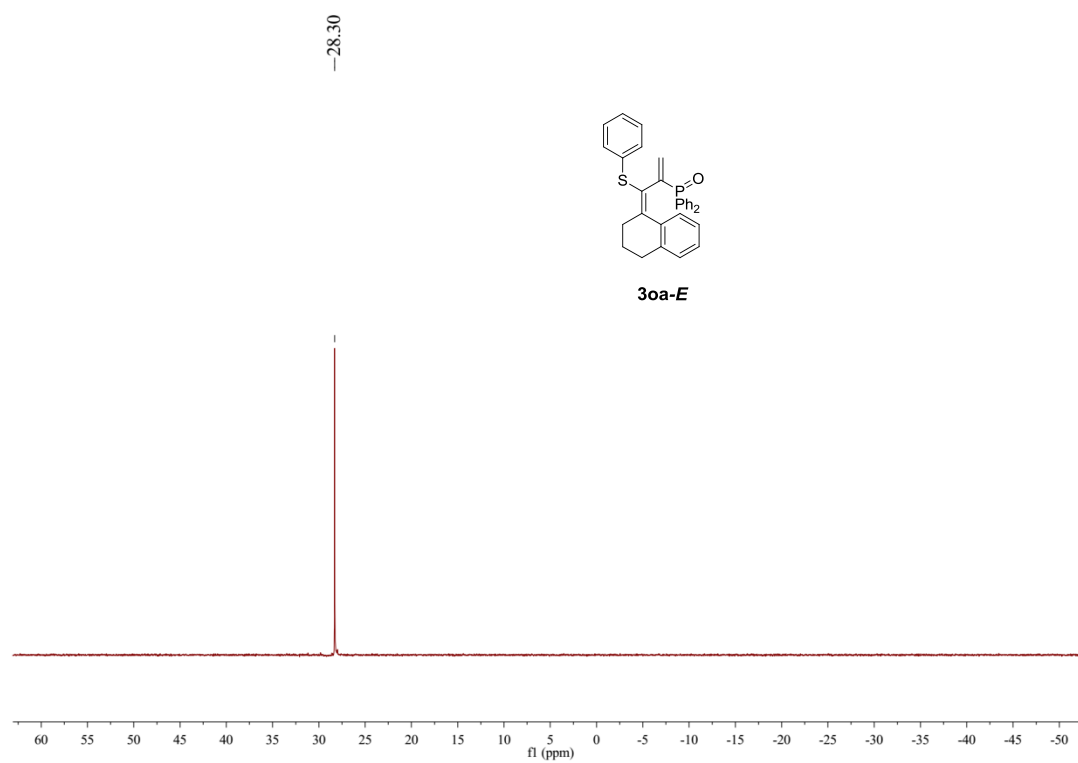
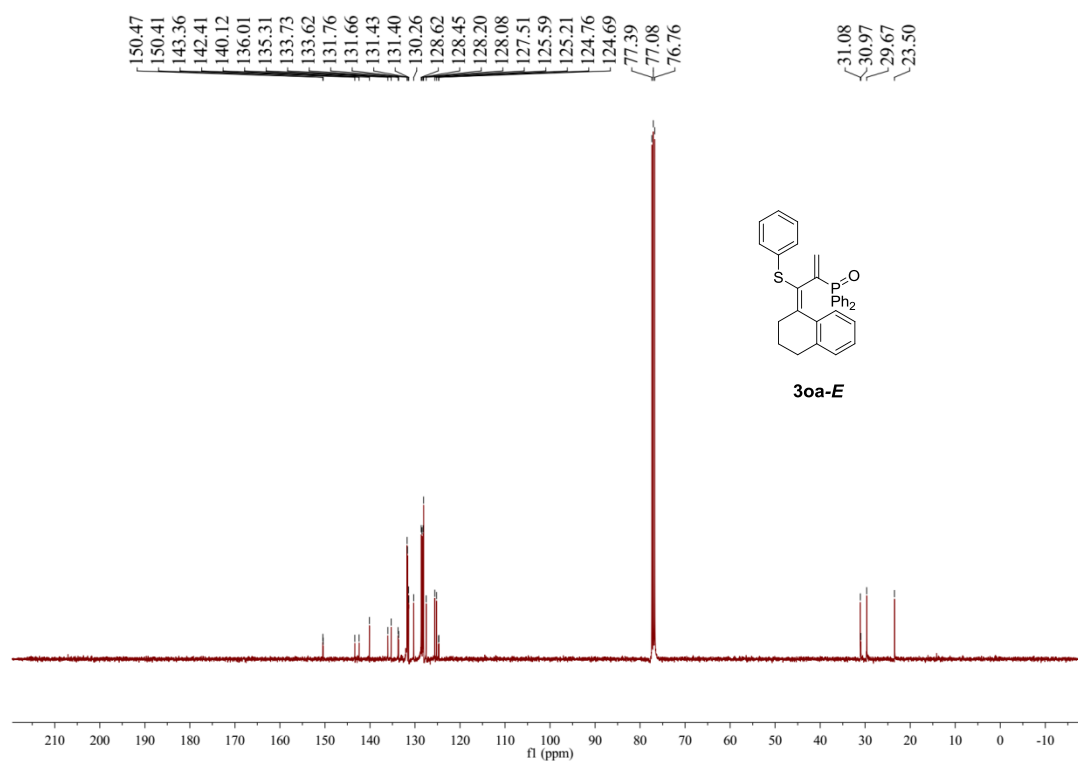


20161109-25 #33 RT: 0.37 AV: 1 NL: 1.32E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

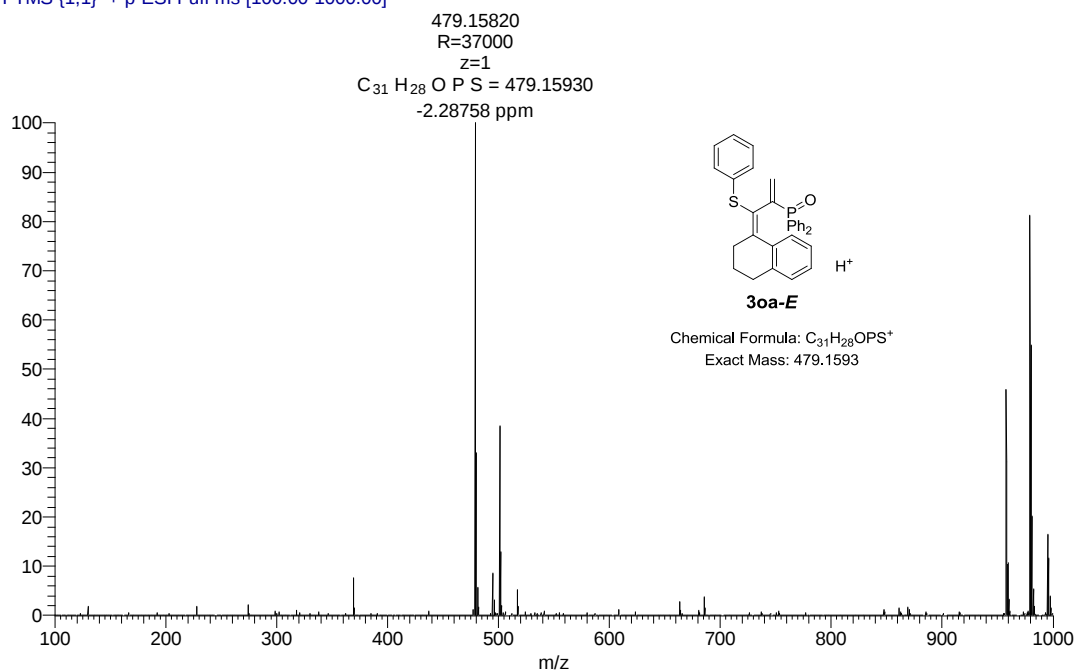


30a-E

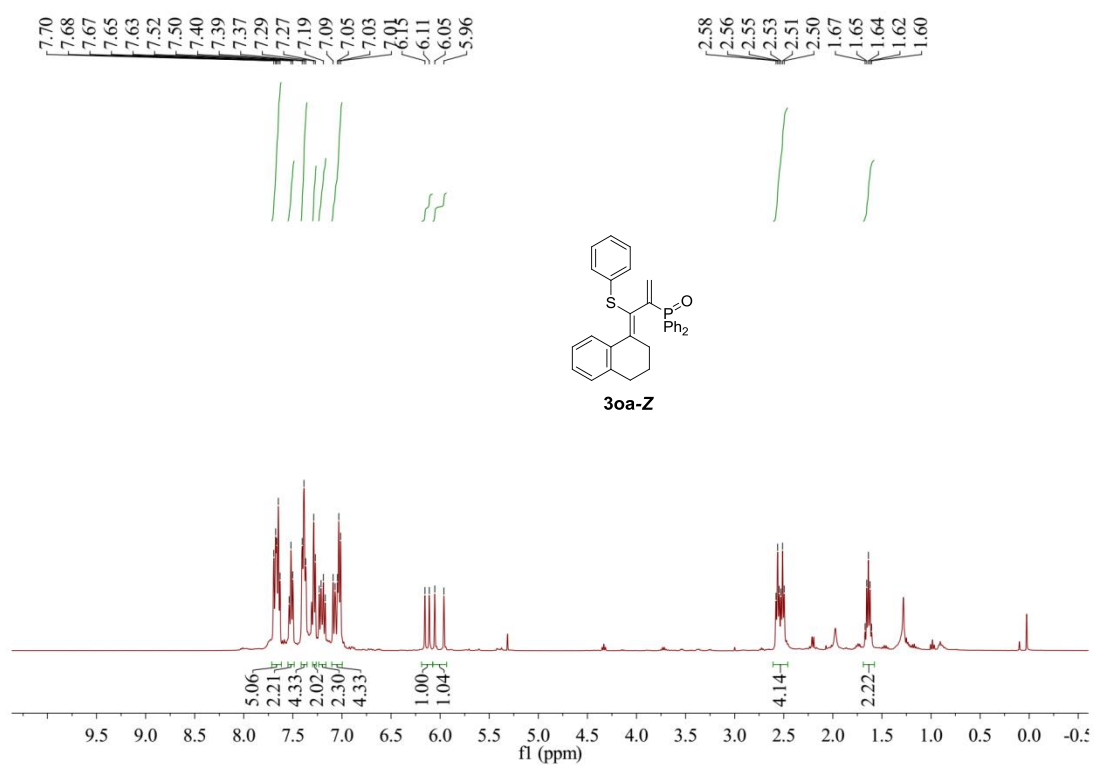


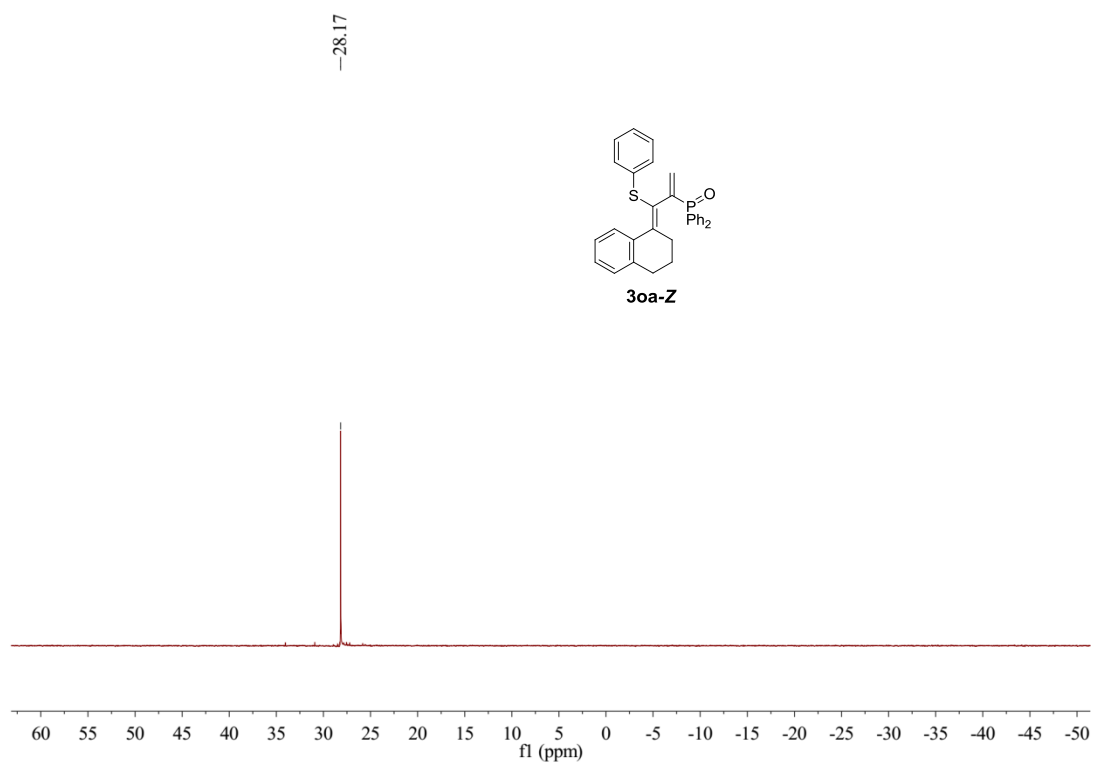
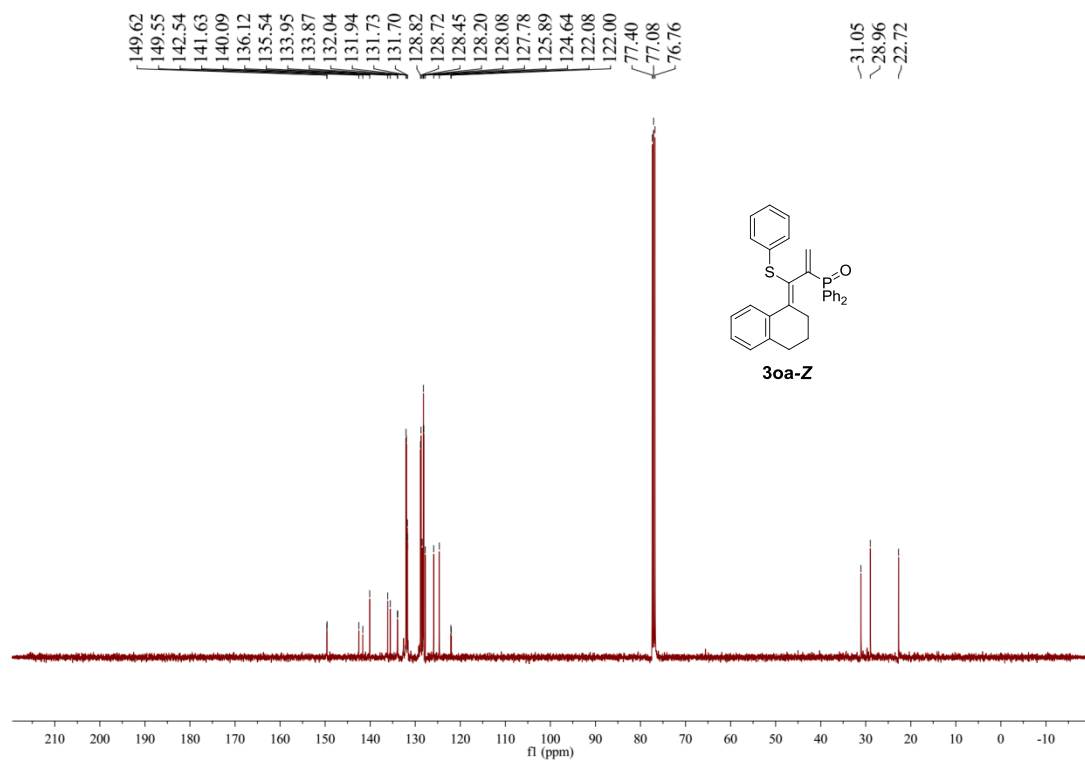


20161109-17 #26 RT: 0.29 AV: 1 NL: 1.47E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

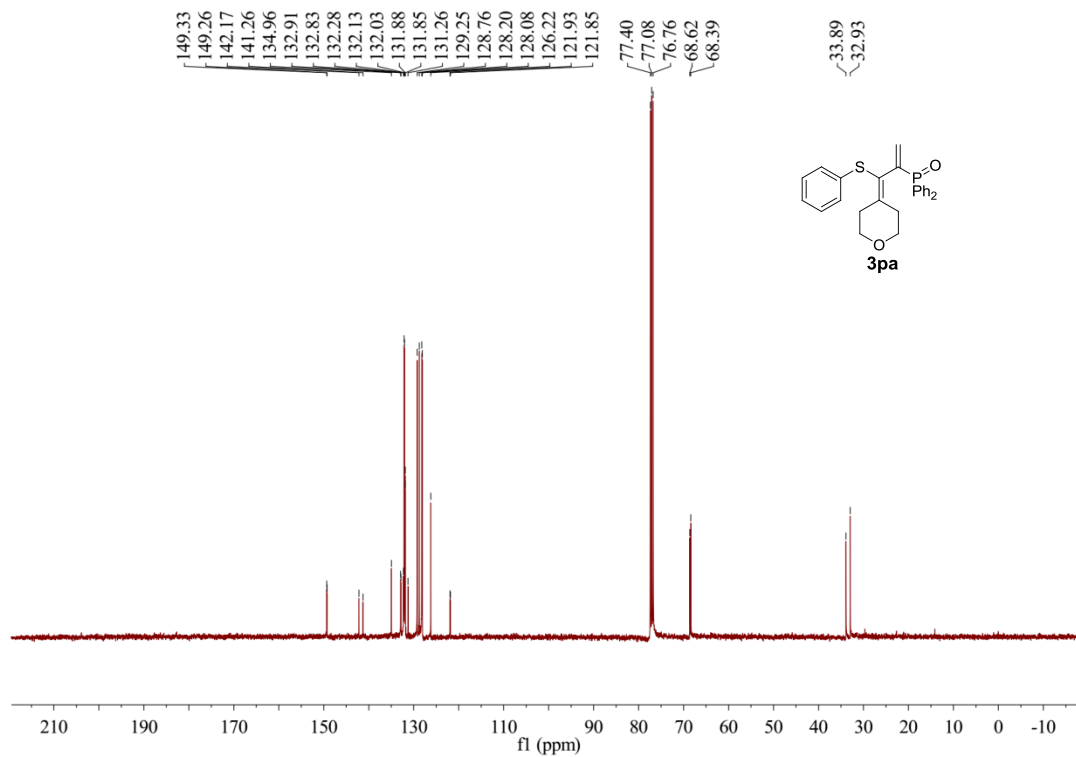
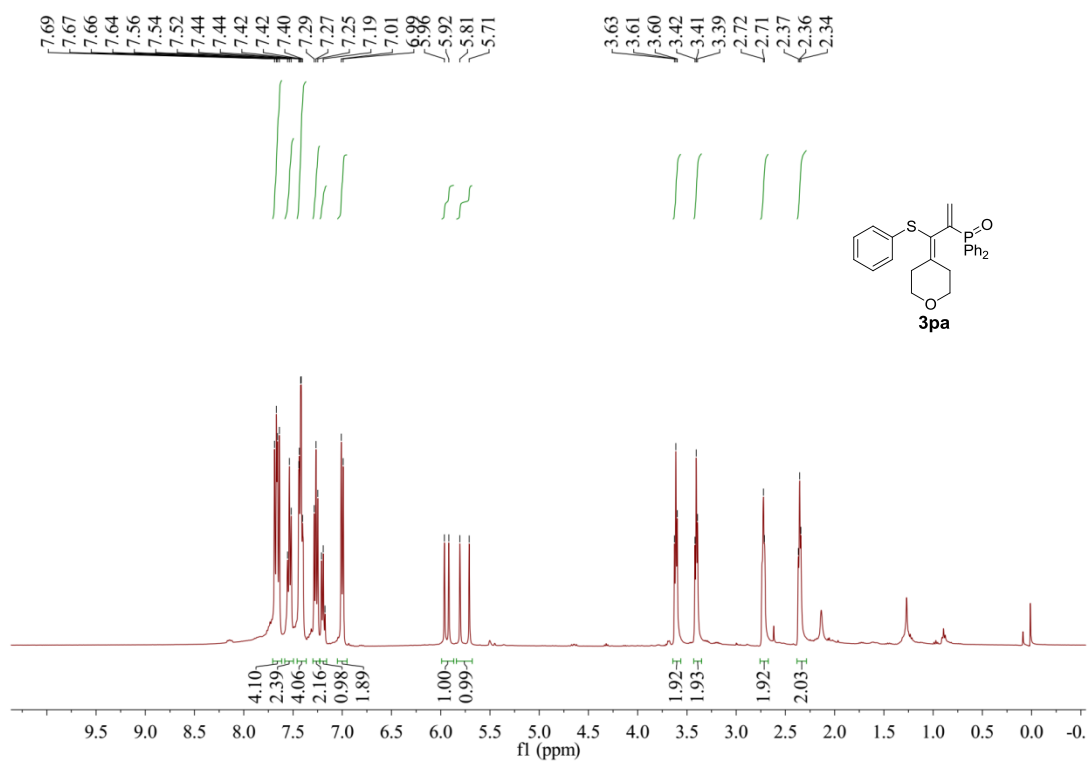


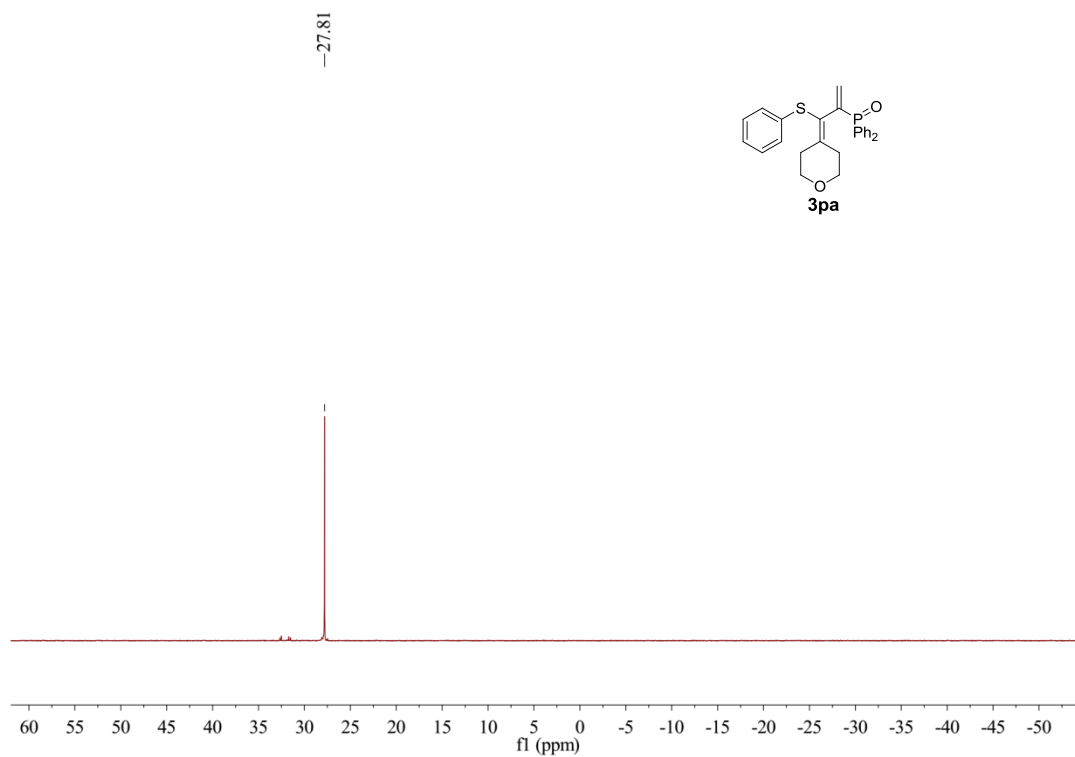
30a-Z



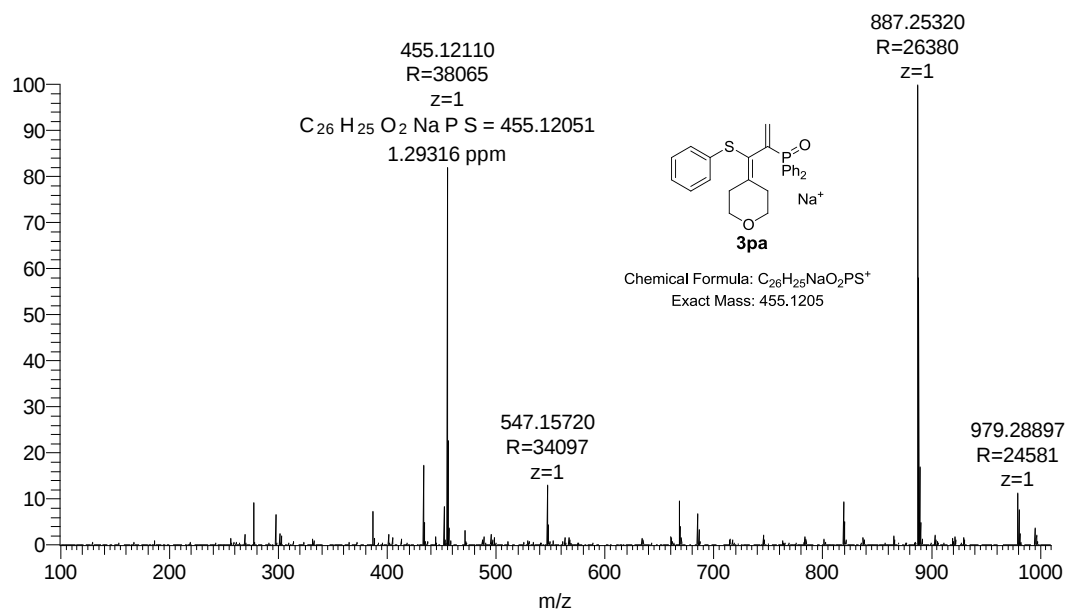


3pa

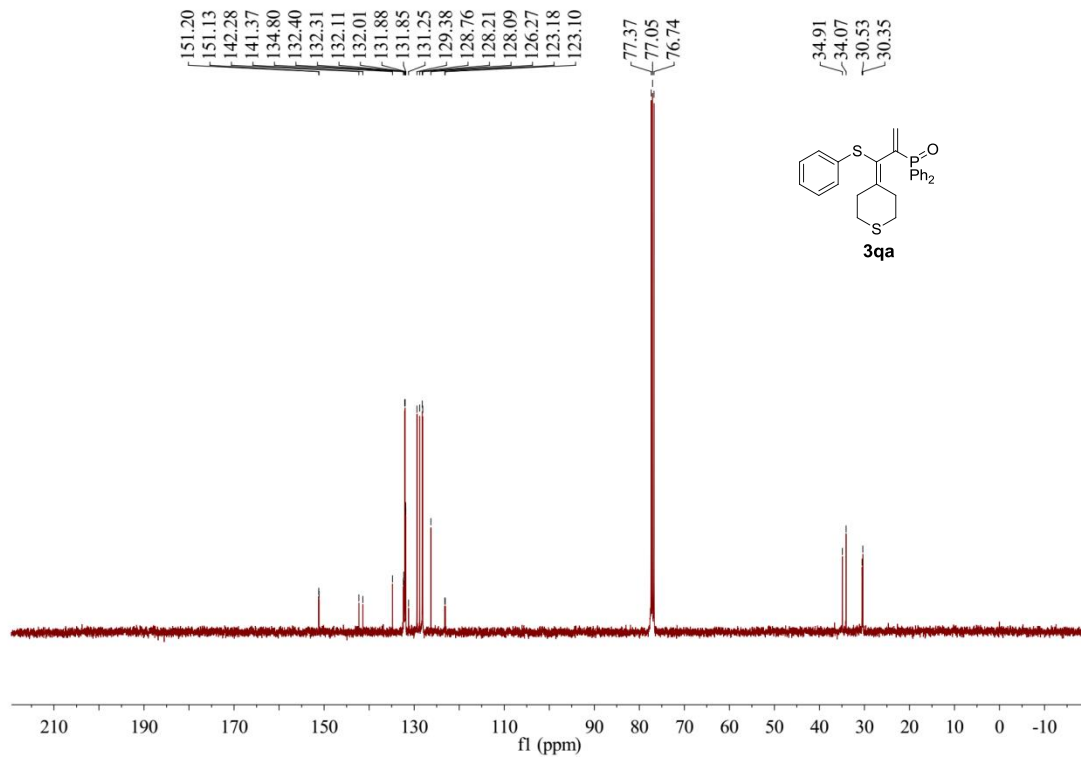
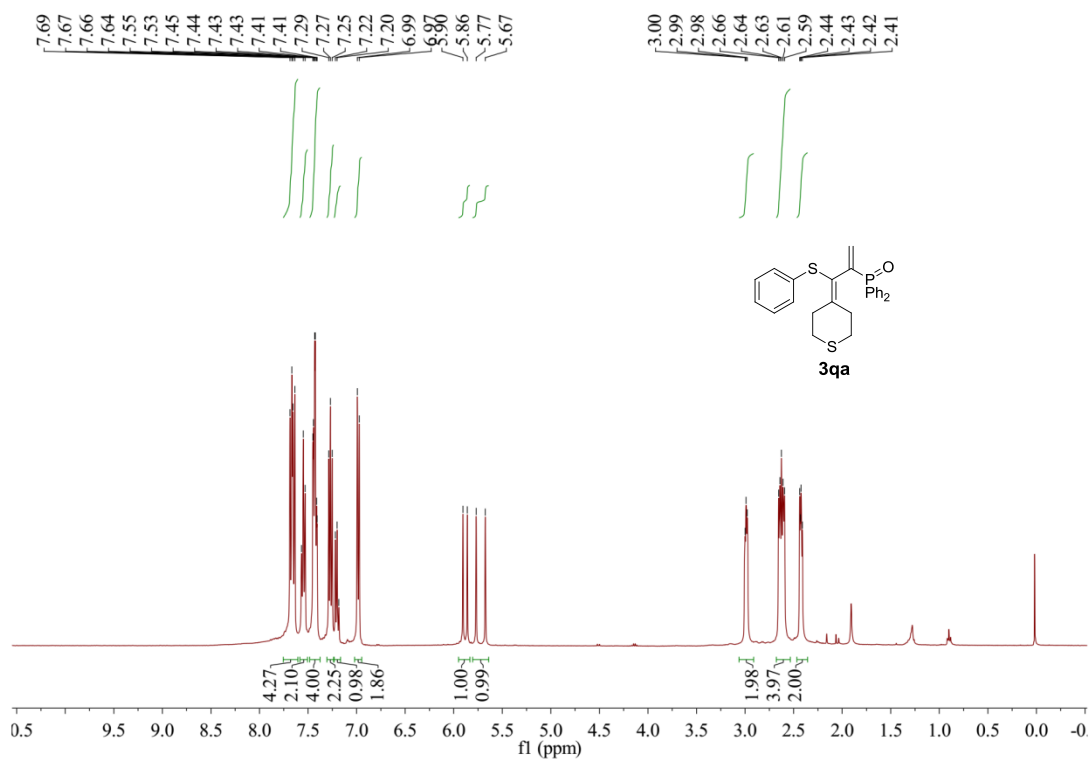


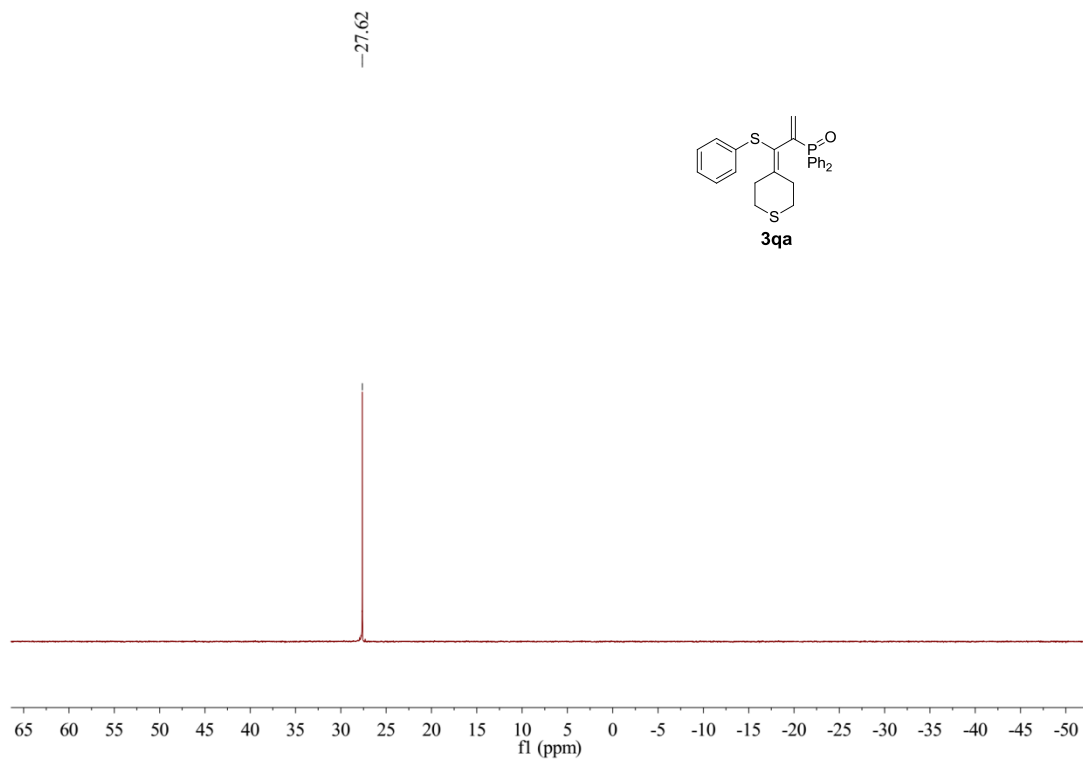


10 #42-43 RT: 0.41-0.42 AV: 2 NL: 5.51E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

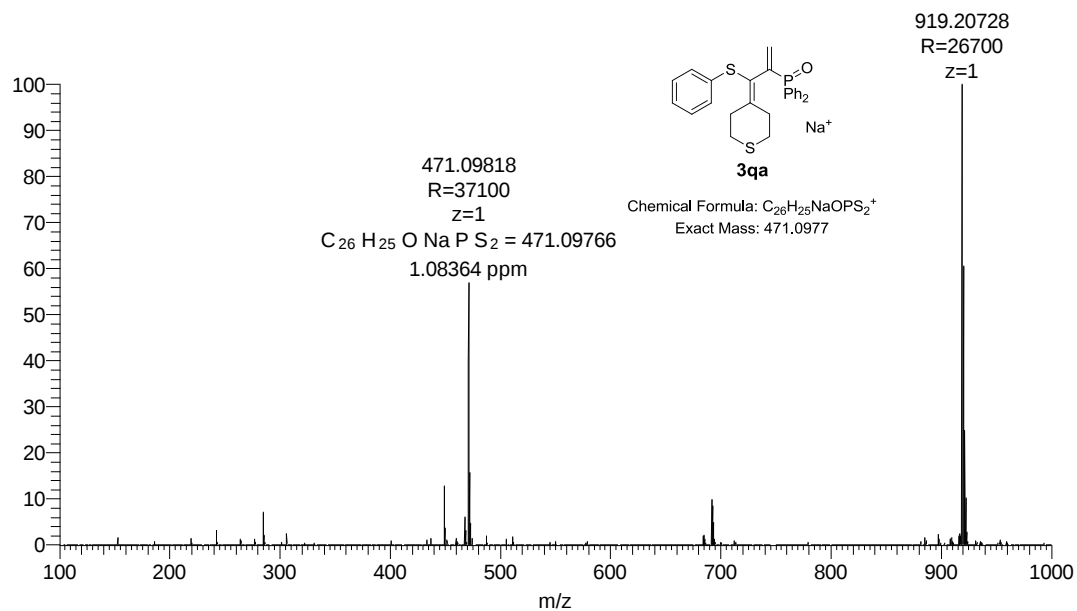


3qa

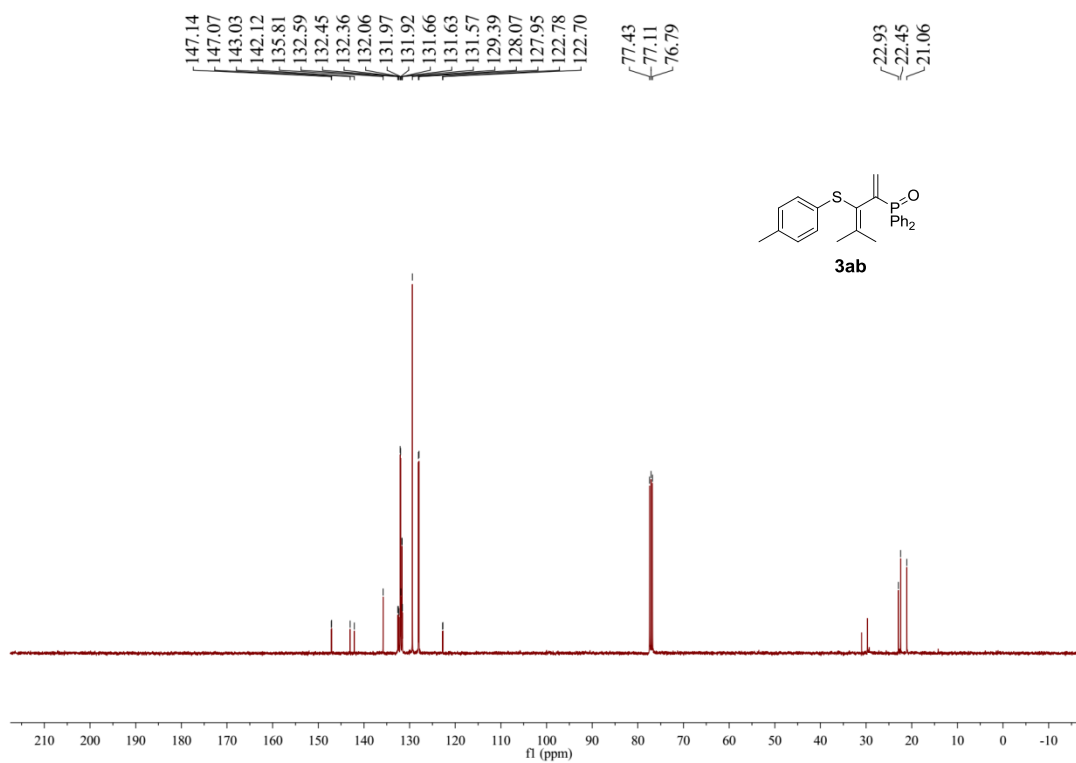
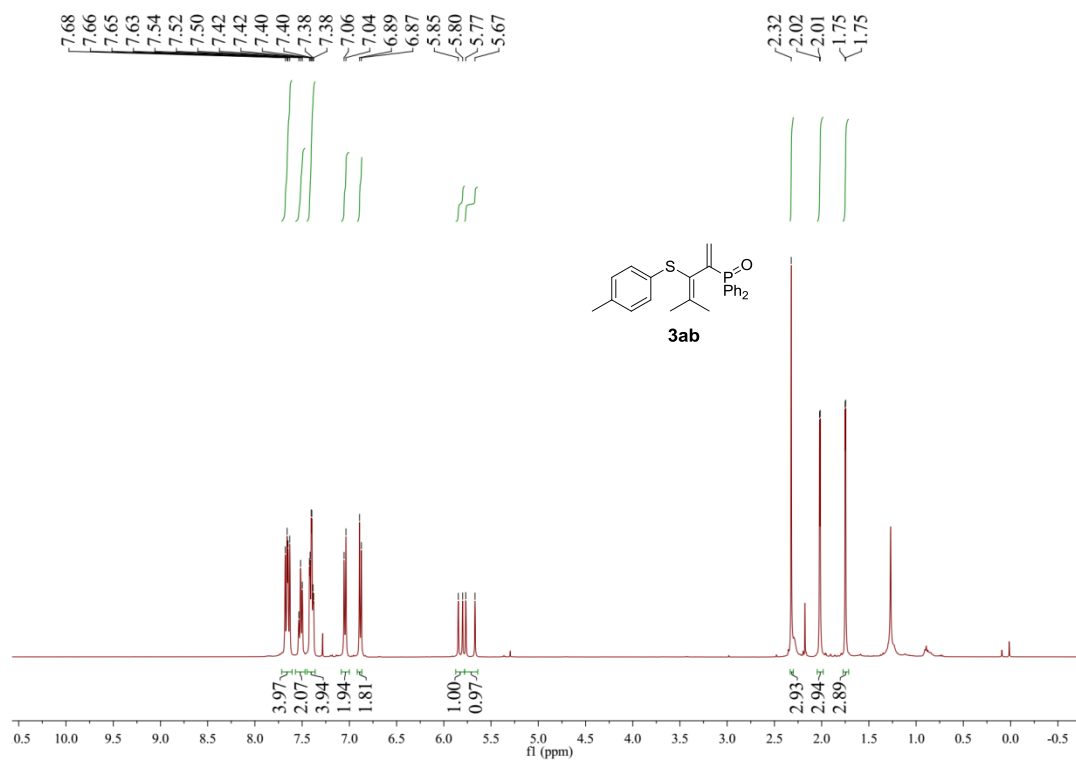


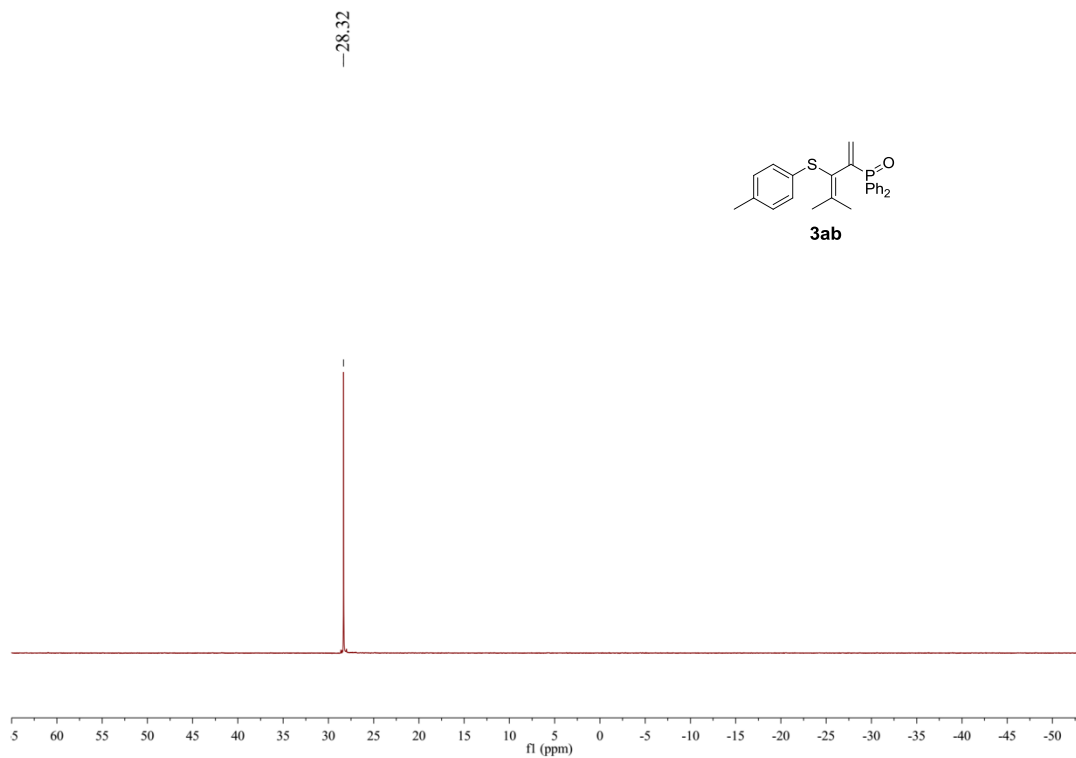


11 #30 RT: 0.30 AV: 1 NL: 1.07E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

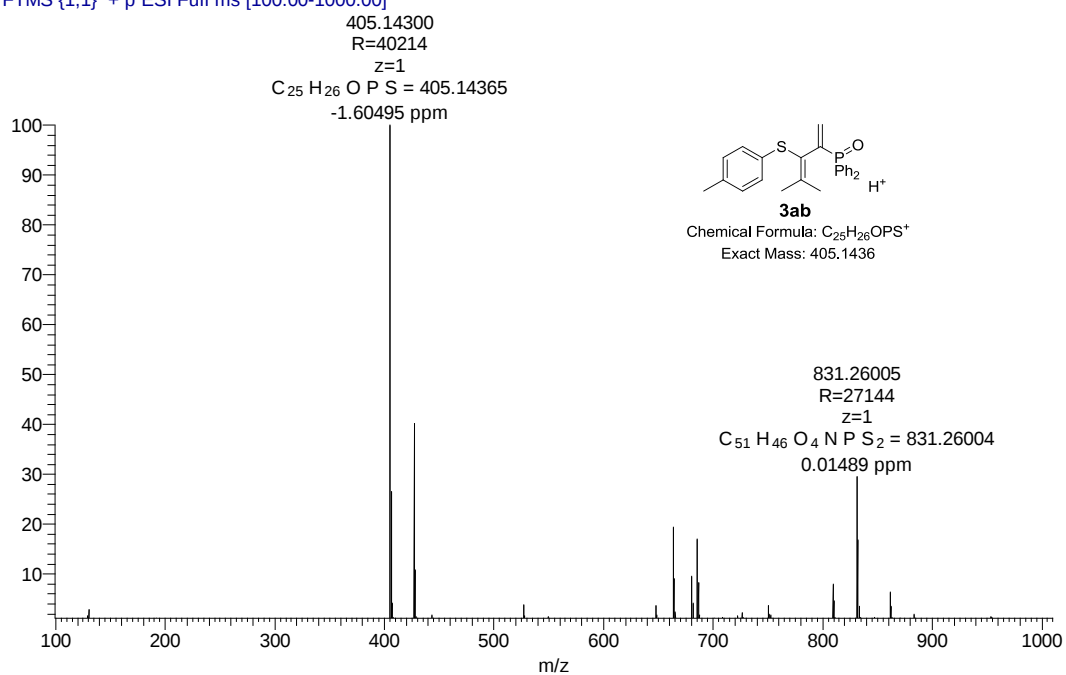


3ab

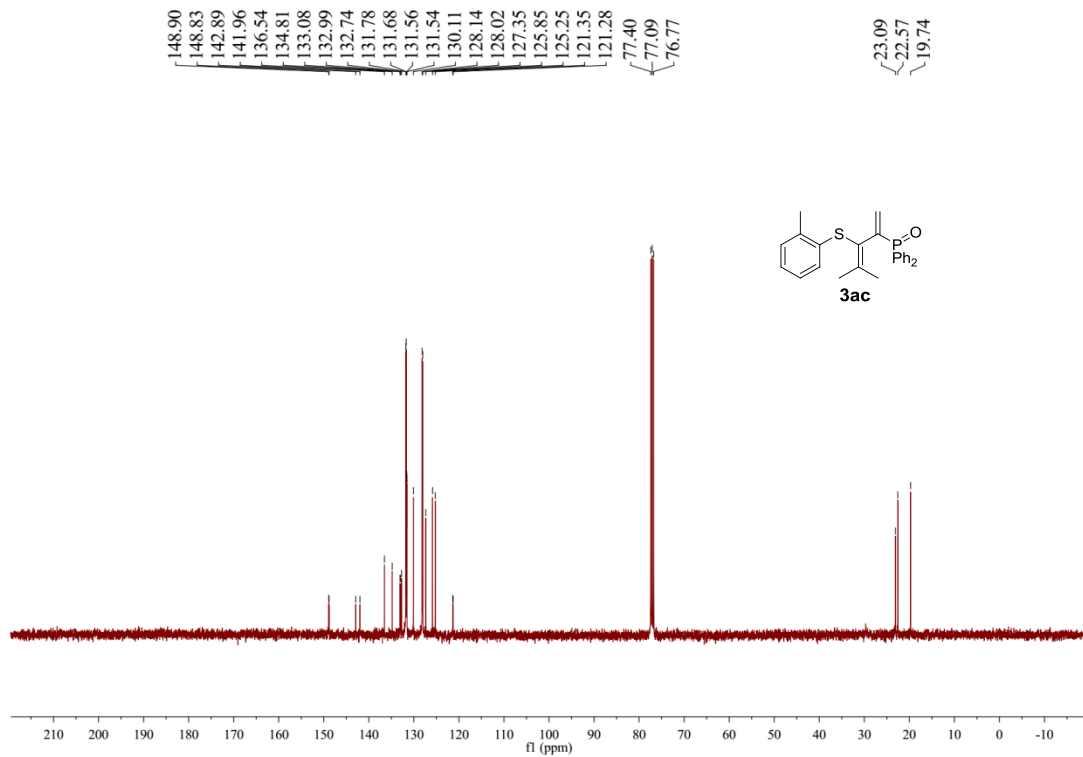
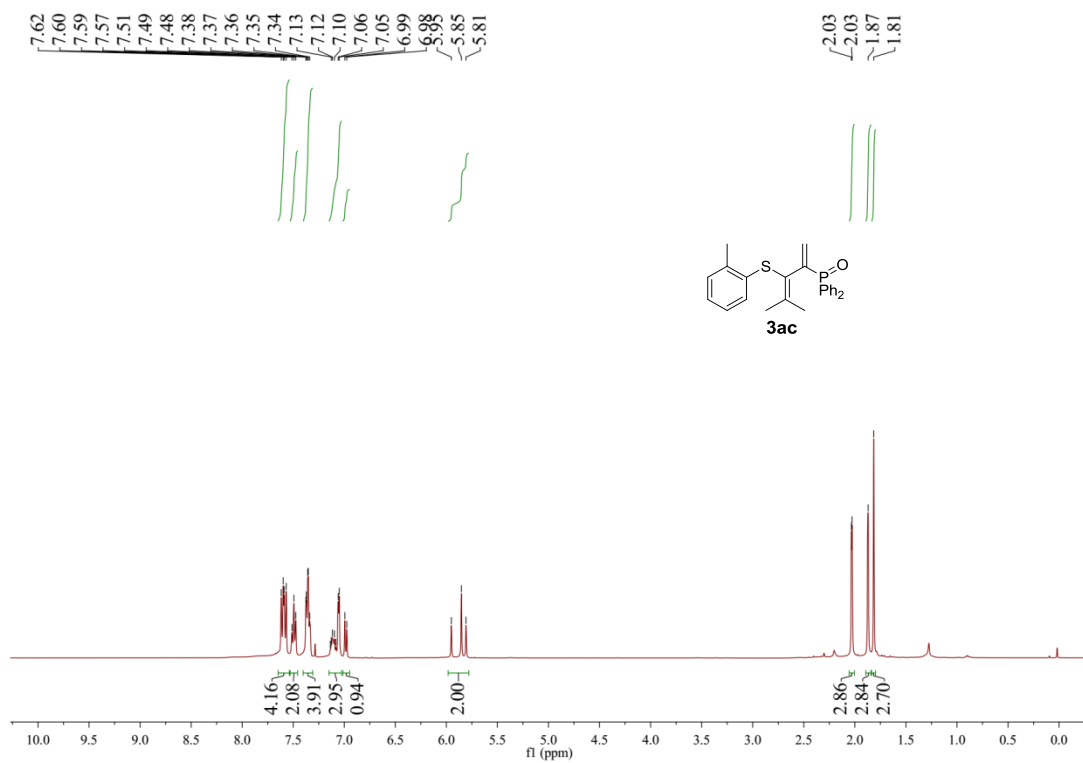


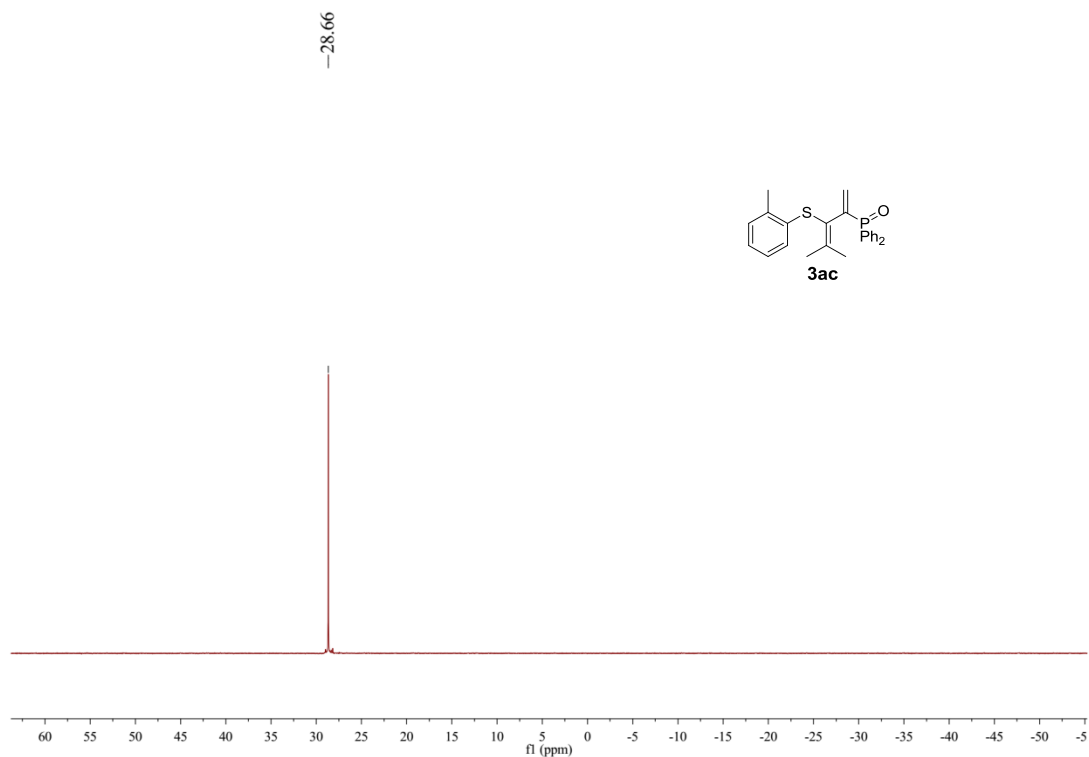


20161109-26 #36-37 RT: 0.41-0.42 AV: 2 NL: 8.99E4
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

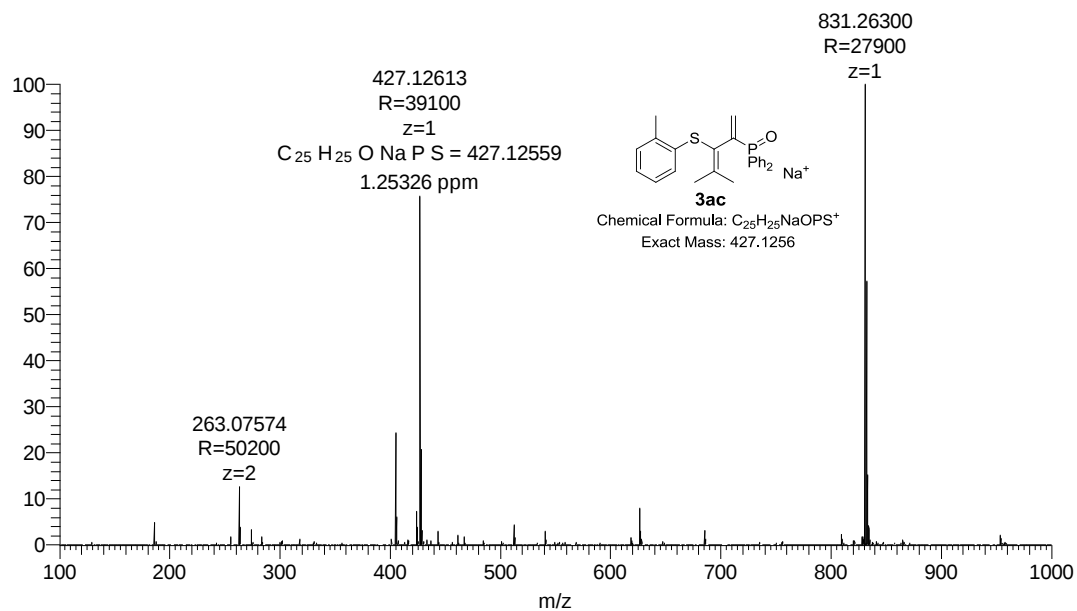


3ac

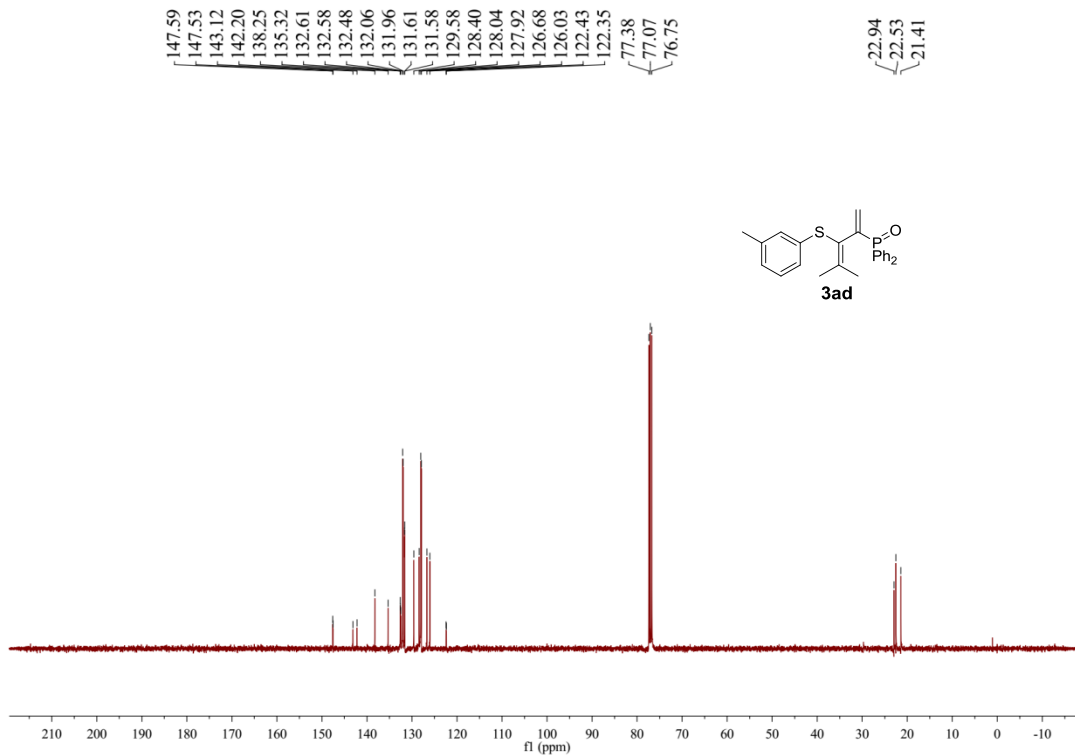
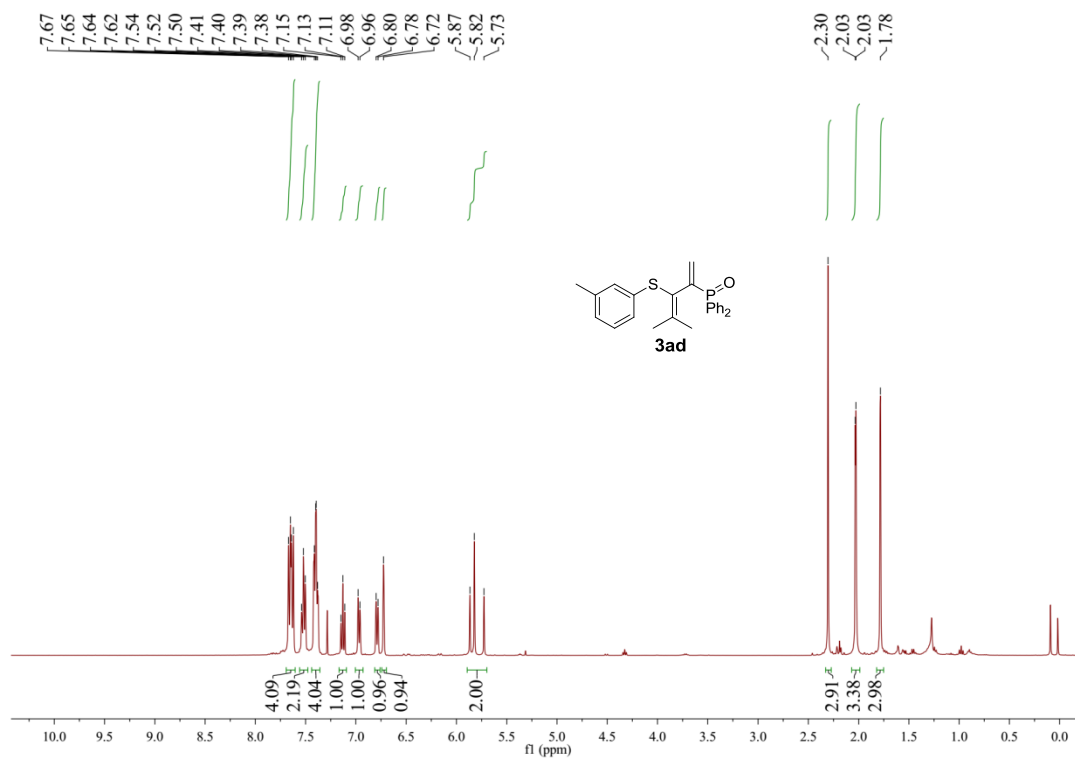


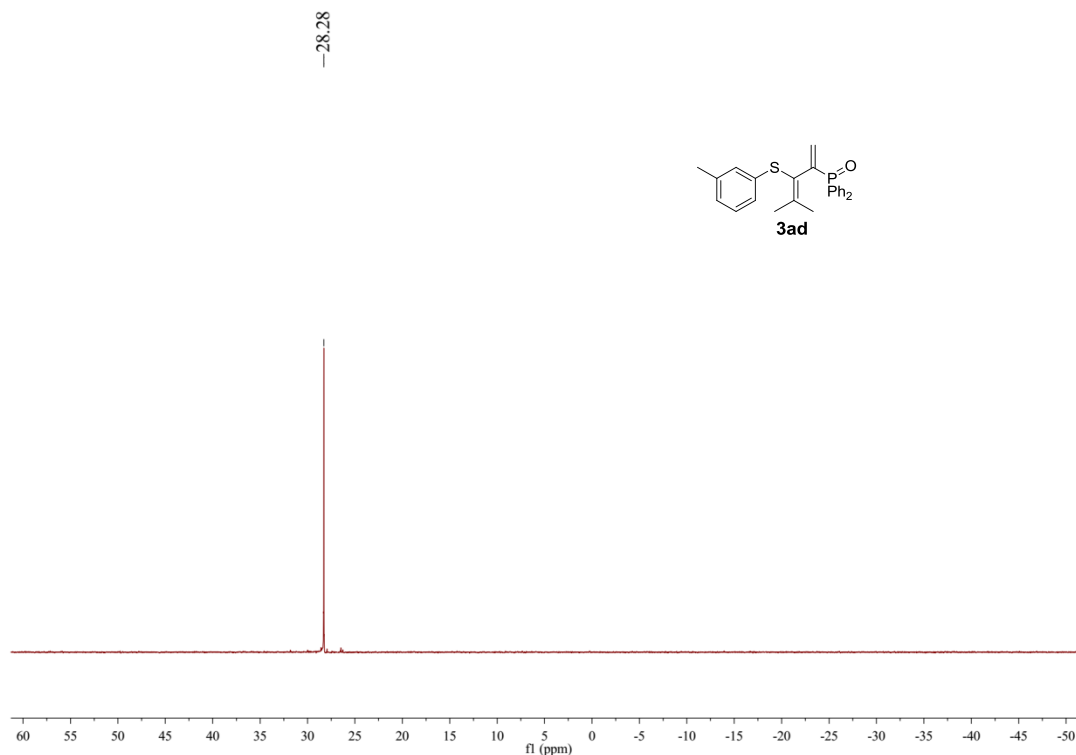


12 #43 RT: 0.41 AV: 1 NL: 8.06E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

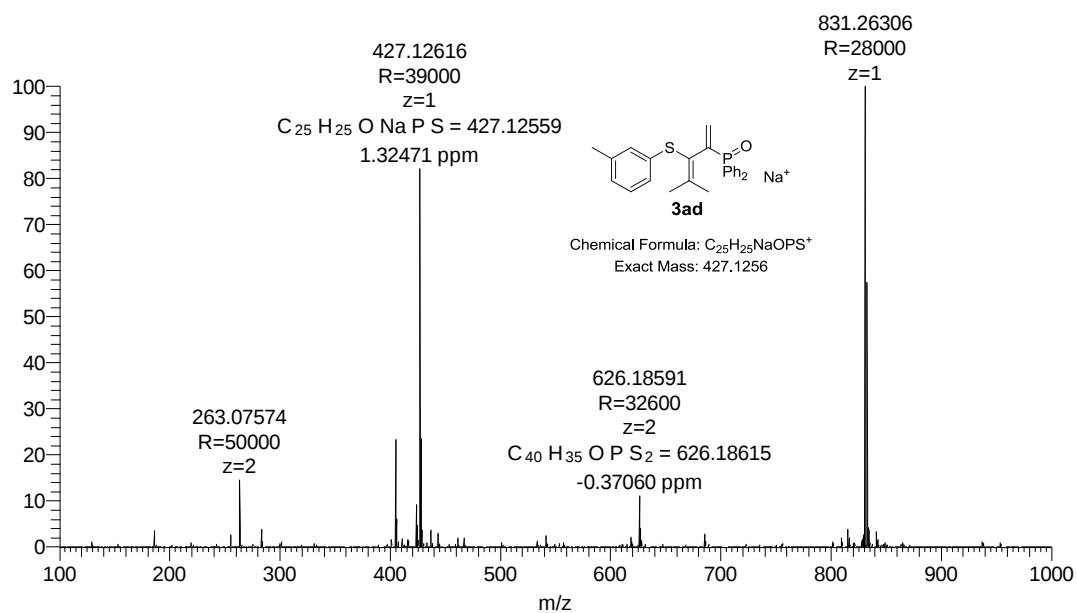


3ad

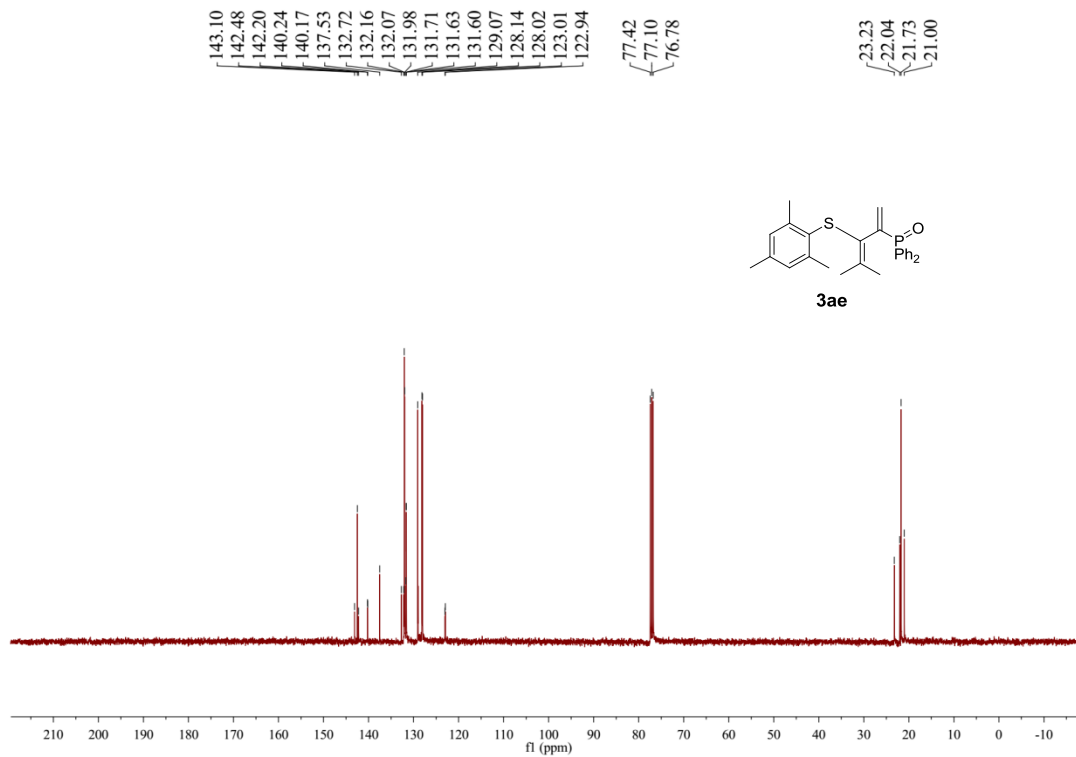
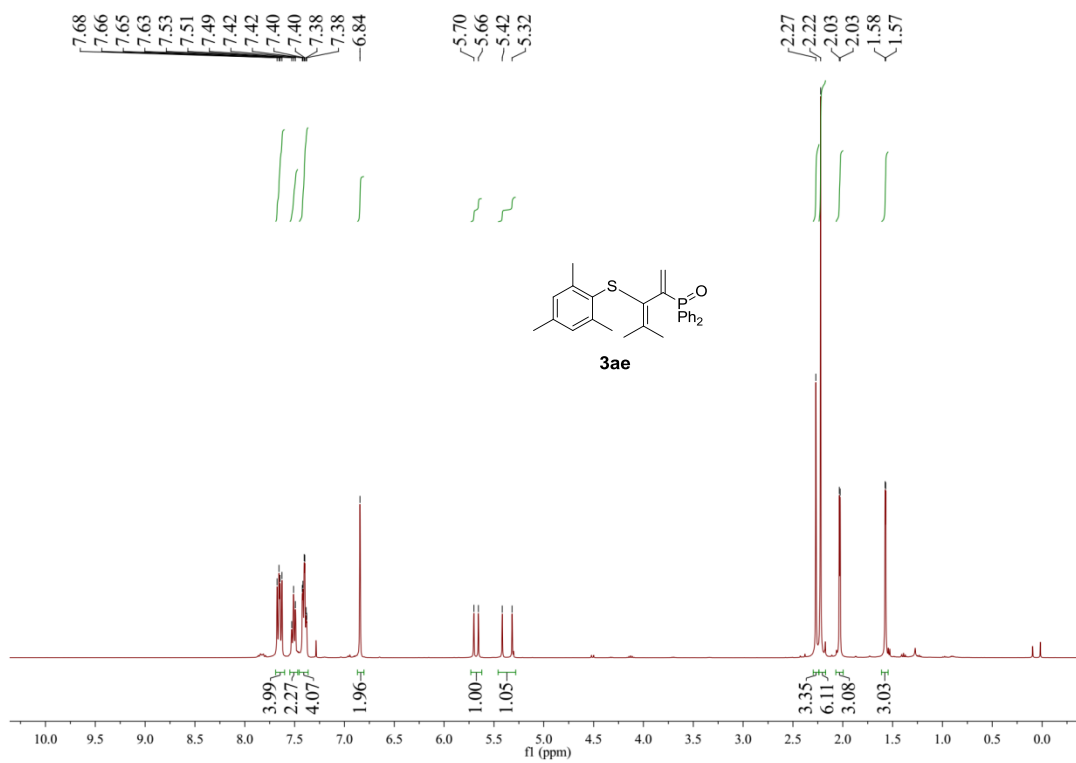


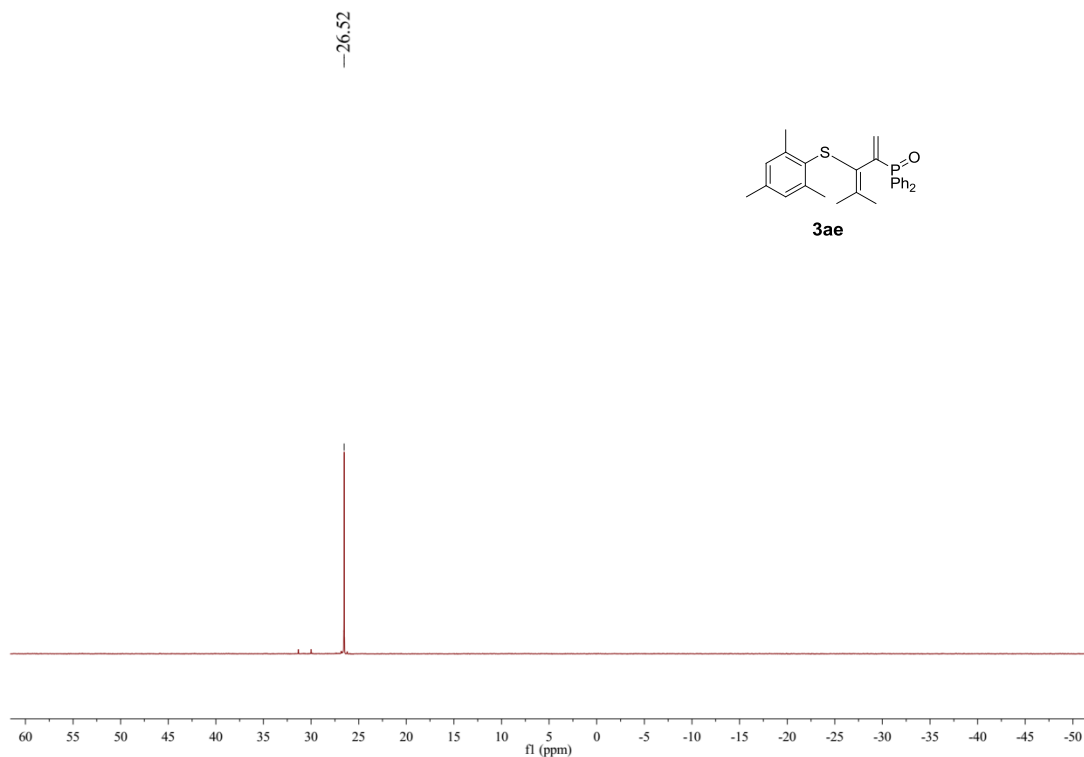


17 #38 RT: 0.36 AV: 1 NL: 6.17E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

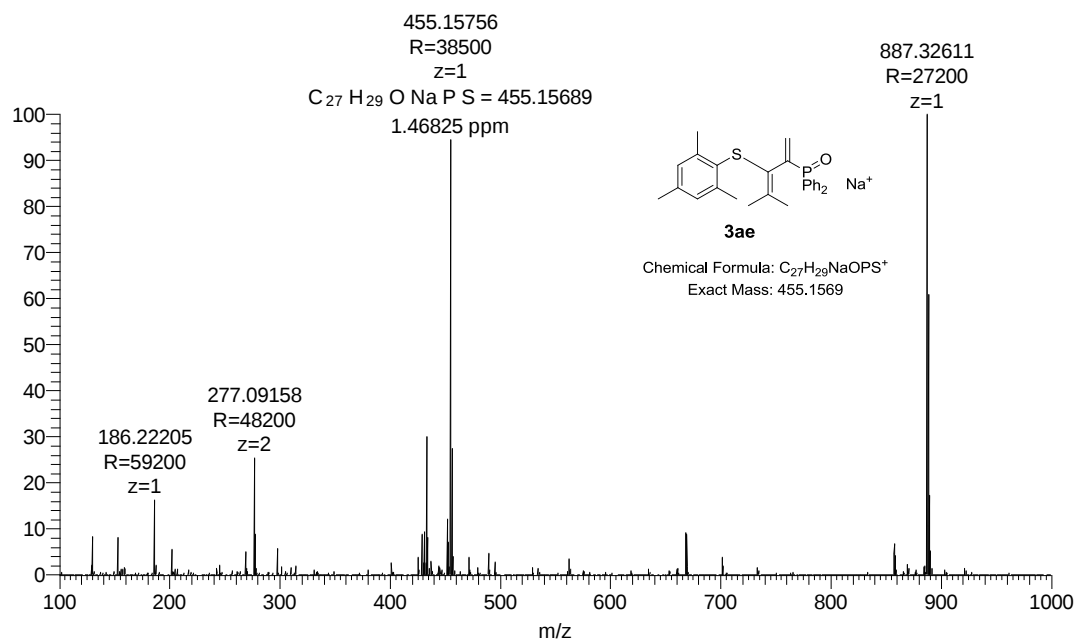


3ae

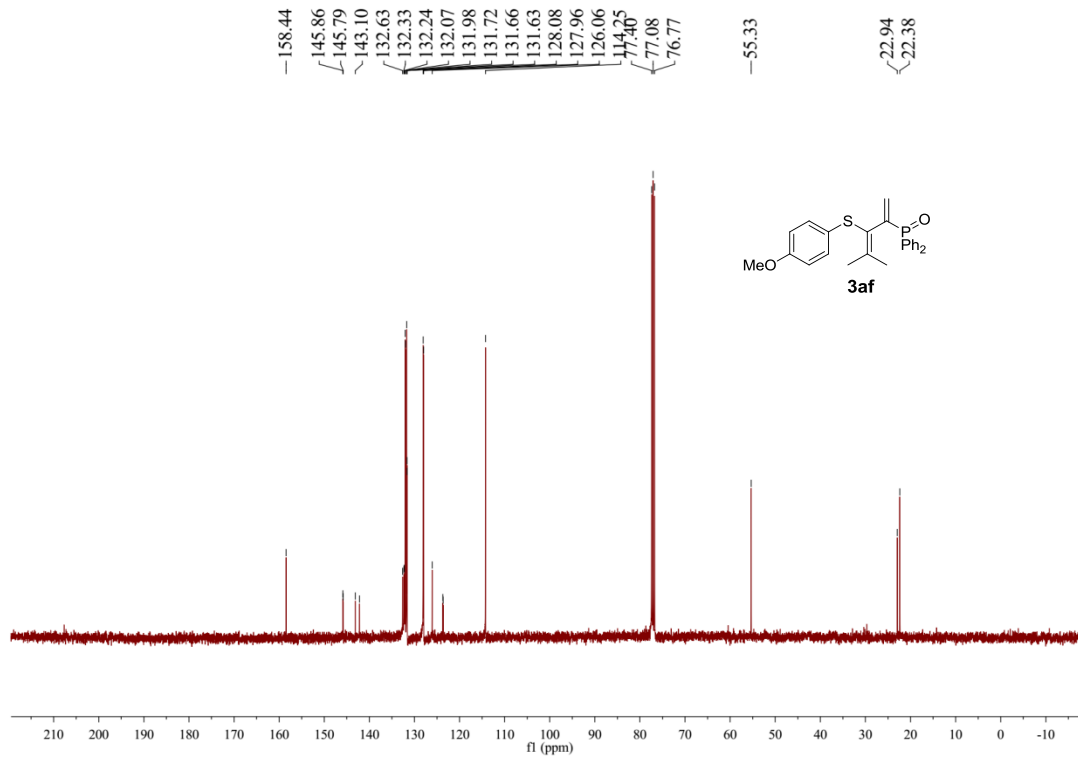
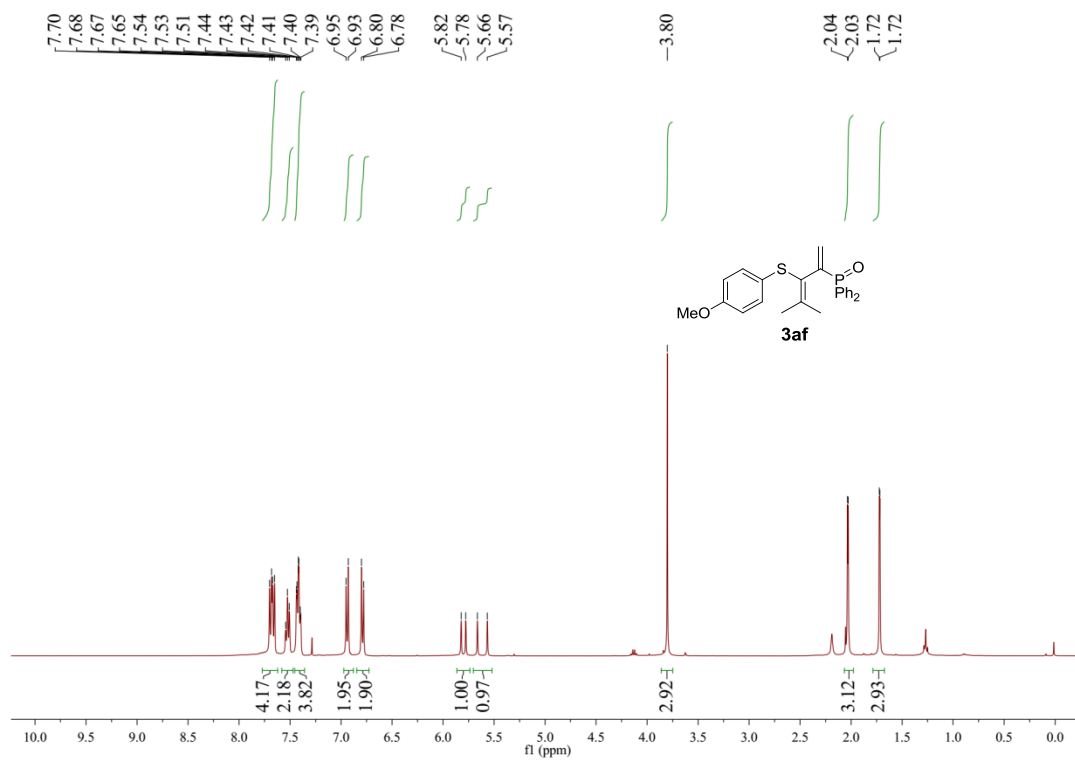


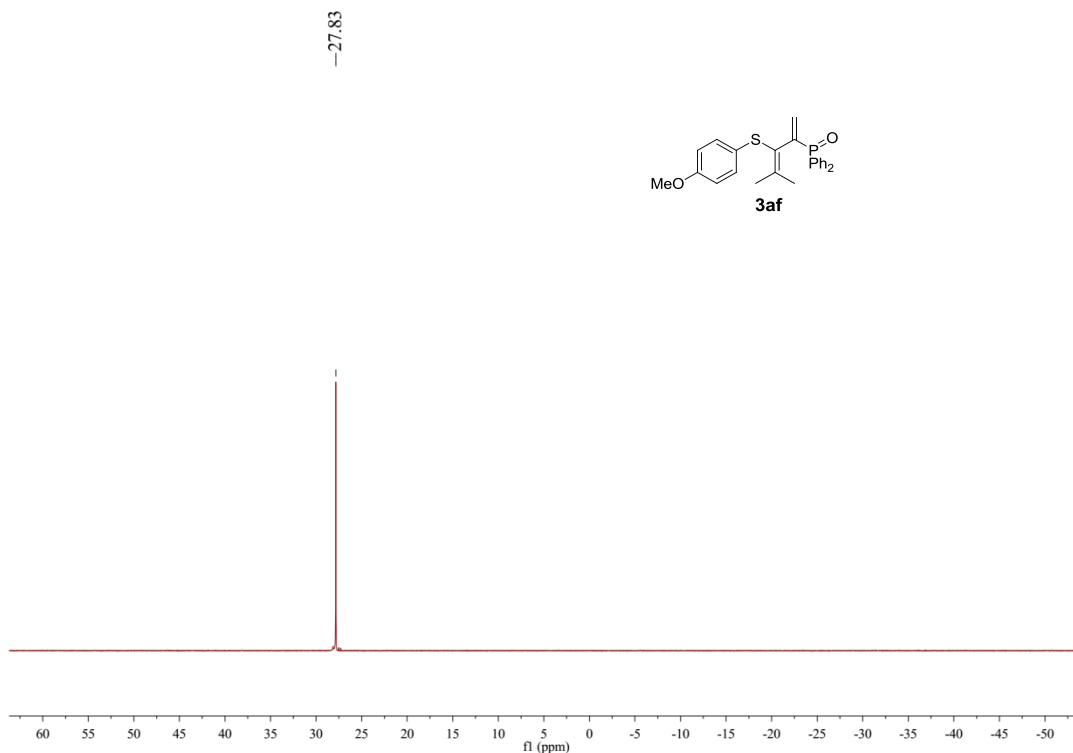


18 #28 RT: 0.28 AV: 1 NL: 3.97E5
 T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

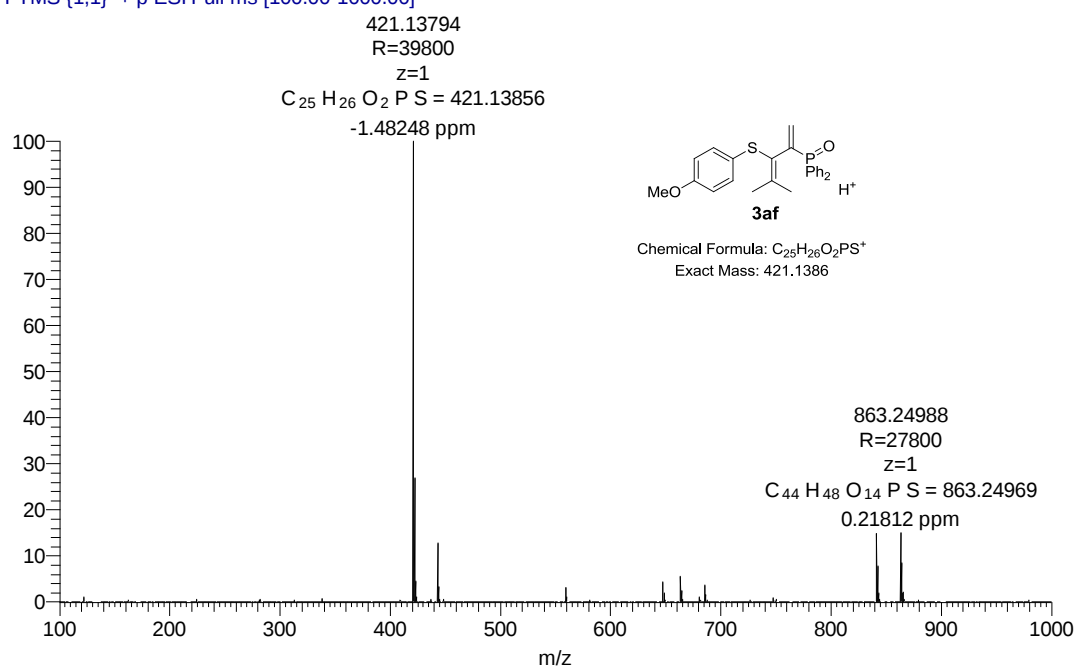


3af

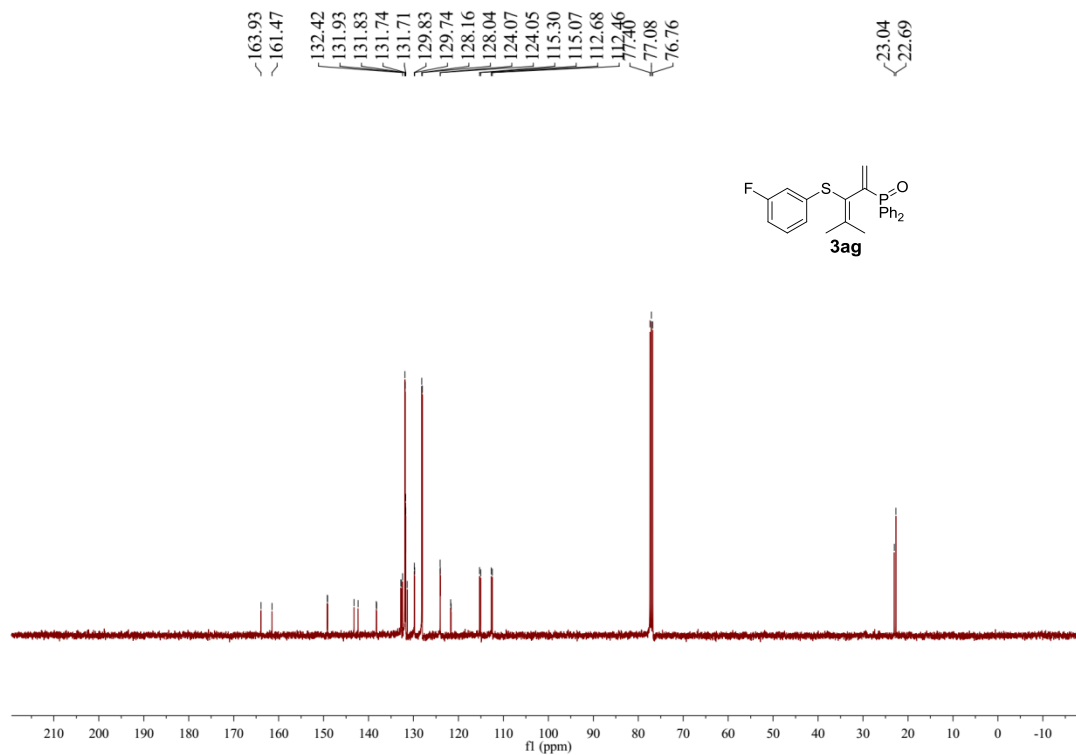
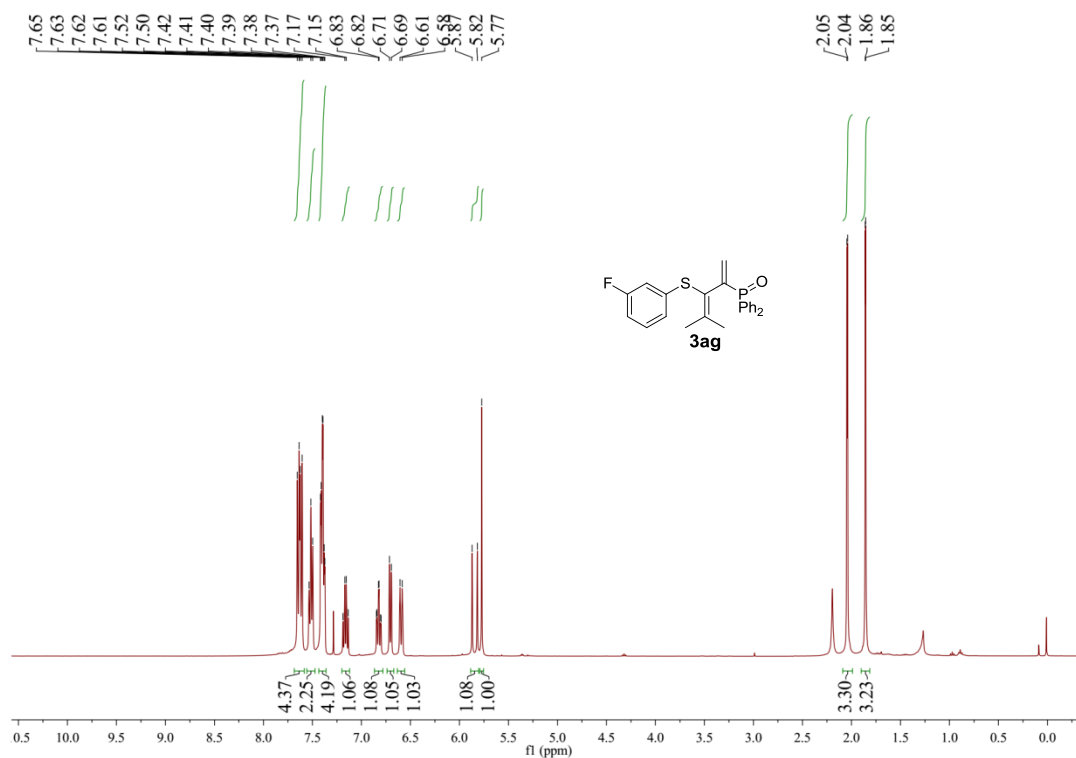


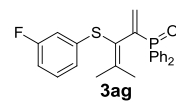
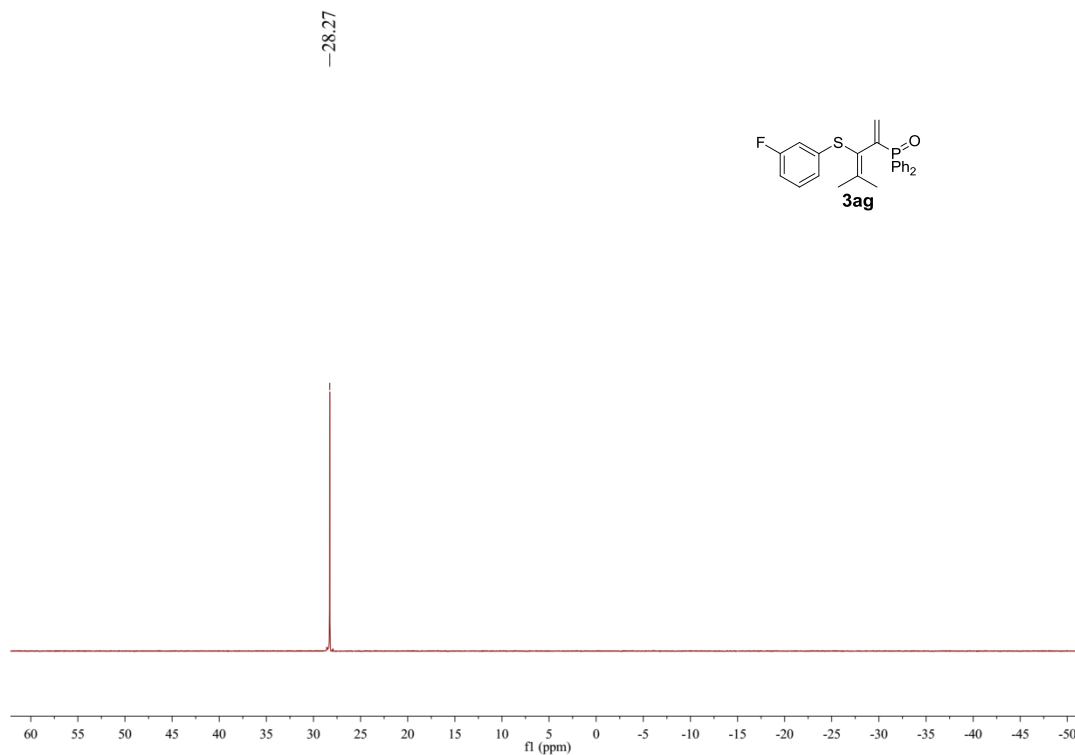


20170117-18 #43 RT: 0.45 AV: 1 NL: 9.11E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

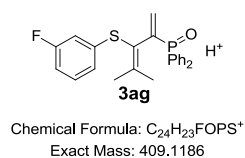
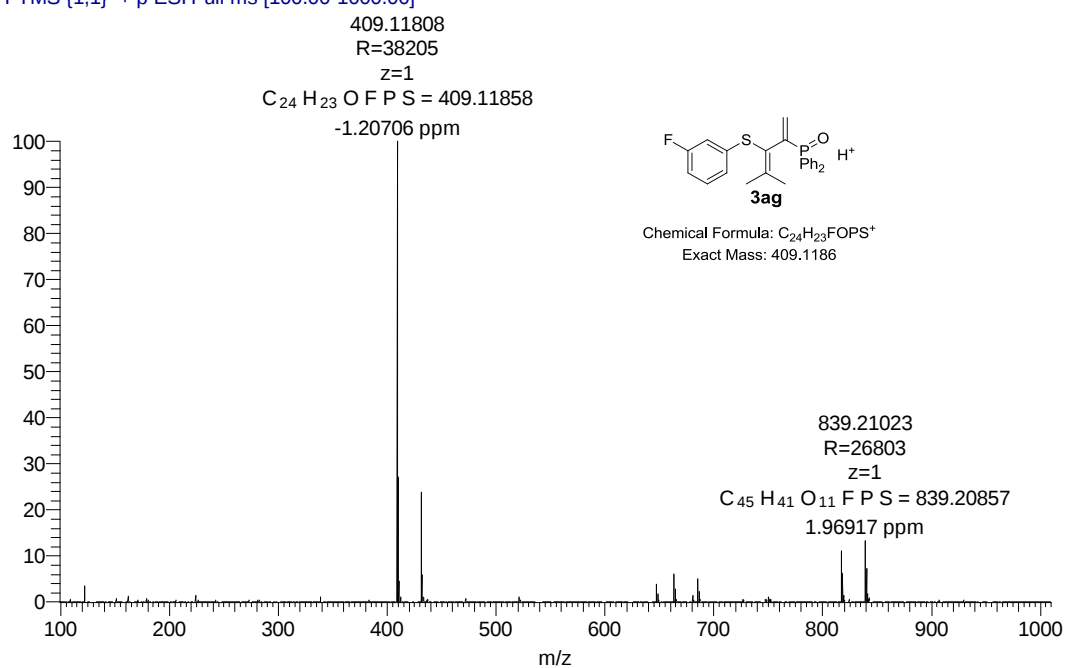


3ag



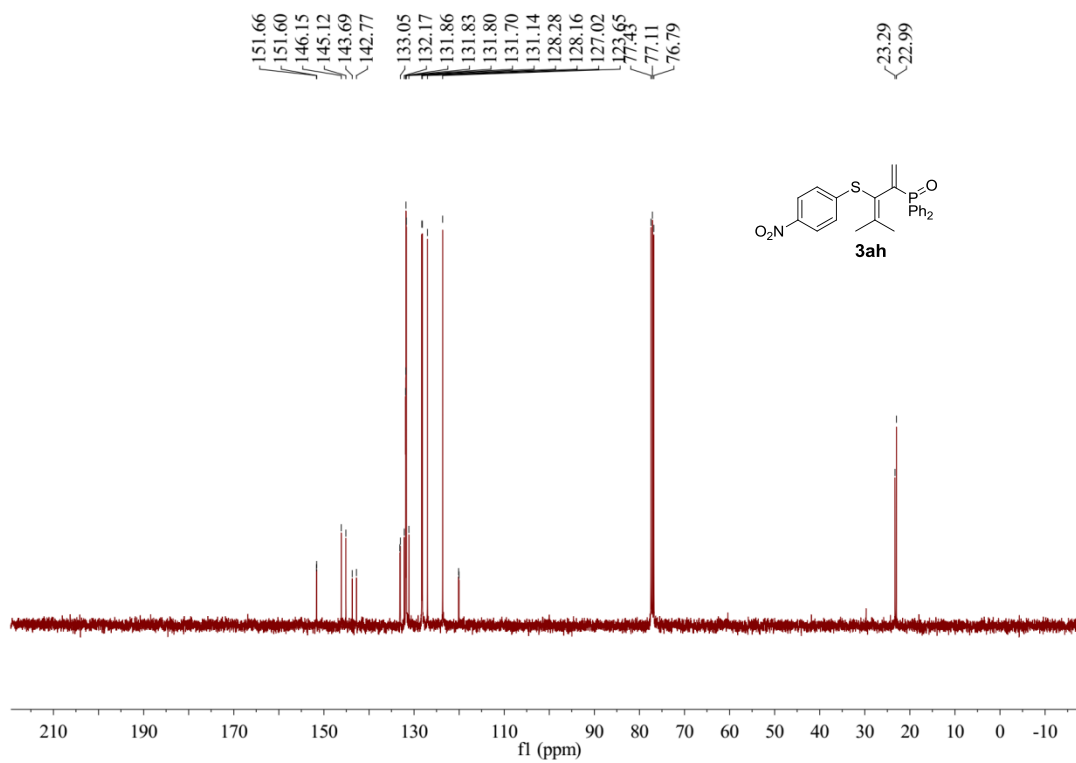
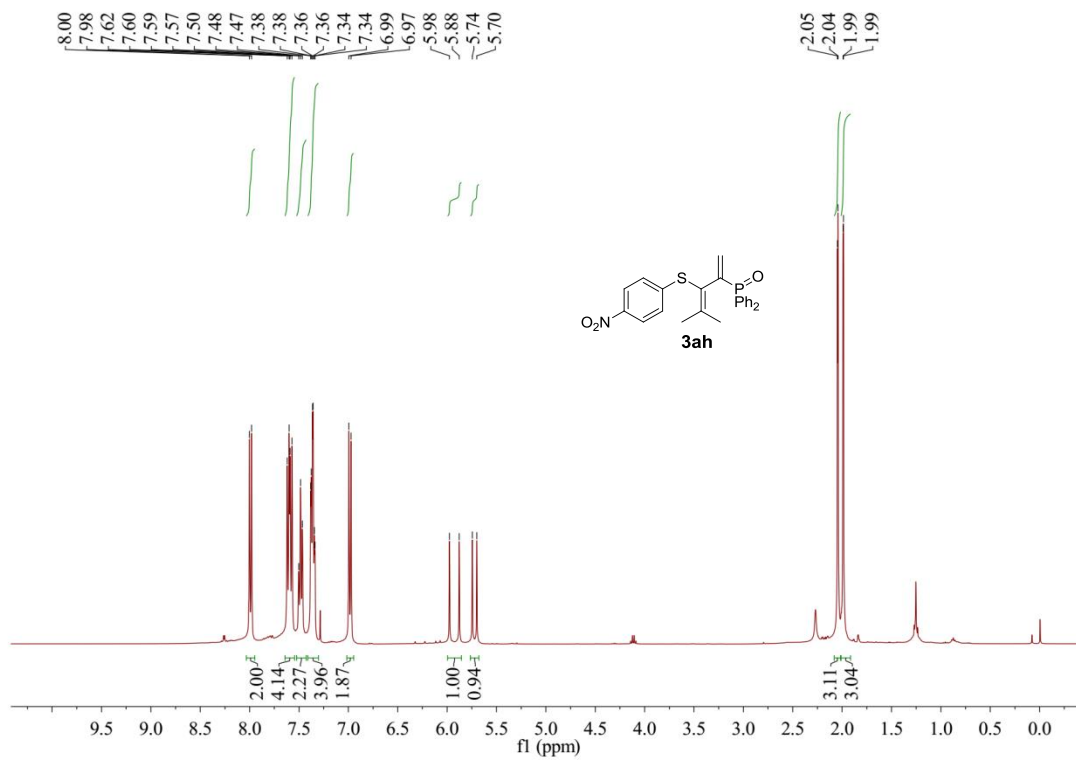


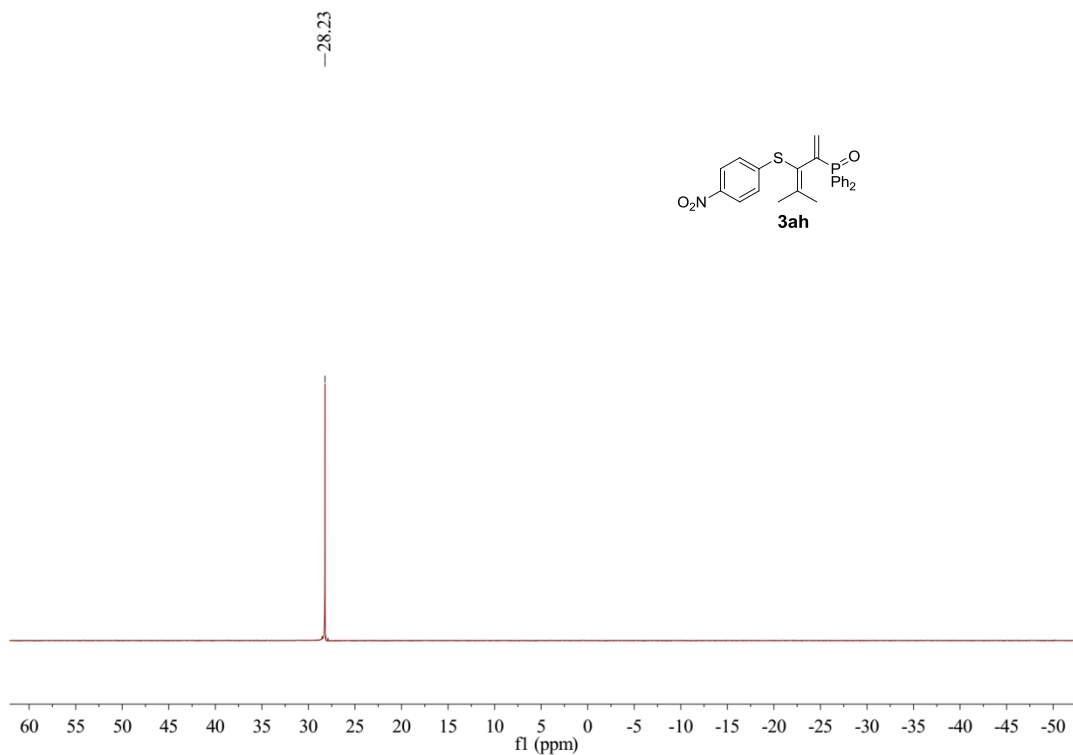
20170117-11 #43-44 RT: 0.44-0.45 AV: 2 NL: 5.37E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]



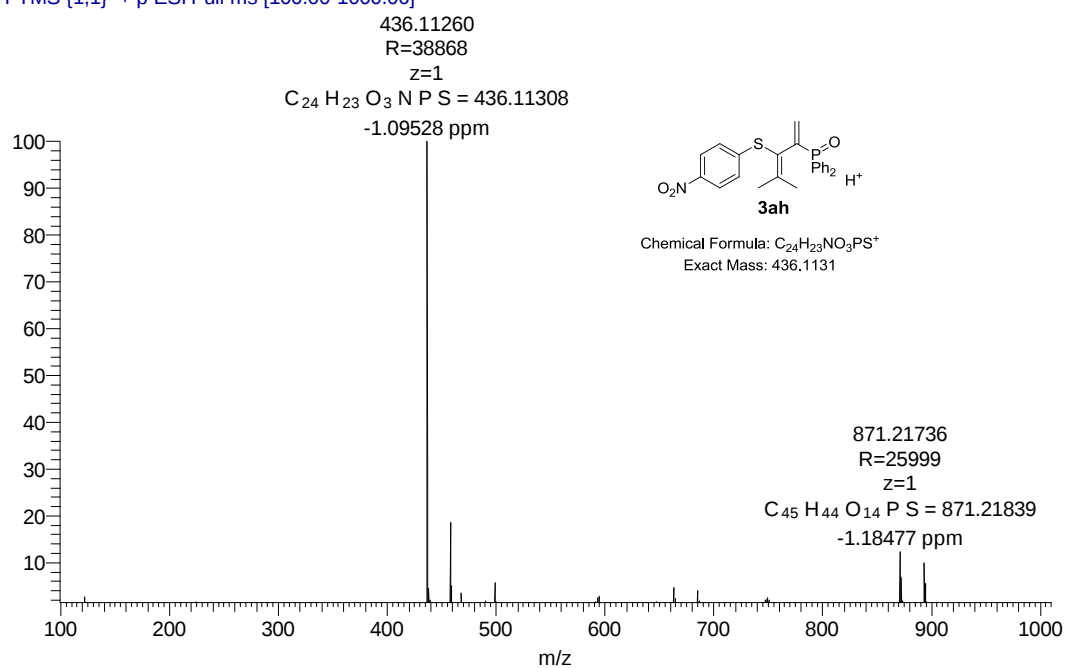
839.21023
R=26803
z=1
C₄₅ H₄₁ O₁₁ F P S = 839.20857
1.96917 ppm

3ah

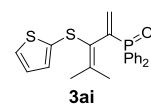
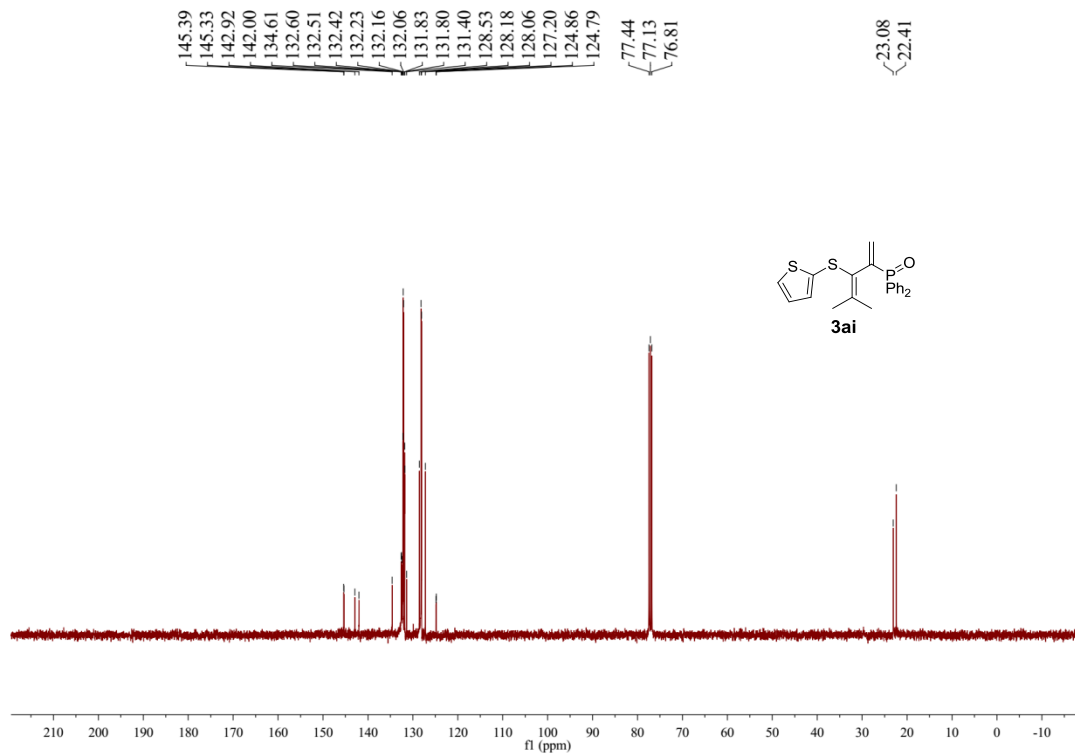
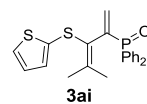
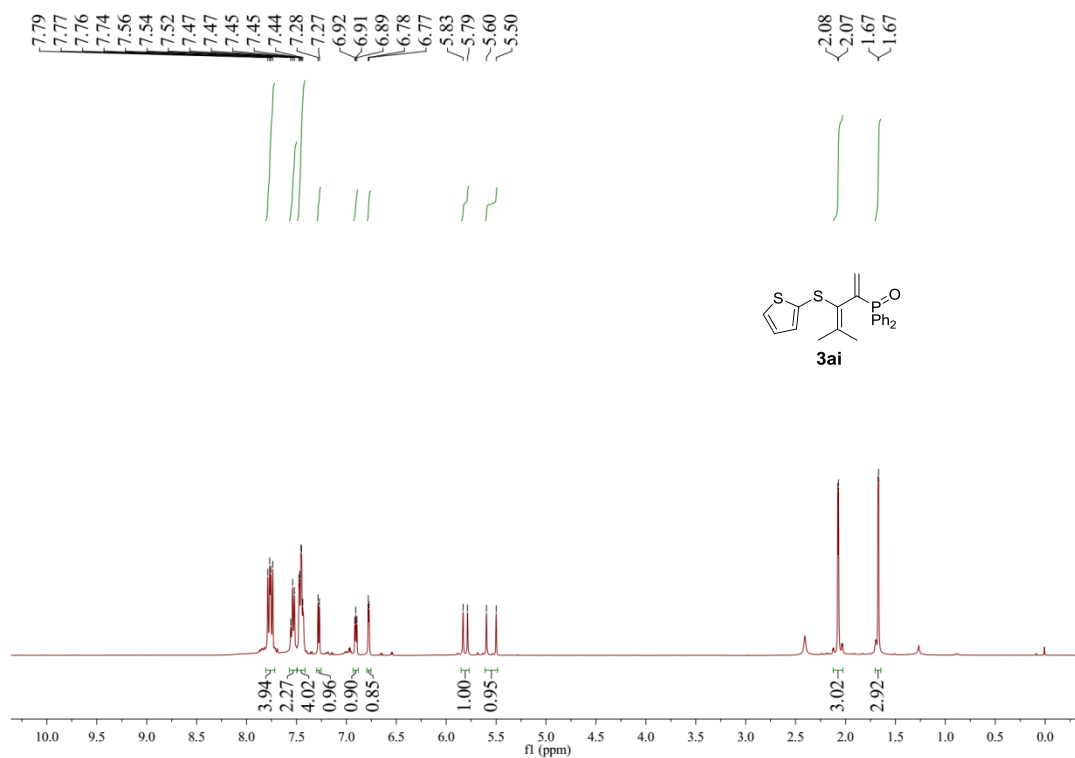


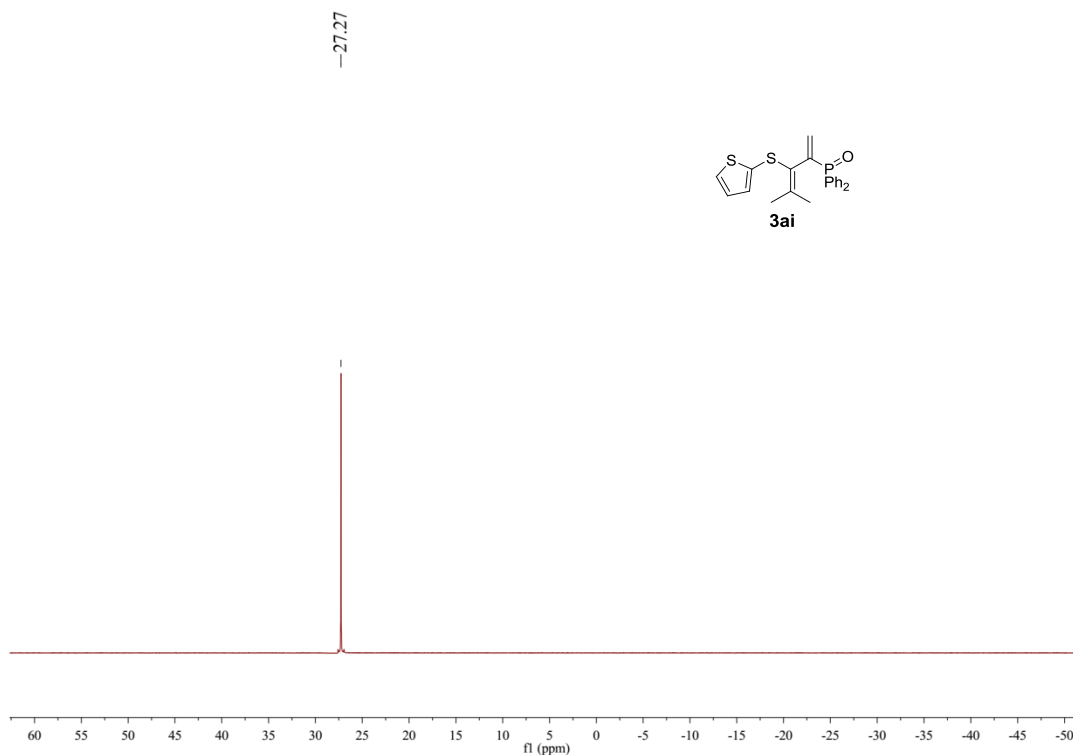


20170117-20 #37-38 RT: 0.40-0.41 AV: 2 NL: 4.80E5
 T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

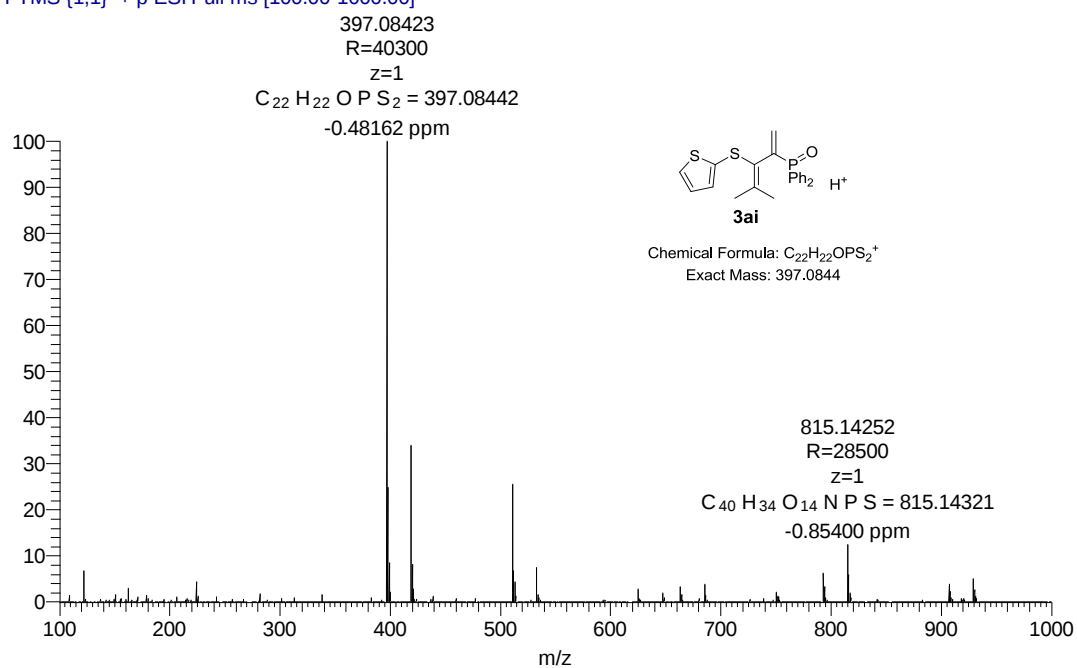


3ai

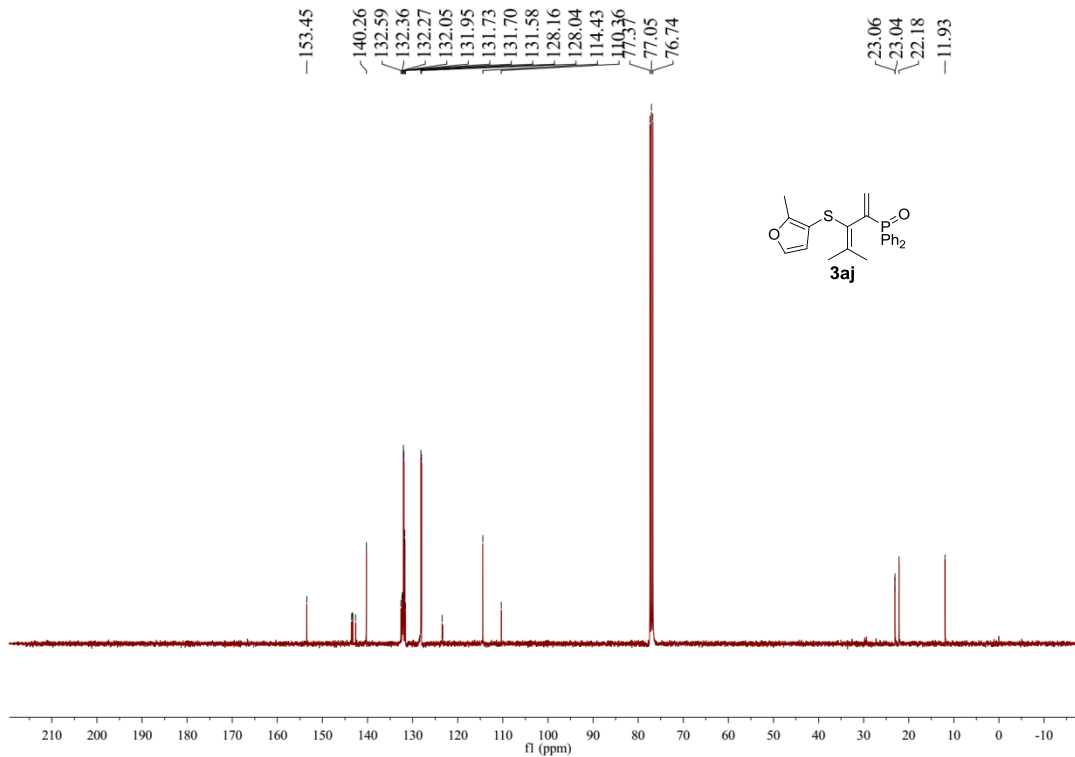
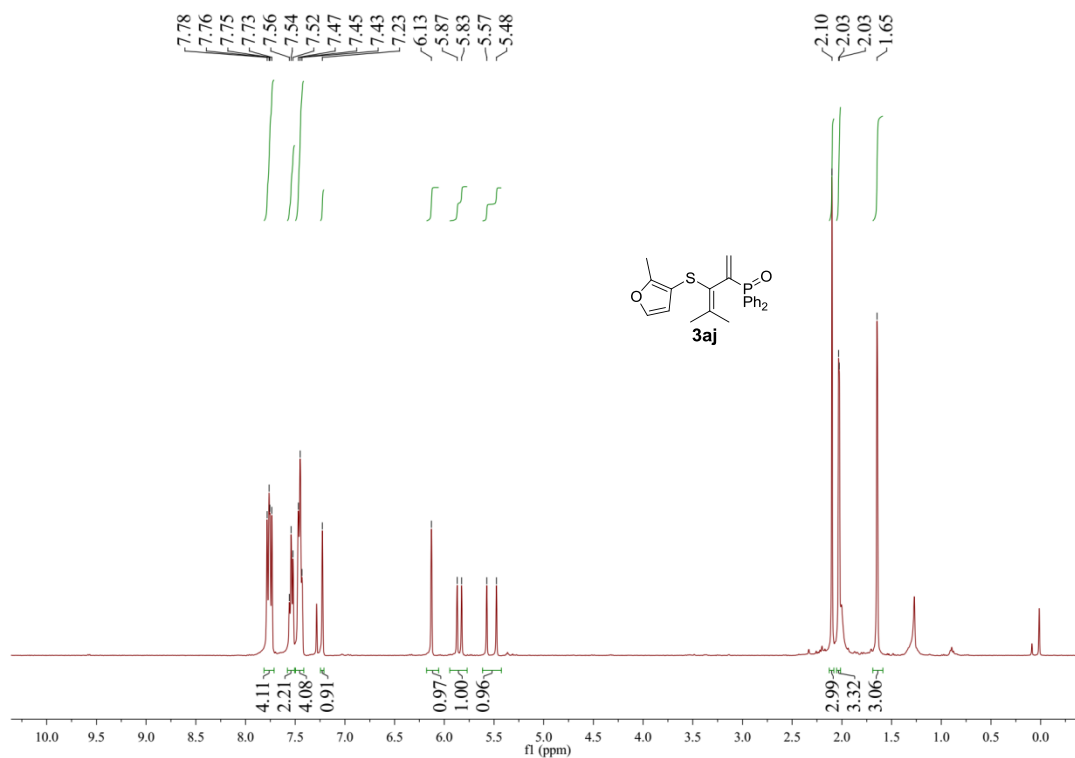


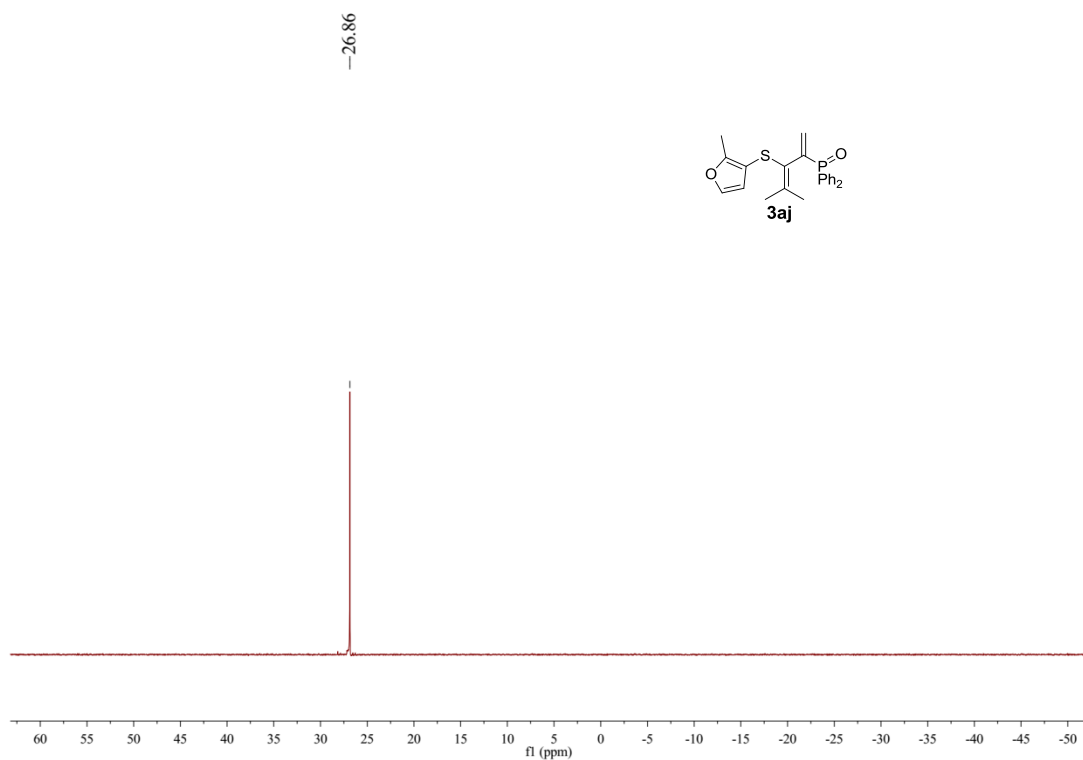


20170117-21 #44 RT: 0.46 AV: 1 NL: 1.80E5
 T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

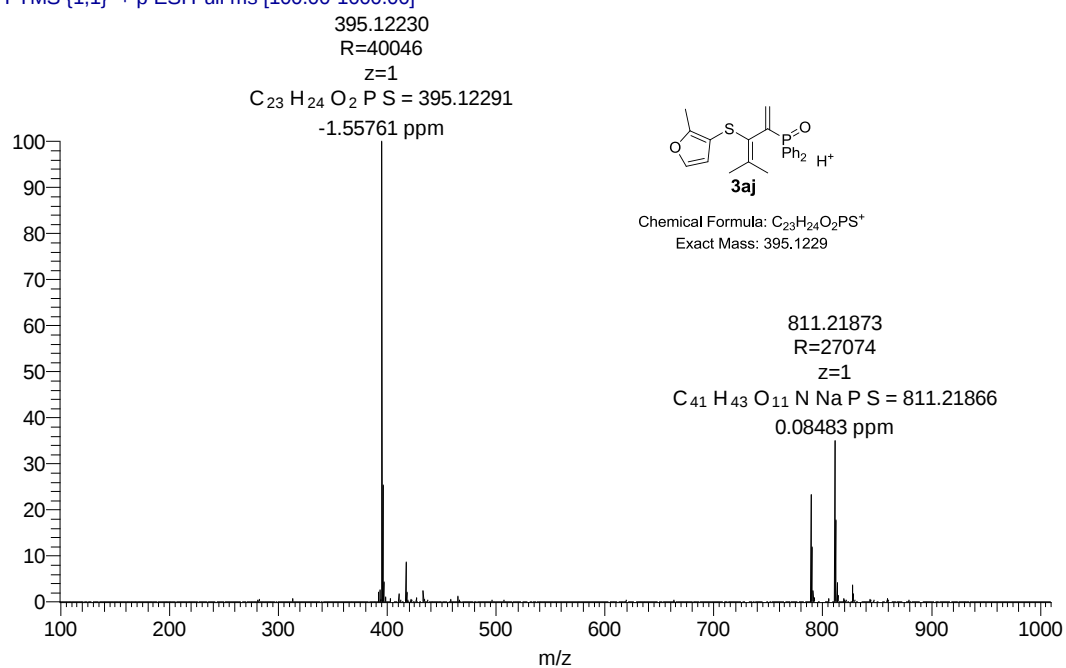


3aj

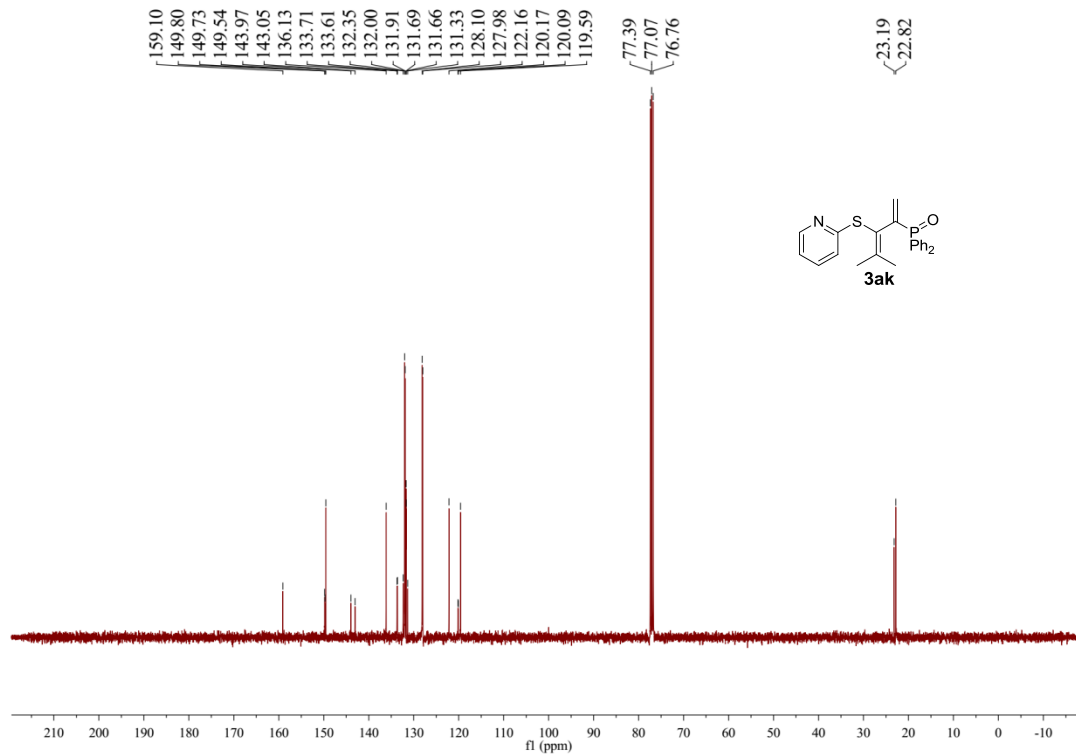
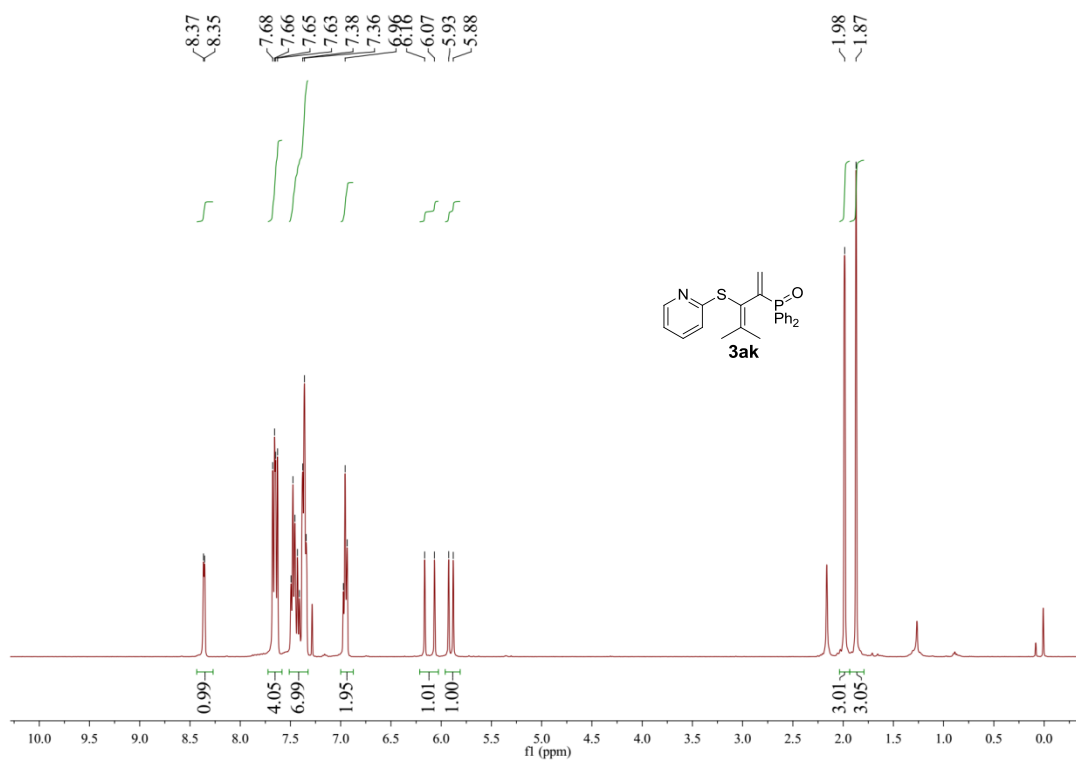


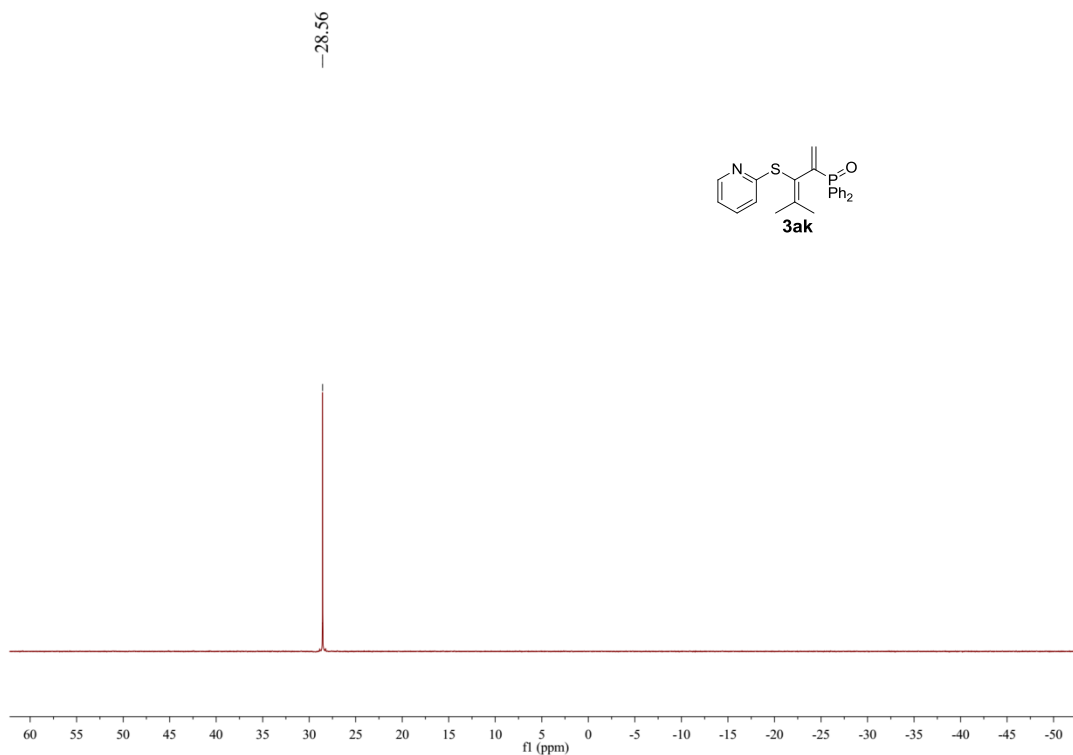


20170117-13 #31-32 RT: 0.32-0.33 AV: 2 NL: 1.64E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]



3ak





20170117-12 #43 RT: 0.43 AV: 1 NL: 1.54E6

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

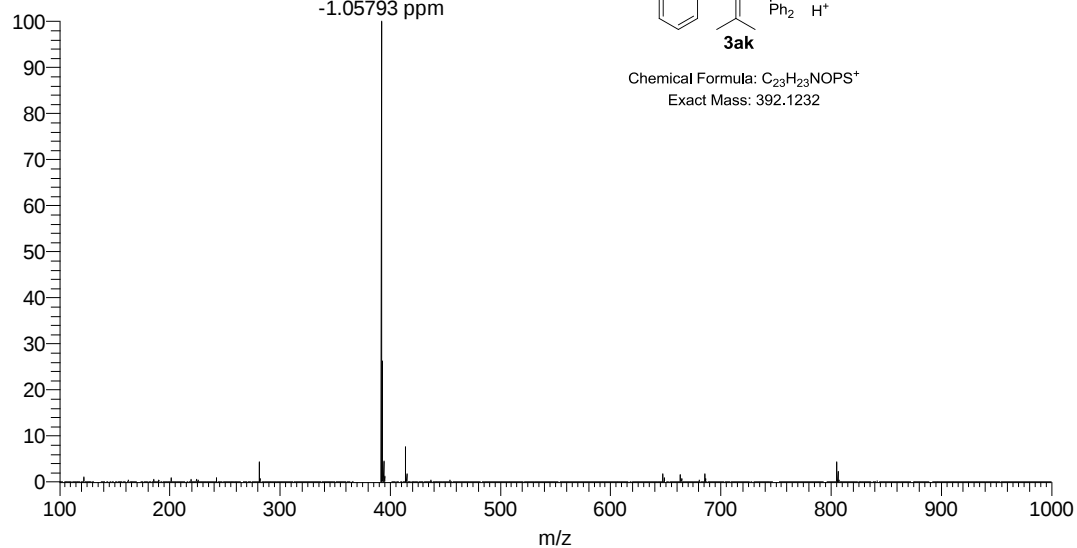
392.12283

R=40800

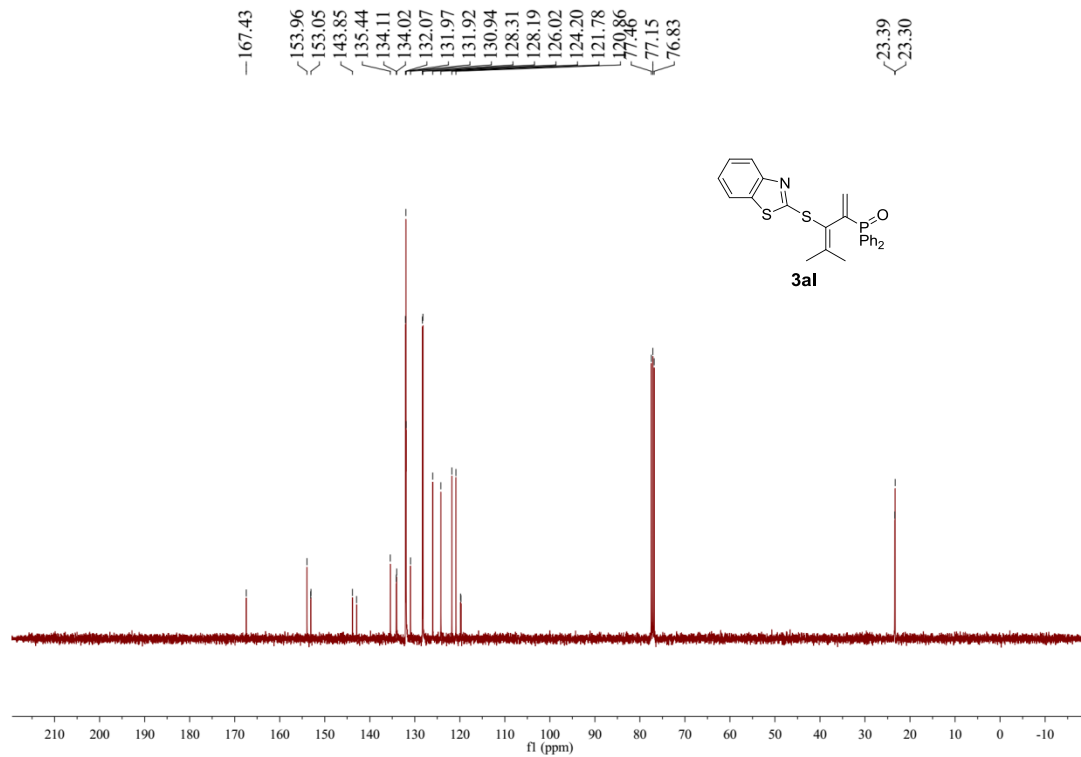
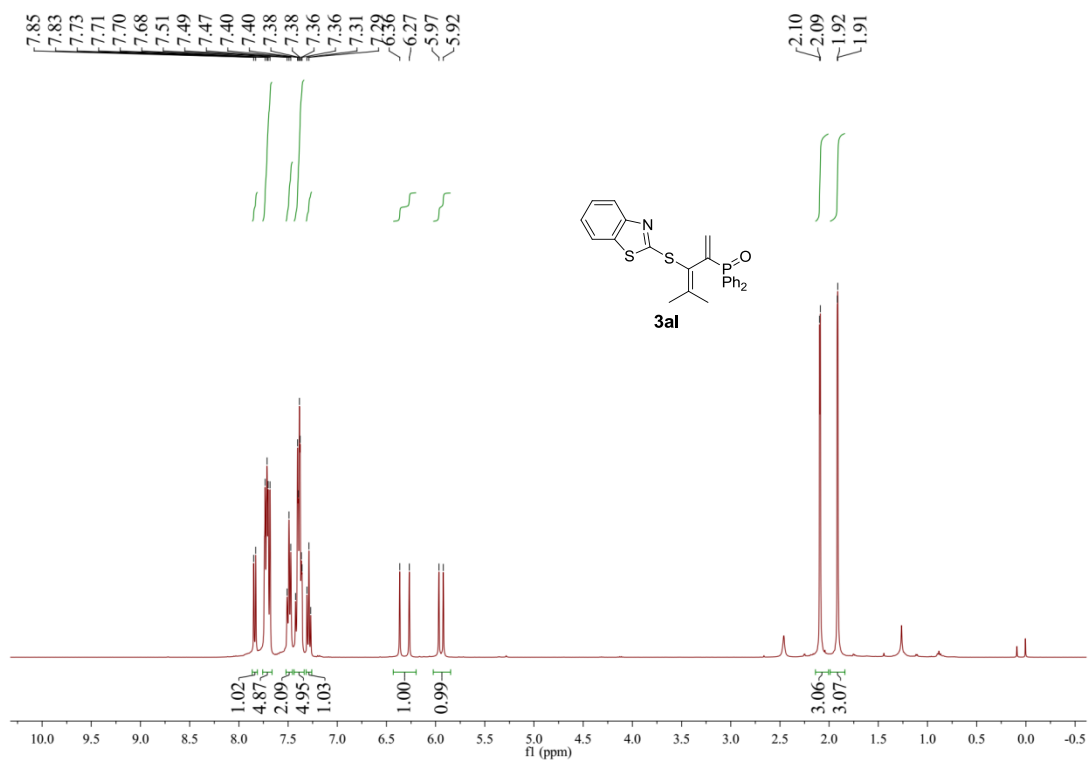
z=1

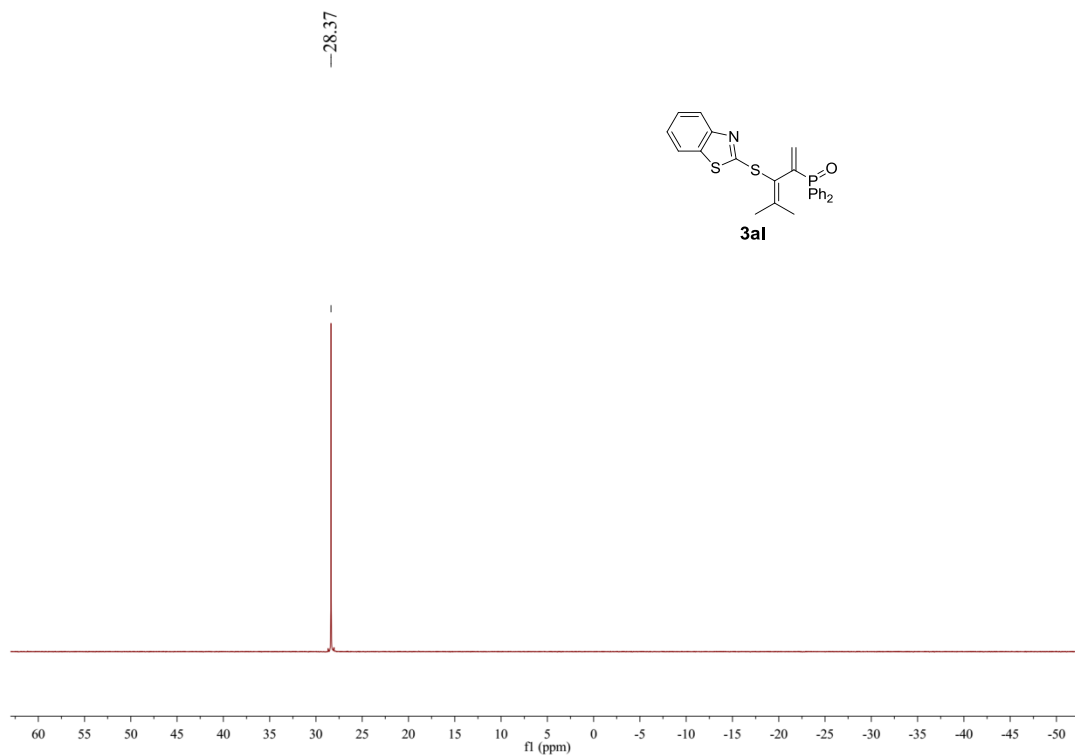
C₂₃ H₂₃ O N P S = 392.12325

-1.05793 ppm



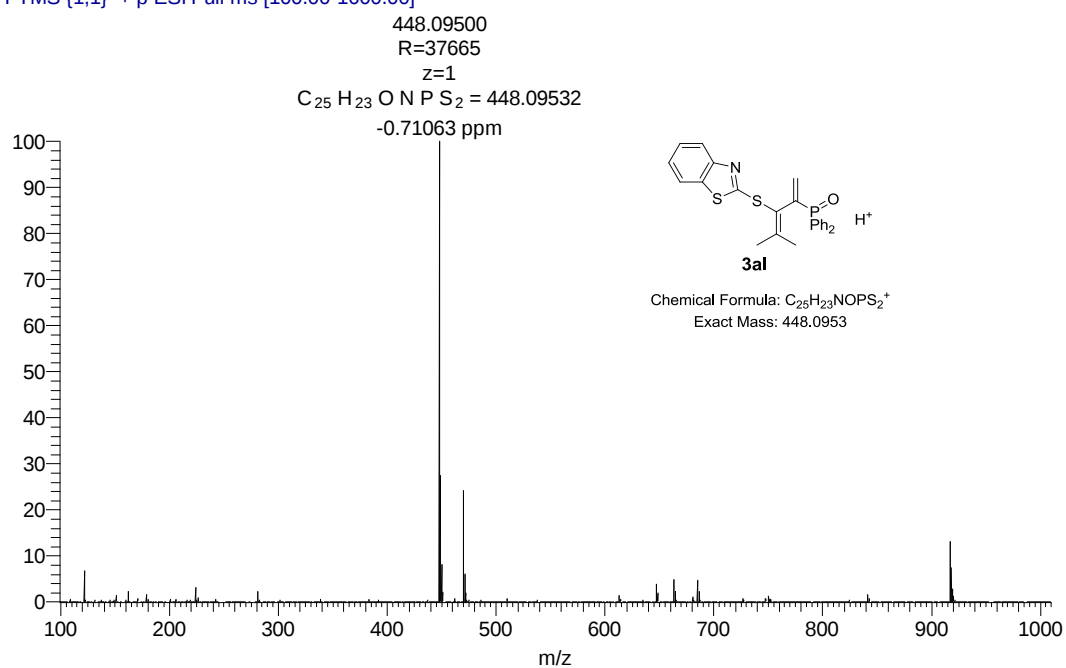
3al



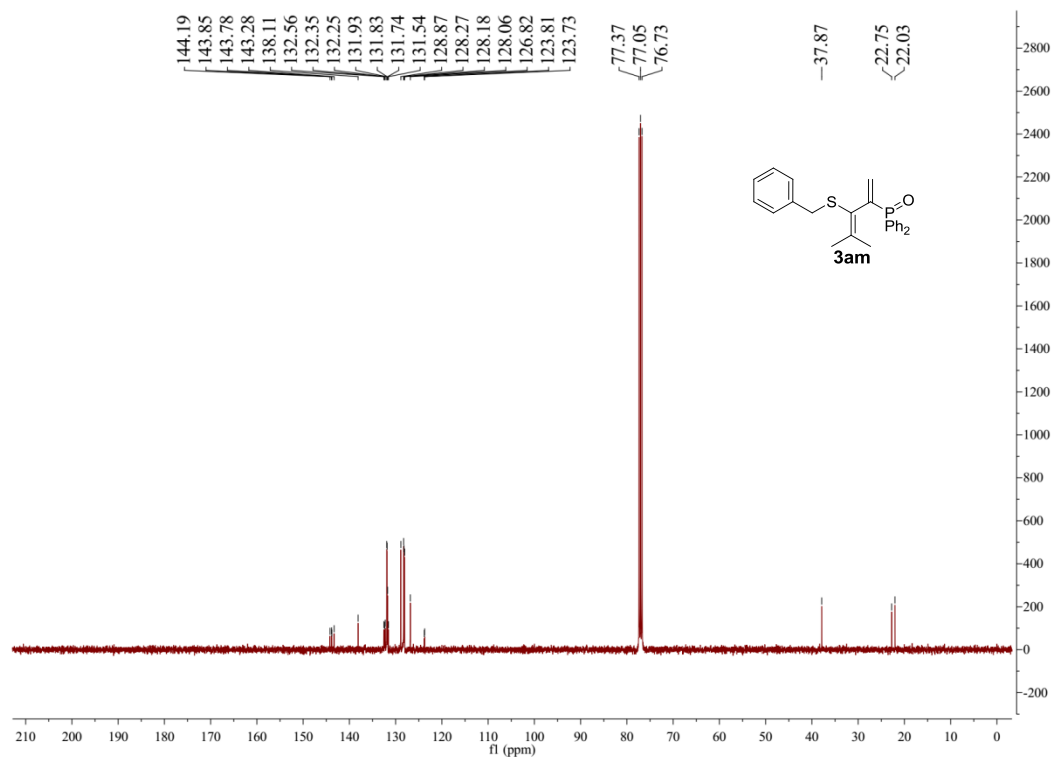
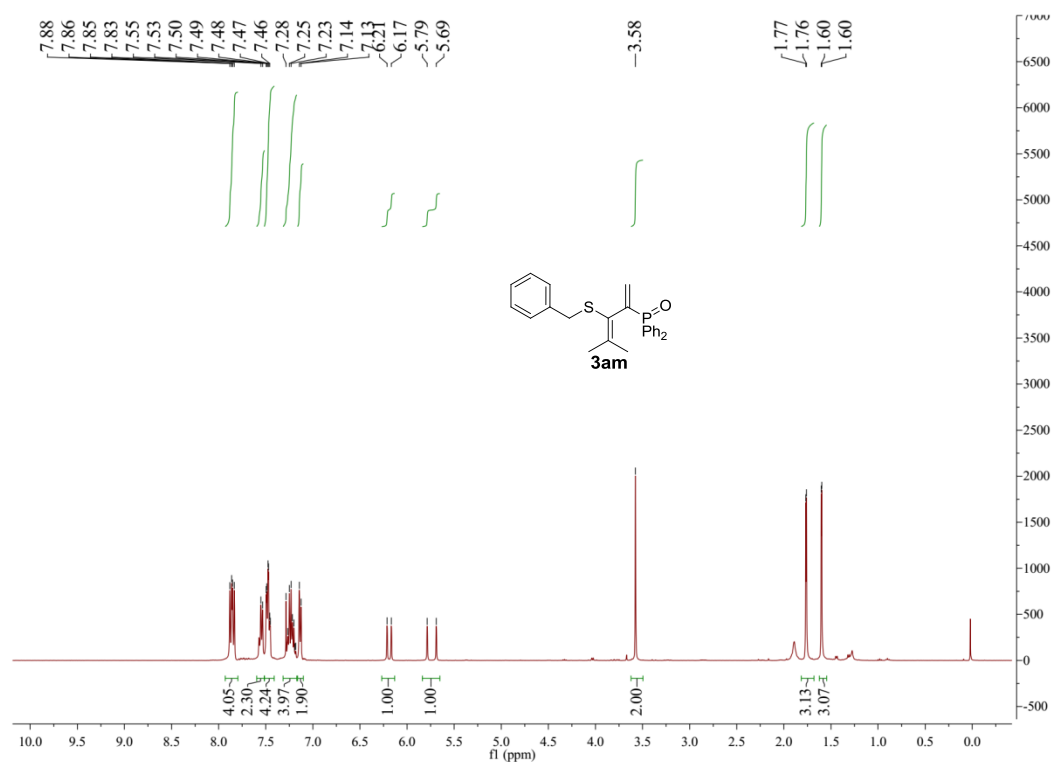


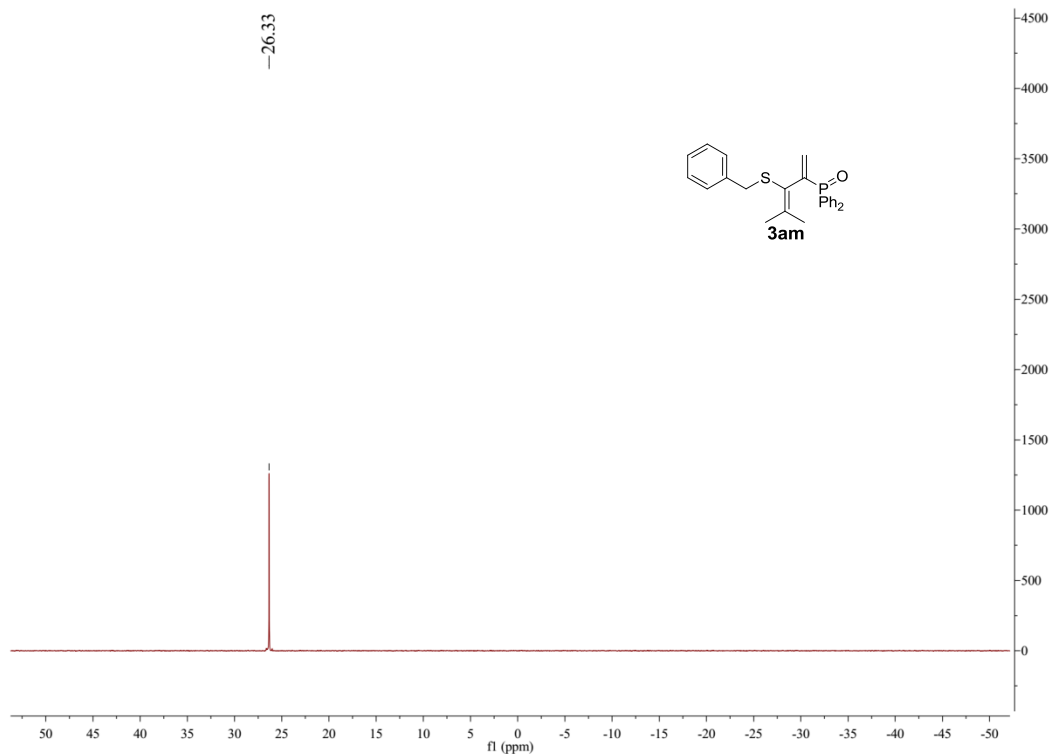
20170117-14 #44-45 RT: 0.46-0.47 AV: 2 NL: 3.10E5

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



3am





20161109-27 #30-31 RT: 0.34-0.35 AV: 2 SB: 29 0.01-0.04 , 0.75-1.02 NL: 7.51E4
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

